

Supporting Information for:

Pyridine Activation via Copper(I)-Catalyzed Annulation toward Indolizines

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General Methods: ^1H NMR and ^{13}C NMR spectra were recorded at room temperature in CDCl_3 , on a Bruker AC-300 (300 and 75.5 MHz), a Bruker AMX-400 (400 and 100 MHz) or a Bruker AV-600 spectrometers. Chemical shifts are given in ppm relative to TMS (^1H , 0.0 ppm) or CDCl_3 (^{13}C , 77.0 ppm). Carbon multiplicities were assigned by DEPT techniques. High-resolution mass spectra (HRMS) were determined by Universidad de Oviedo, Universidad de Burgos and Universidad de Vigo (CACTI) with a Finnigan Mat95 and a VG AutoSpec M Mass Spectrometers respectively.

TLC was performed on aluminum-backed plates with silica gel 60 with F_{254} indicator. All reactions were carried out under nitrogen using standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 . Flash column chromatography was carried out on silica gel (230-240 mesh).

This study was carried out using pyridine derivatives **1a-v** and vinyldiazoacetates **2a-d** (Figure 1). Vinyldiazoacetates were prepared according to literature procedures.¹ 4-

TsO-pyridine **1j** was prepared by tosylation of commercial 4-hydroxypyridine.² All other reagents and solvents used in this work were of the best commercial grade available and used without further purification.

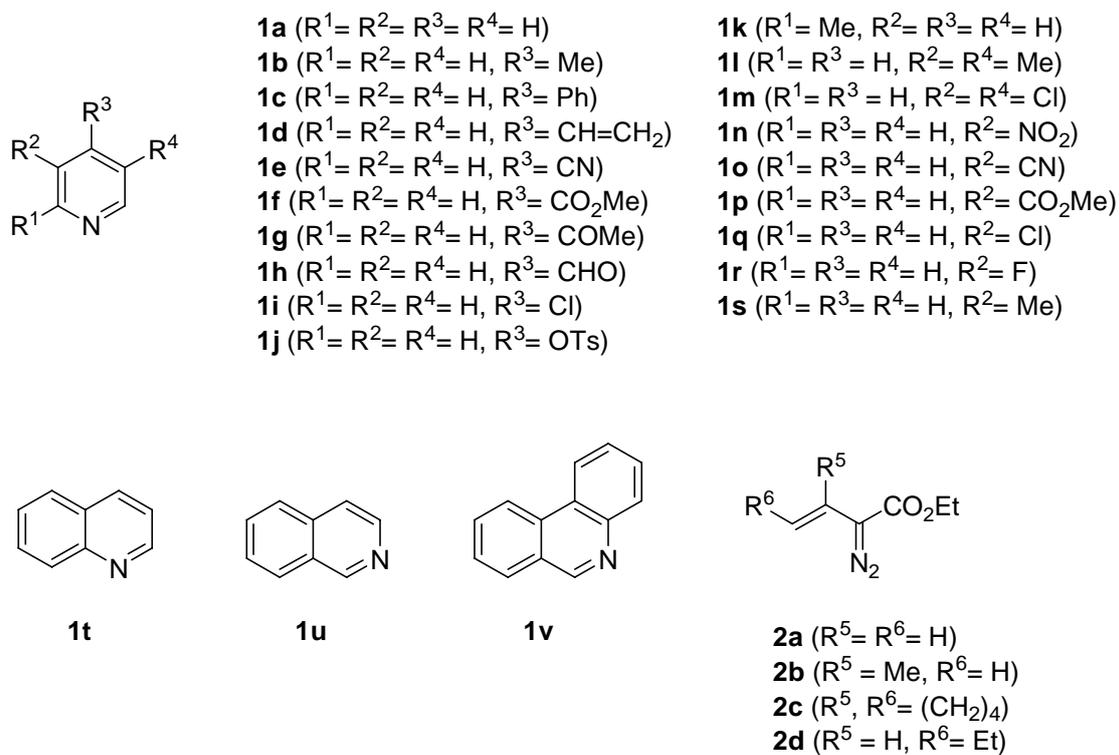
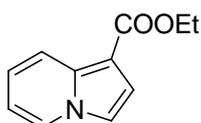


Figure 1. Starting materials used in this work

General Procedure for the Cu(I)-Catalyzed Reaction of Pyridine Derivatives 1 and Vinyldiazoacetates 2: Synthesis of Indolizine Derivatives 3-8

CuBr (3.6 mg, 0.025 mmol) was added to a solution of pyridine **1** (0.5 mmol) and diazocompound **2** (0.5 mmol) in CH₂Cl₂ (5 mL). The mixture was stirred at room temperature with protection from light until disappearance of the starting diazo compound (checked by TLC; 4-14 h). The solvent was removed under reduced pressure and the residue was purified by flash chromatography over a short, light-shielded column of deoxygenated SiO₂ using hexane-ethyl acetate (5:1) as eluent to give the corresponding indolizine derivatives **3-8**.

Some of the reported indolizines are highly sensitive to air and light. Exposure to light and oxygen should be avoided at all steps of the procedure described above.

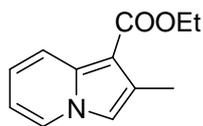


3aa

The general procedure was followed using pyridine **1a** (40 mg) and vinyldiazoacetate **2a** (70 mg). Final chromatographic purification afforded indolizine **3aa** (32 mg, 34%).

Ethyl indolizine-1-carboxylate 3aa: ¹H-NMR (300 MHz, CDCl₃): 1.43 (t, *J* = 7.2 Hz, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 6.6 Hz, 1H), 7.05 (dd, *J* = 9.0 and 6.6 Hz, 1H), 7.24-7.28 (m, 2H), 8.01 (d, *J* = 6.9 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H); ¹³C-NMR (75 Mz, CDCl₃): 14.6 (CH₃), 59.4 (CH₂), 104.0 (C), 112.3 (CH), 113.5 (CH), 116.2 (CH), 119.9 (CH), 122.1 (CH), 125.9 (CH), 135.7 (C), 164.9 (C).

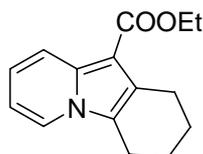
The NMR data of compound **3aa** are consistent with those reported in the literature.³



3ab

The general procedure was followed using pyridine **1a** (40 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3ab** (91 mg, 90%).

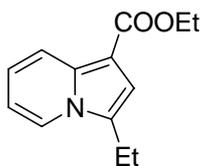
Ethyl 2-methylindolizine-1-carboxylate 3ab: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.43 (t, $J = 7.2$ Hz, 3H), 2.50 (s, 3H), 4.38 (q, $J = 7.2$ Hz, 2H), 6.65 (t, $J = 6.8$ Hz, 1H), 7.00 (t, $J = 8.8$, 1H), 7.07 (s, 1H), 7.90 (d, $J = 6.8$ Hz, 1H), 8.14 (d, $J = 8.8$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.9 (CH_3), 14.6 (CH_3), 59.1 (CH_2), 102.6 (C), 111.9 (CH), 113.2 (CH), 119.7 (CH), 121.8 (CH), 125.2 (CH), 128.5 (C), 136.6 (C), 165.6 (C); HRMS (EI): exact mass calculated for $[\text{C}_{12}\text{H}_{13}\text{NO}_2]^+$ (M^+), 203.0946; found 203.0949.



3ac

The general procedure was followed using pyridine **1a** (40 mg) and vinyl diazoacetate **2c** (97 mg). Final chromatographic purification afforded indolizine **3ac** (61 mg, 50%).

Ethyl 1,2,3,4-tetrahydropyrido[1,2-a]indole-10-carboxylate 3ac: $^1\text{H-NMR}$ (400 MHz, CDCl_3): 1.41 (t, $J = 7.2$ Hz, 3H), 1.86-1.98 (m, 4H), 2.67-2.70 (m, 2H), 3.00-3.03 (m, 2H), 4.36 (q, $J = 7.2$ Hz, 2H), 6.71 (t, $J = 6.8$ Hz, 1H), 6.98-7.02 (m, 1H), 7.71 (d, $J = 6.8$ Hz, 1H), 8.18 (d, $J = 9.2$ Hz, 1H); $^{13}\text{C-NMR}$ (100 Mz, CDCl_3): 14.6 (CH_3), 21.1 (CH_2), 22.3 (CH_2), 23.3 (CH_2), 23.8 (CH_2), 58.9 (CH_2), 100.7 (C), 111.7 (CH), 119.4 (CH), 120.9 (CH), 121.4 (C), 121.7 (CH), 126.8 (C), 135.5 (C), 165.7 (C); HRMS (EI): exact mass calculated for $[\text{C}_{15}\text{H}_{17}\text{NO}_2]^+$ (M^+), 243.1259; found 243.1268.

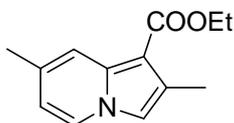


3ad

The general procedure was followed using pyridine **1a** (40 mg) and vinyl diazoacetate **2d** (84 mg). Final chromatographic purification afforded indolizine **3ad** (27 mg, 25%).

Ethyl 3-ethylindolizine-1-carboxylate 3ad: $^1\text{H-NMR}$ (CDCl_3 , 600 MHz): 1.43 (t, $J = 7.2$ Hz, 3H), 1.44 (t, $J = 7.2$ Hz, 3H), 2.81 (q, $J = 7.2$ Hz, 2H), 4.39 (q, $J = 7.2$ Hz, 2H), 6.77 (t, $J = 6.6$ Hz, 1H), 7.04-7.08 (m, 2H), 7.85 (d, $J = 6.6$ Hz, 1H), 8.22 (d, $J = 9.0$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 11.3 (CH_3), 14.7 (CH_3), 19.0 (CH_2), 59.4 (CH_2), 102.8 (C), 112.1 (CH), 112.9 (CH), 120.0 (CH), 121.2 (CH), 122.6 (CH), 127.1 (C), 135.7 (C), 165.2 (C); HRMS (EI): exact mass calculated for $[\text{C}_{13}\text{H}_{15}\text{NO}_2]^+$ (M^+), 217.1103; found 217.1105.

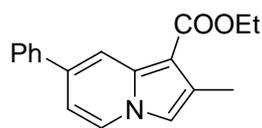
The NMR data of compound **3ad** are consistent with those reported in the literature.³



3bb

The general procedure was followed using 4-methylpyridine **1b** (47 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3bb** (102 mg, 94%).

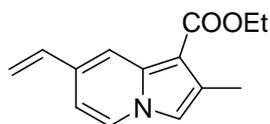
Ethyl 2,7-dimethylindolizine-1-carboxylate 3bb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.42 (t, $J = 7.2$ Hz, 3H), 2.36 (s, 3H), 2.46 (s, 3H), 4.37 (q, $J = 7.2$ Hz, 2H), 6.48 (dd, $J = 6.8$ and 1.6 Hz, 1H), 6.96 (s, 1H), 7.78 (d, $J = 6.8$ Hz, 1H), 7.93 (s, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 13.0 (CH_3), 14.7 (CH_3), 21.4 (CH_3), 59.0 (CH_2), 101.2 (C), 112.6 (CH), 114.5 (CH), 118.2 (CH), 124.7 (CH), 128.1 (C), 132.8 (C), 137.2 (C), 165.8 (C); HRMS (EI): exact mass calculated for $[\text{C}_{13}\text{H}_{15}\text{NO}_2]^+$ (M^+), 217.1103; found 217.1108.



3cb

The general procedure was followed using 4-phenylpyridine **1c** (78 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3cb** (106 mg, 76%).

Ethyl 2-methyl-7-phenylindolizine-1-carboxylate 3cb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.47 (t, $J = 7.2$ Hz, 3H), 2.53 (s, 3H), 4.42 (q, $J = 7.2$ Hz, 2H), 6.98 (dd, $J = 7.2$ and 2.1 Hz, 1H), 7.09 (s, 1H), 7.39-7.51 (m, 3H), 7.69-7.72 (m, 2H), 7.96 (dd, $J = 7.2$ and 0.9 Hz, 1H), 8.46 (s, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 13.0 (CH_3), 14.7 (CH_3), 59.2 (CH_2), 103.2 (C), 111.6 (CH), 113.0 (CH), 116.7 (CH), 125.3 (CH), 126.6 (CH), 127.8 (CH), 128.9 (CH), 129.1 (C), 134.6 (C), 136.9 (C), 139.2 (C), 165.7 (C); HRMS (EI): exact mass calculated for $[\text{C}_{18}\text{H}_{17}\text{NO}_2]^+$ (M^+), 279.1259; found 279.1258.

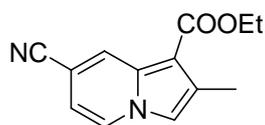


3db

The general procedure was followed using 4-vinylpyridine **1d** (53 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3db** (42 mg, 37%).

Ethyl 2-methyl-7-vinylindolizine-1-carboxylate 3db: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.44 (t, $J = 7.2$ Hz, 3H), 2.48 (s, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 5.33 (d, $J = 10.8$ Hz, 1H), 5.76 (d, $J = 17.4$ Hz, 1H), 6.72 (dd, $J = 17.4$ and 10.8 Hz, 1H), 6.84 (dd, $J = 7.2$ and 1.5 Hz, 1H), 7.03 (s, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 8.06 (s, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.9 (CH_3), 14.6 (CH_3), 59.2 (CH_2), 103.6 (C), 108.9 (CH), 113.7 (CH), 114.4 (CH_2), 118.2 (CH), 125.0 (CH), 128.8 (C), 131.5 (C), 135.7 (CH), 136.6 (C),

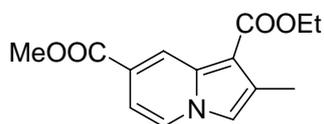
165.6 (C); HRMS (EI): exact mass calculated for $[C_{14}H_{15}NO_2]^+$ (M^+), 229.1103; found 229.1106.



3eb

The general procedure was followed using isonicotinonitrile **1e** (52 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3eb** (84 mg, 74%).

Ethyl 7-cyano-2-methylindolizine-1-carboxylate 3eb: 1H -NMR (400 MHz, $CDCl_3$): 1.45 (t, $J = 7.2$ Hz, 3H), 2.53 (s, 3H), 4.42 (q, $J = 7.2$ Hz, 2H), 6.76 (d, $J = 6.8$ Hz, 1H), 7.25 (s, 1H), 7.95 (d, $J = 6.8$ Hz, 1H), 8.55 (s, 1H); ^{13}C -NMR (75 MHz, $CDCl_3$): 12.8 (CH_3), 14.6 (CH_3), 59.9 (CH_2), 103.6 (C), 107.0 (C), 111.7 (CH), 116.3 (CH), 118.5 (C), 125.3 (CH), 126.3 (CH), 131.1 (C), 133.4 (C), 164.6 (C); HRMS (EI): exact mass calculated for $[C_{13}H_{12}N_2O_2]^+$ (M^+), 228.0899; found 228.0894.

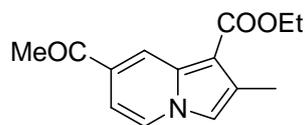


3fb

The general procedure was followed using methyl isonicotinate **1f** (69 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3fb** (111 mg, 85%).

1-Ethyl 7-methyl 2-methylindolizine-1,7-dicarboxylate 3fb: 1H -NMR (400 MHz, $CDCl_3$): 1.46 (t, $J = 7.2$ Hz, 3H), 2.52 (s, 3H), 3.94 (s, 3H), 4.42 (q, $J = 7.2$ Hz, 2H), 7.19 (s, 1H), 7.21 (d, $J = 7.2$ Hz, 1H), 7.89 (d, $J = 7.2$ Hz, 1H), 8.86 (s, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$): 12.9 (CH_3), 14.6 (CH_3), 52.2 (CH_3), 59.6 (CH_2), 106.6 (C), 111.1 (CH), 115.4 (CH), 122.6 (C), 122.7 (CH), 124.5 (CH), 130.4 (C), 134.5 (C), 165.1 (C),

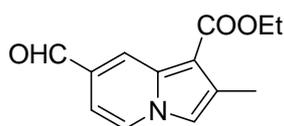
166.2 (C); HRMS (EI): exact mass calculated for $[C_{14}H_{15}NO_4]^+$ (M^+), 261.1001; found 261.1002.



3gb

The general procedure was followed using 4-acetylpyridine **1g** (61 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3gb** (61 mg, 50%).

Ethyl 7-acetyl-2-methylindolizine-1-carboxylate 3gb: 1H -NMR (300 MHz, $CDCl_3$): 1.47 (t, $J = 7.2$ Hz, 3H), 2.52 (s, 3H), 2.65 (s, 3H), 4.42 (q, $J = 7.2$ Hz, 2H), 7.21 (s, 1H), 7.27 (d, $J = 7.2$ Hz, 1H), 7.90 (d, $J = 7.2$ Hz, 1H), 8.81 (d, $J = 0.9$ Hz, 1H); ^{13}C -NMR (75 MHz, $CDCl_3$): 12.9 (CH₃), 14.5 (CH₃), 25.8 (CH₃), 59.6 (CH₂), 107.2 (C), 109.5 (CH), 115.7 (CH), 122.5 (CH), 124.7 (CH), 129.7 (C), 130.4 (C), 134.4 (C), 165.2 (C), 196.3 (C); HRMS (EI): exact mass calculated for $[C_{14}H_{15}NO_3]^+$ (M^+), 245.1052; found 245.1055.

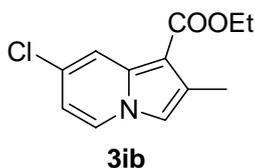


3hb

The general procedure was followed using isonicotinaldehyde **1h** (54 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3hb** (46 mg, 40%).

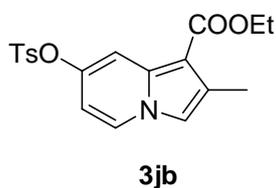
Ethyl 7-formyl-2-methylindolizine-1-carboxylate 3hb: 1H -NMR (400 MHz, $CDCl_3$): 1.46 (t, $J = 7.2$ Hz, 3H), 2.53 (s, 3H), 4.43 (q, $J = 7.2$ Hz, 2H), 7.16 (d, $J = 7.2$ Hz, 1H), 7.27 (s, 1H), 7.93 (d, $J = 7.2$ Hz, 1H), 8.64 (s, 1H), 9.91 (s, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$): 12.9 (CH₃), 14.6 (CH₃), 59.8 (CH₂), 107.8 (CH), 108.3 (C), 116.6 (CH), 125.3

(CH), 127.5 (CH), 129.5 (C), 130.7 (C), 134.3 (C), 165.0 (C), 190.3 (CH); HRMS (EI): exact mass calculated for $[C_{13}H_{13}NO_3]^+$ (M^+), 231.0895; found 231.0894.



The general procedure was followed using 4-chloropyridine **1i** (57 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3ib** (88 mg, 74%)

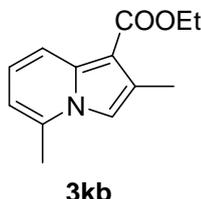
Ethyl 7-chloro-2-methylindolizine-1-carboxylate 3ib: 1H -NMR (400 MHz, $CDCl_3$): 1.43 (t, $J = 7.2$ Hz, 3H), 2.47 (s, 3H), 4.37 (q, $J = 7.2$ Hz, 2H), 6.62 (d, $J = 7.2$ Hz, 1H), 7.03 (s, 1H), 7.80 (d, $J = 7.2$ Hz, 1H), 8.14 (s, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$): 12.8 (CH₃), 14.6 (CH₃), 59.4 (CH₂), 103.0 (C), 113.3 (CH), 113.4 (CH), 118.5 (CH), 125.7 (CH), 128.4 (C), 129.3 (C), 136.2 (C), 165.2 (C); HRMS (EI): exact mass calculated for $[C_{12}H_{12}ClNO_2]^+$ (M^+), 237.0557; found 237.0562.



The general procedure was followed using pyridin-4-yl 4-methylbenzenesulfonate **1j** (125 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3jb** (52 mg, 28%).

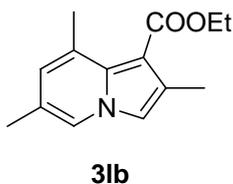
Ethyl 2-methyl-7-(tosyloxy)indolizine-1-carboxylate 3jb: 1H -NMR (300 MHz, $CDCl_3$): 1.35 (t, $J = 7.2$ Hz, 3H), 2.47 (s, 6H), 4.30 (q, $J = 7.2$ Hz, 2H), 6.55 (dd, $J = 7.5$ and 2.7 Hz, 1H), 7.05 (s, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 2.7$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.83 (d, $J = 7.5$ Hz, 1H); ^{13}C -NMR (75 MHz, $CDCl_3$): 12.7 (CH₃), 14.5 (CH₃), 21.7 (CH₃), 59.2 (CH₂), 104.4 (C), 108.6 (CH), 112.0 (CH), 113.5 (CH), 126.3

(CH), 128.6 (CH), 129.89 (CH), 129.94 (C), 132.2 (C), 135.6 (C), 144.4 (C), 145.6 (C), 165.0 (C); HRMS (EI): exact mass calculated for $[C_{19}H_{19}NO_5S]^+$ (M^+), 373.0984; found 373.0988.



The general procedure was followed using 2-methylpyridine **1b** (47 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3kb** (43 mg, 40%).

Ethyl 2,5-dimethylindolizine-1-carboxylate 3kb: 1H -NMR (300 MHz, $CDCl_3$): 1.44 (t, $J = 7.2$ Hz, 3H), 2.54 (s, 3H), 2.55 (s, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 6.55 (d, $J = 6.9$ Hz, 1H), 6.99-7.04 (m, 2H), 8.12 (d, $J = 8.7$ Hz, 1H); ^{13}C -NMR (75 MHz, $CDCl_3$): 13.1 (CH_3), 14.7 (CH_3), 18.8 (CH_3), 59.1 (CH_2), 102.9 (C), 110.2 (CH), 111.6 (CH), 117.3 (CH), 122.2 (CH), 128.6 (C), 133.2 (C), 137.2 (C), 165.8 (C); HRMS (EI): exact mass calculated for $[C_{13}H_{15}NO_2]^+$ (M^+), 217.1103; found 217.1105.



The general procedure was followed using 3,5-dimethylpyridine **1l** (54 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3lb** (76 mg, 66%).

Ethyl 2,6,8-trimethylindolizine-1-carboxylate 3lb: 1H -NMR (400 MHz, $CDCl_3$): 1.40 (t, $J = 7.2$ Hz, 3H), 2.20 (s, 3H), 2.40 (s, 3H), 2.59 (s, 3H), 4.35 (q, $J = 7.2$ Hz, 2H), 6.58 (s, 1H), 6.97 (s, 1H), 7.54 (s, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$): 13.1 (CH_3), 14.5 (CH_3), 17.8 (CH_3), 21.6 (CH_3), 59.6 (CH_2), 104.5 (C), 113.0 (CH), 120.9 (C), 121.2

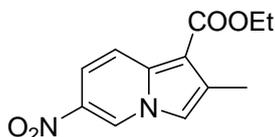
(CH), 126.0 (CH), 127.0 (C), 128.6 (C), 133.7 (C), 166.0 (C); HRMS (EI): exact mass calculated for $[C_{14}H_{17}NO_2]^+$ (M^+), 231.1259; found 231.1261.



3mb

The general procedure was followed using 3,5-dichloropyridine **1m** (74 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **3mb** (81 mg, 60%).

Ethyl 6,8-dichloro-2-methylindolizine-1-carboxylate 3mb: 1H -NMR (300 MHz, $CDCl_3$): 1.41 (t, $J = 7.2$ Hz, 3H), 2.37 (s, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 6.94 (d, $J = 1.5$ Hz, 1H), 7.11 (s, 1H), 7.86 (d, $J = 1.5$ Hz, 1H); ^{13}C -NMR (100 MHz, $CDCl_3$): 11.9 (CH_3), 14.4 (CH_3), 60.6 (CH_2), 108.0 (C), 114.1 (CH), 118.2 (C), 121.5 (CH), 122.1 (CH), 124.8 (C), 128.0 (C), 128.3 (C), 165.1 (C); HRMS (EI): exact mass calculated for $[C_{12}H_{11}Cl_2NO_2]^+$ (M^+), 271.0167; found 271.0169.

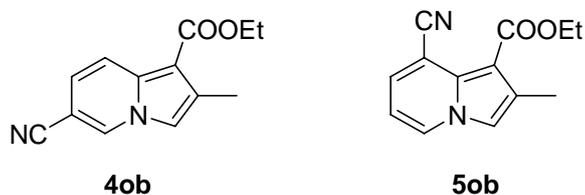


4nb

The general procedure was followed using 3-nitropyridine **1n** (62 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **4nb** (79 mg, 64%).

Ethyl 2-methyl-6-nitroindolizine-1-carboxylate 4nb: 1H -NMR (300 MHz, $CDCl_3$): 1.45 (t, $J = 7.2$ Hz, 3H), 2.53 (s, 3H), 4.41 (q, $J = 7.2$ Hz, 2H), 7.29 (s, 1H), 7.70 (d, $J = 9.9$ Hz, 1H), 8.18 (d, $J = 9.9$ Hz, 1H), 9.03 (s, 1H); ^{13}C -NMR (75 MHz, $CDCl_3$): 13.4 (CH_3), 14.9 (CH_3), 60.3 (CH_2), 108.0 (C), 115.4 (CH), 116.1 (CH), 119.6 (CH), 125.8

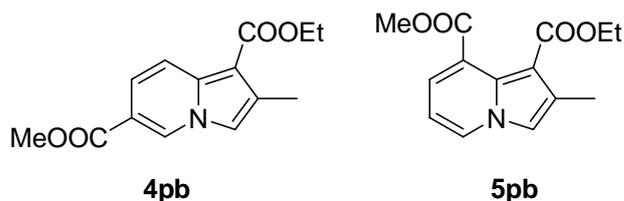
(CH), 132.8 (C), 136.4 (C), 137.2 (C), 165.0 (C); HRMS (EI): exact mass calculated for $[\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4]^+$ (M^+), 248.0797; found 248.0789.



The general procedure was followed using nicotinonitrile **1o** (52 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded a separable 10:1 mixture of indolizines **4ob** (75 mg, 66%) and **5ob** (8 mg, 7%).

Ethyl 6-cyano-2-methylindolizine-1-carboxylate 4ob: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.44 (t, $J = 7.2$ Hz, 3H), 2.51 (s, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 7.04 (d, $J = 9.6$ Hz, 1H), 7.19 (s, 1H), 8.19 (d, $J = 9.6$ Hz, 1H), 8.34 (s, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 13.3 (CH₃), 15.0 (CH₃), 60.2 (CH₂), 98.1 (C), 106.1 (C), 115.0 (CH), 117.5 (C), 120.9 (CH), 121.1 (CH), 131.5 (C), 131.6 (CH), 135.7 (C), 165.2 (C); HRMS (EI): exact mass calculated for $[\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2]^+$ (M^+), 228.0899; found 228.0892.

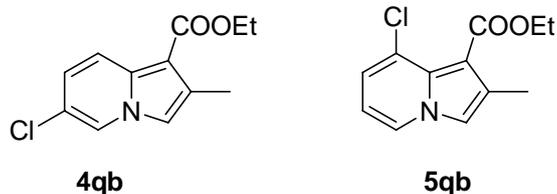
Ethyl 8-cyano-2-methylindolizine-1-carboxylate 5ob: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.46 (t, $J = 7.2$ Hz, 3H), 2.51 (s, 3H), 4.49 (q, $J = 7.2$ Hz, 2H), 6.71 (t, $J = 6.9$ Hz, 1H), 7.24 (s, 1H), 7.50 (d, $J = 6.9$ Hz, 1H), 8.11 (d, $J = 6.9$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.7 (CH₃), 14.5 (CH₃), 59.7 (CH₂), 104.0 (C), 106.2 (C), 110.3 (CH), 114.8 (CH), 117.2 (C), 129.4 (CH), 130.1 (C), 132.1 (CH), 153.1 (C), 164.2 (C); HRMS (EI): exact mass calculated for $[\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2]^+$ (M^+), 228.0899; found 228.0904.



The general procedure was followed using methylnicotinate **1p** (69 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded a separable 3:1 mixture of indolizines **4pb** (52 mg, 40%) and **5pb** (18 mg, 14%).

1-Ethyl 6-methyl 2-methylindolizine-1,6-dicarboxylate 4pb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.44 (t, $J = 7.2$ Hz, 3H), 2.51 (s, 3H), 3.95 (s, 3H), 4.39 (q, $J = 7.2$ Hz, 2H), 7.15 (s, 1H), 7.51 (d, $J = 9.6$ Hz, 1H), 8.12 (d, $J = 9.6$ Hz, 1H), 8.68 (s, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 13.0 (CH_3), 14.6 (CH_3), 52.2 (CH_3), 59.5 (CH_2), 104.4 (C), 114.4 (CH), 115.7 (C), 118.9 (CH), 120.9 (CH), 129.6 (CH), 130.4 (C), 136.8 (C), 165.2 (C), 165.7 (C); HRMS (EI): exact mass calculated for $[\text{C}_{14}\text{H}_{15}\text{NO}_4]^+$ (M^+), 261.1001; found 261.1001.

1-Ethyl 8-methyl 2-methylindolizine-1,8-dicarboxylate 5pb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.38 (t, $J = 7.2$ Hz, 3H), 2.46 (s, 3H), 3.93 (s, 3H), 4.33 (q, $J = 7.2$ Hz, 2H), 6.67 (t, $J = 6.9$ Hz, 1H), 7.16 (s, 1H), 7.27 (d, $J = 6.9$ Hz, 1H), 7.98 (d, $J = 6.9$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.6 (CH_3), 14.4 (CH_3), 52.2 (CH_3), 59.8 (CH_2), 105.4 (C), 110.5 (CH), 113.6 (CH), 123.6 (CH), 124.6 (C), 127.5 (CH), 128.3 (CH), 131.0 (C), 165.4 (C), 167.9 (C); HRMS (EI): exact mass calculated for $[\text{C}_{14}\text{H}_{15}\text{NO}_4]^+$ (M^+), 261.1001; found 261.1005.

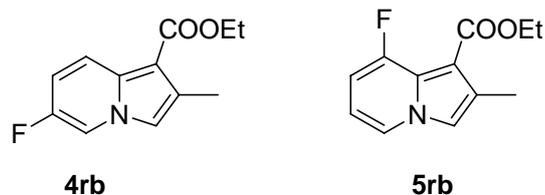


The general procedure was followed using 3-chloropyridine **1q** (57 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded a separable 1:1.5 mixture of indolizines **4qb** (21 mg, 18%) and **5qb** (32 mg 27%).

Ethyl 6-chloro-2-methylindolizine-1-carboxylate 4qb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.43 (t, $J = 7.2$ Hz, 3H), 2.49 (s, 3H), 4.39 (q, $J = 7.2$ Hz, 2H), 6.95 (d, $J = 9.6$ Hz, 1H),

7.06 (s, 1H), 7.95 (s, 1H), 8.11 (d, $J = 9.6$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.9 (CH_3), 14.6 (CH_3), 59.4 (CH_2), 103.7 (C), 113.6 (CH), 120.0 (C), 120.1 (CH), 122.8 (CH), 122.9 (CH), 129.2 (C), 134.6 (C), 165.3 (C); HRMS (EI): exact mass calculated for $[\text{C}_{12}\text{H}_{12}\text{ClNO}_2]^+$ (M^+), 237.0557; found 237.0559.

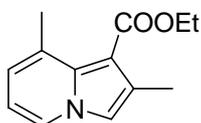
Ethyl 8-chloro-2-methylindolizine-1-carboxylate 5qbb: $^1\text{H-NMR}$ (400 MHz, CDCl_3): 1.42 (t, $J = 7.2$ Hz, 3H), 2.40 (s, 3H), 4.40 (q, $J = 7.2$ Hz, 2H), 6.51 (t, $J = 7.2$ Hz, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 7.14 (s, 1H), 7.82 (d, $J = 7.2$ Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 12.0 (CH_3), 14.4 (CH_3), 60.4 (CH_2), 106.8 (C), 110.7 (CH), 113.6 (CH), 121.5 (CH), 123.8 (CH), 124.5 (C), 127.3 (C), 130.0 (C), 165.6 (C); HRMS (EI): exact mass calculated for $[\text{C}_{12}\text{H}_{12}\text{ClNO}_2]^+$ (M^+), 237.0557; found 237.0554.



The general procedure was followed using 3-fluoropyridine **1r** (49 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded a separable 1:3 mixture of indolizines **4rb** (16 mg, 15%) and **5rb** (50 mg, 45%).

Ethyl 6-fluoro-2-methylindolizine-1-carboxylate 4rb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.43 (t, $J = 7.2$ Hz, 3H), 2.49 (s, 3H), 4.38 (q, $J = 7.2$ Hz, 2H), 6.93 (ddd, $J = 10.0, 8.0$ and 2.0 Hz, 1H), 7.08 (s, 1H), 7.47 (dd, $J = 4.0$ and 2.0 Hz, 1H), 8.14 (dd, $J = 10.0$ and 5.6 Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.9 (CH_3), 14.6 (CH_3), 59.3 (CH_2), 103.5 (C), 111.6 (CH, $J_{\text{C-F}} = 39.0$ Hz), 113.5 (CH, $J_{\text{C-F}} = 24.0$ Hz), 114.3 (CH), 120.4 (CH, $J_{\text{C-F}} = 8.2$ Hz), 129.4 (C), 134.0 (C), 153.4 (C, $J_{\text{C-F}} = 234.0$ Hz), 165.3 (C); $^{19}\text{F-NMR}$ (CDCl_3): -141.67; HRMS (EI): exact mass calculated for $[\text{C}_{12}\text{H}_{12}\text{FNO}_2]^+$ (M^+), 221.0852; found 221.0853.

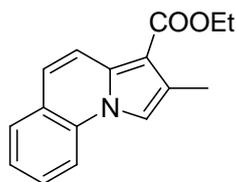
Ethyl 8-fluoro-2-methylindolizine-1-carboxylate 5rb: $^1\text{H-NMR}$ (400 MHz, CDCl_3): 1.40 (t, $J = 7.2$ Hz, 3H), 2.46 (s, 3H), 4.37 (q, $J = 7.2$ Hz, 2H), 6.53-6.57 (m, 1H), 6.64 (dd, $J = 11.6$ and 7.6 Hz, 1H), 7.17 (s, 1H), 7.72 (d, $J = 6.8$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 12.7 (CH_3), 14.4 (CH_3), 59.8 (CH_2), 104.3 (C, $J_{\text{C-F}} = 4.5$ Hz), 105.1 (CH, $J_{\text{C-F}} = 20.2$ Hz), 110.7 (CH, $J_{\text{C-F}} = 7.5$ Hz), 114.9 (CH), 121.6 (CH, $J_{\text{C-F}} = 4.5$ Hz), 126.3 (C, $J_{\text{C-F}} = 33.0$ Hz), 128.6 (C), 154.0 (C, $J_{\text{C-F}} = 252.0$ Hz), 164.7 (C); $^{19}\text{F-NMR}$ (CDCl_3): -116.45; HRMS (EI): exact mass calculated for $[\text{C}_{12}\text{H}_{12}\text{FNO}_2]^+$ (M^+), 221.0852; found 221.0860.



5sb

The general procedure was followed using 3-methylpyridine **1s** (47 mg) and vinyl diazoacetate **2b** (77 mg). Chromatographic purification of the crude reaction afforded a 1:10 mixture of indolizines **4sb** and **5sb** (59 mg, 54%). Spectroscopic data of **5sb** were obtained from this mixture.

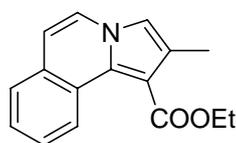
Ethyl 2,8-dimethylindolizine-1-carboxylate 5sb: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.42 (t, $J = 7.2$ Hz, 3H), 2.42 (s, 3H), 2.61 (s, 3H), 4.37 (q, $J = 7.2$ Hz, 2H), 6.54 (t, $J = 6.9$ Hz, 1H), 6.71 (d, $J = 6.9$ Hz, 1H), 7.08 (s, 1H), 7.77 (d, $J = 6.9$ Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 13.0 (CH_3), 14.5 (CH_3), 21.6 (CH_3), 59.8 (CH_2), 105.1 (C), 111.6 (CH), 113.2 (CH), 122.6 (CH), 123.3 (CH), 127.2 (C), 129.2 (C), 134.6 (C), 166.0 (C); HRMS (EI) (mixture of **4sb** and **5sb**): exact mass calculated for $[\text{C}_{13}\text{H}_{15}\text{NO}_2]^+$ (M^+), 217.1103; found 217.1104.



6

The general procedure was followed using quinoline **1t** (65 mg) and vinyldiazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **6** (82 mg, 65%).

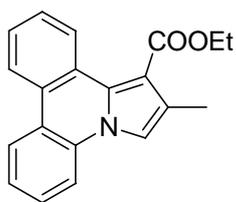
Ethyl 2-methylpyrrolo[1,2-*a*]quinoline-3-carboxylate 6: ¹H-NMR (400 MHz, CDCl₃): 1.46 (t, *J* = 7.2 Hz, 3H), 2.54 (s, 3H), 4.42 (q, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 9.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.54-7.59 (m, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 9.2 Hz, 1H); ¹³C-NMR (100 MHz, CDCl₃): 13.0 (CH₃), 14.6 (CH₃), 59.3 (CH₂), 106.2 (C), 111.8 (CH), 114.4 (CH), 118.7 (CH), 122.9 (CH), 123.8 (C), 124.1 (CH), 126.7 (C), 128.5 (CH), 128.7 (CH), 132.2 (C), 134.6 (C), 165.7 (C); HRMS (EI): exact mass calculated for [C₁₆H₁₅NO₂]⁺ (M⁺), 253.1103; found 253.1103.



7

The general procedure was followed using isoquinoline **1u** (65 mg) and vinyldiazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **7** (101 mg, 80%).

Ethyl 2-methylpyrrolo[2,1-*a*]isoquinoline-1-carboxylate 7: ¹H-NMR (300 MHz, CDCl₃): 1.47 (t, *J* = 7.2 Hz, 3H), 2.45 (s, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 7.07 (s, 1H), 7.44- 7.62 (m, 3H), 7.70 (d, *J* = 7.2 Hz, 1H), 9.30 (d, *J* = 8.4 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): 13.5 (CH₃), 14.5 (CH₃), 60.1 (CH₂), 108.6 (C), 112.9 (CH), 115.1 (CH), 123.7 (CH), 125.5 (C), 125.7 (C), 126.1 (CH), 126.8 (CH), 127.0 (CH), 127.3 (CH), 128.8 (C), 131.6 (C), 166.8 (C); HRMS (EI): exact mass calculated for [C₁₆H₁₅NO₂]⁺ (M⁺), 253.1103; found 253.1104.



8

The general procedure was followed using phenanthridine **1v** (90 mg) and vinyl diazoacetate **2b** (77 mg). Final chromatographic purification afforded indolizine **8** (45 mg, 30%).

Ethyl 2-methylpyrrolo[1,2-*f*]phenanthridine-1-carboxylate 8: $^1\text{H-NMR}$ (300 MHz, CDCl_3): 1.48 (t, $J = 7.2$ Hz, 3H), 2.45 (s, 3H), 4.49 (q, $J = 7.2$ Hz, 2H), 7.40-7.60 (m, 4H), 7.61 (s, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 8.33-8.36 (m, 1H), 8.40 (d, $J = 8.1$ Hz, 1H), 8.97 (dd, $J = 7.1$ and 2.1 Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): 13.2 (CH_3), 14.4 (CH_3), 60.4 (CH_2), 111.0 (C), 112.5 (CH), 115.2 (CH), 121.8 (C), 122.2 (CH), 123.8 (CH), 124.4 (CH), 125.0 (C), 125.2 (C), 126.2 (CH), 126.4 (C), 127.2 (CH), 127.8 (CH), 128.7 (CH), 130.3 (C), 131.9 (C), 167.3 (C); HRMS (EI): exact mass calculated for $[\text{C}_{20}\text{H}_{17}\text{NO}_2]^+$ (M^+), 303.1259; found 303.1268.

Summary of the computational calculations

The transition structures for the reductive elimination on copper(III) metallacycle **III** were fully optimized at the Becke3LYP/6-31G* level of theory, and characterized by computing the vibrational frequencies. The calculations were carried out with the *Gaussian 03* suite of programs.⁴ The regioisomeric transition structures located, corresponding to the reactions of 3-picoline (**TS-a** and **TS-b**) and 3-nitropyridine (**TS-c** and **TS-d**), are shown in Figure 2.

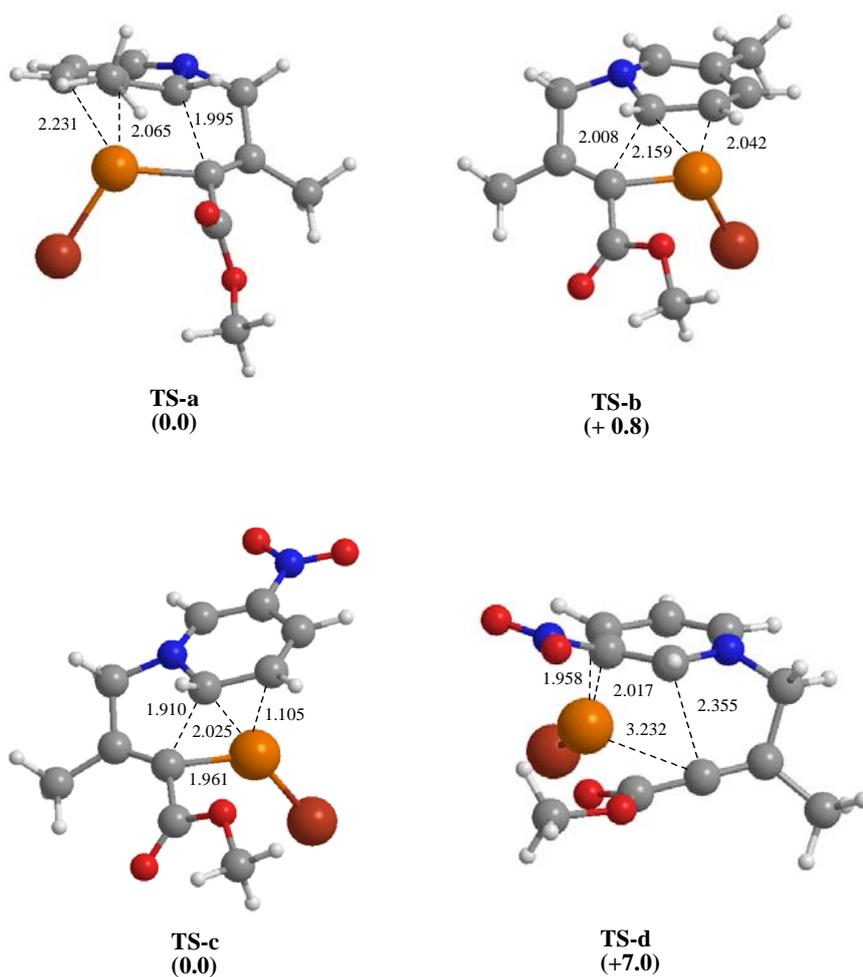


Figure 2. Selected bond lengths (in Å) and relative energies (in Kcal mol⁻¹) of the transition structures located for the reductive elimination on the copper (III) metallacycle **III**.

In the transition structures located, the normal mode corresponding to the imaginary frequency corresponds to the carbon-carbon bond formation between the diazo carbon atom and the carbon atom at positions 2 or 6 of the pyridine and carbon-copper bond breaking, with the exception of **TS-d**, in which, the C-Cu bond is completely broken.

As can be seen, in the case of the 3-picoline, the transition structure **TS-c**, leading to the major regioisomer is preferred by 0.8 Kcal mol⁻¹, whereas for the reaction of 3-nitropyridine, the reductive elimination through transition structure **TS-c** is strongly favored as compared with the regioisomeric **TS-d**.

Cartesian coordinates, total energies (hartrees) and imaginary frequencies (cm⁻¹) of the transition structures located.

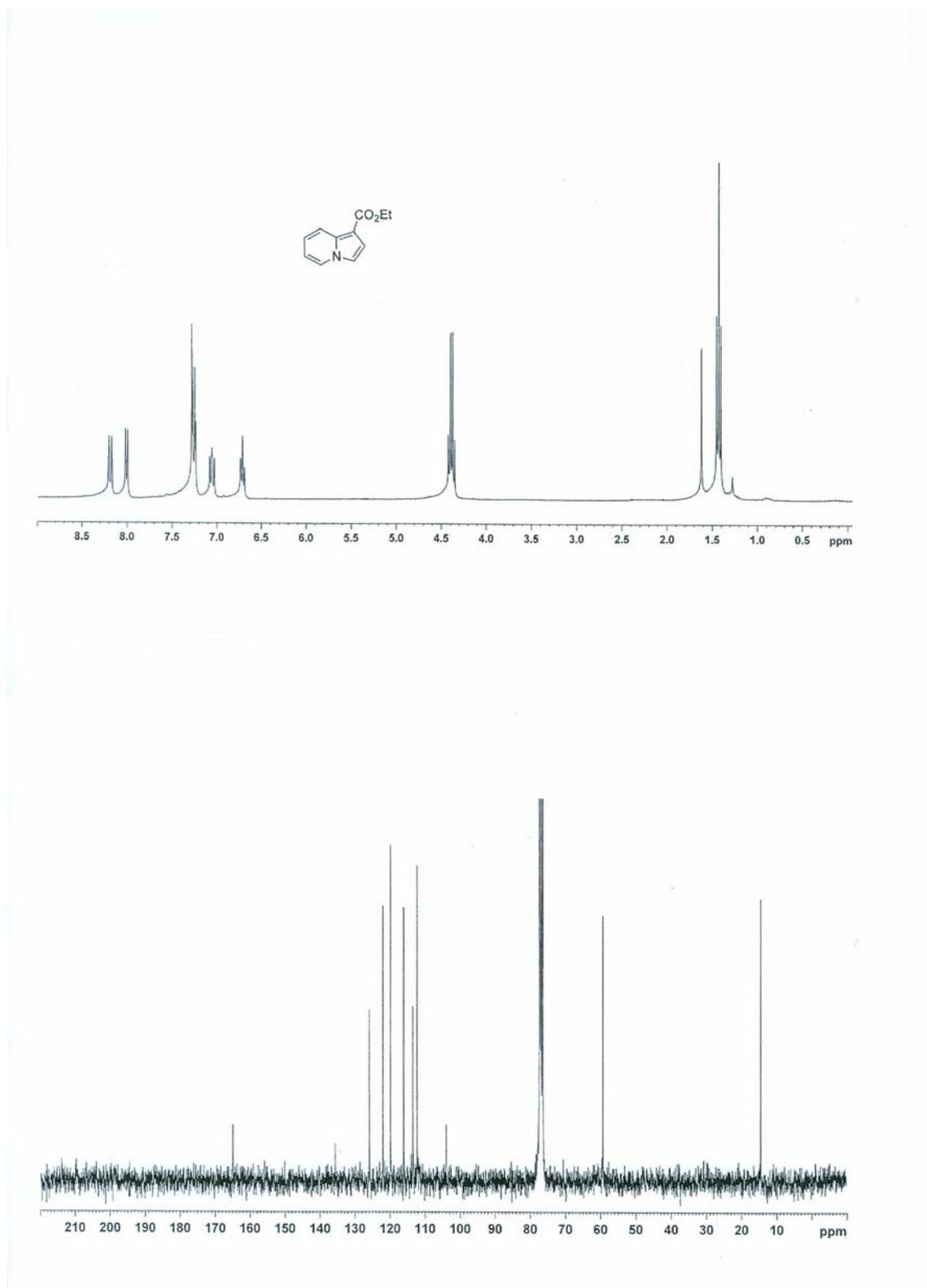
TS-a				TS-b			
C	2.6216	-1.2766	0.0238	C	2.2955	-1.7701	-0.6318
N	2.6216	0.1846	0.0238	N	2.2955	-0.3091	-0.6318
C	0.2457	-0.7858	0.0238	C	-0.0847	-1.2948	-0.6318
C	2.9659	0.8284	-1.1640	C	1.1276	0.1601	-1.2989
C	-1.1639	-0.9355	0.4446	C	-1.5040	-1.5519	-0.9713
C	0.9707	-3.2408	-0.0608	C	0.6577	-3.7428	-0.4993
C	2.4418	2.0246	-1.5192	C	0.7951	1.5711	-1.1023
C	1.4836	2.6806	-0.6474	C	1.1305	2.1567	0.1019
Br	-1.5485	1.1944	-2.4806	Br	-1.7225	0.6117	2.0378
Cu	-0.0015	1.0268	-0.8407	Cu	-0.3252	0.5352	0.2541
C	1.1134	2.0814	0.5408	C	2.0994	1.5050	0.9781
C	1.1708	-1.7524	-0.0657	C	0.8496	-2.2549	-0.5361
C	1.4522	0.6555	0.6925	C	2.6233	0.3212	0.5755
H	3.7242	0.3267	-1.7546	H	1.0523	-0.1761	-2.3287
O	-1.6603	-0.2260	1.3066	O	-2.1483	-2.5651	-0.7999
O	-1.8396	-1.8952	-0.2101	O	-2.0281	-0.4301	-1.5477
H	2.7573	2.5040	-2.4377	H	0.1899	2.0774	-1.8472
C	-3.2521	-1.9574	0.0723	C	-3.4400	-0.4781	-1.8226
H	1.2034	3.7097	-0.8484	H	0.8346	3.1787	0.3167
H	3.0419	-1.6509	0.9706	H	2.9366	-2.1496	0.1708
C	0.3324	2.7589	1.6369	C	2.4873	2.1584	2.2756
H	1.3749	0.3033	1.7175	H	3.3865	-0.1879	1.1546
H	-3.7242	-1.0082	-0.1905	H	-3.9960	-0.5740	-0.8869
H	-3.4245	-2.1728	1.1299	H	-3.6745	-1.3214	-2.4766
H	-3.6345	-2.7630	-0.5545	H	-3.6738	0.4677	-2.3117
H	1.3503	-3.6768	-0.9951	H	1.3111	-4.2401	-1.2299
H	-0.0817	-3.5103	0.0303	H	-0.3808	-4.0173	-0.6837
H	1.5358	-3.7097	0.7577	H	0.9396	-4.1291	0.4903
H	-0.4674	2.1116	2.0122	H	1.6155	2.2490	2.9352
H	-0.1136	3.6923	1.2817	H	2.8849	3.1688	2.1133
H	0.9951	2.9956	2.4806	H	3.2497	1.5770	2.8032
H	3.2592	-1.6553	-0.7823	H	2.7122	-2.1446	-1.5802
E=-4883.52915233 au				E=-4883.52838919 au			
Imag. Freq.= -217.2 cm ⁻¹				Imag. Freq.= -227.8 cm ⁻¹			

TS-c			TS-d		
C	1.8338	-1.5110 -0.3979	C	2.3489	-1.3298 0.0725
N	1.8338	-0.0509 -0.3979	N	2.3489	0.1197 0.0725
C	-0.5205	-0.9563 -0.3979	C	-0.1097	-1.0381 0.0725
C	0.5991	0.4967 -0.9317	C	2.8367	0.8088 -1.0229
C	-1.9445	-1.1384 -0.7907	C	-1.1814	-0.2426 0.4355
C	0.1344	-3.4314 -0.3903	C	0.8279	-3.1384 -0.9567
C	0.4322	1.9636 -0.6681	C	2.4535	2.0804 -1.3074
C	1.3392	2.6701 0.0632	C	1.4282	2.7241 -0.5288
Br	-1.9933	1.0539 2.3876	Br	-0.7636	2.9799 -2.9815
Cu	-0.7192	0.7279 0.5877	Cu	-0.3314	2.0038 -0.9983
C	2.4745	1.9976 0.6246	C	0.9183	1.9857 0.5843
C	0.3827	-1.9538 -0.3529	C	0.9035	-1.7911 -0.2684
C	2.6678	0.6640 0.3890	C	1.3443	0.6437 0.8501
H	0.4584	0.2869 -1.9937	H	3.5711	0.2727 -1.6118
O	-2.6142	-2.1430 -0.6923	O	-1.5892	0.7832 -0.1919
O	-2.4139	0.0290 -1.3083	O	-1.7987	-0.6223 1.5746
H	-0.3281	2.4798 -1.2466	H	2.8881	2.5975 -2.1538
C	-3.8160	0.0395 -1.6484	C	-2.7830	0.2841 2.1057
H	1.2506	3.7416 0.1962	H	1.3501	3.8050 -0.5207
H	2.4351	-1.8878 0.4373	H	2.6298	-1.7070 1.0635
N	3.4400	2.7115 1.4189	N	0.2929	2.7111 1.6873
H	3.5170	0.1438 0.8156	H	1.2192	0.2343 1.8426
H	-4.4163	-0.1302 -0.7519	H	-3.5711	0.4734 1.3737
H	-4.0325	-0.7350 -2.3876	H	-2.3142	1.2269 2.4000
H	-4.0065	1.0312 -2.0574	H	-3.1876	-0.2245 2.9815
H	0.7690	-3.9129 -1.1470	H	1.3290	-3.1080 -1.9337
H	-0.9132	-3.6557 -0.5884	H	-0.2078	-3.4473 -1.1079
H	0.4008	-3.8782 0.5777	H	1.3339	-3.9096 -0.3596
O	4.4163	2.0872 1.8532	O	0.0149	2.0673 2.7041
O	3.2333	3.9129 1.6131	O	0.0603	3.9096 1.5323
H	2.2813	-1.9007 -1.3269	H	3.0795	-1.7005 -0.6511
E=- -5048.70937261 au Imag. Freq.= -224.2cm ⁻¹			E=-5048.69728828au Imag. Freq.= -226.2cm ⁻¹		

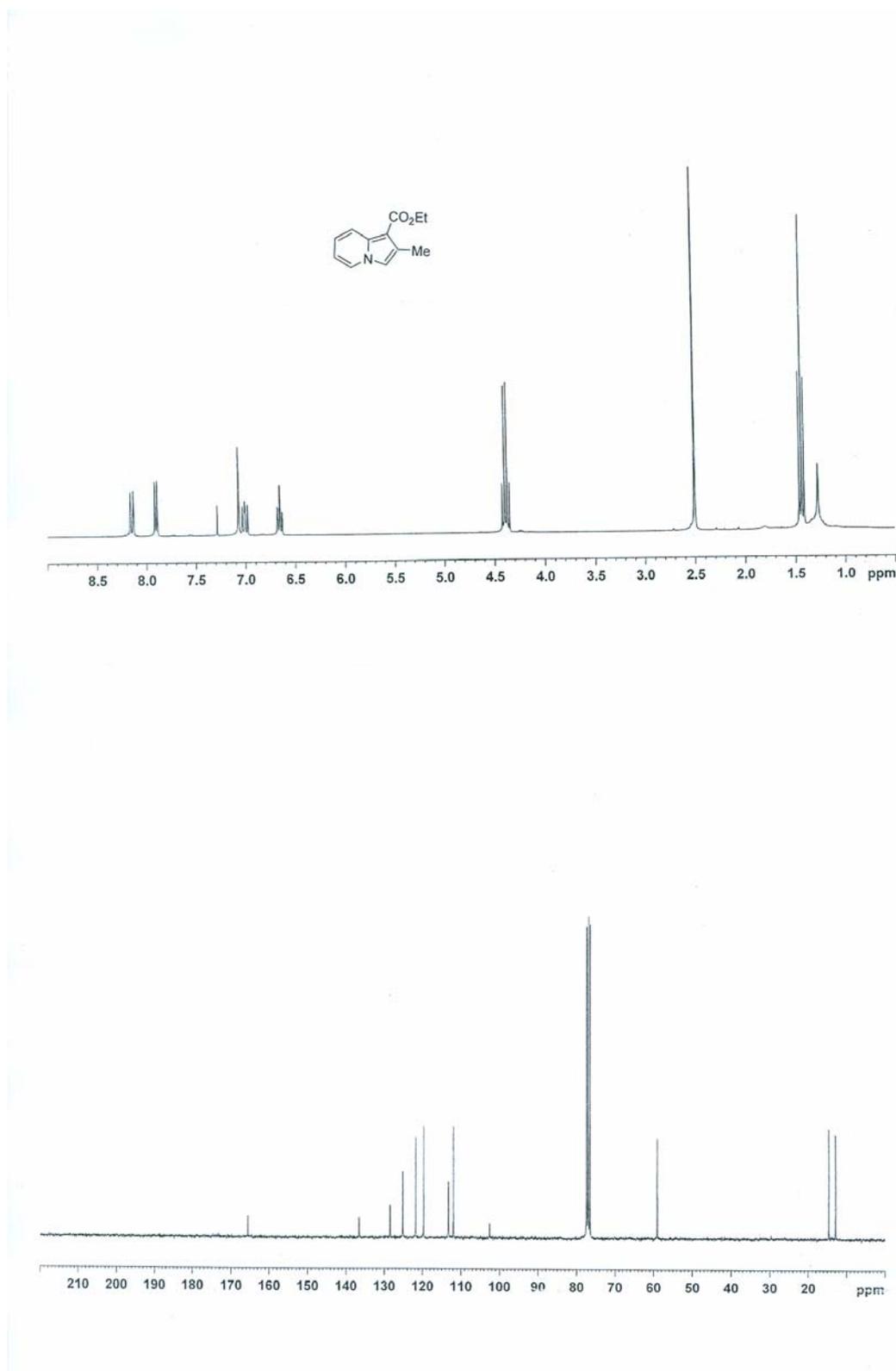
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1. a) Padwa, A.; Kulkarni, Y. S.; Zhang, Z. *J. Org. Chem.* **1990**, *55*, 4144; b) Davies, H. M. L.; Hougland, P. W.; Cantrell, W. R. Jr *Synth. Commun.* **1992**, *22*, 971; c) Manning, J. R.; Davies, H. M. L. *Org. Synth.* **2007**, *84*, 334.
2. Del Giudice, M. R.; Settimi, G.; Delfini, M. *Tetrahedron* **1984**, *40*, 4067.
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4. M. J. Frisch et al. Gaussian 03, Revision B.03, Gaussian, Inc., Pittsburgh PA, 2003. <http://www.gaussian.com>

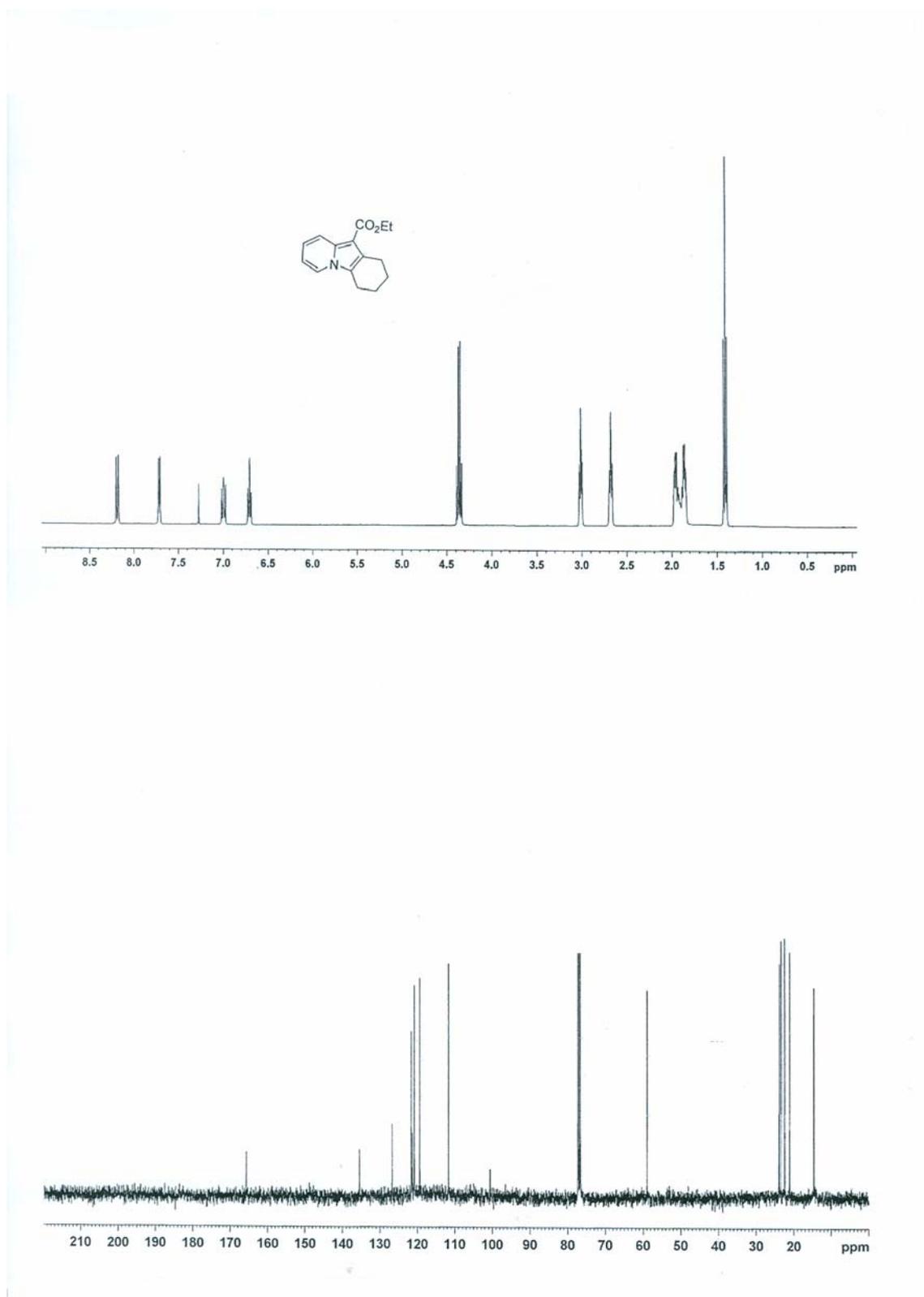
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **3aa**



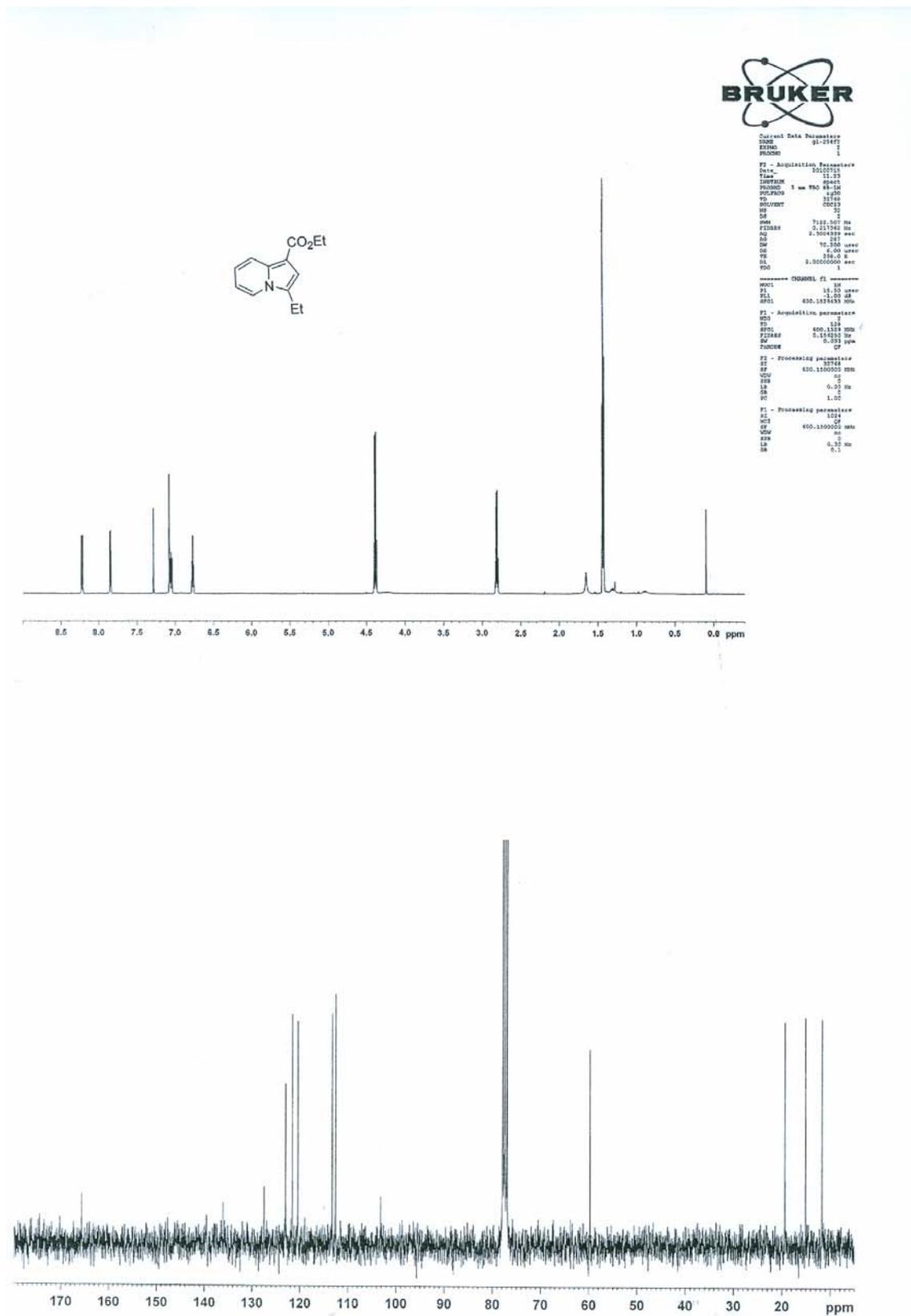
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **3ab**



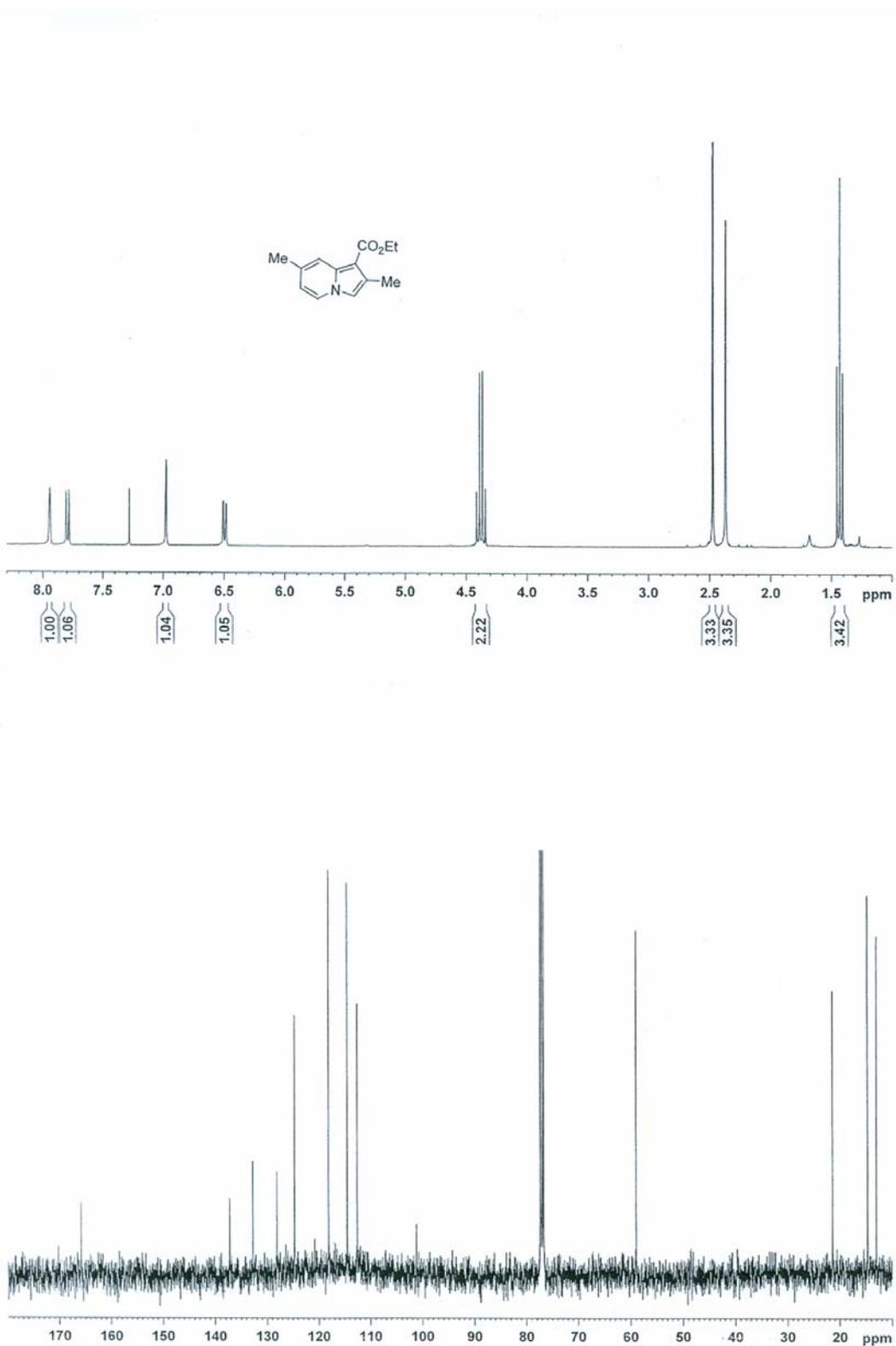
^1H -NMR (400 MHz) and ^{13}C -NMR (100 MHz) spectra of compound **3ac**



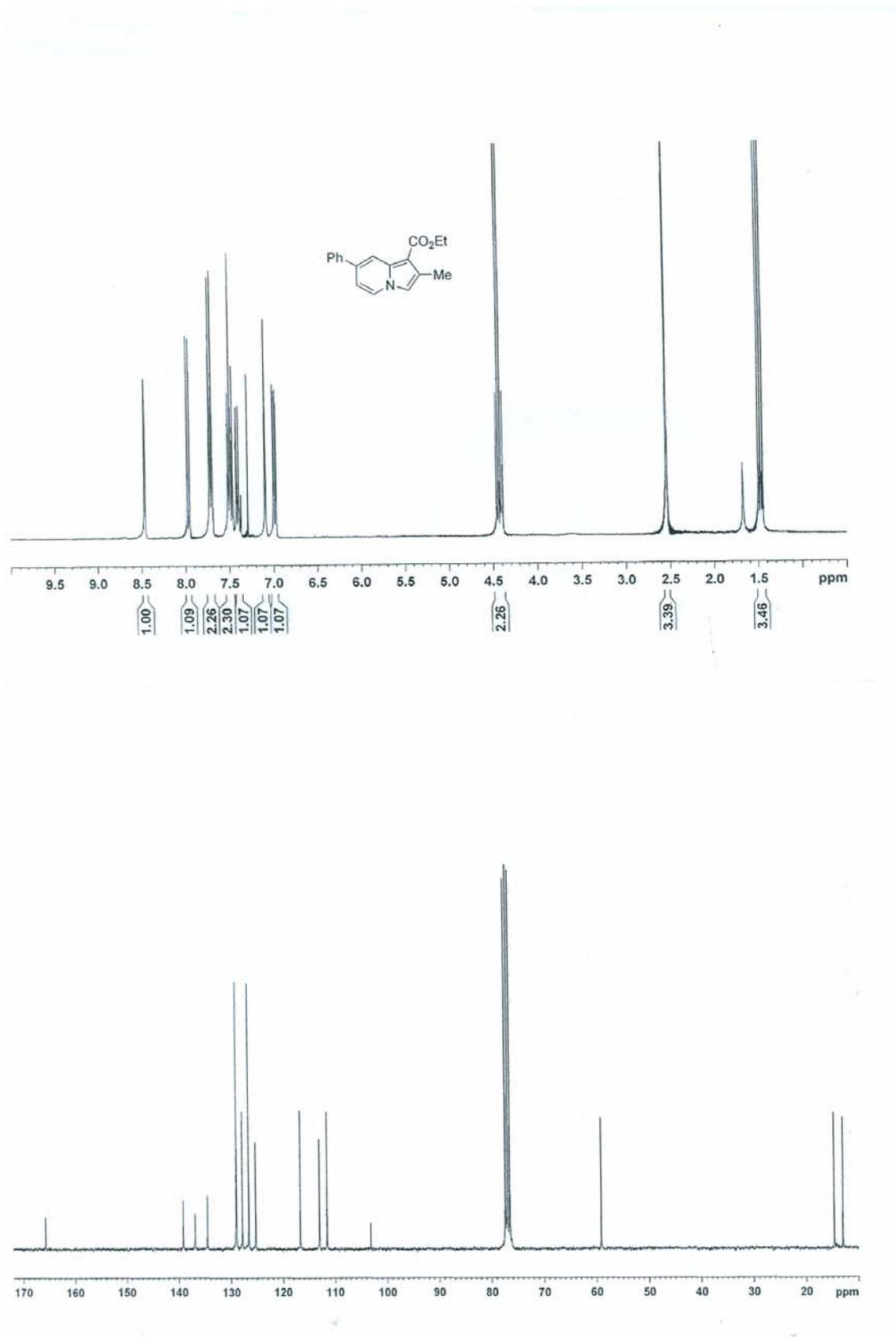
$^1\text{H-NMR}$ (600 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3ad**



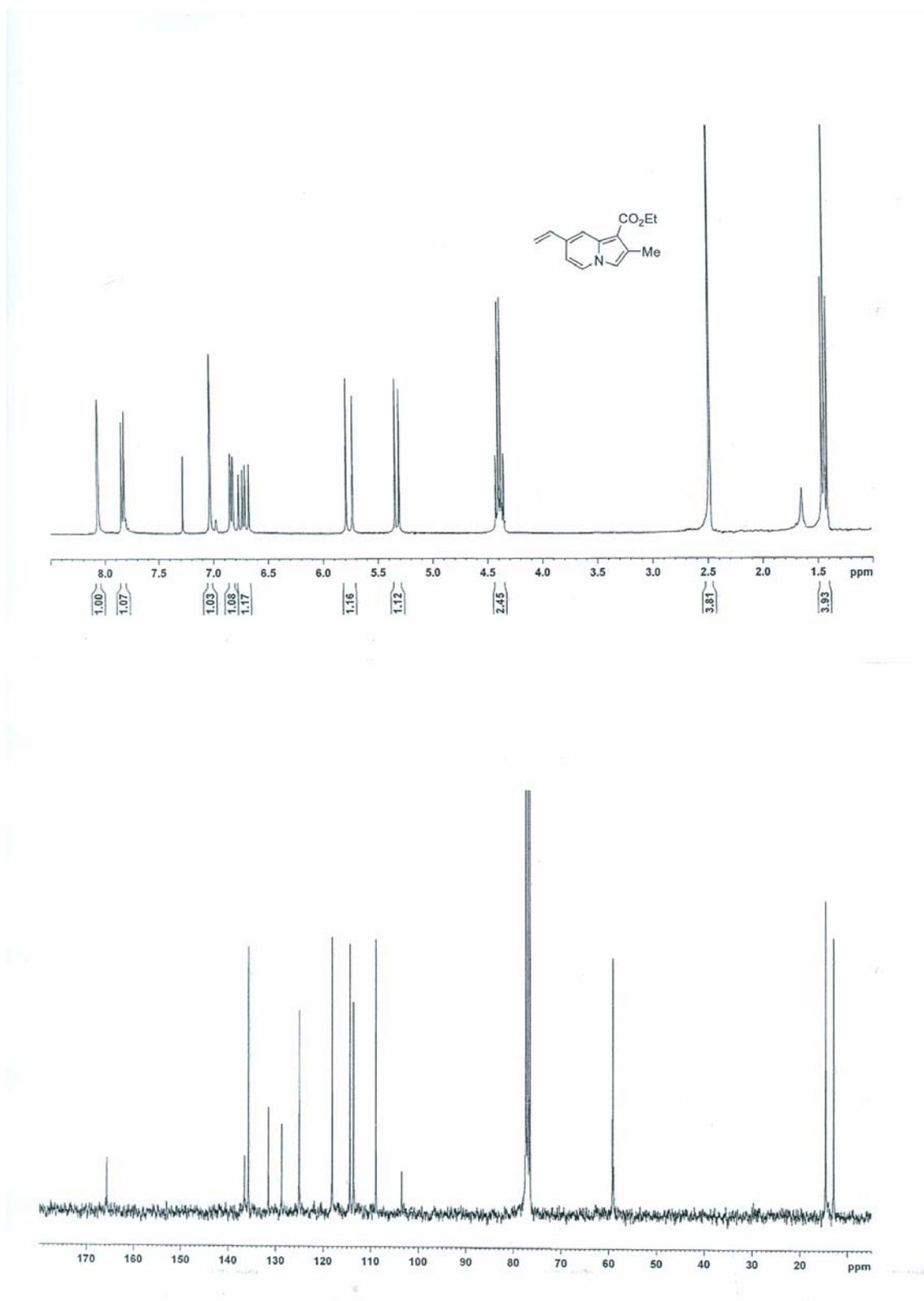
^1H -NMR (300 MHz) and ^{13}C -NMR (100 MHz) spectra of compound **3bb**



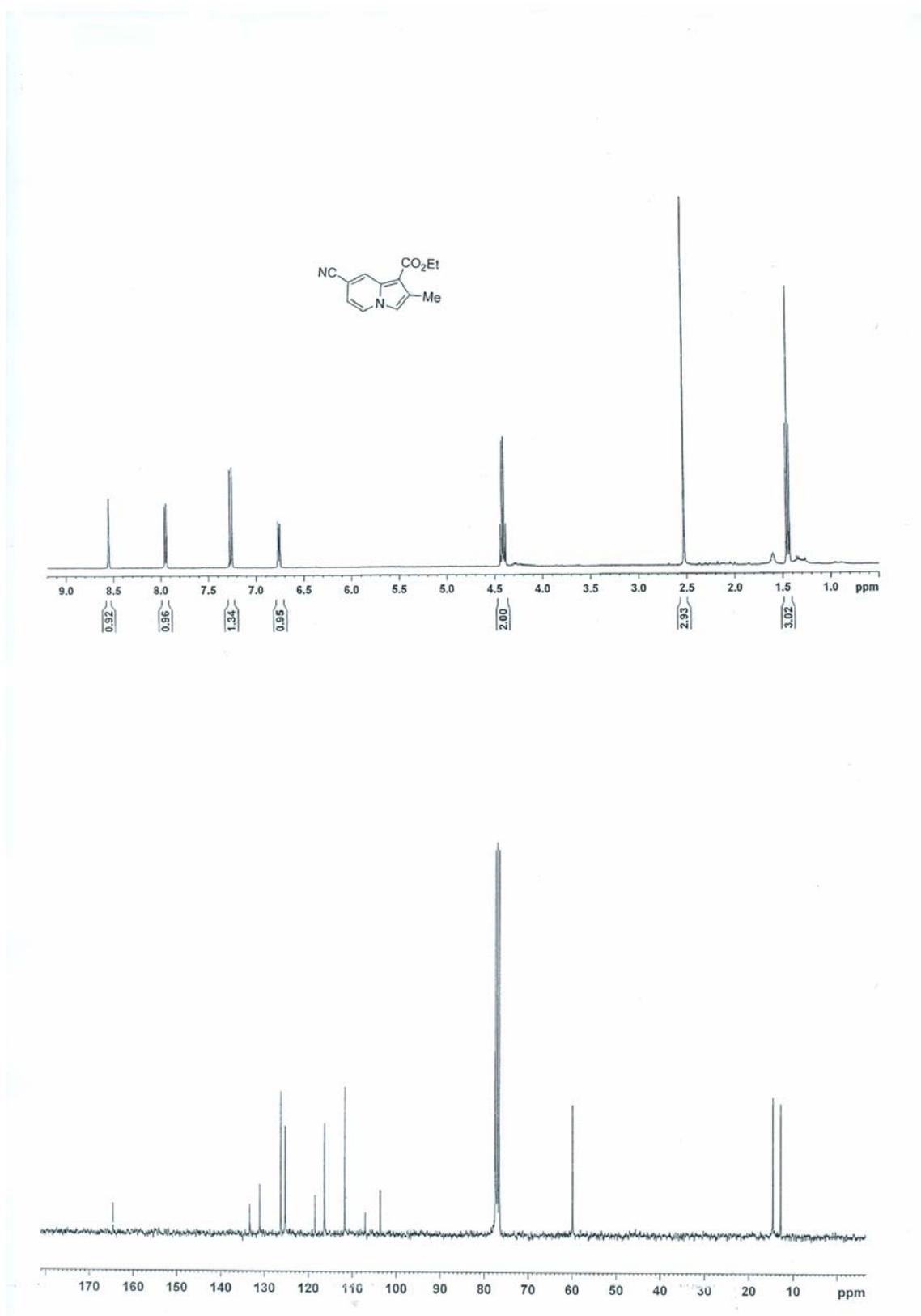
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3cb**



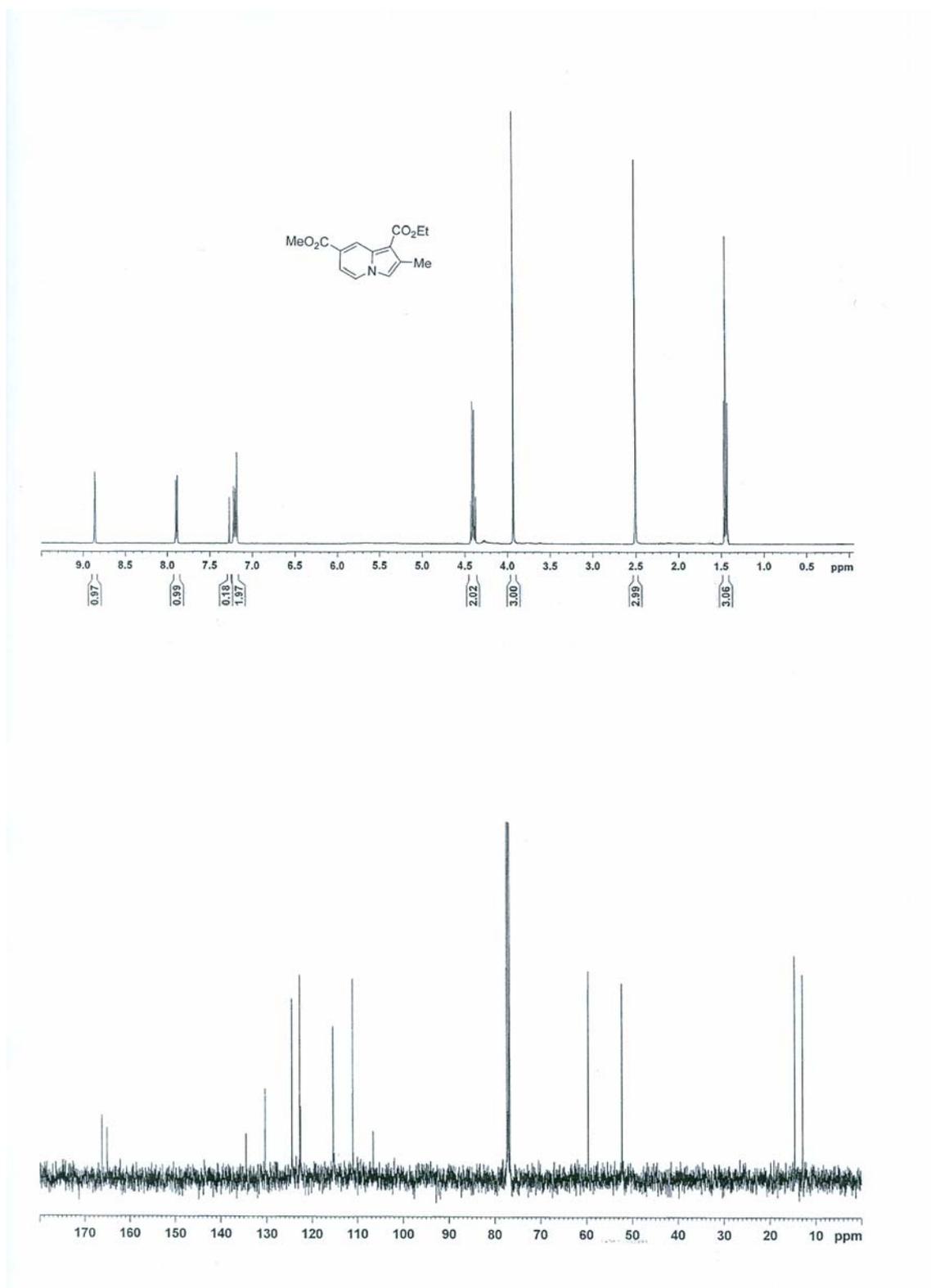
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3db**



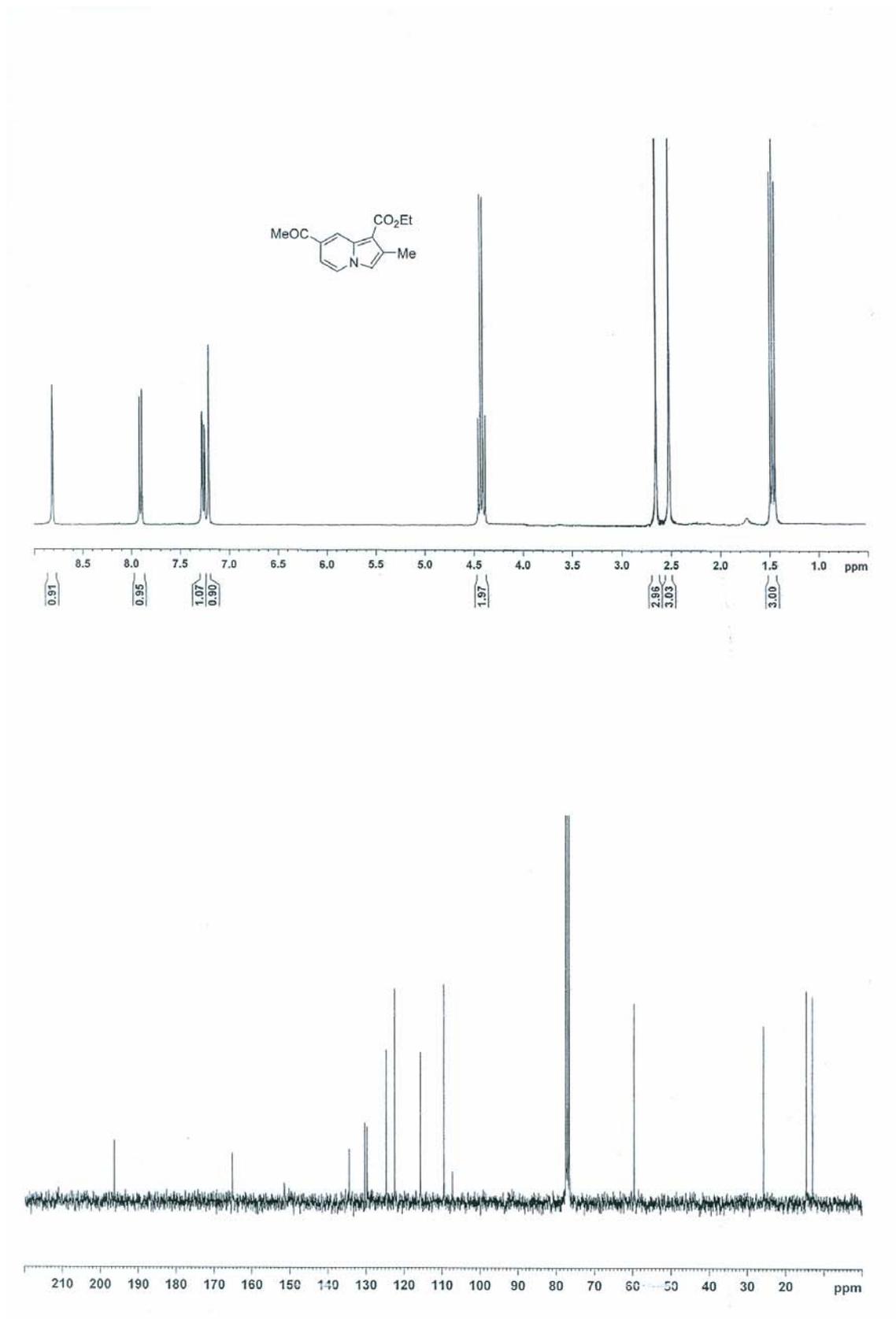
$^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3eb**



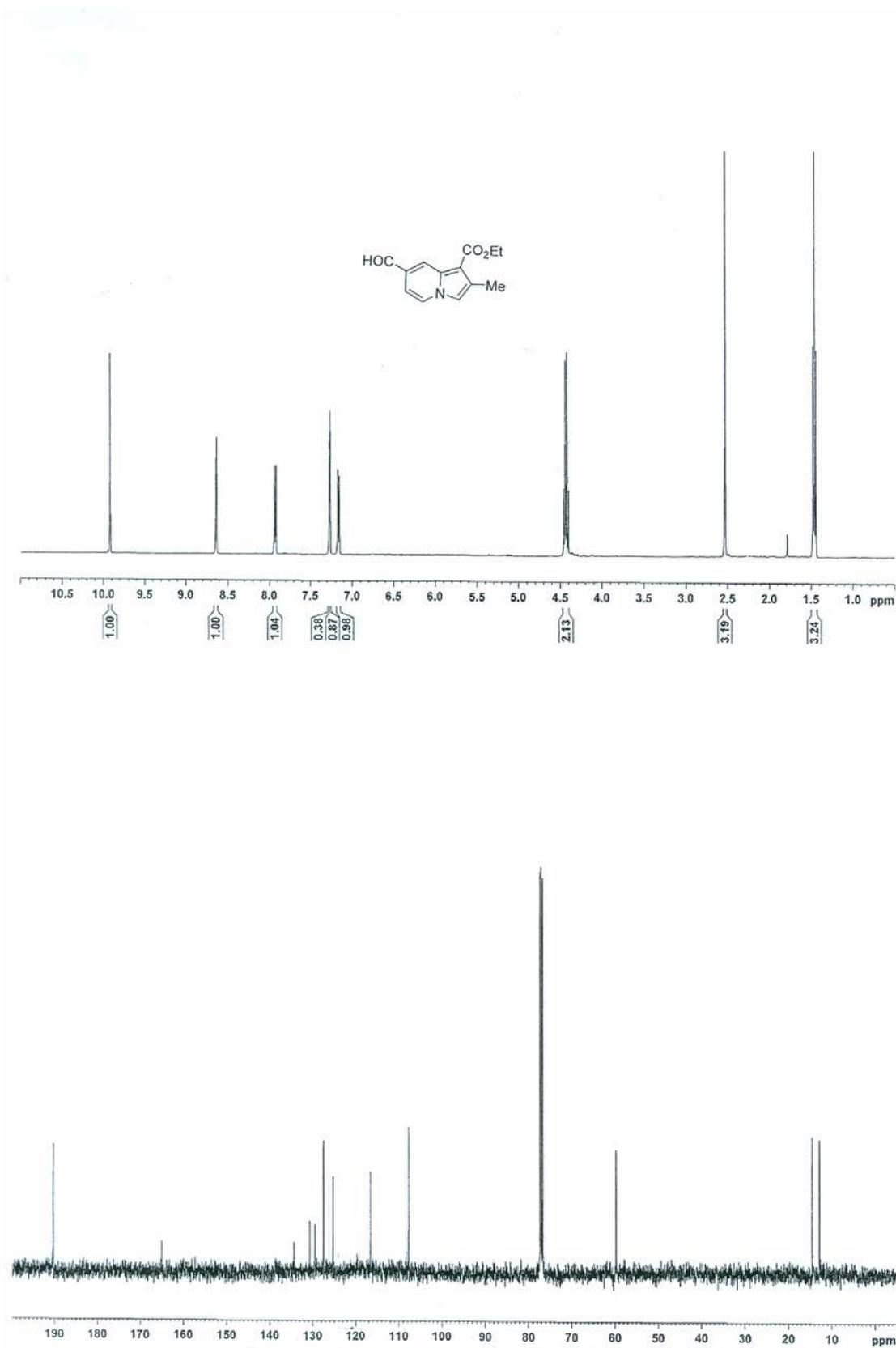
^1H -NMR (400 MHz) and ^{13}C -NMR (100 MHz) spectra of compound **3fb**



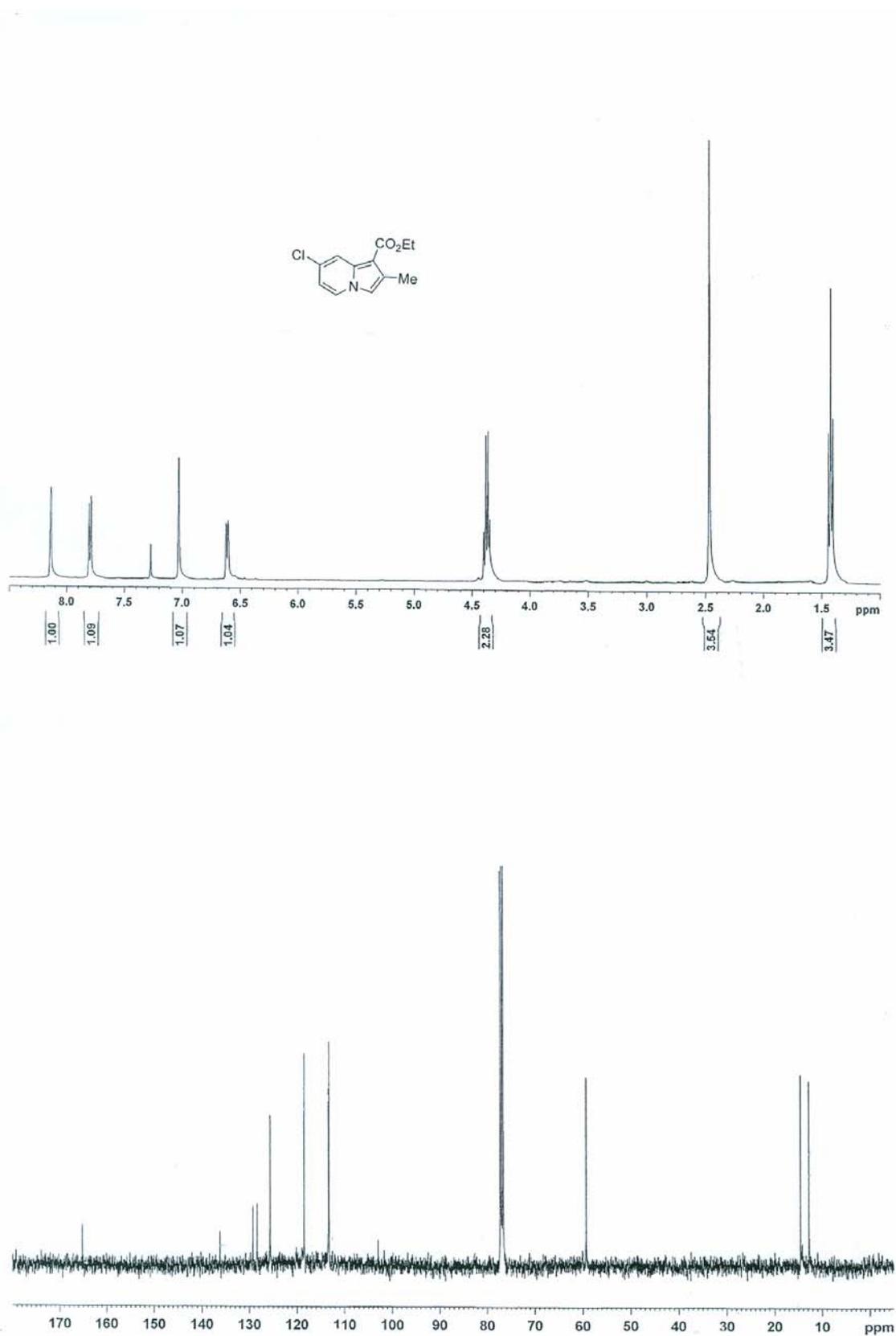
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3gb**



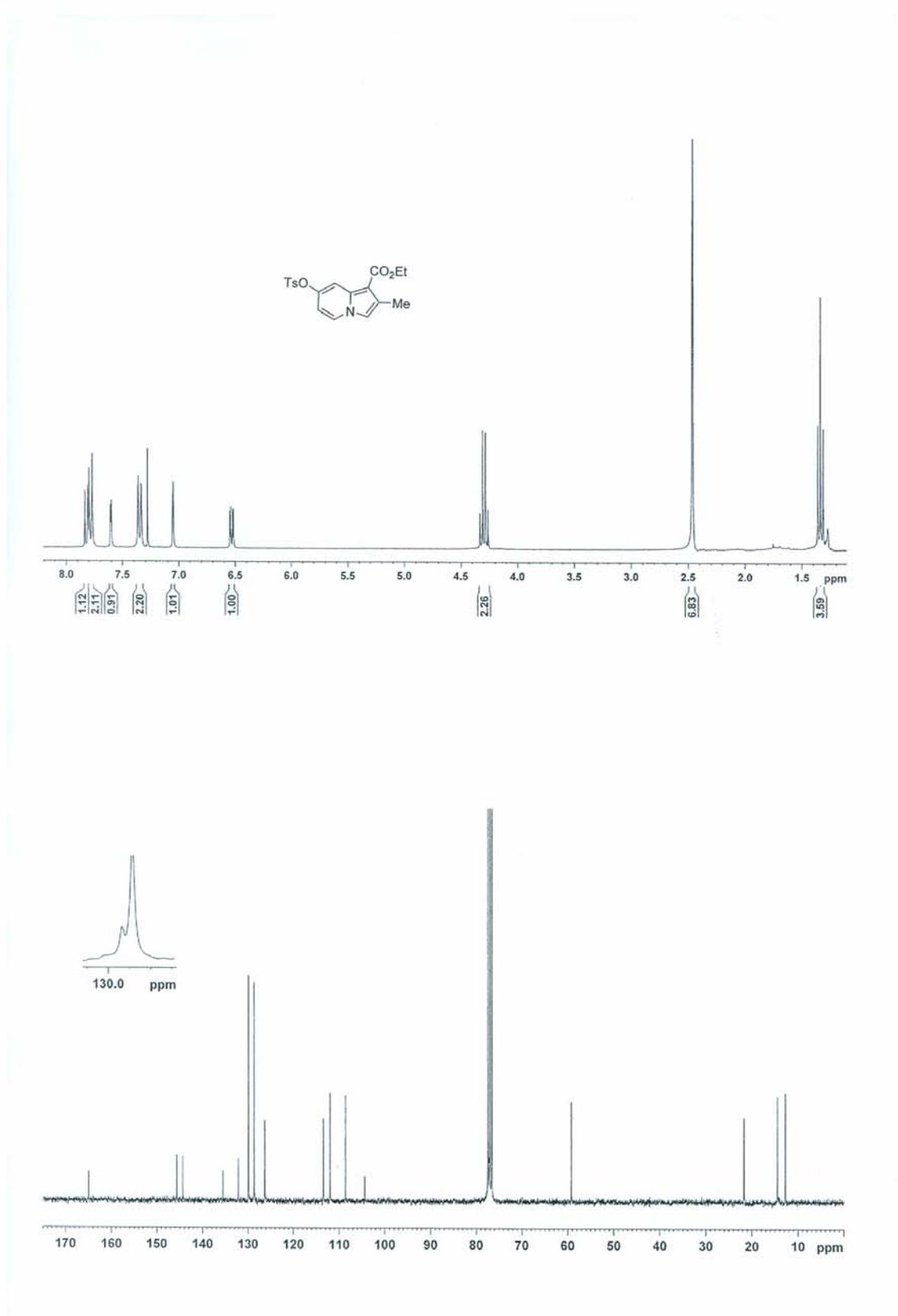
$^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (100 MHz) spectra of compound **3hb**



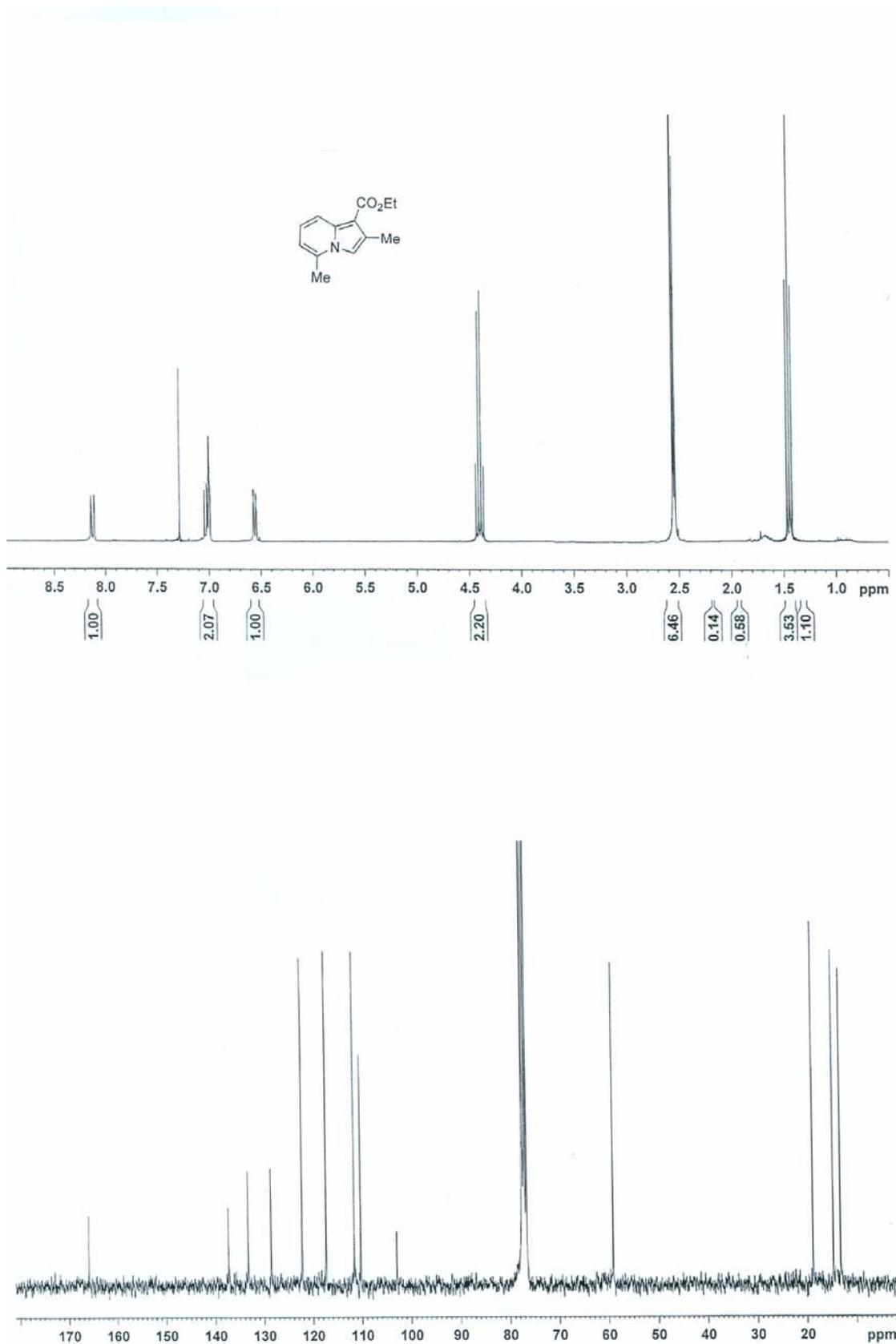
^1H -NMR (400 MHz) and ^{13}C -NMR (100 MHz) spectra of compound **3ib**



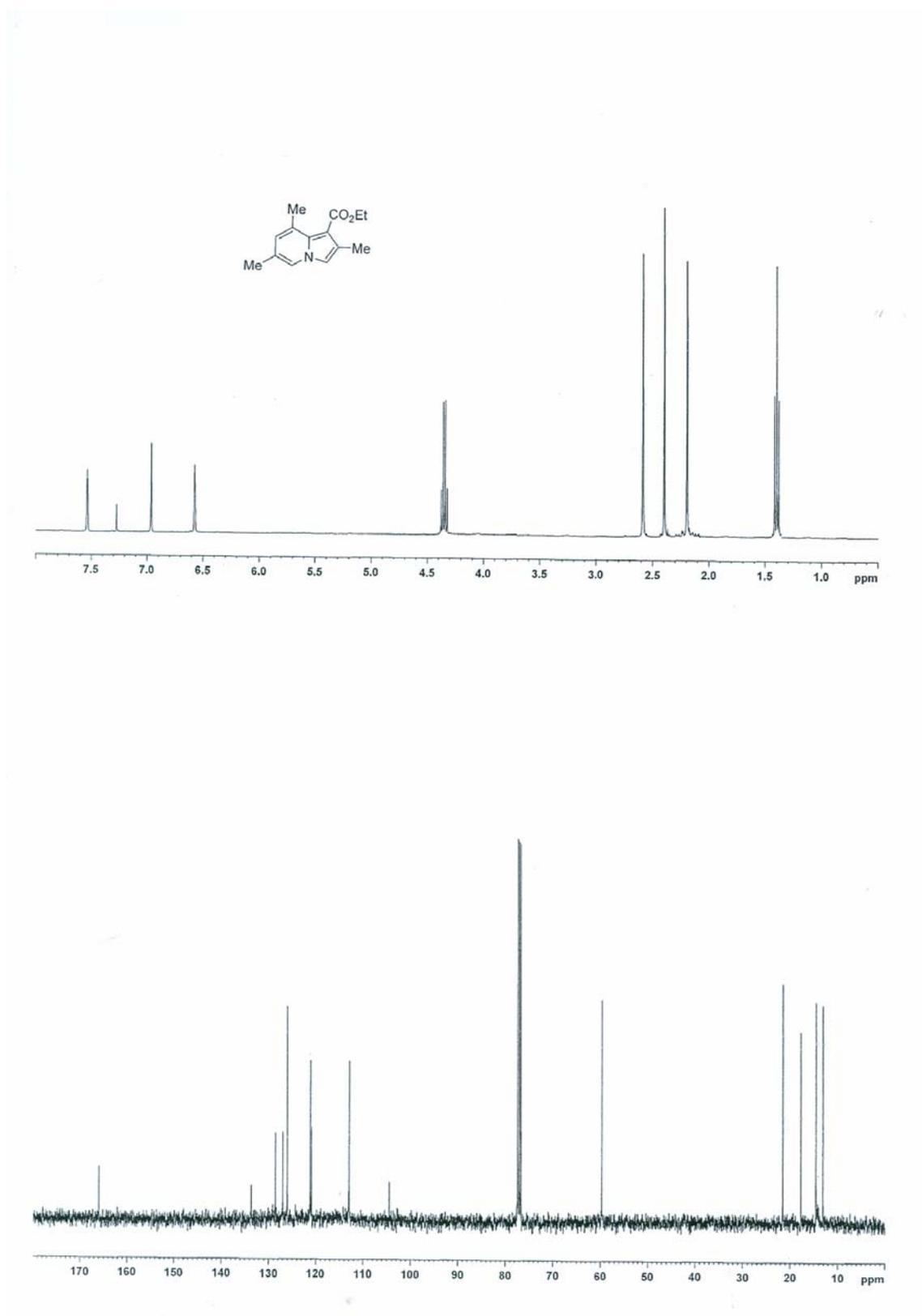
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3jb**



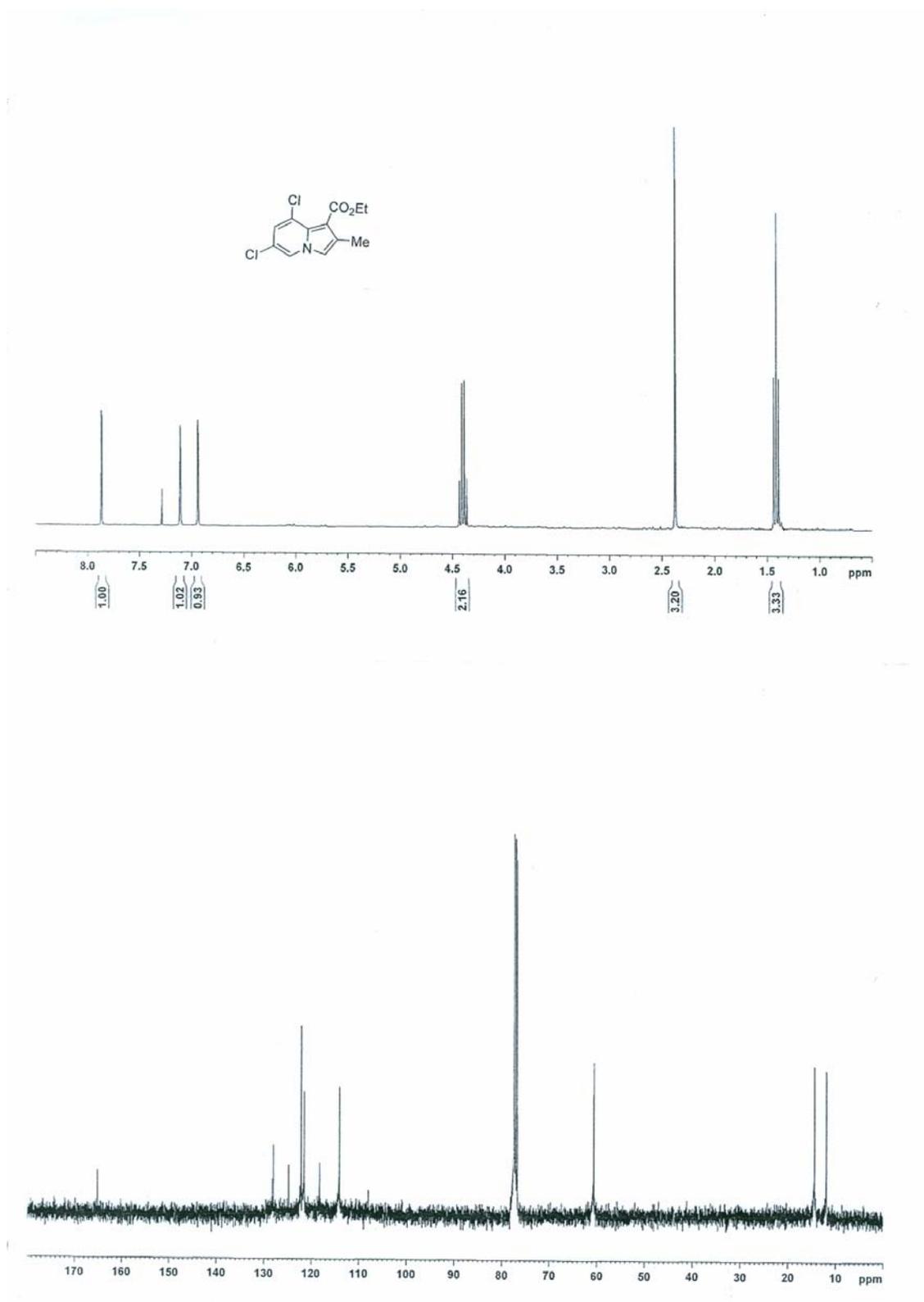
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **3kb**



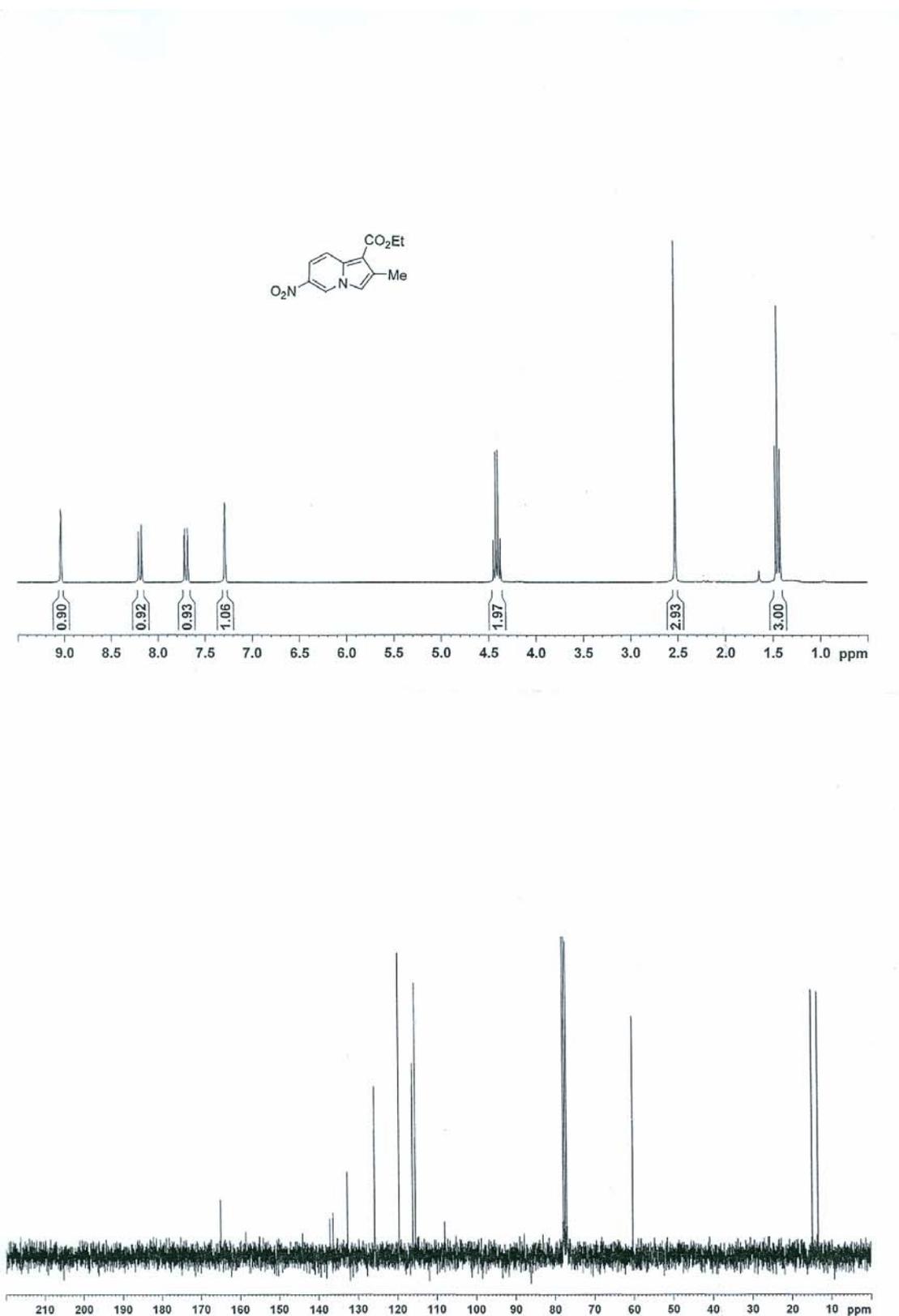
^1H -NMR (400 MHz) and ^{13}C -NMR (100 MHz) spectra of compound **31b**



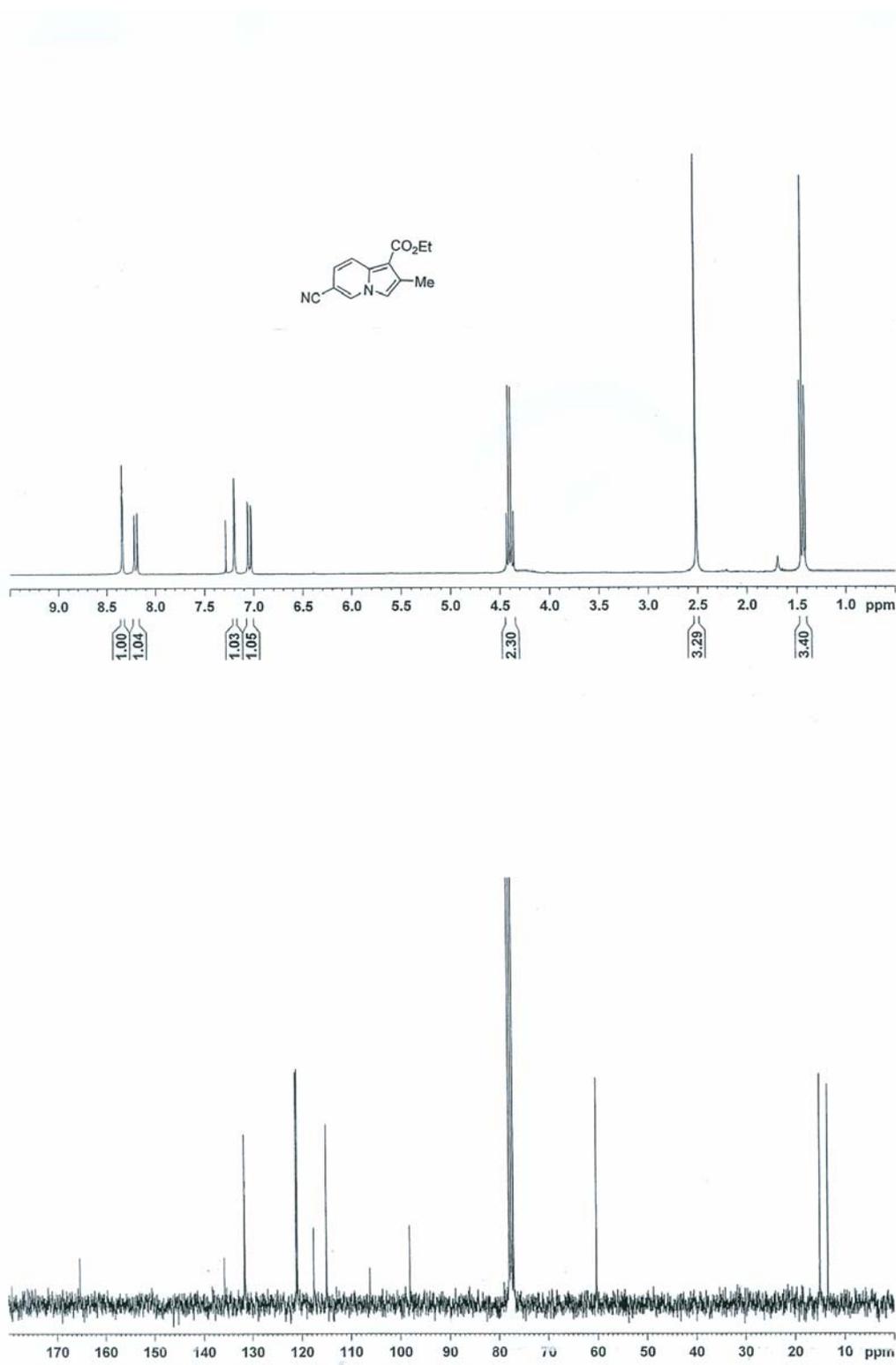
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (100 MHz) spectra of compound **3mb**



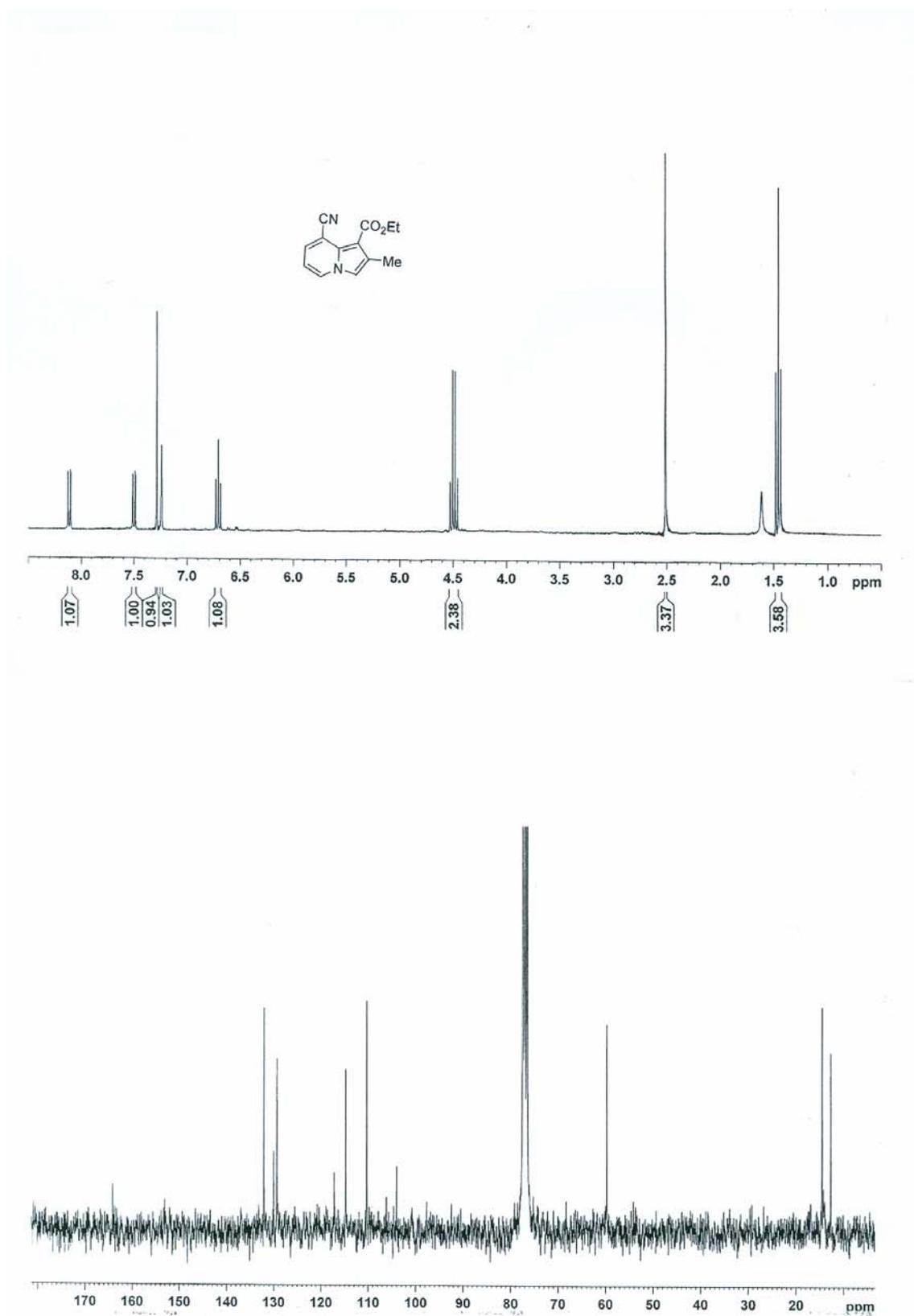
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **4nb**



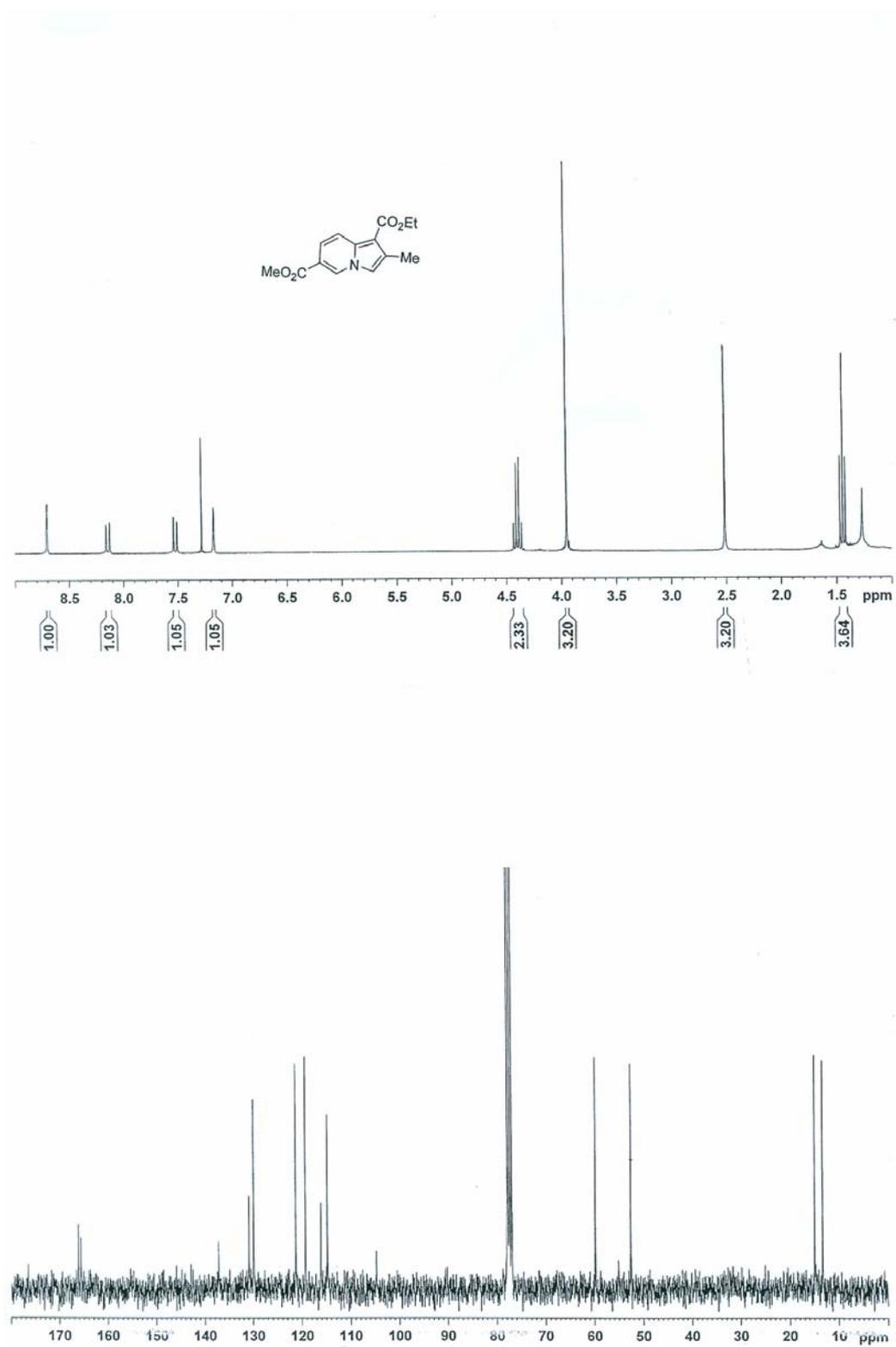
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **4ob**



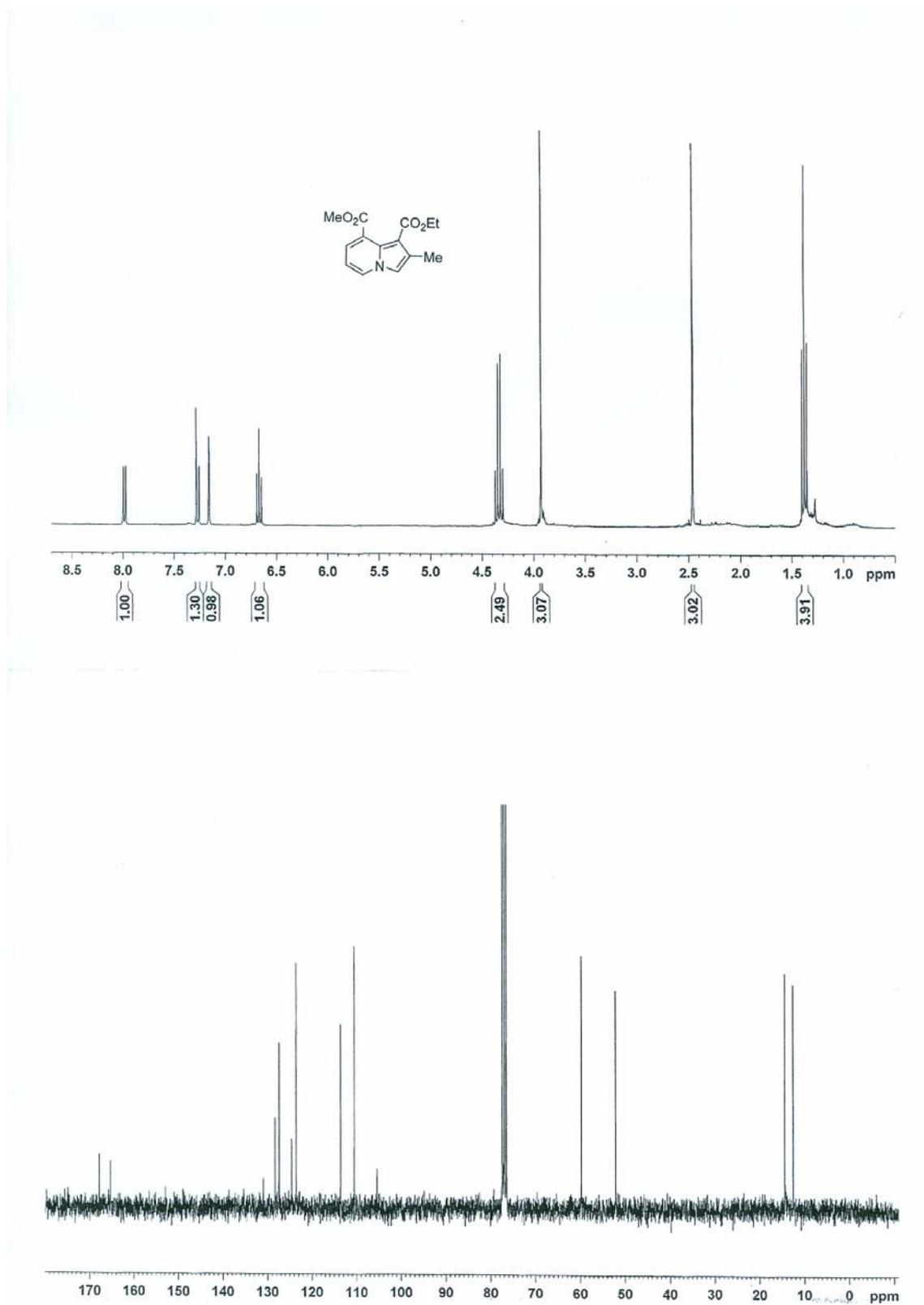
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **5ob**



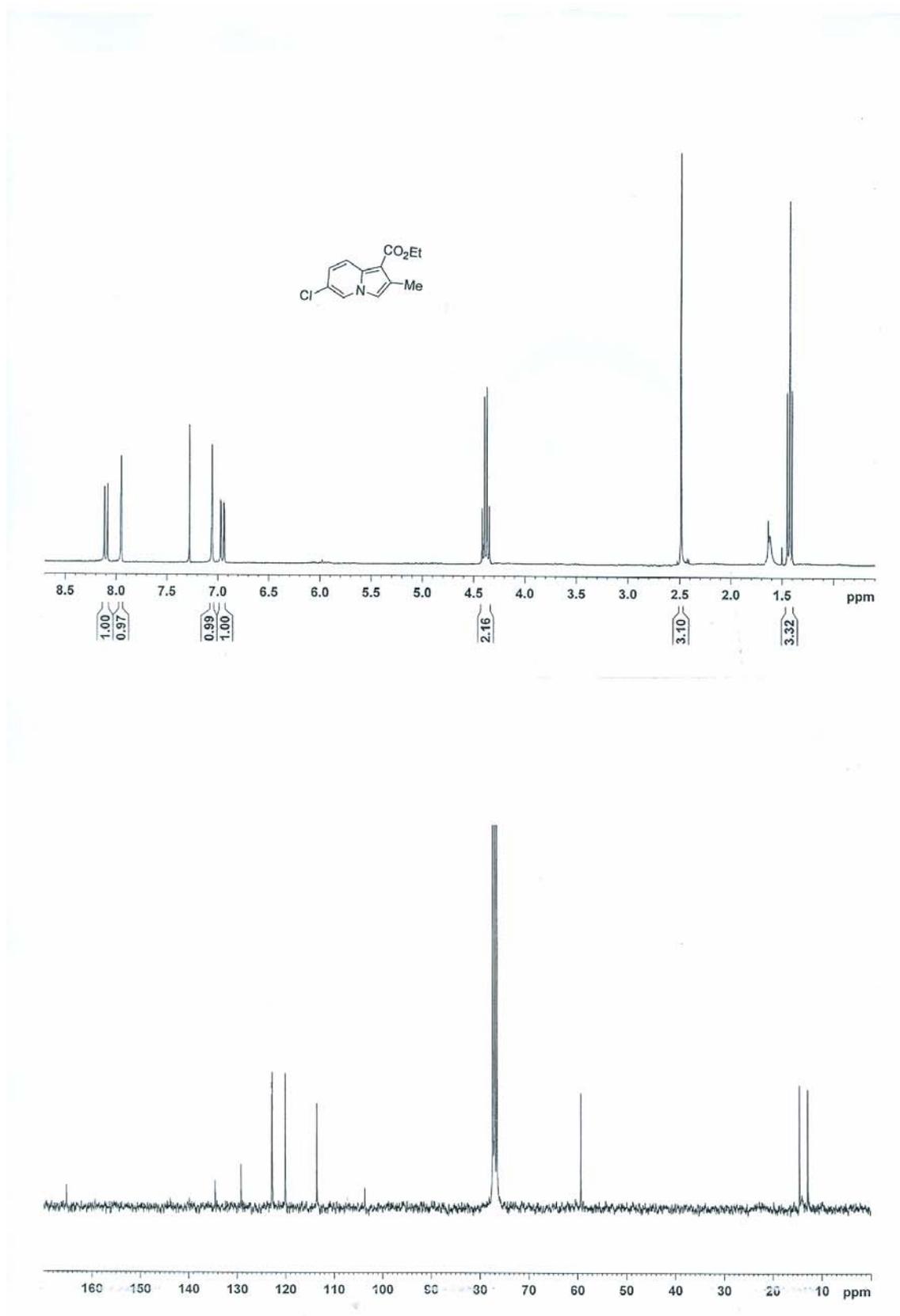
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **4pb**



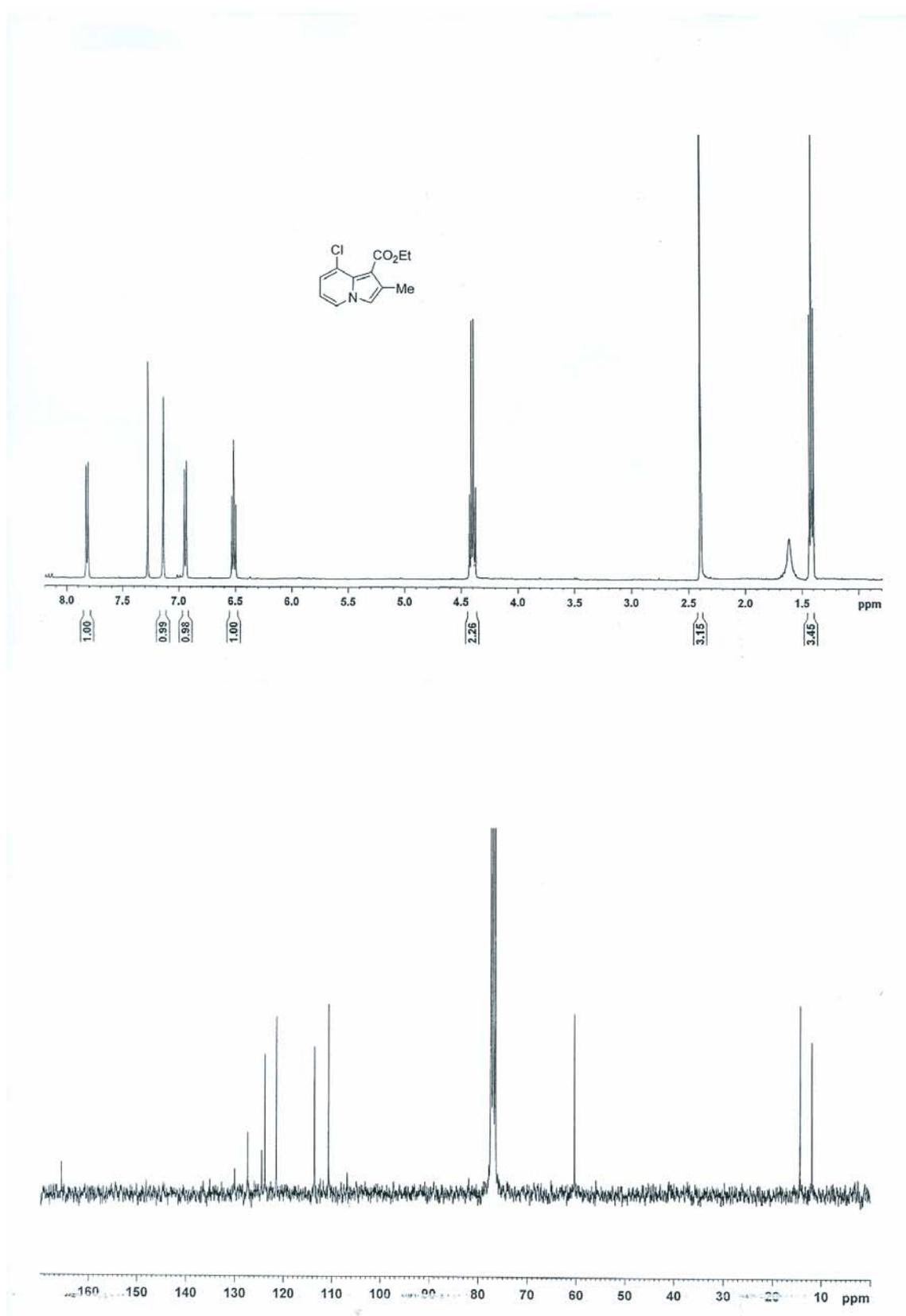
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **5pb**



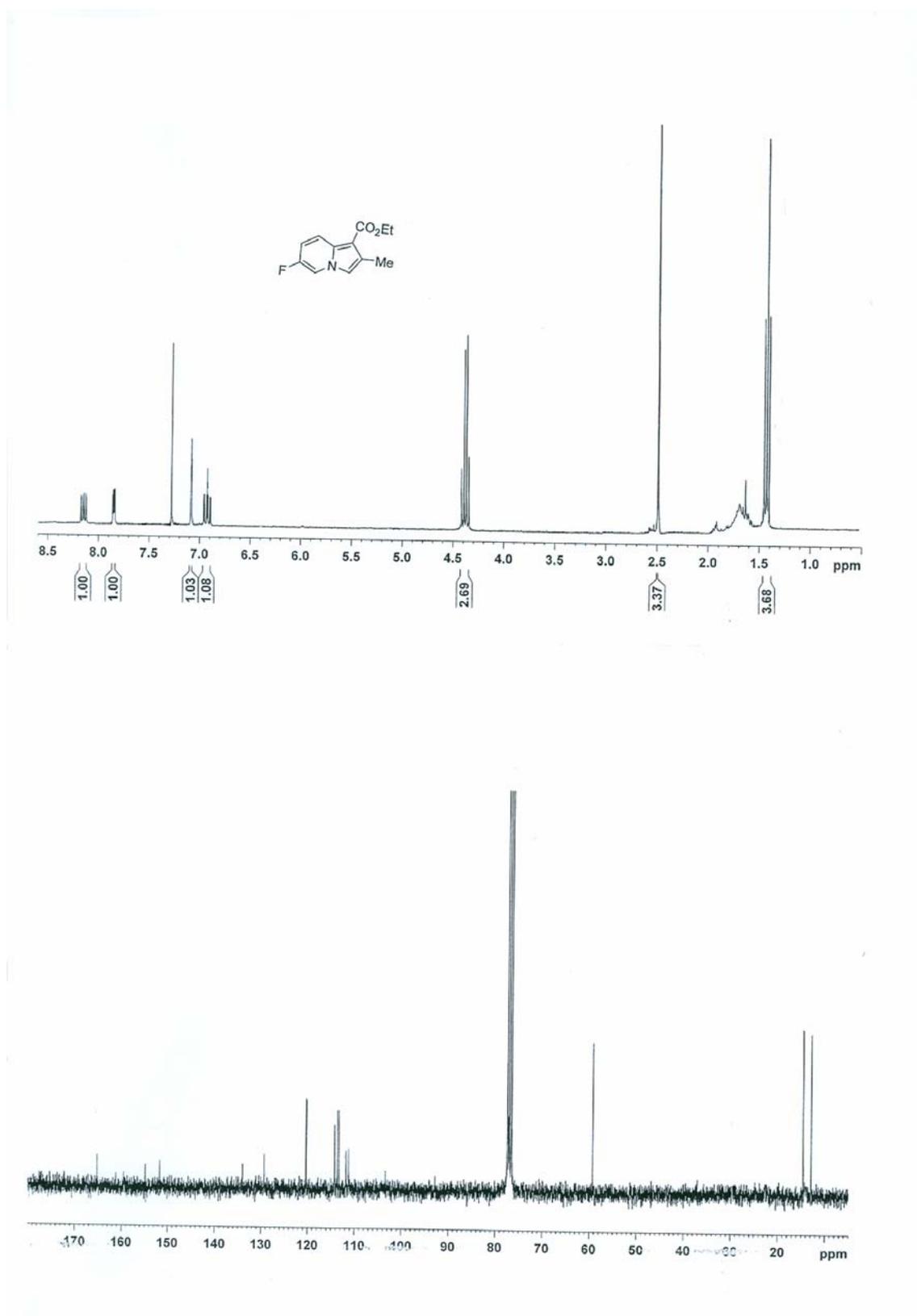
$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **4qb**



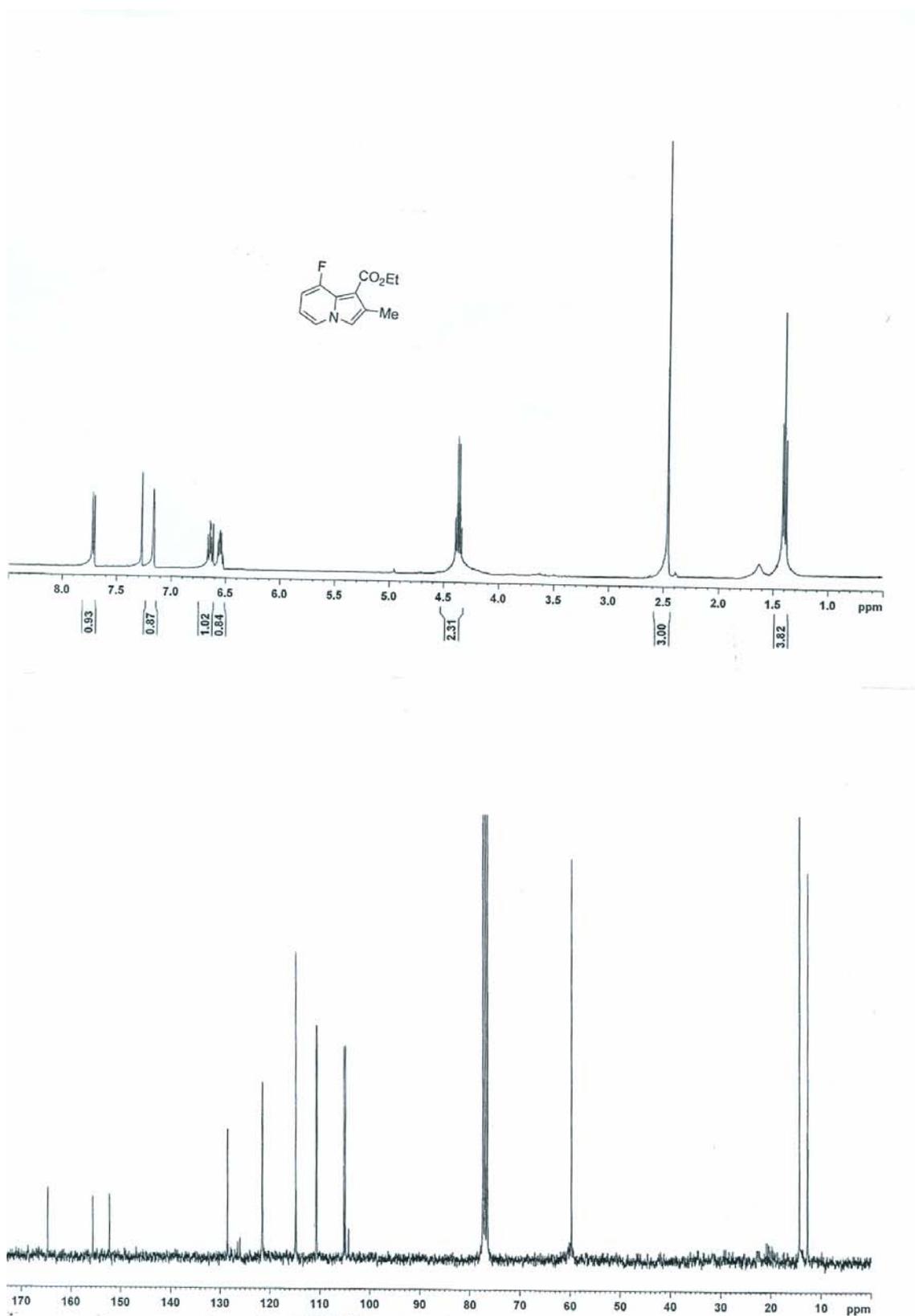
$^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (100 MHz) spectra of compound **5qb**



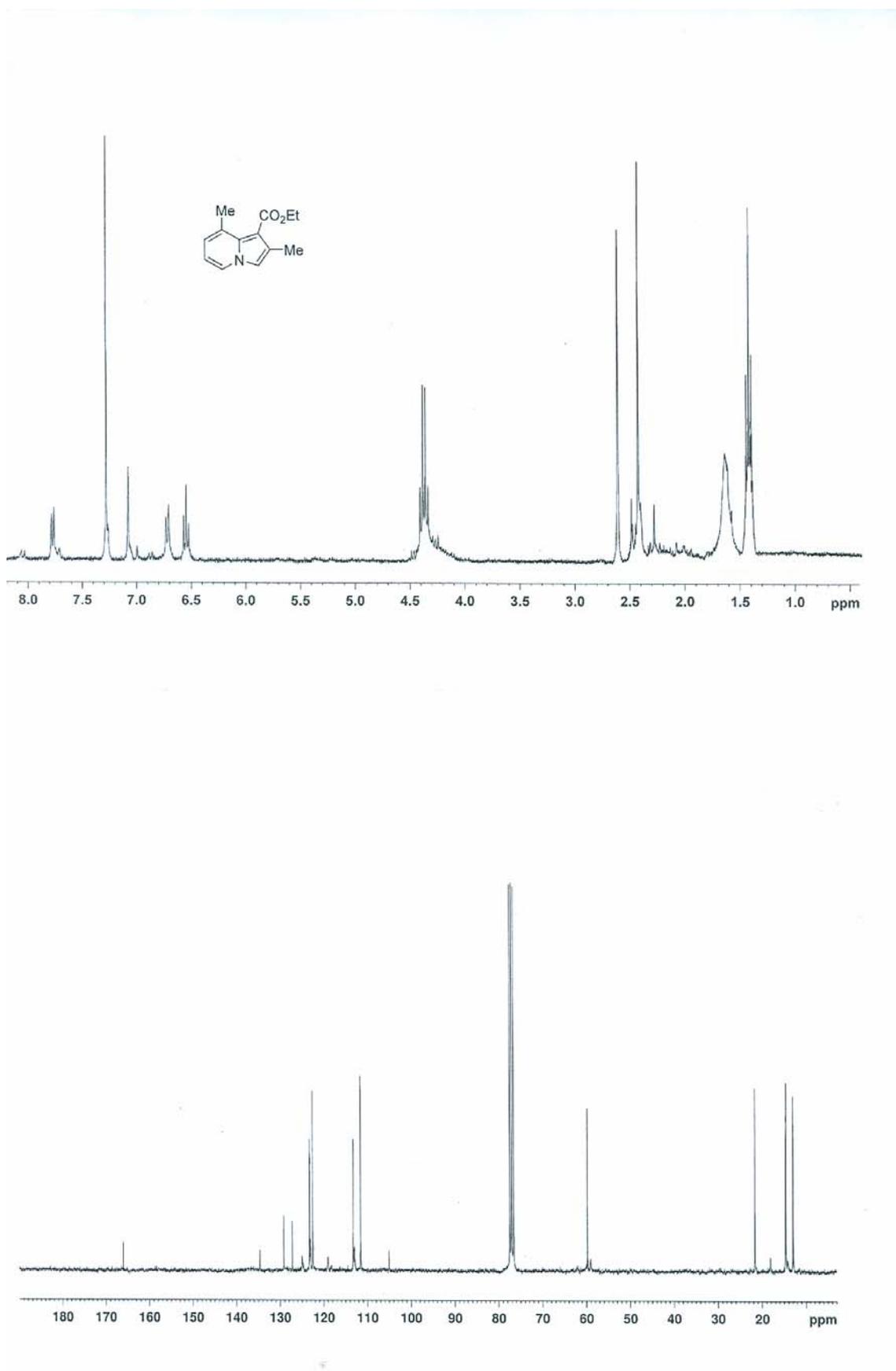
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **4rb**



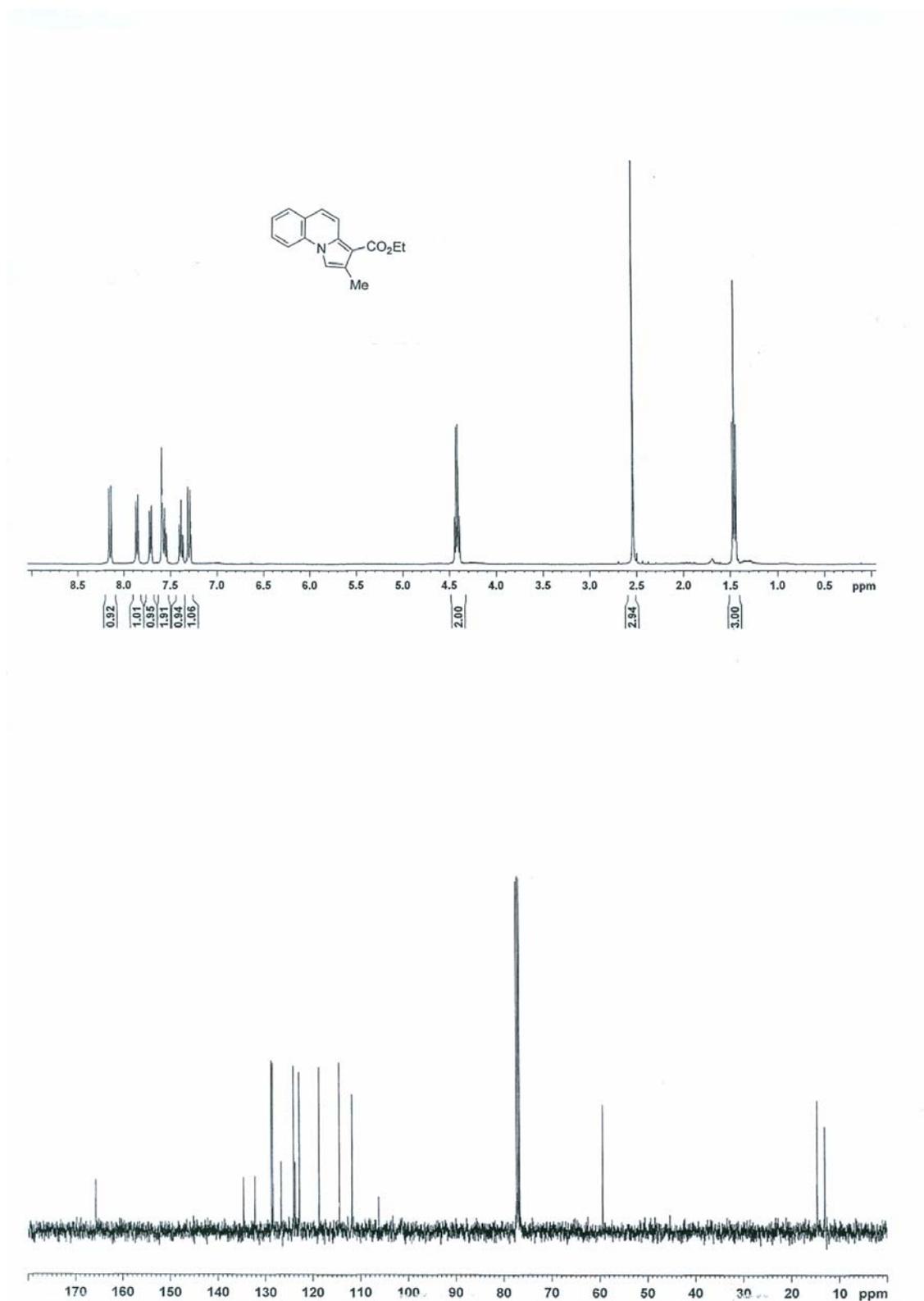
^1H -NMR (400 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **5rb**



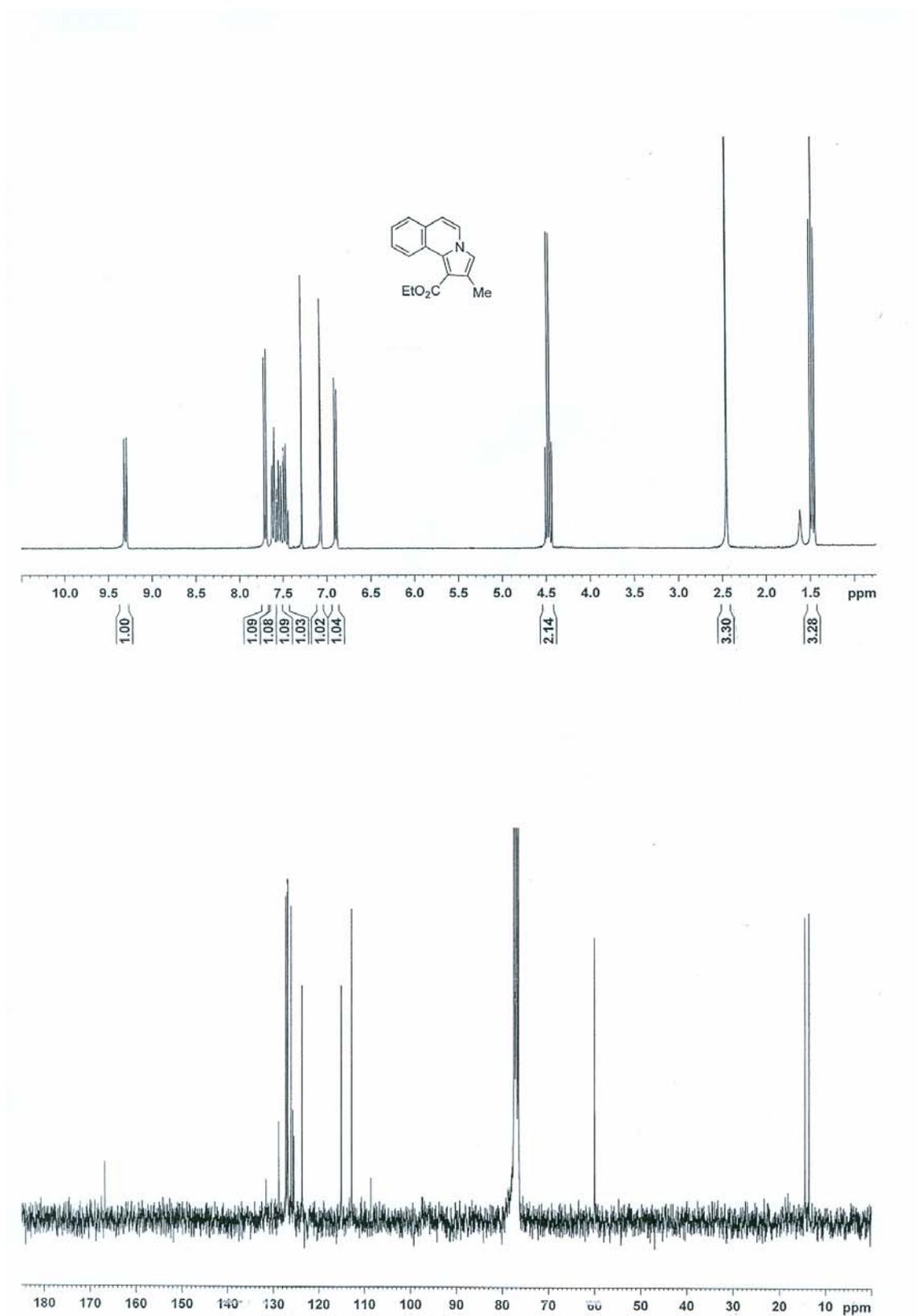
^1H -NMR (300 MHz) and ^{13}C -NMR (75 MHz) spectra of compound **5sb**



$^1\text{H-NMR}$ (400 MHz) and $^{13}\text{C-NMR}$ (100 MHz) spectra of compound **6**



$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) spectra of compound **7**



^1H -NMR (300 MHz) and ^{13}C -NMR (100 MHz) spectra of compound **8**

