Electronic Supplementary Information for

Synthesis of Imidazo and Benzimidazo[2,1-*a*]isoquinolines by Rhodium-Catalyzed Intramolecular Double C-H Bond Activation

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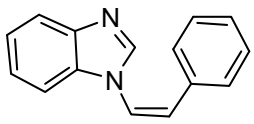
General Information

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts were reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a JASCO Corporation FT/IR-4200 instrument. Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer (EI) or JEOL JMS-T100TD (DART). Melting points were measured using Stanford Research Systems OptiMelt MPA 100. Acetylene derivatives and mesitylene (Sigma Aldrich), $[Cp^*RhCl_2]_2$ and $Cu(OAc)_2$ (Tokyo Chemical Industry Company), Silver salts, imidazoles and dehydrated solvents (Wako Pure Chemical Industries) were purchased and used as received.

General Procedure for preparation of (*Z*)-1-styryl-1*H*-benzimidazole (Table 3, entry 1a):[S1]

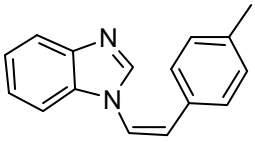


A Schlenk flask was charged with $CsOH{\cdot}H_2O$ (30 mg, 0.18 mmol). NMP (2 mL) and benzimidazole (113 mg, 0.96 mmol) was successively added. The reaction mixture was vigorously stirred and phenylacetylene (100 μL, 0.91 mmol) was added and the mixture stirred for 24 h at 120 ^{0}C. After the reaction was complete, the reaction mixture was allowed to cool, and a 1:1 mixture of ethyl acetate/water (5.0 mL) was added. The organic layer was washed and separated, the aqueous layer was further washed with another 5-mL portion of ethyl acetate, and the combined organic extracts were dried with anhydrous Na_2SO_4. The solvent and volatiles were completely removed under vacuum to give the crude product, and the resulting product was further purified by column chromatography provided (*Z*)-1-styryl-1*H*- benzimidazole with 85% yield.

Rf: (Hexane:ethyl acetate = 8:2) 0.25; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.87-7.83 (m, 2H), 7.38-7.32 (m, 3H), 7.26-7.23 (m, 3H), 7.09-7.07 (m, 2H), 6.87 (d, 1H, *J* = 9.2 Hz), 6.61 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 141.7, 133.3, 132.7, 128.8, 128.5, 128.4, 125.7, 123.8, 123.1, 120.0, 110.3; MS (ESI): *m/z* 221 [M+H].

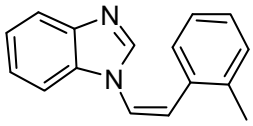
Other (*Z*)-1-styryl-1*H*-imidazole and benzimidazole derivatives (1b-) were synthesized by similar procedures.

(*Z*)-1-(4-Methylstyryl)-1*H*-benzo[*d*]imidazole (Table 3, entry 1b):



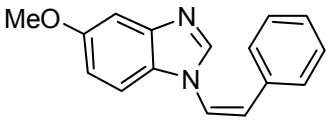
White solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.84-7.77 (m, 2H),

7.30-7.18 (m, 3H), 6.97-6.87 (m, 4H), 6.75 (d, 1H, *J* = 9.2 Hz), 6.53 (d, 1H, *J* = 9.2 Hz), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 138.7, 130.3, 129.6, 128.3, 126.6, 124.0, 123.2, 119.9, 119.2, 110.5, 21.2; MS (ESI): *m/z* 235 [M+H].



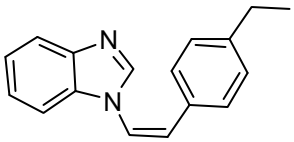
(*Z*)-1-(2-Methylstyryl)-1*H*-benzo[*d*]imidazole (Table 3, entry 1c):

Rf: (Hexane:ethyl acetate = 8:2) 0.37; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.83-7.80 (m, 1H), 7.68 (s, 1H), 7.43-7.41 (m, 1H), 7.36-7.34 (m, 2H), 7.27-7.19 (m, 2H), 7.08- 6.99 (m, 3H), 6.62 (d, 1H, *J* = 9.2 Hz), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 141.3, 136.2, 133.0, 132.7, 130.6, 128.4, 128.1, 126.4, 123.9, 123.2, 121.9, 120.6, 120.0, 110.0, 19.8; MS (ESI): *m/z* 235 [M+H].



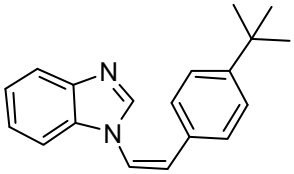
(*Z*)-5-Methoxy-1-styryl-1*H*-benzo[*d*]imidazole (Table 3, entry 1d):

Rf: (Hexane:ethyl acetate = 8:2) 0.22; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.82 (s, 1H), 7.70 (d, 1H, *J* = 7.2 Hz), 7.25-7.22 (m, 4H), 7.05-7.05 (m, 1H), 6.96-6.93 (m, 1H), 6.82 (d, 1H, *J* = 9.2 Hz), 6.72 (m, 1H), 6.61 (d, 1H, *J* = 9.2 Hz), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 157.4, 140.6, 133.3, 128.9, 128.8, 128.5, 128.4, 126.2, 125.9, 120.3, 120.0, 112.9, 93.8, 55.7; MS (ESI): *m/z* 251 [M+H].



(*Z*)-1-(4-Ethylstyryl)-1*H*-benzo[*d*]imidazole (Table 3, entry 1e):

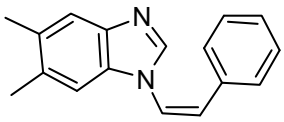
Rf: (Hexane:ethyl acetate = 8:2) 0.18; white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.87-7.82 (m, 2H), 7.36-7.24 (m, 3H), 7.03-6.97 (m, 4H), 6.80-6.79 (m, 1H), 6.57-6.56 (m, 1H), 2.57 (bs, 2H), 1.65 (bs, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 144.9, 141.8, 130.6, 128.4, 128.3, 126.3, 123.8, 123.1, 120.0, 119.3, 110.4, 28.5, 15.2; MS (ESI): *m/z* 249 [M+H].



(*Z*)-1-(4-(*tert*-Butyl)styryl)-1*H*-benzo[*d*]imidazole (Table 3, entry 1f):

Rf: (Hexane:ethyl acetate = 8:2) 0.14; white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.77-7.74 (m, 2H), 7.33-7.31 (m, 1H), 7.25-7.23 (m, 2H), 7.17 (d, 2H, *J* = 8.3 Hz), 6.94 (d, 2H, *J* = 8.3 Hz), 6.73 (d, 1H, *J* = 9.2 Hz), 6.48 (d, 1H, *J* = 9.2 Hz),

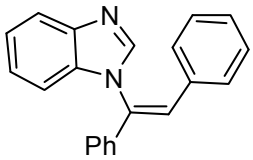
1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 151.6, 143.1, 142.1, 133.0, 130.5, 128.2, 125.7, 125.6, 123.5, 122.7, 120.2, 119.5, 110.2, 34.6, 31.1;
MS (ESI): *m/z* 277 [M+H].



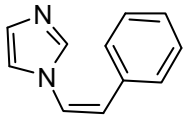
(*Z*)-5,6-Dimethyl-1-styryl-1*H*-benzo[*d*]imidazole (Table 3, entry 1g):

Rf: (Hexane:ethyl acetate = 8:2) 0.16; white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ =7.70 (s, 1H), 7.58 (s, 1H), 7.27-7.24 (m, 3H), 7.15-7.11 (m, 3H), 6.83 (d, 1H, *J* = 9.2 Hz), 6.53 (d, 1H, *J* = 9.2 Hz), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 141.2, 133.7, 132.8, 131.7, 128.9, 128.7, 128.4, 128.2, 126.0, 124.5, 120.5, 120.2, 110.4, 20.5, 20.2; MS (ESI): *m/z* 249 [M+H].

(*Z*)-1-(1,2-Diphenylvinyl)-1*H*-benzo[*d*]imidazole (Table 3, entry 1h):

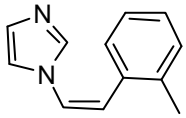


Rf: (Hexane:ethyl acetate = 8:2) 0.24; white solid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.95-7.91 (m, 2H), 7.41-7.18 (m, 11H), 7.03 (d, 1H, *J* = 9.2 Hz), 6.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 143.0, 136.5, 133.6, 132.8, 129.4, 128.9, 128.7, 128.5, 128.4, 126.3, 125.9, 123.9, 123.0, 120.1, 111.6; MS (ESI): *m/z* 297 [M+H].



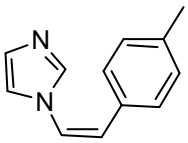
(*Z*)-1-Styryl-1*H*-imidazole (Table 3, entry 1i):

Rf: (Hexane:ethyl acetate = 5:5) 0.25; colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.48 (s, 1H), 7.30-7.26 (m, 3H), 7.12-7.10 (m, 2H), 7.04 (s, 1H), 6.87 (s, 1H), 6.75 (d, 1H, *J* = 9.2 Hz), 6.37 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 136.9, 133.6, 129.5, 128.7, 128.4, 128.2, 126.1, 123.3, 122.3, 118.4; MS (ESI): *m/z* 171 [M+H].



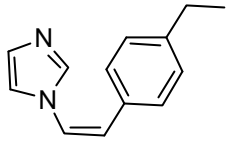
(*Z*)-1-(2-Methylstyryl)-1*H*-imidazole (Table 3, entry 1j):

Rf: (Hexane:ethyl acetate = 3:7) 0.25; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.33 (bs, 1H), 7.19-7.14 (m, 2H), 7.08-7.03 (m, 1H), 6.99 (d, 1H, *J* = 7.3 Hz), 6.86 (bs, 1H), 6.75 (d, 1H, *J* = 9.2 Hz), 6.63 (bs, 1H), 6.21 (d, 1H, *J* = 9.2 Hz), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 136.1, 133.5, 129.3, 128.4, 128.1, 126.1, 122.9, 118.7, 118.4, 21.4; MS (ESI): *m/z* 185 [M+H].



(*Z*)-1-(4-Methylstyryl)-1*H*-imidazole (Table 3, entry 1k):

Rf: (Hexane:ethyl acetate = 3:7) 0.40; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.40 (s, 1H), 7.02-6.97 (m, 3H), 6.90 (d, 2H, *J* = 7.8 Hz), 6.80 (s, 1H), 6.62 (d, 1H, *J* = 9.2 Hz), 6.25 (d, 1H, *J* = 9.2 Hz), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 138.2, 136.8, 130.5, 129.5, 129.4, 129.3, 128.3, 125.9, 123.7, 121.6, 118.4, 21.2; MS (ESI): *m/z* 185 [M+H].



(*Z*)-1-(4-Ethylstyryl)-1*H*-imidazole (Table 3, entry 1l):

Rf: (Hexane:ethyl acetate = 5:5) 0.29; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.43 (s, 1H), 7.04-6.91 (m, 5H), 6.82 (s, 1H), 6.61 (d, 1H, *J* = 9.2 Hz), 6.27 (d, 1H, *J* = 9.2 Hz), 2.54 (q, 2H, *J* = 7.8 Hz), 1.13 (t, 3H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 144.6, 136.8, 130.7, 129.2, 128.4, 128.1, 123.9, 121.5, 118.5, 28.5, 15.3; MS (ESI): *m/z* 199 [M+H].

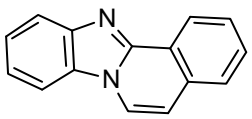
General procedure for intramolecular oxidative coupling:

Procedure 1 (Table 2, entry 6):

An oven-dried screw cap test tube was charged with **1** (0.25 mmol), PivOH (13 mg, 0.5 mmol), $[Cp^*RhCl_2]_2$ (4.7 mg, 3.0 mol%), $Cu(OAc)_2$ (109.0 mg, 0.6 mmol) and anhydrous mesitylene (1.0 mL) and then the tube was sealed. The reaction mixture was allowed to stir at room temperature until the starting material completely dissolved before being placed into an oil bath at 140 ºC for 24 hr. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered and concentrated under reduced pressure. The residue was purified by silica gel, eluting with *n*-hexane/ethyl acetate mixture provided coupling product **2**.

Procedure 2 (Table 2, entry 7):

An oven-dried screw cap test tube was charged with **1** (0.25 mmol), $[Cp^*RhCl_2]_2$ (7.8 mg, 5.0 mol%), $AgSbF_6$ (17.2 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (59.9 mg, 0.30 mmol) and anhydrous mesitylene (1.0 mL) and then the tube was sealed. The reaction mixture was allowed to stir at room temperature until the starting material completely dissolved before being placed into an oil bath at 140 ºC for 24 hr. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered and concentrated under reduced pressure. The residue was purified by silica gel, eluting with *n*-hexane/ethyl acetate mixture provided coupling product **2**.



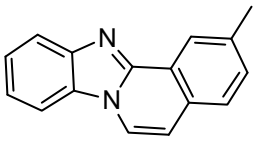
Synthesis of benzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2a):[S2]

An oven-dried screw cap test tube was charged with (*Z*)-1-styryl-1*H*-benzo[*d*]imidazole (55 mg, 0.25 mmol), PivOH (13 mg, 0.5 mmol), $[Cp^*RhCl_2]_2$ (4.7 mg, 3.0 mol%), $Cu(OAc)_2$ (109.0 mg, 0.6 mmol) and anhydrous mesitylene (1.0 mL) was then added and the tube sealed. The reaction mixture was allowed to stir at room temperature until the starting material completely dissolved before being placed into an oil bath at 140 ºC for 24 hr. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, filtered and concentrated under reduced pressure. The residue was purified by silica gel, eluting with *n*-hexane/ethyl acetate mixture provided benzo[4,5]imidazo[2,1-*a*]isoquinoline (**2a**) (41.99 mg) with 77% yields.

Rf: (Hexane:ethyl acetate = 6:4) 0.34; yellow solid; m.p. : 112-114 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.83-8.82 (m, 1H), 8.10 (d, 1H, *J* = 7.3 Hz), 7.96 (d, 1H, *J* = 8.3 Hz), 7.76 (d, 1H, *J* = 7.8 Hz), 7.68-7.61 (m, 3H), 7.44 (t, 1H, *J* = 7.6 Hz), 7.34 (t, 1H, *J* = 7.6 Hz), 7.04 (d, 1H, *J* = 7.3 Hz); ^{13}C NMR (100 MHz, TMS): δ = 146.4, 131.6, 130.4, 129.5, 128.4, 127.0, 125.2, 125.1, 122.6, 122.2, 121.1, 119.3, 111.9, 109.9; MS (ESI): *m/z* 219 [M+H]; HRMS m/z (EI) calcd for $C_{15}H_{10}N_2$ 218.0844: found 218.0843.

Other benzo[4,5]imidazo[2,1-*a*]isoquinoline and imidazo[2,1-*a*]isoquinoline derivatives (2b-p) were synthesized by similar procedures.

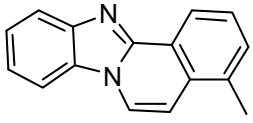
Synthesis of 2-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2b):[S2]



Following the general procedure (**1b**) (*Z*)-1-(3-methylstyryl)-1*H*-benzo[*d*]imidazole undergoes oxidative cross-coupling reaction and provided 2-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (**2b**) (45.8 mg) with 79 % yields.

Rf: (Hexane:ethyl acetate = 6:4) 0.42; yellow solid; m.p. : 122-124 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.57 (s, 1H), 7.98 (d, 1H, *J* = 7.3 Hz), 7.92 (d, 1H, *J* = 7.8 Hz), 7.71 (d, 1H, *J* = 8.2 Hz), 7.53 (d, 1H, *J* = 8.2 Hz), 7.43-7.38 (m, 2H), 7.30 (t, 1H, *J* = 7.6 Hz), 6.94 (d, 1H, *J* = 7.6 Hz), 2.49 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$, TMS): δ = 146.6, 138.6, 131.7, 129.7, 129.3, 126.8, 124.8, 124.7, 122.8, 121.9, 120.3, 119.3, 111.5, 109.8, 21.6; MS (ESI): *m/z* 233 [M+H]; HRMS m/z (EI) calcd for $C_{16}H_{12}N_2$ 232.1000: found 232.1003.

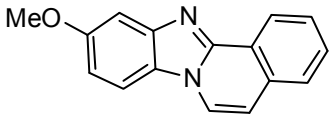
Synthesis of 4-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3,



entry 2c):[S2]

Following the general procedure (**1c**) (*Z*)-1-(2-methylstyryl)-1*H*-benzo[*d*]imidazole undergoes oxidative cross-coupling reaction and provided 4-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (**2c**) (26.5 mg) with 46 % yields.

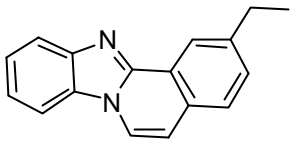
Rf: (Hexane:ethyl acetate = 6:4) 0.22; yellow solid; m.p. : 127-129 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.69 (d, 1H, *J* = 7.3 Hz), 8.12 (d, 1H, *J* = 7.3 Hz), 7.96 (d, 1H, *J* = 7.8 Hz), 7.77 (d, 1H, *J* = 7.3 Hz), 7.53-7.49 (m, 1H), 7.47-7.43 (m, 2H), 7.33 (t, 1H, *J* = 7.3 Hz), 7.17 (d, 1H, *J* = 7.6 Hz), 2.59 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$, TMS): δ = 147.1, 134.3, 132.8, 131.4, 130.5, 128.1, 125.0, 123.2, 122.0, 120.8, 119.4, 109.9, 108.2, 19.4; MS (ESI): *m/z* 233 [M+H]; HRMS m/z (EI) calcd for $C_{16}H_{12}N_2$ 232.1000: found 232.1001.



Synthesis of 10-methoxybenzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2d):

Following the general procedure (**1d**) (*Z*)-5-methoxy-1-styryl-1*H*-benzo[*d*]imidazole undergoes oxidative cross-coupling reaction and provided 10-methoxybenzo[4,5]imidazo[2,1-*a*]isoquinoline (**2d**) (40 mg) with 63 % yields.

Rf: (Hexane:ethyl acetate = 6:4) 0.19; yellow solid; m.p. : 155-156 ^{0}C; IR (KBr) : ν 3057, 2924, 1595, 1452, 1365, 1251, 1168 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.65 (d, 1H, *J* = Hz), 7.88 (d, 1H, *J* = Hz), 7.79 (d, 1H, *J* = Hz), 7.58-7.52 (m, 3H), 7.08-7.02 (2H), 6.86 (d, 1H, *J* = Hz), 3.81 (s, 3H); ^{13}C NMR (100 Hz, $CDCl_3$, TMS): δ = 155.9, 146.3, 137.7, 131.0, 130.1, 129.5, 128.0, 126.9, 126.3, 124.4, 123.5, 121.0, 120.9, 120.1, 114.4, 111.2, 92.8, 55.8; MS (ESI): *m/z* 249 [M+H]; HRMS m/z (EI) calcd for $C_{16}H_{12}N_2O$ 248.0950: found 248.0950.

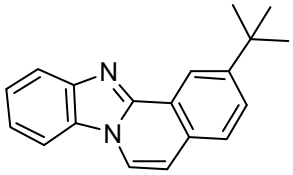


Synthesis of 2-ethylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2e):

Following the general procedure (**1e**) (*Z*)-1-(3-ethylstyryl)-1*H*-benzo[*d*]imidazole undergoes oxidative cross-coupling reaction and provided 2-ethylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (**2e**) (45.5 mg) with 74 % yields.

Rf: (Hexane:ethyl acetate = 7:3) 0.23; yellow solid; m.p. : 73-74 ^{0}C; IR (KBr) : ν 3057, 2932, 1594, 1491, 1447, 1232, 1166 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.65 (s, 1H), 8.03 (d, 1H, *J* =7.3 Hz), 7.95 (d, 1H, *J* = 8.2 Hz), 7.74 (d, 1H, *J* = 8.2 Hz), 7.58 (d, 1H, *J* = 8.2 Hz), 7.46-7.41 (m, 2H), 7.34-7.30 (m, 1H), 6.99 (d, 1H, *J* = 7.3 Hz), 2.81 (q, 2H, *J* = 7.6 Hz), 1.30 (q, 3H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 146.6, 145.1, 130.9, 129.6,

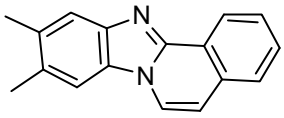
127.0, 124.9, 123.7, 122.0, 120.3, 119.2, 111.8, 109.9, 29.0, 15.5; MS (ESI): *m/z* 247 [M+H]; HRMS m/z (EI) calcd for $C_{17}H_{14}N_2$ 246.1157: found 246.1158.



Synthesis of 2-(*tert*-butyl)benzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2f):

Following the general procedure (**1f**) (*Z*)-1-(4-(*tert*-butyl)styryl)-1*H*-benzo[*d*]imidazole undergoes oxidative cross-coupling reaction and provided 2-(*tert*-butyl)benzo[4,5]imidazo[2,1-a]isoquinoline (**2f**) (47.3 mg) with 69 % yields.

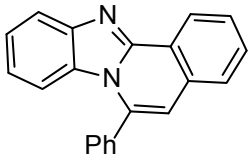
Rf: (Hexane:ethyl acetate = 6:4) 0.77; semi solid; IR (KBr) : ν 3059, 2979, 1597, 1494, 1270, 1192, 1113 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.73 (s, 1H), 8.02-8.0 (m, 1H), 7.95 (d, 1H, *J* = 8.2 Hz), 7.73-7.71 (m, 1H), 7.67-7.65 (m, 1H), 7.60-7.58 (m, 1H), 7.42 (t, 1H, *J* = 8.2 Hz), 7.30 (t, 1H, *J* = 8.2 Hz), 6.95-6.93 (m, 1H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 151.7, 147.5, 143.6, 130.0, 129.3, 128.0, 126.8, 124.5, 123.2, 121.6, 120.0, 120.6, 119.7, 110.0, 109.7, 35.2, 31.3; MS (ESI): *m/z* 275 [M+H]; HRMS m/z (EI) calcd for $C_{19}H_{18}N_2$ 274.1470: found 274.1468.



Synthesis of 9,10-dimethylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2g):[S2]

Following the general procedure (**1g**) (*Z*)-5,6-dimethyl-1-styryl-1*H*-benzo[*d*]imidazole undergoes oxidative cross-coupling reaction and provided 9,10-dimethylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (**2g**) (38.7 mg) with 61 % yields.

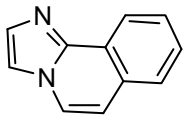
Rf: (Hexane:ethyl acetate = 7:3) 0.33; yellow solid; M P : 179-181 ^0C; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.78-8.76 (m, 1H), 7.98 (d, 1H, *J* = 7.3 Hz), 7.75 (s, 1H), 7.71-7.91 (m, 1H), 7.65-7.62 (m, 2H), 7.55 (s, 1H), 6.99 (d, 1H, *J* = 7.3 Hz), 2.45 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 146.5, 142.2, 133.8, 131.3, 131.2, 129.5, 128.4, 127.9, 126.9, 124.7, 123.6, 121.3, 119.6, 110.8, 109.8, 20.6; MS (ESI): *m/z* 247 [M+H]; HRMS m/z (EI) calcd for $C_{17}H_{14}N_2$ 246.1157: found 246.1159.



Synthesis of 6-phenylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (Table 3, entry 2h):

Following the general procedure (*Z*)-1-(1,2-diphenylvinyl)-1*H*-benzo[*d*]imidazole (**1h**) undergoes oxidative cross-coupling reaction and provided 6-phenylbenzo[4,5]imidazo[2,1-*a*]isoquinoline (**2h**) (45.5 mg) with 62 % yields.

Rf: (Hexane:ethyl acetate = 7:3) 0.26; yellow solid; m.p. : 171-173 ^{0}C; IR (KBr) : ν 3054, 2925, 1645, 1596, 1446, 1232, 1153 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.85-8.83 (m, 1H), 7.91 (d, 1H, *J* = 8.2 Hz), 7.60-7.48 (m, 8H), 7.30 (t, 1H, *J* = 7.8 Hz), 6.91 (t, 1H, *J* = 7.8 Hz), 6.82 (s, 1H), 6.38 (d, 1H, *J* = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 147.8, 143.3, 137.3, 134.3, 131.5, 130.2, 129.8, 129.3, 128.9, 127.9, 126.6, 125.1, 124.3, 122.3, 121.3, 119.3, 114.0, 112.8; MS (ESI): *m/z* 295 [M+H]; HRMS m/z (EI) calcd for $C_{21}H_{14}N_2$ 294.1157: found 294.1158.

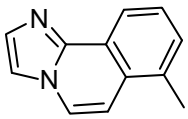


Synthesis of imidazo[2,1-*a*]isoquinoline (Table 3, entry 2i):[S2]

Following the general procedure (*Z*)-1-styryl-1*H*-imidazole (**1i**) undergoes oxidative cross-coupling reaction and provided imidazo[2,1-*a*]isoquinoline (**2i**) (33.2 mg) with 79 % yields.

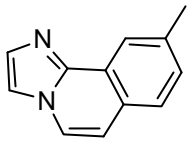
Rf: (Hexane:ethyl acetate = 7:3) 0.21; brown solid; m.p.: 69-71 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.65 (d, 1H, *J* = 7.8 Hz), 7.86 (d, 1H, *J* = 7.3 Hz), 7.65-7.52 (m, 5H), 7.02 (d, 1H, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 142.3, 130.0, 129.4, 128.6, 128.4, 126.9, 123.4, 123.0, 122.9, 114.3, 113.7; MS (ESI): *m/z* 169 [M+H]; HRMS m/z (EI) calcd for $C_{11}H_8N_2$ 168.0687: found 168.0686.

Synthesis of 7-methylimidazo[2,1-*a*]isoquinoline (Table 3, entry 2j):[S2]



Following the general procedure (*Z*)-1-(2-methylstyryl)-1*H*-imidazole (**1j**) undergoes oxidative cross-coupling reaction and provided **7-**methylimidazo[2,1-*a*]isoquinoline (**2j**) (23.2 mg) with 51% yields.

Rf: (Hexane:ethyl acetate = 3:7) 0.34; yellow solid; m.p. : 120-122 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.51 (d, 1H, *J* = 8.3 Hz), 7.87 (d, 1H, *J* = 7.3 Hz), 7.53-7.46 (m, 3H), 7.35 (d, 1H, *J* = 7.3 Hz), 7.15 (d, 1H, *J* = 7.3 Hz), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 143.0, 134.0, 130.4, 129.6, 128.3, 128.0, 123.4, 122.5, 121.5, 113.9, 109.9, 19.4; MS (ESI): *m/z* 183 [M+H]; HRMS m/z (EI) calcd for $C_{12}H_{10}N_2$ 182.0844: found 182.0845.

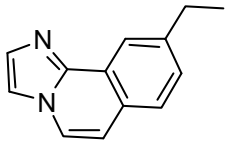


Synthesis of 9-methylimidazo[2,1-*a*]isoquinoline (Table 3, entry 2k):[S2]

Following the general procedure (*Z*)-1-(3-methylstyryl)-1*H*-imidazole (**1k**) undergoes oxidative cross-coupling reaction and provided 9-methylimidazo[2,1-a]isoquinoline (**2k**) (37.7 mg) with 83% yields.

Rf: (Hexane:ethyl acetate = 3:7) 0.36; yellow solid; m.p. : 78-79 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.48 (s, 1H), 7.80 (d, 1H, *J* = 7.3 Hz), 7.55-7.49 (m, 3H), 7.36-7.34 (m,

1H), 6.99 (d, 1H, *J* = 7.3 Hz), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 142.3, 138.9, 130.3, 129.6, 127.3, 126.8, 123.2, 122.9, 122.0, 114.2, 113.7, 21.7; MS (ESI): *m/z* 183 [M+H]; HRMS m/z (EI) calcd for $C_{12}H_{10}N_2$ 182.0844: found 182.0845.



Synthesis of 9-ethylimidazo[2,1-*a*]isoquinoline (Table 3, entry 2l):

Following the general procedure (*Z*)-1-(3-ethylstyryl)-1*H*-imidazole (**1l**) undergoes oxidative cross-coupling reaction and provided 9-ethylimidazo[2,1-*a*]isoquinoline (**2l**) (37.7 mg) with 77 % yields.

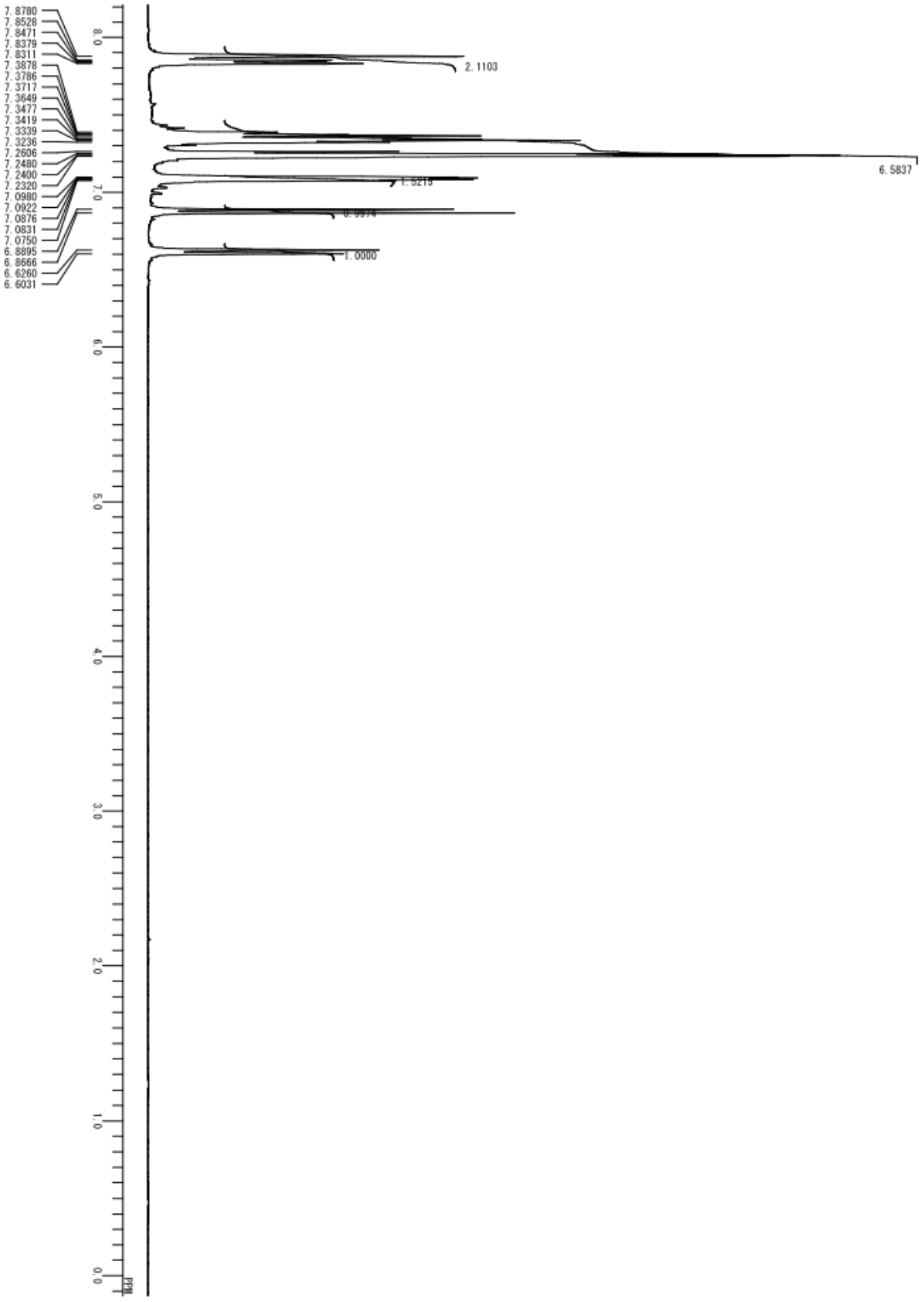
Rf: (Hexane:ethyl acetate = 3:7) 0.40; brown solid; m.p. : 86-87 ^{0}C; IR (KBr) : ν 3093, 2916, 1619, 1518, 1448, 1324, 1267 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 8.54 (s, 1H), 7.82 (d, 1H, *J* = 7.3 Hz), 7.59-7.52 (m, 3H), 7.42-7.39 (m, 1H), 7.03 (d, 1H, *J* = 6.9 Hz), 2.80 (q, 2H, *J* = 7.6 Hz), 1.28 (t, 3H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 145.2, 142.2, 129.5, 129.3, 128.2, 127.6, 127.1, 126.9, 122.7, 122.0, 114.2, 113.9, 29.0, 15.4; MS (ESI): *m/z* 197 [M+H]; HRMS m/z (EI) calcd for $C_{13}H_{12}N_2$ 196.1000: found 196.1000.

References:

(S1) Tzalis, D.; Koradin, C.; Knochel, P. *Tetrahedron Lett.* **1999**, *40*, 6193.

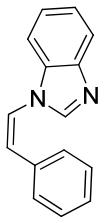
(S2) Sun, M.; Wu, H.; Zheng, J.; Bao, W. *Adv. Synth. Catal.* **2012**, *354*, 835.

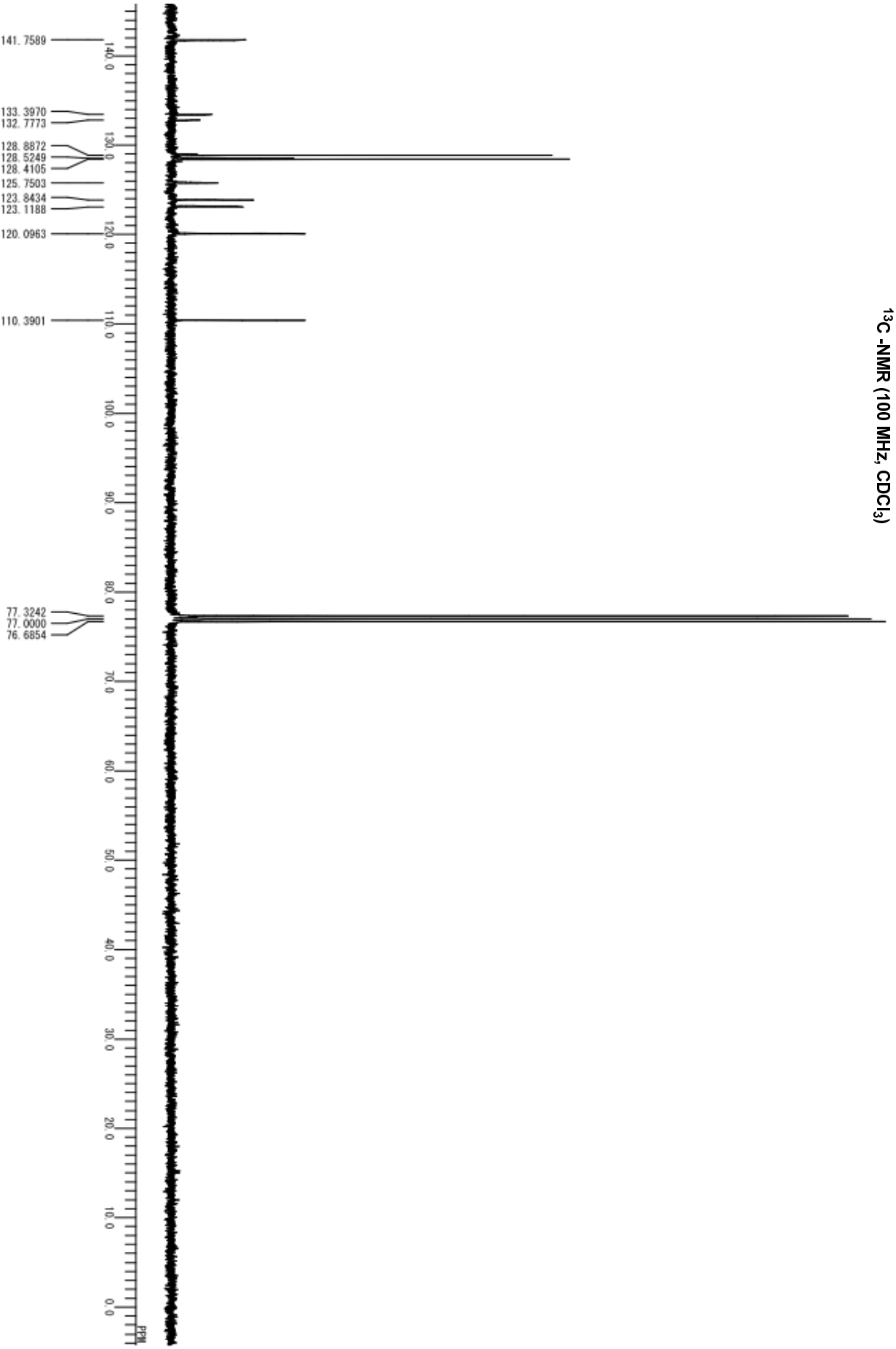
Copies of 1H and 13C- NMR Spectra



^{1}H-NMR (400 MHz, $CDCl_3$)

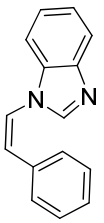
1a

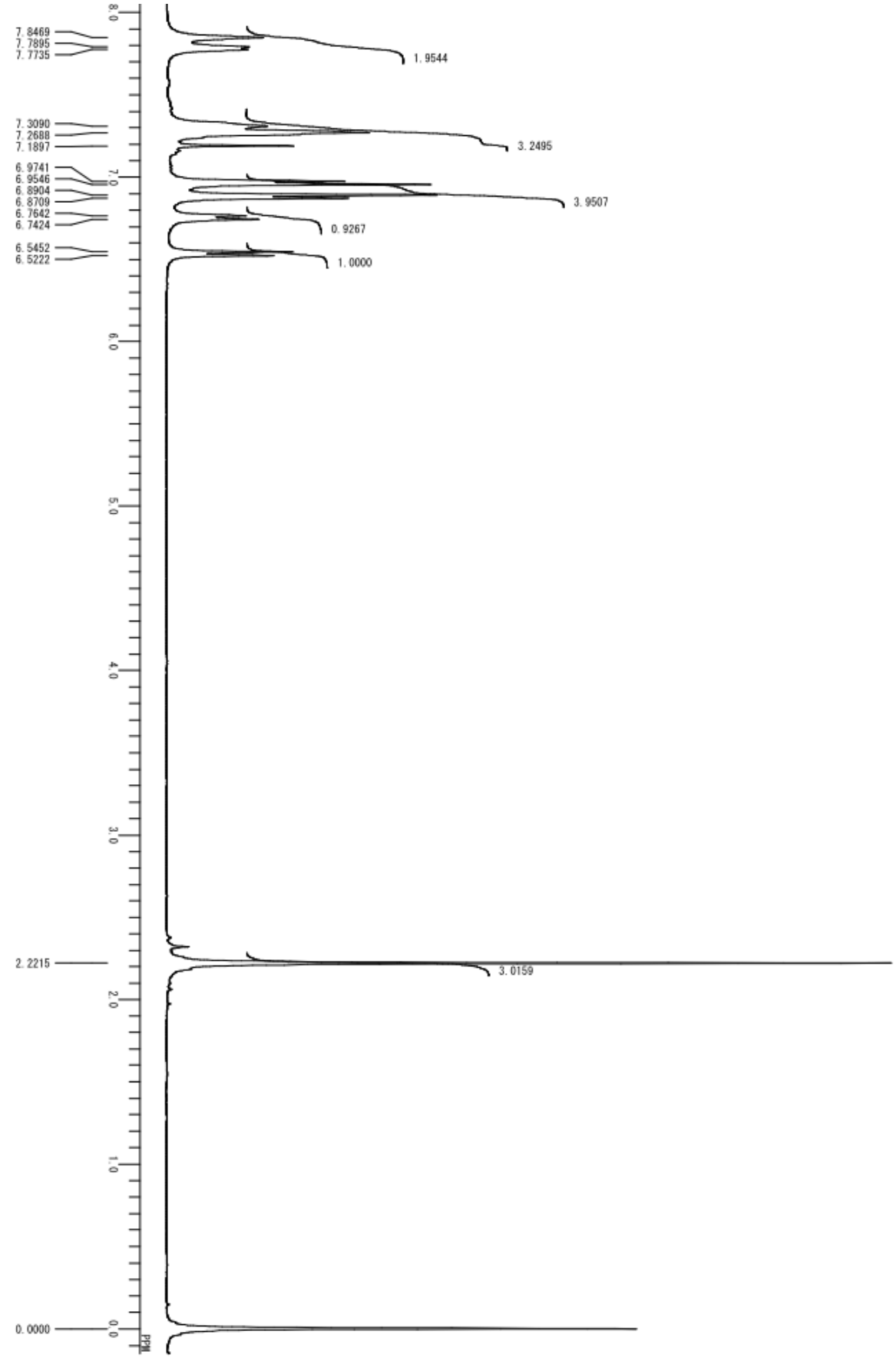




^{13}C -NMR (100 MHz, $CDCl_3$)

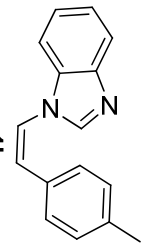
1a

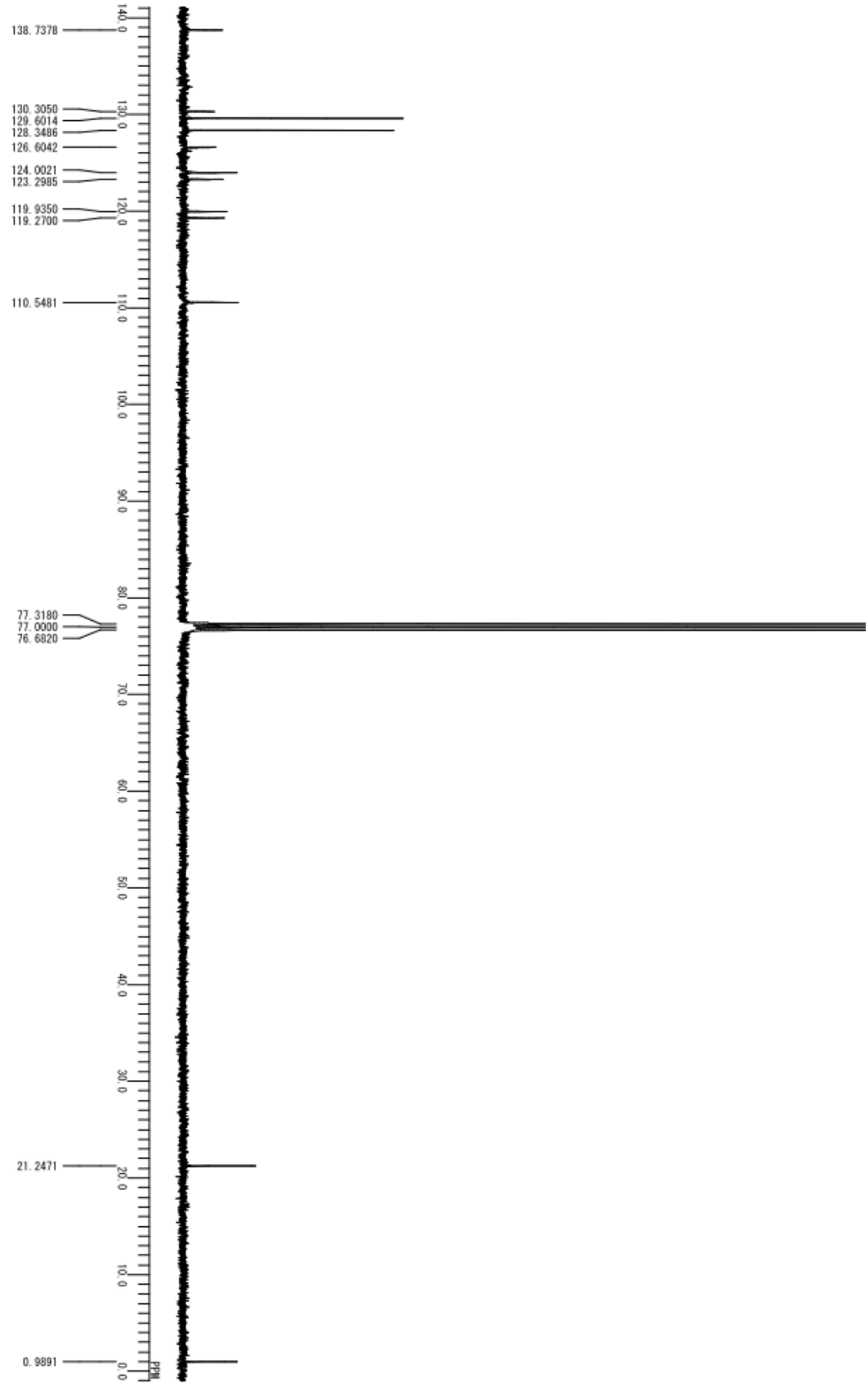




^{1}H -NMR (400 MHz, $CDCl_3$)

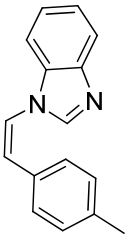
1b

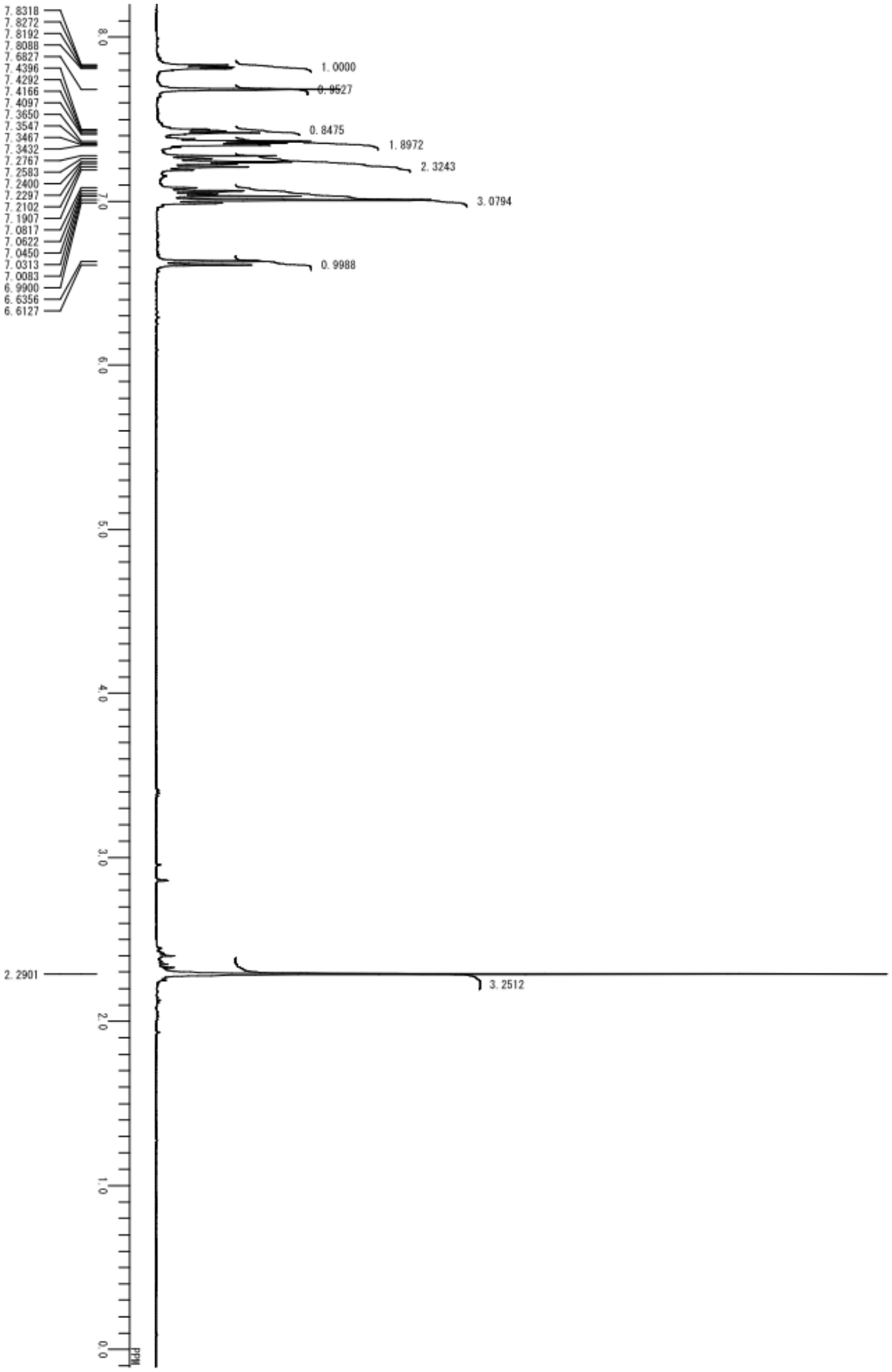




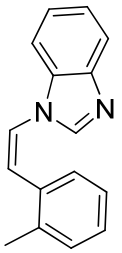
^{13}C -NMR (100 MHz, $CDCl_3$)

1b

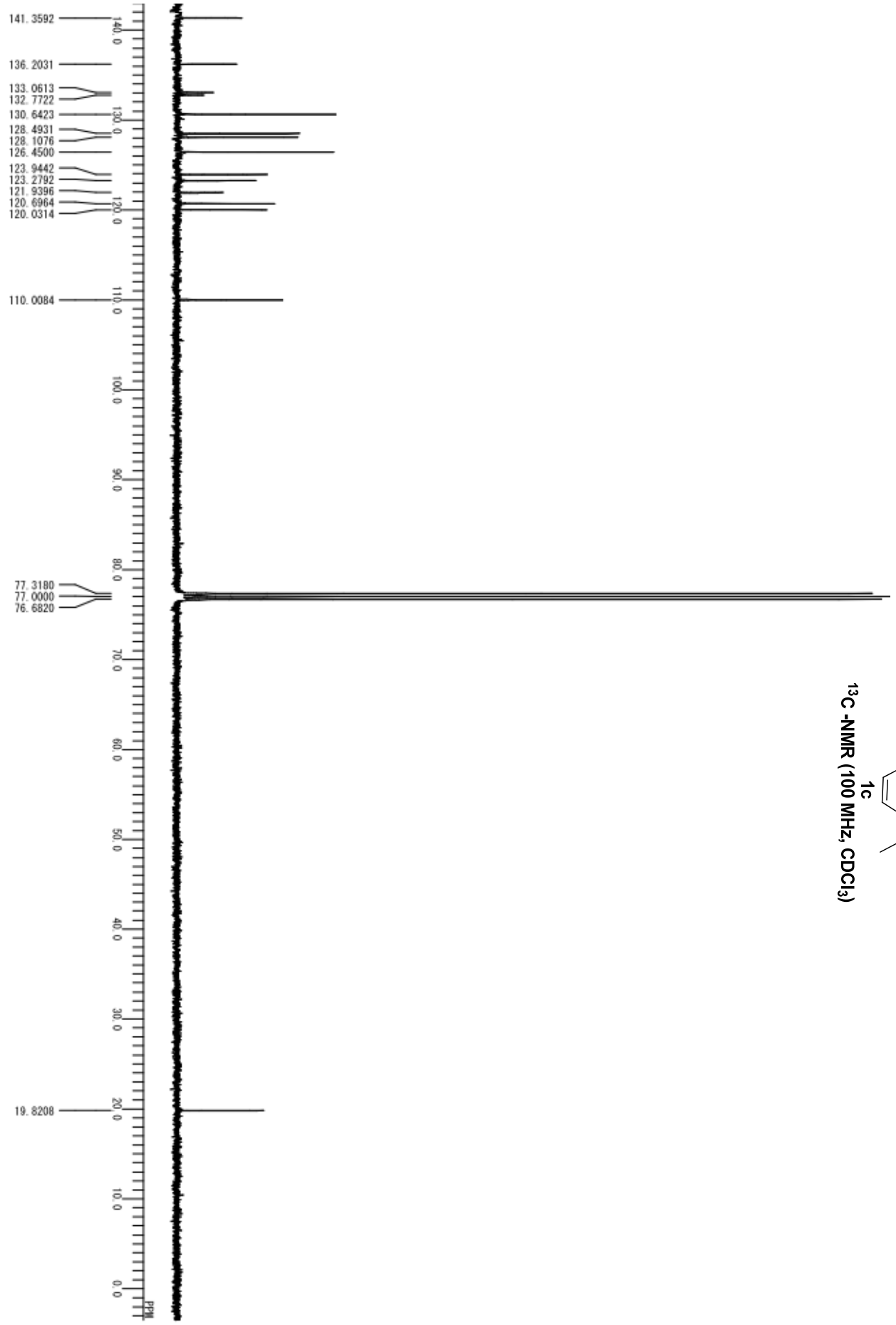




^{1}H-NMR (400 MHz, $CDCl_3$)

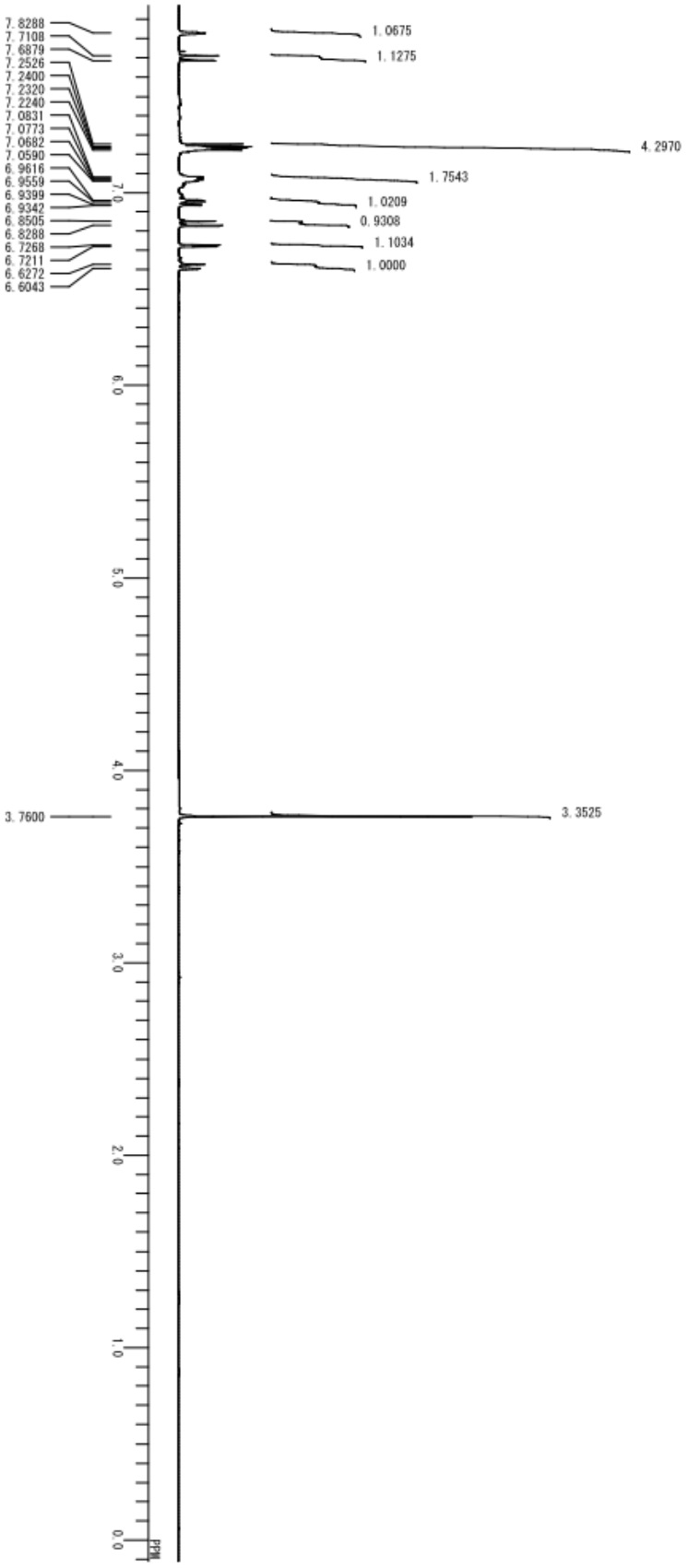


1c



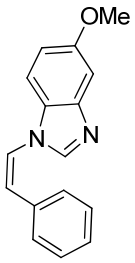
^{13}C -NMR (100 MHz, $CDCl_3$)

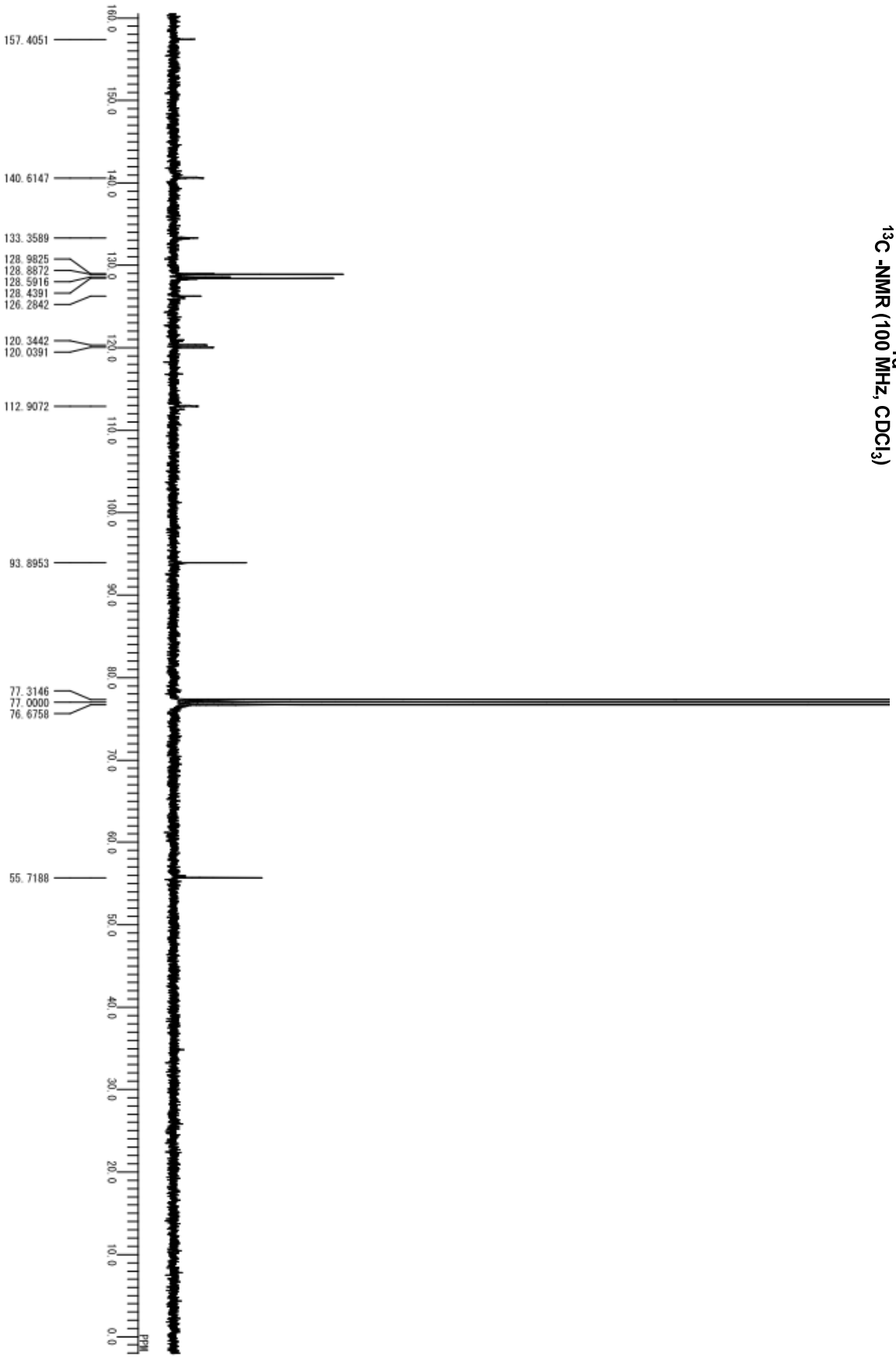
1c



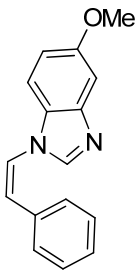
^{1}H-NMR (400 MHz, $CDCl_3$)

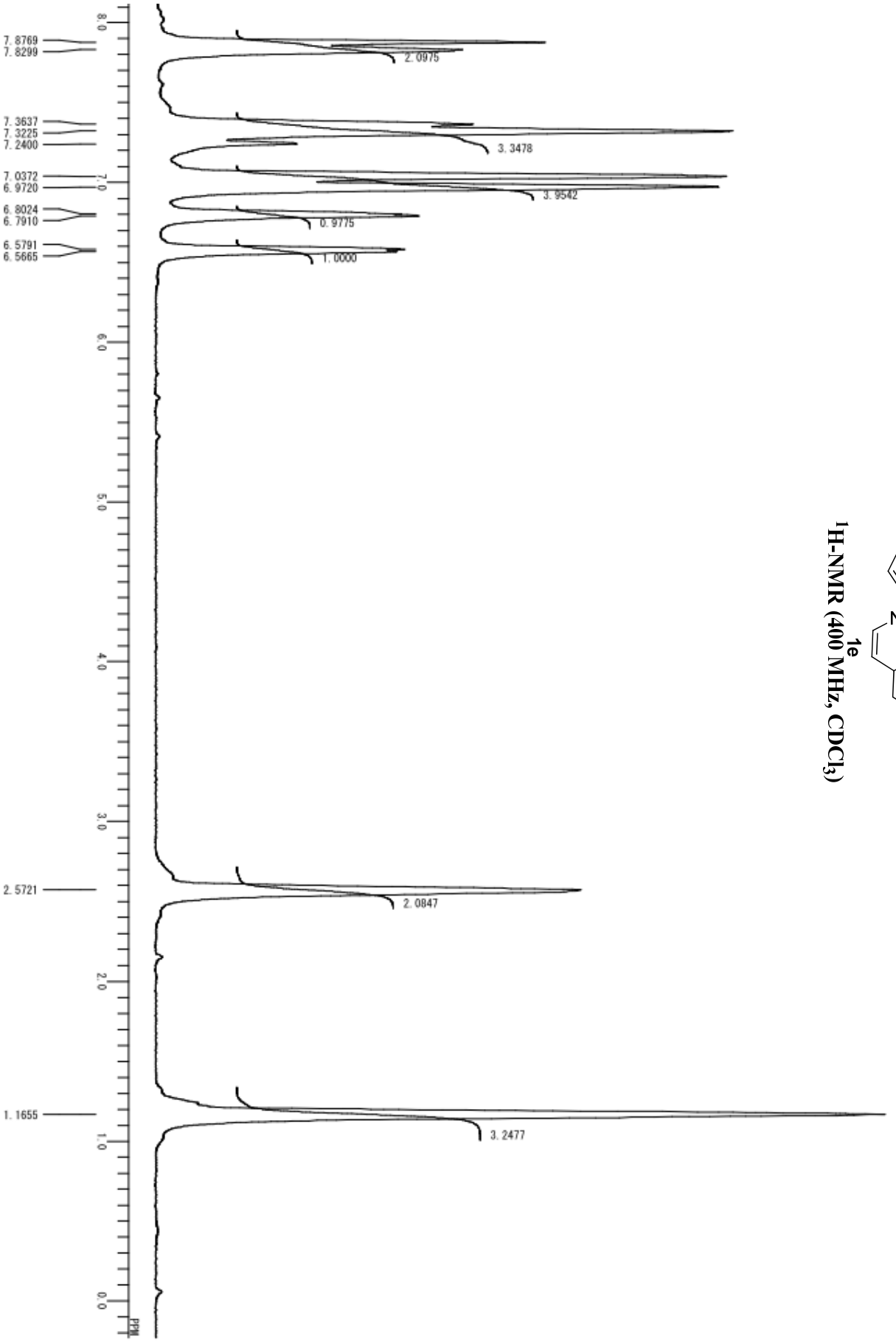
1d





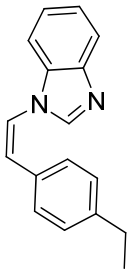
^{13}C -NMR (100 MHz, $CDCl_3$) **1d**

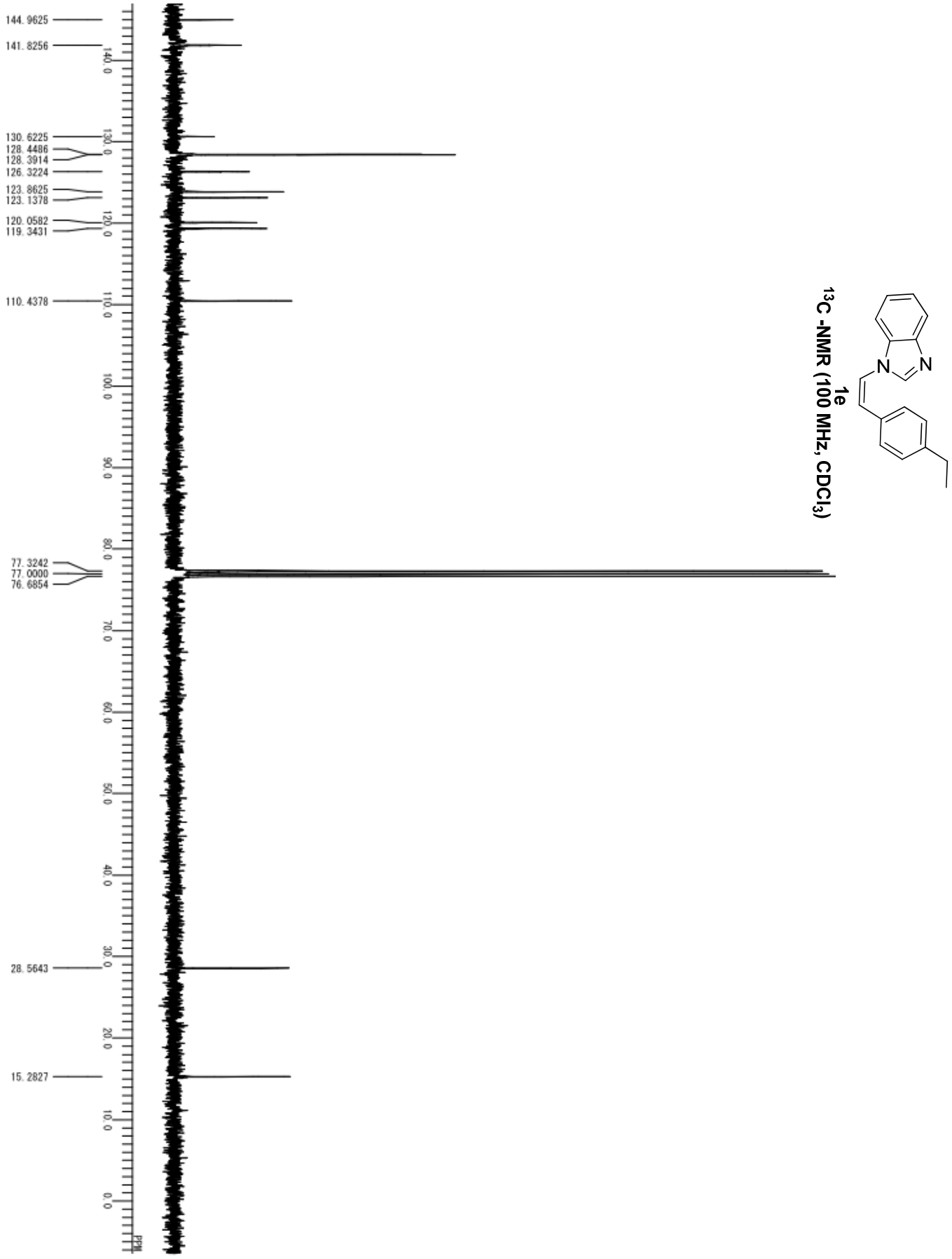


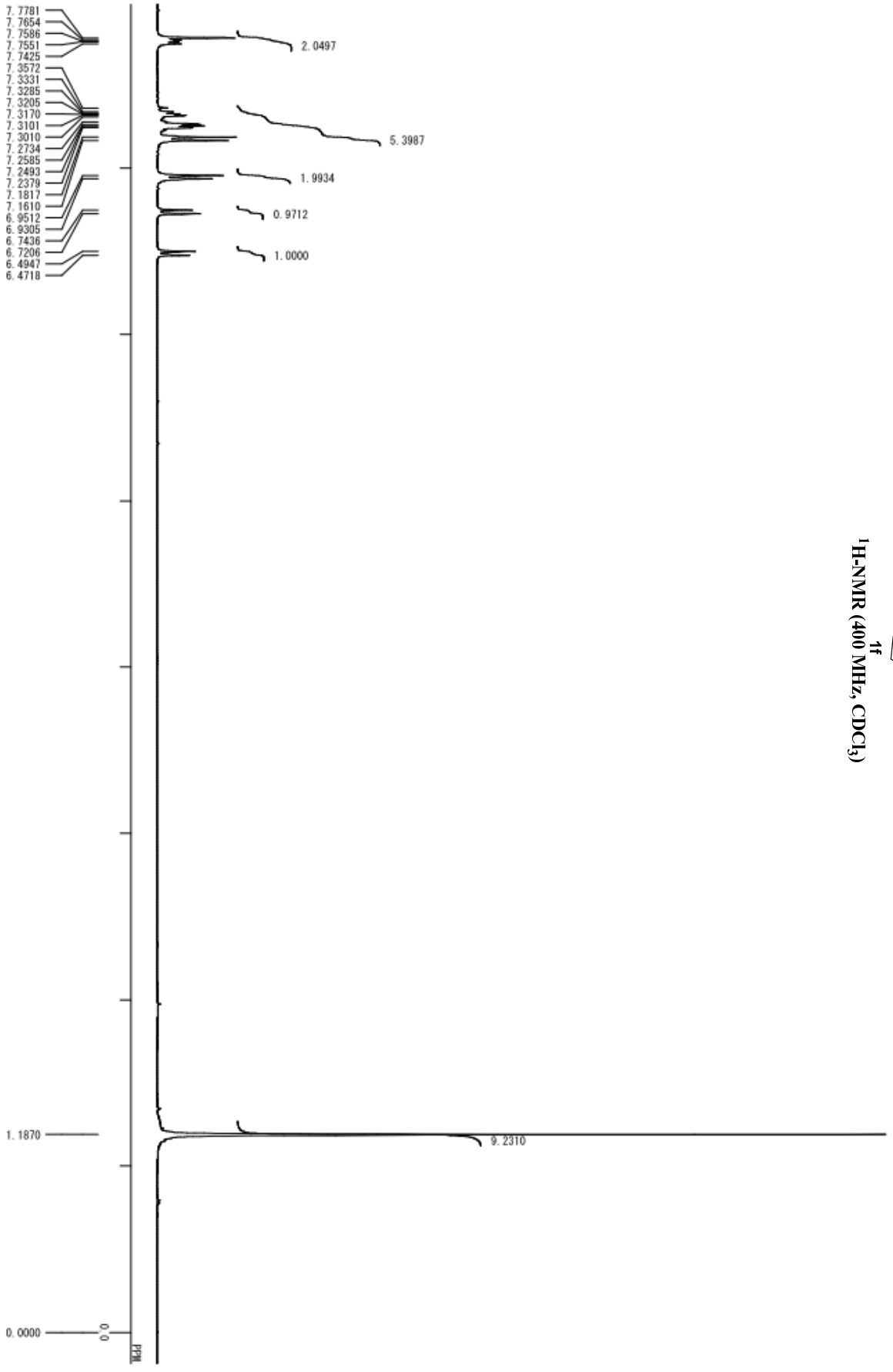


^{1}H-NMR (400 MHz, $CDCl_3$)

1e

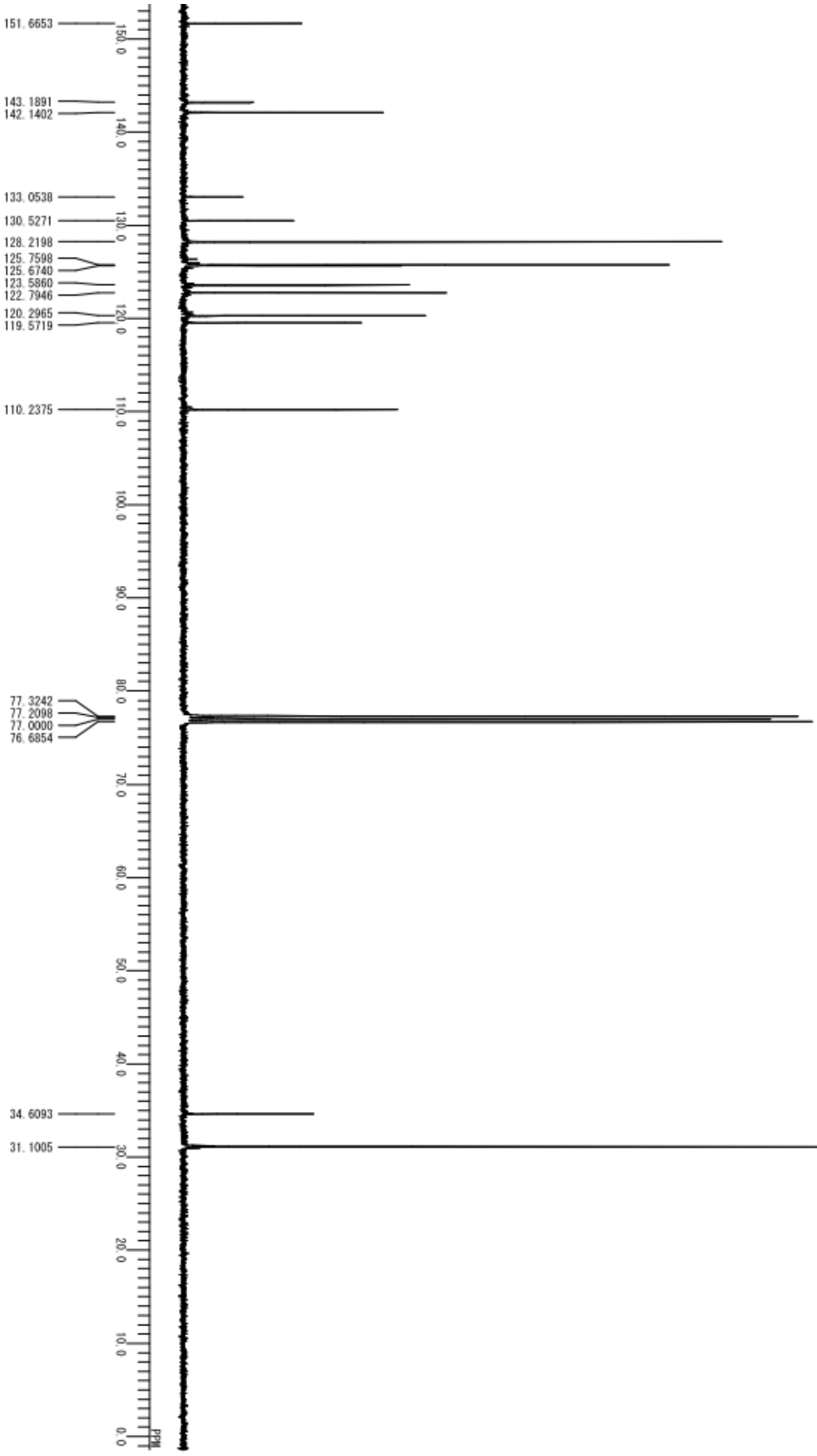






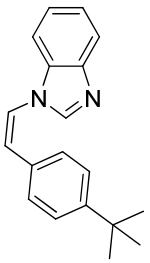
^{1}H-NMR (400 MHz, $CDCl_3$)

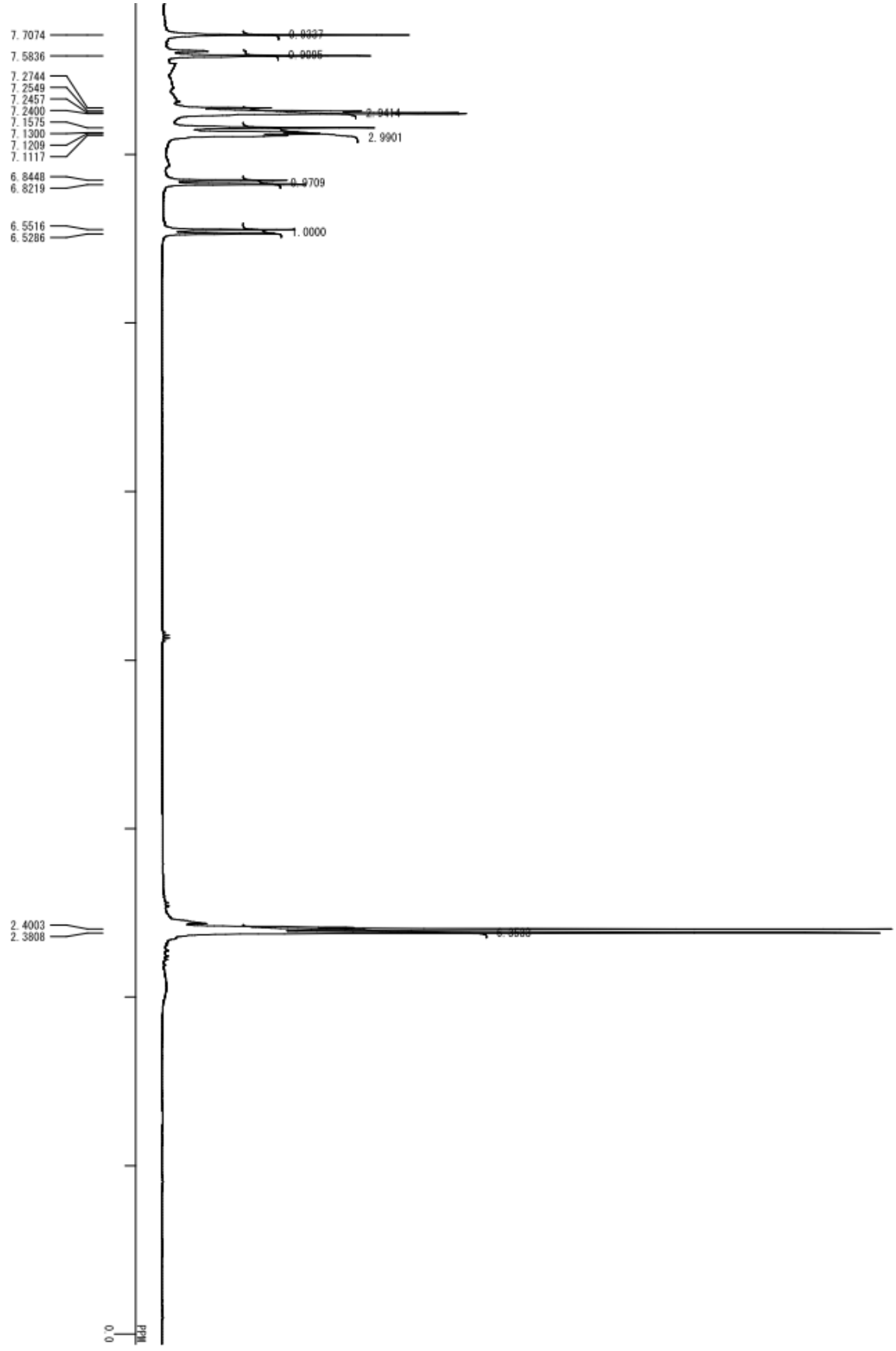
1f



^{13}C -NMR (100 MHz, $CDCl_3$)

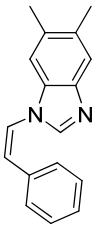
1f

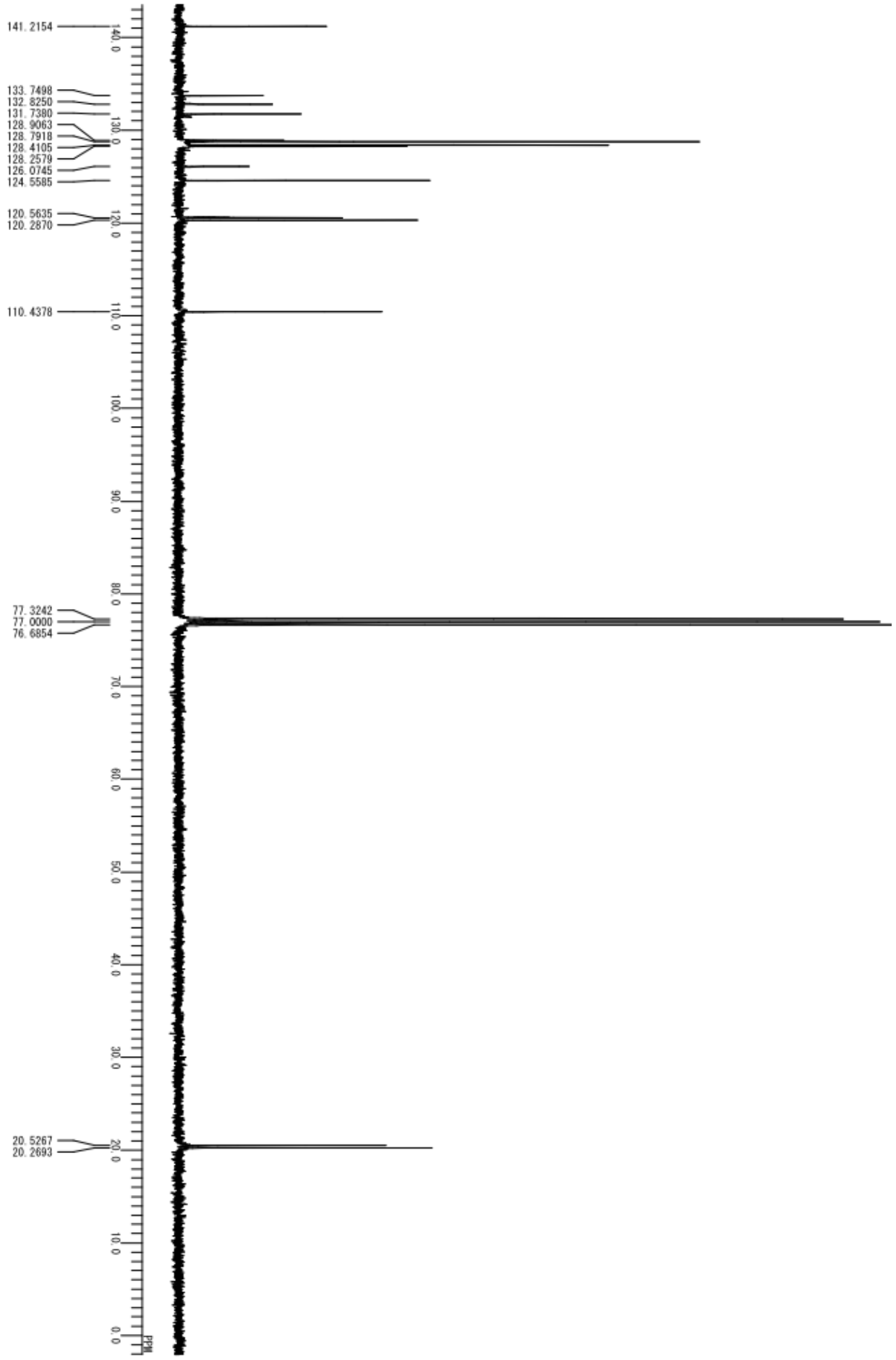




^{1}H-NMR (400 MHz, $CDCl_3$)

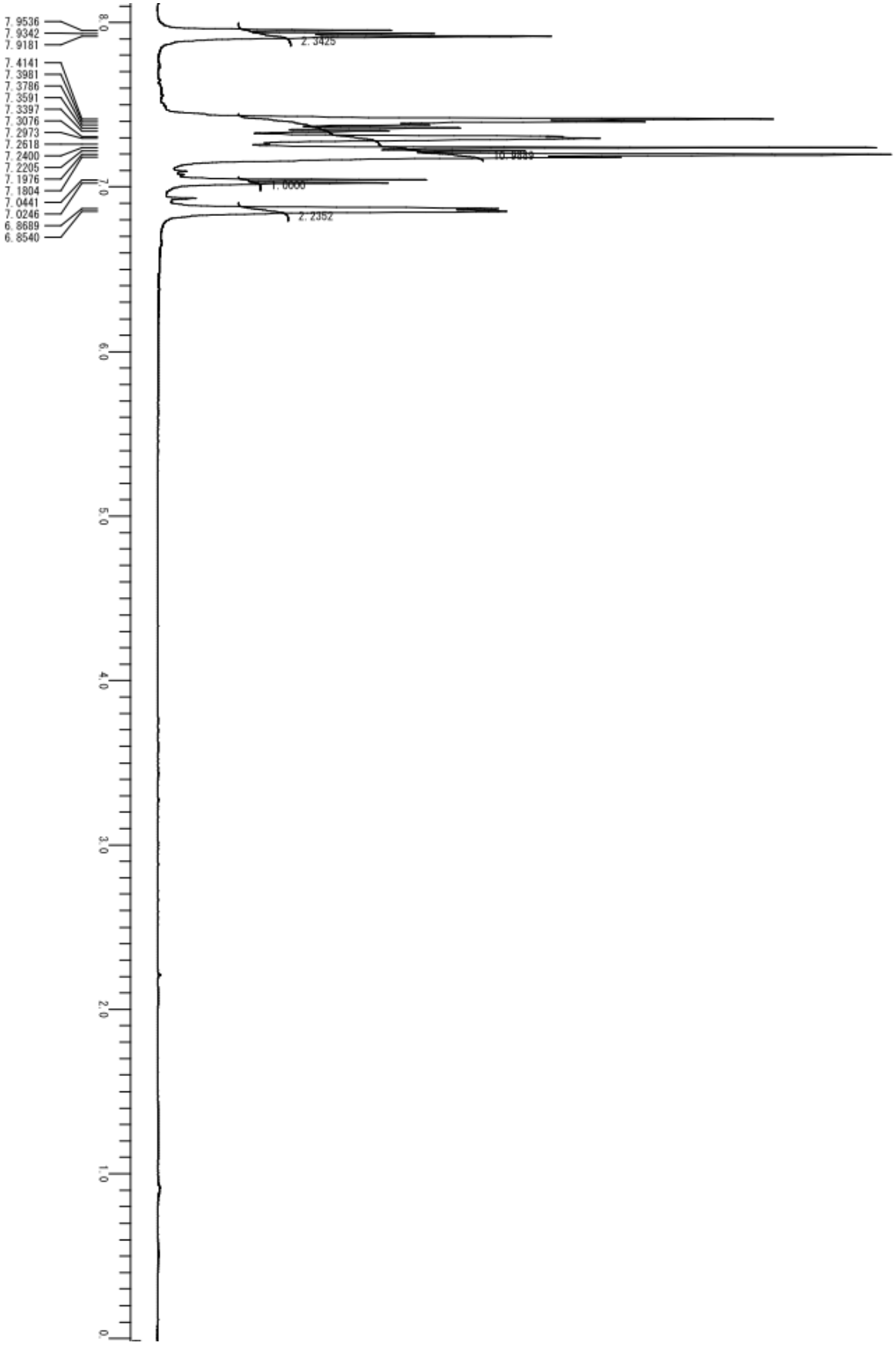
1g





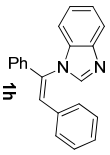
^{13}C-NMR (100 MHz, $CDCl_3$)

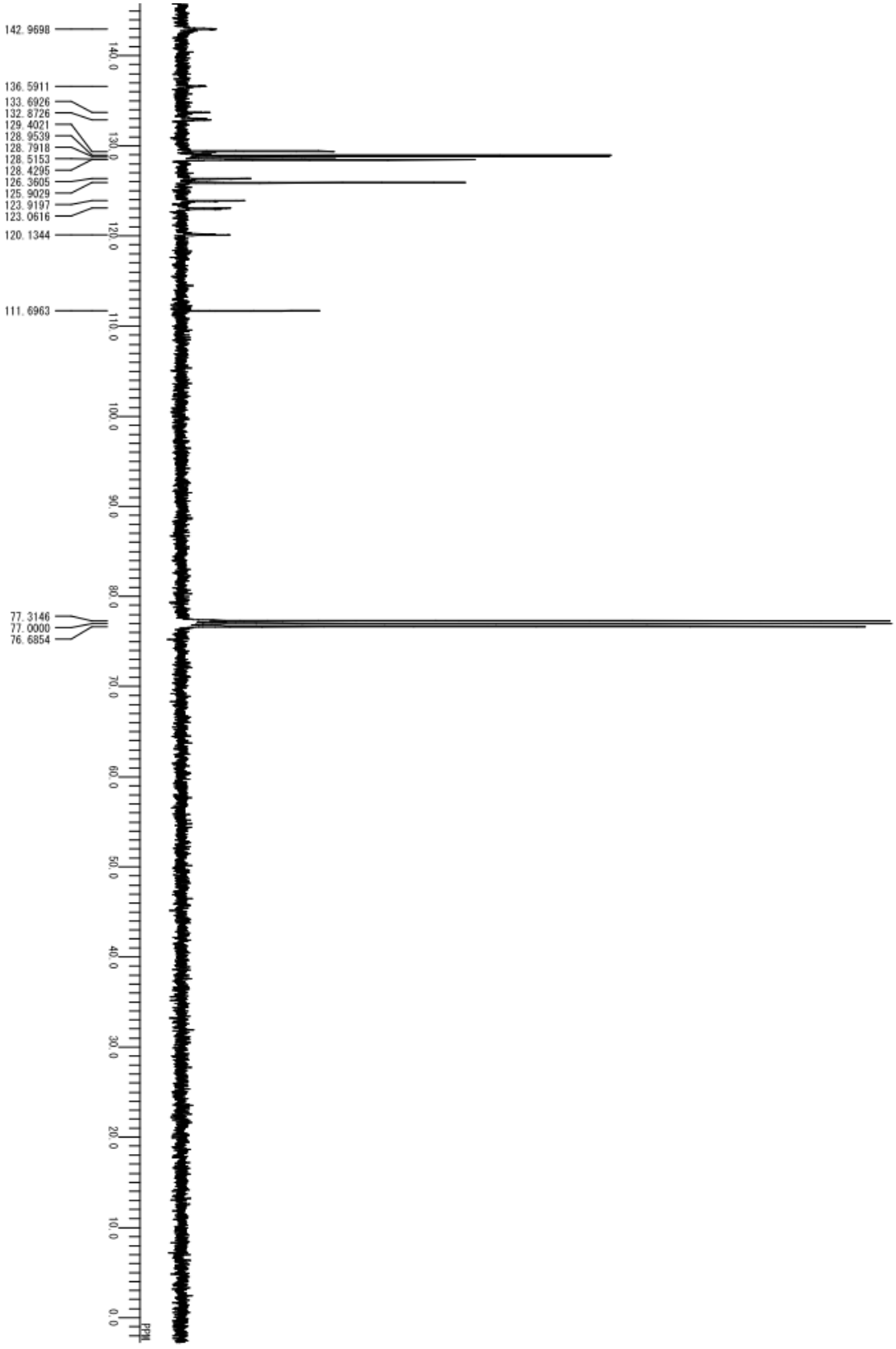
1g



^{1}H-NMR (400 MHz, $CDCl_3$)

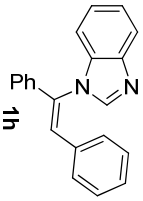
1h

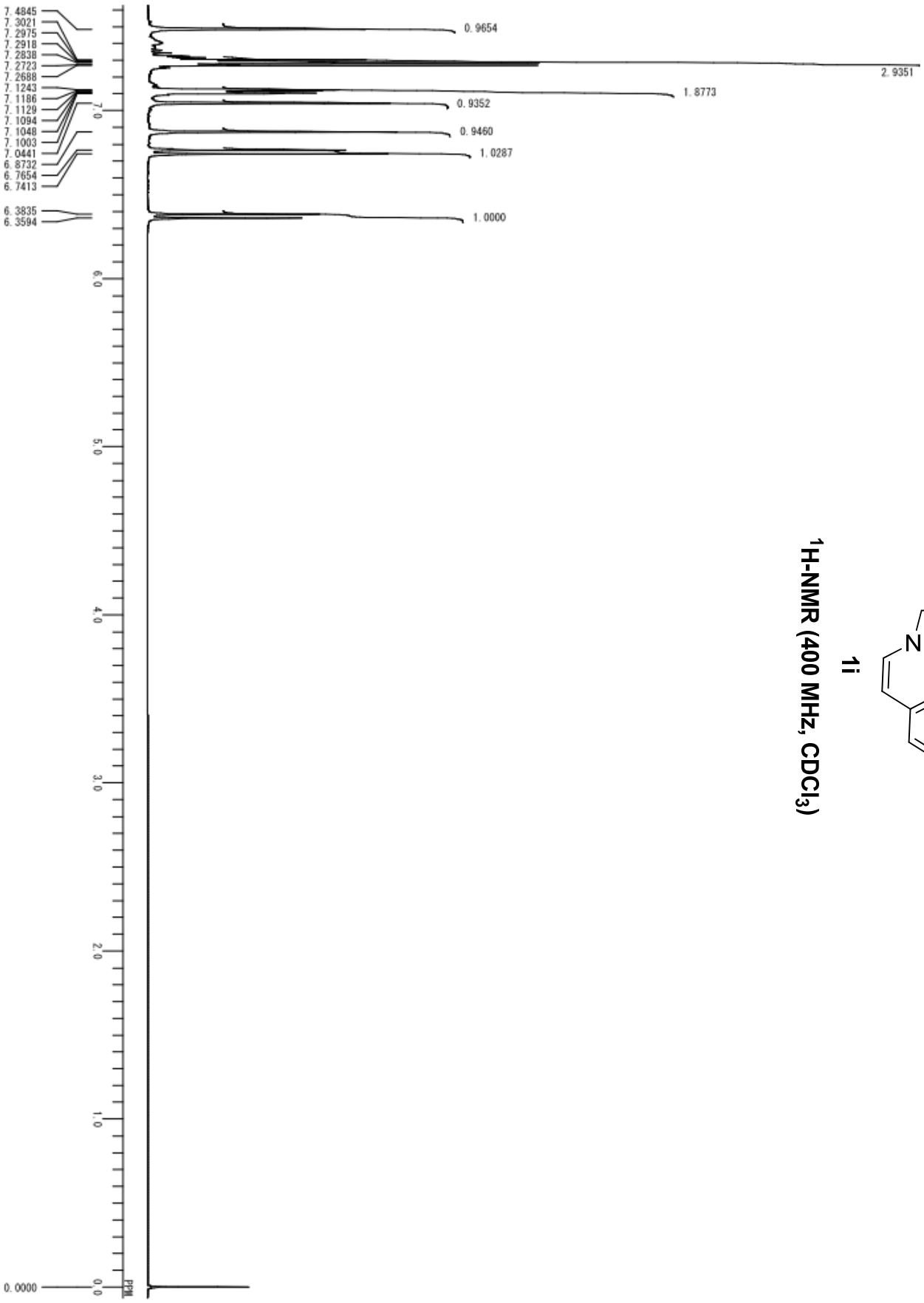




^{13}C-NMR (100 MHz, $CDCl_3$)

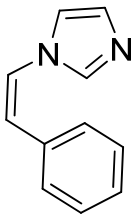
1h

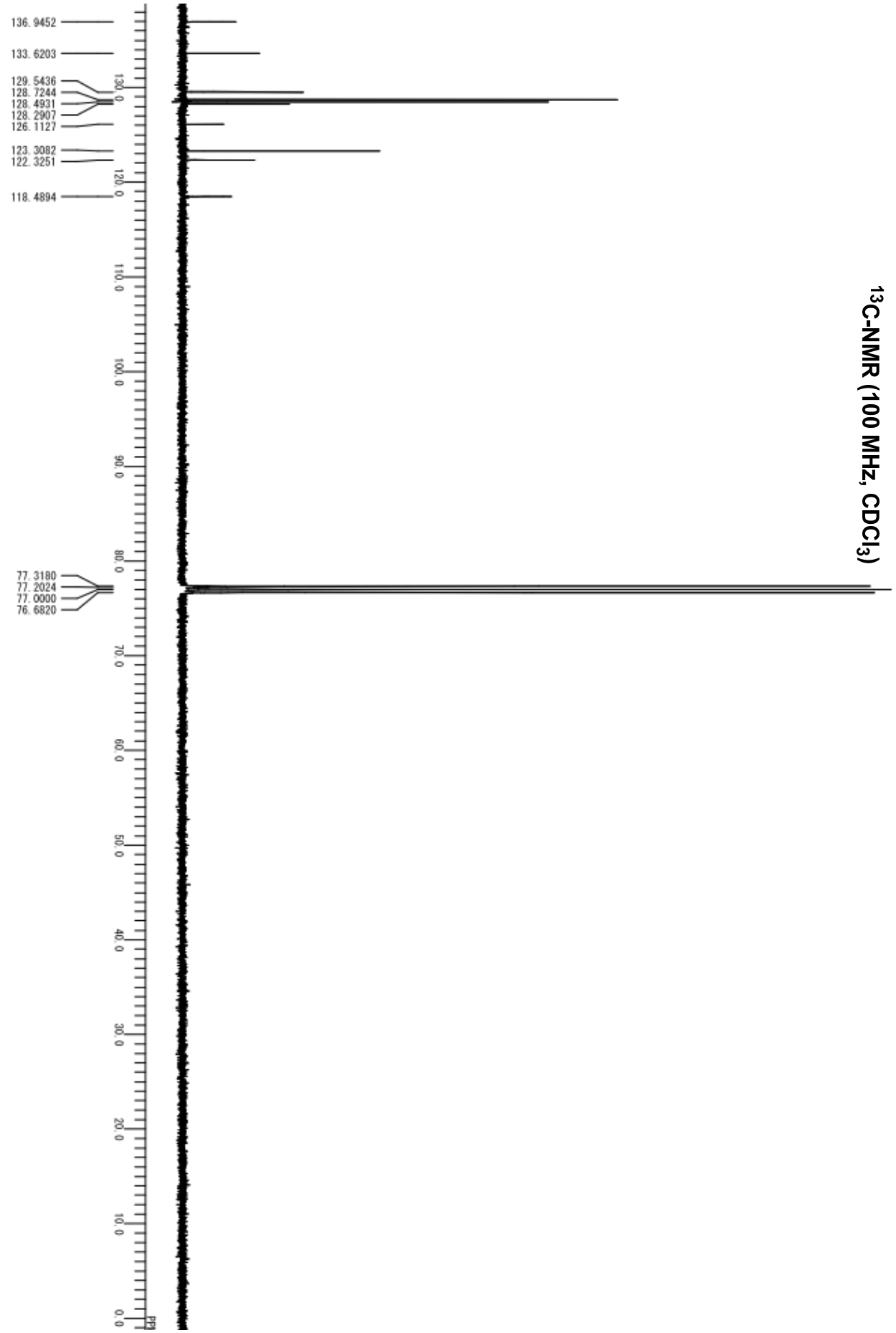




^{1}H-NMR (400 MHz, $CDCl_3$)

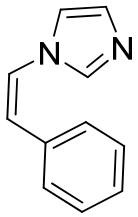
1i

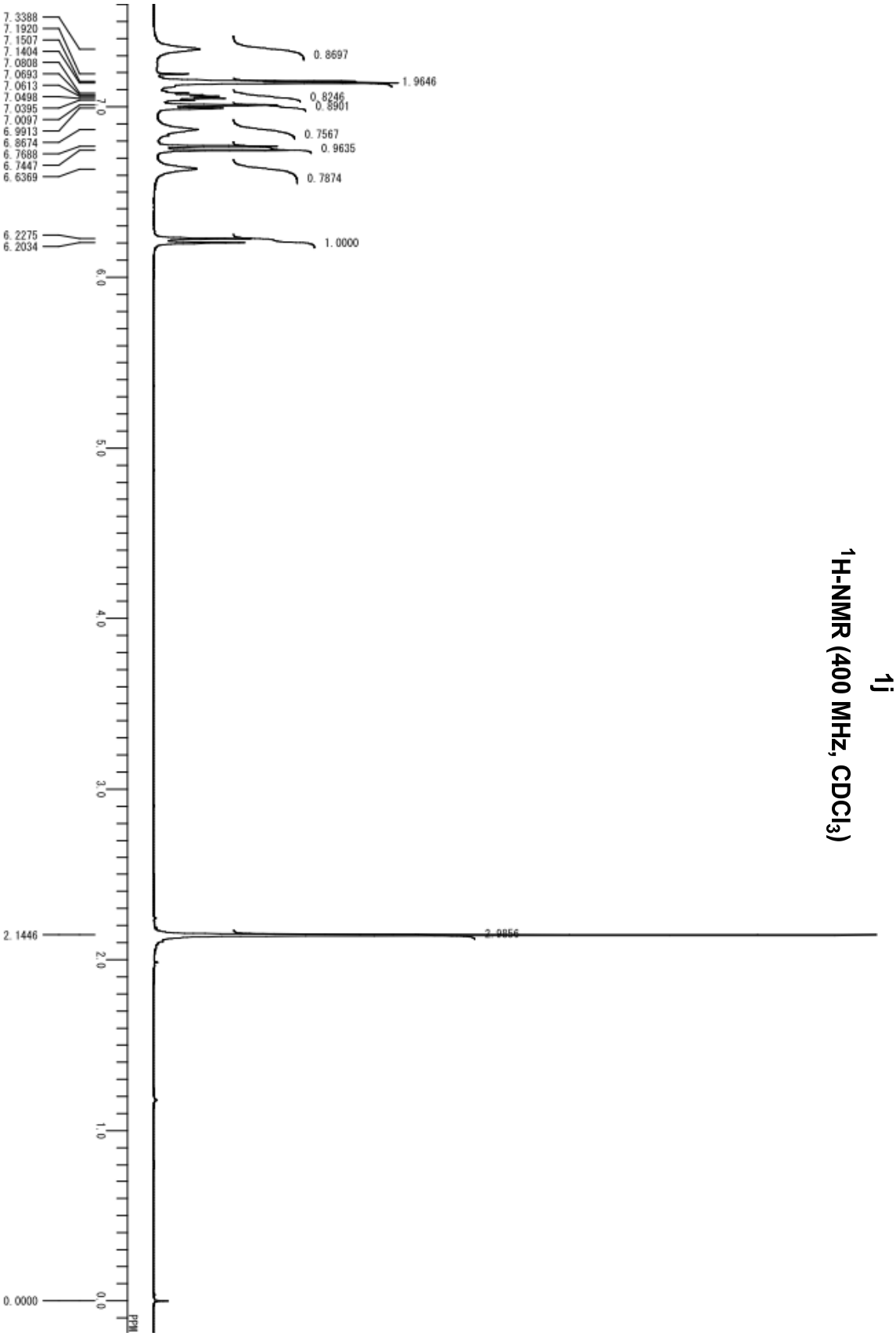




^{13}C-NMR (100 MHz, $CDCl_3$)

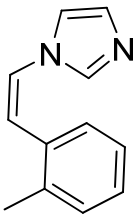
1i

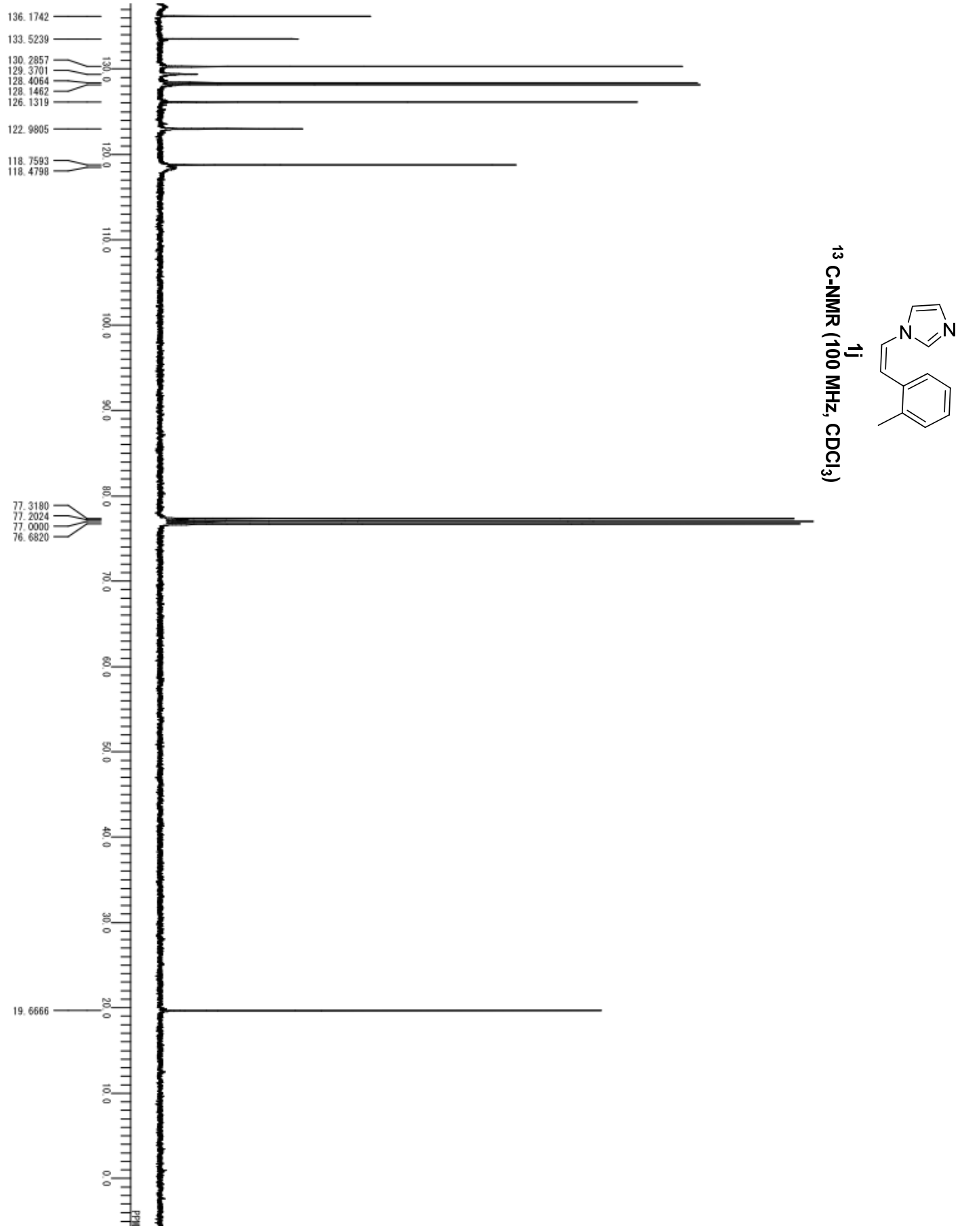




^{1}H-NMR (400 MHz, $CDCl_3$)

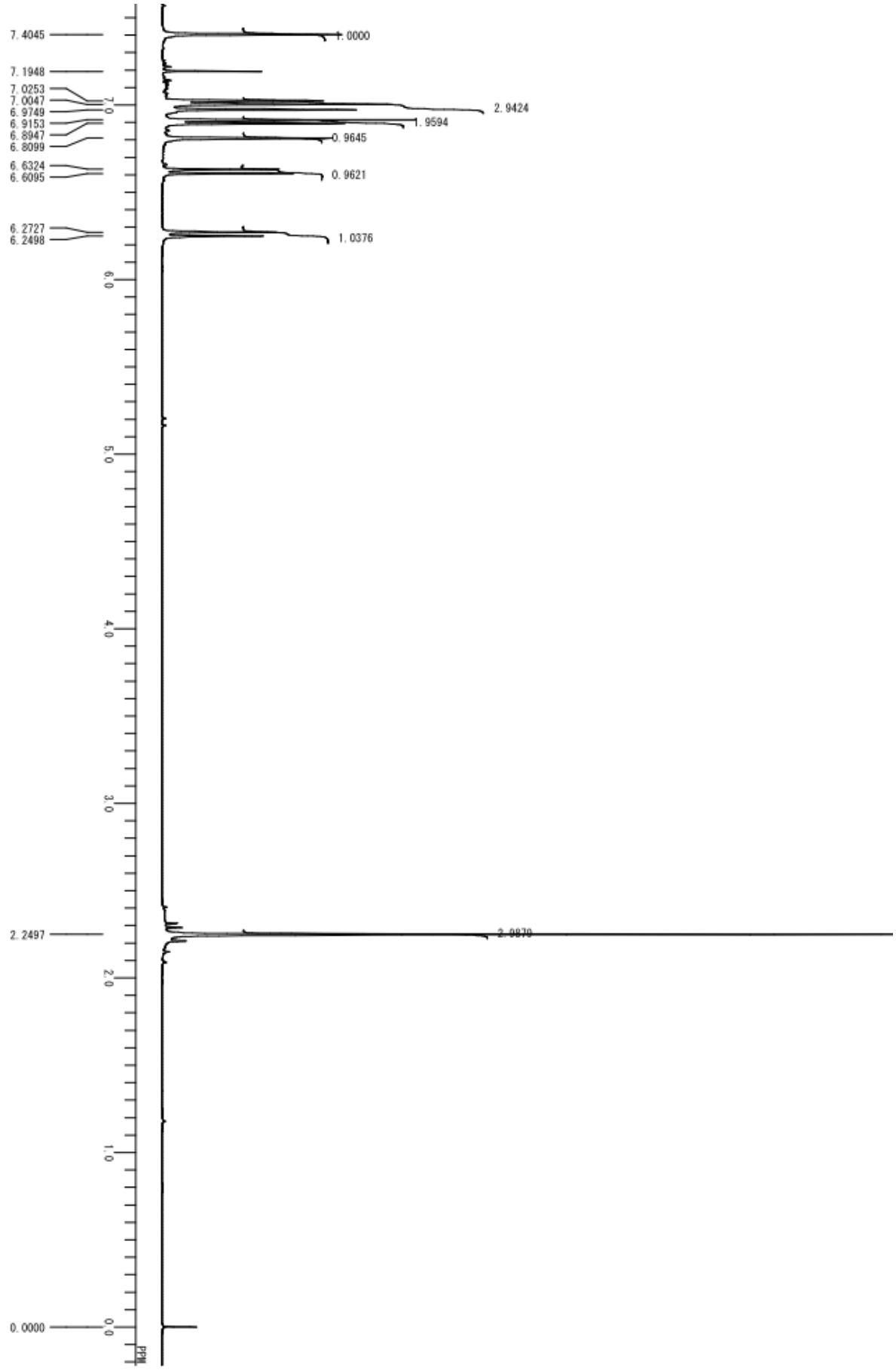
1j





^{13}C-NMR (100 MHz, $CDCl_3$)

1j



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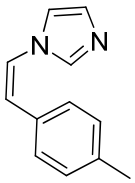
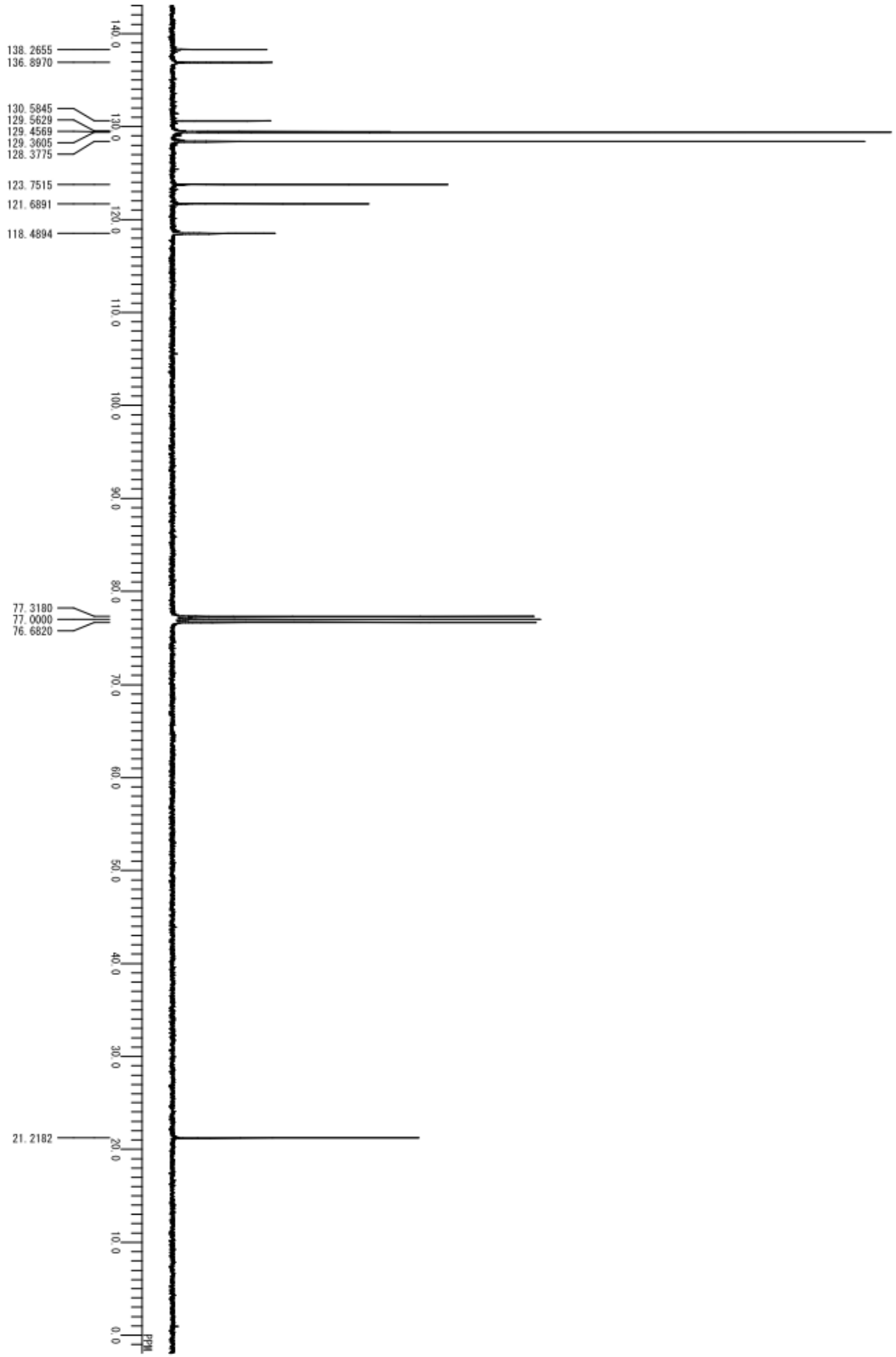
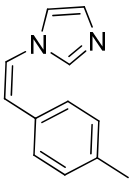
^{1}H-NMR (400 MHz, $CDCl_3$)

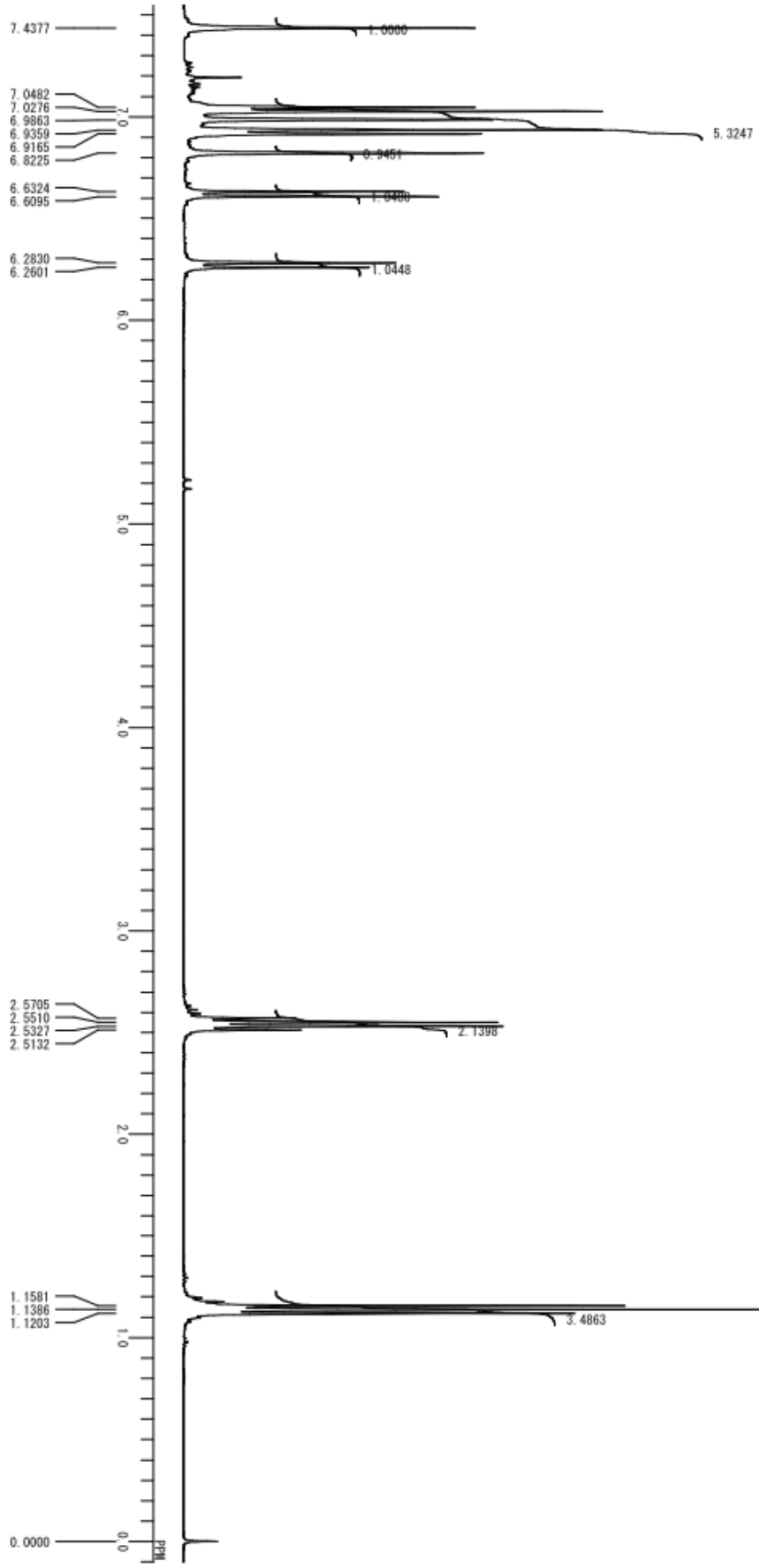




^{13}C-NMR (100 MHz, $CDCl_3$)

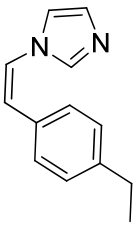
1k

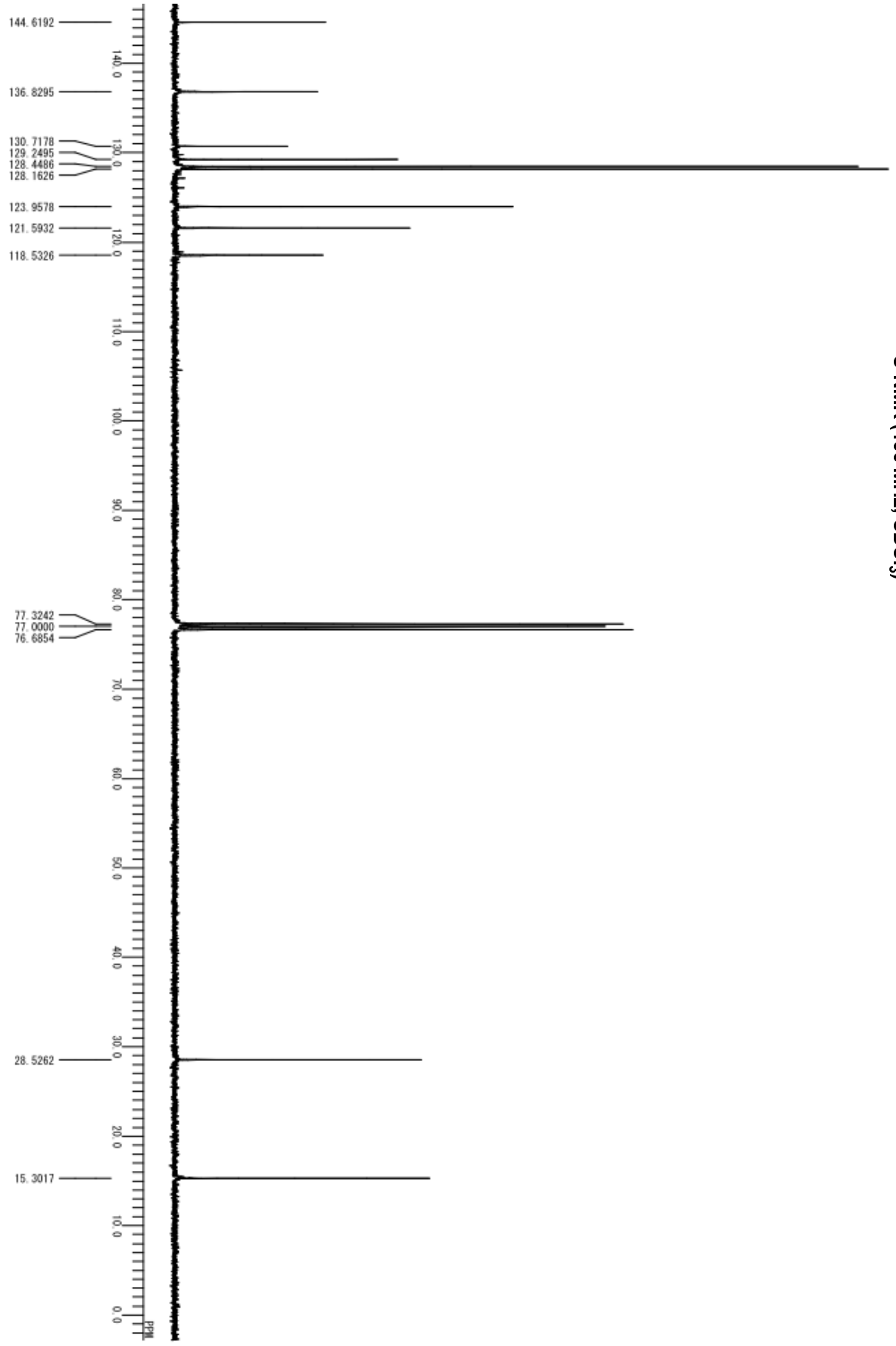




^{1}H-NMR (400 MHz, $CDCl_3$)

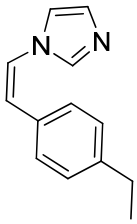
1l

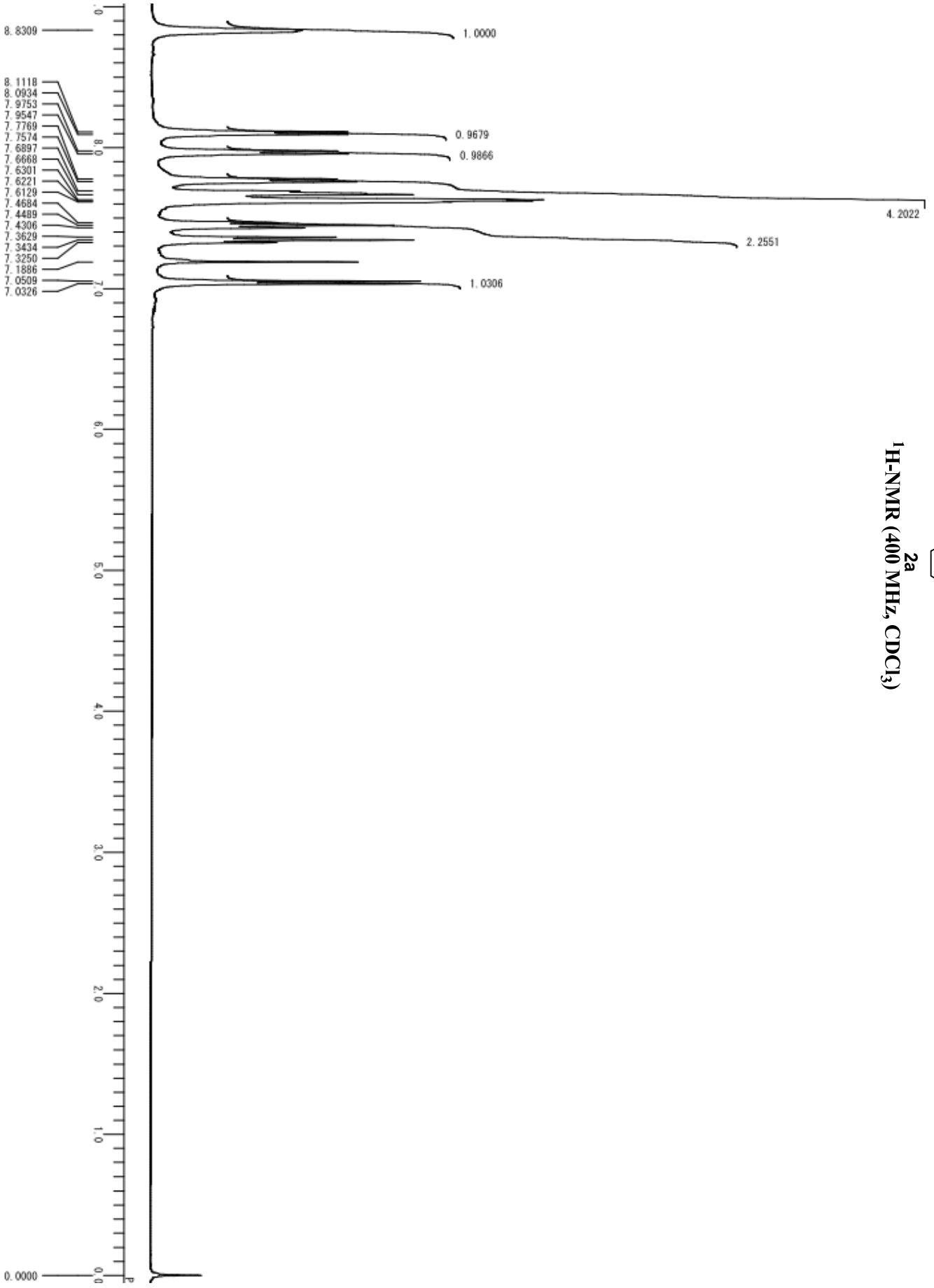




^{13}C-NMR (100 MHz, $CDCl_3$)

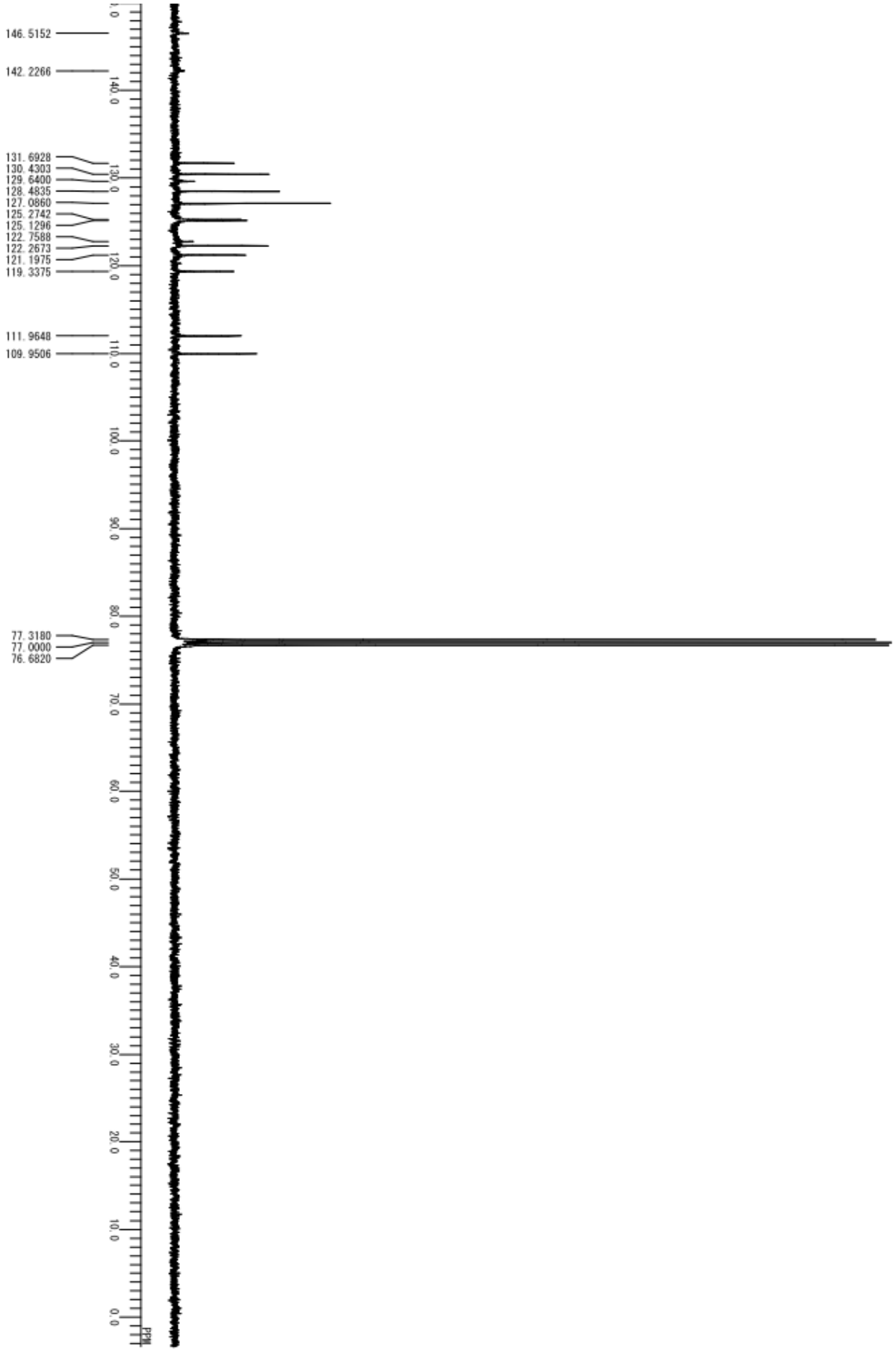
1l





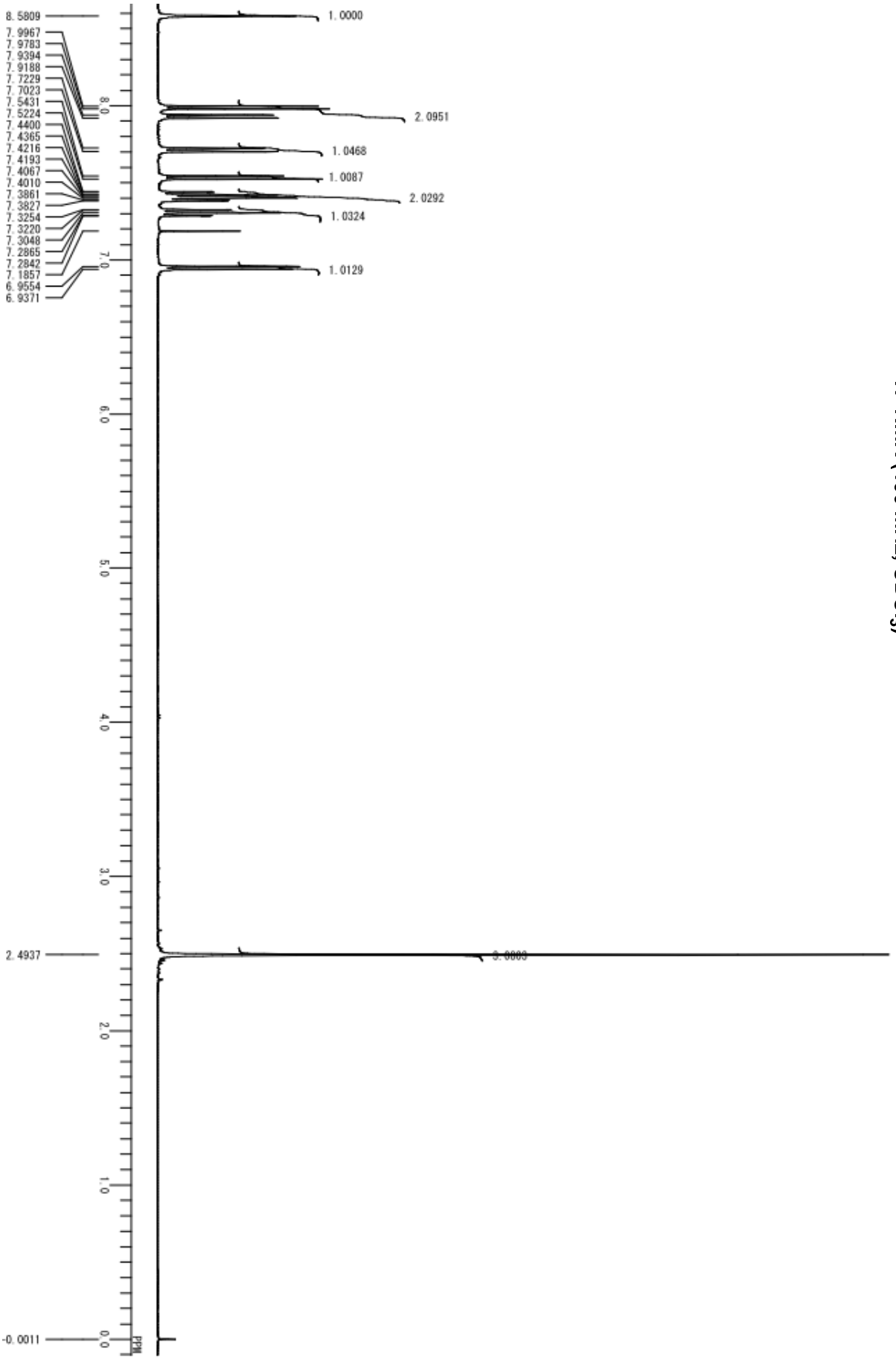
^{1}H-NMR (400 MHz, $CDCl_3$)

2a



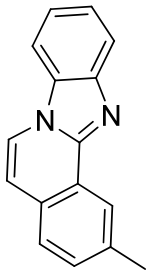
^{13}C -NMR (100 MHz, $CDCl_3$)

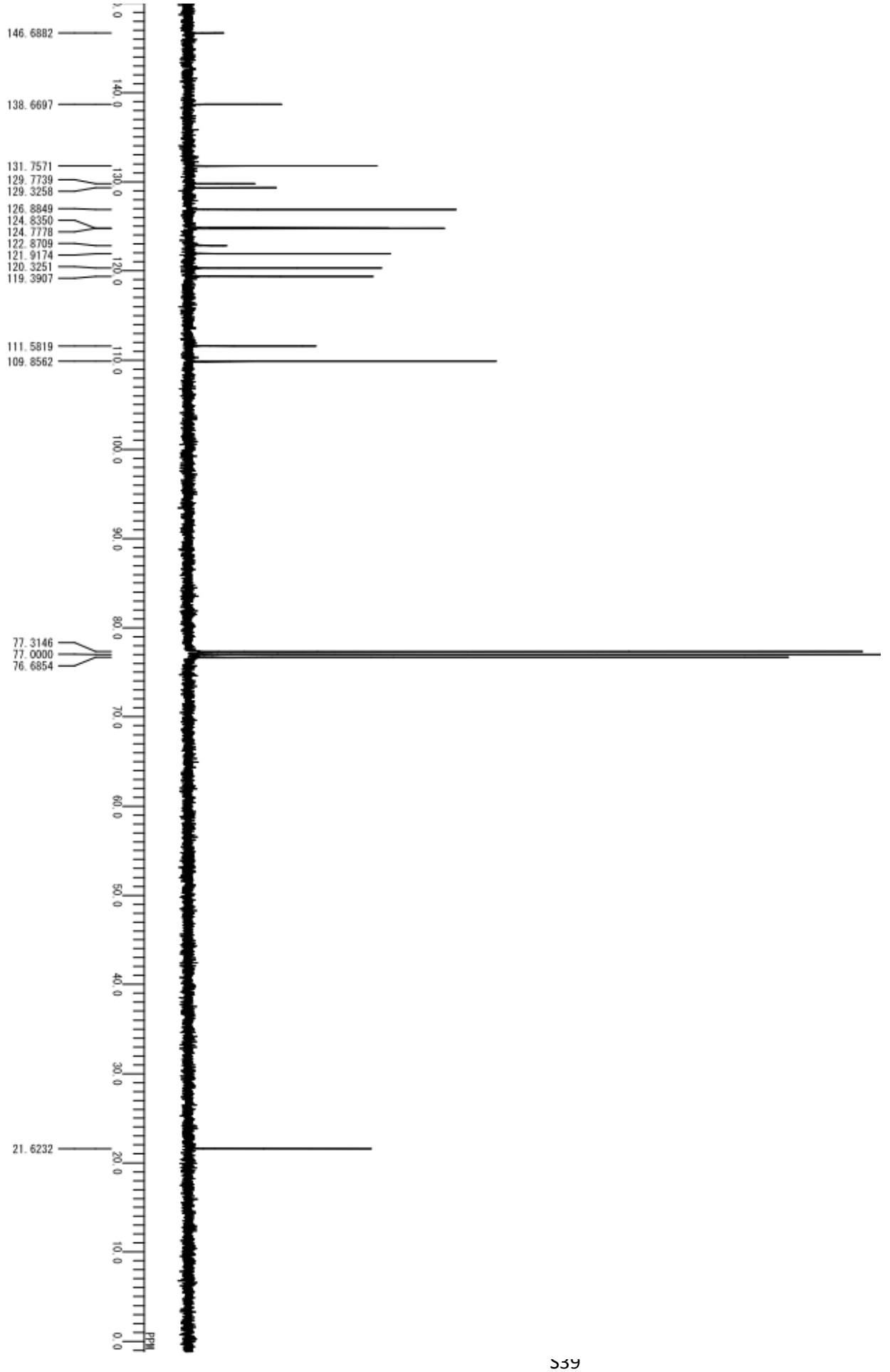
2a



^{1}H -NMR (400 MHz, $CDCl_3$)

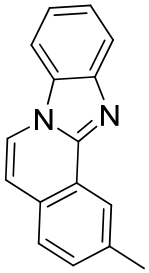
2b

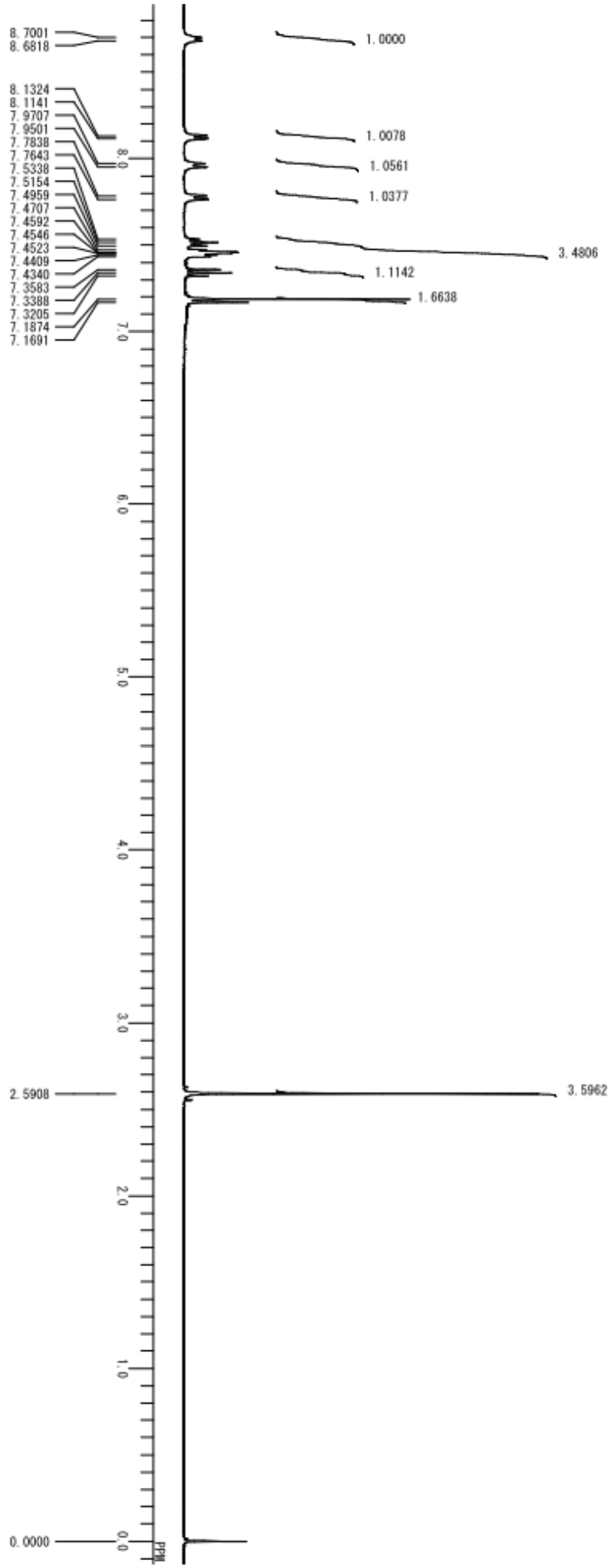




^{13}C -NMR (100 MHz, $CDCl_3$)

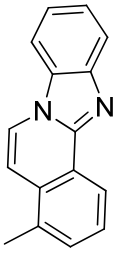
2b

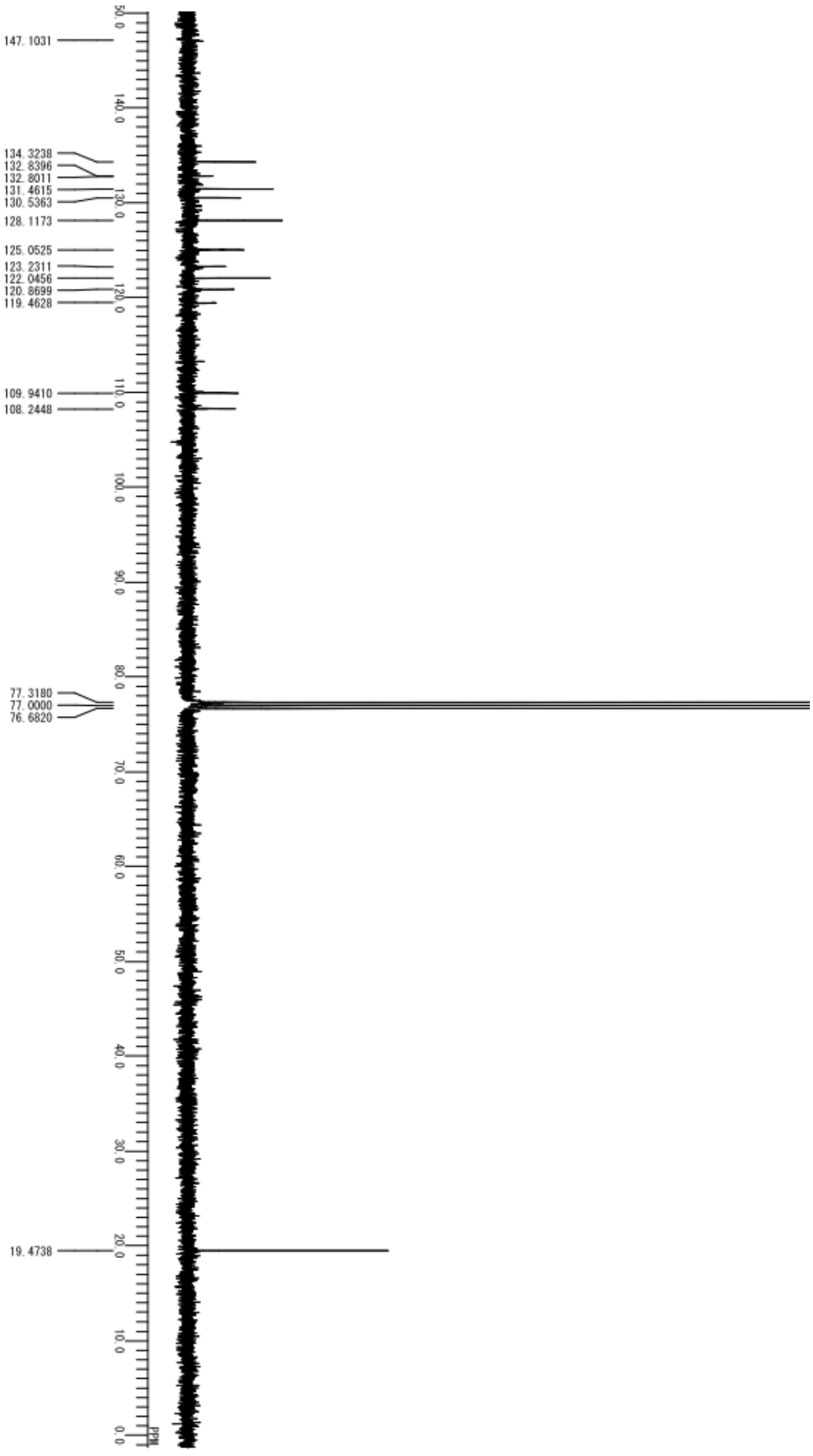




^{1}H-NMR (400 MHz, $CDCl_3$)

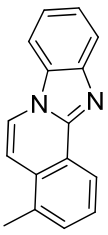
2c

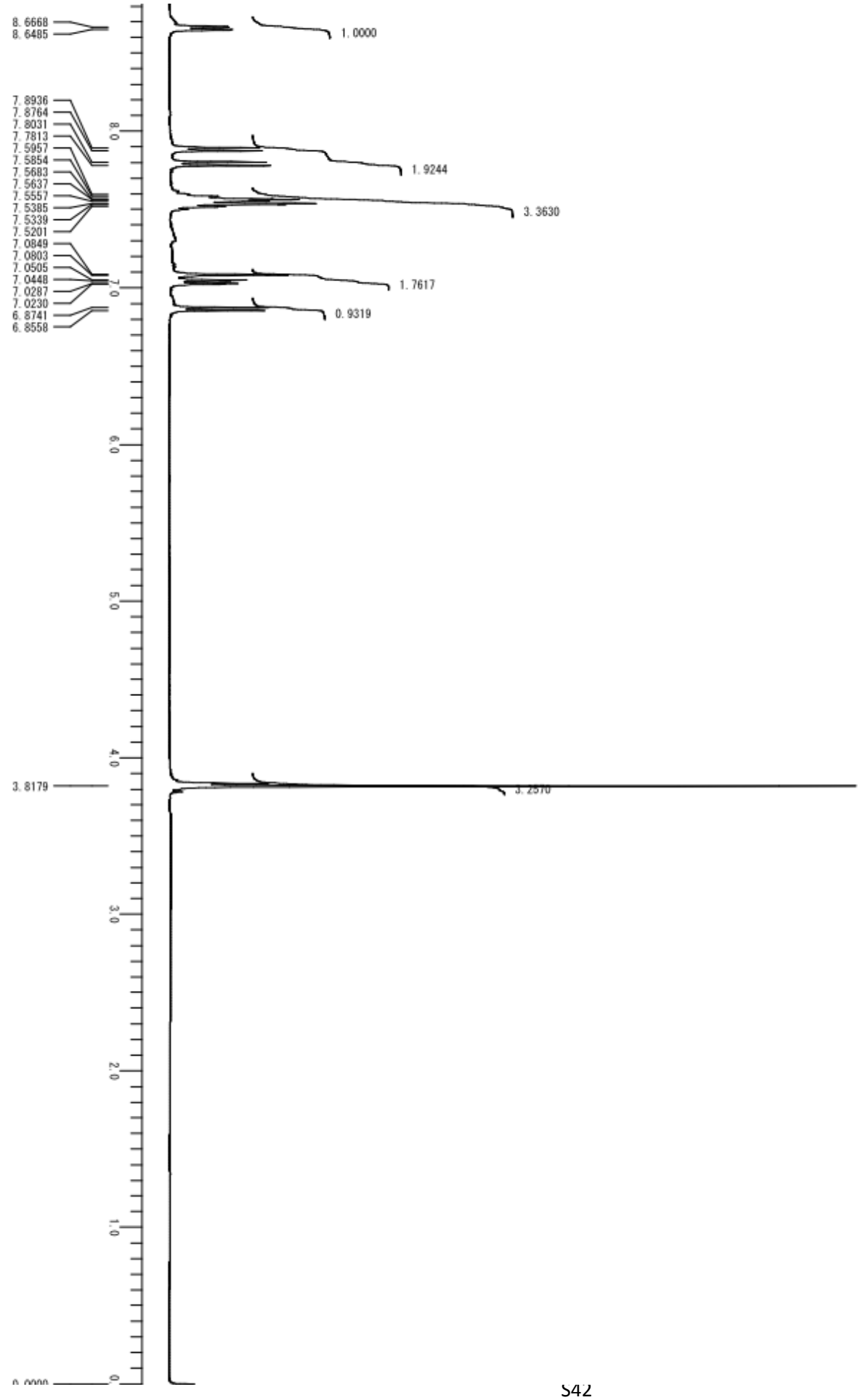




^{13}C -NMR (100 MHz, $CDCl_3$)

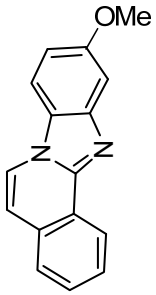
2c

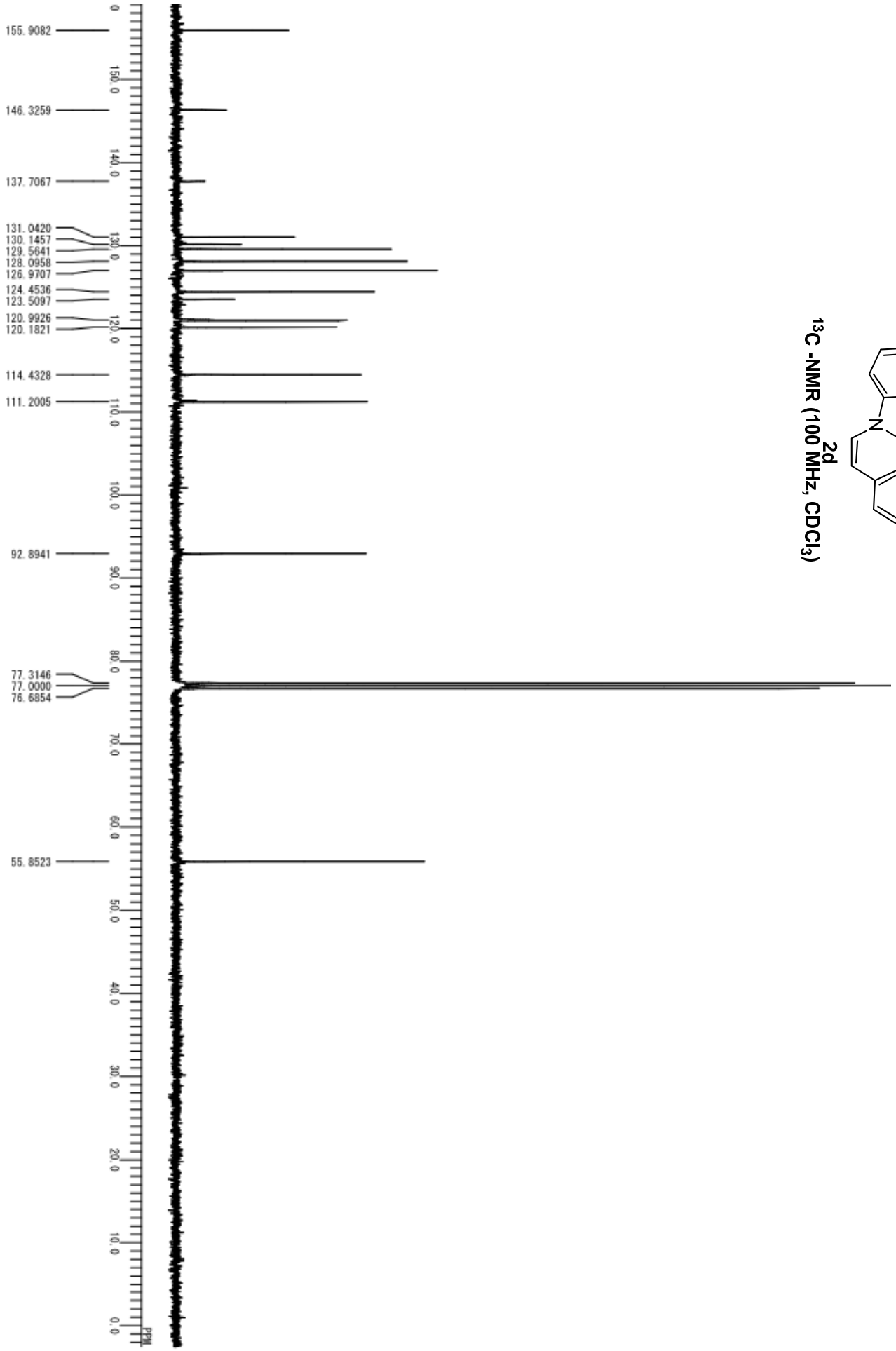




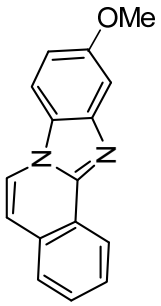
^{1}H-NMR (400 MHz, $CDCl_3$)

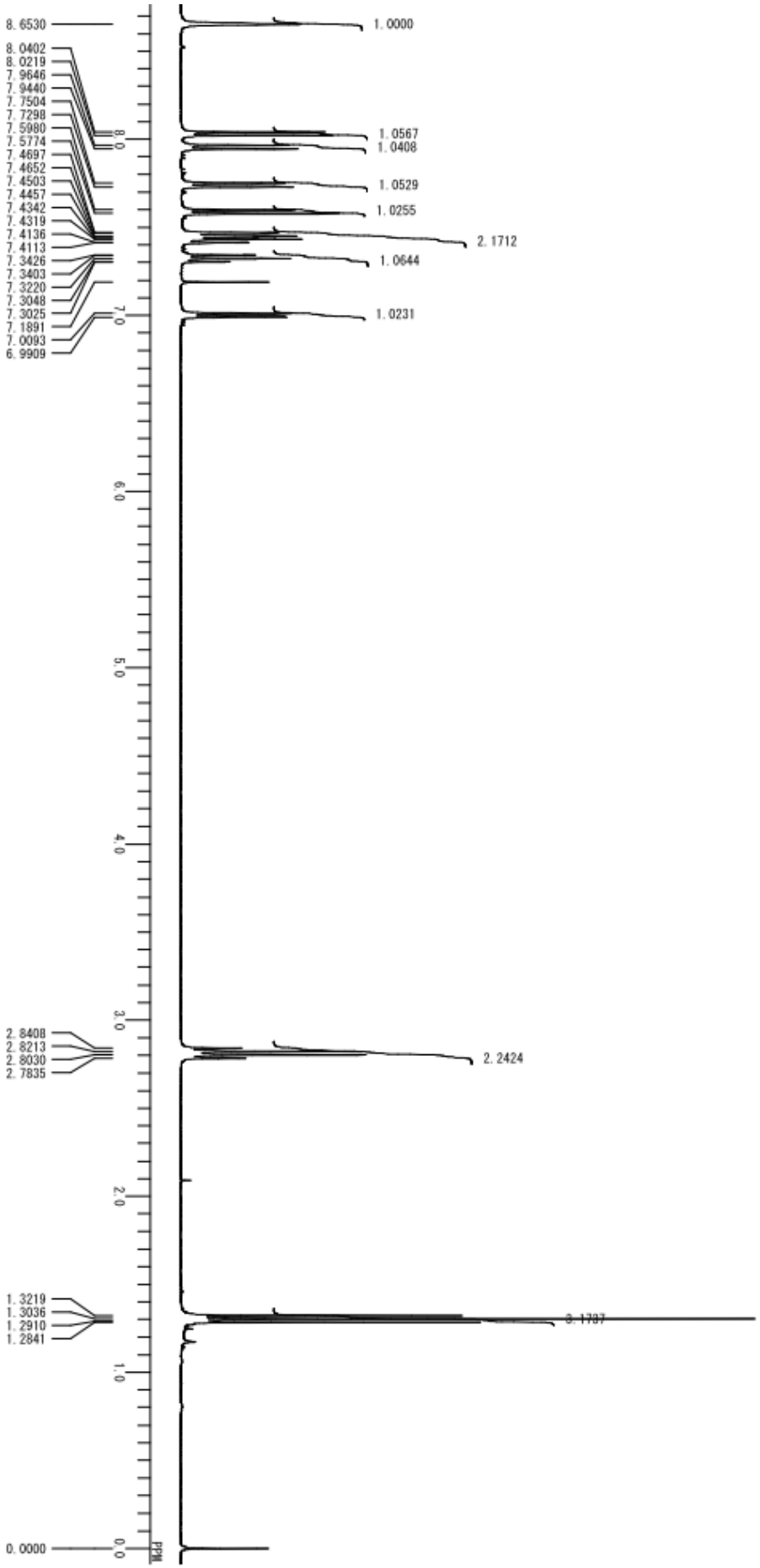
2d



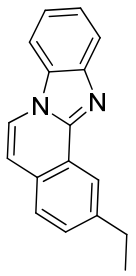


^{13}C -NMR (100 MHz, $CDCl_3$) 2d

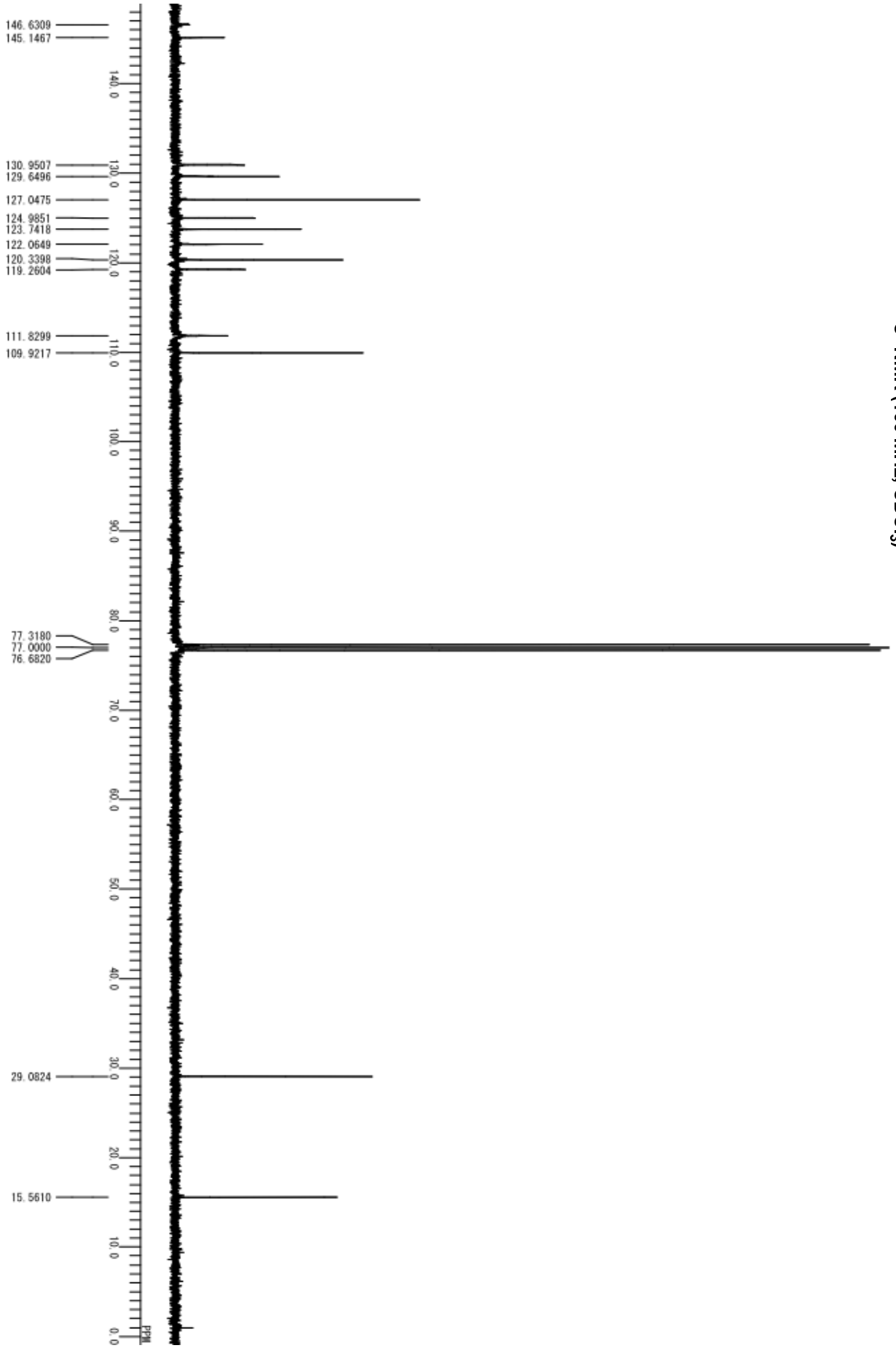




^{1}H-NMR (400 MHz, $CDCl_3$)

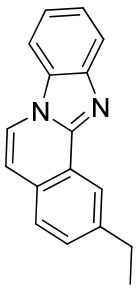


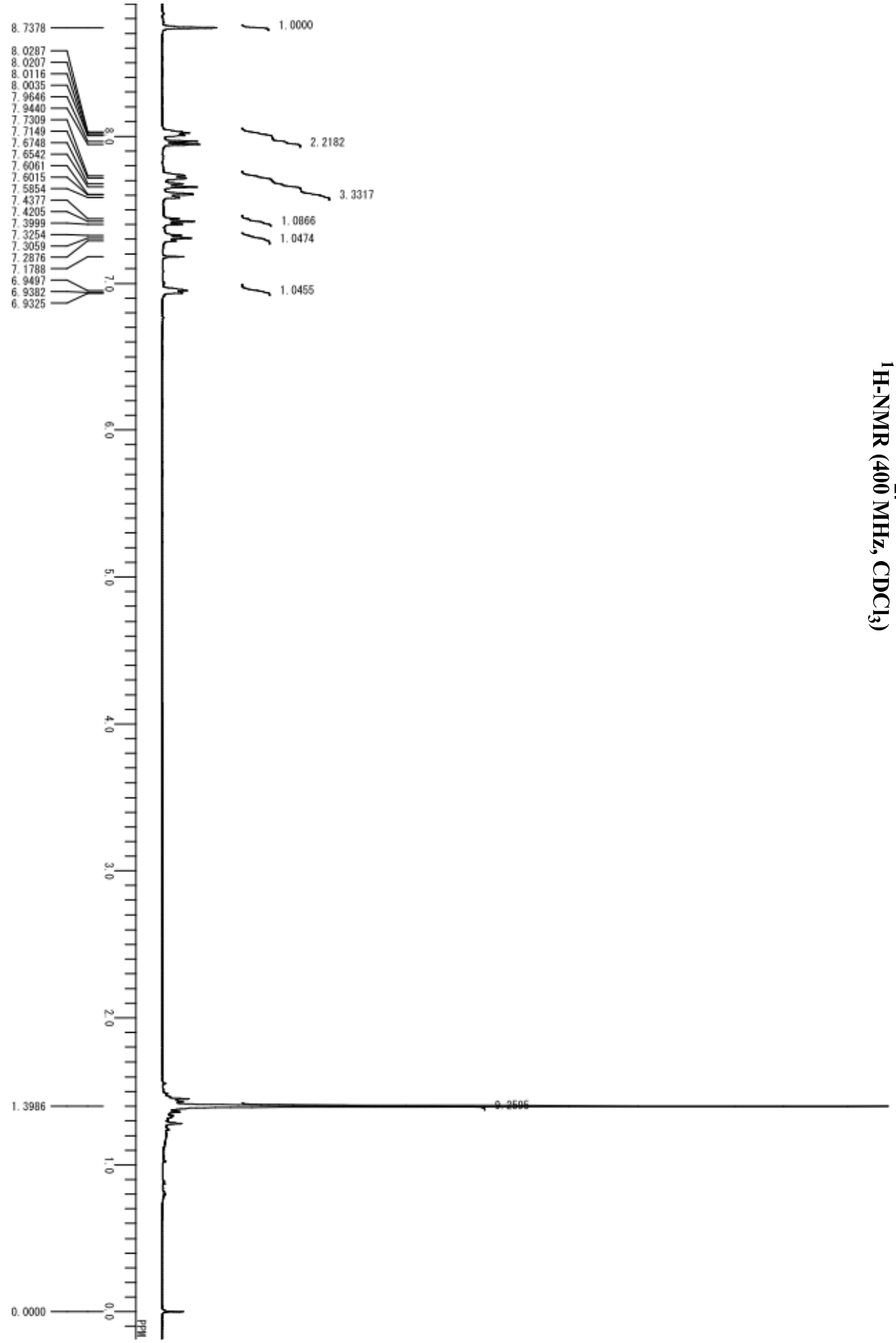
2e



^{13}C -NMR (100 MHz, $CDCl_3$)

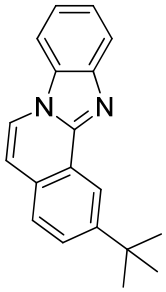
2e

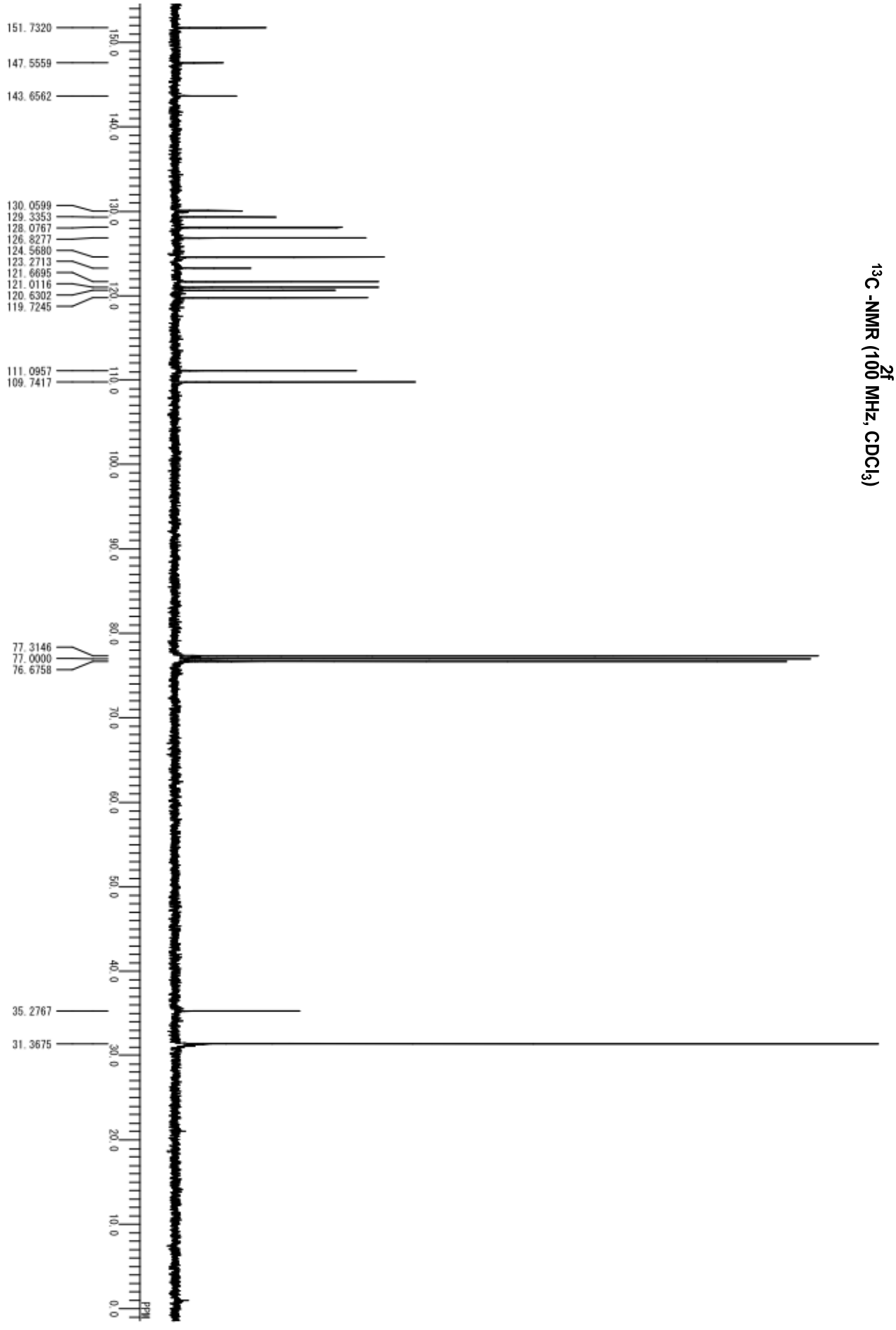




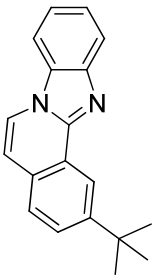
^{1}H-NMR (400 MHz, $CDCl_3$)

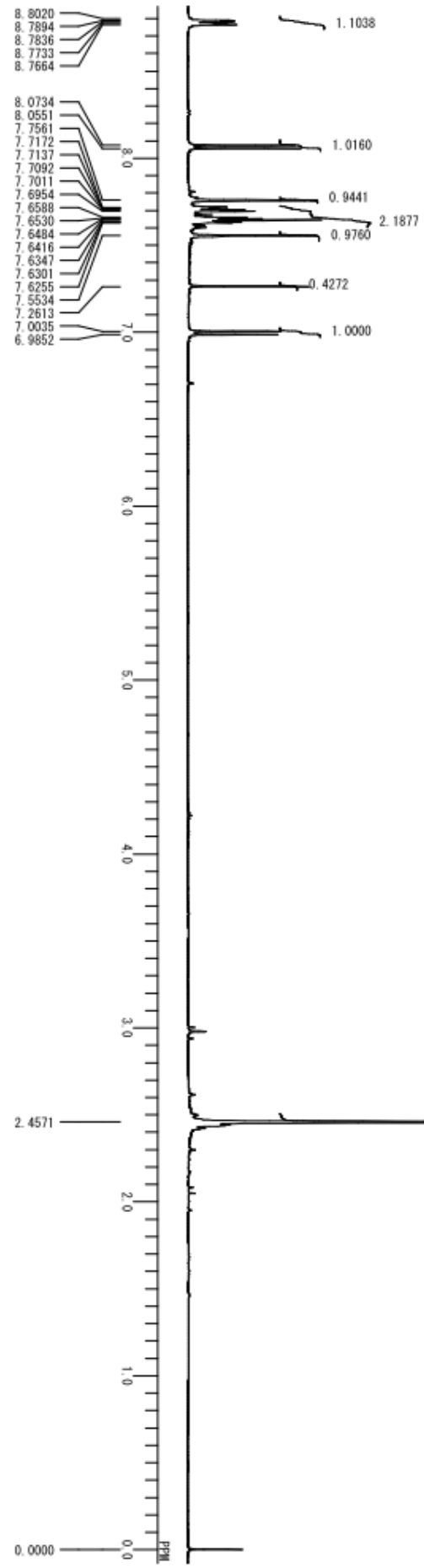
2f





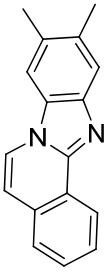
^{13}C -NMR (100 MHz, $CDCl_3$) **2f**

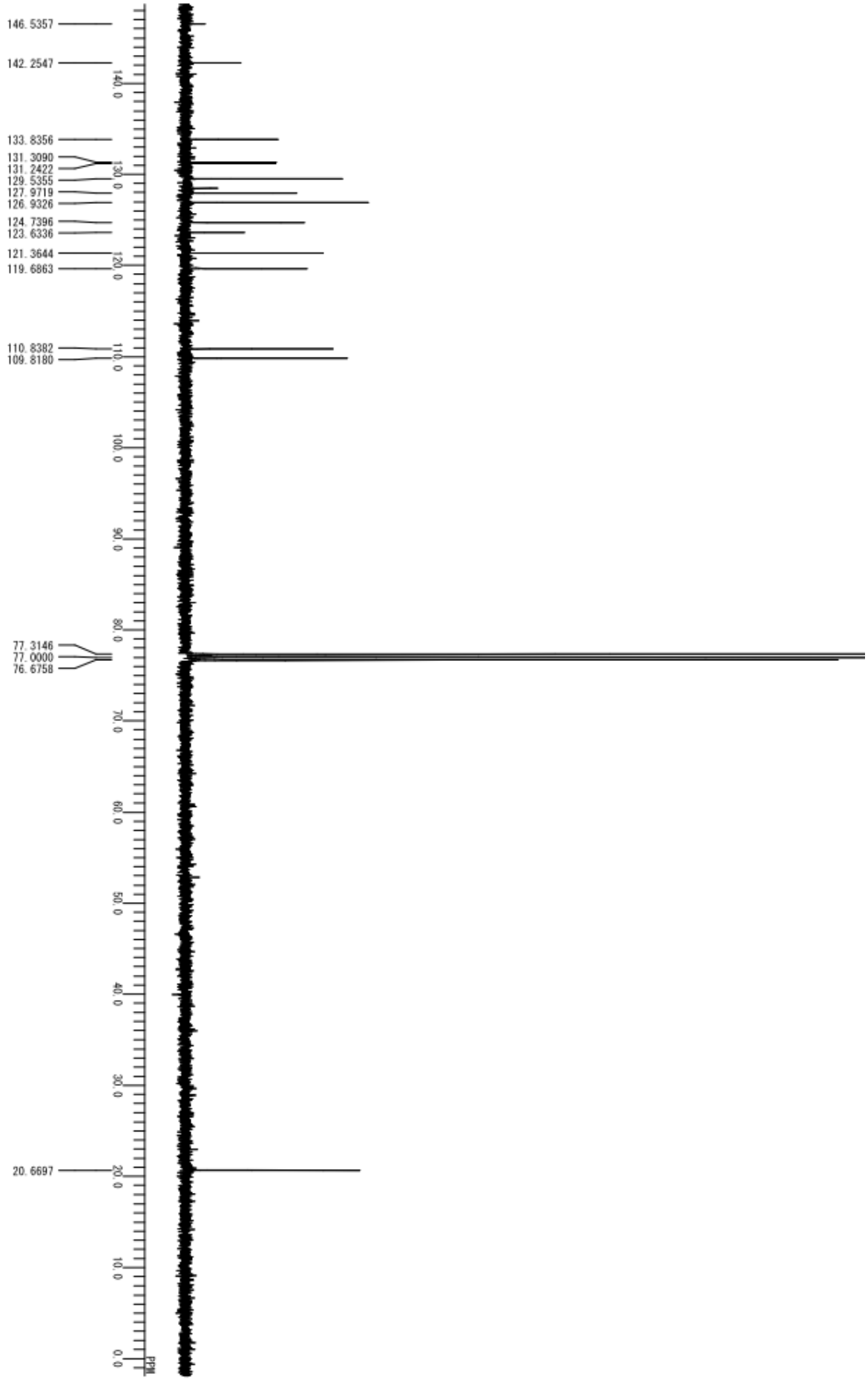




^{1}H-NMR (400 MHz, $CDCl_3$)

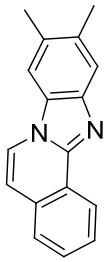
2g

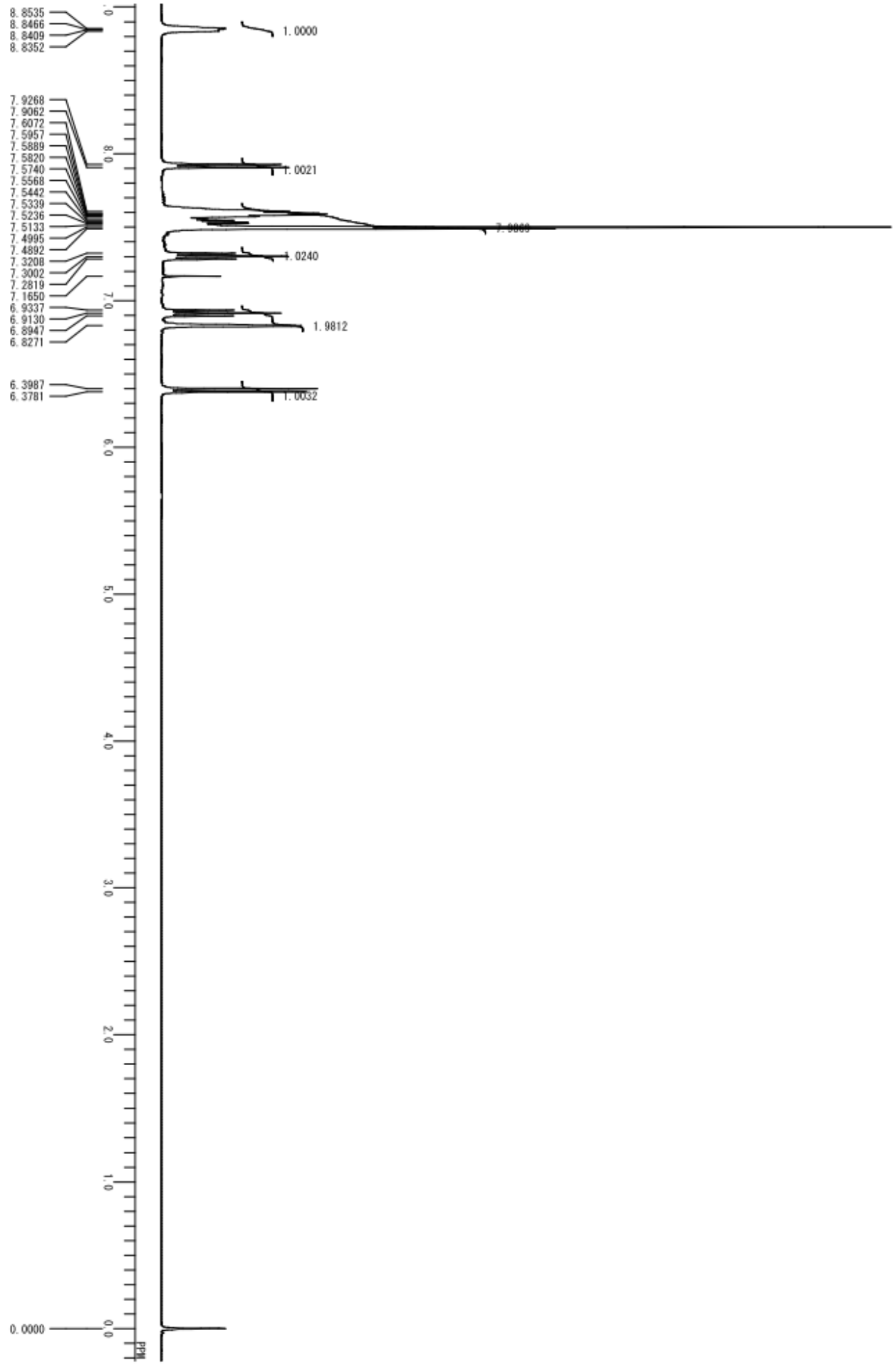




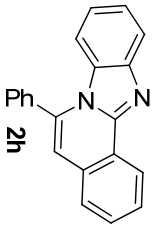
^{13}C -NMR (100 MHz, $CDCl_3$)

2g

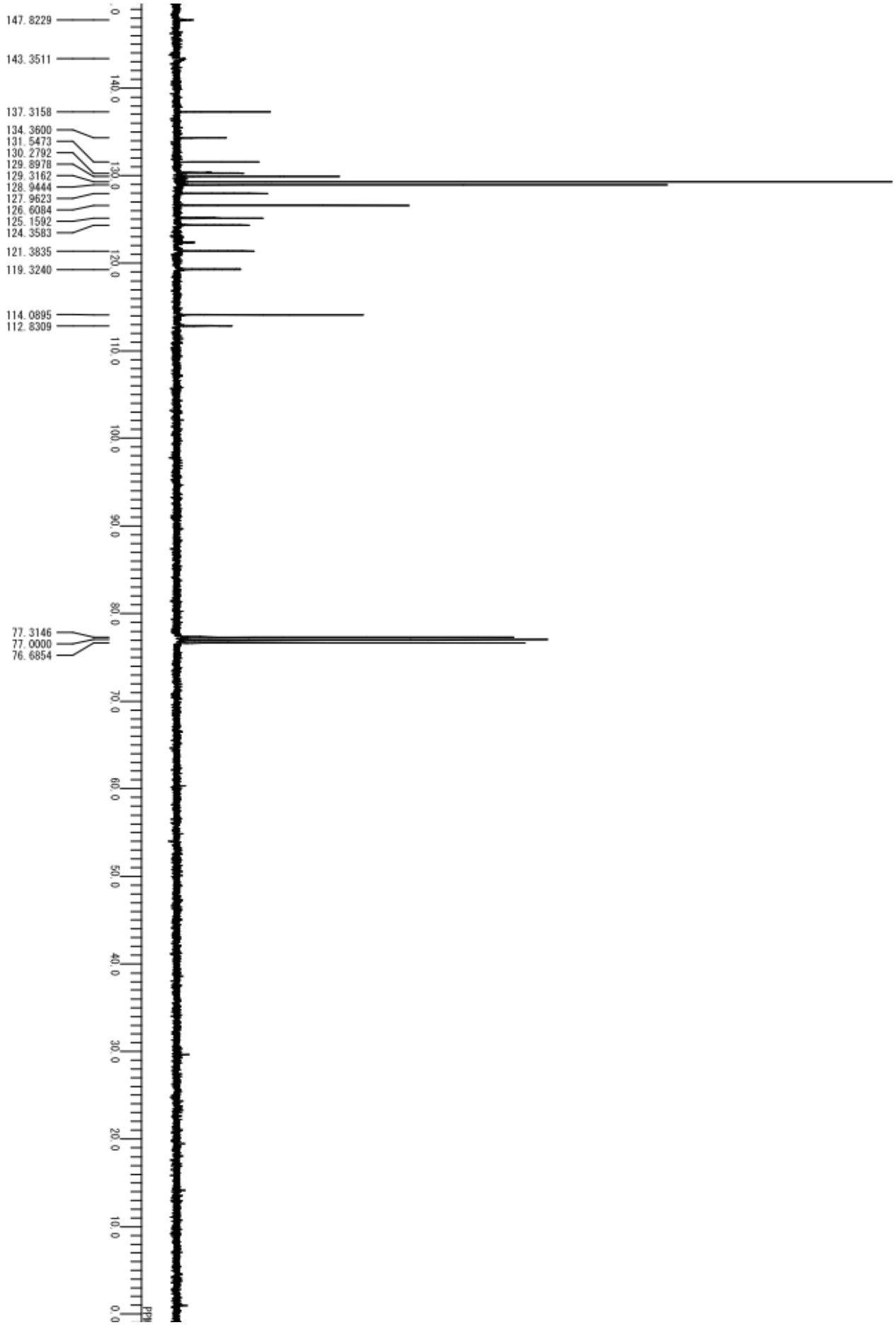




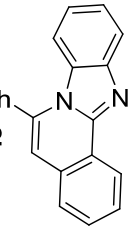
^{1}H-NMR (400 MHz, $CDCl_3$)



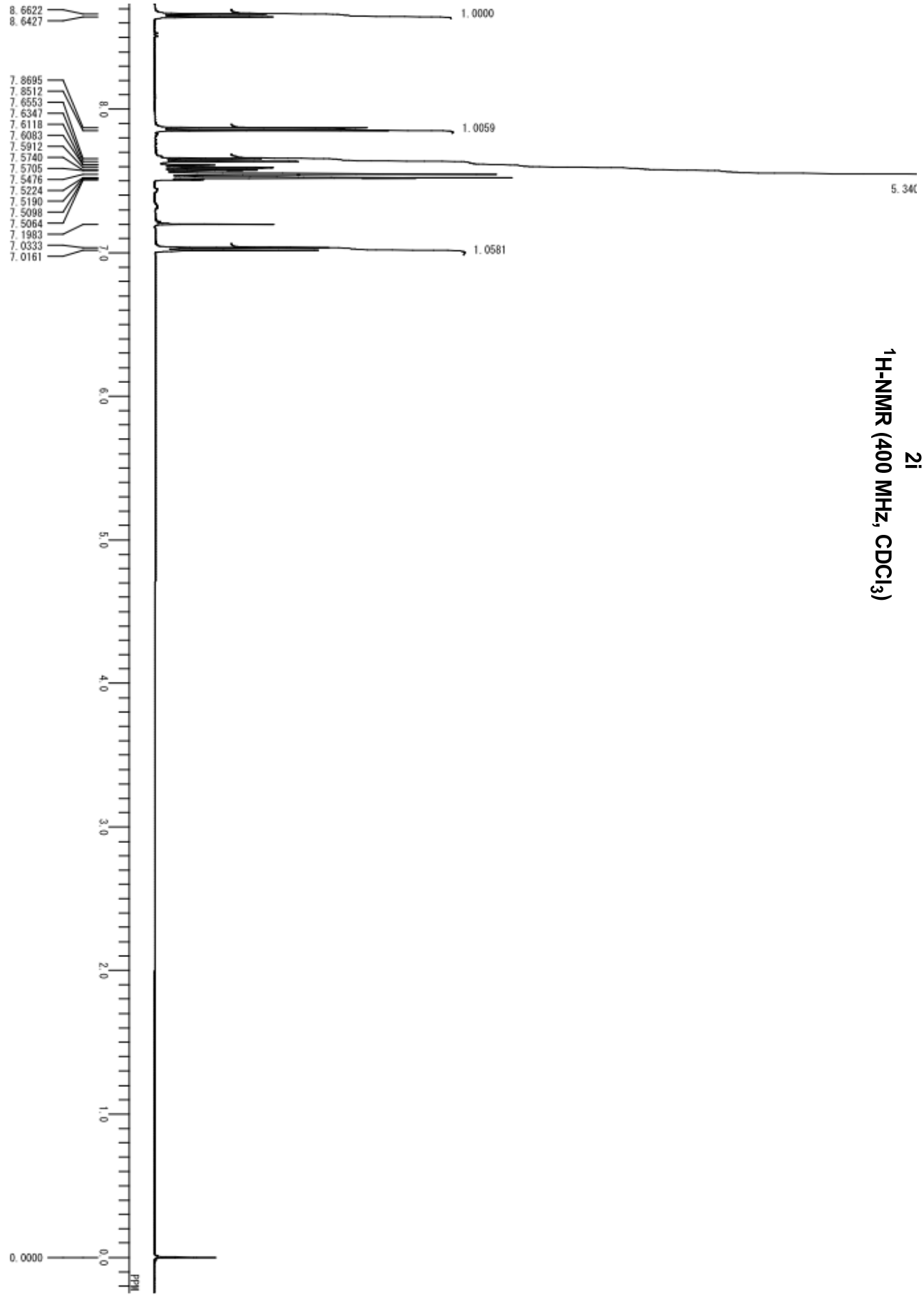
2h



^{13}C -NMR (100 MHz, $CDCl_3$)

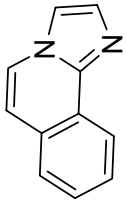


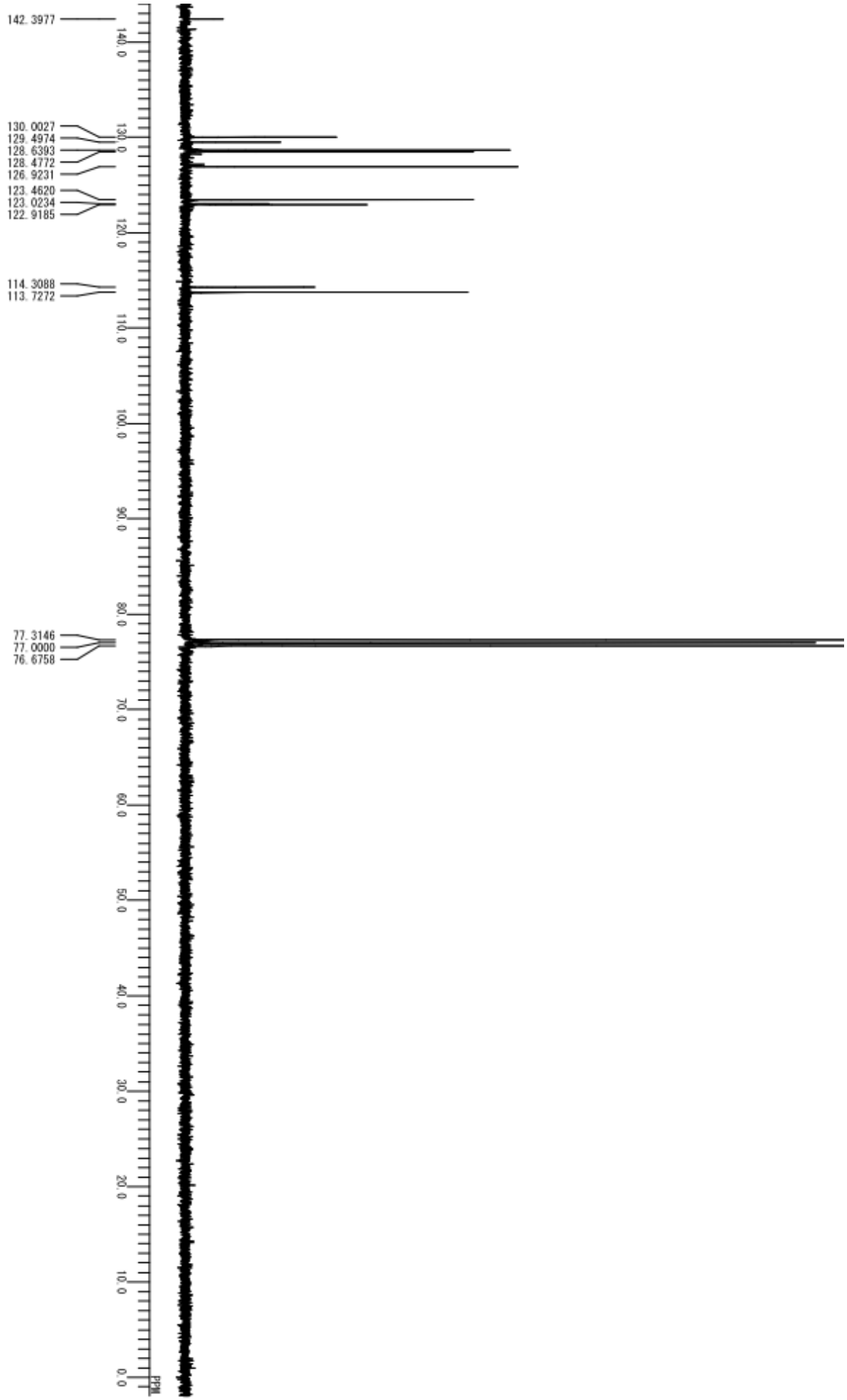
2h



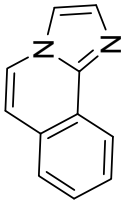
^{1}H-NMR (400 MHz, $CDCl_3$)

2i

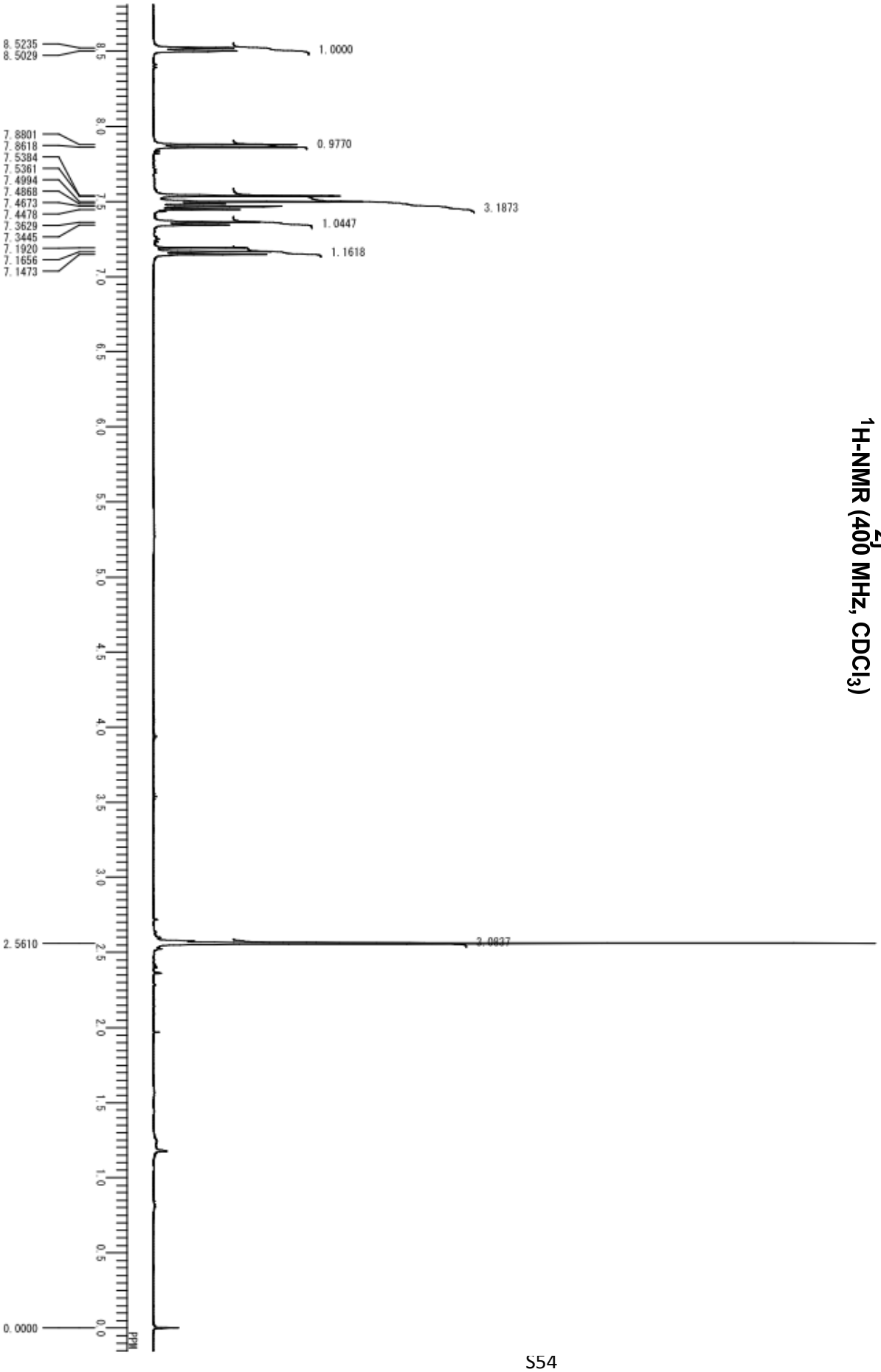




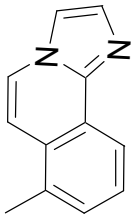
^{13}C-NMR (100 MHz, $CDCl_3$)

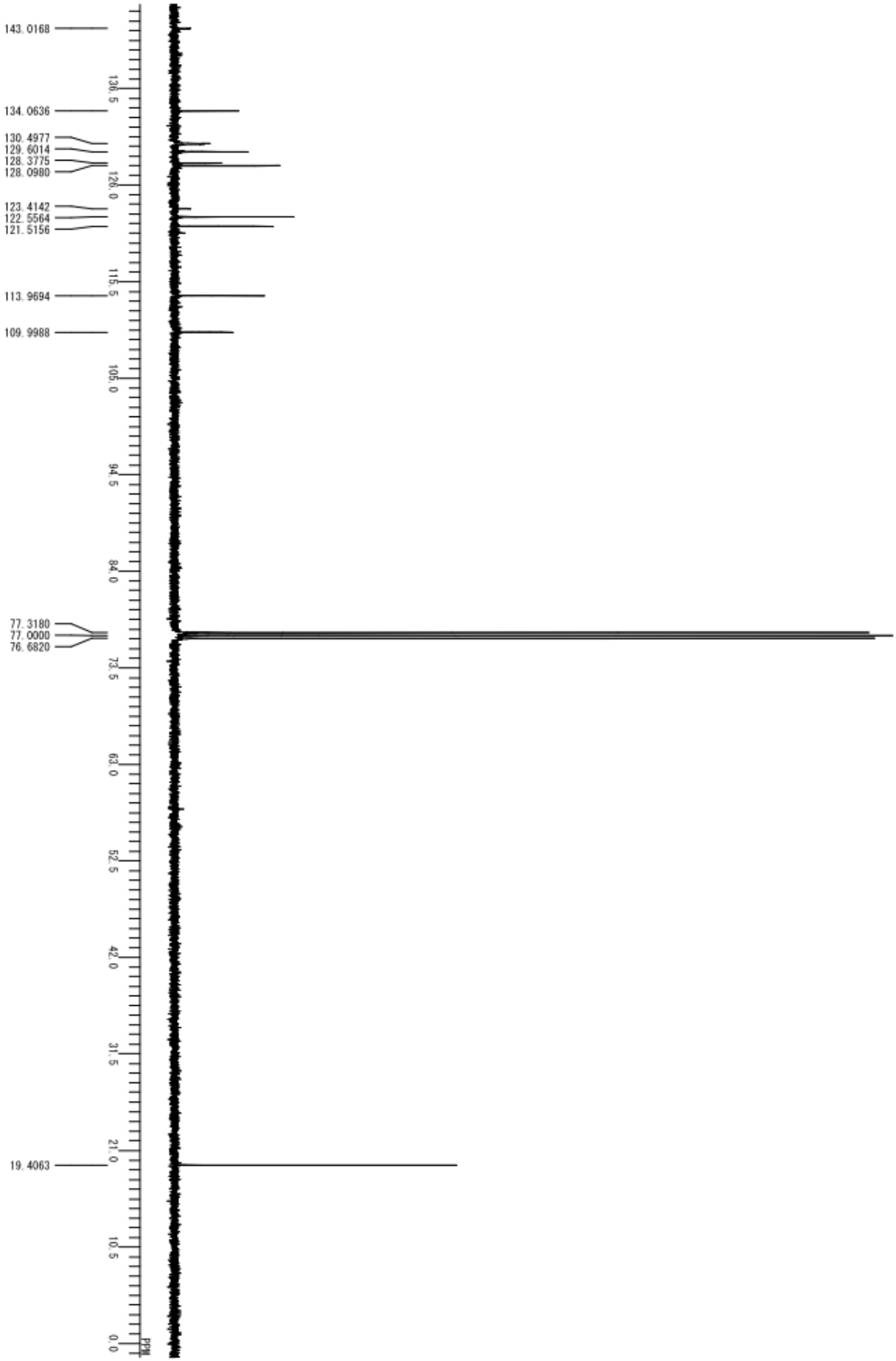


2i



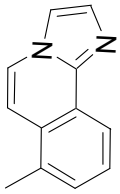
^{1}H-NMR (400 MHz, $CDCl_3$) 2i

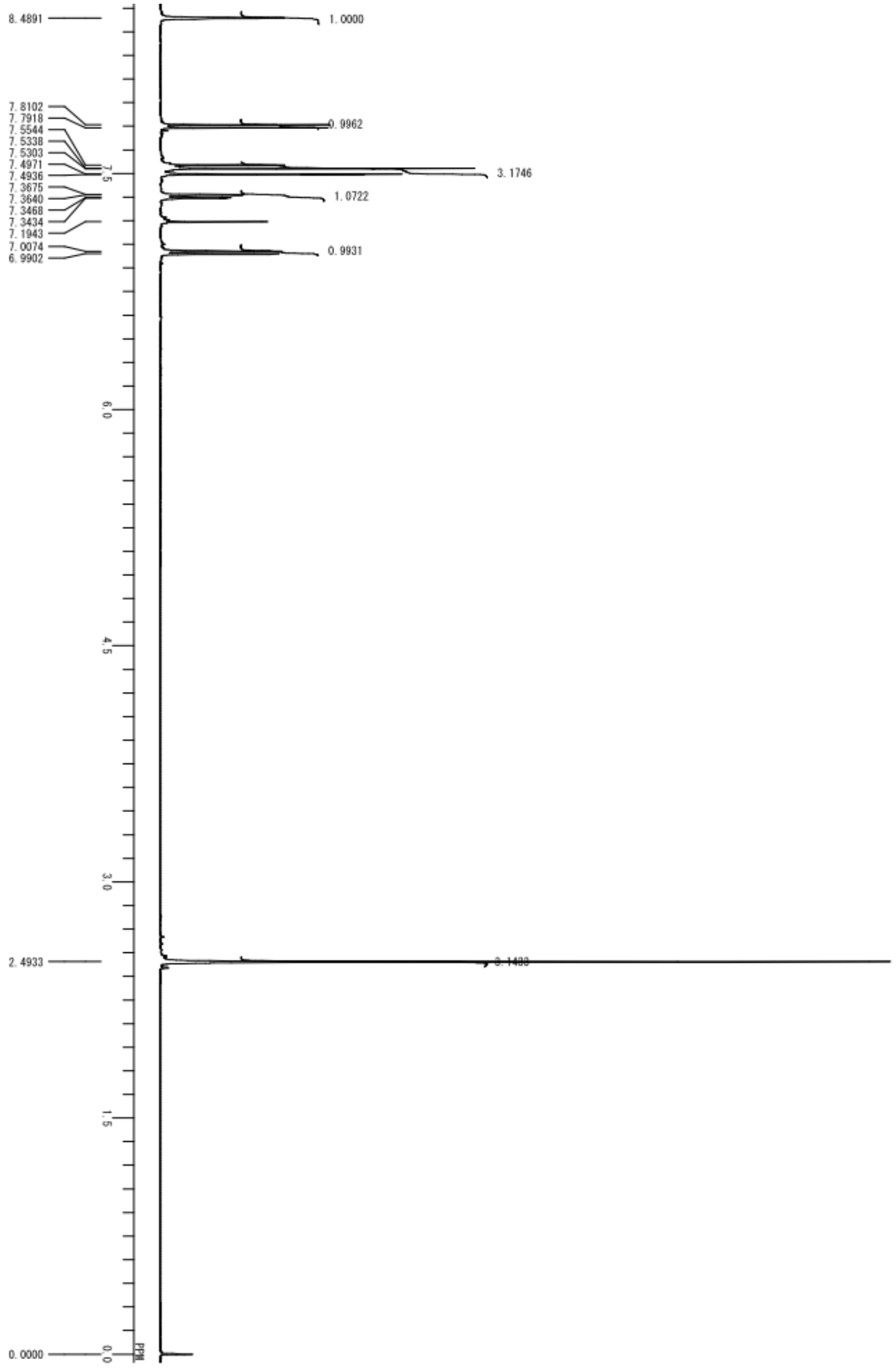




^{13}C-NMR (100 MHz, $CDCl_3$)

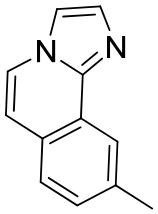
2j

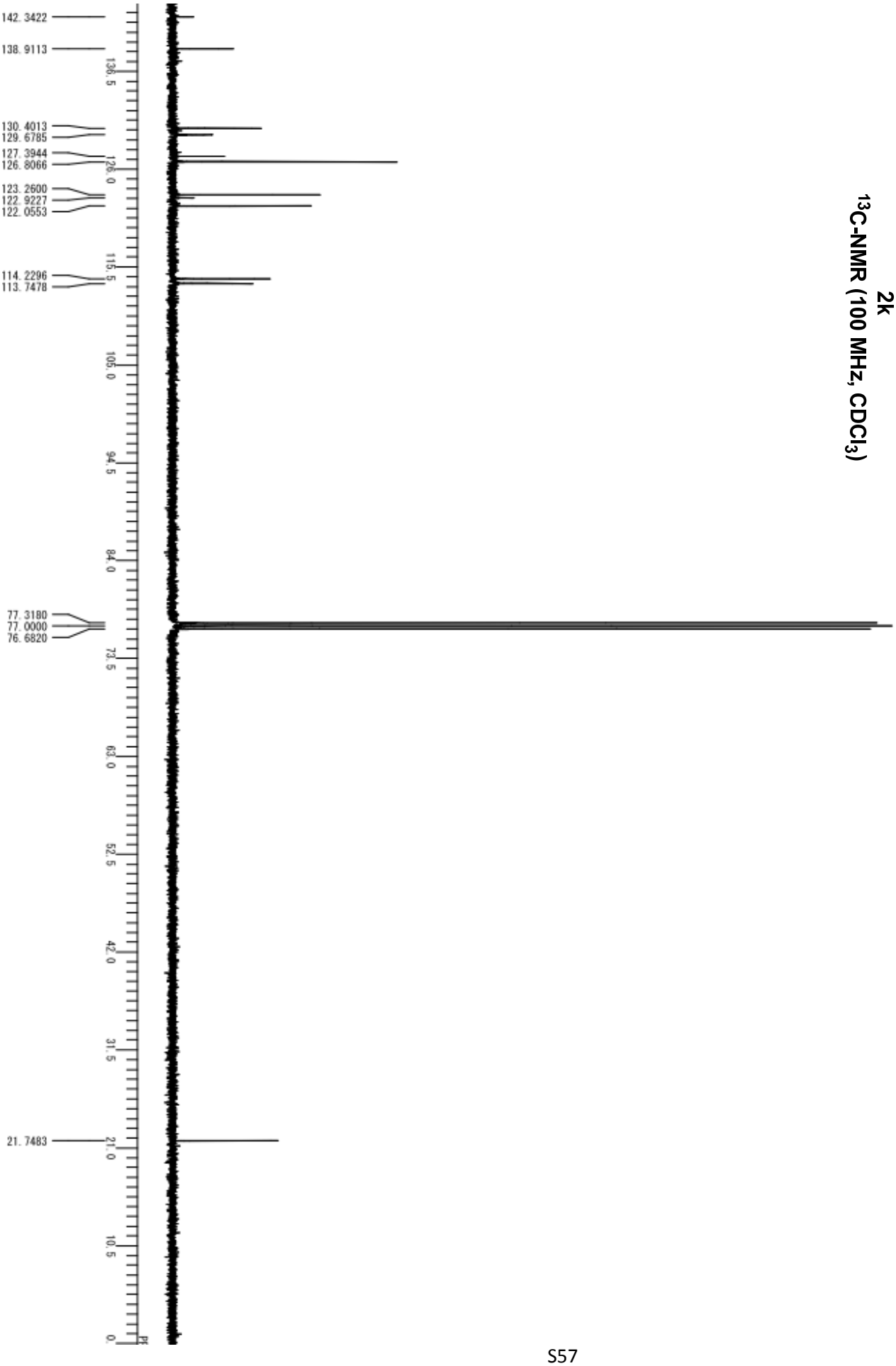




2k

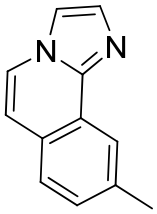
^{1}H-NMR (400 MHz, $CDCl_3$)

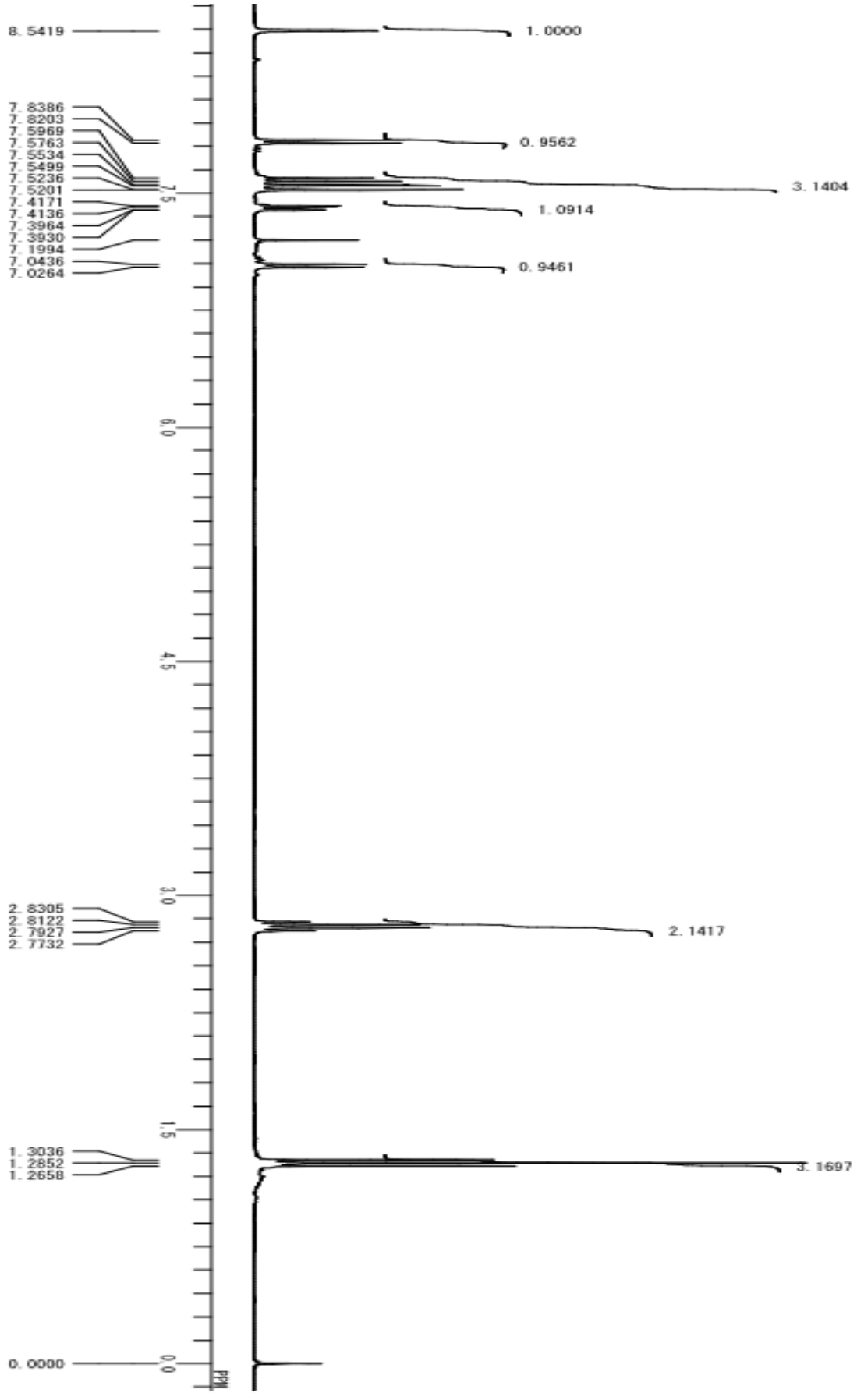




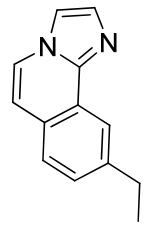
^{13}C-NMR (100 MHz, $CDCl_3$)

2k

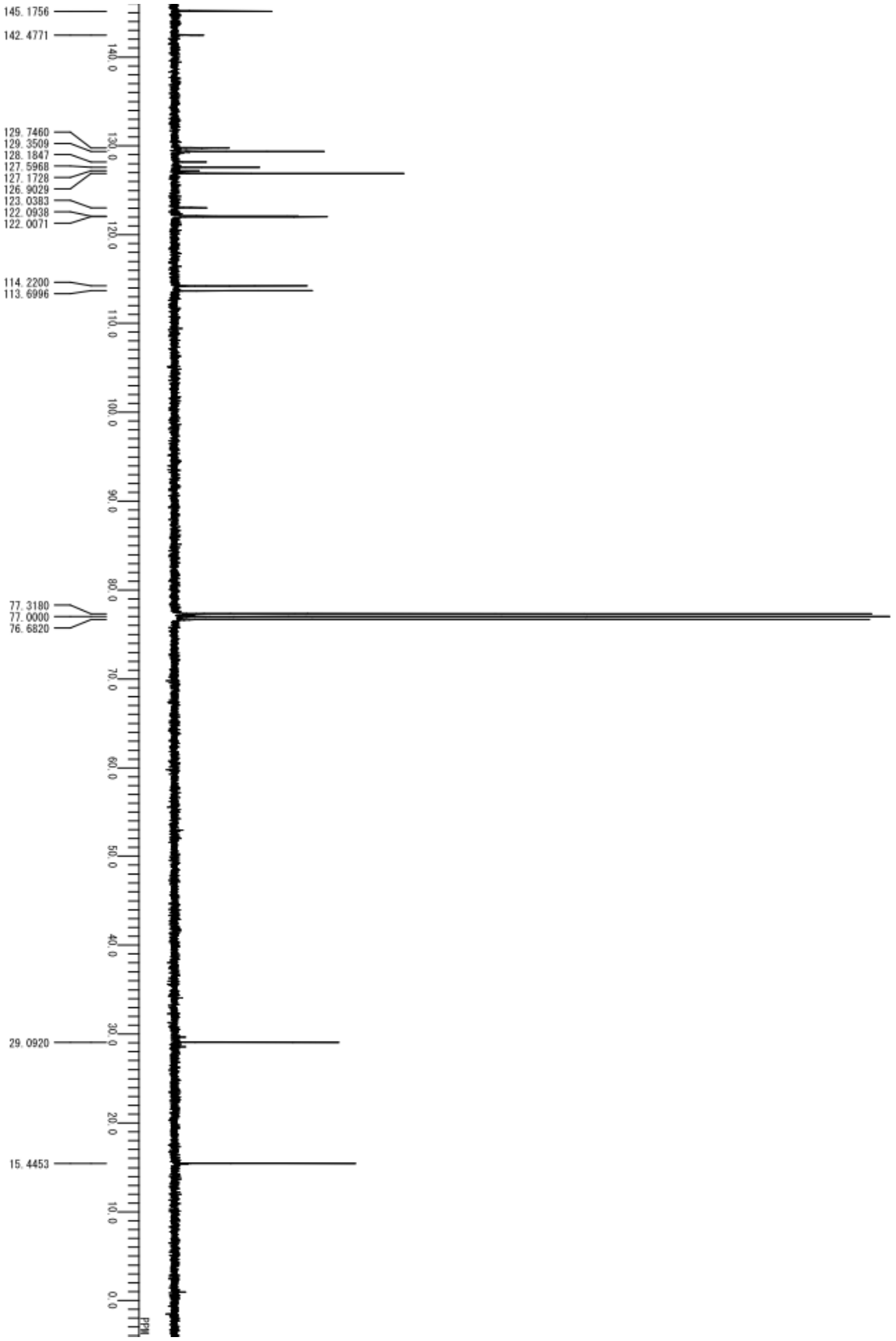




2l



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)

2l