Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Iodoamidation of Olefins with Chloramine Salts and Iodine in Aqueous Media

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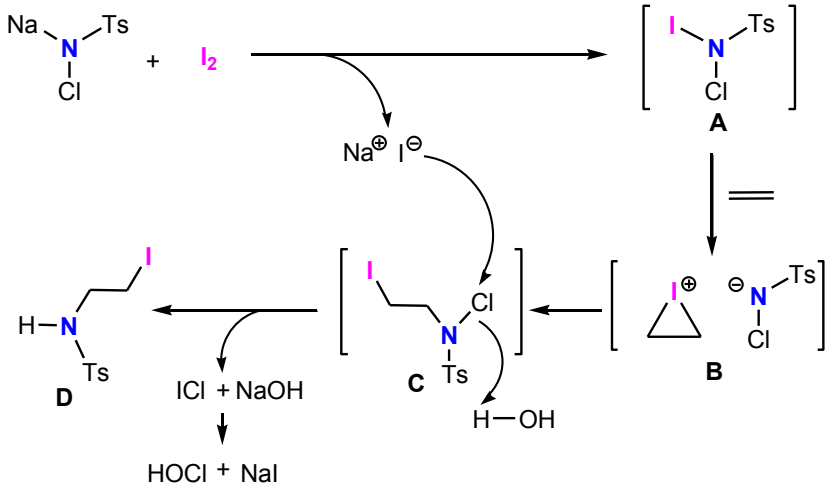
Proposed Reaction Mechanism

Altough the precise mechanisam of the reaction in unclear at presen stage, a proposed mechanism is shown in Scheme S1. Since our previous work[S1a] revealed that the reaction with iodine is very rapid, CT reacts immediately with iodine to form the active species **A.** As shown in Scheme 1, **A** acts as an iodonium source to generate the cyclic iodonium intermediate **B** by reaction with an olefin. In fact, the complete stereoselectivity observed in the reactions (Table 2; entries 6-8, Table3; entries 5-8) support the generation such an intermediate. The formation of a small amount of iodohydrin in some rections (Table 2; entries 6 and 8, Table 3; entry 1) also suggests that an iodonium species is generated. The iodoamidated intermediate **C** is formed by an attack of the nitrogen anion on the cyclic iodonium on the ion pair **B**. The liberated NaI would reduce the N-Cl bond on the intermediate **C** to afford the adduct by reaction with water. The pH of the resulting mixture was around 2, which can be explained by the generation of HOCl, produced by the reaction of liberated ICl with NaOH.



Scheme S1. Proposed Reaction Pathway

Proposed Reaction Process

The proposed mechanism explains why the iodoamidation reaction is specifically induced in aqueous media (Figure 1). Iodine dissolved in olefin layer or water layer reacts with CT to give the species **A**, which rapidly diffuses into olefin layer. In the olefin layer, the reaction of species **A** with the olefin takes place, generating an ion pair consisting of the cyclic iodonium intermediate and the *N*-chloro-*N*-tosyl amide anion, which would rapidly react with each other to give the *N*-chlorinated iodoamide **C**. Since the hydrophilic group, the *N*-chloro-*N*-tosyl group, on intermediate **C** would be located at the interface between the olefin and water layer, sodium iodide in water would attack the chlorine substituent on the nitrogen of **C**, followed by protonation of the amide anion with water. As shown in Table 1, when the reaction was carried out in the absence of water, the amide anion attacks the β-carbon, resulting in the production of aziridines. The use of an acetonitrile-water system (acetonitrile is miscible with water) in the reaction gave an iodohydrine derivative through the attack of water on the cyclic iodonium intermediate, because the ion pair **B** would be stabilized by the high polarity of the co-solvent. In contrast, the use of a hydrophobic organic solvent such as *n*-hexane and CH_2Cl_2 gave compounds that were exclusively iodoamidated.

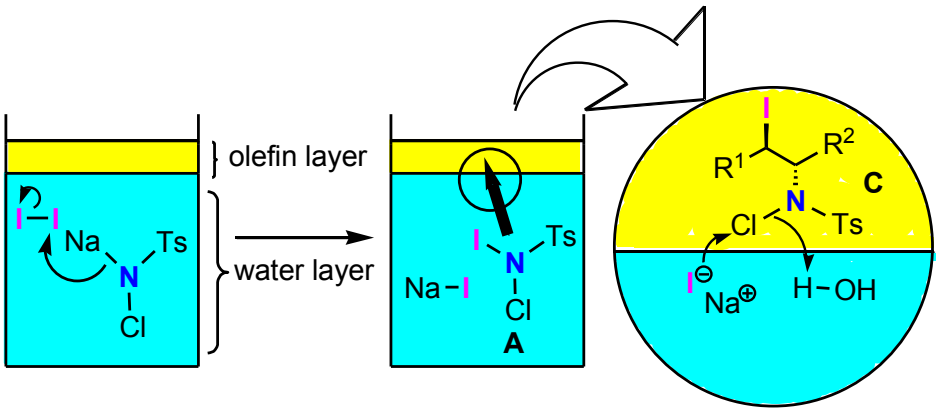
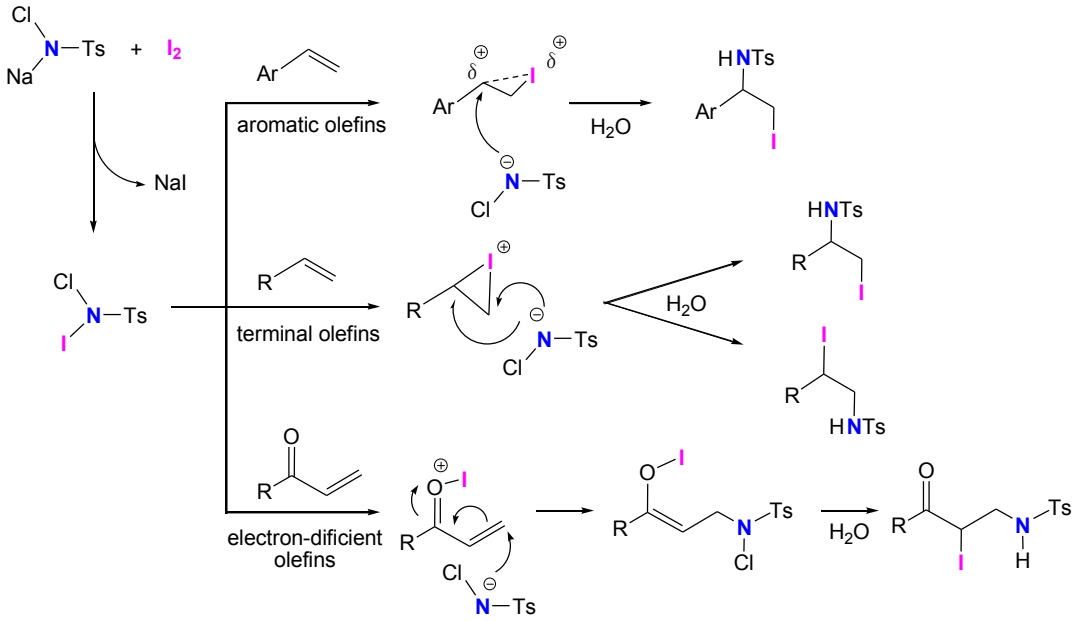


Figure S1. Consideration of Regiochemistry

Consideration of Regiochemistry

Cyclic iodonium intermediates are likely involved in the reaction. In the use of aromatic olefins, the polarity of aqueous media would polarize the benzylic C－I bond. This phenomena would induce the formation of the β-iodinated sulfonamide. As compared with aromatic olefins, aliphatic terminal olefins are not so highly polarized because the positive charge would be shared between the secondary carbon and primary carbon. Thus, a nitrogen nucleophile would attack both the primary carbon and the secondary carbon, leading to the regioisomers. On the other hand, carbonyl groups of electron-deficient olefins would be activated by a iodonium ion acting as a Lewis acid[S2] to induce the 1,4-addition of a nitrogen nucleophile, affording the α-iodo-β-amidated products.



Scheme S2. Consideration of Regiochemistry

General Methods.

Melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were obtained on a JASCO FT/IR-410 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H NMR, 270 MHz; ^{13}C NMR, 68 MHz) using tetramethylsilane as an internal standard. Mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. Elemental analyses were performed at the Analytical Center, Faculty of Engineering, Osaka University. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Co.). Analytical thin-layer chromatography was performed on precoated silica gel glass plates (silica gel 60 F_{254}, 0.25 mm thickness) (Merck Co.). Compounds were visualized by UV light or treatment with an ethanolic solution of phosphomolybdic acid followed by heating. Stereochemistry was determined by the conversion of products **6**[S1a], **7**[S1a], **15**[S1b, S1c], and **16**[S1c] to a known aziridines[S1d]

Typical procedure for the iodoamidation of styrene derivatives with iodine and chloramine-T

Styrene (54 mg, 0.5 mmol) was added to a mixture of chloramine-T (281 mg, 1.0 mmol), iodine (126.8 mg, 0.5 mmol), and water (2.0 mL). The mixture was allowed to stir at room temperature for 1 h. The resulting precipitate was collected by suction filtration and dissolved in acetone (15 mL). The solution was dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate in hexane) gave **1** (147 mg, 73%).

Typical procedure for the iodoamidation of styrene derivatives with iodine and chloramine-T in the case of the addition of a small amount of organic solevent

A small amount of *n*-hexane (100 μL) and styrene (54 mg, 0.5 mmol) were added to a mixture of chloramine-T (281 mg, 1.0 mmol), iodine (126.8 mg, 0.5 mmol), and water (2.0 mL). After stirring for 1 h at room temperature, aqueous $Na_2S_2O_3$ (0.5 M, 5 mL) was added to the reaction mixture and the resulting solution was extracted with Et_2O (20 mL x 3). The combined organic extracts were dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate in hexane) gave **1** (171 mg, 85%).

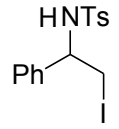
Typical procedure for the iodoamidation of aliphatic olefins and elecron-deficient olefins with chloramine-T

Ethyl acrylate (100 mg, 0.5 mmol) was added to a mixture of chloramine-T (281 mg, 1.0 mmol), iodine (126.8 mg, 0.5 mmol), and water (2.0 mL). After stirring for 1 h at room temperature, aqueous $Na_2S_2O_3$ (0.5 M, 5 mL) was added to the reaction mixture and the resulting solution was extracted with Et_2O (20 mL x 3). The combined organic extracts were dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate in hexane) gave **20** (199 mg, 95%).

A Procedure for the one-pot iodoamidation of ethyl acrylate from $SESNH_2$

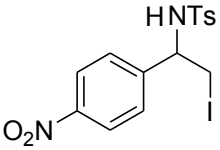
*t*BuOCl (130 mg, 1.2 mmol) was added to a mixture of $SESNH_2$ (181 mg, 1.0 mmol), NaOH aq (1 M , 1 mL), and water (1 mL). After stirring for 1 h at room temperature, iodine (126.8 mg, 0.5 mmol) and ethyl acrylate (100 mg, 0.5 mmol) were added to the aqueous solution, After stirring for 1 h at room temperature, aqueous $Na_2S_2O_3$ (0.5 M, 5 mL) was added to the reaction mixture and the resulting solution was extracted with Et_2O (20 mL x 3). The combined organic extracts were dried over Na_2SO_4 and concentrated to give the crude product. Purification by flash column chromatography (silica gel; ethyl acetate in hexane) gave **17** (152 mg, 73%).

2-iodo-1-phenyl-1-(*p*-toluenesulfonamido)ethane (1)



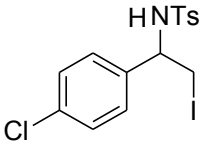
Colorless solid (171 mg, 85%); mp. 126-128 °C; IR (KBr, cm^{-1}) 3243, 1324, 1155; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.36-3.47 (m, 2H), 4.41 (td, 1H, *J* = 6.8, 6.8 Hz), 5.32 (br d, 1H, *J* = 6.8 Hz), 7.06-7.10 (m, 2H), 7.21-7.26 (m, 5H), 7.62 (d, 2H, *J* = 6. 8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.2, 21.6, 58.4, 126.3, 127.0, 128.0, 128.5, 129.4, 136.7, 138.3, 143.3; MS (CI, isobutane): *m/z* (relative intensity, %) 402 ($[M+H]^+$, 100); HRMS (CI, isobutane): *m/z* calcd for $C_{15}H_{17}INO_2S$ (M+H) 400.0025, found 400.0028; Anal. Calcd for $C_{15}H_{16}INO_2S$: C, 44.90; H, 4.02; N, 3.49. Found: C, 45.08; H, 3.76; N, 3.49.

2-iodo-1-(4-nitrophenyl)-1-(*p*-toluenesulfonamido)ethane (2)



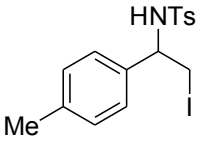
Colorless solid (190 mg, 84%); mp. 165-166 °C; IR (KBr, cm^{-1}) 3257, 1512, 1346, 1315, 1157; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.38 (d, 2H, *J* = 4.3 Hz), 4.52 (td, 1H, *J* = 6.5, 6.5 Hz), 5.32 (br d, 1H, *J* = 6.5 Hz), 7.23-7.26 (m, 2H), 7.34 (d, 2H, *J* = 8.4 Hz), 7.64 (d, 2H, *J* = 8.4 Hz), 8.12 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.3, 21.6, 57.2, 123.7, 127.1, 127.5, 129.6, 136.3, 144.1, 145.6, 147.4; MS (CI, isobutane): *m/z* (relative intensity, %) 447 ($[M+H]^+$, 60), 319 ($[M-I]^+$, 100); HRMS (CI, isobutane): *m/z* calcd for $C_{15}H_{16}IN_2O_4S$ (M+H) 446.9875, found 446.9863; Anal. Calcd for $C_{15}H_{15}IN_2O_4S$: C, 40.37; H, 3.39; N, 6.28. Found: C, 40.66; H, 3.34; N, 6.33.

2-iodo-1-(4-chlorophenyl)-1-(*p*-toluenesulfonamido)ethane (3)



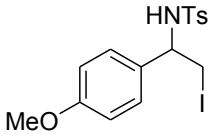
Colorless solid (161 mg, 74%); mp. 156-157 °C; IR (KBr, cm^{-1}) 3273, 1331, 1092; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.37 (d, 2H, *J* = 6.5 Hz), 4.37 (td, 1H, *J* = 6.5, 6.5 Hz), 5.33 (br d, 1H, *J* = 6.5 Hz), 7.03 (d, 2H, *J* = 8.4 Hz), 7.18-7.26 (m, 4H), 7.61 (d, 2H, *J* = 8.4 Hz) ; ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.3, 21.6, 57.2, 127.1, 127.8, 128.7, 129.5, 134.1, 136.5, 136.8, 143.8; MS (CI, isobutane): *m/z* (relative intensity, %) 438 ($[M+H+2]^+$, 27), 436 ($[M+H]^+$, 69), 308 ($[M-I]^+$, 100); HRMS (CI, isobutane): *m/z* calcd for $C_{15}H_{16}ClINO_2S$ (M+H) 434.9557, found 435.9644; Anal. Calcd for $C_{15}H_{15}ClINO_2S$: C, 41.35; H, 3.47; N, 3.21. Found: C, 41.06; H, 3.27; N, 3.23.

2-iodo-1-(4-methylphenyl)-1-(*p*-toluenesulfonamido)ethane (4)



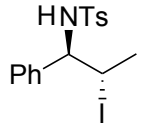
Colorless solid (150 mg, 72%); dec. 154-157 °C; IR (KBr, cm^{-1}) 3238, 1331, 1161; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.40 (s, 3H), 3.35-3.48 (m, 2H), 4.34 (td, 1H, *J* = 6.5, 6.5 Hz), 5.15 (br d, 1H, *J* = 6.5 Hz), 6.96 (d, 2H, *J* = 8.4 Hz), 7.04 (d, 2H, *J* = 8.4 Hz), 7.21 (d, 2H, *J* = 8.4 Hz), 7.64 (d, 2H, *J* = 8.4 Hz) ; ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.7, 21.2, 21.6, 57.9, 126.2, 127.1, 129.2, 129.4, 135.3, 136.7, 138.1, 143.5; MS (CI, isobutane): *m/z* (relative intensity, %) 416 ($[M+H]^+$, 69), 308 ($[M-I]^+$, 100); HRMS (CI, isobutane): *m/z* calcd for $C_{16}H_{19}INO_2S$ (M+H) 416.0108, found 416.0187; Anal. Calcd for $C_{16}H_{18}INO_2S$: C, 46.27; H, 4.37; N, 3.37. Found: C, 46.18; H, 3.29; N, 3.29.

2-iodo-1-(4-methoxyphenyl)-1-(*p*-toluenesulfonamido)ethane (5)



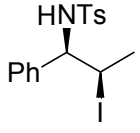
Colorless solid (110 mg, 51%) ; mp. 123-124 °C; IR (KBr, cm^{-1}) 3243, 1315, 1178; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.41 (s, 3H), 3.35-3.48 (m, 2H), 3.77 (s, 3H), 4.34 (td, 1H, *J* = 6.1, 6.1 Hz), 5.09 (br d, 1H, *J* = 6.1 Hz), 6.76 (d, 2H, *J* = 8.9 Hz), 7.00 (d, 2H, *J* = 8.9 Hz), 7.22 (d, 2H, *J* = 8.4 Hz), 7.63 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.9, 21.6, 55.3, 57.7, 113.9, 127.1, 127.6, 129.5, 130.3, 136.7, 143.5, 159.3; MS (CI, isobutane): *m/z* (relative intensity, %) 454 ($[M+Na]^+$,100), 329 ($[M+Na-I]^+$, 98); HRMS (CI, isobutane): *m/z* calcd for $C_{16}H_{18}I\ NO_3SNa$ (M+Na) 453.9950, found 453.9943; Anal. Calcd for $C_{16}H_{18}I\ NO_3SNa$: C, 44.56; H, 4.21; N, 3.25. Found: C, 44.60; H, 3.98; N, 3.21.

(±)-*trans*-1-iodo-2-phenyl-2-(*p*-toluenesulfonamido)propane (6)



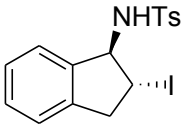
Colorless solid (139 mg, 67%); mp. 145-146 °C; IR (KBr, cm^{-1}) 3276, 1325, 1165; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.78 (d, 3H, *J* = 7.0 Hz), 2.34 (s, 3H), 4.19 (dd, 1H, *J* = 5.1, 8.4 Hz), 4.41-4.45 (m, 1H), 5.34 (br d, 1H, *J* = 8.4 Hz), 7.04-7.21(m, 7H), 7.54 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 24.5, 33.0, 63.2, 127.0, 127.3, 127.9, 127.9, 129.2, 136.8, 136.8, 143.2; MS (CI, isobutane): *m/z* (relative intensity, %) 416 ($[M+H]^+$, 100), 288 ($[M-I]^+$, 55); HRMS (CI, isobutane): *m/z* Calcd for $C_{16}H_{19}INO_2S$ (M+H) 416.0181, found 416.0174.

(±)-*cis*-1-iodo-2-phenyl-2-(*p*-toluenesulfonamido)propane (7)



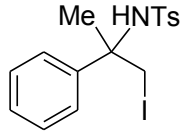
Colorless solid (206 mg, 99%); dec. 130-131 °C; IR (KBr, cm^{-1}) 3261, 1321, 1163; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.89 (d, 3H, *J* = 7.0 Hz), 2.34 (s, 3H), 4.11 (dd, 1H, *J* = 4.9, 8.4 Hz), 4.24-4.33 (m, 1H), 5.31 (br d, 1H, *J* = 8.4 Hz), 7.02-7.28 (m, 7H), 7.56 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.4, 26.1, 35.8, 63.5, 126.5, 127.0, 127.8, 128.2, 129.3, 137.3, 138.5, 143.3; MS (CI, isobutane): *m/z* (relative intensity, %) 416 ($[M+H]^+$, 85), 288 ($[M-I]^+$, 100); HRMS (CI, isobutane): *m/z* Calcd for $C_{16}H_{19}INO_2S$ (M+H) 416.0181, found 416.0172.

(±)-*trans*-2-iodo-1-(*p*-toluenesulfonamido)indane (8)



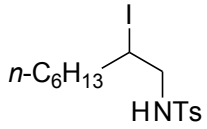
Colorless solid (198 mg, 96%); dec. 143-144 °C; IR (KBr, cm^{-1}) 3269, 1335, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.25 (dd, 1H, *J* = 6.2, 16.7 Hz), 3.58 (dd, 1H, *J* = 6.2, 16.7 Hz), 4.24 (q, 1H, *J* = 6.2 Hz), 4.90 (br d, 1H, *J* = 3.8 Hz), 4.95-4.97 (m, 1H), 7.14-7.37 (m, 6H), 7.85 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.7, 26.5, 43.0, 68.7, 124.4, 124.5, 127.4, 127.7, 129.0, 129.7, 137.2, 139.6, 141.0, 143.8; MS (CI, isobutane): *m/z* (relative intensity, %) 414 ($[M+H]^+$, 100), 286 ($[M-I]^+$, 36); HRMS (CI, isobutane): *m/z* Calcd for $C_{16}H_{17}INO_2S$ (M+H) 414.0025, found 414.0020; Anal. Calcd for $C_{16}H_{16}INO_2S$: C, 46.5; H, 3.90; N, 3.39. Found: C, 46.47; H, 3.79; N, 3.47.

1-iodo-2-phenyl-2-(*p*-toluenesulfonamido)propane (9)



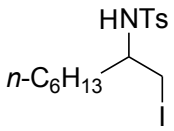
Colorless solid (154 mg, 74%); mp. 92-93 °C; IR (KBr, cm^{-1}) 3263, 1317, 1149; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.76 (s, 3H), 2.41 (s, 3H), 3.59 (d, 1H, *J* = 10.3 Hz), 3.75 (d, 1H, *J* = 10.3 Hz), 5.23 (br s, 1H), 7.19-7.30 (m, 7H), 7.63 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 20.9, 21.5, 26.2, 60.0, 125.6, 126.8, 127.6, 128.2, 129.2, 139.1, 141.1, 142.9; MS (CI, isobutane): *m/z* (relative intensity, %) 416 ($[M+H]^+$, 100), 288 ($[M-I]^+$, 75); HRMS (CI, isobutane): *m/z* calcd for $C_{16}H_{19}INO_2S$ (M+H) 416.0181, found 416.0178; Anal. Calcd for $C_{16}H_{18}INO_2S$: C, 46.27; H, 4.37; N, 3.37. Found: C, 46.39; H, 4.13; N, 3.29.

2-iodo-1-(*p*-toluenesulfonamido)octane (10a)[S3]



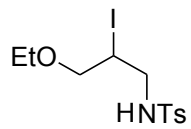
Colorless oil (97 mg, 48%); IR (neat, cm^{-1}) 3452, 1327, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 6.5 Hz), 1.24-1.78 (m, 10H), 2.44 (s, 3H), 3.19-3.34 (m, 2H), 3.97-4.01 (m, 1H), 4.65 (br t, 1H, *J* = 6.5 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 7.75 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 21.6, 22.6, 28.4, 29.2, 31.6, 36.1, 37.3, 50.1, 126.9, 129.7, 136.8, 143.6; MS (CI, isobutane): *m/z* (relative intensity, %) 410 ($[M+H]^+$, 100), 282 ($[M-I]^+$, 40); HRMS (CI, isobutane): *m/z* Calcd for $C_{15}H_{25}INO_2S$ (M+H) 410.0651, found 410.0634.

1-iodo-2-(*p*-toluenesulfonamido)octane (10b)[S4]



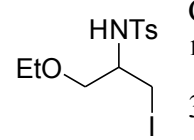
Colorless solid (76 mg, 37%); mp. 91-92 °C; IR (neat, cm^{-1}) 3277, 1331, 1159; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, 3H, *J* = 6.8 Hz), 1.14-1.25 (m, 8H), 1.35-1.60 (m, 2H), 2.43 (s, 3H), 2.89-3.00 (m, 1H), 3.13-3.26 (m, 2H), 4.66 (br d, 1H, *J* = 8.4 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 15.0, 21.6, 22.5, 25.2, 28.7, 31.6, 35.6, 52.5, 126.9, 129.6, 137.7, 143.5; MS (CI, isobutane): *m/z* (relative intensity, %) 410 ($[M+H]^+$, 93), 282 ($[M-I]^+$, 100); HRMS (CI, isobutane): *m/z* Calcd for $C_{15}H_{25}INO_2S$ (M+H) 410.0651, found 410.0642.

1-ethoxy-2-iodo-3-(*p*-toluenesulfonamido)propane (11a)



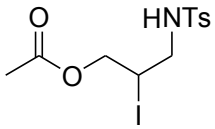
Colorless solid (101 mg, 53%); mp. 45-46 °C; IR (KBr, cm^{-1}) 3284, 1331, 1159; ^1H NMR (270 MHz, $CDCl_3$) δ 1.18 (t, 3H, *J* = 7.0 Hz), 2.44 (s, 3H), 3.35-3.74 (m, 6H), 4.08-4.17 (m, 1H), 5.24 (br t, 1H, *J* = 6.2 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 7.75 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 21.6, 25.8, 48.8, 66.6, 74.2, 126.9, 129.7, 136.7, 143.5; MS (CI, isobutane): *m/z* (relative intensity, %) 384 ($[M+H]^+$, 100), 338 ($[M-OEt]^+$, 42), 256 ($[M-I]^+$, 18); HRMS (CI, isobutane): *m/z* Calcd for $C_{12}H_{19}INO_3S$ (M+H) 384.0130, found 384.0115; Anal. Calcd for $C_{12}H_{19}INO_3S$: C, 37.61; H, 4.73; N, 3.65. Found: C, 37.58; H, 4.54; N, 3.55.

1-etoxy-3-iodo-2-(*p*-toluenesulfonamido)propane (11b)



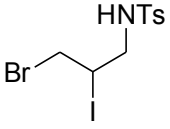
Colorless solid (59 mg, 31%); mp. 55-56 °C; IR (KBr, cm^{-1}) 3196, 1333, 1157; ^1H NMR (270 MHz, $CDCl_3$) δ 1.09 (t, 3H, *J* = 7.02 Hz), 2.44 (s, 3H), 3.18-3.90 (m, 7H), 5.08 (br d, 1H, *J* = 7.3 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 7.77 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.95, 15.2, 21.6, 53.1, 66.8, 70.4, 127.0, 129.7, 137.2, 143.6; MS (CI, isobutane): *m/z* (relative intensity, %) 384 ($[M+H]^+$, 100), 256 ($[M-I]^+$, 21); HRMS (CI, isobutane): *m/z* Calcd for $C_{12}H_{19}INO_3S$ (M+H) 384.0130, found 384.0121.

2-iodo-3-(*p*-toluenesulfonamido)propyl acetate (12a)



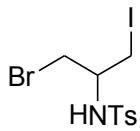
Colorless oil (141 mg, 71%); IR (KBr, cm^{-1}) 3291, 1741, 1331, 1159; ^1H NMR (270 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.44 (s, 3H), 3.31 (t, 2H, 6.5 Hz), 4.11-4.22 (m, 2H), 4.36-4.46 (m, 1H), 5.15 (br t, 2H, *J* = 6.5 Hz), 7.33 (d, 2H, *J* = 8.1 Hz) 7.76 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.6, 26.6, 47.6, 65.9, 126.9, 129.8, 136.6, 143.7, 170.2; MS (CI, isobutane): *m/z* (relative intensity, %) 398 ($[M+H]^+$, 59), 338 ([M-$OCOCH_3$], 100), 270 ($[M-I]^+$, 26); HRMS (CI, isobutane): *m/z* Calcd for $C_{12}H_{17}INO_4S$ (M+H) 397.9923, found 397.9917.

1-bromo-2-iodo-3-(*p*-toluenesulfonamido)propane (13a)



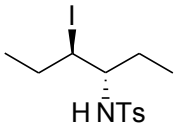
Colorless oil (123 mg, 59%); IR (KBr, cm^{-1}) 3280, 1331, 1159; ^1H NMR (270 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.28-3.39 (m, 1H), 3.45-3.54 (m, 1H), 3.72 (t, 1H, *J* = 10.3 Hz), 3.92 (dd, 1H, *J* = 6.5, 10.3 Hz), 4.26-4.33 (m, 1H), 5.04 (br t, 1H, *J* = 6.5 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 28.9, 34.7, 48.6, 127.0, 129.8, 136.5, 143.8; MS (CI, isobutane): *m/z* (relative intensity, %) 420 ($[M+H+2]^+$, 33), 418 ($[M+H]^+$, 31), 212 ($[M-I-Br]^+$, 100); HRMS (CI, isobutane): *m/z* Calcd for $C_{10}H_{14}BrINO_2S$ (M+H) 417.8973, found 417.8969.

1-bromo-3-iodo-2-(*p*-toluenesulfonamido)propane (13b)



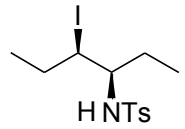
Colorless oil (29 mg, 14%); IR (neat, cm^{-1}) 3269, 1331, 1157; ^1H NMR (270 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.09-3.43 (m, 4H), 3.61-3.66 (m, 1H), 5.04 (br s, 1H), 7.33 (d, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.3, 21.7, 35.8, 53.3, 127.0, 129.9, 136.9, 144.1; MS (CI, isobutane): *m/z* (relative intensity, %) 420 ($[M+H+2]^+$, 92), 418 ($[M+H]^+$, 91), 338 ($[M-Br]^+$, 100), 292 ($[M-I+2]^+$, 43), 290 ($[M-I]^+$, 45), 212 ($[M-I-Br]^+$, 17); HRMS (CI, isobutane): *m/z* Calcd for $C_{10}H_{14}BrINO_2S$ (M+H) 417.8973, found 417.8975.

(3*R,4*S**)-3-iodo-4-(*p*-toluenesulfonamido)hexane (14)**



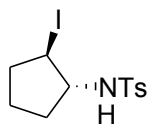
Colorless solid (116 mg, 61%); mp. 110-111 °C; IR (KBr, cm^{-1}) 3277, 1325, 1163; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, 3H, *J* = 7.3 Hz), 0.94 (t, 3H, *J* = 7.3 Hz), 1.33-1.42 (m, 1H), 1.52-1.68 (m, 2H), 1.80-1.86 (m, 1H), 2.44-2.54 (m, 4H), 3.89-3.96 (m, 1H), 4.67 (br d, 1H, *J* = 9.5 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 7.76 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1, 14.6, 21.6, 26.0, 31.1, 49.8, 59.1, 126.8, 129.5, 138.0, 143.4; MS (CI, isobutane): *m/z* (relative intensity, %) 382 ($[M+H]^+$, 96), 254 ($[M-I]^+$, 23); HRMS (CI, isobutane): *m/z* Calcd for $C_{13}H_{21}INO_2S$ (M+H) 382.0338, found 382.0333; Anal. Calcd for $C_{13}H_{20}INO_2S$: C, 40.95; H, 5.29; N, 3.67. Found: C, 41.24; H, 5.10; N, 3.68.

(3*R,4*R**)-3-iodo-4-(*p*-toluenesulfonamido)hexane (15)**



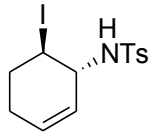
Colorless solid (176 mg, 92%); mp. 115-116 °C; IR (KBr, cm^{-1}) 3253, 1333, 1160; ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (t, 3H, *J* = 7.6 Hz) , 0.97 (t, 3H, *J* = 7.3 Hz) , 1.38-1.88 (m, 4H), 2.43 (s, 3H), 2.72 (td, 1H, *J* = 6.8, 6.8 Hz), 3.97-4.01 (m, 1H), 4.64 (br d, 1H, *J* = 9.5 Hz), 7.29 (d, 2H, *J* = 8.4 Hz), 7.76 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5, 14.7, 21.6, 29.8, 30.8, 46.5, 59.3, 126.8, 129.5, 138.3, 143.3; MS (CI, isobutane): *m/z* (relative intensity, %) 382 ($[M+H]^+$, 100), 254 ($[M-I]^+$, 33); HRMS (CI, isobutane): *m/z* Calcd for $C_{13}H_{21}INO_2S$ (M+H) 328.0338, found 382.0326; Anal. Calcd for $C_{13}H_{20}INO_2S$: C, 40.95; H, 5.29 N, 3.67. Found: C, 41.02; H, 5.01; N, 3.67.

(±) *trans*-2-iodo-1-(*p*-toluenesulfonamide)cyclopentane (16)



Colorless oil (151 mg, 83%); IR (KBr, cm^{-1}) 3245, 1323, 1157; ^1H NMR (270 MHz, $CDCl_3$) δ 1.37-1.48 (m, 1H), 1.68-1.81 (m, 2H), 1.92-2.44 (m, 3H), 2.44 (s, 3H), 3.70-3.77 (m, 1H), 4.00-4.08 (m, 1H), 5.35 (br d, 1H, *J* = 6.5 Hz), 7.31 (d, 2H, *J* = 8.4 Hz), 7.78 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 22.5, 30.0, 30.7, 36.0, 64.5, 127.2, 129.7, 136.7, 143.6; MS (CI, isobutane): *m/z* (relative intensity, %) 366 ($[M+H]^+$, 100), 238 ($[M-I]^+$, 61); HRMS (CI, isobutane): *m/z* Calcd for $C_{12}H_{16}INO_2S$ (M+H) 364.9946, found 364.9950.

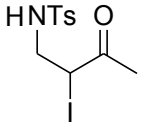
(±) *trans*-4-iodo-3-(*p*-toluenesulfonamide)cyclohexene (17)



Colorless solid (176 mg, 92%); mp. 84-85 °C; IR (KBr, cm^{-1}) 3255, 1331, 1163; ^1H NMR (400 MHz, $CDCl_3$) δ 1.82-1.98 (m, 2H), 2.09-2.18 (m, 2H), 2.45 (s, 3H), 4.01 (br, 1H), 4.37-4.41 (m, 1H), 4.88 (br d, 1H, *J* = 7.3 Hz), 5.32-5.36 (m, 1H), 5.86-5.89 (m, 1H), 7.33 (d, 2H, *J* = 8.4Hz), 7.78 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 24.1, 27.9, 30.3, 55.7, 122.7, 127.0, 129.8, 131.4, 137.0, 143.7; MS (CI, isobutane): *m/z* (relative intensity, %) 378 ($[M+H]^+$, 100), 250 ($[M-I]^+$, 23); HRMS (CI, isobutane): *m/z* Calcd for $C_{13}H_{21}INO_2S$ (M+H) 378.0025, found 378.0020.

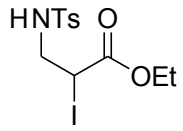
Regiochemistry was determined by 2D NMR.

2-iodo-3-oxo-1-(*p*-toluenesulfonamido)butane (18)



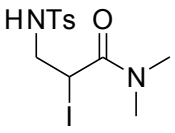
Colorless solid (125 mg, 68%); IR (KBr, cm^{-1}) 3288, 1706, 1329, 1159; ^1H NMR (270 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.43 (s, 3H), 3.26-3.34 (m, 1H), 3.40-3.51 (m, 1H), 4.72 (dd, 1H, *J* = 5.0, 9.3 Hz), 5.51 (br, 1H), 7.32 (d, 2H, *J* = 8.4 Hz), 7.73 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.5, 27.3, 27.5, 46.0, 126.8, 129.7, 136.5, 143.6, 202.3; MS (CI, isobutane): *m/z* (relative intensity, %) 368 ($[M+H]^+$, 100), 240 ($[M-I]^+$, 60); HRMS (CI, isobutane): *m/z* calcd for $C_{11}H_{15}INO_3S$ (M+H) 367.9817, found 367.9813.

ethyl 2-iodo-3-(*p*-toluenesulfonamido)propanoate (19)



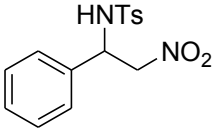
Colorless crystal (189 mg, 95%); mp. 45-47 °C; IR (KBr, cm^{-1}) 3290, 1730, 1331, 1161; ^1H NMR (270 MHz, $CDCl_3$) δ 1.27 (t, 3H, *J* = 7.0 Hz), 2.44 (s, 3H), 3.37-3.46 (m, 2H), 4.20 (q, 2H, *J* = 7.0 Hz), 4.49 (dd, 1H, *J* = 5.4, 9.2 Hz), 5.24 (br, 1H), 7.32 (d, 2H, *J* = 8.1 Hz), 7.73 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.8, 16.9, 21.6, 47.2, 62.4, 126.8, 129.8, 136.7, 143.7, 170.4; MS (CI, isobutane): *m/z* (relative intensity, %) 398 ($[M+H]^+$, 100), 270 ($[M-I]^+$, 64); HRMS (CI, isobutane): *m/z* Calcd for $C_{12}H_{17}INO_4S$ (M+ H) 397.9923, found 397.9928.

2-iodo-*N*, *N*-dimethyl-3-(*p*-toluenesulfonamido)propanamide (20)



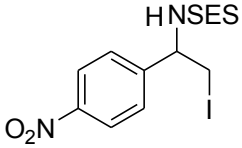
Colorless solid (164 mg, 83%); mp. 109-110 °C; IR (KBr, cm^{-1}) 3201, 1637, 1331, 1161; ^1H NMR (270 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.95 (s, 3H), 2.97 (s, 3H), 3.33-3.43 (m, 1H), 3.52-3.63 (m, 1H), 4.61 (dd, 1H, *J* = 4.7, 10.1 Hz), 5.79 (br, 1H), 7.31 (d, 2H, *J* = 8.1 Hz), 7.73 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 17.0, 21.6, 36.4, 37.8, 47.7, 126.7, 129.6, 136.9, 143.4, 168.6; MS (CI, isobutane): *m/z* (relative intensity, %) 397($[M+H]^+$, 100), 269 ($[M-I]^+$, 27); HRMS (CI): *m/z* calcd for $C_{12}H_{18}IN_2O_3S$ (M+H) 397.0083, found 397.0084; Anal. Calcd for $C_{12}H_{17}IN_2O_3S$: C, 36.37; H, 4.32 N, 7.07. Found: C, 36.46; H, 4.03; N, 7.04.

_N_-(2-nitro-1-phenylethyl)toluenesulfonamide (21)[S5]



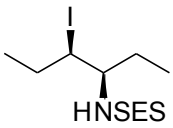
Colorless solid (158 mg, 99%); IR (KBr, cm^{-1}) 3251, 1544, 1381, 1323, 1161; mp. 156-157 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.40 (s, 3H), 4.60 (dd, 1H, *J* = 6.5, 13.2 Hz), 4.82 (dd, 1H, *J* = 6.8, 13.2 Hz), 4.95-5.00 (m, 1H), 5.54 (br d, 1H, *J* = 7.6 Hz), 7.08 (d, 2H, *J* = 8.1 Hz), 7.20-7.26 (m, 5H), 7.64 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.6, 55.4, 78.9, 126.3, 127.0, 128.9, 129.1, 129.6, 135.1, 136.3, 143.9; MS (CI, isobutane): *m/z* (relative intensity, %) 321 ($[M+H]^+$, 3), 260 ($[M-CH_2NO_2]^+$, 34), 172 ($[TsNH_2+H]^+$, 100); HRMS (CI, isobutane): *m/z* Calcd for $C_{15}H_{17}N_2O_4S$ (M+H) 321.0909, found 321.0913; Anal. Calcd for $C_{15}H_{17}N_2O_4S$: C, 56.24; H, 5.03; N, 8.74. Found: C, 56.00; H, 4.77; N, 8.66.

2-iodo-1-(4-nitrophenyl)-1-(2-(trimethylsilyl)ethylsulfonamido)ethane (22)



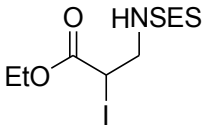
Colorless solid (192 mg, 82%); mp. 129-130 °C; IR (KBr, cm^{-1}) 3274, 1519, 1346, 1273, 1137; ^{1}H NMR (270 MHz, $CDCl_3$) δ -0.01 (s, 9H), 0.94-1.04 (m, 2H), 2.81-2.92 (m, 2H), 2.93-3.00 (m, 2H), 3.46 (td, 1H, *J* = 6.8, 6.8 Hz), 3.58 (td, 1H, *J* = 6.8, 6.8 Hz), 4.73-4.78 (m, 1H), 5.12 (br d, 1H, 7.8 Hz), 7.54 (d, 2H, *J* = 8.6 Hz), 8.26 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ –1.9, 10.6, 10.9, 50.7, 57.5, 124.1, 127.4, 146.6, 147.7; MS (CI, isobutane): *m/z* (relative intensity, %) 457 ($[M+H]^+$, 2) , 443 ($[M-CH_3+2]^+$, 10), 442 ($[M-CH_3+1]^+$, 19), 441 ($[M-CH_3]^+$, 100), 313 ($[M-CH_3-I]^+$, 100); HRMS (CI, isobutane): *m/z* Calcd for $C_{13}H_{22}IN_2O_4SSi$ (M+ H) 457.0114, found 457.0096.

(3*R,4*R**)-3-iodo-4-(2-(trimethylsilyl)ethylsulfonamido)hexane (23)**



Colorless solid (190 mg, 97%); mp. 79-80 °C; IR (KBr, cm^{-1}) 3257, 1315, 1142; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 9H) , 0.95 (t, 3H, *J* = 11.2 Hz) , 1.04-1.10 (m, 5H), 1.67 (td, 2H, *J* = 7.3, 7.3 Hz) 1.81-2.12 (m, 2H) 2.77-2.82 (m, 1H), 2.97 (td, 2H, J = 5.9, 5.9 Hz), 4.11-4.17(m, 1H) , 4.28 (br d, 1H, *J* = 4.9 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.86, 10.7, 10.9, 14.7, 31.1, 31.5, 47.3, 51.0, 59.3; MS (CI, isobutane): *m/z* (relative intensity, %) 392 ($[M+H]^+$, 11), 378 ($[M-CH_3+2]^+$, 9) , 377 ($[M-CH_3+1]^+$, 16), 376 ($[M-CH_3]^+$, 100), 254 ($[M-I]^+$, 3); HRMS (CI, isobutane): *m/z* Calcd for $C_{13}H_{21}INO_2S$ (M+H) 392.0576, found 392.0580.

ethyl 2-iodo-3-(2-(trimethylsilyl)ethylsulfonamido)propanoate (24)



Colorless oil (149 mg, 73%); IR (KBr, cm^{-1}) 3217, 1726, 1323, 1257, 1140; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.98-1.05 (m, 2H), 1.30 (t, 3H, *J* = 7.3 Hz), 2.93-3.00 (m, 2H), 3.53-3.63 (m, 2H), 4.20-4.29 (m, 2H), 4.56 (dd, 1H, *J* = 3.5 Hz, 9.7 Hz), 5.02 (br t, 1H, *J* = 6.8 Hz); ^{13}C NMR (68 MHz, $CDCl_3$) δ −1.9, 10.7, 13.8, 17.7, 47.4, 49.8, 62.4, 170.5; MS (CI, isobutane): *m/z* (relative intensity, %) 408 ($[M+H]^+$, 50), 270 ($[M-I]^+$, 64); HRMS (CI, isobutane): *m/z* Calcd for $C_{10}H_{23}INO_4SSi$ (M+ H) 408.0162, found 408.0174.

X-ray Structure Analysis.

All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation. The structure of **8** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are summarized in Table S1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-778523 for **8**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

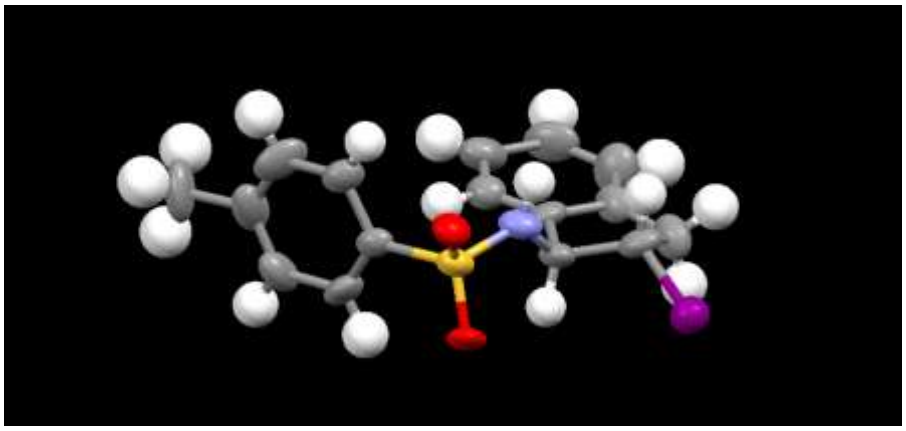


Figure S2. Molecular structure of **8** (trans adduct).

Table S1: Crystallographic data for **8**

	8
Empirical formula	$C_{16}H_{16}O_2NSI$
Formula weight	413.27
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a [Å]	5.1624(2)
b [Å]	17.4656(6)
c [Å]	18.1124(6)
V [Å^3]	7762.7(10)
Z	4
D_{calcd} [g cm^{-3}]	1.681
μ(Cu Kα) [cm^{-1}]	166.275
T [°C]	-100.0
λ(Cu Kα) [Å]	1.54187
*R*1[a]	0.0759
*wR*2[b]	0.2140

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

References

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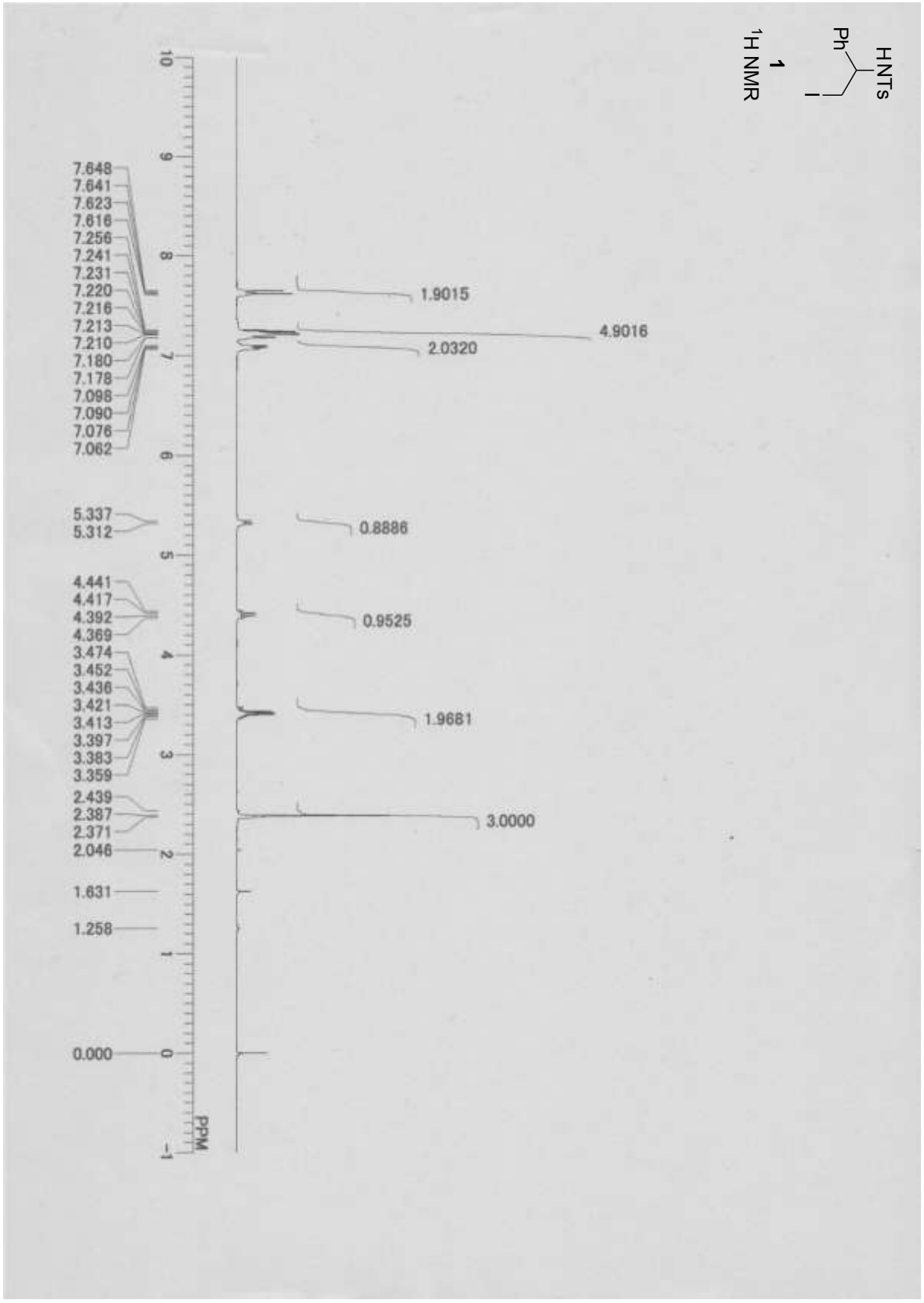
S2 J. S. Yadav, B. V. S. Reddy, M. S. Reddy and A. R. Prasad, *Tetrahedron Lett*., 2002, **43**, 9703.

S3 S. Minakata, T. Hotta, Y. Oderaotoshi and M. Komatsu, *J. Org. Chem.,* 2006, **71**, 7471.

S4 S. Minakata, Y. Okada, Y. Oderaotoshi and M. Komatsu, *Org. Lett.,* 2005, **7**, 3509.

S5 F. Gao, M. Deng and C. Qian, *Tetrahedron,* 2005, **61**, 12238.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7.220
7.216
7.213
7.210
7.180
7.178
7.098
7.090
7.076
7.062
5.337
5.312
4.441
4.417
4.392
4.369
3.474
3.452
3.436
3.421
3.413
3.397
3.383
3.359
2.439
2.387
2.371
2.046
1.631
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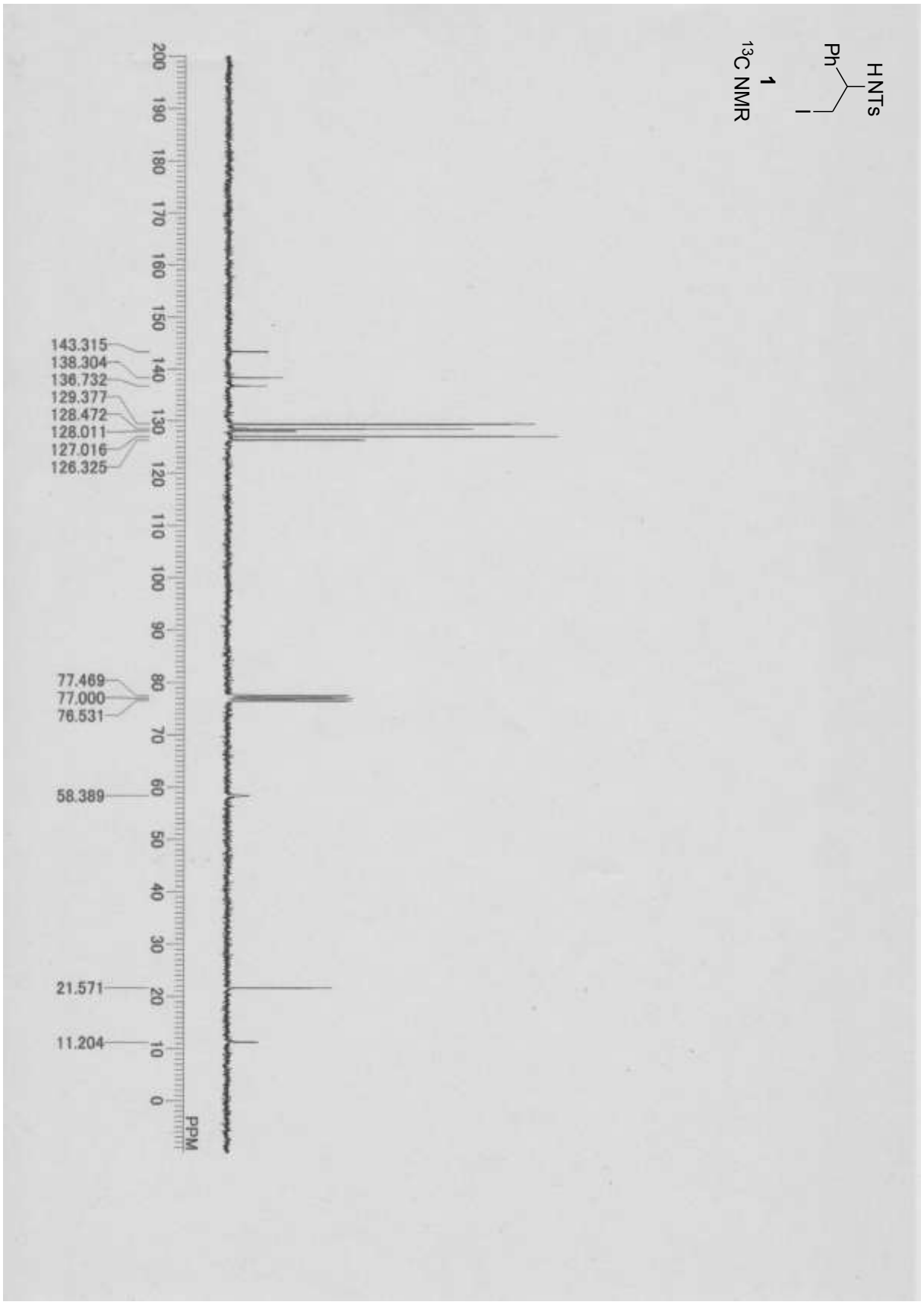
1.9015
4.9016
2.0320
0.8886
0.9525
1.9681
3.0000
PPM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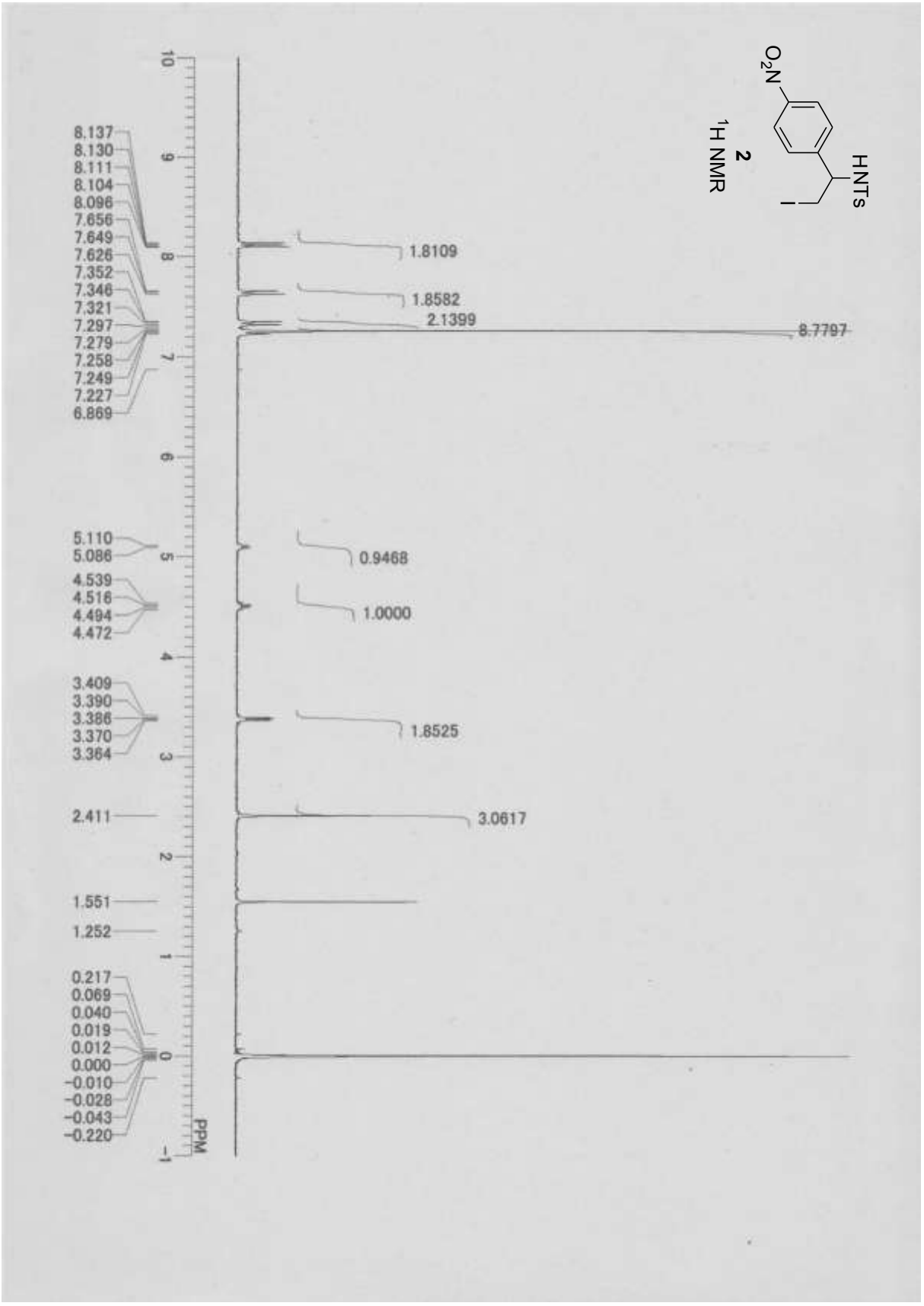
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7.626
7.352
7.346
7.321
7.297
7.279
7.258
7.249
7.227
6.869
5.110
5.086
4.539
4.516
4.494
4.472
3.409
3.390
3.386
3.370
3.364
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1.252
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0.069
0.040
0.019
0.012
0.000
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-0.028
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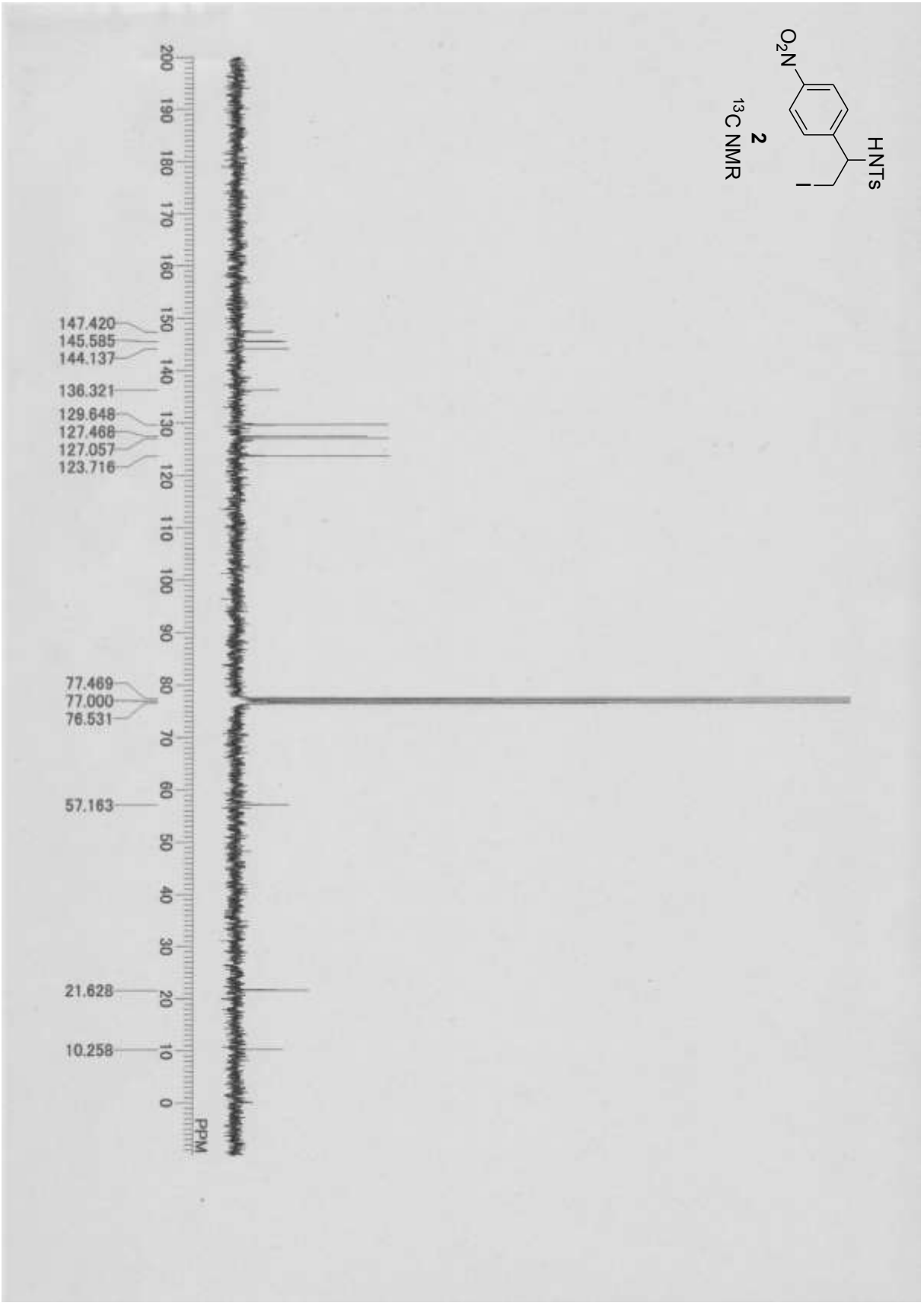
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77.000
76.531
57.163
21.628
10.258
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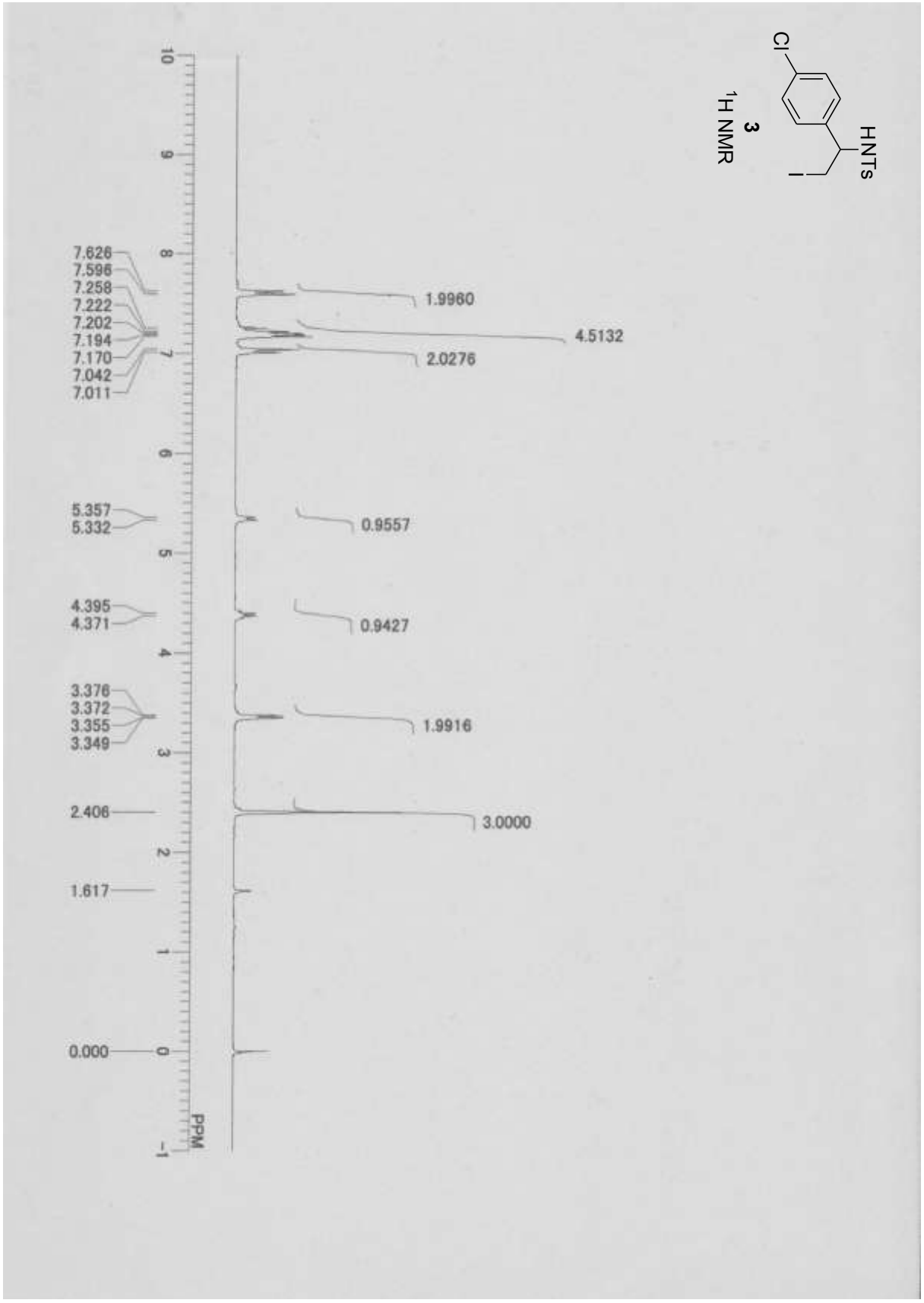
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7.011
5.357
5.332
4.395
4.371
3.376
3.372
3.355
3.349
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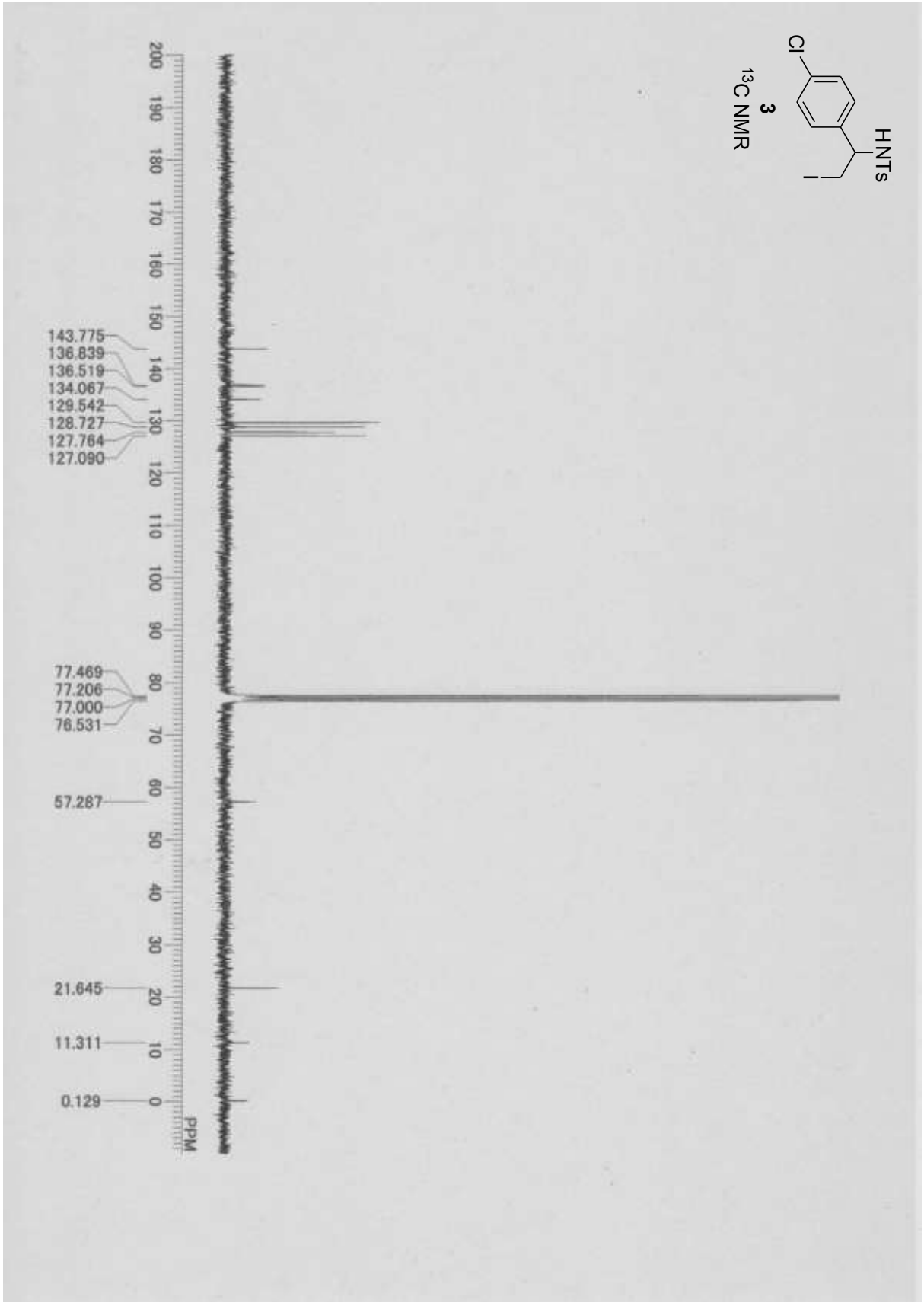
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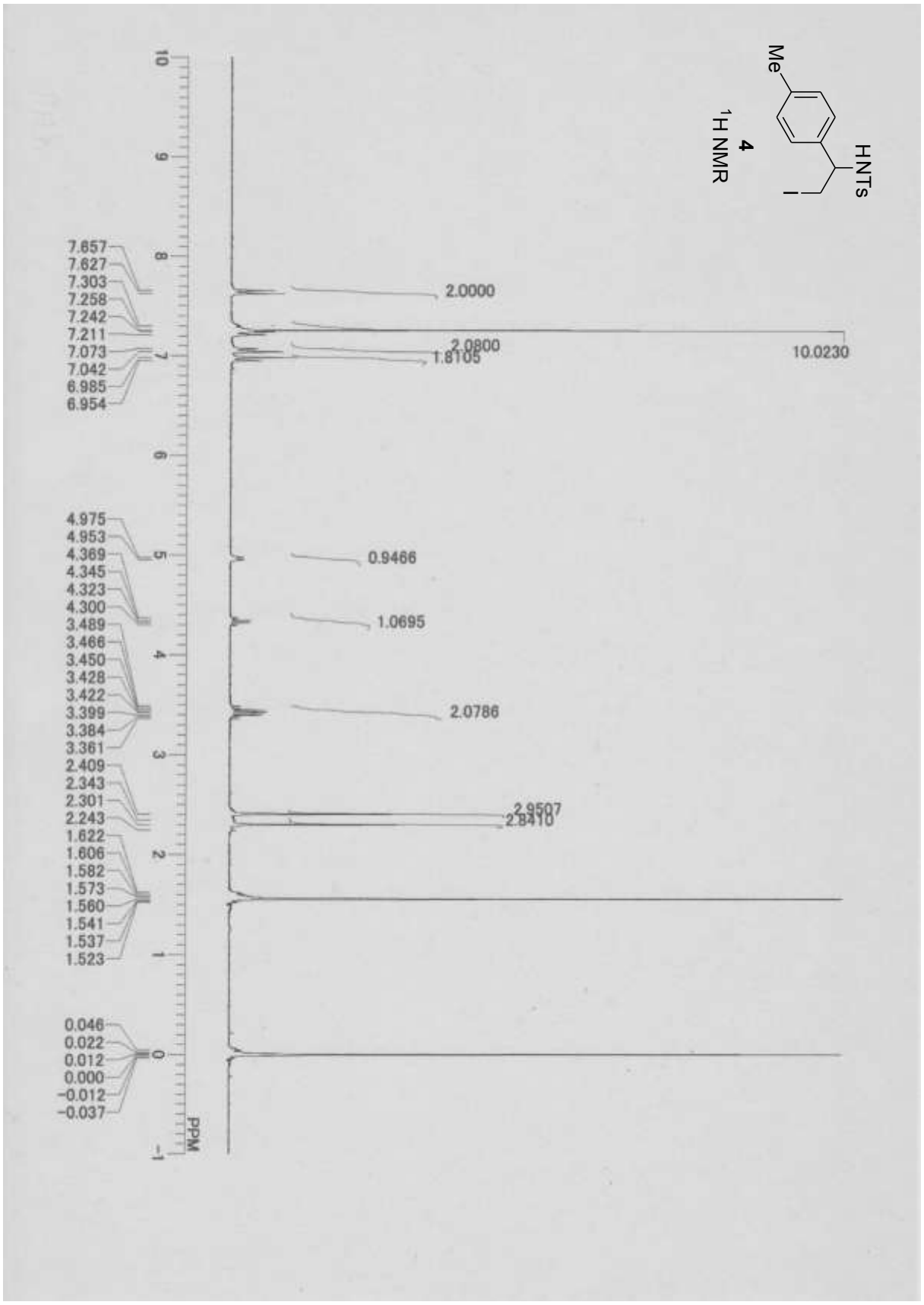
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4.975
4.953
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4.345
4.323
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3.466
3.450
3.428
3.422
3.399
3.384
3.361
2.409
2.343
2.301
2.243
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1.606
1.582
1.573
1.560
1.541
1.537
1.523
0.046
0.022
0.012
0.000
-0.012
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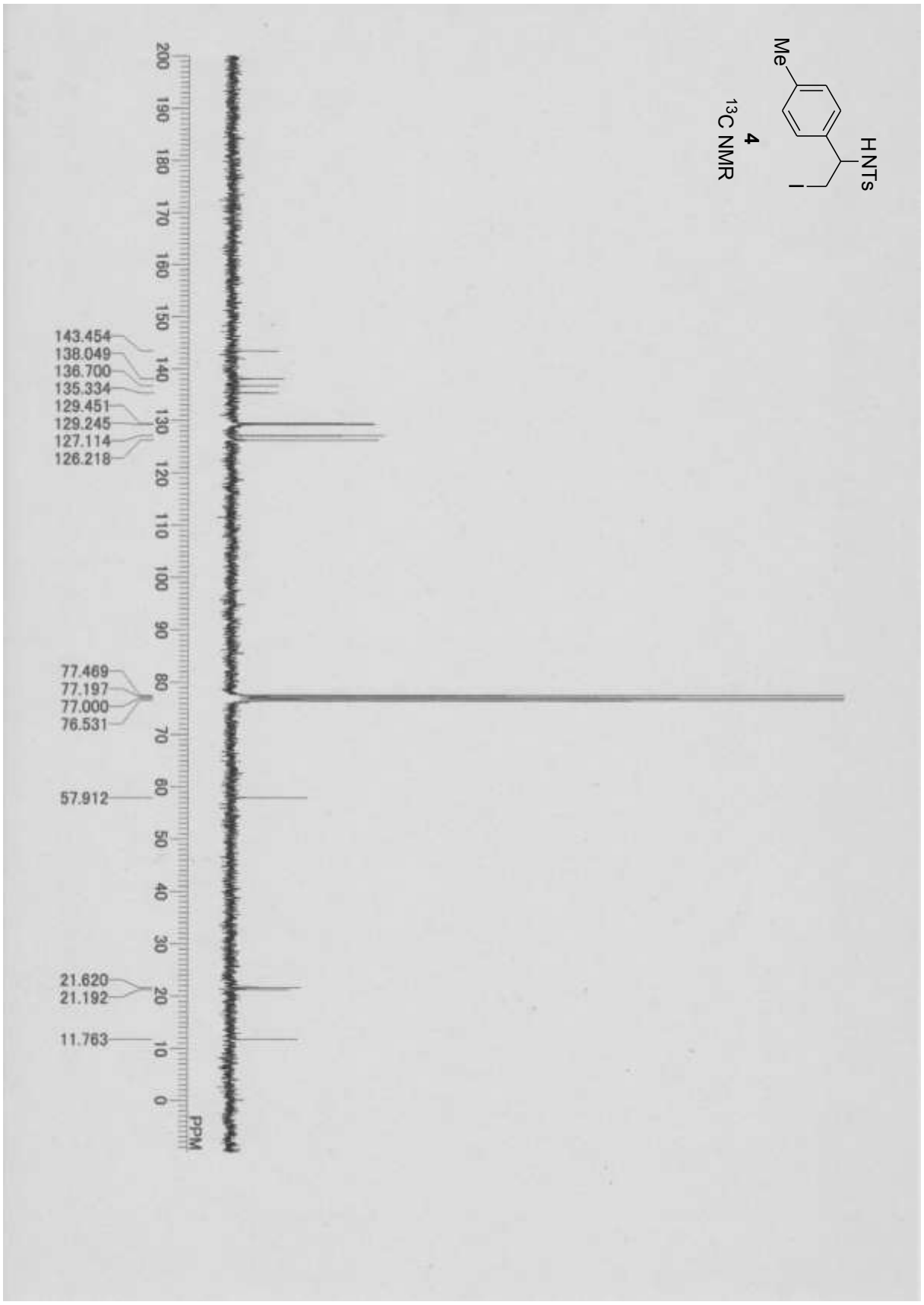
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I
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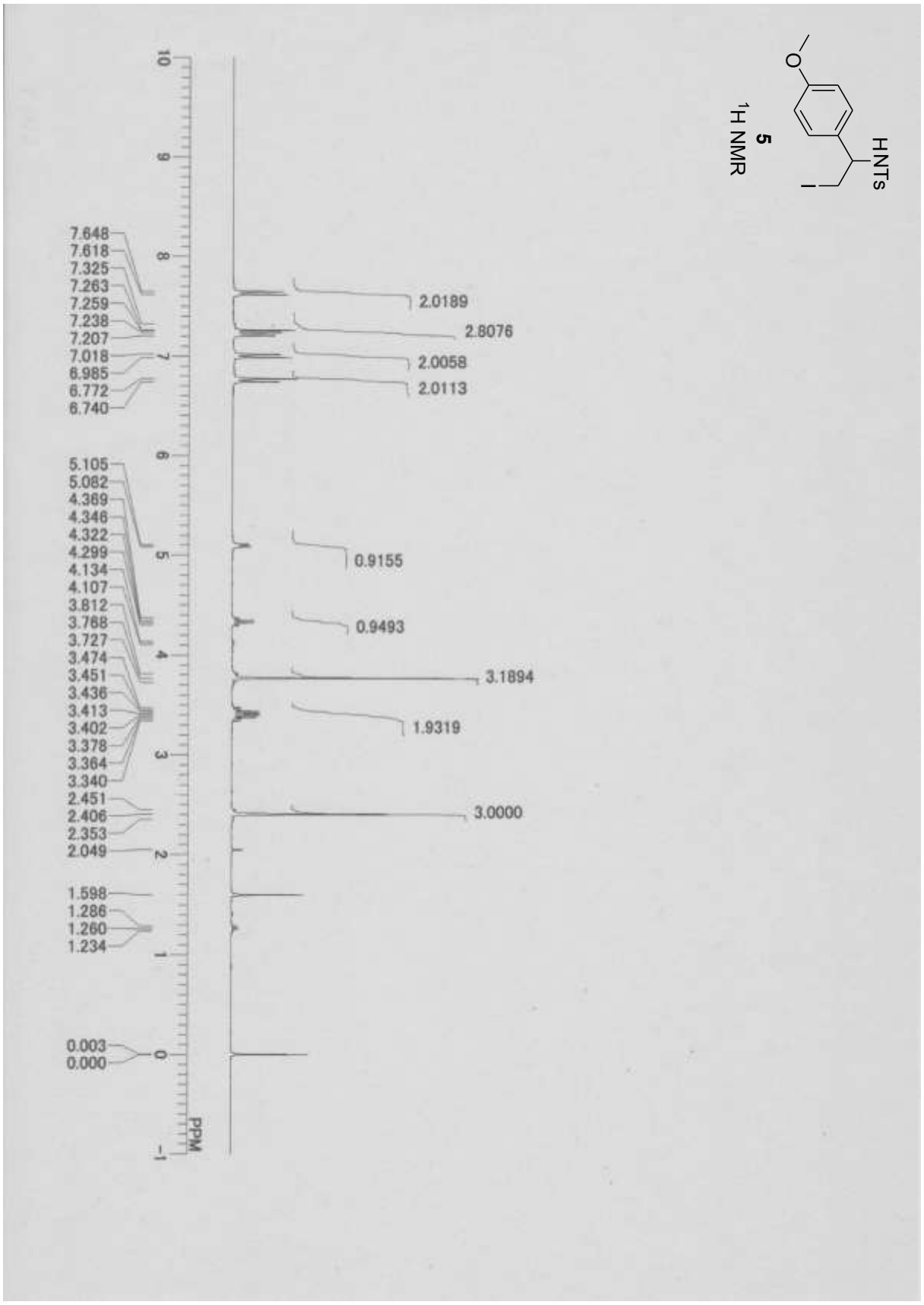
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6.740
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5.082
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4.346
4.322
4.299
4.134
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3.727
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1.260
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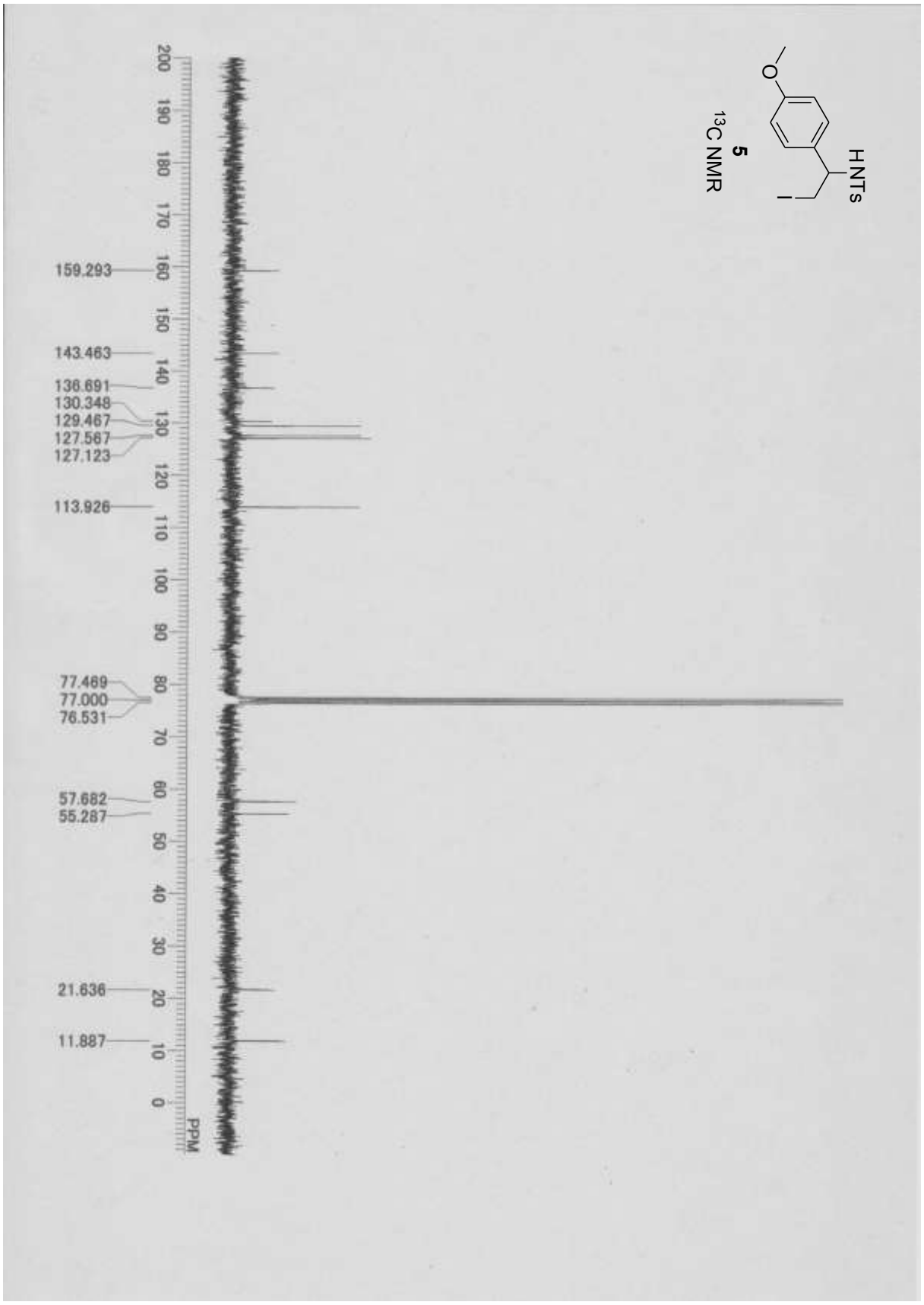
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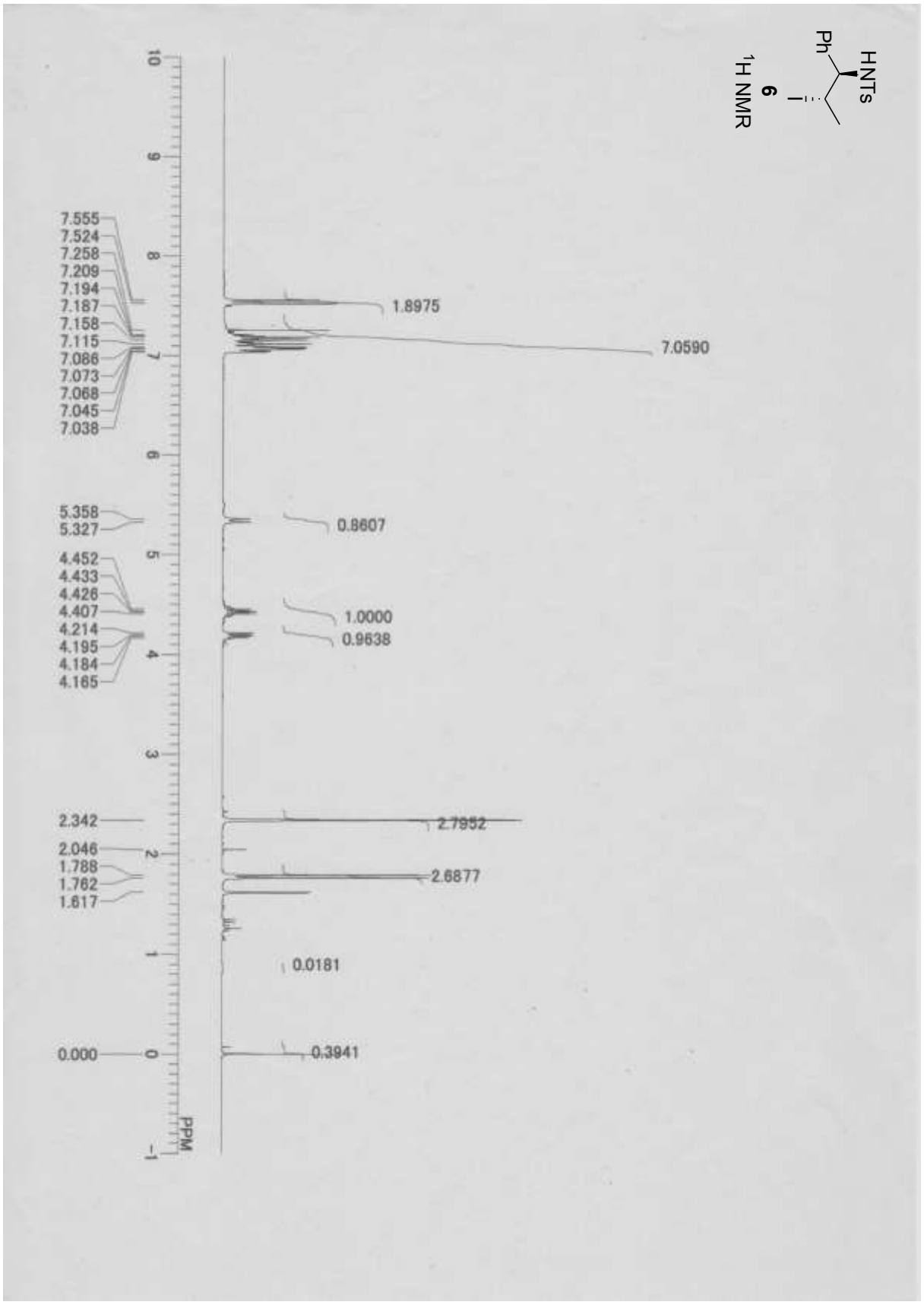
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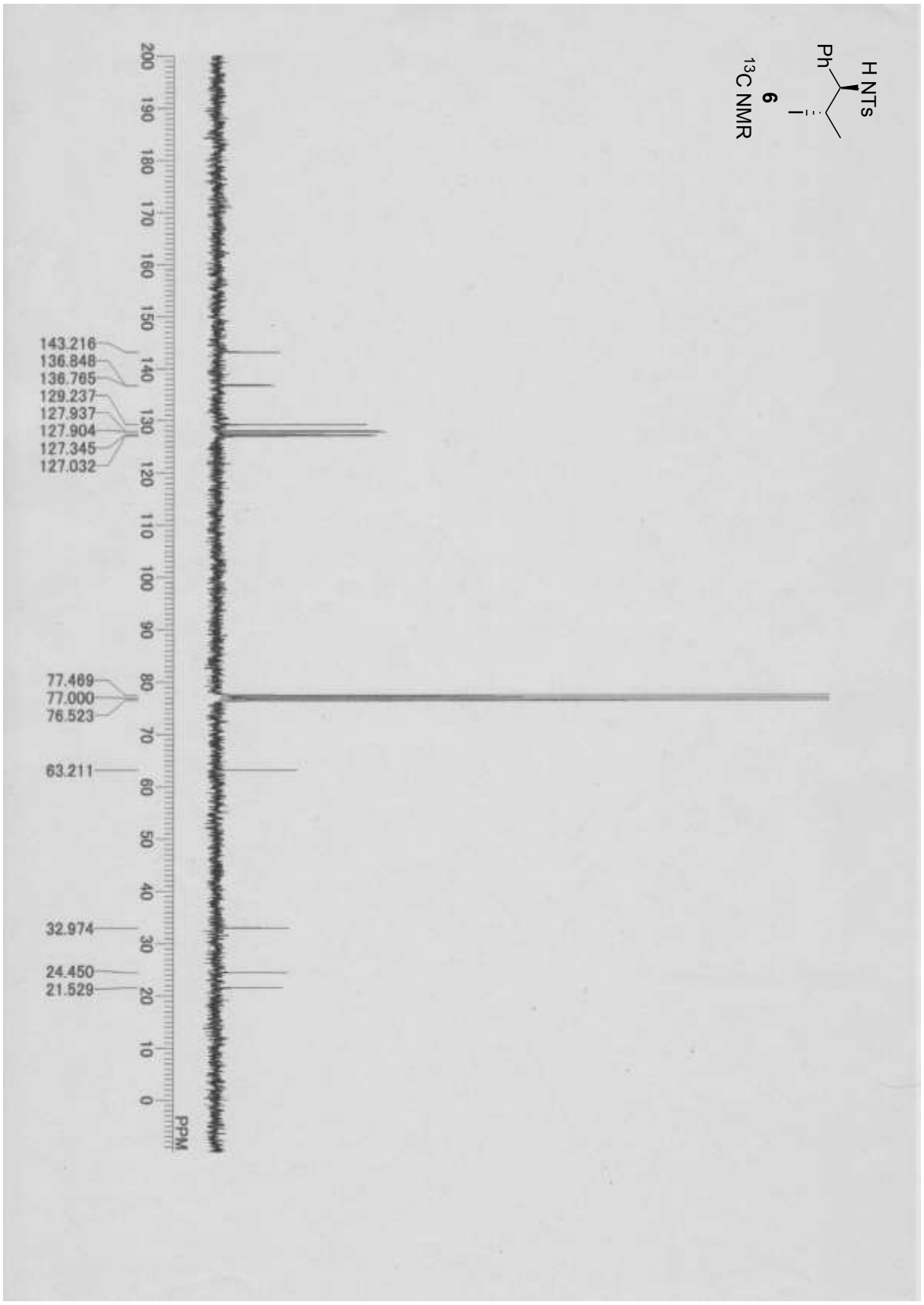
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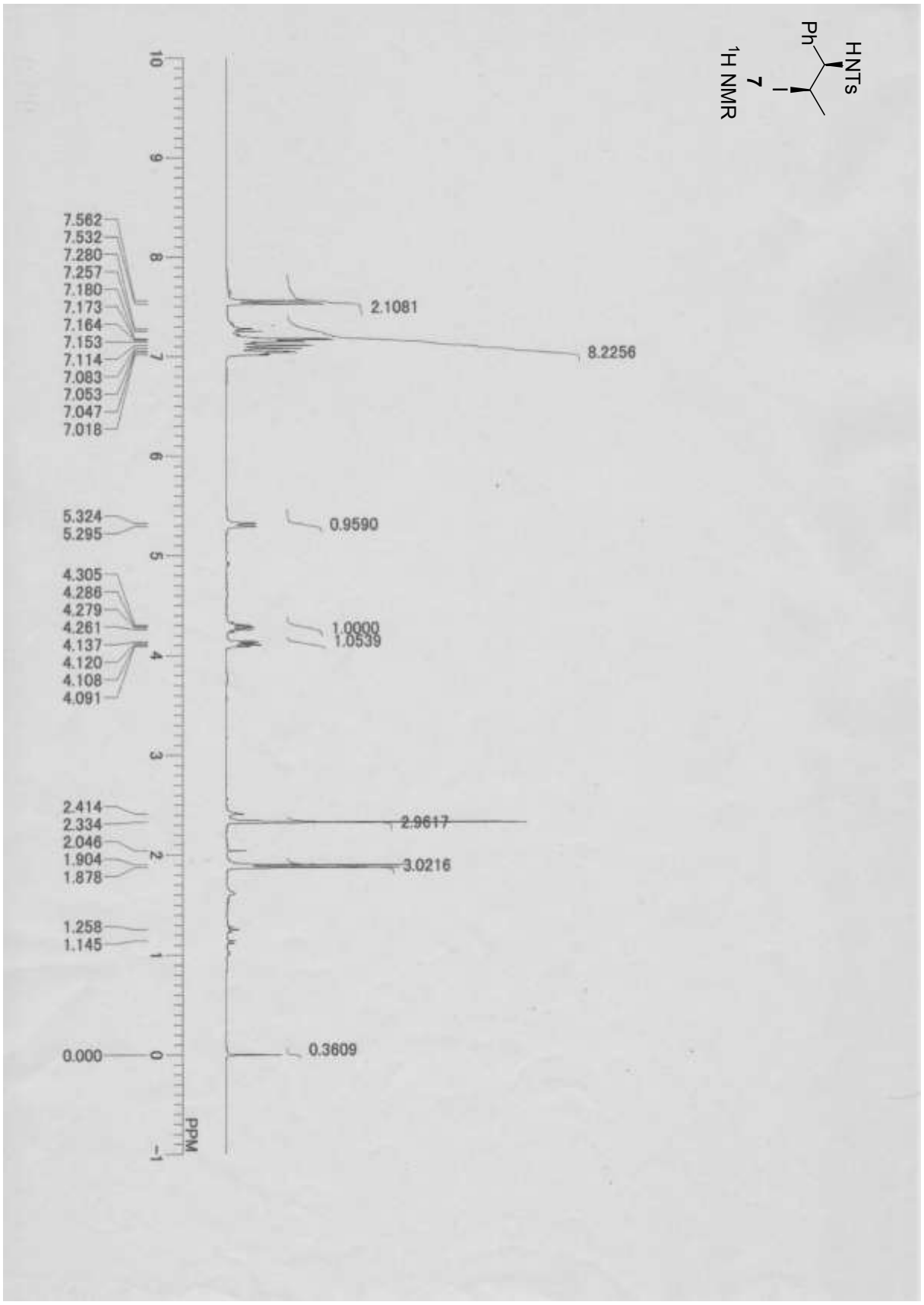
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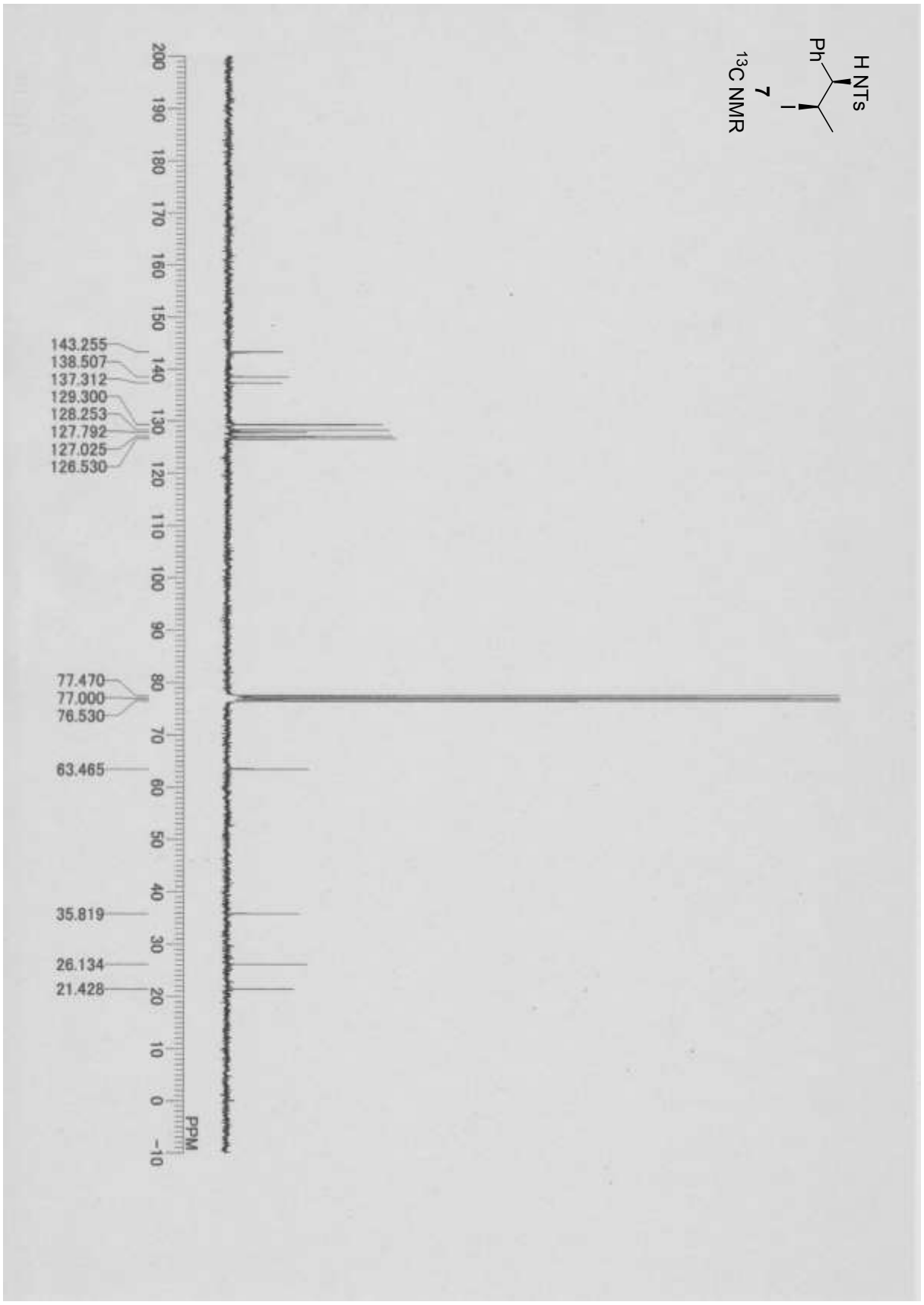
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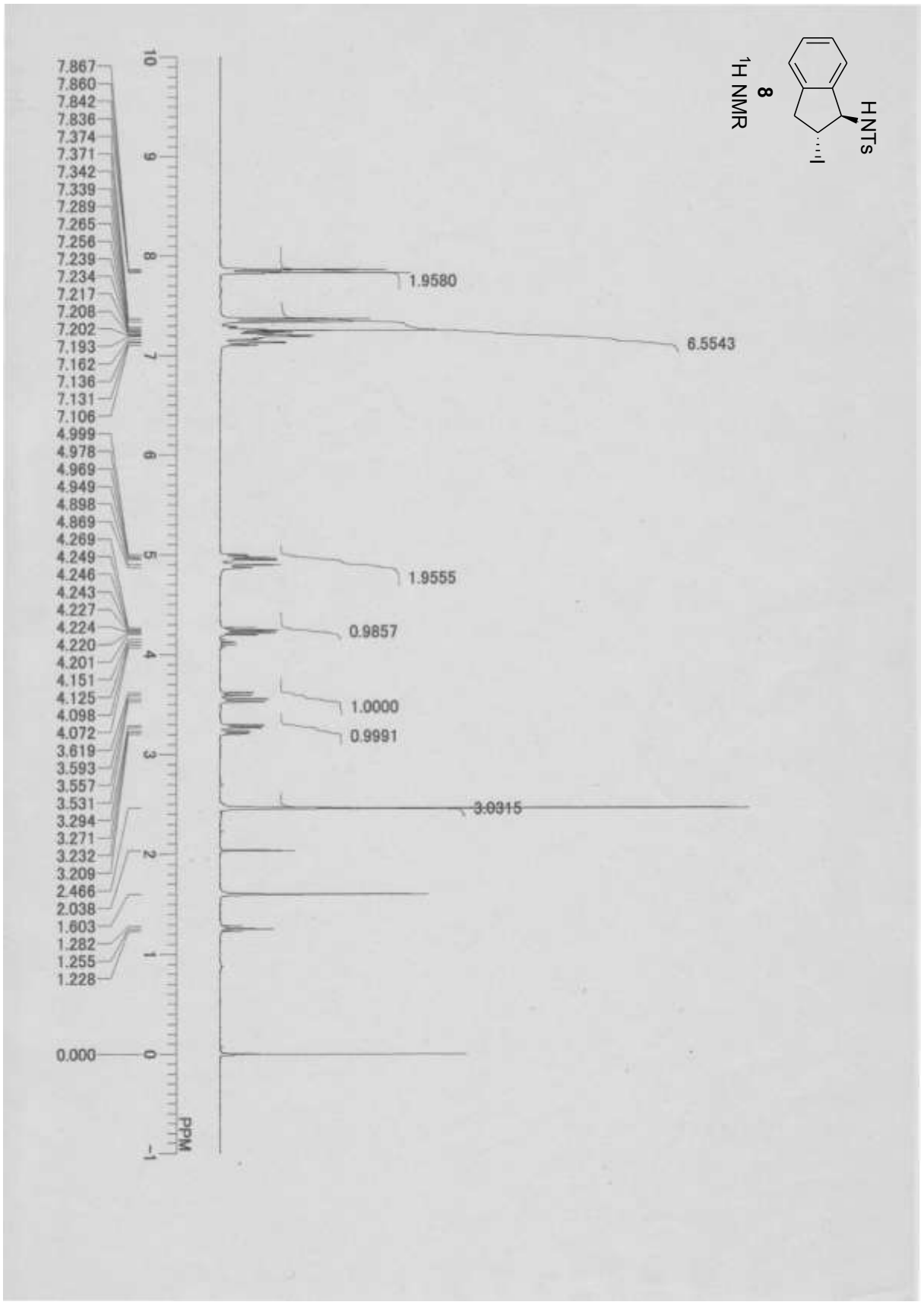
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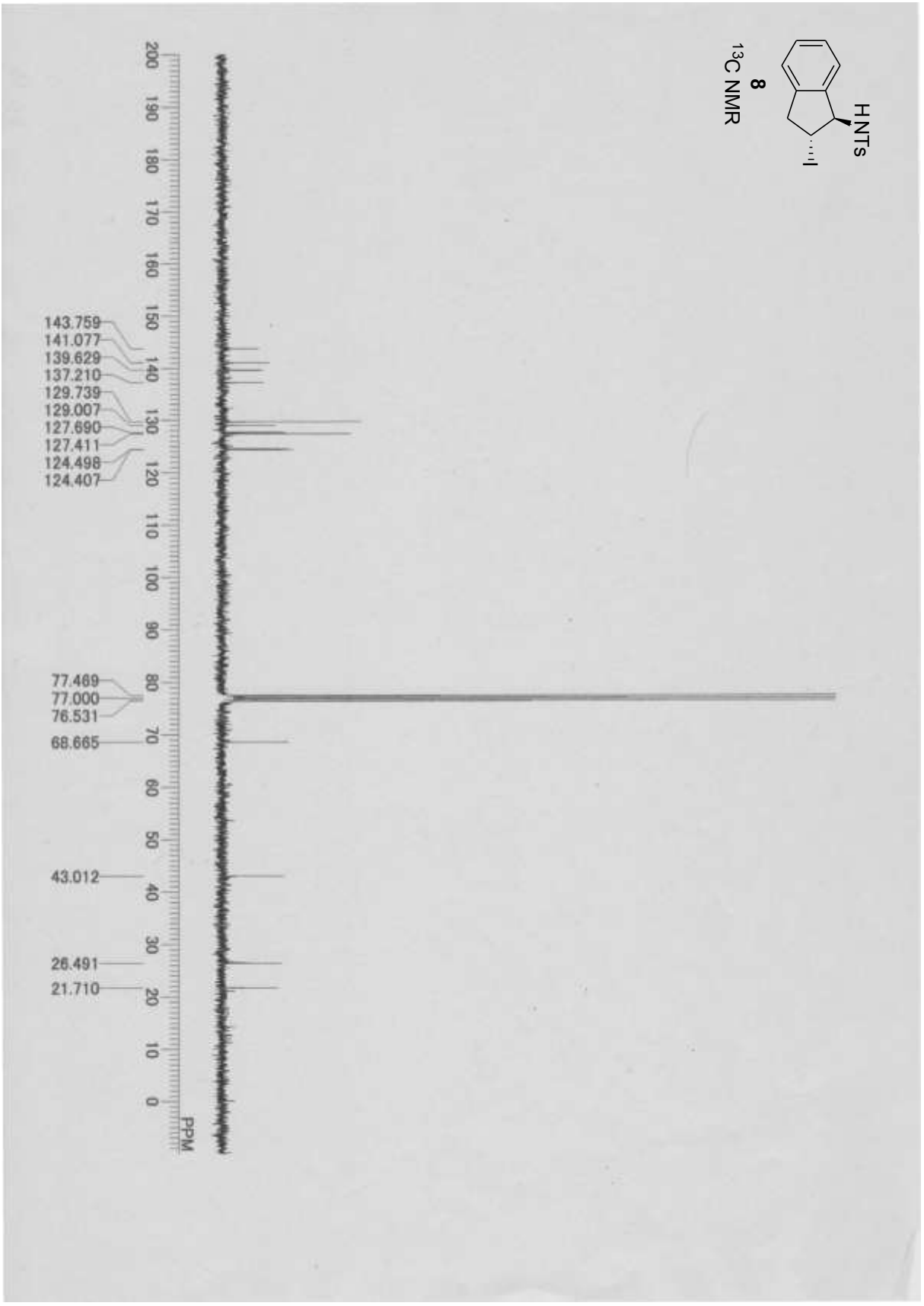
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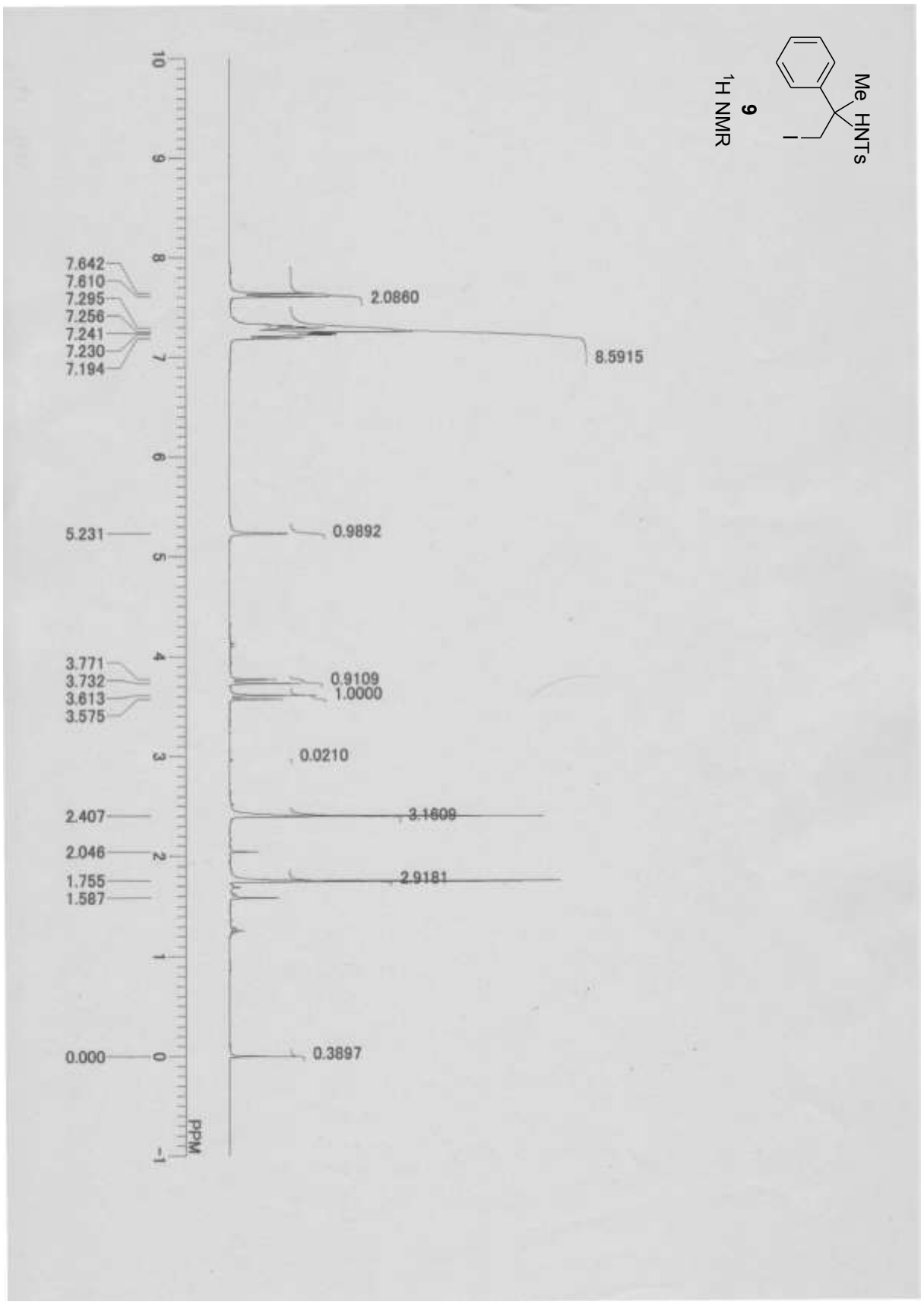
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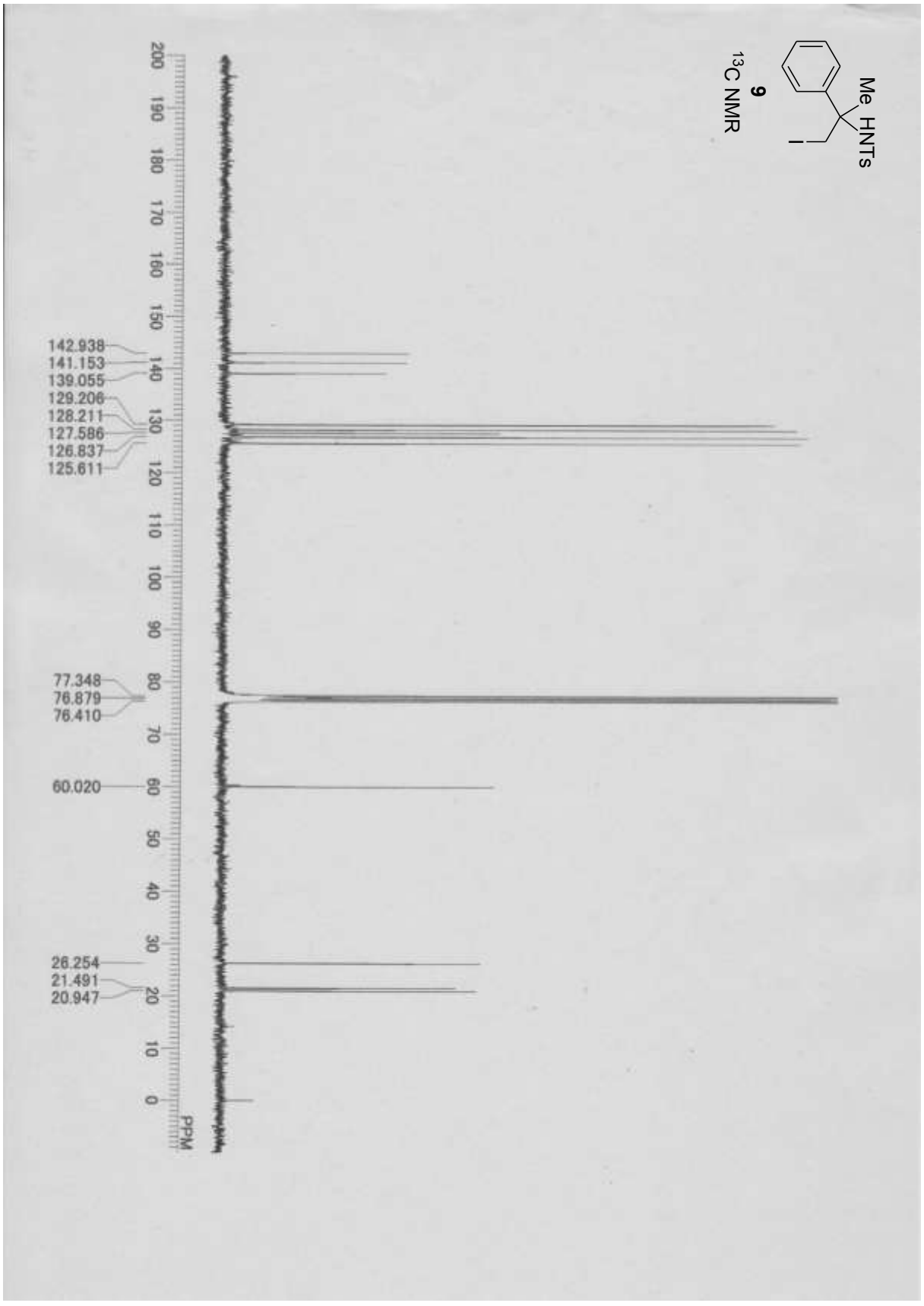
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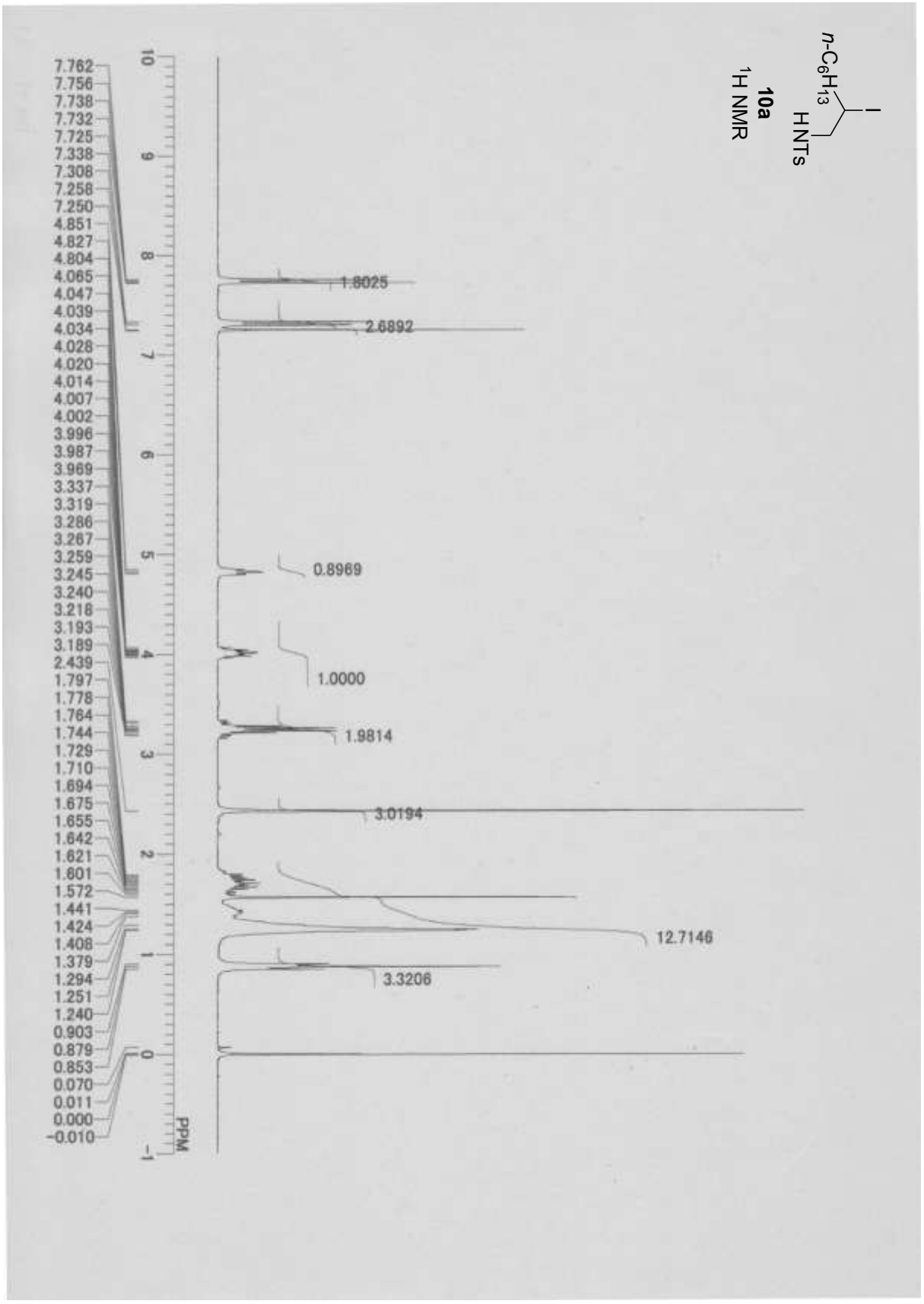
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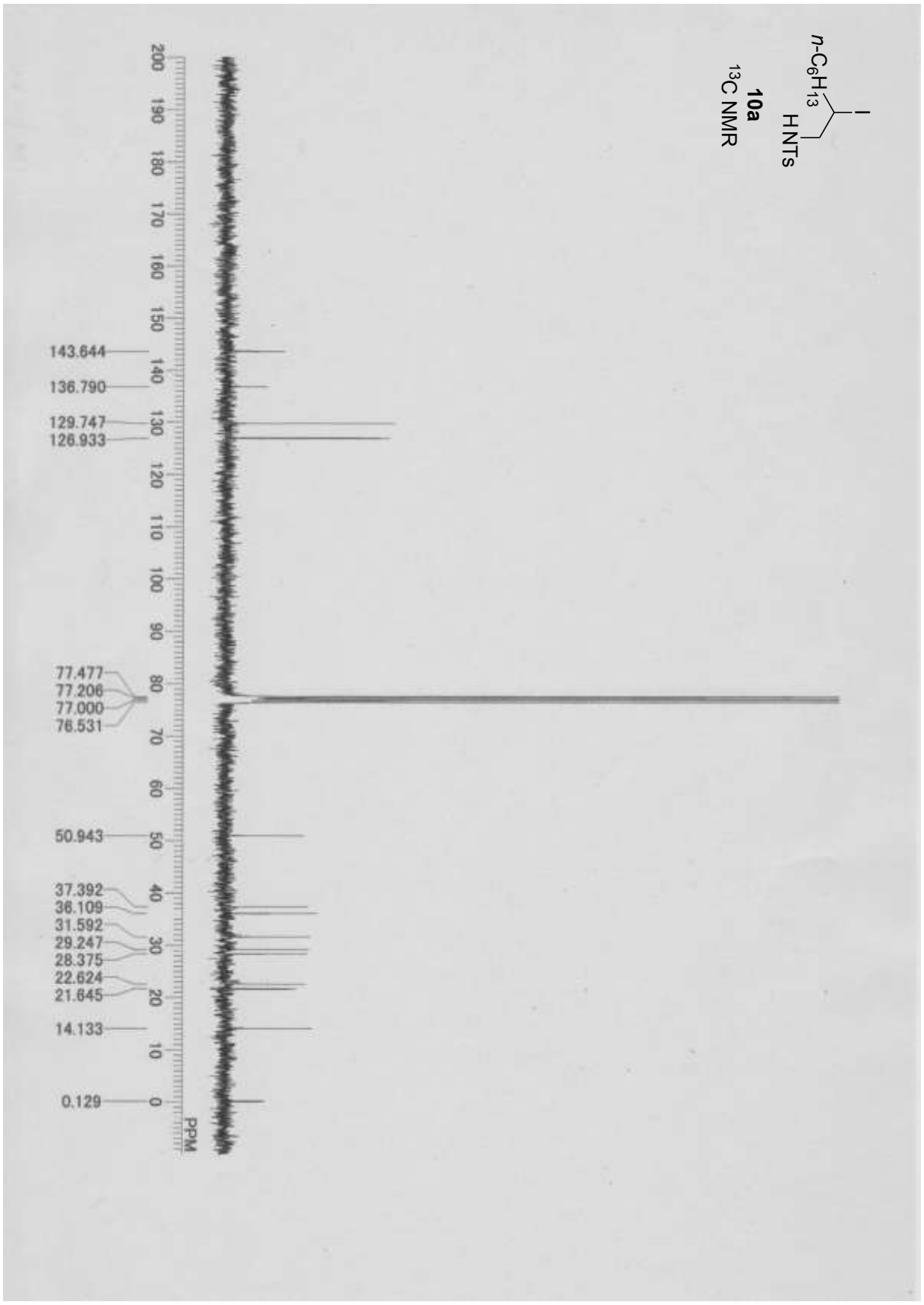
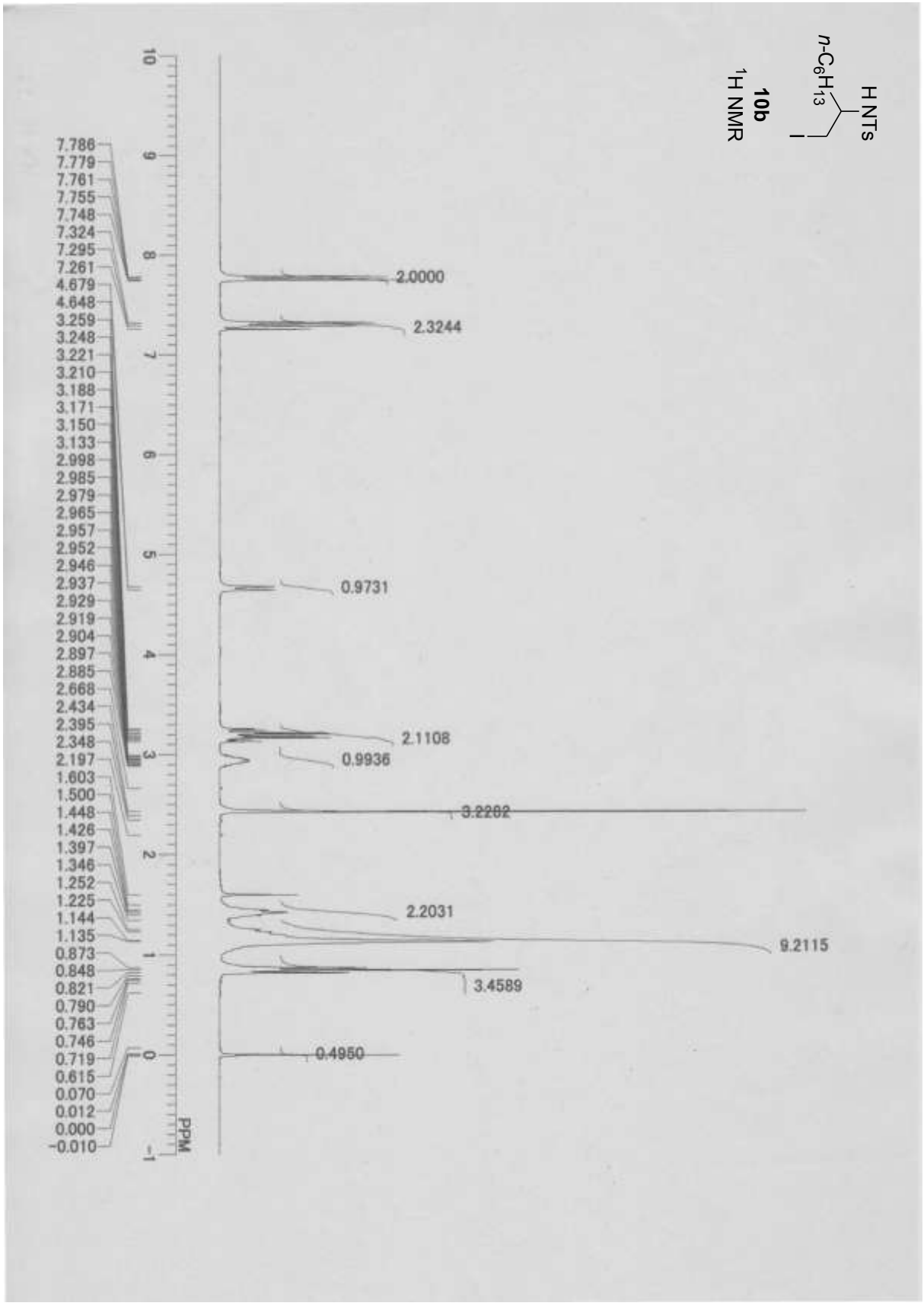
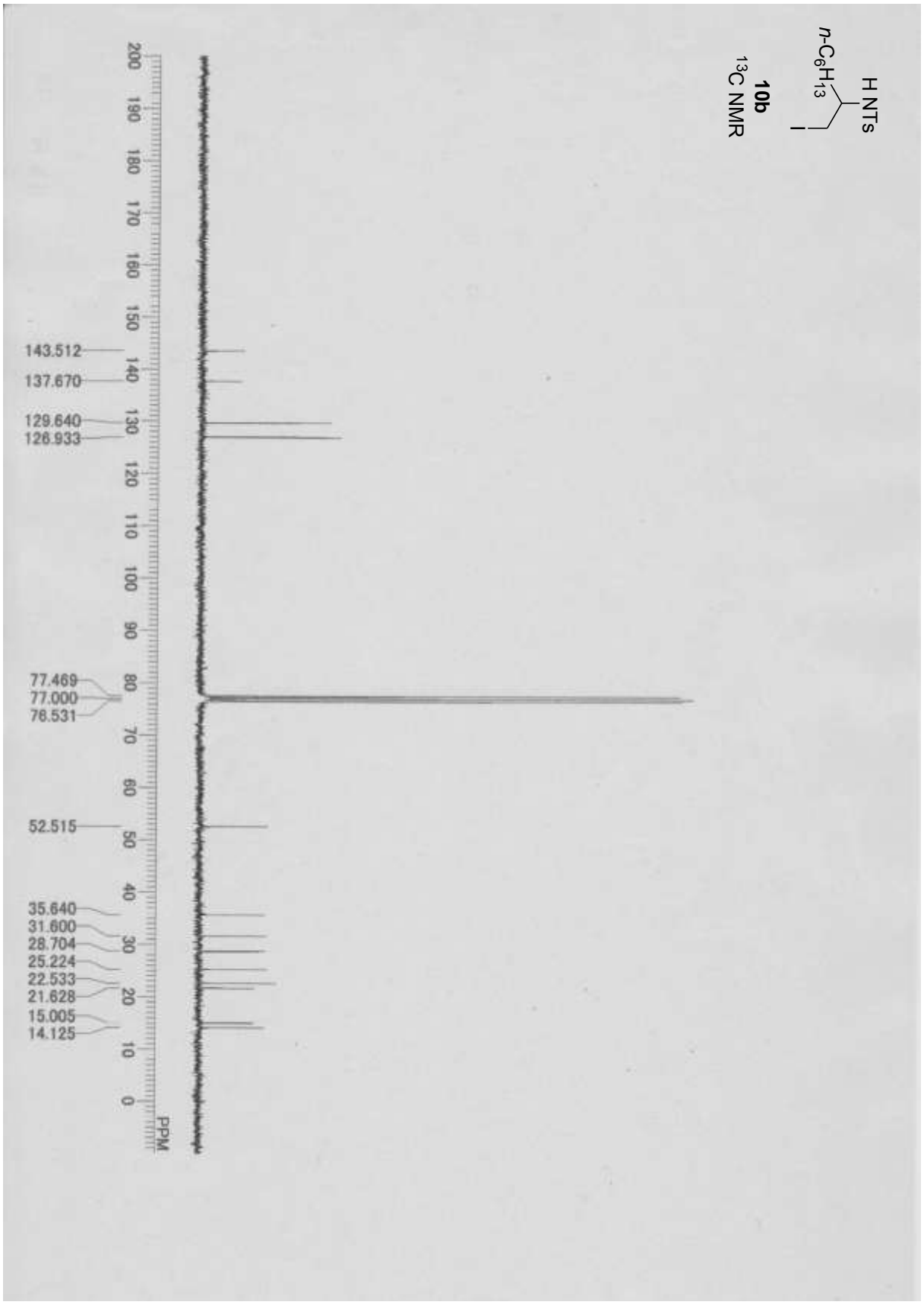
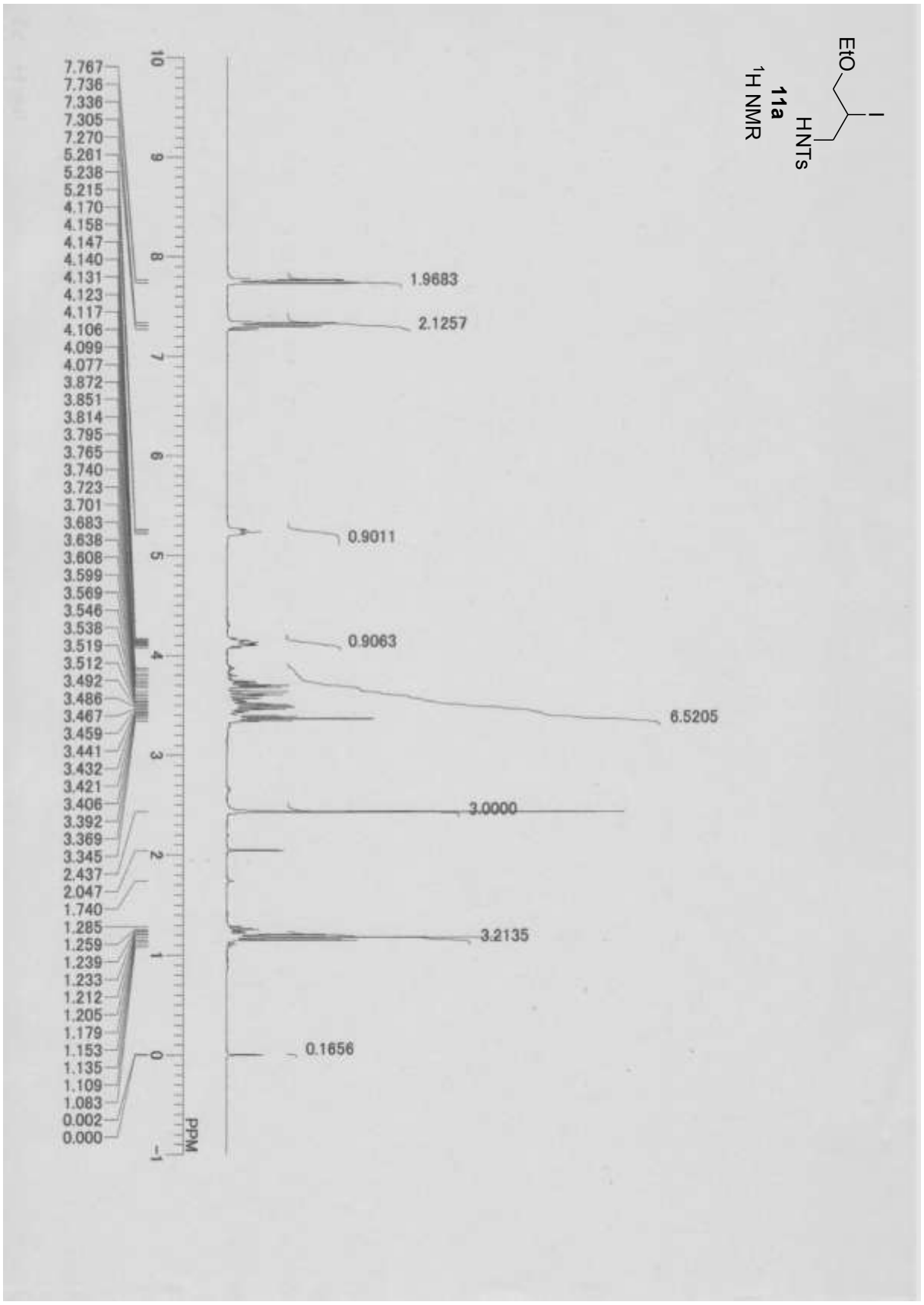
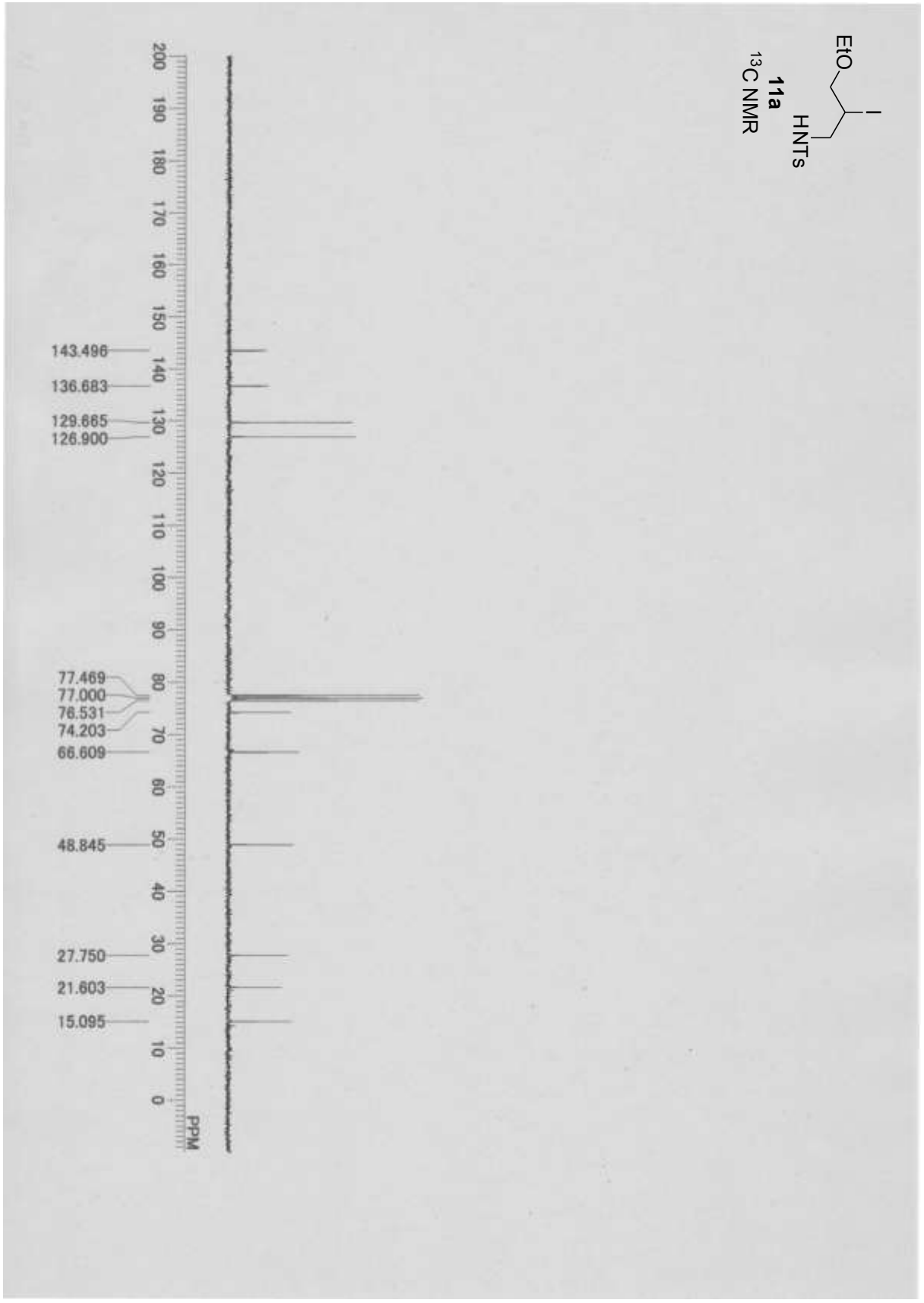
3.3206
PPM

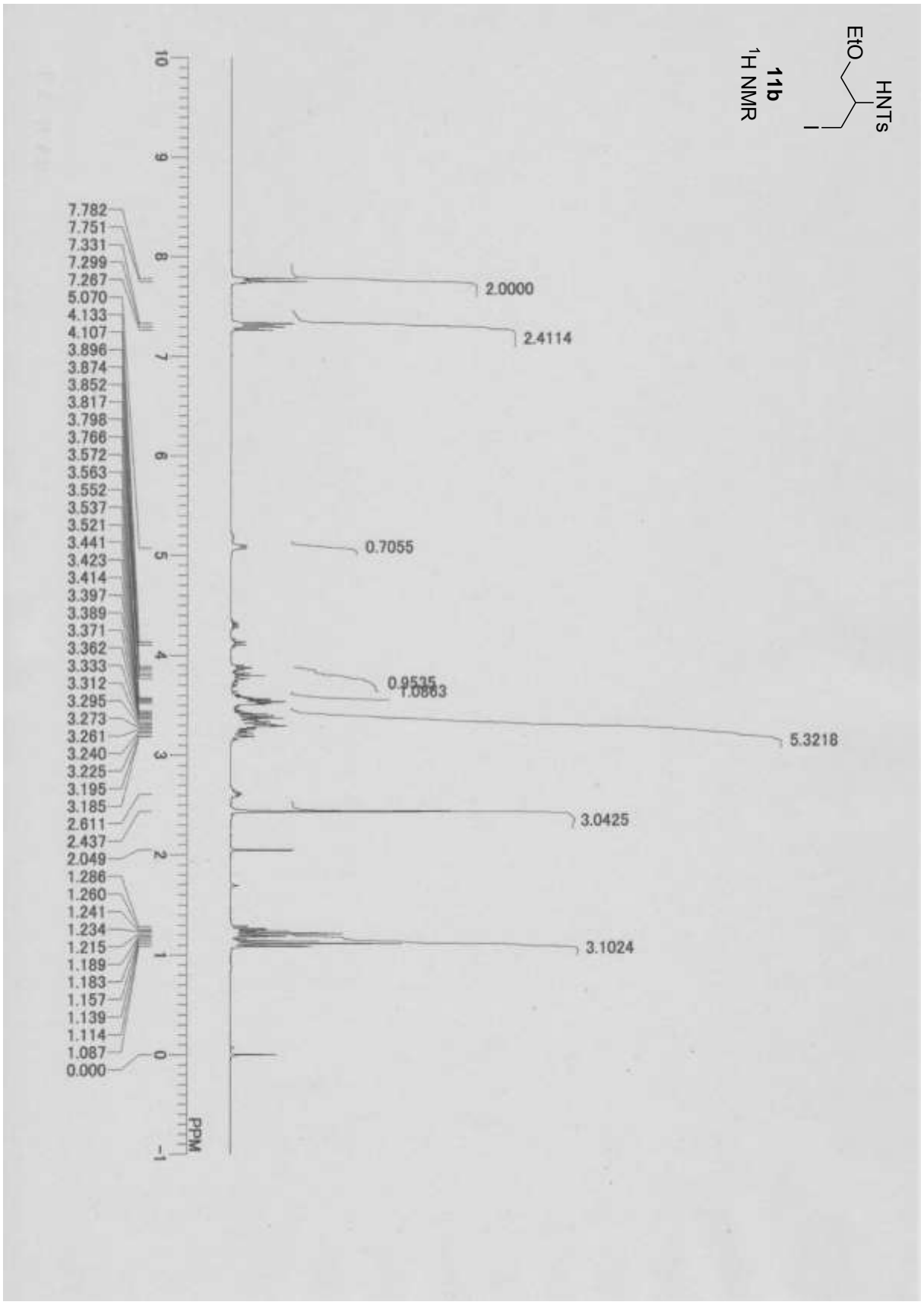

10a
13C NMR
n-C6H13
I
HNTs
143.644
136.790
129.747
126.933
77.477
77.206
77.000
76.531
50.943
37.392
36.109
31.592
29.247
28.375
22.624
21.645
14.133
0.129
PPM

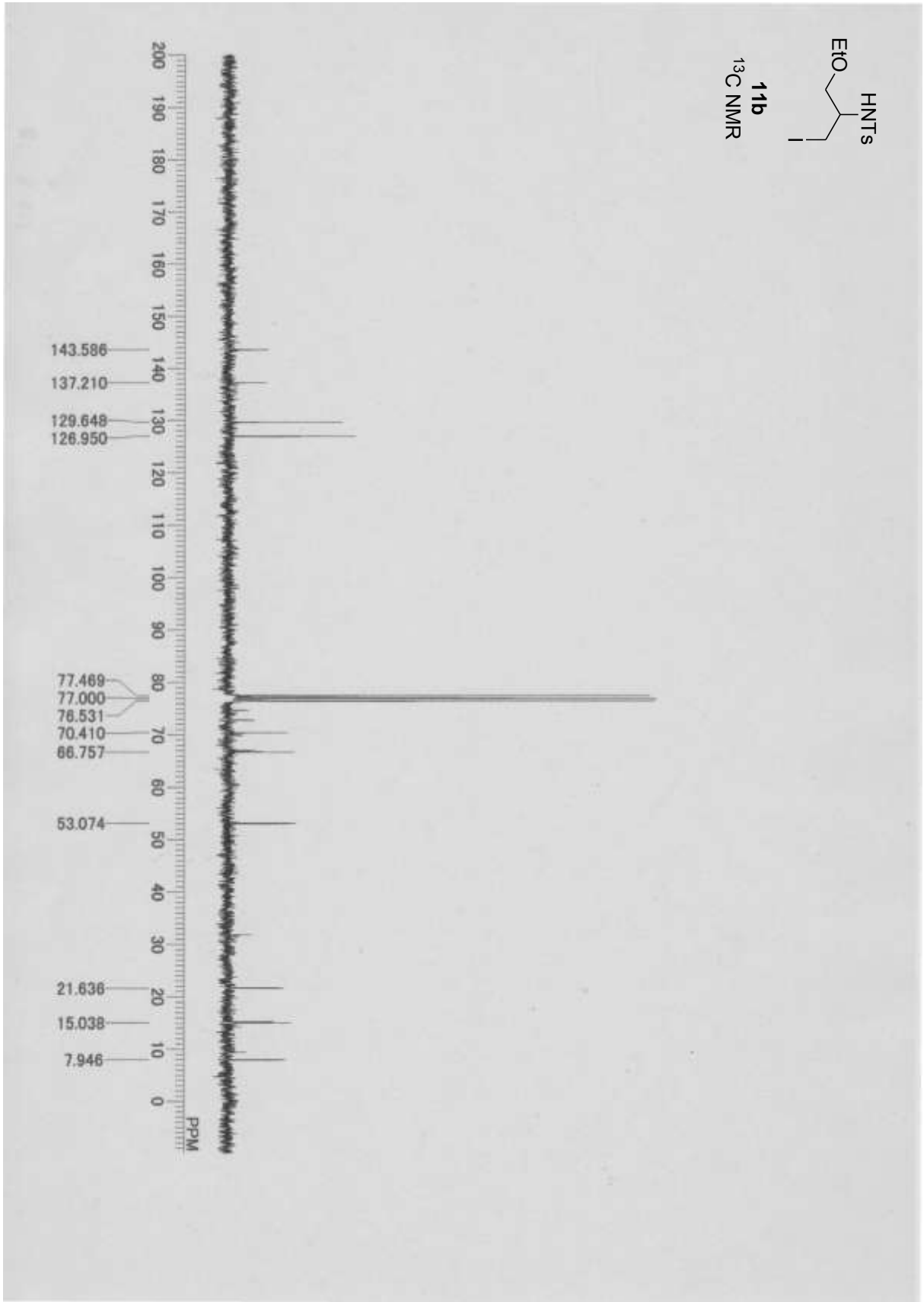

10b
^{1}H NMR
H NTs
n-C_6H_{13}
I
7.786
7.779
7.761
7.755
7.748
7.324
7.295
7.261
4.679
4.648
3.259
3.248
3.221
3.210
3.188
3.171
3.150
3.133
2.998
2.985
2.979
2.965
2.957
2.952
2.946
2.937
2.929
2.919
2.904
2.897
2.885
2.668
2.434
2.395
2.348
2.197
1.603
1.500
1.448
1.426
1.397
1.346
1.252
1.225
1.144
1.135
0.873
0.848
0.821
0.790
0.763
0.746
0.719
0.615
0.070
0.012
0.000
-0.010
2.0000
2.3244
0.9731
2.1108
0.9936
3.2202
2.2031
9.2115
3.4589
0.4950
PPM

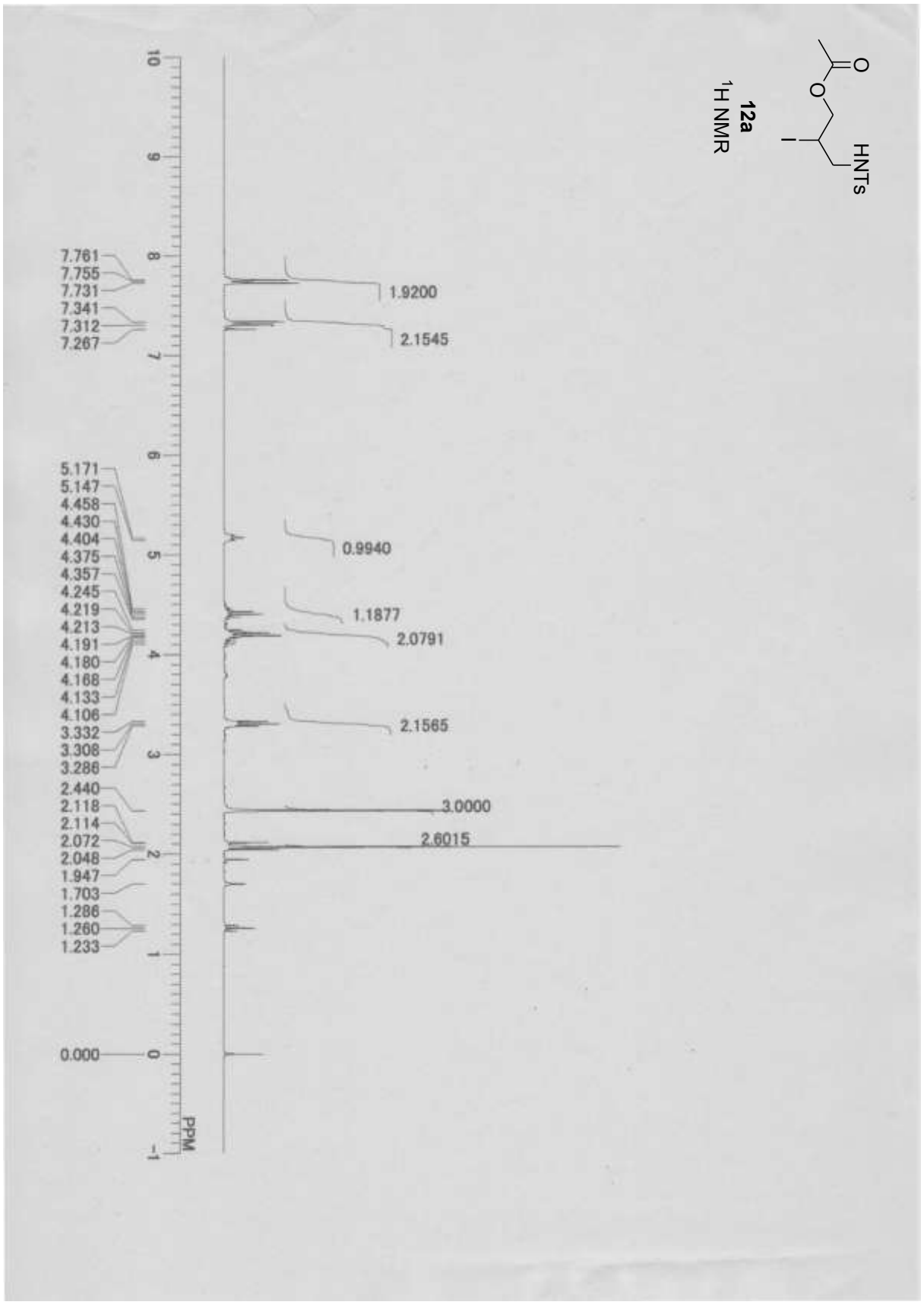

H NTs
n-C6H13
I
10b
13C NMR
143.512
137.670
129.640
126.933
77.469
77.000
76.531
52.515
35.640
31.600
28.704
25.224
22.533
21.628
15.005
14.125
PPM

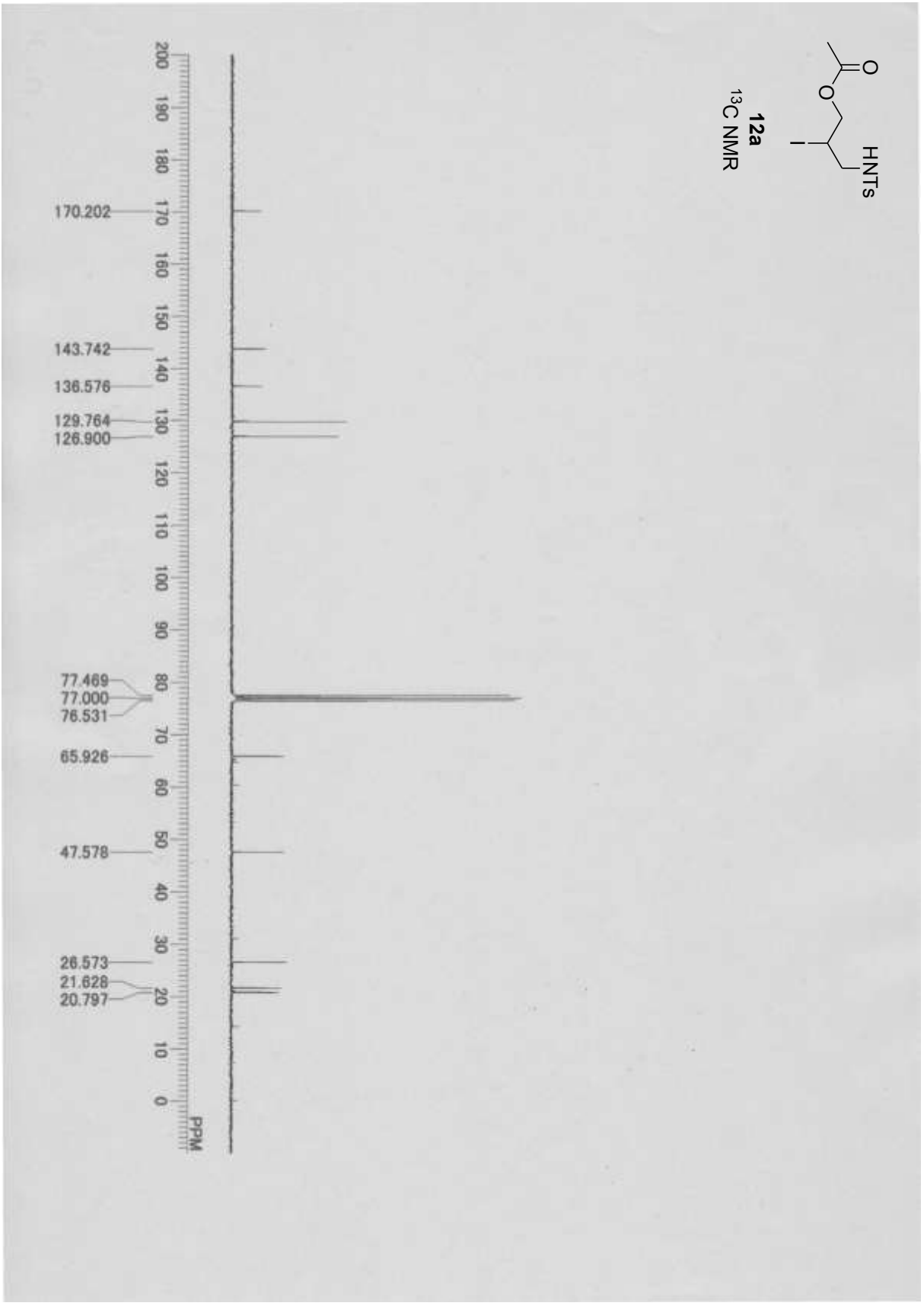

EtO
I
HNTs
11a
1H NMR
7.767
7.736
7.336
7.305
7.270
5.261
5.238
5.215
4.170
4.158
4.147
4.140
4.131
4.123
4.117
4.106
4.099
4.077
3.872
3.851
3.814
3.795
3.765
3.740
3.723
3.701
3.683
3.638
3.608
3.599
3.569
3.546
3.538
3.519
3.512
3.492
3.486
3.467
3.459
3.441
3.432
3.421
3.406
3.392
3.369
3.345
2.437
2.047
1.740
1.285
1.259
1.239
1.233
1.212
1.205
1.179
1.153
1.135
1.109
1.083
0.002
0.000
1.9683
2.1257
0.9011
0.9063
6.5205
3.0000
3.2135
0.1656
PPM

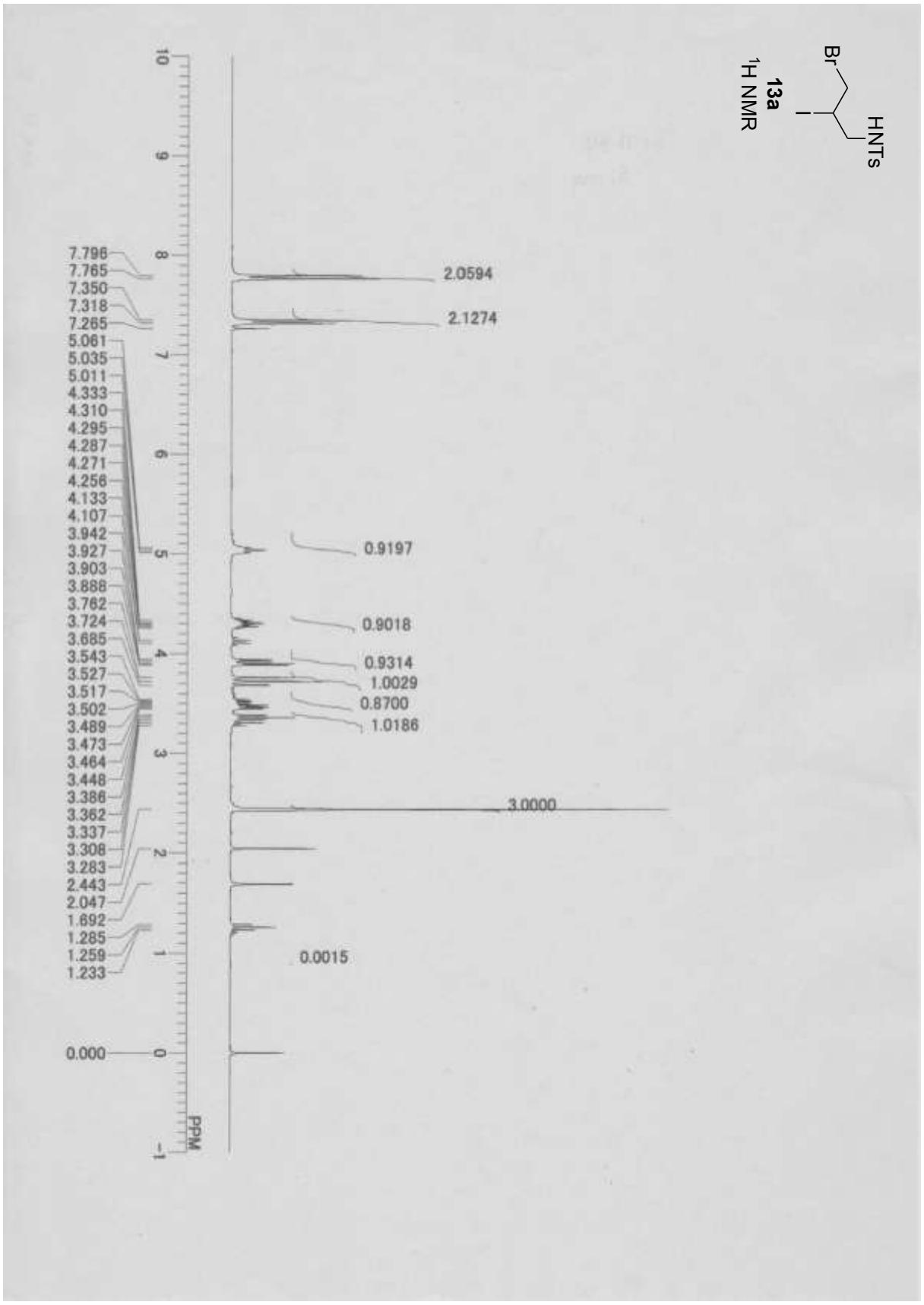

EtO
I
HNTs
11a
13C NMR
143.496
136.683
129.665
126.900
77.469
77.000
76.531
74.203
66.609
48.845
27.750
21.603
15.095
PPM

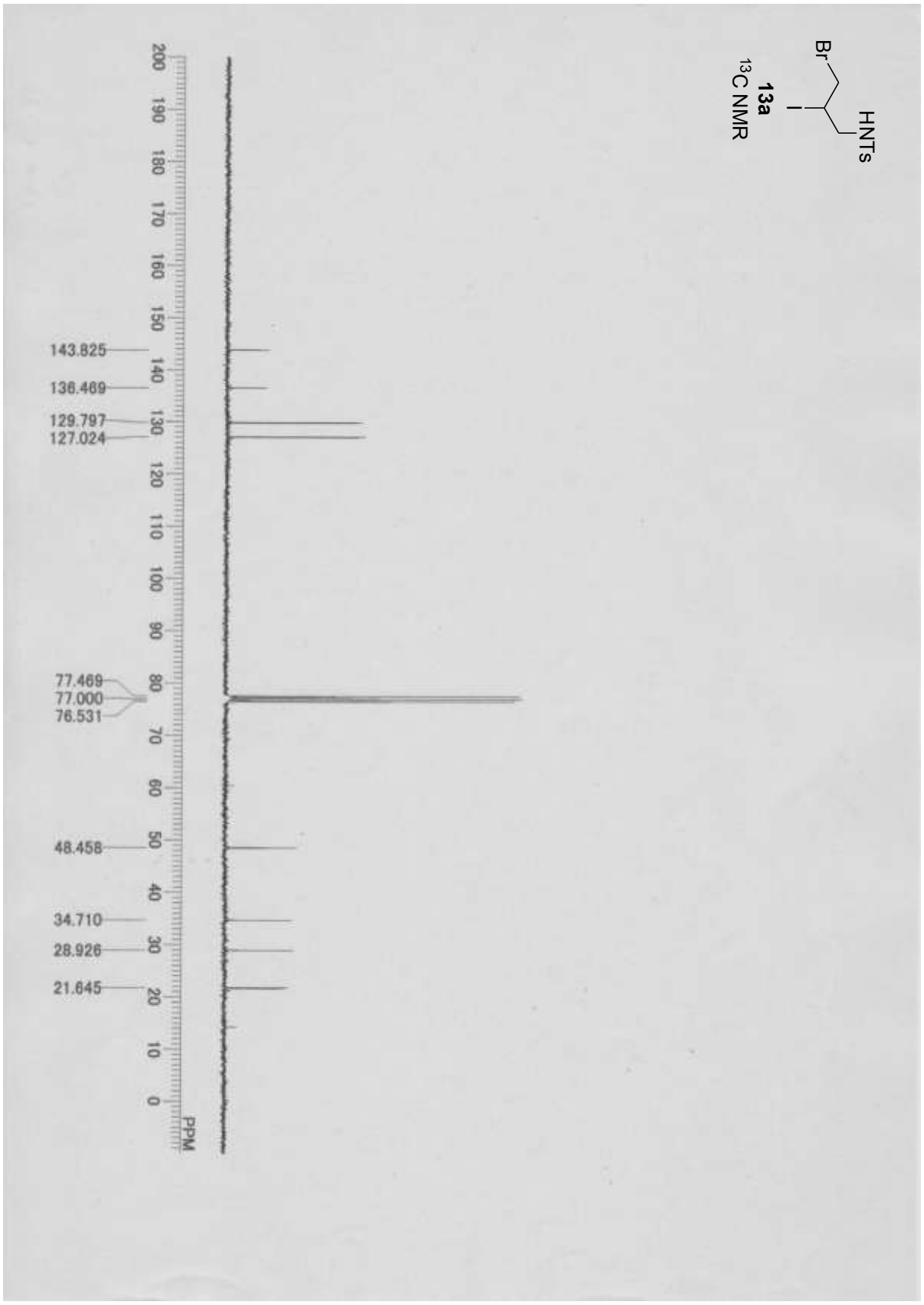

11b
^{1}H NMR
EtO
HNTs
I
7.782
7.751
7.331
7.299
7.267
5.070
4.133
4.107
3.896
3.874
3.852
3.817
3.798
3.766
3.572
3.563
3.552
3.537
3.521
3.441
3.423
3.414
3.397
3.389
3.371
3.362
3.333
3.312
3.295
3.273
3.261
3.240
3.225
3.195
3.185
2.611
2.437
2.049
1.286
1.260
1.241
1.234
1.215
1.189
1.183
1.157
1.139
1.114
1.087
0.000
2.0000
2.4114
0.7055
0.9535
1.0863
5.3218
3.0425
3.1024
PPM

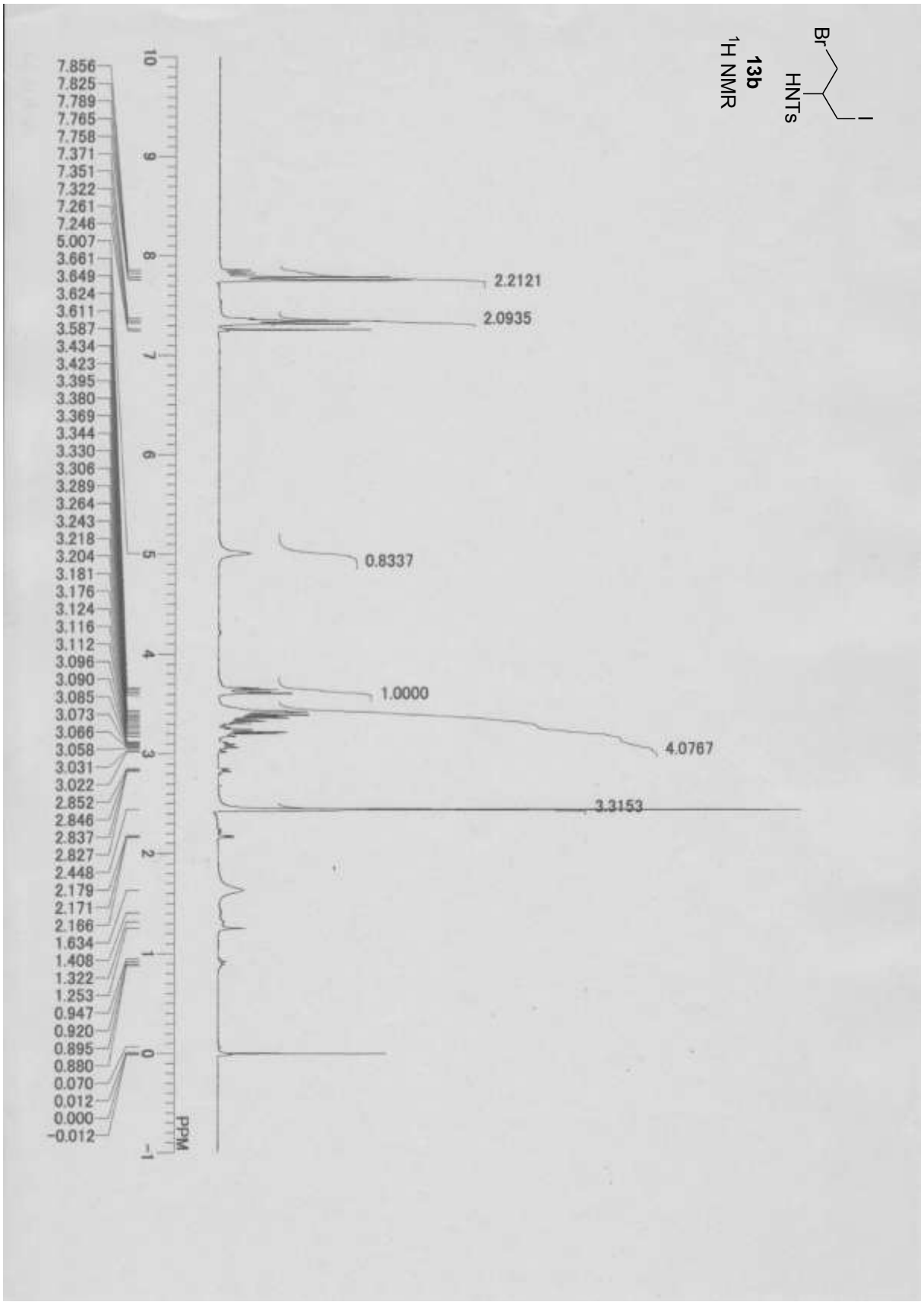

EtO
HNTs
I
11b
13C NMR
143.586
137.210
129.648
126.950
77.469
77.000
76.531
70.410
66.757
53.074
21.636
15.038
7.946
PPM

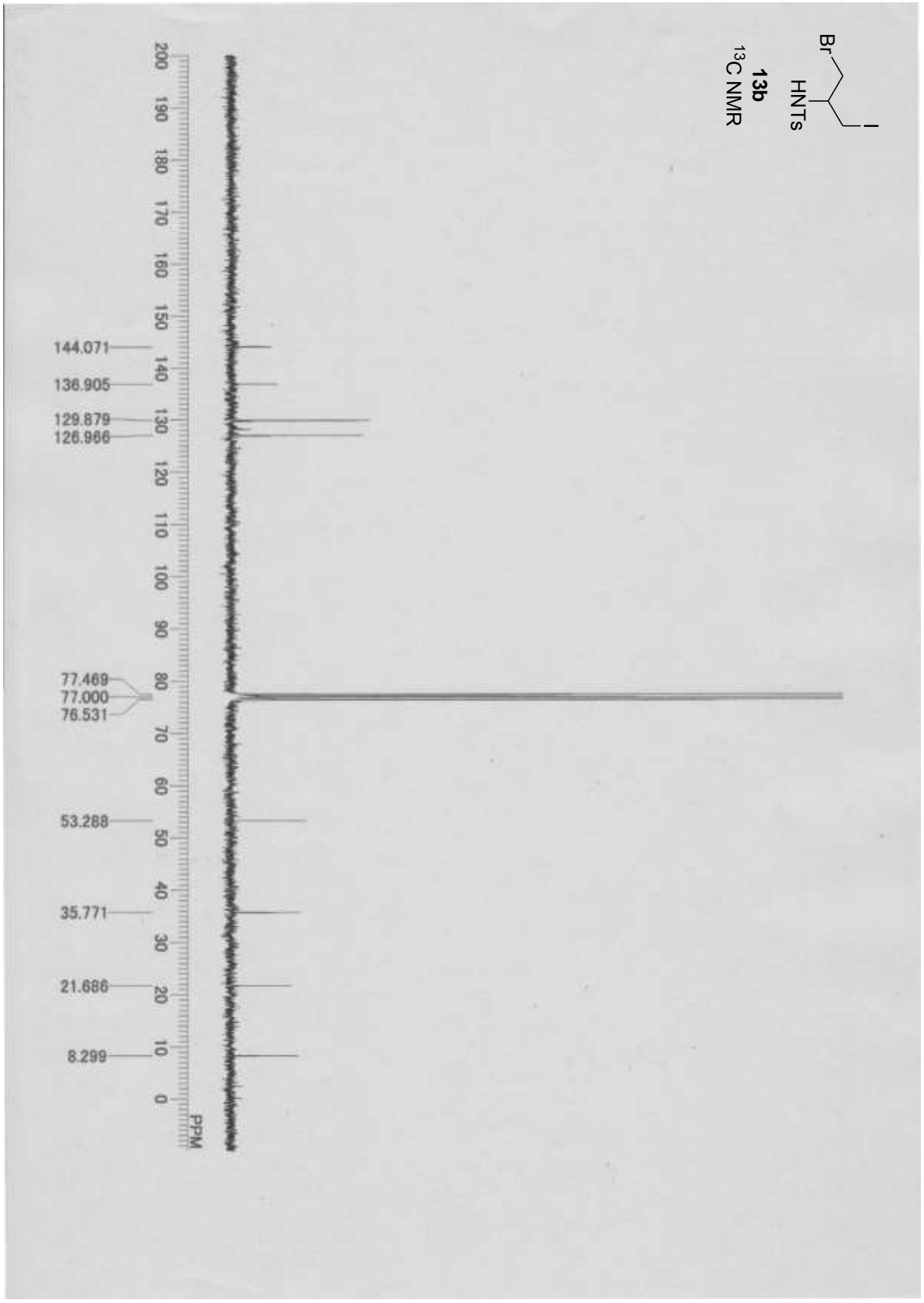

12a
1H NMR
O
O
I
HNTs
7.761
7.755
7.731
7.341
7.312
7.267
5.171
5.147
4.458
4.430
4.404
4.375
4.357
4.245
4.219
4.213
4.191
4.180
4.168
4.133
4.106
3.332
3.308
3.286
2.440
2.118
2.114
2.072
2.048
1.947
1.703
1.286
1.260
1.233
0.000
1.9200
2.1545
0.9940
1.1877
2.0791
2.1565
3.0000
2.6015
PPM

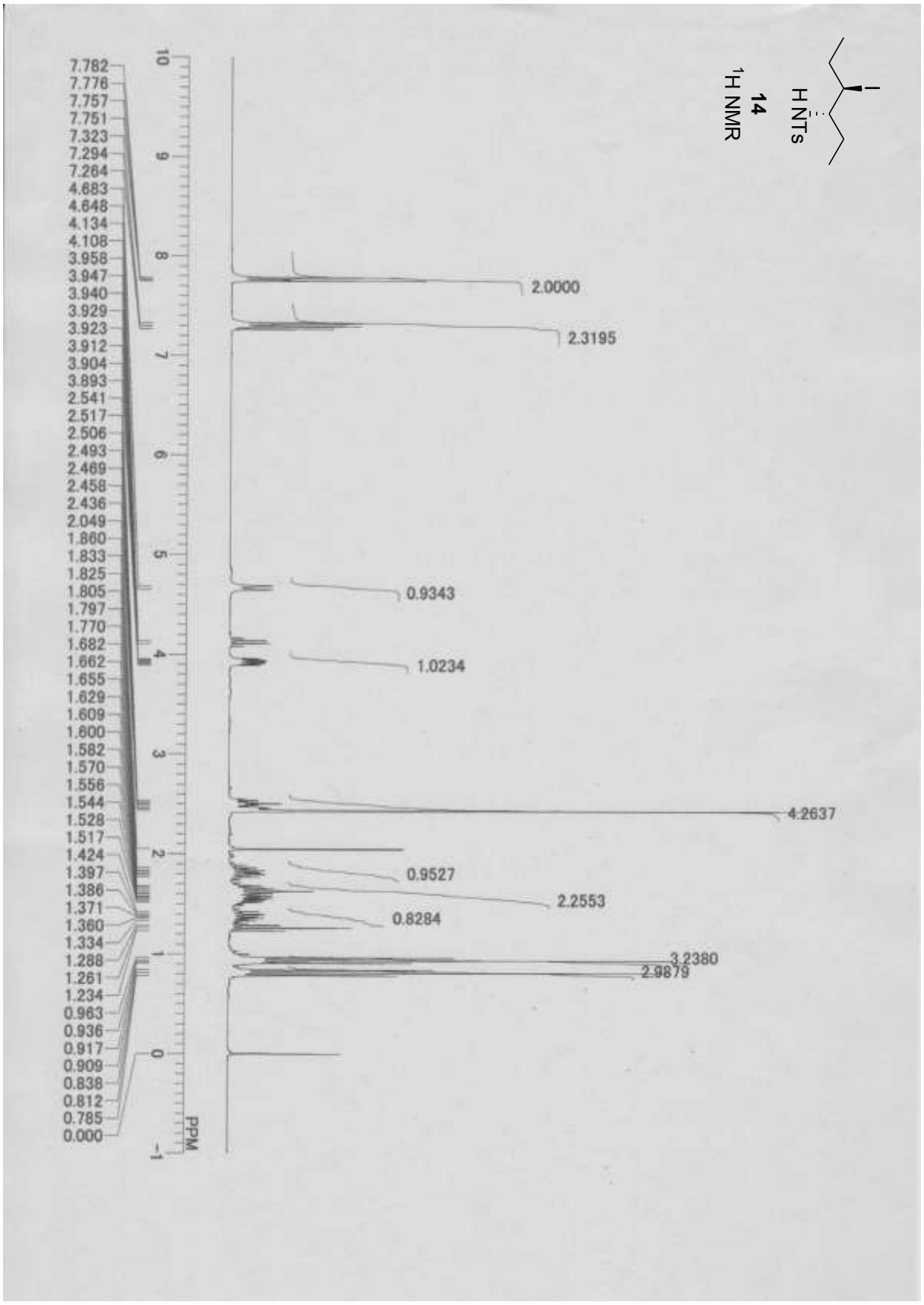

12a
13C NMR
HNTs
170.202
143.742
136.576
129.764
126.900
77.469
77.000
76.531
65.926
47.578
26.573
21.628
20.797
PPM

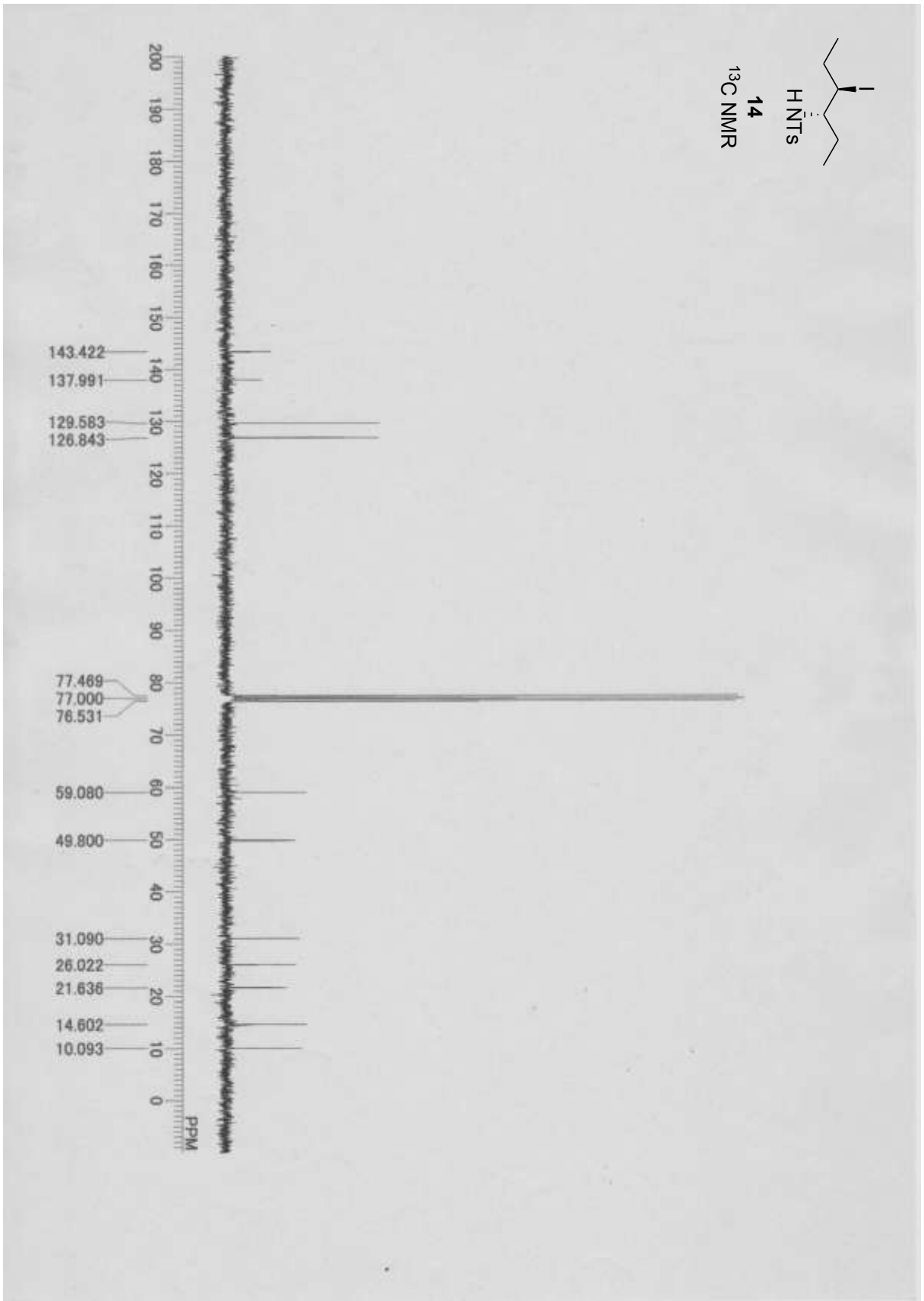

13a
^{1}H NMR
Br
I
HNTs
7.796
7.765
7.350
7.318
7.265
5.061
5.035
5.011
4.333
4.310
4.295
4.287
4.271
4.256
4.133
4.107
3.942
3.927
3.903
3.888
3.762
3.724
3.685
3.543
3.527
3.517
3.502
3.489
3.473
3.464
3.448
3.386
3.362
3.337
3.308
3.283
2.443
2.047
1.692
1.285
1.259
1.233
0.000
2.0594
2.1274
0.9197
0.9018
0.9314
1.0029
0.8700
1.0186
3.0000
0.0015
PPM

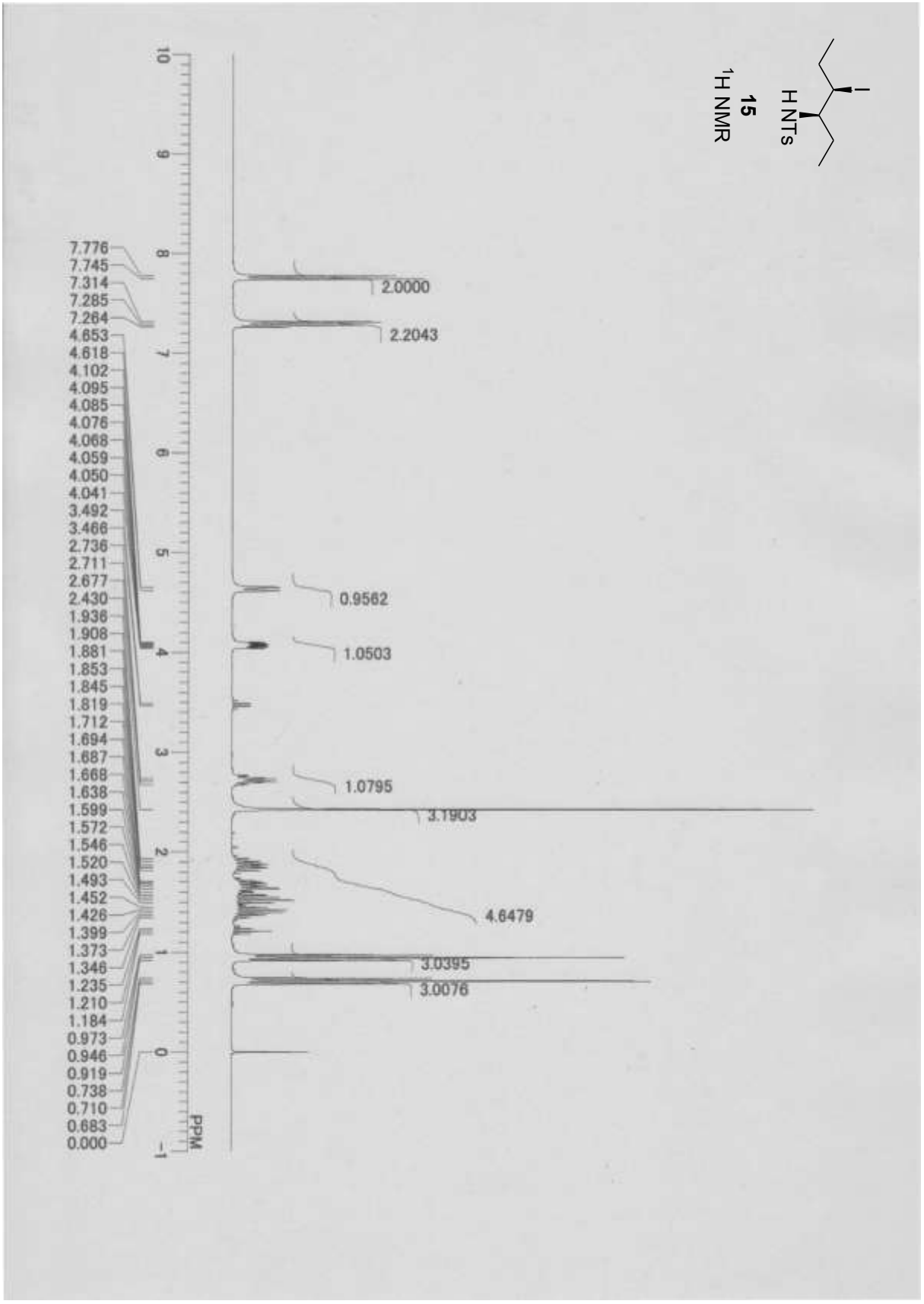

Br
HNTs
13a
13C NMR
143.825
136.469
129.797
127.024
77.469
77.000
76.531
48.458
34.710
28.926
21.645
PPM

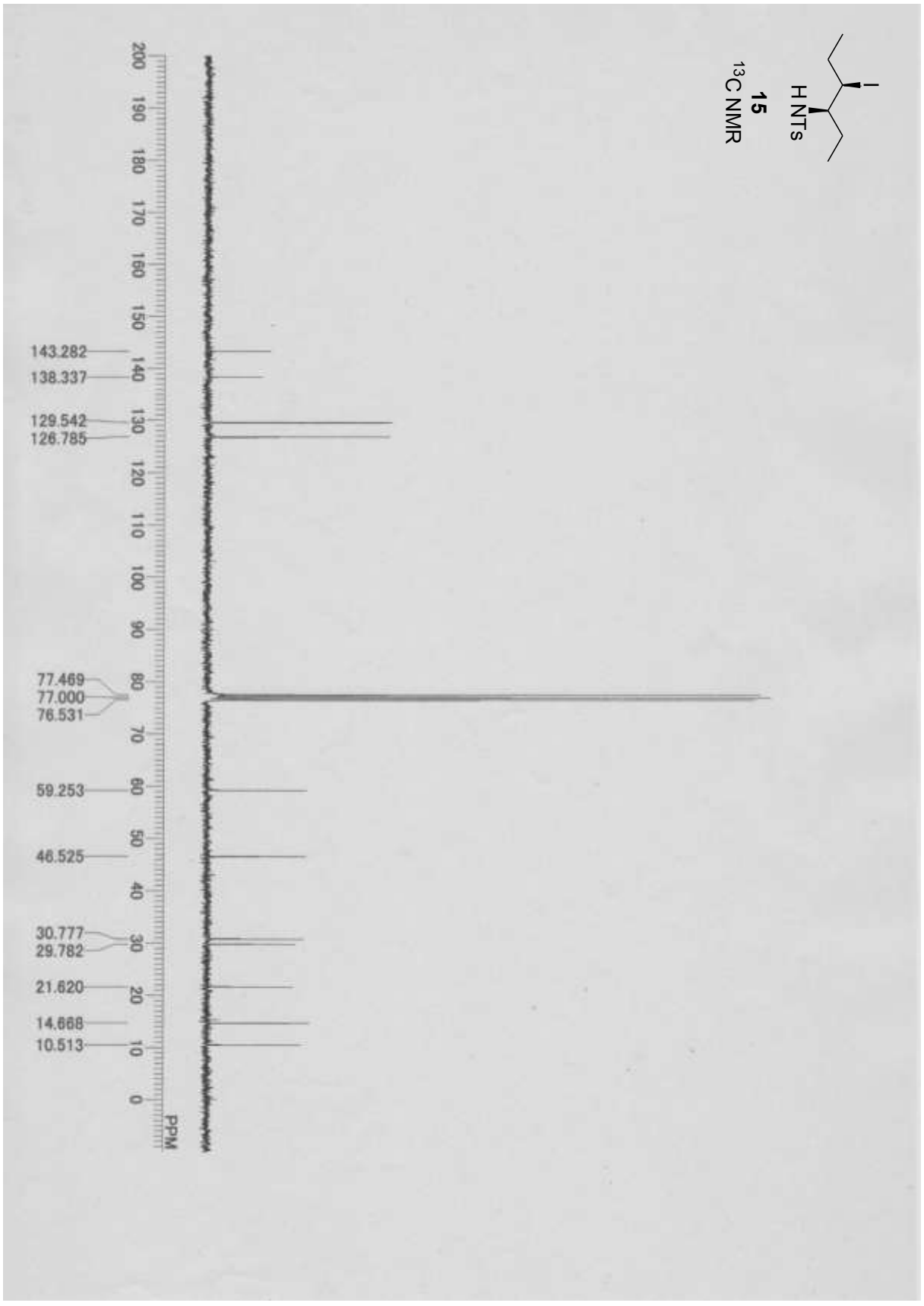

13b
^{1}H NMR
Br
HNTs
I
7.856
7.825
7.789
7.765
7.758
7.371
7.351
7.322
7.261
7.246
5.007
3.661
3.649
3.624
3.611
3.587
3.434
3.423
3.395
3.380
3.369
3.344
3.330
3.306
3.289
3.264
3.243
3.218
3.204
3.181
3.176
3.124
3.116
3.112
3.096
3.090
3.085
3.073
3.066
3.058
3.031
3.022
2.852
2.846
2.837
2.827
2.448
2.179
2.171
2.166
1.634
1.408
1.322
1.253
0.947
0.920
0.895
0.880
0.070
0.012
0.000
-0.012
2.2121
2.0935
0.8337
1.0000
4.0767
3.3153
PPM

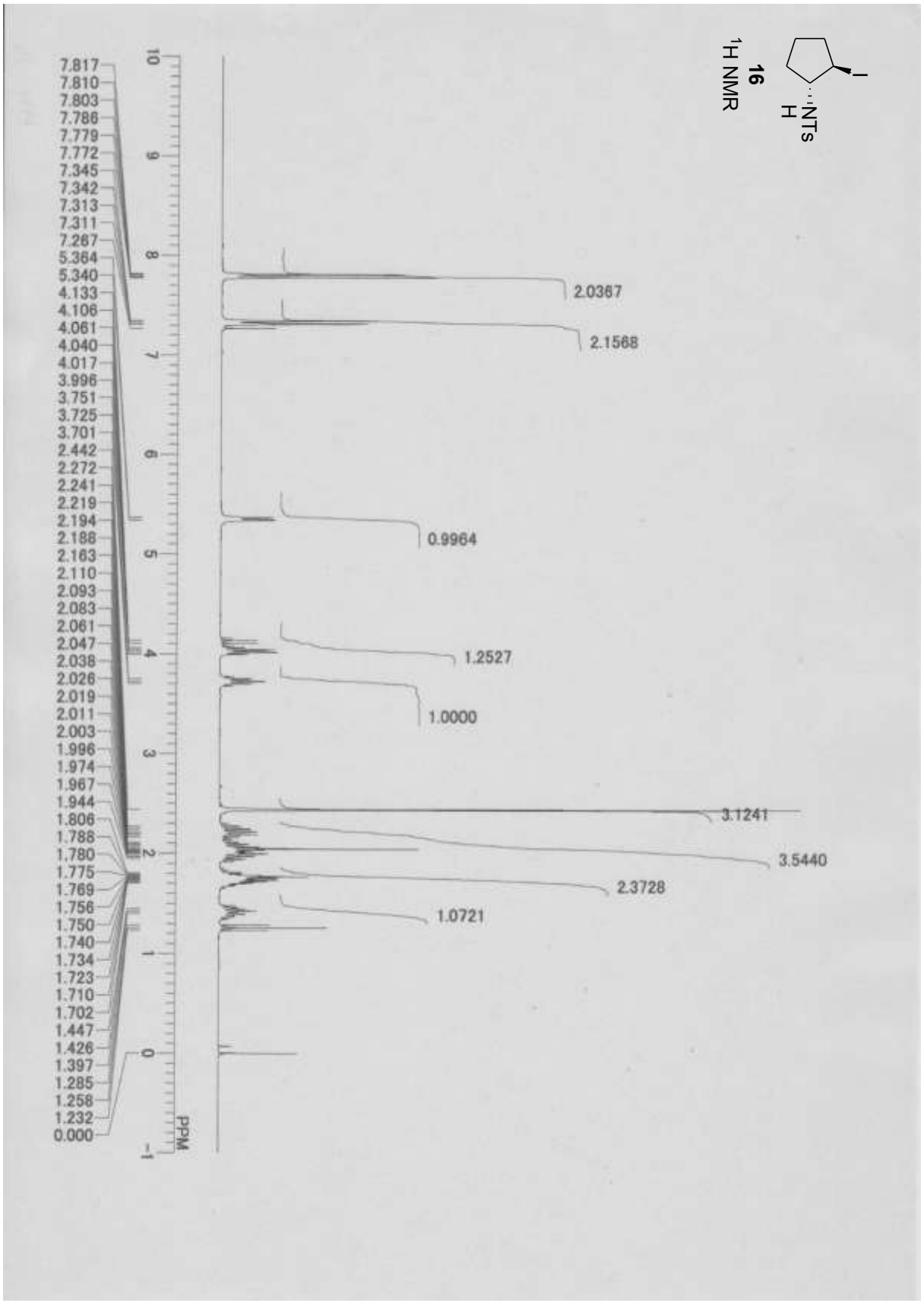

Br
HNTs
I
13b
13C NMR
144.071
136.905
129.879
126.966
77.469
77.000
76.531
53.288
35.771
21.686
8.299
PPM

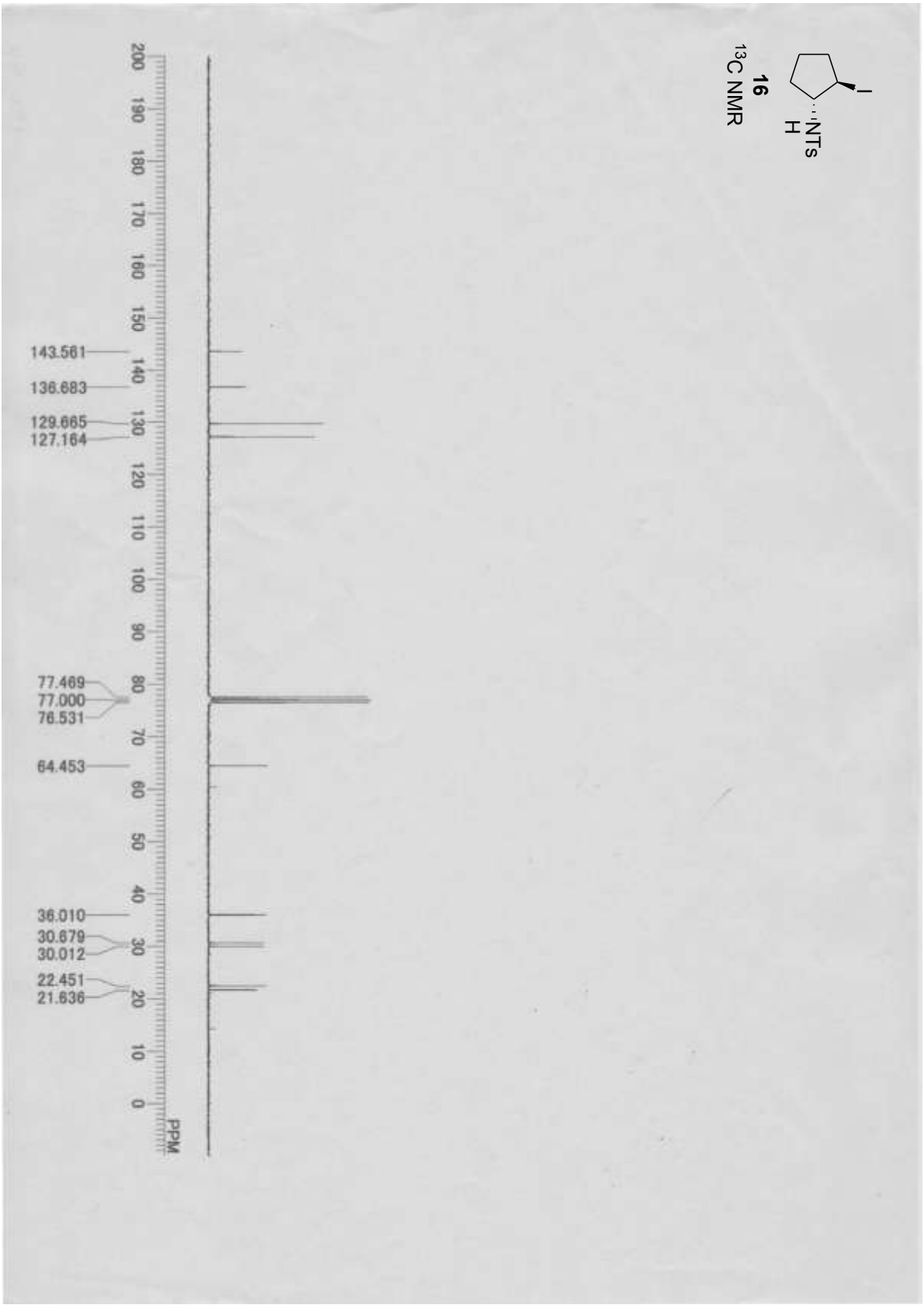

14
^{1}H NMR
H NTs
7.782
7.776
7.757
7.751
7.323
7.294
7.264
4.683
4.648
4.134
4.108
3.958
3.947
3.940
3.929
3.923
3.912
3.904
3.893
2.541
2.517
2.506
2.493
2.469
2.458
2.436
2.049
1.860
1.833
1.825
1.805
1.797
1.770
1.682
1.662
1.655
1.629
1.609
1.600
1.582
1.570
1.556
1.544
1.528
1.517
1.424
1.397
1.386
1.371
1.360
1.334
1.288
1.261
1.234
0.963
0.936
0.917
0.909
0.838
0.812
0.785
0.000
2.0000
2.3195
0.9343
1.0234
4.2637
0.9527
2.2553
0.8284
3.2380
2.9879
PPM

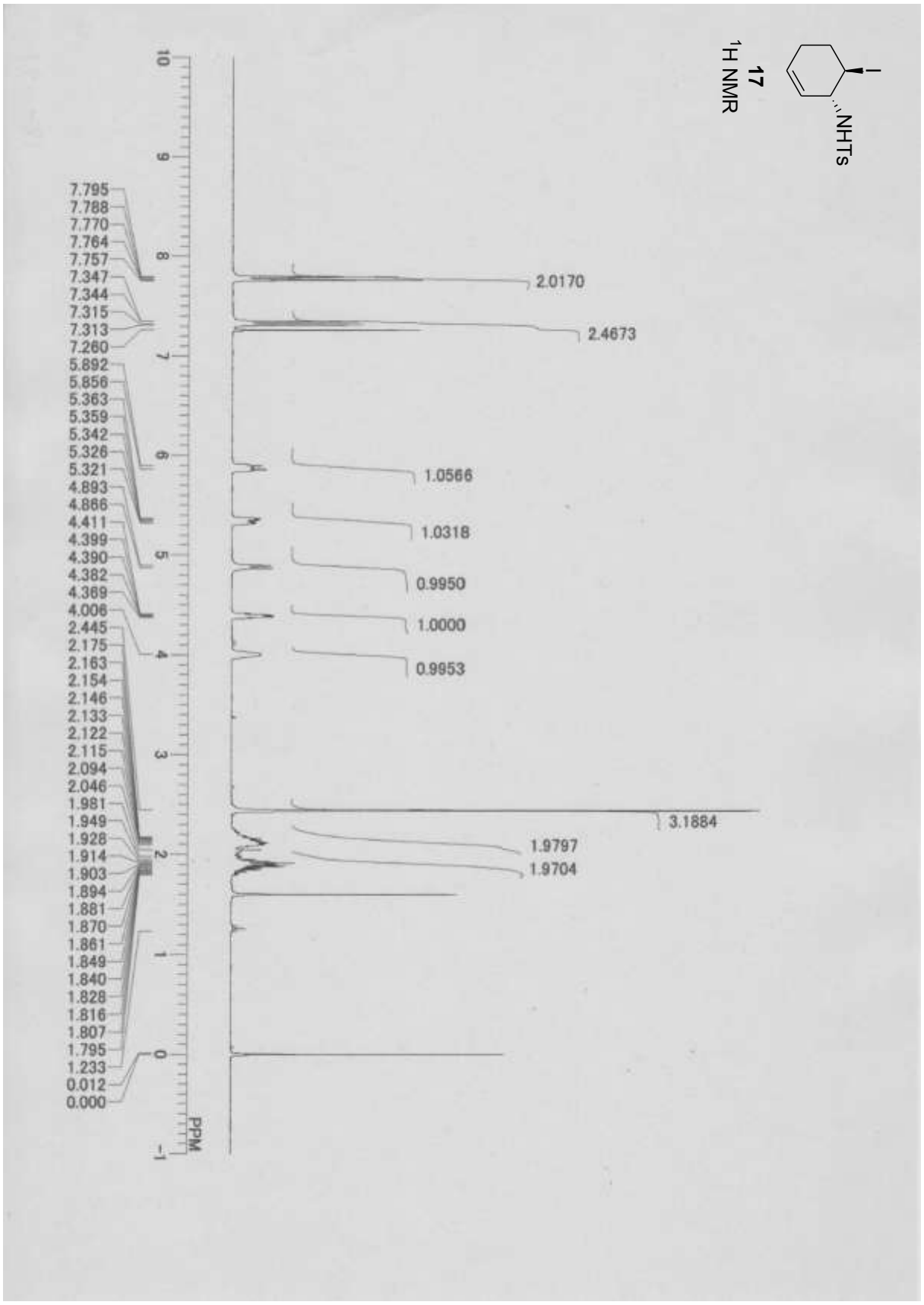

14
^{13}C NMR
143.422
137.991
129.583
126.843
77.469
77.000
76.531
59.080
49.800
31.090
26.022
21.636
14.602
10.093
PPM

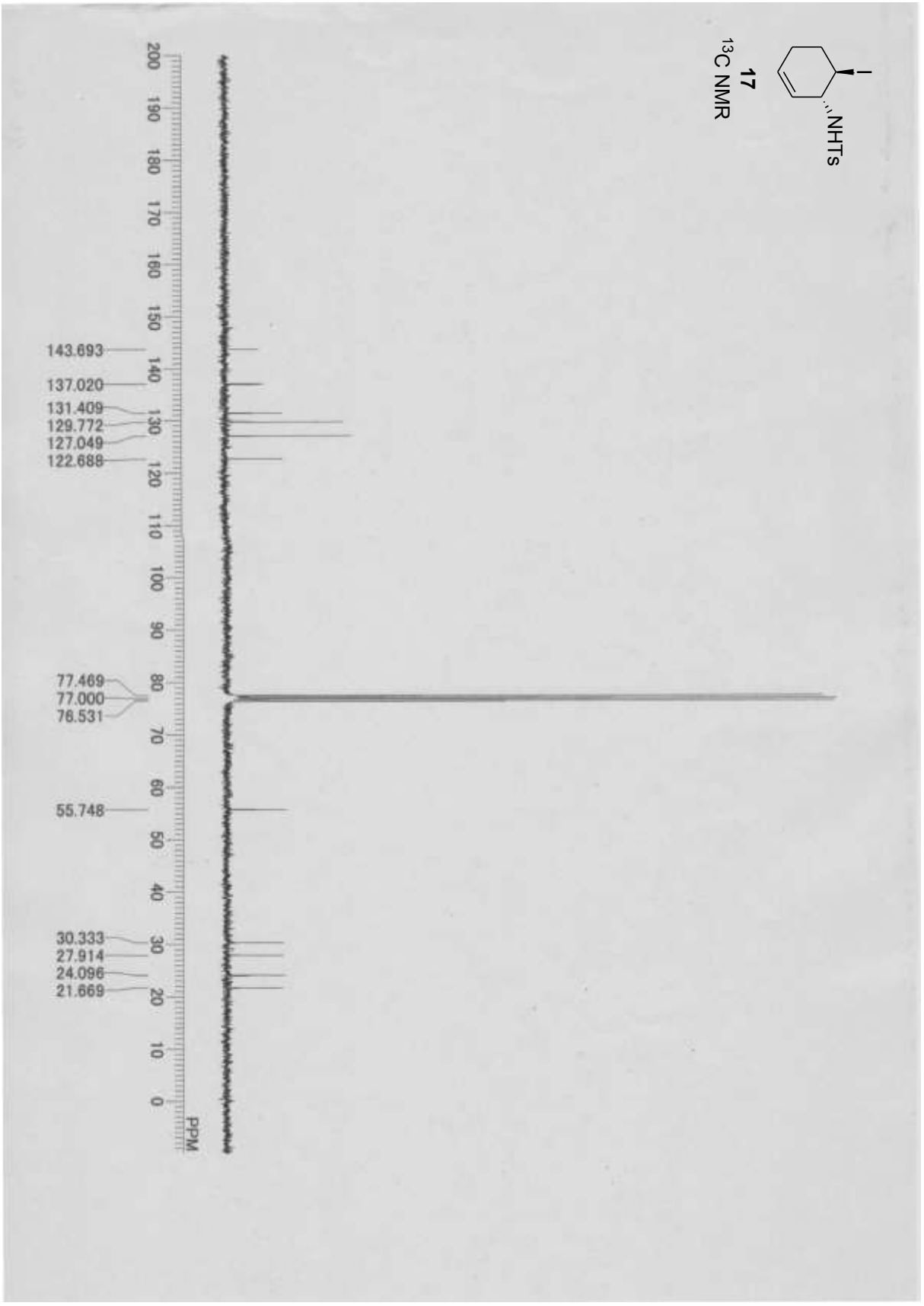

15
^{1}H NMR
H NTs
7.776
7.745
7.314
7.285
7.264
4.653
4.618
4.102
4.095
4.085
4.076
4.068
4.059
4.050
4.041
3.492
3.466
2.736
2.711
2.677
2.430
1.936
1.908
1.881
1.853
1.845
1.819
1.712
1.694
1.687
1.668
1.638
1.599
1.572
1.546
1.520
1.493
1.452
1.426
1.399
1.373
1.346
1.235
1.210
1.184
0.973
0.946
0.919
0.738
0.710
0.683
0.000
2.0000
2.2043
0.9562
1.0503
1.0795
3.1903
4.6479
3.0395
3.0076
PPM

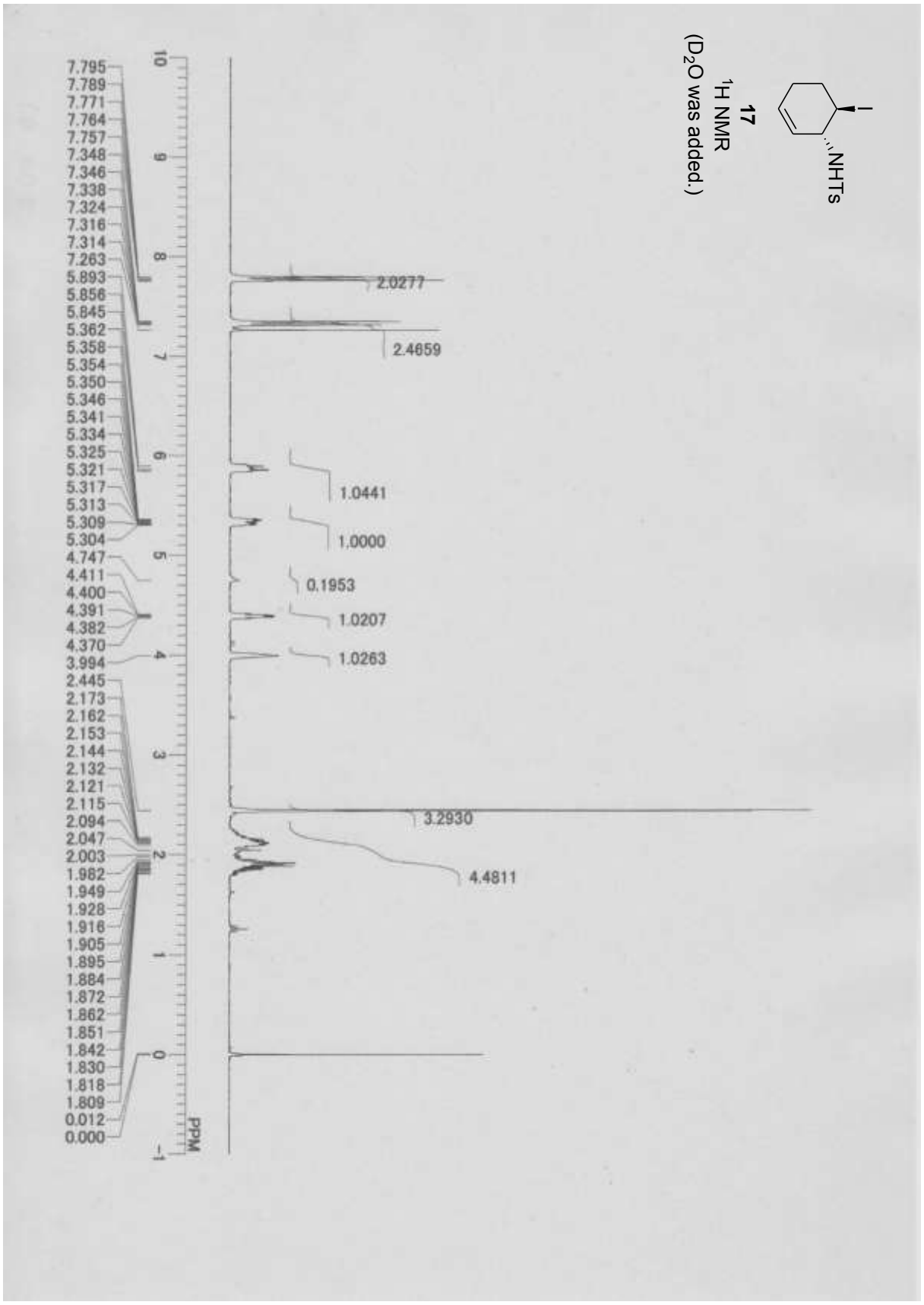

15
^{13}C NMR
HNTs
143.282
138.337
129.542
126.785
77.469
77.000
76.531
59.253
46.525
30.777
29.782
21.620
14.668
10.513
PPM

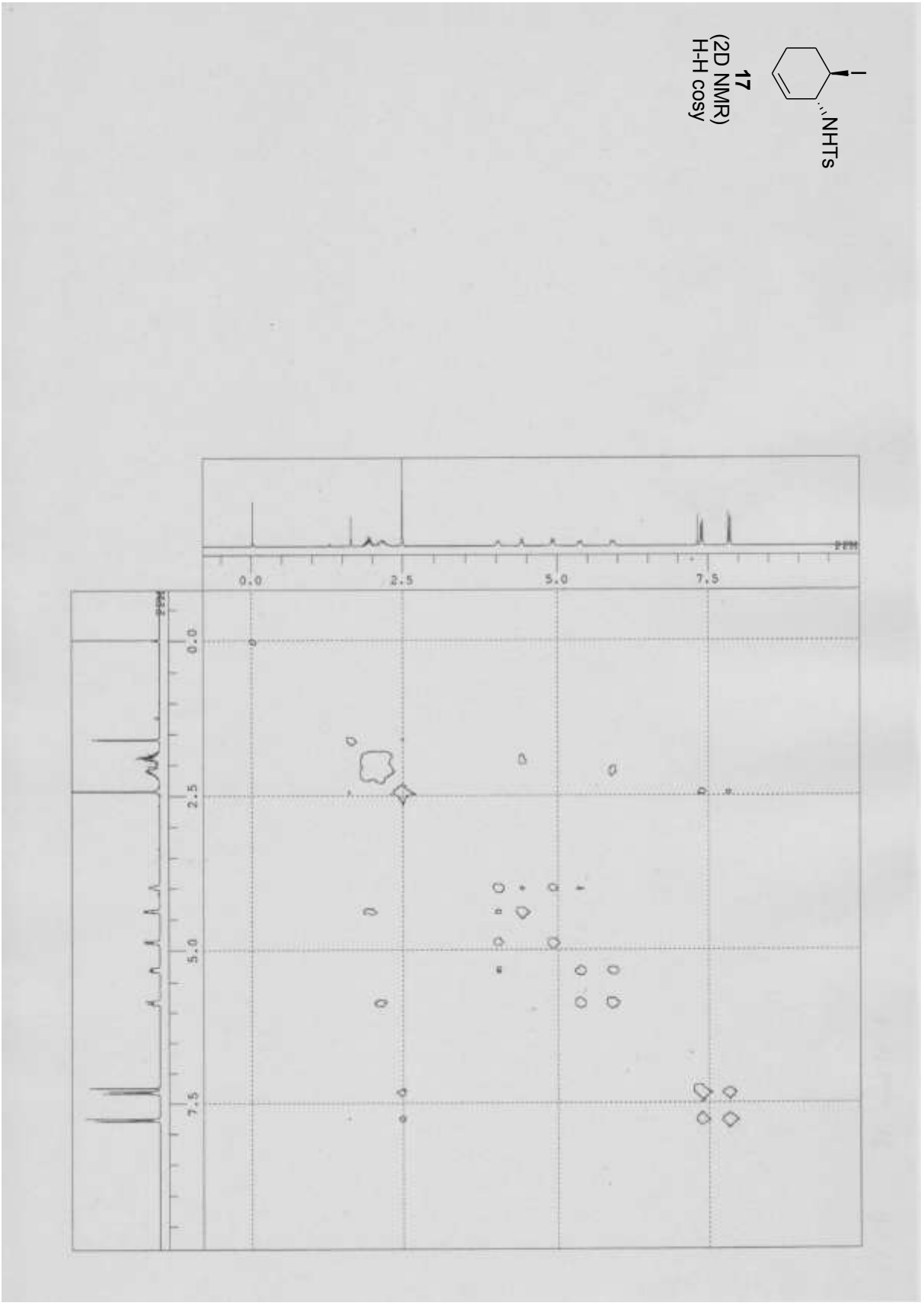

16
1H NMR
NTs
H
I
7.817
7.810
7.803
7.786
7.779
7.772
7.345
7.342
7.313
7.311
7.267
5.364
5.340
4.133
4.106
4.061
4.040
4.017
3.996
3.751
3.725
3.701
2.442
2.272
2.241
2.219
2.194
2.188
2.163
2.110
2.093
2.083
2.061
2.047
2.038
2.026
2.019
2.011
2.003
1.996
1.974
1.967
1.944
1.806
1.788
1.780
1.775
1.769
1.756
1.750
1.740
1.734
1.723
1.710
1.702
1.447
1.426
1.397
1.285
1.258
1.232
0.000
PPM
2.0367
2.1568
0.9964
1.2527
1.0000
3.1241
3.5440
2.3728
1.0721

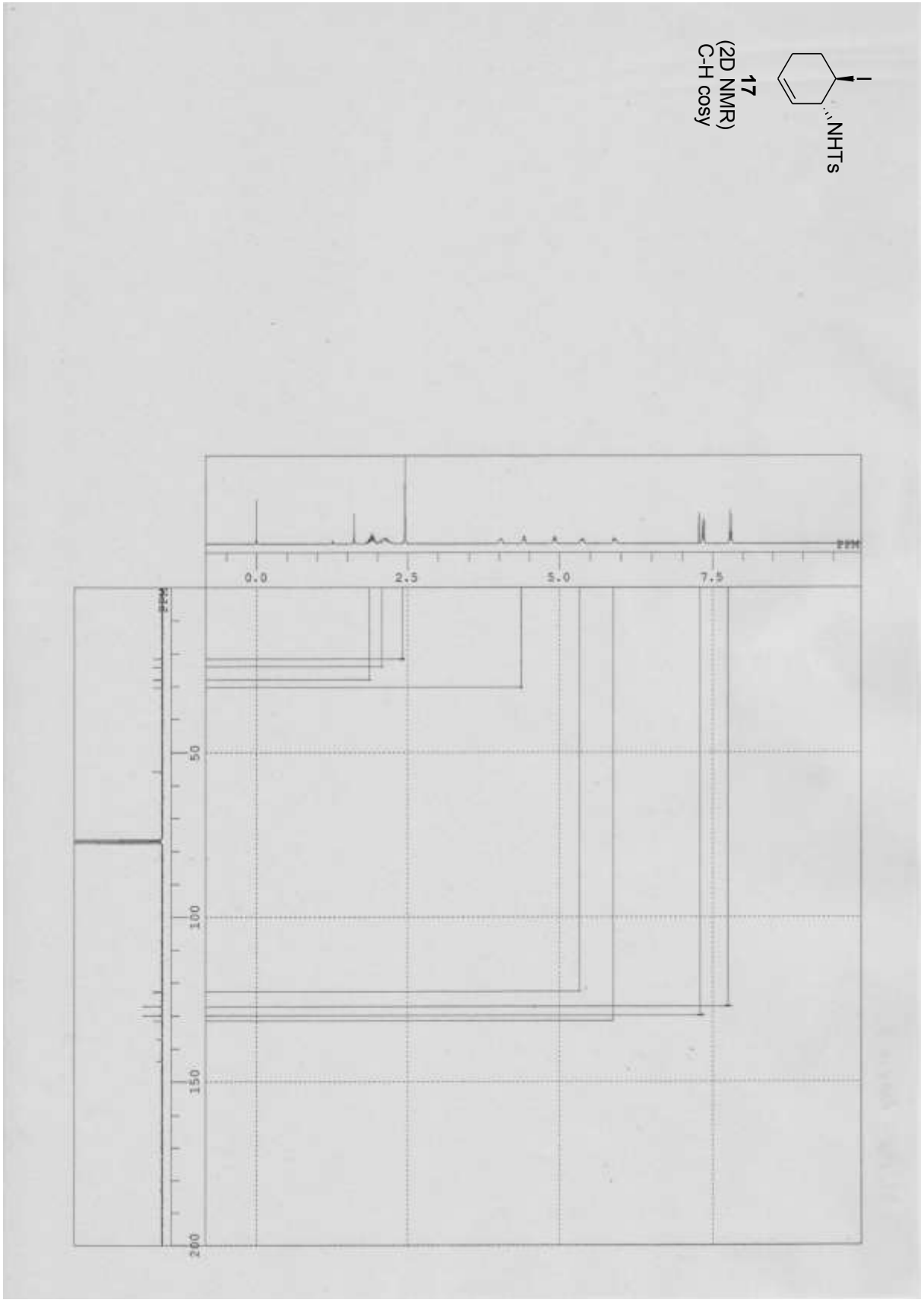

16
^{13}C NMR
NTs
H
I
143.561
136.683
129.665
127.164
77.469
77.000
76.531
64.453
36.010
30.679
30.012
22.451
21.636
PPM

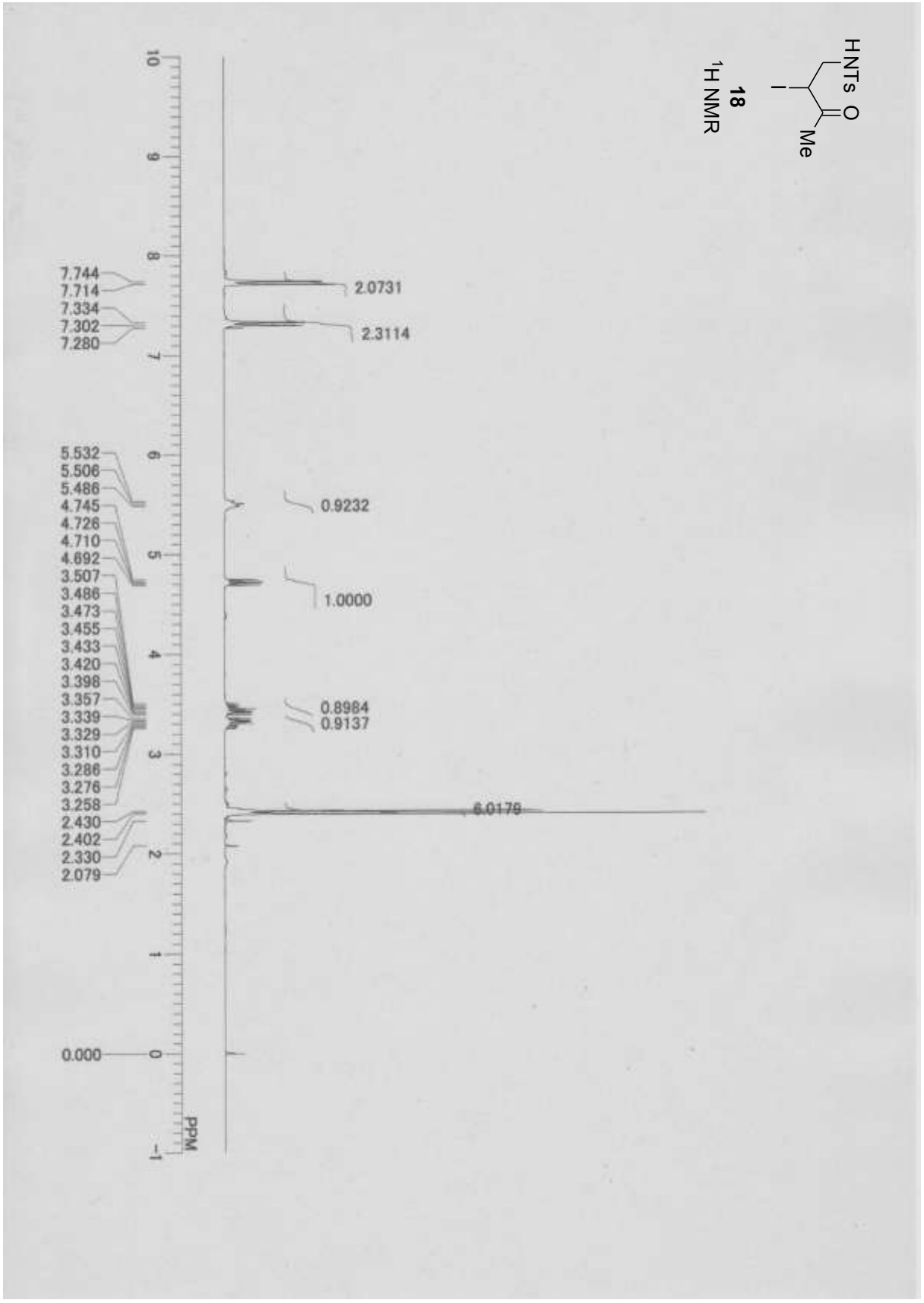

17
^{1}H NMR
NHTs
7.795
7.788
7.770
7.764
7.757
7.347
7.344
7.315
7.313
7.260
5.892
5.856
5.363
5.359
5.342
5.326
5.321
4.893
4.866
4.411
4.399
4.390
4.382
4.369
4.006
2.445
2.175
2.163
2.154
2.146
2.133
2.122
2.115
2.094
2.046
1.981
1.949
1.928
1.914
1.903
1.894
1.881
1.870
1.861
1.849
1.840
1.828
1.816
1.807
1.795
1.233
0.012
0.000
2.0170
2.4673
1.0566
1.0318
0.9950
1.0000
0.9953
3.1884
1.9797
1.9704
PPM

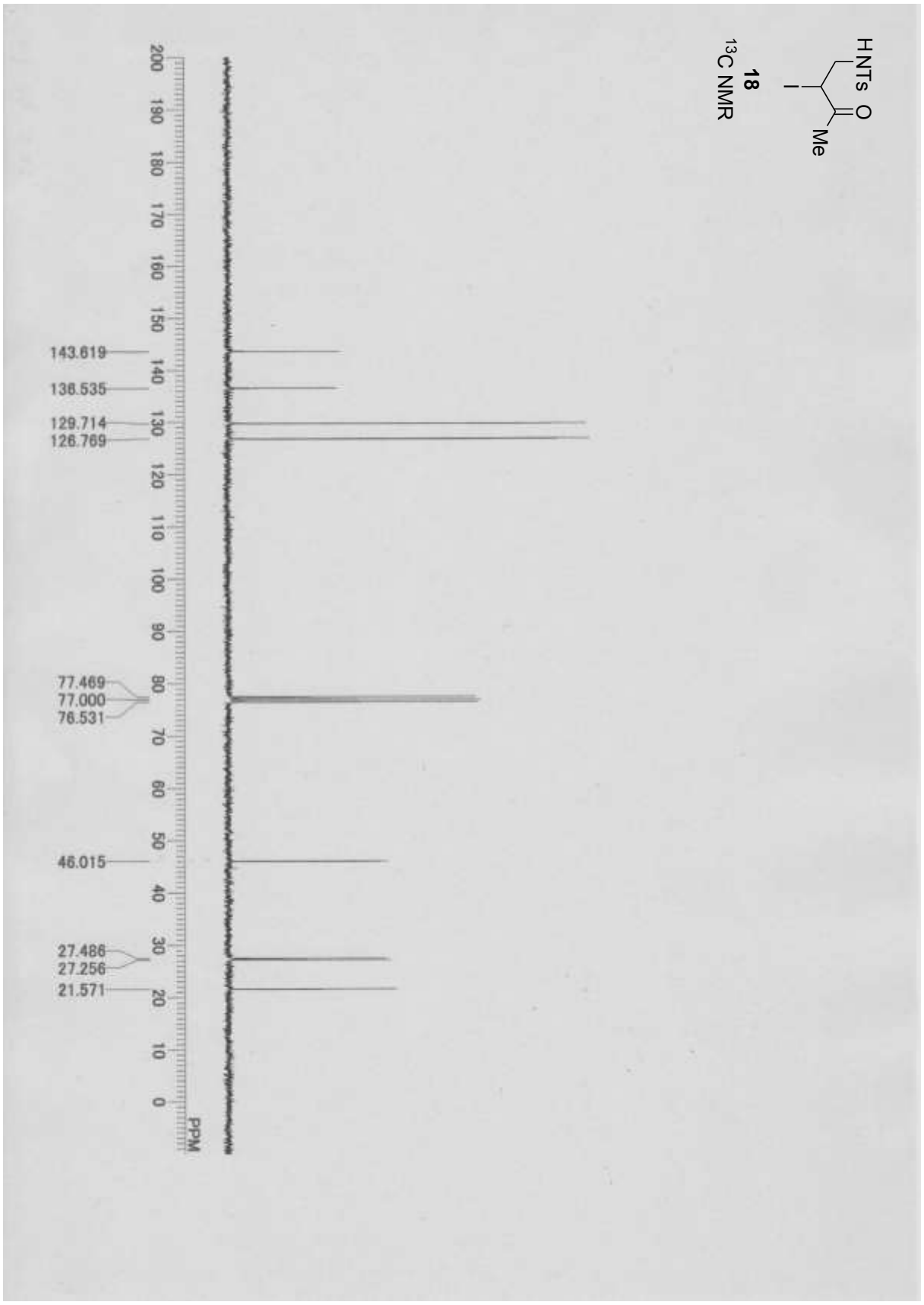

17
^{13}C NMR
NHTs
143.693
137.020
131.409
129.772
127.049
122.688
77.469
77.000
76.531
55.748
30.333
27.914
24.096
21.669
PPM

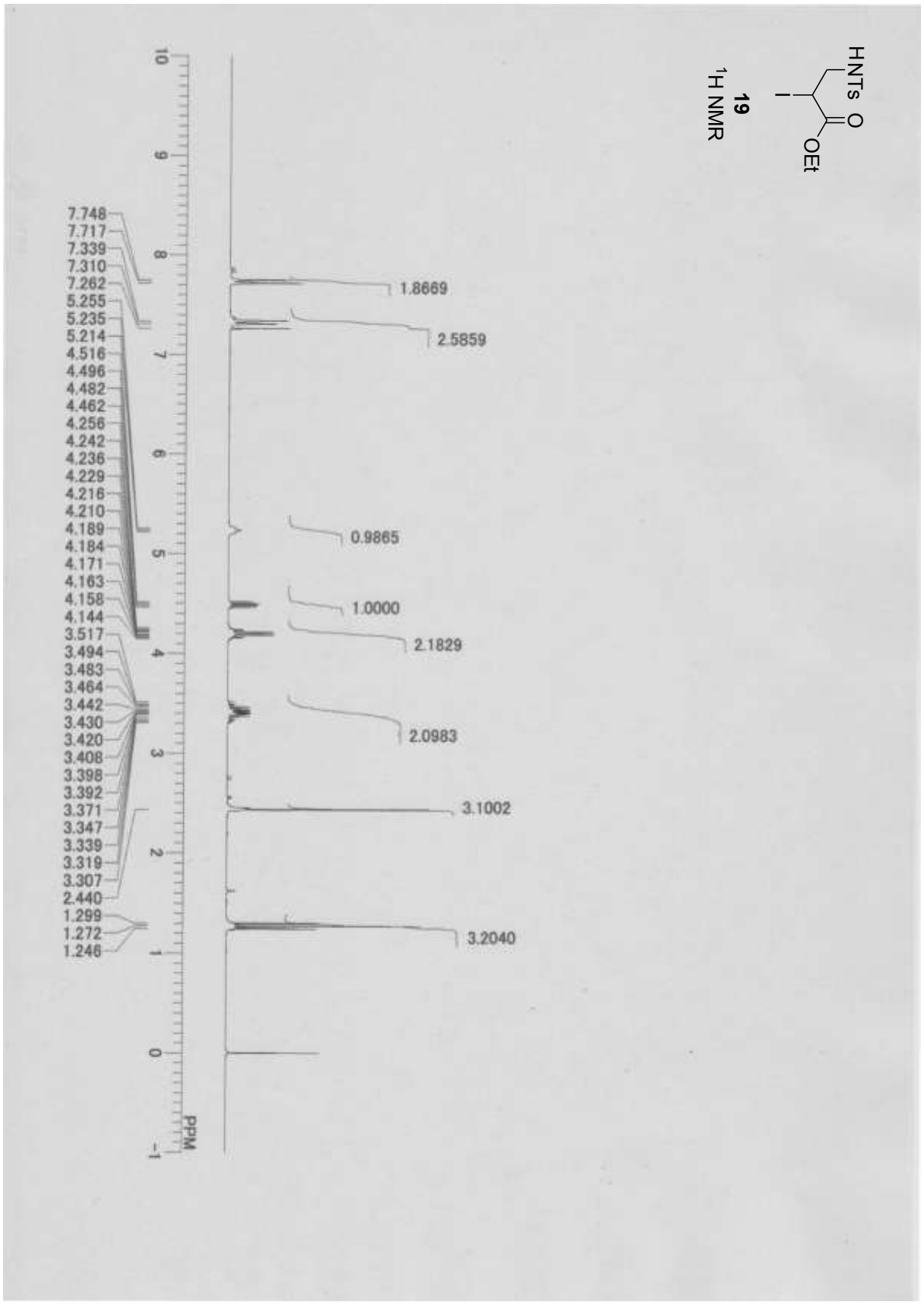

NHTs
17
^{1}H NMR
(D_2O was added.)
7.795
7.789
7.771
7.764
7.757
7.348
7.346
7.338
7.324
7.316
7.314
7.263
5.893
5.856
5.845
5.362
5.358
5.354
5.350
5.346
5.341
5.334
5.325
5.321
5.317
5.313
5.309
5.304
4.747
4.411
4.400
4.391
4.382
4.370
3.994
2.445
2.173
2.162
2.153
2.144
2.132
2.121
2.115
2.094
2.047
2.003
1.982
1.949
1.928
1.916
1.905
1.895
1.884
1.872
1.862
1.851
1.842
1.830
1.818
1.809
0.012
0.000
2.0277
2.4659
1.0441
1.0000
0.1953
1.0207
1.0263
3.2930
4.4811
PPM

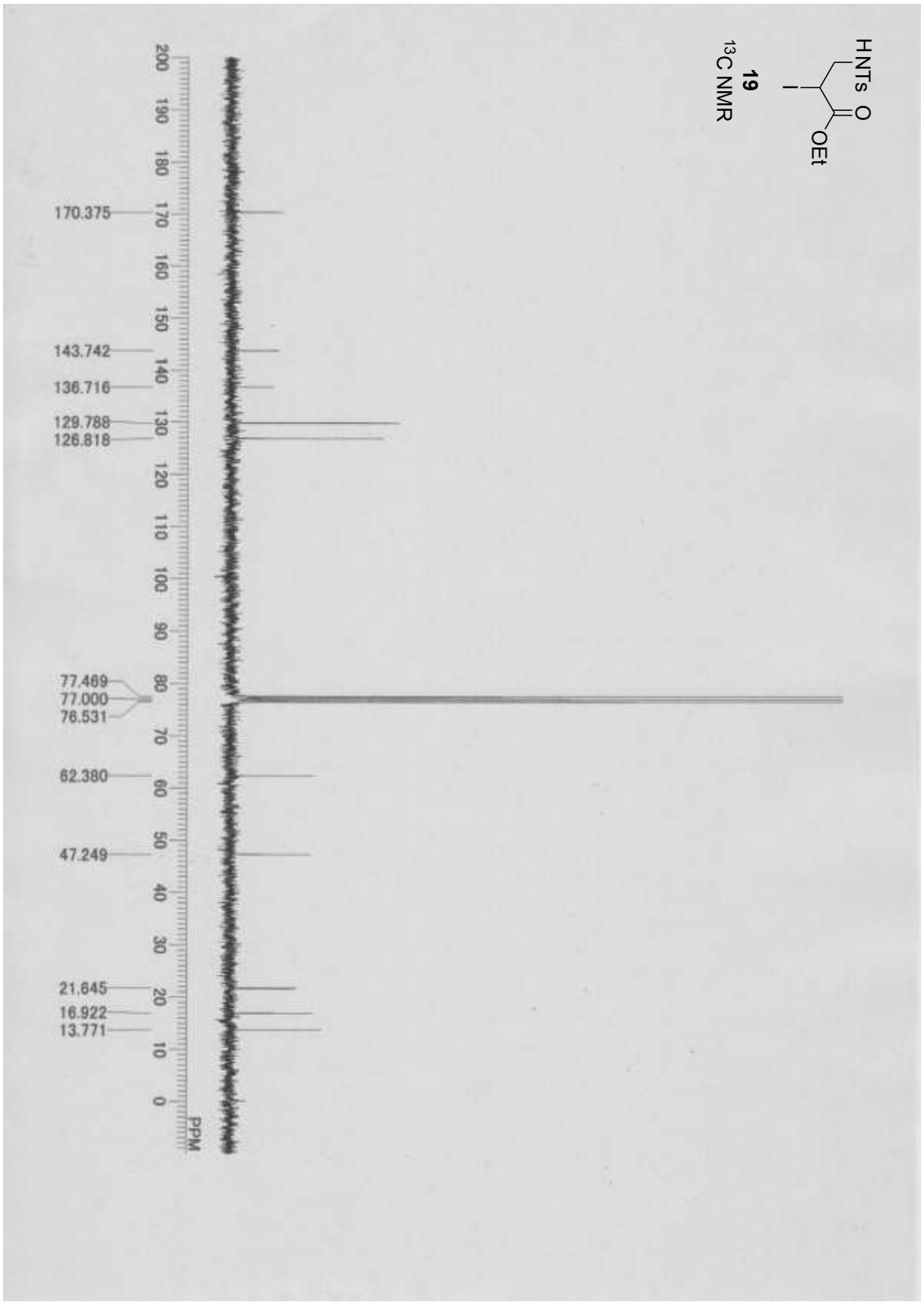

NHTs
17
(2D NMR)
H-H cosy
0.0
2.5
5.0
7.5
PPM

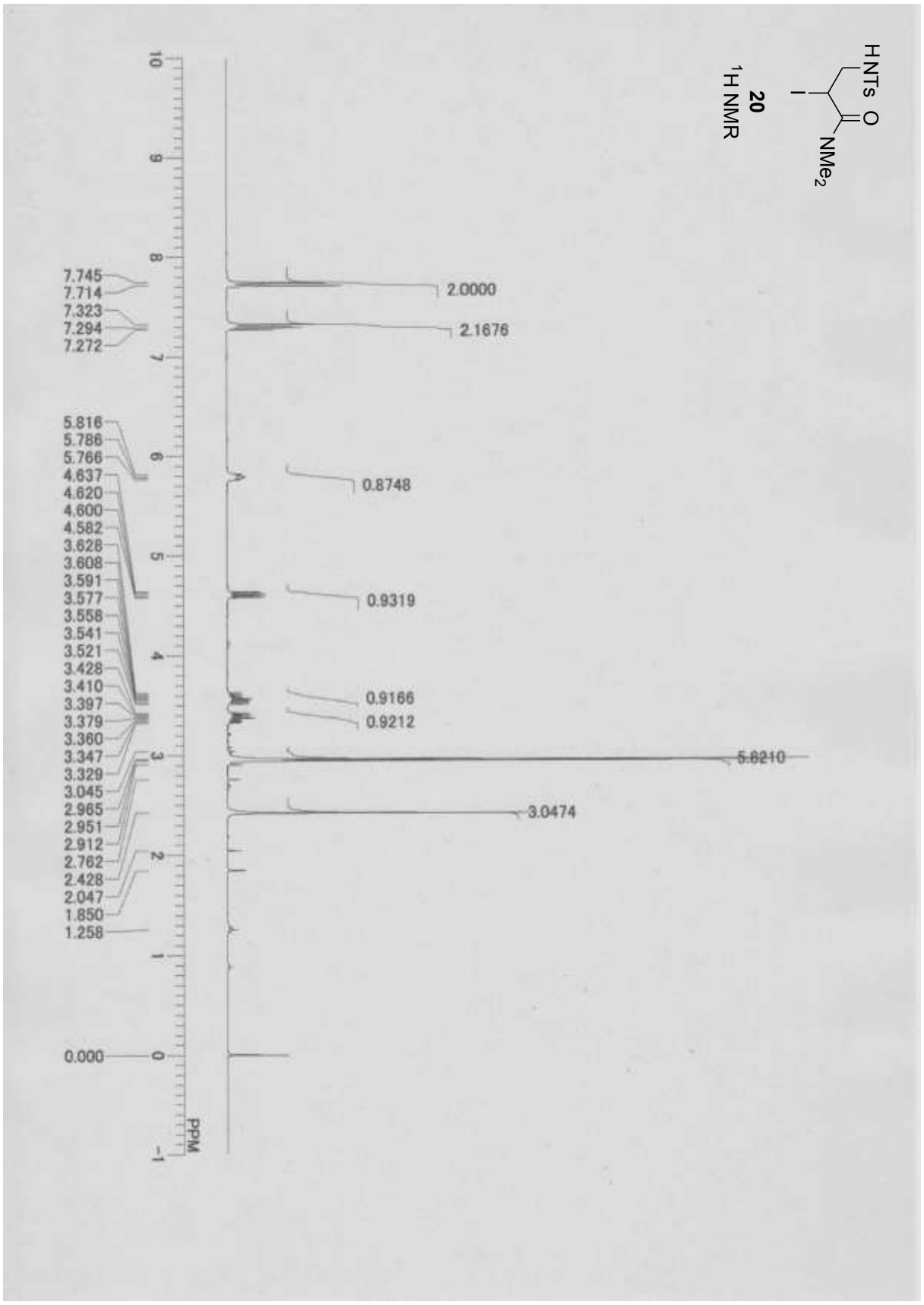

NHTs
17
(2D NMR)
C-H cosy
0.0
2.5
5.0
7.5
50
100
150
200

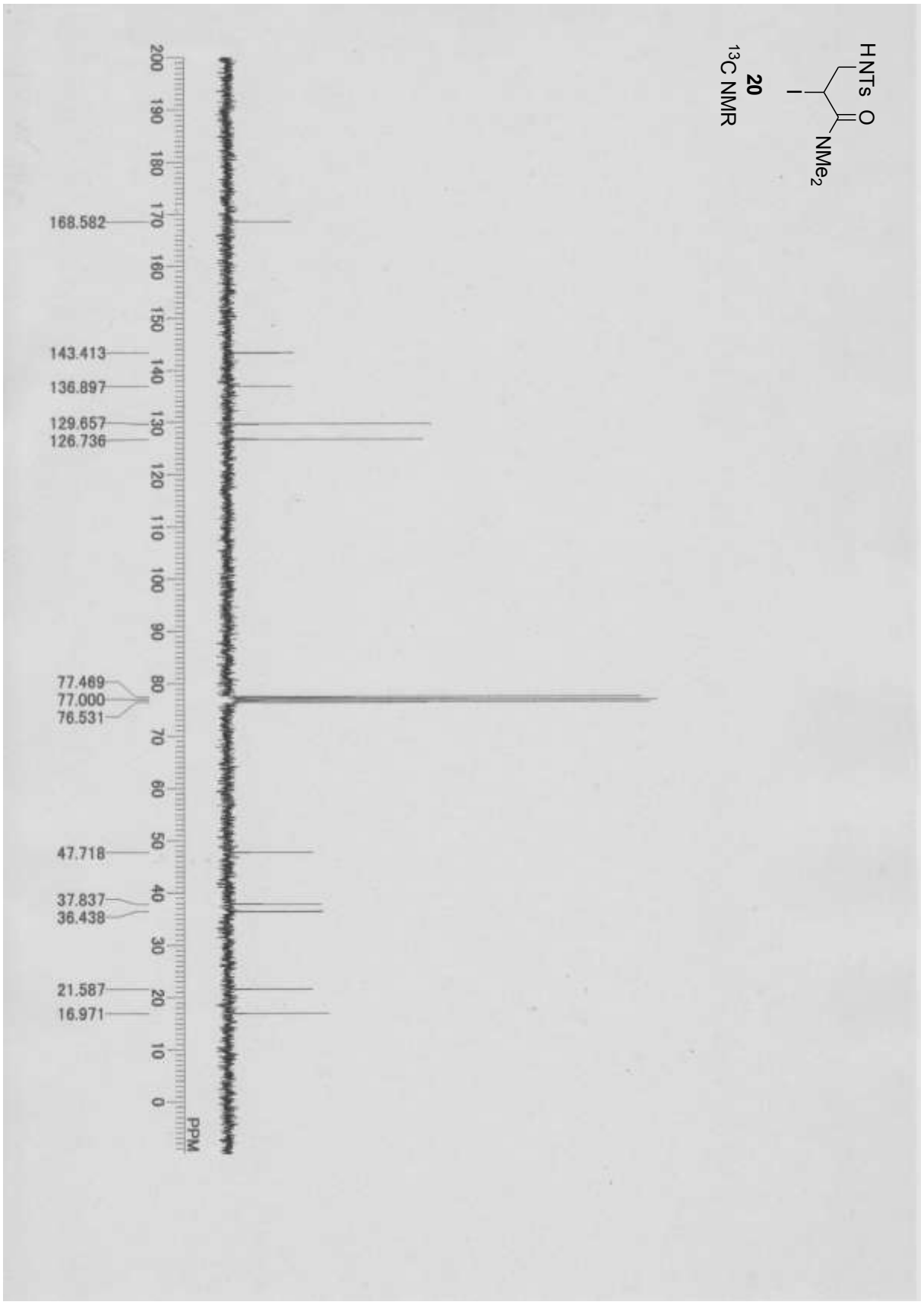

HNTs O
I
Me
18
1H NMR
7.744
7.714
7.334
7.302
7.280
5.532
5.506
5.486
4.745
4.726
4.710
4.692
3.507
3.486
3.473
3.455
3.433
3.420
3.398
3.357
3.339
3.329
3.310
3.286
3.276
3.258
2.430
2.402
2.330
2.079
0.000
2.0731
2.3114
0.9232
1.0000
0.8984
0.9137
6.0179
ppm

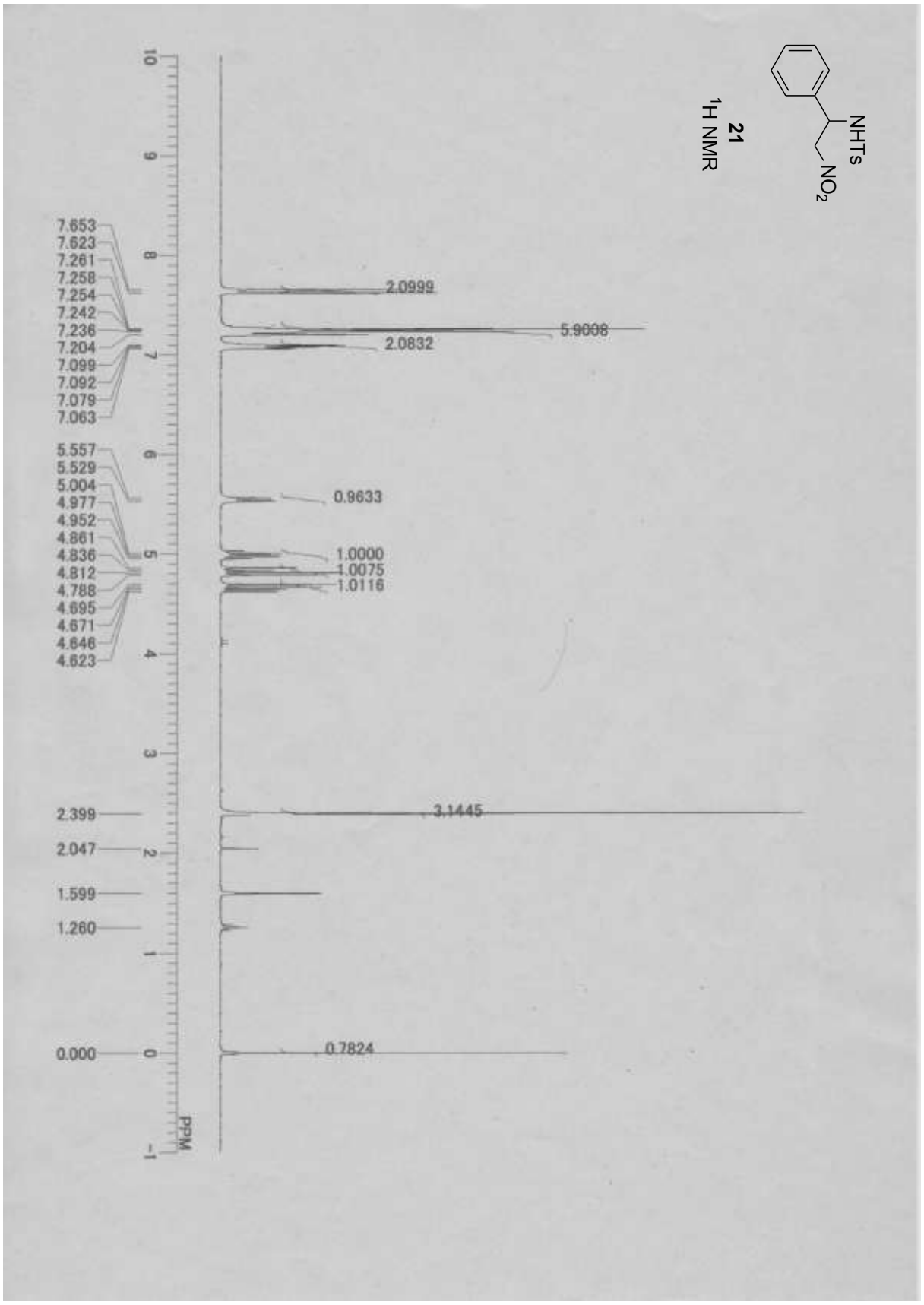

HNTs O
Me
I
18
13C NMR
143.619
138.535
129.714
126.769
77.469
77.000
76.531
46.015
27.486
27.256
21.571
PPM

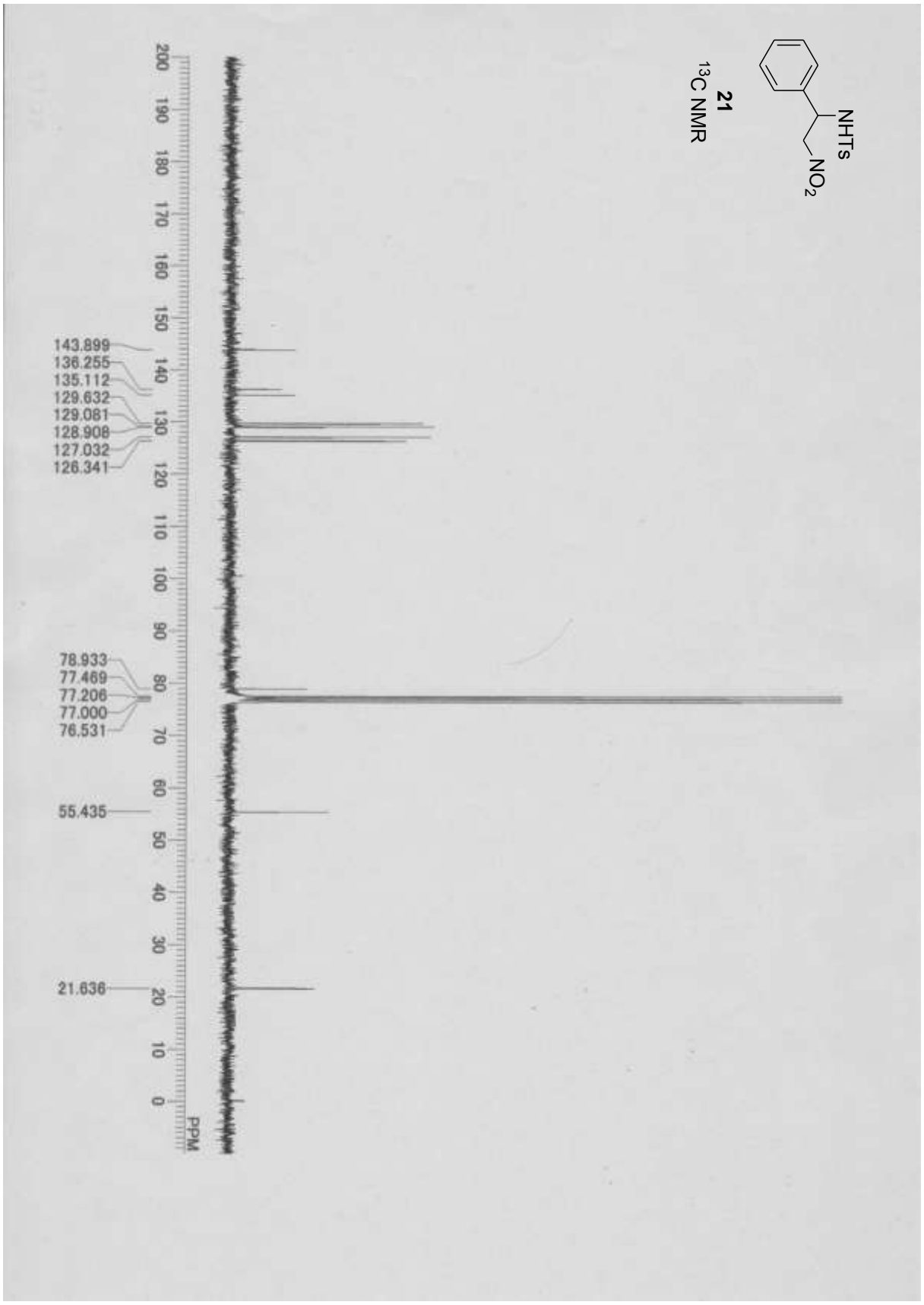

HNTs O
I
OEt
19
1H NMR
7.748
7.717
7.339
7.310
7.262
5.255
5.235
5.214
4.516
4.496
4.482
4.462
4.256
4.242
4.236
4.229
4.216
4.210
4.189
4.184
4.171
4.163
4.158
4.144
3.517
3.494
3.483
3.464
3.442
3.430
3.420
3.408
3.398
3.392
3.371
3.347
3.339
3.319
3.307
2.440
1.299
1.272
1.246
1.8669
2.5859
0.9865
1.0000
2.1829
2.0983
3.1002
3.2040
PPM

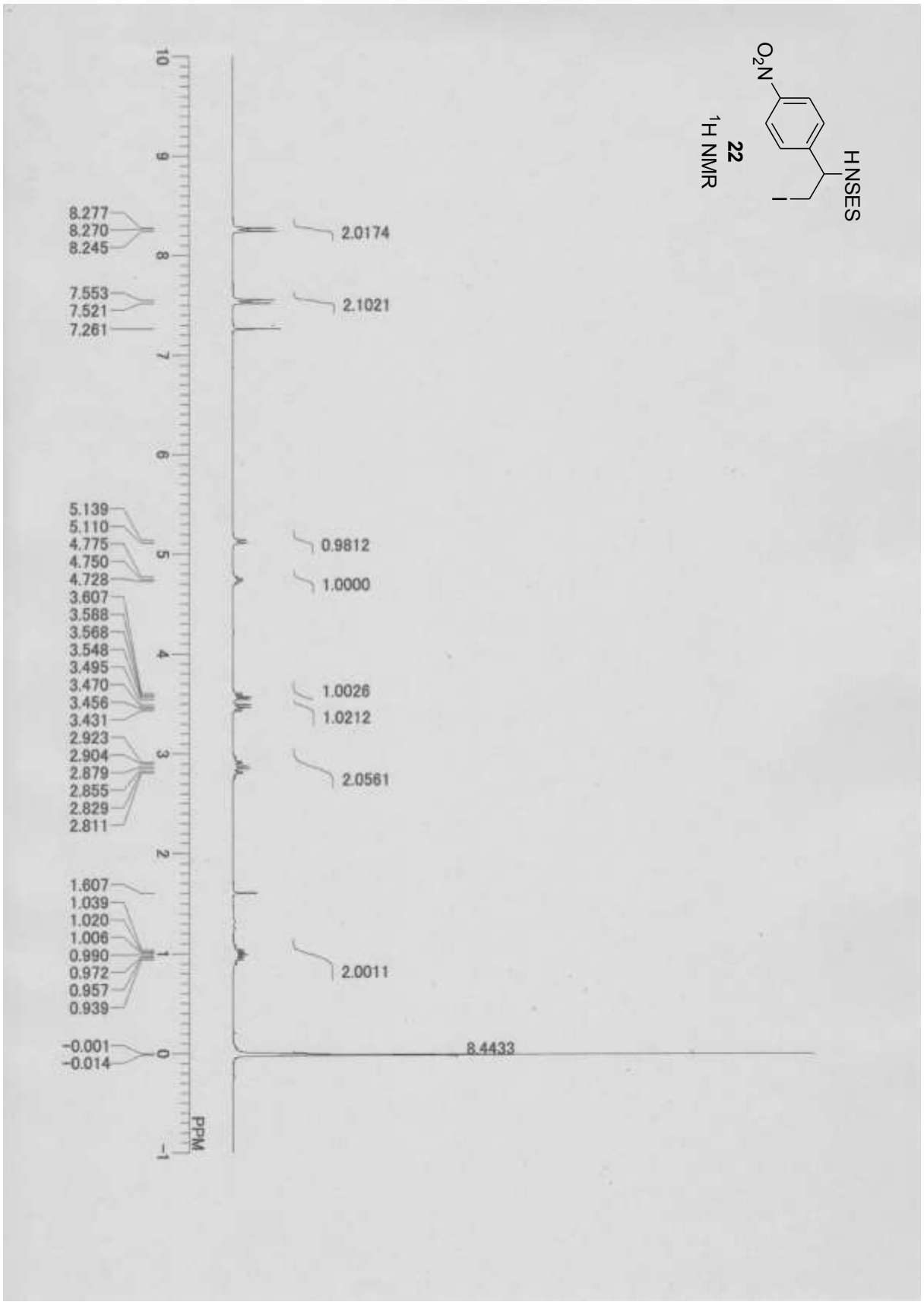

HNTs O
I
OEt
19
13C NMR
170.375
143.742
136.716
129.788
126.818
77.469
77.000
76.531
62.380
47.249
21.645
16.922
13.771
PPM

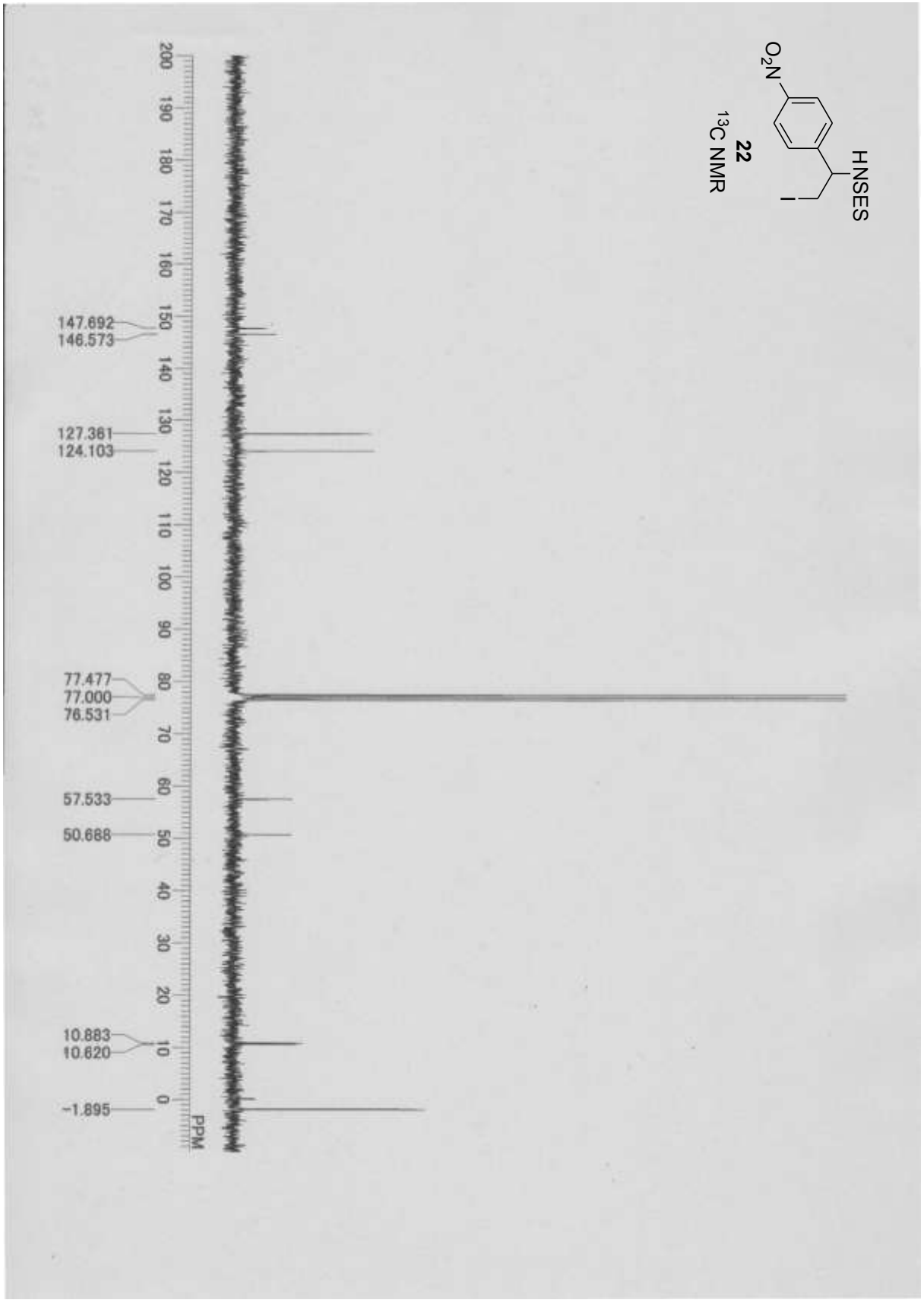

HNTs O
I
NMe2
20
1H NMR
7.745
7.714
7.323
7.294
7.272
5.816
5.786
5.766
4.637
4.620
4.600
4.582
3.628
3.608
3.591
3.577
3.558
3.541
3.521
3.428
3.410
3.397
3.379
3.360
3.347
3.329
3.045
2.965
2.951
2.912
2.762
2.428
2.047
1.850
1.258
0.000
2.0000
2.1676
0.8748
0.9319
0.9166
0.9212
5.8210
3.0474
PPM

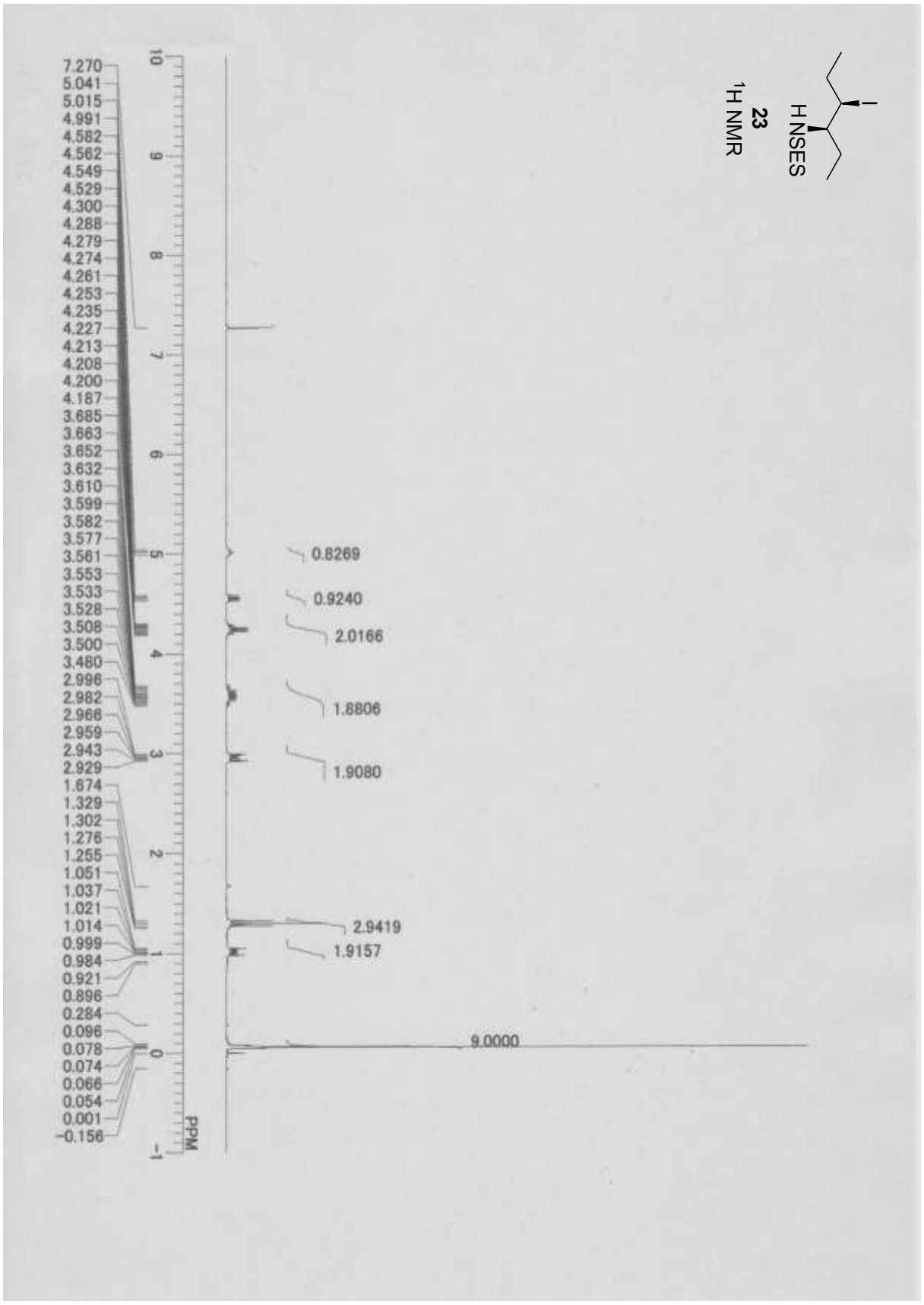

HNTs O
I
NMe2
20
13C NMR
168.582
143.413
136.897
129.657
126.736
77.469
77.000
76.531
47.718
37.837
36.438
21.587
16.971
PPM

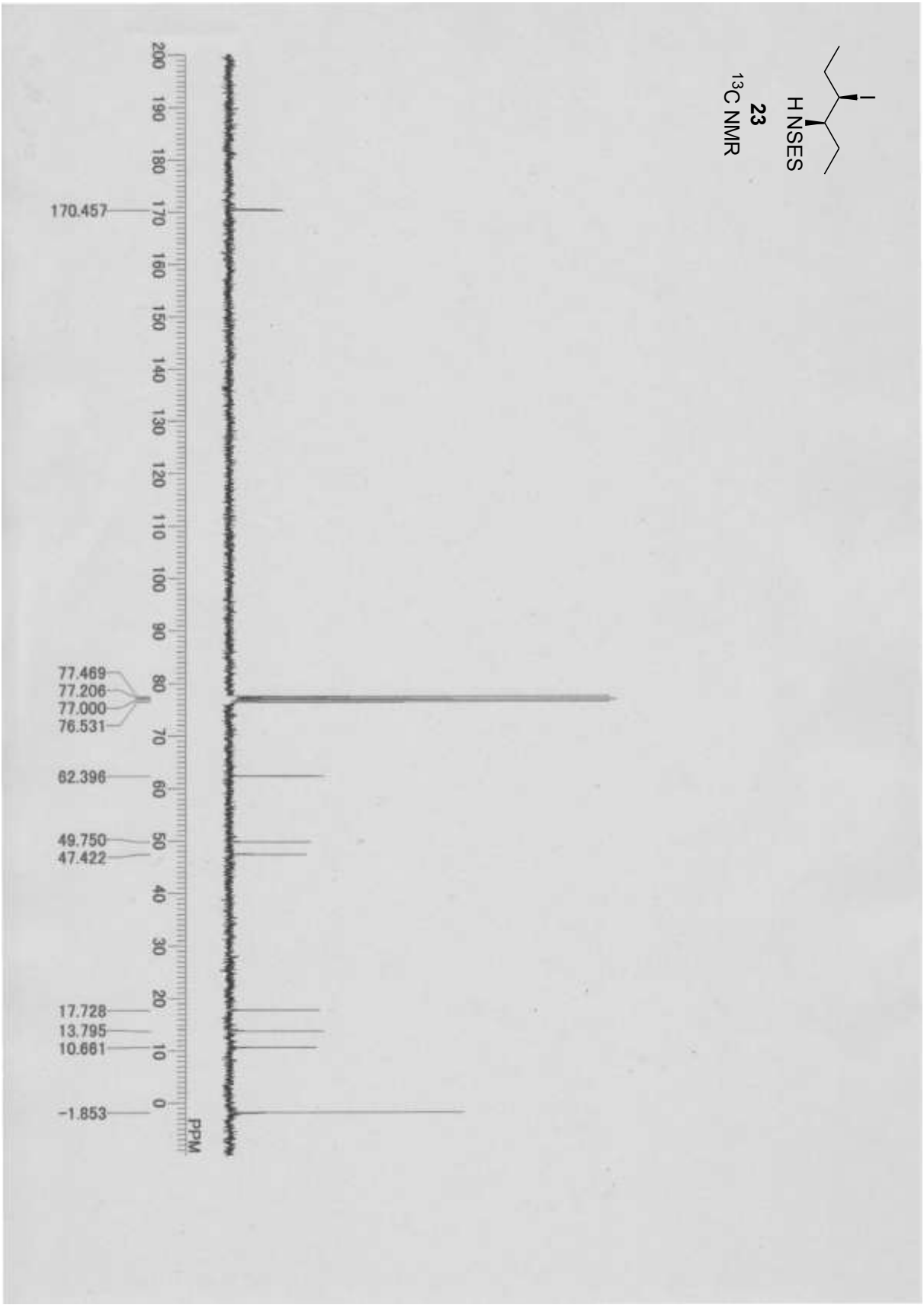

21
1H NMR
NHTs
NO2
7.653
7.623
7.261
7.258
7.254
7.242
7.236
7.204
7.099
7.092
7.079
7.063
5.557
5.529
5.004
4.977
4.952
4.861
4.836
4.812
4.788
4.695
4.671
4.646
4.623
2.399
2.047
1.599
1.260
0.000
2.0999
5.9008
2.0832
0.9633
1.0000
1.0075
1.0116
3.1445
0.7824
PPM


21
^{13}C NMR
NHTs
NO_2
143.899
136.255
135.112
129.632
129.081
128.908
127.032
126.341
78.933
77.469
77.206
77.000
76.531
55.435
21.636
PPM


22
^{1}H NMR
O_2N
HNSES
I
8.277
8.270
8.245
7.553
7.521
7.261
5.139
5.110
4.775
4.750
4.728
3.607
3.588
3.568
3.548
3.495
3.470
3.456
3.431
2.923
2.904
2.879
2.855
2.829
2.811
1.607
1.039
1.020
1.006
0.990
0.972
0.957
0.939
-0.001
-0.014
2.0174
2.1021
0.9812
1.0000
1.0026
1.0212
2.0561
2.0011
8.4433
PPM


O_2N
HNSES
I
22
^{13}C NMR
147.692
146.573
127.361
124.103
77.477
77.000
76.531
57.533
50.688
10.883
10.620
-1.895
PPM


23
^{1}H NMR
H NSES
7.270
5.041
5.015
4.991
4.582
4.562
4.549
4.529
4.300
4.288
4.279
4.274
4.261
4.253
4.235
4.227
4.213
4.208
4.200
4.187
3.685
3.663
3.652
3.632
3.610
3.599
3.582
3.577
3.561
3.553
3.533
3.528
3.508
3.500
3.480
2.996
2.982
2.966
2.959
2.943
2.929
1.674
1.329
1.302
1.276
1.255
1.051
1.037
1.021
1.014
0.999
0.984
0.921
0.896
0.284
0.096
0.078
0.074
0.066
0.054
0.001
-0.156
0.8269
0.9240
2.0166
1.8806
1.9080
2.9419
1.9157
9.0000
PPM


HNSES
23
13C NMR
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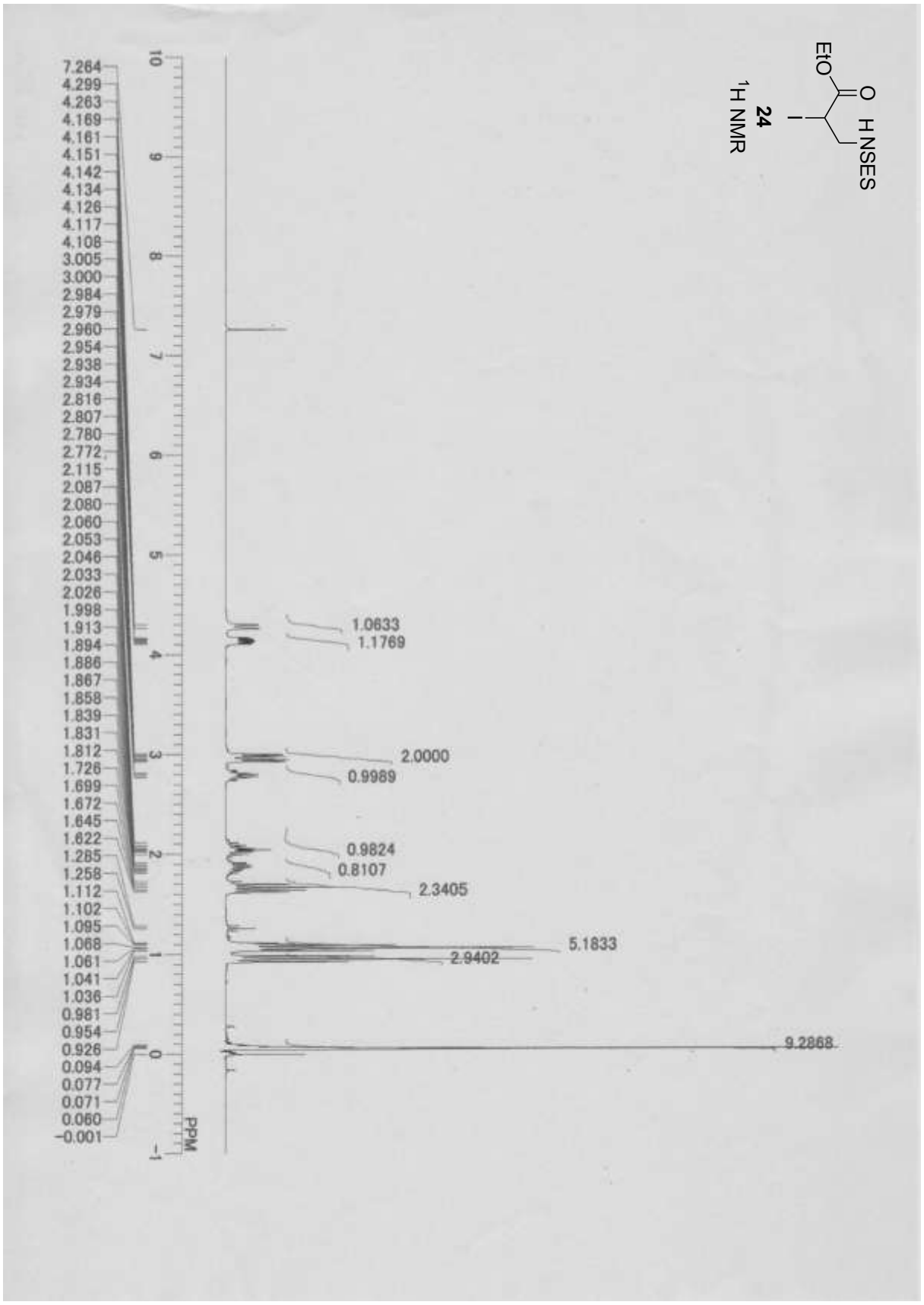
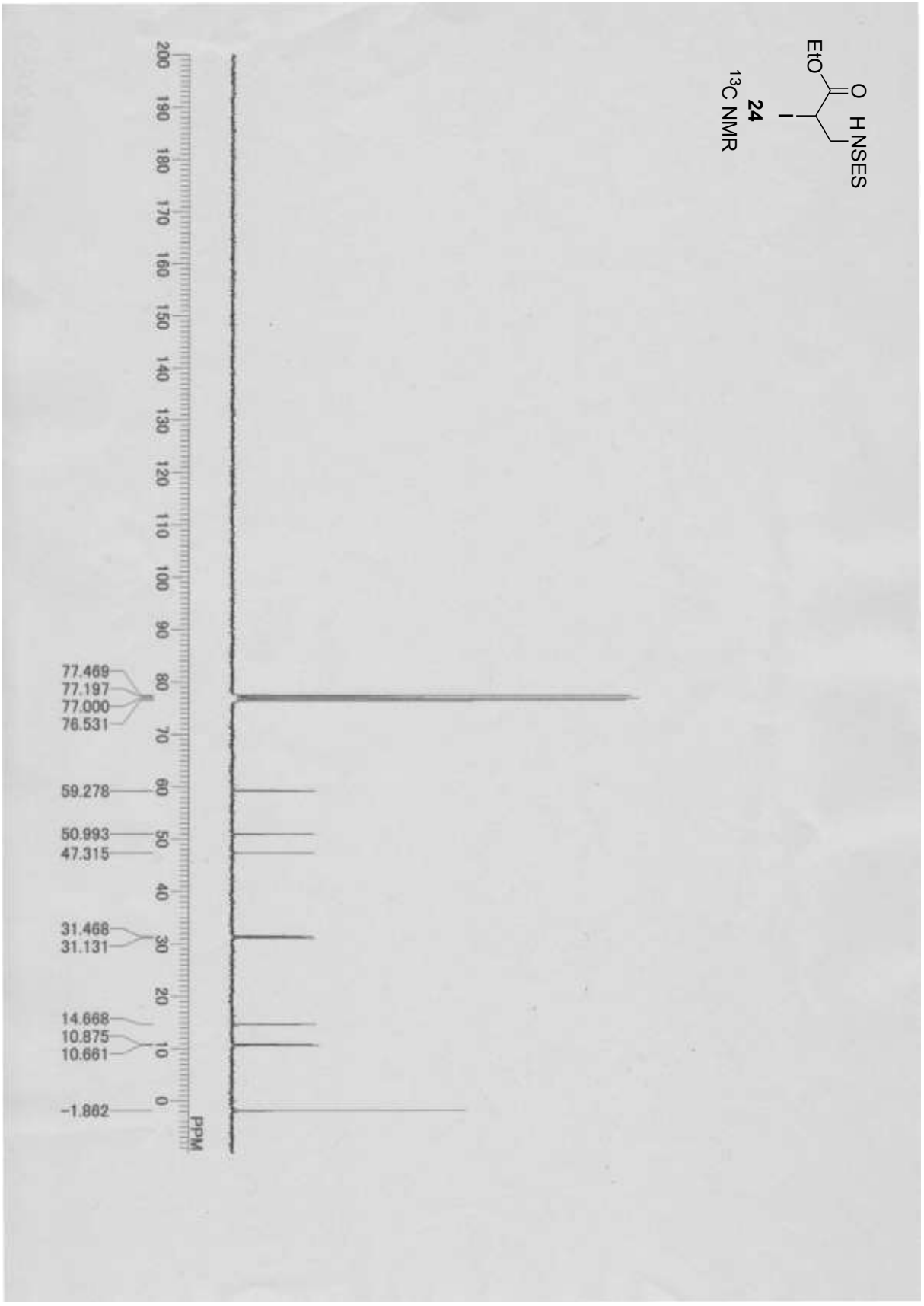
77.206
77.000
76.531
62.396
49.750
47.422
17.728
13.795
10.661
-1.853
PPM


24
^{1}H NMR
EtO
O
HNSES
I
7.264
4.299
4.263
4.169
4.161
4.151
4.142
4.134
4.126
4.117
4.108
3.005
3.000
2.984
2.979
2.960
2.954
2.938
2.934
2.816
2.807
2.780
2.772
2.115
2.087
2.080
2.060
2.053
2.046
2.033
2.026
1.998
1.913
1.894
1.886
1.867
1.858
1.839
1.831
1.812
1.726
1.699
1.672
1.645
1.622
1.285
1.258
1.112
1.102
1.095
1.068
1.061
1.041
1.036
0.981
0.954
0.926
0.094
0.077
0.071
0.060
-0.001
1.0633
1.1769
2.0000
0.9989
0.9824
0.8107
2.3405
5.1833
2.9402
9.2868
PPM


EtO
O
H
N
SES
I
24
^{13}C NMR
77.469
77.197
77.000
76.531
59.278
50.993
47.315
31.468
31.131
14.668
10.875
10.661
-1.862
PPM