Supporting information.

Regio- and stereocontrolled opening of three-membered heterocyclic rings: a greener approach.

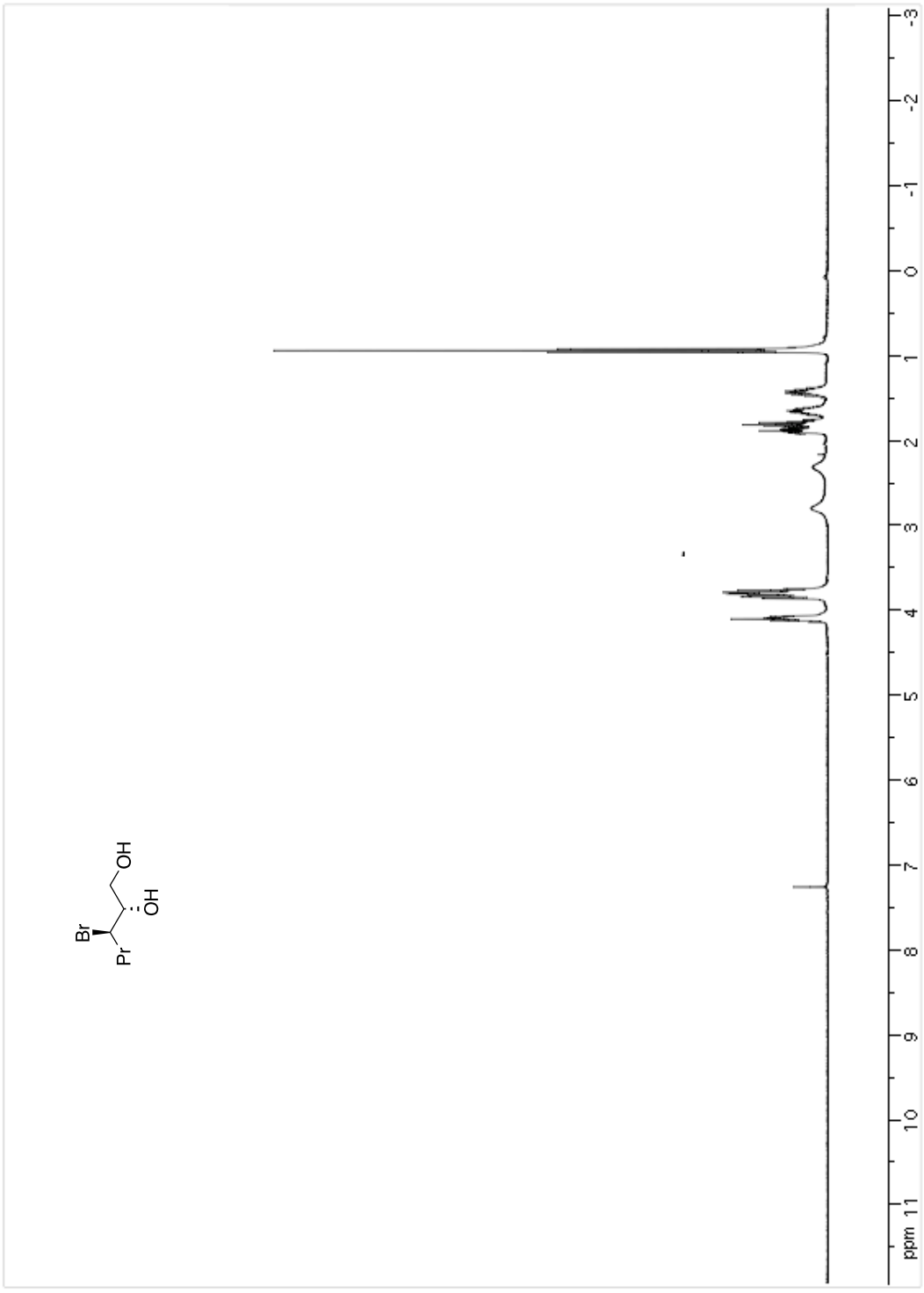
Characterization of known compounds.

(*2S*,3R) ethyl 3-bromo-2-hydroxyhexanoate (17):** pail yellow oil (93-95% yield); ^{1}H NMR (300 MHz $CDCl_3$) δ: 4.38 (1H, d, *J* 3.1 Hz, C<u>H</u>OH), 4.2 (2H, q, *J* 7.2 Hz, COC<u>H</u>$_2$CH$_3$), 4.18-4.1 (1H, m, C<u>H</u>Br), 3.48 (1H, br s, O<u>H</u>), 1.96-1.75 (2H, m, C<u>H</u>$_2$CH$_2$CH$_3$), 1.72-1.36 (2H, m, CH$_2$C<u>H</u>$_2$CH$_3$), 1.31 (3H, t, *J* 7.2 Hz, COCH$_2$C<u>H</u>$_3$), 0.95 (3H, t, *J* 7.4, CH$_2$CH$_2$C<u>H</u>$_3$); ^{13}C NMR (75 MHz $CDCl_3$) δ: 165.6, 74.5, 62.4, 57.3, 32.2, 25.9, 13.2, 14.3; HRMS (ES Q-TOF): [M+H]+, found. 239.0280 $C_8H_{15}BrO_3$ requires 239.0283.

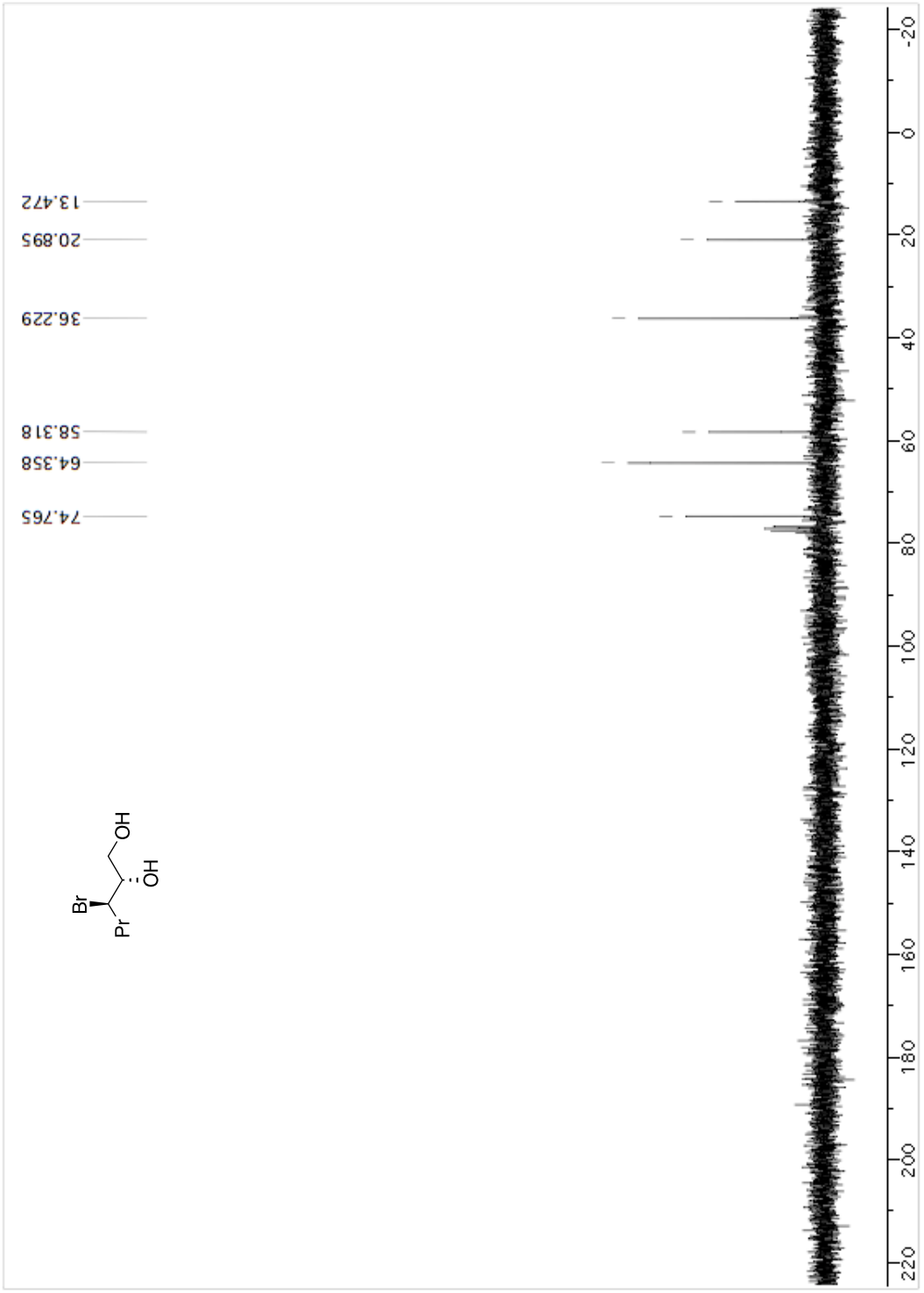
(*E*)-ethyl 3-((4*R,5*S**)-2-oxo-4-propyloxazolidin-5-yl)acrylate (20)**: pail yellow oil (96-97% yield); ^{1}H NMR (300 MHz $CDCl_3$) δ: 6.96 (1H, dd, *J* 5.1, 15.4 Hz, C<u>H</u>=CHCO), 6.42 (1H, br s, N<u>H</u>), 6.06 (1H, dd, *J* 1.5, 15.4 Hz, CH=C<u>H</u>CO), 4.74 (1H, ddd, *J* 1.5, 6.6 Hz, C<u>H</u>CH=CH), 4.2 (2H, q, *J* 7.2 Hz, COC<u>H</u>$_2$CH$_3$), 3.54 (1H, dd, *J* 6.6 Hz, C<u>H</u>NH), 1.90-1.42 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$), 1.31 (3H, t, *J* 7.2 Hz, COCH$_2$C<u>H</u>$_3$), 0.95 (3H, t, *J* 7.4, CH$_2$CH$_2$C<u>H</u>$_3$); ^{13}C NMR (75 MHz $CDCl_3$) δ: 165.5, 158.4, 141.8, 123.2, 80.2, 60.9, 57.7, 37.0, 18.6, 14.1, 13.7; HRMS (ES Q-TOF): [M+H]+, found. 228.1239 $C_{11}H_{17}NO_4$ requires 228.1236

NMR spectra of unknown compounds.

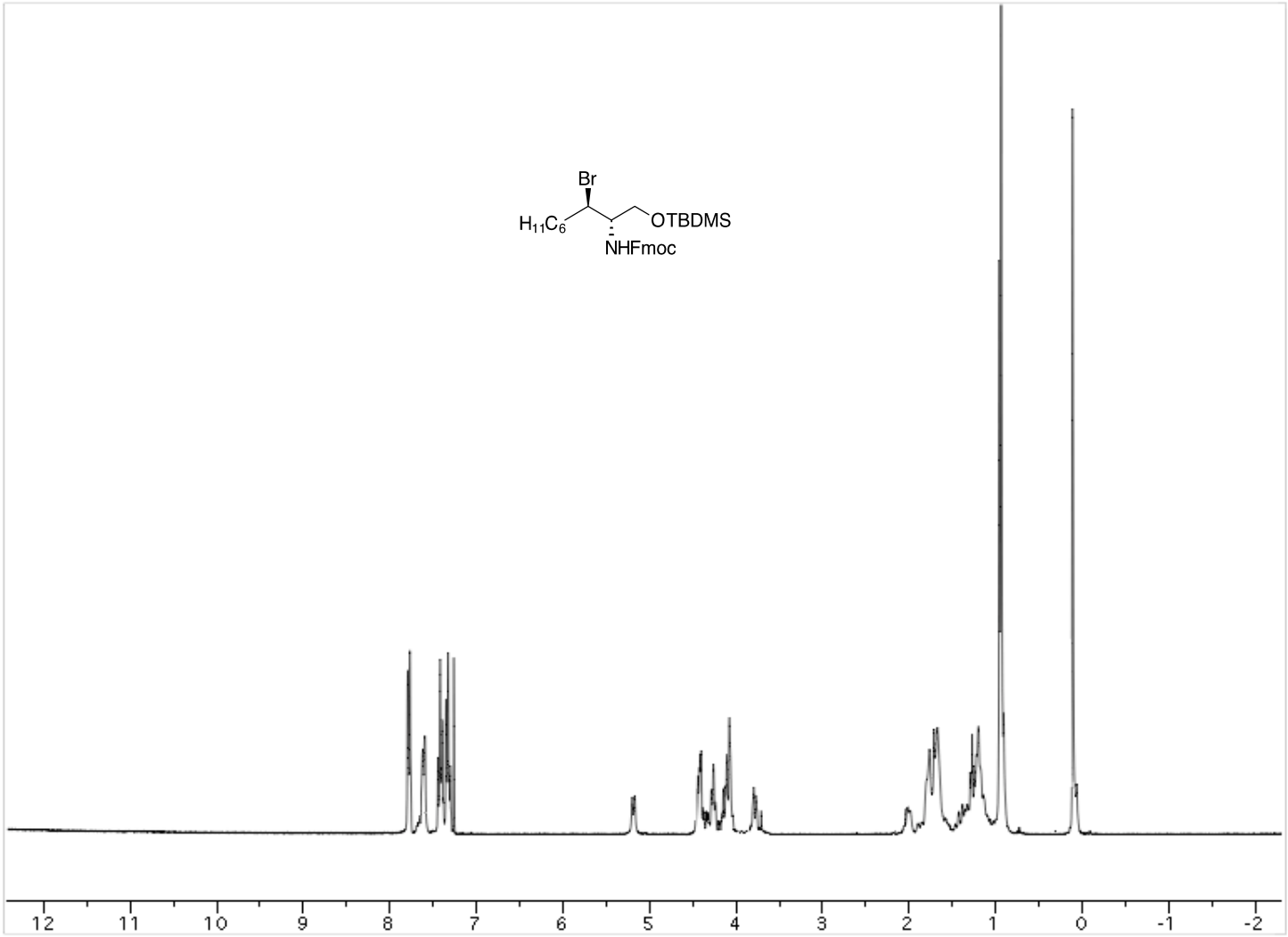
(2*S,3*R**)-3-bromo-hexan-1,2-diol (15)**



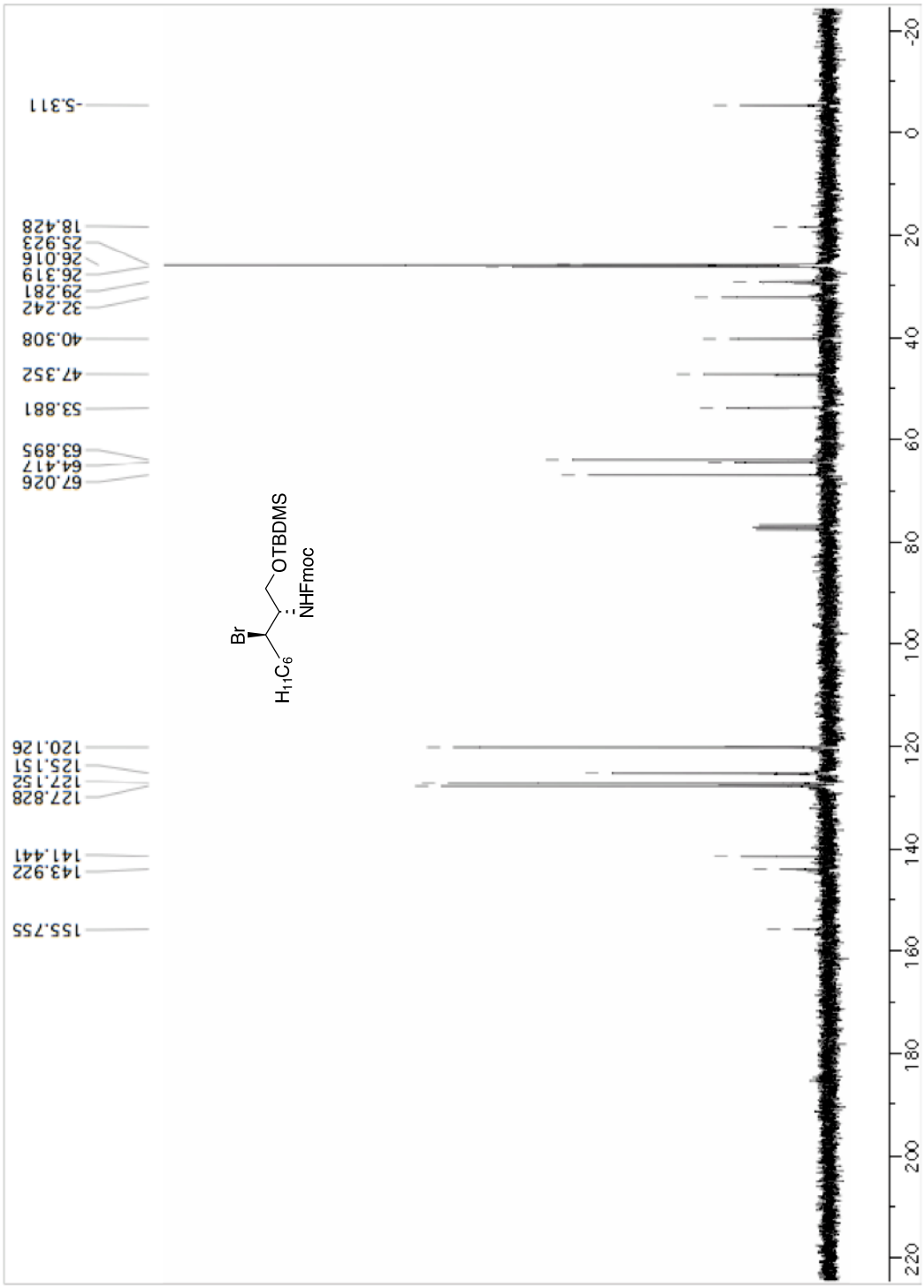
(2*S,3*R**)-3-bromo-hexan-1,2-diol (15)**



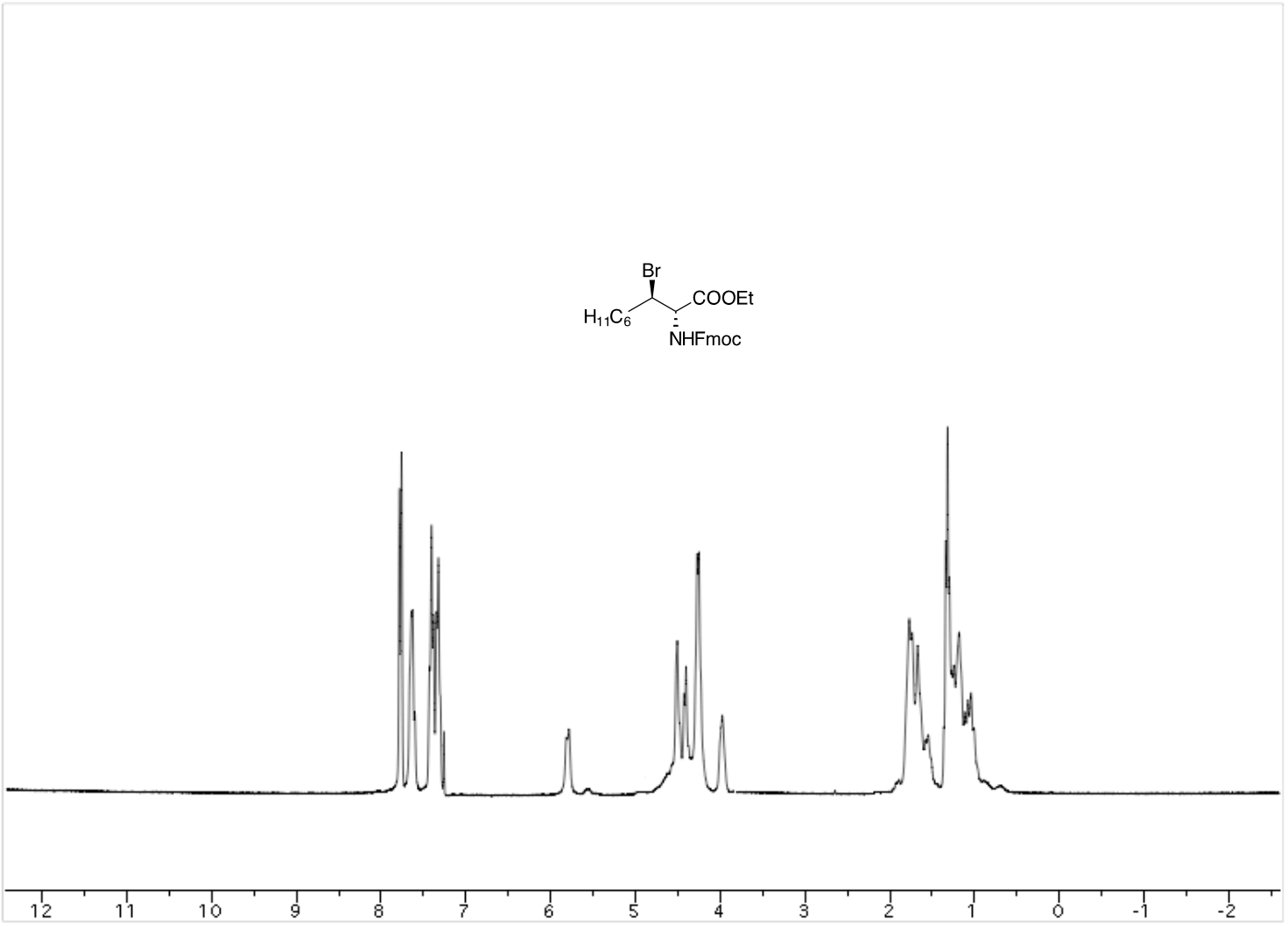
(*2S*,3R)-2-(N-9-fluorenylmethyloxycarbonyl)amino-3-bromo-3-cyclohexyl-(O-tert-butyl dimethylsilyl)propanol (16)**:



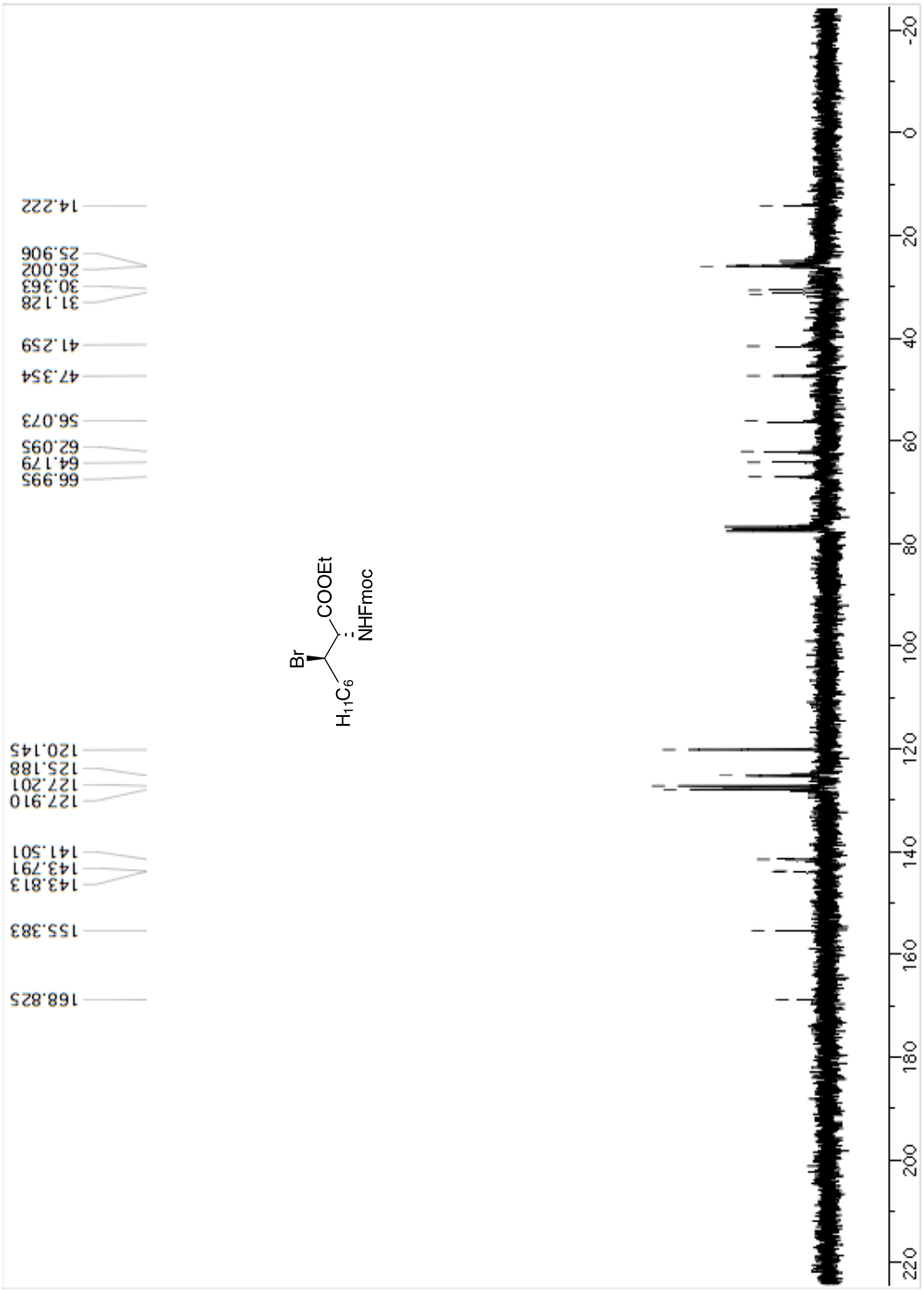
(2*S,3*R**)-2-(N-9-fluorenylmethyloxycarbonyl)amino-3-bromo-3-cyclohexyl-(O-tert-butyl dimethylsilyl)propanol (16):**



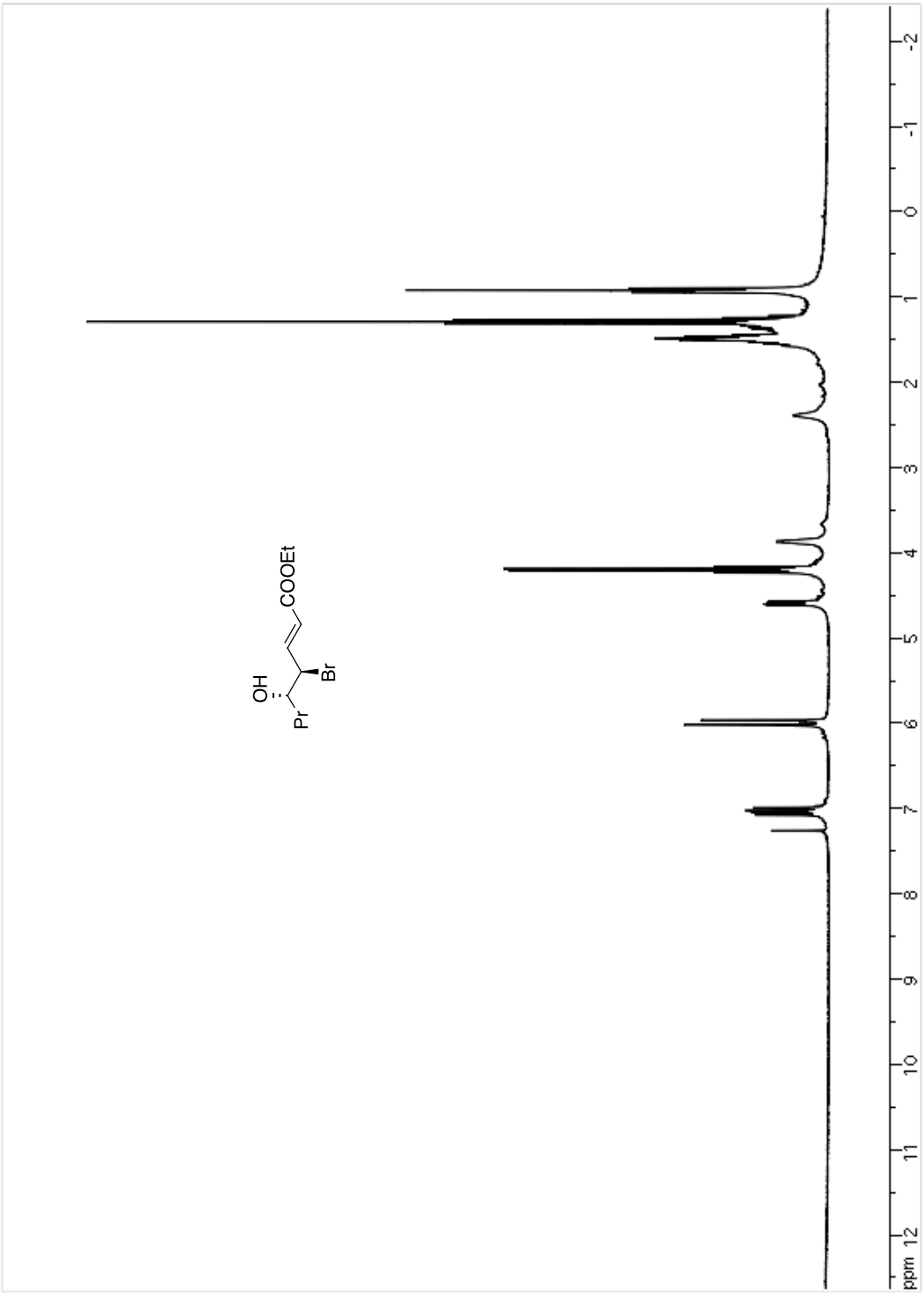
(*2S*, 3R)-ethyl 2-(N-9-fluorenylmethyloxycarbonyl)amino-3-bromo-3-cyclohexylpropanoate (18)**:



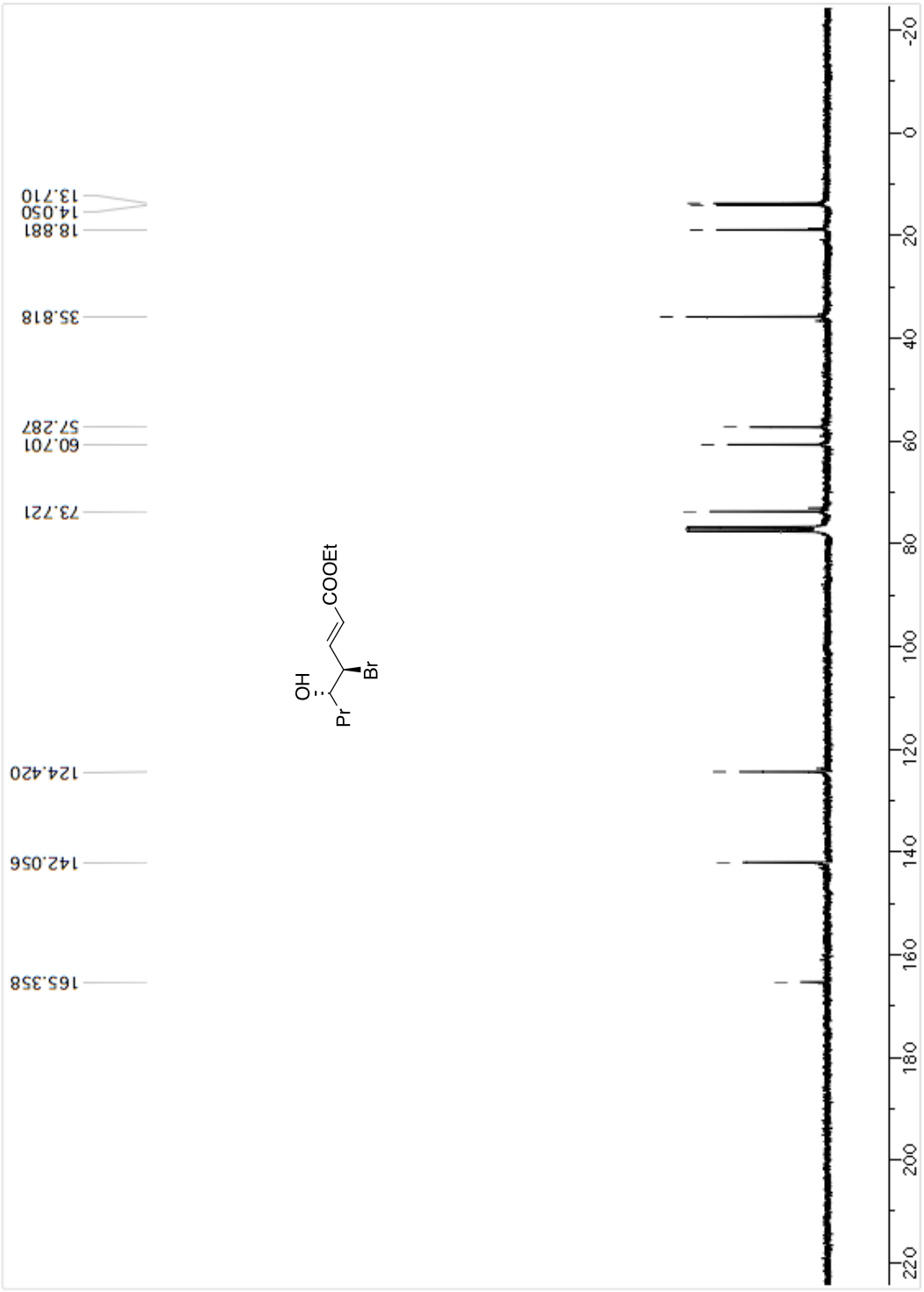
(2*S, 3*R**)-ethyl 2-(N-9-fluorenylmethyloxycarbonyl)amino-3-bromo-3-cyclohexylpropanoate (18):**



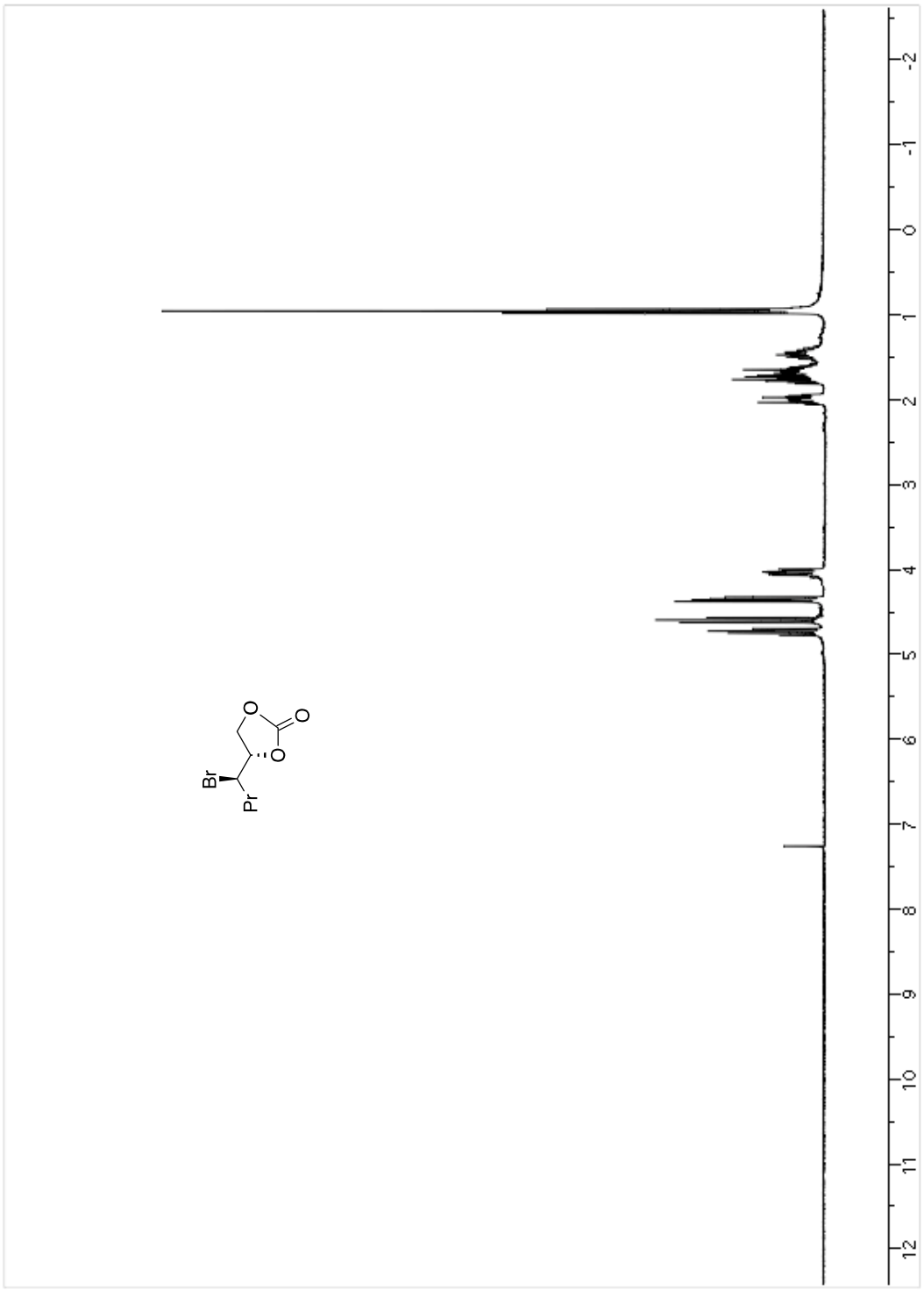
***(E)*-(4*R**,5*S**)-ethyl 4-bromo-5-hydroxyoct-2-enoate (19):**



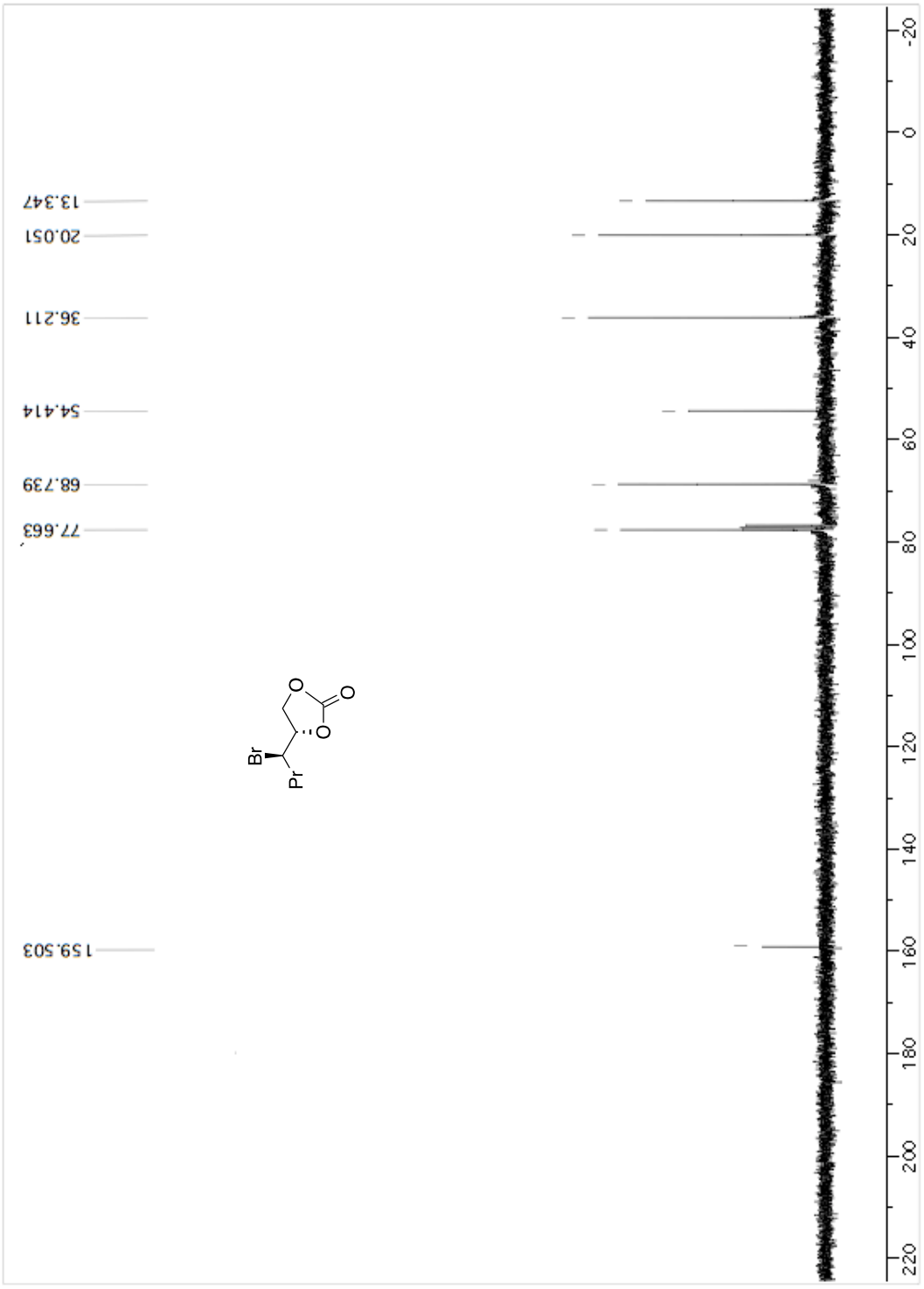
***(E)*-(4*R**,5*S**)-ethyl 4-bromo-5-hydroxyoct-2-enoate (19):**



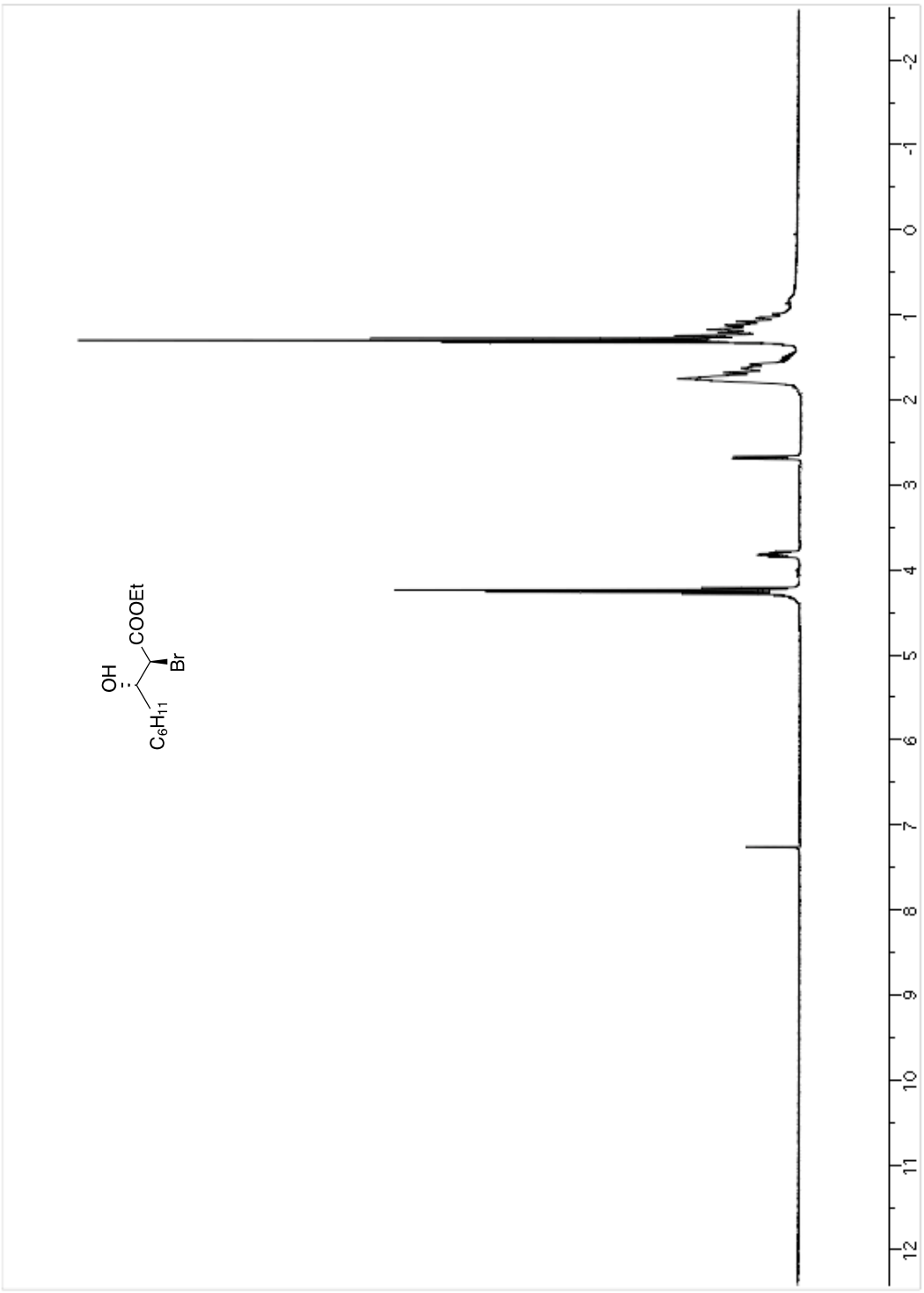
(*S)-4-((*R**)-1-bromobutyl)-1,3-dioxolan-2-one (21):**



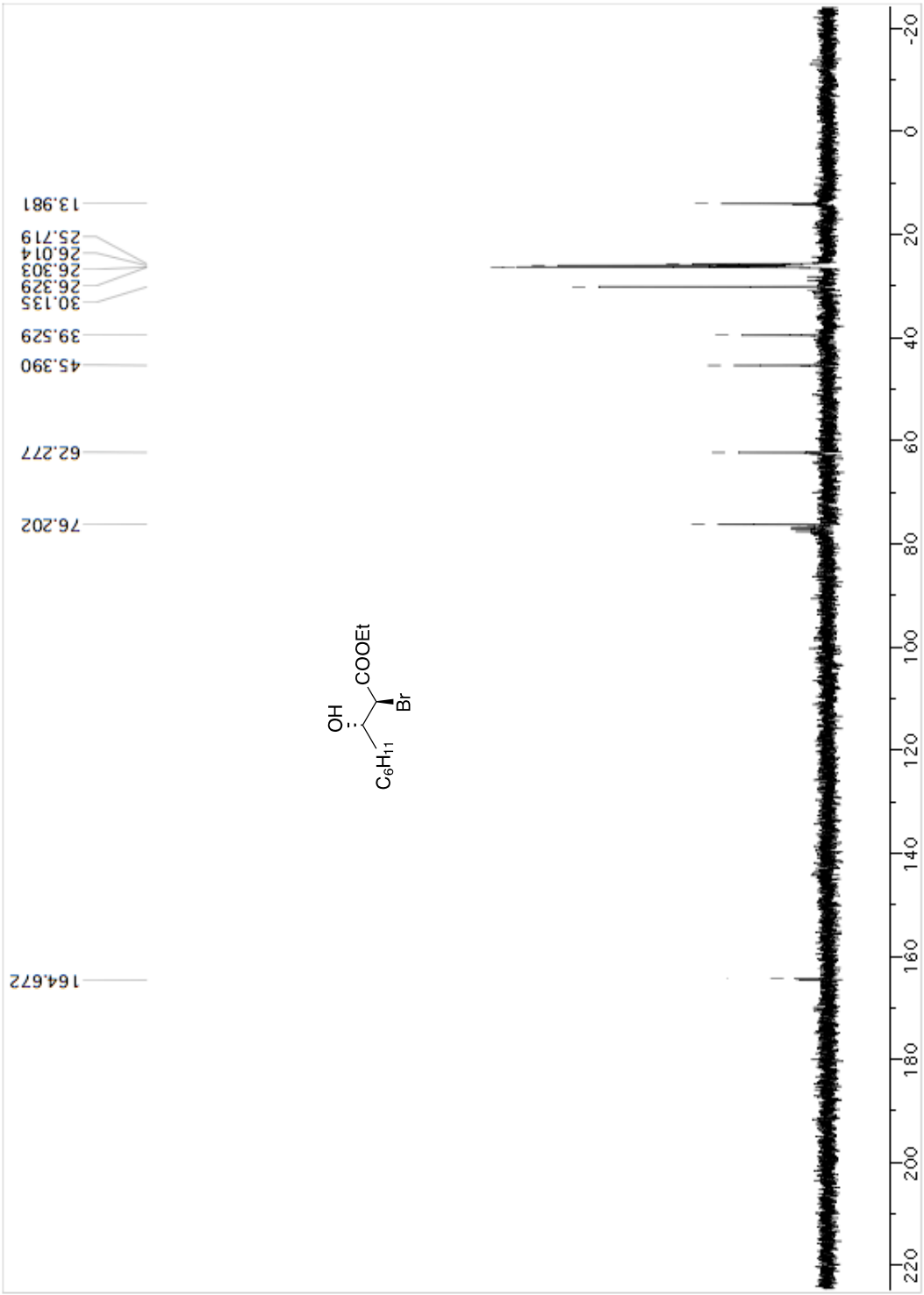
(*S)-4-((*R**)-1-bromobutyl)-1,3-dioxolan-2-one (21):**



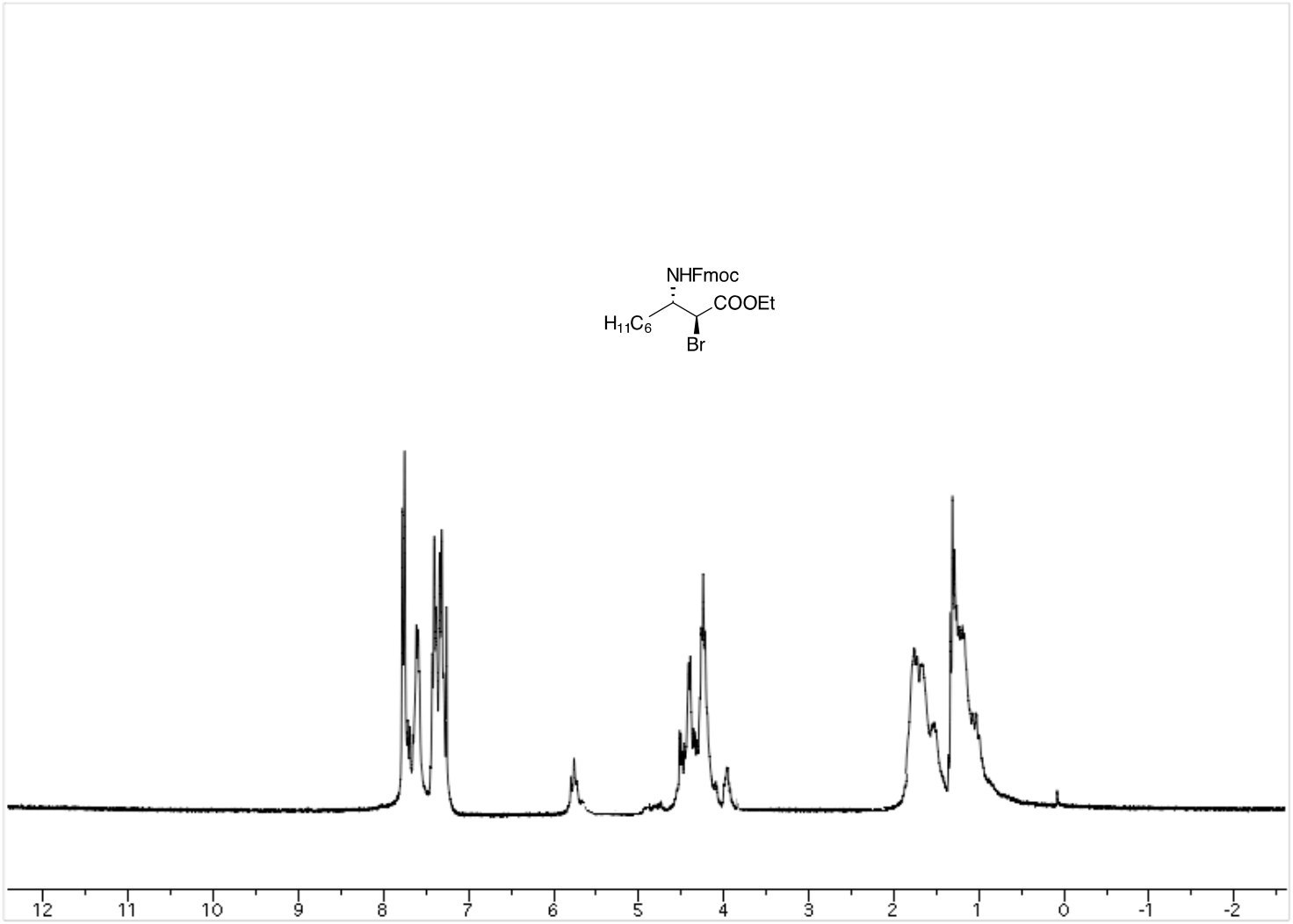
(2*S,3*S**) ethyl 2-bromo-3-cyclohexyl-3-hydroxypropa noate (22):**



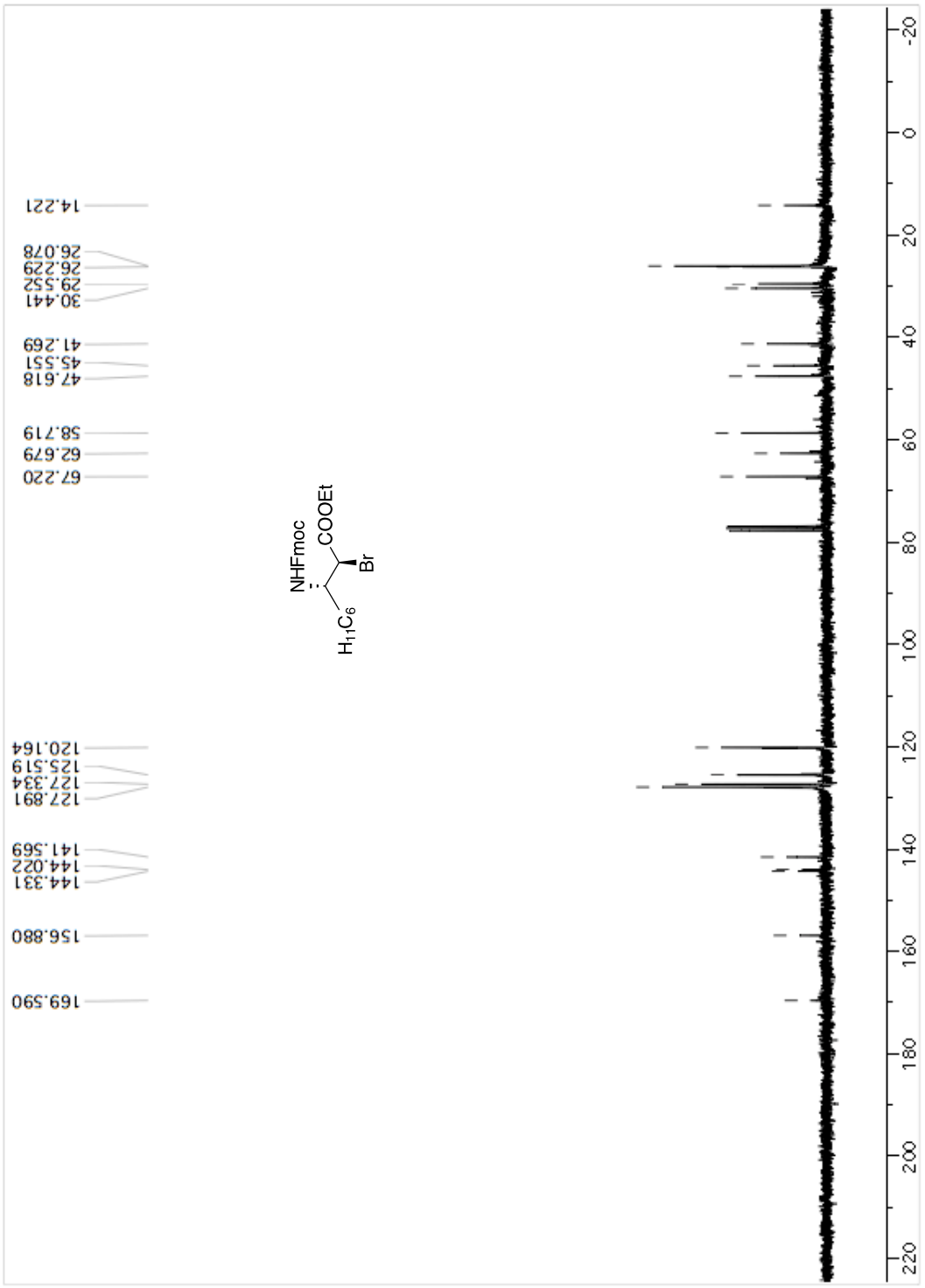
(2*S,3*S**) ethyl 2-bromo-3-cyclohexyl-3-hydroxypropa noate (22):**



(2*S,3*S**)-ethyl 3-(N-9-fluorenylmethyloxycarbonyl)amino-2-bromo-3-cyclohexyl propanoate (23):**

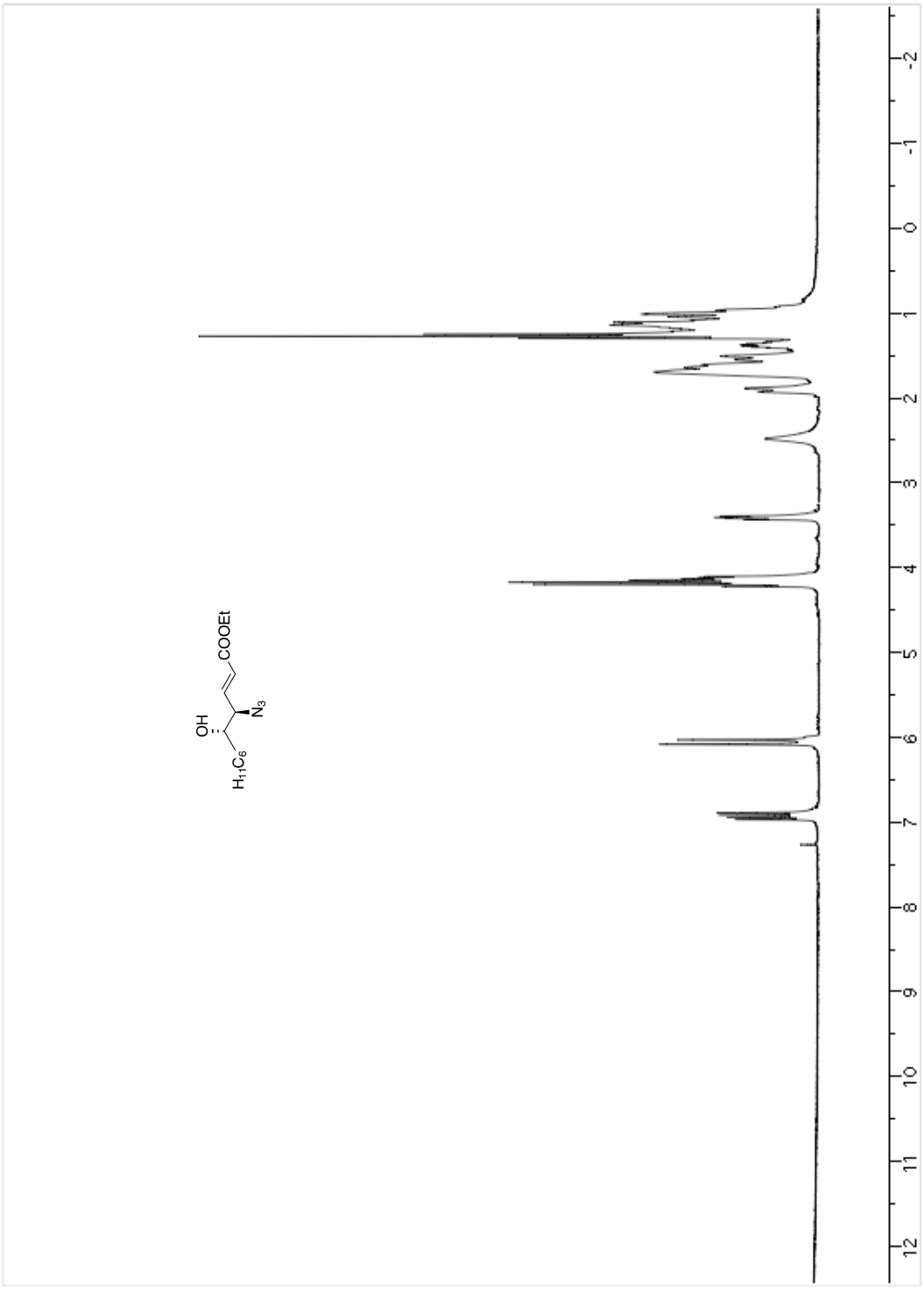


(2*S,3*S**)-ethyl 3-(*N*-9-fluorenylmethyloxycarbonyl)amino-2-bromo-3-cyclohexyl propanoate (23):**

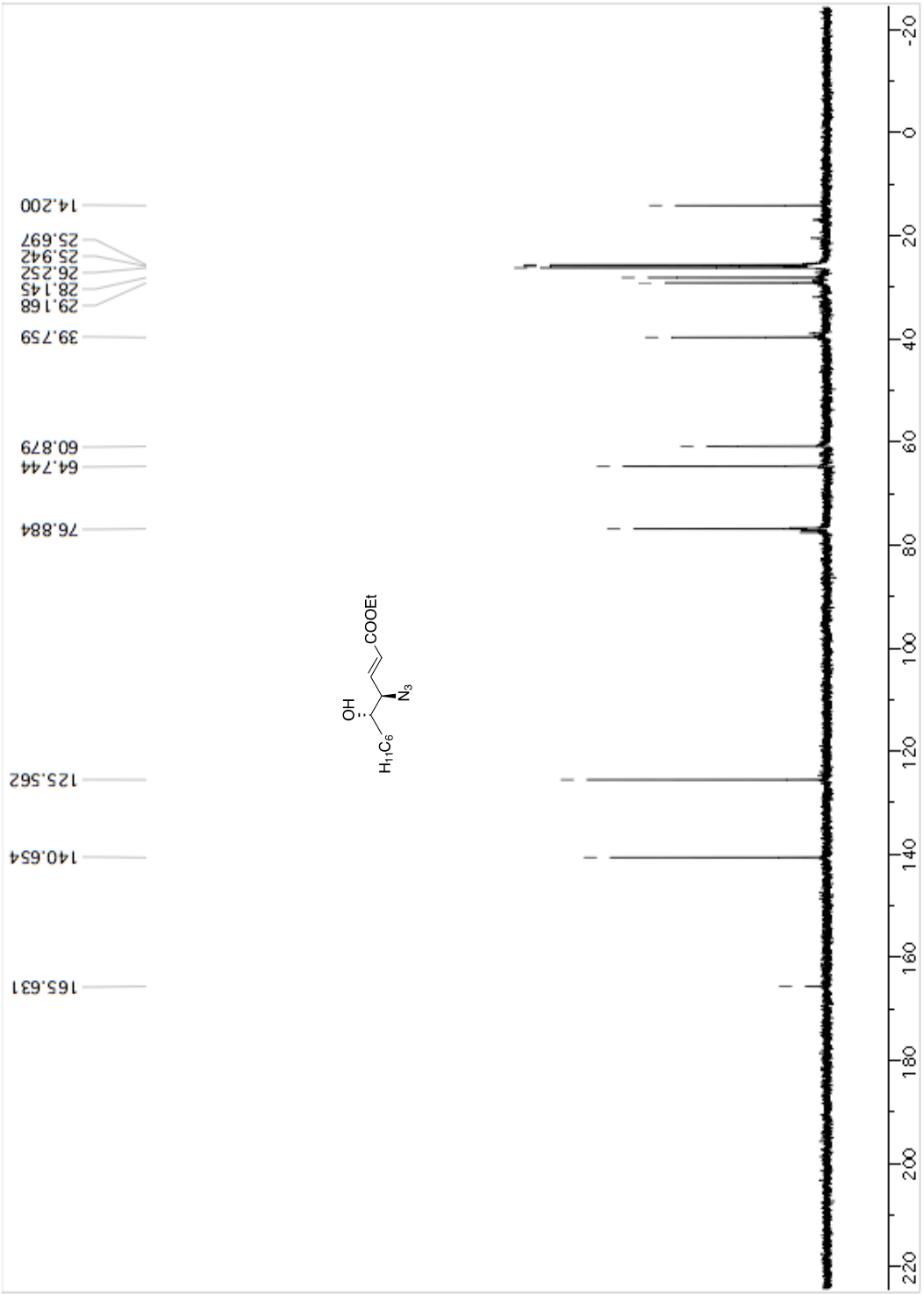


(E)

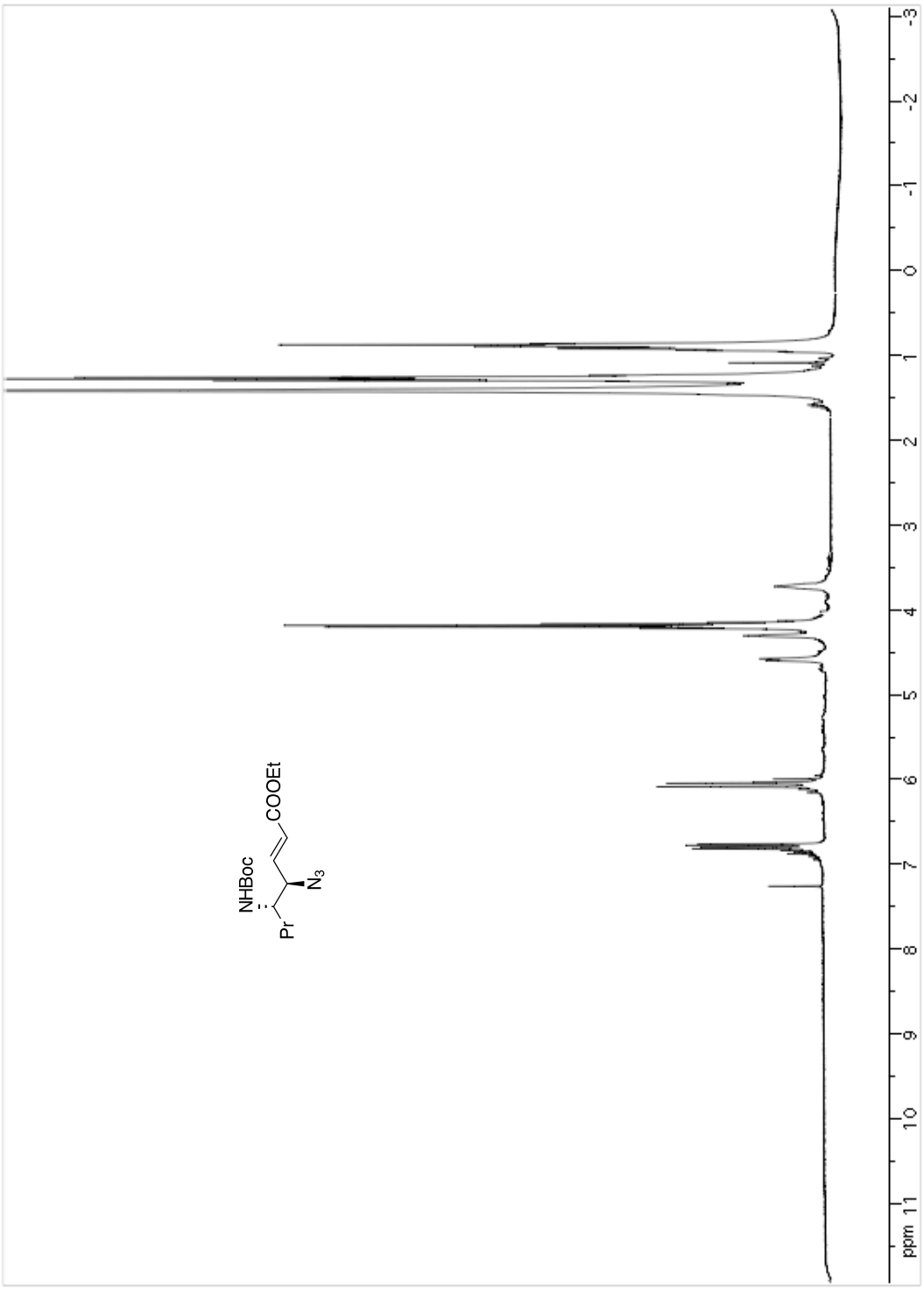
(4*R,5*S**)-ethyl 4-azido-5-cyclohexyl-5-hydroxypent-2-enoate (24):**



(*E*) (4*R,5*S**)-ethyl 4-azido-5-cyclohexyl-5-hydroxypent-2-enoate (24):**



(*E*) (4*R,5*S**)-ethyl-4-azido-5-(*tert*-butoxycarbonyl)amino-oct-2-enoate (25):**



(*E*) (4*R,5*S**)-ethyl-4-azido-5-(*tert*-butoxycarbonyl)amino-oct-2-enoate (25):**