Supporting information

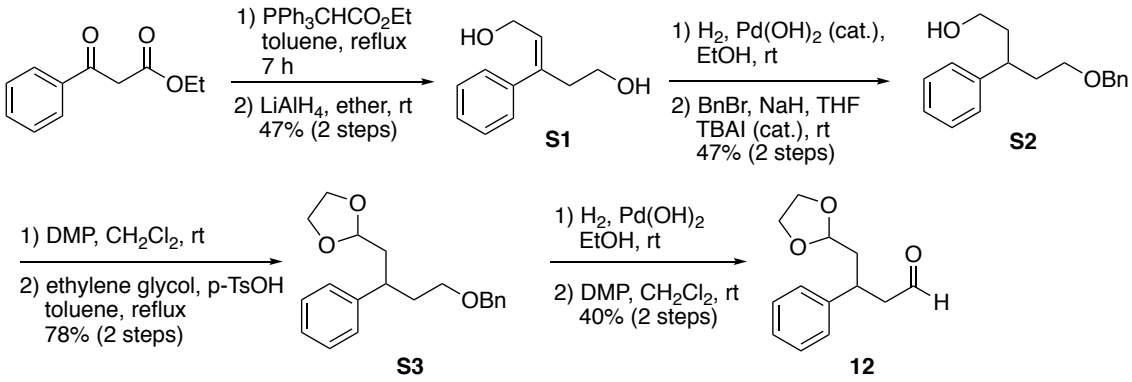
The one-pot synthesis of pyridine derivatives from the corresponding 1,5-dicarbonyl compounds

Hiromichi Mihara, Takeru Miyakoshi, Yui Kikuchi, Hiroyuki Konno*

Department of Biological Engineering, Graduate School of Science and Engineering, Yamagata University, Yonezawa, Yamagata 992-8510, Japan

General

All solvents were reagent grade. CH_2Cl_2 was distilled from CaH_2 and THF from Na. All commercial reagents were of the highest purity available. ^1H (400, 500 or 600 MHz) and ^{13}C NMR (100, 125 or 150 MHz) spectra were recorded on JNM-ECX400, JNM-ECX500 or JNM-ECA600 spectrometers. Chemical shifts are expressed in ppm relative to $CHCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C). Analytical TLC was performed on Merck Silica gel $60F_{254}$. Crude products were purified by column chromatography on Silica Gel 60 N [Kanto, particle size, (spherical, neutral) 63-210 μm or 100-200 μm]. Mass spectra were obtained using a JEOL AccuTOF JMS-T100LC (ESIMS). GC-MS. IR spectra were recorded at FT/IR-460 plus (JASCO, Tokyo, Japan).



3-Phenylpent-2-ene-1,5-diol (S1)

A phosphorus ylide (5.22 g, 15.0 mmol) was added to a solution of ethyl benzoylacetate (860 μL, 5.00 mmol) in toluene (16 mL), and the mixture was heated under reflux for 7 h. The reaction solution was cooled to room temperature and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:2) to give crude diester as a yellow oil. Under a nitrogen atmosphere, a ether suspension of $LiAlH_4$ (343 mg, 9.03 mmol) was cooled to 0 °C. Ether solution (5 mL) of crude diester was slowly added dropwise. After completion of the dropwise addition, the ice water bath was removed and the reaction solution was stirred at room temperature. After 2 h, the mixture was cooled to 0 °C and sequentially diluted with H_2O (343 μL), 1 M NaOH (343 μL) and H_2O (1.03 mL). The mixture was stirred for 1 h, diluted with AcOEt (30 mL), filtered through Celite, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 5:1) to give unsaturated diol (**S1**) (423 mg, 2 steps, 47%) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (t, J = 6.0 Hz, 2H), 3.54 (t, J = 6.0 Hz, 2H), 4.20 (d, J = 7.2 Hz, 2H), 6.08 (t, J =

7.2 Hz, 1H), 7.23-7.35 (m, 5H). K. Sato, Y. Masui, M. Onaka, *Bull. Chem. Soc. Jpn,* 2017, **90**, 1318.

5-(Benzyloxy)-3-phenylpentan-1-ol (S2)

A catalytic amount of 1 M NaOH was added to a suspension of $Pd(OH)_2$ (catalytic amount) and **S1** (1.25 g, 7.01 mmol) in EtOH (16 mL). The reaction vessel was flushed with hydrogen gas and the reaction solution was stirred vigorously for 1 h under hydrogen atmosphere (1 atm). The reaction solution was filtered through Celite and washed with EtOH. The filtrate was concentrated under reduced pressure to give saturated diol. This compound was used in the next reaction without purification. Sodium hydride (244 mg, 6.10 mmol) was added to a solution of diol in THF (30 mL) at 0 °C and the mixture stirred at room temperature for 1 h. Benzyl bromide (858 μL, 7.17 mmol) and a catalytic amount of TBAI were added and the mixture was stirred at room temperature for 5 h. The reaction solution was cooled to 0 °C, diluted with water, and concentrated under reduced pressure. The aqueous layer was extracted with AcOEt, the organic layer was washed with H_2O, brine and dried with $MgSO_4$ and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:1) to give benzyl ether (**S2**) (635 mg, 2 steps, 47%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79-1.95 (m, 3H), 2.01-2.10 (m, 1H), 2.47 (br, 1H), 2.86-2.96 (m, 1H), 3.25-3.13 (m, 1H), 3.36-3.50 (m, 3H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 7.18-7.47 (m, 10H) ppm. ^{13}C NMR (600 MHz, $CDCl_3$) δ 36.7, 39.0, 39.6, 60.9, 68.3, 73.0, 126.4, 127.6, 127.7, 127.8, 128.4, 128.6, 138.4, 144.5. IR (film) ν max cm^{-1}: 3378, 2931, 2858. MS (ESI) *m/z*: calcd. for $C_{18}H_{22}NaO_2$ $[M+H]^+$ 293.2, found 293.2.

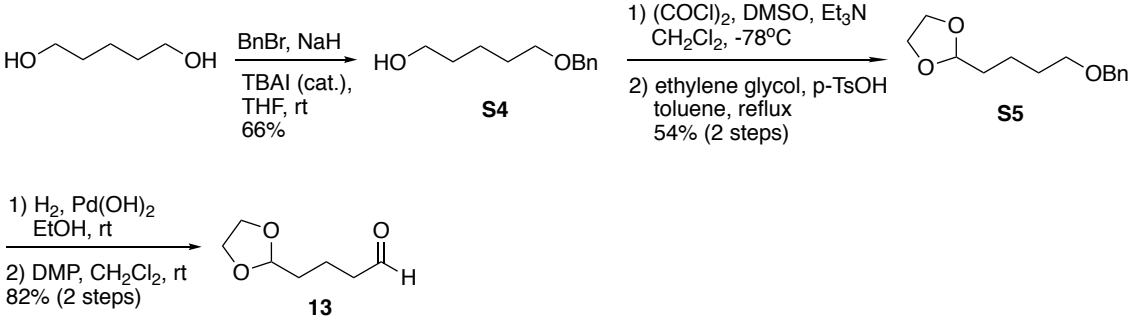
2-[4-(Benzyloxy)-2-phenylbutyl]-1,3-dioxolane (S3)

DMP (1.92 g, 4.53 mmol) was added to a solution of **S2** (635 mg, 2.35 mmol) in CH_2Cl_2 (14 mL) and stirred for 1 h. $NaHCO_3$ aq. and excess $Na_2S_2O_3$ aq. were added to the reaction solution. After the solid component had dissolved, the aqueous layer was extracted with CH_2Cl_2. The organic layer was washed with H_2O and brine, and dried with anhydrous $MgSO_4$. The filtrate was concentrated under reduced pressure to give aldehyde as a colorless oil. This compound was used in the next reaction without purification. Ethylene glycol (594 μL, 10.7 mmol) and catalytic amount of *p*-TsOH was added to toluene solution (10 mL) of aldehyde and the mixture was refluxed for 2 h. Water produced by the reaction was removed by azeotropic distillation using a Dean-Stark apparatus. The reaction solution was cooled and $NaHCO_3$ aq. was added. The aqueous layer was extracted with ether, the organic layer was washed with H_2O, brine and dried with $MgSO_4$, and the

filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:4) to give acetal protected compound (**S3**) (572 mg, 2 steps 78%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87-2.03 (m, 2H), 2.08-2.19 (m, 2H), 3.06-3.14 (m, 1H), 3.29-3.42 (m, 2H), 3.72-3.81 (m, 2H), 3.90-3.97 (m, 2H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.64-4.68 (m, 1H), 7.19-7.41 (m, 10H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 36.9, 38.5, 40.9, 64.8, 65.4, 68.2, 72.9, 103.1, 126.4, 127.7, 127.8, 128.4, 128.5, 138.6, 144.1. IR (film) ν max cm^{-1}: 2947, 2926, 2881. MS (ESI) *m/z*: calcd. for $C_{20}H_{24}NaO_3$ $[M+H]^+$ 335.2, found 335.2.

4-(1,3-Dioxolan-2-yl)-3-phenylbutanal (12)

S3 (156 mg, 0.500 mmol) was added to a suspension of $Pd(OH)_2$ (catalytic amount) in EtOH (7 mL). The reaction vessel was flushed with hydrogen gas and the reaction solution was stirred vigorously for 1 h under a hydrogen atmosphere (1 atm). The reaction solution was filtered through Celite and washed with EtOH. The filtrate was concentrated under reduced pressure to give the crude alcohol as a colorless oil. This compound was used in the next reaction without purification. DMP (172 mg, 0.406 mmol) was added to a solution of the alcohol (111 mg, 0.500 mmol) in CH_2Cl_2 (10 mL) and stirred for 3 h. $NaHCO_3$ aq. and excess $Na_2S_2O_3$ aq. were added to the reaction solution. After the solid component had dissolved, the aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:2) to give aldehyde (**12**) (45 mg, 2 steps, 40%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88-1.95 (m, 1H), 2.02-2.08 (m, 1H), 2.70-2.86 (m, 2H), 3.44-3.51 (m, 1H), 3.73-3.81 (m, 2H), 3.89-3.96 (m, 2H), 4.63 (dd, *J* = 6.3, 3.2 Hz, 1H), 7.18-7.36 (m, 5H), 9.64 (t, *J* = 1.8 Hz, 1H). G. Chelucci, *Synthesis* 1991, **6**, 474.



5-(Benzyloxy)-pentan-1-ol (S4)

Sodium hydride (2.4 g, 60.0 mmol) was added to a solution of pentane-1,5-diol (5.26 mL,

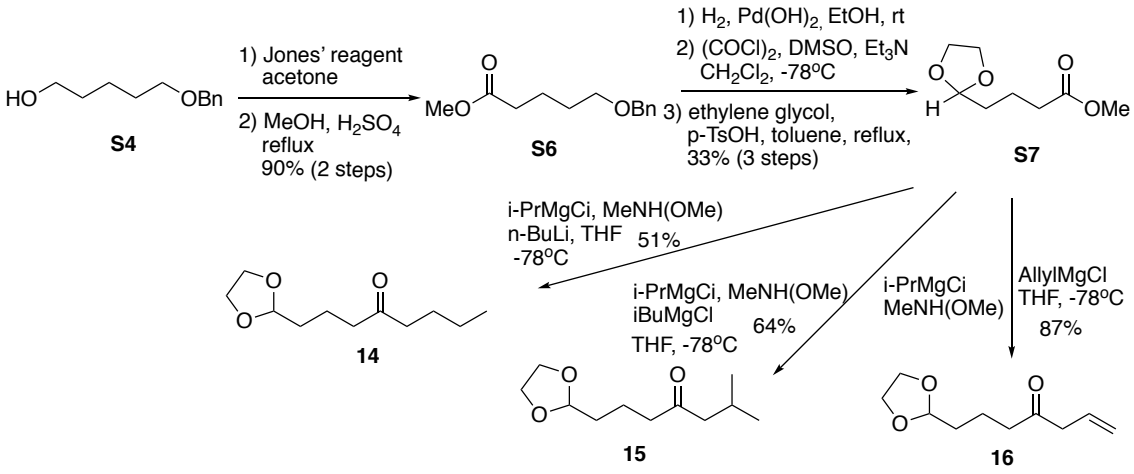
50.0 mmol) in THF (80 mL) at 0 °C, and the mixture was stirred for 1 h. Benzyl bromide (6.6 mL, 55.2 mmol), and a catalytic amount of TBAI were added and mixture was stirred at room temperature for 15 h. The reaction solution was cooled to 0 °C, H_2O was added, and the mixture was concentrated under reduced pressure. The aqueous layer was extracted with AcOEt, the organic layer was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:2) to give benzyl ether (**S4**) (6.4 g, 66%) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.39-1.44 (m, 2H), 1.51-1.56 (m, 2H), 1.60-1.65 (m, 2H), 2.42 (brs, 1H), 3.46 (t, *J* = 6.6 Hz, 2H), 3.56 (t, *J* = 6.0 Hz, 2H), 4.48 (s, 2H), 7.24-7.34 (m, 5H). J. L. Kiappes, M. L. Hill, D. S. Alonzi, J. L. Miller, I. Ren, A. C. Sayce, A. T. Caputo, A. Kato, N. Zitzmann, *Org. Lett.*, 2018, **13**, 60.

2-[4-(Benzyloxy)-butyl]-1,3-dioxolane (S5)

A solution of dimethyl sulfoxide (2.3 mL, 32.4 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of oxalyl chloride (1.4 mL, 16.3 mmol) in CH_2Cl_2 (30 mL) at -78 °C. After 10 min, a solution of **S4** (1.60 g, 8.24 mmol) in CH_2Cl_2 (20 mL) was added and reaction solution was stirred at -78 °C for 30 min. Triethylamine (6.8 mL, 48.8 mmol) was added dropwise and the temperature was kept at -78 °C for 10 min, then gradually raised to room temperature. NH_4Cl aq. was added, the aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure to give the aldehyde as a colorless oil. This compound was used in the next reaction without purification. Ethylene glycol (1.4 mL, 25.1 mmol) and catalytic amount of *p*-TsOH was added to a solution of aldehyde in toluene (40 mL) and the mixture was heated under reflux for 5 h. Water produced by the reaction was removed by azeotropic distillation using a Dean-Stark apparatus. The reaction solution was cooled and $NaHCO_3$ aq. was added. The aqueous layer was extracted with ether, the organic layer was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:4) to give acetal protected compound (**S5**) (1.05 g, 2 steps 54%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.49-1.54 (m, 2H), 1.64-1.69 (m, 4H), 3.46 (t, *J* = 7.2 Hz, 2H), 3.77-3.85 (m, 2H), 3.89-3.95 (m, 2H), 4.48 (s, 2H), 4.83 (t, *J* = 4.8 Hz, 1H), 7.23-7.35 (m, 5H). J. L. Kiappes, M. L. Hill, D. S. Alonzi, J. L. Miller, I. Ren, A. C. Sayce, A. T. Caputo, A. Kato, N. Zitzmann, *Org. Lett.*, 2018, **13**, 60.

4-(1,3-Dioxolan-2-yl)-butanal (13)

S5 (946 mg, 4.00 mmol) was added to a suspension of $Pd(OH)_2$ (catalytic amount) in EtOH (13 mL). The reaction vessel was flushed with hydrogen gas and the reaction solution was stirred vigorously for 1 h under a hydrogen atmosphere (1 atm). The reaction solution was filtered through Celite and washed with EtOH. The filtrate was concentrated under reduced pressure to obtain alcohol. This compound was used in the next reaction without purification. DMP (3.41 g, 8.04 mmol) was added to a solution of alcohol (585 mg, 4.00 mmol) in CH_2Cl_2 (25 mL) and stirred for 5 h. $NaHCO_3$ aq. and excess $Na_2S_2O_3$ aq. were added to the reaction solution. After the solid component had dissolved, the aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with H_2O, brine and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:1) to give aldehyde (**13**) (473 mg, 2 steps, 82%) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 1.61-1.72 (m, 4H), 2.43 (td, J = 7.2, 1.2 Hz, 2H), 3.75-3.80 (m, 2H), 3.86-3.91 (m, 2H), 4.79 (t, J = 4.2 Hz, 1H), 9.69 (t, J = 1.2 Hz, 1H). L. Panella, A. M. Aleixandre, G. J. Kruidhof, J. Robertus, B. L. Feringa, J. G. de Vries, A. J. Minnaard, *J. Org. Chem.*, 2006, **71**, 2026.



Methyl 5-(benzyloxy)-pentanoate (S6)

Jones' reagent was added dropwise to a solution of **S4** (2.53 g, 13.0 mmol) in acetone (20 mL), until the solution was persistenty orange. After stirring the reaction solution for a further 10 min, isopropanol was added until the reaction solution turned green. The solution was concentrated under reduced pressure and the aqueous layer was extracted with ether. The organic layer was washed with H_2O, brine and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. This residue was used in the next reaction without purification. Sulfuric acid (2.8 mL) was added dropwise to a carboxylic

acid (2.71 g, 13.0 mmol) in MeOH solution (30 mL) at 0 °C. The mixture was heated under reflux for 3 h. The reaction solution was cooled to room temperature and concentrated under reduced pressure. The aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with $NaHCO_3$ aq., H_2O, brine and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:3) to give methyl ester (**S6**) (2.60 g, 2 steps, 90%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54-1.77 (m, 4H), 2.33 (t, J = 7.6 Hz, 2H), 3.47 (t, J = 6.2 Hz, 2H), 3.65 (s, 3H), 4.49 (s, 2H), 7.26-7.34 (m, 5H). L. Boerjesson, I. Csoeregh, C. J. Welch, *J. Org. Chem*., 1995, **60**, 2989.

Methyl 4-(1,3-dioxolan-2-yl)butanoate (S7)

S6 (2.60 g, 11.7 mmol) was added to a suspension of $Pd(OH)_2$ (catalytic amount) in MeOH (40 mL). The reaction vessel was flushed with hydrogen gas and the reaction solution was stirred vigorously for 11 h under a hydrogen atmosphere (1 atm). The reaction solution was filtered through Celite and washed with MeOH. The filtrate was concentrated under reduced pressure to give alcohol as a colorless oil. This compound was used in the next reaction without purification. A solution of oxalyl chloride (3.0 mL, 34.9 mmol) in CH_2Cl_2 (30 mL) was cooled to -78 °C and a solution of dimethyl sulfoxide (3.4 mL, 47.9 mmol) in CH_2Cl_2 (20 mL) was slowly added dropwise. After 10 min, a solution of alcohol in CH_2Cl_2 (20 mL) was added and the reaction solution was stirred at -78 °C. After 30 min, the reaction was diluted by the dropwise addition of triethylamine (10 mL, 71.7 mmol) and after 10 min at -78 °C for 10 min, it was allowed to warm to room temperature. NH_4Cl aq. was added, the aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with H_2O, brine and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure to obtain an aldehyde compound as a colorless oil. This compound was used in the next reaction without purification. Ethylene glycol (1.3 mL, 23.3 mmol) and catalytic amount of *p*-TsOH was added to a solution of aldehyde in toluene (60 mL) and the mixture was heated under reflux for 3 h. H_2O produced by the reaction was removed by azeotropic distillation using a Dean-Stark apparatus. The reaction solution was cooled and $NaHCO_3$ aq. was added. The aqueous layer was extracted with ether, the organic layer was washed with H_2O, brine and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:1) to give **S7** (672 mg, 3 steps, 33%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57-1.70 (m, 4H), 2.28 (t, J = 7.5 Hz, 2H), 3.57 (s, 3H), 3.73-3.78 (m, 2H), 3.83-3.90 (m, 2H), 4.76 (t, J = 4.5 Hz, 1H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 19.3, 33.0, 33.7, 51.4, 64.8, 104.0, 173.7. IR (film) ν max cm^{-1}: 2953,

2884, 2768, 1737. MS (EI) *m/z*: calcd. for $C_6H_{13}O_4$ $[M-C_2H_2]^+$ 149.1, found 149.1.

1-(1,3-Dioxolan-2-yl)-octan-4-one (14)

Under a nitrogen atmosphere, a solution of i-PrMgCl (1.3 M, 1.85 mL, 2.40 mmol) was added dropwise to a solution of *N, O*-dimethylhydroxylamine hydrochloride (117 mg, 1.20 mmol) and **S7** (130 μL, 0.80 mmol) in THF (4 mL) at 0 °C. After stirring for 30 min, a solution of BuLi in hexane (2.5 M, 0.96 mL, 2.40 mmol) was added, and the mixture stirred at -78 °C. After 3 h, NH_4Cl aq. was added, the temperature was raised to room temperature, and concentrated under reduced pressure. The aqueous layer was extracted with AcOEt, the organic layers was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure to obtain cyclization precursor (**14**) (82 mg, 51%) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.23-1.29 (m, 2H), 1.48-1.53 (m, 2H), 1.60-1.69 (m, 4H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 3.77-3.83 (m, 2H), 3.89-3.94 (m, 2H), 4.81 (t, *J* = 4.2 Hz, 1H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 13.9, 18.2, 22.4, 26.0, 33.1, 42.3, 42.5, 64.9, 104.3, 211.0. IR (film) ν max cm^{-1}: 2957, 2933, 2874, 1713. MS (EI) *m/z*: calcd. for $C_{11}H_{20}O_3$ $[M]^+$ 200.3, found 200.2.

1-(1,3-Dioxolan-2-yl)-6-methylheptan-4-one (15)

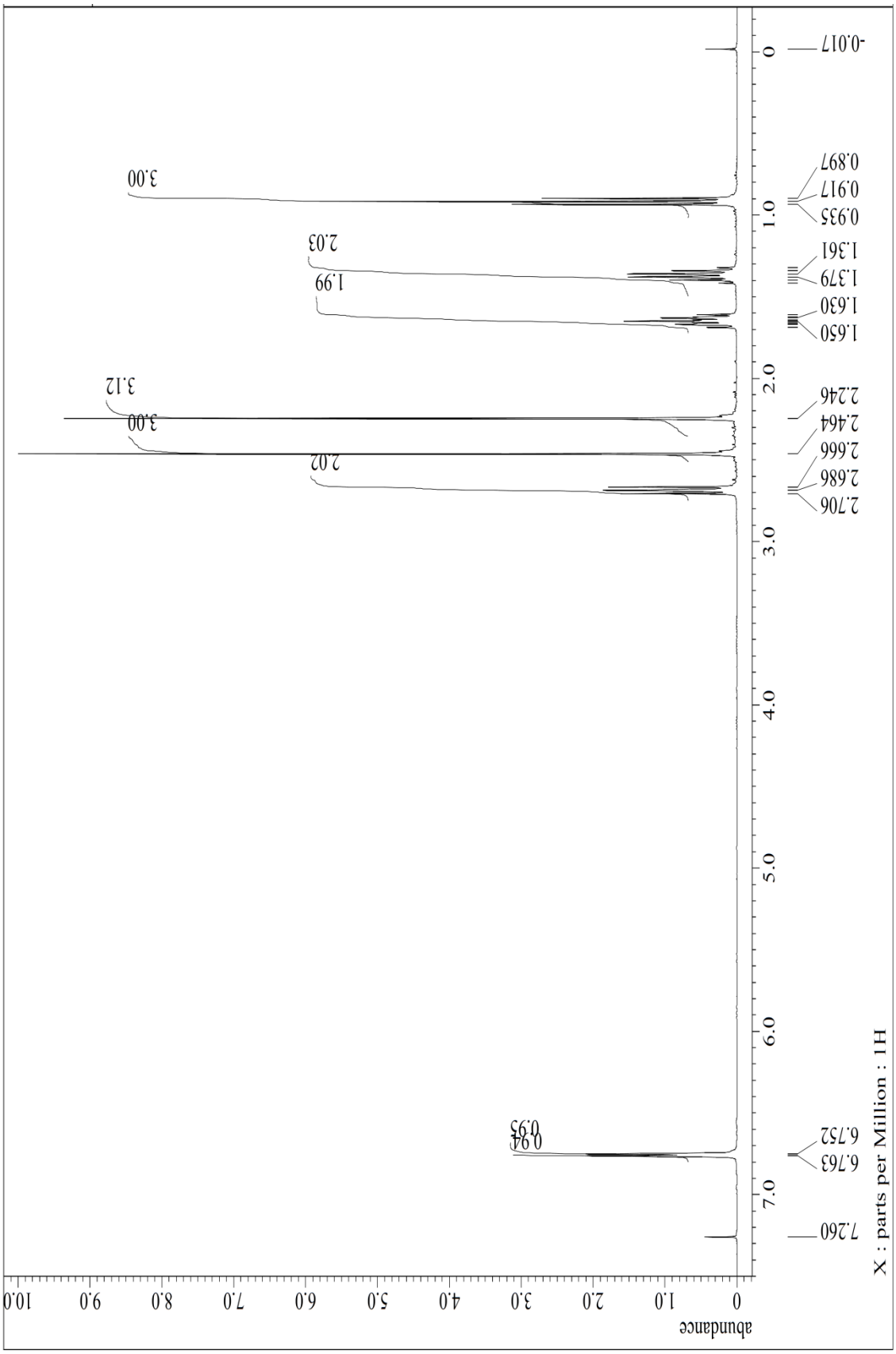
Under a nitrogen atmosphere, a solution of i-PrMgCl (1.3 M, 1.85 mL, 2.40 mmol) was added dropwise to a solution of *N, O*-dimethylhydroxylamine hydrochloride (117 mg, 1.20 mmol) and **S7** (130 μL, 0.80 mmol) in THF (4 mL) at 0 °C. After stirring for 30 min, a solution of Grignard reagent in hexane (2.0 M, 4.0 mL, 8.0 mmol) was added, and the mixture stirred at -78 °C. After 1 h, NH_4Cl aq. was added, the temperature was raised to room temperature, and concentrated under reduced pressure. The aqueous layer was extracted with AcOEt, the organic layer was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure to obtain cyclization precursor (**15**) (102 mg, 64%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, *J* = 7.0 Hz, 6H), 1.50-1.66 (m, 4H), 2.01-2.09 (m, 1H), 2.20 (d, *J* = 7.0 Hz, 2H), 2.37 (t, *J* = 7.0 Hz, 2H), 3.73-3.79 (m, 2H), 3.84-3.91 (m, 2H), 4.76 (t, *J* = 4.5 Hz, 1H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 18.2, 22.6, 24.6, 33.1, 42.9, 51.8, 64.9, 104.3, 210.6. IR (film) ν max cm^{-1}: 2956, 2932, 2872, 1711. MS (EI) *m/z*: calcd. for $C_{11}H_{20}O_3$ $[M]^+$ 200.3, found 200.2.

7-(1,3-Dioxolan-2-yl)-hept-1-en-4-one (16)

Under a nitrogen atmosphere, a solution of i-PrMgCl (1.3 M, 7.0 mL, 9.10 mmol) was added dropwise to a solution of *N, O*-dimethylhydroxylamine hydrochloride (439 mg,

mmol) was added dropwise to a solution of *N, O*-dimethylhydroxylamine hydrochloride (439 mg, 4.50 mmol) and **S7** (439 μL, 3.00 mmol) in THF (15 mL) at 0 °C. After 30 min, Grignard reagent in ether solution (0.7 M, 8.0 mL, 5.60 mmol) was added dropwise at 0 °C. After raising to room temperature and stirring for 4 h, the reaction solution was poured into NH_4Cl aq. cooled to 0 °C. The solution was concentrated under reduced pressure, the aqueous layer was extracted with CH_2Cl_2, the organic layer was washed with H_2O, NaCl aq. and dried with $MgSO_4$, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt:hexane = 1:2) to give cyclization precursor (**16**) (481 mg, 87%) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.61-1.72 (m, 4H), 2.47 (t, J = 7.2 Hz, 2H), 3.14 (d, J = 7.2 Hz, 2H), 3.78-3.83 (m, 2H), 3.89-3.95 (m, 2H), 4.81 (t, J = 4.2 Hz, 1H), 5.08-5.15 (m, 2H), 5.85-5.92 (m, 1H). ^{13}C NMR (600 MHz, $CDCl_3$) δ 18.0, 33.0, 41.9, 47.7, 64.9, 104.3, 118.8, 130.7, 208.4. IR (film) ν max cm^{-1}: 2954, 2884, 2769, 1714. MS (EI) *m/z*: calcd. for $C_{10}H_{16}O_3$ $[M]^+$ 184.1, found 184.2.

^{1}H NMR of **5**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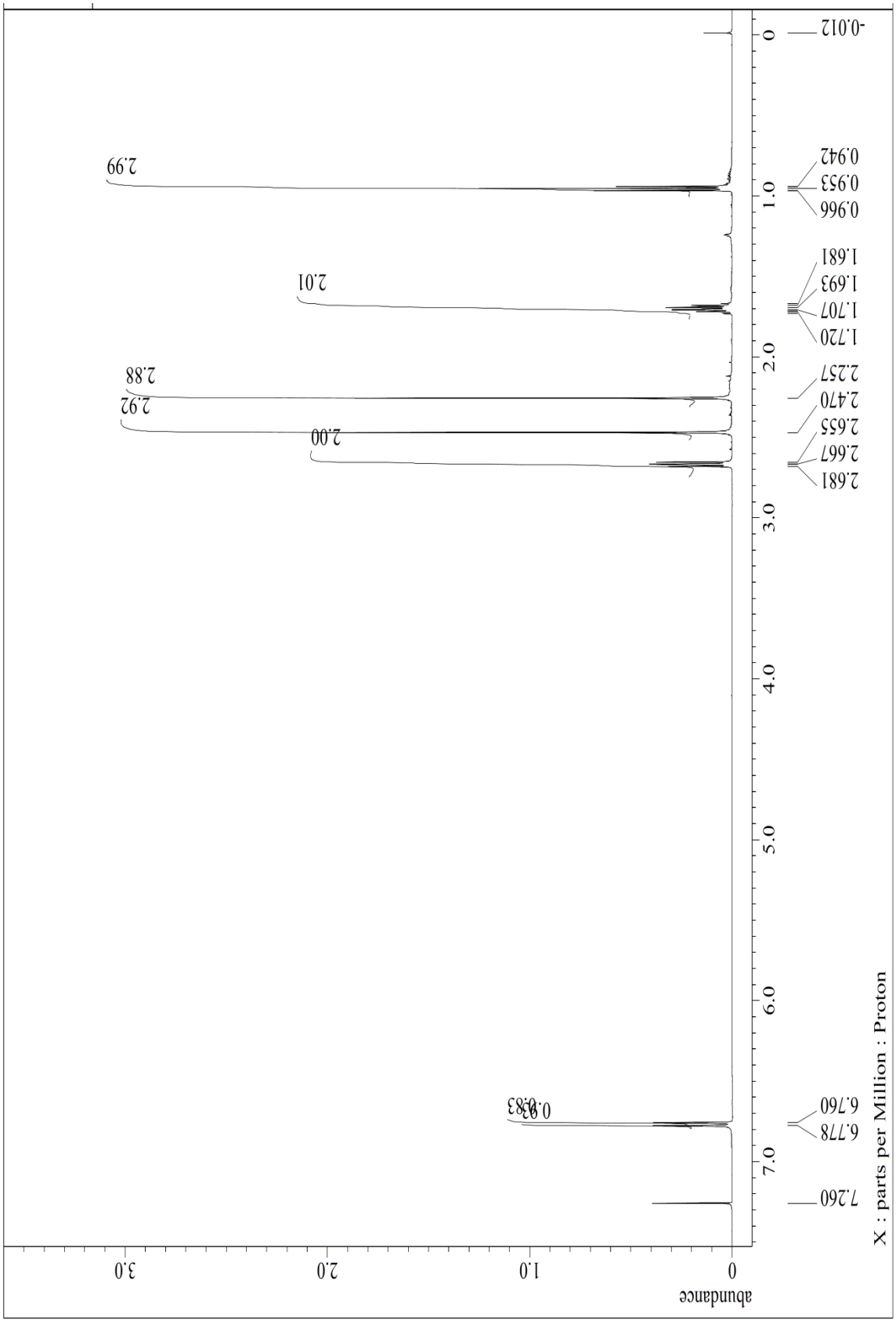
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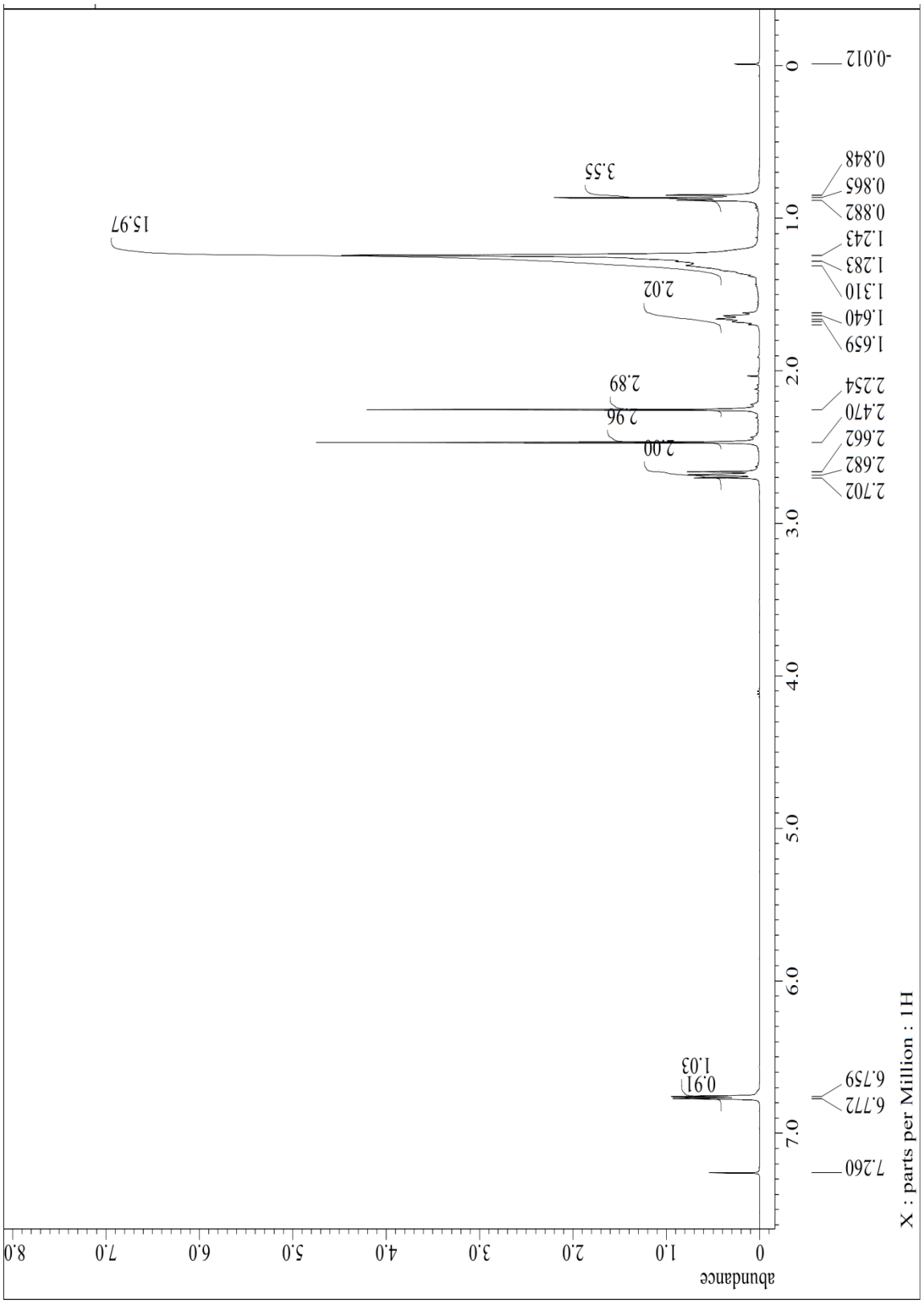
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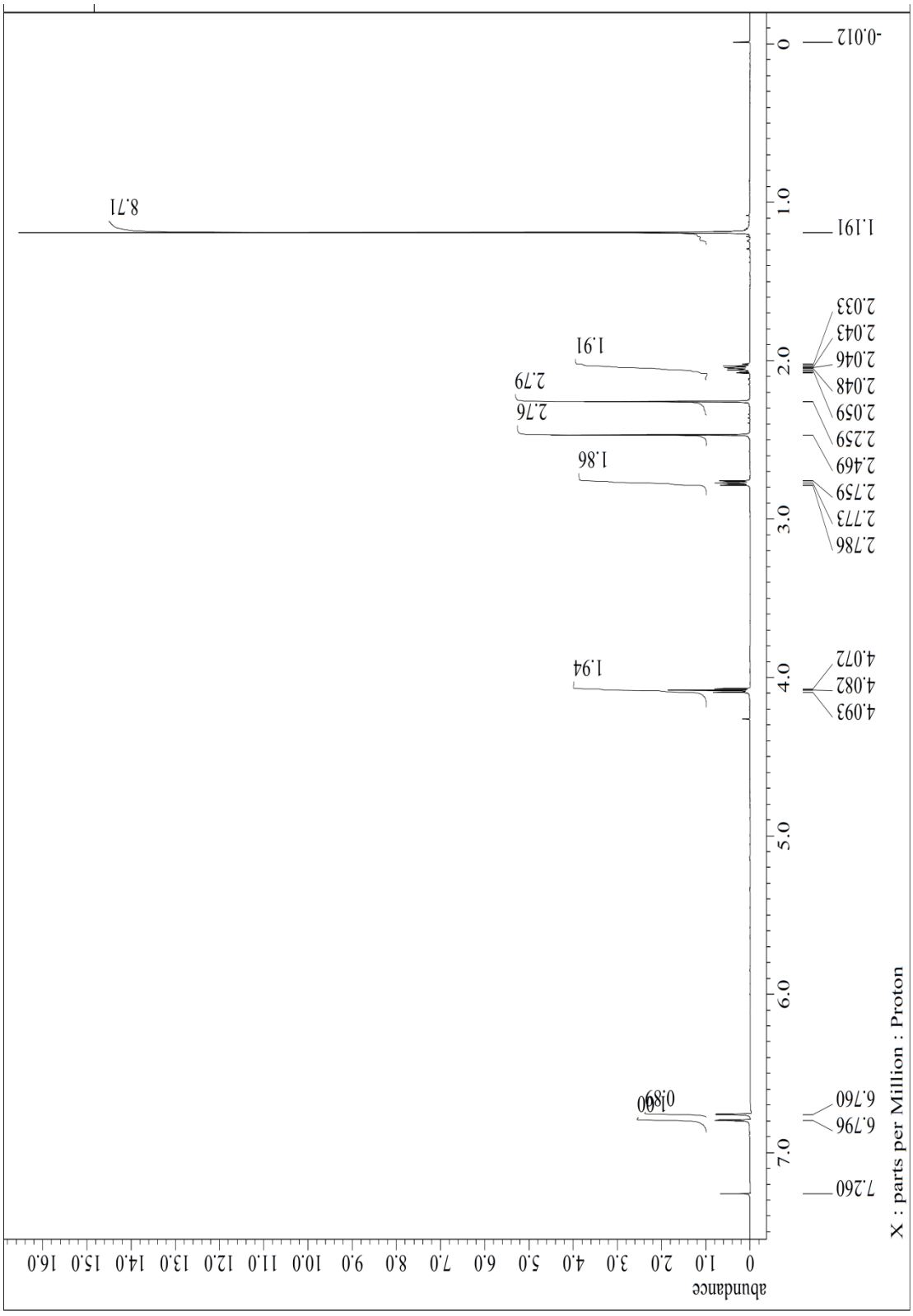
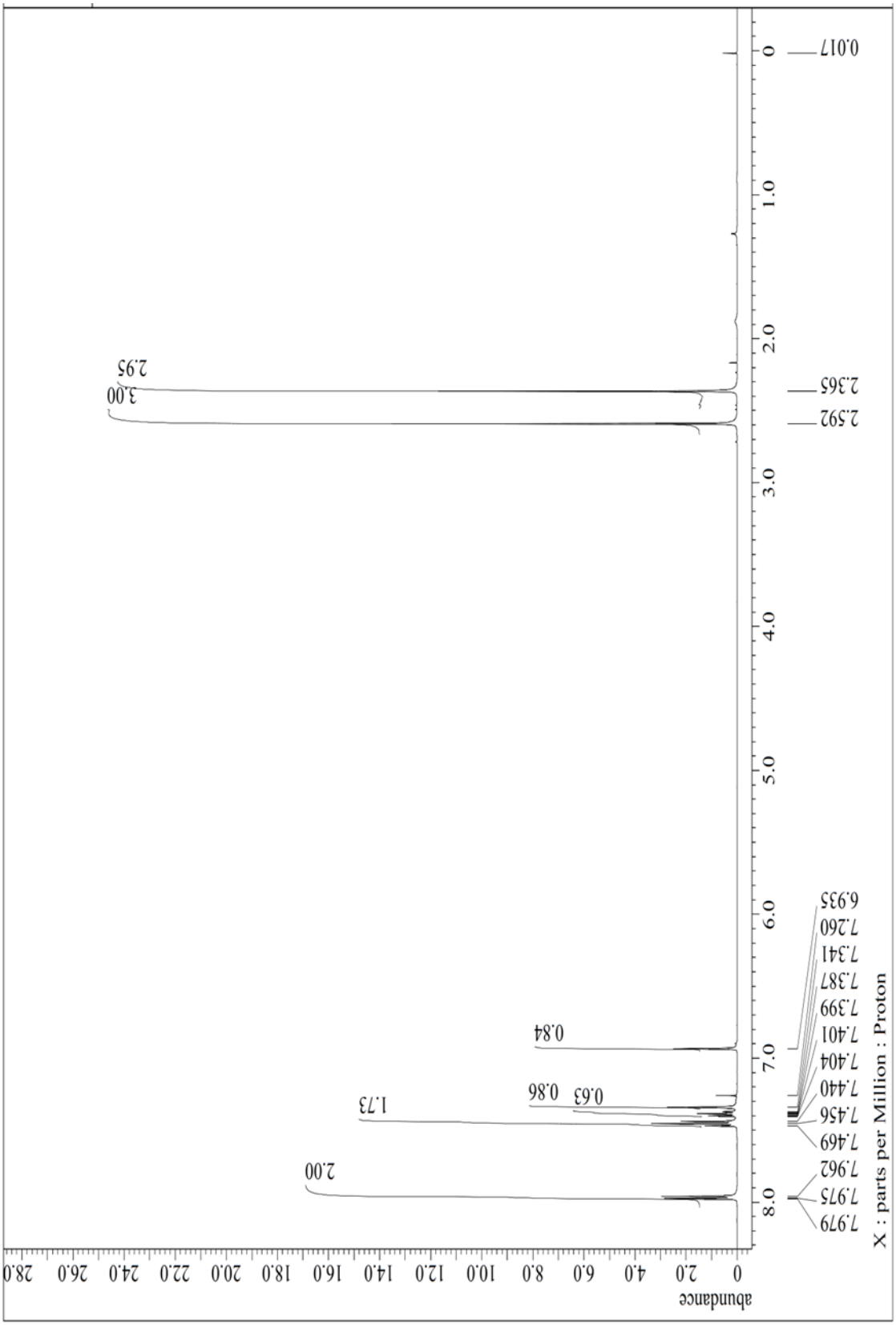
abundance

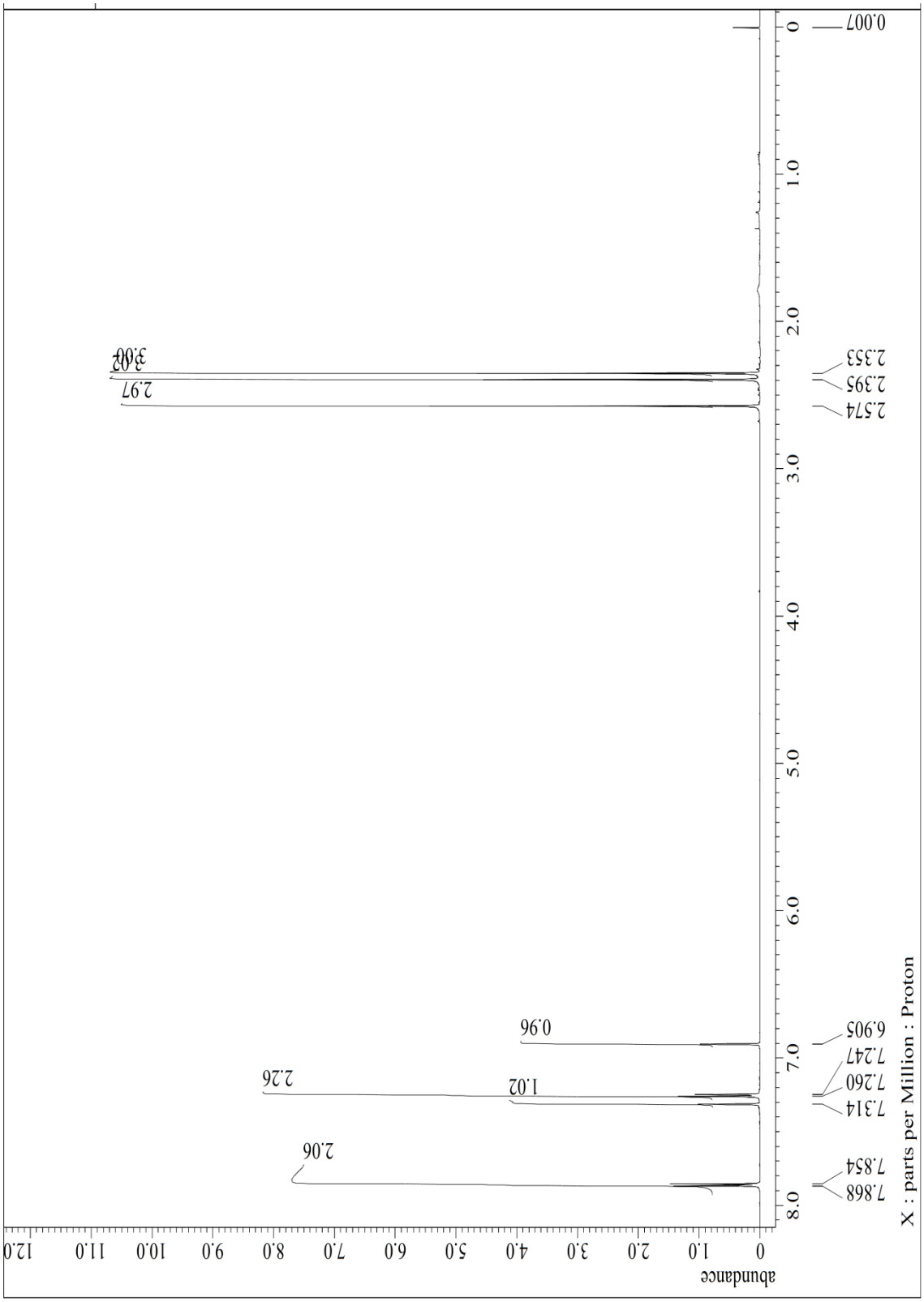
^{1}H NMR of **20**


-0.012
1.191
2.033
2.043
2.046
2.048
2.059
2.259
2.469
2.759
2.773
2.786
4.072
4.082
4.093
6.760
6.796
7.260
8.71
1.91
2.79
2.76
1.86
1.94
1.89
1.00
X : parts per Million : Proton
abundance

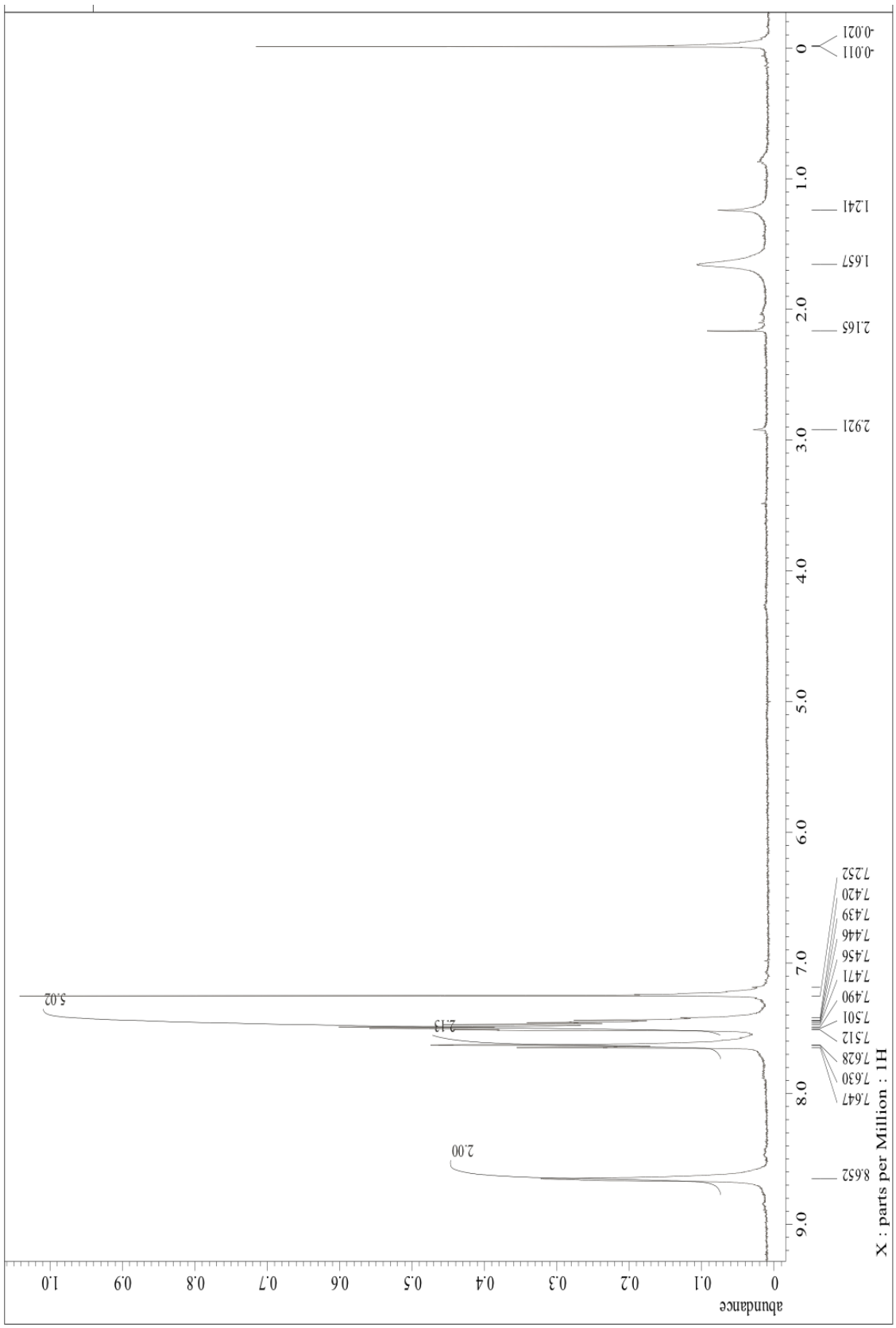
^{1}H NMR of **21**


0.017
2.365
2.592
3.00
2.95
0.84
0.63
0.86
1.73
2.00
7.979
7.975
7.962
7.469
7.456
7.440
7.404
7.401
7.399
7.387
7.341
7.260
6.935
X : parts per Million : Proton
abundance

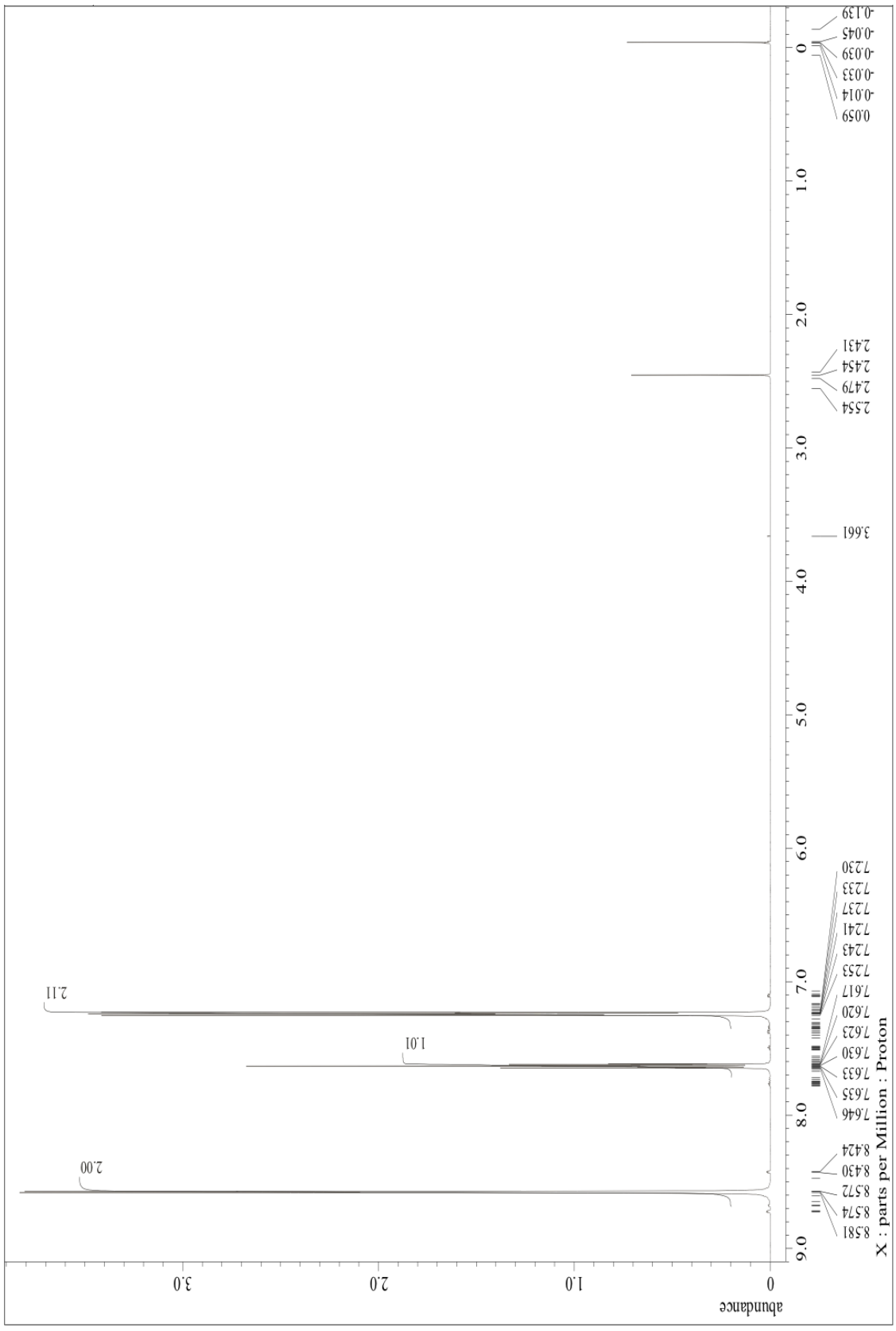
^{1}H NMR of **22**


X : parts per Million : Proton
abundance
0.007
2.353
2.395
2.574
3.00
3.02
2.97
6.905
7.247
7.260
7.314
7.854
7.868
0.96
1.02
2.26
2.06

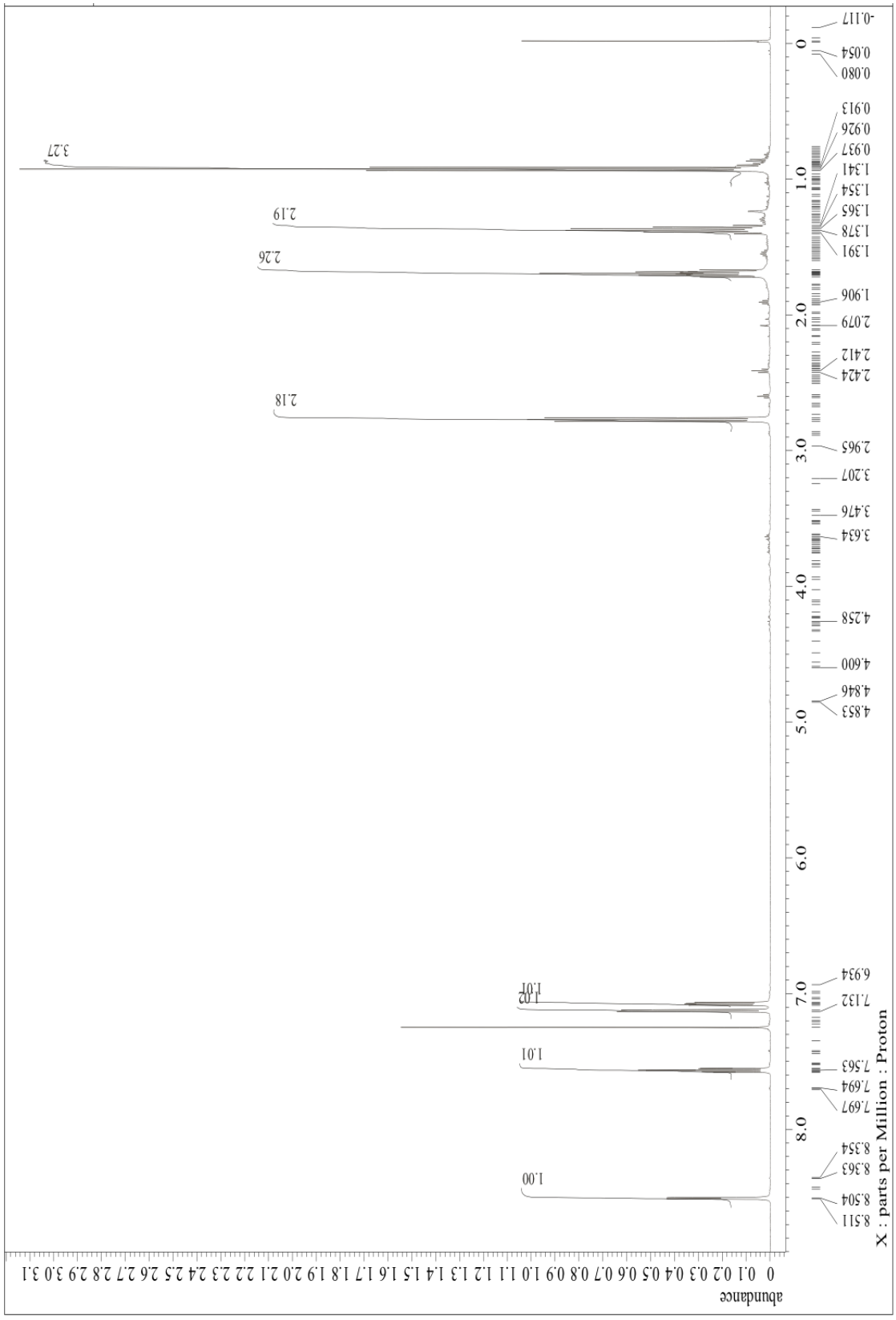
^{1}H NMR of **23**


X : parts per Million : 1H
abundance
-0.021
-0.011
1.241
1.657
2.165
2.921
5.02
2.13
2.00
8.652
7.647
7.630
7.628
7.512
7.501
7.490
7.471
7.456
7.446
7.439
7.420
7.252

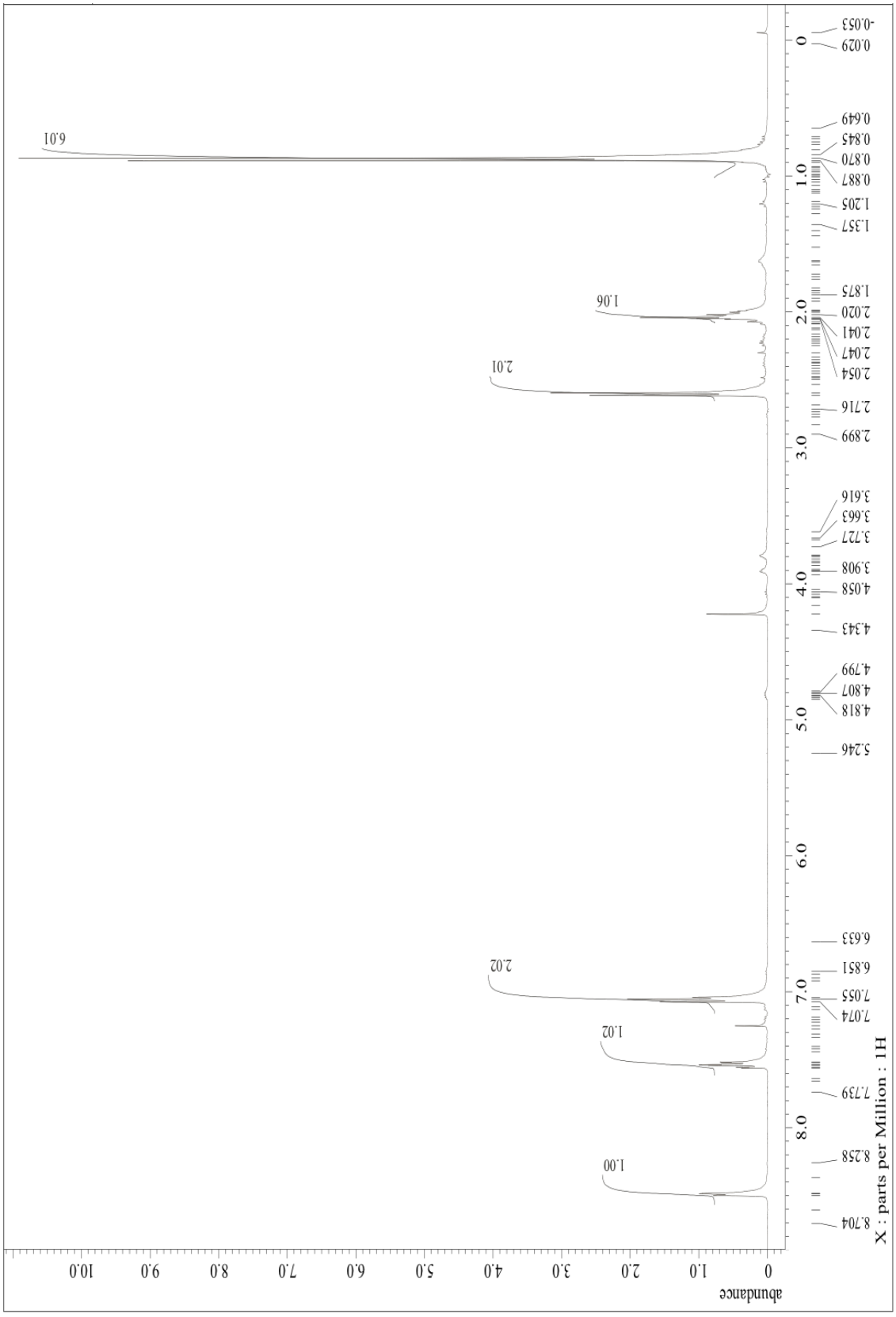
^{1}H NMR of **24**



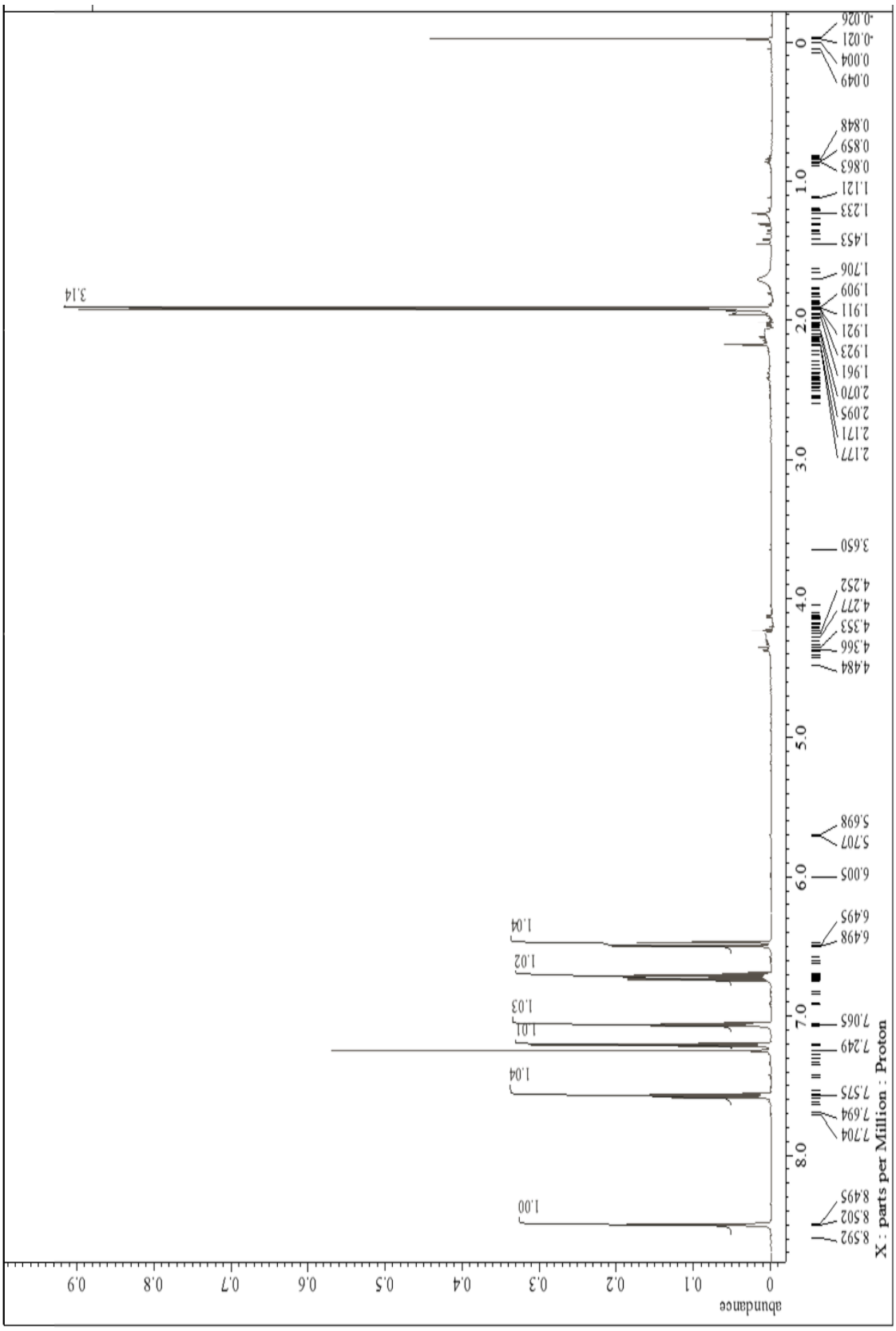
^{1}H NMR of **25**


X : parts per Million : Proton
abundance
8.511
8.504
8.363
8.354
7.697
7.694
7.563
7.132
6.934
4.853
4.846
4.600
4.258
3.634
3.476
3.207
2.965
2.424
2.412
2.079
1.906
1.391
1.378
1.365
1.354
1.341
0.937
0.926
0.913
0.080
0.054
-0.117
1.00
1.01
1.02
1.01
2.18
2.26
2.19
3.27

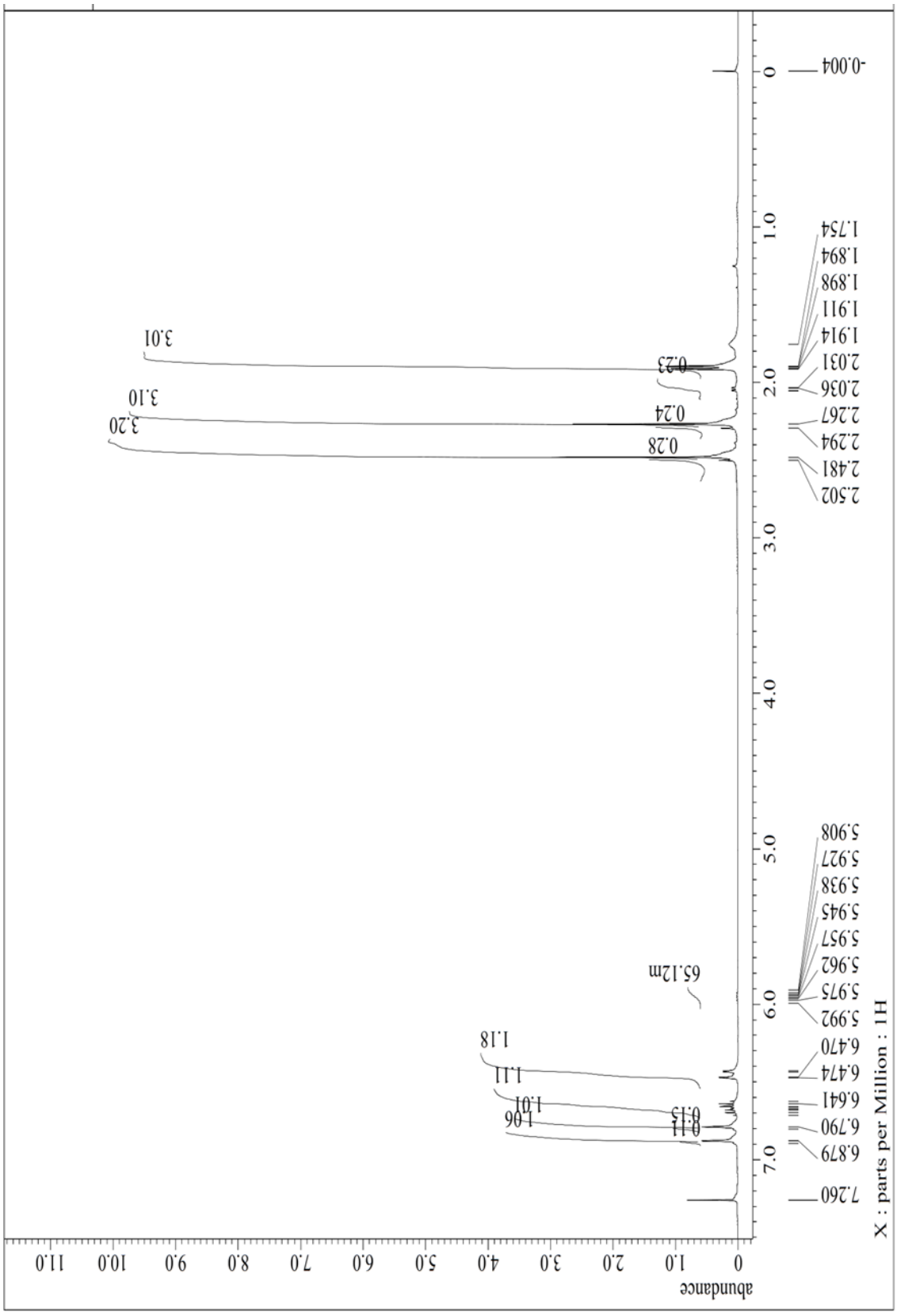
^{1}H NMR of **26**


X : parts per Million : 1H
abundance
-0.053
0.029
0.649
0.845
0.870
0.887
1.205
1.357
1.875
2.020
2.041
2.047
2.054
2.716
2.899
3.616
3.663
3.727
3.908
4.058
4.343
4.799
4.807
4.818
5.246
6.633
6.851
7.055
7.074
7.739
8.258
8.704
6.01
1.06
2.01
2.02
1.02
1.00

^{1}H NMR of **27**


X : parts per Million : Proton
abundance
8.592
8.502
8.495
7.704
7.694
7.575
7.249
7.065
6.498
6.495
6.005
5.707
5.698
4.484
4.366
4.353
4.277
4.252
3.650
2.177
2.171
2.095
2.070
1.961
1.923
1.921
1.911
1.909
1.706
1.453
1.233
1.121
0.863
0.859
0.848
0.049
0.004
-0.021
-0.026
3.14
1.00
1.04
1.01
1.03
1.02
1.04

^{1}H NMR of **28**


X : parts per Million : 1H
abundance
7.260
6.879
6.790
6.641
6.474
6.470
5.992
5.975
5.962
5.957
5.945
5.938
5.927
5.908
2.502
2.481
2.294
2.267
2.036
2.031
1.914
1.911
1.898
1.894
1.754
-0.004
3.01
3.10
3.20
0.23
0.24
0.28
65.12m
1.18
1.11
1.01
1.06
0.15
0.11