Supporting Information

Identification of Isoafricanol and its Terpene Cyclase in Streptomyces violaceusniger by CLSA-NMR

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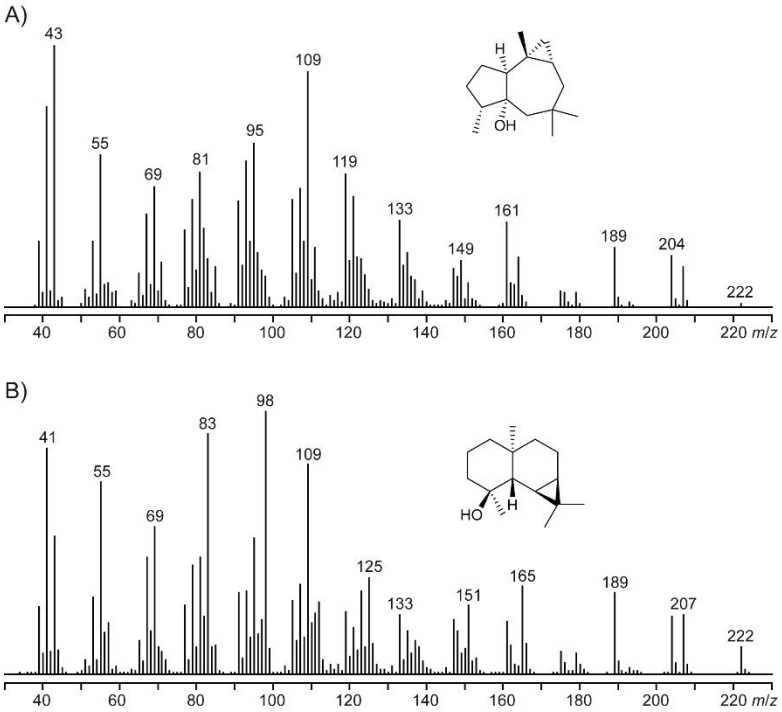


Figure 1 Mass spectra of (A) the sesquiterpene alcohol **X** (identified as isoafricanol), and (B) maaliol (closest hit in our mass spectral libraries).

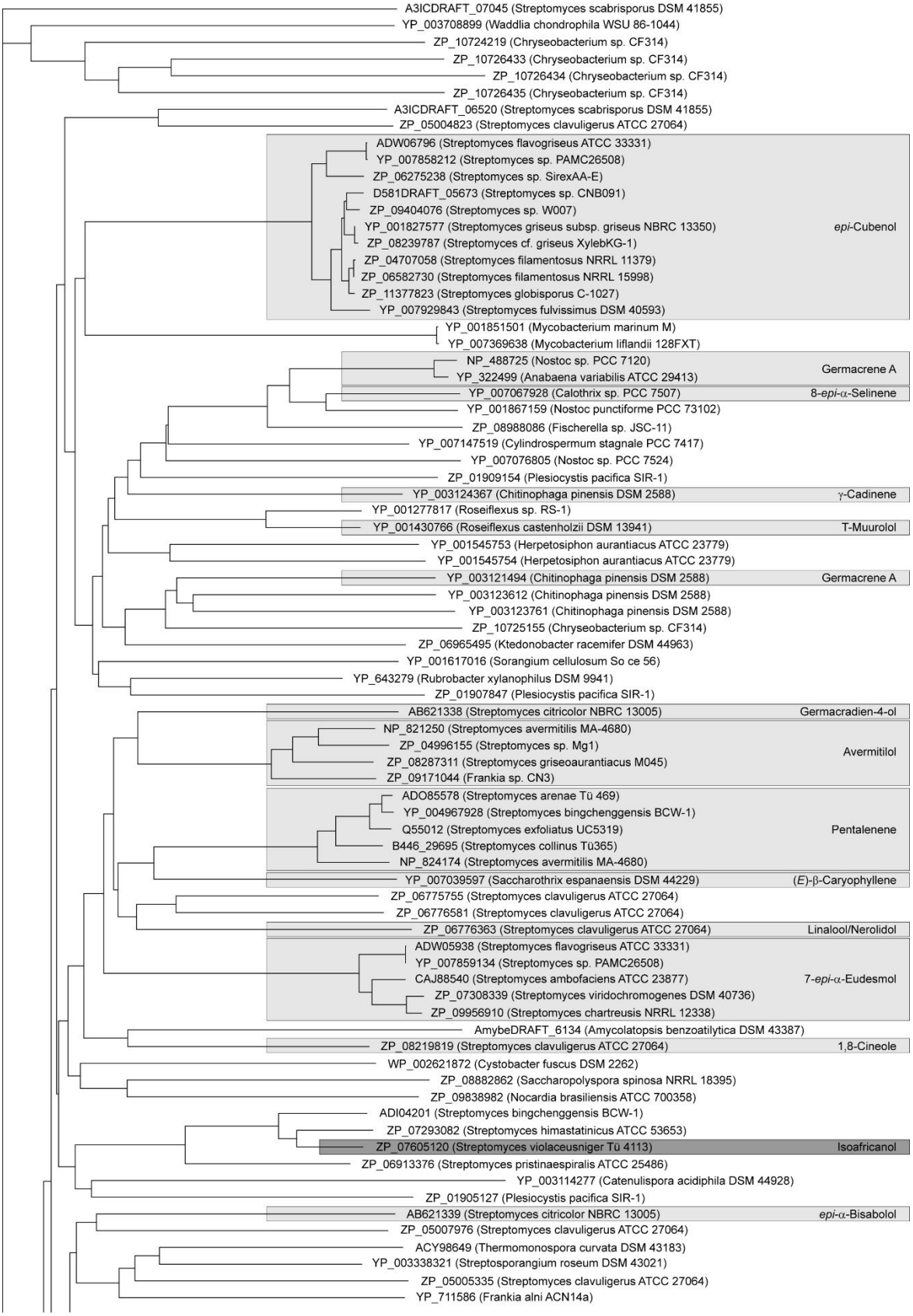


Figure 2 Phylogenetic tree of bacterial terpene cyclases. Enzymes characterised in previous studies are shown in light grey boxes, the isoafricanol synthase identified in this study is shown in a dark grey box.

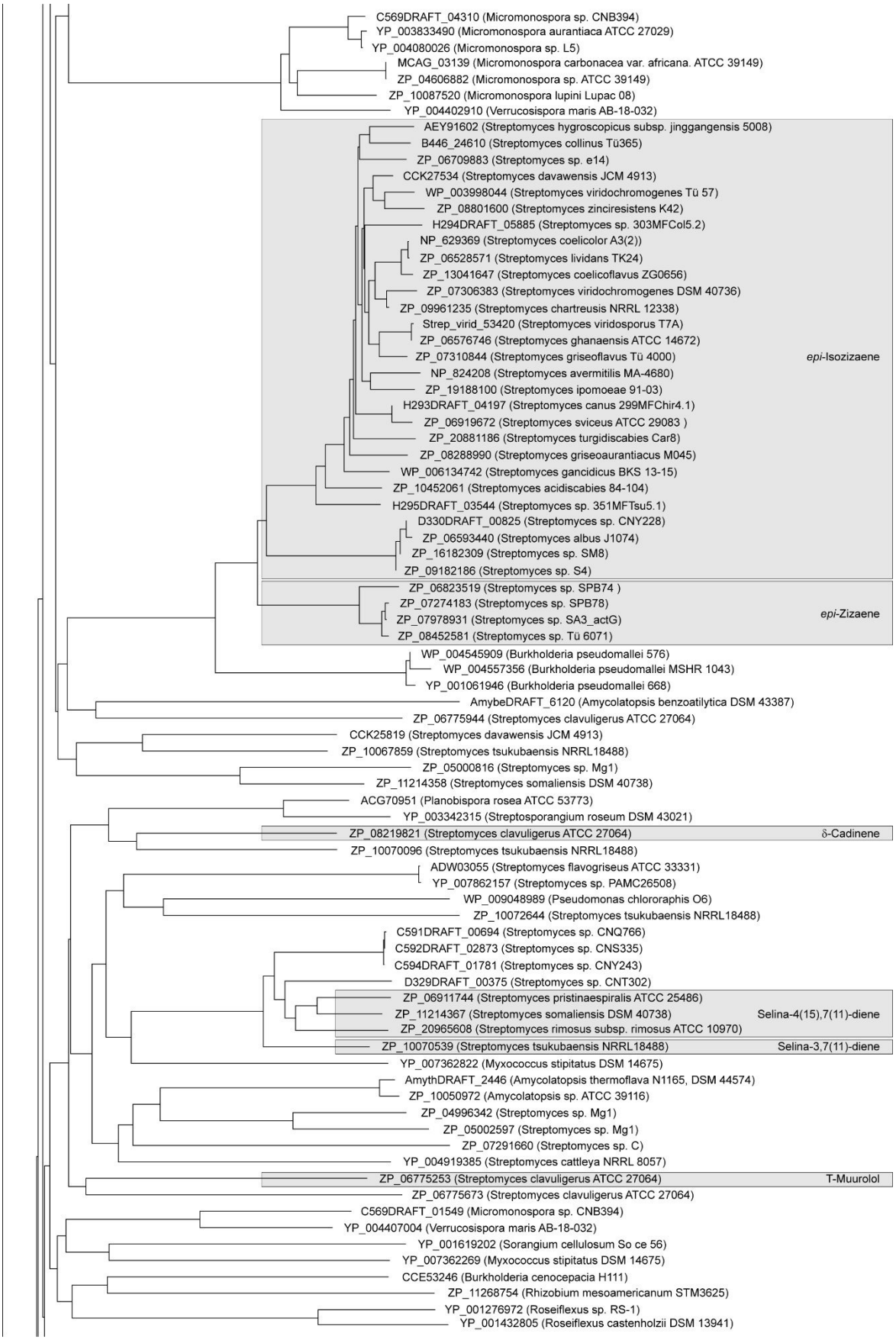


Figure 2 Phylogenetic tree of bacterial terpene cyclases. Enzymes characterised in previous studies are shown in light grey boxes, the isoafricanol synthase identified in this study is shown in a dark grey box.

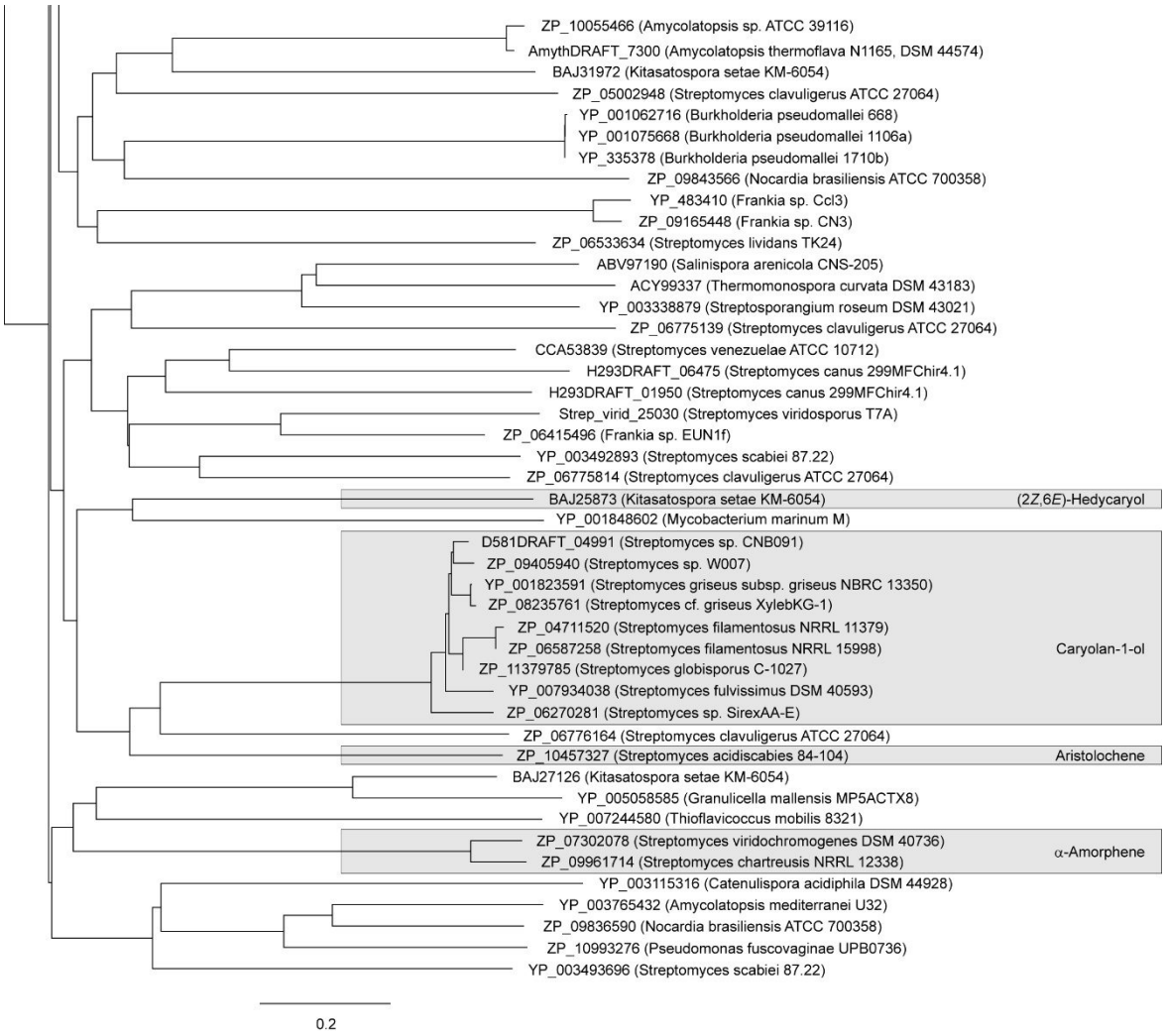


Figure 2 Phylogenetic tree of bacterial terpene cyclases. Enzymes characterised in previous studies are shown in light grey boxes, the isoafricanol synthase identified in this study is shown in a dark grey box.

Table 1

^{13}C-NMR data obtained in feeding experiments					**^{13}C-NMR data of known sesquiterpene alcohols**						
9a*	**9b***	**9c**	**9d**	**9e**	**16a**[1]	**16b**[2]	**16c**[1]	**16d**[2]	**16e**[3]	**17a**[4]	**17b**[4]
		85.7 (C_q)			85.7	85.5	87.3	84.2	80.8	81.3	80.2
		53.8 (CH)			53.8	52.4	55.9	54.7	51.7	48.6	48.7
			46.4 (CH_2)		46.4	51.3	50.1	52.3	49.7	48.0	48.5
45.6 (CH)					45.6	50.0	45.1	46.5	47.7	43.3	44.9
		40.9 (CH_2)			40.9	44.5	40.3	44.1	38.8	43.2	43.5
34.0 (C_q)					34.0	35.6	34.3	35.3	35.2	41.4	42.0
				31.6 (CH_3)	31.6	34.2	32.0	34.1	31.9	34.0	34.0
	31.3 (CH_2)				31.3	32.9	31.7	?[a]	29.3	33.3	33.4
	31.1 (CH_3)				31.1	25.9	31.4	30.5	29.1	25.6	24.1
			23.4 (CH_2)		23.5	25.8	26.0	25.5	29.0	24.4	23.6
	22.6 (CH_2)				22.6	25.8	23.6	23.8	27.4	23.7	22.9
				22.1 (CH_3)	22.1	24.0	22.9	23.7	23.8	23.3	22.4
			20.9 (CH)		20.9	22.7	21.5	22.9	21.6	21.8	21.8
18.6 (C_q)					18.7	18.4	18.2	18.3	17.7	20.6	20.7
				12.3 (CH_3)	12.3	18.3	15.3	12.8	12.3	19.6	19.7

[a]Missing information in original publication.

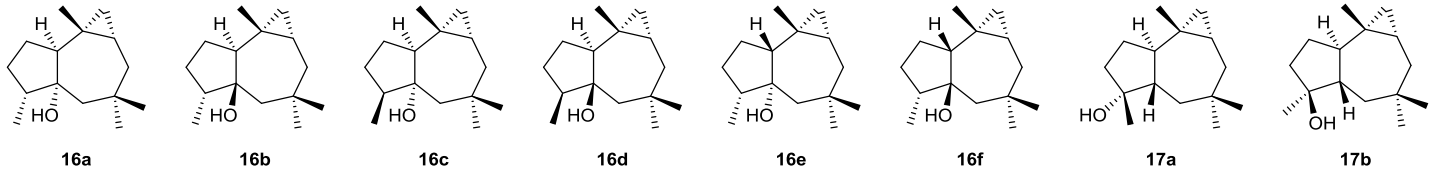
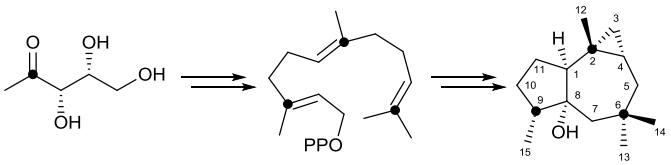
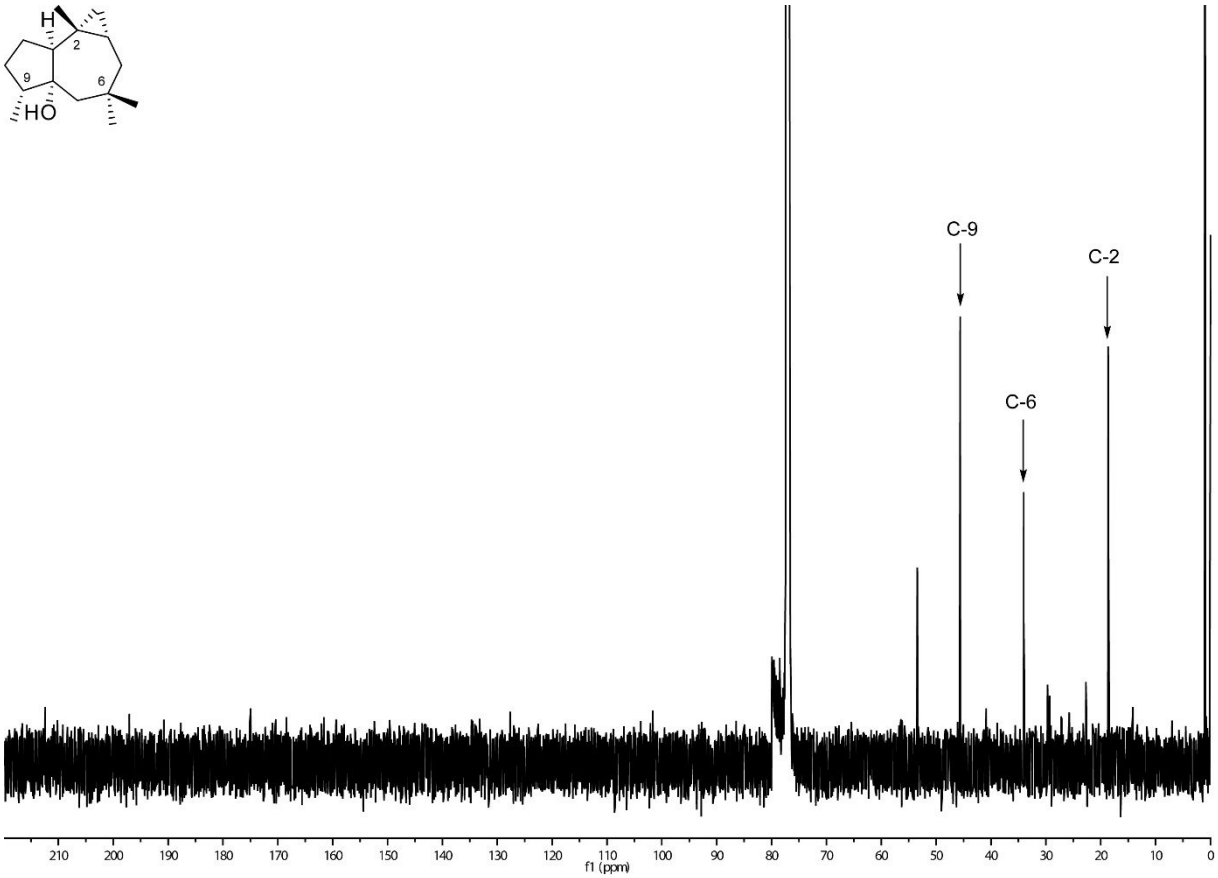
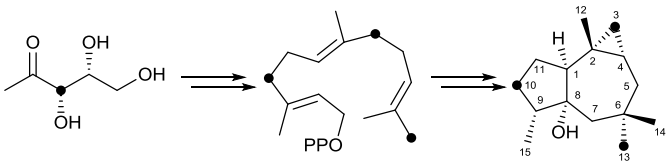


Figure 3 Structures of isoafricanol (**16a**), its stereoisomers (**16b – 16f**), and of the constitutional isomers leptographiol (**17a**) and isoleptographiol (**17b**). These two constitutional isomers were included in this overview, because their formation can be easily explained by capture of the first cationic intermediate along the biosynthetic pathway to **3** with water (Scheme 3 of main text). NMR data of **16f** are not available from the literature.

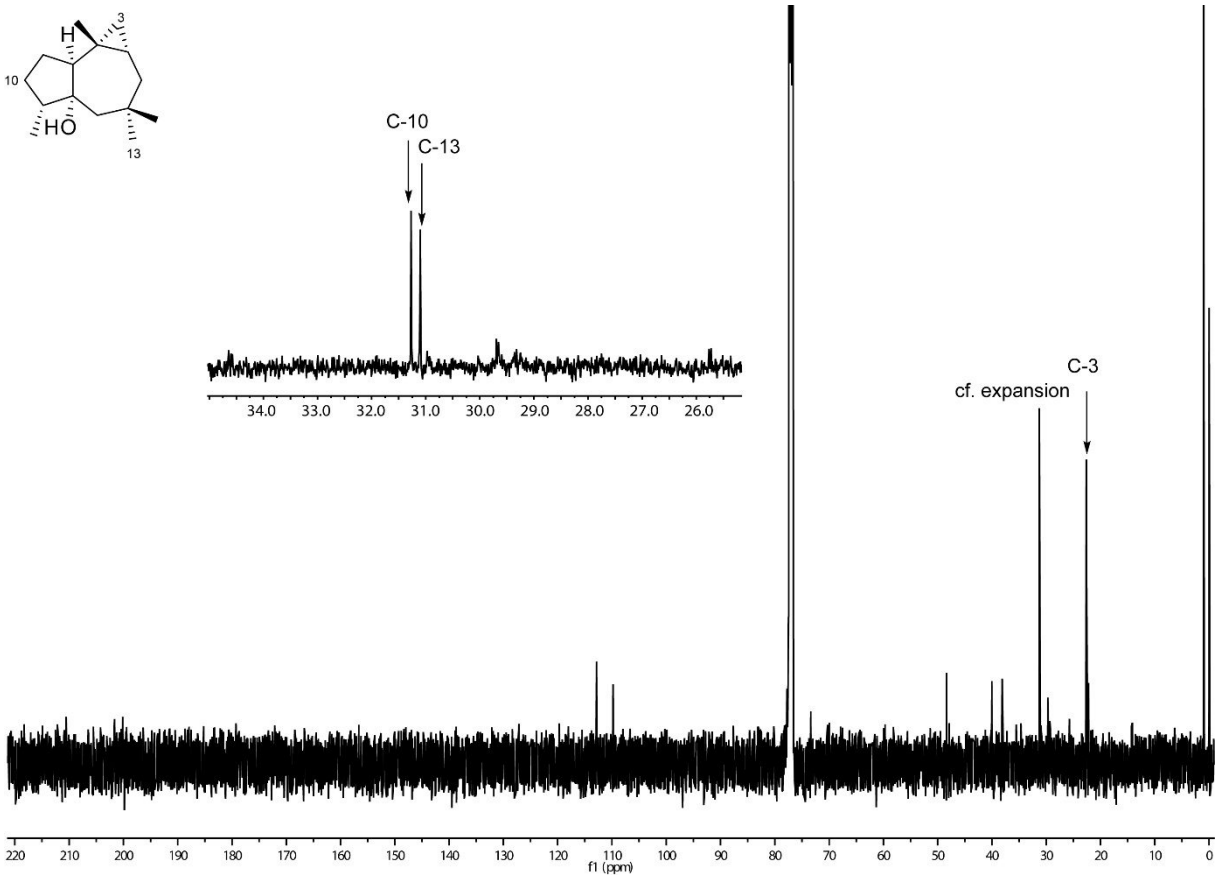


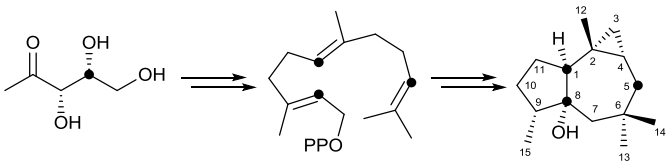
9a [3,7,11-$^{13}C_3$]FPP [2,6,9-$^{13}C_3$]-**16a**



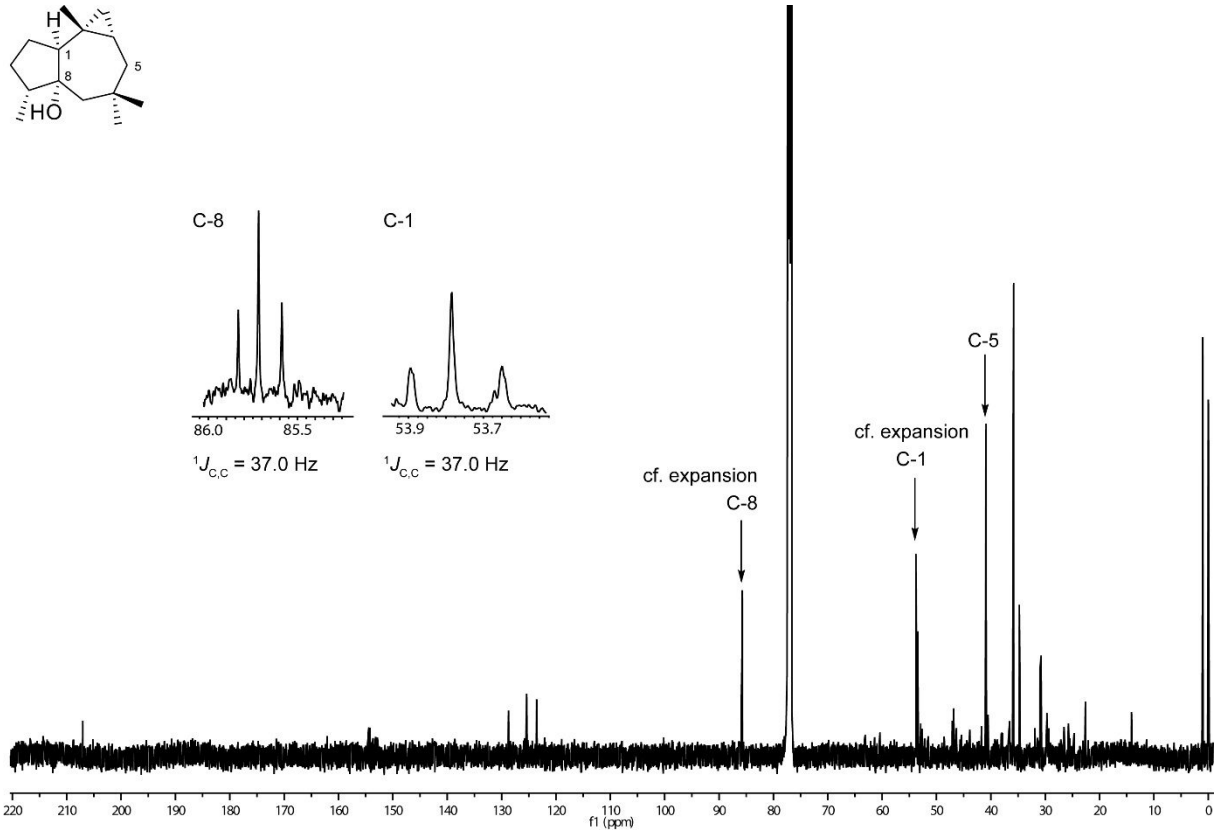


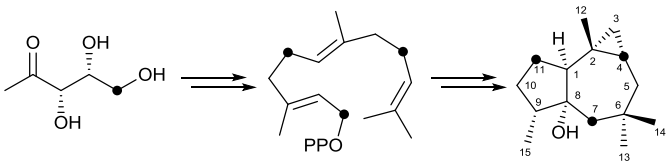
9b [4,8,12-$^{13}C_3$]FPP [3,10,13-$^{13}C_3$]-**16a**



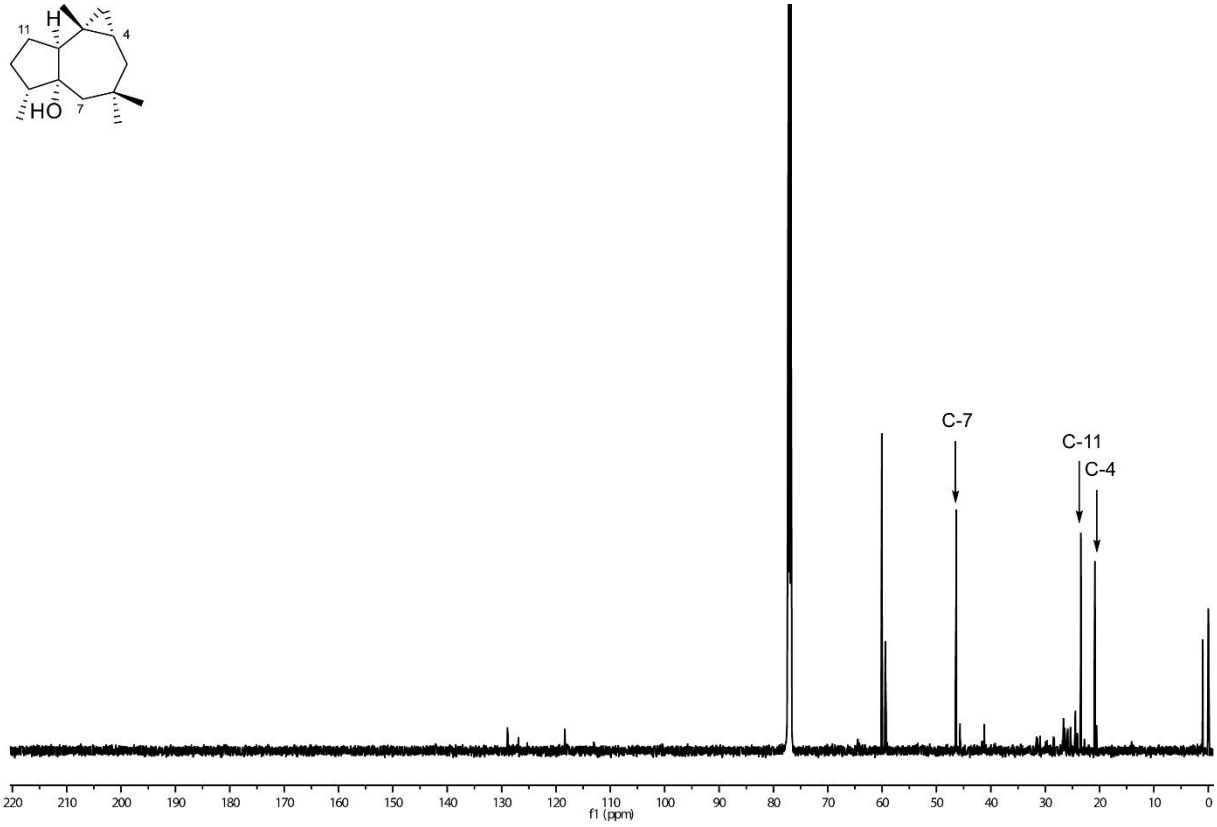


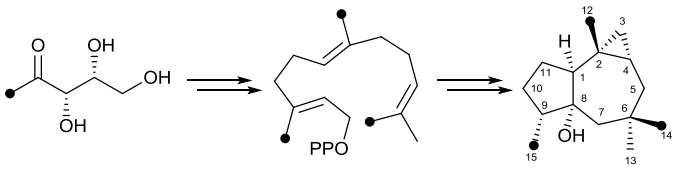
9c [2,6,10-$^{13}C_3$]FPP [1,5,8-$^{13}C_3$]-**16a**



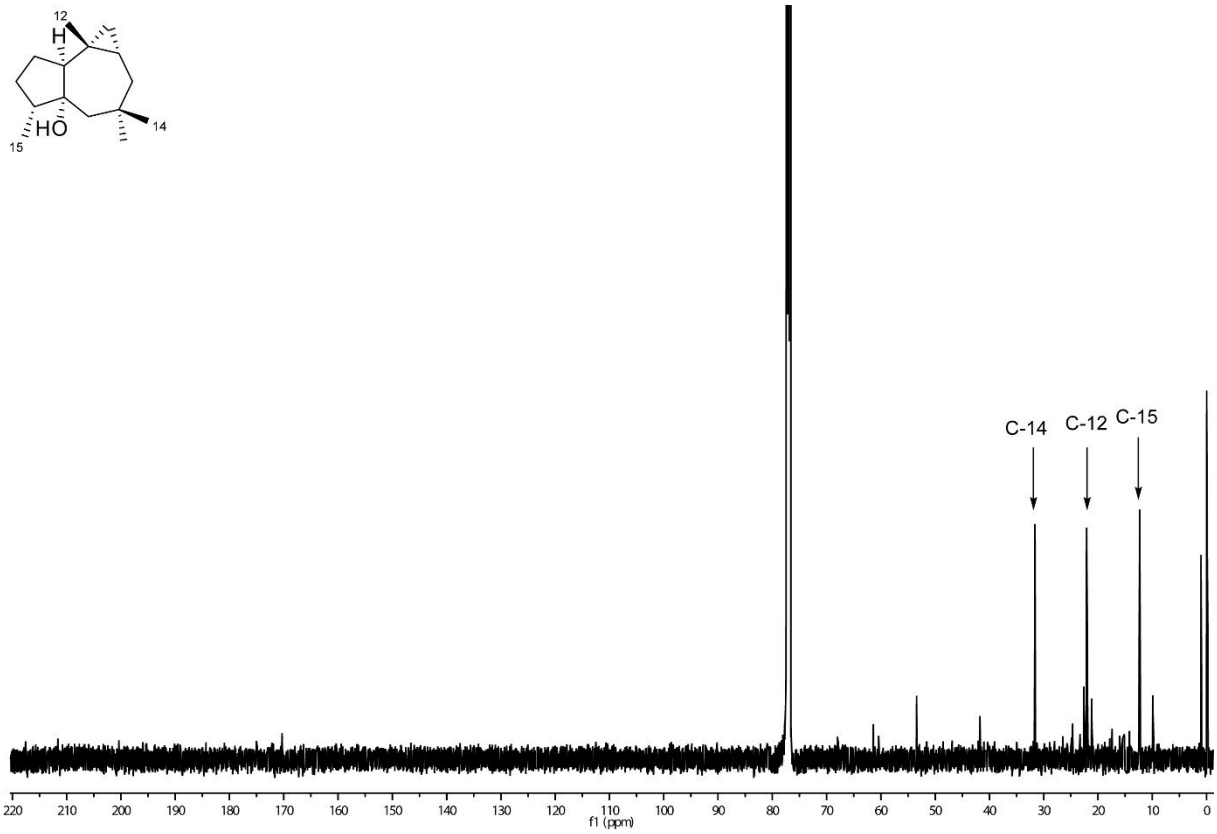


9d [1,5,9-$^{13}C_3$]FPP [4,7,11-$^{13}C_3$]-**16a**





9e [13,14,15-$^{13}C_3$]FPP [12,14,15-$^{13}C_3$]-**16a**



General Methods. Chemicals were purchased from Acros Organics (Geel, Belgium) or Sigma Aldrich Chemie GmbH (Steinheim, Germany) and used without further purification. All non-aqueous reactions were performed under an inert atmosphere (N_2) in flame-dried flasks. Solvents were purified by distillation and dried according to standard methods. Thin-layer chromatography was performed with 0.2 mm precoated plastic sheets Polygram® Sil G/UV254 (Machery-Nagel). Column chromatography was carried out using Merck silica gel 60 (70-200 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker DRX-400 (400 MHz) and AV III-400 (400 MHz) spectrometers, and were referenced against TMS (δ = 0.00 ppm) for ^{1}H-NMR and $CDCl_3$ (δ = 77.01 ppm) for ^{13}C-NMR. The enhanced ^{13}C-NMR signals of ^{13}C-labelled carbons are indicated by $^{13}C_q$, ^{13}CH, $^{13}CH_2$, or $^{13}CH_3$, respectively. Coupling constants for ^{13}C satellites of ^{1}H NMR signals are marked with an asterisk ($^1J_{C,H*}$). UV spectra were obtained using a Varian Cary 100 Bio, and IR spectra were recorded with a Bruker Tensor 27 ATR (attenuated total reflectance). Specific rotations were measured using a Dr. Kernchen Propol Digital Automatic Polarimeter. GC-MS analyses of synthetic compounds were carried out with an HP6890 gas chromatograph connected to an HP5973 mass selective detector fitted with a BPX-5 fused silica capillary column (25 m, 0.25 mm i. d., 0.25 µm film). Instrumental parameters were (1) inlet pressure, 77.1 kPa, He 23.3 mL min^{-1}, (2) injection volume, 2 µL, (3) transfer line, 300 °C, and (4) electron energy 70 eV. The GC was programmed as follows: 5 min at 50 °C increasing at 10 °C min^{-1} to 320 °C, and operated in split mode (20:1, 60 s valve time). The carrier gas was He at 1 mL min^{-1}. Retention indices (I) were determined from a homologous series of n-alkanes (C_8-C_{38}).

Culture conditions. The actinomycete Streptomyces violaceusniger Tü4113 was obtained from Hans-Peter Fiedler (Tübingen). The bacteria were grown in 65.GYM medium (glucose: 4.0 g, yeast extract: 4.0 g, malt extract: 10.0 g, $CaCO_3$: 2.0 g, agar: 12.0 g, H_2O: 1000 mL; if liquid medium $CaCO_3$ was not added). The bacteria were inoculated in liquid medium (100 mL) and incubated in a rotary shaker at 28 °C for 3 days. An agar plate was inoculated with 1 mL culture volume, followed by drying on air. Incubation at 28 °C was continued for 1 day prior to CLSA analysis.

Collection of volatiles. The volatile metabolites that were emitted by the agar plate cultures were trapped by use of the closed-loop stripping analysis (CLSA).[5] Therefore the agar plate was put into a closed vessel containing a char-coal filter (Chromtech GmbH, Idstein, Precision Char Coal Filter 5 mg). The charcoal filter was removed from the apparatus after 18-24 h and eluted with ~50 µL of pure dichloromethane. The extract was directly analysed by GC/MS and the rest of the sample stored at -80 °C.

GC/MS. GC-MS analyses were carried out on an Agilent 7890A connected with an Agilent 5975C inert mass detector fitted with a HP-5 fused silica capillary column (30 m, 0.25 mm i. d., 0.25 µm film, Agilent). GC conditions were as follows: inlet pressure 77.1 kPa, He 23.3 mL min^{-1}, injection volume 1.5 µL, transfer line 300 °C, electron energy 70 eV. The operation mode was splitless (60 s valve time) and the carrier gas was He at 1.2 mL min^{-1}. The GC was programmed as follows: 5 min at 50 °C increasing with 5 °C min^{-1} to 320 °C.

Feeding experiments. The synthetic isotopomers of ^{13}C-labelled deoxyxylulose (**9a** – **9e**) were fed to the agar plate cultures by mixing the pure compound (1 mM) with the agar medium before gelation. The agar plate was inoculated with a liquid culture of S. violaceusniger and incubated at 28°C for one day. The agar plate was placed in a CLSA and the volatiles were collected for three days. The charcoal filter was removed every day and the collected volatiles were extracted with $CDCl_3$ (~50 µL). The extracts were combined and the ^{13}C-NMR and DEPT spectra were recorded on an AV II-600 spectrometer with cryoprobe at 150 MHz. The NMR signals were referenced against TMS (δ = 0.00 ppm) for ^{1}H-NMR and $CDCl_3$ (δ = 77.01 ppm) for ^{13}C-NMR.

Synthesis of ^{13}C-labelled isotopomers of deoxyxylulose

Preparation of ethyl [1-^{13}C]-(E)-4-(Benzyloxy)but-2-enoate (5a). A solution of [1-^{13}C]triethyl phosphonoacetate (**4a**) (4.00 g, 17.8 mmol, 1.0 eq.) in dry THF (9 mL) was slowly added to a suspension of NaH (60% dispersed in mineral oil; 710 mg, 17.8 mmol, 1 eq.) in THF (18 mL) at 0°C. Benzyloxyacetaldehyde (3.99 g, 26.7 mmol, 1.5 eq.) was then added. The mixture was slowly warmed to room temperature and stirred over night. After consumption of the starting material as indicated by TLC analysis, the reaction was quenched by the addition of saturated NH_4Cl solution. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica gel with hexane/EtOAc (10:1) afforded compound **5a** (2.89 g, 13.1 mmol, 74%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.27 (m, 5H, 5x CH), 6.99 (ddt, $^3J_{C,H}$ = 6.8 Hz, $^3J_{H,H}$ = 15.8 Hz, $^3J_{H,H}$ = 4.4 Hz, 1H, CH), 6.13 (ddt, $^2J_{C,H}$ = 3.4 Hz, $^3J_{H,H}$ = 15.8 Hz, $^4J_{H,H}$ = 2.0 Hz, 1H, CH), 4.57 (s,

$^{1}J_{C,H^*}$ = 141.8 Hz, 2H, CH_2), 4.20 (dq, $^{3}J_{C,H}$ = 3.0 Hz, $^{3}J_{H,H}$ = 7.1 Hz, 2H, CH_2), 4.19 – 4.16 (m, 2H, CH_2), 1.29 (t, $^{3}J_{H,H}$ = 7.1 Hz, $^{1}J_{C,H^*}$ = 127.0 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.3 (^{13}CO), 144.2 ($^{2}J_{C,C}$ = 1.1 Hz, CH), 137.7 (C_q), 128.4 (2x CH), 127.8 (CH), 127.6 (2x CH), 121.4 (d, $^{1}J_{C,C}$ = 75.0 Hz, CH), 72.7 (CH_2), 68.6 (d, $^{3}J_{C,C}$ = 6.8 Hz, CH_2), 60.3 (d, $^{2}J_{C,C}$ = 2.3 Hz, CH_2), 14.2 (d, $^{3}J_{C,C}$ = 2.1 Hz, CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3065 (w), 3033 (w), 2983 (w), 2939 (w), 2904 (w), 2871 (w), 1680 (s), 1497 (w), 1453 (w), 1366 (w), 1294 (m), 1245 (m), 1153 (m), 1116 (m), 1028 (m), 997 (m), 738 (m), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 221 (<1) $[M]^+$, 192 (3), 176 (3), 158 (8), 146 (8), 132 (8), 115 (20), 105 (12), 91 (100), 79 (24), 65 (30), 51 (13), 39 (20); GC (BPX-5) I = 1754.

Preparation of ethyl [2-^{13}C]-(E)-4-(Benzyloxy)but-2-enoate (5b). Same procedure as for **5a** with [2-^{13}C]triethyl phosphonoacetate (**4b**) as starting material. Yield: 3.97 g (17.6 mmol, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.39 (m, 5H, 5x CH), 6.99 (ddt, $^{2}J_{C,H}$ = 3.0 Hz, $^{3}J_{H,H}$ = 4.3 Hz, $^{3}J_{H,H}$ = 15.7 Hz, 1H, CH), 6.14 (ddt, $^{1}J_{C,H}$ = 164.4 Hz, $^{3}J_{H,H}$ = 15.7 Hz, $^{3}J_{H,H}$ = 2.0 Hz, 1H, ^{13}CH), 4.57 (s, $^{1}J_{CH^*}$ = 141.8 Hz, CH_2), 4.21 (q, $^{3}J_{H,H}$ = 7.2 Hz, 2H, CH_2), 4.20 – 4.16 (m, 2H, CH_2), 1.30 (t, $^{3}J_{H,H}$ = 7.2 Hz, $^{1}J_{C,H^*}$ = 127.0 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.2 (d, $^{1}J_{C,C}$ = 75.0 Hz, CO), 144.1 (d, $^{1}J_{C,C}$ = 71.6 Hz, CH), 137.7 (C_q), 128.4 (2x CH), 127.7 (CH), 127.6 (2x CH), 121.4 (^{13}CH), 72.7 (CH_2), 68.6 (CH_2), 60.3 (d, $^{3}J_{C,C}$ = 0.8 Hz, CH_2), 14.2 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3066 (w), 3033 (w), 2983 (w), 2939 (w), 2904 (w), 2871 (w), 1717 (s), 1634 (w), 1497 (w), 1453 (w), 1368 (w), 1296 (m), 1266 (m), 1176 (m), 1116 (w), 1030 (m), 976 (w), 739 (w), 698 (m) cm^{-1}; EIMS (70 eV) m/z (%) = 221 (<1) $[M]^+$, 192 (3), 176 (2), 158 (7), 147 (7), 130 (10), 115 (17), 105 (12), 91 (100), 79 (24), 65 (30), 51 (13), 40 (13); GC (BPX-5) I = 1754.

Preparation of [1-^{13}C]-(E)-4-(benzyloxy)-N-methoxy-N-methylbut-2-enamide (6a). To a slurry of Me(MeO)NH·HCl (3.72 g, 38.1 mmol, 3 eq.) and the ester **5a** (2.81 g, 10.7 mmol, 1 eq.) in dry THF was added freshly prepared iPrMgCl in THF (25.4 mL, 2.0 M, 50.8 mmol, 4 eq.) at -20°C. After consumption of the starting material as followed by TLC, the reaction was quenched with saturated NH_4Cl solution. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel with hexane/EtOAc (2:1) to yield the pure Weinreb amide **6a** (2.01 g, 8.53 mmol, 67%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.27 (m, 5H, 5x CH), 7.01 (ddt, $^{3}J_{C,H}$ = 6.2 Hz, $^{3}J_{H,H}$ = 15.6 Hz, $^{3}J_{H,H}$ = 4.4 Hz, 1H, CH), 6.73 – 6.67 (m, 1H, CH), 4.58 (s, $^{1}J_{C,H^*}$ = 141.5 Hz, 2H, CH_2), 4.22 (ddd, $^{3}J_{H,H}$ = 4.3 Hz, $^{4}J_{H,H}$ = 2.0 Hz, $^{4}J_{C,H}$ = 1.3 Hz, 2H, CH_2), 3.70 (s, $^{1}J_{C,H^*}$ = 144.5 Hz, 3H, CH_3), 3.25 (d, $^{2}J_{C,H}$ = 2.0 Hz, $^{1}J_{C,H^*}$ = 139.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4 (^{13}CO), 142.7 (d, $^{2}J_{C,C}$ = 1.0 Hz, CH), 137.8 (C_q), 128.4 (2x CH), 127.7 (CH), 127.6 (2x CH), 118.7 (d, $^{1}J_{C,C}$ = 67.4 Hz, CH), 72.6 (CH_2), 69.0 (d, $^{3}J_{C,C}$ = 6.1 Hz, CH_2), 61.7 (CH_3), 32.3 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3063 (w), 3031 (w), 2938 (w), 2861 (w), 1722 (w), 1658 (m), 1598 (s), 1497 (w), 1453 (w), 1408 (w), 1371 (s), 1264 (m), 1170 (m), 1118 (s), 993 (s), 965 (s), 810 (w), 740 (s), 699 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 236 (<1) $[M]^+$, 176 (13), 158 (11), 129 (6), 115 (4), 105 (2), 91 (100), 77 (8), 65 (15), 56 (6), 39 (11); GC (BPX-5) I = 1986.

Preparation of [2-^{13}C]-(E)-4-(benzyloxy)-N-methoxy-N-methylbut-2-enamide (6b). Same procedure as for **6a** with **5b** as starting material. Yield: 2.53 g (10.8 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.27 (m, 5H, 5x CH), 7.01 (ddt, $^{2}J_{C,H}$ = 2.3 Hz, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = 4.3 Hz, 1H, CH), 6.70 (ddt, $^{3}J_{H,H}$ = 15.5 Hz, $^{1}J_{C,H}$ = 162.4 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H, ^{13}CH), 4.58 (s, $^{1}J_{C,H^*}$ = 141.4 Hz, 2H, CH_2), 4.22 (ddd, $^{3}J_{H,H}$ = 4.3 Hz, $^{4}J_{H,H}$ = 1.9 Hz, $^{3}J_{C,H}$ = 5.1 Hz, 2H, CH_2), 3.70 (s, $^{1}J_{C,H^*}$ = 144.4 Hz, 3H, CH_3), 3.25 (s, $^{1}J_{C,H^*}$ = 139.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.4 (d, $^{1}J_{C,C}$ = 68.1 Hz, CO), 142.7 (d, $^{1}J_{C,C}$ = 73.2 Hz, CH), 137.8 (C_q), 128.4 (2x CH), 127.7 (CH), 127.6 (2x CH), 118.8 (^{13}CH), 72.6 (CH_2), 69.0 (d, $^{2}J_{C,C}$ = 0.6 Hz, CH_2), 61.7 (CH_3), 32.3 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3063 (w), 3031 (w), 2968 (w), 2938 (w), 2897 (w), 2860 (w), 1722 (w), 1653 (s), 1620 (m), 1452 (m), 1415 (m), 1381 (s), 1261 (w), 1173 (w), 1119 (m), 998 (s), 964 (s), 816 (w), 740 (s), 699 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 236 (1) $[M]^+$, 176 (37), 158 (30), 146 (4), 130 (25), 115 (9), 105 (4), 91 (100), 77 (18), 65 (34), 56 (14), 40 (15); GC (BPX-5) I = 1988.

Preparation of [2-^{13}C]-(E)-5-(benzyloxy)pent-3-en-2-one (7a). To a solution of the Weinreb amide **6a** (2.48 g, 10.5 mmol, 1 eq.) in dry THF (10.5 mL) was added dropwise a solution of MeMgBr (10.5 mL, 3 M in Et_2O, 31.5 mmol, 3.0 eq.) at 0°C. The reaction mixture was stirred for 2 h at 0°C, warmed to room temperature and then quenched with 2 N HCl. The aqueous layer was extracted three times with Et_2O. The combined extracts were dried with $MgSO_4$ and concentrated under reduced pressure. Column chromatography on silica gel with hexane/EtOAc (10:1) afforded the pure methyl ketone **7a** (1.15 g, 6.0 mmol, 71%) as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.28 (m, 5H, 5x CH), 6.80 (ddt, $^{3}J_{H,H}$ = 16.1 Hz, $^{3}J_{C,H}$ = 6.3 Hz, $^{3}J_{H,H}$ = 4.5 Hz, 1H, CH), 6.28 (ddt, $^{3}J_{H,H}$ = 16.1 Hz, $^{2}J_{C,H}$ = 2.5 Hz, $^{4}J_{H,H}$ = 2.0 Hz, 1H, CH), 4.57 (s, $^{1}J_{C,H^*}$ = 141.9 Hz, 2H, CH_2), 4.21 – 4.19 (m, 2H, CH_2), 2.26 (d, $^{2}J_{C,H}$ = 5.9 Hz, $^{1}J_{C,H^*}$ = 145.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz,

$CDCl_3$) δ = 198.3 (^{13}CO), 143.1 (d, $^2J_{C,C}$ = 1.6 Hz, CH), 137.6 (C_q), 130.3 (d, $^1J_{C,C}$ = 53.0 Hz, CH), 128.5 (2x CH), 127.9 (CH), 127.7 (2x CH), 72.9 (CH_2), 68.8 (d, $^3J_{C,C}$ = 6.0 Hz), 27.2 (d, $^1J_{C,C}$ = 42.3, CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3065 (w), 3034 (w), 2940 (w), 1722 (s), 1700 (s), 1670 (s), 1496 (w), 1454 (w), 1360 (w), 1257 (w), 1206 (m), 1171 (w), 1097 (m), 1070 (w), 1025 (w), 979 (m), 748 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 161 (4), 146 (10), 132 (8), 116 (2), 105 (5), 91 (100), 85 (8), 77 (18), 65 (21), 51 (11), 44 (23); GC (BPX-5) I = 1639.

Preparation of [3-^{13}C]-(E)-5-(benzyloxy)pent-3-en-2-one (7b). Same procedure as for **7a** with **6b** as starting material. Yield: 1.71 g (8.96 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39 – 7.28 (m, 5H, 5x CH), 6.80 (ddt, $^2J_{C,H}$ = 1.6 Hz, $^3J_{H,H}$ = 16.1 Hz, $^3J_{H,H}$ = 4.5 Hz, 1H, CH), 6.27 (ddt, $^3J_{H,H}$ = 16.1 Hz, $^1J_{C,H}$ = 159.4 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H, ^{13}CH), 4.57 (s, $^1J_{C,H*}$ = 142.1 Hz, 2H, CH_2), 4.21 (ddd, $^3J_{H,H}$ = 4.5 Hz, $^4J_{H,H}$ = 2.0 Hz, $^3J_{C,H}$ = 4.5 Hz, 2H, CH_2), 2.27 (d, $^3J_{C,H}$ = 1.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.1 (d, $^1J_{C,C}$ = 53.0 Hz, CO), 142.9 (d, $^1J_{C,C}$ = 69.2 Hz, CH), 137.6 (C_q), 130.3 (^{13}CH), 128.5 (2x CH), 127.9 (CH), 127.7 (2x CH), 72.9 (CH_2), 68.8 (CH_2), 27.2 (d, $^2J_{C,C}$ = 15.1 Hz, CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3065 (w), 3034 (w), 2941 (w), 2908 (w), 1700 (s), 1600 (w), 1497 (w), 1454 (w), 1361 (m), 1284 (m), 1249 (m), 1205 (m), 1167 (m), 1095 (m), 1068 (m), 977 (m), 916 (w), 747 (s), 696 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 161 (7), 146 (12), 132 (10), 117 (2), 105 (5), 91 (100), 85 (11), 77 (17), 65 (22), 51 (11), 43 (23); GC (BPX-5) I = 1639.

Preparation of [2-^{13}C]-(3S,4R)-5-(benzyloxy)-3,4-dihydroxypentan-2-one (8a). According to Walsh and Sharpless,[8] AD-mix β (8.3 g), $K_2OsO_4{\cdot}2H_2O$ (22 mg, 0.06 mmol, 0.01 eq.), $NaHCO_3$ (1.49 g, 17.7 mmol, 3.0 eq.), and $MeSO_2NH_2$ (562 mg, 5.91 mmol, 1.0 eq.) were suspended in a 1:1 mixture of distilled water and ^{t}BuOH (60 mL, 1:1). After cooling to 0 °C compound **7a** (1.13 g, 5.91 mmol, 1.0 eq.) dissolved in a small amount of toluene was added dropwise to give a final concentration of 0.1 M of the ketone in the reaction mixture. The reaction was stirred overnight at 0 °C, and then diluted with ethyl acetate. $Na_2S_2O_5$ (8.87 g, 46.7 mmol, 7.9 eq.) was added carefully in small portions. The mixture was extracted with ethyl acetate (3x), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel with hexane/EtOAc (2:1) gave **8a** (962 mg, 4.27 mmol, 72%) as colorless oil. $[\alpha]^{21.8}_D$ = +26.3 (c 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.28 (m, 5H, 5x CH), 4.57 (s, $^1J_{C,H*}$ = 142.1 Hz, 2H, CH_2), 4.24 – 4.18 (m, 2H, 2x CH), 3.73 (br s, 1H, OH), 3.64 (dd, $^2J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 5.9 Hz, 1H, CH), 3.61 (dd, $^2J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 6.3 Hz, 1H, CH), 2.45 (br s, 1H, OH), 2.27 (d, $^2J_{C,H}$ = 6.1 Hz, $^1J_{C,H*}$ = 128.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.1 (^{13}CO), 137.6 (C_q), 128.5 (2x CH), 127.9 (CH), 127.8 (2x CH), 77.1 (d, $^1J_{C,C}$ = 39.0 Hz, CH), 73.6 (CH_2), 71.0 (d, $^3J_{C,C}$ = 3.1 Hz, CH_2), 70.4 (CH), 25.5 (d, $^1J_{C,C}$ = 42.2 Hz) ppm; IR (ATR) $\tilde{\nu}$ = 3432 (br), 3065 (w), 3032 (w), 2933 (w), 2872 (w), 1703 (s), 1676 (s), 1602 (w), 1495 (w), 1453 (m), 1361 (w), 1273 (m), 1207 (m), 1177 (w), 1070 (s), 1026 (m), 743 (m), 714 (s), 699 (s) cm^{-1}; EIMS (70 eV, MSTFA) m/z (%) = 325 (5), 219 (52), 193 (10), 179 (5), 147 (23), 131 (10), 117 (8), 103 (10), 91 (100), 73 (64), 65 (14), 44 (17); GC (BPX-5, MSTFA) I = 1903.

Preparation of [3-^{13}C]-(3S,4R)-5-(benzyloxy)-3,4-dihydroxypentan-2-one (8b). Same procedure as for **8a** with **7c** as starting material. Yield: (1.49 g, 6.6 mmol, 75%). $[\alpha]^{20.8}_D$ = +12.5 (c 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.27 (m, 5H, 5x CH), 4.56 (s, 2H, CH_2), 4.22 (br d, $^1J_{C,H}$ = 144.3 Hz, 1H, ^{13}CH), 4.20 (m, 1H, CH), 3.74 (br s, 1H, OH), 3.65 – 3.58 (m, 1H, CH), 2.53 (br s, 1H, OH), 2.26 (d, $^3J_{C,H}$ = 1.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.2 (CO), 137.6 (C_q), 128.5 (2x CH), 127.9 (CH), 127.8 (2x CH), 77.2 (^{13}CH), 73.6 (CH_2), 71.0 (CH_2), 70.4 (d, $^1J_{C,C}$ = 39.6 Hz, CH), 25.5 (d, $^2J_{C,C}$ = 3.2 Hz) ppm; IR (ATR) $\tilde{\nu}$ = 3427 (br), 3069 (w), 2944 (w), 2884 (s), 1688 (s), 1602 (w), 1583 (w), 1495 (w), 1452 (m), 1421 (w), 1323 (m), 1274 (m), 1181 (w), 1114 (m), 1099 (m), 1070 (m), 1025 (w), 932 (m), 707 (s) cm^{-1}; EIMS (70 eV, MSTFA) m/z (%) = 326 (7), 219 (56), 206 (7), 193 (9), 179 (8), 147 (29), 131 (10), 117 (9), 103 (10), 91 (100), 73 (67), 59 (10), 43 (17); GC (BPX-5, MSTFA) I = 1903.

Preparation of [4-^{13}C]-(3S,4R)-5-(benzyloxy)-3,4-dihydroxypentan-2-one (8c). Same procedure as for **8a** with **7c** as starting material. Yield: (951 mg, 4.2 mmol, 87%). $[\alpha]^{24.4}_D$ = +33.2 (c 1.20, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.28 (m, 5H, 5x CH), 4.57 (s, 2H, CH_2), 4.23 (dd, $^3J_{H,H}$ = 1.9 Hz, $^2J_{C,H}$ = 1.9 Hz, 1H, CH), 4.21 (ddt, $^1J_{C,H}$ = 145.3 Hz, $^3J_{H,H}$ = 6.2, $^3J_{H,H}$ = 2.1 Hz, 1H, ^{13}CH), 3.73 (br s, 1H, OH), 3.62 (m, 2H, CH_2), 2.38 (br s, 1H, OH), 2.27 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.1 (C_q), 137.6 (C_q), 128.5 (2x CH), 127.9 (CH), 127.8 (2x CH), 77.2 (d, $^1J_{C,C}$ = 39.2 Hz, CH), 73.6 (d, $^2J_{C,C}$ = 4.0 Hz, CH_2), 70.4 (^{13}CH), 25.5 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3428 (br), 3064 (w), 2868 (w), 1714 (s), 1496 (w), 1359 (m), 1244 (m), 1112 (s), 1072 (s), 1027 (s), 738 (s), 698 (s) cm^{-1}; EIMS (70 eV, MSTFA) m/z (%) = 369 (<1) $[M]^+$, 326 (6), 264 (1), 248 (2), 232 (2), 218 (48), 206 (5), 194 (7), 179 (5), 147 (16), 130 (11), 118 (6), 103 (6), 91 (100), 73 (60), 59 (8), 43 (18); GC (BPX-5, MSTFA) I = 1901.

Preparation of [5-^{13}C]-(3S,4R)-5-(benzyloxy)-3,4-dihydroxypentan-2-one (8d). Same procedure as for **8a** with **7d** as starting material. Yield: (1.76 g, 7.8 mmol, 91%). $[\alpha]^{24.5}_{D}$ = +44.4 (c 4.85, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.25 (m, 5H, 5x CH), 4.54 (d, $^2J_{C,H}$ = 4.0 Hz, 2H, CH_2), 4.20 – 4.15 (m, 2H, 2x CH), 3.82 (br s, 1H, OH), 3.61 (ddd, $^1J_{C,H}$ = 142.1 Hz, $^2J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 5.8 Hz, 1H, $^{13}CH_2$), 3.58 (ddd, $^1J_{C,H}$ = 143.4 Hz, $^2J_{H,H}$ = 9.5 Hz, $^3J_{H,H}$ = 6.5 Hz, 1H, CH_2), 2.85 (br s, 1H, OH), 2.22 (s, $^1J_{C,H*}$ = 128.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.2 (d, $^3J_{C,C}$ = 3.1 Hz, C_q), 137.5 (d, $^3J_{C,C}$ = 2.5 Hz, C_q), 128.3 (2x CH), 127.7 (CH), 127.6 (2x CH), 77.2 (CH), 73.5 (d, $^2J_{C,C}$ = 1.3 Hz, CH_2), 70.7 ($^{13}CH_2$), 70.4 (CH, J = 29.2 Hz), 25.5 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3432 (br), 3063 (w), 3031 (w), 2863 (w), 1715 (s), 1453 (w), 1359 (w), 1247 (w), 1121 (s), 1072 (s), 741 (m), 700 (m) cm^{-1}; EIMS (70 eV, MSTFA) m/z (%) = 369 (<1) $[M]^+$, 326 (1), 218 (21), 205 (1), 193 (3), 179 (2), 158 (1), 147 (7), 130 (6), 115 (2), 103 (4), 91 (100), 73 (44), 65 (8), 43 (14); GC (BPX-5, MSTFA) I = 1901.

Preparation of [2-^{13}C]-(3S,4R)-2-methoxy-2-methyltetrahydrofuran-3,4-diol (9a*). Compound **8a** (950 mg, 4.2 mmol, 1 eq.) was dissolved in MeOH (22 mL). A catalytic amount of Pd/C (450 mg, 5% Pd, 0.21 mmol, 0.05 eq.) was added and the reaction mixture was stirred for 2 h in a H_2 atmosphere (40 bar) at 40°C. Pure **9a*** (570 mg, 3.85 mmol, 91%) was obtained as colorless oil by filtration via a plug of silica gel and removal of the solvent under reduced pressure (1:1 mixture of two diastereomers). $[\alpha]^{22}_{D}$ = –29.8 (c 0.4, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.37 – 4.21 (m, 3H), 4.11 (dd, J = 9.8, 7.1 Hz, 1H), 3.91 (d, J = 1.6 Hz, 1H), 3.85 (d, J = 6.0 Hz, 1H), 3.67 – 3.61 (m, 2H), 3.28 (d, $^3J_{C,H}$ = 3.8 Hz, 3H, OCH_3), 3.26 (d, $^3J_{C,H}$ = 3.8 Hz, 3H, OCH_3), 1.44 (d, $^2J_{C,H}$ = 4.8 Hz, 3H, CH_3), 1.40 (d, $^2J_{C,H}$ = 4.9 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 112.2 ($^{13}C_q$), 107.9 ($^{13}C_q$), 85.4 (d, $^1J_{C,C}$ = 47.1 Hz, CH), 84.2 (d, $^1J_{C,C}$ = 48.5 Hz, CH), 79.5 (d, $^2J_{C,C}$ = 2.5 Hz, CH), 78.0 (d, $^2J_{C,C}$ = 3.3 Hz, CH), 74.5 (CH_2), 72.8 (CH_2), 51.0 (d, $^2J_{C,C}$ = 2.2 Hz, OCH_3), 50.8 (d, $^2J_{C,C}$ = 2.1 Hz, OCH_3), 20.9 (d, $^1J_{C,C}$ = 48.1 Hz, CH_3), 18.4 (d, $^1J_{C,C}$ = 48.8 Hz, CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3387 (br), 2945 (w), 2890 (w), 2834 (w), 1462 (w), 1379 (w), 1179 (w), 1087 (s), 999 (s), 867 (m), 846 (m), 767 (w), 647 (w) cm^{-1}; EIMS (70 eV, MSTFA) m/z (%) = 262 (6) $[M–OCH_3]^+$, 232 (3), 217 (38), 203 (6), 191 (23), 172 (6), 147 (77), 129 (21), 113 (8), 101 (10), 89 (19), 73 (100), 59 (23), 45 (22); HRMS (ESI) m/z $[M+Na]^+$ calcd. 172.06613, obsd. 172.06617.

Preparation of [3-^{13}C]-(3S,4R)-2-methoxy-2-methyltetrahydrofuran-3,4-diol (9b*). Same procedure as for **9a*** with **8b** as starting material. Yield: (865 mg, 5.84 mmol, 91%). $[\alpha]^{22}_{D}$ = –23.0 (c 0.5, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.37 – 4.20 (m, 3H), 4.12 – 4.01 (m, 2H), 3.71 – 3.61 (m, 3H), 3.27 (s, 3H, OCH_3), 3.25 (s, 3H, OCH_3), 1.43 (d, $^3J_{C,H}$ = 3.2 Hz, 3H, CH_3), 1.39 (d, $^3J_{C,H}$ = 2.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 112.2 (d, $^1J_{C,C}$ = 48.5 Hz, C_q), 107.9 (d, $^1J_{C,C}$ = 47.1 Hz, C_q), 85.4 (^{13}CH), 84.2 (^{13}CH), 79.5 (d, $^1J_{C,C}$ = 40.8 Hz, CH), 78.0 (d, $^1J_{C,C}$ = 41.2 Hz, CH), 74.5 (d, $^2J_{C,C}$ = 1.4 Hz, CH_2), 72.8 (d, $^2J_{C,C}$ = 3.0 Hz, CH_2), 51.0 (OCH_3), 50.8 (d, $^3J_{C,C}$ = 2.7 Hz, OCH_3), 20.9 (d, $^2J_{C,C}$ = 3.3 Hz, CH_3), 18.4 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3379 (br), 2945 (w), 2891 (w), 2835 (w), 1466 (w), 1381 (w), 1177 (w), 1107 (m), 1066 (s), 1000 (s), 863 (m), 813 (w), 763 (w) cm^{-1}; EIMS (70 eV, MSTFA) m/z (%) = 262 (10) $[M–OCH_3]^+$, 232 (5), 218 (52), 204 (10), 192 (22), 172 (10), 163 (5), 147 (86), 130 (38), 114 (12), 101 (13), 89 (24), 73 (100), 59 (34), 45 (30); HRMS (ESI) m/z $[M+Na]^+$ calcd. 172.06613, obsd. 172.06611.

Preparation of [4-^{13}C]deoxyxylulose (9c). According to Meyer et al.,[9] Compound **8d** (14 mg, 0.06 mmol, 1.0 eq.) was dissolved in 2 mL ^{i}PrOH/H_2O (9:1) and treated with Pd/C (6 mg, 5% Pd, 0.003 mmol, 0.05 eq.). The reaction mixture was stirred under an atmosphere of H_2 (40 bar) at 40 °C for 12 h and was then filtered via Celite. Removal of the solvent under reduced pressure yielded **9d** (7 mg, 0.05 mmol, 85%) as colorless oil. $[\alpha]^{24.9}_{D}$ = –3.4 (c 1.50, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.40 (t, $^3J_{H,H}$ = 2.0 Hz, CH), 4.15 – 3.96 (m, 1H, ^{13}CH), 3.73 – 3.59 (m, 2H, CH_2), 2.28 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 215.9 (C_q), 80.0 (d, $^1J_{C,C}$ = 39.4 Hz, CH), 74.3 (^{13}CH), 65.1 (d, $^1J_{C,C}$ = 53.4 Hz, CH_2), 28.6 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3364 (br), 2975 (m), 2935 (m), 1713 (s), 1454 (m), 1243 (w), 1068 (s), 1042 (s), 1010 (s), 987 (s) cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd. 158.05048, obsd. 158.05048.

Preparation of [5-^{13}C]deoxyxylulose (9d). According to Meyer et al.,[9] Compound **8d** (450 mg, 2.0 mmol, 1.0 eq.) was dissolved in 40 mL ^{i}PrOH/H_2O (9:1) and treated with Pd/C (210 mg, 5% Pd, 0.1 mmol, 0.05 eq.). The reaction mixture was stirred under an atmosphere of H_2 (40 bar) at 40 °C for 90 min and was then filtered via Celite. Removal of the solvent under reduced pressure yielded **9d** (268 mg, 1.98 mmol, 99%) as colorless oil. $[\alpha]^{24.9}_{D}$ = –0.5 (c 1.55, MeOH); ^{1}H NMR (400 MHz, D_2O) δ = 4.42 (t, $^3J_{H,H}$ = 1.8 Hz, 1H, CH), 4.22 – 4.17 (m, 1H, CH), 3.77 (ddd, $^1J_{C,H}$ = 143.2 Hz, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 5.7 Hz, 1H, $^{13}CH_2$), 3.66 (ddd, $^1J_{C,H}$ = 144.5 Hz, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 7.2 Hz, 1H, $^{13}CH_2$), 2.30 (s, $^1J_{C,H*}$ = 128.6 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 215.9 (d, $^3J_{C,C}$ = 3.0 Hz, C_q), 80.0 (CH), 74.3 (d, $^1J_{C,C}$ = 43.0 Hz, CH), 65.1 ($^{13}CH_2$), 28.6 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3371 (br), 2938 (w), 2883 (w), 1711 (s), 1417 (m), 1359 (m), 1117 (s), 1076 (m), 1024 (m), 971 (m) cm^{-1}; HRMS (ESI) m/z $[M+Na]^+$ calcd. 158.05048, obsd. 158.05048.

Preparation of ethyl [2-^{13}C]-(E)-4-((tert-butyldimethylsilyl)oxy)but-2-enoate (10b). A solution of diisopropylamine (2.3 g, 22.5 mmol, 1.0 eq.) in 200 mL of anhydrous THF was cooled to 0 °C and treated with a 1.6 M solution of n-BuLi (14.1 mL, 22.5 mmol, 1.0 eq.) in hexane. It was stirred for 1 h at 0 °C and then [2-^{13}C]triethyl phosphonoacetate (**4b**), (5.1 g, 22.5 mmol, 1.0 eq.) was added dropwise. Stirring was continued for further 1 h after which 2-((tert-butyldimethylsilyl)oxy)acetaldehyde (4.4 g, 22.5 mmol, 1.0 eq.) was added dropwise. The reaction mixture was stirred for 3 h at 0 °C and then quenched by addition of water. It was extracted three times with diethyl ether, dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (40:1) afforded compound **10b** (4.0 g, 16.5 mmol, 73%) and minor amounts of the Z-isomer (625 mg, 2.6 mmol, 11%) as colorless liquids. (E)-**10b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.99 (ddt, $^3J_{H,H}$ = 15.5 Hz, $^2J_{C,H}$ = 3.3 Hz, $^3J_{H,H}$ = 3.3 Hz, $^1J_{C,H^*}$ = 156.0 Hz, 1H, CH), 6.09 (ddt, $^1J_{C,H}$ = 164.8 Hz, $^3J_{H,H}$ = 15.5 Hz, $^4J_{H,H}$ = 2.4 Hz, 1H, ^{13}CH), 4.34 (ddd, $^3J_{C,H}$ = 5.0 Hz, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,H}$ = 2.3 Hz, 2H, CH_2), 4.20 (q, $^3J_{H,H}$ = 7.1 Hz, $^1J_{C,H^*}$ = 147.1 Hz, 2H, CH_2), 1.30 (t, $^3J_{H,H}$ = 7.1 Hz, $^1J_{C,H^*}$ = 127.0 Hz, 3H, CH_3), 0.92 (s, $^1J_{C,H^*}$ = 125.2 Hz, $^3J_{Si,H}$ = 5.9 Hz, 9H, 3x CH_3), 0.08 (s, $^1J_{C,H^*}$ = 118.5 Hz, $^2J_{Si,H}$ = 6.3 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7 (C_q, $^1J_{C,C}$ = 75.3 Hz), 147.3 (CH, $^1J_{C,C}$ = 72.6 Hz), 119.6 (^{13}CH), 62.2 (CH_2), 60.3 (CH_2, $^3J_{C,C}$ = 1.0 Hz), 25.8 (3x CH_3), 18.3 (C_q), 14.3 (CH_3), -5.5 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 2955 (w), 2932 (w), 1719 (s), 1636 (w), 1290 (m), 1255 (s), 1133 (s), 958 (m), 833 (s), 776 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 245 (<1) [M]$^+$, 230 (2), 216 (1), 200 (13), 188 (33), 160 (61), 132 (13), 103 (67), 86 (6), 75 (100), 57 (16), 41 (23); GC (BPX-5) I = 1461. (Z)-**10b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.36 (dt, $^3J_{H,H}$ = 11.7 Hz, $^3J_{H,H}$ = 4.7 Hz, $^1J_{C,H^*}$ = 157.4 Hz, 1H, CH), 5.73 (ddt, $^1J_{C,H}$ = 164.5 Hz, $^3J_{H,H}$ = 11.7 Hz, $^4J_{H,H}$ = 2.5 Hz, 1H, ^{13}CH), 4.76 (ddd, $^3J_{H,H}$ = 4.7 Hz, $^4J_{H,H}$ = 2.5 Hz, $^3J_{C,H}$ = 3.8, $^1J_{C,H^*}$ = 145.9 Hz, 2H, CH_2), 4.16 (q, $^3J_{H,H}$ = 7.2 Hz, $^1J_{C,H^*}$ = 147.3 Hz, 2H, CH_2), 1.28 (t, $^3J_{H,H}$ = 7.2 Hz, $^1J_{C,H^*}$ = 127.0 Hz, 3H, CH_3), 0.91 (s, $^1J_{C,H^*}$ = 125.0 Hz, $^3J_{Si,H}$ = 5.8 Hz, 9H, 3x CH_3), 0.08 (s, $^1J_{C,H^*}$ = 118.7 Hz, $^2J_{Si,H}$ = 6.2 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.1 (C_q, $^1J_{C,C}$ = 73.9 Hz), 152.2 (CH, $^1J_{C,C}$ = 68.7 Hz), 118.0 (^{13}CH), 61.7 (CH_2), 60.1 (CH_2, $^3J_{C,C}$ = 1.3 Hz), 25.9 (3x CH_3), 18.3 (C_q), 14.2 (CH_3), -5.3 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 2956 (w), 2931 (w), 1716 (s), 1620 (w), 1255 (m), 1184 (s), 1090 (s), 1034 (m), 835 (s), 806 (m), 775 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 245 (<1) [M]$^+$, 230 (1), 216 (1), 200 (12), 188 (65), 160 (70), 132 (14), 114 (5), 103 (12), 86 (6), 75 (100), 57 (15), 41 (24); GC (BPX-5) I = 1387.

Preparation of ethyl [1-^{13}C]-(E)-4-((tert-butyldimethylsilyl)oxy)but-2-enoate (10a). Same procedure as for **10b** with [1-^{13}C]triethyl phosphonoacetate (**4a**) as starting material. Yield: (E)-**10a** (3.3 g, 13.5 mmol, 76%), (Z)-**10a** (377 mg, 1.5 mmol, 9%). (E)-**10a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (ddt, $^3J_{H,H}$ = 15.5 Hz, $^2J_{C,H}$ = 6.8 Hz, $^3J_{H,H}$ = 3.5 Hz, $^1J_{C,H^*}$ = 156.2 Hz, 1H, ^{13}CH), 6.09 (ddt, $^3J_{H,H}$ = 15.5, $^3J_{C,H}$ = 3.5, $^4J_{H,H}$ = 2.3 Hz, $^1J_{C,H^*}$ = 164.3 Hz, 1H, CH), 4.34 (ddd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,H}$ = 2.3, $^4J_{C,H}$ = 1.6 Hz, 2H, CH_2), 4.21 (dq, $^3J_{H,H}$ = 7.2 Hz, $^3J_{C,H}$ = 3.1 Hz, $^1J_{C,H^*}$ = 147.2 Hz, 2H, CH_2), 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, $^1J_{C,H^*}$ = 127.0 Hz, 3H, CH_3), 0.92 (s, $^1J_{C,H^*}$ = 125.1 Hz, $^3J_{Si,H}$ = 5.9 Hz, 9H, 3x CH_3), 0.08 (s, $^1J_{C,H^*}$ = 118.6 Hz, $^2J_{Si,H}$ = 6.3 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7 ($^{13}C_q$), 147.3 (d, $^2J_{C,C}$ = 1.4 Hz, CH), 119.7 (d, $^1J_{C,C}$ = 74.6 Hz, CH), 62.2 (d, $^2J_{C,C}$ = 6.8 Hz, CH_2), 60.3 (d, $^3J_{C,C}$ = 2.3 Hz, CH_2), 25.8 (3x CH_3), 18.3 (C_q), 14.3 (d, $^3J_{C,C}$ = 2.2 Hz, CH_3), -5.5 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 2955 (w), 2932 (w), 1683 (s), 1659 (w), 1469 (w), 1269 (m), 1138 (s), 1037 (m), 958 (m), 834 (s), 776 (s) cm^{-1}. EIMS (70 eV) m/z (%) = 245 (<1) [M]$^+$, 230 (1), 200 (14), 188 (31), 160 (52), 131 (10), 115 (5), 103 (71), 86 (5), 75 (100), 57 (19), 41 (17). GC (BPX-5) I = 1461; (Z)-**10a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.36 (ddt, $^3J_{C,H}$ = 14.8 Hz, $^3J_{H,H}$ = 11.7 Hz, $^3J_{H,H}$ = 4.8 Hz, $^1J_{C,H^*}$ = 157.3 Hz, 1H, CH), 5.74 (ddt, $^3J_{H,H}$ = 11.7 Hz, $^4J_{H,H}$ = 2.5 Hz, $^2J_{C,H}$ = 2.5 Hz, $^1J_{C,H^*}$ = 164.3 Hz, 1H, CH), 4.76 (ddd, $^3J_{H,H}$ = 4.7 Hz, $^4J_{H,H}$ = 2.5 Hz, $^4J_{C,H}$ = 1.5 Hz, $^1J_{C,H^*}$ = 145.6 Hz, 2H, CH_2), 4.17 (dq, $^3J_{C,H}$ = 3.1 Hz, $^3J_{H,H}$ = 7.2 Hz, $^1J_{C,H^*}$ = 147.2 Hz, 2H, CH_2), 1.28 (t, $^3J_{H,H}$ = 7.2 Hz, $^1J_{C,H^*}$ = 127.0 Hz, 3H, CH_3), 0.91 (s, $^1J_{C,H^*}$ = 125.0 Hz, $^3J_{Si,H}$ = 6.0 Hz, 9H, 3x CH_3), 0.08 (s, $^1J_{C,H^*}$ = 118.5 Hz, $^2J_{Si,H}$ = 6.2 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.2 ($^{13}C_q$), 152.2 (d, $^2J_{C,C}$ = 0.9 Hz, CH), 118.0 (d, $^1J_{C,C}$ = 73.8 Hz, CH), 61.7 (d, $^2J_{C,C}$ = 1.8 Hz, CH_2), 60.1 (d, $^3J_{C,C}$ = 2.3 Hz, CH_2), 25.9 (3x CH_3), 18.3 (C_q), 14.2 (d, $^3J_{C,C}$ = 2.2 Hz, CH_3), -5.3 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 2956 (w), 2932 (w), 1677 (m), 1645 (w), 1468 (w), 1406 (w), 1255 (m), 1158 (m), 1090 (s), 1035 (m), 835 (s), 775 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 245 (<1) [M]$^+$, 230 (1), 200 (14), 188 (31), 160 (52), 131 (10), 115 (5), 99 (14), 86 (5), 75 (100), 57 (19), 41 (17); GC (BPX-5) I = 1387.

Preparation of [2-^{13}C]-(E)-4-((tert-butyldimethylsilyl)oxy)but-2-en-1-ol (11b). Compound **10b** (4.0 g, 16.3 mmol, 1.0 eq.) was dissolved in 160 mL of anhydrous THF and cooled to -78 °C. A 1 M solution of DIBAL-H (34.2 mL, 34.2 mmol, 2.1 eq.) in hexane was added dropwise and stirring was continued for 2 h at -78 °C. It was warmed to 0 °C and then quenched with a sat. solution of sodium tartrate. The reaction mixture was extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (4:1) yielded **11b** (3.2 g, 15.5 mmol, 95%) as colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.86 (ddtt, $^1J_{C,H}$ = 156.2, $^3J_{H,H}$ = 15.4 Hz, $^3J_{H,H}$ = 5.5 Hz, $^4J_{H,H}$ = 1.8 Hz, 1H, ^{13}CH), 5.82 – 5.75 (m, 1H, CH), 4.21 – 4.13 (m, 4H, 2x CH_2), 1.60

(br s, 1H, OH), 0.92 (s, $^{1}J_{C,H*}$ = 125.2 Hz, $^{3}J_{Si,H}$ = 6.0 Hz, 9H, 3x CH_3), 0.08 (s, $^{1}J_{C,H*}$ = 118.5 Hz, $^{2}J_{Si,H}$ = 6.2 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 130.9 (CH, $^{1}J_{C,C}$ = 84.2 Hz), 129.0 (^{13}CH), 63.1 (CH_2), 63.1 (CH_2, $^{1}J_{C,C}$ = 46.5 Hz), 25.9 (3x CH_3), 18.4 (C_q), -5.3 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3340 (br), 2954 (w), 2930 (w), 1465 (w) 1254 (m), 1088 (m), 833 (s), 775 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 203 (<1) $[M]^+$, 185 (1), 146 (10), 128 (9), 112 (2), 100 (3), 75 (100), 57 (7), 41 (19); GC (BPX-5) I = 1303.

Preparation of [1-^{13}C]-(E)-4-((tert-butyldimethylsilyl)oxy)but-2-en-1-ol (11a). Same procedure as for **11b** with **10a** as starting material. Yield: (2.67 g, 13.1 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.92 – 5.76 (m, 2H, 2x CH), 4.20 – 4.17 (m, 2H, CH_2), 4.07 (dddt, $^{1}J_{C,H}$ = 142.3 Hz, $^{3}J_{H,H}$ = 5.2, $^{4}J_{H,H}$ = 1.2, $^{5}J_{H,H}$ = 0.9, 2H, $^{13}CH_2$), 1.54 (br s, 1H, OH), 0.92 (s, $^{1}J_{C,H*}$ = 125.1 Hz, $^{3}J_{Si,H}$ = 5.9, 9H, 3x CH_3), 0.08 (s, $^{1}J_{C,H*}$ = 118.6 Hz, $^{2}J_{Si,H}$ = 6.2 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 131.0 (d, $^{2}J_{C,C}$ = 1.3 Hz, CH), 129.0 (d, $^{1}J_{C,C}$ = 46.4 Hz, CH), 63.3 ($^{13}CH_2$), 63.3 (d, $^{1}J_{C,C}$ = 46.2 Hz, CH_2), 25.9 (3x CH_3), 18.4 (C_q), -5.2 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3283 (br), 2919 (w), 2863 (w), 1415 (w), 1366 (w), 1225 (w), 1072 (s), 969 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 203 (<1) $[M]^+$, 171 (1), 146 (14), 128 (14), 112 (2), 99 (5), 88 (3), 75 (100), 57 (12), 41 (18); GC (BPX-5) I = 1303.

Preparation of [3-^{13}C]-(E)-((4-(benzyloxy)but-2-en-1-yl)oxy)(tert-butyl)dimethylsilane (12b). NaH (60% in mineral oil, 1.2 g, 30.8 mmol, 2.0 eq.) was suspended in 40 mL of anhydrous THF and cooled to 0 °C. Alcohol **11b** (3.1 g, 15.4 mmol, 1.0 eq.) was added dropwise. After gas evolution diminished (~15 min) benzyl bromide (5.3 g, 30.8 mmol, 2.0 eq.) and anhydrous DMF (2.4 mL, 30.8 mmol, 2.0 eq.) were added and stirring was continued for 3 h at room temperature. The reaction mixture was quenched by the addition of a sat. aqueous solution of NH_4Cl followed by extraction with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (40:1) yielded **12b** (4.3 g, 14.5 mmol, 94%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.25 (m, 5H, 5x CH), 5.85 (ddtt, $^{1}J_{C,H}$ = 156.3 Hz, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = 5.9 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1H, ^{13}CH), 5.89 – 5.81 (m, 1H, CH), 4.51 (s, $^{1}J_{C,H*}$ = 141.1 Hz, 2H, CH_2), 4.21 – 4.18 (m, 2H, CH_2), 4.05 – 4.02 (m, 2H, CH_2), 0.91 (s, $^{1}J_{C,H*}$ = 125.1 Hz, $^{3}J_{Si,H}$ = 5.8 Hz, 9H, 3x CH_3), 0.07 (s, $^{1}J_{C,H*}$ = 118.4 Hz, $^{2}J_{Si,H}$ = 6.3 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.4 (C_q), 132.6 (CH, $^{1}J_{C,C}$ = 73.3 Hz), 128.4 (2x CH), 127.7 (2x CH), 127.6 (CH), 126.3 (^{13}CH), 72.1 (CH_2, $^{3}J_{C,C}$ = 3.1 Hz), 70.2 (CH_2, $^{1}J_{C,C}$ = 48.1 Hz), 63.2 (CH_2), 25.9 (3x CH_3), 18.4 (C_q), -5.2 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3031 (w), 2954 (w), 2855 (w), 1485 (w), 1359 (w), 1253 (m), 1089 (m), 1006 (w), 834 (s), 775 (s), 696 (m), 671 (m) cm^{-1}; EIMS (70 eV) m/z (%) = 293 (<1) $[M]^+$, 236 (7), 218 (1), 165 (40), 135 (41), 114 (11), 101 (17), 91 (100), 75 (35), 59 (9), 41 (11); GC (BPX-5) I = 1913.

Preparation of [4-^{13}C]-(E)-((4-(benzyloxy)but-2-en-1-yl)oxy)(tert-butyl)dimethylsilane (12a). Same procedure as for **12b** with **11a** as starting material. Yield: (3.64 g, 12.4 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.26 (m, 5H, 5x CH), 5.84 – 5.81 (m, 2H, 2x CH), 4.52 (d, $^{3}J_{C,H}$ = 4.0 Hz, $^{1}J_{C,H*}$ = 141.2 Hz, 2H, CH_2), 4.22 – 3.85 (m, $^{1}J_{C,H}$ = 141.1 Hz, 2H, $^{13}CH_2$), 4.20 – 4.19 (m, 2H, CH_2), 0.91 (s, $^{1}J_{C,H*}$ = 125.2 Hz, $^{3}J_{Si,H}$ = 5.9 Hz, 9H, 3x CH_3), 0.07 (s, $^{1}J_{C,H*}$ = 118.5 Hz, $^{2}J_{Si,H}$ = 6.1 Hz, 6H, 2x CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.4 (d, $^{3}J_{C,C}$ = 2.8 Hz, C_q), 132.6 (d, $^{2}J_{C,C}$ = 1.6 Hz, CH), 128.4 (2x CH), 127.7 (2x CH), 127.6 (CH), 126.3 (d, $^{1}J_{C,C}$ = 47.4 Hz, CH), 72.1 (d, $^{2}J_{C,C}$ = 1.4 Hz, CH_2), 70.2 ($^{13}CH_2$), 63.2 (d, $^{3}J_{C,C}$ = 6.4 Hz, CH_2), 26.0 (3x CH_3), 18.4 (C_q), -5.2 (2x CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3032 (w), 2954 (w), 2886 (w), 1460 (w), 13880 (w), 1253 (m), 1096 (m), 969 (m), 834 (s), 776 (s), 734 (m), 671 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 293 (<1) $[M]^+$, 236 (13), 218 (3), 165 (62), 135 (60), 114 (24), 101 (28), 91 (100), 75 (48), 57 (15), 41 (14); GC (BPX-5) I = 1913.

Preparation of [3-^{13}C]-(E)-4-(benzyloxy)but-2-en-1-ol (13b). Compound **12b** (4.2 g, 14.4 mmol, 1.0 eq.) was dissolved in 140 mL THF and cooled to 0 °C. A 1 M solution of TBAF (15.8 mL, 15.8 mmol, 1.1 eq.) in THF was added and stirred for 2 h at 0 °C. The reaction mixture was diluted with H_2O and extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (2:1) yielded **13b** (2.3 g, 11.9 mmol, 89%) as colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 – 7.27 (m, 5H, 5x CH), 5.85 (ddtt, $^{1}J_{C,H}$ = 155.6 Hz, $^{3}J_{H,H}$ = 15.5 Hz, $^{3}J_{H,H}$ = 5.8 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H, ^{13}CH), 5.95 – 5.88 (m, 1H, CH), 4.51 (s, $^{1}J_{C,H*}$ = 141.4 Hz, 2H, CH_2), 4.17 – 4.14 (m, 2H, CH_2), 4.06 – 4.03 (m, 2H, CH_2), 1.84 (br s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.1 (C_q), 132.2 (d, $^{1}J_{C,C}$ = 71.8 Hz, CH), 128.4 (2x CH), 127.7 (^{13}CH), 127.6 (2x CH), 127.3 (CH), 72.3 (CH_2, $^{3}J_{C,C}$ = 3.2 Hz), 70.0 (CH_2, $^{1}J_{C,C}$ = 47.0 Hz), 62.9 (CH_2, $^{2}J_{C,C}$ = 1.0 Hz) ppm; IR (ATR) $\tilde{\nu}$ = 3377 (br), 3063 (w), 2920 (w), 1496 (w), 1359 (w), 1091 (s), 1000 (s), 967 (s), 736 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 179 (<1) $[M]^+$, 161 (1), 142 (1), 130 (4), 108 (12), 91 (100), 77 (22), 65 (23), 51 (16), 40 (15); GC (BPX-5) I = 1593.

Preparation of [4-^{13}C]-(E)-4-(benzyloxy)but-2-en-1-ol (13a). Same procedure as for **13b** with **12a** as starting material. Yield: (2.1 g, 11.7 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 – 7.25 (m, 5H, 5x CH), 5.95 – 5.79 (m, 2H, 2x CH), 4.52 (d, $^{3}J_{C,H}$ = 4.1 Hz, $^{1}J_{C,H^*}$ =141.5 Hz, 2H, CH_2), 4.14 – 4.13 (m, 2H, CH_2), 4.03 (dddt, $^{1}J_{C,H}$ = 141.6 Hz, $^{3}J_{C,H}$ = 5.4 Hz, $^{4}J_{H,H}$ = 1.2 Hz, $^{5}J_{H,H}$ = 1.2 Hz, 2H, $^{13}CH_2$), 1.81 (br s, 1H, OH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2 (d, $^{3}J_{C,C}$ = 3.0 Hz, C_q), 132.2 (d, $^{2}J_{C,C}$ = 1.5 Hz, CH), 128.4 (2x CH), 127.8 ($^{1}J_{C,C}$ = 48.2 Hz, CH), 127.7 (2x CH), 127.6 (CH), 72.3 (d, $^{2}J_{C,C}$ = 1.4 Hz, CH_2), 70.0 ($^{13}CH_2$), 62.9 (d, $^{3}J_{C,C}$ = 6.4 Hz, CH_2) ppm; IR (ATR) $\tilde{\nu}$ = 3377 (br), 3063 (w), 3030 (w), 2852 (w), 1496 (w), 1453 (w), 1355 (w), 1206 (w), 1088 (s), 998 (s), 736 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 179 (<1) $[M]^+$, 134 (3), 108 (11), 91 (100), 77 (18), 65 (19), 51 (10), 39 (9); GC (BPX-5) I = 1593.

Preparation of [3-^{13}C]-(E)-4-(benzyloxy)but-2-enal (14b). According to Fournier et al.,[6] a solution of IBX (3.9 g, 14.0 mmol, 1.1 eq.) in 120 mL anhydrous DMSO was treated with alcohol **13b** (2.3 g, 12.8 mmol, 1.0 eq.) and stirred over night at room temperature. The reaction mixture was carefully diluted with diethyl ether and a sat. aqueous solution of $NaHCO_3$. The aqueous layer was extracted three times with diethyl ether and the combined organic layers were dried over $MgSO_4$ before concentration under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (5:1) yielded aldehyde **14b** (1.2 g, 6.9 mmol, 54%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.56 (dd, $^{3}J_{H,H}$ = 7.9 Hz, $^{3}J_{C,H}$ = 1.0 Hz, $^{1}J_{C,H^*}$ = 172.4 Hz, 1H, CHO), 7.36 – 7.26 (m, 5H, 5x CH), 6.82 (ddt, $^{1}J_{C,H}$ = 153.7, $^{3}J_{H,H}$ = 15.9 Hz, $^{3}J_{H,H}$ = 4.3 Hz, 1H, ^{13}CH), 6.38 (ddt, $^{3}J_{H,H}$ = 15.9, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 2.0 Hz, 1H, CH), 4.57 (s, $^{1}J_{C,H^*}$ = 142.2 Hz, 2H, CH_2), 4.26 (ddd, $^{2}J_{C,H}$ = 5.2 Hz, $^{3}J_{H,H}$ = 4.2 Hz, $^{4}J_{H,H}$ = 2.0 Hz, 2H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.3 (CHO, $^{2}J_{C,C}$ = 4.3 Hz), 153.0 (^{13}CH), 137.4 (C_q), 131.8 (d, $^{1}J_{C,C}$ = 68.9 Hz, CH), 128.5 (2x CH), 127.9 (CH), 127.6 (2x CH), 73.0 (CH_2, $^{3}J_{C,C}$ = 3.6 Hz), 68.5 (CH_2, $^{1}J_{C,C}$ = 46.1 Hz) ppm; IR (ATR) $\tilde{\nu}$ = 3064 (w), 2842 (w), 1684 (s), 1496 (w), 1359 (w), 1105 (s), 1016 (m), 967 (s), 737 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 177 (<1) $[M]^+$, 159 (2), 147 (12), 130 (6), 119 (4), 105 (9), 91 (100), 77 (24), 65 (23), 51 (18), 40 (20); GC (BPX-5) I = 1553.

Preparation of [4-^{13}C]-(E)-4-(benzyloxy)but-2-enal (14a). Same procedure as for **14b** with **13a** as starting material. Yield: (1.84 g, 10.4 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.58 (d, $^{3}J_{H,H}$ = 7.9 Hz, $^{1}J_{C,H^*}$ = 172.4 Hz, $^{3}J_{C,H^*}$ = 25.8 Hz, 1H, CHO), 7.39 – 7.28 (m, 5H, 5x CH), 6.85 (ddt, $^{3}J_{H,H}$ = 15.8 Hz, $^{2}J_{C,H}$ = 5.2, $^{3}J_{H,H}$ = 4.2 Hz, 1H, CH), 6.41 (dddt, $^{3}J_{H,H}$ = 15.8 Hz, $^{3}J_{H,H}$ = 7.8 Hz, $^{3}J_{C,H}$ = 5.4 Hz, $^{4}J_{H,H}$ = 1.9 Hz, 1H, CH), 4.60 (d, $^{3}J_{C,H}$ = 4.3 Hz, $^{1}J_{C,H^*}$ = 141.9 Hz, 2H, CH_2), 4.28 (ddd, $^{1}J_{C,H}$ = 141.9 Hz, $^{3}J_{H,H}$ = 4.2 Hz, $^{4}J_{H,H}$ = 1.9 Hz, 2H, $^{13}CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.2 (d, $^{3}J_{C,C}$ = 7.3 Hz, C_q), 152.9 (d, $^{1}J_{C,C}$ = 46.0 Hz, CH), 137.4 (d, $^{3}J_{C,C}$ = 2.8 Hz, C_q), 131.8 (CH), 128.5 (2x CH), 128.0 (CH), 127.7 (2x CH), 73.0 (d, $^{2}J_{C,C}$ = 1.3 Hz, CH_2), 68.6 ($^{13}CH_2$) ppm; IR (ATR) $\tilde{\nu}$ = 3064 (w), 3032 (w), 2860 (w), 2835 (w), 1686 (s), 1496 (w), 1453 (w), 1354 (w), 1206 (w), 1097 (s), 1024 (m), 965 (s), 738 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 177 (<1) $[M]^+$, 146 (12), 131 (6), 119 (3), 105 (7), 91 (100), 77 (21), 65 (22), 51 (11), 40 (11); GC (BPX-5) I = 1553.

Preparation of [4-^{13}C]-(E)-5-(benzyloxy)but-3-en-2-ol (15b). According to Stipa et al.,[7] a 3 M solution of MeMgBr (6.8 mL, 20.3 mmol, 3.0 eq.) was diluted with 60 mL of anhydrous Et_2O and cooled to 0 °C. Slowly aldehyde **14b** (1.2 g, 6.76 mmol, 1.0 eq.) in 20 mL of anhydrous Et_2O was added and the reaction mixture stirred over night at room temperature. It was quenched by the carefully addition of a sat. aqueous solution of NH_4Cl. It was extracted three times with diethyl ether, dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (3:1) yielded **15b** (1.12 g, 5.82 mmol, 86%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.26 (m, 5H, 5x CH), 5.78 (ddt, $^{1}J_{C,H}$ = 155.4 Hz, $^{3}J_{H,H}$ = 15.6 Hz, $^{3}J_{H,H}$ = 5.8 Hz, 1H, ^{13}CH), 5.81 (dddt, $^{3}J_{H,H}$ = 15.6 Hz, $^{3}J_{H,H}$ = 6.1 Hz, $^{2}J_{C,H}$ = 2.6 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 1H, CH), 4.52 (s, 2H, CH_2), 4.36 – 4.28 (m, 1H, CH), 4.01 (dddd, $^{3}J_{H,H}$ = 5.7 Hz, $^{2}J_{C,H}$ = 4.5 Hz, $^{4}J_{H,H}$ = 1.4 Hz, $^{5}J_{H,H}$ = 0.8 Hz, 2H, CH_2), 1.73 (br s, 1H, OH), 1.27 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2 (C_q), 137.1 (CH, $^{1}J_{C,C}$ = 72.0 Hz), 128.4 (2x CH), 127.7 (2x CH), 127.6 (CH), 126.2 (^{13}CH), 72.3 (CH_2, $^{3}J_{C,C}$ = 3.3 Hz), 70.1 (CH_2, $^{1}J_{C,C}$ = 48.0 Hz), 68.2 (CH, $^{2}J_{C,C}$ = 1.1 Hz), 23.2 (CH_3, $^{3}J_{C,C}$ = 3.1 Hz) ppm; IR (ATR) $\tilde{\nu}$ = 3381 (br), 3030 (w), 2972 (w), 1496 (w), 1453 (w), 1362 (w), 1111 (m), 1060 (s), 968 (s), 736 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 193 (<1) $[M]^+$, 175 (2), 160 (1), 146 (1), 130 (5), 108 (11), 91 (100), 77 (15), 65 (16), 51 (14), 39 (13); GC (BPX-5) I = 1601.

Preparation of [5-^{13}C]-(E)-5-(benzyloxy)but-3-en-2-ol (15a). Same procedure as for **15b** with **14a** as starting material. Yield: (1.79 g, 9.3 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 – 7.25 (m, 5H, 5x CH), 5.85 – 5.73 (m, 2H, 2x CH), 4.52 (d, $^{3}J_{C,H}$ = 4.1 Hz, 2H, CH_2), 4.35 – 4.29 (m, 1H, CH), 4.01 (ddd, $^{1}J_{C,H}$ = 141.3 Hz, $^{3}J_{C,H}$ = 4.4 Hz, $^{4}J_{C,H}$ = 0.8 Hz, 2H, $^{13}CH_2$), 1.70 (br s, 1H, OH), 1.28 (d, $^{3}J_{H,H}$ = 6.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.2 (d, $^{3}J_{C,C}$ = 2.8 Hz, C_q), 137.2 (d, $^{2}J_{C,C}$ = 1.4 Hz, CH), 128.4 (2x CH), 127.7 (2x CH), 127.6 (CH), 126.2 (d, $^{1}J_{C,C}$ = 48.0 Hz, CH), 70.1 ($^{13}CH_2$), 68.2 (d, $^{3}J_{C,C}$ = 6.1 Hz, CH), 23.2 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3375 (br), 3064 (w), 3031 (w), 2972 (w), 1497 (w), 1362 (w), 1108 (m), 1060 (s), 1026 (s), 969 (s),

737 (s), 697 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 193 (<1) $[M]^+$, 175 (3), 160 (2), 148 (2), 131 (4), 108 (34), 91 (100), 77 (35), 65 (38), 51 (19), 43 (48); GC (BPX-5) I = 1601.

Preparation of [4-^{13}C]-(E)-5-(benzyloxy)but-3-en-2-one (7c). To a solution of IBX (1.74 g, 6.23 mmol, 1.1 eq.) in 60 mL of anhydrous DMSO was added alcohol **15b** (1.1 g, 5.7 mmol, 1.0 eq.) and the reaction was stirred for 4 h at room temperature. The reaction was stopped by addition of a sat. aqueous solution of $NaHCO_3$ and extracted three times with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. Purification of the residue by flash silica gel chromatography with hexane/EtOAc (5:1) yielded **7c** (955 mg, 5.0 mmol, 88%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.29 (m, 5H, 5x CH), 6.80 (ddt, $^1J_{C,H}$ = 155.3 Hz, $^3J_{H,H}$ = 16.1 Hz, $^3J_{H,H}$ = 4.5 Hz, 1H, ^{13}CH), 6.38 – 6.32 (m, 1H, CH), 4.57 (s, $^1J_{C,H^*}$ = 141.8 Hz, 2H, CH_2), 4.20 (ddd, $^2J_{C,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.6 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, CH_2), 2.27 (d, $^4J_{H,H}$ = 0.6 Hz, $^1J_{C,H^*}$ = 127.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.2 (C_q, $^2J_{C,C}$ = 1.7 Hz), 143.0 (^{13}CH), 137.6 (C_q), 130.3 (CH, $^1J_{C,C}$ = 68.8 Hz), 128.5 (2x CH), 127.9 (CH), 127.7 (2x CH), 73.0 (CH_2, $^3J_{C,C}$ = 3.7 Hz), 68.8 (CH_2, $^1J_{C,C}$ = 46.2 Hz), 27.2 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3063 (w), 2858 (w), 1673 (s), 1610 (m), 1452 (w), 1358 (s), 1253 (s), 1114 (s), 1025 (m), 970 (m), 737 (s), 698 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 191 (<1) $[M]^+$, 161 (4), 146 (8), 133 (6), 116 (2), 105 (6), 91 (100), 77 (18), 65 (19), 51 (15), 43 (28); GC (BPX-5) I = 1635.

Preparation of [5-^{13}C]-(E)-5-(benzyloxy)but-3-en-2-one (7d). Same procedure as for **7c** with **15a** as starting material. Yield: (1.66 g, 8.7 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 – 7.28 (m, 5H, 5x CH), 6.80 (ddt, $^3J_{H,H}$ = 16.1 Hz, $^2J_{C,H}$ = 5.0 Hz, $^3J_{H,H}$ = 4.5 Hz, 1H, CH), 6.35 (ddt, $^3J_{H,H}$ = 16.1 Hz, $^3J_{C,H}$ = 6.1 Hz, $^4J_{H,H}$ = 1.9 Hz, 1H, CH), 4.57 (d, $^3J_{C,H}$ = 4.3 Hz, 2H, CH_2), 4.20 (ddd, $^1J_{C,H}$ = 142.1 Hz, $^3J_{H,H}$ = 4.5 Hz, $^4J_{H,H}$ = 2.0 Hz, 2H, $^{13}CH_2$), 2.26 (s, $^1J_{C,H^*}$ = 127.3 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.1 (d, $^3J_{C,C}$ = 6.0 Hz, C_q), 143.0 (d, $^1J_{C,C}$ = 46.1 Hz, CH), 137.6 (d, $^3J_{C,C}$ = 2.8 Hz, C_q), 130.3 (CH), 128.5 (2x CH), 127.9 (CH), 127.7 (2x CH), 68.8 ($^{13}CH_2$), 27.2 (CH_3) ppm; IR (ATR) $\tilde{\nu}$ = 3063 (w), 3031 (w), 2859 (w), 1674 (s), 1632 (m), 1496 (w), 1358 (m), 1253 (s), 1106 (s), 968 (m), 738 (s), 698 (s) cm^{-1}; EIMS (70 eV) m/z (%) = 191 (<1) $[M]^+$, 161 (2), 145 (6), 133 (6), 105 (5), 91 (100), 77 (15), 65 (19), 43 (29); GC (BPX-5) I = 1635.

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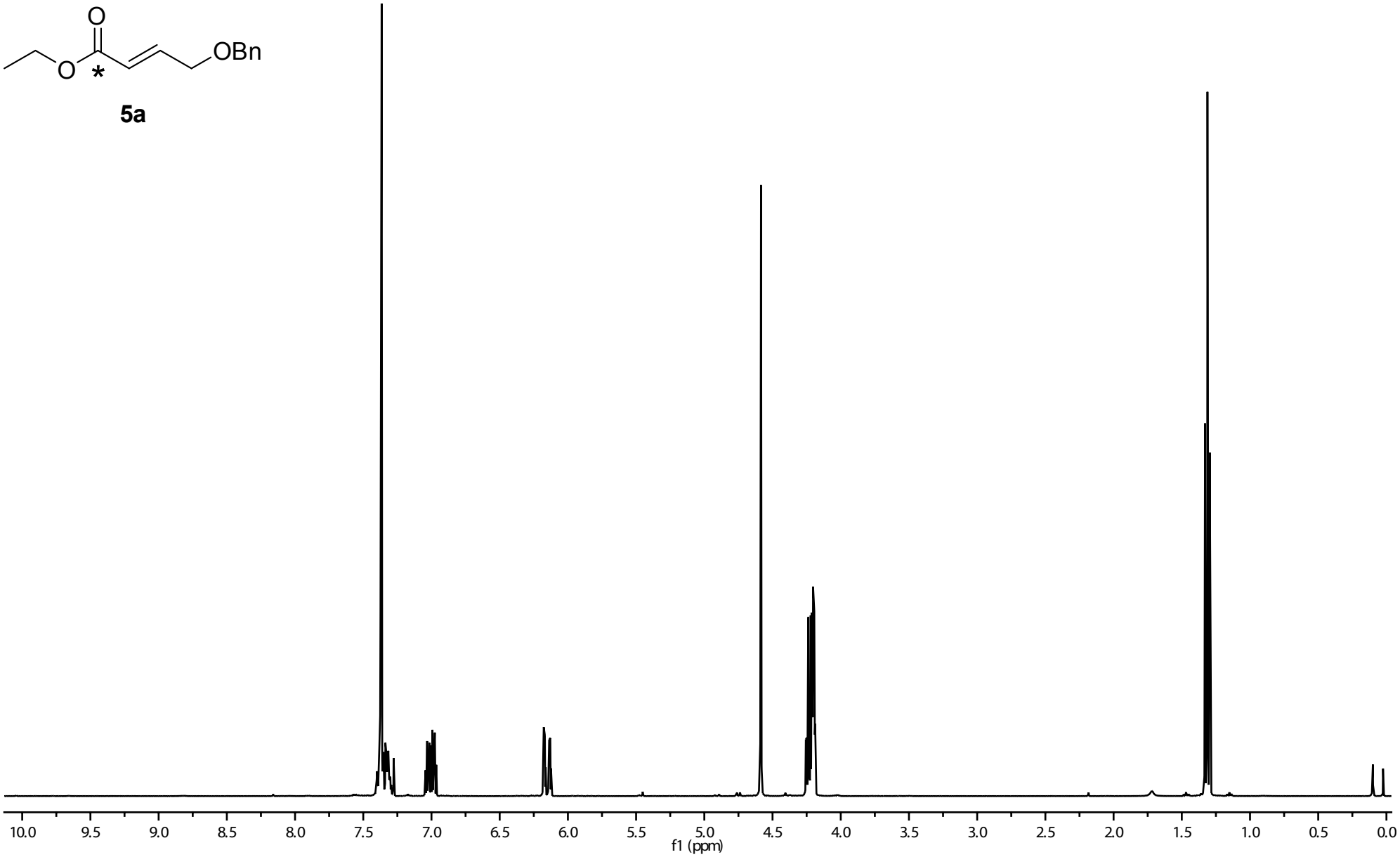
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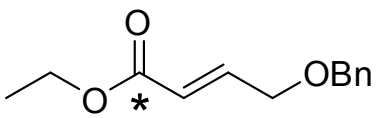
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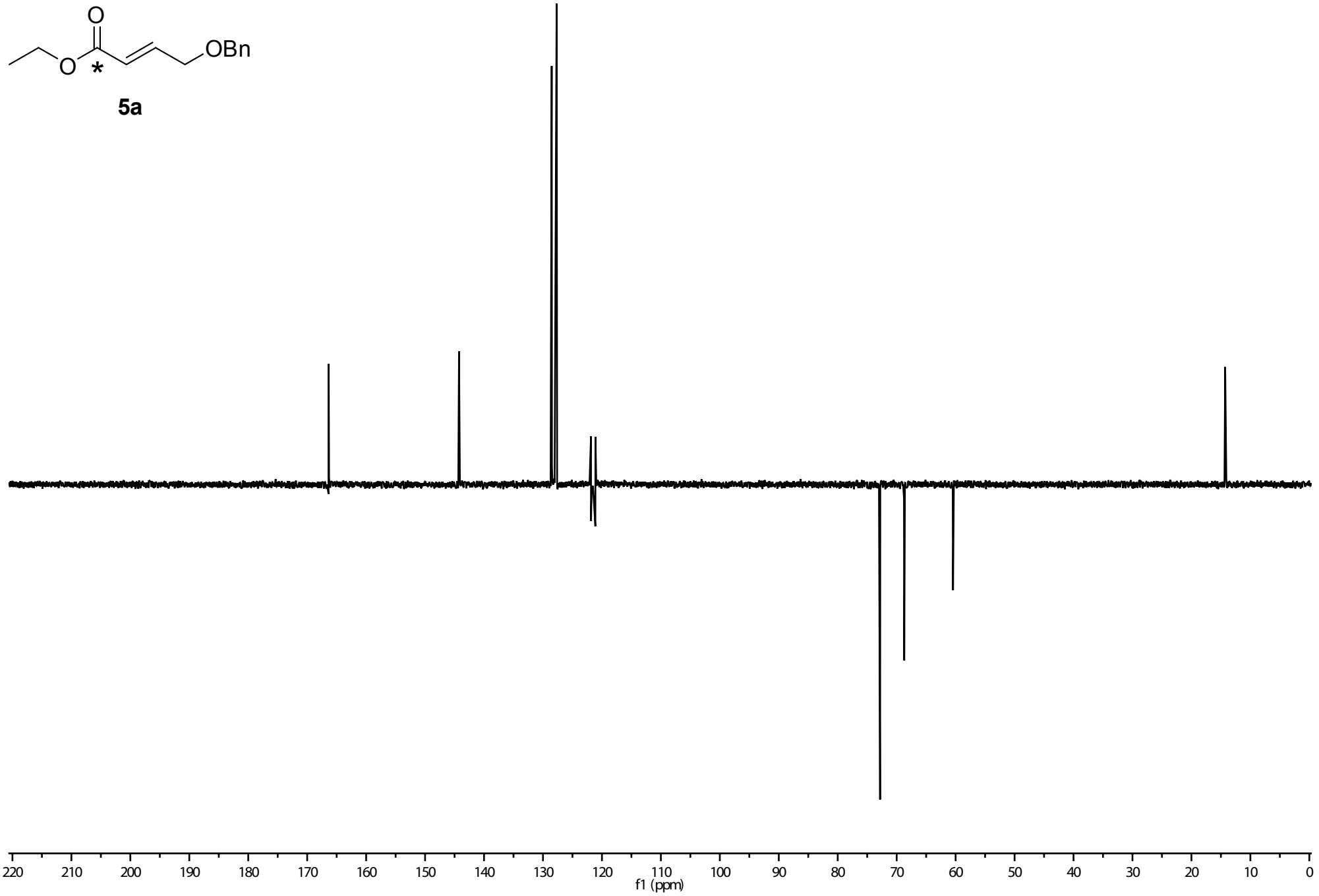
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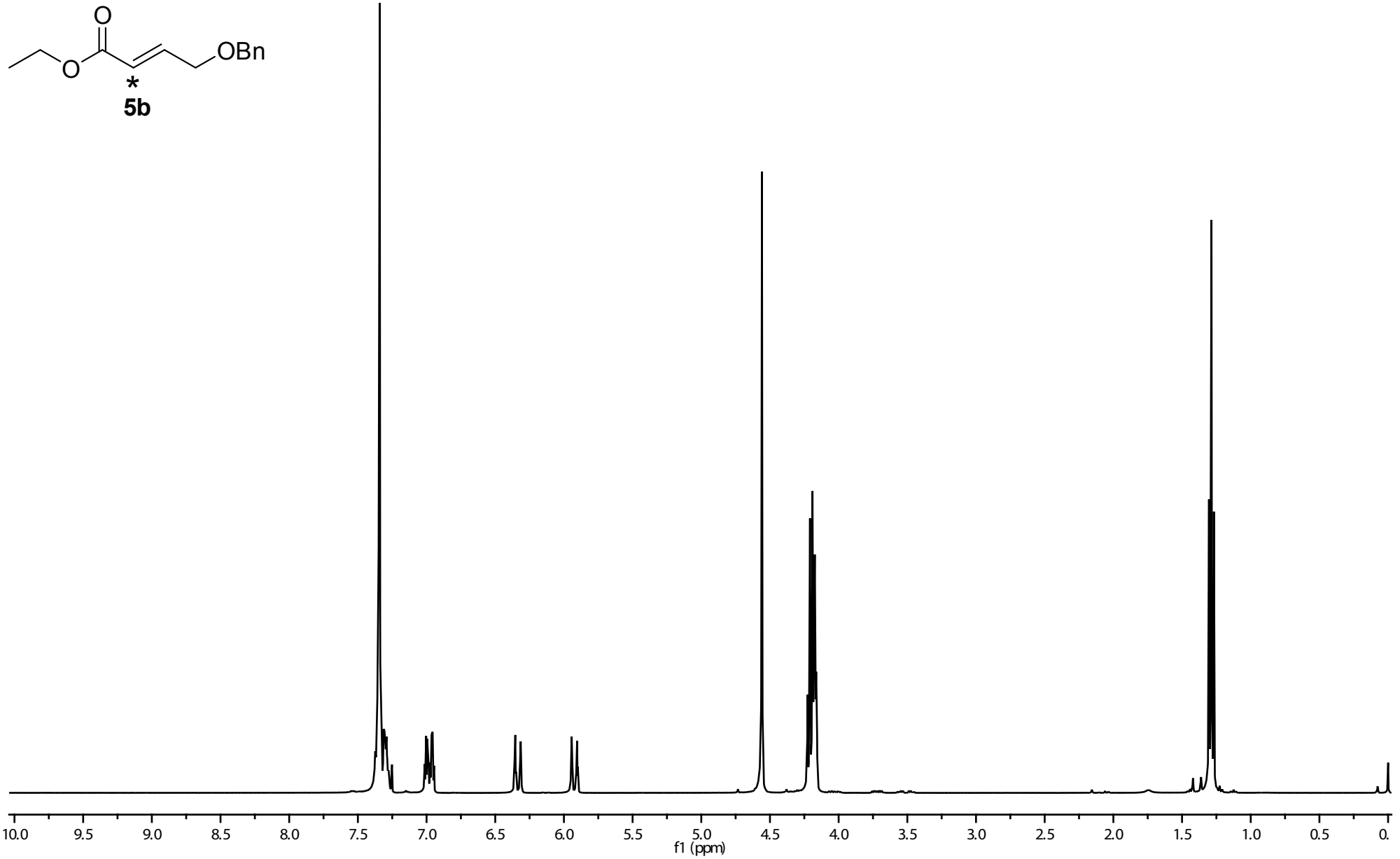
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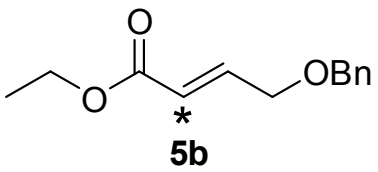
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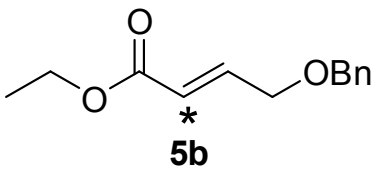
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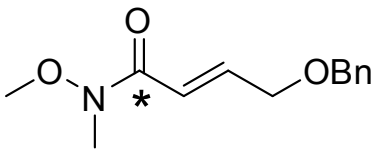
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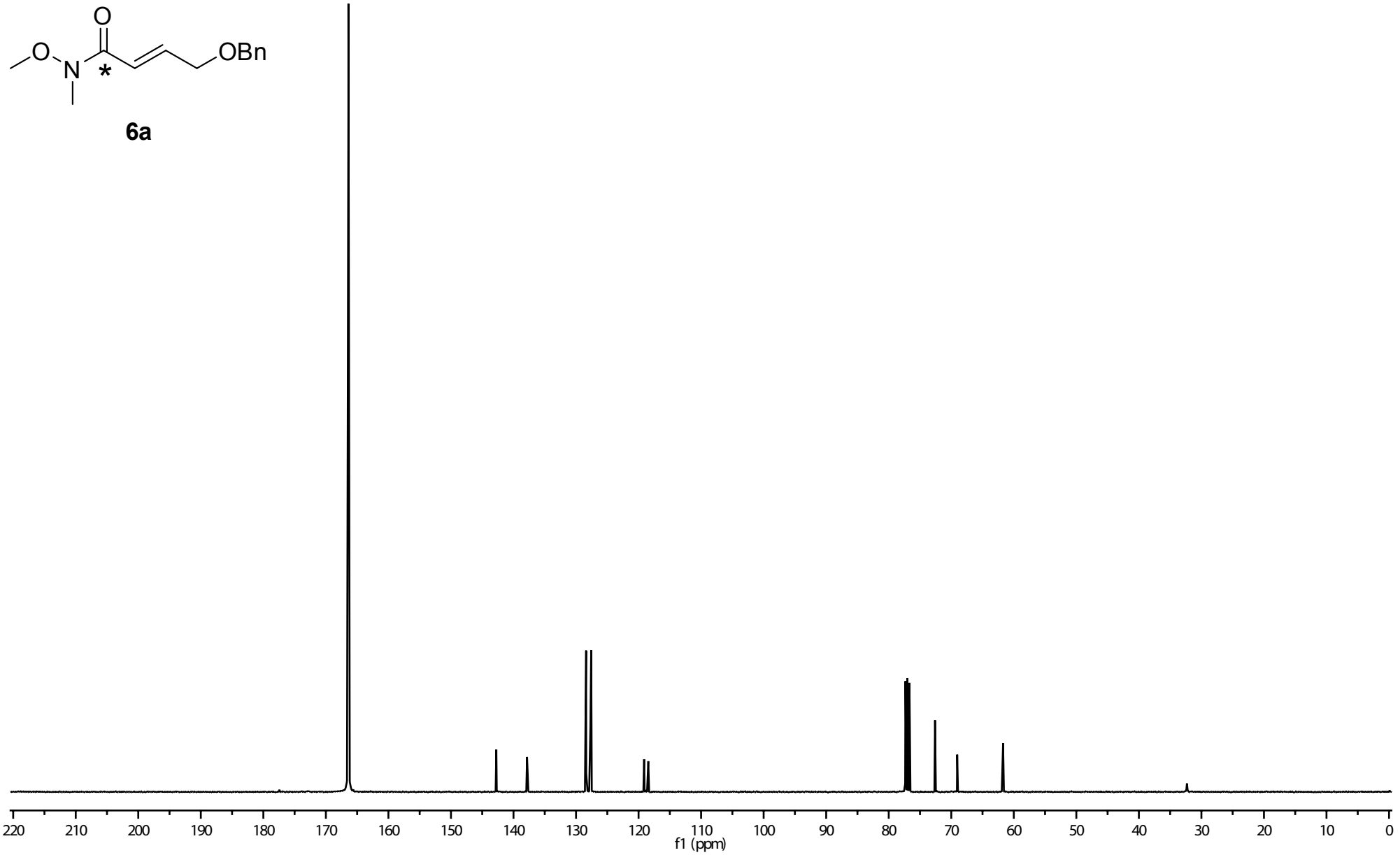
f1 (ppm)


O
O
N
*
OBn
6a
220
210
200
190
180
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90
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50
40
30
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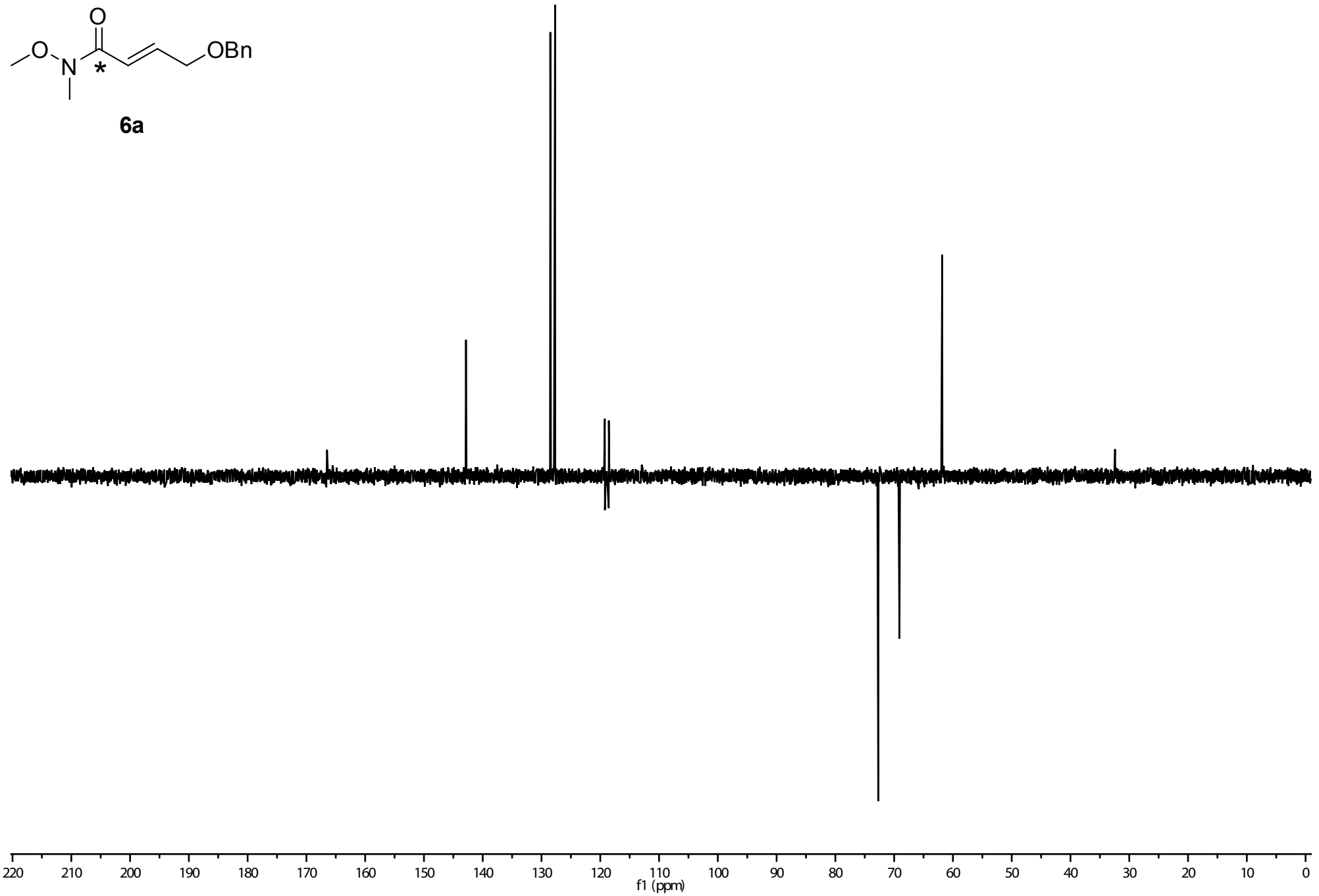
f1 (ppm)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O
N
*
OBn
6a
220
210
200
190
180
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90
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70
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40
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10
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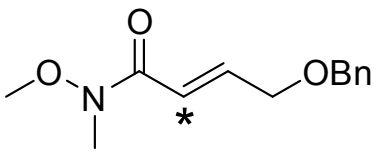
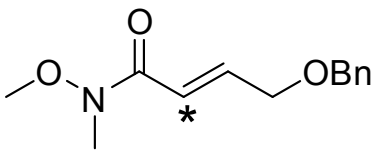
f1 (ppm)


O
O
N
OBn
*

6b

10.0
9.5
9.0
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
f1 (ppm)


O
O
N
OBn
*

6b

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210
200
190
180
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130
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90
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70
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40
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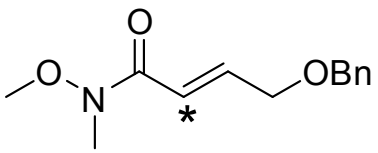
f1 (ppm)


O
O
N
OBn
*

6b

220
210
200
190
180
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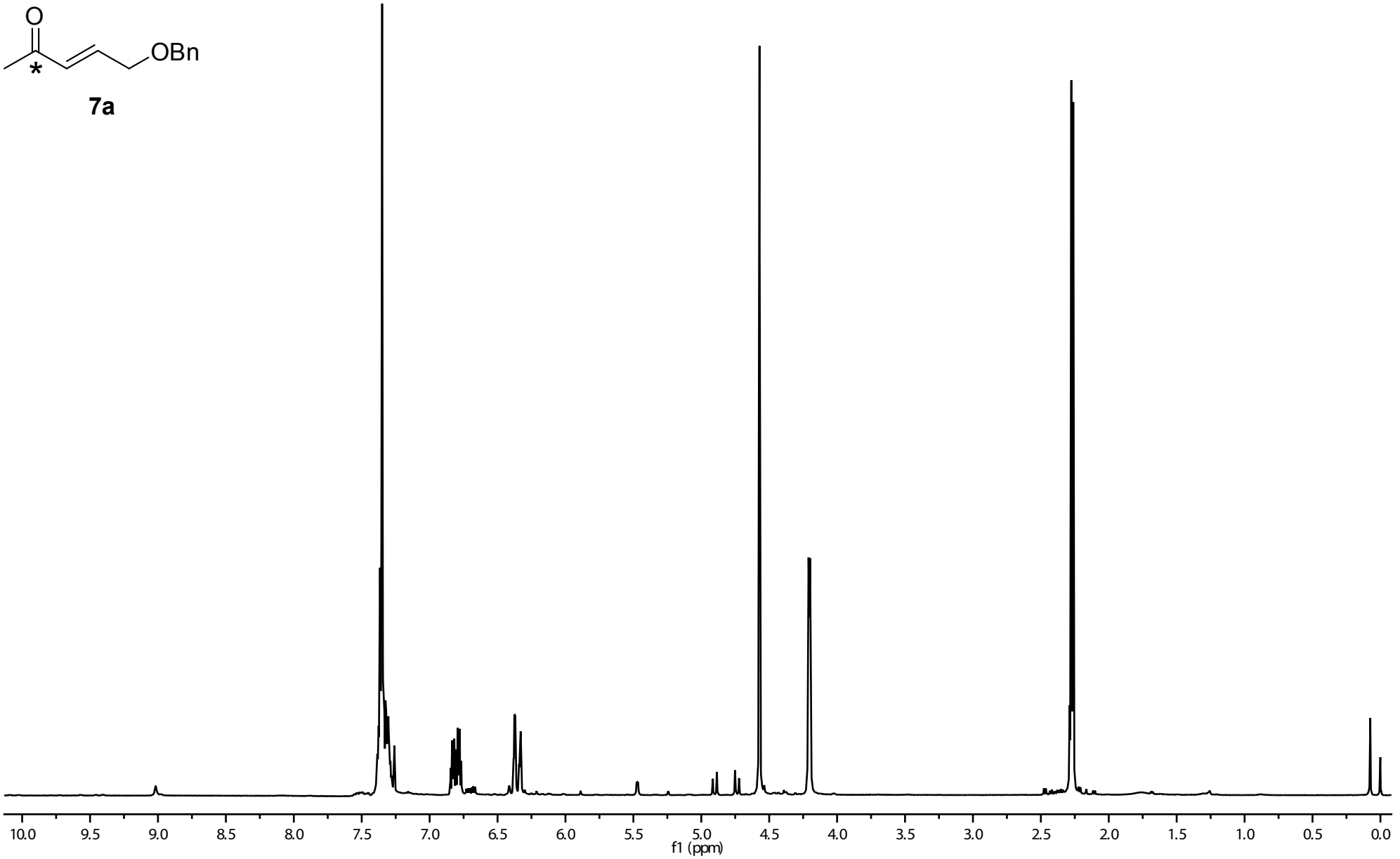
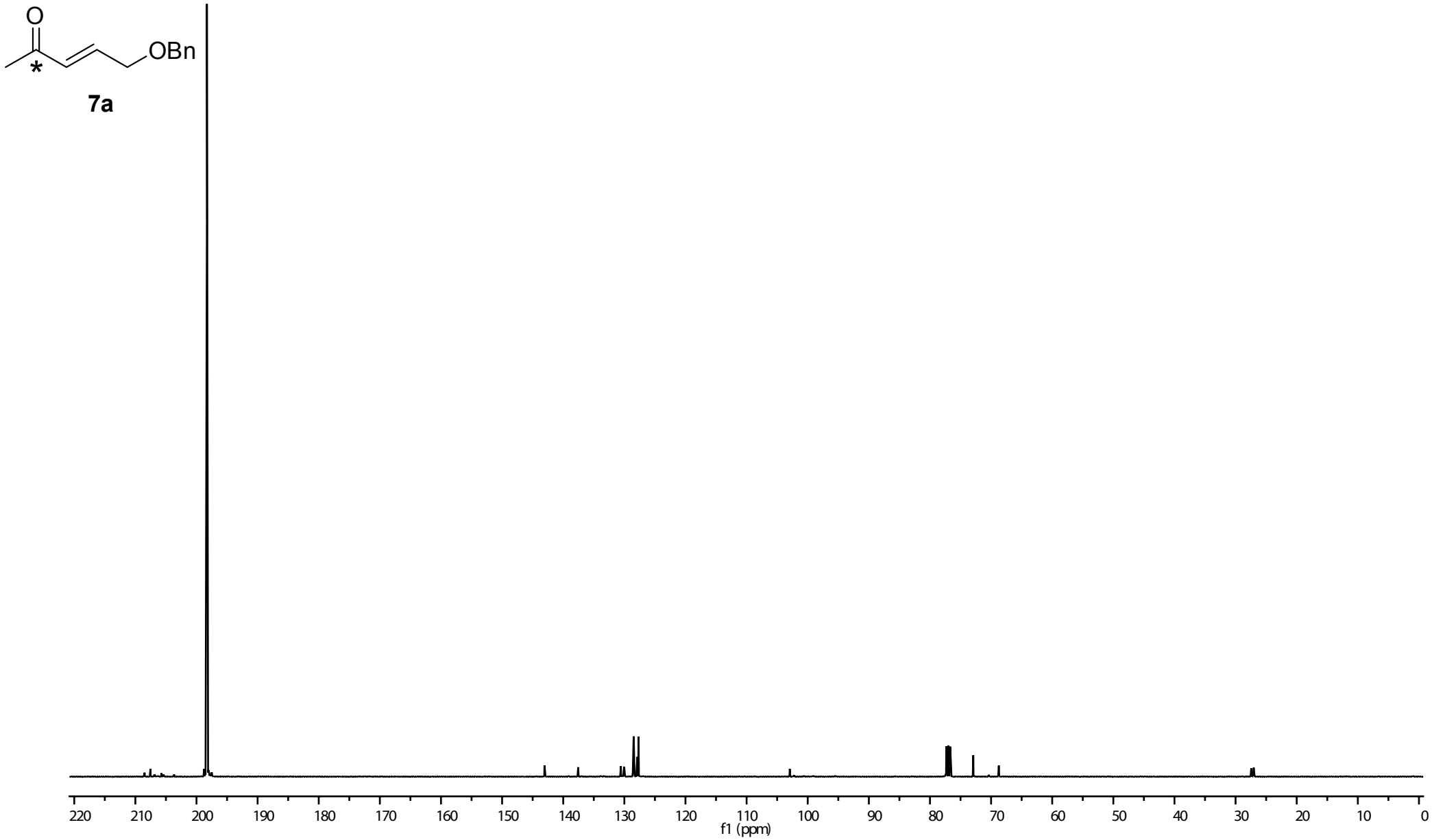
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OBn
*
7a
10.0
9.5
9.0
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
f1 (ppm)


O
OBn
*
7a
220
210
200
190
180
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130
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110
100
90
80
70
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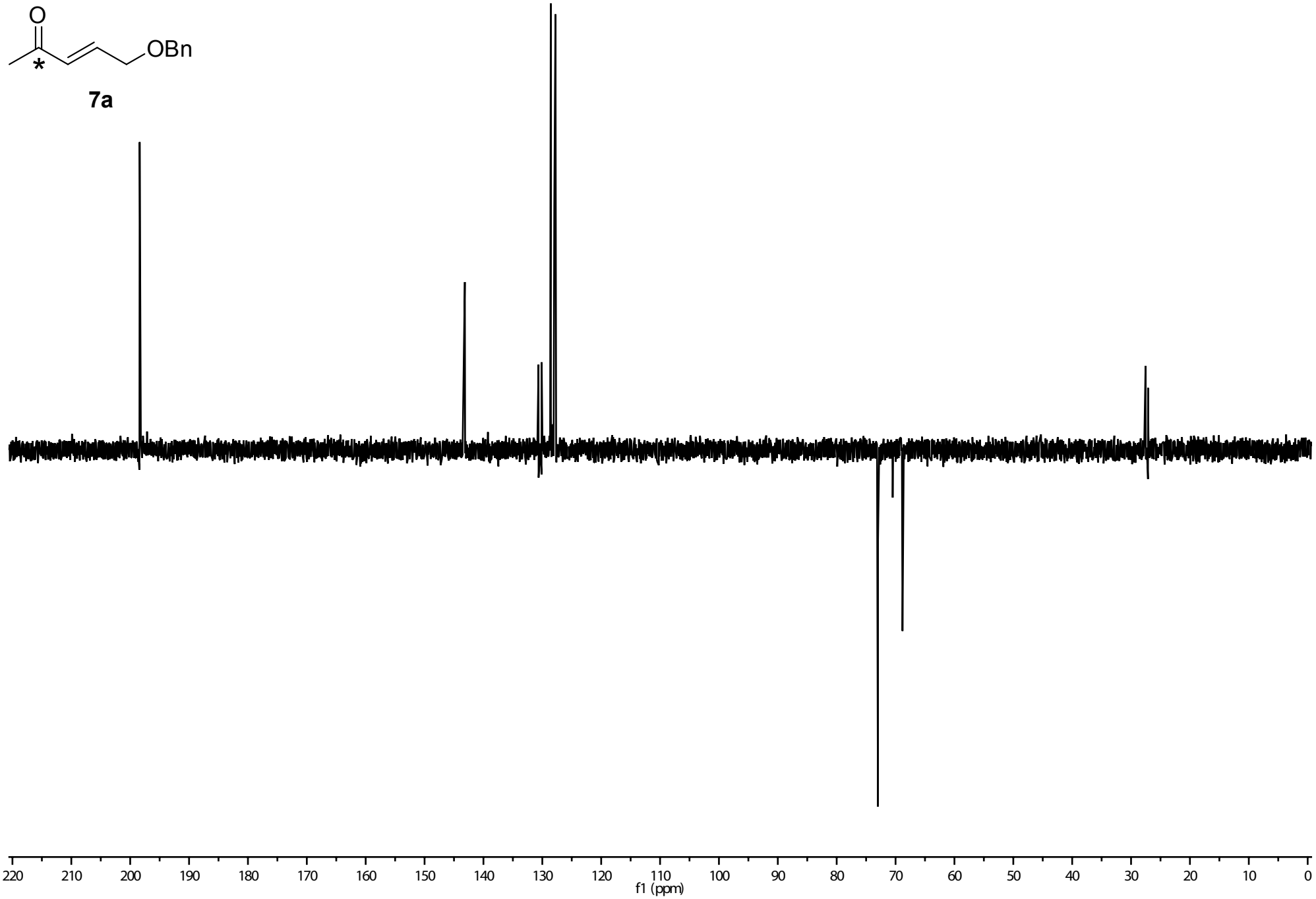
50
40
30
20
10
0
f1 (ppm)


O
OBn
*
7a
220
210
200
190
180
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150
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130
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110
100
90
80
70
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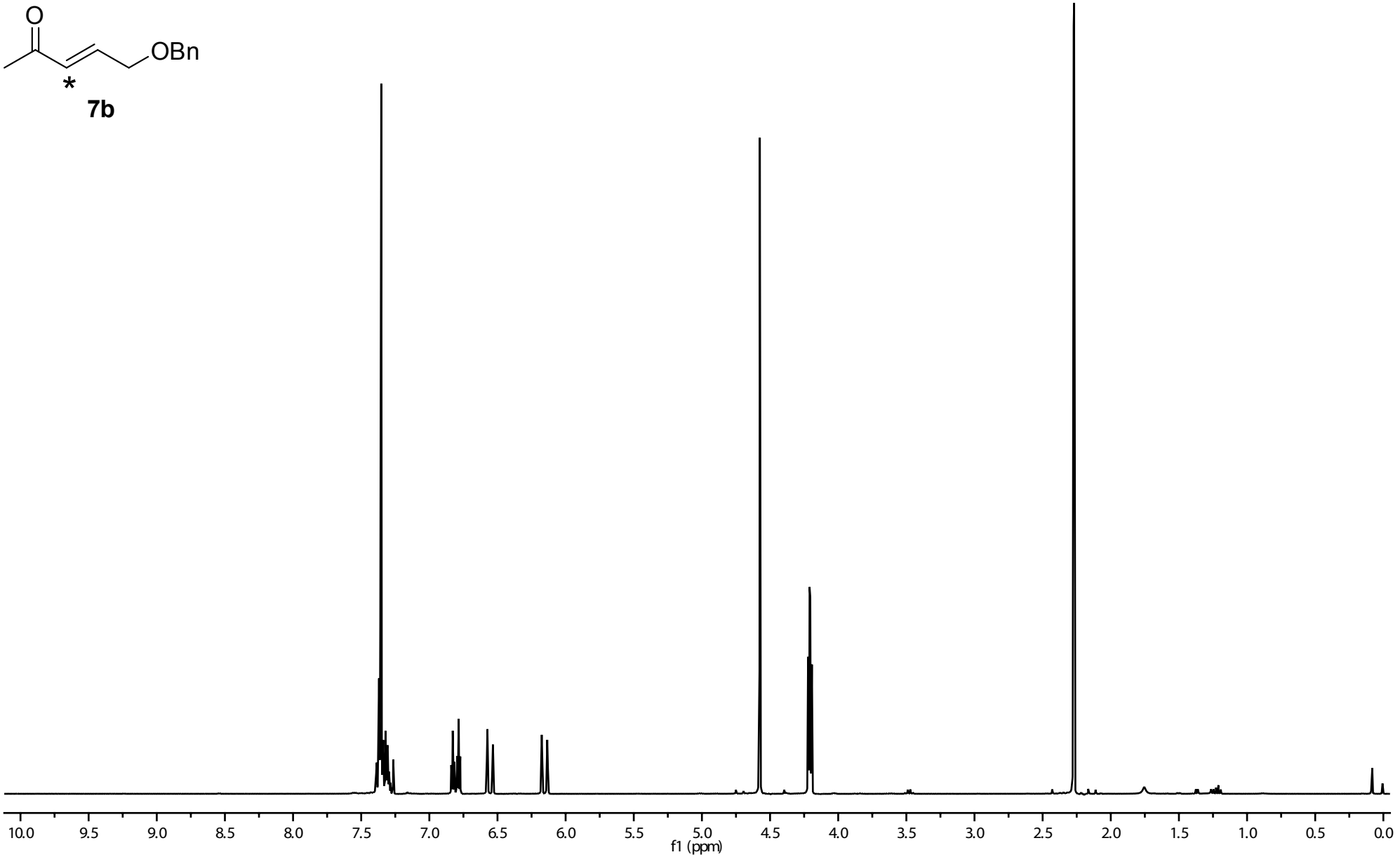
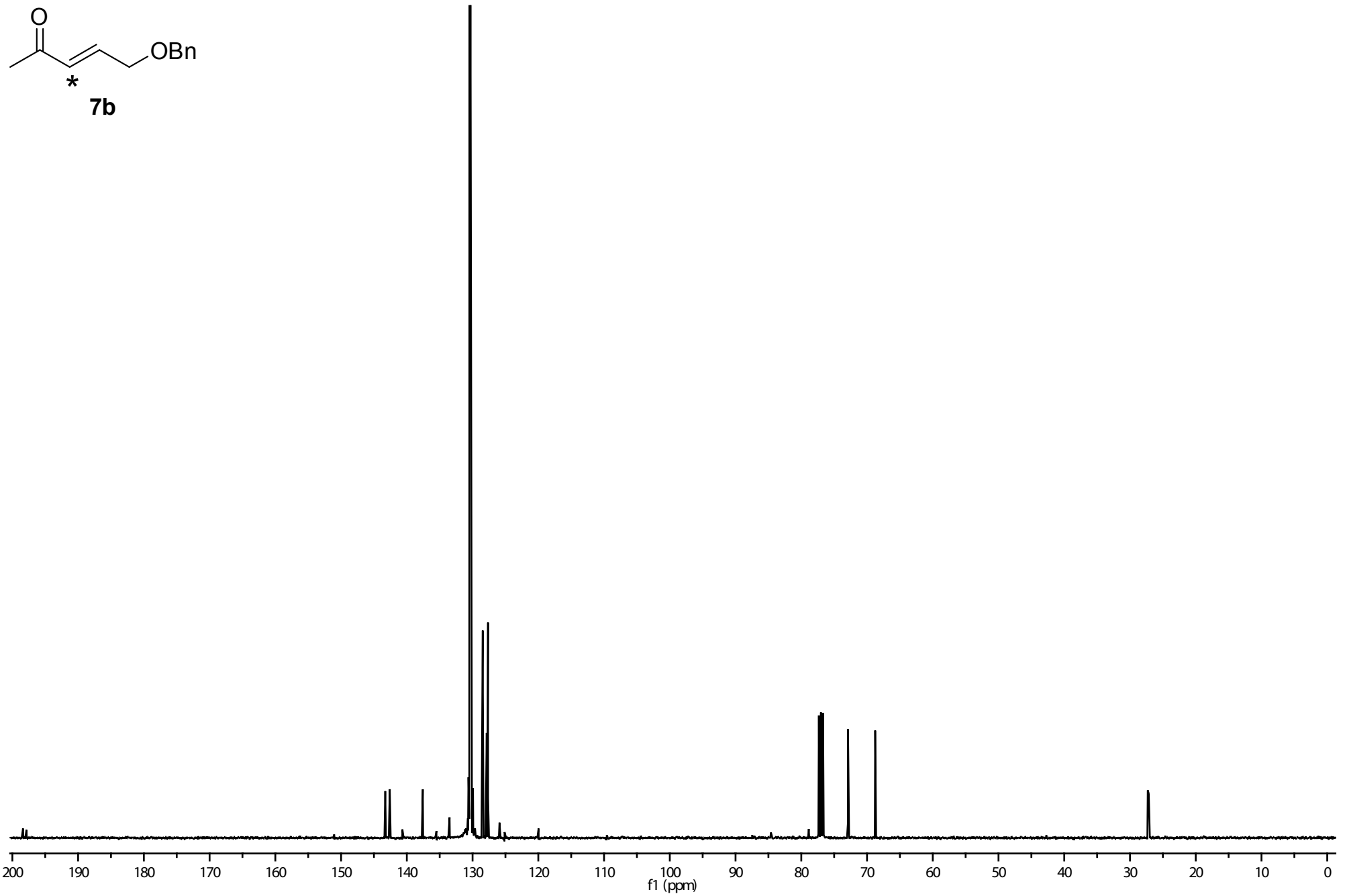
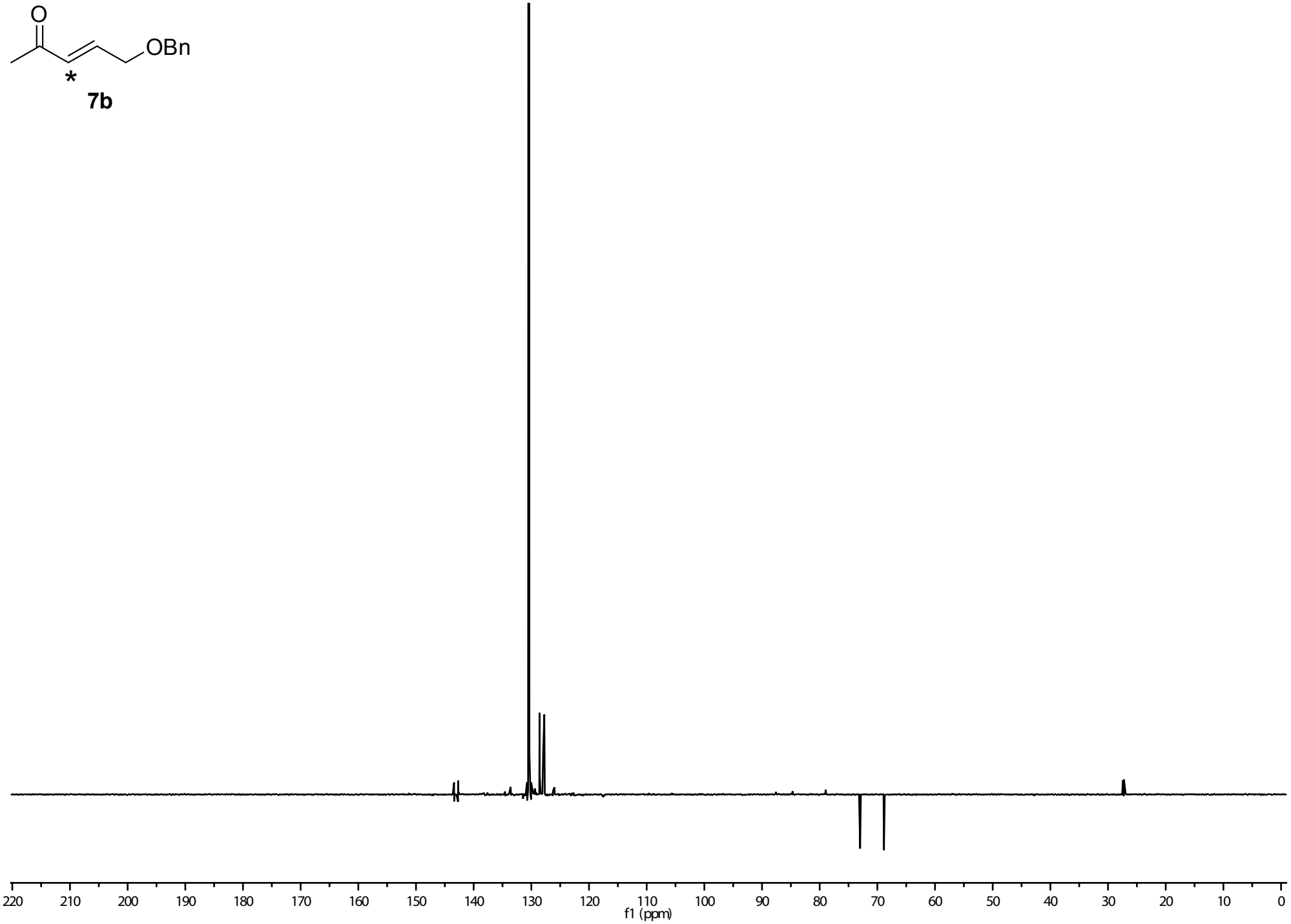
50
40
30
20
10
0
f1 (ppm)


O
OBn
*
7b
10.0
9.5
9.0
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
f1 (ppm)


O
OBn
*
7b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OBn
*
7b
220
210
200
190
180
170
160
150
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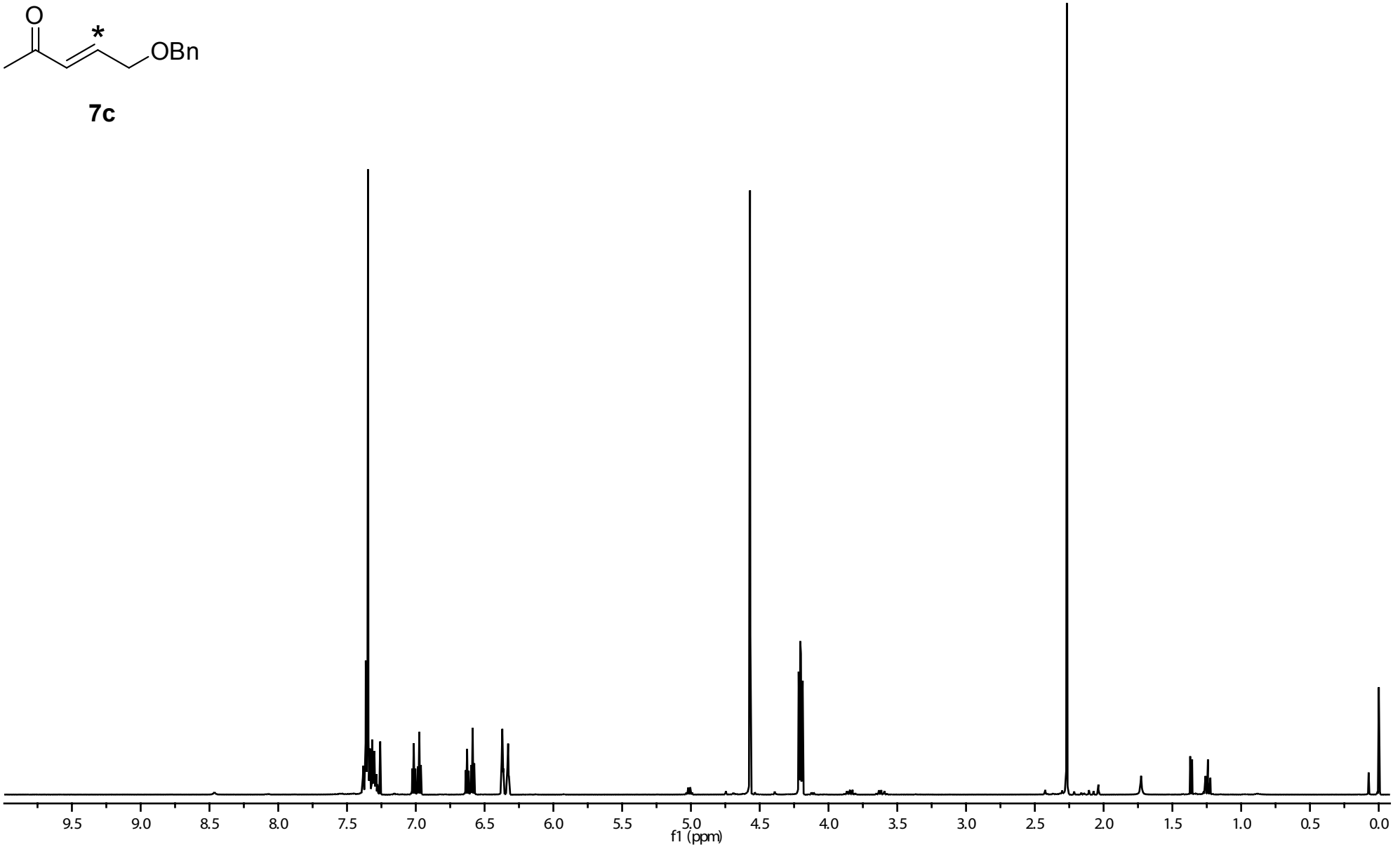
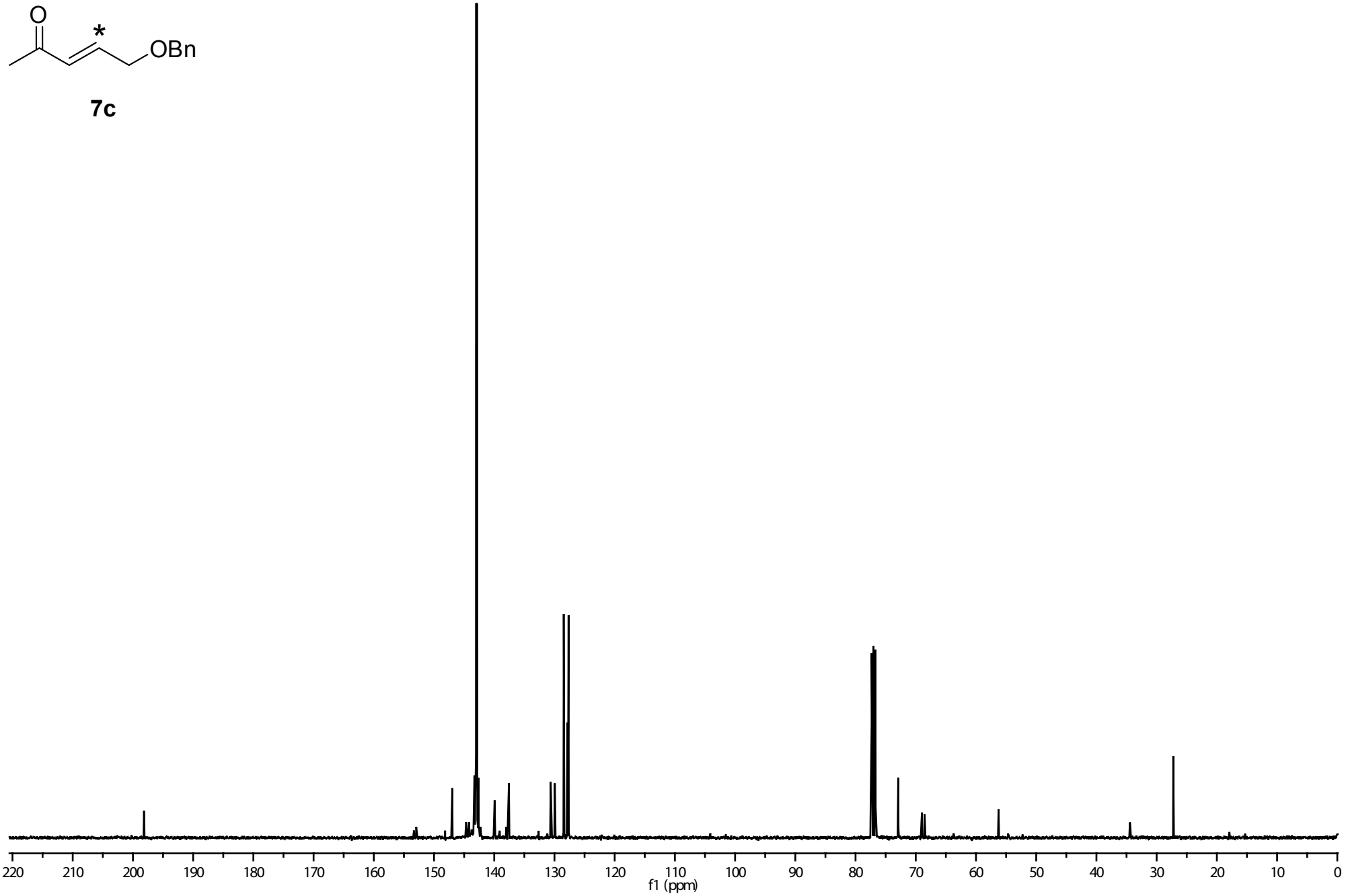
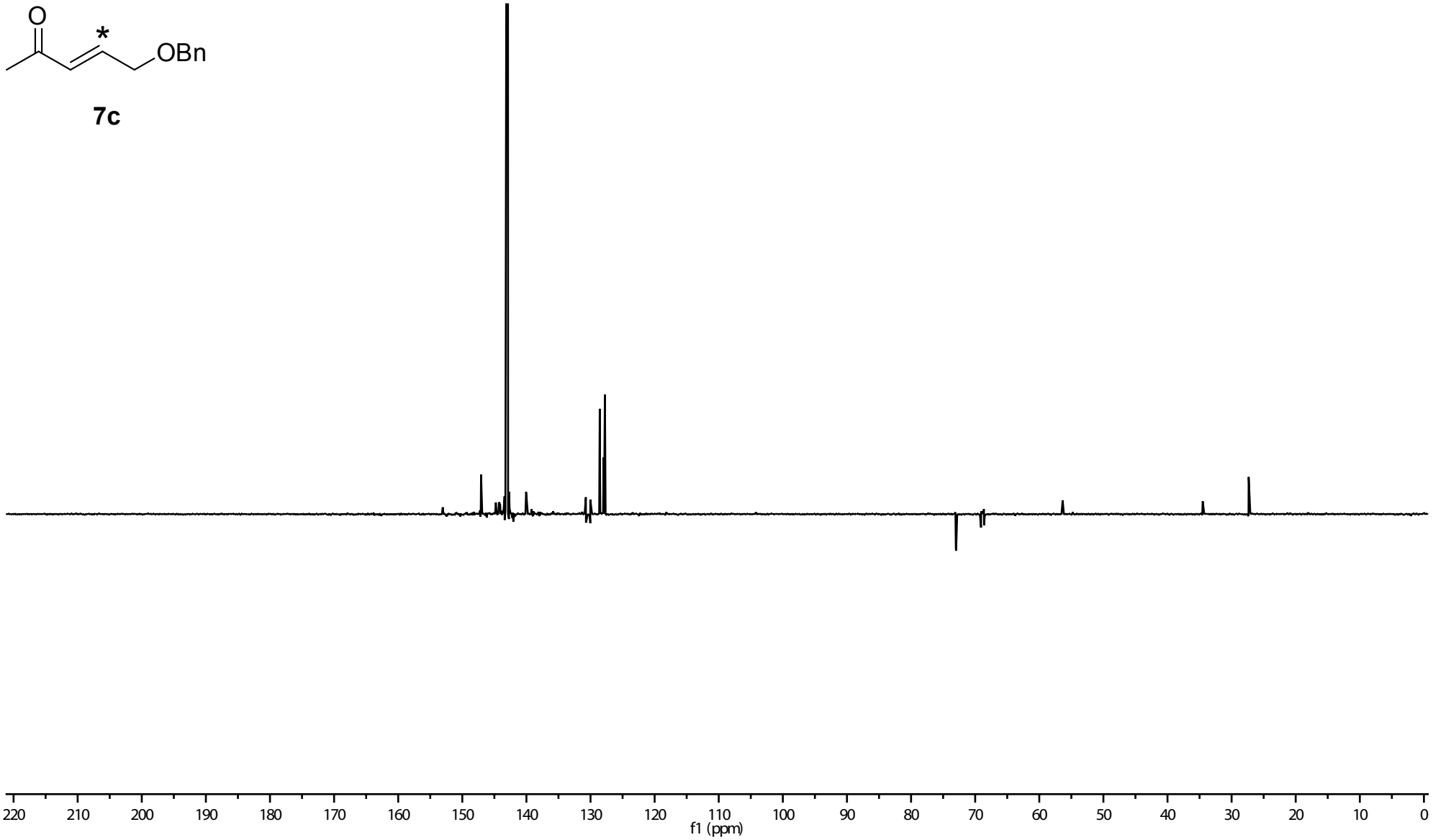
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
*
OBn
7c
9.5
9.0
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
f1 (ppm)


O
*
OBn
7c
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
*
OBn
7c
220
210
200
190
180
170
160
150
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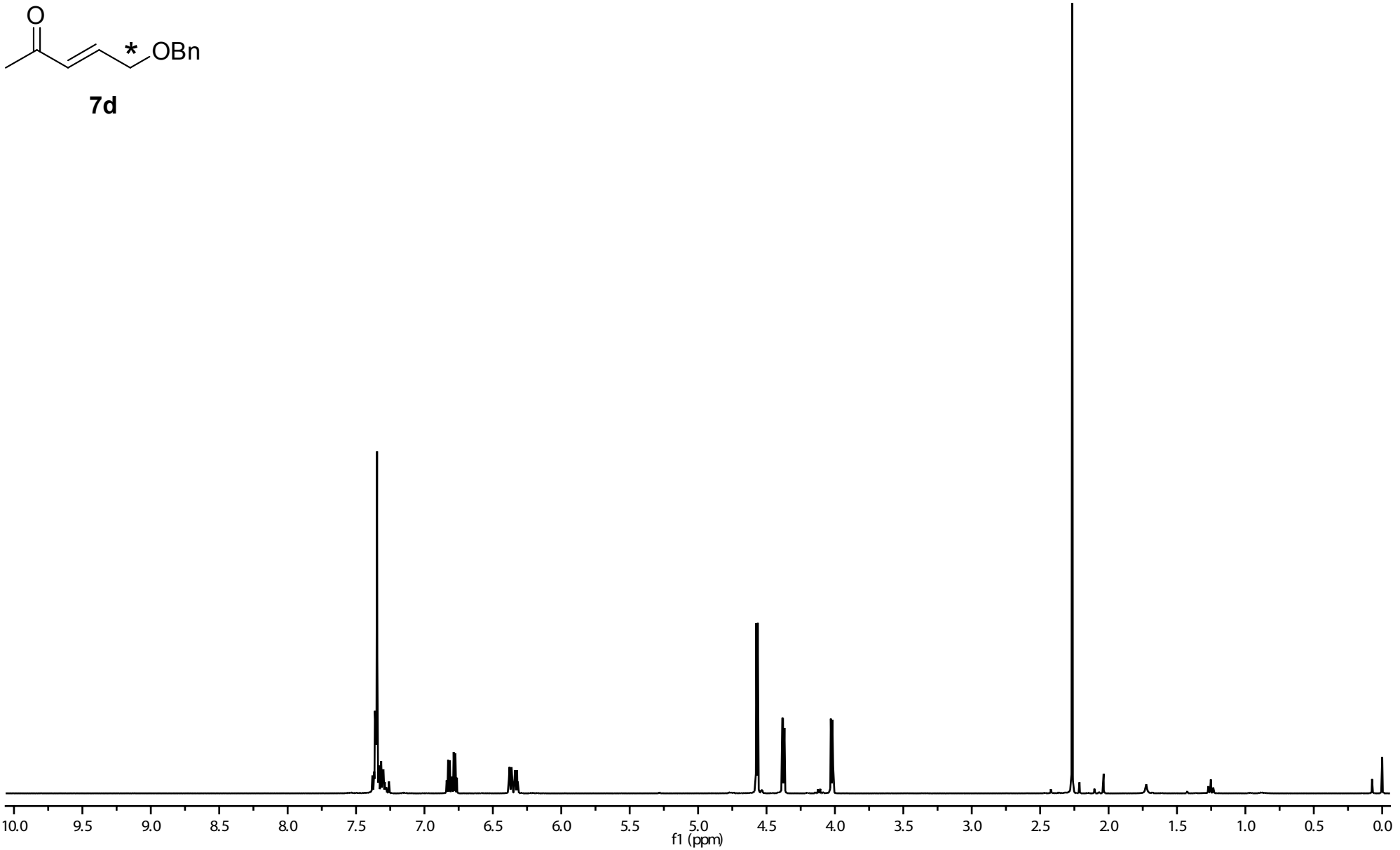
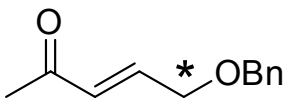
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
*
OBn
7d
10.0
9.5
9.0
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
f1 (ppm)


O
*
OBn

7d

220
210
200
190
180
170
160
150
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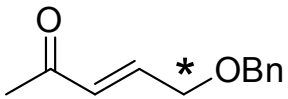
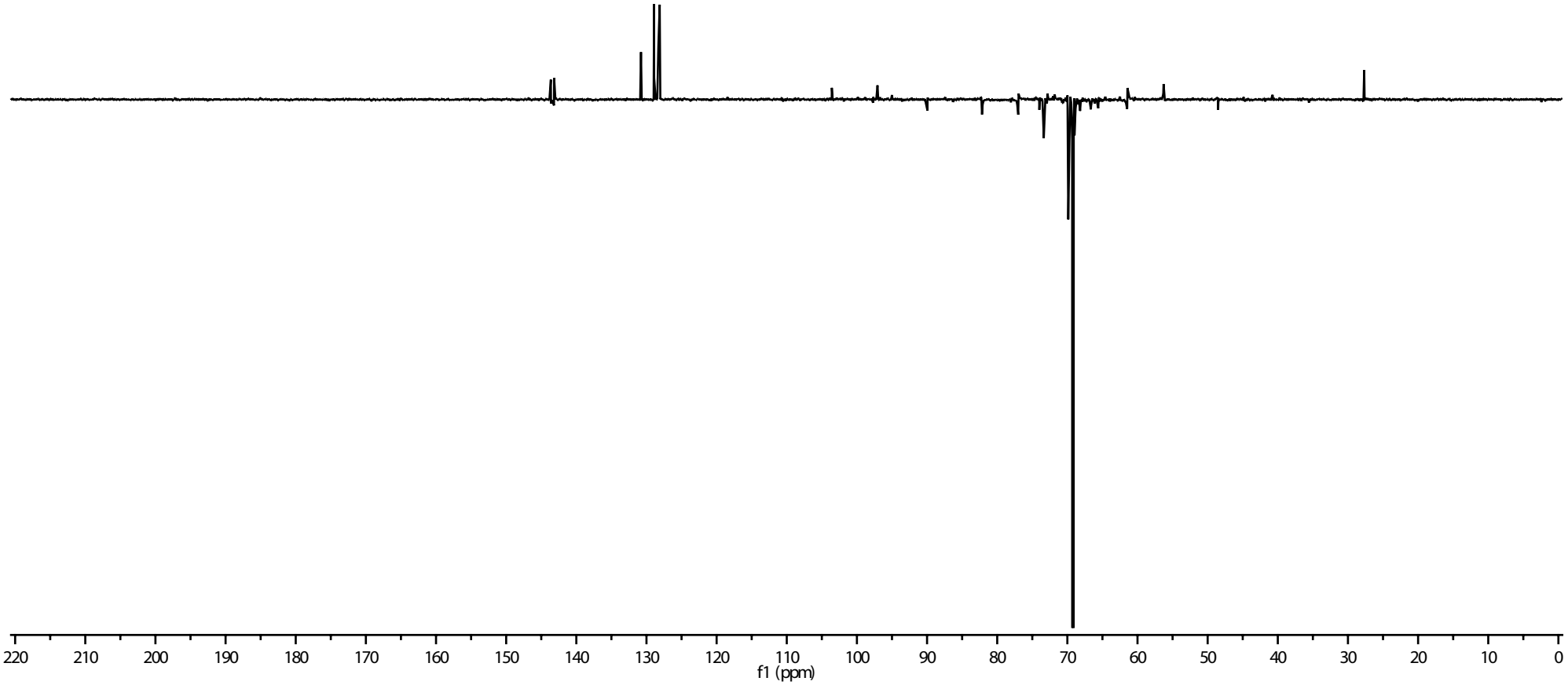
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
*
OBn

7d


220
210
200
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180
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160
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100
90
80
70
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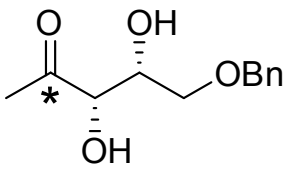
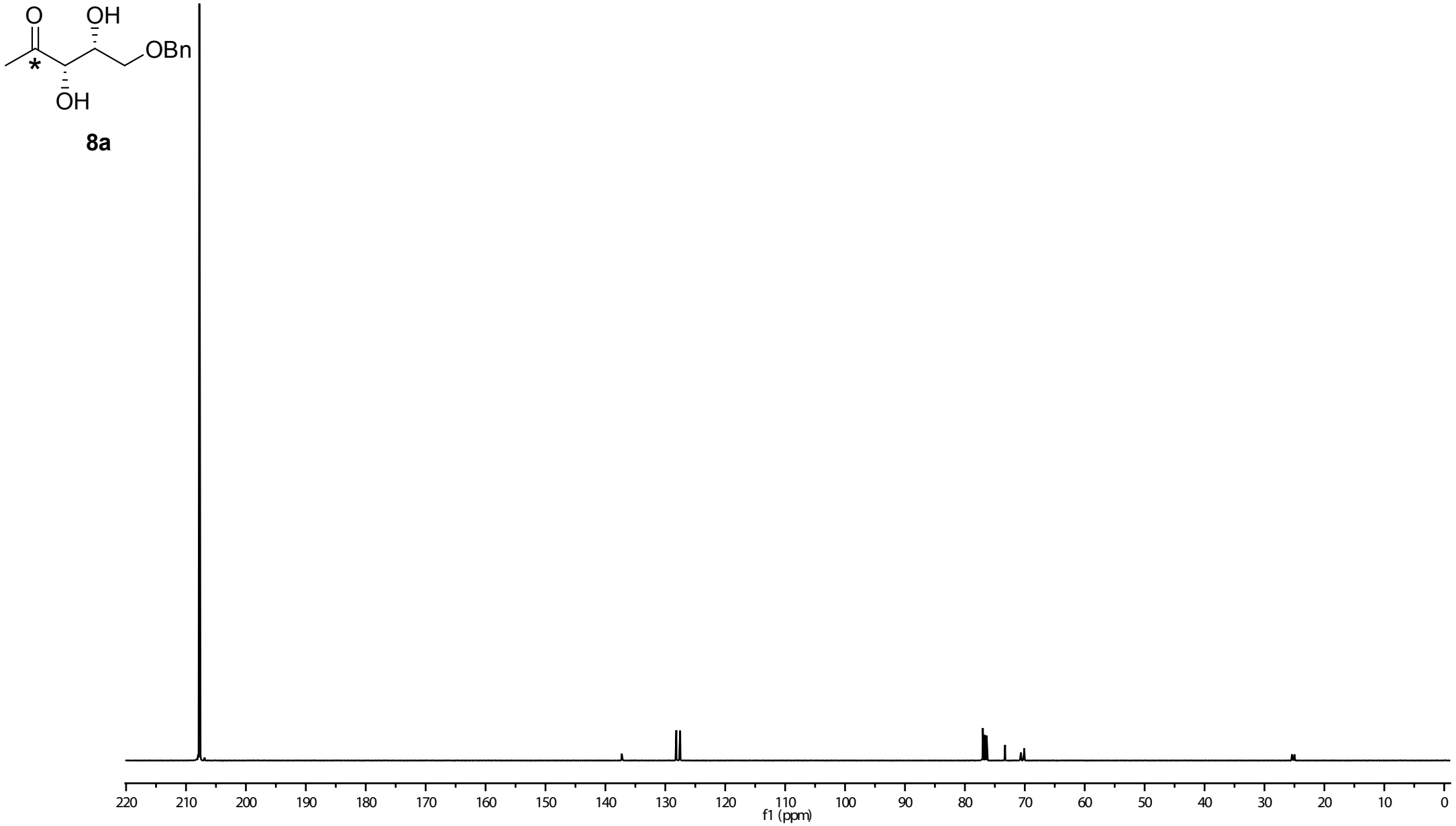
50
40
30
20
10
0
f1 (ppm)


O
OH
OBn
*
OH

8a

10.0
9.5
9.0
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
f1 (ppm)


O
OH
OBn
*
OH
8a
220
210
200
190
180
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150
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130
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90
80
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50
40
30
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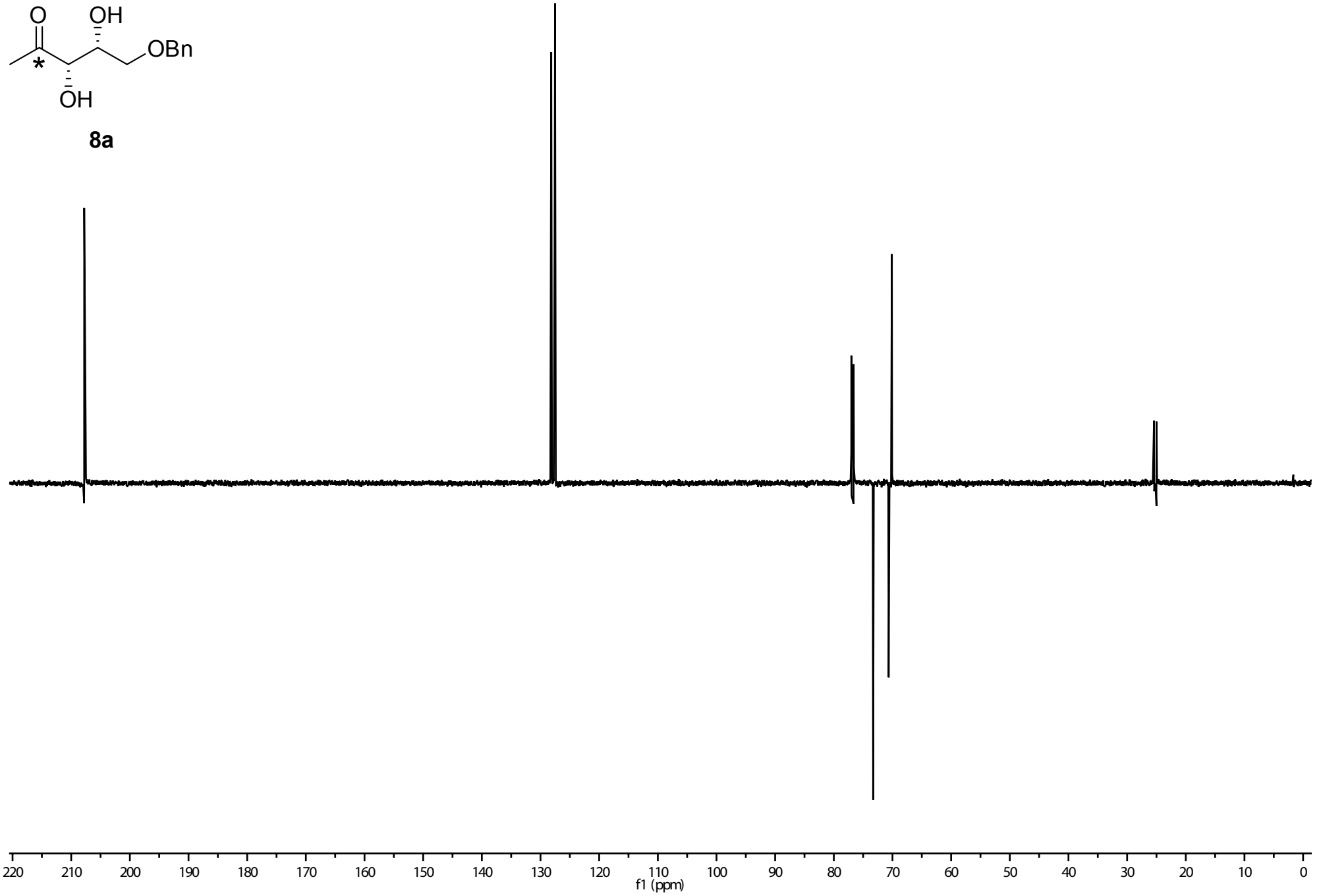
10
0
f1 (ppm)


O
OH
OBn
*
OH
8a
220
210
200
190
180
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150
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130
120
110
100
90
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70
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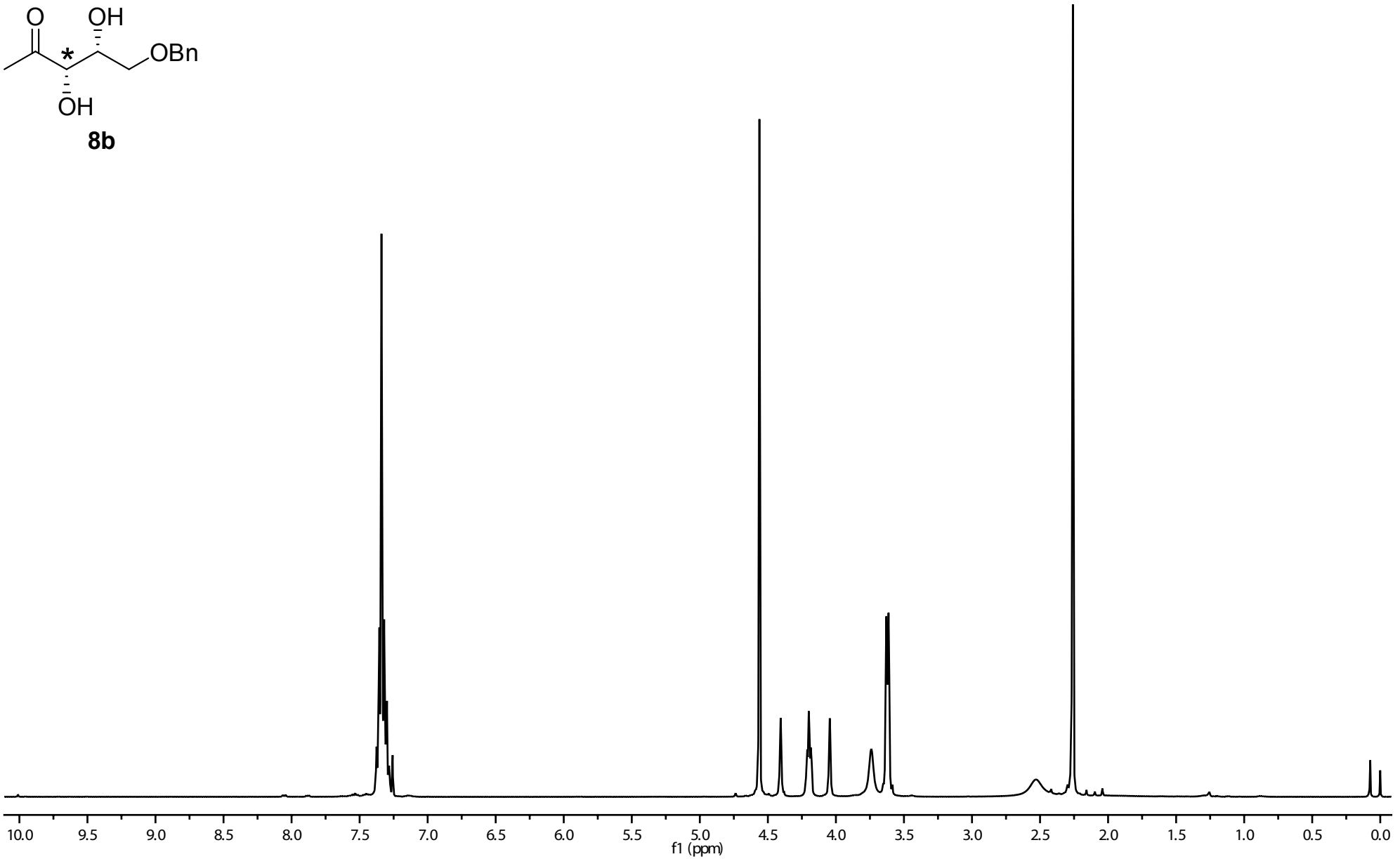
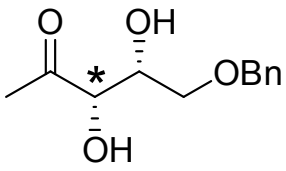
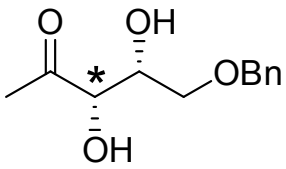
50
40
30
20
10
0
f1 (ppm)


O
OH
OBn
OH
*
8b
10.0
9.5
9.0
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
f1 (ppm)


O
OH
*
OBn
OH

8b

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
*
OBn
OH

8b

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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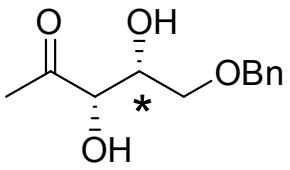
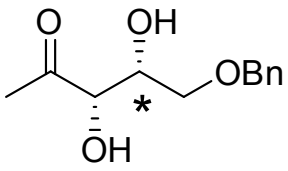
50
40
30
20
10
0
f1 (ppm)


O
OH
OBn
*
OH

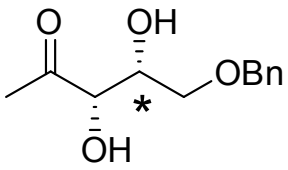
8c

10.0
9.5
9.0
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
f1 (ppm)


O
OH
OBn
*
OH

8c

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
OBn
*
OH

8c

220
210
200
190
180
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160
150
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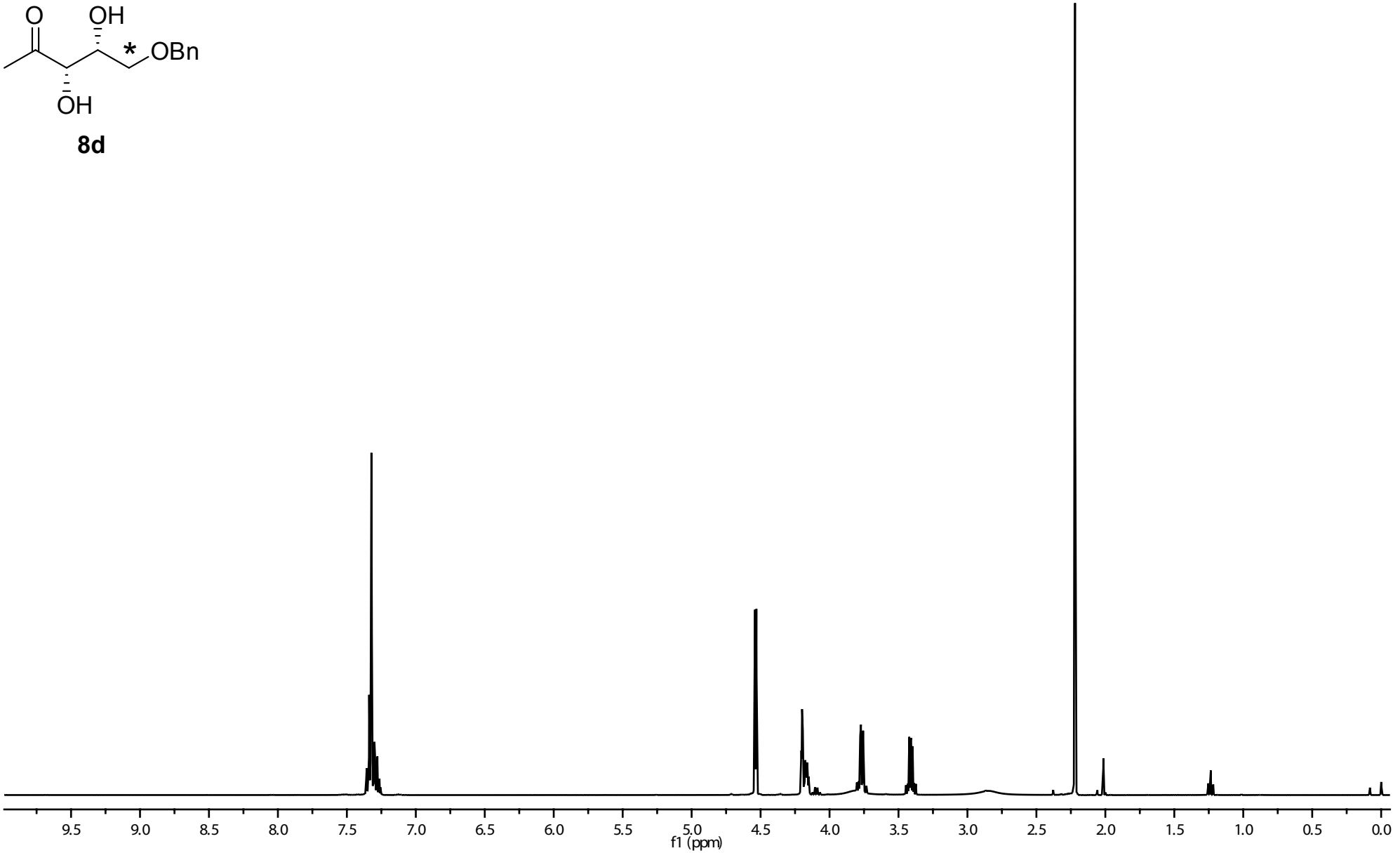
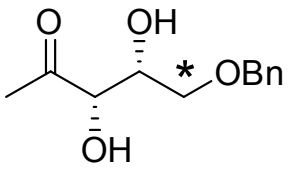
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

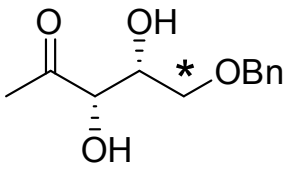

O
OH
*
OBn
OH
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

8d

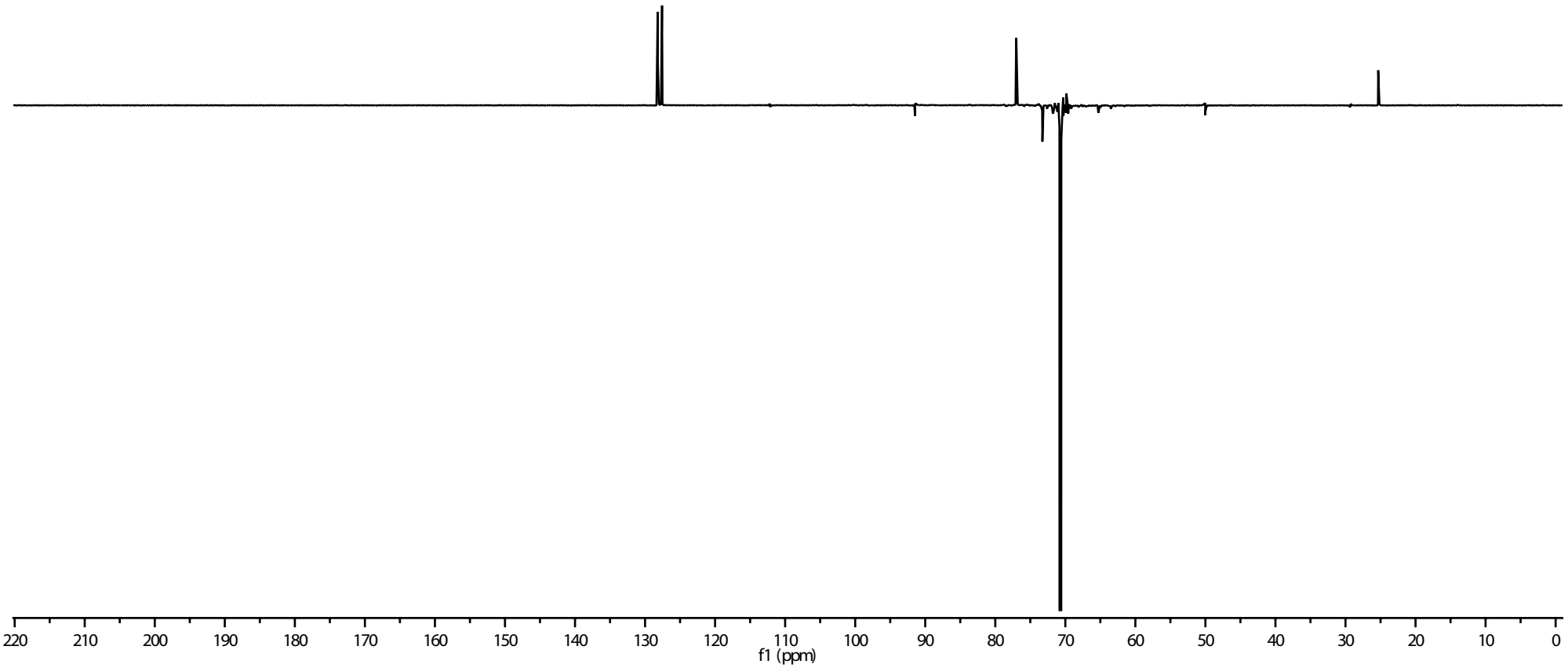

O
OH
*
OBn
OH

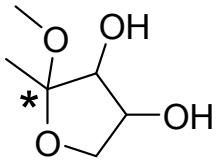
8d

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
*
OBn
OH

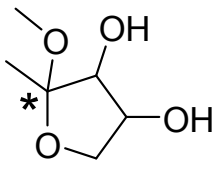
8d


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
*
OH
O

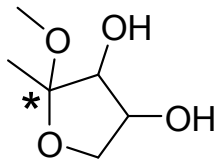
9a

10.0
9.5
9.0
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
f1 (ppm)


O
OH
*
OH
O

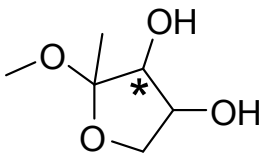
9a

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
*
OH
O

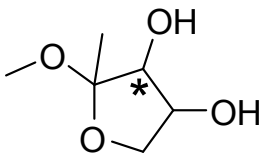
9a

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OH
O
*
OH
O

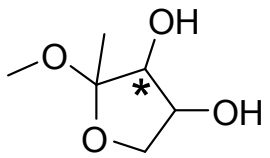
9b

10.0
9.5
9.0
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
f1 (ppm)


OH
O
*
OH
O

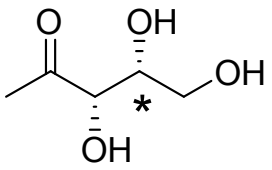
9b

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
O
*
OH
O

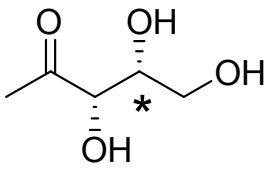
9b

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
OH
*
OH

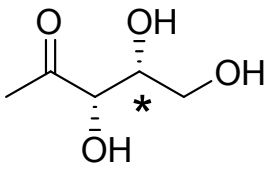
9c

10.0
9.5
9.0
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
f1 (ppm)


O
OH
OH
*
OH

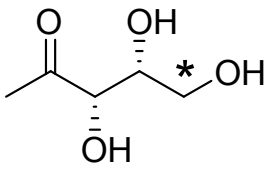
9c

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
OH
*
OH

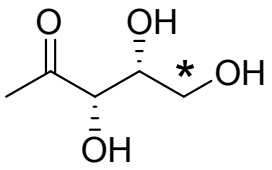
9c

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
*
OH
OH

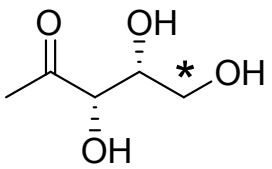
9d

10.0
9.5
9.0
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.
f1 (ppm)


O
OH
*
OH
OH

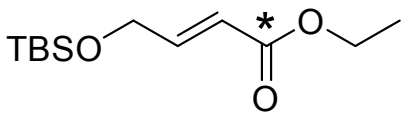
9d

240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
OH
*
OH
OH

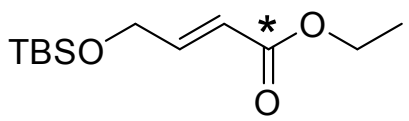
9d

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TBSO
*
O
O

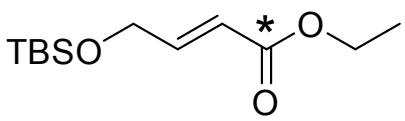
(*E*)-**10a**

10.0
9.5
9.0
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
f1 (ppm)


TBSO
*
O
O

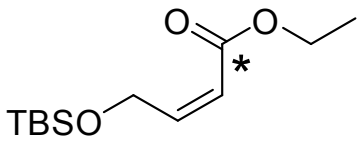
(*E*)-**10a**

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
*
O
O

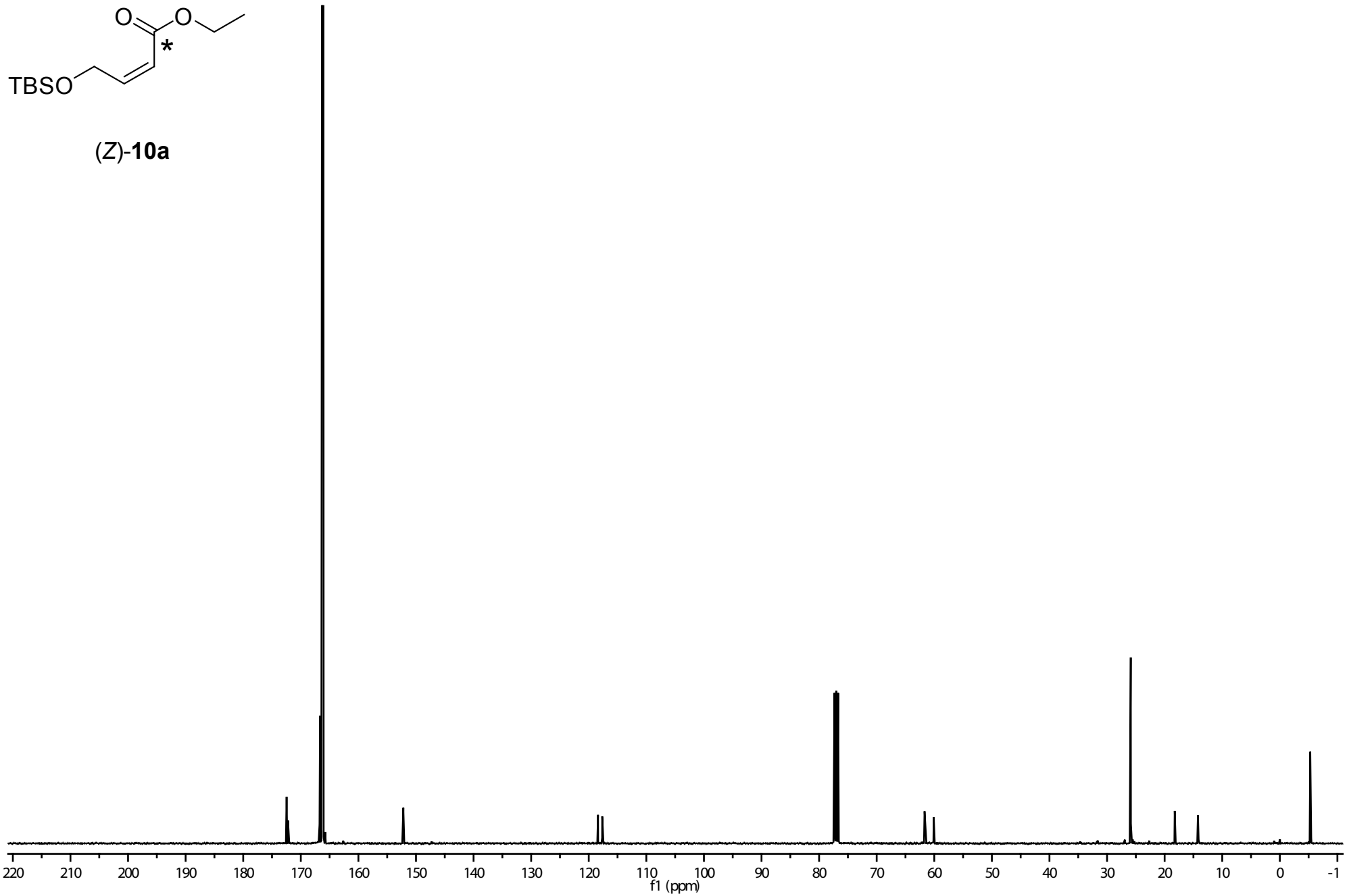
(*E*)-**10a**

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

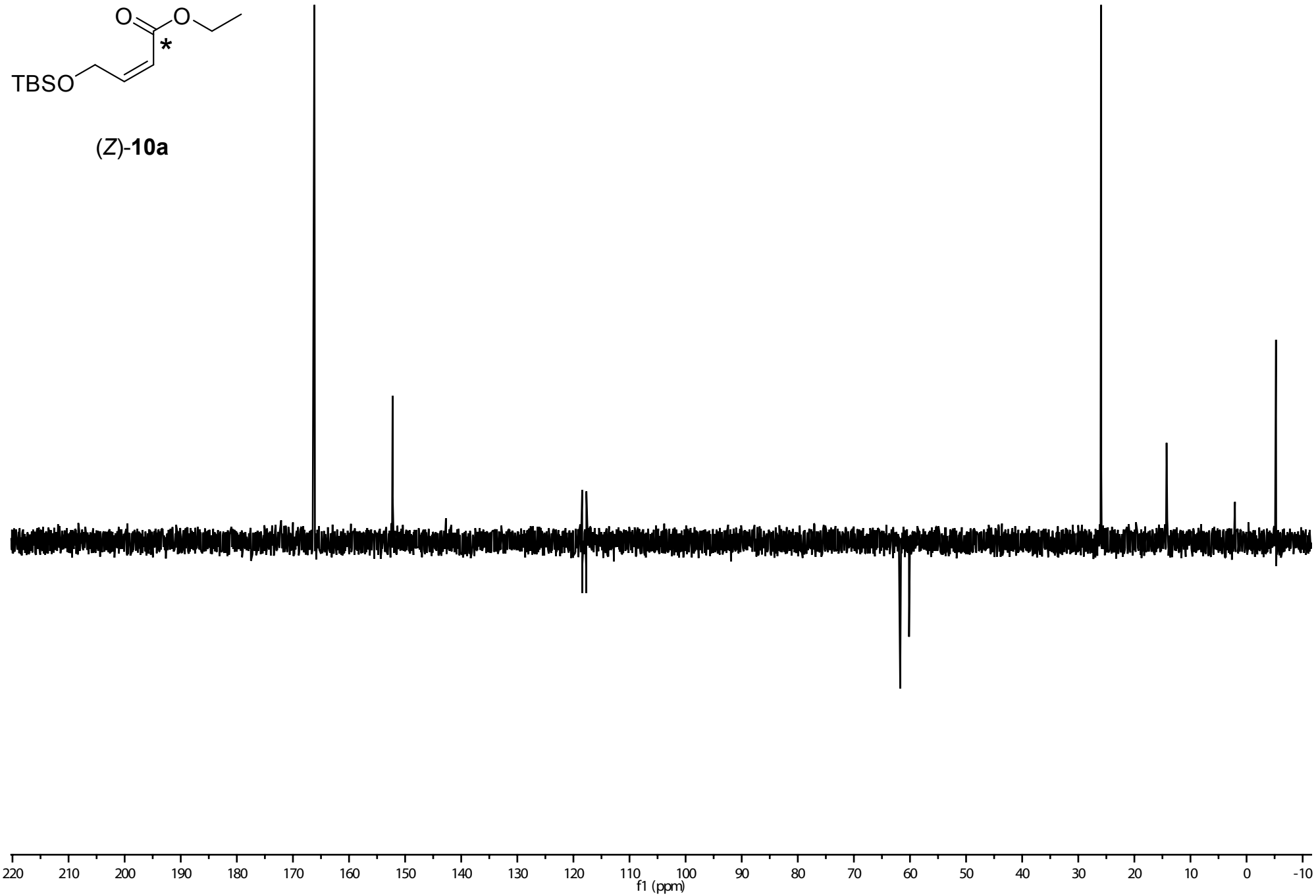

O
O
*
TBSO

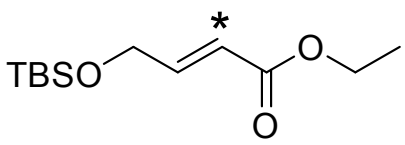
(*Z*)-**10a**

9.5
9.0
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
f1 (ppm)


O
O
*
TBSO
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

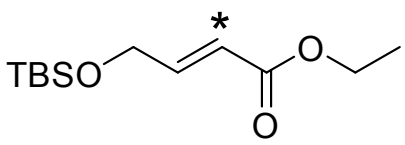
(*Z*)-**10a**


O
O
*
TBSO
(Z)-10a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
*
O
O

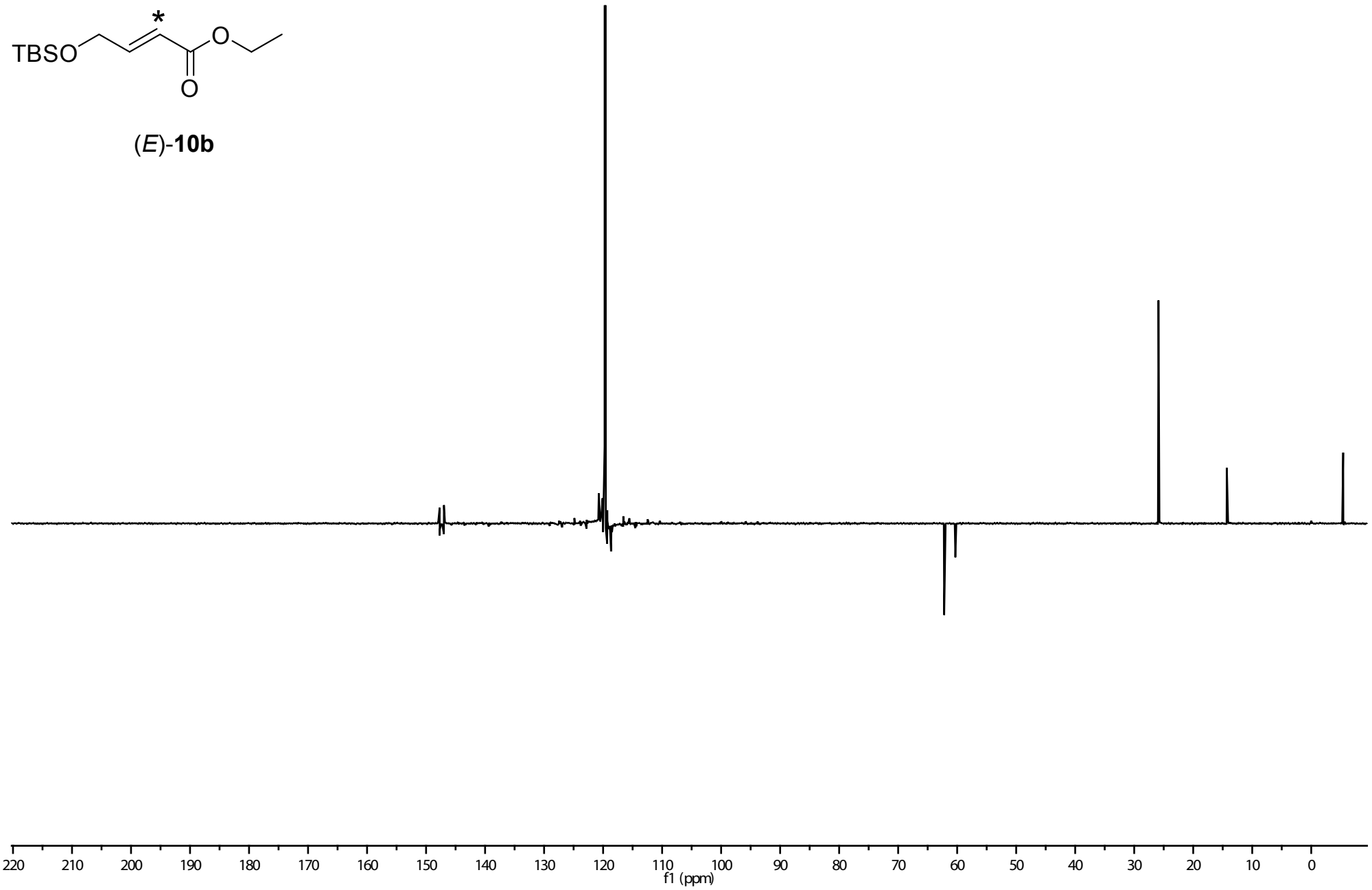
(*E*)-**10b**

10.0
9.5
9.0
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
f1 (ppm)

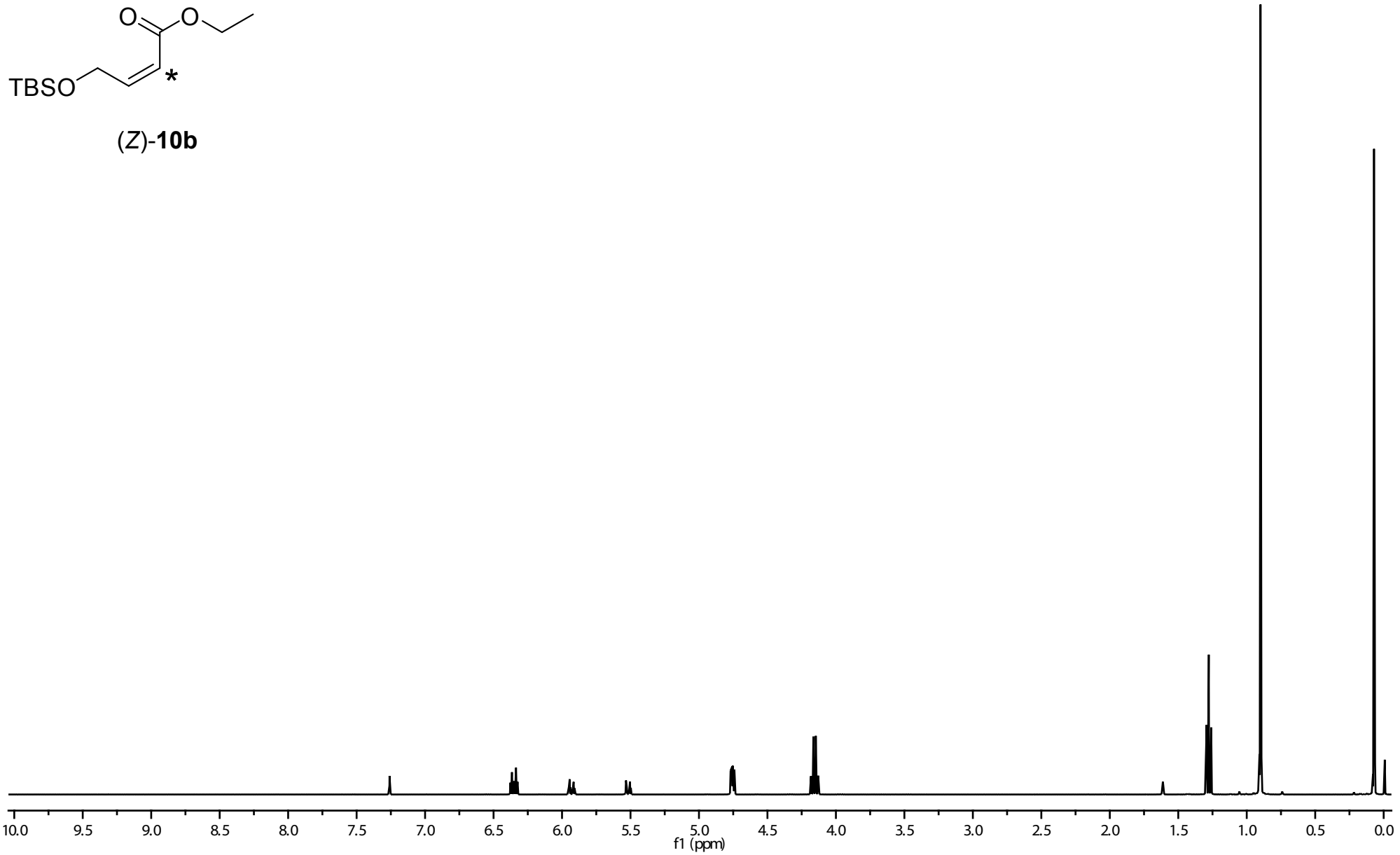

TBSO
*
O
O

(*E*)-**10b**

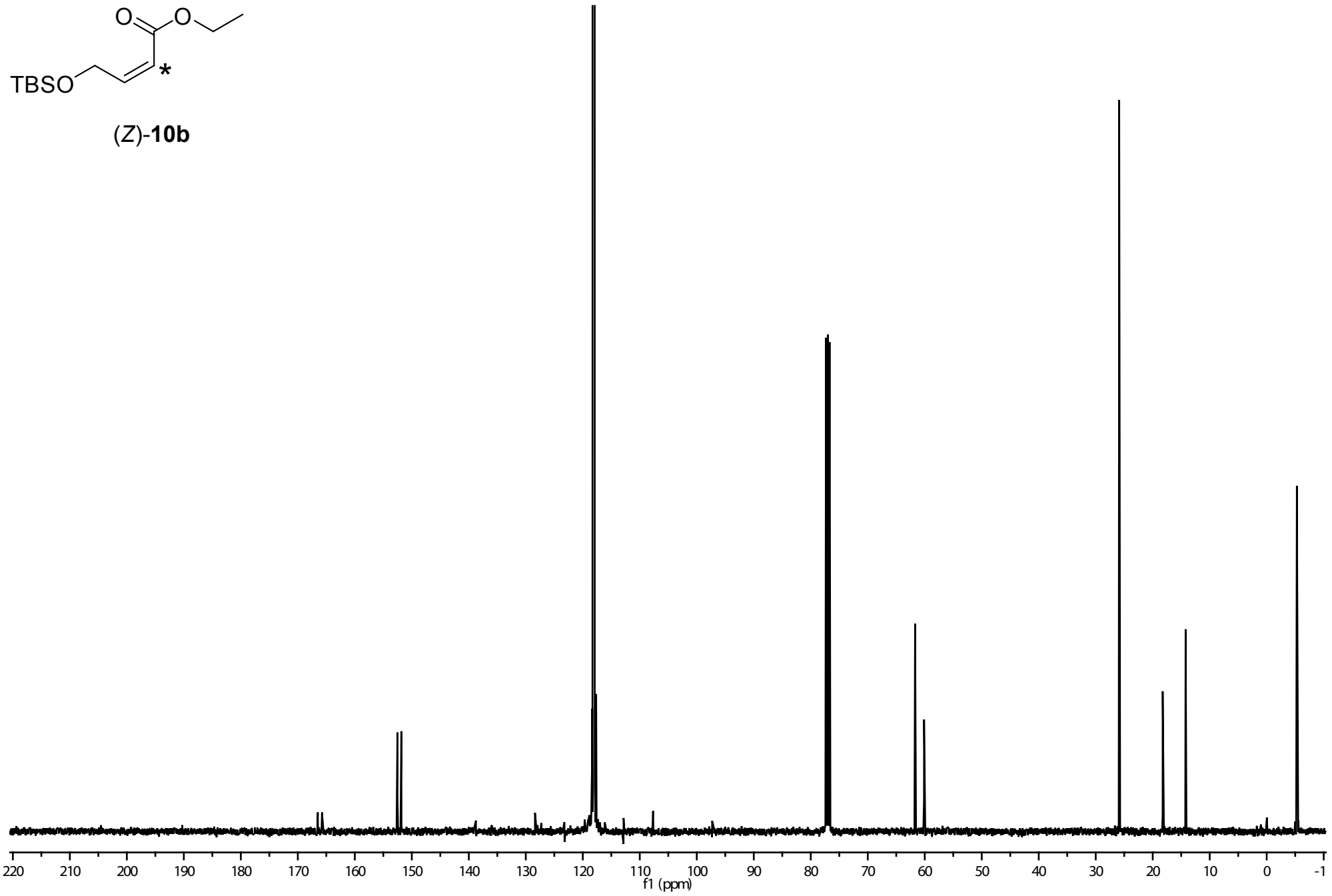
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

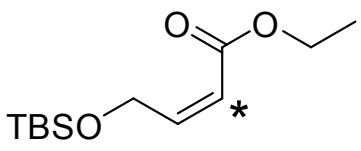

TBSO
*
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(*E*)-**10b**


O
O
TBSO
*
10.0
9.5
9.0
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
f1 (ppm)

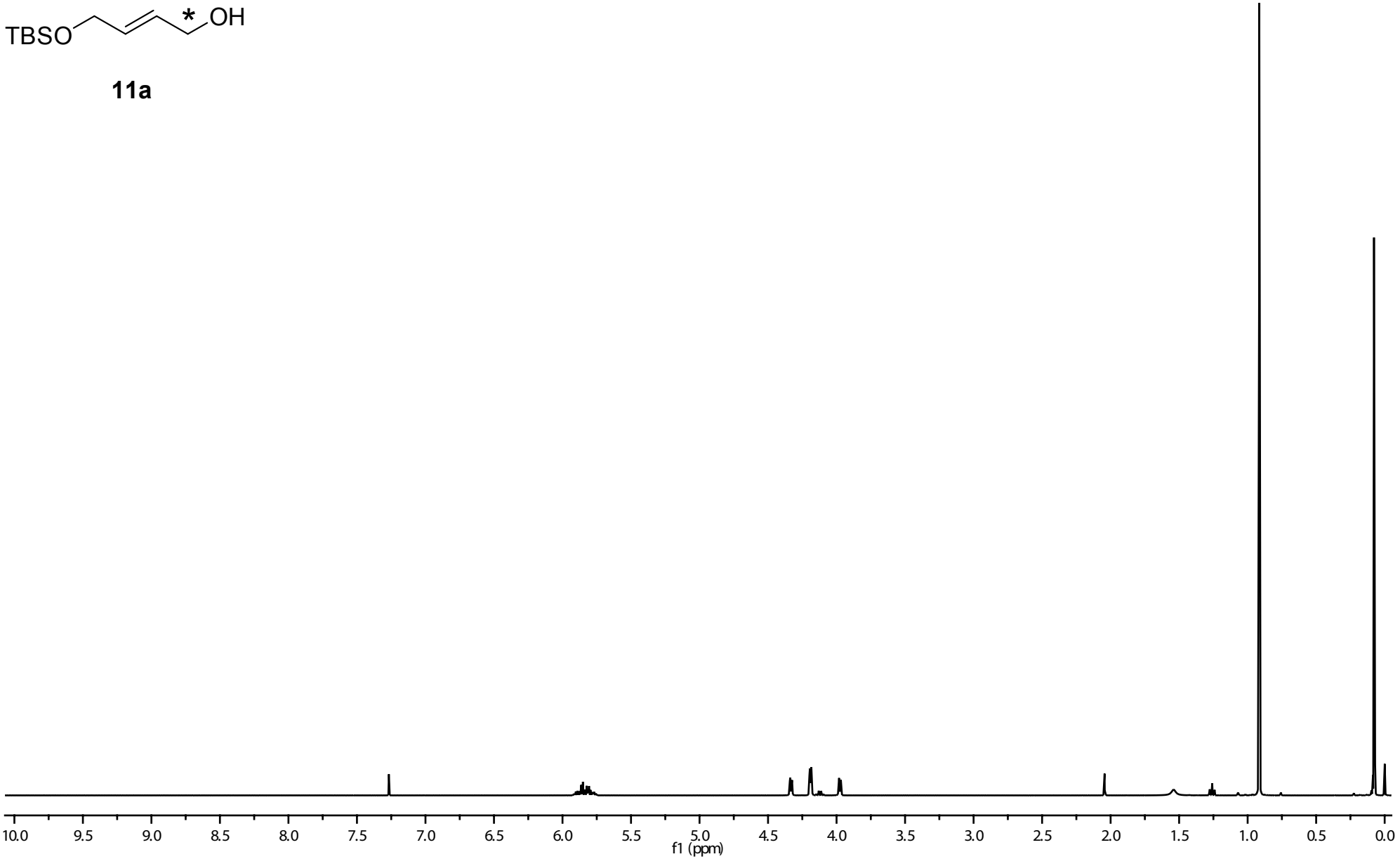
(*Z*)-**10b**

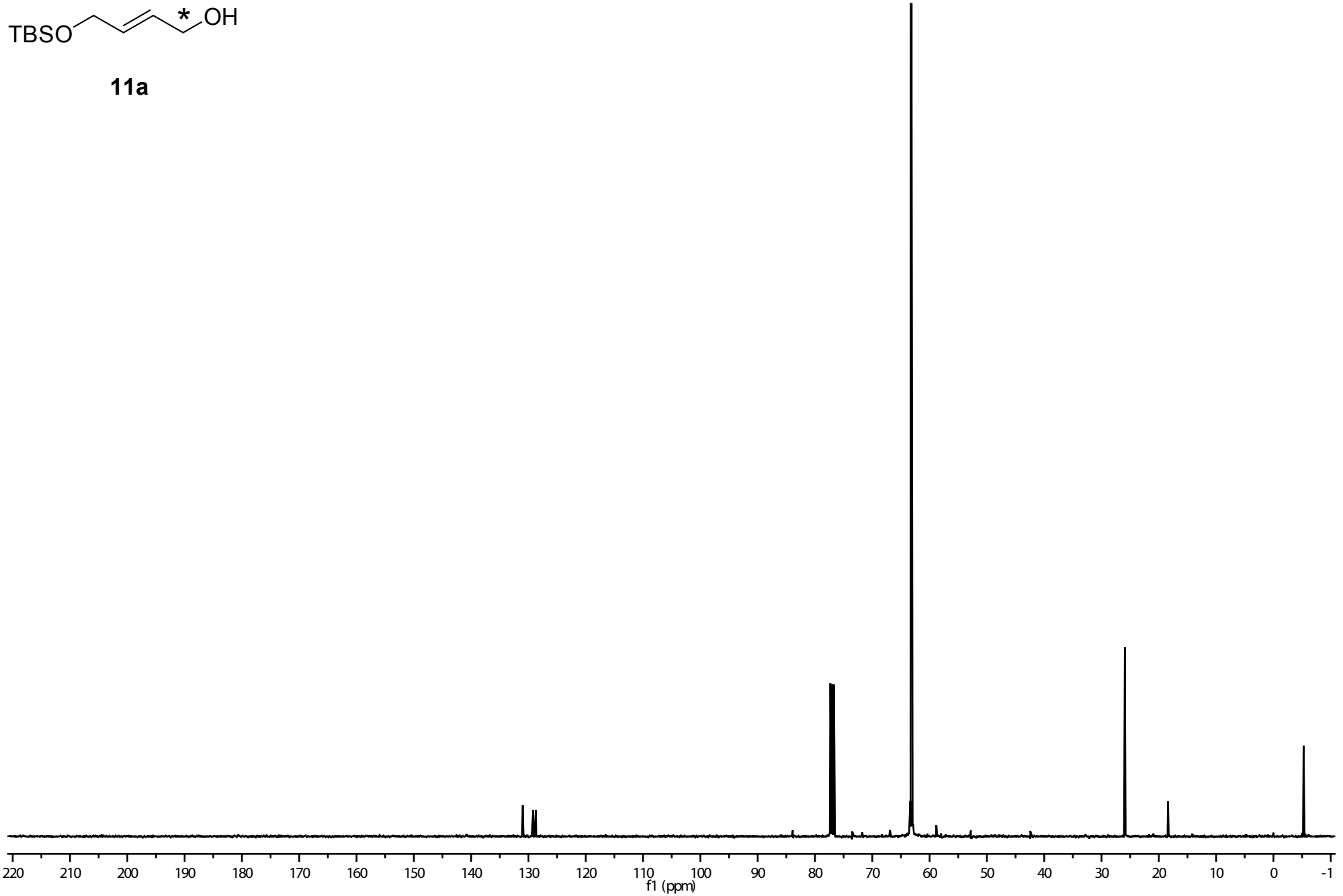

O
O
TBSO
*
(Z)-10b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

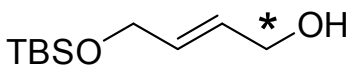

O
O
TBSO
*

(*Z*)-**10b**

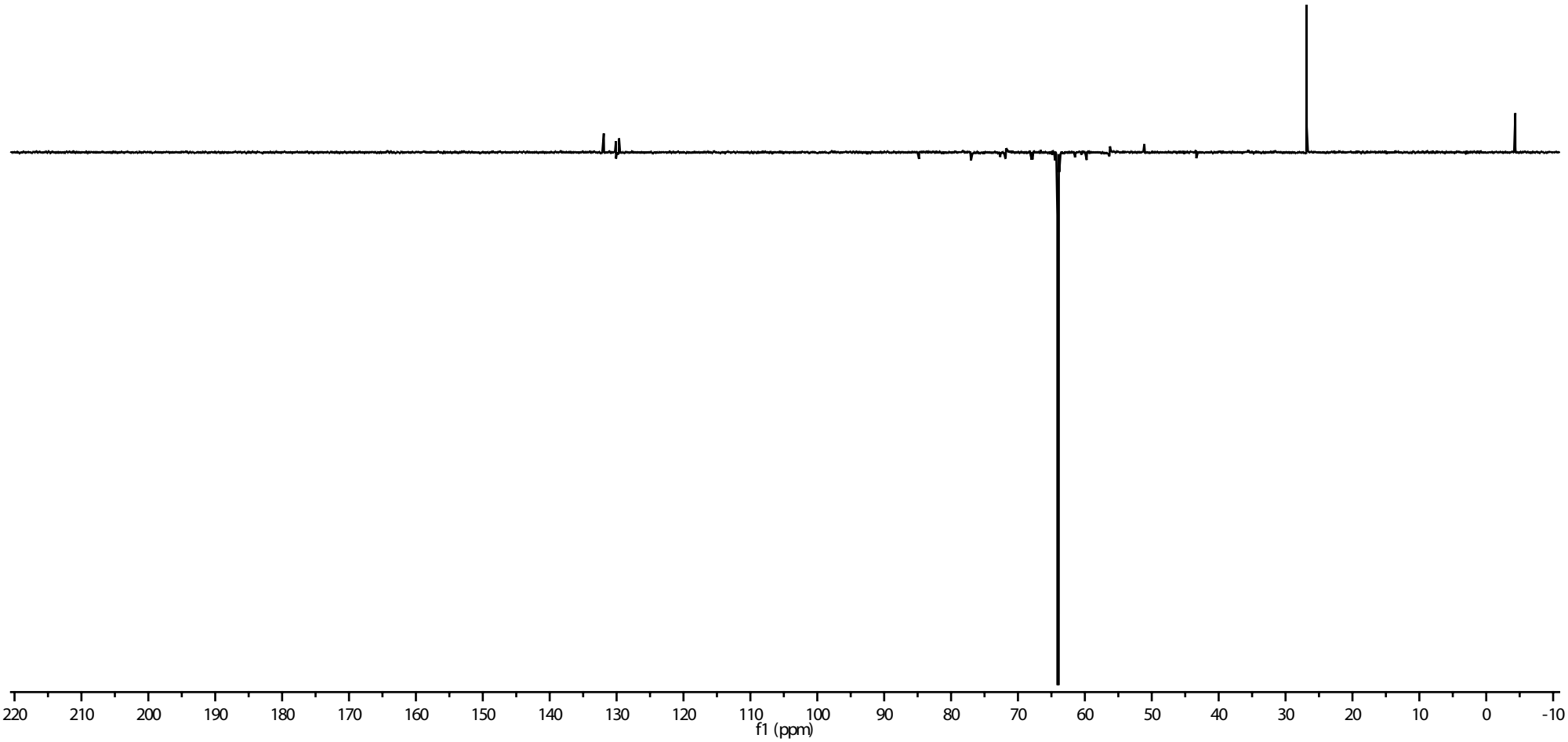
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

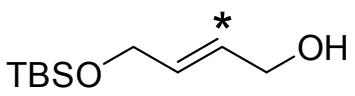

TBSO
*
OH
11a
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TBSO
*
OH
11a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


TBSO
*
OH

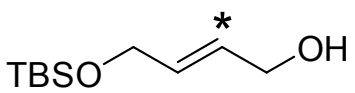
11a


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
OH
*

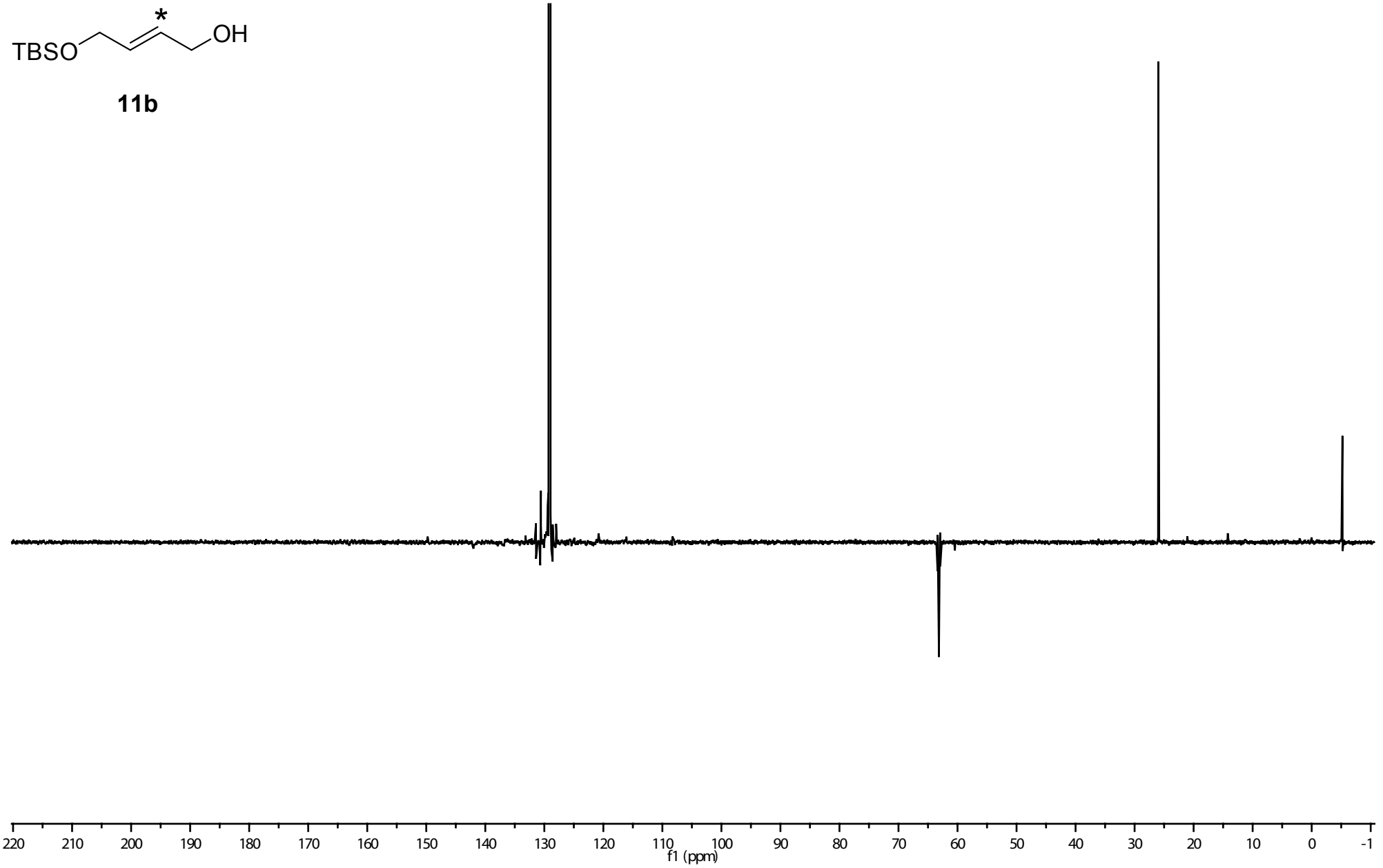
11b

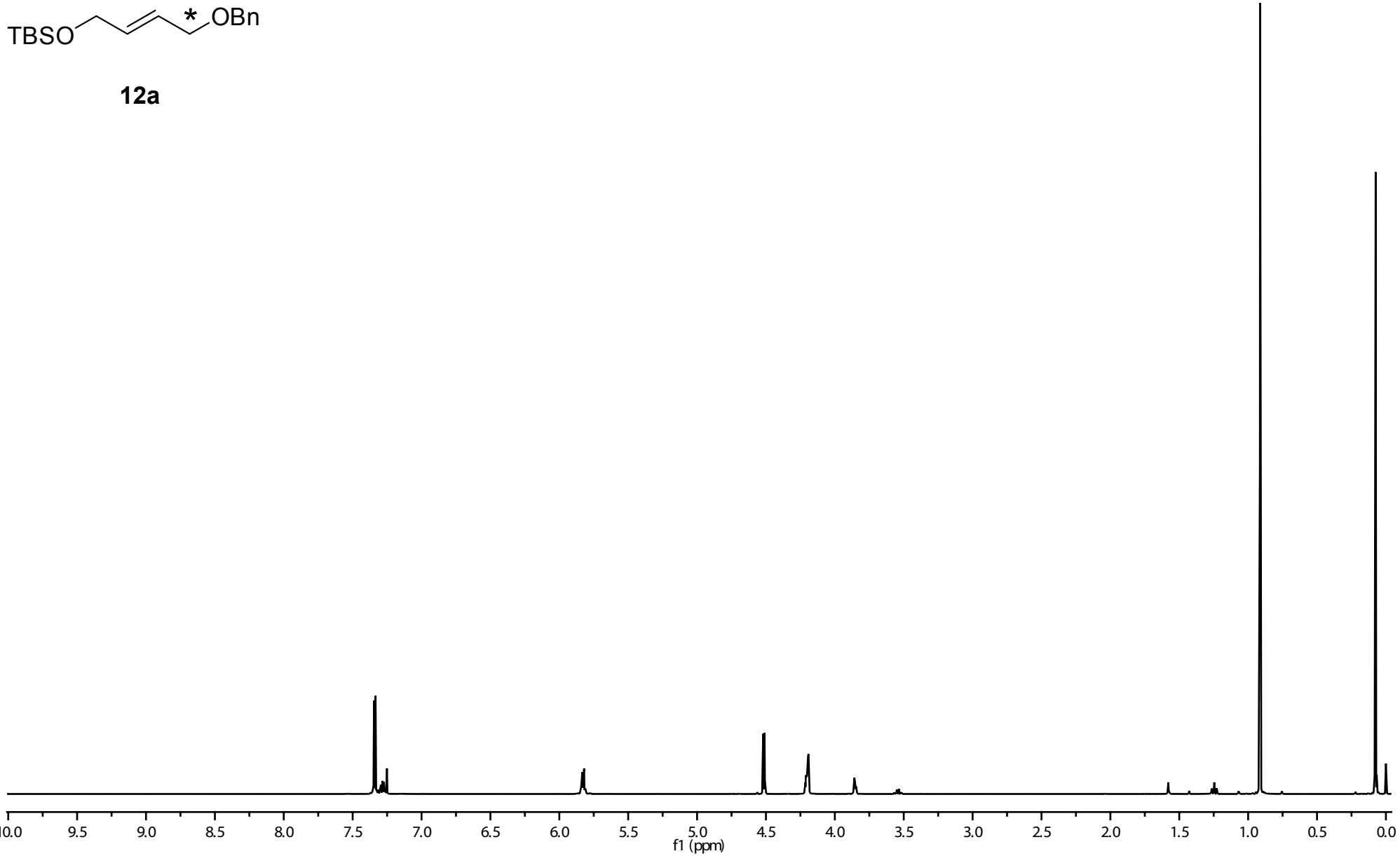
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

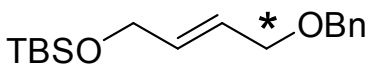

TBSO
OH
*

11b

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

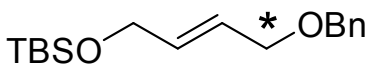

TBSO
OH
*
11b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


TBSO
*
OBn
12a
10.0
9.5
9.0
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
f1 (ppm)

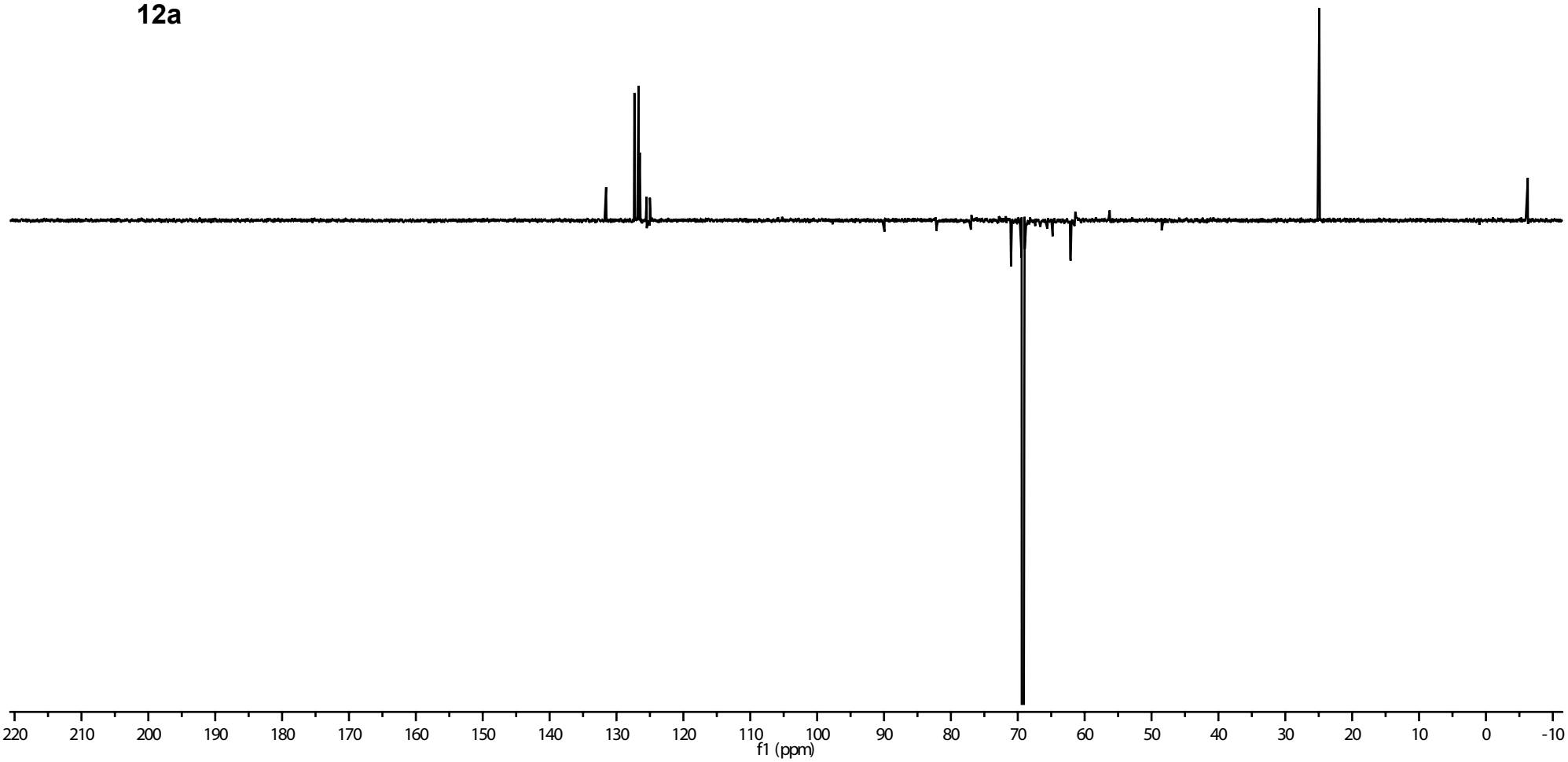

TBSO
*
OBn

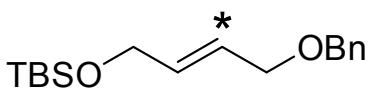
12a

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TBSO
*
OBn

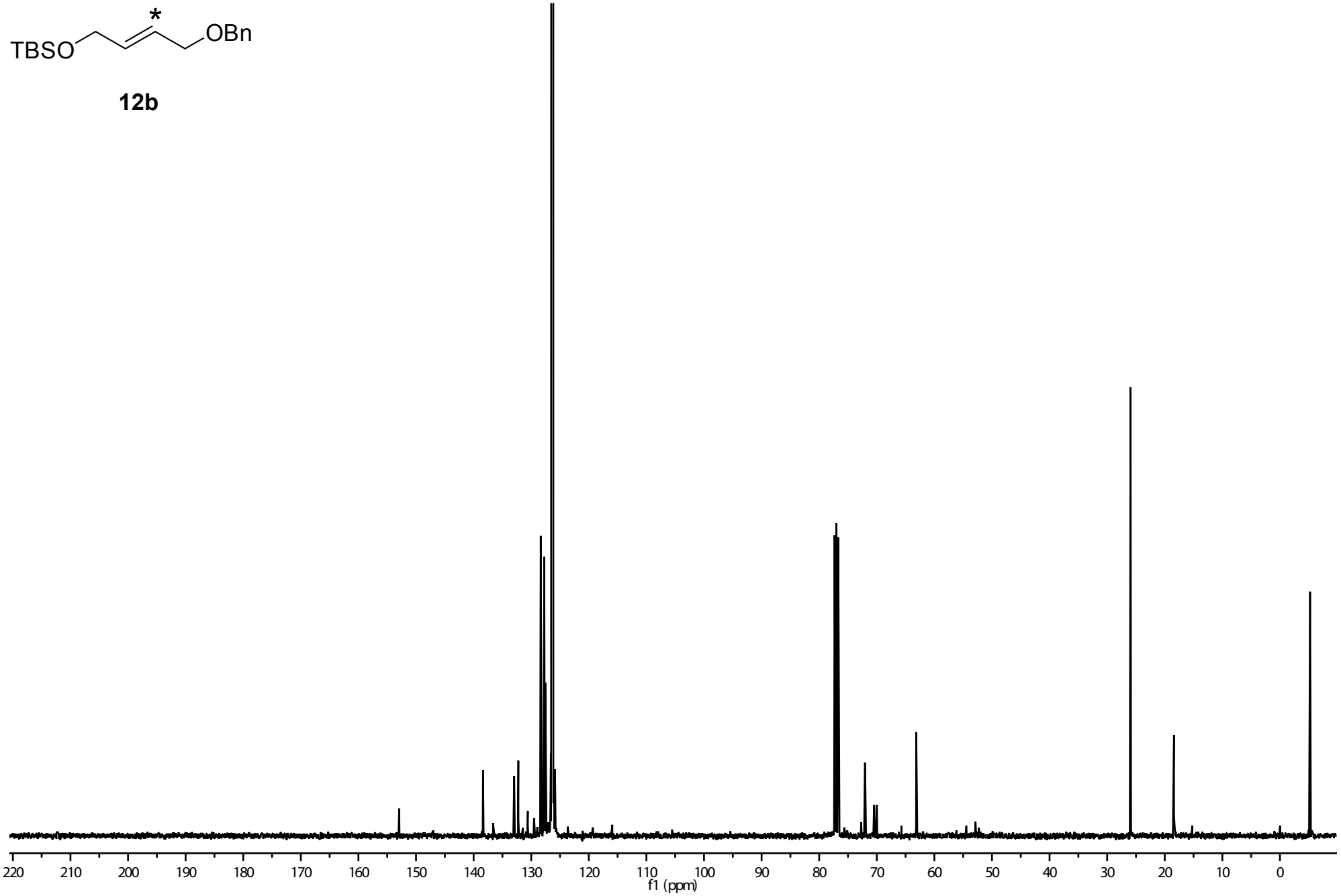
12a

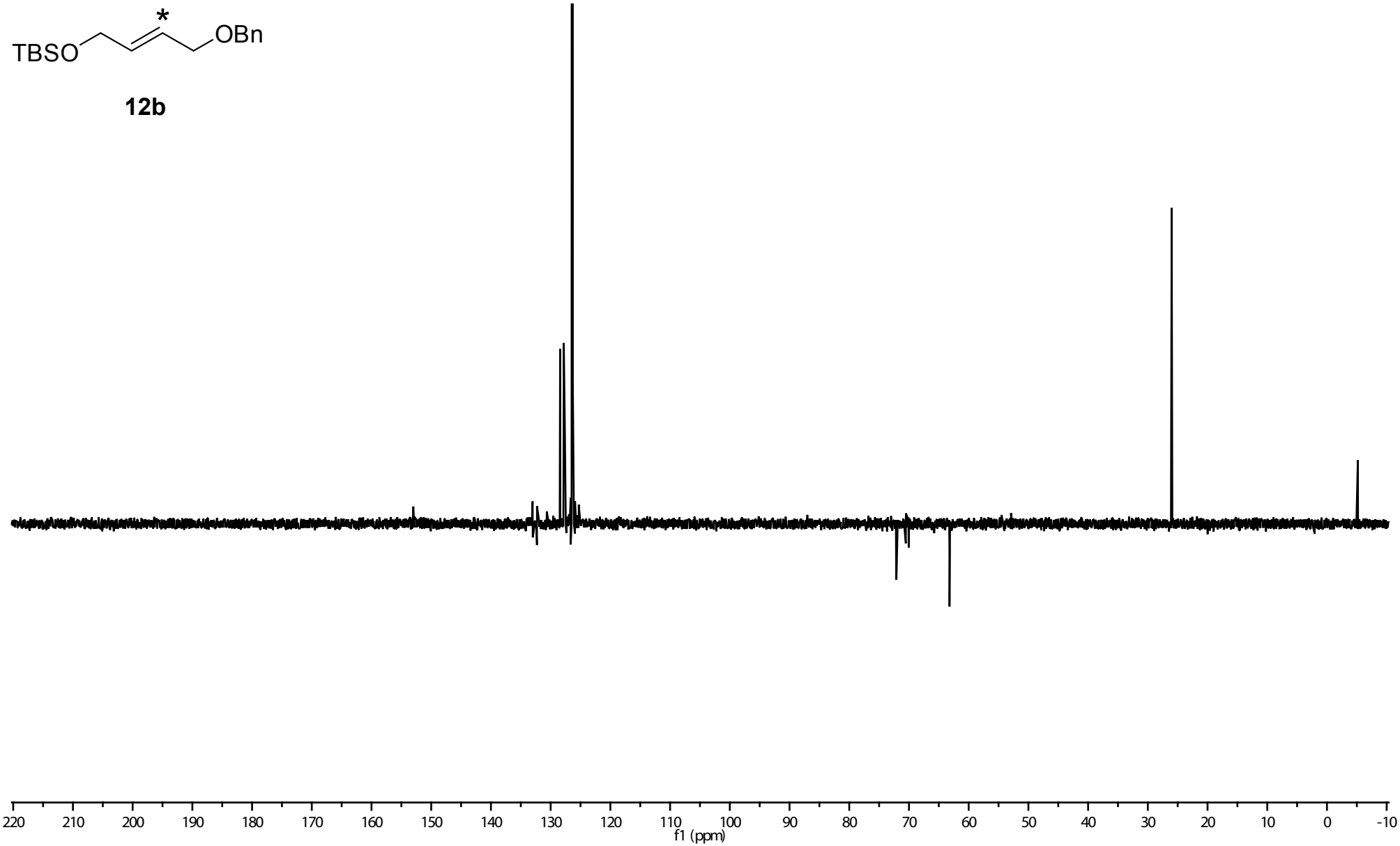

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

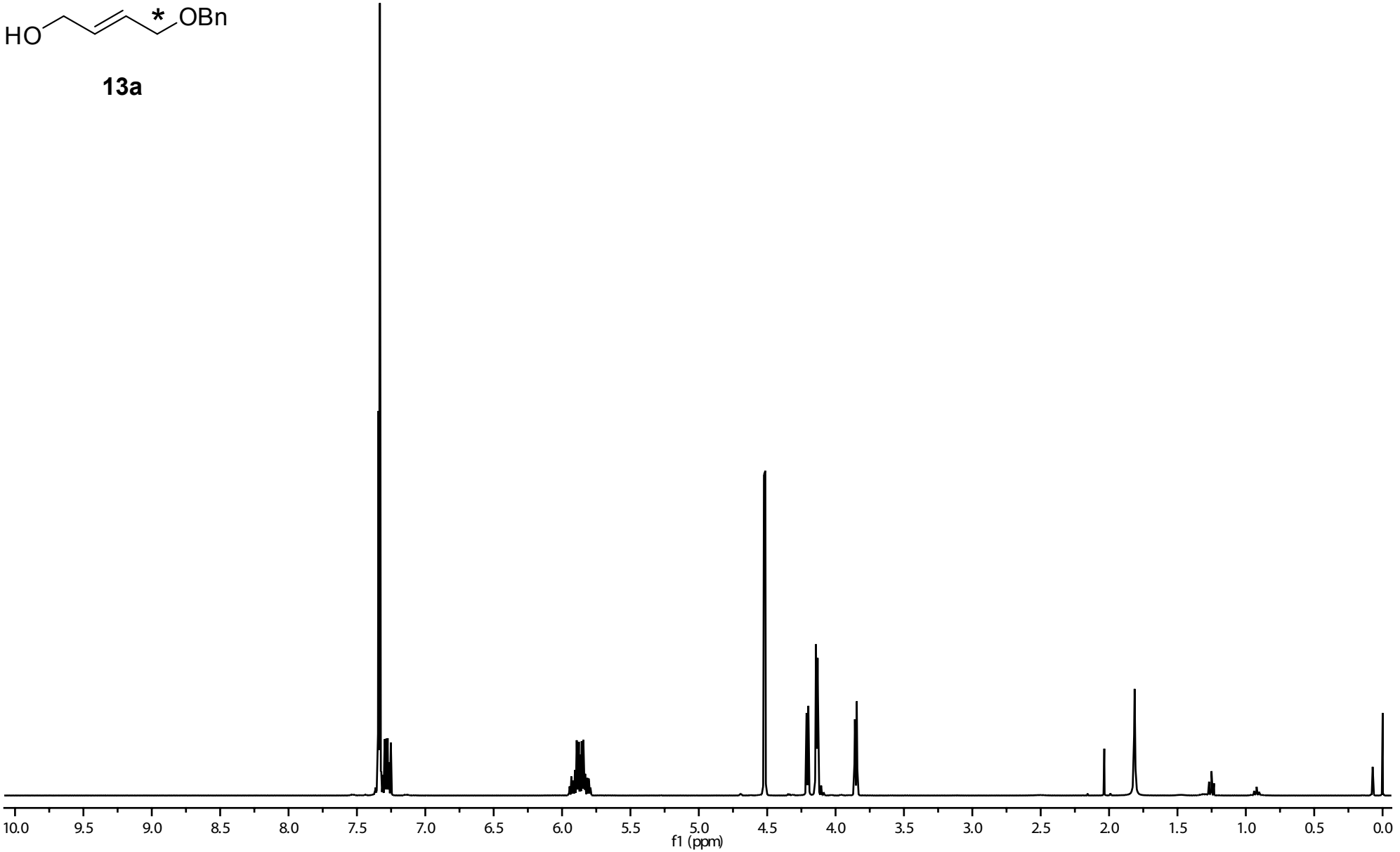

TBSO
*
OBn

12b

10.0
9.5
9.0
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
f1 (ppm)


TBSO
*
OBn
12b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TBSO
*
OBn
12b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
*
OBn
13a
10.0
9.5
9.0
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
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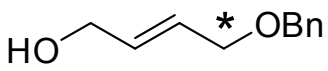
0.0
f1 (ppm)


HO
*
OBn

13a

220
210
200
190
180
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50
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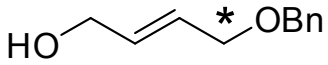
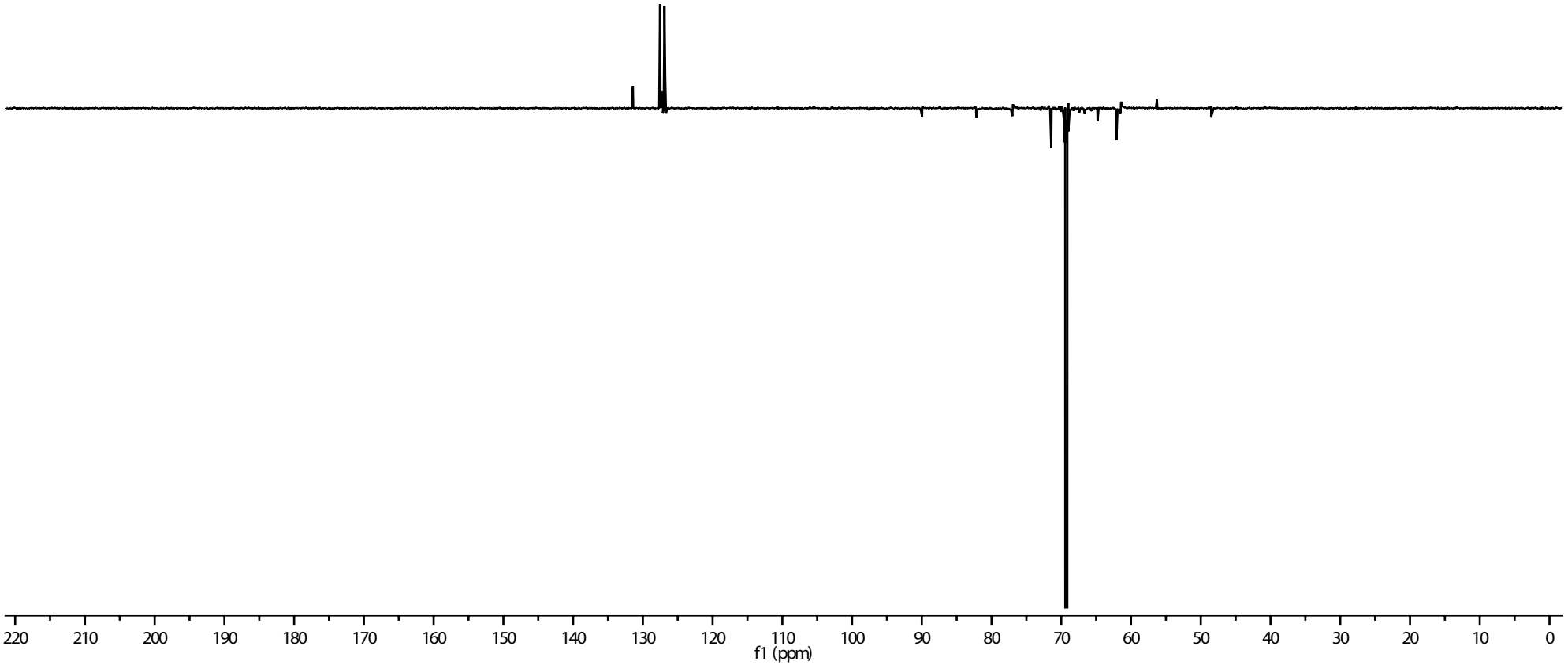
f1 (ppm)


HO
*
OBn

13a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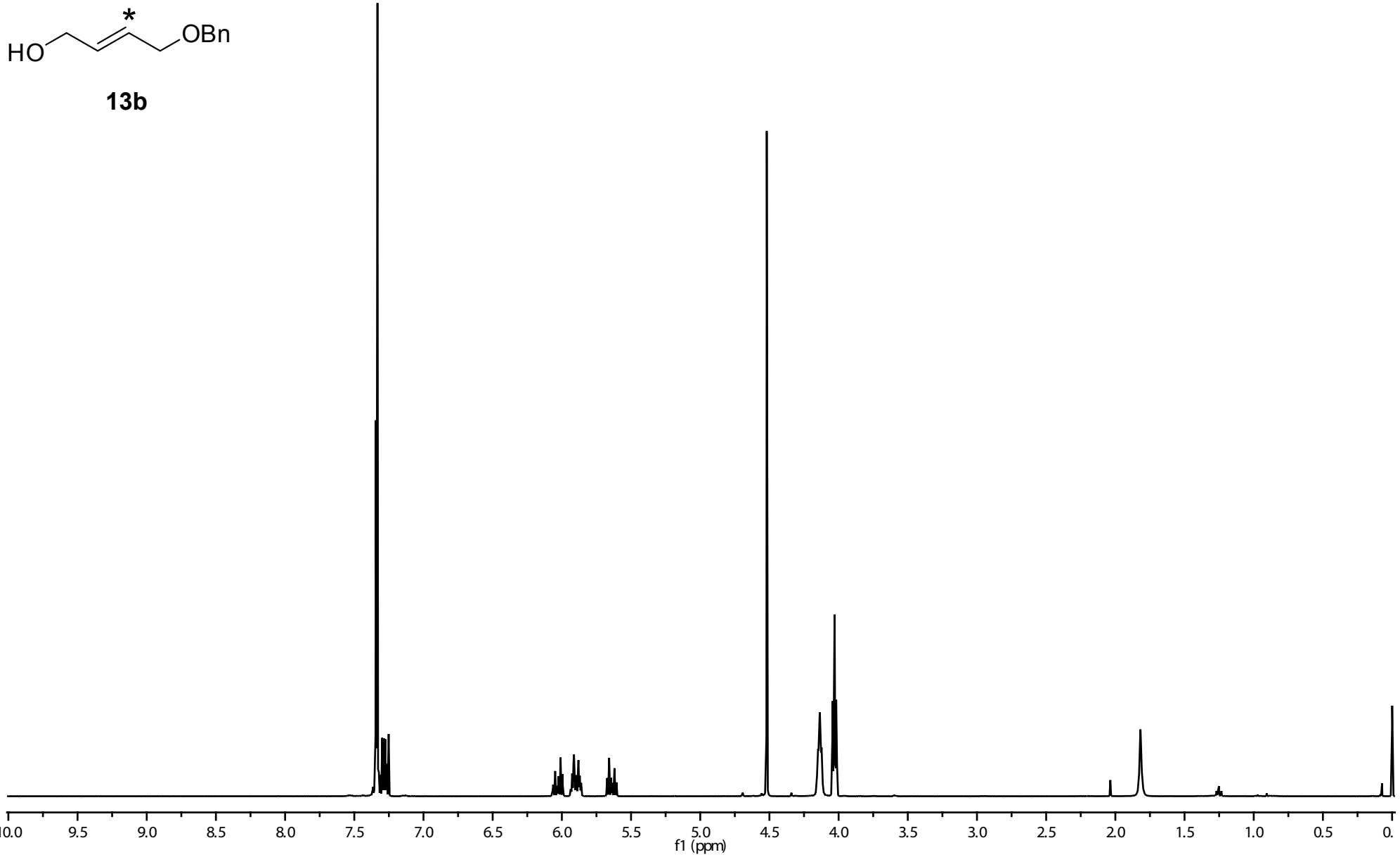
HO
OBn
*
13b
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
2.0
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1.0
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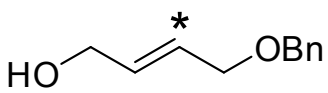
0.
f1 (ppm)


HO
OBn
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13b

220
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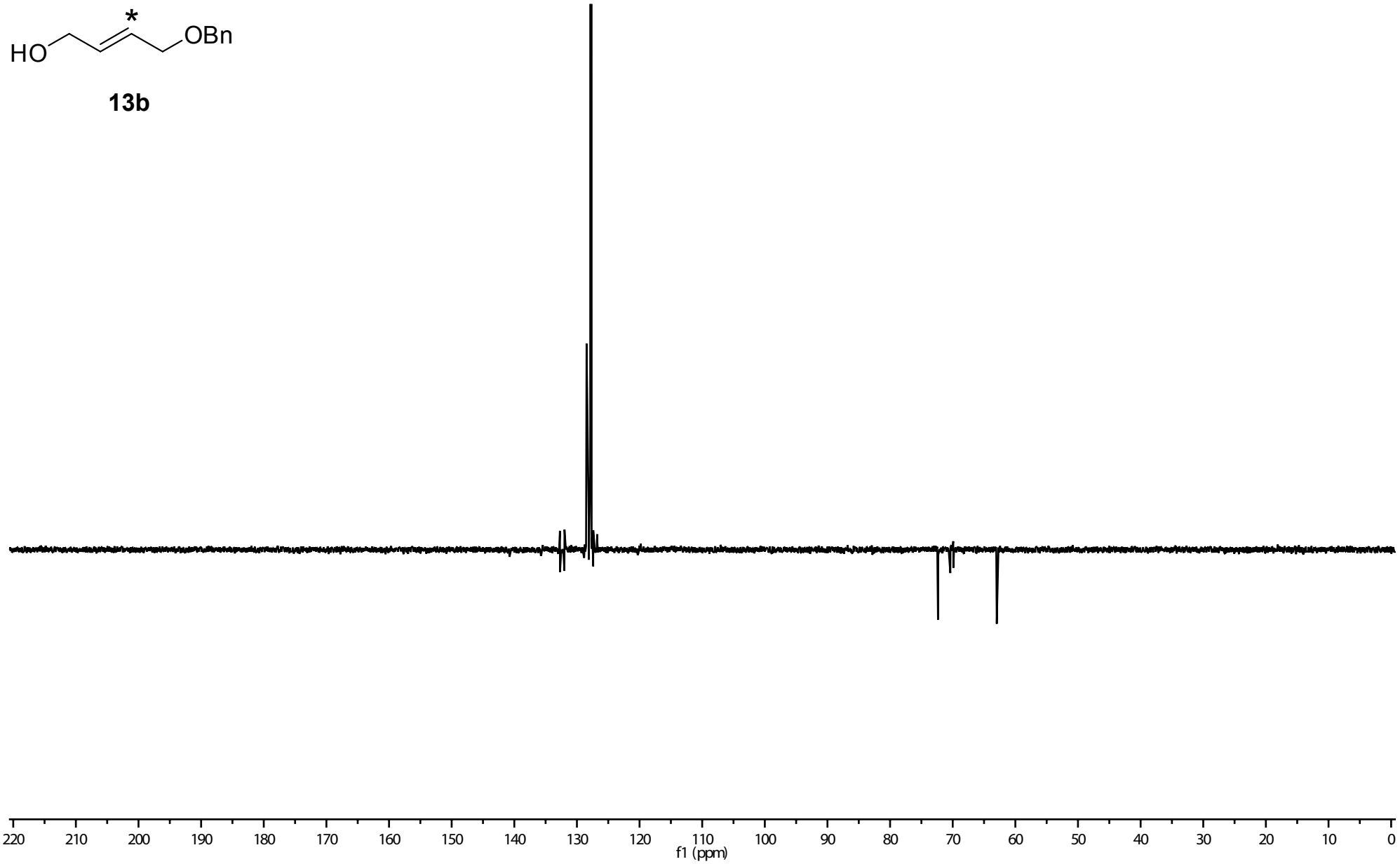
f1 (ppm)


HO
OBn
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13b
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10
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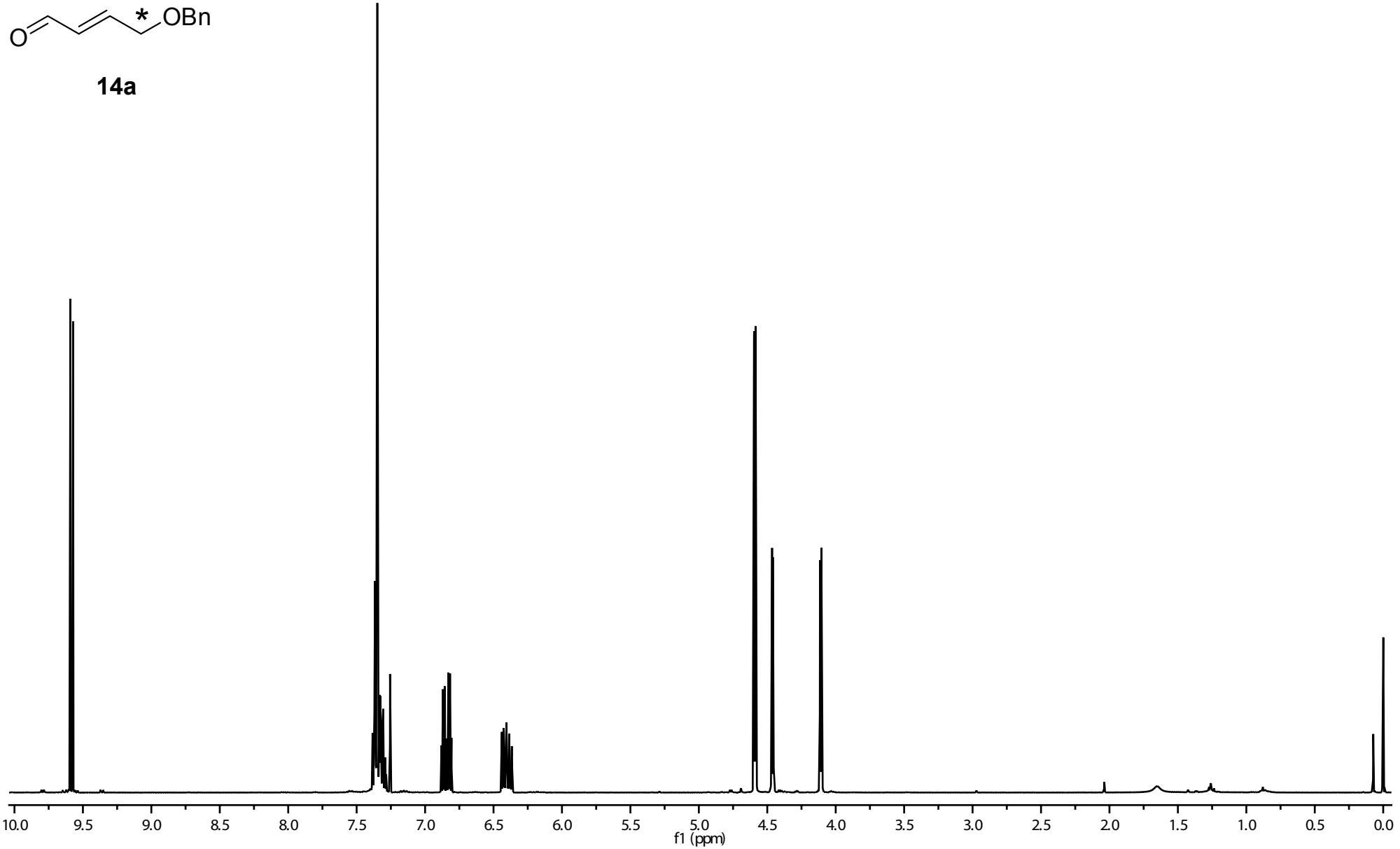
f1 (ppm)


O
*
OBn
14a
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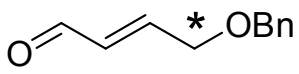
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
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OBn

14a

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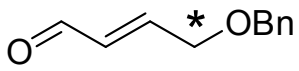
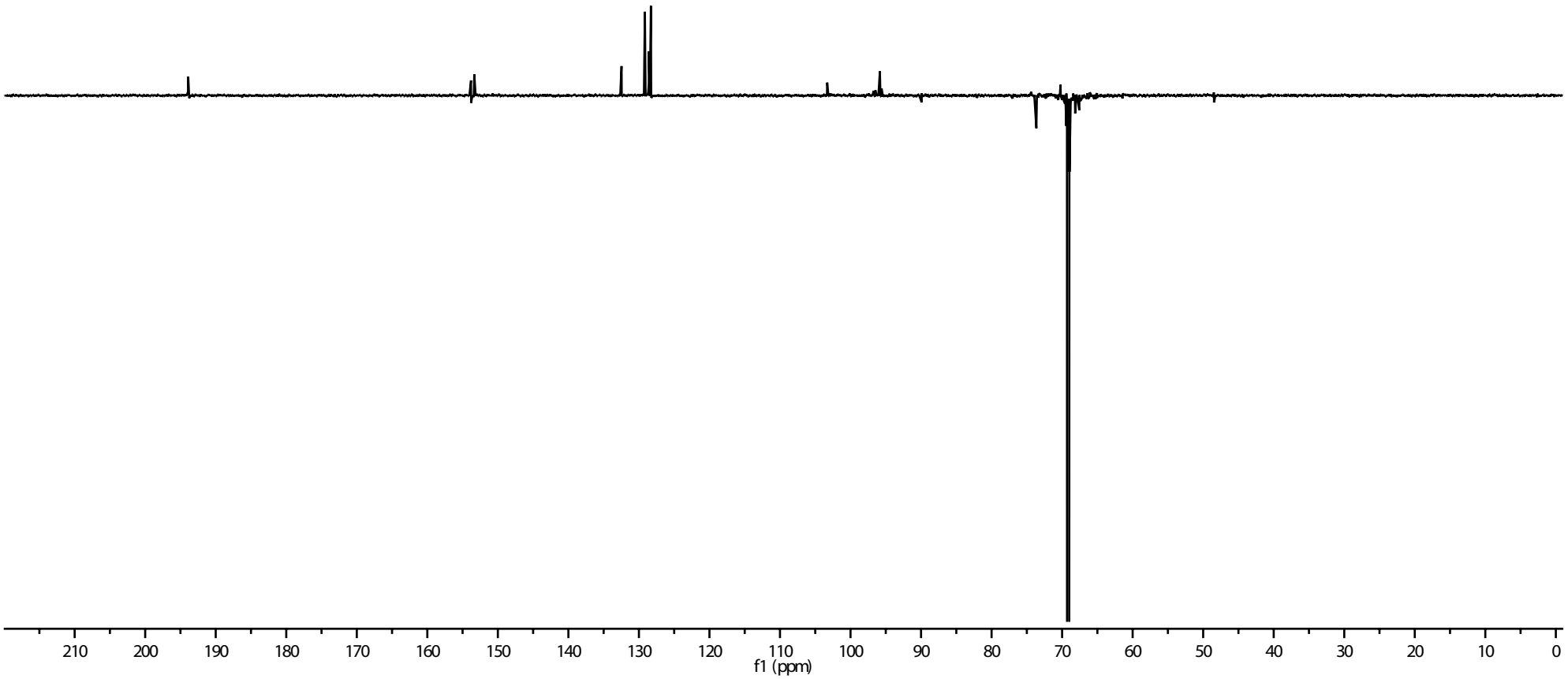
f1 (ppm)


O
*
OBn

14a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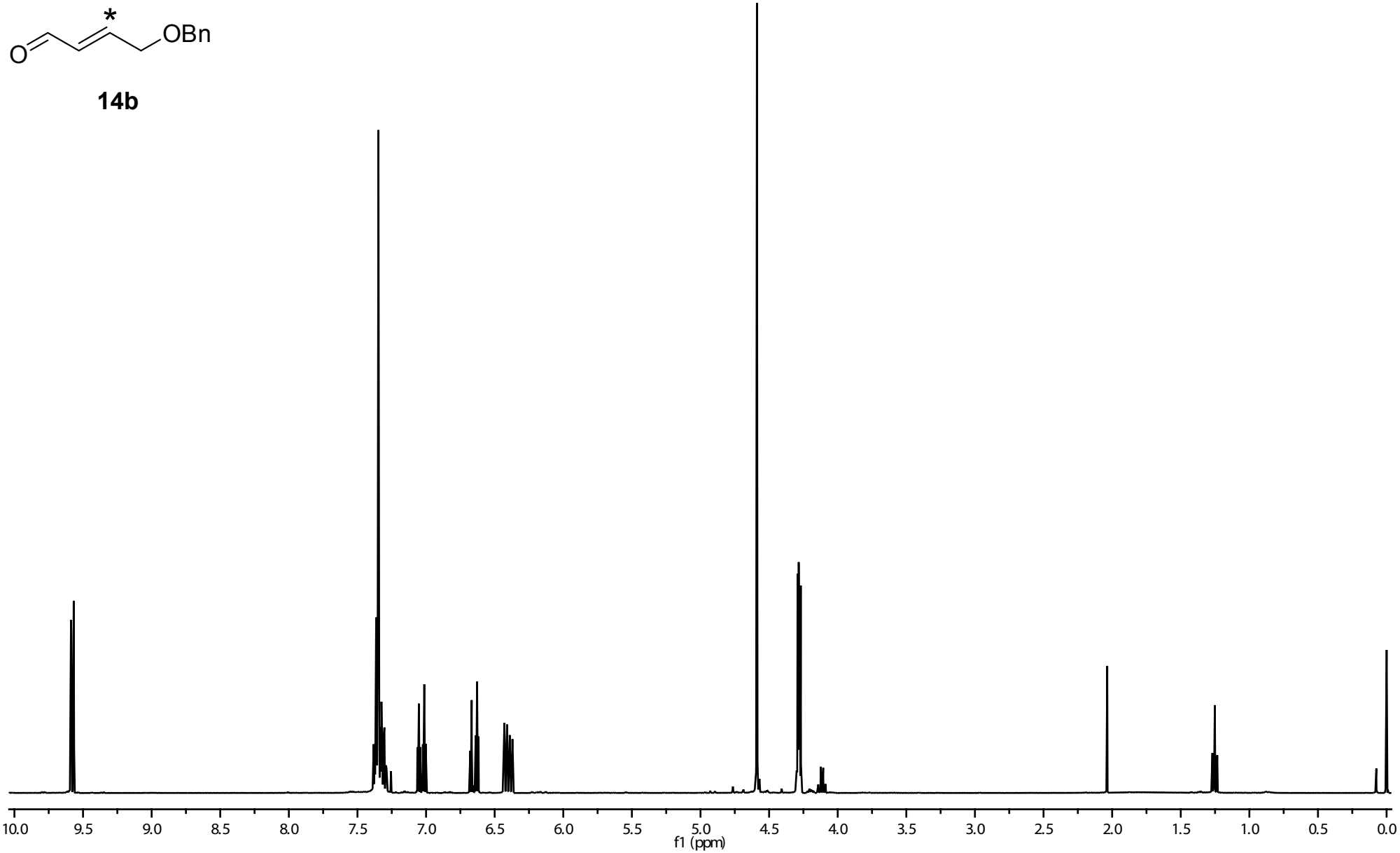
f1 (ppm)


O
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OBn
14b
10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.0
2.5
2.0
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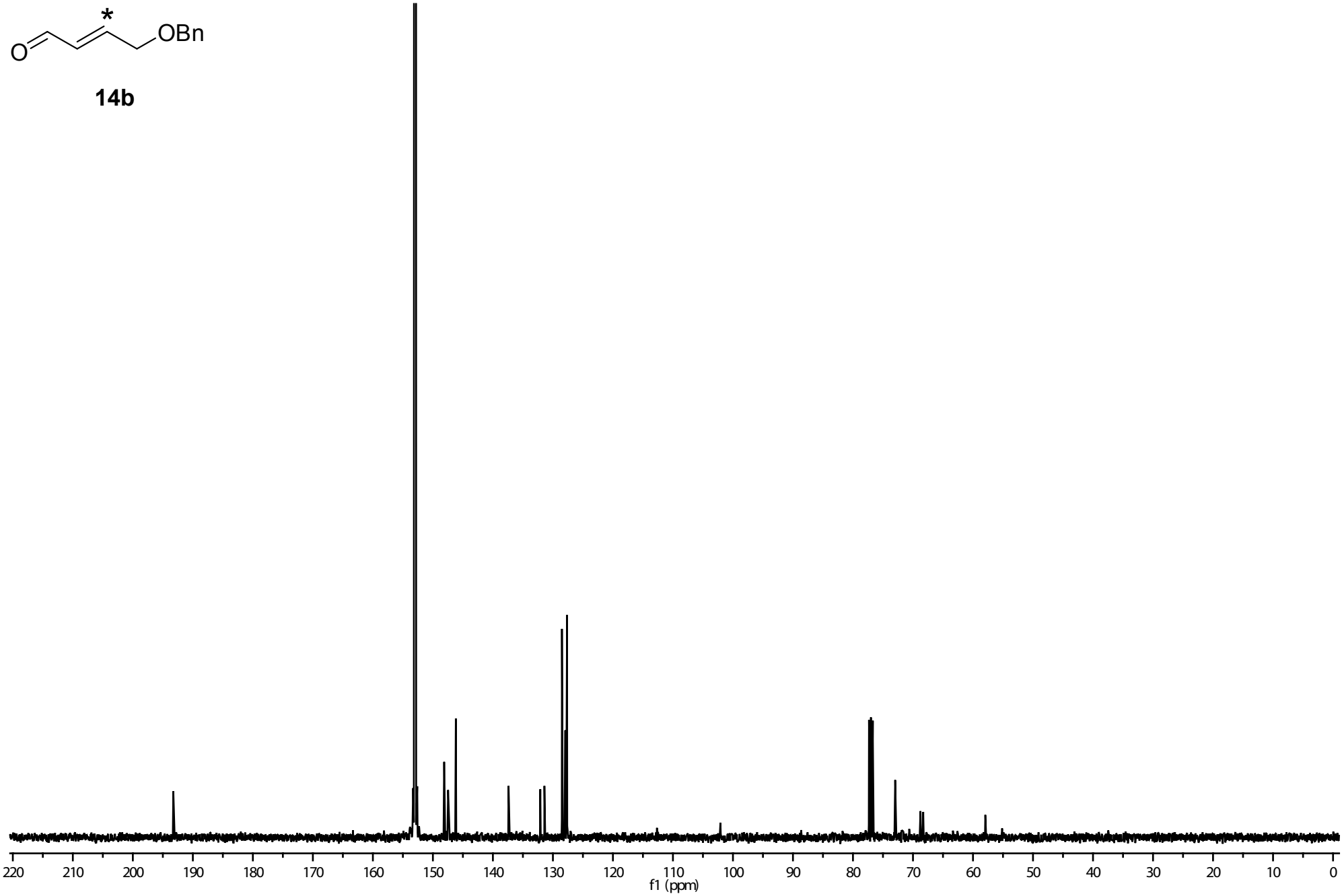
1.0
0.5
0.0
f1 (ppm)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OBn
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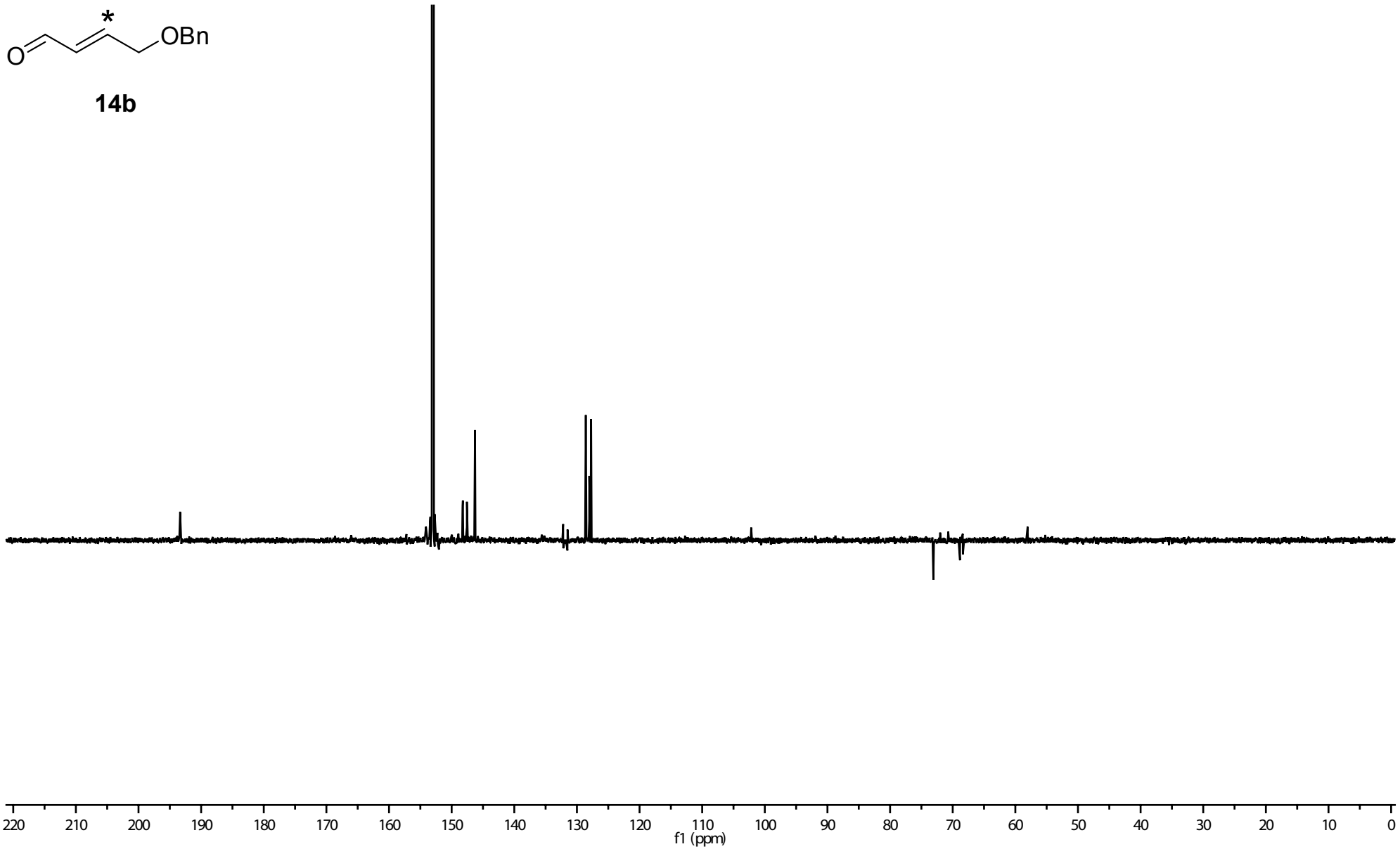
f1 (ppm)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OBn
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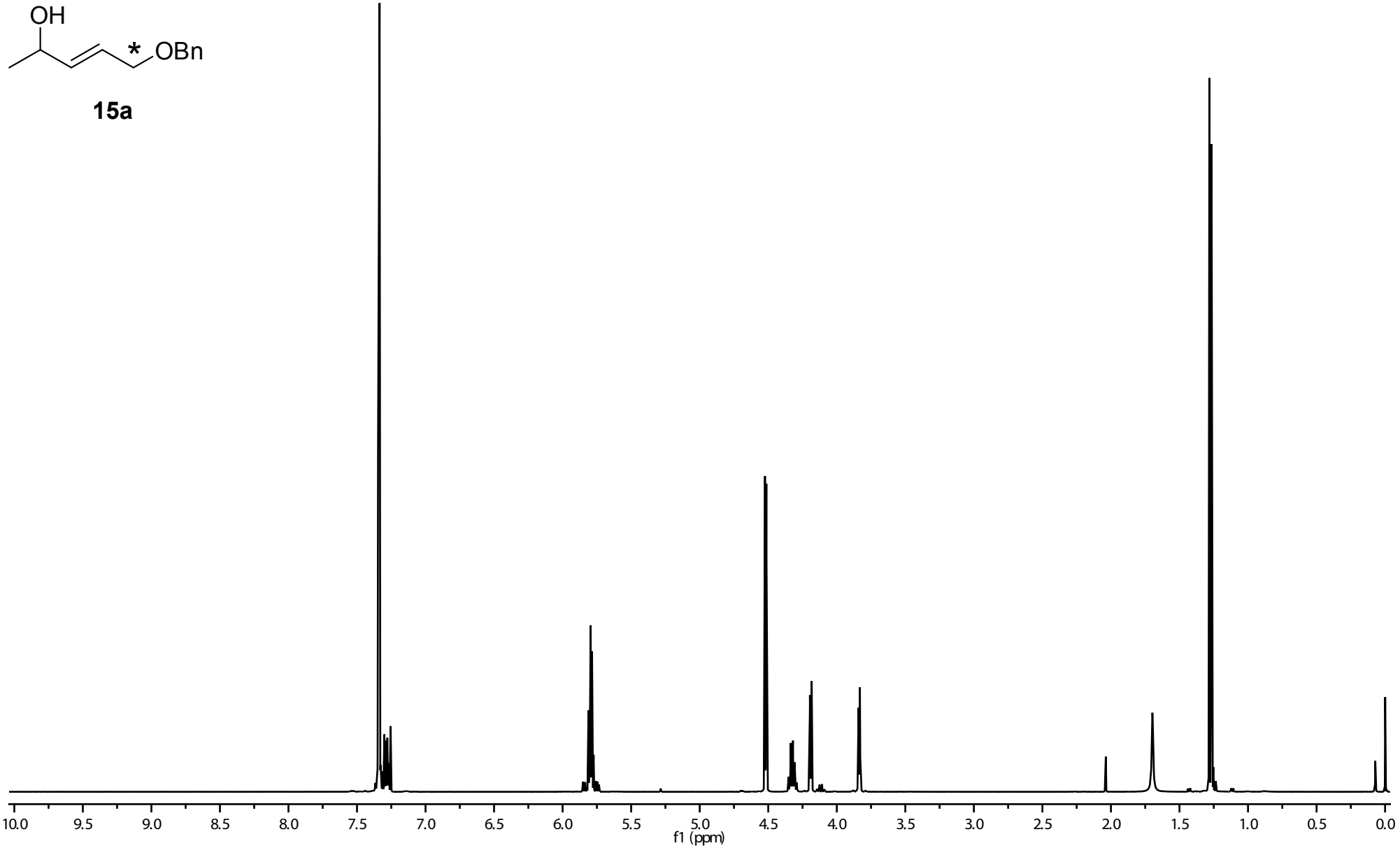
f1 (ppm)


OH
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OBn
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9.0
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7.5
7.0
6.5
6.0
5.5
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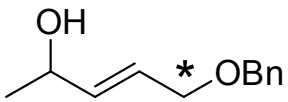
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
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OBn

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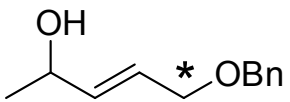
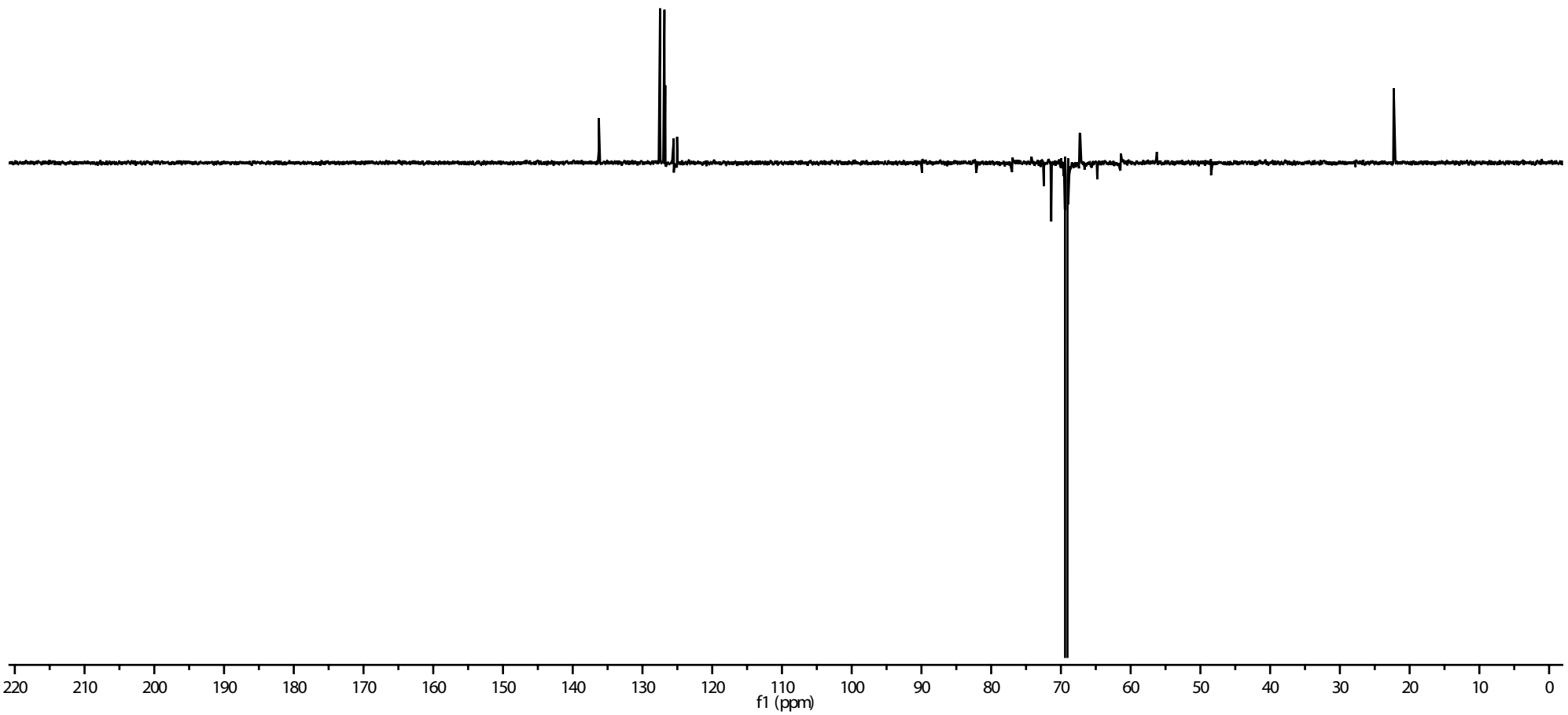
f1 (ppm)


OH
*
OBn

15a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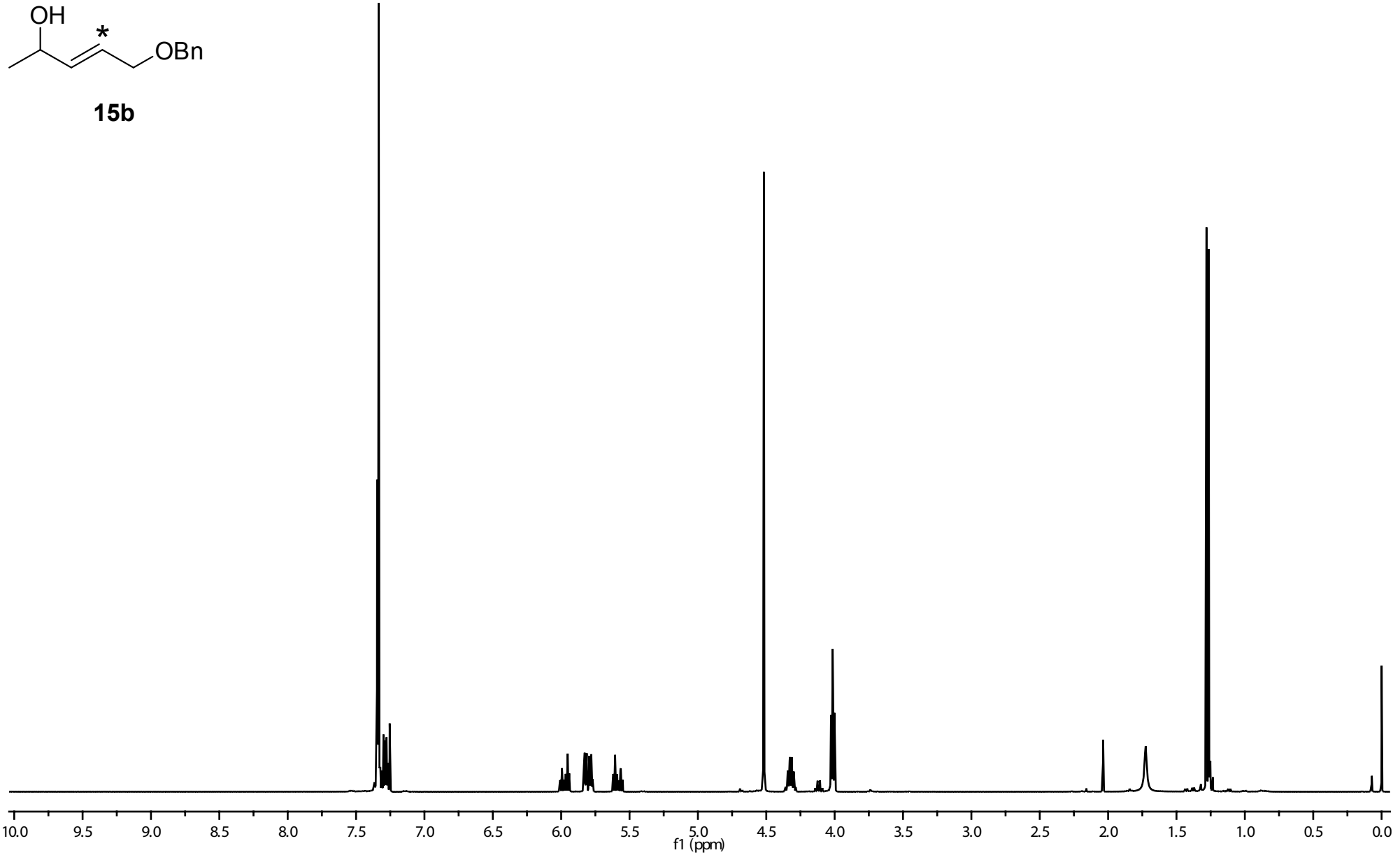
f1 (ppm)


OH
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OBn
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1.0
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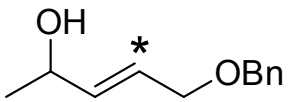
f1 (ppm)


OH
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OBn

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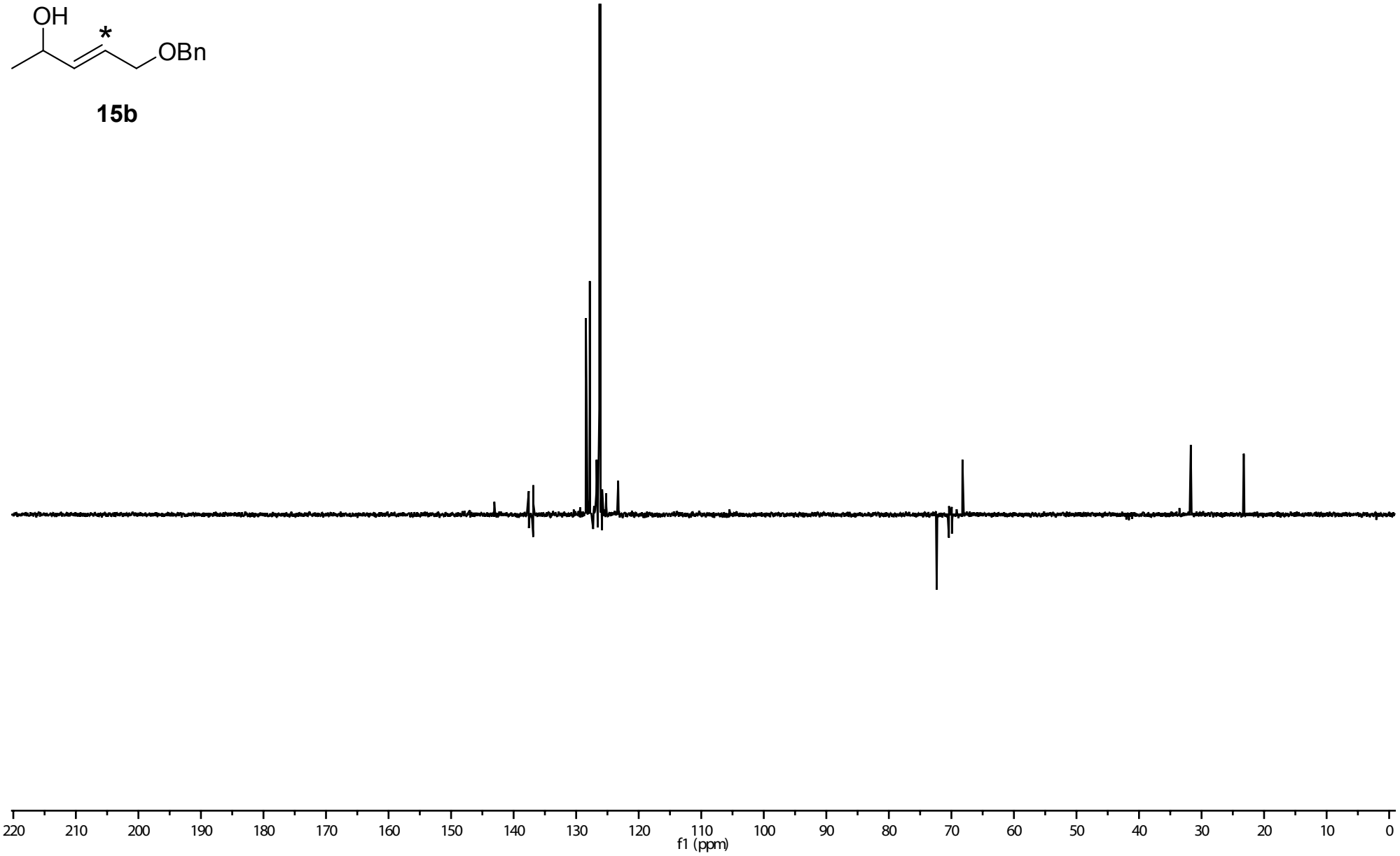
OH
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OBn
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f1 (ppm)