Supporting Information for:

Cobalt(III) Porphyrin Catalyzed Aza-Diels–Alder Reaction

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Contents

Instrumentation and Chemicals

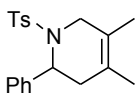
All manipulations of oxygen– and moisture–sensitive materials were conducted in a dry box or with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane (^{1}H) as an internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration, and identification. High–resolution mass spectra were obtained with a Thermo Fisher SCIENTIFIC EXACTIVE spectrometer. X-Ray data were taken on a Bruker Smart APEX X-Ray diffracto- meter equipped with a large area CCD detector. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC–908 equipped with JAIGEL–1H and –2H columns (toluene as an eluent). Infrared spectra (IR) spectra were determined on a SHIMADZU IR Affinity–1 spectrometer. Melting points were determined using a YANAKO MP–500D. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 μm). Toluene and cobalt(II) acetate were purchased from Wako Pure Chemical Co.[1-3] Free base *meso*-tetraphenylporphine and $AgSbF_6$ were purchased from Strem chemicals. Dienes were purchased from TCI. Aldimines were prepared according to the reported procedure.[4,5] Unless otherwise noted, commercially available reagents were used without purification.

Experimental Procedure and Characterization Data for Products.

Prepapration of [Co(TPP)]SbF$_6$.[1-3] Cobalt(II) porphyrin ([Co(TPP)]) was prepared with free base tetraphenyl porphyrin (TPP) and cobalt(II) acetate by refluxing in DMF. The [Co(TPP)] was then oxidized by air with hydrogen chloride solution of MeOH to afford [Co(TPP)]Cl, which was purified with recrystallization in chloroform. X-Ray single crystal analysis was performed to confirm the formation of [Co(TPP)]Cl. The cationic cobalt complex was prepared following reported procedure: [Co(TPP)]Cl (311 mg, 0.44 mmol) and $AgSbF_6$ (137 mg, 0.4 mmol) was dissolved in dry CH_2Cl_2 (10 ml) and stirred for 6 h in dry box. The reaction mixture was filtered and concentrated to dryness. The complex was used without further purification. Other cobalt complexes were also prepared by this procedure.

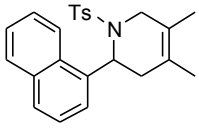
General procedure. The reaction was performed in a 15 mL sealed tube equipped with a Teflon−coated magnetic stirrer bar. A diene (0.8 mmol) were added to a solution of imine (0.4 mmol) and [Co(TPP)]SbF_6 (3.6 mg, 4.0 μmol) in toluene (4 mL) in a dry box. The flask was taken outside the dry box and stirred at ambient temperature for the indicated time under argon atmosphere. The resulting reaction mixture was filtered through a silica gel pad, concentrated *in vacuo*. The residue was purified by flash silica gel column chromatography (20 g, 2x15 cm, hexane/ethyl acetate = 5:1) to give the corresponding product.

4,5-Dimethyl-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3aa**).



Yield: 92%. Mp. 87−89 ℃ (ethyl acetate). TLC: R_f = 0.37 (hexane/ethyl acetate = 7:1) ^{1}H NMR ($CDCl_3$) δ 7.65 (dt, *J* = 7.0, 2.0 Hz, 2H), 7.20−7.28 (m, 7H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.21−3.25 (m, 1H), 2.40 (s, 3H), 2.31−2.37 (m, 1H), 2.19 (d, *J* = 17.5 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.14, 139.95, 137.98, 129.58, 128.55, 127.56, 127.54, 127.27, 123.44, 122.50, 53.75, 45.16, 32.78, 21.69, 18.82, 16.21. IR (KBr): 2919, 1927, 1596, 1522, 1517, 1352, 1330, 1279, 1162, 1090, 1009, 856, 814 cm^{-1}. HRMS (ESI$^+$) found 342.1512, calcd for $[M+H]^+$ 342.1522.

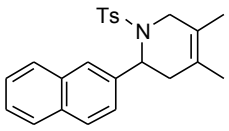
4,5-Dimethyl-2-(naphthalen-1-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ba**).



Yield: 89%. Mp. 155−157 ℃ (ethyl acetate). TLC: R_f = 0.36 (hexane/ethyl acetate = 7:1). ^{1}H NMR ($CDCl_3$) δ 8.66 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.62 (t, *J* = 8.5 Hz, 1H), 7.51 (t, *J* = 8.5 Hz, 1H), 7.32 (t, *J* = 8.5 Hz, 1H), 7.19−7.24 (m, 3H), 6.06 (d, *J* = 7.5 Hz, 1H), 3.77 (d, *J* = 18.0 Hz, 1H), 3,17 (d, *J* = 18.0 Hz, 1H), 2.49−2.54 (m, 1H), 2.40 (s, 3H), 2.22 (d, *J* = 18.0 Hz, 1H), 1.53 (s, 3H), 1.50 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.33, 137.50, 135.09, 134.16, 131.86, 129.30, 128.96, 128.74, 127.60, 126.82, 125.90, 124.87, 124.59,

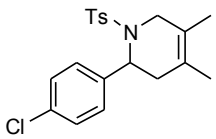
124.43, 124.30, 122.59, 50.71, 45.49, 32.84, 21.62, 18.40, 16.40. IR (KBr): 3065, 2908, 2882, 1598, 1511, 1442, 1338, 1303, 1183, 1163, 1139, 1054, 919, 815 cm^{-1}. HRMS (ESI^+) found 392.1666, calcd for $[M+H]^+$ 392.1679.

4,5-Dimethyl-2-(naphthalen-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ca**).



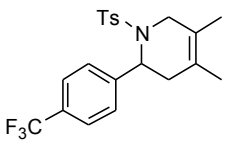
Yield: 83%. Mp. 100–102 ℃ (ethyl acetate). TLC: R_f = 0.41 (hexane/ethyl acetate = 5:1) ^1H NMR ($CDCl_3$) δ 7.71–7.81 (m. 3H), 7.68–7.70 (m, 2H), 7.56 (s, 1H), 7.44–7.47 (m, 3H), 7.20–7.22 (m, 2H), 5.39 (d, *J* = 6.5 Hz, 1H), 3.93 (d *J* = 18.5 Hz. 1H), 3.27 (d, *J* = 18.5 Hz, 1H), 2.32–2.43 (m, 2H), 2.39 (s, 3H), 1.62 (s, 3H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.19, 137.95, 137.20, 133.25, 132.86, 129.58, 128.32, 128.25, 127.68, 127.22, 126.16, 126.13, 126.04, 125.95, 123.34, 122.58, 53.88, 45.29, 32.57, 21.64, 18.84, 16.22. IR (KBr): 2978, 2880, 1596, 1507, 1493, 1457, 1437, 1386, 1378, 1339, 1320, 1292, 1107, 949, 841 cm^{-1}. HRMS (ESI^+) found 392.1666, calcd for $[M+H]^+$ 392.1679.

2-(4-Chlorophenyl)-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3da**).



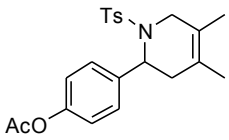
Yield: 90%. Mp. 110–112 ℃ (ethyl acetate). TLC: R_f = 0.41 (hexane/ethyl acetate = 7:1) ^1H NMR ($CDCl_3$) δ 7.64 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.20–7.24 (m, 4H), 7.15–7.18 (m, 2H), 5.18 (d, *J* = 6.5 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.19–3.23 (m, 1H), 2.40 (s, 3H), 2.30–2.36 (m, 1H), 2.14 (d, *J* = 17.5 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.43, 138.44, 137.74, 133.36, 129.65, 128.93, 128.66, 127.18, 123.18, 122.59, 53.14, 45.10, 32.68, 21.68, 18.81, 16.18. IR (KBr): 2922, 2856, 1595, 1492, 1447, 1325, 1292, 1159, 1089, 1011, 922, 816, 715 cm^{-1}. HRMS (ESI^+) found 342.1512, calcd for $[M+H]^+$ 342.1522. HRMS (ESI^+) found 376.1121, calcd for $[M+H]^+$ 342.1133.

4,5–Dimethyl–1–tosyl–2–(4–(trifluoromethyl)phenyl)–1,2,3,6–tetrahydropyridine (**3ea**).



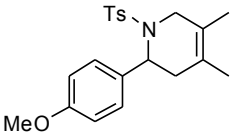
Yield: 85%. Mp. 93–95 ℃ (ethyl acetate). TLC: R_f = 0.29 (hexane/ethyl acetate/triethylamine = 20:1:0.02) ^1H NMR ($CDCl_3$) δ 7.63 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.33–7.35 (m, 2H), 7.21–7.24 (m, 2H), 5.25 (d, *J* = 6.5 Hz, 1H), 3.89 (d, *J* = 17.5 Hz, 1H), 3.21–3.26 (m, 1H), 2.40 (s, 3H), 2.36–2.39 (m, 1H), 2.19 (d, *J* = 17.5 Hz, 1H), 1.58 (s, 3H), 1.53 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 144.09, 143.47, 137.53, 129.68, 129.67 (q, *J* = 32.2 Hz), 127.84, 127.19, 125.50 (q, *J* = 3.8 Hz), 124.29 (q, *J* = 272.1), 123.13, 122.66, 53.46, 45.30, 32.83, 21.65, 18.84, 16.20. IR (KBr): 2920, 2880, 2858, 1620, 1437, 1413, 1342, 1322, 1183, 1141, 1114, 1107, 1063, 1038, 922, 814 cm^{-1}. HRMS (ESI^+) found 410.1382, calcd for $[M+H]^+$ 410.1396.

4-(4,5-Dimethyl-1-tosyl-1,2,3,6-tetrahydropyridin-2-yl)phenyl acetate (**3fa**).



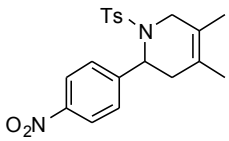
Yield: 85%. Mp. 125–127 ℃ (ethyl acetate). TLC: R_f = 0.30 (hexane/ethyl acetate = 3:1) ^{1}H NMR ($CDCl_3$) δ 7.64 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.21–7.25 (m, 4H), 6.97 (dt, *J* = 8.5, 2.0 Hz, 2H), 5.20 (d, *J* = 6.5 Hz, 1H), 3.86 (d, *J* = 17.5 Hz, 1H), 3.23 (d, *J* = 17.5 Hz, 1H), 2.30–2.36 (m, 1H), 2.28 (s, 3H), 2.15 (d, *J* = 17.5 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 169.50, 150.04, 143.23, 137.75, 137.43, 129.60, 128.62, 127.17, 123.22, 122.52, 121.54, 53.20, 45.04, 32.76, 21.64, 21.28, 18.76, 16.19. IR (KBr): 2923, 2860, 1754, 1597, 1508, 1447, 1322, 1220, 1209, 1156, 1066, 1012, 912, 805 cm^{-1}. HRMS (ESI$^+$) found 400.1563, calcd for $[M+H]^+$ 400.1577.

2-(4-Methoxyphenyl)-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ga**).



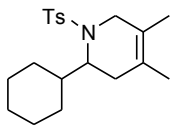
Yield: 83%. Mp. 120–122 ℃ (ethyl acetate). TLC: R_f = 0.37 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.63–7.65 (m, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.16 (dt, *J* = 8.5, 2.0 Hz, 2H), 6.78 (dt, *J* = 8.5, 2.0 Hz, 2H), 5.18 (d, *J* = 7.0 Hz, 1H), 3.84 (d, *J* = 17.5 Hz, 1H), 3.77 (s, 3H), 3.18–3.22 (m, 1H), 2.40 (s, 3H), 2.30–2.36 (m, 1H), 2.14 (d, *J* = 17.5 Hz, 1H), 1.57 (s, 3H), 1.52 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 158.99, 143.09, 137.98, 131.94, 129.55, 128.76, 127.22, 123.43, 122.45, 113.82, 55.42, 53.19, 44.98, 32.86, 21.68, 18.78, 16.21. IR (KBr): 2906, 2842, 1609, 1513, 1442, 1379, 1333, 1302, 1254, 1167, 1138, 1088, 1031, 916, 816 cm^{-1}. HRMS (ESI$^+$) found 372.1616, calcd for $[M+H]^+$ 372.1628.

4,5-Dimethyl-2-(4-nitrophenyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ha**).



Yield: 77%. Mp. 141–143 ℃ (ethyl acetate). TLC: R_f = 0.35 (hexane/ethyl acetate = 3:1) ^{1}H NMR ($CDCl_3$) δ 8.12 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.66 (dt *J* = 8.5, 2.0 Hz, 2H), 7.40–7.43 (m, 2H), 7.25–7.26 (m, 2H), 5.29 (d, *J* = 6.5 Hz, 1H), 3.89 (d, *J* = 17.5 Hz, 1H), 3.21–3.26 (m, 1H), 2.42 (s, 3H), 2.38–2.40 (m, 1H), 2.20 (d, *J* = 17.5 Hz, 1H), 1.59 (s, 3H), 1.53 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 147.51, 147.43, 143.70, 137.44, 129.82, 128.39, 127.18, 123.81, 123.01, 122.88, 53.33, 45.33, 32.74, 21.72, 18.91, 16.22. IR (KBr): 2919, 1927, 1596, 1522, 1517, 1352, 1330, 1279, 1162, 1090, 1009, 856, 814 cm^{-1}. HRMS (ESI$^+$) found 387.1361, calcd for $[M+H]^+$ 387.1373.

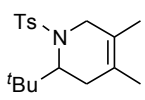
2-Cyclohexyl-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ia**).



Yield: 87%. Mp. 133–135 ℃ (ethyl acetate). TLC: R_f = 0.42 (hexane/ethyl acetate = 7:1) ^{1}H NMR ($CDCl_3$) δ 7.62–7.64 (m, 2H), 7.21–7.23 (m, 2H),

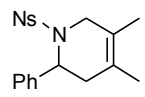
3.86 (d, J = 18.0 Hz, 1H), 3.63 (td, J = 4.5, 2.5 Hz, 1H), 3.43 (d, J = 18.0, 1H), 2.39 (s, 3H), 1.70–1.86 (m, 5H), 1.59–1.64 (m, 2H), 1.53 (s, 3H), 1.44 (s, 3H), 1.31–1.39 (m, 1H), 1.12–1.25 (m, 3H), 0.96–1.04 (m, 1H), 0.86–092 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 142.81, 138.73, 129.53, 126.99, 123.21, 121.20, 56.56, 45.56, 37.64, 31.05, 30.54, 30.36, 26.53, 26.35, 26.26, 21.67, 19.07, 15.98. IR (KBr): 2926, 2856, 2848, 1595, 1452, 1437, 1327, 1266, 1163, 1080, 1005, 925, 816 cm^{-1}. HRMS (ESI$^+$) found 348.1980, calcd for $[M+H]^+$ 348.1992.

2-*tert*-Butyl-4,5-dimethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ja**).



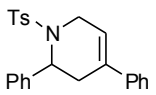
Yield: 83%. Mp. 104–106 ℃ (ethyl acetate). TLC: R_f = 0.33 (hexane/ethyl acetate = 10:1) ^{1}H NMR ($CDCl_3$) δ 7.61–7.64 (m, 2H), 7.21–7.23 (m, 2H), 3.95 (d, J = 18.5 Hz, 1H), 3.74 (d, J = 8.0 Hz, 1H), 3.59 (d, J = 18.5, 1H), 2.39 (s, 3H), 1.72–1.84 (m, 2H), 1.48 (s, 3H), 1.44 (s, 3H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 142.87, 138.27, 129.55, 127.04, 124.08, 120.78, 58.35, 46.81, 36.34, 29.12, 28.15, 21.68, 18.67, 15.97. IR (KBr): 2972, 2935, 2865, 1595, 1476, 1400, 1328, 1182, 1160, 1142, 1089, 1011, 920, 817, 732 cm^{-1}. HRMS (ESI$^+$) found 322.1824, calcd for $[M+H]^+$ 322.1835.

4,5-Dimethyl-1-(2-nitrophenylsulfonyl)-2-phenyl-1,2,3,6-tetrahydropyridine (**3ka**).



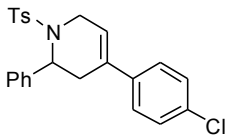
Yield: 64%. TLC: R_f = 0.41 (hexane/ethyl acetate = 2:1) ^{1}H NMR ($CDCl_3$) δ 7.98 (dd, J = 7.5, 1.0 Hz, 1H), 7.60–7.69 (m, 3H), 7.21–7.28 (m, 5H), 5.26 (d, J = 6.5 Hz, 1H), 3.83 (d, J = 18.0 Hz, 1H), 3.36 (d, J = 18.0 Hz, 1H), 2.62–2.68 (m, 1H), 2.34 (d, J = 17.5 Hz, 1H), 1.68 (s, 3H), 1.57 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 139.25, 133.47, 131.83, 130.84, 128.68, 127.82, 127.47, 124.50, 123.61, 122.59, 109.98, 54.30, 45.41, 33.34, 18.90, 16.15. (One signal emerged.) IR (neat): 2916, 2856, 1547, 1538, 1451, 1372, 1346, 1173, 1068, 1012, 777 cm^{-1}. HRMS (ESI$^+$) found 373.1205, calcd for $[M+H]^+$ 373.1217.

2,4-Diphenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ab**).



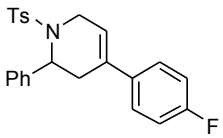
Yield: 91%. Mp. 33–35 ℃ (ethyl acetate). TLC: R_f = 0.26 (hexane/ethyl acetate = 7:1) ^{1}H NMR ($CDCl_3$) δ 7.73 (dd, J = 8.0, 1.0 Hz, 2H), 7.30–7.35 (m, 4H), 7.21–7.27 (m, 8H), 5.90 (t, J = 2.0 Hz, 1H), 5.47 (d, J = 6.0 Hz, 1H), 4.33 (d, J = 19.0 Hz, 1H), 3.55 (dd, J = 19.0, 2.0 Hz, 1H), 2.81 (d, J = 17.5 Hz, 1H), 2.67–2.72 (m, 1H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.36, 140.44, 139.16, 137.76, 134.40, 129.72, 128.62, 128.56, 127.74, 127.68, 127.44, 127.17, 125.16, 120.21, 53.37, 41.49, 28.72, 21.58. IR (KBr): 3060, 3030, 2923, 1598, 1494, 1446, 1372, 1345, 1324, 1304, 1289, 1155, 1090, 927, 820 cm^{-1}. HRMS (ESI$^+$) found 390.1507, calcd for $[M+H]^+$ 390.1522.

4-(4-Chlorophenyl)-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ac**).



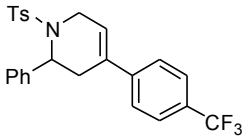
Yield: 87%. Mp. 47–49 ℃ (ethyl acetate). TLC: R_f = 0.37 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.22–7.31 (m, 9H), 7.16–7.19 (m, 2H), 5.90–5.92 (m, 1H), 5.46 (d, *J* = 6.5 Hz, 1H), 4.30–4.35 (m, 1H), 3.52–3.57 (m, 1H), 2.77 (d, *J* = 17.5 Hz, 1H), 2.65–2.72 (m, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.50, 139.05, 138.90, 137.75, 133.62, 133.49, 129.79, 128.83, 128.68, 127.82, 127.42, 127.27, 126.49, 120.85, 53.35, 41.48, 28.79, 21.67. IR (KBr): 3029, 2853, 1595, 1496, 1407, 1338, 1333, 1283, 1161, 1155, 1090, 927, 820, 737 cm^{-1}. HRMS (ESI$^+$) found 424.1119, calcd for $[M+H]^+$ 424.1133.

4-(4-Fluorophenyl)-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ad**).



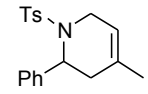
Yield: 90%. Mp. 129–131 ℃ (ethyl acetate). TLC: R_f = 0.36 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.71–7.74 (m, 2H), 7.19–7.33 (m, 9H), 6.98–7.03 (m, 2H), 5.85–5.87 (m, 1H), 5.46 (d, *J* = 6.5 Hz, 1H), 4.32–4.38 (m, 1H), 3.52–3.57 (m, 1H), 2.78 (d, *J* = 17.0 Hz, 1H), 2.66–2.73 (m, 1H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 162.52 (d, *J* = 245.8 Hz), 143.46, 139.15, 137.79, 136.65 (d, *J* = 3.4 Hz), 133.60, 129.78, 128.66, 127.80, 127.44, 127.28, 126.83 (d, *J* = 7.6 Hz), 120.23, 115.53 (d, *J* = 21.5 Hz), 53.40, 41.46, 29.06, 21.66. IR (KBr): 2885, 2852, 1596, 1512, 1495, 1460, 1334, 1282, 1220, 1156, 1100, 1045, 930, 727 cm^{-1}. HRMS (ESI$^+$) found 408.1416, calcd for $[M+H]^+$ 408.1428.

2-Phenyl-1-tosyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyridine (**3ae**).



Yield: 83%. Mp. 45–47 ℃ (ethyl acetate). TLC: R_f = 0.41 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.71–7.73 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22–7.29 (m, 7H), 5.99–6.01 (m, 1H), 5.47 (d, *J* = 5.5 Hz, 1H), 4.32–4.38 (m, 1H), 3.53–3.59 (m, 1H), 2.80 (d, *J* = 17.5 Hz, 1H), 2.69–2.76 (m, 1H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.91, 143.60, 138.92, 137.70, 133.55, 130.27 (q, *J* = 24.4 Hz), 129.83, 128.72, 127.88, 127.36, 127.27, 125.67 (q, *J* = 2.6 Hz), 125.51, 124.29 (q, *J* = 272.1 Hz), 122.48, 53.32, 41.51, 28.72, 21.65. IR (KBr): 3063, 3032, 2926, 1682, 1598, 1494, 1466, 1410, 1306, 1287, 1262, 1215, 1069, 1016, 906, 845 cm^{-1}. HRMS (ESI$^+$) found 458.1381, calcd for $[M+H]^+$ 458.1396.

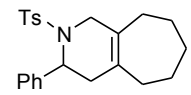
4-Methyl-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3af**).



Yield: 71%. Mp. 101–103 ℃ (ethyl acetate). TLC: R_f = 0.40 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.65 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.20–7.27 (m, 7H), 5.27–5.28 (m, 2H), 4.02–4.07 (m, 1H), 3.28–3.35 (m, 1H), 2.39 (s, 3H), 2.29–2.35 (m,

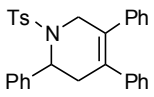
1H), 2.21 (d, *J* = 17.0 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.18, 139.68, 137.97, 131.65, 129.64, 128.56, 127.63, 127.51, 127.28, 117.72, 53.40, 41.06, 31.55, 23.43, 21.69. IR (KBr): 3027, 2851, 1595, 1493, 1451, 1368, 1324, 1258, 1147, 1093, 1030, 923, 815 cm^{-1}. HRMS (ESI$^+$) found 328.1354, calcd for $[M+H]^+$ 328.1366.

3-Phenyl-2-tosyl-2,3,4,5,6,7,8,9-octahydro-1H-cyclohepta[c]pyridine (**3ag**).



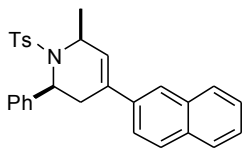
Yield: 88%. Mp. 88–89 ℃ (ethyl acetate). TLC: R_f = 0.53 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.23–7.33 (m, 7H), 5.22 (d, *J* = 6.5 Hz, 1H), 3.92 (d, *J* = 18.5 Hz, 1H), 3.27 (d, *J* = 18.5 Hz, 1H), 2.42 (s, 3H), 2.37–2.39 (m, 1H), 2.21 (d, *J* = 18.0 Hz, 1H), 2.09–2.15 (m, 1H), 1.88–1.93 (m, 3H), 1.61–1.75 (m, 2H), 1.27–1.45 (m, 3H), 1.15–1.22 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 143.15, 139.85, 137.93, 131.08, 130.18, 129.56, 128.46, 127.58, 127.53, 127.27, 53.30, 44.95, 34.79, 32.61, 32.27, 31.87, 26.12, 26.09, 21.66. IR (neat): 2915, 2845, 1597, 1451, 1343, 1329, 1165, 1156, 1101, 1087, 816 cm^{-1}. HRMS (ESI$^+$) found 382.1822, calcd for $[M+H]^+$ 382.1835.

2,4,5-Triphenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ah**).



Yield: 50%. Mp. 134–136 ℃ (ethyl acetate). TLC: R_f = 0.39 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.0 Hz, 2H), 7.28–7.31 (m, 3H), 7.08–7.12 (m, 6H), 6.84–6.86 (m, 2H), 6.75–6.77 (m, 2H) 5.46 (t, *J* = 4.0 Hz, 1H), 4.48 (d, *J* = 18.5 Hz, 1H), 3.68 (dt, *J* = 18.5, 3.0 Hz, 1H), 2.74–2.76 (m, 2H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 143.60, 141.37, 139.52, 139.31, 137.80, 132.33, 131.75, 129.80, 128.92, 128.79, 128.67, 128.25, 128.16, 127.94, 127.56, 127.45, 127.14, 126.88, 53.83, 45.17, 32.41, 21.71. IR (KBr): 3049, 2922, 1598, 1493, 1344, 1165, 1094, 1070, 981, 912, 812 cm^{-1}. HRMS (ESI$^+$) found 466.1820, calcd for $[M+H]^+$ 466.1835.

(*2S**,*6S**)-6-Methyl-4-(naphthalen-2-yl)-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ai**).



Yield: 70%. Mp. 67–69 ℃ (ethyl acetate). TLC: R_f = 0.38 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.79–7.83 (m, 5H), 7.75 (s, 1H), 7.44–7.54 (m, 5H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21–7.26 (m, 3H), 6.06 (dd, *J* = 3.0 Hz, 1H), 5.53 (d, *J* = 6.0 Hz, 1H), 4.63–4.69 (m, 1H), 3.04 (d, *J* = 17.0 Hz, 1H), 2.45 (dddd, *J* = 17.0, 6.0, 3.0, 3.0 Hz, 1H), 2.41 (s, 3H), 0.93 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 143.47, 140.74, 138.33, 137.29, 133.60, 133.04, 132.45, 130.09, 128.40, 128.33, 128.31, 127.81, 127.58, 127.03, 126.69, 126.34, 123.82, 123.46, 52.13, 50.65, 26.51, 22.69, 21.75. (Two signals emerged.) IR (KBr): 3058, 2928, 1597, 1495, 1451, 1381, 1329, 1281, 1160, 1100, 995, 815 cm^{-1}. HRMS (ESI$^+$) found 454.1822, calcd for $[M+H]^+$ 454.1835.

(*2S**,*6R**)-6-Methyl-4-(naphthalen-2-yl)-2-phenyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ai'**).

Yield: 13%. Mp. 46–48 ℃ (ethyl acetate). TLC: R_f = 0.32 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.75–7.79 (m, 3H), 7.68–7.69 (m, 1H), 7.40–7.47 (m, 5H), 7.28–7.30 (m, 2H), 7.14–7.17 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.20 (dd, *J* = 4.0, 2.0 Hz, 1H), 5.35 (dd, *J* = 5.5 Hz, 1H), 4.70–4.75 (m, 1H), 3.22 (ddd, *J* = 16.5, 5.5 1.0 Hz, 1H), 3.11 (dddd, *J* = 16.5, 5.5, 2.0, 2.0 Hz, 1H), 2.35 (s, 3H), 1.54 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 142.64, 139.93, 139.66, 137.71, 134.45, 133.58, 133.01, 129.26, 128.40, 128.30, 128.25, 128.16, 128.00, 127.76, 127.46, 127.14, 126.52, 126.17, 124.06, 123.68, 56.82, 51.52, 32.55, 21.87, 21.62. IR (KBr): 3029, 2926, 1597, 1452, 1382, 1324, 1159, 1094, 1009, 848 cm^{-1}. HRMS (ESI$^+$) found 454.1820, calcd for $[M+H]^+$ 454.1835.

(*1R**,*3R**,*4S**)-3-Phenyl-2-tosyl-2-azabicyclo[2.2.2]oct-5-ene (**3aj**).

Yield: 55%. Mp. 186–188 ℃ (ethyl acetate). TLC: R_f = 0.39 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.62 (dt, *J* = 8.0, 2.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.0, 2H), 7.24–7.26 (m, 2H), 6.61 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 5.92 (ddd, *J* = 8.0, 5.5, 1.0 Hz, 1H), 4.60–4.63 (m, 1H), 4.18 (s, 1H), 2.57–2.59 (m, 1H), 2.42 (s, 3H), 2.16–2.22 (m, 1H), 1.46 (ddt, *J* = 12.0, 10.0, 4.0, 1H), 1.39 (ddt, *J* = 12.0, 12.0, 4.0 Hz, 1H), 0.85–0.91 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 143.48, 141.02, 135.63, 134.09, 131.80, 129.57, 128.42, 128.40, 127.12, 126.62, 62.23, 49.77, 38.59, 26.75, 21.75, 15.89. IR (KBr): 3062, 3023, 2965, 1599, 1493, 1366, 1344, 1304, 1164, 1096, 1053, 1015, 922, 816 cm^{-1}. HRMS (ESI$^+$) found 340.1353, calcd for $[M+H]^+$ 340.1366.

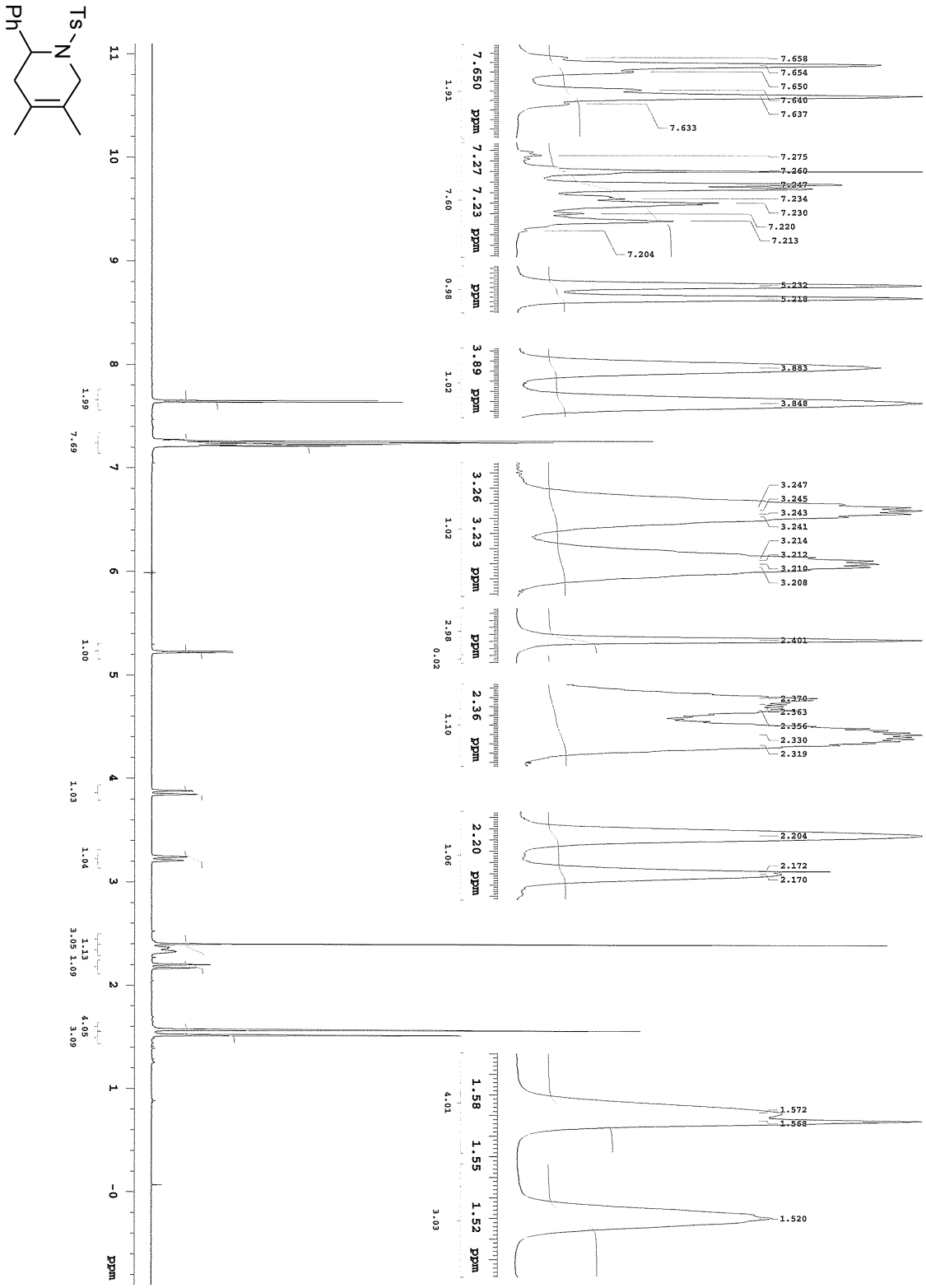
(*1R**,*3S**,*4S**)-3-Phenyl-2-tosyl-2-azabicyclo[2.2.2]oct-5-ene (**3aj'**).

Yield: 8%. Mp. 174–176 ℃ (ethyl acetate). TLC: R_f = 0.45 (hexane/ethyl acetate = 5:1) ^{1}H NMR ($CDCl_3$) δ 7.58 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.09–7.17 (m, 7H), 6.61 (ddd, *J* = 8.0, 6.5, 1.5 Hz, 1H), 5.96 (dd, *J* = 6.5 Hz, 1H), 4.67–4.69 (m, 2H), 2.77–2.81 (m, 1H), 2.37 (s, 3H), 1.94 (ddt, *J* = 13.0, 9.5, 3.5 Hz, 1H), 1.58–1.68 (m, 1H), 1.39 (ddt, *J* = 12.5, 12.5, 3.5 Hz, 1H), 1.19–1.25 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 143.12, 142.35, 137.96, 134.35, 132.48, 129.40, 127.77, 127.64, 127.06, 126.93, 62.77, 49.33, 39.65, 25.38, 22.55, 21.65. IR (KBr): 3060, 2961, 2874, 1598, 1447, 1373, 1344, 1323, 1159, 1099, 1063, 962, 923, 763 cm^{-1}. HRMS (ESI$^+$) found 340.1353, calcd for $[M+H]^+$ 340.1366.

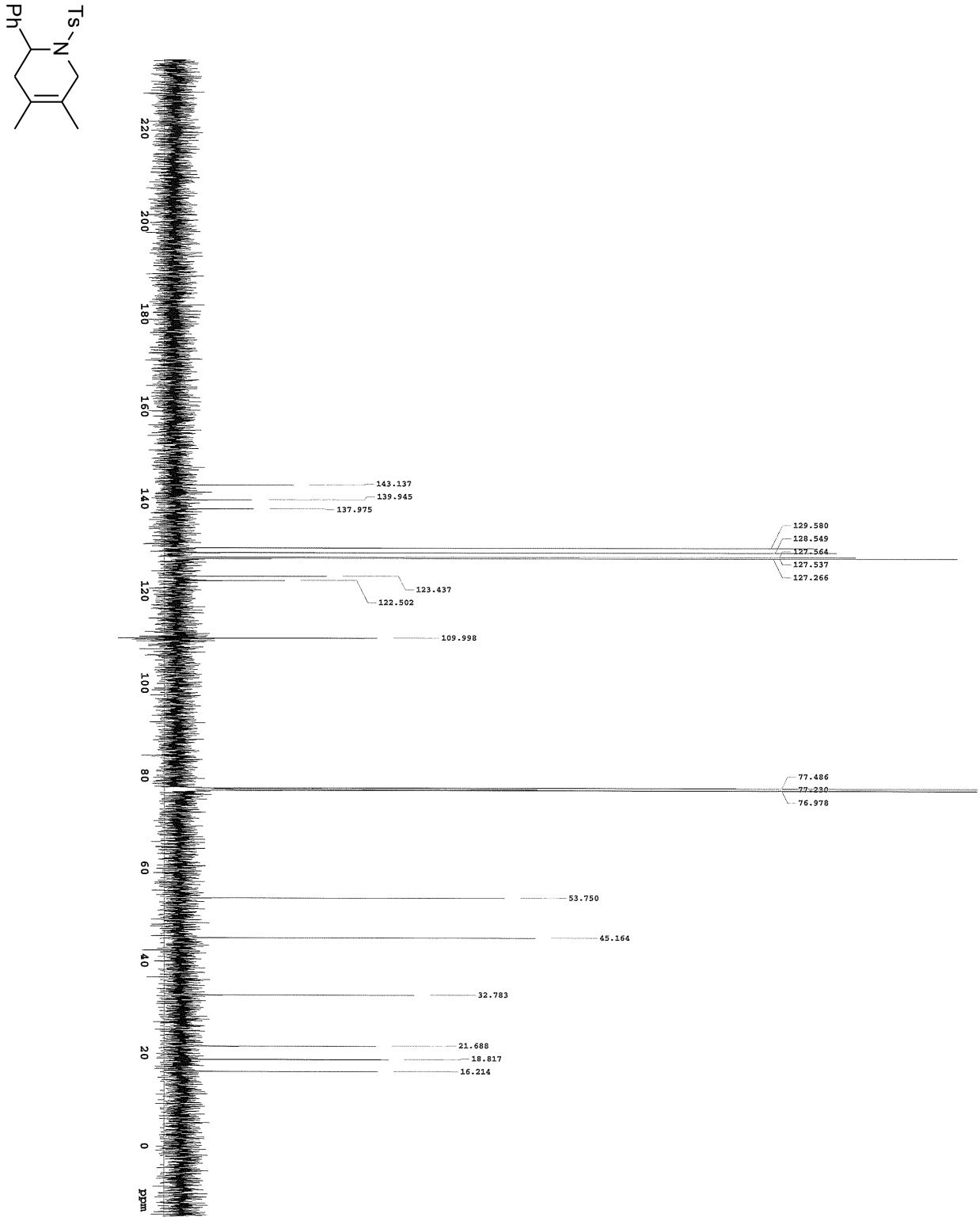
(*2S**,*6S**)-6-Methyl-2-(naphthalen-1-yl)-4-(naphthalen-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3bi**).Yield: 59%. Mp. 226–228 ℃ (chloroform). TLC: R_f 0.30 (hexane/ethyl acetate = 7:1) ^{1}H NMR ($CDCl_3$) δ 9.01 (d, *J* = 8.5 Hz, 1H), 7.82–7.90 (m, 6H), 7.76–7.84 (m, 2H), 7.69–7.72 (m, 1H), 7.47–7.57 (m, 4H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.25–7.28 (m, 3H), 6.39 (d, *J* = 6.5 Hz, 1H), 6.06 (dd, *J* = 4.0, 2.0 Hz, 1H), 4.55 (m, 1H), 3.12 (d, *J* = 17.5 Hz, 1H), 2.99–3.05 (m, 1H), 2.37 (s, 3H), 0.46 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 143.87, 137.57, 137.35, 135.92, 134.25, 134.16, 133.63, 133.09, 132.56, 129.85, 129.20, 128.79, 128.39, 128.34, 128.08, 127.82, 126.82, 126.66, 126.31, 126.05, 125.80, 125.78, 125.19, 124.77, 124.01, 123.70, 50.75, 49.75, 28.89, 21.73, 19.96. IR (KBr): 3105, 3020, 2960, 2853, 1597, 1510, 1448, 1381, 1335, 1323, 1282, 1163, 1099, 981, 816 cm^{-1}. HRMS (ESI^+) found 504.1980, calcd for $[M+H]^+$ 504.1992.

1H and 13C NMR Spectrum

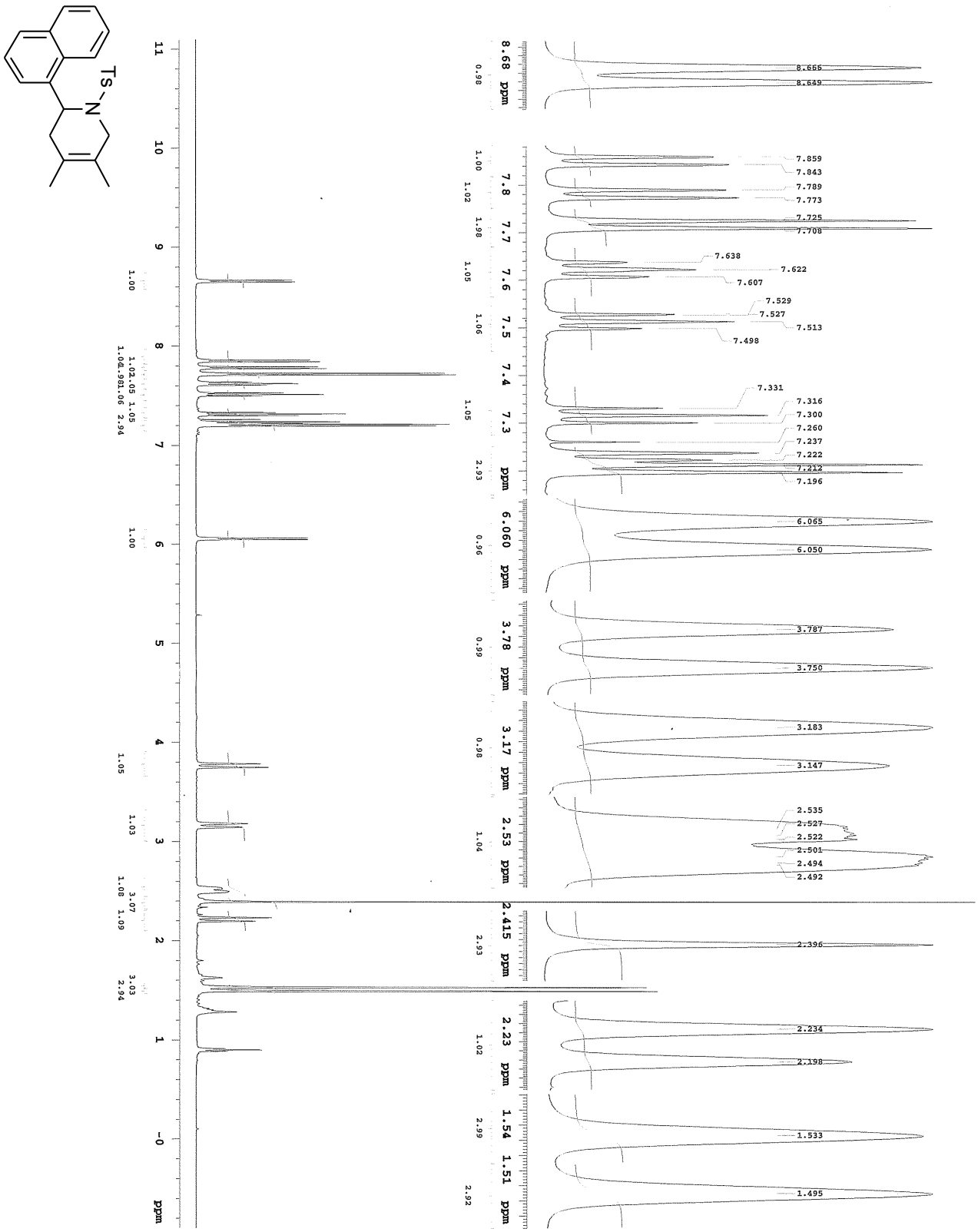
3aa (500 MHz, $CDCl_3$)



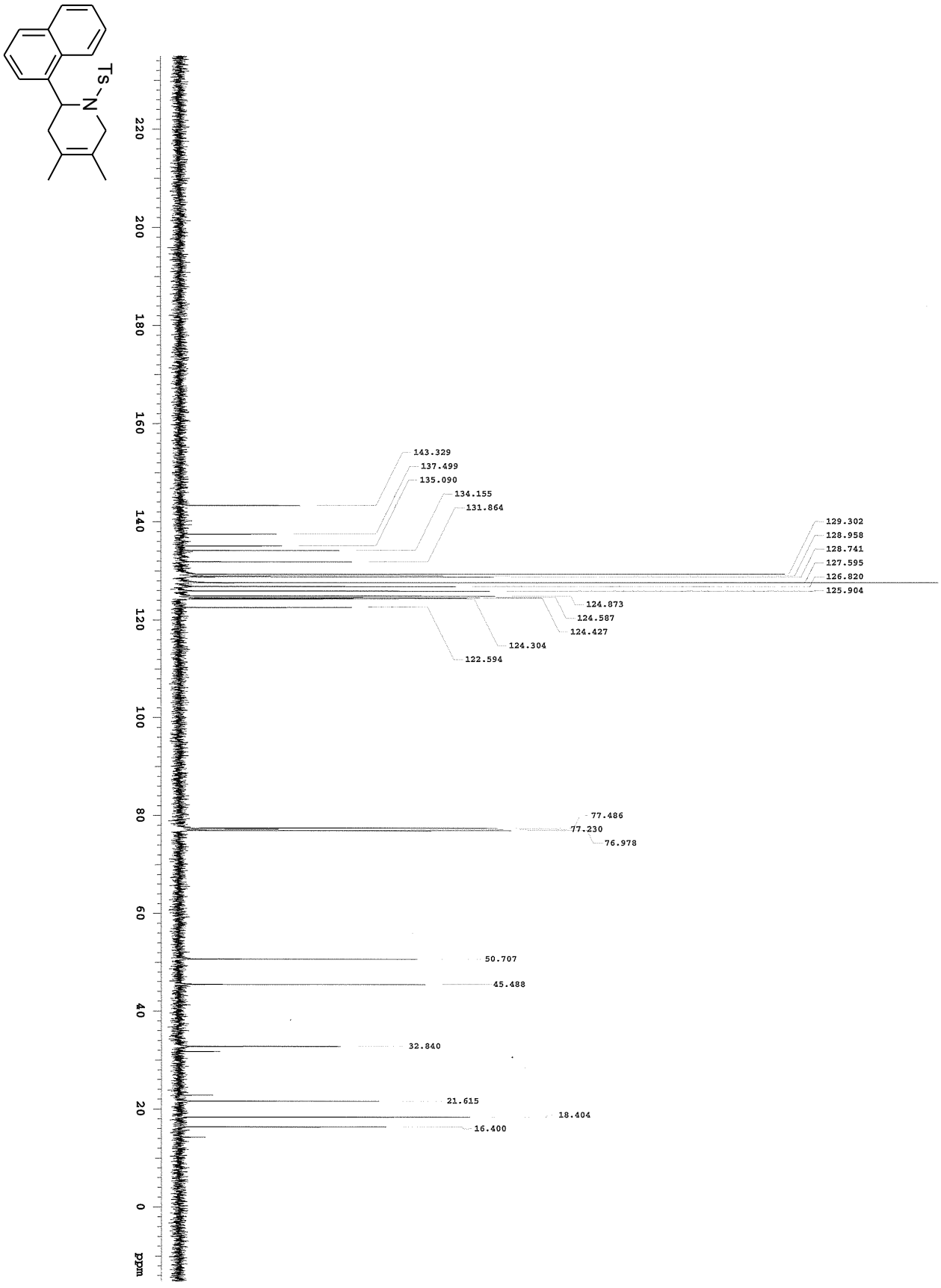
3aa (125.7 MHz, $CDCl_3$)



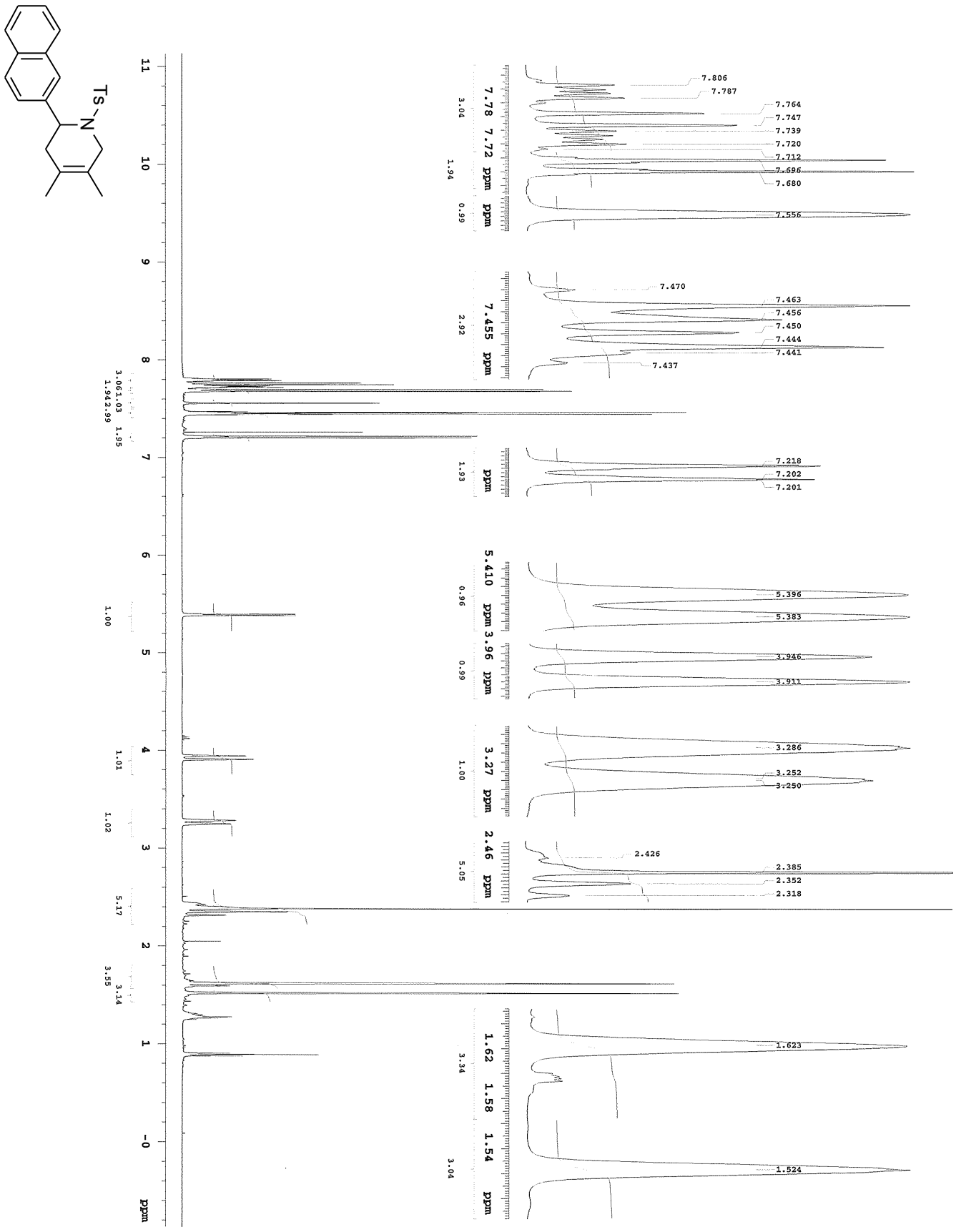
3ba (500 MHz, $CDCl_3$)



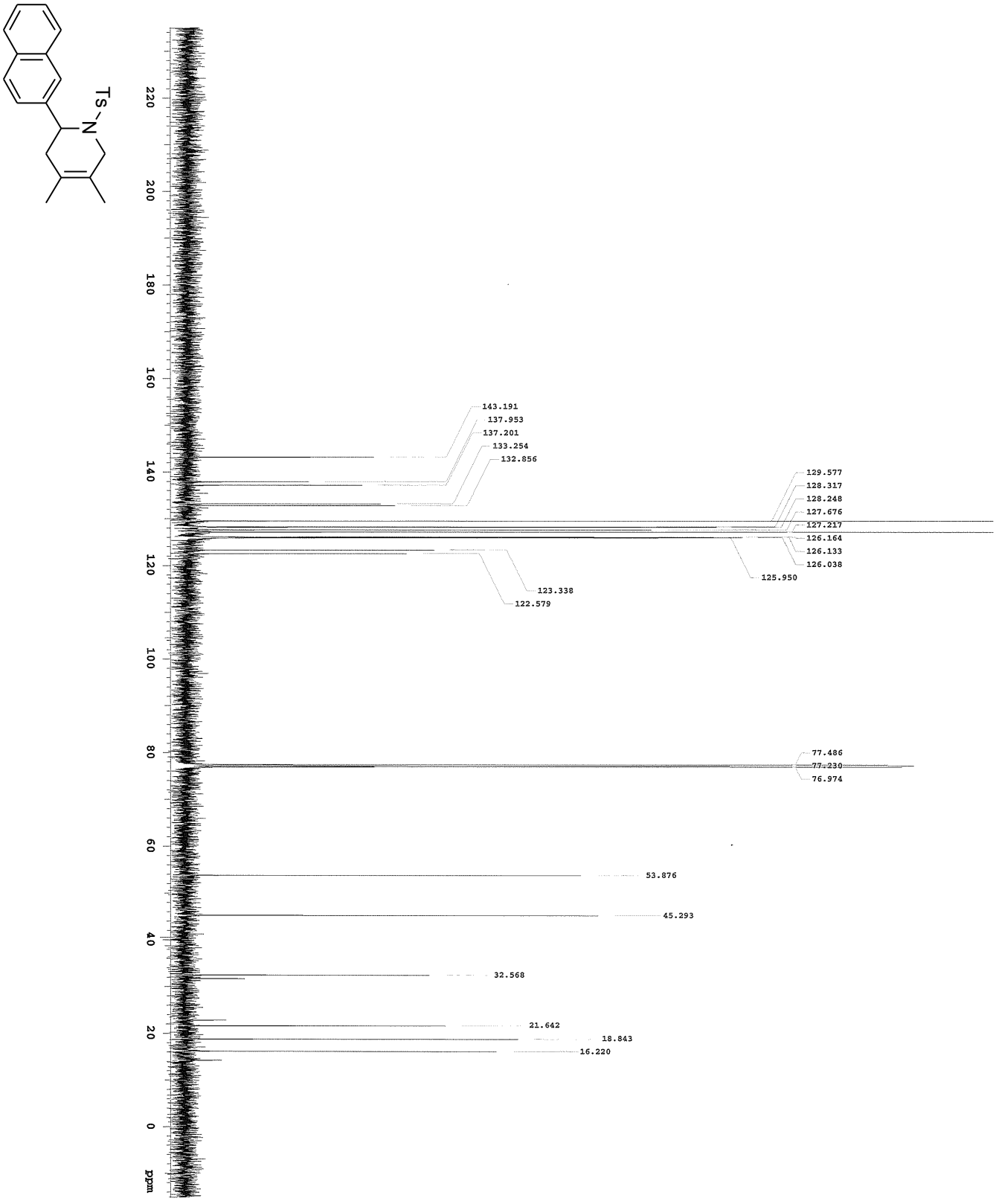
3ba (125.7 MHz, $CDCl_3$)



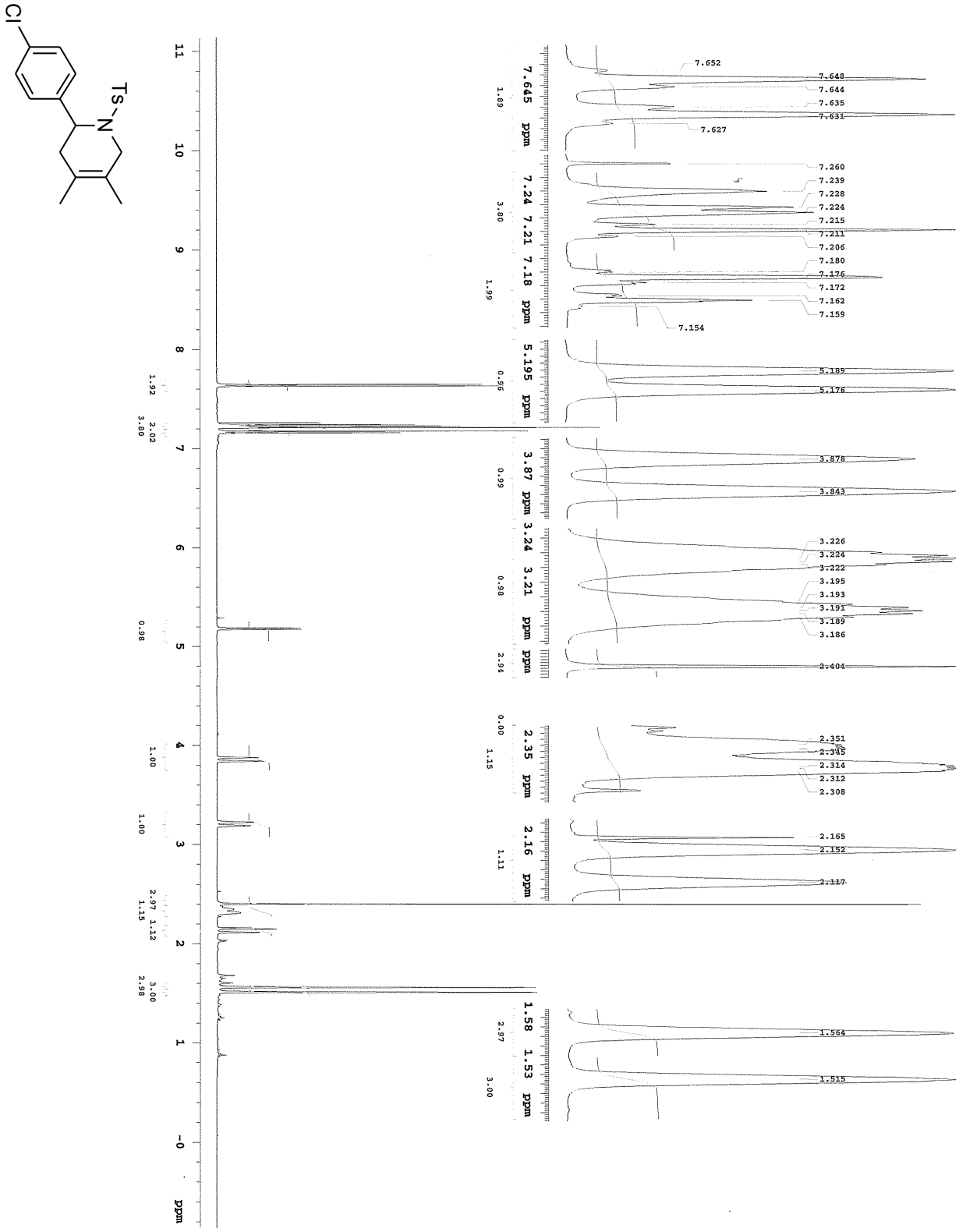
3ca (500 MHz, $CDCl_3$)



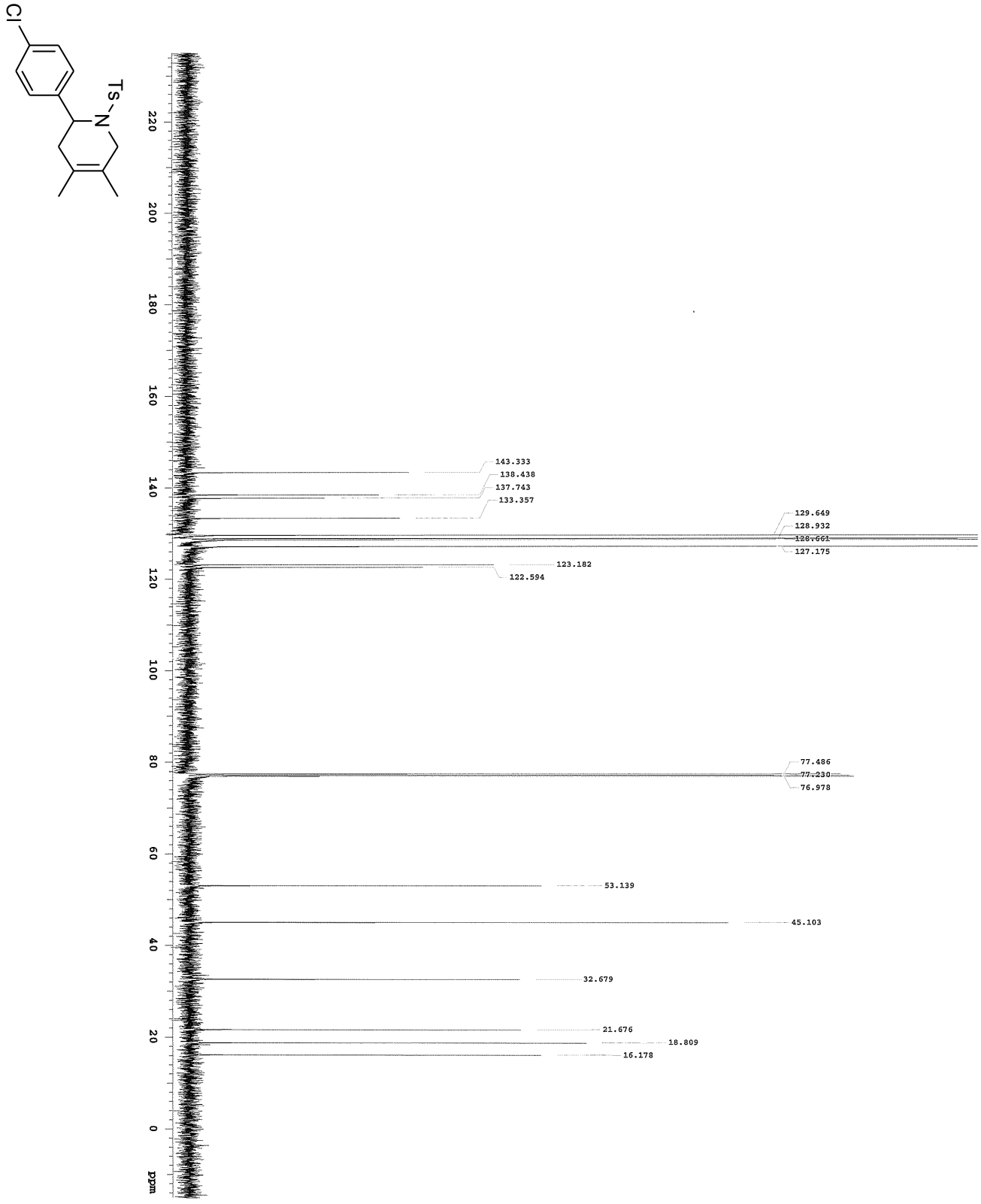
3ca (125.7 MHz, $CDCl_3$)



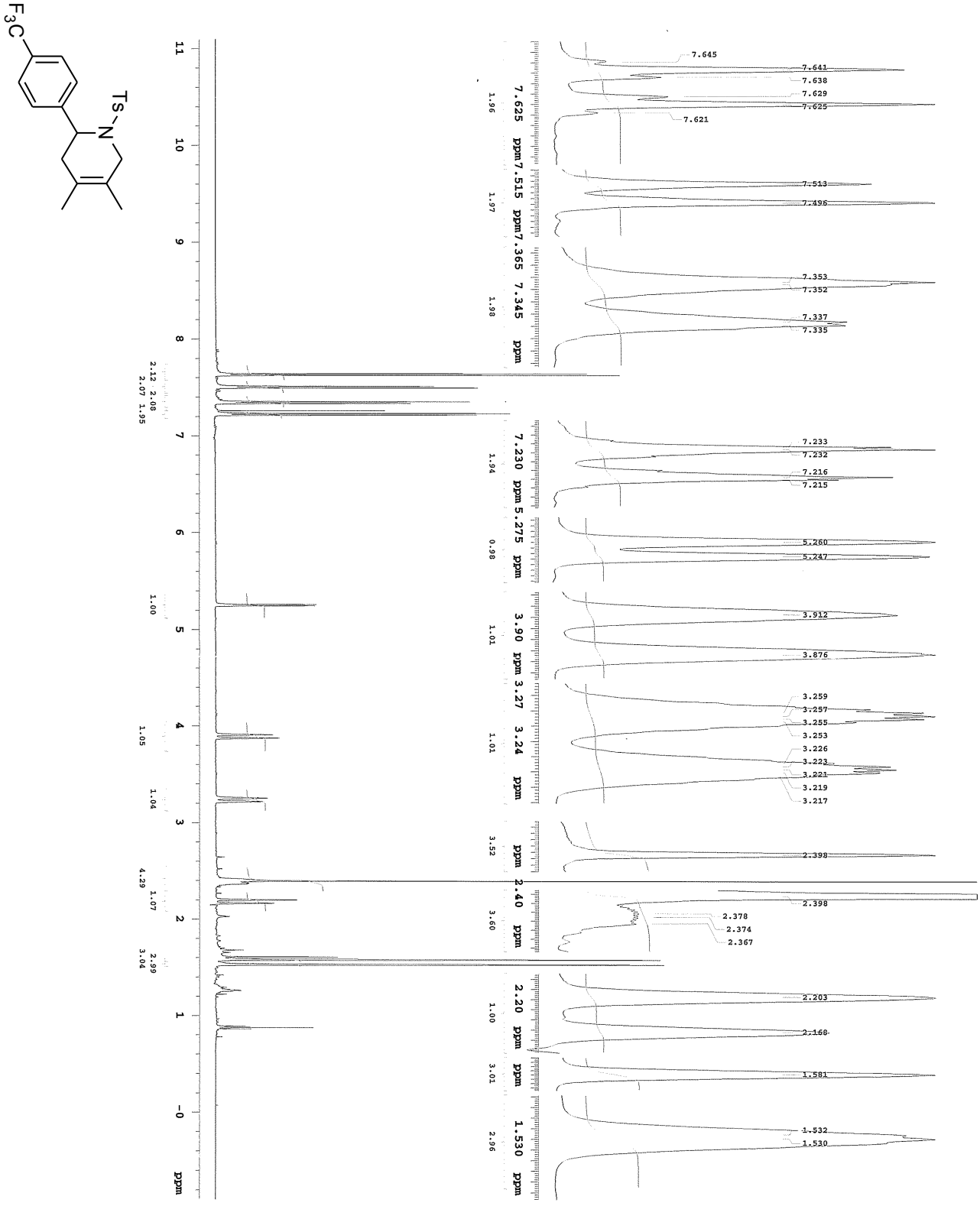
3da (500 MHz, $CDCl_3$)



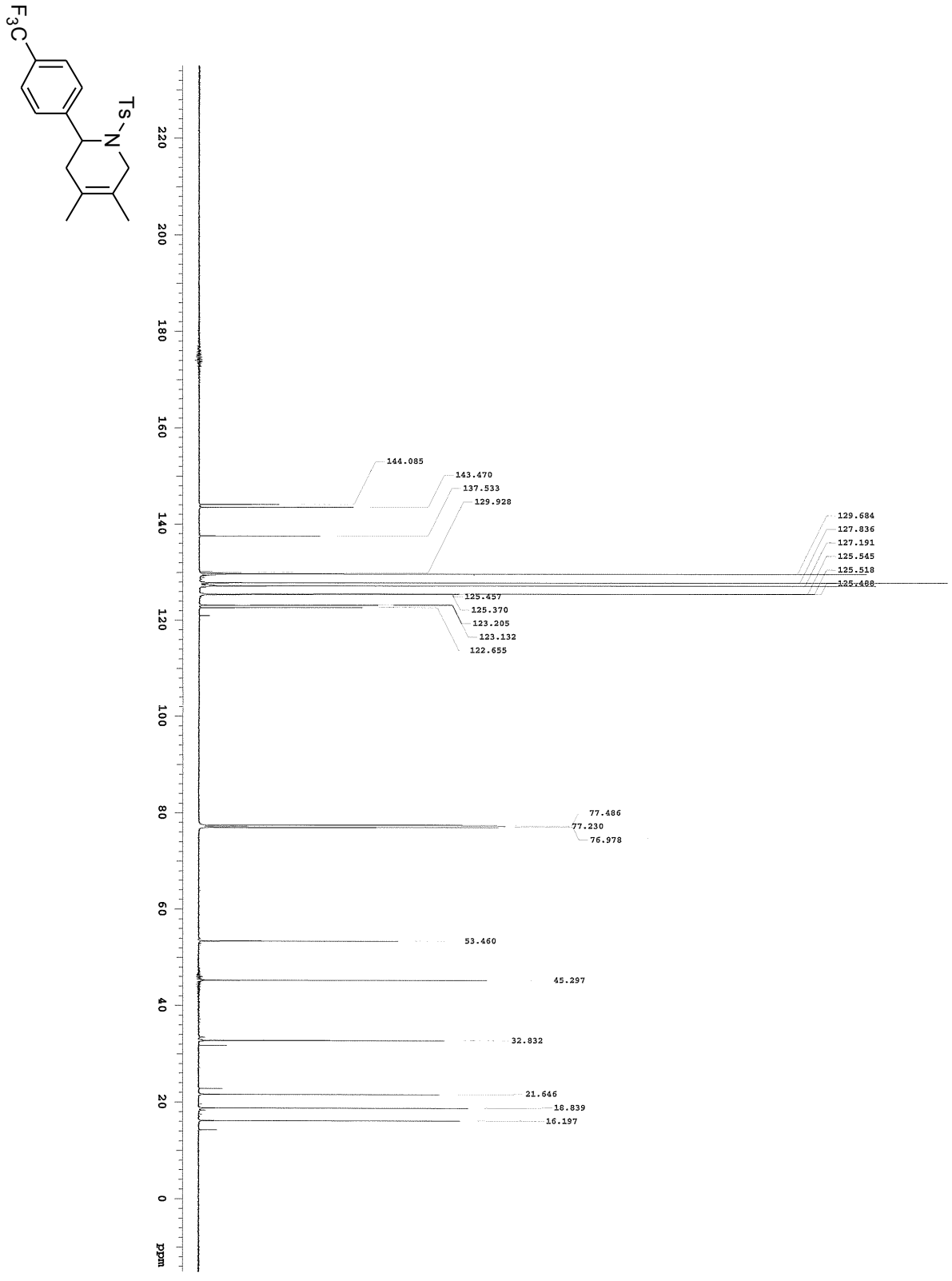
3da (125.7 MHz, $CDCl_3$)



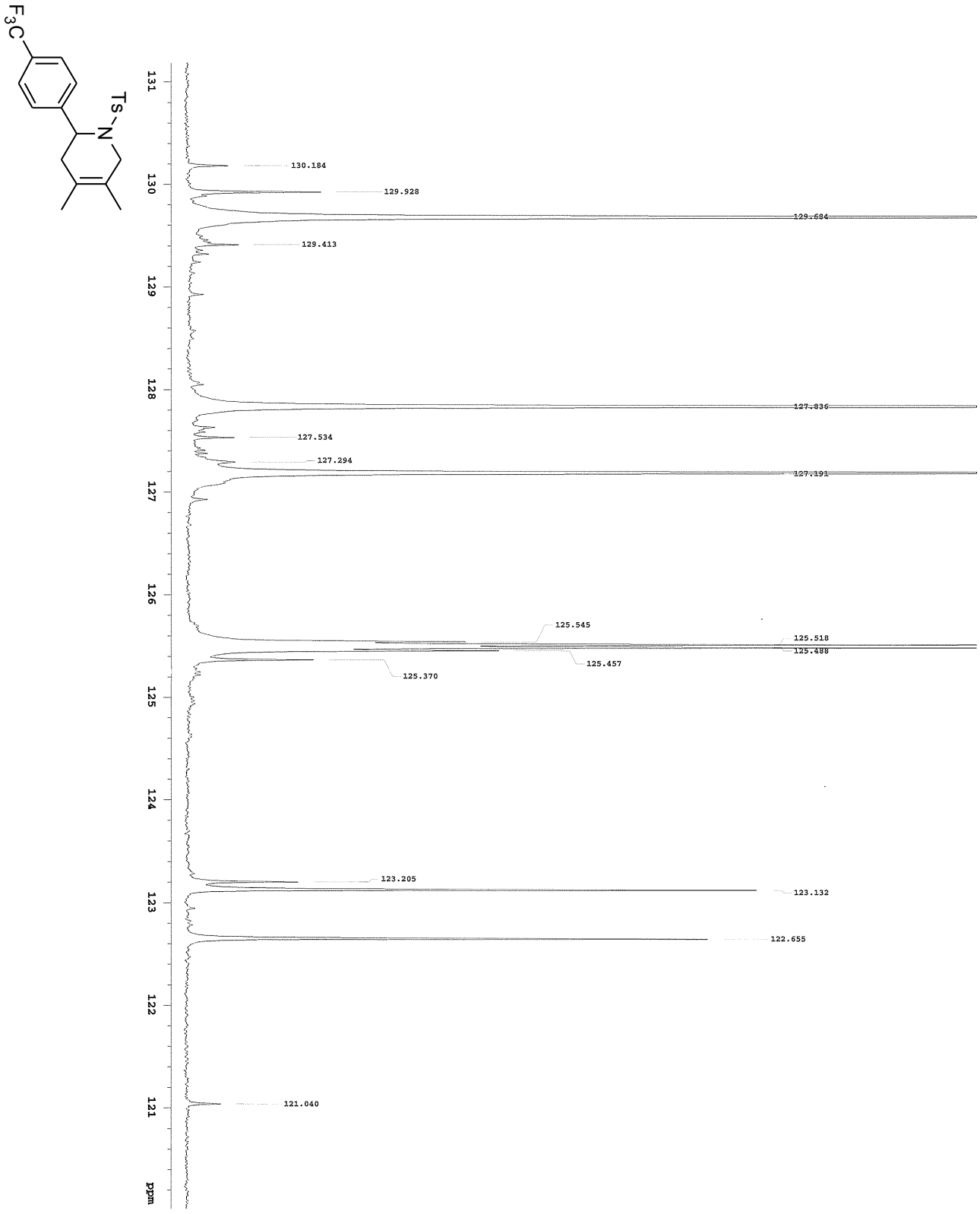
3ea (500 MHz, $CDCl_3$)



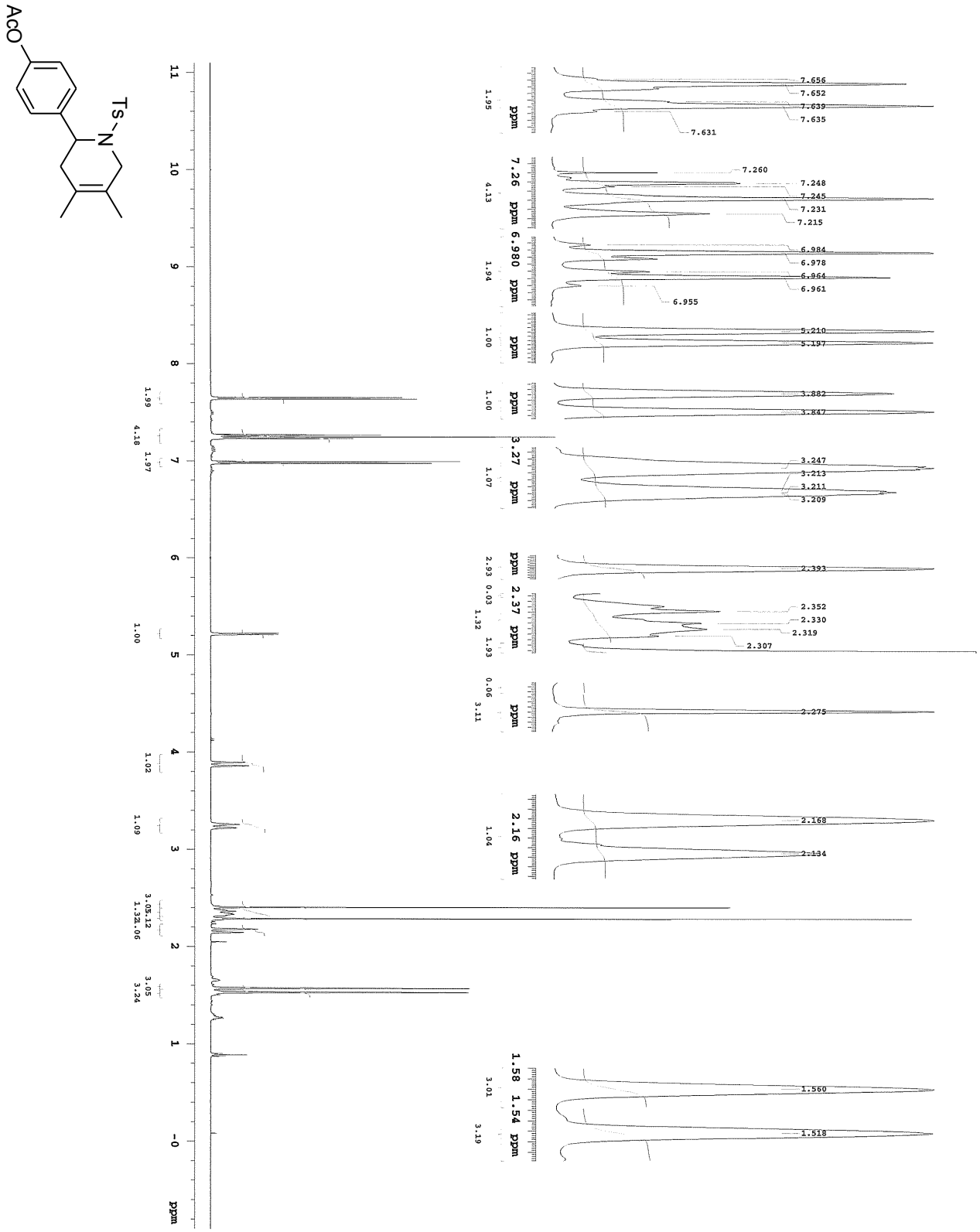
3ea (125.7 MHz, $CDCl_3$)



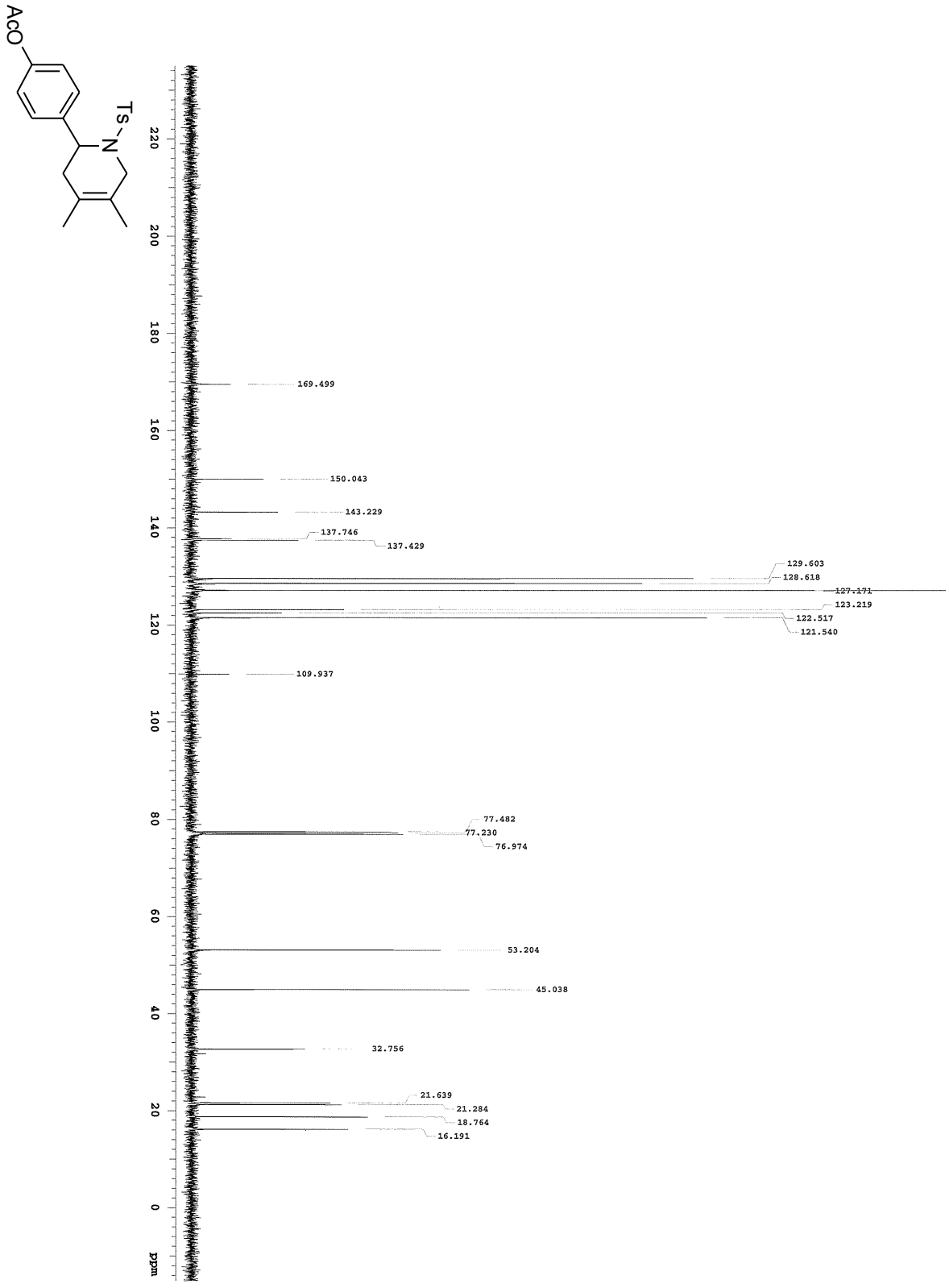
3ea (125.7 MHz, $CDCl_3$)



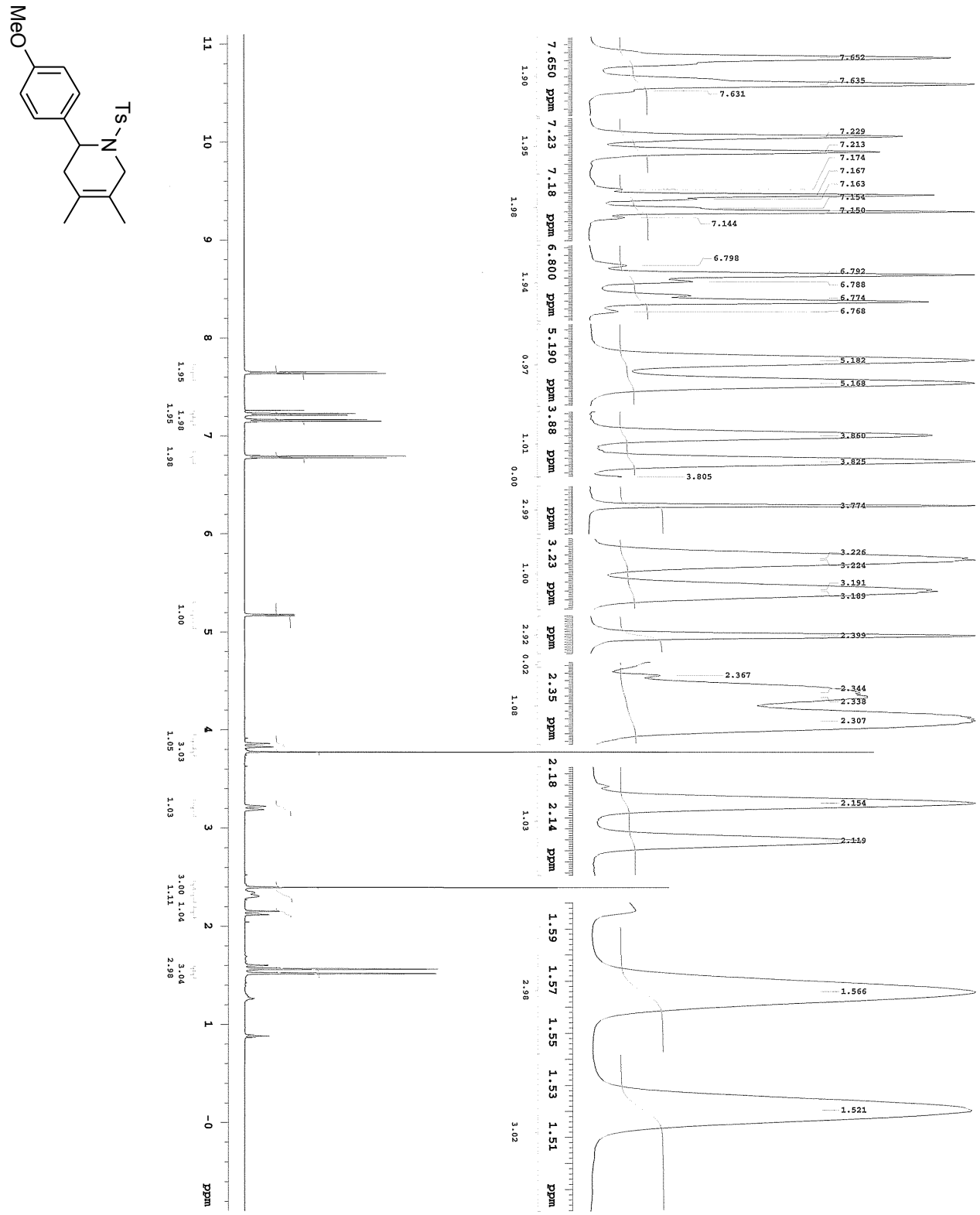
3fa (500 MHz, $CDCl_3$)



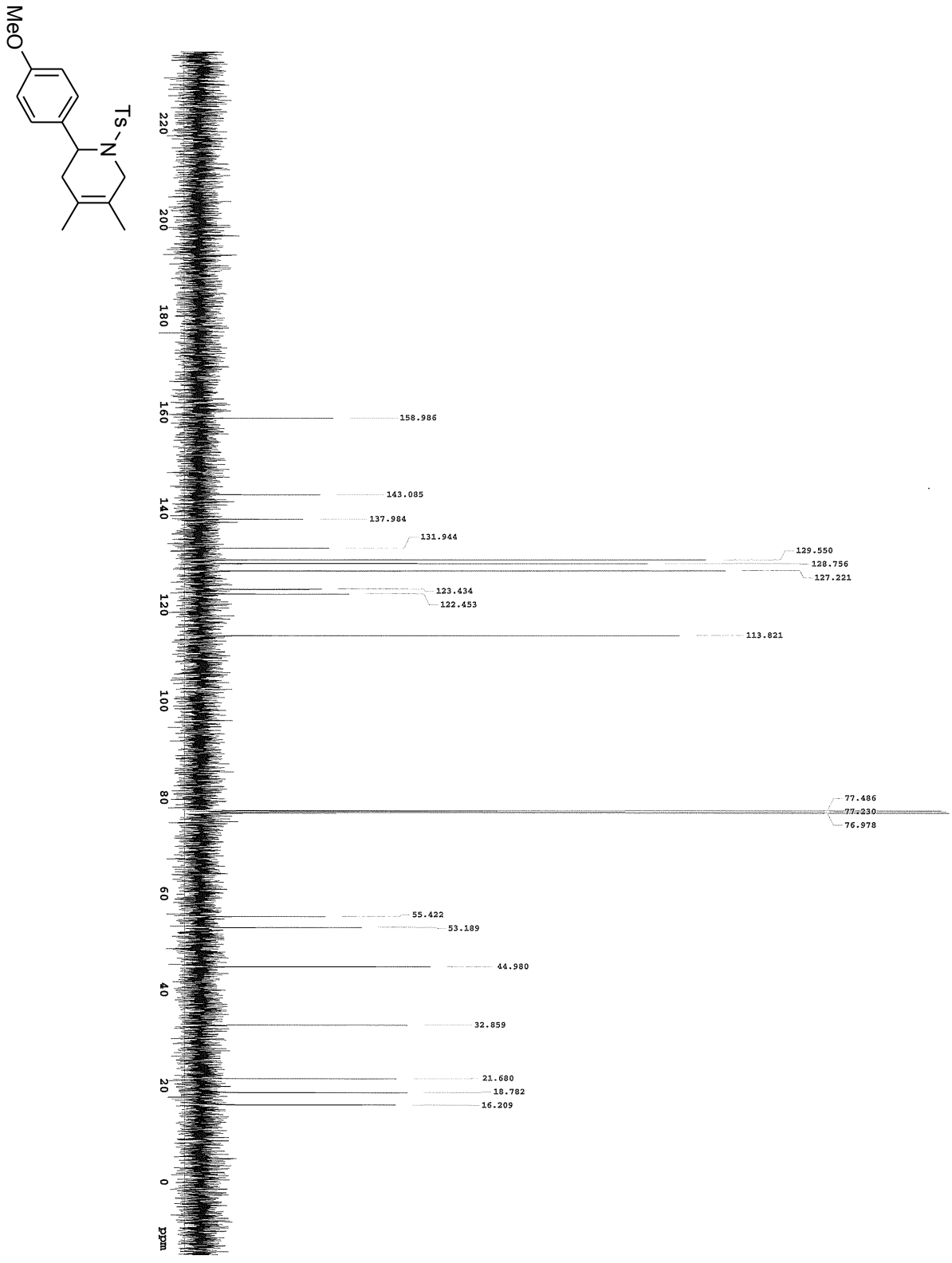
3fa (125.7 MHz, $CDCl_3$)



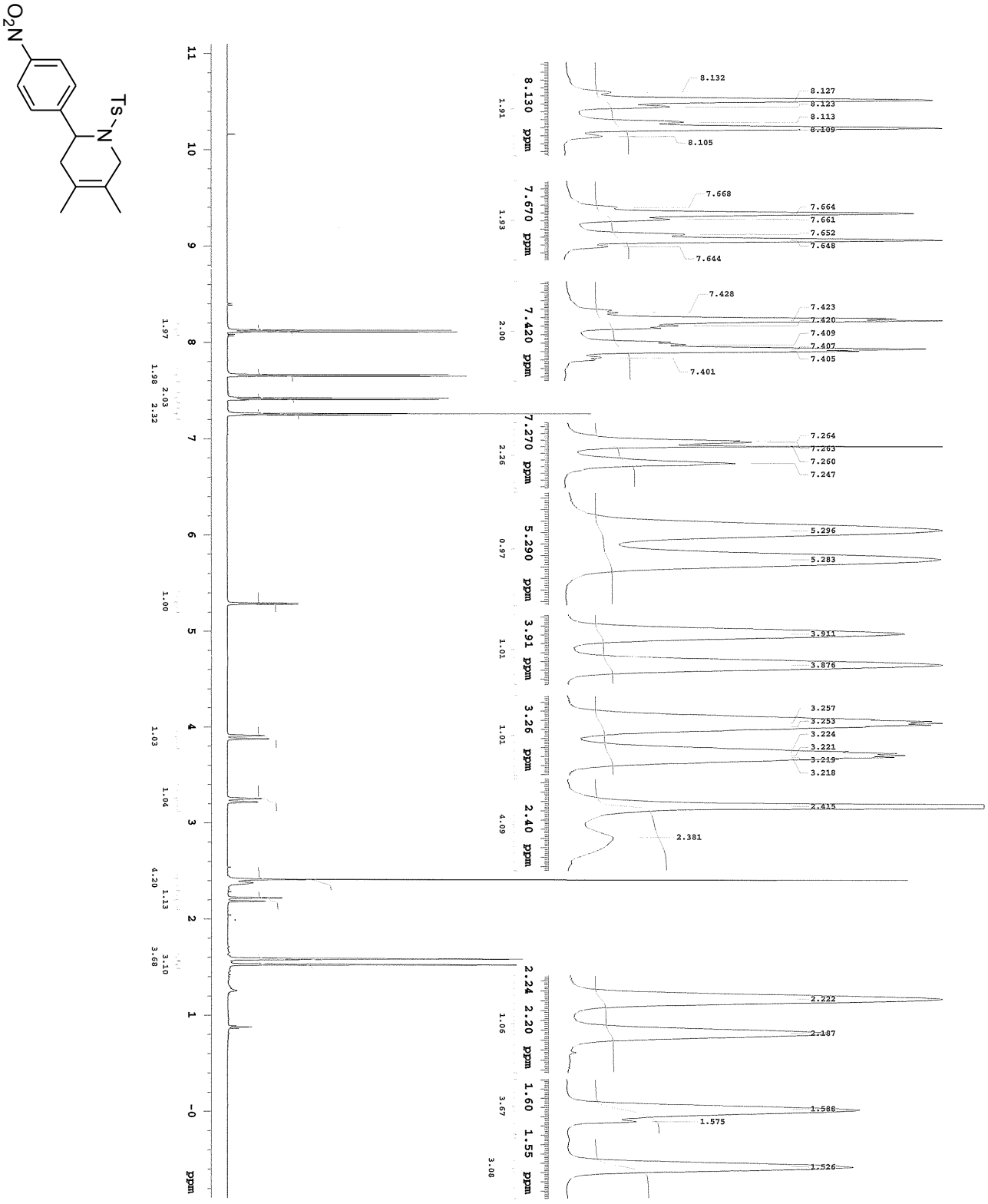
3ga (500 MHz, $CDCl_3$)



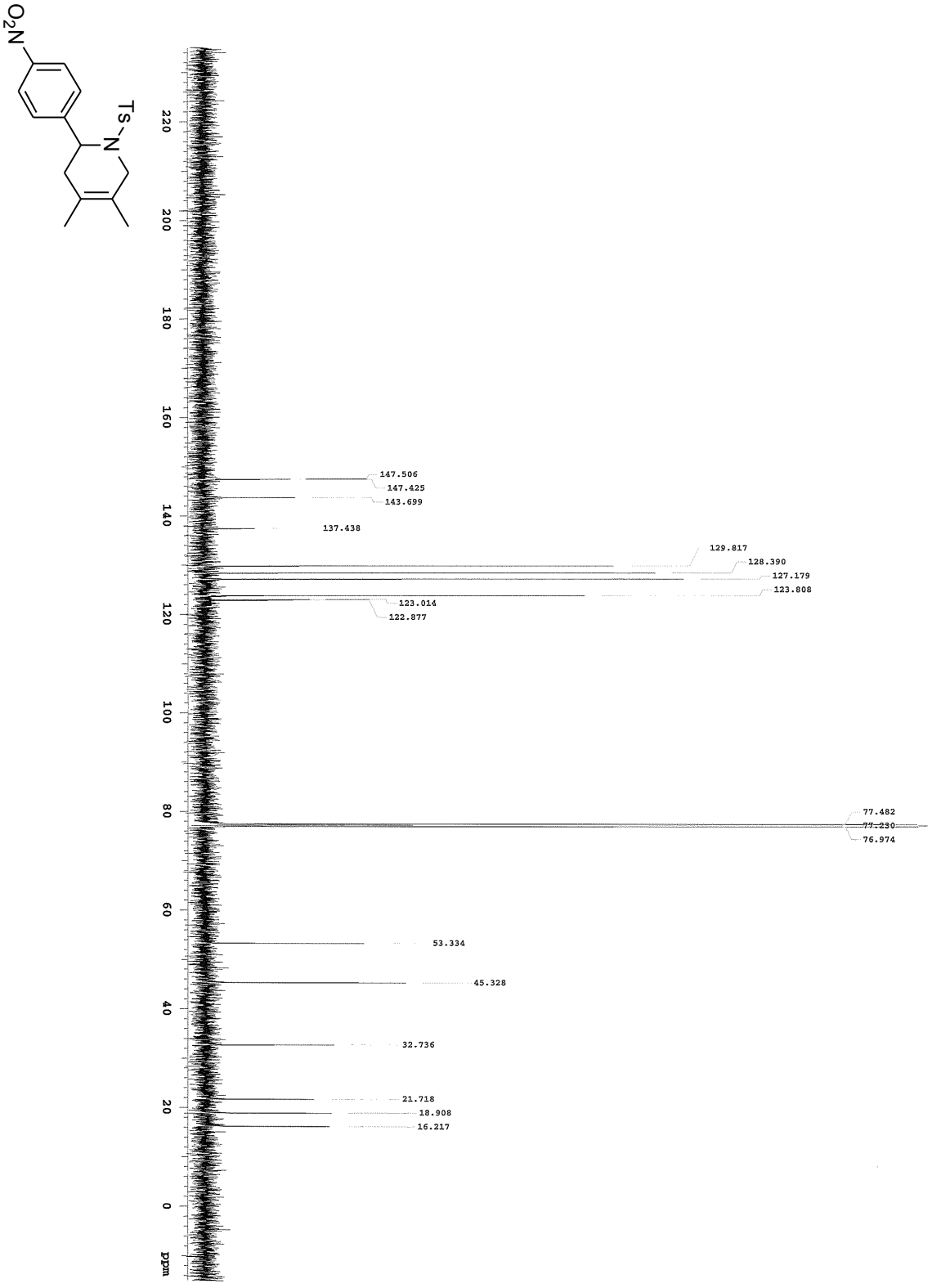
3ga (125.7 MHz, $CDCl_3$)



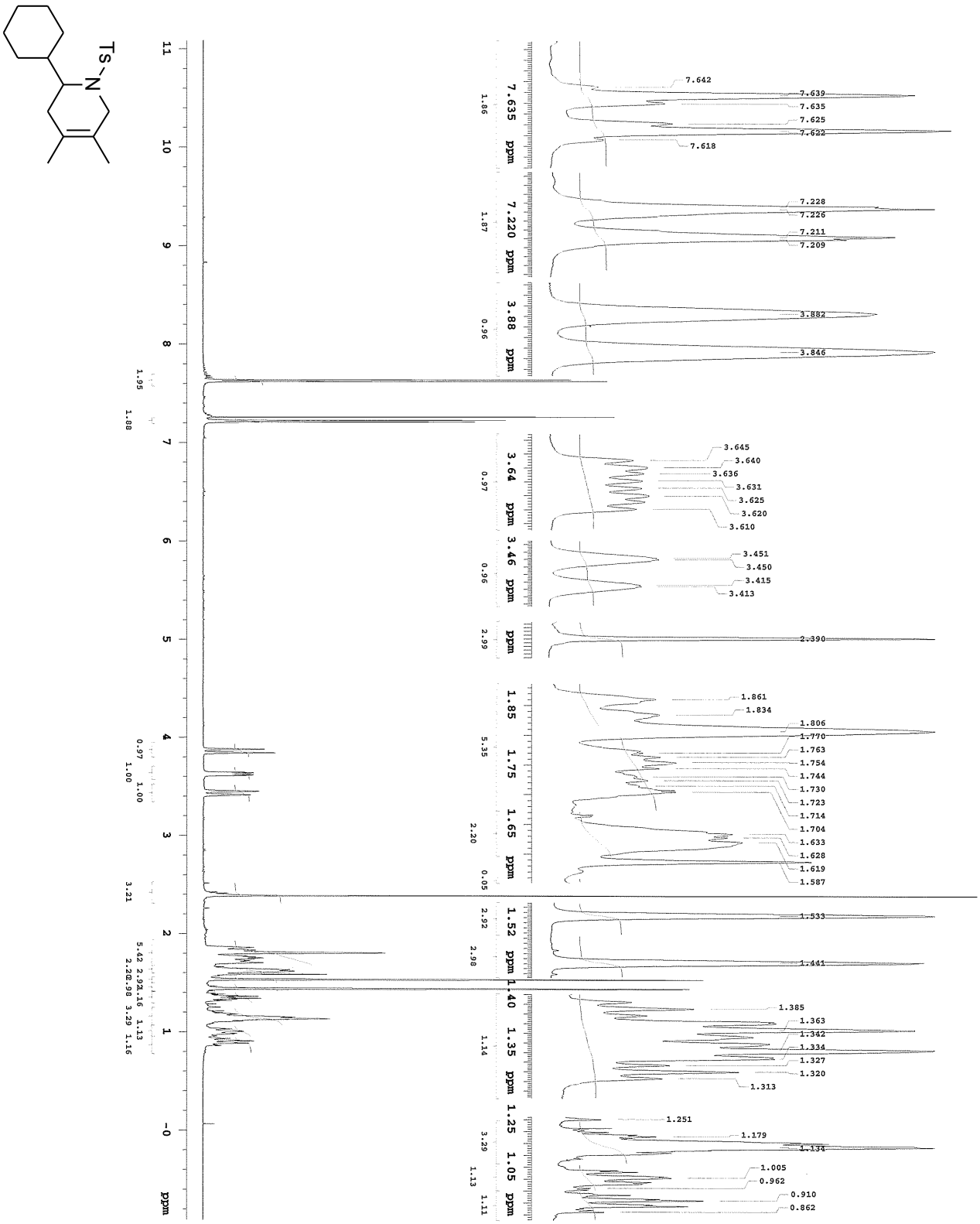
3ha (500 MHz, $CDCl_3$)



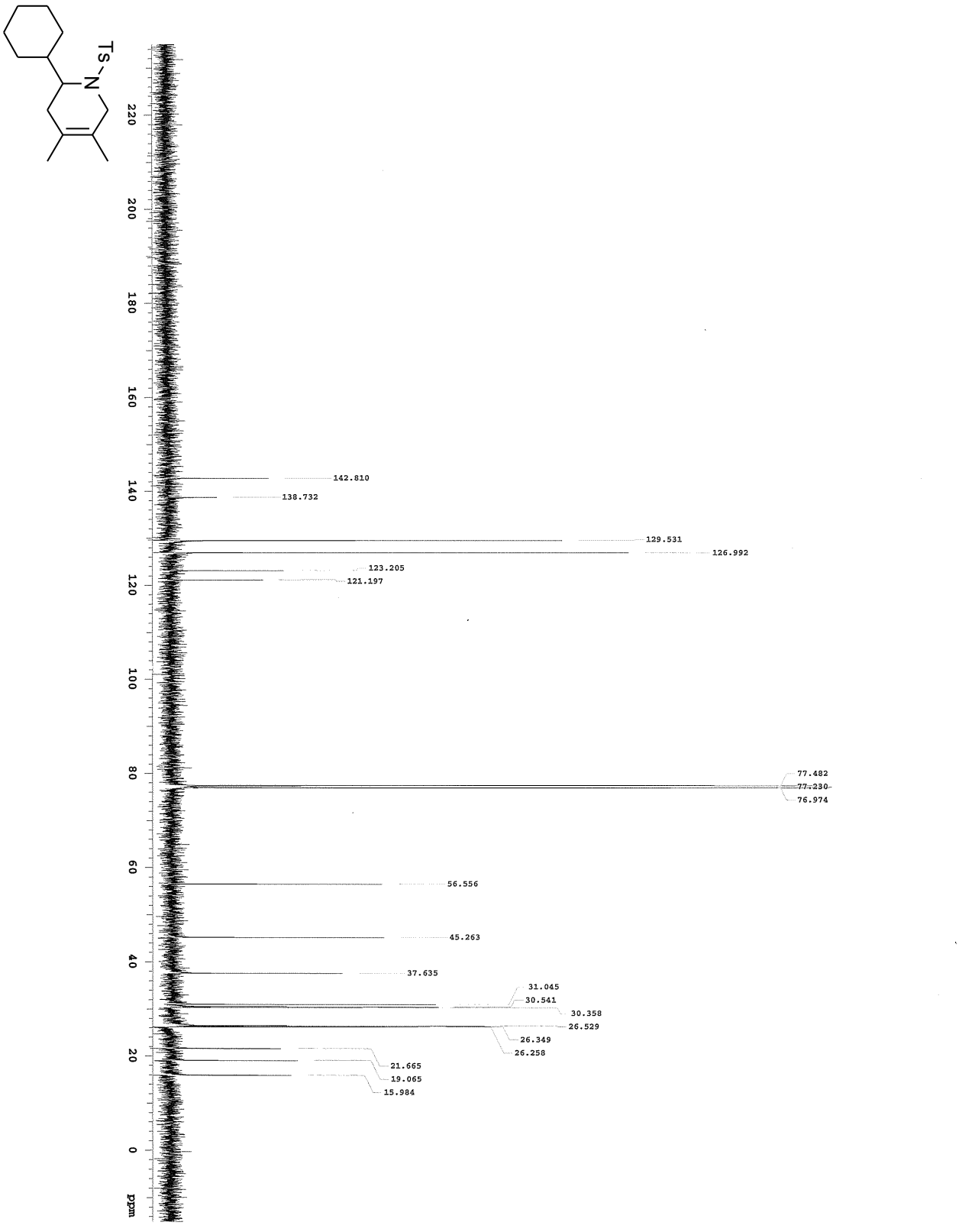
3ha (125.7 MHz, $CDCl_3$)



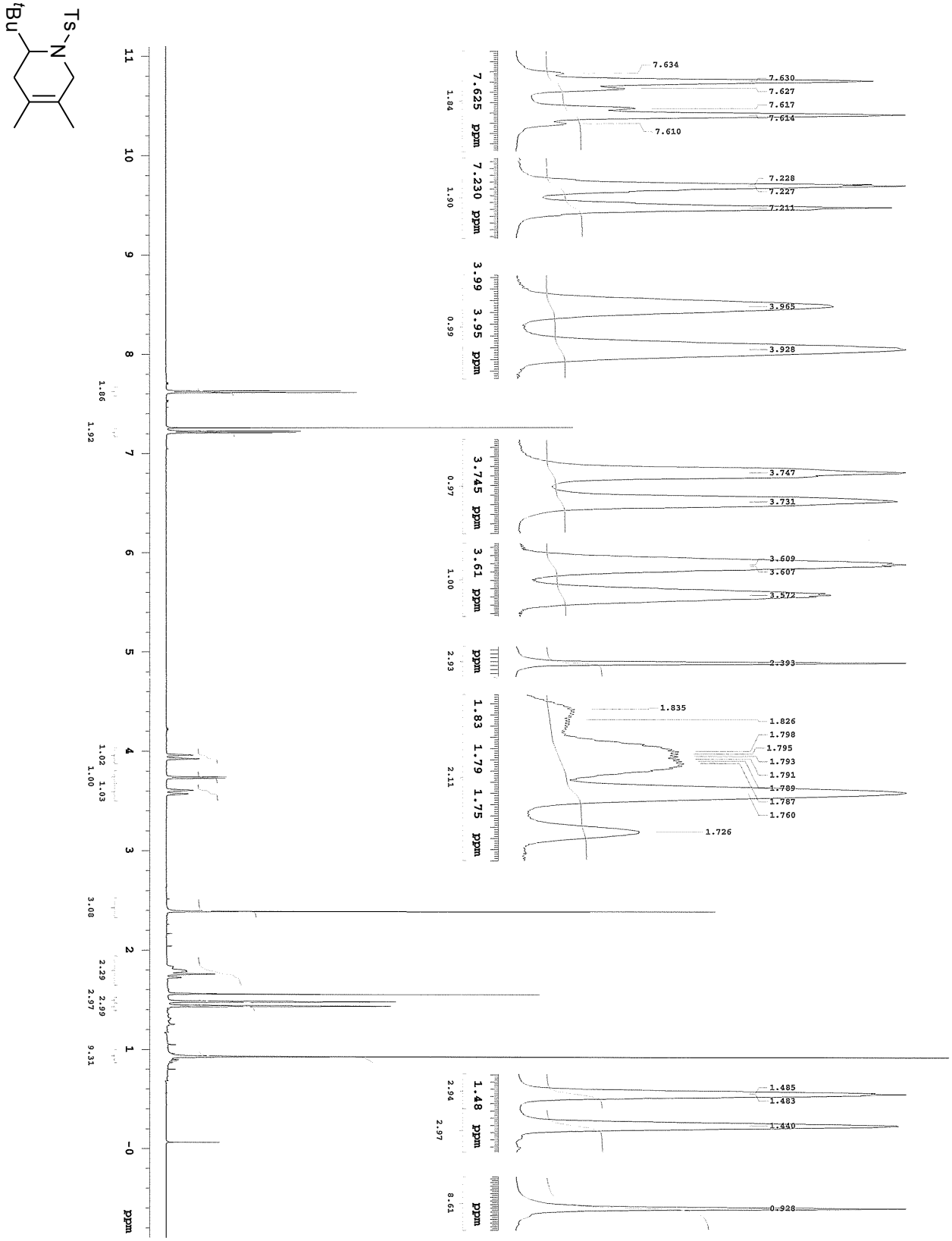
3ia (500 MHz, $CDCl_3$)



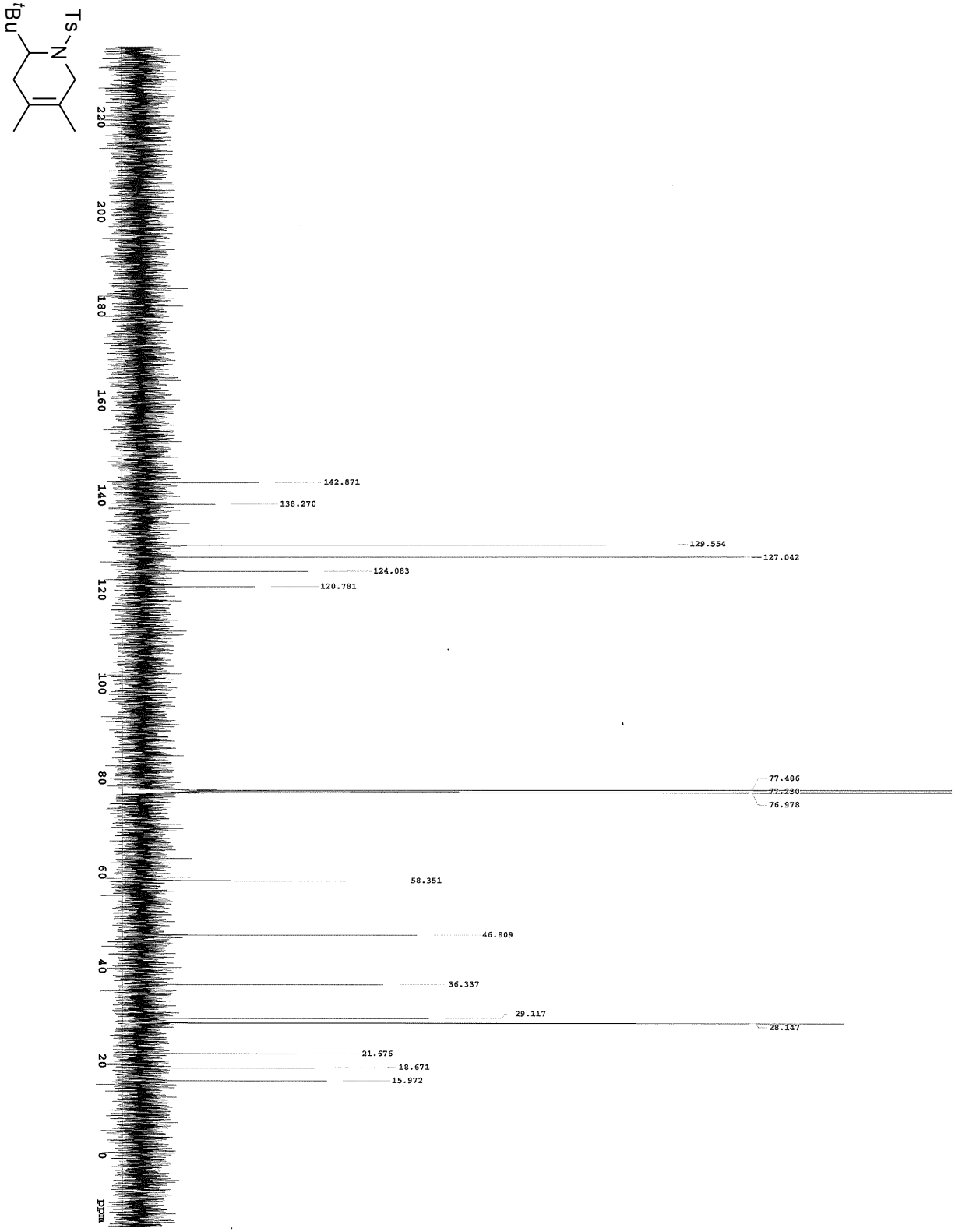
3ia (125.7 MHz, $CDCl_3$)



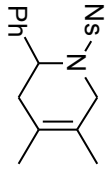
3ja (500 MHz, $CDCl_3$)

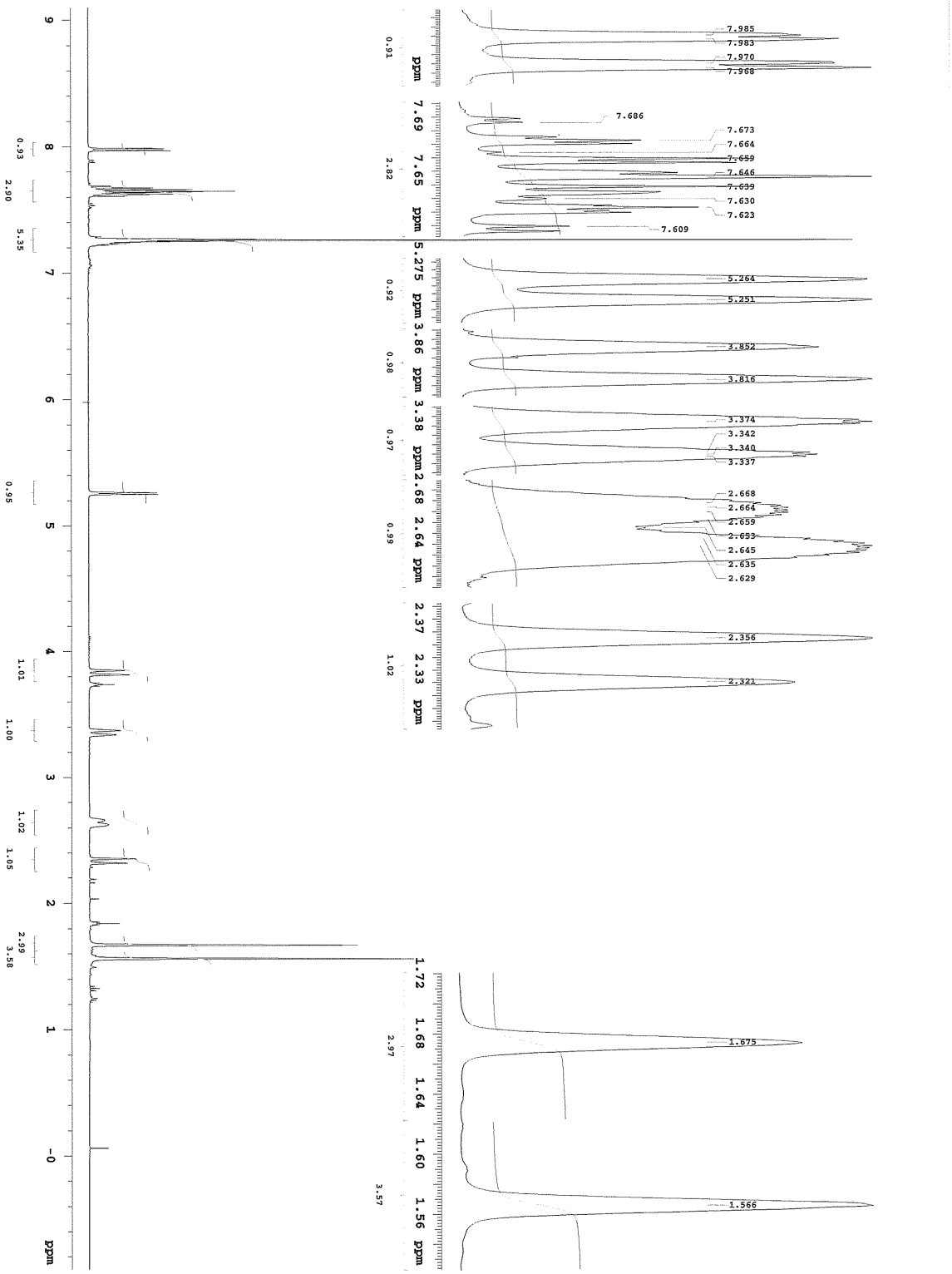


3ja (125.7 MHz, $CDCl_3$)

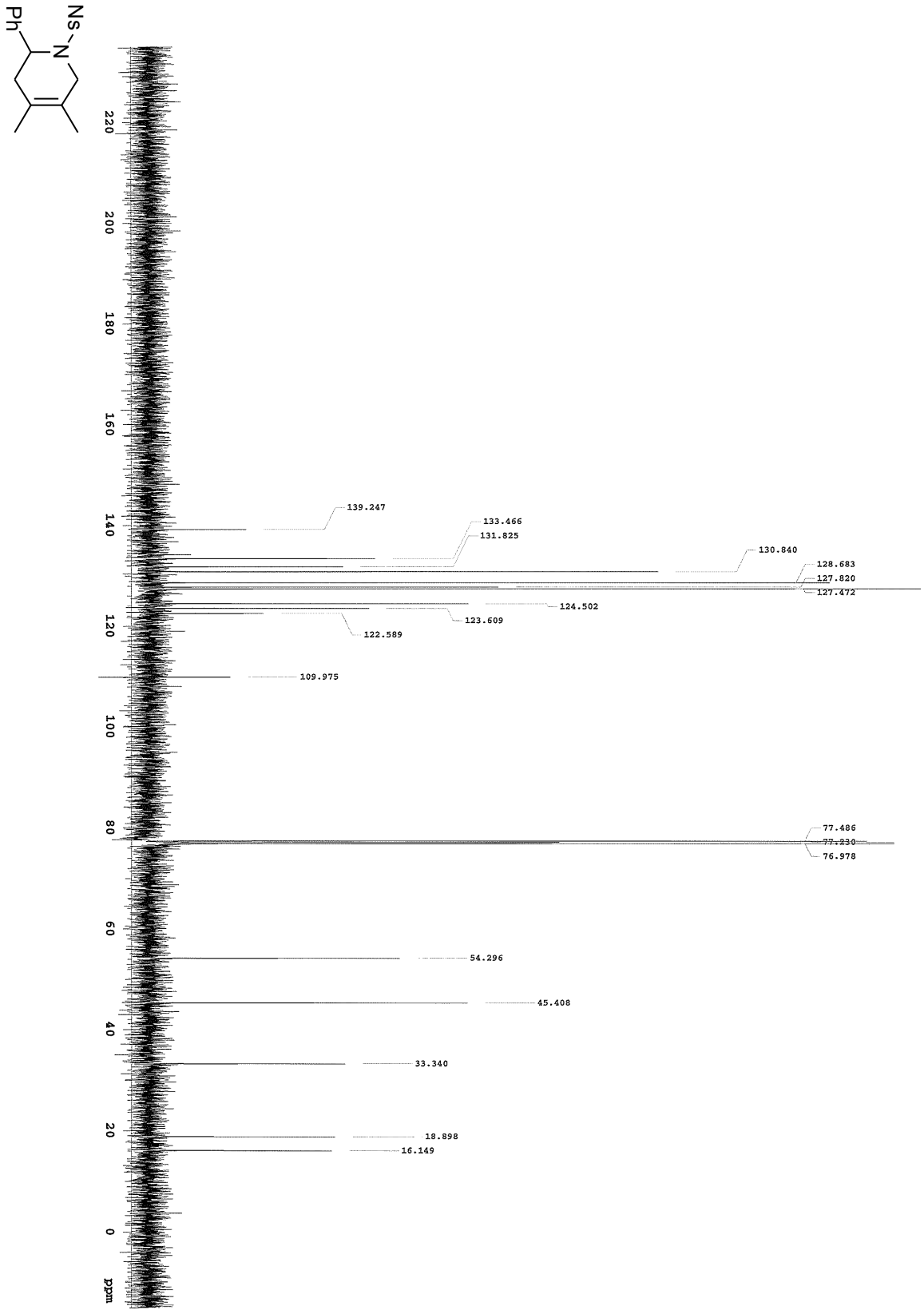


3ka (500 MHz, $CDCl_3$)

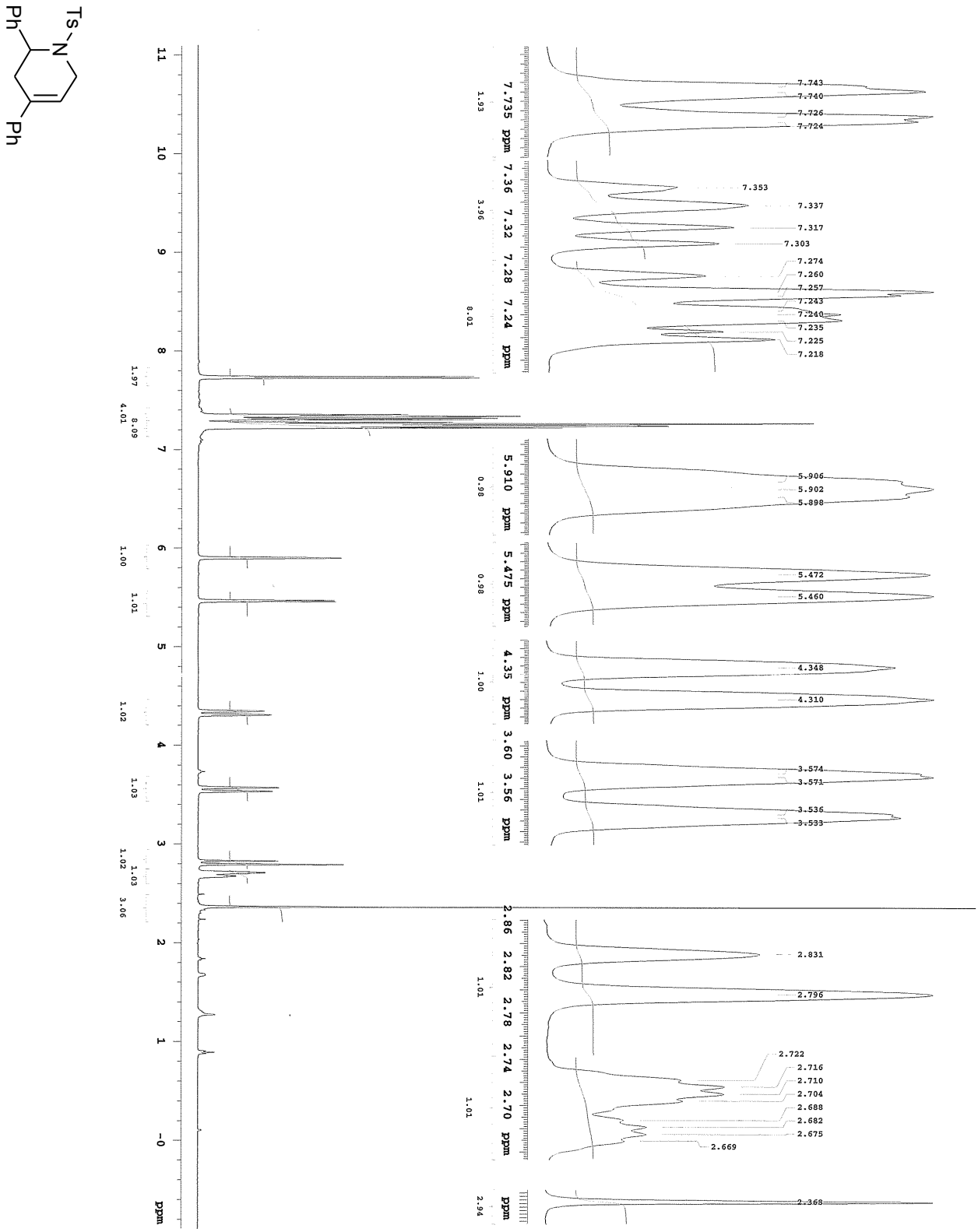




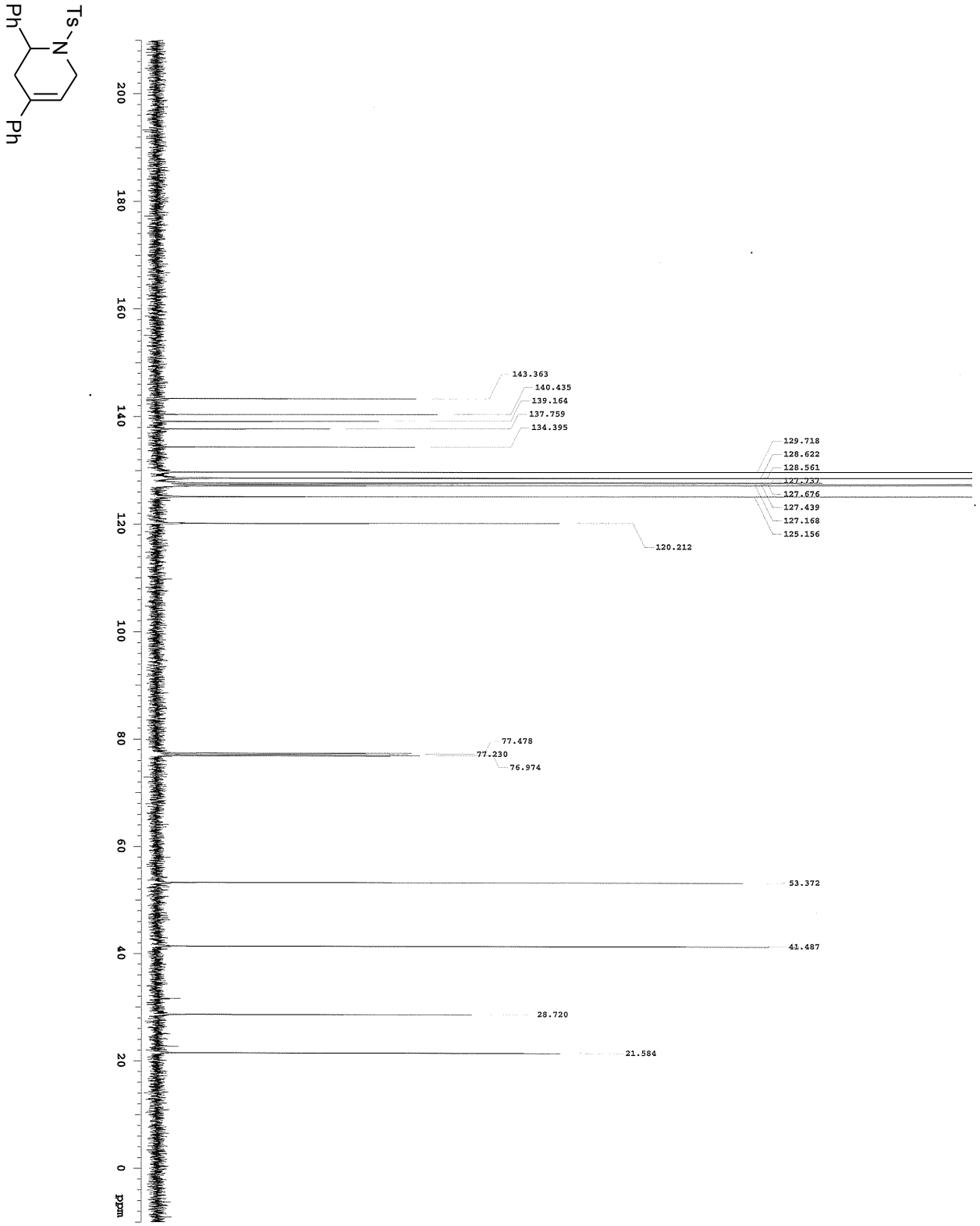
3ka (125.7 MHz, $CDCl_3$)



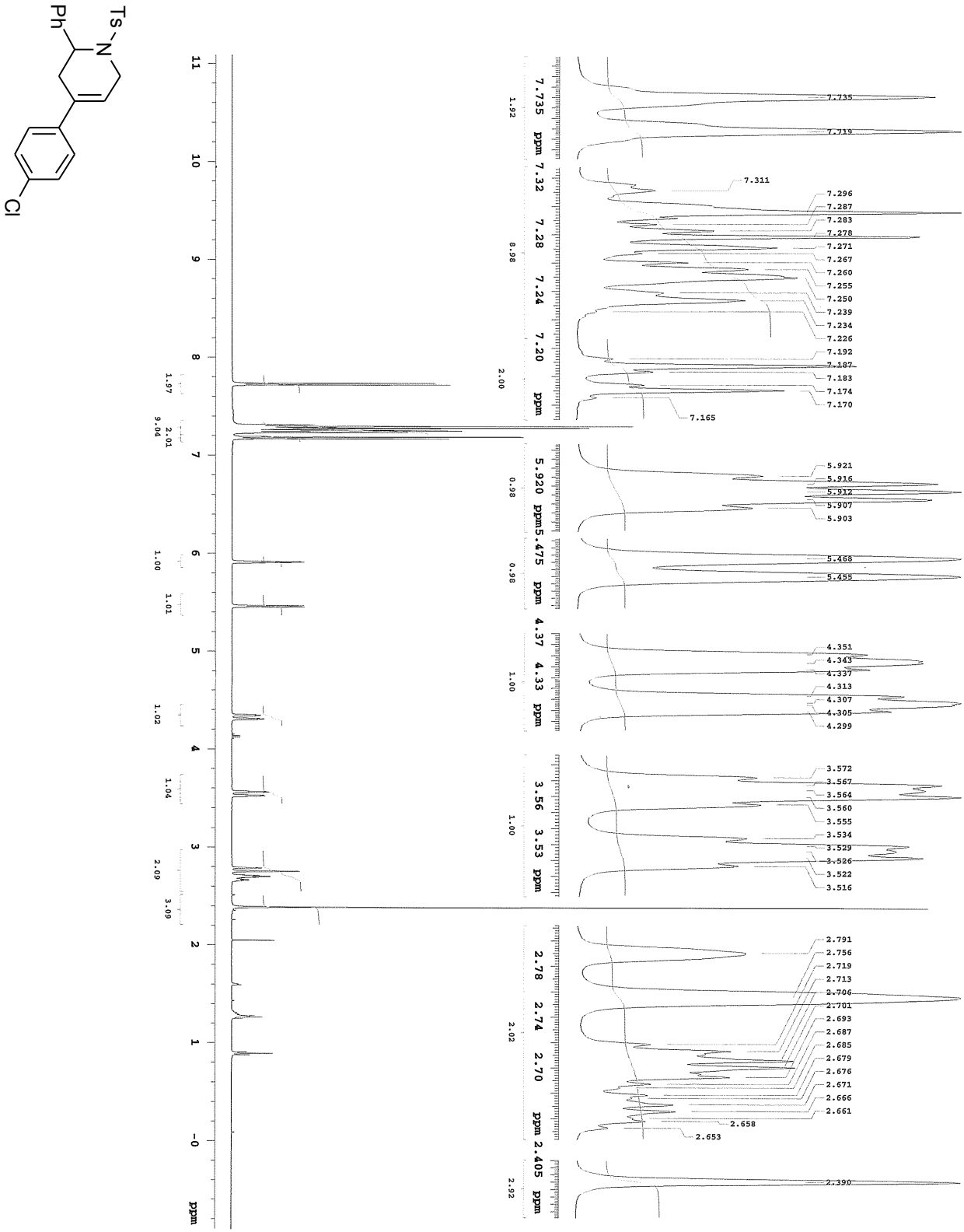
3ab (500 MHz, $CDCl_3$)



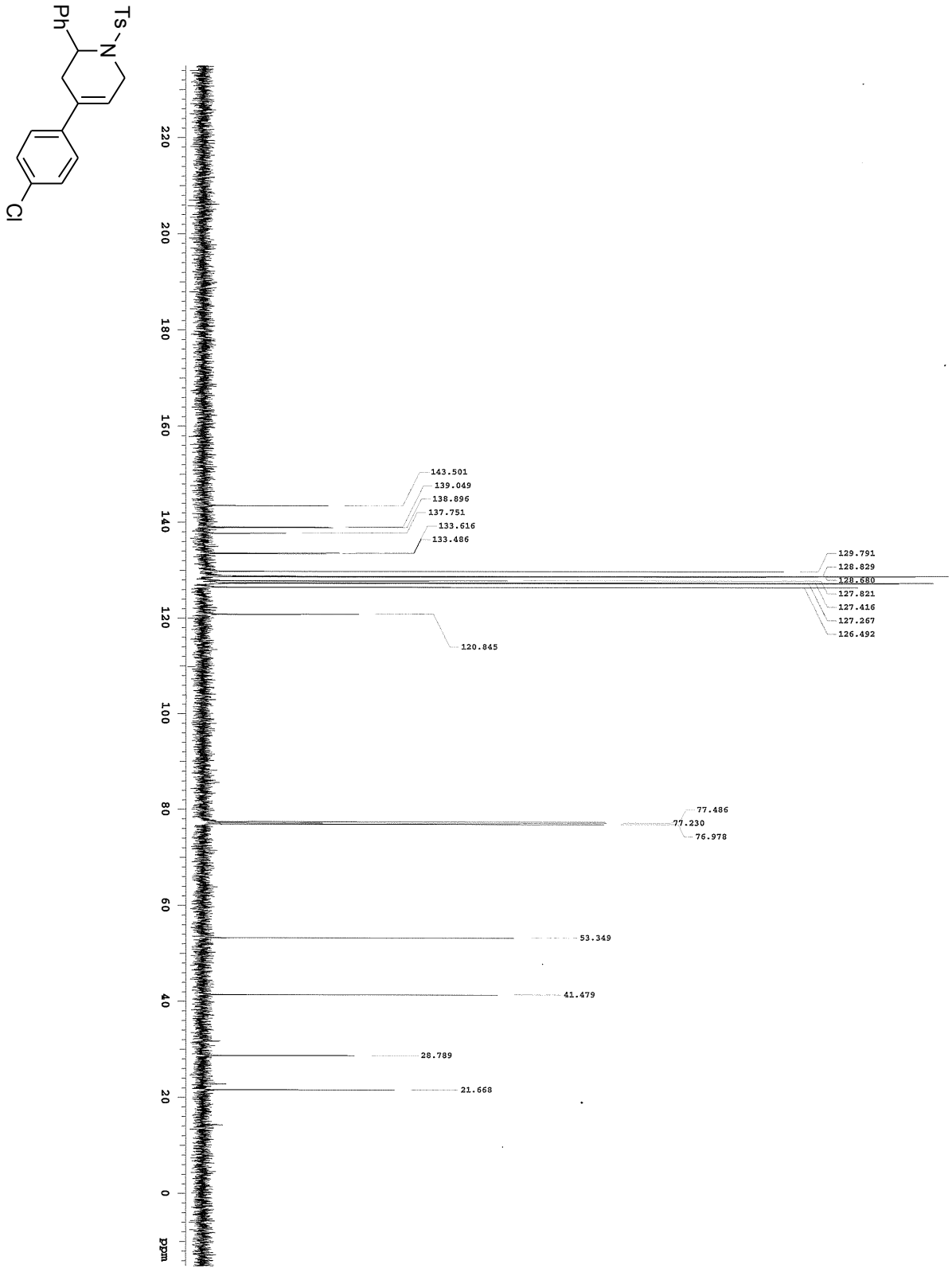
3ab (125.7 MHz, $CDCl_3$)



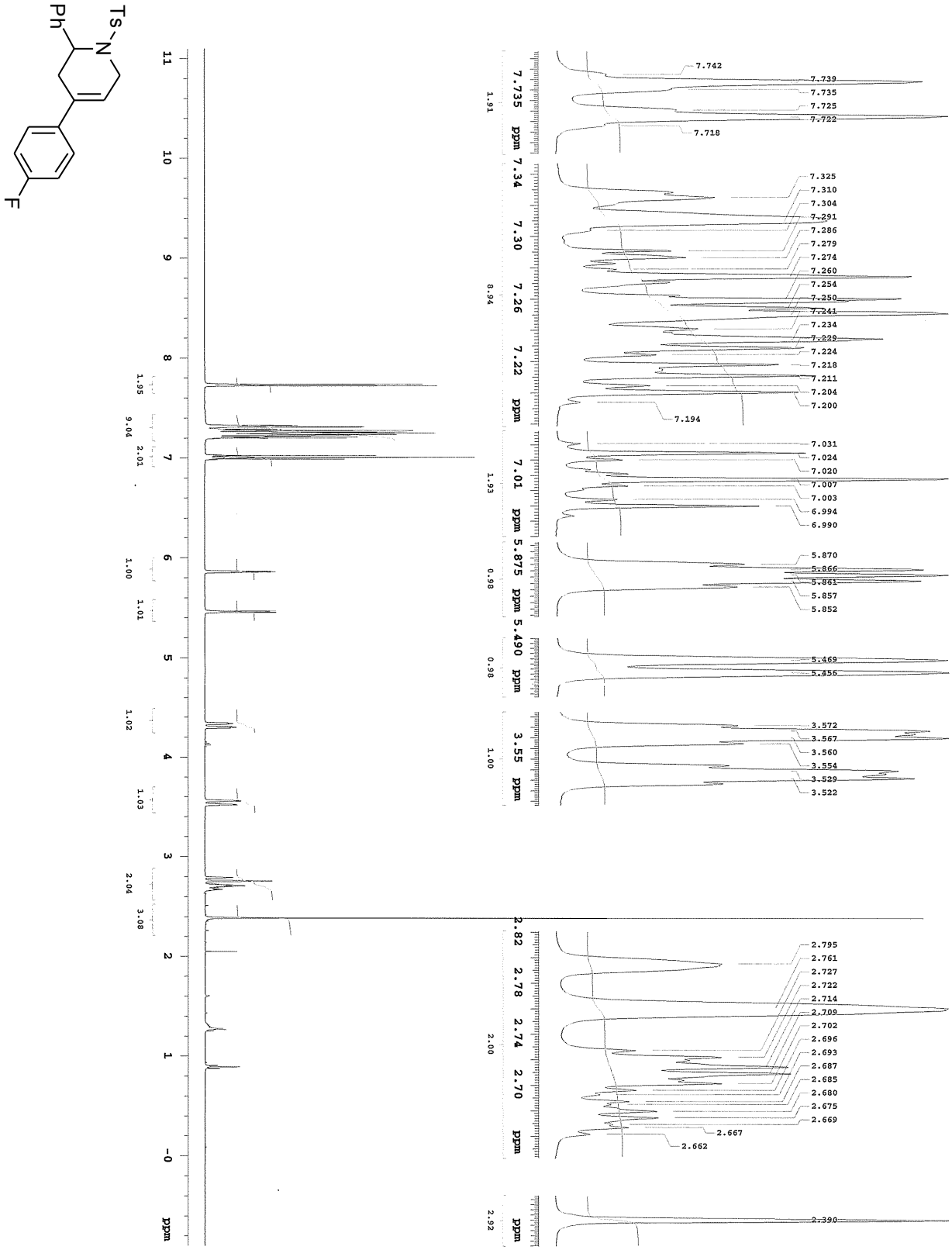
3ac (500 MHz, $CDCl_3$)



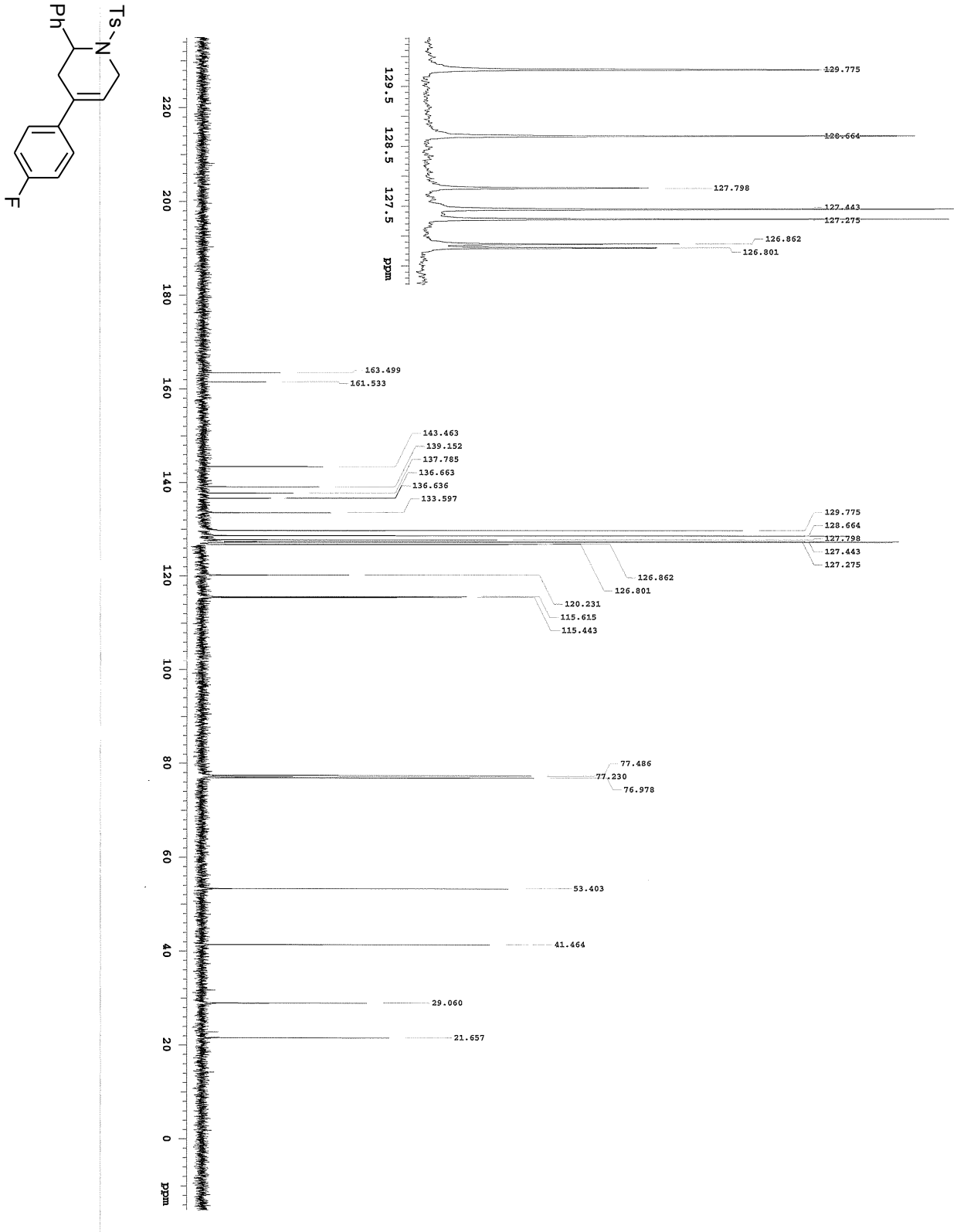
3ac (125.7 MHz, $CDCl_3$)



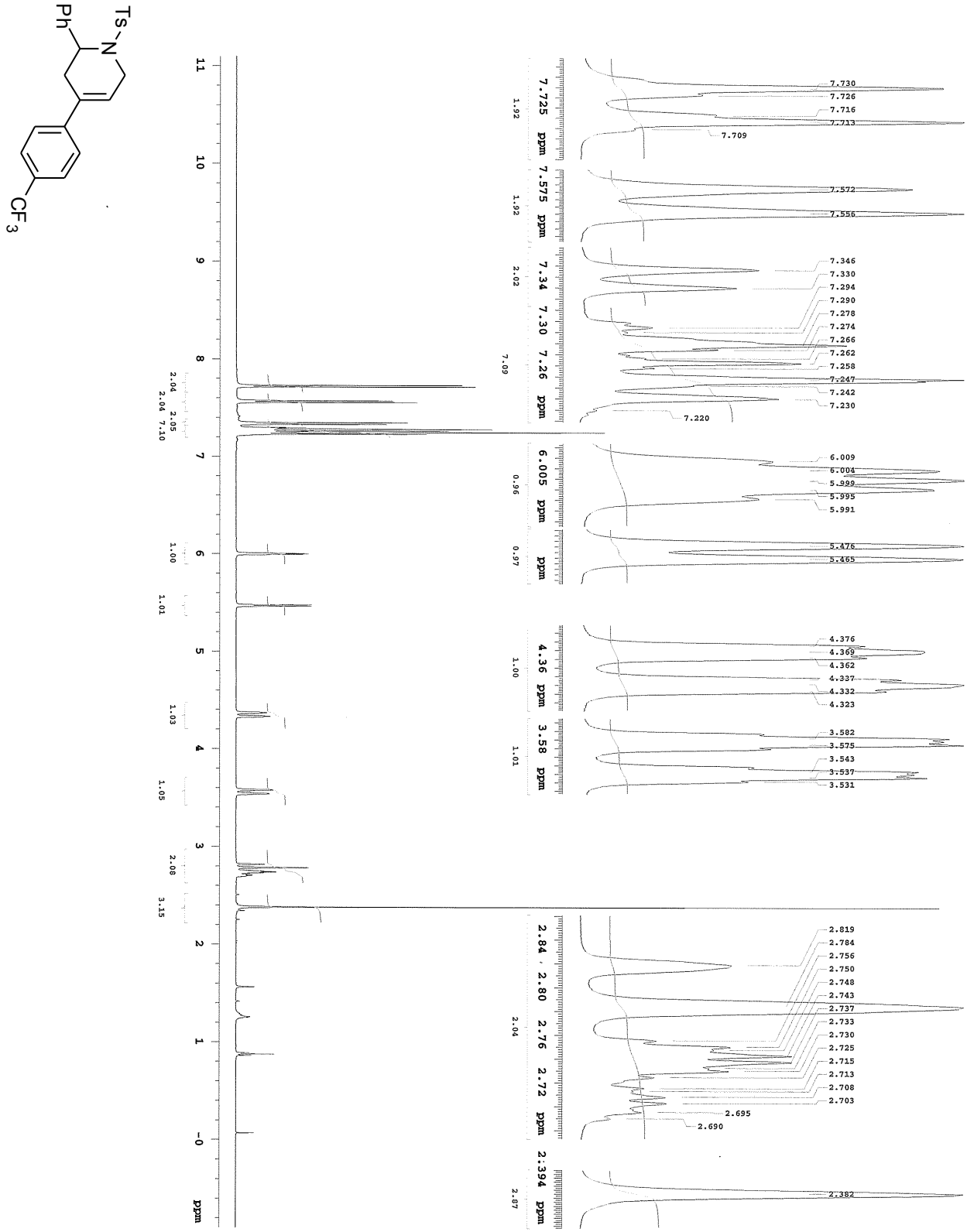
3ad (500 MHz, $CDCl_3$)



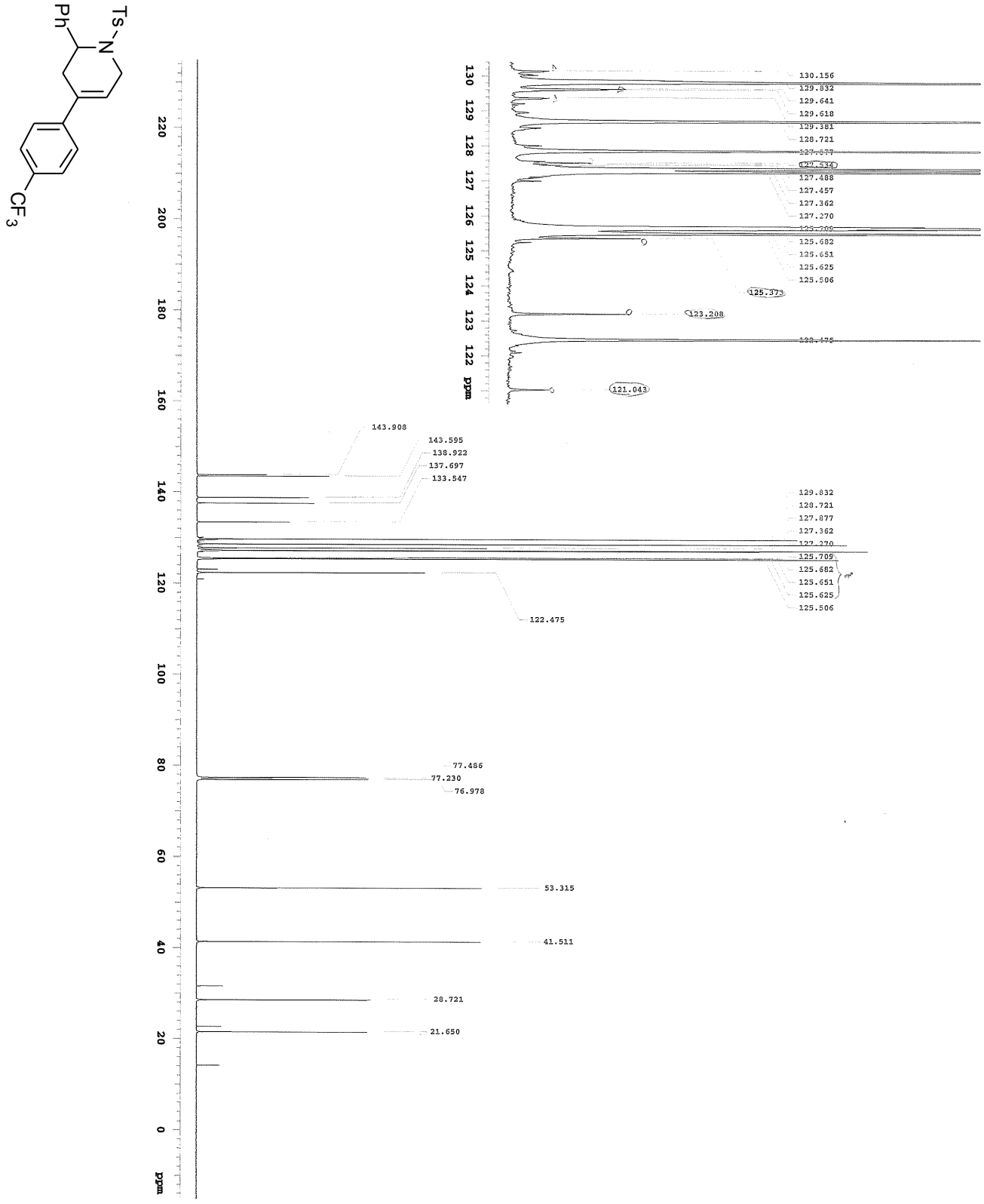
3ad (125.7 MHz, $CDCl_3$)



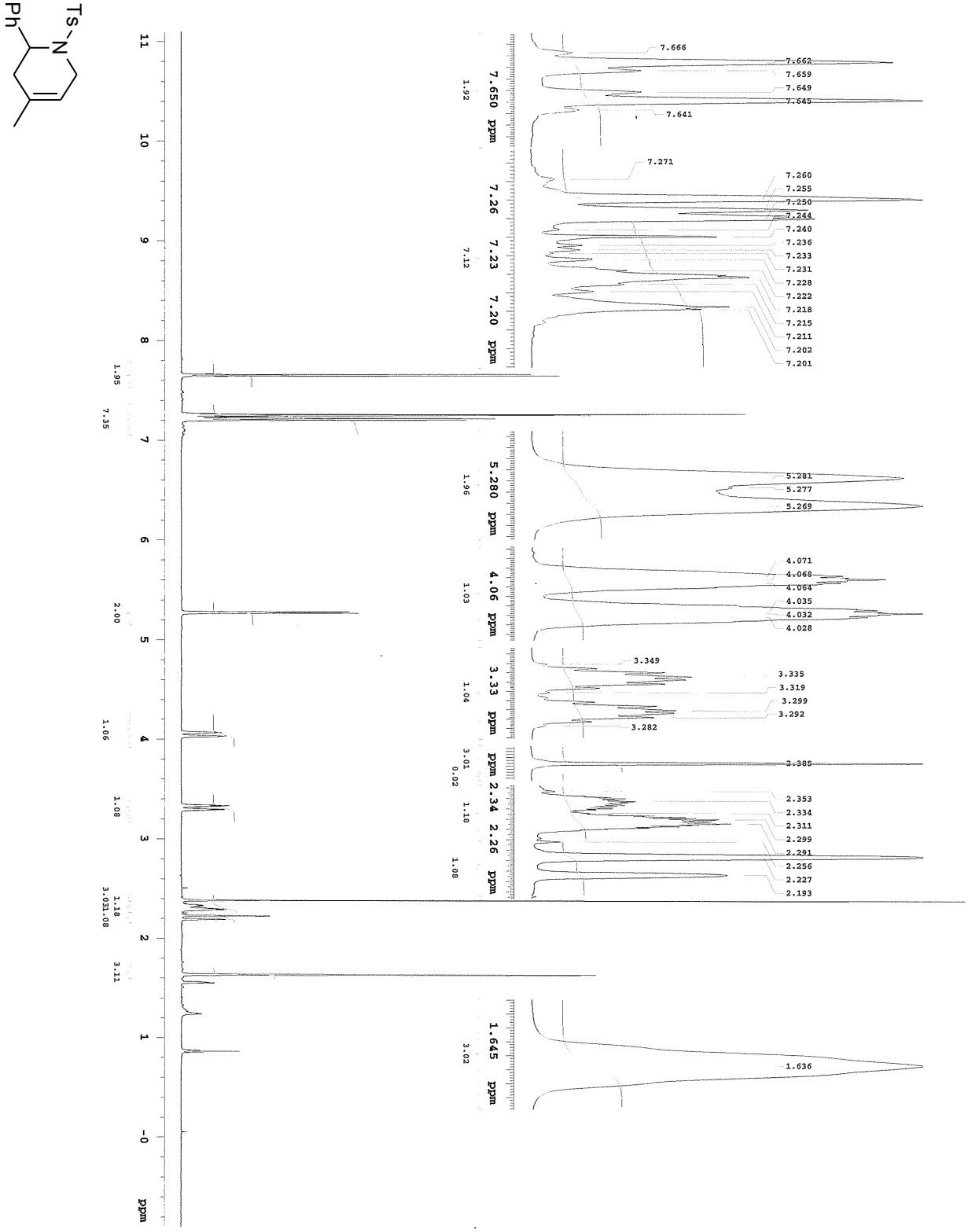
3ae (500 MHz, $CDCl_3$)



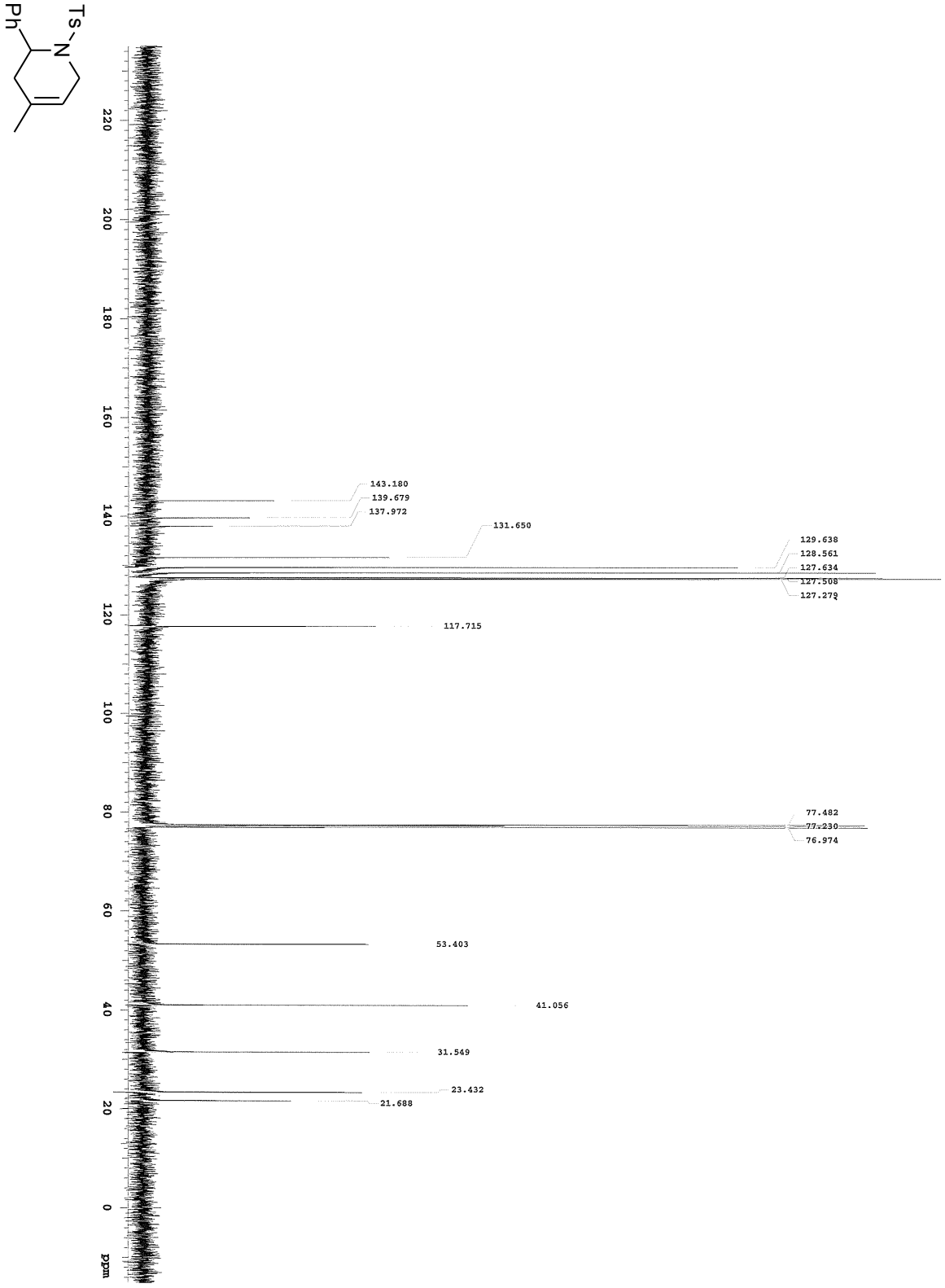
3ae (125.7 MHz, $CDCl_3$)



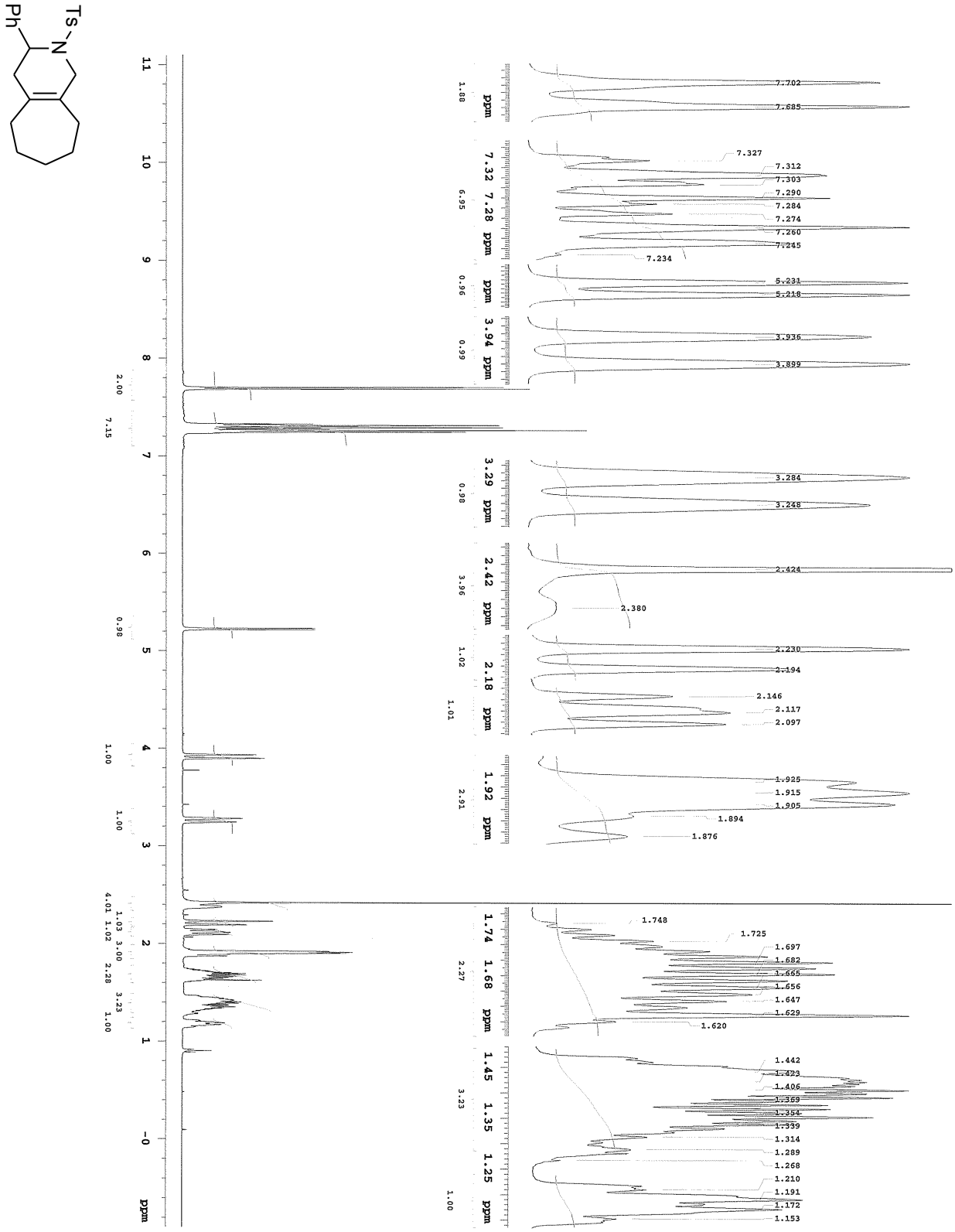
3af (500 MHz, $CDCl_3$)



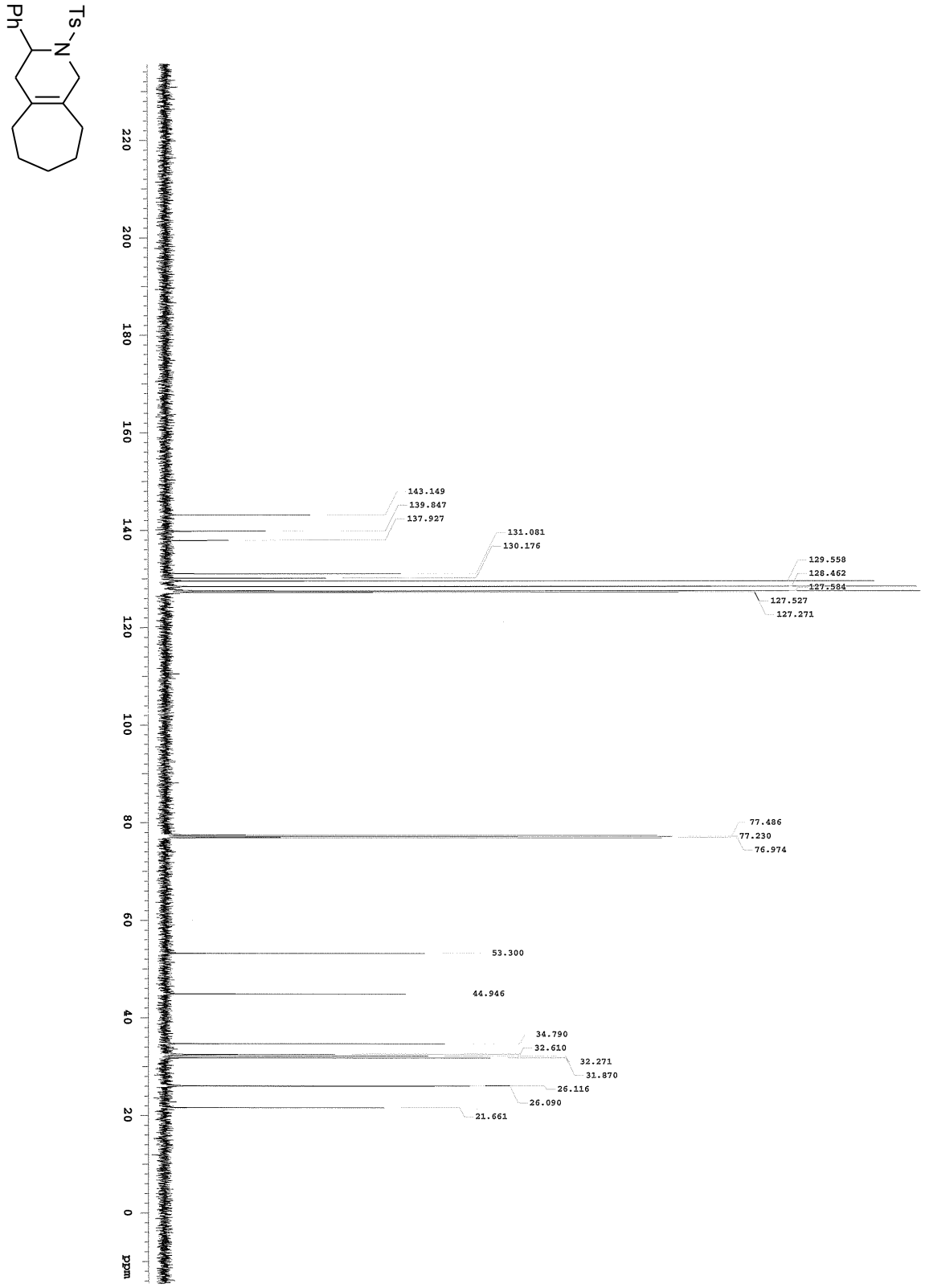
3af (125.7 MHz, $CDCl_3$)



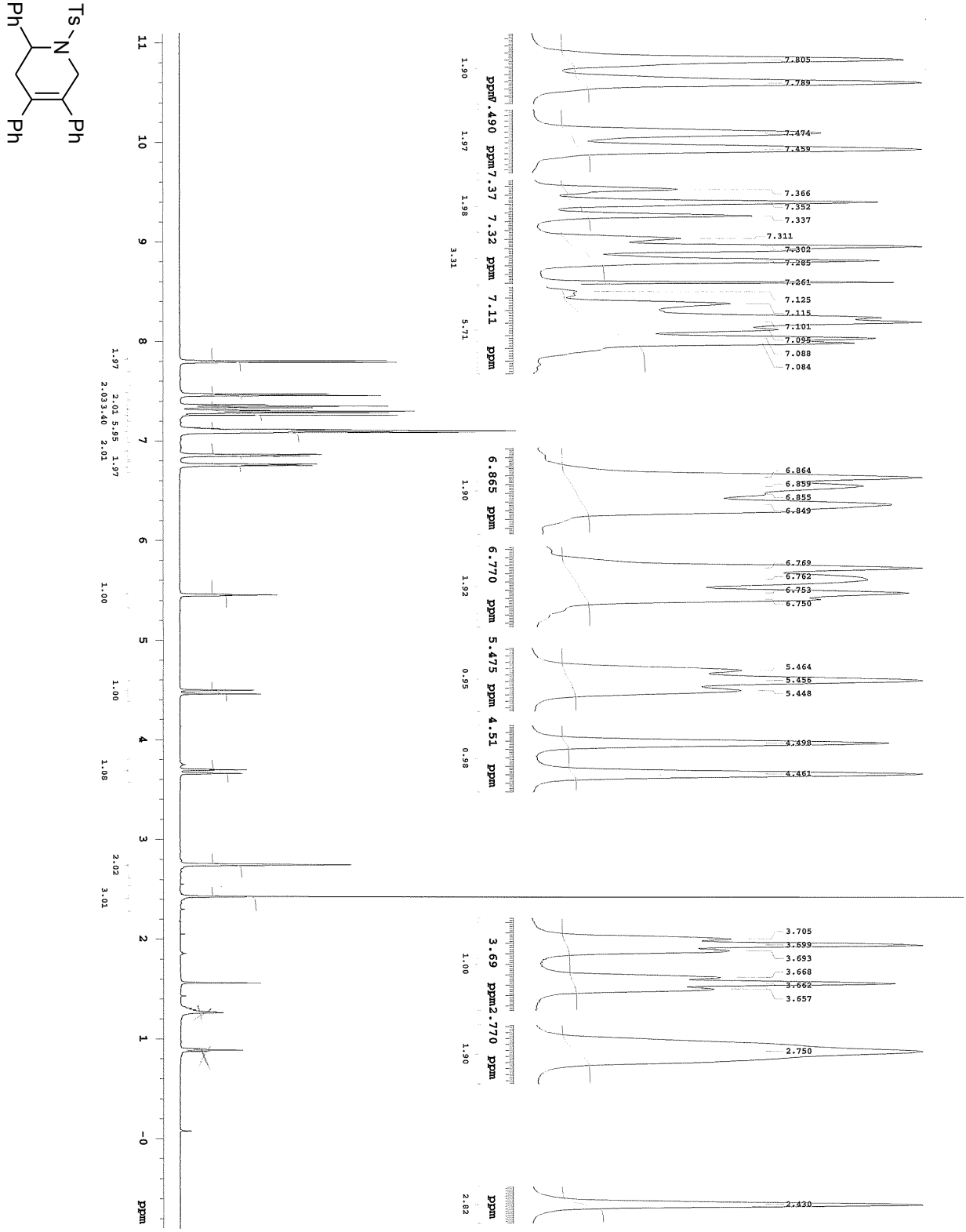
3ag (500 MHz, $CDCl_3$)



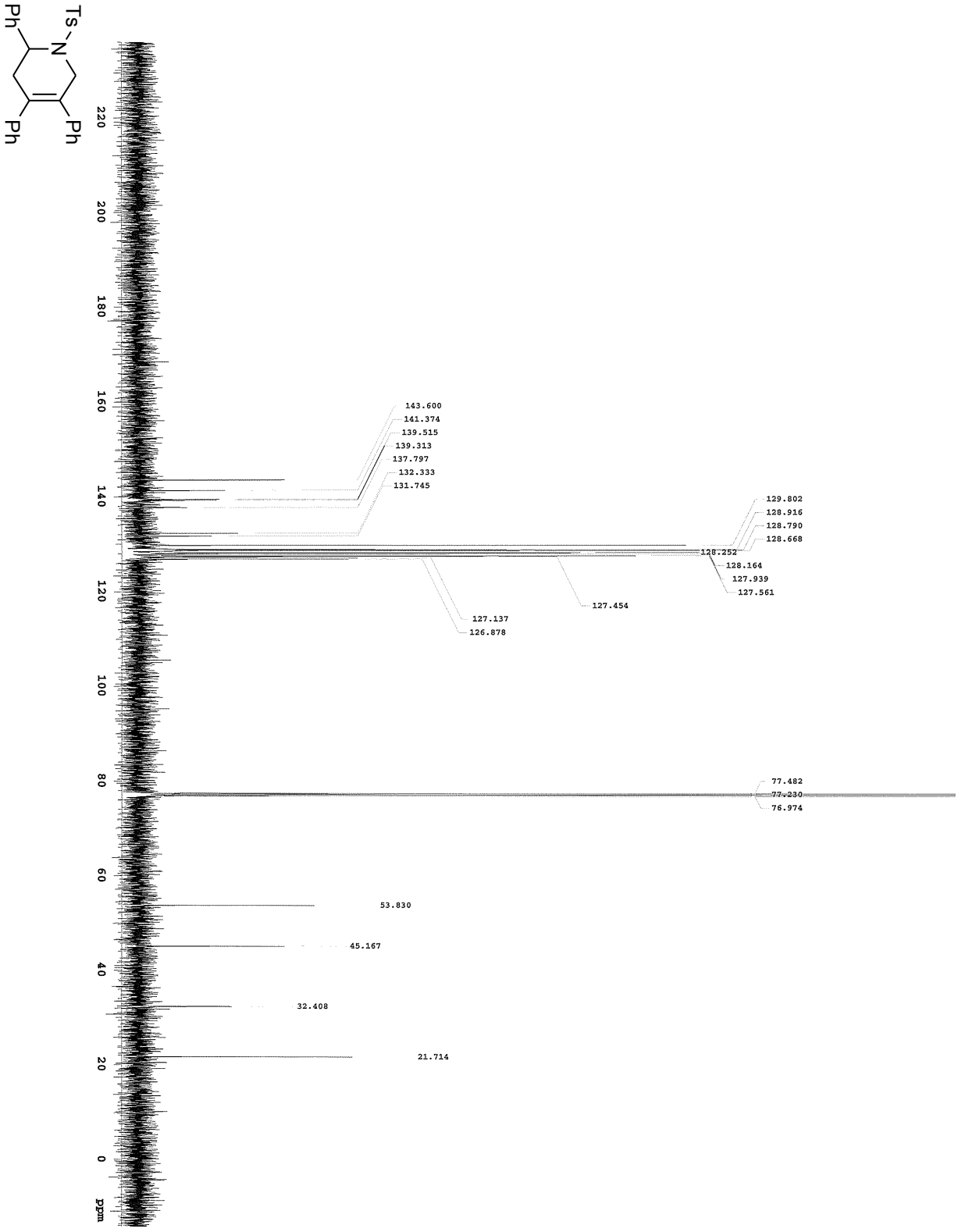
3ag (125.7 MHz, $CDCl_3$)



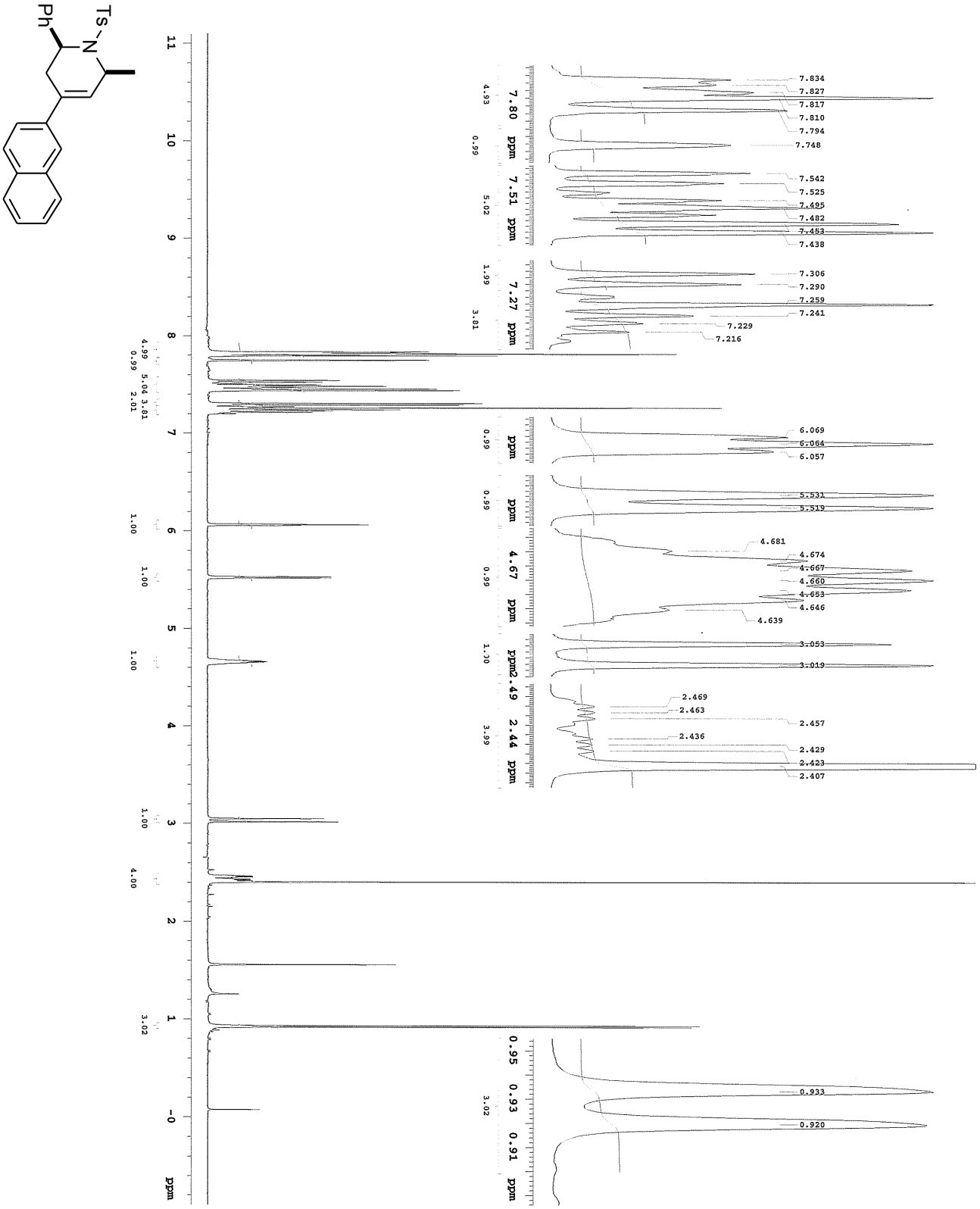
3ah (500 MHz, $CDCl_3$)



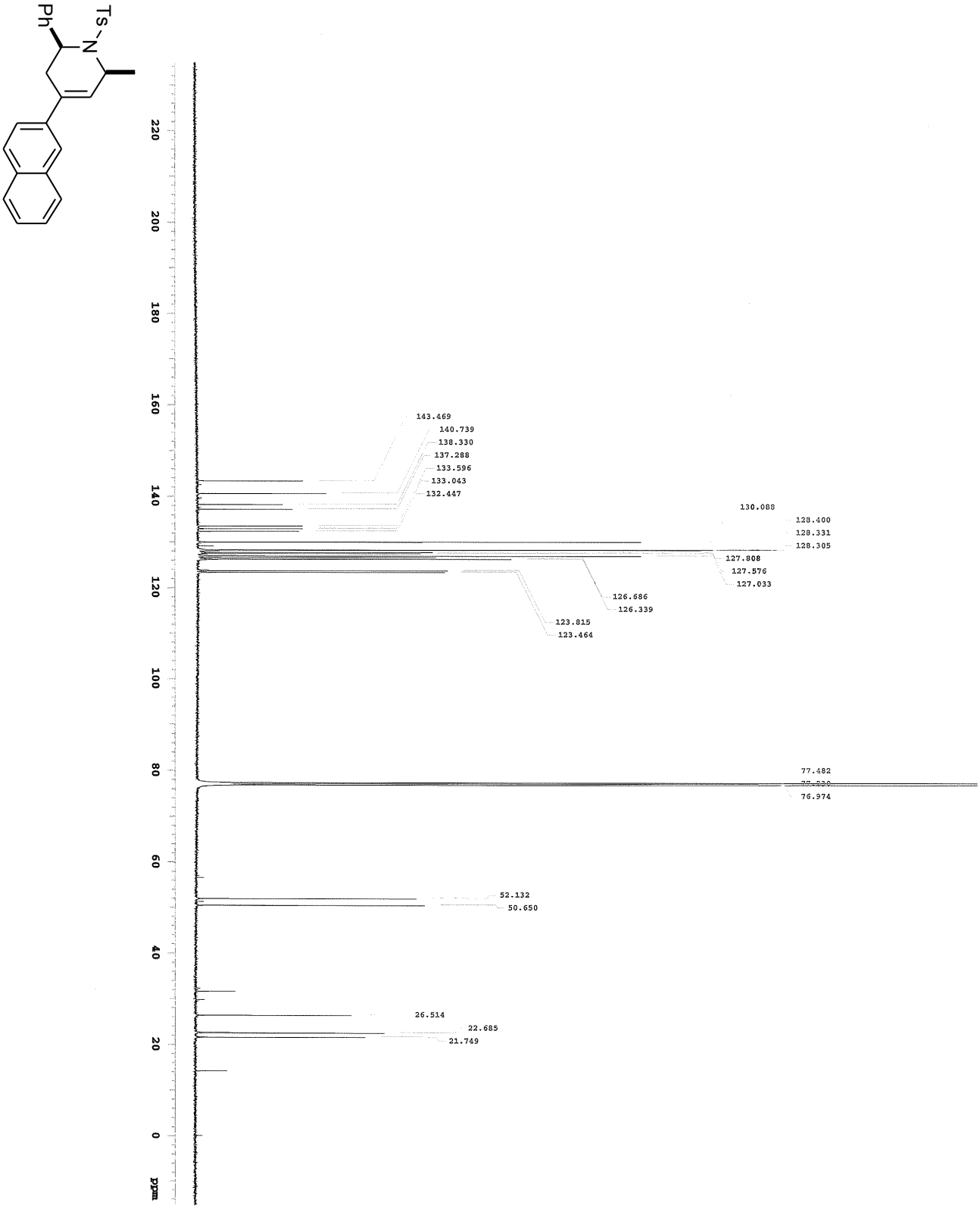
3ah (125.7 MHz, $CDCl_3$)



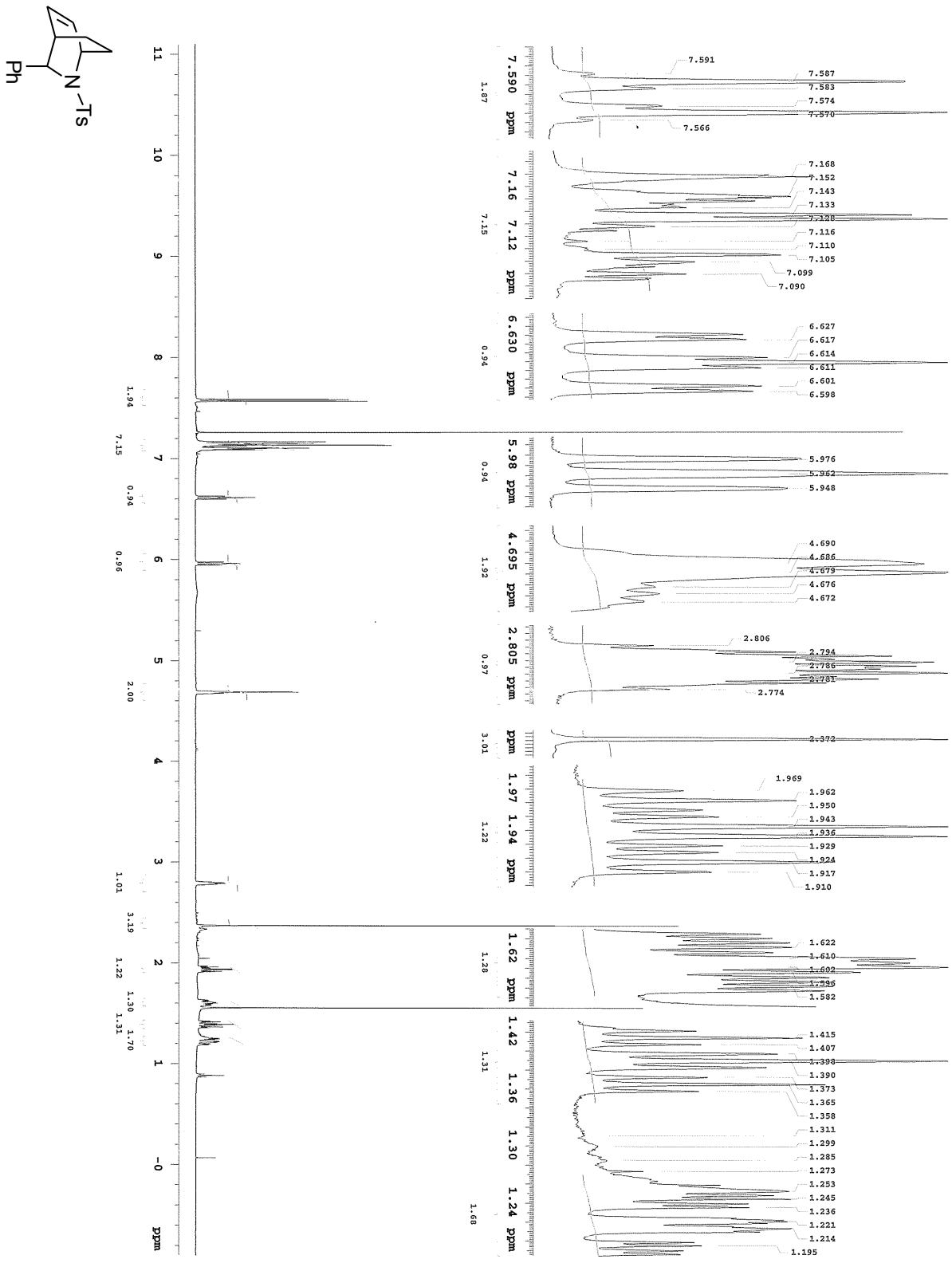
3ai (500 MHz, $CDCl_3$)



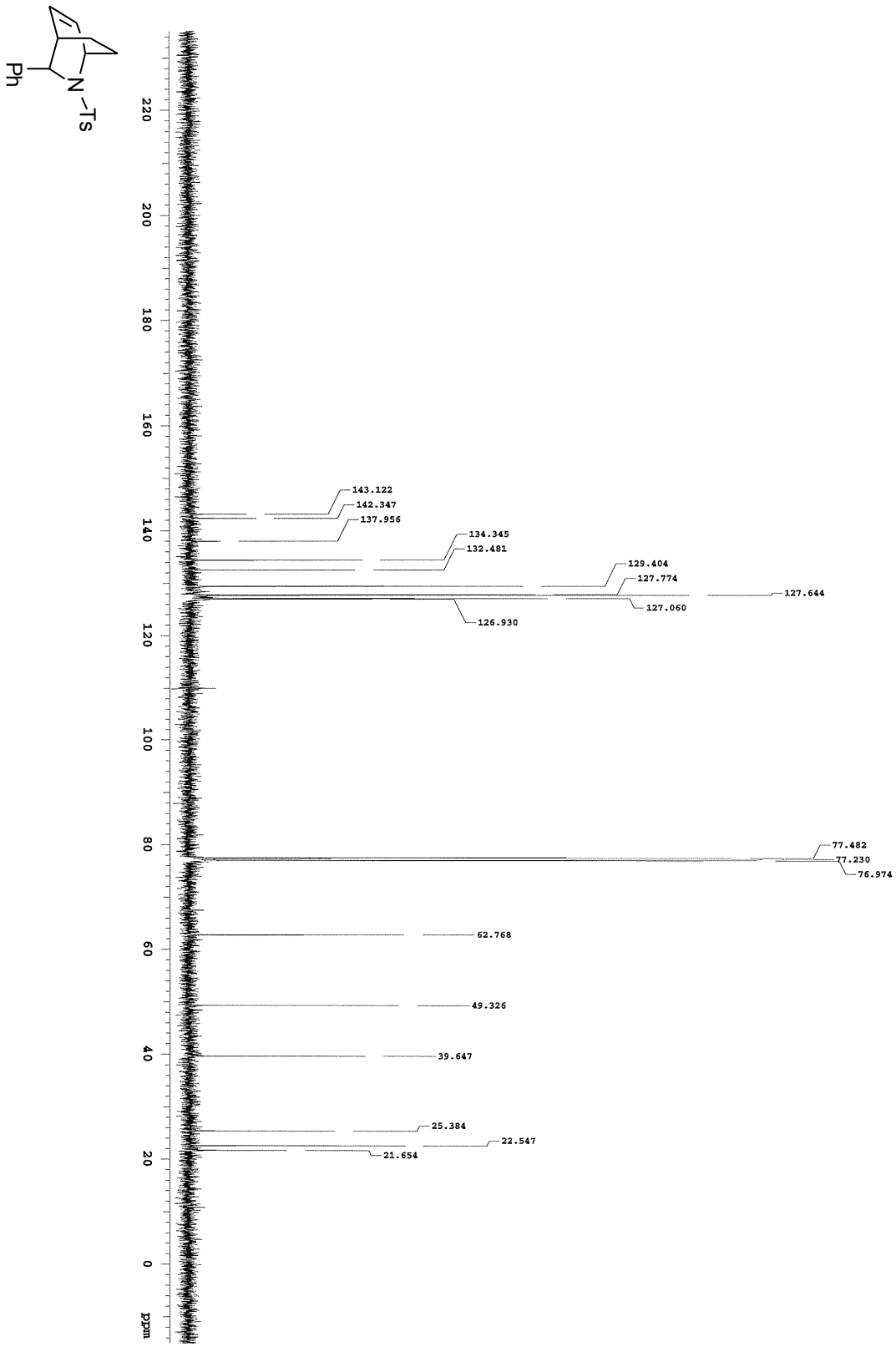
3ai (125.7 MHz, $CDCl_3$)



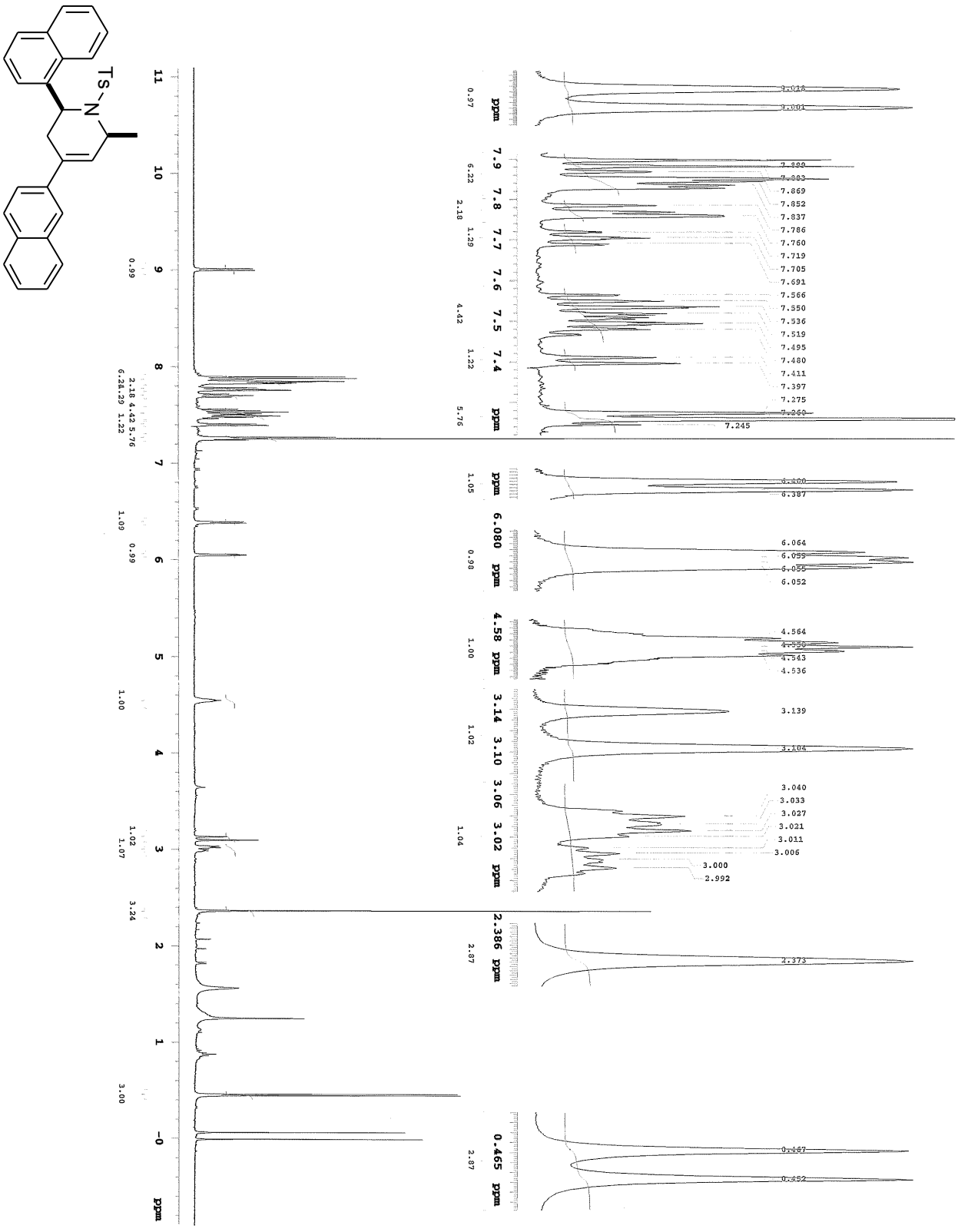
3aj (500 MHz, $CDCl_3$)



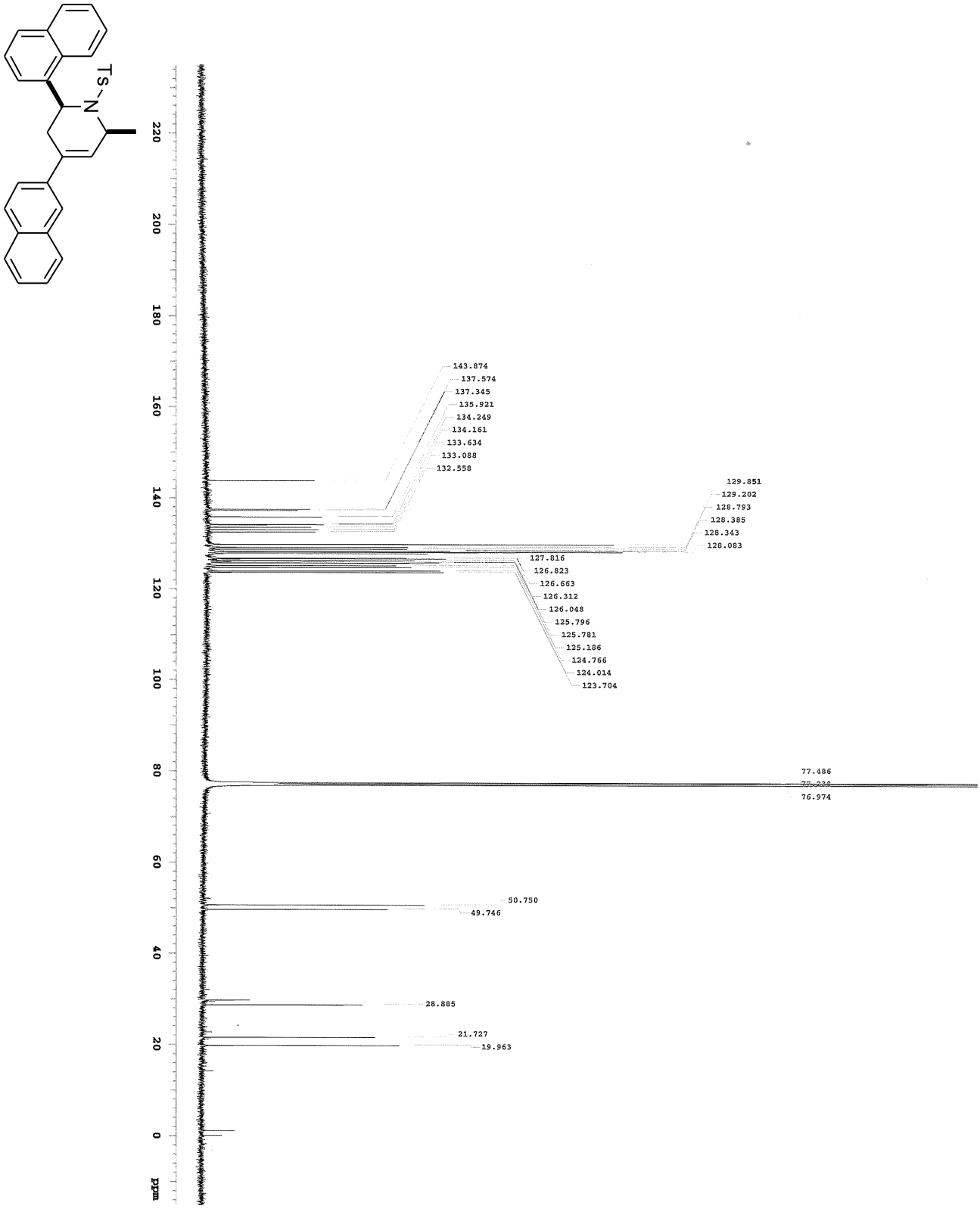
3aj (125.7 MHz, $CDCl_3$)



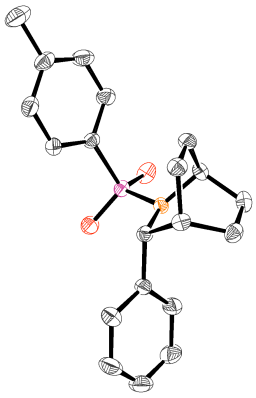
3bi (500 MHz, $CDCl_3$)



3bi (125.7 MHz, $CDCl_3$)

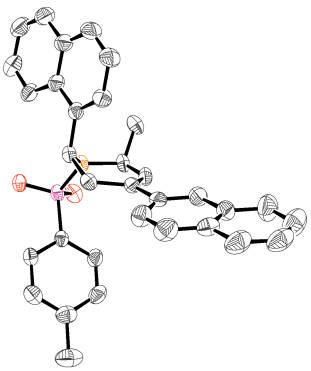


ORTEP Drawing of 3aj



Identification code	**3aj**	
Empirical formula	$C_{20}\ H_{21}\ N\ O_2\ S$	
Formula weight	339.44	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 7.819(3) Å	α= 90°
	b = 11.480(4) Å	β= 105.707(6)°
	c = 9.859(4) Å	γ = 90°
Volume	851.8(5) $Å^3$	
Z	2	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	0.202 mm^{-1}	
F(000)	360	
Crystal size	0.10 x 0.10 x 0.10 mm^3	
Theta range for data collection	2.15 to 26.82°.	
Index ranges	-9<=h<=7, -14<=k<=13, -12<=l<=9	
Reflections collected	5118	
Independent reflections	3275 [R(int) = 0.0170]	
Completeness to theta = 26.82°	98.5 %	
Absorption correction	None	
Max. and min. transmission	0.9801 and 0.9801	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3275 / 1 / 218	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0960	
R indices (all data)	R1 = 0.0385, wR2 = 0.0973	
Absolute structure parameter	0.62(6)	
Largest diff. peak and hole	0.361 and -0.196 $e.Å^{-3}$	

ORTEP Drawing of 3bi



Identification code	**3bi**	
Empirical formula	C34 H30 Cl3 N O2 S	
Formula weight	623.00	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6082(17) Å	α= 72.785(3)°.
	b = 11.0420(19) Å	β= 75.236(3)°.
	c = 14.459(2) Å	γ = 79.948(3)°.
Volume	1555.4(4) $Å^3$	
Z	2	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	648	
Crystal size	0.10 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.51 to 27.01°.	
Index ranges	-13<=h<=12, -12<=k<=14, -13<=l<=18	
Reflections collected	9537	
Independent reflections	6581 [R(int) = 0.0179]	
Completeness to theta = 27.01⁻	96.8 %	
Absorption correction	None	
Max. and min. transmission	0.9617 and 0.9617	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6581 / 0 / 372	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.2530	
R indices (all data)	R1 = 0.1245, wR2 = 0.2867	
Largest diff. peak and hole	0.783 and -0.374 e.$Å^{-3}$	

References

1. For synthesis of [Co(TPP)], see: (a) Shirazi, A.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 3420. (b) Aldler, A. D.; Longo, F. R.; Varadi, V. *Inorg. Synth.* **1976**, *16*, 213.
2. For synthesis of [Co(TPP)]Cl, see: (a) Fukuzumi, S.; Miyamoto, K.; Suenobu, T.; Caemelbecke, E. V.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 2880.
3. For synthesis of $[Co(TPP)]^+$, see: (a) Fukuzumi, S.; Mochizuki, S.; Tanaka, T. *Inorg. Chem.* **1990**, *29*, 653. (b) Fukuzumi, S.; Okamoto, K.; Tokuda, Y.; Gros, C. P.; Guilard, R. *J. Am. Chem. Soc.* **2004**, *126*, 17059.
4. Love, B. E.; Raje, P. S.; Williams II, T. C. *Synlett*, **1994**, 493.
5. Kiss, E.; Markó, I. E.; Guillaume, M. *Tetrahedron*, **2011**, 9173.