Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Metal-free reduction of the greenhouse gas sulfur hexafluoride, formation of SF_5 containing ion pairs and the application in fluorinations

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General: Unless otherwise stated, all commercially available compounds were used as provided without further purification. Tetrakis-dimethylaminoethylene (TDAE) was purchased from Acros. Sulfur Hexafluoride (SF_6) was supplied by Solvay. The solvents used in reactions were of p.a. grade, dried and degassed by standard techniques.[1] Acetonitrile was distilled over P_4O_{10} and subsequently over CaH_2 under argon prior to use. The reactions were performed in a glovebox or by using standard Schlenk techniques. Solvents for chromatography were of technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator, visualized by irradiation with UV light or by basic potassium permanganate staining reagent. Column chromatography was performed using silica gel Merck 60 (particle size 0.063-0.2 mm). Solvent mixtures are understood as volume/volume. ^{1}H-, ^{13}C-, and ^{19}F NMR spectra were recorded on a Varian VNMR 400, VNMR 600 and Mercury 300 spectrometers in $CDCl_3$ CD_2Cl_2, C_6D_6, CD_3OD and DMSO-d_6. The NMR data are reported in the following order: chemical shift (δ) in ppm; multiplicity (denoted as follows: s – singlet, d – doublet, t – triplet, q – quartet, quint – quintet, sept – septet, m – multiplet) and the coupling constants (*J*) (given in Hertz (Hz)). The ^{19}F solid-state NMR measurements were performed using a Bruker DSX500 spectrometer working at a ^{19}F resonance frequency of 470.51 MHz. Most of the spectra were recorded at 30 °C using a 2.5 mm MAS probe-body and a spinning speed of 35 kHz by employing a one pulse sequence. The used pulse length was 7 µs, the dwell time 0.5 µs, and the recycle delay is 1 s or 2 s, depending on the sample. The position of the spinning sidebands was identified by comparison of spectra recorded at different spinning speeds. The use of other experimental conditions than these ones is stated in the text. The ^{19}F NMR spectrum of the probe-body was acquired using the same pulse sequence and experimental parameters and then subtracted from the experimental data. All spectra of solid state ^{19}F NMR were externally calibrated by the trifluoroethanol ^{19}F NMR chemical shift.

Mass spectra (ME-EI, 70 eV and MS-CI, Methane) were conducted on a Finnigan SSQ 7000 spectrometer. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer (The air-sensitive samples were recorded on a Bruker Alpha FT-IR spectrometer in the glove box using the platinum single reflection diamond ATR module) and are reported in cm^{-1}. The following abbreviations were used for the intensities of the IR absorption bands: (vs) − very strong, (s) − strong, (m) − medium, (w) − weak.

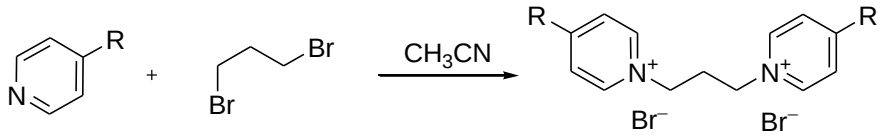
Electrochemical measurements were performed using the Metrohm Autolab all-in-one potentiostat PGSTAT 101 (Nova 1.10.1.9) electrochemical analyzer using a standard three-electrode 25 mL cyclic voltammetry cell equipped with a platinum working electrode (ø = 1 mm), platinum wire auxiliary electrode and a non-aqueous Ag/Ag^+ (0.1 M, n-Bu_4NClO_4 + 0.01 M

$AgNO_3$) system in acetonitrile as the reference electrode with the voltage scan rates from 50 to 100 mV/s. The 5 mM solutions of the investigated compounds were in the 0.1 M solution of [n-Bu_4N]ClO_4 (supporting electrolyte), which were thoroughly bubbled with dry argon for 15 minutes to remove any oxygen before experiment and kept under positive pressure of argon. Under these experimental conditions the ferrocene/ferricinium couple, used as internal standard for potential measurements,[6] was located at $E_{1/2}$ = + 0.086 V in acetonitrile.

Preparation of the starting materials

Potassium graphite (KC_8) was prepared according to a literature protocol.[2]

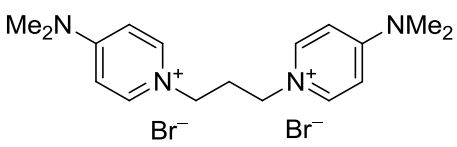
Experimental procedure for the synthesis of 1aa and 1 bb:



R = Me_2N (**1aa**); t-Bu (**1bb**)

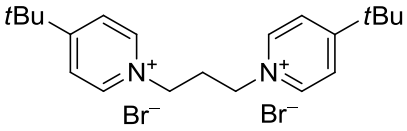
Into a thick-wall glass vessel equipped with a Teflon screw-cap and a stir bar, was loaded the corresponding 4-substituted pyridine (110 mmol. 1.1 equiv.), 50 mL of dry acetonitrile and 1,3-dibrompropane (50 mmol, 0.5 equiv.). The colorless clear reaction mixture was stirred at 120 °C for 12 h (*Caution*: the autogenous pressure occurs, open cap only after cooling to r.t.!). The completion of the reaction was checked by TLC (EtOAc:Hex, 1:4). The resulting slurry was poured into 200 mL of Et_2O, stirred for additional 30 min and filtered through a sintered glass filter. The white solid material was washed with Et_2O (20 mL×3) and dried under dynamic vacuum at 80 °C or 18 h.

1,1'-(propane-1,3-diyl)-bis(4-(dimethylamino)pyridin-1-ium) dibromide 1aa



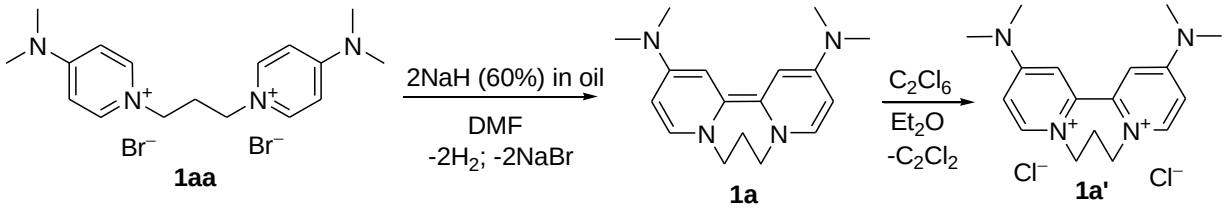
The compound was obtained as white crystals. Yield: 95%. Mp = 193-195 °C (199-203 °C lit.).[3] **^{1}H NMR** (400 MHz, CD_3OD) δ = 8.38 (d, *J* = 7.3 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 4H), 4.45 (t, *J* = 7.6 Hz, 4H), 3.4 (s, 12H), 2.59 (quint, *J* = 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ = 157.9 (s, 2C_{quat}), 143.1 (s, 4*C*H), 109.2 (s, 4*C*H), 55.5 (s, 2CH_2), 40.5 (s, 6CH_3), 32.9 (s, CH_2). **IR** (KBr, cm^{-1}) ν_{max} = 3401 (s), 3034 (m), 2312 (w), 2097 (w), 1895 (w), 1641 (s), 1559 (s), 1401 (s), 1178 (s), 1064 (s), 947 (s), 821 (s). **MS** (EI): m/z (%) 284 (40) $[M-2]^{2+}$ (M_{theor}^{2+} $2Br^-$ = 446.2). The analytical data are consistent with the previously published reports.[3]

1,1'-(propane-1,3-diyl)-bis(4-(dimethylamino)pyridin-1-ium) dibromide 1bb



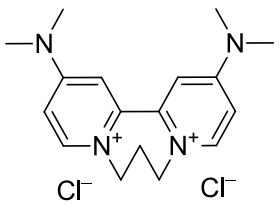
The compound was obtained as a white solid. Yield: 92%. **^{1}H NMR** (400 MHz, CD_3OD) δ = 9.04 (dd, *J* = 5.7, 3.5 Hz, 4H), 8.19 (d, *J* = 7.0 Hz, 4H), 4.95 – 4.74 (m, 4H), 2.91 – 2.73 (m, 2H), 1.46 (s, 18H). **^{13}C NMR** (101 MHz, CD_3OD) δ = 173.1 (s, 2C_{quat}), 145.5 (s, 4*C*H), 126.8 (s, 4*C*H), 58.3 (s, 2CH_2), 37.6 (s, *C*H_2), 33.5 (s, 2C_{quat}), 30.2 (s, 6*C*H_3). **IR** (KBr, cm^{-1}) ν_{max} = 3364 (s), 2961 (s), 2313 (w), 2062 (w), 1971 (w), 1740 (s), 1638(s), 1454 (s), 1368 (s), 1210 (s), 1114 (m), 845 (s). **MS** (EI): m/z 310 (1) $[M]^{2+}$, 176 (12) [M-(4-*t*BuPy)]$^{+}$, 135 (98) [4-*t*BuPy]$^{+}$ (M_{theor}^{2+} $2Br^{-}$ = 472.3).

Experimental procedure for the synthesis of *1a'*:



In a Schlenk tube (250 mL) equipped with a highly efficient stir bar was placed dried **1aa** salt (25 mmol) followed by NaH (60% in oil, 250 mmol) under argon. The mixture was cooled to −10 °C and DMF (75 mL) was added via cannula. The reaction mixture turned pink and hydrogen evolution was observed. The tube was warmed up to room temperature and stirred for additional 4 h. The resulting deep violet solution was transferred through a cannula to the solution of C_2Cl_6 in Et_2O (25 mmol in 100 mL of Et_2O). A fine precipitate was formed upon dilution with additional 200 mL of Et_2O and the product was filtered through a cannula under argon, washed with Et_2O (20 mL×2) and dried under dynamic vacuum. (The product is stable to oxygen but traps moisture from the air immediately). Residual NaH, NaHal and the e-donor were suspended in hexane and quenched with *i*PrOH.

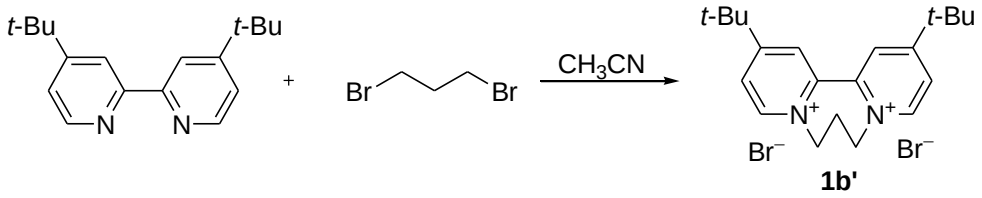
2,12-bis(dimethylamino)-7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine-5,9-diium iodide 1a'



The compound was obtained as brown crystals. Yield: 86%. Mp = 290-295 °C. **^{1}H NMR** (400 MHz, CD_3OD) δ = 8.37 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 3.1 Hz, 2H), 7.16 (dd, *J* = 7.6, 3.1 Hz, 2H), 4.64 – 4.50 (m, 2H), 4.18 – 3.99 (m, 2H), 3.44 (s, 6H), 3.36 (s, 6H), 2.63 – 2.50 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ = 158.5 (s, 2C_{quat}), 144.8 (s, 2C_{quat}), 144.6 (s, 2*C*H), 113.0 (s, 2*C*H), 109.5 (s, 2*C*H), 52.9 (s, 2CH_2), 41.2 (dd, *J* = 9.0, 4.2 Hz), 41.0 (dd, *J* = 8.0, 3.5 Hz), 30.3 (s,

CH_2). **IR** (solid, cm^{-1}) ν_{max} = 3021 (w), 2975 (w), 2948 (w), 1636 (s), 1573 (s), 1530 (m), 1510 (w), 1428 (m), 1406 (m), 1373 (m), 1346 (w), 1322 (m), 1262 (m), 1234 (w), 1224 (w), 1199 (w), 1181 (m), 1172 (m), 1123 (m), 1081 (m), 1053 (m), 1030 (m), 999 (w), 894 (m), 853 (m), 833 (m), 810 (m), 783 (m), 657 (w), 530 (w), 469 (w). **MS** (EI): m/z (%) 284 (72) $[M]^{2+}$ (M_{theor}^{2+} $2Cl^-$ = 355.3). The analytical data are consistent with the previously published reports.[4]

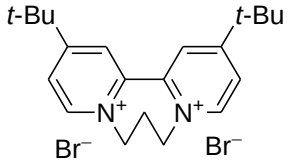
Experimental procedure for the synthesis of *1b'*:



1b'

Into a thick-wall vessel equipped with a Teflon screw-cap and a stir bar was loaded 2,2'-(di-*tert*-butyl)bipyridine (50 mmol. 1.0 equiv.), 50 mL of dry acetonitrile and 1,3-dibromopropane (55 mmol, 1.1 equiv.). The reaction mixture was stirred at 120 °C for 12 h. (*Caution*: the autogenous pressure occurs, open cap only after cooling to r.t.!). The completion of reaction was checked by TLC (EtOAc:Hex, 1:4). The resulting slurry was poured into 200 mL of Et_2O, stirred for additional 30 min and filtered through a sintered glass filter. The obtained yellow solid was washed with Et_2O (20 mL×3) and dried under dynamic vacuum at 80 °C for 18 h.

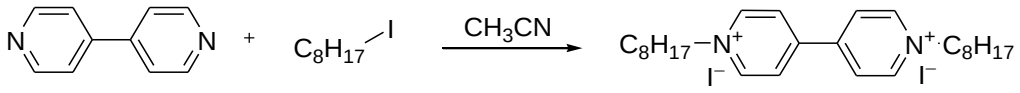
2,12-di-tert-butyl-7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine-5,9-diium dibromide 1b'



1b'

Yield: 89%. Mp > 300 °C (decomp). **^{1}H NMR** (400 MHz, CD_3OD) δ = 9.22 (d, *J* = 6.5 Hz, 2H), 8.62 (d, *J* = 2.2 Hz, 2H), 8.45 (dd, *J* = 6.5, 2.2 Hz, 2H), 5.11 – 4.98 (m, 2H), 4.65 – 4.42 (m, 2H), 2.92 (ddd, *J* = 9.0, 7.1, 3.8 Hz, 2H), 1.56 (s, 18H). **^{13}C NMR** (101 MHz, CD_3OD) δ = 175.0 (s, 2C_{quat}), 147.9 (s, 2*C*H), 145.1 (s, 2C_{quat}), 130.9 (s, 2*C*H), 129.1 (s, 2*C*H), 56.4 (s, CH_2), 38.4 (s, CH_2), 31.5 (s, 2C_{quat}), 30.2 (s, 6CH_3). **IR** (solid, cm^{-1}) ν_{max} = 3022(w), 2960 (s), 2874 (w), 1623 (s), 1571 (w), 1558 (m), 1512 (m), 1486 (w), 1465 (m), 1437 (s), 1418 (w), 1400 (w), 1375 (m), 1358 (m), 1341 (m), 1302 (m), 1253 (m), 1208 (m), 1182 (m), 1144 (m), 1116 (m), 1103 (s), 1091 (s), 1035 (m), 992 (m), 935 (m), 909 (m), 873 (m), 864 (s), 854 (m), 854 (w), 828 (w), 777(w), 745 (m), 683 (m), 612 (s), 531 (s), 529 (w), 518 (m), 495 (m), 480 (m), 464 (s), 430(m). **MS** (EI): m/z (%) 310 (6) $[M]^{2+}$, 253 (10) $[M\text{-}t\text{Bu}]^{2+}$ (M_{theor}^{2+} $2Br^-$ = 470.3).

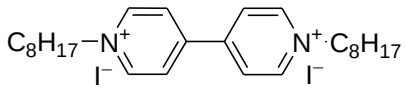
Experimental procedure for synthesis of (VC8^{2+} 2I^{-}) *1c'*:



1c'

Into a thick-wall glass vessel equipped with a Teflon screw-cap and a stir bar were loaded 4,4'-bipyridine (50 mmol. 1.0 equiv.), 50 mL of dry acetonitrile and 1-iodooctane (110 mmol, 2.05 equiv.). The orange reaction mixture was stirred at 120 °C for 12 h. (*Caution*: the autogenous pressure occurs, open cap only after cooling to r.t.!). The completion of reaction was checked by TLC (EtOAc:Hex, 1:4). The resulting slurry was poured into 200 mL of Et_2O, stirred for additional 30 min and filtered through a sintered glass filter. The obtained deep orange solid was washed with Et_2O (20 mL×3) and dried under dynamic vacuum at 80 °C for 18 h.

1,1'-dioctyl-[4,4'-bipyridine]-1,1'-diium iodide (VC8^{2+} 2I) 1c'

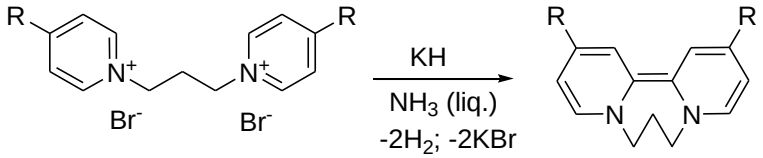


1c'

Yield: 85%. Mp = 288-290 °C (dec.). **^{1}H NMR** (600 MHz, CD_3OD) δ = 9.34 (d, *J* = 6.8 Hz, 4H), 8.73 (d, *J* = 6.6 Hz, 4H), 4.88 – 4.74 (m, 4H), 2.18 – 2.06 (m, 4H), 1.52 – 1.39 (m, 8H), 1.39 – 1.25 (m, 12H), 0.90 (t, *J* = 6.9 Hz, 6H). **^{13}C NMR** (151 MHz, CD_3OD) δ = 149.8 (s, 2C_{quat}), 145.7 (s, 4*C*H), 127.1 (s, 4*C*H), 61.9 (s, 2CH_2), 31.5 (s, 2CH_2), 31.2 (s, 2CH_2), 28.8 (s, 2CH_2), 28.7 (s, 2CH_2), 25.8 (s, 2CH_2), 22.3 (s, 2CH_2), 13.1 (s, 2CH_3). **IR** (KBr, cm^{-1}) ν_{max} = 3380 (s), 3026 (s), 2924 (s), 2308 (w), 2088 (w), 1920 (w), 1638 (s), 1558 (s), 1441 (s), 1178 (s), 1062 (s), 956 (m), 820 (s), 727 (m). **MS** (ESI): m/z (%) 383 (23) $[M+1]^{2+}$ (M_{theor}^{2+} 2I^{-} = 636.4).

General procedures for synthesis of e-donors 1a-c:

General procedure A:

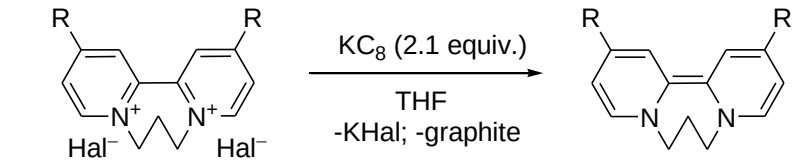


R = Me_2N (**1aa**), *t*Bu (**1bb**) R = Me_2N (**1a**), *t*Bu (**1b**)

In a glovebox, a mixture of **1aa** or **1bb** (20 mmol, 1 equiv.) and KH (~95%, washed 3 times with hexane, 100 mmol, 5 equiv.) was placed in a Schlenk-flask. The reaction vessel was taken outside and equipped with a dry-ice condenser and an oil bubbler under argon up-flow. Under stirring, the argon was substituted with ammonia until ca. 100 mL of the liquid condensed. The purple

reaction mixture was left at reflux for 3 h and then was allowed to evaporate overnight at ambient temperature. The solid was extracted with dry and degassed toluene, and the extract was filtered. The solvent was removed *in vacuo* to afford **1a** (**1b**) as a deep-purple highly moisture and oxygen sensitive solid which can be further purified by crystallization from toluene (**1a**) or hexane (**1b**).

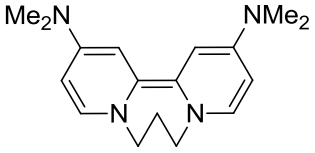
General procedure B:



R = Me_2N (**1a'**), *t*Bu (**1b'**) R = Me_2N (**1a**), *t*Bu (**1b**)

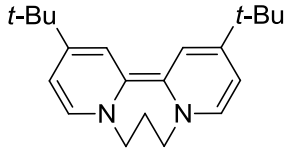
In a glovebox, a vial equipped with a stir bar was loaded with **1a'** or **1b'** (2 mmol, 1 equiv.), potassium graphite (KC_8) (0.57 g, 4.2 mmol) and cooled to −20 °C. THF (20 mL) was added in a single portion. The color of the mixture turned immediately from yellow to purple-black and the golden-brown color of KC_8 disappeared. The reaction mixture was stirred for 1h. Inorganic products were filtered off and the solvent was removed *in vacuo* to afford the pure **1a** (**1b**) as a dark, deep colored, moisture and highly oxygen sensitive solid which can be further purified by crystallization from toluene (**1a**) or hexane (**1b**). This method provides ca. 95% pure products.

N^1,N^1,N^{12},N^{12}-tetramethyl-7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine-2,12-diamine 1a



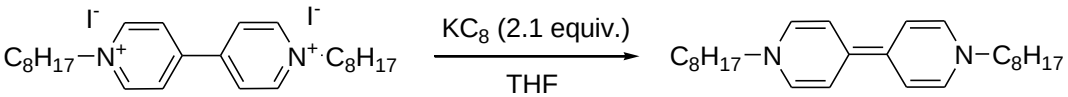
The compound was obtained according to *General Procedure A* as a black-purple microcrystalline solid. Mp = 128-131 °C. Yield: 67%. **^{1}H NMR** (600 MHz, C_6D_6) δ = 5.63 (d, *J* = 7.5 Hz, 2H), 5.17 (d, *J* = 2.0 Hz, 2H), 4.92 (dd, *J* = 7.5, 2.4 Hz, 2H), 3.01 (t, *J* = 6.2 Hz, 4H), 2.46 (s, 12H), 0.97 (quint, *J* = 6.1 Hz, 2H). **^{13}C NMR** (151 MHz, C_6D_6) δ = 143.4 (s, 2C_{quat}), 138.3 (s, 2*C*H), 115.7 (s, 2C_{quat}), 95.9 (s, 2*C*H), 95.5 (s. 2*C*H), 52.2 (s, 2CH_2), 40.4 (s, 6CH_3), 24.1 (s, CH_2). **IR** (solid, cm^{-1}) ν_{max} = 2940 (w), 2914 (w), 2856 (w), 2818 (w), 2761 (w), 1632(s), 1620 (s), 1579 (w), 1555 (s), 1531 (w), 1471 (w), 1442 9s), 1360 (s), 1339 (s), 1319 (s), 1262 (w), 1240 (m), 1208 (m), 1192 (m), 1166 (w), 1130 (s), 1096 (m), 1084 (w), 1060 (s), 999 (m), 980 (m), 957 (m), 935 (s), 909 (m), 814 (m), 786 (s), 766 (s), 745 (m), 728 (m), 707 (w), 690 (s), 658 (m), 644 (w), 502 (m), 486 (s) 425 (s). The analytical data are consistent with the previously published report.[3b]

2,12-di-tert-butyl-7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine 1b



The compound was obtained according to *General Procedure B* on a 8 mmol scale as a black-purple microcrystalline solid. Mp = 118-120 °C. Yield: 88%. **^{1}H NMR** (600 MHz, C_6D_6) δ = 6.16 (d, *J* = 1.8 Hz, 2H), 5.54 (d, *J* = 7.4 Hz, 2H), 4.95 (dd, *J* = 7.4, 2.0 Hz, 2H), 2.92 (t, *J* = 6.3 Hz, 4H), 1.10 (s, 18H), 0.84 (quint, *J* = 6.3 Hz, 2H). **^{13}C NMR** (151 MHz, C_6D_6) δ = 139.8 (s, 2C_{quat}), 137.0 (s, 2*C*H), 118.6 (s, 2C_{quat}), 113.6 (s, 2*C*H), 100.1 (s, 2*C*H), 51.7 (s, 2CH_2), 33.7 (s, 2C_{quat}), 29.2 (s, 6CH_3), 22.01 (s, *C*H_2). **IR** (solid, cm^{-1}) ν_{max} = 2946 (s), 2900 (w), 2861 (m), 1617 (s), 1561 (m), 1472 (w), 1458 (m), 1432 (s), 1389 (w), 1373 (s), 1352 (s), 1329 (s), 1259 (s), 1242 (s), 1202 (s), 1185 (s), 1163 (s), 1123 (s), 1108 (w), 1060 (s), 1022 (w), 933 (w), 979 (w), 904 (w), 841 (s), 806 (s), 725 (s), 684 (w), 668 (s), 646 (w), 530 (w), 502 (m), 418 (s).

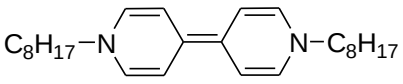
Experimental procedure for synthesis of neutral dioctyl viologen (VC_8) 1c:



1c' **1c**

In a glovebox, to a vial equipped with a stir bar were added **1c'** (2 mmol), potassium graphite (KC_8) (0.57 g, 4.2 mmol) and dry, degassed, precooled to −20 °C THF (20 mL). The color of the mixture turned from dark orange to yellow and the golden-brown color of KC_8 disappeared. The reaction mixture was stirred for 18 h. Inorganic products were filtered off and the solvent was removed *in vacuo* to afford pure 1,1'-dioctyl-1H,1'H-4,4'-bipyridinylidene (92 %) as a deep red, moisture and highly oxygen sensitive solid.

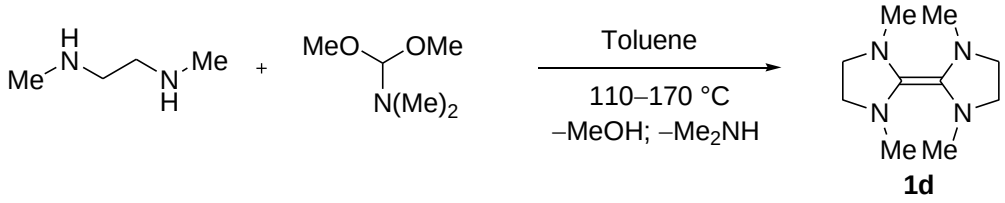
1,1'-dioctyl-1H,1'H-4,4'-bipyridinylidene 1c'



1c

Mp = 48-50 °C. **^{1}H NMR** (600 MHz, C_6D_6) δ = 5.57 (d, *J* = 8.0 Hz, 4H), 5.48 (d, *J* = 8.0 Hz, 4H), 2.52 (t, *J* = 7.0 Hz, 4H), 1.32 – 1.25 (m, 4H), 1.24 – 1.15 (m, 12H), 1.15 – 1.06 (m, 8H), 0.91 (t, J = 7.2 Hz, 6H). **^{13}C NMR** (151 MHz, C_6D_6) δ = 128.9 (s, 4CH), 109.2 (s, 2C_{quat}), 107.9 (s, 4*C*H), 53.6 (s, 2CH_2), 32.3 (s, 2CH_2), 30.3 (s, 2CH_2), 29.7 (s, 2CH_2), 29.7 (s, 2CH_2), 26.9 (s, 2CH_2), 23.1 (s, 2CH_2), 14.4 (s, 2CH_3). **IR** (C_6H_{14}, cm^{-1}) ν_{max} = 3424 (w), 3055(w), 2923 (s), 2325 (w), 2096 (w), 1915 (w), 1809 (w), 1638 (s), 1363 (s), 1179 (s), 1001 (s), 732 (s).

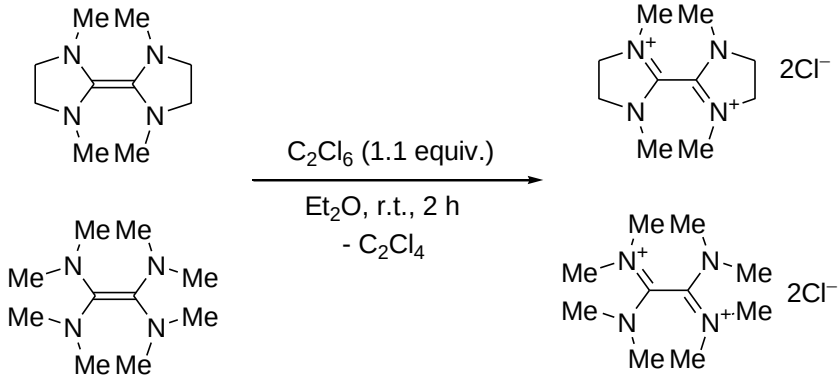
Experimental procedure for synthesis of 1,1',3,3'-tetramethyl-1,1',3,3',4,4',5,5'-octahydro-2,2'-biimidazolylidene 1d:



1d

Into a Schlenk-tube equipped with a stir bar under argon was added, dry degassed toluene (10 mL), *N*,*N*'-dimethyl-ethylenediamine (6.39 mL, 1 equiv., 59.4 mmol) and DMF-DMA (10 mL, 1.28 equiv., 76 mmol). The reaction mixture was stirred at r.t for 1 h and then with up-flow of argon a Liebig condenser with an oil bubbler was placed on the top. The Schlenk tube was heated to 110 °C under very slow argon flow. During the distillation of dimethylamine and MeOH the temperature of the oil-bath was gradually increased to 170 °C until toluene (110 °C by thermometer *on-top*) started to distill off. After the distillation of toluene ceased, the system was cooled under positive pressure of argon and the condenser was removed. The residual toluene was removed *in vacuo* at r.t.; the product solidified to give white solid. The compound was stored in the glovebox. Yield: 65%. Mp = 20-22 °C. ^{1}H NMR (400 MHz, C_6D_6) δ = 2.76 (s, 8H), 2.61 (s, 12H). **^{13}C NMR** (101 MHz, C_6D_6) δ = 129.6 (s, C_{quat}), 52.7 (s, 2CH_2), 40.3 (s, 4CH_3). The analytical data are consistent with the previously published report.[5]

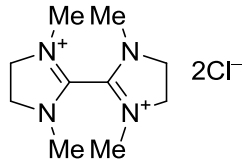
Experimental procedure for the synthesis of 1,1',3,3'-tetramethyl-1,1',3,3',4,4',5,5'-octahydro-2,2'-biimidazolyliden-dium dichloride 1d' and octamethylethene-1,1,2,2-tetraaminium dichloride 1e':



In a glovebox a solution of the electron donor in Et_2O (1 mmol in 4 mL) was prepared. To that a solution of C_2Cl_6 in Et_2O (1 mmol in 4 mL) was added and the mixture was stirred for 2 h. A fine microcrystalline precipitate formed and was filtered through a glass-filter, washed with Et_2O

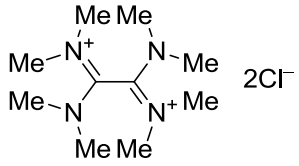
(5 mL×2) and dried under dynamic vacuum. (The products trap moisture from the air immediately but are oxygen stable).

1,1',3,3'-tetramethyl-1,1',3,3',4,4',5,5'-octahydro-2,2'-biimidazolyliden-dium dichloride 1d'



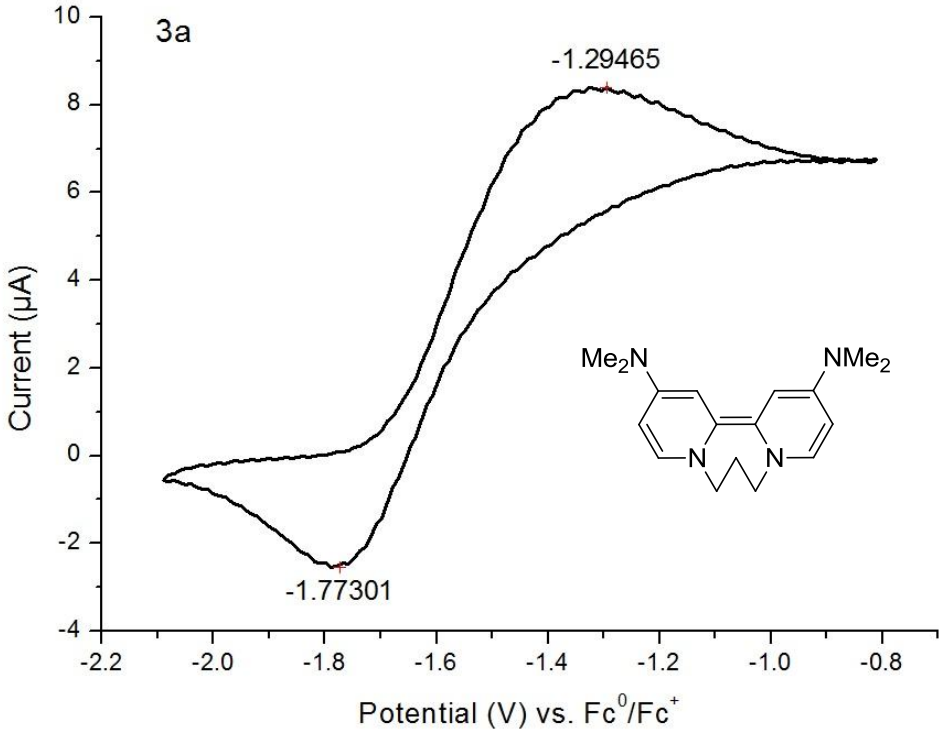
The compound was obtained as white crystals. Yield: 91%. Mp =210-212 °C. **^{1}H NMR** (600 MHz, CD_3OD) δ = 4.31 (s, 8H), 3.33 (s, 12H). **^{13}C NMR** (151 MHz, CD_3OD) δ = 150.9 (s, 2C_{quat}), 53.5 (s, 4CH_2), 35.2 (d, $J^1_{(N\text{-}C)}$ = 4.6 Hz, 4CH_3). **IR** (solid, cm^{-1}) ν_{max} = 2971 (m), 1638 (vs), 1543 (w), 1447 (m), 1417 (m), 1288 (s), 1217 (m), 1134 (w), 1104 (m), 897 (m), 876 (w), 713 (m), 694 (m), 604 (w). **MS** (EI): m/z (%) 167 (40) $[M-2CH_3]^{2+}$ (M_{theor}^{2+} $2Cl^-$ = 267.2).

Octamethylethene-1,1,2,2-tetraaminium dichloride 1e'

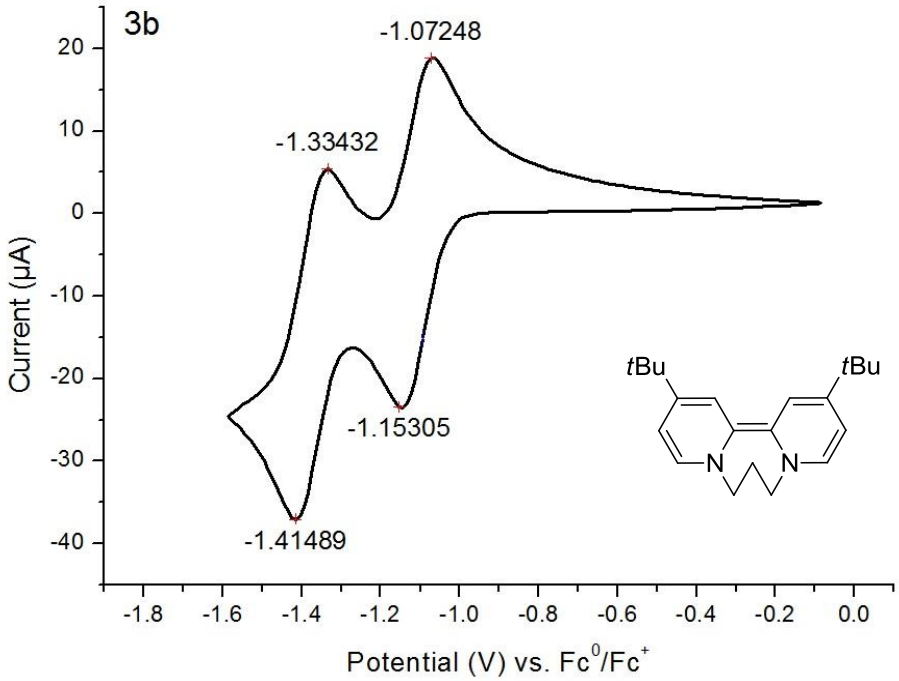


The compound was obtained as white crystals. Yield: 87%. Mp =250-252 °C. **^{1}H NMR** (600 MHz, CD_3OD) δ = 3.61 (s, 12H), 3.33 (s, 12H). **^{13}C NMR** (151 MHz, CD_3OD) δ = 157.3 (s, 2C_{quat}), 44.07 (d, $J^1_{(N\text{-}C)}$ = 4.7 Hz, 2CH_3), 43.3 (d, $J^1_{(N\text{-}C)}$ = 3.6 Hz, 2CH_3). **IR** (solid, cm^{-1}) ν_{max} = 2989 (w), 1670 (vs), 1520 (w), 1474 (w), 1403 (s), 1263 (m), 1212 (m), 1191 (m), 1150 (w), 1108 (w), 1069 (w), 890 (m), 874 (s), 772 (vs), 729 (w), 710 (w), 683 (s), 653 (m). **MS** (EI): m/z (%)170 (100) $[M\text{-}2CH_3]^{2+}$, 185 (50) $[M\text{-}CH_3]^{2+}$, 200 (64) $[M]^{2+}$ (M_{theor}^{2+} $2Cl^-$ = 271.2). The analytical data are consistent with the previously published report.[7]

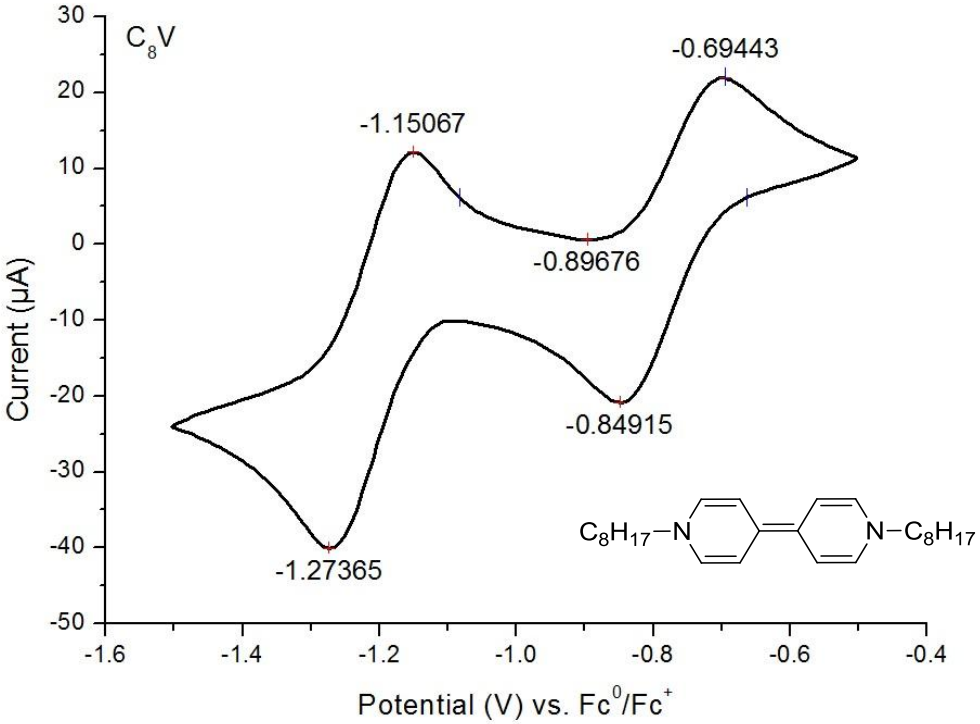
Cyclic voltammograms of the e-donors:



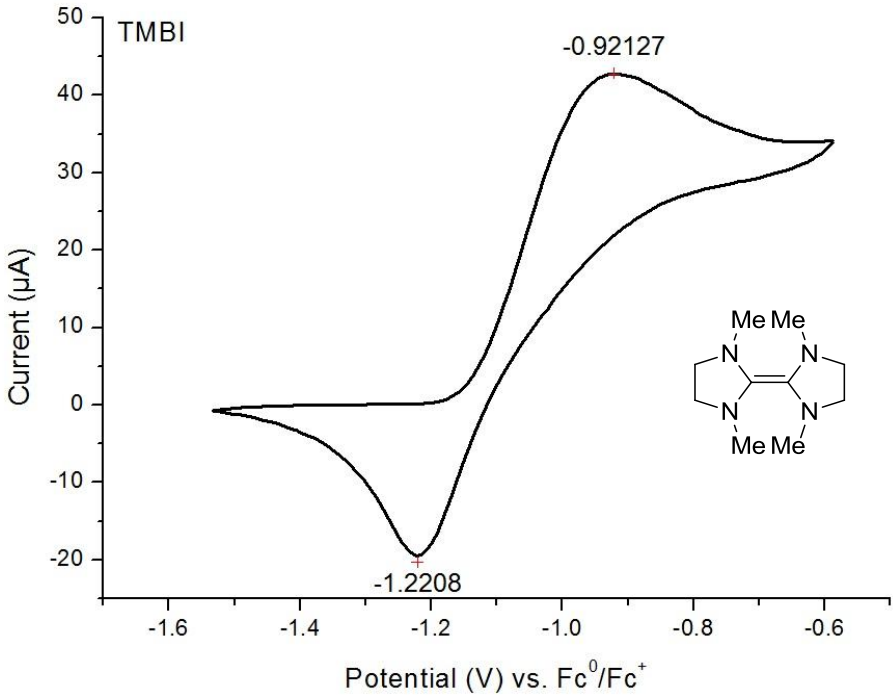
$E_{1/2}$ = −1.53 V vs $Cp_2Fe^{+/0}$ (**$E_{1/2}$ = −1.13 V vs SCE**)



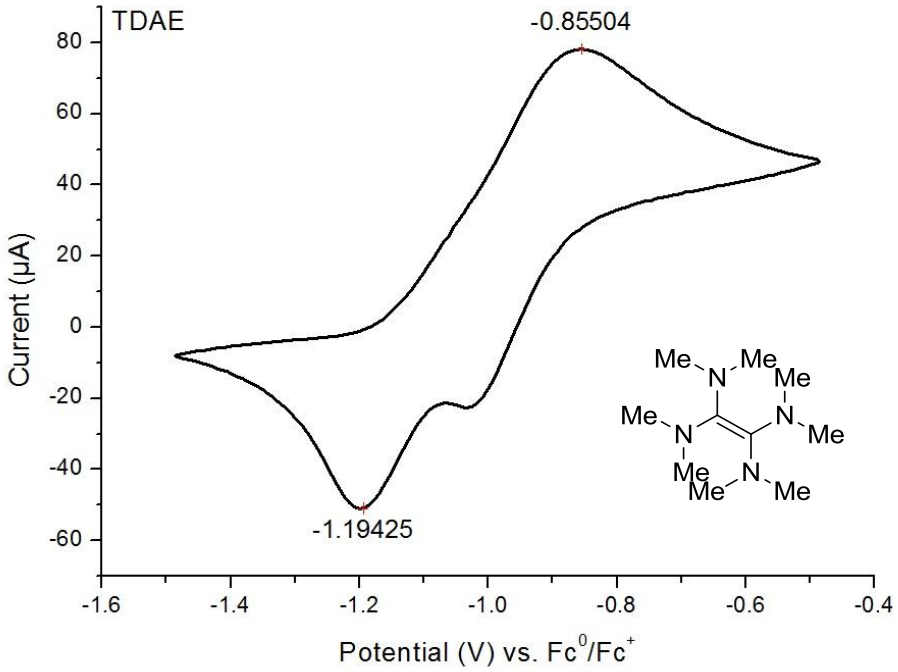
$E^1_{1/2}$ = −1.37 V vs $Cp_2Fe^{+/0}$ (**$E^1_{1/2}$ = −0.97 V vs SCE**)
$E^2_{1/2}$ = −1.11 V vs $Cp_2Fe^{+/0}$ (**$E^2_{1/2}$ = −0.71 V vs SCE**)



$E^1_{1/2}$ = −1.21 V vs $Cp_2Fe^{+/0}$ (**$E^1_{1/2}$ = −0.81 V vs SCE**)
$E^2_{1/2}$ = −0.77 V vs $Cp_2Fe^{+/0}$ (**$E^2_{1/2}$ = −0.37 V vs SCE**)

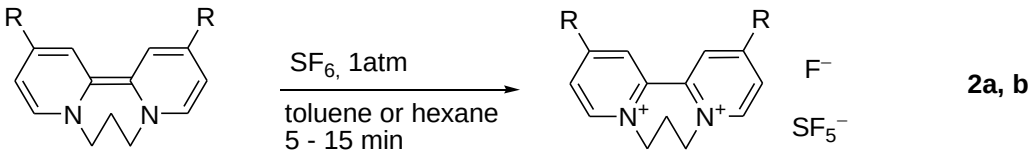


$E_{1/2}$ = −1.07 V vs $Cp_2Fe^{+/0}$ (**$E_{1/2}$ = −0.67 V vs SCE**)



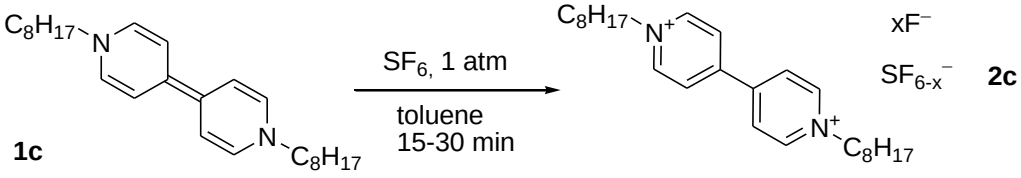
$E_{1/2}$ = −1.02 V vs $Cp_2Fe^{+/0}$ (**$E_{1/2}$ = −0.62 V vs SCE**)

General experimental procedure for the reaction of super e-donors with SF_6:

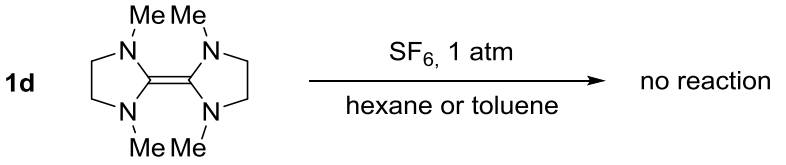


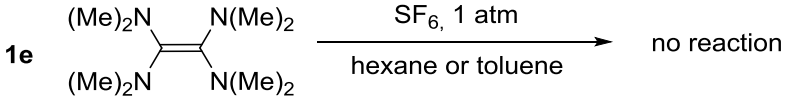
2a, b

R = Me_2N (**1a**), *t*Bu (**1b**)



1c **2c**





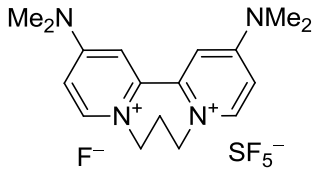
Analytical scale (NMR-experiment)

In a J. Young NMR-tube was placed an e-donor **1a-1e** followed by addition of C_6D_6. The tube was removed from the glovebox and ^{1}H- and ^{13}C NMR spectra were recorded. Subsequently the tube was opened and argon was replaced by SF_6 within 1 minute. The NMR tube was quickly closed and vigorously shaken. After several minutes the color changed and a precipitate formation was observed. The consumption of e-donor was confirmed by ^{1}H- and ^{13}C NMR spectroscopy, no signals except for SF_6 were detected in the ^{19}F NMR spectra. The reaction with TMBI **1d** and TDAE **1e** did not provide the desired product.

Preparative scale

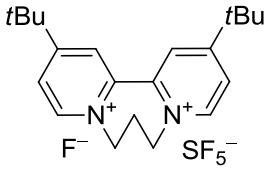
In a Schlenk tube (25 mL) equipped with a stir bar the e-donor (1 mmol) was added and the appropriate dry degassed solvent (10 mL) – toluene (for TDAE – hexane, see below). After the solution was formed, the tube was removed from the glovebox, the cap was substituted with a rubber septum and SF_6 was introduced via balloon. The reaction took place within minutes. Nevertheless, the stirring was kept overnight. The solvent was filtered off via cannula and the residue was dried *in vacuo* at r.t. for 10 min. The product was transferred to the glovebox and stored at −30 °C.

2,12-bis-(dimethylamino)-7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine-5,9-diium fluoride pentafluorosulfide 2a



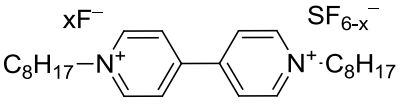
Compound **2a** was obtained as a brown microcrystalline powder. Mp = 146-148 °C (decomp). In a scale up experiment, from 0.6 g of the starting material 0.78 g of the product was obtained. **^{1}H NMR** (400 MHz, CD_3OD) δ = 8.31 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 3.1 Hz, 2H), 7.17 (dd, *J* = 7.6, 3.1 Hz, 2H), 4.61 – 4.42 (m, 2H), 4.06 (ddd, *J* = 14.7, 9.8, 8.3 Hz, 2H), 3.40 (s, 6H), 3.36 (s, 6H), 2.59 – 2.45 (m, 2H). **^{13}C NMR** (101 MHz, CD_3OD) δ = 158.5 (s, 2C_{quat}), 145.0 (s, 2C_{quat}), 144.6 (s, 2*C*H), 112.4 (s, 2*C*H), 109.5 (s, 2*C*H), 52.8 (s, 2CH_2), 40.81 (s, 2CH_3), 40.73 (s, 2CH_3), 30.29 (s, CH_2). **^{19}F NMR** (376 MHz, CD3OD) δ = −165.2 (s, F^-), -276.0 (sept, $J^2_{(D-F)}$ = 7.1 Hz, CD_3F from the reaction with CD_3OD). **IR** (solid, cm^{-1}) ν_{max} = 2931 (w), 1917 (w), 1714 (w), 1640 (m), 1534 (w), 1486 (m), 1445 (w), 1402 (w), 1363 (m), 1334 (w), 1262 (m), 1242 (m), 1216 (w), 1199 (w), 1181 (m), 1150 (m), 1121 (m), 1070 (m), 1059 (m), 1030 (m), 999 (w), 968 (w), 928 (w), 889 (m), 873 (m), 859 (w), 834 (m), 783 (s, SF_5^-), 738 (m), 698 (w), 655 (w), 575 (vs, SF_5^-), 516 (w), 465 (s, SF_5^-). **MS** (EI): m/z (%) 284 (100) $[M]^+$ (M_{theor}^{2+} F^-/ SF_5^-= 430.5).

2,12-di-tert-butyl-7,8-dihydro-6H-dipyrido[1,2-a:2',1'-c][1,4]diazepine-5,9-diium fluoride pentafluorosulfide 2b



Compound **2b** was obtained as brown-grey microcrystalline powder. In a scale up experiment, from 2.74 g of the starting material 3.35 g of the product was obtained. Mp = 116-118 °C (decomp). **^{1}H NMR** (600 MHz, CD_3OD) δ = 9.17 (d, *J* = 6.5 Hz, 2H), 8.54 (d, *J* = 2.2 Hz, 2H), 8.47 (dd, *J* = 6.5, 2.2 Hz, 2H), 5.05 – 4.96 (m, 2H), 4.46 (ddd, *J* = 14.4, 9.7, 8.8 Hz, 2H), 2.92 – 2.82 (m, 2H), 1.56 (s, 18H). **^{13}C NMR** (151 MHz, CD_3OD) δ = 175.4 (s, 2C_{quat}), 148.1 (s, 2*C*H), 145.2 (s, 2C_{quat}), 130.3 (s, 2*C*H), 129.1 (s, 2*C*H), 56.2 (s, 2CH_2), 38.4 (s, *C*H_2), 31.5 (s, 2C_{quat}), 30.1 (s. 6*C*H_3). **^{19}F NMR** (564 MHz, CD_3OD) δ = −171.6 (s, F^-), −276.0 (sept, $J^2_{(D-F)}$ = 7.1 Hz; CD_3F from the reaction with CD_3OD). **IR** (solid, cm^{-1}) ν_{max} = 2960 (s), 2873 (w), 1627(s), 1575 (w), 1562(w), 1512 (w), 1480 (w), 1435 (w), 1414 (w), 1393 (w), 1371 (w), 1334 (w), 1308 (w), 1256 (m), 1211 (w), 1186 (w), 1144 (w), 1118 (w), 1102 (w), 1032 (w), 933 (w), 907(w), 855 (m), 788 (m, SF_5^-), 744 (w), 616 (m), 575 (vs, SF_5^-), 534 (m), 517 (w), 493 (w), 464 (s, SF_5^-), 430 (w). **MS** (EI): m/z (%) 310 (92) $[M]^+$ (M_{theor}^{2+} F^-/ SF_5^-= 456.5).

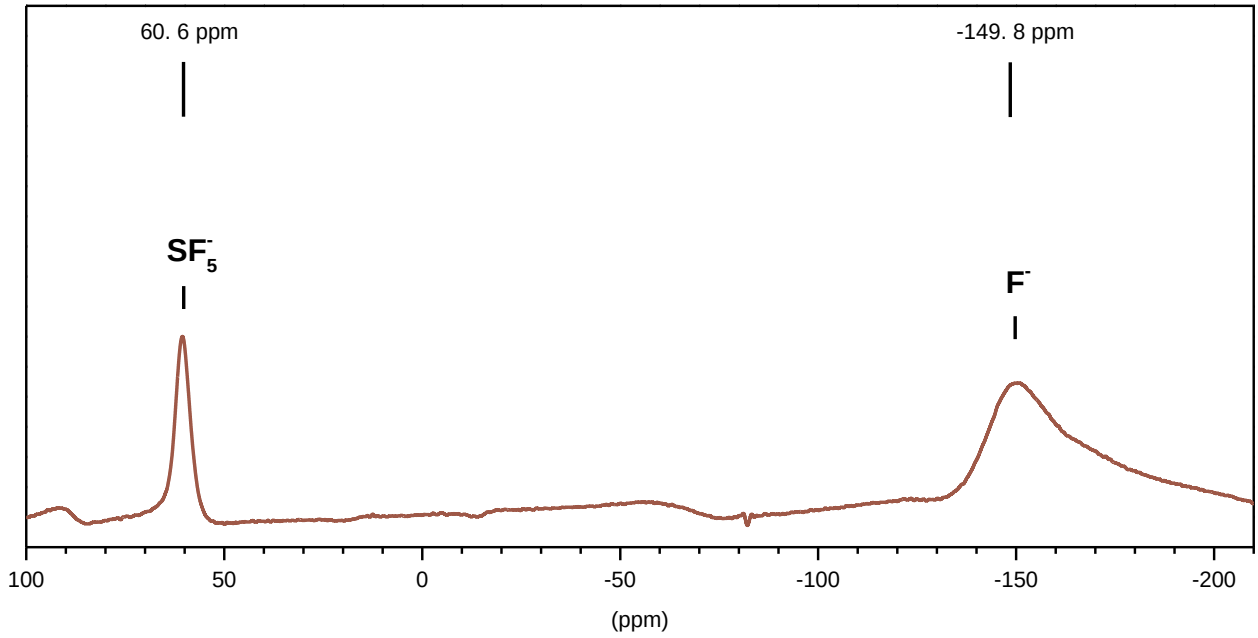
1,1'-dioctyl-[4,4'-bipyridine]-1,1'-diium *x*-fluoride (6-*x*)fluorosulfide 2c



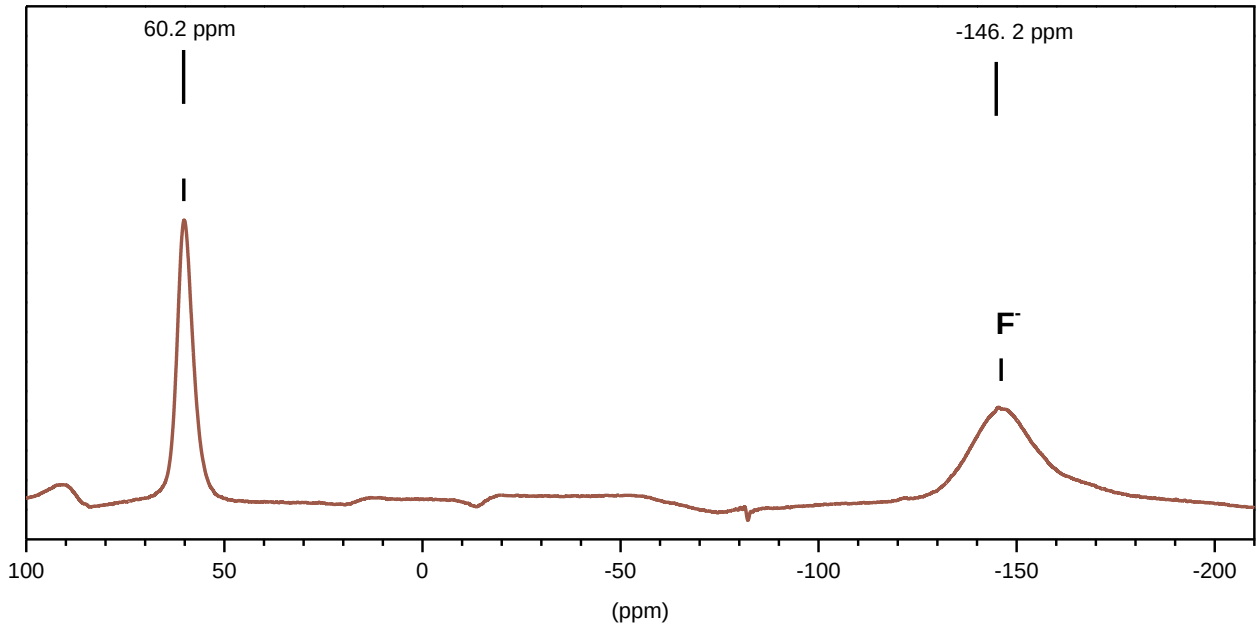
Compound **2c** was obtained as a blue-green solid. Mp = 118-120 °C (dec.). **^{1}H NMR** (400 MHz, CD_3OD) δ = 9.09 (br. s, 1H), 8.80 (br. s, 1H), 8.49 (br. s, 1H), 7.96 (br. s, 1H), 4.99 (br. s, 7H), 2.04 (br. s, 1H), 1.90 (br. s, 5H), 1.31 (br. s, 36H), 0.88 (br. s, 18H). **^{13}C NMR** (101 MHz, CD_3OD) δ = 151.2 (s), 145.8 (s), 126.5 (s), 123.0 (s), 32.8 (s), 32.3 (s), 29.6 (s), 29.5 (s), 26.6 (s), 23.5 (s), 23.1 (s), 14.4 (s). **^{19}F NMR** (376 MHz, CD_3OD) δ = −161.35 (s, F^-).

^{19}F NMR studies of the products 2:

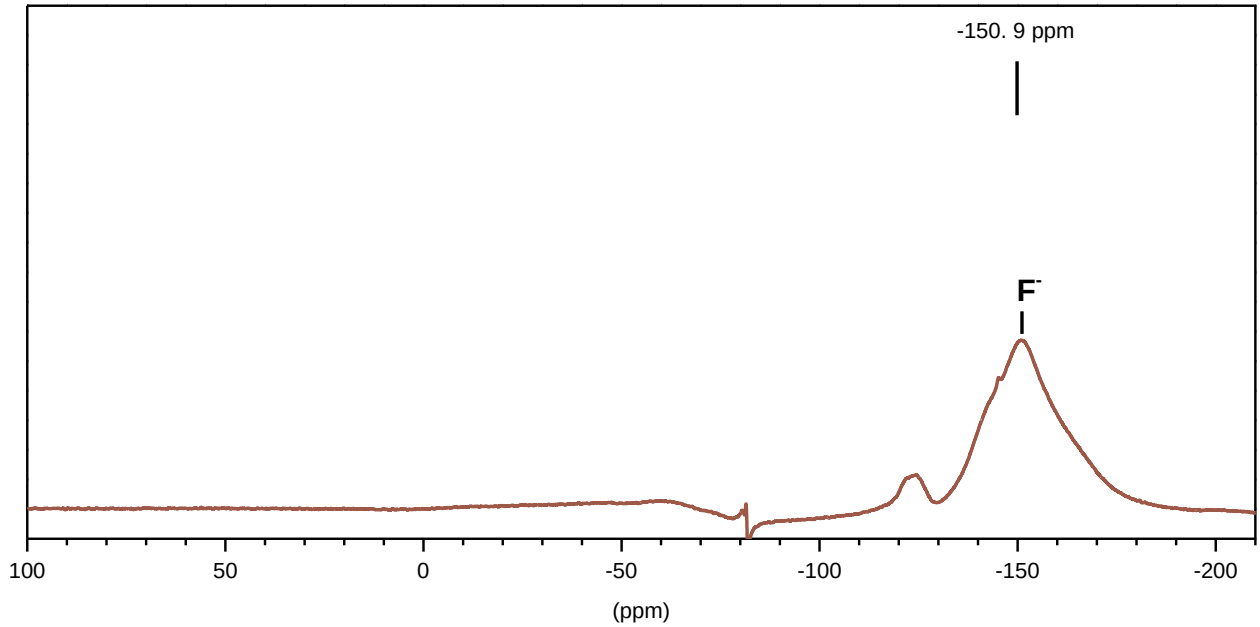
The ^{19}F solid-state NMR spectrum of **2a** measured at 30 °C with a spinning speed of 35 kHz.



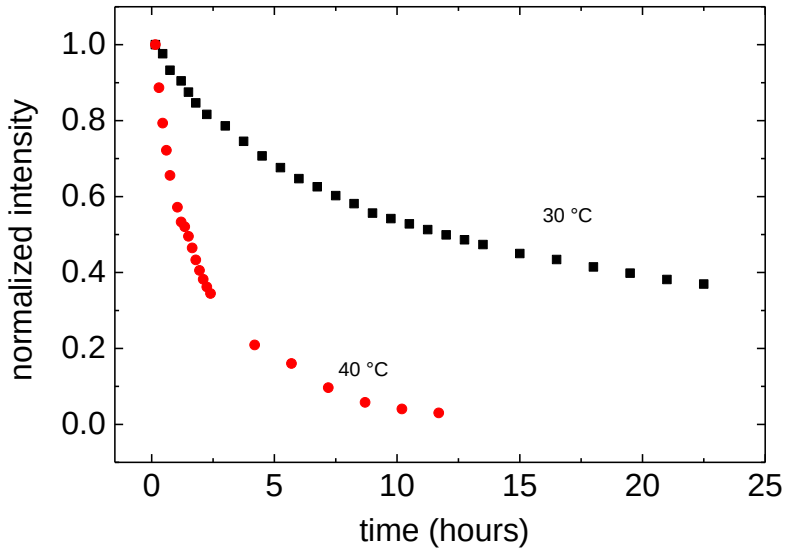
The ^{19}F solid-state NMR spectrum of **2b** measured at 30 °C with a spinning speed of 35 kHz.



^{19}F solid-state NMR spectrum of product **2c** measured at 30 °C and using a spinning speed of 35 kHz. No signal at +60 ppm detected.

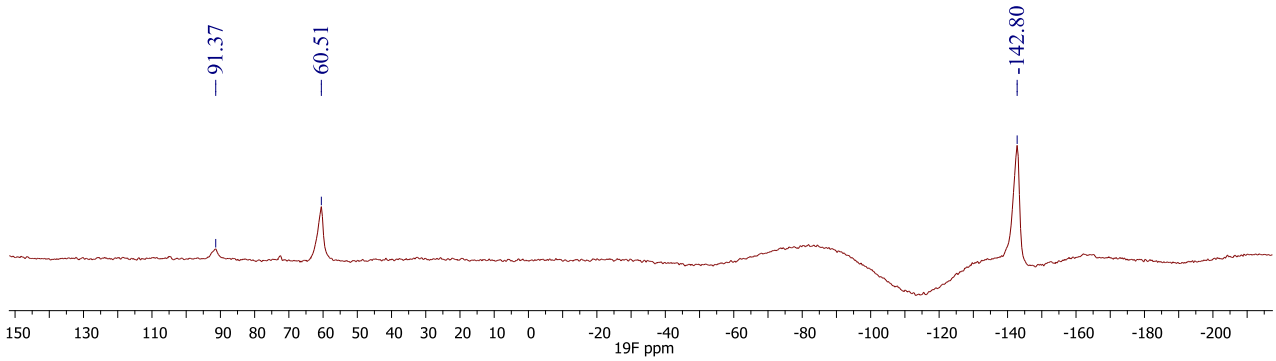


The plot of intensity decay of the signal at +60 ppm was obtained for **2b**, the measuring time for each point was about 9 min. Comparison of the kinetic curves at 30 °C and 40 °C indicates the existence of two processes characterized by fast and slow decay rate.



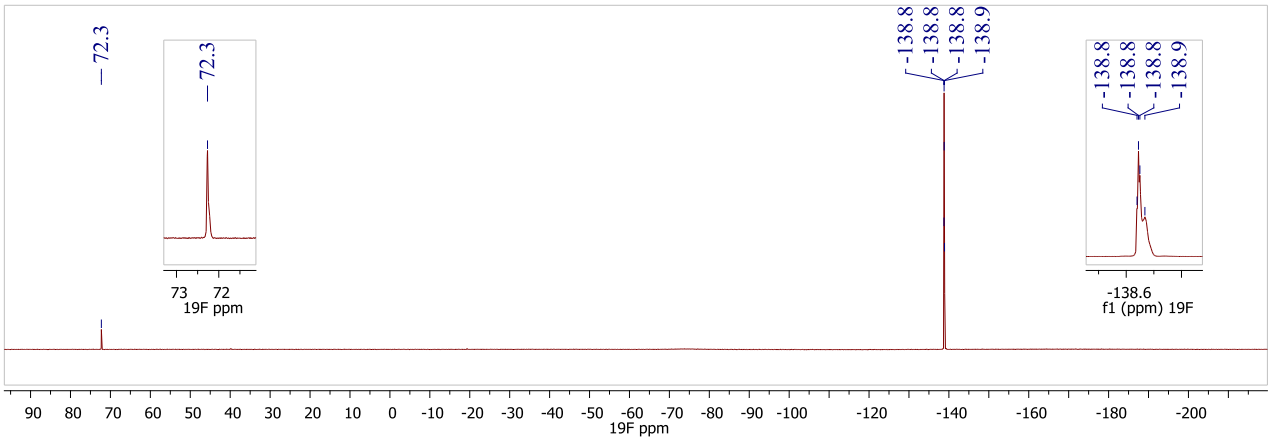
^{19}F NMR studies of products 2 in liquid state:

^{19}F NMR spectrum of **2b** at −30 °C in CD_3CN.



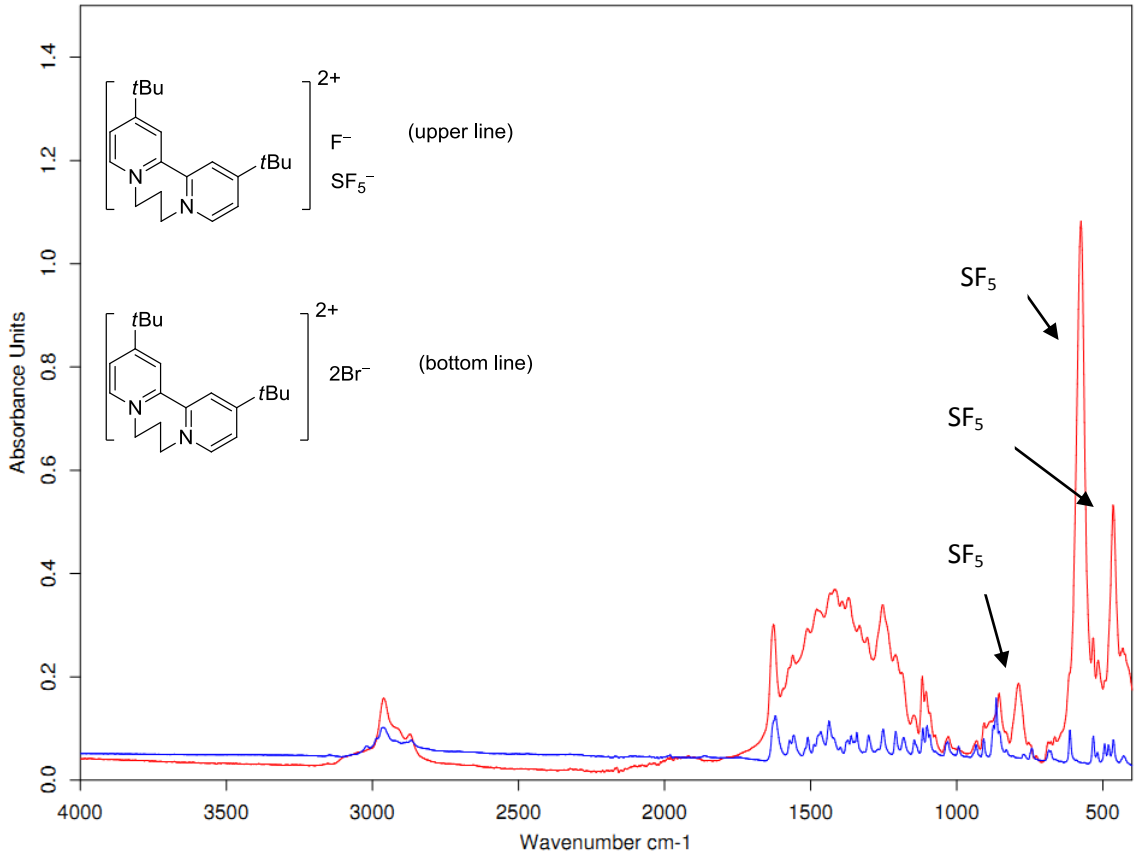
The obtained signals of SF_5^- (δ= 60.5 ppm) and F^- (δ= −142.8 ppm) in solution are similar to those ones obtained in the ^{19}F solid-state NMR experiment.

The ^{19}F NMR spectrum of **2b** at −30 °C in SO_2.



The signal at δ = −72.3 ppm is attributed SOF_2 which could formed from the reaction of SF_5^- with SO_2.

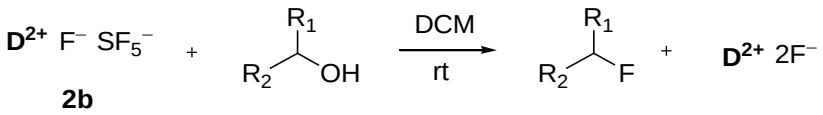
IR studies of the SF_6 reduction products and parental organic donors dihalides:



The IR spectra of the **2b** (upper line) and parental **[1b^{2+}]2Br^{-}** (bottom line) at r.t.

Reactions of product 2b as a SF_4-analog:

- **Reaction of 2b with alcohols**

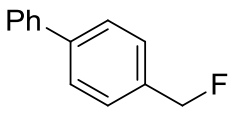


In a glovebox, into a Schlenk tube equipped with a stir bar, was placed salt **2b** (0.5 mmol) followed by addition of benzyl alcohol (0.25 mmol) and dry degassed solvent (DCM or DMF, 1 mL) under vigorous stirring. The tube was removed from the glovebox. After 2 h of stirring at r.t. to the reaction mixture was added $PhCF_3$ (0.25 mmol) as an internal standard and the yield was determined by quantitative ^{19}F NMR spectrum analysis. The sample for analysis was obtained by water work-up and purified by column chromatography using pentane as eluent.

- **Reactivity test of salts 2a-c in deoxofluorinations of benzyl alcohol:**

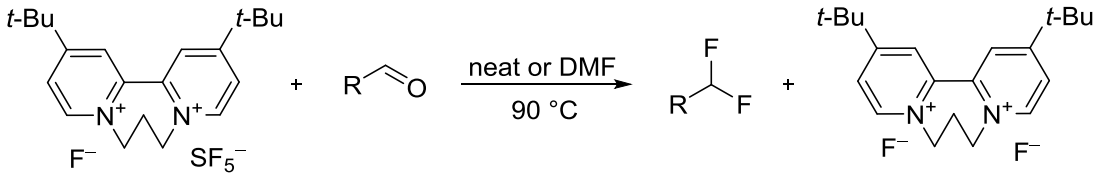
In a glovebox, a Schlenk-tube equipped with a stir bar was loaded with salt **2** (0.25 mmol) followed by addition of benzyl alcohol (0.25 mmol) and dry degassed solvent (DCM or DMF, 1 mL) under vigorous stirring. The tube was removed from the glovebox. After 2 h of stirring at r.t. to the reaction mixture was added $PhCF_3$ (0.25 mmol) as an internal standard and the yield was determined by quantitative ^{19}F NMR spectrum analysis.

4-(fluoromethyl)-1,1'-biphenyl



The product was obtained as a white solid. Yield 64%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 – 7.58 (m, 4H), 7.49 – 7.43 (m, 4H), 7.40 – 7.34 (m, 1H), 5.43 (d, $J^2_{(H-F)}$ = 47.9 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 141.7 (d, $J^6_{(C-F)}$ = 3.2 Hz, C_{quat}), 140.6 (d, $J^7_{(C-F)}$ = 1.1 Hz, C_{quat}), 135.1 (d, $J^2_{(C-F)}$= 16.8 Hz, C_{quat}), 128.8 (s, 2*C*H), 128.1 (d, $J^4_{(C-F)}$ = 5.5 Hz, 2*C*H), 127.5 (s, 2*C*H), 127.4 (d, $J^5_{(C-F)}$ = 1.1 Hz, 2*C*H), 127.1 (s, *C*H_2), 84.4 (d, $J^1_{(C-F)}$ = 165.9 Hz, *C*H_2). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −206.2 (t, $J^2_{(H-F)}$ = 47.9 Hz, 1F). **IR** ($CHCl_3$, cm^{-1}) ν_{max} = 3040 (m), 2929 (s), 2334 (w), 2080 (w), 1897 (m), 1729 (s), 1606 (m), 1473 (s), 1384 (s), 1269 (s), 1121 (m), 977 (s), 832 (s), 755 (s). **MS** (CI): m/z (%) 167 (100) $[M-F]^+$, 187 (67) $[M+1]^+$ (M_{theor} = 186.2).

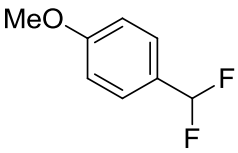
- **Reaction with aldehydes**



R = p-MeO-C_6H_4, 43% after the column chromatography

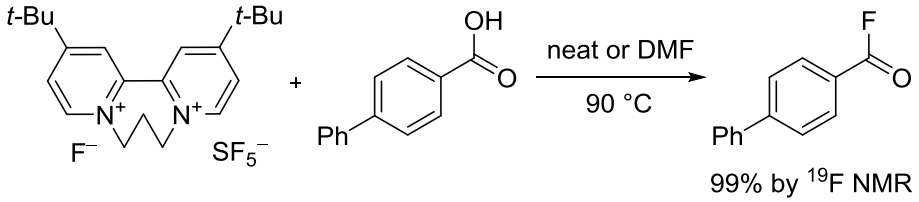
In a Schlenk tube equipped with a stir bar was loaded with salt **2b** (0.5 mmol) followed by benzaldehyde (0.25 mmol) and then dry, degassed DMF (1 mL) was added under vigorous stirring. The tube was removed from the glovebox and left under stirring at 90 °C in an oil-bath. After 12 h to the tube was added $PhCF_3$ (0.25 mmol) as an internal standard and the yield was determined by quantitative ^{19}F NMR spectrum analysis. The reaction was also successfully performed under neat conditions but with more vigorous stirring. The sample for analysis was obtained by water work-up (or upon addition of silica and DCM (5 mL) and evaporating the solvent) and purified by column chromatography (pentane: Et_2O mixtures as eluent).

4-(difluoromethyl)-anisole



The product was obtained as light orange oil. Yield: 43%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.60 (t, $J^1_{(H\text{-}F)}$ = 56.8 Hz, 1H), 3.84 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −108.32 (d, $J^1_{(H\text{-}F)}$ = 56.8 Hz, 2F). **IR** ($CHCl_3$, cm^{-1}) ν_{max} = 2922 (s), 2857 (s), 2324 (w), 2092 (w), 1923 (w), 1724 (m), 1606 (m), 1511 (w), 1457 (m), 1374 (w), 1258 (s), 1165 (w), 1018 (s), 863 (m), 796 (s), 693 (m).

Reaction with carboxylic acids



99% by ^{19}F NMR

In a glovebox, a Schlenk tube equipped with a stir bar was loaded with salt **2b** (0.5 mmol) followed by addition of benzoic acid (0.25 mmol) and dry degassed DMF (1 mL) under vigorous stirring. The tube was removed from the glovebox and stirred at 90 °C in an oil-bath. After 1 h to the tube was added $PhCF_3$ (0.25 mmol) as an internal standard and the yield was determined by quantitative ^{19}F NMR spectrum analysis.

Literature

[1] a) D. D. Perrin, W. L. F. Armarego, Purification of Laboratory Chemicals (Pergamon Press, Oxford, 1988) 3rd Ed.; b) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518.

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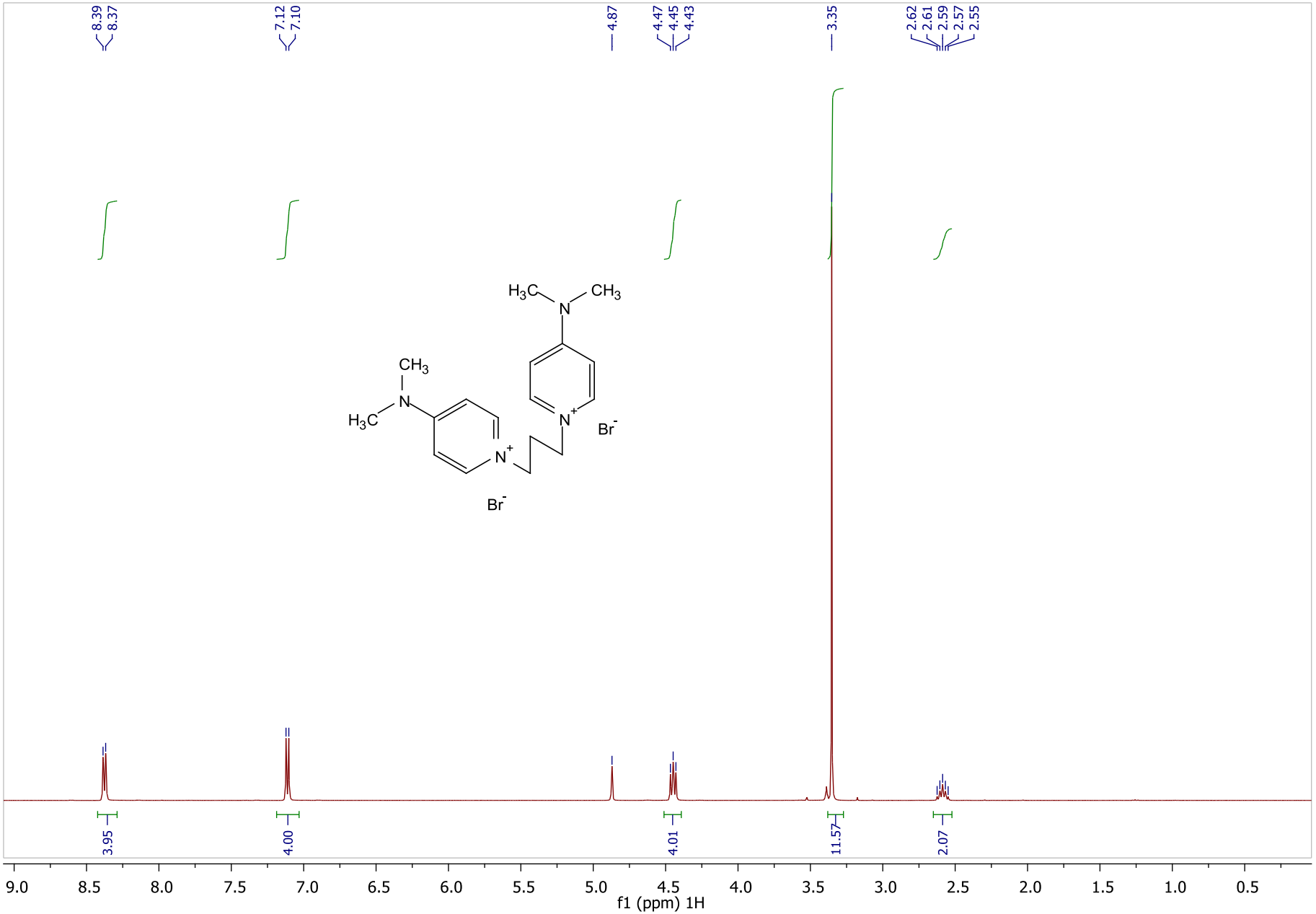
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7.10
4.87
4.47
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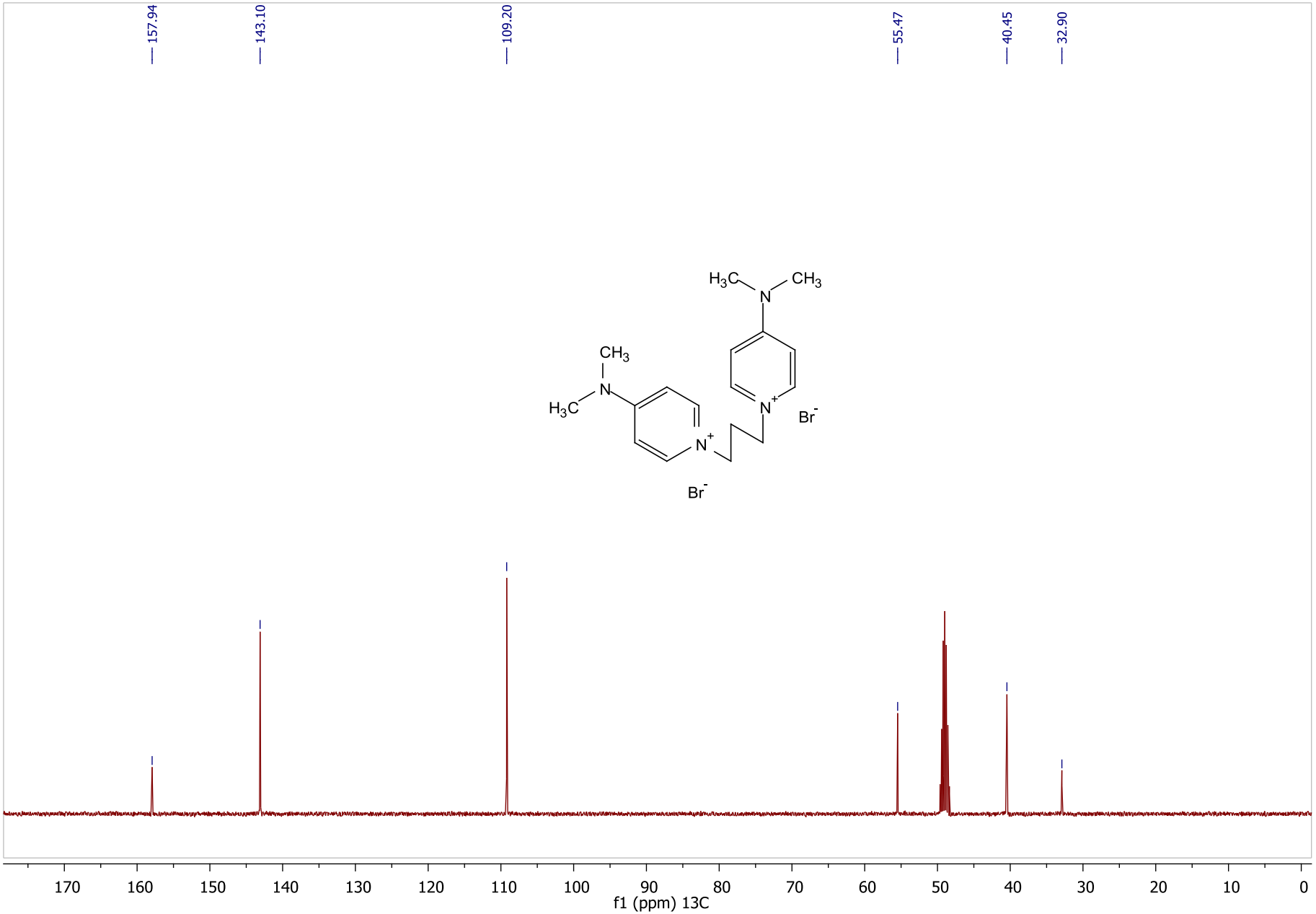
4.43
3.35
2.62
2.61
2.59
2.57
2.55
H3C
CH3
N
CH3
H3C
N
N+
Br-
N+
Br-
3.95
4.00
4.01
11.57
2.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm) 1H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143.10
109.20
55.47
40.45
32.90
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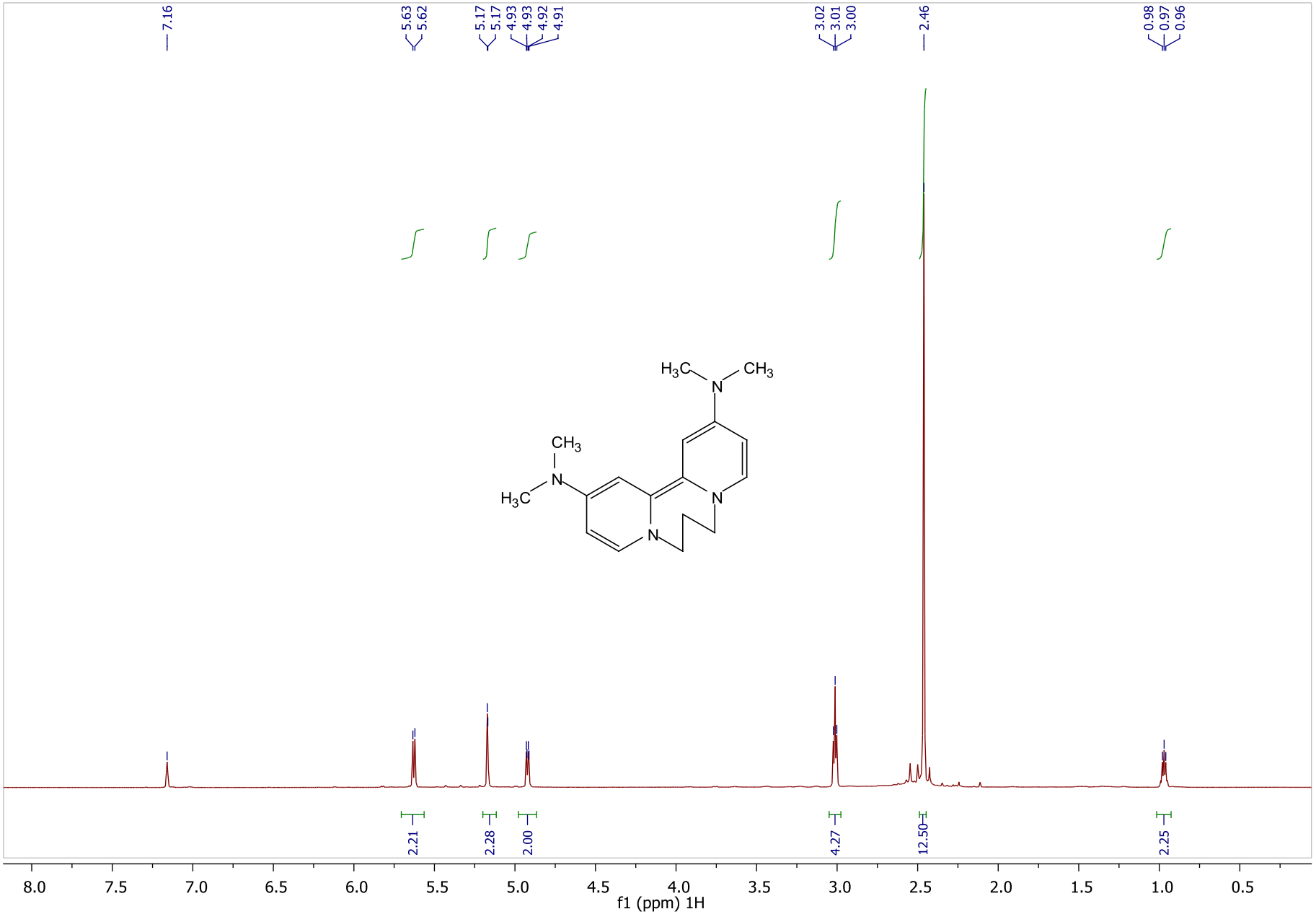
CH3
N
CH3
N
H3C
N+
Br-
N+
Br-
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C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4.93
4.93
4.92
4.91
3.02
3.01
3.00
2.46
0.98
0.97
0.96
H3C
CH3
N
CH3
N
H3C
N
N
2.21
2.28
2.00
4.27
12.50
2.25
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
3.5
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2.5
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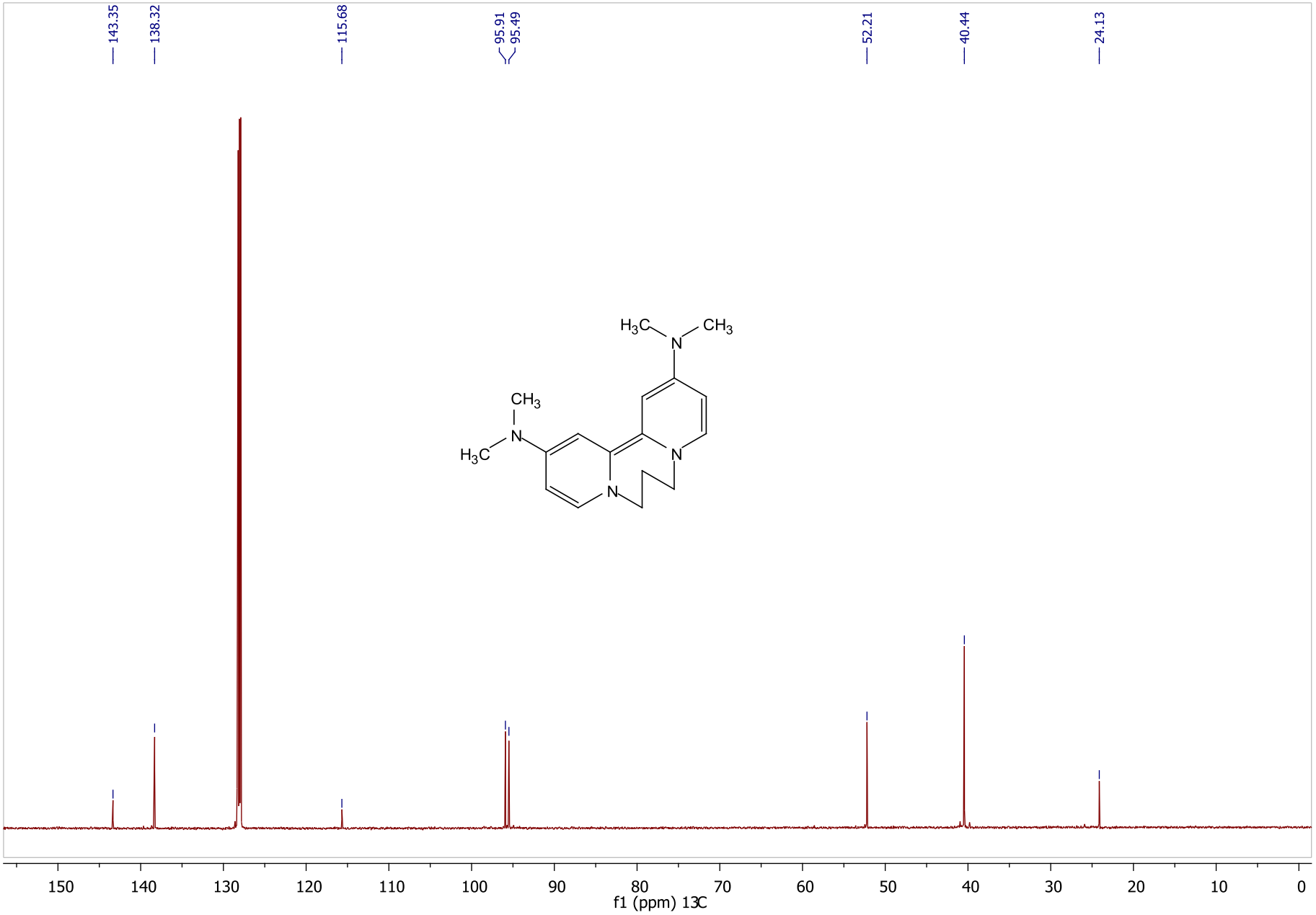
1.5
1.0
0.5
f1 (ppm) 1H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138.32
115.68
95.91
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40.44
24.13
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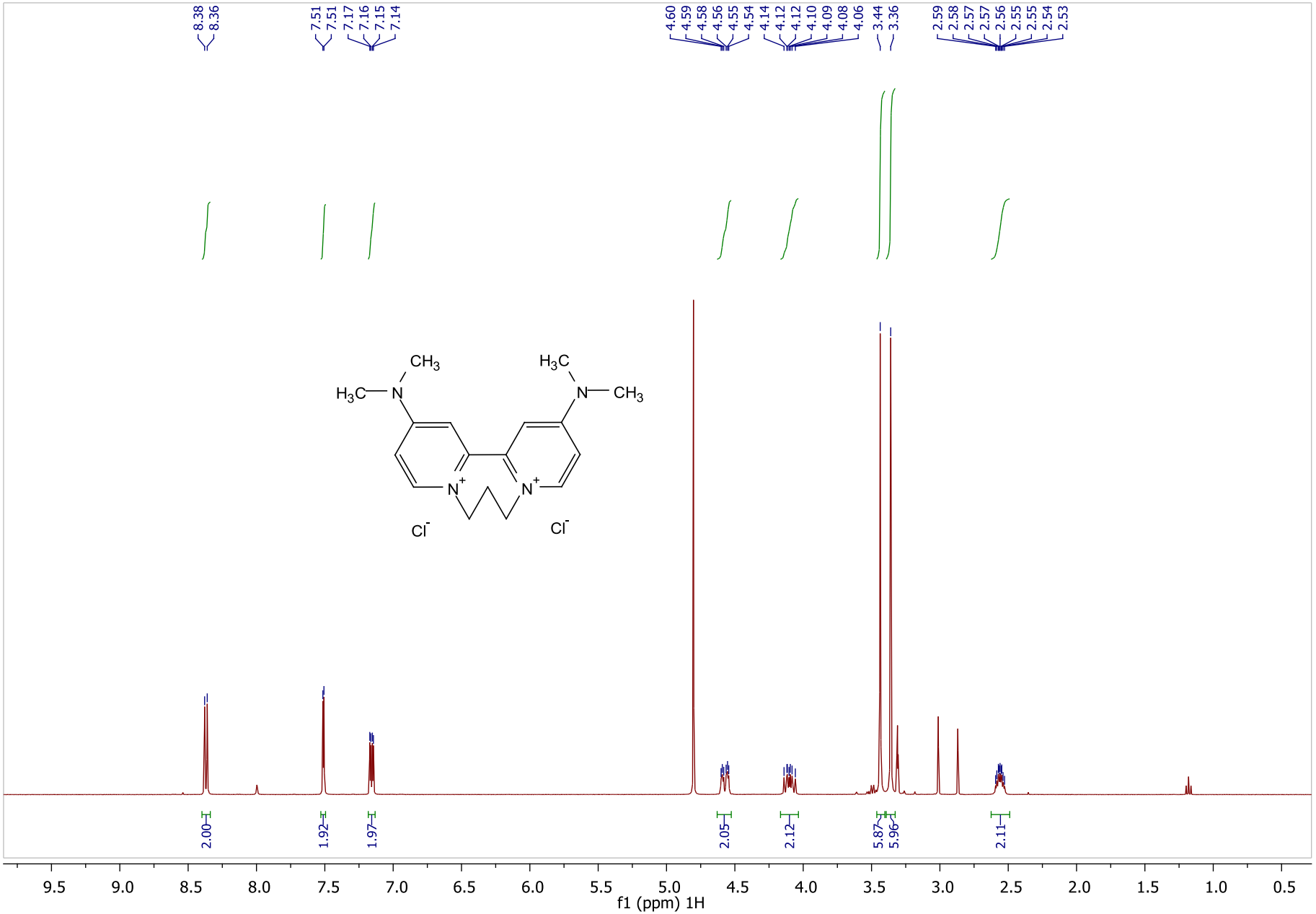
N
CH3
N
H3C
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C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4.59
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4.55
4.54
4.14
4.12
4.12
4.10
4.09
4.08
4.06
3.44
3.36
2.59
2.58
2.57
2.57
2.56
2.55
2.55
2.54
2.53
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H3C
N
H3C
N
CH3
N+
N+
Cl-
Cl-
2.00
1.92
1.97
2.05
2.12
5.87
5.96
2.11
9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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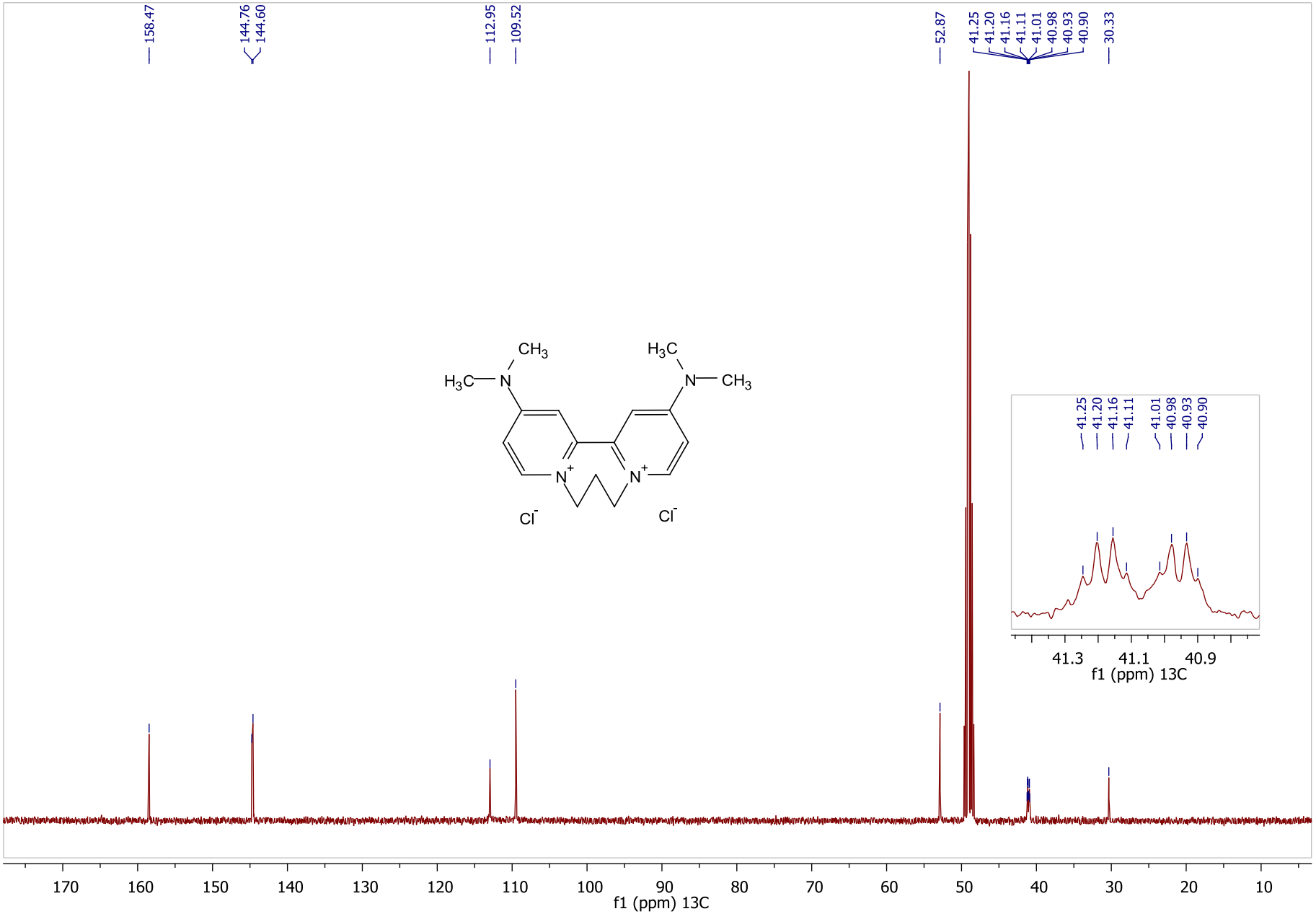
2.0
1.5
1.0
0.5
f1 (ppm) 1H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109.52
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41.20
41.16
41.11
41.01
40.98
40.93
40.90
30.33
CH3
H3C
N
H3C
N
CH3
N+
N+
Cl-
Cl-
41.3
41.1
40.9
f1 (ppm) 13C
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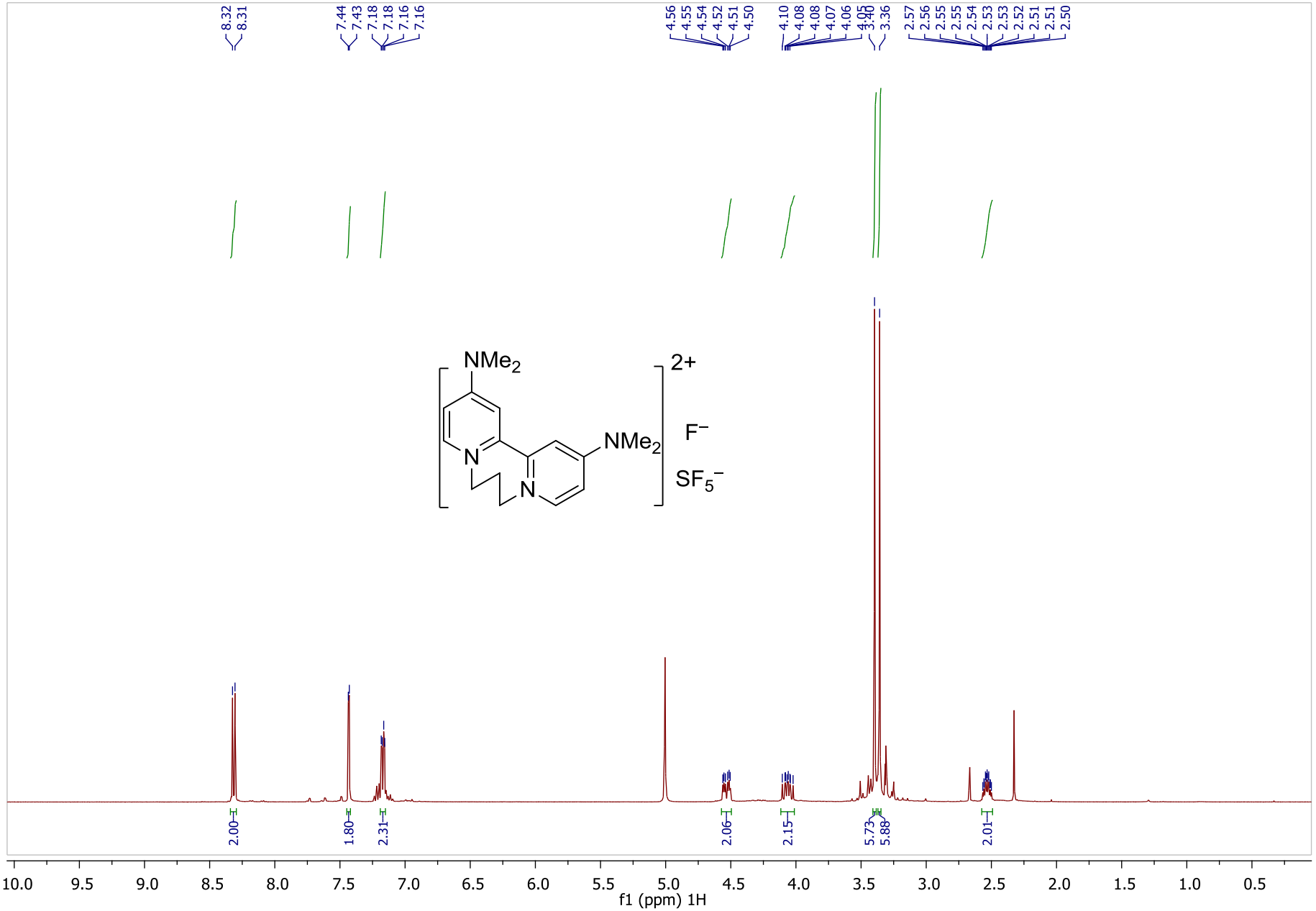
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C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7.16
7.16
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4.50
4.10
4.08
4.08
4.07
4.06
4.05
3.40
3.36
2.57
2.56
2.55
2.55
2.54
2.53
2.53
2.52
2.51
2.51
2.50
NMe2
NMe2
N
N
2+
F−
SF5−
2.00
1.80
2.31
2.06
2.15
5.73
5.88
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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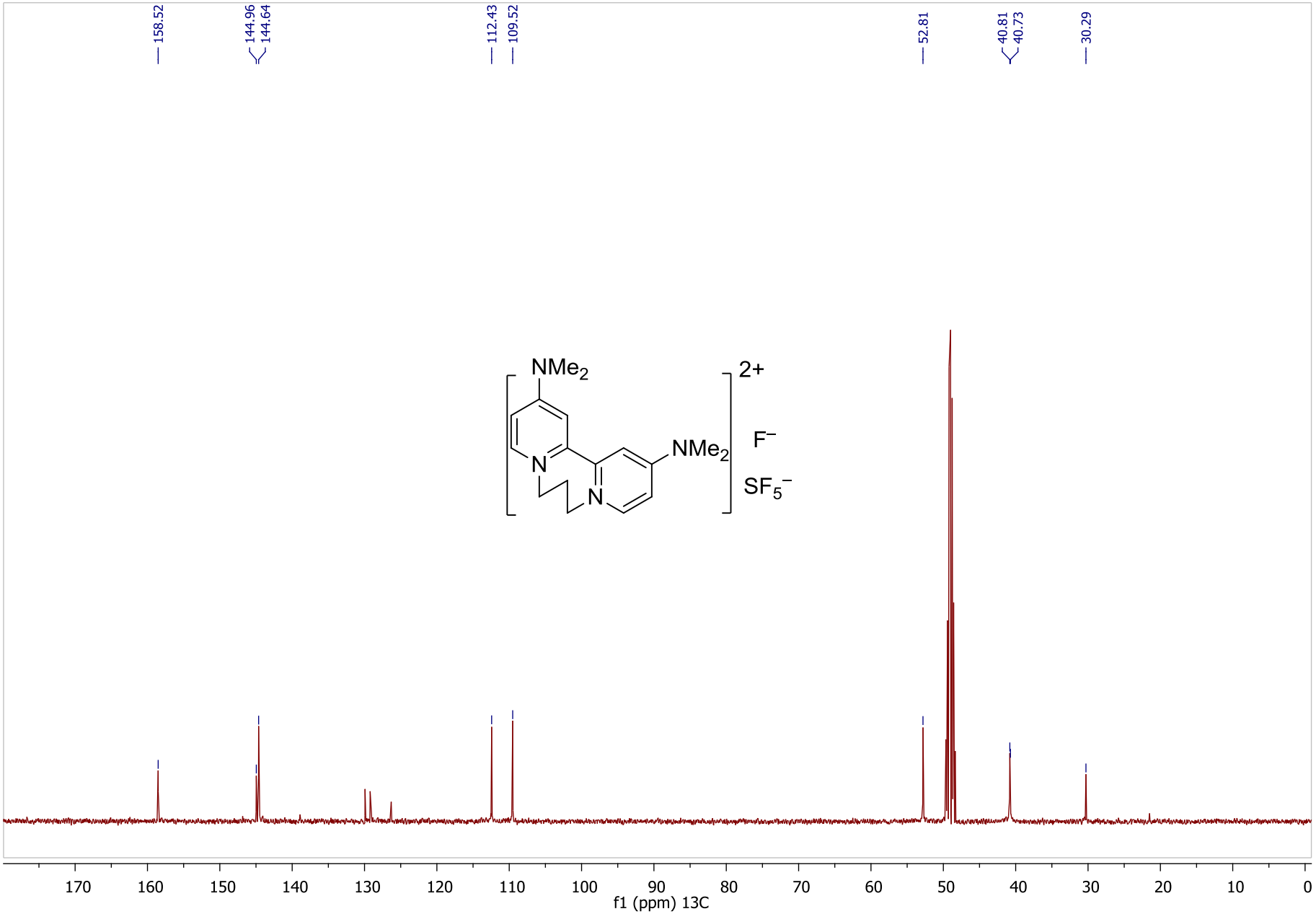
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm) 1H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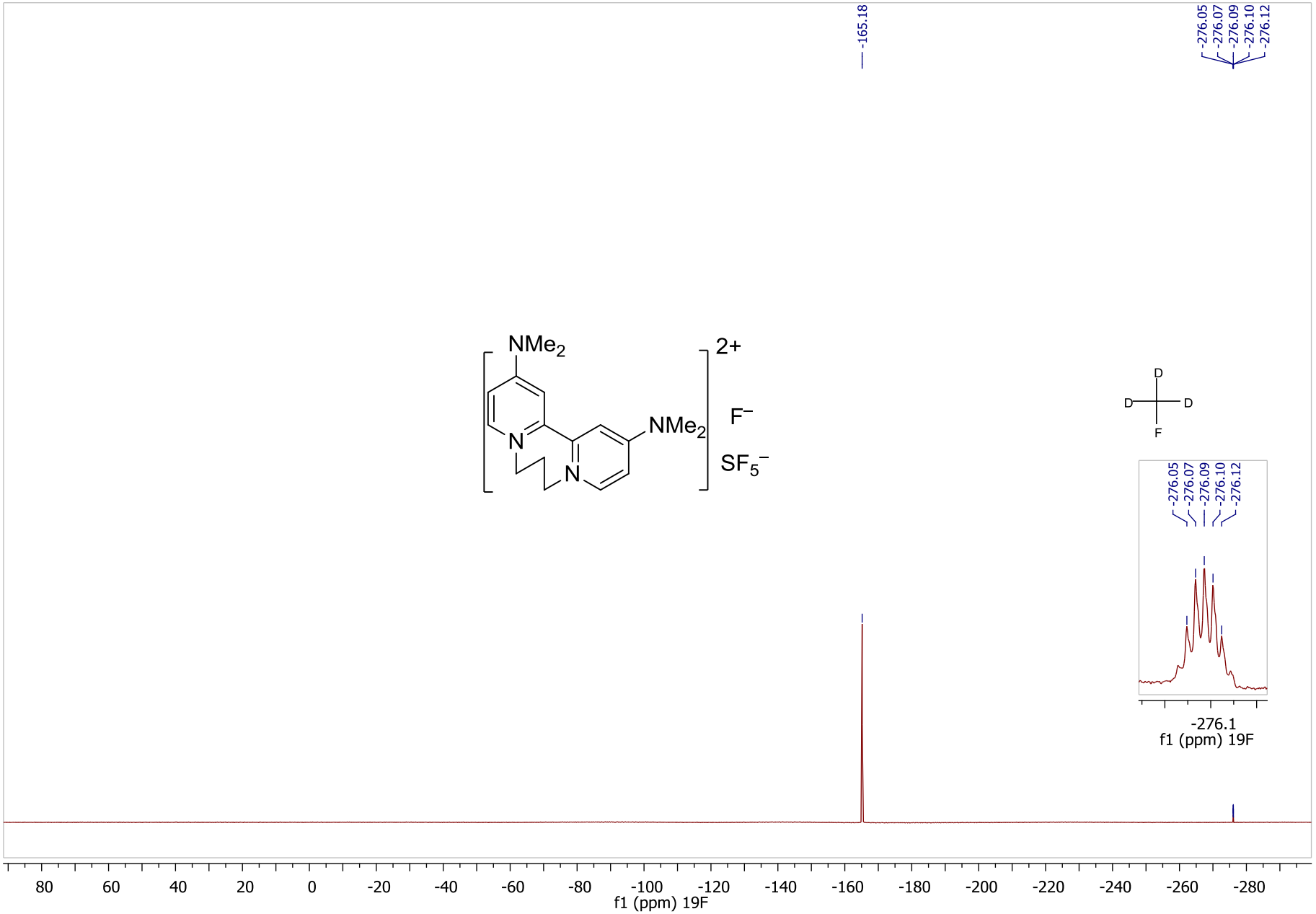
112.43
109.52
52.81
40.81
40.73
30.29
NMe2
NMe2
N
N
2+
F−
SF5−
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C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-276.07
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-276.10
-276.12
NMe2
2+
NMe2
F−
SF5−
N
N
D
D
D
F
-276.05
-276.07
-276.09
-276.10
-276.12
-276.1
f1 (ppm) 19F
80
60
40
20
0
-20
-40
-60
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-100
-120
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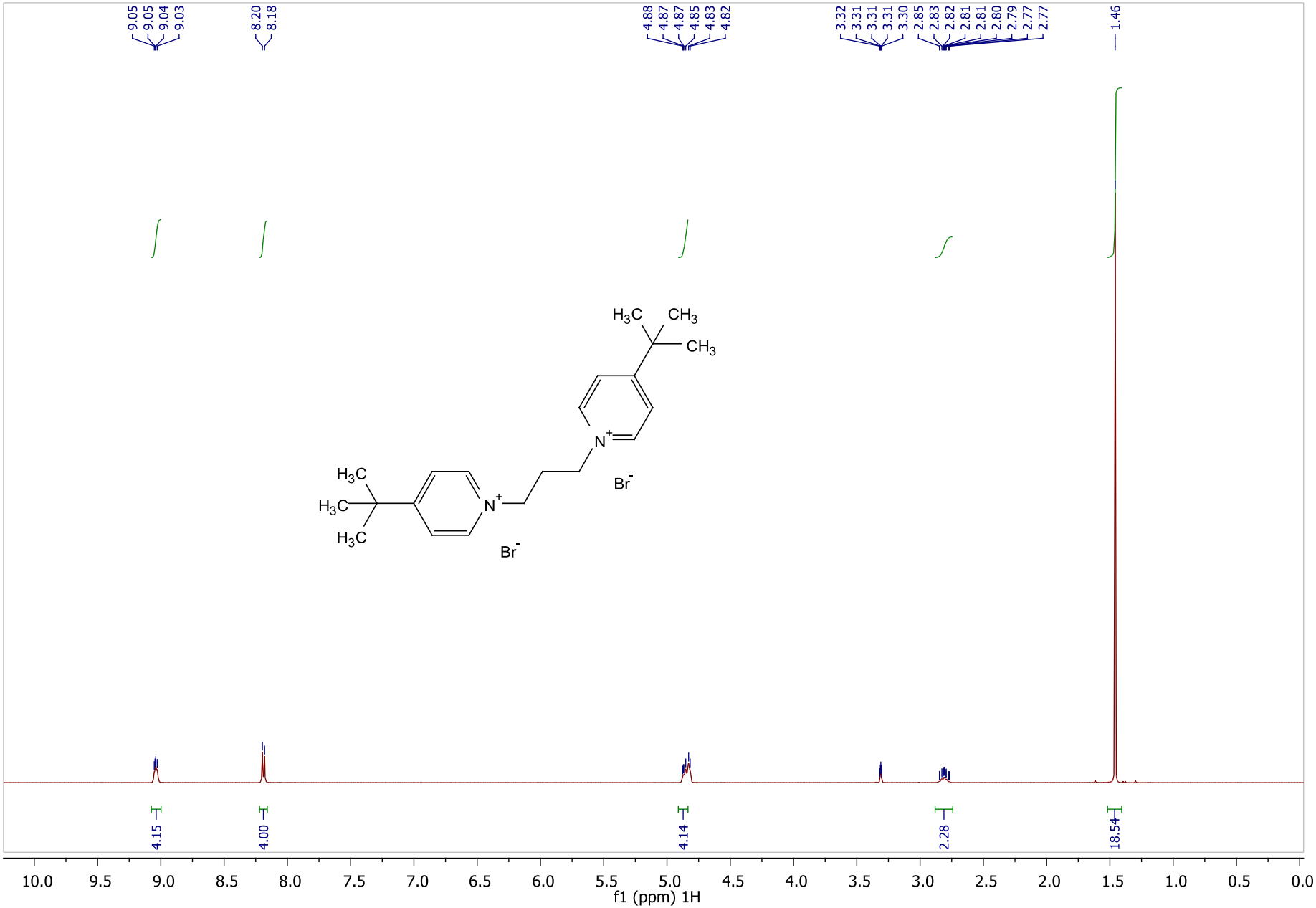
-160
-180
-200
-220
-240
-260
-280
f1 (ppm) 19F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2.83
2.82
2.81
2.81
2.80
2.79
2.77
2.77
1.46
H3C
CH3
CH3
N+
Br-
H3C
H3C
H3C
N+
Br-
4.15
4.00
4.14
2.28
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
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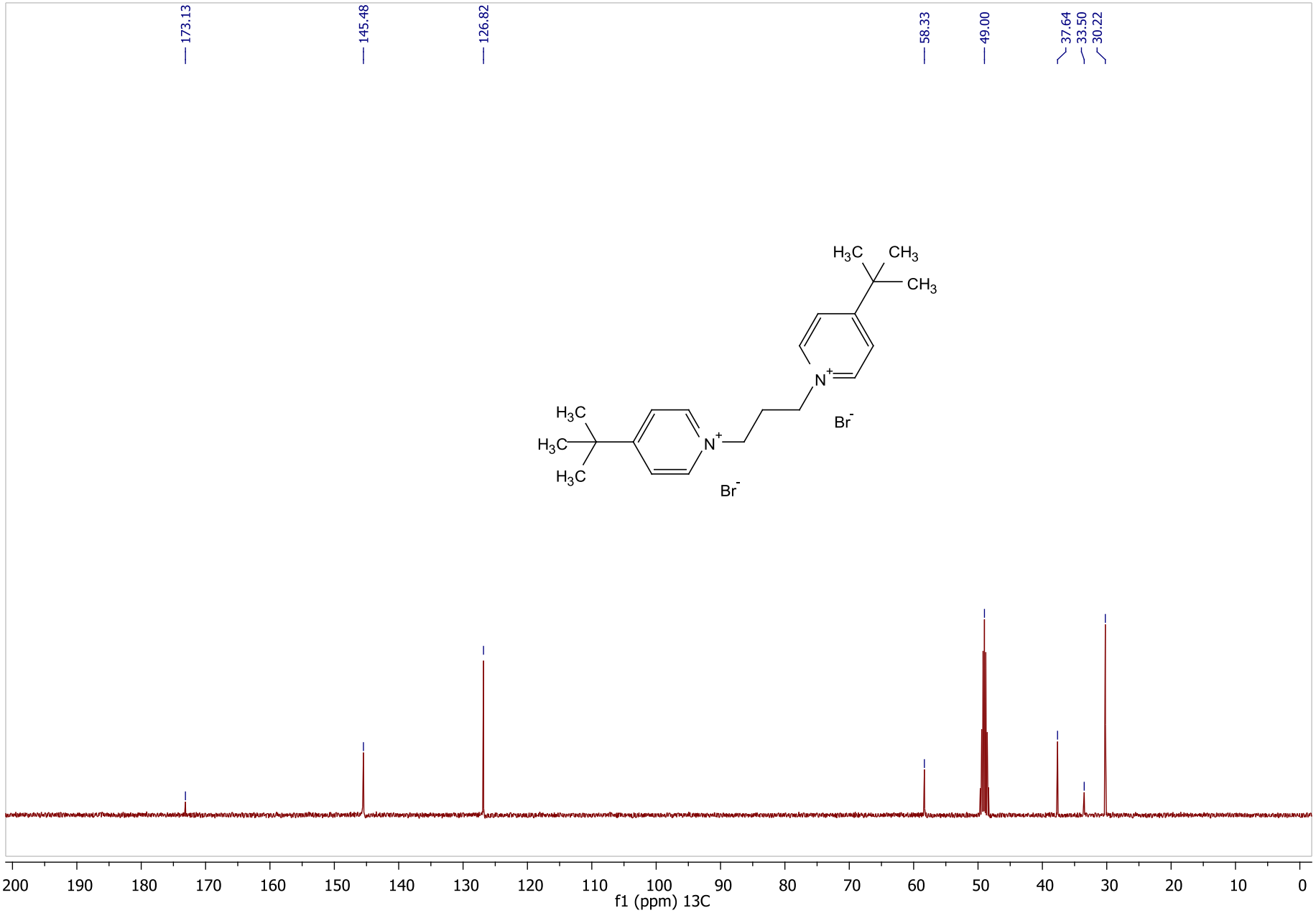
f1 (ppm) 1H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37.64
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30.22
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CH3
N+
Br-
H3C
H3C
H3C
N+
Br-
200
190
180
170
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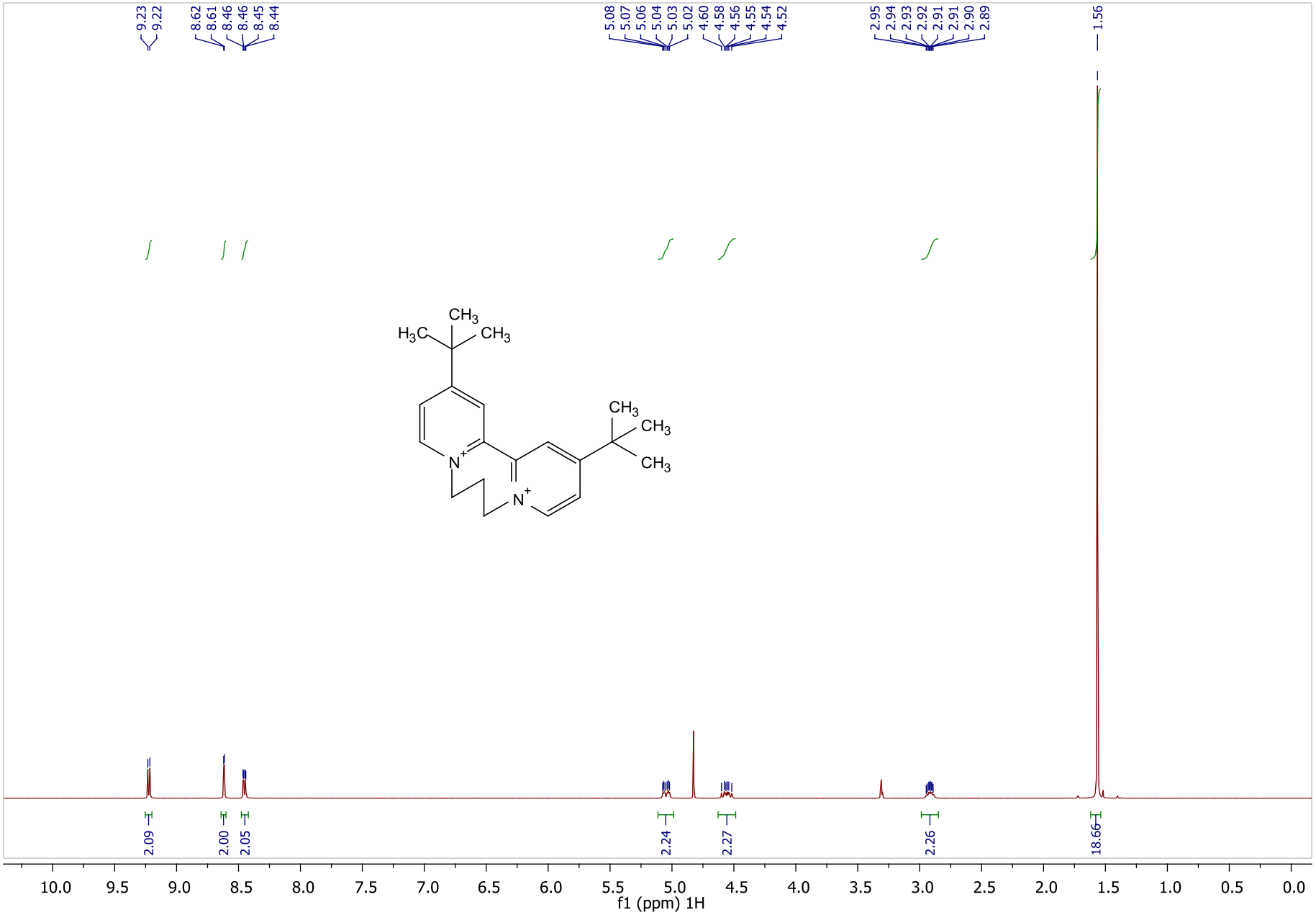
f1 (ppm) 13C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2.92
2.91
2.91
2.90
2.89
1.56
CH3
H3C
CH3
CH3
CH3
CH3
N+
N+
2.09
2.00
2.05
2.24
2.27
2.26
18.66
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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5.0
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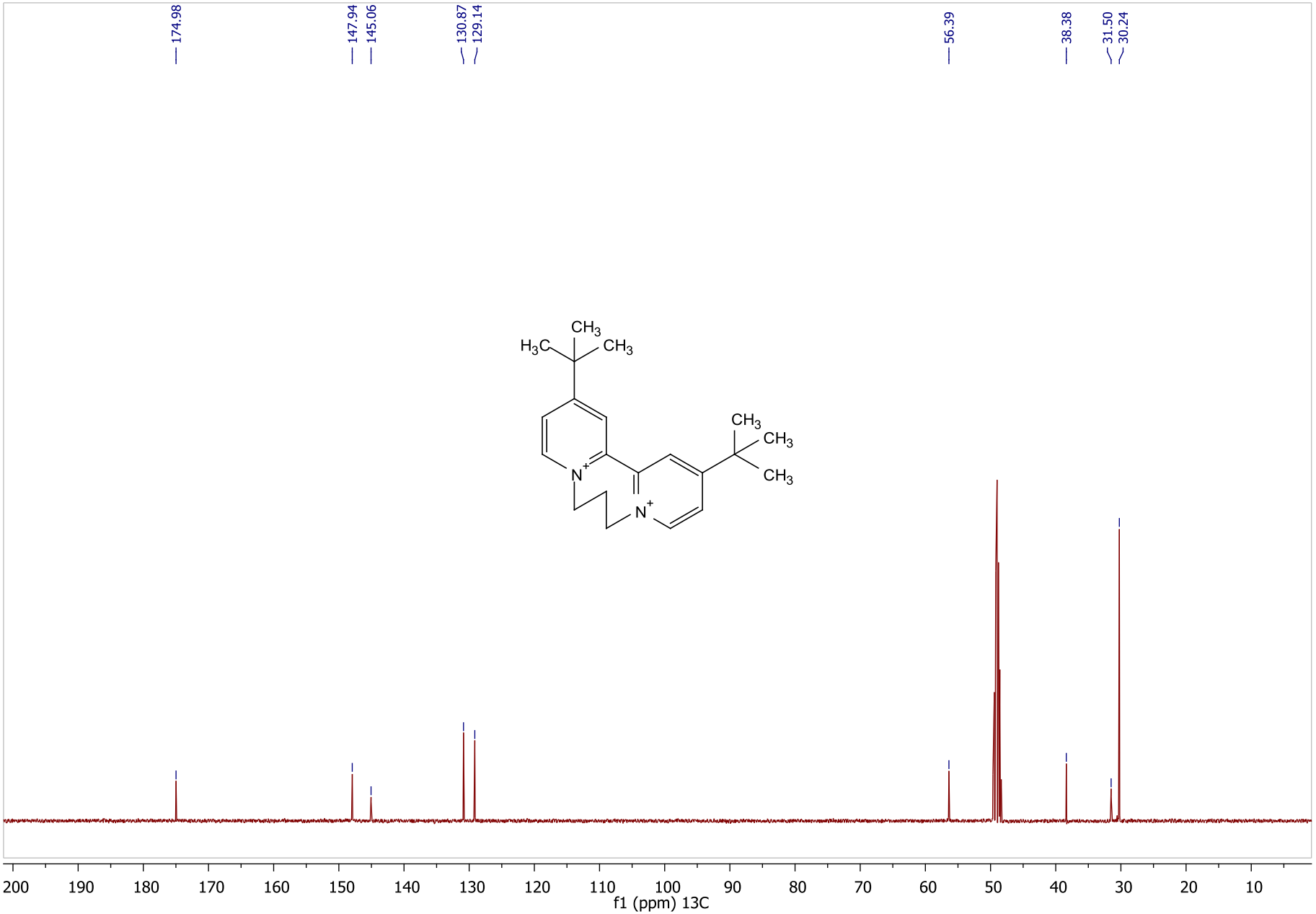
f1 (ppm) 1H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56.39
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31.50
30.24
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H3C
CH3
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CH3
N+
N+
200
190
180
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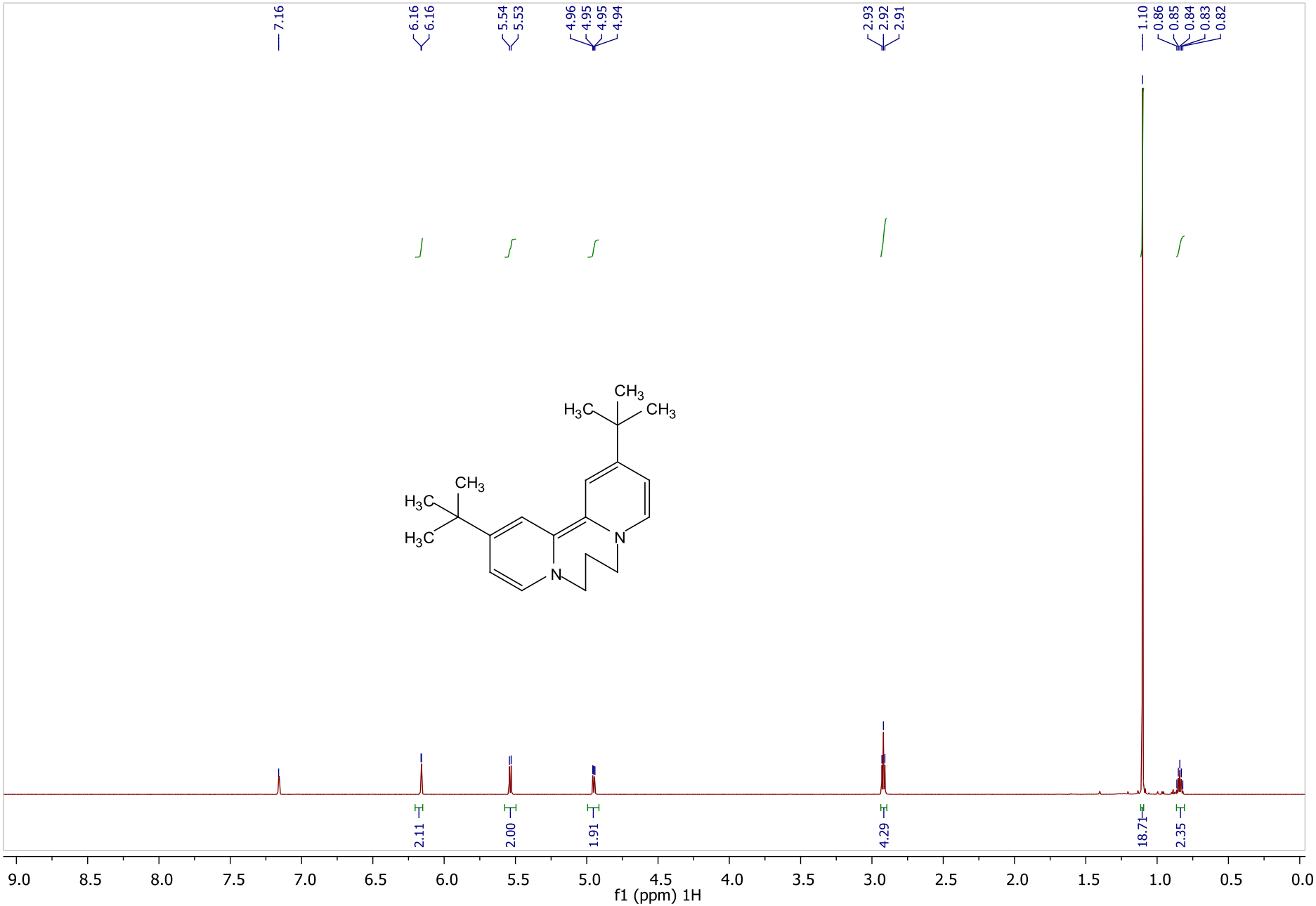
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C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6.16
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5.53
4.96
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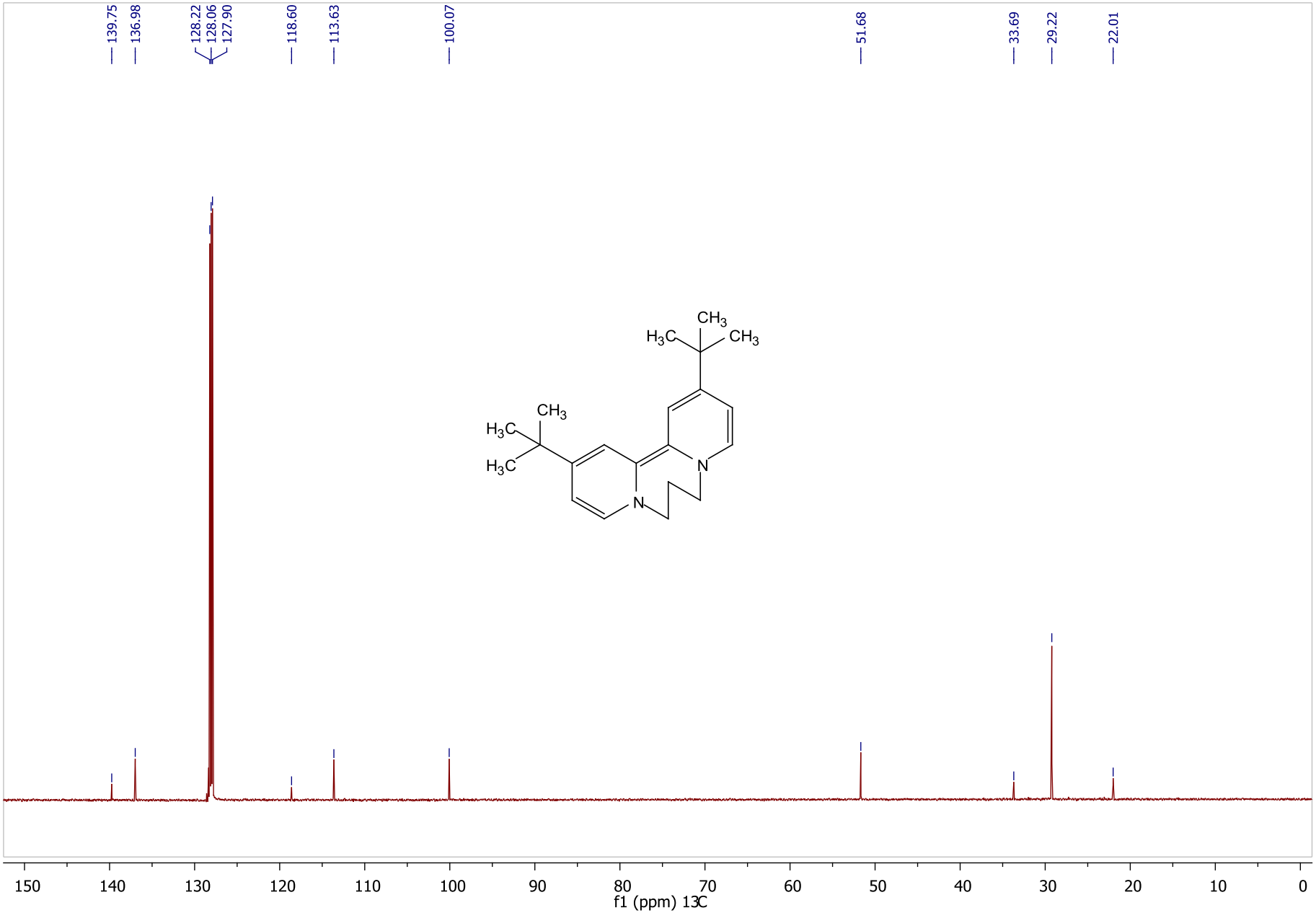
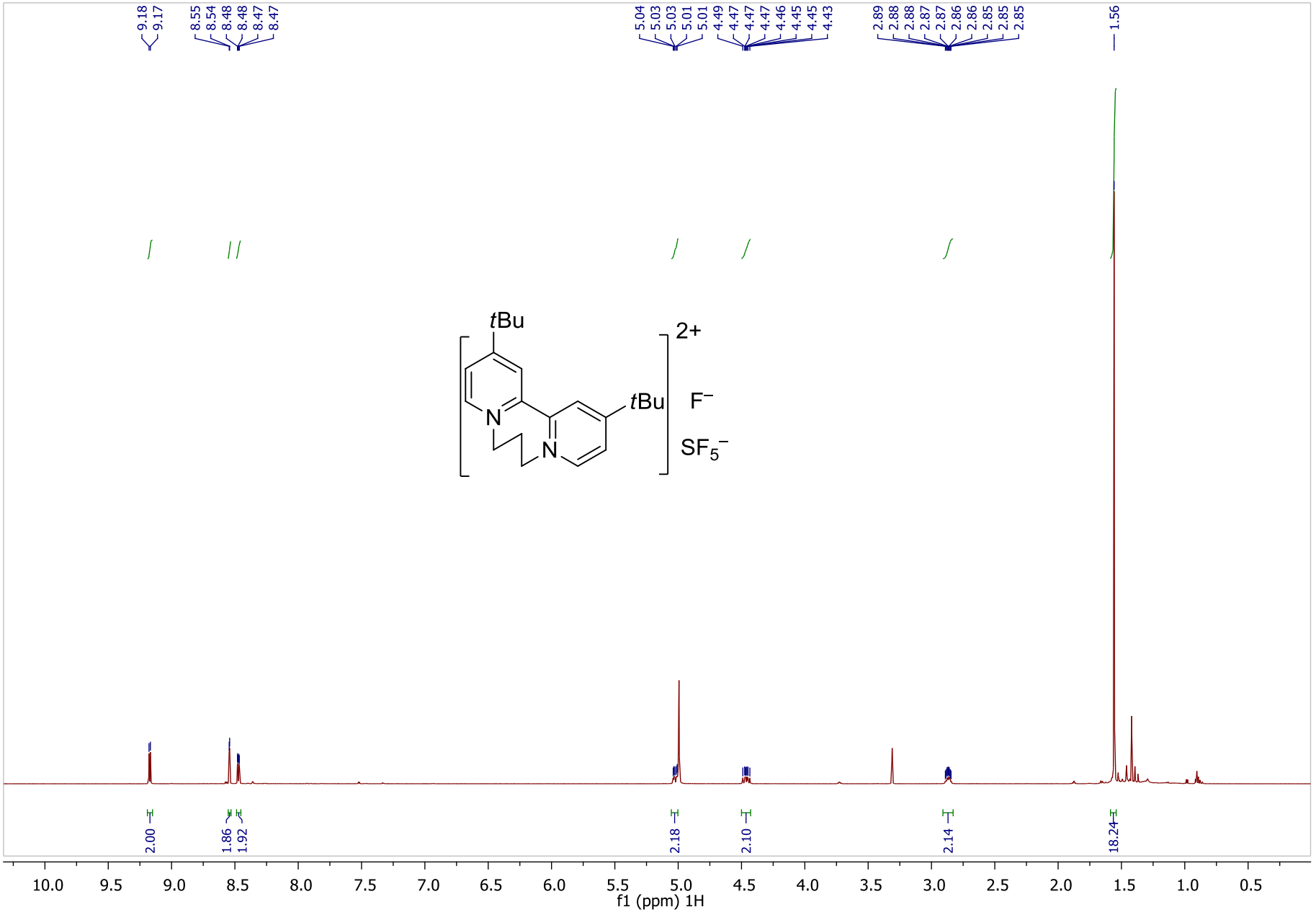
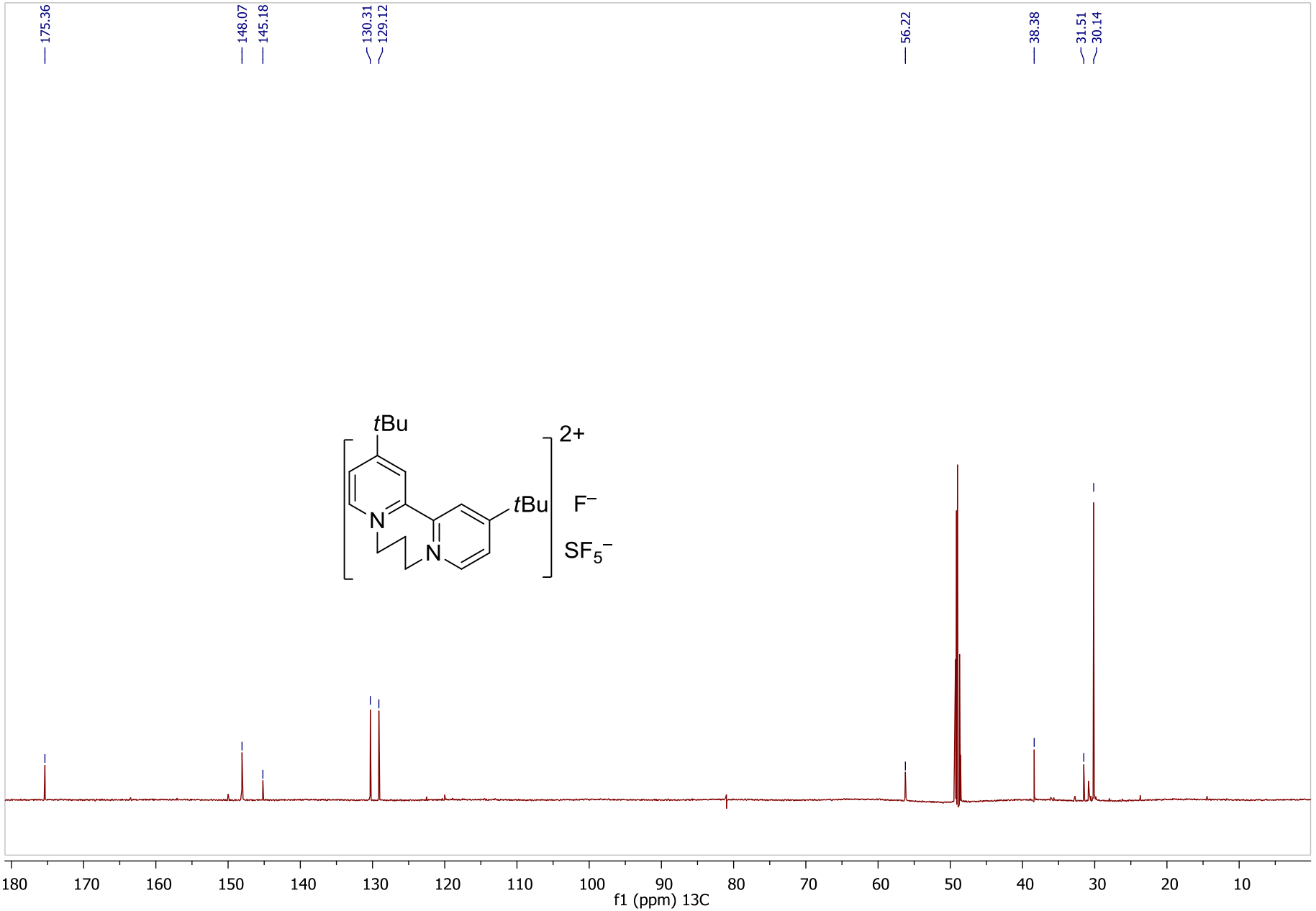
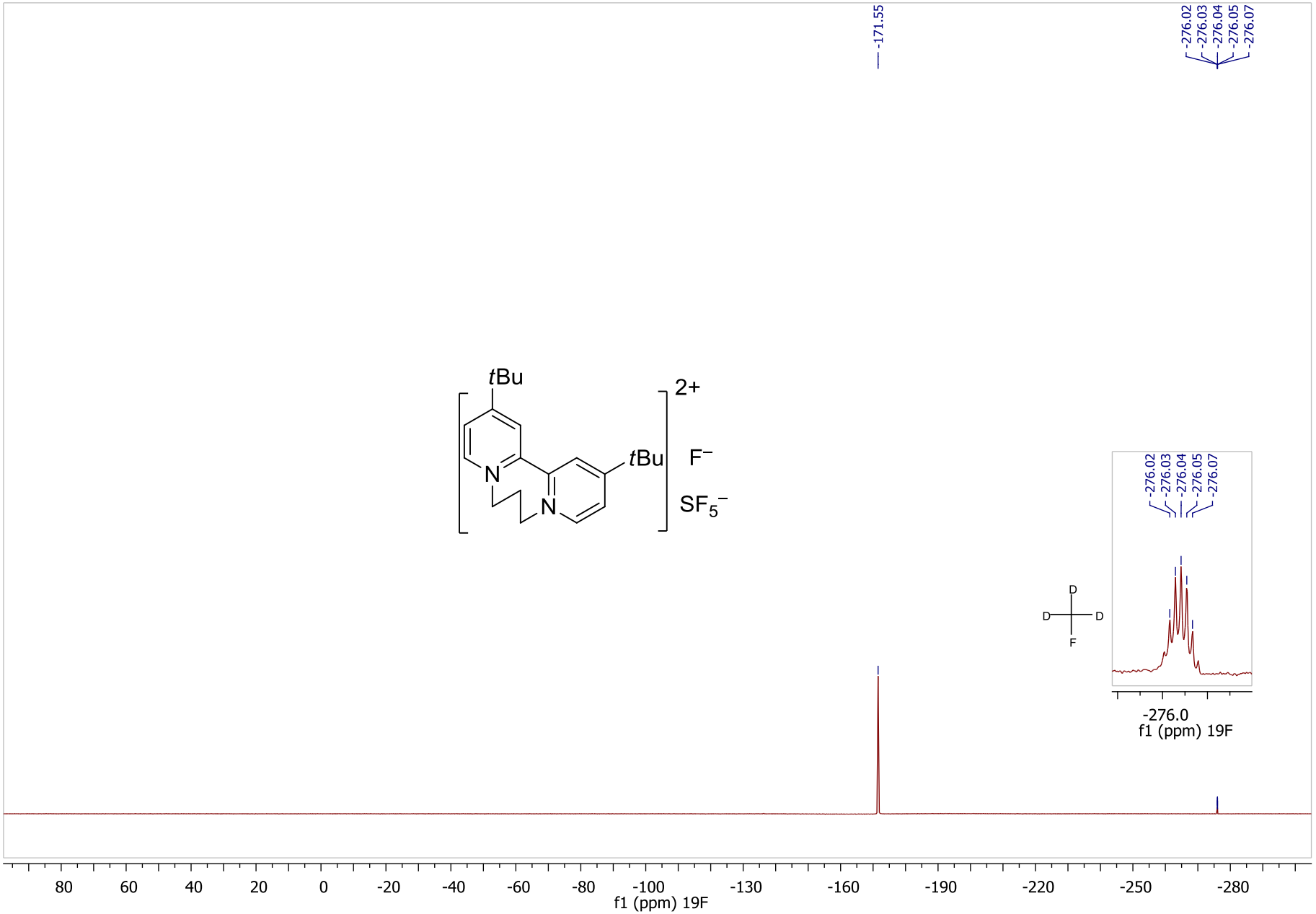
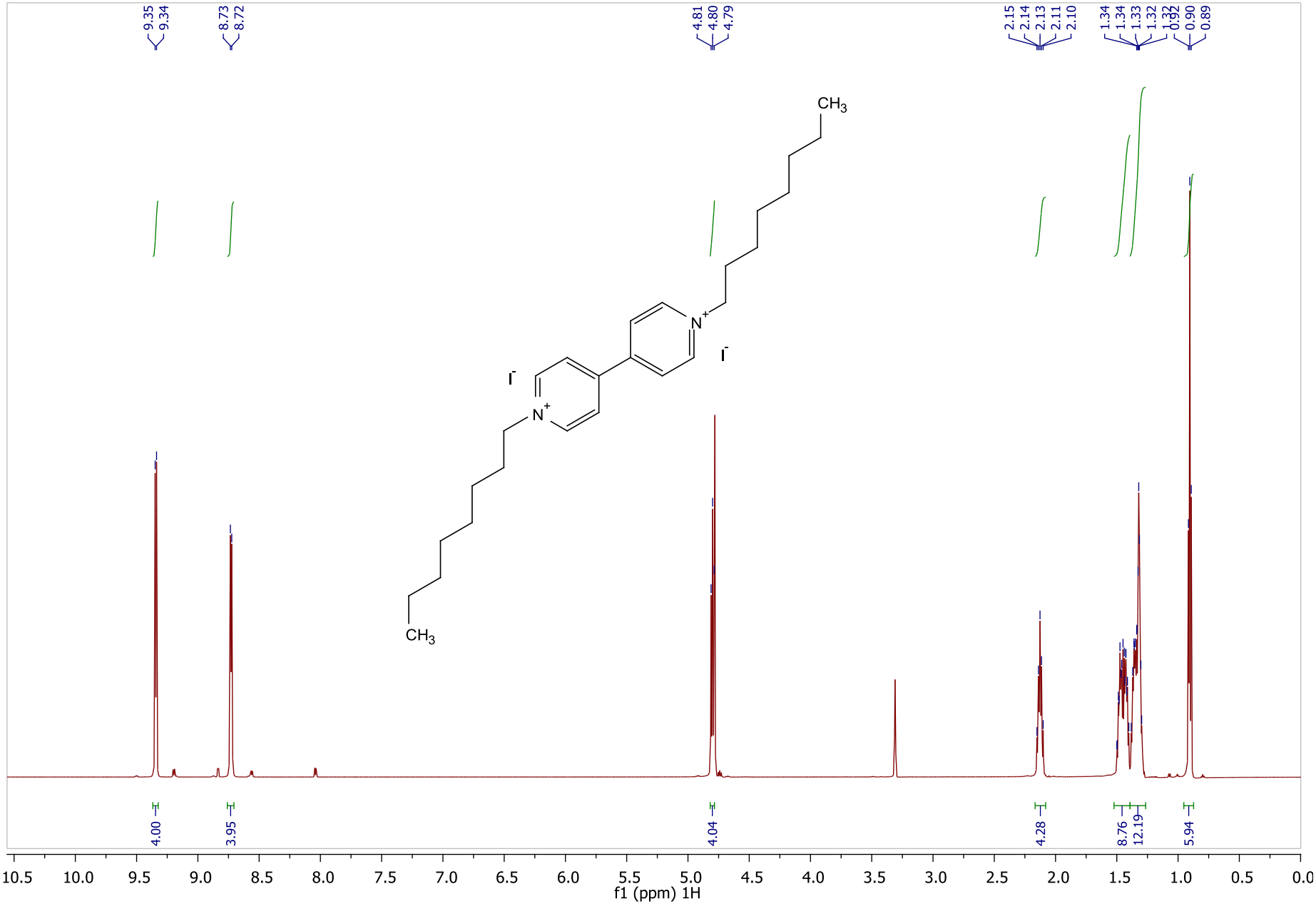
4.95
4.94
2.93
2.92
2.91
1.10
0.86
0.85
0.84
0.83
0.82
CH3
H3C
CH3
CH3
H3C
H3C
N
N
2.11
2.00
1.91
4.29
18.71
2.35
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm) 1H

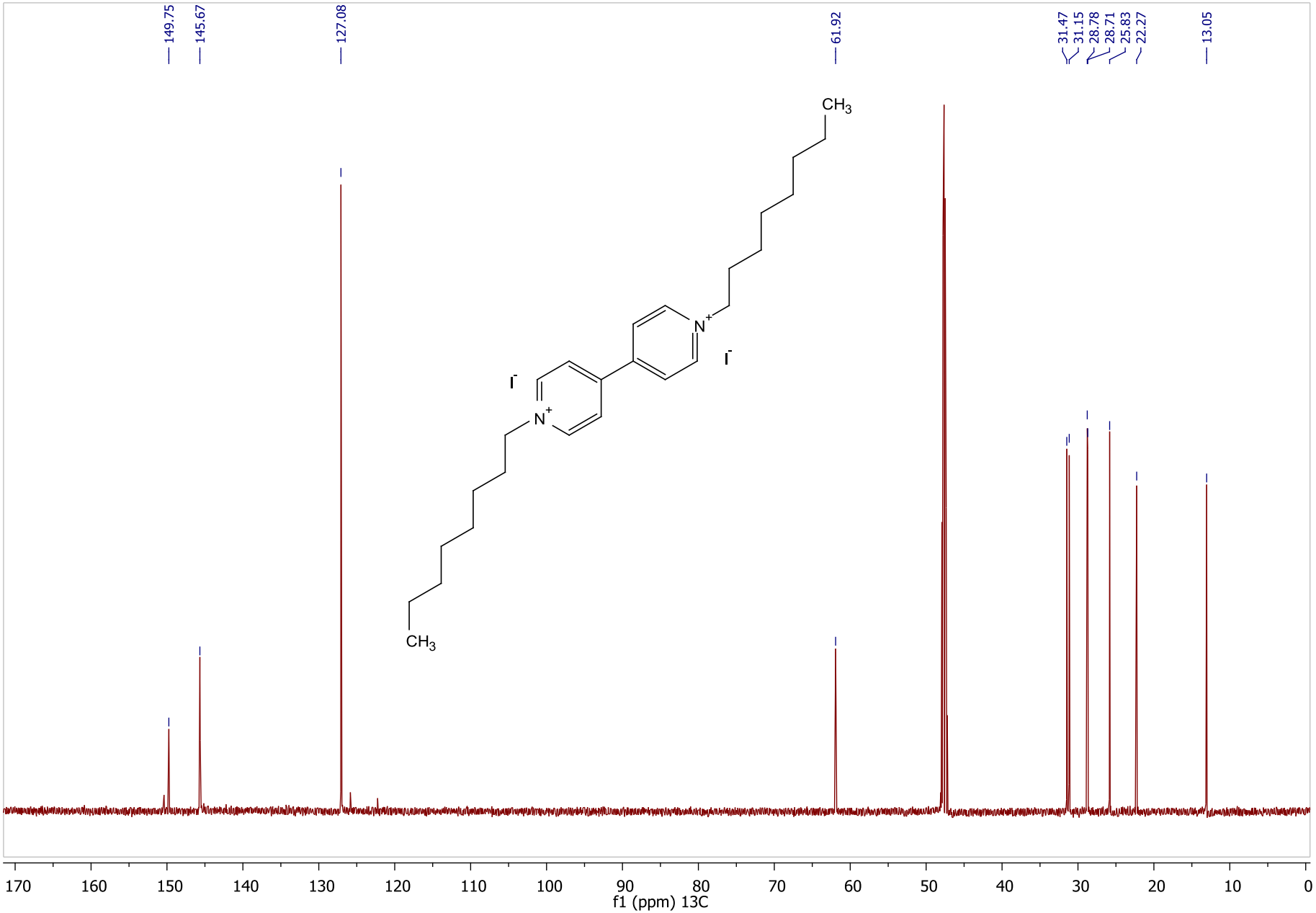

139.75
136.98
128.22
128.06
127.90
118.60
113.63
100.07
51.68
33.69
29.22
22.01
CH3
H3C
CH3
CH3
H3C
H3C
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

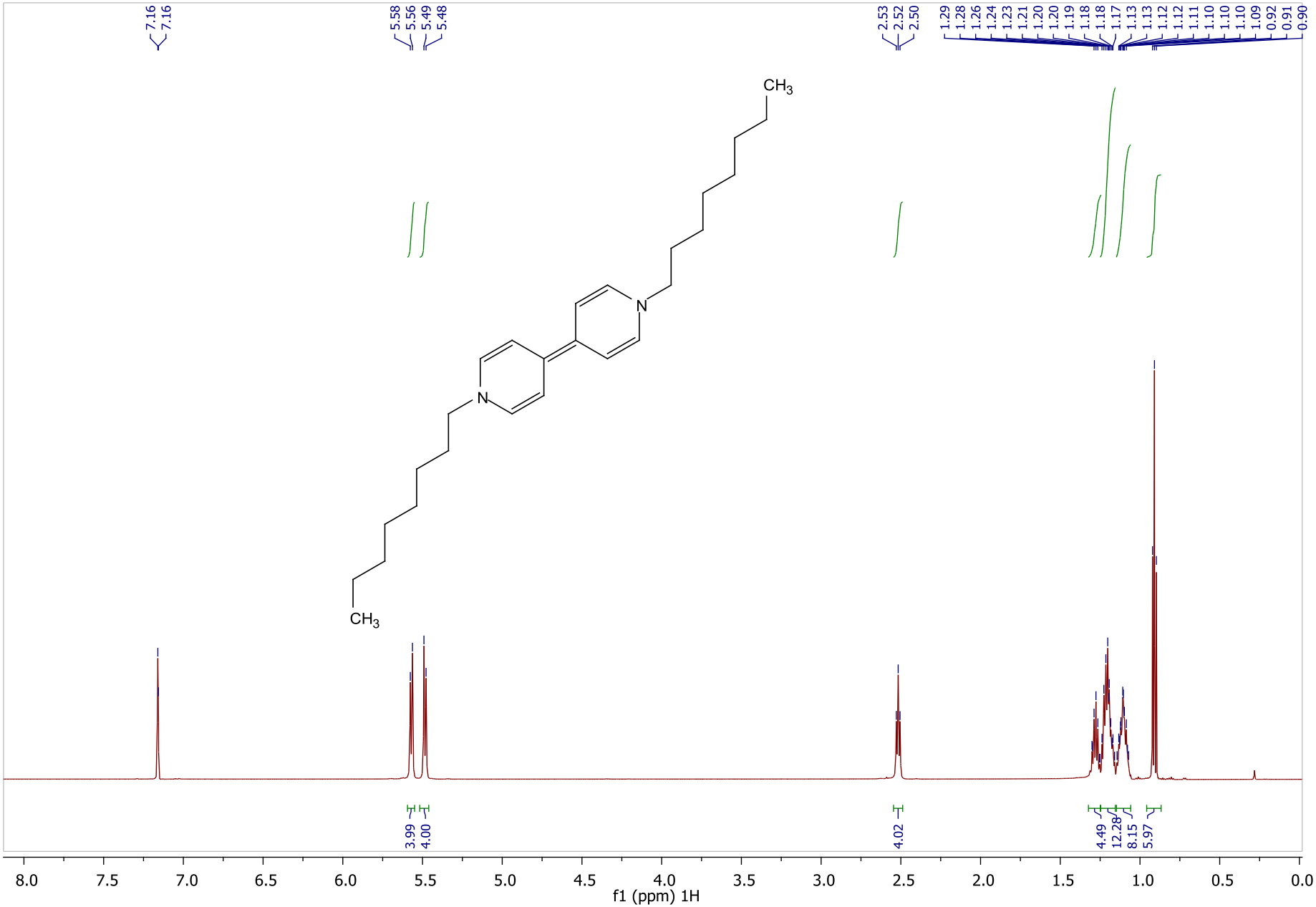

9.18
9.17
8.55
8.54
8.48
8.48
8.47
8.47
5.04
5.03
5.03
5.01
5.01
4.49
4.47
4.47
4.47
4.46
4.45
4.45
4.43
2.89
2.88
2.88
2.87
2.87
2.86
2.86
2.85
2.85
2.85
1.56
tBu
tBu
N
N
2+
F⁻
SF5⁻
2.00
1.86
1.92
2.18
2.10
2.14
18.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm) 1H

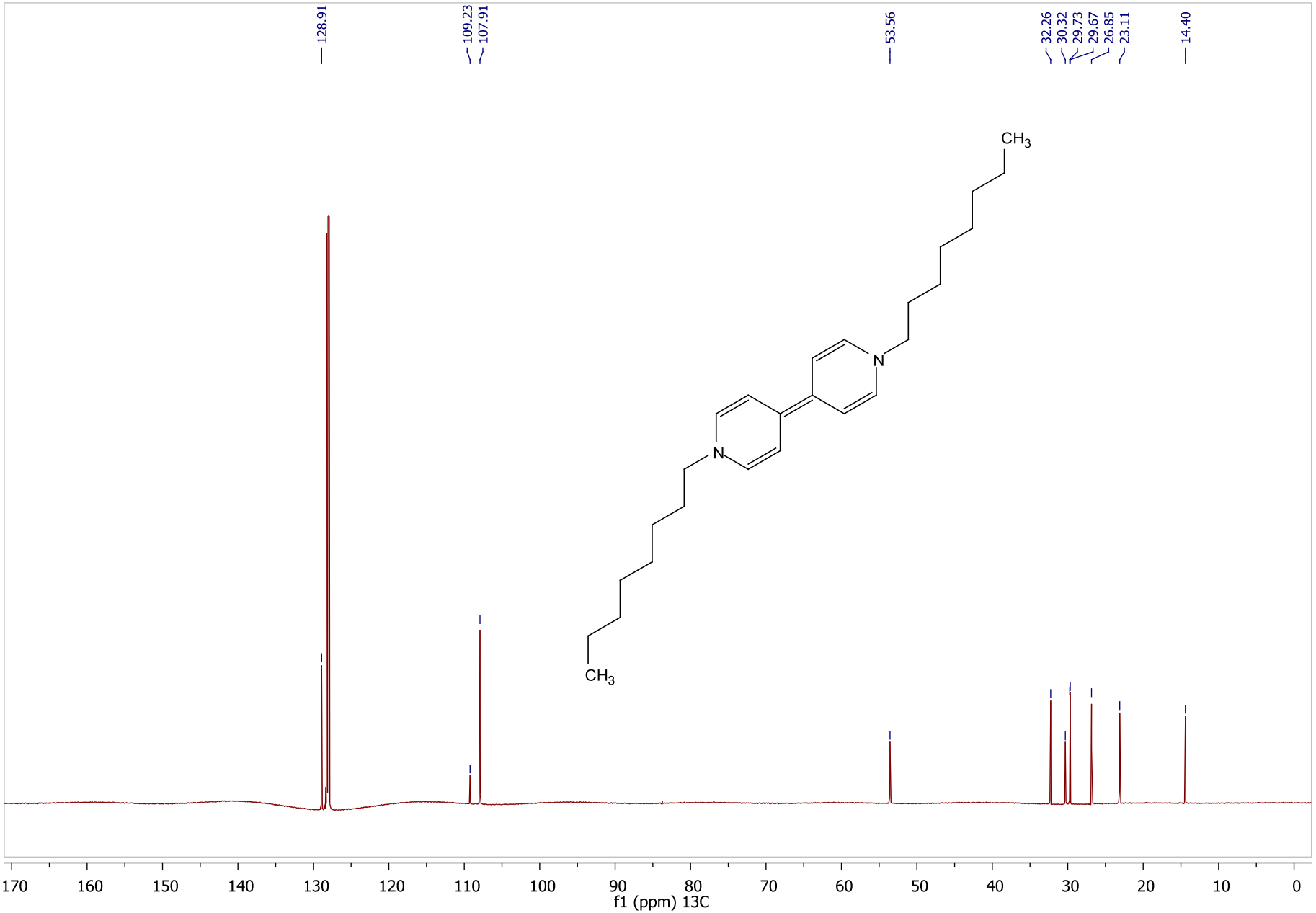

175.36
148.07
145.18
130.31
129.12
56.22
38.38
31.51
30.14
tBu
tBu
N
N
2+
F⁻
SF5⁻
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm) 13C

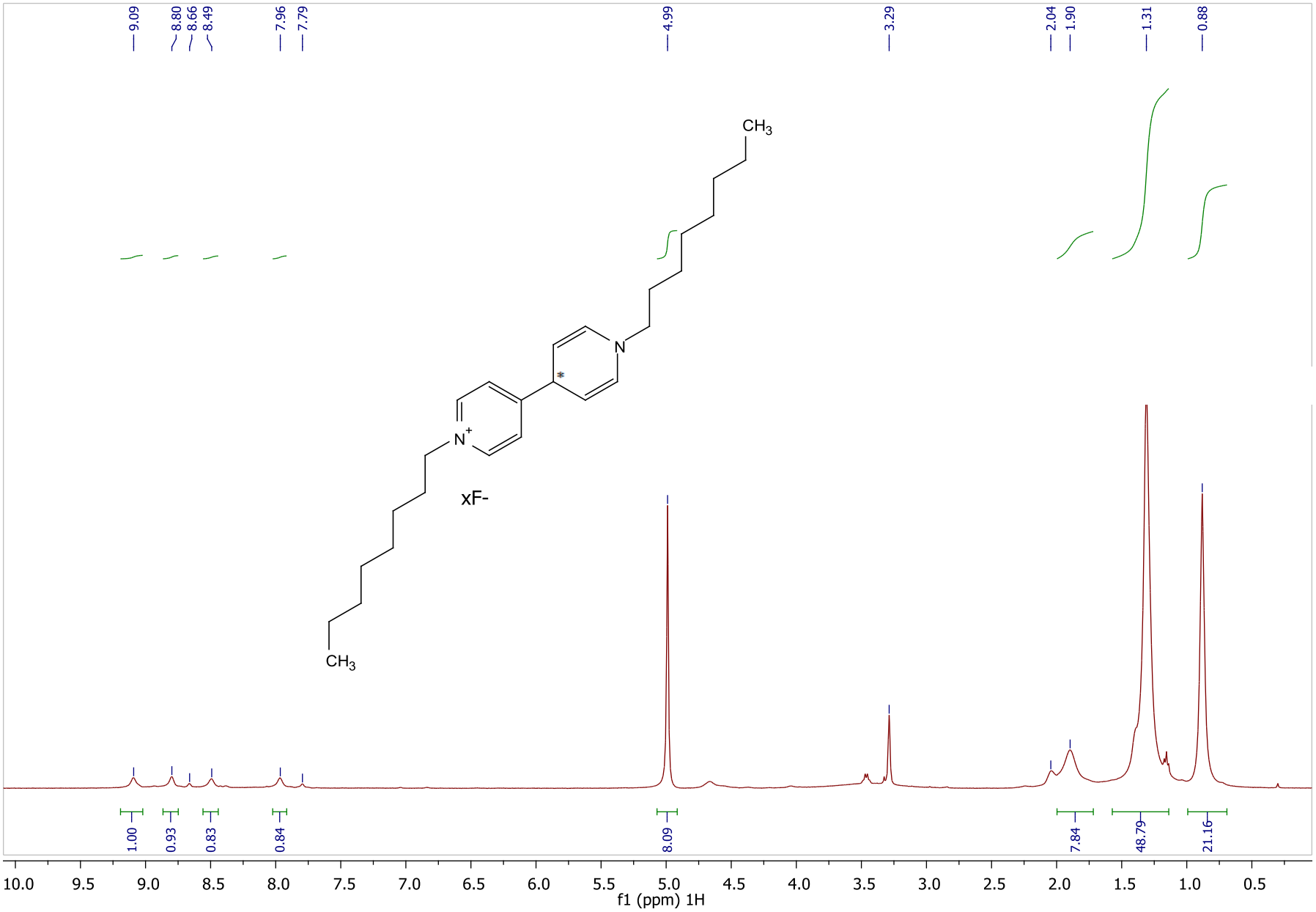

-171.55
-276.02
-276.03
-276.04
-276.05
-276.07
tBu
tBu
2+
F⁻
SF5⁻
N
N
D
D
D
F
-276.0
f1 (ppm) 19F
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
-280
f1 (ppm) 19F

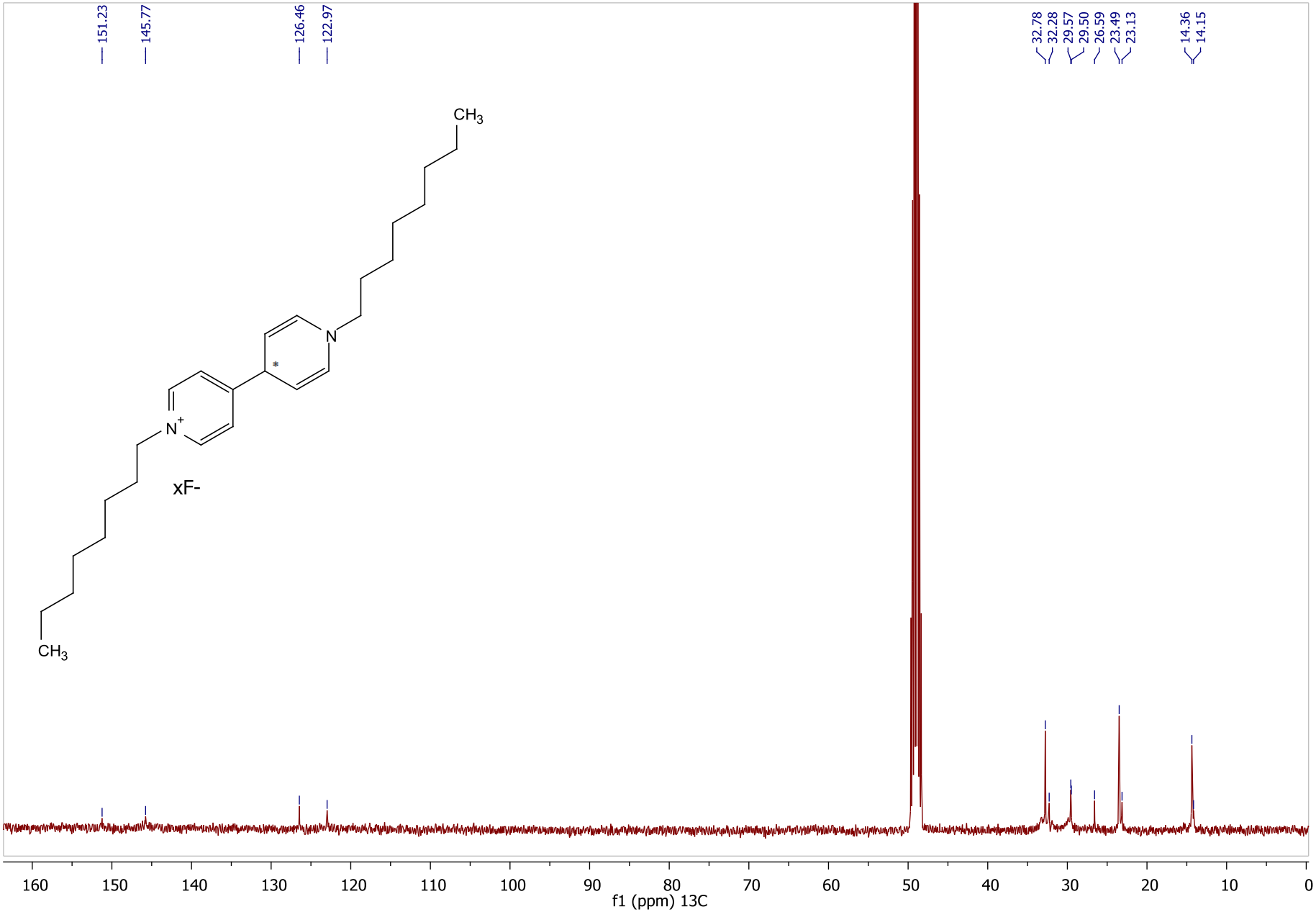

9.35
9.34
8.73
8.72
4.81
4.80
4.79
2.15
2.14
2.13
2.11
2.10
1.34
1.34
1.33
1.32
0.92
0.90
0.89
CH3
N+
I-
I-
N+
CH3
4.00
3.95
4.04
4.28
8.76
12.19
5.94
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm) 1H

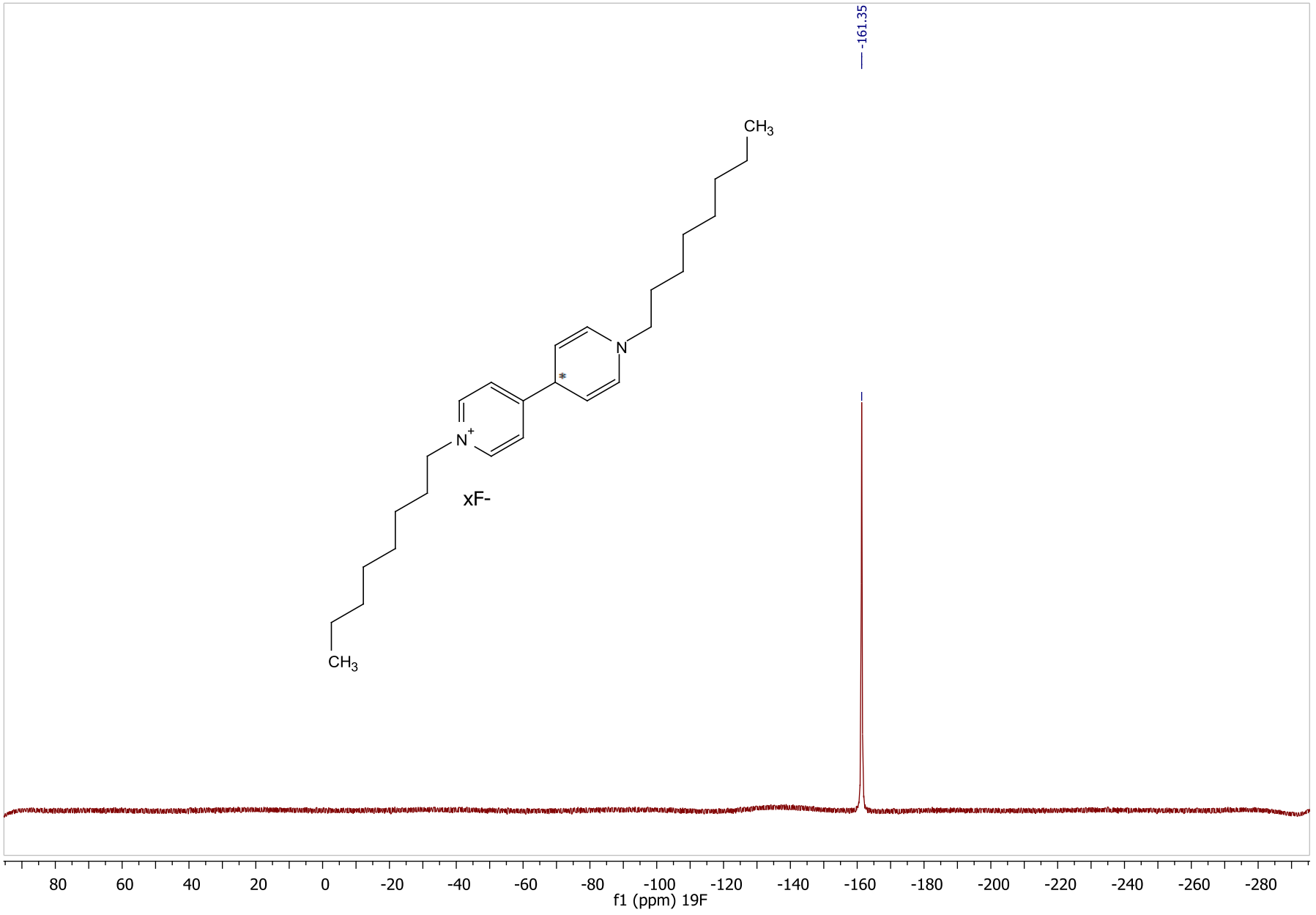

149.75
145.67
127.08
61.92
31.47
31.15
28.78
28.71
25.83
22.27
13.05
CH3
N+
I-
I-
N+
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

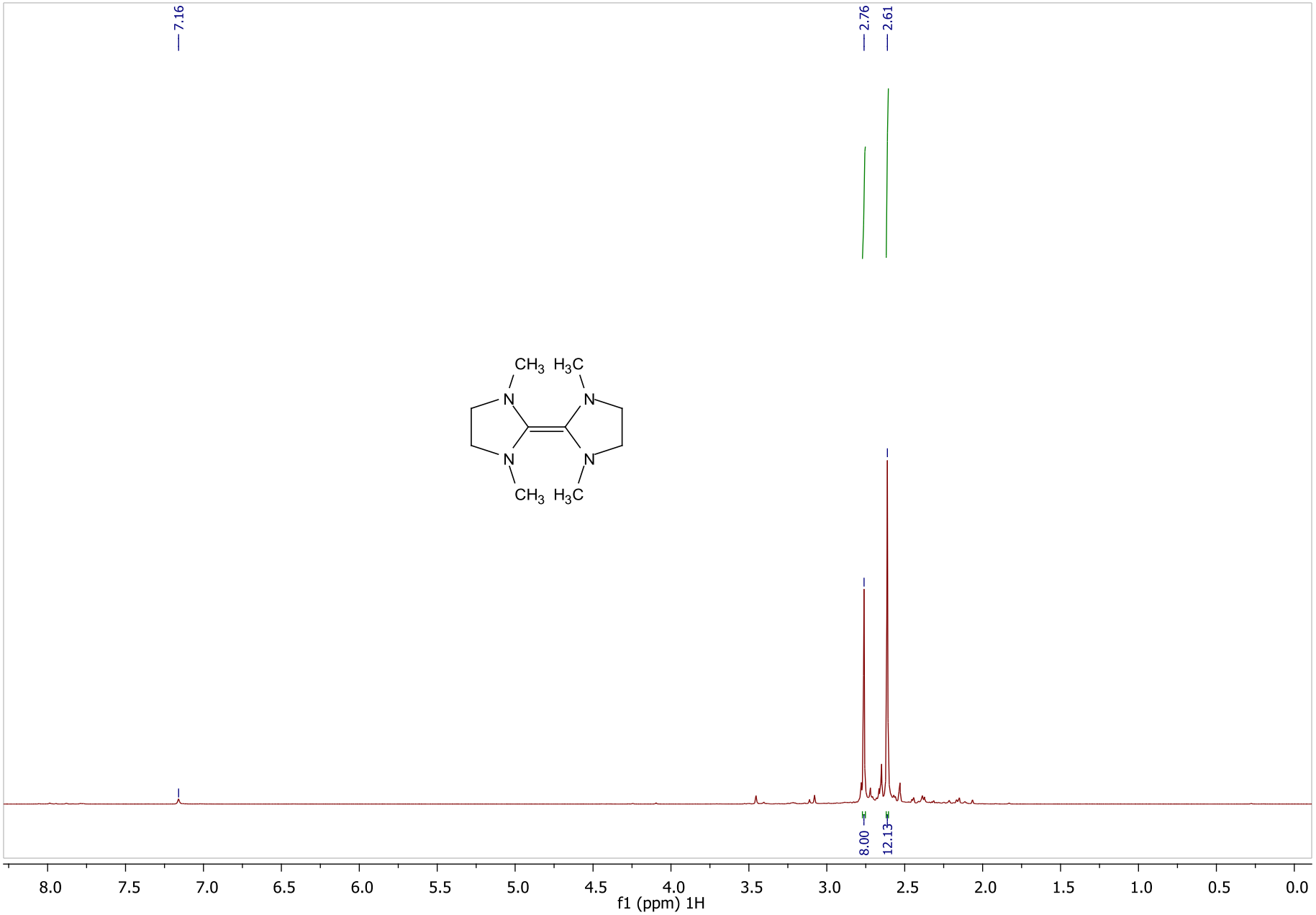

7.16
7.16
5.58
5.56
5.49
5.48
2.53
2.52
2.50
1.29
1.28
1.26
1.24
1.23
1.21
1.20
1.20
1.19
1.18
1.18
1.17
1.13
1.13
1.12
1.12
1.11
1.10
1.10
1.10
1.09
0.92
0.91
0.90
CH3
N
N
CH3
3.99
4.00
4.02
4.49
12.28
8.15
5.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm) 1H

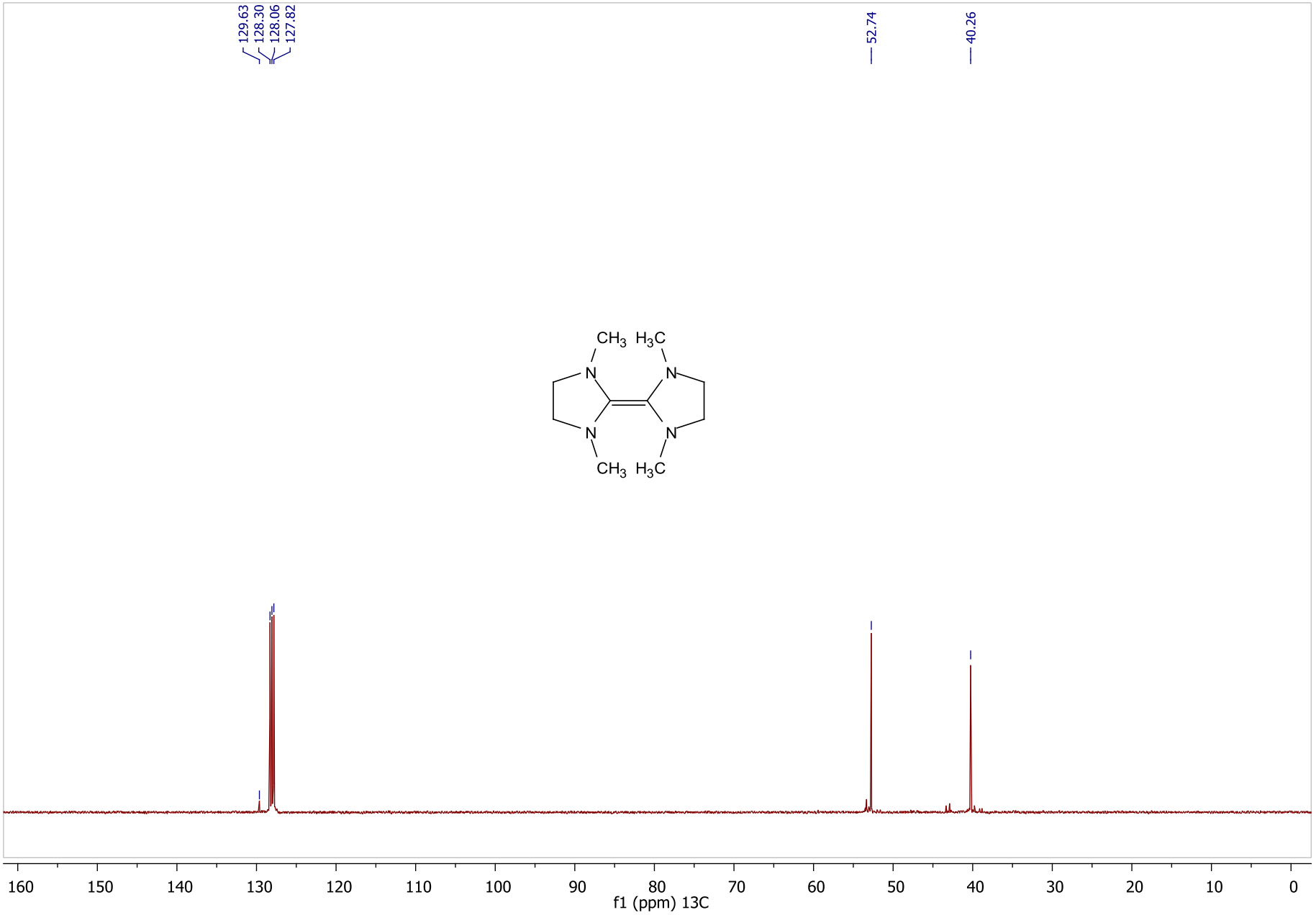

128.91
109.23
107.91
53.56
32.26
30.32
29.73
29.67
26.85
23.11
14.40
CH3
N
N
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

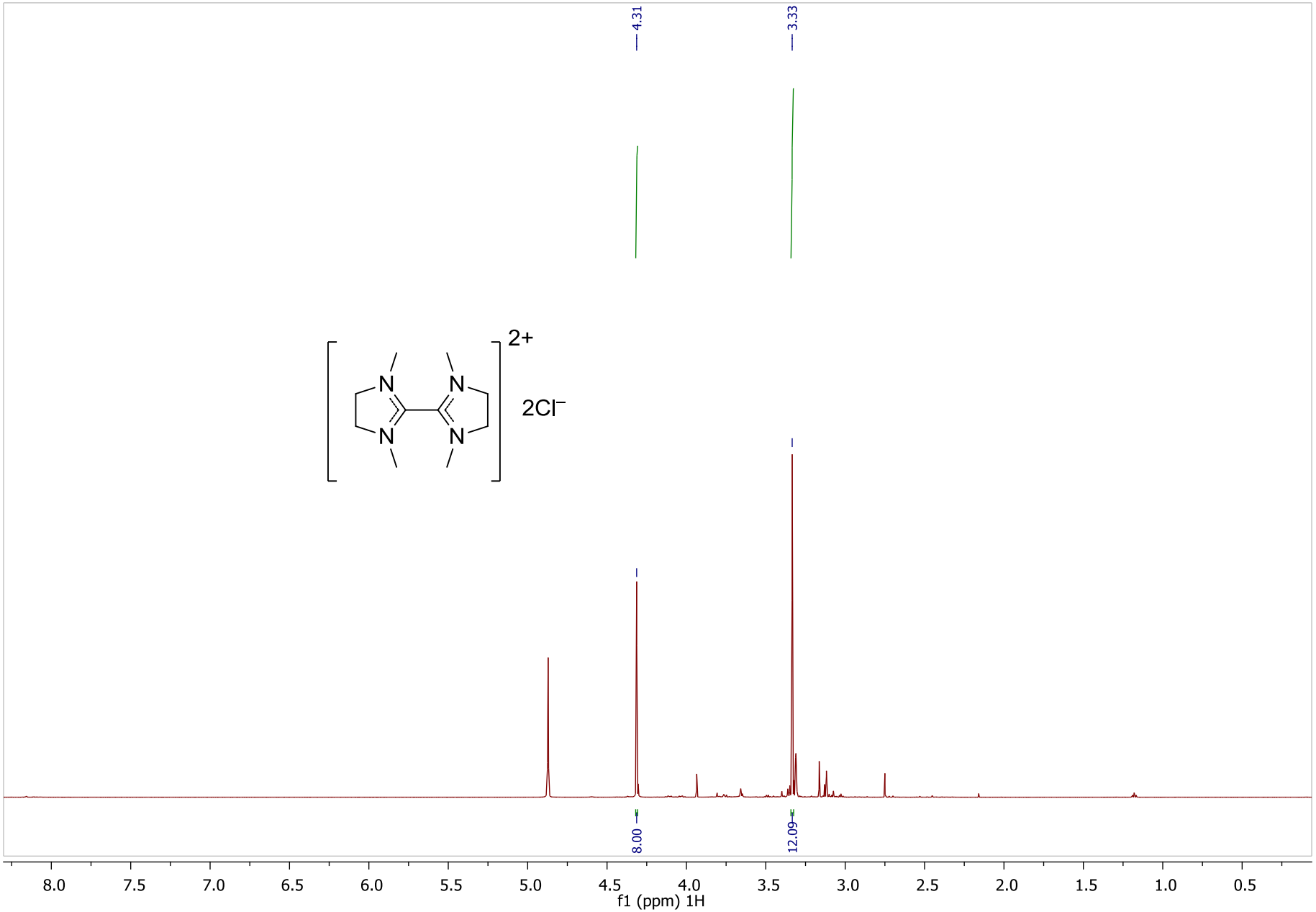

9.09
8.80
8.66
8.49
7.96
7.79
4.99
3.29
2.04
1.90
1.31
0.88
CH3
N
N+
xF-
CH3
1.00
0.93
0.83
0.84
8.09
7.84
48.79
21.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm) 1H

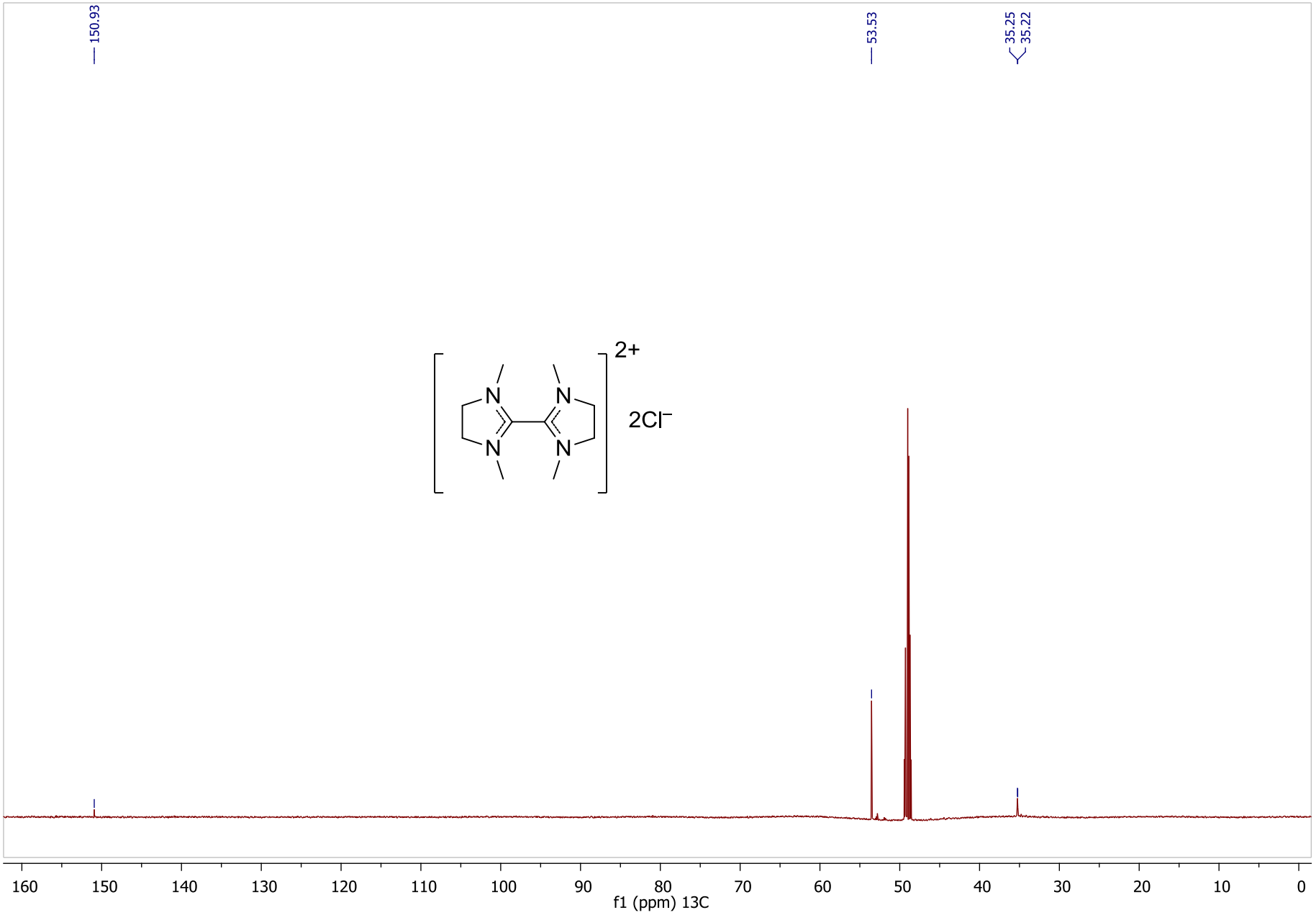

151.23
145.77
126.46
122.97
32.78
32.28
29.57
29.50
26.59
23.49
23.13
14.36
14.15
CH3
N
N+
xF-
CH3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

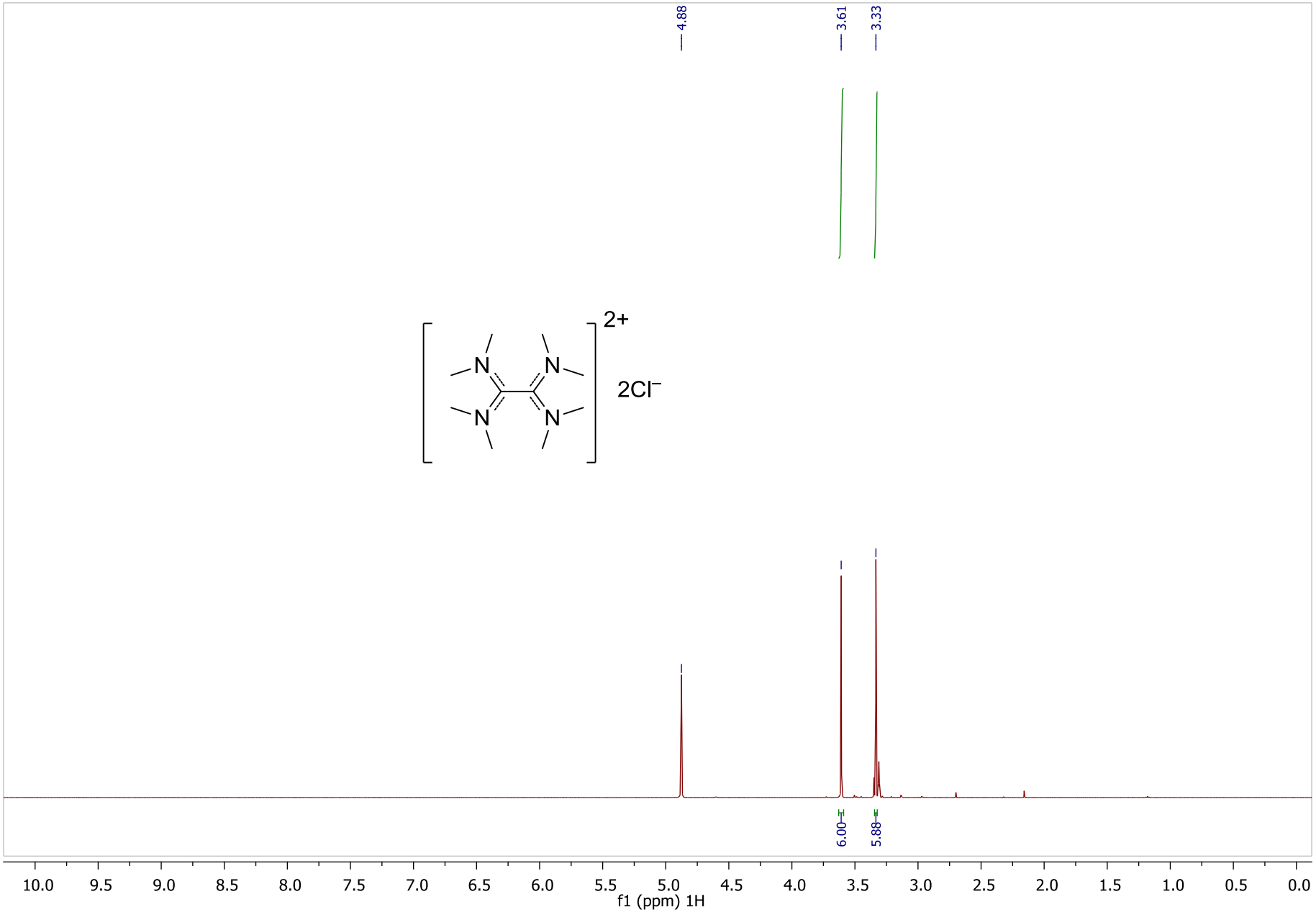

-161.35
CH3
N
N+
xF-
CH3
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
f1 (ppm) 19F

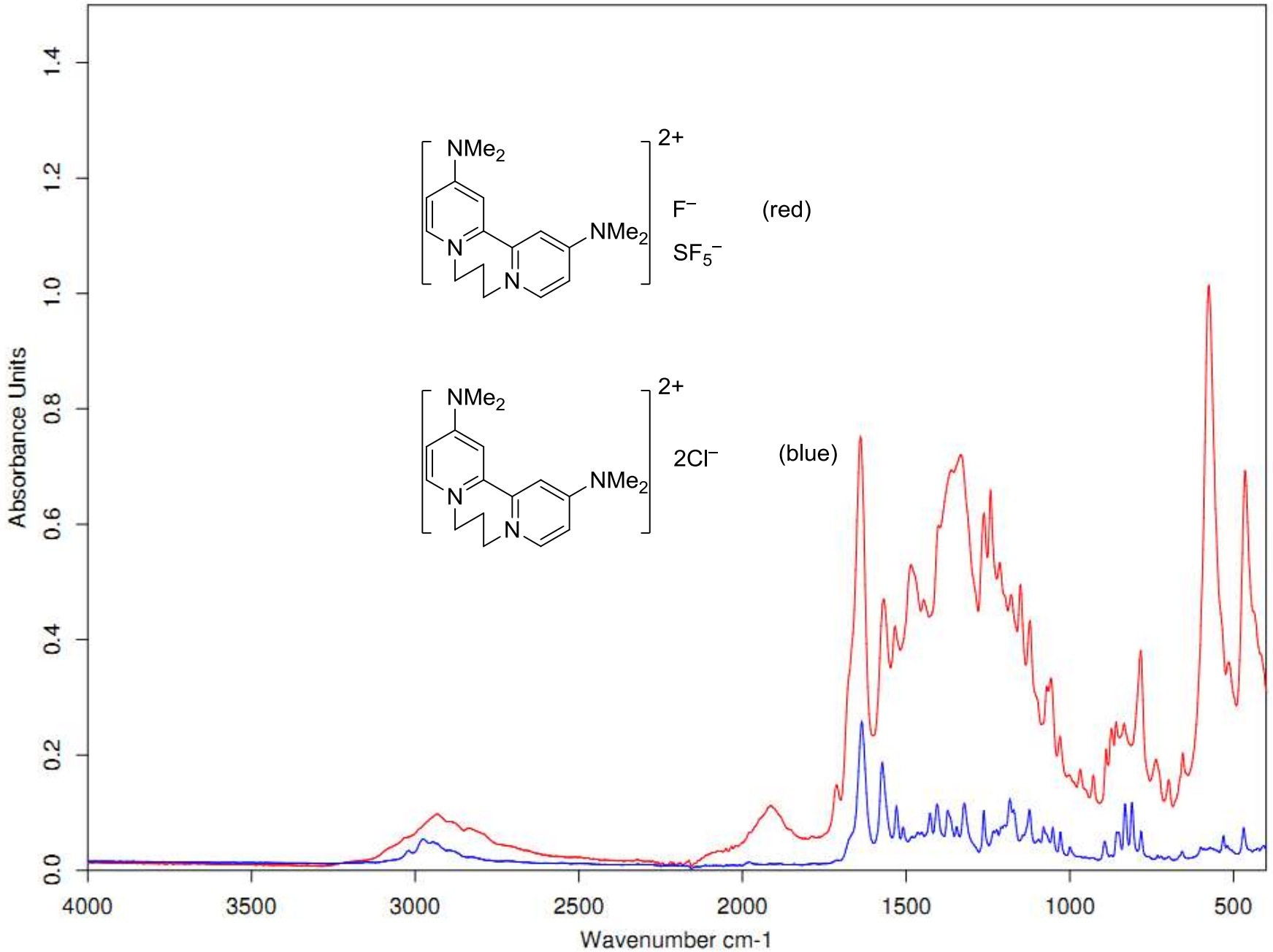

7.16
2.76
2.61
CH3 H3C
N
N
N
N
CH3 H3C
8.00
12.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm) 1H


129.63
128.30
128.06
127.82
52.74
40.26
CH3 H3C
N
N
N
N
CH3 H3C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C

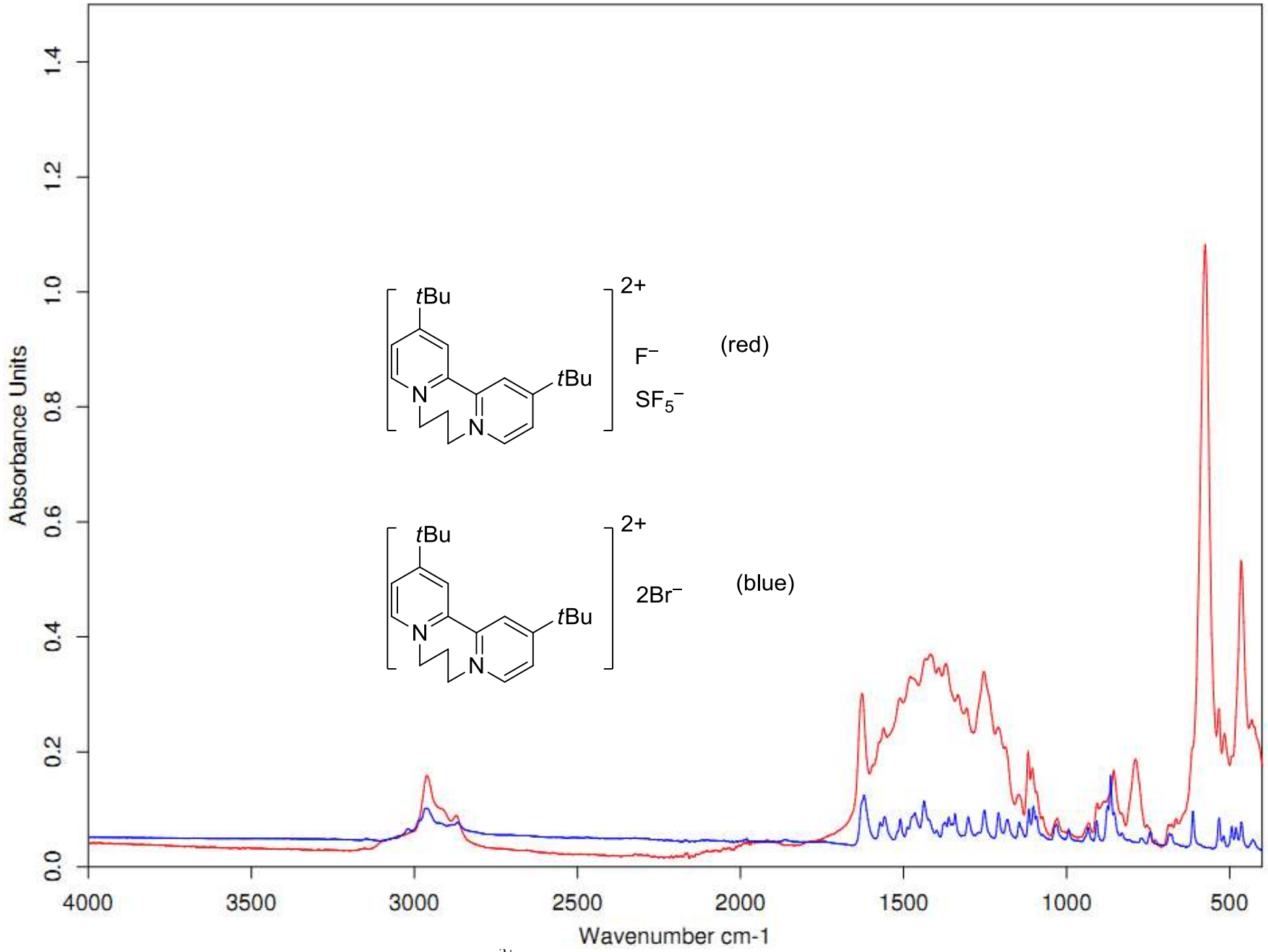

4.31
3.33
2+
2Cl⁻
N
N
N
N
8.00
12.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm) 1H


150.93
53.53
35.25
35.22
2+
2Cl⁻
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm) 13C


4.88
3.61
3.33
2+
N
N
N
N
2Cl⁻
6.00
5.88
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm) 1H



The IR spectra of the **2a** (upper red line) and parental $D^{2+}2Cl^{-}$ **1a'** (bottom blue line) at r.t.



The IR spectra of the **2b** (upper red line) and parental $D^{2+}2Br^{-}$ **1b'** (bottom blue line) at r.t.