Supplementary Information

A Simple Amine Protection Strategy for Olefin Metathesis Reactions

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Experimental Section

All chemicals were purchased from Aldrich and used without further purification unless stated otherwise. Anhydrous *p*-toluenesulphonic acid was dried under vacuum (1 mmHg) at 100-110°C for 4h. Dichloromethane was dried over $CaCl_2$, distilled from CaH and degassed by applying an argon sparge prior to use in all metathesis reactions.[10] The following primary amines were synthesised according to literature procedures: 10-undecen-1-amine,[11] *N*-benzyl-2-propen-1-amine[12] and 2-allyl-4-penten-1-amine.[13] Melting points (m.p.) were measured on a Stuart Scientific SMP 3 melting point apparatus. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a Brüker DPX 300 MHz spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C) or a Brüker DRX 400 MHz spectrometer (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR), as solutions in deuterated solvents as specified. The ^{13}C NMR spectra were recorded using a JMOD pulse sequence or proton decoupled pulse sequence unless stated otherwise. Low-resolution electrospray ionisation (LR-ESI) mass spectra were recorded on a Micromass Platform II API QMS-quadrupole electrospray mass spectrometer as specified. $[M]^+$ denotes the molecular ion. High-resolution electrospray (HR-MS) were recorded on a Brüker BioApex 47e Fourier Transform mass spectrometer and were recorded as specified.

Two methods were used to prepare the olefinic ammonium salts: Method A was *via* direct salt formation by acid/base exchange,[14] and Method B was *via* HCl salt formation followed by silver salt precipitation. The yields of the olefinic ammonium salt starting materials obtained using either procedure (A or B), were near quantitative in all cases.

Method A: A solution of *p*-toluenesulphonic acid (3 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of olefinic amine (3 mmol) in CH_2Cl_2 (10 mL) at room temperature. After stirring for 10 min, the turbid mixture became clear. The solvent was then removed by rotary evaporation and the resultant amine salt was dried on a high vacuum pump.

Method B: A solution of silver salt (1 mmol) in EtOH (5 mL) was added to a stirred solution of the olefinic ammonium chloride (1 mmol) in EtOH (5 mL) at room temperature. The reaction mixture became cloudy upon addition of the silver salt. After 10 min, the mixture was gravity filtered to remove precipitated AgCl. The ethanolic filtrate was then evaporated by rotary evaporation and the resultant amine salt was dried on a high vacuum pump.

Characterisation data for olefinic ammonium salts:

3-Butenyl ammonium triflate (**4b**): colourless solid, m.p. 135-137°C; ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 5.73-5.67 (m, 1H); 5.25-5.19 (m, 2H); 3.09 (t, 2H, *J* 7.1 Hz); 2.44 (q, 2H, *J* 7.1 Hz); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, d_4-MeOH): 32.6, 39.9, 119.2, 134.0. $\underline{C}F_3$ not observed.

3-Butenyl ammonium tetrafluoroborate (**4c**): colourless solid, m.p. 141-143°C; ^{1}H n.m.r. (400 MHz, d_6-Acetone): δ 5.91-5.81 (m, 1H), 5.25-5.12 (m, 2H), 3.26 (t, 2H, *J* 7.4 Hz), 2.57 (q, 2H, *J* 7.4 Hz); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, d_4-MeOD): 32.6, 40.0, 119.2, 134.1.

3-Butenyl ammonium tosylate (**4d**): colourless solid, m.p. 104-106°C; ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.75 (d, 2H, *J* 8.1 Hz, ArH); 7.19 (d, 2H, *J* 8.1 Hz, ArH); 5.61-5.53 (m, 1H); 5.03-4.98 (m, 2H); 2.83 (t, 2H, *J* 7.6 Hz); 2.36 (s, 3H); 2.28 (q, 2H, *J* 7.6 Hz); NH_3 not detected due to exchange. ^{13}C n.m.r. (100 MHz, $CDCl_3$): 142.8, 141.1, 132.8, 129.3, 126.1, 118.6, 39.3, 31.6, 21.5.

2-Propenyl ammonium tosylate (**4e**): colourless solid, m.p. 98-99°C; ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.85 (bs, 3H, NH_3); 7.73 (d, 2H, *J* 7.7 Hz, ArH); 7.17 (d, 2H, *J* 7.7 Hz, ArH); 5.83-5.72 (m, 1H); 5.27-5.16 (m, 2H); 2.36 (s, 3H, Ar-CH_3). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.2, 141.0, 129.7, 129.2, 126.2, 121.1, 42.2, 21.5.

N-Benzyl-2-propenyl ammonium tosylate (**4f**): colourless solid, m.p. 121-122°C; ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 9.13 (bs, 2H, NH_2); 7.69 (d, 2H, *J* 8.4 Hz); 7.43 (m, 2H); 7.28 (m, 3H); 7.18 (d, 2H, *J* 8.4 Hz); 6.00-5.86 (m, 1H); 5.36-5.29 (m, 2H); 4.06 (t, 2H, *J* 5.4 Hz); 3.45 (q, 2H, *J* 6.1 Hz); 2.38 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.7, 140.4, 130.3, 130.2, 129.2, 129.0, 128.9, 127.9, 125.9, 123.8, 49.5, 48.3, 21.3.

1-Methylcarboxy-3-butenyl ammonium tosylate (**4h**): colourless solid, m.p. 110-112°C; ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.75 (d, 2H, *J* 8.2 Hz, ArH); 7.15 (d, 2H, *J* 8.2 Hz, ArH); 5.68-5.58 (m, 1H); 5.13-5.02 (m, 2H); 4.06 (t, 1H, *J* 6.0 Hz); 3.64 (s, 3H, OMe); 2.58 (dt, 2H, *J* 6.4 Hz, *J* 1.2 Hz); 2.35 (s, 3H); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, $CDCl_3$): 169.4, 141.7, 140.5, 130.4, 129.0, 126.3, 120.9, 52.8, 52.7, 34.6, 21.4.

10-Undecenylammonium tosylate (**4i**): colourless semi-solid. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.73 (d, 2H, *J* 8.0 Hz, ArH); 7.51 (bs, 3H, NH_3); 7.16 (d, 2H, *J* 8.0 Hz, ArH); 5.84-5.75 (m, 1H); 5.01-4.91 (m, 2H); 2.77 (bs, 2H); 2.36 (s, 3H); 2.04-1.99 (m, 2H), 1.48 (m, 2H), 1.38-1.06 (m, 12H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.3, 140.6, 139.3, 129.3, 126.2, 114.4, 40.3, 34.0, 29.7, 29.6, 29.3, 29.2, 29.1, 27.6, 26.5, 21.6.

10-Undecenylammonium chloride (**4j**): colourless semi-solid. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 8.30 (bs, 3H, NH_3); 5.84-5.75 (m, 1H); 5.01-4.91 (m, 2H); 2.98 (bs, 2H); 2.03 (m, 2H), 1.77 (m, 2H), 1.42-1.25 (m, 12H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 139.3, 114.3, 34.0, 32.8, 29.7, 29.6, 29.2, 29.1, 28.0, 26.8, 25.9.

2-Allyl-4-pentenyl ammonium tosylate (**4k**): colourless semi solid; ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.73 (d, 2H, *J* 8.0 Hz); 7.59 (bs, 3H, NH_3); 7.18 (d, 2H, *J* 8.0 Hz); 5.64-5.54 (m, 2H); 5.05-4.97 (m, 4H); 2.77 (t, 2H, *J* 6.0 Hz, NCH_2); 2.33 (s, 3H, $ArCH_3$); 2.03 (m, 4H, CH_2); 1.82 (p, 1H, *J* 6.4 Hz). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.1, 140.8, 135.0, 130.7, 129.3, 126.2, 43.0, 35.6, 35.0, 21.5.

Diallyl ammonium tosylate (**4l**): colourless ionic liquid. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 8.95 (bs, 2H, NH_2); 7.73 (d, 2H, *J* 8.4 Hz); 7.19 (d, 2H, *J* 8.4 Hz); 5.98-5.83 (m, 2H); 5.42-5.36 (m, 4H); 3.59 (q, 4H, *J* 5.6 Hz); 2.38 (s, 3H). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.8 (*i*-ArC), 140.8 (*p*-ArC), 129.1 (*m*-ArCH), 128.0 (*o*-ArCH), 126.1 (=CH), 124.2 (=CH_2), 48.5 (*N*-CH_2), 21.5 (CH_3).

N,N',-Dimethyl diallyl ammonium tosylate (**4m**): colourless solid, m.p. 45-49°C; ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 7.77 (d, 2H, *J* 8.0 Hz); 7.14 (d, 2H, *J* 8.0 Hz); 5.97-5.89 (m, 2H); 5.79-

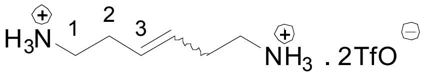
5.67 (m, 4H); 4.16 (d, 4H, *J* 7.2 Hz, CH_2); 3.20 (s, 6H, NCH_3); 2.33 (s, 3H, $ArCH_3$). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 143.9, 139.2, 129.5, 128.6, 125.8, 124.4, 65.7, 49.5, 21.2.

Ammonium tosylate metathesis products (5d-l):

The following is an example of a conventional metathesis procedure for the metathesis of alkenyl ammonium tosylates (**4**): Under an inert atmosphere of nitrogen, a Schlenk tube was charged with 3-butenyl ammonium tosylate (**4d**) (52 mg, 0.15 mmol), 2nd gen. Hoveyda-Grubbs second generation catalyst (4.8 mg, 5 mol%) and a small magnetic stir bar. The CH_2Cl_2 (2mL) was added through a rubber septum and the tube was sealed and heated at reflux under nitrogen for 24 hours. The vessel was then cooled to room temperature and the reaction solvent was removed by rotary evaporation. Crystallization from icec-cold acetone and filtration gave 3-hexene-1,6-diammonium-ditosylate (**5d**) (50 mg, 95%) as a colourless, microcrystalline solid.

The following is an example of a microwave assisted metathesis procedure for the metathesis of alkenyl ammonium tosylates (**4**): Under an inert atmosphere of nitrogen, a quartz microwave vessel was charged with allylammonium tosylate (**4e**) (50 mg, 0.22 mmol), Hoveyda-Grubbs second generation catalyst (6.9 mg, 5 mol%), CH_2Cl_2 (2mL) and a small magnetic stir bar. The vessel was sealed and irradiated in a CEM discovery microwave (Benchmate) at 100˚C, 100 watts for 2 h with cooling. The vessel was cooled to room temperature and solvent removed by rotary evaporation. Crystallization from cooled CH_2Cl_2 and filtration gave pure 2-butene-1,4-diammonium-ditosylate (**5e**) (47 mg, 74%) as a colourless, microcrystalline solid.

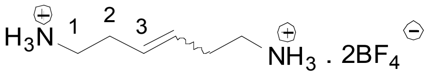
3-Hexene-1,6-diammonium ditriflate (**5b**)



Conventional: Crystallized from CH_2Cl_2 as a light brown solid (39 mg, 83% yield). Note: The product formed a gel during the reaction, m.p. 223°C (dec); ^1H n.m.r. (200 MHz, *d*$_4$-MeOD): δ 5.62 (m, 2H, =CH); 3.12 (t, *J* 7.2 Hz, 4H, NCH_2); 2.48 (m, 4H, =CH<u>CH</u>$_2$). ^{13}C n.m.r. (100

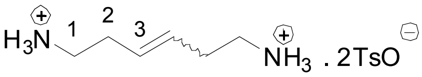
MHz, d_4-MeOD): 129.9 (C3), 128.8 (OTf), 40.1 (C1), 31.5 (C2). HR-MS (ESI, +ve, MeOH): Calculated m/z 115.1232; Observed m/z 115.1230 $[M\text{-}2TfOH+H]^+$.

3-Hexene-1,6-diammonium ditetrafluoroborate (**5c**)



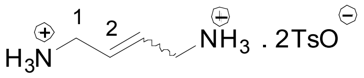
Conventional: 91% conversion, as determined by ^{1}H n.m.r. spectroscopy. The compound could be precipitated from acetone but decomposed during filtration. ^{1}H n.m.r. (400 MHz, d_4-MeOD): δ 5.63 (m, 2H, =CH); 3.01 (t, *J* 7.2 Hz, 4H, NCH_2); 2.40 (m, 4H, $=CH\underline{CH_2}$); NH not detected due to exchange.

3-Hexene-1,6-diammonium-ditosylate (**5d**)



Conventional: Crystallized from CH_2Cl_2, 92% yield.
Microwave: Crystallized from CH_2Cl_2, 95% yield.
m.p. 181-184°C; ^{1}H n.m.r. (200 MHz, D_2O): δ 7.76 (d, *J* 8.1 Hz, 4H, ArH); 7.44 (d, *J* 8.1 Hz, 4H, ArH); 5.68 (m, 2H, =CH); 3.12 (t, *J* 7.2 Hz, 4H, NCH_2); 2.48 (m, 10H, $ArCH_3$, $=CH\underline{CH_2}$); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, d_4-MeOH): 143.5 (TsO^-), 141.8 (TsO^-), 130.1 (C3), 129.9 (TsO^-), 126.9 (TsO^-), 40.3 (C1), 31.5 (C2), 21.3 (CH_3). HR-MS (ESI, +ve, MeOH): Calculated *m/z* 115.1230; Observed *m/z* 115.1230 $[M\text{-}2TsOH+H]^+$.

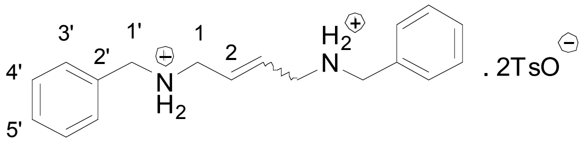
2-Butene-1,4-diammonium ditosylate (**5e**)



Conventional: Crystallized from CH_2Cl_2, 40 % yield.
Microwave: Crystallized from CH_2Cl_2, 74 % yield (13% using 1 mol% cat. loading).
m.p. 238-242°C; ^{1}H n.m.r. (300 MHz, D_2O): δ 7.77 (d, *J* 8.2 Hz, 4H, ArH); 7.45 (d, *J* 8.2 Hz, 4H, ArH); 6.06 (m, 2H, =CH); 3.74 (m, 4H, NCH_2); 2.47 (m, 6H, $ArCH_3$); NH not detected

due to exchange. ^{13}C n.m.r. (100 MHz, *d$_4$*-MeOD): 143.4 (TsO$^-$), 141.9 (TsO$^-$), 129.9 (TsO$^-$), 129.6 (C2), 126.9 (TsO$^-$), 41.6 (C1), 21.3 (CH$_3$). HR-MS (ESI, +ve, MeOH): Calculated *m/z* 87.0917; Observed *m/z* 87.0919 [M-2TsOH+H]$^+$.

N^1,*N*^{4}-Dibenzyl-2-butene-1,4-diammonium ditosylate (**5f**)

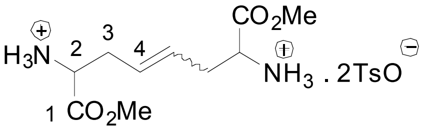


Conventional: Crystallization did not yield product (23% conversion by ^{1}H n.m.r. spectroscopy).

Microwave: Crystallized from acetone, 46% yield.

m.p. 190.5-192.5 °C; ^{1}H n.m.r. (400 MHz, *d*$_4$-MeOD): 7.69 (d, *J* 8.0 Hz, 4H, ArH); 7.45 (m, 10H, <u>Ph</u>CH$_2$); 7.23 (d, *J* 8.0 Hz, 4H, ArH); 6.12 (m, 2H, =CH); 4.20 (s, 4H, Ph<u>CH$_2$</u>); 3.31 (d, *J* 4.4 Hz, 4H, NCH$_2$); 2.36 (s, 6H, Ar<u>CH$_3$</u>); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz *d*$_4$-MeOD): 143.5 (TsO$^-$), 142.0 (TsO$^-$), 132.8 (C2), 131.2 (C3'), 130.9 (TsO$^-$), 130.5 (C4'), 130.4 (TsO$^-$), 130.1 (C5'), 127.1 (C2), 52.1 (C1'), 49.3 (C1), 21.4 (CH$_3$). HR-MS (ESI, +ve, MeOH): Calculated *m/z* 267.1856; Observed *m/z* 267.1854 [M-2TsOH+H]$^+$.

1,6-Di(methylcarboxy)-3-hexene-1,6-diammonium ditosylate (**5h**)

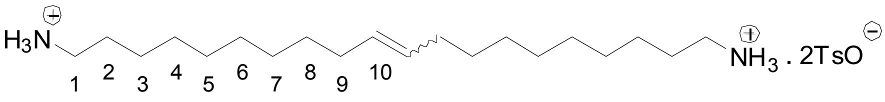


Conventional: Crystallized from CH$_2$Cl$_2$, 92 % yield.

Microwave: Crystallized from CH$_2$Cl$_2$, 90 % yield.

m.p. 214-216°C; ^{1}H n.m.r. (300 MHz, *d$_4$*-MeOD): δ 7.70 (d, *J* 8.0 Hz, 4H, ArH); 7.24 (d, *J* 8.0 Hz, 4H, ArH); 5.68 (m, 2H, =CH); 4.14 (q, *J* 6.4 Hz, 2H, NCH); 3.83 (s, 6H, OMe); 2.76-2.63 (m, 4H, =CH<u>CH$_2$</u>); 2.37 (s, 6H, ArCH$_3$); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, *d*$_4$-MeOH): 170.3 (CO), 143.5 (TsO$^-$), 141.8 (TsO$^-$), 129.9 (TsO$^-$), 128.0 (C4), 126.9 (TsO$^-$), 53.7 (OCH$_3$), 53.5 (C2), 31.5 (C3), 21.3 (CH$_3$). HR-MS (ESI, +ve, MeOH): Calculated m/z 231.1339; Observed m/z 231.1338 [M - 2TsOH + H]$^+$.

10-Icosene-1,20-diammonium ditosylate (**5i**)

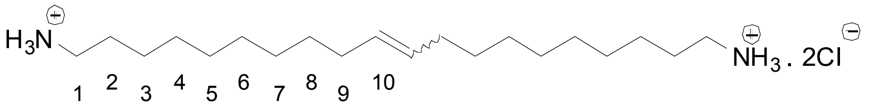


Conventional: Crystallized from Acetone, 92% yield. Isomerisation observed.

Microwave: Crystallized from Acetone, 88% yield. Isomerisation observed.

^{1}H n.m.r. (400 MHz, d_4-MeOD): δ 7.71 (d, *J* 8.0 Hz, 4H, o-ArH); 7.24 (d, *J* 8.0 Hz, 4H, m-ArH); 5.35-5.40 (m, 2H, =CH); 2.90 (t, *J* 8.0 Hz, 4H, NCH_2); 2.37 (s, 6H, $ArCH_3$); 1.95-2.05 (m, 4H, =CH$\underline{CH_2}$); 1.63 (m, 4H, $NCH_2\underline{CH_2}$); 1.30 (bs, 24H, 6 × CH_2); NH not detected due to exchange. LRMS (ESI, +ve, MeOH): Showed significant isomerisation; Calculated m/z 311.3; Observed m/z 311.3 ± 14n [M - 2TsOH + H ± $(CH_2)_n$]$^+$.

10-Icosene-1,20-diammonium dichloride (**5j**)

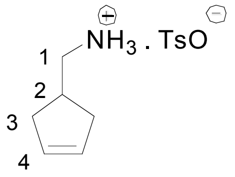


Conventional: Crystallized from CH_2Cl_2, 81% yield.

Microwave: Crystallized from CH_2Cl_2, 82% yield.

^{1}H n.m.r. (400 MHz, d_4-MeOD): δ 5.39 (s, 2H); 2.91 (t, *J* 7.6 Hz, 4H); 2.21 (bs, 4H); 1.66 (bs, 4H); 1.49-1.31 (bm, 24H); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, d_4-MeOD): 131.4 (C10), 40.8 (C1), 34.8 (C9), 33.6 (C2), 30.8 (C8), 30.4 (C7), 30.2 (C6), 30.1 (C5), 28.6 (C4), 27.5 (C3). HR-MS (ESI, +ve, MeOH): Calculated m/z 311.3421; Observed m/z 311.3422 [M – 2HCl + H]$^+$.

1-(3-Cyclopentenyl)methylammonium tosylate (**5k**)

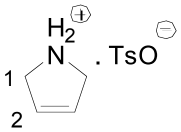


Conventional: Crystallization did not give product (>95 % conversion by ^{1}H n.m.r. spectroscopy)

Microwave: Crystallization did not give product (>95% conversion by ^{1}H n.m.r. spectroscopy)

^{1}H n.m.r. (400 MHz, $CDCl_3$): 7.73 (d, *J* 7.6 Hz, 2H); 7.61, (bs, 3H, NH_3); 7.15 (d, *J* 7.6 Hz, 2H); 5.52 (bs, 2H, =CH); 2.72 (bs, 2H, CH_2); 2.45-2.25 (bm, 6H, CH, CH_2, $ArCH_3$); 2.02-1.75-1 (bm, 2H, CH_2). ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.3 (TsO^-), 140.6 (TsO^-), 129.0 (C4), 128.9 (TsO^-), 125.9 (TsO^-), 44.8 (C1), 36.5 (C3), 35.3 (C2), 21.5 (CH_3). HR-MS (ESI, +ve, MeOH): Calculated *m/z* 98.0964; Observed *m/z* 98.0958 $[M-TsOH+H]^+$.

2,5-Dihydro-1*H*-pyrrolium tosylate (**5l**)

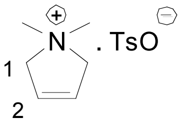


Conventional: Crystallization did not yield product (quant. conversion by ^{1}H n.m.r. spectroscopy)

Microwave: Crystallization did not yield product (quant. conversion by ^{1}H n.m.r. spectroscopy)

M.p. 115-117°C. ^{1}H n.m.r. (300 MHz $CDCl_3$): 7.69 (d, *J* 7.4 Hz, 2H); 7.16 (d, *J* 7.4 Hz, 2H); 5.75 (bs, 2H, =CH); 4.09 (bs, 4H, N-CH_2); 2.40 (s, 3H, Ar-CH_3); NH not detected due to exchange. ^{13}C n.m.r. (100 MHz, $CDCl_3$): 141.4 (TsO^-), 140.9 (TsO^-), 129.2 (TsO^-), 126.0 (TsO^-), 125.1 (C2), 52.4 (C1), 21.3 (CH_3). HR-MS (ESI, +ve, MeOH): Calculated *m/z* 70.0651; Observed *m/z* 70.0658 $[M-TsOH+H]^+$.

N,*N*'-Dimethyl-2,5-dihydro-1*H*-pyrrolium tosylate (**5m**)



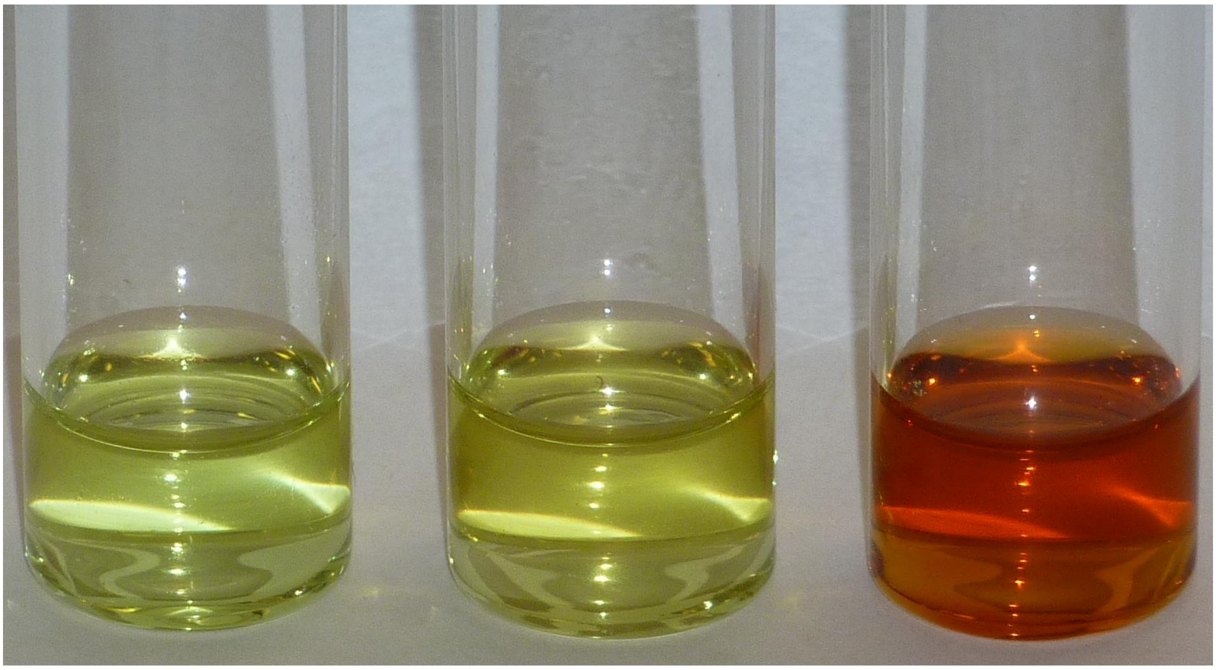
Conventional: Crystallization did not yield product (9% conversion by ^{1}H n.m.r. spectroscopy)

Microwave: Crystallization did not yield product (>95% conversion by ^{1}H n.m.r. spectroscopy)

^{1}H n.m.r. (200 MHz $CDCl_3$): 7.66 (d, *J* 7.8 Hz, 2H); 7.10 (d, *J* 7.8 Hz, 2H); 5.76 (bs, 2H, =CH); 4.31 (bs, 4H, NCH_2); 3.32 (s, 6H, NCH_3); 2.30 (s, 3H, Ar$\underline{CH_3}$). ^{13}C n.m.r. (100 MHz

$CDCl_3$): 143.6 (TsO^-), 139.5 (TsO^-), 128.7 (TsO^-), 125.8 (TsO^-), 124.8 (C2), 72.4 (NCH_3), 53.9 (C1), 21.2 (Ar$\underline{CH_3}$). HR-MS (ESI, +ve, MeOH): Calculated *m/z* 98.0964; Observed *m/z* 98.0969 $[M\text{-}TsOH+H]^+$.

Qualitative assessment of catalyst activity



(a) (b) (c)

Figure 2: (a) 1mg HGII in 1mL of CH_2Cl_2; (b) 1mg HGII with 50mg of allylammonium tosylate (**4e**) in 1 mL of CH_2CH_2; (c) 1mg HGII in CH_2Cl_2 with 50mg of allylamine (**4a**) in CH_2Cl_2. All solutions stirred for 20 minutes prior to taking the photo.

Reactions outcomes reveal that **4e** (middle vial) can undergo cross metathesis to **5e**, whereas **4a** (right vial) fails to produce any product **5a** under metathesis conditions. The above picture illustrates colourimetric assessment of catalyst activity when working with olefinic amines.

References

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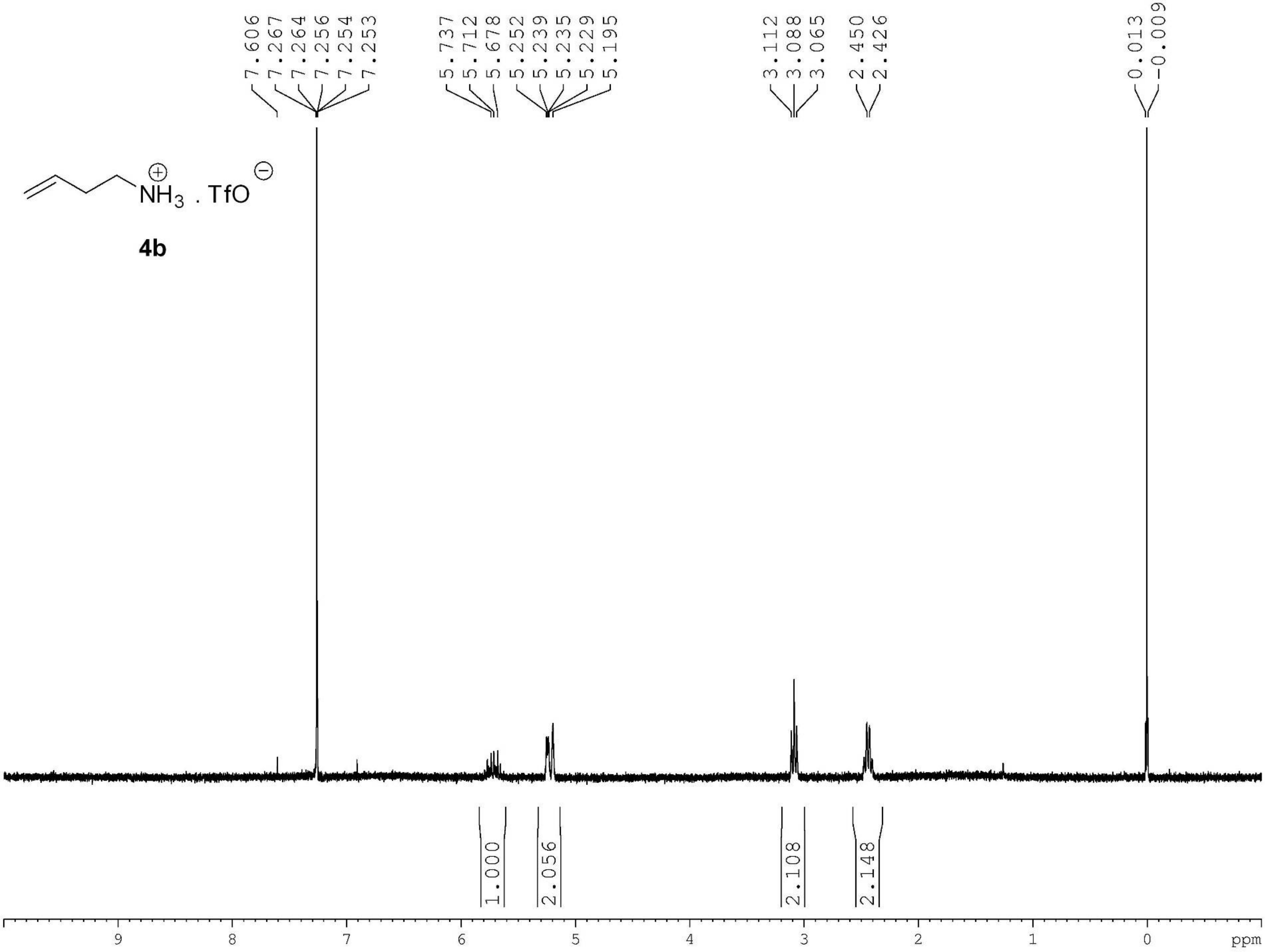
14. G. Asensio, R. Mello, C. Boix-Bernardini, M. Gonzalez-Nunez, G. Castellano, *J. Org. Chem.,* 1995, **60**, 3692.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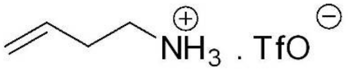
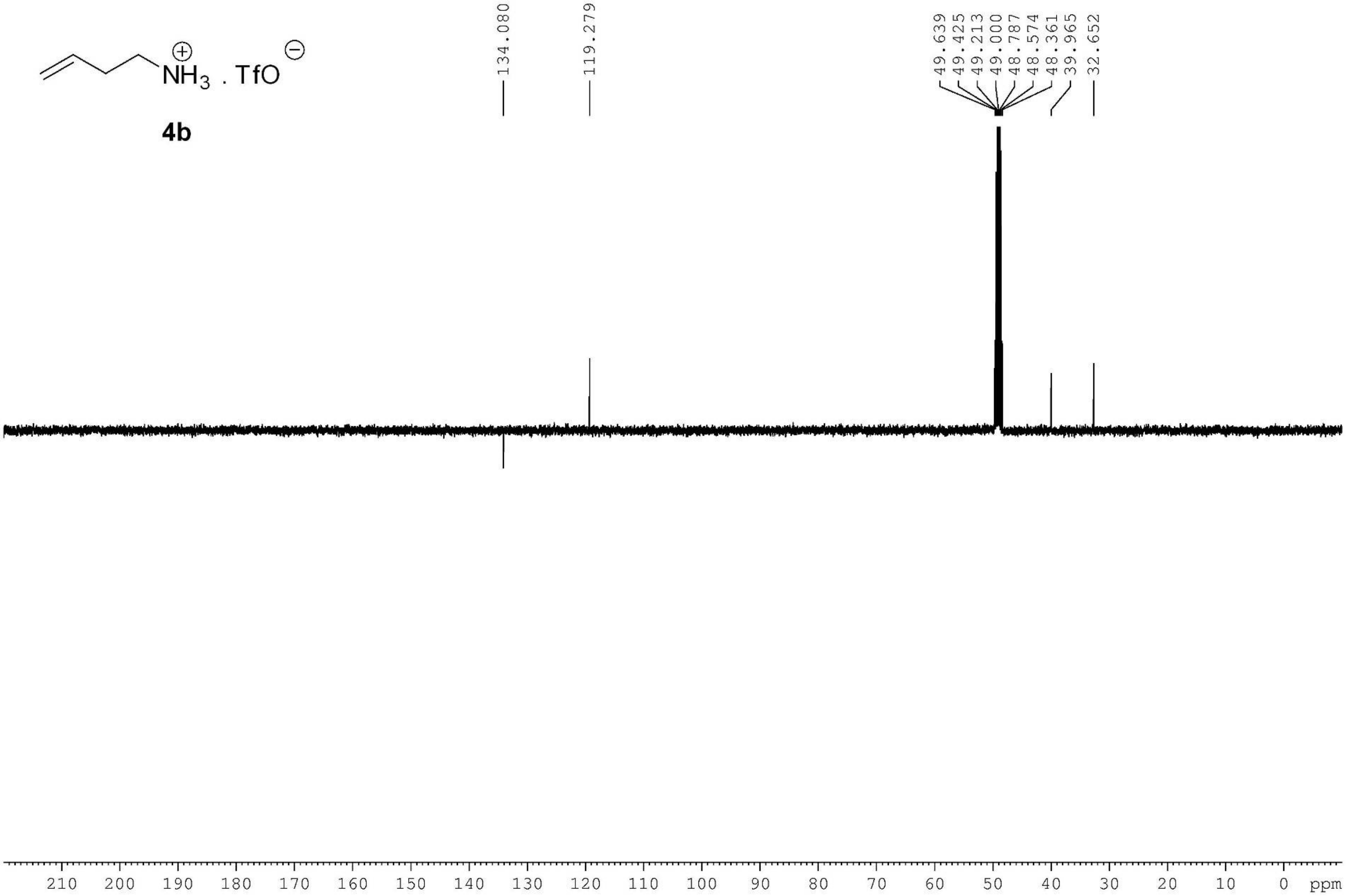
7.267
7.264
7.256
7.254
7.253
5.737
5.712
5.678
5.252
5.239
5.235
5.229
5.195
3.112
3.088
3.065
2.450
2.426
0.013
-0.009
NH3 . TfO
4b
1.000
2.056
2.108
2.148
9
8
7
6
5
4
3
2
1
0
ppm


NH3 . TfO

4b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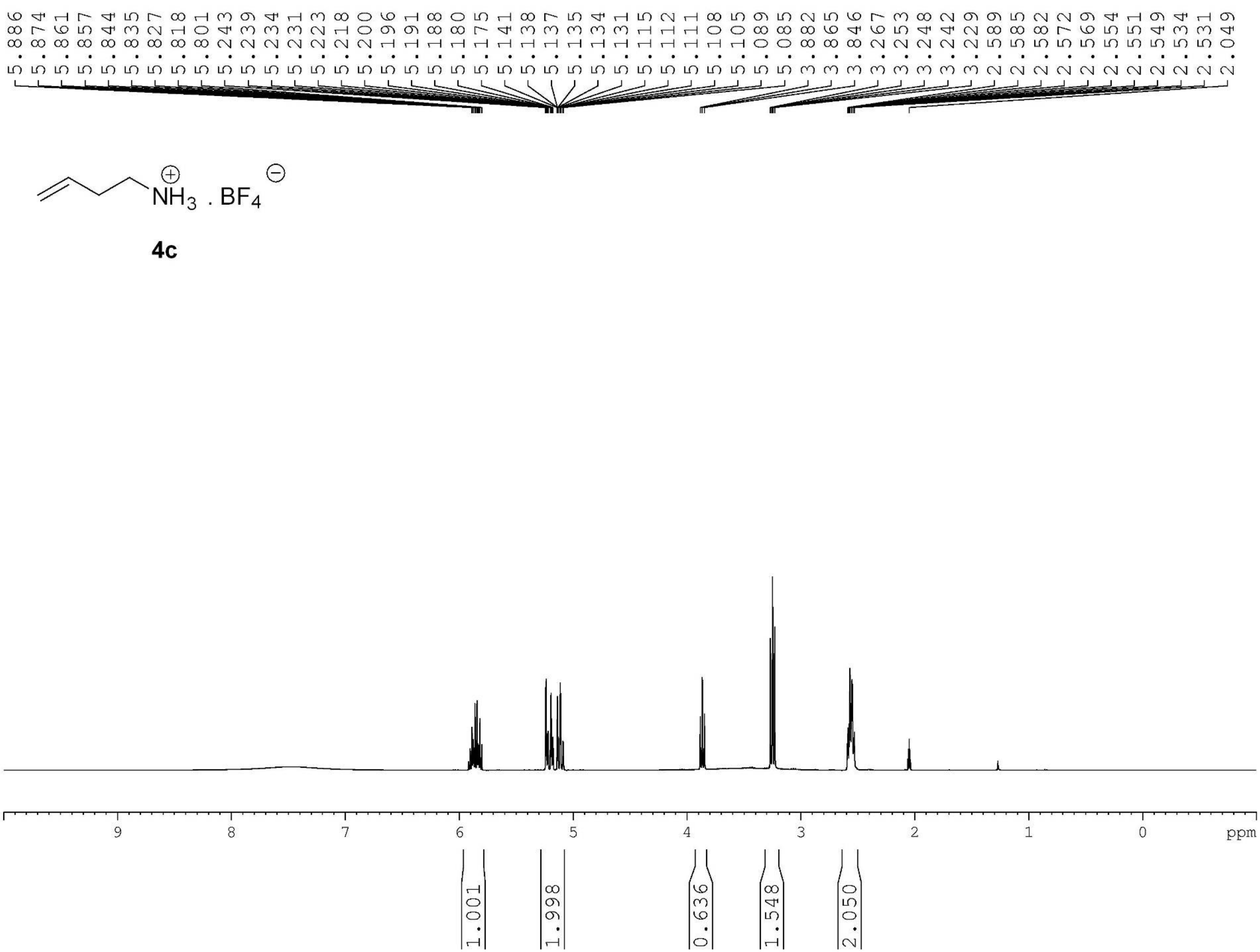
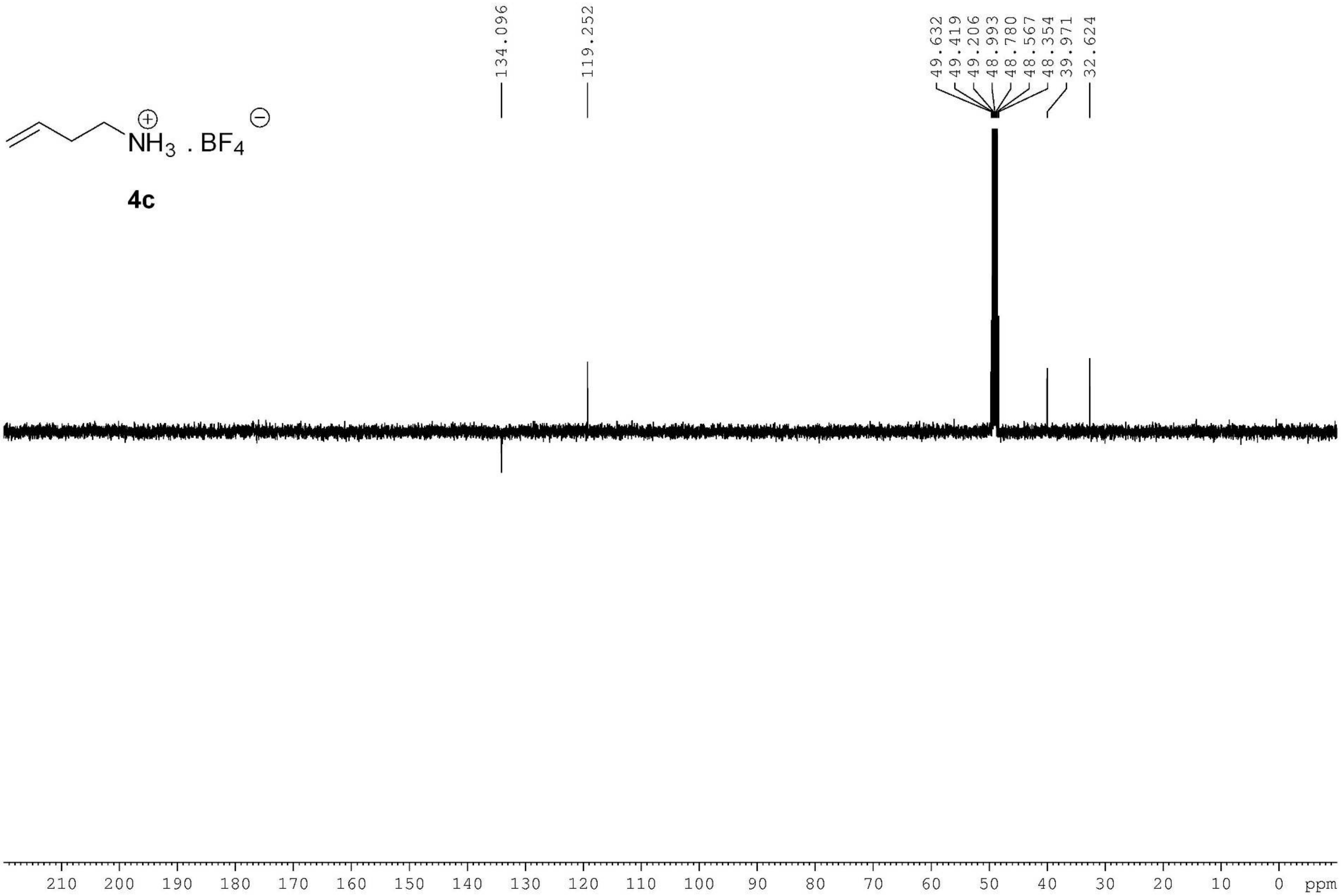
119.279
49.639
49.425
49.213
49.000
48.787
48.574
48.361
39.965
32.652
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



4c
5.886
5.874
5.861
5.857
5.844
5.835
5.827
5.818
5.801
5.243
5.239
5.234
5.231
5.223
5.218
5.200
5.196
5.191
5.188
5.180
5.175
5.141
5.138
5.137
5.135
5.134
5.131
5.115
5.112
5.111
5.108
5.105
5.089
5.085
3.882
3.865
3.846
3.267
3.253
3.248
3.242
3.229
2.589
2.585
2.582
2.572
2.569
2.554
2.551
2.549
2.534
2.531
2.049
9
8
7
6
5
4
3
2
1
0
ppm
1.001
1.998
0.636
1.548
2.050

NH3
. BF4

4c


134.096
119.252
49.632
49.419
49.206
48.993
48.780
48.567
48.354
39.971
32.624
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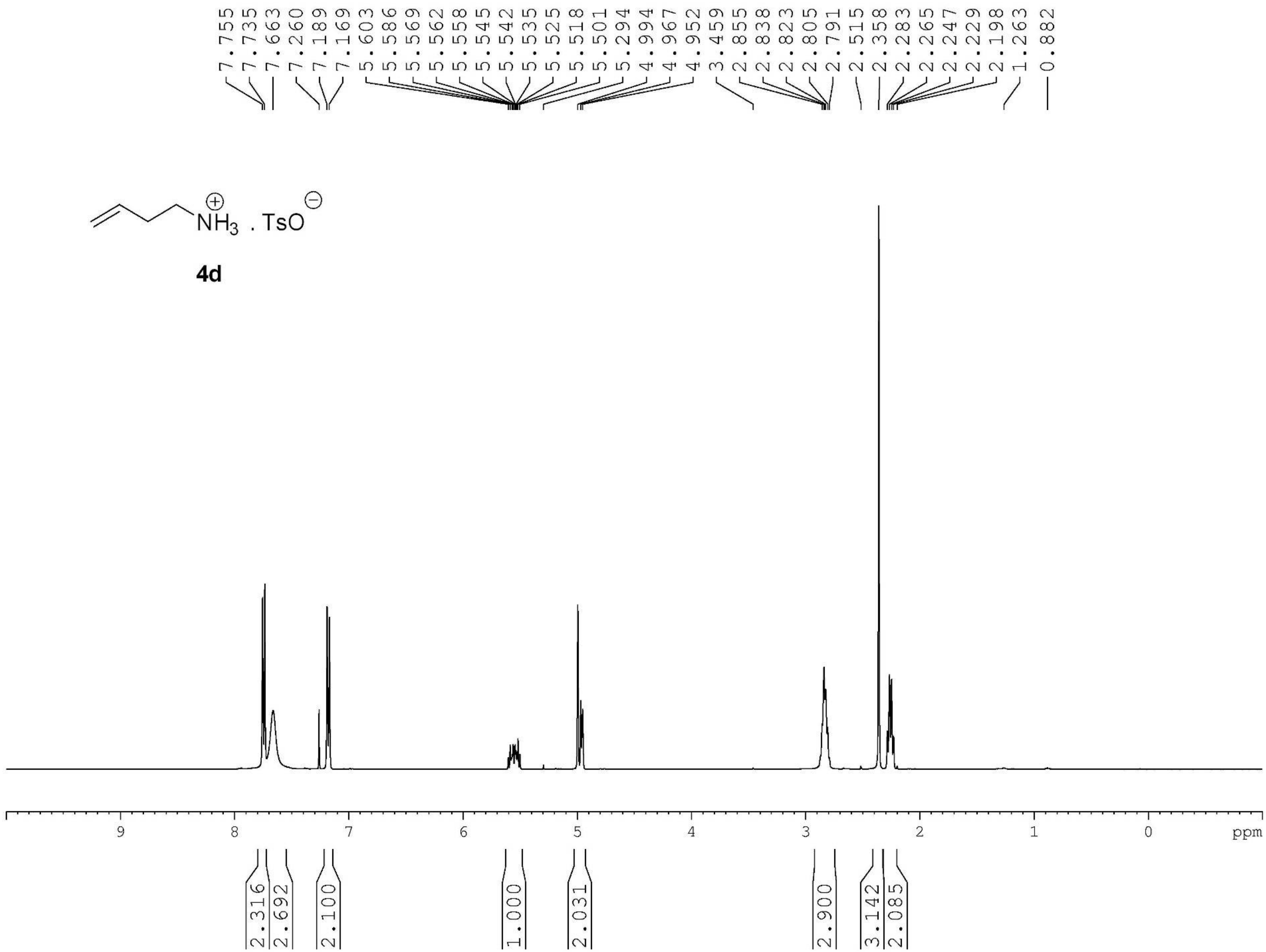
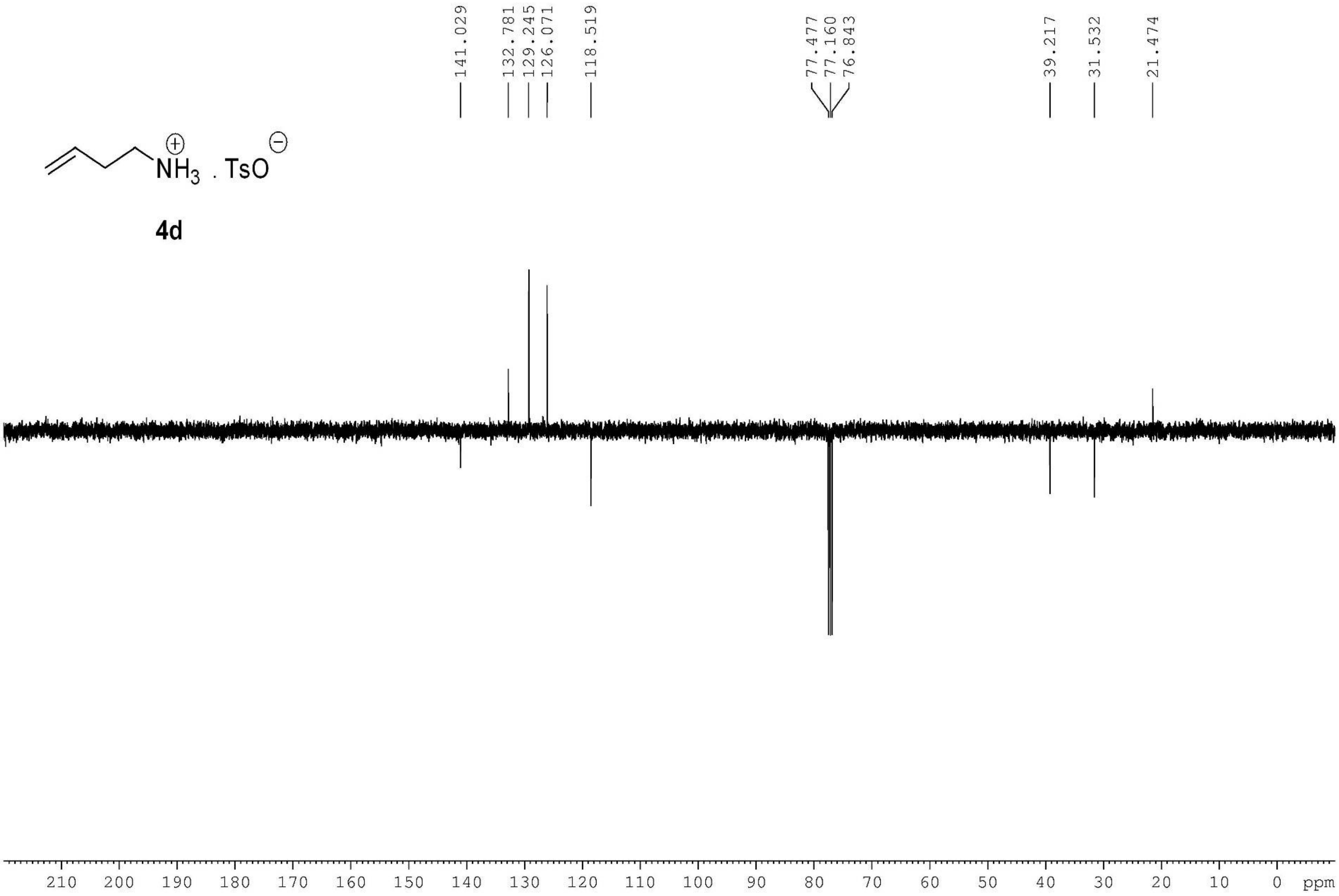
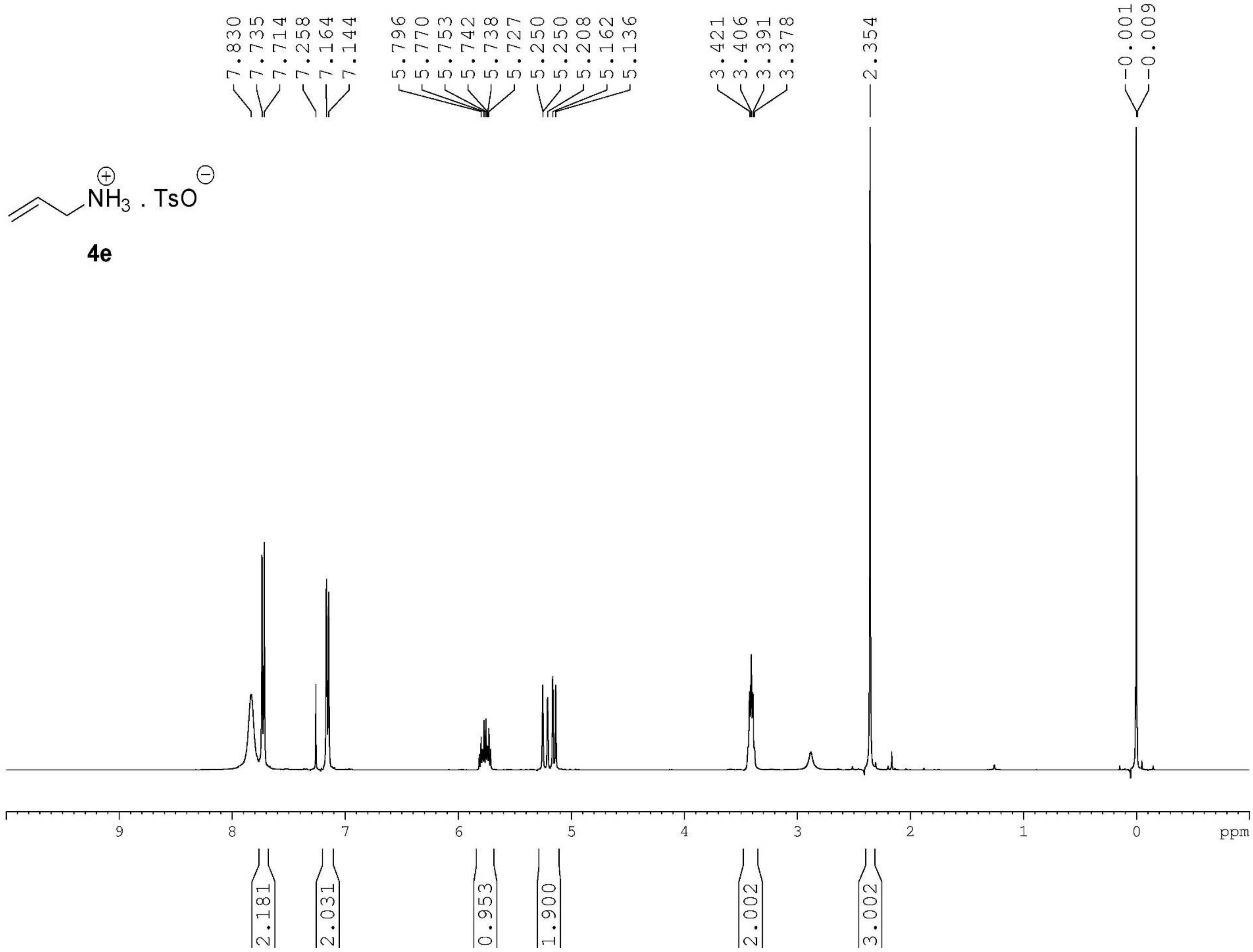
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.755
7.735
7.663
7.260
7.189
7.169
5.603
5.586
5.569
5.562
5.558
5.545
5.542
5.535
5.525
5.518
5.501
5.294
4.994
4.967
4.952
3.459
2.855
2.838
2.823
2.805
2.791
2.515
2.358
2.283
2.265
2.247
2.229
2.198
1.263
0.882
NH3 . TsO
4d
9
8
7
6
5
4
3
2
1
0
ppm
2.316
2.692
2.100
1.000
2.031
2.900
3.142
2.085


NH3
TsO

4d

141.029
132.781
129.245
126.071
118.519
77.477
77.160
76.843
39.217
31.532
21.474
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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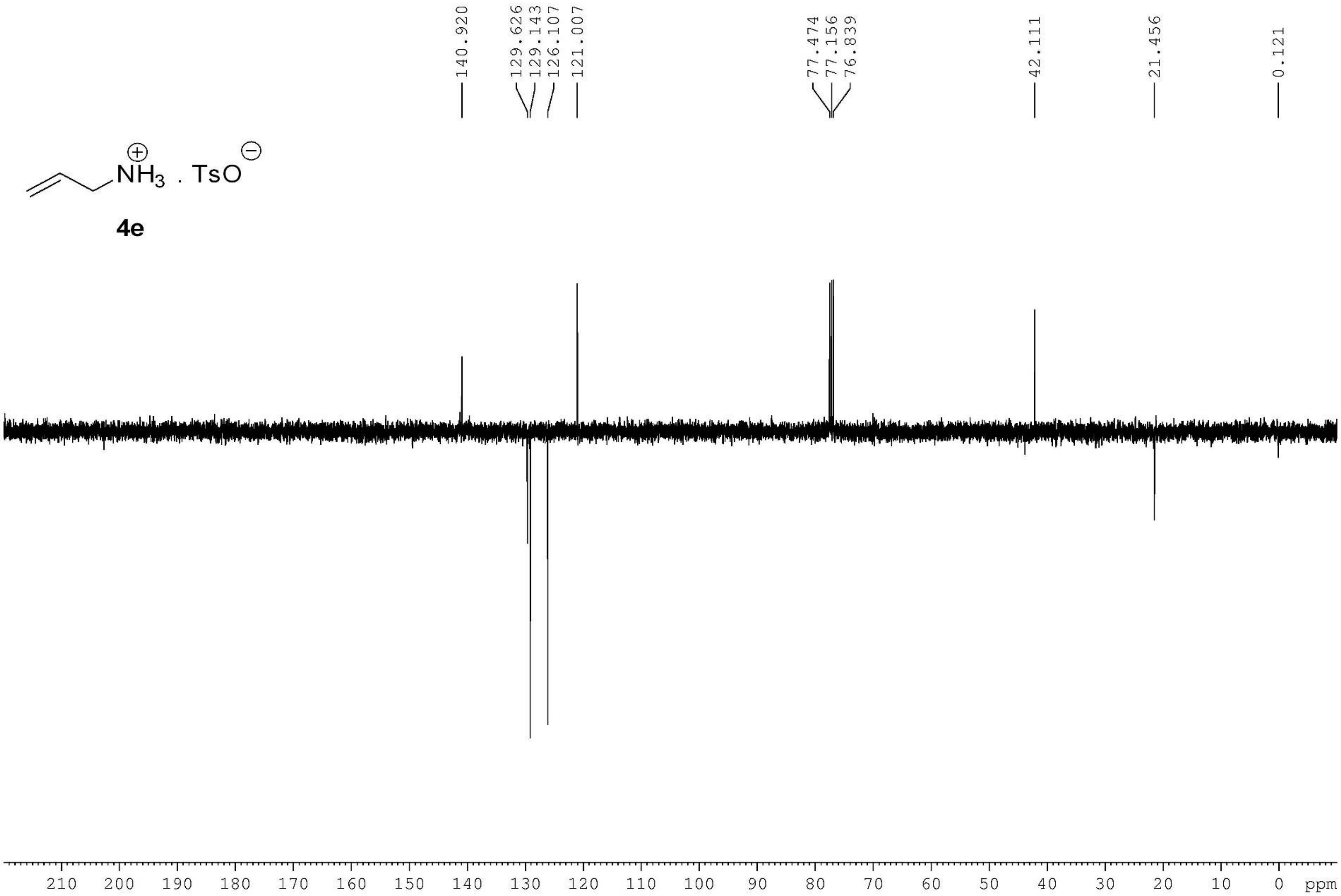
7.735
7.714
7.258
7.164
7.144
5.796
5.770
5.753
5.742
5.738
5.727
5.250
5.250
5.208
5.162
5.136
3.421
3.406
3.391
3.378
2.354
-0.001
-0.009
NH_3^+ . TsO^-
9
8
7
6
5
4
3
2
1
0
ppm
2.181
2.031
0.953
1.900
2.002
3.002

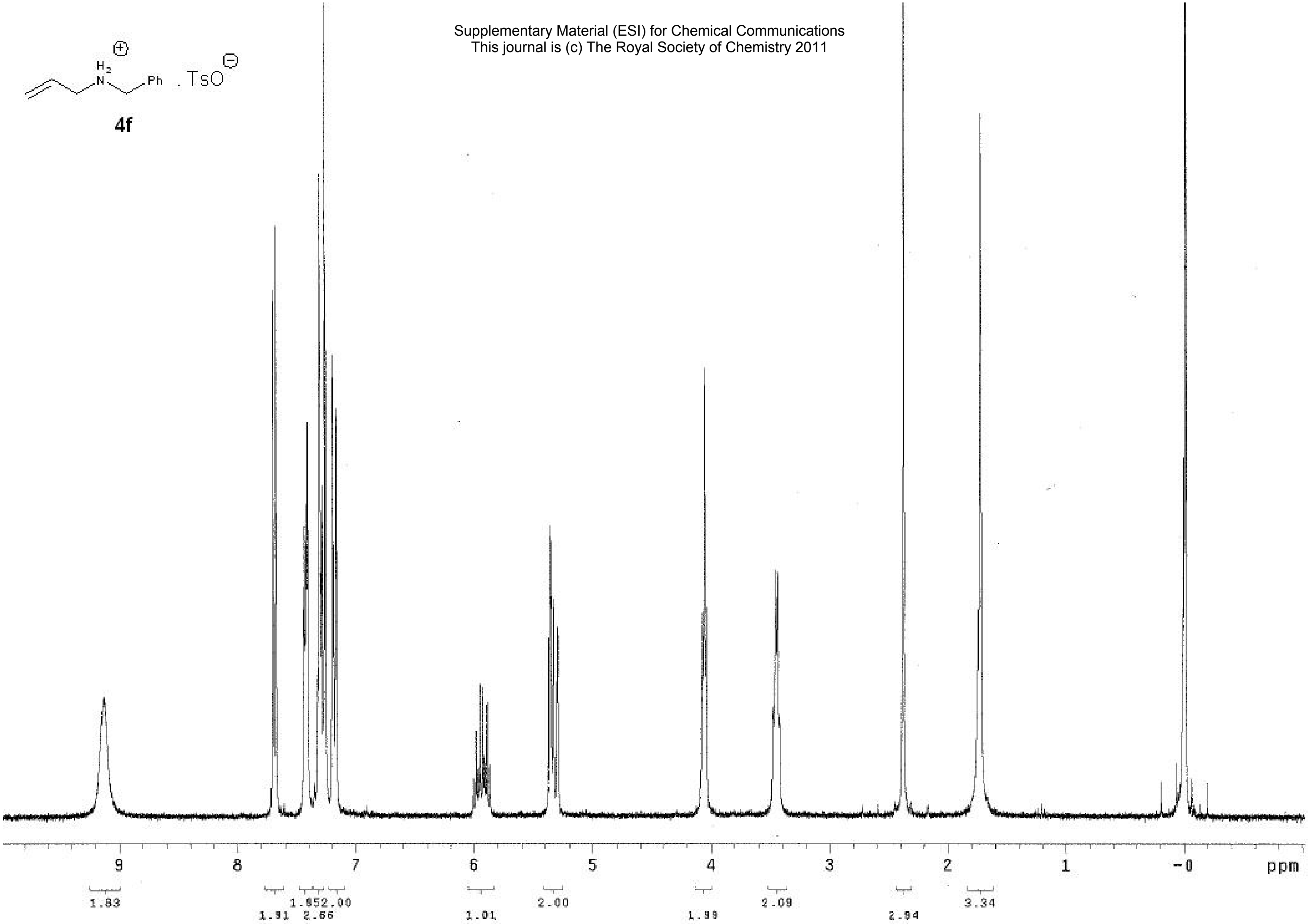
4e

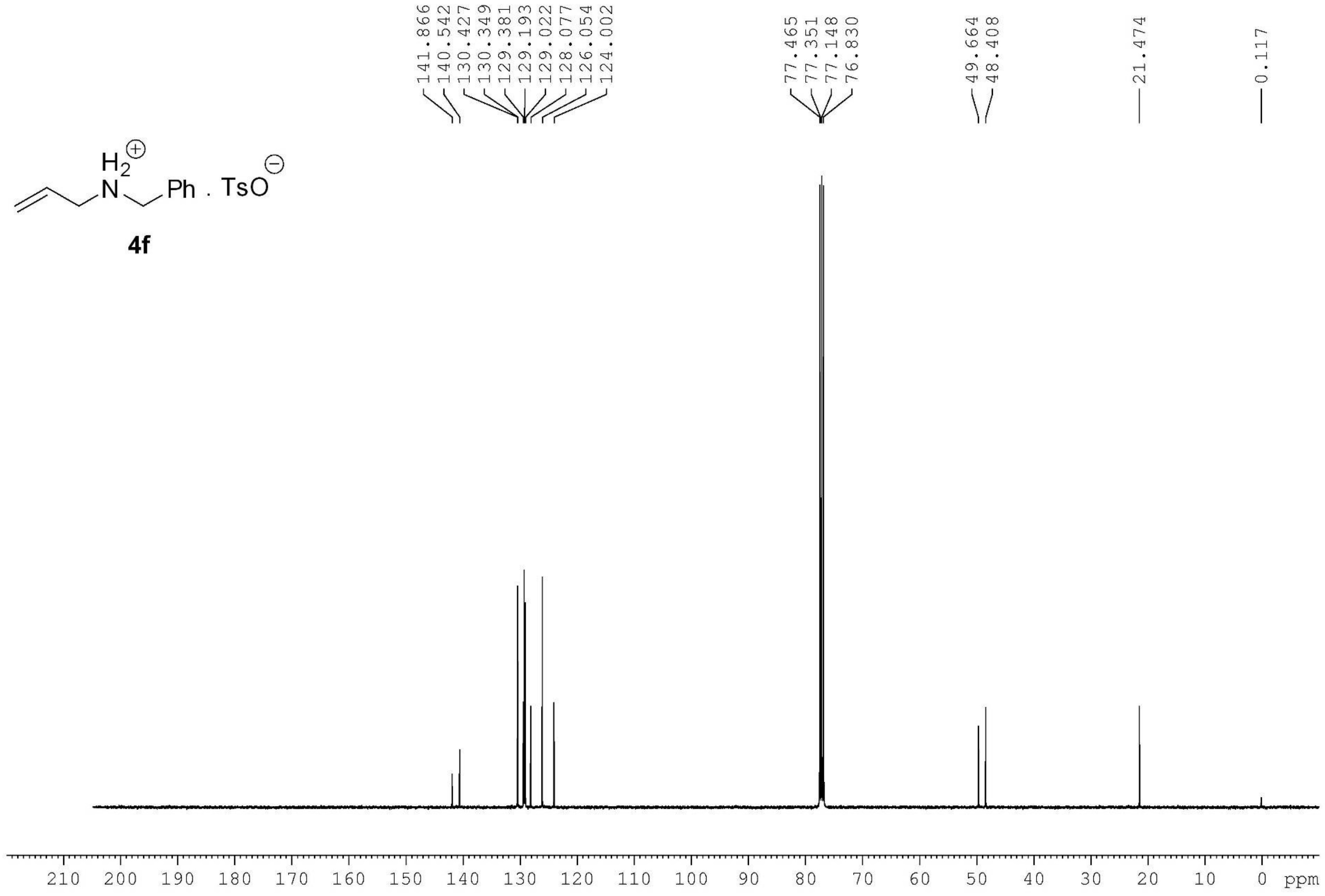

140.920
129.626
129.143
126.107
121.007
77.474
77.156
76.839
42.111
21.456
0.121
NH3 . TsO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4e

H2
N
Ph
. TsO

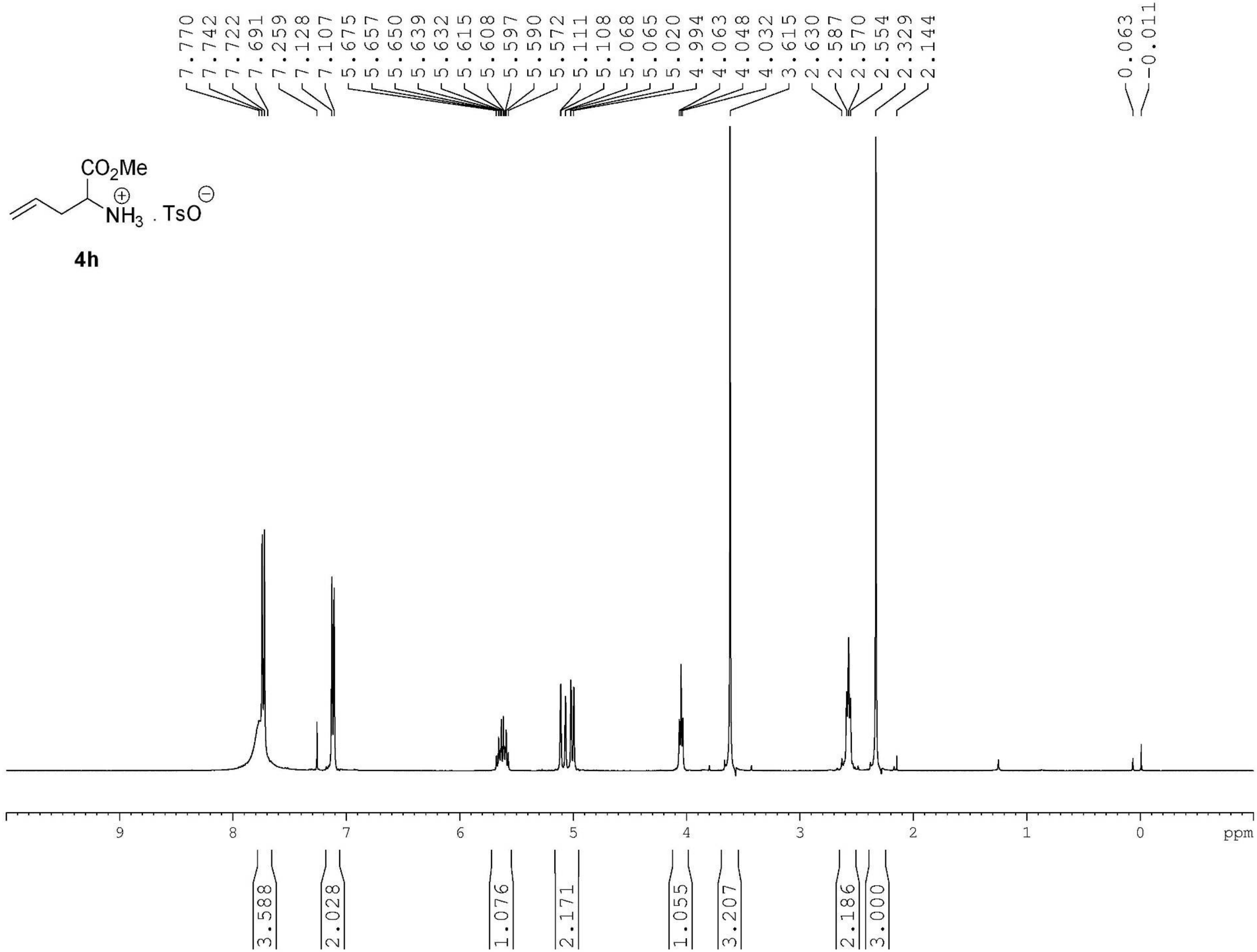
4f


9
8
7
6
5
4
3
2
1
-0
ppm
1.83
1.91
1.85
2.00
2.66
1.01
2.00
1.99
2.09
2.94
3.34

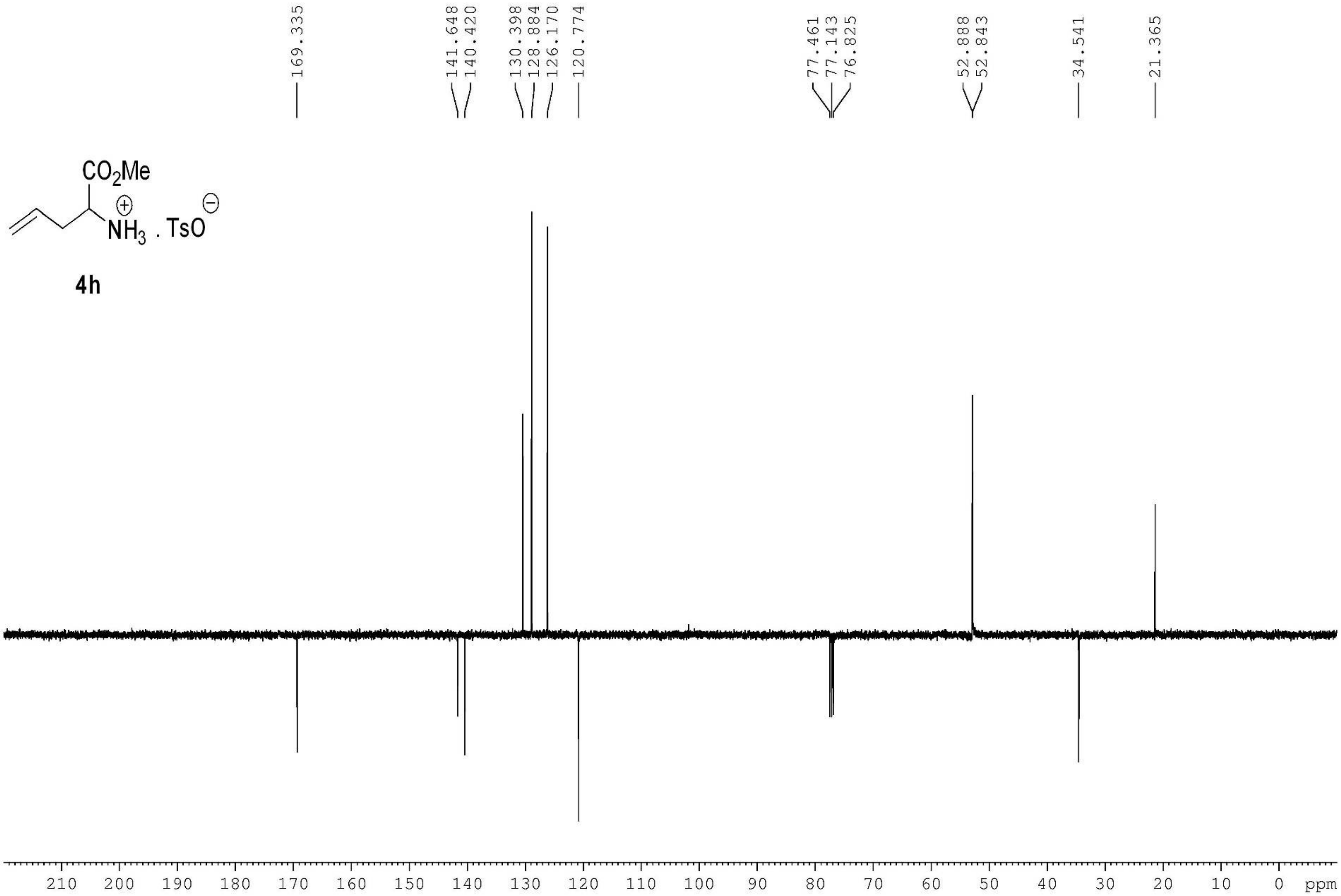


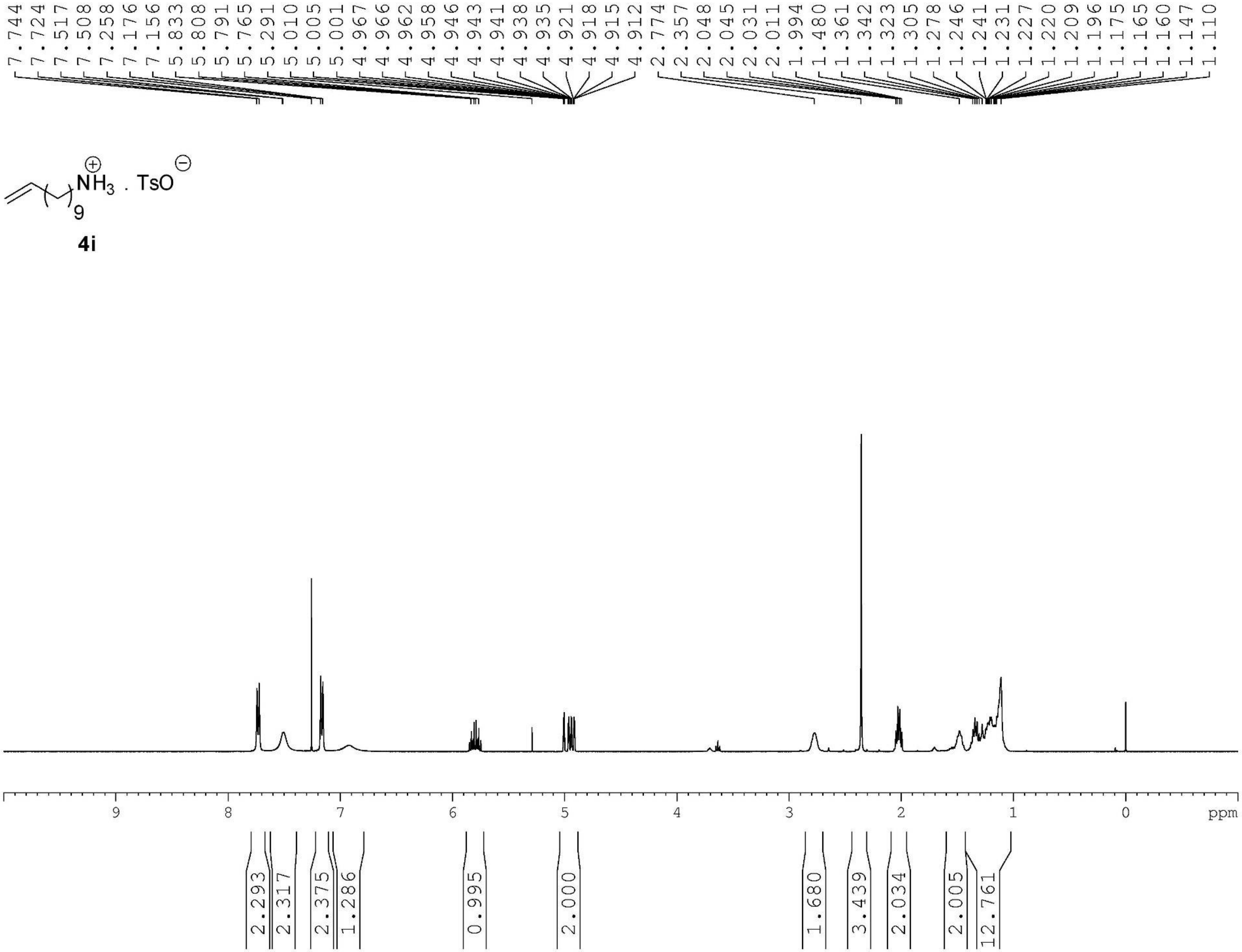
4f

H2⊕
N
Ph . TsO⊖
141.866
140.542
130.427
130.349
129.381
129.193
129.022
128.077
126.054
124.002
77.465
77.351
77.148
76.830
49.664
48.408
21.474
0.117
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.770
7.742
7.722
7.691
7.259
7.128
7.107
5.675
5.657
5.650
5.639
5.632
5.615
5.608
5.597
5.590
5.572
5.111
5.108
5.068
5.065
5.020
4.994
4.063
4.048
4.032
3.615
2.630
2.587
2.570
2.554
2.329
2.144
0.063
-0.011
CO2Me
NH3
TsO
9
8
7
6
5
4
3
2
1
0
ppm
3.588
2.028
1.076
2.171
1.055
3.207
2.186
3.000

4h


169.335
141.648
140.420
130.398
128.884
126.170
120.774
77.461
77.143
76.825
52.888
52.843
34.541
21.365
CO2Me
NH3 . TsO
4h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.724
7.517
7.508
7.258
7.176
7.156
5.833
5.808
5.791
5.765
5.291
5.010
5.005
5.001
4.967
4.966
4.962
4.958
4.946
4.943
4.941
4.938
4.935
4.921
4.918
4.915
4.912
2.774
2.357
2.048
2.045
2.031
2.011
1.994
1.480
1.361
1.342
1.323
1.305
1.278
1.246
1.241
1.231
1.227
1.220
1.209
1.196
1.175
1.165
1.160
1.147
1.110
NH3 . TsO
9
9
8
7
6
5
4
3
2
1
0
ppm
2.293
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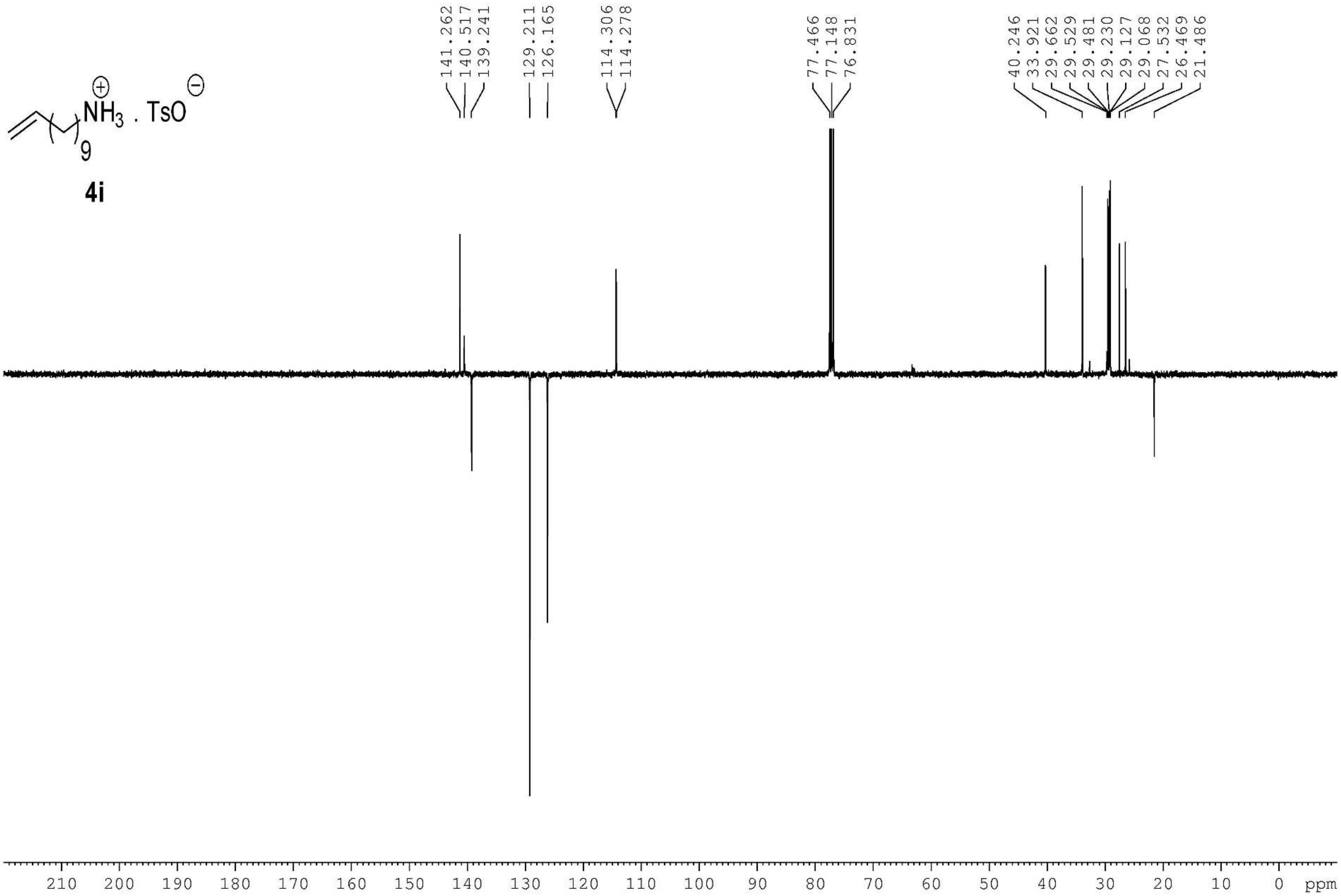
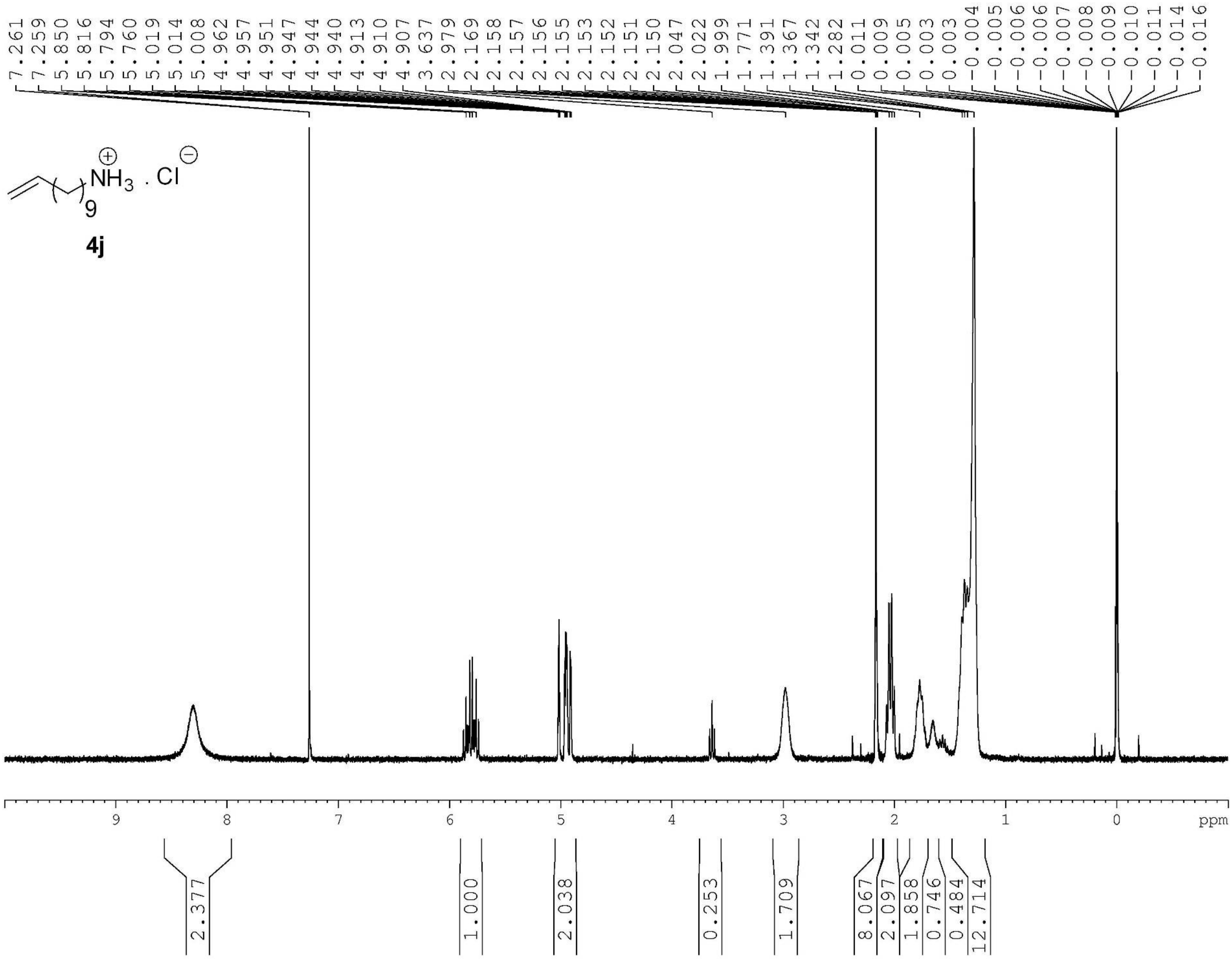
2.375
1.286
0.995
2.000
1.680
3.439
2.034
2.005
12.761

4i


NH3 . TsO
9
4i
141.262
140.517
139.241
129.211
126.165
114.306
114.278
77.466
77.148
76.831
40.246
33.921
29.662
29.529
29.481
29.230
29.127
29.068
27.532
26.469
21.486
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.259
5.850
5.816
5.794
5.760
5.019
5.014
5.008
4.962
4.957
4.951
4.947
4.944
4.940
4.913
4.910
4.907
3.637
2.979
2.169
2.158
2.157
2.156
2.155
2.153
2.152
2.151
2.150
2.047
2.022
1.999
1.771
1.391
1.367
1.342
1.282
0.011
0.009
0.005
0.003
0.003
-0.004
-0.005
-0.006
-0.006
-0.007
-0.008
-0.009
-0.010
-0.011
-0.014
-0.016
NH3 . Cl
9
9
8
7
6
5
4
3
2
1
0
ppm
2.377
1.000
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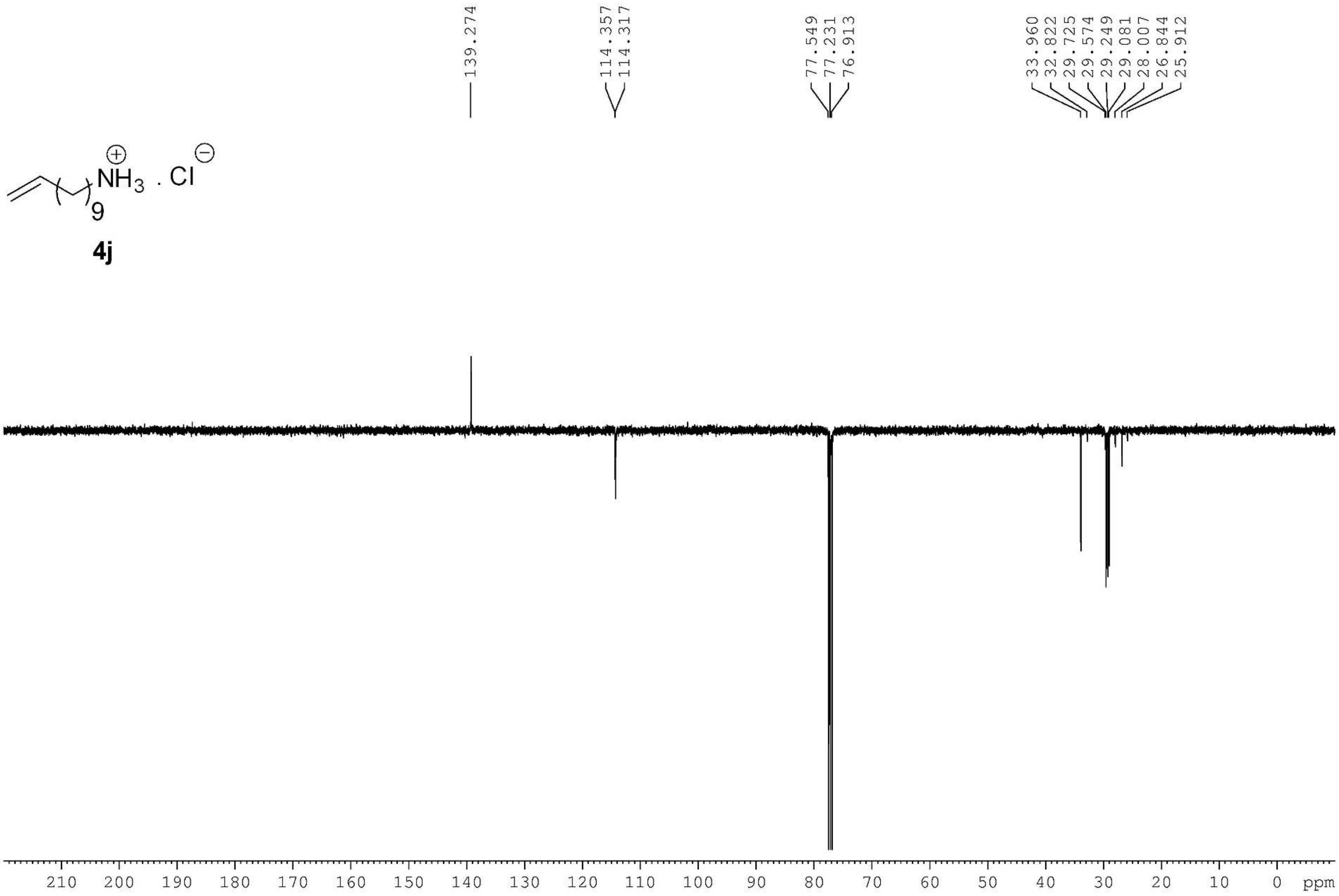
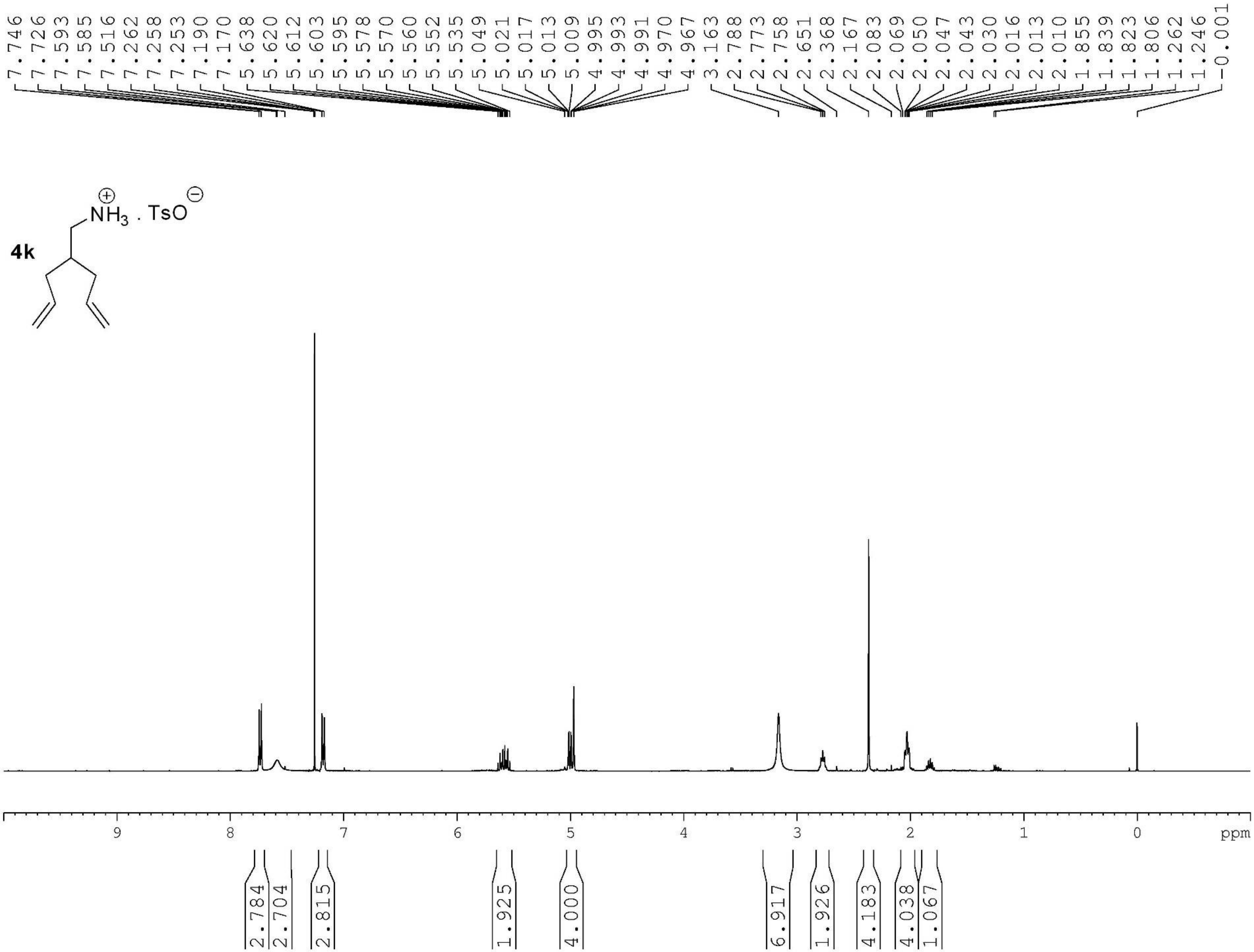
0.253
1.709
8.067
2.097
1.858
0.746
0.484
12.714

4j



4j

139.274
114.357
114.317
77.549
77.231
76.913
33.960
32.822
29.725
29.574
29.249
29.081
28.007
26.844
25.912
NH3 . Cl
9
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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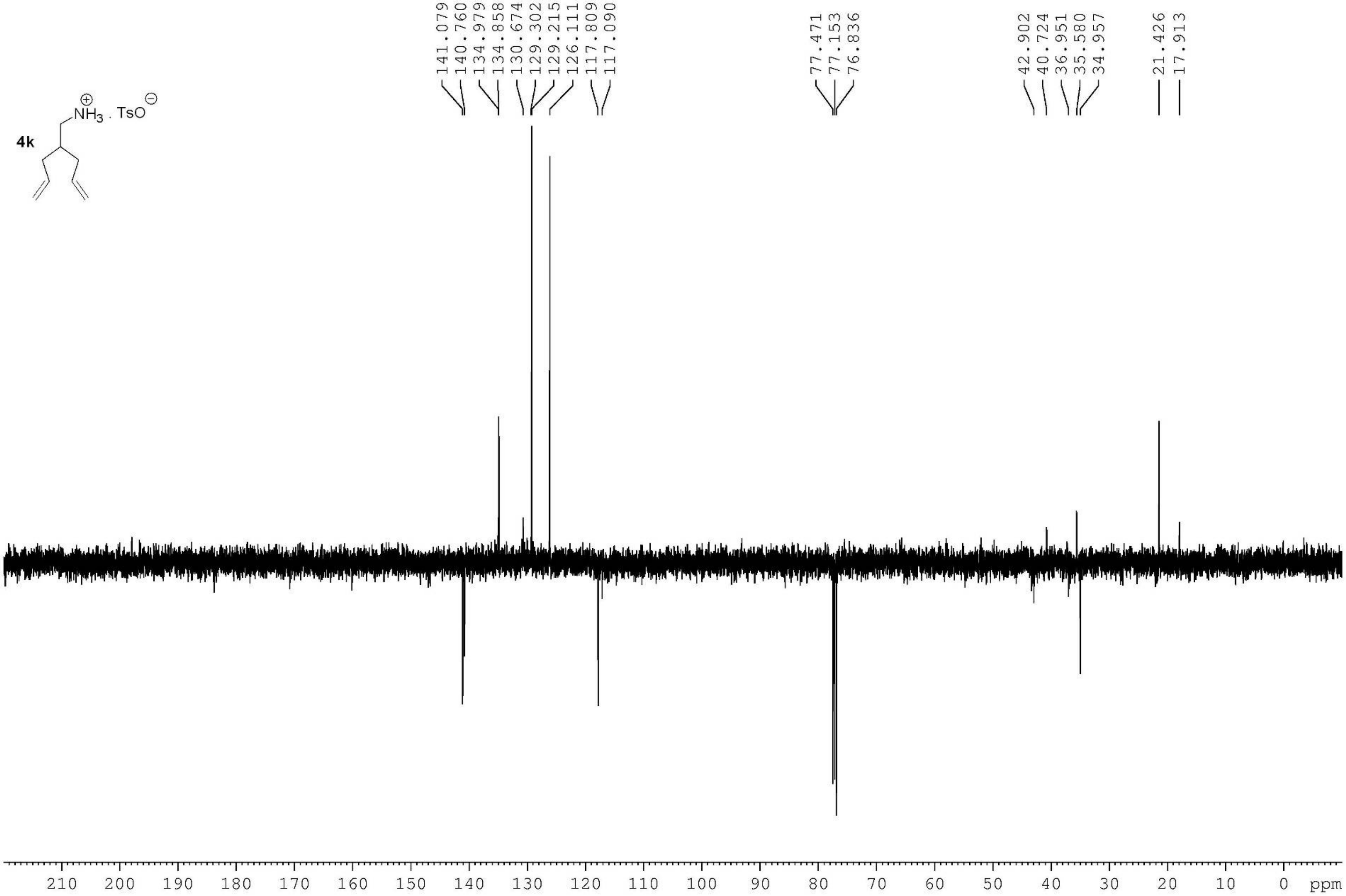
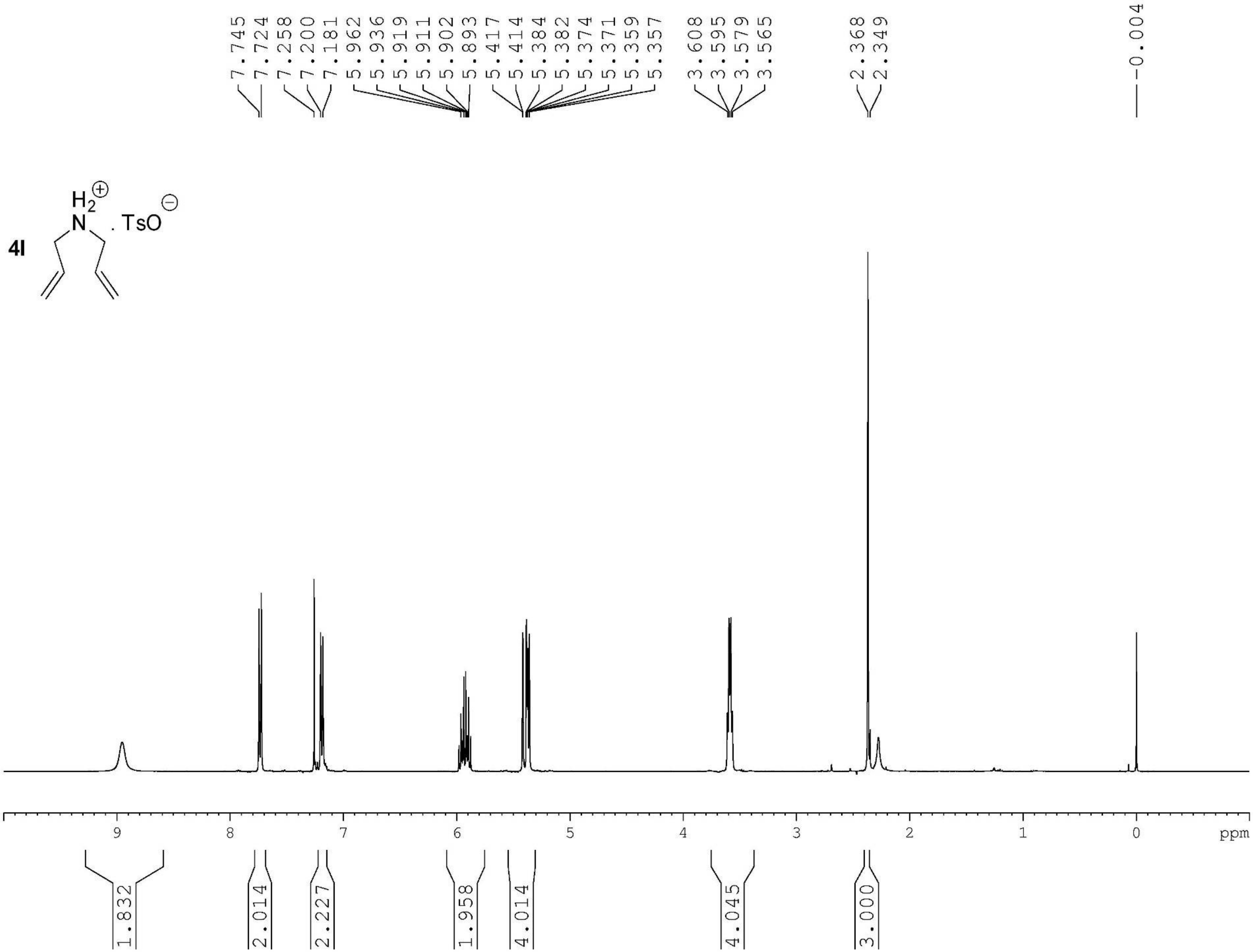
7.262
7.258
7.253
7.190
7.170
5.638
5.620
5.612
5.603
5.595
5.578
5.570
5.560
5.552
5.535
5.049
5.021
5.017
5.013
5.009
4.995
4.993
4.991
4.970
4.967
3.163
2.788
2.773
2.758
2.651
2.368
2.167
2.083
2.069
2.050
2.047
2.043
2.030
2.016
2.013
2.010
1.855
1.839
1.823
1.806
1.262
1.246
-0.001
4k
NH3 . TsO
9
8
7
6
5
4
3
2
1
0
ppm
2.784
2.704
2.815
1.925
4.000
6.917
1.926
4.183
4.038
1.067

4k


NH3 ⊕
. TsO ⊖
141.079
140.760
134.979
134.858
130.674
129.302
129.215
126.111
117.809
117.090
77.471
77.153
76.836
42.902
40.724
36.951
35.580
34.957
21.426
17.913
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4l


H2
N
. TsO
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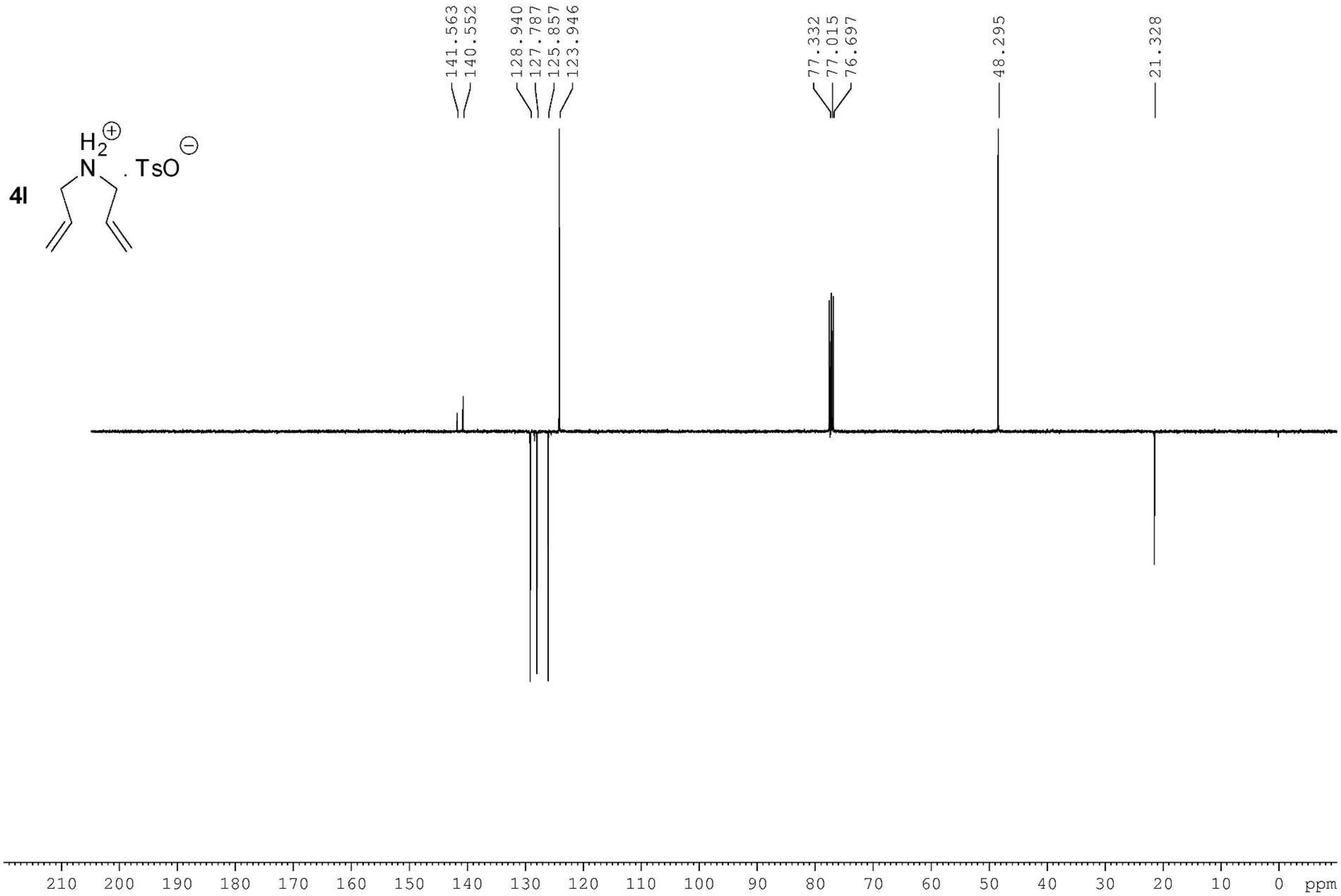
5.962
5.936
5.919
5.911
5.902
5.893
5.417
5.414
5.384
5.382
5.374
5.371
5.359
5.357
3.608
3.595
3.579
3.565
2.368
2.349
-0.004
9
8
7
6
5
4
3
2
1
0
ppm
1.832
2.014
2.227
1.958
4.014
4.045
3.000

4l

H2
N
. TsO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127.787
125.857
123.946
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77.015
76.697
48.295
21.328
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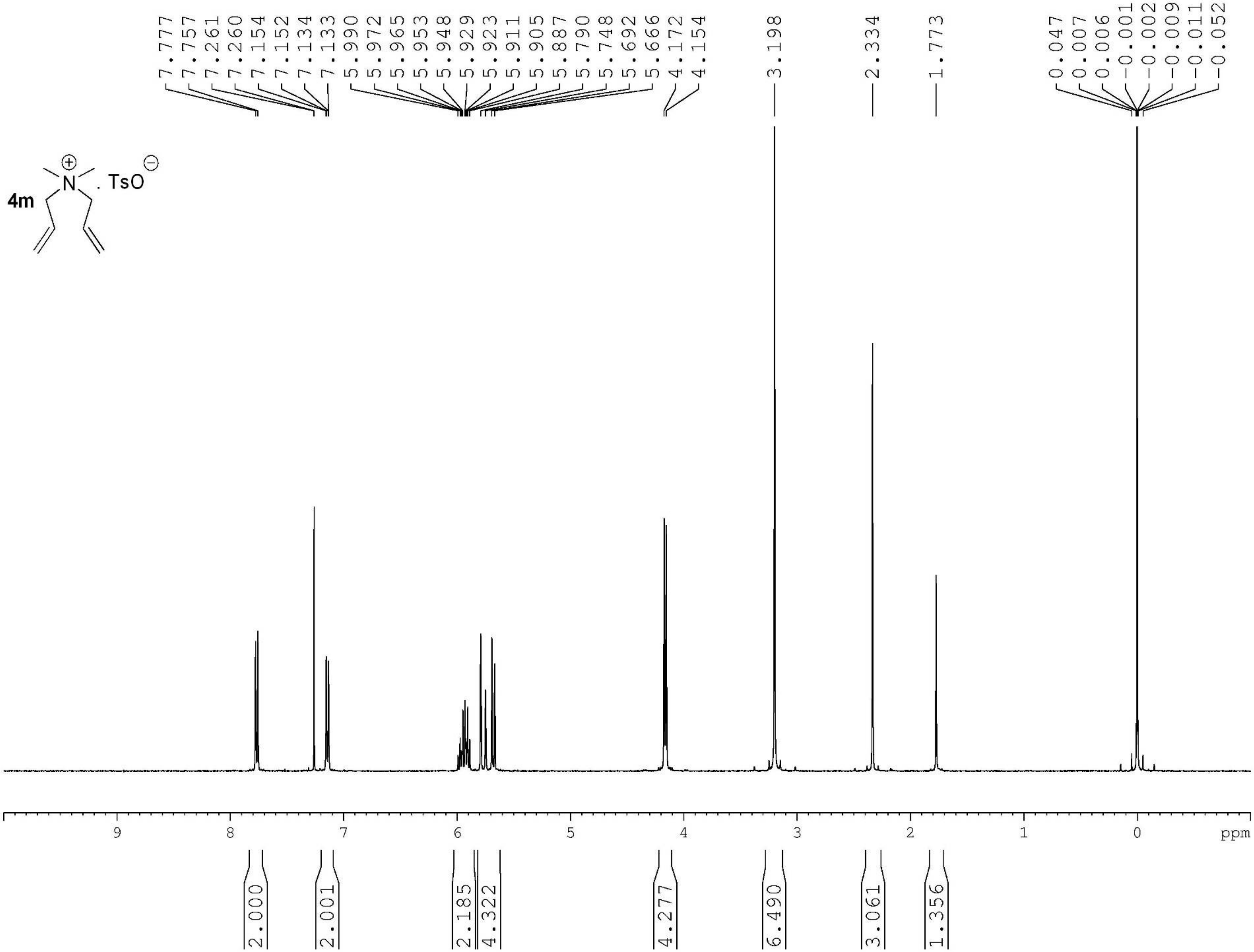
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4m


N
TsO
7.777
7.757
7.261
7.260
7.154
7.152
7.134
7.133
5.990
5.972
5.965
5.953
5.948
5.929
5.923
5.911
5.905
5.887
5.790
5.748
5.692
5.666
4.172
4.154
3.198
2.334
1.773
0.047
0.007
0.006
-0.001
-0.002
-0.009
-0.011
-0.052
9
8
7
6
5
4
3
2
1
0
ppm
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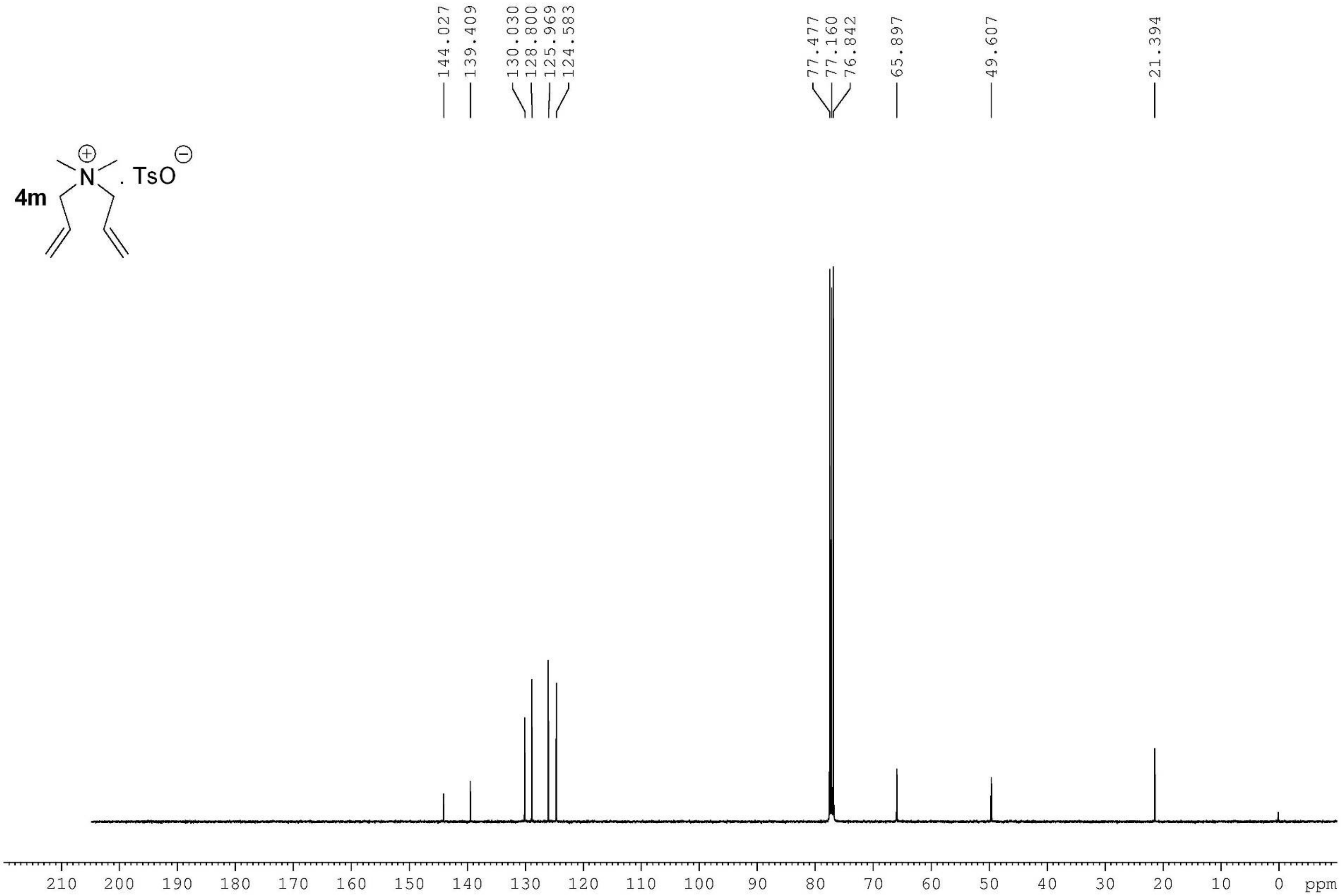
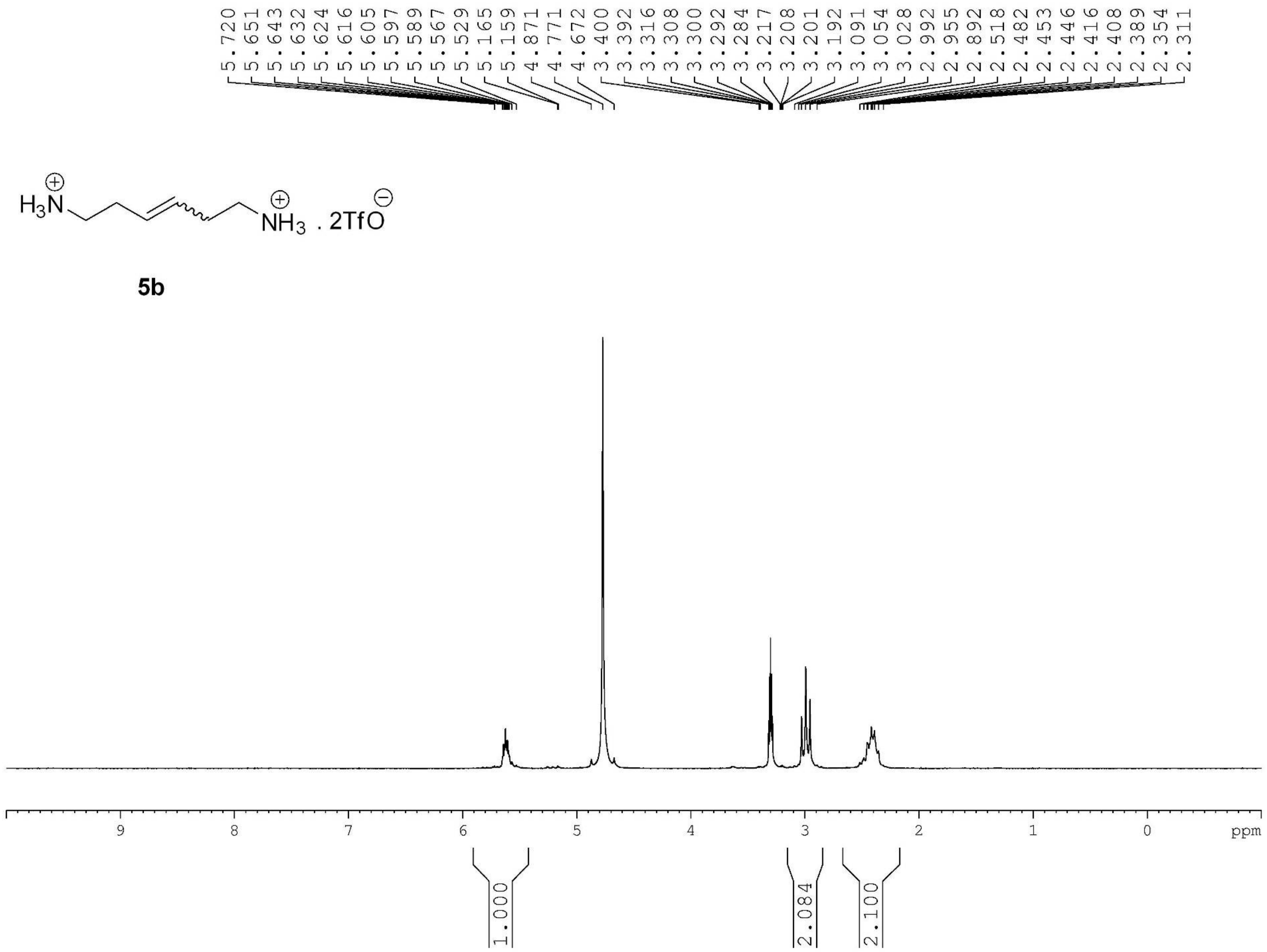
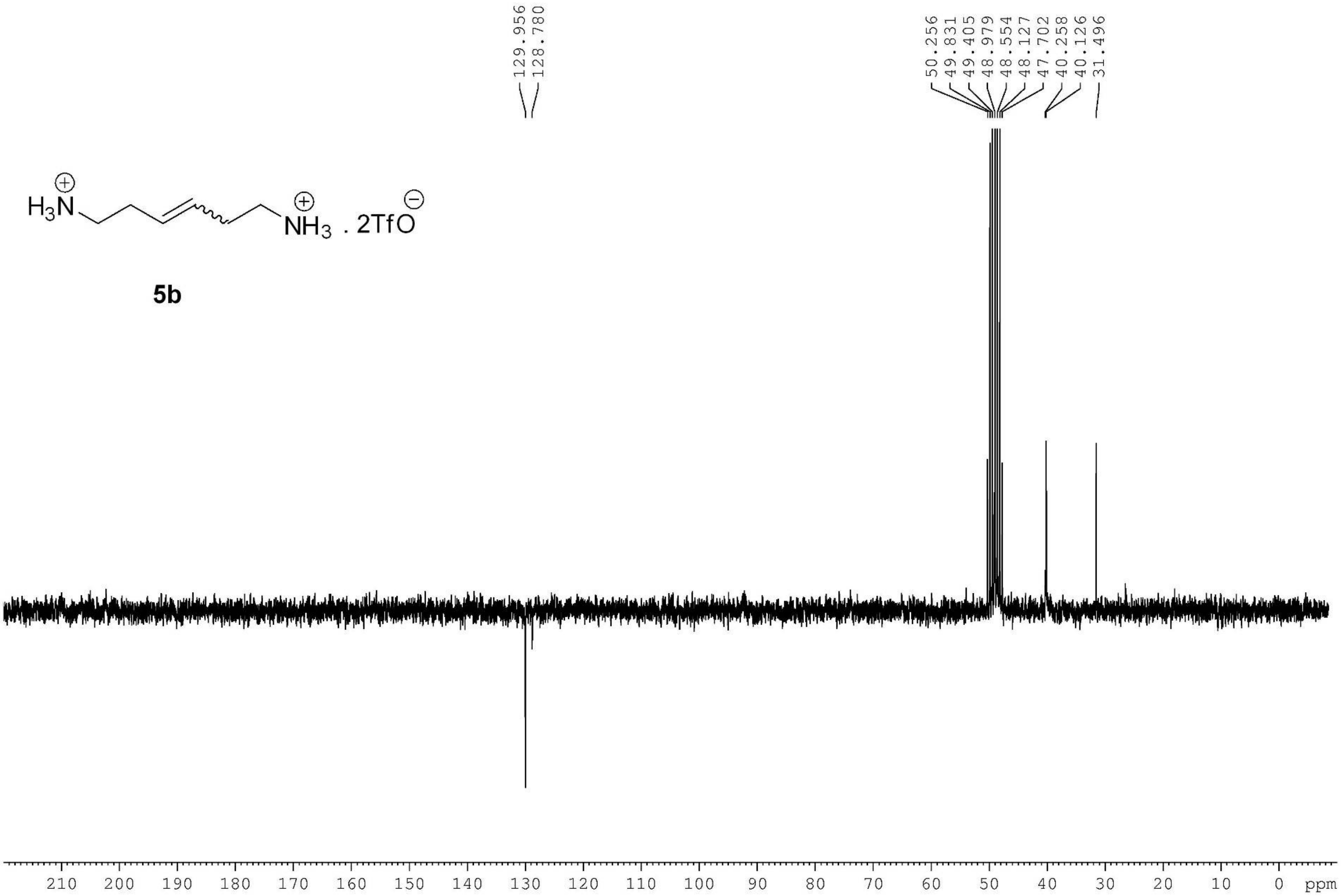
4.322
4.277
6.490
3.061
1.356


4m
N
. TsO
144.027
139.409
130.030
128.800
125.969
124.583
77.477
77.160
76.842
65.897
49.607
21.394
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


H3N⊕
⊕NH3
. 2TfO⊖

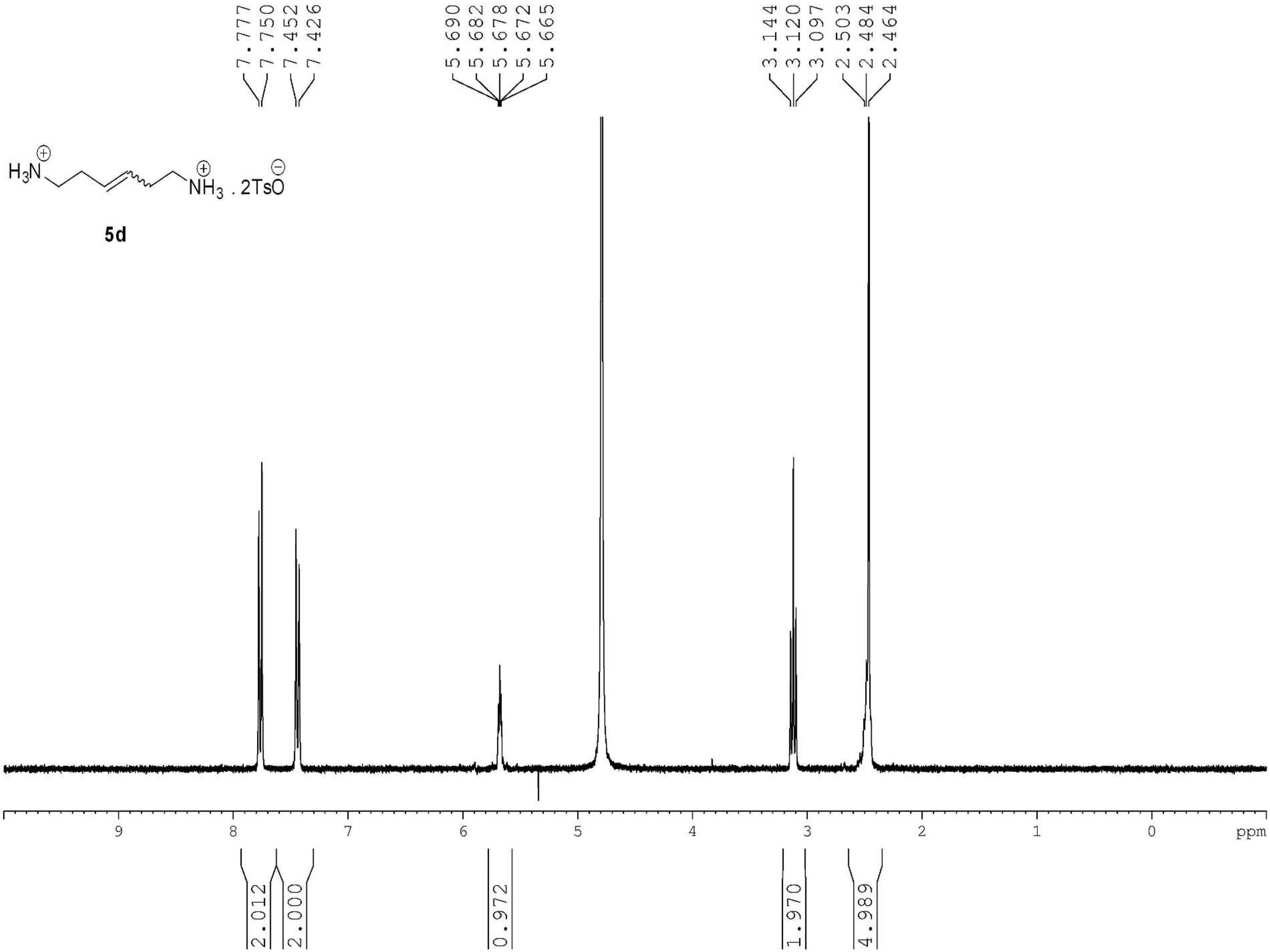
5b

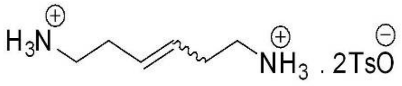
5.720
5.651
5.643
5.632
5.624
5.616
5.605
5.597
5.589
5.567
5.529
5.165
5.159
4.871
4.771
4.672
3.400
3.392
3.316
3.308
3.300
3.292
3.284
3.217
3.208
3.201
3.192
3.091
3.054
3.028
2.992
2.955
2.892
2.518
2.482
2.453
2.446
2.416
2.408
2.389
2.354
2.311
9
8
7
6
5
4
3
2
1
0
ppm
1.000
2.084
2.100



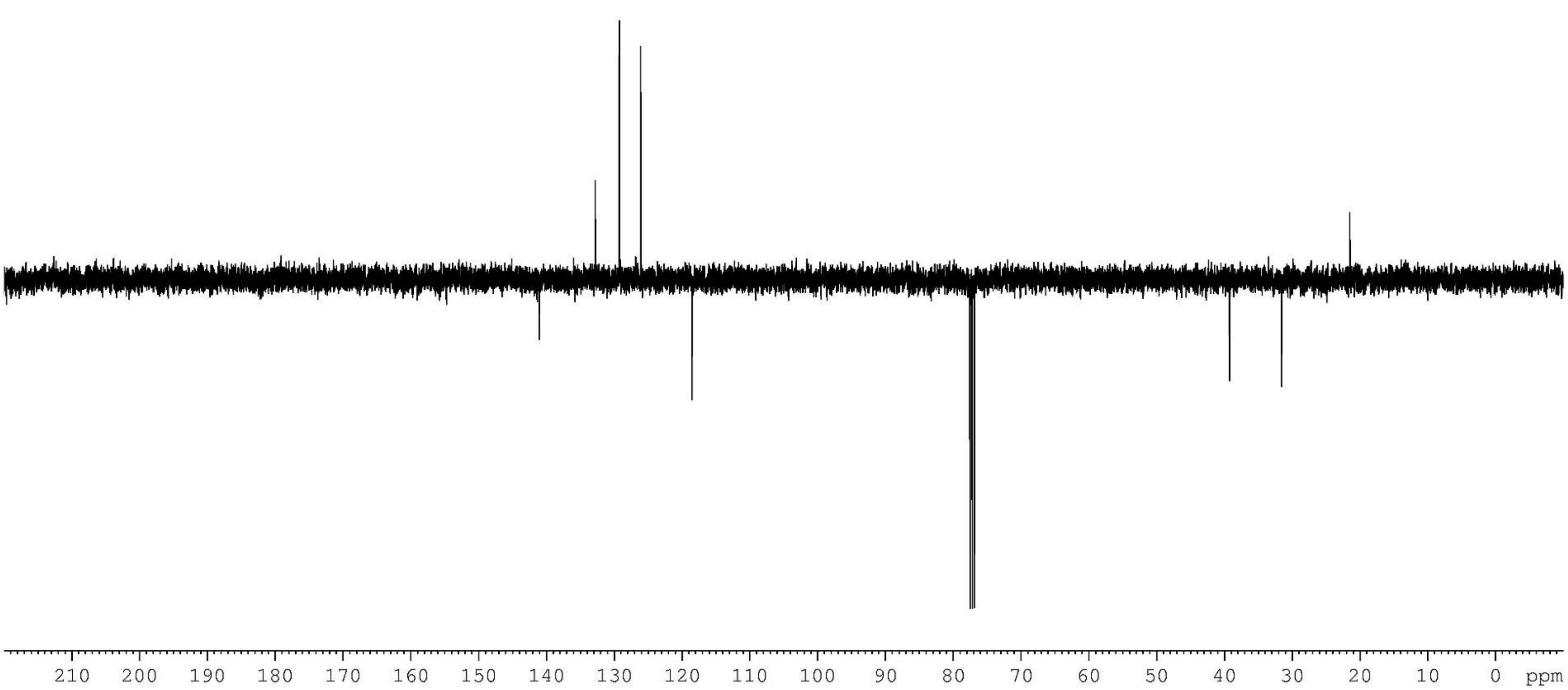
5b

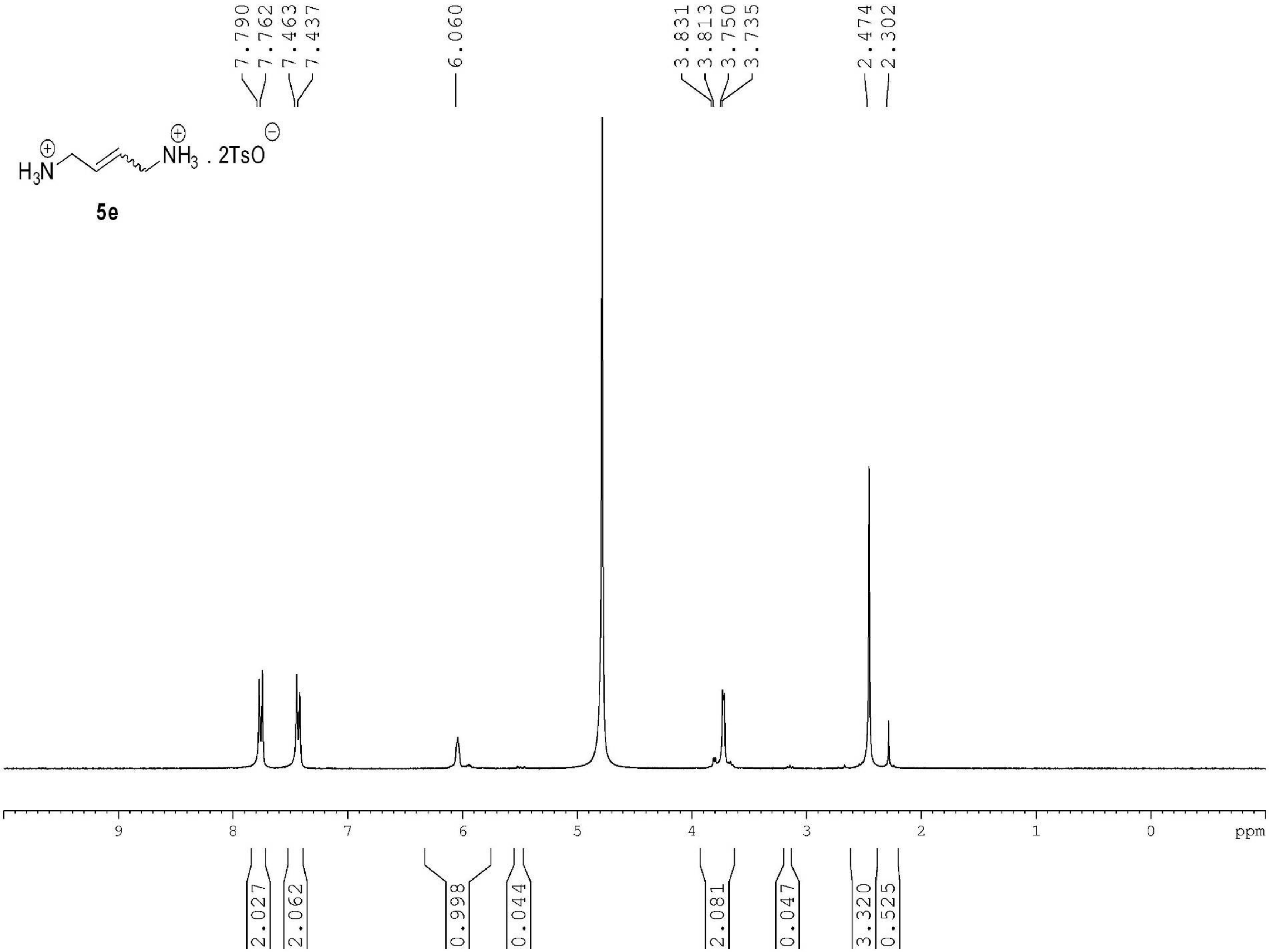
129.956
128.780
50.256
49.831
49.405
48.979
48.554
48.127
47.702
40.258
40.126
31.496
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.777
7.750
7.452
7.426
5.690
5.682
5.678
5.672
5.665
3.144
3.120
3.097
2.503
2.484
2.464
$H_3\overset{\oplus}{N}$ … $\overset{\oplus}{N}H_3$. 2TsO$^{\ominus}$
5d
9
8
7
6
5
4
3
2
1
0
ppm
2.012
2.000
0.972
1.970
4.989


H3N
NH3 . 2TsO

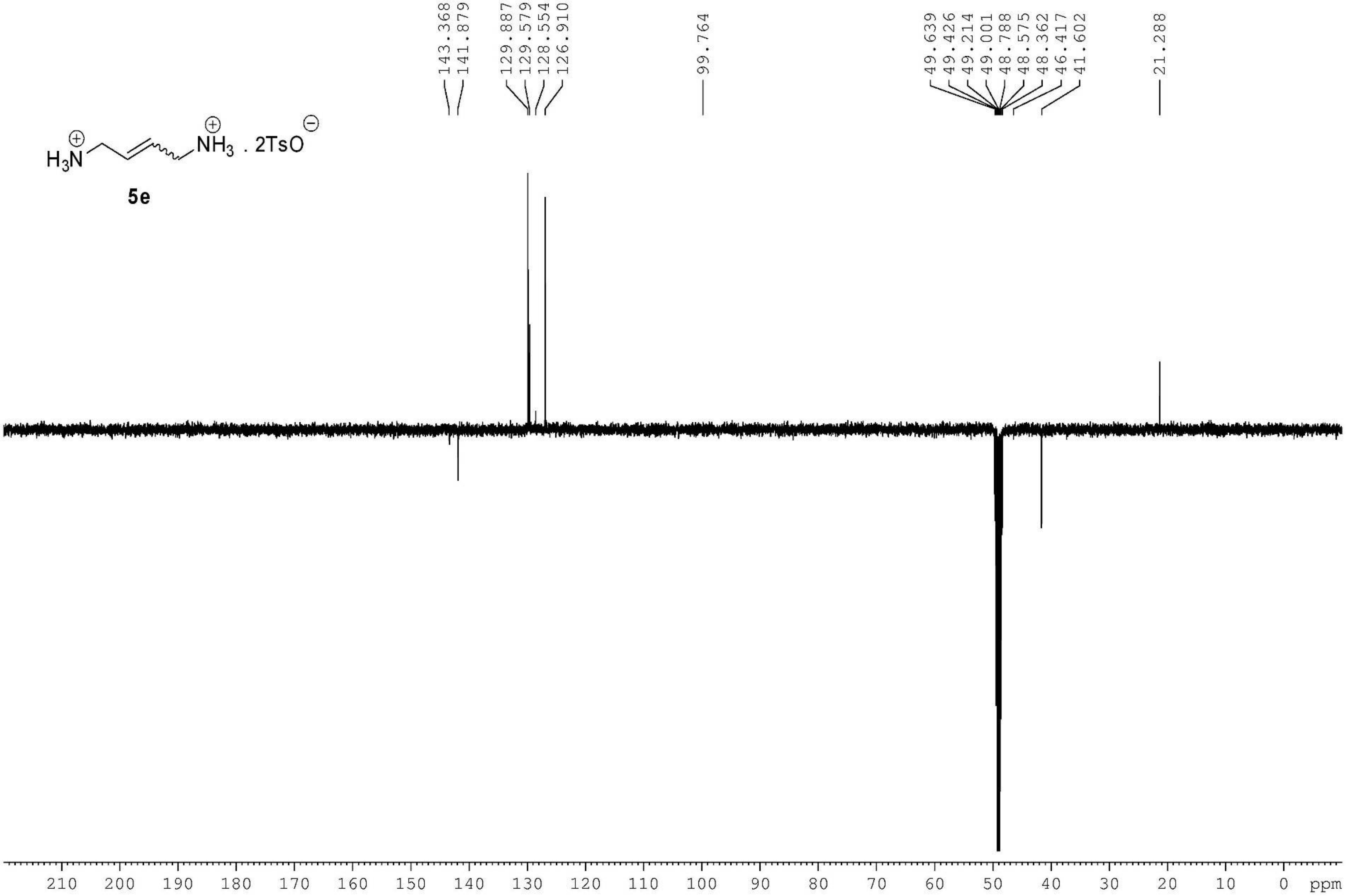
5d


141.028
132.780
129.244
126.070
118.517
77.476
77.159
76.841
39.215
31.531
21.472
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



5e

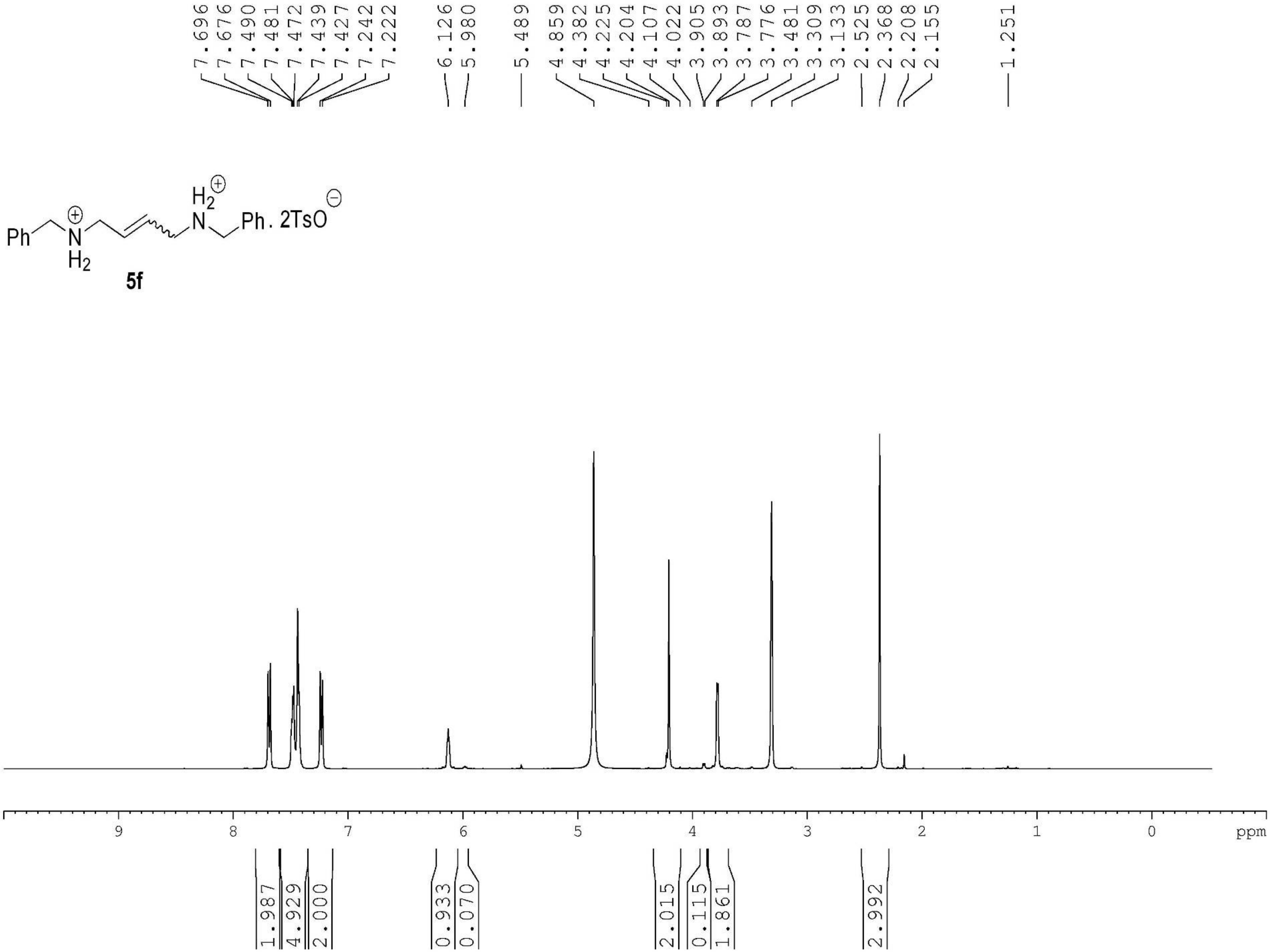
7.790
7.762
7.463
7.437
6.060
3.831
3.813
3.750
3.735
2.474
2.302
H3N⊕
NH3⊕ . 2TsO⊖
9
8
7
6
5
4
3
2
1
0
ppm
2.027
2.062
0.998
0.044
2.081
0.047
3.320
0.525

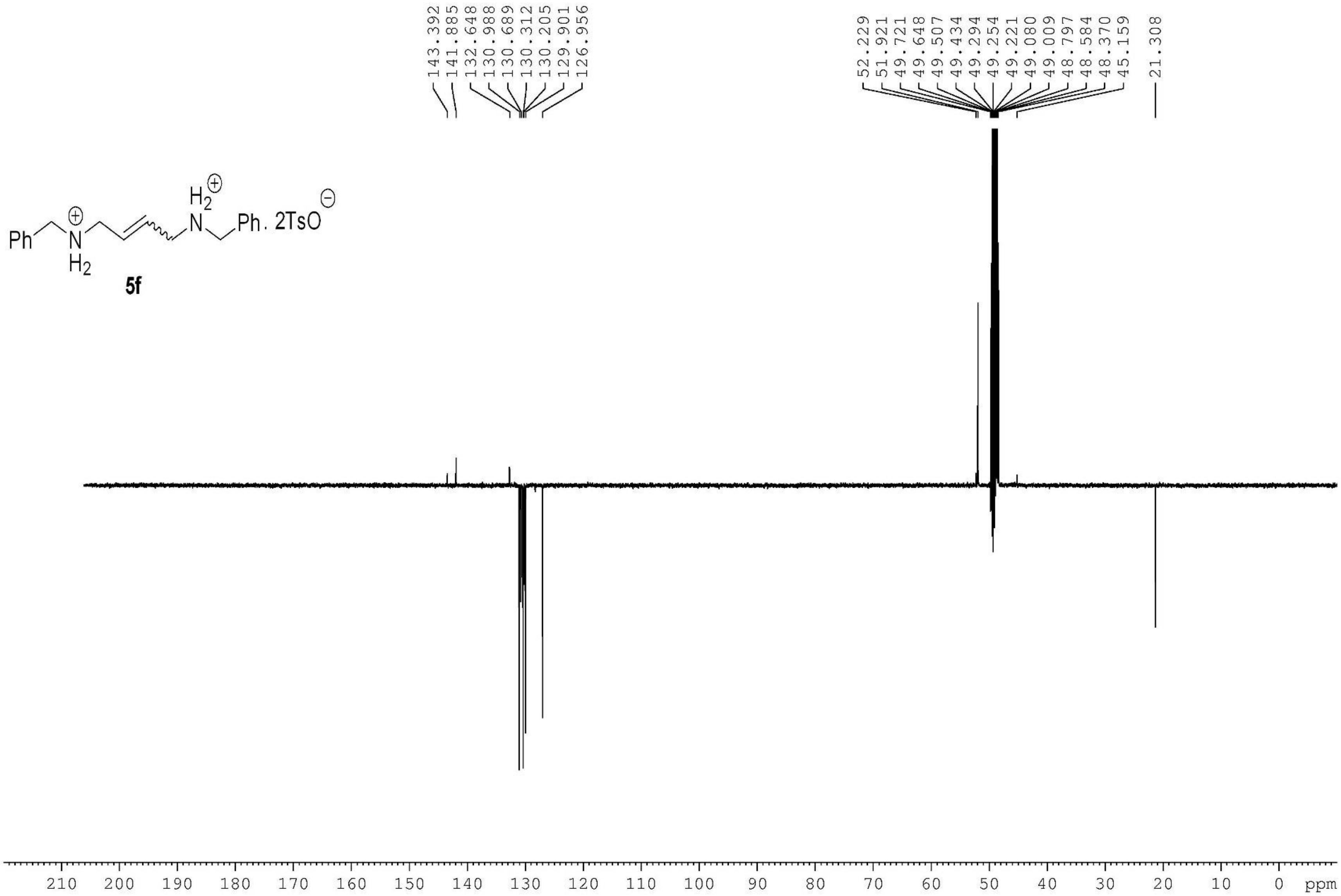

143.368
141.879
129.887
129.579
128.554
126.910
99.764
49.639
49.426
49.214
49.001
48.788
48.575
48.362
46.417
41.602
21.288
$H_3\overset{\oplus}{N}$
$\overset{\oplus}{N}H_3$. 2TsO$^{\ominus}$
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

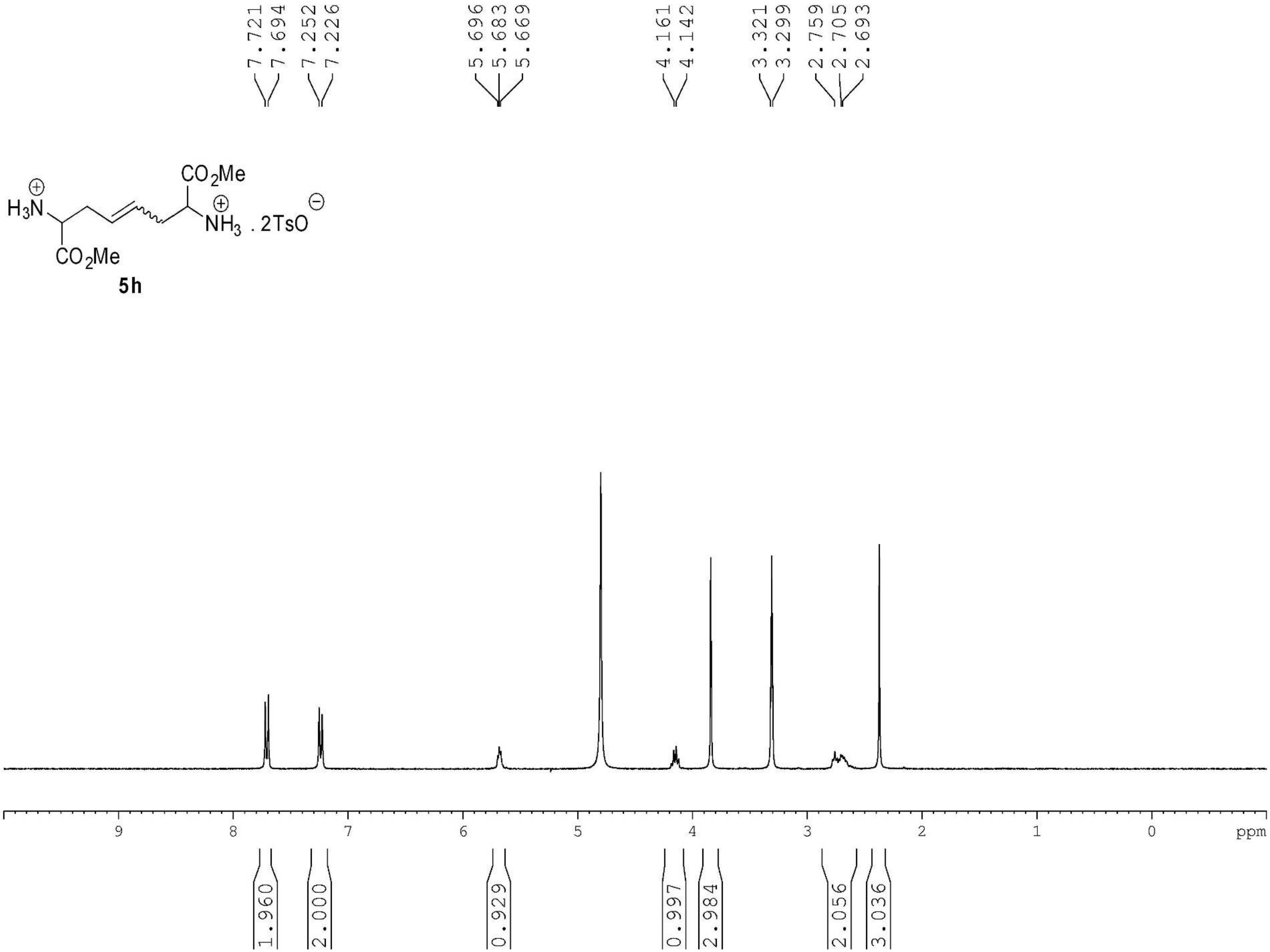
5e

Ph
N
H2
H2
N
Ph. 2TsO

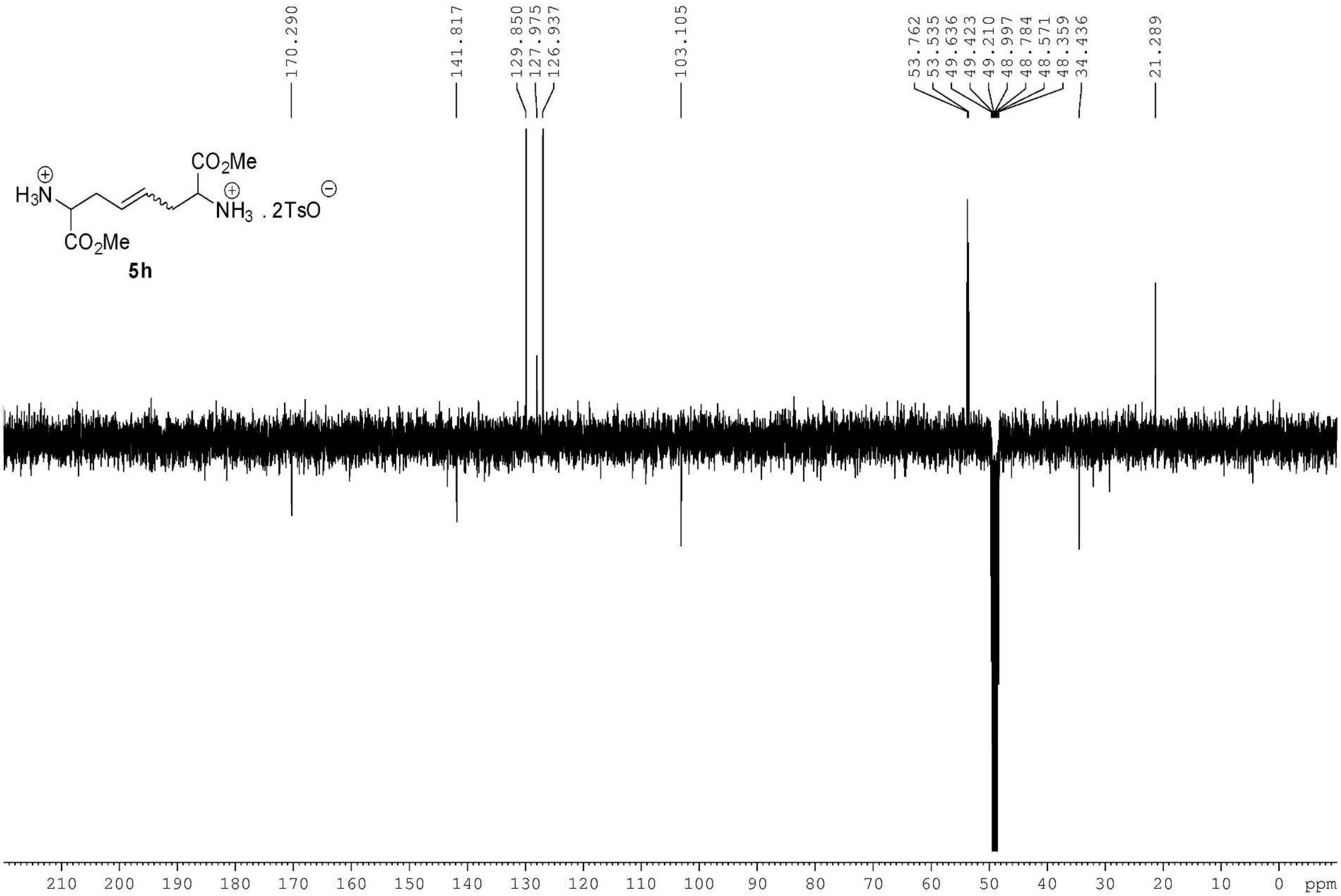
5f


7.696
7.676
7.490
7.481
7.472
7.439
7.427
7.242
7.222
6.126
5.980
5.489
4.859
4.382
4.225
4.204
4.107
4.022
3.905
3.893
3.787
3.776
3.481
3.309
3.133
2.525
2.368
2.208
2.155
1.251
9
8
7
6
5
4
3
2
1
0
ppm
1.987
4.929
2.000
0.933
0.070
2.015
0.115
1.861
2.992


143.392
141.885
132.648
130.988
130.689
130.312
130.205
129.901
126.956
52.229
51.921
49.721
49.648
49.507
49.434
49.294
49.254
49.221
49.080
49.009
48.797
48.584
48.370
45.159
21.308
Ph
N
H2
H2
N
Ph. 2TsO
5f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

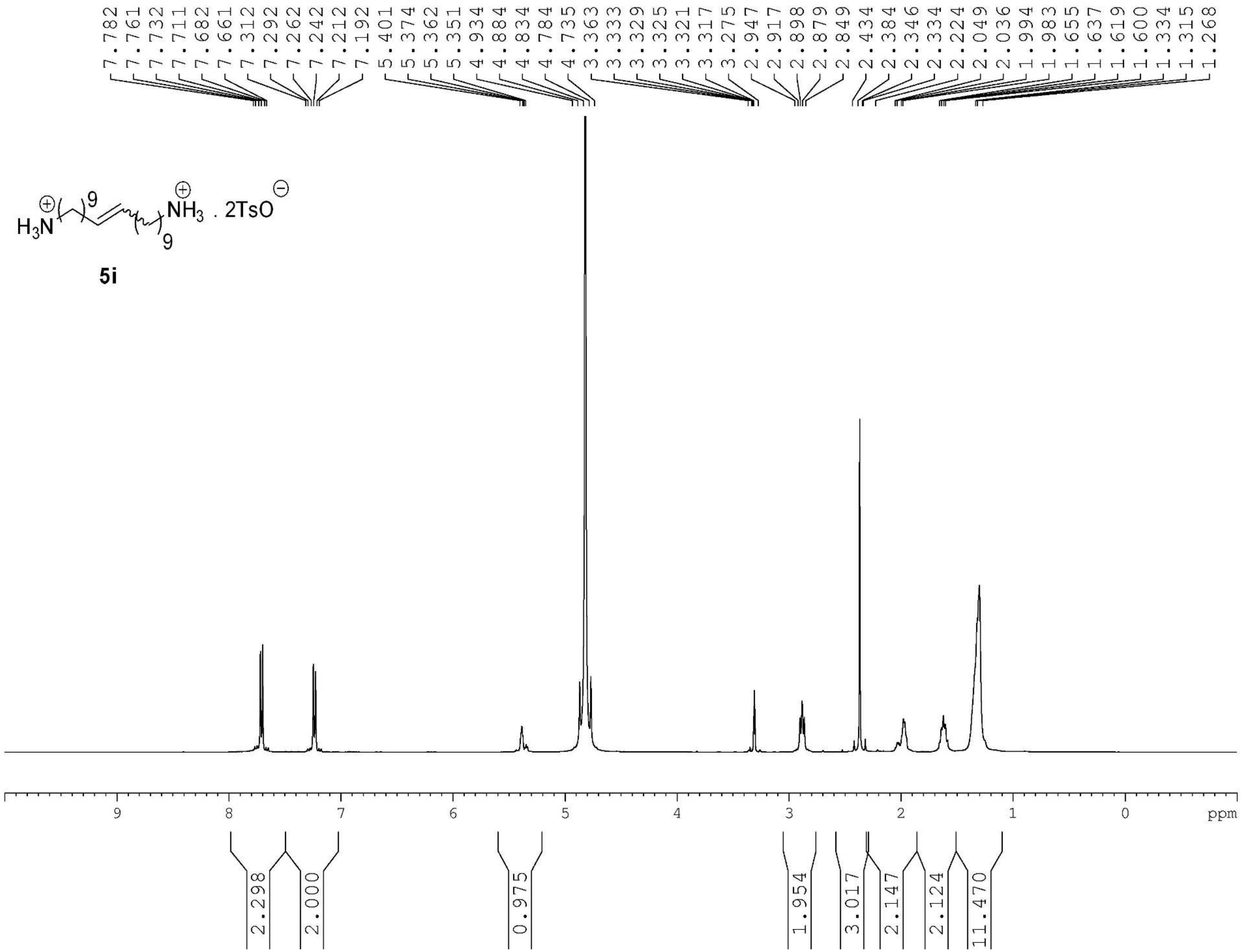


5h
7.721
7.694
7.252
7.226
5.696
5.683
5.669
4.161
4.142
3.321
3.299
2.759
2.705
2.693
9
8
7
6
5
4
3
2
1
0
ppm
1.960
2.000
0.929
0.997
2.984
2.056
3.036


170.290
141.817
129.850
127.975
126.937
103.105
53.762
53.535
49.636
49.423
49.210
48.997
48.784
48.571
48.359
34.436
21.289
CO2Me
H3N
NH3
. 2TsO
CO2Me
5h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

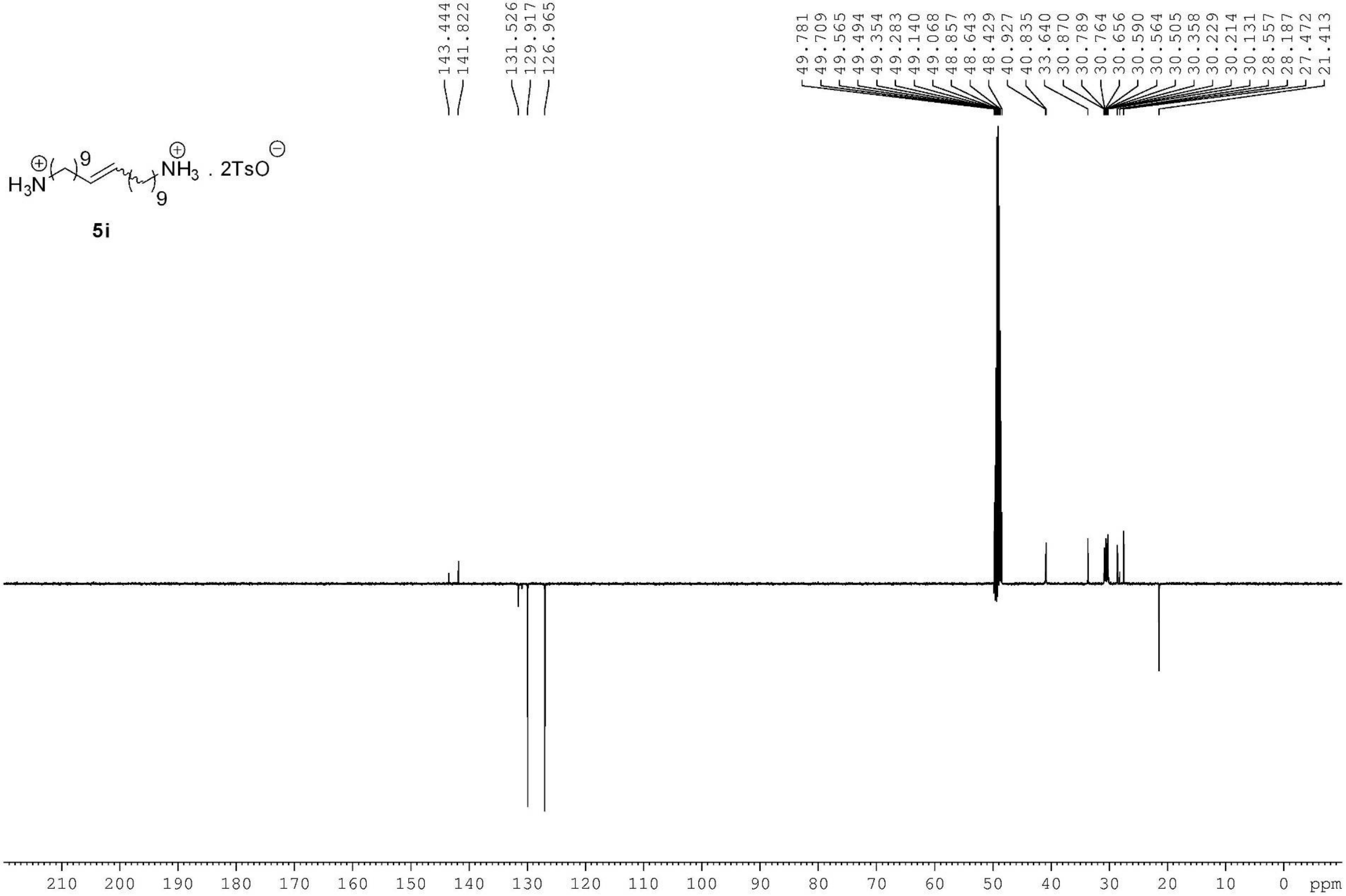
H3N
9
NH3
. 2TsO
9

5i


7.782
7.761
7.732
7.711
7.682
7.661
7.312
7.292
7.262
7.242
7.212
7.192
5.401
5.374
5.362
5.351
4.934
4.884
4.834
4.784
4.735
3.363
3.333
3.329
3.325
3.321
3.317
3.275
2.947
2.917
2.898
2.879
2.849
2.434
2.384
2.346
2.334
2.224
2.049
2.036
1.994
1.983
1.655
1.637
1.619
1.600
1.334
1.315
1.268
9
8
7
6
5
4
3
2
1
0
ppm
2.298
2.000
0.975
1.954
3.017
2.147
2.124
11.470

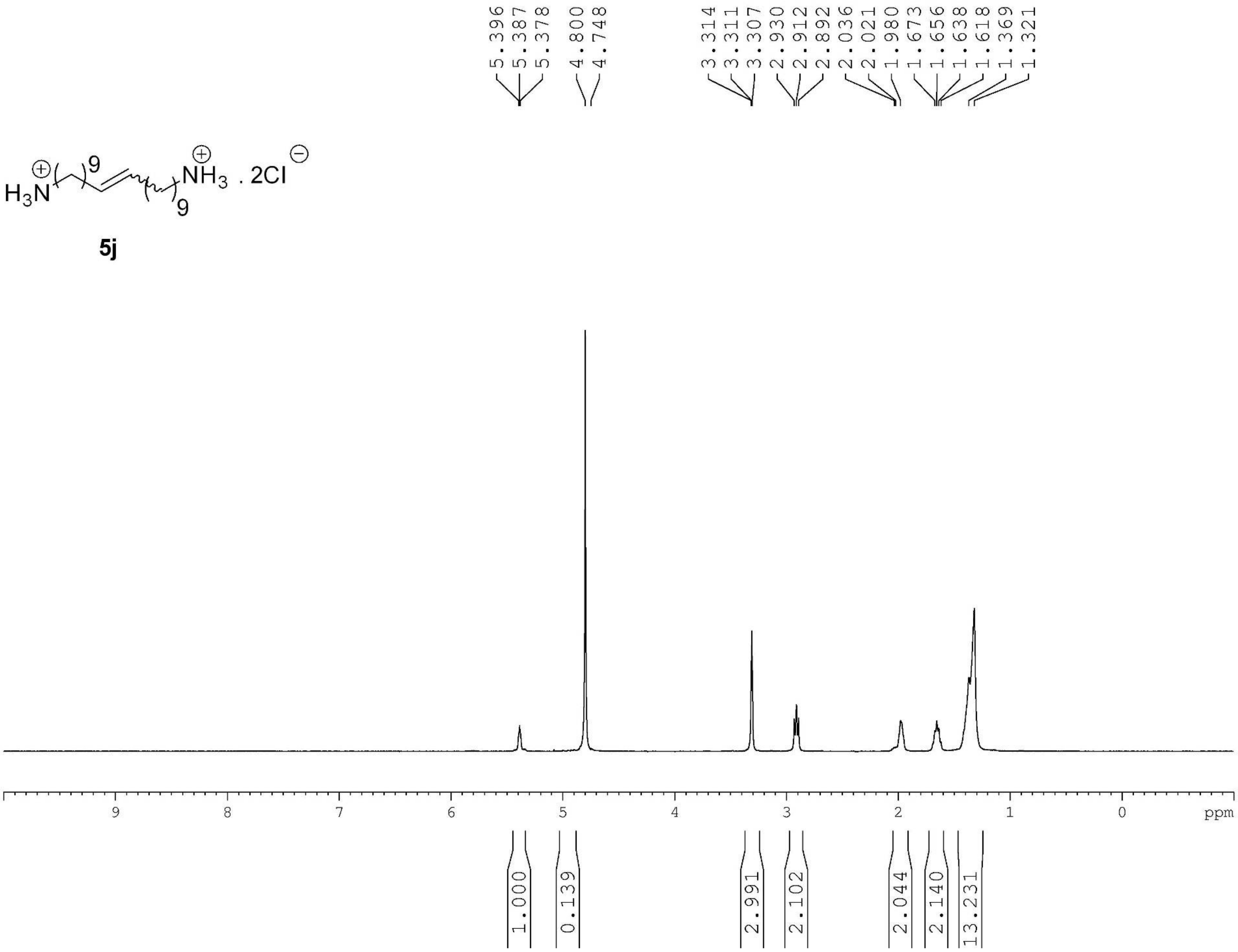
H3N
9
NH3
9
. 2TsO

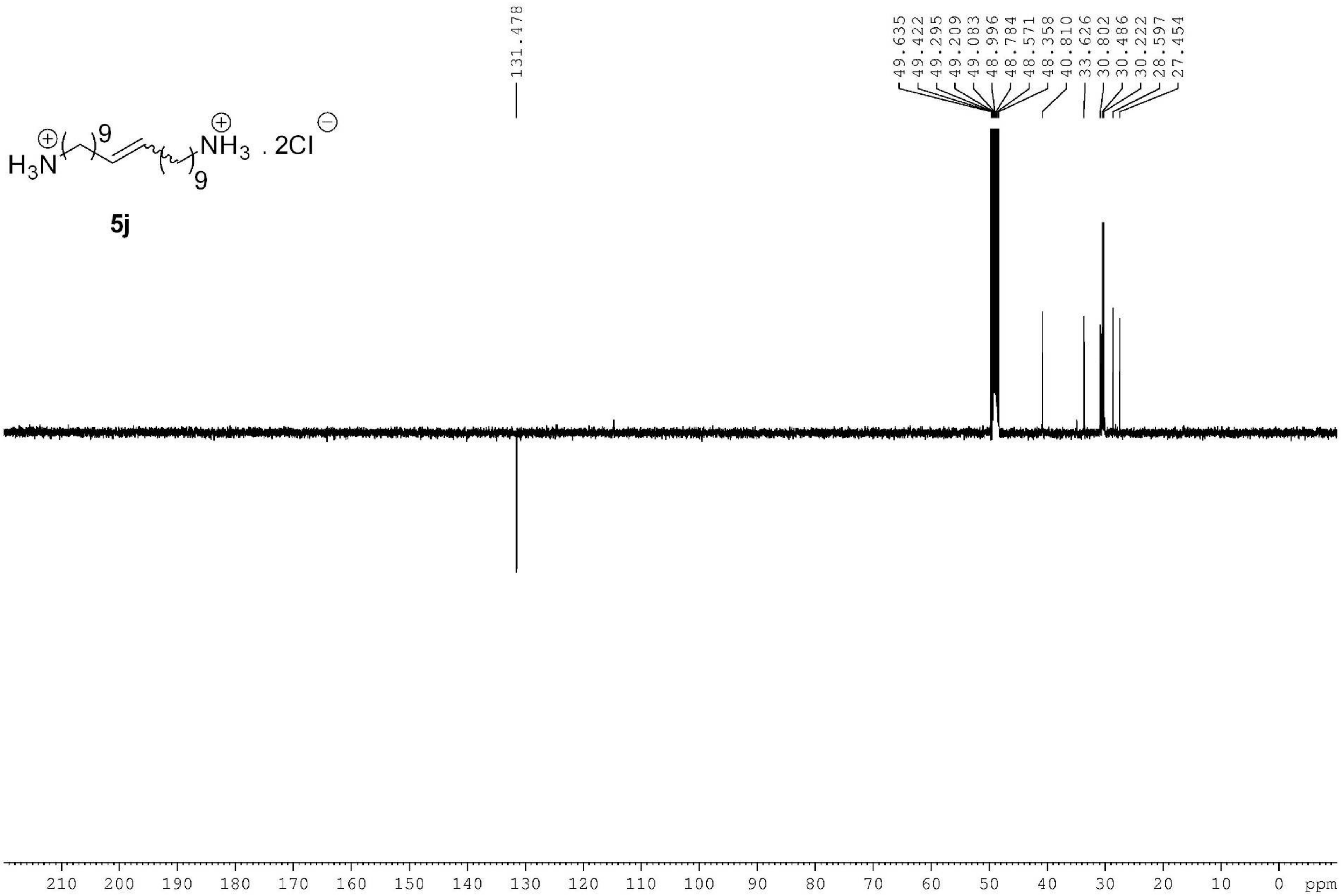
5i


143.444
141.822
131.526
129.917
126.965
49.781
49.709
49.565
49.494
49.354
49.283
49.140
49.068
48.857
48.643
48.429
40.927
40.835
33.640
30.870
30.789
30.764
30.656
30.590
30.564
30.505
30.358
30.229
30.214
30.131
28.557
28.187
27.472
21.413
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

H3N⊕
9
9
NH3⊕
. 2Cl⊖

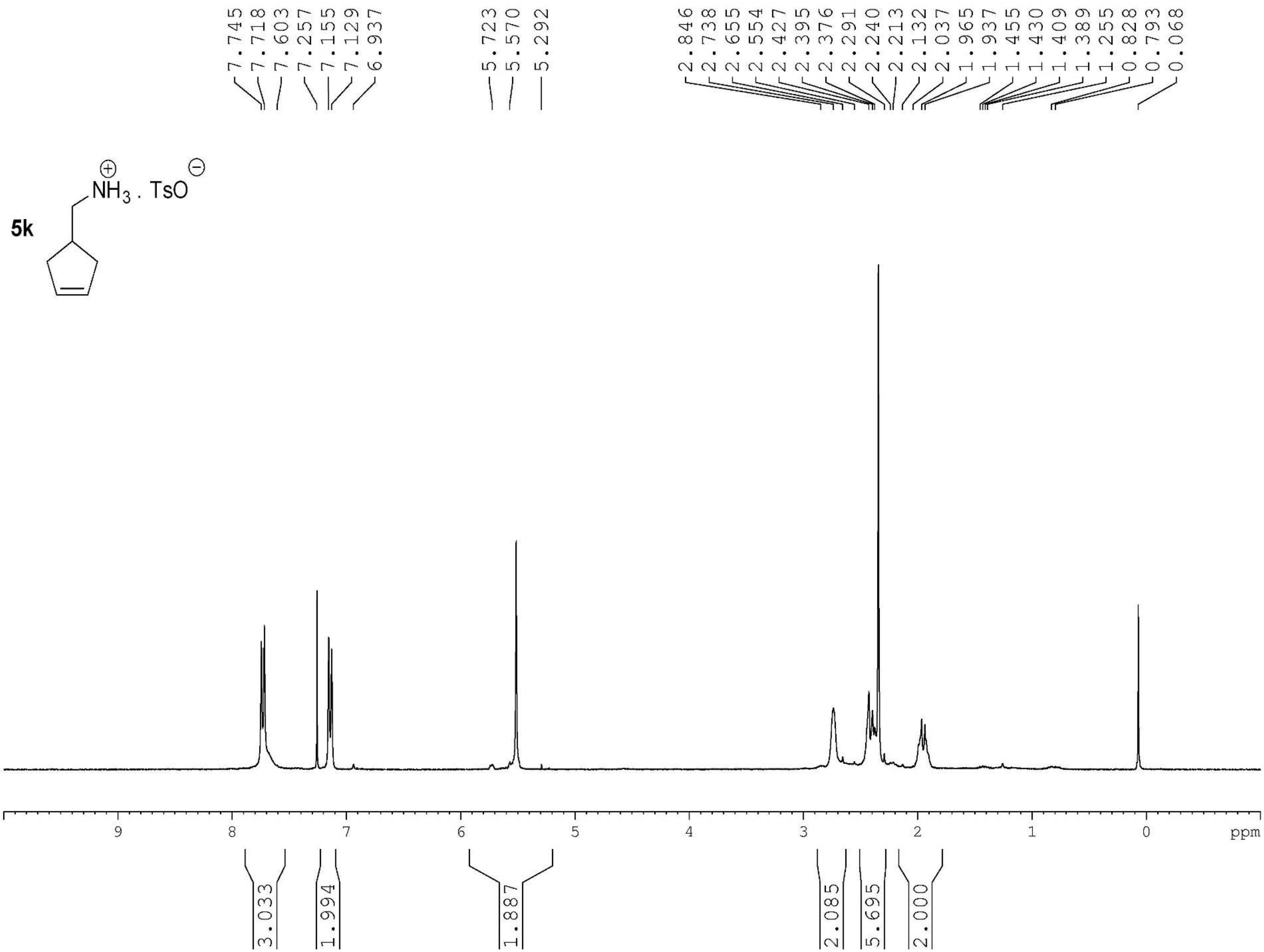
5j


5.396
5.387
5.378
4.800
4.748
3.314
3.311
3.307
2.930
2.912
2.892
2.036
2.021
1.980
1.673
1.656
1.638
1.618
1.369
1.321
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.139
2.991
2.102
2.044
2.140
13.231

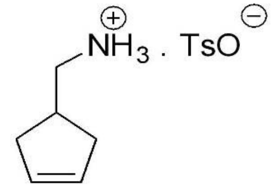

131.478
49.635
49.422
49.295
49.209
49.083
48.996
48.784
48.571
48.358
40.810
33.626
30.802
30.486
30.222
28.597
27.454
H3N
9
NH3
9
. 2Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

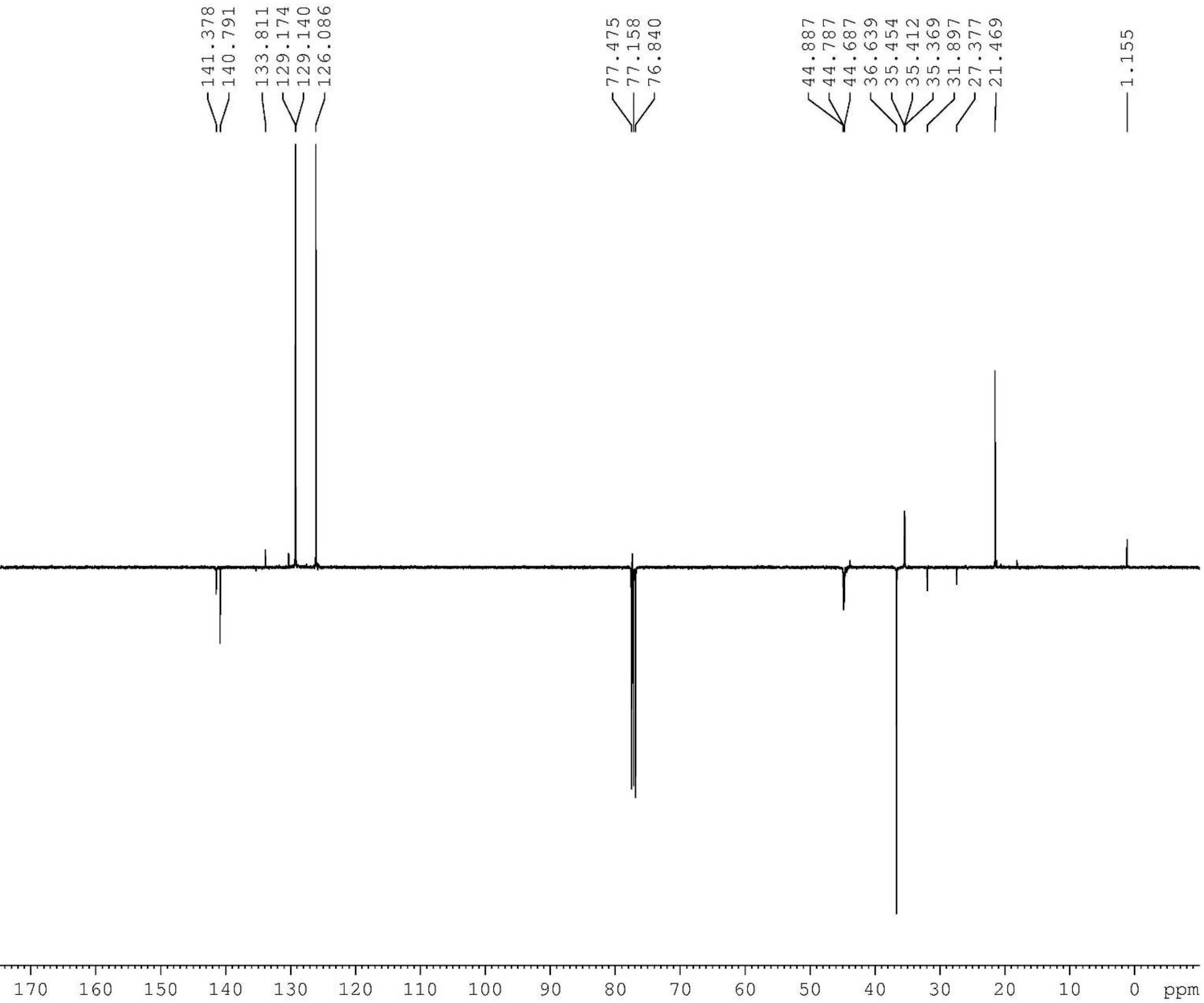
5j

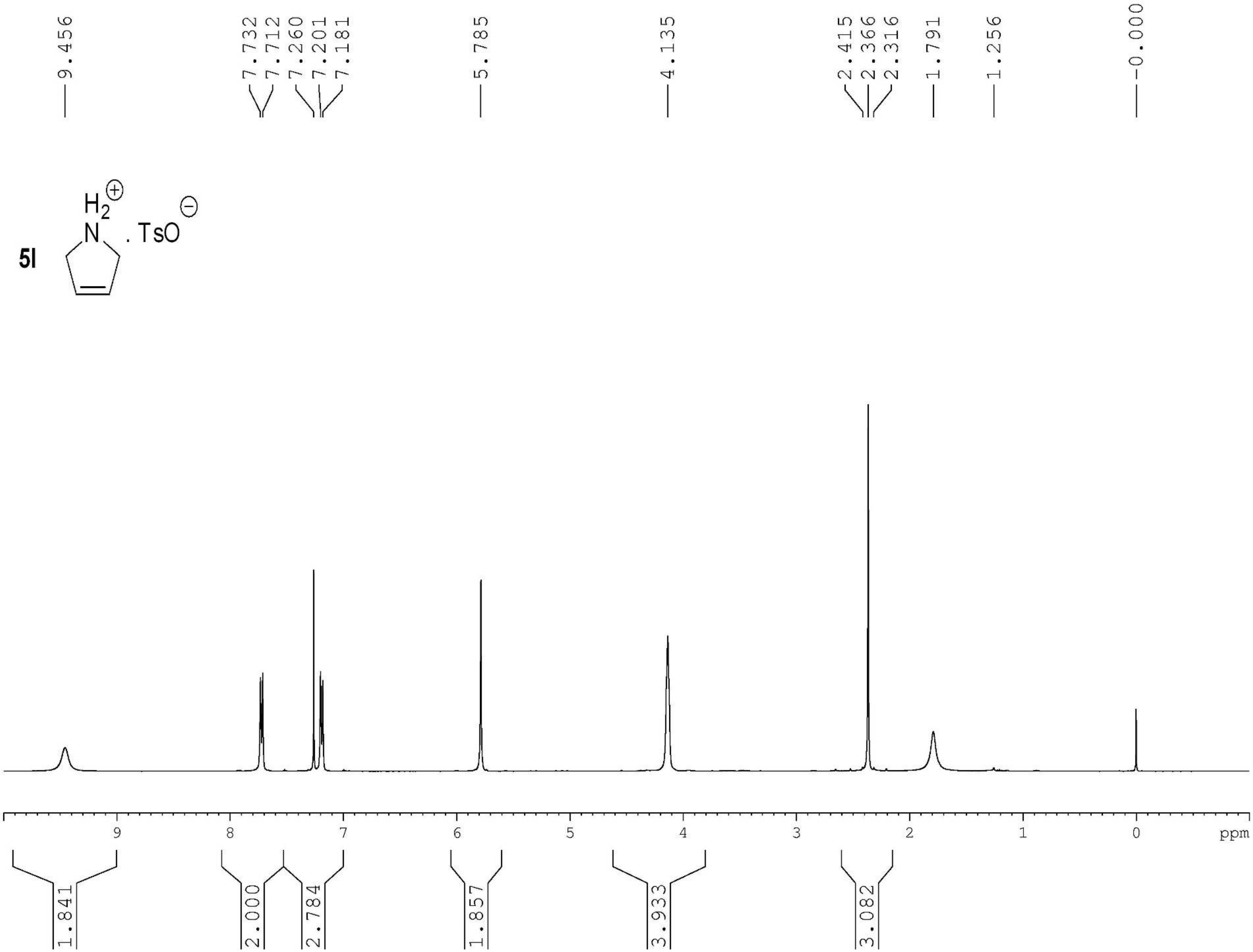
5k


NH3 . TsO
7.745
7.718
7.603
7.257
7.155
7.129
6.937
5.723
5.570
5.292
2.846
2.738
2.655
2.554
2.427
2.395
2.376
2.291
2.240
2.213
2.132
2.037
1.965
1.937
1.455
1.430
1.409
1.389
1.255
0.828
0.793
0.068
9
8
7
6
5
4
3
2
1
0
ppm
3.033
1.994
1.887
2.085
5.695
2.000

5k

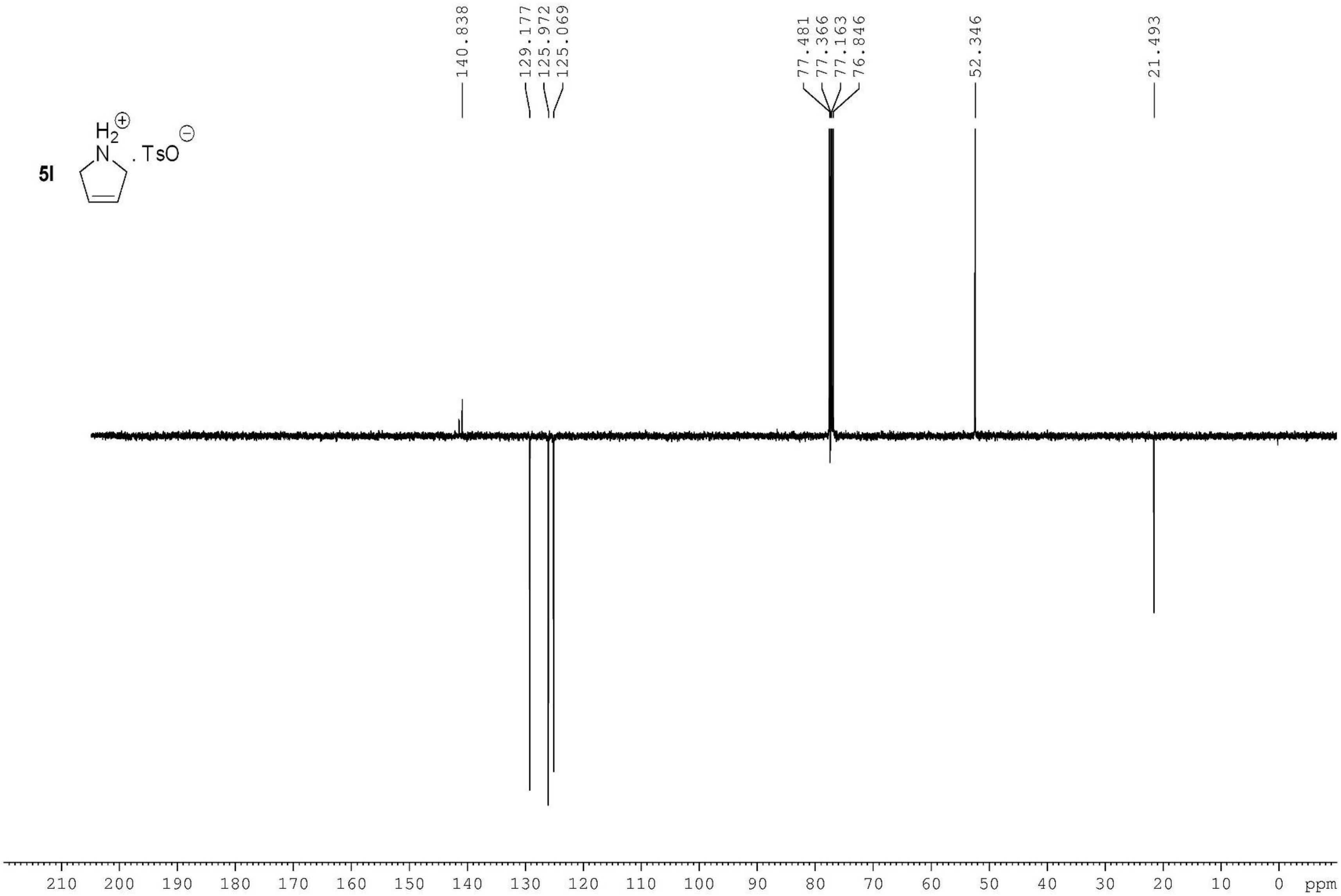

$\overset{\oplus}{N}H_3$. TsO$^{\ominus}$

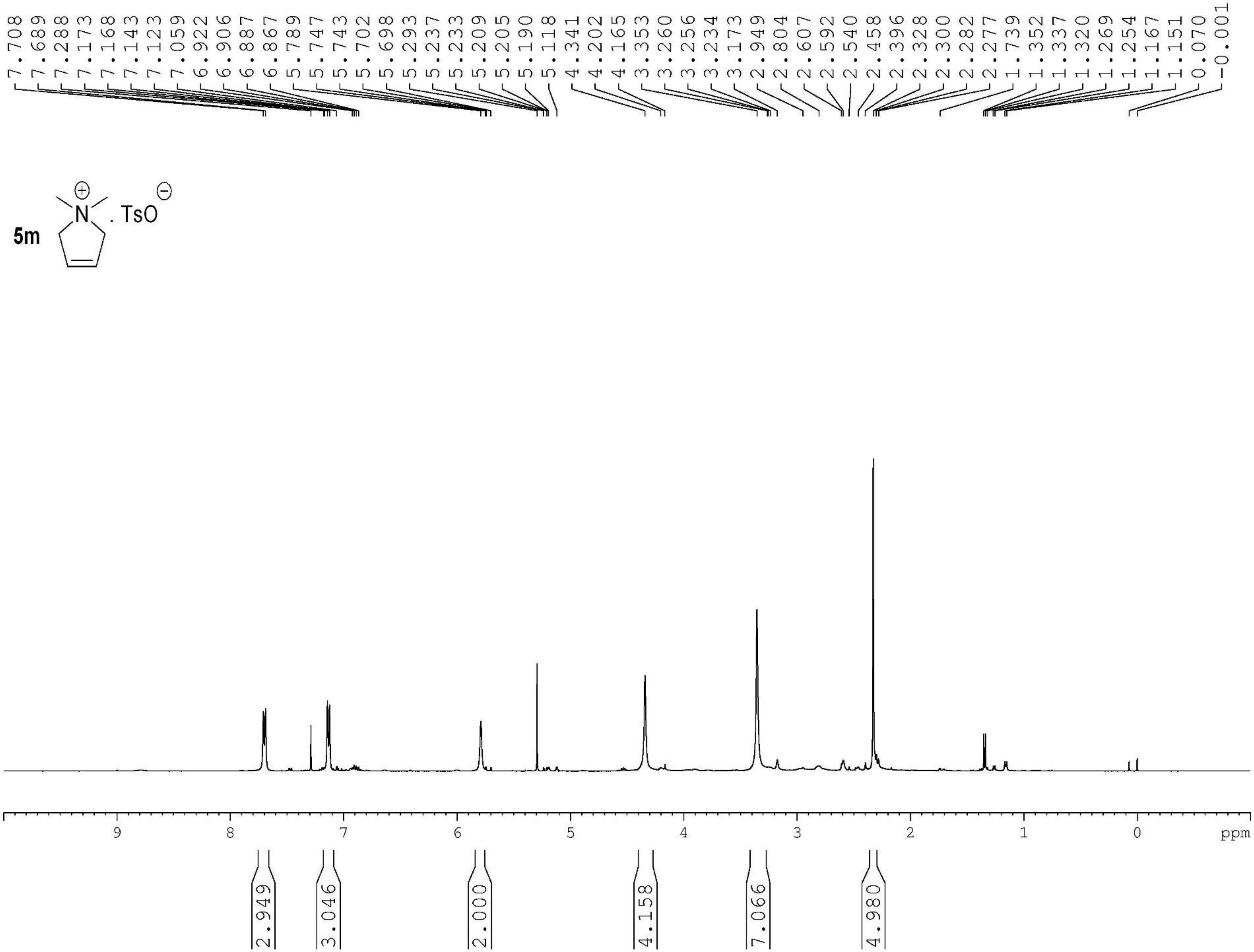

141.378
140.791
133.811
129.174
129.140
126.086
77.475
77.158
76.840
44.887
44.787
44.687
36.639
35.454
35.412
35.369
31.897
27.377
21.469
1.155
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



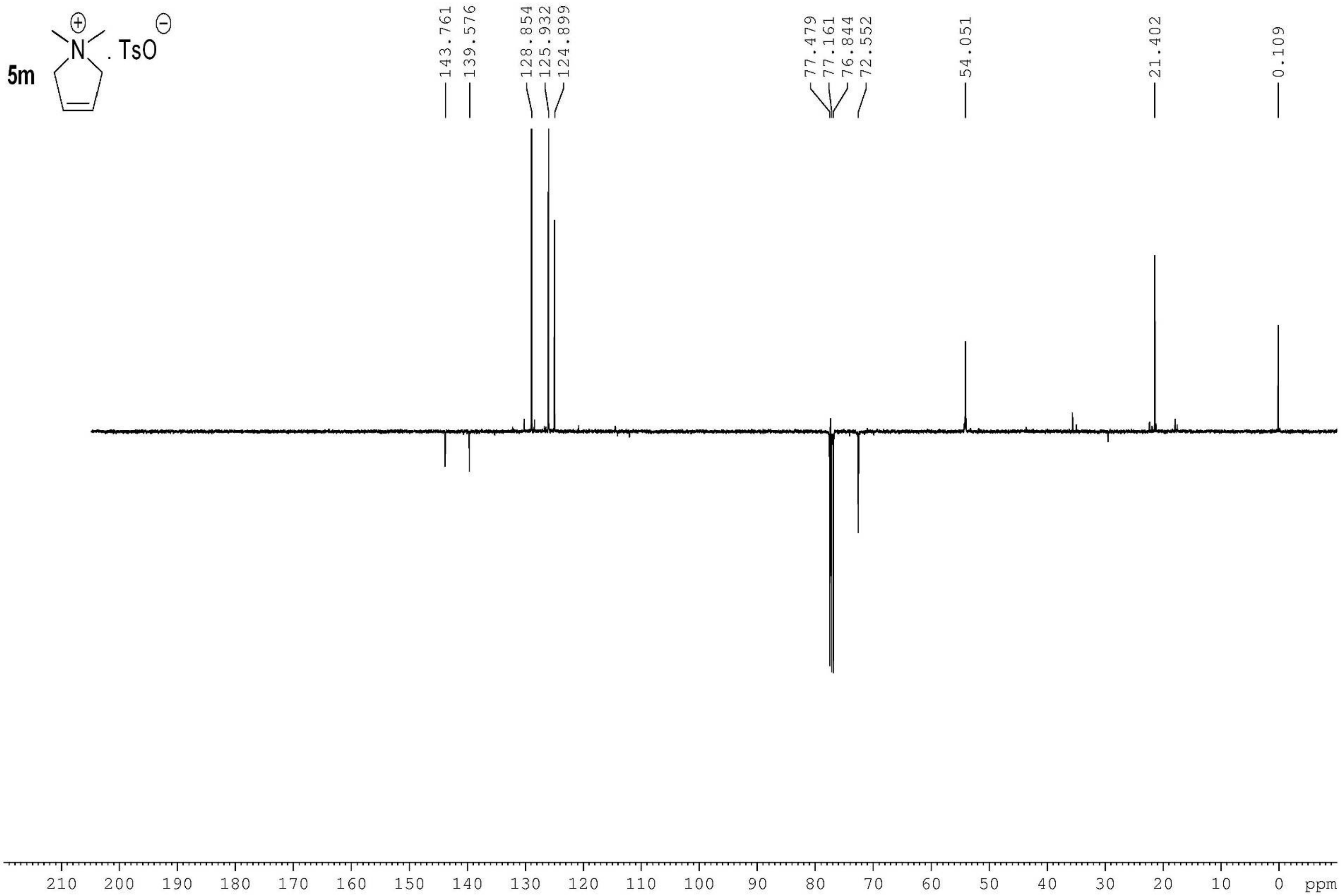
5l

9.456
7.732
7.712
7.260
7.201
7.181
5.785
4.135
2.415
2.366
2.316
1.791
1.256
-0.000
H_2
N
. TsO
9
8
7
6
5
4
3
2
1
0
ppm
1.841
2.000
2.784
1.857
3.933
3.082


140.838
129.177
125.972
125.069
77.481
77.366
77.163
76.846
52.346
21.493
5l
H_2 ⊕
N
. TsO ⊖
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.708
7.689
7.288
7.173
7.168
7.143
7.123
7.059
6.922
6.906
6.887
6.867
5.789
5.747
5.743
5.702
5.698
5.293
5.237
5.233
5.209
5.205
5.190
5.118
4.341
4.202
4.165
3.353
3.260
3.256
3.234
3.173
2.949
2.804
2.607
2.592
2.540
2.458
2.396
2.328
2.300
2.282
2.277
1.739
1.352
1.337
1.320
1.269
1.254
1.167
1.151
0.070
-0.001
5m
N
. TsO
9
8
7
6
5
4
3
2
1
0
ppm
2.949
3.046
2.000
4.158
7.066
4.980

5m


. TsO
143.761
139.576
128.854
125.932
124.899
77.479
77.161
76.844
72.552
54.051
21.402
0.109
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm