Electronic Supplementary Information

Synthesis of fused bis-indazoles/indazoles *via* one-pot sequential strategy

Kishan Gugulothu,[a] Ramanna Jatoth,[a] Peramalla Edukondalu,[a] Anusha Vanga,[a] Raghavender Matta,[a] K. Shiva Kumar,[a,b]*

[a]Department of Chemistry, Osmania University, Hyderabad-500 007, India
[b]Department of Chemistry, School of Physical Sciences, Central University of Kerala, Kasaragod, Kerala 671320, India

Table of contents Page No

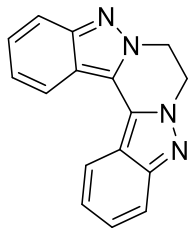
1. General methods: Unless stated otherwise, solvents and chemicals were obtained from commercial sources and were used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light or iodine spray. Flash chromatography was performed on silica gel (100-200 mesh) using hexane and ethyl acetate. Melting points were recorded on a DBK digital melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 or 400 or 125 or 100 Bruker Biospin A III FT-NMR spectrometer. ^{1}H and ^{13}C NMR spectra were determined in $CDCl_3$ and DMSO-d_6 solutions by using 500 or 400 or 125 or 100 MHz spectrometers, respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), dd (doublet of doublet), t (triplet) and m (multiplet). Coupling constants (J) are given in hertz. High-resolution mass spectra were recorded on a Bruker maxis-TOF mass spectrometer.

All starting materials 2-azidobenzaldehyde, substituted 2-azidobenzaldehyde (**1a**[1], **1c**[1], **1e**[1], **1g**[1], **1b**[2] and **1d-1f**[3]) and 2-(1*H*-indol-1-yl)ethan-1-amine[4] were prepared according to the known literature procedure.

2. General procedure and characterisation of annulated bi indazoles (**3aa-3af**)

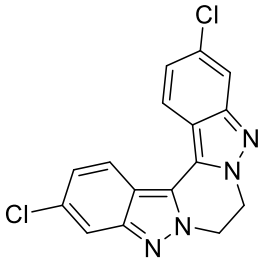
2-Azidobenzaldehyde (**1**) (0.50 mmol), diamine (**2**) (0.25 mmol) were taken in a oven dried Schlenck tube and it was closed with nitrogen balloon and stirred for 40 min at 110 ^{o}C. The completion of first step was monitored by TLC. Upon cooling to room temperature, $Pd(OAc)_2$ (5 mol %), $Cu(OAc)_2$ (50 mol %), and DMF (2 mL) solvent were added in same pot and resulting mixture was heated at 100 ^{o}C for 4 h. After completion of the reaction, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (2×20 mL). The organic layers were collected, combined and washed by saturated sodium bicarbonate, brine and dried with Na_2SO_4 and concentrated under vacuum to give the crude, which was further purified by flash column chromatography, was performed on silica gel (100-200 mesh) using hexane and ethyl acetate as eluent to afford the desired product (**3**).

7,8-Dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3aa)



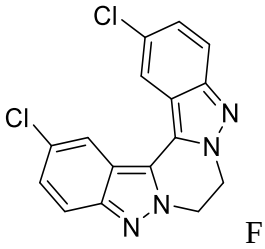
The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), ethane-1,2-diamine (**2a**) (0.016 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3aa** (96 mg, 74%) as a Brown solid; mp = 139-141 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.27 (dd, J = 11.6, 8.4 Hz, 2H), 4.97 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1 (2C), 126.9 (2C), 125.2 (2C), 123.3 (2C), 120.1 (2C), 118.0 (2C), 117.9 (2C), 47.9 (2C); **HR-MS**: (ESI+) m/z calculated for $[C_{16}H_{13}N_4]^+$ = $[M + H]^+$ 261.1135, found 261.1135.

3,12-Dichloro-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3ba)



The general procedure was followed by using 2-azido-4-chlorobenzaldehyde (**1b**) (90.5 mg, 0.5 mmol), ethane-1,2-diamine (**2a**) (0.016 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ba** (118 mg, 72%) as a Yellow solid; mp = 288-290 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$+TFA(1:0.3)) δ 8.17 (d, J = 8.8 Hz, 2H), 7.91 (s, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.28 (s, 4H**); ^{13}C NMR** (100 MHz, $CDCl_3$+TFA(1:0.3)) δ 146.7 (2C), 136.7 (2C), 127.4 (2C), 121.0 (2C), 116.4 (2C), 116.0 (2C), 115.6 (2), 47.0 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{16}H_{11}Cl_2N_4]^+$ = $[M + H]^+$ 329.0355, found 329.0355.

2,13-Dichloro-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3ca)

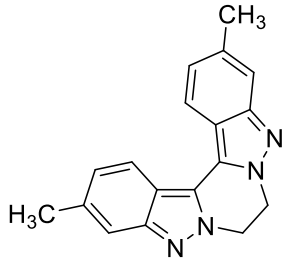


F

The general procedure was followed by using 2-azido-5-chlorobenzaldehyde (**1c**) (90.5 mg, 0.5 mmol), ethane-1,2-diamine (**2a**) (0.016 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ca** (121 mg, 74%) as a Brown solid; mp = 280-282 ^oC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (500 MHz, $CDCl_3$+TFA (1:0.1)) δ 8.04 (s, 2H), 7.78 (d, J = 9.5 Hz, 2H), 7.45 (d, J = 9 Hz, 2H), 5.12 (s, 4H); **^{13}C NMR** (100 MHz,

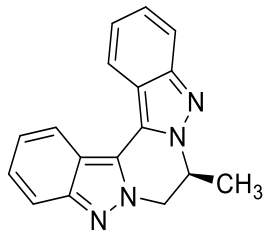
$CDCl_3$+TFA (1:0.1)) δ 146.1 (2C), 130.9 (2C), 130.3 (2C), 124.7 (2C), 118.6 (4C), 118.3 (2C), 47.2 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{16}H_{11}Cl_2N_4]^+ = [M + H]^+$ 329.0355, found 329.0353.

3,12-Dimethyl-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3da)



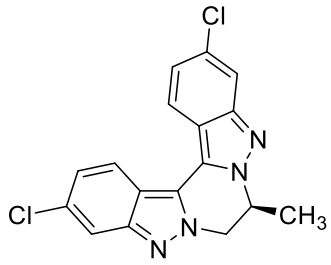
The general procedure was followed by using 2-azido-4-methylbenzaldehyde (**1d**) (80.5 mg, 0.5 mmol), ethane-1,2-diamine (**2a**) (0.016 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3da** (100.8 mg, 70%) as a Brown solid; mp = 242-244 ^oC; R_f = 0.5 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.8 Hz, 2H), 7.62 (s, 2H), 7.30 (d, J = 8.4 Hz, 2H), 5.17 (s, 4H), 2.56 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4 (2C), 140.0 (2C), 127.9 (2C), 125.4 (2C), 119.5 (2C), 116.2 (2C), 115.0 (2C), 46.8 (2C), 22.1 (2C)**; HR-MS** (ESI+) m/z calculated for $[C_{18}H_{17}N_4]^+ = [M + H]^+$ 289.1448, found 289.1447.

(S)-7-Methyl-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3ab)



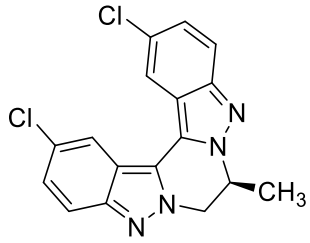
The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), propane-1,2-diamine (**2b**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ab** (98 mg, 72%) as a Yellow solid; mp = 178-180 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.4 Hz, 2H), 7.79 (dd, J = 8.4, 4.4 Hz, 2H), 7.40 (t, J = 7 Hz, 2H), 7.30 – 7.26 (m, 2H), 5.18-4.98 (m, 2H), 4.71 (dd, J = 13.6, 5.6 Hz, 1H), 1.74 (d, J = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 149.0, 126.9, 126.7, 124.9, 124.3, 123.2, 123.2, 120.3(2C), 118.2, 118.1 (2C), 117.9, 54.4, 53.6, 17.9; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{15}N_4]^+ = [M + H]^+$ 275.1291, found 275.1292.

(S)-3,12-Dichloro-7-methyl-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3bb)



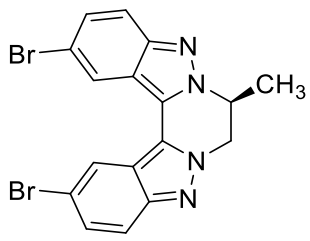
The general procedure was followed by using 2-azido-4-chlorobenzaldehyde (**1b**) (90.5 mg, 0.5 mmol), propane-1,2-diamine (**2b**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3bb** (116 mg, 68%) as a Off white solid; mp = 240-242 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, CDCl3) δ 8.04 (d, J = 7.6 Hz, 2H), 7.78 (s, 2H), 7.22 (s, 2H), 5.30 – 4.70 (m, 3H), 1.74 (d, J = 3.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$+TFA(1:0.3)) δ 148.1, 148.1, 148.0, 148.0, 135.1, 134.7, 126.2(2C), 125.2, 124.3, 121.1, 121.0, 116.5, 116.2, 54.4, 52.6, 18.1; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{13}Cl_2N_4]^+ = [M + H]^+$ 343.0512, found 343.0512.

(S)-2,13-Dichloro-7-methyl-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3cb)



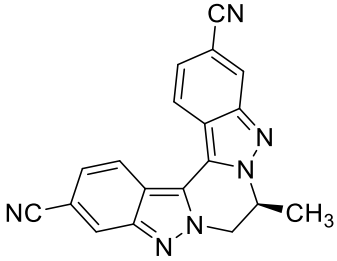
The general procedure was followed by using 2-azido-5-chlorobenzaldehyde (**1c**) (90.5 mg, 0.5 mmol), propane-1,2-diamine (**2b**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3cb** (123 mg, 72%) as a Brown solid; mp = 222-224 ^oC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.61 (d, J = 6 Hz, 2H), 7.30 – 7.18 (m, 2H), 5.03 – 4.87 (m, 2H), 4.58 (dd, J = 13.2, 5.6 Hz, 1H), 1.65 (d, J = 6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 147.2, 129.1, 129.1, 128.2, 128.2, 124.1, 123.6, 119.8, 119.6, 118.7, 118.7, 118.3, 118.0, 54.4, 53.6, 17.6; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{13}Cl_2N_4]^+ = [M + H]^+$ 343.0512, found 343.0541.

(S)-2,13-Dibromo-7-methyl-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole) (3eb)



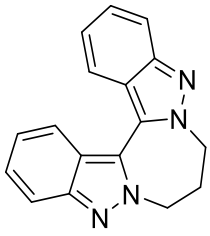
The general procedure was followed by using 2-azido-5-bromobenzaldehyde (**1e**) (113 mg, 0.5 mmol), propane-1,2-diamine (**2b**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3eb** (139 mg, 65%) as a Yellow solid; mp = 230-232 °C; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (s, 2H), 7.68 – 7.65 (m, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 5.15 – 5.10 (m, 1H), 5.00 – 4.96 (m, 1H), 4.71 – 4.66 (m, 1H), 1.74 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 147.4, 130.6, 130.5, 123.9, 123.4, 122.1, 122.1, 120.0, 119.8, 119.1, 118.8, 117.0, 117.0, 54.5, 53.6, 17.6; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{13}Br_2N_4]^+ = [M + H]^+$ 430.9501, found 430.9501.

(*S*)-7-Methyl-7,8-dihydropyrazino[1,2-*b*:4,3-*b*']bis(indazole)-3,12-dicarbonitrile (3fb)



The general procedure was followed by using 3-azido-4-formylbenzonitrile (**1f**) (86 mg, 0.5 mmol), propane-1,2-diamine (**2b**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3fb** (102 mg, 63%) as a Beige solid; mp = 296-298 °C; R_f = 0.5 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 4.4 Hz, 2H), 8.28 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.59-7.55 (m, 2H), 5.51 – 5.44 (m, 1H), 5.21 (dd, *J* = 14.4, 4.8 Hz, 1H), 5.05 – 5.00 (m, 1H), 1.77 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 146.4, 125.4(2C), 125.0, 124.6, 124.5, 121.7, 121.6, 119.7, 119.2, 118.5, 115.7, 112.9, 111.6, 111.3, 55.0, 53.1, 17.9; **HR-MS** (ESI+) m/z calculated for $[C_{19}H_{13}N_6]^+ = [M + H]^+$ 325.1196, found 325.1196.

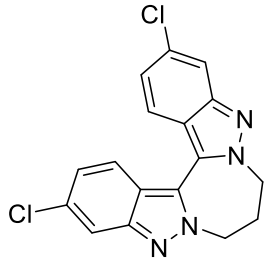
8,9-Dihydro-7H-[1,4]diazepino[1,2-*b*:4,3-*b*']bis(indazole) (3ac)



The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), propane-1,3-diamine (**2c**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ac** (96 mg, 70%) as a Brown solid; mp = 200-202 °C; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 4H), 7.42 – 7.38 (m, 2H), 7.25 (m, 2H), 4.65 (t, *J* = 7 Hz, 4H), 2.91 – 2.84 (m, 2H); **^{13}C NMR**

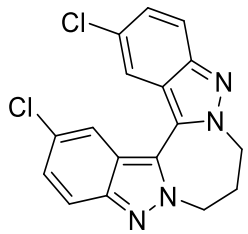
(100 MHz, $CDCl_3$) δ 148.3 (2C), 126.7 (2C), 125.3 (2C), 123.1 (2C), 121.1 (2C), 119.9 (2C), 117.9 (2C), 49.1 (2C), 31.6; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{15}N_4]^+ = [M + H]^+$ 275.1291, found 275.1300.

3,13-Dichloro-8,9-dihydro-7H-[1,4]diazepino[1,2-*b*:4,3-*b'*]bis(indazole) (3bc)



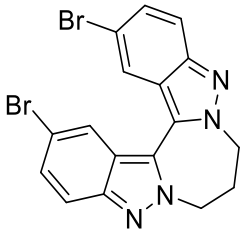
The general procedure was followed by using 2-azido-4-chlorobenzaldehyde (**1b**) (90.5 mg, 0.5 mmol), propane-1,3-diamine (**2c**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3bc** (123 mg, 72%) as a Brown solid; mp = 257-259 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 1.6, 0.4 Hz, 2H), 7.63 (dd, J = 8.8, 0.4 Hz, 2H), 7.11 (dd, J = 8.8, 1.6 Hz, 2H), 4.57 (t, J = 7 Hz, 4H), 2.82 – 2.75 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5 (2C), 132.8 (2C), 125.2 (2C), 124.8 (2C), 120.8 (2C), 119.4 (2C), 117.1 (2C), 49.3 (2C), 31.3; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{13}Cl_2N_4]^+ = [M + H]^+$ 343.0512, found 343.0516.

2,14-Dichloro-8,9-dihydro-7*H*-[1,4]diazepino[1,2-*b*:4,3-*b'*]bis(indazole) (3cc)



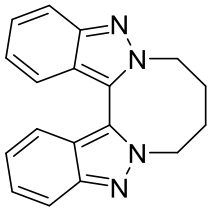
The general procedure was followed by using 2-azido-5-chlorobenzaldehyde (**1c**) (90.5 mg, 0.5 mmol), propane-1,3-diamine (**2c**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3cc** (119.7 mg, 70%) as a Brown solid; mp = 283-285 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$+TFA(1:0.2)) δ 7.89 – 7.84 (m, 4H), 7.61 (d, J = 8.4 Hz, 2H), 4.83 (s, 4H), 3.02 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$+TFA(1:0.2)) δ 144.7 (2C), 131.3 (2C), 131.0 (2C), 125.0 (2C), 121.3 (2C), 118.2 (2C), 118.1 (2C), 49.0 (2C), 31.1; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{13}Cl_2N_4]^+ = [M + H]^+$ 343.0512, found 343.0523.

2,14-Dibromo-8,9-dihydro-7H-[1,4]diazepino[1,2-*b*:4,3-*b'*]bis(indazole) (3ec)



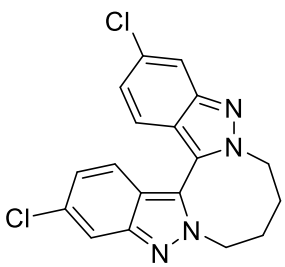
The general procedure was followed by using 2-azido-5-bromobenzaldehyde (**1e**) (113 mg, 0.5 mmol), propane-1,3-diamine (**2c**) (0.021 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ec** (141.8 mg, 66%) as a Brown solid; mp = 286-288 ºC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 – 7.93 (m, 2H), 7.68 (d, *J* = 9 Hz, 2H), 7.46 (dd, *J* = 9, 1.5 Hz, 2H), 4.61 (t, *J* = 6.5 Hz, 4H), 2.88 - 2.83 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.8 (2C), 130.5 (2C), 124.1 (2C), 122.1 (2C), 121.7 (2C), 119.8 (2C), 117.1 (2C), 49.2 (2C), 31.4; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{13}Br_2N_4]^+ = [M + H]^+$ 430.9501, found 430.9500.

7,8,9,10-Tetrahydro-[1,4]diazocino[1,2-*b*:4,3-*b*']bis(indazole) (3ad)



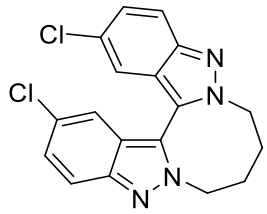
The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), butane-1,4-diamine (**2d**) (0.025 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ad** (93.6 mg, 65%) as a Off white solid; mp = 201-203 ºC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 2H), 4.92 – 4.87 (m, 2H), 3.94 – 3.88 (m, 2H), 2.32 – 2.30 (m, 2H), 2.13 – 2.09 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3 (2C), 126.6 (2C), 124.0 (2C), 122.9 (2C), 122.1 (2C), 119.7 (2C), 117.7 (2C), 52.2 (2C), 28.7 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{18}H_{17}N_4]^+ = [M + H]^+$ 289.1448, found 289.1456.

3,14-Dichloro-7,8,9,10-tetrahydro-[1,4]diazocino[1,2-*b*:4,3-*b*']bis(indazole) (3bd)



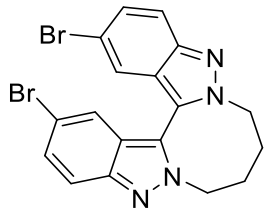
The general procedure was followed by using 2-azido-4-chlorobenzaldehyde (**1b**) (90z.5 mg, 0.5 mmol), butane-1,4-diamine (**2d**) (0.025 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3bd** (121 mg, 68%) as a Off white solid; mp = 221-223 ^oC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$+TFA(1:0.1)) δ 7.93 (s, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 5.14 – 5.09 (m, 2H), 4.02 (dd, J = 14.4, 10 Hz, 2H), 2.46 – 2.38 (m, 2H), 2.21 – 2.14 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$+TFA(1:0.1)) δ 145.5 (2C), 136.9 (2C), 127.3 (2C), 124.8 (2C), 120.5 (2C), 120.0 (2C), 115.1 (2C), 52.2 (2C), 27.5 (2); **HR-MS** (ESI+) m/z calculated for $[C_{18}H_{15}Cl_2N_4]^+$ = $[M + H]^+$ 357.0668, found 357.0668.

2,15-Dichloro-7,8,9,10-tetrahydro-[1,4]diazocino[1,2-b:4,3-b']bis(indazole) (3cd)



The general procedure was followed by using 2-azido-5-chlorobenzaldehyde (**1c**) (90.5 mg, 0.5 mmol), butane-1,4-diamine (**2d**) (0.025 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3cd** (124.6 mg, 70%) as a Pink solid; mp = 285-287 ^oC; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$+TFA (1:0.3)) δ 7.91 (d, J = 6.8 Hz, 2H), 7.70 – 7.63 (m, 4H), 5.17 – 5.14 (m, 2H), 4.09 – 4.04 (m, 2H), 2.46 – 2.43 (m, 2H), 2.21 (dd, J = 9.6, 2.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$+ TFA (1:0.3)) δ 146.6 (2C), 129.0 (2C), 128.2 (2C), 123.0 (2C), 122.5 (2C), 119.4 (2C), 118.1 (2C), 52.3 (2C), 28.7(2C); **HR-MS** (ESI+) m/z calculated for $[C_{18}H_{15}Cl_2N_4]^+$ = $[M + H]^+$ 357.0668, found 357.0663.

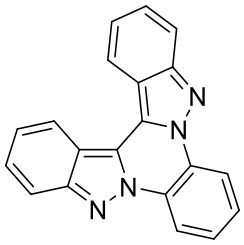
2,15-Dibromo-7,8,9,10-tetrahydro-[1,4]diazocino[1,2-*b*:4,3-*b'*]bis(indazole) (3ed)



The general procedure was followed by using 2-azido-5-bromobenzaldehyde (**1e**) (113 mg, 0.5 mmol), butane-1,4-diamine (**2d**) (0.025 mL, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ed** (148.7 mg, 67%) as a Brown solid; mp = 291-293 ^oC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 4H), 7.39 (dd, J = 8.8, 1.6 Hz, 2H), 4.79 (dd, J = 14, 6.8 Hz, 2H), 3.80 – 3.73 (m, 2H), 2.24 (dd, J

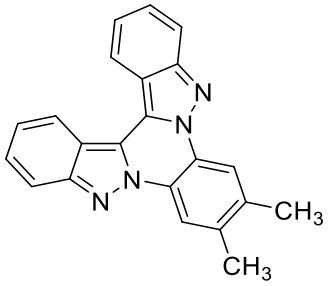
= 11.2, 7.6 Hz, 2H), 2.04 – 1.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7 (2C), 130.5(2C), 123.2 (2C), 122.8 (2C), 121.5 (2C), 119.6 (2C), 116.8 (2C), 52.3 (2C), 28.6 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{18}H_{15}Br_2N_4]^+ = [M + H]^+$ 444.9658, found 444.9658.

Diindazolo[2,3-*a*:3',2'-*c*]quinoxaline (3ae)



The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), benzene-1,2-diamine (**2e**) (27 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3ae** (103 mg, 67%) as a Yellow solid; mp = 288-290 ^oC; R_f = 0.5 (20% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78 (dd, J = 6.0, 3.6 Hz, 2H), 8.55 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.8 Hz, 2H), 7.96 (dd, J = 6.4, 3.2 Hz, 2H), 7.79 (t, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6 (2C), 129.8 (2C), 129.3 (2C), 124.8 (2C), 124.1 (2C), 124.1 (2C), 120.2 (2C), 117.5 (2C), 116.2 (2C), 116.0 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{20}H_{13}N_4]^+ = [M + H]^+$ 309.1135, found 309.1134.

8,9-Dimethyldiindazolo[2,3-*a*:3',2'-*c*]quinoxaline (3af)

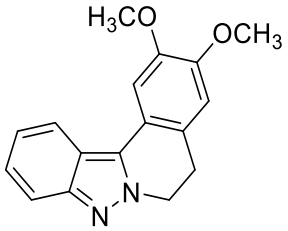


The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), 4,5-dimethylbenzene-1,2-diamine (**2f**) (34 mg, 0.25 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **3af** (110.8 mg, 66%) as a Yellow solid; mp = 282-284 ^oC; R_f = 0.5 (20% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 – 8.27 (m, 4H), 7.86 (d, J = 6.0 Hz, 2H), 7.60 (s, 2H), 7.41 (s, 2H), 2.45 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7 (2C), 140.3 (2C), 130.2 (2C), 124.3 (2C), 123.7 (2C), 122.2 (2C), 120.4 (2C), 117.3 (2C), 116.0 (2C), 115.8 (2C), 19.9 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{22}H_{17}N_4]^+ = [M + H]^+$ 337.1448, found 337.1446.

3. General procedure and characterisation of annulated indazoles (5aa-5fc)

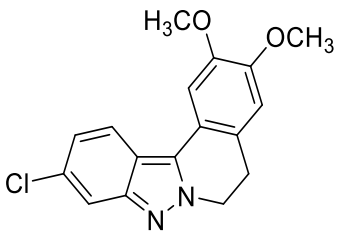
2-Azidobenzaldehyde (**1**) (0.50 mmol), aryl/heteroaryl benzyl amines (**4**) (0.50 mmol) were taken in a oven dried Schlenck tube and it was closed with nitrogen balloon and stirred for 40 min at 110 ^{o}C. The completion of first step was monitored by TLC. Upon cooling to room temperature, $Pd(OAc)_2$ (5 mol %), $Cu(OAc)_2$ (50 mol %), and DMF (2 mL) solvent were added in same pot and resulting mixture was heated at 100 ^{o}C for 4 h. After completion of the reaction, the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (2×20 mL). The organic layers were collected, combined and washed by saturated sodium bicarbonate, brine and dried with Na_2SO_4 and concentrated under vacuum to give the crude, which was further purified by flash column chromatography, was performed on silica gel (100-200 mesh) using hexane and ethyl acetate as eluent to afford the desired product (**5**).

2,3-Dimethoxy-5,6-dihydroindazolo[3,2-*a*]isoquinoline (5aa)



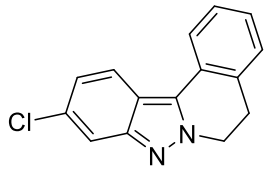
The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), 2-(3,4-dimethoxyphenyl)ethan-1-amine (**4a**) (0.084 mL, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5aa** (98 mg, 70%) as a White solid; mp = 177-179 ^{o}C (Lit[5] 180-182 ^{o}C); R_f = 0.5 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.48 (s, 1H), 7.33 (t J = 7.4 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 6.86 (s, 1H), 4.63 (t, J = 6.8 Hz, 2H), 4.03 (s, 3H), 3.95 (s, 3H), 3.22 (t, J = 6.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 148.5, 148.4, 130.7, 126.0, 125.0, 121.9, 120.7, 120.0, 117.8, 117.5, 111.56 107.3, 56.2, 56.0, 47.9, 28.8.

10-Chloro-2,3-dimethoxy-5,6-dihydroindazolo[3,2-a]isoquinoline (5ba)



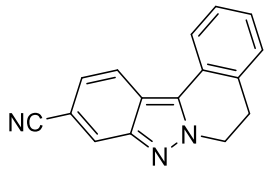
The general procedure was followed by using 2-azido-4-chlorobenzaldehyde (**1b**) (90.5 mg, 0.5 mmol), 2-(3,4-dimethoxyphenyl)ethan-1-amine (**4a**) (0.084 mL, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5ba** (113 mg, 72%) as a Yellow solid; mp = 148-150 ^oC[6]; R_f = 0.4 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 1H), 7.70 (s, 1H), 7.40 (s, 1H), 7.10 (d, J = 8.8 Hz, 1H), 6.85 (s, 1H), 4.59 (t, J = 6.8 Hz, 2H), 4.02 (s, 3H), 3.95 (s, 3H), 3.21 (t, J = 6.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 148.7, 148.5, 131.9, 131.3, 125.1, 123.1, 121.3, 120.1, 116.8, 116.0, 111.6, 107.4, 56.3, 56.1, 47.9, 28.7.

10-Chloro-5,6-dihydroindazolo[3,2-a]isoquinoline (5bb)



The general procedure was followed by using 2-azido-4-chlorobenzaldehyde (**1b**) (90.5 mg, 0.5 mmol), 2-phenylethan-1-amine (**4b**) (0.062 mL, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5bb** (91.4 mg, 72%) as a Off white solid; mp = 98-100 ^oC; R_f = 0.5 (30% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.71 – 7.71 (m, 1H), 7.43 – 7.39 (m, 1H), 7.35 – 7.29 (m, 2H), 7.12 (dd, J = 8.8, 1.6 Hz, 1H), 4.63 (t, J = 7.0 Hz, 2H), 3.28 (t, J = 76.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 132.0, 132.0, 131.1, 128.4, 128.3, 127.8, 127.4, 124.0, 123.6, 121.6, 117.0, 116.6, 47.8, 29.0; **HR-MS** (ESI+) m/z calculated for $[C_{15}H_{12}ClN_2]^+$ = $[M + H]^+$ 255.0684, found 255.0685.

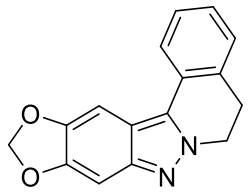
5,6-Dihydroindazolo[3,2-a]isoquinoline-10-carbonitrile (5fb)



The general procedure was followed by using 3-azido-4-formylbenzonitrile (**1f**) (86 mg, 0.5 mmol), 2-phenylethan-1-amine (**4b**) (0.062 mL, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5fb** (75.9 mg, 62%) as a Off white solid; mp = 148-150 ^oC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 6.0 Hz, 1H), 7.37 – 7.33 (m, 2H),

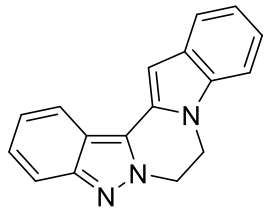
7.29 (d, *J* = 8.8 Hz, 1H), 4.69 (t, *J* = 6.8 Hz, 2H), 3.31 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 132.0, 131.7, 128.8, 128.5, 128.0, 127.0, 125.0, 124.0, 123.0, 122.0, 119.6, 119.5, 109.3, 48.3, 29.0; **HR-MS** (ESI+) m/z calculated for $[C_{16}H_{12}N_3]^+ = [M + H]^+$ 246.1026, found 246.1025.

5,6-Dihydro-[1,3]dioxolo[4',5':5,6]indazolo[3,2-*a*]isoquinoline (5gb)



The general procedure was followed by using 6-azidobenzo[d][1,3]dioxole-5-carbaldehyde (**1g**) (95.5 mg, 0.5 mmol), 2-phenylethan-1-amine (**4b**) (0.062 mL, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5gb** (83 mg, 63%) as a Brown solid; mp = 196-198 ^oC; R_f = 0.5 (30% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.01 (s, 1H), 5.99 (s, 2H), 4.54 (t, *J* = 6.6 Hz, 2H), 3.24 (t, *J* = 6.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 146.0, 145.8, 131.9, 130.2, 128.3, 128.0, 127.6, 127.5, 123.3, 113.4, 101.0, 95.8, 94.6, 47.5, 29.3; **HR-MS** (ESI+) m/z calculated for $[C_{16}H_{13}N_2O_2]^+ = [M + H]^+$ 265.0972, found 265.0975.

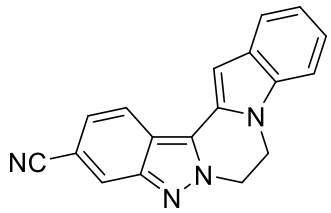
7,8-Dihydroindolo[2',1':3,4]pyrazino[1,2-b]indazole (5ac)



The general procedure was followed by using 2-azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), 2-(1H-indol-1-yl)ethan-1-amine (**4c**) (80 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5ac** (90.6 mg, 70%) as a Brown solid; mp = 105-107 ^oC; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 1H), 7.23 – 7.15 (m, 2H), 7.03 (s, 1H), 4.89 (t, *J* = 6.0 Hz, 2H), 4.55 (t, *J* = 5.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 136.3, 129.2, 127.8, 126.7, 126.5, 123.0, 122.5, 121.3, 120.7, 119.9, 118.3, 117.6,

109.0, 98.8, 47.8, 40.6; **HR-MS** (ESI+) m/z calculated for $[C_{17}H_{14}N_3]^+ = [M + H]^+$ 260.1182, found 260.1181.

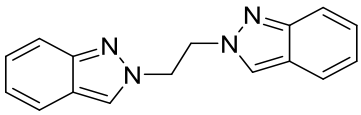
7,8-Dihydroindolo[2',1':3,4]pyrazino[1,2-*b*]indazole-3-carbonitrile (5fc)



The general procedure was followed by using 3-azido-4-formylbenzonitrile (**1f**) (86 mg, 0.5 mmol), 2-(1H-indol-1-yl)ethan-1-amine (**4c**) (80 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6mg, 0.025 mmol) and $Cu(OAc)_2$ (45.5 mg, 0.25 mmol) to yielded **5fc** (90.8 mg, 64%) as a Beige solid; mp = 270-272 °C; R_f = 0.5 (50% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 – 8.14 (m, 2H), 7.76 (d, J = 4.8 Hz, 1H), 7.49-7.26 (m, 5H), 5.11 (s, 2H), 4.66 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 137.2, 131.2, 128.5, 125.8, 125.0, 123.6, 122.5, 122.4, 122.0, 121.3, 118.7, 113.5, 113.2, 109.6, 104.6, 47.7, 39.9; **HR-MS** (ESI+) m/z calculated for $[C_{18}H_{13}N_4]^+ = [M + H]^+$ 285.1135, found 285.1130.

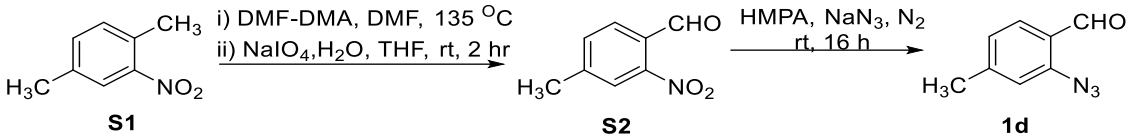
3. Preparation of 1,2-Di(2H-indazol-2-yl)ethane (3aa')

2-Azidobenzaldehyde (**1a**) (73.5 mg, 0.5 mmol), ethane-1,2-diamine (**2a**) (0.016 mL, 0.25 mmol) were taken in a oven dried Schlenck tube and it was closed with nitrogen balloon and stirred for 40 min at 110 °C. the mixture was cooled to room temperature, diluted with water (10 mL) and extracted with ethyl acetate (2×20 mL). The organic layers were collected and dried with Na_2SO_4 and concentrated under vacuum to give the crude, which was further purified by flash column chromatography, was performed on silica gel (100-200 mesh) using hexane and ethyl acetate as eluent to afford the desired product (**3aa'**) (107 mg, 82% yield).



Brown solid; mp = 178-180 °C; R_f = 0.4 (40% EA/Hexane); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.10 (s, 2H), 7.60 (dd, J = 8.4, 3.6 Hz, 4H), 7.21 (t, 7.6 Hz, 2H), 6.99 (dd, J = 8.0, 7.2 Hz, 2H), 5.05 (s, 4H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 148.7 (2C), 126.0 (2C), 125.0 (2C), 121.6 (2C), 121.5 (2C), 121.1 (2C), 117.4 (2C), 53.1 (2C); **HR-MS** (ESI+) m/z calculated for $[C_{16}H_{15}N_4]^+ = [M + H]^+$ 262.1213, found 263.1294.

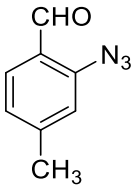
4. Preparation of 2-Azido-4-methylbenzaldehyde (1d):



N, N-Dimethylformamide dimethyl acetal (DMF-DMA) (7.6 g, 39.7 mmol) was added to a stirred solution of 1, 4-dimethyl-2-nitrobenzene (2 g, 13.2 mmol) in DMF (59 mL). After being heated at 140 °C for 72 h, the dark red solution was cooled to room temperature and added quickly to a rapidly stirred solution of $NaIO_4$ (8.7 g, 40.7 mmol) in H_2O (60 mL) and DMF (20 mL) at 0 °C. The reaction flask was washed with DMF (5 mL) at 0 °C and added to $NaIO_4$ mixture. The reaction was stirred at 0 °C for 2 h before being warmed to room temperature. The orange solution was filtered and rinsed with methyl *tert*-butyl ether (200 mL). The filtrate was then washed with H_2O (20 mL×3). The organic layer was dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the crude product was purified by flash column chromatography to afford 4-methyl-2-nitrobenzaldehyde (**S-1**) (1.6 g, 74 % yield)[7].

To a stirring solution of 4-methyl-2-nitrobenzaldehyde (**S2**) (1.6 g, 9.69 mmol) in HMPA (20 ml) was added sodium azide (1.2 g, 19.39 mmol). The reaction mixture was stirred at room temperature and monitored by TLC. After consumption of the starting material, the mixture was diluted with ice-cold water and extracted with ethyl acetate (3 × 25 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated to give the crude compound, which was further purified by column chromatography to afford **1d** (1.1 g, 71% yield).

2-Azido-4-methylbenzaldehyde (1d):



Yellow crystal; mp = 39 - 41 °C; R_f = 0.4 (5% EA/Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.06 – 7.03 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.3, 146.9, 142.8, 129.0, 126.0, 124.8, 119.3, 21.9**.**

5. X-ray Data: The quality single crystals suitable for SC-XRD experiments of all the three compounds were obtained from CH_3CN:$CHCl_3$ (50;50) solvent by the slow evaporation

method. The single-crystal X-ray diffraction measurements were performed to determine the crystal structure of three compounds using APEX3 (Bruker, 2016; Bruker D8 Venture photon 100 CMOS detector) diffractometer having graphite-monochromatized (MoKα = 0.71073 Å). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5º steps φ/ω. The data were collected with a time frame of 10 sec for the three components by setting the sample to detector distance fixed at 40 cm. The data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2018) was used for structure solution and full-matrix least-squares refinement on F^2.[8] The program(s) used to refine the molecular structures of **3ac**, **3ad** and **3cd** are SHELXL 2018/3 (Sheldrick, 2018). All non-hydrogen atoms were refined by the anisotropic method and hydrogen atoms were either refined or placed in calculated positions. All the structural refinements converged to good R-factors, as listed in Table S1. The molecular graphics of ORTEP diagrams were performed by XP software. The crystal symmetry of the three components was cross-checked by running the cif files through PLATON (Spek, 2020) software and notified that no additional symmetry was observed.

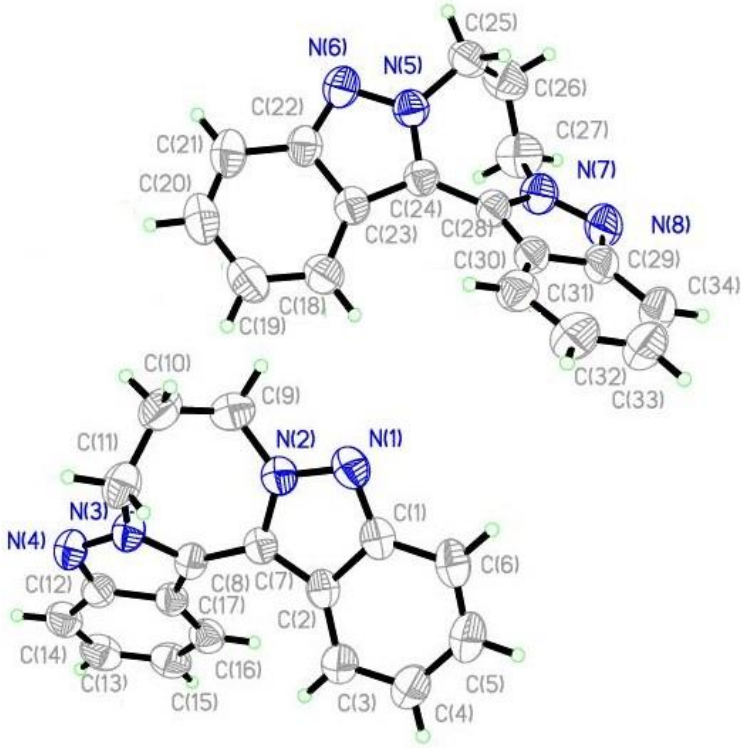


Figure 1. ORTEP diagram of of **3ac (CCDC 2127856)**, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

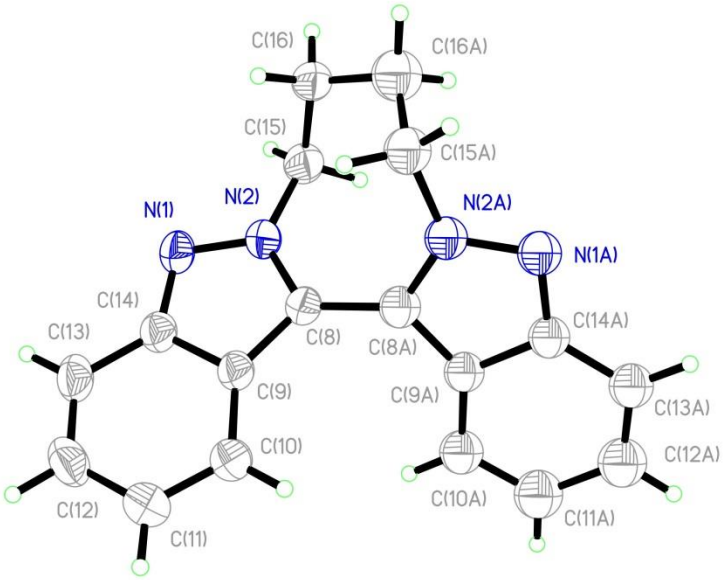


Figure 2. ORTEP diagram of **3ad CCDC** 2127858, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

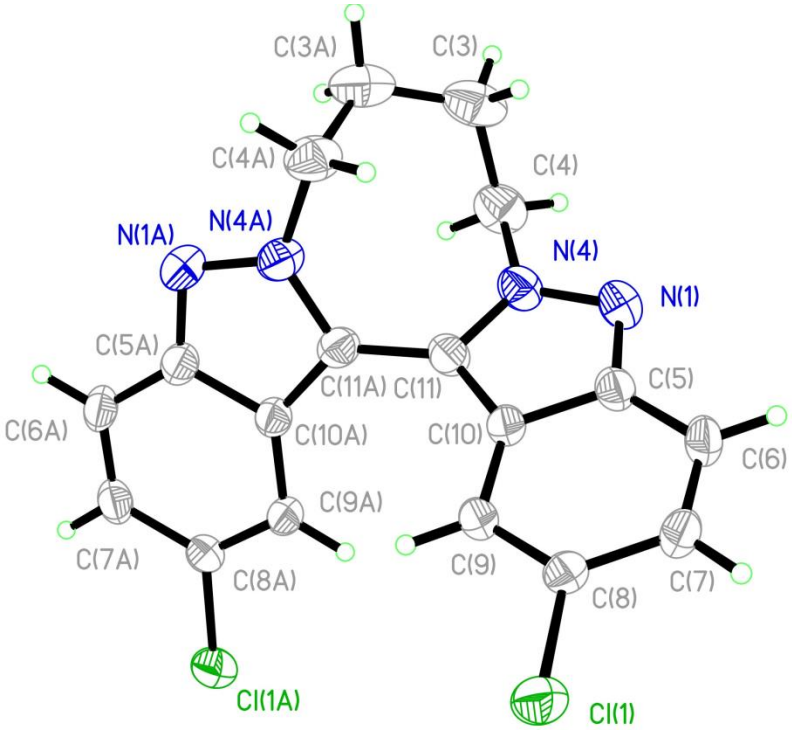


Figure 3. ORTEP diagram of **3cd CCDC** 2127855, the asymmetric unit contains a single molecule. Herein, the ellipsoids are drawn with a 50% probability.

Table S2. Crystallographic parameters detail of compounds **3ac, 3ad** and **3cc.**

Parameters	**3ac (CCDC 2127856)**	**3ad (CCDC 2127858)**	**3cd (CCDC 2127855)**
Chemical formula	C_{17} H_{14} N_4	C_{18} H_{16} N_4	C_{18} H_{14} Cl_2 N_4
Formula weight (Mr)	274.32	288.35	357.23
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P21/c	C2/c	C2/c
Temperature, T (K)	273(2)	273(2)	273(2)
a/Å	17.887(3)	12.637(1)	11.589(1)
b/Å	10.805(1)	14.143(1)	9.126(1)
c/Å	15.510(1)	9.403(1)	15.336(1)
α/°	90	90	90
β/°	113.27(1)	122.24(1)	91.15(1)
γ/°	90	90	90
Volume, V/Å^3	2753.8(1)	1421.5(1)	1621.6(2)
Z		4	4
Source of radiation	Mo Kα radiation, λ = 0.71073 Å	Mo Kα radiation, λ = 0.71073 Å	Mo Kα radiation, λ = 0.71073 Å
Dc/g cm^{-3}	1.323	1.347	1.463
Crystal description and color	Plate, yellow	Plate, colorless	Block, colorless
μ, mm^{-1}	0.082	0.083	0.407
Data collection			
Diffractometer	Bruker D8 Venture photon 100 CMOS detector	Bruker D8 Venture photon 100 CMOS detector	Bruker D8 Venture photon 100 CMOS detector
Absorption correction	multi-scan SADABS; Bruker, 2016	multi-scan SADABS; Bruker, 2016	multi-scan SADABS; Bruker, 2016
T_{min}, T_{max}	0.981, 0.988	0.980, 0.987	0.979, 0.987
Total reflections	47963	47462	40455
Unique reflections	6812	3539	3461
Reflection at I > 2σ (I)	4245	2323	2821
2θ range [°]	2.256-28.308	2.388-26.386	2.657-28.298
Limiting indices	-23<h<23 -14<k<14 -20<l<20	-15<h<15 -17<k<17 -11<l<11	-15<h<15 -12<k<12 -20<l<20
Refinement			

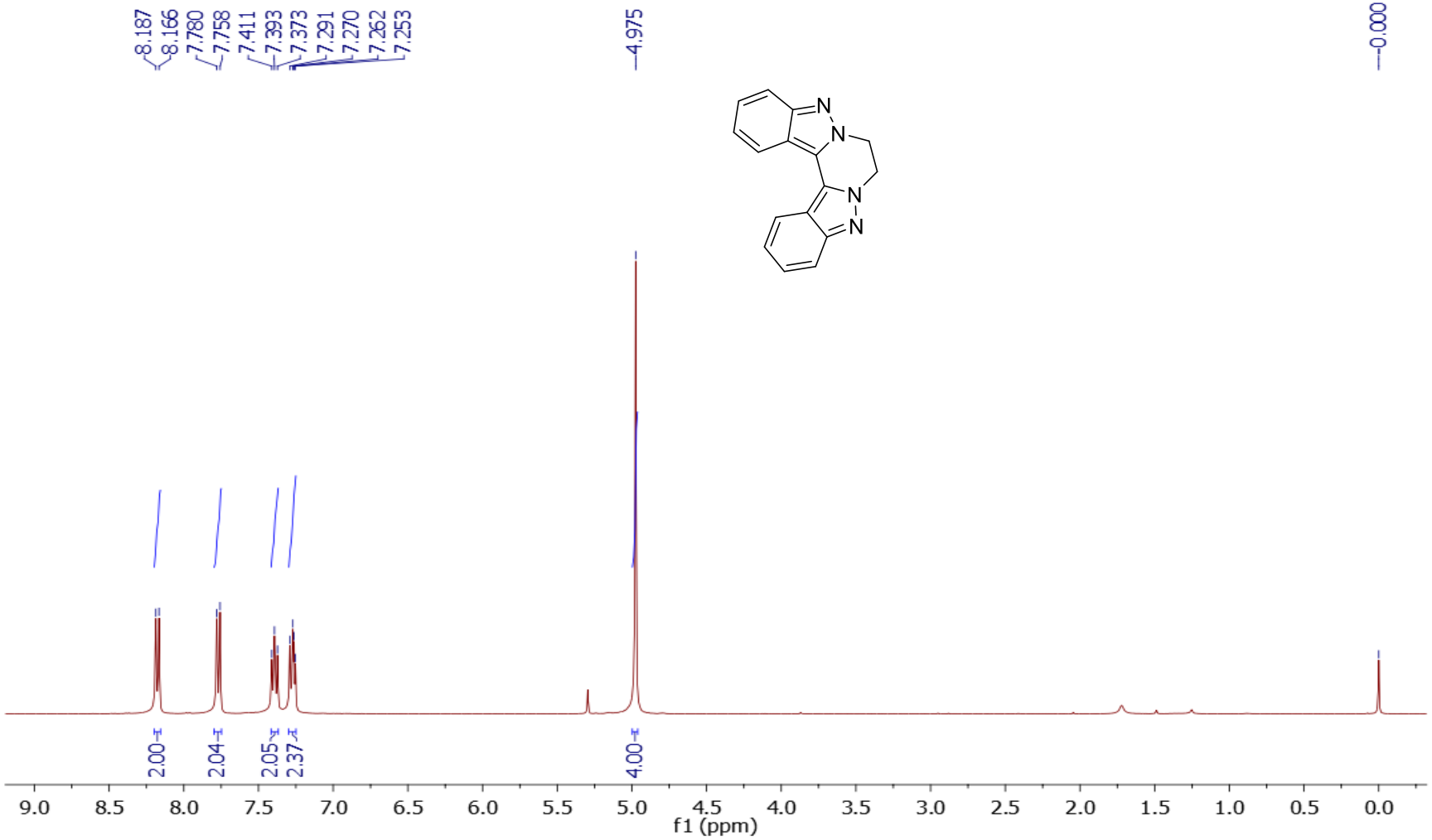
F(0 0 0)	1152	608	736
No. of restraints	0	0	0
H-atom treatment	Constr	Constr	Constr
No. of parameters	379	100	109
R_1, I > 2σ (I)	0.0529	0.0428	0.0645
wR_2 I > 2σ (I)	0.1423	0.1237	0.1643
GoF on F^2	1.005	0.965	1.161
CCDC No.	2127856	2127858	2127855

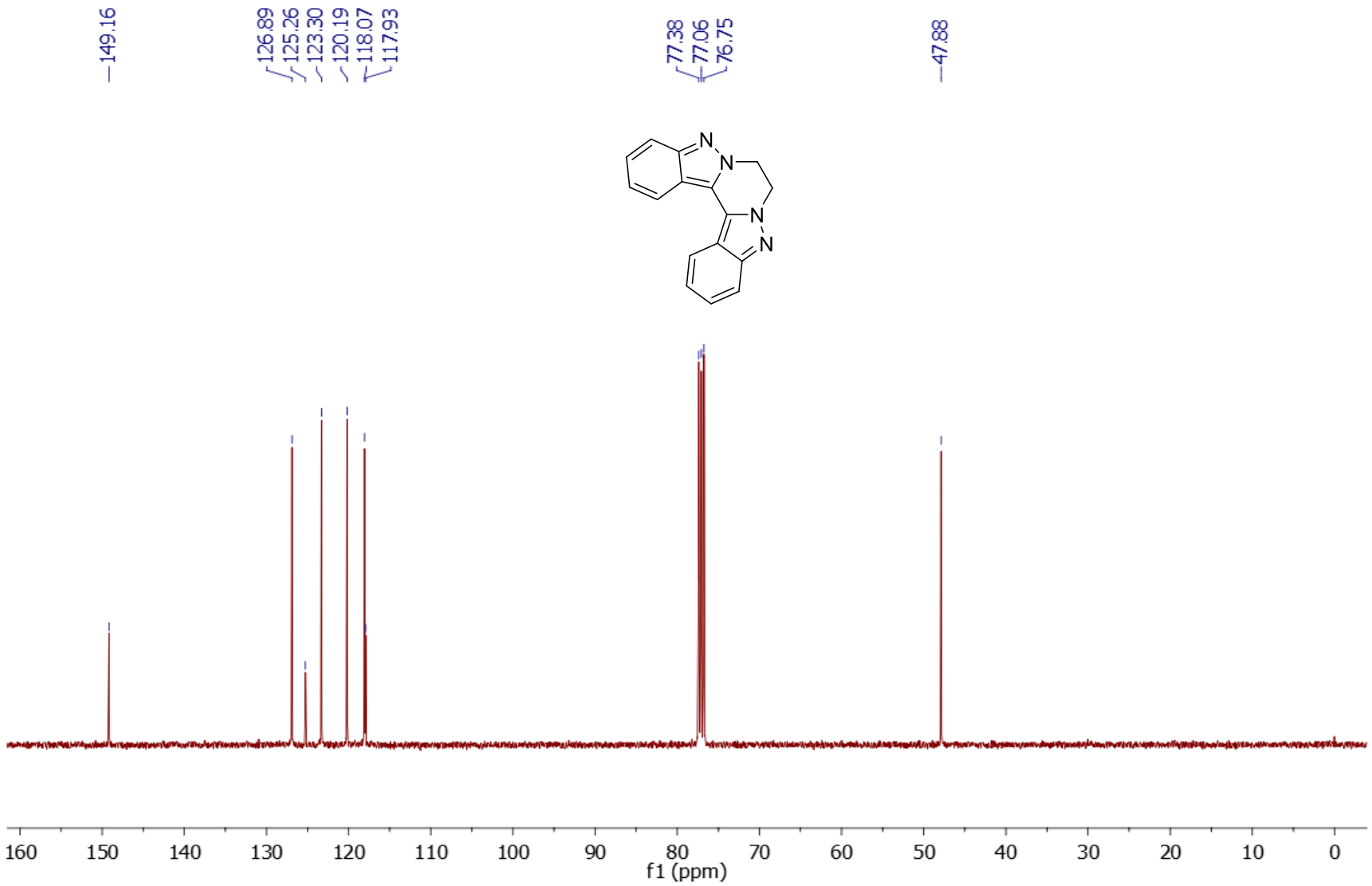
6. References

1. J. Hu, Y. Cheng, Y. Yang, Y. Rao, *Chem. Commun*., 2011, **47**, 10133-10135.
2. S. Vidyacharan, A. Murugan, D. S. Sharada, *J. Org. Chem*., 2016, **81**, 2837-2848.
3. G. A. Abeykoon, J. J. Sahn, S. F. Martin, *Tetrahedron Lett*., 2021, **66**, 6855–6858
4. N. Gigant, E. Claveau, P. Bouyssou, I. Gillaizeau, *Org. Lett*., 2012, **14**, 844-847.
5. D. Sawant, R. Kumar, P. R. Maulik, B. Kundu, *Org. Lett.*, 2006, **8**, 1525-1528.
6. D. Sawant, R. Kumar, P. R. Maulik, B. Kundu, *Org. Lett.*, 2006, **8**, 1525-1528.
7. L. Yang, L. Shi, Q. Xing, K.-W. Huang, C. Xia, F. Li, *ACS Catal*., 2018, **8**, 10340-10348
8. Sheldrick, G. M. SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement. University of Göttingen, Göttingen, 1997.

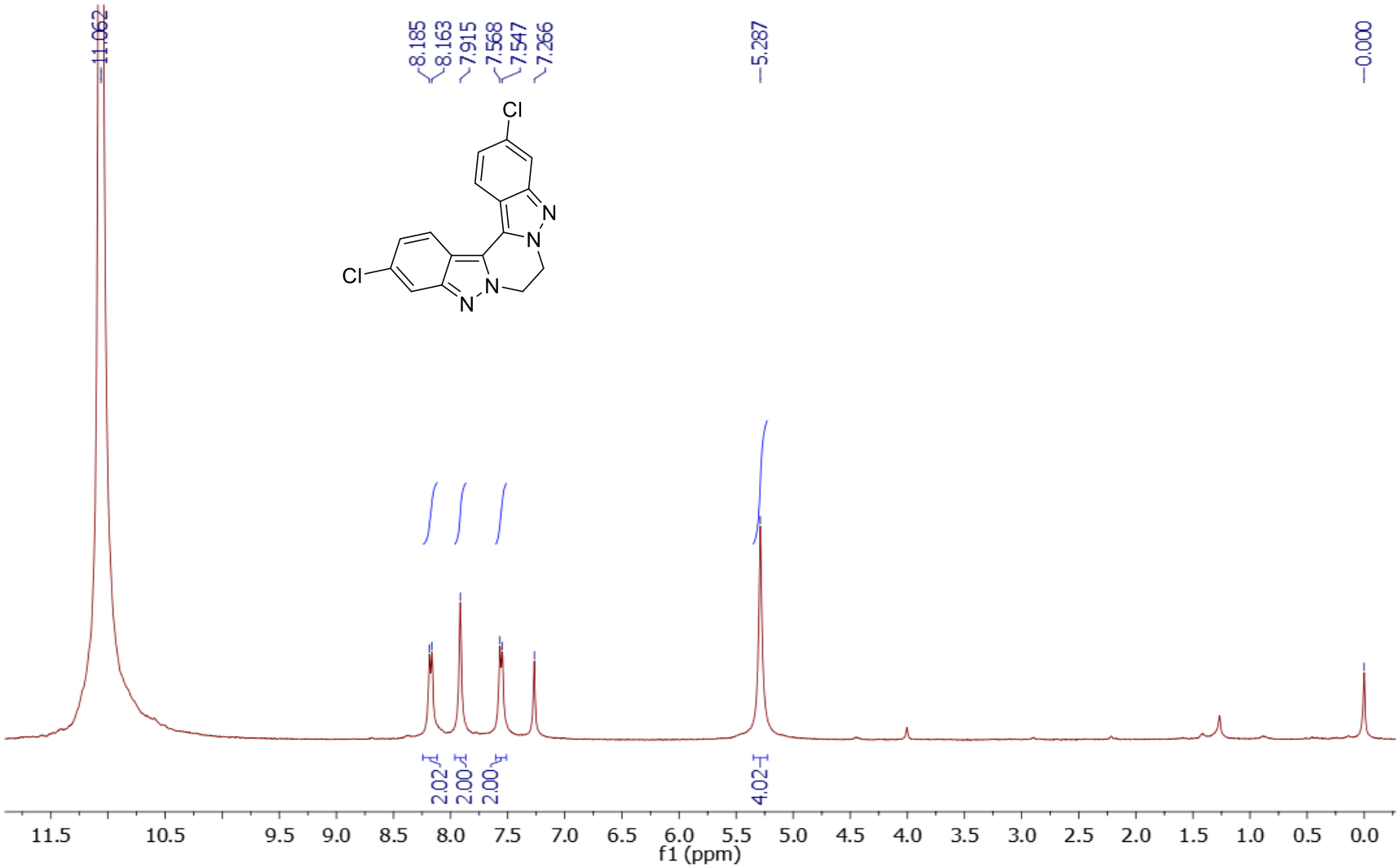
7. Copies of ^{1}H and ^{13}C NMR spectra of products

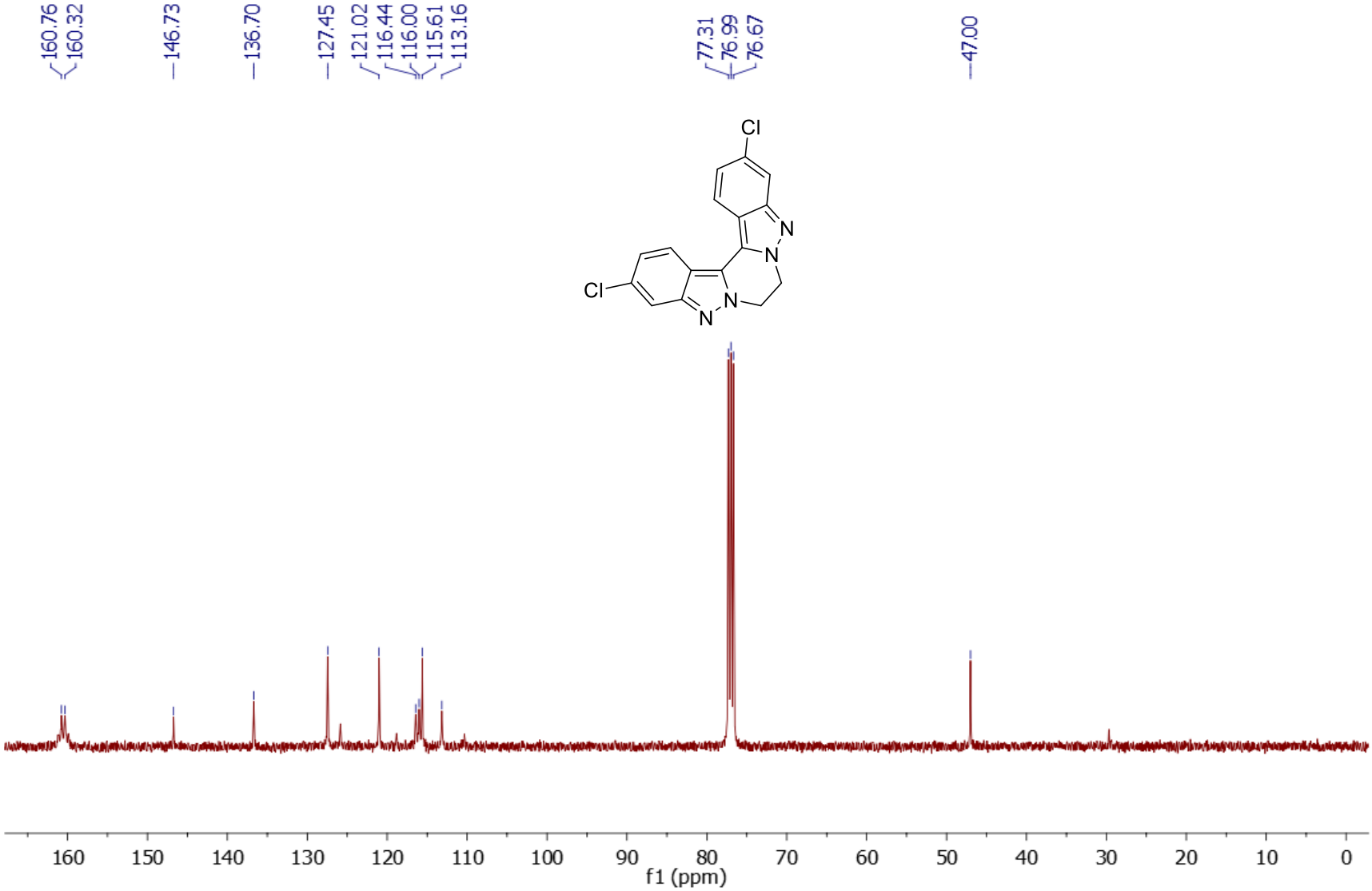
Compound 3aa



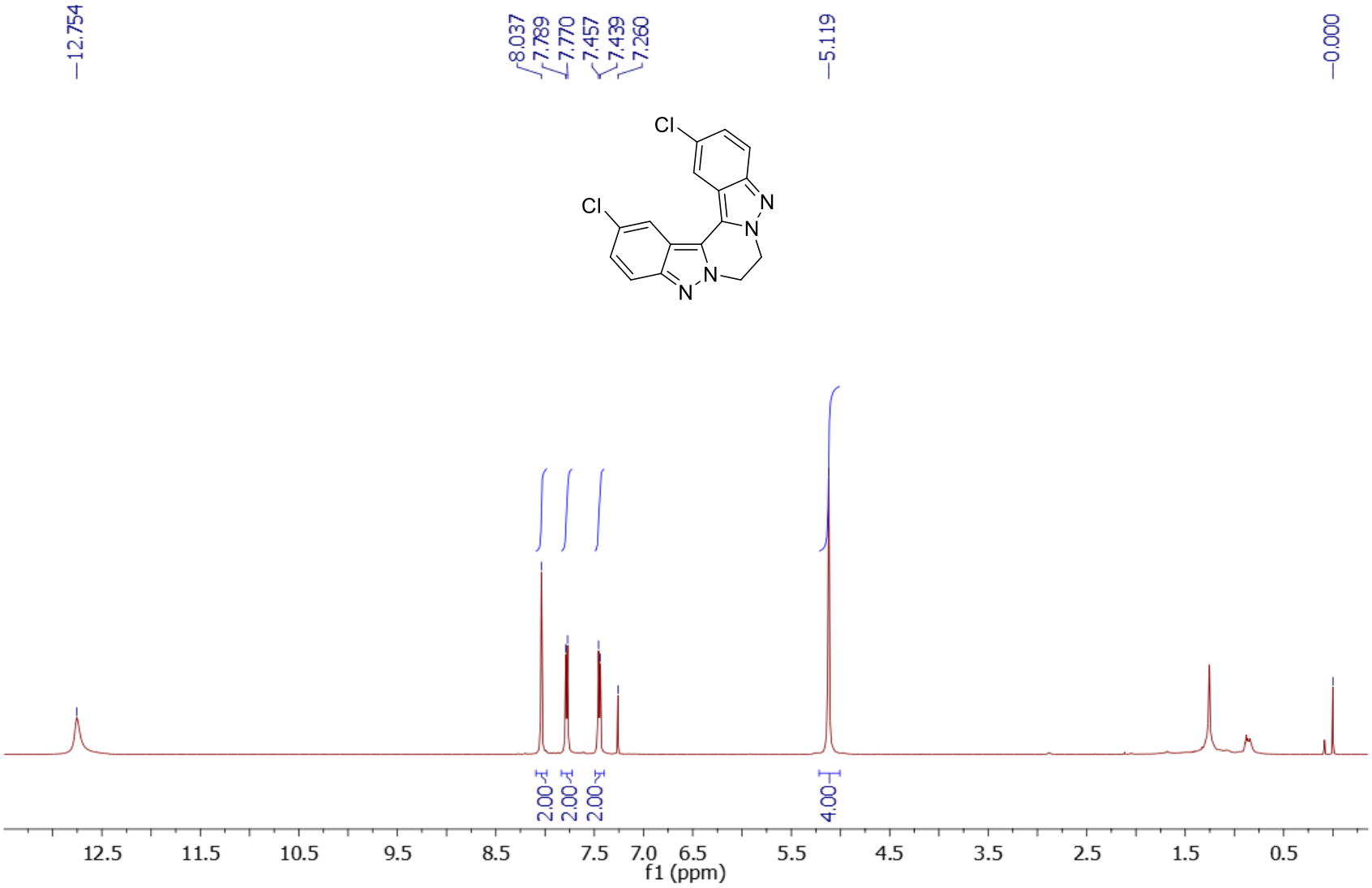

149.16
126.89
125.26
123.30
120.19
118.07
117.93
77.38
77.06
76.75
47.88
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

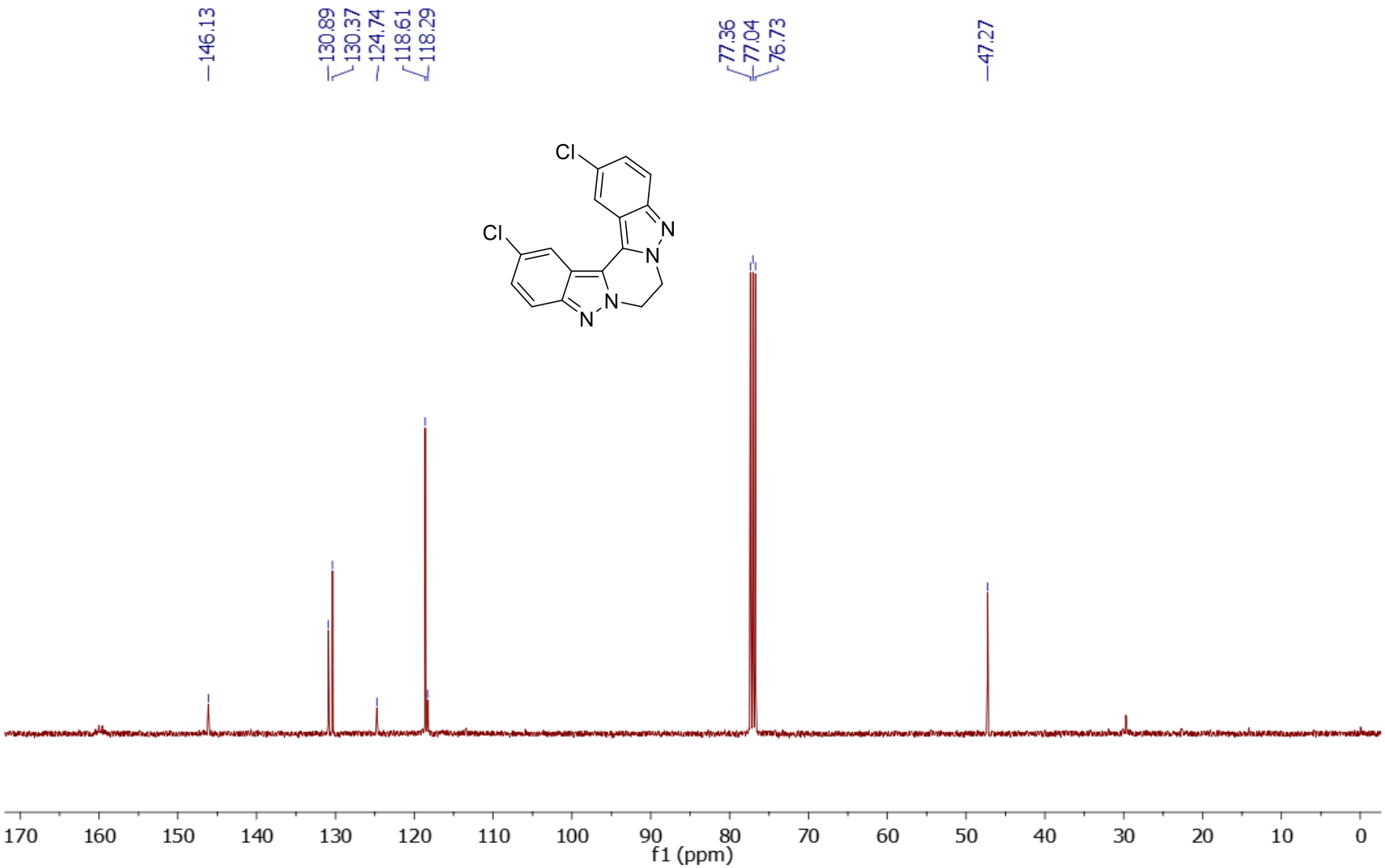
Compound 3ba



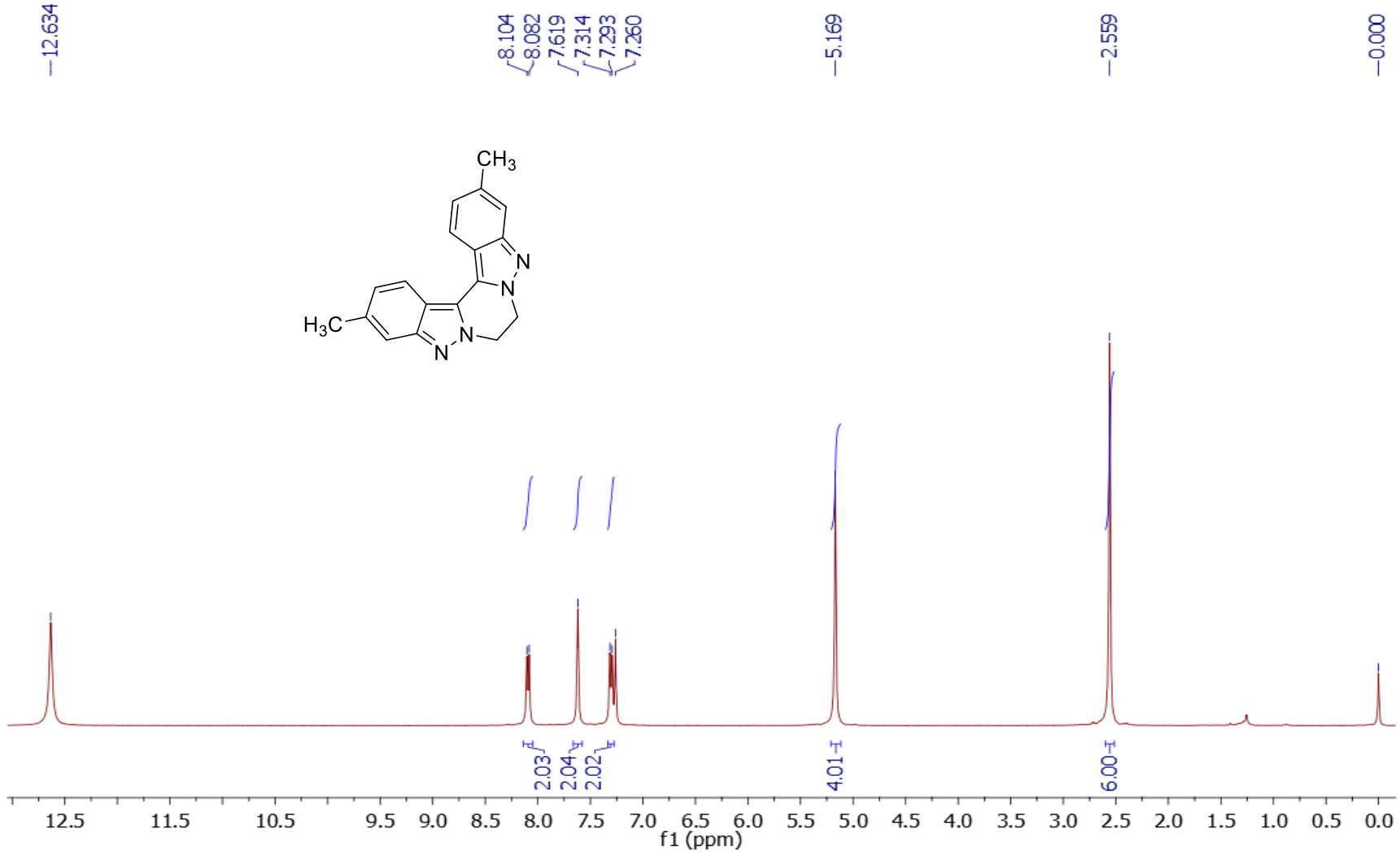

160.76
160.32
146.73
136.70
127.45
121.02
116.44
116.00
115.61
113.16
77.31
76.99
76.67
47.00
Cl
Cl
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

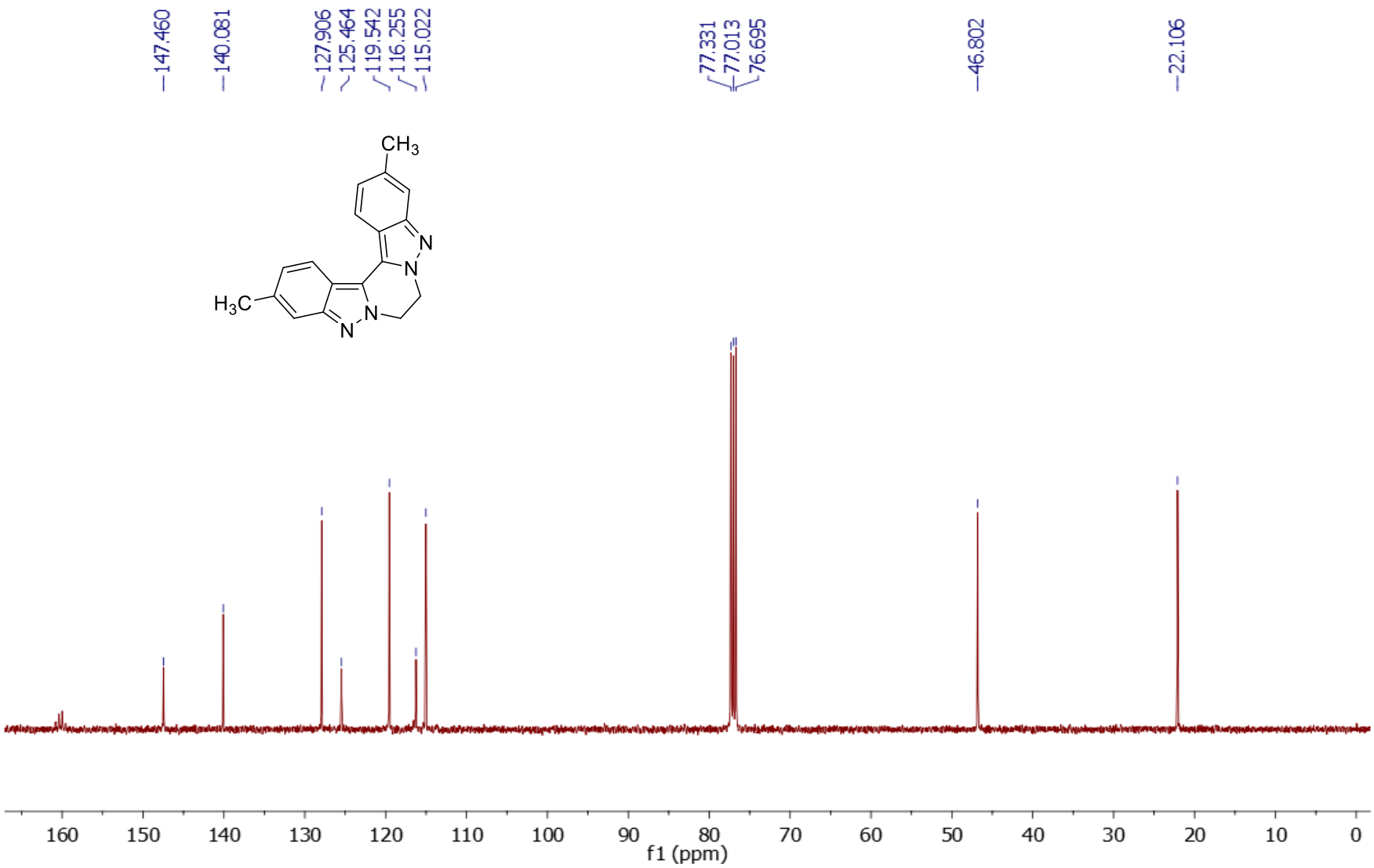
Compound 3ca



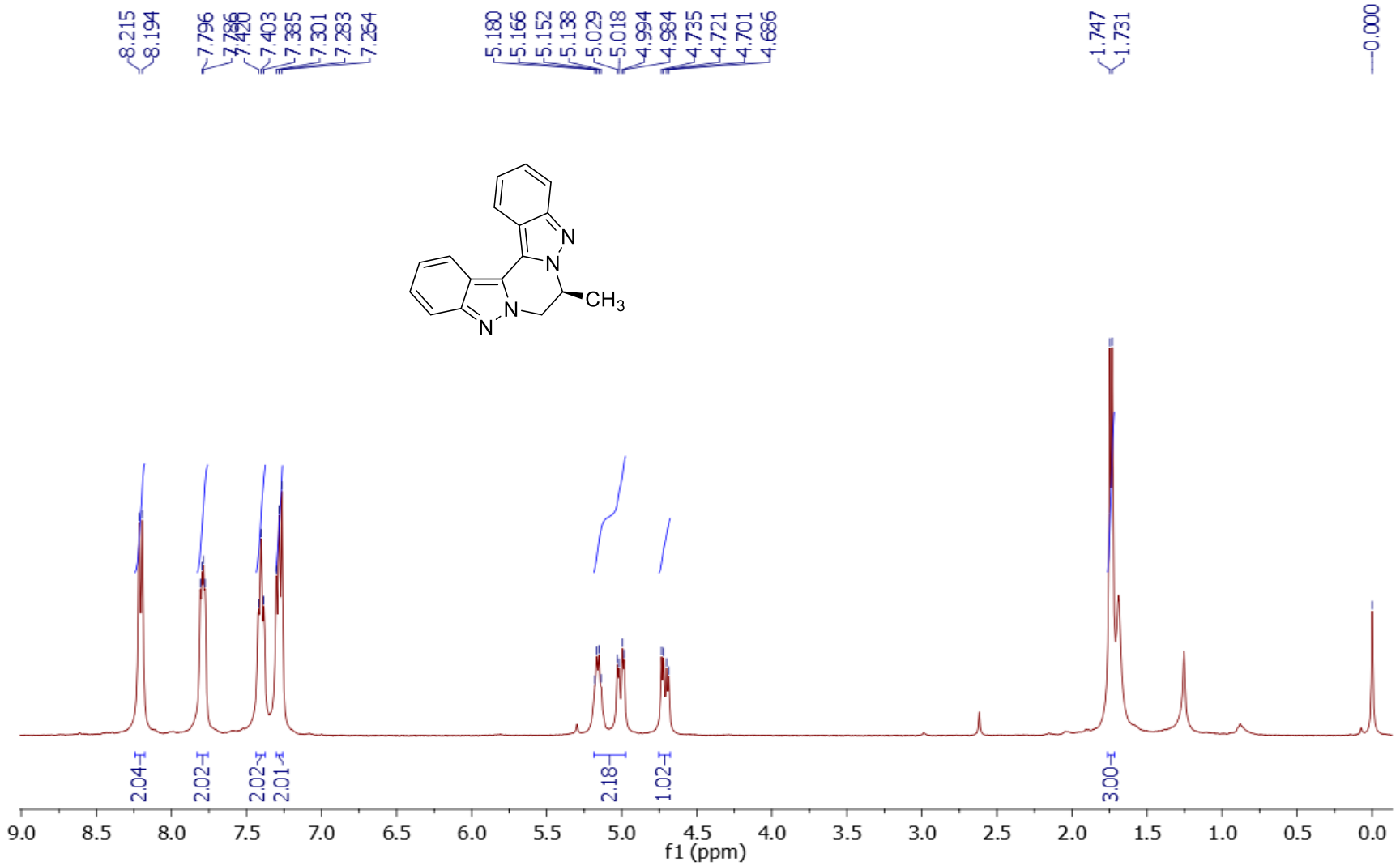

146.13
130.89
130.37
124.74
118.61
118.29
77.36
77.04
76.73
47.27
Cl
Cl
N
N
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

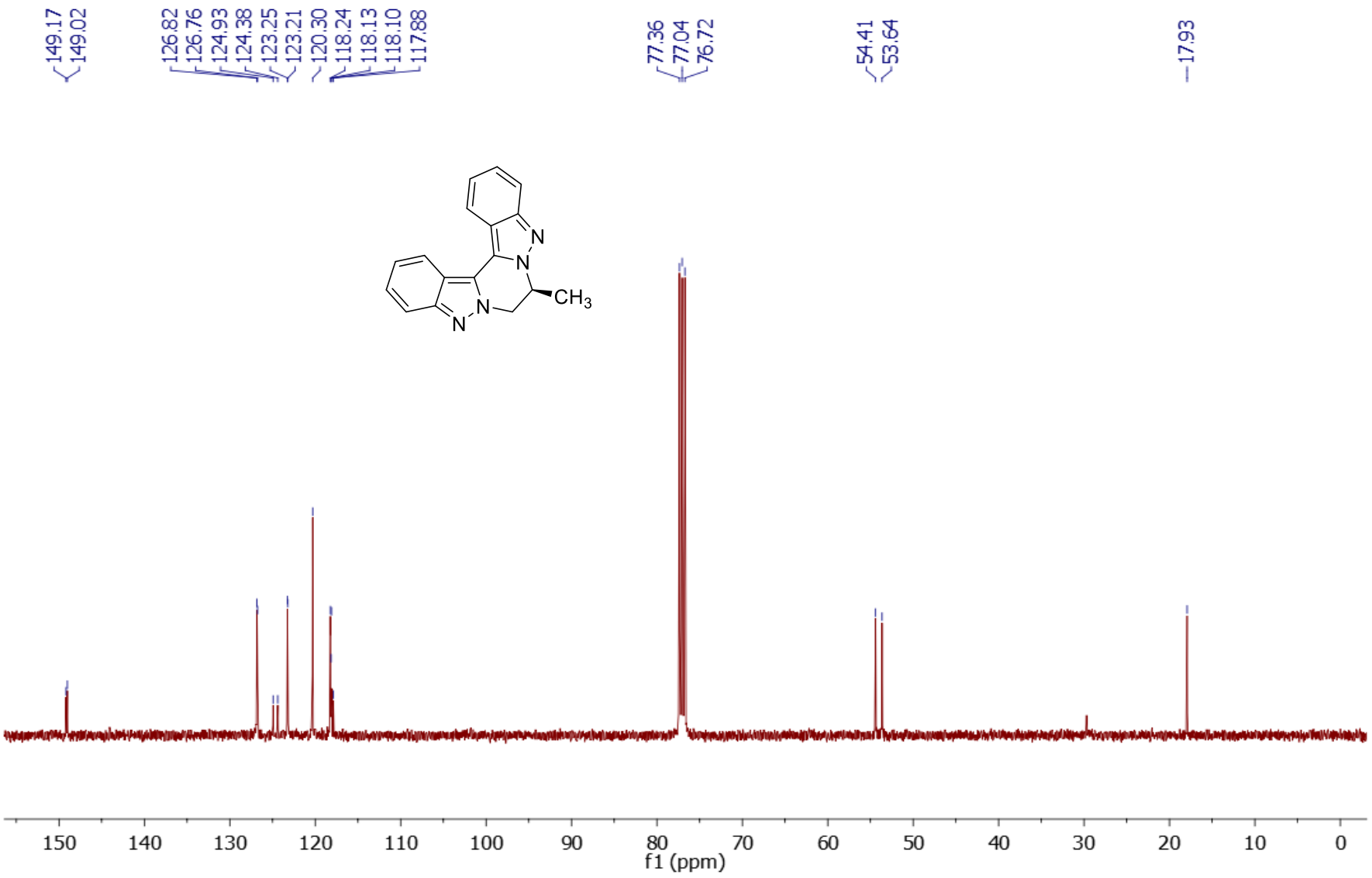
Compound 3da



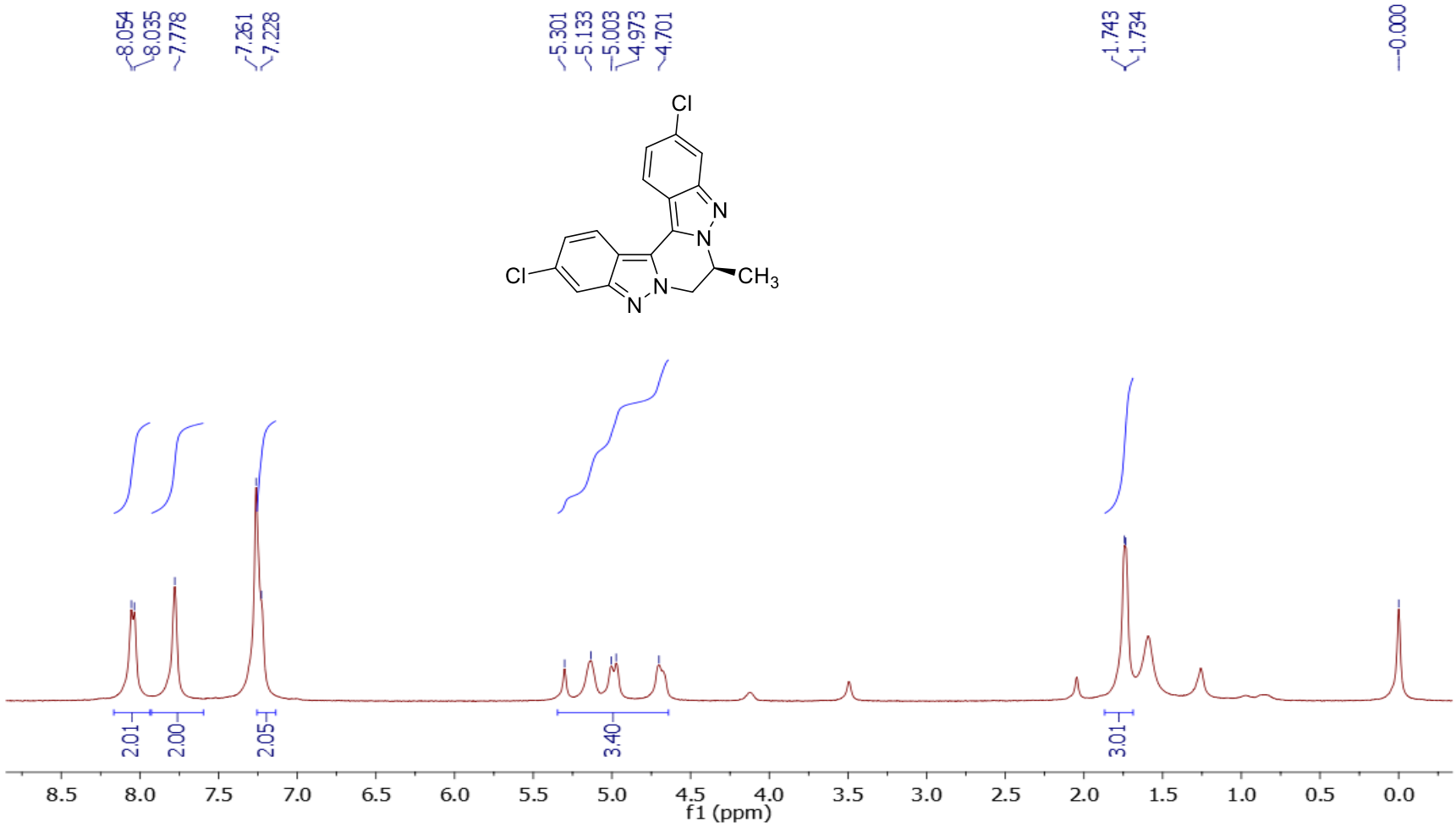

147.460
140.081
127.906
125.464
119.542
116.255
115.022
77.331
77.013
76.695
46.802
22.106
CH3
H3C
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

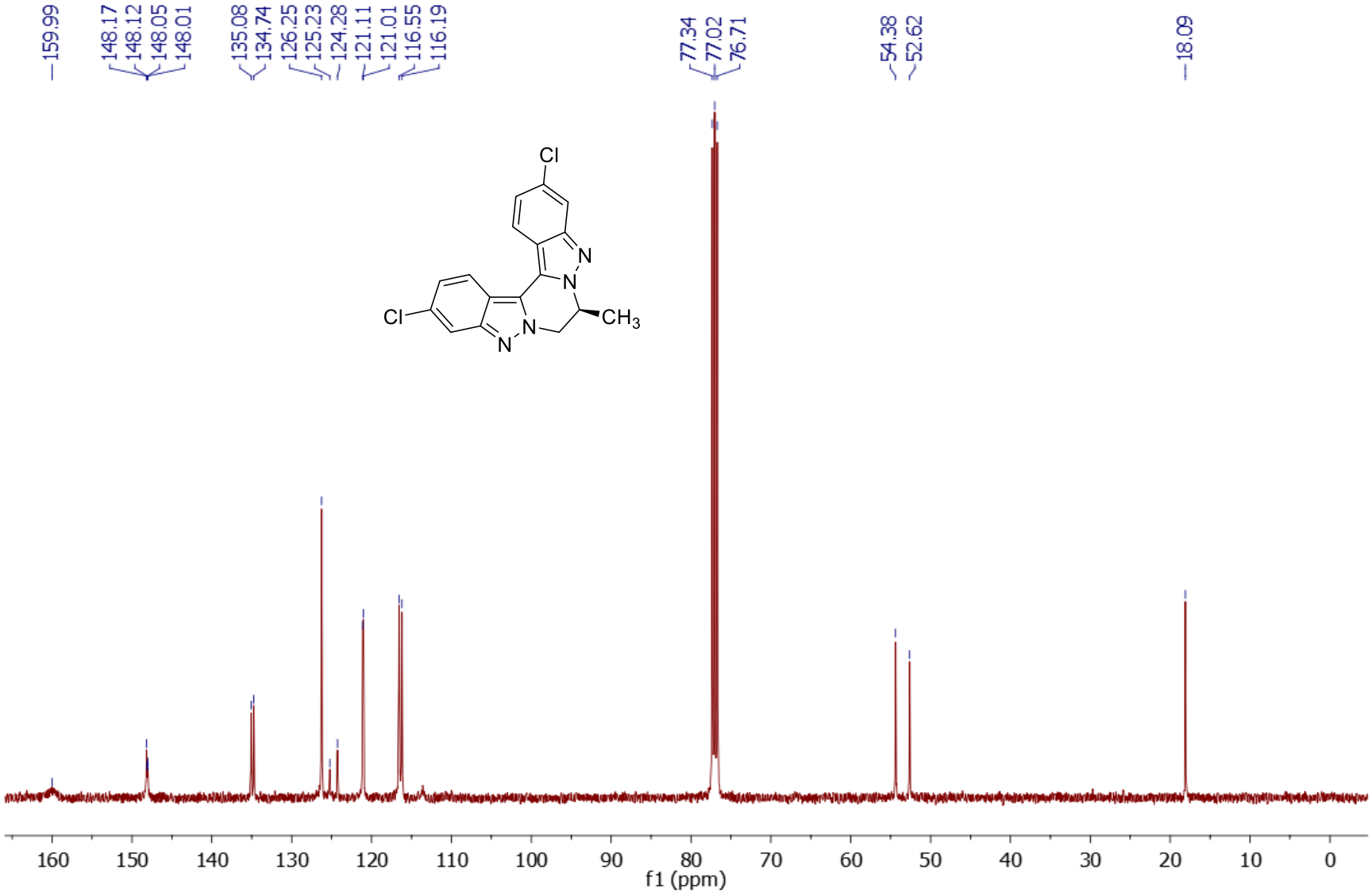
Compound 3ab



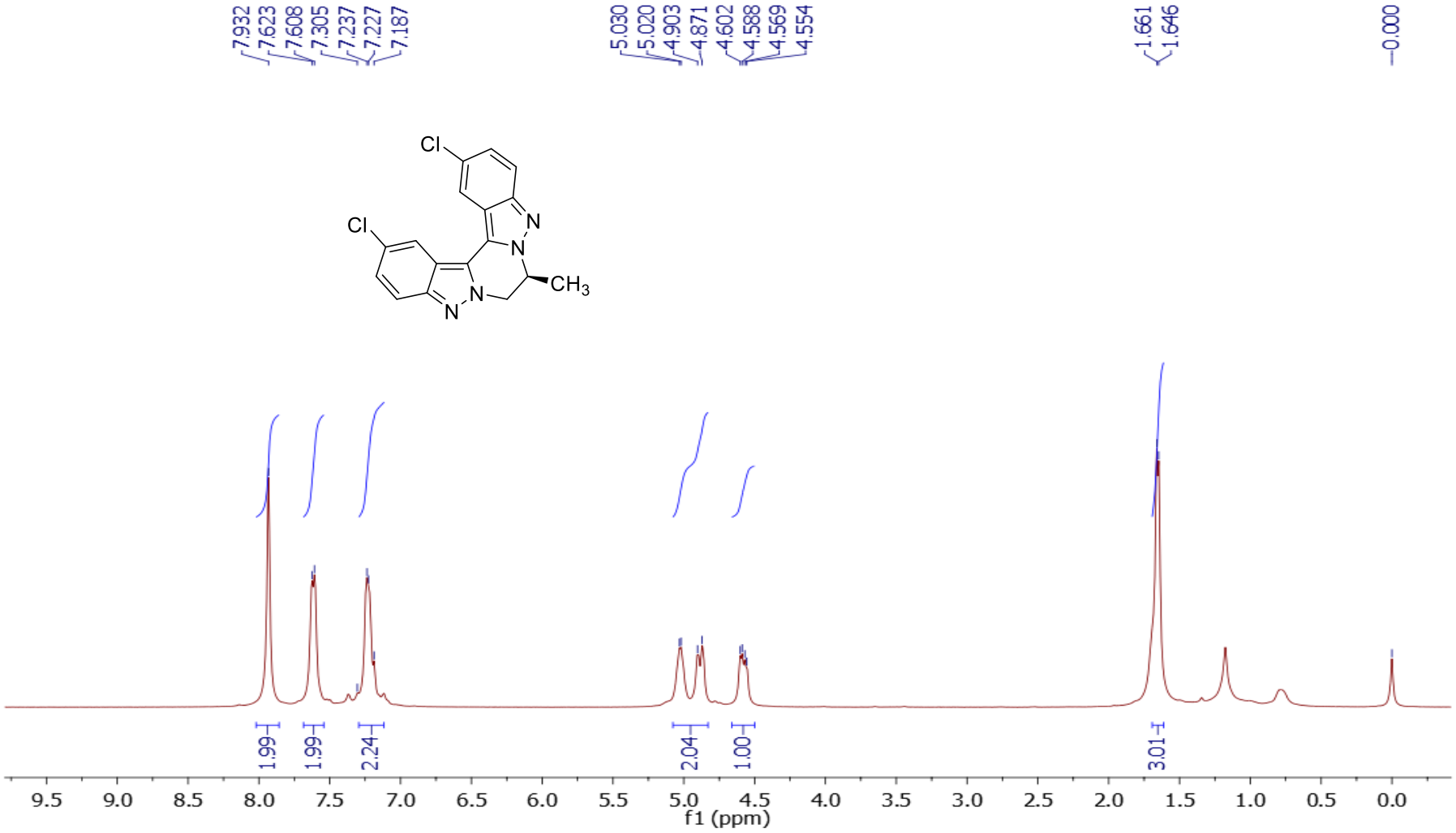

149.17
149.02
126.82
126.76
124.93
124.38
123.25
123.21
120.30
118.24
118.13
118.10
117.88
77.36
77.04
76.72
54.41
53.64
17.93
N
N
N
N
CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

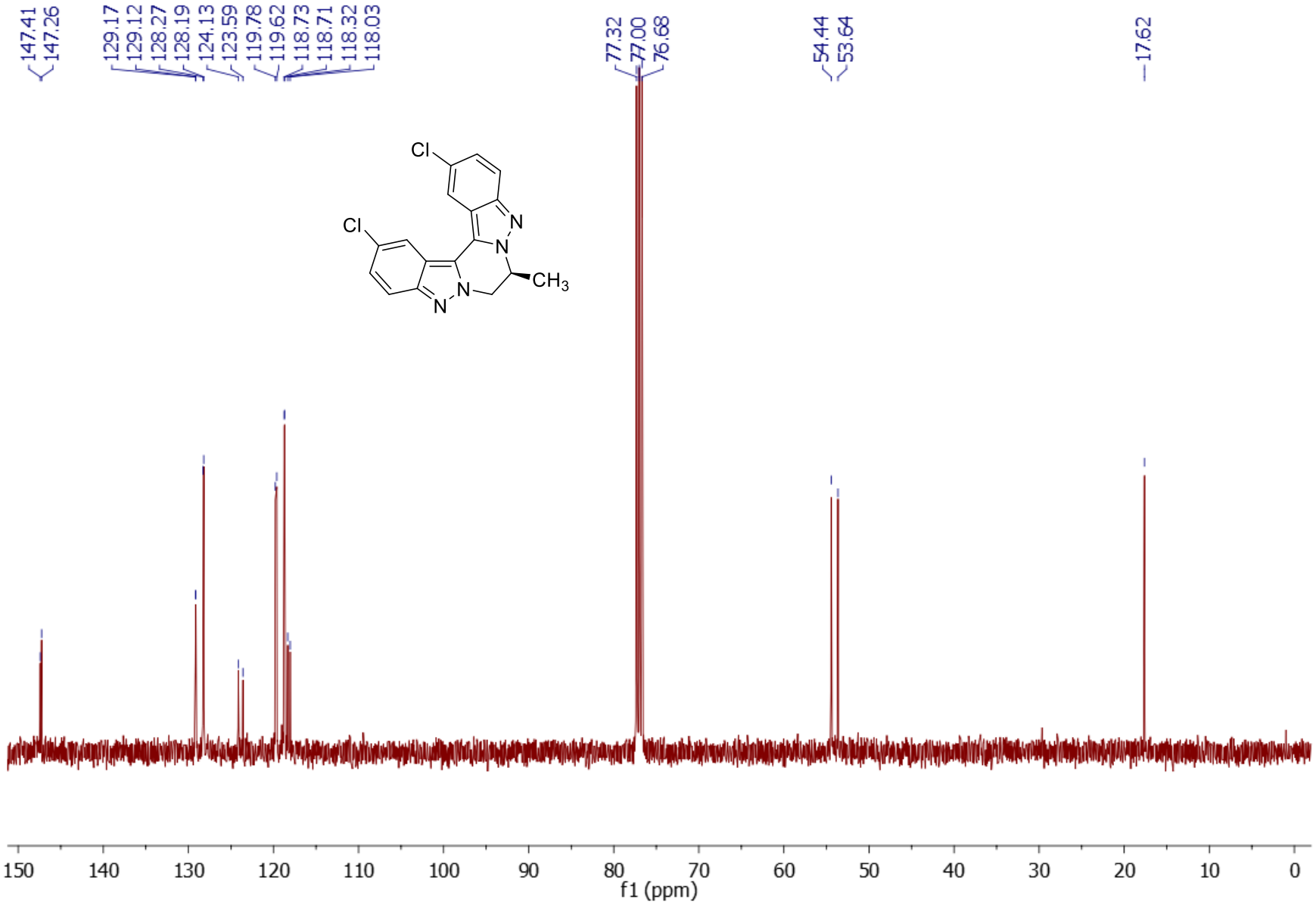
Compound 3bb



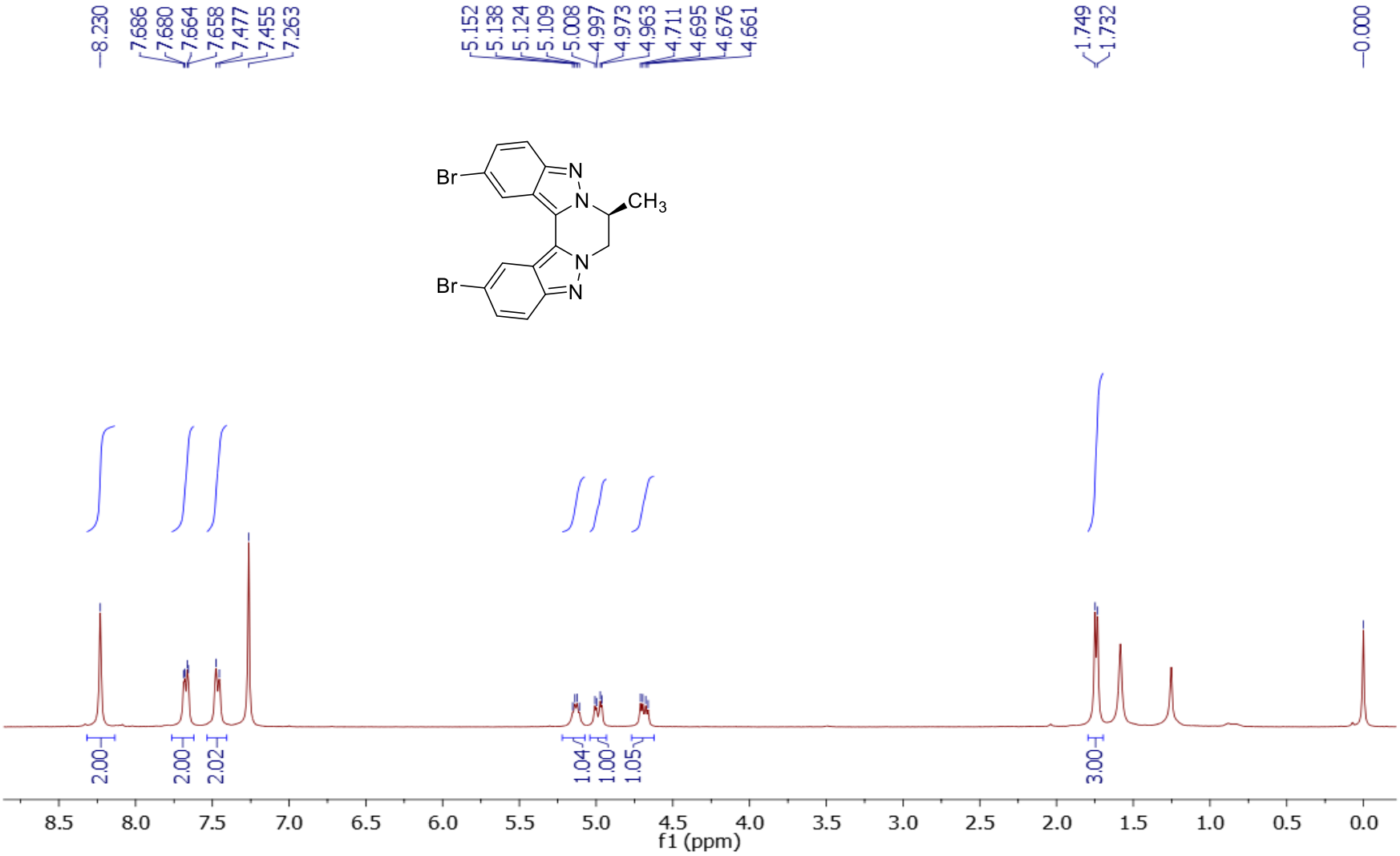

159.99
148.17
148.12
148.05
148.01
135.08
134.74
126.25
125.23
124.28
121.11
121.01
116.55
116.19
77.34
77.02
76.71
54.38
52.62
18.09
Cl
N
N
Cl
N
N
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

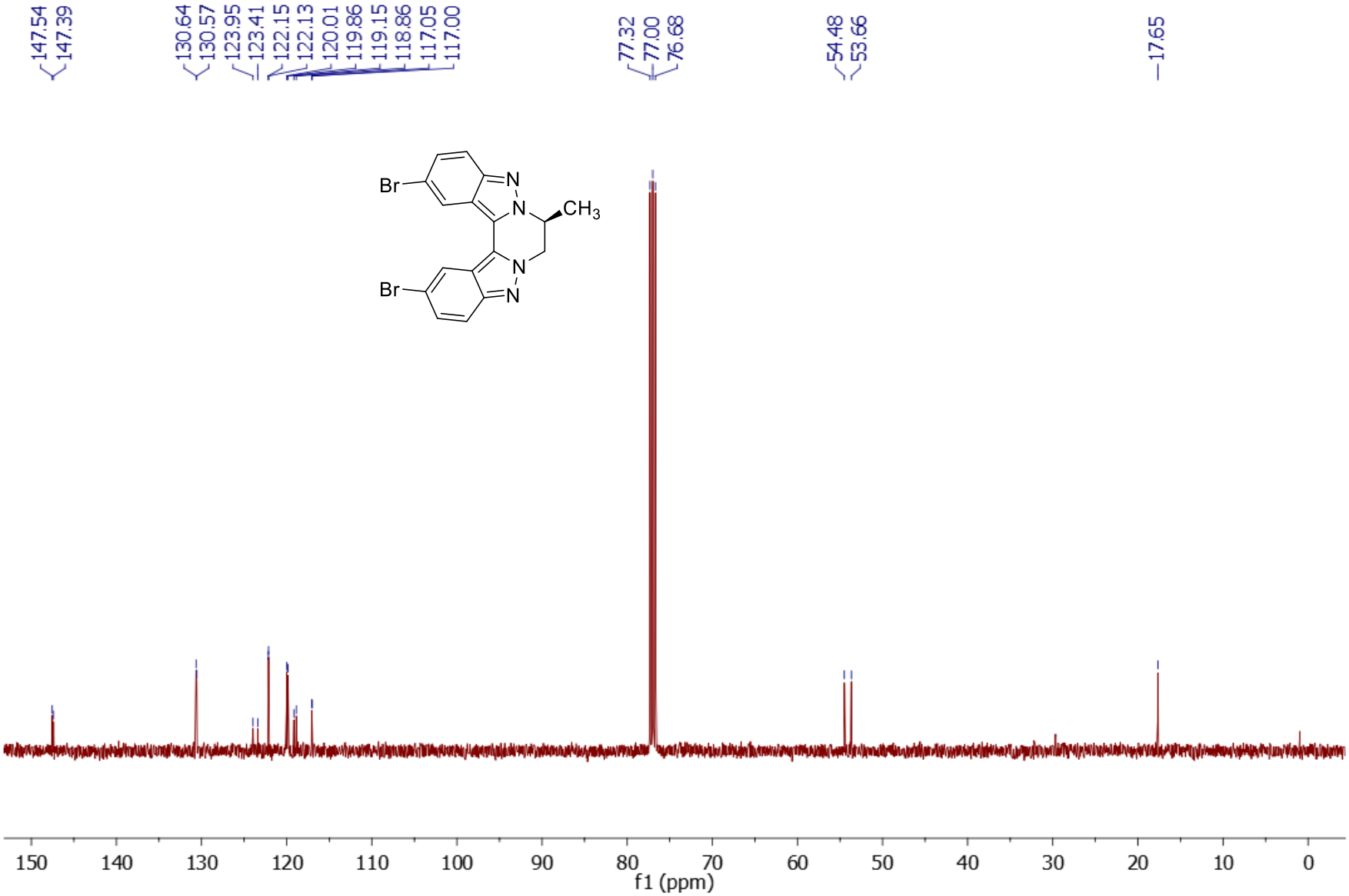
Compound 3cb



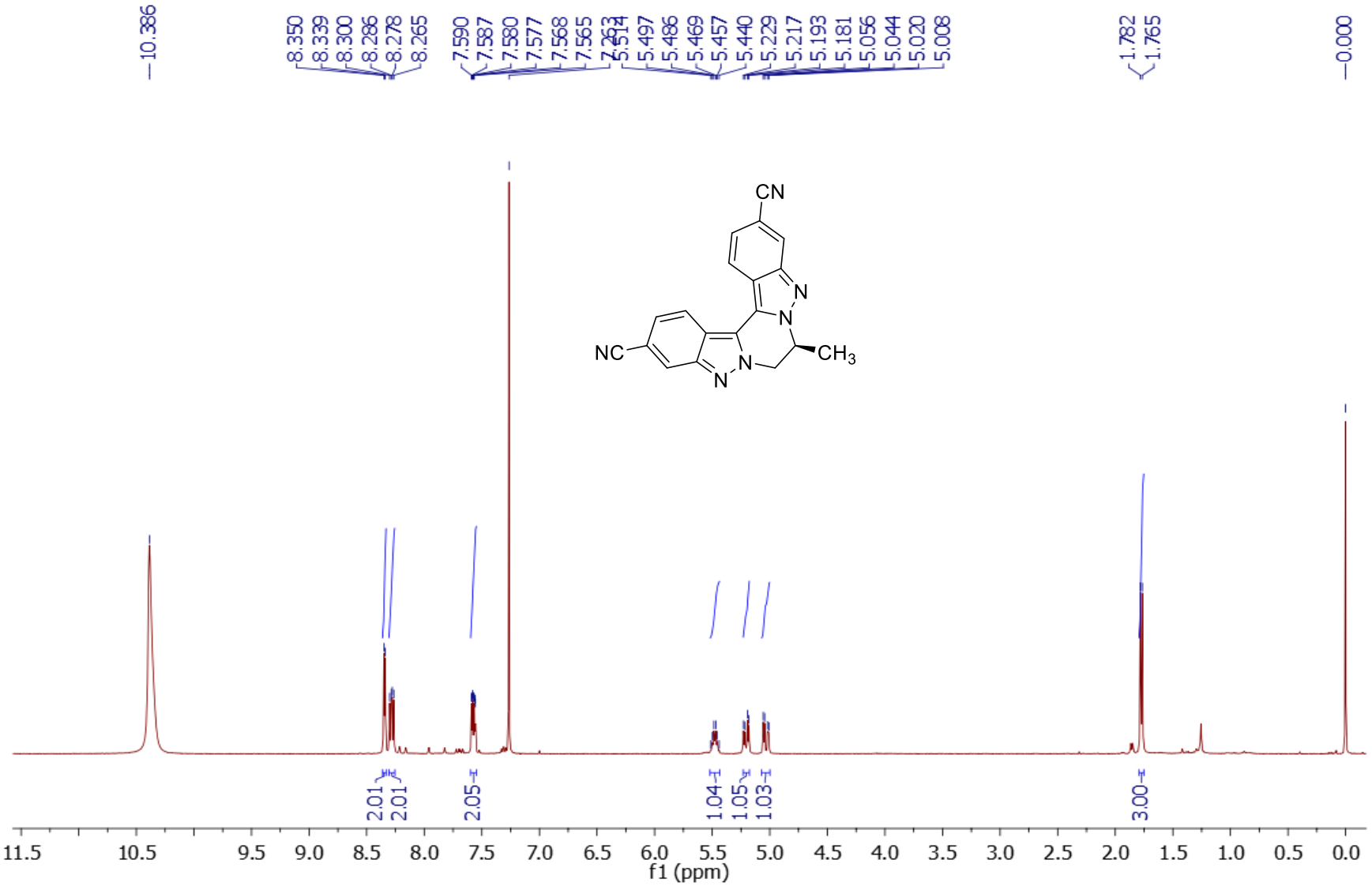

147.41
147.26
129.17
129.12
128.27
128.19
124.13
123.59
119.78
119.62
118.73
118.71
118.32
118.03
77.32
77.00
76.68
54.44
53.64
17.62
Cl
Cl
N
N
N
N
CH3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

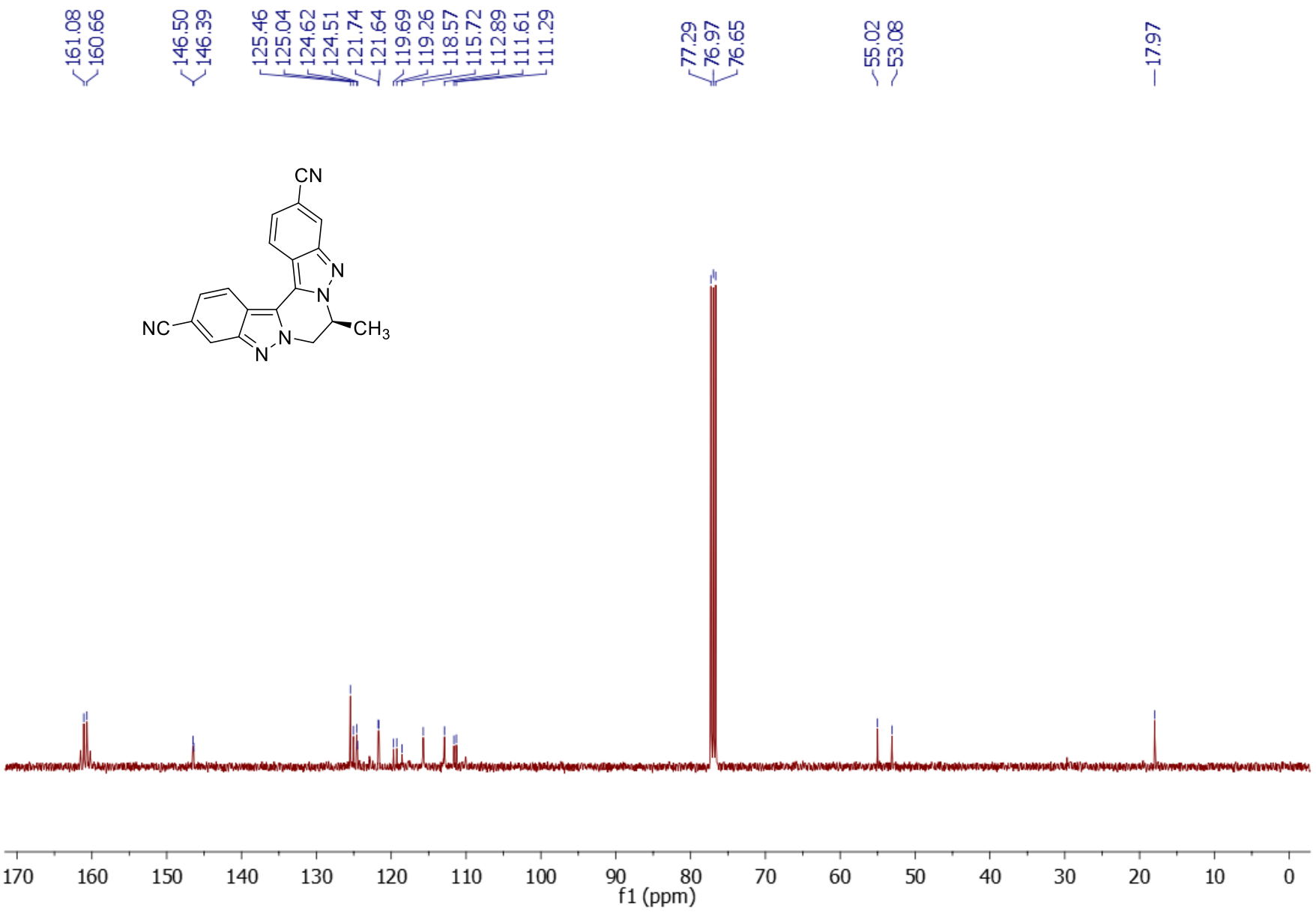
Compound 3eb



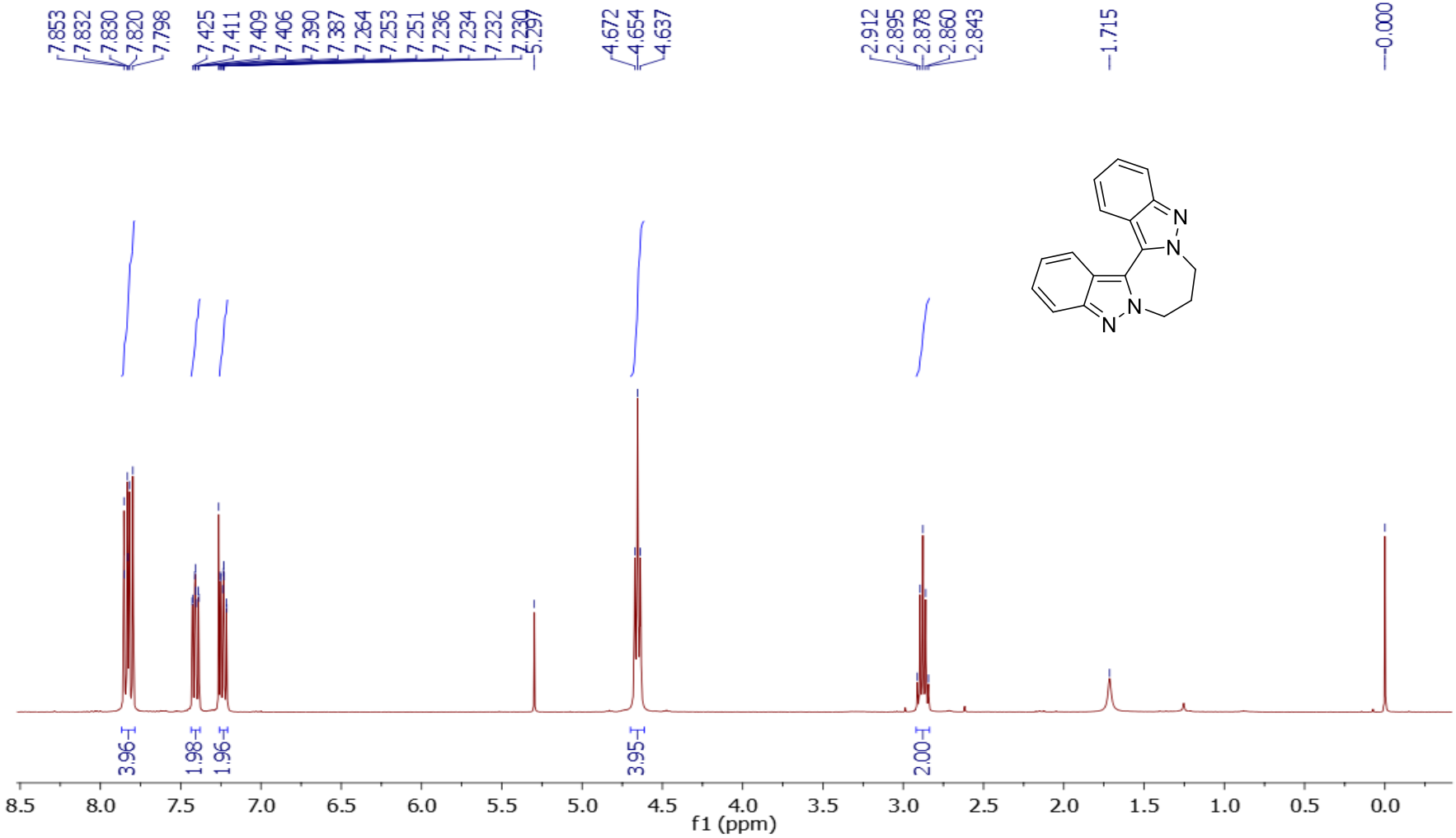

147.54
147.39
130.64
130.57
123.95
123.41
122.15
122.13
120.01
119.86
119.15
118.86
117.05
117.00
77.32
77.00
76.68
54.48
53.66
17.65
Br
N
N
CH3
N
Br
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

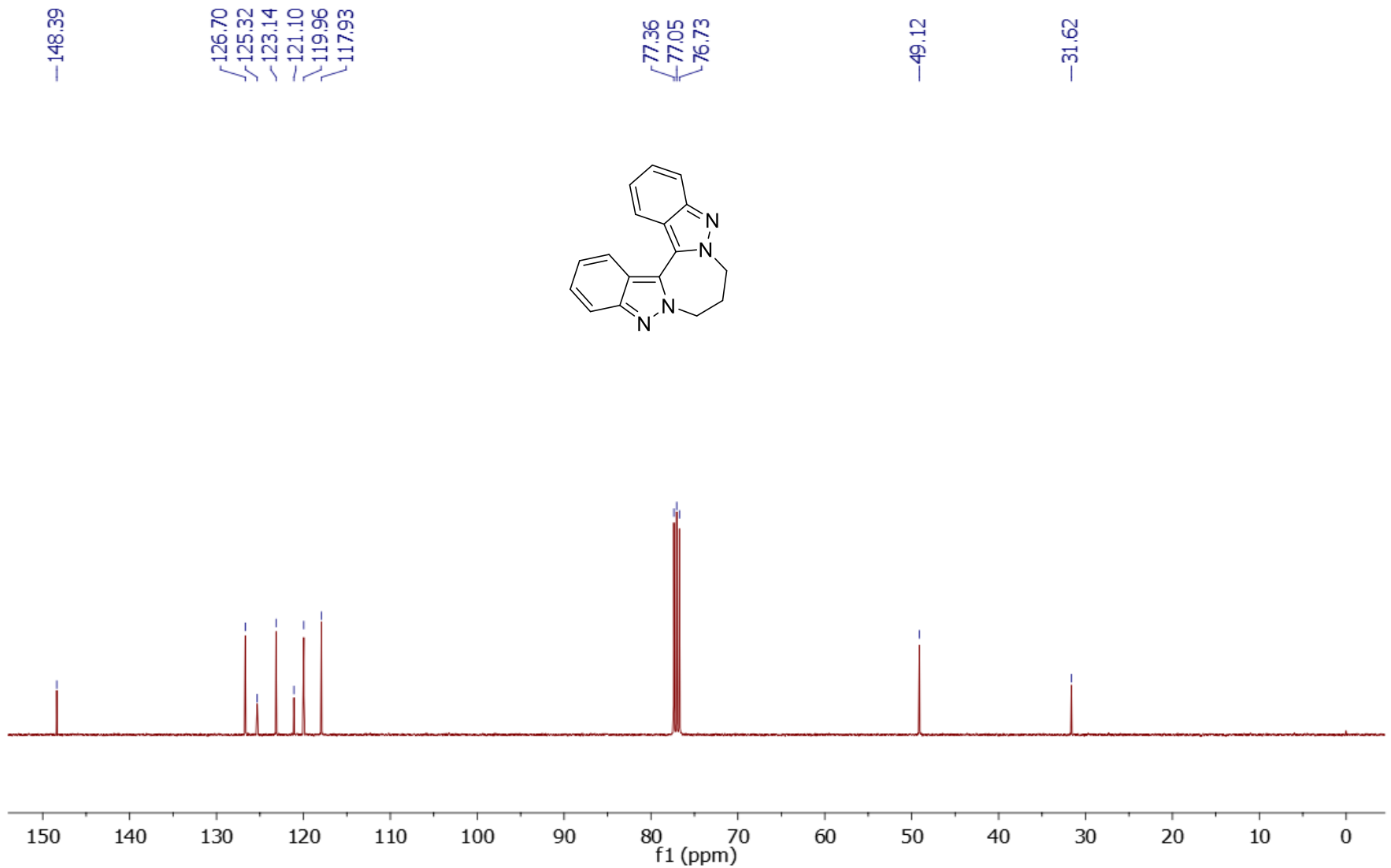
Compound 3fb



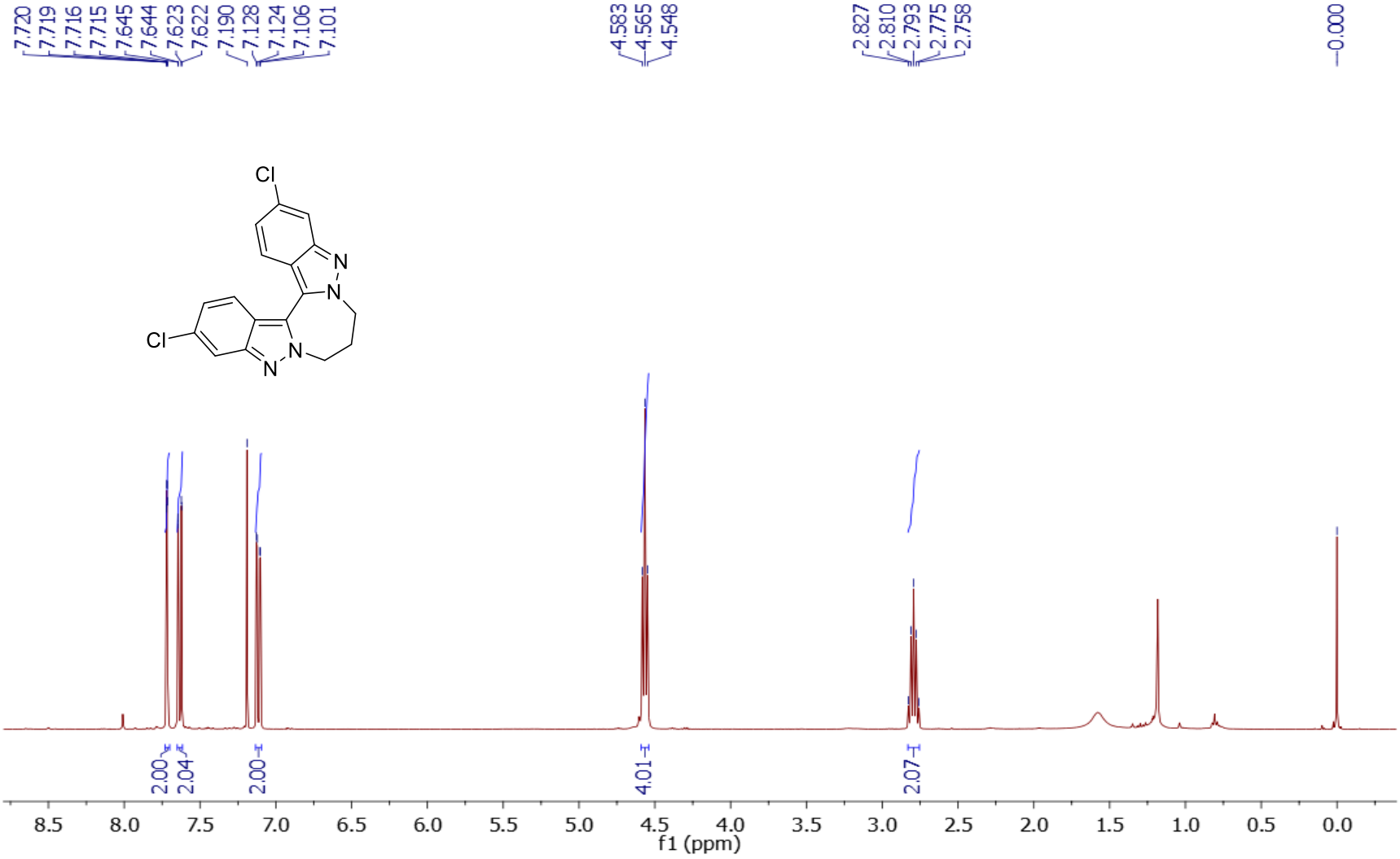

161.08
160.66
146.50
146.39
125.46
125.04
124.62
124.51
121.74
121.64
119.69
119.26
118.57
115.72
112.89
111.61
111.29
77.29
76.97
76.65
55.02
53.08
17.97
CN
NC
N
N
N
N
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

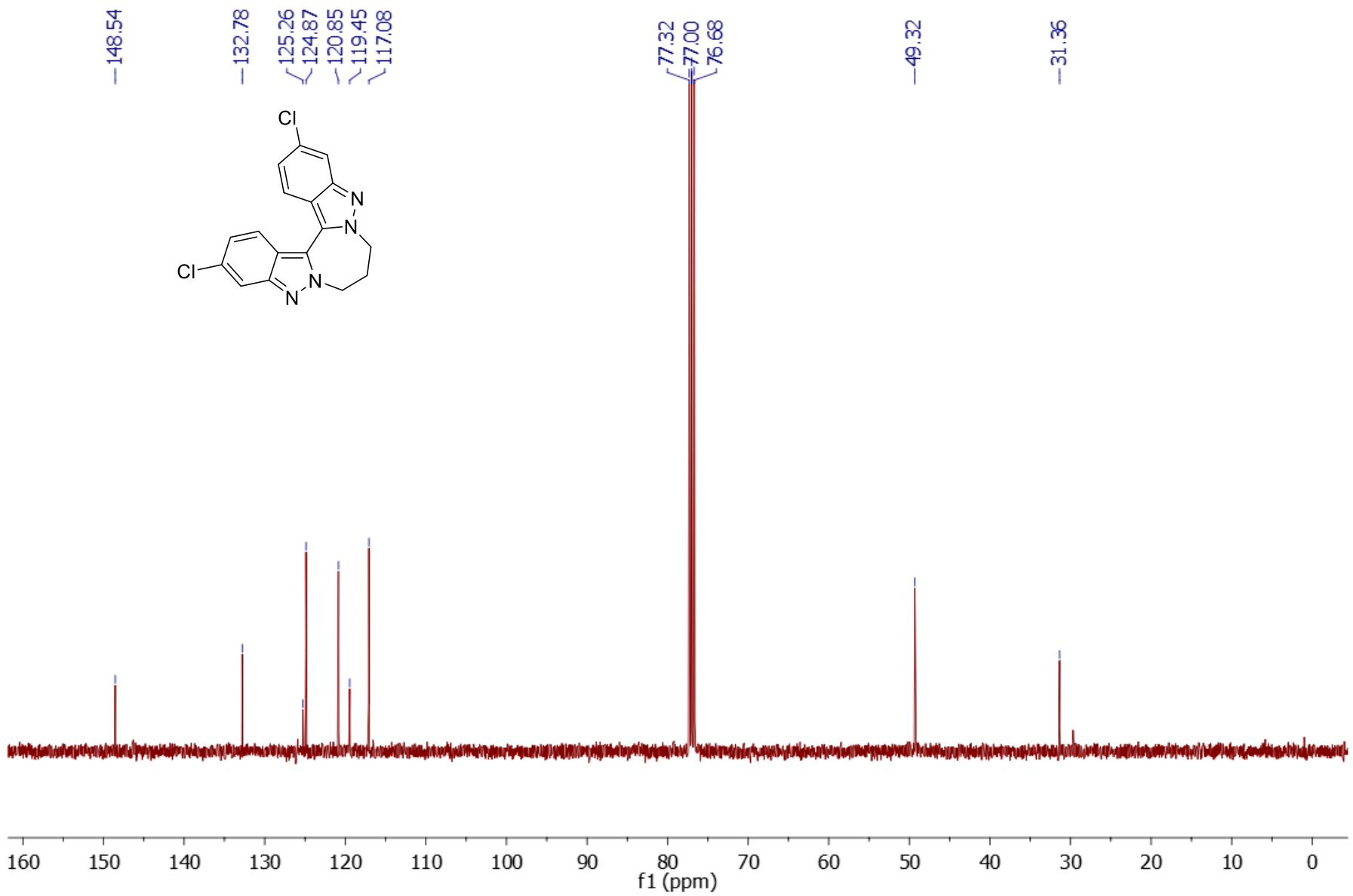
Compound 3ac



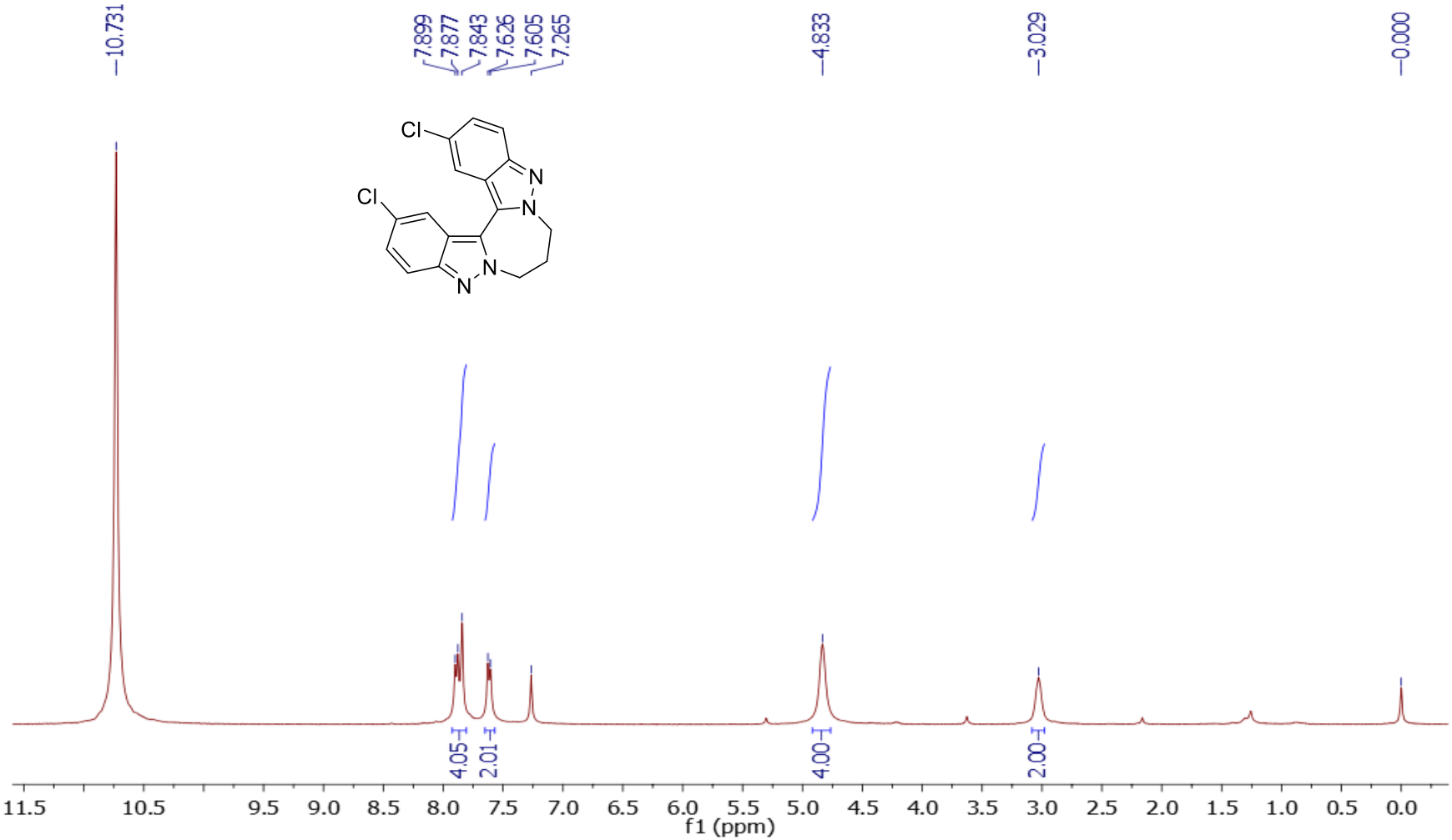

148.39
126.70
125.32
123.14
121.10
119.96
117.93
77.36
77.05
76.73
49.12
31.62
N
N
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

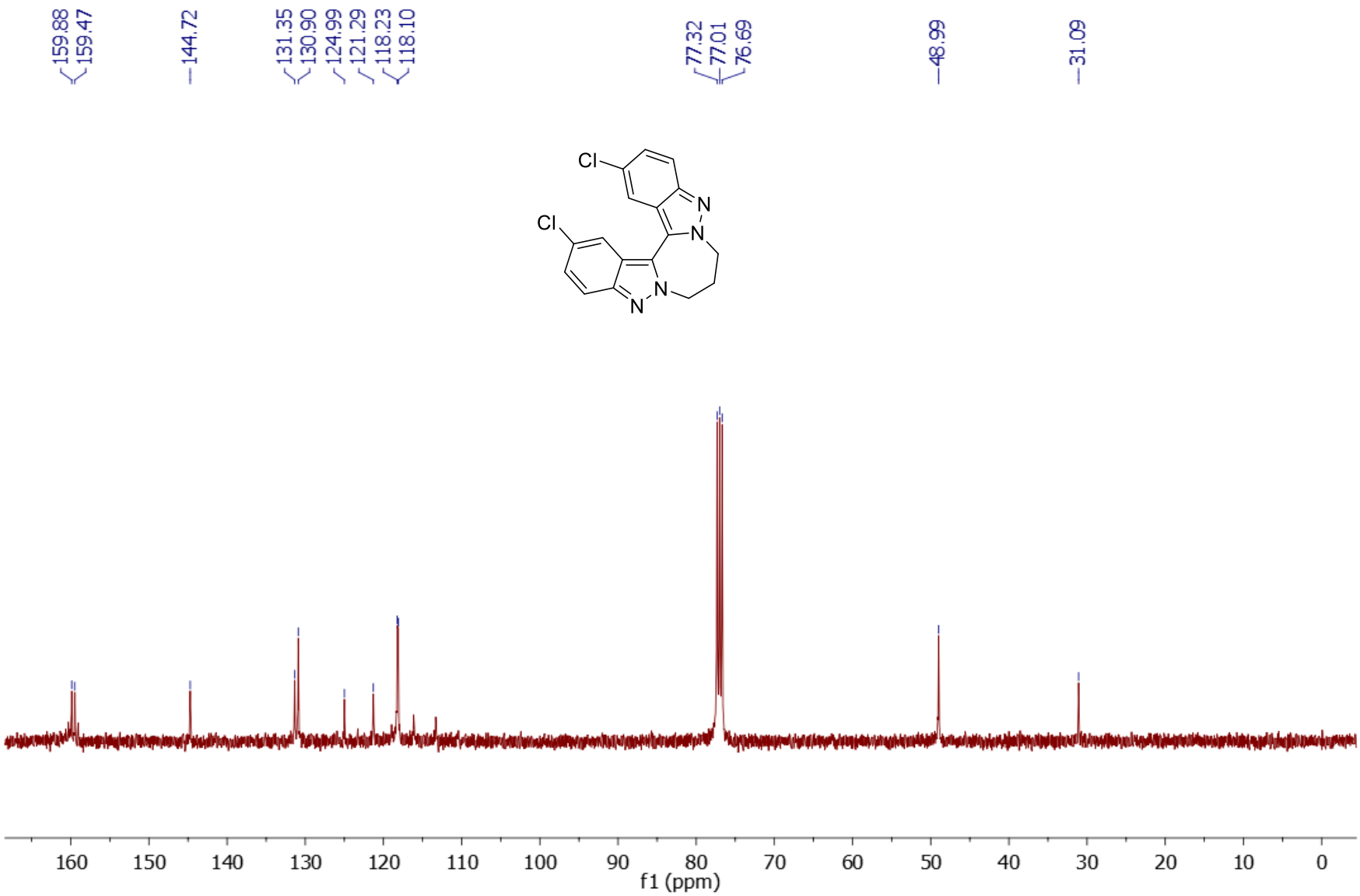
Compound 3bc



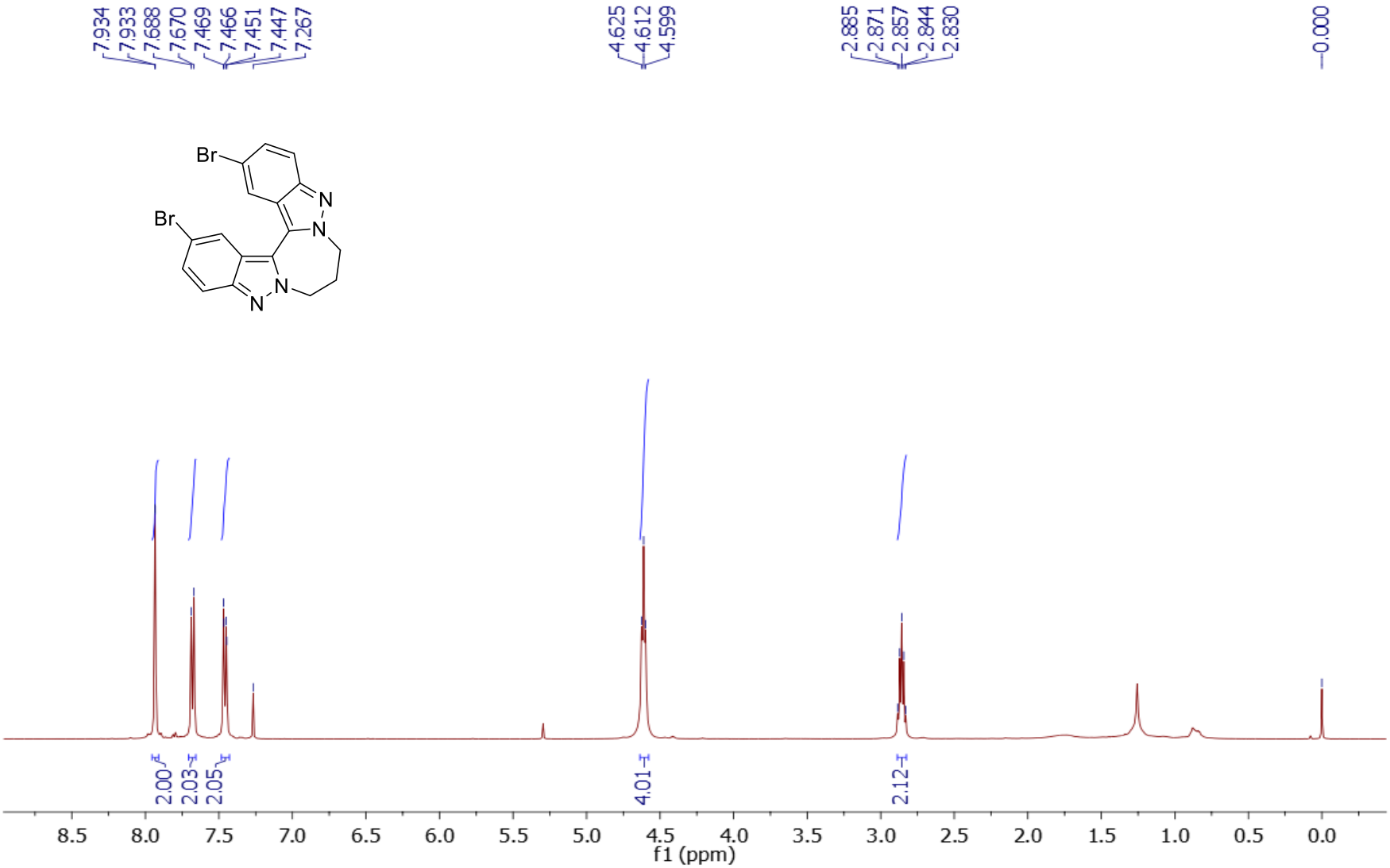

148.54
132.78
125.26
124.87
120.85
119.45
117.08
77.32
77.00
76.68
49.32
31.36
Cl
Cl
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

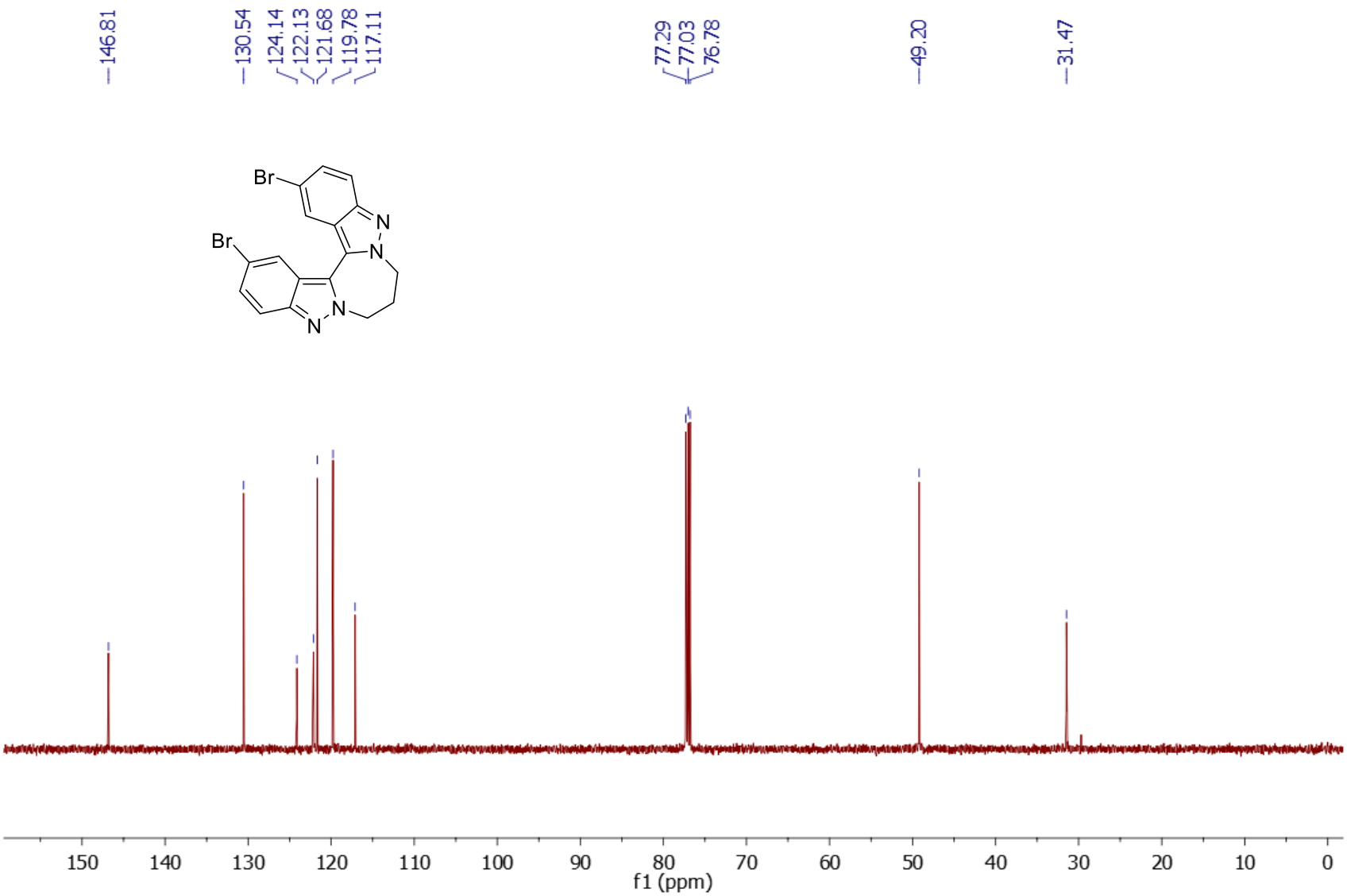
Compound 3cc



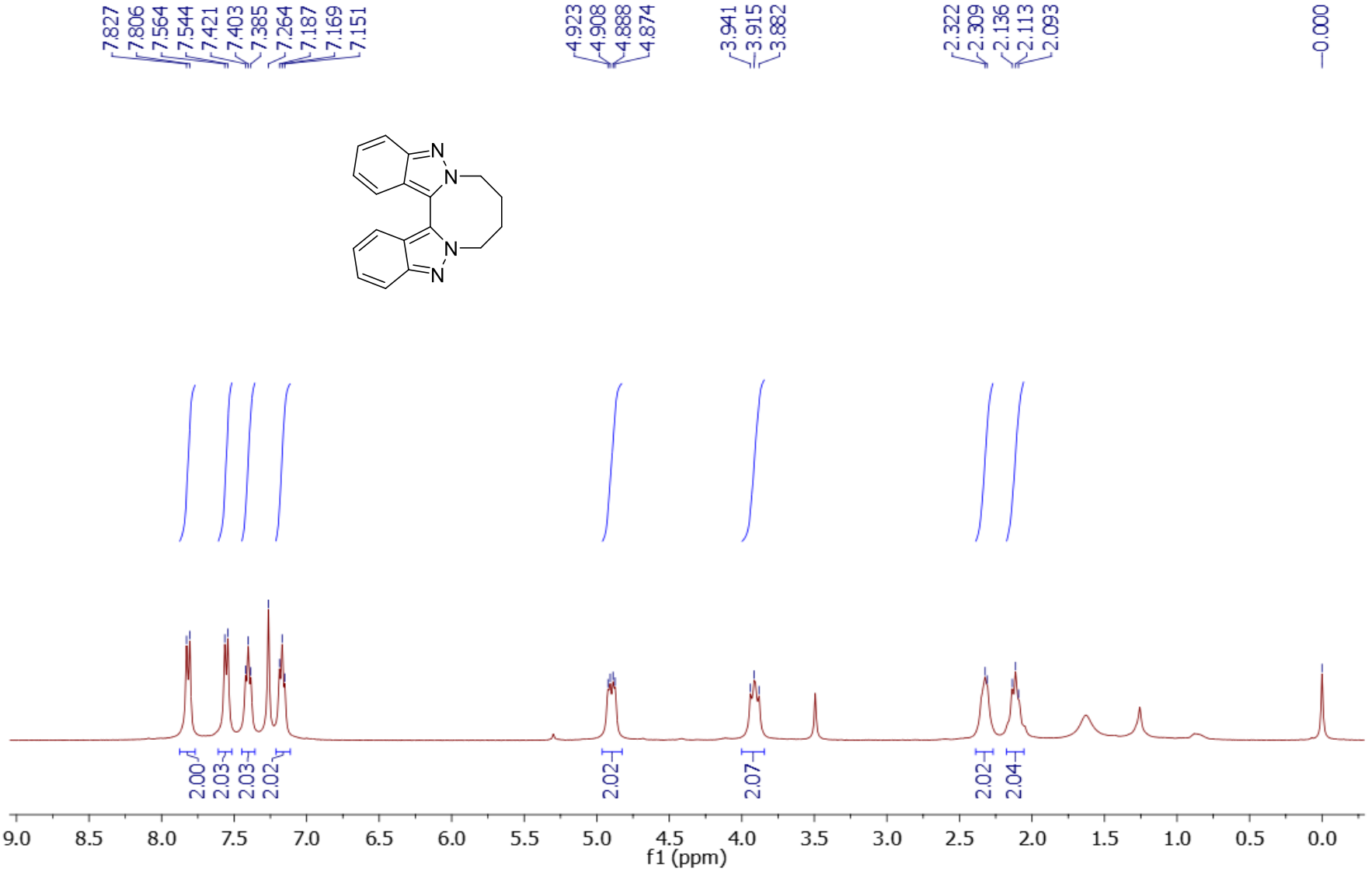

159.88
159.47
144.72
131.35
130.90
124.99
121.29
118.23
118.10
77.32
77.01
76.69
48.99
31.09
Cl
Cl
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

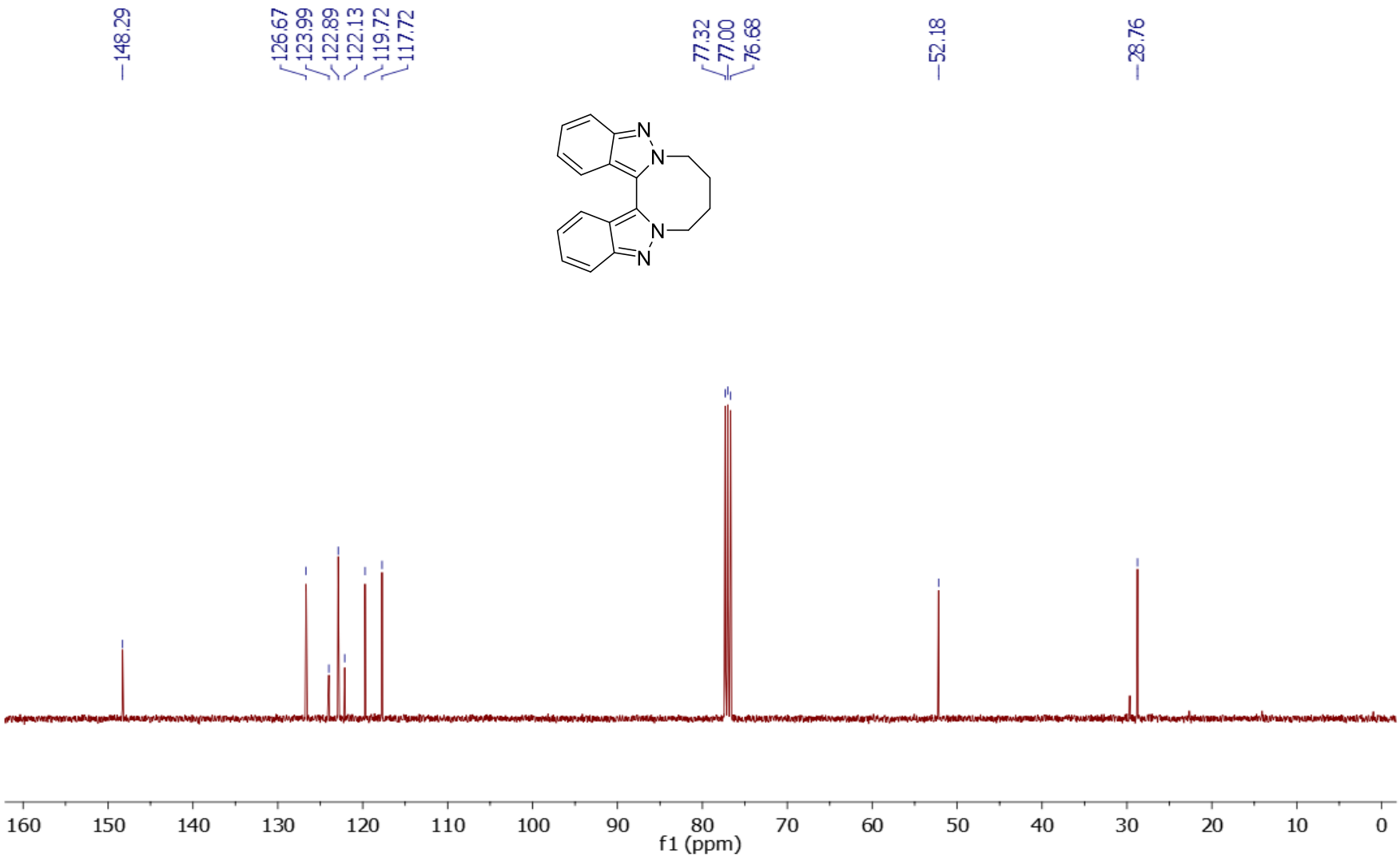
Compound 3ec



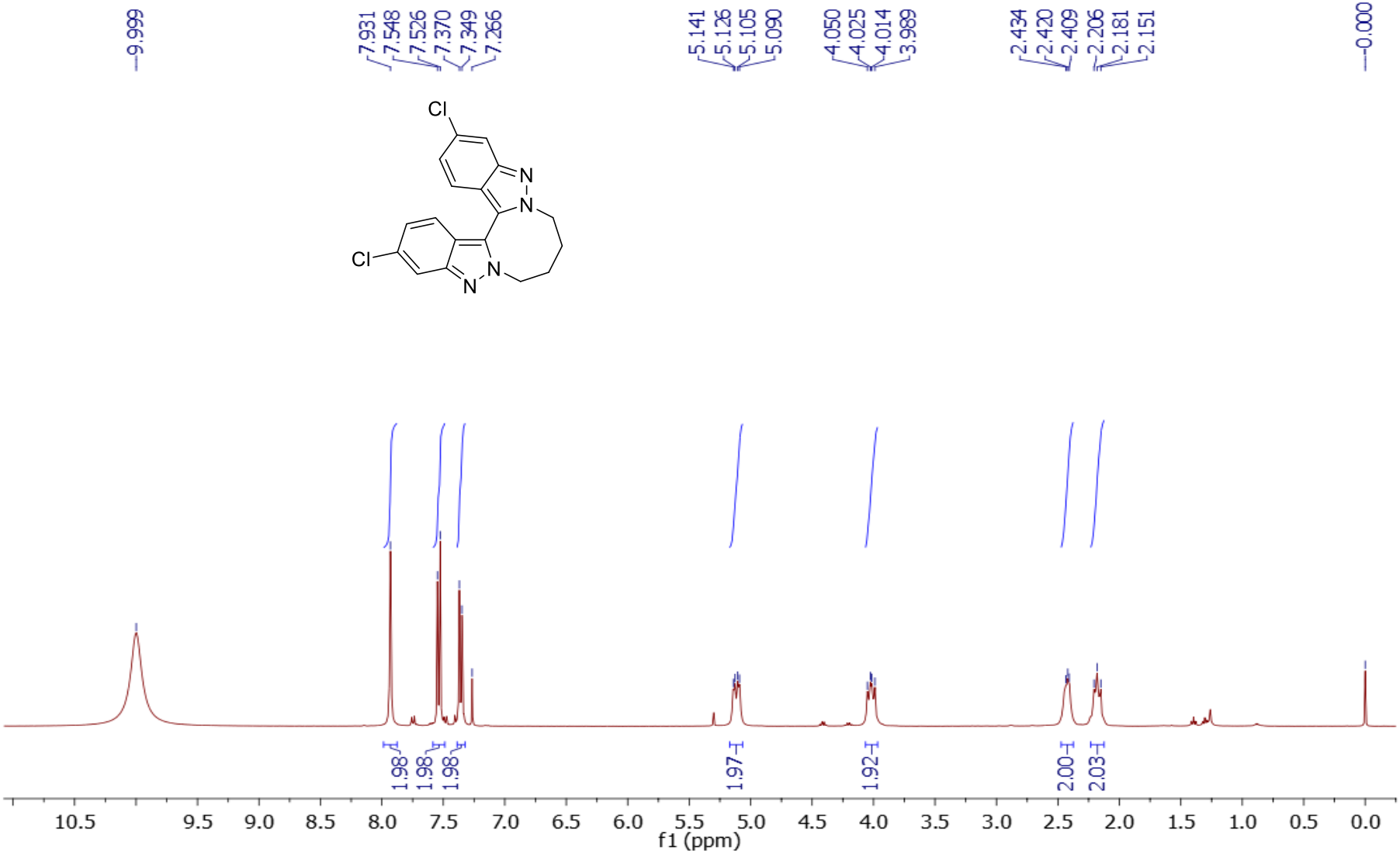

146.81
130.54
124.14
122.13
121.68
119.78
117.11
77.29
77.03
76.78
49.20
31.47
Br
Br
N
N
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

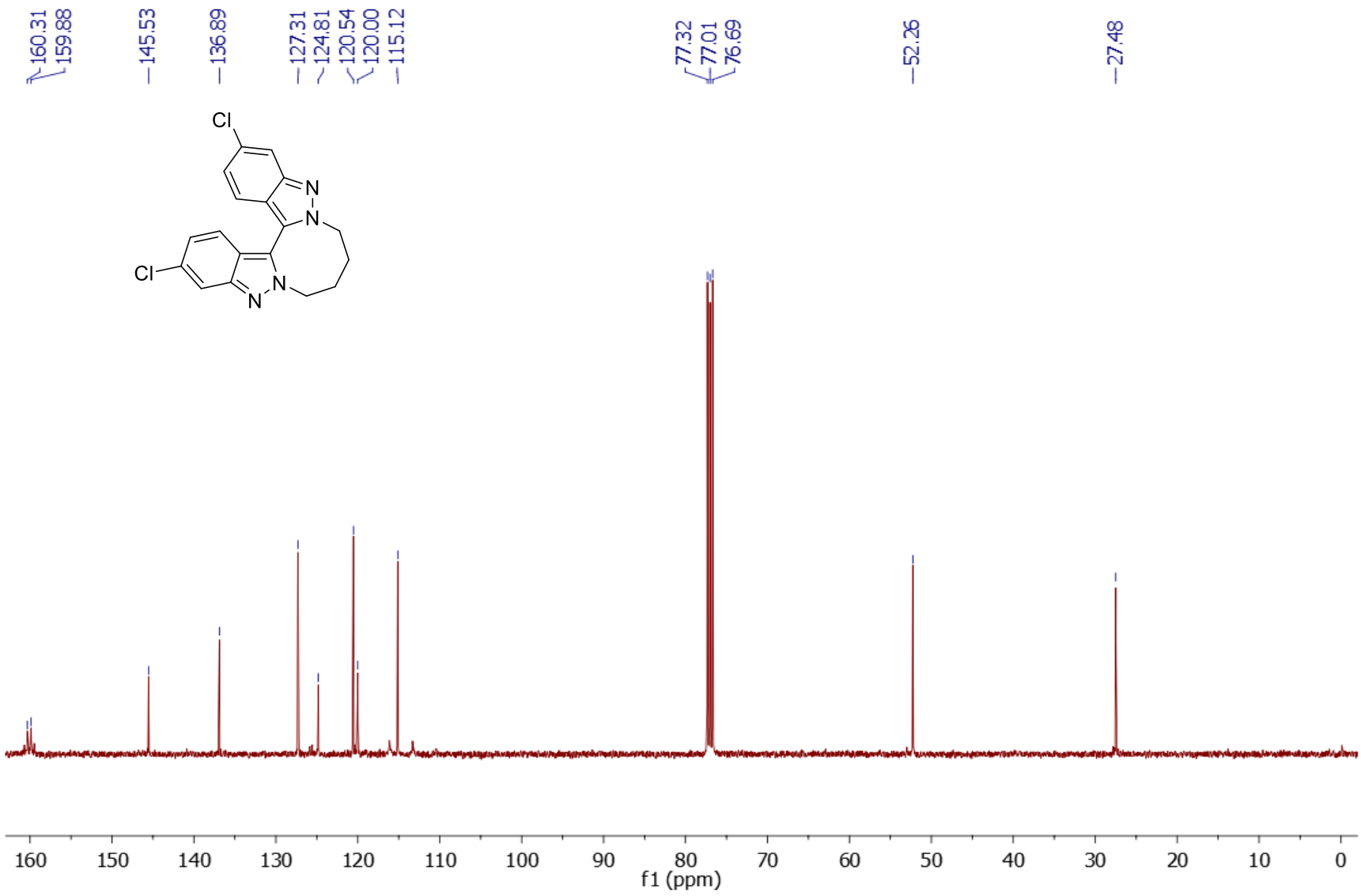
Compound 3ad



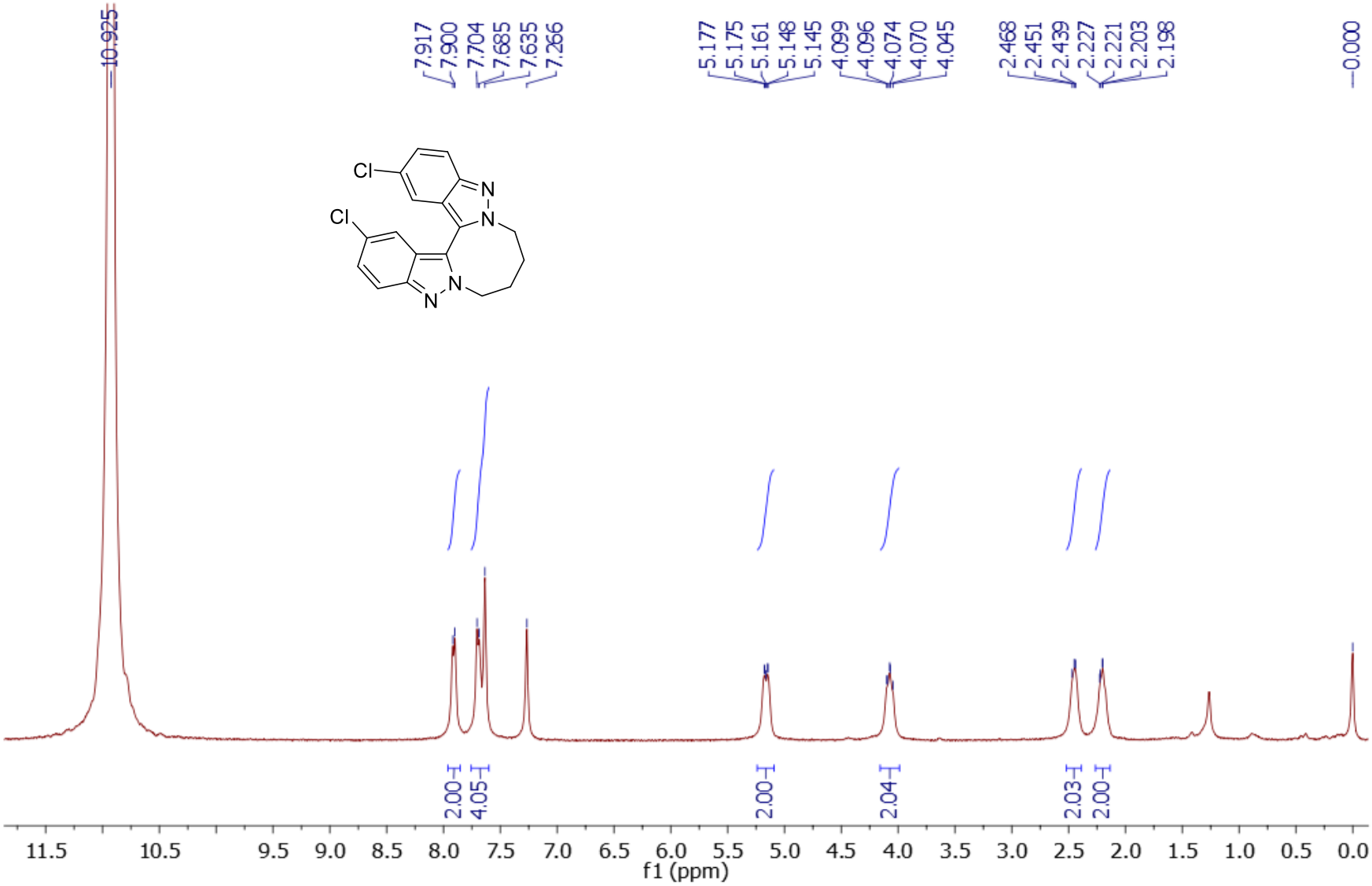

148.29
126.67
123.99
122.89
122.13
119.72
117.72
77.32
77.00
76.68
52.18
28.76
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

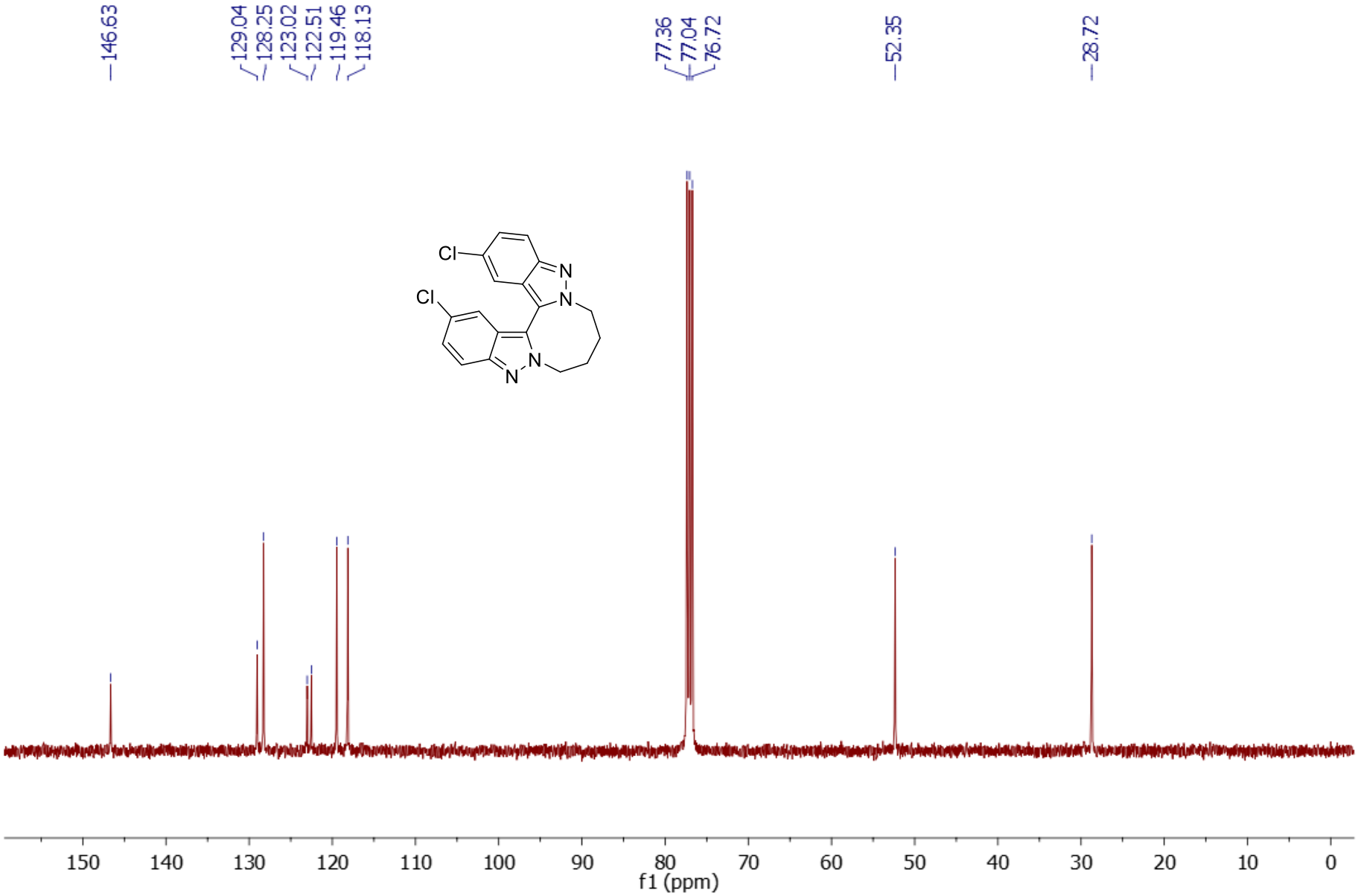
Compound 3bd



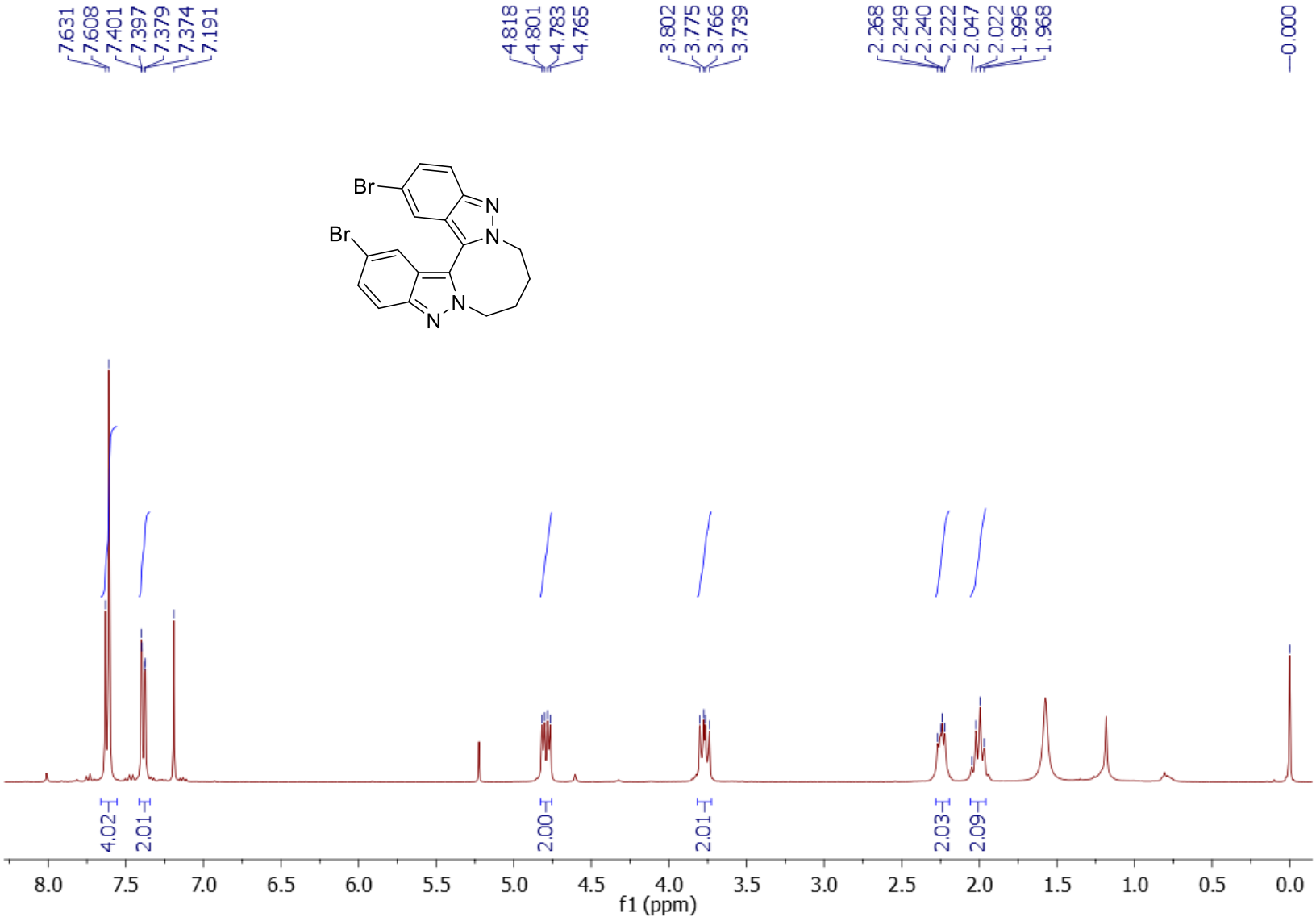

160.31
159.88
145.53
136.89
127.31
124.81
120.54
120.00
115.12
77.32
77.01
76.69
52.26
27.48
Cl
Cl
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

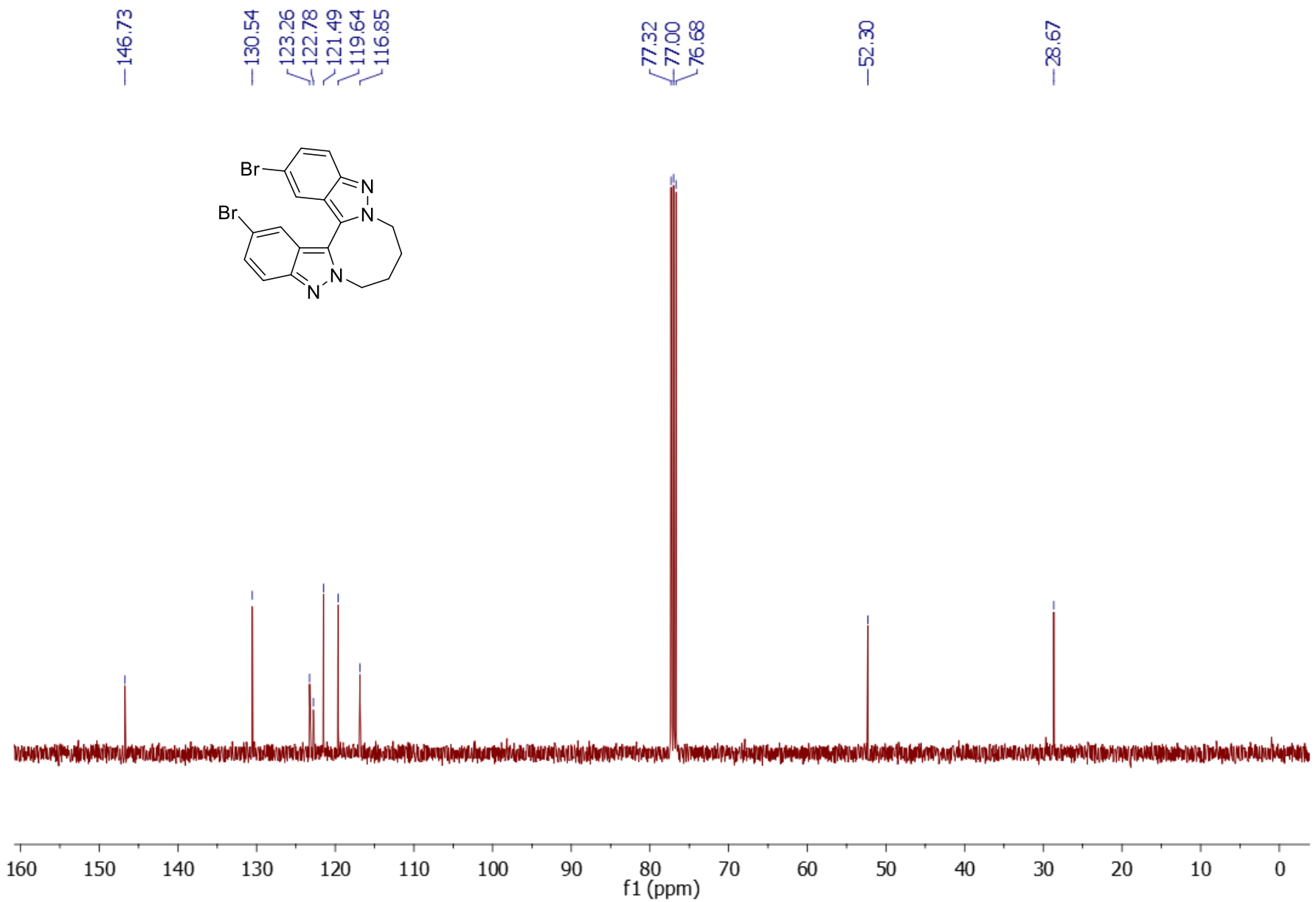
Compound 3cd



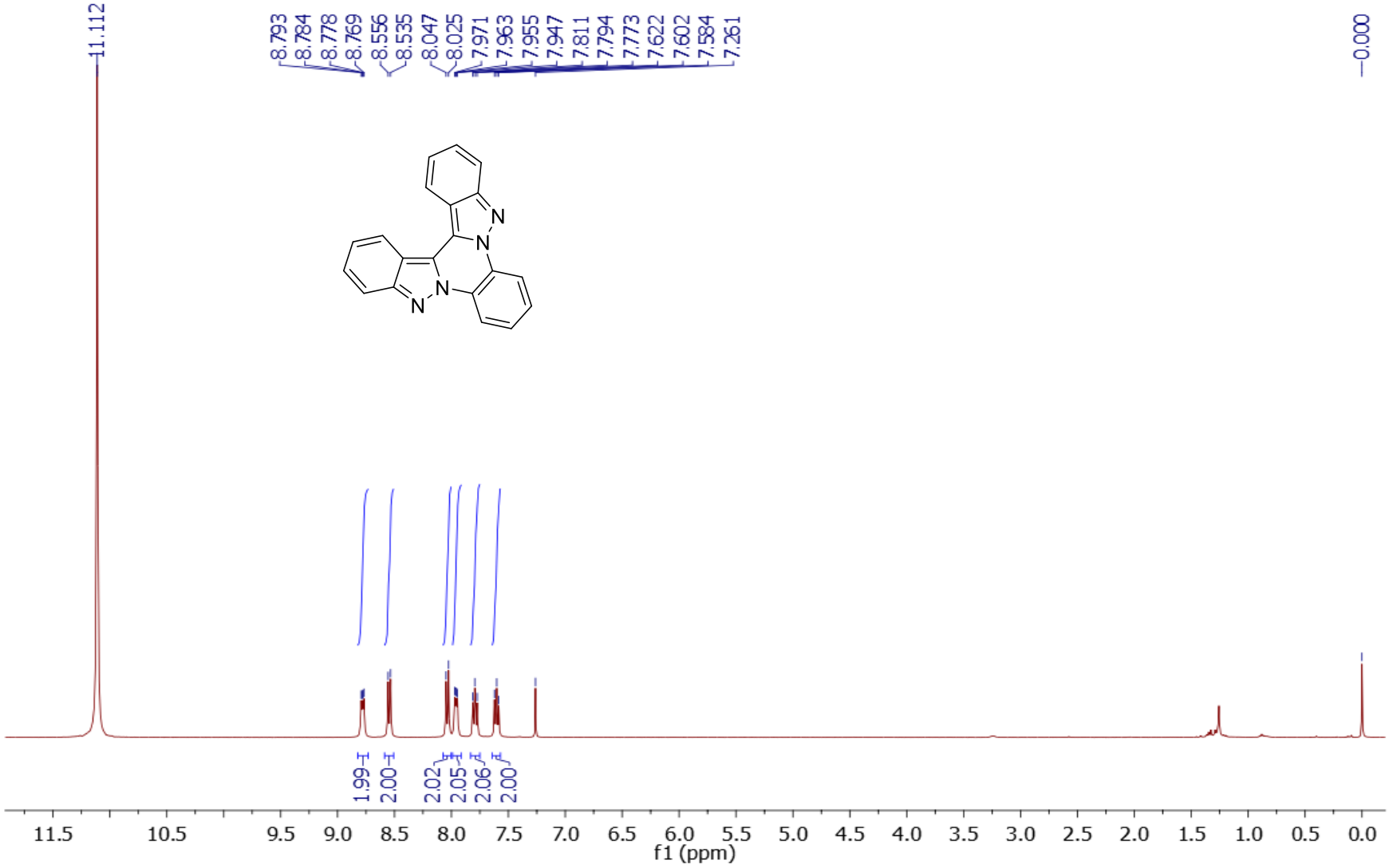

146.63
129.04
128.25
123.02
122.51
119.46
118.13
77.36
77.04
76.72
52.35
28.72
Cl
Cl
N
N
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

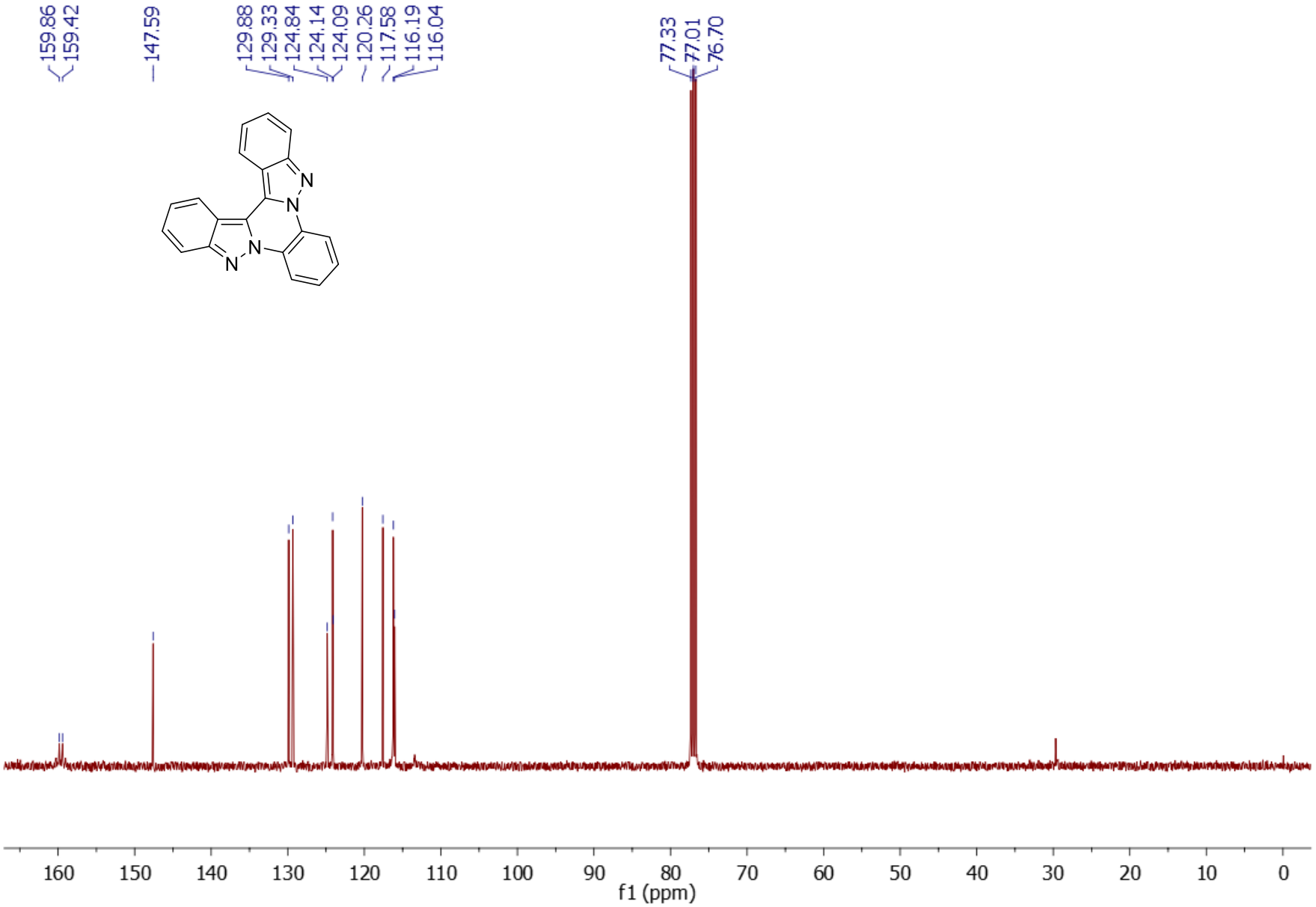
Compound 3ed



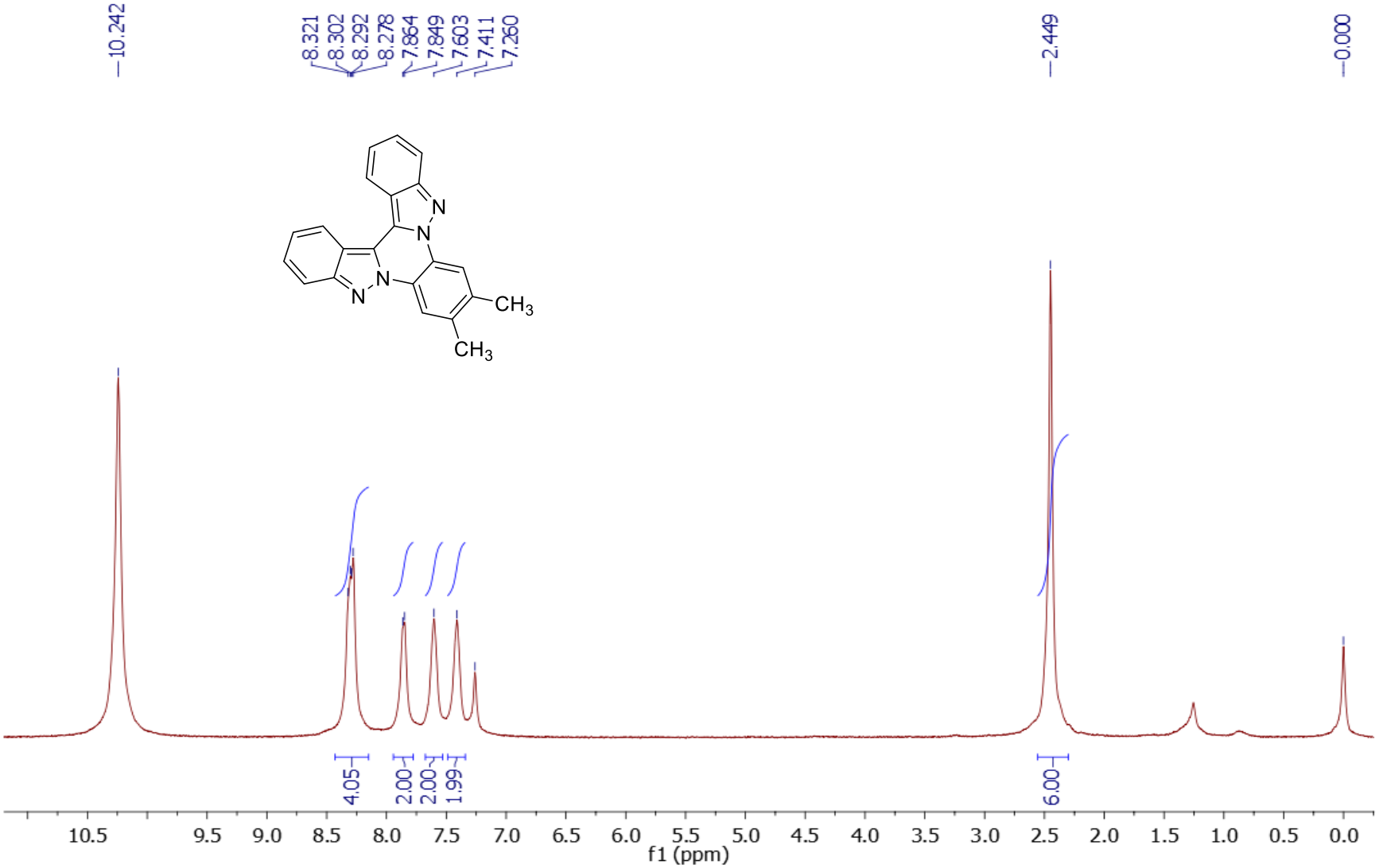

146.73
130.54
123.26
122.78
121.49
119.64
116.85
77.32
77.00
76.68
52.30
28.67
Br
Br
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

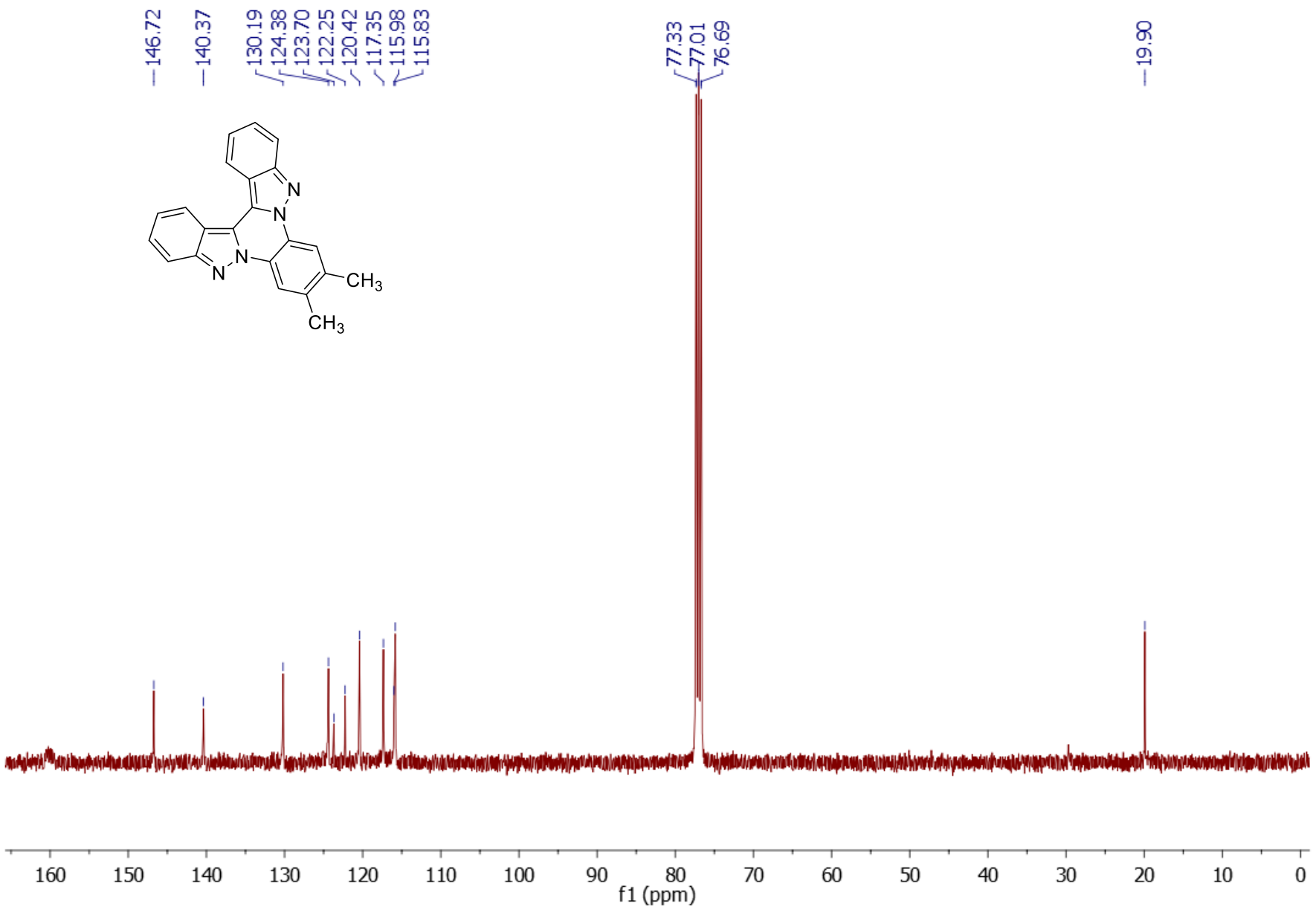
Compound 3ae



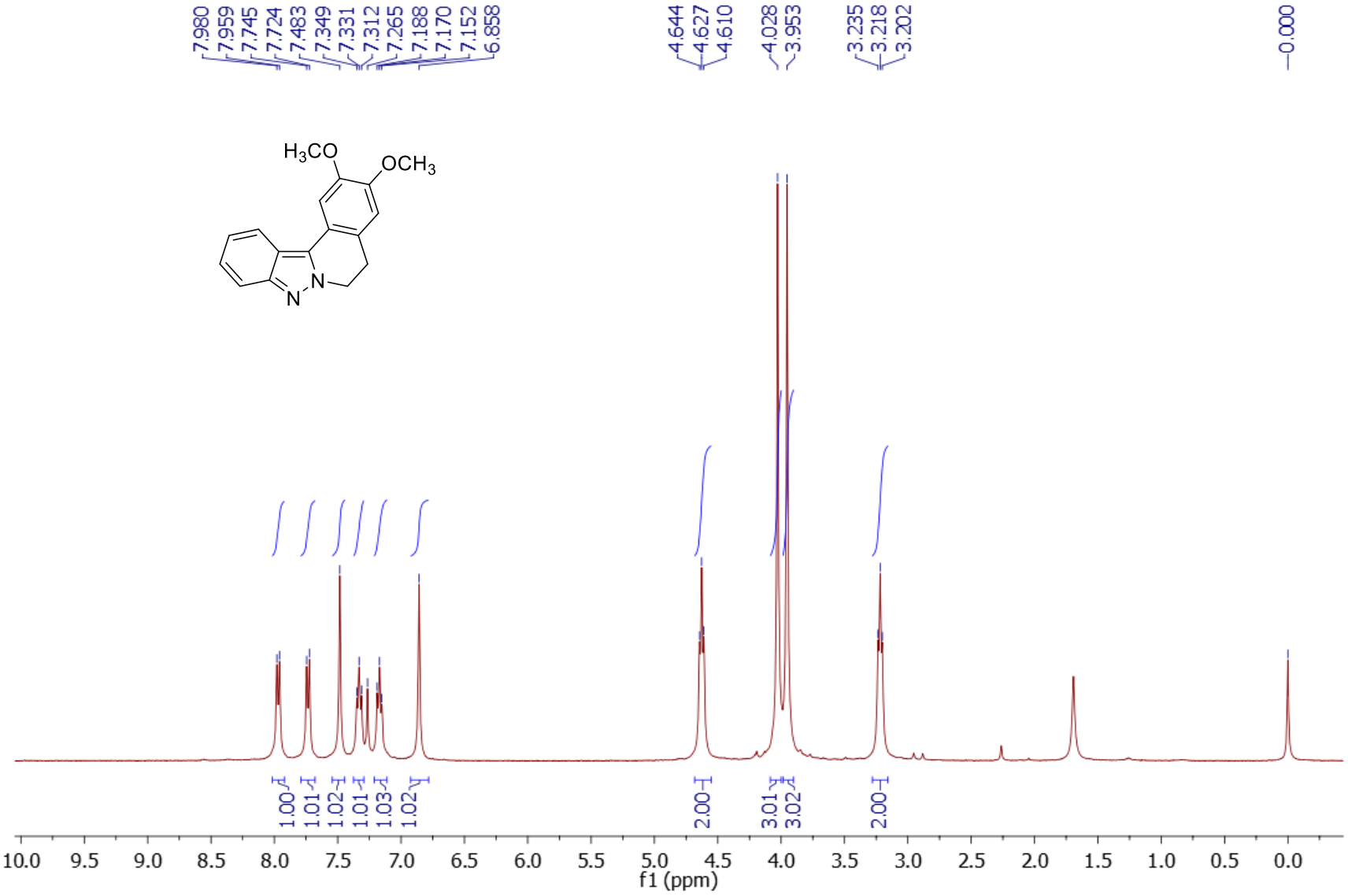

159.86
159.42
147.59
129.88
129.33
124.84
124.14
124.09
120.26
117.58
116.19
116.04
77.33
77.01
76.70
N
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

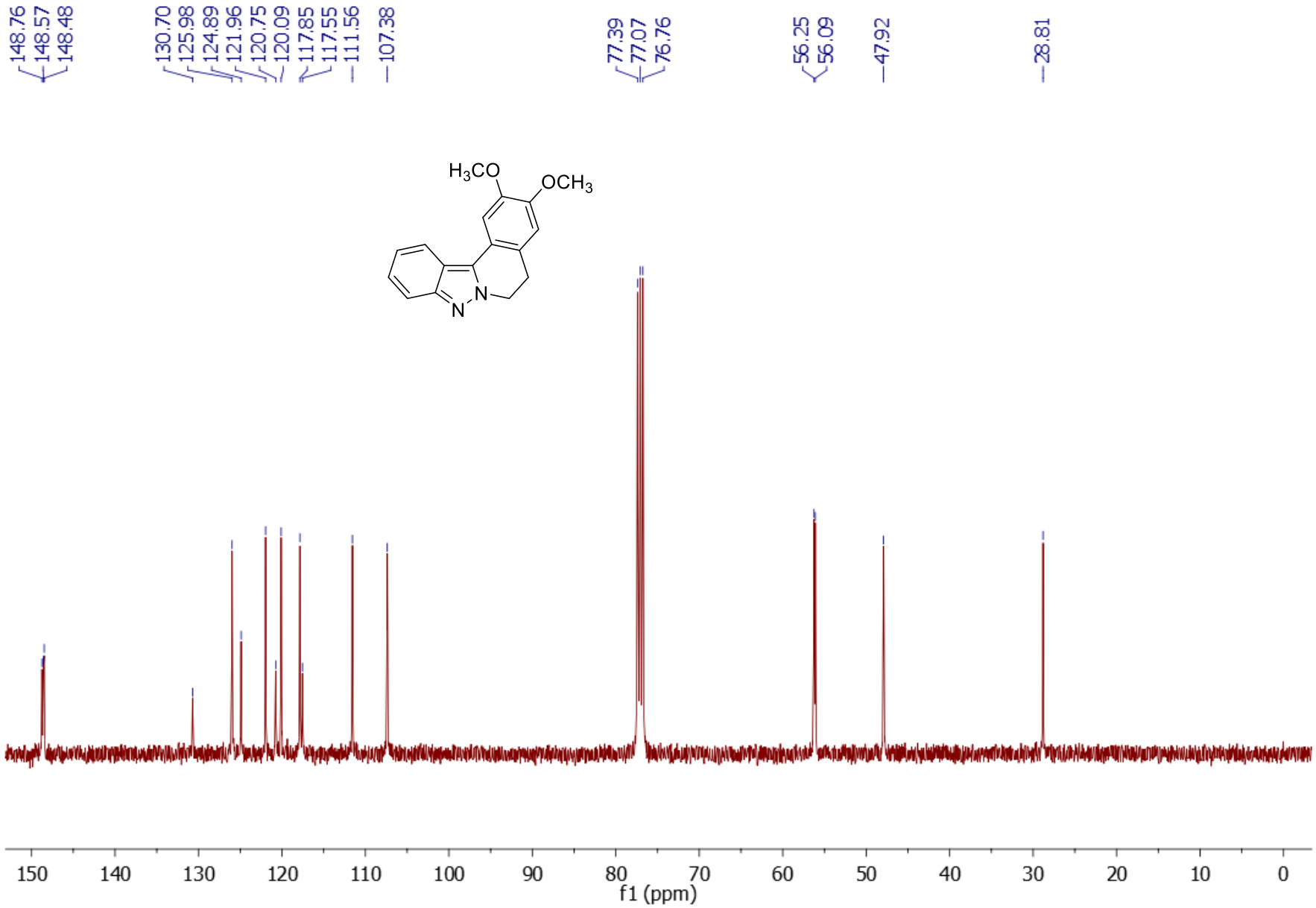
Compound 3af



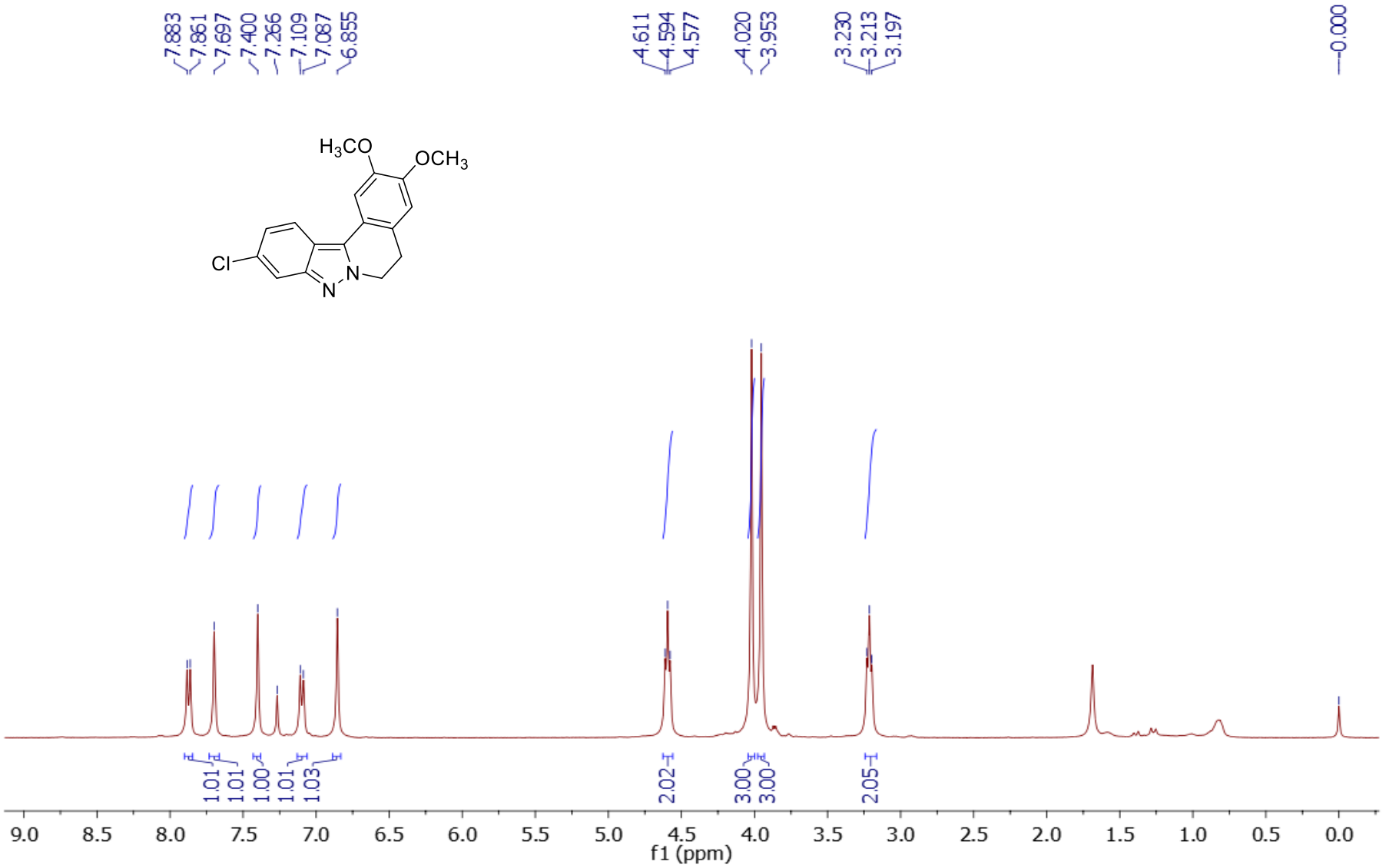

146.72
140.37
130.19
124.38
123.70
122.25
120.42
117.35
115.98
115.83
77.33
77.01
76.69
19.90
N
N
N
N
CH3
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

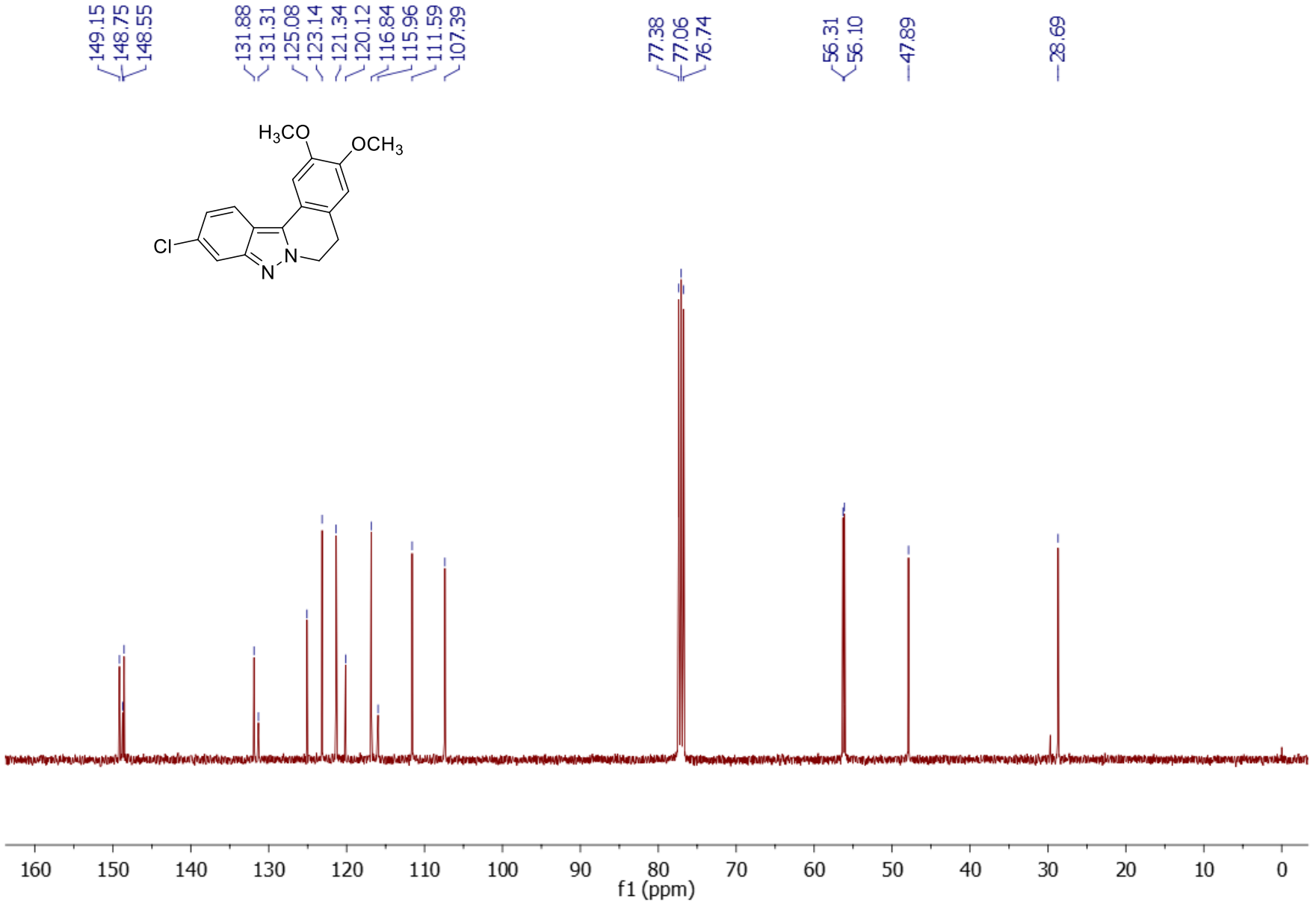
Compound 5aa



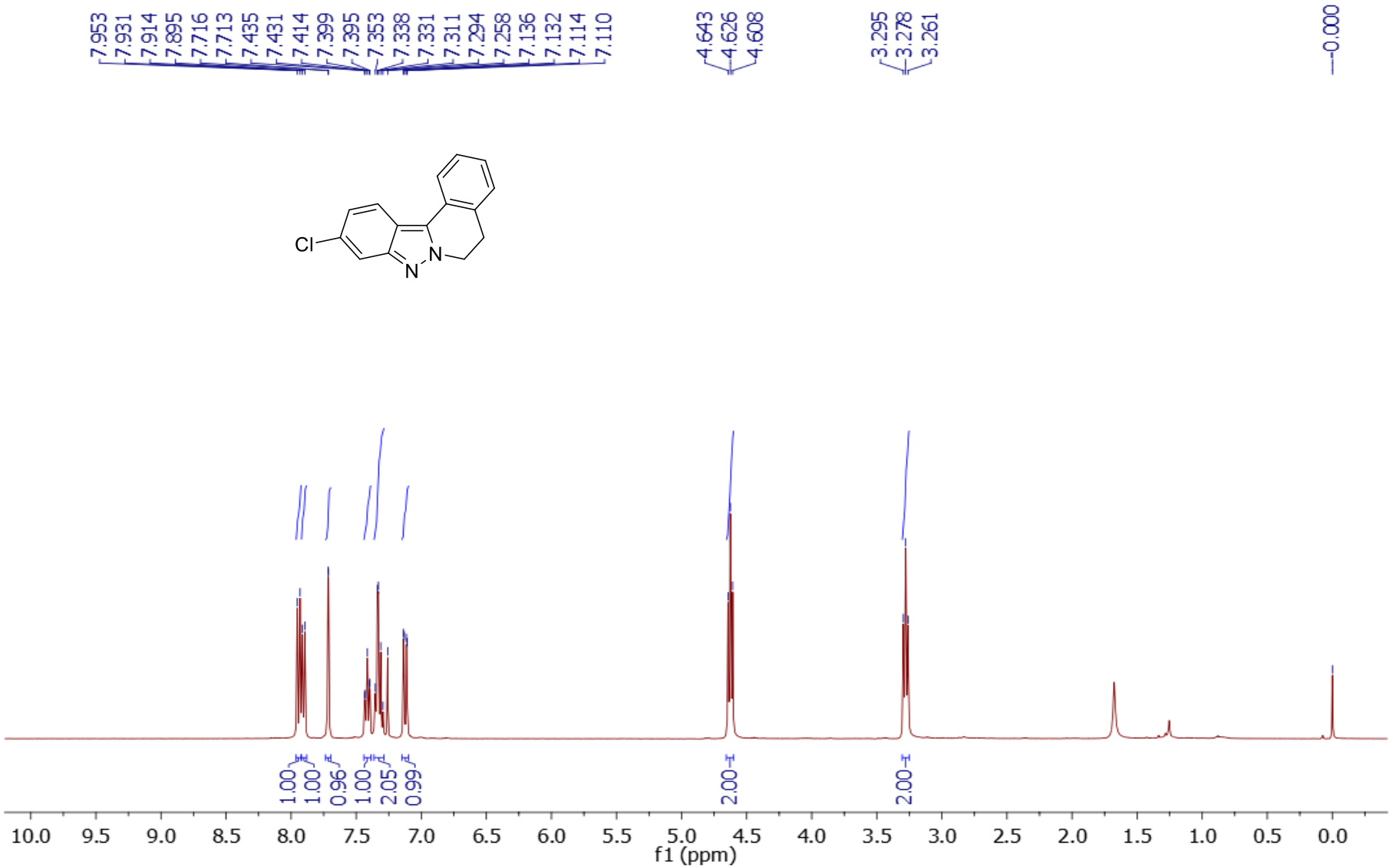

148.76
148.57
148.48
130.70
125.98
124.89
121.96
120.75
120.09
117.85
117.55
111.56
107.38
77.39
77.07
76.76
56.25
56.09
47.92
28.81
H3CO
OCH3
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

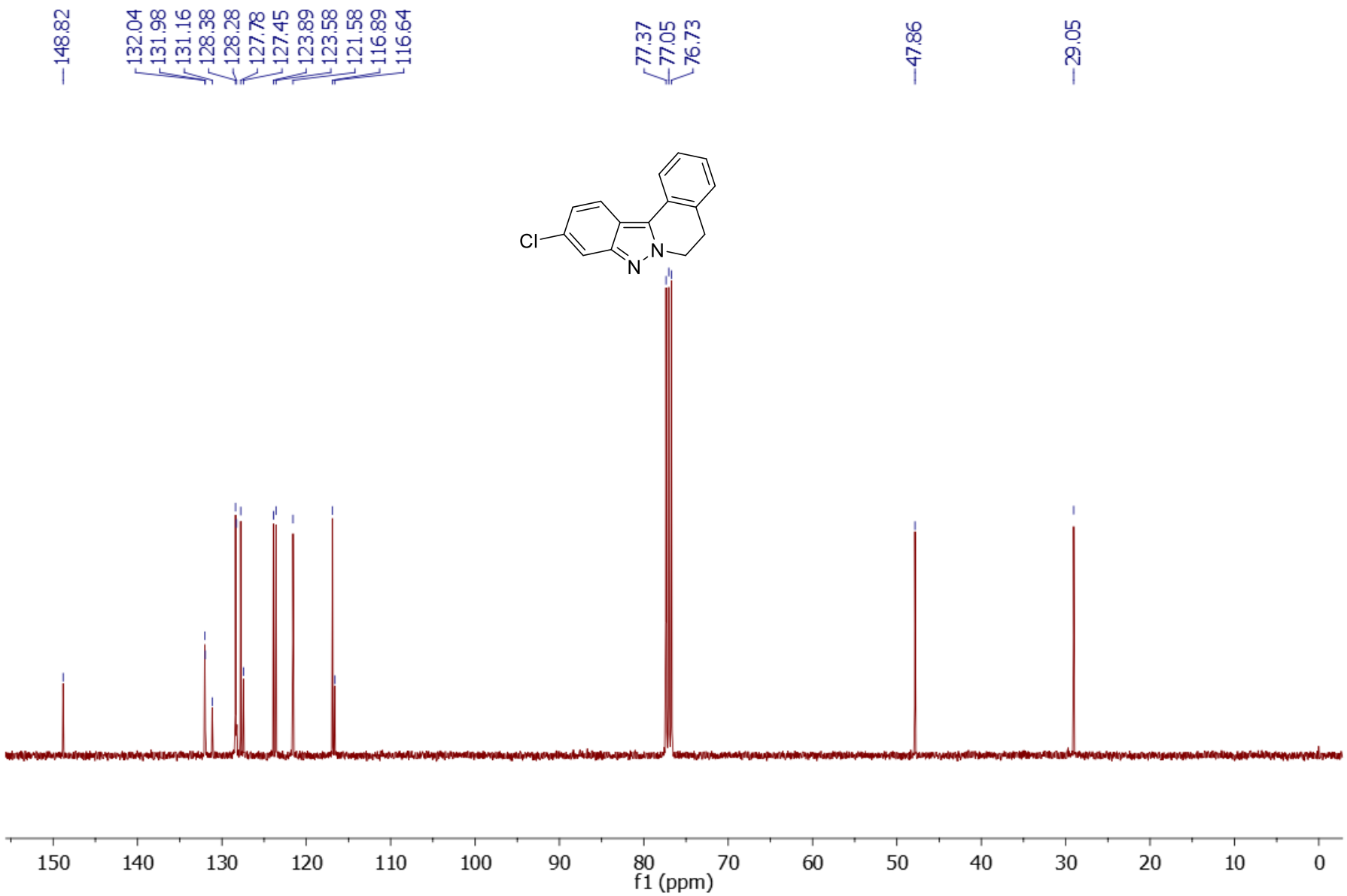
Compound 5ba



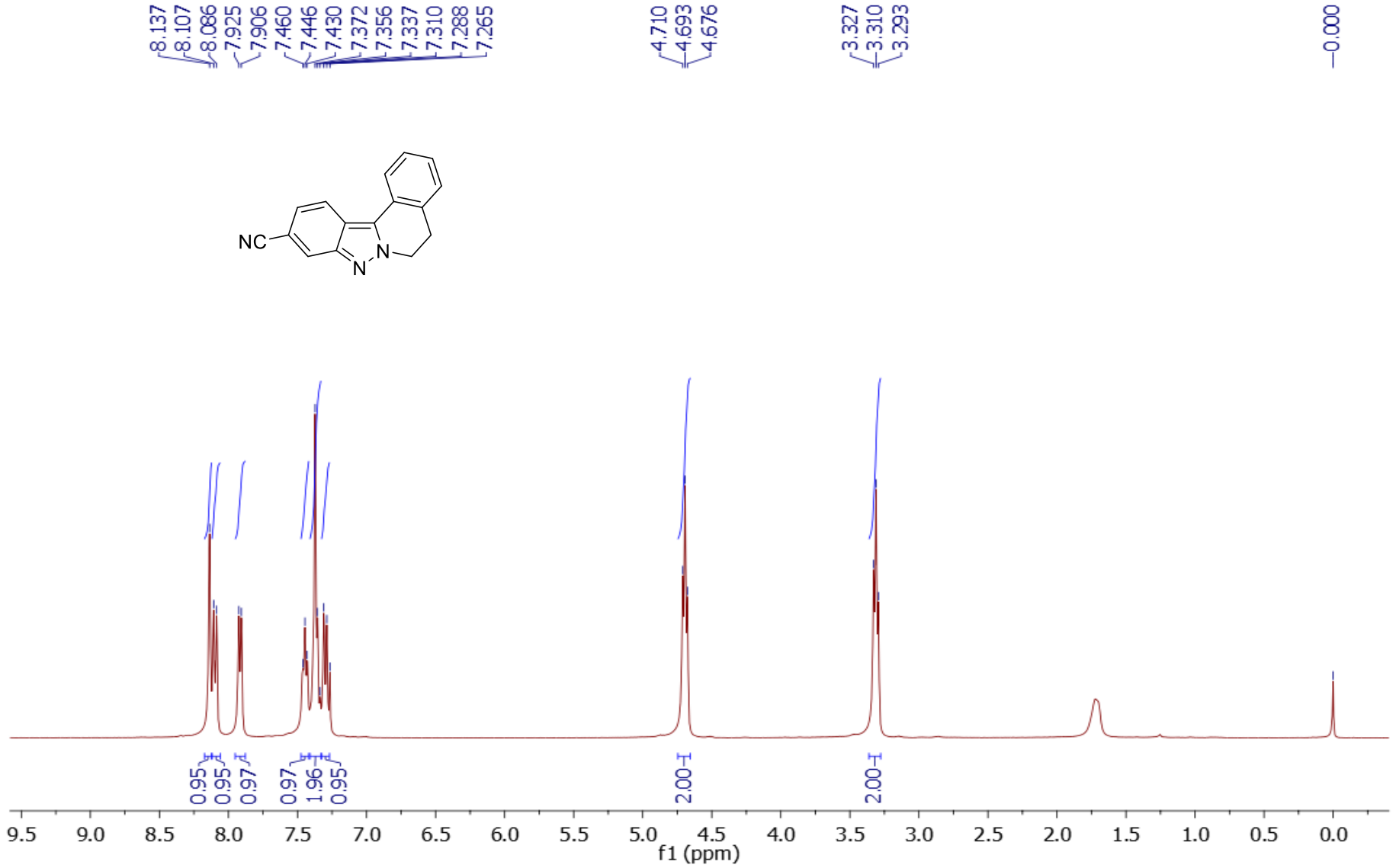

149.15
148.75
148.55
131.88
131.31
125.08
123.14
121.34
120.12
116.84
115.96
111.59
107.39
77.38
77.06
76.74
56.31
56.10
47.89
28.69
H3CO
OCH3
Cl
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

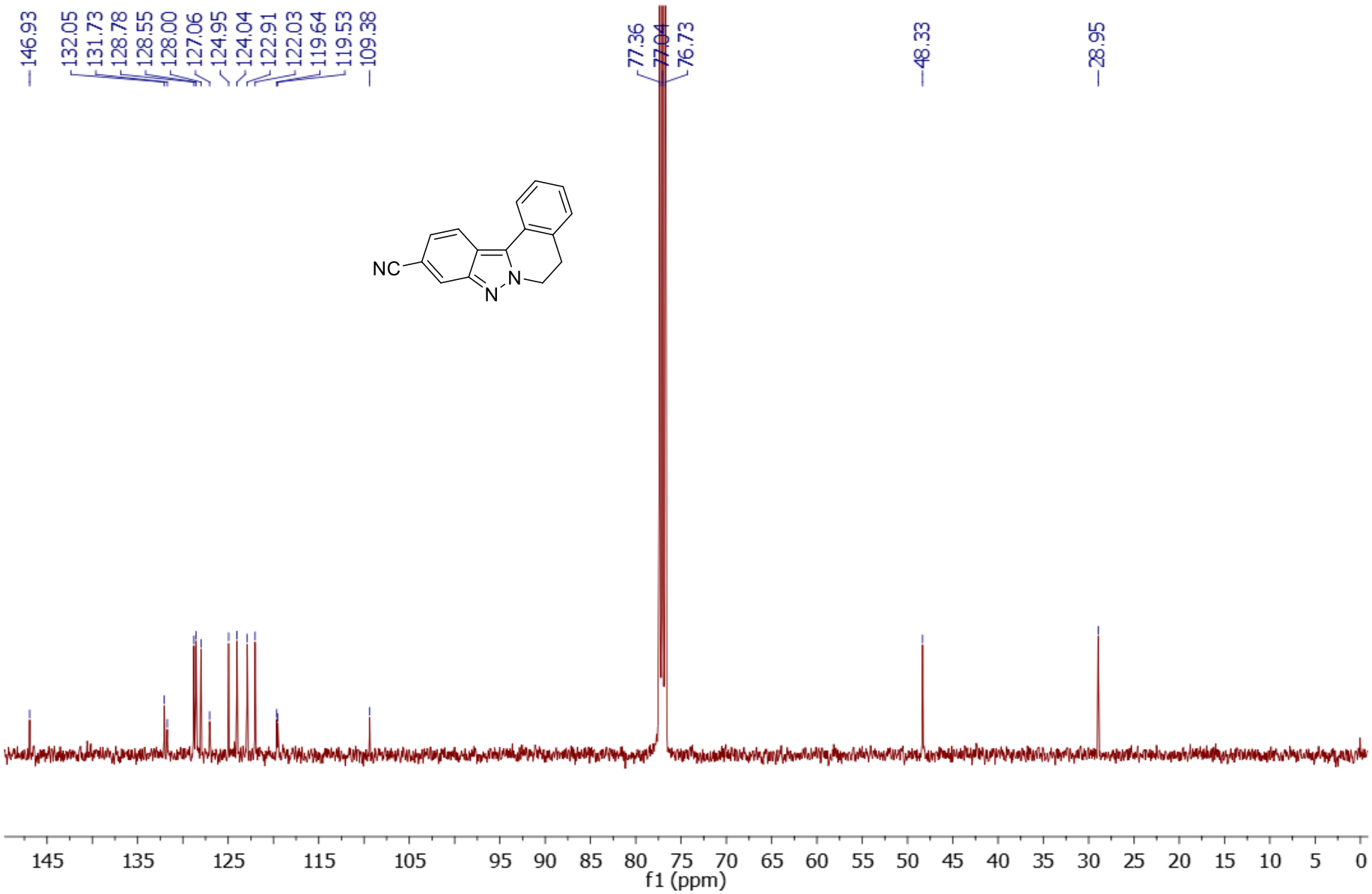
Compound 5bb



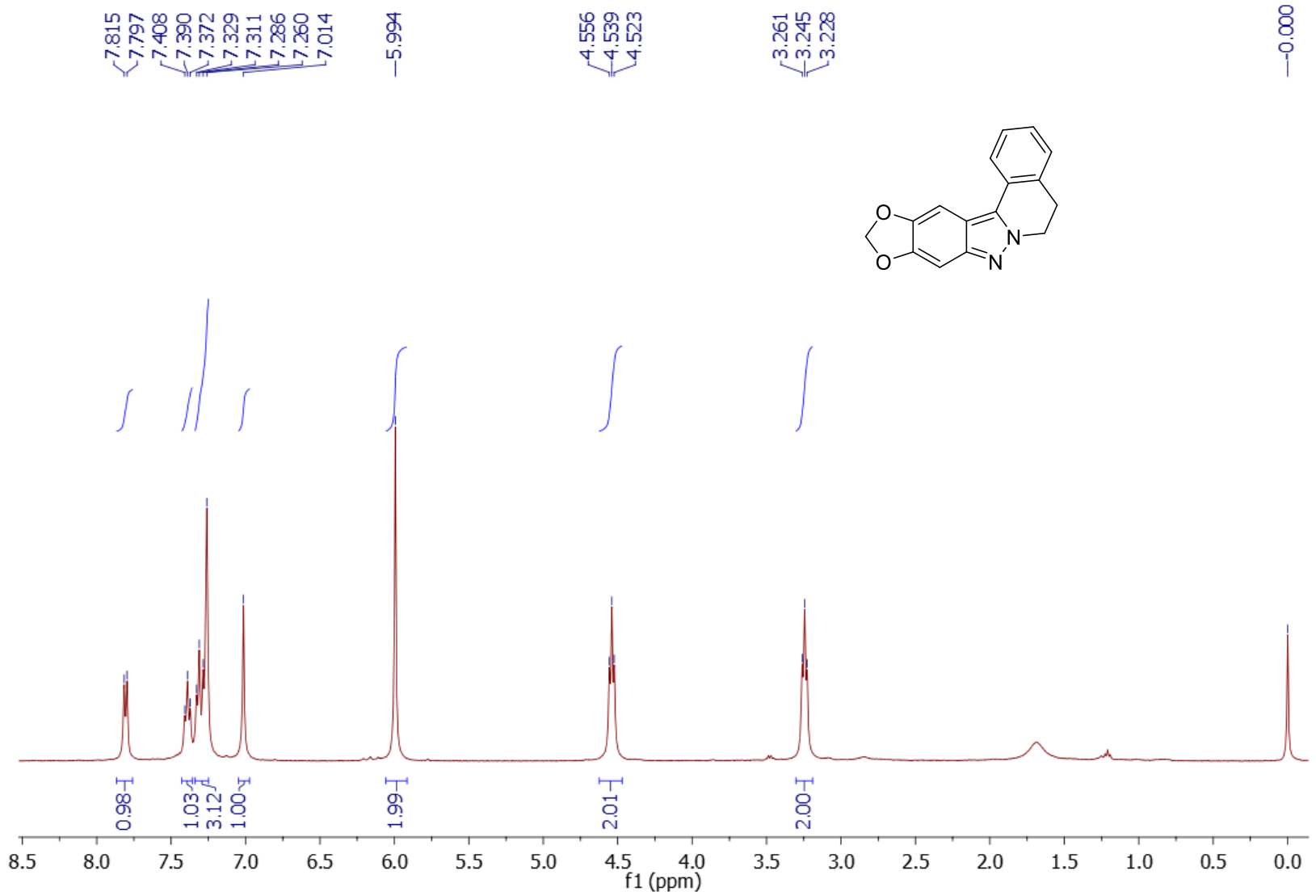

148.82
132.04
131.98
131.16
128.38
128.28
127.78
127.45
123.89
123.58
121.58
116.89
116.64
77.37
77.05
76.73
47.86
29.05
Cl
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

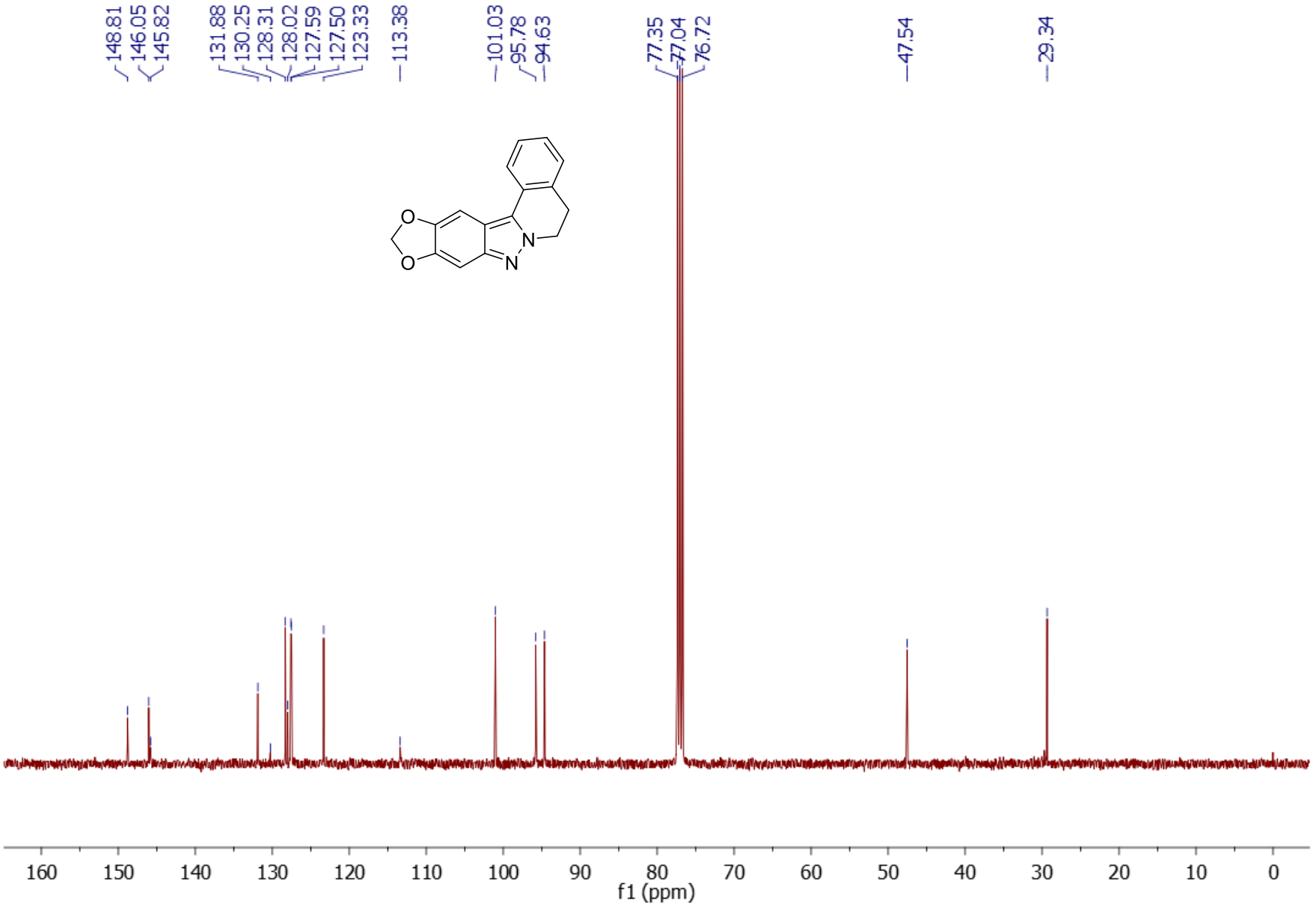
Compound 5fb



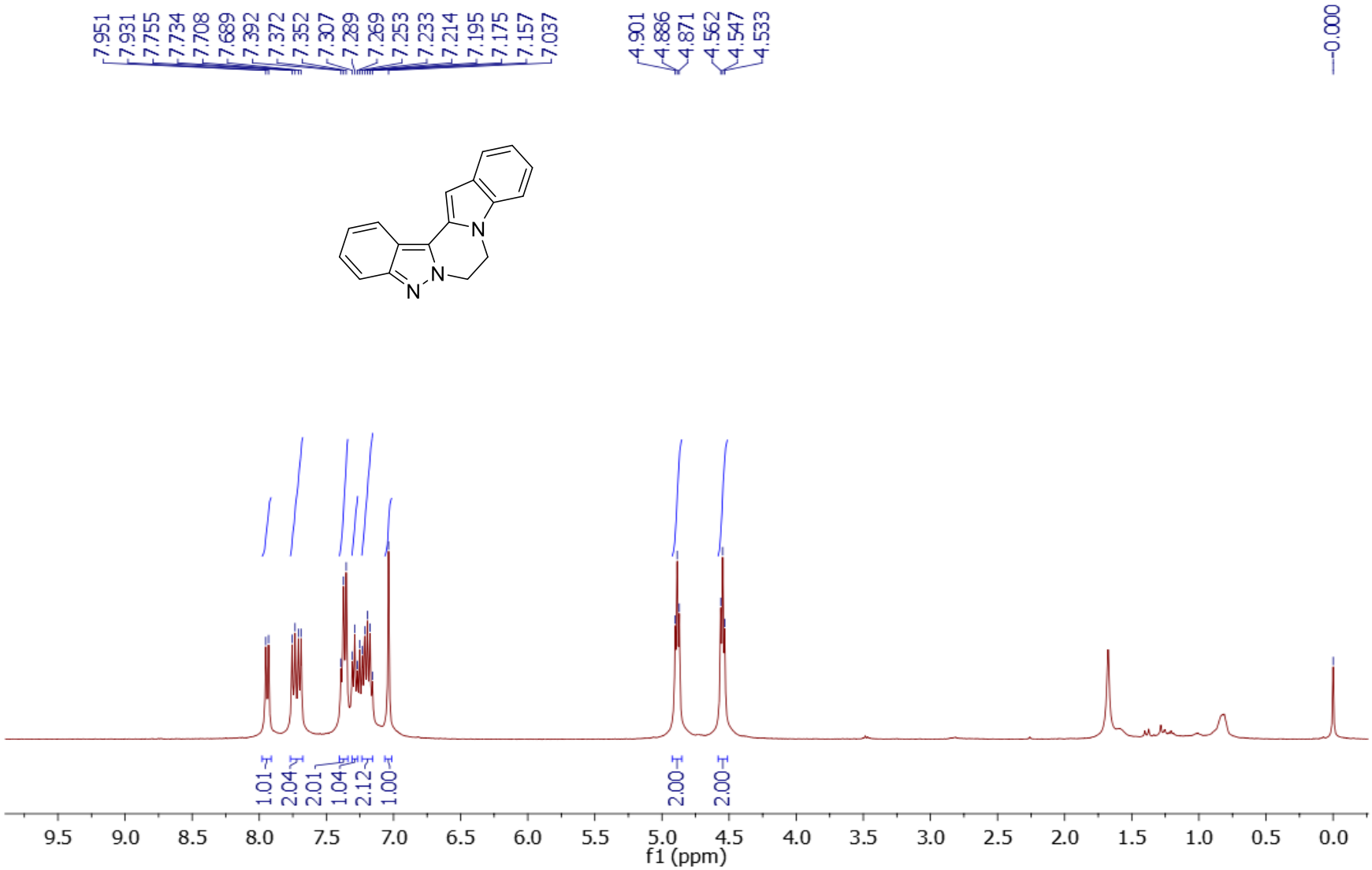

146.93
132.05
131.73
128.78
128.55
128.00
127.06
124.95
124.04
122.91
122.03
119.64
119.53
109.38
77.36
77.04
76.73
48.33
28.95
NC
N
N
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

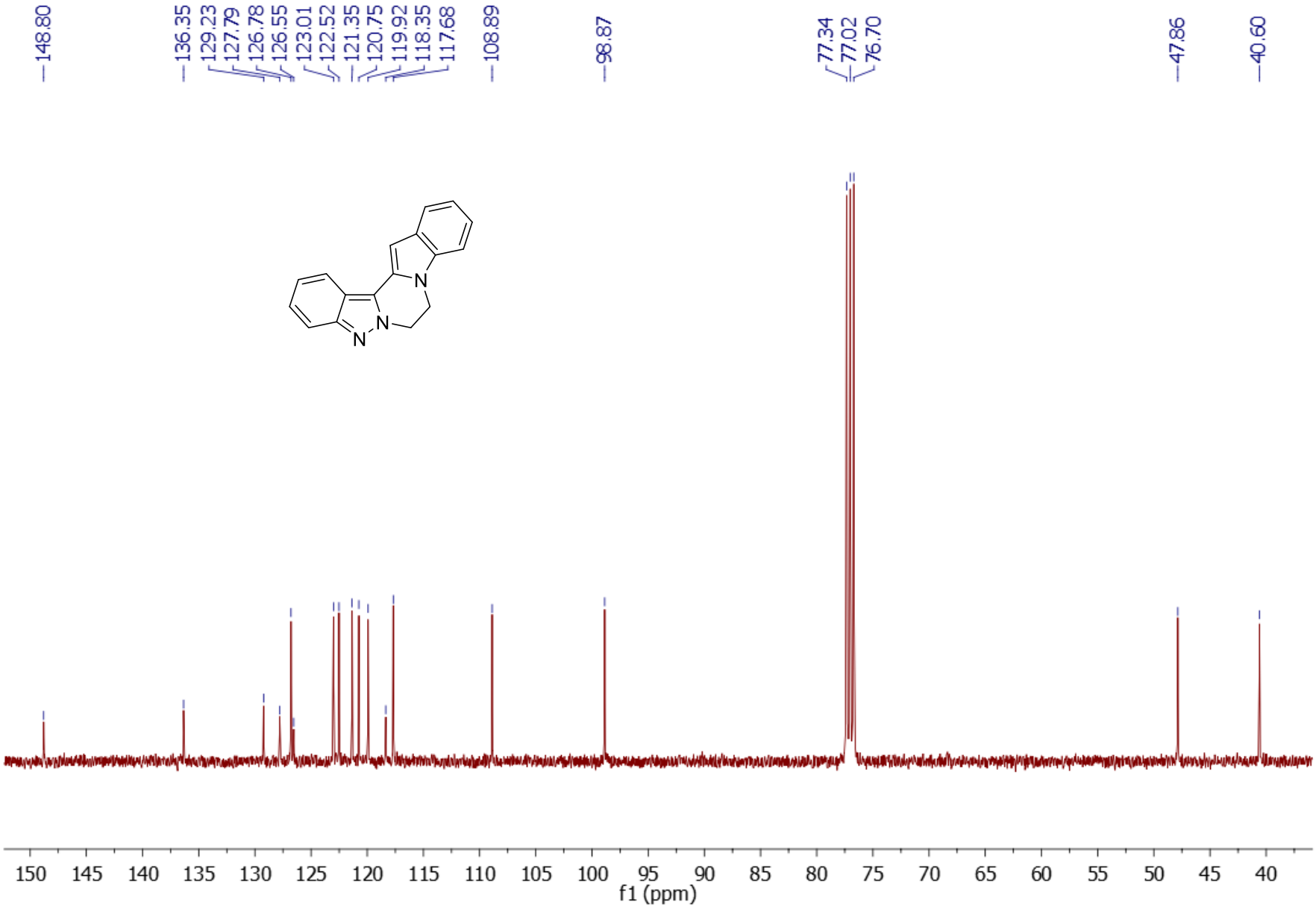
Compound 5gb



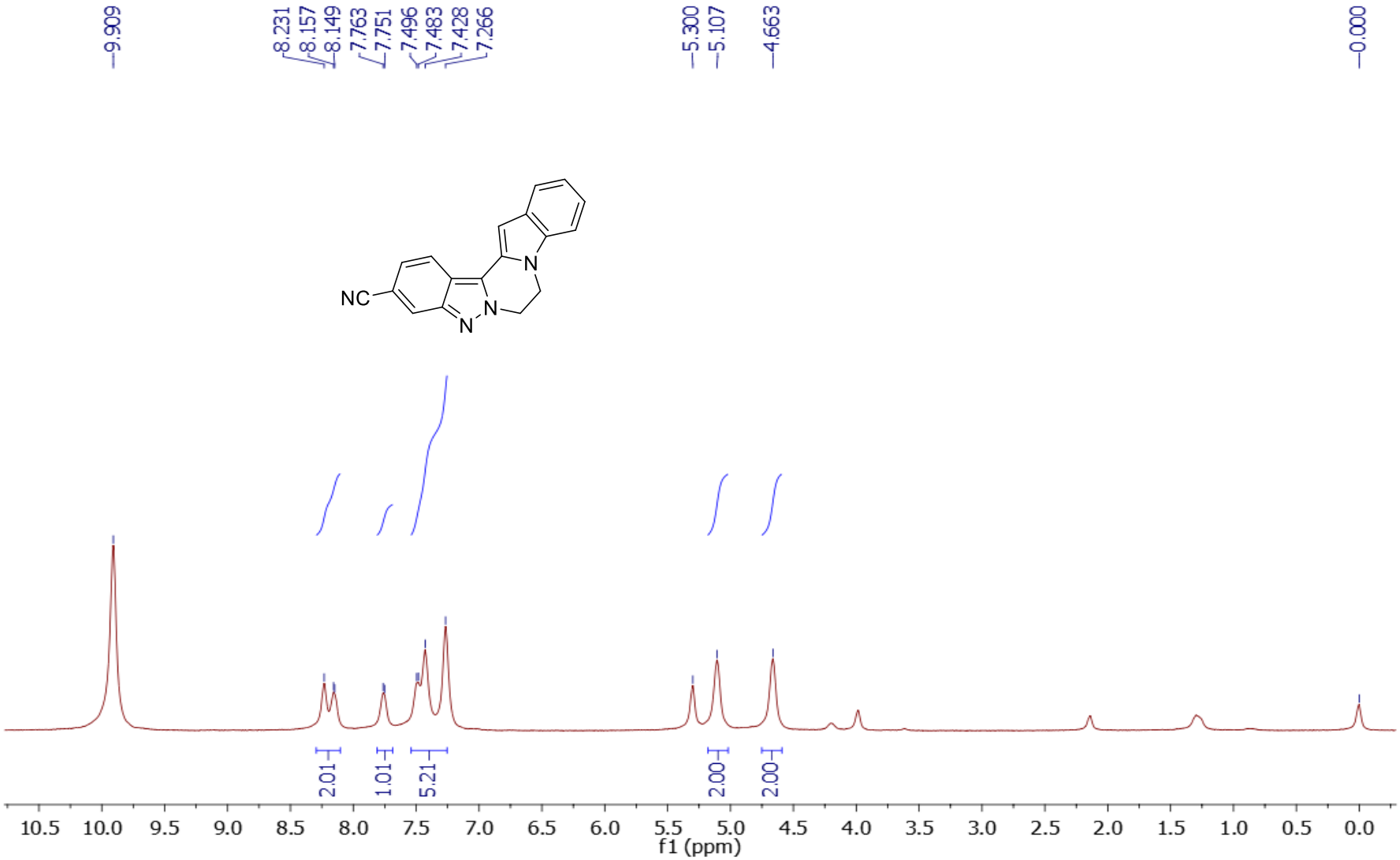

148.81
146.05
145.82
131.88
130.25
128.31
128.02
127.59
127.50
123.33
113.38
101.03
95.78
94.63
77.35
77.04
76.72
47.54
29.34
O
O
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

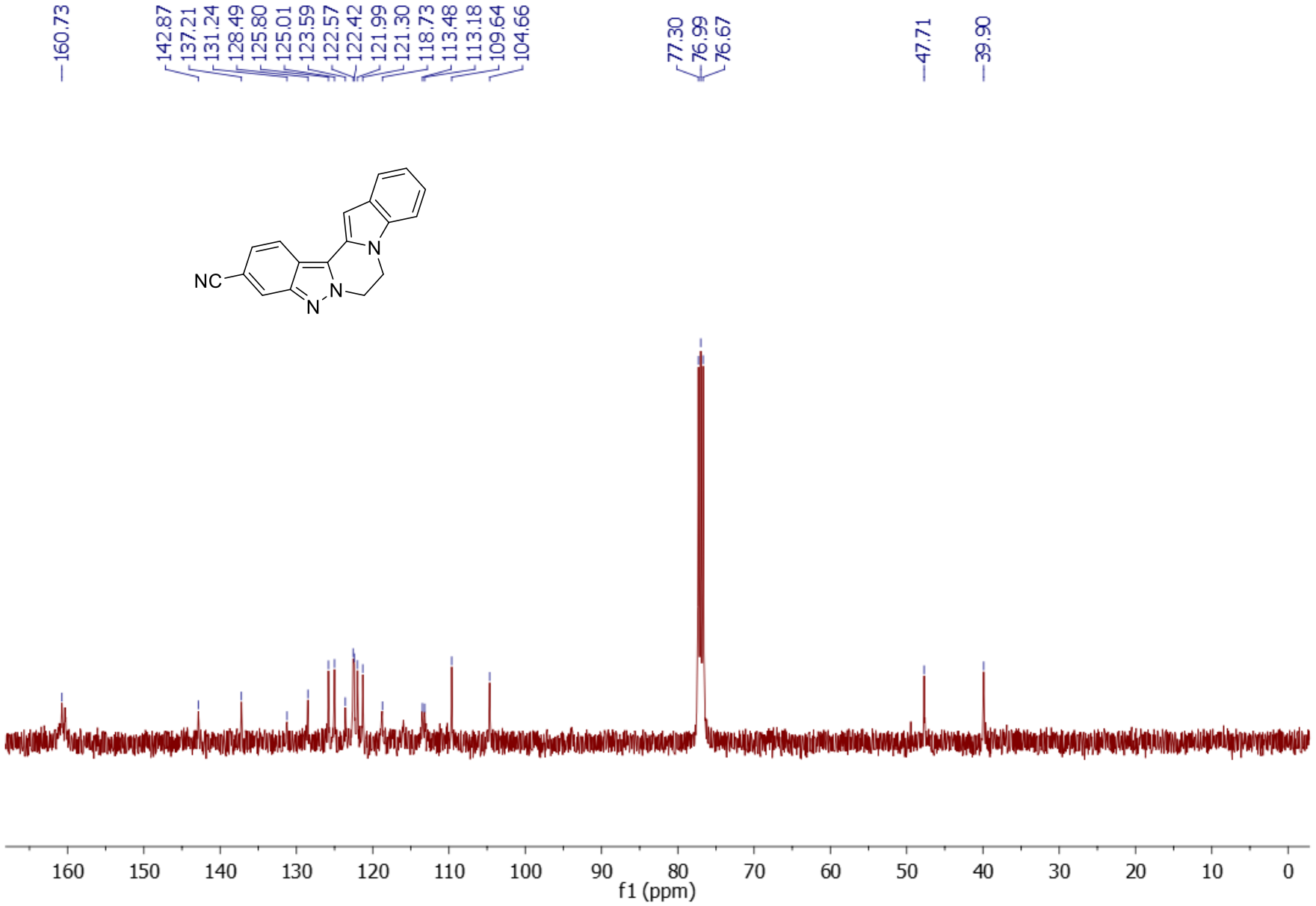
Compound 5ac



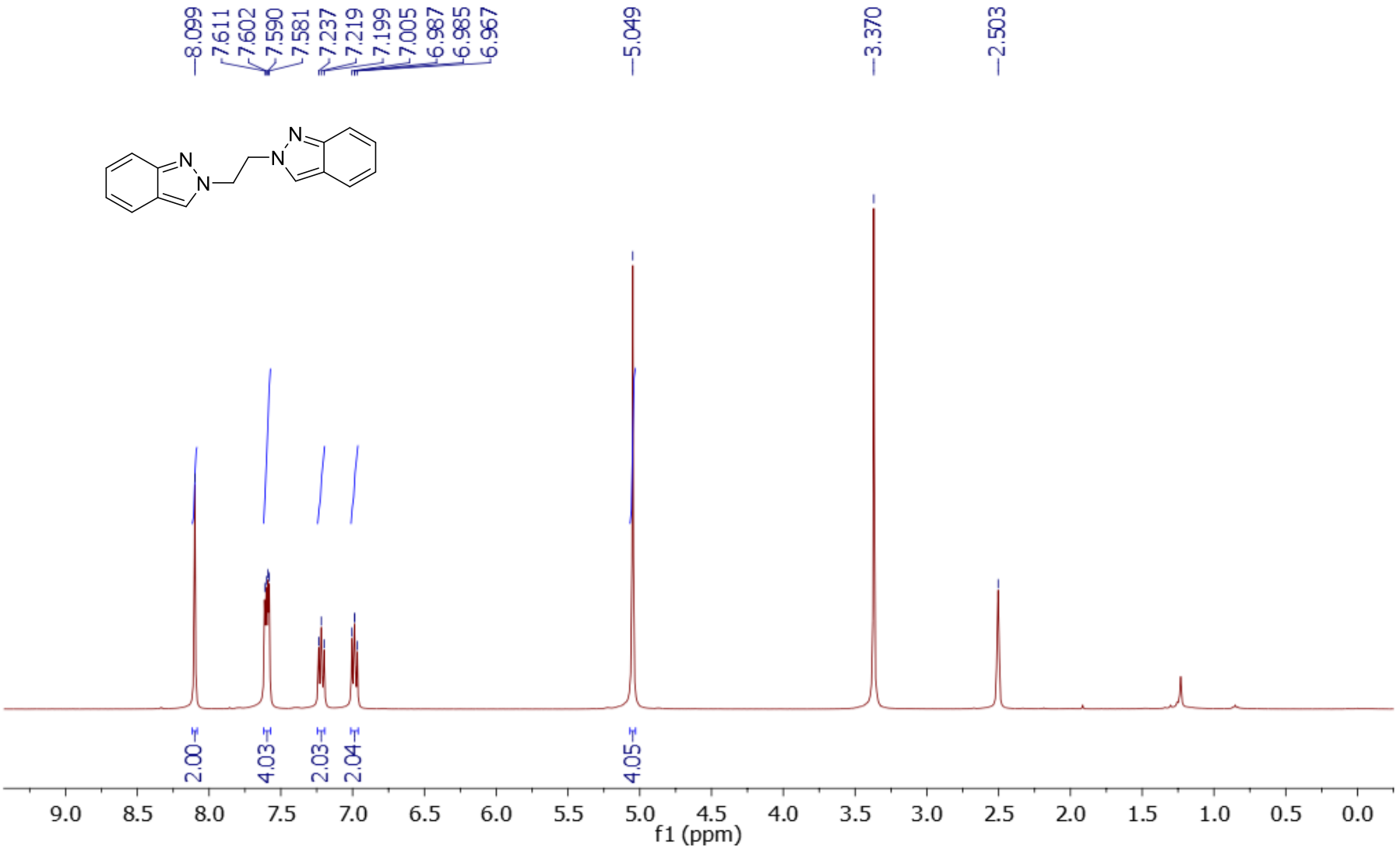

148.80
136.35
129.23
127.79
126.78
126.55
123.01
122.52
121.35
120.75
119.92
118.35
117.68
108.89
98.87
77.34
77.02
76.70
47.86
40.60
N
N
N
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)

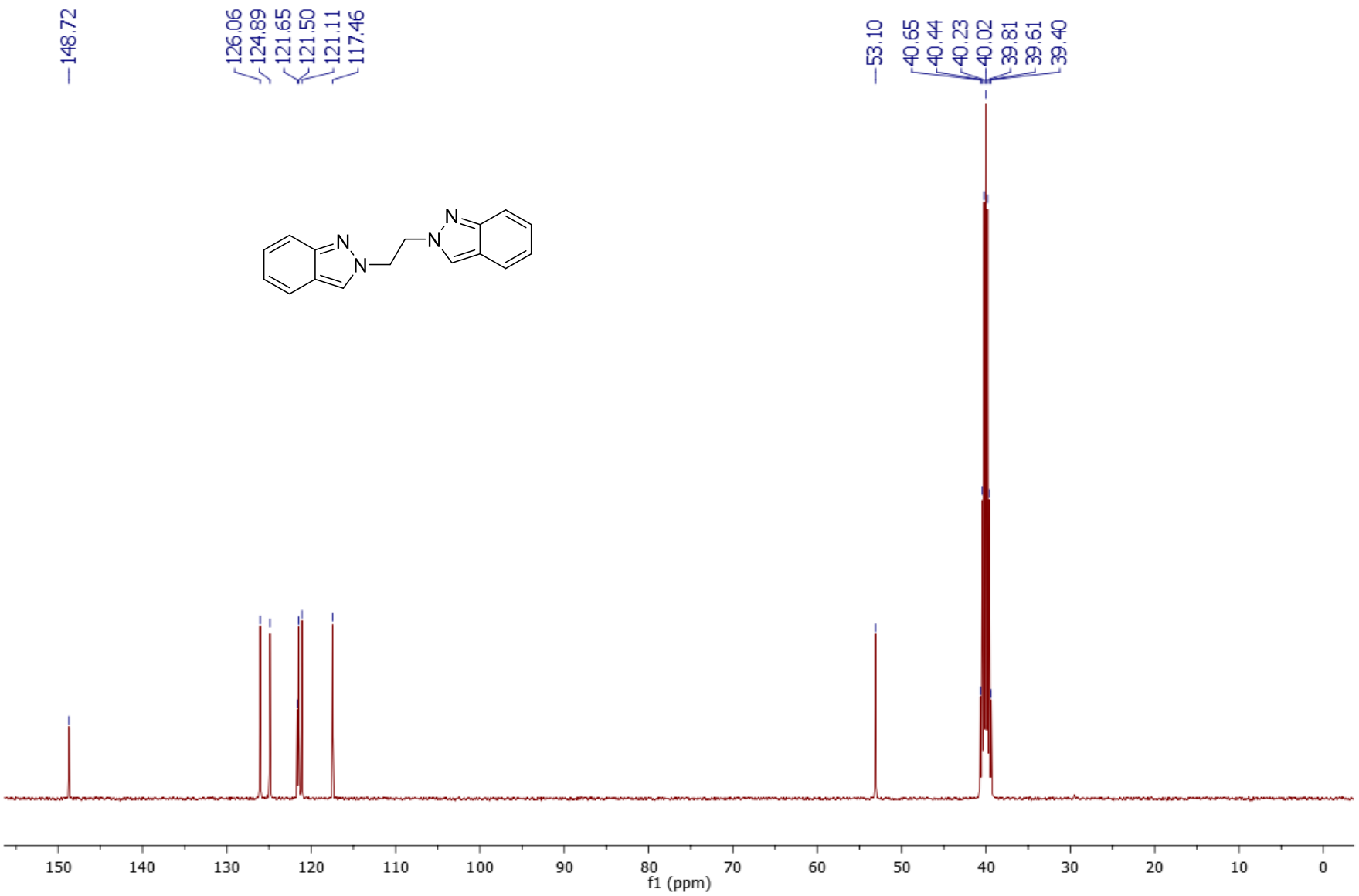
Compound 5fc



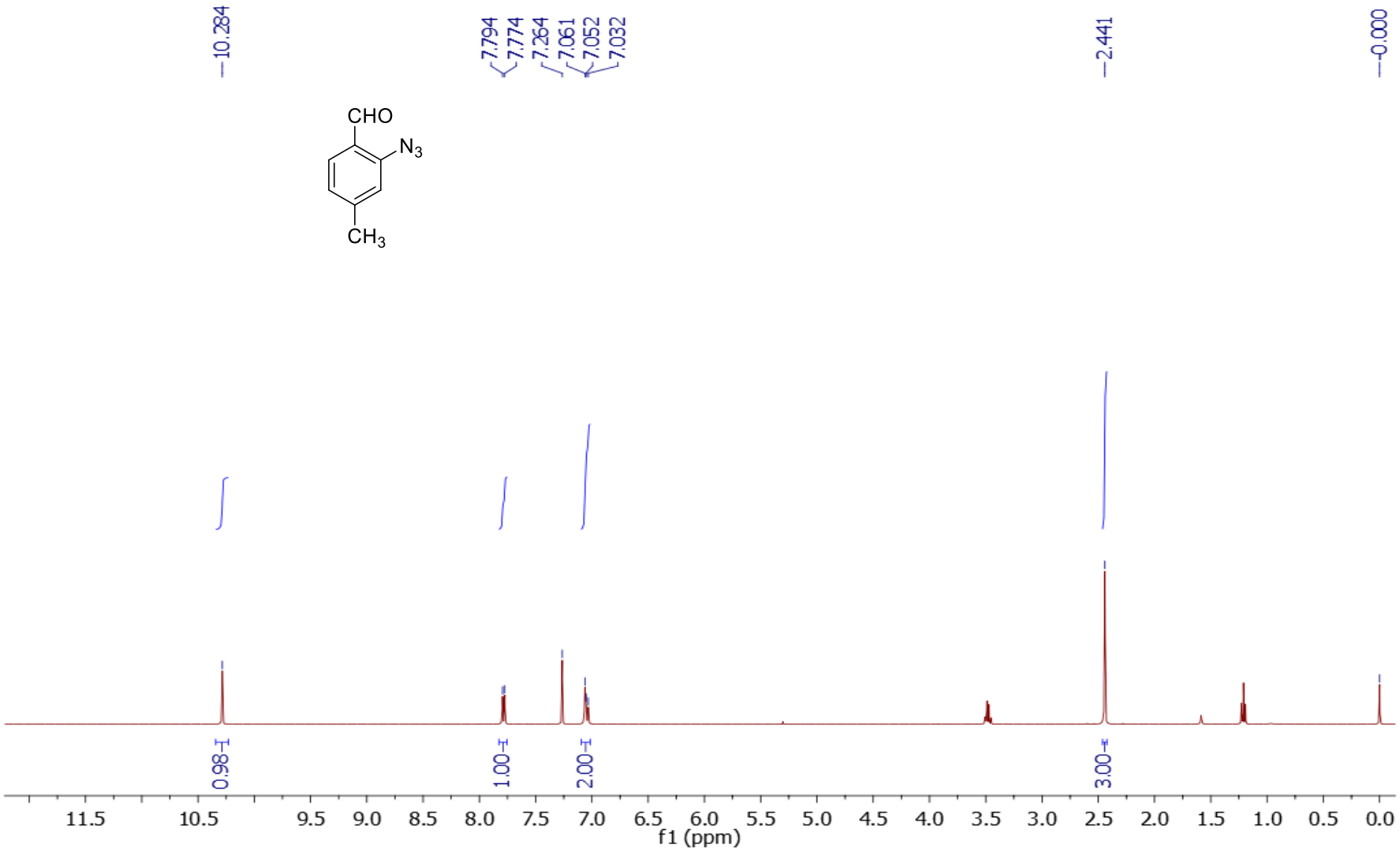

160.73
142.87
137.21
131.24
128.49
125.80
125.01
123.59
122.57
122.42
121.99
121.30
118.73
113.48
113.18
109.64
104.66
77.30
76.99
76.67
47.71
39.90
NC
N
N
N
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

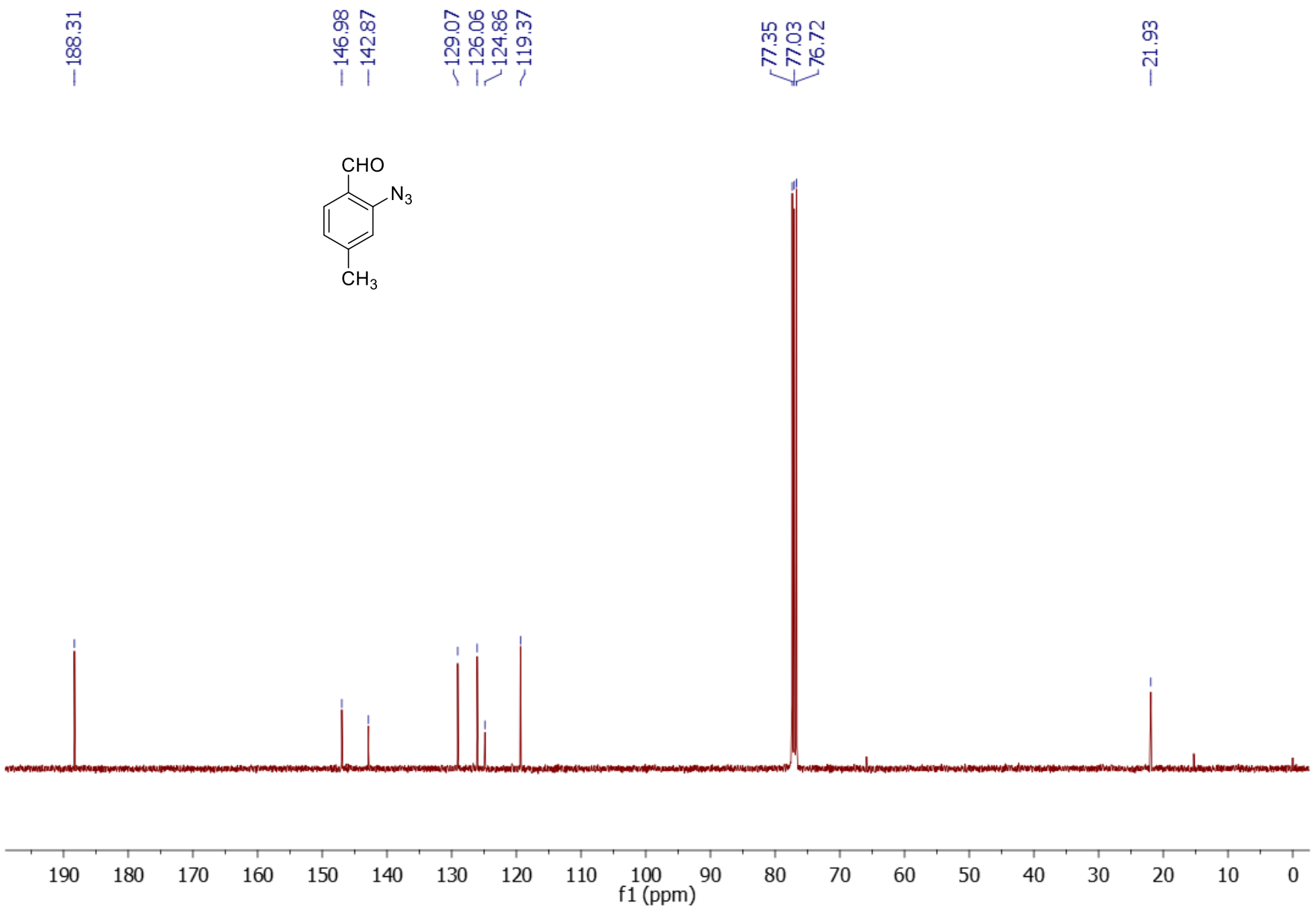
Compound 3aa′




148.72
126.06
124.89
121.65
121.50
121.11
117.46
53.10
40.65
40.44
40.23
40.02
39.81
39.61
39.40
N
N
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound 1d


10.284
7.794
7.774
7.264
7.061
7.052
7.032
2.441
0.000
CHO
N3
CH3
0.98
1.00
2.00
3.00
11.5
10.5
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)


188.31
146.98
142.87
129.07
126.06
124.86
119.37
77.35
77.03
76.72
21.93
CHO
N3
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)