Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Serendipitous Base Catalysed Condensation-Heteroannulation of Iminoesters: A Regioselective Route to Synthesis of 4,6-Disubstituted 5-Azaindoles

Premansh Dudhe,[a] Krishnan Venkatasubbaiah,[c] Biswarup Pathak,[a] and Venkatesh Chelvam*[a,b]

a. Discipline of Chemistry, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore-453 552, India
b. Discipline of Biosciences and Biomedical Engineering, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore-453 552, India
c. School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar-752 050, Odisha, India
*Corresponding author e-mail: cvenkat@iiti.ac.in

Supporting Information

Table of Contents

List of Abbreviations

NMR = Nuclear Magnetic Resonance
s = singlet
d = doublet
dd = doublet of doublets
dt = doublet of triplets
t = triplet
q = quartet
m = multiplet
HRMS = High Resolution Mass Spectroscopy
IR = Infrared Spectroscopy
m.p.= melting point
TLC = Thin Layer Chromatography
UV = Ultraviolet light
nm = nanometer
equiv. = equivalents
mmol = milli mol
mL = milli Litres
mg = milligrams
gms = Grams
R_f= Retention factor
DMF = *N,N*-Dimethyl formamide
DCM = Dichloromethane
DMA = *N,N*-Dimethyl acetamide
THF = Tetrahydrofuran
ACN = Acetonitrile
EtOAc =Ethyl Acetate
MS = Molecular Sieves
DIPEA = *N,N*-Diisopropylethylamine
DBU =1,8-Diazabicyclo[5.4.0]undec-7-ene
DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
MQ = milli Q

General Remarks

All reactions were carried out in oven dried glass wares with magnetic stirring.**1e**, **2a**, **2c**, **2d** along with other reagents were obtained from commercial supplier and used without further purification. NMR spectra were recorded on AvanceIII 400 Ascend Bruker. $CDCl_3$ and D_2O were used as NMR solvents. Chemical shifts (*δ)* reported as part per million (ppm) and TMS was used as internal reference. High resolution mass spectra were obtained through Bruker Daltonik High Performance LC MS (Electrospray Ionization Quadrupole time-of-flight) spectrometer. X-ray structure analysis was carried out at Single crystal X-ray diffractometer Bruker KAPPA APEXII. Melting points (m.p.) are uncorrected and were measured on Veego melting point apparatus (Capillary method). Analytical thin layer chromatography (TLC) was carried out on silica gel plates (silica gel 60 F254 aluminium supported plates); the visualization was accomplished with an UV lamp (254 nm and 365 nm) and using chemical staining with Brady's reagent, $KMnO_4$, ninhydrin, iodine, and bromocresol. Column chromatography was performed using silica gel (100–200 mesh or 230–400 mesh) and neutral alumina (175 mesh). DMF, DCM, DMA, toluene, and acetonitrile were dried using $CaH_2$and distilled over flame-dried 4Å molecular sieves. THF and Et_2O were dried over Na/benzophenone and stored over flame-dried 4Å molecular sieves under inert atmosphere prior to use. Organic bases including DIPEA, Et_3N, and DBU were stored over anhydrous KOH pellets.

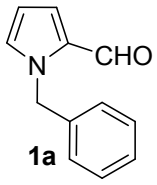
Optimization of reaction conditions for formation of 3aa

Table S1. Optimization of reaction conditions for formation of 3aa

S.No	Aldehyde (equiv.)	Aminoester HCl (equiv.)	Base (equiv.)	Solvent	Additive	Temperature	Reaction Time	Yield*
1.	**1a** (1.0)	**2a** (1.0)	DIPEA (3.5)	Toluene	4Å MS	Reflux	48 h	38% (**3aa**)
2.	**1a** (1.0)	**2a** (1.0)	Et_3N (3.5)	Toluene	4Å MS	Reflux	48 h	No product
3.	**1a** (2.0)	**2a** (1.0)	NaH (3.5)	THF	-	RT to reflux	24 h	No product
4.	**1a** (2.0)	**2a** (1.0)	K_2CO_3 (6.5)	Et_2O	-	RT to reflux	24 h	No product
5.	**1a** (2.0)	**2a** (1.0)	Cs_2CO_3 (2.0)	DMF	-	RT to reflux	24 h	No product
6.	**1a** (2.0)	**2a** (1.0)	DIPEA (3.5)	-	-	150°C/Sealed tube	6 h	58% (**3aa**)
7.	**1a** (1.0)	**2a** (5.0)	DIPEA (15.0)	-	-	100°C/Sealed tube	48 h	34% (**3aa**)
8.	**1a** (2.0)	**2a** (1.0)	DBU (3.5)	-	-	150°C/Sealed tube	6 h	31% (**3aa**)
9.	**1a**(2.0)	**2a** (1.0)	DIPEA (3.5)	-	-	150°C/200mbar (microwave)	10 min	Trace (**3aa**)
10.	**1a** (2.0)	**2a** (1.0)	DIPEA (3.5)	-	DDQ (1.0)	150°C/Sealed tube	16 h	No product
11.	**1a** (2.0)	**2a** (1.0)	DIPEA (3.5)	-	-	50°C/Sealed tube	24 h	No product

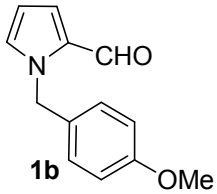
equiv. = no. of equivalents;*isolated yield

Typical Experimental Procedures



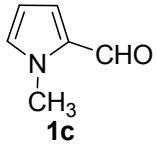
1a

1-Benzyl-1H-pyrrole-2-carbaldehyde (**1a**). Crushed potassium hydroxide (1.175 gm, 21 mmol) was dissolved in dimethyl sulfoxide (5 mL) in a round-bottom flask (100 mL) by stirring for 5 min at room temperature. Solid pyrrole-2-carboxaldehyde (500 mg, 5.25 mmol) was added to the reaction mixture in one portion and stirred for 45 min at the same temperature. Subsequently, the reaction mixture was cooled to 0 °C and benzyl bromide (1.25 mL, 10.5 mmol) was added through a glass syringe drop-wise over a period of 5 min. The reaction mixture was warmed to room temperature, monitored by TLC and stirred for another 45 min. After the completion of reaction, the reaction mixture was quenched with milli-Q water (MQ, 10 mL) and extracted with diethyl ether (3×10 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (100–200 mesh) column chromatography using hexane:EtOAc (99.5:0.5) as eluent to afford **1a**. Yield 85% (824 mg); Yellow oily liquid; R_f 0.50 (9:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.27–7.13(m, 3H), 7.12–7.00 (m, 2H), 6.93–6.80 (m, 2H), 6.18 (dd, J = 3.2, 2.7 Hz, 1H), 5.47 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 137.6, 131.6, 131.4, 128.7, 127.7, 127.3, 124.8, 110.2, 52.0.



1b

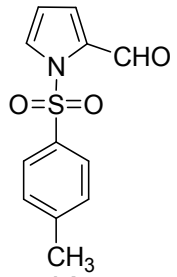
1-(4-Methoxybenzyl)-1H-pyrrole-2-carbaldehyde (**1b**). Under inert atmosphere, in a two-neck round-bottom flask (50 mL), sodium hydride (55–60% suspension in oil, 100 mg, 2.52 mmol) was suspended in dry dimethyl formamide (3 mL) at room temperature. Pyrrole-2-carboxaldehyde (200 mg, 2.10 mmol) was added to the reaction mixture in one portion and stirred for 30 min at the same temperature. Subsequently, the reaction mixture was cooled to 0 °C and 4-methoxy benzyl chloride (0.34 mL, 2.52 mmol) was added through a glass syringe drop-wise over a period of 5 min under inert atmosphere. The reaction mixture was allowed to warm to room temperature, stirred for another 2 h and monitored by TLC. After the completion of the reaction, the reaction mixture was quenched with milli-Q water (MQ, 10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:EtOAc (98.0:2.0) as eluent to afford **1b**. Yield 95% (430 mg); Dark yellow oily liquid; R_f 0.45 (4:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.13 (d, J = 8.3 Hz, 2H), 6.98–6.91 (m, 2H), 6.83 (d, J = 8.3 Hz, 2H), 6.24 (dd, J = 2.8, 2.4 Hz, 1H), 5.48 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 159.2, 131.5, 131.2, 129.6, 128.9, 124.9, 114.1, 110.1, 55.3, 51.5.



1c

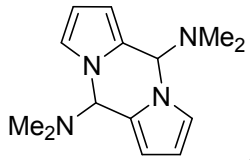
1-Methyl-1H-pyrrole-2-carbaldehyde (**1c**). Potassium tertiary butoxide (1.188 gm, 10.50 mmol) and 18-crown-6 ether (0.16 mL, 0.72 mmol) were suspended in diethyl ether (10 mL) in a two-

neck round-bottom flask (50 mL) at room temperature. Pyrrole-2-carboxaldehyde (1.0 gm, 10.50 mmol) was added to the reaction mixture in one portion and stirred for 15 min at the same temperature. Subsequently, the reaction mixture was cooled to 0 °C and methyl iodide (0.32 mL, 5.25 mmol) was added through a glass syringe drop-wise over a period of 5 min. Reaction mixture was allowed to warm to room temperature, stirred for another 24 h and monitored by TLC. After the completion of reaction, the reaction mixture was quenched with milli-Q water (MQ, 10 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:EtOAc (99:1) as eluent to afford **1c**. Yield 83% (950 mg); Light yellow liquid; R_f 0.25 (4:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 6.98–6.88 (m, 1H), 6.88–6.83 (m, 1H), 6.25–6.17 (m, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ179.6, 132.1, 132.0, 124.1, 109.5, 36.5.

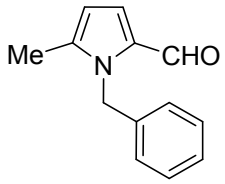


1d

1-Tosyl-1H-pyrrole-2-carbaldehyde (**1d**). Sodium hydride (55–60% suspension in oil, 50 mg, 1.31 mmol) was suspended in dry dimethyl formamide (3 mL) in a two-neck round-bottom flask (50 mL) at room temperature under an inert atmosphere. Pyrrole-2-carboxaldehyde (100 mg, 1.05 mmol) was added to the reaction mixture in one portion at 0 °C and stirred for 20 min. Subsequently, tosyl chloride (200 mg, 1.05 mmol) was added in one portion and reaction mixture was stirred at room temperature overnight (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with milli-Q water (MQ, 10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:EtOAc (95:5) as eluent to afford **1d**. Yield 80% (210 mg); Yellow liquid; R_f 0.25 (9:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.64–7.55 (m, 1H), 7.30 (d, J = 8.3 Hz, 2H), 7.14 (dd, J = 3.3, 1.2 Hz, 1H), 6.39 (dd, J = 3.3, 3.0 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 146.0, 130.2, 129.6, 129.5, 127.8, 127.5, 124.5, 112.4, 38.0.

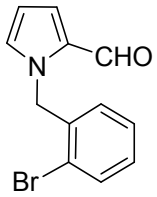


N^5,*N*^{5},*N*^{10},*N*^{10}*-tetramethyl-5,10-dihydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diamine*. A solution of pyrrole-2-carboxaldehyde (500 mg, 5.25 mmol) in dimethylamine (1.05 mL, 40% in H_2O) was stirred at room temperature for 3 h. The precipitated solid was collected by filtration and dried under reduced pressure. The crude solid was recrystallized from hot EtOAc (10 mL) and hexane (5 mL) to afford the dimer.[6] Yield 67% (430 mg); Pink solid; R_f 0.30 (8:2 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–6.91 (m, 2H), 6.29–6.23 (m, 2H), 6.20–6.13 (m, 2H), 5.87 (s, 2H), 2.22 (s, 12H).[1]



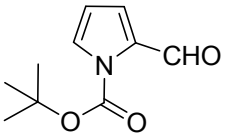
1f

1-Benzyl-5-methyl-1H-pyrrole-2-carbaldehyde (**1f**). Freshly prepared N^5,N^5,N^{10},N^{10}-tetramethyl-5,10-dihydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diamine (1.0 gm, 4.09 mmol) was dissolved in dry THF (15 mL) in a round bottom flask (100 mL) under an inert atmosphere at 0 °C. *n*-BuLi (1.6 M in hexane, 5.62 mL, 9.00 mmol) was added to the reaction mixture slowly, through a glass syringe over a period of 10 min at the same temperature. The reaction mixture warmed to 5 °C and continued for stirring for another 2 h. The reaction mixture was once again cooled to 0 °C and methyl iodide (1.02 mL, 16.36 mmol) was added through a glass syringe over a period of 10 min. The reaction mixture was warmed to room temperature and stirred for 5 h. Saturated $NaHCO_3$ (25 mL) and MQ water (25 mL) were added and the mixture was heated at 80 °C for 16 h. The reaction mixture was extracted with DCM (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue with crushed KOH (1.234 gm, 22.00 mmol) were dissolved in DMSO (6 mL) in a round bottom flask (100 mL) at room temperature with stirring. Benzyl bromide (0.98 mL, 8.25 mmol) was added using a glass syringe drop-wise over a period of 10 min and further stirred for overnight at room temperature. The reaction mixture was quenched with milli-Q water (15 mL) and extracted with EtOAc (5 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:acetone (96:4) as eluent to afford **1f**.Yield 55% (600 mg); Dark yellow oily liquid; R_f 0.45 (9:1 hexane-acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.37–7.17 (m, 3H), 6.97 (m, 2H), 6.91 (d, J = 3.8 Hz, 1H), 6.08 (d, J = 3.8 Hz, 1H), 5.63 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 140.9, 137.6, 131.8, 128.7, 127.2, 126.2, 125.2, 110.4, 48.3, 12.2.



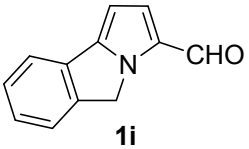
1g

1-(2-Bromobenzyl)-1H-pyrrole-2-carbaldehyde (**1g**). Sodium hydride (55–60% suspension in oil, 100 mg, 2.52 mmol) was suspended in dry dimethyl formamide (2 mL) in a two-neck round-bottom flask (50 mL) at room temperature under an inert atmosphere. Pyrrole-2-carboxaldehyde (200 mg, 2.10 mmol) was added to the reaction mixture in one portion and stirred for 20 min at the same temperature. Subsequently, the reaction mixture was cooled to 0 °C and 2-bromobenzyl chloride (0.31 mL, 2.52 mmol) was added using a glass syringe drop-wise over a period of 5 min. The reaction mixture was warmed to room temperature and stirred for further 2 h (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with milli-Q water (10 mL) and extracted with EtOAc(3 × 5 mL). The combined organic layers was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:EtOAc (99.0:1.0) as eluent to afford **1g**. Yield 78% (430 mg); White solid; R_f 0.60 (8:2hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.19 (dd, J = 7.5, 7.5 Hz,1H),7.12 (dd, J = 7.8, 7.3 Hz, 1H), 7.00 (d, J = 3.0 Hz, 1H), 6.98–6.93 (m, 1H), 6.67(d, J = 7.5 Hz, 1H), 6.30 (dd, J = 3.0, 2.6 Hz, 1H), 5.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 137.1, 132.8, 131.7, 131.5, 129.2, 128.3, 127.9, 124.7, 122.7, 110.4, 52.1.



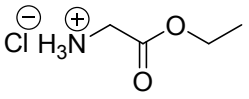
1h

Tert-butyl 2-formyl-1H-pyrrole-1-carboxylate (**1h**). Pyrrole-2-carboxaldehyde (500 mg, 5.25 mmol) and *N*,*N*-dimethylamino pyridine (65 mg, 0.52 mmol) were dissolved in acetonitrile (5 mL) in a two-neck round-bottom flask (50 mL) at room temperature. Boc anhydride (1.44 mL, 6.30 mmol) was added to the reaction mixture through a glass syringe over a period of 5 min at room temperature under inert atmosphere and stirred for further 2 h (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with milli-Q water (10 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:EtOAc (99:1) as eluent to afford **1h**. Yield 92% (950 mg); Pale yellow oily liquid; R_f 0.35 (9:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ10.30 (s, 1H), 7.44–7.39 (m, 1H), 7.16 (d, J = 2.5 Hz, 1H), 6.26 (dd, J = 3.3, 2.5 Hz, 1H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 148.4, 134.8, 127.4, 121.2, 111.7, 85.8, 28.0.



1i

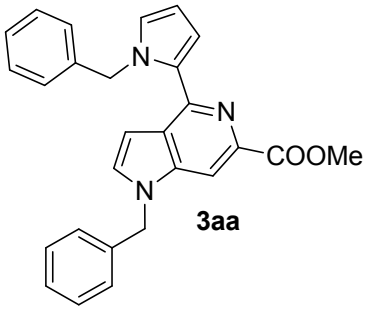
5H-Pyrrolo[2,1-a]isoindole-3-carbaldehyde (**1i**). *1-(2-Bromobenzyl)-1H-pyrrole-2-carbaldehyde* (**1g**, 300 mg, 1.14 mmol) was dissolved in dry *N*,*N*-Dimethyl acetamide (DMA, 2 mL) in a three-neck round-bottom flask (50 mL) and the solution was degassed (through N_2 bubbling). KOAc (112 mg, 1.14 mmol) and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) were added to the reaction mixture at room temperature in one portion. The reaction mixture was heated at 140 °C using oil bath under inert atmosphere, monitored by TLC for another 7 h. After the completion of reaction, the reaction mixture was quenched with brine (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified over silica gel (230–400 mesh) column chromatography using hexane:EtOAc (98:2) as eluent to afford **1i**. Yield 76% (160 mg); Yellow crystalline solid; m.p. = 128–130 °C; R_f 0.70 (2:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.69–7.59 (m, 1H), 7.53–7.46 (m, 1H), 7.45–7.29 (m, 2H), 7.12–7.03 (m, 1H), 6.52–6.41 (m, 1H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 146.1, 141.9, 131.4, 129.8, 128.2, 127.4, 125.7, 123.5, 120.5, 101.3, 52.4.



2b

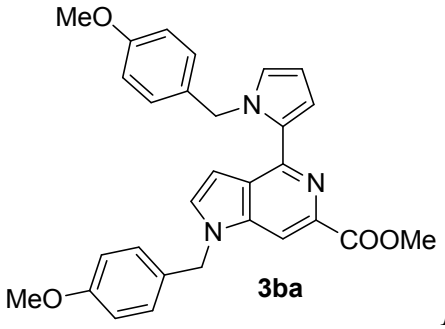
Glycine ethyl ester HCl salt (**2b**). Glycine (5.0gm, 66.60 mmol) was suspended in dry ethanol (30 mL) in around-bottom flask (250 mL). The suspension was cooled to 0 °C and thionyl chloride (7.3 mL, 100 mmol) was added drop-wise through a glass syringe over a period of 10 min. The reaction mixture was refluxed overnight and monitored using TLC. The excess solvent was evaporated under reduced pressure and the residue was further washed with diethyl ether(3 × 10 mL) to afford **2b**. Crude yield 97% (8.980 gm); Off white solid; ^{1}H NMR (400 MHz, D_2O) δ 4.29 (q, J = 7.3 Hz, 2H), 3.90 (s, 2H), 1.28 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, D_2O) δ 168.2, 63.4, 40.3, 13.2.

General procedure for synthesis of *Alkyl 4-(1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* derivatives (**3aa–fa**). A mixture of glycine alkyl ester hydrochloride (**2a–c**, 1 mmol), aldehyde (**1a–i**, 2 mmol) and *N*,*N*-Diisopropylethylamine (DIPEA, 3.5 mmol) was heated at 150 °C for 6–12 h in a sealed tube (25 mL, Borosilicate) with constant stirring (monitored by TLC). The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (1 × 10 mL) and washed with brine (1 × 10 mL). The reaction mixture was further extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and purified over neutral alumina (175 mesh) column chromatography using hexane-EtOAc solvent mixture as eluent.



3aa

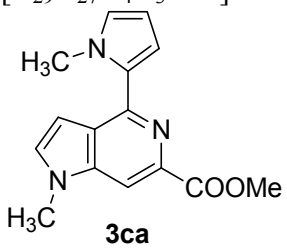
Methyl1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3aa**). According to the general procedure mentioned above, **1a** (100 mg, 0.54 mmol), **2a** (34 mg, 0.27 mmol) and DIPEA (0.165 mL, 0.95 mmol) were heated in a sealed tube at 150 °C for 6 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (94:6) as eluent; Yield 58% (66 mg); Yellow crystalline solid; m.p. = 134–136 °C; R_f 0.65 (2:1 hexane-EtOAc); IR (KBr) 3028 (=C–H), 2922–2850 (C–H), 1722 (C=O), 1712–1554 (C=C), 1357 (C–H bend), 779 (=C–H bend) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.35–7.27 (m, 3H), 7.24 (d, J = 3.2 Hz, 1H), 7.18–7.13 (m, 2H), 7.12–7.08 (m, 3H), 7.07–7.02 (m, 2H), 6.91 (d, J = 3.2 Hz, 1H), 6.90–6.87 (m, 1H), 6.82 (dd, J = 3.7, 1.7 Hz, 1H), 6.29 (dd, J = 2.9, 2.3 Hz, 1H), 5.88 (s, 2H), 5.34 (s, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 145.8, 140.5, 139.6, 138.7, 136.2, 131.2, 130.4, 129.0, 128.2, 128.2, 127.1, 127.0, 126.8, 125.7, 125.0, 113.2, 108.2, 105.7, 103.7, 52.5, 51.7, 50.2; HRMS (ESI) calcd for [$C_{27}H_{23}N_3O_2$+H^+] 422.1863, found 422.1859.



3ba

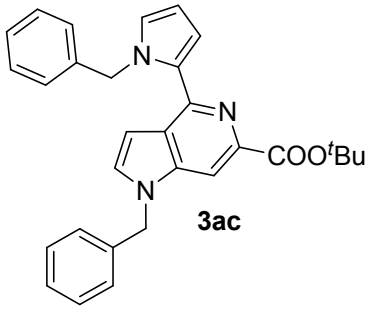
Methyl1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3ba**). According to the general procedure mentioned above, **1b** (100 mg, 0.46 mmol), **2a** (29 mg, 0.23 mmol) and DIPEA (0.140 mL, 0.81 mmol) were heated in a sealed tube at 150 °C for 6 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (88:12) as eluent; Yield 61% (68 mg); Yellow liquid; R_f0.60 (1:1 hexane-EtOAc); IR (KBr) 3073 (=C–H), 2958–2851 (C–H), 1743 (C=O), 1109–1029 (C–O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.22 (d, J = 3.2 Hz, 1H), 7.08 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2 H), 6.90–6.81 (m, 4H), 6.78 (dd, J = 3.5, 1.5 Hz, 1H), 6.69 (d, J = 8.8 Hz, 2H), 6.25 (dd, J = 3.3, 2.6 Hz, 1H), 5.77 (s, 2H), 5.28 (s, 2H), 3.97 (s, 3H), 3.78 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 158.8, 157.8, 145.1, 139.6, 137.9, 130.9, 130.3, 129.6, 127.9, 127.8, 127.4, 124.7,

124.4, 113.7, 112.9, 112.5, 107.3, 105.0, 102.8, 54.6, 54.4, 51.7, 50.4, 49.0; HRMS (ESI) calcd for $[C_{29}H_{27}N_4O_3+H^+]$ 482.2074, found 482.2074.



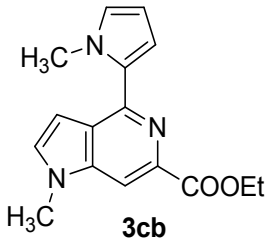
3ca

Methyl1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3ca**). According to the general procedure mentioned above, **1c** (100 mg, 0.92 mmol), **2a** (29 mg, 0.46 mmol) and DIPEA (0.281 mL, 1.61 mmol) were heated in a sealed tube at 150 °C for 6 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (92:8) as eluent; Yield 48% (59 mg);Yellowish-brown liquid; R_f 0.60 (1:1 hexane-EtOAc); IR (KBr) 3126–3084 (=C–H), 2926–2852 (C–H), 1732 (C=O), 1714–1556 (C=C), 1350 (C–H bend), 721 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.24–7.17 (m, 1H), 6.89–6.81 (m, 1H), 6.80–6.74 (m, 1H), 6.73–6.68 (m, 1H), 6.25–6.13 (m, 1H), 4.03 (s, 3H), 3.97 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 145.7, 140.7, 138.5, 132.0, 130.7, 126.2, 124.9, 112.6, 107.5, 105.5, 103.1, 52.5, 36.4, 33.1; HRMS (ESI) calcd for $[C_{15}H_{15}N_3O_2+H^+]$ 270.1237, found 270.1233.



3ac

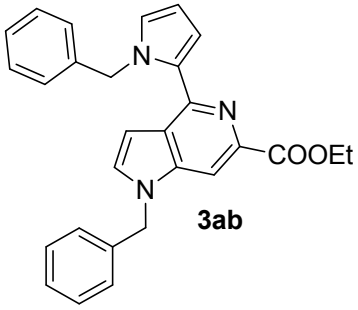
Tert-butyl-1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3ac**). According to the general procedure mentioned above, **1a** (100 mg, 0.54 mmol), **2c** (45 mg, 0.27 mmol) and DIPEA (0.165 mL, 1.61 mmol) were heated in a sealed tube at 150 °C for 8 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (95:5) as eluent; Yield 40% (50 mg); Yellow liquid; R_f 0.50 (4:1 hexane-EtOAc); IR (KBr) 3063 (=C–H), 2976–2849 (C–H), 1732 (C=O), 1701–1564 (C=C), 1363 (C–H bend), 723 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.37–7.26 (m, 3H), 7.22 (d, J = 3.2 Hz, 1H), 7.19–7.04 (m, 7H), 6.91 (d, J = 3.2 Hz, 1H), 6.89–6.82 (m, 2H), 6.26 (dd, J = 3.2, 3.0 Hz, 1H), 6.03 (s, 2H), 5.33 (s, 2H), 1.59 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 145.4, 140.7, 140.2, 139.8, 136.3, 130.9, 130.5, 129.0, 128.3, 128.1, 127.2, 127.0, 126.8, 125.8, 124.3, 113.3, 108.1, 105.0, 103.5, 81.1, 51.8, 50.1, 28.3; HRMS (ESI) calcd for $[C_{30}H_{29}N_3O_2+H^+]$ 464.2333, found 464.2334.



3cb

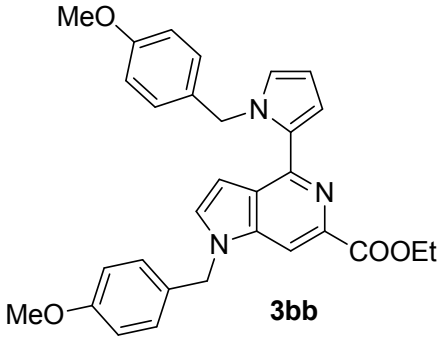
Ethyl1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3cb**). According to the general procedure mentioned above, **1c** (100 mg, 0.92 mmol), **2b** (64 mg, 0.46 mmol) and DIPEA (0.281 mL, 1.61 mmol) were heated in a sealed tube at 150 °C for 7 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (92:8) as eluent Yield 46% (60 mg); Light yellow liquid; R_f 0.50 (2:1 hexane-EtOAc); IR (KBr) 3077 (=C–H), 2957–2850 (C–H), 1731 (C=O), 1714–1558 (C=C), 1374 (C–H

bend),725 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.24–7.19 (m, 1H), 6.92–6.85 (m, 1H), 6.83–6.78 (m, 1H), 6.78–6.72 (m, 1H), 6.27–6.19 (m, 1H), 4.46 (q, J = 6.8 Hz, 2H), 4.10 (s, 3H), 3.88 (s, 3H), 1.45 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 145.5, 140.7, 138.7, 131.9, 130.7, 126.3, 124.6, 112.7, 107.5, 105.2, 103.0, 61.3, 36.6, 33.1, 14.4; HRMS (ESI) calcd for $[C_{16}H_{17}N_3O_2+H^+]$ 284.1394, found 284.1389.



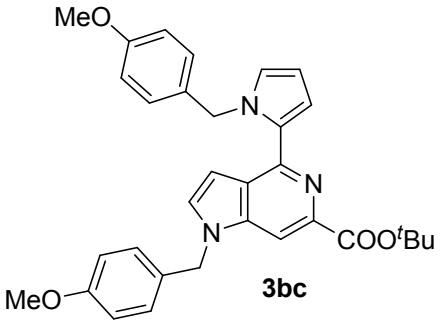
3ab

Ethyl1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3ab**). According to the general procedure mentioned above, **1a** (100 mg, 0.54 mmol), **2b** (38 mg, 0.27 mmol) and DIPEA (0.165 mL, 0.95 mmol) were heated in a sealed tube at 150 °C for 6 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (94:6) as eluent; Yield 55% (65 mg); Yellow liquid; R_f 0.60 (4:1 hexane-EtOAc); IR (KBr) 3056 (=C–H), 2977–2851 (C–H), 1729 (C=O), 1712–1554 (C=C), 1367 (C–H bend), 726 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.38–7.26 (m, 3H), 7.26–7.21 (m, 1H), 7.19–7.13 (m, 2H), 7.13–7.02 (m, 5H), 6.95–6.90 (m, 1H), 6.90–6.86 (m, 1H), 6.85–6.80 (m, 1H), 6.33–6.24 (m, 1H), 5.94 (s, 2H), 5.35 (s, 2H), 4.41 (q, J = 6.8 Hz, 2H), 1.38 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 145.7, 140.6, 139.7, 139.0, 136.3, 131.1, 130.4, 129.0, 128.3, 128.2, 127.2, 127.0, 126.8, 125.8, 124.8, 113.3, 108.2, 105.5, 103.6, 61.3, 51.7, 50.2, 14.4; HRMS (ESI) calcd for $[C_{28}H_{25}N_3O_2+H^+]$ 436.2020, found 436.2024.



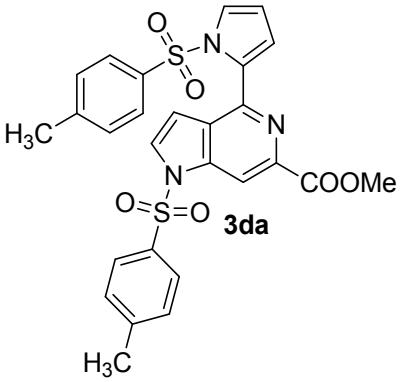
3bb

Ethyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3bb**). According to the general procedure mentioned above, **1b** (100 mg, 0.46 mmol), **2b** (32 mg, 0.23 mmol) and DIPEA (0.140 mL, 0.81 mmol); Yield 60% (68 mg) were heated in a sealed tube at 150 °C for 8 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (90:10) as eluent; Yellow liquid; R_f 0.55 (2:1 hexane-EtOAc); IR (KBr) 3067 (=C–H), 2955–2852 (C–H), 1738 (C=O),1713–1515 (C=C),1369 (C–H bend), 1106–1028 (C–O), 727 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.21 (d, J = 3 Hz, 1H), 7.08 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 3.0 Hz, 1H), 6.87–6.82 (m, 3H), 6.80 (dd, J = 3.3, 1.2 Hz, 1H), 6.69 (d, J = 8.8 Hz, 2H), 6.26 (dd, J = 3.0, 2.5 Hz, 1H), 5.83 (s, 2H), 5.28 (s, 2H), 4.43 (q, J = 7.0 Hz, 2H), 3.78 (s, 3H), 3.70 (s, 3H), 1.40 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 159.5, 158.5, 145.7, 140.4, 138.9, 131.7, 130.9, 130.3, 128.6, 128.6, 128.2, 125.4, 124.8, 114.4, 113.7, 113.2, 108.0, 105.5, 103.5, 61.3, 55.3, 55.2, 51.1, 49.7, 14.4; HRMS (ESI) calcd for $[C_{30}H_{29}N_3O_4+H^+]$ 496.2231, found 496.2230.



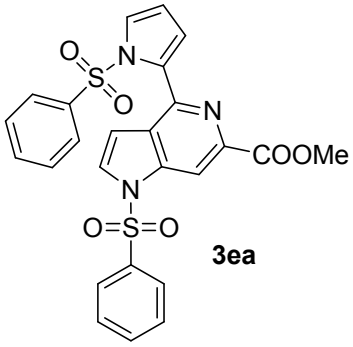
3bc

Tert-butyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3bc**). According to the general procedure mentioned above, **1b** (100 mg, 0.46 mmol), **2c** (39 mg, 0.23 mmol) and DIPEA (0.140 mL, 0.81 mmol) were heated in a sealed tube at 150 °C for 7 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (9:1) as eluent; Yield 42% (50 mg); Yellow-orange oily liquid; R_f 0.55 (2:1 hexane-EtOAc); IR (KBr) 3066 (=C-H), 2995–2833 (C-H), 1730 (C=O), 1715–1554 (C=C), 1366 (C–H bend), 1113–1033 (C–O), 727 (=C–H bend) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.19 (d, J = 3.3 Hz, 1H), 7.08 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 3.3 Hz, 1H), 6.87–6.79 (m, 4H), 6.69 (d, J = 8.5 Hz, 2H), 6.25 (dd, J = 3.5, 2.4 Hz, 1H), 5.93 (s, 2H), 5.26 (s, 2H), 3.78 (s, 3H), 3.69 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.5, 158.5, 145.4, 140.6, 140.1, 131.8, 130.7, 130.4, 128.7, 128.6, 128.3, 125.5, 124.3, 114.4, 113.7, 113.3, 108.0, 105.0, 103.4, 81.1, 55.3, 55.2, 51.3, 49.7, 28.3; HRMS (ESI) calcd for [$C_{32}H_{33}N_3O_4$+H$^+$] 524.2544, found 524.2551.



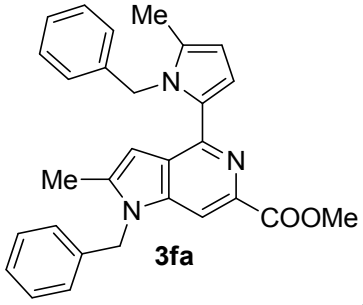
3da

Methyl 1-tosyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3da**). According to the general procedure mentioned above, **1d** (100 mg, 0.40 mmol), **2a** (25 mg, 0.20 mmol) and DIPEA (0.122 mL, 0.70 mmol) were heated in a sealed tube at 150 °C for 12 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (85:15) as eluent; Yield 47% (52 mg); Off white solid; m.p. = 120–122 °C; R_f 0.50 (1:1 hexane-EtOAc); IR (KBr) 3132–3064 (=C–H), 2955–2850 (C–H), 1728 (C=O), 1710–1512 (C=C), 1371 (C–H bend), 1309 (N–S=O), 1145 (S=O), 725 (=C–H bend) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 3.8 Hz, 1H), 7.41–7.36 (m, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.29–7.25 (m, 2H), 6.66 (d, J = 3.8 Hz, 1H), 6.41–6.36 (m, 1H), 6.33 (dd, J = 3.3, 2.6 Hz, 1H), 4.03 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 146.2, 145.5, 145.0, 142.0, 139.3, 136.0, 134.8, 131.0, 130.5, 130.2, 129.8, 129.3, 128.3, 127.2, 124.3, 117.3, 112.2, 110.2, 108.1, 53.0, 29.8, 21.7; HRMS (ESI) calcd for [$C_{27}H_{23}N_3O_6S_2$+H$^+$] 550.1101, found 550.1096.



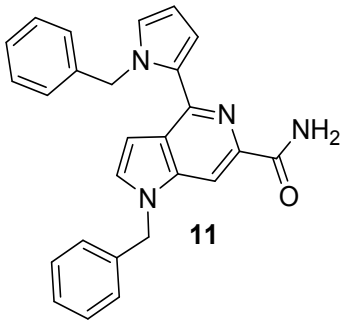
3ea

Methyl 1-(phenylsulfonyl)-4-(1-(phenylsulfonyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3ea**). According to the general procedure mentioned above, **1e** (100 mg, 0.43 mmol), **2a** (27 mg, 0.21 mmol) and DIPEA (0.128 mL, 0.74 mmol) were heated in a sealed tube at 150 °C for 12 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (85:15) as eluent; Yield 45% (49 mg); Yellow solid; m.p. = 104–106 °C; R_f 0.50 (1:1 hexane-EtOAc); IR (KBr) 3132–3064 (=C–H), 3005–2850 (C–H), 1728 (C=O), 1710–1512 (C=C), 1371 (C–H bend), 1309 (N–S=O), 1145 (S=O), 725 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.06 (d, J = 7.5 Hz, 2H), 7.99 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 3.8 Hz, 1H), 7.67–7.43 (m, 6H), 7.40 (dd, J = 3.0, 1.5 Hz, 1H), 6.67 (d, J = 3.8 Hz, 1H), 6.42 (dd, J = 3.0, 1.5 Hz, 1H), 6.35 (dd, J = 3.3, 2.5 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 145.3, 142.1, 139.3, 139.0, 137.7, 134.8, 133.8, 131.0, 129.8, 129.6, 129.3, 129.1, 128.1, 127.1, 124.4, 117.5, 112.3, 110.1, 108.2, 52.9; HRMS (ESI) calcd for $[C_{25}H_{19}N_3O_6S_2+Na^+]$ 544.0607, found 544.0603.



3fa

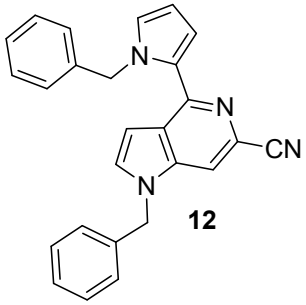
Methyl 1-benzyl-4-(1-benzyl-5-methyl-1H-pyrrol-2-yl)-2-methyl-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3fa**). According to the general procedure mentioned above, **1f** (100 mg, 0.50 mmol), **2a** (32 mg, 0.25 mmol) and DIPEA (0.150 mL, 0.88 mmol) were heated in a sealed tube at 150 °C for 6 h. After workup, the crude residue was purified through alumina (neutral, 175 mesh) column chromatography using hexane-EtOAc (90:10) as eluent; Yield 64% (72 mg); Yellow liquid; R_f 0.55 (2:1 hexane-EtOAc); IR (KBr) 3027 (=C–H), 2949–2852 (C–H), 1727 (C=O), 1712–1539 (C=C), 1355 (C-H bend), 782 (=C-H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.43–7.26 (m, 3H), 7.19–7.01 (m, 3H), 6.99–6.90 (m, 2H), 6.89–6.82 (m, 2H), 6.80–6.66 (m, 2H), 6.12–6.02 (m, 1H), 5.92 (s, 2H), 5.33 (s, 2H), 3.87 (s, 3H), 2.38 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta^{13}C$ NMR (100 MHz, $CDCl_3$) δ 167.5, 144.7, 141.4, 140.5, 139.9, 138.0, 136.5, 133.2, 130.4, 129.5, 129.0, 128.2, 127.7, 126.3, 126.1, 126.0, 112.3, 107.5, 105.1, 102.5, 52.3, 47.8, 46.8, 12.9, 12.7; HRMS (ESI) calcd for $[C_{29}H_{27}N_3O_2+H^+]$ 450.2176, found 450.2173.



11

1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxamide (**11**). In a round-bottom flask (100 mL), Methyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3aa**,100 mg,0.24 mmol) and KOH (14 mg, 0.24 mmol) was dissolved in methanol (5 mL) at room temperature under continuous stirring. Aqueous ammonia (25%, 0.350 mL, 9.40 mmol) was added to the mixture dropwise using a glass syringe over a period of 10 min. The reaction mixture was stirred at the room temperature for further 24 h. After the completion of the reaction, MeOH was evaporated under reduced pressure. MilliQ water (5 mL) and EtOAc (5 mL) was added to the residue and organic layer was separated. The aqueous phase was further extracted with EtOAc (5 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified using EtOAc as eluent over neutral alumina (175 mesh) column chromatography; Yield 78% (150 mg); Yellow gummy liquid; R_f 0.50 (EtOAc); IR (KBr) 3431 (N–H), 3033 (=C–H), 2960–2852 (C–H), 1677 (C=O), 1562 (C–N bend), 1376–1360 (C–H bend), 1296–1029 (C–O), 726 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ8.07 (s, 1H), 7.38–7.19 (m, 7H), 7.16–7.06 (m, 3H), 6.95 (d, J = 3.0 Hz, 1H), 6.92–6.85 (m, 2H), 6.85–6.78 (m, 1H), 6.40 (dd, J = 3.0, 2.6 Hz, 1H), 5.59 (s, 2H), 5.38 (s, 2H), 4.89 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 144.1, 141.1, 140.0, 136.3, 131.0, 129.0, 129.0, 128.7, 128.1, 127.0, 127.0, 126.9, 126.1, 125.3, 124.9, 112.6, 108.8, 103.5, 103.0, 51.3, 50.2; MS (ESI) calcd for [$C_{26}H_{22}N_4O$+H^+] 407.1866, found 407.2023.*

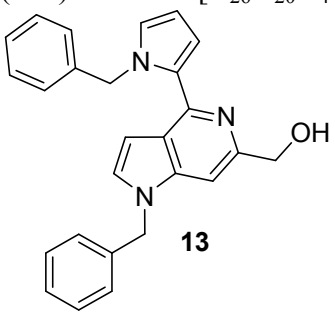
*The compound **11** is unstable in polar solvent to record a good HRMS.



12

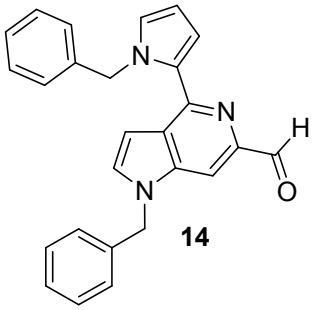
1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbonitrile (**12**). An oven-dried single neck round-bottom flask (25 mL) was charged with 1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxamide (**11**,40 mg, 0.098 mmol) and $POCl_3$ (5 mL) was added dropwise using a glass syringe over a period of 20 min at room temperature. A reflux condenser was fixed to the round bottom flask and the reaction mixture was heated at 60 °C and stirred for overnight. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with toluene (5 mL) and the solvent was evaporated under reduced pressure. Saturated $NaHCO_3$ (10 mL) was added slowly to the reaction mixture to neutralizeexcess phosphorous oxychloride. The aqueous phase was extracted with EtOAc (5 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified using hexane-EtOAC (90:10) as eluent over neutral alumina (175 mesh) column chromatography to afford **12**; Yield 66% (25 mg); colorless liquid; R_f 0.20 (2:1 hexane-EtOAc); IR (KBr) 3431 (N–H), 3031 (=C–H), 2960–2852 (C–H), 2223 (–C≡N stretch), 1588–1530 (C=C), 1376–1360 (C–H bend), 725 (=C–H bend) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.39–7.31 (m, 3H), 7.30 (d, J = 3.0 Hz, 1H), 7.22–7.02 (m, 7H), 6.94 (d, J

= 3.0 Hz, 1H), 6.93–6.89 (m, 1H), 6.85 (dd, J = 3.5, 1.2 Hz, 1H), 6.31 (dd, J = 3.0, 2.4 Hz, 1H), 5.75 (s, 2H), 5.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 139.2, 135.5, 131.7, 129.5, 129.2, 128.5, 128.5, 128.4, 127.2, 127.0, 126.9, 126.6, 124.6, 123.1, 119.2, 114.1, 109.1, 108.4, 104.1, 52.1, 50.6; HRMS (ESI) calcd for [$C_{26}H_{20}N_4$+H^+] 389.1761, found 389.1777.



13

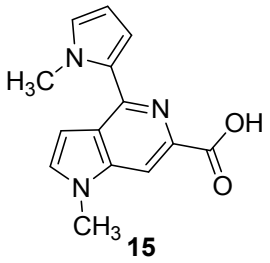
(1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)methanol (**13**). In a two-neck round-bottom flask (50 mL), Methyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3aa**, 250 mg, 0.59 mmol) was dissolved in dry THF (5 mL) under an inert atmosphere. The reaction mixture was cooled to 0 °C before addition of solid $LiAlH_4$ (68 mg, 1.78 mmol) in single portion. The reaction mixture was warmed to room temperature and further stirred for 20 min. After the consumption of ester **3aa**, as confirmed by TLC, the reaction mixture was quenched with saturated NH_4Cl (10 mL) solution and further diluted with EtOAc (10 mL). The aqueous layer was extracted using EtOAc (10 × 3 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, evaporated under reduced pressure, and the crude residue was purified over neutral alumina (175 mesh) column chromatography using hexane-EtOAC (75:25) as eluent; Yield 94% (220 mg); colorless liquid; R_f 0.35 (2:1 hexane-EtOAc); IR (KBr) 3414 (O–H), 3028 (=C–H), 2958–2850 (C–H), 1695–1559 (C=C), 1357 (C–H bend), 1100–1023 (C–O stretch) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.36–7.17 (m, 6H), 7.13 (d, J = 3.3 Hz, 1H), 7.07 (dd, J = 7.5, 8.0 Hz, 4H), 6.90 (s, 1H), 6.89–6.80 (m, 3H), 6.36 (dd, J = 3.0, 2.6 Hz, 1H), 5.65 (s, 2H), 5.28 (s, 2H), 4.63 (s, 2H), 3.24 (brs, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 144.7, 141.6, 139.7, 136.6, 131.1, 129.2, 129.0, 128.5, 128.0, 127.0, 126.8, 126.3, 125.2, 122.7, 112.6, 108.5, 103.0, 99.0, 64.7, 51.7, 50.1; HRMS (ESI) calcd for [$C_{26}H_{23}N_3O$+H^+] 394.1914, found 394.1913.



14

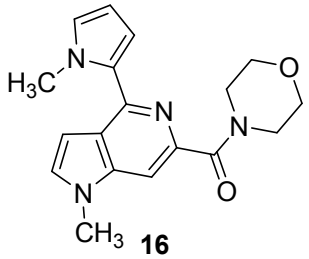
1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbaldehyde (**14**). A solution of (1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)methanol (**13**, 100 mg, 0.25 mmol) was prepared in dichloromethane (5 mL) in around-bottom flask (100 mL) and solid MnO_2 (326 mg, 3.75 mmol) was added in single portion. A double-walled reflux condenser was fixed to the round-bottom flask and reaction mixture was refluxed overnight. After the completion of reaction, solvent was evaporated under reduced pressure. The residual mixture was purified over neutral alumina (175 mesh) column chromatography using hexane-EtOAc (95:5) as eluent; Yield 70% (70 mg); Off white liquid; R_f 0.55 (2:1 hexane-EtOAc); IR (KBr) 3030 (=C–H), 2960–2852 (C–H), 1696 (C=O), 1606–1556 (C=C), 1358–1331 (C–H bend), 1287–1079 (C–O), 725 (=C–H bend) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.83 (s, 1H), 7.42–7.27 (m, 4H),* 7.23–7.02 (m, 7H), 6.98–6.93 (m, 1H), 6.92–6.88 (m, 1H), 6.88–6.82 (m, 1H), 6.42–6.28 (m, 1H), 5.81 (s, 2H), 5.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 146.3, 145.1, 140.4, 139.5, 136.0, 132.3, 130.3, 129.1, 128.4, 128.3, 127.0*,

126.8, 126.2, 125.9, 113.3, 108.5, 103.7, 102.2, 51.9, 50.4; HRMS (ESI) calcd for [$C_{26}H_{21}N_3O$+H^+] 392.1757, found 392.1756.
*higher intensity carbon



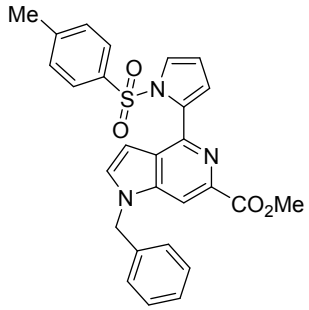
15

1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylic acid (**15**). Around-bottom flask (50 mL) was charged with Methyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**3ca**, 200 mg, 0.74 mmol) dissolved in THF (3 mL). 1M aqueous LiOH solution (2.5 mL) was addedat room temperature and the reaction mixture was stirred for 3 h at the same temperature (monitored by TLC). After the consumption of **3ca**, diethyl ether (10 mL) and saturated $NaHCO_3$ (10 mL) was added to the reaction mixture. The aqueous layer was separated and acidified to pH 4 (by dropwise addition of 6N HCl). The aqueous phase was extracted with EtOAc (5 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to give crude product **15** which was utilized in the next step without further purification; Crude yield 90% (172 mg); Yellow oily liquid; R_f 0.10 (EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.32 (d, *J* = 3.0 Hz, 1H), 6.90 (d, *J* = 3.0 Hz, 1H), 6.86 (m, 1H), 6.77 (dd, *J* = 3.5, 1.3 Hz, 1H), 6.29 (dd, *J* = 2.8, 2.4 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 142.8, 140.3, 135.8, 132.0, 128.2, 125.8, 124.5, 112.6, 107.3, 102.9, 102.7, 35.3, 32.3; HRMS (ESI) calcd for [$C_{14}H_{13}N_3O_2$+H^+] 256.1081, found 256.1066.



16

(1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)(morpholino)methanone (**16**). A two-neck round-bottom flask (50 mL) was charged with unpurified **15** (100 mg, 0.39 mmol**)** dissolved in dry DMF (4 mL) under an inert atmosphere. The reaction mixture was cooled briefly to 0°C before addition of morpholine (0.13 mL, 1.57 mmol), *1-ethyl-3-(3-dimethylaminopropyl)carbodiimide* (300 mg, 1.57 mmol), hydroxybenzotriazole (212 mg, 1.57 mmol) and DIPEA (0.54 mL, 3.13 mmol) in a sequential manner under constant stirring. The reaction mixture was warmed to room temperature, stirred for further 16 h. After the consumption of **15** as confirmed by TLC, cold brine (10 mL) was added to the reaction mixture. The reaction mixture was extracted with EtOAc (10 × 3 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated, and purified over neutral alumina (175 mesh) column chromatography using hexane-EtOAc (50:50) as eluent; Yield 49% (60 mg); White crystalline solid; m.p. = 95–96 °C; R_f 0.40 (1:1 hexane-EtOAc); IR (KBr) 3065 (=C–H), 2957–2850 (C–H),1682 (C=O), 1641–1513 (C=C),1371 (C–H bend), 723 (=C–H bend) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.65 (s, 1H), 7.17 (d, *J* = 3.0 Hz, 1H), 6.82 (d, *J* = 3.0 Hz, 1H), 6.80–6.77 (m, 1H), 6.76–6.71 (m, 1H), 6.25 (dd, *J* = 2.8, 2.4 Hz, 1H), 3.97 (s, 3H), 3.92–3.76 (m, 9H), 3.72–3.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 169.2, 144.2, 144.1, 141.1, 131.1, 130.9, 125.9, 123.4, 112.6, 107.6, 104.3, 102.8, 67.3, 67.0, 48.1, 43.1, 36.6, 32.9; HRMS (ESI) calcd for [$C_{18}H_{20}N_4O_2$+H^+] 325.1659, found 325.1655.



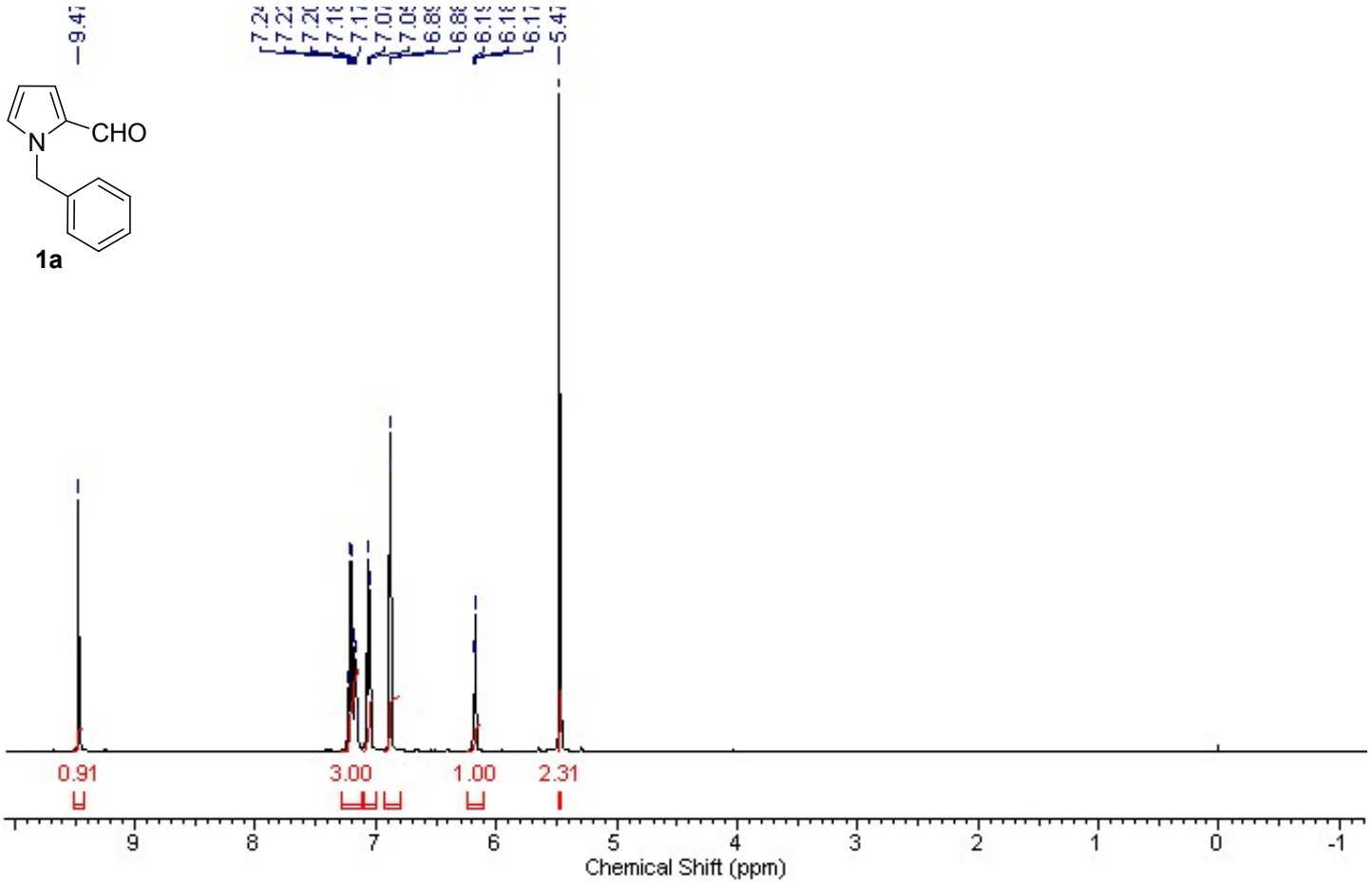
17

Methyl 1-benzyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate (**17**). A mixture of N-benzyl pyrrole-2-aldehyde (37 mg, 0.20 mmol) and N-tosyl pyrrole-2-aldehyde (50 mg, 0.20 mmol), glycinemethyl ester hydrochloride (25 mg, 0.20 mmol) and DIPEA (0.12 mL, 0.70 mmol) was heated in a sealed tube at 150 °C for 6 h. The crude mixture was diluted with CH_2Cl_2 (10 mL) and washed with brine solution (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated, and purified over neutral alumina (175 mesh) column chromatography using hexane-EtOAc (80:20) as eluent; Yield 41% (40 mg); White crystalline solid; m.p. = 130–32 °C; R_f 0.22 (3:1 hexane-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.34–7.09 (m, 9H), 6.54–6.47 (m, 1H), 6.45–6.37 (m, 1H), 6.29 (dd, J = 2.8, 2.4 Hz, 1H), 5.34 (s, 2H), 3.92 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 144.8, 144.6, 139.9, 139.0, 136.3, 136.0, 132.1, 131.8, 129.6, 129.1, 128.34, 128.31, 128.2, 127.1, 123.7, 116.7, 111.9, 107.7, 103.4, 52.7, 50.4, 21.7; HRMS (ESI) calcd for [$C_{27}H_{23}N_3O_4S$+H^+] 486.1409, found 486.1452.

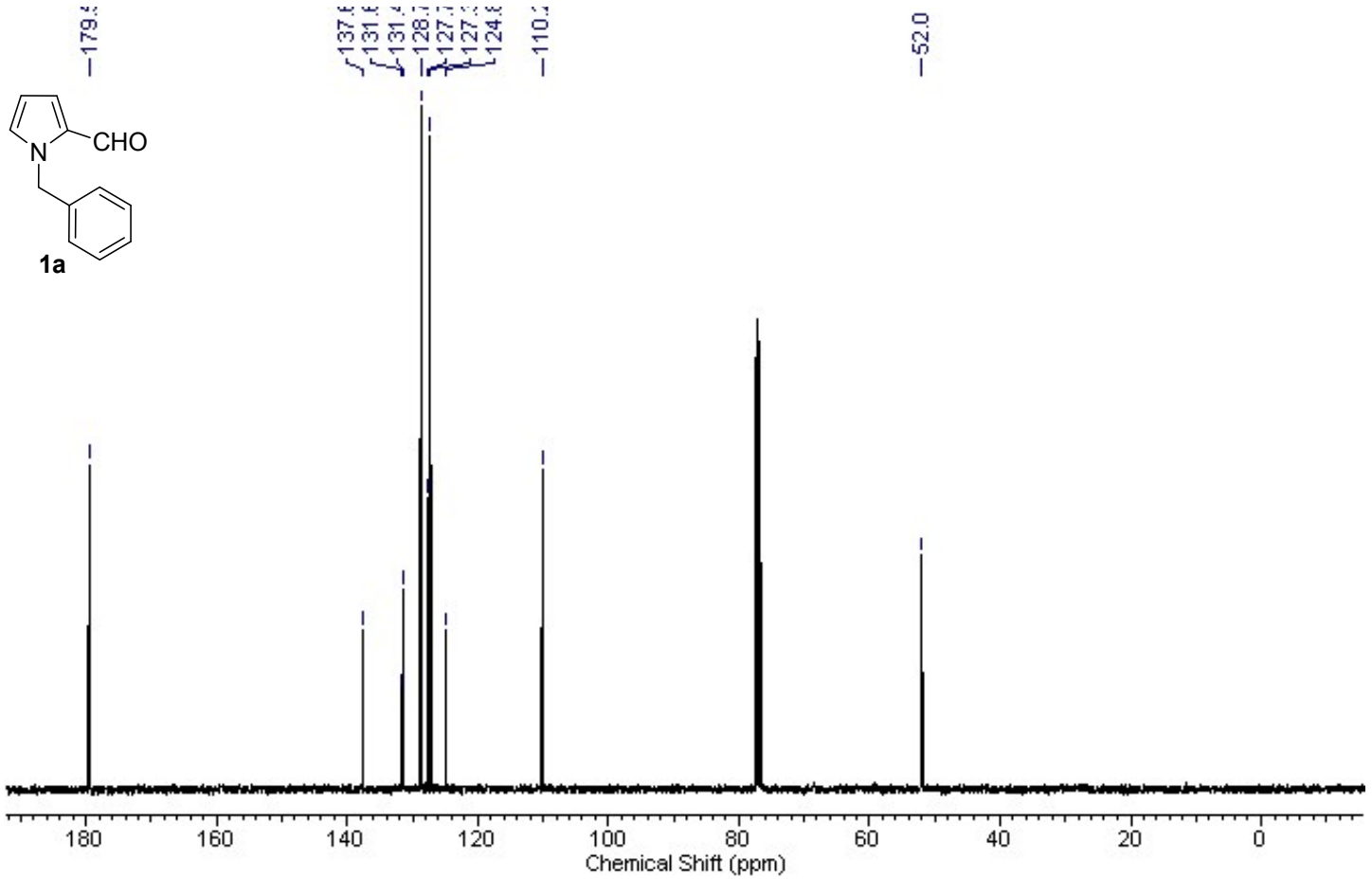
5. Computational details: The density functional theoretical calculations are done at B3LYP/6-311++G** level of theory using Gaussian 09 D.01 program.[2–4]

6. Copies of ^{1}Hand ^{13}C NMR spectra for newly synthesized compounds

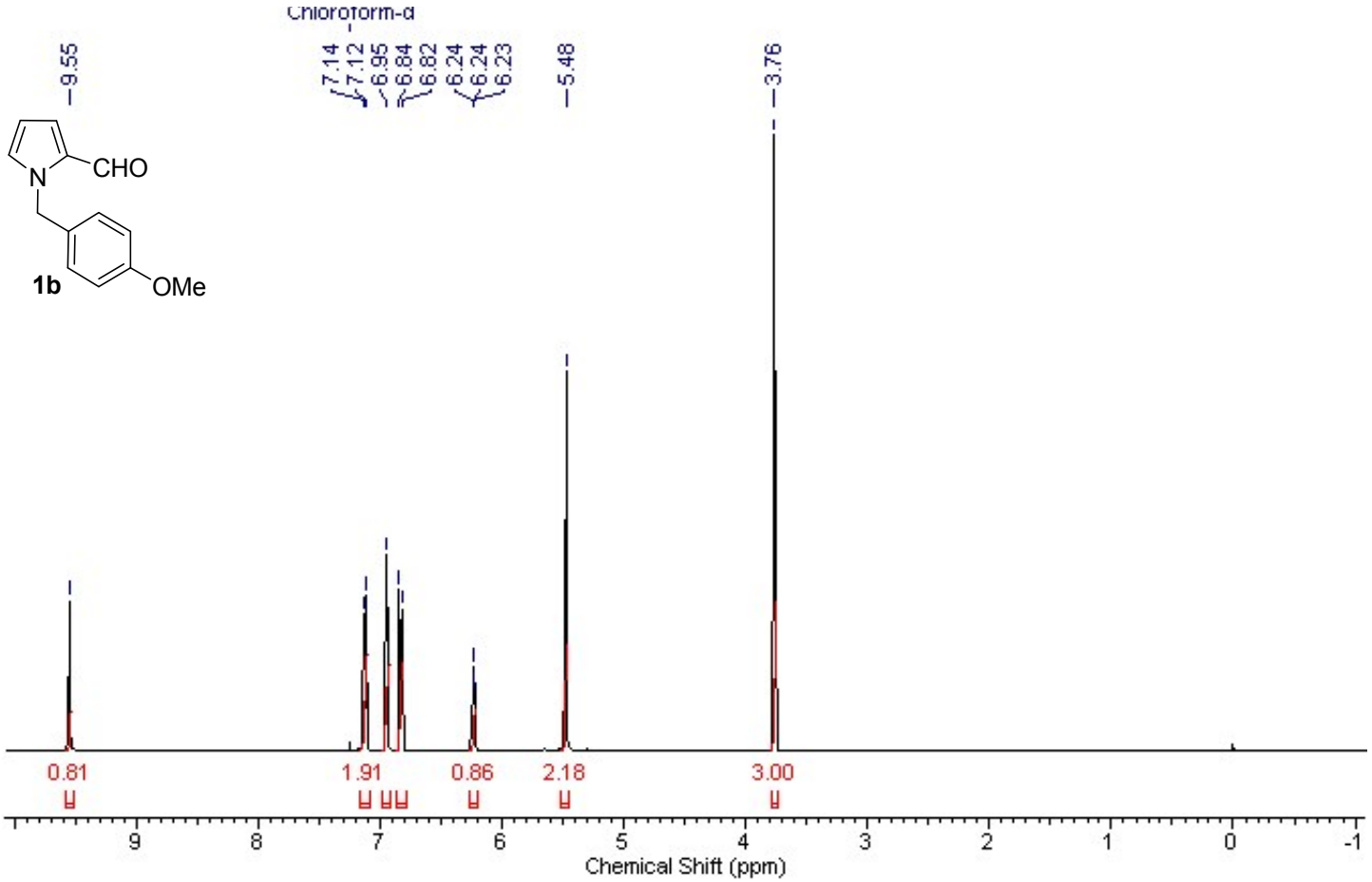
^{1}H NMR spectrum of*1-Benzyl-1H-pyrrole-2-carbaldehyde* (**1a**)



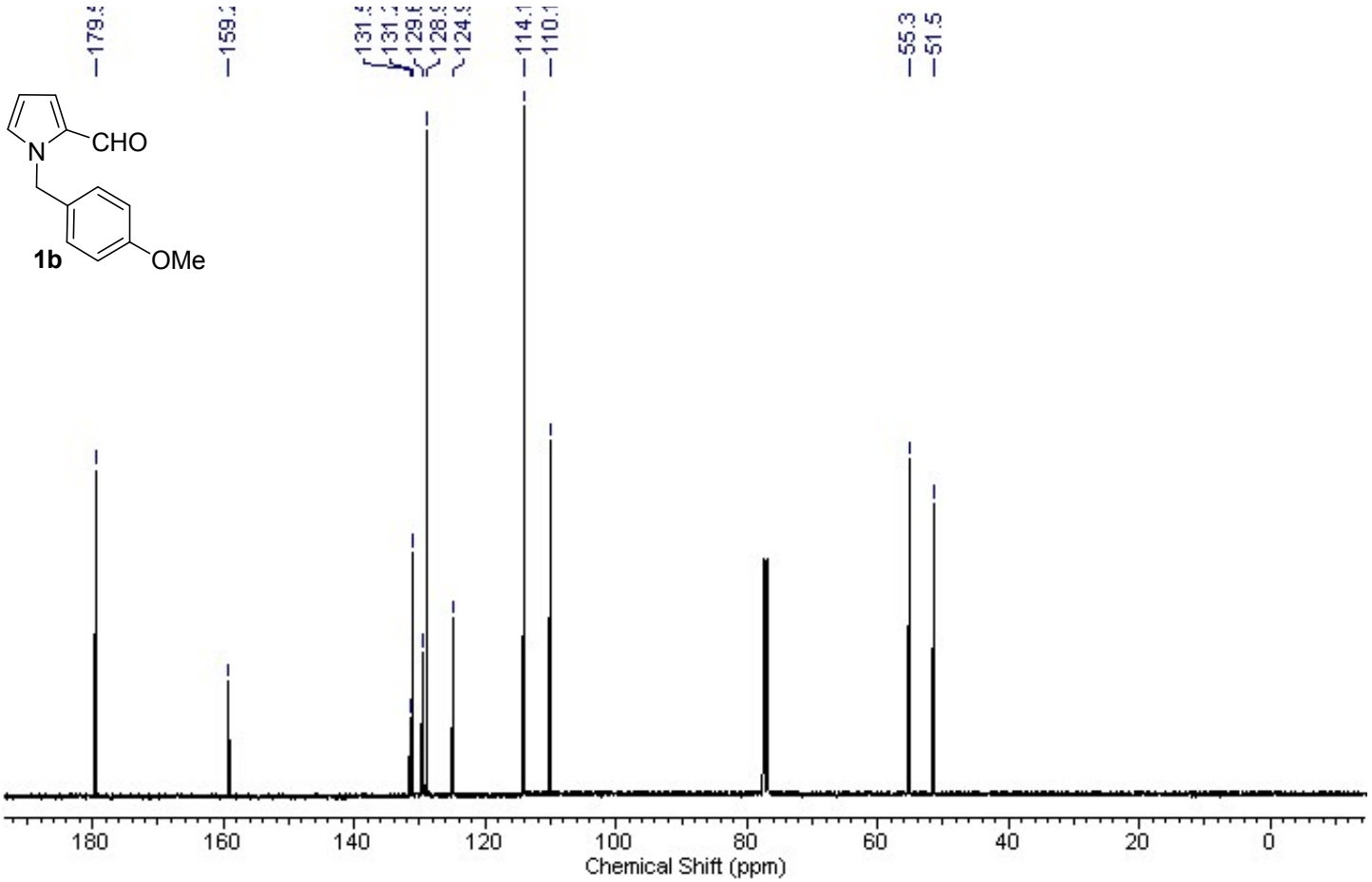
^{13}C NMR spectrum of*1-Benzyl-1H-pyrrole-2-carbaldehyde* (**1a**)



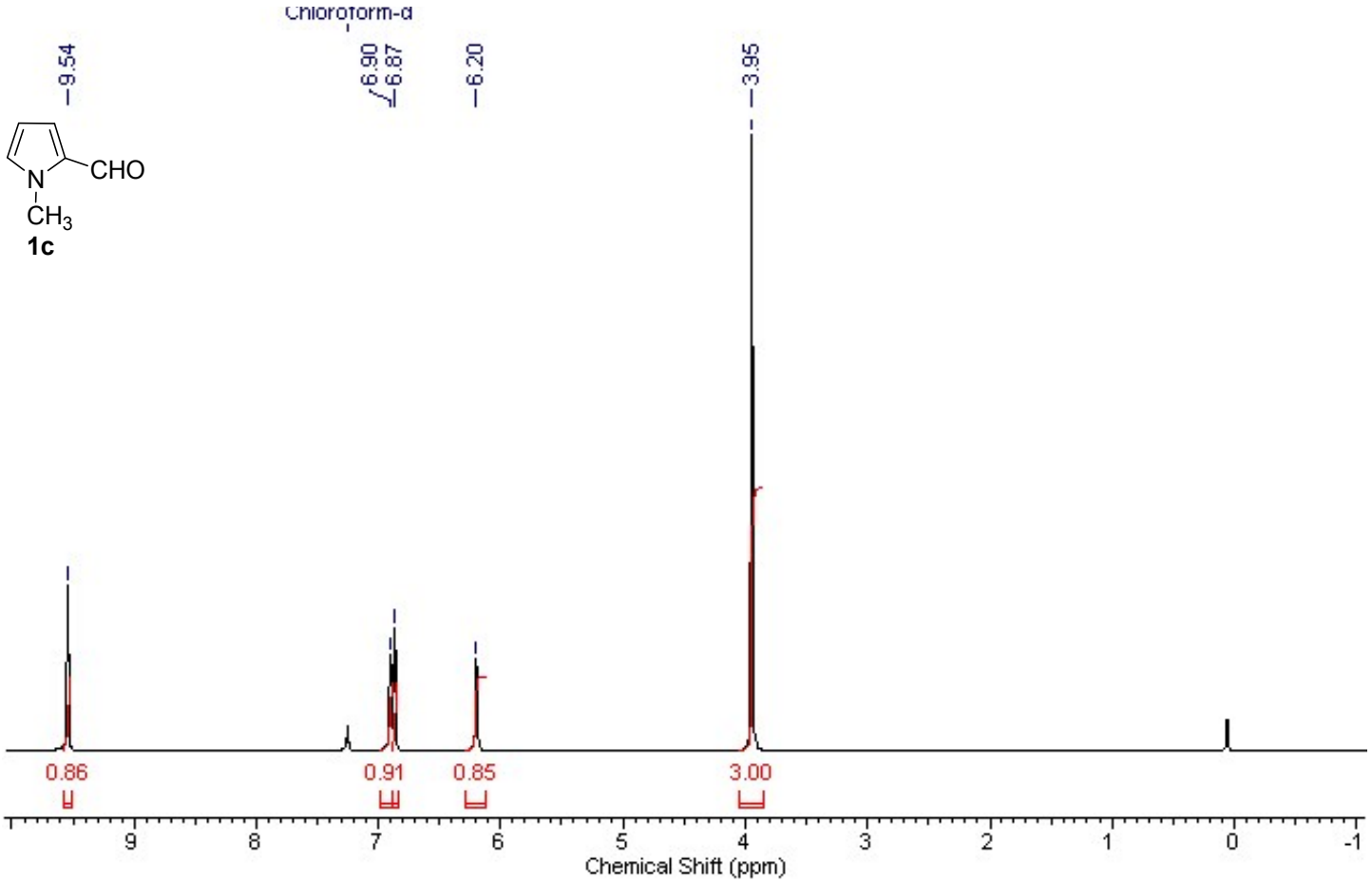
^{1}H NMR spectrum of*1-(4-Methoxybenzyl)-1H-pyrrole-2-carbaldehyde* (**1b**)



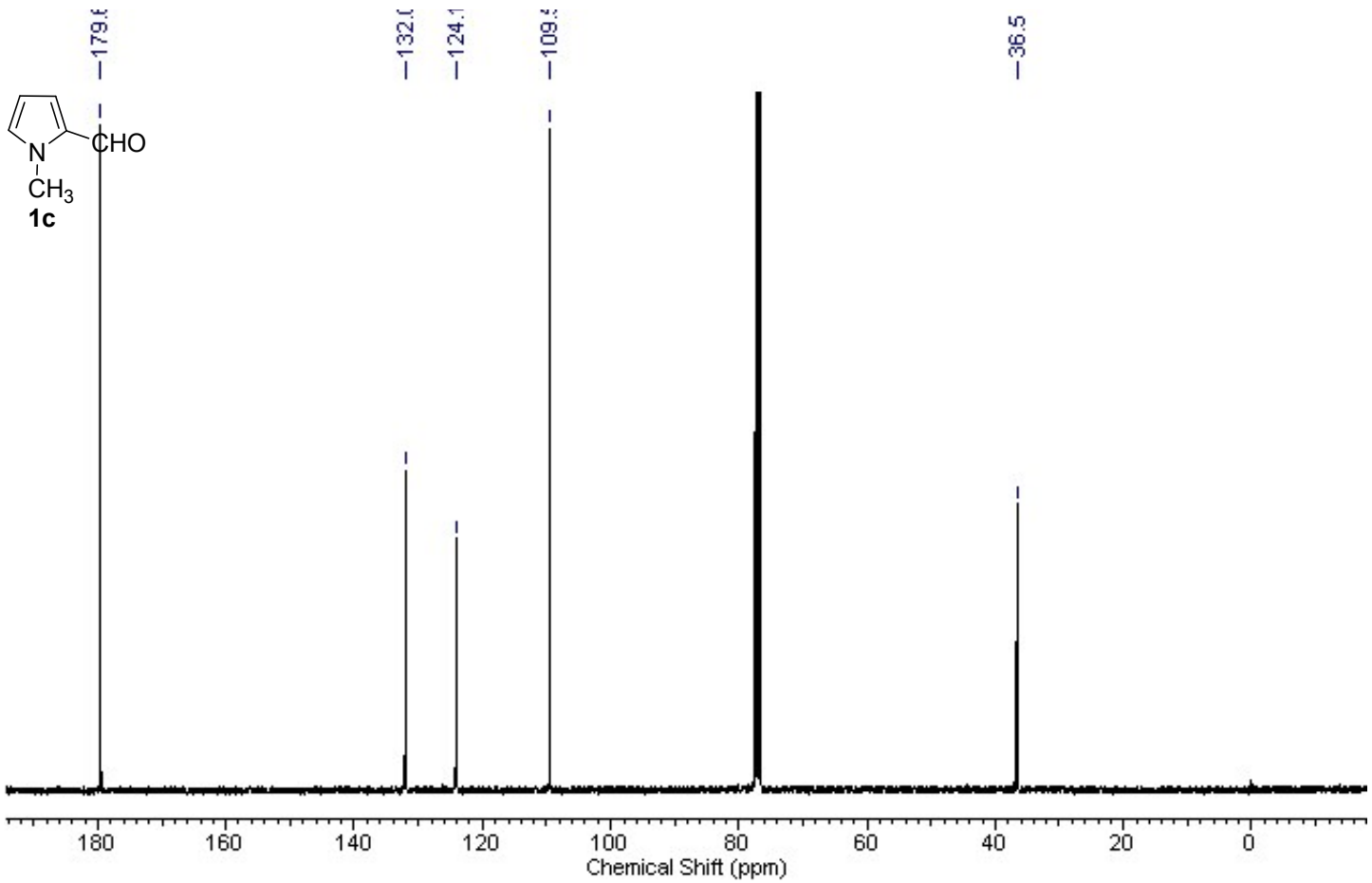
^{13}C NMR spectrumof1-(4-Methoxybenzyl)-1H-pyrrole-2-carbaldehyde (**1b**)



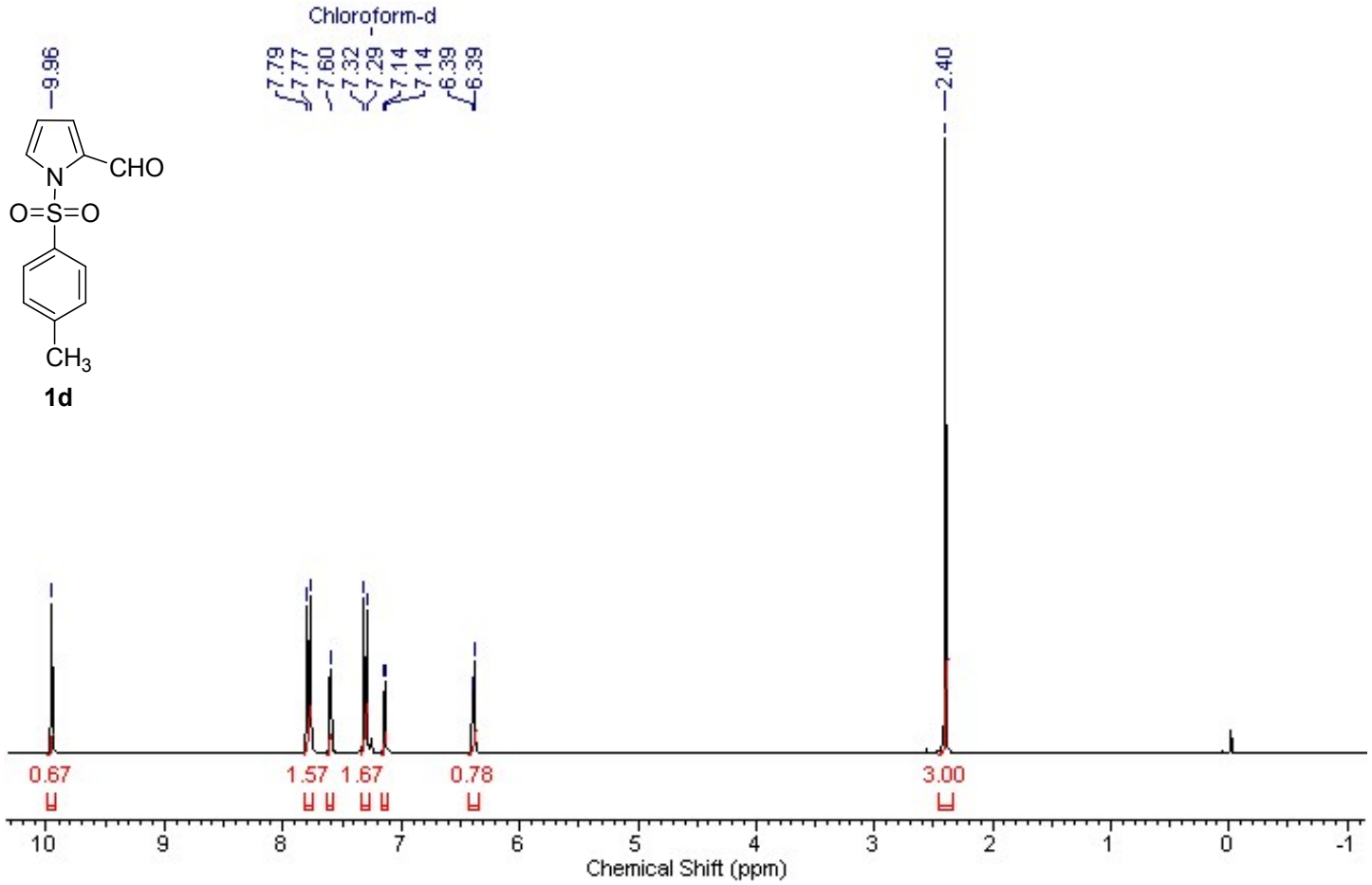
^{1}H NMR spectrum of*1-Methyl-1H-pyrrole-2-carbaldehyde* (**1c**)



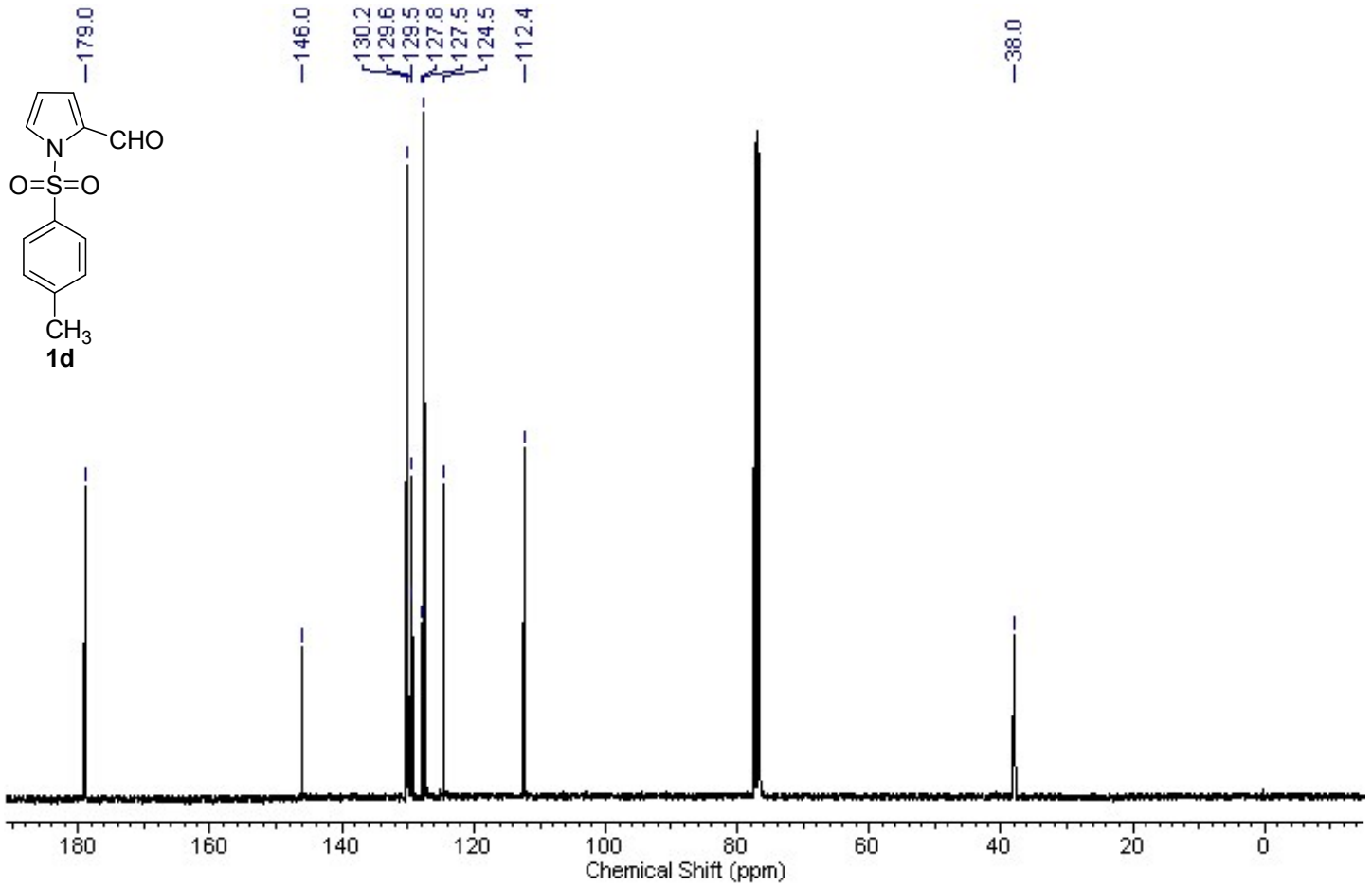
^{13}C NMR spectrum of*1-Methyl-1H-pyrrole-2-carbaldehyde* (**1c**)



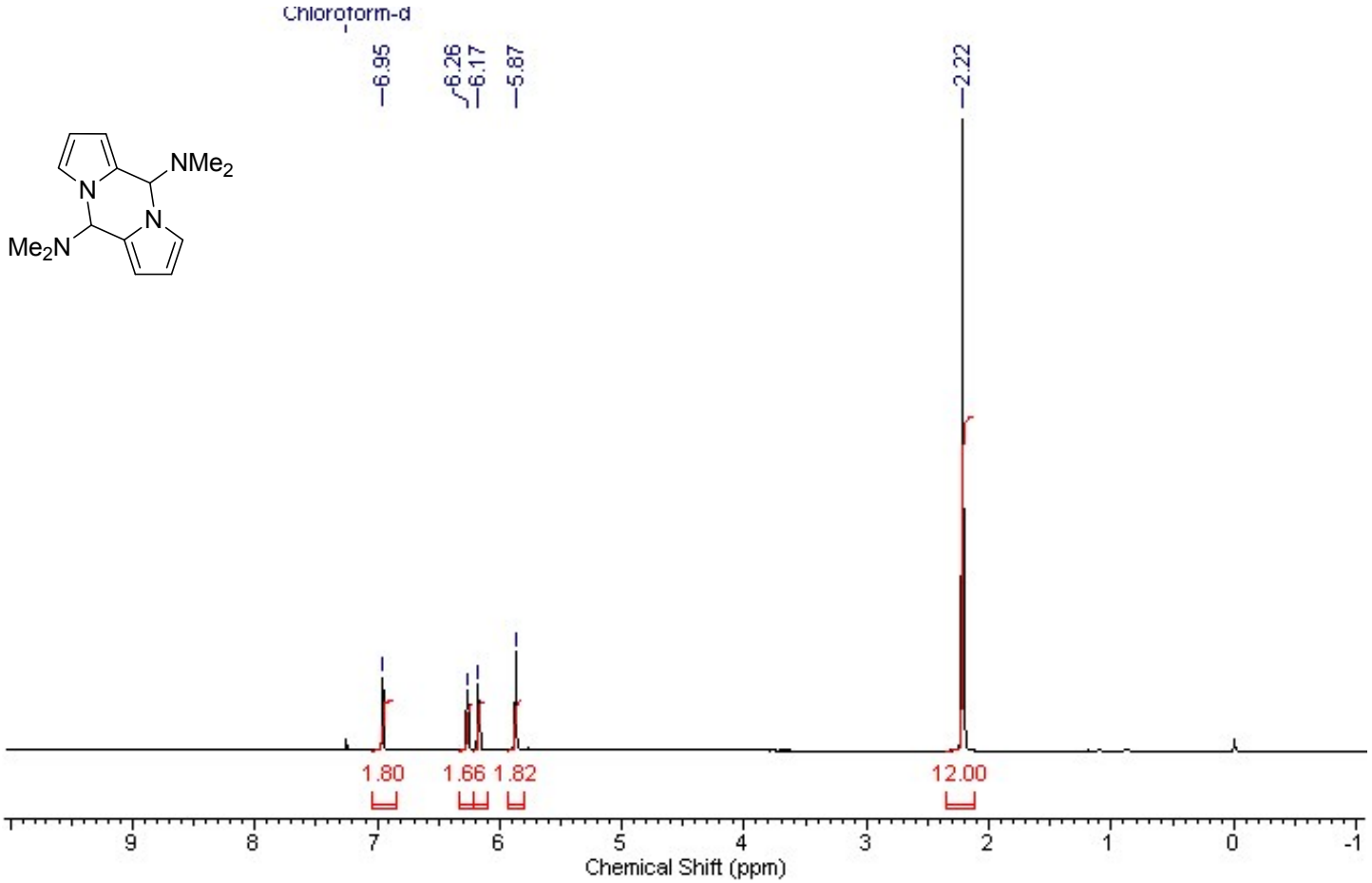
^{1}H NMR spectrumof1-Tosyl-1H-pyrrole-2-carbaldehyde (**1d**)



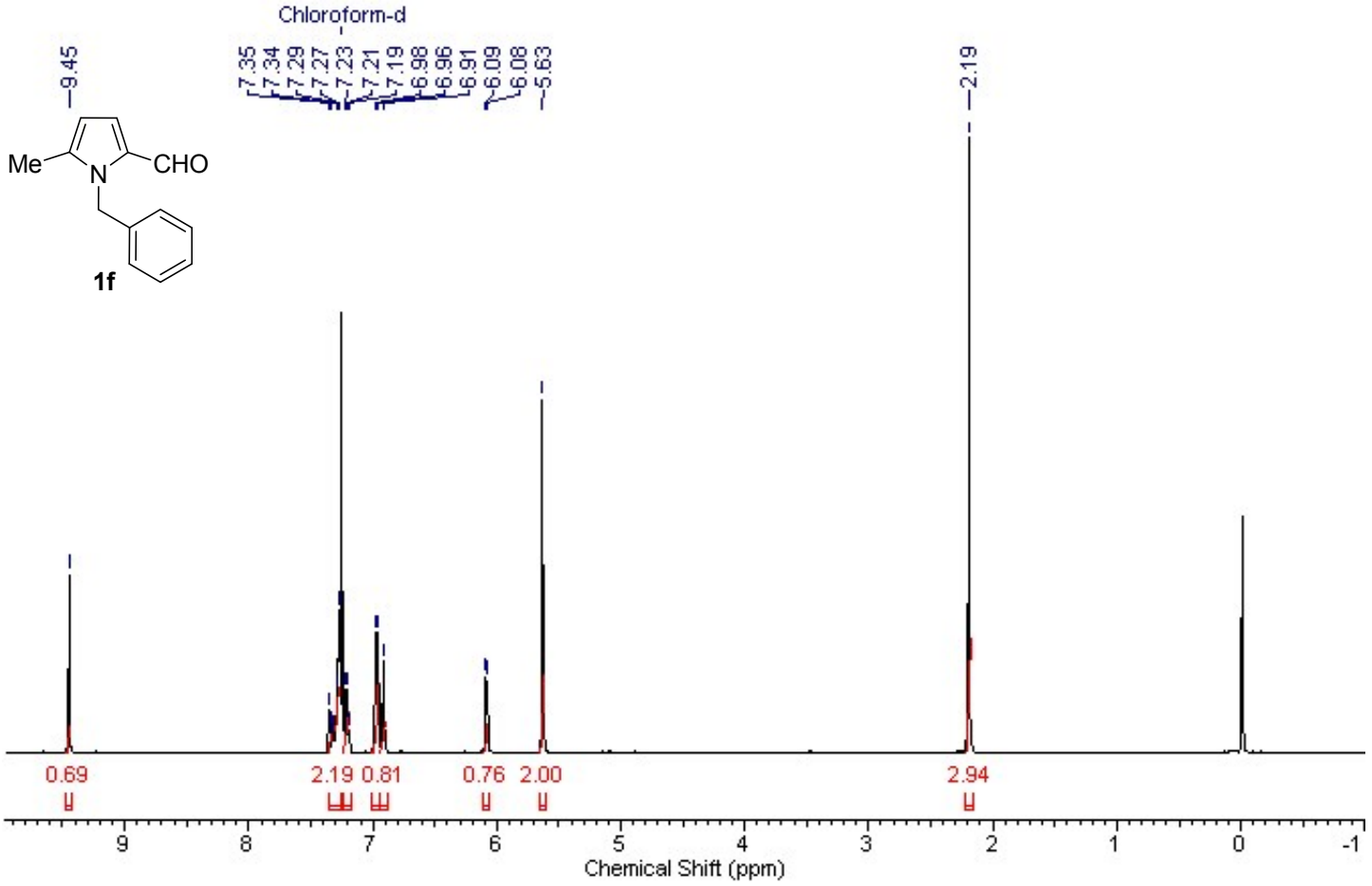
^{13}C NMR spectrum of1-Tosyl-1H-pyrrole-2-carbaldehyde (**1d**)



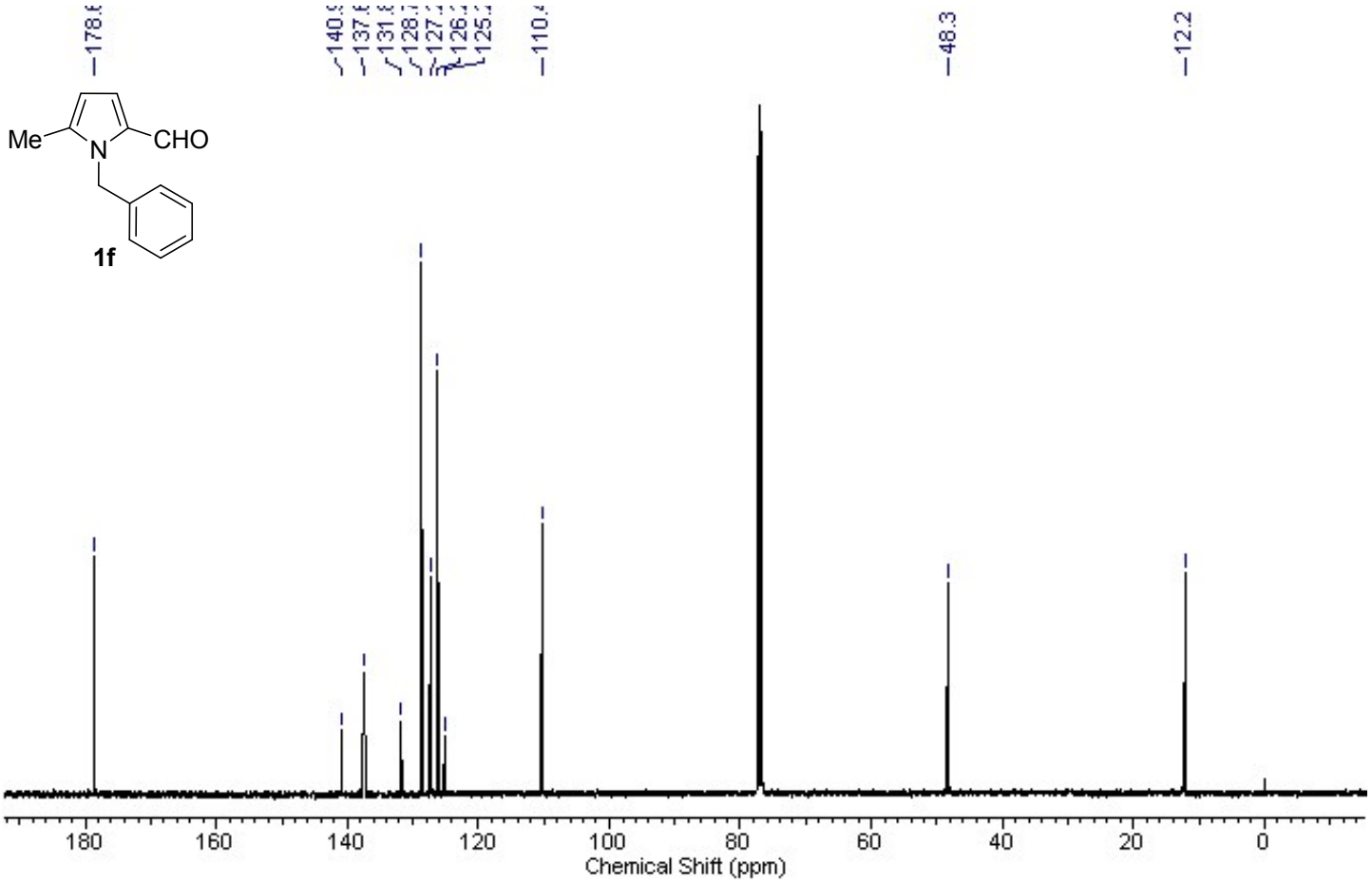
^{1}H NMR spectrum of *N5,N5,N10,N10-tetramethyl-5,10-dihydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-diamine*



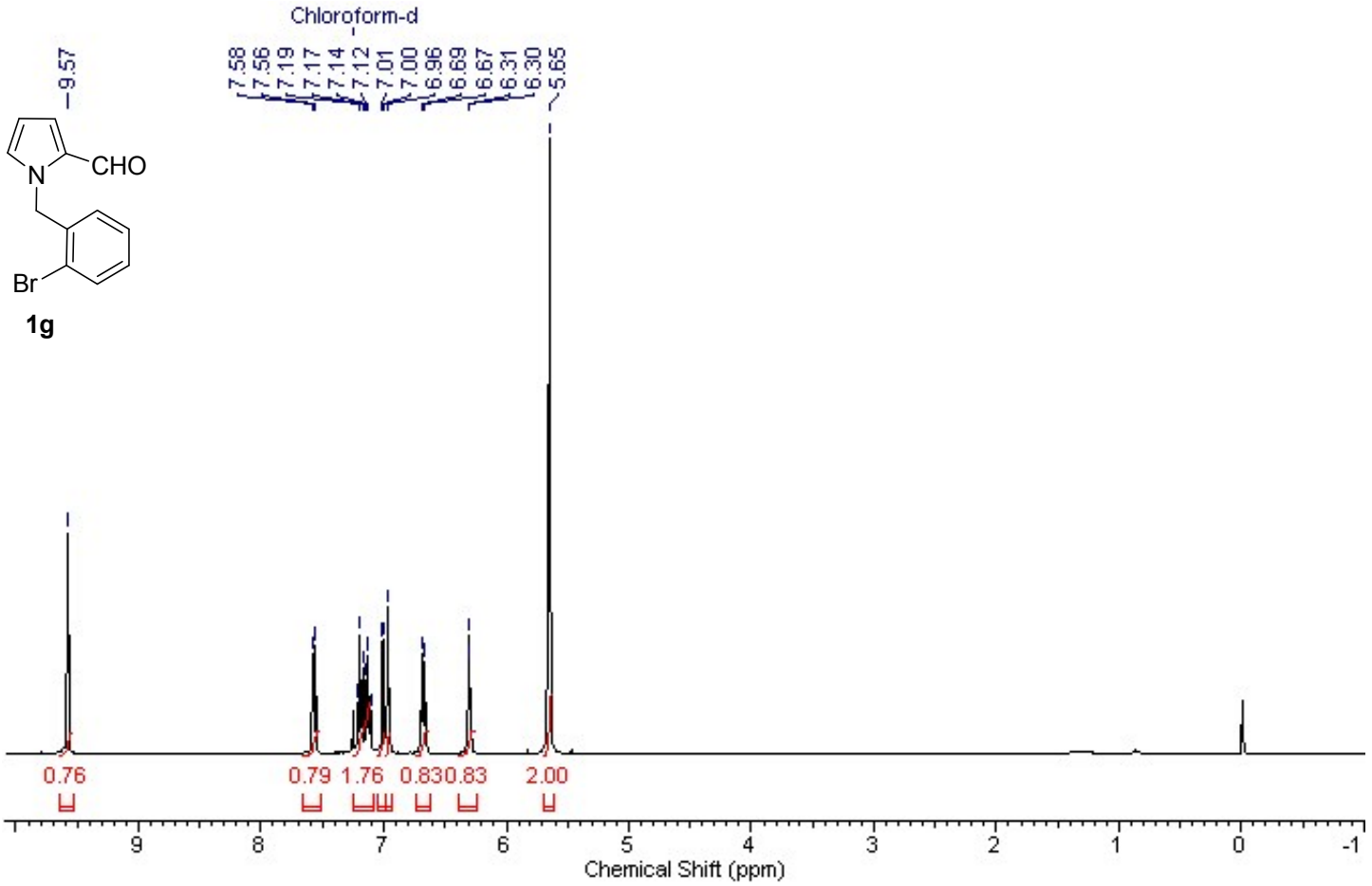
^{1}H NMR spectrum of *1-Benzyl-5-methyl-1H-pyrrole-2-carbaldehyde* (**1f**)



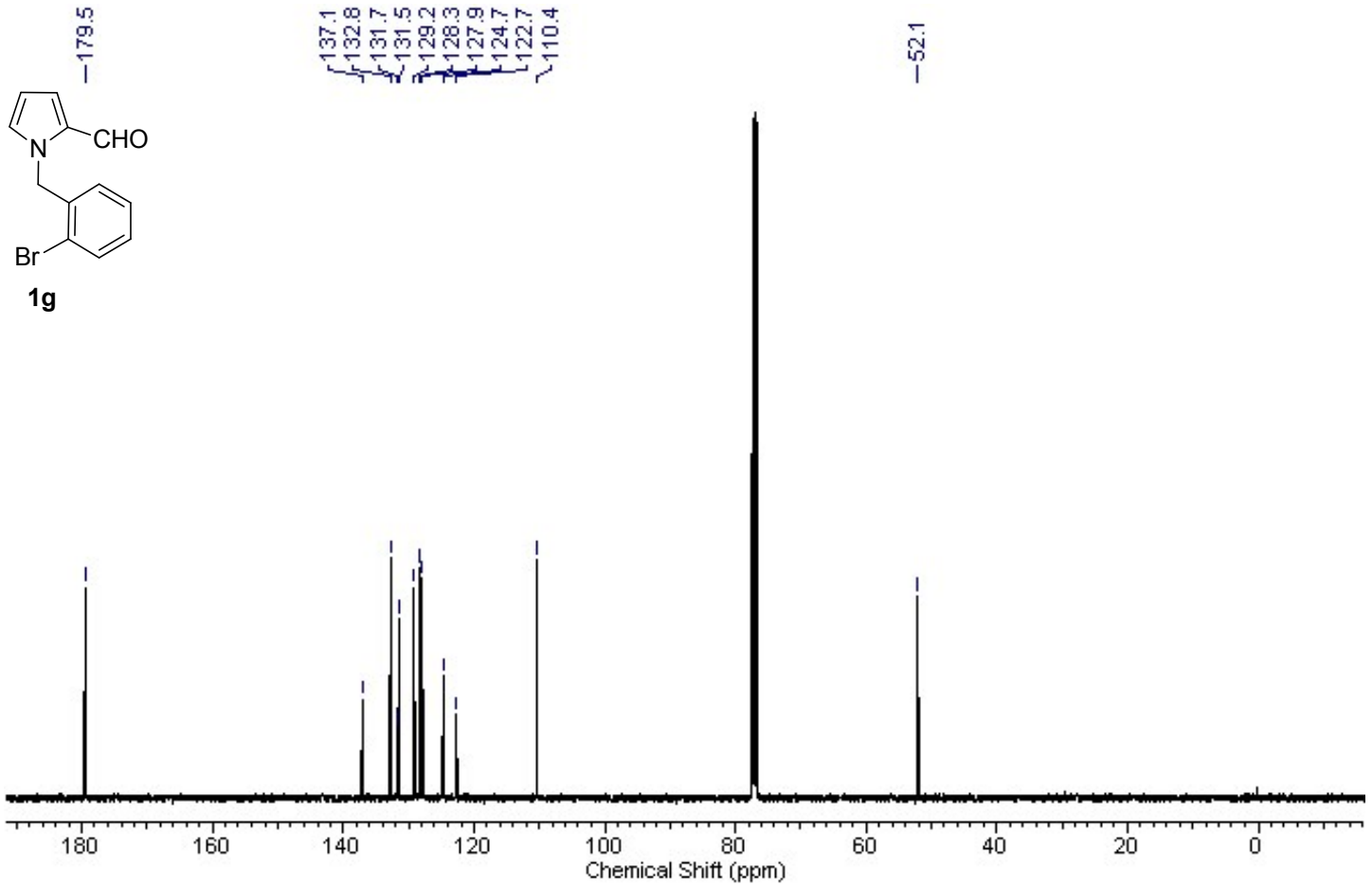
^{13}C NMR spectrum of ***1-****Benzyl-5-methyl-1H-pyrrole-2-carbaldehyde* (**1f**)



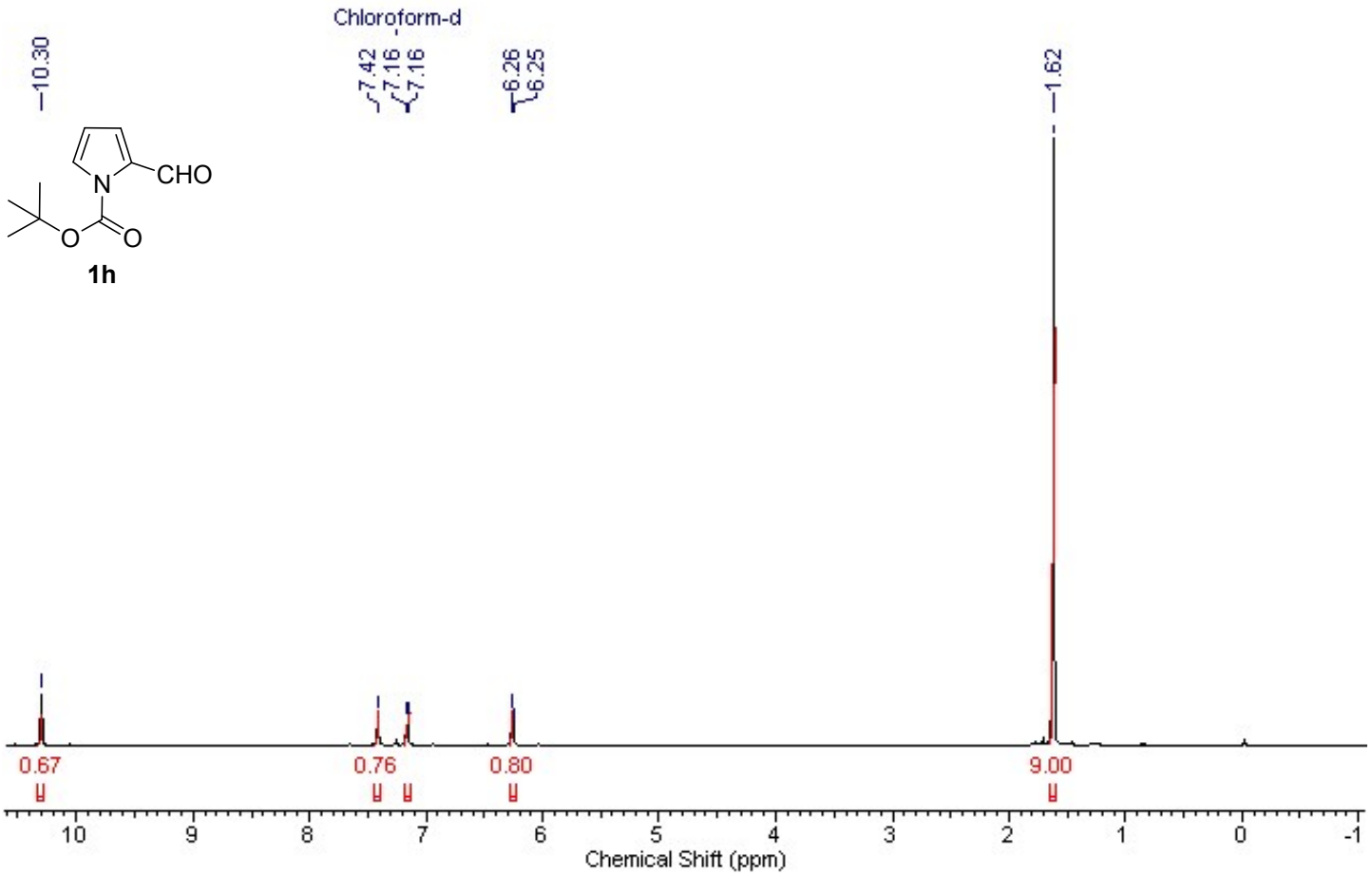
^{1}H NMR spectrumof *1-(2-Bromobenzyl)-1H-pyrrole-2-carbaldehyde* (**1g**)



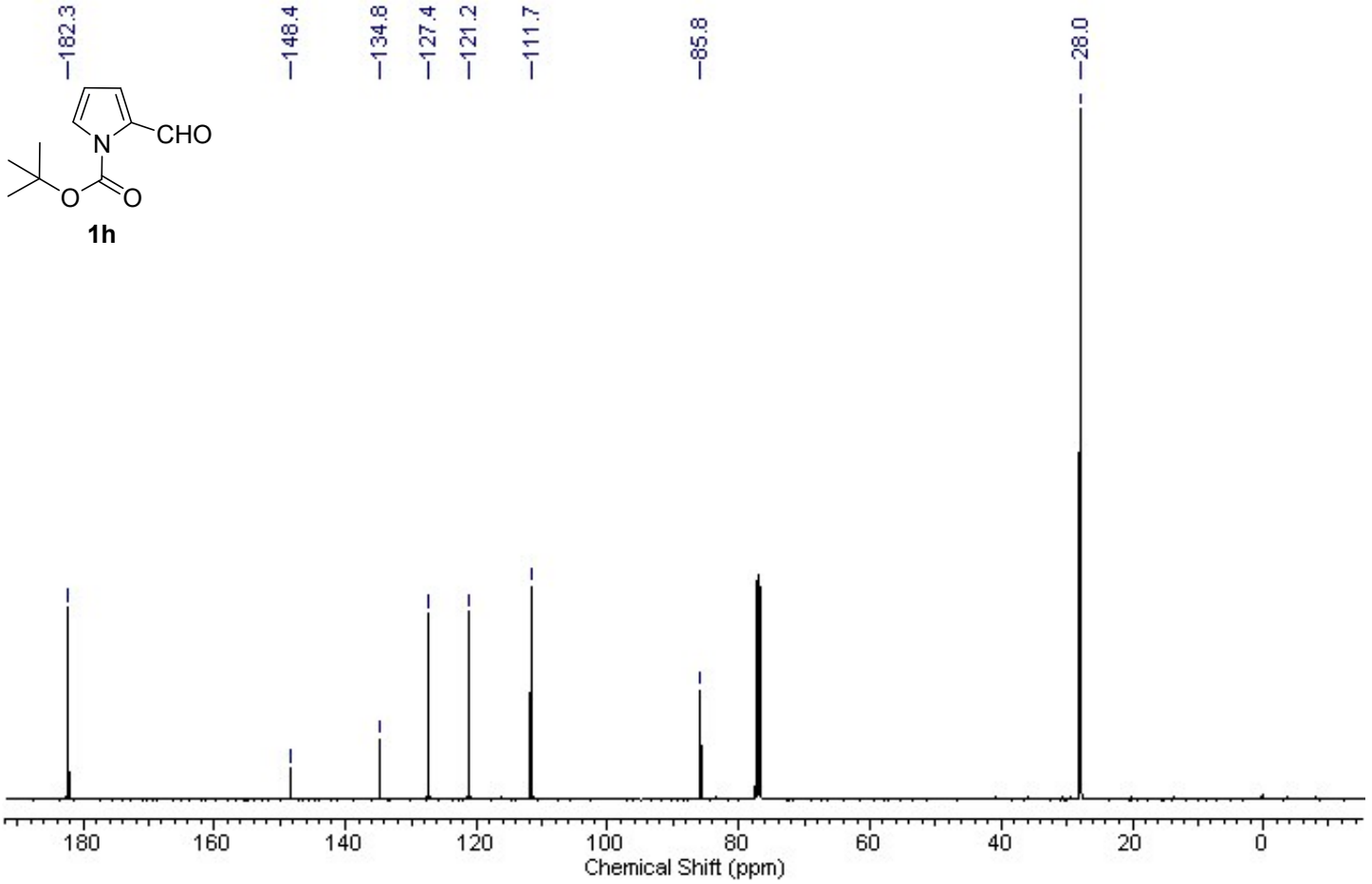
^{13}C NMR spectrum of *1-(2-Bromobenzyl)-1H-pyrrole-2-carbaldehyde* (**1g**)



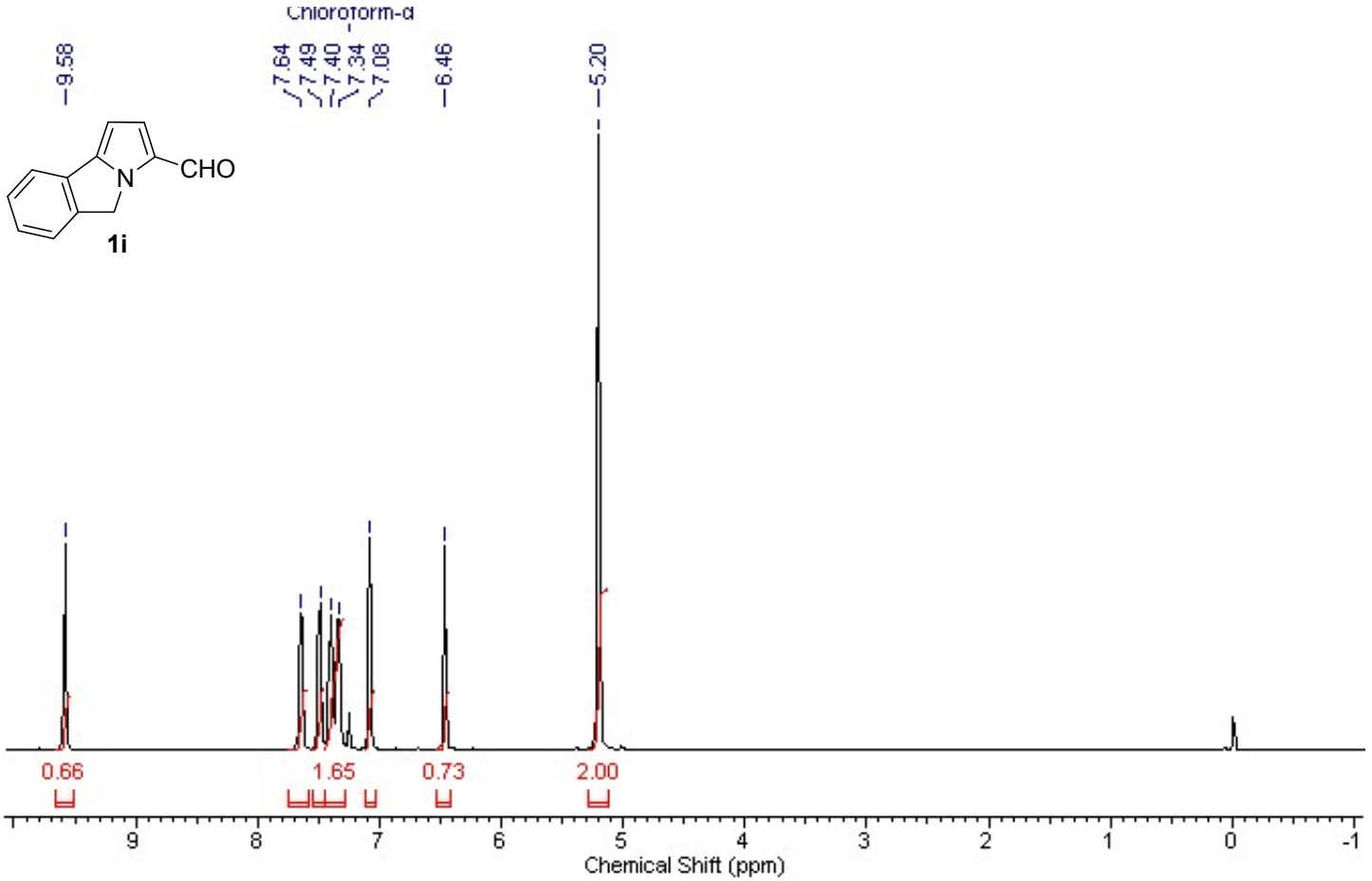
^{1}H NMR spectrumofT*ert-butyl 2-formyl-1H-pyrrole-1-carboxylate* (**1h**)



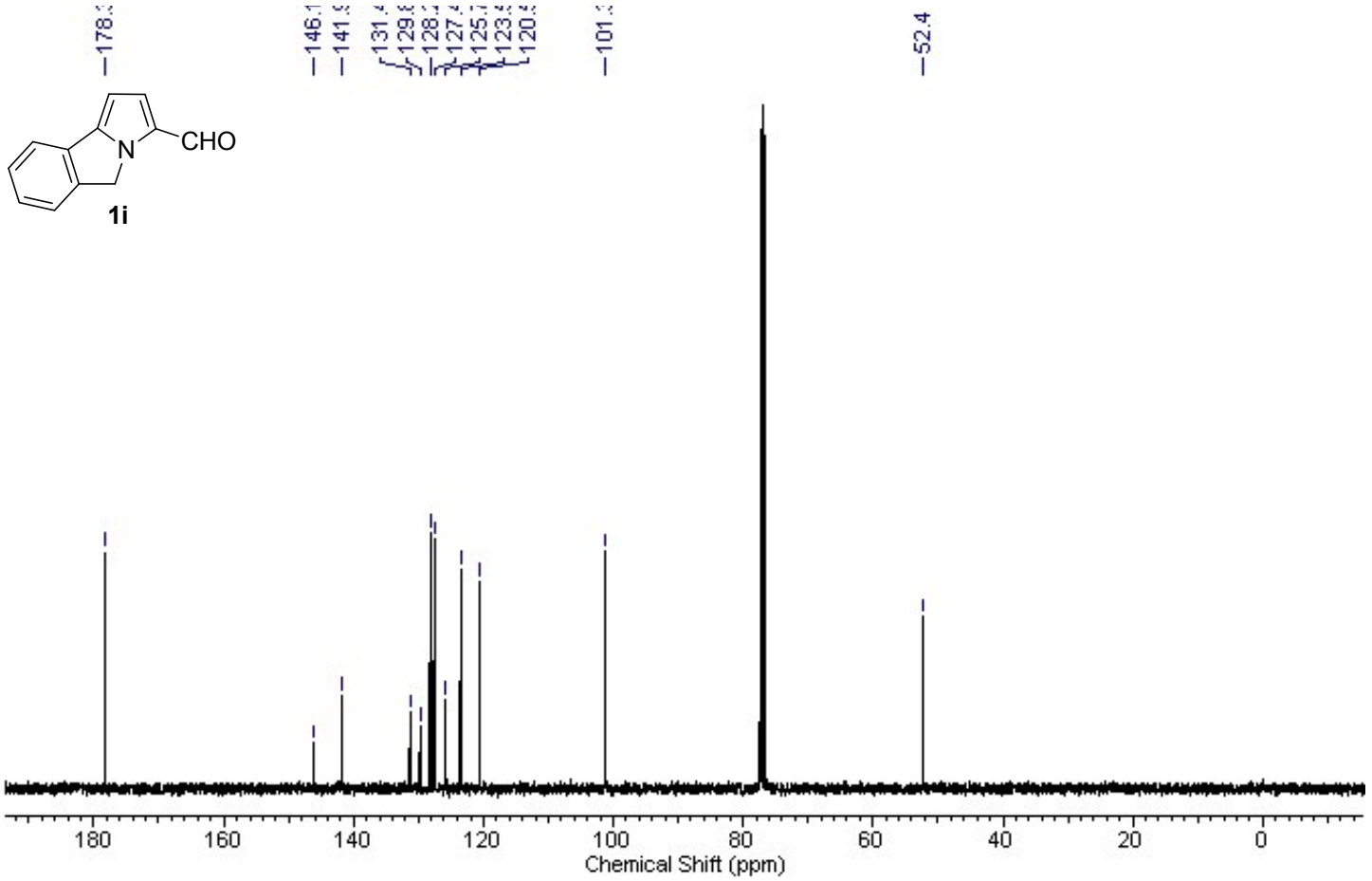
^{13}C NMR spectrum of*Tert-butyl 2-formyl-1H-pyrrole-1-carboxylate* (**1h**)



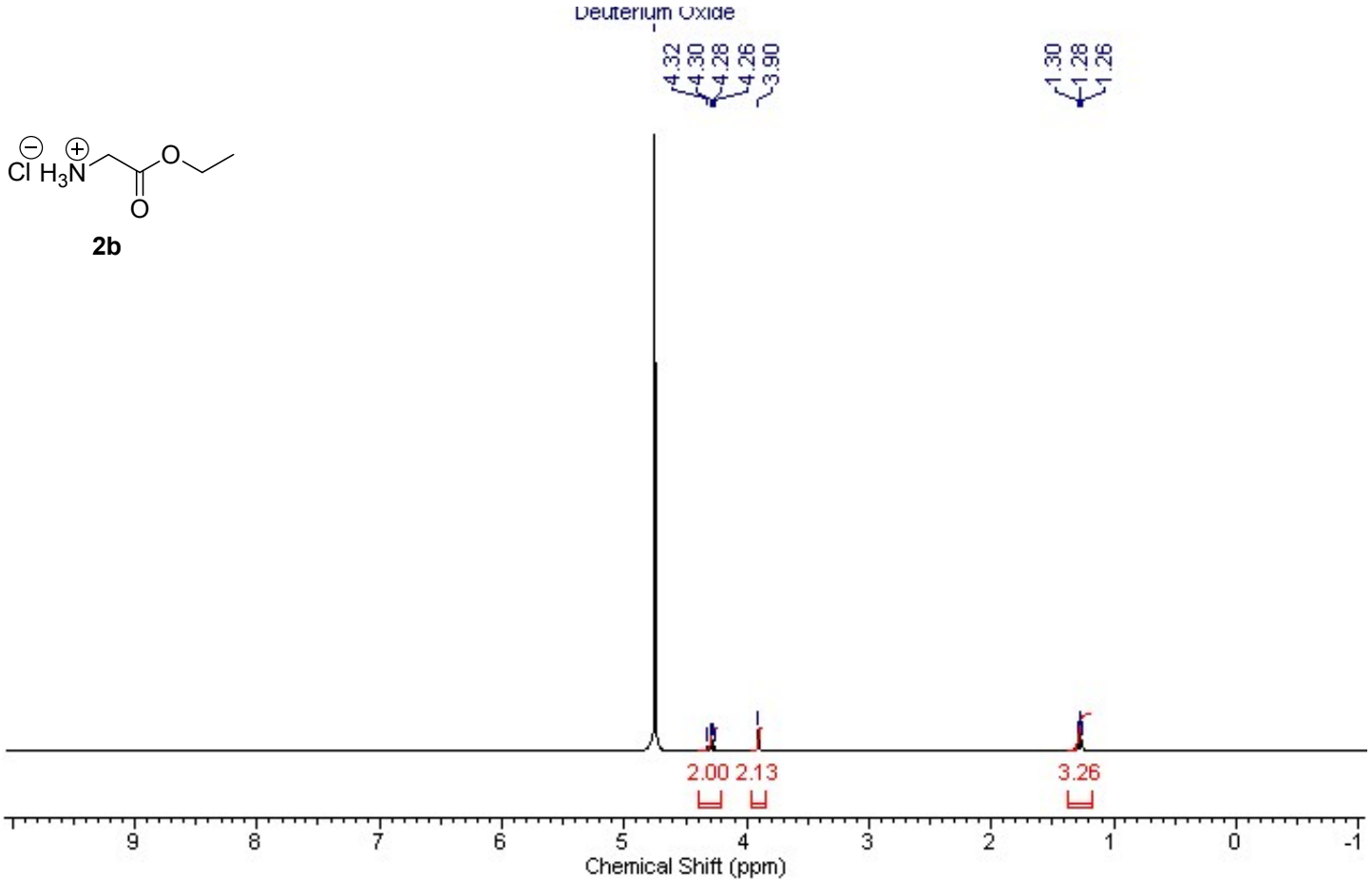
^{1}H NMR spectrum of *5H-Pyrrolo[2,1-a]isoindole-3-carbaldehyde* (**1i**)



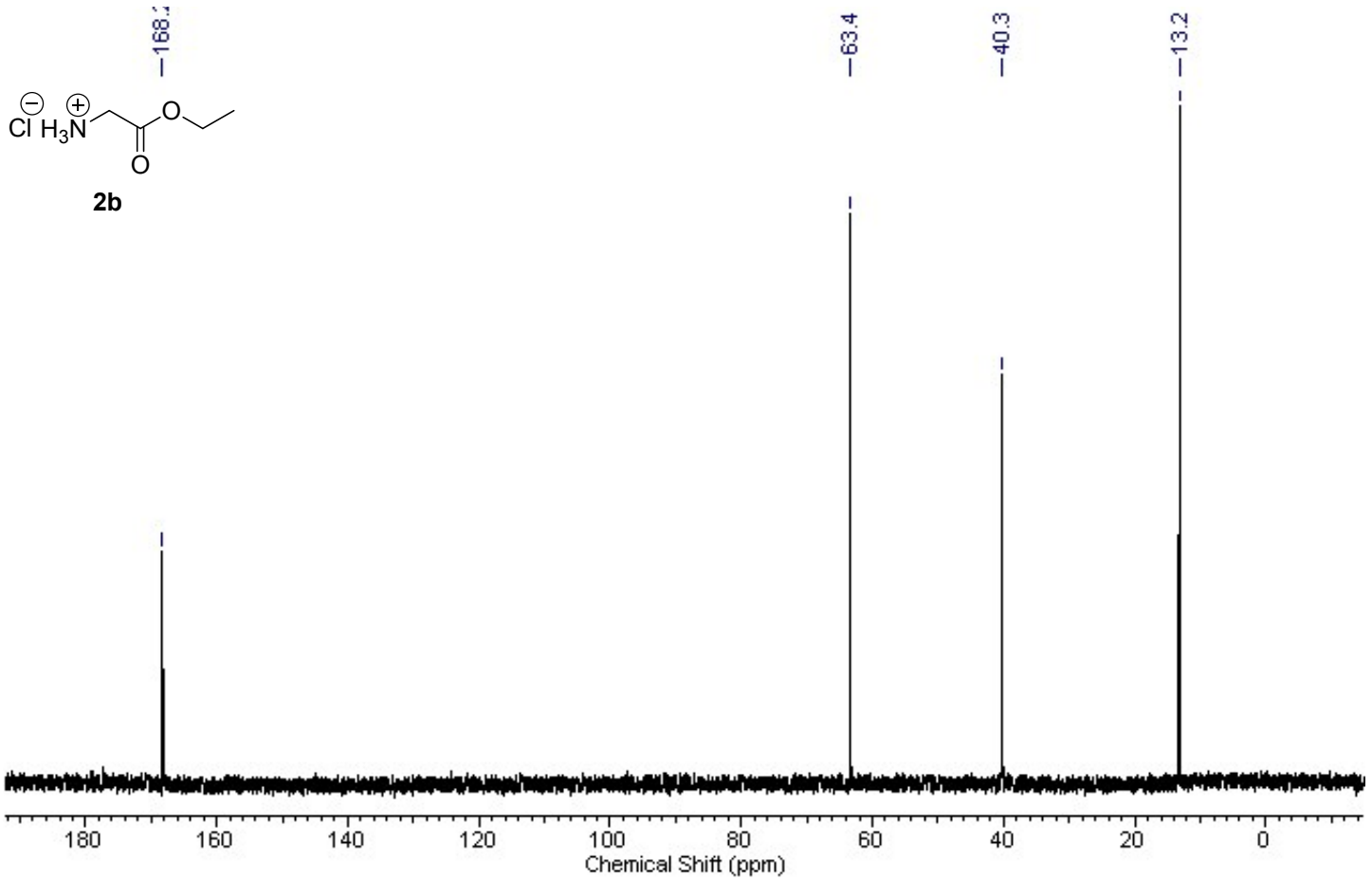
^{13}C NMR spectrum of *5H-Pyrrolo[2,1-a]isoindole-3-carbaldehyde* (**1i**)



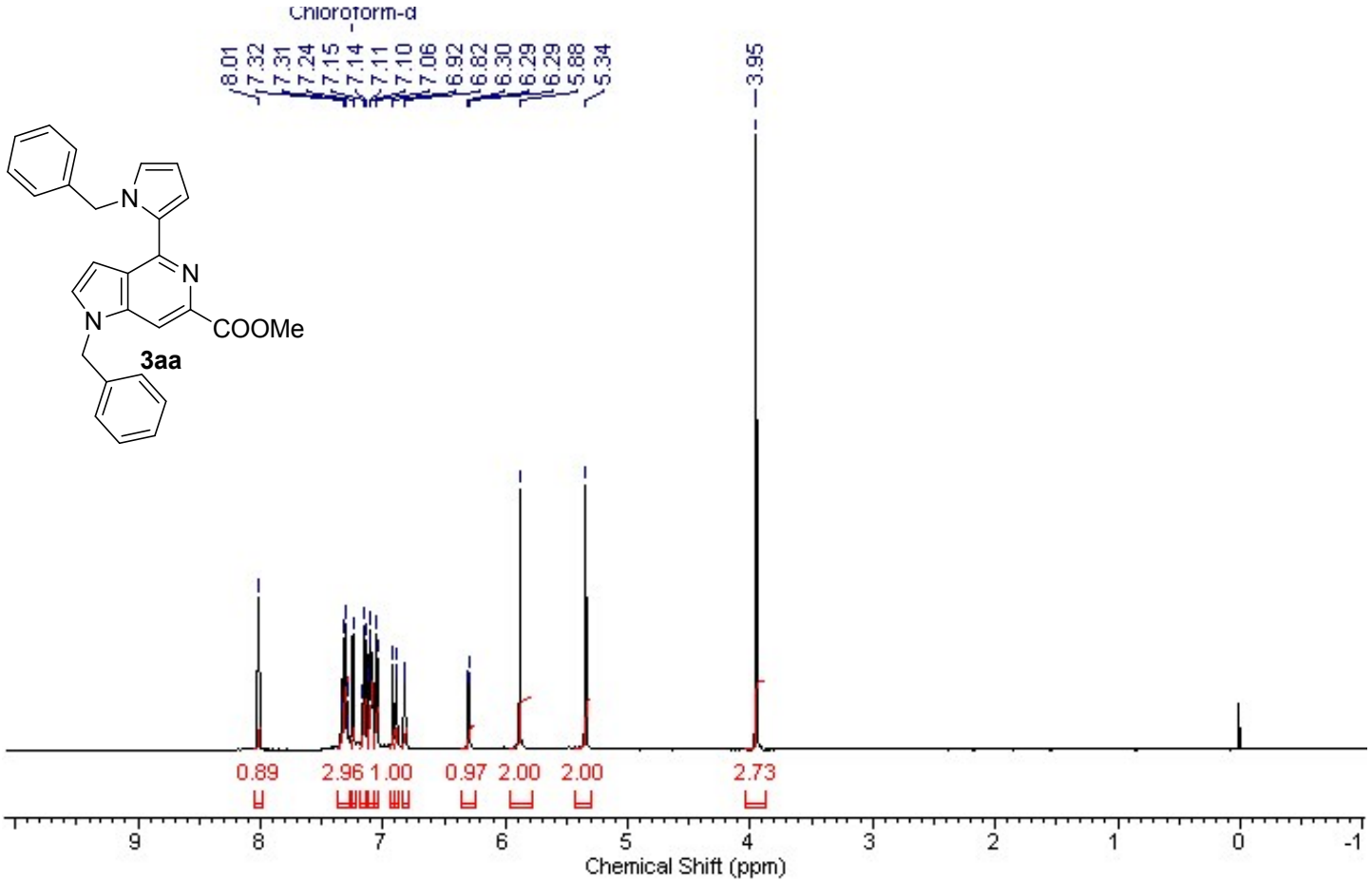
^{1}H NMR spectrum of *Glycine ethyl ester HCl salt* (**2b**)



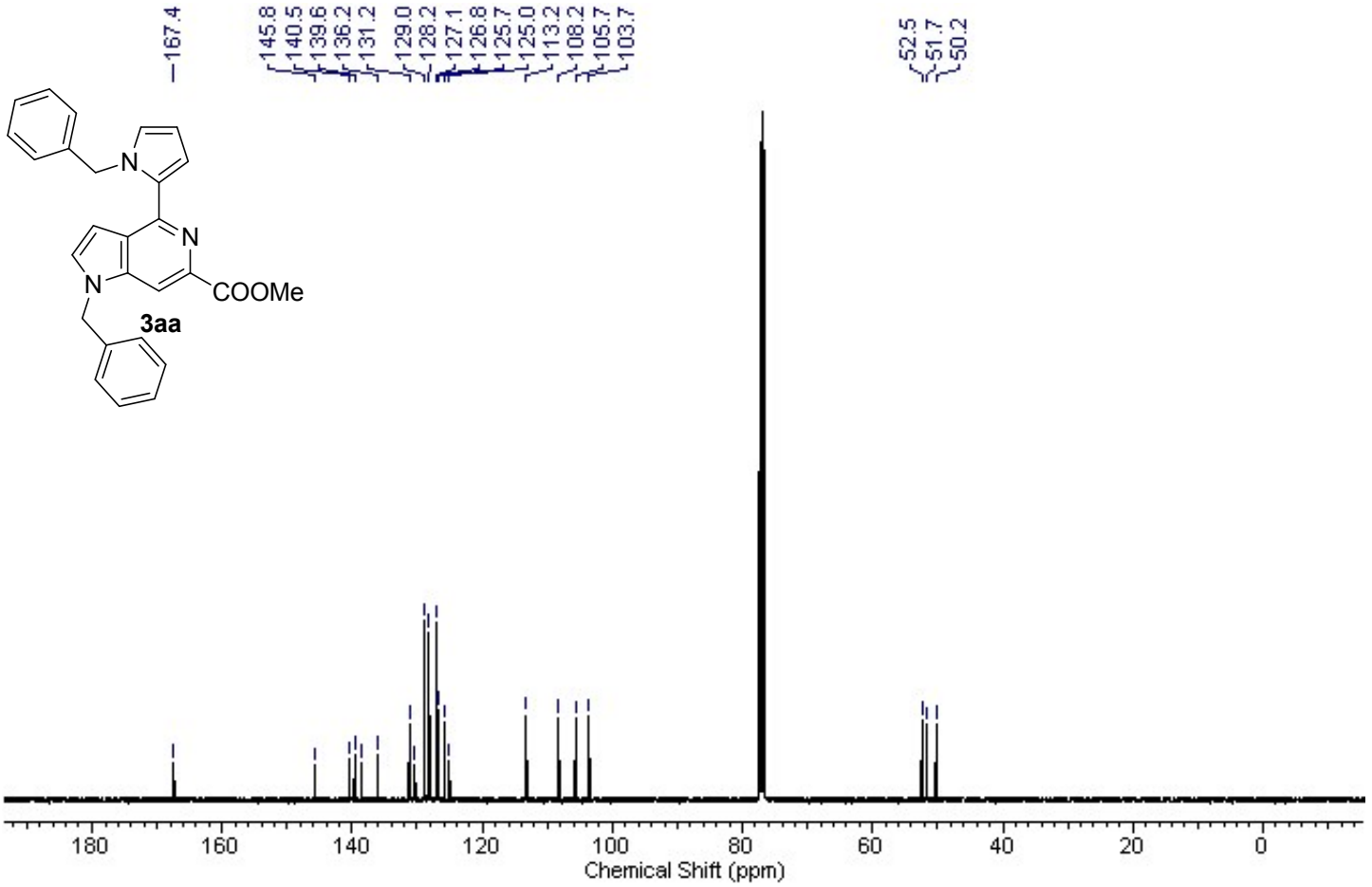
^{13}C NMR spectrum of *Glycine ethyl ester HCl salt* (**2b**)



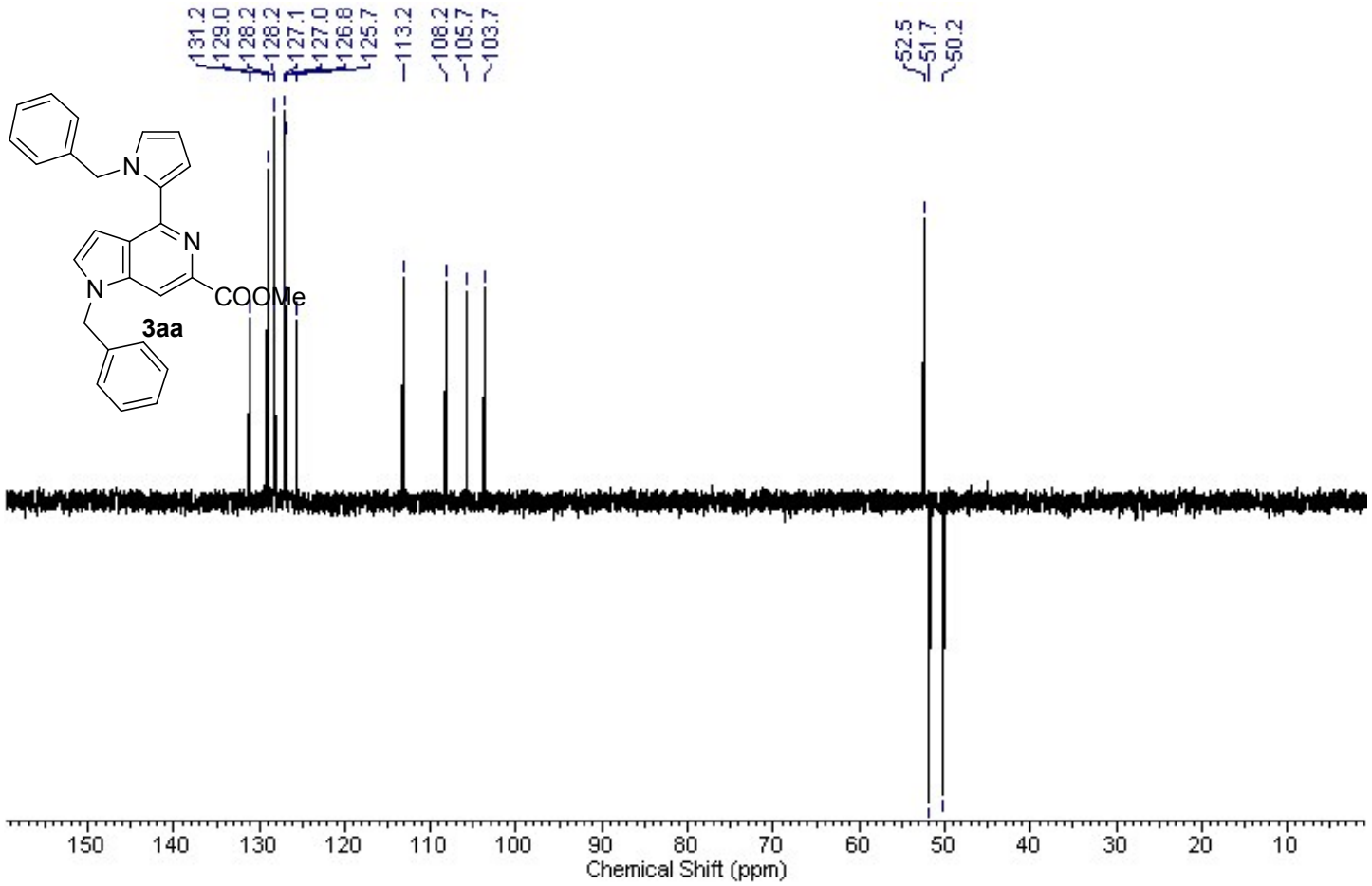
^{1}H NMRspectrum (500 MHz) of*Methyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3aa**)



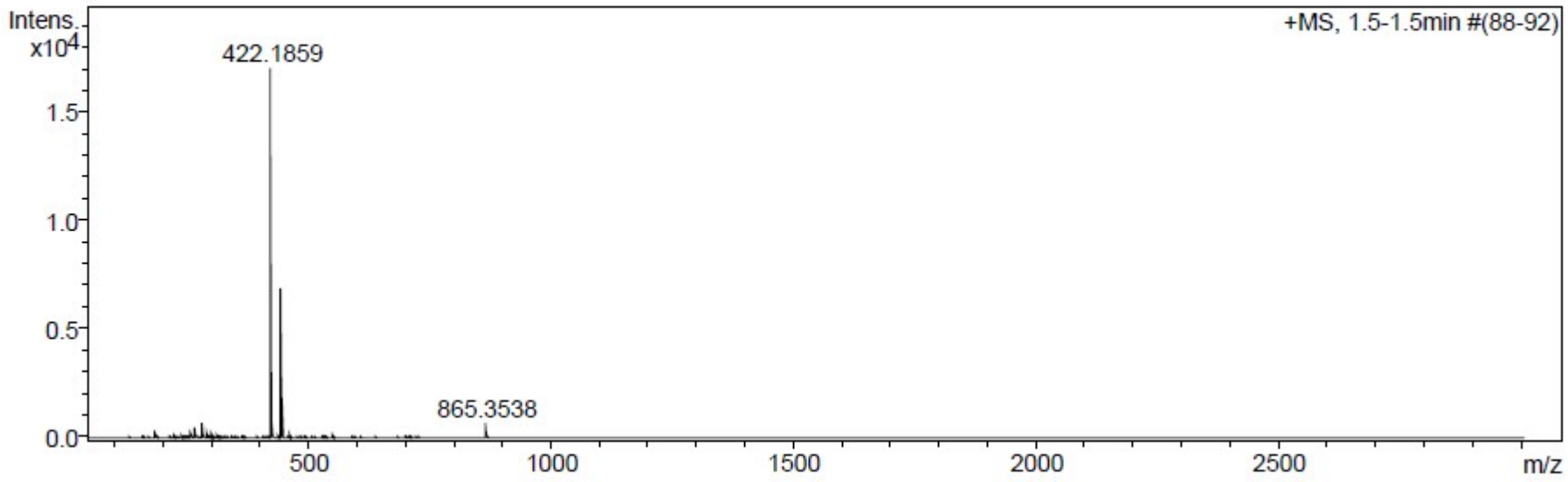
^{13}C NMR spectrum of *Methyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3aa**)



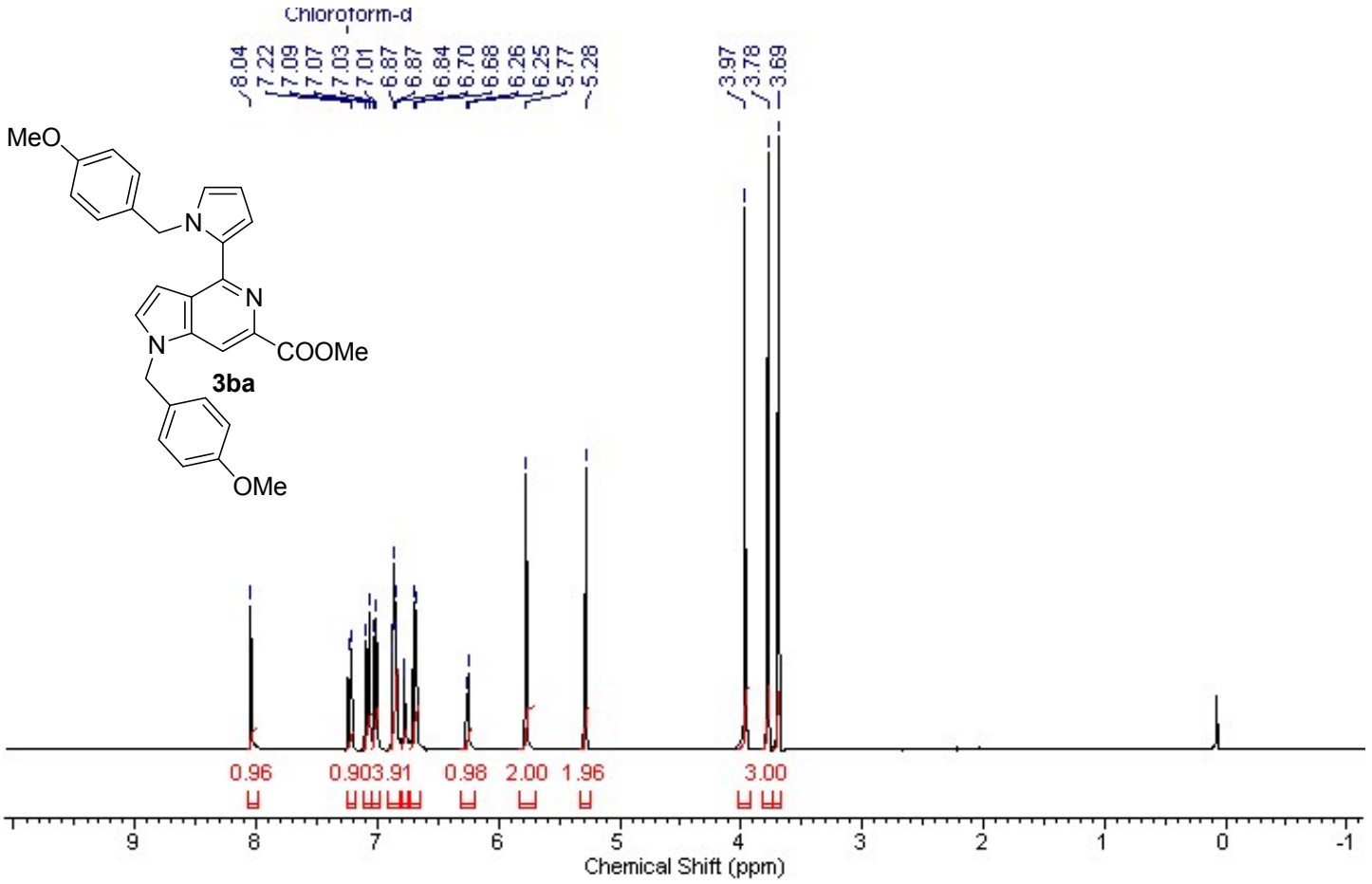
DEPT-135°spectrum of *Methyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3aa**)



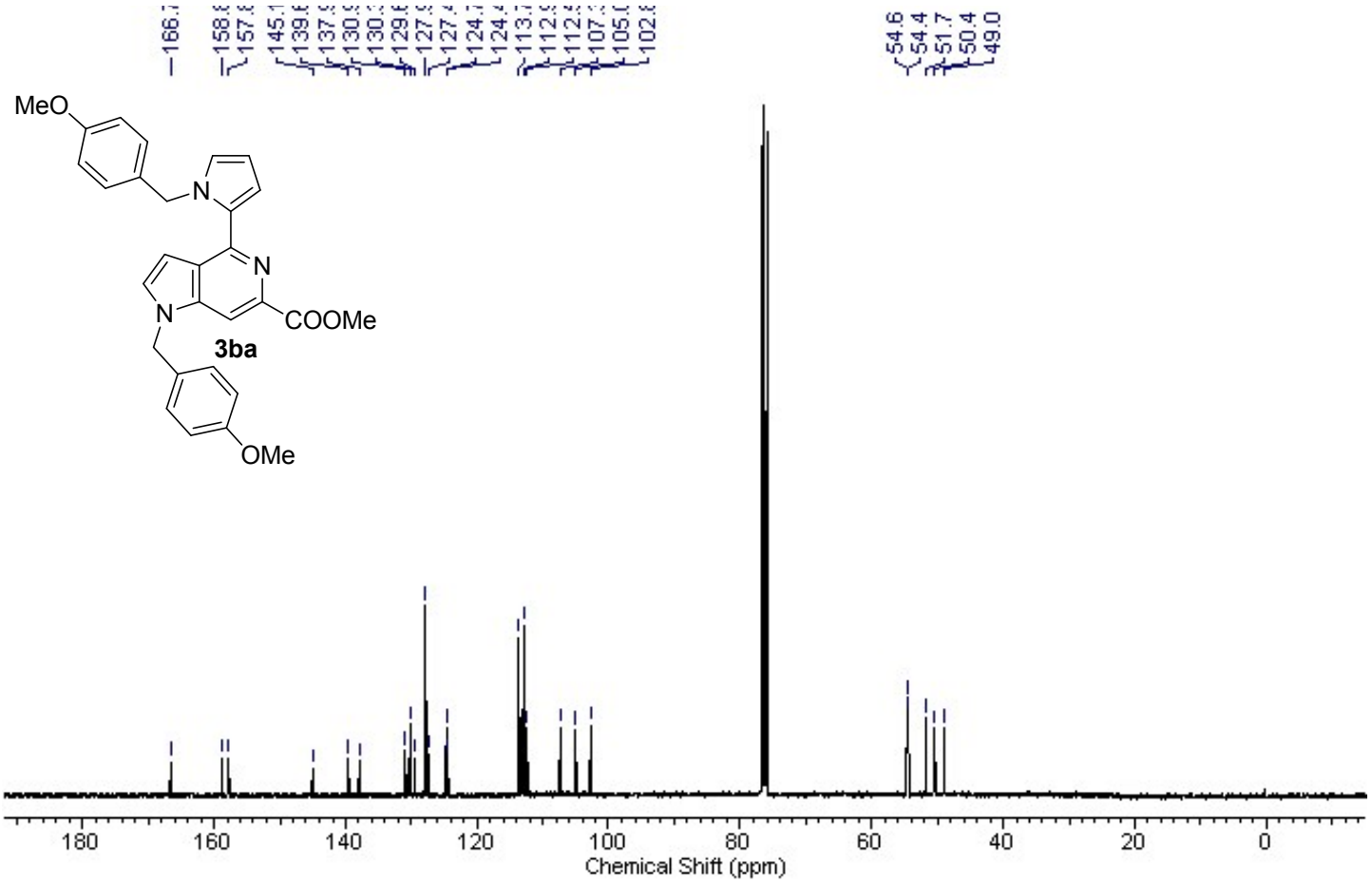
HRMS data of *Methyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3aa**)



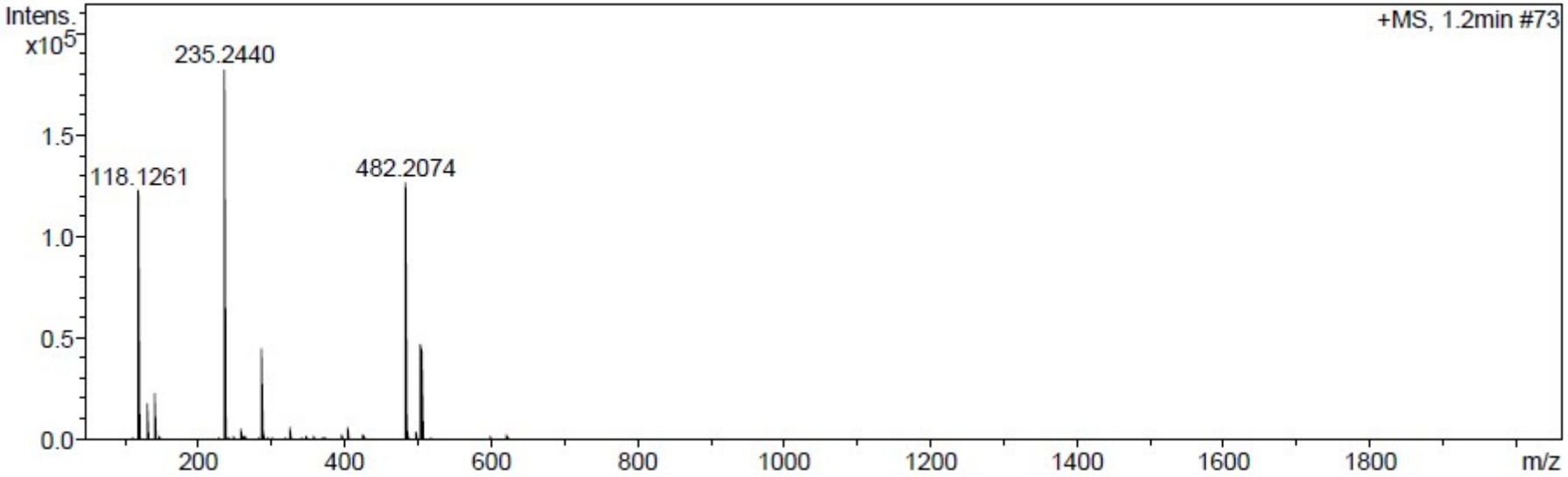
^{1}H NMR spectrum of *Methyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ba**)



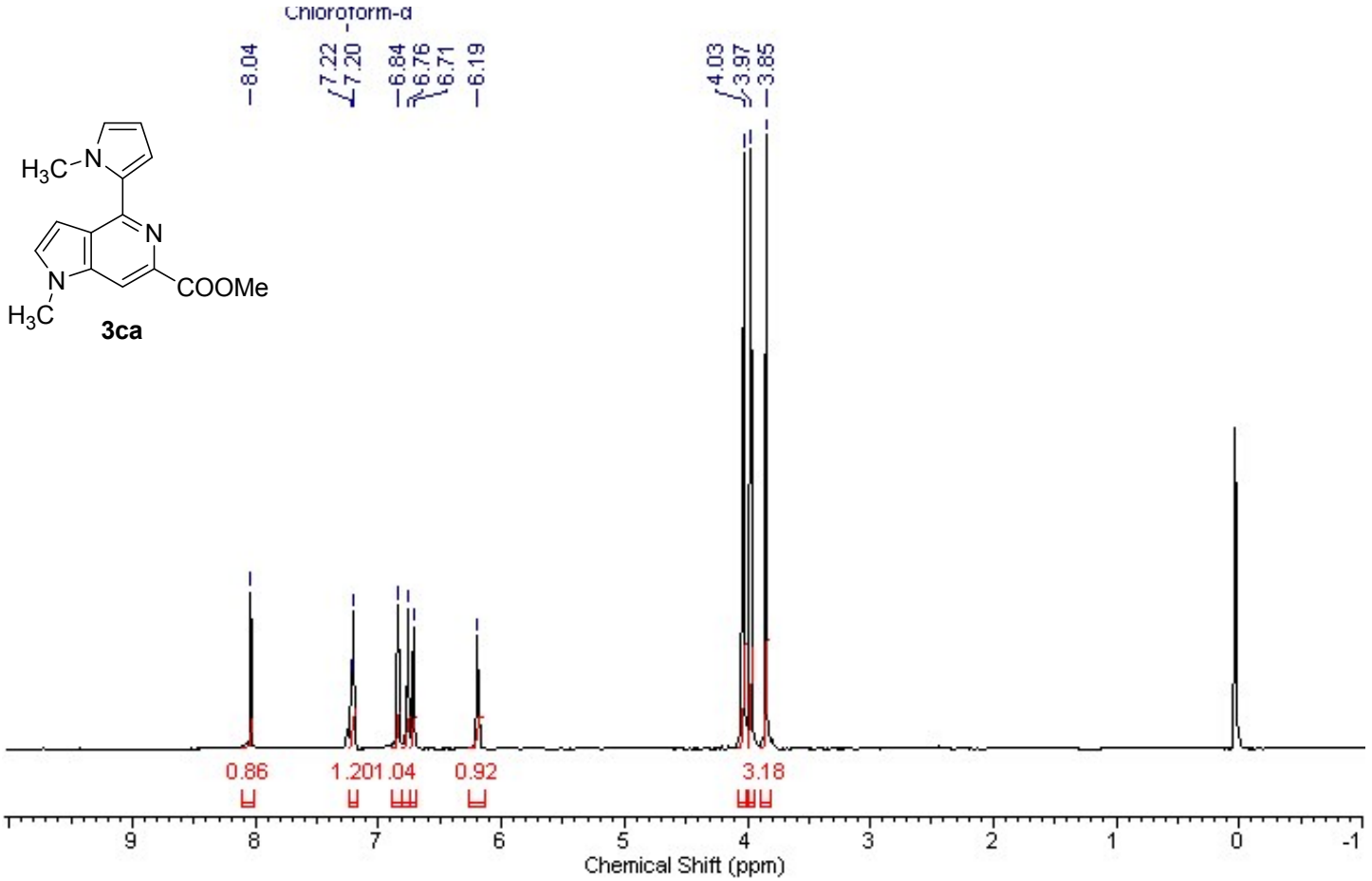
^{13}C NMR spectrum of *Methyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ba**)



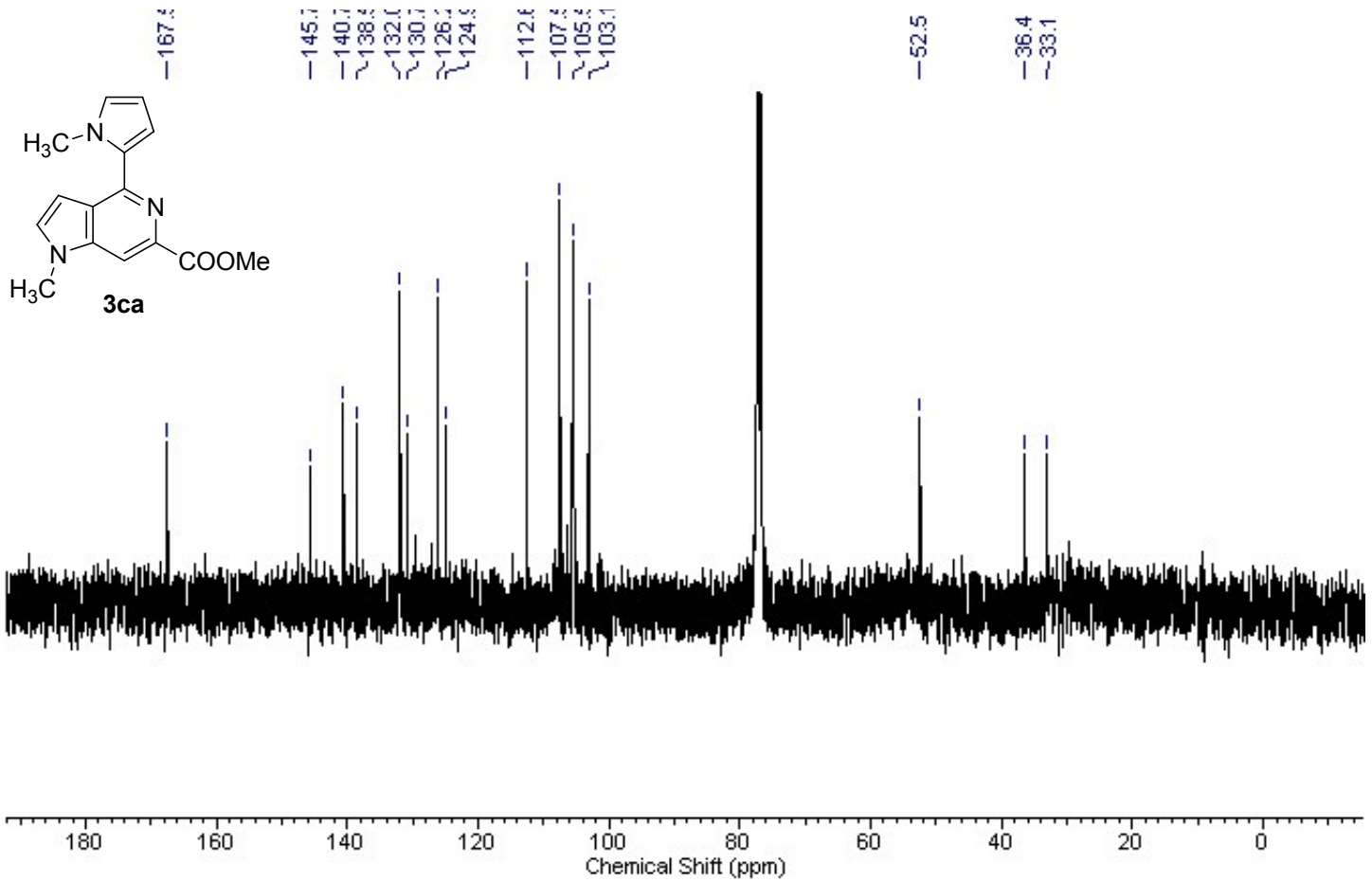
HRMS data of *Methyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ba**)



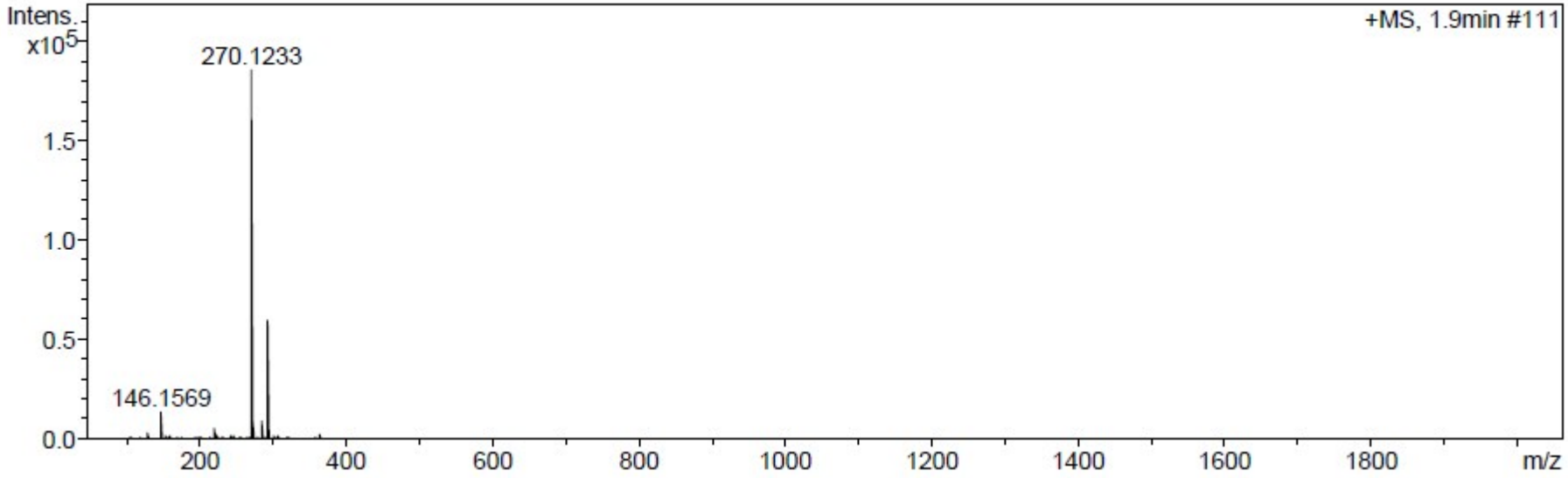
^{1}H NMR spectrum of *Methyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ca**)



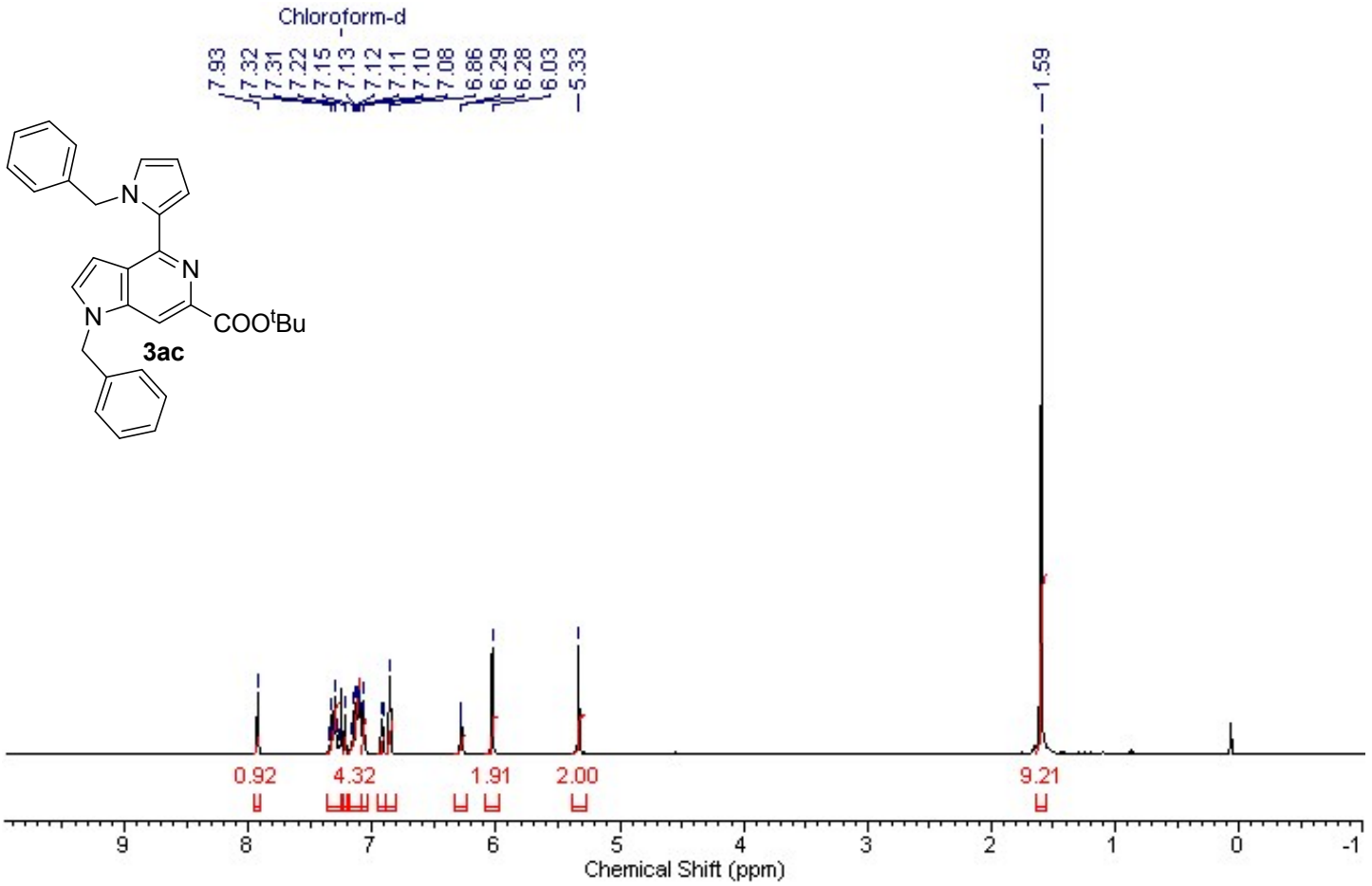
^{13}C NMR spectrum of *Methyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ca**)



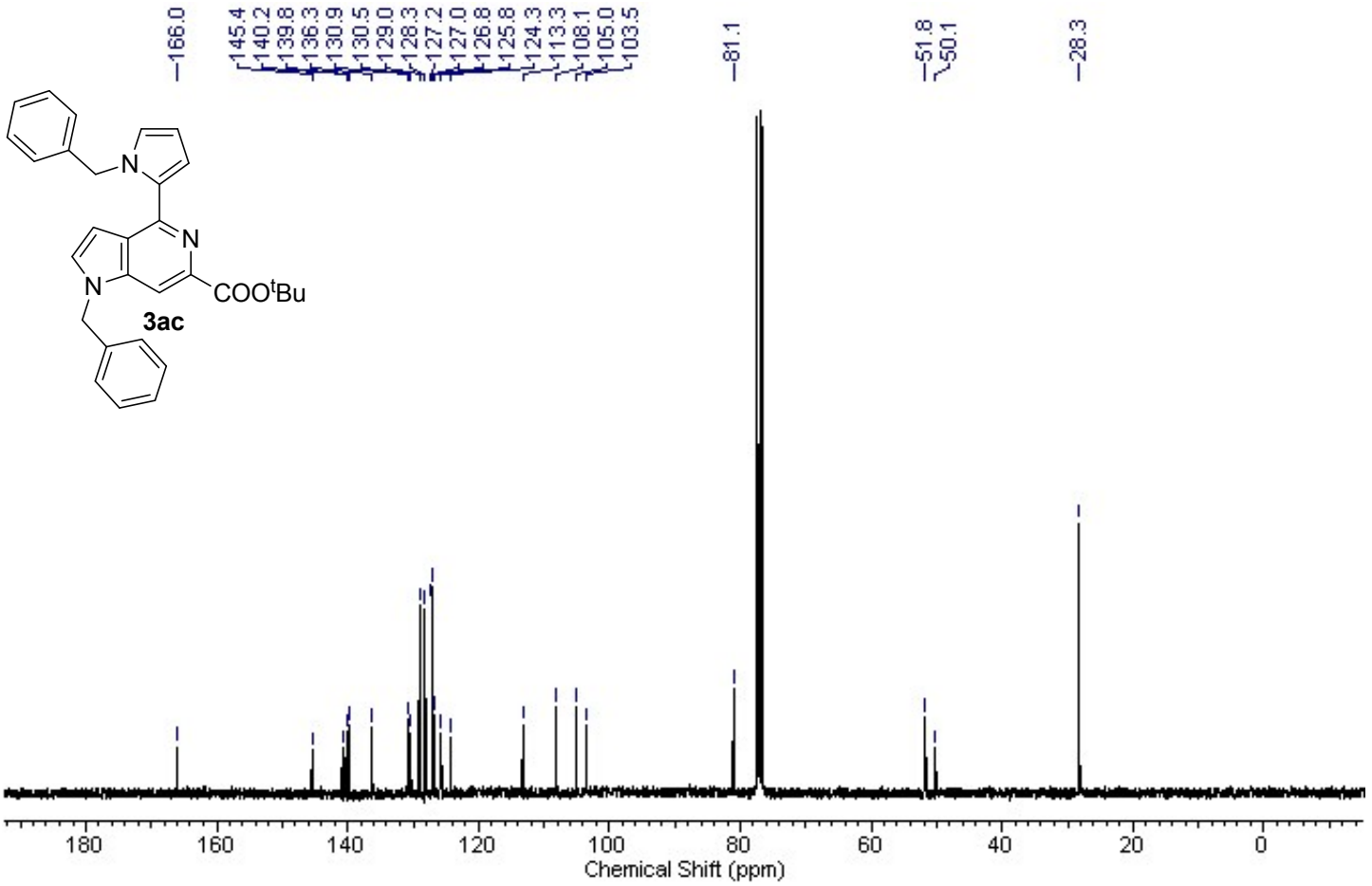
HRMS data of *Methyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ca**)



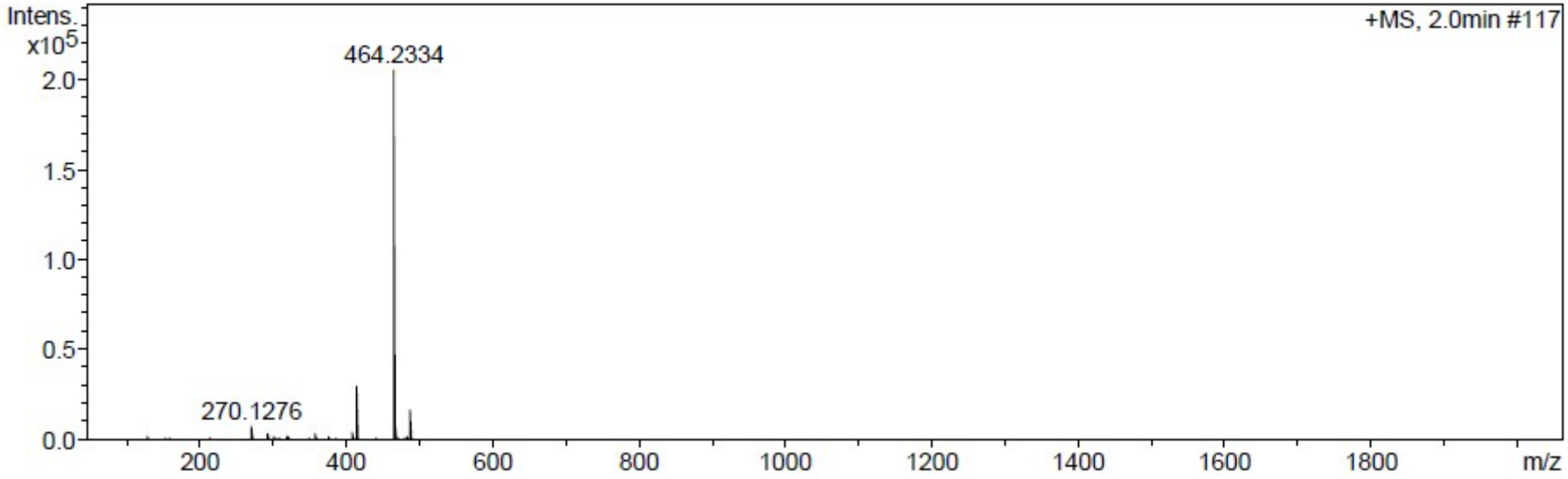
^{1}H NMR spectrum of *Tert-butyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ac**)



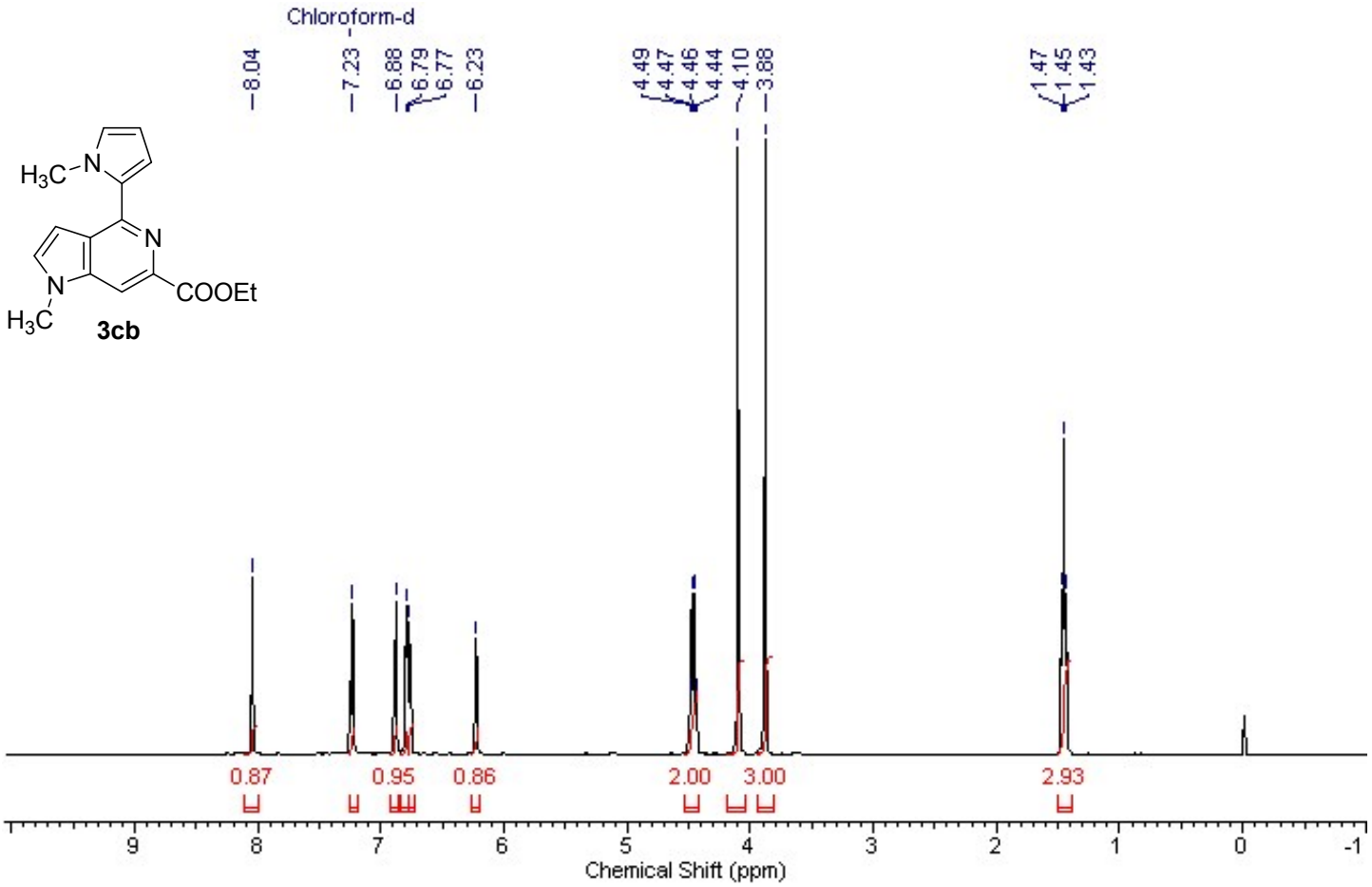
^{13}C NMR spectrum of *Tert-butyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ac**)



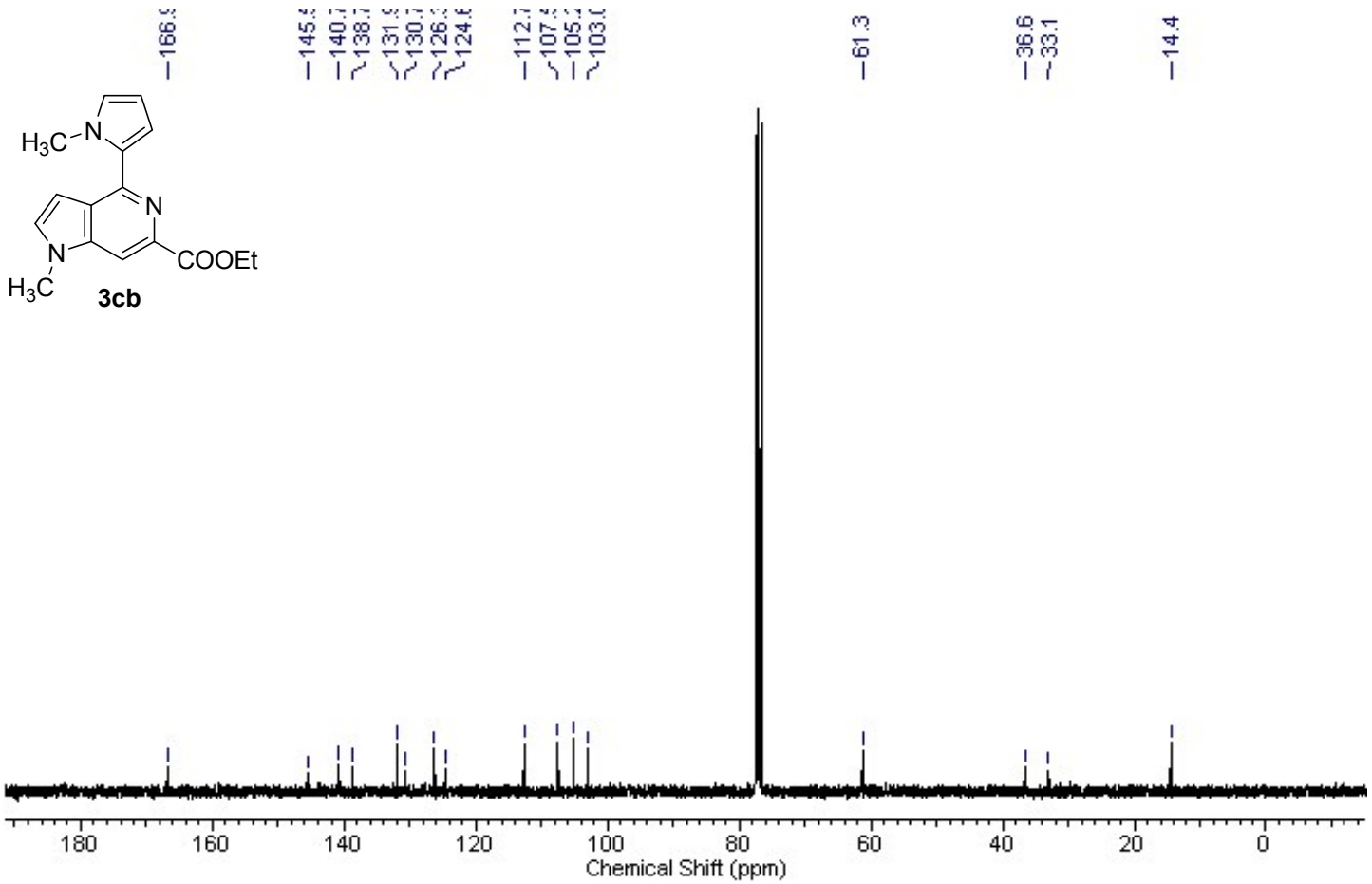
HRMS data of *Tert-butyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ac**)



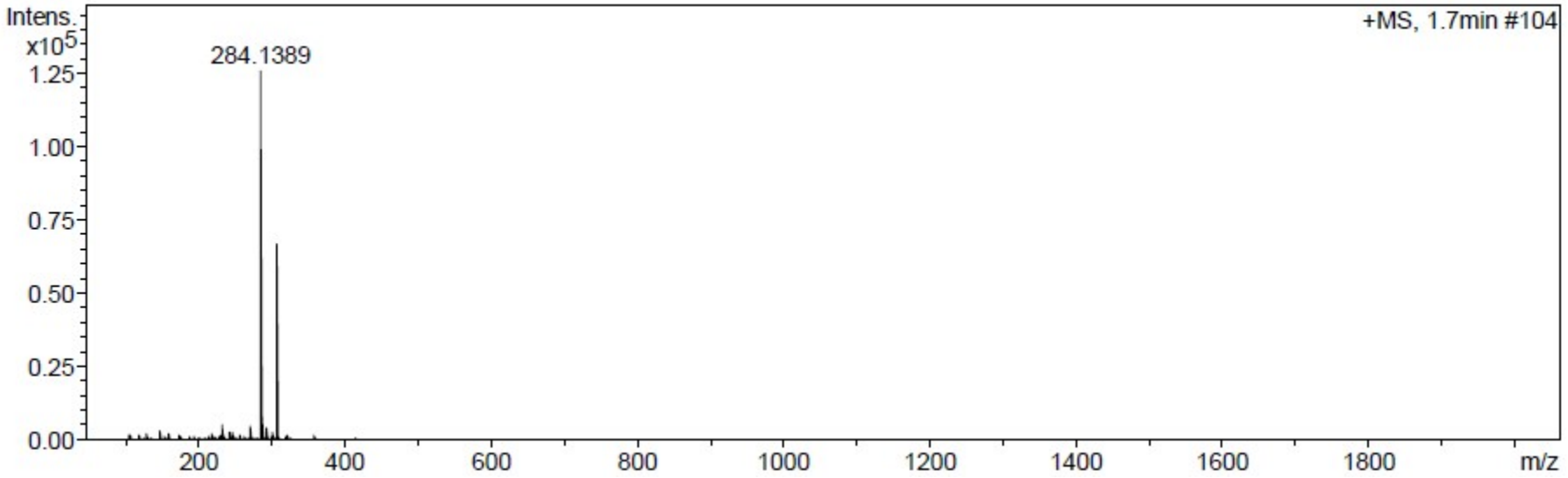
^{1}H NMR spectrum of *Ethyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3cb**)



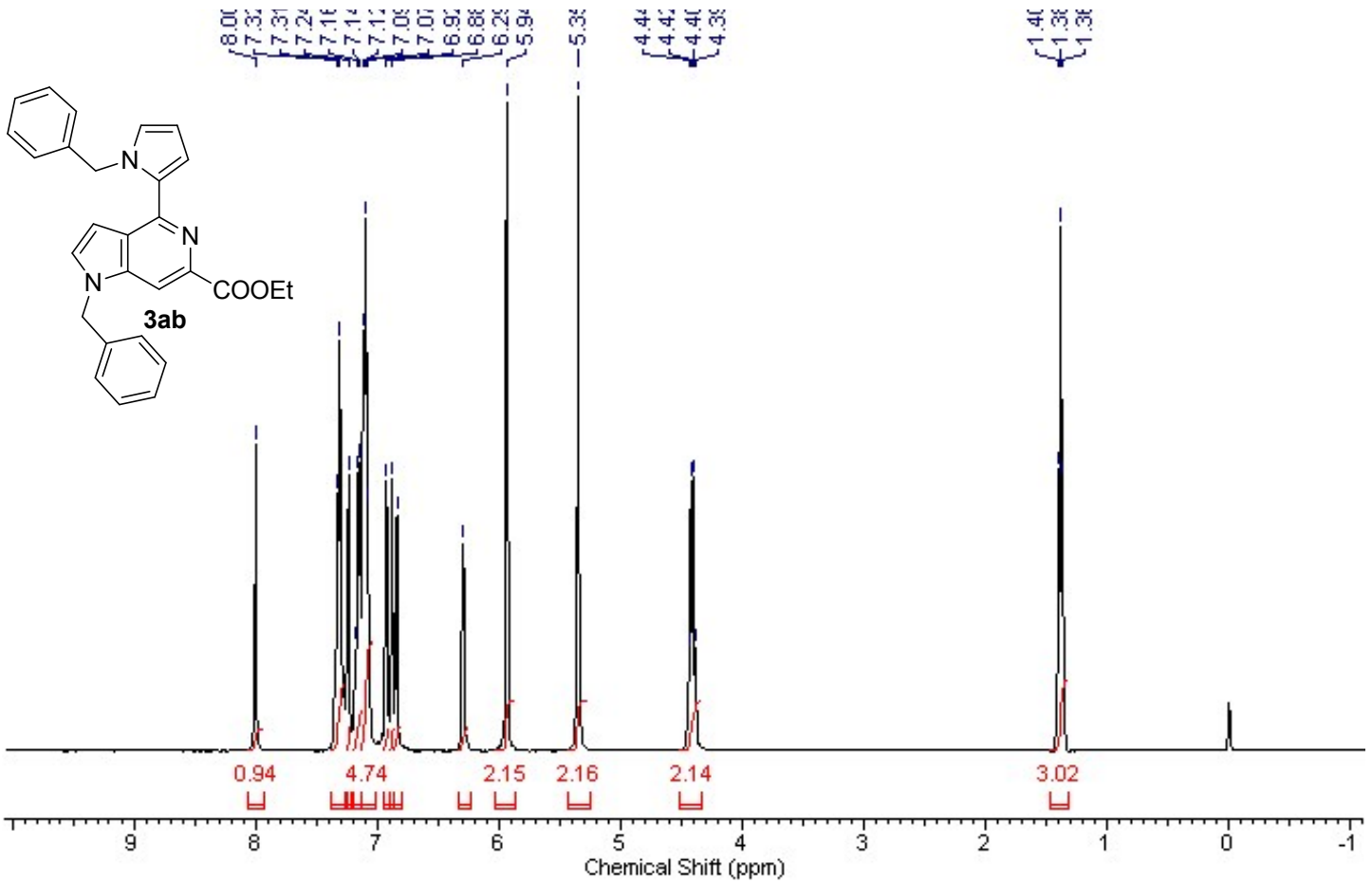
^{13}C NMR spectrum of *Ethyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3cb**)



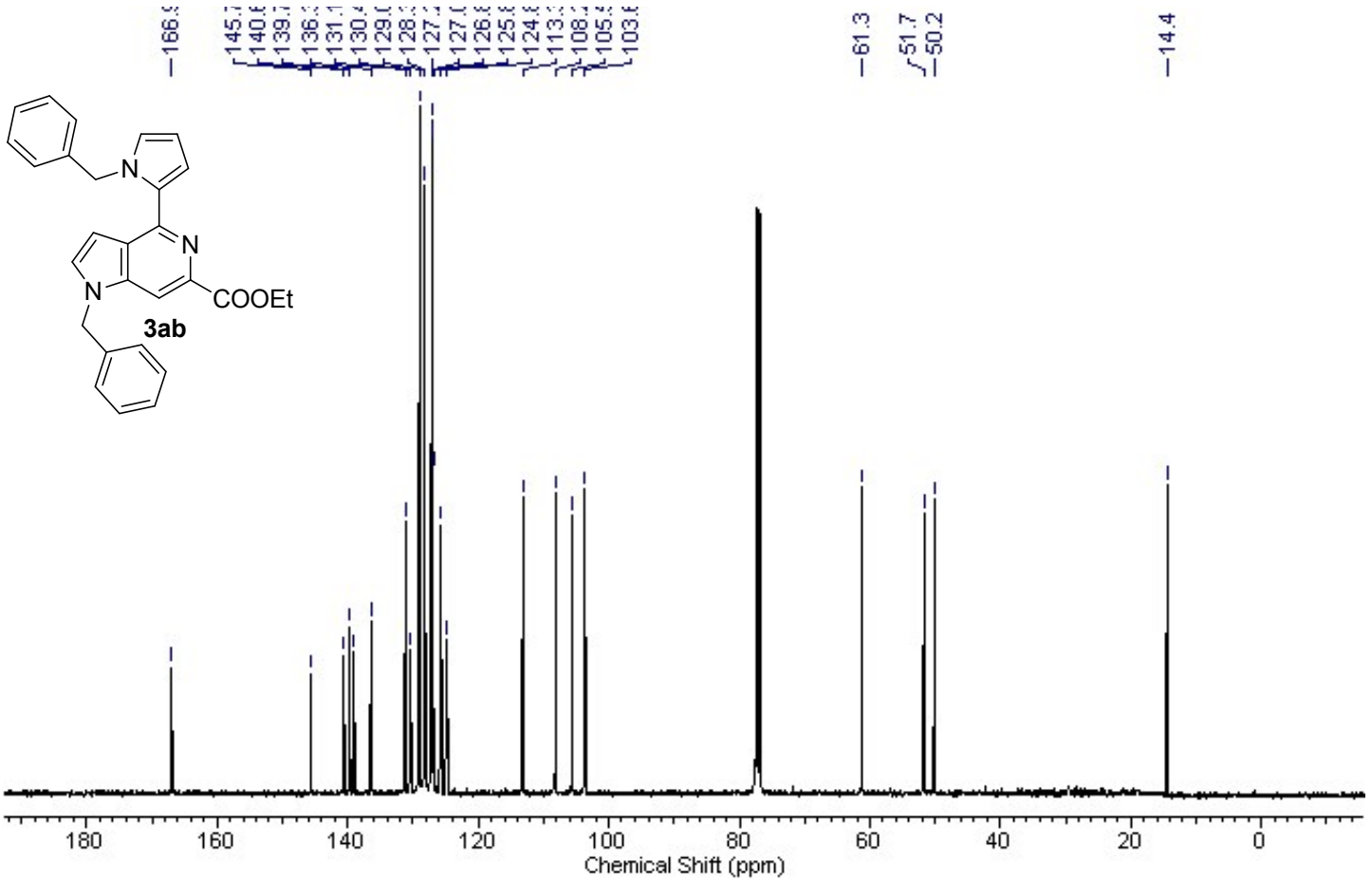
HRMS data of *Ethyl 1-methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3cb**)



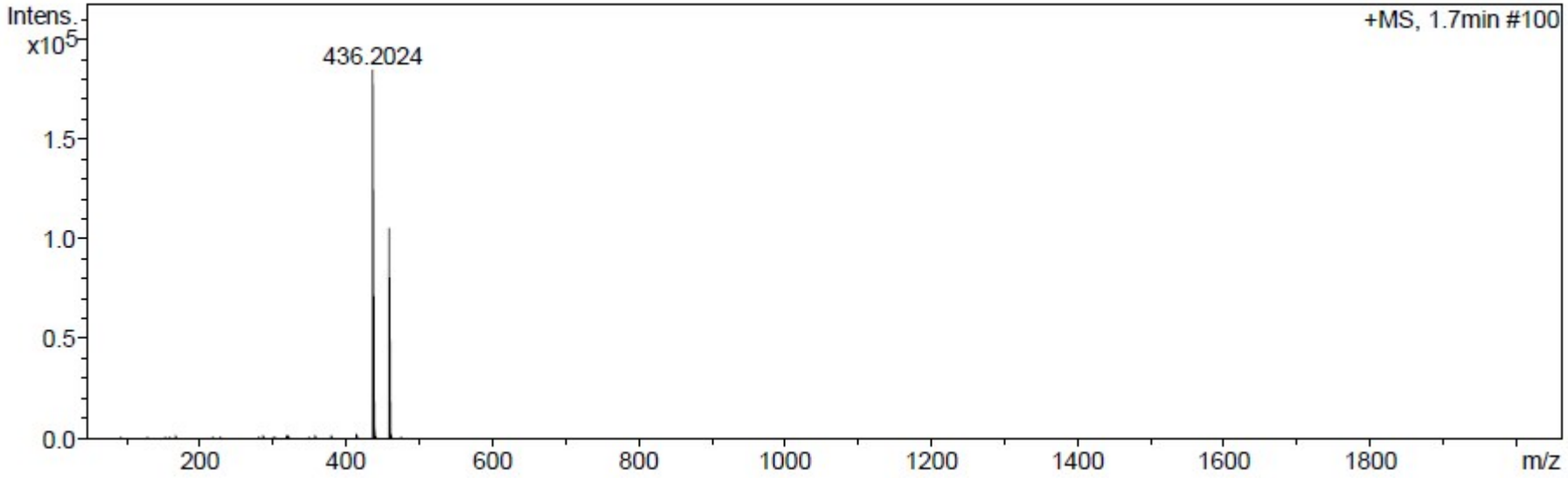
^{1}H NMR spectrum of *Ethyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ab**)



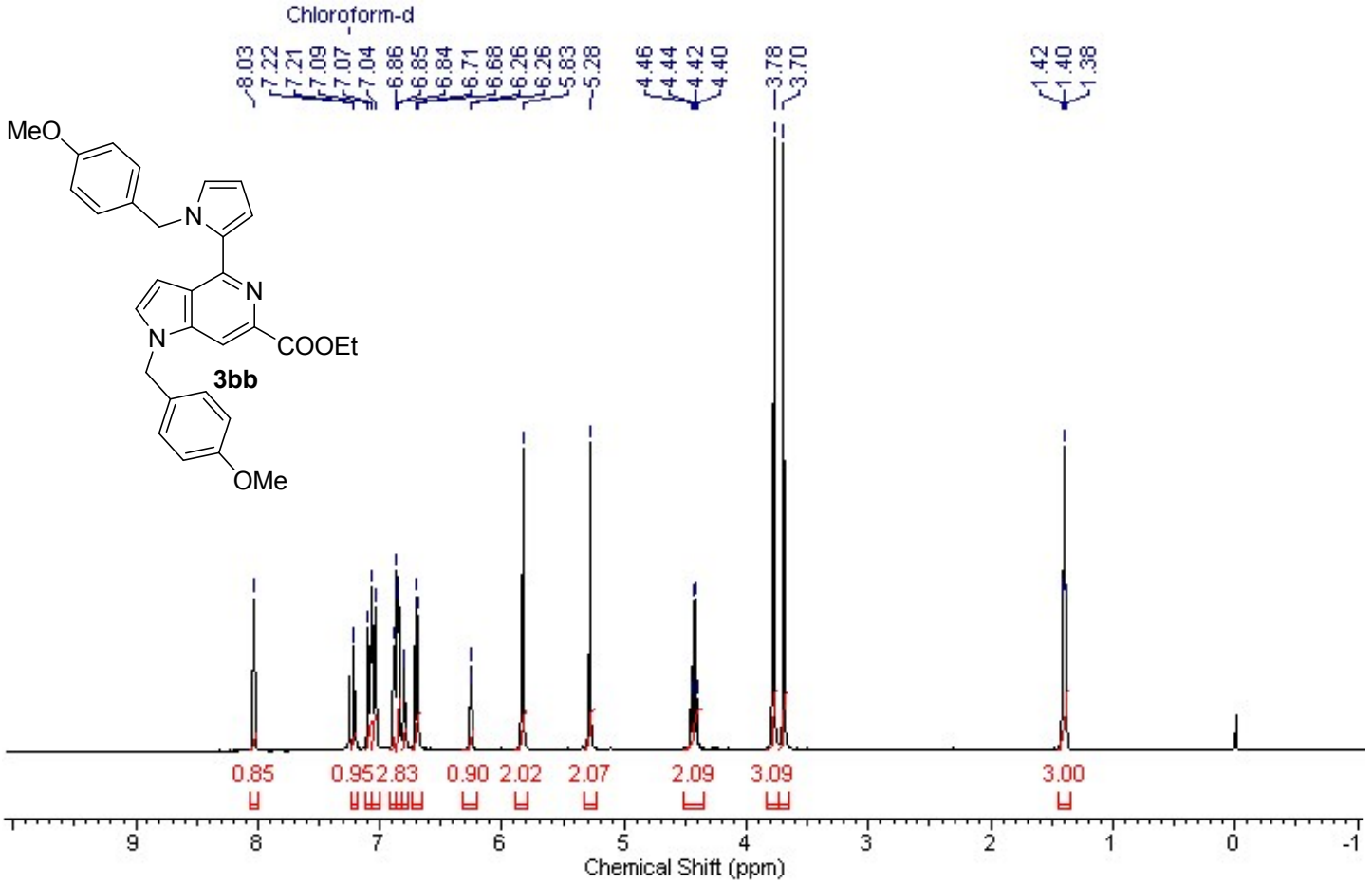
^{13}C NMR spectrum of *Ethyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ab**)



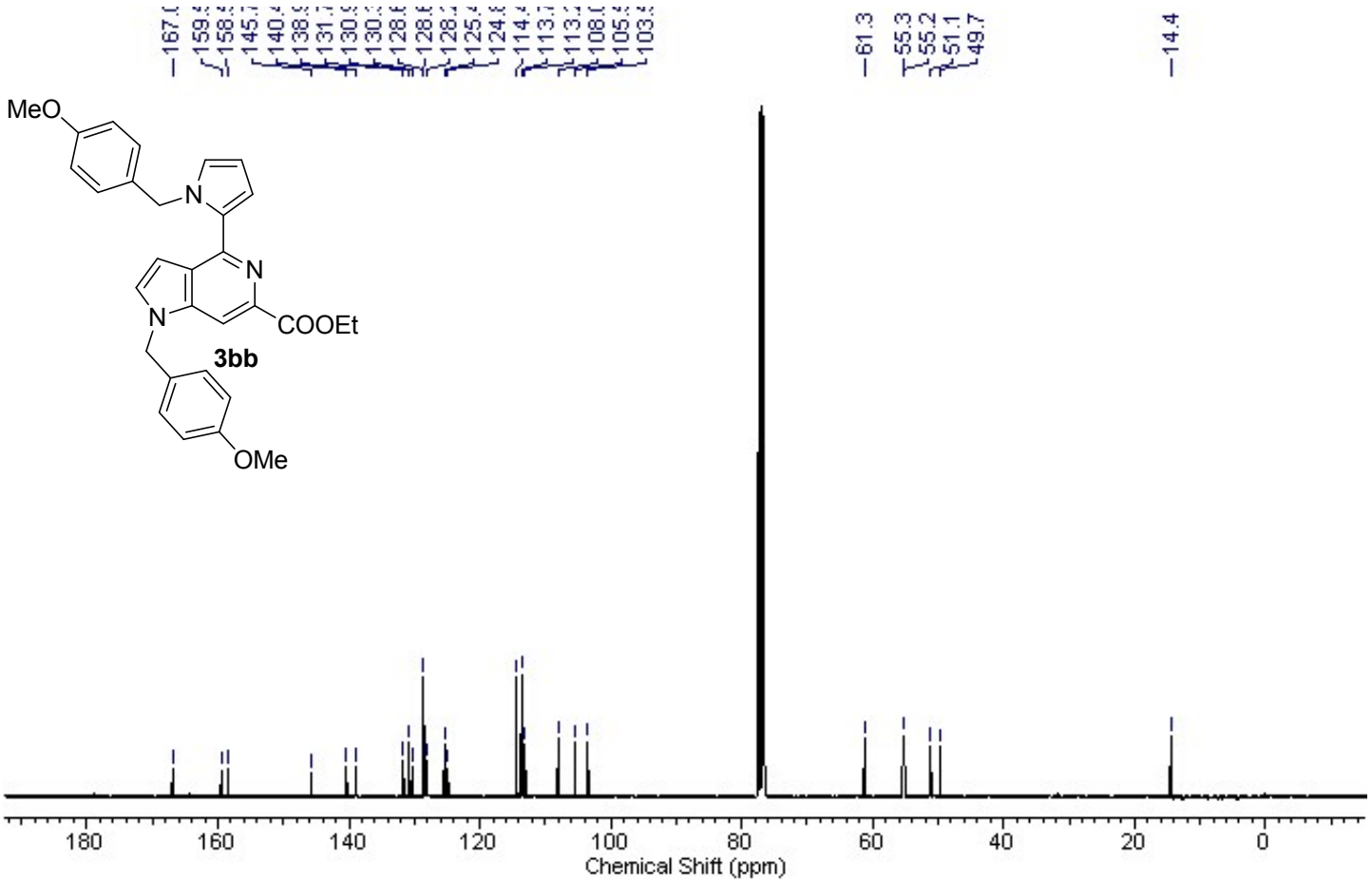
HRMS data of *Ethyl 1-benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ab**)



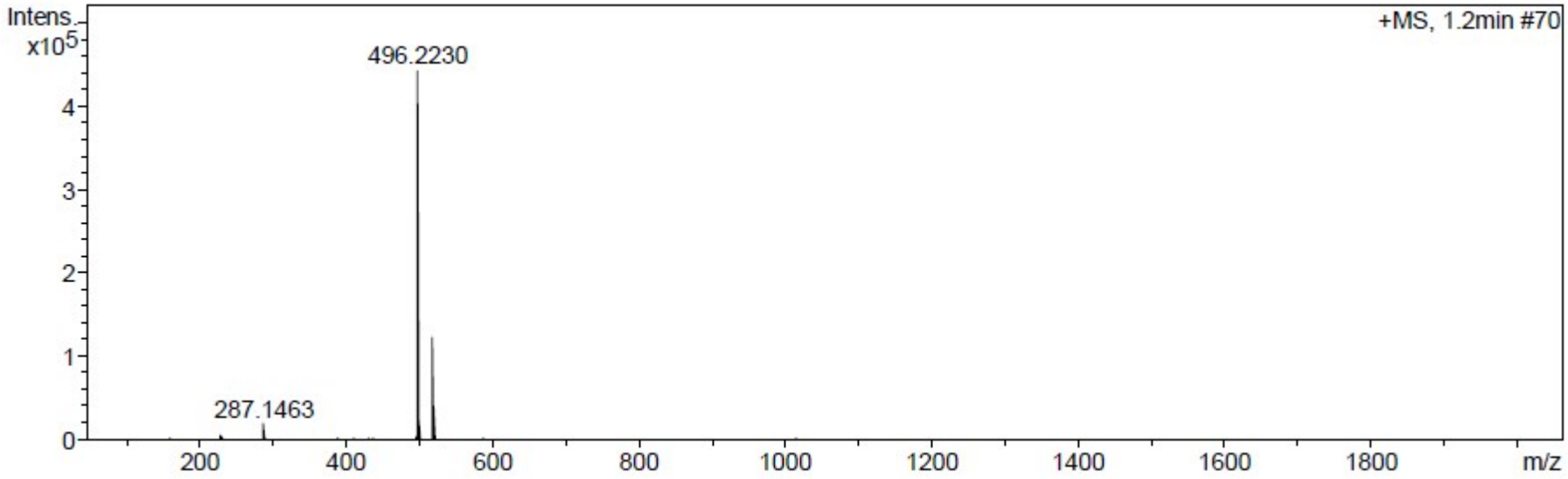
[1]H NMR spectrum of *Ethyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3bb**)



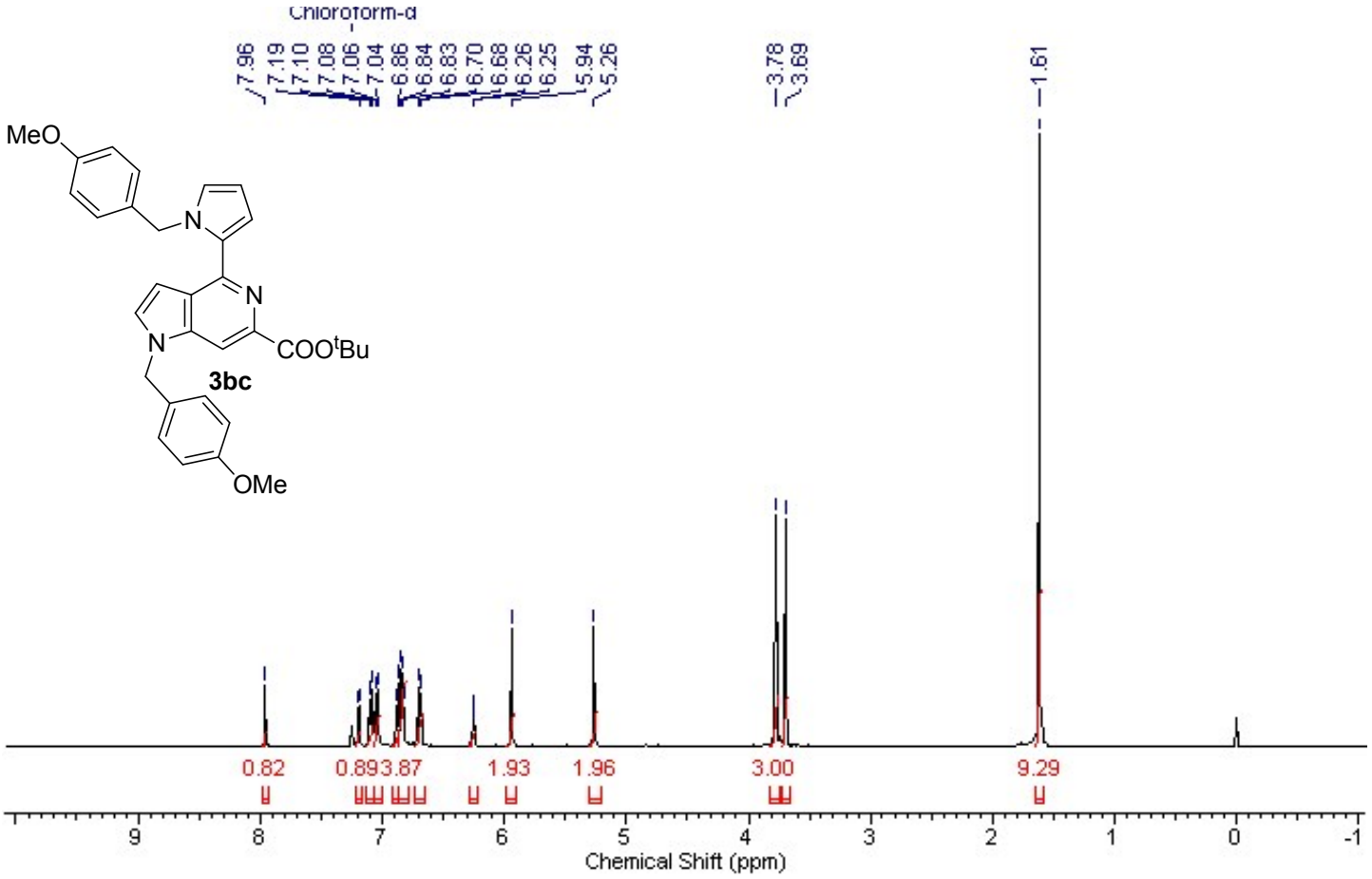
^{13}C NMR spectrum of *Ethyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3bb**)



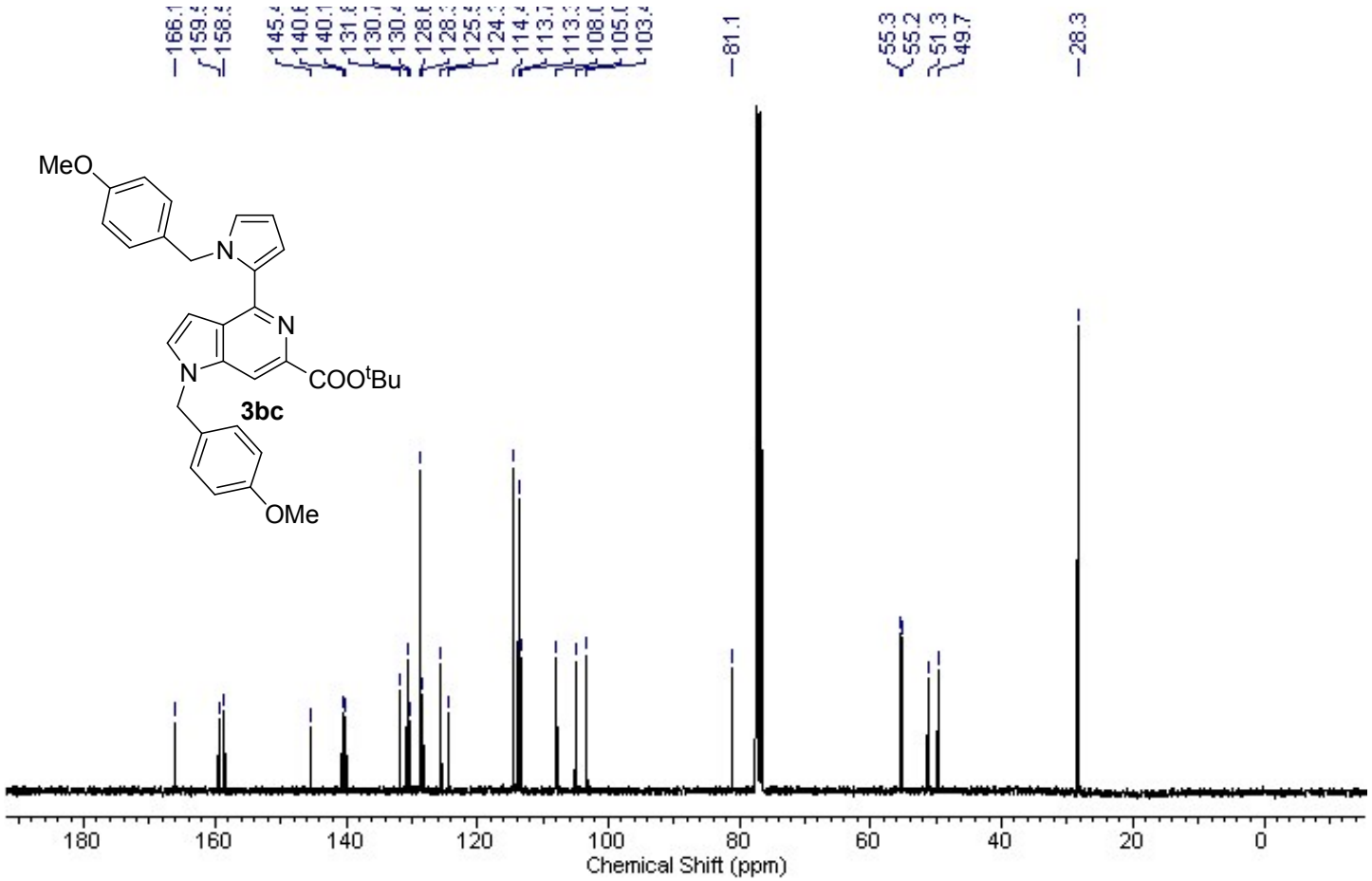
HRMS data of *Ethyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3bb**)



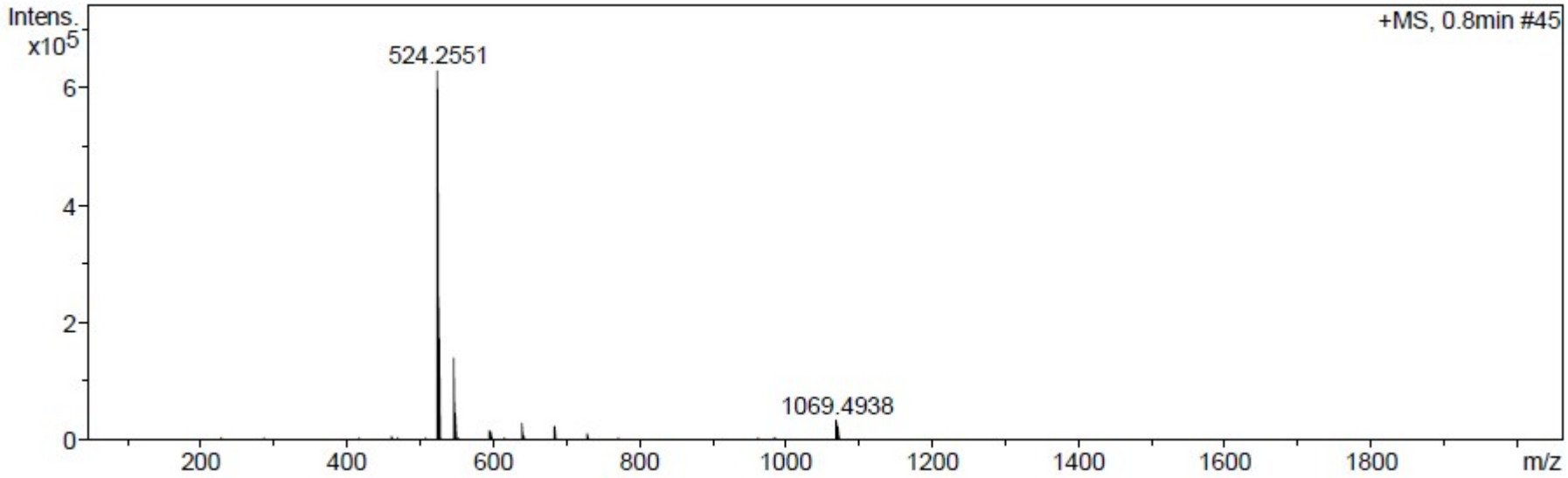
^{1}H NMR spectrum of *Tert-butyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3bc**)



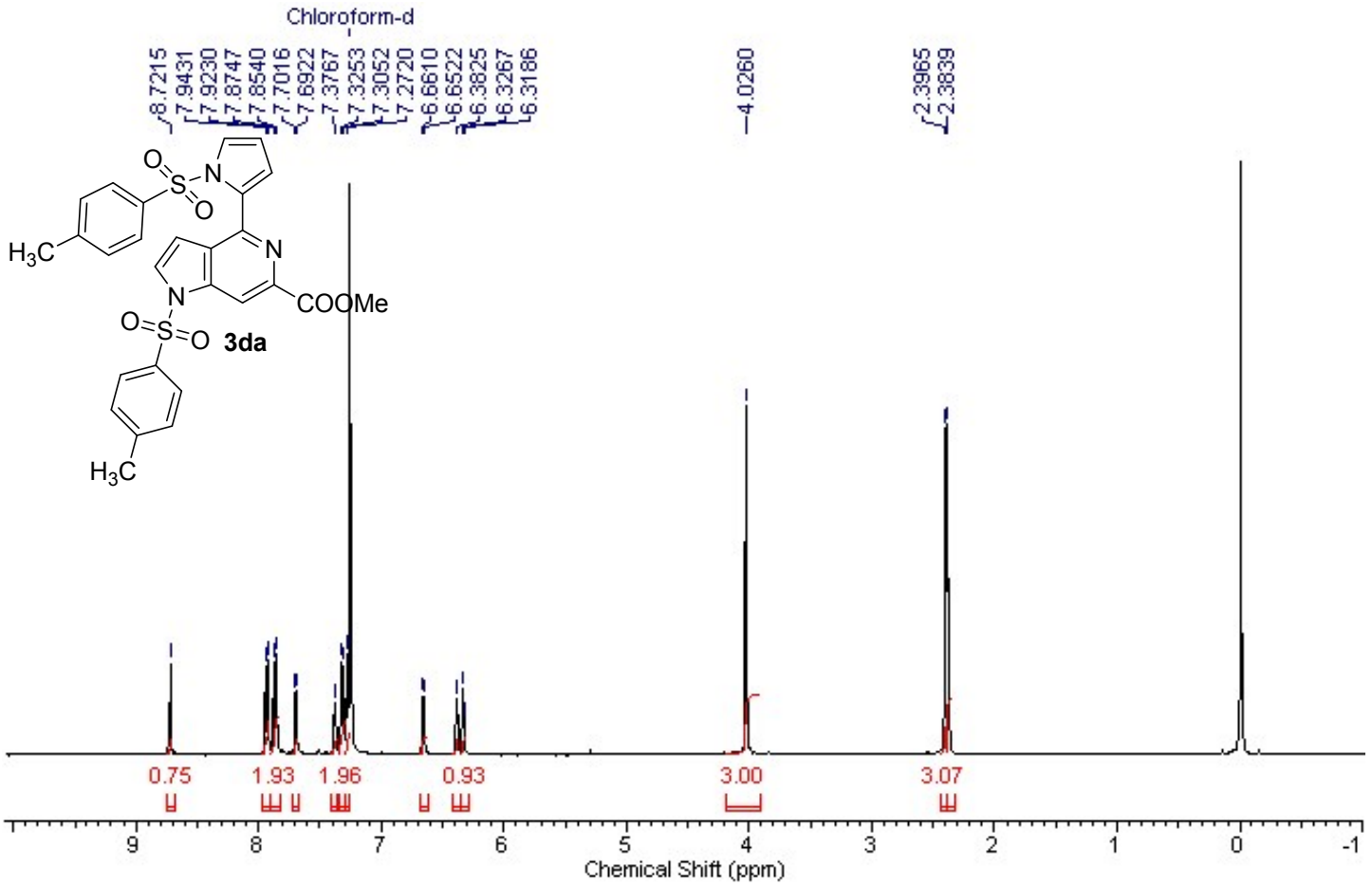
^{13}C NMR spectrum of *Tert-butyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3bc**)



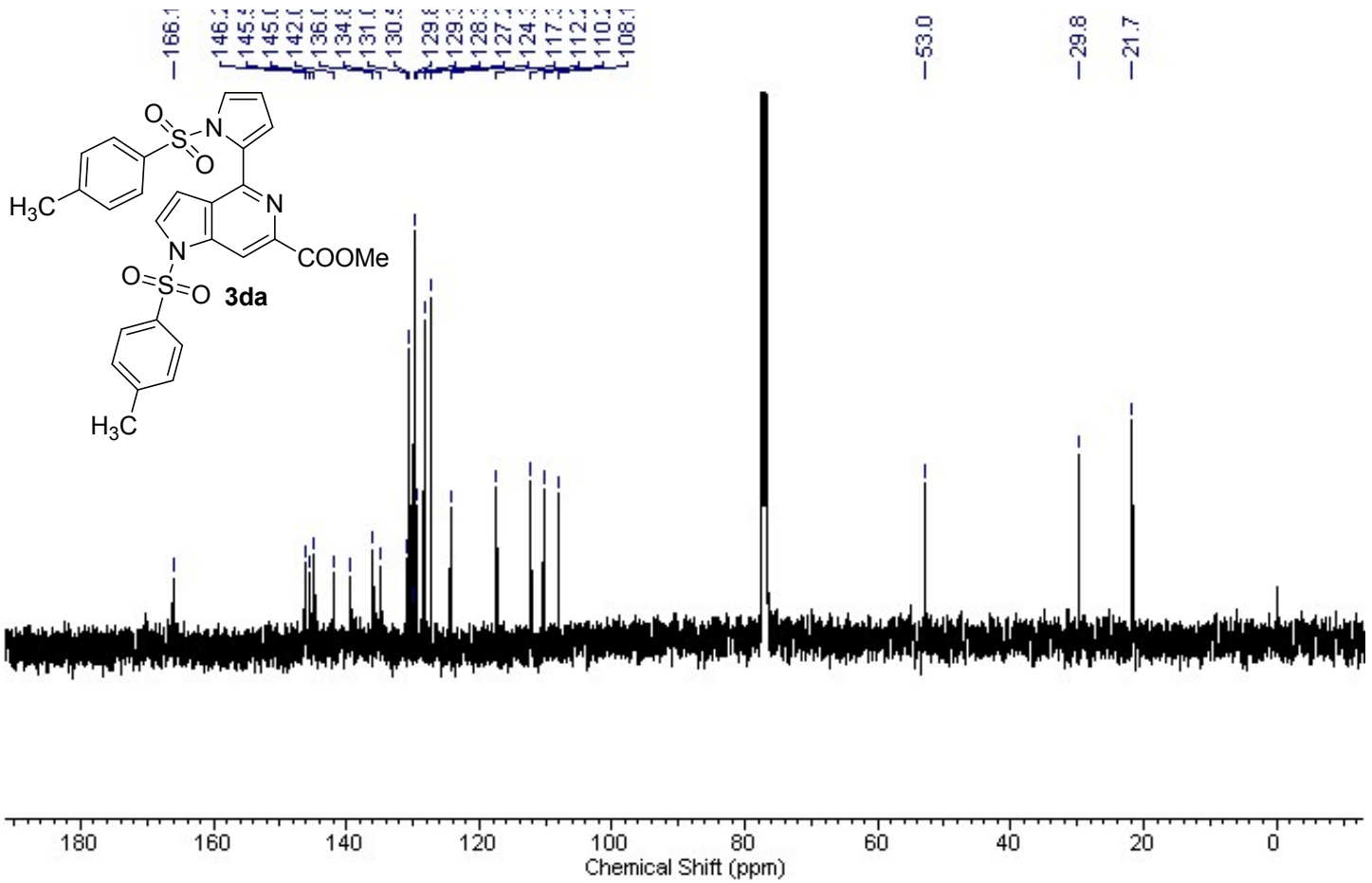
HRMS data of *Tert-butyl 1-(4-methoxybenzyl)-4-(1-(4-methoxybenzyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3bc**)



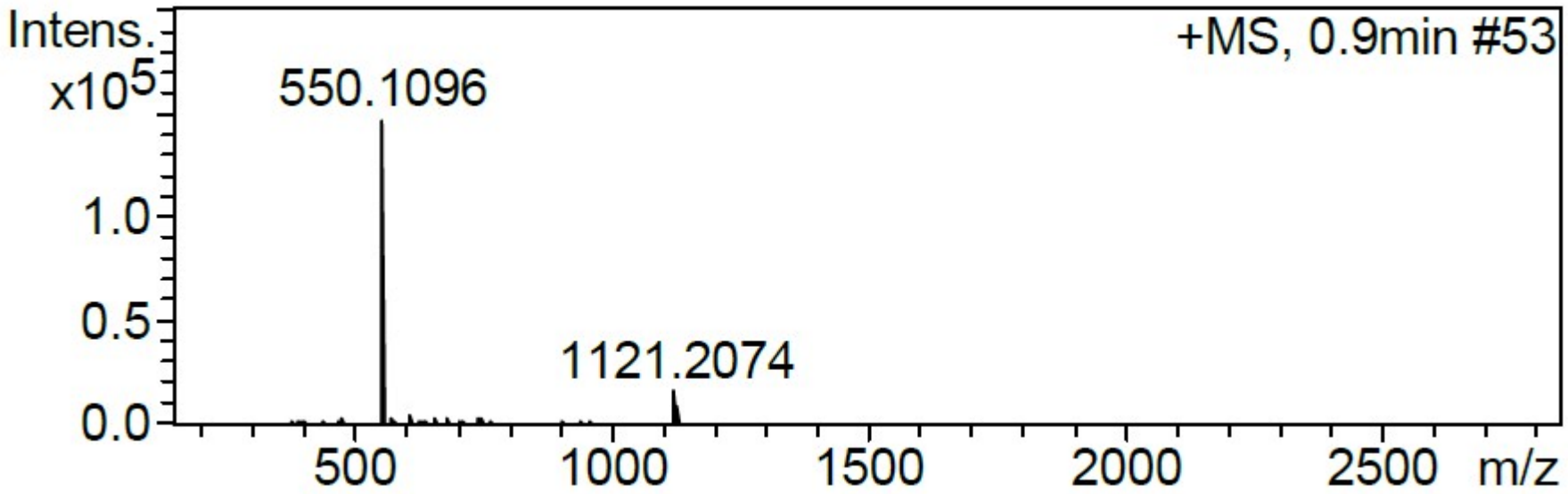
^{1}H NMR spectrum of *Methyl 1-tosyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3da**)



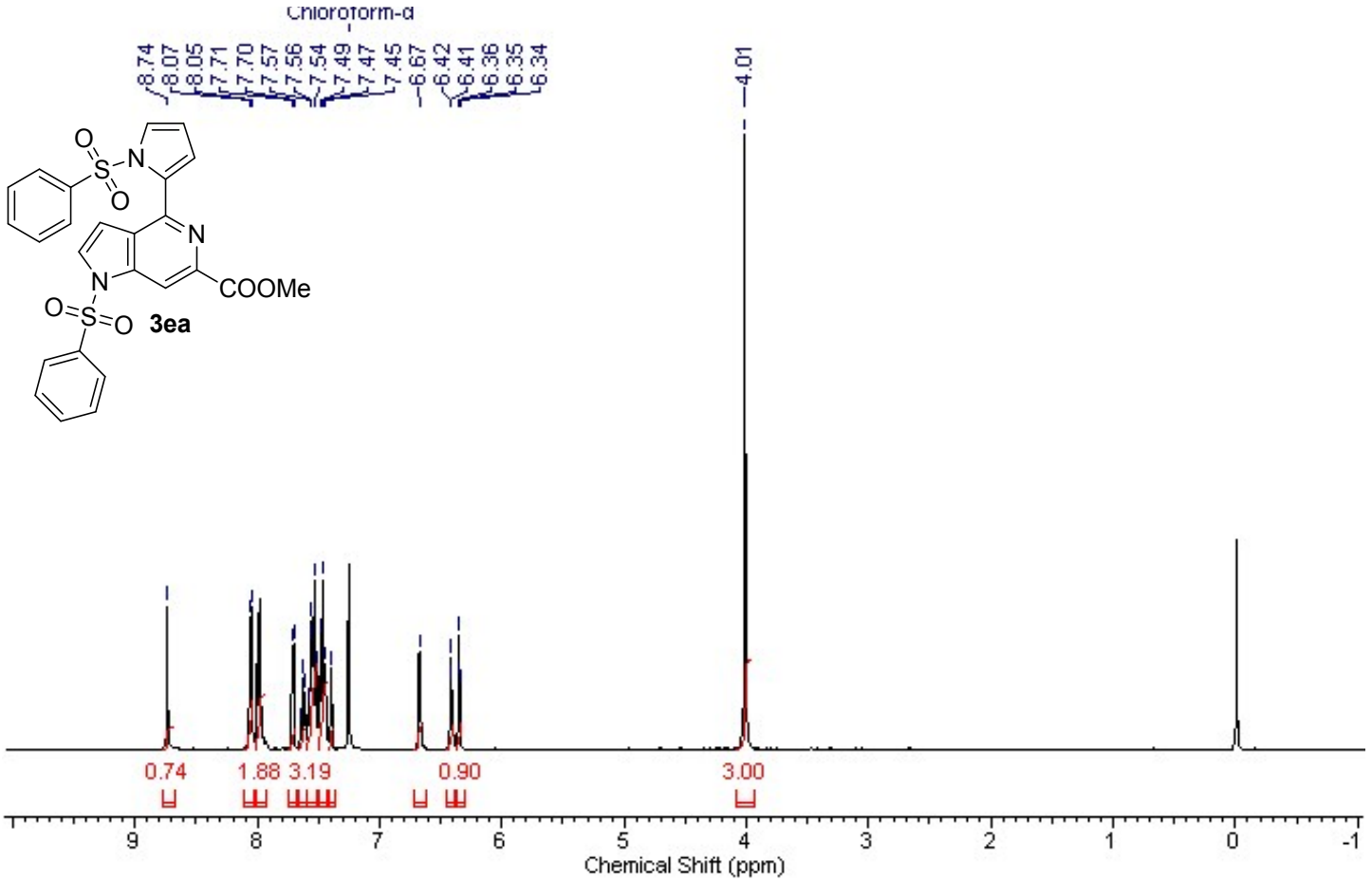
^{13}C NMR spectrum of *Methyl 1-tosyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3da**)



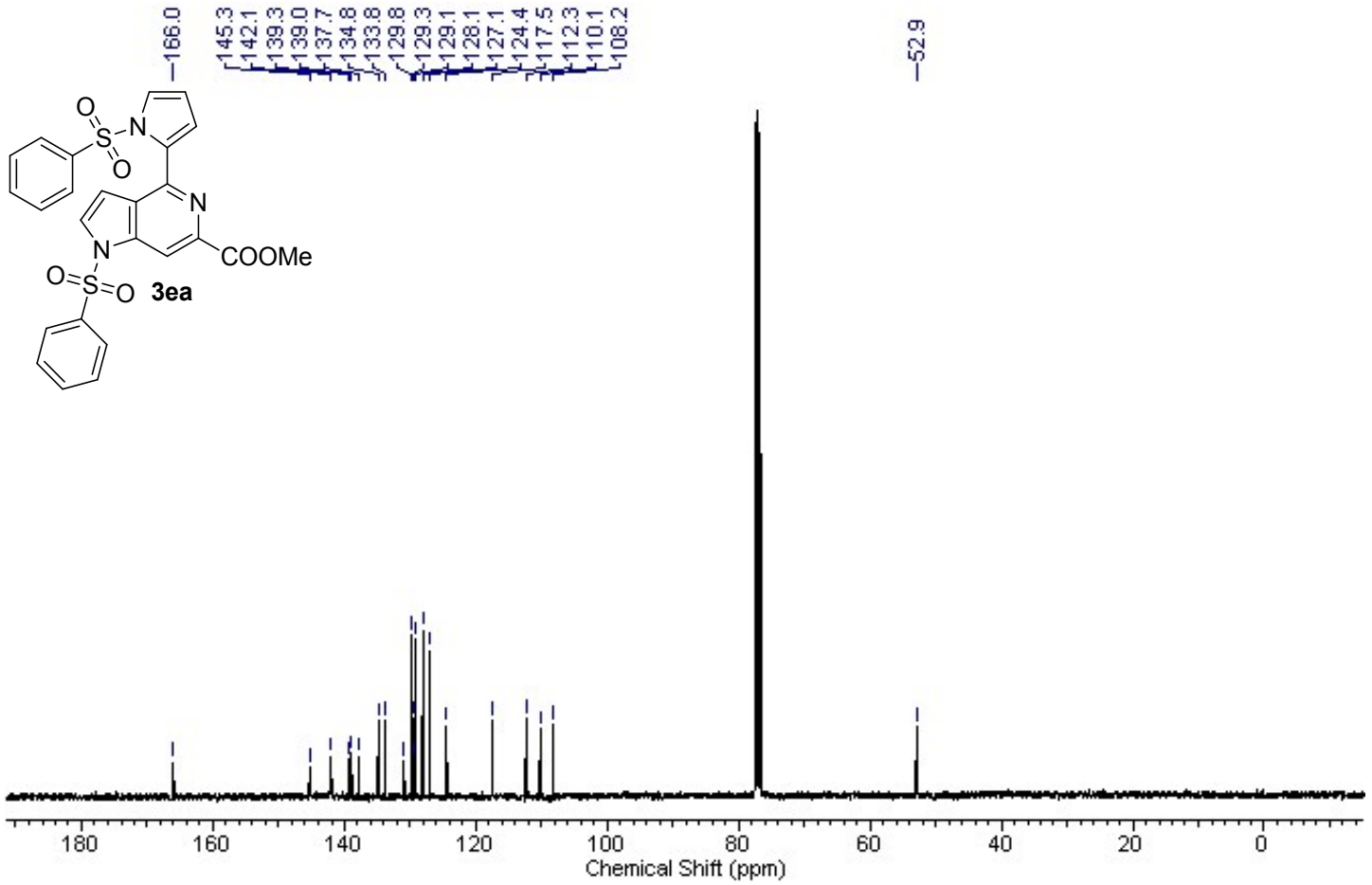
HRMS data of *Methyl 1-tosyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3da**)



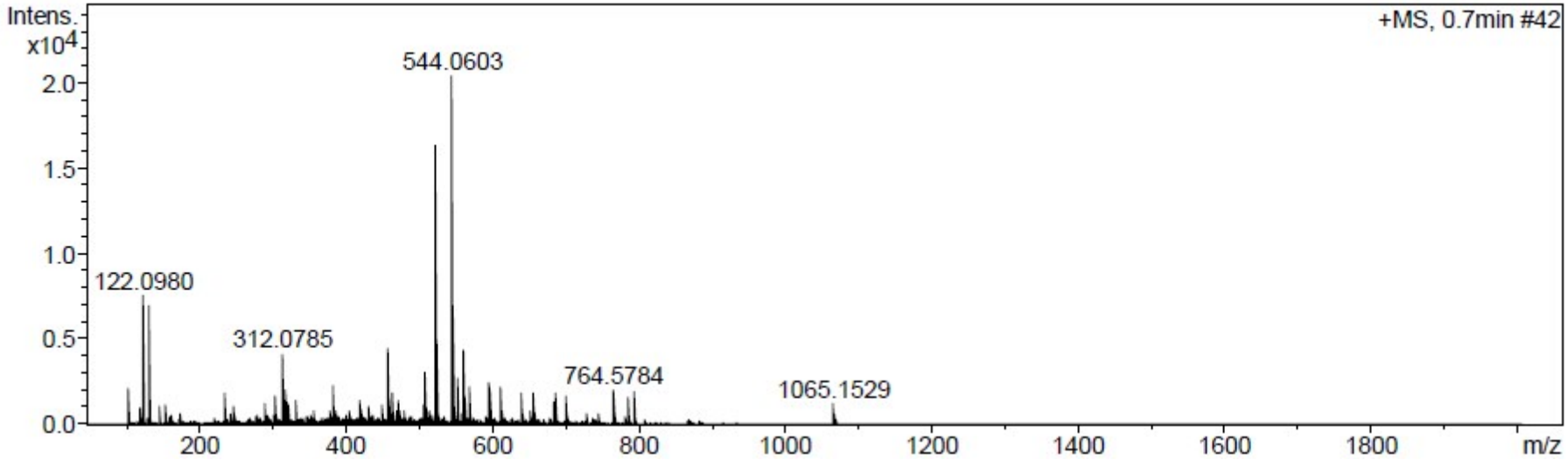
^{1}H NMR spectrum of *Methyl 1-(phenylsulfonyl)-4-(1-(phenylsulfonyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ea**)



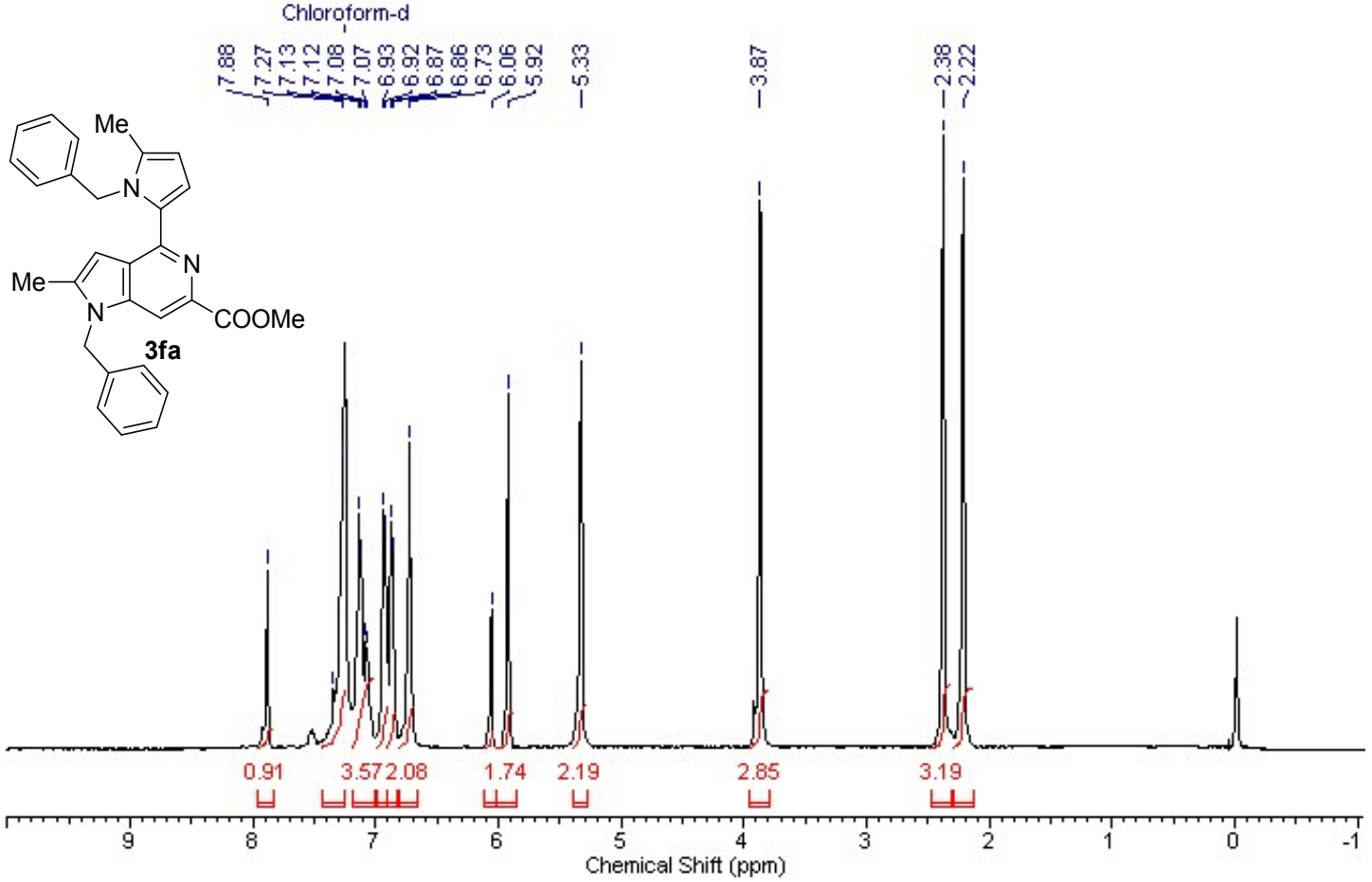
^{13}C NMR spectrum of *Methyl 1-(phenylsulfonyl)-4-(1-(phenylsulfonyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ea**)



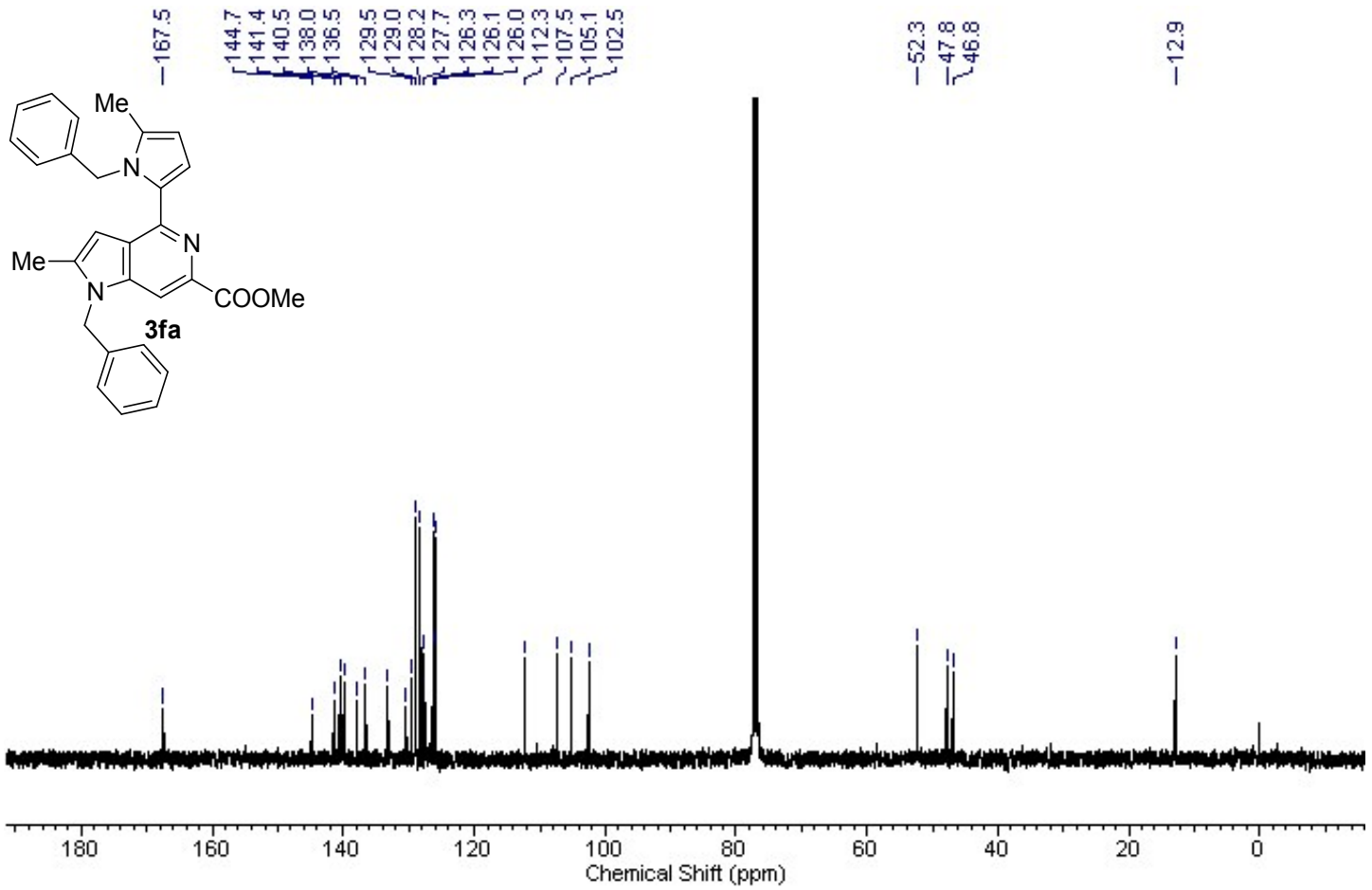
HRMS data of *Methyl 1-(phenylsulfonyl)-4-(1-(phenylsulfonyl)-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3ea**)



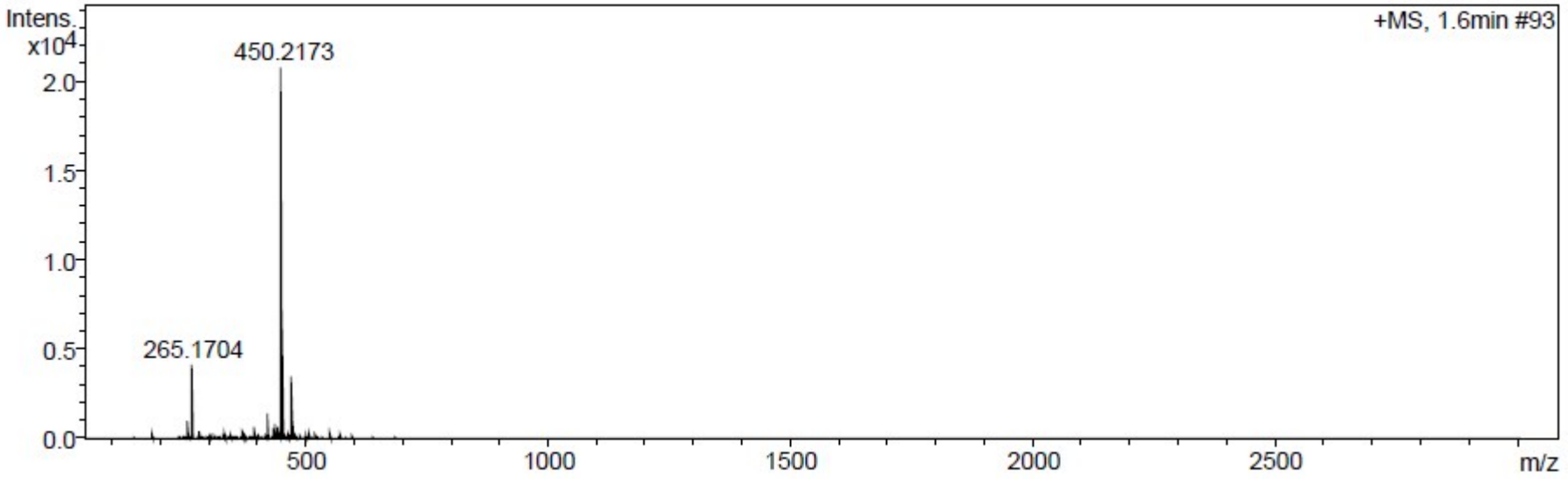
^{1}H NMR spectrum of*Methyl 1-benzyl-4-(1-benzyl-5-methyl-1H-pyrrol-2-yl)-2-methyl-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3fa**)



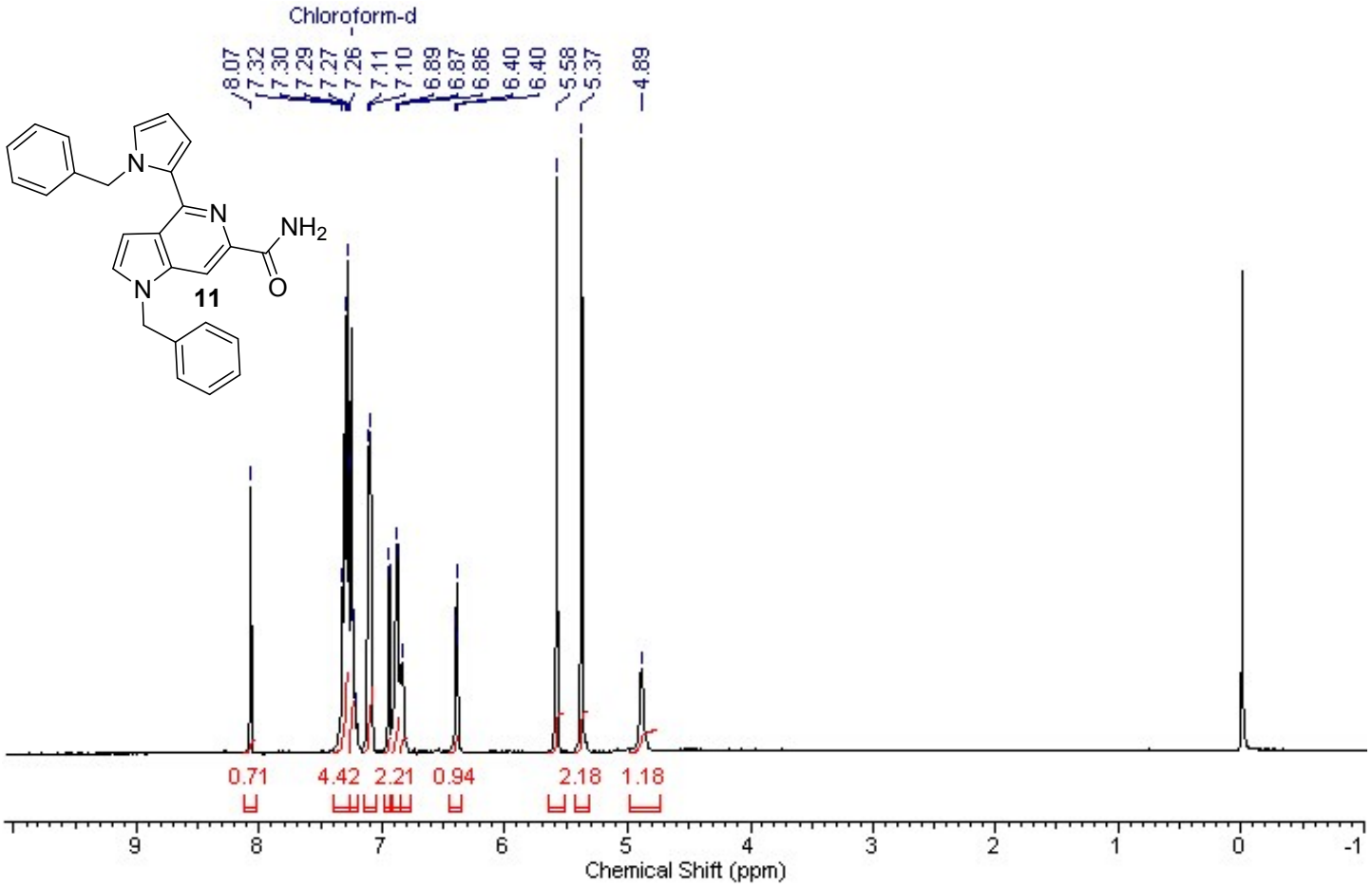
^{13}C NMR spectrum of *Methyl 1-benzyl-4-(1-benzyl-5-methyl-1H-pyrrol-2-yl)-2-methyl-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3fa**)



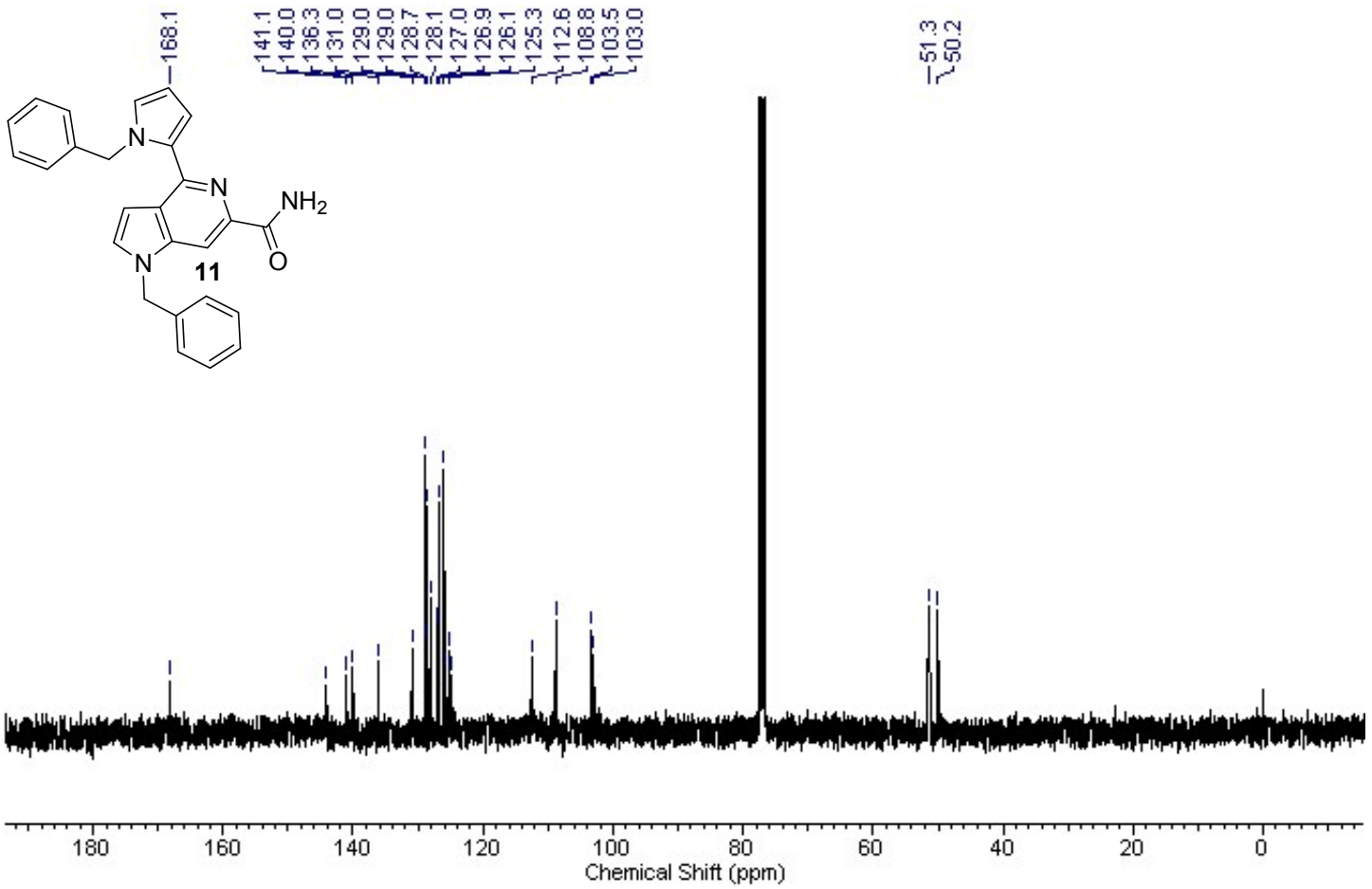
HRMS data of *Methyl 1-benzyl-4-(1-benzyl-5-methyl-1H-pyrrol-2-yl)-2-methyl-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**3fa**)



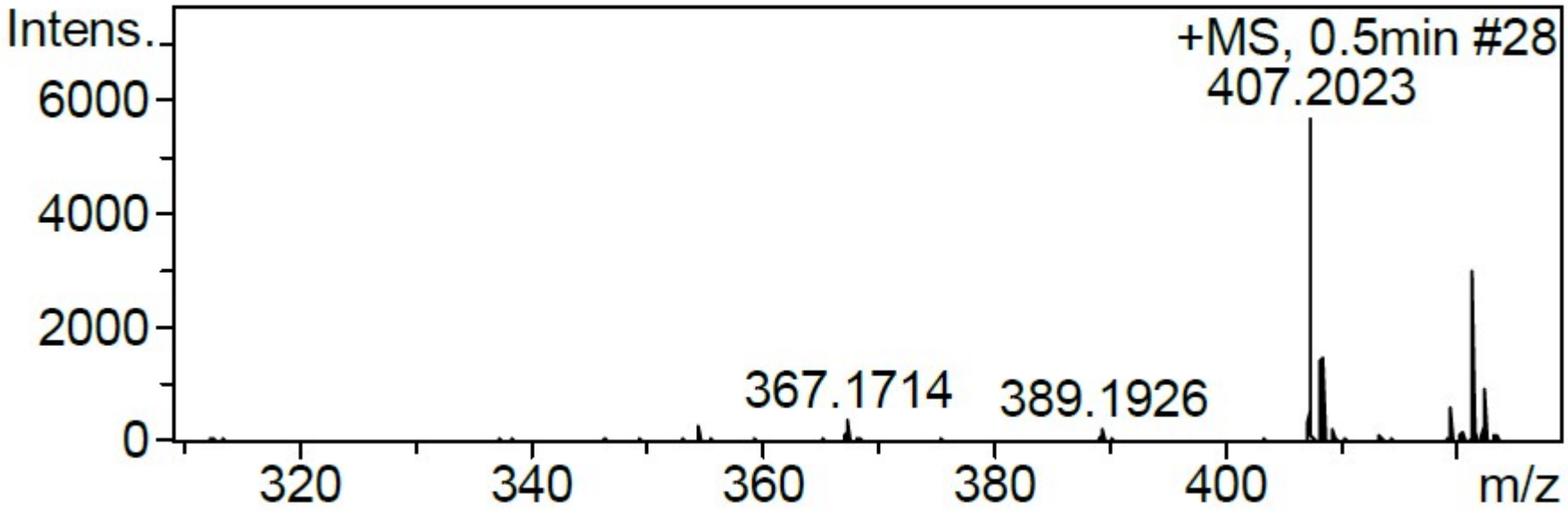
^{1}H NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxamide* (**11**)



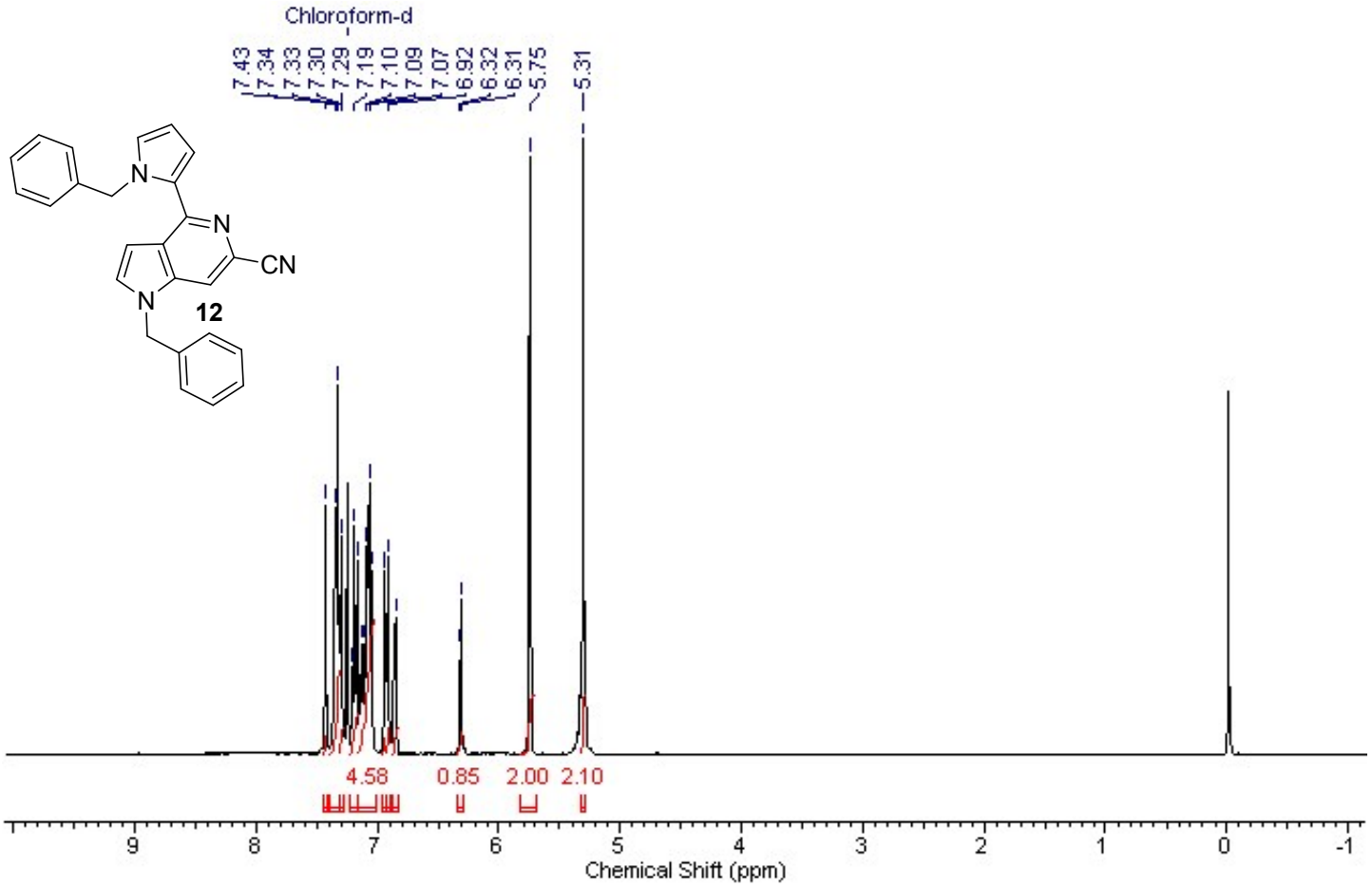
^{13}C NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxamide* (**11**)



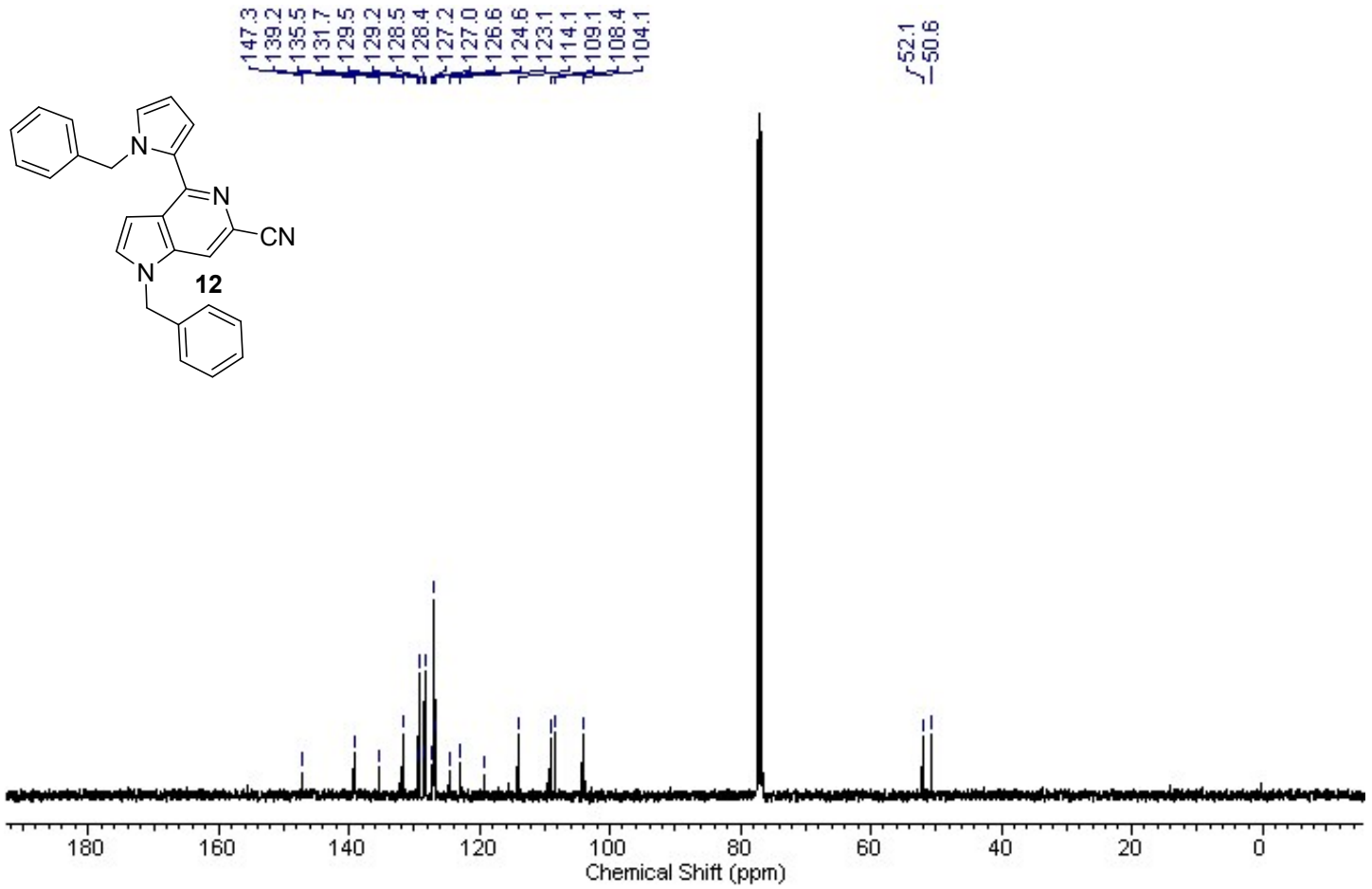
Mass data of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxamide* (**11**)



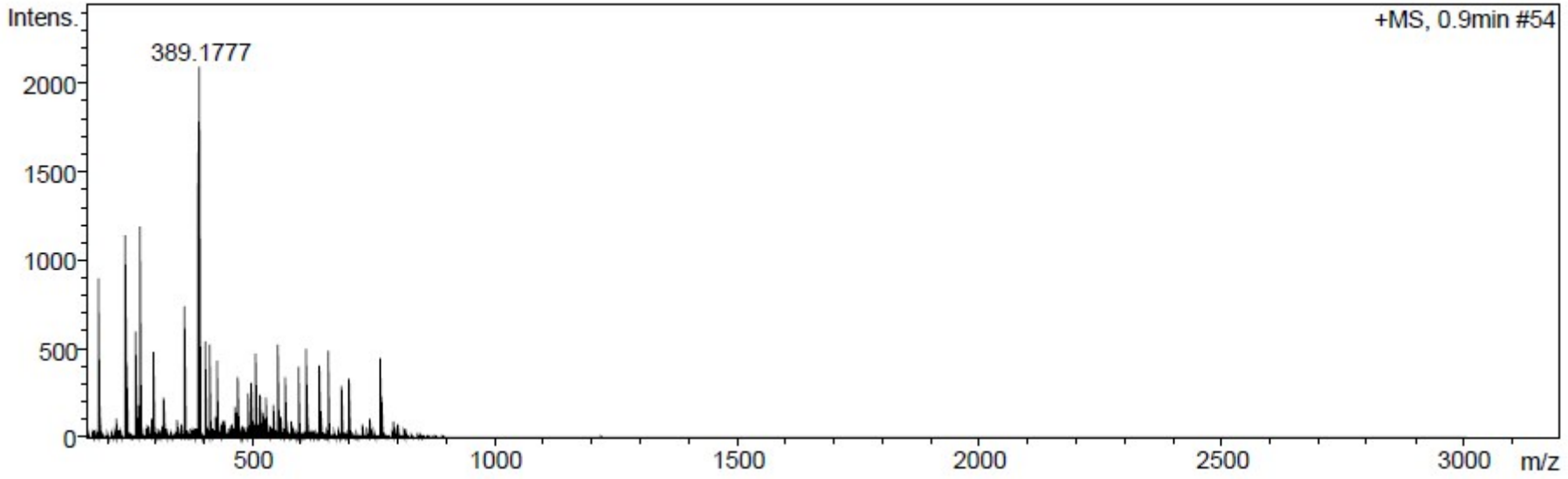
^{1}H NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbonitrile* (**12**)



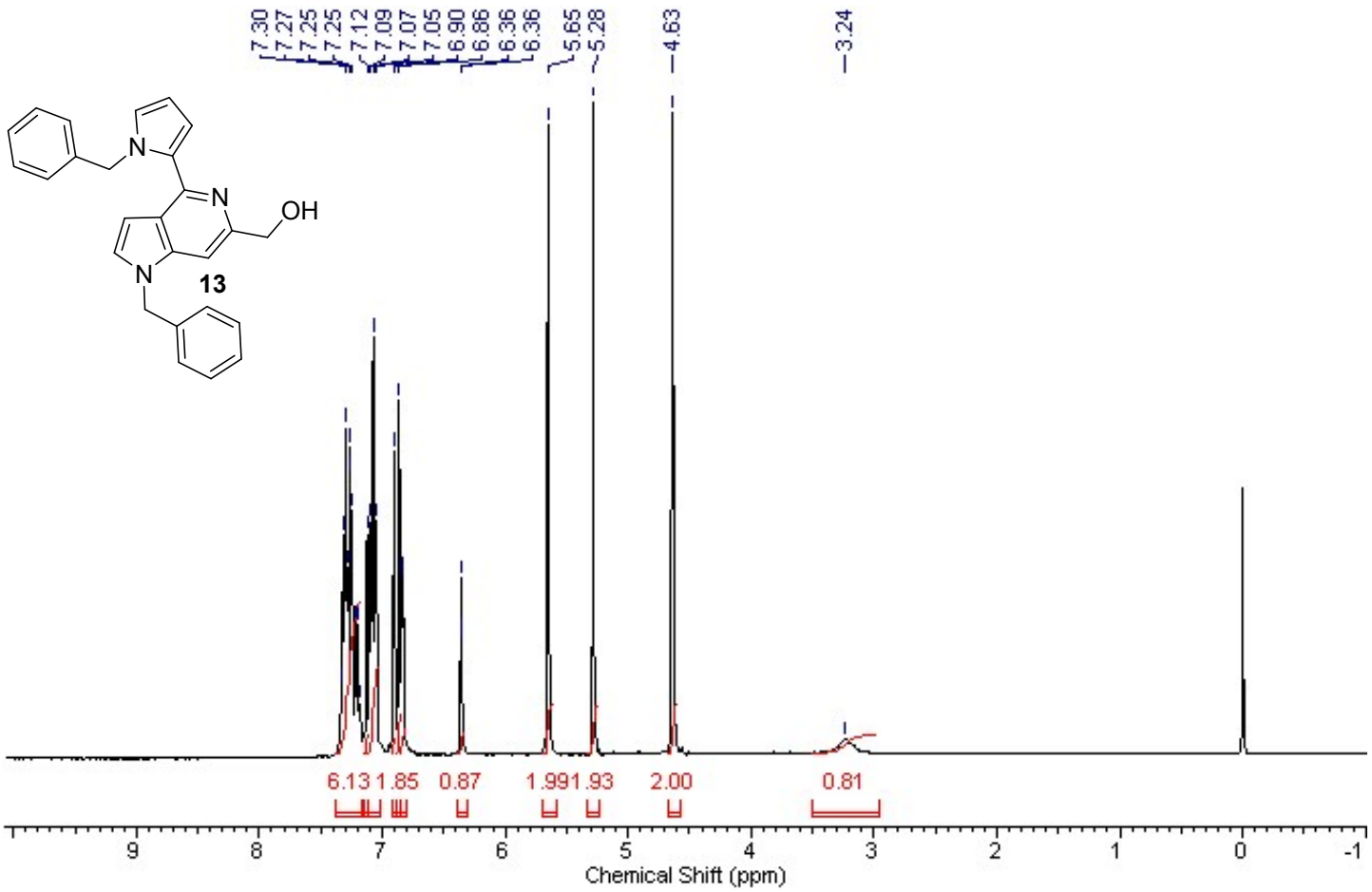
^{13}C NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbonitrile* (**12**)



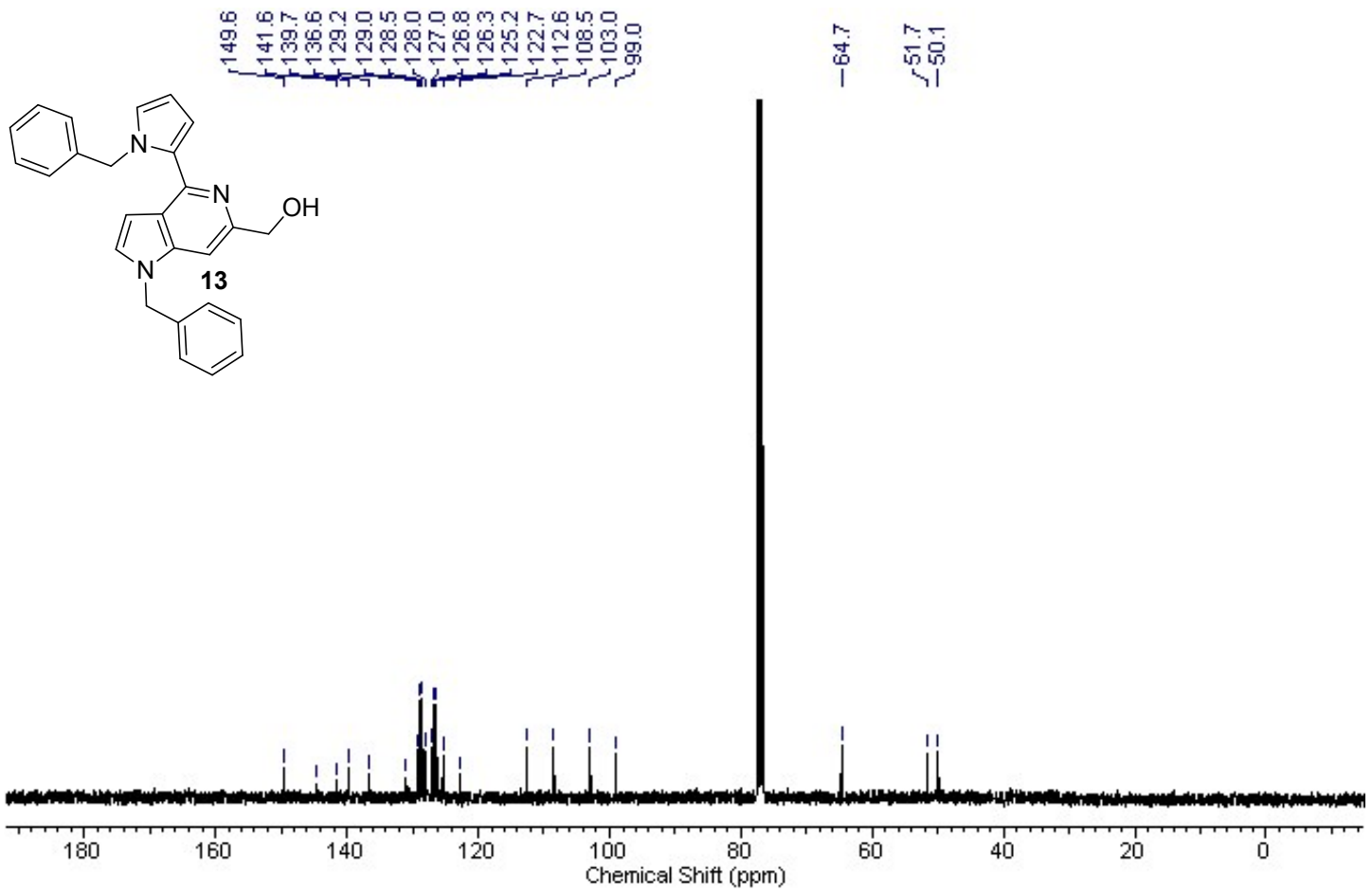
HRMS data of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbonitrile* (**12**)



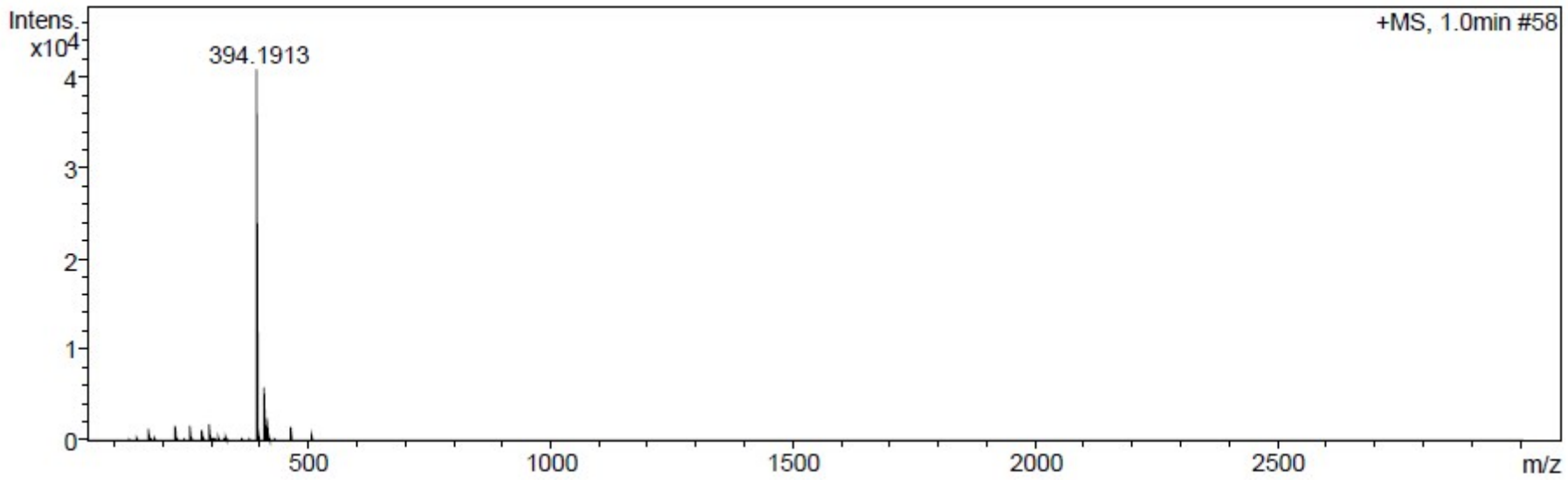
^{1}H NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)methanol* (**13**)



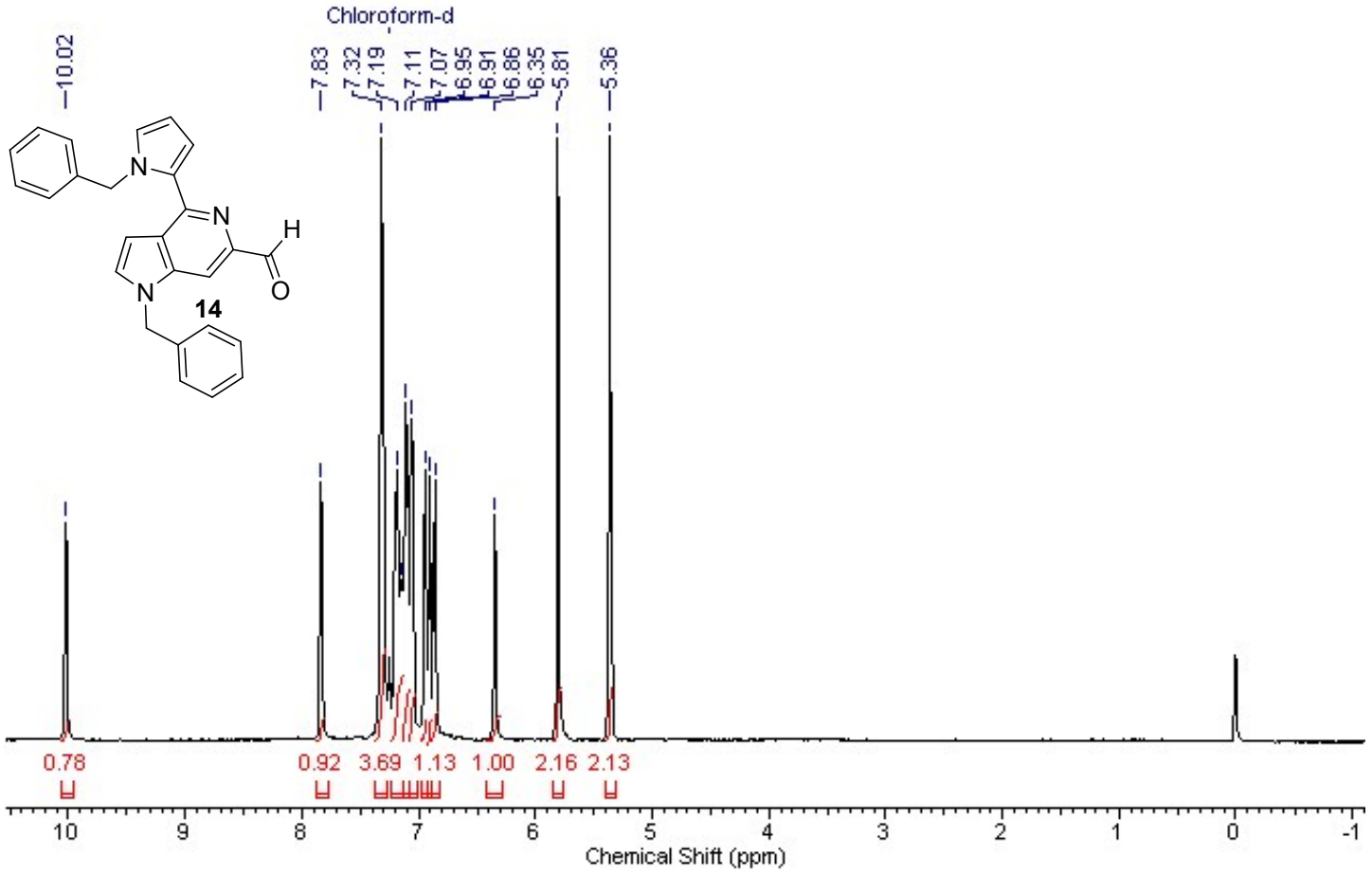
^{13}C NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)methanol* (**13**)



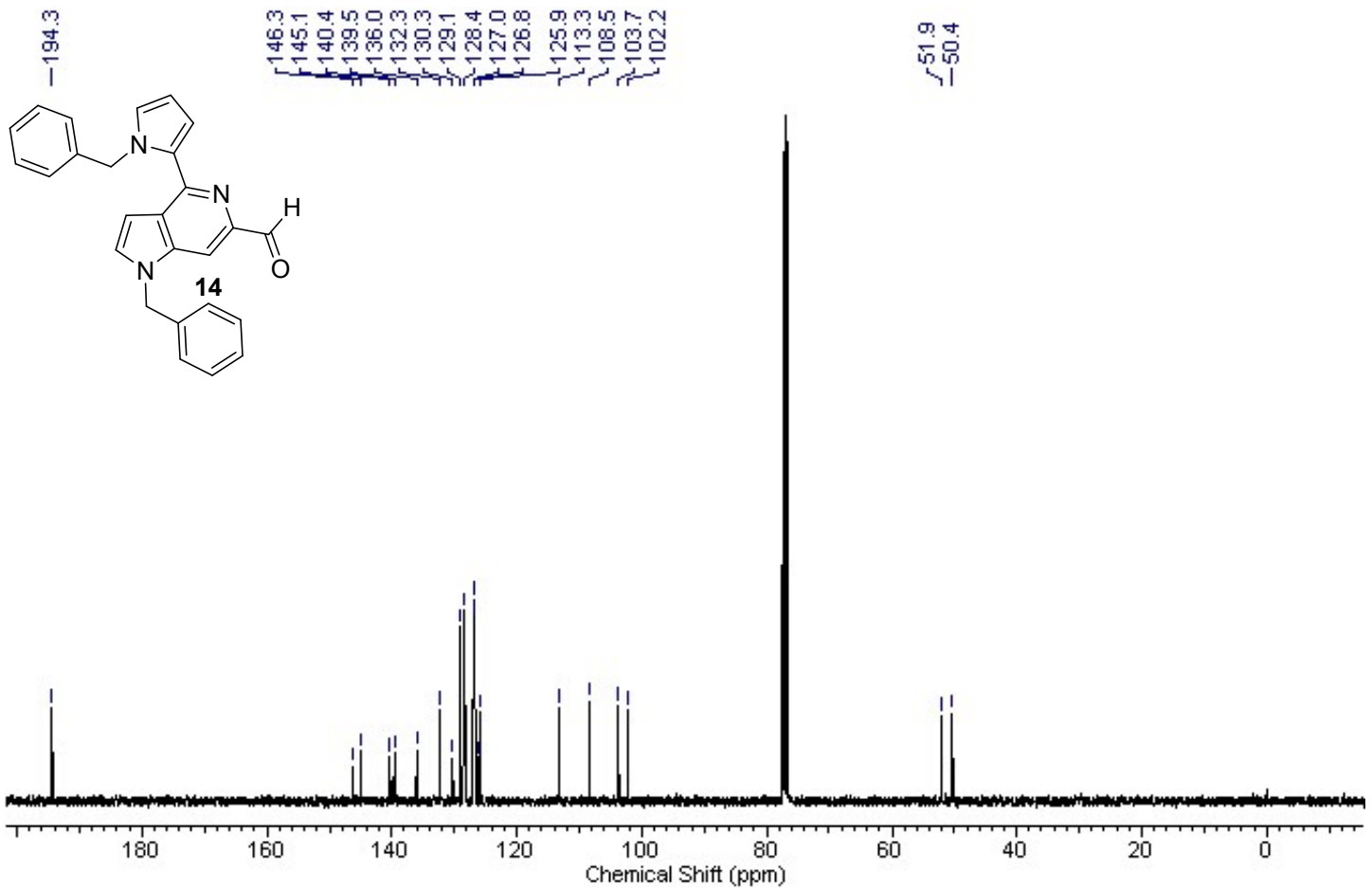
HRMS data of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)methanol* (**13**)



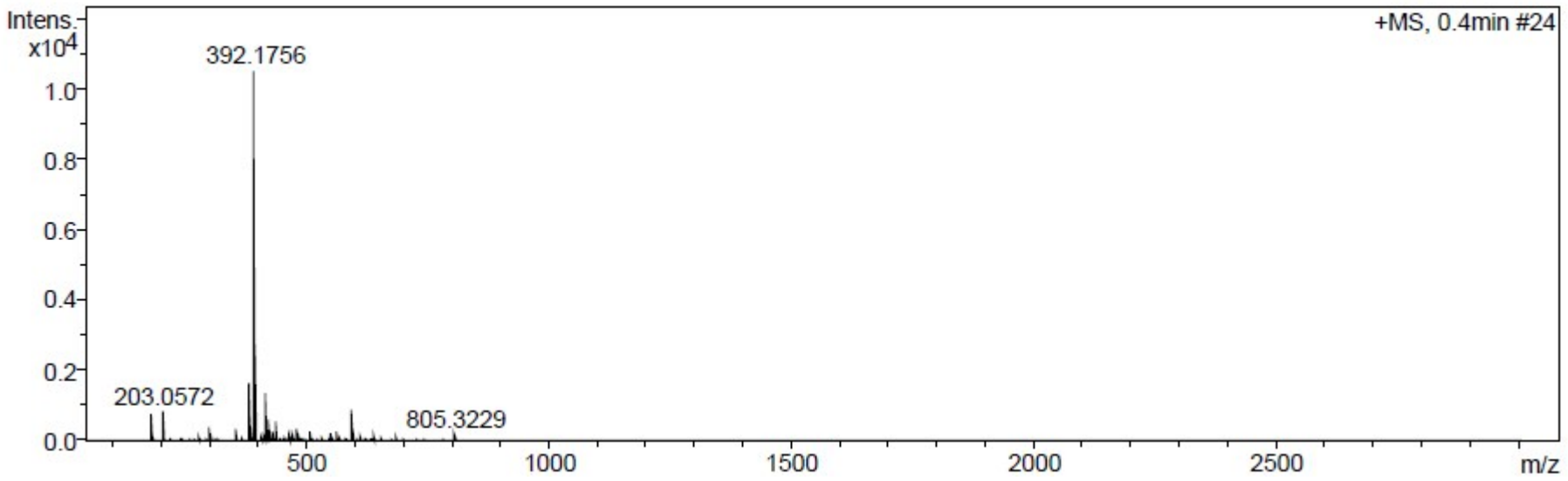
^{1}H NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbaldehyde* (**14**)



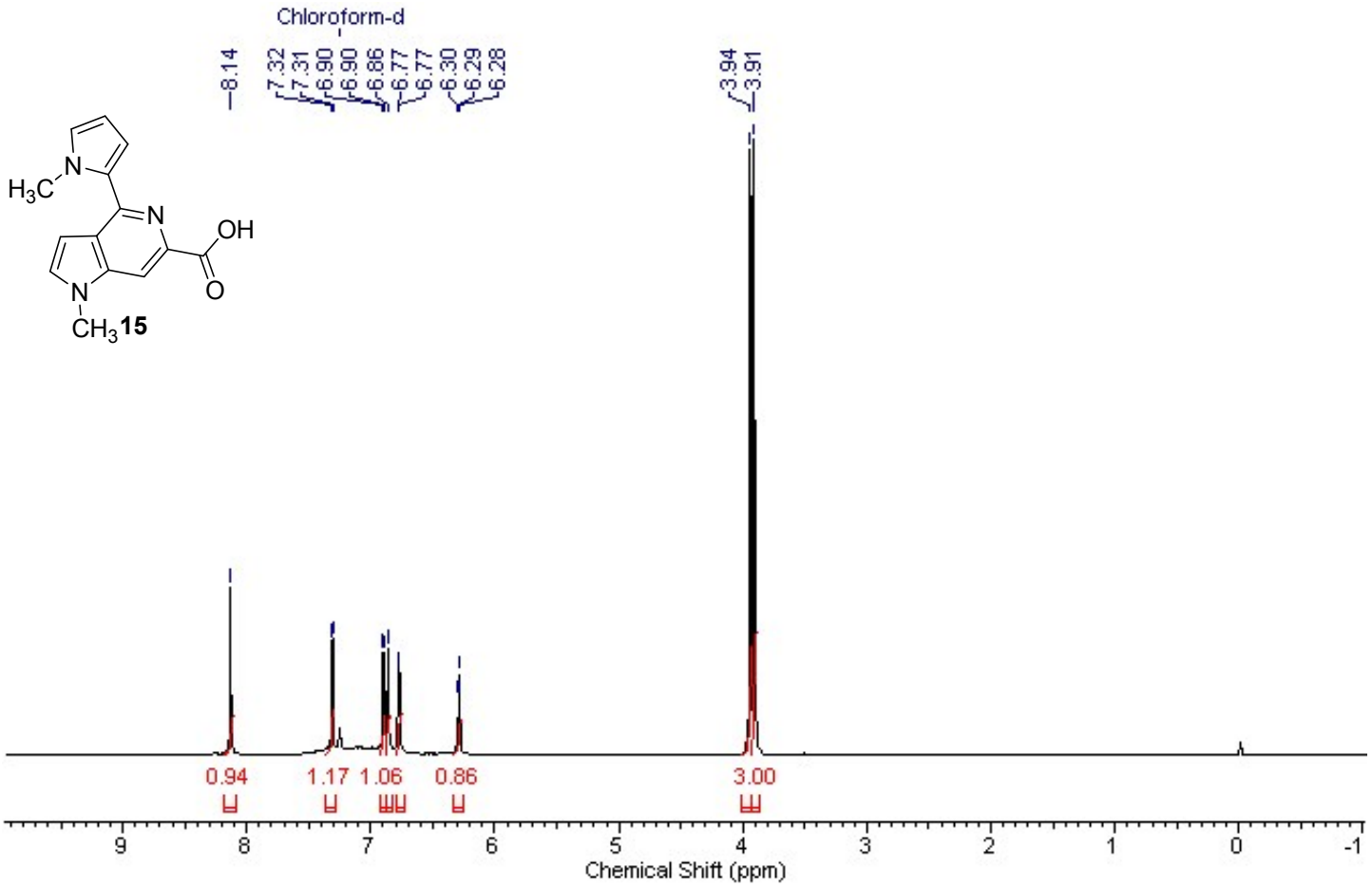
^{13}C NMR spectrum of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbaldehyde* (**14**)



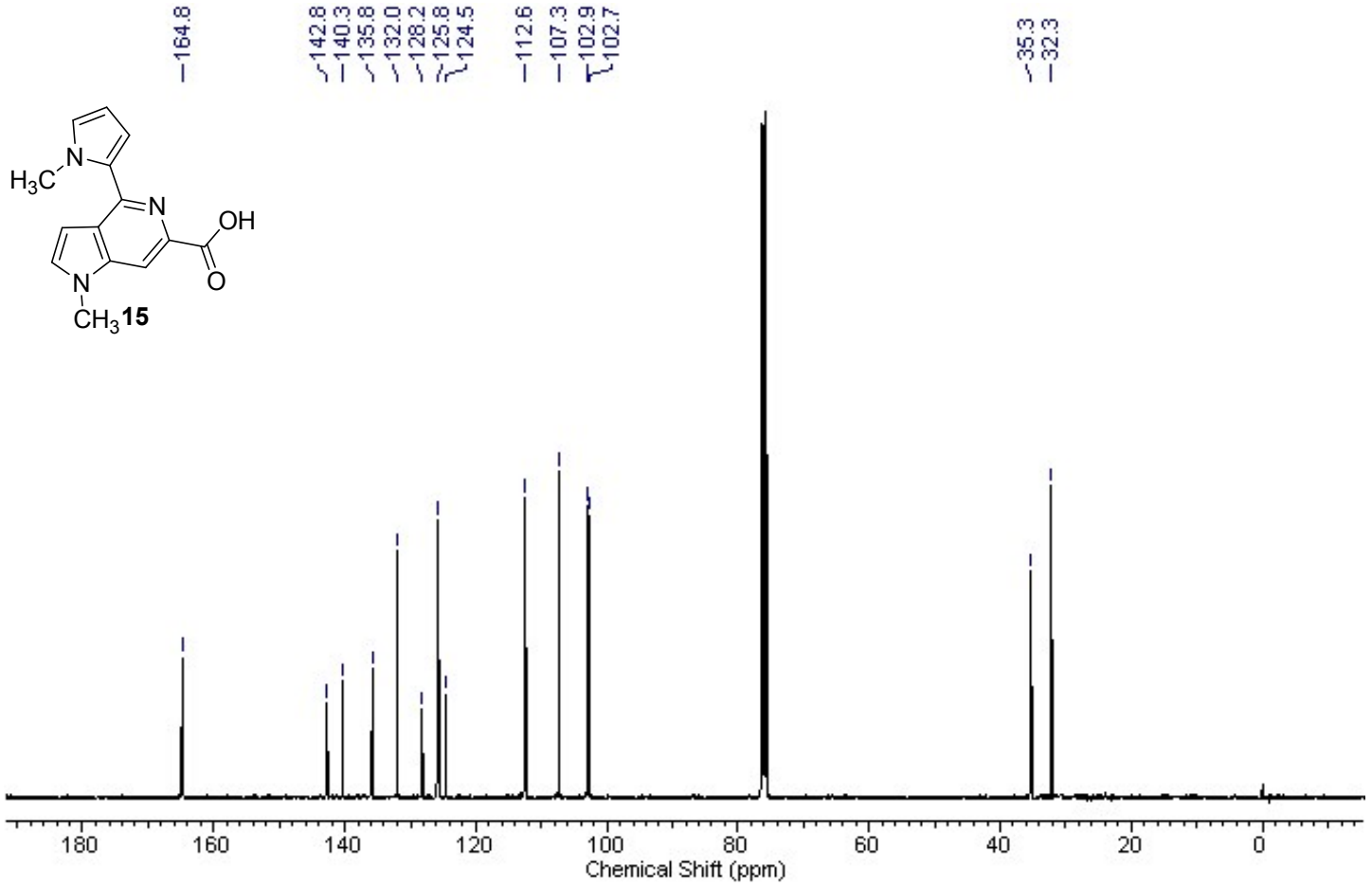
HRMS data of *1-Benzyl-4-(1-benzyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carbaldehyde* (**14**)



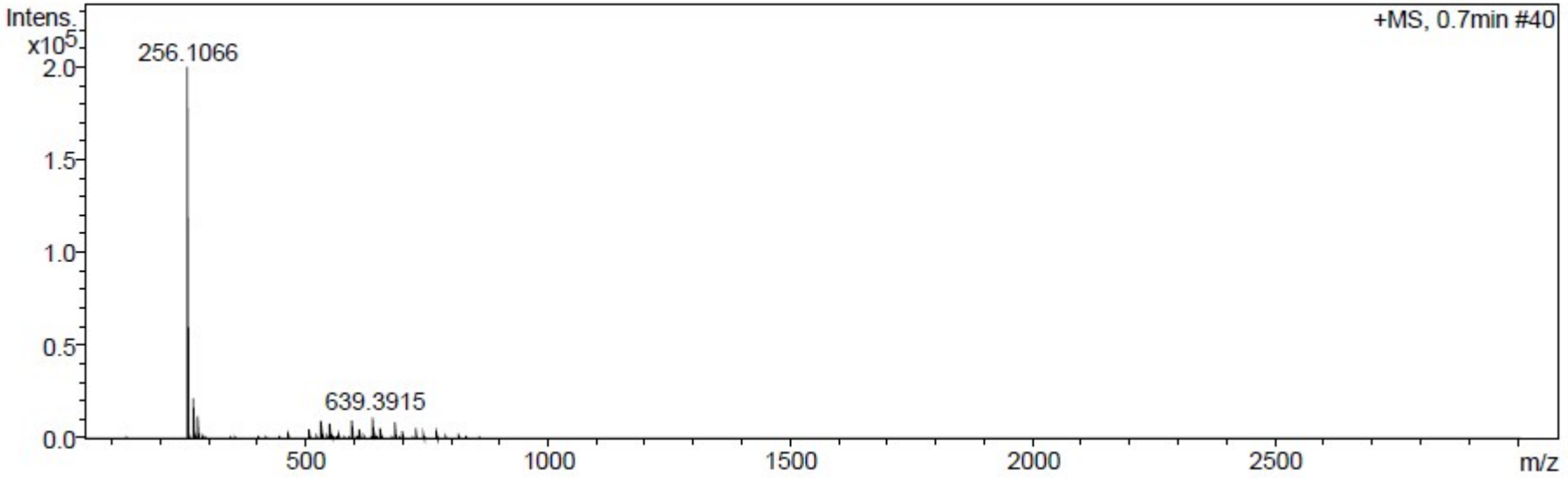
Crude ^{1}H NMR spectrum of *1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylic acid* (**15**)



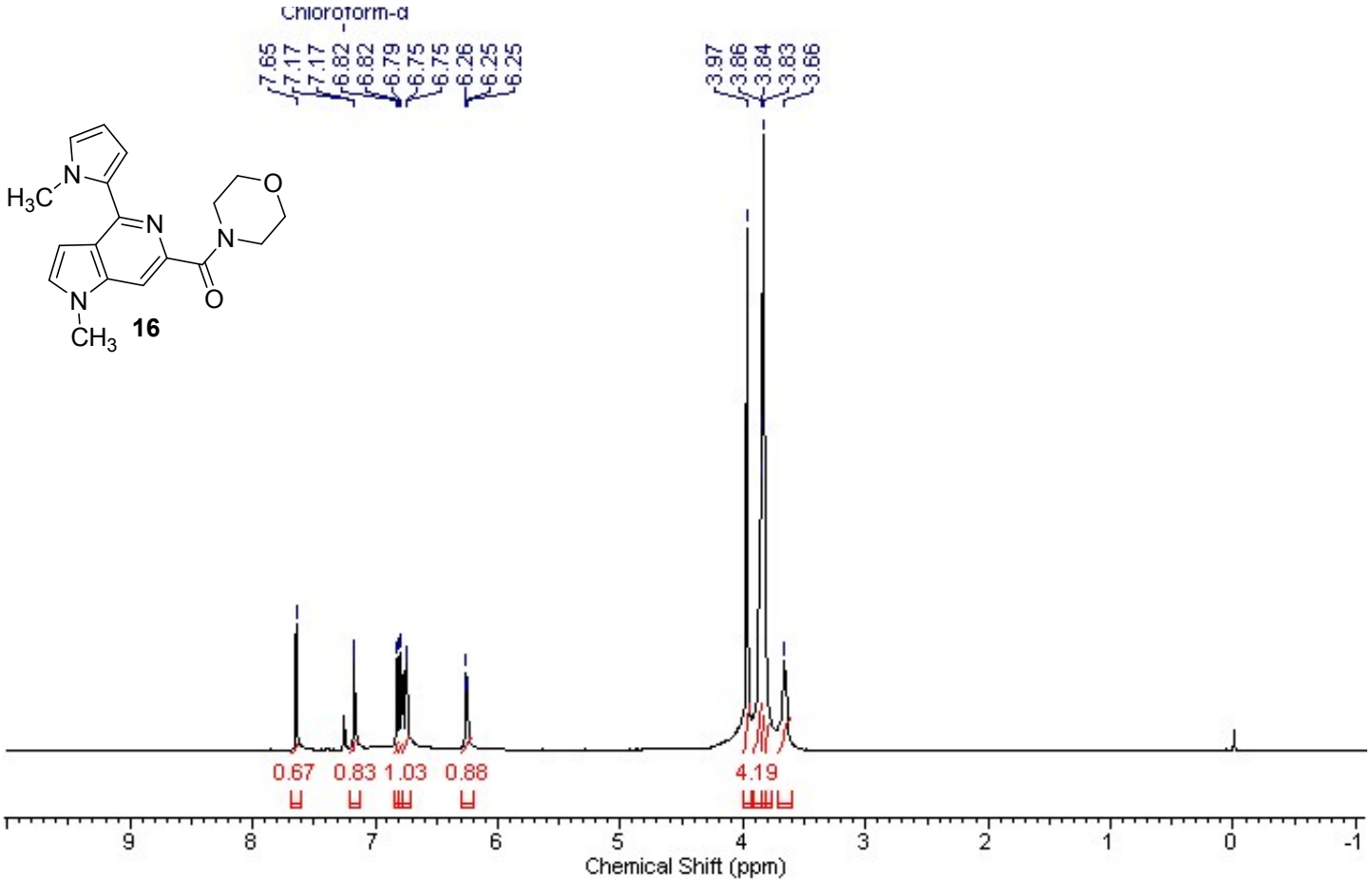
Crude ^{13}C NMR spectrum of *1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylic acid* (**15**)



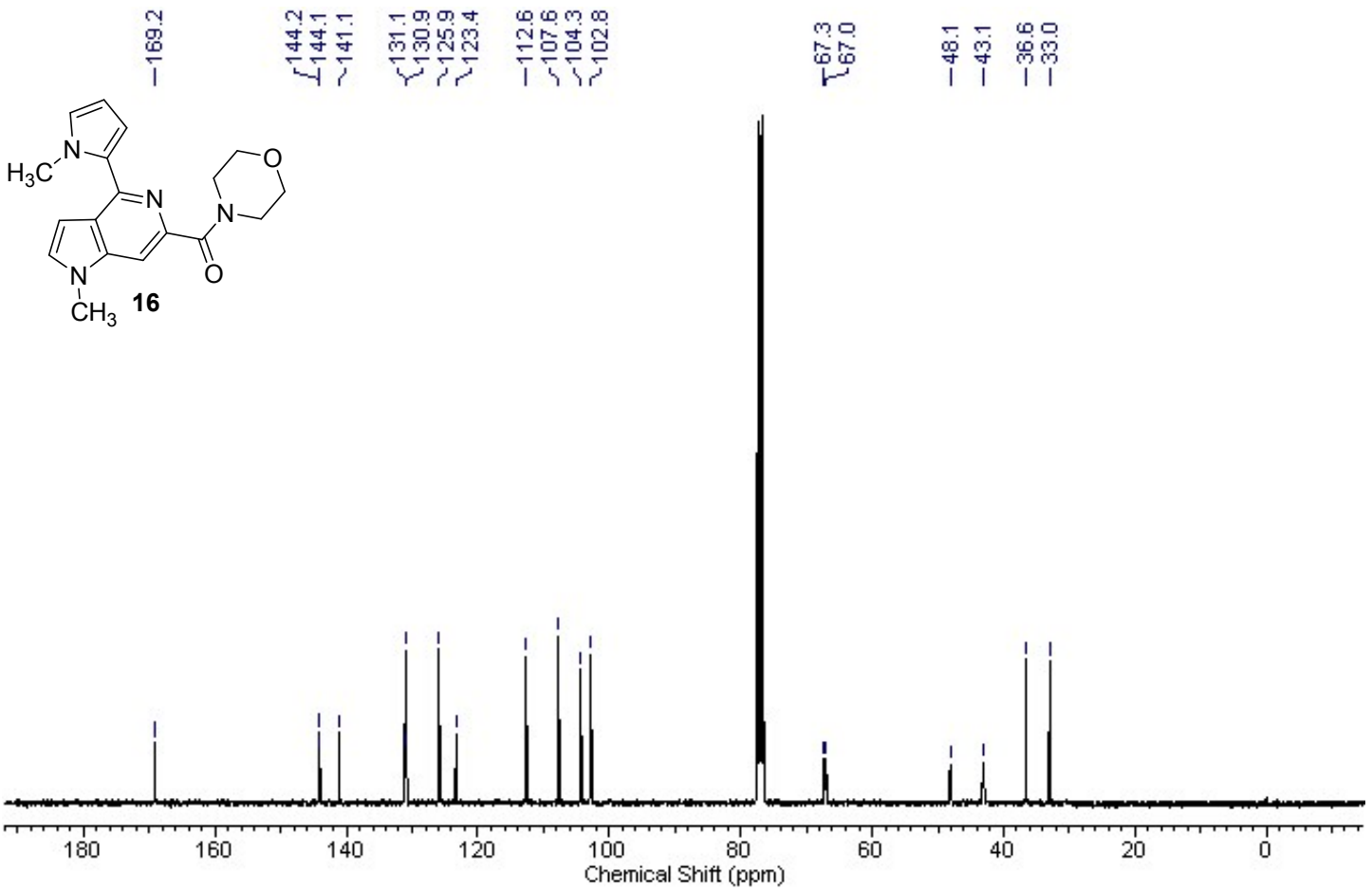
HRMS data of *1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylic acid* (**15**)



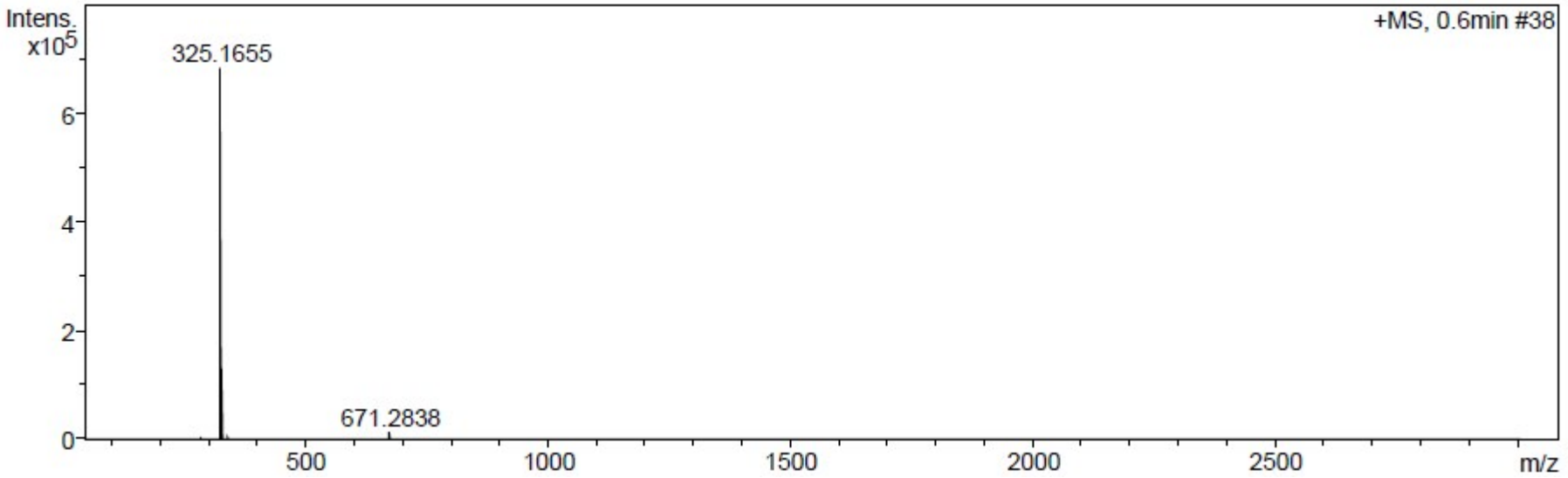
^{1}H NMR spectrum of 1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)(morpholino)methanone (**16**)



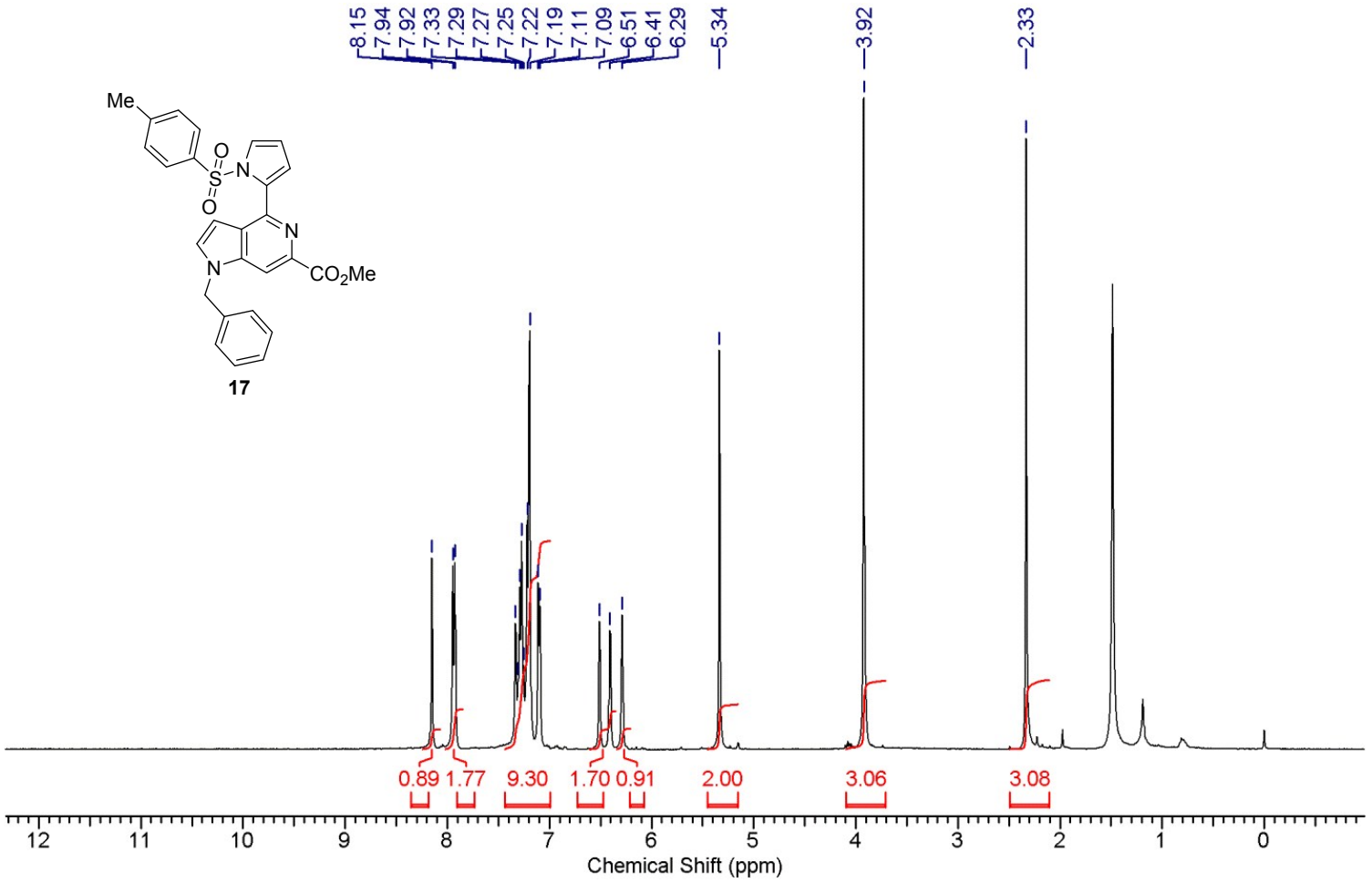
^{13}C NMR spectrum of *1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)(morpholino)methanone* (**16**)



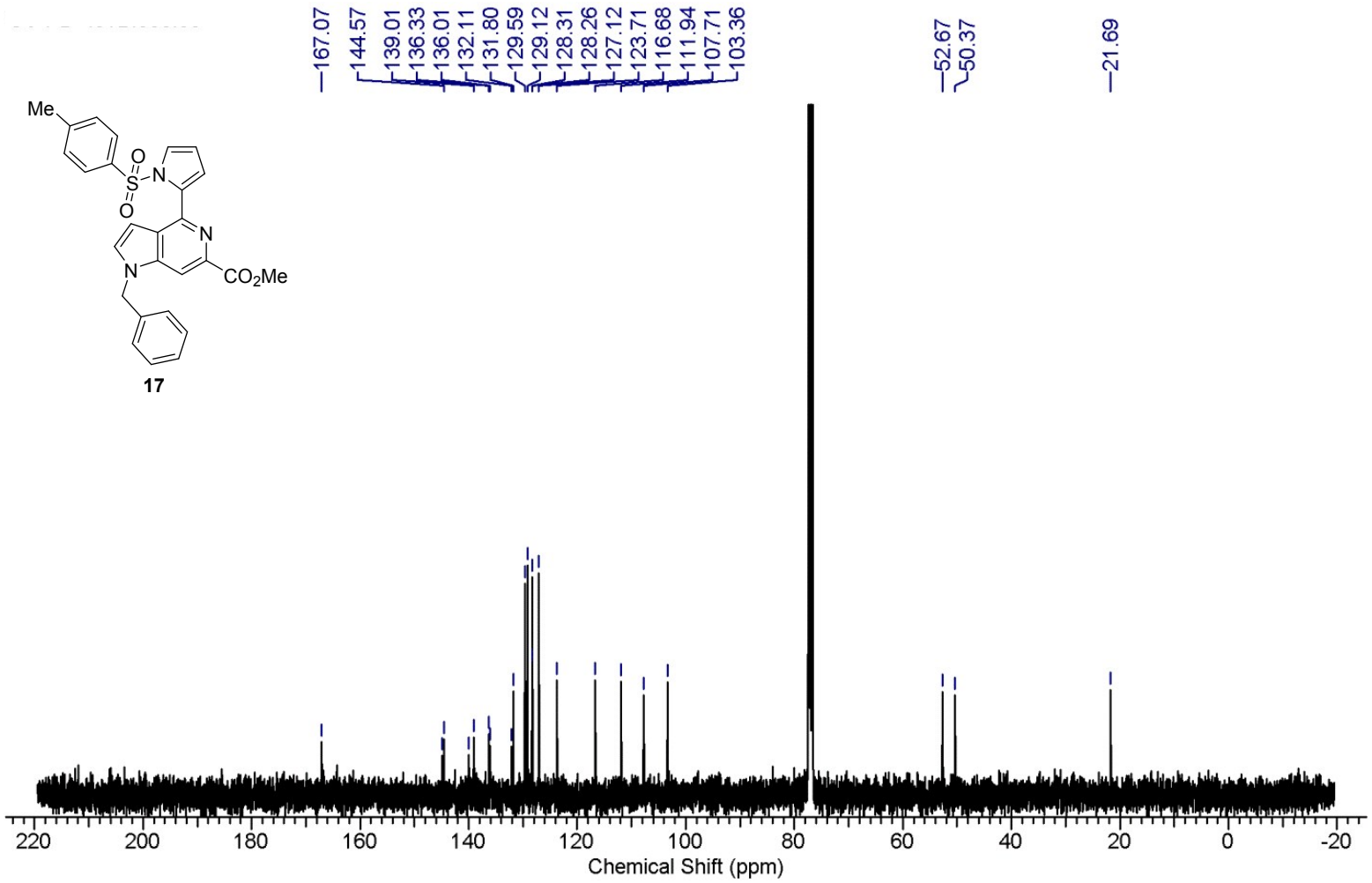
HRMS data of *1-Methyl-4-(1-methyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridin-6-yl)(morpholino)methanone* (**16**)



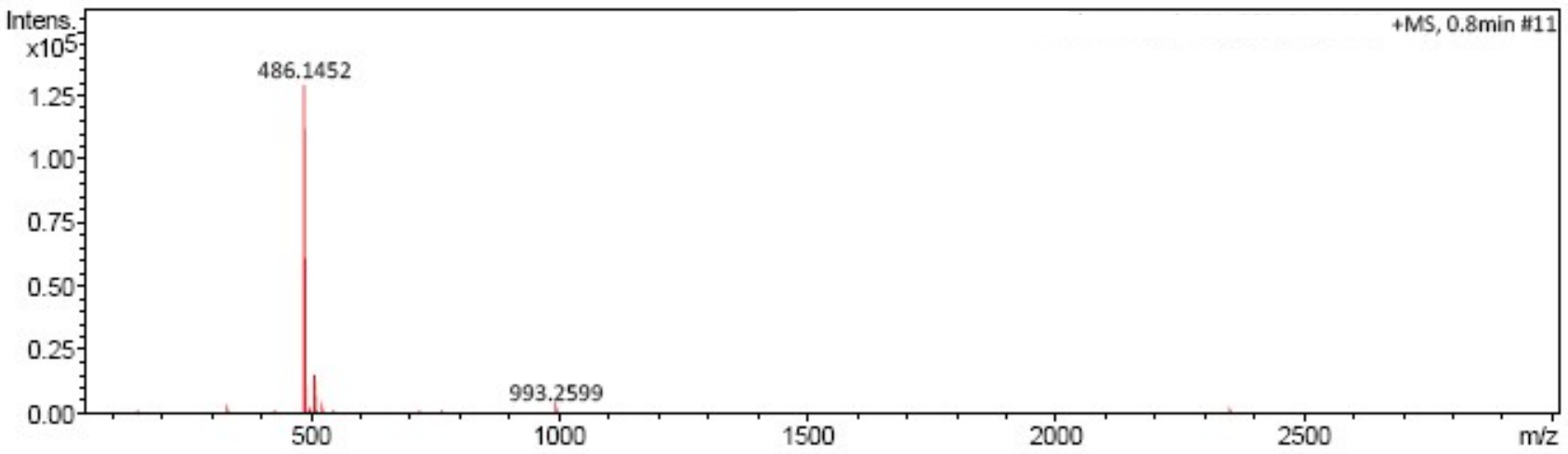
^{1}H NMR spectrum of *Methyl 1-benzyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**17**).



^{13}C NMR spectrum of *Methyl 1-benzyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**17**).



HRMS data of *Methyl 1-benzyl-4-(1-tosyl-1H-pyrrol-2-yl)-1H-pyrrolo[3,2-c]pyridine-6-carboxylate* (**17**).



References

1. Slight modification of method reported by- V. K. Outlaw, F. B. d'Andrea, C. A. Townsend, Org. Lett. 2015, 17, 1822–1825.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, ¨O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, 2009.
3. A. D. Becke, Phys. Rev. A, 1988, 38, 3098–3100.
4. Lee, W. Yang and R. G. Parr, Phys. Rev. B: Condens. Matter Phys., 1988, 37, 785–789.