Supporting Information

Catalyst-controlled reversal of chemoselectivity in acylation of 2-aminopentane-1,5-diol derivatives

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Content:

General

^{1}H and ^{13}C NMR spectra were obtained with JEOL JMN 400 spectrometer at 400 and 100 MHz, respectively, with chemical shifts being given in ppm units (tetramethylsilane or the solvent residual signal for $CDCl_3$, acetone-d_6, CD_3OD, and DMSO-d_6 as internal standard, indicating 0, 7.24, 2.04, 3.30, and 2.49 respectively). IR spectra were recorded with a JASCO FT/IR-300 spectrometer. Specific rotation was measured with a Horiba SEPA-200 automatic digital polarimeter. MS spectra were recorded with a JEOL JMS 700 mass spectrometer. TLC analysis and preparative TLC were performed on commercial glass plates bearing a 0.25 mm layer or 0.5 mm layer of Merck Kiesel-gel 60 F_{254}. Silica gel chromatography was performed with Silica gel 60 N (spherical, neutral, 40-50 μm, Kanto Chemical Co., Inc.), or Silica gel 60 N (spherical, neutral, 53-210 μm, Kanto Chemical Co., Inc.). Dry solvents (THF, DMF, and CH_2Cl_2 <50 ppm water contents) were purchased from Kanto Chemical Co., Inc. and used without further purification.

List of abbreviation

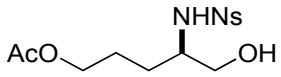
AcOEt	ethyl acetate
DMAP	4-dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
EDCI	1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
HOBt	1-hydroxybenzotriazole
NMM	*N*-methylmorpholine
NMO	*N*-methylmorpholine oxide
THF	tetrahydrofuran
TPAP	tetrapropylammonium perruthenate

General procedure for chemoselective acylation for Table 1

To a solution of diol substrate (20.0 mg, 1.0 equiv.), catalyst (10 mol%) and 2,4,6-collidine (1.7 equiv.) in $CHCl_3$ (concentration of the substrate: 0.01 M) was added acetic anhydride (1.03 equiv.) at –60 °C. The resulting mixture was stirred at the same temperature for 24 h. The reaction was quenched with MeOH (10 mL), and the solvent was evaporated. The residue was dissolved in AcOEt, washed with 1*N* HCl, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography or prep. TLC on silica gel to afford the mono- and the diacetates. Regioselectivity of the monoacetate was determined by the integration of ^{1}H NMR.

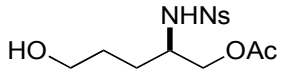
Spectral data for monoacetates 2, 3, and diacetate in Table 1

(*R*)-5-Hydroxy-4-(2-nitrophenylsulfonamido)pentyl acetate (2)



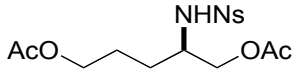
Colorless oil. $[\alpha]_D^{20}$ = +47 (c = 0.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.13 (m, 1H), 7.91–7.86 (m, 1H), 7.78–7.72 (m, 2H), 5.57 (s, 1H), 4.03–3.98 (m, 2H), 3.61–3.50 (m, 3H), 2.03 (s, 3H), 1.86-1.52 (5H, m). ^{13}C NMR ($CDCl_3$) δ 171.1, 147.7, 134.7, 133.5, 133.0, 130.6, 125.4, 64.7, 63.6, 56.3, 28.4, 24.9, 20.9. IR (KBr) 3485, 3236, 2934, 2876, 1719, 1592, 1365, 1340 cm^{-1}. MS (FAB) m/z 347 ($M+H^+$, 3). HRMS (FAB) Calcd for $C_{13}H_{19}N_2O_7S$ $(M+H)^+$ 347.0913, Found, 347.0917.

(*R*)-5-Hydroxy-2-(2-nitrophenylsulfonamido)pentyl acetate (3)



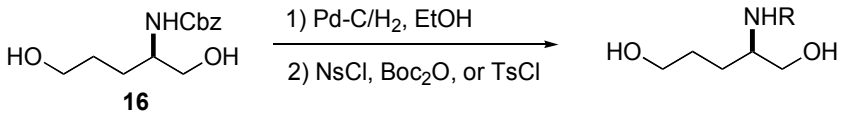
Colorless powder. M.p. 70–72 °C. $[\alpha]_D^{20}$ =+126 (c = 0.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.12 (m, 1H), 7.92–7.85 (m, 1H), 7.80–7.71 (m, 2H), 5.83 (d, *J* = 7.8 Hz, 1H), 3.99 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.94 (dd, *J* = 11.4, 5.5 Hz, 1H), 3.79 (s, 1H), 3.63 (s, 2H), 1.95 (s, 1H), 1.87 (s, 3H), 1.73–1.52 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 170.6, 147.6, 134.9, 133.5, 133.0, 130.5, 125.3, 65.6, 62.0, 53.6, 28.9, 28.2, 20.5. IR (KBr): 3531, 3320, 2949, 2889, 1738, 1541, 1430, 1366, 1241 cm^{-1}. MS (FAB) m/z 369 ($M+Na^+$, 10), 347 ($M+H^+$, 15). HRMS (FAB) Calcd for $C_{13}H_{19}N_2O_7S$ $(M+H)^+$ 347.0913, Found 347.0920.

(*R*)-2-(2-Nitrophenylsulfonamido)pentane-1,5-diyl diacetate (1-diacetate)



Colorless oil. $[\alpha]_D^{20}$ = +128 (c = 0.08, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.12 (m, 1H), 7.93–7.86 (m, 1H), 7.80–7.73 (m, 2H), 5.54 (d, *J* = 8.7 Hz, 1H), 4.10–4.00 (m, 2H), 3.97 (dd, *J* = 4.4, 11.7 Hz, 1H), 3.91 (dd, *J* = 4.4, 11.7 Hz, 1H), 3.80–3.71 (m, 1H), 2.05 (s, 3H), 1.89 (s, 3H), 1.82–1.74 (m, 1H), 1.70–1.61 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 171.1, 170.5, 147.7, 134.9, 133.6, 133.1, 130.5, 125.5, 65.4, 63.5, 53.5, 29.0, 24.8, 20.9, 20.5. IR (KBr) 3306, 2959, 1731, 1592, 1541, 1430, 1366, 1243 cm^{-1}. MS (FAB) m/z 411 ($M+Na^+$, 10), 389 ($M+H^+$, 10). HRMS (FAB) Calcd for $C_{15}H_{21}N_2O_8S$ $(M+H)^+$ 389.1018, Found 389.1030.

Preparation of diol substrates 1, 15, and 17 for Tables 1 and 3



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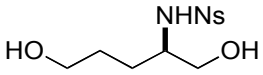
To a suspension of 10% Pd-C (~10 wt% of starting material) in EtOH was added **16**,[1] and the reaction mixture was stirred for 24 h at room temperature under H_2 atmosphere. Then the mixture was filtered and the filtrate was evaporated to afford a corresponding amino alcohol. To a solution of an amino alcohol in THF-DMF was added an appropriate acid anhydride, or sulfonyl chloride in the presence of Et_3N to afford corresponding *N*-protected diol substrates.

For synthesis of substrates **1**, **15**,[2] and **17**,[3] NsCl, Boc_2O, and TsCl, were employed, respectively, in the *N*-protection step.

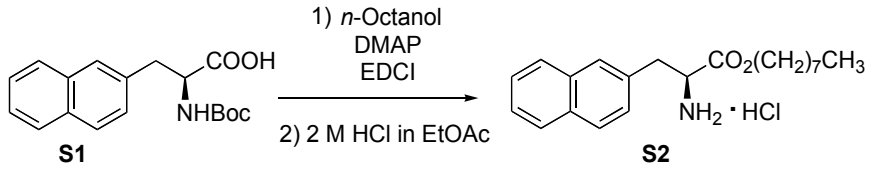
(*R*)-*N*-(1,5-Dihydroxypentan-2-yl)-2-nitrobenzenesulfonamide (1)



Colorless powder. M.p. 70–73 °C. $[\alpha]_D^{20}$ = +24 (c = 0.33, MeOH). ^{1}H NMR (acetone-d_6) δ 8.19–8.14 (m, 1H), 7.98–7.83 (m, 3H), 6.49 (s, 1H), 3.92 (s, 1H), 3.60–3.41 (m, 6H), 2.93 (s, 2H), 1.79–1.38 (m, 4H). ^{13}C NMR (acetone-d_6) δ 148.8, 135.5, 134.5, 133.5, 131.2, 125.6, 64.7, 62.1, 57.4, 28.9. IR (KBr) 3538, 3321, 2928, 1594, 1537, 1362 cm^{-1}. MS (FAB) m/z 305 ($M+H^+$, 10). HRMS (FAB) Calcd for $C_{12}H_{17}N_2O_6S$ $(M+H)^+$ 305.0807, Found 305.0807.

Preparation of catalyst 7

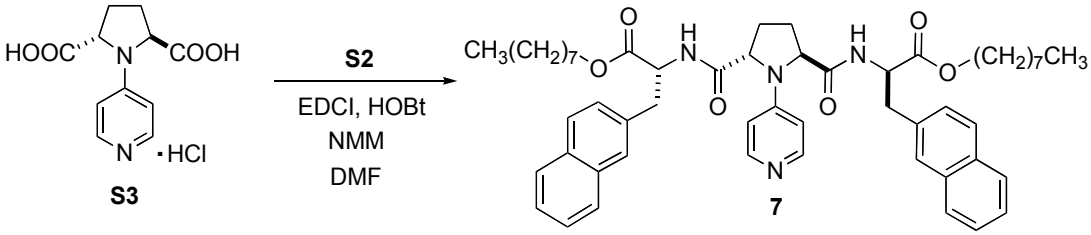
(*R*)-Octyl 2-amino-3-(naphthyl-2-yl)propanoate hydrochloride (S2)



To a solution of (*R*)-*N*-Boc-(2-naphthyl)alanine (**S1**) (2.8 g, 8.9 mmol) and *n*-octanol (4.9 mL, 31 mmol) in CH_2Cl_2 were added EDCI (6.0 g, 31 mmol) and DMAP (109 mg, 0.89 mmol) at 0 °C. After stirring at room temperature for 4 h, the reaction mixture was diluted with EtOAc and washed successively with 1 M aq. HCl, saturated aq. $NaHCO_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The residue was purified by SiO_2 column chromatography (*n*-hexane : AcOEt = 5 : 1) to give (*R*)-*N*-Boc-(2-naphthyl)alanine *n*-octyl ester (3.2 g, 85%). To a solution of (*R*)-*N*-Boc-(2-naphthyl)alanine *n*-octyl ester (3.2 g) in AcOEt (20 mL) was added 4 *N* HCl in AcOEt at 0 °C. Then the mixture was warmed to rt and stirred for 3 h at the same temperture. The mixture was evaporated and the residue was recrystallized to afford **S2** (2.1 g, 62% in two steps).

Colorless powder. M.p. 131–132 ºC. $[\alpha]_D^{21}$ = –50 (*c* 0.70 , CH_3OH). ^1H NMR (400 MHz, DMSO-d_6) δ 8.55 (t, *J* = 5.5 Hz, 1H), 8.49 (br s, 3H), 7.94–7.78 (m, 3H), 7.73 (s, 1H), 7.55–7.41 (m, 2H), 7.43(d, *J* = 8.7 Hz, 1H), 4.18–3.97 (m, 1H), 3.26 (dd, *J* = 13.3, 6.4 Hz, 1H), 3.18 (dd, *J* = 13.3, 7.8 Hz, 1H), 3.17–3.10 (m, 1H), 2.92–2.76 (m, 1H), 1.39–0.86 (m, 12H), 0.84 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.4, 133.0, 132.8, 132.2, 128.1, 127.9, 127.7, 127.5, 126.1, 125.8, 53.5, 38.6, 37.2, 31.3, 28.7, 28.6, 26.3, 22.1, 14.0. IR (KBr) 3328, 2926, 2853, 1658, 1561 cm^{-1}. MS (FAB) *m/z* (rel intensity) 327 ($M+H^+$, 100), 310 (5), 170 (60), 130 (10). HRMS (FAB) Calcd for $C_{21}H_{29}NO_2$ $(M+H)^+$ 327.2198, Found 327.2198.

(2*S*,5*S*)-2,5-Bis[(2*R*)-3-(naphthyl-2-yl)-1-octyloxy-1-oxopropan-2-ylaminocarbonyl]-1-(pyridin-4-yl)pyrrolidine (7)



To a solution of (2*S*,5*S*)-1-(pyridin-4-yl)pyrrolidine-2,5-dicarboxylic acid hydrochloride (**S3**)[4] (100 mg, 0.37 mmol) in DMF were successively added **S2** (400 mg, 1.1 mmol), NMM (240 μg, 2.2 mmol), HOBt (150 mg, 1.1 mmol), and EDCI (210 mg, 1.1 mmol) at room temperature. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with AcOEt, washed saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and evaporated in *vacuo*. The residue was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 10 : 1) to give a

crude residue, which was recrystallized to give **7** (133 mg, 54%).

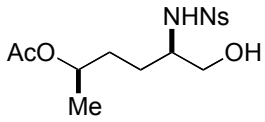
M.p. 136.0–137.0 ºC. $[\alpha]_D^{21}$ = –95 (*c* 0.83, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.0 Hz, 2H), 7.88–7.68 (m, 2H), 7.67–7.52 (m, 4H), 7.51– 7.34 (m, 4H), 7.33–7.12 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.15 (d, *J* = 6.0 Hz, 2H), 6.09 (d, *J* = 8.2 Hz, 2H), 5.01– 4.80 (m, 2H), 4.27–3.96 (m, 6H), 3.15 (d, *J* = 5.5 Hz, 4H), 2.30–1.79 (m, 4H), 1.70–1.49 (m, 4H), 1.48–1.06 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 170.8, 150.2, 149.6, 133.1, 132.6, 132.4, 128.4, 127.8, 127.7, 127.5, 126.7, 126.3, 125.9, 108.2, 66.0, 62.3, 52.4, 37.5, 31.7, 29.1, 28.4, 25.8, 22.6, 14.1. IR (KBr) 3302, 2926, 2855, 1735, 1661, 1600, 1229 cm^{-1}. MS (FAB) *m/z* (rel intensity) 855 ($M+H^+$, 40), 827 (5), 697 (5), 500 (40), 344 (5), 198 (5), 145 (100). HRMS (FAB) Calcd for $C_{53}H_{66}N_4O_6$ $(M+H)^+$ 855.5060, Found 855.5079. Anal Calcd for $C_{53}H_{66}N_4O_6$: C, 74.44; H, 7.78; N, 6.55, Found: C, 74.14; H, 7.78; N, 6.47.

General procedure for chemoselective acylation for Table 2

To a solution of diol substrate (20.0 mg, 1.0 equiv.), catalyst (20 mol%) and 2,4,6-collidine (1.7 equiv.) in $CHCl_3$ (concentration of the substrate: 0.01 M) was added acetic anhydride (1.03 equiv.) at –60 °C. The resulting mixture was stirred at the same temperature for 24 h. The reaction was quenched with MeOH (10 mL), and the solvent was evaporated. The residue was dissolved in AcOEt, washed with 1*N* HCl, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography or prep. TLC on silica gel to afford the mono- and diacetates. Regioselectivity of the monoacetate was determined by the integration of ^{1}H NMR.

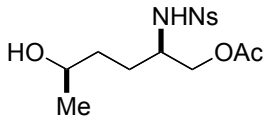
Spectral data for Table 2

(2*R*,5*R*)-6-Hydroxy-5-(2-nitrophenylsulfonamido)hexan-2-yl acetate (8-*sec*-OAc)



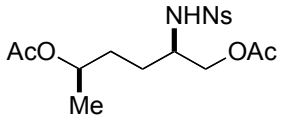
Colorless oil. $[\alpha]_D^{20}$ = –17 (c = 0.27, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.12 (m, 1H), 7.91–7.85 (m, 1H), 7.78–7.71 (m, 2H), 5.58 (br s, 1H), 4.90–4.70 (m, 1H), 3.63–3.41 (m, 3H), 2.00 (s, 3H), 1.86 (s, 1H), 1.72–1.47 (m, 4H), 1.14 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.8, 147.7, 134.7, 133.5, 132.9, 130.7, 125.4, 70.4, 64.6, 56.7, 32.0, 27.8, 21.3, 19.9. IR (KBr) 3527, 3337, 2962, 1717, 1540, 1261 cm^{-1}. MS (FAB) m/z 383 ($M+Na^+$, 20), 361 ($M+H^+$, 2). HRMS (FAB) Calcd for $C_{14}H_{21}N_2O_7S$ $(M+H)^+$ 361.1070, Found 361.1081.

(2*R*,5*R*)-5-Hydroxy-2-(2-nitrophenylsulfonamido)hexyl acetate (8-*pri*-OAc)



Colorless oil. $[\alpha]_D^{20}$ = +92 (c = 0.27, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.13 (m, 1H), 7.91–7.85 (m, 1H), 7.78–7.71 (m, 2H), 5.72 (d, *J* = 8.7 Hz, 1H), 4.02–3.90 (m, 2H), 3.84–3.71 (m, 2H), 1.89 (s, 3H), 1.80–1.35 (m, 5H), 1.17 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.6, 147.7, 135.0, 133.5, 133.0, 130.5, 125.4, 67.8, 65.5, 53.8, 34.6, 29.0, 23.9, 20.5. IR (KBr) 3538, 3315, 2965, 1735, 1542 cm^{-1}. MS (FAB) m/z 361 ($M+H^+$, 2). HRMS (FAB) Calcd for $C_{14}H_{21}N_2O_7S$ $(M+H)^+$ 361.1069, Found 361.1061.

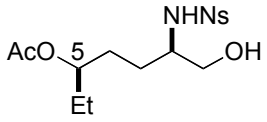
(2*R*,5*R*)-2-(2-Nitrophenylsulfonamido)hexane-1,5-diyl diacetate (8-diacetate)



Colorless oil. $[\alpha]_D^{20}$ = +105 (c = 0.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.11 (m, 1H), 7.93–7.86 (m, 1H), 7.80–7.72 (m, 2H), 5.52 (d, *J* = 8.7 Hz, 1H), 4.92–4.80 (m, 1H), 3.96 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.88 (dd, *J* = 11.4, 4.1Hz, 1H), 3.71 (s, 1H), 2.03 (s, 3H), 1.90 (s, 3H), 1.69–1.51 (m, 4H), 1.18 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.7, 170.4, 147.7, 134.9, 133.6, 133.1, 130.5, 125.5, 70.3, 65.4, 53.9, 32.1, 28.6, 21.3, 20.5, 20.0. IR (KBr) 3287, 2919, 1731, 1540 cm^{-1}. MS (FAB) m/z 403 ($M+H^+$, 5), 344 (10). HRMS (FAB) Calcd for $C_{16}H_{23}N_2O_8S$ $(M+H)^+$ 403.1175, Found 403.1155.

(3*R*,6*R*)-7-Hydroxy-6-(2-nitrophenylsulfonamido)heptan-3-yl acetate (9-*sec*-OAc)

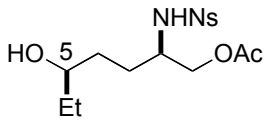
(The *R* configurations at C(5) {according to the nomenclature: 3-posiiton} was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



Colorless oil. $[\alpha]_D^{20}$ = +12 (c = 0.45, $CHCl_3$). ^{1}H NMR (acetone-d_6) δ 8.19–8.13 (m, 1H), 7.95–7.80 (m, 3H), 6.49 (s, 1H), 4.68 (s, 1H), 3.94 (t, *J* = 5.3 Hz, 1H), 3.60–3.30 (m, 3H), 1.96 (s, 3H), 1.80–1.33 (m, 6H), 0.79 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (acetone-d_6) δ 170.7, 148.8, 135.4, 134.6, 133.5, 131.3, 125.6, 75.4, 64.8, 64.7, 57.6, 28.3, 27.5, 21.0, 9.7. IR (KBr) 3526, 3335, 2968, 1717, 1542 cm^{-1}. MS (FAB) m/z 375 ($M+H^+$, 5), 345 (2), 315 (3). HRMS (FAB) Calcd for $C_{15}H_{23}N_2O_7S$ $(M+H)^+$ 375.1226, Found 375.1216.

(2*R*,5*R*)-5-Hydroxy-2-(2-nitrophenylsulfonamido)heptyl acetate (9-*pri*-OAc)

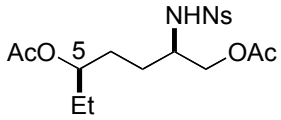
(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



Colorless oil. $[\alpha]_D^{20}$ = +82 (c = 0.16, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.14 (m, 1H), 7.90–7.85 (m, 1H), 7.78–7.71 (m, 2H), 5.71 (d, *J* = 8.7 Hz, 1H), 3.98 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.94 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.82–3.74 (m, 1H), 3.49 (br s, 1H), 1.90 (s, 3H), 1.80–1.30 (m, 6H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (acetone-d_6) δ 170.7, 148.8, 135.5, 134.7, 133.5, 131.3, 125.6, 72.7, 72.6, 66.5, 55.0, 33.8, 31.1, 20.5, 10.2. IR (KBr) 3530, 3327, 2964, 2925, 1736, 1542, 1365 cm^{-1}. MS (FAB) m/z 374 (M^+, 2), 122 (60). HRMS (FAB) Calcd for $C_{15}H_{22}N_2O_7S$ $(M)^+$ 374.1148, Found 374.1155.

(2*R*,5*R*)-2-(2-Nitrophenylsulfonamido)heptane-1,5-diyl diacetate (9-diacetate)

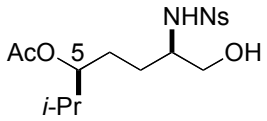
(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



Colorless oil. $[\alpha]_D^{20}$ = +95 (c = 0.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.11 (m, 1H), 7.93–7.86 (m, 1H), 7.81–7.73 (m, 2H), 5.52 (d, *J* = 8.7 Hz, 1H), 4.79–4.72 (m, 1H), 3.96 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.88 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.69 (s, 1H), 2.04 (s, 3H), 1.90 (s, 3H), 1.69–1.48 (m, 7H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.9, 170.5, 147.7, 134.9, 133.6, 133.1, 130.5, 125.5, 74.7, 65.4, 53.9, 29.8, 28.4, 27.0, 21.2, 20.5, 9.5. IR (KBr) 3304, 2968, 1732, 1541, 1430, 1365 cm^{-1}. MS (FAB) m/z 429 ($M+Na^+$, 3), 417 ($M+H^+$, 2), 357 (2). HRMS (FAB) Calcd for $C_{17}H_{25}N_2O_8S$ $(M+H)^+$ 417.1331, Found 417.1348.

(3*S*,6*R*)-7-Hydroxy-2-methyl-6-(2-nitrophenylsulfonamido)heptan-3-yl acetate (10-*sec*-OAc)

(The *R* configurations at C(5) {according to the nomenclature: 3-posiiton} was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)

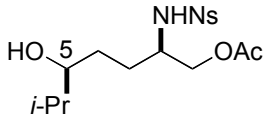


Colorless oil. $[\alpha]_D^{20}$ = –3.6 (c = 0.71, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.12 (m, 1H), 7.89–7.84 (m, 1H), 7.80–7.70 (m, 2H), 5.63 (d, *J* = 7.8 Hz, 1H), 4.70–4.55 (m, 1H), 3.61–3.43 (m, 3H), 2.09 (s,

1H), 2.03 (s, 3H), 1.78–1.66 (m, 1H), 1.56-1.25 (m, 4H), 0.80 (d, J = 6.4 Hz, 3H), 0.79 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 171.1, 147.7, 134.7, 133.5, 132.9, 130.7, 125.3, 64.7, 56.8, 31.3, 27.9, 27.4, 21.1, 18.3, 17.6. IR (KBr) 3522, 3342, 2965, 1715, 1540 cm^{-1}. MS (FAB) m/z 411 ($M+Na^+$, 20), 389 ($M+H^+$, 15). HRMS (FAB) Calcd for $C_{16}H_{25}N_2O_7S$ $(M+H)^+$: 389.1382, Found: 389.1372.

(2*R*,5*S*)-5-Hydroxy-6-methyl-2-(2-nitrophenylsulfonamido)heptyl acetate (10-*pri*-OAc)

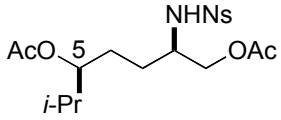
(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



Colorless oil. $[\alpha]_D^{20}$ = +56 (c = 0.32, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19-8.12 (m, 1H), 7.90–7.85 (m, 1H), 7.79–7.71 (m, 2H), 5.72 (d, J = 8.7 Hz, 1H), 4.02–3.91 (m, 2H), 3.83–3.74 (m, 1H), 3.35–3.27 (m, 1H), 1.91 (sl, 3H), 1.85–1.57 (m, 5H), 1.39–1.25 (m, 1H), 0.85 (d, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 170.6, 147.7, 135.0, 133.5, 133.0, 130.6, 125.3, 65.7, 54.0, 33.9, 29.6, 29.4, 20.6, 18.6, 17.2. IR (KBr) 3546, 3339, 2960, 1733, 1540 cm^{-1}. MS (FAB) m/z 389 ($M+H^+$, 2), 371 (2), 345 (1). HRMS (FAB) Calcd for $C_{16}H_{25}N_2O_7S$ $(M+H)^+$ 389.1382, Found 389.1376.

(2*R*,5*S*)-6-Methyl-2-(2-nitrophenylsulfonamido)heptane-1,5-diyl diacetate (10-diacetate)

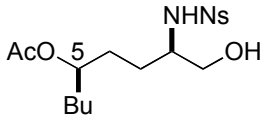
(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



Colorless oil. $[\alpha]_D^{20}$ = +72 (c = 0.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.11 (m, 1H), 7.93–7.85 (m, 1H), 7.80–7.69 (m, 2H), 5.51 (d, J = 8.7 Hz, 1H), 4.73–4.63 (m, 1H), 3.97 (dd, J = 11.4, 4.1 Hz, 1H), 3.88 (dd, J = 11.7, 4.1 Hz, 1H), 3.74–3.64 (m, 1H), 2.05 (s, 3H), 1.91 (s, 3H), 1.81–1.38 (m, 6H), 0.83 (d, J = 6.9 Hz, 3H), 0.82 (d, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 171.0, 170.5, 147.7, 134.9, 133.6, 133.1, 130.5, 125.4, 65.5, 54.0, 31.5, 28.7, 27.4, 21.1, 20.5, 18.3, 17.6. IR (KBr) 3306, 2964, 1731, 1542 cm^{-1}. MS (FAB) m/z 431 ($M+H^+$, 2), 308 (2), 122 (55). HRMS (FAB) Calcd for $C_{18}H_{27}N_2O_8S$ $(M+H)^+$ 431.1488, Found: 431.1480.

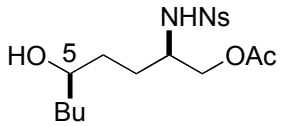
(2*R*,5*R*)-1-Hydroxy-2-(2-nitrophenylsulfonamido)nonan-5-yl acetate (11-*sec*-OAc)

(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



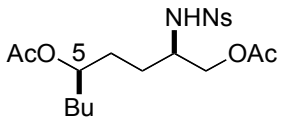
Colorless oil. $[\alpha]_D^{20}$ = +9.1 (c = 0.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.11 (m, 1H), 7.91–7.85 (m, 1H), 7.78–7.71 (m, 2H), 5.56 (d, *J* = 7.8 Hz, 1H), 4.76 (s, 1H), 3.63–3.40 (m, 3H), 2.01 (s, 3H), 1.82 (s, 1H), 1.64–1.10 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.9, 147.7, 134.7, 133.5, 132.9, 130.7, 125.4, 73.7, 64.7, 56.8, 33.7, 30.3, 27.7, 27.3, 22.5, 21.2, 13.9. IR (KBr) 3338, 2957, 2872, 1716, 1541 cm^{-1}. MS (FAB) m/z 403 ($M+H^+$, 15), 343 (30). HRMS (FAB) Calcd for $C_{17}H_{27}N_2O_7S$ $(M+H)^+$: 403.1539, Found: 403.1542.

(2*R*,5*R*)-5-Hydroxy-2-(2-nitrophenylsulfonamido)nonyl acetate (11-*pri*-OAc)



Colorless oil. $[\alpha]_D^{20}$ = +81 (c = 0.26, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.11 (m, 1H), 7.92–7.85 (m, 1H), 7.78–7.70 (m, 2H), 5.71 (d, *J* = 8.7 Hz, 1H), 3.98 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.93 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.83–3.72 (m, 1H), 3.61–3.52 (m, 1H), 1.90 (s, 3H), 1.82–1.71 (m, 1H), 1.67–1.53 (m, 3H), 1.46–1.20 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.6, 147.7, 135.1, 133.5, 133.0, 130.5, 125.4, 71.8, 65.6, 53.9, 37.5, 32.9, 29.0, 27.7, 22.6, 20.5, 14.0. IR (KBr) 3545, 3334, 2931, 2861,1732, 1541,1436, 1364, 1238cm^{-1}. MS (FAB) m/z 403 ($M+H^+$, 5). HRMS (FAB) Calcd for $C_{17}H_{27}N_2O_7S$ $(M+H)^+$ 403.1539, Found: 403.1551.

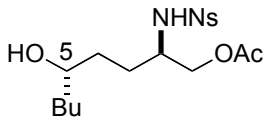
(2*R*,5*R*)-2-(2-nitrophenylsulfonamido)nonane-1,5-diyl diacetate (11-diacetate)



Colorless oil. $[\alpha]_D^{20}$ = +66 (c = 0.28, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.11 (m, 1H,), 7.92–7.86 (m, 1H), 7.80–7.71 (m, 2H), 5.52 (d, *J* = 8.7 Hz, 1H), 4.81 (s, 1H), 3.96 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.88 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.69 (s, 1H), 2.03 (s, 3H), 1.90 (s, 3H), 1.73–1.39 (m, 6H), 1.34–1.16 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.9, 170.5, 147.7, 134.9, 133.5, 133.1, 130.5, 125.4, 73.6, 65.4, 53.9, 33.8, 30.3, 28.4, 27.3, 22.5, 21.2, 20.5, 14.0. IR (KBr) 3306, 3098, 2957, 2932, 1732, 1541, 1429, 1365, 1241cm^{-1}. MS (FAB) m/z 445 ($M+H^+$, 5), 467 ($M+Na^+$, 10). HRMS

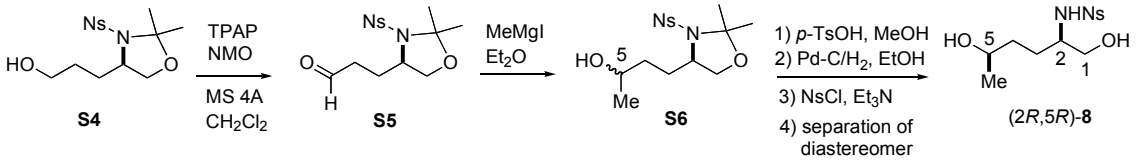
(FAB) Calcd for $C_{19}H_{29}N_2O_8S$ $(M+H)^+$ 445.1645, Found 445.1656.

(2*R*,5*S*)-5-Hydroxy-2-(2-nitrophenylsulfonamido)nonyl acetate (5-*epi*-11-*pri*-OAc)



Colorless oil. $[\alpha]_D^{20}$ = +78 (c = 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.17–8.14 (m, 1H), 7.90–7.88 (m, 1H), 7.78–7.72 (m, 2H), 5.62 (d, *J* = 8.7 Hz, 1H), 3.98 (dd, *J* = 4.1, 11.4 Hz, 1H), 3.93 (dd, *J* = 5.0, 11.4 Hz, 1H), 3.81–3.73 (m, 1H), 3.63–3.52 (m, 1H), 1.90 (s, 3H), 1.73–1.23 (m, 10H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 170.6, 147.7, 135.0, 133.5, 133.0, 130.5, 125.4, 71.1, 65.7, 53.7, 37.3, 32.7, 28.3, 27.7, 22.6, 20.5, 14.0. IR (KBr) 3334, 2956, 2930, 2857, 1738, 1542, 1427, 1364, 1241 cm^{-1}. MS (FAB) m/z 425 $(M+Na)^+$. HRMS (FAB) Calcd for $C_{17}H_{26}N_2O_7SNa$ $(M+Na)^+$ 425.1358, Found 425.1356.

Typical procedure for synthesis of diol substrates for Table 2: Preparation of *N*-((2*R*,5*R*)-1,5-dihydroxyhexan-2-yl)-2-nitrobenzenesulfonamide (8)



To a solution of **S4**[1] (6.0 g, 20 mmol) in CH_2Cl_2 were added NMO (3.0 g, 26 mmol) and MS4Å (10 g) at rt under Ar atmosphere. After being stirred at 0°C, TPAP (238 mg, 0.68 mmol) was added and stirred for 48 h at rt. The mixture was filtered through a pad of celite and the filtrate was evaporated *in vacuo* to give a residue The residue was purified by SiO_2 column chromatography (*n*-hexane : AcOEt = 7 : 1) to give **S5**[5] (4.2 g, 71%). To a solution of MeMgI (3.0 equiv.) in Et_2O was added **S5** (500 mg, 1.5 mmol, 1.0 equiv.) at –10 °C under Ar atmosphere. After being stirred for 1 h at –10 °C, the reaction was quenched with sat. aq. NH_4Cl, and extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered and evaporated to give a residue. The residue was purified by SiO_2 column chromatography (*n*-hexane : AcOEt = 1 : 1) to give **S6** (343 mg, 65%) as a diastereomeric mixture due to the newly formed stereogenic center at C(5).

To a solution of a diastereomeric mixture of **S6** (303 mg, 0.85 mmol) in MeOH was added catalytic amount of *p*-TsOH·H_2O (51 mg, 0.27 mmol, 0.3 equiv.). After being stirred for 24 h at rt, the solvent was evaporated to give a residue. The residue was partitioned between AcOEt and sat. aq. $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and evaporated to give a residue. To a suspension of 10% Pd-C (30 mg, ~10 wt % of starting material) in EtOH was added the residue, and the reaction

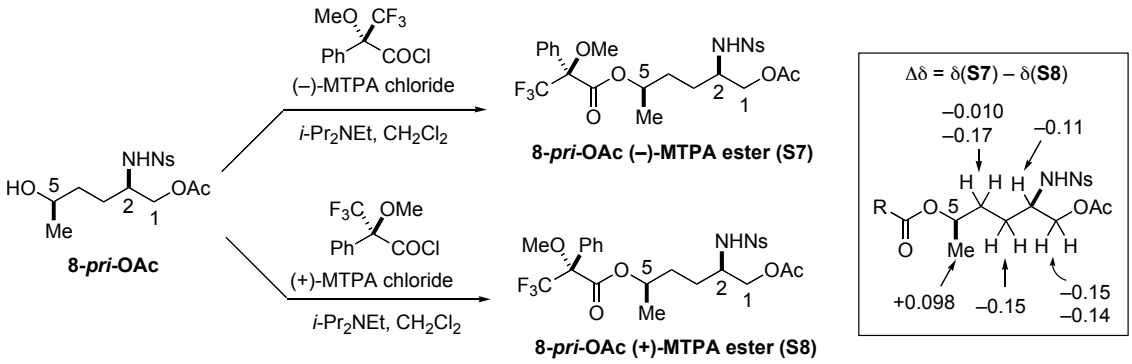
mixture was stirred for 9 h at room temperature under H_2 atmosphere. The mixture was filtered, and the filtrate was evaporated to afford an amino alcohol.

To a solution of an amino alcohol (1.0 equiv.) in THF were added 2-nitrobenzenesulfonyl chloride (240mg, 1.1 mmol, 1.1 equiv.) and Et_3N (0,20 mL, 1.4 mmol, 1.5 equiv.) at 0 °C. After being stirred for 4 h at rt, the reaction was quenched with sat. aq. NH_4Cl, and extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered and evaporated to give a residue. The residue was purified by SiO_2 column chromatography ($CHCl_3$: MeOH = 10 : 1) to give **8** (287 mg, 92% over 3 steps) as a diastereomeric mixture. The diastereomers (2*R*,5*R*)-**8** and (2*R*,5*S*)-**8** were separated by prep. HPLC (**(**$CHCl_3$: MeOH = 85 : 15). The absolute configuration at C(5) of (2*R*,5*R*)-**8** was determined by modified Mosher's method[6] as described below.

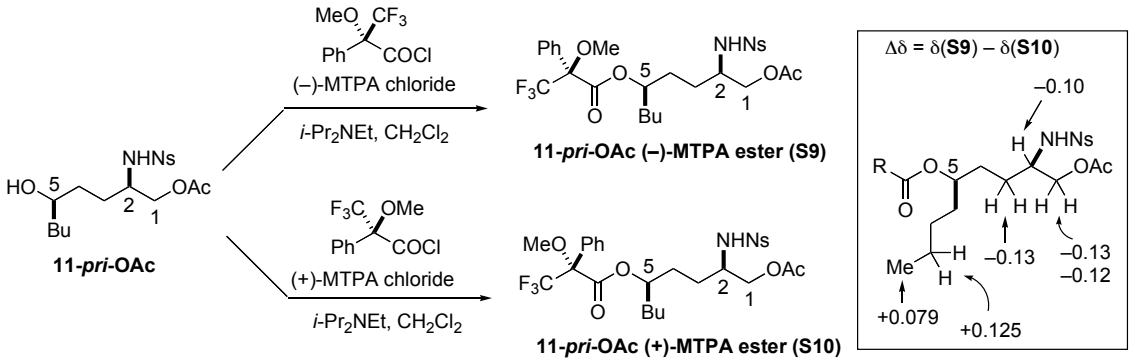
According to this typical procedure, substrates **9**, **10**, **11** and 5-*epi*-**11** were prepared by addition of the corresponding Grignard reagent toward aldehyde **S5**. The absolute configurations at C(5) of these substrates were tentatively assigned according to their reactivity toward chemoselective acylation with catalyst **7**.

Modified Mosher's method[6] for determination of the absolute configuration at C(5) of 8 and 11

One of the diastereomer of **8**, obtained from the above typical procedure, was acetylated under the conditions for Table 2, entry 1 (DMAP catalysis) to afford **8-*pri*-OAc**. The secondary-OH at C(5) of **8-*pri*-OAc** was further acylated with (–)-MTPA and (+)-MTPA chloride in the presence of *i*-Pr_2NEt in CH_2Cl_2 to give the corresponding MTPA esters **S7** and **S8**, respectively. After assignment of the chemical shifts of each proton by 1H-1H COSY spectra, the values, Δδ = δ(**S7**) – δ(**S8**), were calculated. From the data as shown below, the absolute stereochemistry of C(5) of **8** was determined to *R*. This (2*R*,5*R*)-**8** isomer was employed as a substrate for entries 1 and 2 in Table 2.



The same procedure was employed for **11** to determine the absolute stereochemistry at C(5). One of the diastereomer of **11**, obtained from the above typical procedure, was acetylated with DMAP to afford **11-*pri*-OAc**. After esterification of **11-*pri*-OAc** with (–)-MTPA and (+)-MTPA chloride, the values, Δδ = δ(**S9**) – δ(**S10**), from the corresponding MTPA esters were calculated as shown below.



Since the signals of hydrogens adjacent to C(5) overlaps each other, the chemical shifts of the indicated hydrogens were observed for the assignment of the absolute stetreochemistry at C(5). Thus, the absolute stereochemistry of C(5) of **11** was also determined to *R*. This (2*R*,5*R*)-**11** and (2*R*,5*S*)-*epi*-**11** isomers were employed as substrates for entries 5 and 6 in Table 2, respectively.

8-*pri*-OAc (–)-MTPA ester (S7)

^{1}H-NMR (CD_3OD) δ: 8.10–8.04 (m, 1H), 7.85–7.73 (m, 3H), 7.52–7.36 (m, 5H), 5.08–4.96 (m, 1H), 3.822 (dd, *J* = 4.6, 11.0 Hz, 1H), 3.754 (dd, *J* = 6.4, 11.0 Hz, 1H), 3.53 (s, 3H), 3.57–3.45 (center of the signal: 3.516 ppm) (m, 1H), 1.77 (s, 3H), 1.66–1.56 (m, 1H), 1.66–1.52 (center of the signal: 1.610 ppm) (m, 1H), 1.51–1.39 (center of the signal: 1.450 ppm) (m, 1H), 1.39–1.30 (center of the signal: 1.345 ppm) (m, 1H), 1.265 (d, *J* = 6.0 Hz, 3H).

8-*pri*-OAc (+)-MTPA ester (S8)

^{1}H-NMR (CD_3OD) δ: 8.12–8.05 (m, 1H), 7.84–7.73 (m, 3H), 7.51–7.38 (m, 5H), 5.08–4.97 (m, 1H), 3.970 (dd, *J* = 5.0, 11.5 Hz, 1H), 3.892 (dd, *J* = 6.4, 11.5 Hz, 1H), 3.68–3.57 (center of the signal: 3.623 ppm) (m, 1H), 3.48 (s, 3H), 1.79 (s, 3H), 1.70–1.54 (center of the signal: 1.620 ppm) (m, 2H) 1.56–1.42 (center of the signal: 1.490 ppm) (m, 1H), 1.167 (d, *J* = 6.0 Hz, 3H).

11-*pri*-OAc (–)-MTPA ester (S9)

^{1}H-NMR (CD_3OD) δ: 8.10–8.04 (m, 1H), 7.85–7.74 (m, 3H), 7.53–7.37 (m, 5H), 5.01–4.92 (m, 1H), 3.843 (dd, *J* = 5.0, 11.4 Hz, 1H), 3.773 (dd, *J* = 6.9, 11.4 Hz, 1H), 3.55–3.46 (center of the signal: 3.5050 ppm) (m, 1H), 3.51 (s, 3H), 1.80 (s, 3H), 1.68–1.52 (center of the signals: 1.600 ppm) (m, 2H), 1.60–1.44 (center of the signal: 1.610 ppm) (m, 2H), 1.43–1.22 (center of the signal: 1.325 ppm) (m, 4H), 1.32–1.14 (m, 2H), 0.886 (d, *J* = 7.3 Hz, 3H).

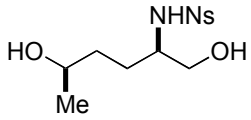
12-*pri*-OAc (+)-MTPA ester (S10)

^{1}H-NMR (CD_3OD) δ: 8.12–8.05 (m, 1H), 7.85–7.73 (m, 3H), 7.53–7.37 (m, 5H), 5.03–4.92 (m, 1H),

3.974 (dd, J = 5.0, 11.4 Hz, 1H), 3.897 (dd, J = 6.4, 11.4 Hz, 1H), 3.67–3.54 (center of the signal: 3.6050 ppm) (m, 1H), 3.50 (s, 3H), 1.81 (s, 3H), 1.73–1.62 (center of the signal: 1.675 ppm) (m, 4H) 1.62–1.50 (center of the signal: 1.575 ppm) (m, 1H), 1.52–1.39 (center of the signal: 1.455 ppm) (m, 2H), 1.28–1.12 (center of the signal: 1.200 ppm) (m, 1H), 1.12–0.96 (center of the signal: 1.040 ppm) (m, 2H), 0.807 (d, J = 7.3 Hz, 3H).

Spectral data of diol substrates 8–11 in Table 2

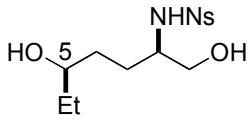
***N*-((2*R*,5*R*)-1,5-Dihydroxyhexan-2-yl)-2-nitrobenzenesulfonamide (8)**



Colorless oil. $[\alpha]_D^{20}$ = +1.7 (c = 0.53, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.19–8.12 (m, 1H), 7.89-7.83 (m, 1H), 7.77–7.71 (m, 2H), 5.90 (d, J = 7.3 Hz, 1H), 3.74 (s, 1H), 3.60–3.47 (m, 3H), 2.65 (s, 1H), 2.09 (s, 1H), 1.75–1.69 (m, 1H), 1.56–1.45 (m, 2H), 1.38–1.24 (m, 1H), 1.12 (d, J = 6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 147.7, 134.7, 133.5, 132.9, 130.7, 125.3, 67.9, 64.3, 56.6, 34.6, 28.1, 23.7. IR (KBr) 3545, 3350, 2965, 2928, 2881, 2367, 2328, 1541, 1418, 1362, 1166. MS (FAB) m/z 341 ($M+Na^+$, 3), 319 ($M+H^+$, 5). HRMS (FAB) Calcd for $C_{12}H_{19}N_2O_6S$ $(M+H)^+$ 319.0964, Found 319.0978.

***N*-((2*R*,5*R*)-1,5-Dihydroxyheptan-2-yl)-2-nitrobenzenesulfonamide (9)**

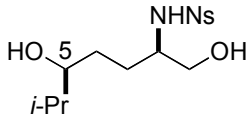
(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



Colorless oil. $[\alpha]_D^{20}$ = –11 (c = 0.87, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 8.18–8.09 (m, 1H), 7.90–7.81 (m, 1H), 7.79–7.69 (m, 2H), 6.00 (d,, J = 8.2 Hz, 1H), 3.62–3.38 (m, 4H), 3.28 (s, 1H), 2.58 (s, 1H), 1.83–1.67 (m, 1H), 1.57–1.42 (m, 2H), 1.36 (t, J = 7.3 Hz, 2H), 1.29–1.18 (m, 1H), 0.84 (t, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 147.6, 134.6, 133.5, 132.9, 130.6, 125.2, 73.1, 64.1, 56.7, 32.3, 30.3, 28.0, 9.8. IR (KBr) 3534, 3348, 2934, 2878, 1541, 1362 cm^{-1}. MS (FAB) m/z (rel intensity) 333 ($M+H^+$, 1). HRMS (FAB) Calcd for $C_{13}H_{21}N_2O_6S$ $(M+H)^+$ 333.1120, Found 333.1104.

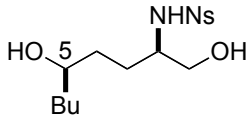
***N*-((2*R*,5*S*)-1,5-Dihydroxy-6-methylheptan-2-yl)-2-nitrobenzenesulfonamide (10)**

(The *R* configurations at C(5) was tentatively assigned according to its reactivity toward chemoselective acylation with catalyst **7**.)



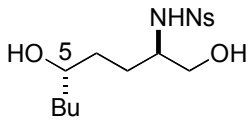
Colorless oil. $[\alpha]_D^{20} = -24$ (c = 1.39, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 8.18–8.12 (m, 1H), 7.88–7.82 (m, 1H), 7.79–7.68 (m, 2H), 5.92 (d, *J* = 7.3 Hz, 1H), 3.62–3.47 (m, 3H), 3.31-3.22 (m, 1H), 3.01 (s, 1H), 2.23 (s, 1H), 1.84–1.72 (m, 1H), 1.60–1.40 (m, 3H), 1.29–1.15 (m, 1H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 147.6, 134.7, 133.5, 132.9, 130.6, 125.2, 64.3, 56.8, 33.8, 29.6, 28.6, 18.5, 17.3. IR (KBr) 3530, 3349, 2959, 2875, 1541, 1362 cm^{-1}. MS (FAB) m/z 347 ($M+H^+$, 5), 186 (2). HRMS (FAB) Calcd for $C_{14}H_{23}N_2O_6S$ $(M+H)^+$ 347.1276, Found 347.1288.

***N*-((2*R*,5*R*)-1,5-Dihydroxynonan-2-yl)-2-nitrobenzenesulfonamide (11)**



Colorless oil. $[\alpha]_D^{20} = -8.7$ (c = 0.32, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 8.18–8.10 (m, 1H), 7.89–7.81 (m, 1H), 7.78–7.67 (m, 2H), 5.98 (d, *J* = 7.8 Hz, 1H), 3.62–3.42 (m, 4H), 2.42 (s, 1H), 1.80–1.69 (m, 1H), 1.58–1.42 (m, 2H), 1.36–1.14 (m, 7H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 147.6, 134.7, 133.4, 132.9, 130.6, 125.2, 71.7, 64.2, 56.7, 37.3, 32.8, 28.0, 27.6, 22.6, 14.0. IR (KBr) 3534, 3351, 2931, 1542, 1362 cm^{-1}. MS (FAB) m/z 361 ($M+H^+$, 1), 383 ($M+Na^+$, 1). HRMS (FAB) Calcd for $C_{15}H_{25}N_2O_6S$ $(M+H)^+$ 361.1433, Found 361.1421.

***N*-((2*R*,5*S*)-1,5-Dihydroxynonan-2-yl)-2-nitrobenzenesulfonamide (5-*epi*-11)**



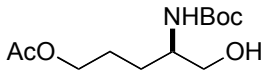
Colorless needles. M.p. 69–71 ºC. $[\alpha]_D^{20} = -7.9$ (c = 0.51, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 8.17–8.13 (m, 1H), 7.87–7.82 (m, 1H), 7.77–7.70 (m, 2H), 5.92 (d, *J* = 5.5 Hz, 1H), 3.60–3.45 (m, 4H), 2.87 (s, 1H), 2.23 (s, 1H), 1.71–1.59 (m, 2H), 1.45–1.15 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 147.6, 134.6, 133.4, 132.8, 130.7, 125.2, 71.2, 64.7, 56.5, 37.2, 32.5, 27.7, 27.4, 22.6, 14.0. IR (KBr) 3520, 3320, 2960, 2933, 2869, 1538, 1356, 1328 cm^{-1}. MS (FAB) m/z 361 ($M+H^+$, 30), 383 ($M+Na^+$, 55). HRMS (FAB) Calcd for $C_{15}H_{25}N_2O_6S$ $(M+H)^+$ 361.1433, Found 361.1443.

General procedure for chemoselective acylation for Table 3

To a solution of diol substrate (20.0 mg, 1.0 equiv.), catalyst (10 mol%) and 2,4,6-collidine (1.7 equiv.) in the solvent depicted in Table 3, was added acetic anhydride (1.03 equiv.) at the temperature indicated in Table 3. The resulting mixture was stirred at the same temperature for 24 h. The reaction was quenched with MeOH (10 mL), and the solvent was evaporated. The residue was dissolved in AcOEt, washed with 1*N* HCl, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude compound was purified by column chromatography or prep. TLC on silica gel to afford the mono- and the diacetates. Regioselectivity of the monoacetate was determined by the integration of ^{1}H NMR.

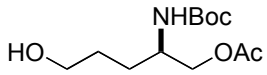
Spectral data for Table 3

(*R*)-4-(*tert*-Butoxycarbonylamino)-5-hydroxypentyl acetate (15-5-OAc)



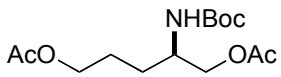
Colorless oil. $[\alpha]_D^{20}$ = +17 (c = 0.36, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 4.71 (s, 1H), 4.08 (t, *J* = 6.2 Hz, 2H), 3.66 (s, 3H), 3.58 (s, 3H), 2.46 (s, 1H), 2.05 (s, 3H), 1.81–1.56 (m, 4H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 171.2, 156.4, 79.7, 65.7, 64.2, 52.4, 28.3, 28.0, 25.3, 21.0. IR (KBr) 3369, 2976, 2937, 1739, 1714, 1692, 1524, 1391, 1366 cm^{-1}. MS (FAB) m/z 284 ($M+Na^+$, 12), 262 ($M+H^+$, 10). HRMS (FAB) Calcd for $C_{12}H_{24}NO_5$ $(M+H)^+$ 262.1654, Found 262.1642.

(*R*)-2-(*tert*-Butoxycarbonylamino)-5-hydroxypentyl acetate (15-1-OAc)



Colorless oil. $[\alpha]_D^{20}$ = +35 (c = 0.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 4.70 (s, 1H), 4.15–4.01 (m, 2H), 3.89 (br s, 1H), 3.68 (s, 2H), 2.08 (s, 3H), 1.70–1.55 (m, 4H), 1.44 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 171.0, 155.7, 79.6, 66.3, 62.3, 49.3, 28.7, 28.4, 28.3, 20.8. IR (KBr) 3354, 2976, 2937, 1714, 1694, 1530, 1391, 1366 cm^{-1}. MS (FAB) m/z 284 ($M+Na^+$, 15), 262 ($M+H^+$, 15). HRMS (FAB) Calcd for $C_{12}H_{24}NO_5$ $(M+H)^+$ 262.1655, Found 262.1664.

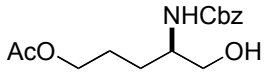
(*R*)-2-(*tert*-Butoxycarbonylamino)pentane-1,5-diyl diacetate (15-diacetate)



Colorless oil. $[\alpha]_D^{20}$ = +24 (c = 0.48, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 4.56 (d, *J* = 8.2 Hz, 1H), 4.13–4.00 (m, 4H), 3.88 (s, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.80–1.50 (m, 4H),, 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 171.1, 170.9, 155.4, 79.6, 66.3, 64.0, 49.3, 28.5, 28.3, 25.2, 21.0, 20.8. IR (KBr)

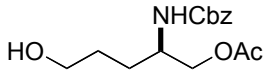
3368, 2976, 1740, 1714, 1520, 1455, 1366 cm^{-1}. MS (FAB) m/z 326 ($M+Na^+$, 20), 304 ($M+H^+$, 15). HRMS (FAB) Calcd for $C_{14}H_{26}NO_6$ $(M+H)^+$ 304.1760, Found 304.1754.

(*R*)-4-(Benzyloxycarbonylamino)-5-hydroxypentyl acetate (16-5-OAc)



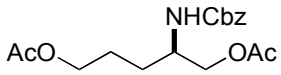
Colorless oil. $[\alpha]_D^{20}$ = +52 (c = 0.07, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.35 (s, 5H), 5.10 (s, 2H), 4.99 (s, 1H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.75–3.56 (m, 3H), 2.29 (s, 1H), 2.04 (s, 3H), 1.80–1.48 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 171.2, 156.6, 136.2, 128.5, 128.2, 128.1, 66.9, 65.2, 64.1, 52.8, 27.9, 25.3, 21.0. IR (KBr) 3332, 2955, 1714, 1702, 1538, 1244 cm^{-1}. MS (FAB) m/z 296 ($M+H^+$, 5), 264 (5). HRMS (FAB) Calcd for $C_{15}H_{22}NO_5$ $(M+H)^+$ 296.1498, Found 296.1487.

(*R*)-2-(Benzyloxycarbonylamino)-5-hydroxypentyl acetate (16-1-OAc)



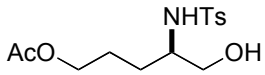
Colorless oil. $[\alpha]_D^{20}$ = +56 (c = 0.05, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.35 (s, 5H), 5.15–4.92 (m, 3H), 4.15–4.00 (m, 2H), 3.95 (s, 1H), 3.66 (s, 2H), 2.03 (s, 3H), 1.70–1.45 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 171.0, 156.1, 136.3, 128.5, 128.2, 128.1, 66.8, 66.0, 62.2, 50.0, 28.6, 28.2, 20.8. IR (KBr) 3332, 2948, 2871, 1697, 1538, 1235 cm^{-1}. MS (FAB) m/z 296 ($M+H^+$,10), 264 (4). HRMS (FAB) Calcd for $C_{15}H_{22}NO_5$ $(M+H)^+$ 296.1498, Found 296.1487.

(*R*)-2-(Benzyloxycarbonylamino)pentane-1,5-diyl diacetate (16-diacetate)



Colorless powder. M.p. 65–67 ºC. $[\alpha]_D^{20}$ = +44 (c = 0.03, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.36 (s, 5H), 5.20–5.05 (m, 2H), 4.83 (d, *J* = 8.7 Hz, 2H), 4.15–4.03 (m, 4H), 3.98–3.91 (m, 1H), 2.05 (s, 6H), 1.80–1.40 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 171.1, 170.9, 155.9, 136.3, 128.5, 128.2, 128.1, 66.9, 66.0, 63.9, 50.0, 28.4, 25.1, 20.9, 20.8. IR (KBr) 3319, 2960, 1733, 1685, 1545, 1235 cm^{-1}. MS (FAB) m/z 360 ($M+Na^+$, 20), 338 ($M+H^+$, 18). HRMS (FAB) Calcd for $C_{17}H_{24}NO_6$ $(M+H)^+$ 338.1604, Found 338.1588.

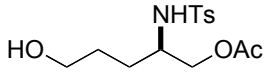
(*R*)-5-Hydroxy-4-(4-methylphenylsulfonamido)pentyl acetate (17-5-OAc)



Colorless oil. $[\alpha]_D^{20}$ = +24 (c = 0.08, $CHCl_3$). ^1H NMR ($CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J*

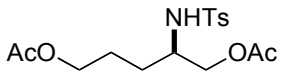
= 8.2 Hz, 2H), 5.24 (d, *J* = 6.4 Hz, 1H), 3.97–3.87 (m, 2H), 3.59–3.44 (m, 2H), 3.31–3.22 (m, 1H), 2.43 (s, 4H), 2.01 (s, 3H), 1.62–1.40 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 171.2, 143.6, 137.5, 129.7, 127.0, 64.5, 63.8, 55.1, 28.2, 24.8, 21.5, 20.9. IR (KBr) 3503, 3282, 2955, 2885, 1735, 1597, 1435, 1325 cm^{-1}. MS (FAB) m/z 338 ($M+Na^+$, 50), 316 ($M+H^+$, 48). HRMS (FAB) Calcd for $C_{14}H_{22}NO_5S$ $(M+H)^+$ 316.1219, Found 316.1219.

(*R*)-5-Hydroxy-2-(4-methylphenylsulfonamido)pentyl acetate (17-1-OAc)



Colorless powder. M.p. 66–68 ºC. $[\alpha]_D^{20}$ = +22 (c = 0.05, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 5.17 (d, *J* = 8.2 Hz, 1H), 3.99 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.87 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.66–3.47 (m, 3H), 2.43 (s, 3H), 1.93 (s, 3H), 1.67–1.55 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 170.9, 143.5, 137.9, 129.7, 127.0, 65.8, 62.3, 52.6, 29.0, 28.0, 21.5, 20.6. IR (KBr) 3414, 3131, 2901, 1713, 1594, 1442, 1331 cm^{-1}. MS (FAB) m/z 338 ($M+Na^+$, 20), 316 ($M+H^+$, 40). HRMS (FAB) Calcd for $C_{14}H_{22}NO_5S$ $(M+H)^+$ 316.1218, Found 316.1223.

(*R*)-2-(4-Methylphenylsulfonamido)pentane-1,5-diyl diacetate (17-diacetate)



Colorless oil. $[\alpha]_D^{20}$ = +7.7 (c = 0.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 4.76 (d, *J* = 8.2 Hz, 1H), 4.05–3.93 (m, 3H), 3.85 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.56–3.45 (m, 1H), 2.43 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.70–1.50 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 171.0, 170.8, 143.6, 137.9, 129.8, 127.0, 65.6, 63.7, 52.5, 29.0, 24.7, 21.5, 20.9, 20.6. IR (KBr) 3283, 2956, 2928, 1739, 1434, 1365, 1242 cm^{-1}. MS (FAB) m/z 380 ($M+Na^+$, 20), 358 ($M+H^+$, 20). HRMS (FAB) Calcd for $C_{16}H_{24}NO_6S$ $(M+H)^+$ 358.1324, Found 358.1338.

References

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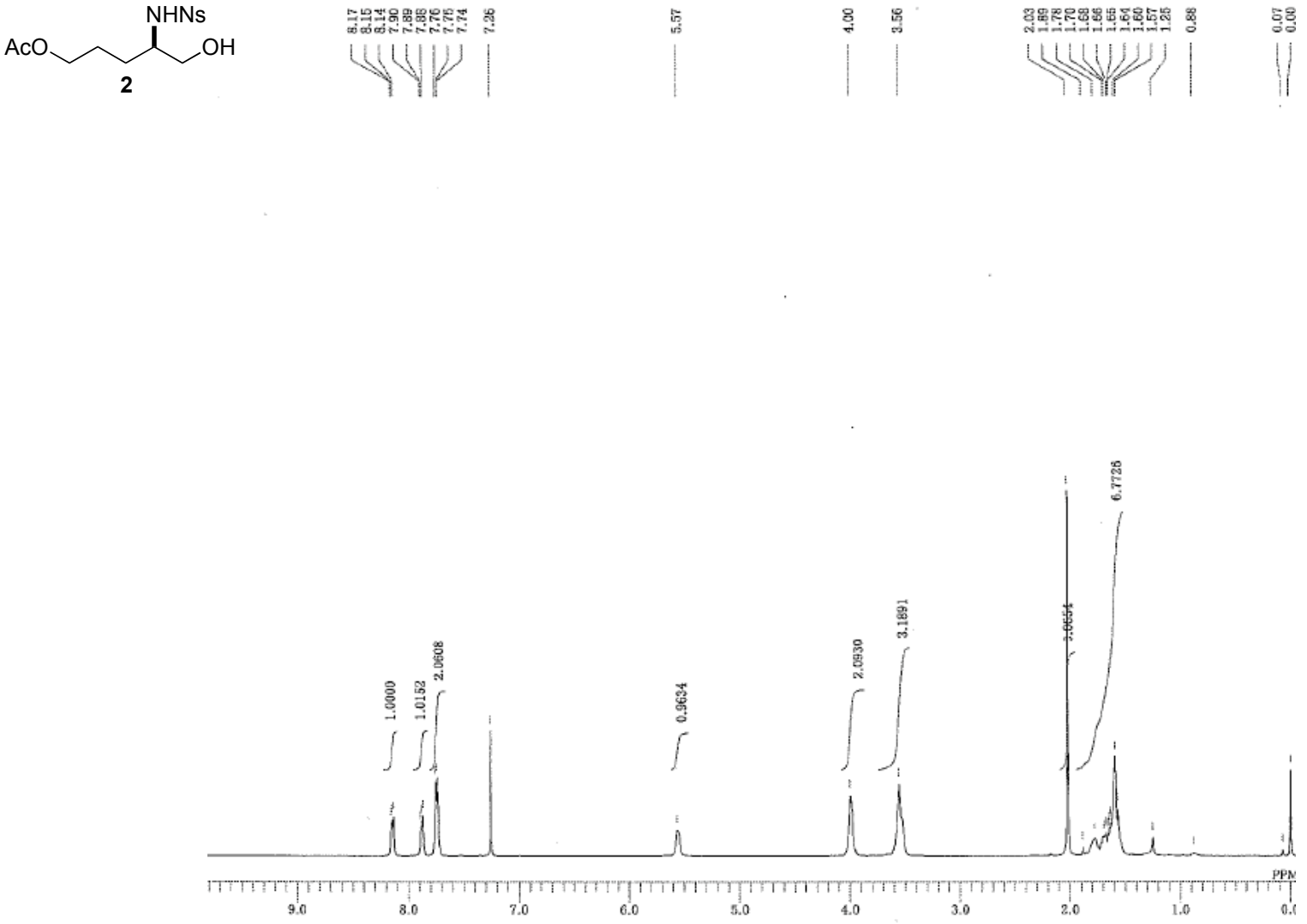
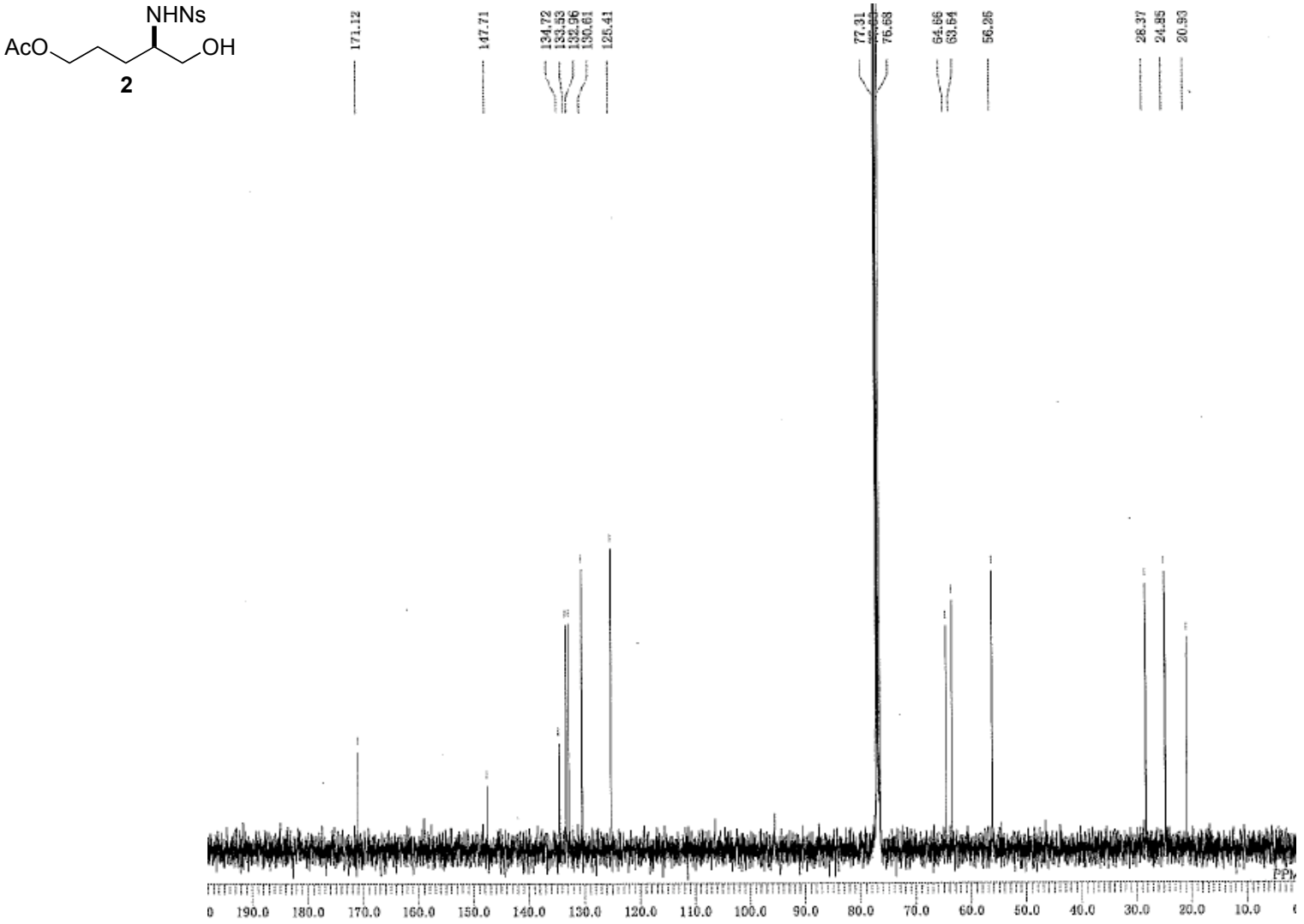
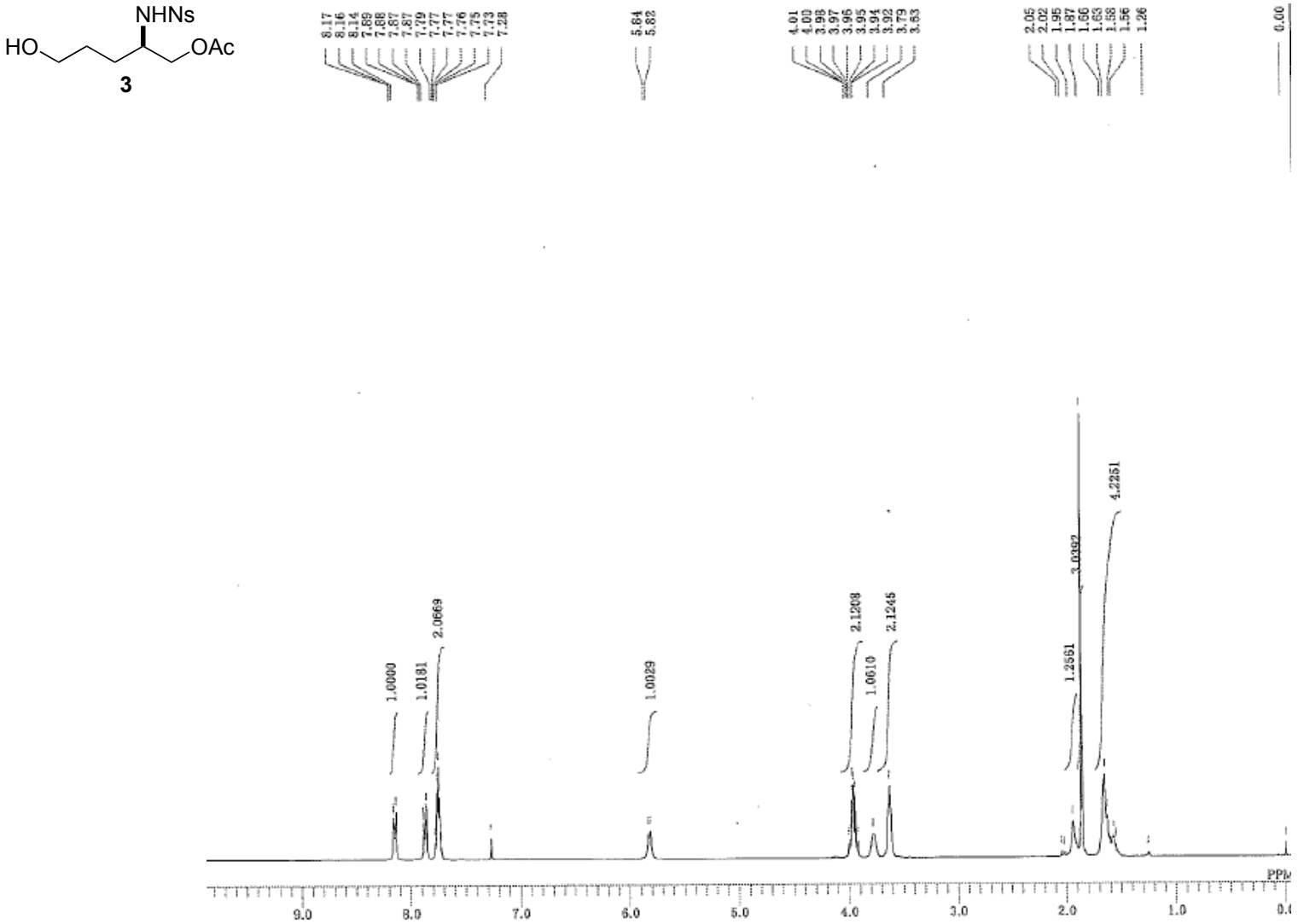
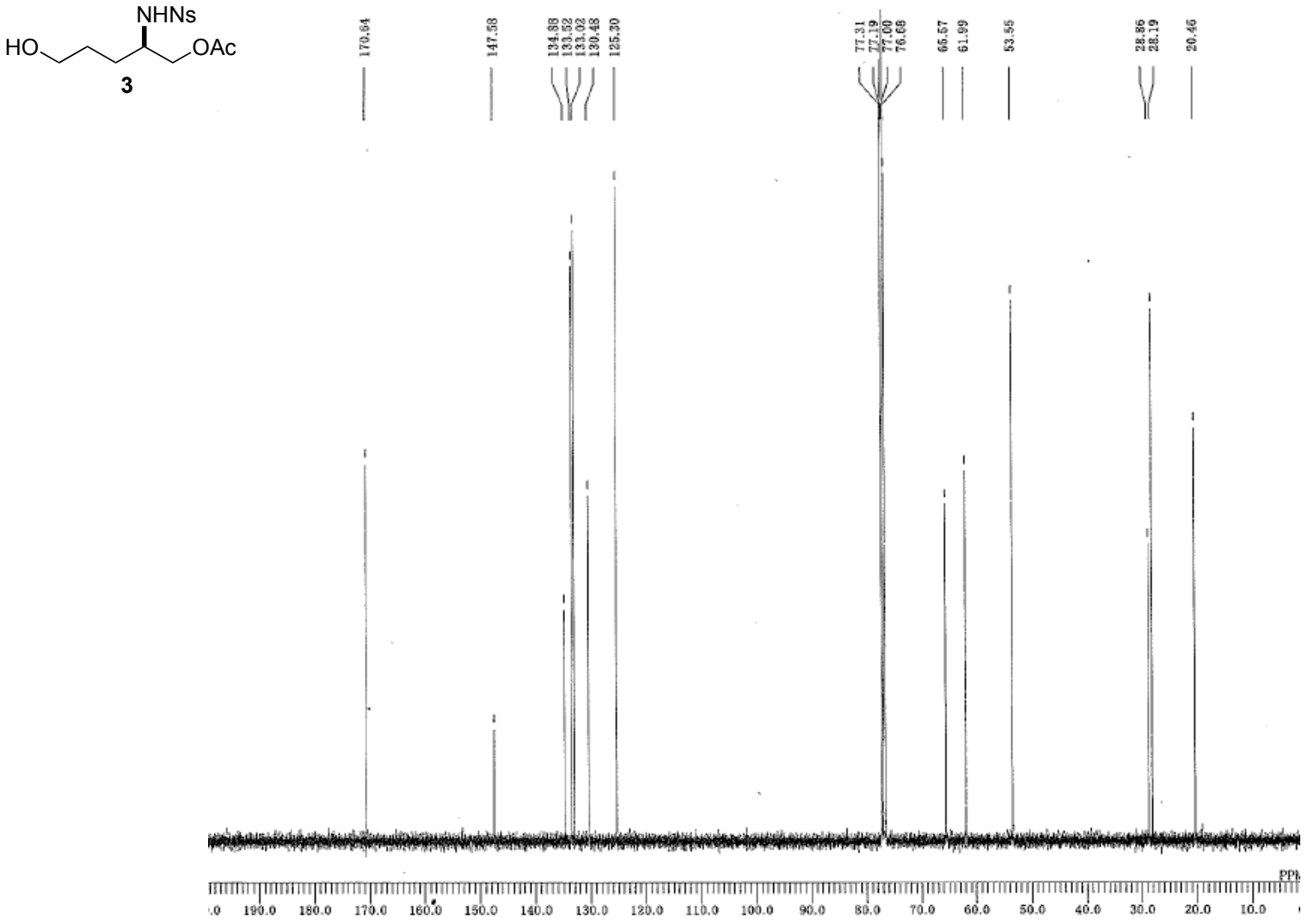
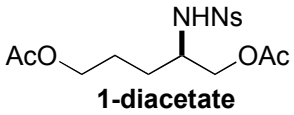


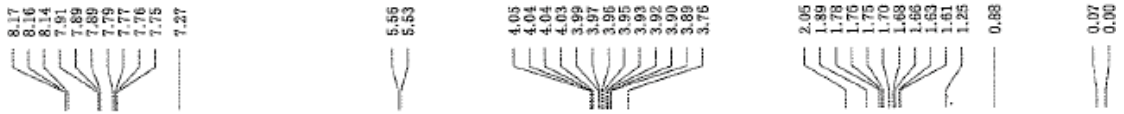


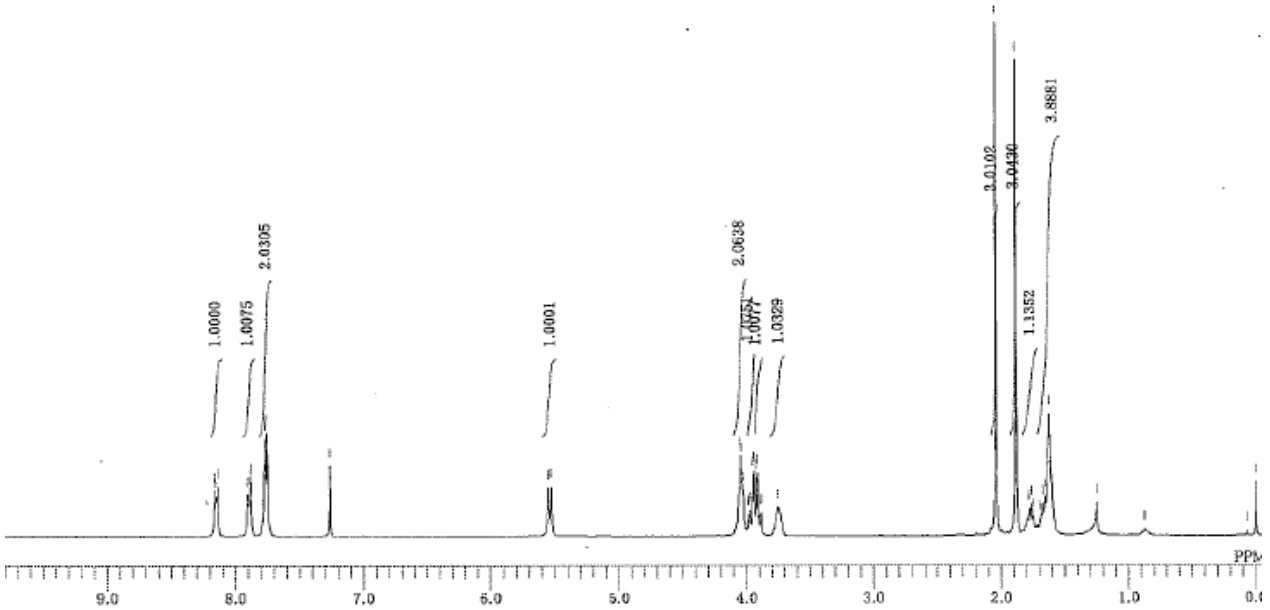


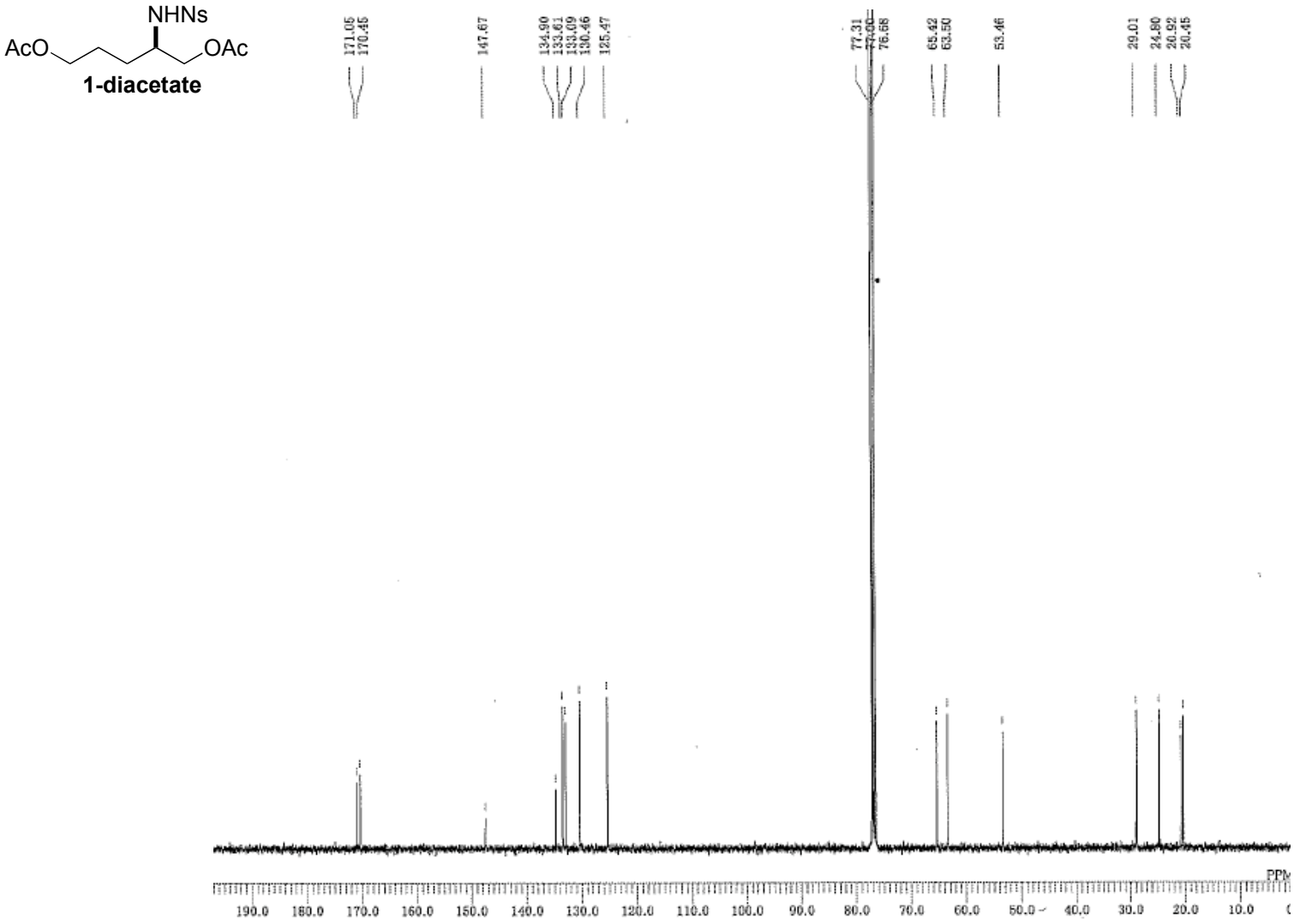


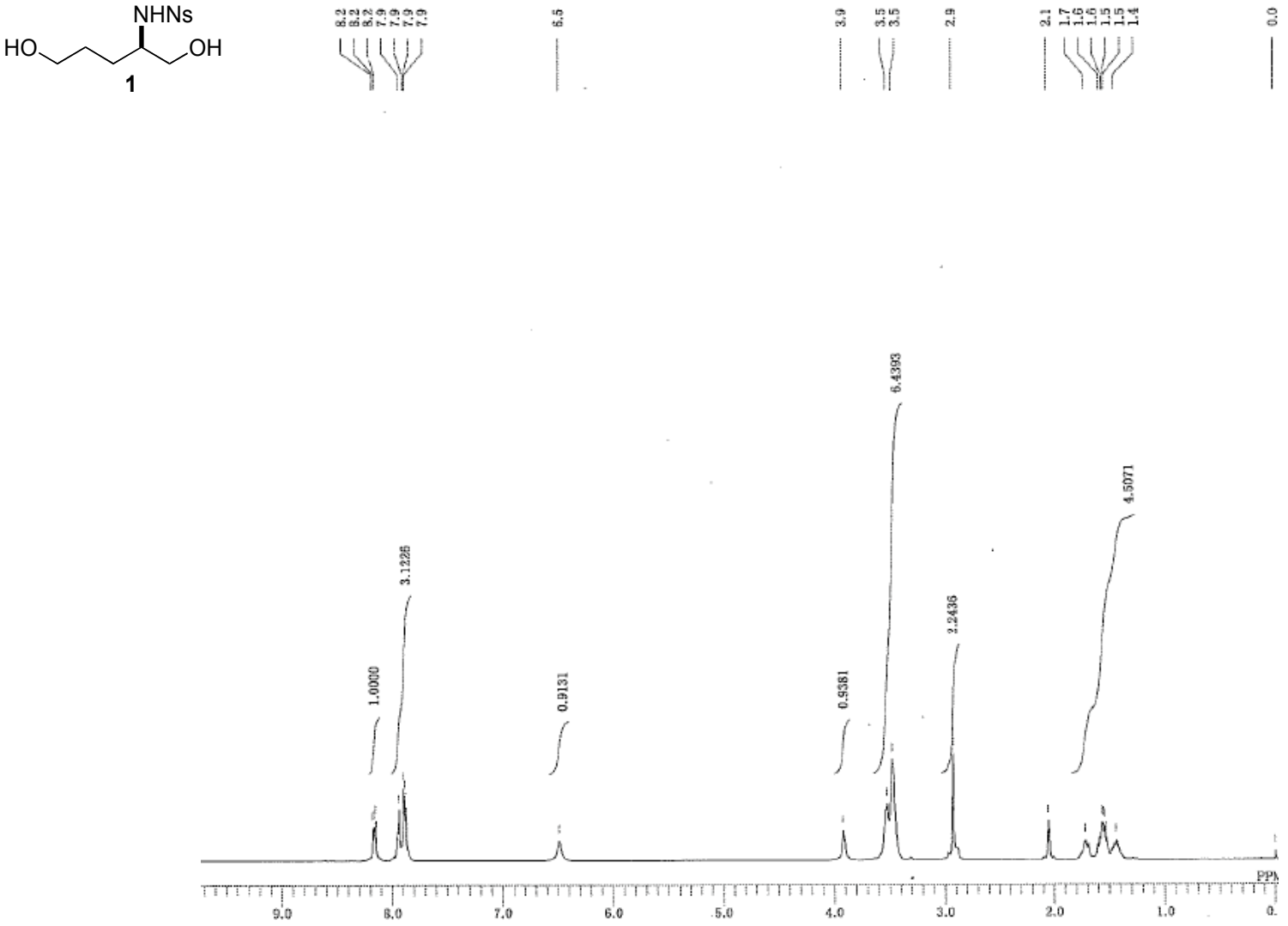


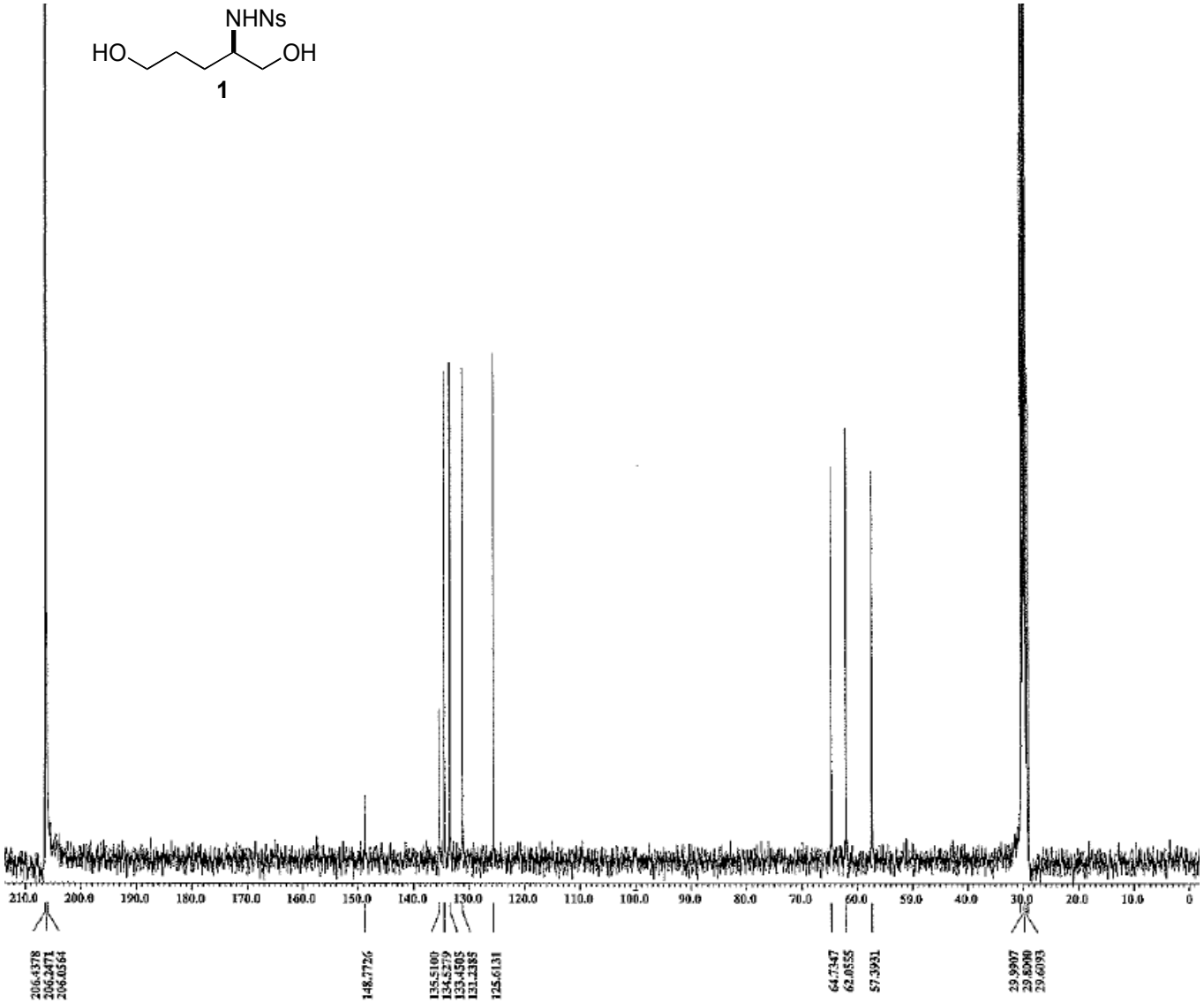
1-diacetate

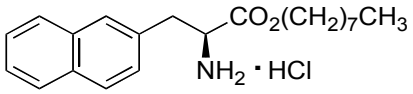




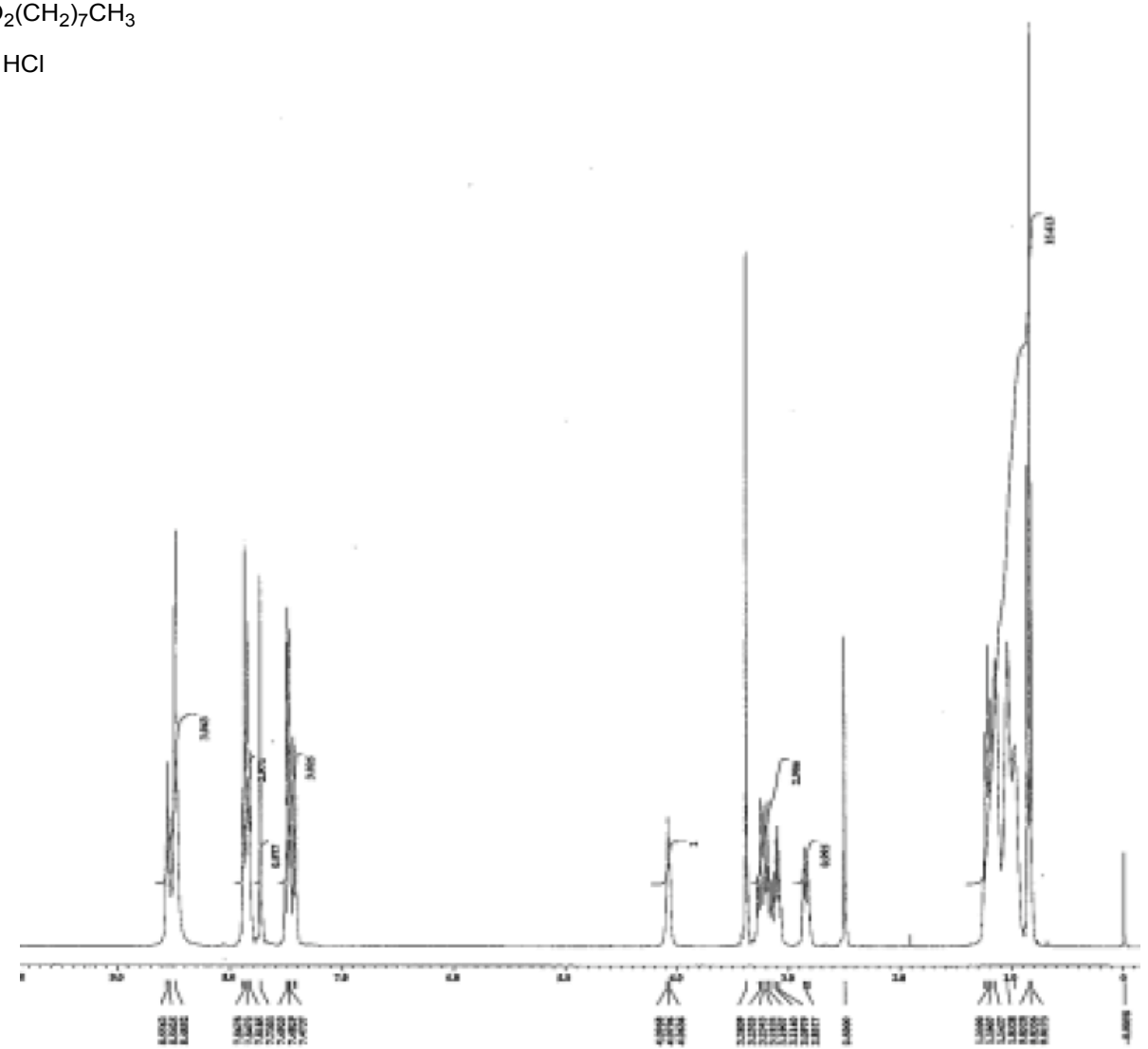


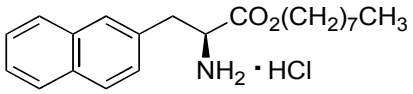




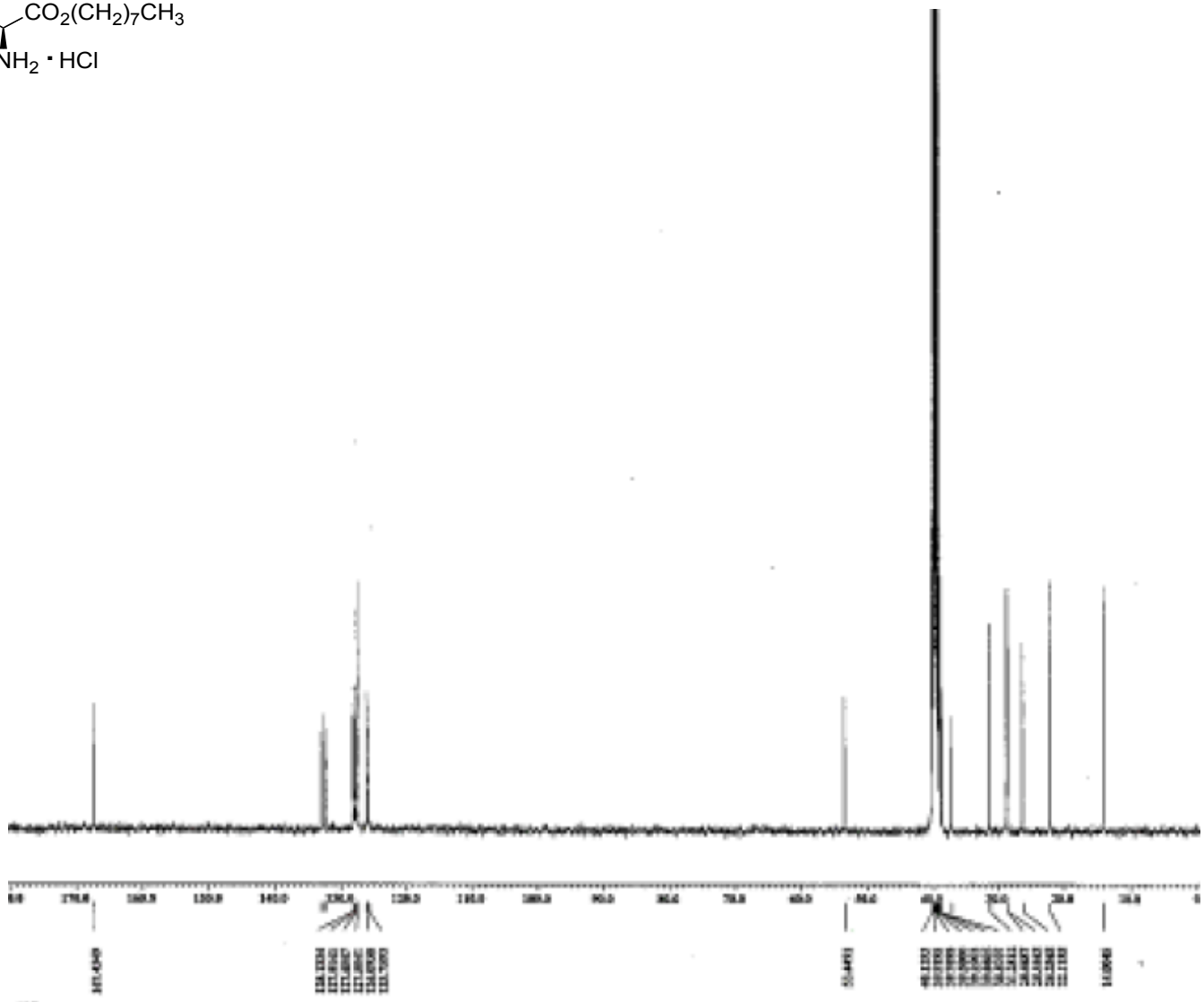


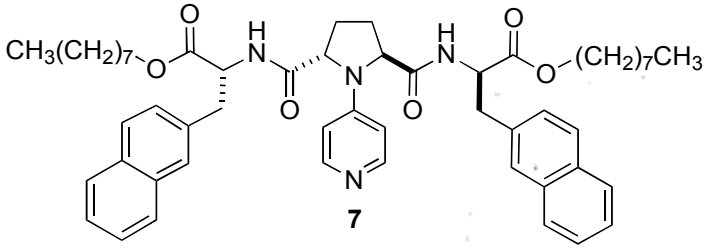
S2





S2





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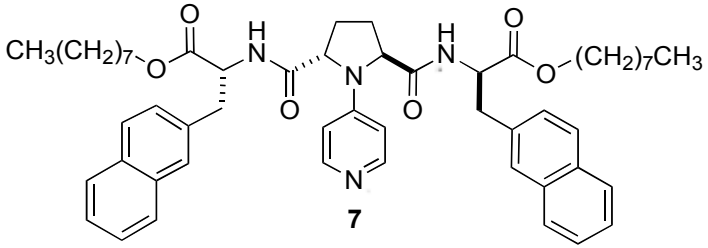

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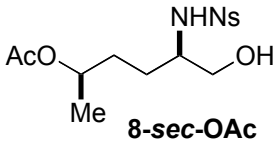
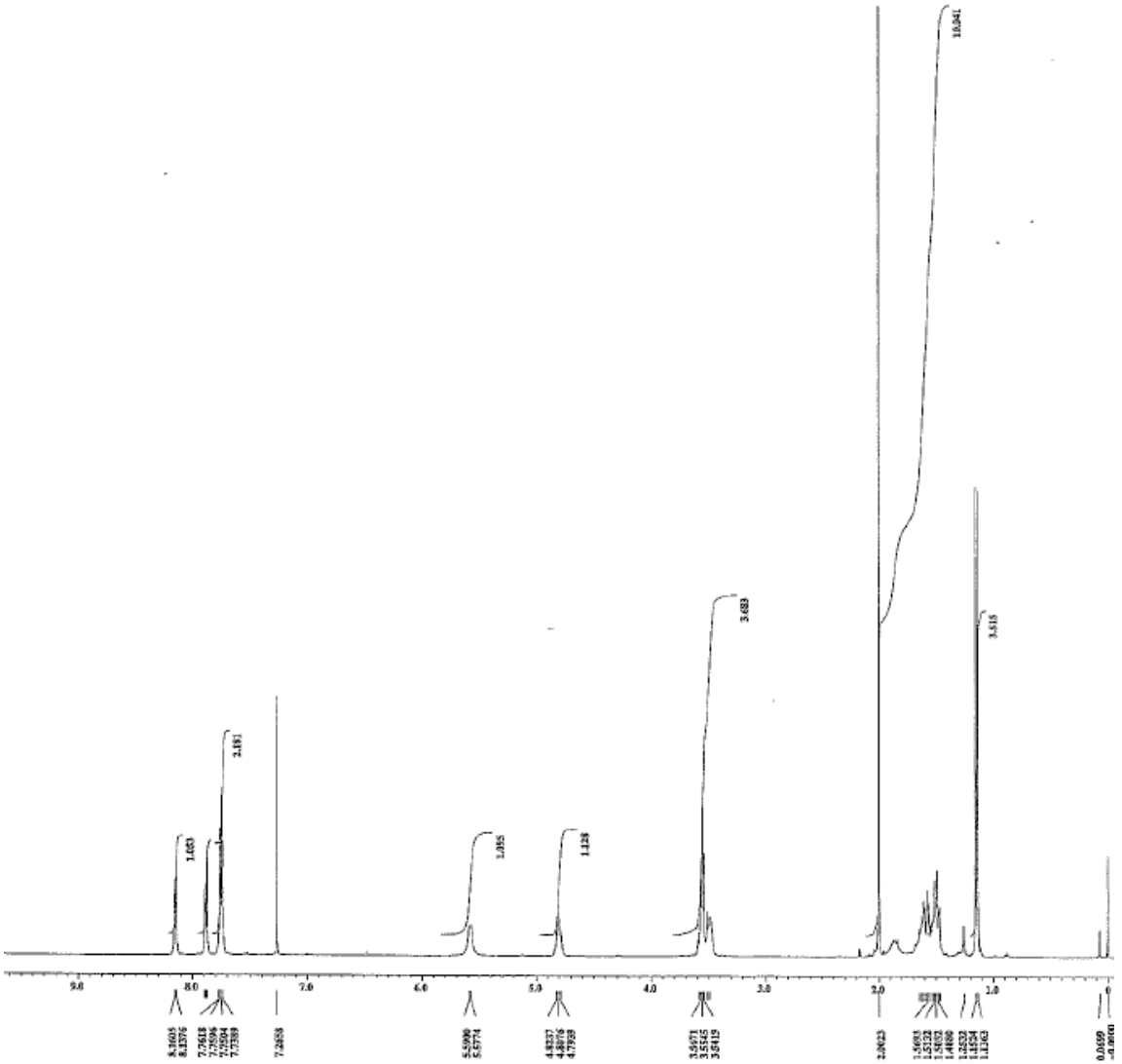
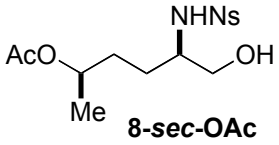


8-*sec*-OAc





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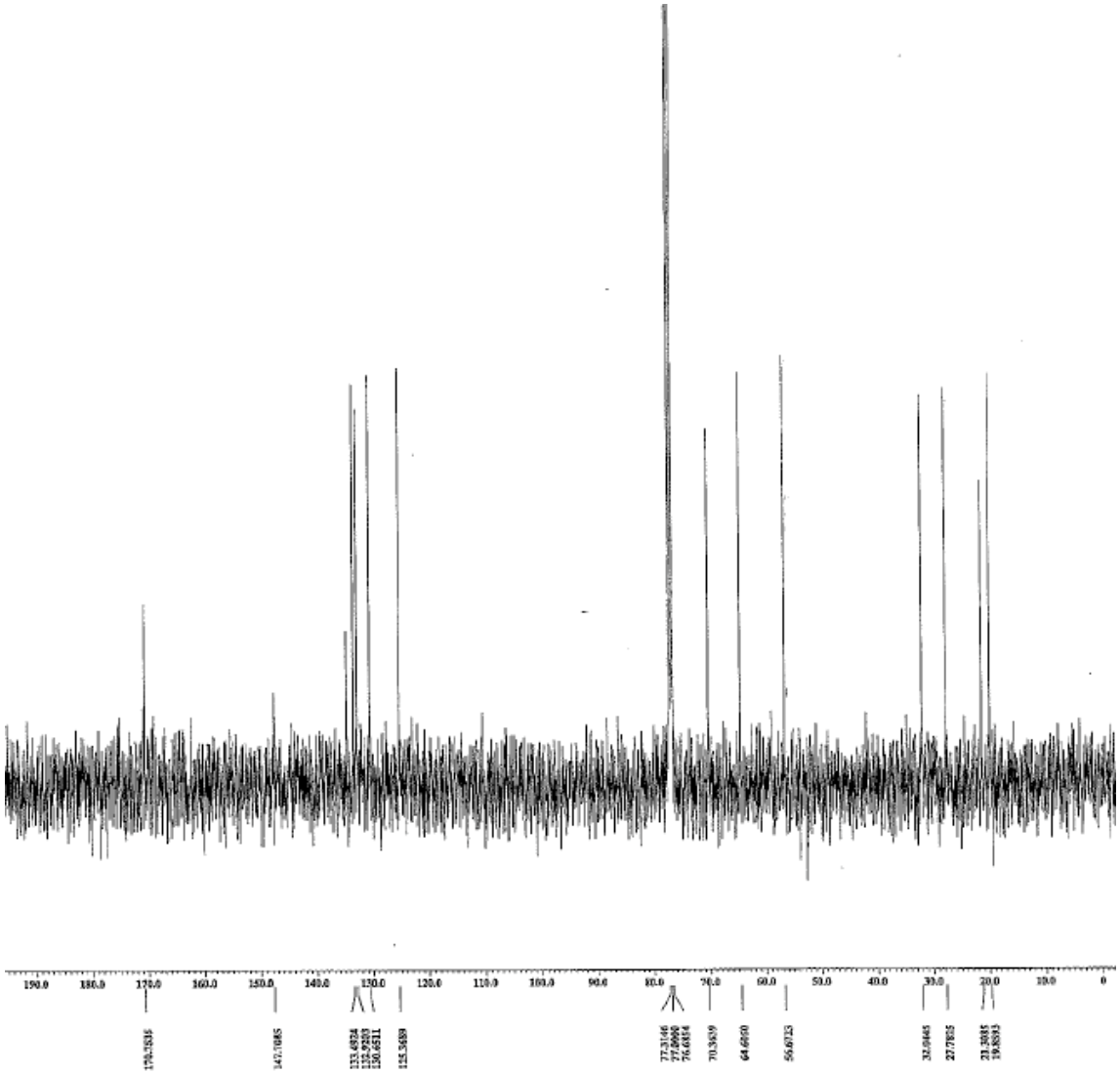
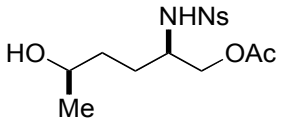
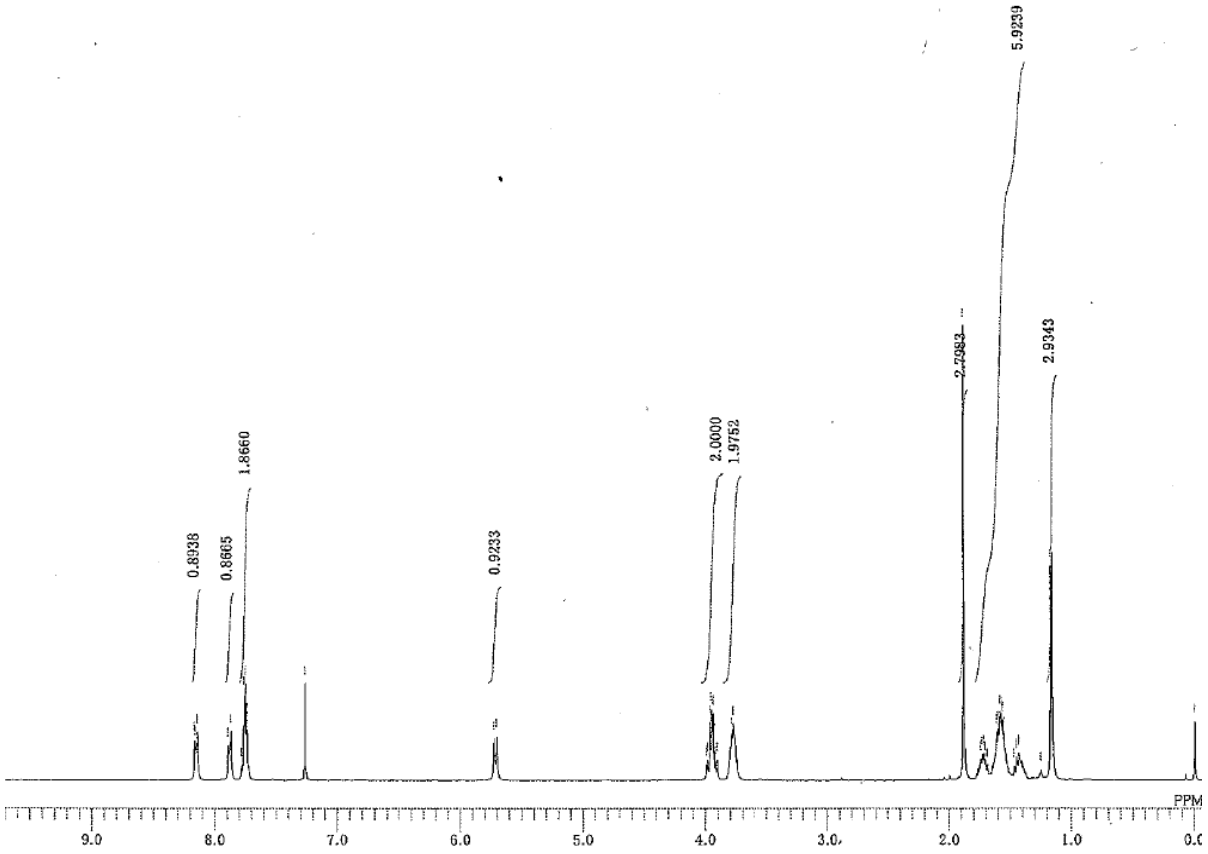
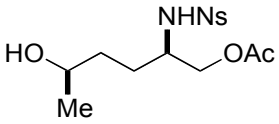


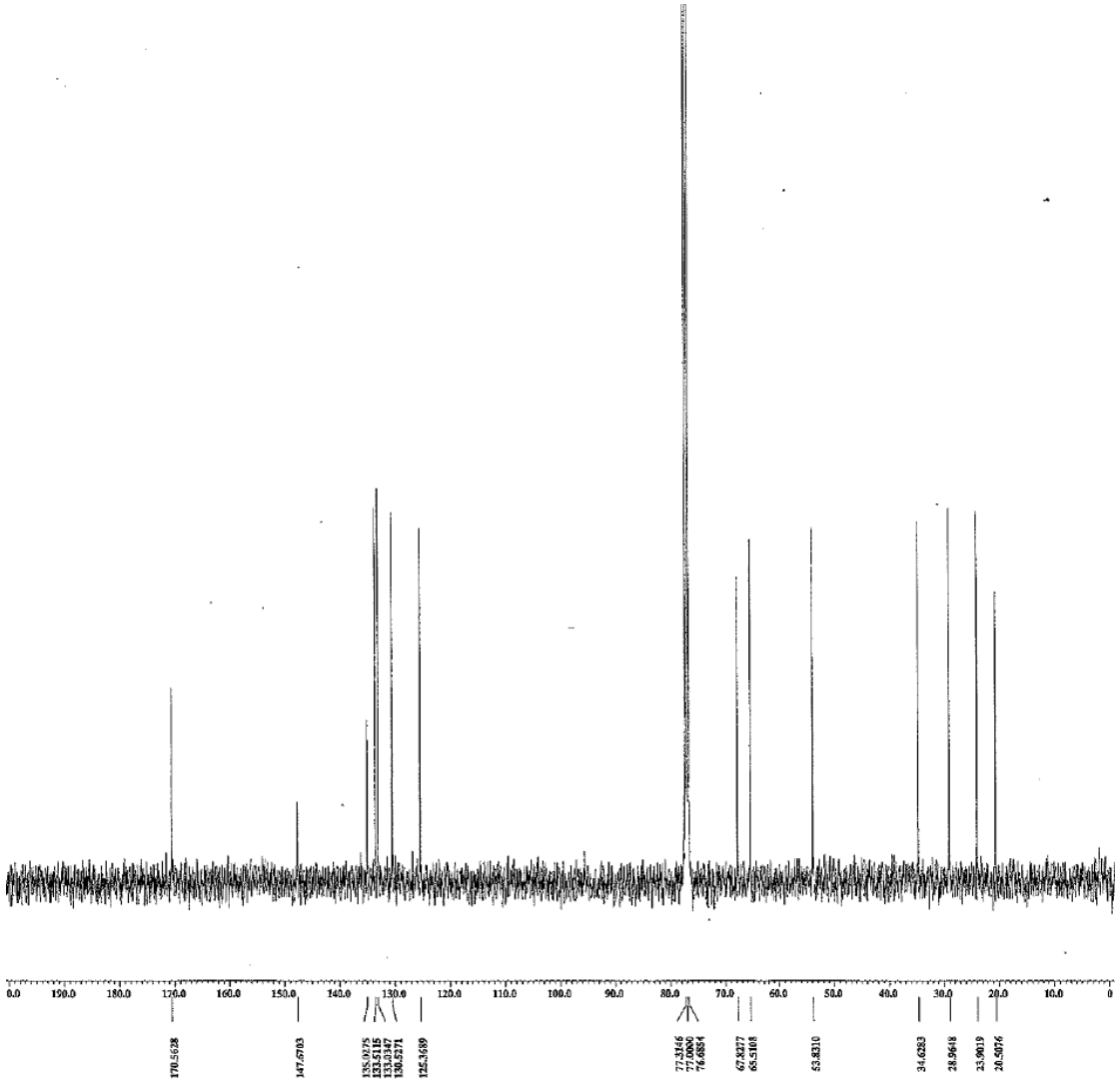


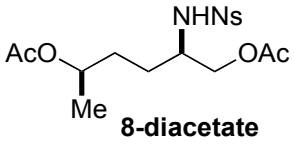
8-*pri*-OAc



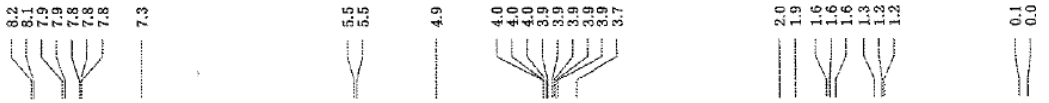


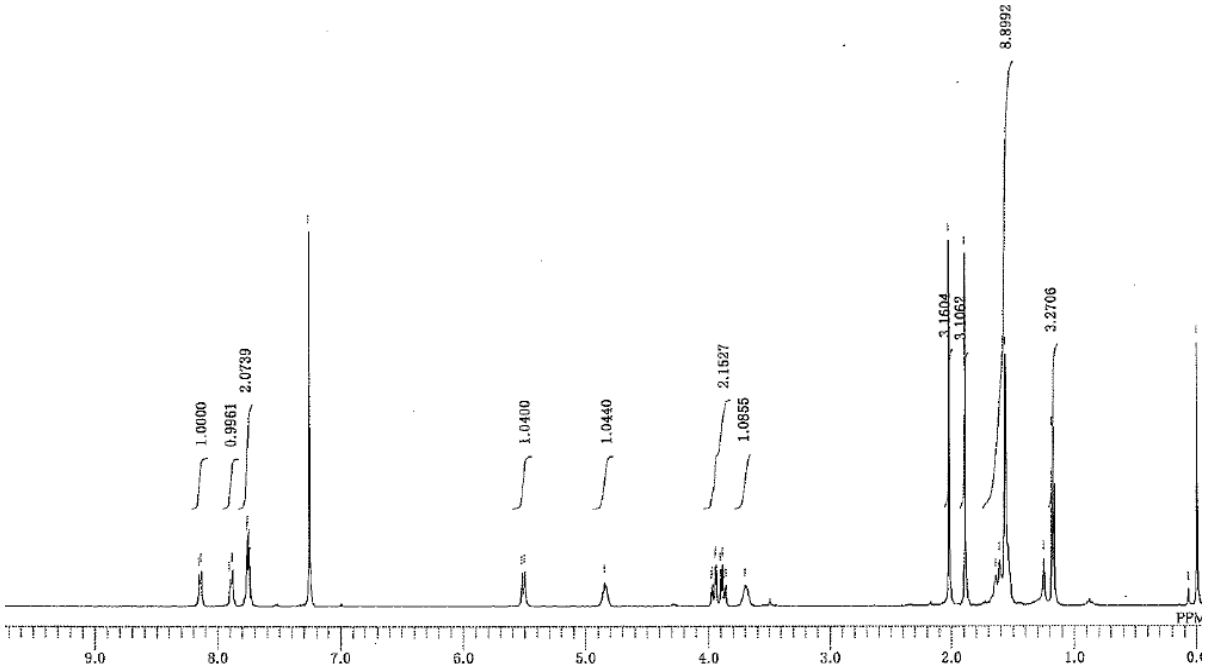
8-*pri*-OAc

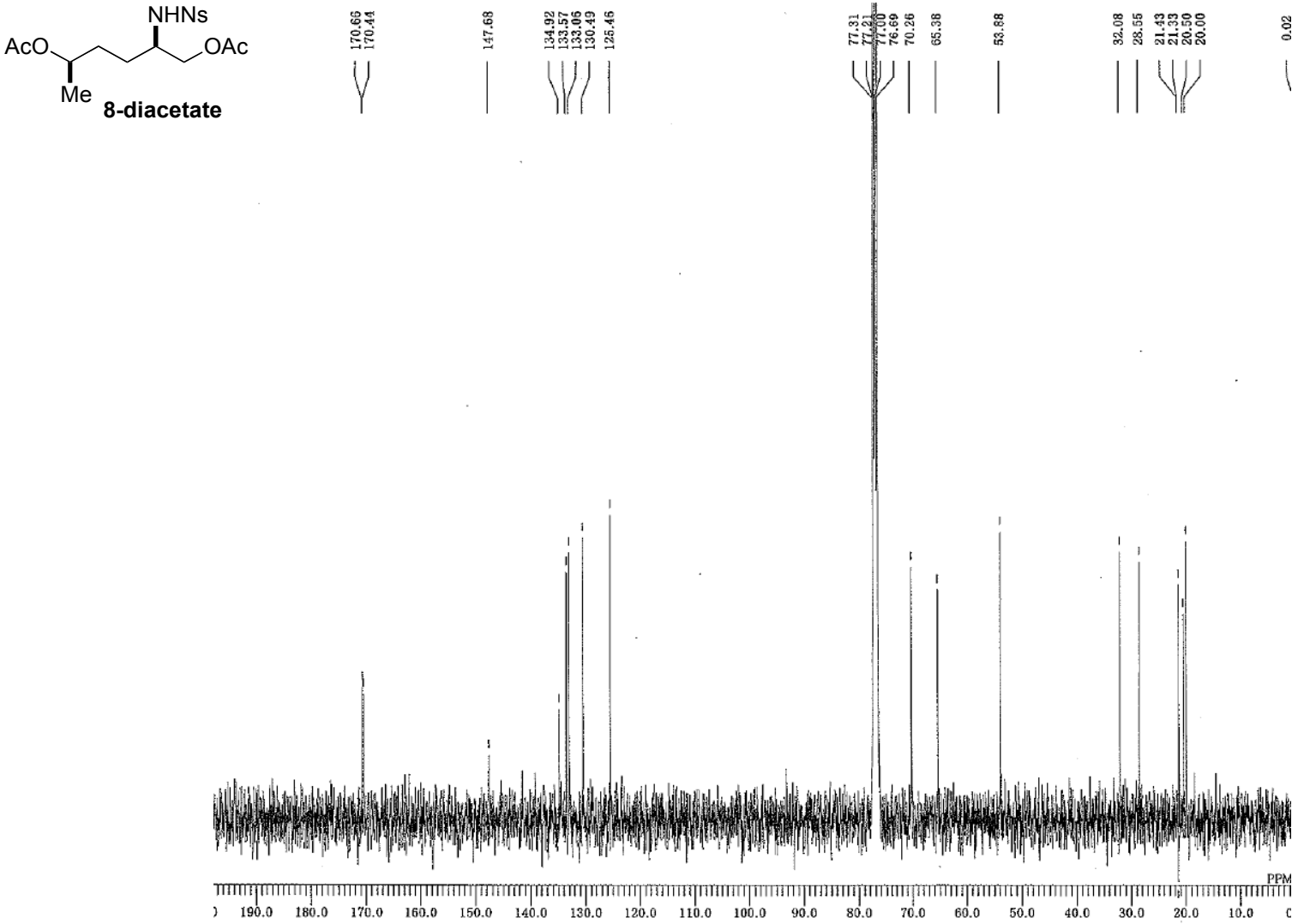


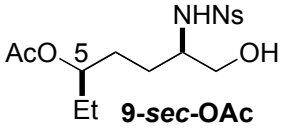


8-diacetate



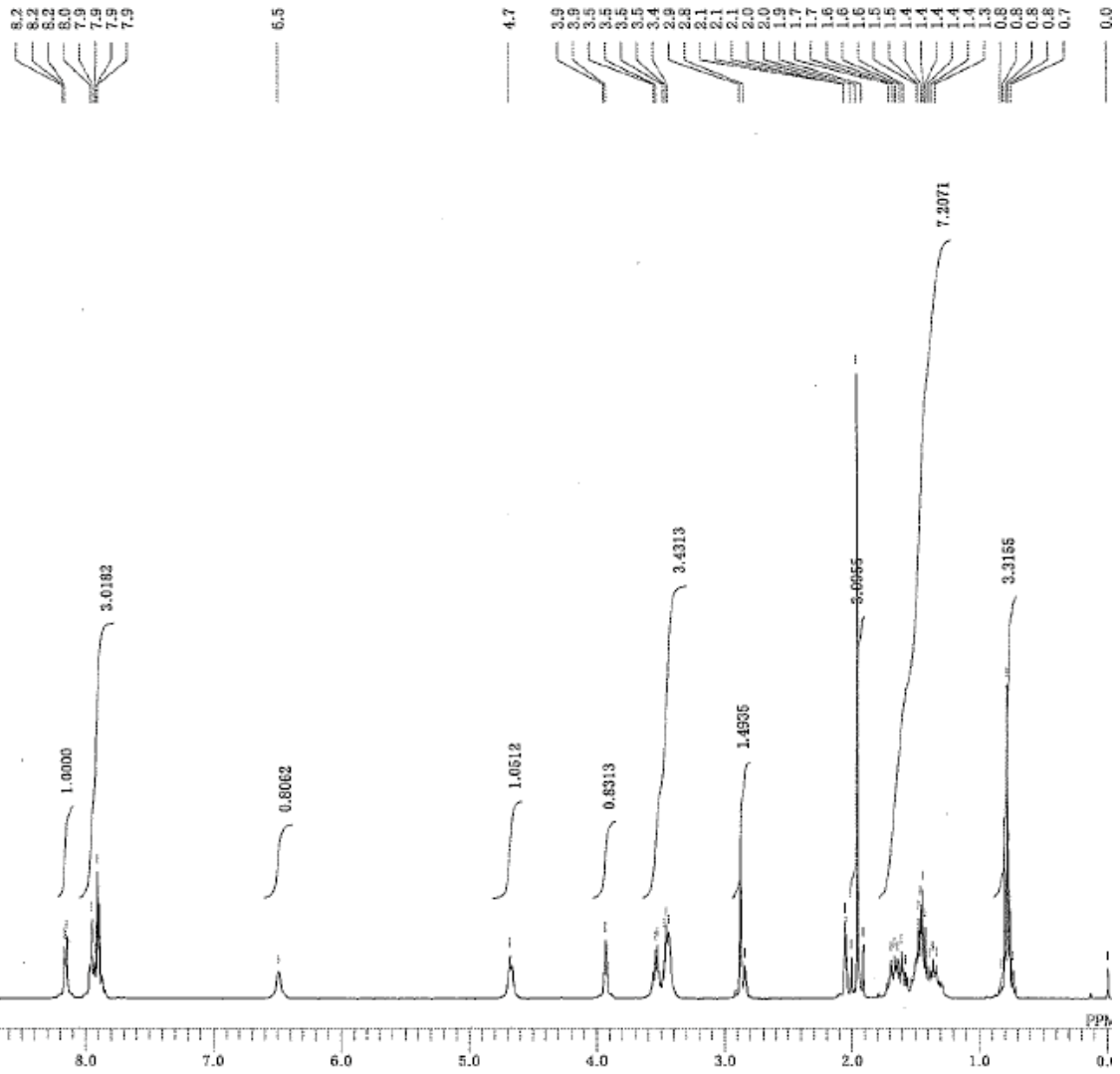


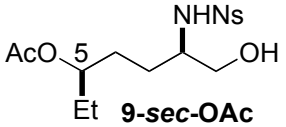




9-*sec*-OAc

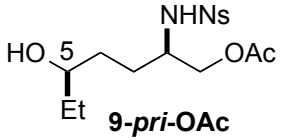
The absolute configuration at C(5) was tetatively assigned.





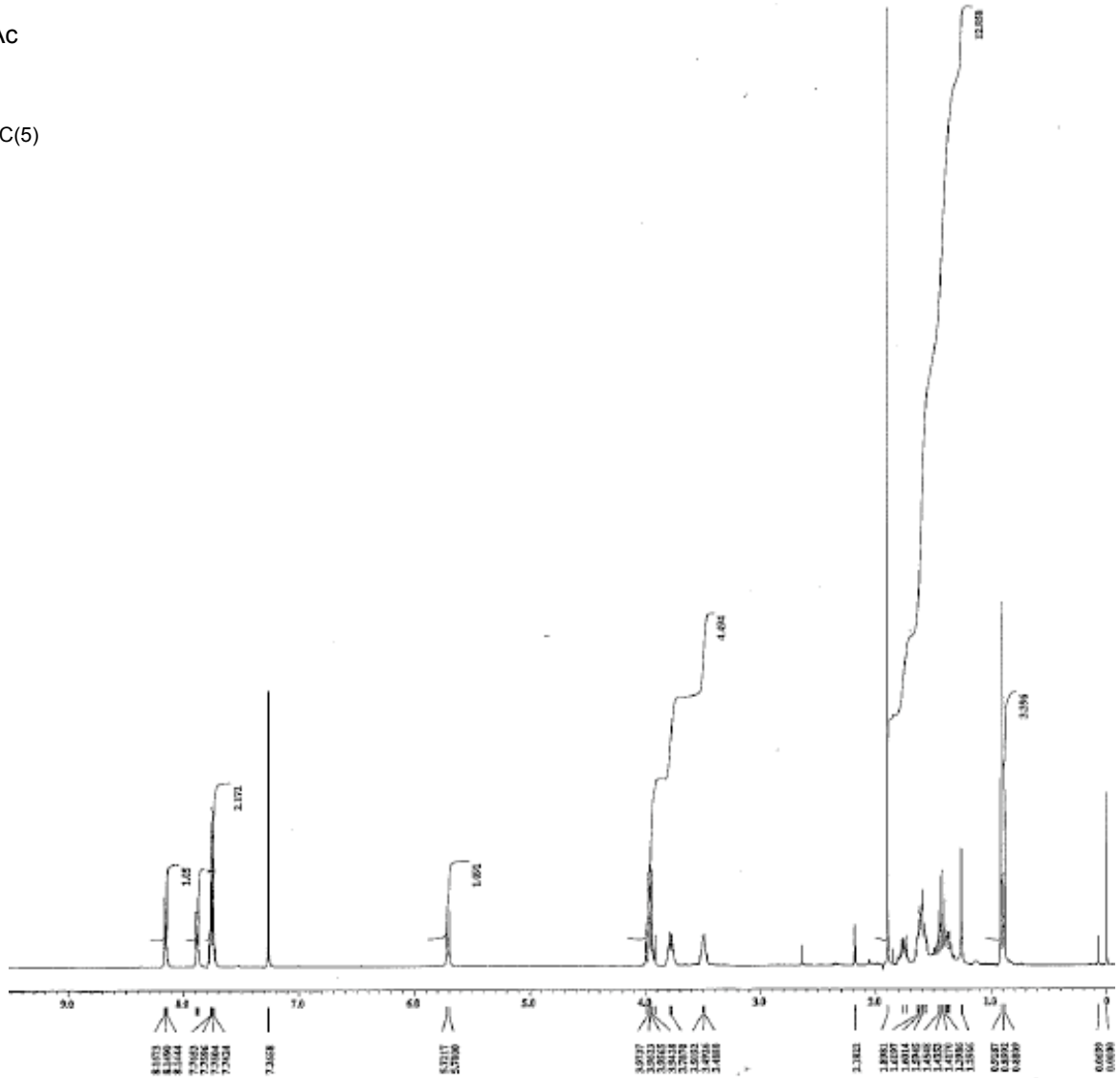
9-*sec*-OAc

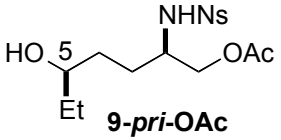
The absolute configuration at C(5) was tetatively assigned.



9-*pri*-OAc

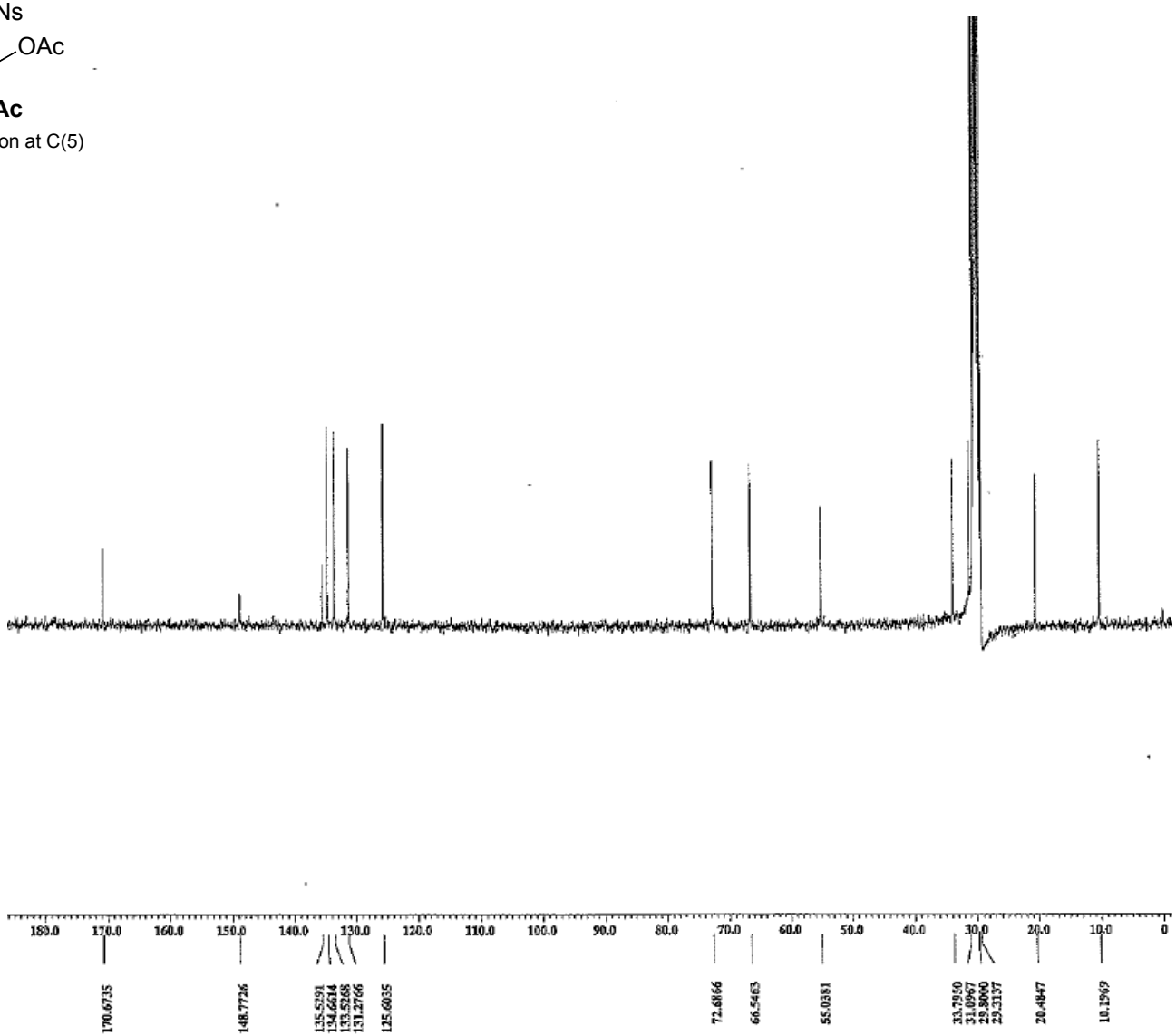
The absolute configuration at C(5) was tetatively assigned.

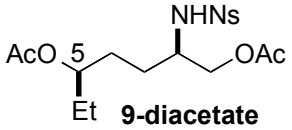




9-*pri*-OAc

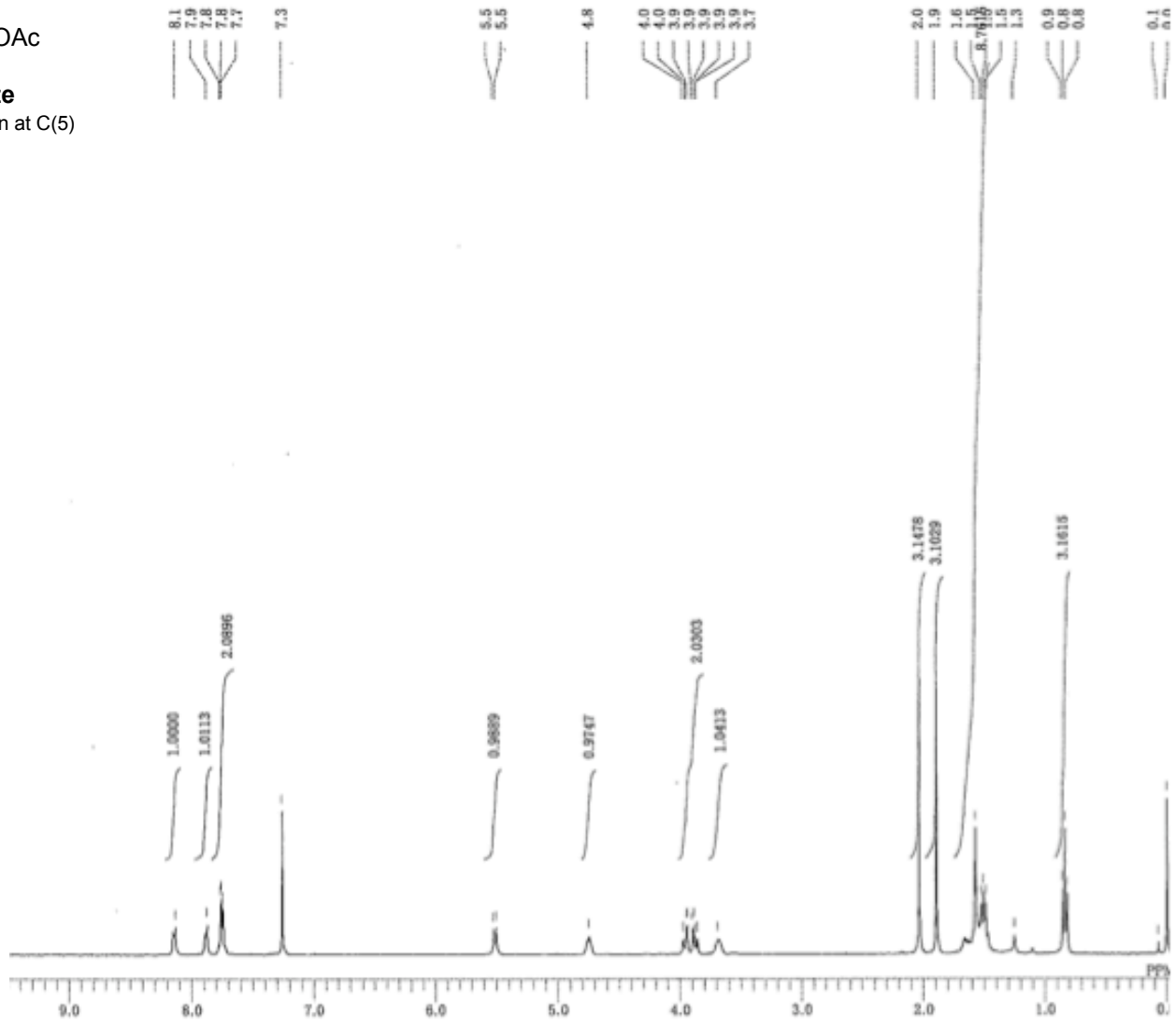
The absolute configuration at C(5) was tetatively assigned.

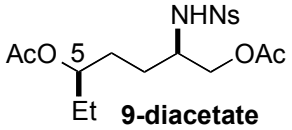




9-diacetate

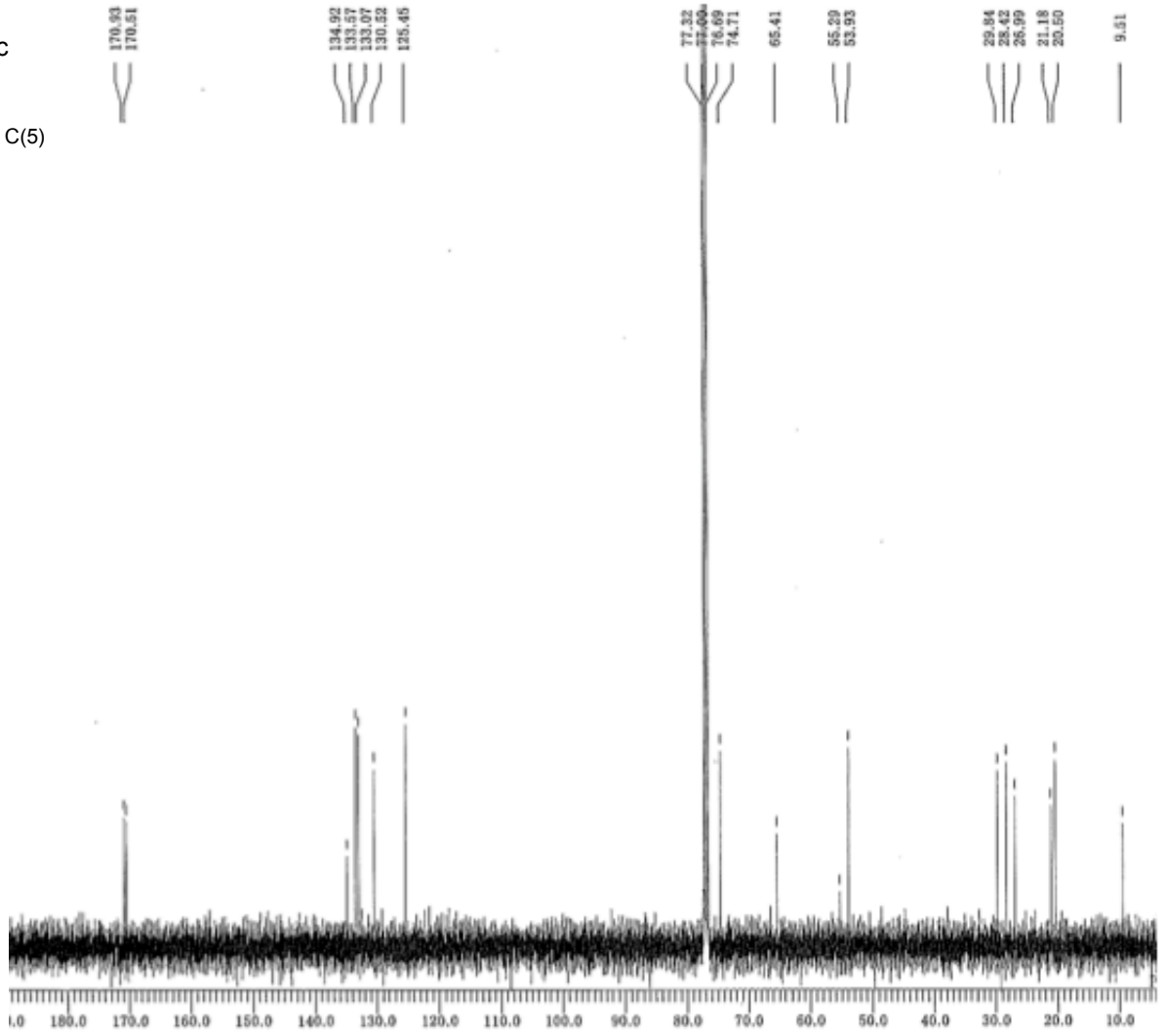
The absolute configuration at C(5) was tetatively assigned.

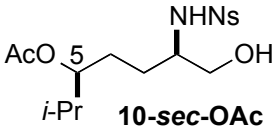




9-diacetate

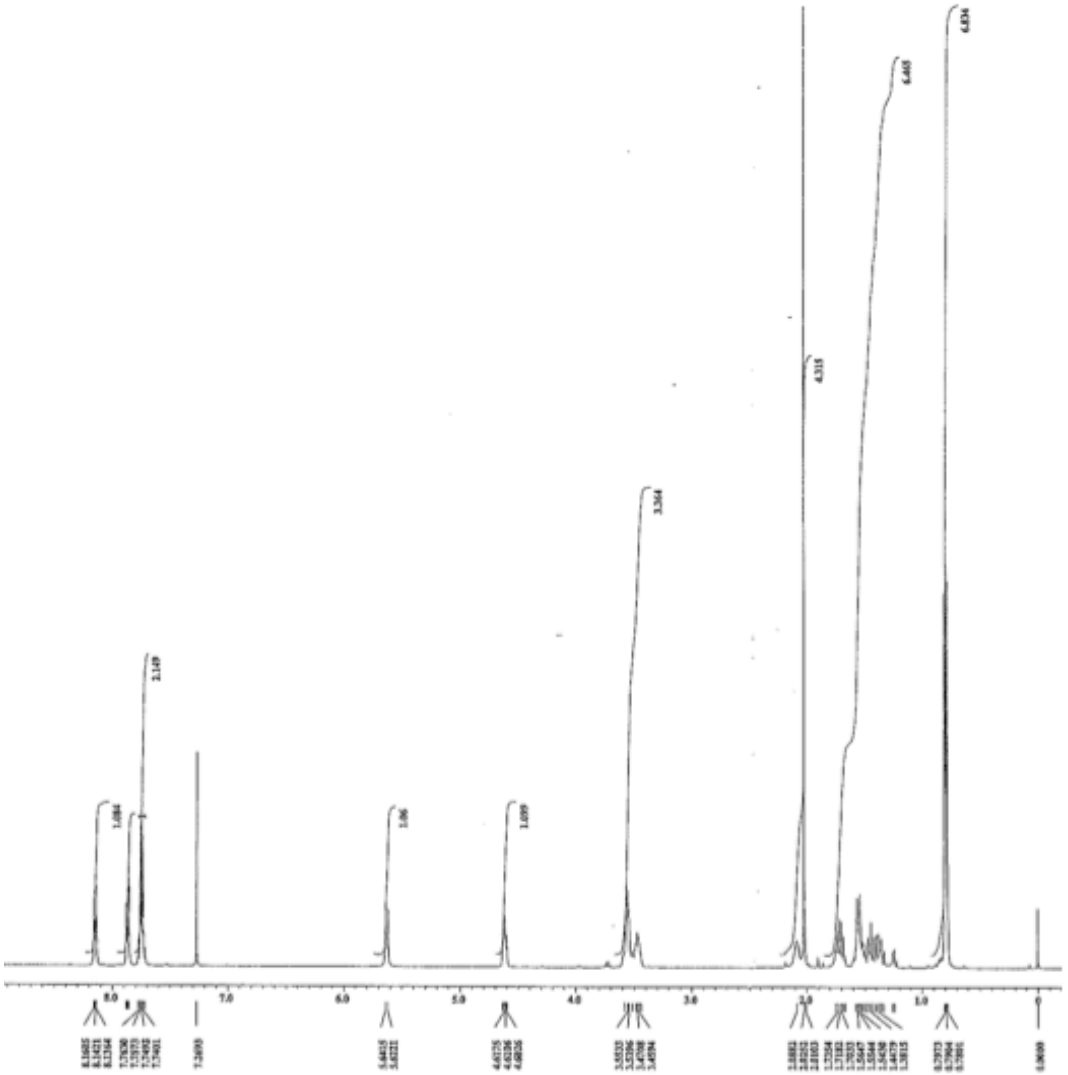
The absolute configuration at C(5) was tetatively assigned.

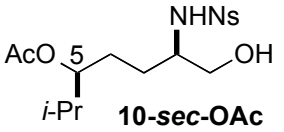




10-*sec*-OAc

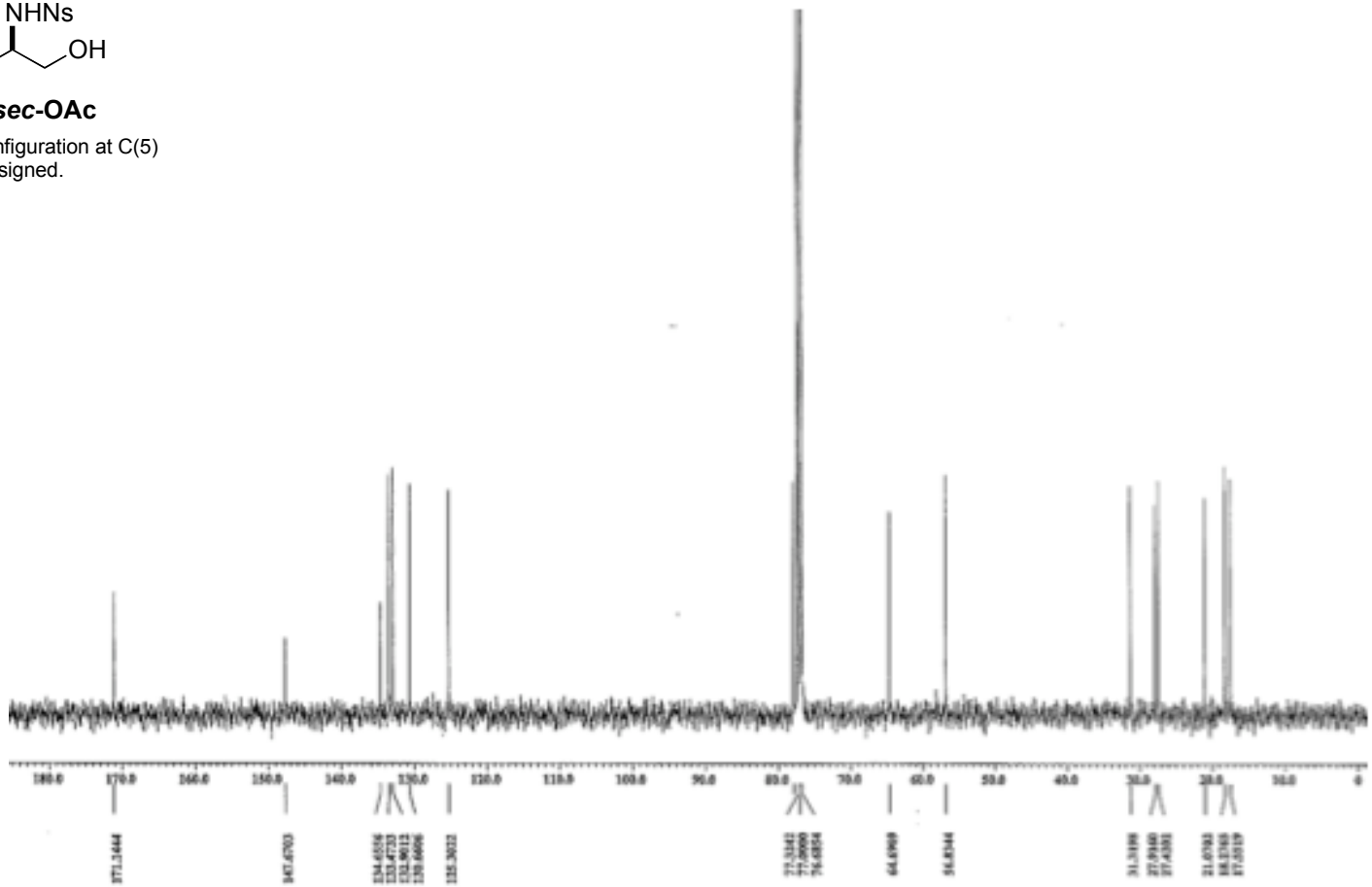
The absolute configuration at C(5) was tetatively assigned.

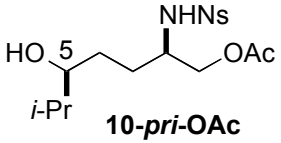




10-*sec*-OAc

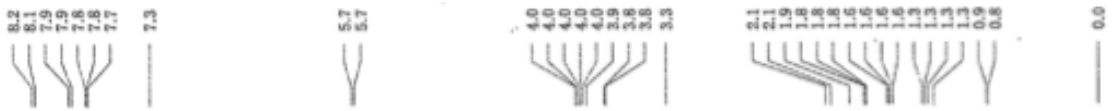
The absolute configuration at C(5) was tetatively assigned.

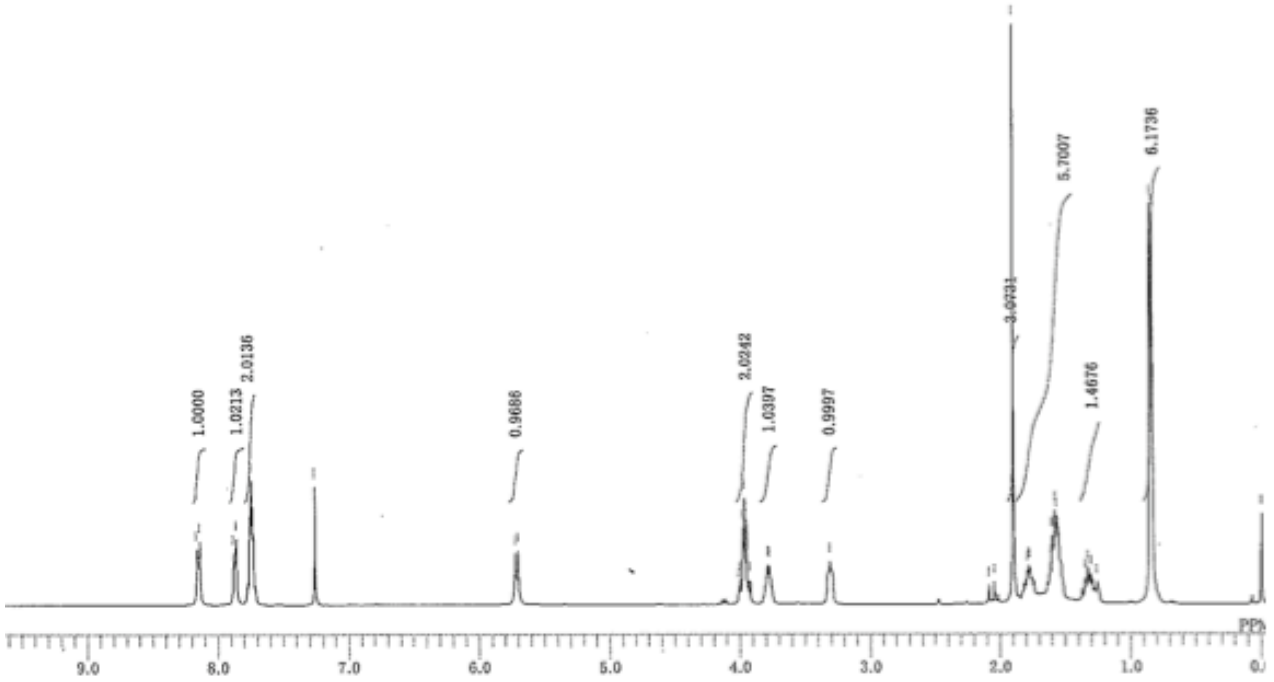


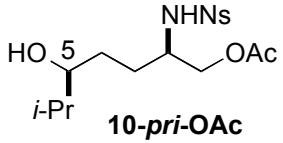


10-*pri*-OAc

The absolute configuration at C(5) was tetatively assigned.

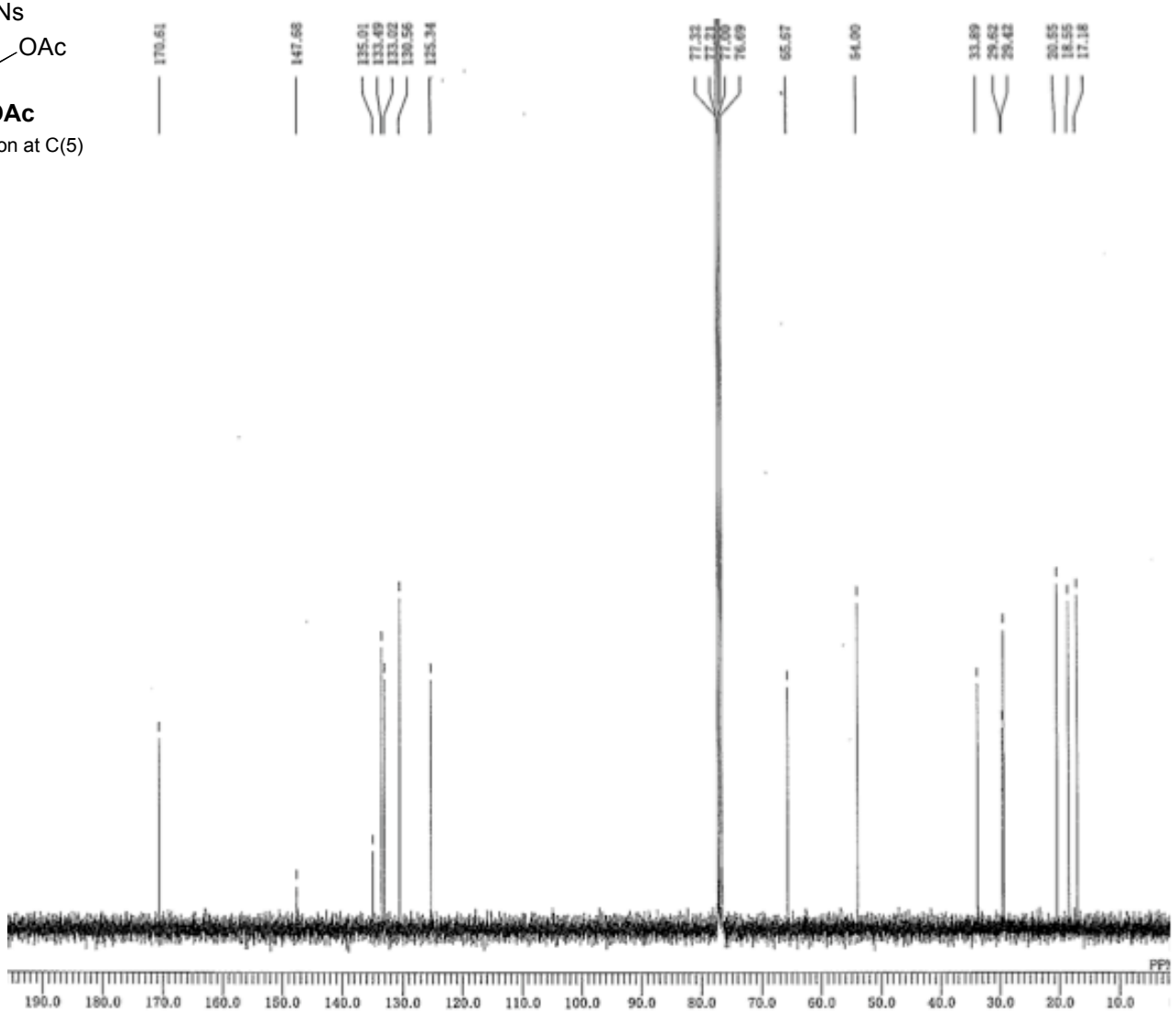


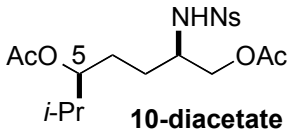




10-*pri*-OAc

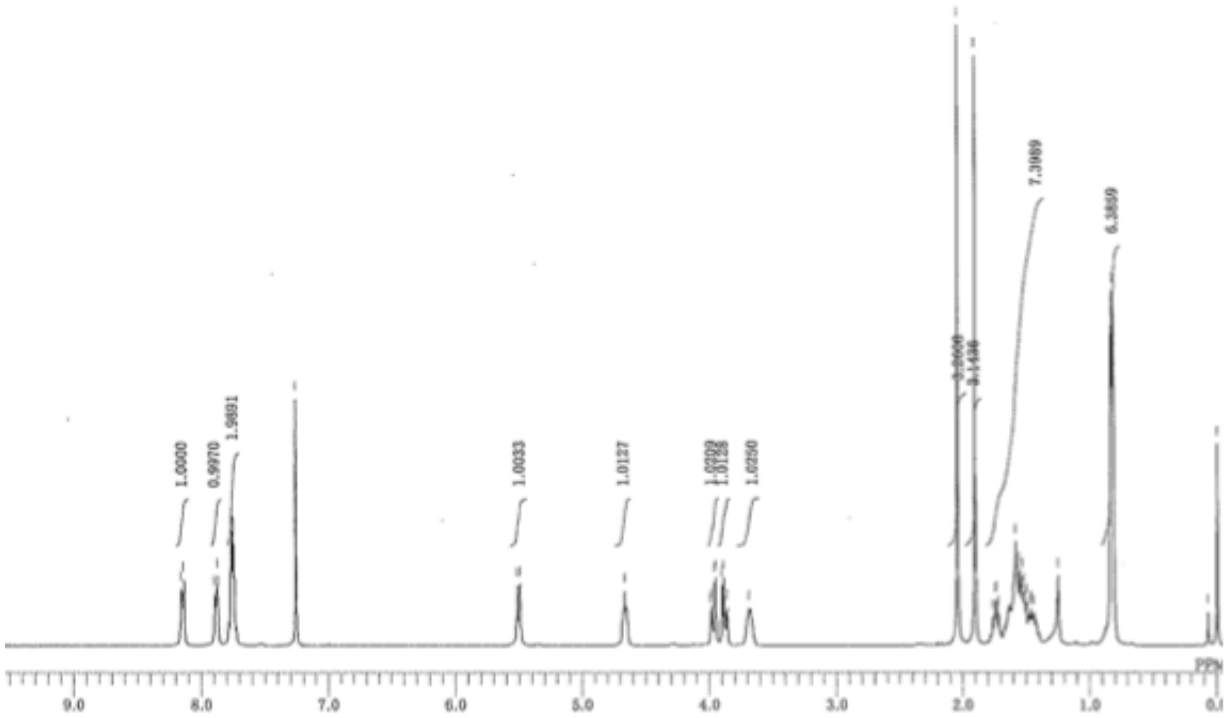
The absolute configuration at C(5) was tetatively assigned.

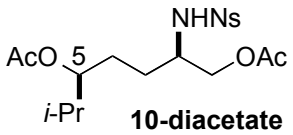




10-diacetate

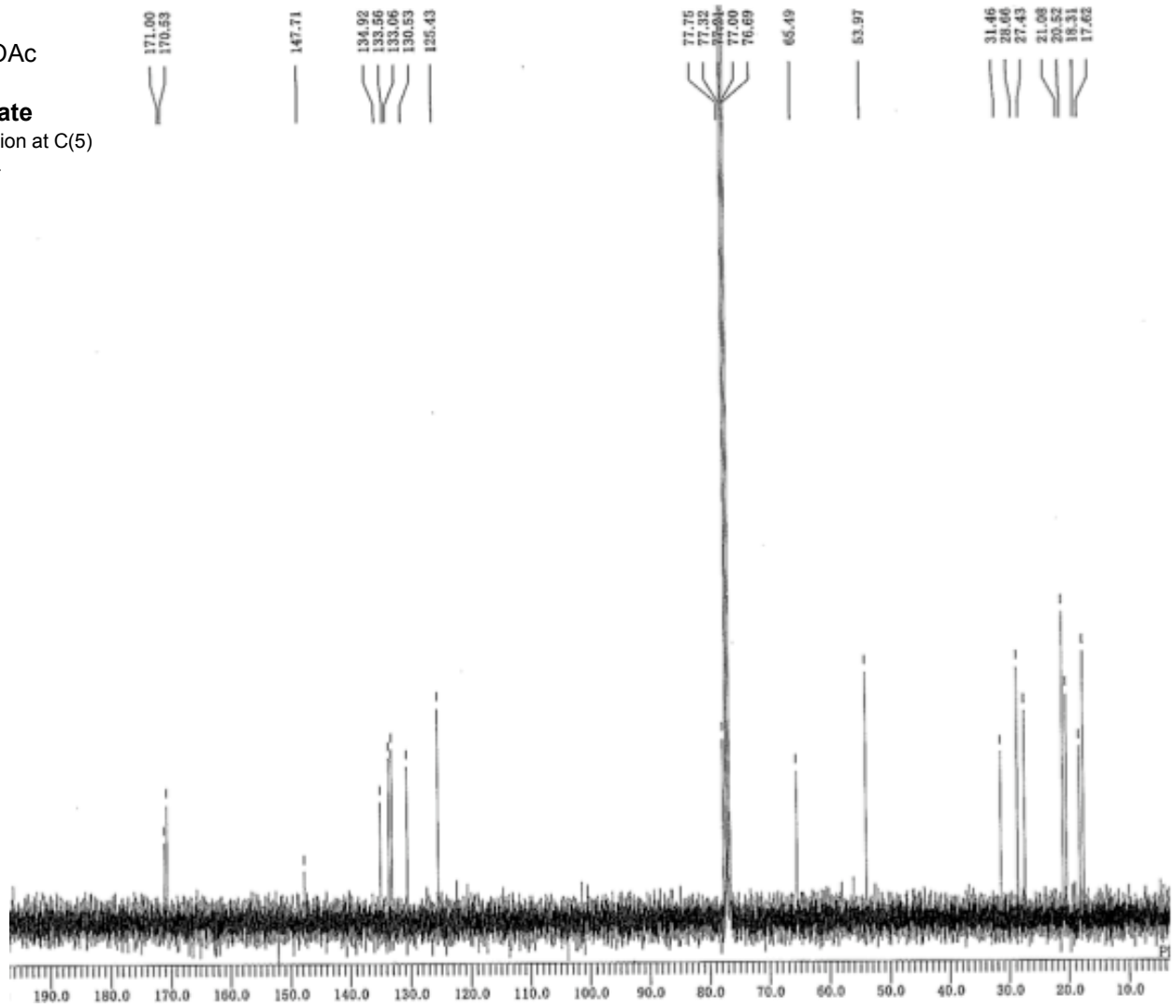
The absolute configuration at C(5) was tetatively assigned.

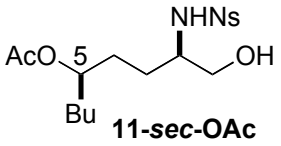




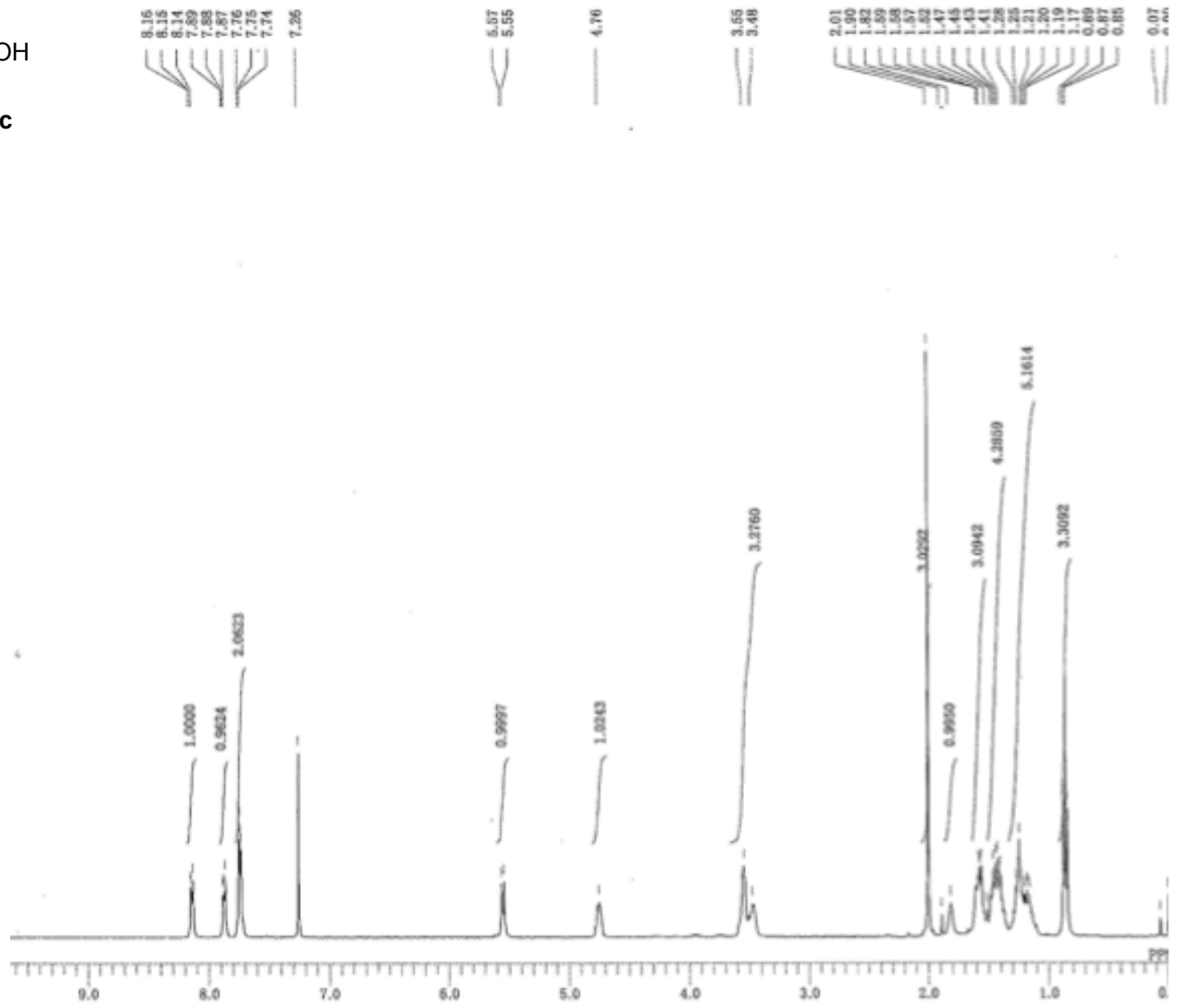
10-diacetate

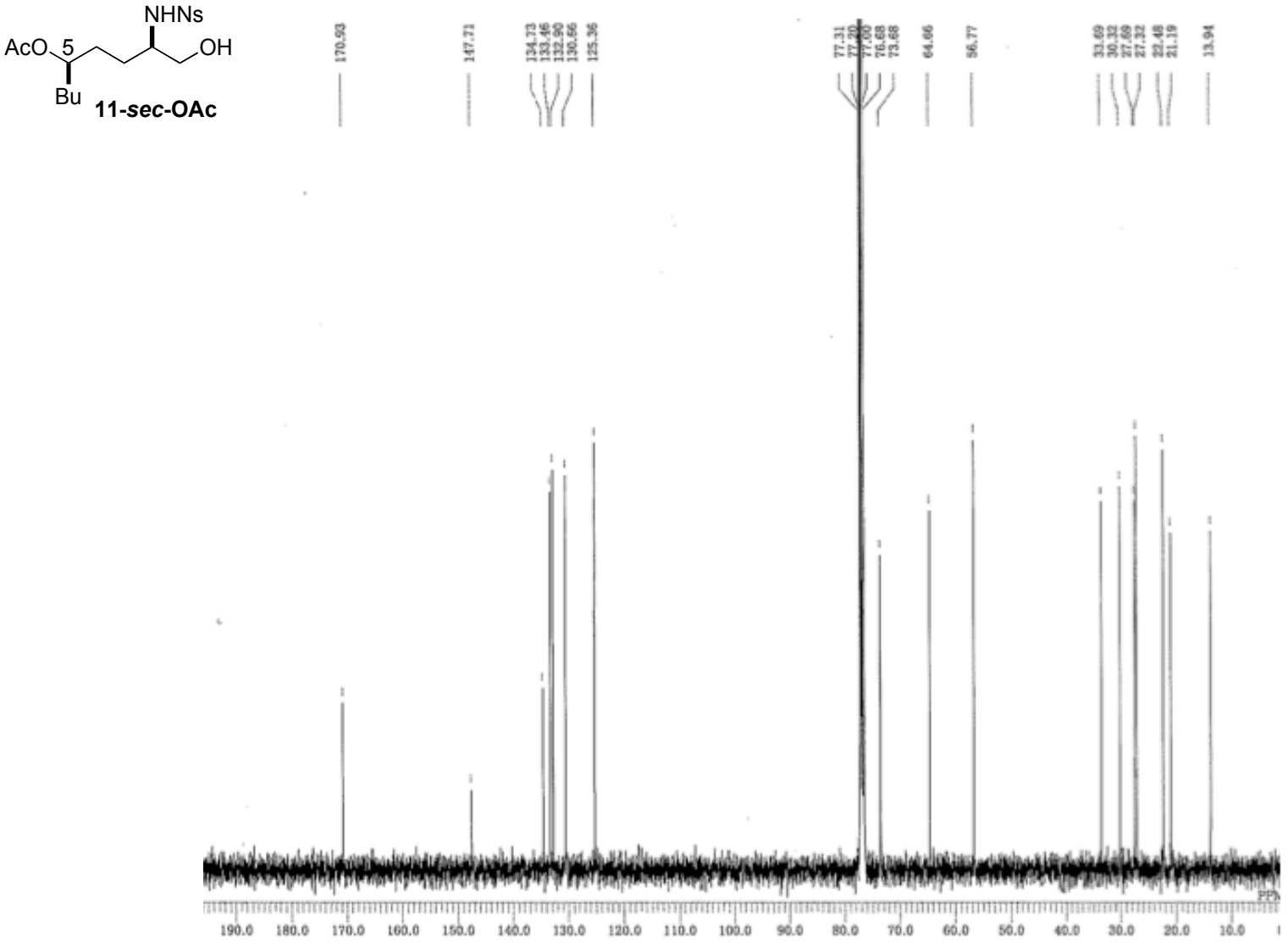
The absolute configuration at C(5) was tetatively assigned.

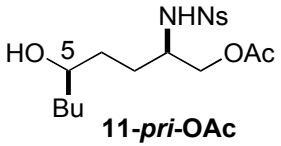




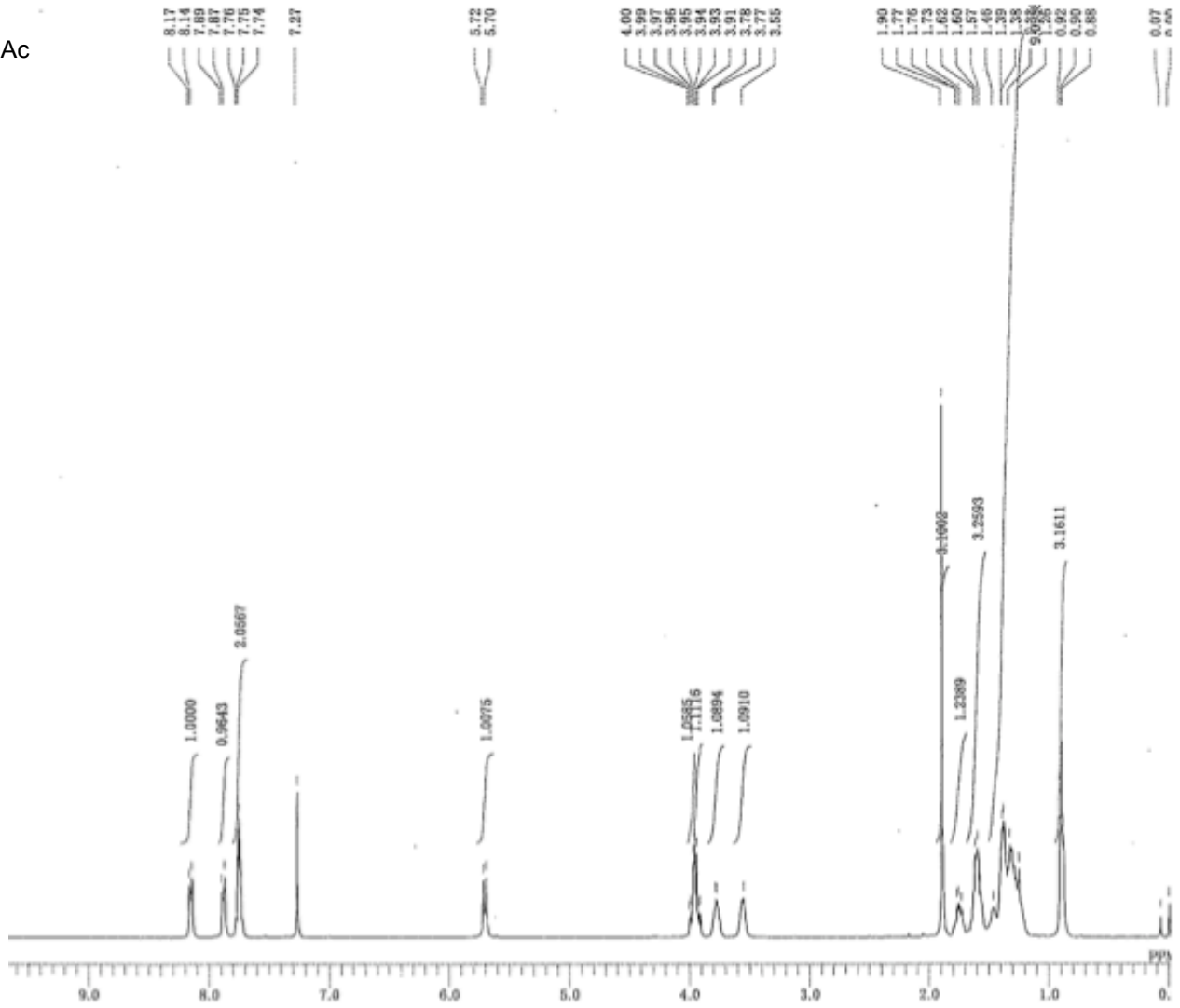
11-*sec*-OAc

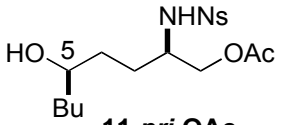




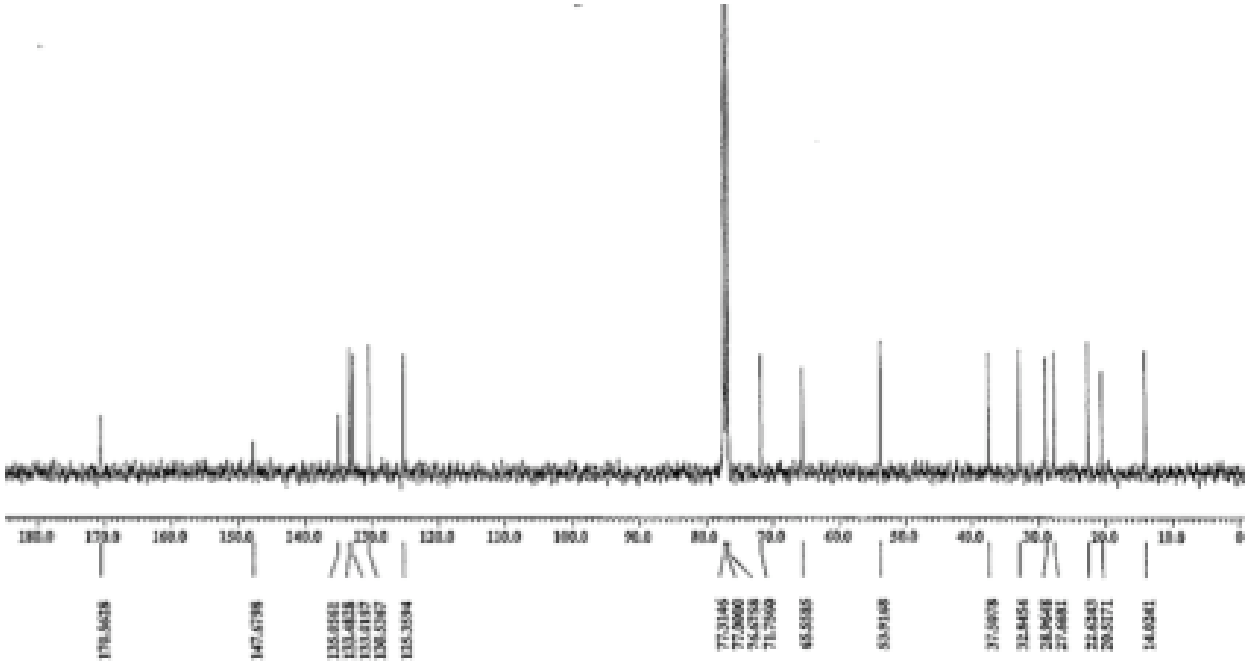


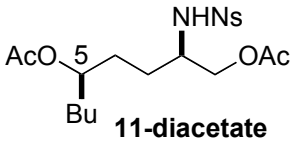
11-*pri*-OAc



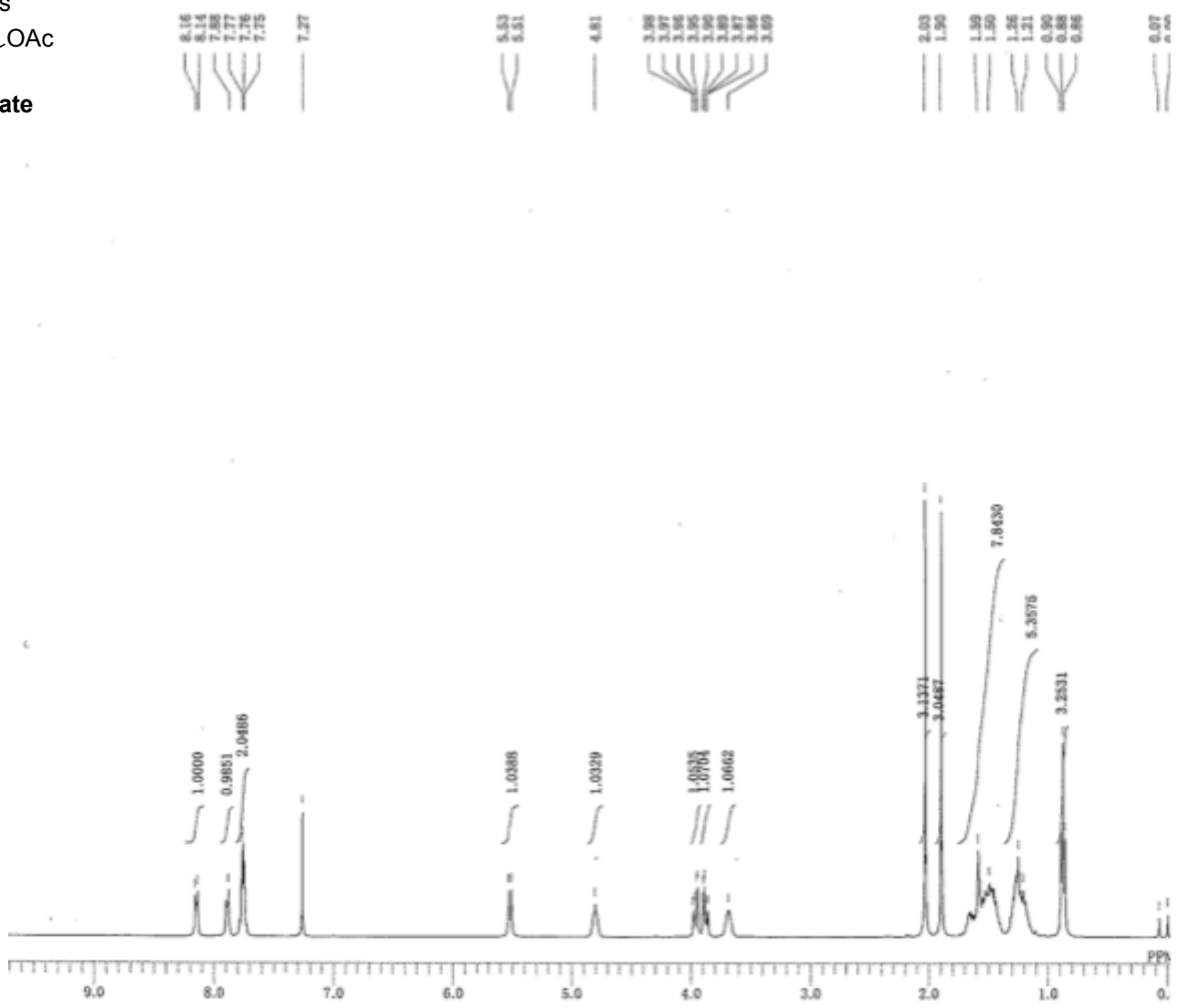


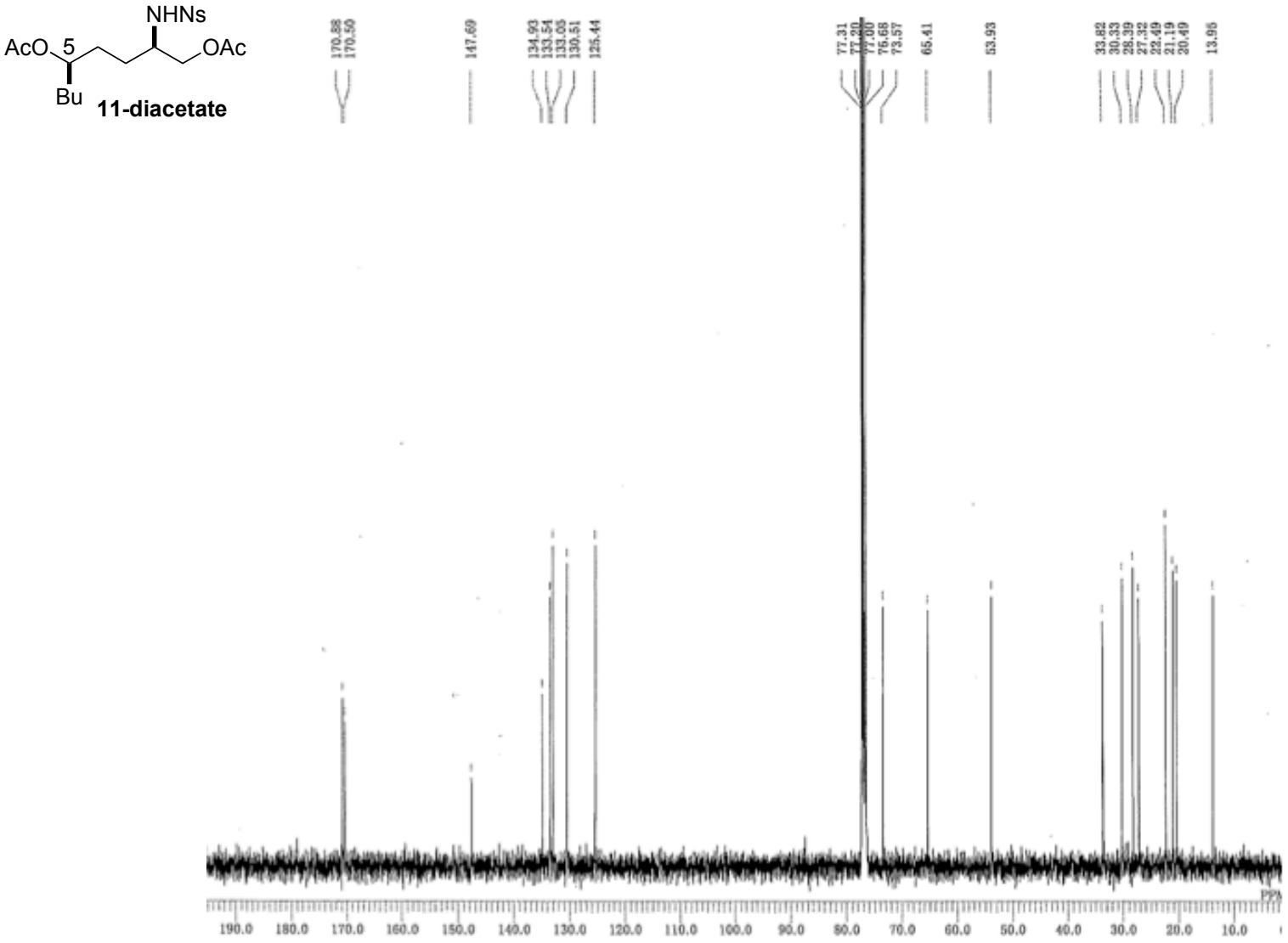
11-*pri*-OAc

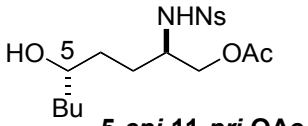




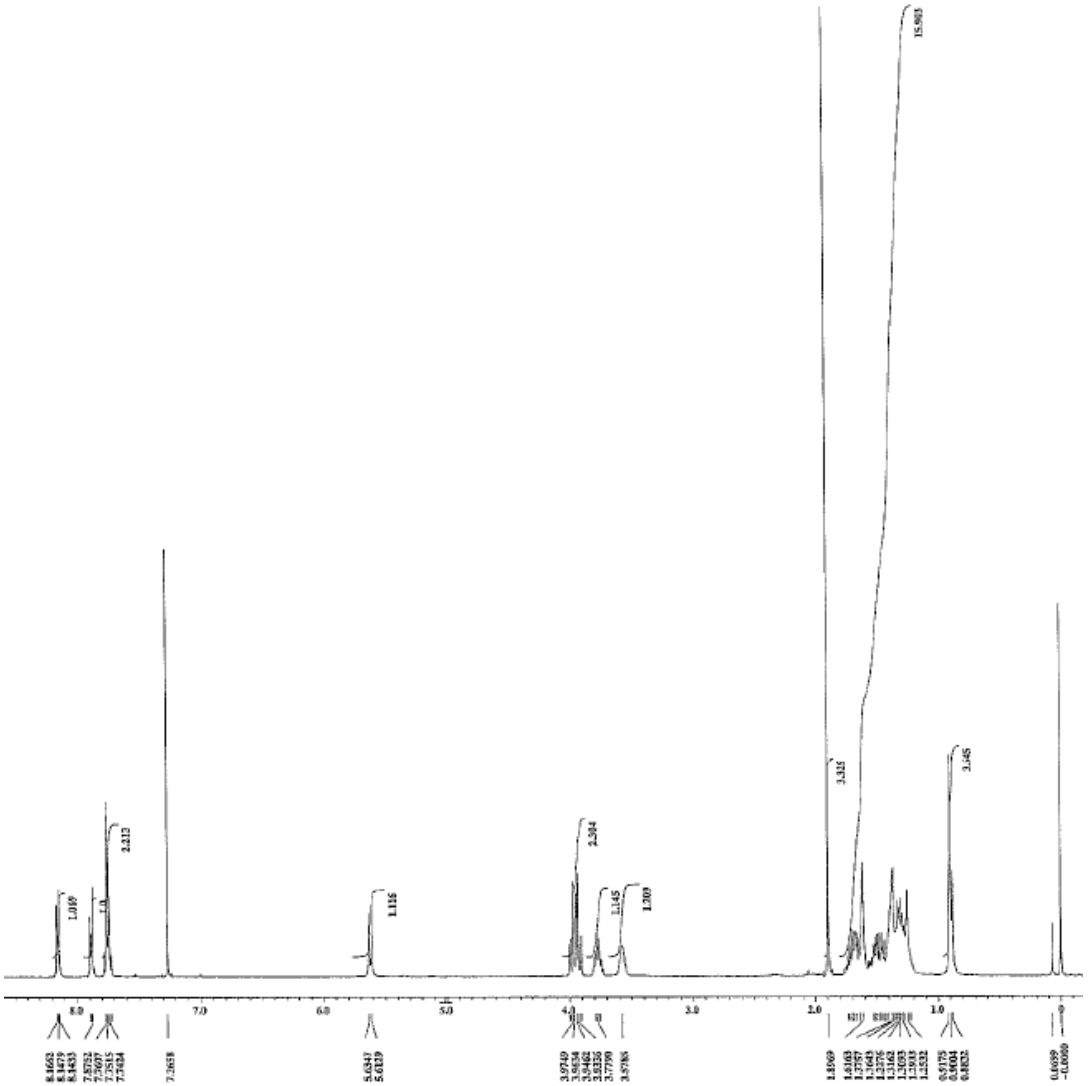
11-diacetate

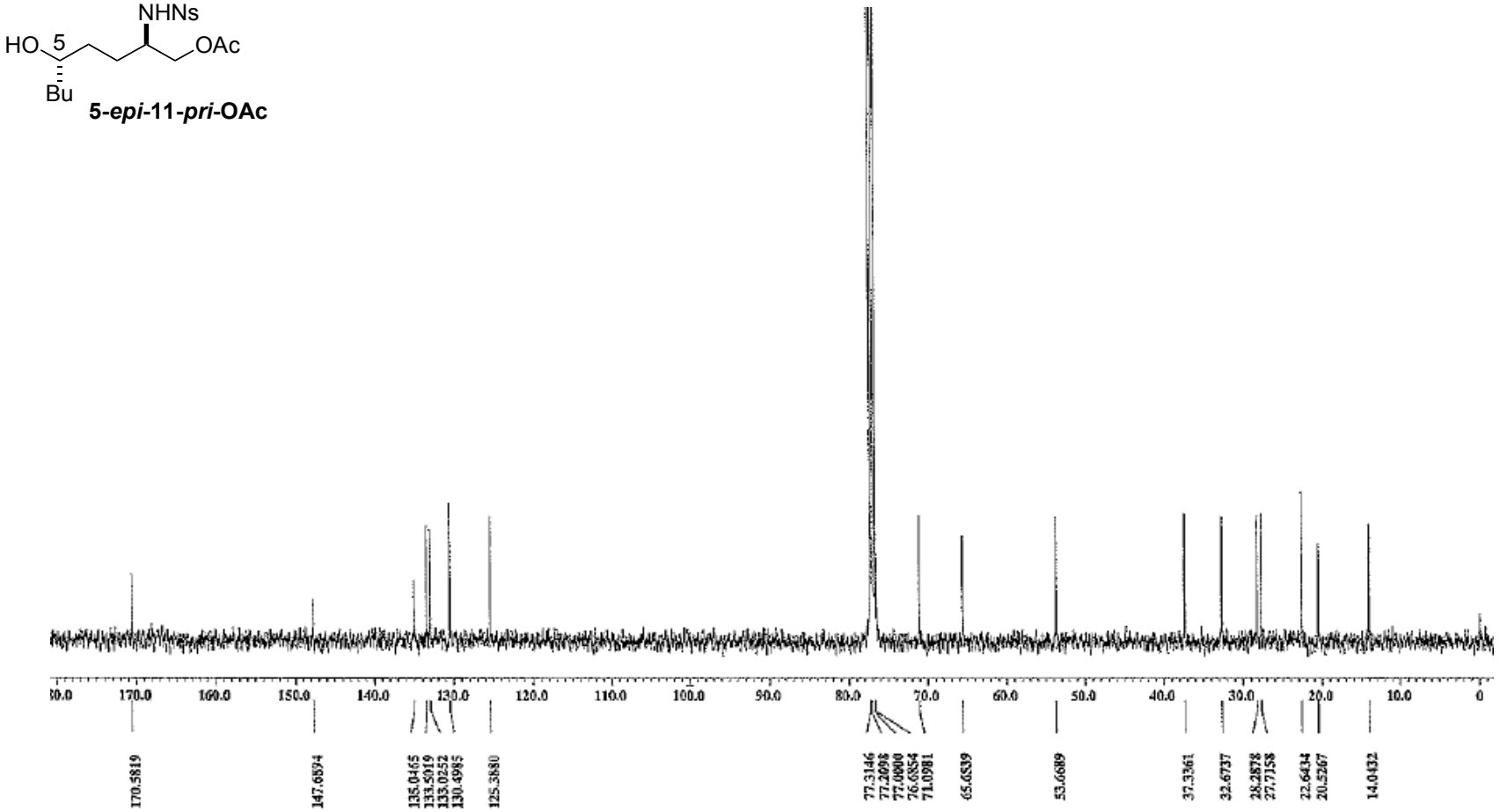




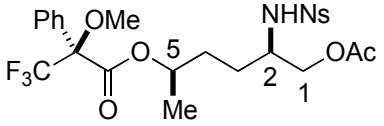


5-*epi*-11-*pri*-OAc

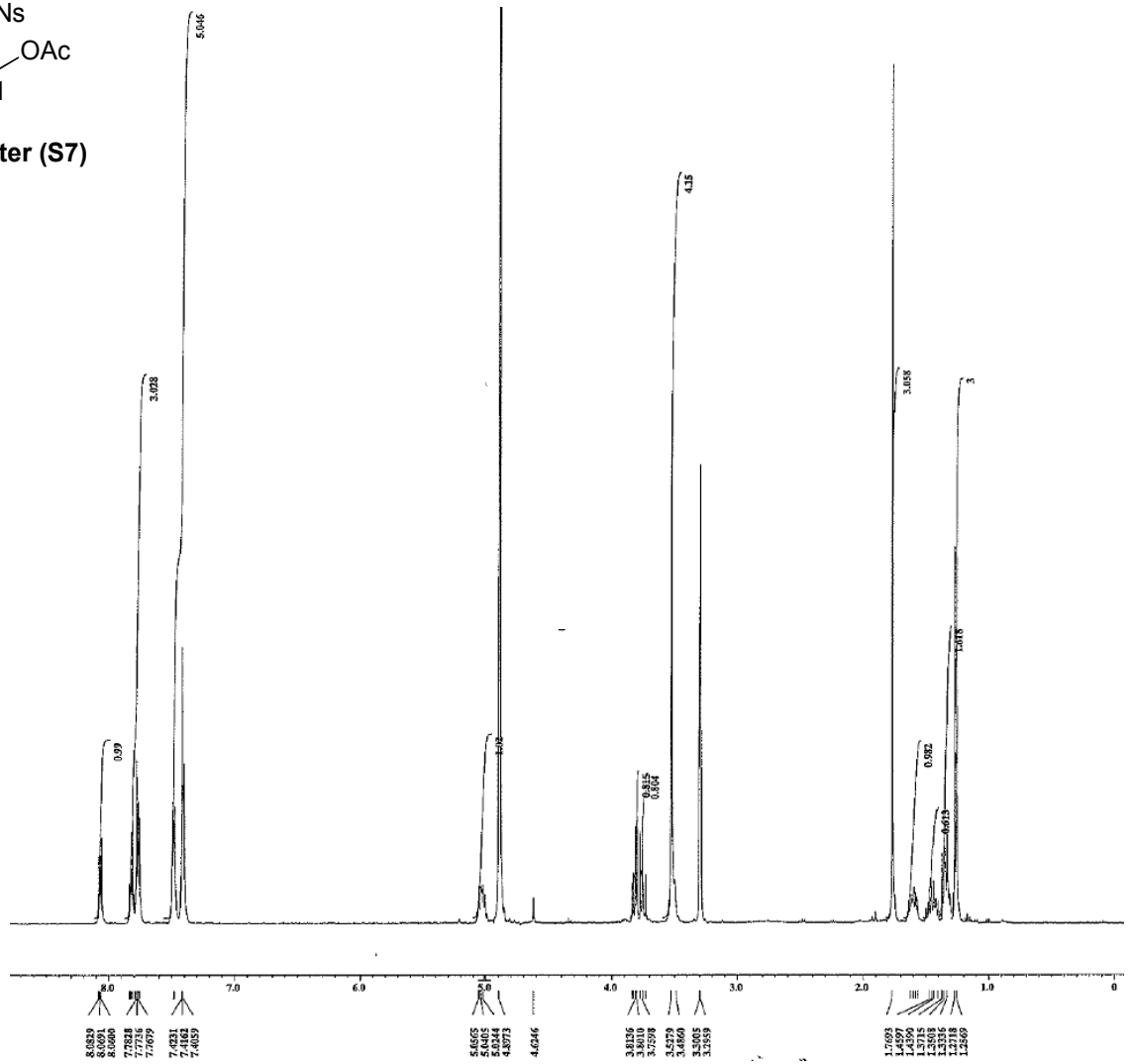


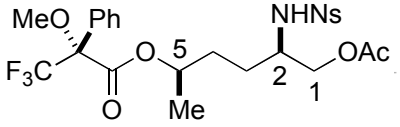


5-*epi*-11-*pri*-OAc

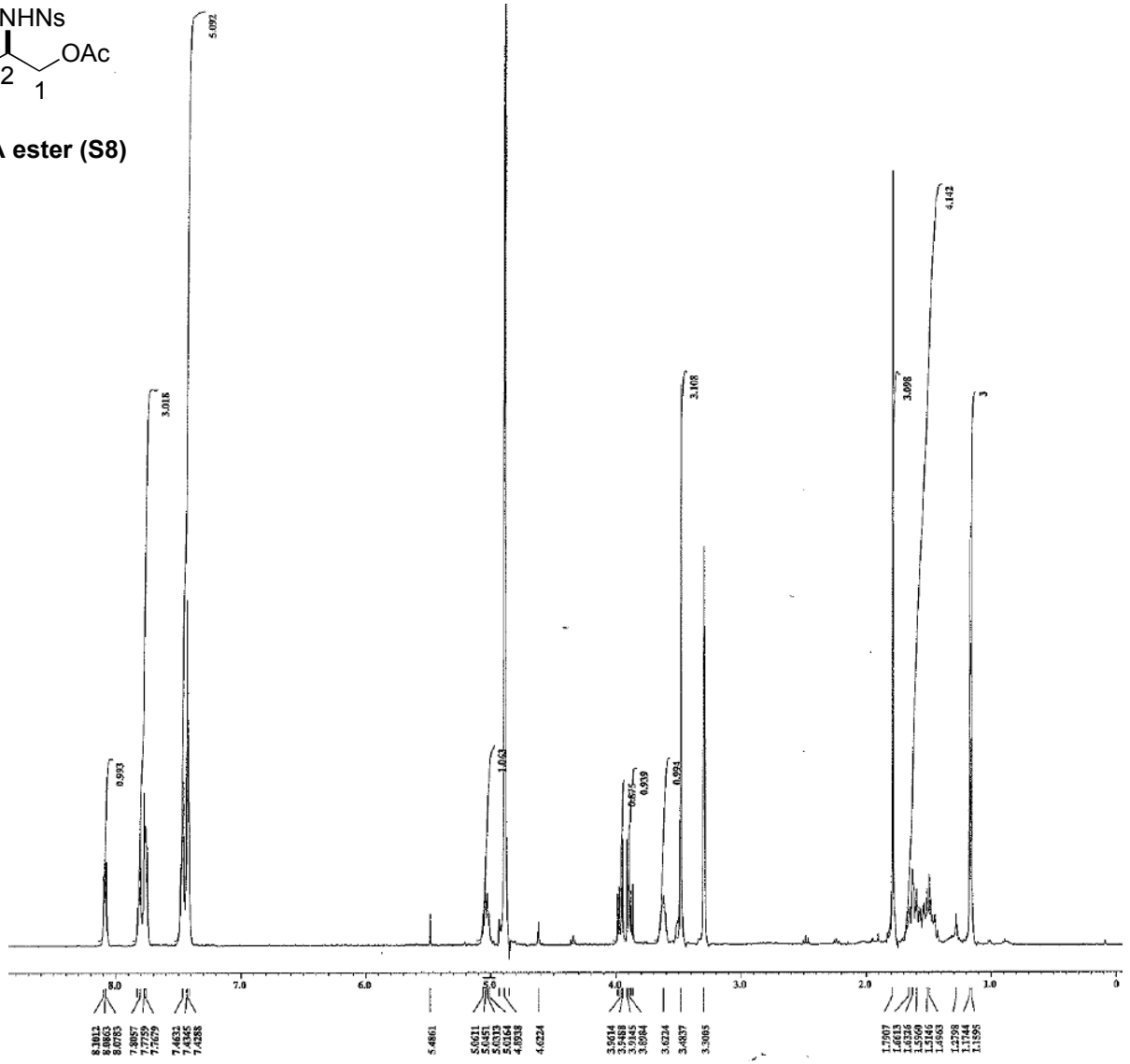


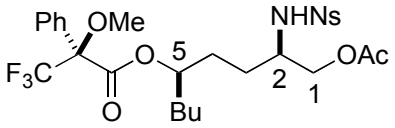
8-*pri*-OAc (–)-MTPA ester (S7)



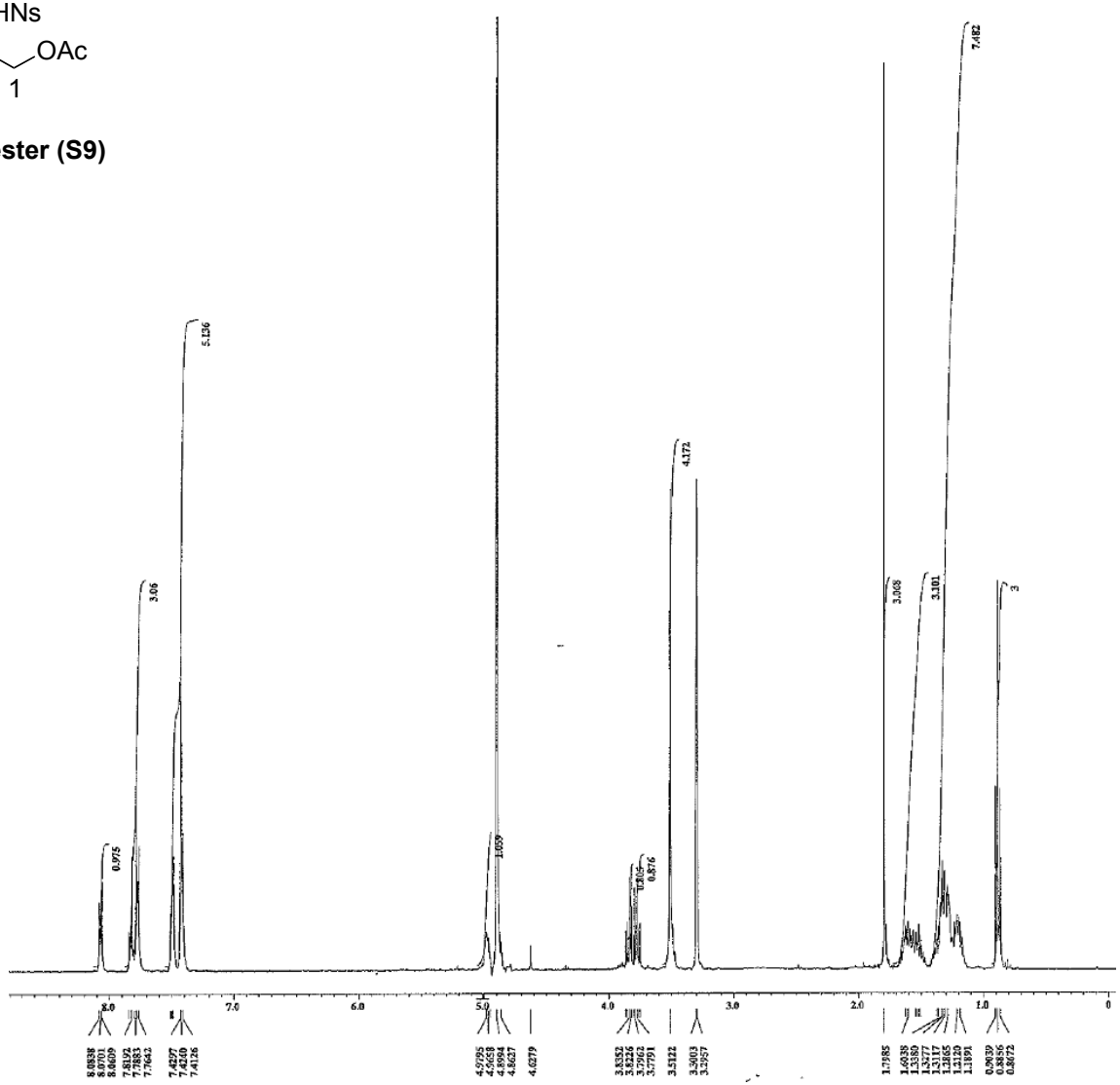


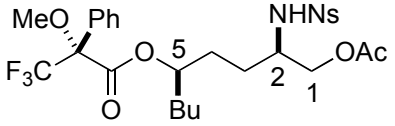
8-*pri*-OAc (+)-MTPA ester (S8)



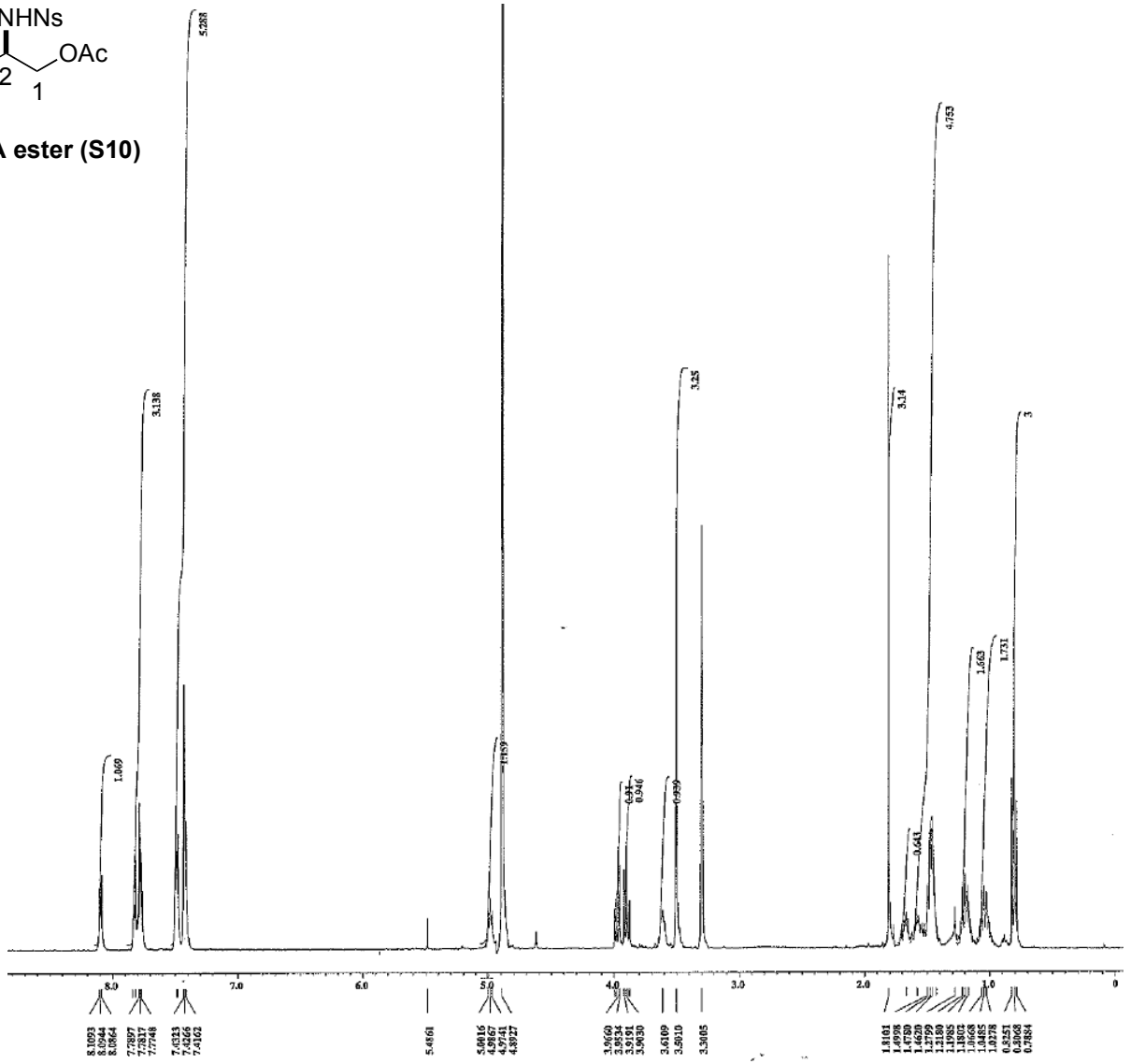


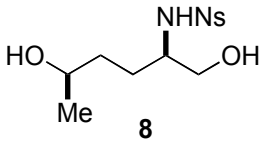
11-*pri*-OAc (–)-MTPA ester (S9)





11-*pri*-OAc (+)-MTPA ester (S10)





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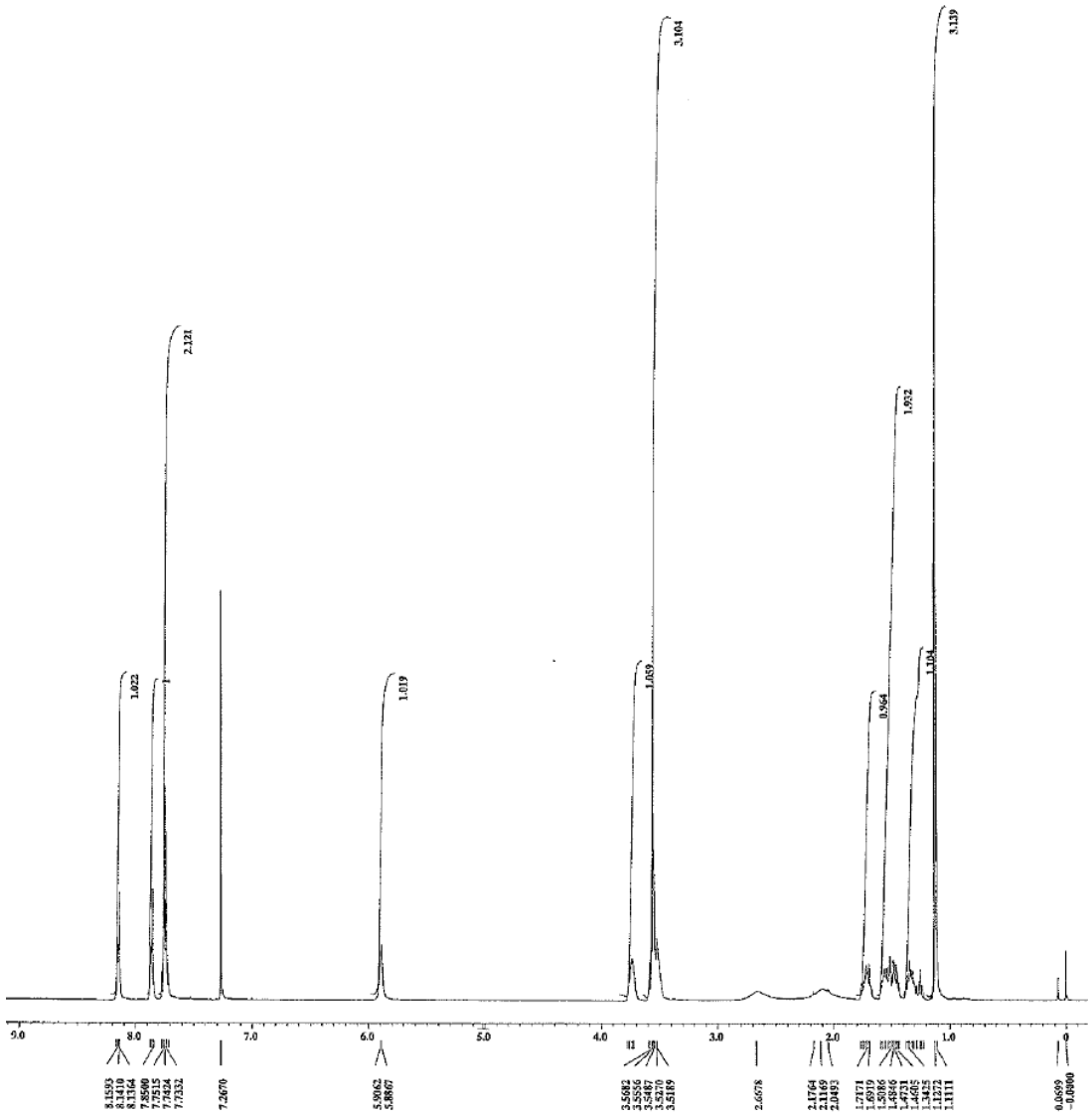

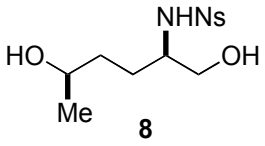

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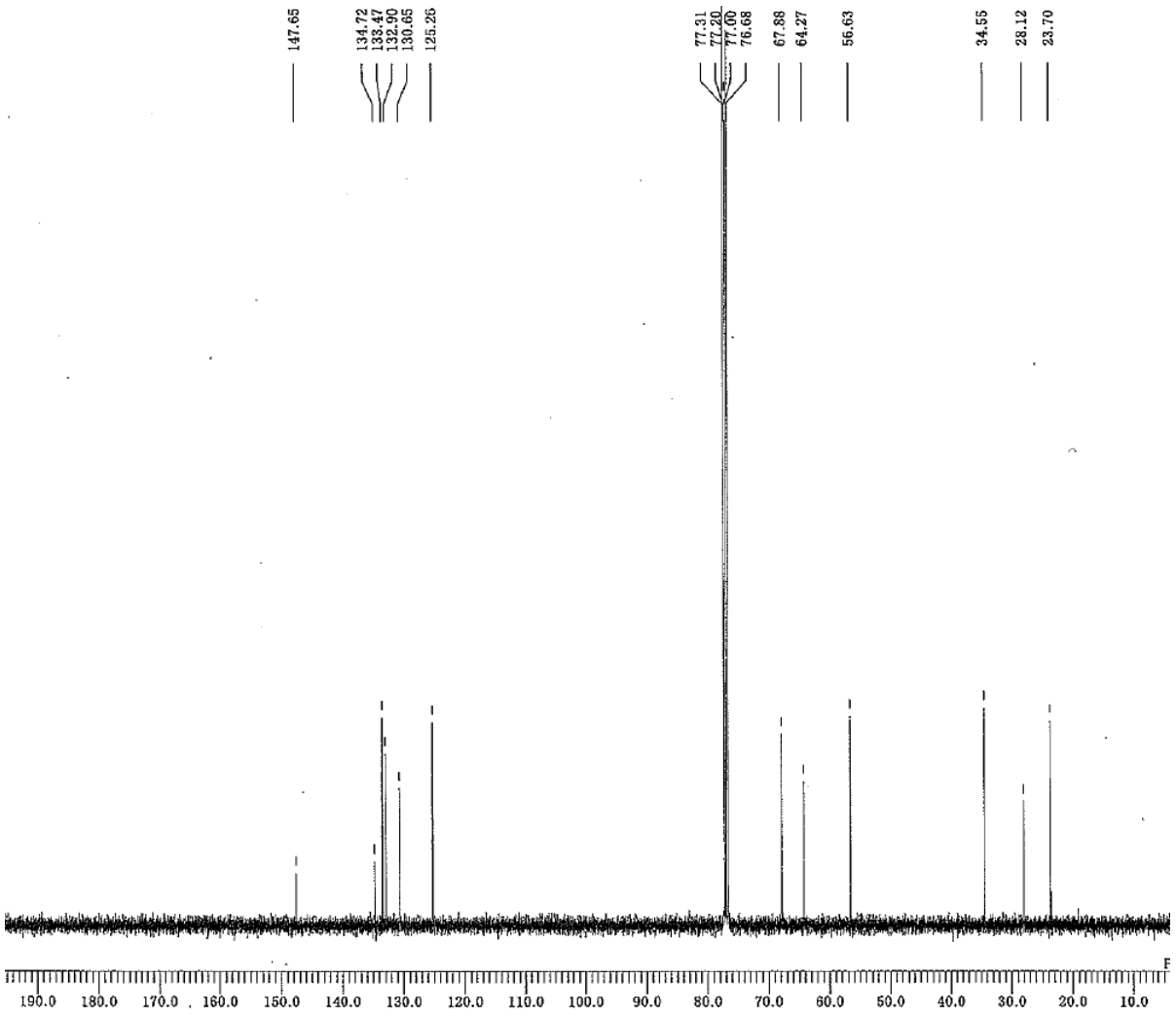
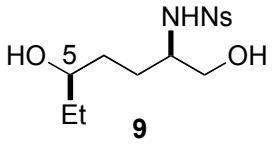
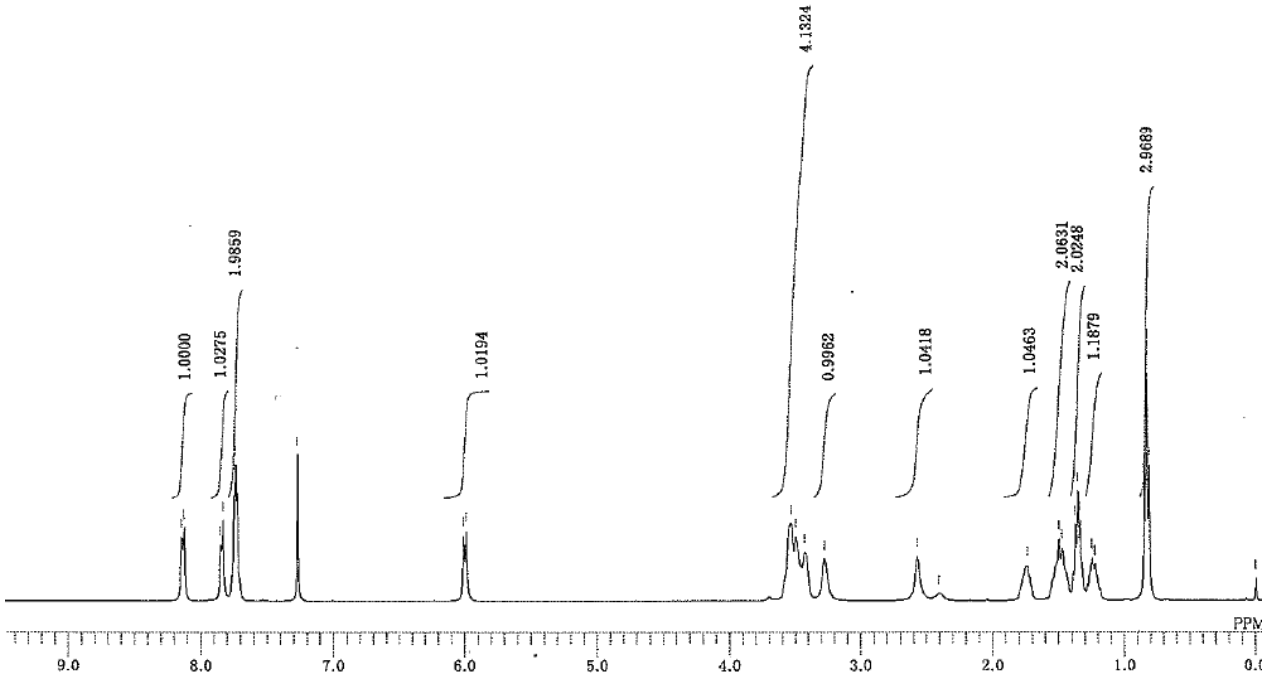
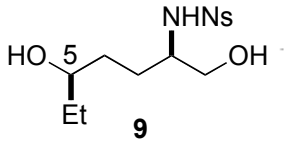




9

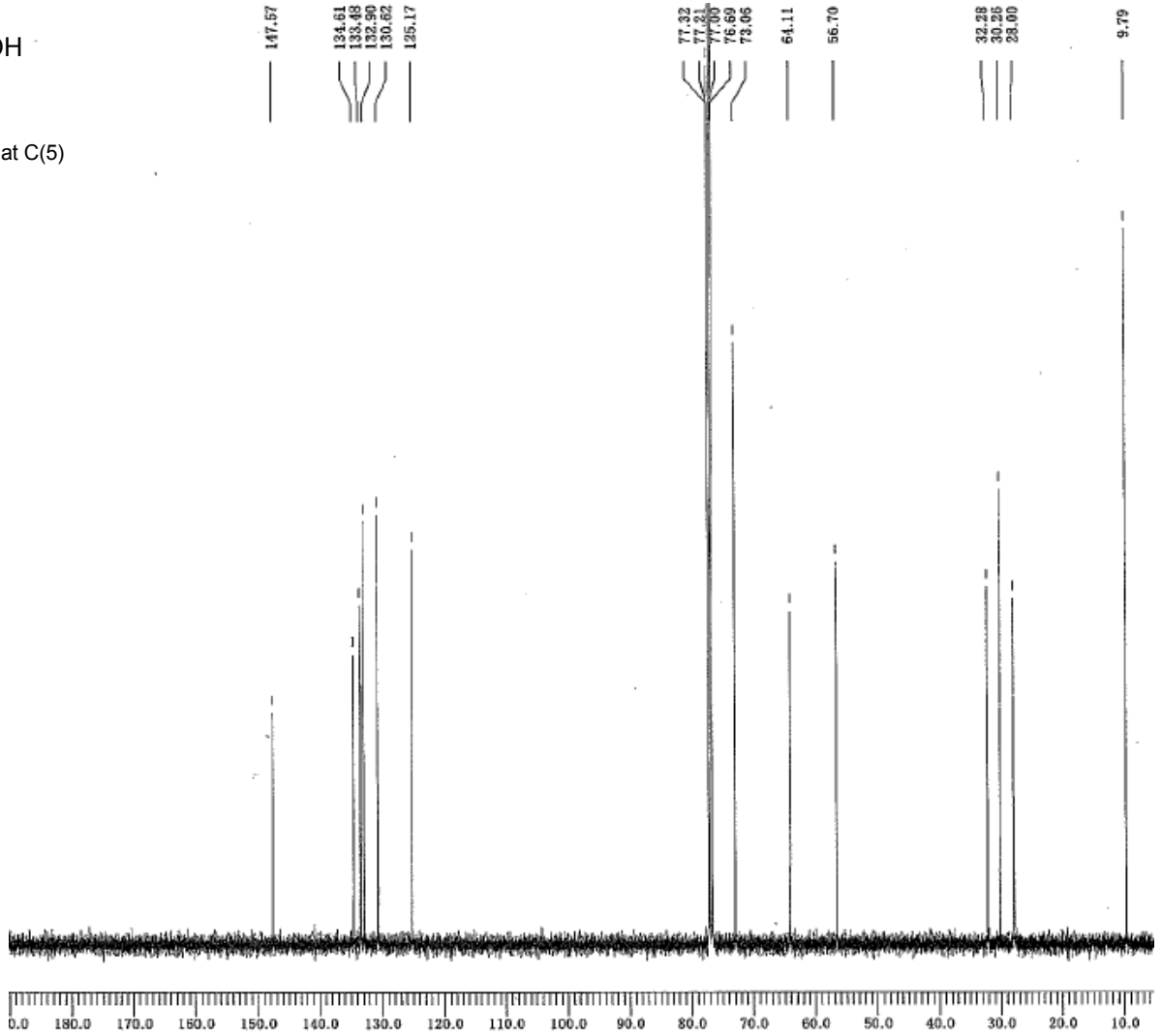
The absolute configuration at C(5) was tetatively assigned.

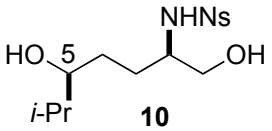




9

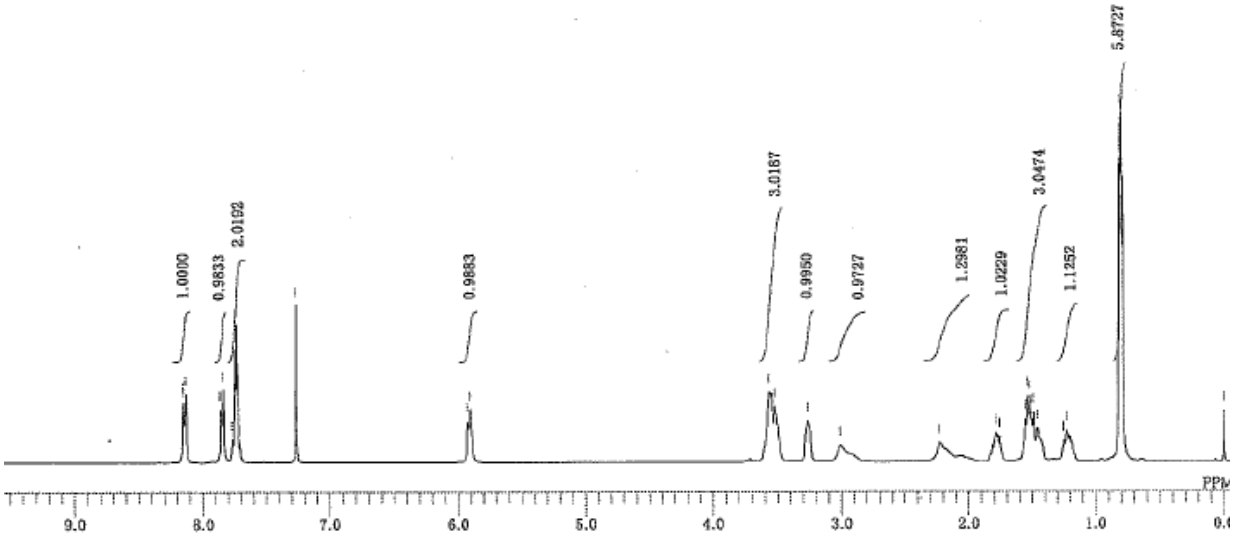
The absolute configuration at C(5) was tetatively assigned.

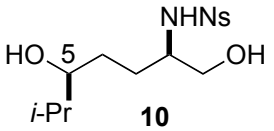




10

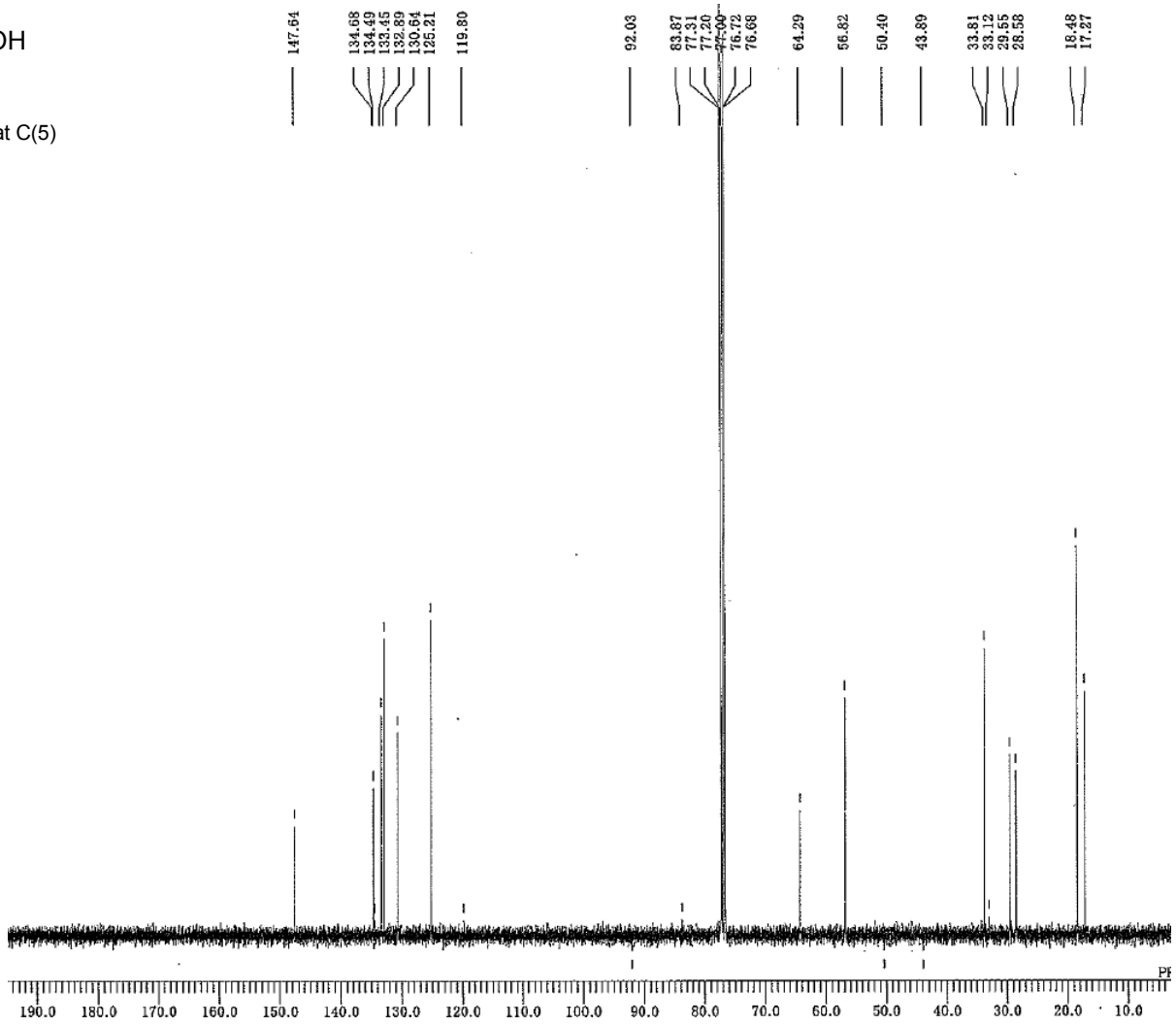
The absolute configuration at C(5) was tetatively assigned.

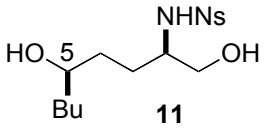




10

The absolute configuration at C(5) was tetatively assigned.





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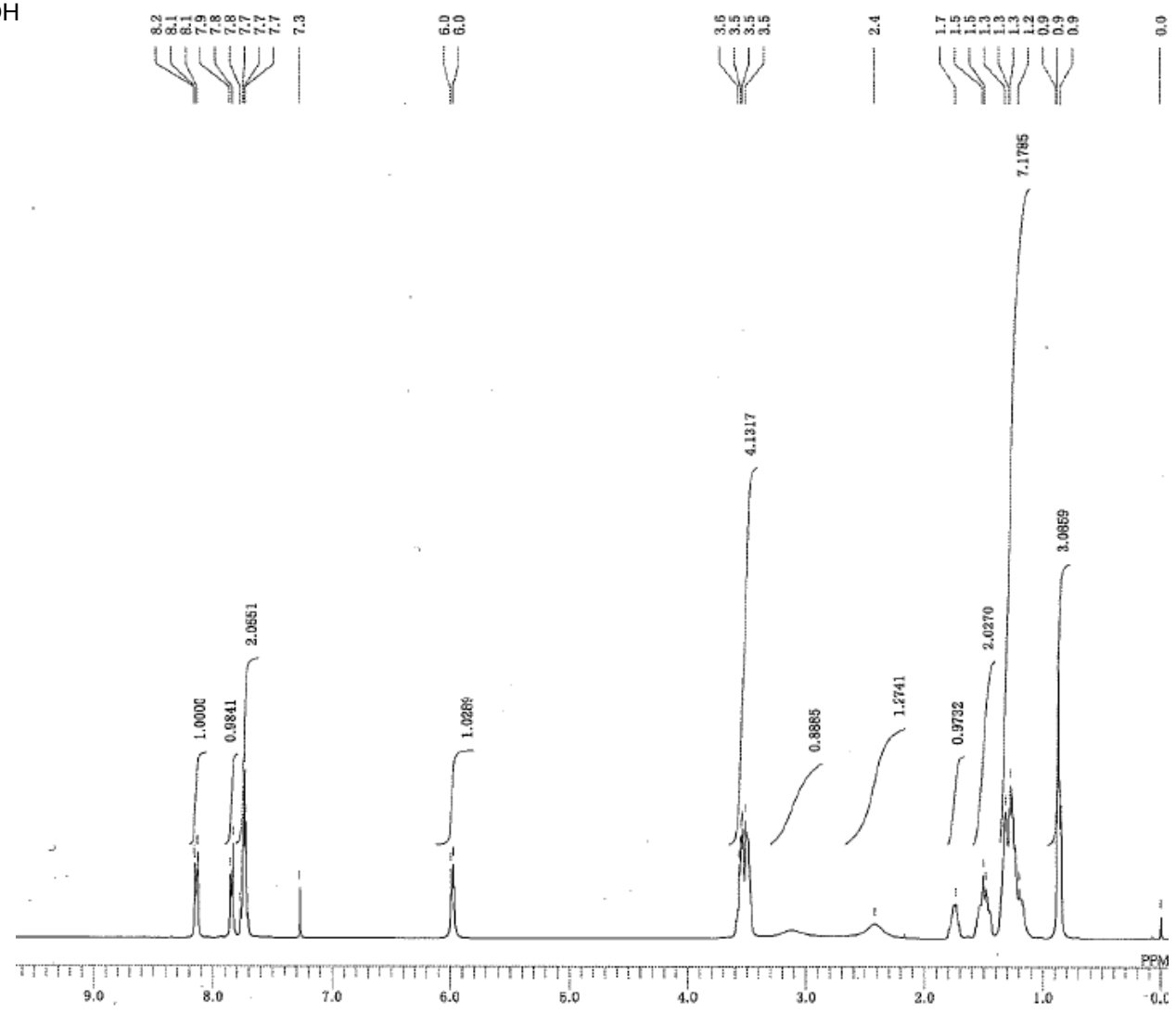

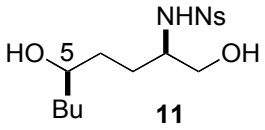

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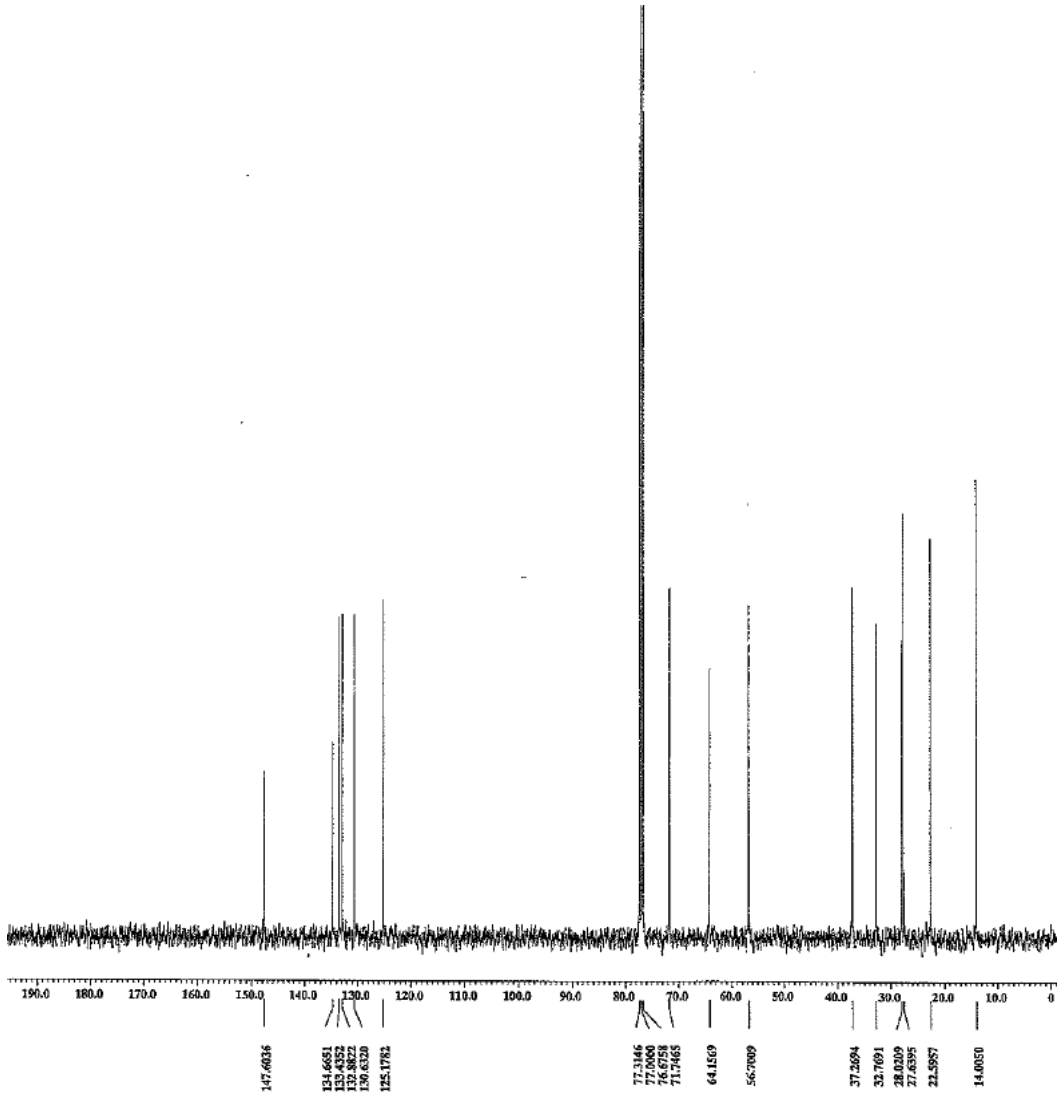
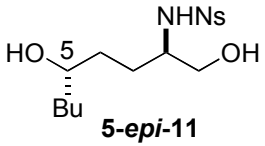
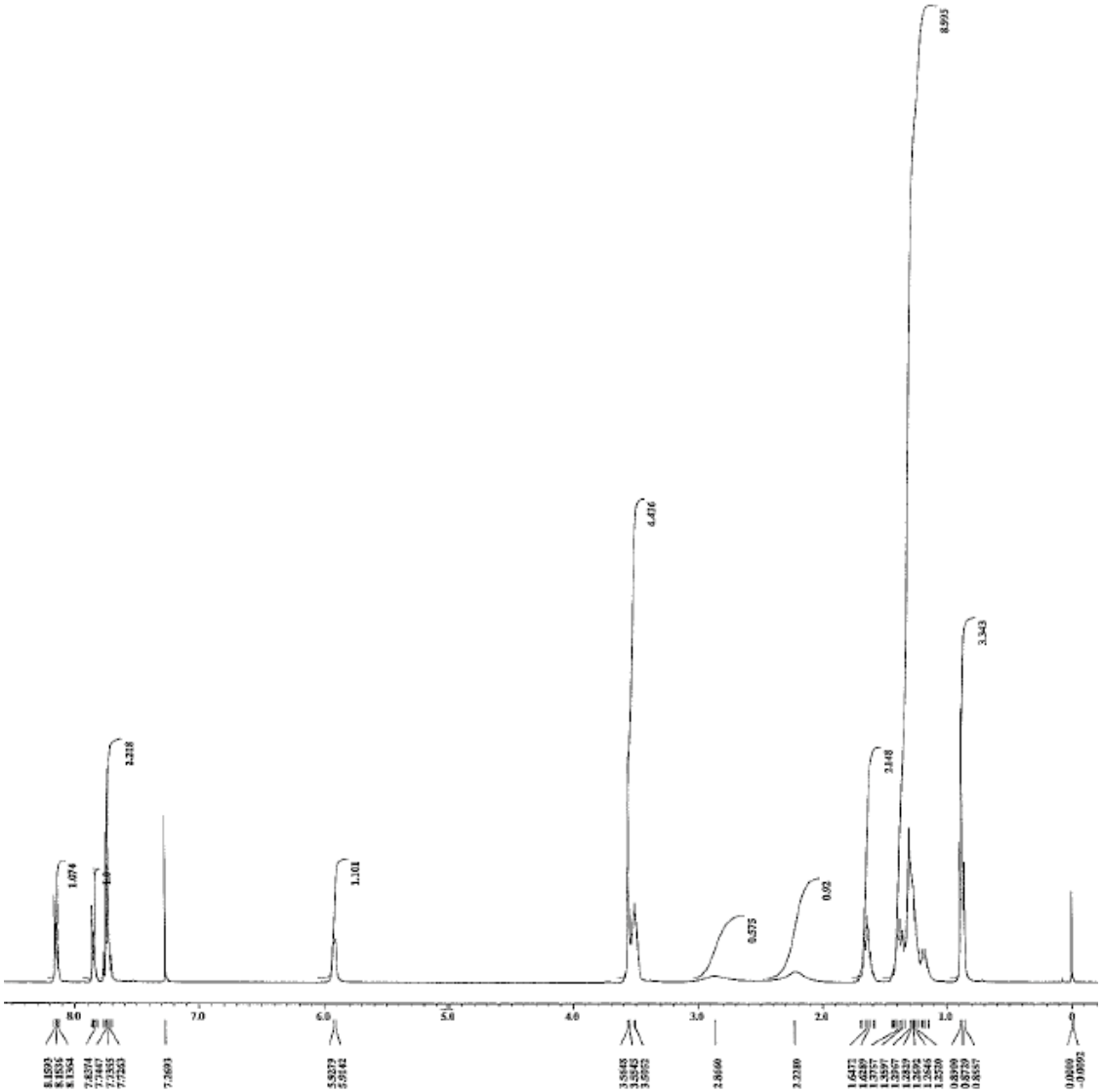
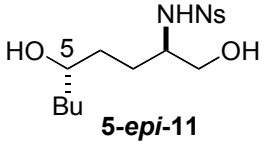




5-*epi*-11





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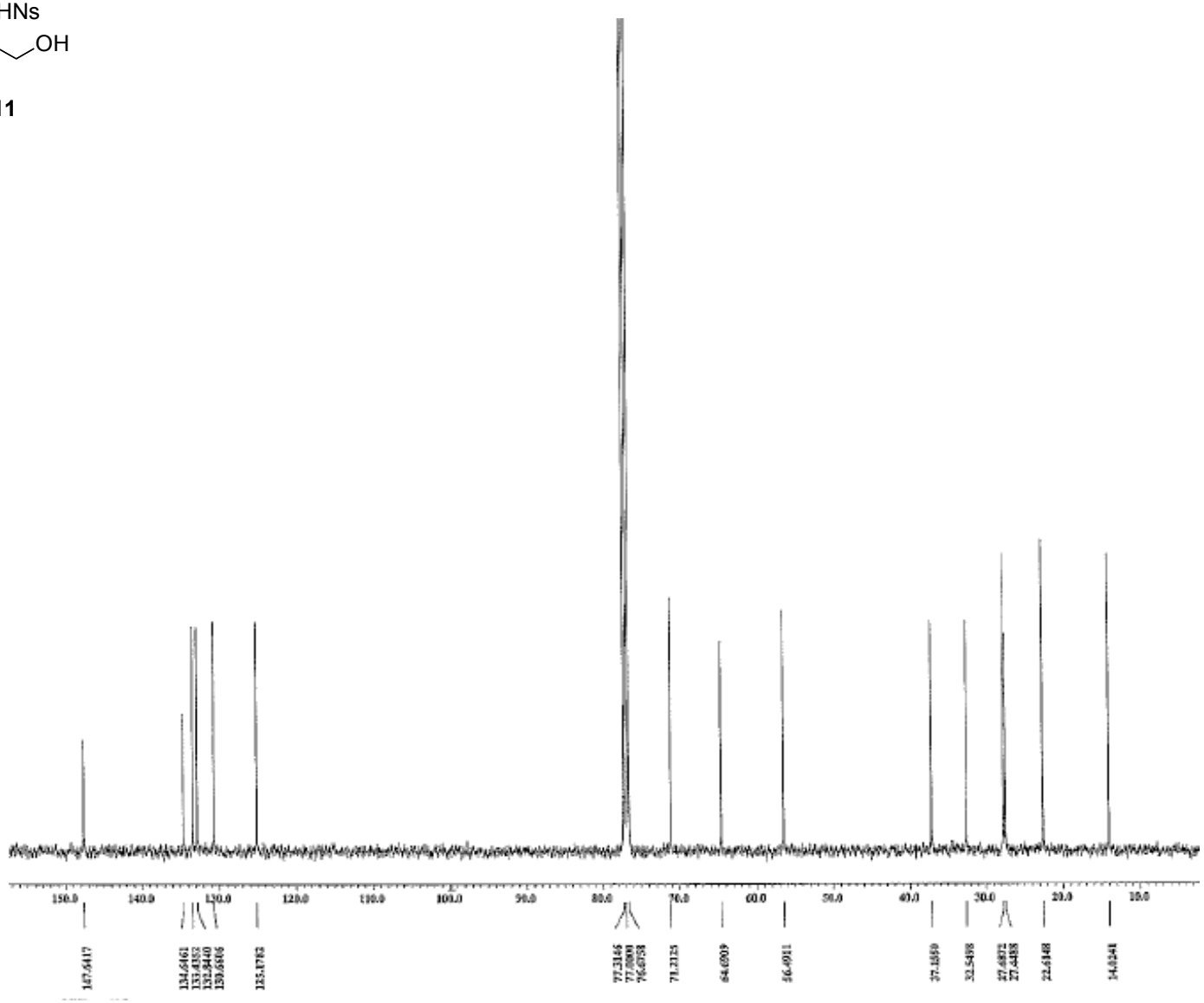
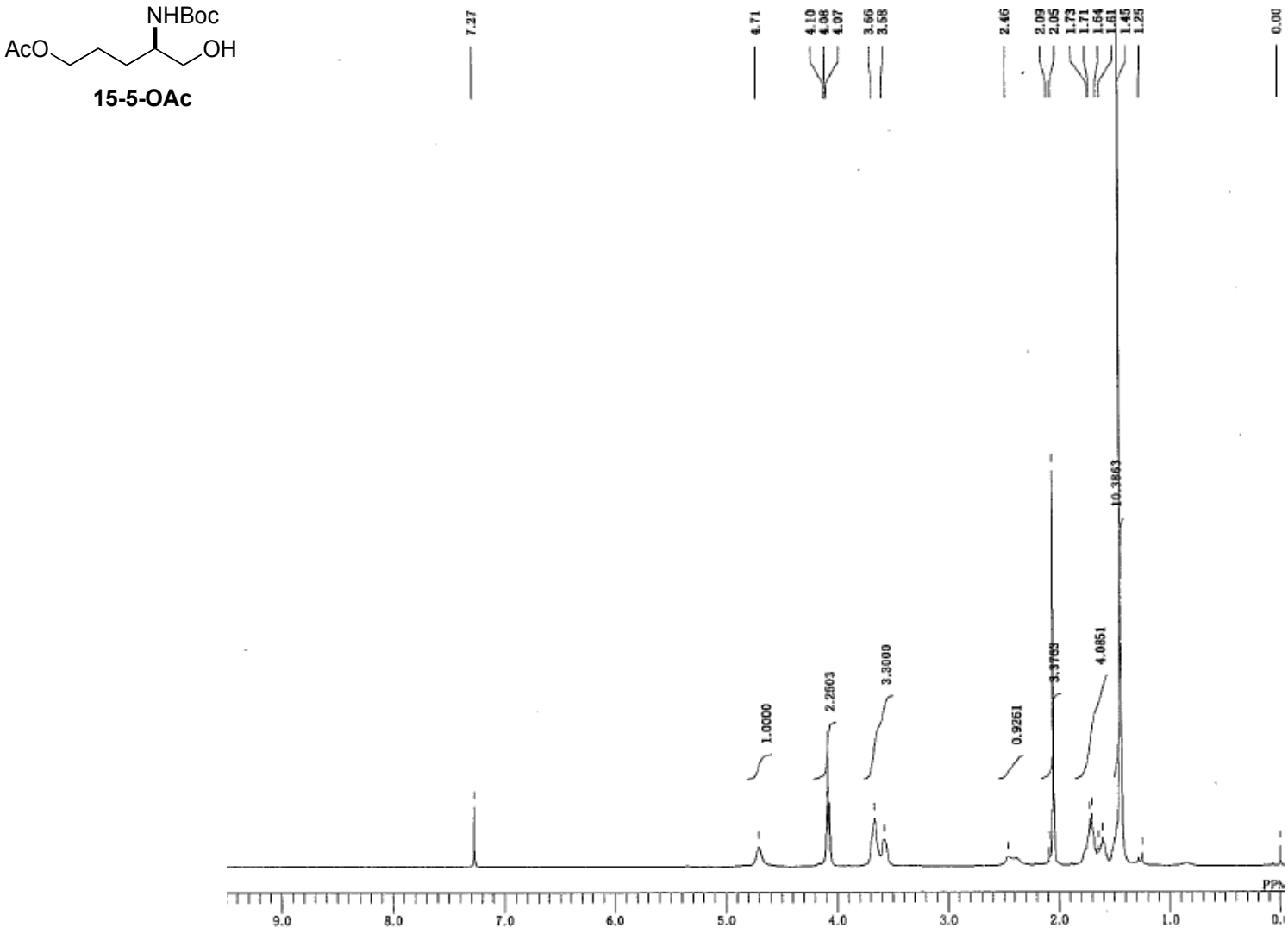
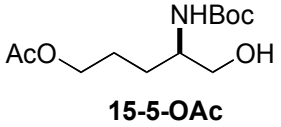
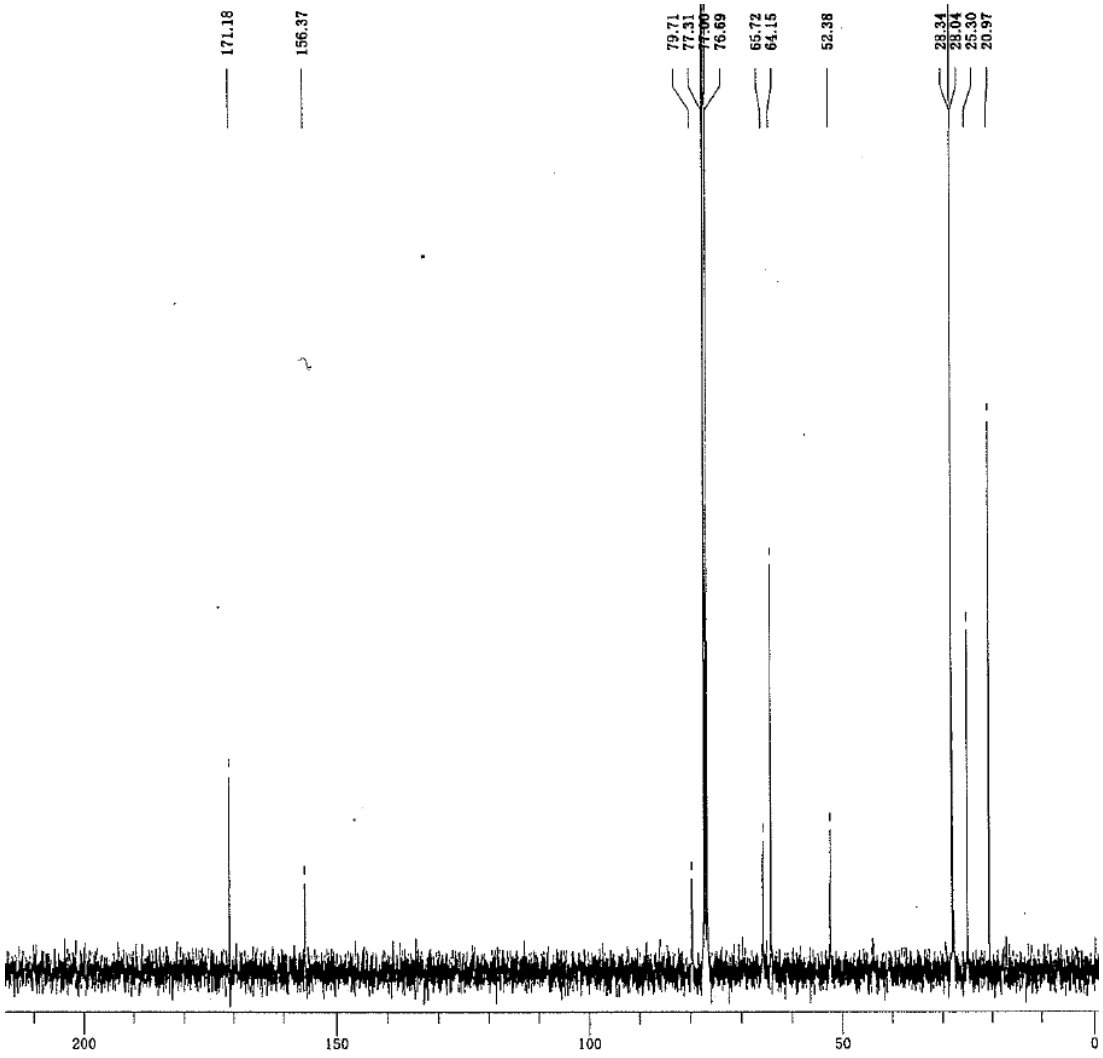
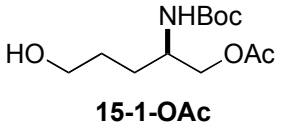




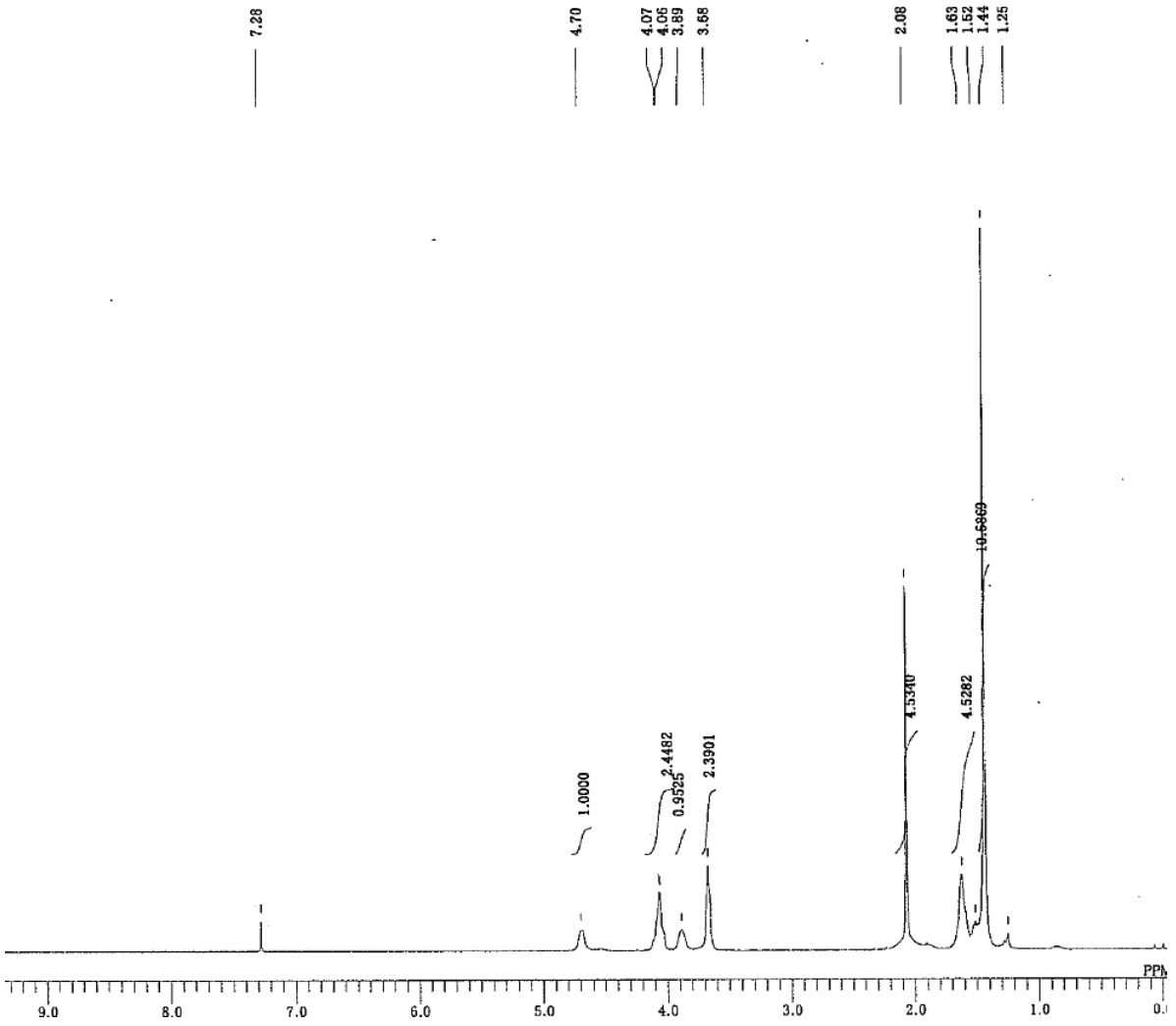


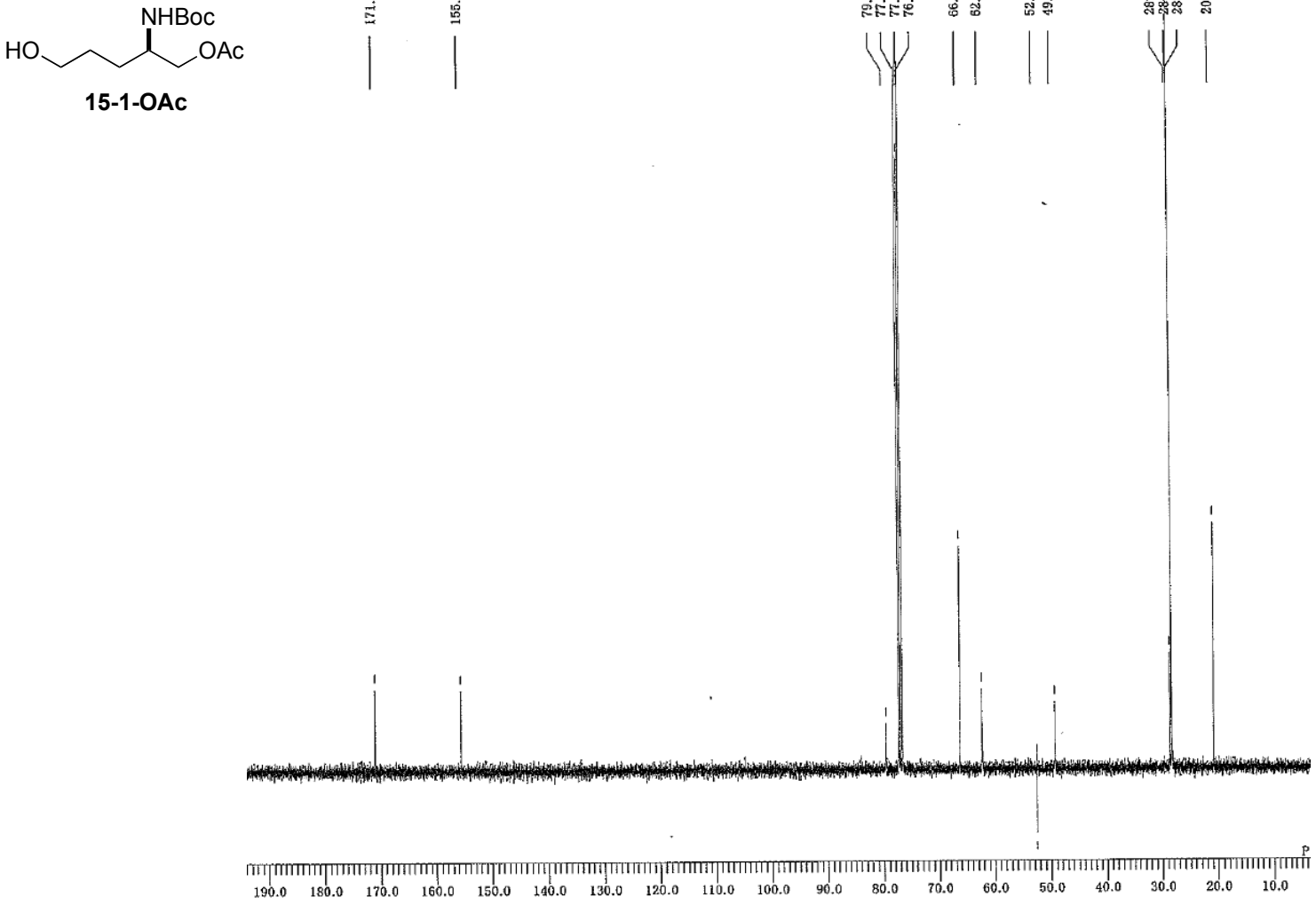
15-5-OAc

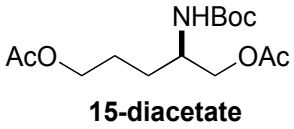




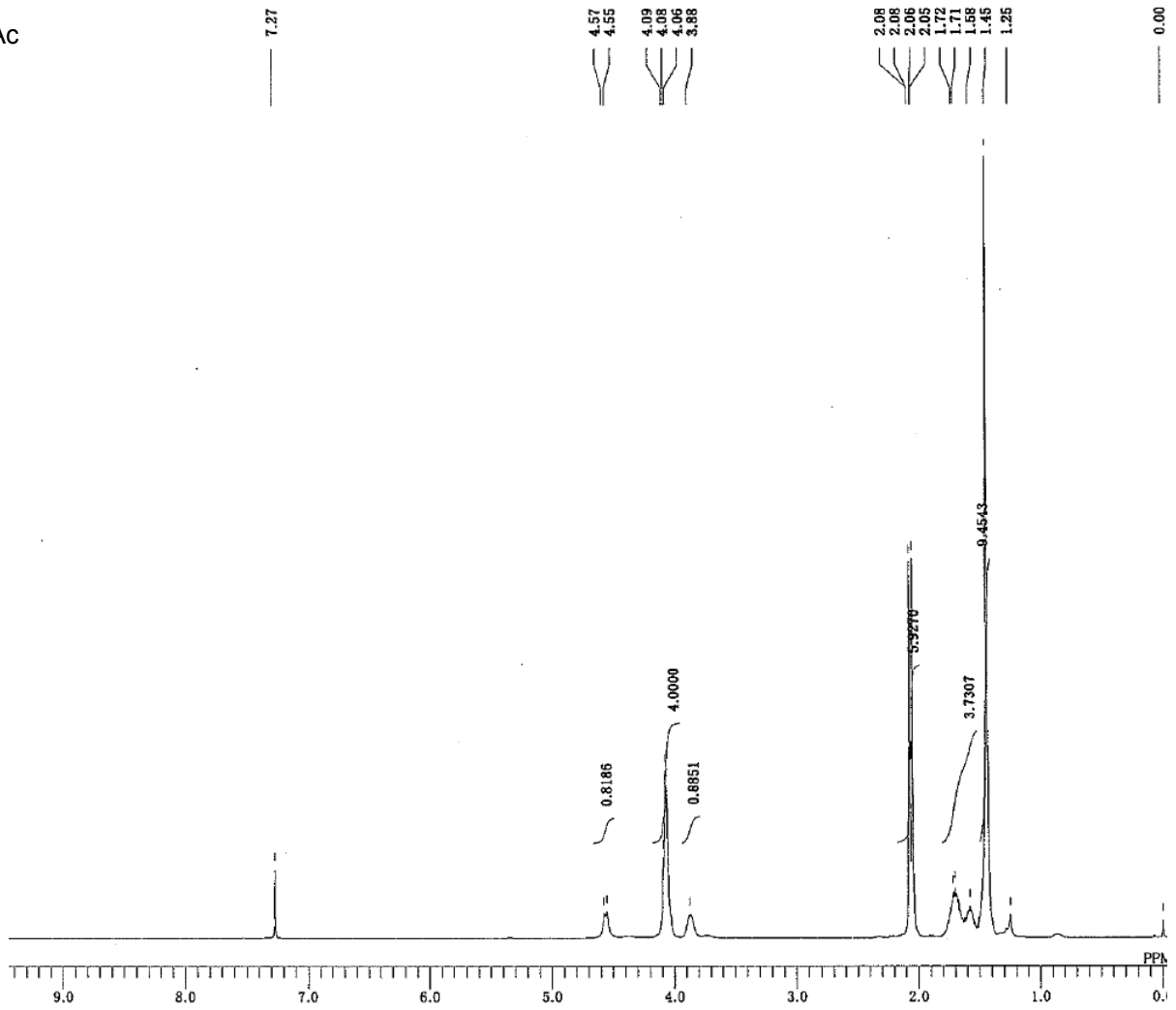
15-1-OAc

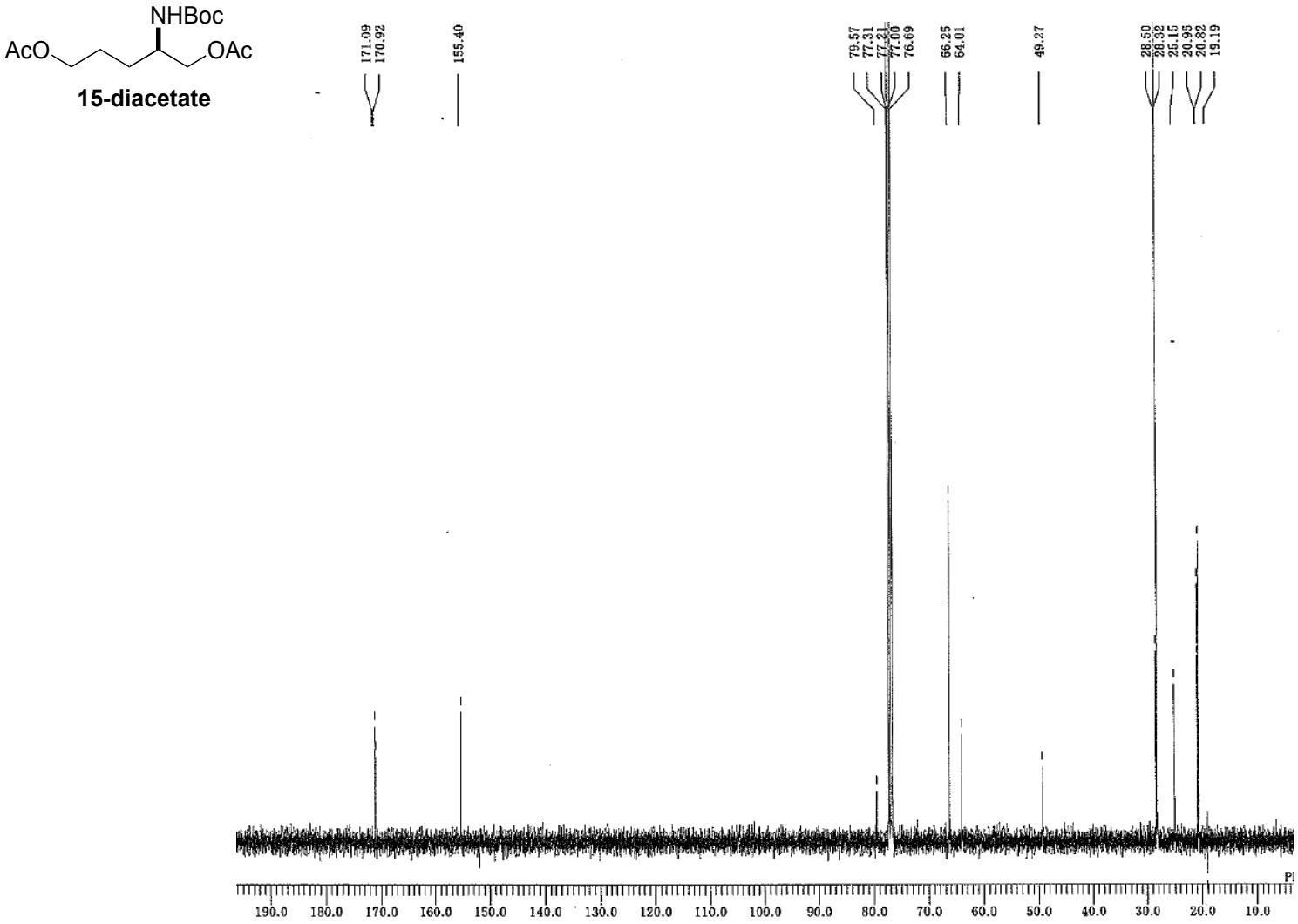


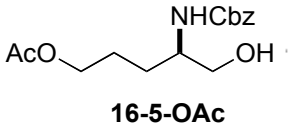




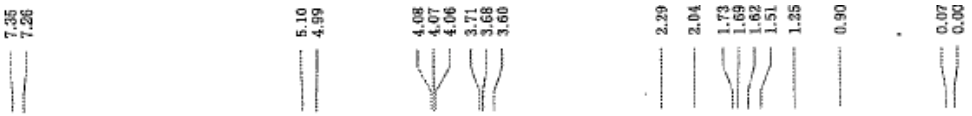
15-diacetate

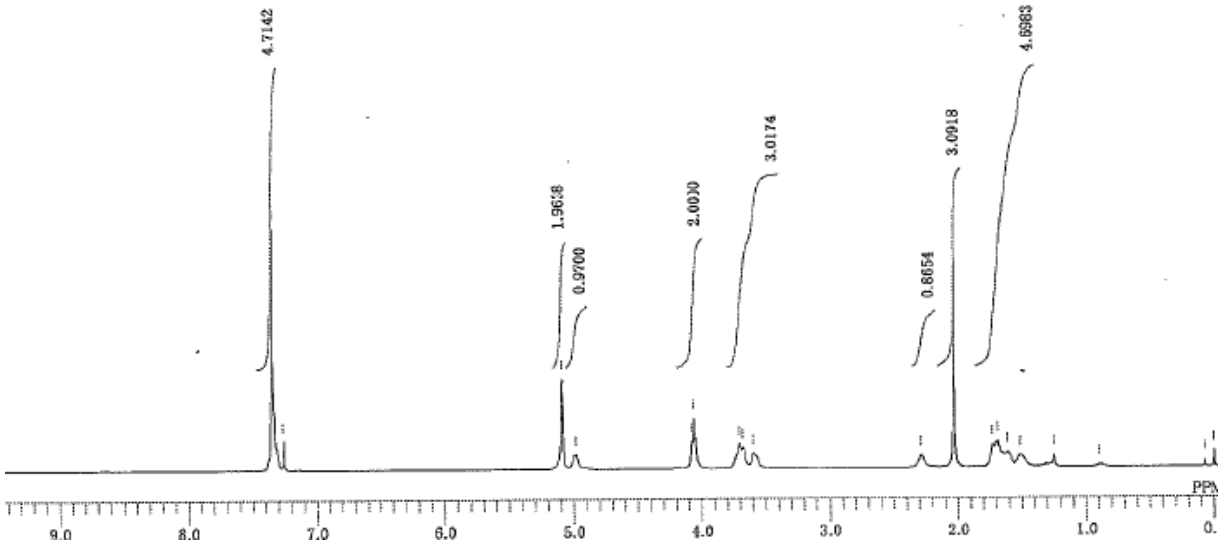


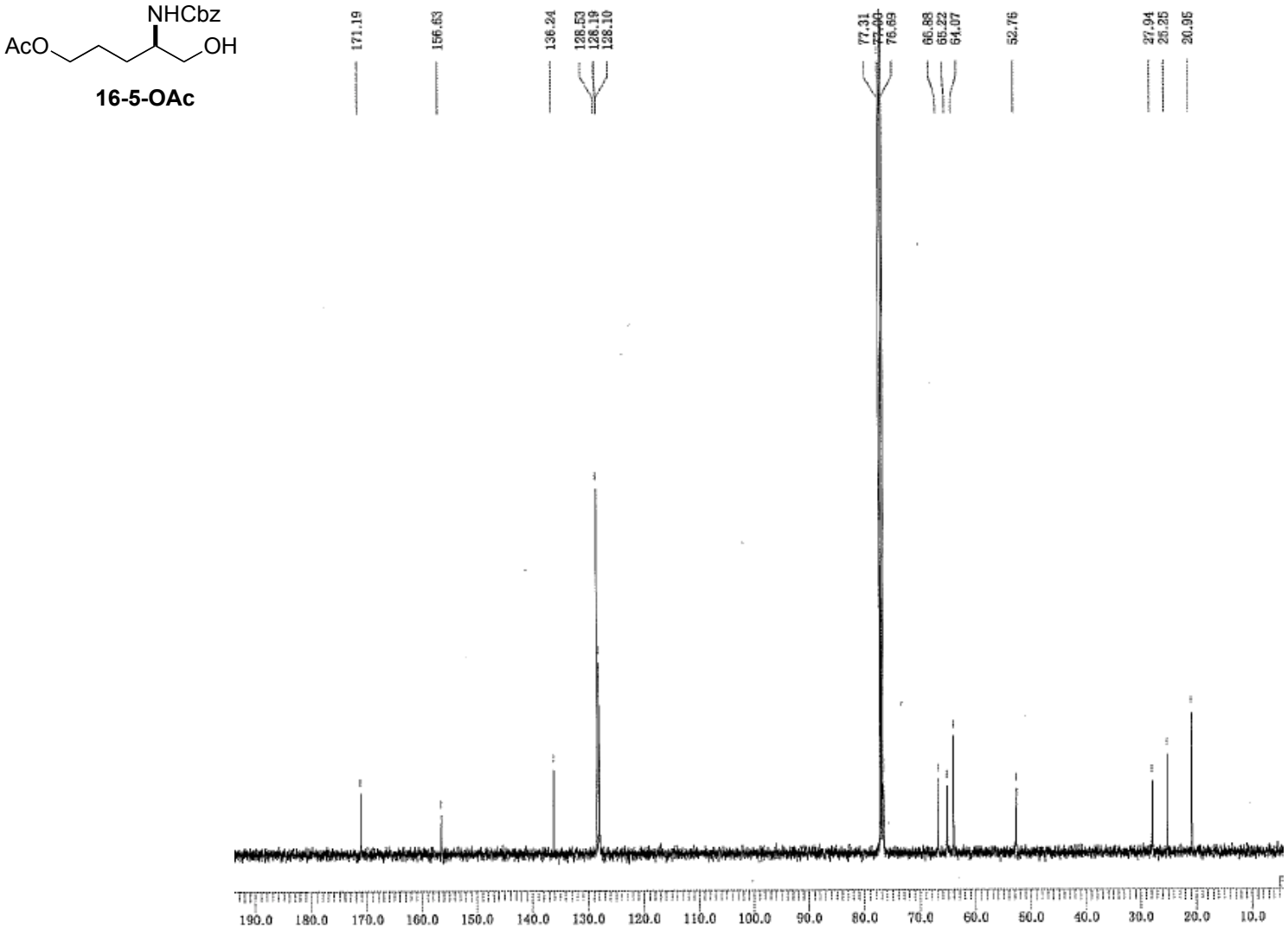


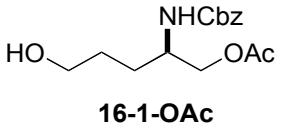


16-5-OAc

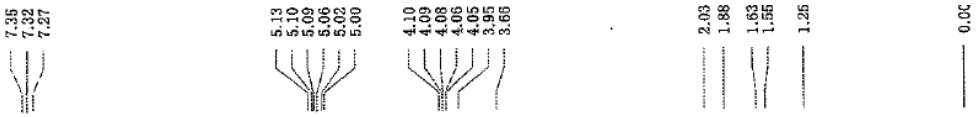


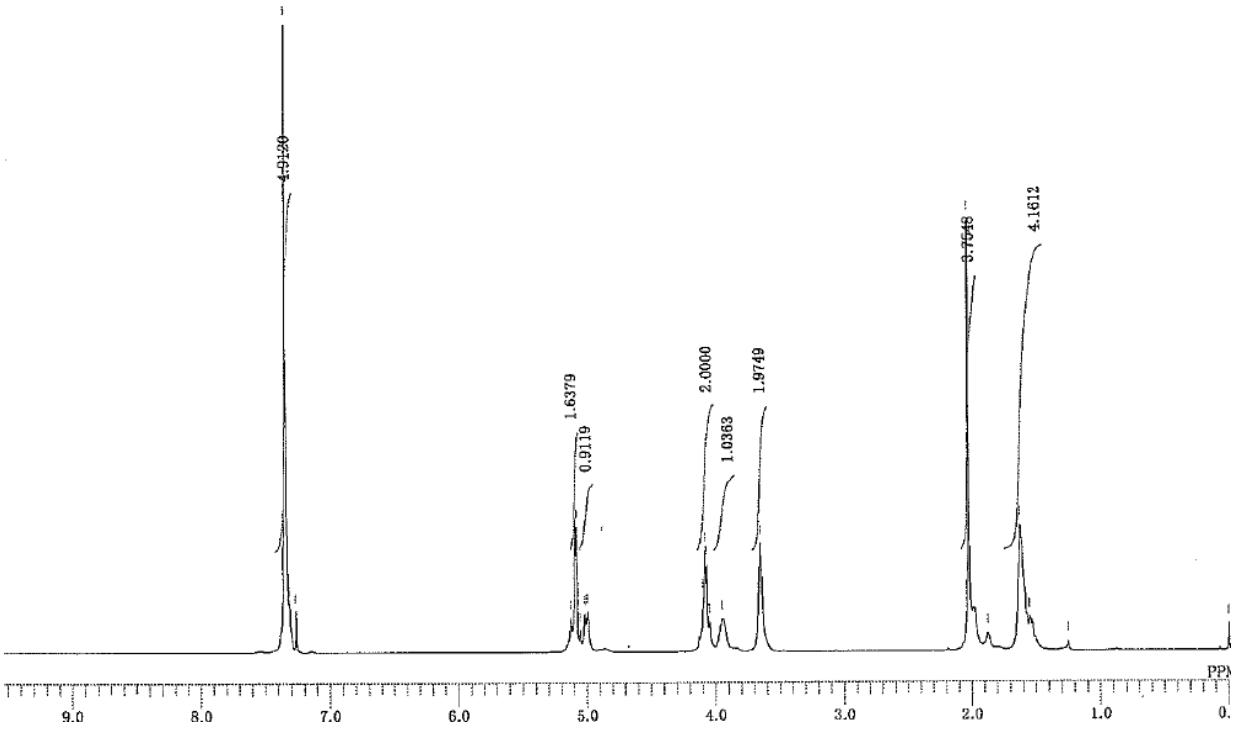


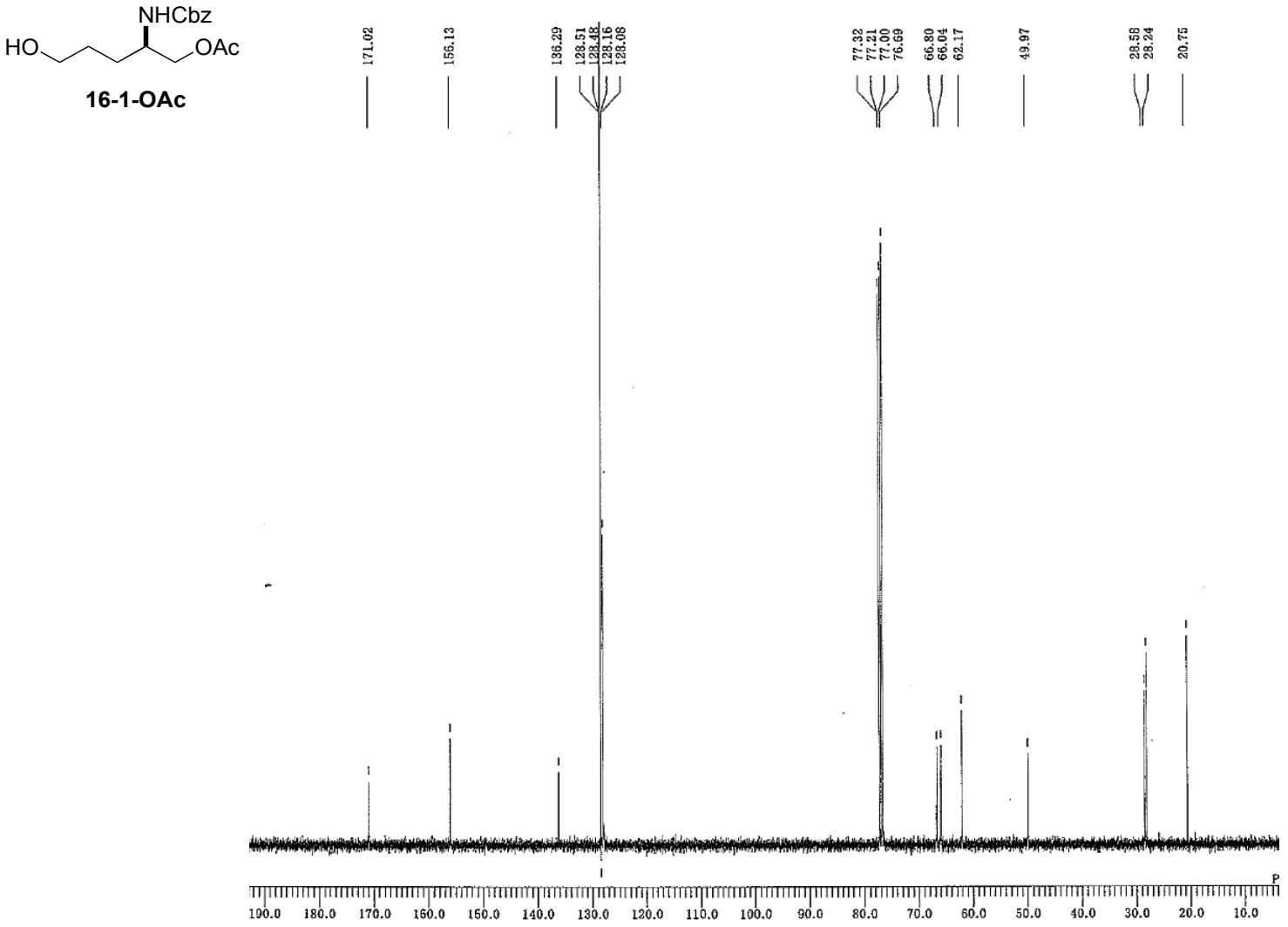


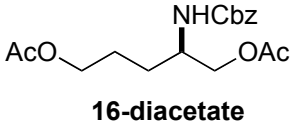


16-1-OAc

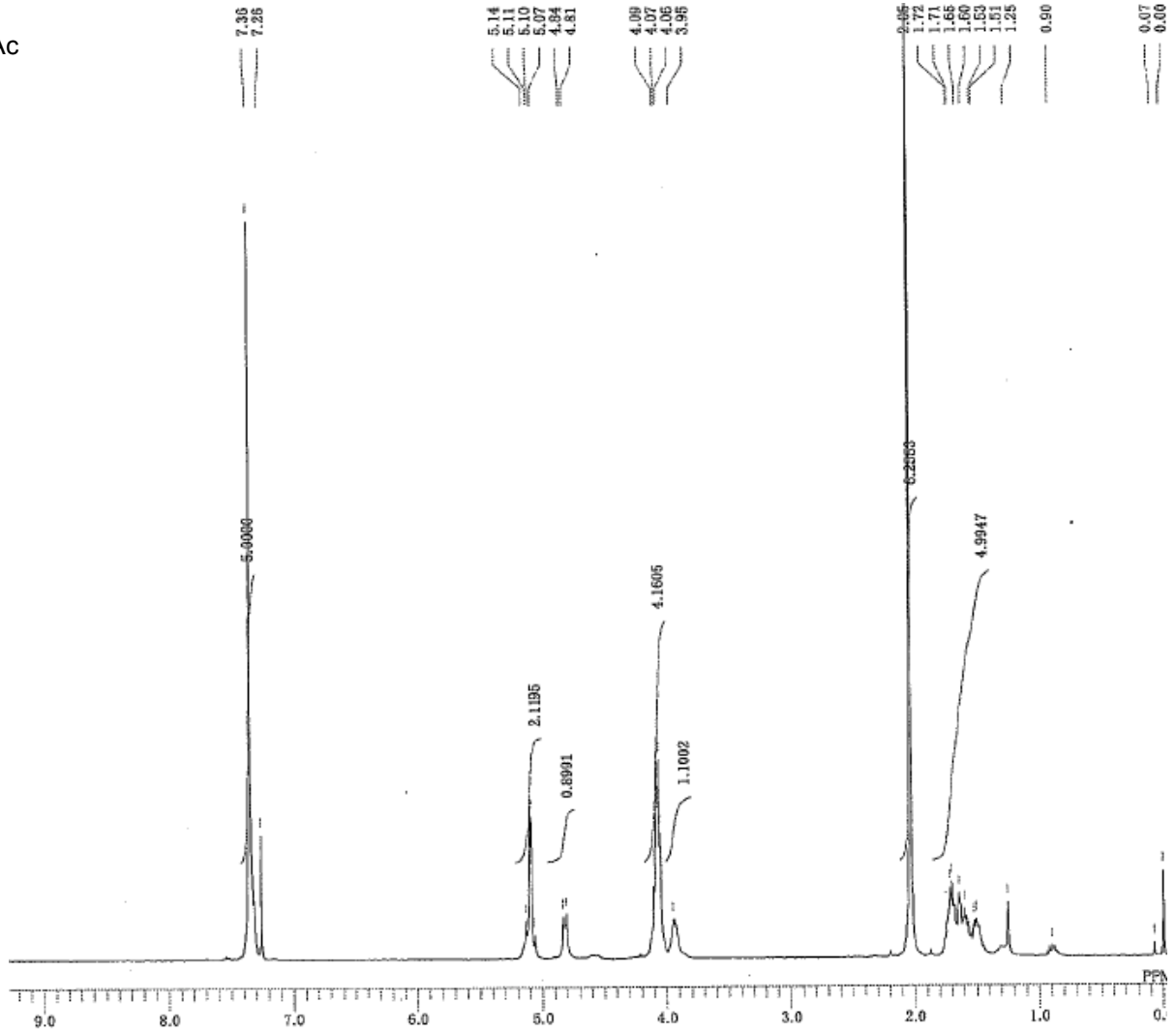


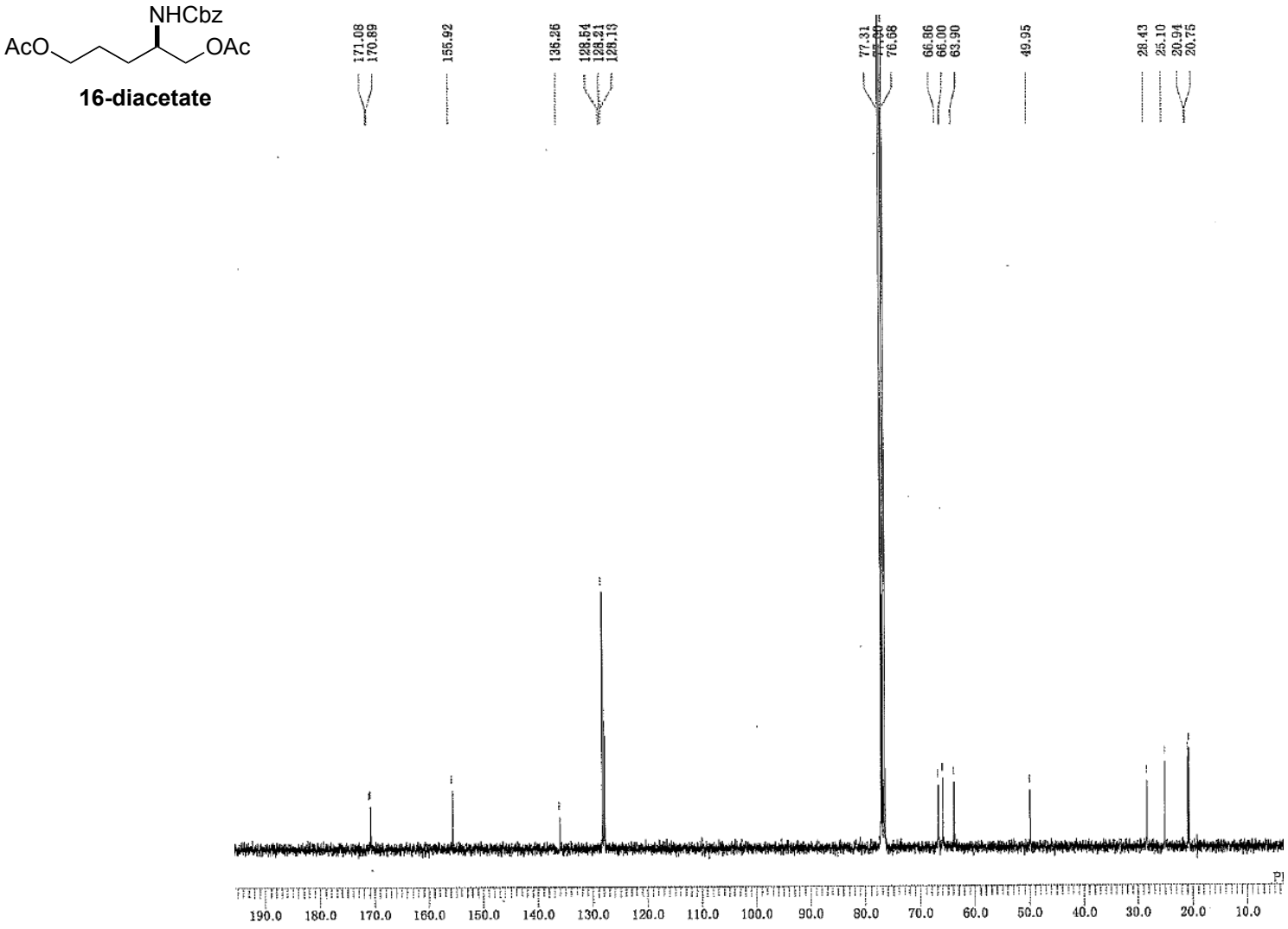


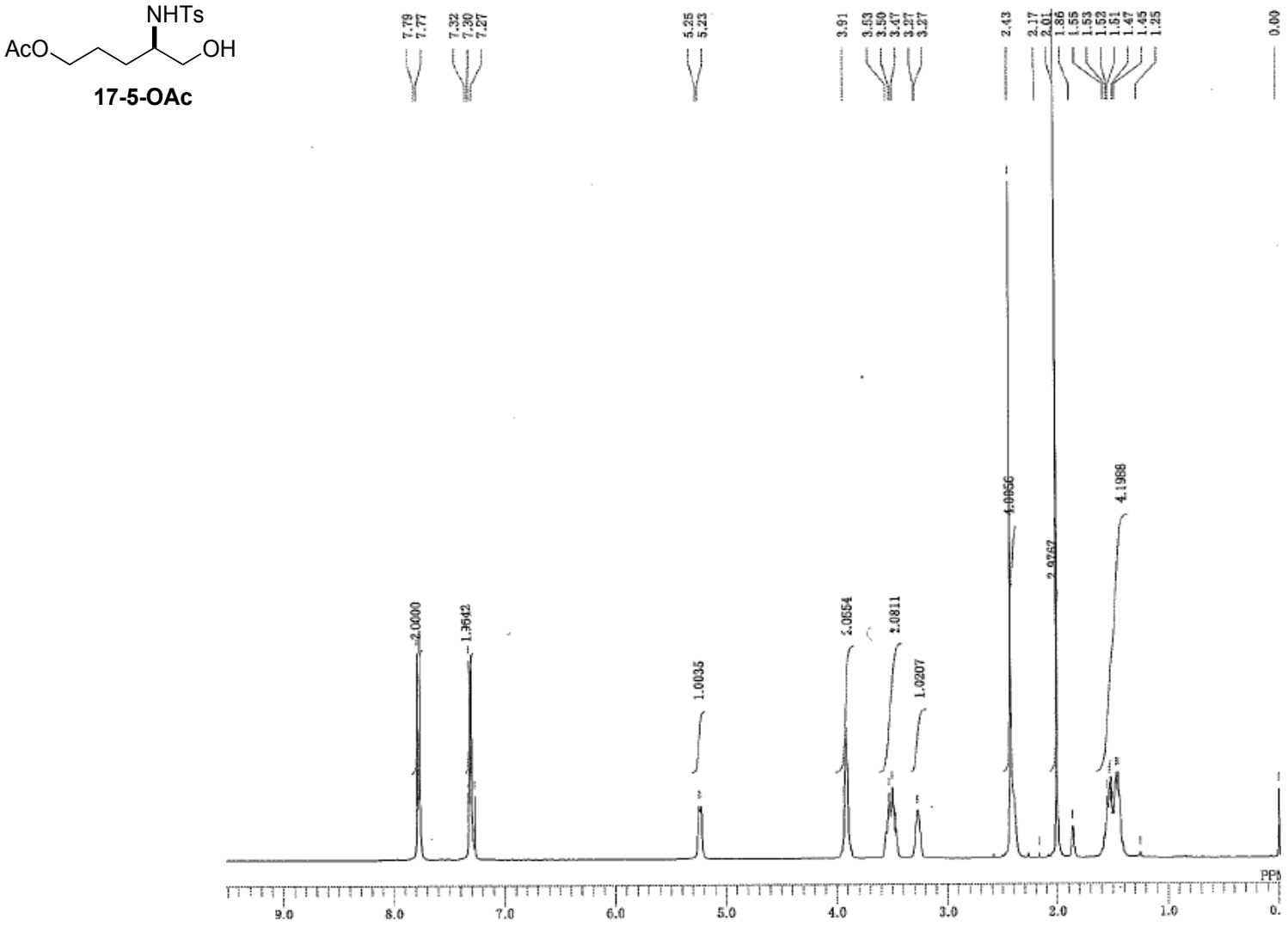


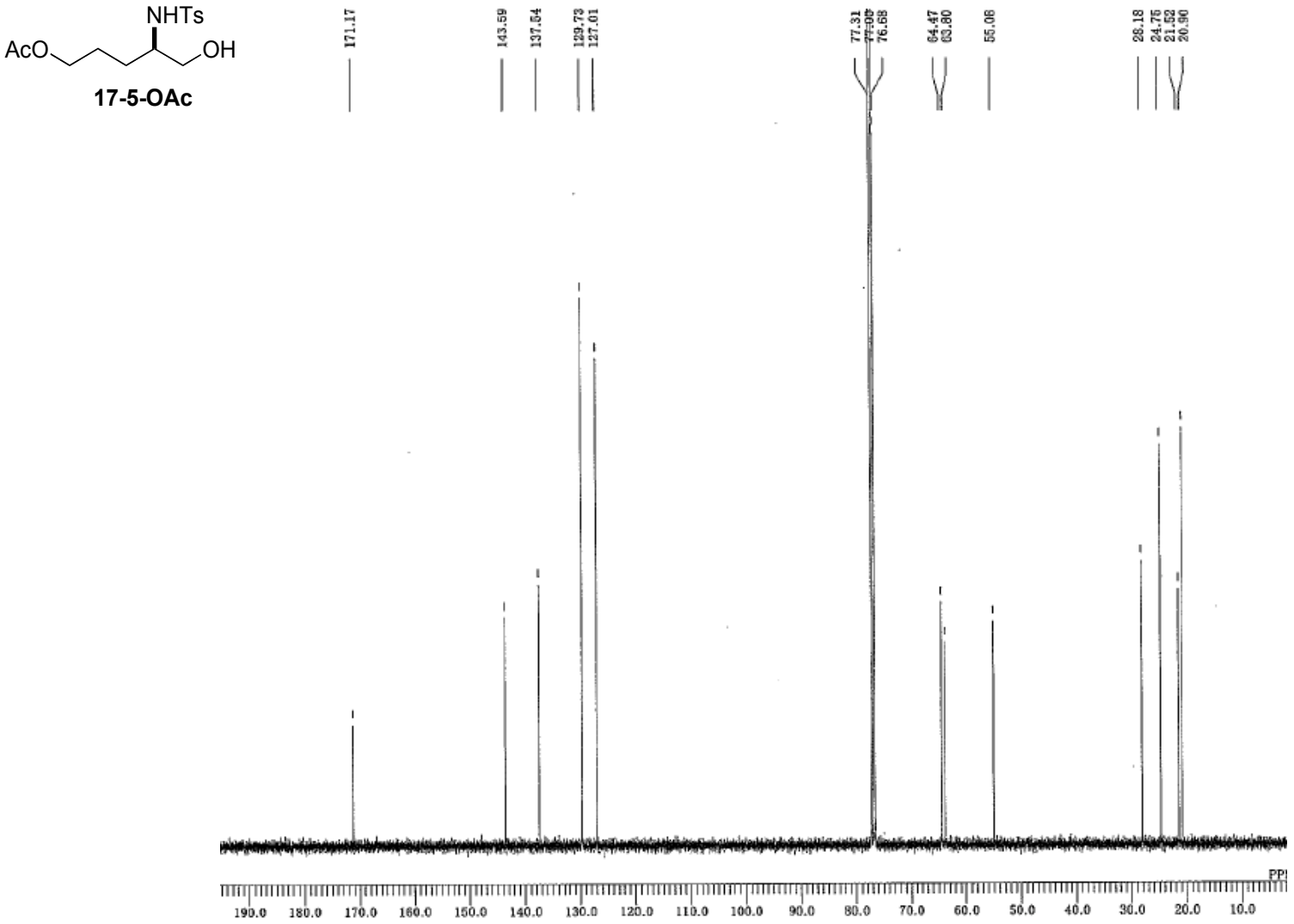


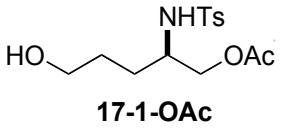
16-diacetate



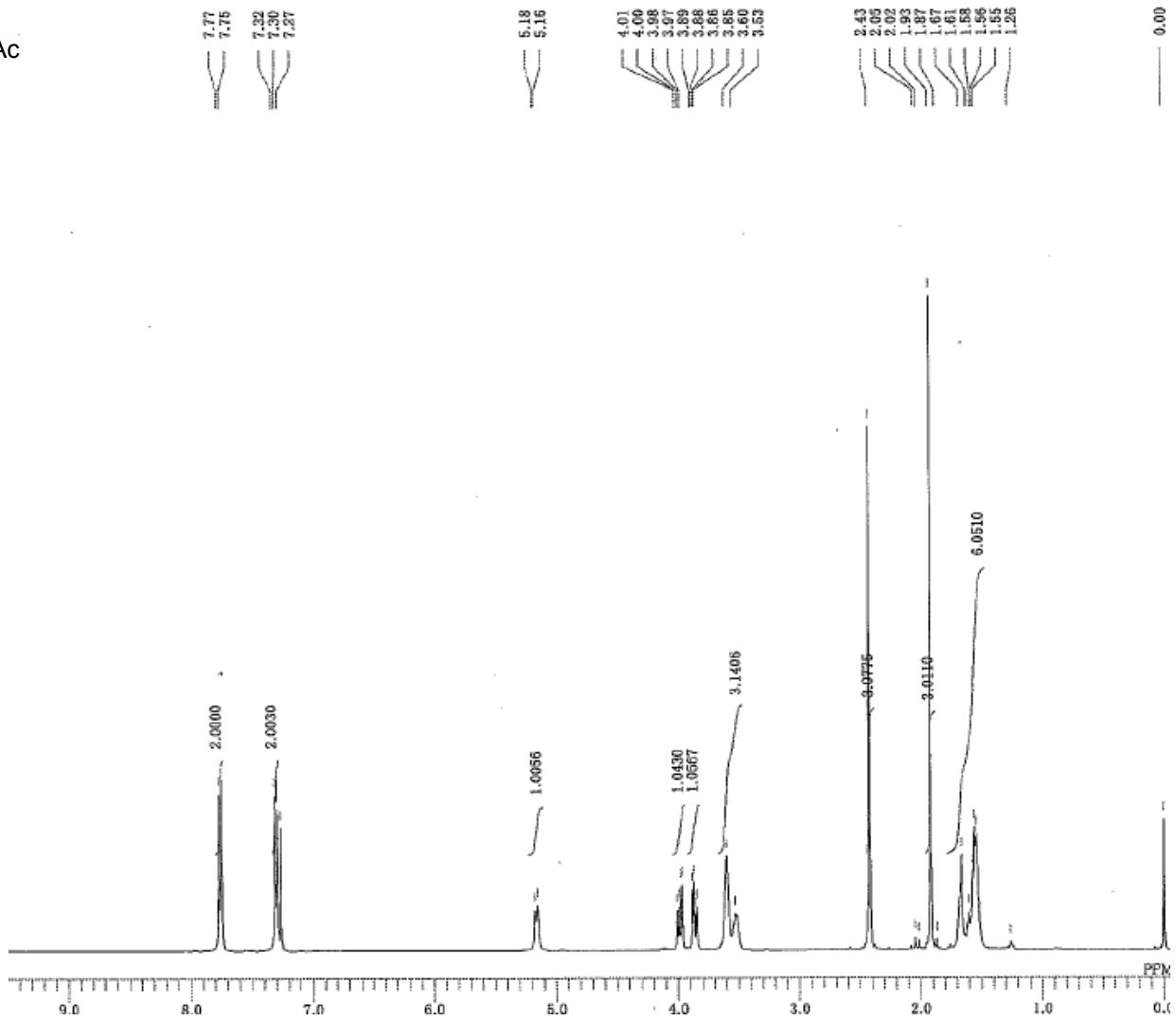


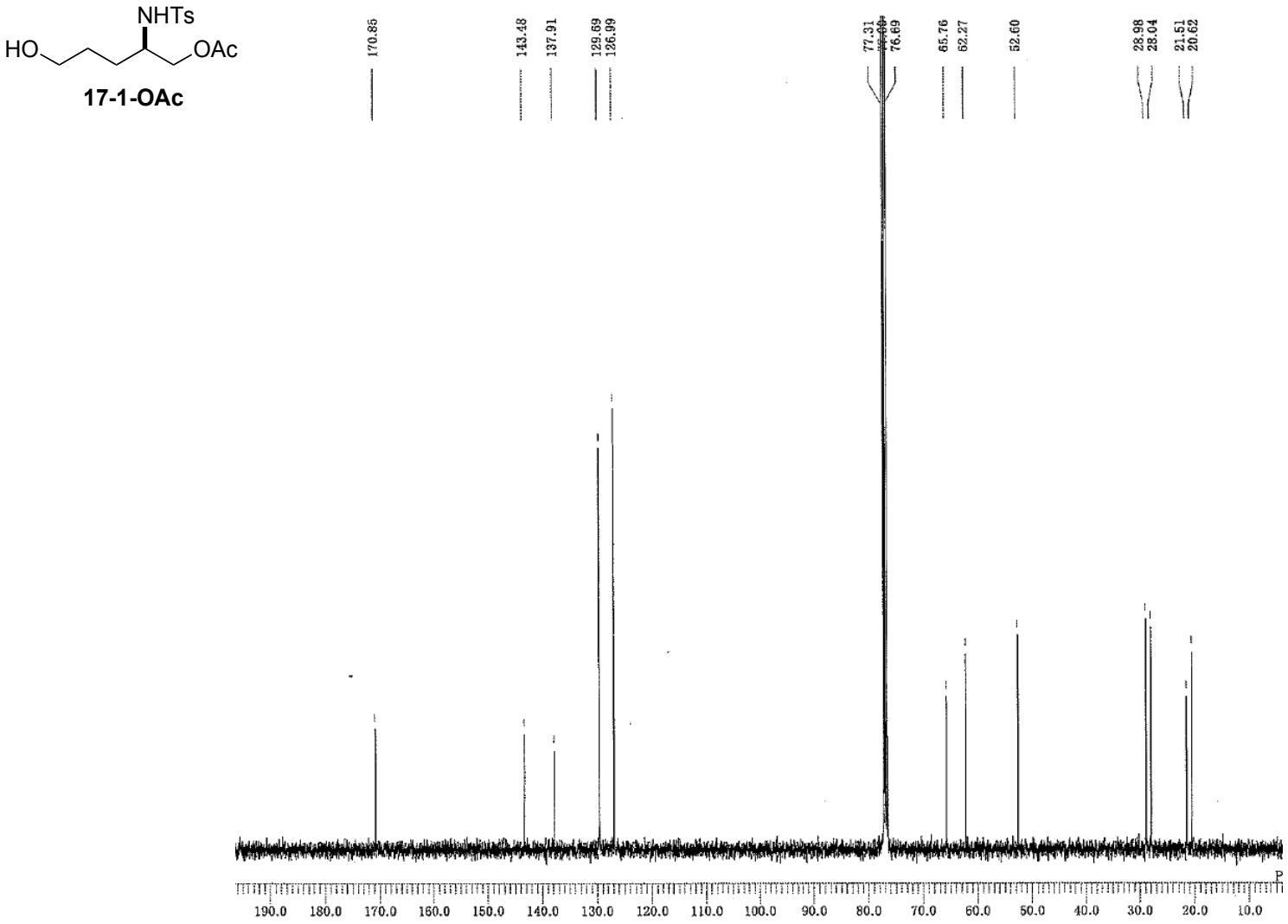


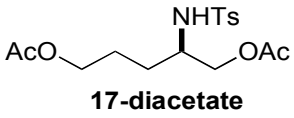




17-1-OAc







17-diacetate