Supporting Information for

Synthesis of α,α,α',α'-Tetrachloro Δ^1-bipyrrolines and 4,8-Dichloro-2,6-diazasemibuvallenes

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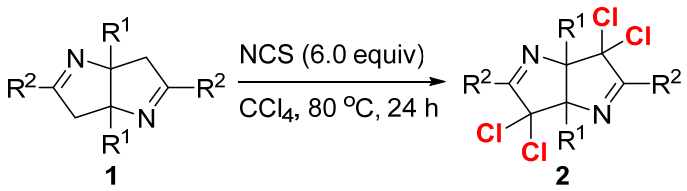
Contents

1) Experimental details and characterization data for all new compounds

General Methods: All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a Mikrouna Super (1220/750) glovebox. The nitrogen in the glove box was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. ^{n}BuLi and ^{t}BuLi were obtained from Acros. Δ^1-Bipyrrolines were prepared according to the reported method.[1]

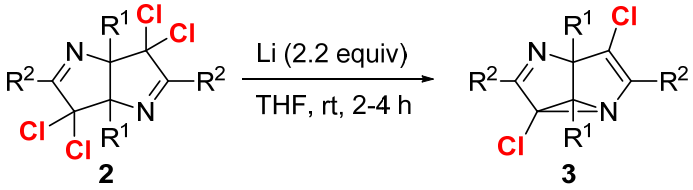
NMR spectroscopic measurements were carried out using Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) or a JEOL-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization).

a) Synthesis of α,α,α',α'-tetrachloro Δ^1-bipyrrolines[1]



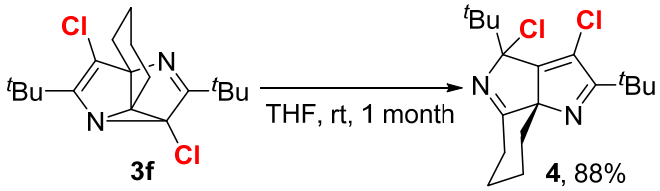
NCS (12.0 mmol, 1.626 g) was added to a solution of Δ^1-bipyrroline **1** (2.0 mmol) in 15 ml CCl_4 in a 50 ml Schlenk tube, the mixture was stirred at 80 °C for 24 h. The reaction mixture was then quenched with water and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow solid, which was purified by column chromatography (Petrol Ether: Ethyl Acetate = 50:1) to afford products α,α,α',α'-tetrachloro-Δ^1-bipyrrolines **2a-g**. Single crystals of **2g** suitable for X-ray structural analysis were grown in hexane/dichloromethane at room temperature.

b) Synthesis of 4,8-dichloro-2,6-diazasemibuvallenes

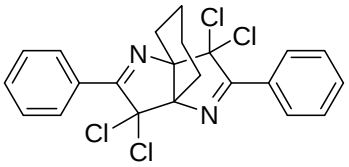


Li (1.1 mmol, 8.4 mg) was added to a solution of α,α,α',α'-tetrachloro-Δ^1-bipyrrolines **2** (0.5 mmol) in 5 ml THF in a 25 ml round-bottom flask in glove box, the mixture was stirred at room temperature for 2-4 h. The solvent was evaporated in vacuo to give a brown solid. This solid was dissolved in THF-d_8 and monitored by NMR to comfirm α,α,α',α'-tetrachloro-Δ^1-bipyrroline was totally disappeared. The THF and THF-d_8 were evaporated in vacuo to give a brown solid again. Then the 4,8-dichloro-2,6-diazasemibuvallene was extracted by diethyl ether from brown solid. At the same time, the salt (LiCl) was removed.

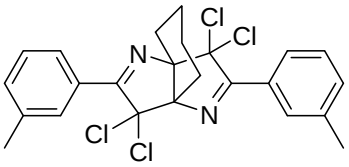
c) Rearrangement reaction of 4,8-dichloro-2,6-diazasemibuvallene



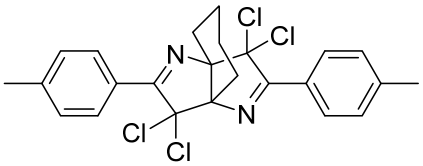
4,8-Dichloro 2,6-diazasemibuvallene **3f** (0.3 mmol) was dissolved in THF-d_8 at room temperature in glove box and was monitored by NMR. 4,8-Dichloro 2,6-diazasemibuvallene **3f** was completely transformed to **4** in one month. The solvent was evaporated in vacuo to give a yellow solid, which was purified by column chromatography (Petrol Ether: Ethyl Acetate = 100:1) to afford pure product **4** (90 mg) in 88% yield. Single crystals of **4** suitable for X-ray structural analysis were grown in hexane at room temperature.



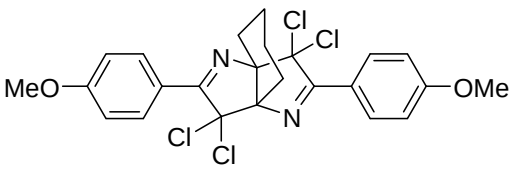
2a: Yellow solid, isolated yield 89% (802 mg). ^{1}H NMR (300MHz, THF-d_8, 25 ^{o}C): δ = 1.59 (br, 2H, CH_2), 1.83 (br, 2H, CH_2), 2.24 (br, 2H, CH_2), 2.86-2.91 (m, 2H, CH_2), 7.42-7.44 (m, 6H, C_6H_5), 8.19 (br, 4H, C_6H_5); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 22.2 (2 CH_2), 30.1 (2 CH_2), 81.5 (2 quat. C), 94.0 (2 quat. C), 128.4 (4 CH), 129.5 (2 CH), 129.7 (4 CH), 131.8 (2 quat. C), 166.1 (2 C=N). HRMS: *m/z*: calcd for $C_{22}H_{19}Cl_4N_2$ $[M+H]^+$: 451.0375, found: 451.0372.



2b: Yellow solid, isolated yield 79% (755 mg). ^{1}H NMR (400MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 1.60-1.66 (m, 2H, CH_2), 1.86-1.87 (m, 2H, CH_2), 2.23-2.28 (m, 2H, CH_2), 2.36 (s, 6H, CH_3), 2.92-2.95 (m, 2H, CH_2), 7.30 (d, *J* = 8 Hz, 4H, C_6H_5), 7.88 (s, 2H, C_6H_5), 7.98-7.99 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 ^{o}C): δ = 21.4 (2 CH_2), 22.3 (2 CH_2), 30.1 (2 CH_3), 81.4 (2 quat. C), 94.1 (2 quat. C), 126.7 (2 CH), 128.1 (2 CH), 129.4 (2 quat. C), 130.1 (2 CH), 132.5 (2 CH), 138.1 (2 quat. C), 166.2 (2 C=N). HRMS: *m/z*: calcd for $C_{24}H_{23}Cl_4N_2$ $[M+H]^+$: 479.0610, found: 479.0610.

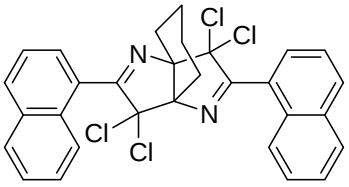


2c: Yellow solid, isolated yield 73% (678 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.52-1.56 (m, 2H, CH_2), 1.57-1.60 (m, 2H, CH_2), 1.80-1.81 (m, 2H, CH_2), 2.34 (s, 6H, CH_3), 2.84-2.88 (m, 2H, CH_2), 7.21 (d, *J* = 8 Hz, 4H, C_6H_5), 8.07 (d, *J* = 8 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 21.6 (2 CH_2), 23.3 (2 CH_2), 31.3 (2 CH_3), 82.4 (2 quat. C), 95.3 (2 quat. C), 127.8 (2 quat. C), 129.7 (4 CH), 130.5 (4 CH), 143.0 (2 quat. C), 166.0 (2 C=N). HRMS: *m/z*: calcd for $C_{24}H_{23}Cl_4N_2$ $[M+H]^+$: 479.0610, found: 479.0615.

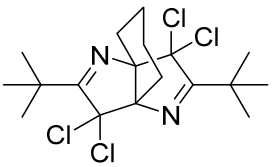


2d: Yellow solid, isolated yield 67% (683 mg). ^{1}H NMR

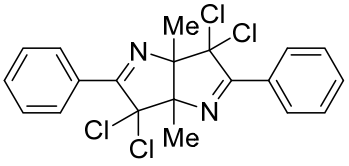
(400MHz, $CDCl_3$, TMS, 25 °C): δ = 1.54-1.62 (m, 2H, CH_2), 1.85 (br, 2H, CH_2), 2.18-2.23 (m, 2H, CH_2), 2.88-2.92 (m, 2H, CH_2), 3.93 (s, 6H, CH_3), 6.94 (d, *J* = 8 Hz, 3H, C_6H_5), 8.09-8.14 (m, 5H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ = 20.1 (2 CH_2), 30.3 (2 CH_2), 56.3 (2 CH_3O), 81.4 (2 quat. C), 93.7 (1 quat. C), 111.2 (1 quat. C), 122.5 (1 quat. C), 122.6 (1 quat. C), 129.6 (4 CH), 131.5 (4 CH), 157.6 (2 quat. C), 164.2 (2 C=N). HRMS: *m/z*: calcd for $C_{24}H_{23}Cl_4O_2N_2$ $[M+H]^+$: 511.0437, found: 511.0442.



2e: Yellow solid, isolated yield 70% (770 mg). ^1H NMR (400MHz, $CDCl_3$, TMS, 25 °C): δ = 1.25-1.27 (m, 1H, CH_2), 1.91-2.03 (m, 3H, CH_2), 2.45-2.50 (m, 2H, CH_2), 3.02-3.06 (m, 1H, CH_2), 7.24-7.30 (m, 2H, C_6H_5), 7.43-7.46 (m, 2H, C_6H_5), 7.56-7.59 (m, 2H, C_6H_5), 7.86 (d, *J* = 8 Hz, 2H, C_6H_5), 7.99 (d, *J* = 8 Hz, 2H, C_6H_5), 8.14-8.20 (m, 4H, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ = 22.4 (2 CH_2), 29.9 (2 CH_2), 82.5 (2 quat. C), 96.1 (2 quat. C), 124.3 (2 CH), 125.5 (2 CH), 126.2 (2 CH), 127.1 (2 CH), 127.2 (2 quat. C), 128.3 (2 CH), 128.4 (2 CH), 131.3 (2 CH), 132.2 (2 quat. C), 133.7 (2 quat. C), 167.5 (2 C=N). HRMS: *m/z*: calcd for $C_{30}H_{23}Cl_4N_2$ $[M+H]^+$: 551.0610, found: 551.0597.

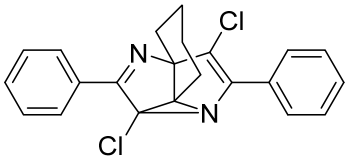


2f: Colorless solid, isolated yield 85% (697 mg). ^1H NMR (400MHz, $CDCl_3$, TMS, 25 °C): δ = 1.37 (s, 18H, CH_3), 1.41-1.44 (m, 2H, CH_2), 1.75-1.77 (m, 2H, CH_2), 2.17-2.19 (m, 2H, CH_2), 2.65-2.69 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, TMS, 25 °C): δ = 22.4 (2 CH_2), 28.9 (2 CH_2), 29.4 (6 CH_3), 37.2 (2 quat. C), 79.9 (2 quat. C), 95.0 (2 quat. C) 174.8 (2 C=N). HRMS: *m/z*: calcd for $C_{18}H_{27}Cl_4N_2$ $[M+H]^+$: 411.0915, found: 411.0923.

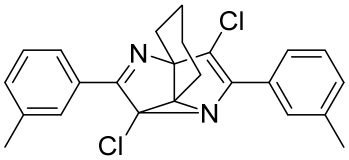


2g: Yellow solid, isolated yield 80% (678 mg). ^1H NMR (400MHz, THF-d_8, 25 °C): δ = 1.74 (s, 6H, CH_3), 7.39-7.43 (m, 4H, C_6H_5), 7.46-7.48 (m, 2H, C_6H_5), 8.12 (d, *J* = 8 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 °C): δ = 16.86 (2 CH_3), 85.69 (2 quat. C), 93.9 (2 quat. C), 129.2 (4 CH), 130.3 (2 CH), 130.5 (4 CH), 132.6 (2 quat. C), 167.7 (2 C=N).

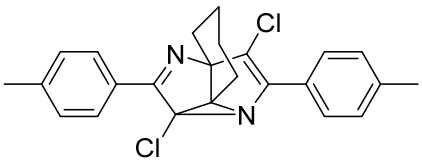
HRMS: *m/z*: calcd for $C_{20}H_{17}Cl_4N_2$ $[M+H]^+$: 425.0140, found: 425.0133.



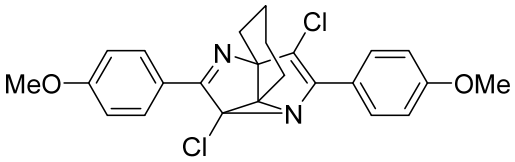
3a: Yellow solid, isolated yield 85% (162 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.29-1.33 (m, 2H, CH_2), 1.70-1.77 (m, 4H, CH_2), 2.39-2.42 (m, 2H, CH_2), 7.31-7.33 (m, 6H, C_6H_5), 7.77-7.80 (m, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 22.1 (2 CH_2), 25.9 (2 CH_2), 79.1 (2 quat. C), 109.1 (2 quat. C), 128.7 (4 CH), 129.1 (4 CH), 130.6 (2 CH), 133.4 (2 quat. C), 150.5 (2 C=N). Elemental Analysis Calcd (%) for $C_{22}H_{18}Cl_2N_2$: C, 69.30; H, 4.76; N, 7.35; Found: C, 69.15; H, 4.53; N, 7.22.



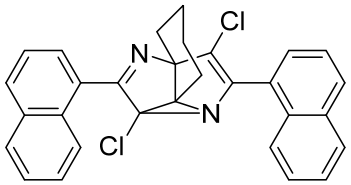
3b: Yellow solid, isolated yield 82% (196 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 0.86-0.89 (m, 2H, CH_2), 1.26-1.28 (m, 2H, CH_2), 1.75-1.79 (m, 2H, CH_2), 2.30 (s, 6H, CH_3), 2.39-2.43 (m, 2H, CH_2), 7.13-7.15 (m, 2H, C_6H_5), 7.19-7.22 (m, 2H, C_6H_5), 7.57 (d, *J* = 8Hz, 2H, C_6H_5), 7.64 (s, 2H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 20.5 (2 CH_2), 21.2 (2 CH_2), 24.9 (2 CH_3), 78.1 (2 quat. C), 108.0 (2 quat. C), 125.1 (2 CH), 127.9 (2 CH), 128.3 (2 CH), 130.2 (2 CH), 132.5 (2 quat. C), 137.7 (2 quat. C), 149.7 (2 C=N). Elemental Analysis Calcd (%) for $C_{24}H_{22}Cl_2N_2$: C, 70.42; H, 5.42; N, 6.84; Found: C, 70.17; H, 5.26; N, 6.78.



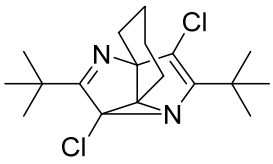
3c: Yellow solid, isolated yield 81% (194 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.26-1.31 (m, 2H, CH_2), 1.69-1.74 (m, 4H, CH_2), 2.26 (s, 6H, CH_3), 2.26-2.42 (m, 2H, CH_2), 7.12 (d, *J* = 8 Hz, 4H, C_6H_5), 7.67 (d, *J* = 8 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 21.5 (2 CH_2), 22.1 (2 CH_2), 25.9 (2 CH_3), 78.9 (2 quat. C), 108.5 (2 quat. C), 128.7 (4 CH), 129.7 (4 CH), 130.8 (2 quat. C), 140.7 (2 quat. C), 150.3 (2 C=N). Elemental Analysis Calcd (%) for $C_{24}H_{22}Cl_2N_2$: C, 70.42; H, 5.42; N, 6.84; Found: C, 70.20; H, 5.16; N, 6.63.



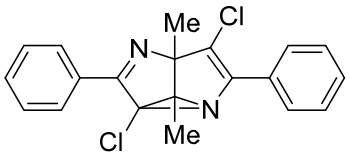
3d: Yellow solid, isolated yield 73% (160 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.26-1.30 (m, 4H, CH_2), 1.70-1.76 (m, 2H, CH_2), 2.36-2.40 (m, 2H, CH_2), 3.87 (s, 6H, OCH_3), 7.08 (d, *J* = 8 Hz, 3H, C_6H_5), 7.71-7.74 (d, *J* = 8 Hz, 2H, C_6H_5); 7.85 (br, 3H, C_6H_5), ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 22.1 (2 CH_2), 25.8 (2 CH_2), 56.8 (2 CH_3O), 79.0 (2 quat. C), 108.4 (1 quat. C), 112.8 (1 quat. C), 123.1 (1 quat. C), 126.6 (1 quat. C), 128.9 (4 CH), 130.3 (4 CH), 148.6 (2 quat. C), 157.4 (2 C=N). Elemental Analysis Calcd (%) for $C_{24}H_{22}Cl_2N_2O_2$: C, 65.31; H, 5.02; N, 6.35; Found: C, 65.80; H, 5.11; N, 6.14.



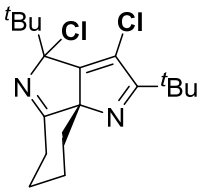
3e: Yellow solid, isolated yield 76% (182 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.25-1.30 (m, 2H, CH_2), 1.86-1.89 (m, 2H, CH_2), 2.01 (br, 2H, CH_2), 3.51-2.54 (m, 2H, CH_2), 7.24-7.28 (m, 2H, C_6H_5), 7.37-7.38 (m, 4H, C_6H_5), 7.40-7.44 (m, 2H, C_6H_5), 7.87-7.89 (m, 2H, C_6H_5), 7.92-7.93 (m, 2H, C_6H_5), 8.19-8.21 (m, 2H, C_6H_5); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 22.2 (2 CH_2), 26.2 (2 CH_2), 80.3 (2 quat. C), 112.6 (2 quat. C), 125.6 (2 CH), 126.7 (2 CH), 126.9 (2 CH), 127.3 (2 CH), 129.2 (2 CH), 129.6 (2 CH), 130.4 (2 quat. C), 131.2 (2 CH), 132.1 (2 quat. C), 134.8 (2 quat. C), 152.0 (2 C=N). Elemental Analysis Calcd (%) for $C_{30}H_{22}Cl_2N_2$: C, 74.85; H, 4.61; N, 5.82; Found: C, 75.80; H, 4.53; N, 5.64.



3f: Yellow solid, isolated yield 94% (160 mg). ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.24 (s, 18H, CH_3), 1.42-1.50 (m, 3H, CH_2), 1.62-1.70 (m, 3H, CH_2), 2.20-2.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 21.1 (2 CH_2), 24.8 (2 CH_2), 27.6 (6 CH_3), 34.6 (2 quat. C), 77.5 (2 quat. C), 108.3 (2 quat. C), 157.7 (2 C=N). Elemental Analysis Calcd (%) for $C_{18}H_{26}Cl_2N_2$: C, 63.34; H, 7.68; N, 8.21; Found: C, 63.60; H, 7.86; N, 8.03.



3g: Yellow solid, in situ NMR yield 50%. ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.54 (s, 6H, CH_3), 7.31-7.33 (m, 6H, C_6H_5), 7.78 (d, *J* = 8 Hz, 4H, C_6H_5); ^{13}C NMR (100 MHz, 25 ^{o}C): δ = 13.4 (2 CH_3), 80.6 (2 quat. C), 108.6 (2 quat. C), 128.8 (4 CH), 129.2 (2 CH), 130.5 (4 CH), 133.6 (2 quat. C), 150.4 (2 C=N).



4: Colorless solid, isolated yield 88% (90 mg). ^{1}H NMR (400MHz, $CDCl_3$, TMS, 25 ^{o}C): ^{1}H NMR (400MHz, THF-d_8, 25 ^{o}C): δ = 1.26-1.27 (m, 2H, CH_2), 1.35 (s, 9H, CH_3), 1.46 (s, 9H, CH_3), 1.62-1.65 (m, 2H, CH_2), 1.85-1.94 (m, 2H, CH_2), 2.38-2.42 (m, 1H, CH_2), 2.75-2.78 (m, 1H, CH_2); ^{13}C NMR (100 MHz, THF-d_8, 25 ^{o}C): δ = 21.2 (1 CH_2), 23.6 (1 CH_2), 27.3 (3 CH_3), 27.7 (3 CH_3), 33.6 (1 CH_2), 35.7 (1 CH_2), 36.9 (1 quat. C), 38.0 (1 quat. C), 77.2 (1 quat. C), 87.6 (1 quat. C), 91.1 (1 quat. C), 119.7 (1 quat. C), 172.0 (1 C=N), 181.0 (1 C=N). HRMS: *m/z*: calcd for $C_{18}H_{27}Cl_2N_2$ $[M+H]^+$: 341.1473, found: 341.1477.

2) X-ray crystallographic studies

The single crystals of **2g**, and **4** suitable for X-ray analysis were grown as shown in the experimental section. Data collections for **2g** and **4** were performed at 180 K on SuperNova diffractometer, using monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the CrystalClear (Rigaku Inc. 2007) program package for **2g** and **4**. The raw frame data were processed using CrystalClear (Rigaku Inc. 2007) for **2g** and **4** to yield the reflection data file. The structures of **2g** and **4** were solved by use of SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **2g** and **4** are summarized in Table S1 - Table S4. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1036087 (**2g**), CCDC 1036088 (**4**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [2,3]

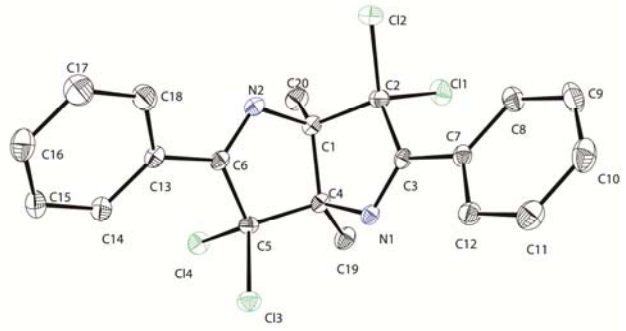


Figure S1. ORTEP drawing of **2g** with 30% probability thermal ellipsoids.

Table S1. **Crystal data and structure refinement for 2g**.

Identification code	**2g**
Empirical formula	$C_{20}H_{16}Cl_4N_2$
Formula weight	426.15
Temperature/K	180.01(10)

Crystal system	orthorhombic
Space group	Pbca
a/Å	11.2813(6)
b/Å	14.1148(7)
c/Å	24.5832(14)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	3914.4(4)
Z	8
$\rho_{calc}g/cm^3$	1.446
μ/mm^{-1}	0.611
F(000)	1744.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	Mo Kα (λ = 0.7107)
2Θ range for data collection/°	5.78 to 52.04
Index ranges	$-10 \leq h \leq 13$, $-17 \leq k \leq 17$, $-30 \leq l \leq 20$
Reflections collected	10680
Independent reflections	3848 [R_{int} = 0.0391, R_{sigma} = 0.0473]
Data/restraints/parameters	3848/0/299
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0361, wR_2 = 0.0726
Final R indexes [all data]	R_1 = 0.0582, wR_2 = 0.0821
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.27

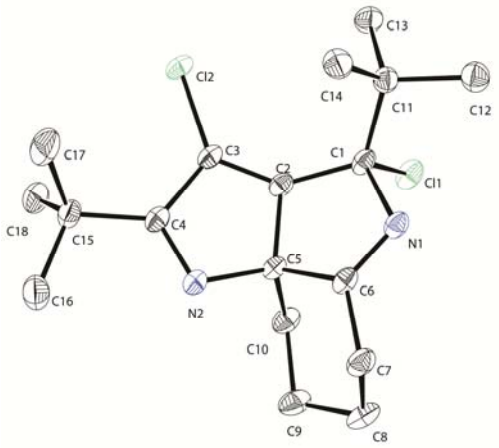


Figure S2. ORTEP drawing of **4** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table S2. **Crystal data and structure refinement for 4**.

Identification code	**4**
Empirical formula	$C_{18}H_{26}Cl_2N_2$
Formula weight	341.31
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.3474(7)
b/Å	9.8657(7)
c/Å	12.3923(9)
α/°	66.695(7)
β/°	69.579(7)
γ/°	62.115(7)
Volume/Å^3	908.60(14)
Z	2
ρ_{calc}g/cm^3	1.248
μ/mm^{-1}	0.356
F(000)	364.0

Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.794 to 52.044
Index ranges	$-11 \leq h \leq 11$, $-10 \leq k \leq 12$, $-14 \leq l \leq 15$
Reflections collected	6880
Independent reflections	3578 [R_{int} = 0.0300, R_{sigma} = 0.0505]
Data/restraints/parameters	3578/0/205
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0548, wR_2 = 0.1337
Final R indexes [all data]	R_1 = 0.0800, wR_2 = 0.1527
Largest diff. peak/hole / e $Å^{-3}$	1.57/-0.27

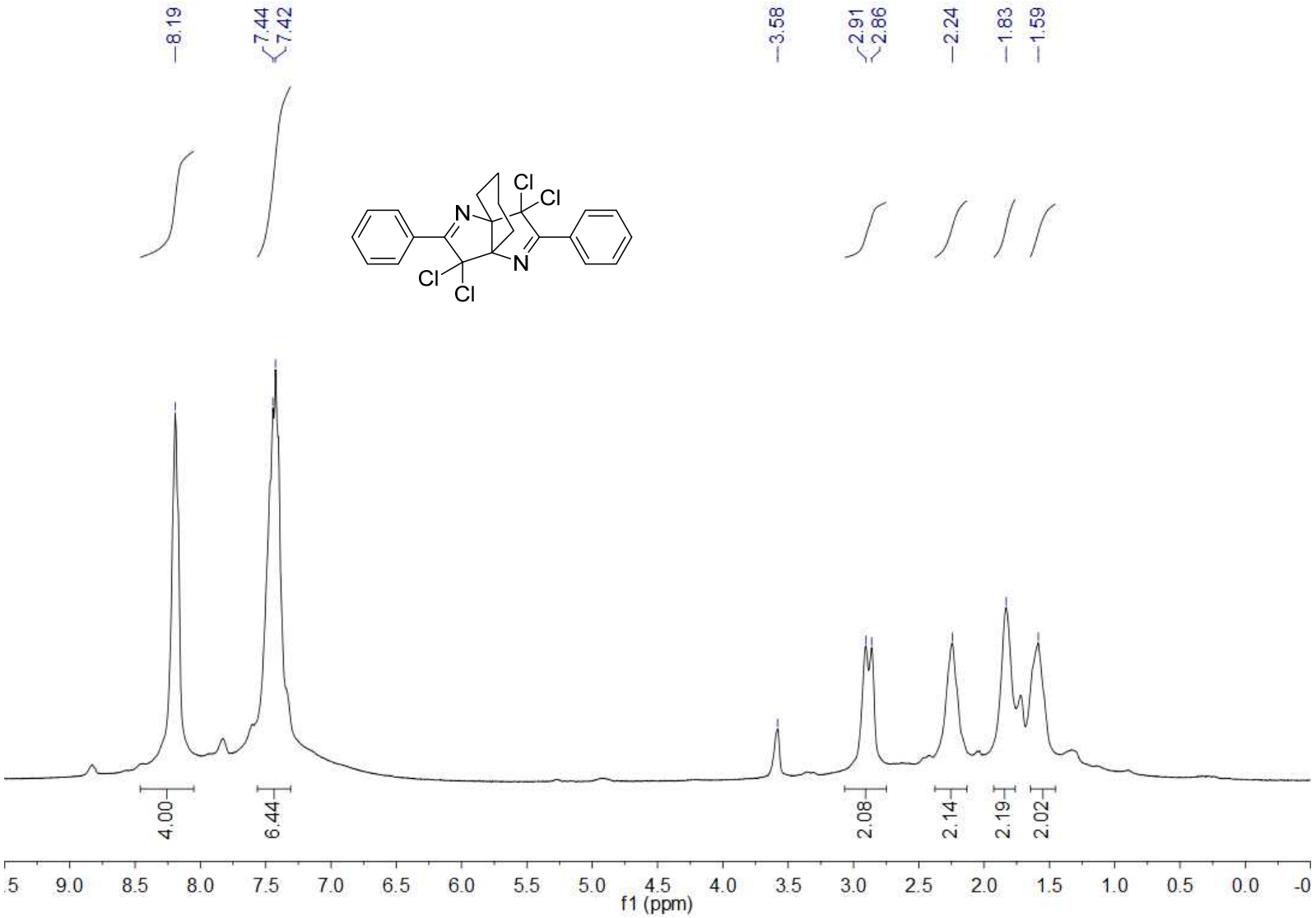
3) References

(1) Yu, N.; Wang, C.; Zhao, F.; Liu, L.; Zhang, W.-X.; Xi, Z. *Chem.-Eur. J.* **2008**, *14*, 5670.

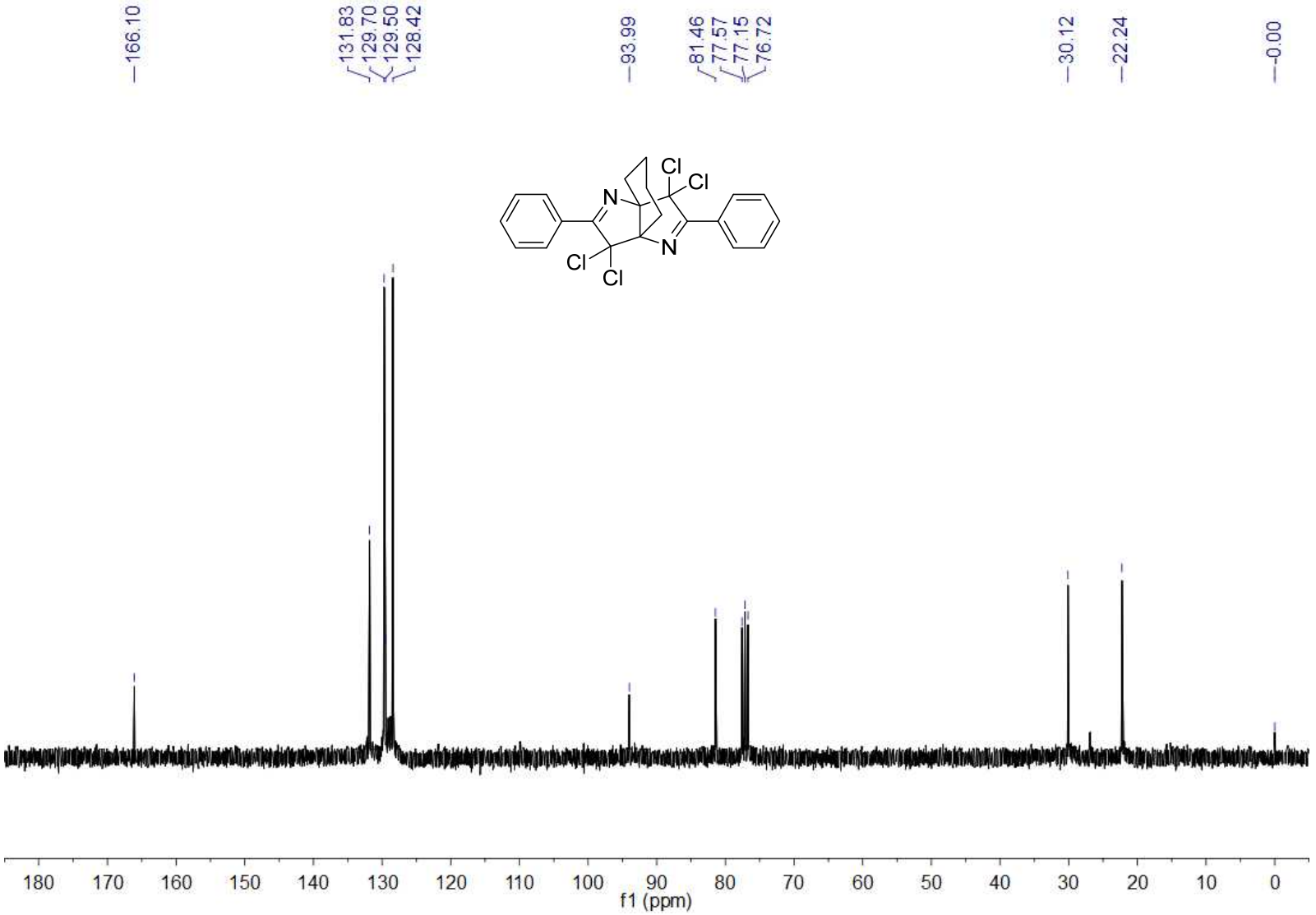
(2) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: *Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.: (Madison, WI, 1997).

4) Copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds

2a-^{1}H NMR



2a-^{13}C NMR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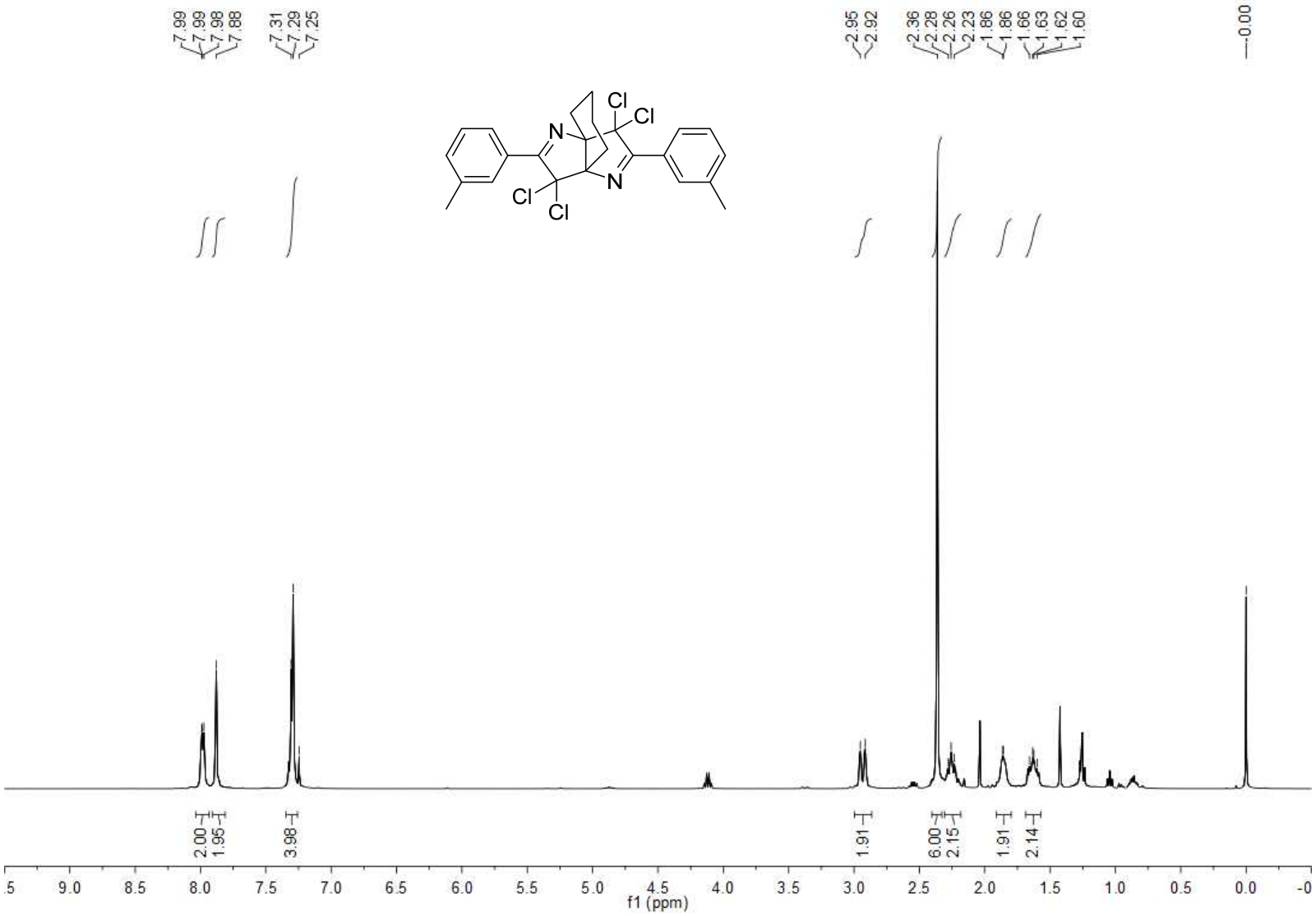
129.50
128.42
93.99
81.46
77.57
77.15
76.72
30.12
22.24
0.00
Cl
Cl
N
N
Cl
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2b-^{1}H NMR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1.86
1.66
1.63
1.62
1.60
0.00
Cl
Cl
N
N
Cl
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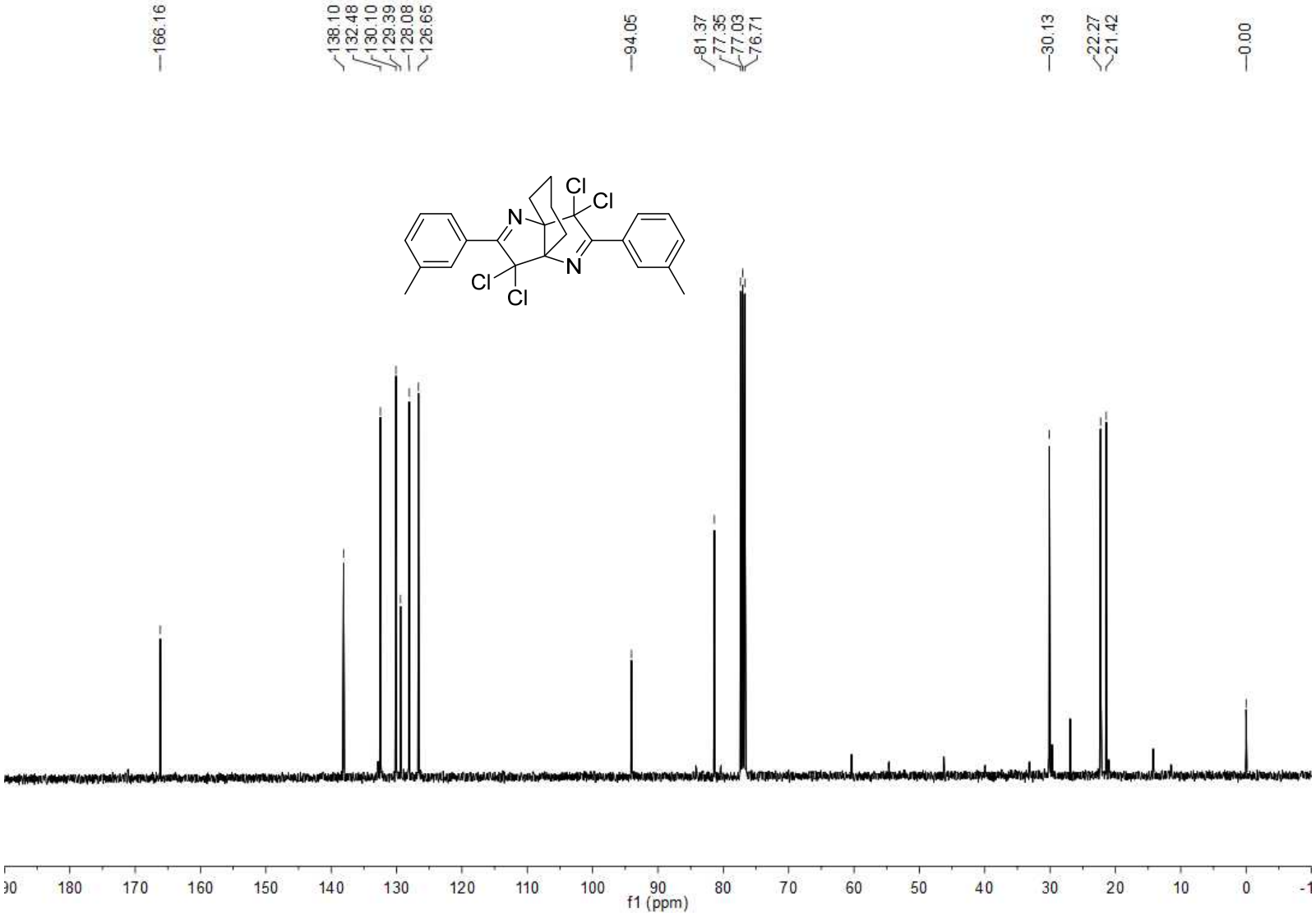
1.91
2.14
f1 (ppm)

2b-^{13}C NMR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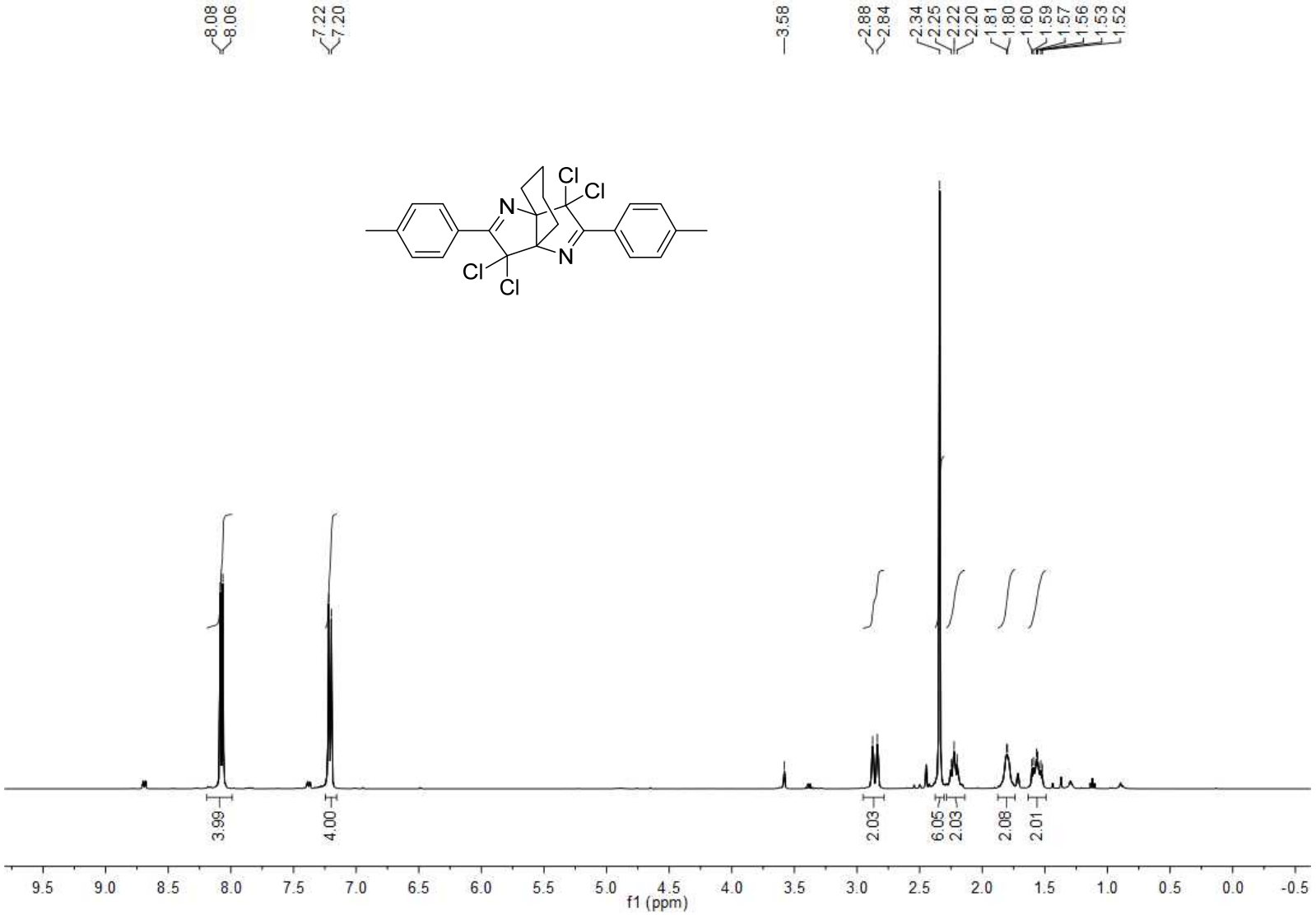
Cl
Cl
f1 (ppm)

2c-^{1}H NMR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1.80
1.60
1.59
1.57
1.56
1.53
1.52
Cl
Cl
N
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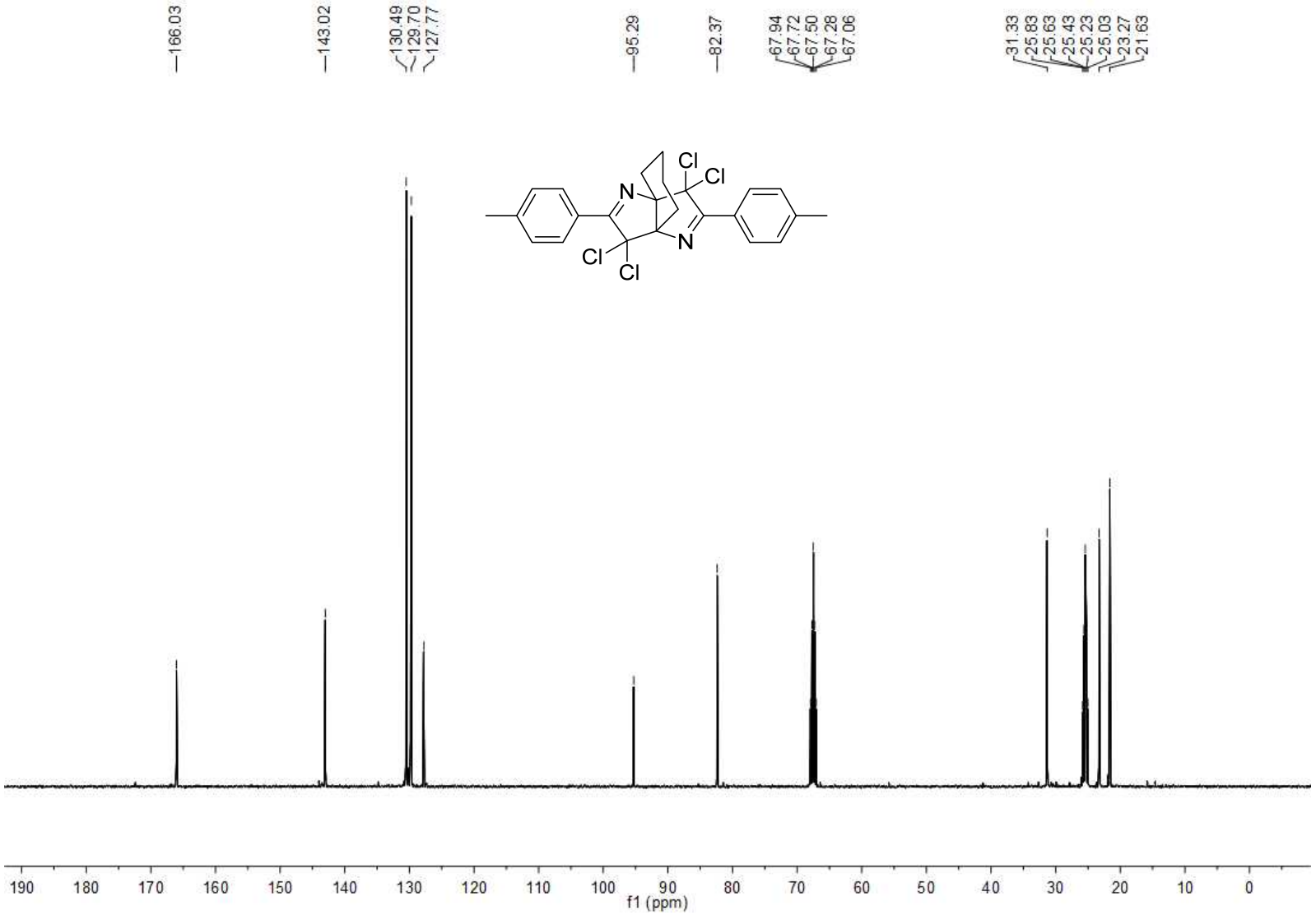
2.01
f1 (ppm)

2c-^{13}C NMR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25.83
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25.43
25.23
25.03
23.27
21.63
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Cl
N
N
Cl
Cl
190
180
170
160
150
140
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80
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10
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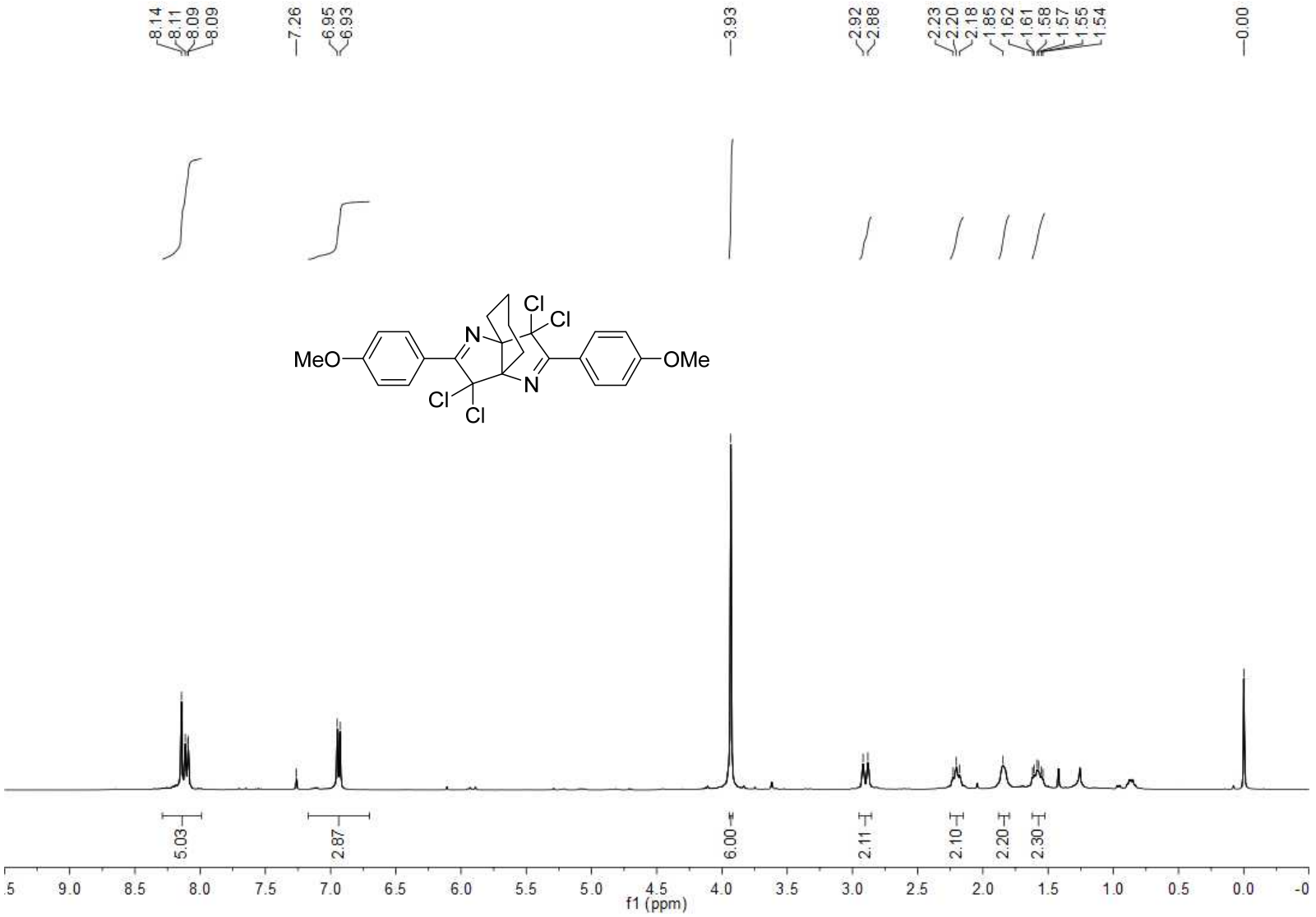
f1 (ppm)

2d-^{1}H NMR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2.18
1.85
1.62
1.61
1.58
1.57
1.55
1.54
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MeO
OMe
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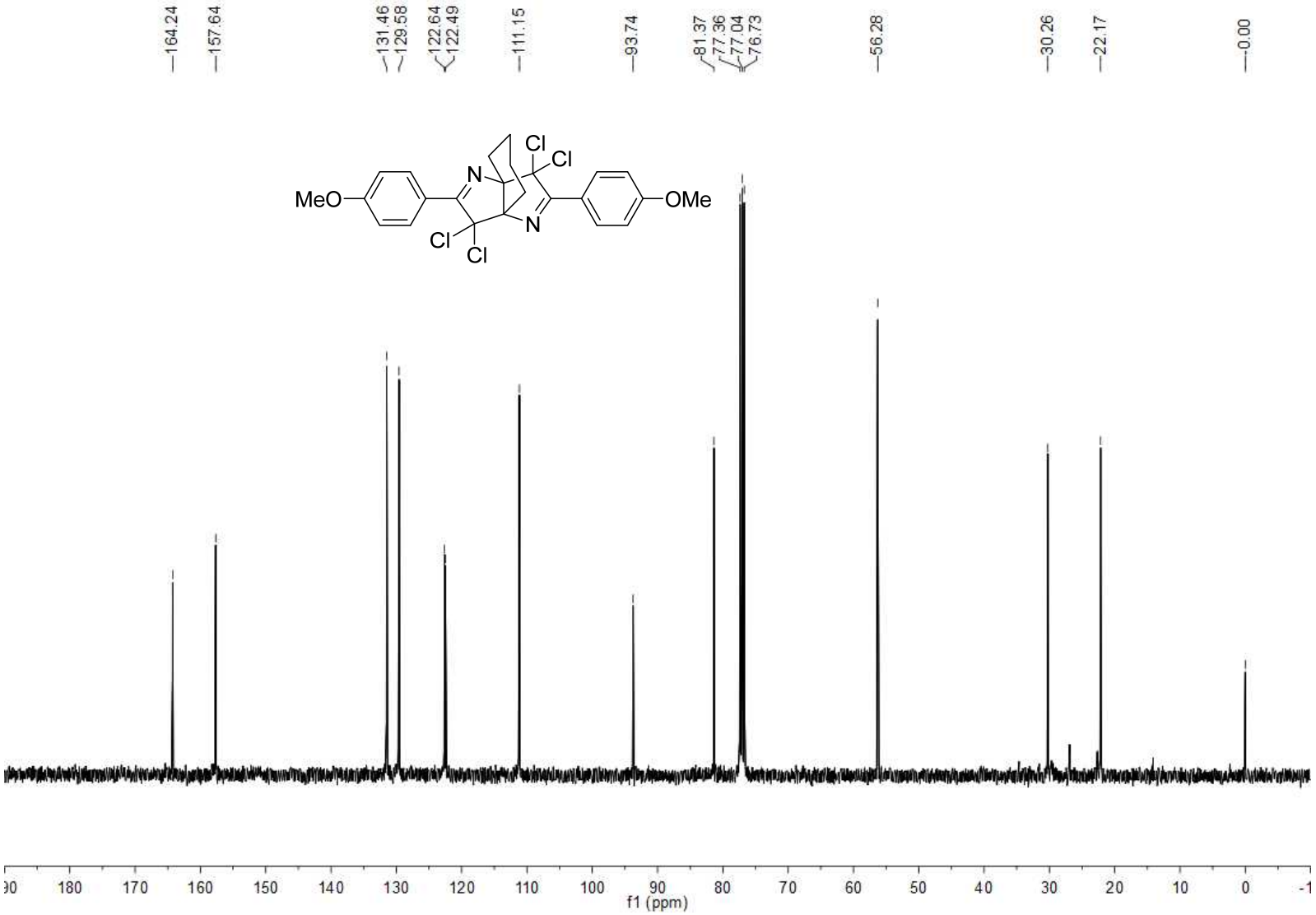
2.30
f1 (ppm)

2d-^{13}C NMR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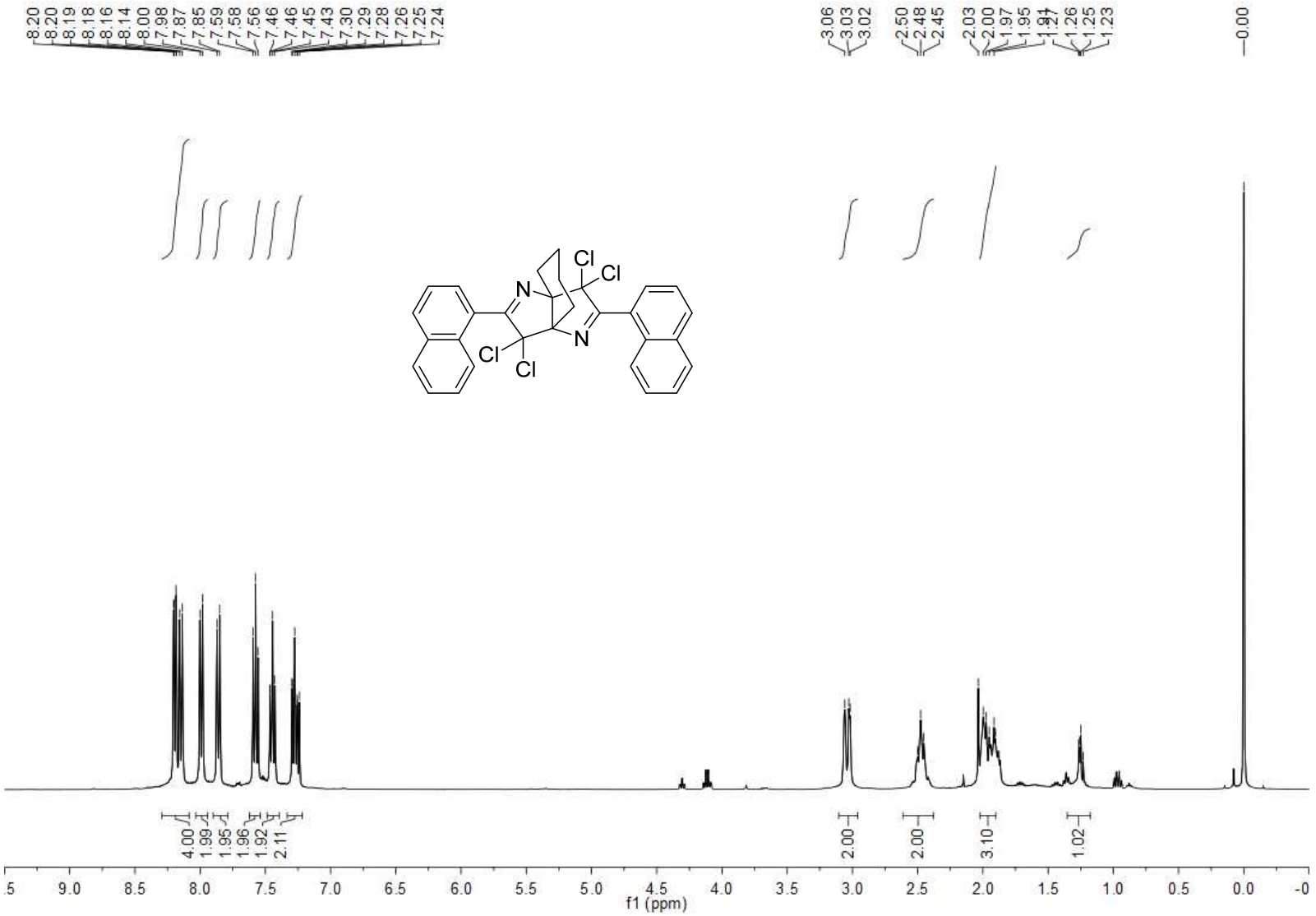
Cl
Cl
Cl
Cl
f1 (ppm)

2e-^{1}H NMR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7.26
7.25
7.24
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3.03
3.02
2.50
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2.45
2.03
2.00
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1.95
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1.25
1.23
0.00
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Cl
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N
Cl
Cl
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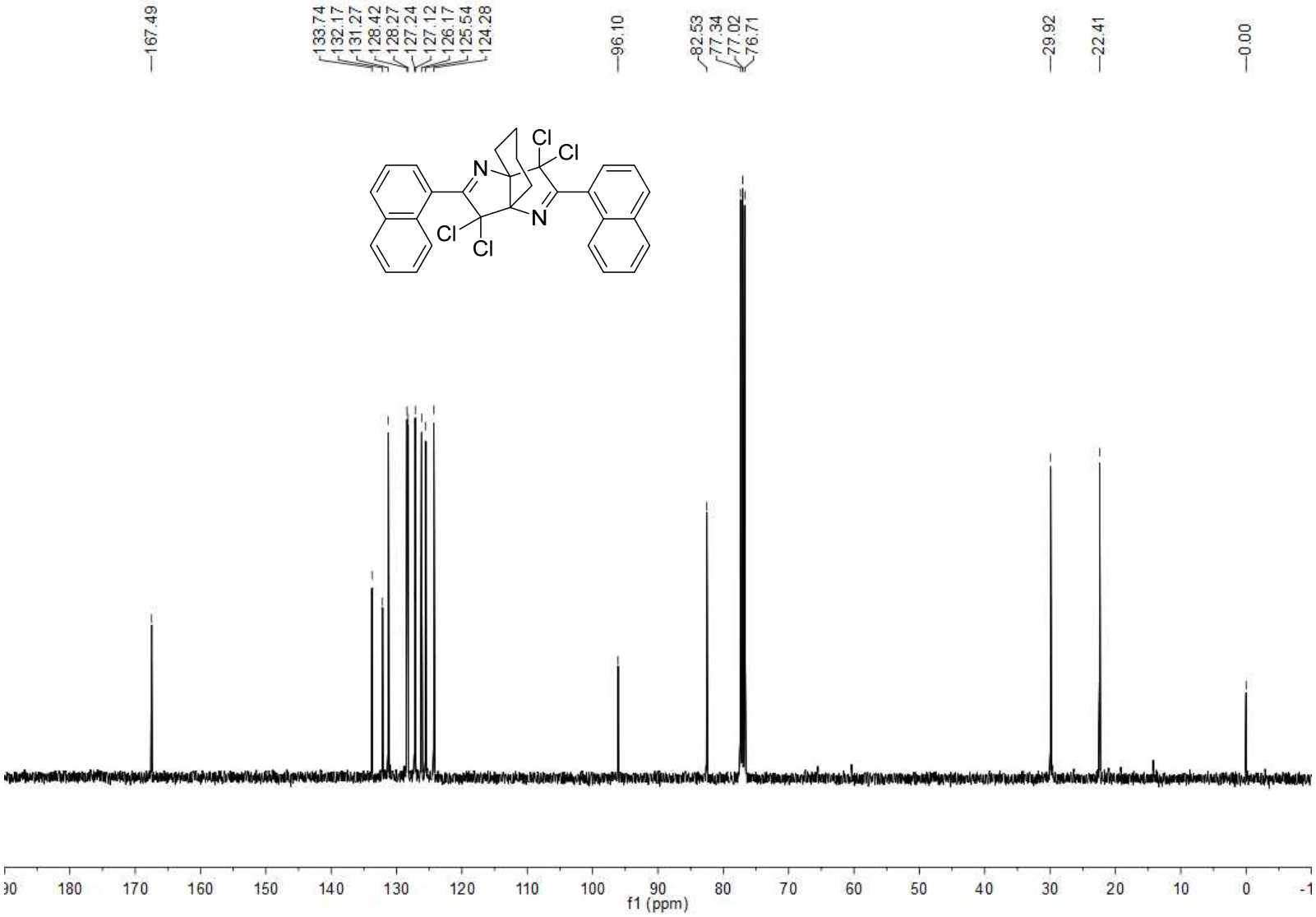
2.00
2.00
3.10
1.02
f1 (ppm)

2e-^{13}C NMR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77.34
77.02
76.71
29.92
22.41
0.00
Cl
Cl
N
N
Cl
Cl
180
170
160
150
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10
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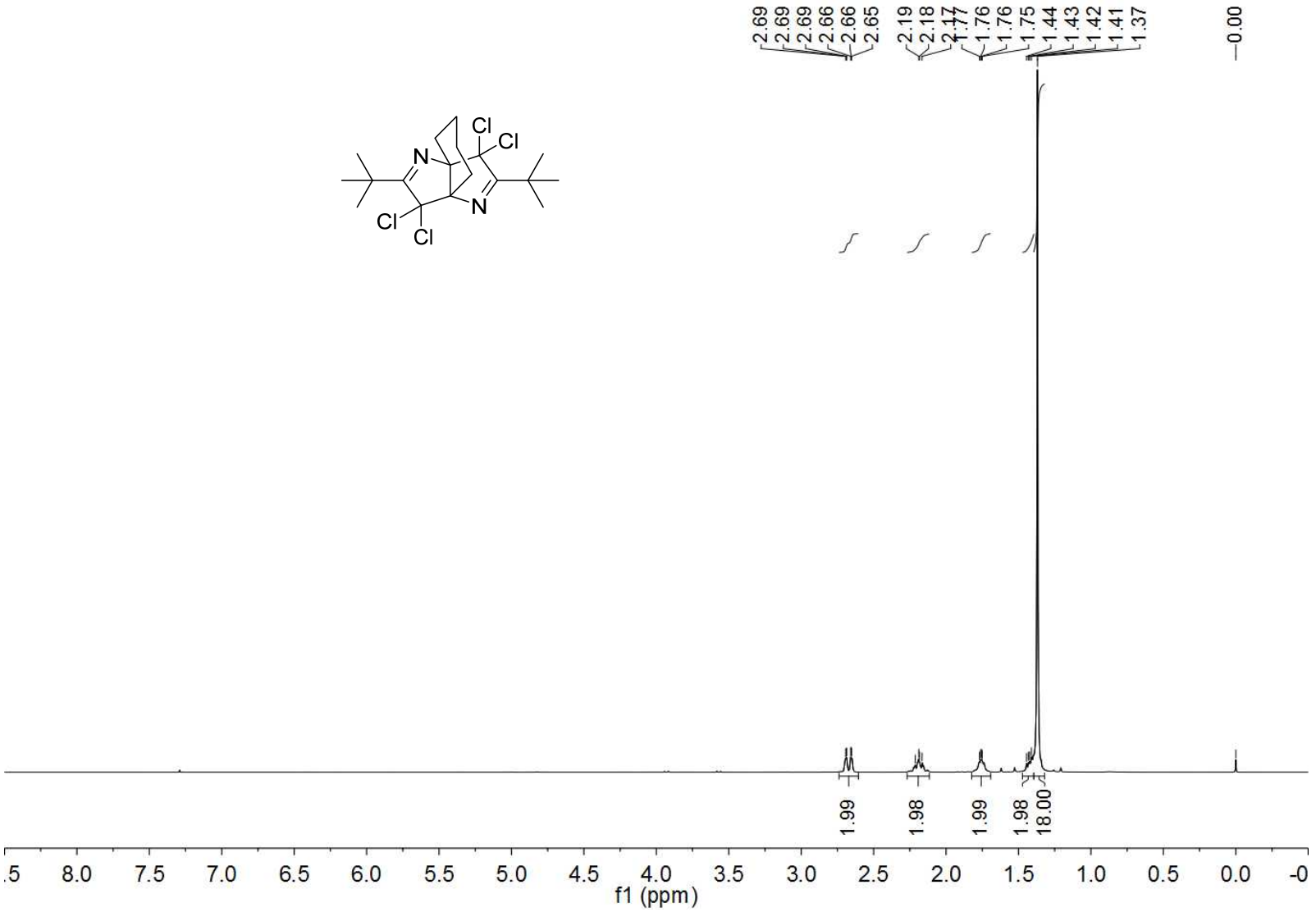
f1 (ppm)

2f-^{1}H NMR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Cl
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6.5
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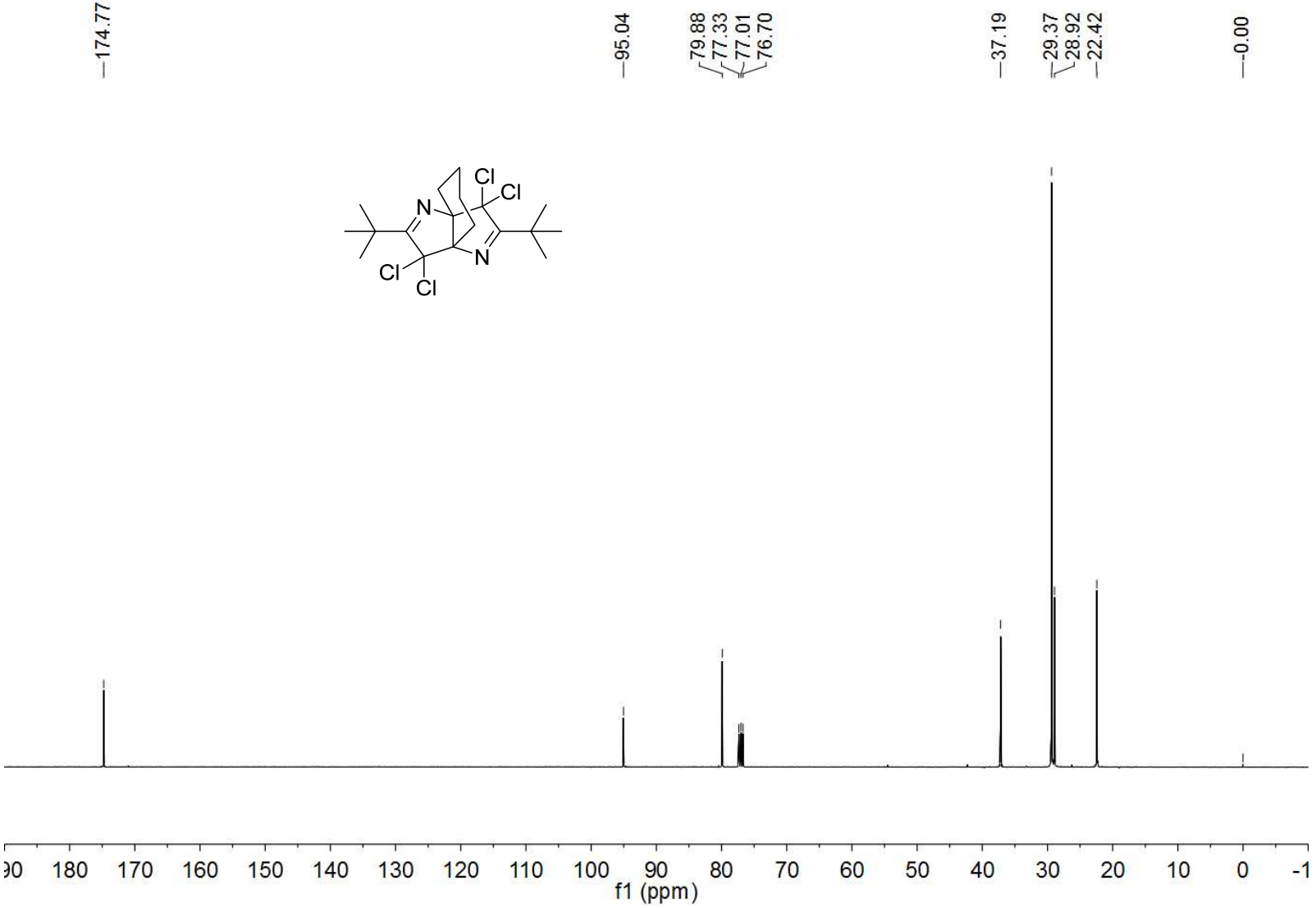
2f-^{13}C NMR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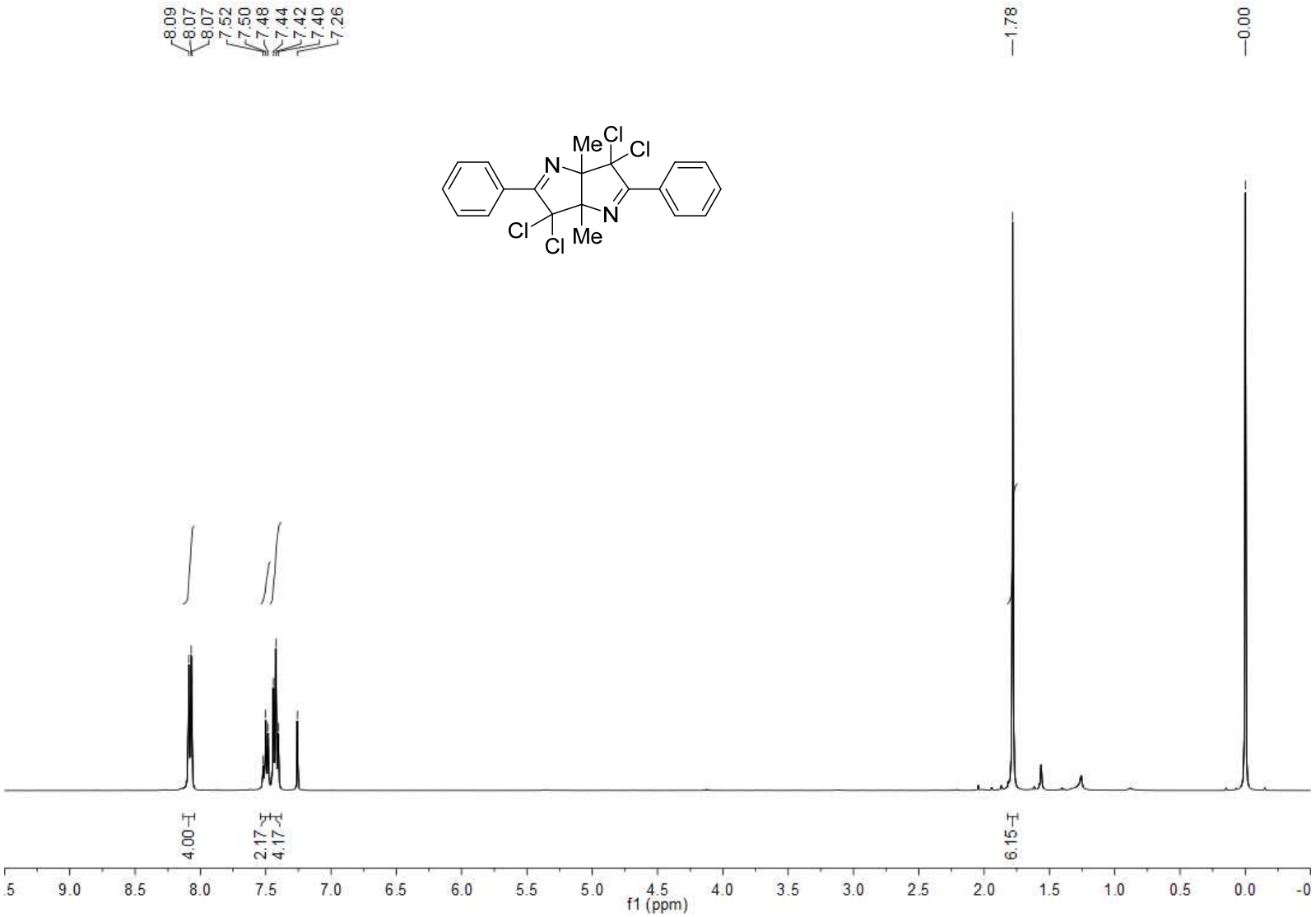
N
Cl
Cl
f1 (ppm)

2g-^{1}H NMR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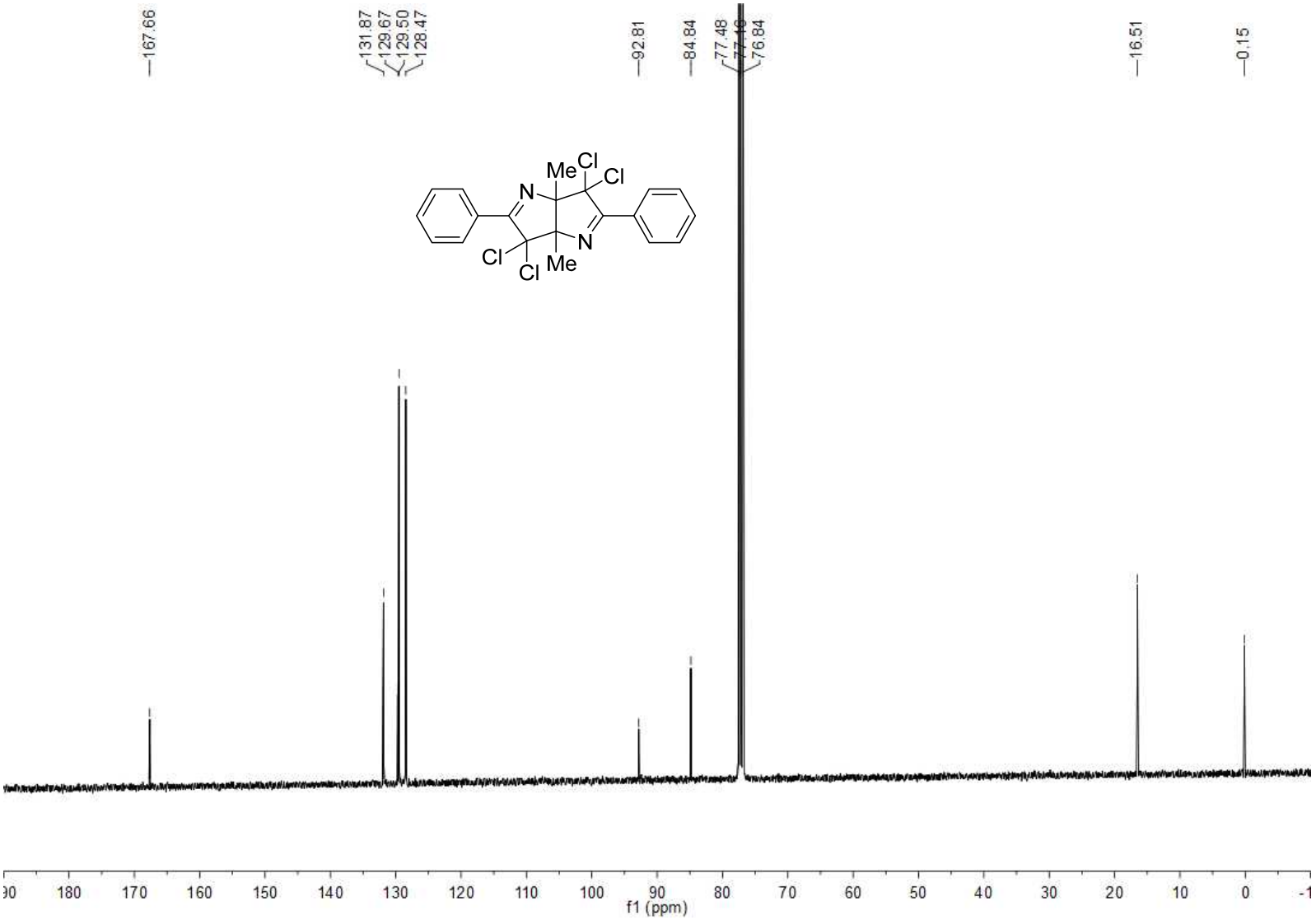
6.15
f1 (ppm)

2g-^{13}C NMR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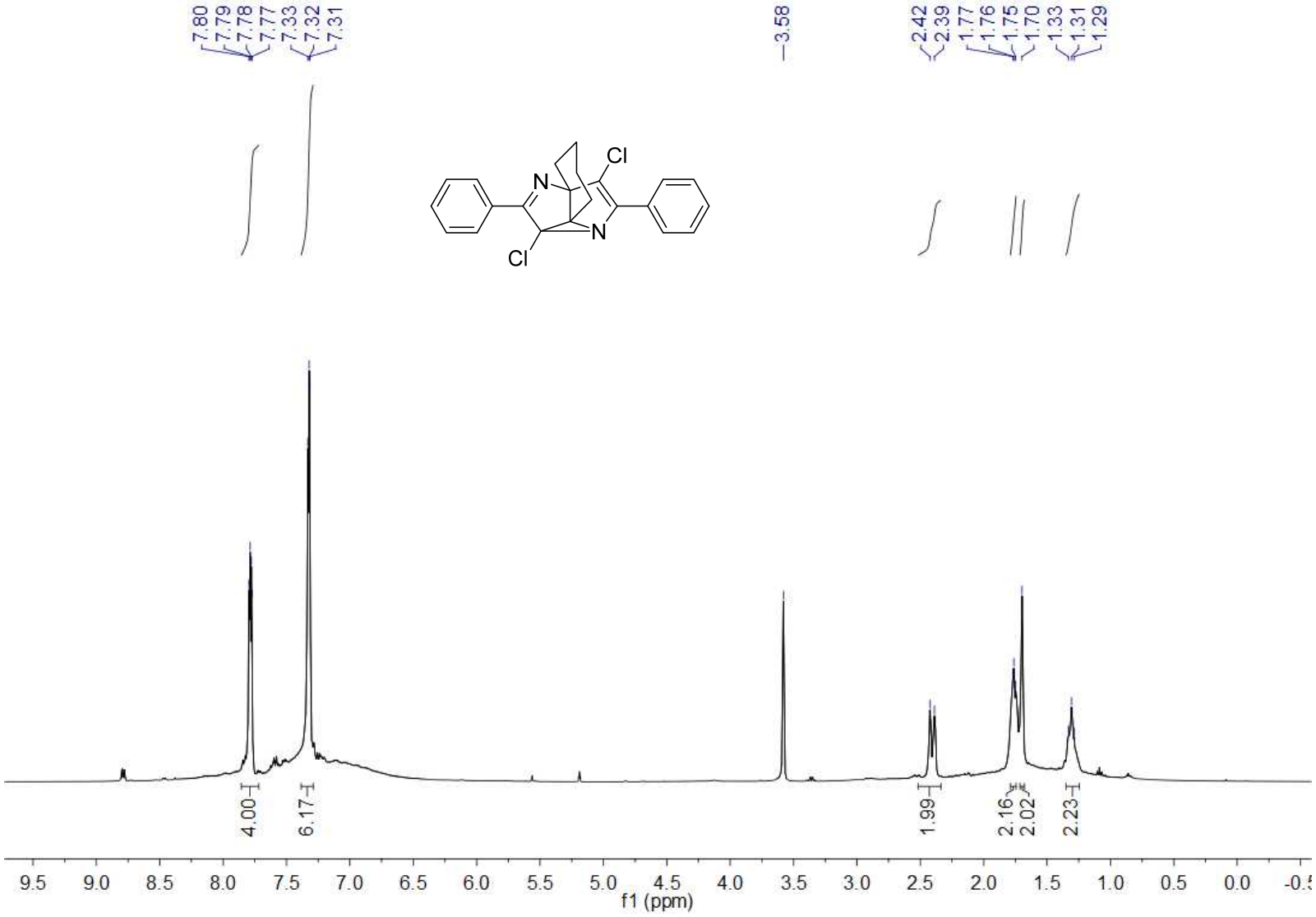
f1 (ppm)

3a-^{1}H NMR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1.31
1.29
Cl
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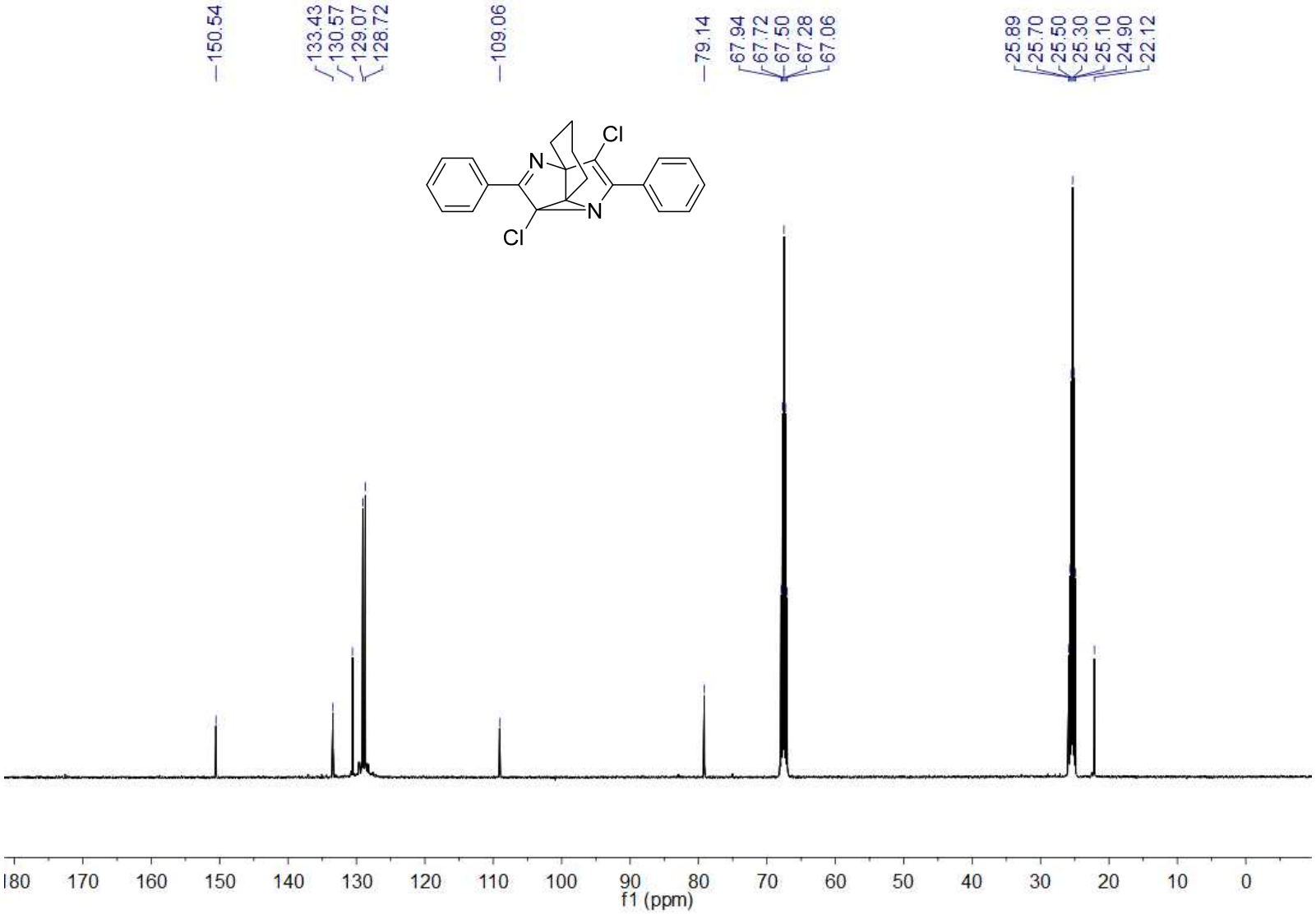
N
Cl
4.00
6.17
1.99
2.16
2.02
2.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3a-^{13}C NMR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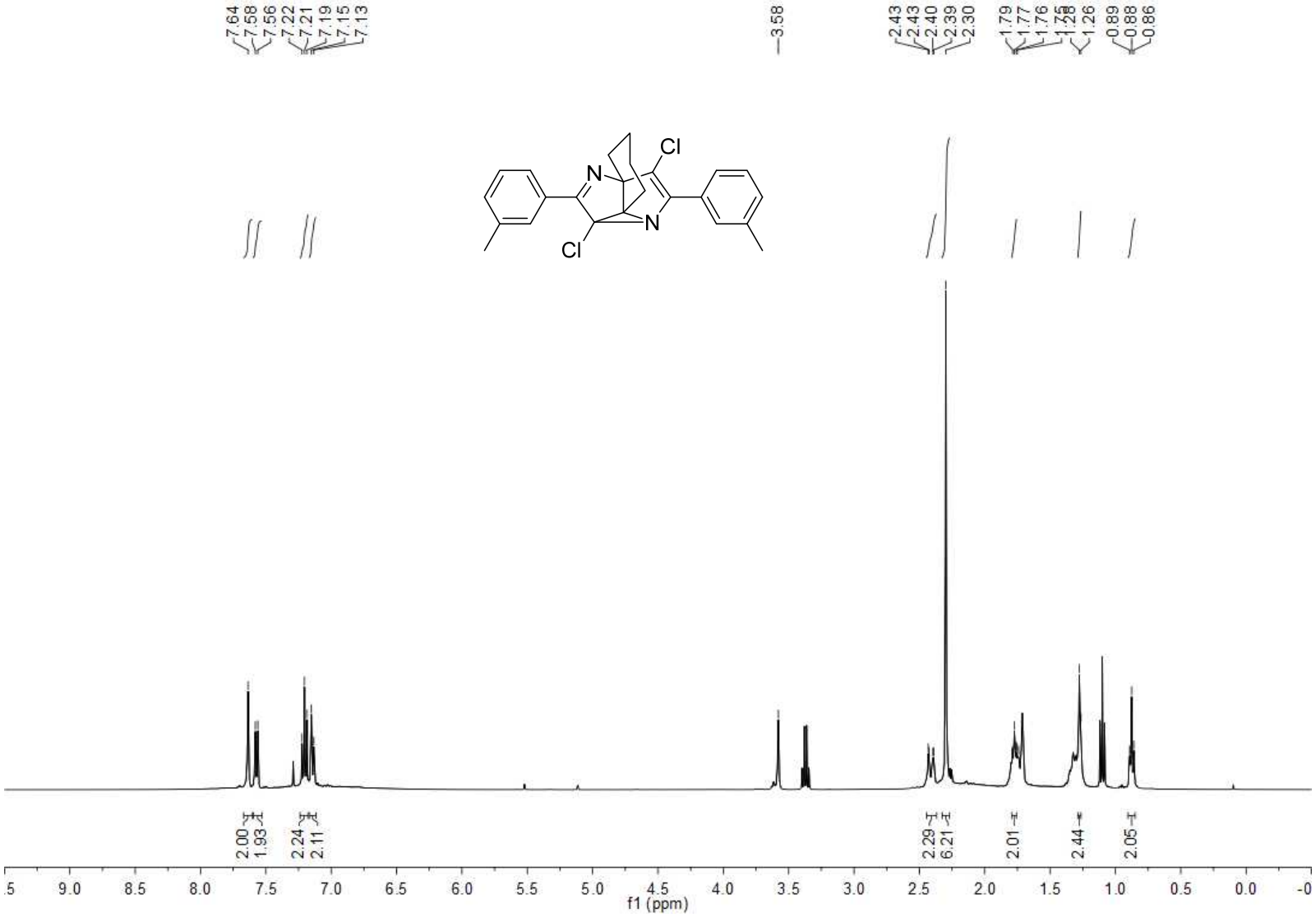
f1 (ppm)

3b-^{1}H NMR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Cl
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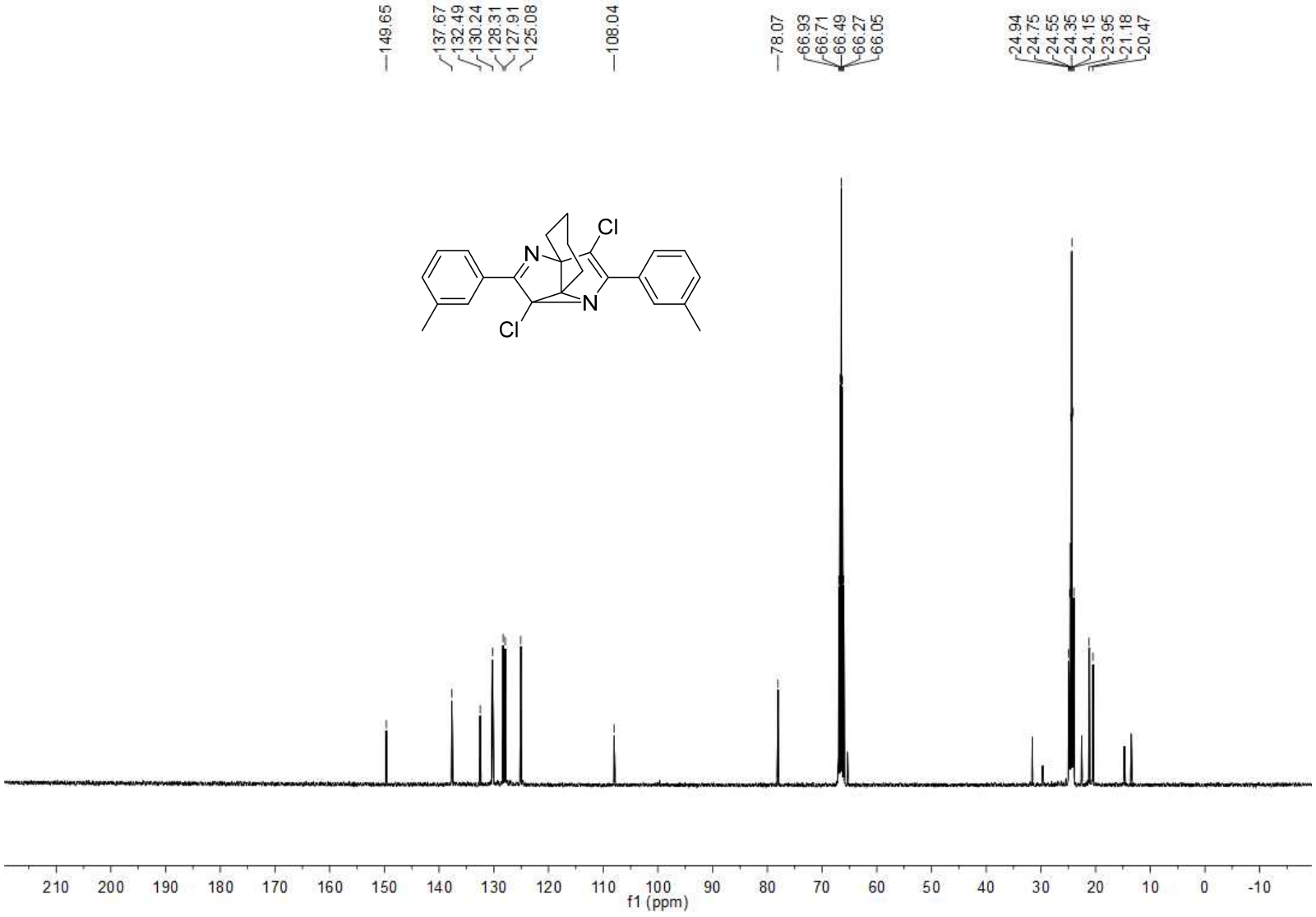
f1 (ppm)

3b-^{13}C NMR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66.27
66.05
24.94
24.75
24.55
24.35
24.15
23.95
21.18
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Cl
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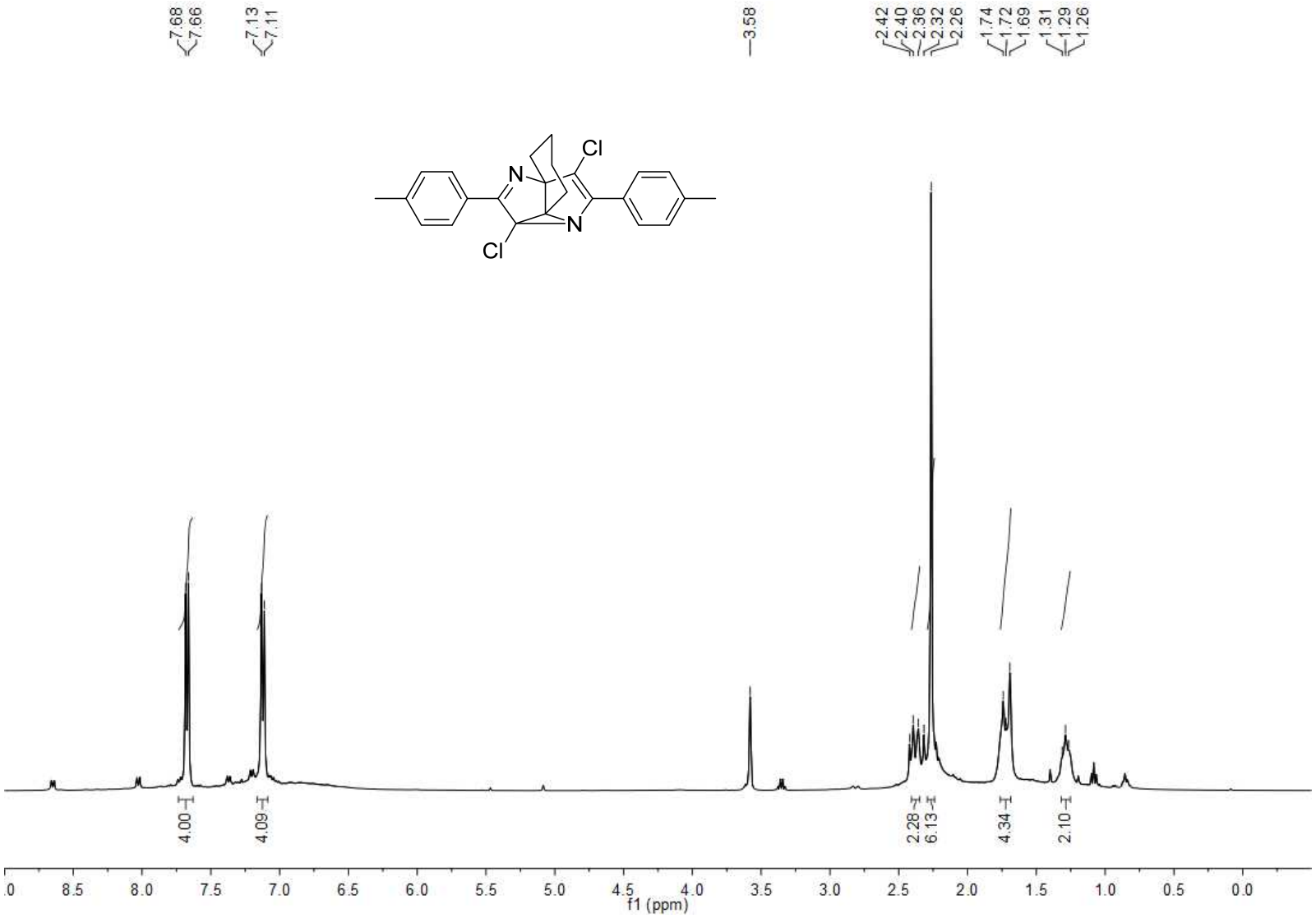
f1 (ppm)

3c-^{1}H NMR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1.26
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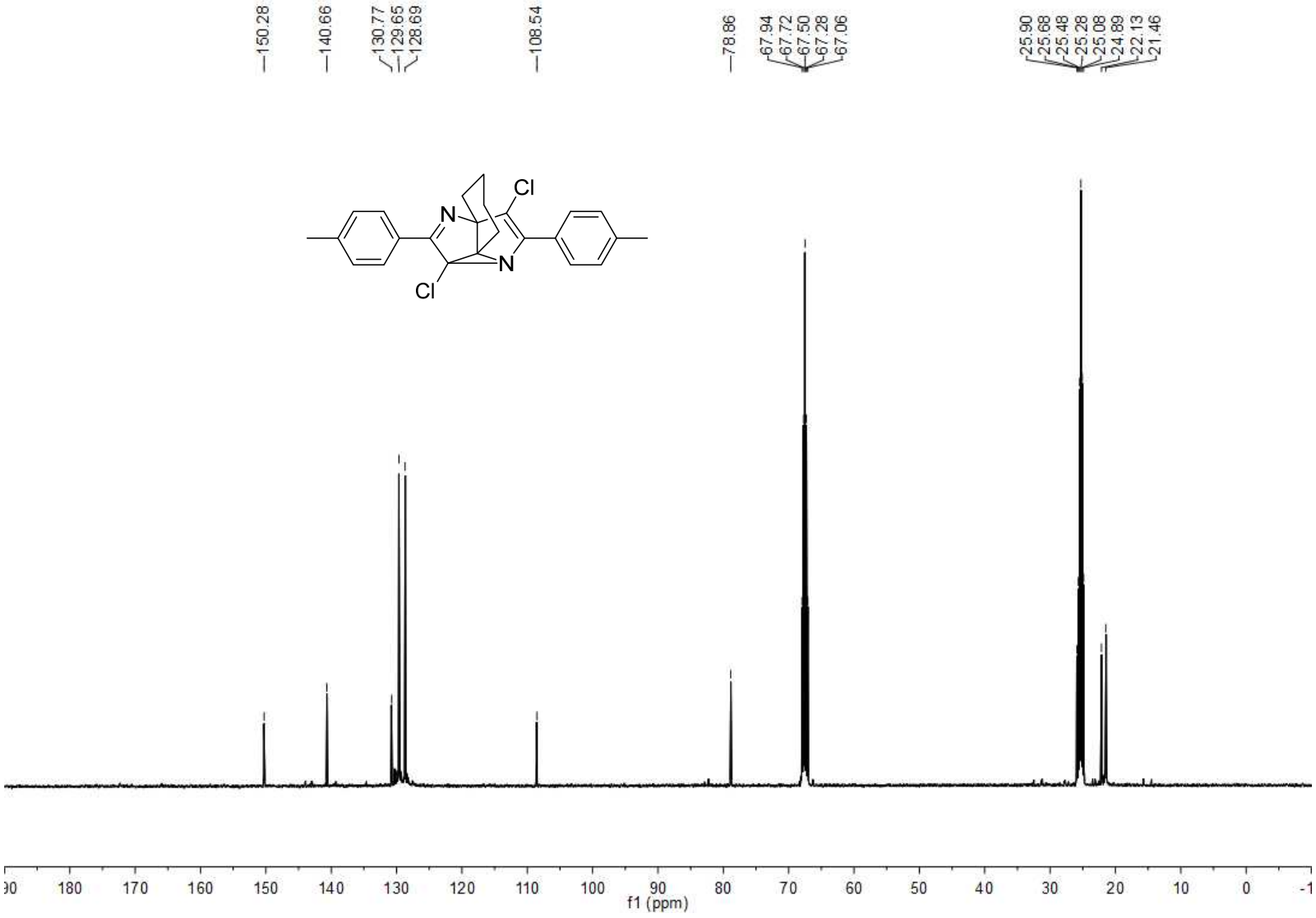
f1 (ppm)

3c-^{13}C NMR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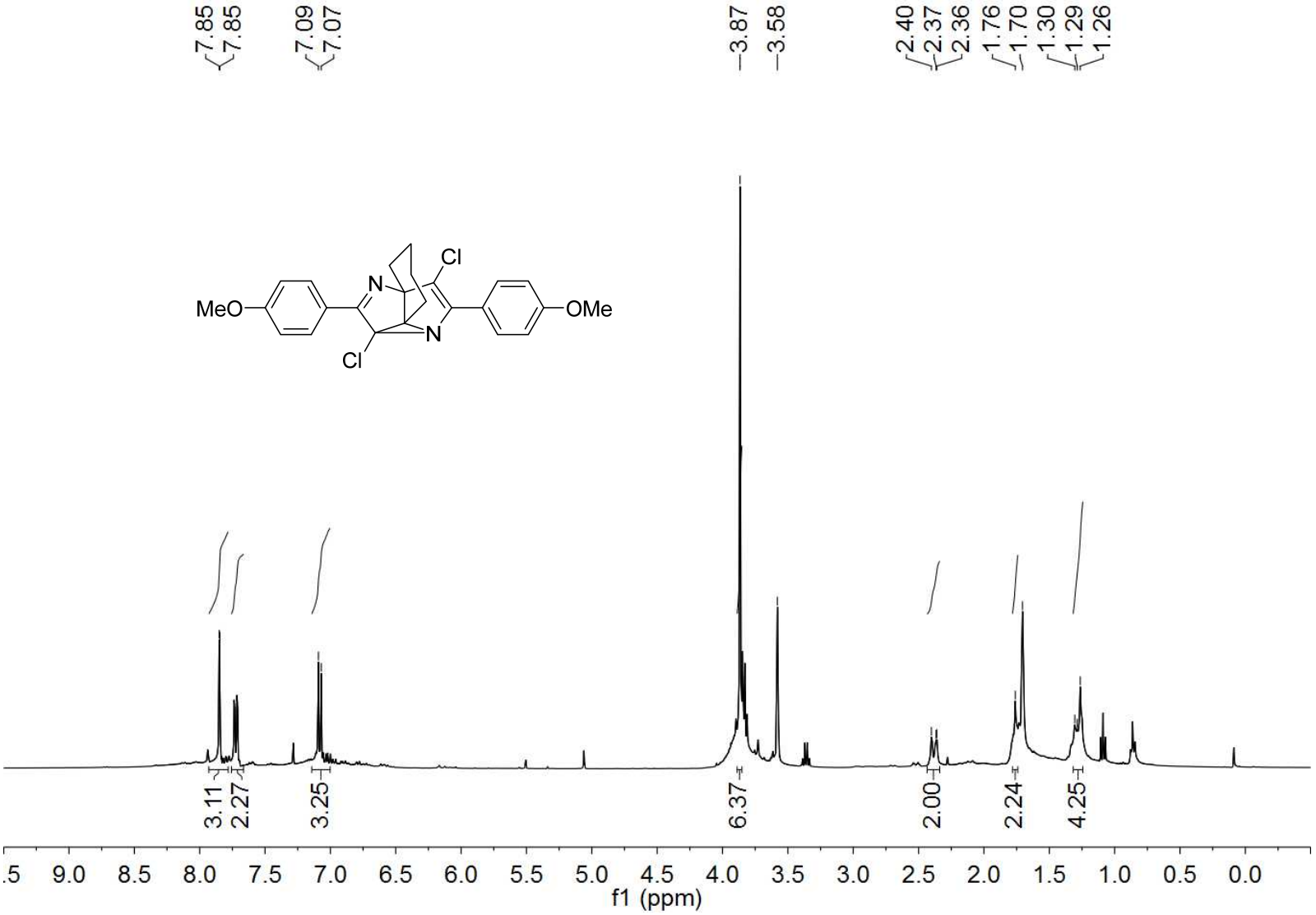
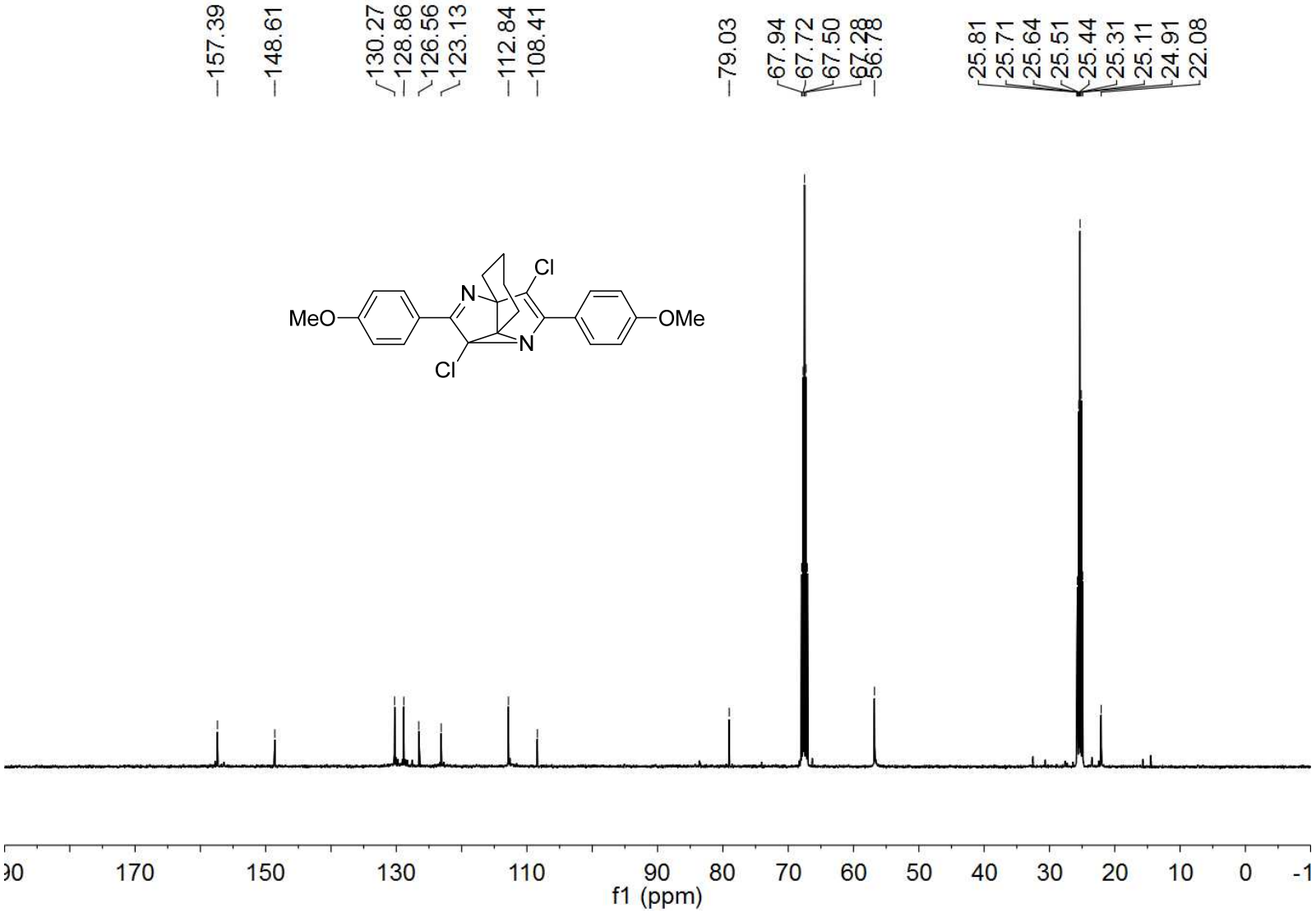
25.28
25.08
24.89
22.13
21.46
Cl
N
N
Cl
f1 (ppm)

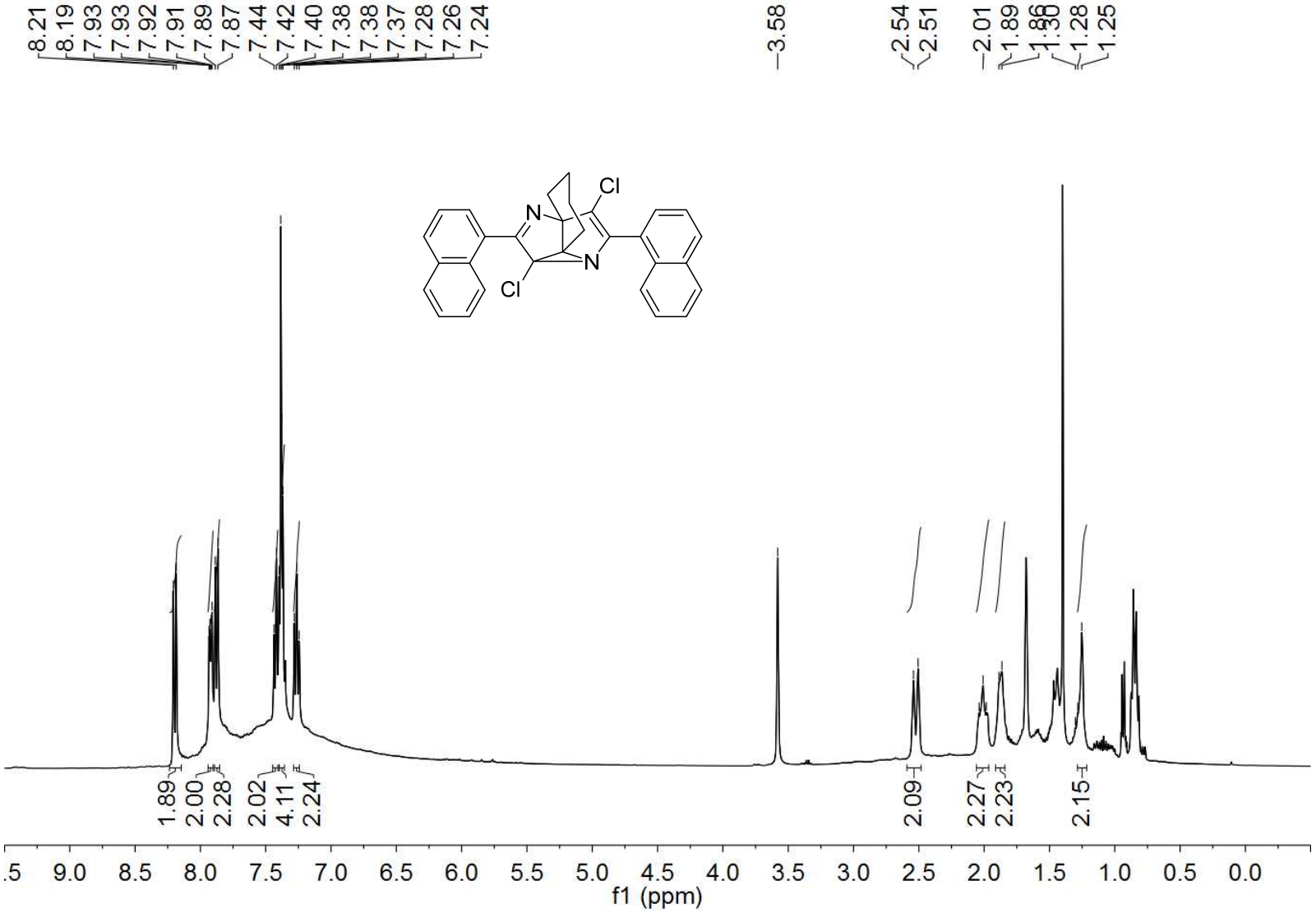
3d-^{1}H NMR


7.85
7.85
7.09
7.07
3.87
3.58
2.40
2.37
2.36
1.76
1.70
1.30
1.29
1.26
Cl
N
MeO
OMe
N
Cl
3.11
2.27
3.25
6.37
2.00
2.24
4.25
f1 (ppm)

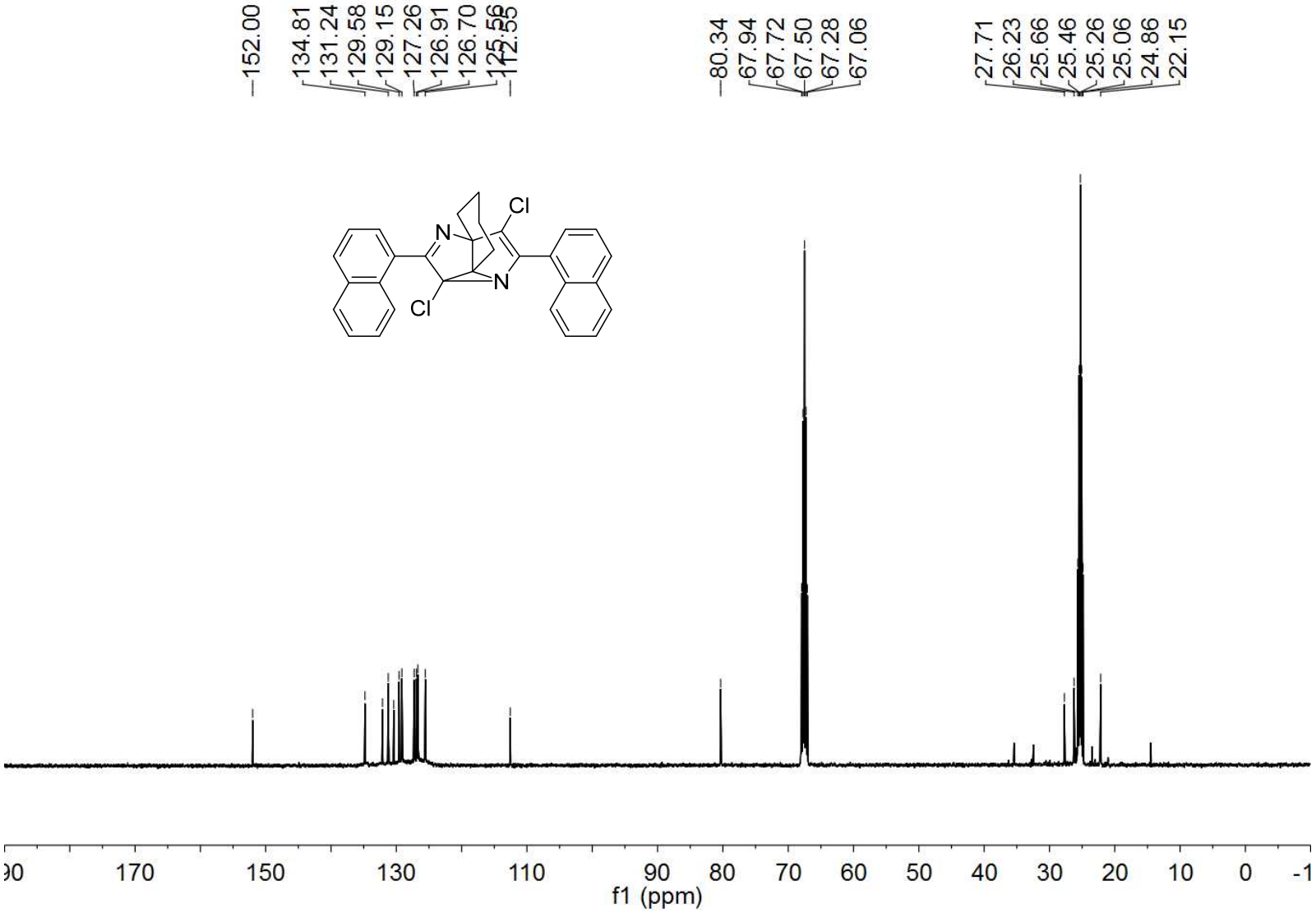
3d-^{13}C NMR


157.39
148.61
130.27
128.86
126.56
123.13
112.84
108.41
79.03
67.94
67.72
67.50
67.28
56.78
25.81
25.71
25.64
25.51
25.44
25.31
25.11
24.91
22.08
MeO
OMe
Cl
Cl
N
N
f1 (ppm)

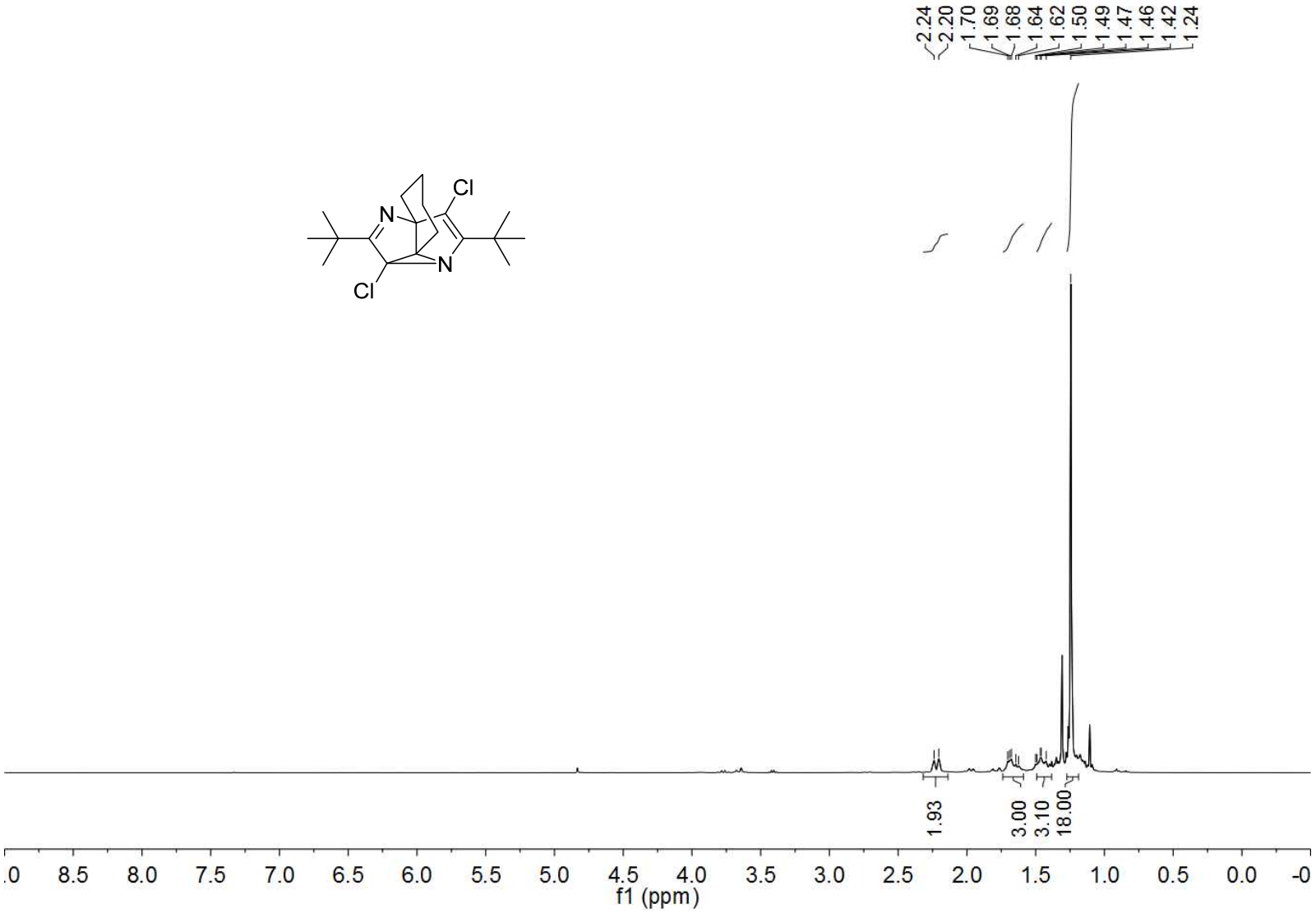
3e-^{1}H NMR


8.21
8.19
7.93
7.93
7.92
7.91
7.89
7.87
7.44
7.42
7.40
7.38
7.38
7.37
7.28
7.26
7.24
3.58
2.54
2.51
2.01
1.89
1.86
1.30
1.28
1.25
Cl
N
N
Cl
1.89
2.00
2.28
2.02
4.11
2.24
2.09
2.27
2.23
2.15
f1 (ppm)

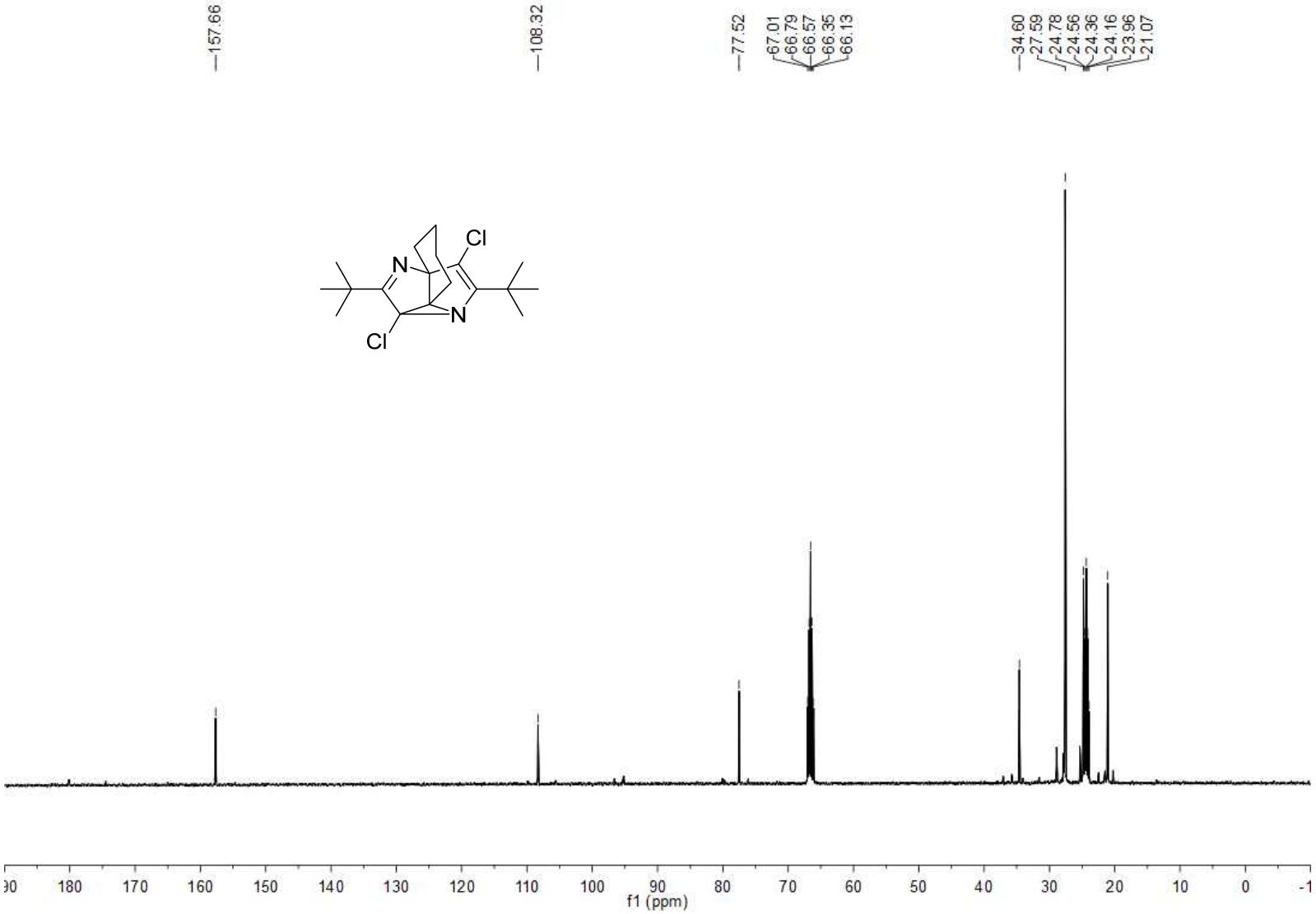
3e-^{13}C NMR


152.00
134.81
131.24
129.58
129.15
127.26
126.91
126.70
125.56
125.55
80.34
67.94
67.72
67.50
67.28
67.06
27.71
26.23
25.66
25.46
25.26
25.06
24.86
22.15
Cl
N
N
Cl
f1 (ppm)

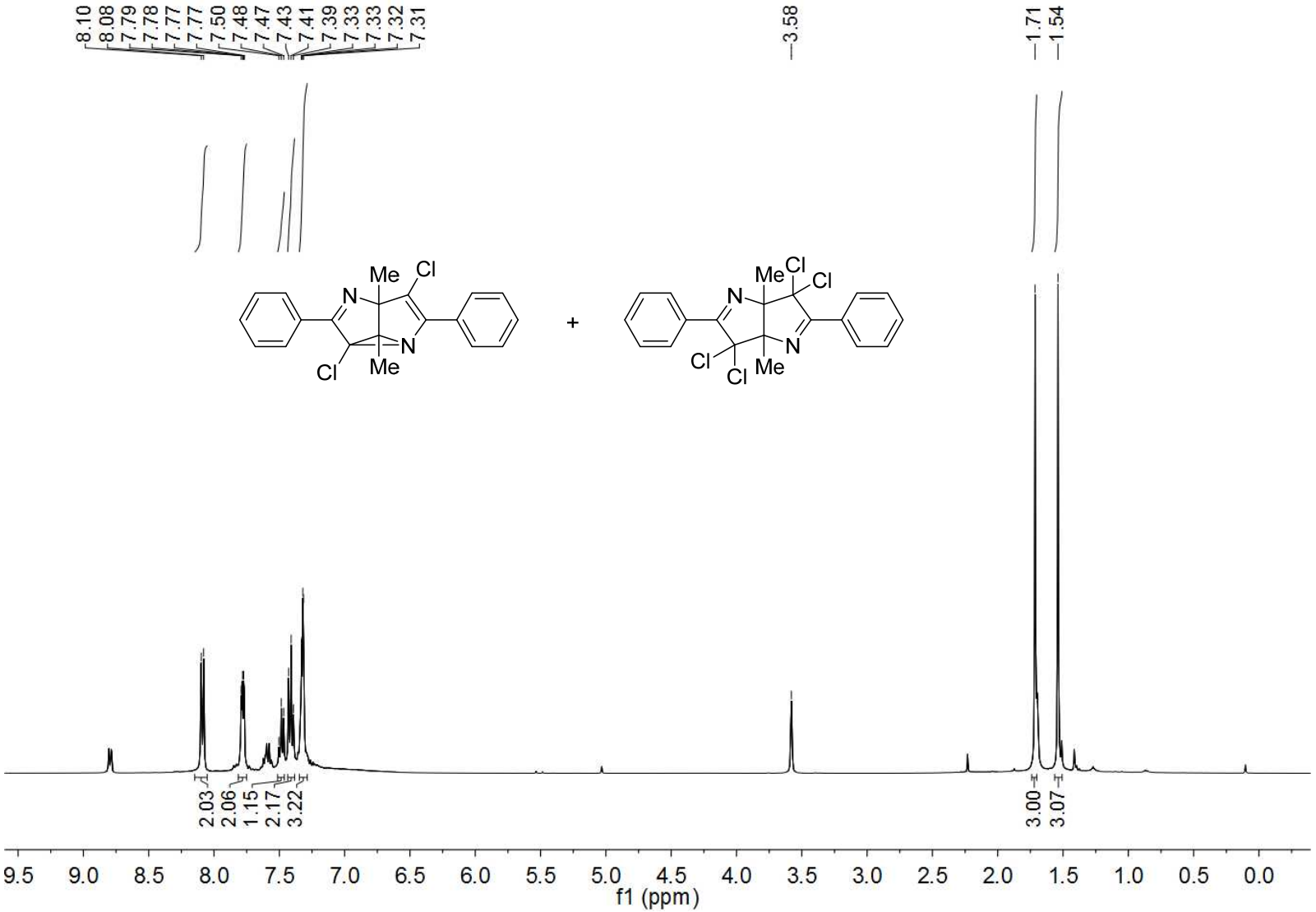
3f-^{1}H NMR


2.24
2.20
1.70
1.69
1.68
1.64
1.62
1.50
1.49
1.47
1.46
1.42
1.24
Cl
N
N
Cl
1.93
3.00
3.10
18.00
.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
f1 (ppm)

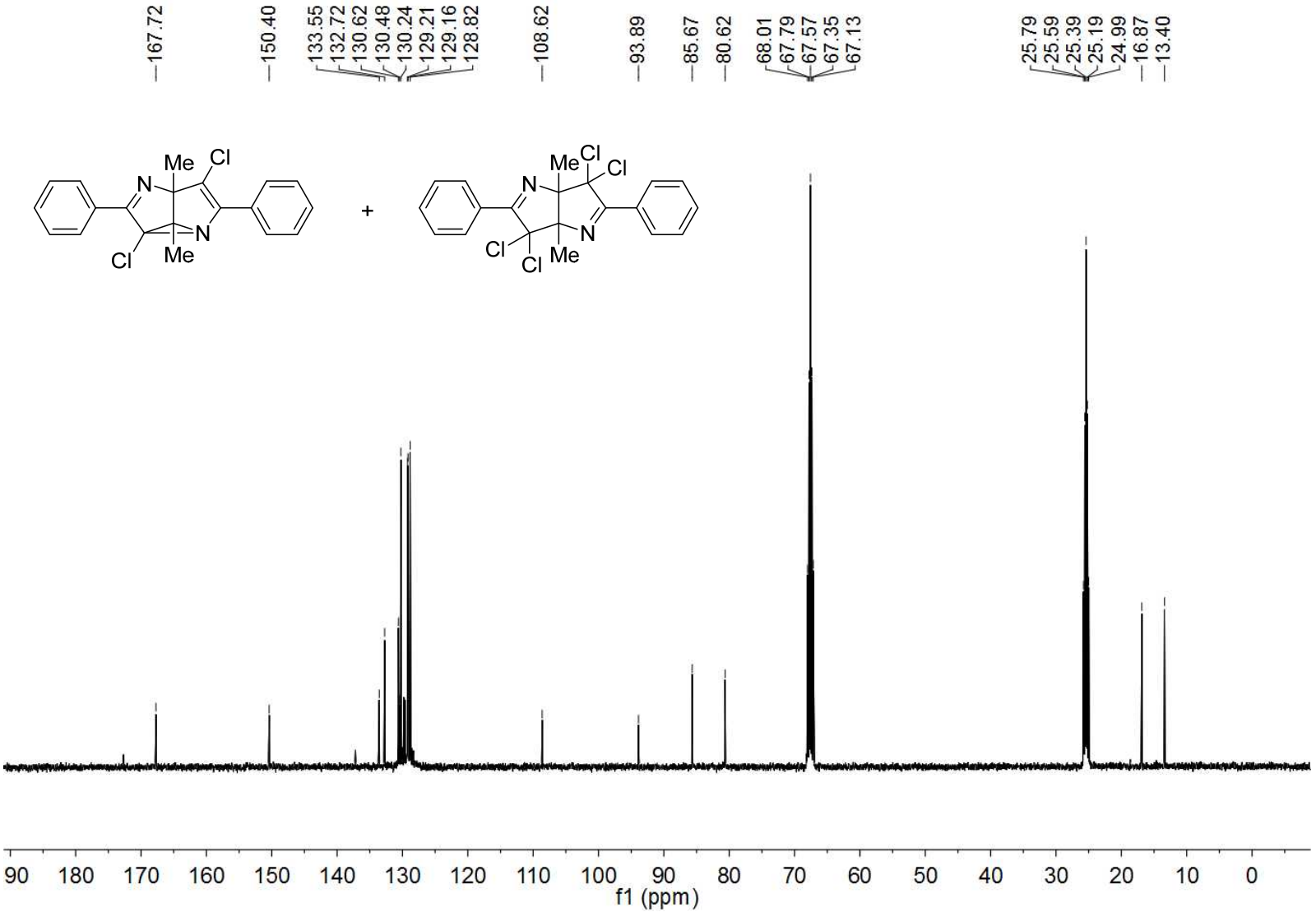
3f-^{13}C NMR


157.66
108.32
77.52
67.01
66.79
66.57
66.35
66.13
34.60
27.59
24.78
24.56
24.36
24.16
23.96
21.07
Cl
N
N
Cl
f1 (ppm)

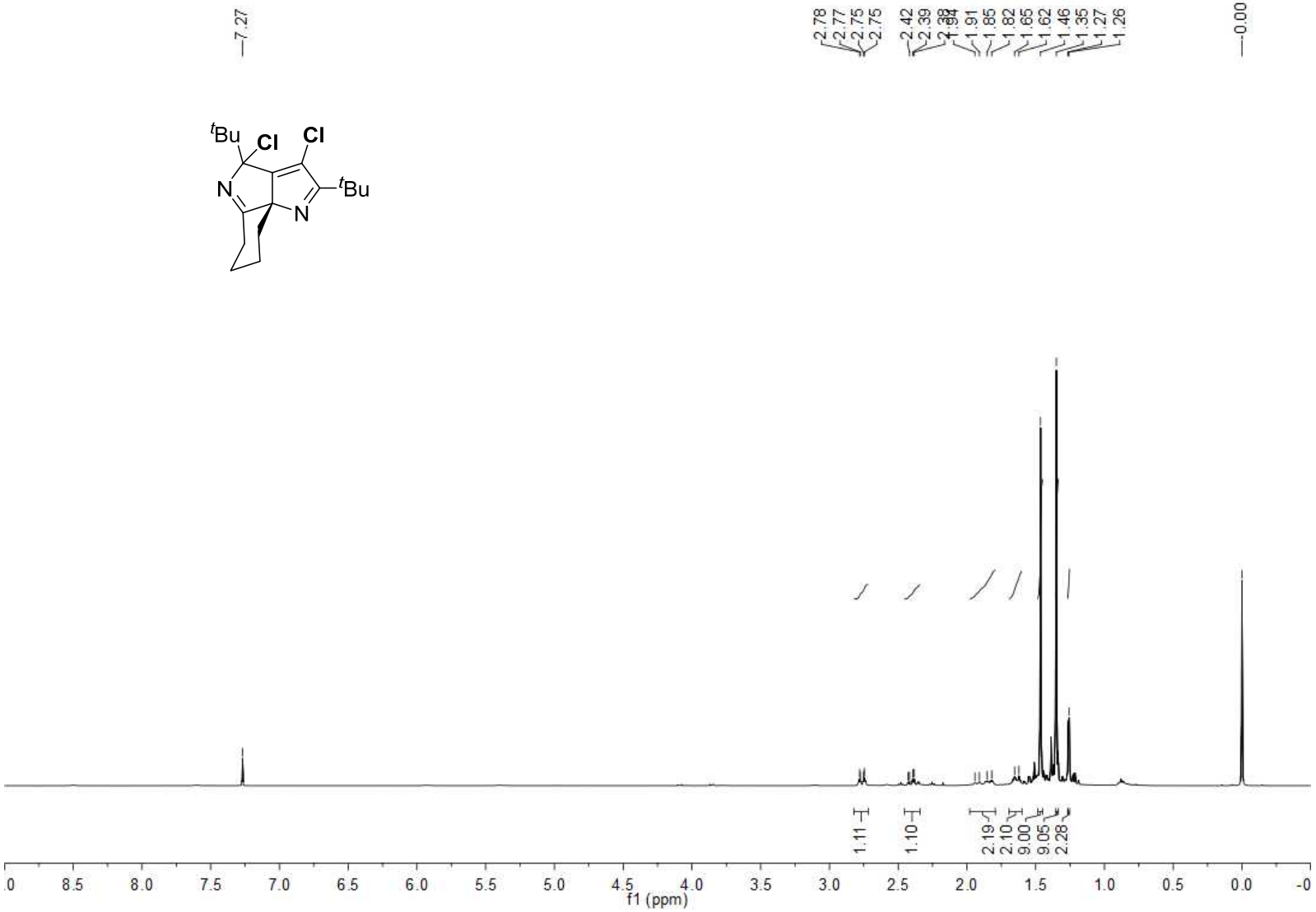
3g-in situ ^{1}H NMR (including 2g)



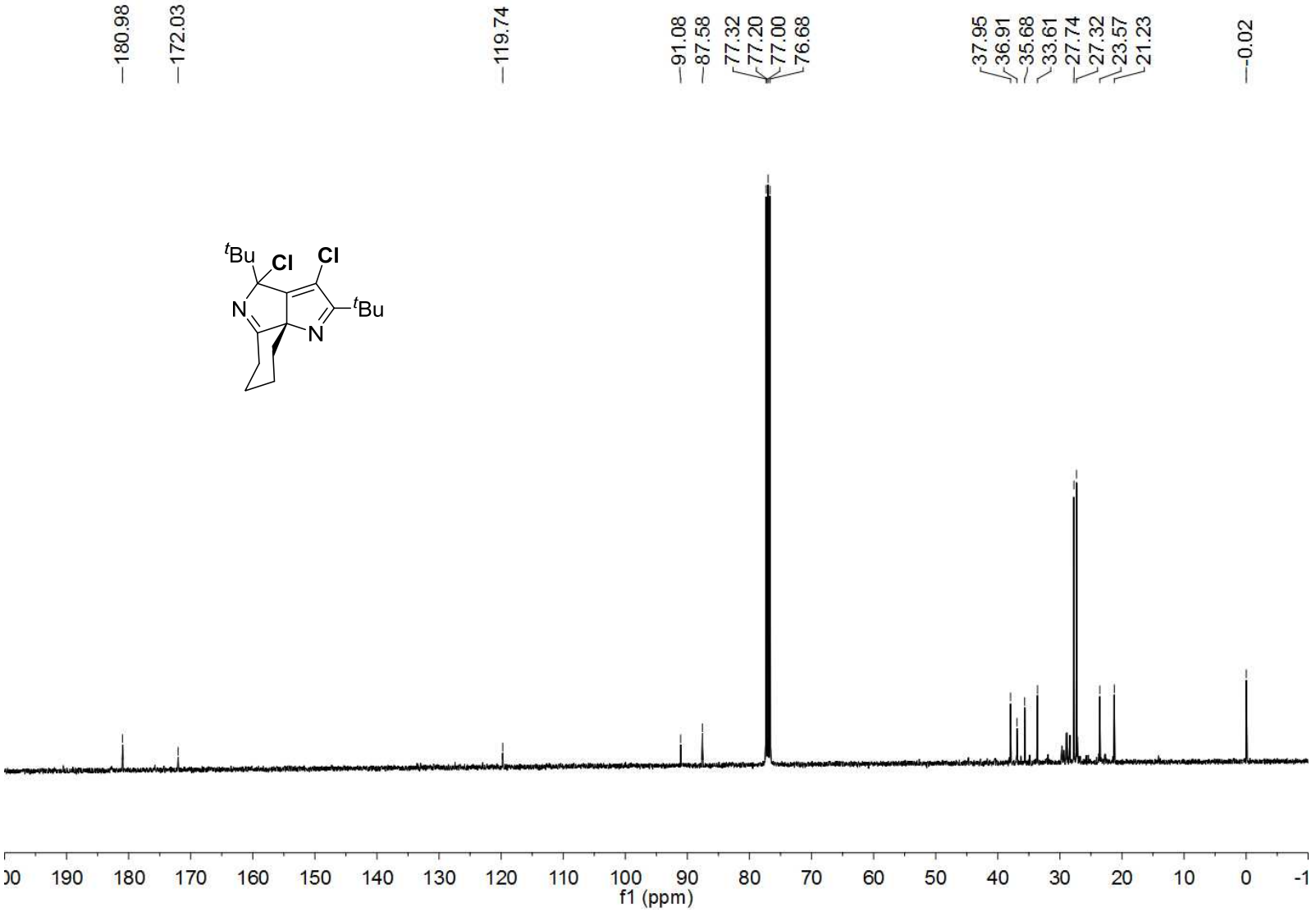
3g-in situ ^{13}C NMR (including 2g)



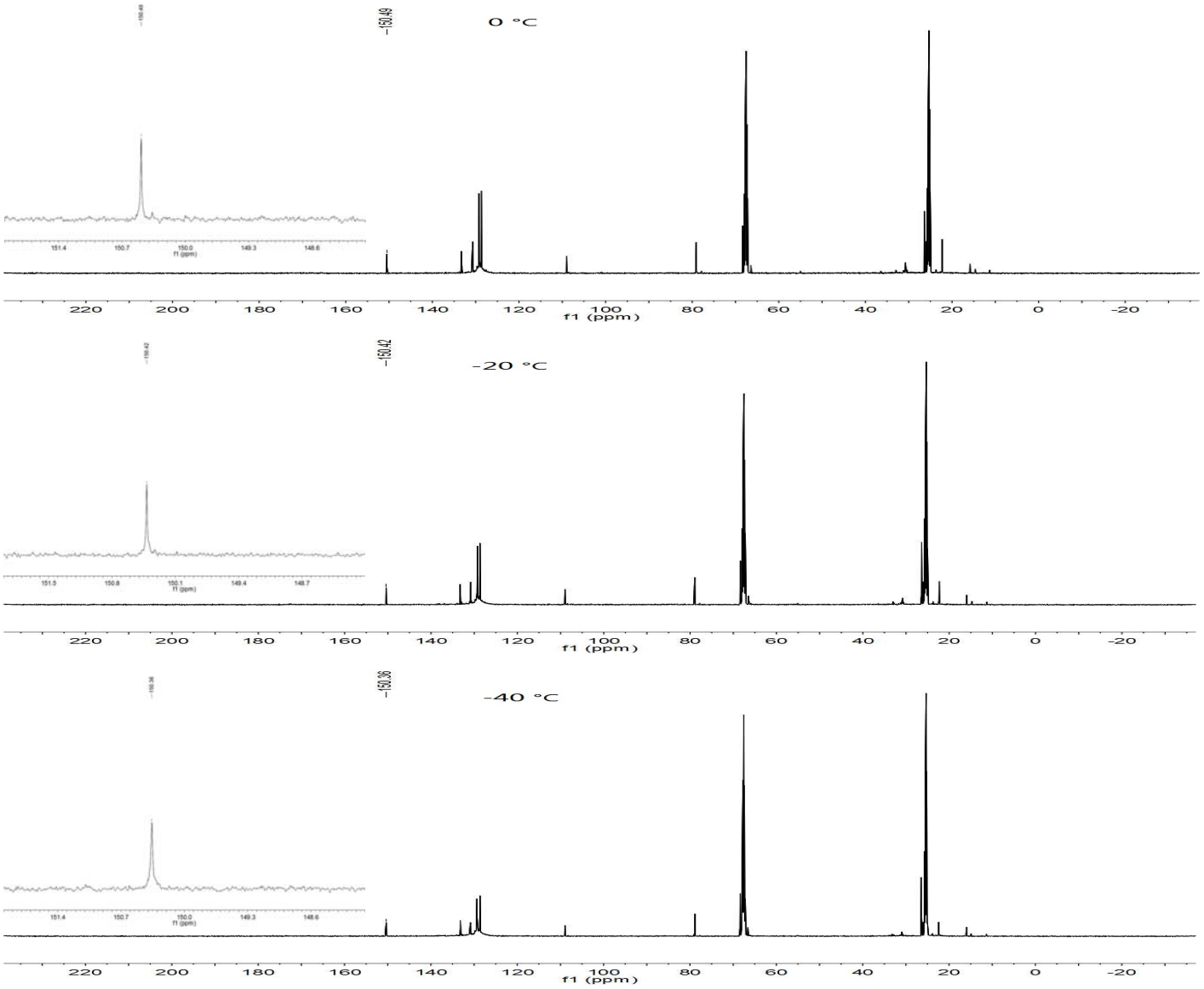
4-^{1}H NMR

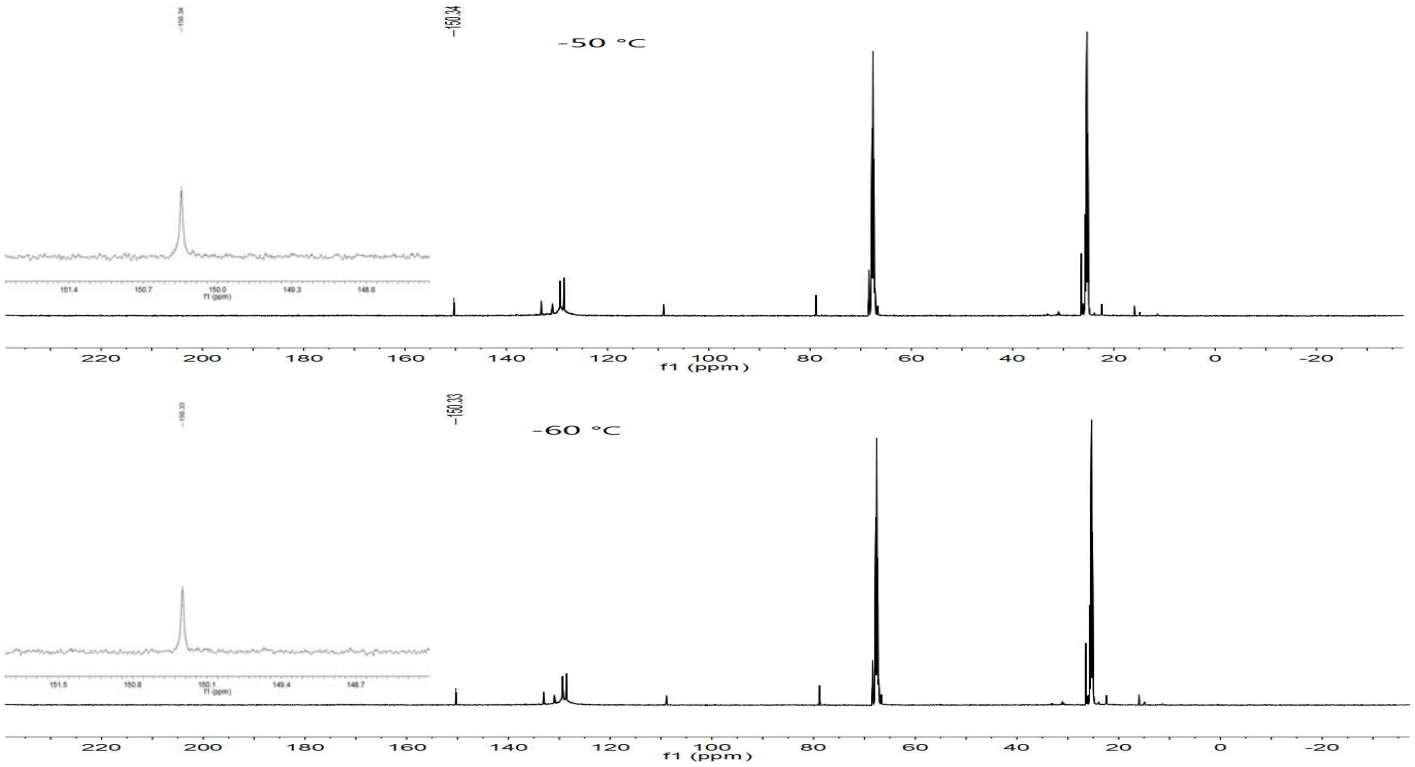

7.27
2.78
2.77
2.75
2.75
2.42
2.39
1.91
1.85
1.82
1.65
1.62
1.46
1.35
1.27
1.26
0.00
tBu
Cl
Cl
tBu
N
N
1.11
1.10
2.19
2.10
9.00
9.05
2.28
f1 (ppm)

4-^{13}C NMR


180.98
172.03
119.74
91.08
87.58
77.32
77.20
77.00
76.68
37.95
36.91
35.68
33.61
27.74
27.32
23.57
21.23
0.02
tBu
Cl
Cl
tBu
N
N
f1 (ppm)

Low temperature NMR spectra for 3a




-150.04
-50 °C
151.4
150.7
150.0
149.3
148.6
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)
-150.03
-60 °C
151.5
150.8
150.1
149.4
148.7
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
f1 (ppm)