Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

DDQ: the chlorinating reagent and oxidant for the ligand-directed ortho-chlorination of 2-arylpyridines

Qian Zhang, Fan Yang* and Yangjie Wu*

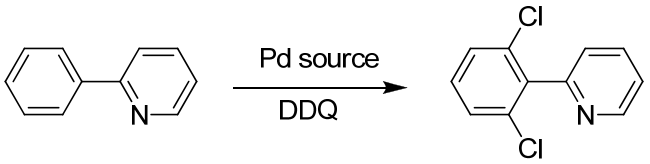
The College of Chemistry and Molecular Engineering, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, People's Republic of China

Tel/Fax: (+86)-371-6797-9408. E-mail: yangf@zzu.edu.cn; wyj@zzu.edu.cn

Contents

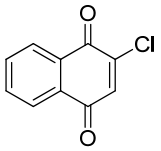
Optimization process data in detail

Table 1. Optimization of the Reaction Conditions[a]

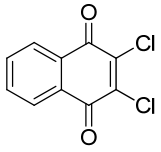


1a **2a**

Entry	Palladium Source (mol%)	T (^{o}C)	Solvent	Yield (%)[b]
1	$PdCl_2$ (5)	120	DMSO	10
2	$PdCl_2$ (5)	120	NMP	23
3	$PdCl_2$ (5)	reflux	H_2O	0
4	$PdCl_2$ (5)	120	HOAc	0
5	$PdCl_2$ (5)	reflux	toluene	56
6	$PdCl_2$ (5)	120	chlorobenzene	70
7	**$PdCl_2$ (5)**	**120**	**DMF**	**88**
8	$PdCl_2$ (5)	120	DMF/H_2O (1:1)	62
9[c]	$PdCl_2$ (5)	120	DMF	55
10	$PdCl_2$ (5)	100	DMF	56
11[d]	$PdCl_2$ (5)	120	DMF	89
12[e]	$PdCl_2$ (5)	120	DMF	77
13	$Pd(OAc)_2$ (5)	120	DMF	68
14	Pd_2dba_3 (2.5)	120	DMF	57
15[f]	$PdCl_2$ (5)	120	DMF	0
16[g]	$PdCl_2$ (5)	120	DMF	0



A1



A2

[a] Reaction conditions: **1a** (0.3 mmol), palladium catalyst, and DDQ (3 equiv) in 2 mL of solvent under a nitrogen atmosphere at 120 ^{o}C for 3 h. [b] Isolated yield. [c] DDQ (2 equiv). [d] For 5 h. [e] Under air. [f] 2-Chlorobenzoquinone (**A1**) (3 equiv)was used as the chlorinating reagent. [g] 2,3-Dichloro-1,4-naphthoquinone (**A2**) (3 equiv) was used as the chlorinating reagent.

Experimental Section

General details

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured by using a WC-1 microscopic apparatus. GC analysis was performed on Agilent 4890D gas chromatograph. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High resolution mass spectra were measured on a UHPLC Q-TOF HR-MS. The single crystal X-ray diffraction study was measured on a Xcalibur, Eos, Gemini diffractometer. Dichloromethane, ethyl acetate and hexane were used for column chromatography without further purification, and other solvents were purified according to the standard methods. The chemicals were obtained from commercial sources and used as-received unless otherwise noted.

General procedure for the palladium-catalyzed chlorination of 2-arylpyridines

General procedure for the synthesis of **2j**: to a solution of 2-(4-methoxyphenyl)-5-methylpyridine (0.3 mmol) in DMF (2 mL), DDQ (0.9 mmol) and $PdCl_2$ (5 mol%) were added. The resulting mixture was heated at 120 ^{o}C for 3 h. After the reaction was complete, the mixture was added into

H_2O (25 mL) and extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent *in vacuo*, the residue was purified by column chromatography (petroleum/ethyl acetate=10:1) to afford the pure product. The yield of the isolated product was 99%.

2-(2,6-Dichlorophenyl)pyridine (**2a**)[1]

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.30 (m, 1H), 7.32–7.35 (m, 2H), 7.39–7.42 (m, 2H), 7.81 (td, J = 7.70 Hz, 1.80 Hz, 1H), 8.74–8.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.9, 125.0, 128.1, 129.8, 134.6, 136.4, 138.4, 149.6, 155.5; HRMS-ESI (m/z) calcd for $C_{11}H_8Cl_2N$ ($M+H^+$): 224.0034, found: 224.0034.

2-[(2-Benzyloxy-6-chloro)phenyl]pyridine (**2b**)

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02 (s, 2H), 6.92 (d, J = 8.32 Hz, 1H), 7.09–7.17 (m, 3H), 7.21–7.29 (m, 5H), 7.35 (d, J = 7.76 Hz, 1H), 7.74 (td, J = 7.68 Hz, 1.40 Hz, 1H), 8.75 (d, J = 4.48 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.6, 110.6, 121.3, 121.4, 124.7, 125.6, 126.7, 127.4, 128.8, 129.0, 133.1, 135.0, 135.7, 148.4, 153.9, 156.3; HRMS-ESI (m/z) calcd for $C_{18}H_{15}ClNO$ ($M+H^+$): 296.0842, found: 296.0841.

2-[(2-Butoxy-6-chloro)phenyl]pyridine (**2c**)

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78 (t, J = 7.40 Hz, 3H), 1.15–1.25 (m, 2H), 1.48–1.55 (m, 2H), 3.87 (t, J = 6.36 Hz, 2H), 6.84 (d, J = 8.32 Hz, 1H), 7.04 (d, J = 8.00 Hz, 1H), 7.19–7.30 (m, 3H), 7.70 (td, J = 7.72 Hz, 1.48 Hz, 1H), 8.69 (d, J = 4.44 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6, 17.9, 29.9, 67.6, 109.8, 120.6, 121.1, 124.6, 128.6, 128.7, 132.9, 134.8, 148.2, 154.0, 156.8; HRMS-ESI (m/z): calcd for $C_{15}H_{17}ClNO$ ($M+H^+$) 262.0999, found: 262.0998.

2-[(2-Chloro-5-methoxy)phenyl]pyridine (**2d**)

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 6.87 (dd, J = 8.72 Hz, 2.88 Hz, 1H), 7.12 (d, J = 2.92 Hz, 1H), 7.24–7.27 (m, 1H), 7.34 (d, J = 8.80 Hz, 1H), 7.63 (d, J = 7.80 Hz, 1H), 7.73 (t, J = 7.60 Hz, 1H), 8.69 (d, J = 4.48 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.5, 115.0, 115.1, 121.4, 122.3, 123.8, 129.8, 134.8, 138.8, 148.4, 155.7, 157.3; HRMS-ESI (m/z) calcd for $C_{12}H_{11}ClN$ ($M+H^+$): 220.0529, found: 220.0523.

2-[(2-Chloro-5-methoxy)phenyl]-5-methylpyridine (**2e**)

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 3.82 (s, 3H), 6.87 (dd, J = 8.72 Hz, 2.76 Hz, 1H), 7.13 (d, J = 2.76 Hz, 1H), 7.34 (d, J = 8.80 Hz, 1H), 7.56 (s, 2H), 8.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 54.6, 114.8, 115.0, 122.5, 123.3, 129.8, 131.1, 135.4, 138.8, 148.9, 153.0, 157.4; HRMS-ESI (m/z): calcd for $C_{13}H_{13}ClN$ ($M+H^+$): 234.0686, found: 234.0681.

2-[(2-Chloro-5-methyl)phenyl]pyridine (**2f**)

Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 7.11 (dd, J = 8.12 Hz, 1.56 Hz, 1H), 7.22–7.26 (m, 1H), 7.32 (d, J = 8.12 Hz, 1H), 7.40 (d, J = 1.24 Hz, 1H), 7.62 (d, J = 7.84 Hz, 1H), 7.71 (td, J = 7.76 Hz, 1.56 Hz, 1H), 8.69 (d, J = 4.56 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 121.3, 123.9, 128.0, 128.8, 129.3, 131.1, 134.7, 135.9, 137.7, 148.5, 155.9; HRMS-ESI (m/z) calcd for $C_{12}H_{11}ClN$ ($M+H^+$): 204.0580, found: 204.0575.

2-[(2-Chloro-5-methyl)phenyl]-5-methylpyridine (**2g**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.36 (s, 3H), 7.09 (d, J = 7.40 Hz, 1H), 7.31 (d, J = 8.16 Hz, 1H), 7.39 (s, 1H), 7.53 (s, 2H), 8.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.2, 19.8, 123.3, 128.0, 128.8, 129.1, 130.8, 131.0, 135.3, 135.8, 137.7, 148.9, 153.1; HRMS-ESI (m/z) calcd for $C_{13}H_{13}ClN$ ($M+H^+$): 218.0737, found: 218.0741.

2-[(2-Chloro-5-isobutoxy)phenyl]pyridine (**2h**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, J = 6.72 Hz, 6H), 2.00–2.13 (m, 1H), 3.74 (d, J = 6.44 Hz, 2H), 6.88 (dd, J = 8.76 Hz, 2.88 Hz, 1H), 7.14 (d, J = 2.84 Hz, 1H), 7.26 (t, J = 7.28 Hz, 1H), 7.32–7.36 (m, 1H), 7.63–7.66 (m, 1H), 7.71–7.76 (m, 1H), 8.67–8.71 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 18.3, 27.3, 73.8, 115.4, 115.9, 121.4, 123.9, 129.8, 134.8, 135.7, 138.8, 148.5, 155.9, 157.1; HRMS-ESI (m/z) calcd for $C_{15}H_{17}ClNO$ ($M+H^+$): 262.0999, found: 262.0996.

2-[(2,6-Dichloro-4-methoxy)phenyl]pyridine (**2i**)[1]
Yellow solid, mp 76–78 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 6.96 (s, 2H), 7.30–7.34 (m, 2H), 7.79 (td, J = 7.72 Hz, 1.56 Hz, 1H), 8.74 (d, J = 3.48 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 113.9, 122.6, 125.4, 130.8, 134.8, 136.1, 149.3, 155.2, 159.5; HRMS-ESI (m/z) calcd for $C_{12}H_{10}Cl_2NO$ ($M+H^+$): 254.0139, found: 254.0139.

2-[(2,6-Dichloro-4-methoxy)phenyl]-5-methylpyridine (**2j**)
White solid, mp 106–108 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.83 (s, 3H), 6.95 (s, 2H), 7.21 (d, J = 7.88 Hz, 1H), 7.57–7.61 (m, 1H), 8.56 (dd, J = 1.48 Hz, 0.68 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 55.6, 113.9, 124.8, 130.8, 132.1, 134.9, 136.6, 149.8, 152.4, 159.4; HRMS-ESI (m/z) calcd for $C_{13}H_{12}Cl_2NO$ ($M+H^+$): 268.0296, found: 268.0302.

2-{[2,6-Dichloro-4-(*tert*-butyl)]phenyl}pyridine (**2k**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 7.30–7.33 (m, 2H), 7.40 (s, 2H), 7.80 (td, J = 7.68 Hz, 1.12 Hz, 1H), 8.74 (d, J = 4.68 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.8, 34.8, 122.6, 124.9, 125.2, 133.9, 135.2, 136.1, 149.4, 153.7, 155.4; HRMS-ESI (m/z) calcd for $C_{15}H_{16}Cl_2N$ ($M+H^+$): 280.0660, found: 280.0669.

2-{[2,6-Dichloro-4-(*tert*-butyl)]phenyl}-5-methylpyridine (**2l**)
Light yellow solid, mp 128–130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 9H), 2.41 (s, 3H), 7.23 (d, J = 7.88 Hz, 1H), 7.39 (s, 2H), 7.61 (dd, J = 7.92 Hz, 1.56 Hz, 1H), 8.57 (d, J = 0.68 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 31.0, 35.0, 124.5, 125.4, 132.4, 134.3, 135.4, 136.8, 150.1, 152.8, 153.7; HRMS-ESI (m/z) calcd for $C_{16}H_{18}Cl_2N$ ($M+H^+$): 294.0816, found: 294.0818.

2-[(2,6-Dichloro-4-methyl)phenyl]pyridine (**2m**)[1]
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 7.23 (s, 2H), 7.31–7.35 (m, 2H), 7.80 (td, J = 7.68 Hz, 1.60 Hz, 1H), 8.75 (d, J = 4.40 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7, 122.7, 125.1, 128.6, 134.0, 135.4, 136.2, 140.3, 149.5, 155.5; HRMS-ESI (m/z) calcd for $C_{12}H_{10}Cl_2N$ ($M+H^+$): 238.0190, found: 238.0198.

2-[(2,6-Dichloro-4-methyl)phenyl]-5-methylpyridine (**2n**)
White solid, mp 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.41 (s, 3H), 7.22–7.24 (m, 3H), 7.61 (d, J = 7.72 Hz, 1H), 8.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 20.6, 124.4, 128.5, 132.2, 134.1, 135.2, 136.7, 140.1, 149.8, 152.5; HRMS-ESI (m/z) calcd for $C_{13}H_{12}Cl_2N$ ($M+H^+$): 252.0347, found: 252.0355.

2-(2,6-Dichlorophenyl)-5-methylpyridine (**2o**)
Yellow solid, mp 90–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.23–7.29 (m, 2H), 7.38–7.41 (m, 2H), 7.63 (dd, J = 7.92 Hz, 1.60 Hz, 1H), 8.59 (t, J = 0.56 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 124.2, 127.9, 129.5, 132.4, 134.6, 136.8, 138.1, 149.8, 152.4; HRMS-ESI (m/z) calcd for $C_{12}H_{10}Cl_2N$ ($M+H^+$): 238.0190, found: 238.0194.

2-[(4-Bromo-2,6-dichloro)phenyl]pyridine (**2p**)
White solid, mp 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.37 (m, 2H), 7.59 (s, 2H), 7.81 (td, J = 7.76 Hz, 1.72 Hz, 1H), 8.74–8.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.0, 123.0, 124.8, 130.7, 135.2, 136.3, 137.3, 149.6, 154.4; HRMS-ESI (m/z) calcd for $C_{11}H_7BrCl_2N$ ($M+H^+$): 301.9139, found: 301.9143.

2-[(4-Bromo-2,6-dichloro)phenyl]-5-methylpyridine (**2q**)
White solid, mp 100–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.21 (d, J = 7.88 Hz, 1H), 7.57–7.64 (m, 3H), 8.58 (d, J = 0.52 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 121.8, 124.2, 130.7, 132.7, 135.4, 136.8, 137.3, 150.0, 151.5; HRMS-ESI (m/z) calcd for $C_{12}H_9BrCl_2N$ ($M+H^+$): 315.9295, found: 315.9304.

2-[(2,6-Dichloro-4-fluoro)phenyl]pyridine (**2r**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, J = 8.20 Hz, 2H), 7.30–7.38 (m, 2H), 7.82 (td, J = 7.72 Hz, 1.40 Hz, 1H), 8.75 (d, J = 4.56 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.7 (d, J = 24.3 Hz), 122.9, 125.1, 134.7 (d, J = 4.1 Hz), 135.2 (d, J = 11.5 Hz), 136.3, 149.5, 154.5, 161.3 (d, J = 251.4 Hz); HRMS-ESI (m/z) calcd for $C_{11}H_7Cl_2FN$ ($M+H^+$): 241.9940, found: 241.9945.

2-[(2,6-Dichloro-4-fluoro)phenyl]-5-methylpyridine (**2s**)
White solid, mp 99–102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.42 (s, 3H), 7.16–7.23 (m, 3H), 7.61–7.64 (m, 1H), 8.57–8.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 115.6 (d, J = 24.3 Hz), 124.5, 132.6, 134.7 (d, J = 3.9 Hz), 135.4 (d, J = 11.5 Hz), 136.8, 150.0, 151.6, 161.2 (d, J = 251.2 Hz); HRMS-ESI (m/z) calcd for $C_{12}H_9Cl_2FN$ ($M+H^+$): 256.0096, found: 256.0096.

2-[(2,6-Dichloro-4-ethoxycarbonyl)phenyl]pyridine (**2t**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (t, J = 7.16 Hz, 3H), 4.42 (q, J = 7.16 Hz, 2H), 7.33–7.40 (m, 2H), 7.84 (td, J = 7.72 Hz, 1.72 Hz, 1H), 8.07 (s, 2H), 8.76–8.79 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.2, 60.9, 122.3, 123.8, 128.1, 131.2, 133.9, 135.6, 141.1, 148.8, 153.8, 163.2; HRMS-ESI (m/z) calcd for $C_{14}H_{12}Cl_2NO_2$ ($M+H^+$): 296.0245, found: 296.0248.

2-[(2,6-Dichloro-4-ethoxycarbonyl)phenyl]-5-methylpyridine (**2u**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (t, J = 7.12 Hz, 3H), 2.43 (s, 3H), 4.41 (q, J = 7.12 Hz, 2H), 7.22–7.28 (m, 1H), 7.64 (d, J = 7.72 Hz, 1H), 8.06 (s, 2H), 8.60 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 18.3, 61.8, 124.1, 129.0, 131.9, 132.9, 135.0, 136.9, 142.1, 150.1, 151.8, 164.1; HRMS-ESI (m/z) calcd for $C_{15}H_{14}Cl_2NO_2$ ($M+H^+$): 310.0402, found: 310.0407.

10-Chlorobenzo[h]quinoline (**2v**)[1]
Light yellow solid, mp 64–66 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.56 (m, 2H), 7.67 (d, J = 8.80 Hz, 1H), 7.75 (d, J = 8.76 Hz, 1H), 7.81 (d, J = 7.76 Hz, 2H), 8.13–8.17 (m, 1H), 9.09–9.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.7, 126.6, 127.5, 127.6, 127.7, 127.8, 128.2, 131.5, 132.3, 135.7, 136.3, 146.5, 147.6; HRMS-ESI (m/z) calcd for $C_{13}H_9ClN$ ($M+H^+$): 214.0424, found: 214.0418.

2-[2-(3-Chlorothienyl)]pyridine (**2w**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00 (d, J = 5.32 Hz, 1H), 7.18–7.23 (m, 1H), 7.35 (d, J = 5.32 Hz, 1H), 7.75 (td, J = 7.92 Hz, 1.72 Hz, 1H), 8.23 (d, J = 8.12 Hz, 1H), 8.61 (d, J = 4.64 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.5, 121.9, 122.2, 126.3, 129.8, 136.4, 136.8, 149.3, 150.8; HRMS-ESI (m/z) calcd for C_9H_7ClNS ($M+H^+$): 195.9988, found: 195.9996.

2-[2-(3-Chlorothienyl)]-5-methylpyridine (**2x**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H), 6.99 (d, J = 5.32 Hz, 1H), 7.32 (d, J = 5.32 Hz, 1H), 7.56 (d, J = 8.12 Hz, 1H), 8.11 (d, J = 8.20 Hz, 1H), 8.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 120.3, 121.5, 125.8, 129.9, 132.1, 137.0, 137.2, 148.3, 149.9; HRMS-ESI (m/z) calcd for $C_{10}H_9ClNS$ ($M+H^+$): 210.0144, found: 210.0148.

{[5-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)]phenyl}pyridine (**3a**)
Light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 12H), 2.29 (s, 3H), 3.81 (s, 3H), 6.85–6.88 (m, 1H), 7.28 (t, J = 8.00 Hz, 1H), 7.42–7.48 (m, 2H), 7.52–7.55 (m, 1H), 8.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 24.0, 54.3, 82.5, 110.7, 113.7, 118.1, 119.2, 128.6, 130.7, 136.3, 139.9, 149.0, 153.5, 159.0; HRMS-ESI (m/z) calcd for C_9H_7ClNS ($M+H^+$-Bpin): 200.1075, found: 200.1087.

Crystal data for compound 2j:

The molecular structure of the dichlorinated product (**2j**) was unambiguously determined by the single crystal X-ray diffraction study (Fig. 1). CCDC 917218 contains the supplementary crystallographic data for **2j**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/datarequest/cif. Crystal, data for compound **2j**: $C_{13}H_{11}Cl_2NO$, M = 268.13, Triclinic, a = 6.2427(4) Å, α = 74.492(6)^o, b = 8.5337(6) Å, β = 77.526(6)^o, c = 12.7695(10) Å, γ = 81.552(5)^o, V = 637.16(8) Å^3, T = 291.15 K, space group = Pī, Z = 2, Number of reflections = 4499, Independent reflections = 2279, [R(int) = 0.0212], Final R indices [I>2σ (I)] R_1 = 0.0389, wR_2 = 0.1078, R indices (all data) R_1 = 0.0443, wR_2 = 0.1131.

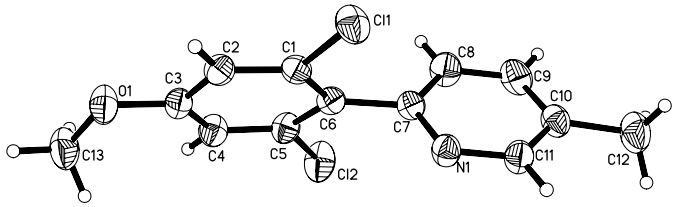
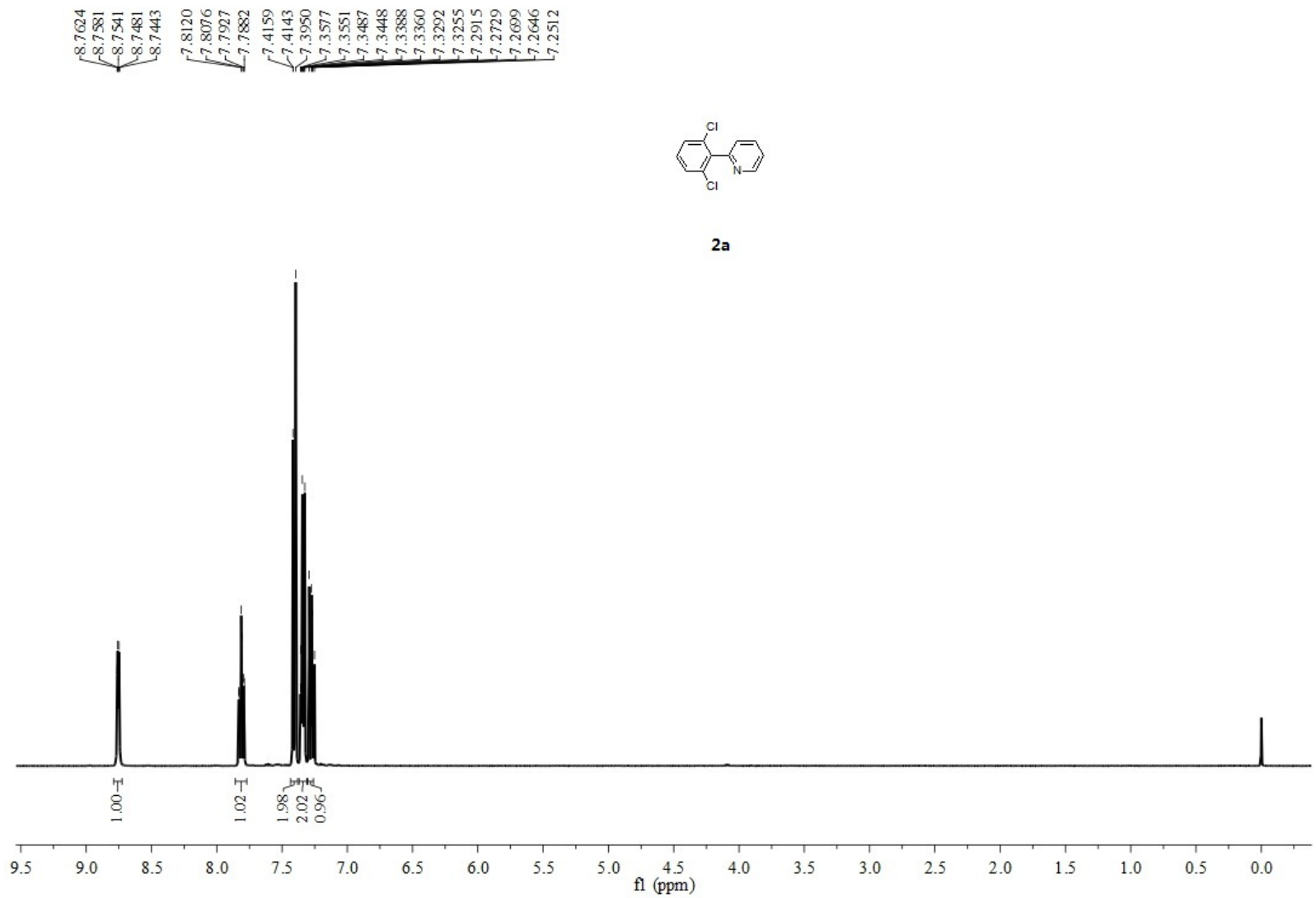
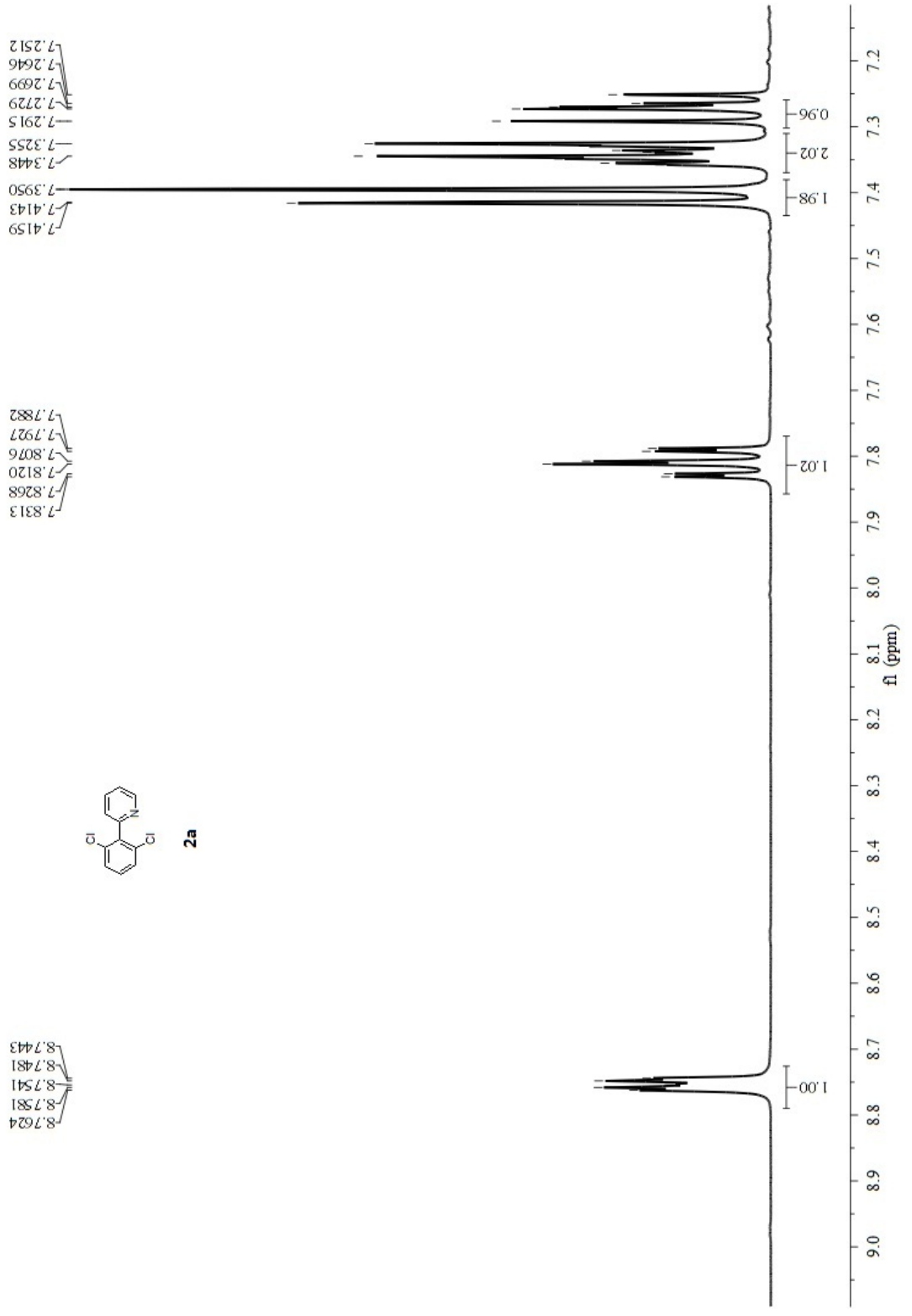


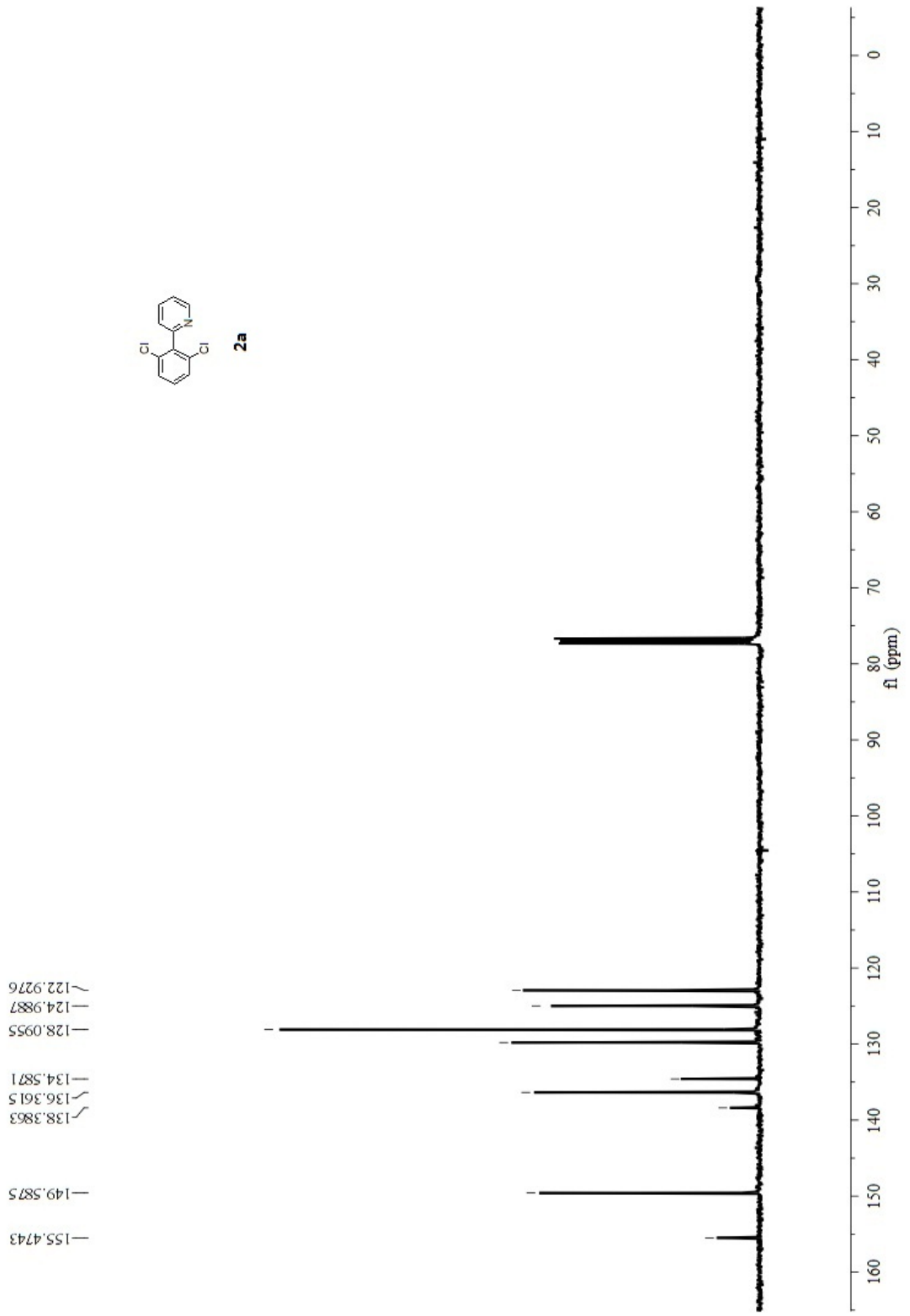
Figure 1. Molecular structure of **2j**

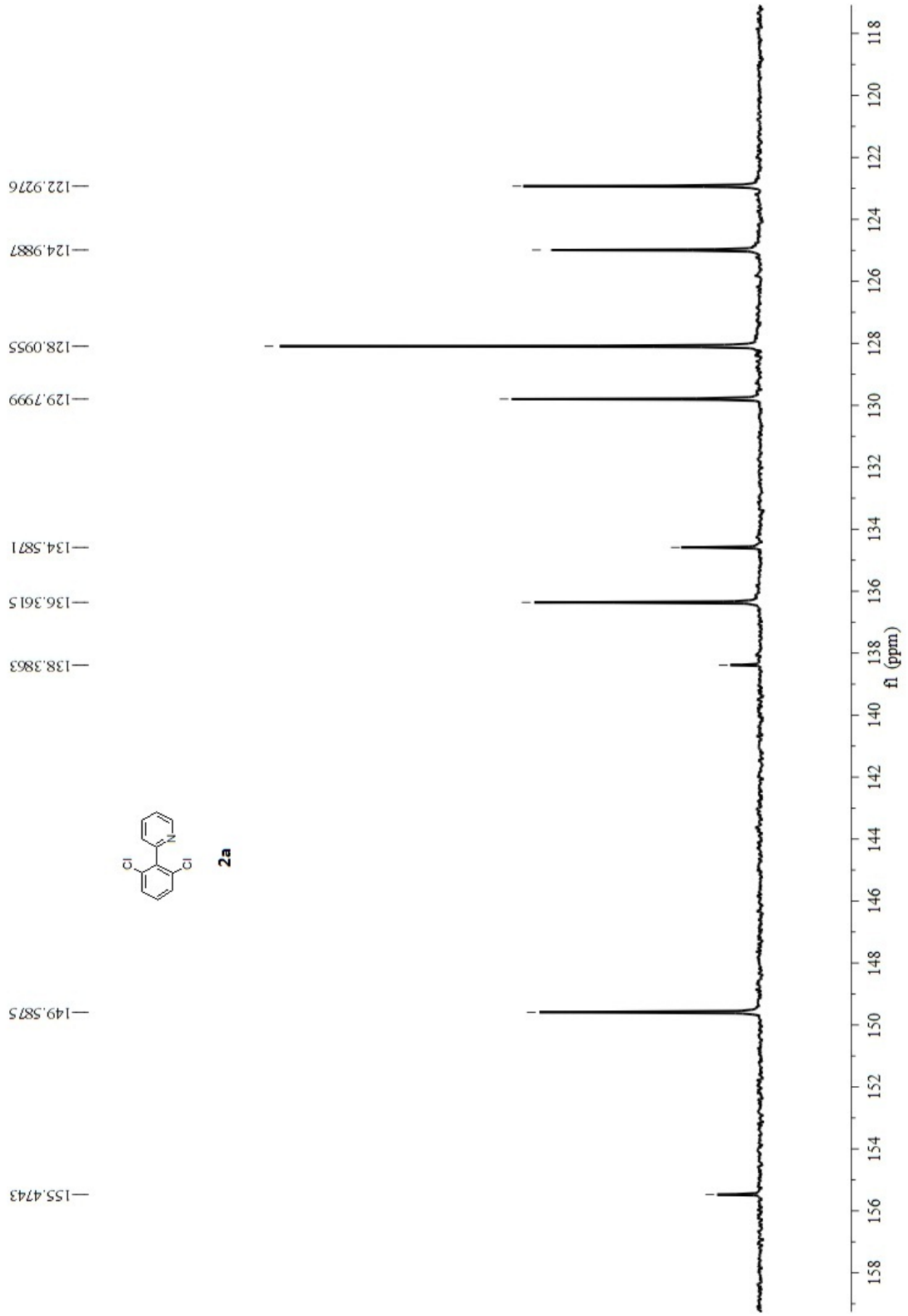
Refrences:

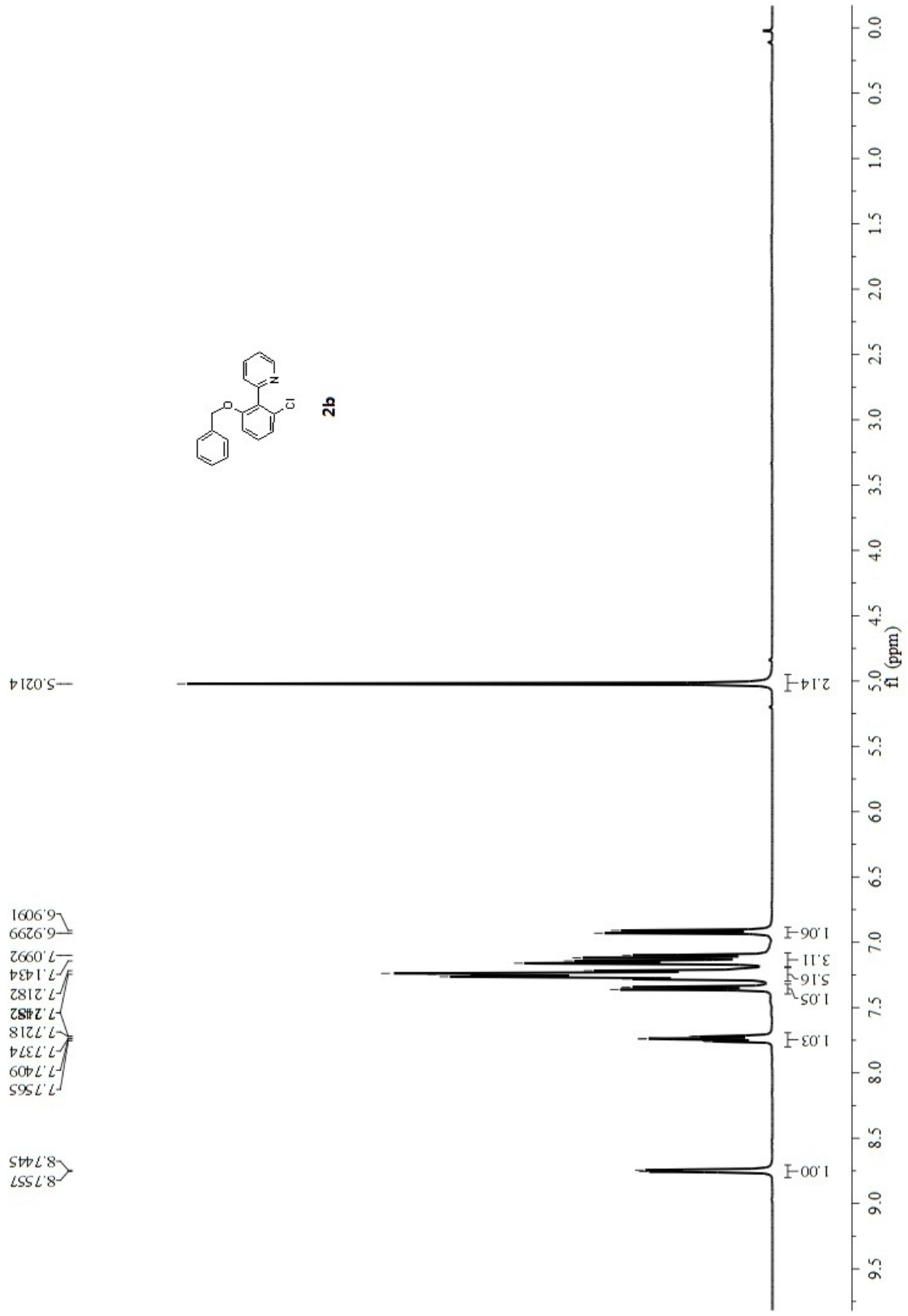
[1] X. Chen, X. S. Hao, C. E. Goodhue, J. Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790.

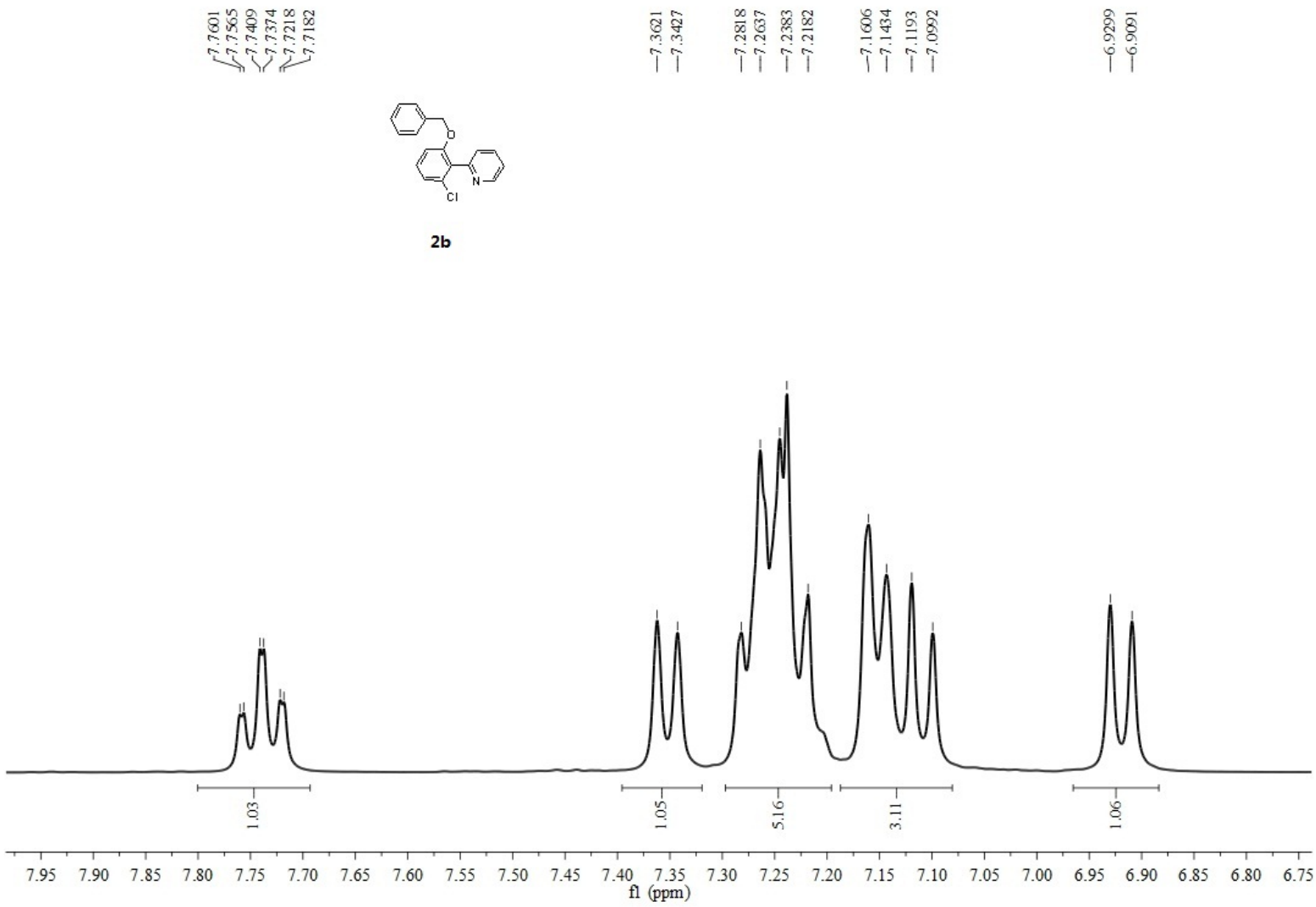

8.7624
8.7581
8.7541
8.7481
8.7443
7.8120
7.8076
7.7927
7.7882
7.4159
7.4143
7.3950
7.3577
7.3551
7.3487
7.3448
7.3388
7.3360
7.3292
7.3255
7.2915
7.2729
7.2699
7.2646
7.2512
Cl
N
Cl
2a
1.00
1.02
1.98
2.02
0.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


8.7624
8.7581
8.7541
8.7481
8.7443
8.3313
8.3268
8.3120
8.3076
8.2927
8.2882
7.4159
7.4143
7.3950
7.3448
7.3255
7.2915
7.2729
7.2699
7.2646
7.2512
1.00
1.02
1.98
2.02
0.96
f1 (ppm)
2a

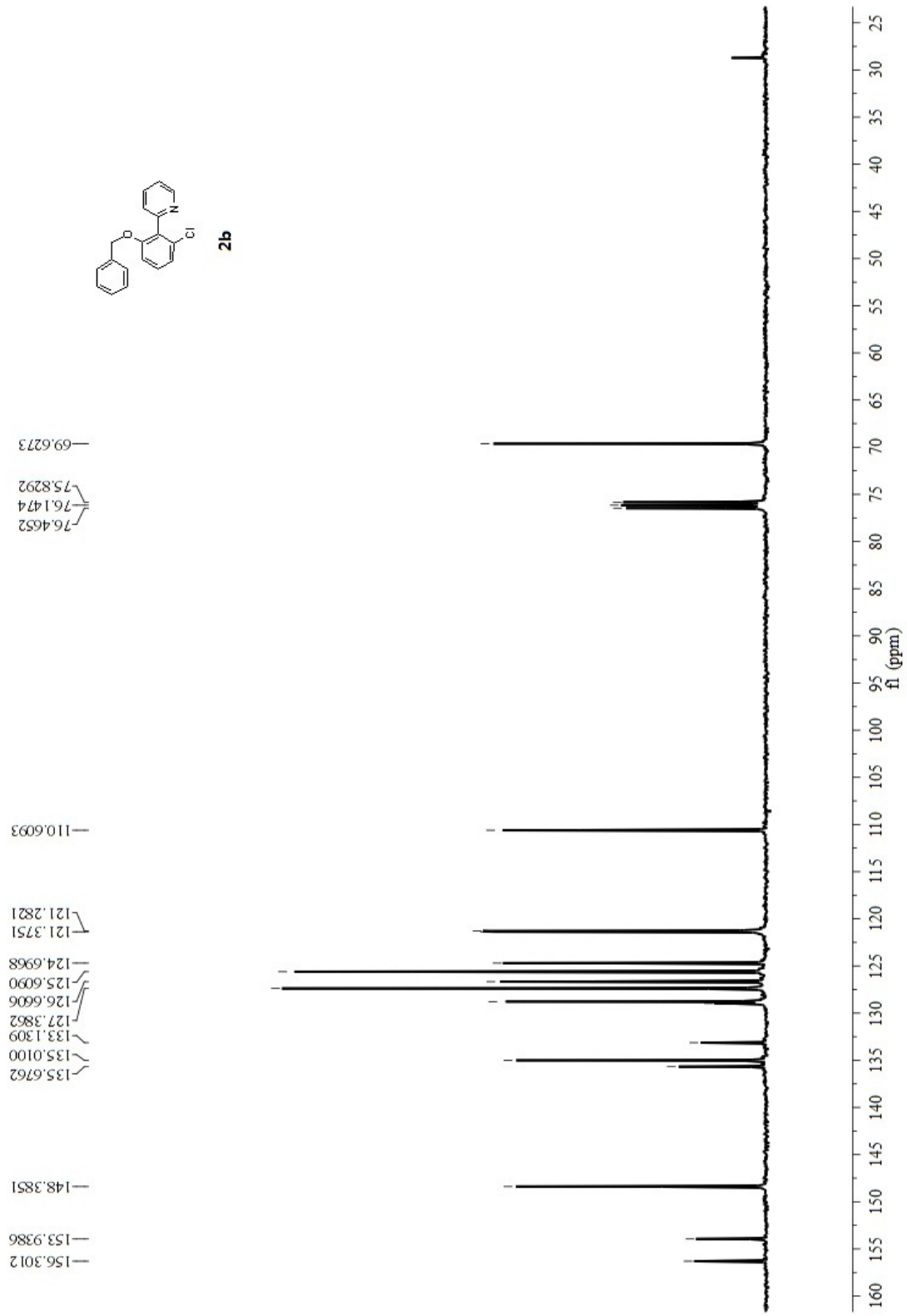

2a
Cl
Cl
N
155.4743
149.5875
138.3863
136.3615
134.5871
128.0955
124.9887
122.9276
f1 (ppm)

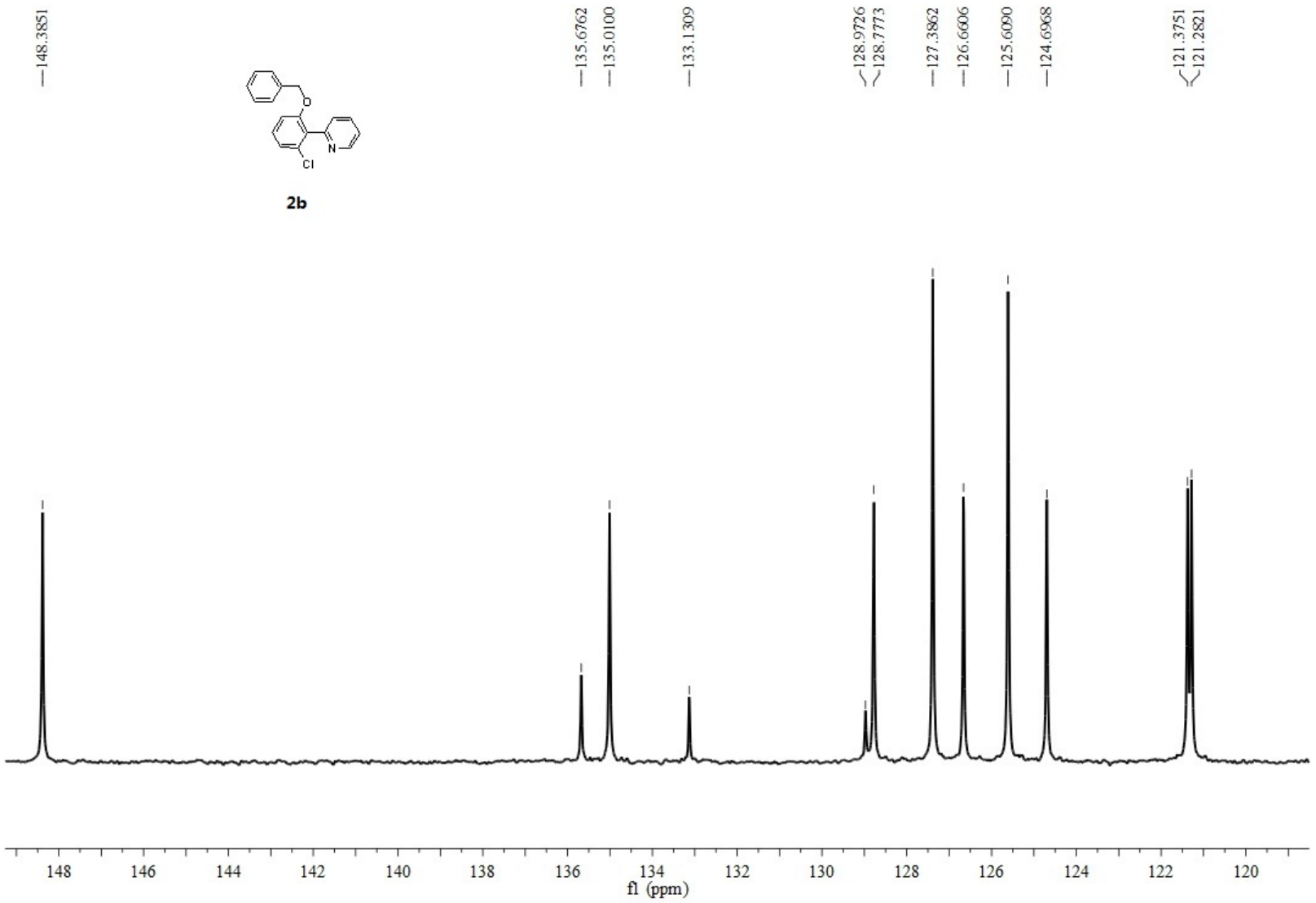

155.4743
149.5875
138.3863
136.3615
134.5871
129.7999
128.0955
124.9887
122.9276
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
f1 (ppm)
Cl
Cl
N
2a


2b
N
O
Cl
8.7557
8.7445
7.7565
7.7409
7.7374
7.7218
7.2482
7.2182
7.1434
7.0992
6.9299
6.9091
5.0214
1.00
1.03
1.05
5.16
3.11
1.06
2.14
f1 (ppm)


7.7601
7.7565
7.7409
7.7374
7.7218
7.7182
7.3621
7.3427
7.2818
7.2637
7.2383
7.2182
7.1606
7.1434
7.1193
7.0992
6.9299
6.9091
O
N
Cl
1.03
1.05
5.16
3.11
1.06
7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75
f1 (ppm)

2b


2b
N
O
Cl
69.6273
75.8292
76.1474
76.4652
110.6093
121.2821
121.3751
124.6968
125.6090
126.6606
127.3862
133.1309
135.0100
135.6762
148.3851
153.9386
156.3012
f1 (ppm)

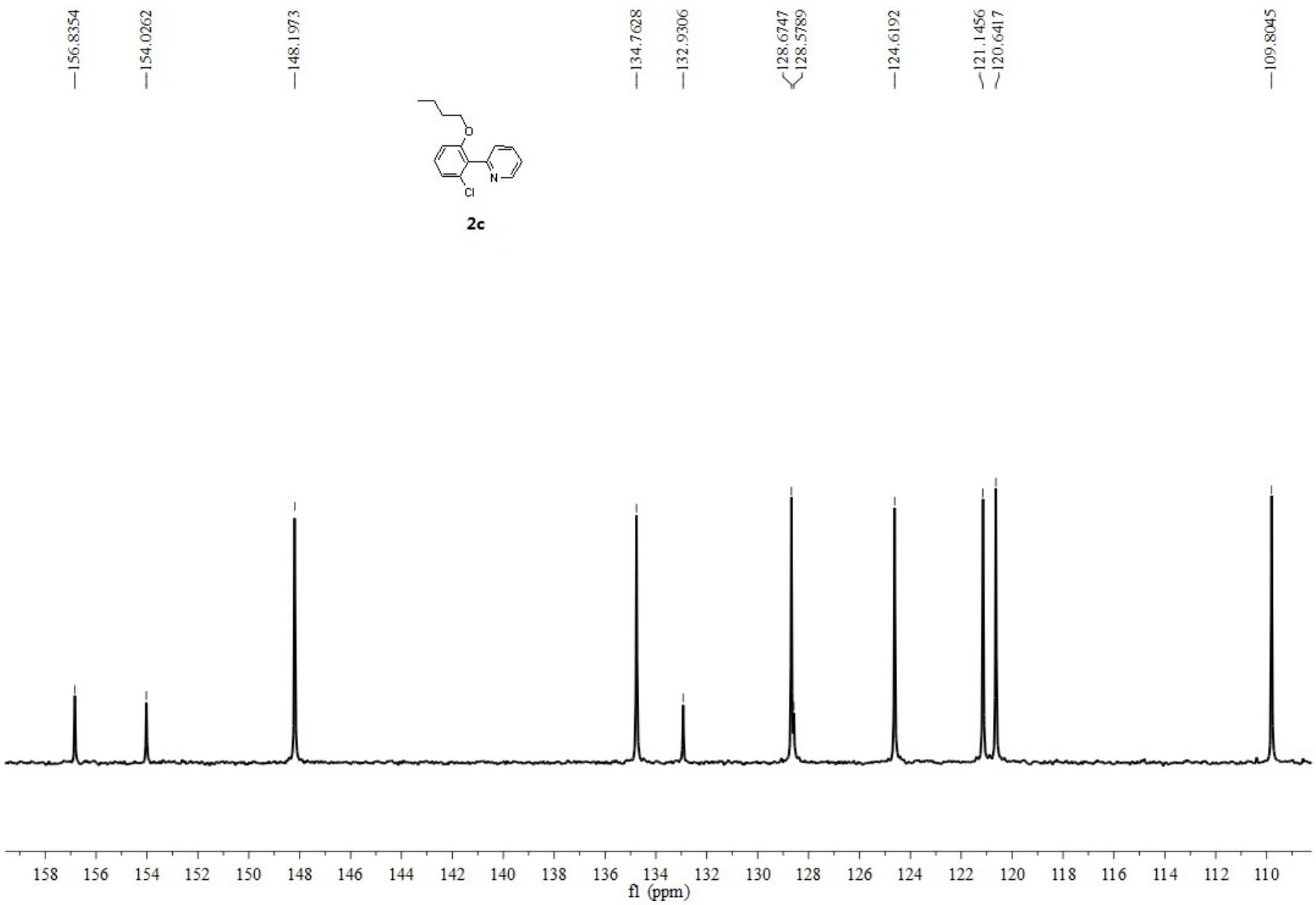

148.3851
135.6762
135.0100
133.1309
128.9726
128.7773
127.3862
126.6606
125.6090
124.6968
121.3751
121.2821
O
N
Cl
2b
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
f1 (ppm)

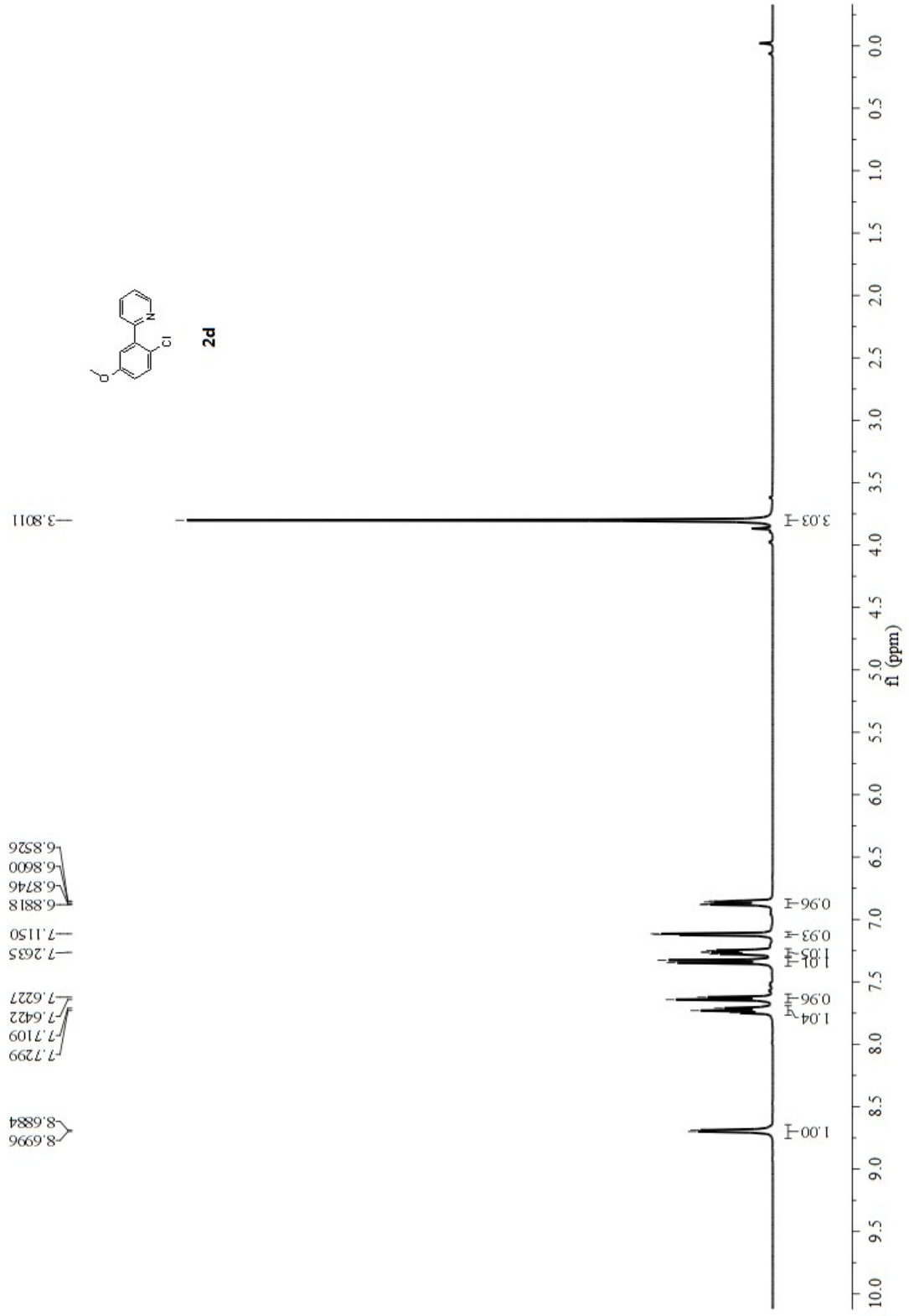
8.6925
8.6814
7.7071
7.7034
7.6880
7.6843
7.2902
7.2211
7.2004
7.0328
6.8569
6.8361
3.8866
3.8707
3.8548
1.5495
1.5331
1.5159
1.4966
1.4805
1.1868
0.7963
0.7778
0.7593
1.00
1.02
3.12
1.01
1.04
2.14
2.16
2.51
3.29
f1 (ppm)
2c

8.6925
8.6814
7.7264
7.7225
7.7071
7.7034
7.6880
7.6842
7.2902
7.2707
7.2532
7.2415
7.2211
7.2113
7.2004
7.0528
7.0328
6.8569
6.8361
2c
1.00
1.02
3.12
1.01
1.04
f1 (ppm)

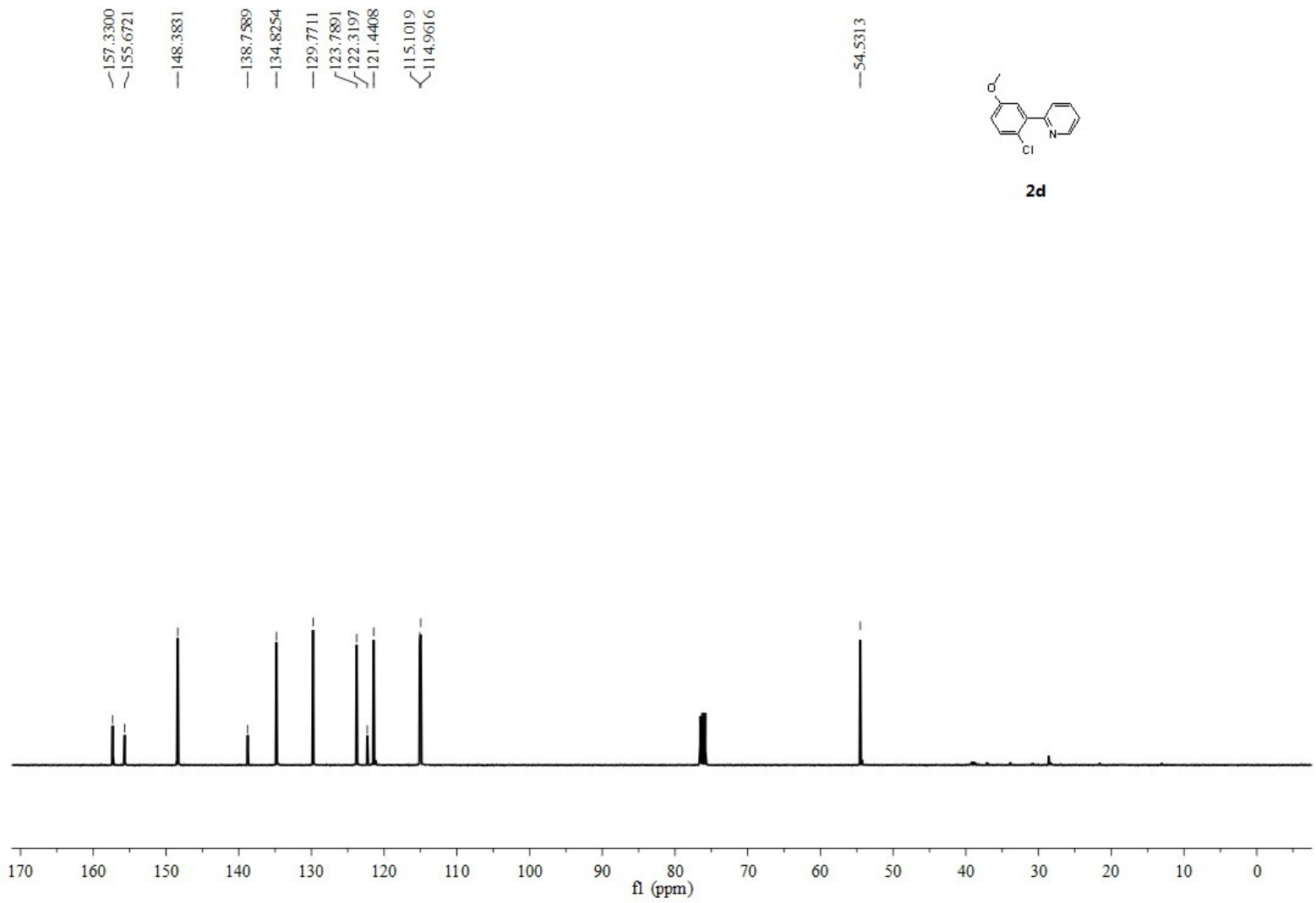
3.8866
3.8707
3.8548
1.5495
1.5331
1.5159
1.4966
1.4805
1.2423
1.2054
1.1868
1.1684
1.1502
0.7963
0.7778
0.7593
2c
2.14
3.29
2.51
2.16
f1 (ppm)

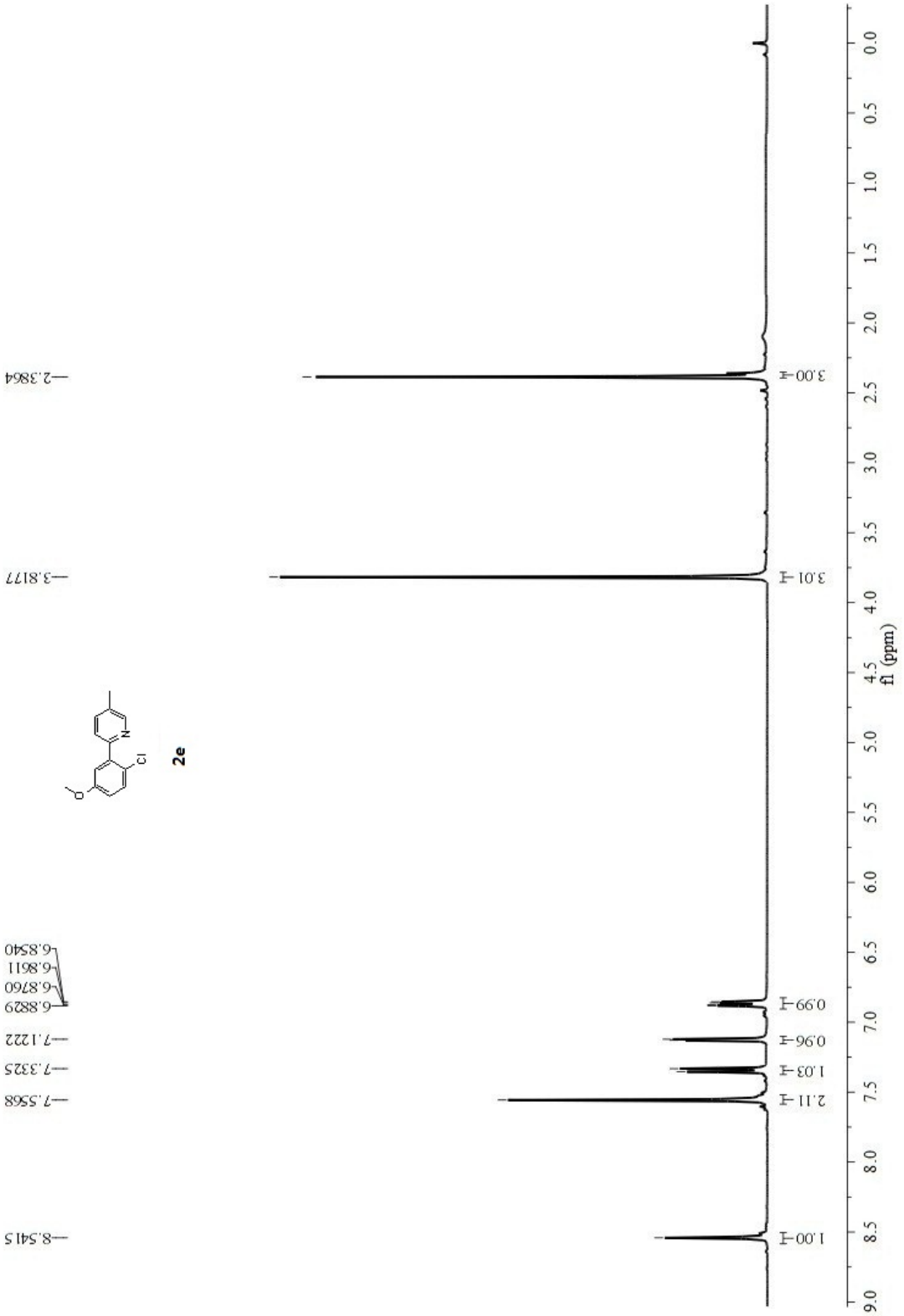
156.8354
154.0262
148.1973
134.7628
132.9306
128.5789
124.6192
121.1456
120.6417
109.8045
67.6214
29.9096
17.9265
12.6114
2c
f1 (ppm)


156.8354
154.0262
148.1973
134.7628
132.9306
128.6747
128.5789
124.6192
121.1456
120.6417
109.8045
O
N
Cl
2c
158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110
f1 (ppm)

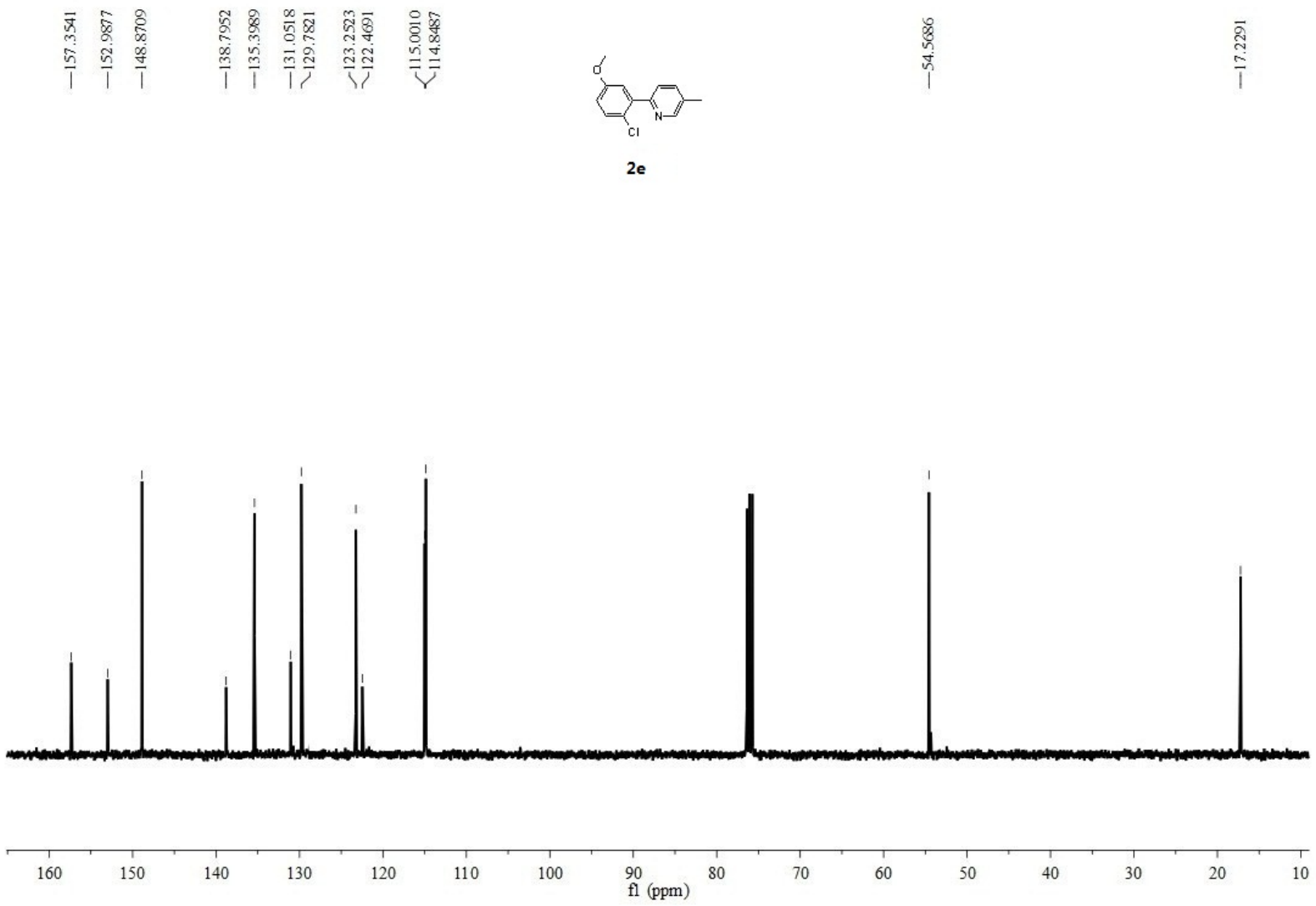

2d
8.6996
8.6884
7.7299
7.7109
7.6422
7.6227
7.2635
7.1150
6.8818
6.8746
6.8600
6.8526
3.8011
1.00
1.04
0.96
1.01
1.05
0.93
0.96
3.03
f1 (ppm)

8.6996
8.6884
7.7488
7.7299
7.7109
7.6422
7.6227
7.3473
7.3253
7.2635
7.2607
7.2472
7.1223
7.1150
6.8818
6.8746
6.8600
6.8526
2d
1.00
0.96
1.04
1.01
1.05
0.93
0.96
f1 (ppm)


157.3300
155.6721
148.3831
138.7589
134.8254
129.7711
123.7891
122.3197
121.4408
115.1019
114.9616
54.5313
O
N
Cl
2d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

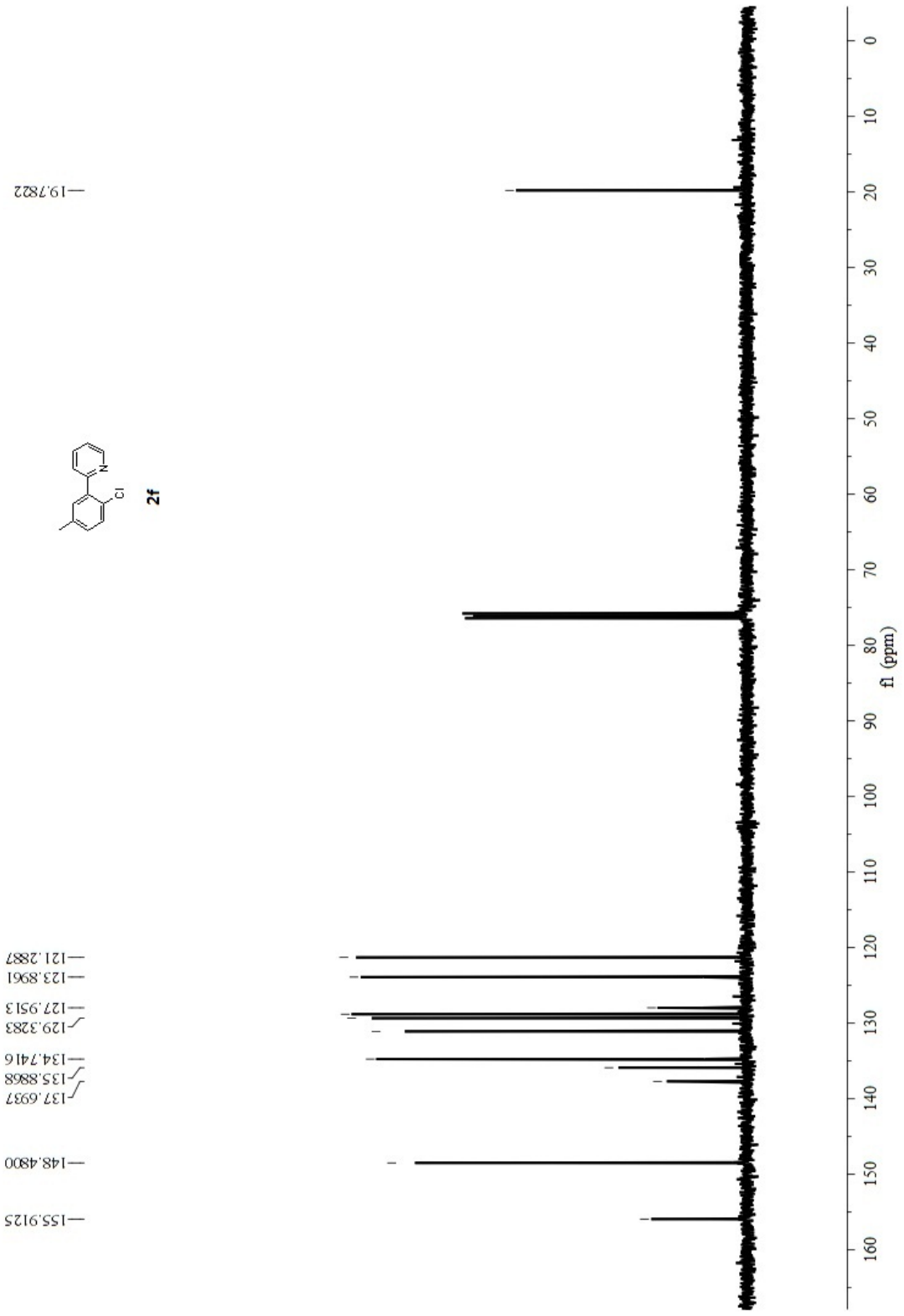

8.5415
7.5568
7.3325
7.1222
6.8829
6.8760
6.8611
6.8540
3.8177
2.3864
1.00
2.11
1.03
0.96
0.99
3.01
3.00
f1 (ppm)
2e

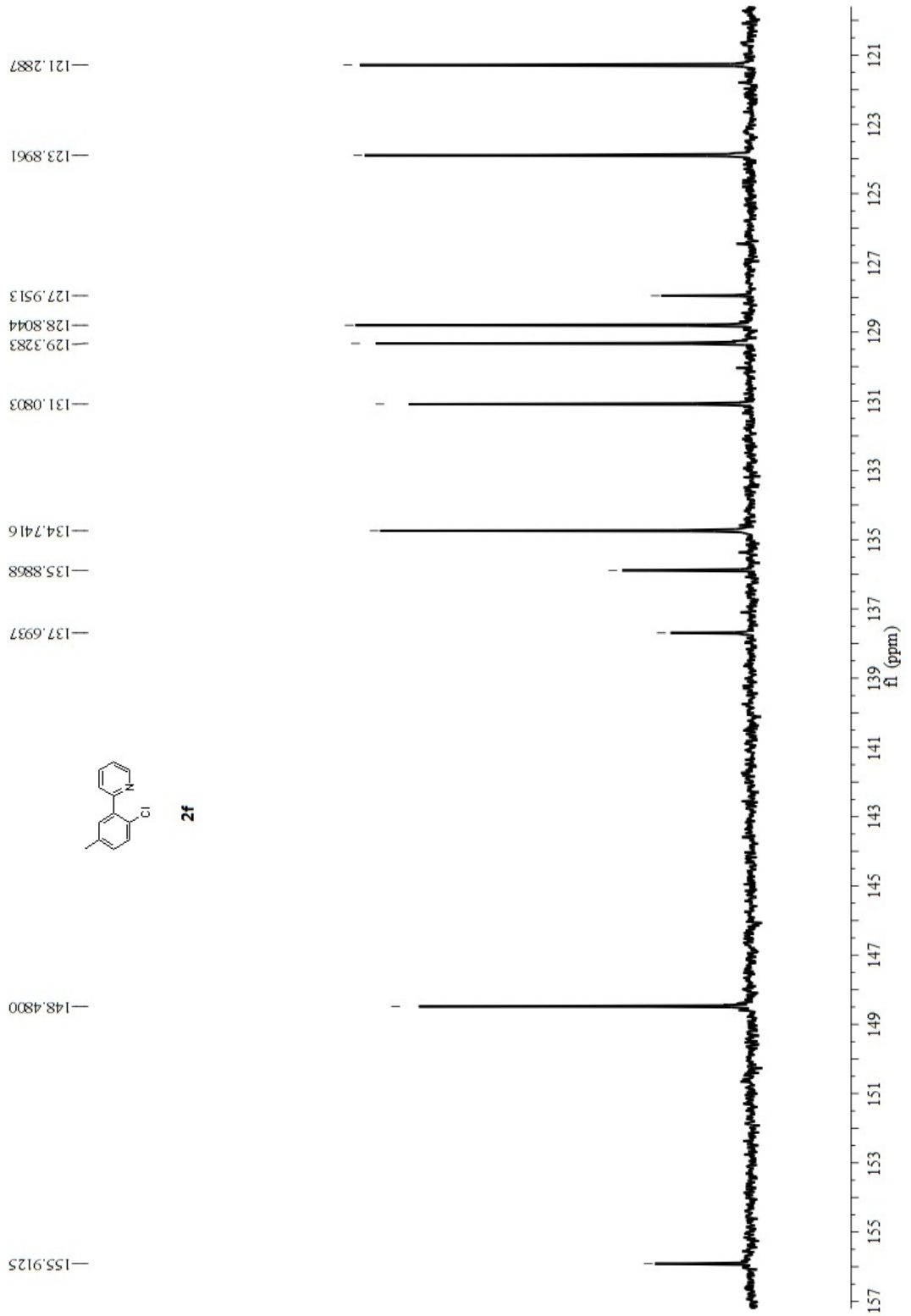
8.5415
7.5568
7.3545
7.3325
7.1291
7.1222
6.8829
6.8760
6.8611
6.8540
2e
1.00
2.11
1.03
0.96
0.99
f1 (ppm)

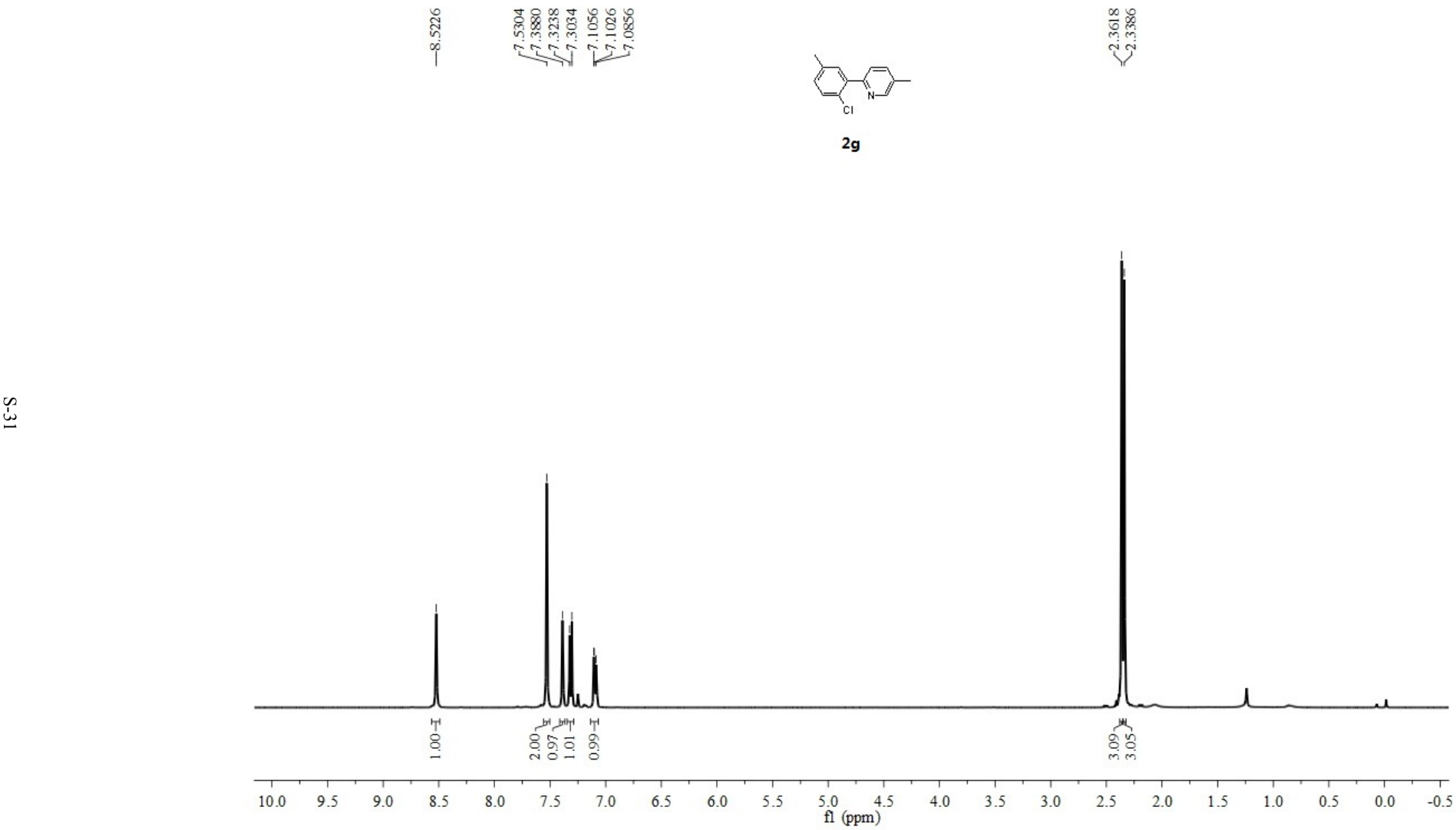

157.3541
152.9877
148.8709
138.7952
135.3989
131.0518
129.7821
123.2523
122.4691
115.0010
114.8487
54.5686
17.2291
O
N
Cl
2e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

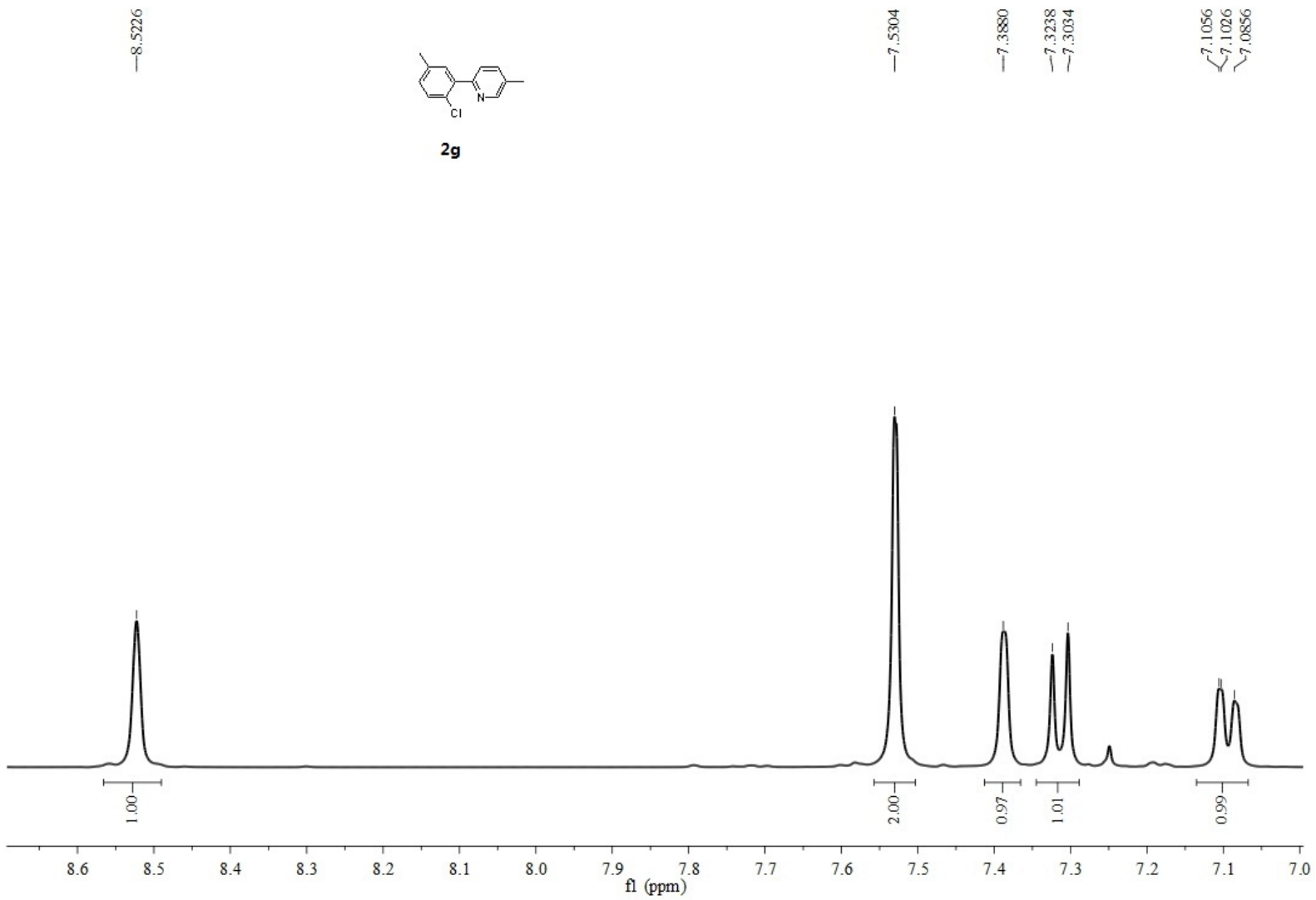
2f
8.6971
8.6857
7.7099
7.6947
7.6907
7.6332
7.6136
7.4008
7.3977
7.3335
7.3132
7.2549
7.2421
7.2388
7.2257
7.1207
7.1168
7.1004
7.0966
2.3405
2.97
1.00
1.01
1.00
0.99
0.98
1.07
0.99
f1 (ppm)

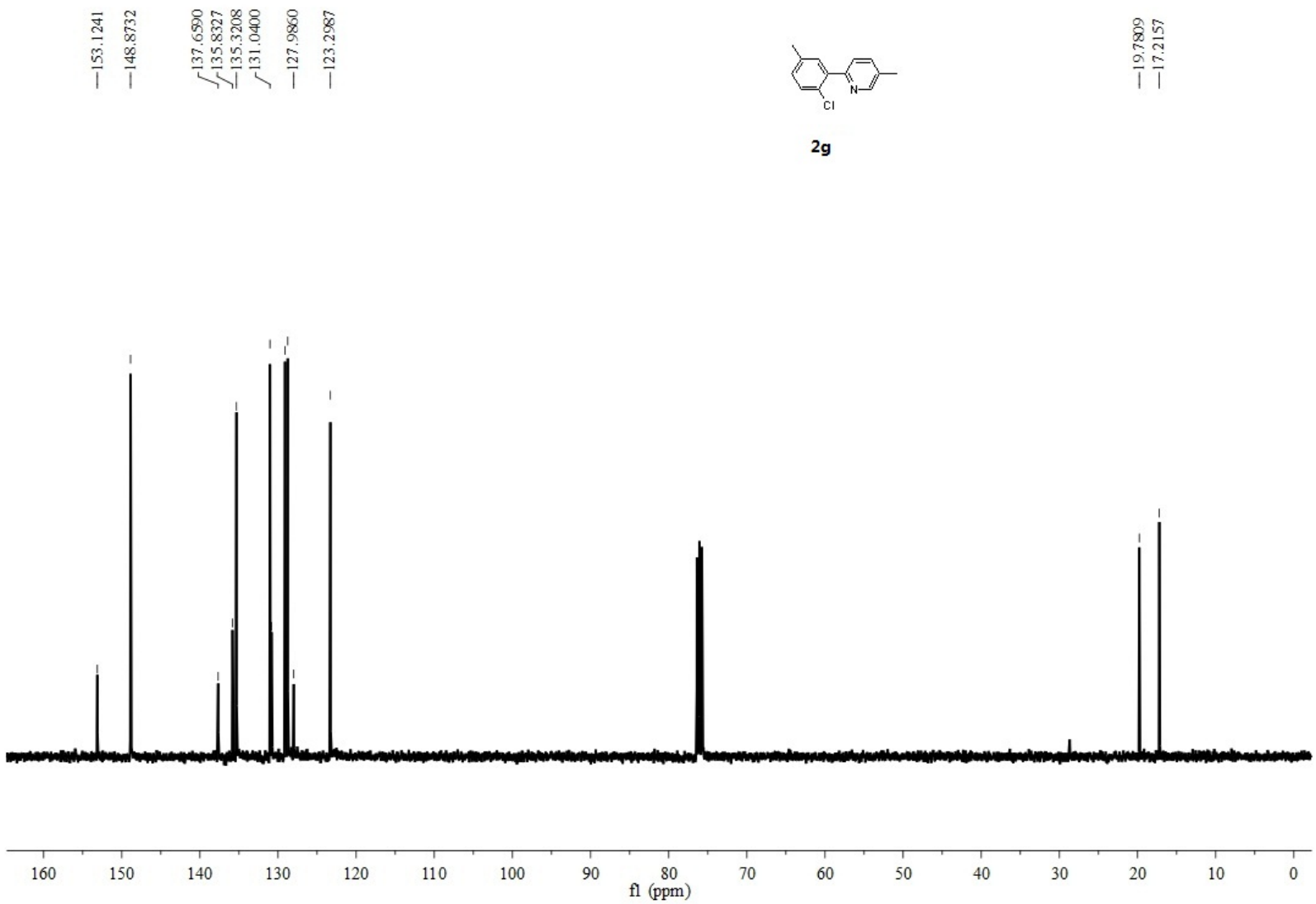
8.6971
8.6857
7.4008
7.3977
7.3335
7.3132
7.2549
7.2421
7.2388
7.2257
7.1207
7.1168
7.1004
7.0966
7.7330
7.7291
7.7136
7.7099
7.6947
7.6907
7.6332
7.6136
1.00
1.01
1.00
0.98
1.07
0.99
f1 (ppm)
2f

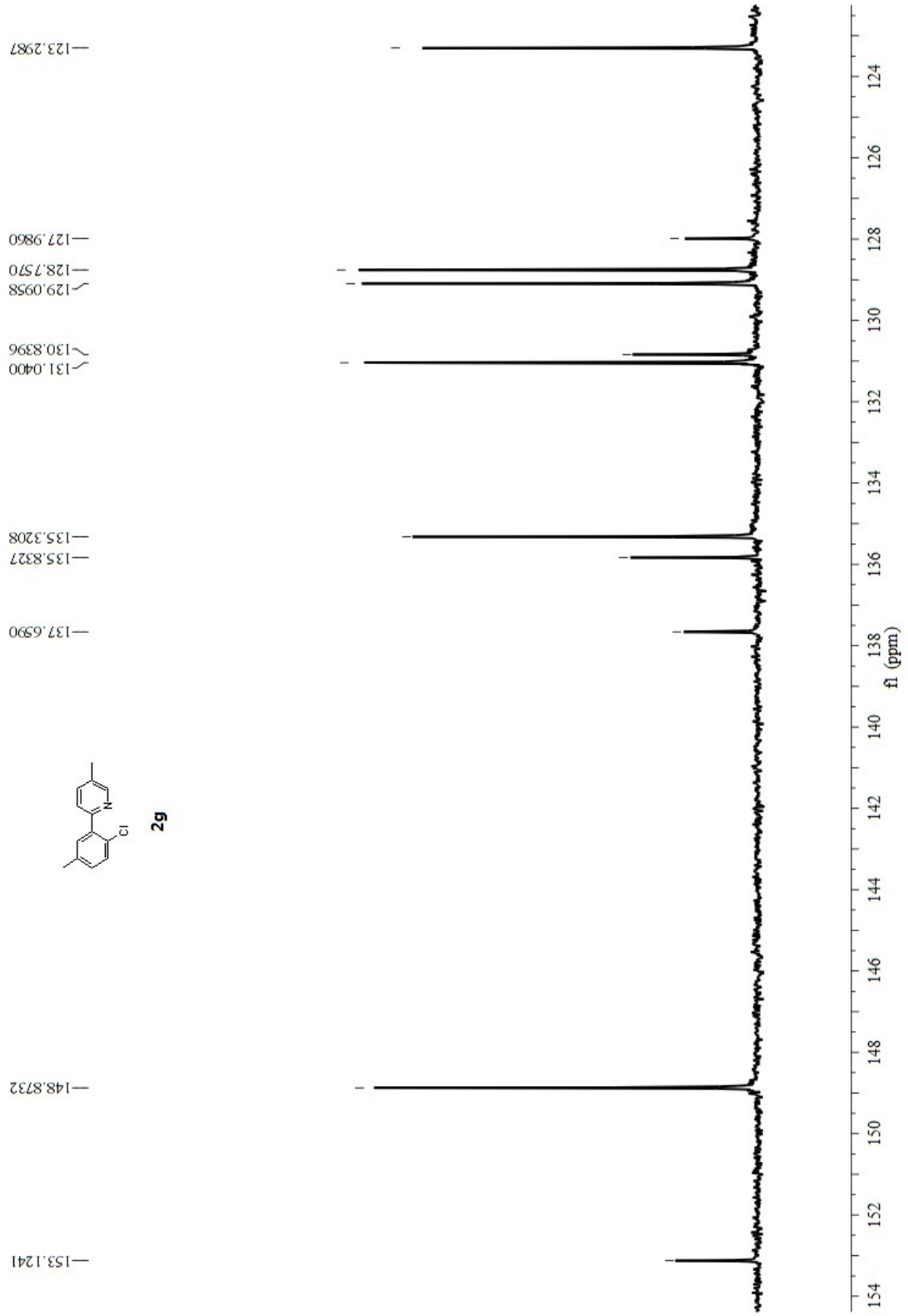

155.9125
148.4800
137.6937
135.8868
134.7416
129.3283
127.9513
123.8961
121.2887
19.7822
2f
f1 (ppm)

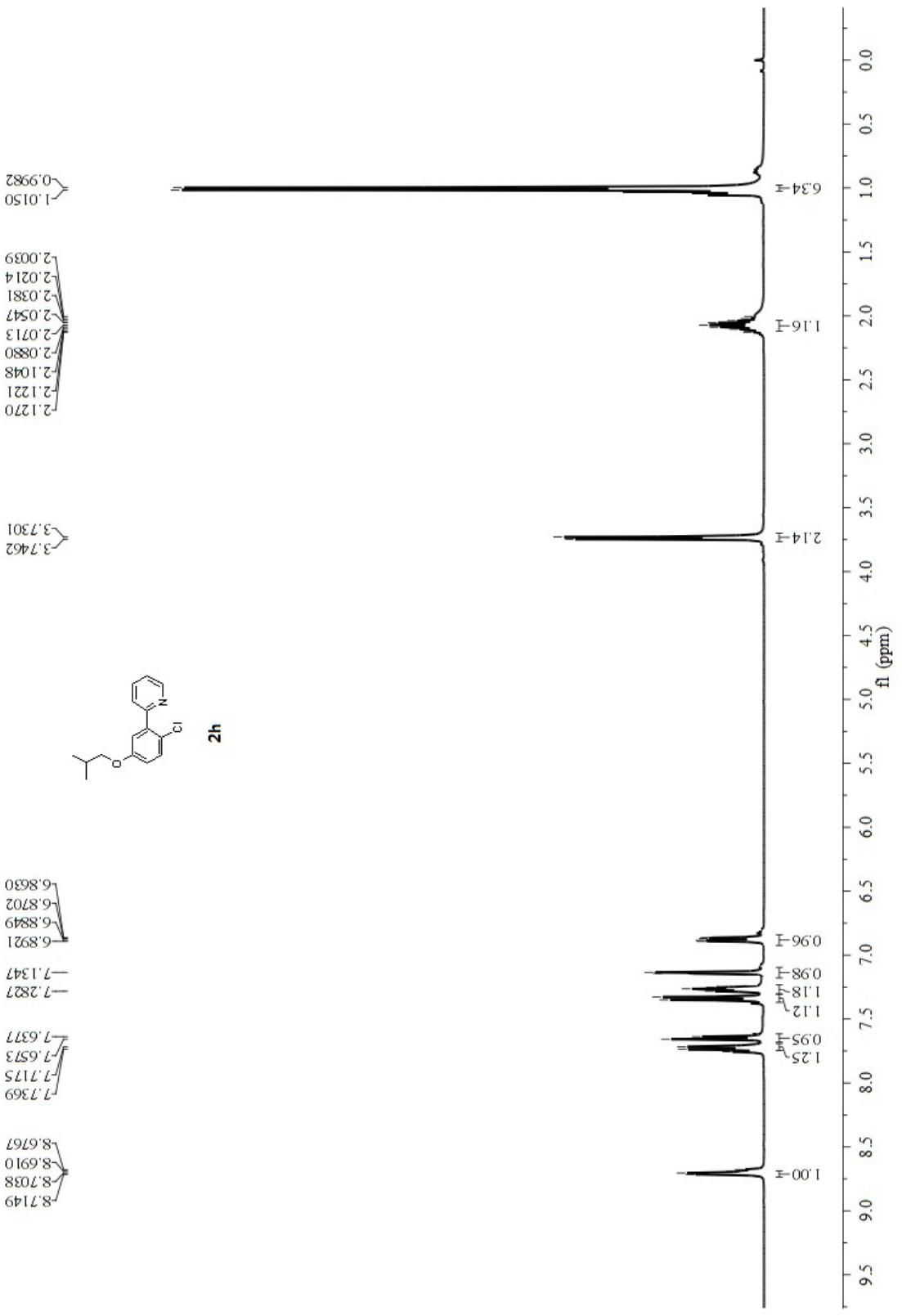

155.9125
148.4800
137.6937
135.8868
134.7416
131.0803
129.3283
128.8044
127.9513
123.8961
121.2887
2f
Cl
N
157
155
153
151
149
147
145
143
141
139
137
135
133
131
129
127
125
123
121
f1 (ppm)


8.5226
7.5304
7.3880
7.3238
7.3034
7.1056
7.1026
7.0856
2.3618
2.3386
Cl
N
2g
1.00
2.00
0.97
1.01
0.99
3.09
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

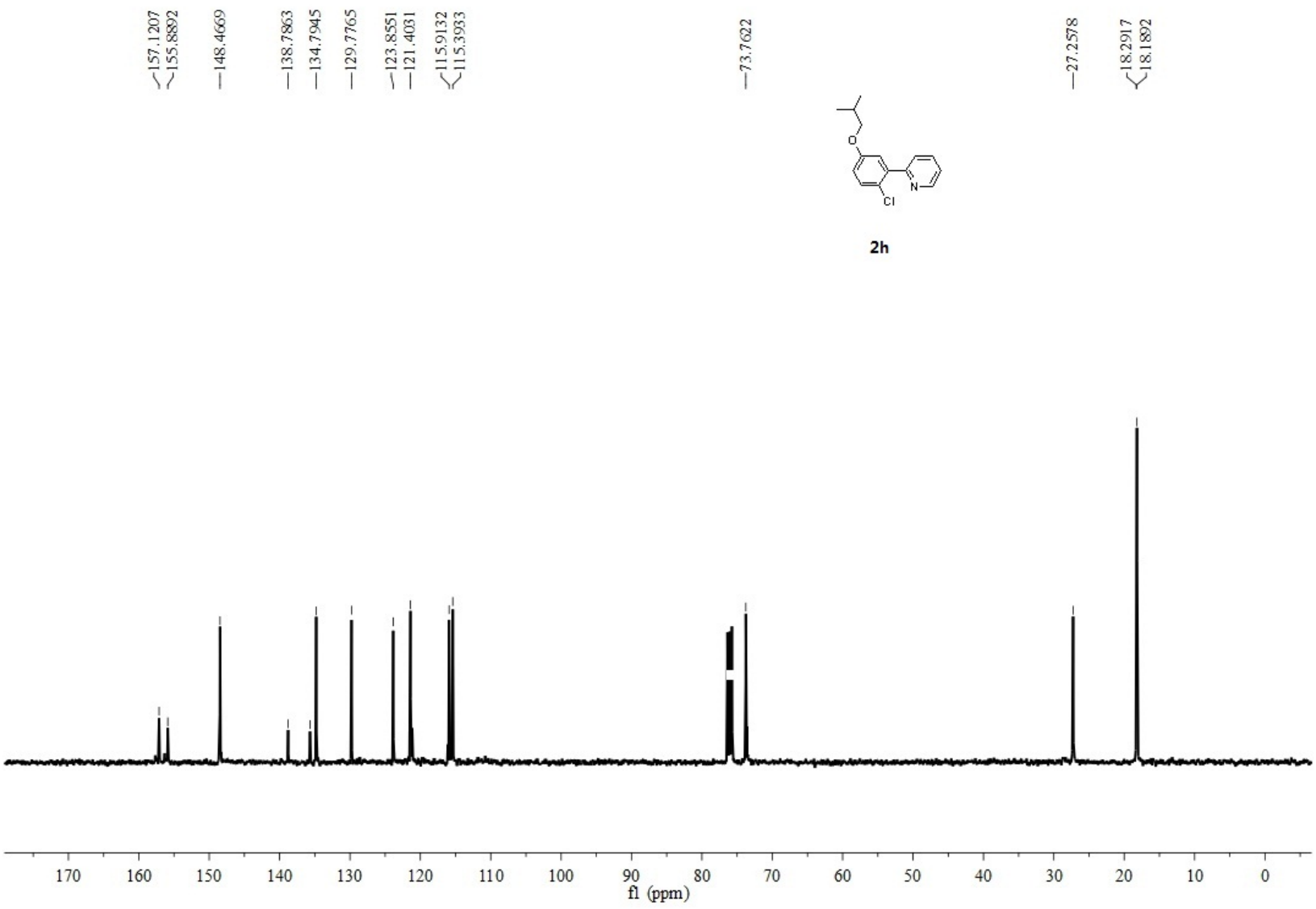

8.5226
7.5304
7.3880
7.3238
7.3034
7.1056
7.1026
7.0856
Cl
N
2g
1.00
2.00
0.97
1.01
0.99
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)

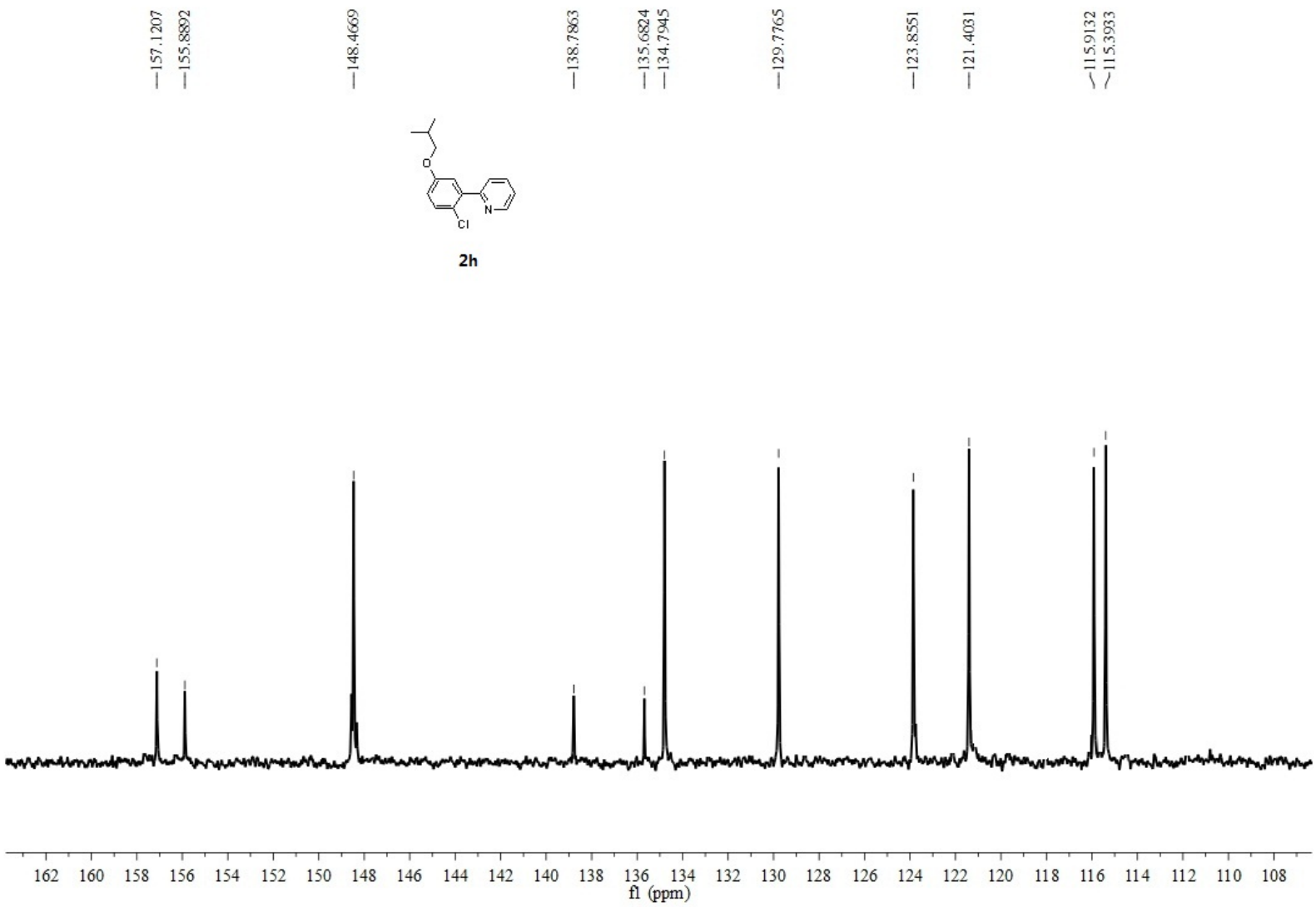

153.1241
148.8732
137.6590
135.8327
135.3208
131.0400
127.9860
123.2987
19.7809
17.2157
Cl
N
2g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

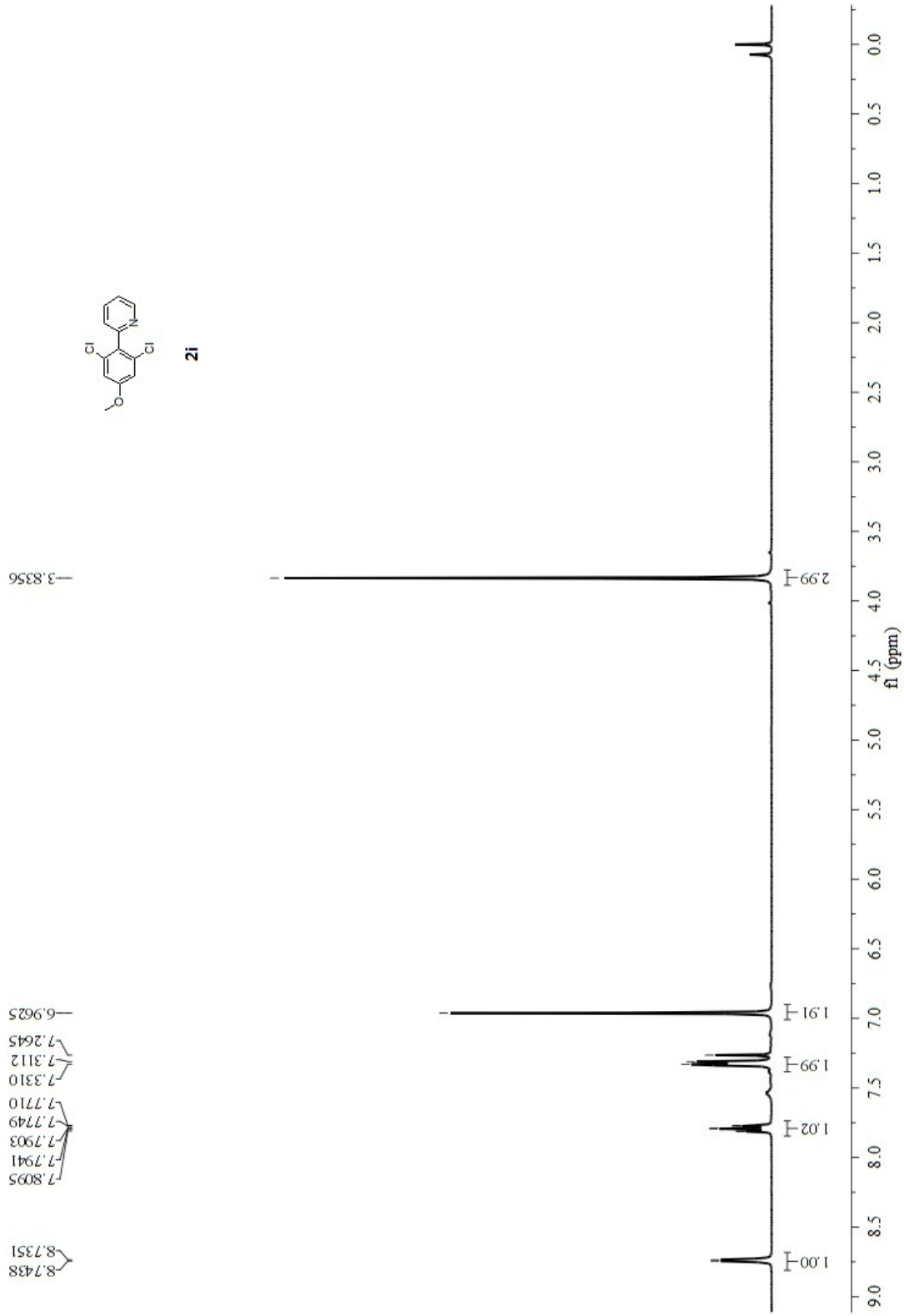

153.1241
148.8732
137.6590
135.8327
135.3208
131.0400
130.8396
129.0958
128.7570
127.9860
123.2987
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
f1 (ppm)
N
Cl
2g


8.7149
8.7038
8.6910
8.6767
7.7369
7.7175
7.6573
7.6377
7.2827
7.1347
6.8921
6.8849
6.8702
6.8630
3.7462
3.7301
2.1270
2.1221
2.1048
2.0880
2.0713
2.0547
2.0381
2.0214
2.0039
1.0150
0.9982
2h
1.00
0.95
1.25
1.12
1.18
0.98
0.96
2.14
1.16
6.34
f1 (ppm)

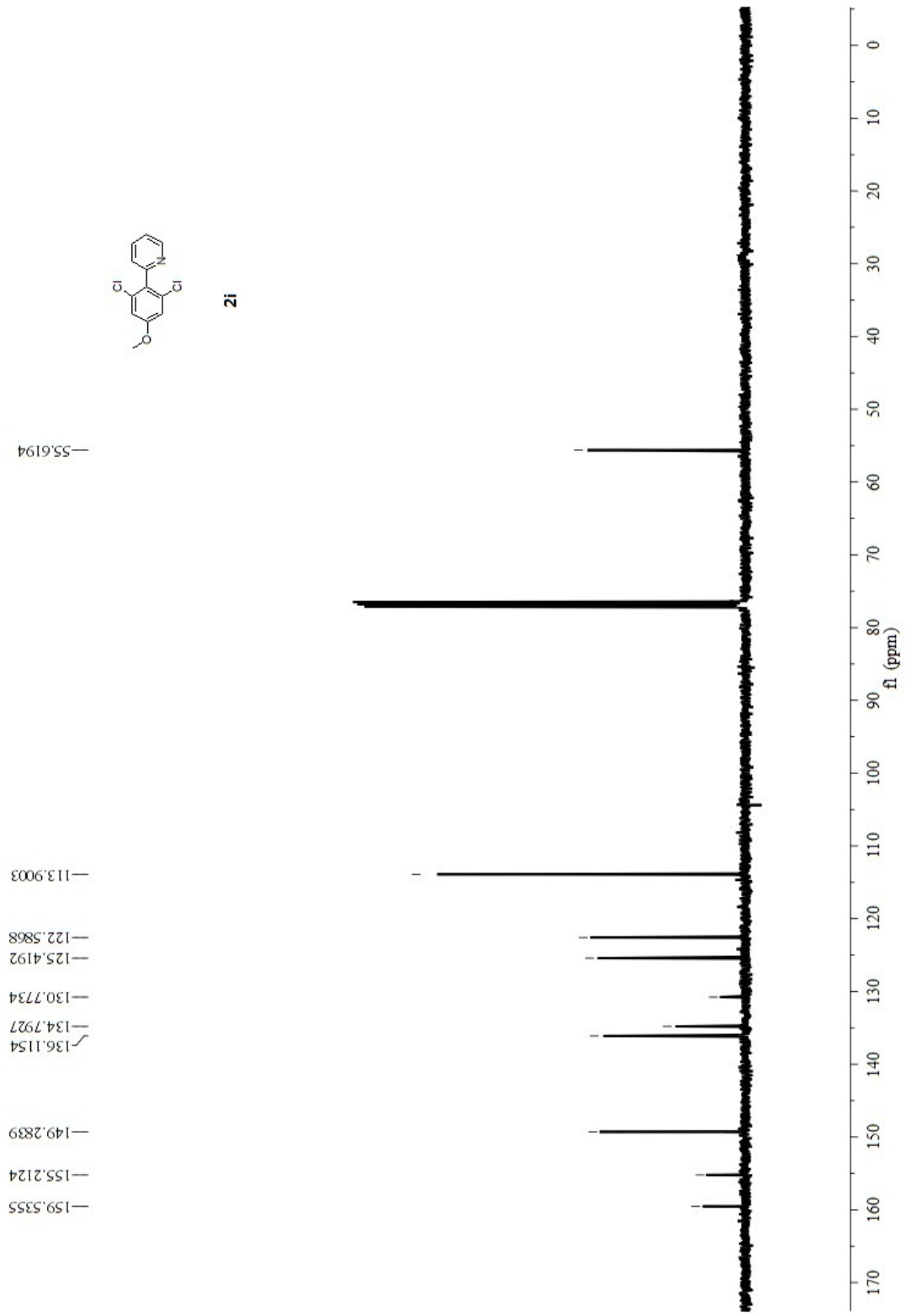
8.7149
8.7038
8.6910
8.6767
7.7559
7.7369
7.7175
7.6573
7.6377
7.3502
7.3375
7.3282
7.2827
7.2636
7.2524
7.1418
7.1347
6.8921
6.8849
6.8702
6.8630
2h
1.00
1.25
0.95
1.12
1.18
0.98
0.96
f1 (ppm)

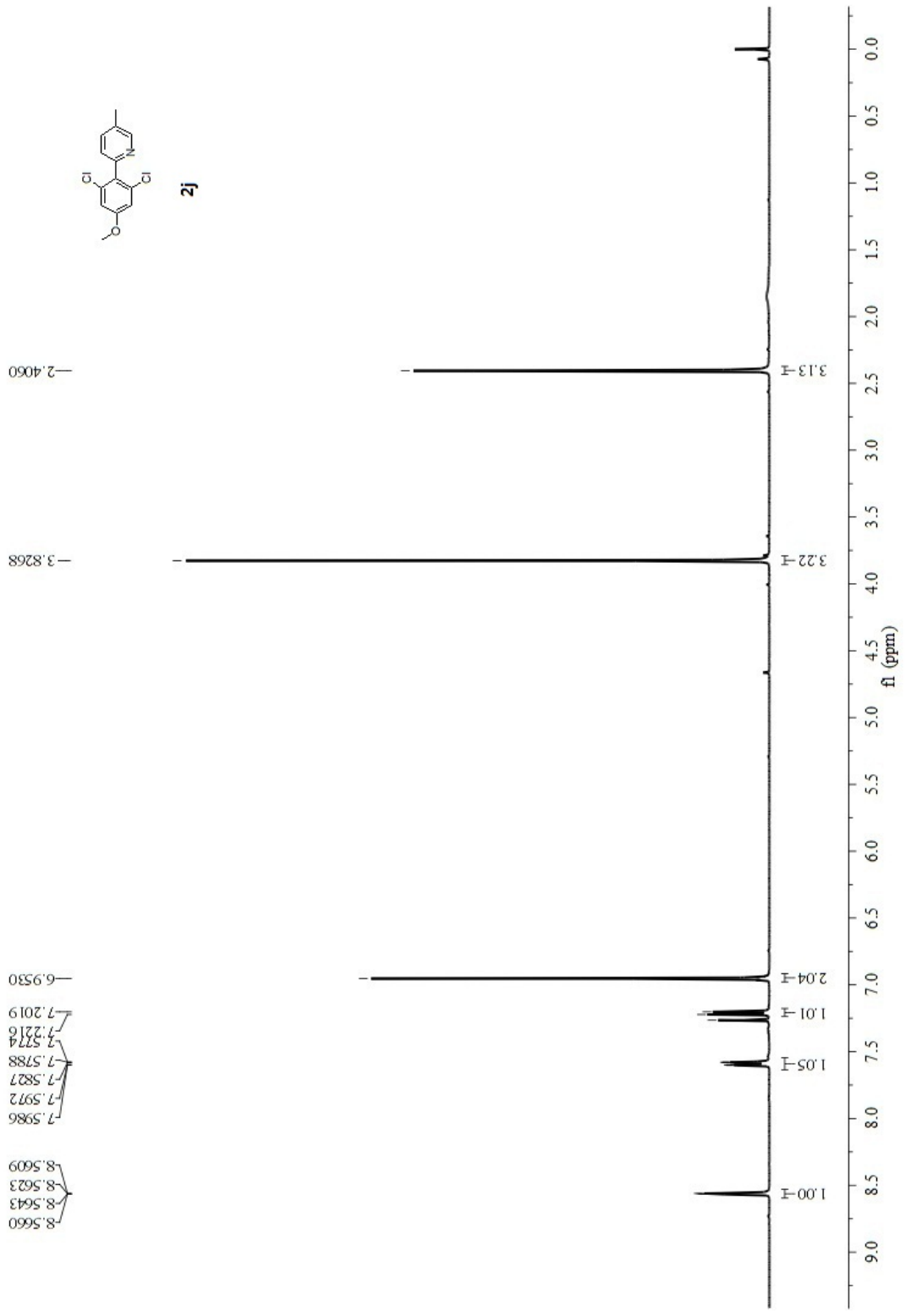

157.1207
155.8892
148.4669
138.7863
134.7945
129.7765
123.8551
121.4031
115.9132
115.3933
73.7622
27.2578
18.2917
18.1892
O
N
Cl
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


157.1207
155.8892
148.4669
138.7863
135.6824
134.7945
129.7765
123.8551
121.4031
115.9132
115.3933
O
N
Cl
2h
162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)

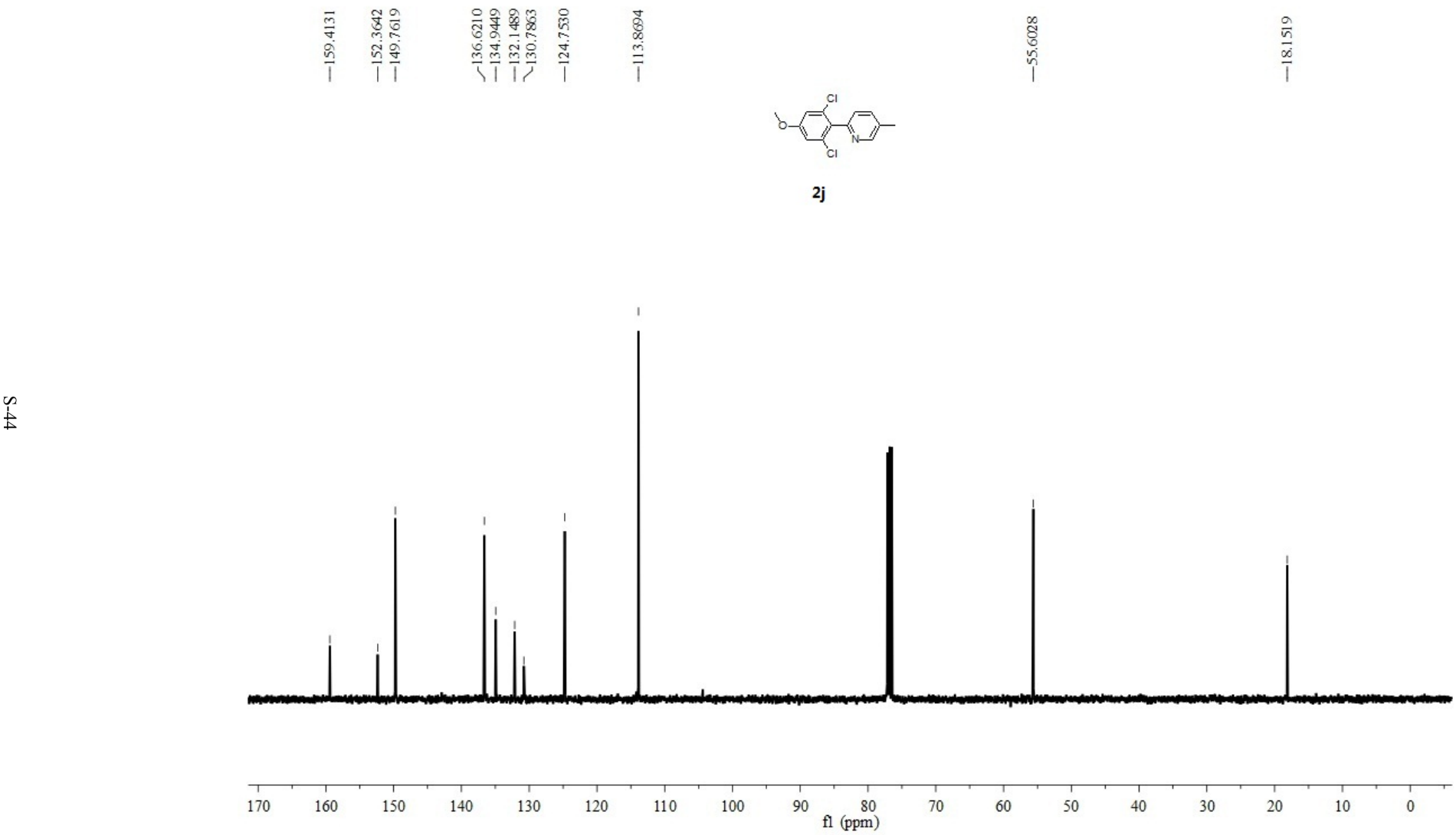

2i
8.7438
8.7351
7.8095
7.7941
7.7903
7.7749
7.7710
7.3310
7.3112
7.2645
6.9625
3.8356
1.00
1.02
1.99
1.91
2.99
f1 (ppm)

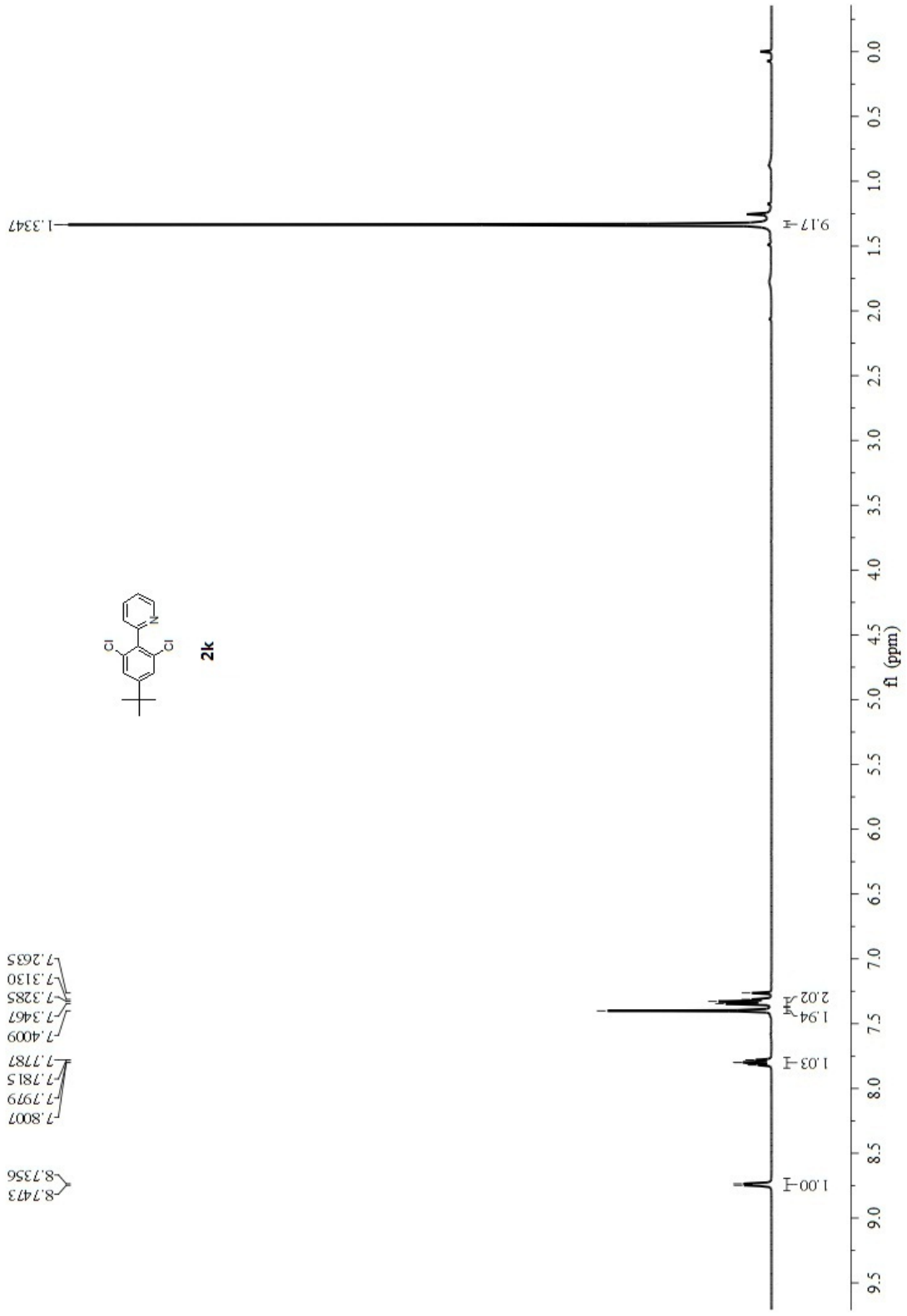
8.7438
8.7351
7.8134
7.8095
7.7941
7.7903
7.7749
7.7710
7.3310
7.3112
7.2645
6.9625
1.00
1.02
1.99
1.91
f1 (ppm)
2i


2i
55.6194
113.9003
122.5868
125.4192
130.7734
134.7927
136.1154
149.2839
155.2124
159.5355
f1 (ppm)

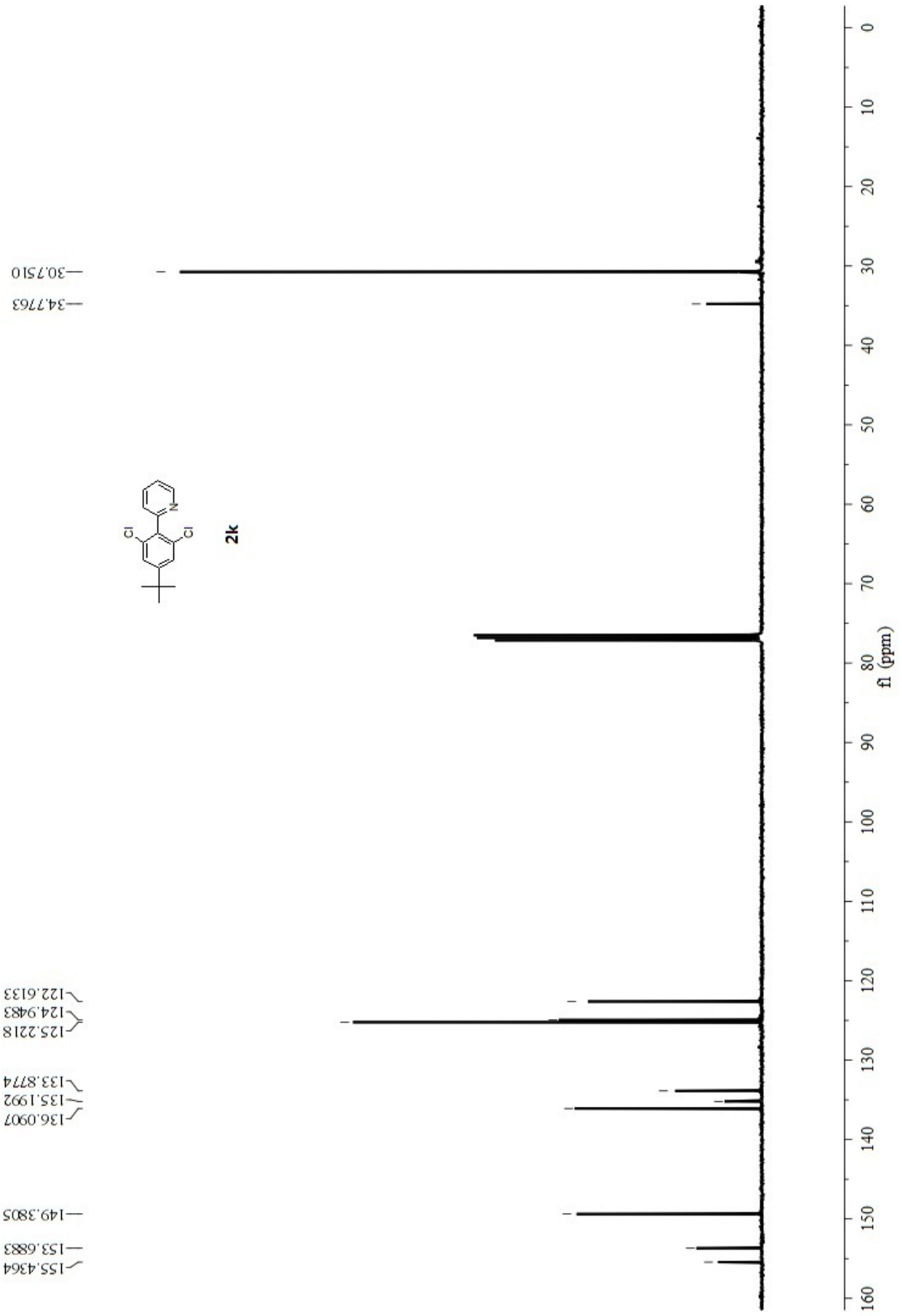

2j
8.5660
8.5643
8.5623
8.5609
7.5986
7.5972
7.5827
7.5788
7.5774
7.2216
7.2019
6.9530
3.8268
2.4060
1.00
1.05
1.01
2.04
3.22
3.13
f1 (ppm)

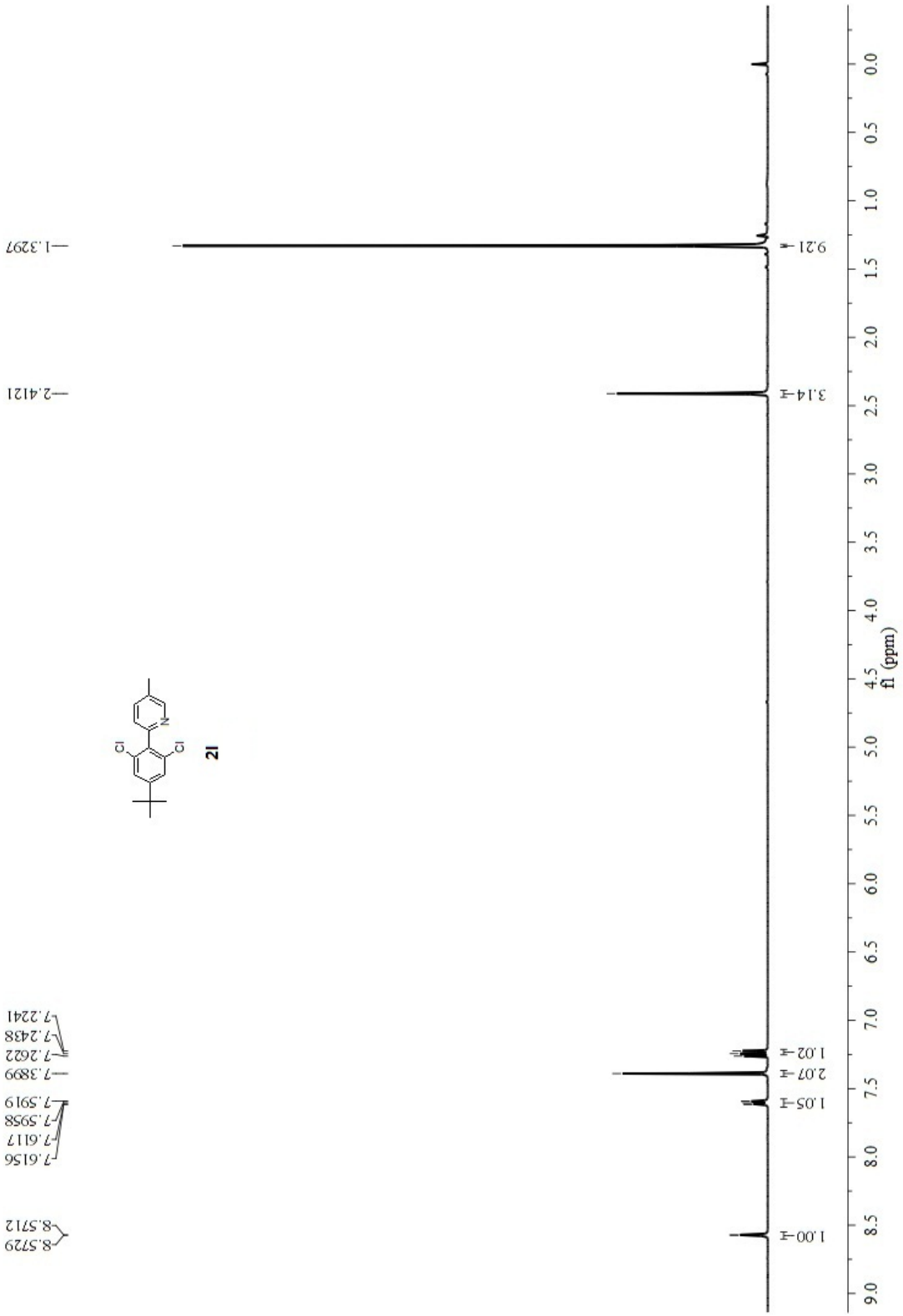
8.5660
8.5643
8.5623
8.5609
7.6025
7.5986
7.5972
7.5827
7.5788
7.5774
7.2646
7.2216
7.2019
6.9530
2j
1.00
1.05
1.01
2.04
f1 (ppm)


159.4131
152.3642
149.7619
136.6210
134.9449
132.1489
130.7863
124.7530
113.8694
55.6028
18.1519
Cl
O
N
Cl
2j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

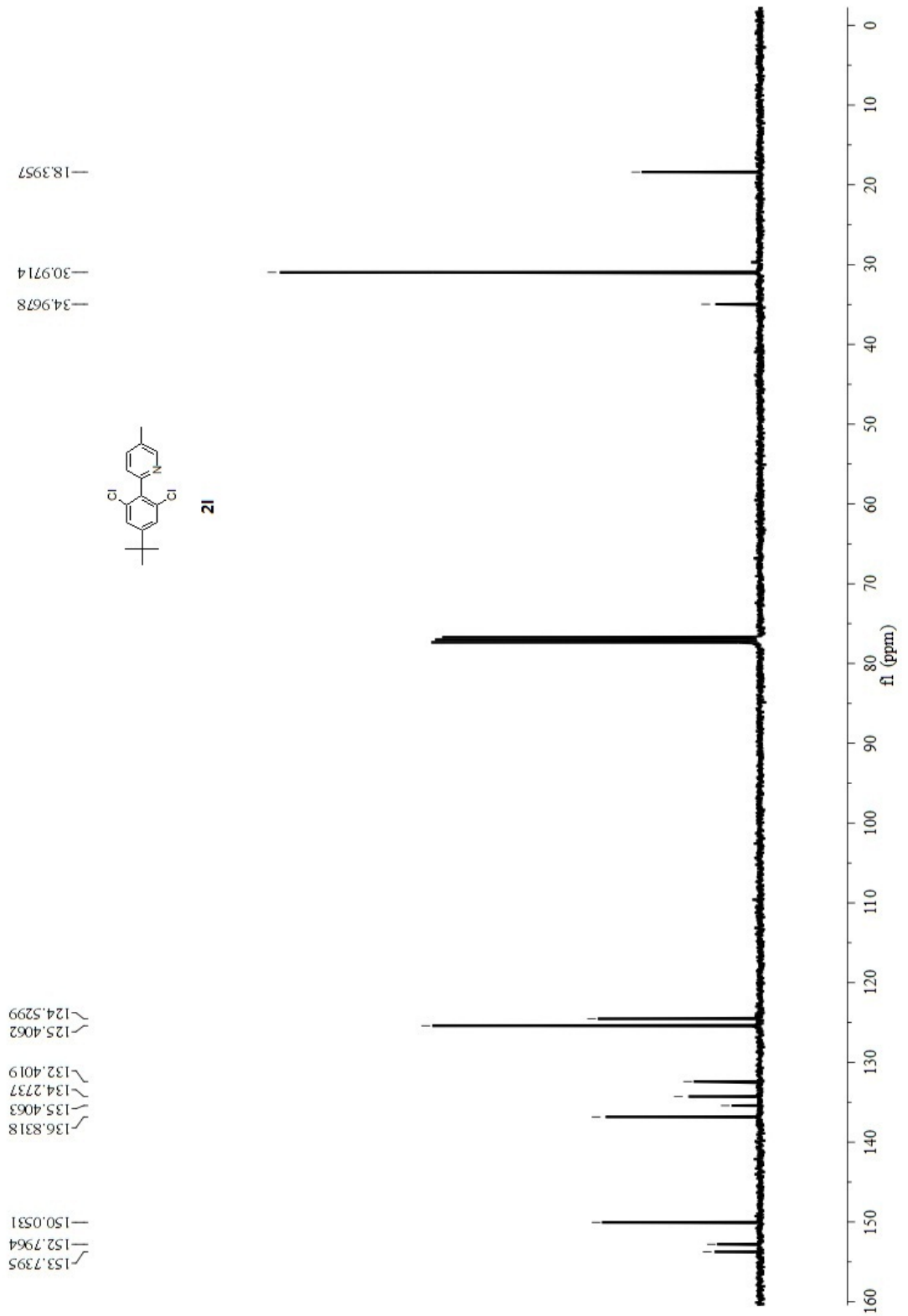

1.3347
9.17
8.7473
8.7356
7.8007
7.7979
7.7815
7.7787
7.4009
7.3467
7.3285
7.3130
7.2635
1.00
1.03
1.94
2.02
2k
f1 (ppm)

8.7356
8.7473
8.8199
8.8171
8.8007
7.7979
7.7815
7.7787
7.4009
7.3285
7.3130
7.2635
1.00
1.03
1.94
2.02
f1 (ppm)
2k


155.4364
153.6883
149.3805
136.0907
135.1992
133.8774
125.2218
124.9483
122.6133
34.7763
30.7510
2k
Cl
Cl
N
f1 (ppm)

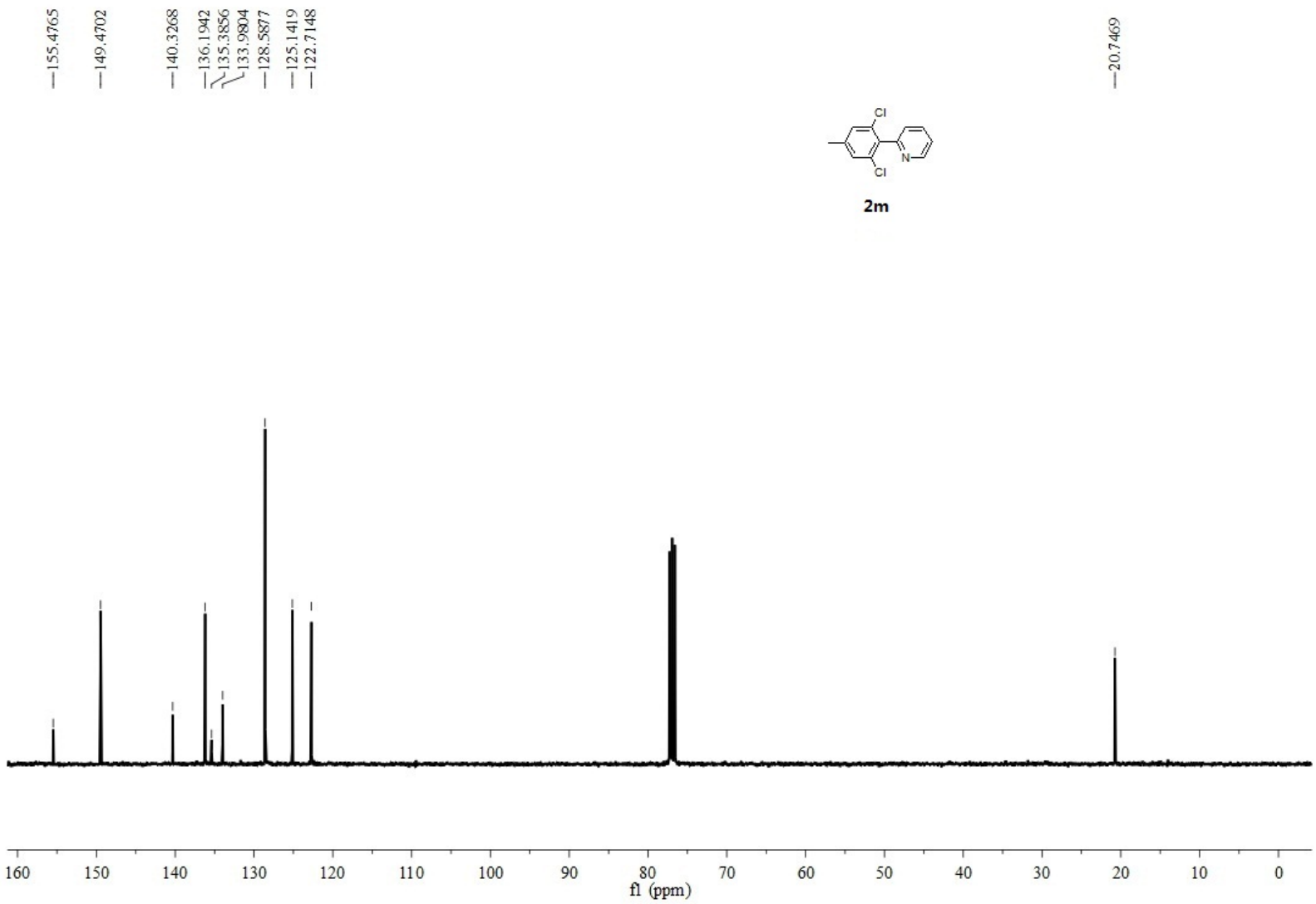

8.5729
8.5712
7.6156
7.6117
7.5958
7.5919
7.3899
7.2622
7.2438
7.2241
1.3297
2.4121
1.00
1.05
2.07
1.02
3.14
9.21
f1 (ppm)
2l

8.5729
8.5712
7.6156
7.6117
7.5958
7.5919
7.3899
7.2622
7.2438
7.2241
1.00
1.05
2.07
1.02
f1 (ppm)
2l

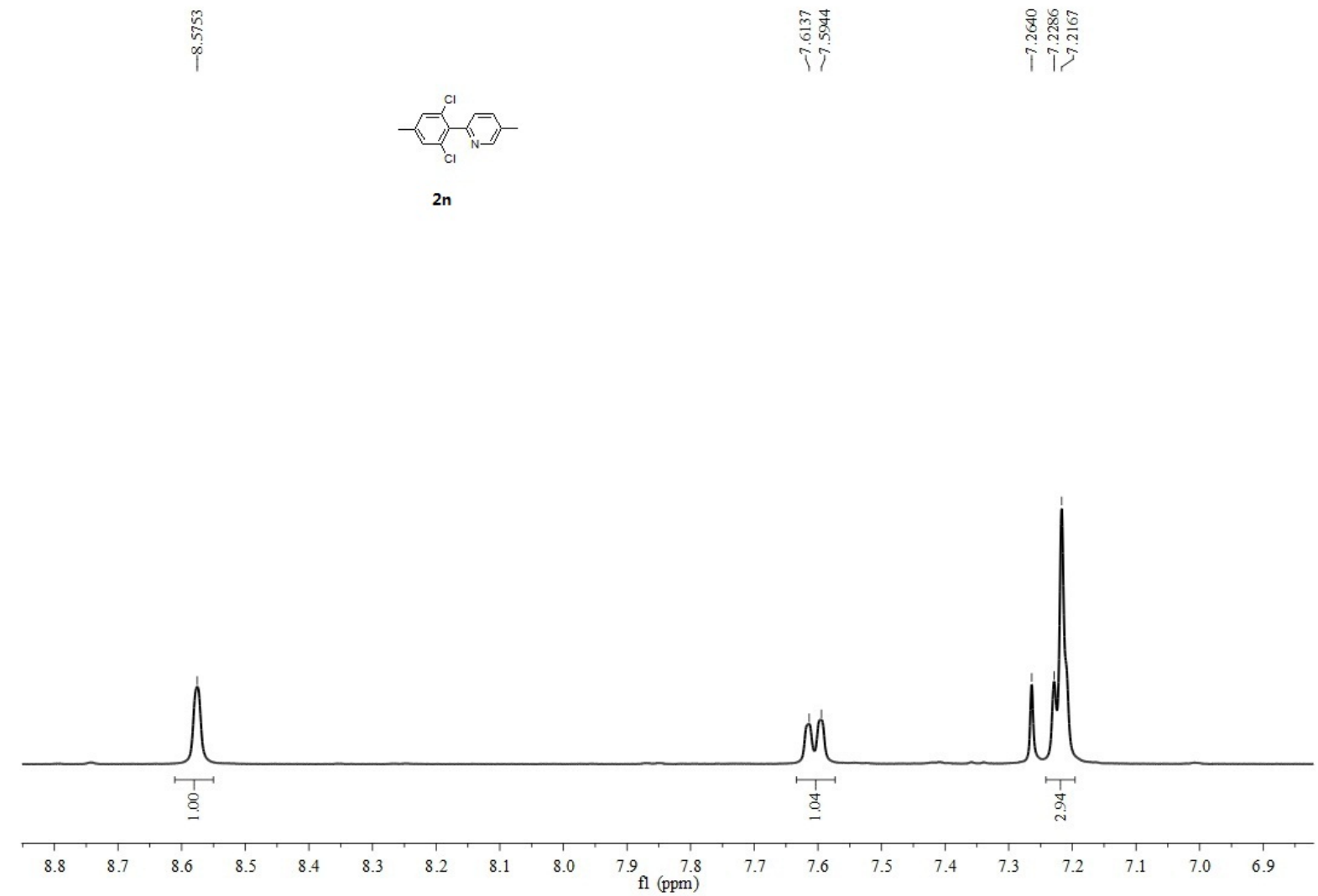

153.7395
152.7964
150.0531
136.8318
135.4063
134.2737
132.4019
125.4062
124.5299
34.9678
30.9714
18.3957
2l
Cl
Cl
N
f1 (ppm)

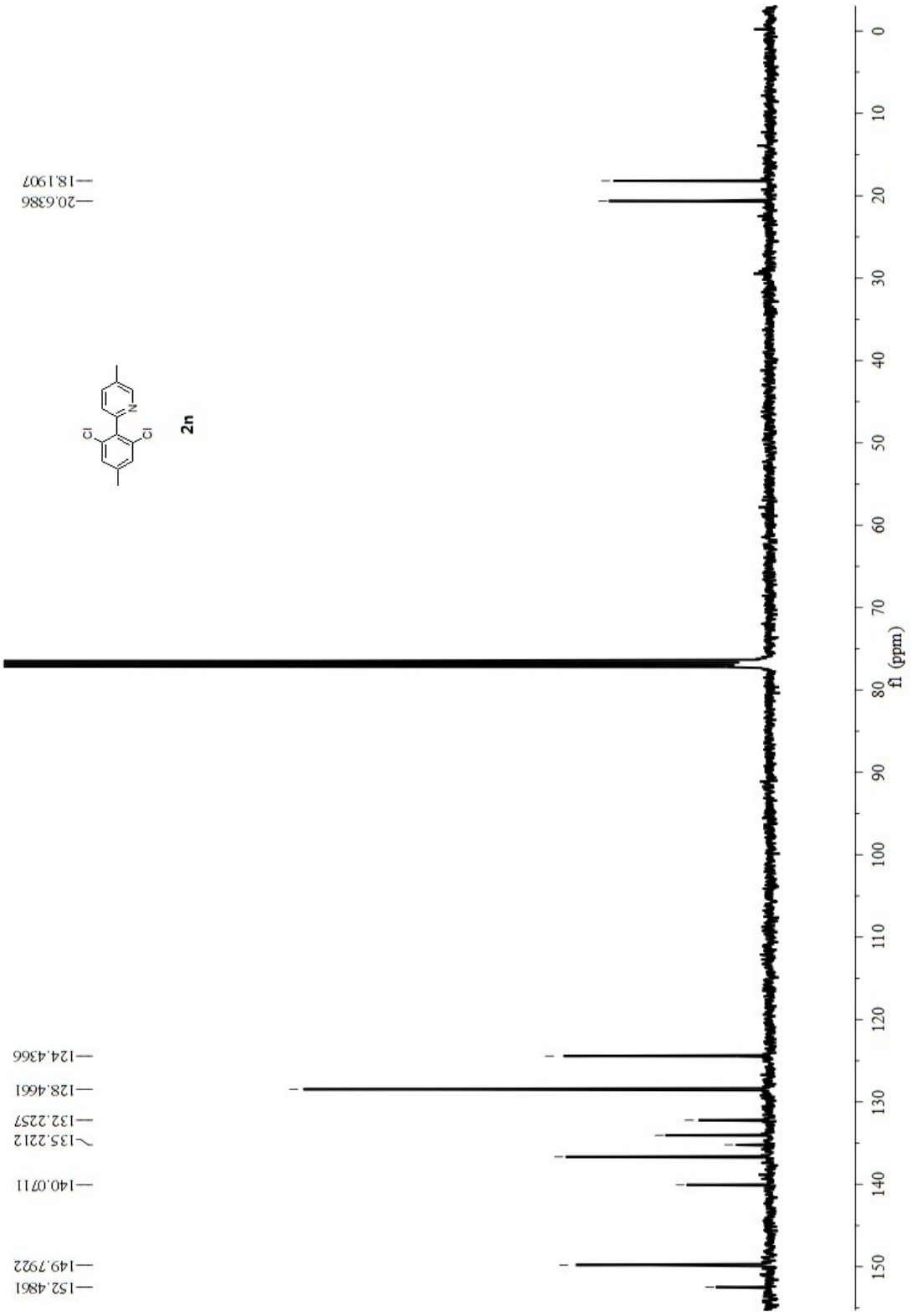
8.7511
8.7401
7.7972
7.7931
7.7779
7.7739
7.3415
7.3299
7.3107
7.2653
7.2265
2.3649
1.00
1.03
2.01
1.91
3.13
2m
Cl
Cl
N
f1 (ppm)

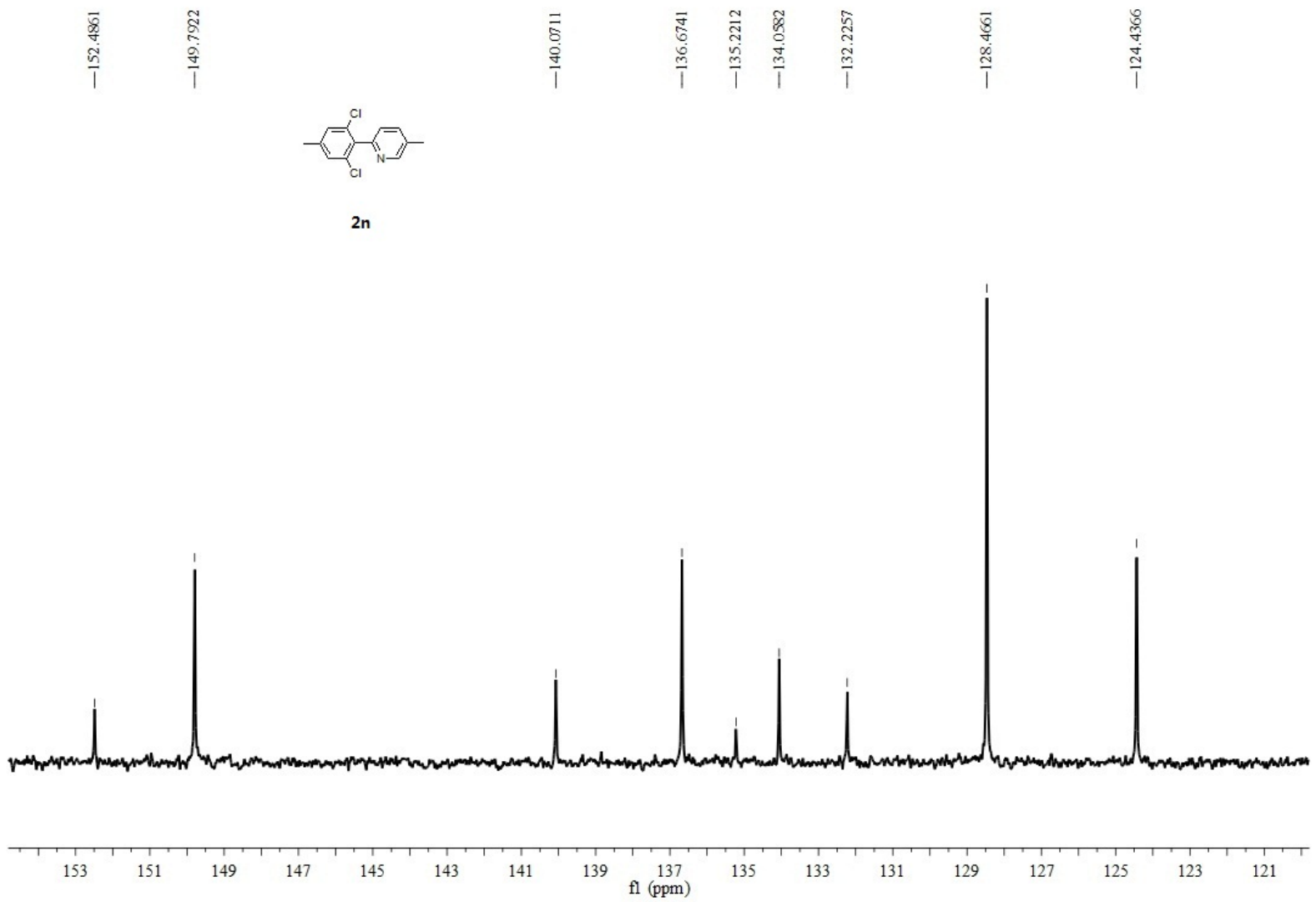
8.7511
8.7401
8.1640
8.1240
7.9972
7.9931
7.7779
7.7739
7.3415
7.3299
7.3107
7.2653
7.2265
2m
Cl
Cl
N
1.00
1.03
2.01
1.91
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)


155.4765
149.4702
140.3268
136.1942
135.3856
133.9804
128.5877
125.1419
122.7148
20.7469
Cl
Cl
N
2m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

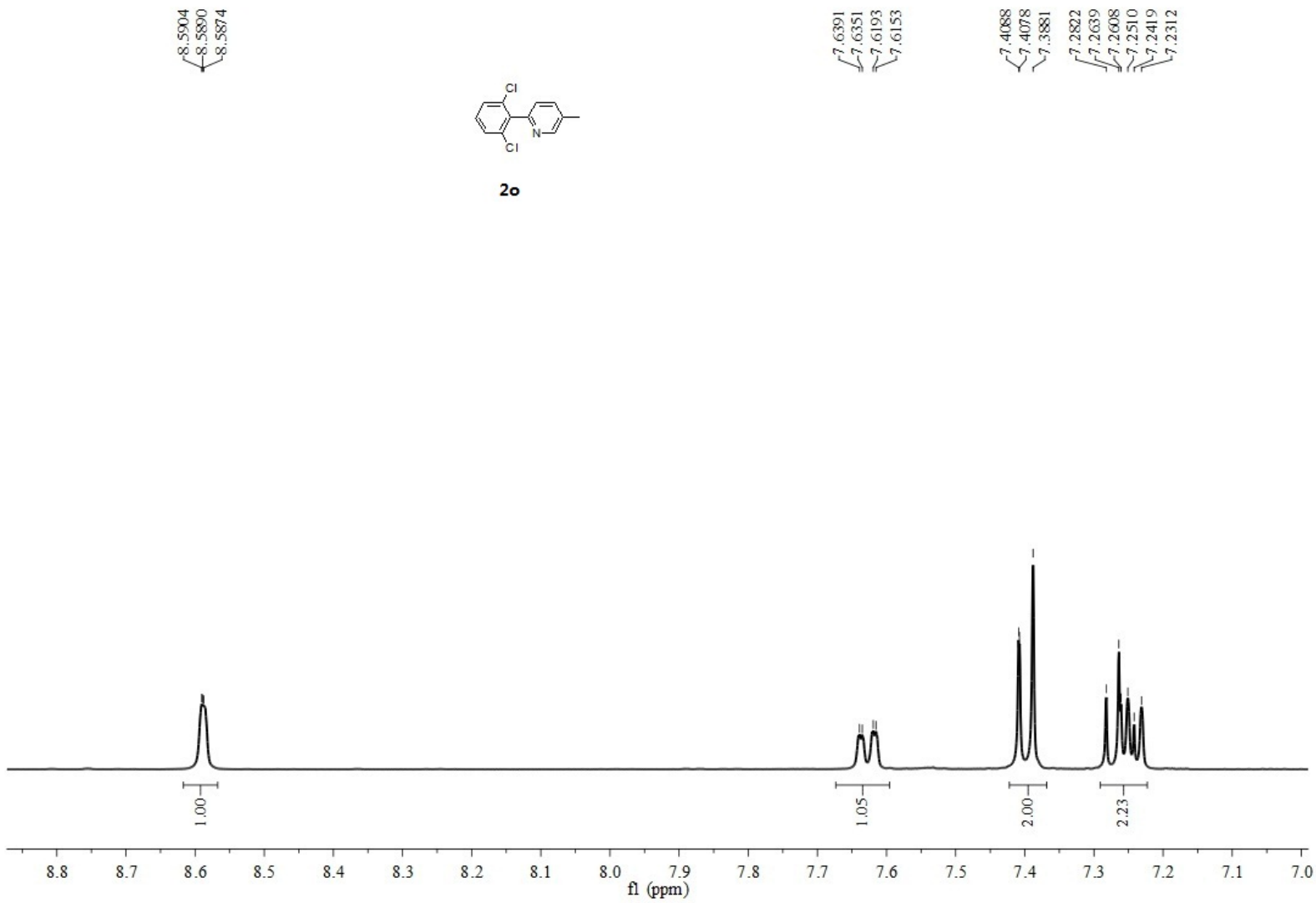
8.5753
7.6137
7.5944
7.2640
7.2286
7.2167
2.4144
2.3605
2n
1.00
1.04
2.94
3.01
3.07
f1 (ppm)


8.5753
7.6137
7.5944
7.2640
7.2286
7.2167
Cl
Cl
N
2n
1.00
1.04
2.94
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)

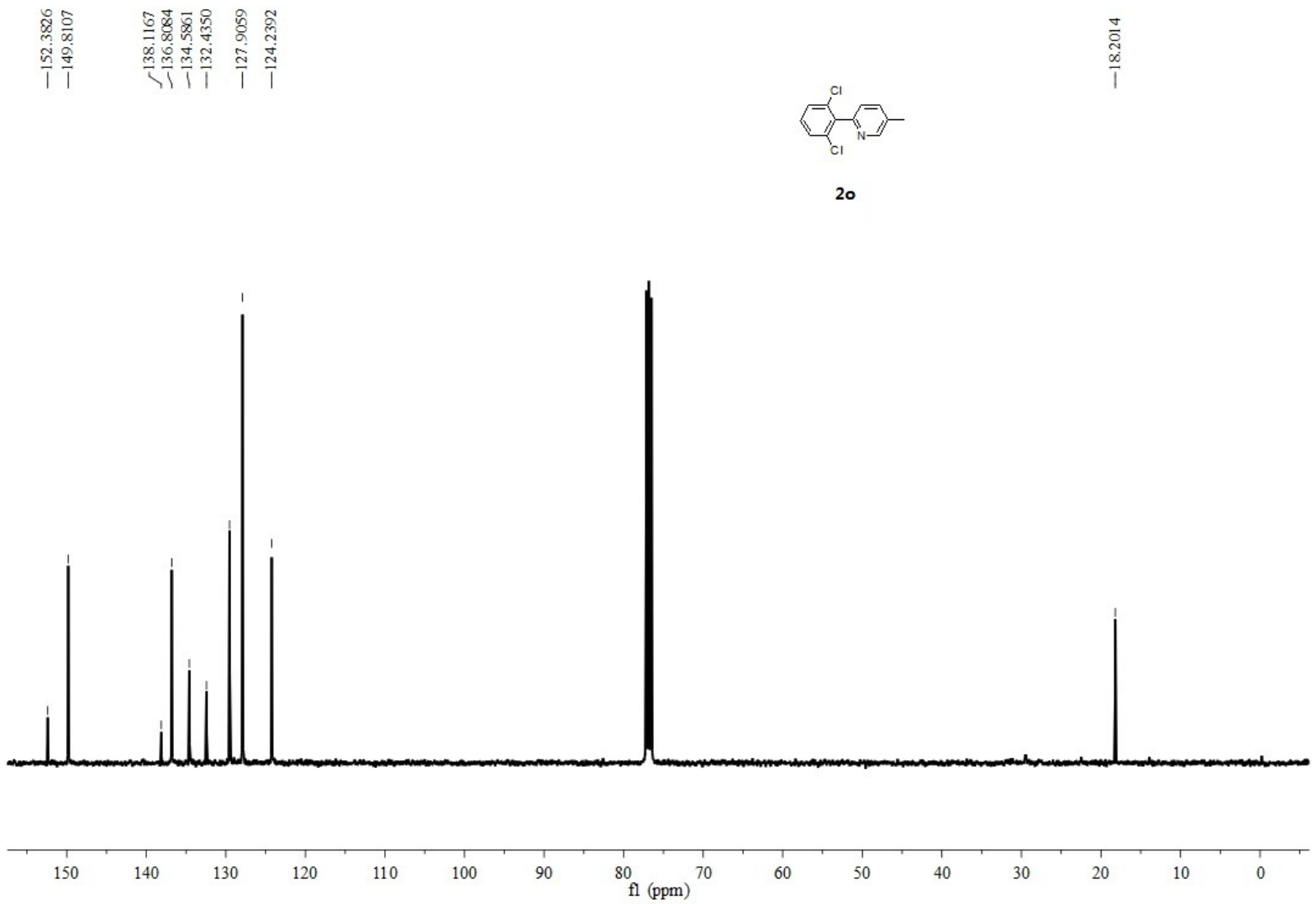

18.1907
20.6386
2n
Cl
Cl
N
152.4861
149.7922
140.0711
135.2212
132.2257
128.4661
124.4366
f1 (ppm)

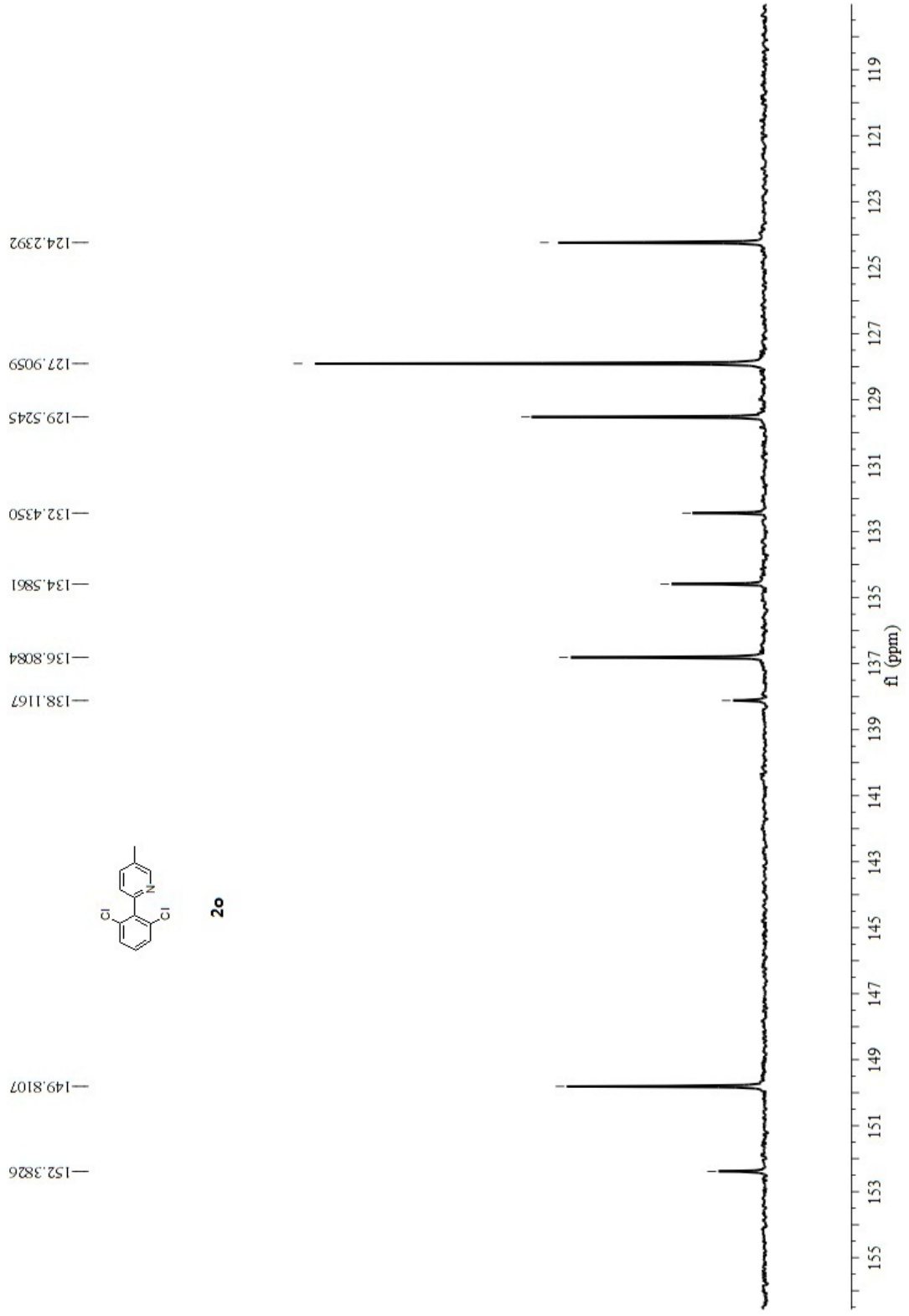

152.4861
149.7922
140.0711
136.6741
135.2212
134.0882
132.2257
128.4661
124.4366
Cl
Cl
N
2n
153
151
149
147
145
143
141
139
137
135
133
131
129
127
125
123
121
f1 (ppm)

8.5904
8.5890
8.5874
7.6391
7.6351
7.6193
7.6153
7.4088
7.4078
7.3881
7.2822
7.2639
7.2608
7.2510
7.2419
7.2312
2.4232
2o
3.11
1.00
2.23
2.00
1.05
1.00
f1 (ppm)

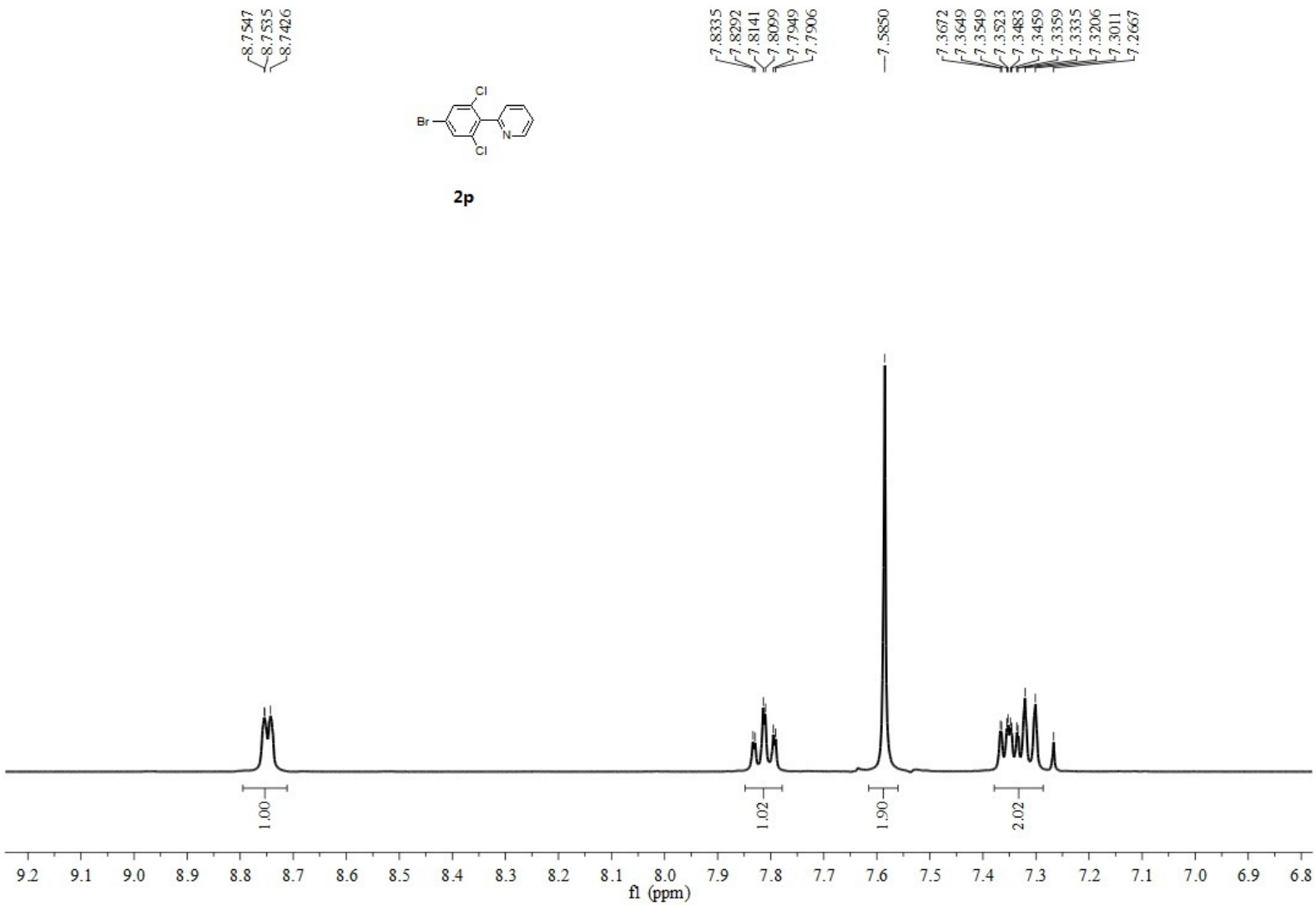

8.5904
8.5890
8.5874
7.6391
7.6351
7.6193
7.6153
7.4088
7.4078
7.3881
7.2822
7.2639
7.2608
7.2510
7.2419
7.2312
Cl
Cl
N
1.00
1.05
2.00
2.23
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
f1 (ppm)

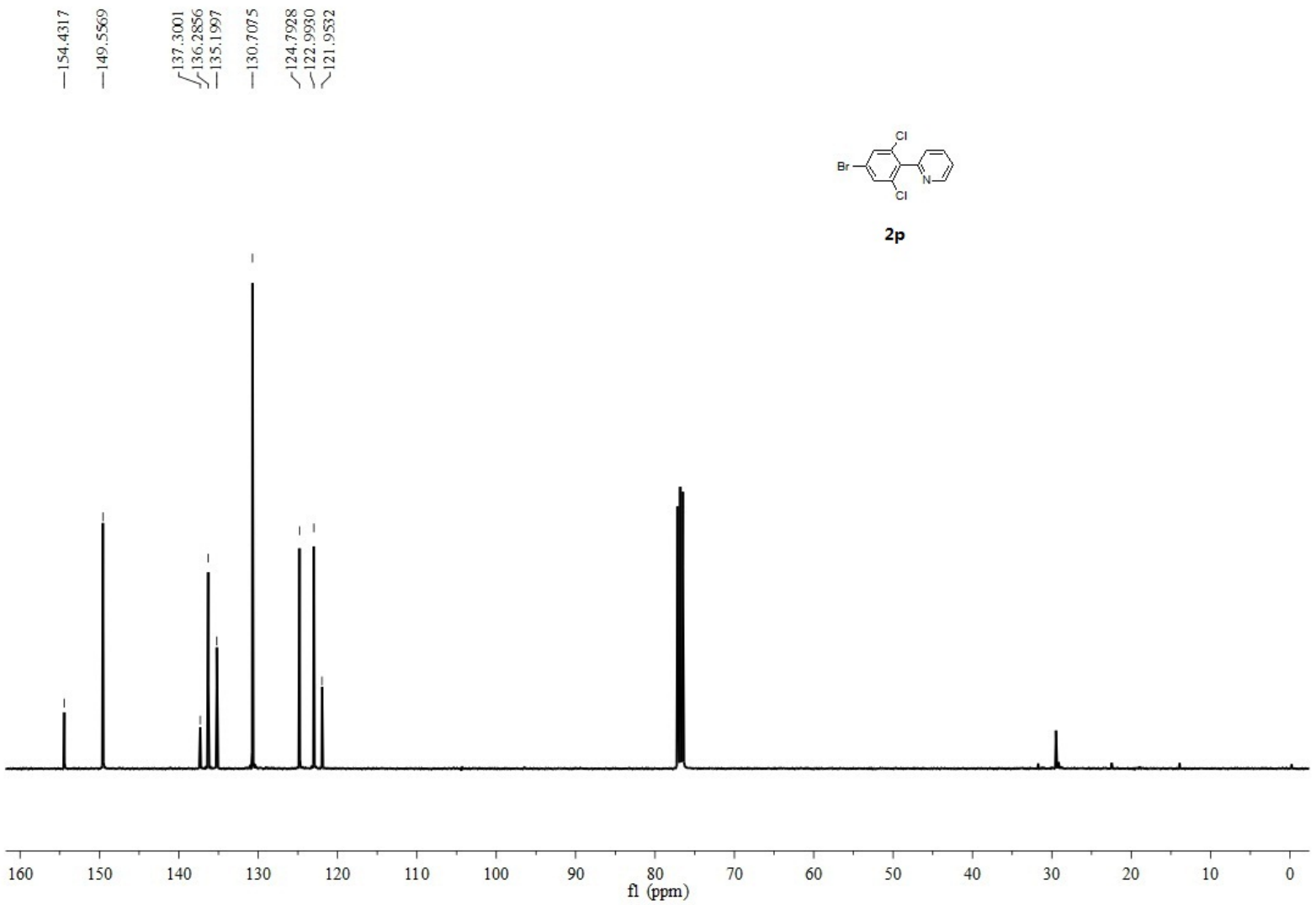
2o


152.3826
149.8107
138.1167
136.8084
134.5861
132.4350
127.9059
124.2392
18.2014
Cl
Cl
N
2o
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


124.2392
127.9059
129.5245
132.4350
134.5861
136.8084
138.1167
149.8107
152.3826
2o
Cl
Cl
N
155
153
151
149
147
145
143
141
139
137
135
133
131
129
127
125
123
121
119
f1 (ppm)

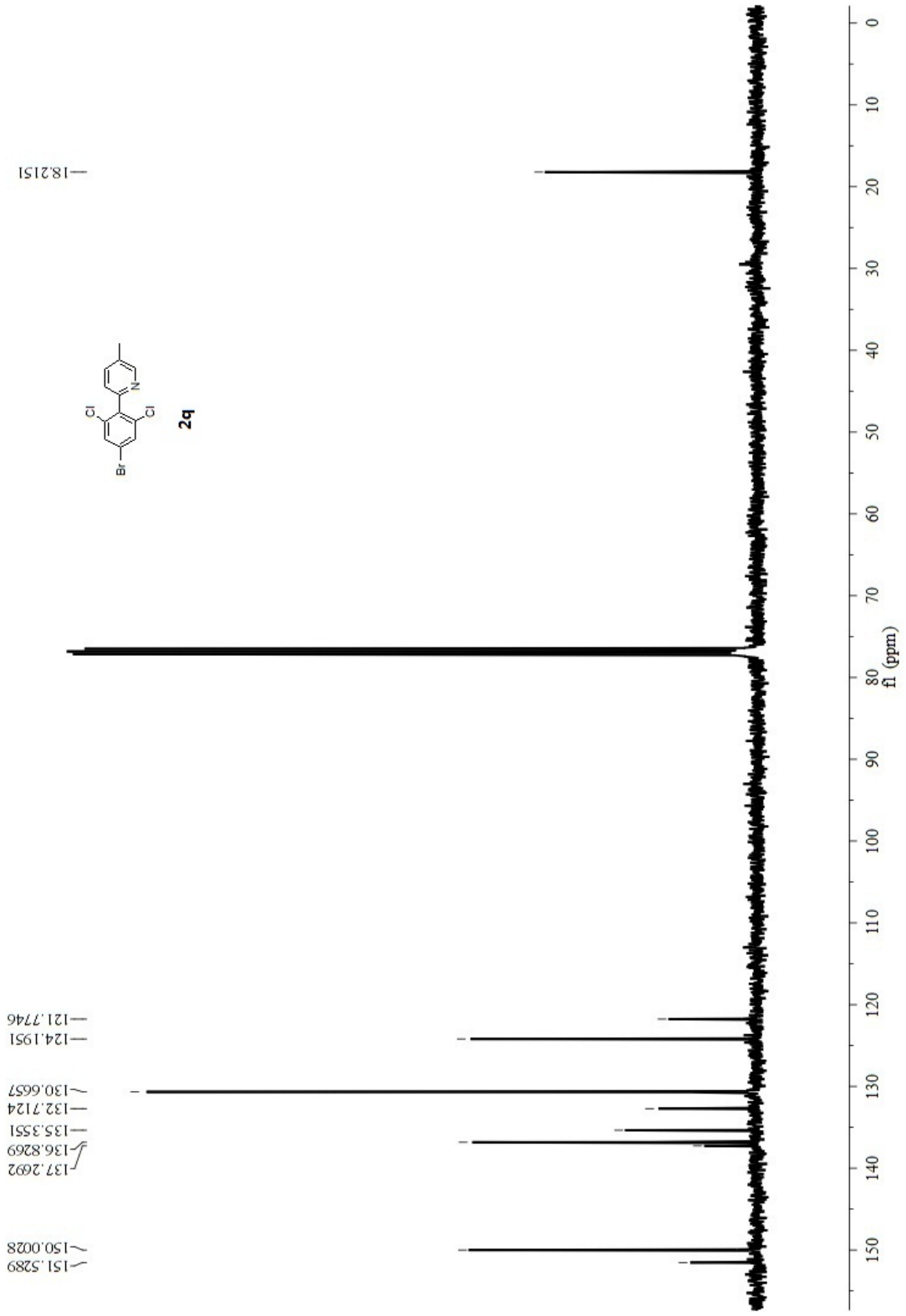
8.7547
8.7535
8.7426
7.8141
7.8099
7.7949
7.7906
7.5850
7.3672
7.3649
7.3549
7.3523
7.3483
7.3459
7.3359
7.3335
7.3206
7.3011
7.2667
Cl
Cl
Br
N
2p
1.00
1.02
1.90
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


8.7547
8.7535
8.7426
7.8335
7.8292
7.8141
7.8099
7.7949
7.7906
7.5850
7.3672
7.3649
7.3549
7.3523
7.3483
7.3459
7.3359
7.3335
7.3206
7.3011
7.2667
Cl
Br
N
Cl
2p
1.00
1.02
1.90
2.02
9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)


154.4317
149.5569
137.3001
136.2856
135.1997
130.7075
124.7928
122.9930
121.9532
Cl
Br
N
Cl
2p
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

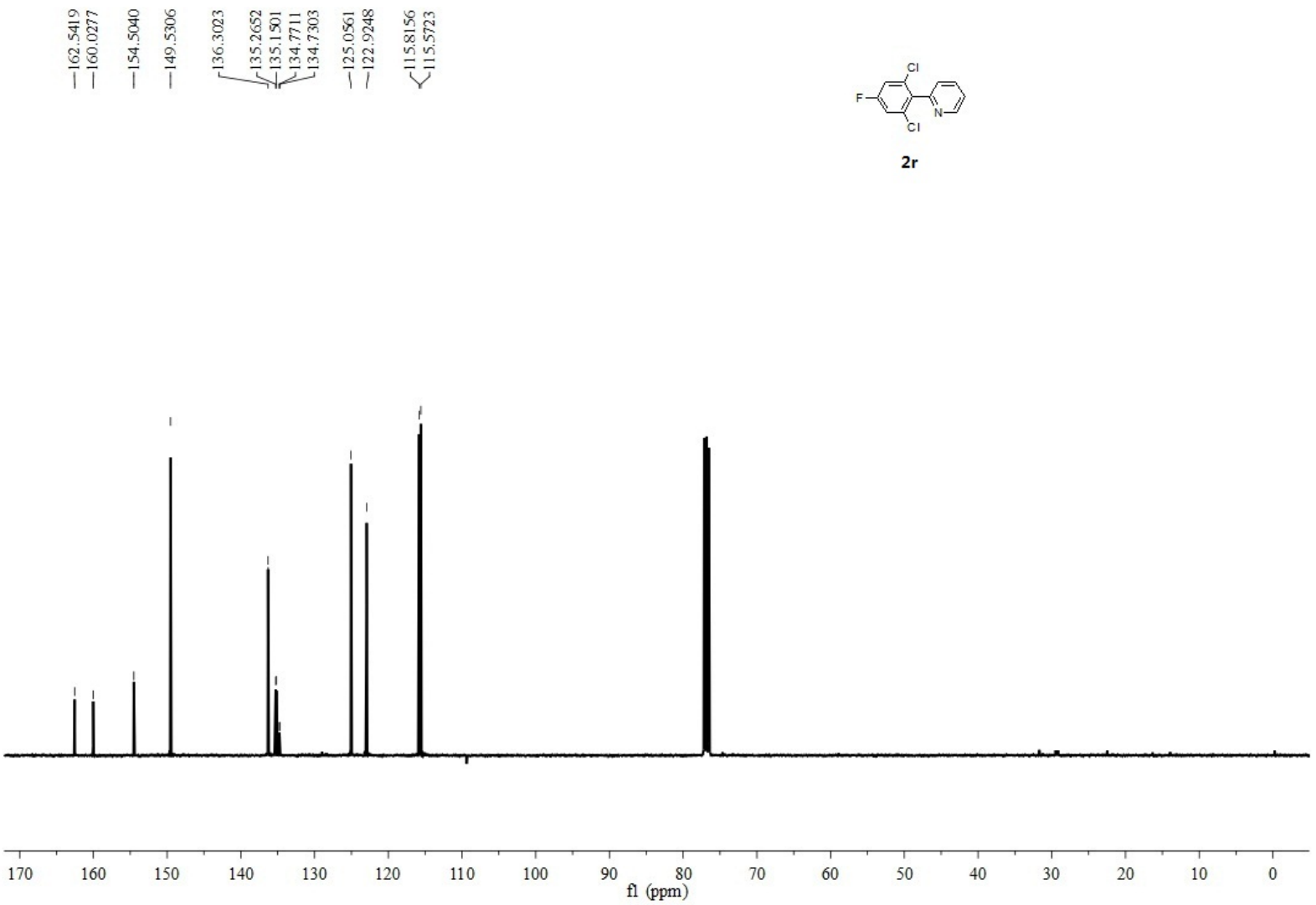
8.5796
8.5783
7.6341
7.6306
7.6144
7.5756
7.2658
7.2197
7.2000
2.4218
1.00
3.04
0.98
3.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
Cl
Cl
Br
N
2q

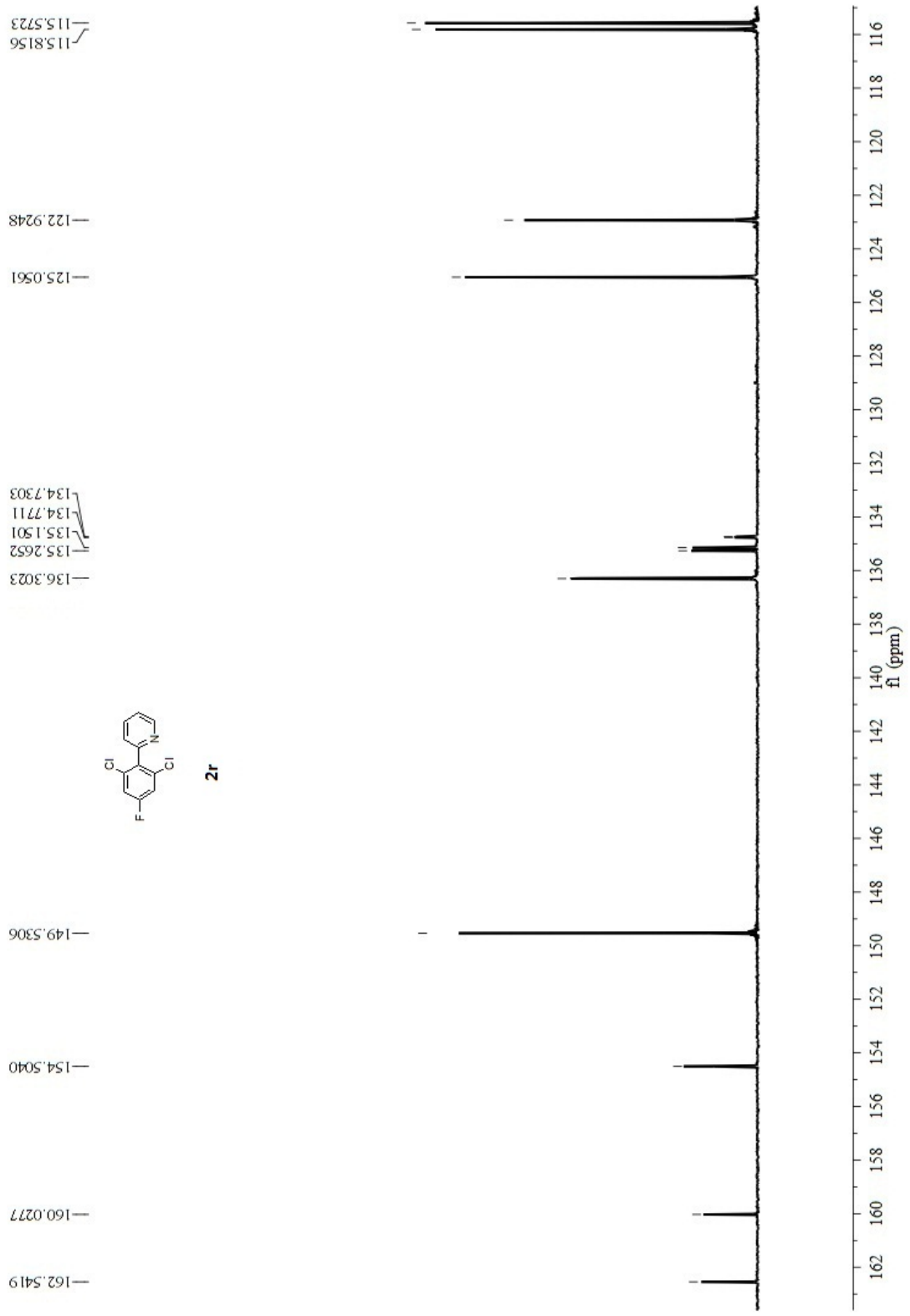
8.5796
8.5783
7.6341
7.6306
7.6144
7.5756
7.2658
7.2197
7.2000
1.00
3.04
0.98
f1 (ppm)
2q


151.5289
150.0028
137.2692
136.8269
135.3551
132.7124
130.6657
124.1951
121.7746
18.2151
2q
Cl
Cl
Br
N
f1 (ppm)

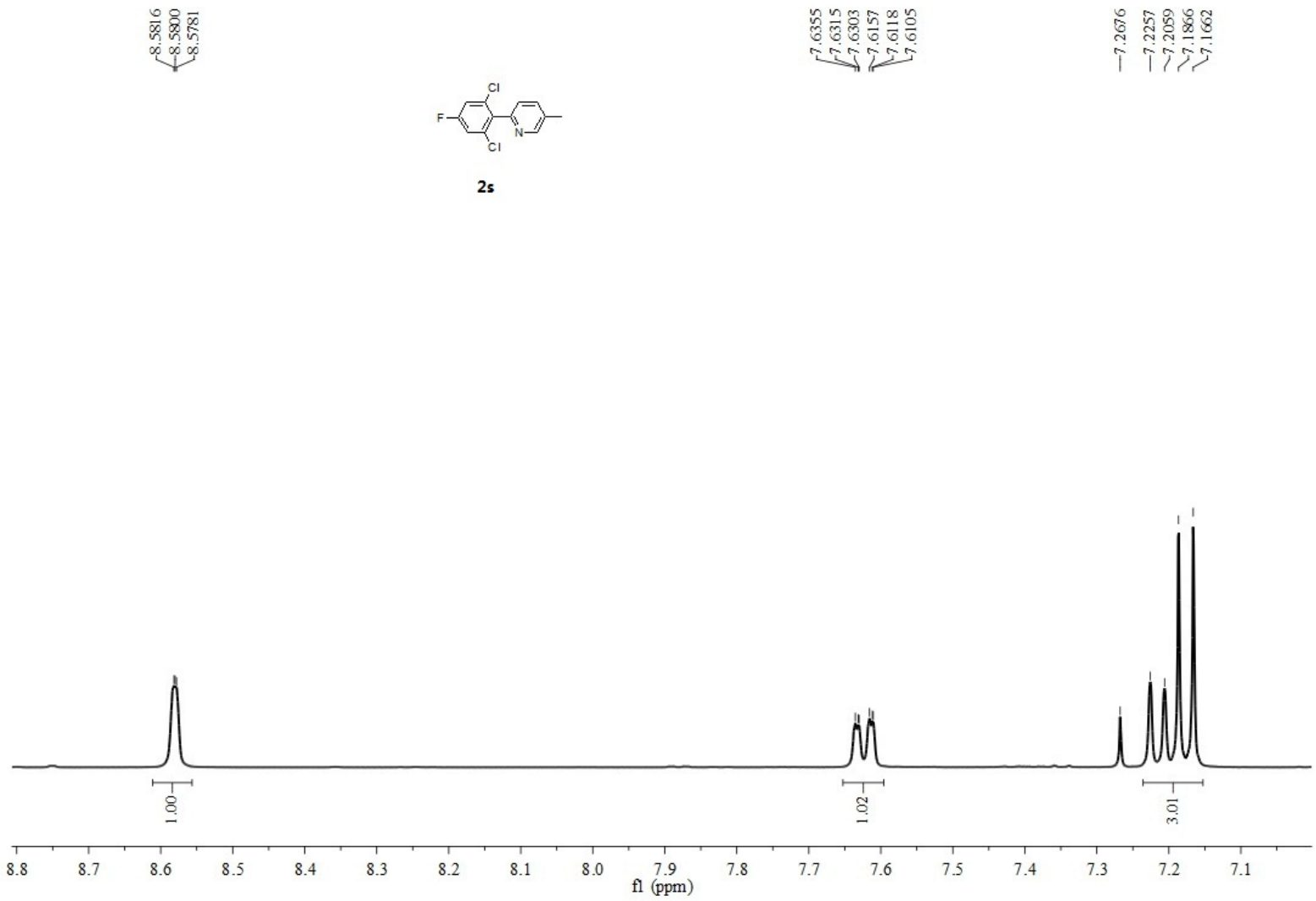
8.7574
8.7460
7.8200
7.8166
7.8008
7.7973
7.3696
7.3568
7.3521
7.3315
7.3119
7.2690
7.1976
7.1771
Cl
Cl
F
N
2r
1.00
1.02
2.05
1.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

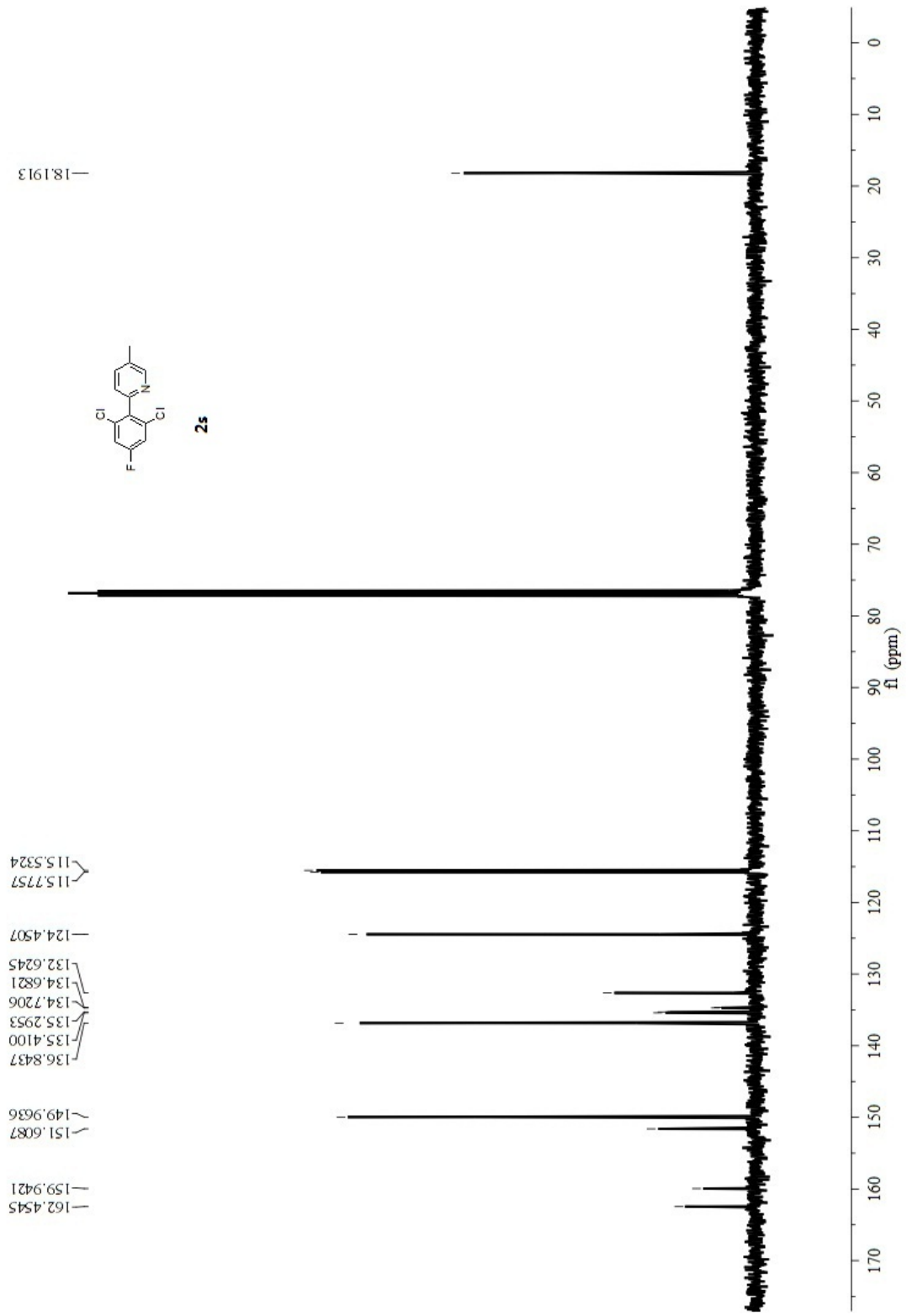
8.7574
8.7460
7.8393
7.8358
7.8200
7.8166
7.8008
7.7973
7.3696
7.3568
7.3321
7.3315
7.3119
7.2690
7.1976
7.1771
2r
1.00
1.02
2.05
1.99
f1 (ppm)

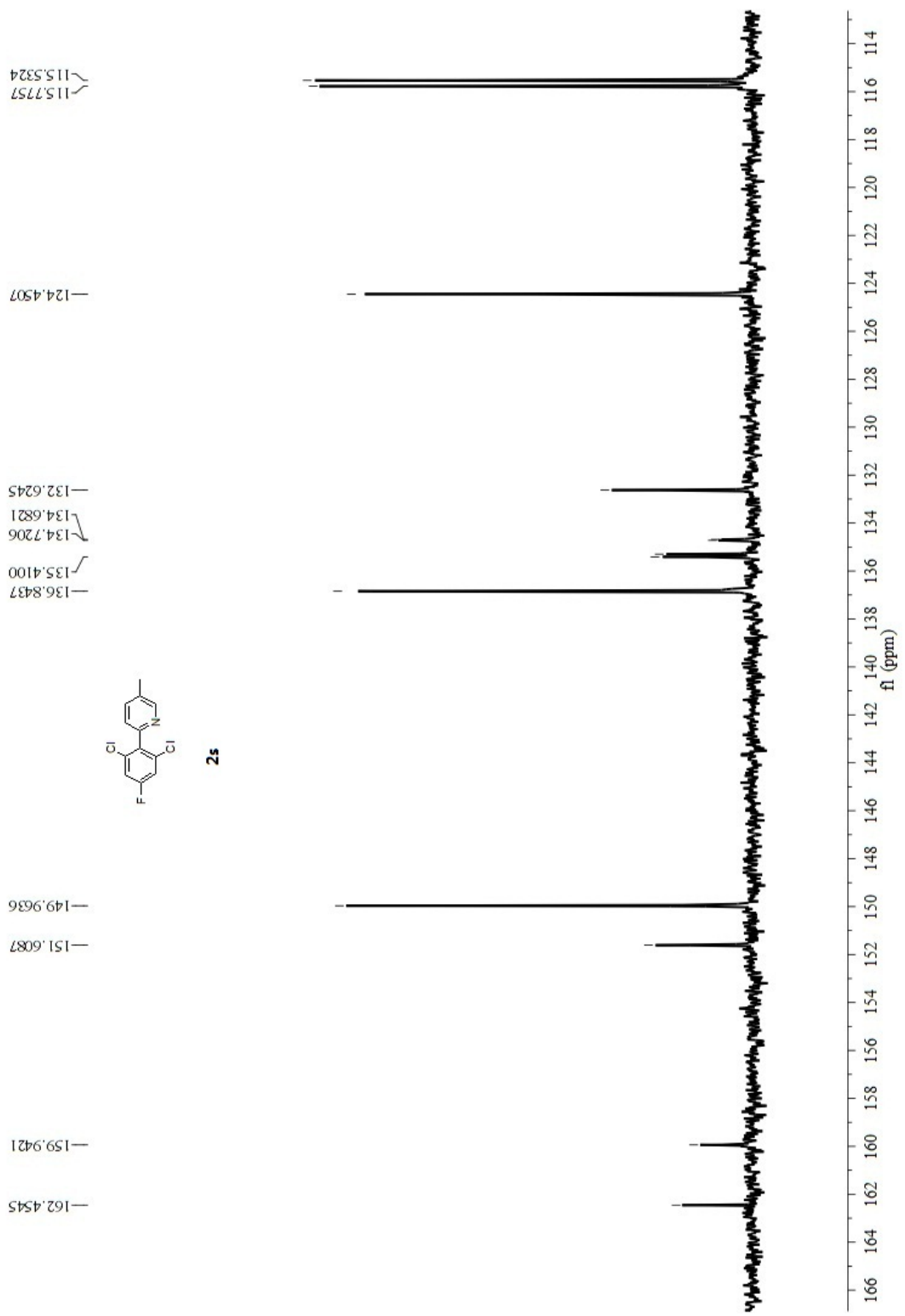

162.5419
160.0277
154.5040
149.5306
136.3023
135.2652
135.1501
134.7711
134.7303
125.0561
122.9248
115.8156
115.5723
Cl
F
Cl
N
2r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

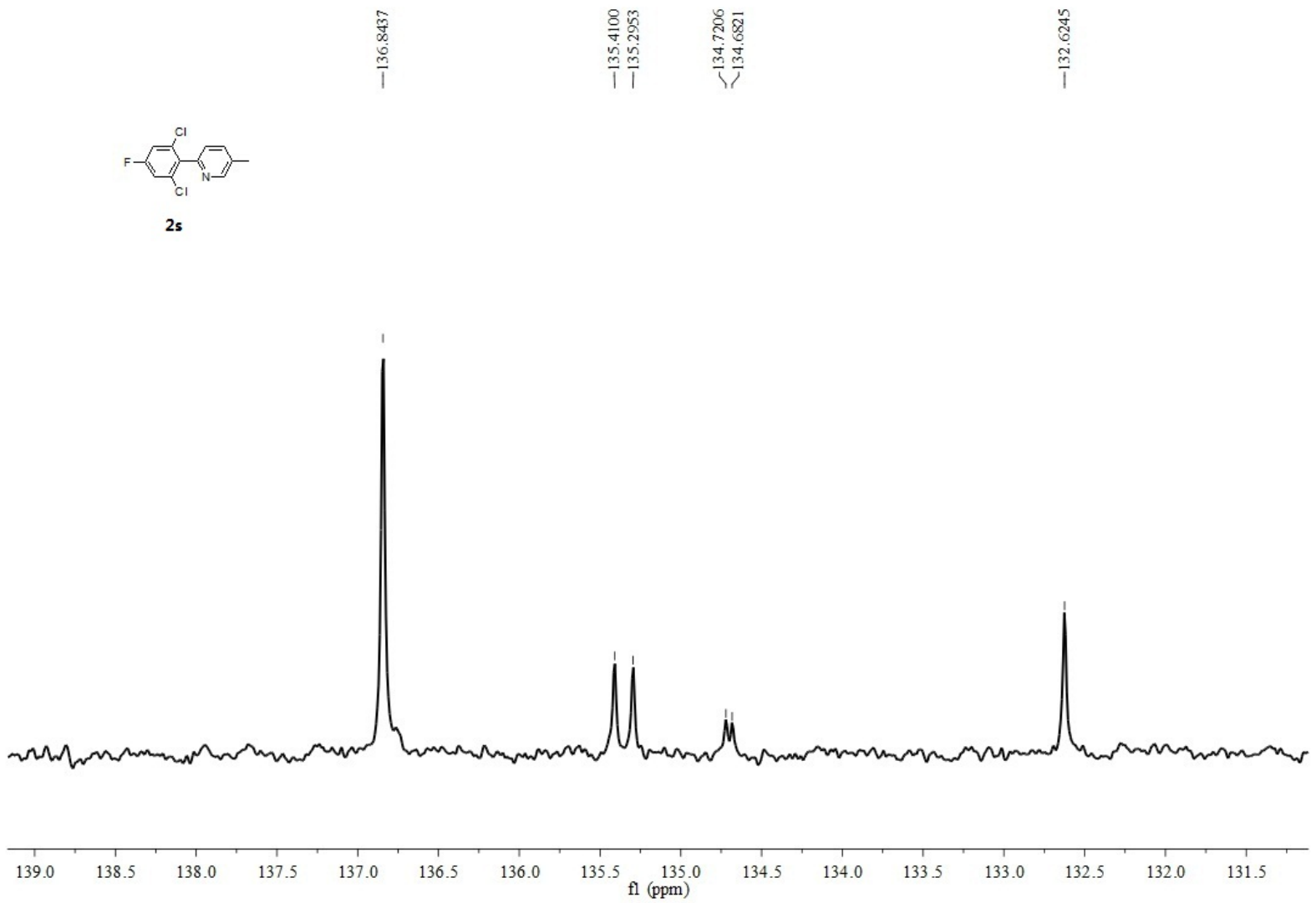

162.5419
160.0277
154.5040
149.5306
136.3023
135.2652
135.1501
134.7711
134.7303
125.0561
122.9248
115.8156
115.5723
2r
F
Cl
Cl
N
162 160 158 156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116
f1 (ppm)

8.5816
8.5800
8.5781
7.6355
7.6157
7.6118
7.6105
7.2676
7.2257
7.2059
7.1866
7.1662
2.4221
Cl
Cl
F
N
2s
3.15
3.01
1.02
1.00
f1 (ppm)


8.5816
8.5800
8.5781
7.6355
7.6315
7.6303
7.6157
7.6118
7.6105
7.2676
7.2257
7.2059
7.1866
7.1662
Cl
F
Cl
N
2s
1.00
1.02
3.01
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)

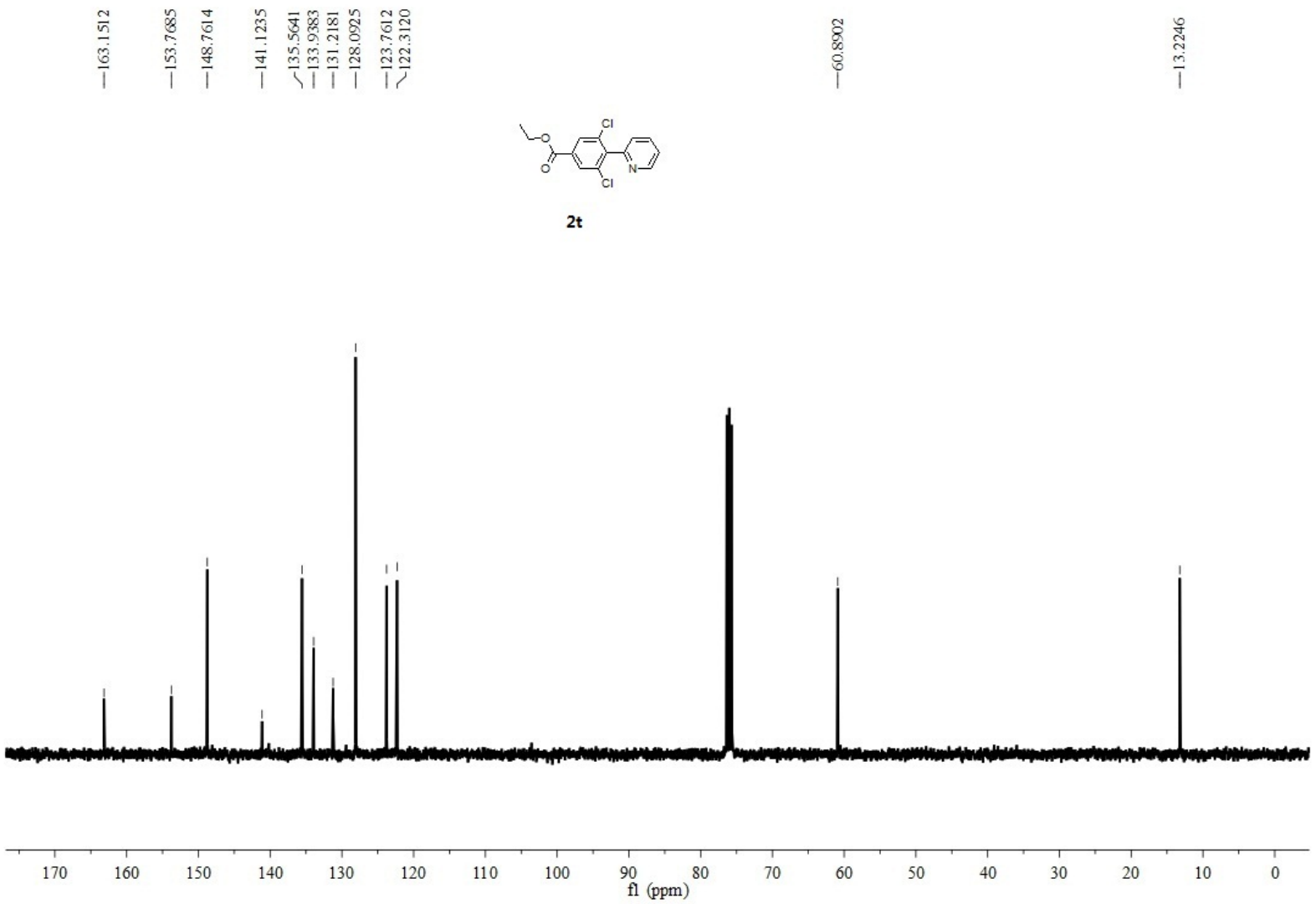

18.1913
115.5324
115.7757
124.4507
132.6245
134.6821
134.7206
135.2953
135.4100
136.8437
149.9636
151.6087
159.9421
162.4545
2s
Cl
Cl
F
N
f1 (ppm)


162.4545
159.9421
151.6087
149.9636
136.8437
135.4100
134.7206
134.6821
132.6245
124.4507
115.7757
115.5324
2s
f1 (ppm)


136.8437
135.4100
135.2953
134.7206
134.6821
132.6245
Cl
F
N
Cl
2s
139.0
138.5
138.0
137.5
137.0
136.5
136.0
135.5
135.0
134.5
134.0
133.5
133.0
132.5
132.0
131.5
f1 (ppm)

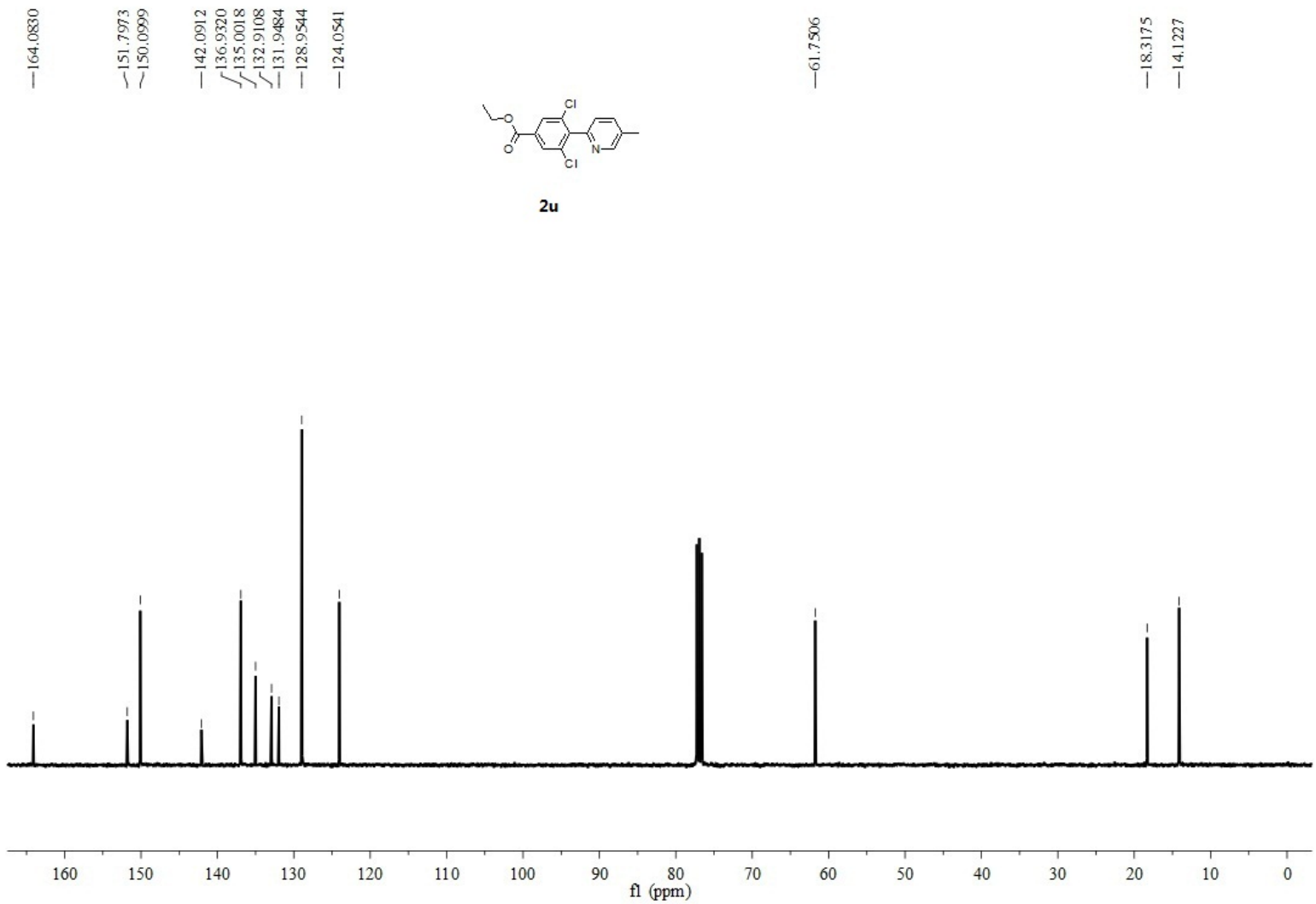
8.7807
8.7795
8.7687
8.0725
7.8233
7.3981
7.3955
7.3858
7.3831
7.3790
7.3764
7.3666
7.3641
7.3519
7.3325
7.2718
4.4480
4.4301
4.4123
4.3945
1.4447
1.4269
1.4090
2t
1.00
1.95
1.05
2.05
2.07
3.18
f1 (ppm)

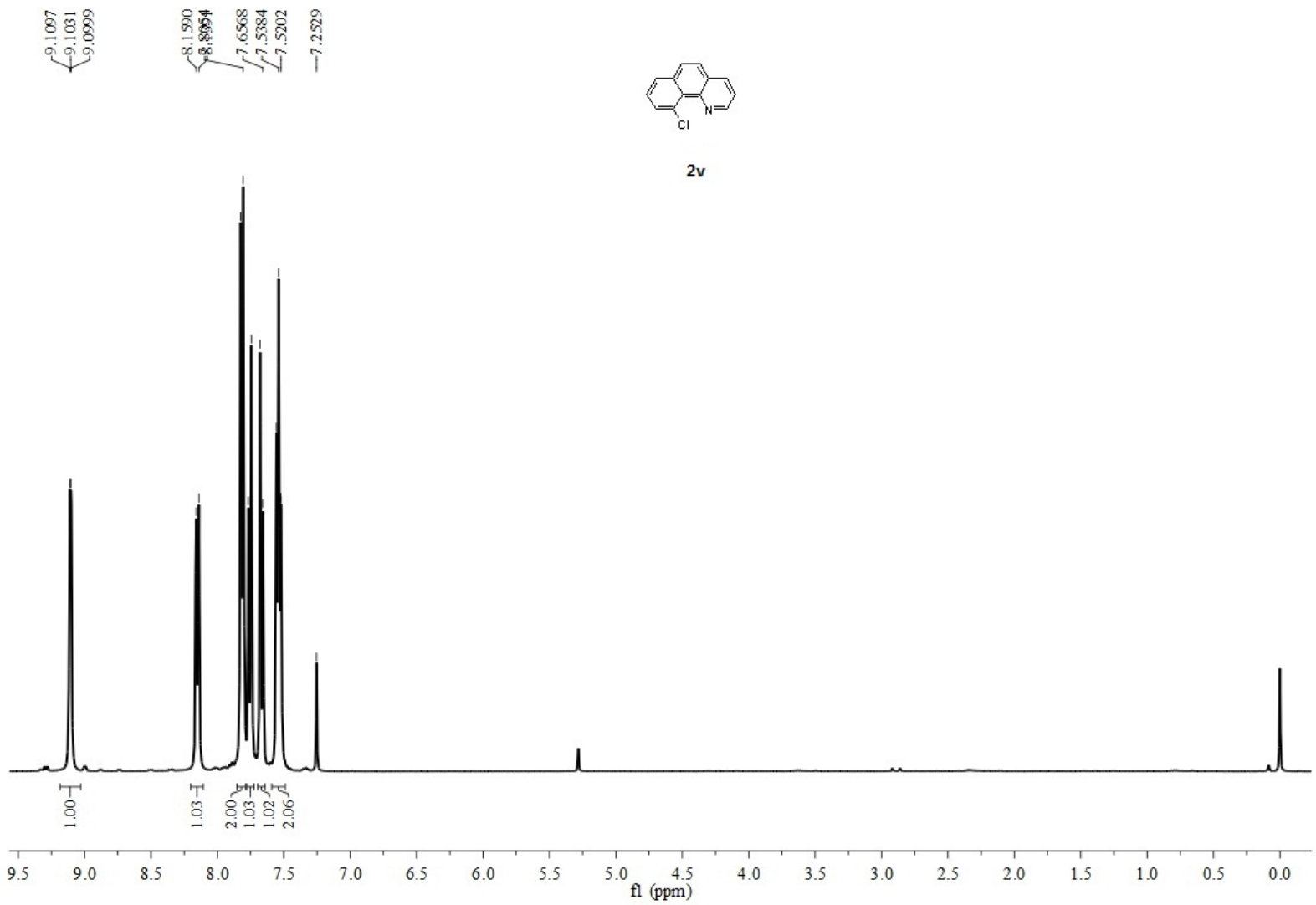
8.7807
8.7795
8.7687
8.0725
7.8663
7.8620
7.8470
7.8427
7.8277
7.8233
7.3981
7.3955
7.3858
7.3831
7.3790
7.3764
7.3666
7.3641
7.3519
7.3325
7.2718
2t
1.00
1.95
1.05
2.05
f1 (ppm)

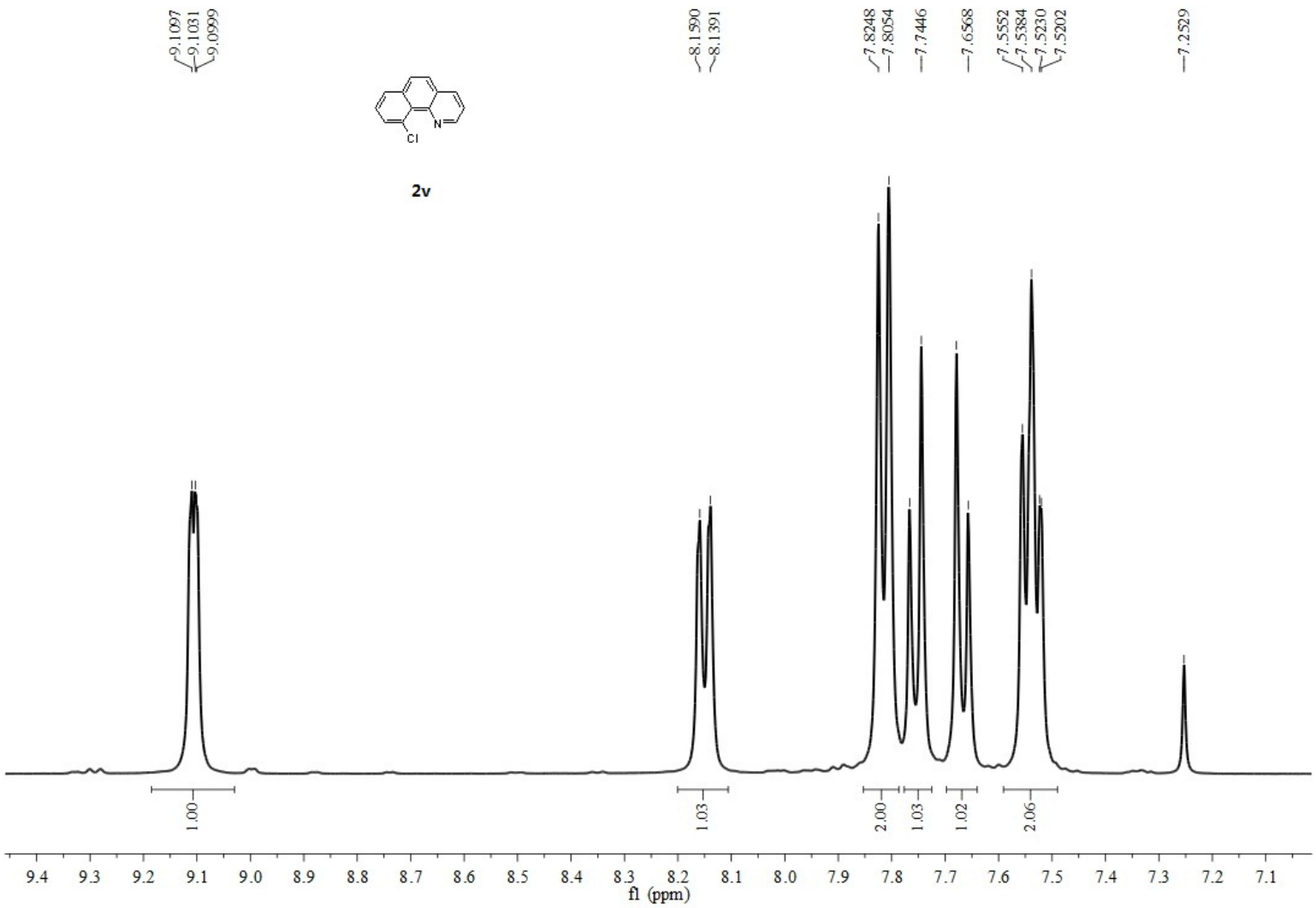

163.1512
153.7685
148.7614
141.1235
135.5641
133.9383
131.2181
128.0925
123.7612
122.3120
60.8902
13.2246
Cl
O
O
N
Cl
2t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

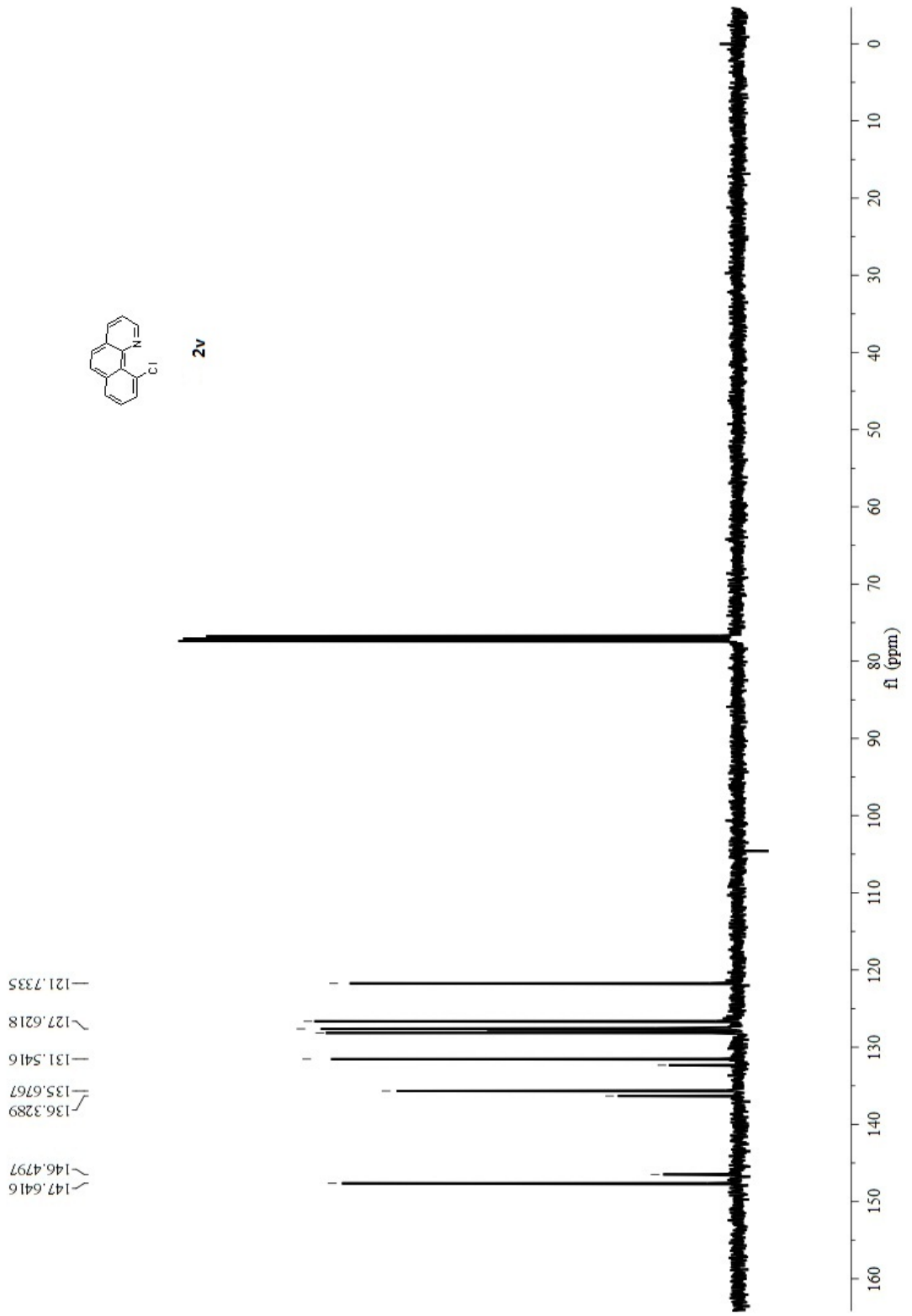
8.5987
8.0598
7.6537
7.6344
7.2716
7.2456
7.2259
4.4419
4.4241
4.4064
4.3886
2.4340
1.4407
1.4229
1.4052
1.00
1.92
1.01
1.14
2.06
3.00
3.05
f1 (ppm)
2u

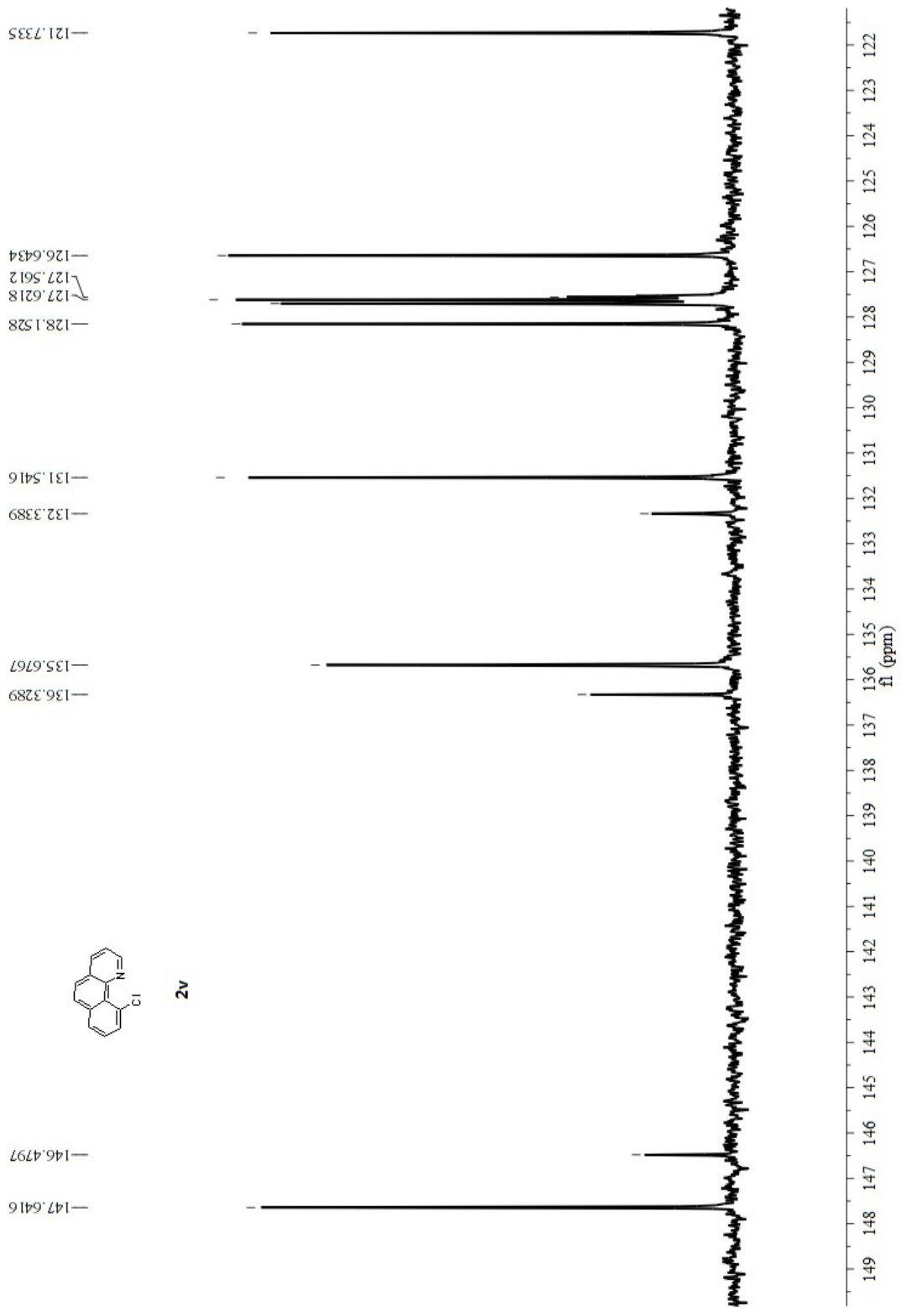
8.5987
8.0598
7.6537
7.6344
7.2716
7.2456
7.2259
2u
1.00
1.92
1.01
1.14
f1 (ppm)

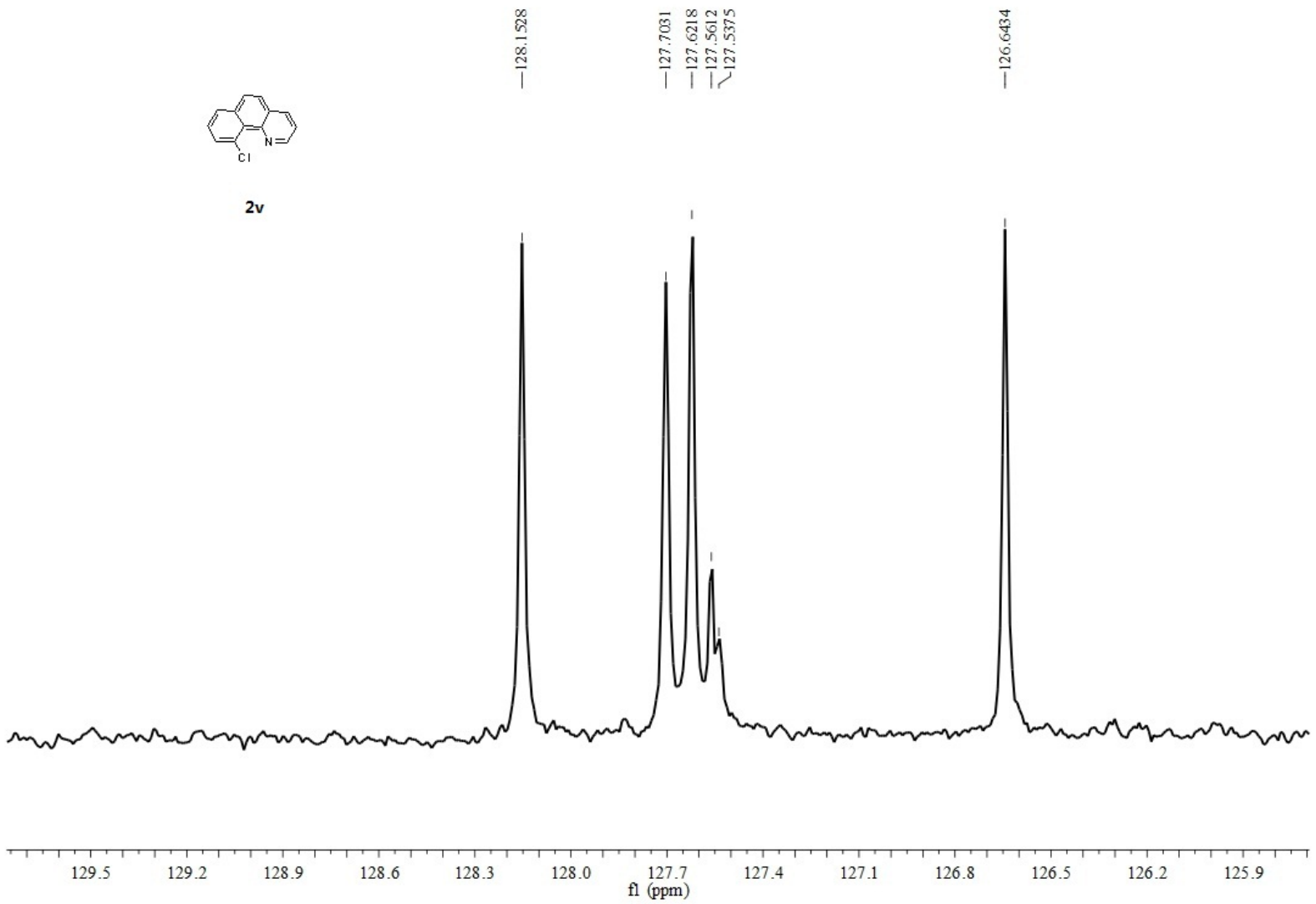

164.0830
151.7973
150.0999
142.0912
136.9320
135.0018
132.9108
131.9484
128.9544
124.0541
61.7506
18.3175
14.1227
Cl
Cl
N
O
O
2u
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

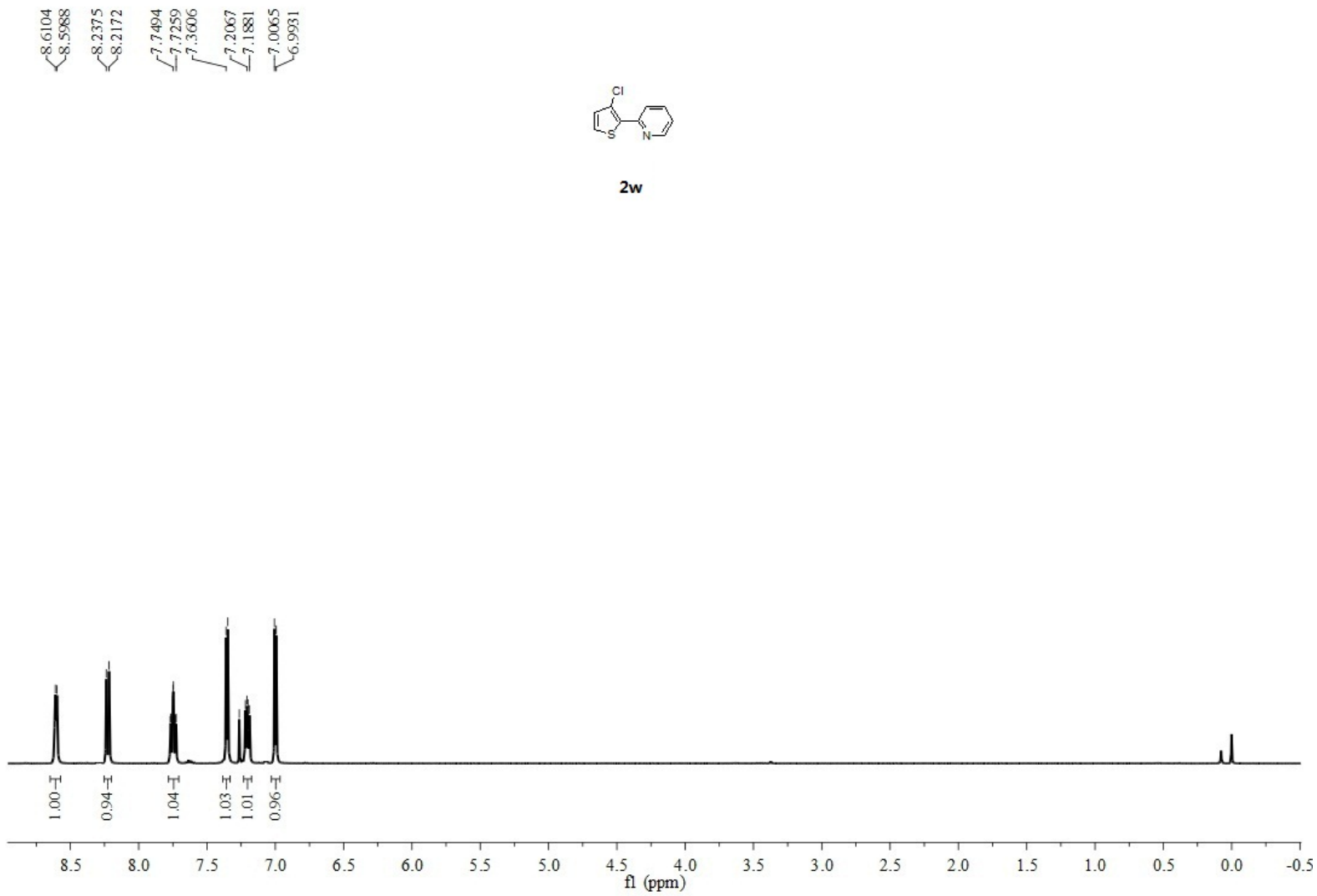

9.1097
9.1031
9.0999
8.1590
7.6568
7.5384
7.5202
7.2529
Cl
N
2v
1.00
1.03
2.00
1.03
1.02
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


9.1097
9.1031
9.0999
8.1590
8.1391
7.8248
7.8054
7.7446
7.6568
7.5552
7.5384
7.5230
7.5202
7.2529
Cl
N
2v
1.00
1.03
2.00
1.03
1.02
2.06
9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
f1 (ppm)


2v
Cl
N
147.6416
146.4797
136.3289
135.6767
131.5416
127.6218
121.7335
f1 (ppm)


147.6416
146.4797
136.3289
135.6767
132.3389
131.5416
128.1528
127.6218
127.5612
126.6434
121.7335
2v
Cl
N
149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)

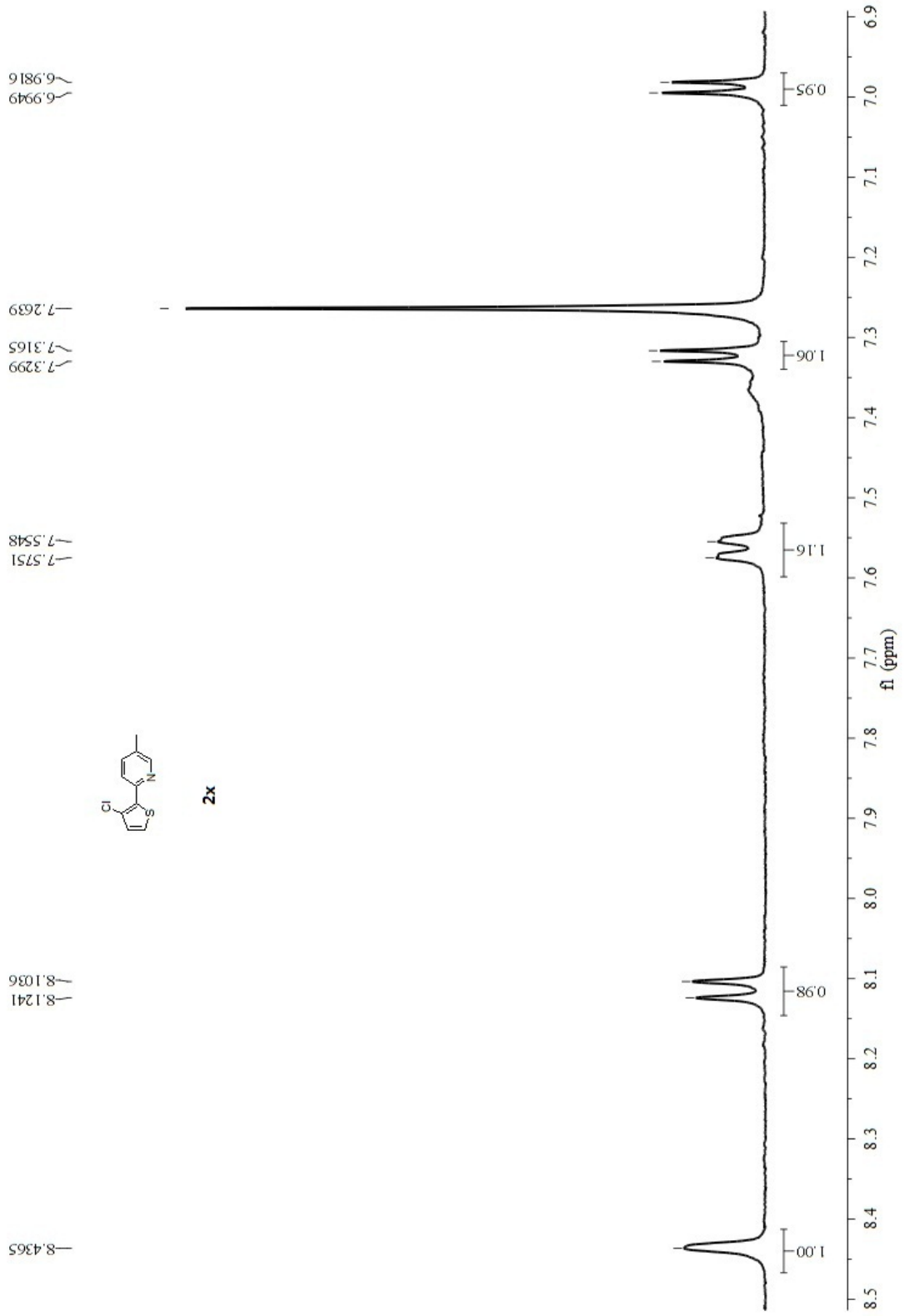

128.1528
127.7031
127.6218
127.5612
127.5375
126.6434
Cl
N
2v
129.5
129.2
128.9
128.6
128.3
128.0
127.7
127.4
127.1
126.8
126.5
126.2
125.9
f1 (ppm)

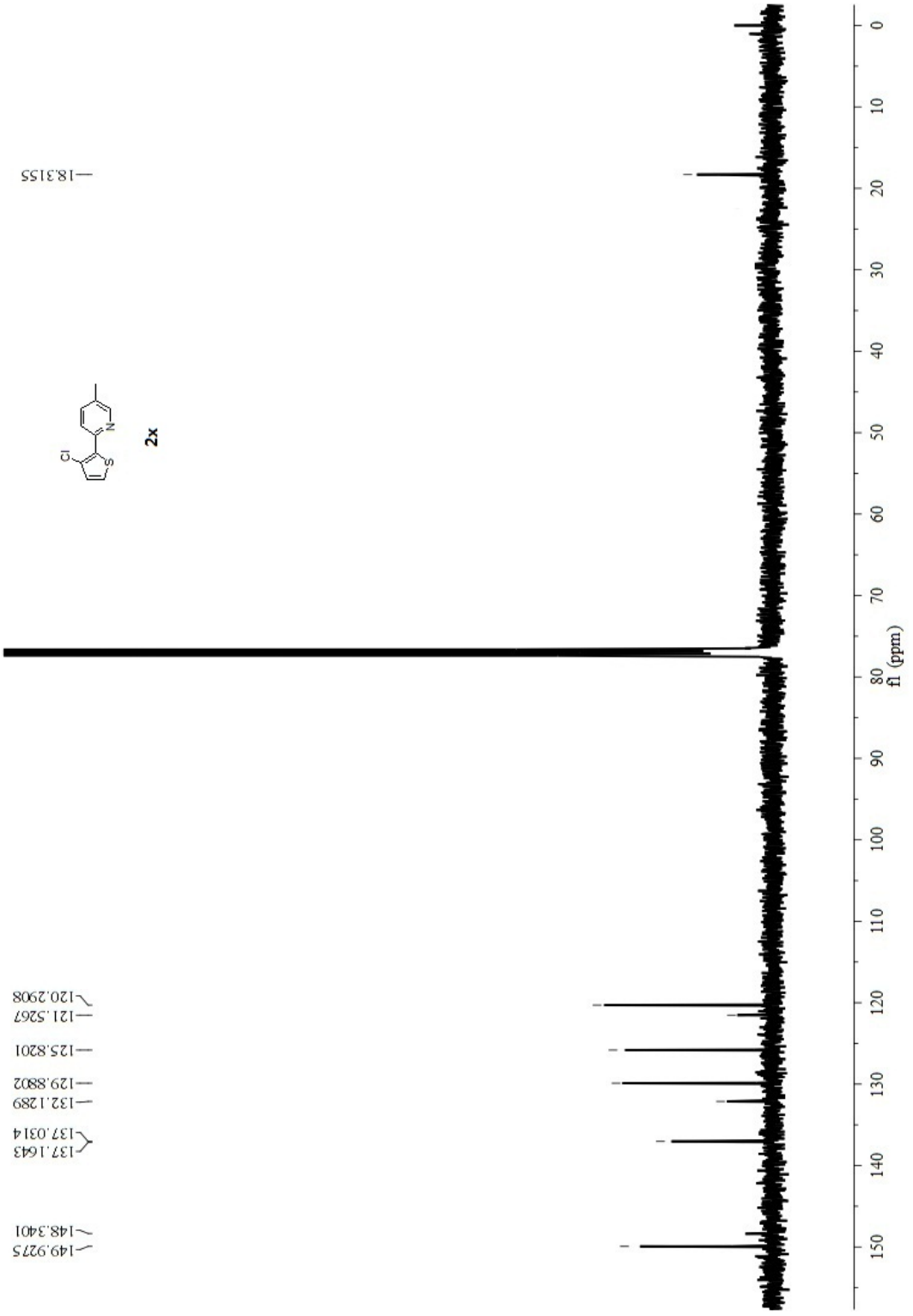

8.6104
8.5988
8.2375
8.2172
7.7494
7.7259
7.3606
7.2067
7.1881
7.0065
6.9931
Cl
S
N
2w
1.00
0.94
1.04
1.03
1.01
0.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

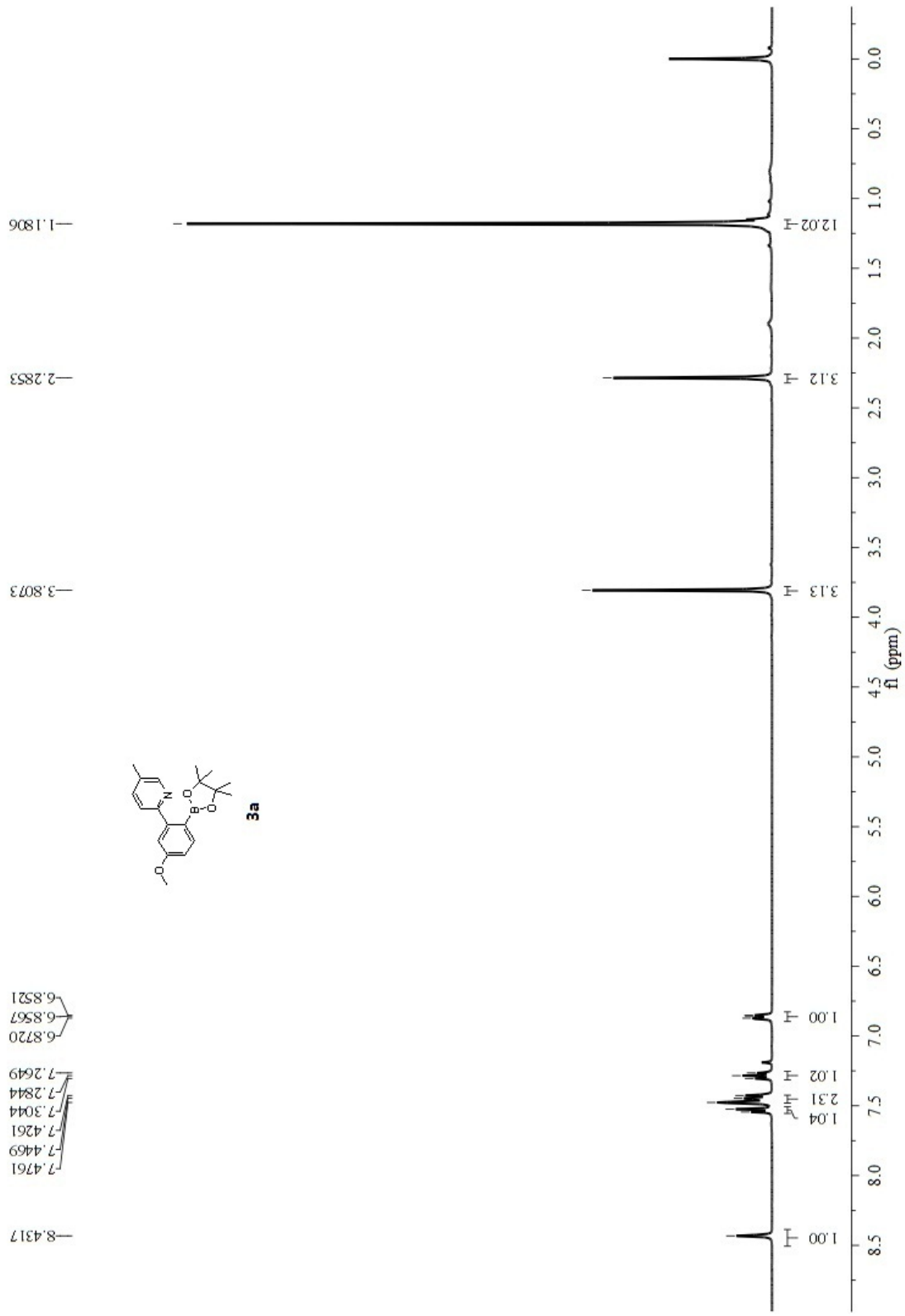
8.6104
8.5988
8.2375
8.2172
7.7692
7.7649
7.7494
7.7456
7.7301
7.7259
7.3606
7.3473
7.2639
7.2190
7.2067
7.2005
7.1881
7.0065
6.9931
2w
1.00
0.94
1.04
1.03
1.01
0.96
f1 (ppm)

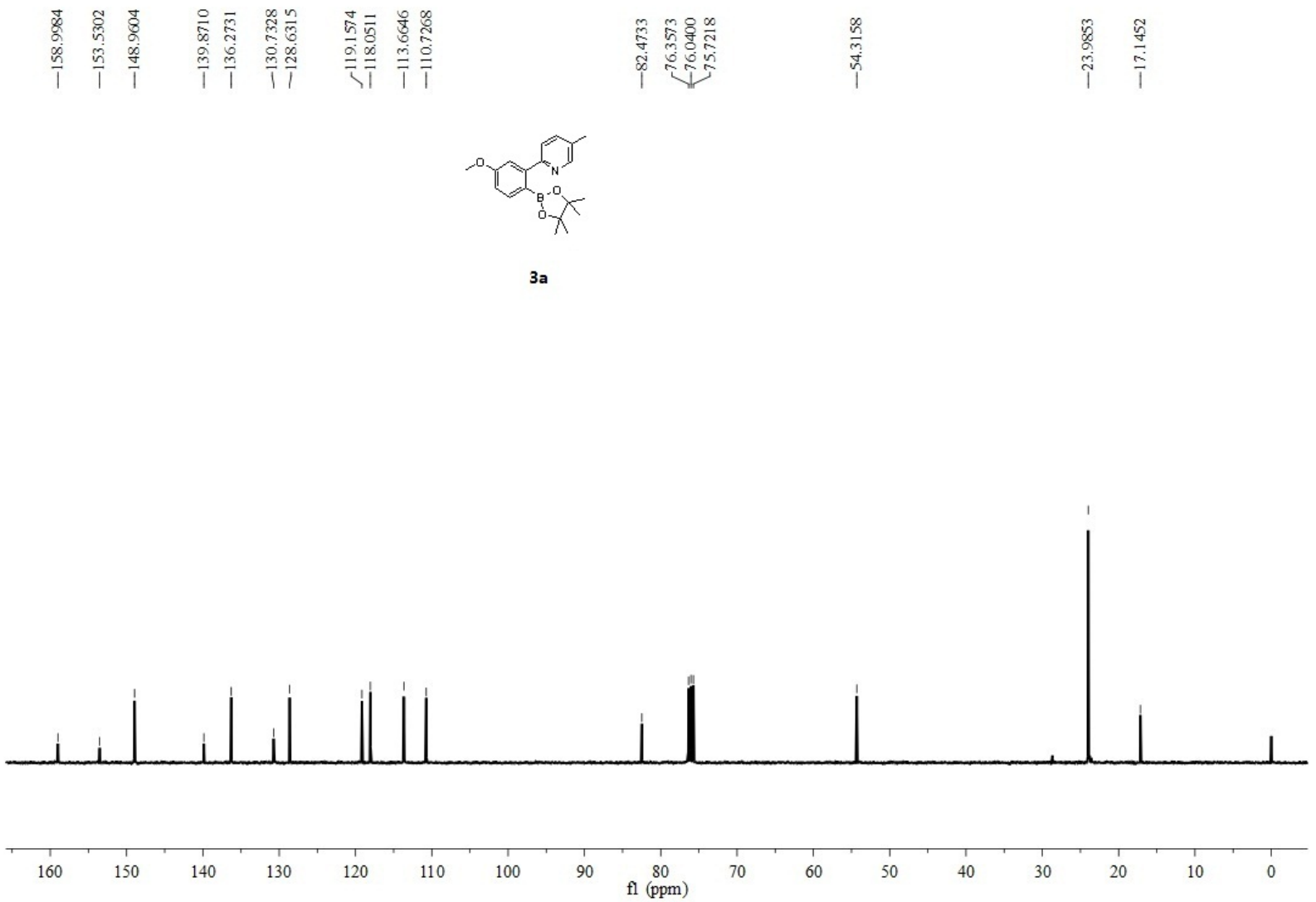
150.7559
149.2959
136.8385
136.3800
129.8093
126.2604
122.1838
121.8939
120.4943
2w
f1 (ppm)

8.4365
8.1241
8.1036
7.5751
7.5548
7.2639
6.9949
6.9816
2.3640
1.00
0.98
1.16
1.06
0.95
3.05
2x
f1 (ppm)


8.4365
8.1241
8.1036
7.5751
7.5548
7.3299
7.3165
7.2639
6.9949
6.9816
1.00
0.98
1.16
1.06
0.95
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f1 (ppm)
2x
Cl
S
N


18.3155
2x
149.9275
148.3401
137.1643
137.0314
132.1289
129.8802
125.8201
121.5267
120.2908
f1 (ppm)


8.4317
7.4761
7.4469
7.4261
7.3044
7.2844
7.2649
6.8720
6.8567
6.8521
3.8073
2.2853
1.1806
1.00
1.02
2.31
1.04
1.00
3.13
3.12
12.02
3a
f1 (ppm)


158.9984
153.5302
148.9604
139.8710
136.2731
130.7328
128.6315
119.1574
118.0511
113.6646
110.7268
82.4733
76.3573
76.0400
75.7218
54.3158
23.9853
17.1452
O
N
B
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3a

The reductive product of DDQ detected by GC-Mass: