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Chan-Lam *N*-arylation and C–H amination with heteroaromatic ring-NH: An approach to access extended-fused imidazo[1,2-*a*]-pyridines/pyrazines

Sankar Kumar Guchhait* and Meenu Saini

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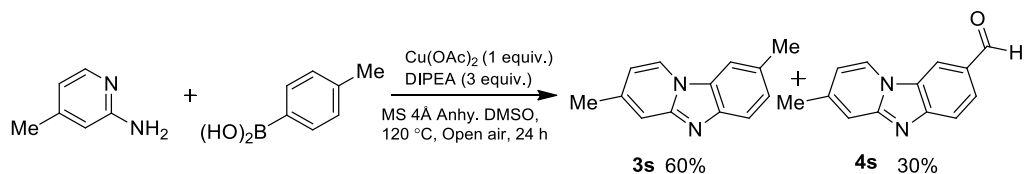
I. General information

All reactants and reagents were obtained from the commercial source and used without further purification. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance DPX 400 spectrometer in $\text{CDCl}_3/\text{DMSO}-d_6$ using TMS as an internal standard. J values are given in Hz. The IR spectra were recorded on a Nicolet FT-IR Impact 410 instrument. HRMS (ESI) were recorded with Bruker-Maxis mass spectrometers. The reactions were monitored by TLC (Merck®, Silica gel 60 F254, 0.25 mm). The products were purified by column chromatography silica gel 100-200 (Merck, silica gel 100-200 mesh, neutral, spherical) or neutral alumina column chromatography. Evaporation of solvents was performed at reduced pressure, using a Büchi rotary evaporator.

Representative experimental procedure for synthesis of 8-methylbenzo[4,5]imidazo[1,2-*a*]pyridine (**3a**, entry 1, Table 2):

A 25 mL dry two-necked round bottom flask equipped with a magnetic stirrer and guard tube containing calcium chloride was charged with 2-Aminopyridine (94mg, 1.0 mmol), *p*-Tolylboronic acid (270 mg, 2 mmols.), DIPEA (0.54 mL, 3mmols.) and $\text{Cu}(\text{OAc})_2$ (181 mg, 1 mmol) in anhydrous DMSO solution (3 mL) with molecular sieves (200 mg). The mixture was heated at 120 °C for 24 h. An aqueous solution of ammonium hydroxide was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with brine, and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate/Hexane (30%) as eluting solvent. It afforded the product **3a** (154 mg, 85% yield).

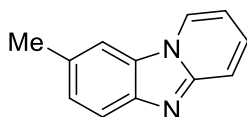
Products (Table 2, Products **3b-3v**) were also prepared following this representative procedure



Scheme S1: Formation of unexpected product 8-methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbaldehyde(4s)

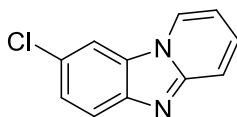
II. Spectral data of synthesized compounds

8-Methylbenzo[4,5]imidazo[1,2-*a*]pyridine(3a):



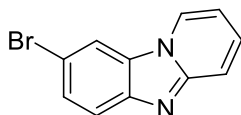
White solid; 154 mg, 85 %; m.p: 83-85 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.37 (d, $J = 6.8$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 7.67-7.65 (m, 2H), 7.39-7.35 (m, 2H), 6.80 (dd, $J = 6.7, 6.4$ Hz, 1H), 2.59 (s, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 148.2, 142.5, 131.1, 128.7, 127.4, 125.0, 119.4, 117.9, 110.11, 110.10, 21.9 ppm; HRMS (ESI) m/z : calcd. for $\text{C}_{12}\text{H}_{11}\text{N}_2$ $[\text{M}+\text{H}]^+$ 183.0922, found: 183.0916.

8-Chlorobenzo[4,5]imidazo[1,2-*a*]pyridine (3b):



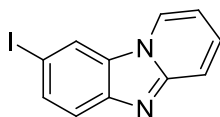
White solid; 132 mg, 70 %; m.p: 110-112 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.40 (d, $J = 6.8$ Hz, 1H), 7.92 (d, $J = 1.7$ Hz, 1H), 7.87 (d, $J = 8.7$ Hz, 1H), 7.71 (d, $J = 9.2$ Hz, 1H), 7.52-7.44 (m, 2H), 6.90 (dd, $J = 6.7, 6.7$ Hz, 1H) ppm; $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 149.1, 142.9, 129.7, 129.0, 126.6, 126.4, 125.0, 120.8, 118.2, 110.8, 110.5 ppm; HRMS (ESI) m/z : calcd. for $\text{C}_{11}\text{H}_8\text{ClN}_2$ $[\text{M}+\text{H}]^+$ 203.0376, found: 203.0378.

8-Bromobenzo[4,5]imidazo[1,2-a]pyridine (Product 3c):



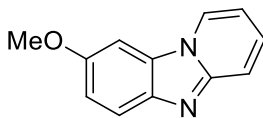
Pale Yellow solid; 166 mg, 68 %; m.p: 150-152 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 6.8 Hz, 1H), 8.04 (d, *J* = 1.7 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 9.2 Hz, 1H), 7.61 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.45 (ddd, *J* = 6.6, 6.6, 1.2 Hz, 1H), 6.87 (ddd, *J* = 6.8, 6.8, 0.8 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.9, 143.3, 129.8, 129.5, 129.0, 125.0, 121.2, 118.2, 113.7, 113.5, 110.8 ppm; HRMS (ESI) *m/z*: calcd. for C₁₁H₈Br⁷⁹N₂ [M+H]⁺ 246.9871, found: 246.9869.

8-Iodobenzo[4,5]imidazo[1,2-a]pyridine(3d):



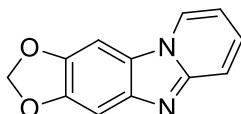
White solid; 154 mg, 78 %; m.p: 181-183 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.41 (d, *J* = 6.8 Hz, 1H), 8.27 (d, *J* = 1.3 Hz, 1H), 7.80 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.72 (m, 2H), 7.48 (ddd, *J* = 8.0, 7.8, 1.1 Hz, 1H), 6.90 (dd, *J* = 6.8, 6.7 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.6, 143.8, 134.5, 130.2, 129.9, 125.1, 121.6, 119.6, 118.1, 110.9, 83.3 ppm; MS (ESI) *m/z*: calcd. for C₁₁H₈I⁷⁹N₂ [M+H]⁺ 295.09, found: 295.16.

8-Methoxybenzo[4,5]imidazo[1,2-a]pyridine (3e):



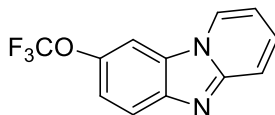
Dark brown solid; 130mg, 66 %; m.p: 155-156 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.34 (d, *J* = 6.8 Hz, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.66 (d, *J* = 9.2 Hz, 1H), 7.34 (dd, *J* = 7.7, 7.6 Hz, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.81 (dd, *J* = 6.7, 6.6 Hz, 1H), 3.94 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 155.4, 148.0, 138.9, 128.7, 128.1, 124.7, 120.5, 118.1, 115.9, 110.1, 93.2, 58.0 ppm; HRMS (ESI) *m/z*: calcd. for C₁₂H₁₀N₂O[M+H]⁺ 199.0871, found: 199.0864.

[1,3]Dioxolo[4'',5'':4',5']benzo[1',2':4,5]imidazo[1,2-*a*]pyridine(3f):



Off white solid; 161 mg, 76 %; m.p: >200 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 6.8 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.33-7.28 (m, 3H), 6.83 (dd, *J* = 6.7, 6.7 Hz, 1H), 6.08 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.9, 147.5, 144.2, 140.0, 127.0, 124.1, 122.7, 117.6, 110.4, 101.5, 98.8, 90.4 ppm. HRMS (ESI) *m/z*: calcd. for C₁₂H₈N₂O₂[M+H]⁺ 213.0664, found: 213.0664.

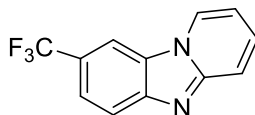
8-(Trifluoromethoxy)benzo[4,5]imidazo[1,2-*a*]pyridine (3g):



White solid; 163 mg, 65%; m.p: 110-112 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.43 (d, *J* = 7.0 Hz, 1H), 7.94 (d, *J* = 8.9 Hz, 1H), 7.80 (s, 1H), 7.73 (d, *J* = 9.2 Hz, 1H), 7.50-7.43 (m, 2H), 6.92 (dd, *J* = 6.7, 6.7 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 149.9, 143.3, 142.9, 129.8,

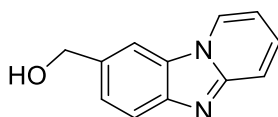
128.2, 125.1, 120.71(q, $J = 256$ Hz), 120.70, 119.9, 118.3, 110.8, 103.9 ppm; HRMS (ESI) m/z : calcd. for $C_{12}H_8F_3N_2O$ $[M+H]^+$ 253.0588, found: 253.0574.

8-(Trifluoromethyl)benzo[4,5]imidazo[1,2-*a*]pyridine(3h):



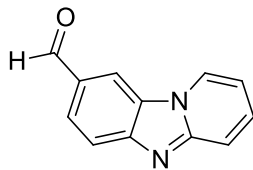
Pale Yellow solid; 169 mg, 72 %; m.p.: 90-91 °C; 1H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, $J = 6.8$ Hz, 1H), 8.22 (s, 1H), 8.03 (d, $J = 8.6$ Hz, 1H), 7.79 (dd, $J = 9.0, 7.7$ Hz, 2H), 7.55 (ddd, $J = 6.7, 6.6, 1.1$ Hz, 1H), 6.98 (dd, $J = 6.8, 6.7$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 150.3, 146.5, 130.7, 128.0, 125.3, 124.7(q, $J = 270$ Hz) 123.1, 122.7, 122.4 (q, $J = 3$ Hz), 120.3, 118.3, 111.2, 108.5(q, $J = 5$ Hz); HRMS (ESI) m/z : calcd. for $C_{11}H_7F_3N_2$ $[M+H]^+$ 237.0639, found: 237.0641.

Benzo[4,5]imidazo[1,2-*a*]pyridin-8-ylmethanol (3i):



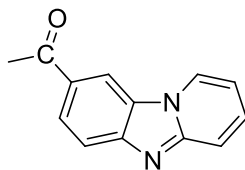
White solid; 114 mg, 58 %; m.p.: >200 °C; 1H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, $J = 6.8$ Hz, 1H), 7.94 (s, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 9.2$ Hz, 1H), 7.50 (dd, $J = 8.4, 1.1$ Hz, 1H), 7.44 (ddd, $J = 6.6, 6.6, 1.1$ Hz, 1H), 6.87 (dd, $J = 6.7, 6.1$ Hz, 1H), 4.94 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 144.0, 138.4, 134.3, 129.4, 125.1, 119.8, 118.0, 110.4, 108.9, 65.5 ppm. HRMS (ESI) m/z : calcd. for $C_{12}H_{10}N_2O$ $[M+H]^+$ 199.0871, found: 199.0860.

Benzo[4,5]imidazo[1,2-*a*]pyridine-8-carbaldehyde (3j):



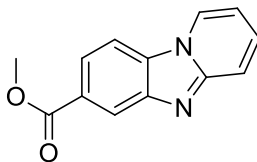
White solid; 82 mg, 42 %; m.p: >200 °C; ¹H NMR (400 MHz, CDCl₃): δ 10.13 (s, 1H), 8.58 (d, *J* = 6.7 Hz, 1H), 8.47 (s, 1H), 8.04 ((dd, *J* = 8.4, 1.0 Hz, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 9.2 Hz, 1H), 7.58 (dd, *J* = 8.6, 7.2 Hz, 1H), 7.00 (dd, *J* = 6.7, 6.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 191.2, 151.2, 149.0, 131.6, 129.6, 129.0, 127.5, 125.8, 120.0, 118.3, 112.7, 111.7 ppm; HRMS (ESI) *m/z*: calcd. for C₁₂H₈N₂O[M+H]⁺ 197.0715, found: 197.0707.

1-(Benzo[4,5]imidazo[1,2-*a*]pyridin-8-yl)ethanone(3k):



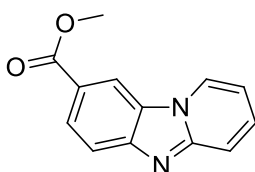
White solid; 105 mg, 50 %; m.p: >200 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.57 (s, 1H), 8.54 (d, *J* = 6.7 Hz, 1H), 8.11 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.89 (d, *J* = 8.6, 1H), 7.71 (d, *J* = 9.2 Hz, 1H), 7.52 (dd, *J* = 8.2, 7.5 Hz, 1H), 6.94 (dd, *J* = 6.7, 6.7 Hz, 1H), 2.72 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 197.2, 150.8, 147.8, 131.2, 130.0, 128.7, 126.3, 125.7, 119.2, 118.1, 111.4, 111.3, 26.8 ppm; HRMS (ESI) *m/z*: calcd. for C₁₃H₁₀N₂O[M+H]⁺ 211.0871, found: 211.0871.

Methyl benzo[4,5]imidazo[1,2-*a*]pyridine-7-carboxylate (3l):



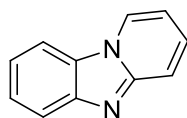
White solid; 124 mg, 55 %; m.p: >200 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.67 (s, 1H), 8.48 (d, *J* = 6.7 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.5, 1H), 7.75 (d, *J* = 9.2, 1H), 7.49 (dd, *J* = 8.4, 6.8 Hz 1H), 6.92 (dd, *J* = 6.7, 6.7, 1H), 4.01 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 167.3, 149.8, 144.0, 131.6, 130.1, 127.6, 125.3, 122.3, 122.1, 118.4, 111.0, 110.3, 52.3 ppm; HRMS (ESI) *m/z*: calcd. for C₁₃H₁₀N₂O₂[M+H]⁺ C 227.0820, found: 227.0814.

Methyl benzo[4,5]imidazo[1,2-*a*]pyridine-8-carboxylate (3m):



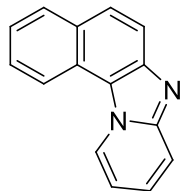
White solid; 135 mg, 60 %; m.p: 179-181 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.71 (s, 1H), 8.59 (d, *J* = 6.7 Hz, 1H), 8.25 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.6, 1H), 7.77 (d, *J* = 9.1, 1H), 7.56 (dd, *J* = 8.8, 7.0 Hz, 1H), 6.98 (dd, *J* = 6.7, 6.7, 1H), 4.01 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 167.2, 150.5, 147.8, 130.9, 128.4, 126.8, 125.6, 122.5, 119.3, 118.2, 113.1, 111.2, 52.2 ppm; HRMS (ESI) *m/z*: calcd. for C₁₃H₁₀N₂O₂[M+H]⁺ 227.0820, found: 227.0817.

Benzo[4,5]imidazo[1,2-*a*]pyridine(3n):



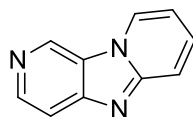
White solid; 134 mg, 80 %; m.p: 181-182 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.44 (d, *J* = 6.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 9.1, 1H), 7.54 (dd, *J* = 7.7, 7.6, 1H), 7.44-7.36 (m, 2H), 6.84 (dd, *J* = 6.7, 6.6, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.5, 144.5, 129.3, 128.6, 125.6, 125.2, 121.0, 119.9, 118.0, 110.4, 110.3 ppm; HRMS (ESI) *m/z*: calcd. for C₁₁H₈N₂[M+H]⁺ 169.0765, found: 169.0761.

Naphtho[2',3':4,5]imidazo[1,2-*a*]pyridine(3o):



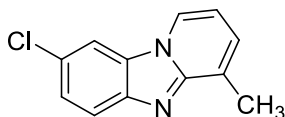
White solid; 122 mg, 56 %; m.p: 160-162 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.15 (d, *J* = 6.9 Hz, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.10 (d, *J* = 8.0 Hz 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 7.94-7.89 (m, 2H), 7.75 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.57 (dd, *J* = 7.5, 7.4, 1H), 7.48 (dd, *J*= 8.4, 7.2, 1H) 7.07 (dd, *J*= 6.7, 6.7, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 147.7, 143.1, 130.3, 130.0, 127.7, 127.0, 126.94, 126.91, 124.0, 122.9, 121.5, 120.1, 119.1, 118.3, 111.9 ppm; HRMS (ESI) *m/z*: calcd. for C₁₅H₁₀N₂ [M+H]⁺ 219.0922, found: 219.0911.

Imidazo[1,2-*a*:5,4-*c'*]dipyridine (3p):



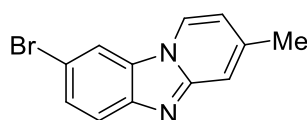
White solid; 98 mg, 58 %; m.p: 135-137 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.63 (s, 1H), 9.28 (d, *J* = 6.7 Hz, 1H), 8.53 (d, *J* = 4.1 Hz, 1H), 7.79-7.72 (m, 3H), 7.16 (dd, *J* = 5.8, 6.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, *d*₆-DMSO): δ 150.1, 148.7, 144.4, 136.2, 133.3, 128.6, 127.5, 117.4, 113.8, 112.2 ppm; HRMS (ESI) *m/z*: calcd. for C₁₀H₇N₃ [M+H]⁺ 170.0718, found: 170.0719.

8-Chloro-4-methylbenzo[4,5]imidazo[1,2-*a*]pyridine(3q):



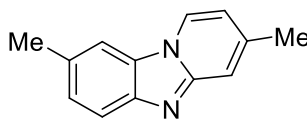
White solid; 118 mg, 55 %; m.p: 131-132 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.26 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.49 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.25 (d, *J* = 6.7 Hz, 1H), 6.81 (dd, *J* = 6.8, 6.8 Hz, 1H), 2.70 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 149.7, 142.6, 129.5, 128.09, 128.02, 126.5, 126.2, 122.7, 120.8, 110.9, 110.7, 17.5 ppm; HRMS (ESI) *m/z*: calcd. for C₁₂H₉CIN₂ [M+H]⁺ 217.0532, found: 217.0524.

8-Bromo-4-methylbenzo[4,5]imidazo[1,2-*a*]pyridine(3r):



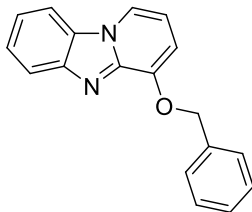
White solid; 135 mg, 52 %; m.p: >200 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, *J* = 7.0 Hz, 1H), 7.98 (d, *J* = 1.6 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.42 (s, 1H), 6.70 (d, *J* = 6.9 Hz, 1H), 2.47 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 149.5, 143.3, 141.4, 129.5, 128.6, 124.1, 120.8, 116.1, 113.7, 113.3, 113.2, 21.9 ppm; HRMS (ESI) *m/z*: calcd. for C₁₂H₁₀Br⁷⁹N₂ [M+H]⁺ 261.0027, found: 261.0020.

3,8-Dimethylbenzo[4,5]imidazo[1,2-*a*]pyridine(3s):



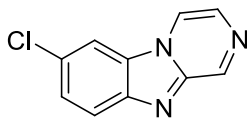
White solid; 177 mg, 60 %; m.p: 134-135 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, *J* = 7.0 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 1H), 7.65 (s, 1H), 7.42 (s, 1H), 7.34 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.66 (dd, *J* = 7.0, 1.2 Hz, 1H), 2.59 (s, 3H), 2.47 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.3, 142.7, 140.2, 130.6, 128.7, 127.1, 124.0, 119.1, 115.9, 112.9, 109.9, 21.87, 21.82 ppm; HRMS (ESI) *m/z*: calcd. for C₁₃H₁₂N₂ [M+H]⁺ 197.1078, found: 197.1069.

2-(Benzyloxy)benzo[4,5]imidazo[1,2-*a*]pyridine (3t):



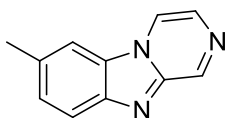
Black solid; 137 mg, 50 %; m.p: 97-99 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.07 (m, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.55-7.51 (m, 3H), 7.41-7.34 (m, 4H), 6.72-6.69 (m, 2H), 5.41 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 148.0, 144.0, 143.6, 135.9, 129.3, 128.6, 128.1, 127.5, 125.4, 121.3, 120.5, 117.8, 110.5, 110.0, 106.2, 70.9 ppm; HRMS (ESI) *m/z*: calcd. for C₁₈H₁₄N₂O[M+H]⁺ 275.1184, found: 275.1186.

7-Chlorobenzo[4,5]imidazo[1,2-*a*]pyrazine (3u):



White solid; 107 mg, 53 %; m.p: 142-143 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.30 (s, 1H), 8.28 (dd, *J* = 4.6, 1.4 Hz, 1H), 8.01-7.98 (m, 3H), 7.60 (dd, *J* = 9.0, 1.7 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 146.0, 142.77, 142.70, 129.1, 128.19, 128.11, 127.6, 122.5, 117.6, 111.2 ppm; HRMS (ESI) *m/z*: calcd. for C₁₀H₆ClN₃ [M+H]⁺ 204.0328, found: 204.0328.

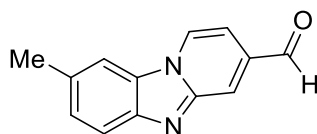
7-Methylbenzo[4,5]imidazo[1,2-*a*]pyrazine (3v):



White solid; 78 mg, 43 %; m.p: 163-164 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.25 (s, 1H), 9.05 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.22 (s, 1H), 8.00 (d, *J* = 4.6 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.48 (dd, *J* = 8.5, 1.2 Hz, 1H), 2.57 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 145.6, 142.7, 141.9, 133.7, 129.2, 127.8, 126.9, 120.8, 117.7, 110.6, 21.9 ppm; HRMS (ESI) *m/z*: calcd. for C₁₁H₉N₃ [M+H]⁺ 184.0875, found: 184.0877.

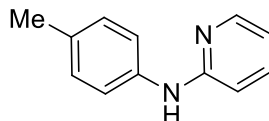
III. Spectral data of intermediates and side product and intermediates

8-Methylbenzo[4,5]imidazo[1,2-*a*]pyridine-3-carbaldehyde(4s):



Yellow solid; 63 mg, 30 %; m.p: 114-115 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 10.09 (s, 1H), 9.12-9.09 (m, 1H), 8.40(s, 1H), 8.18 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 2.56 (s, 3H) ppm; ¹³C NMR (100 MHz, *d*₆-DMSO): 191.9, 146.3, 143.3, 135.7, 132.3, 128.9, 128.0, 127.6, 124.5, 119.4, 111.8, 104.9, 21.5 ppm; HRMS (ESI) *m/z*: calcd. for C₁₃H₁₀N₂O [M+H]⁺ 211.0871, found: 211.0860.

N-(*p*-Tolyl)pyridin-2-amine (3ai):

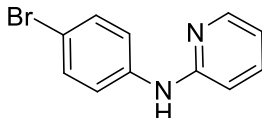


White solid; 165 mg, 90 %; m.p: 103-104 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.20 (dd, *J* = 4.8, 0.9 Hz, 1H), 7.47 (ddd, *J* = 7.2, 7.2, 1.8 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.71 (dd, *J* = 6.3, 5.7 Hz, 1H), 2.35 (s, 3H) ppm; ¹³C NMR (100

MHz, CDCl₃): δ 156.4, 148.4, 137.8, 137.6, 132.7, 129.8, 121.2, 114.5, 107.6, 20.8 ppm;

HRMS (ESI) m/z : calcd. for C₁₂H₁₂N₂ [M+H]⁺ 185.1078, found: 185.1071.

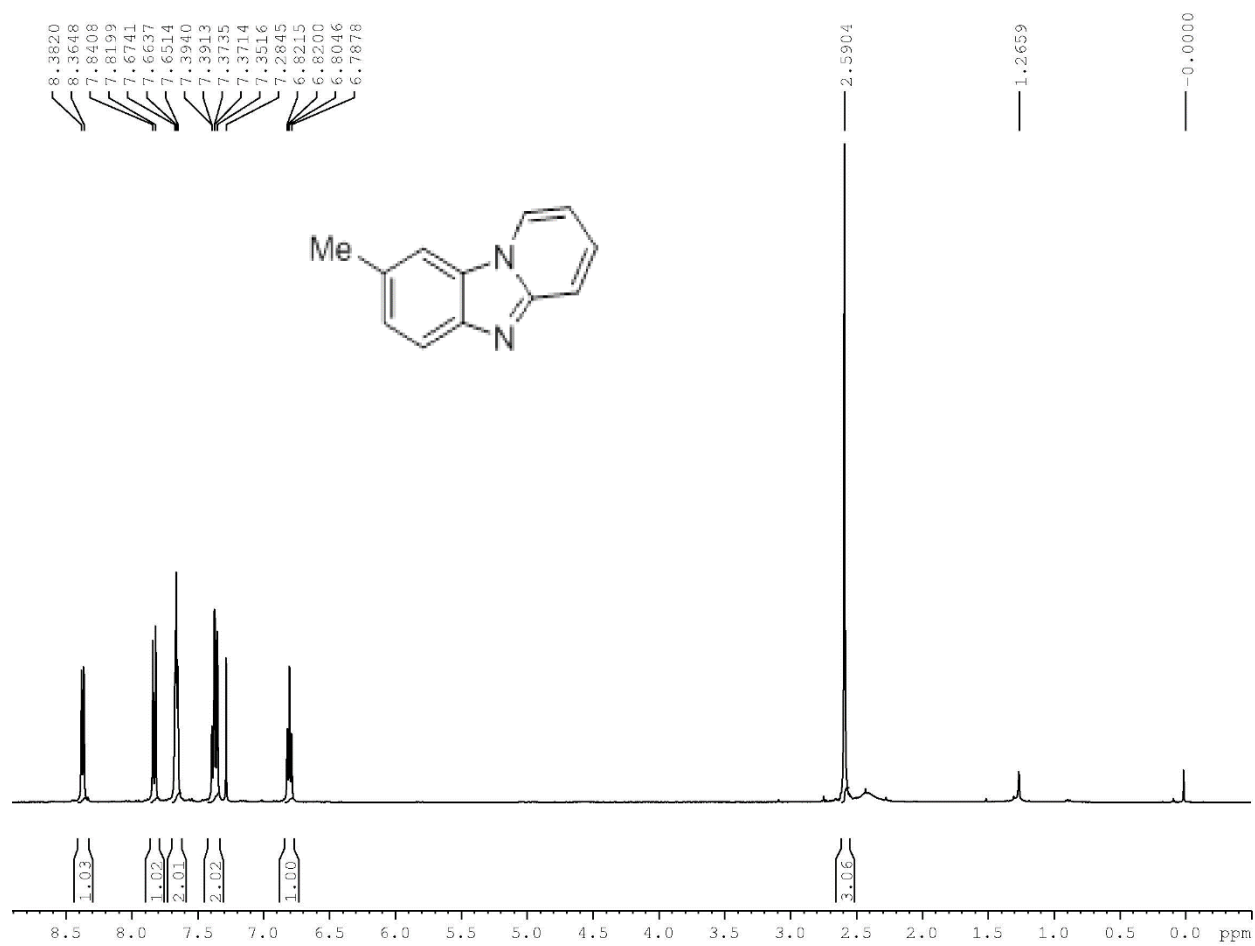
***N*-(4-Bromophenyl)pyridin-2-amine (3ci):**



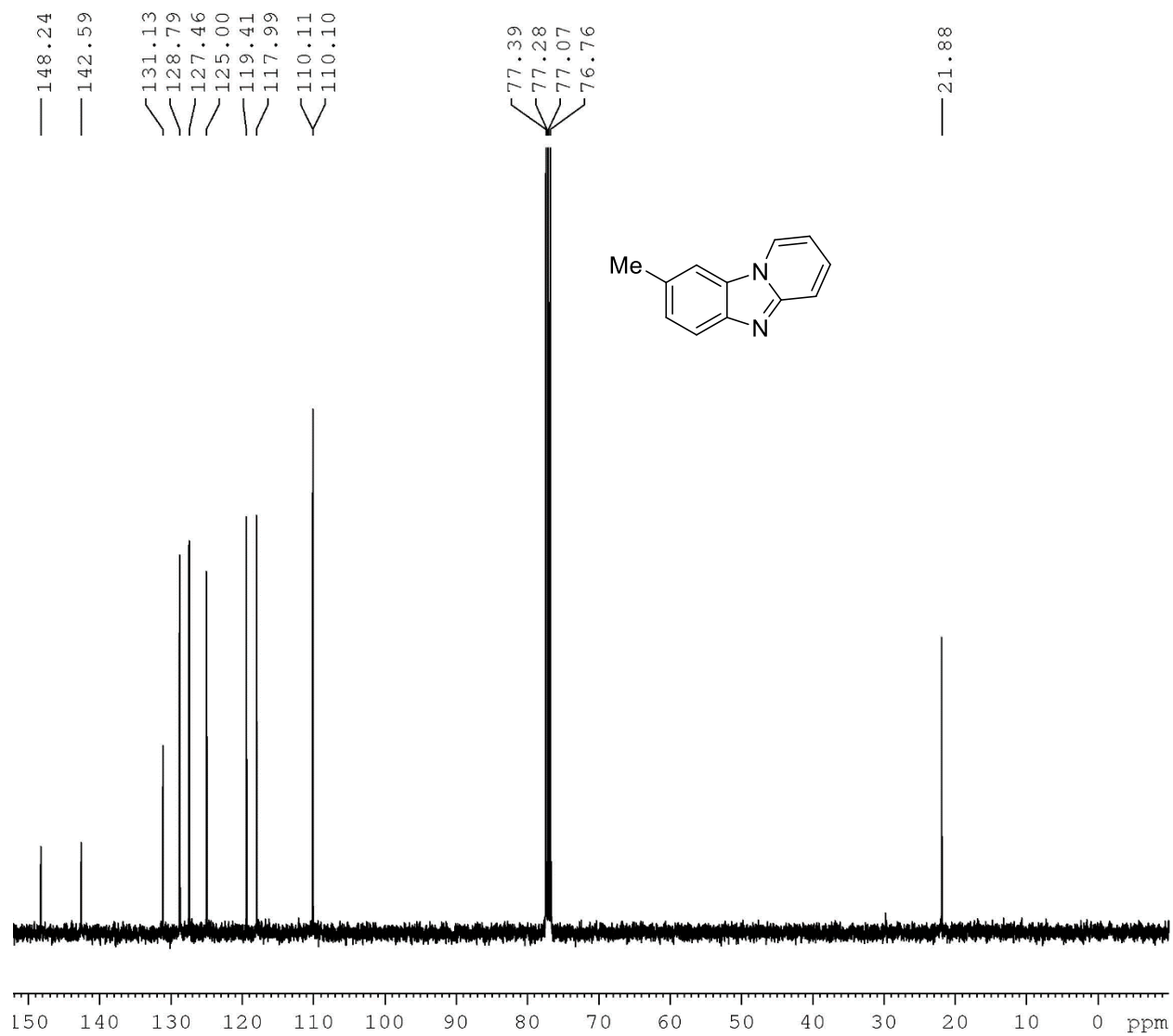
White solid; 204 mg, 82 %; m.p: 130-131 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.24 (br s, 1H), 7.53 (ddd, J = 7.9, 7.7, 1.4 Hz, 1H), 7.44 (d, J = 8.7, 2H), 7.28 (d, J = 8.7, 2H), 6.84-6.77 (m, 2H), 6.69 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 155.4, 148.3, 139.6, 137.9, 132.1, 121.4, 115.5, 114.7, 108.8 ppm; HRMS (ESI) m/z : calcd. for C₁₁H₉Br⁷⁹N₂ [M+H]⁺ 249.0027, found: 249.0014.

IV. ^1H NMR and ^{13}C NMR Spectra

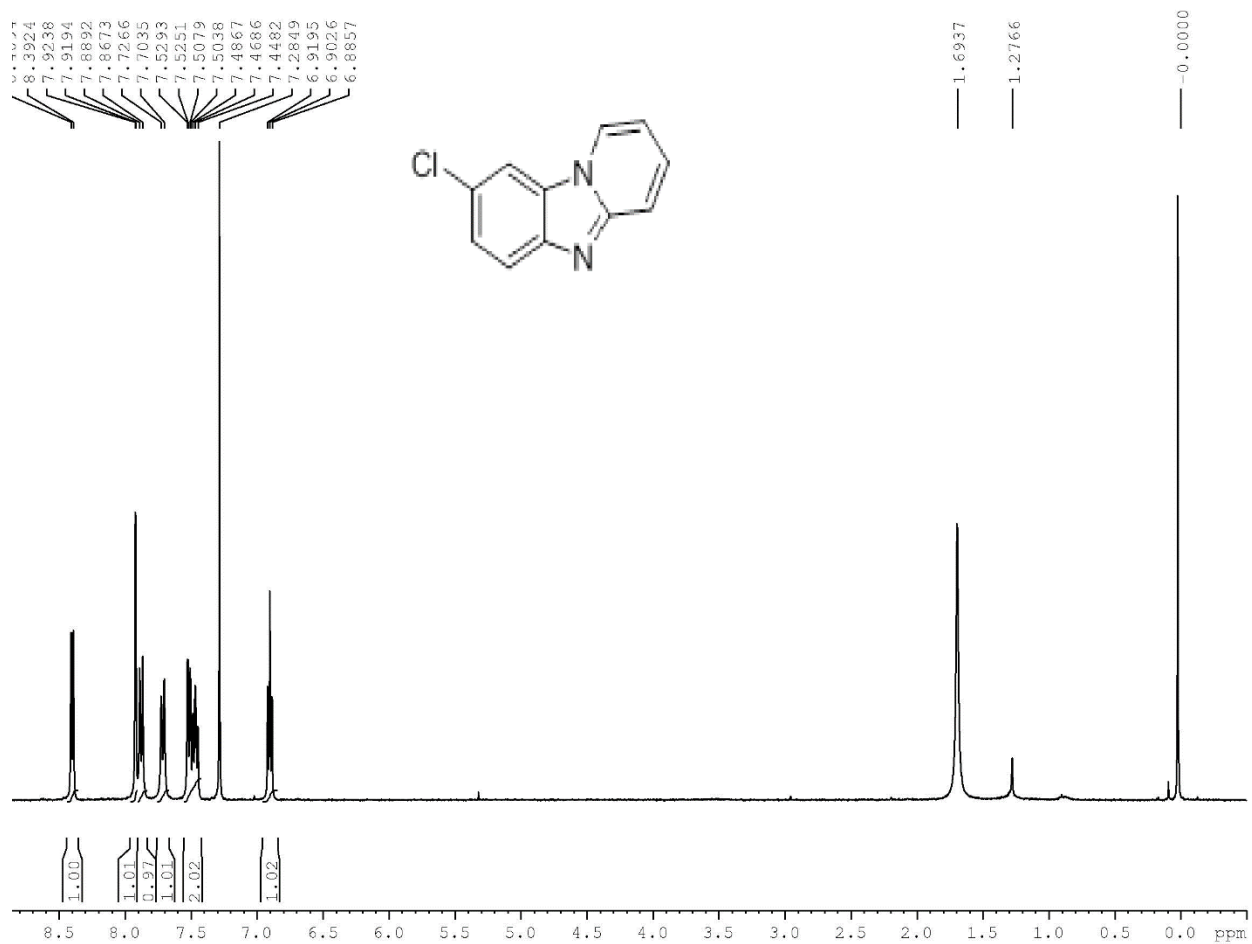
^1H NMR spectra of compound 3a



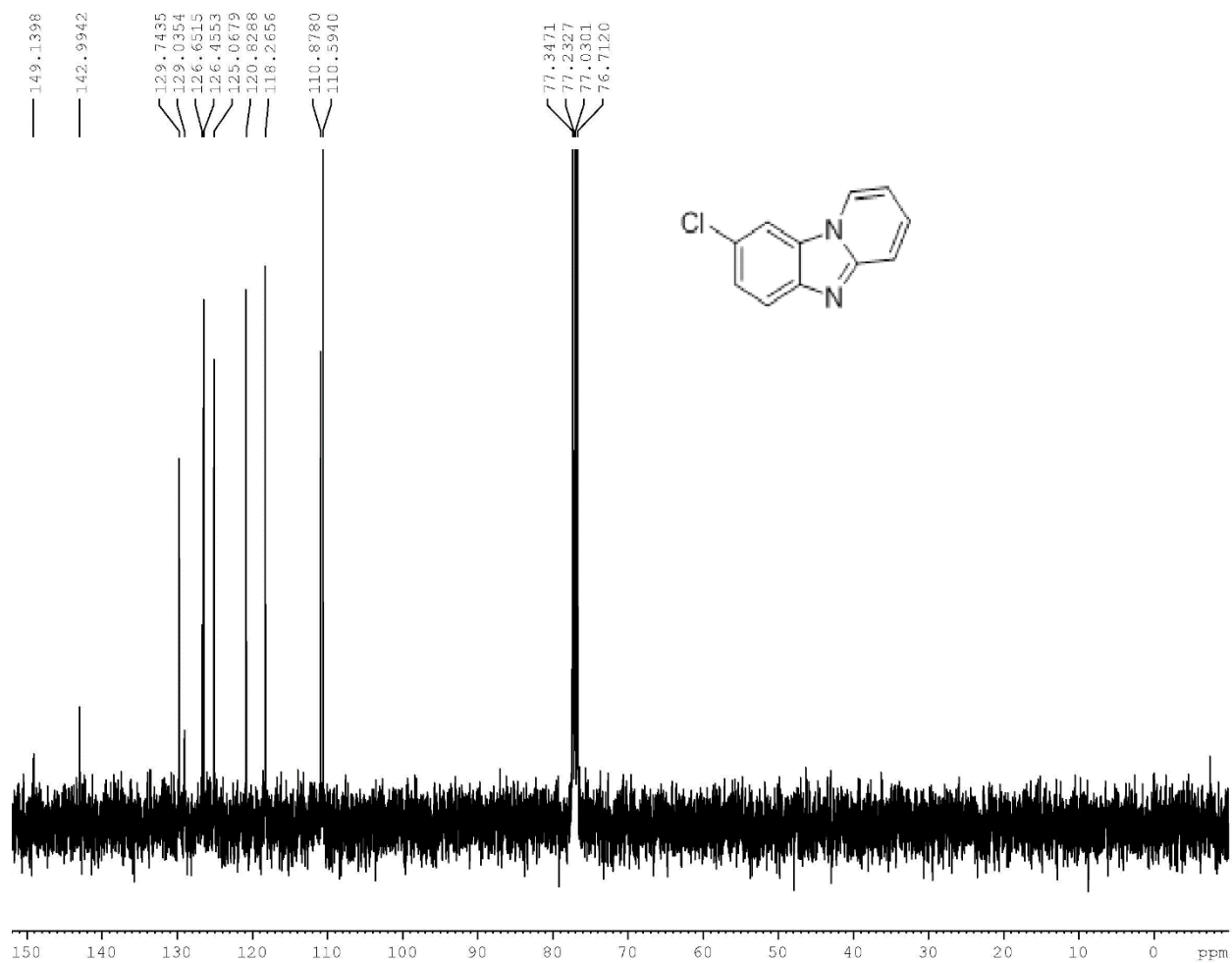
¹³C NMR spectra of compound 3a



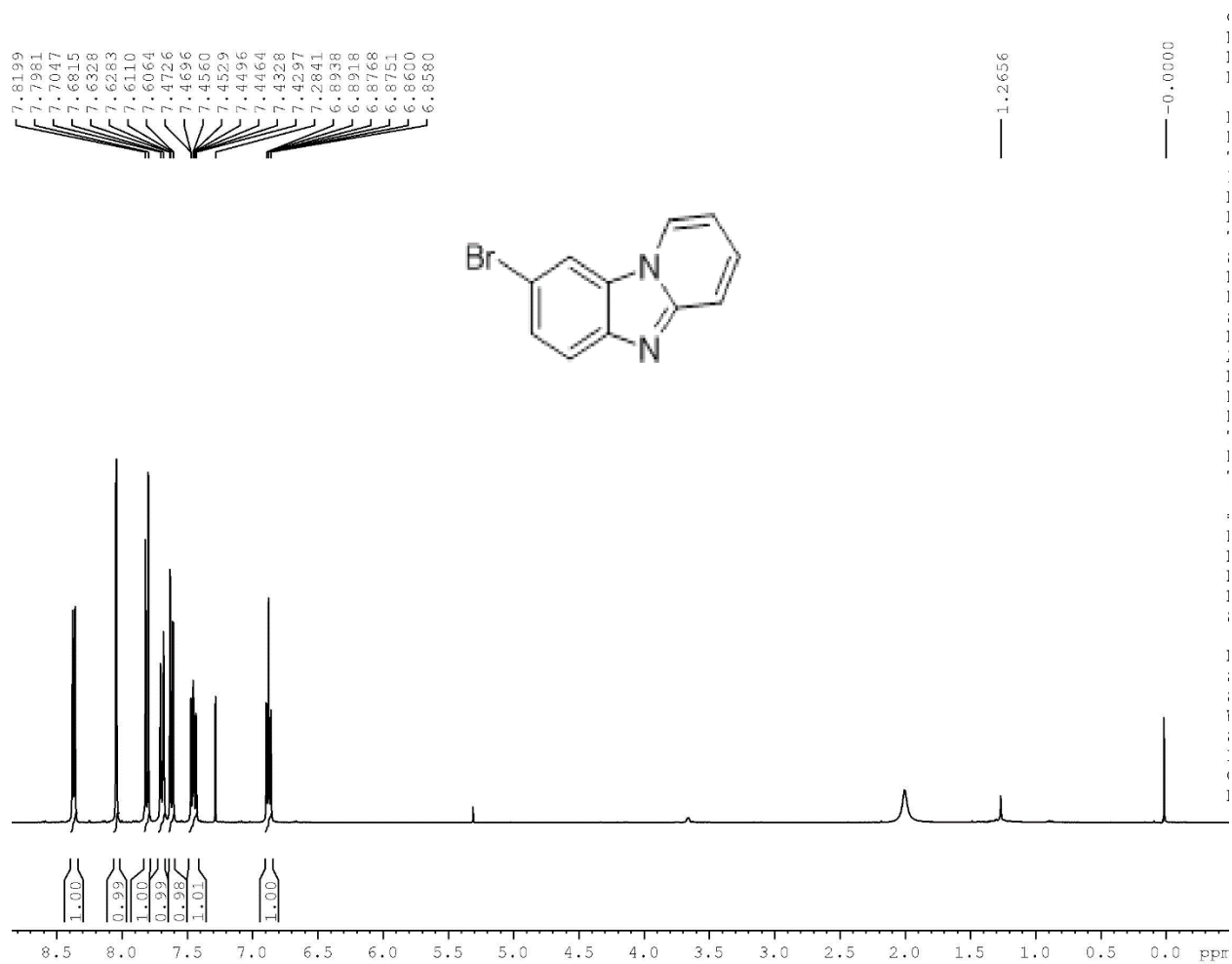
¹H NMR spectra of compound 3b



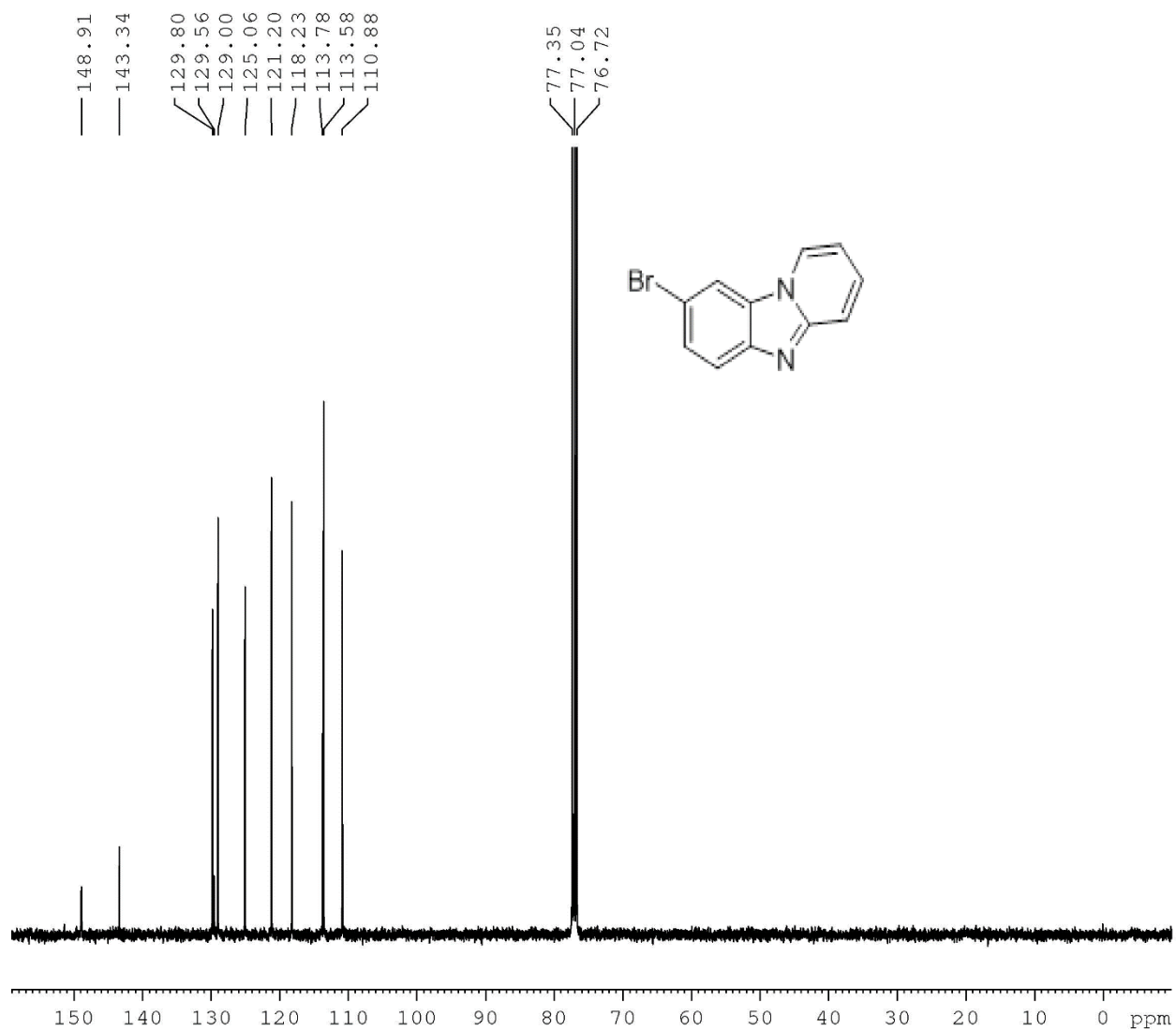
¹³C NMR spectra of compound 3b



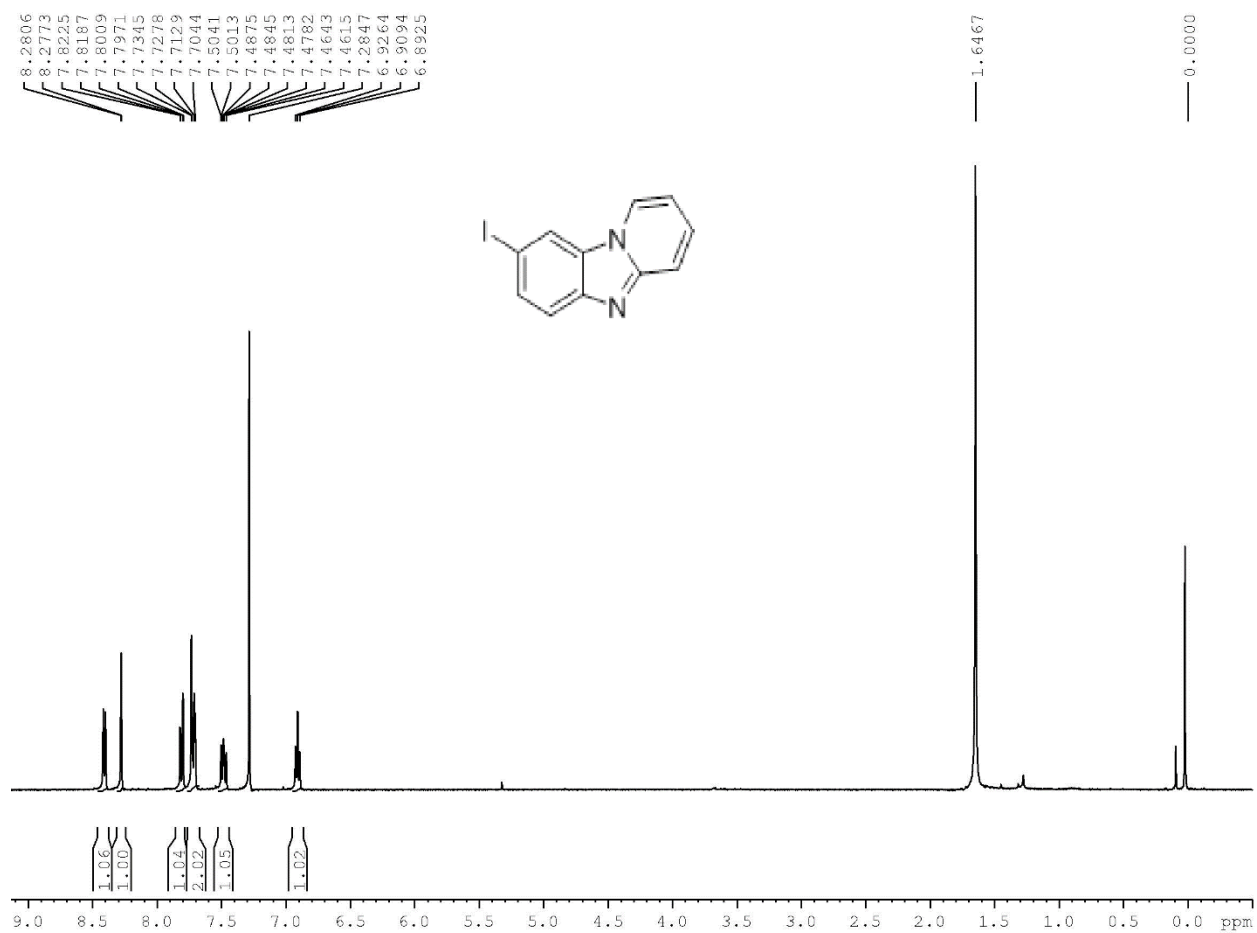
¹H NMR spectra of compound 3c



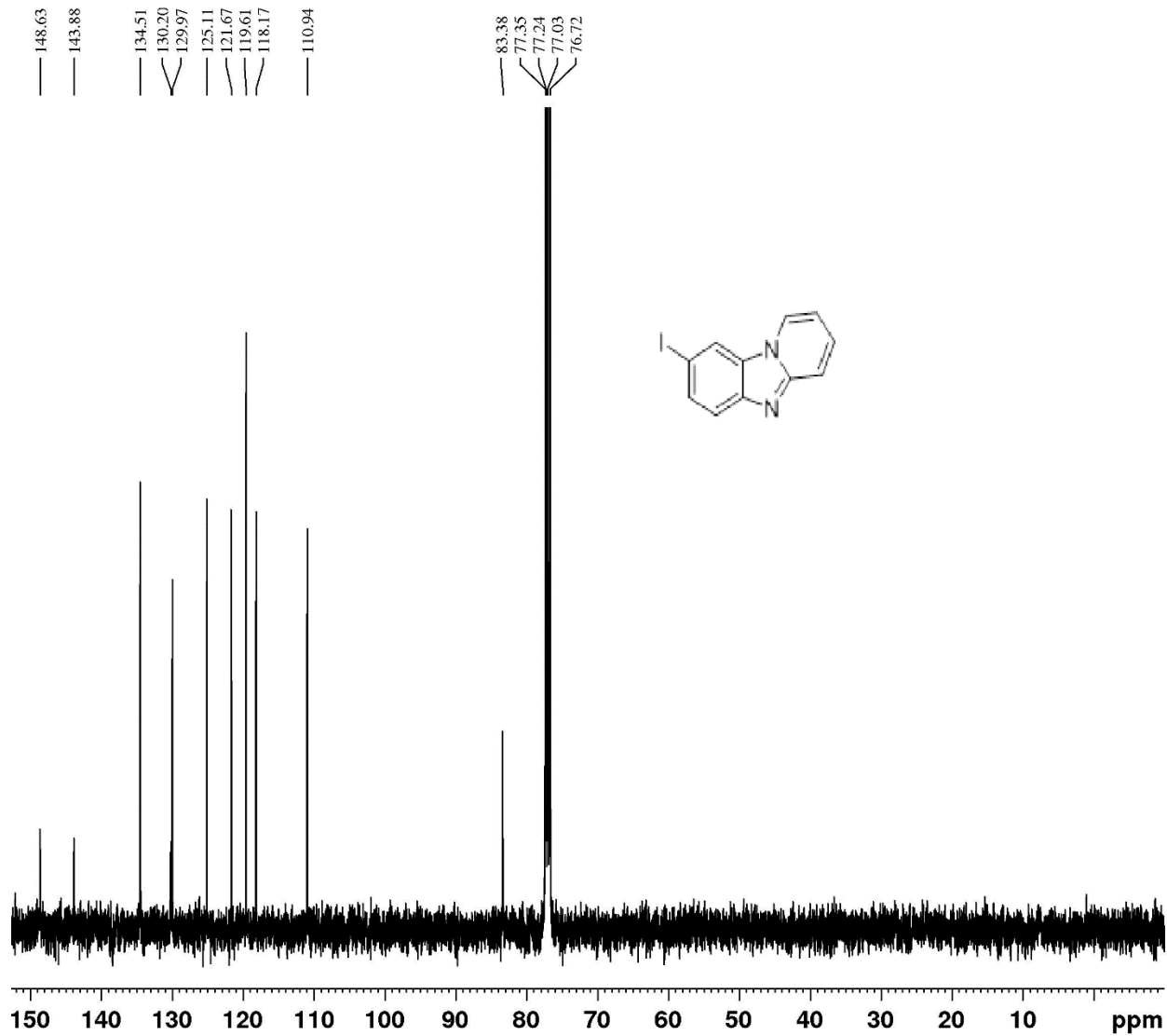
¹³C NMR spectra of compound 3c



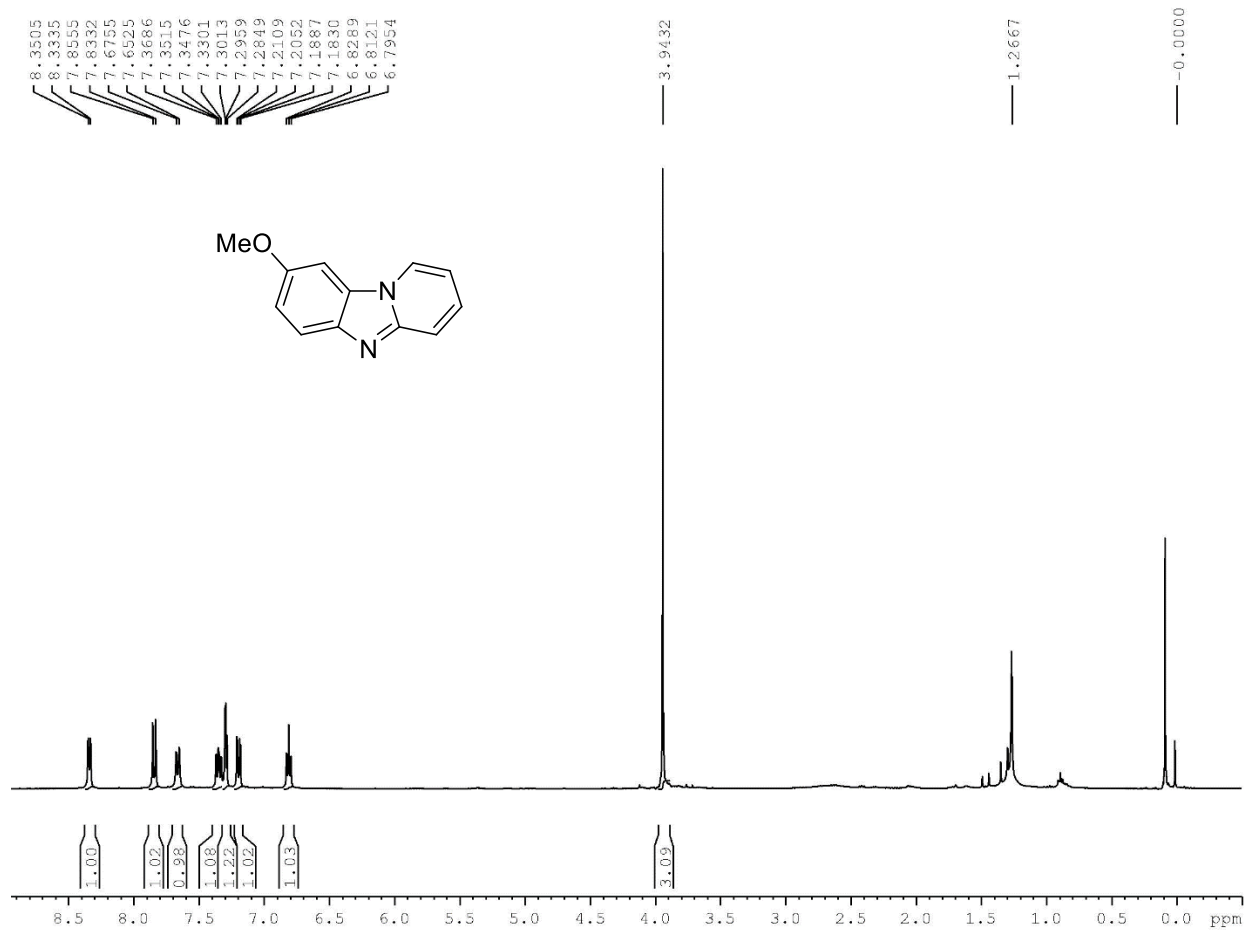
¹H NMR spectra of compound 3d



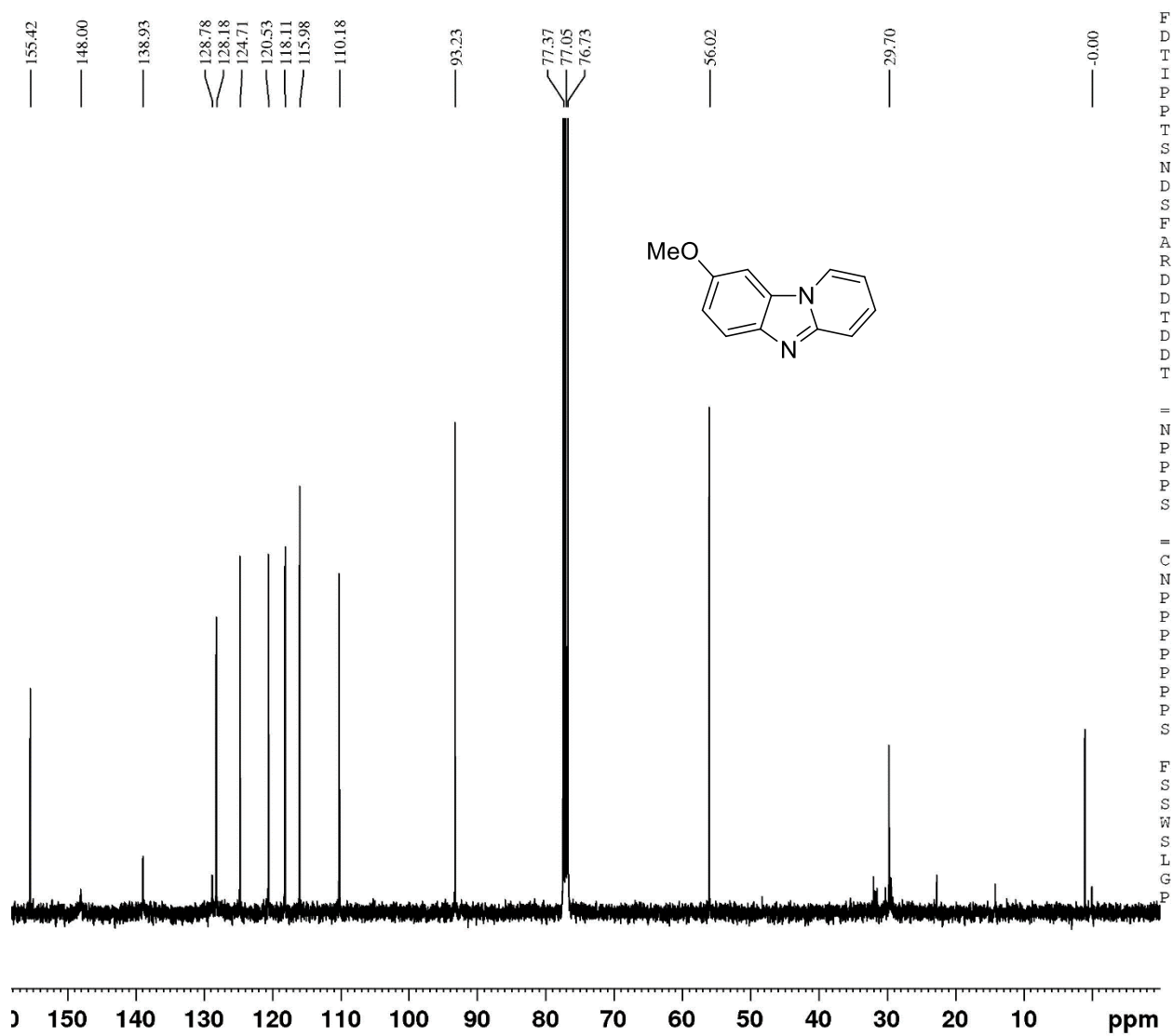
¹³C NMR spectra of compound 3d



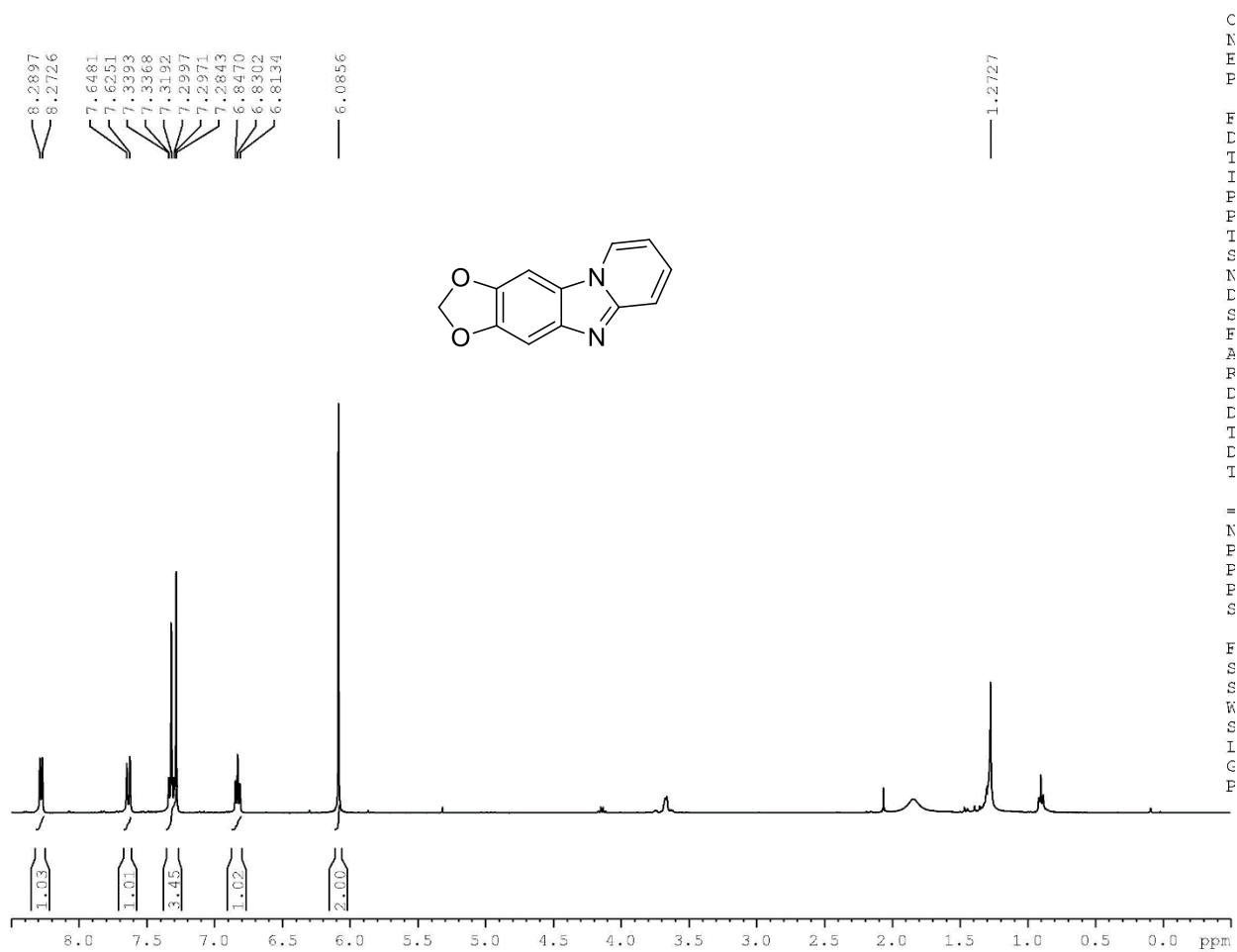
¹H NMR spectra of compound 3e



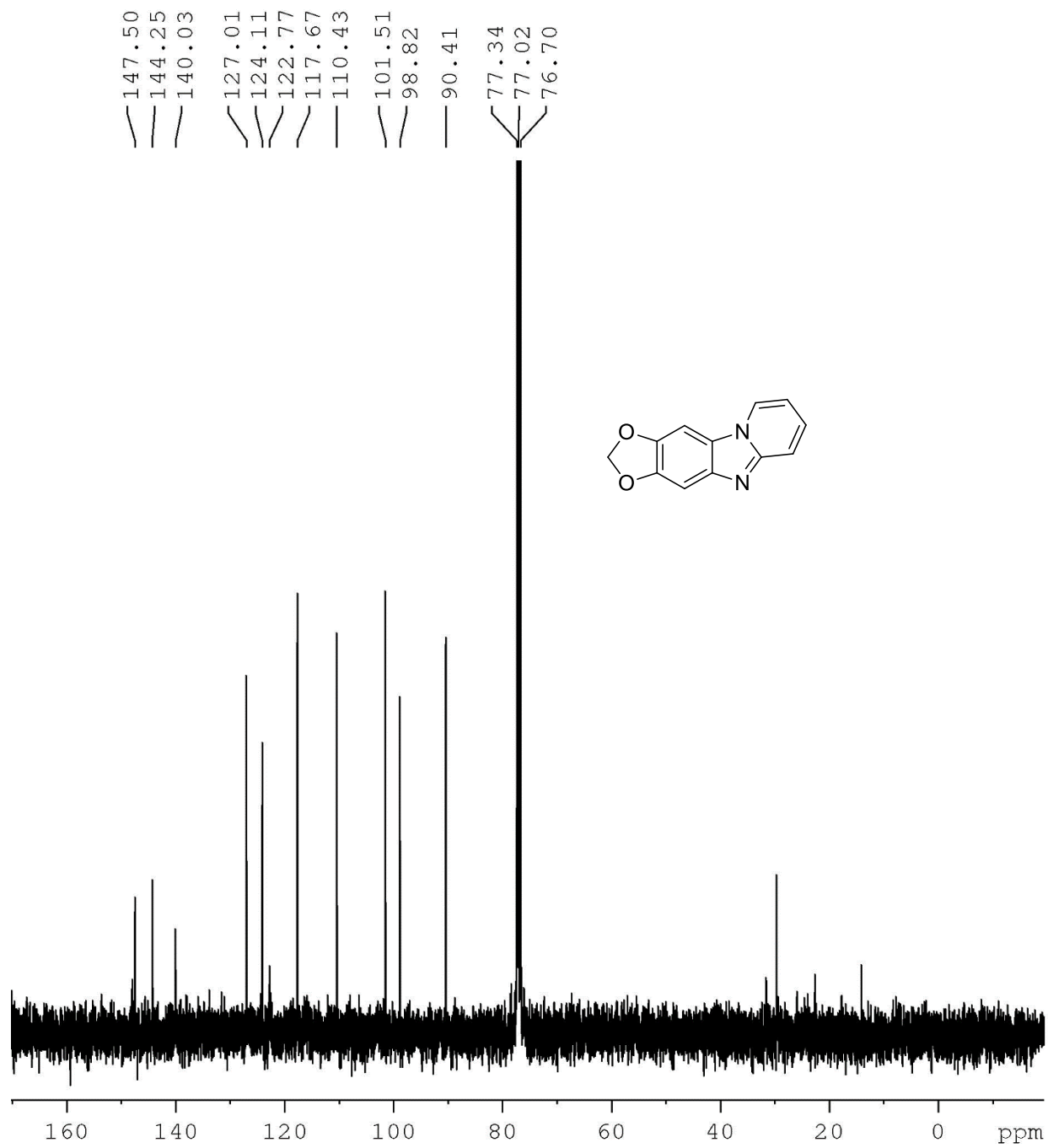
¹³C NMR spectra of compound 3e



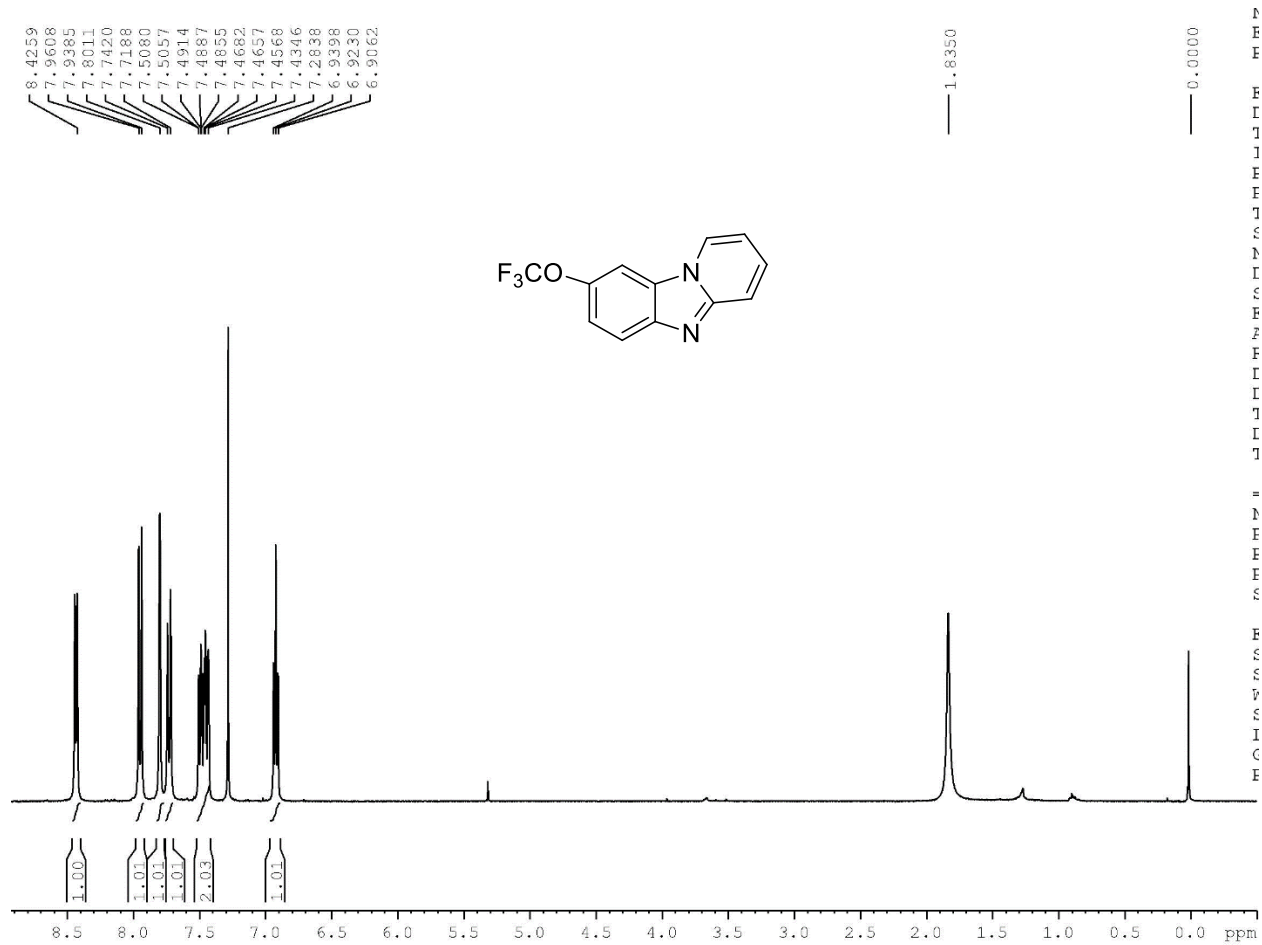
¹H NMR spectra of compound 3f



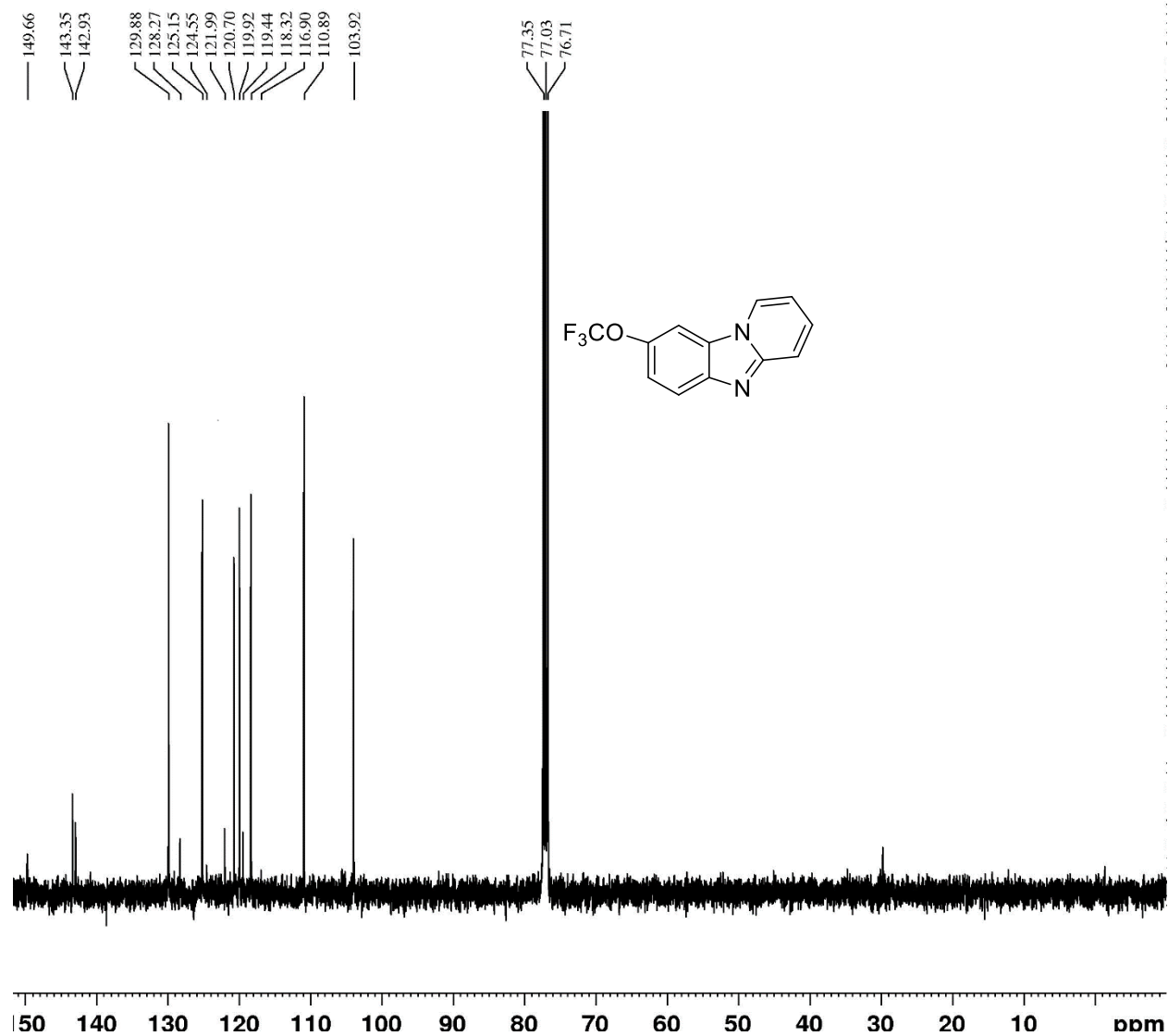
¹³C NMR spectra of compound 3f



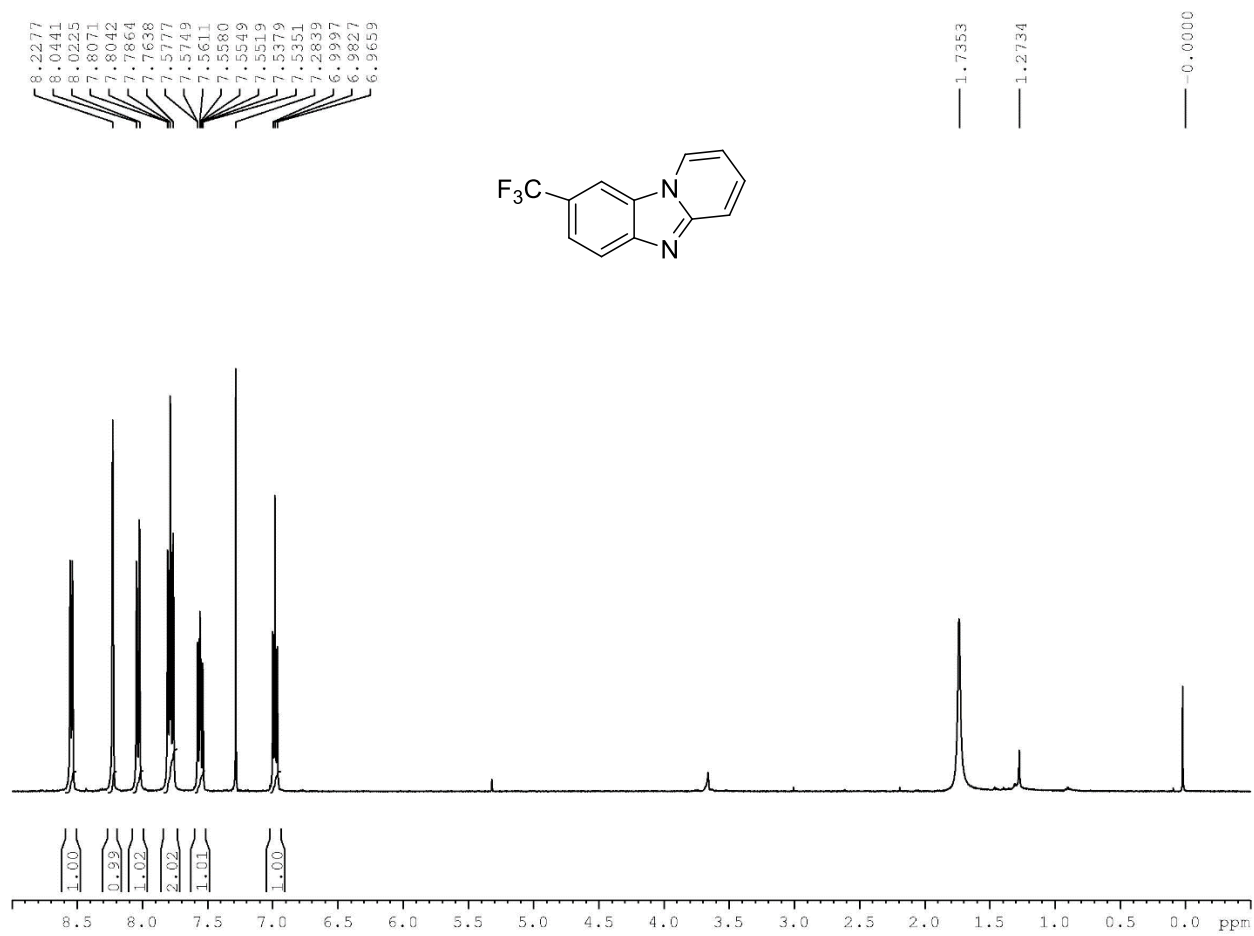
¹H NMR spectra of compound 3g



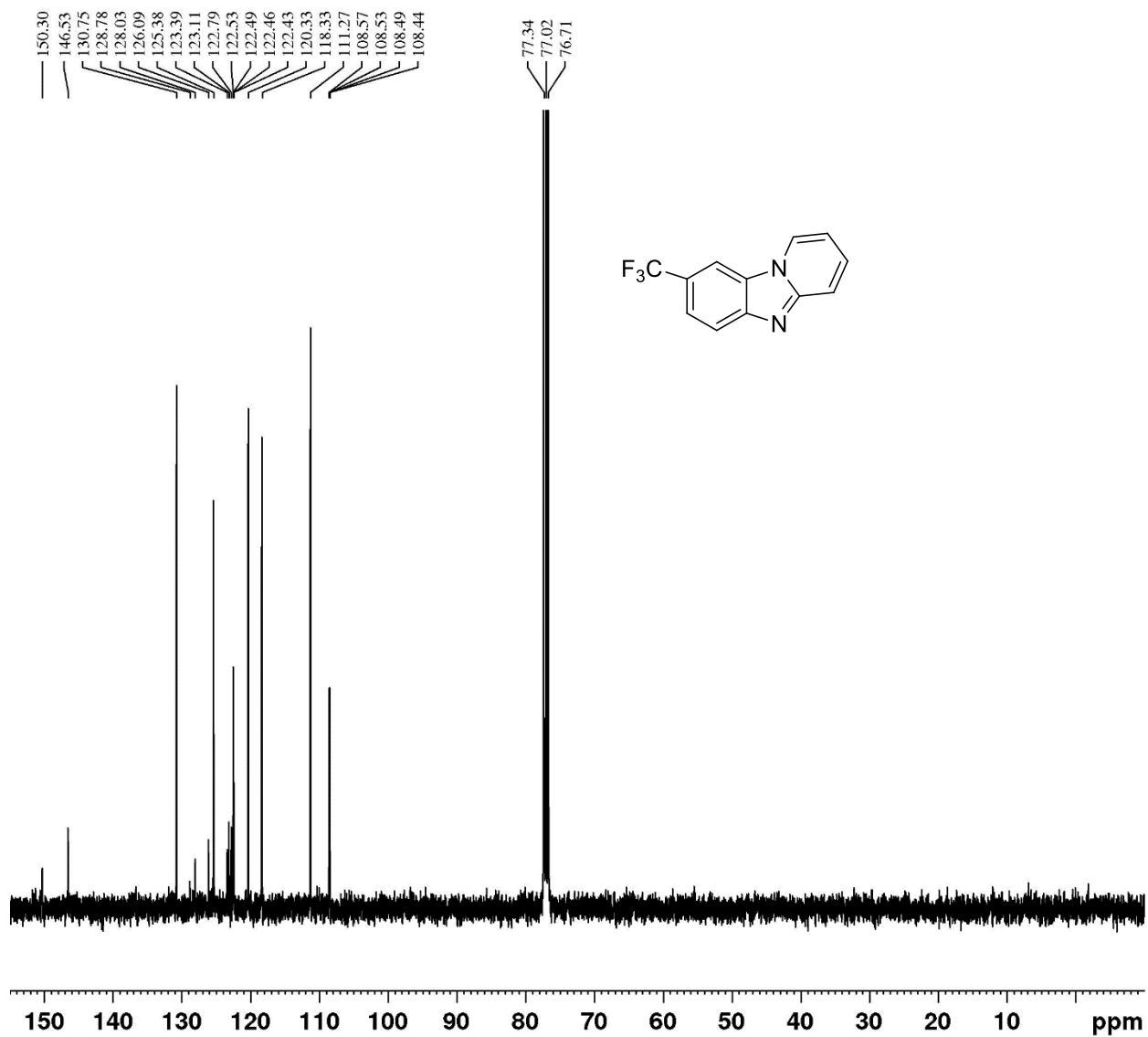
¹³C NMR spectra of compound 3g



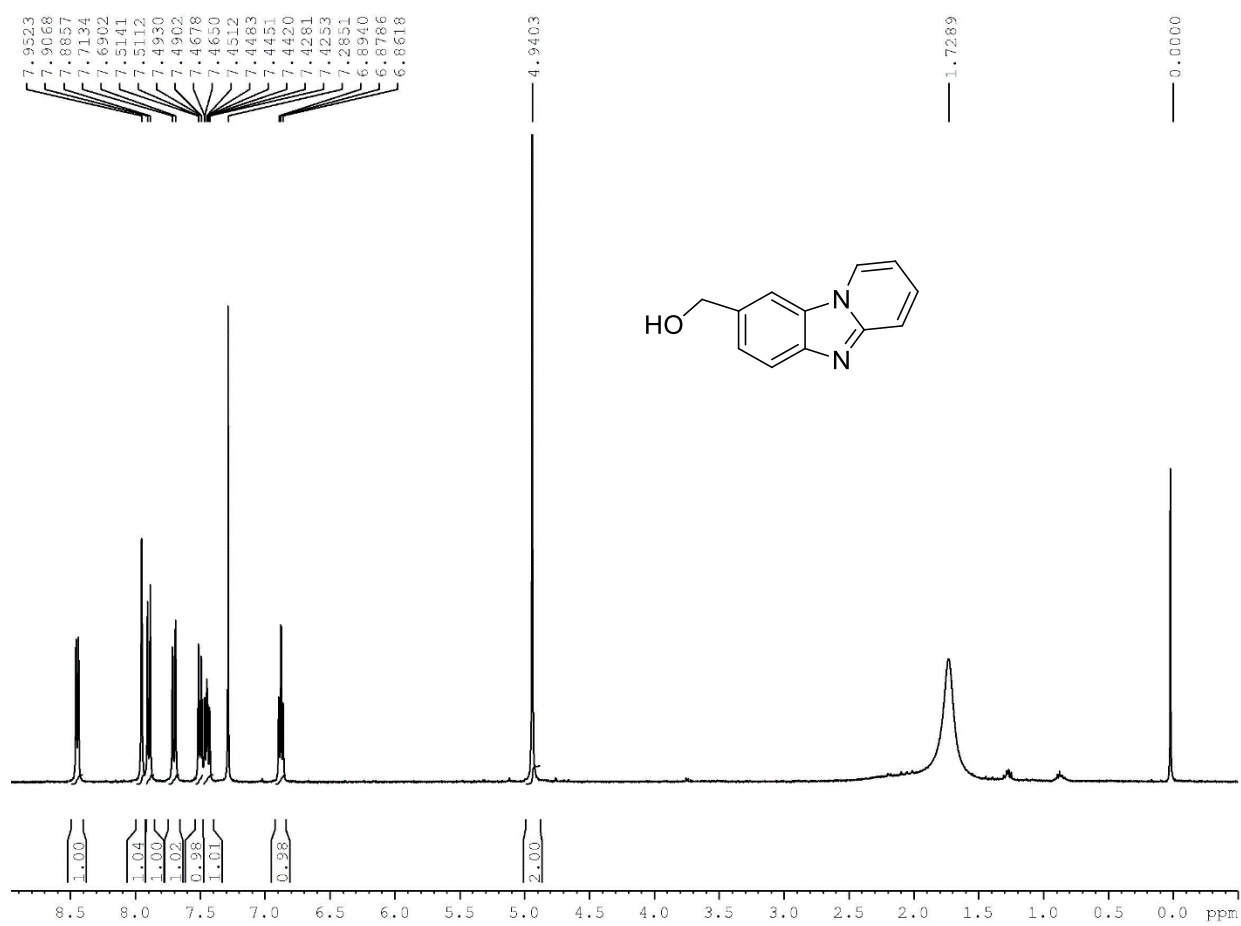
¹H NMR spectra of compound 3h



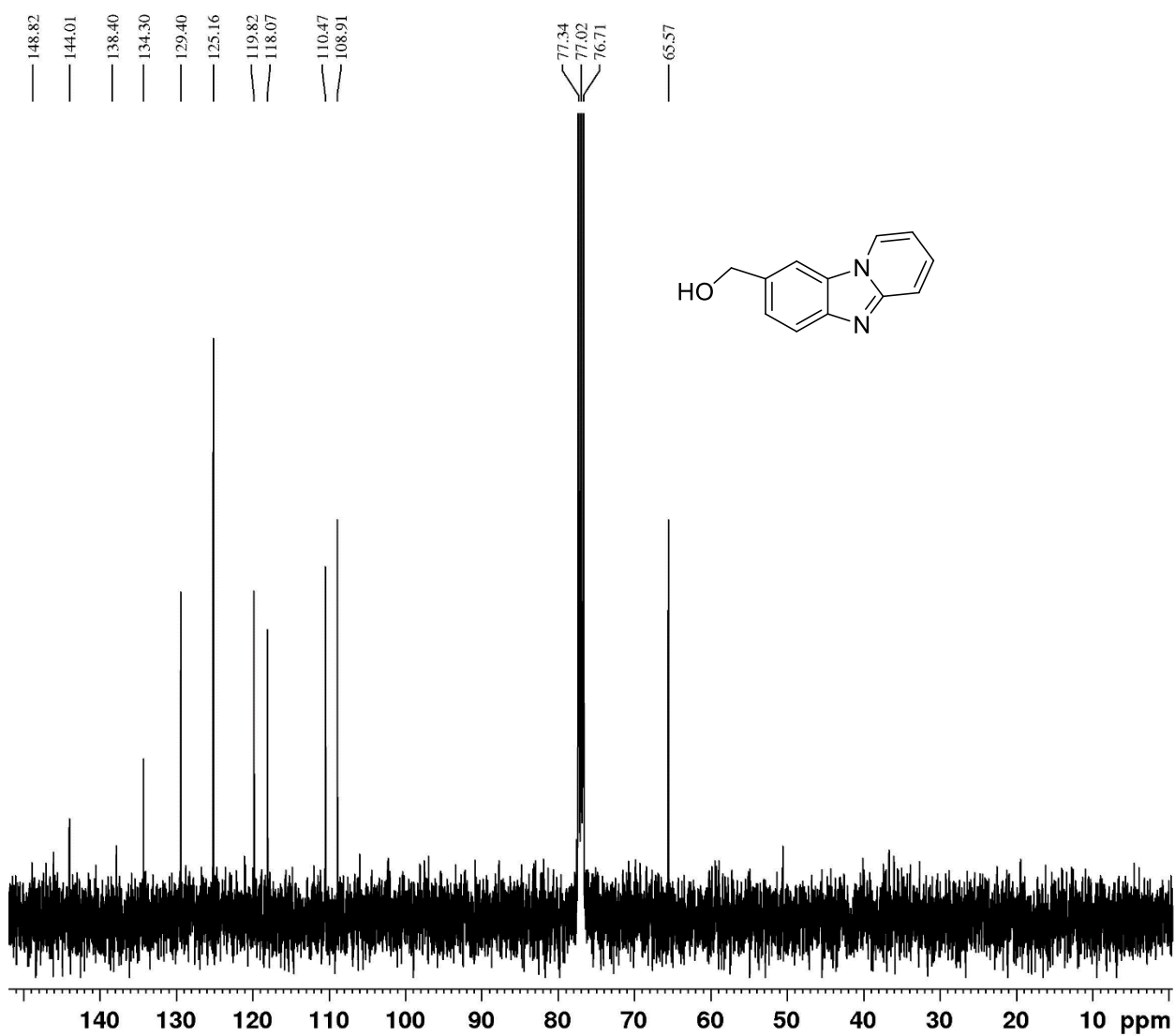
¹³C NMR spectra of compound 3h



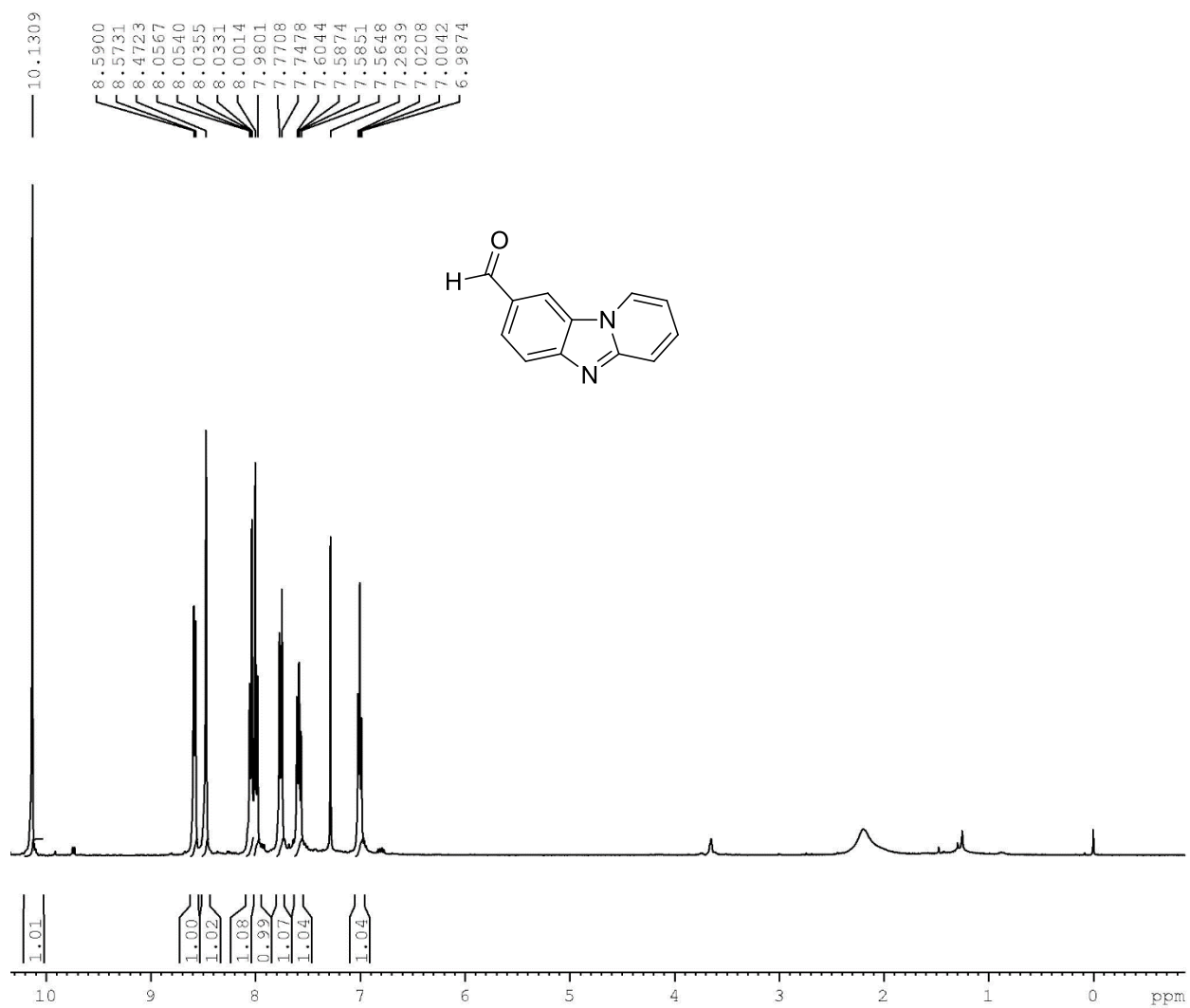
¹H NMR spectra of compound 3i



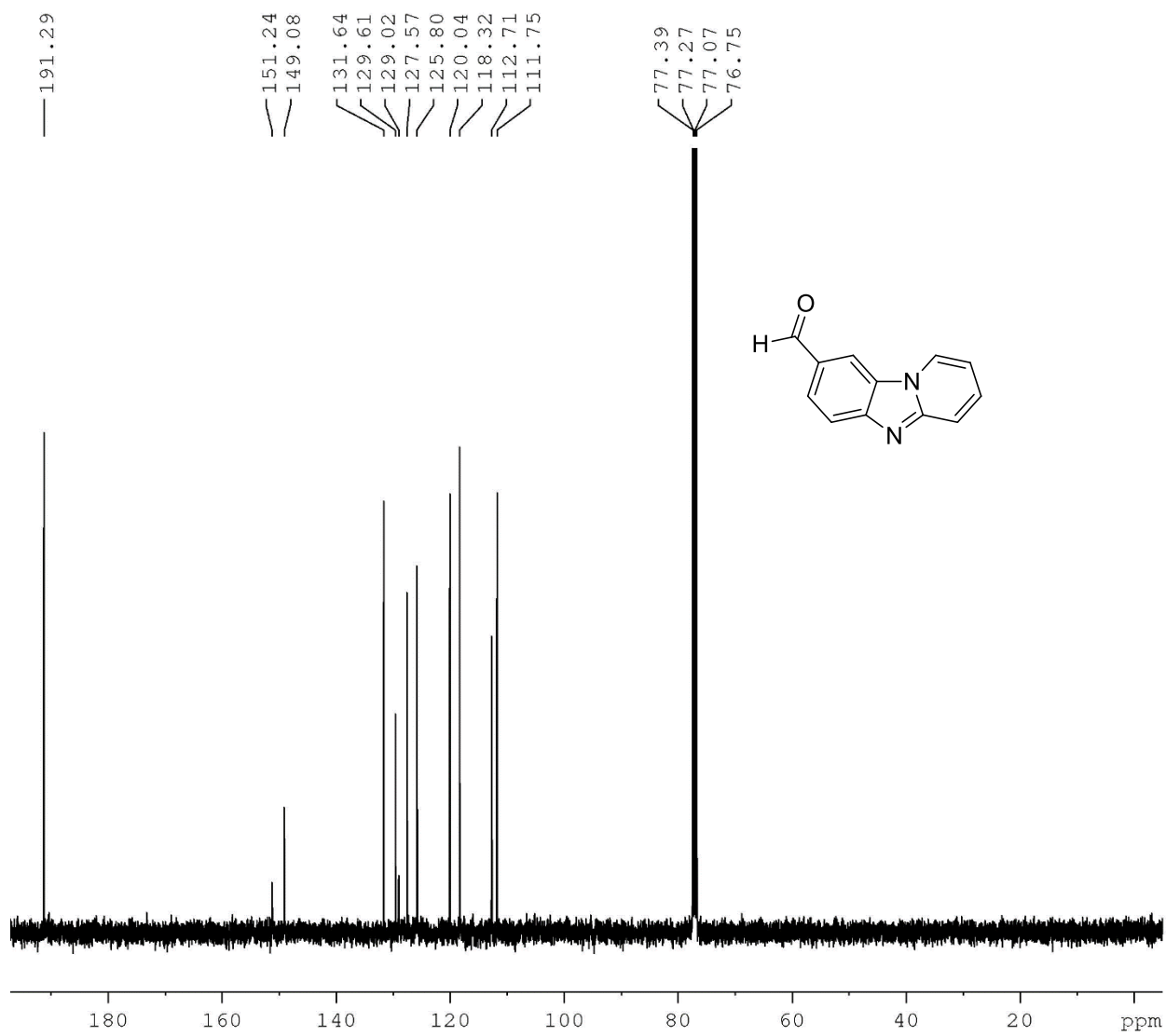
^{13}C NMR spectra of compound 3i



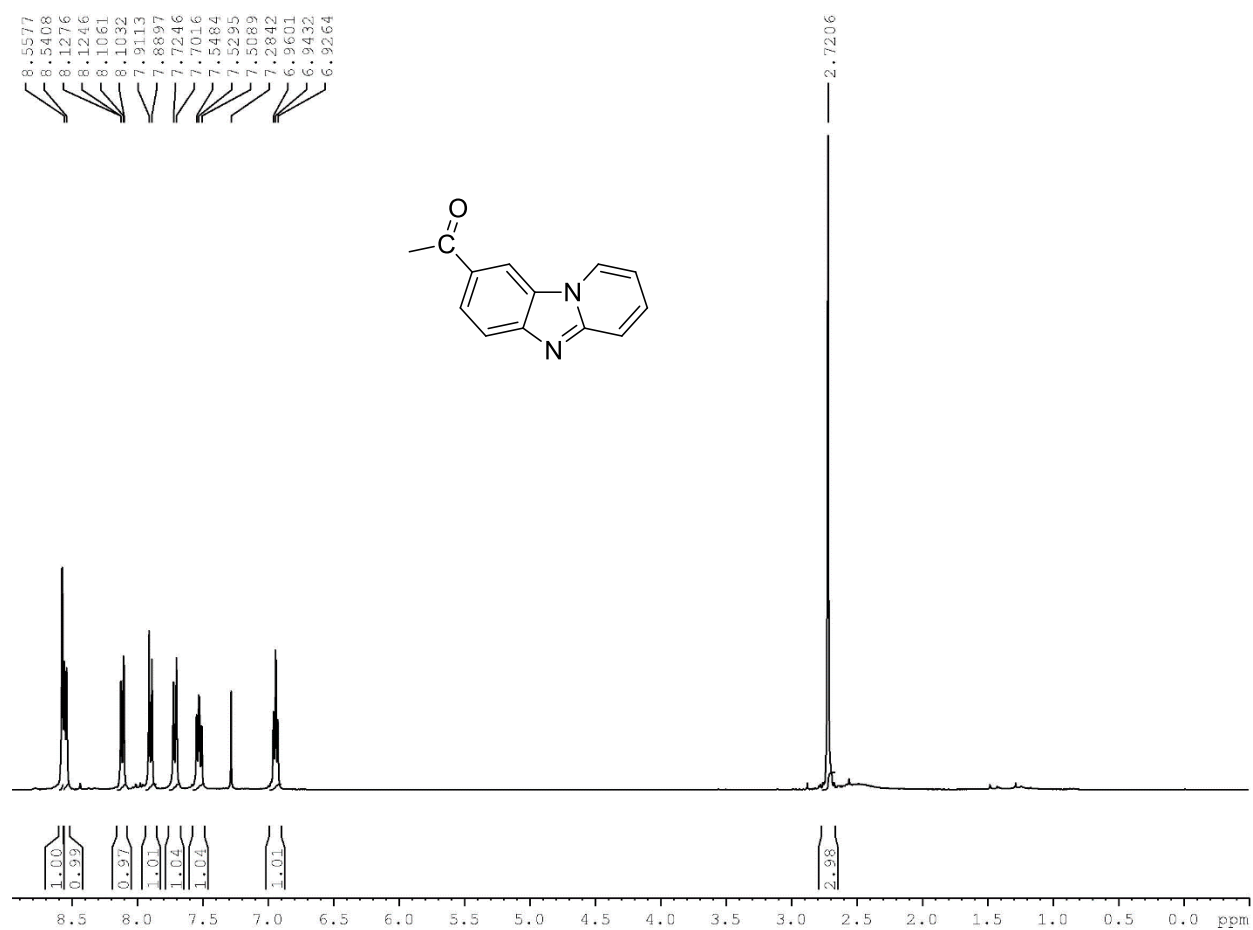
¹H NMR spectra of compound 3j



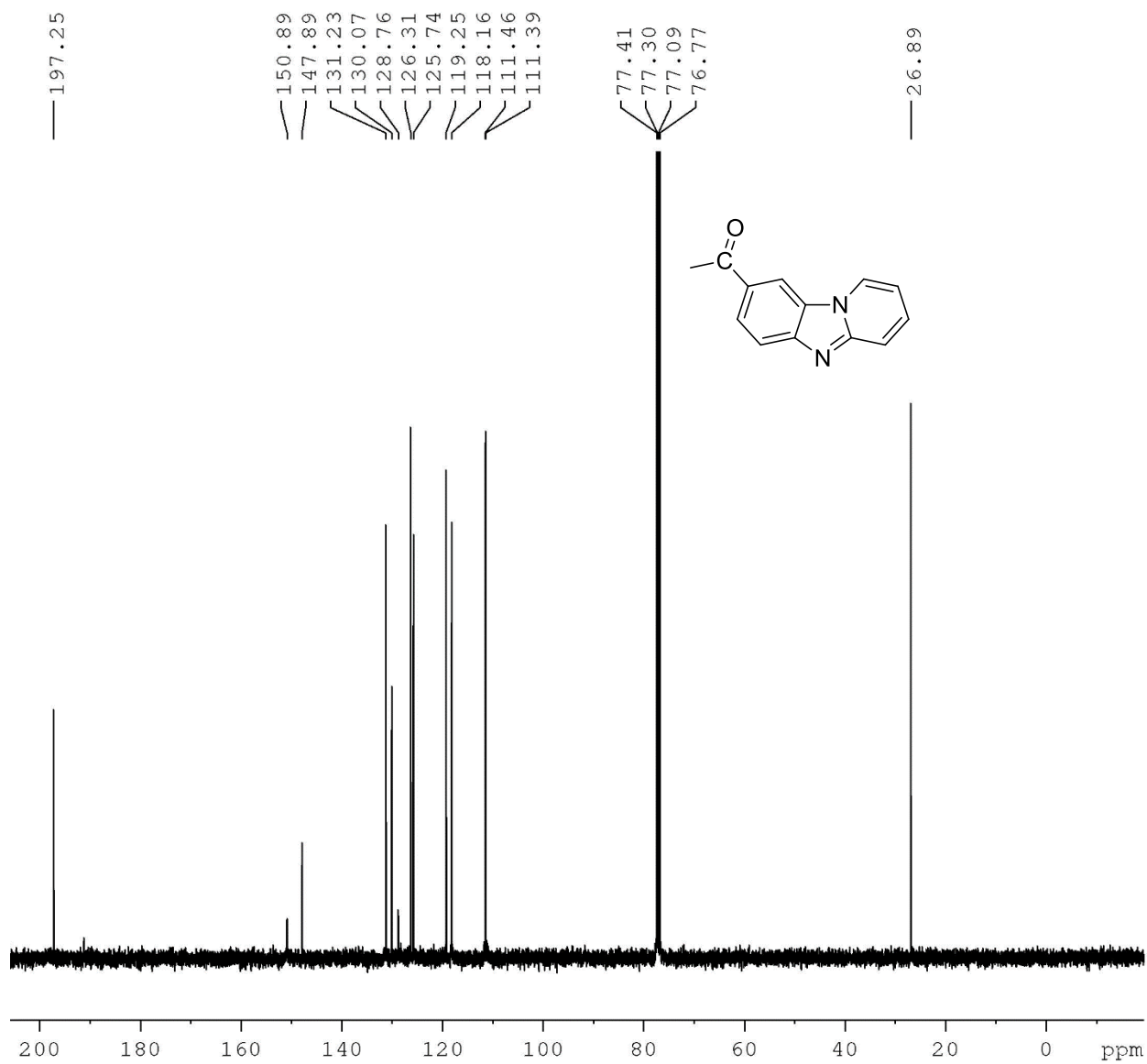
^{13}C NMR spectra of compound 3j



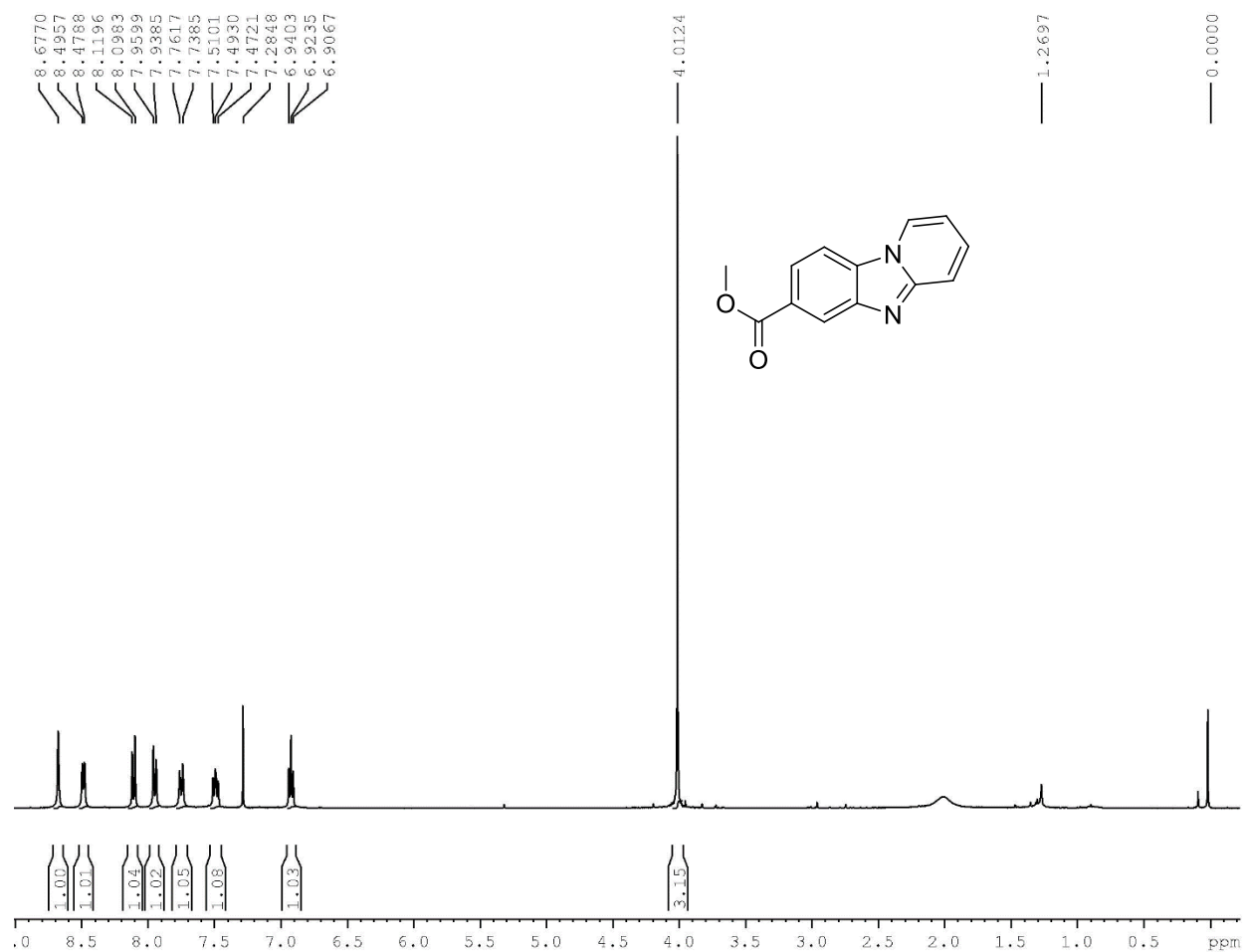
¹H NMR spectra of compound 3k



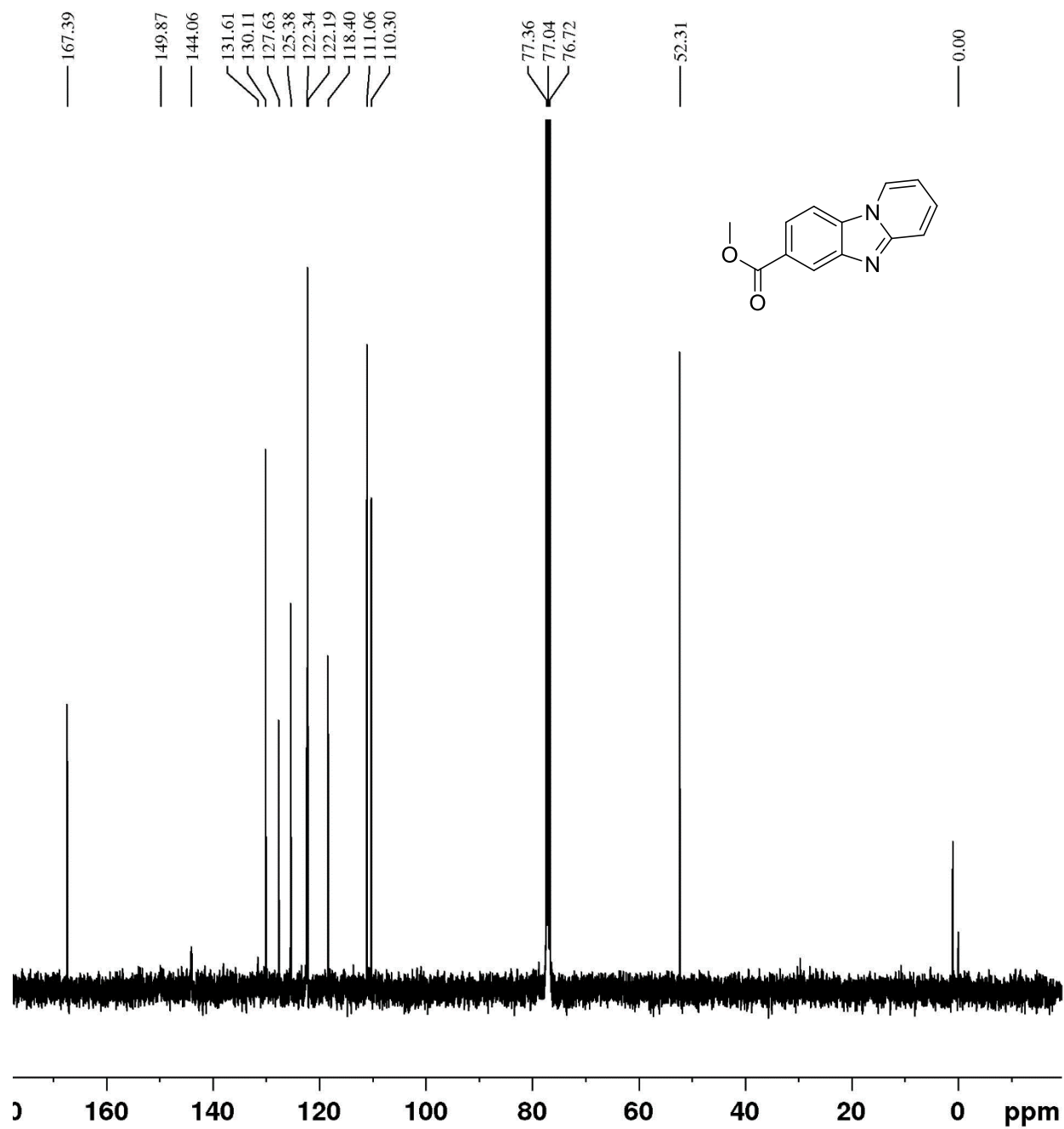
¹³C NMR spectra of compound 3k



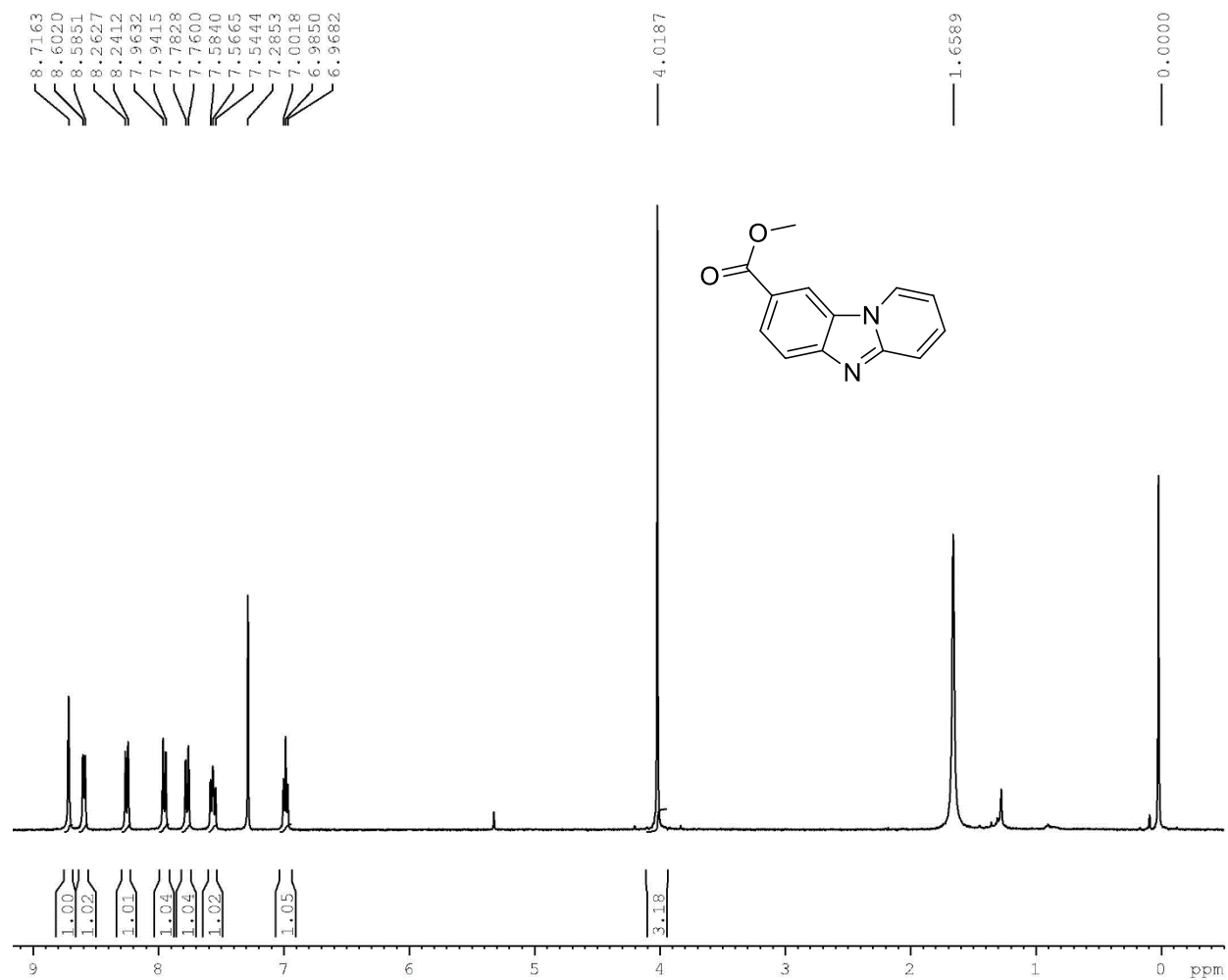
¹H NMR spectra of compound 3l



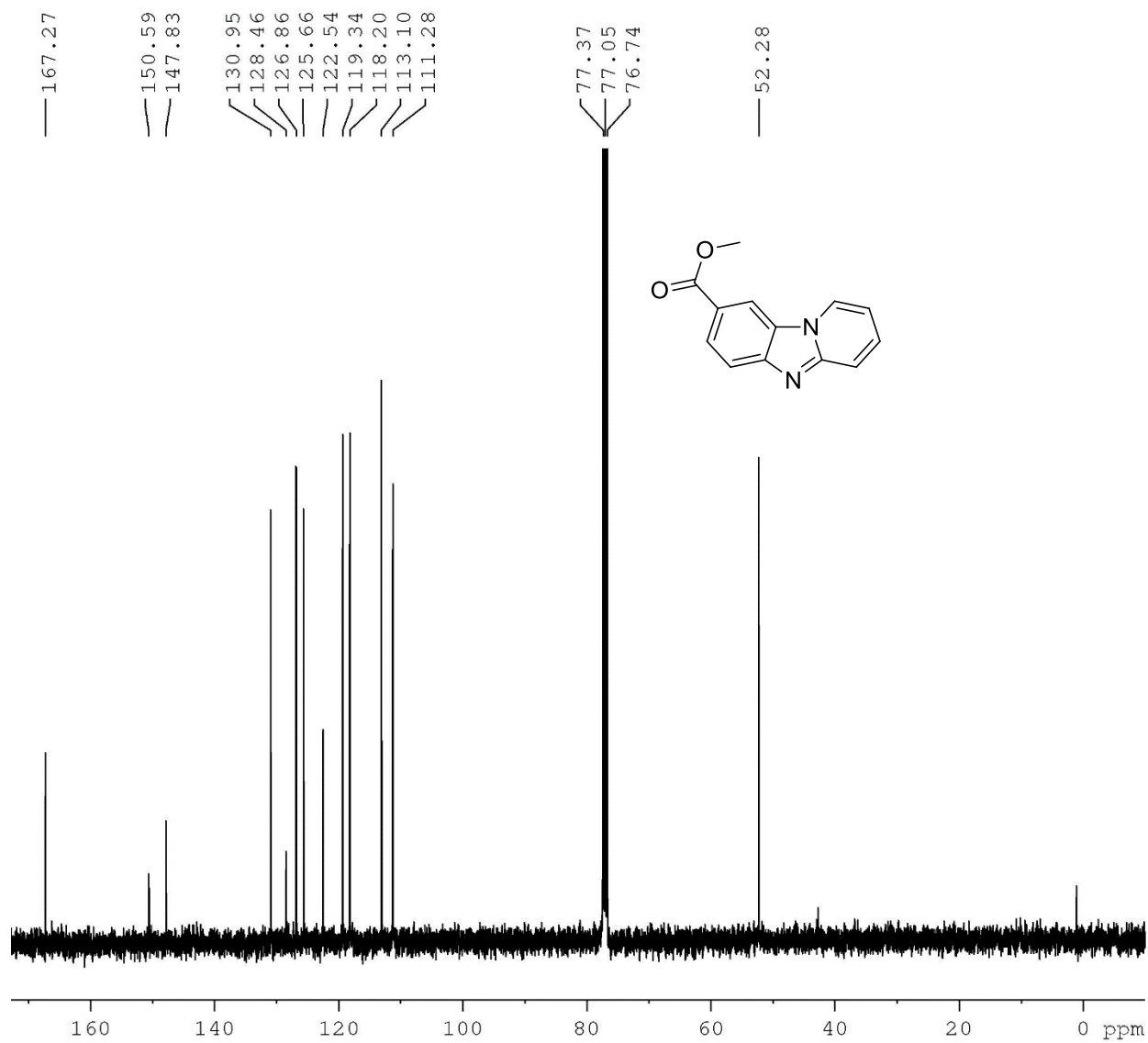
¹³C NMR spectra of compound 31



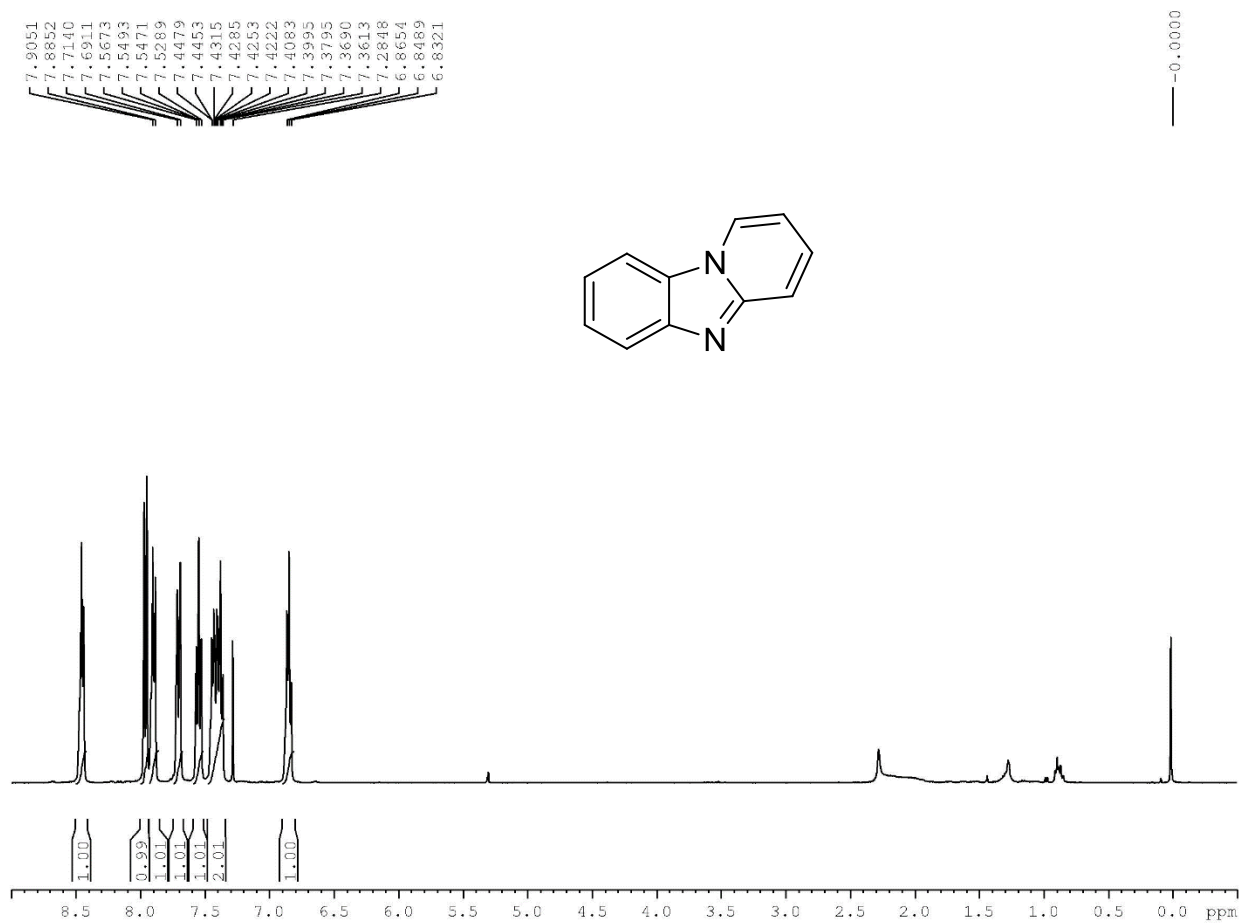
¹H NMR spectra of compound 3m



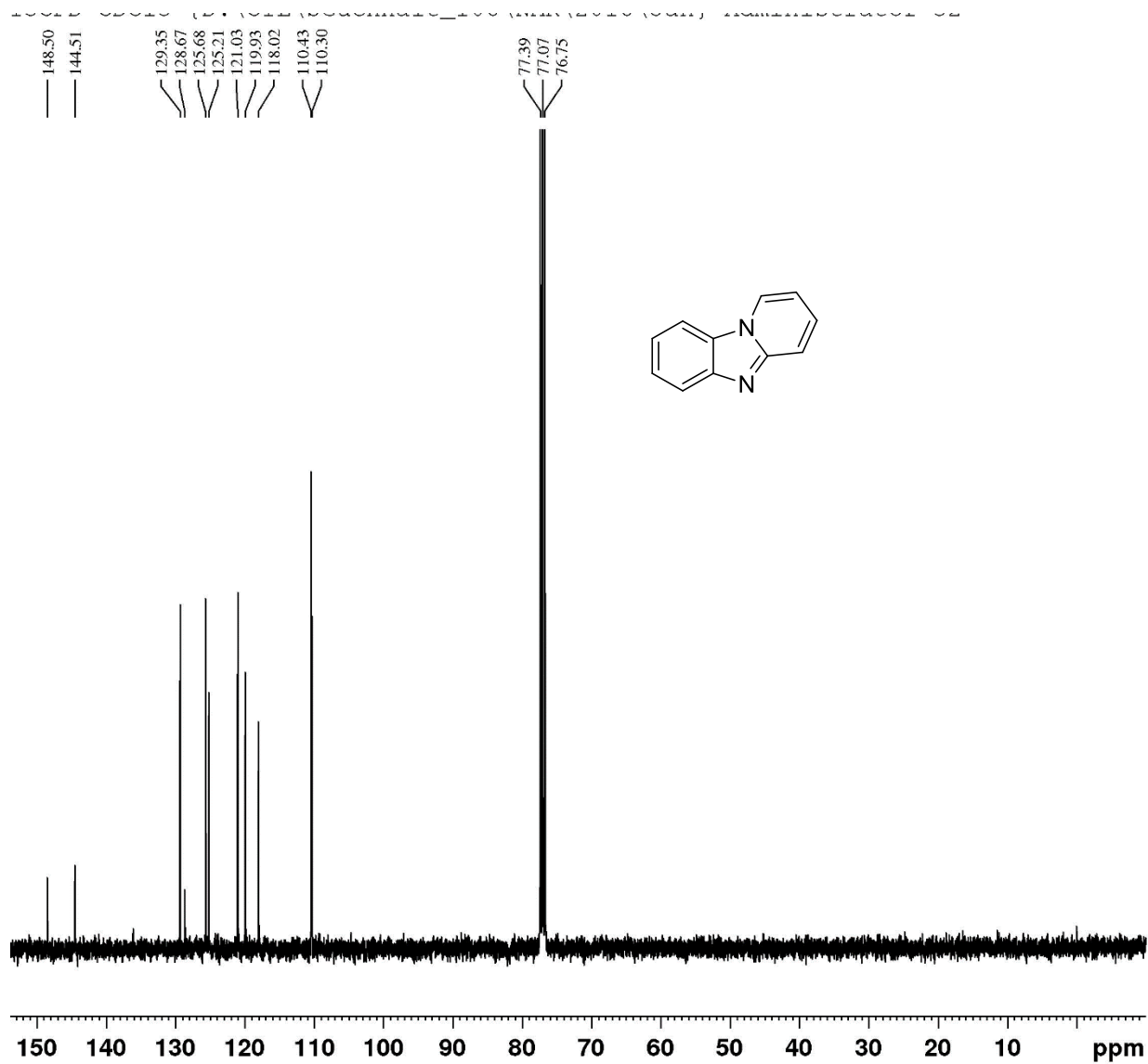
¹³C NMR spectra of compound 3m



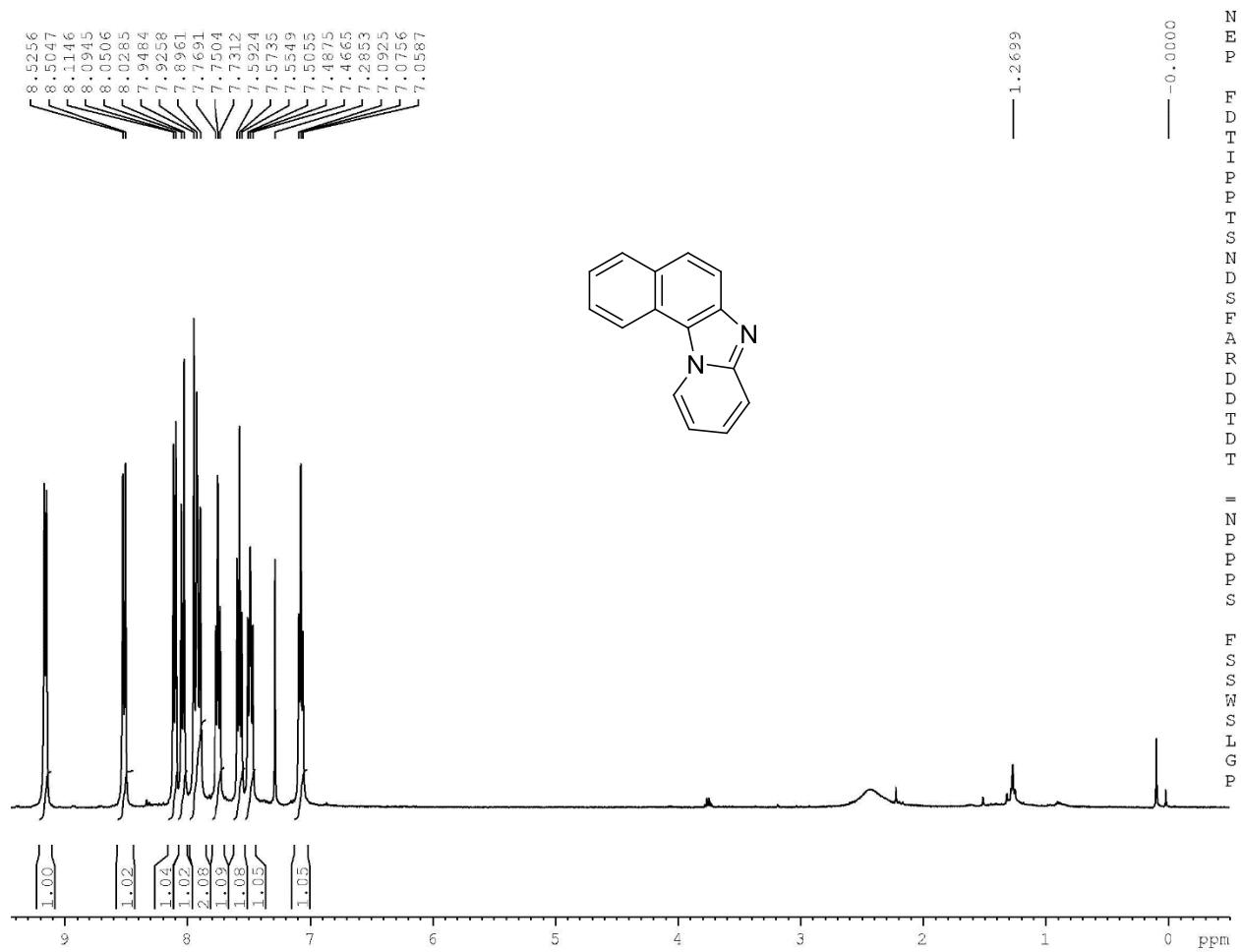
¹H NMR spectra of compound 3n



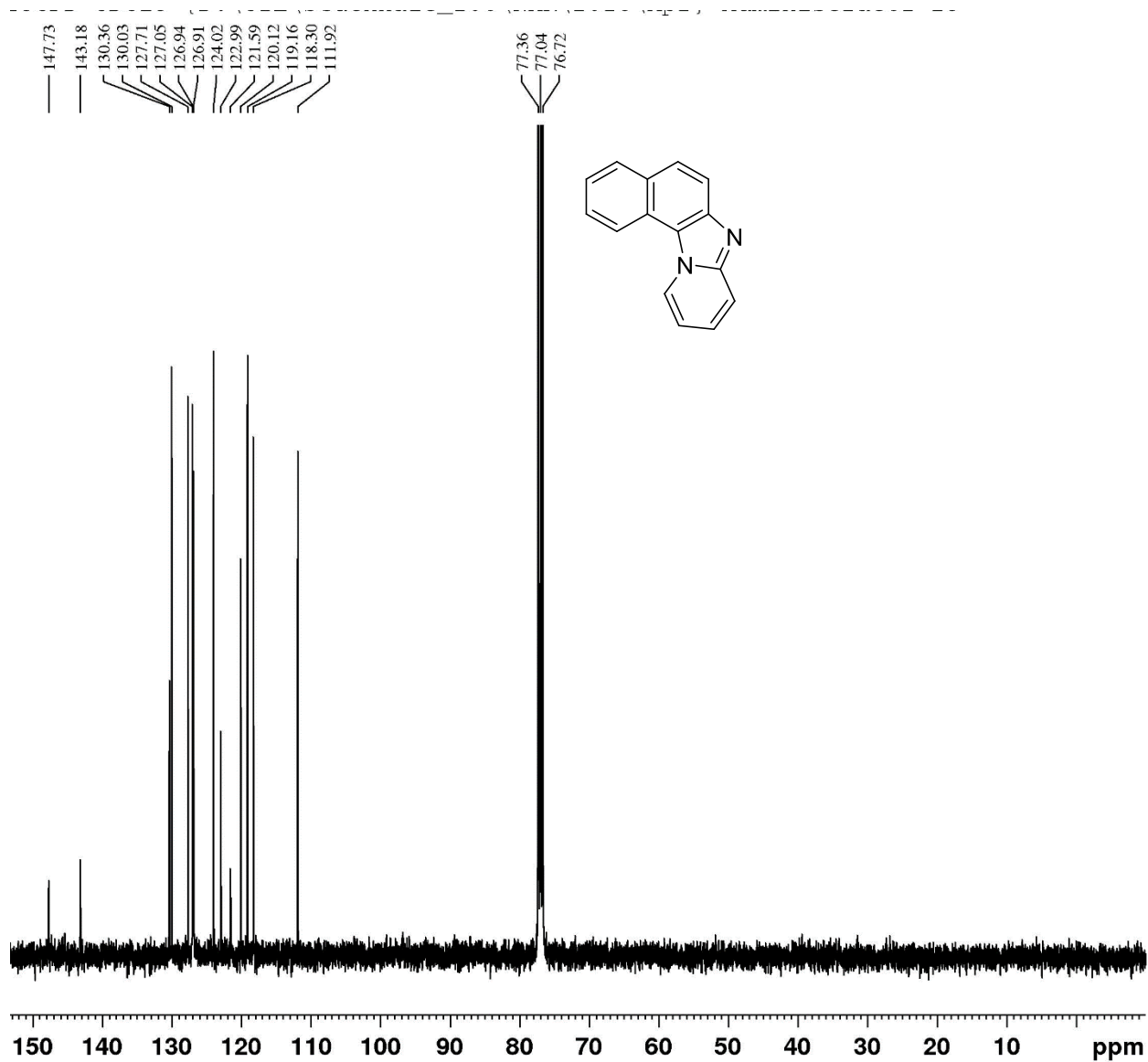
¹³C NMR spectra of compound 3n



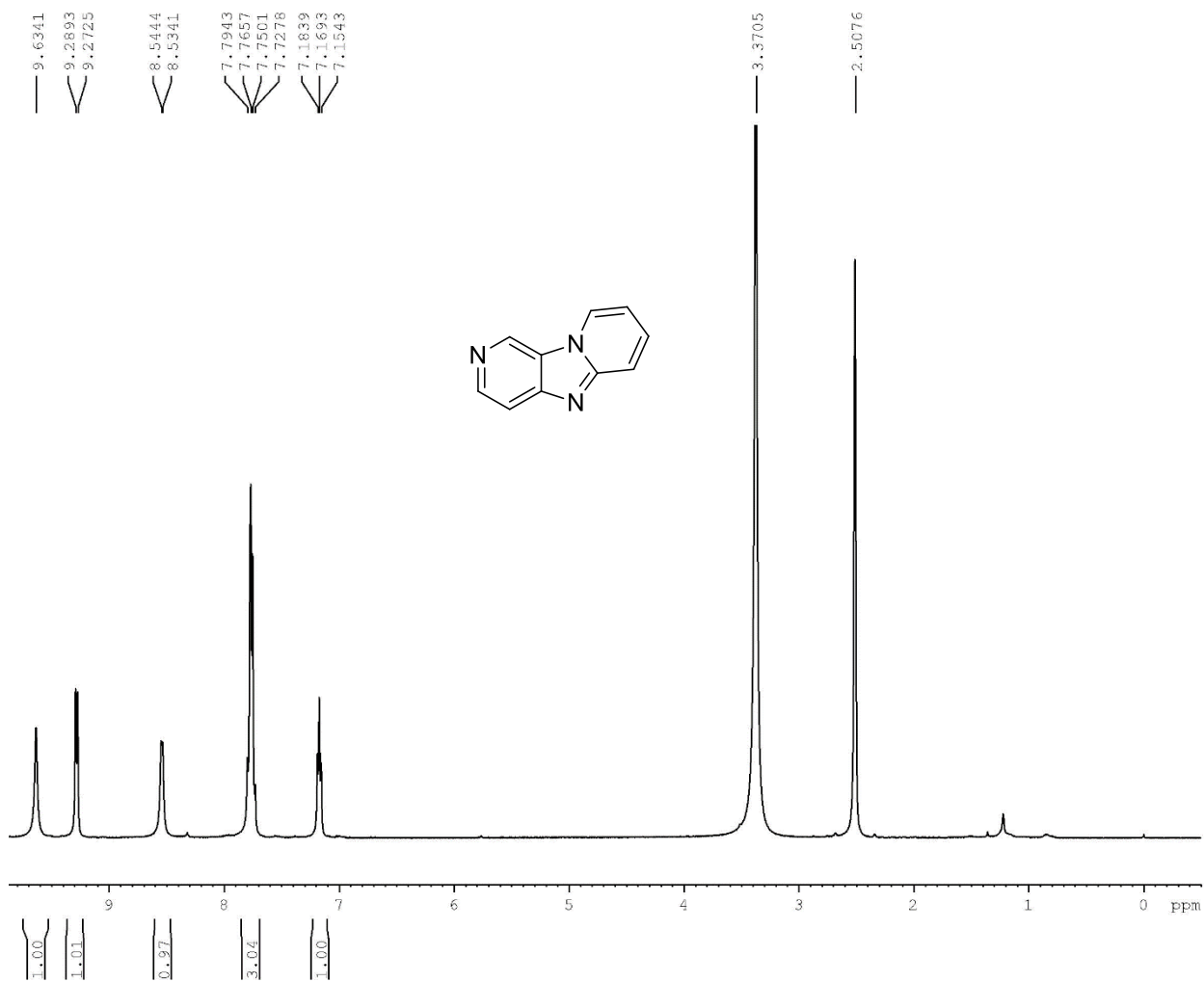
¹H NMR spectra of compound 3o



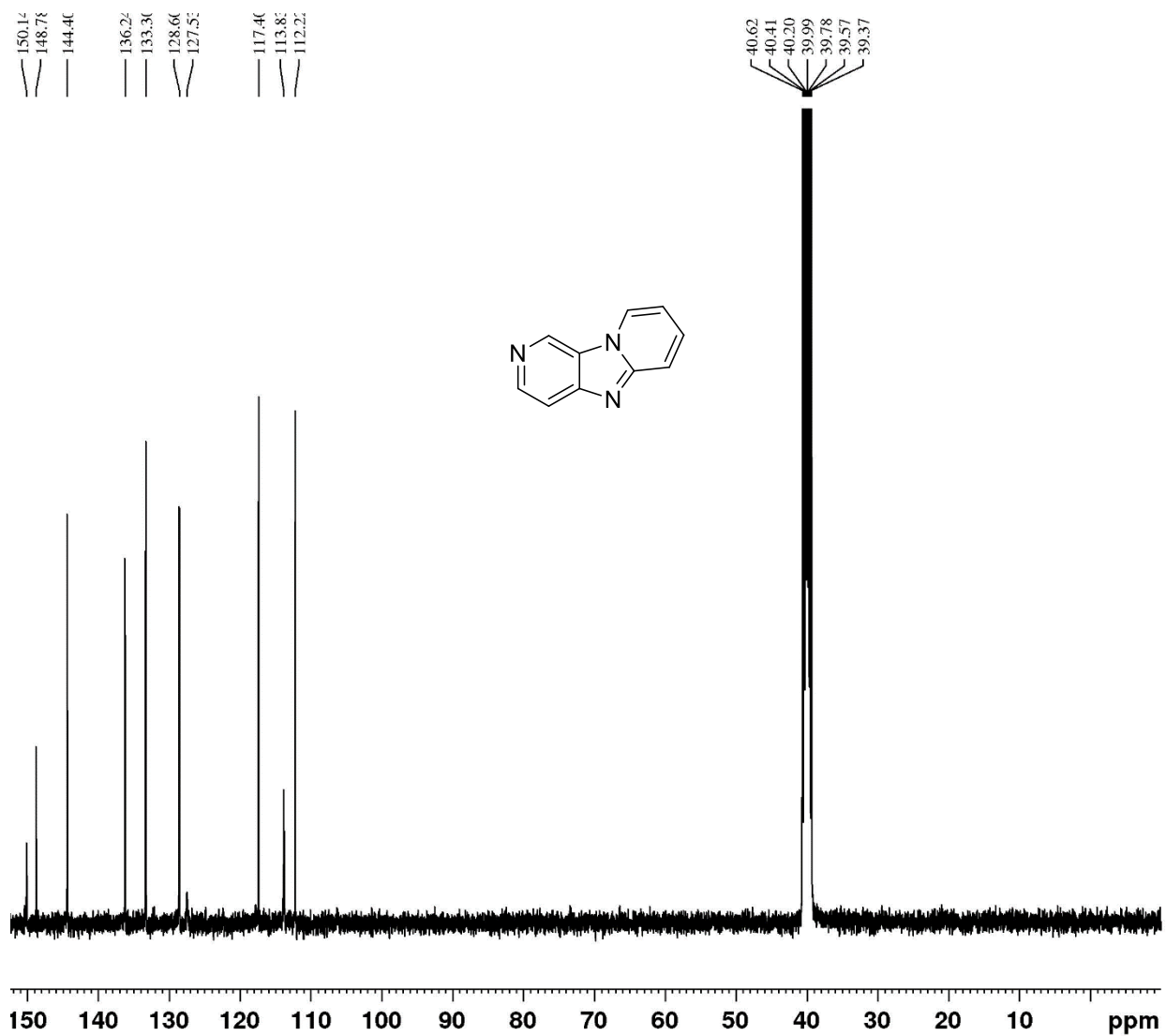
¹³C NMR spectra of compound 3o



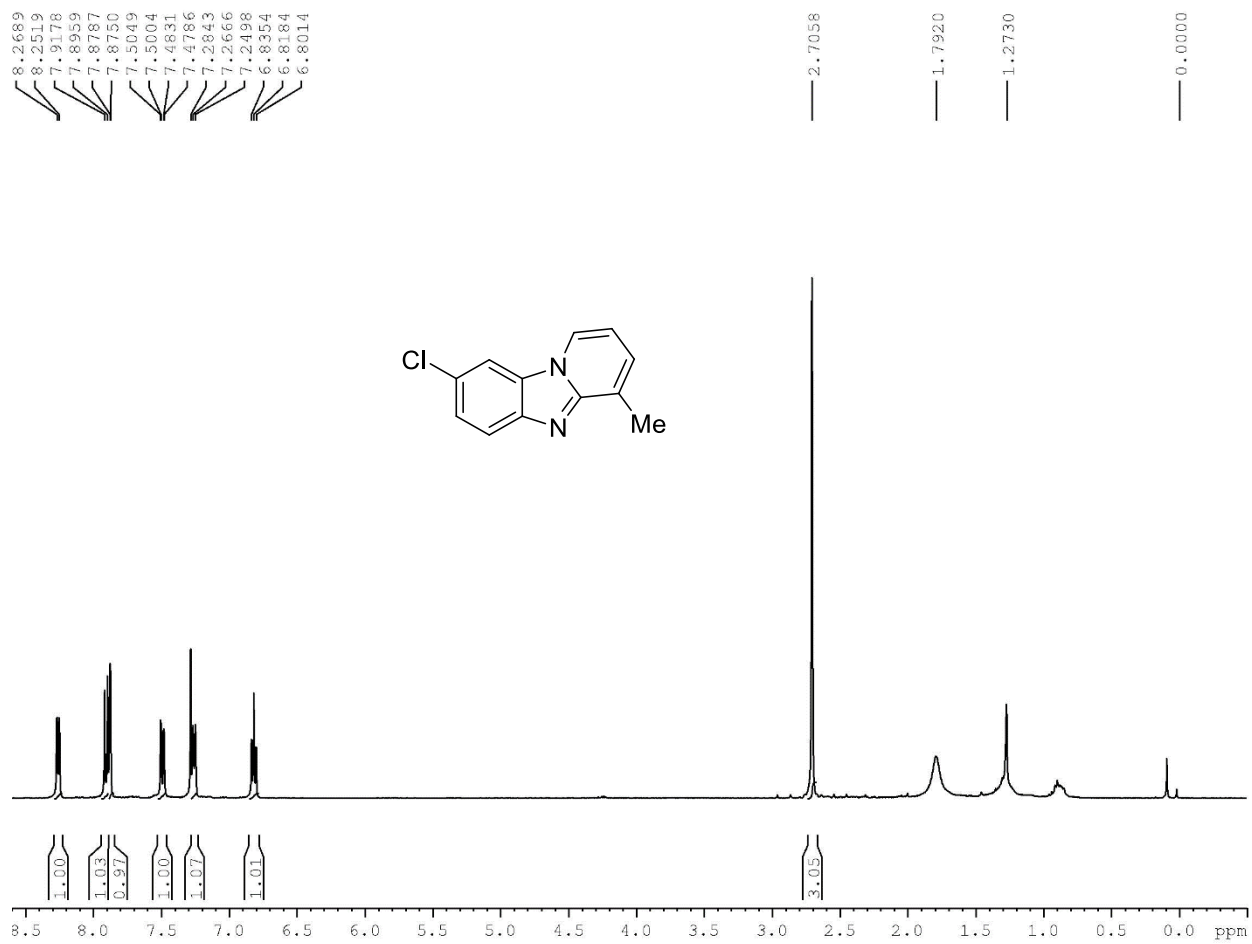
¹H NMR spectra of compound 3p



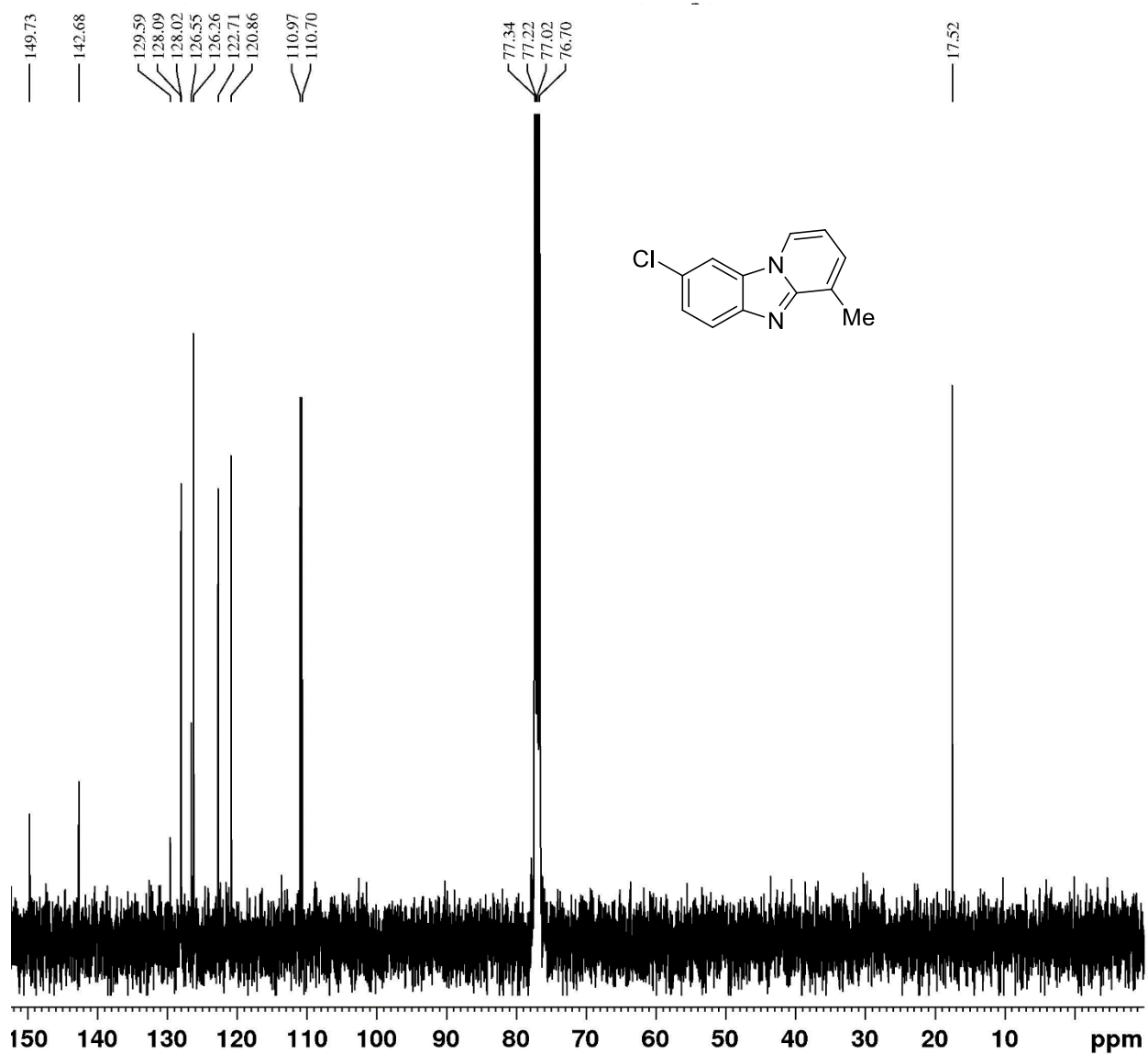
¹³C NMR spectra of compound 3p



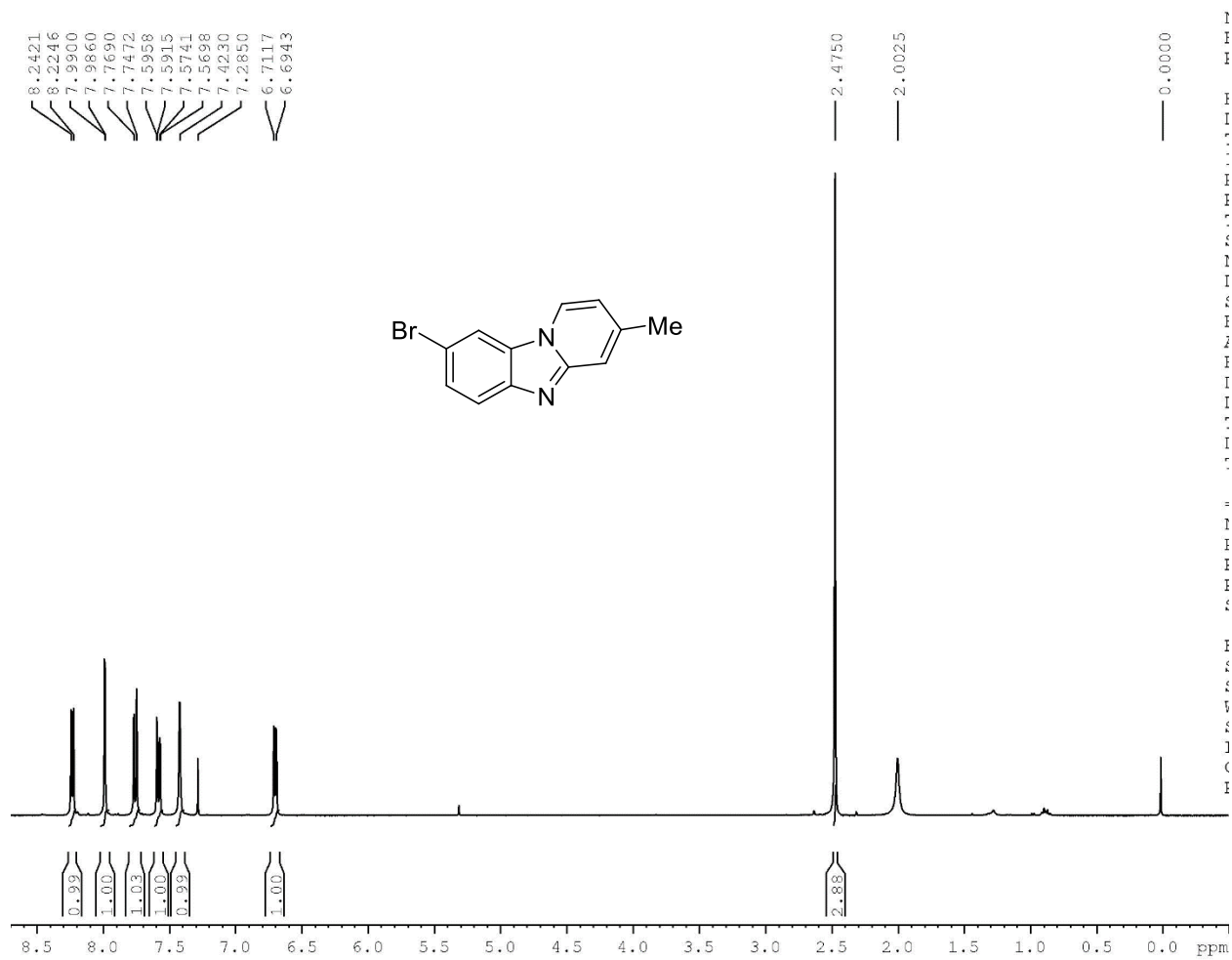
¹H NMR spectra of compound 3q



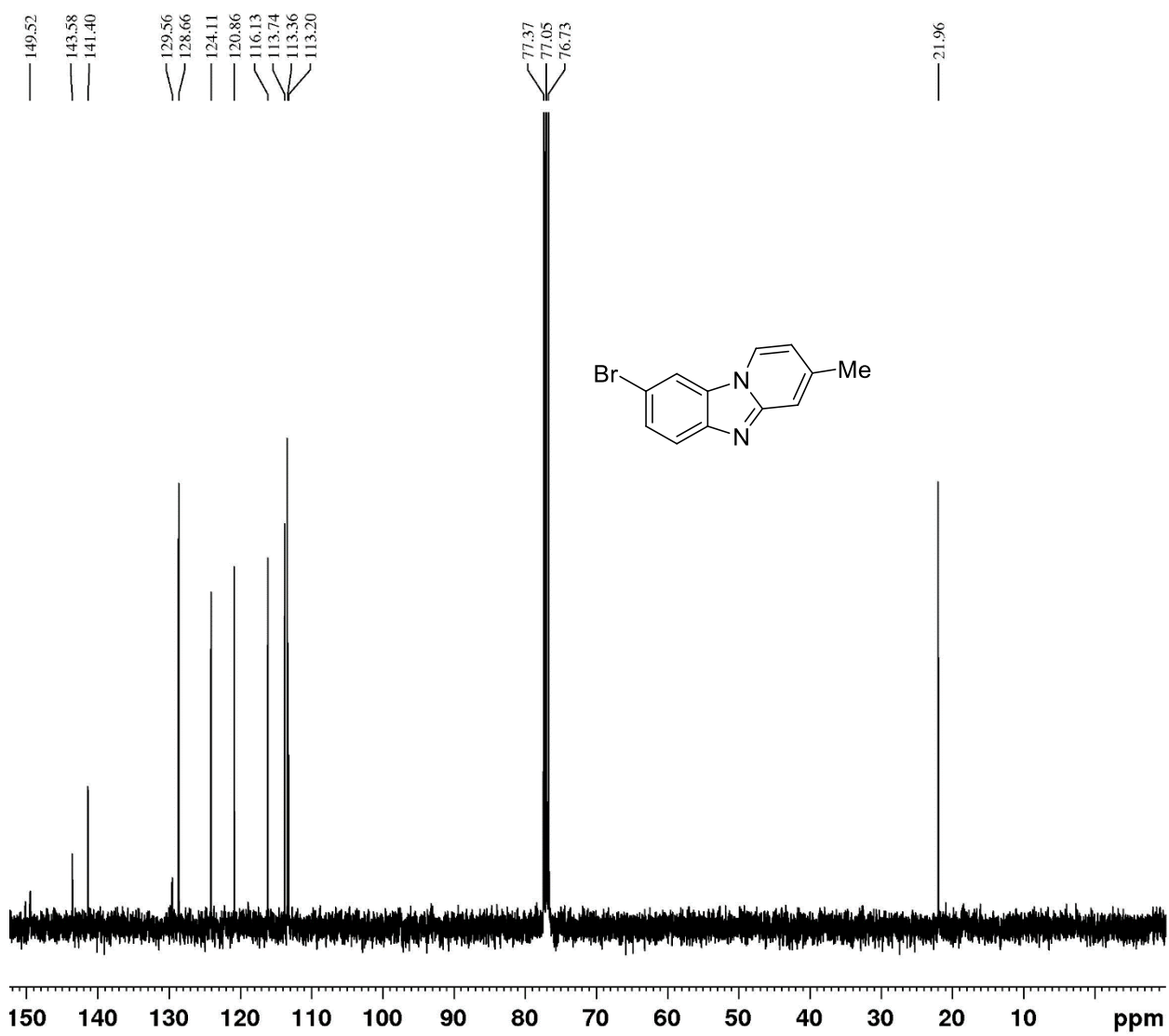
¹³C NMR spectra of compound 3q



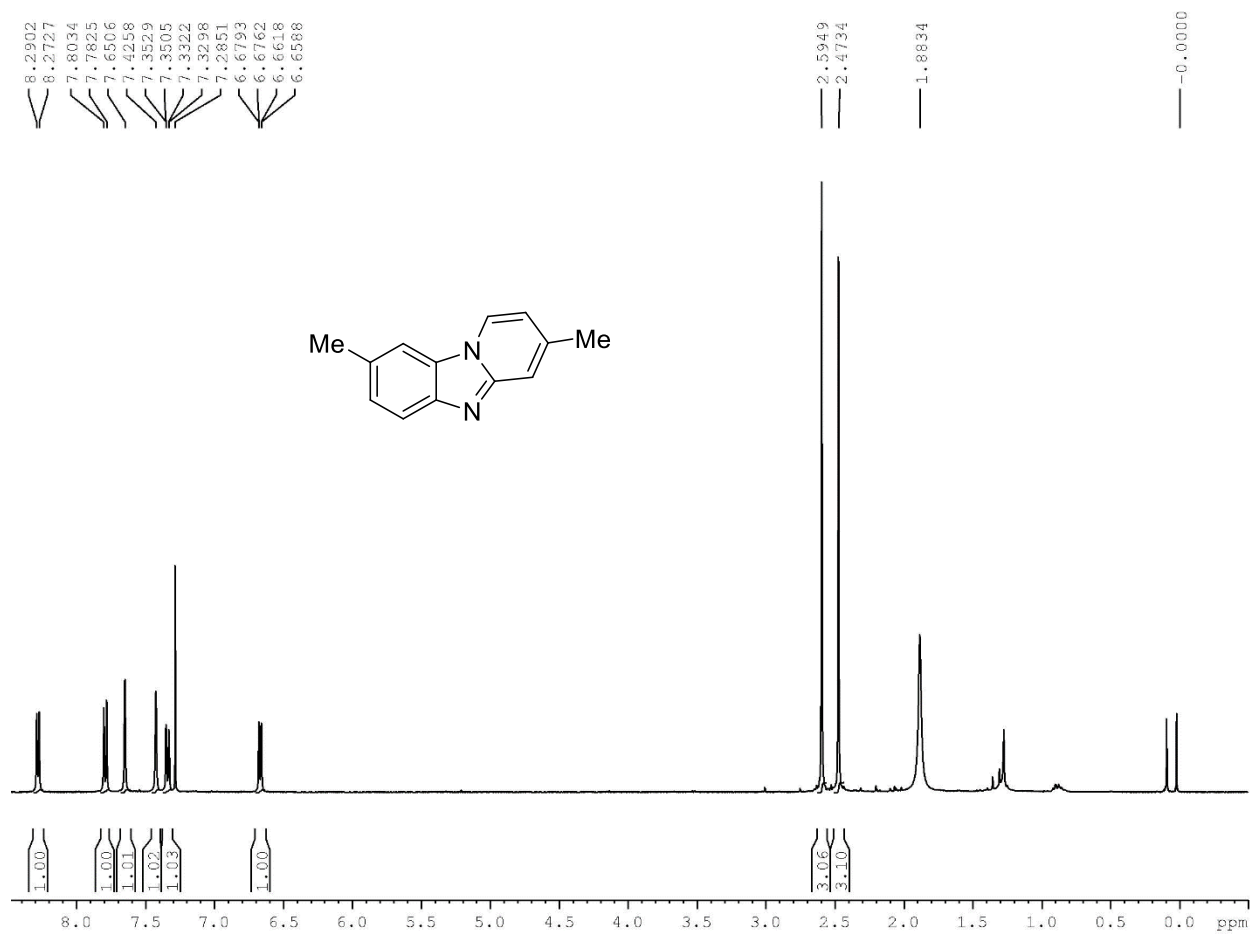
¹H NMR spectra of compound 3r



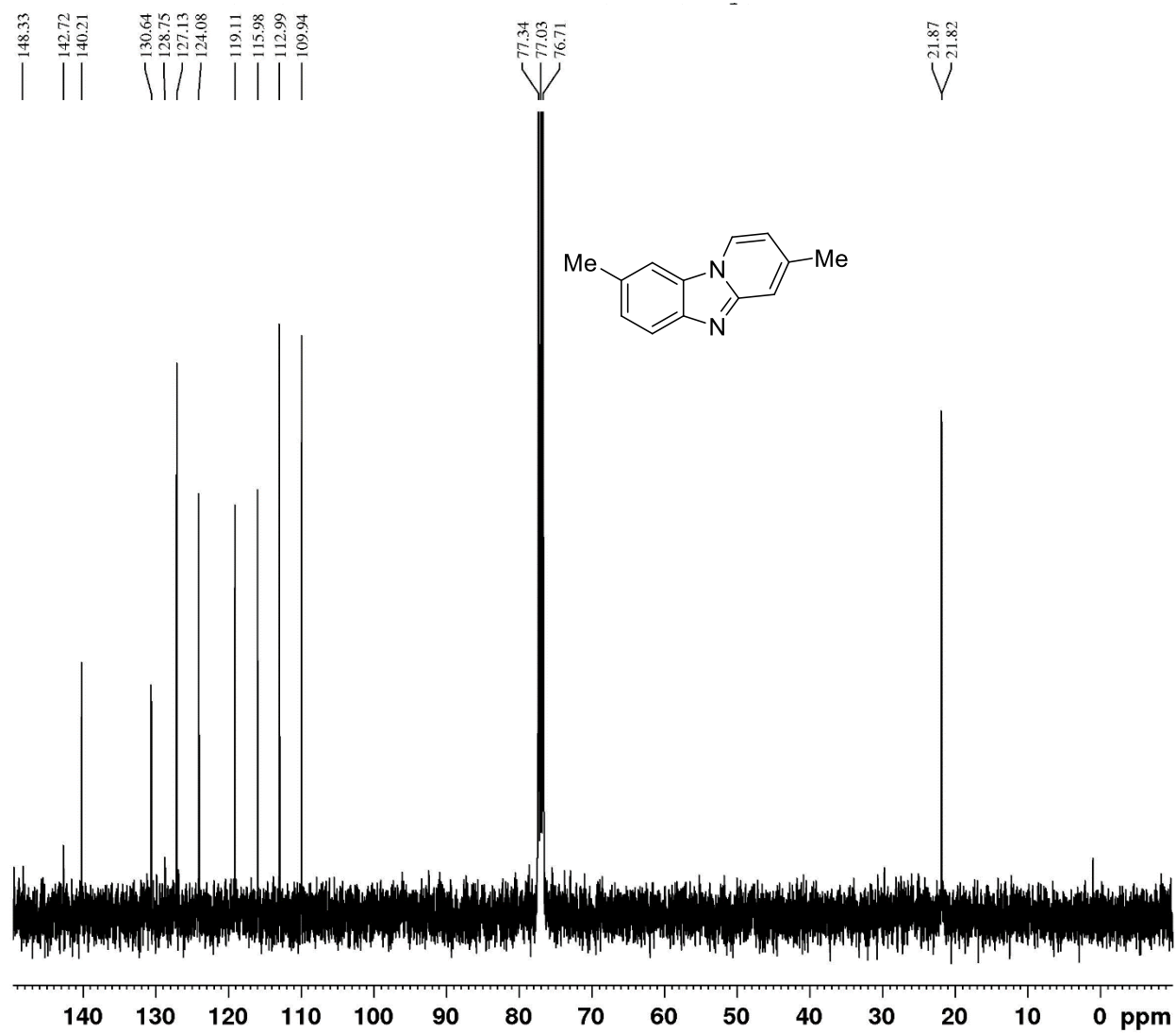
¹³C NMR spectra of compound 3r



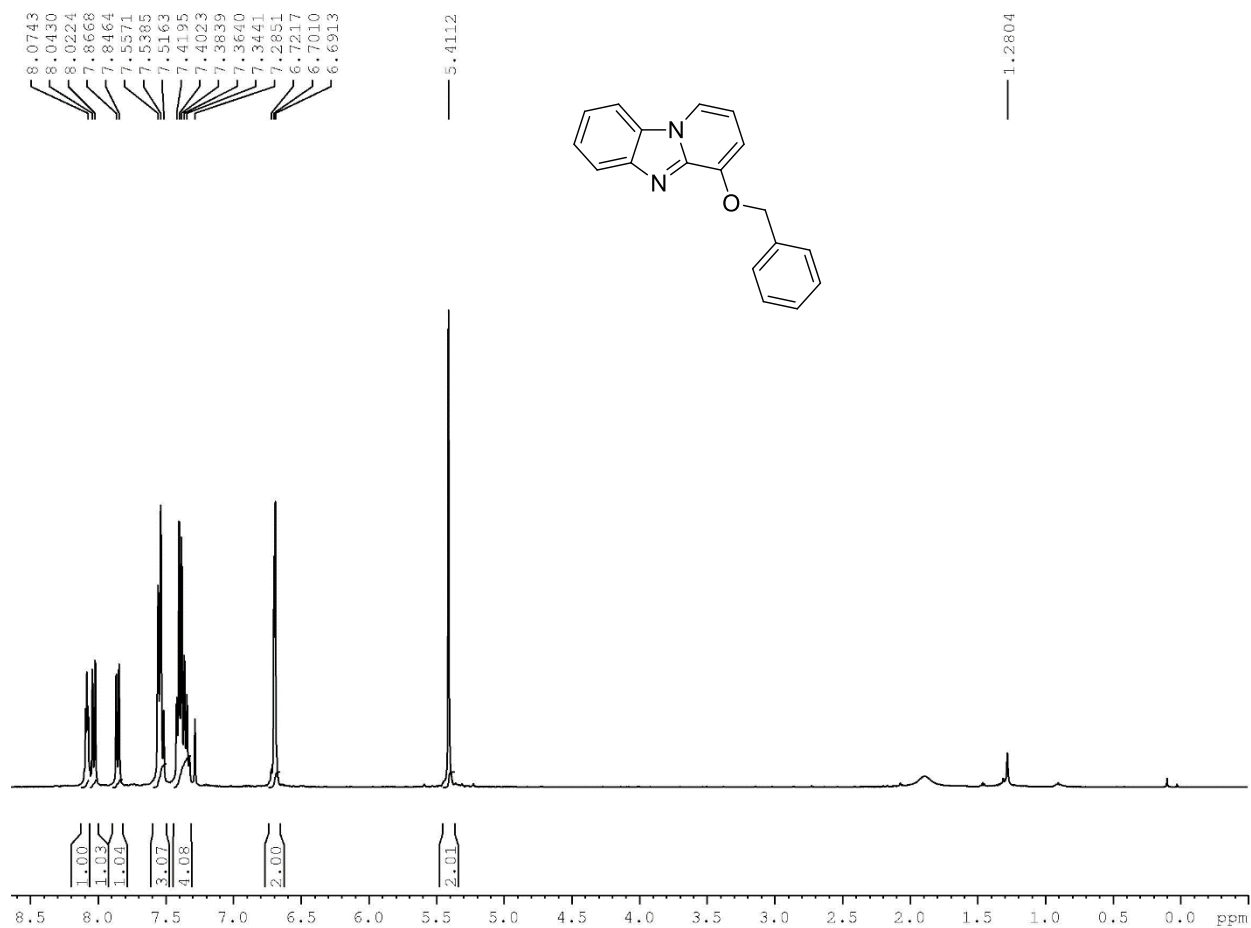
¹H NMR spectra of compound 3s



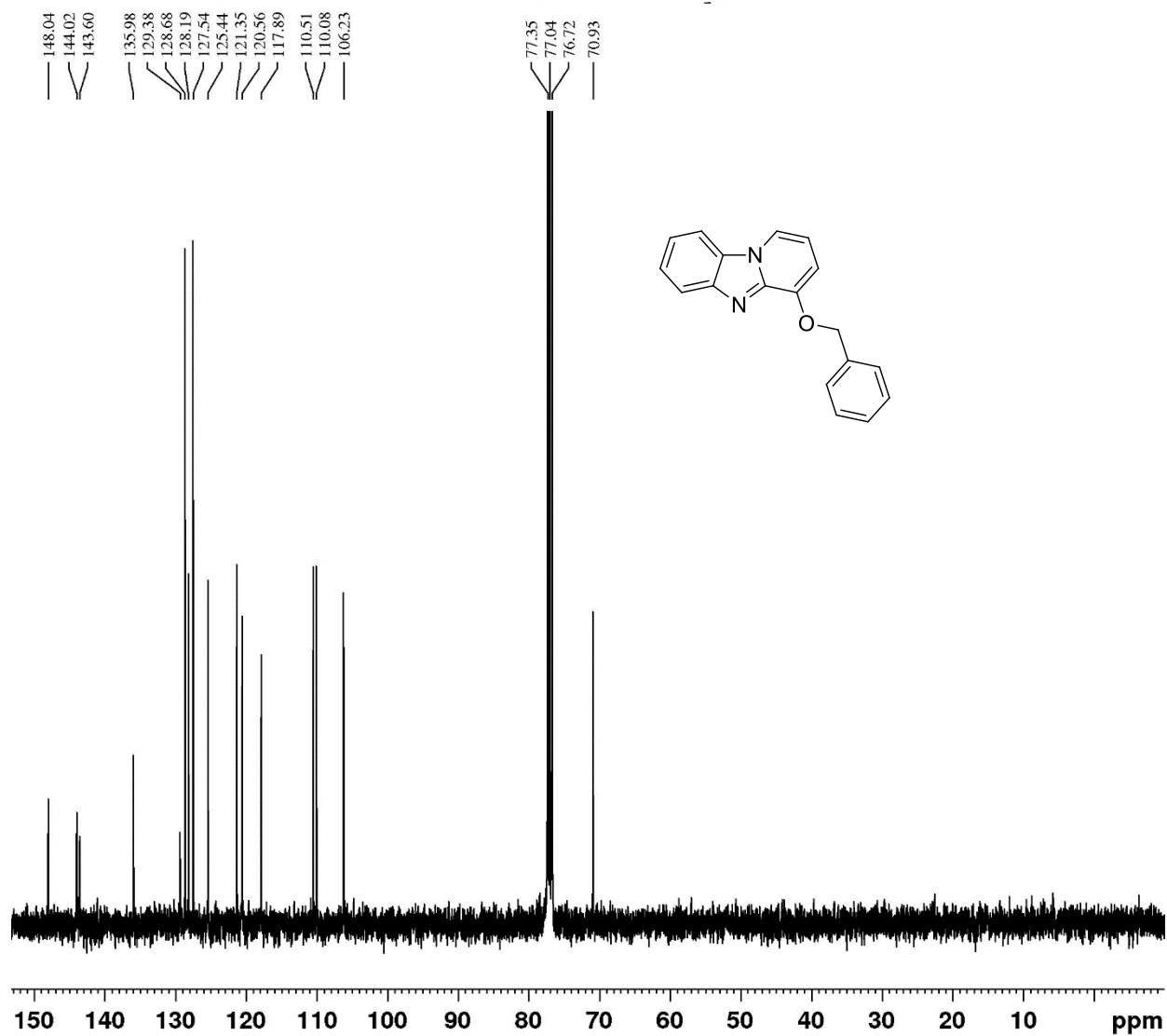
¹³C NMR spectra of compound 3s



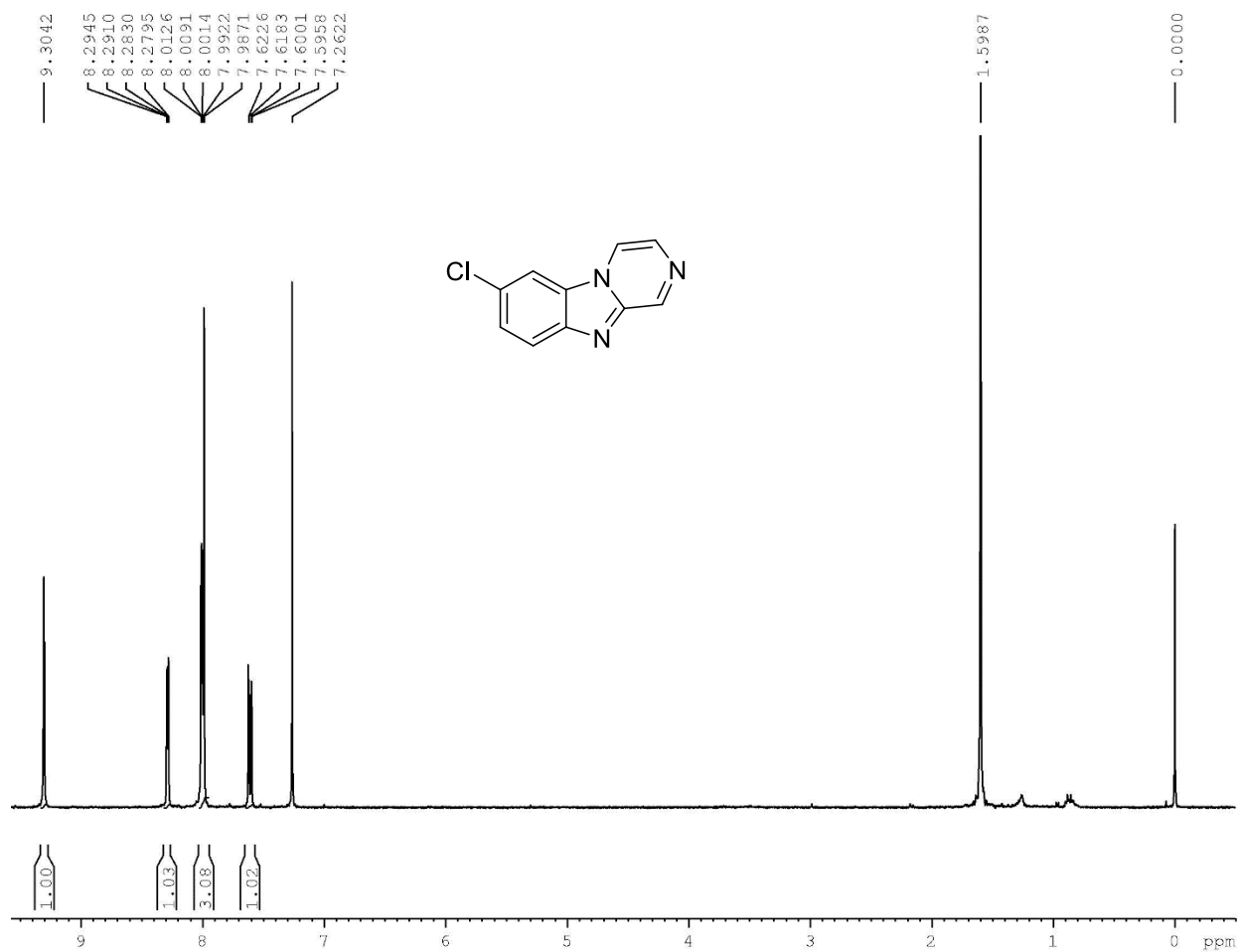
¹H NMR spectra of compound 3t



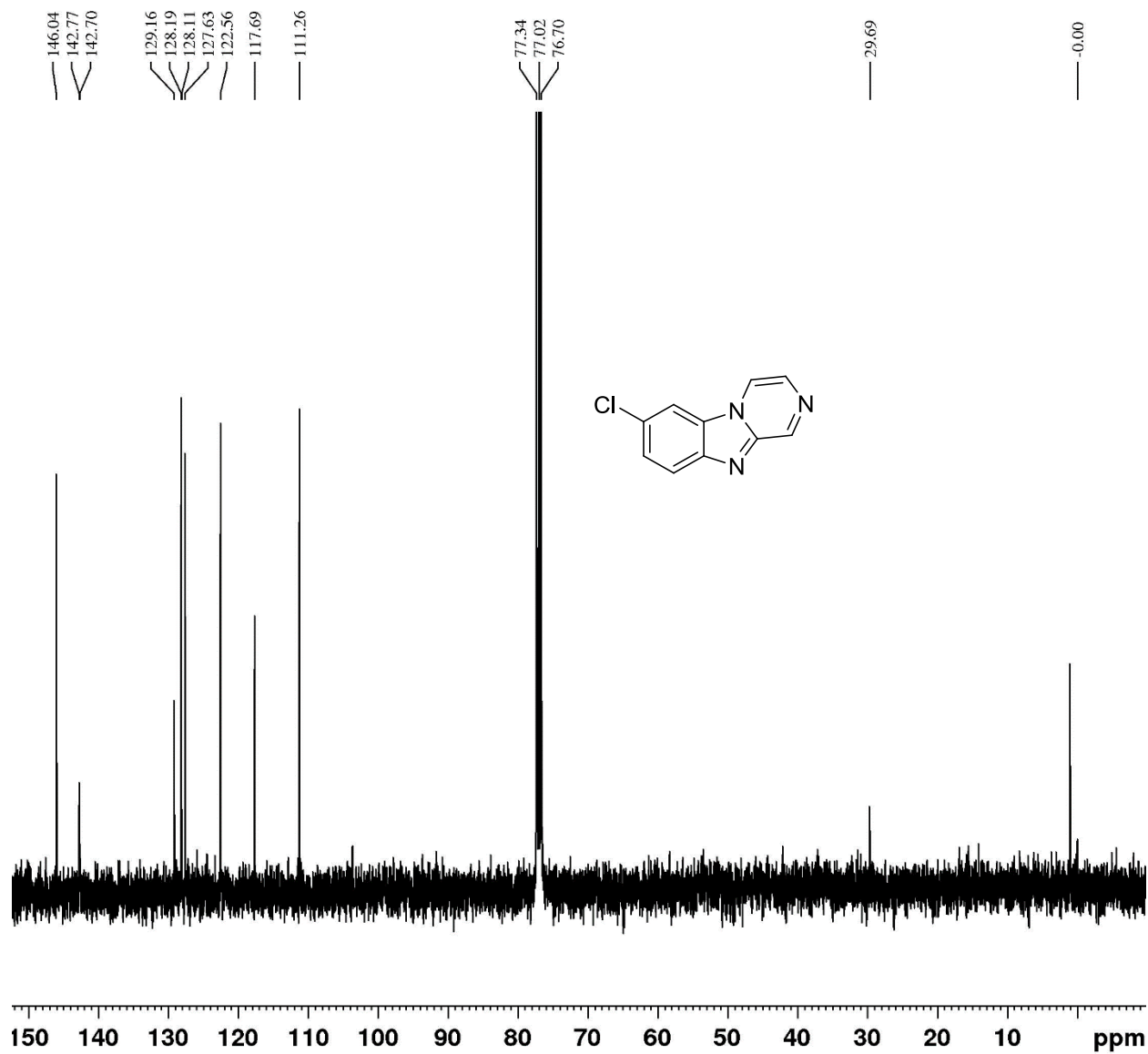
¹³C NMR spectra of compound 3t



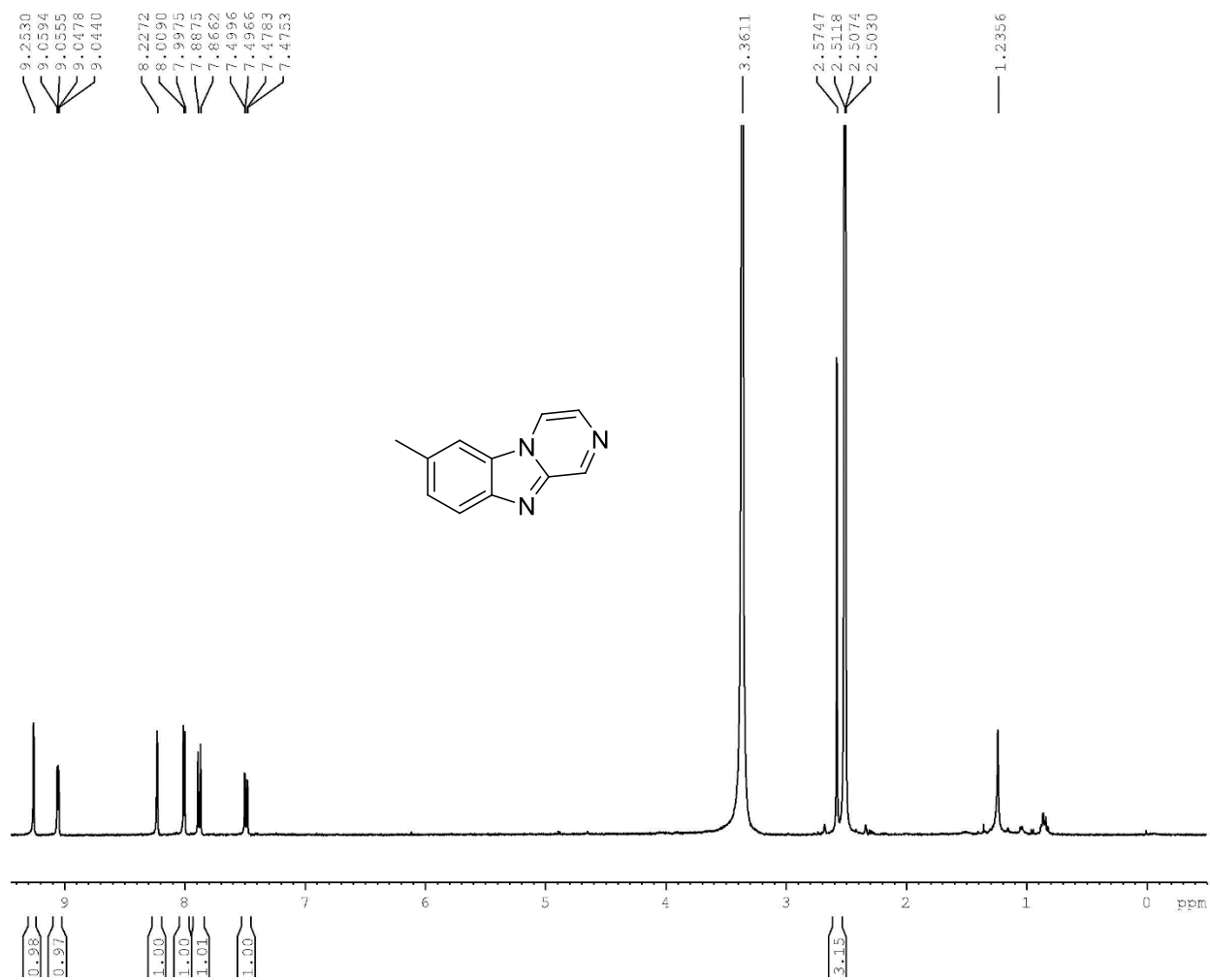
¹H NMR spectra of compound 3u



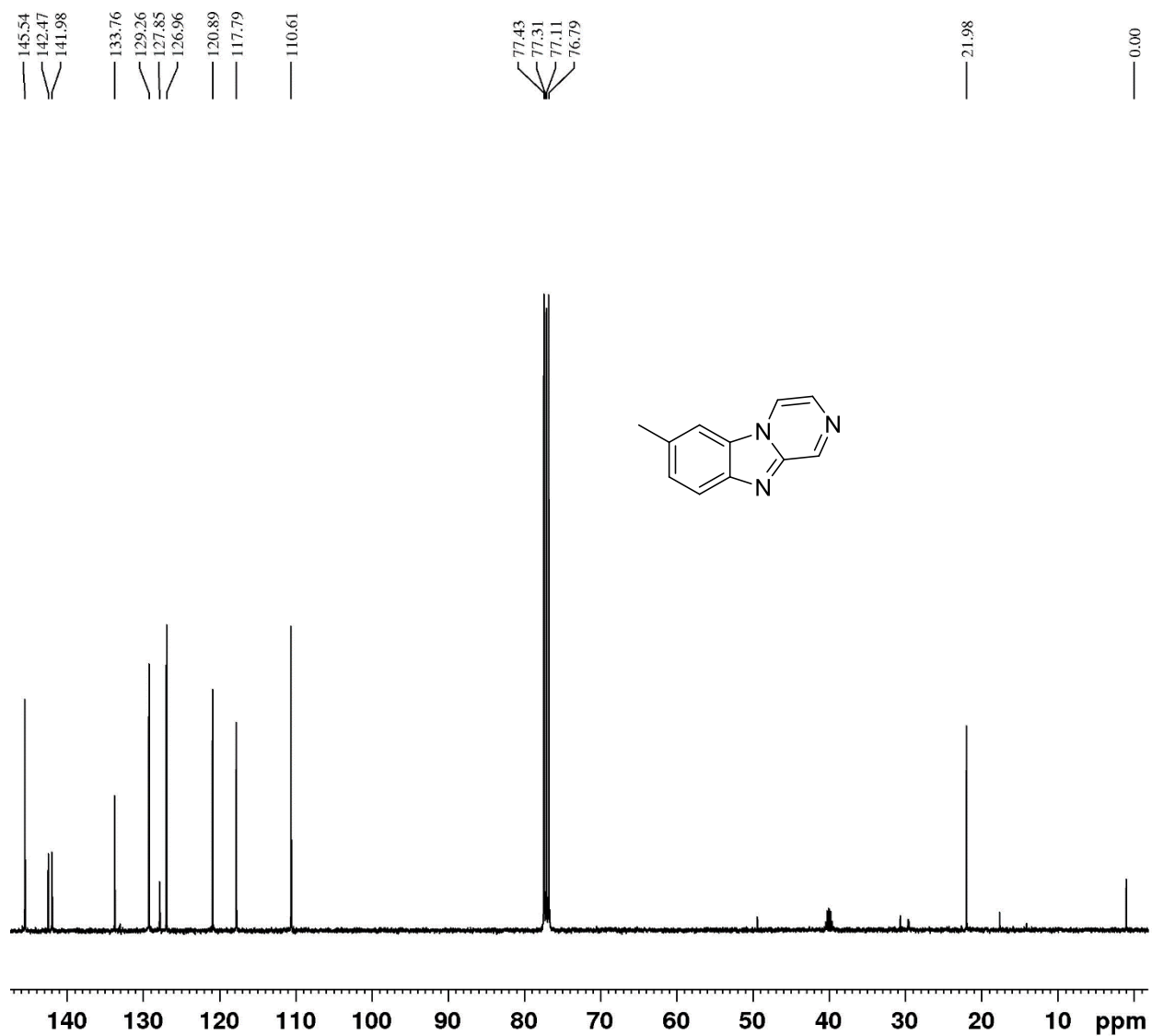
¹³C NMR spectra of compound 3u



¹H NMR spectra of compound 3v

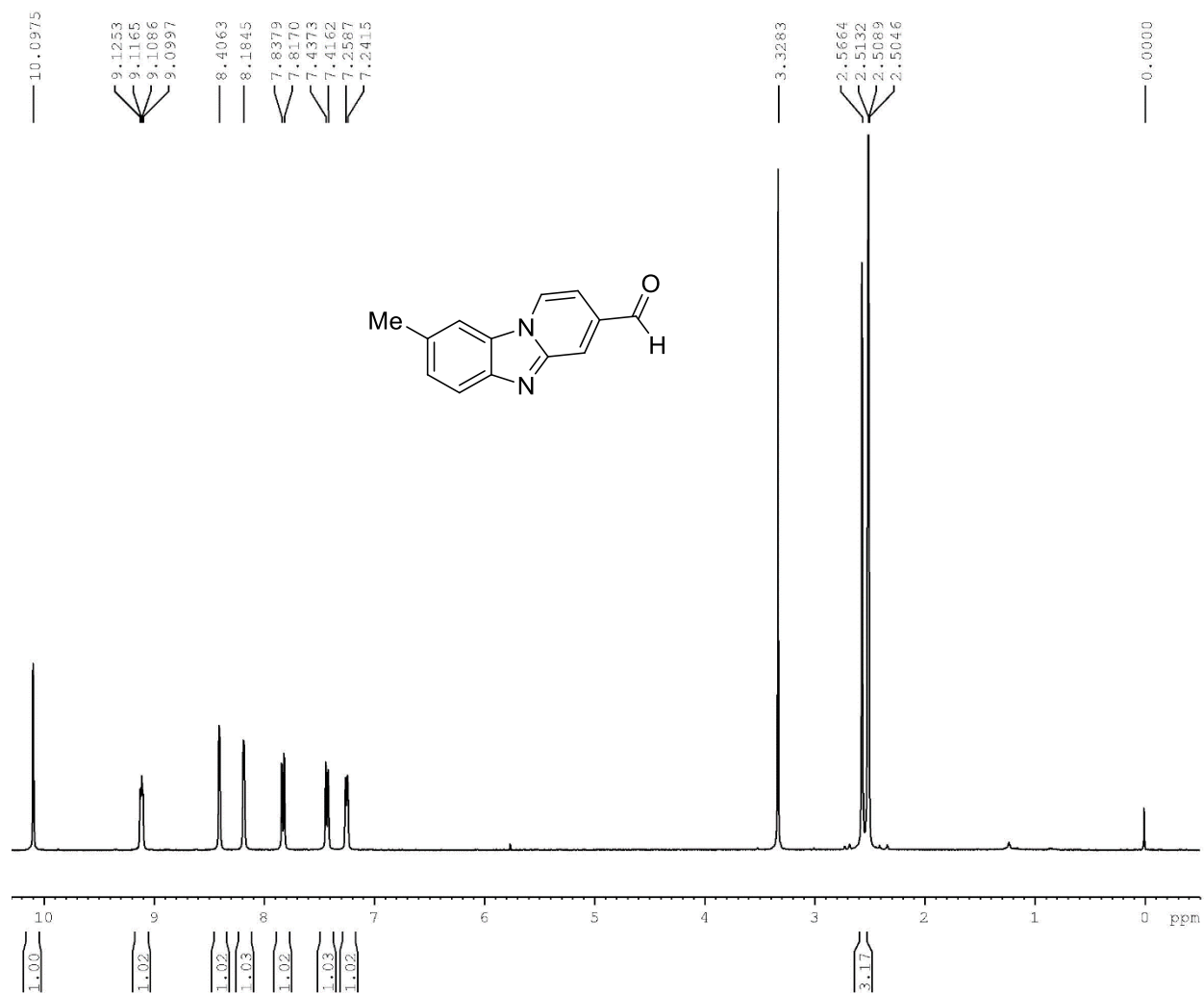


¹³C NMR spectra of compound 3v

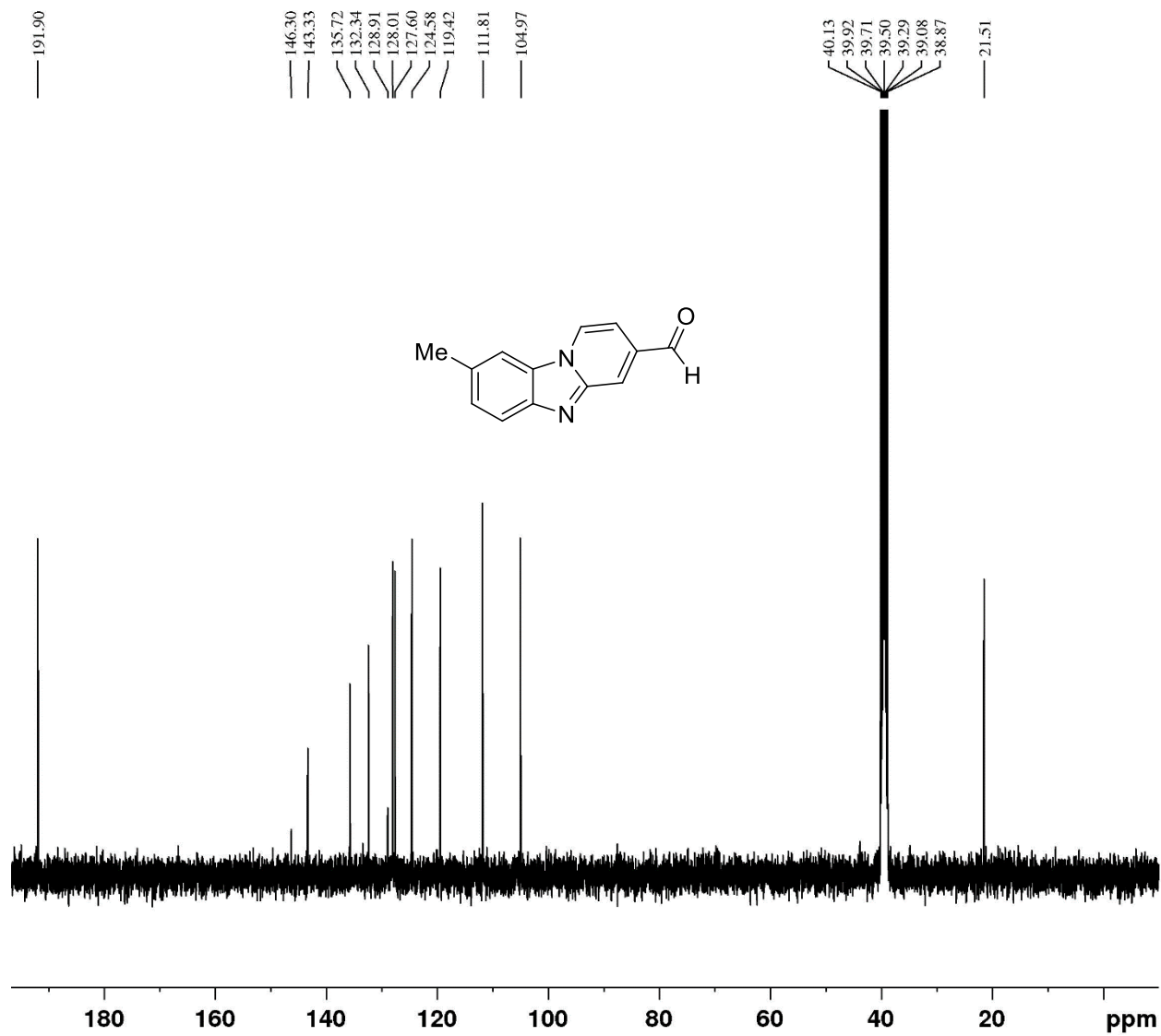


Spectral data of intermediates and side product and intermediates

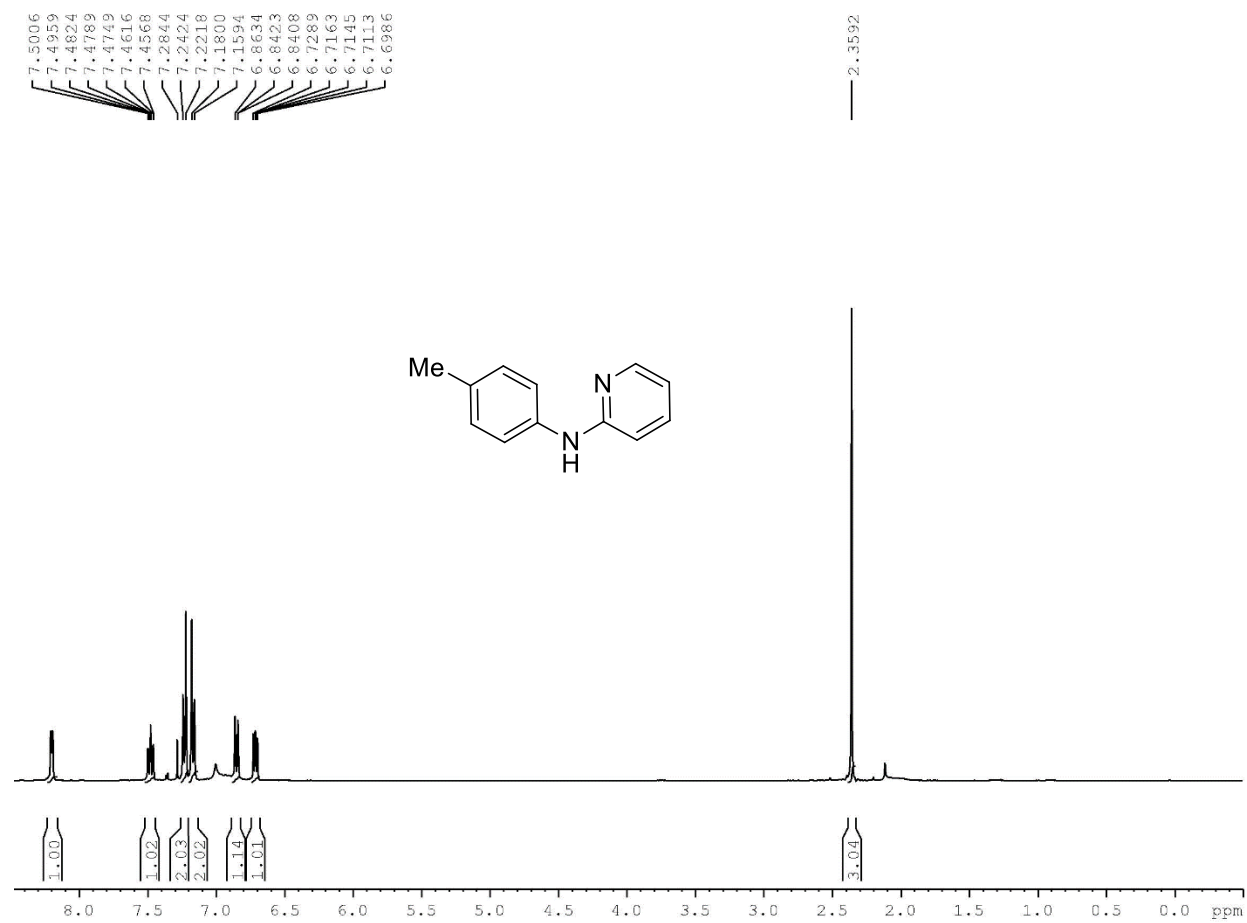
¹H NMR spectra of compound 4s



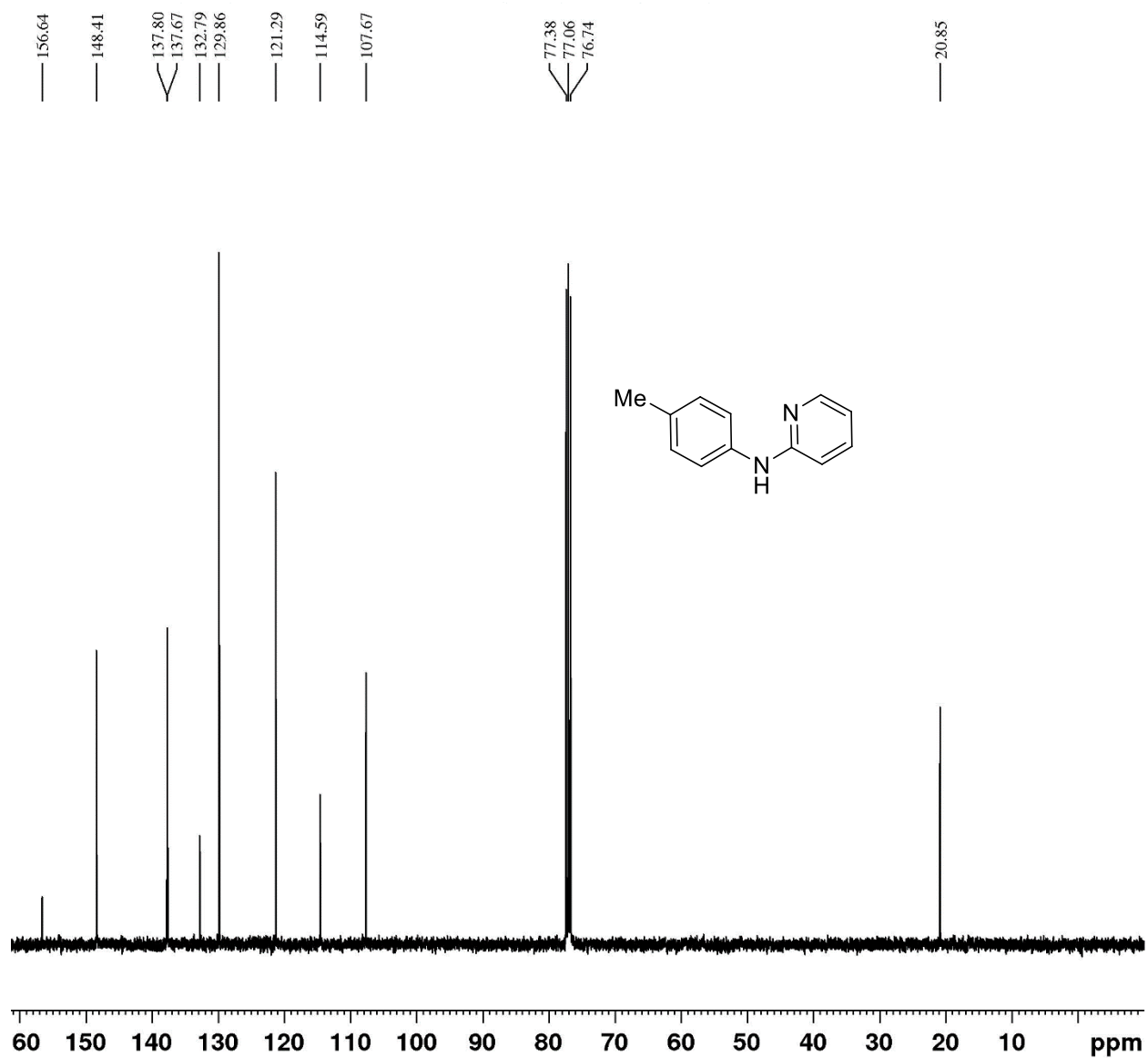
¹³C NMR spectra of compound 4s



¹H NMR spectra of compound 3ai



¹³C NMR spectra of compound 3ai

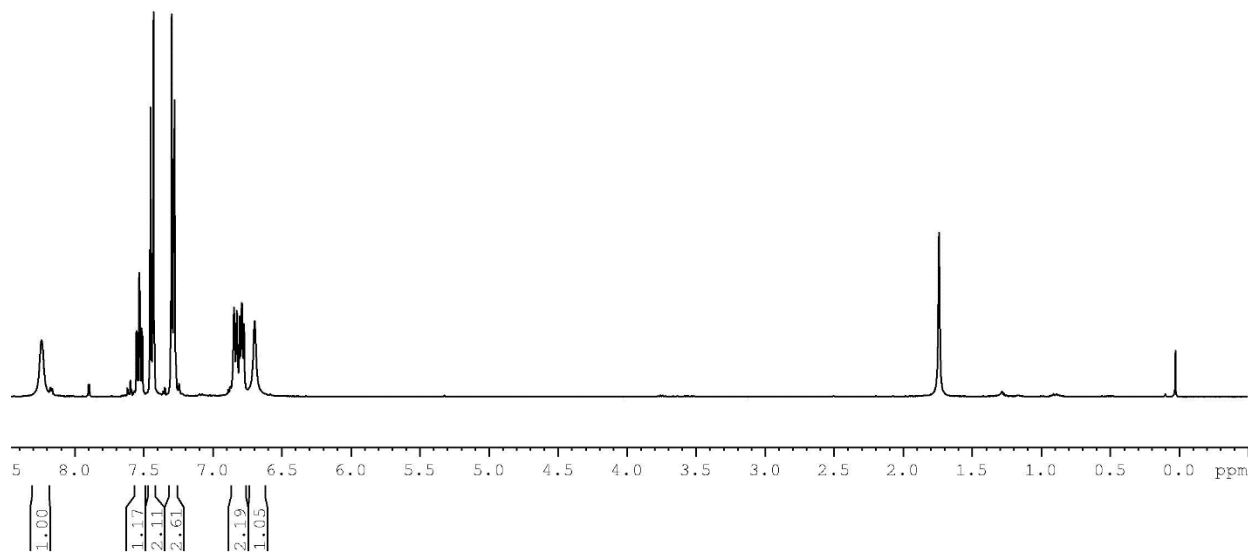
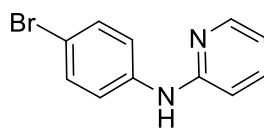


¹H NMR spectra of compound 3ci

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6.7741
6.6966

1.7382

0.0000



¹³C NMR spectra of compound 3ci

