One-Step Construction of Tetrahydro-5*H*-indolo[3,2-*c*]quinolines from Benzyl Azides and Indoles via a Cascade Reaction Sequence

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Supporting Information

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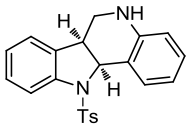
Part 1. Experimental Procedures and Analytical Data

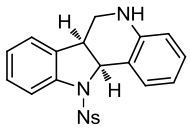
General Methods. Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 (^{1}H at 400 MHz and ^{13}C at 100 MHz) using TMS as the internal standard. Column chromatography was performed on silica gel. Commercially available reagents and solvents were used without further purification.

Compounds **1a**–**1g**,[1] **2a**–**2e**,[2] and **2f**–**2l**[3] were synthesized according to the literature procedures.

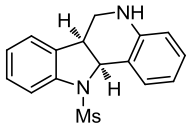
General Procedure for the Synthesis of 3.[4] To a solution of **1** (1.1 mmol) in toluene (5.0 mL) at 0 ^{o}C was added TfOH (107 μL, 1.2 mmol). After the mixture was stirred at 0 ^{o}C for 15 min, a solution of **2** (1.0 mmol) in toluene (5.0 mL) was added. The reaction mixture was warmed to room temperature, stirred for 1.5 h, neutralized by slowly adding solid $NaHCO_3$ (100 mg), and diluted with DCM and H_2O. The two layers were separated and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried (Na_2SO_4), filtrated, and concentrated to give a residue, which was purified by flash chromatography (petroleum ether/DCM/EtOAc, 20:1:1) to afford **3**.



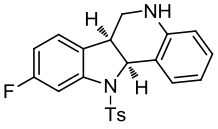
11-Tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3a). White solid; mp 207–208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.07 (d, J = 8.8 Hz, 1H), 3.41-3.49 (m, 2H), 5.45 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 8.4 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 6.99 (t, J = 7.2 Hz, 1H), 7.07-7.23 (m, 5H), 7.51 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 40.7, 41.3, 61.6, 115.1, 119.2, 120.1, 120.6, 123.1, 125.7, 126.9, 128.0, 128.3, 129.5, 131.3, 135.1, 135.4, 142.3, 143.8, 145.7. HRMS (ESI) Calcd for $C_{22}H_{20}N_2O_2S$ + H 377.1318; found 377.1322.



11-(2-Nitrophenylsulfonyl)-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3b). Yellow solid; mp 188–190 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.40 (dd, J = 12.8, 3.2 Hz, 1H), 3.54 (d, J = 8.4 Hz, 1H), 3.63 (d, J = 12.4 Hz, 1H), 5.61 (br s, 1H), 5.74 (d, J = 8.4 Hz, 1H), 6.44 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 7.14-7.18 (m, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.65-7.69 (m, 1H), 7.72-7.74 (m, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 39.8, 40.4, 62.2, 114.8, 117.1, 117.8, 118.9, 124.2, 124.5, 125.8, 127.9, 128.3, 129.6, 129.8, 130.1, 132.0, 135.2, 135.3, 140.4, 147.1, 147.8. HMRS (ESI) Calcd for $C_{21}H_{17}N_3O_4S$ + H 408.1013; found 408.1010.

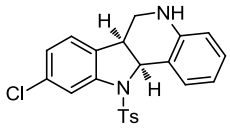


11-(Methylsulfonyl)-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3c). White solid; mp 184–185 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.96 (s, 3H), 3.45 (dd, J = 12.4, 3.2 Hz, 1H), 3.70 (dt, J = 12.4, 2.8 Hz, 1H), 4.12 (d, J = 8.8 Hz, 1H), 5.54 (d, J = 8.8 Hz, 1H), 5.55 (br s, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.59 (t, J = 7.6 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 7.14-7.18 (m, 2H), 7.20-7.23 (m, 1H), 7.39-7.41 (m, 1H), 7.44 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 36.4, 40.2, 40.8, 61.1, 114.6, 117.0, 117.8, 120.2, 124.3, 125.2, 127.6, 127.9, 130.3, 135.3, 142.0, 147.0. HMRS (ESI) Calcd for $C_{16}H_{16}N_2O_2S$ + Na 323.0825; found 323.0833.

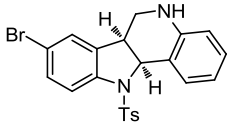


9-Fluoro-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3f). White solid; mp 189–190 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.08 (d, J = 8.4 Hz, 1H), 3.45 (d, J = 3.2 Hz, 2H), 3.55 (br s, 1H), 5.47 (d, J = 8.4 Hz, 1H), 6.41 (d, J =

8.0 Hz, 1H), 6.79-6.85 (m, 2H), 6.99-7.04 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.35 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 40.4, 41.5, 62.4, 108.0 (d, *J* = 27.0 Hz), 112.5 (d, *J* = 22.0 Hz), 115.2, 119.5, 120.4, 123.8 (d, *J* = 9.0 Hz), 127.0, 128.5, 129.7, 130.4 (d, *J* = 3.0 Hz), 131.3, 135.5, 143.8 (d, *J* = 12.0 Hz), 144.1, 145.7, 162.6 (d, *J* = 243.0 Hz). HMRS (ESI) Calcd for $C_{22}H_{19}FN_2O_2S$ + H 395.1224; found 395.1232.

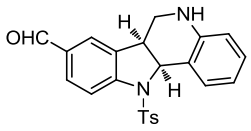


9-Chloro-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3g). White solid; mp 206–208 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.06 (d, *J* = 8.0 Hz, 1H), 3.44 (d, *J* = 3.2 Hz, 2H), 3.54 (br s, 1H), 5.46 (d, *J* = 8.4 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 7.6 Hz, 1H), 6.98-7.03 (m, 2H), 7.09 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 40.6, 41.3, 62.2, 115.2, 119.5, 120.3, 120.3, 124.0, 125.8, 127.0, 128.6, 129.8, 131.3, 133.6, 133.7, 135.5, 143.6, 144.1, 145.6. HMRS (ESI) Calcd for $C_{22}H_{19}ClN_2O_2S$ + H 411.0929; found 411.0924.

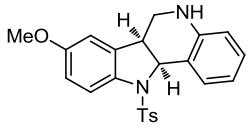


8-Bromo-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3h). White solid; mp 132–133 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.33 (s, 3H), 3.09 (d, *J* = 8.4 Hz, 1H), 3.25 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.52-3.56 (m, 1H), 5.52 (d, *J* = 2.0 Hz, 1H), 5.61 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 7.29-7.33 (m, 3H), 7.37-7.39 (m, 1H), 7.43 (s, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.0, 39.9, 40.4, 61.9, 114.8, 117.3, 117.8, 119.5, 120.4, 126.9, 127.3, 128.1, 129.9, 130.3, 130.6, 134.8, 138.6, 141.1, 144.2, 146.8. HMRS (ESI) Calcd for $C_{22}H_{19}BrN_2O_2S$ + Na 477.0243;

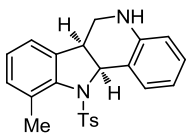
found 477.0243.



11-Tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline-8-carbaldehyde (3i). Yellow solid; mp 184–185 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 3.22 (d, J = 8.8 Hz, 1H), 3.49-3.58 (m, 2H), 3.53 (br s, 1H), 5.56 (d, J = 8.8 Hz, 1H), 6.41 (d, J = 7.6 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.64 (s, 1H), 7.70-7.75 (m, 2H), 7.82 (d, J = 7.6 Hz, 1H), 9.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 40.9, 41.3, 62.4, 115.3, 119.4, 119.5, 120.1, 123.5, 126.8, 128.7, 129.9, 131.3, 132.2, 134.0, 135.7, 136.2, 144.4, 145.7, 148.1, 191.0. HMRS (ESI) Calcd for $C_{23}H_{20}N_2O_3S$ + H 405.1267; found 405.1258.

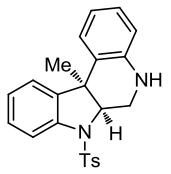


8-Methoxy-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3j). White solid; mp 220–222 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.33 (s, 3H), 2.94 (d, J = 8.0 Hz, 1H), 3.24 (dd, J = 12.4, 3.2 Hz, 1H), 3.49 (dd, J = 12.8, 2.8 Hz, 1H), 3.70 (s, 3H), 5.52 (d, J = 8.4 Hz, 1H), 6.40 (d, J = 7.6 Hz, 1H), 6.63 (t, J = 7.2 Hz, 1H), 6.75-6.79 (m, 2H), 6.91 (t, J = 8.0 Hz, 1H), 7.27-7.30 (m, 3H), 7.50-7.54 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.0, 39.7, 40.2, 55.4, 61.8, 109.8, 112.9, 114.6, 117.1, 119.6, 119.7, 126.9, 127.9, 129.8, 130.3, 134.6, 134.9, 137.6, 143.9, 146.8, 157.7. HMRS (ESI) Calcd for $C_{23}H_{22}N_2O_3S$ + H 407.1424; found 407.1416.

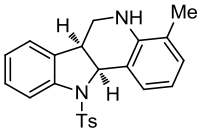


10-Methyl-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3k). White solid; mp 149–151 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 2.47 (s, 3H),

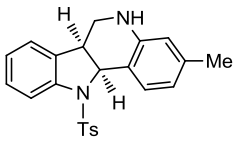
2.73 (d, *J* = 7.6 Hz, 1H), 3.32-3.40 (m, 2H), 3.45 (br s, 1H), 5.40 (d, *J* = 7.6 Hz, 1H), 6.31 (d, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.6 Hz, 1H), 6.89-6.97 (m, 2H), 7.05-7.12 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 21.6, 39.7, 41.4, 62.9, 114.9, 118.8, 120.1, 120.4, 126.6, 127.6, 128.1, 129.5, 130.6, 131.0, 133.4, 135.1, 137.8, 141.6, 143.9, 145.3. HMRS (ESI) Calcd for $C_{23}H_{22}N_2O_2S$ + H 391.1475; found 391.1480.



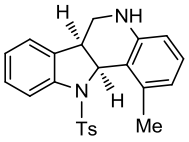
11b-Methyl-7-tosyl-6,6a,7,11b-tetrahydro-5*H*-indolo[2,3-*c*]quinoline (3l). White solid; mp 167–168 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 2.39 (s, 3H), 3.33 (dd, *J* = 11.2, 8.0 Hz, 1H), 3.53 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.84 (br s, 1H), 4.22 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.18-7.22 (m, 2H), 7.25-7.27 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 30.5, 45.4, 45.8, 69.1, 115.4, 115.5, 119.0, 123.9, 124.2, 126.3, 126.9, 127.3, 127.9, 128.0, 129.7, 135.5, 139.1, 139.9, 144.1, 144.9. HMRS (ESI) Calcd for $C_{23}H_{22}N_2O_2S$ + H 391.1475; found 391.1468.



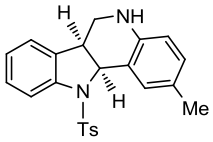
4-Methyl-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3m). White solid; mp 238–240 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.37 (s, 3H), 3.06 (d, *J* = 8.4 Hz, 1H), 3.46 (dd, *J* = 12.4, 3.6 Hz, 1H), 3.56 (dd, *J* = 12.0, 2.8 Hz, 1H), 5.48 (d, *J* = 8.8 Hz, 1H), 6.75 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 7.08-7.23 (m, 5H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9, 21.5, 40.7, 41.3, 62.0, 118.4, 120.0, 120.2, 121.7, 123.2, 125.6, 127.0, 128.0, 129.2, 129.4, 129.5, 135.2, 135.7, 142.5, 143.7, 144.0. HMRS (ESI) Calcd for $C_{23}H_{22}N_2O_2S$ + H 391.1475; found 391.1468.



3-Methyl-11-tosyl-6,6a,11,11a-tetrahydro-*5H*-indolo[3,2-*c*]quinoline (3n). White solid; mp 278–280 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.37 (s, 3H), 3.06 (t, J = 4.4 Hz, 1H), 3.45 (t, J = 3.6 Hz, 2H), 5.43 (d, J = 8.4 Hz, 1H), 6.21 (s, 1H), 6.64 (dd, J = 7.6, 0.8 Hz, 1H), 7.05-7.22 (m, 5H), 7.51 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.5, 40.8, 41.4, 61.6, 115.5, 117.9, 120.1, 120.5, 123.1, 125.6, 127.0, 128.0, 129.5, 131.2, 135.1, 135.7, 138.3, 142.3, 143.7, 145.5 {Note: Compound **3n** was contaminated with a small amount of **3o** due to difficult separation of the two regioisomers}. HRMS (ESI) Calcd for $C_{23}H_{22}N_2O_2S$ + H 391.1475; found 391.1484.

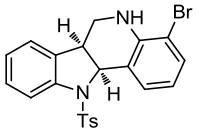


1-Methyl-11-tosyl-6,6a,11,11a-tetrahydro-*5H*-indolo[3,2-*c*]quinoline (3o). White solid; mp 205–206 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.72 (s, 3H), 2.94 (t, J = 3.6 Hz, 1H), 3.18 (dd, J = 12.0, 4.0 Hz, 1H), 3.30 (dd, J = 12.0, 2.8 Hz, 1H), 5.66 (d, J = 7.6 Hz, 1H), 6.23 (d, J = 8.0 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 7.03-7.09 (m, 3H), 7.15 (t, J = 7.2 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 29.7, 41.3, 41.4, 63.2, 113.5, 117.5, 121.6, 122.1, 123.3, 126.3, 127.7, 127.8, 128.4, 129.2, 135.2, 137.2, 141.7, 143.3, 143.8, 146.5. HRMS (ESI) Calcd for $C_{23}H_{22}N_2O_2S$ + H 391.1475; found 391.1477.

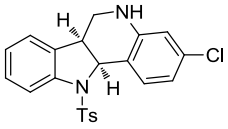


2-Methyl-11-tosyl-6,6a,11,11a-tetrahydro-*5H*-indolo[3,2-*c*]quinoline (3p). White

solid; mp 180–182 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.17 (s, 3H), 2.32 (s, 3H), 3.03 (d, J = 8.4 Hz, 1H), 3.24 (dd, J = 12.4, 3.2 Hz, 1H), 3.47 (dd, J = 12.4, 2.8 Hz, 1H), 5.29 (br s, 1H), 5.53 (d, J = 8.8 Hz, 1H), 6.32 (d, J = 8.0 Hz, 1H), 6.74 (dd, J = 8.4, 1.6 Hz, 1H), 7.10 (td, J = 6.8, 0.4 Hz, 1H), 7.18-7.21 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.34 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.3, 21.0, 40.0, 40.3, 61.6, 114.8, 118.7, 119.6, 124.1, 125.5, 125.5, 126.8, 127.6, 128.7, 129.8, 130.4, 135.0, 135.9, 141.7, 144.0, 144.6. HRMS (ESI) Calcd for $C_{23}H_{22}N_2O_2S$ + H 391.1475; found 391.1471.

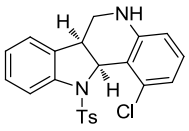


4-Bromo-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3q). White solid; mp 210–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.05 (d, J = 8.4 Hz, 1H), 3.47 (dd, J = 12.4, 3.2 Hz, 1H), 3.56-3.61 (m, 1H), 4.24 (br s, 1H), 5.44 (d, J = 8.4 Hz, 1H), 6.67 (t, J = 8.0 Hz, 1H), 7.07-7.09 (m, 1H), 7.12-7.18 (m, 3H), 7.21-7.25 (m, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 40.6, 41.0, 61.6, 109.2, 119.3, 120.1, 122.1, 123.3, 125.9, 127.0, 128.2, 129.6, 130.7, 131.6, 134.7, 135.5, 142.2, 142.9, 144.0. HRMS (ESI) Calcd for $C_{22}H_{19}BrN_2O_2S$ + H 455.0423; found 455.0414.

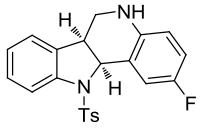


3-Chloro-11-tosyl-6,6a,11,11a-tetrahydro-*5H*-indolo[3,2-*c*]quinoline (3r). White solid; mp 239–240 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.32 (s, 3H), 3.04 (d, J = 8.4 Hz, 1H), 3.29 (dd, J = 12.4, 3.2 Hz, 1H), 3.53 (dd, J = 12.8, 2.0 Hz, 1H), 5.56 (d, J = 8.4 Hz, 1H), 5.84 (br s, 1H), 6.44 (d, J = 2.0 Hz, 1H), 6.65 (dd, J = 8.4, 2.4 Hz, 1H), 7.11 (td, J = 7.2, 0.8 Hz, 1H), 7.19-7.23 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.38 (dd, J = 8.0, 0.8 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.0, 39.5, 40.1, 60.9, 113.4, 116.6, 118.5, 118.6, 124.1, 125.7,

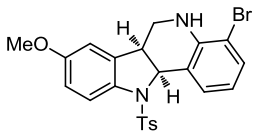
126.8, 127.9, 129.8, 132.1, 132.4, 134.9, 135.3, 141.4, 144.1, 148.1. HRMS (ESI) Calcd for $C_{22}H_{19}ClN_2O_2S$ + H 411.0929; found 411.0925.



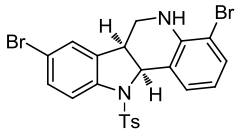
1-Chloro-11-tosyl-6,6a,11,11a-tetrahydro-*5H*-indolo[3,2-*c*]quinoline (3s). White solid; mp 178–180 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.29 (s, 3H), 3.06 (t, J = 3.6 Hz, 1H), 3.15 (m, 2H), 5.73 (d, J = 7.2 Hz, 1H), 5.93 (br s, 1H), 6.35 (d, J = 8.0 Hz, 1H), 6.60 (d, J = 7.2 Hz, 1H), 6.90 (t, J = 8.0 Hz, 1H), 7.09-7.22 (m, 5H), 7.34-7.39 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.9, 39.7, 40.6, 62.7, 113.5, 115.2, 117.6, 120.4, 124.3, 126.1, 127.5 (possibly corresponding to 2 carbon signals), 129.1, 129.2, 135.0, 135.9, 137.0, 142.6, 143.7, 149.5. HRMS (ESI) Calcd for $C_{22}H_{19}ClN_2O_2S$ + H 411.0929; found 411.0938.



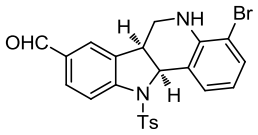
2-Fluoro-11-tosyl-6,6a,11,11a-tetrahydro-*5H*-indolo[3,2-*c*]quinoline (3t). White solid; mp 211–213 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.32 (s, 3H), 3.09 (d, J = 8.4 Hz, 1H), 3.27 (dd, J = 12.4, 3.2 Hz, 1H), 3.50 (d, J = 12.4 Hz, 1H), 5.50 (br s, 1H), 5.58 (d, J = 8.8 Hz, 1H), 6.43 (q, J = 4.8 Hz, 1H), 6.81 (td, J = 8.4, 3.2 Hz, 1H), 7.10 (td, J = 6.8, 0.4 Hz, 1H), 7.19-7.22 (m, 2H), 7.29 (d, J = 7.6 Hz, 3H), 7.40 (dd, J = 8.4, 0.8 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.0, 40.1, 40.1, 61.3, 115.2 (d, J = 23.0 Hz), 115.6 (d, J = 22.0 Hz), 115.9 (d, J = 7.0 Hz), 118.4, 121.0 (d, J = 7.0 Hz), 124.2, 125.6, 126.9, 127.8, 129.9, 134.8, 135.4, 141.5, 143.6, 144.2, 154.6 (d, J = 231.0 Hz). HRMS (ESI) Calcd for $C_{22}H_{19}FN_2O_2S$ + H 395.1224; found 395.1230.



4-Bromo-8-methoxy-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3u). White solid; mp 220–221 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.33 (s, 3H), 2.98 (d, J = 8.0 Hz, 1H), 3.29 (dd, J = 12.8, 3.2 Hz, 1H), 3.62-3.66 (m, 1H), 3.70 (s, 3H), 5.22 (d, J = 2.8 Hz, 1H), 5.60 (d, J = 8.4 Hz, 1H), 6.62 (t, J = 8.0 Hz, 1H), 6.77-6.79 (m, 2H), 7.25-7.31 (m, 4H), 7.53-7.58 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.9, 39.6, 40.2, 55.3, 61.7, 108.1, 109.9, 113.0, 117.9, 119.6, 122.1, 126.9, 129.8, 130.0, 131.4, 134.3, 134.7, 137.0, 143.5, 144.0, 157.7. HRMS (ESI) Calcd for $C_{23}H_{21}BrN_2O_3S$ + H 485.0529; found 485.0519.



4,8-Dibromo-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline (3v). White solid; mp 253–254 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.33 (s, 3H), 3.15 (d, J = 8.0 Hz, 1H), 3.32-3.35 (m, 1H), 3.68 (d, J = 13.2 Hz, 1H), 5.28 (d, J = 2.8 Hz, 1H), 5.70 (d, J = 8.4 Hz, 1H), 6.63 (t, J = 8.0 Hz, 1H), 7.27-7.33 (m, 4H), 7.39-7.41 (m, 2H), 7.58-7.62 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.9, 39.6, 40.2, 61.8, 108.2, 117.9, 118.1, 120.3, 121.9, 126.9, 127.3, 129.9, 130.8 (possibly corresponding to 2 carbon signals), 131.5, 134.6, 137.9, 140.9, 143.5, 144.3. HMRS (ESI) Calcd for $C_{22}H_{18}Br_2N_2O_2S$ + H 554.9348; found 554.9340.



4-Bromo-11-tosyl-6,6a,11,11a-tetrahydro-5*H*-indolo[3,2-*c*]quinoline-8-carbalde hyde (3w). Yellow solid; mp 250–252 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.32 (s, 3H), 3.29 (d, J = 8.8 Hz, 1H), 3.38 (dd, J = 13.2, 3.2 Hz, 1H), 3.78 (d, J = 12.8 Hz, 1H), 5.34 (d, J = 2.4 Hz, 1H), 5.83 (d, J = 8.8 Hz, 1H), 6.64 (t, J = 8.0 Hz, 1H), 7.27-7.33 (m, 3H), 7.57 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4

Hz, 2H), 7.72 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 9.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 21.0, 39.5, 40.0, 62.2, 108.3, 118.1, 118.2, 121.9, 124.4, 126.8, 129.9, 130.0 (possibly corresponding to 2 carbon signals), 131.7, 133.7, 134.9, 136.2, 143.7, 144.5, 146.8, 191.7. HMRS (ESI) Calcd for $C_{23}H_{19}BrN_2O_3S$ + H 483.0373; found 483.0369.

Part 2. Copies of NMR Spectra for New Compounds

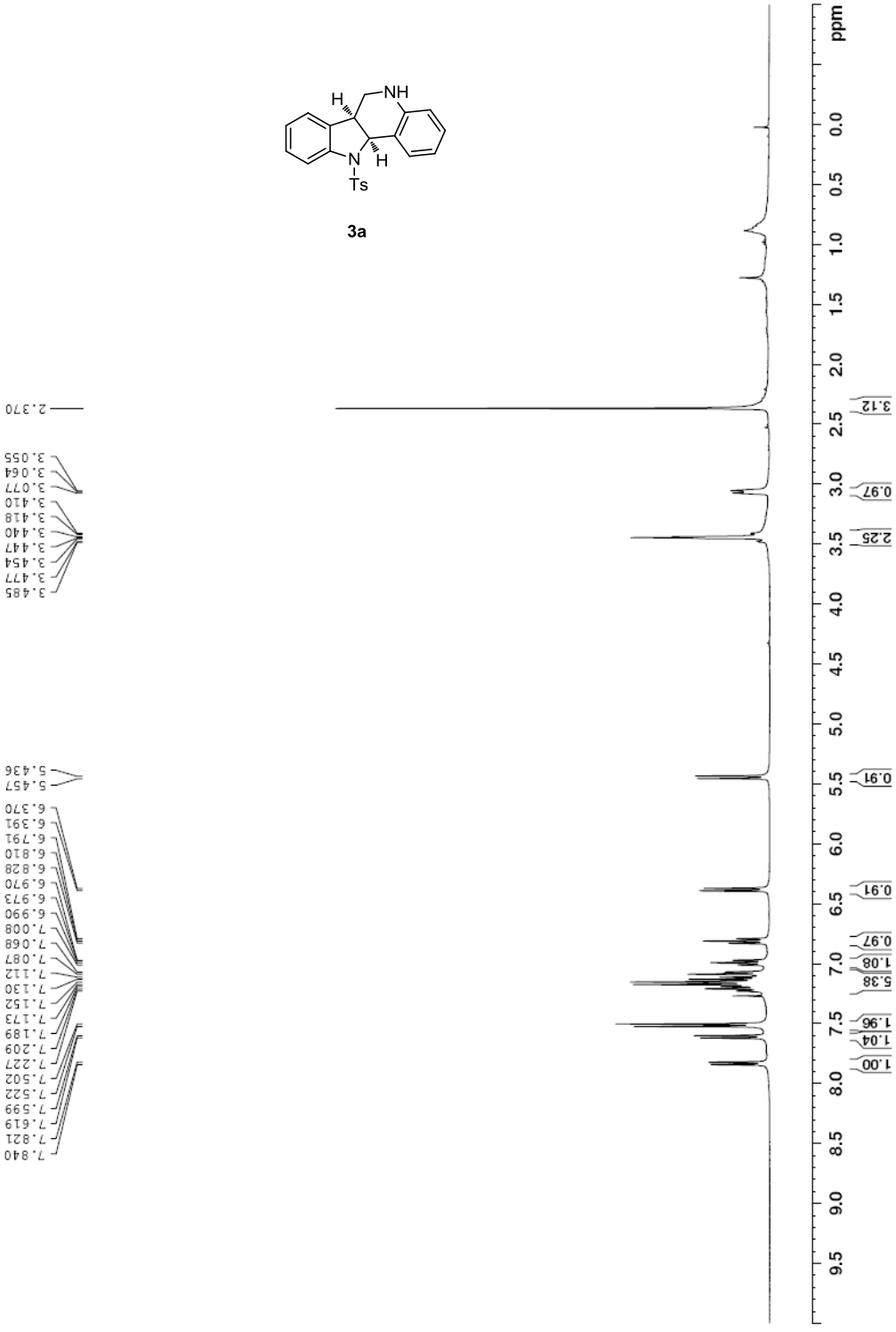


Fig. S1. ^{1}H NMR of 3a (400 MHz, $CDCl_3$)

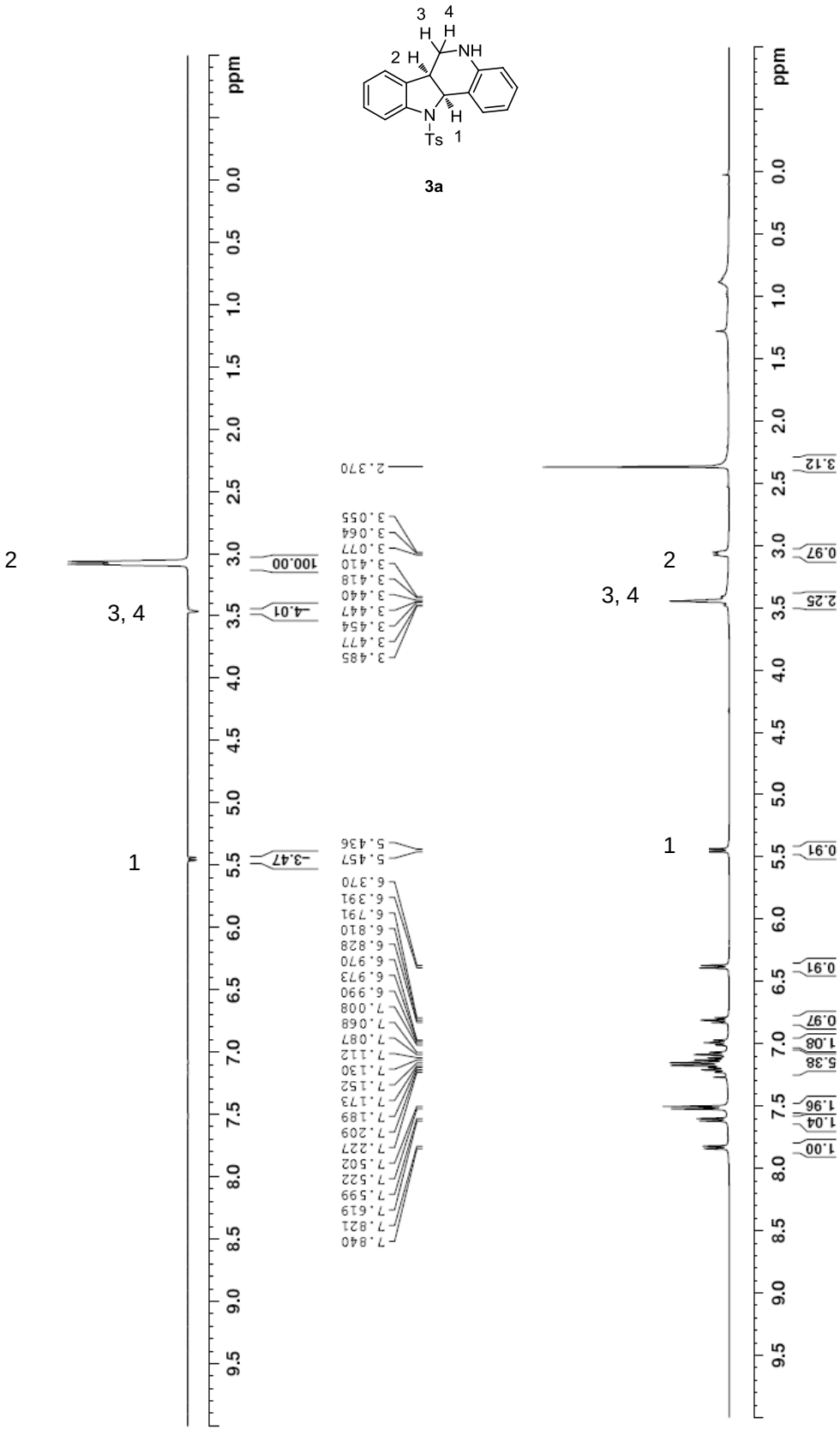


Fig. S2. 1D NOE Correlation of 3a (400 MHz, $CDCl_3$)

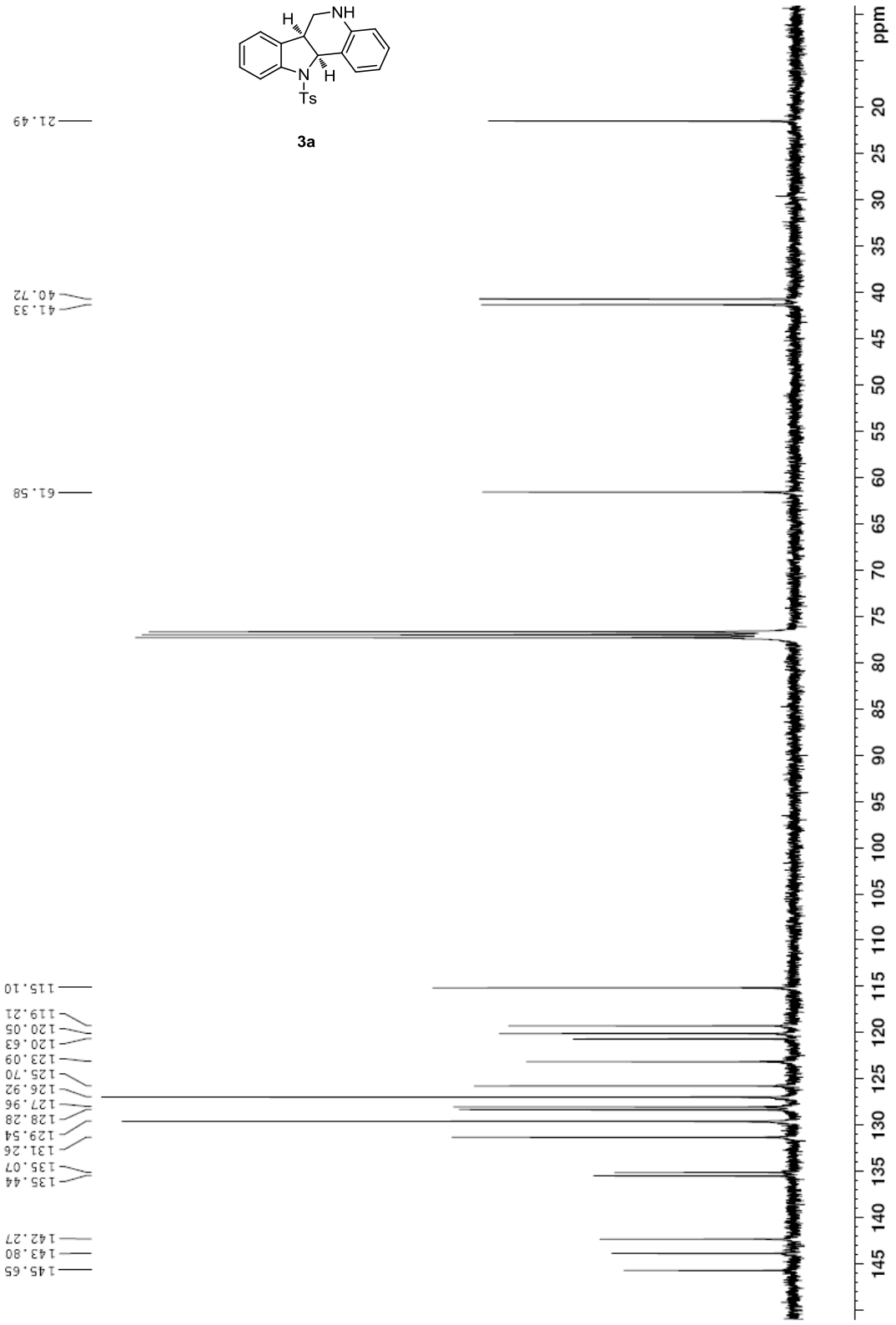


Fig. S3. ^{13}C NMR of 3a (100 MHz, $CDCl_3$)

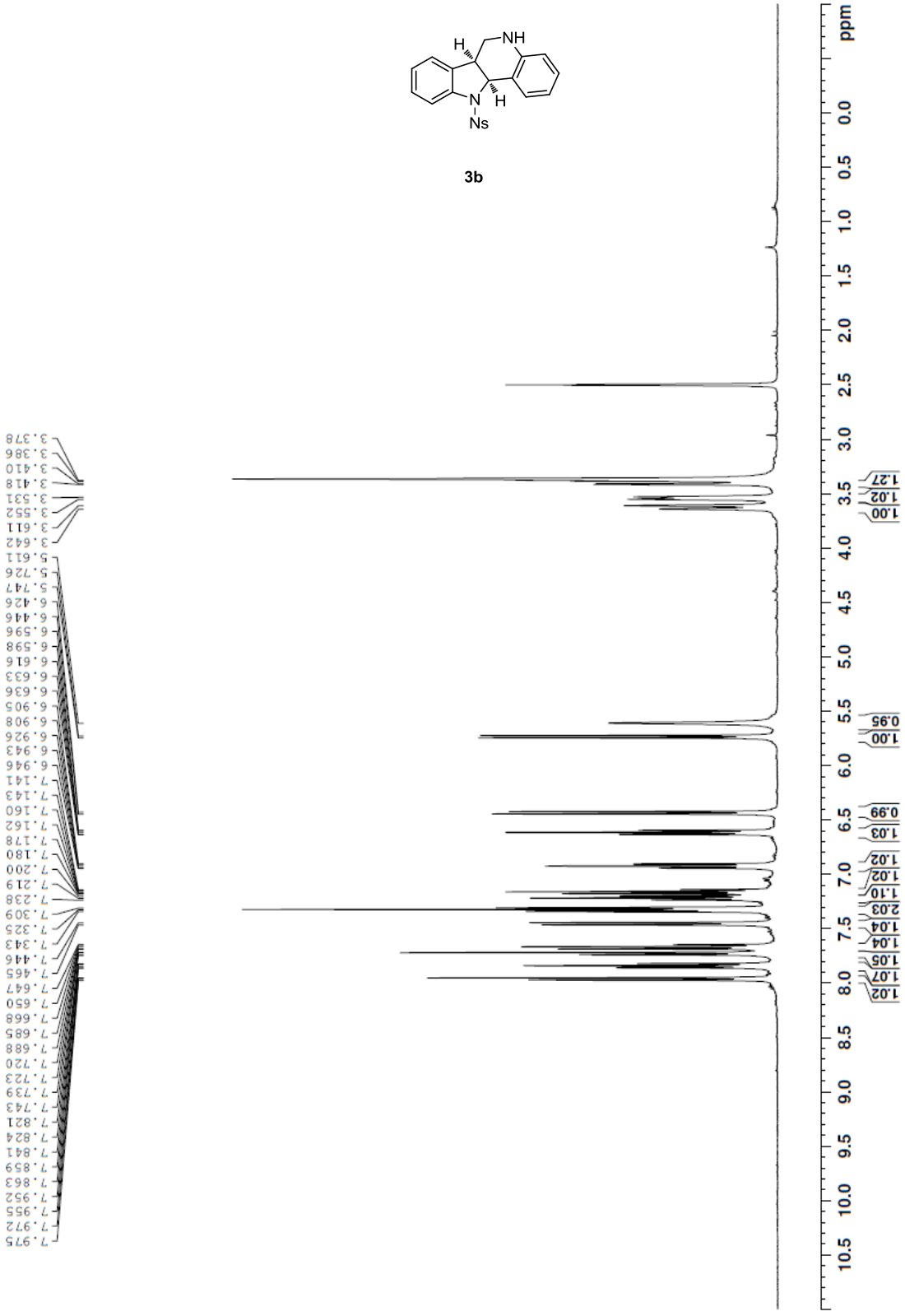


Fig. S4. ^{1}H NMR of 3b (400 MHz, DMSO-d_6)

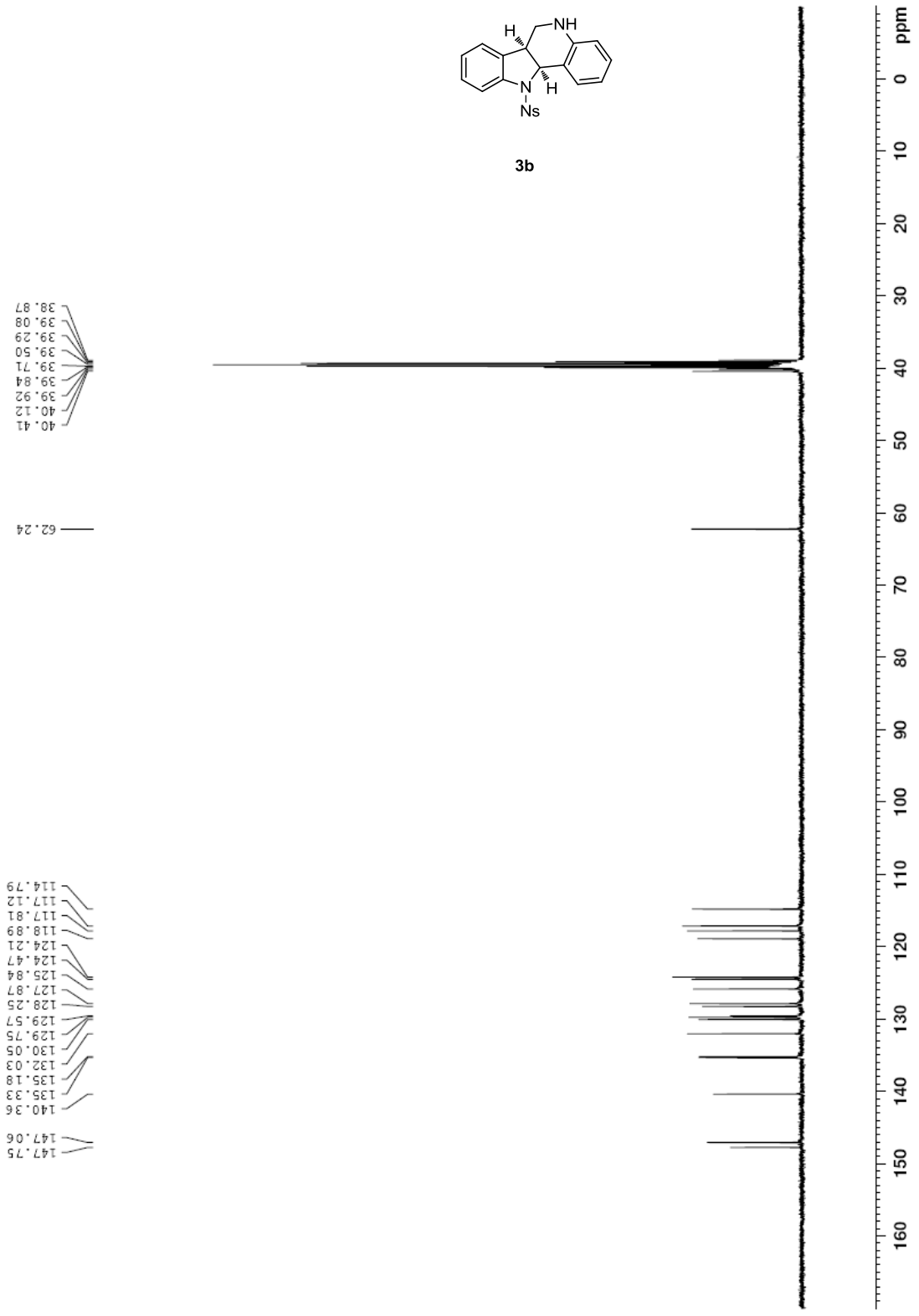


Fig. S5. ^{13}C NMR of 3b (100 MHz, DMSO-d_6)

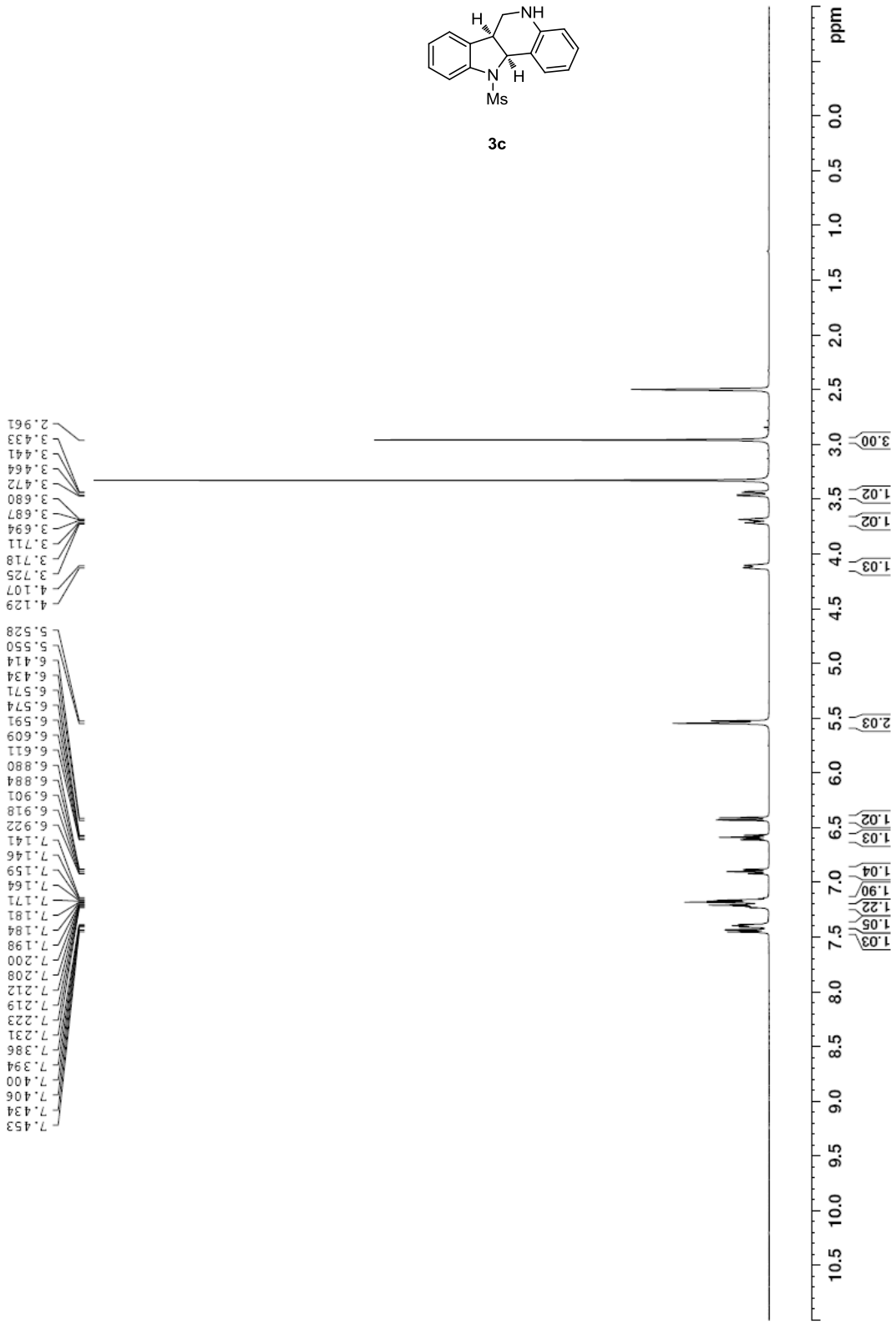


Fig. S6. ^{1}H NMR of 3c (400 MHz, DMSO-d_6)

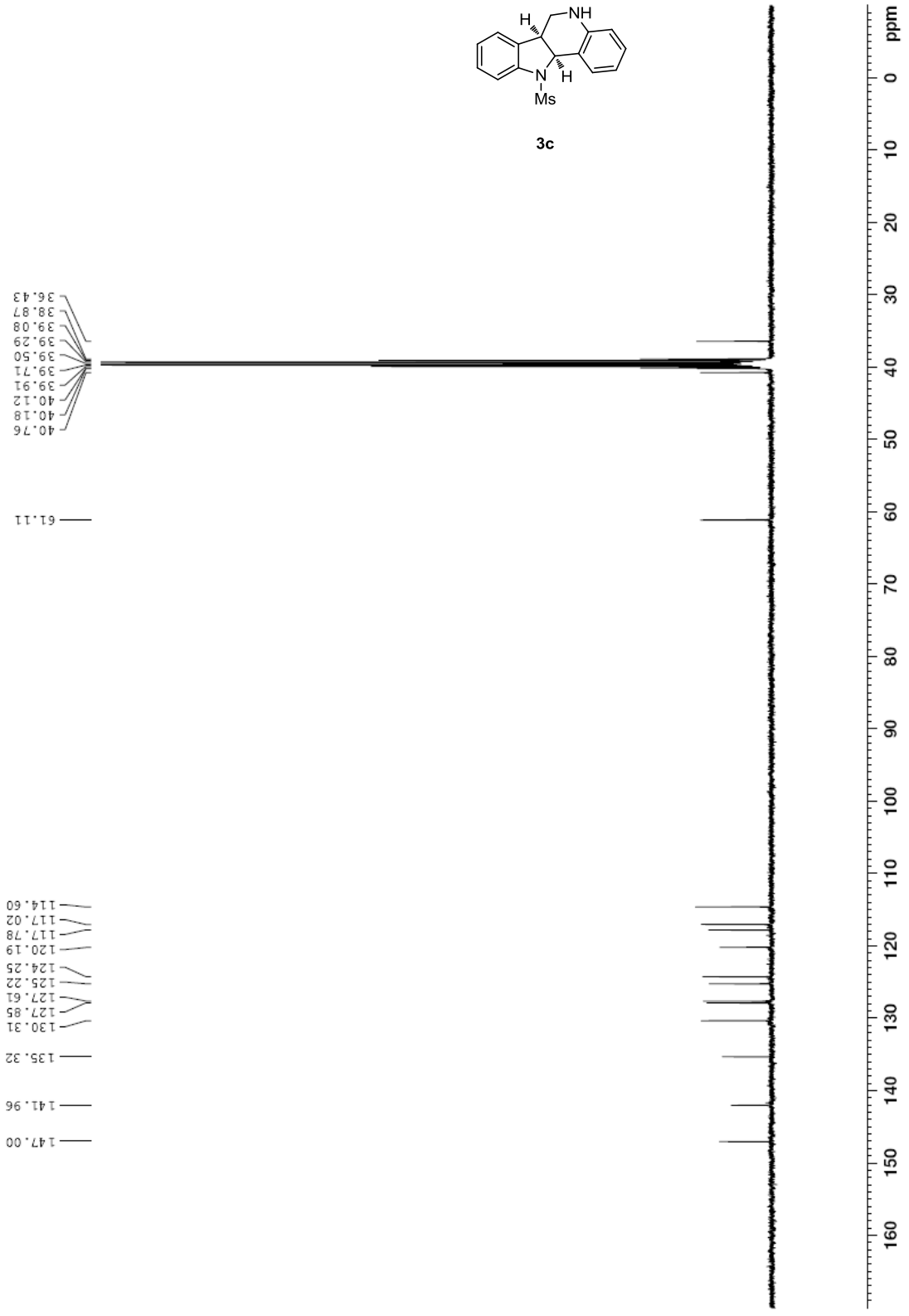


Fig. S7. ^{13}C NMR of 3c (100 MHz, DMSO-d_6)

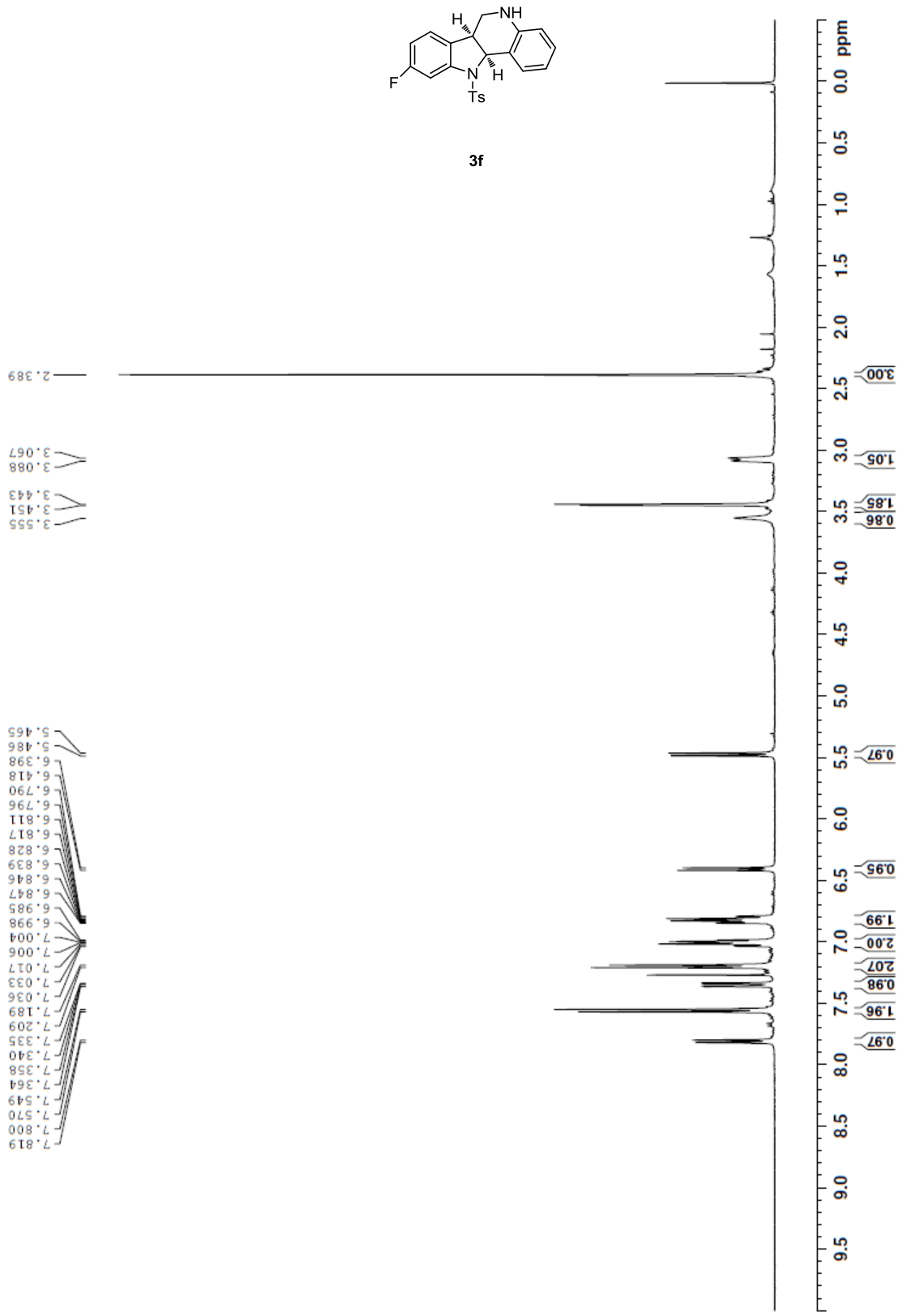


Fig. S8. ^{1}H NMR of 3f (400 MHz, $CDCl_3$)

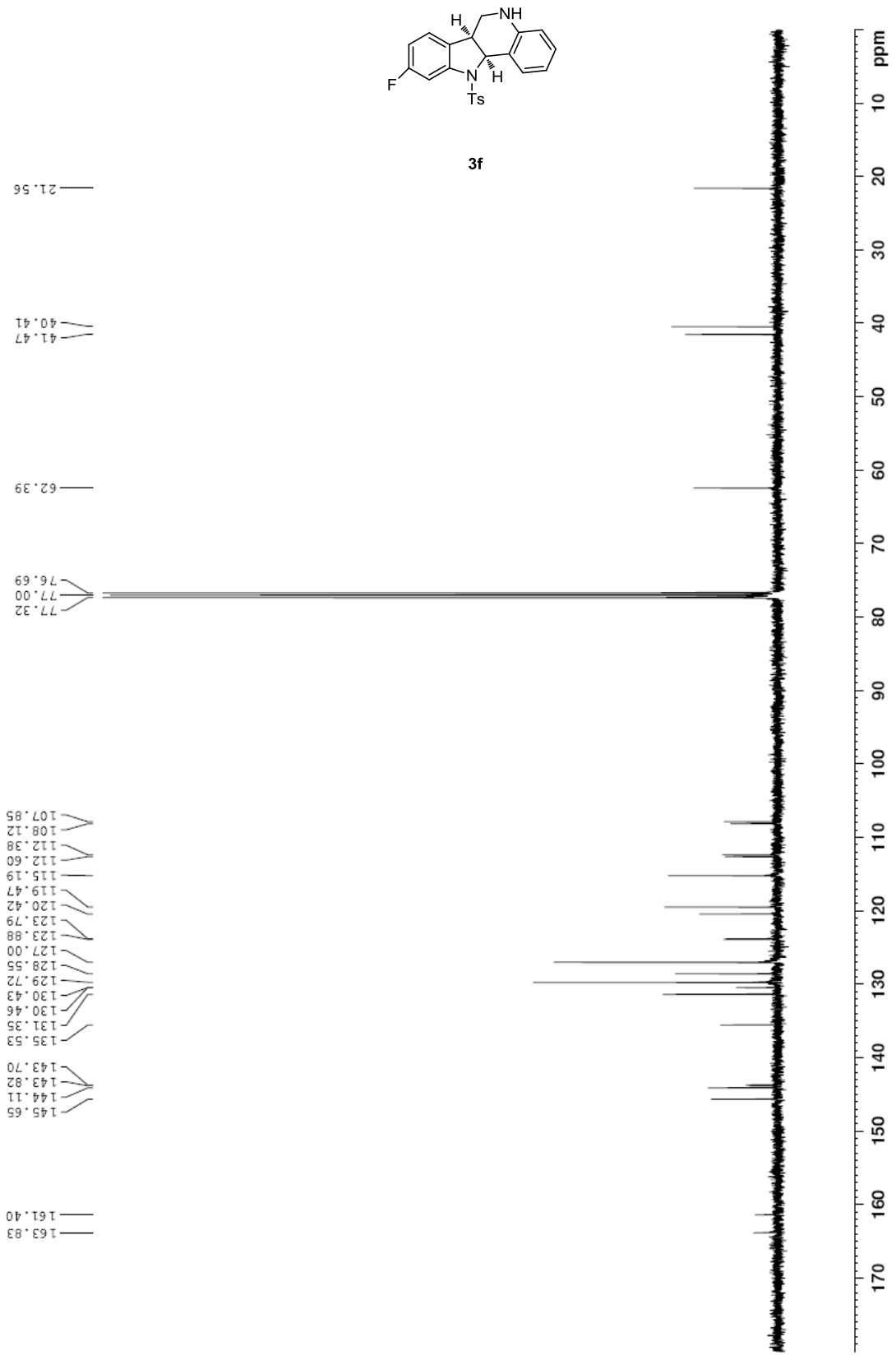


Fig. S9. ^{13}C NMR of 3f (100 MHz, $CDCl_3$)

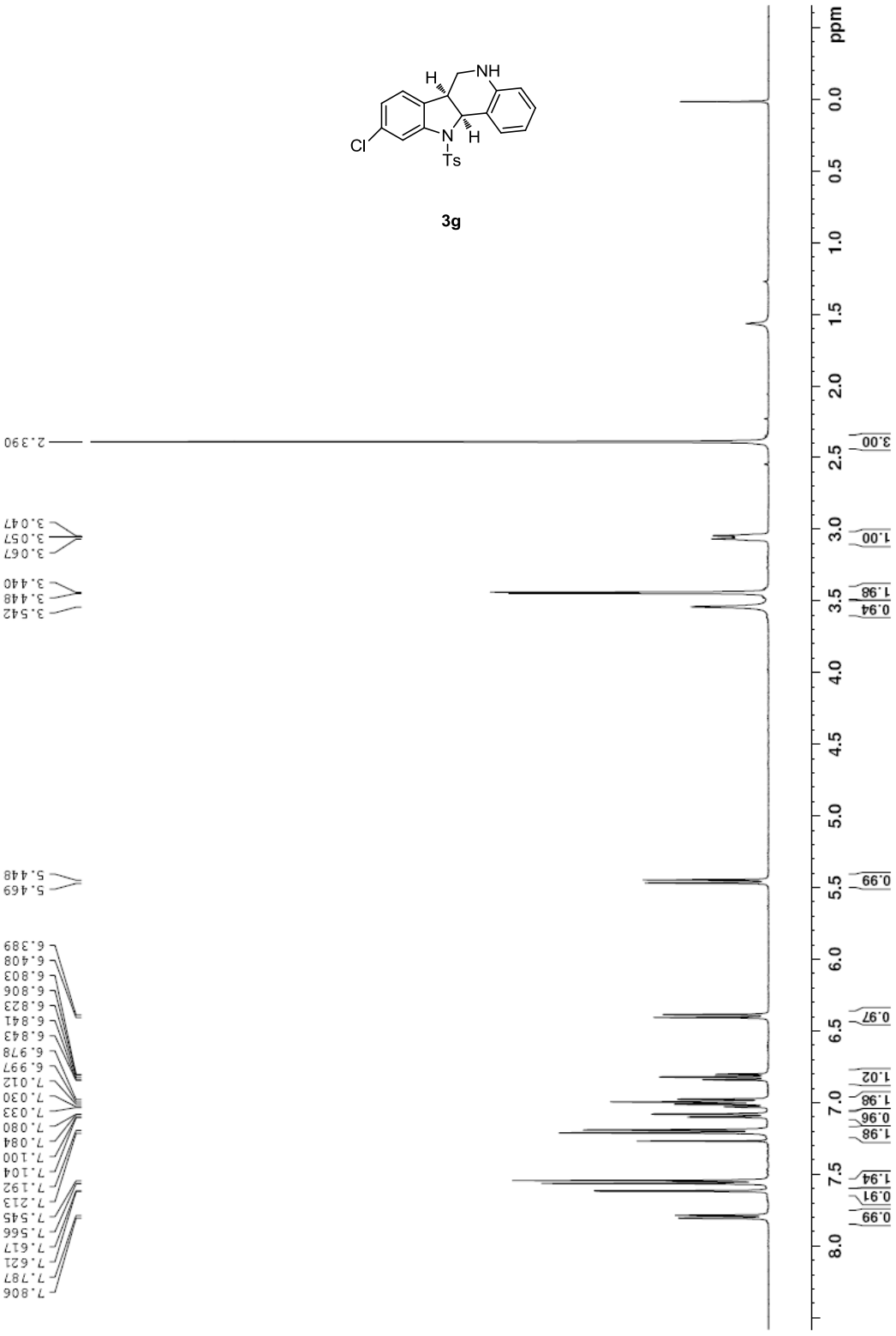


Fig. S10. ^{1}H NMR of 3g (400 MHz, $CDCl_3$)

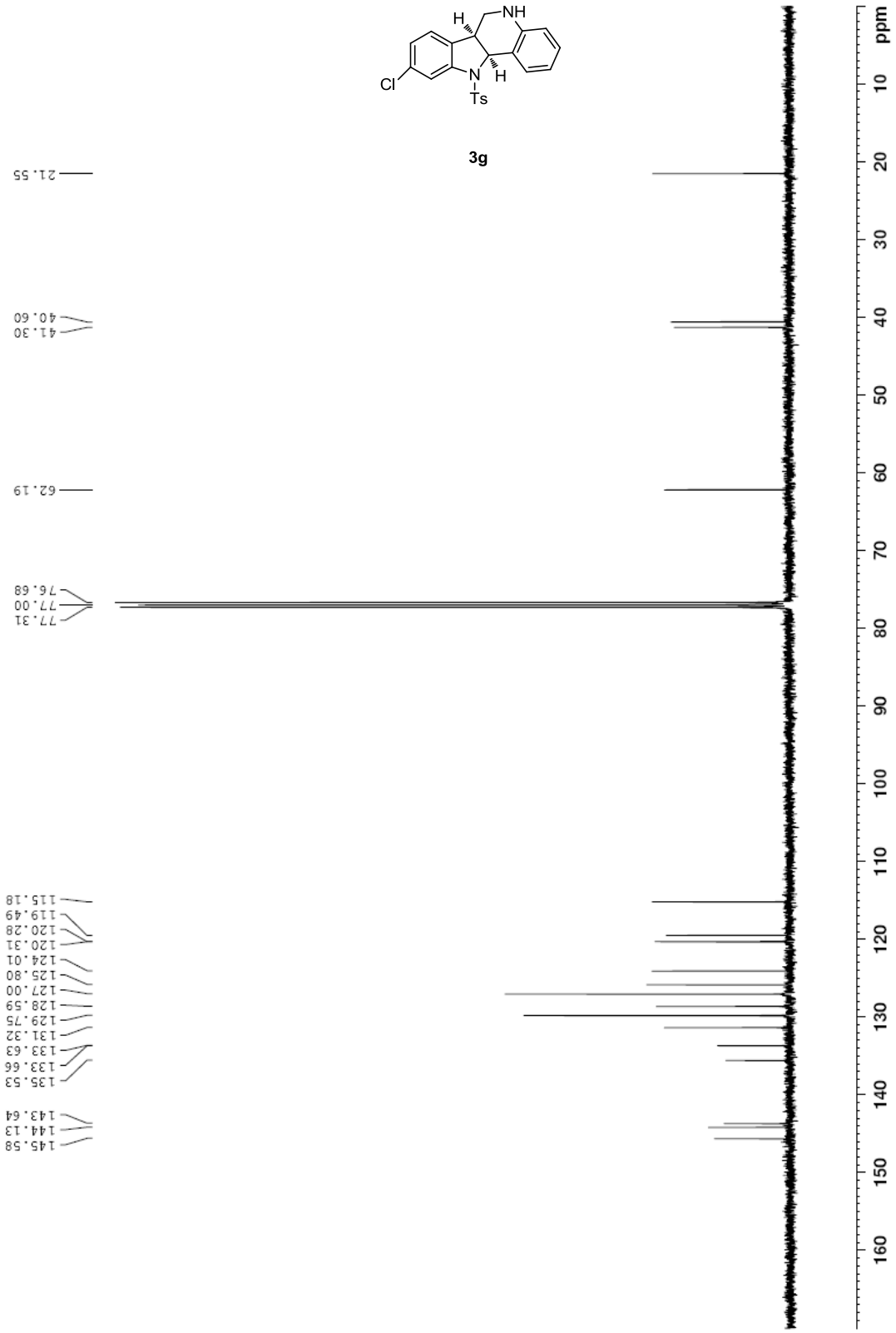


Fig. S11. ^{13}C NMR of 3g (100 MHz, $CDCl_3$)

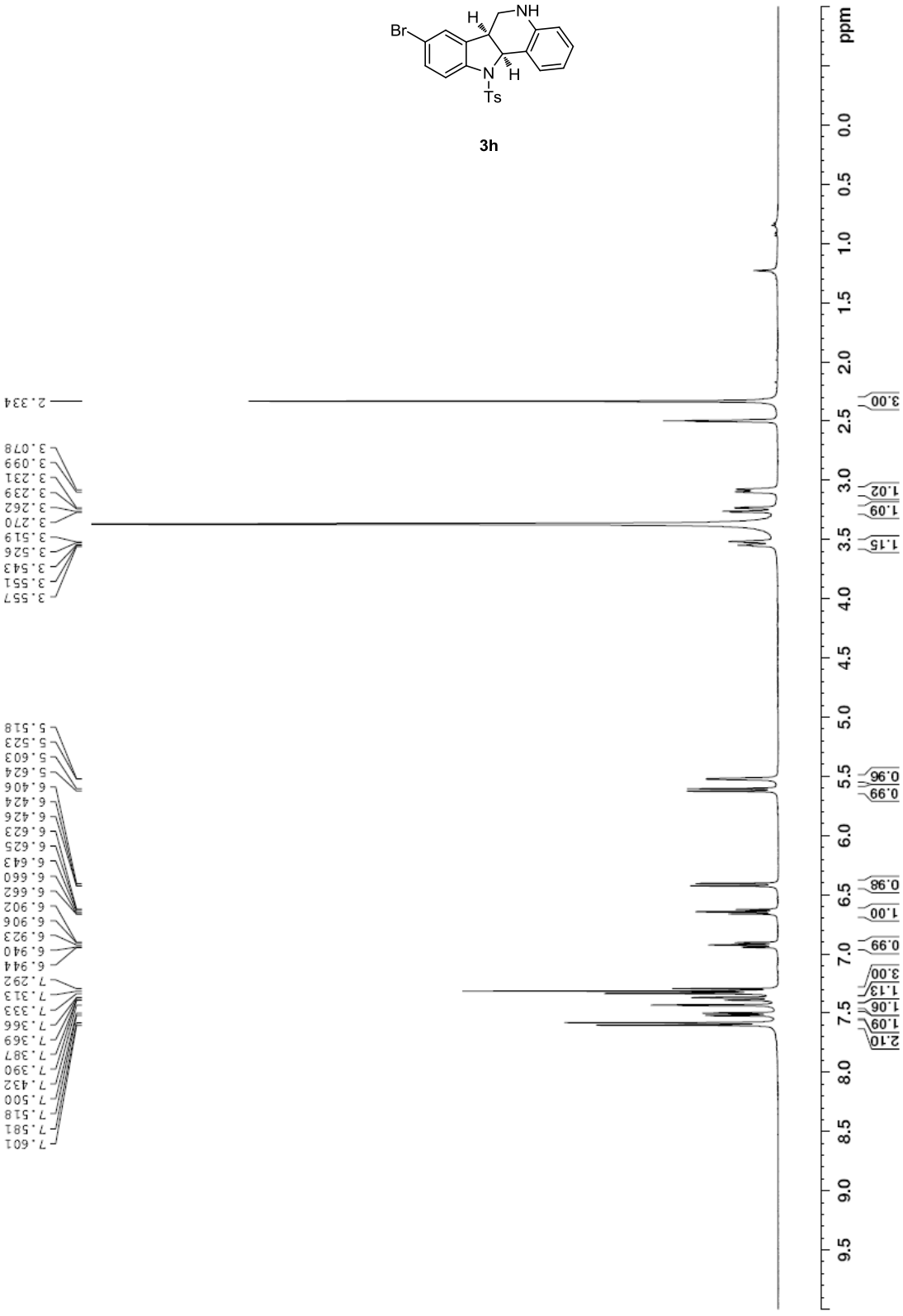


Fig. S12. ^{1}H NMR of 3h (400 MHz, DMSO-d_6)

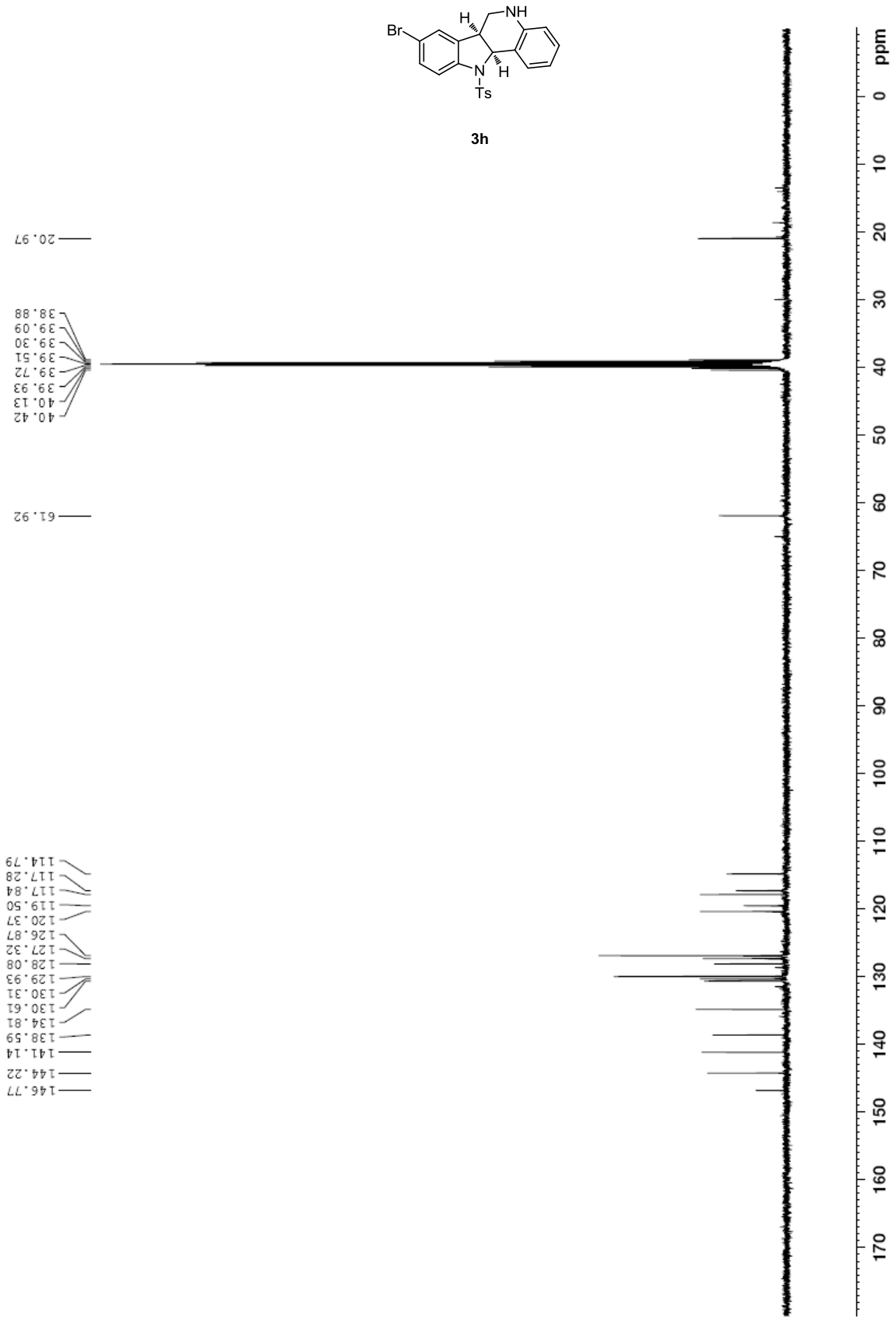


Fig. S13. ^{13}C NMR of 3h (100 MHz, DMSO-d_6)

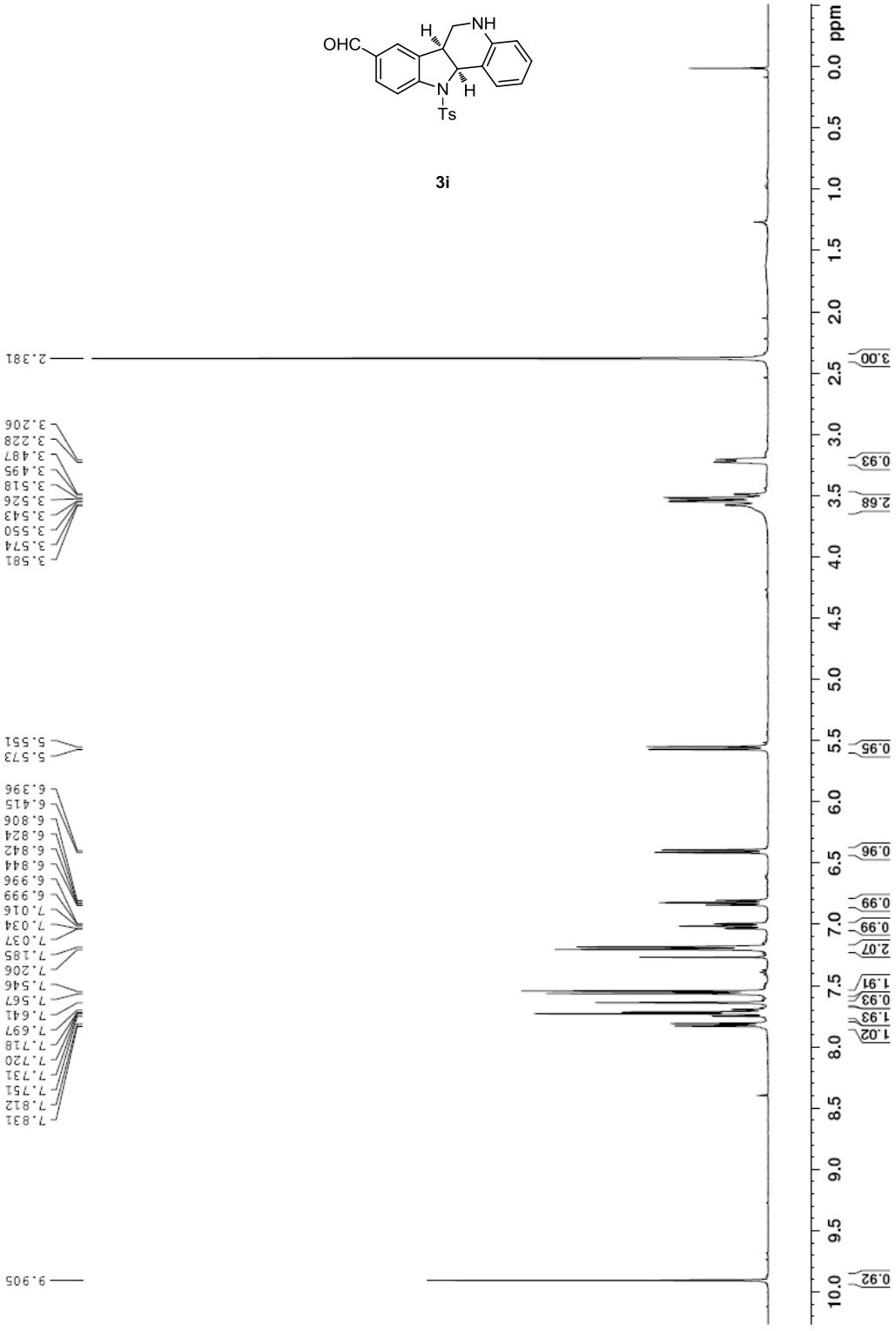


Fig. S14. ^{1}H NMR of 3i (400 MHz, $CDCl_3$)

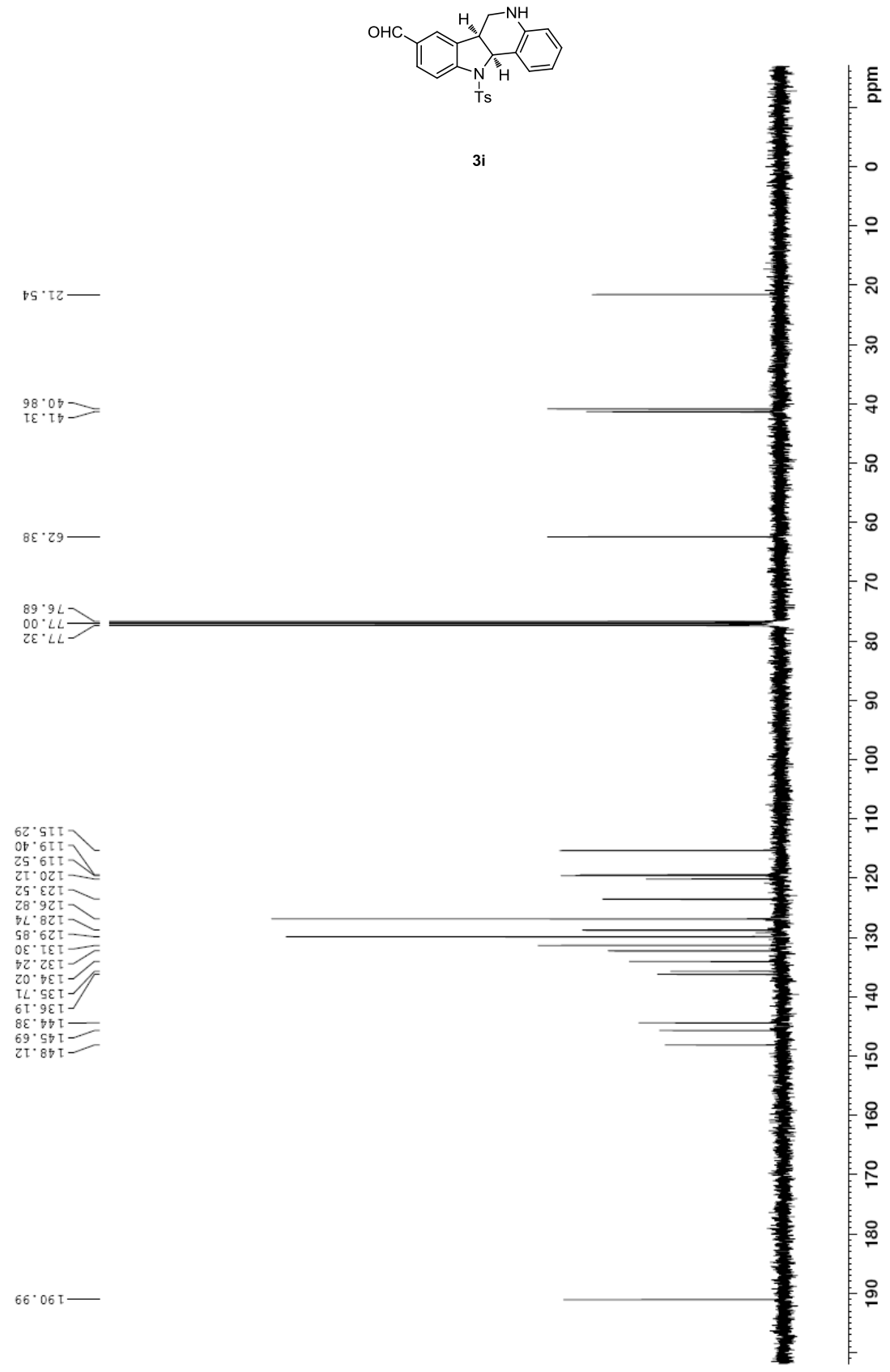


Fig. S15. ^{13}C NMR of 3i (100 MHz, $CDCl_3$)

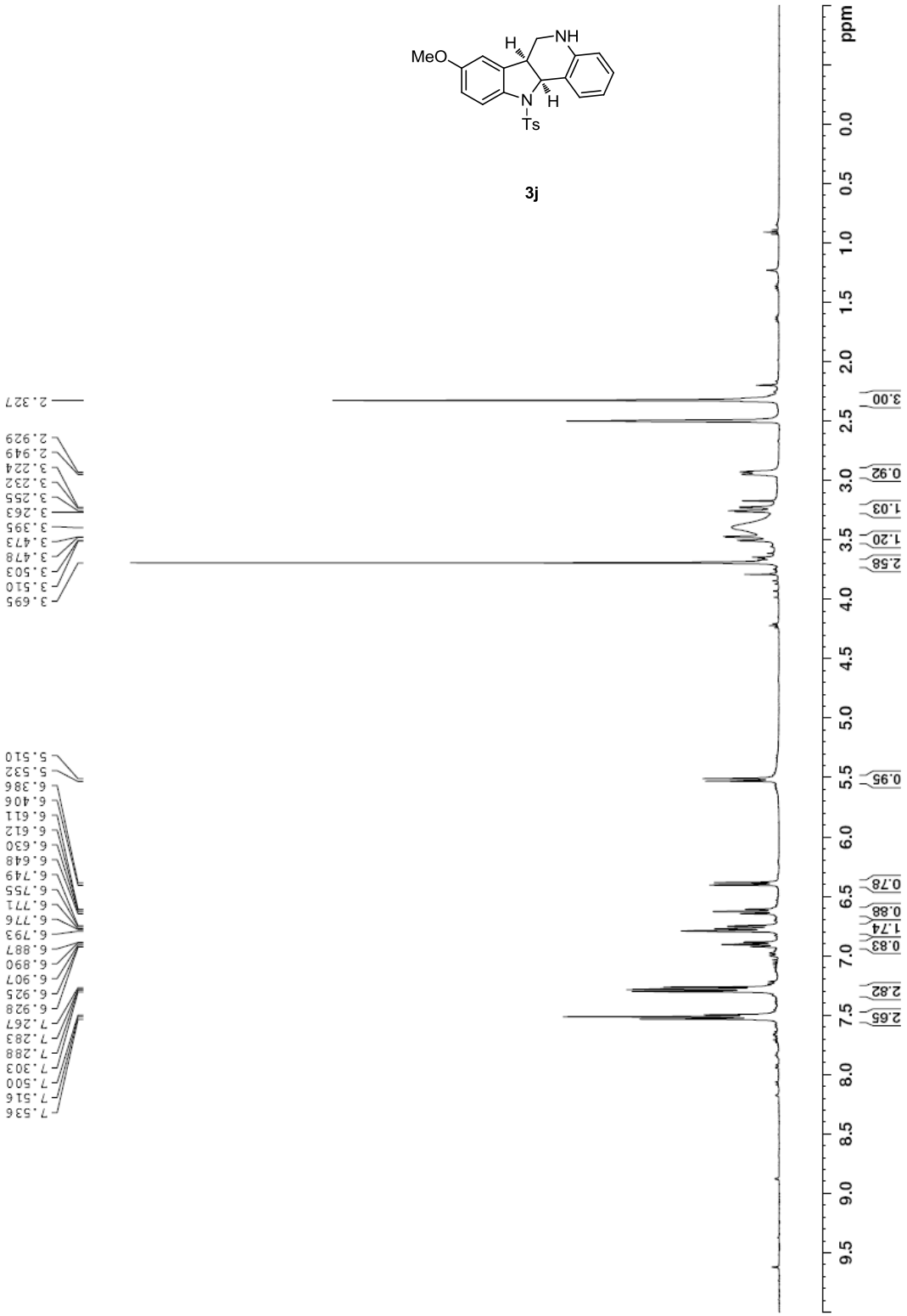


Fig. S16. ^{1}H NMR of 3j (400 MHz, DMSO-d_6)

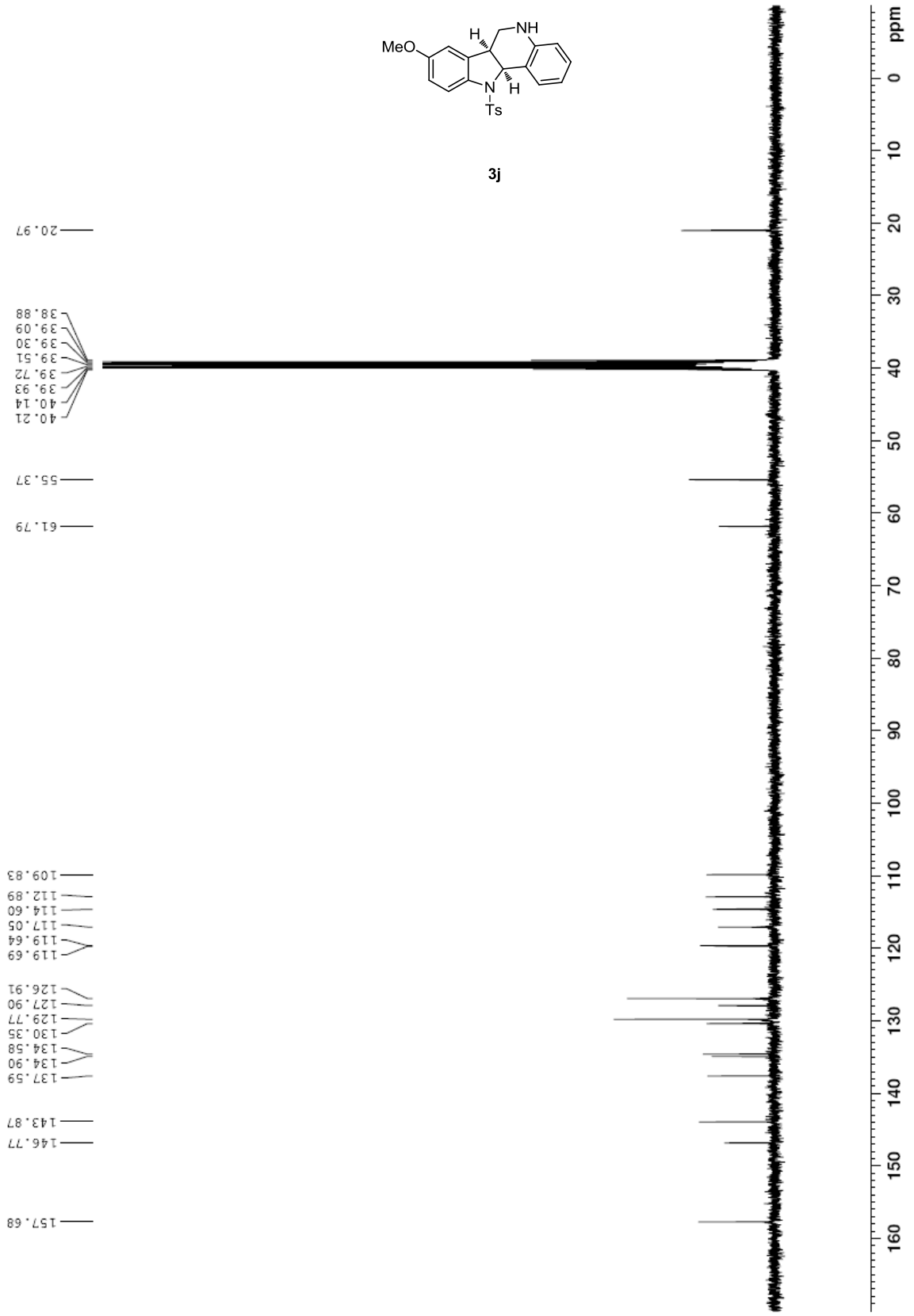


Fig. S17. ^{13}C NMR of 3j (100 MHz, DMSO-d_6)

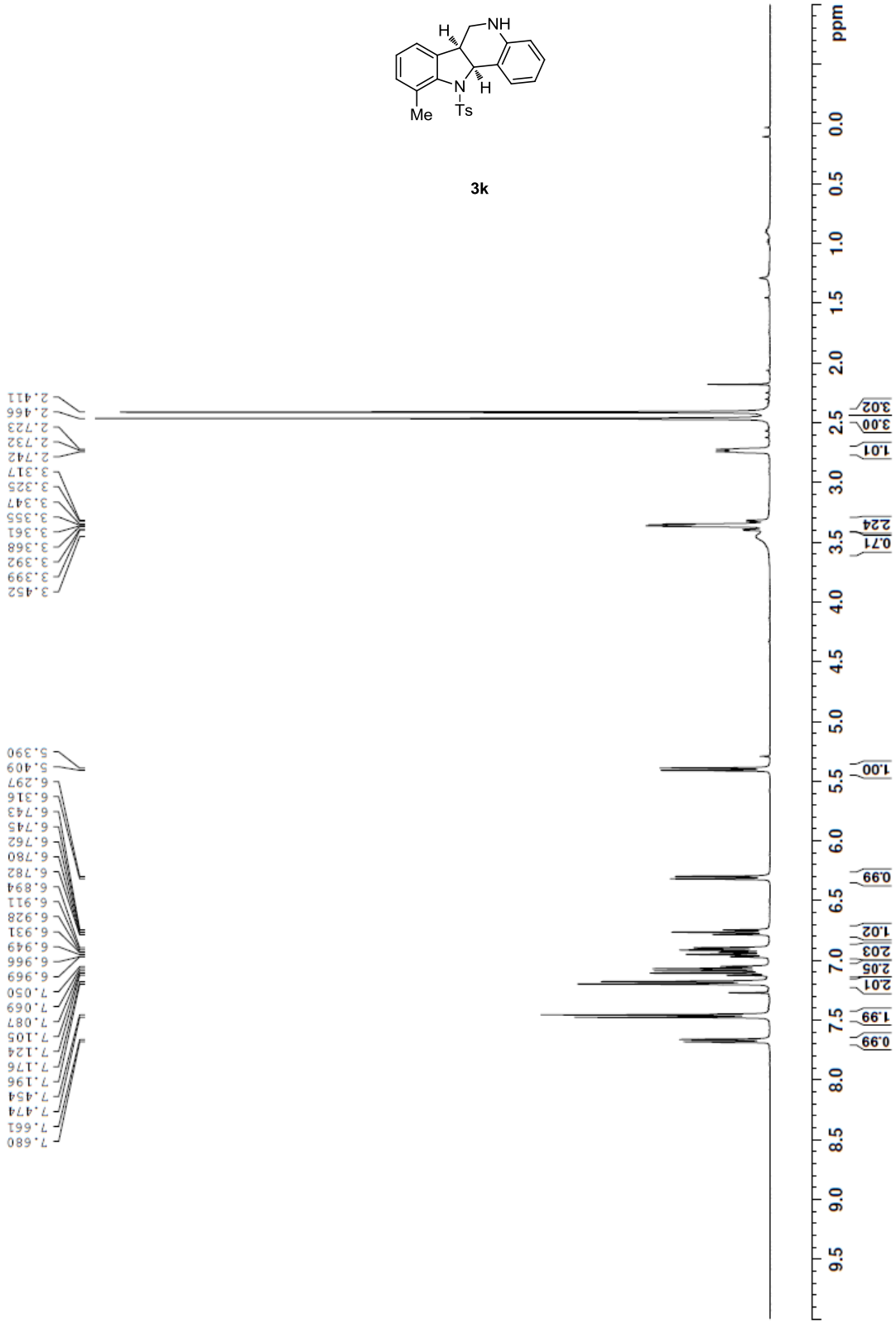


Fig. S18. ^{1}H NMR of 3k (400 MHz, $CDCl_3$)

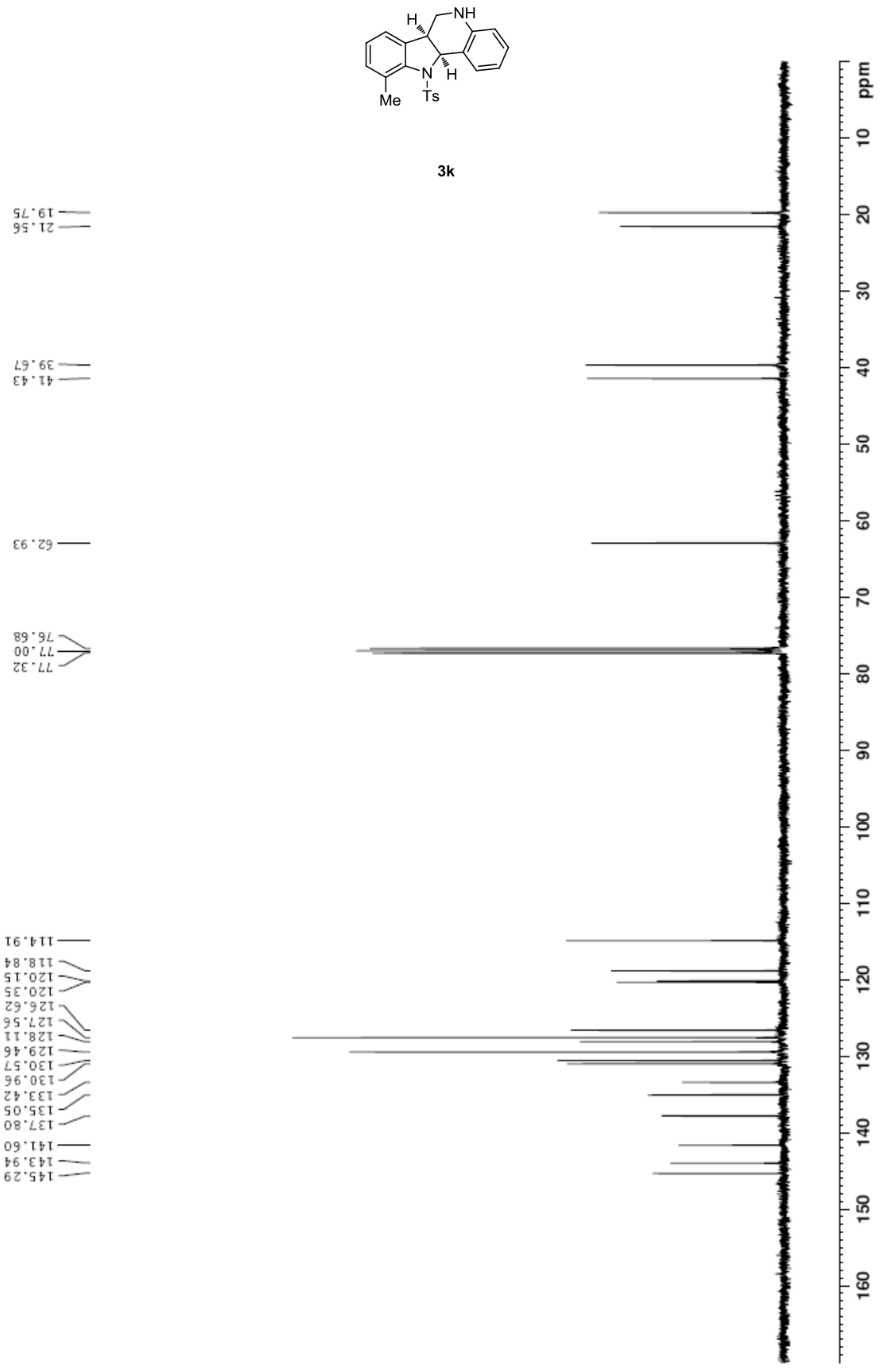


Fig. S19. ^{13}C NMR of 3k (100 MHz, $CDCl_3$)

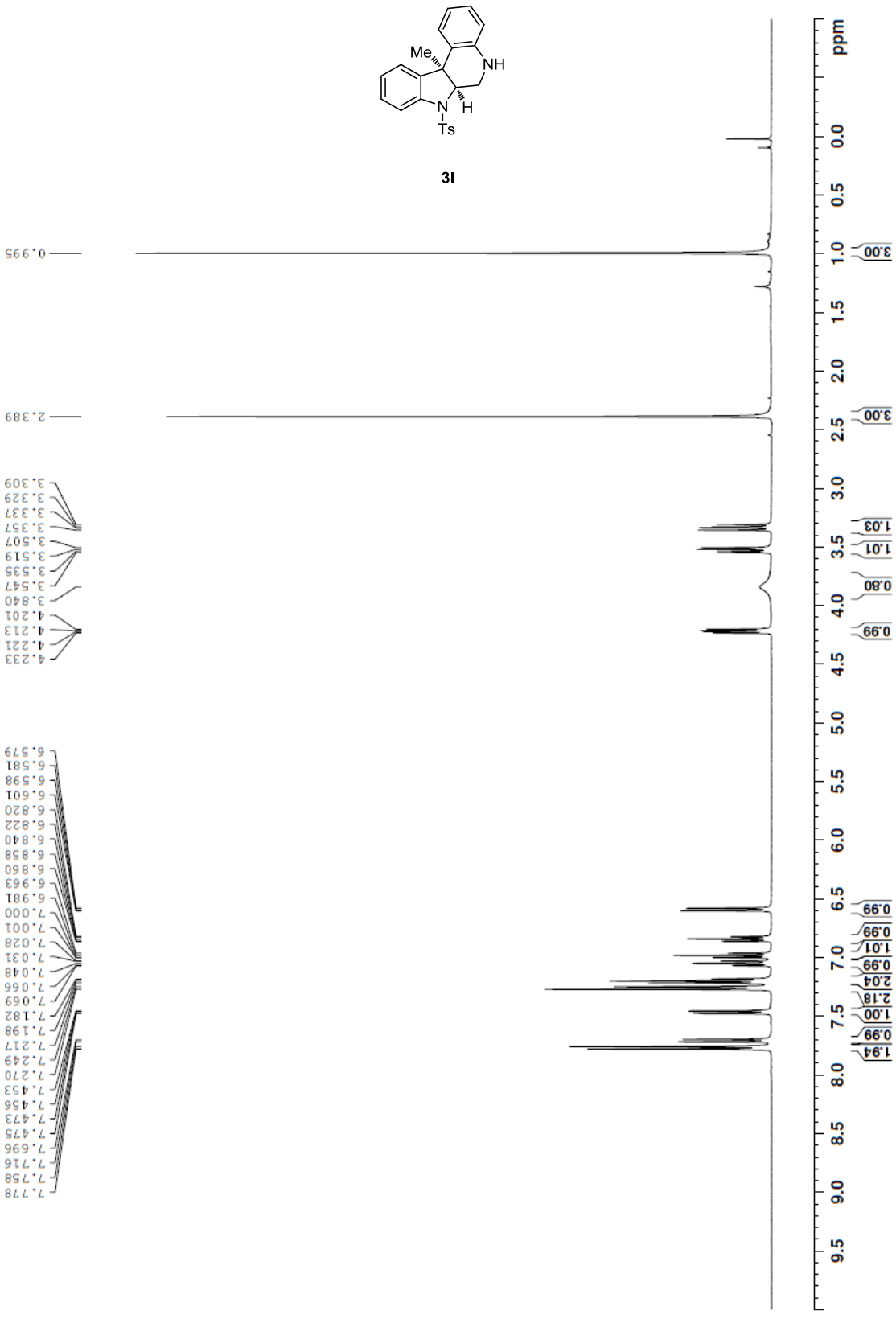


Fig. S20. ^{1}H NMR of 3l (400 MHz, $CDCl_3$)

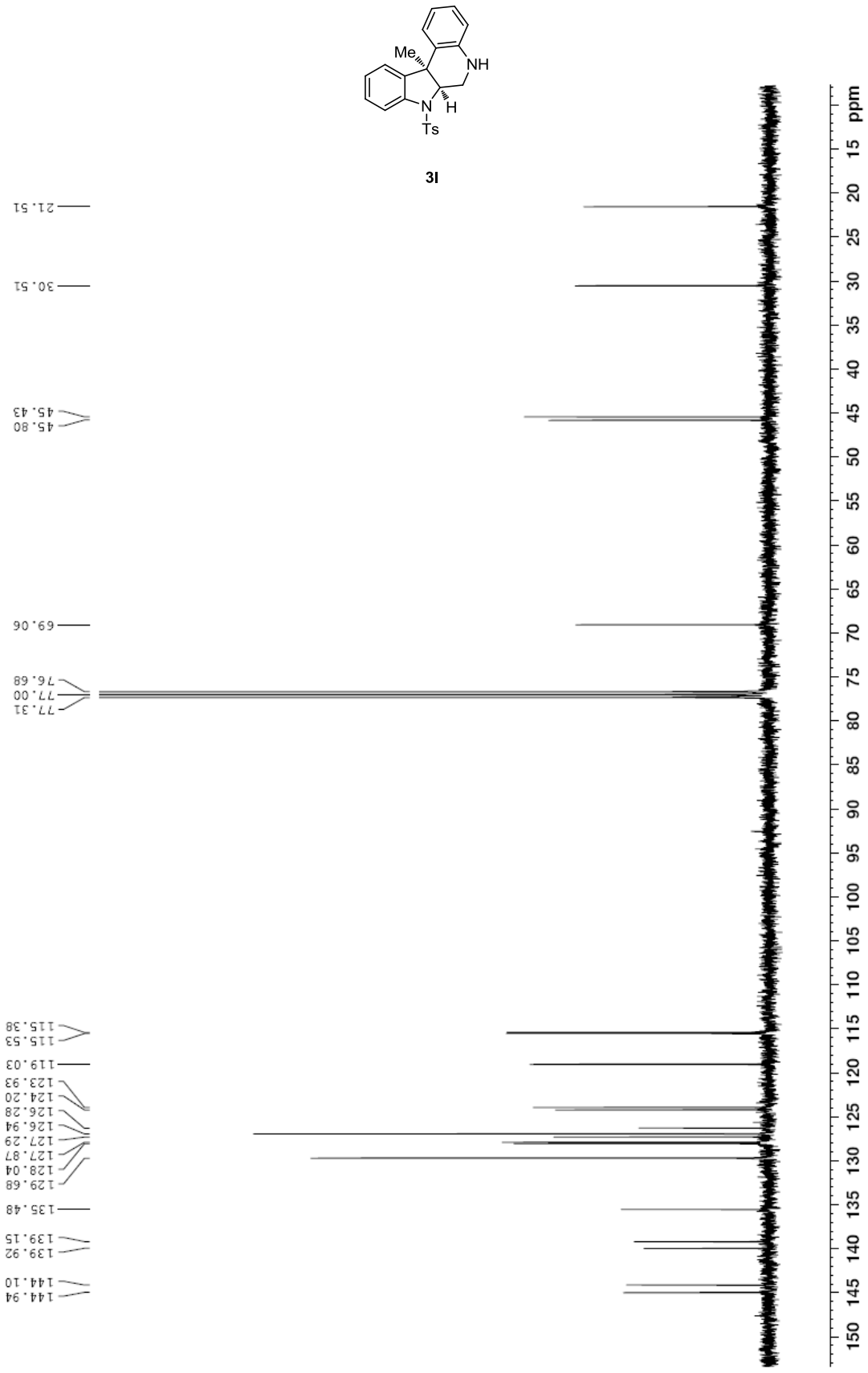


Fig. S21. ^{13}C NMR of 3l (100 MHz, $CDCl_3$)

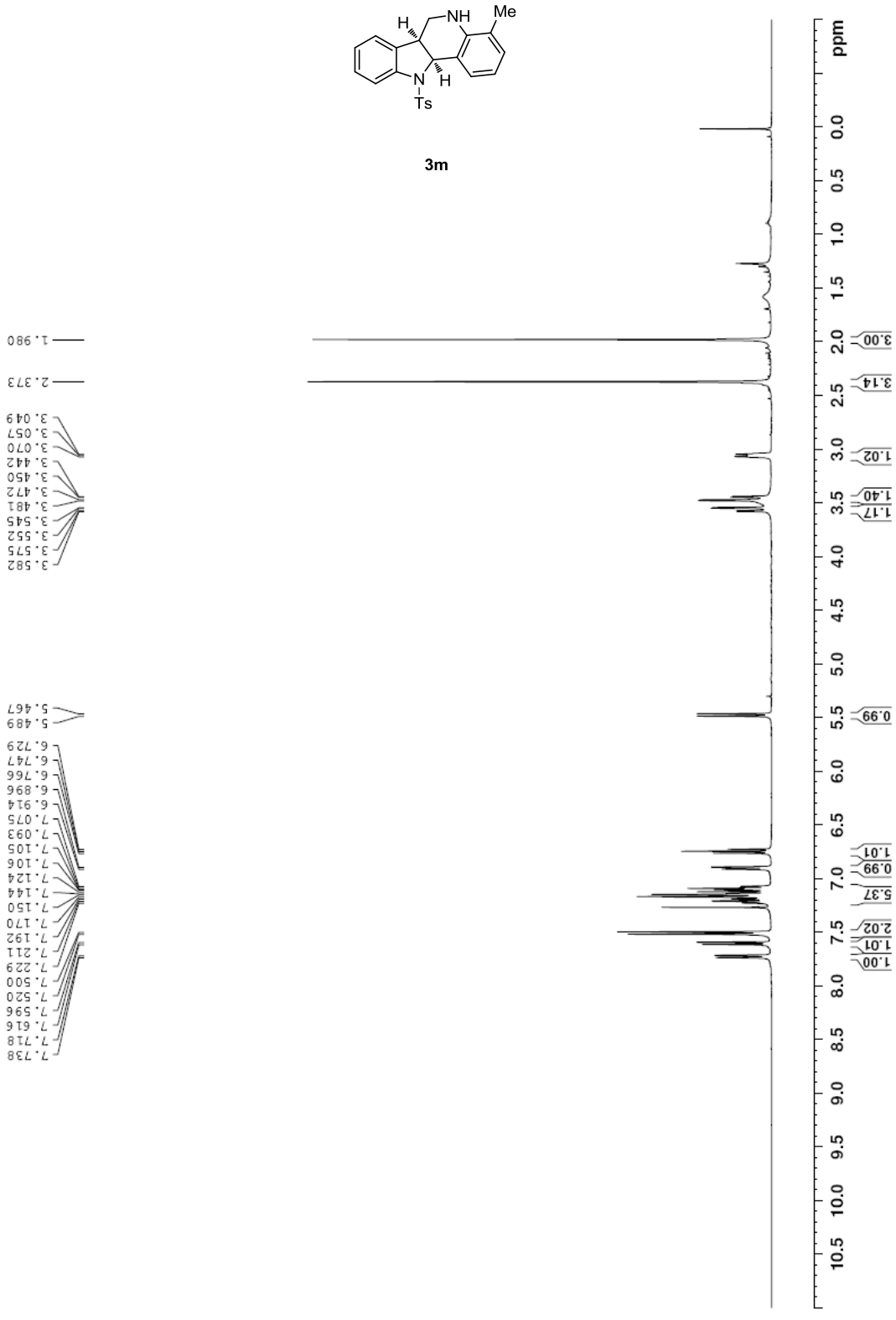


Fig. S22. ^{1}H NMR of 3m (400 MHz, $CDCl_3$)

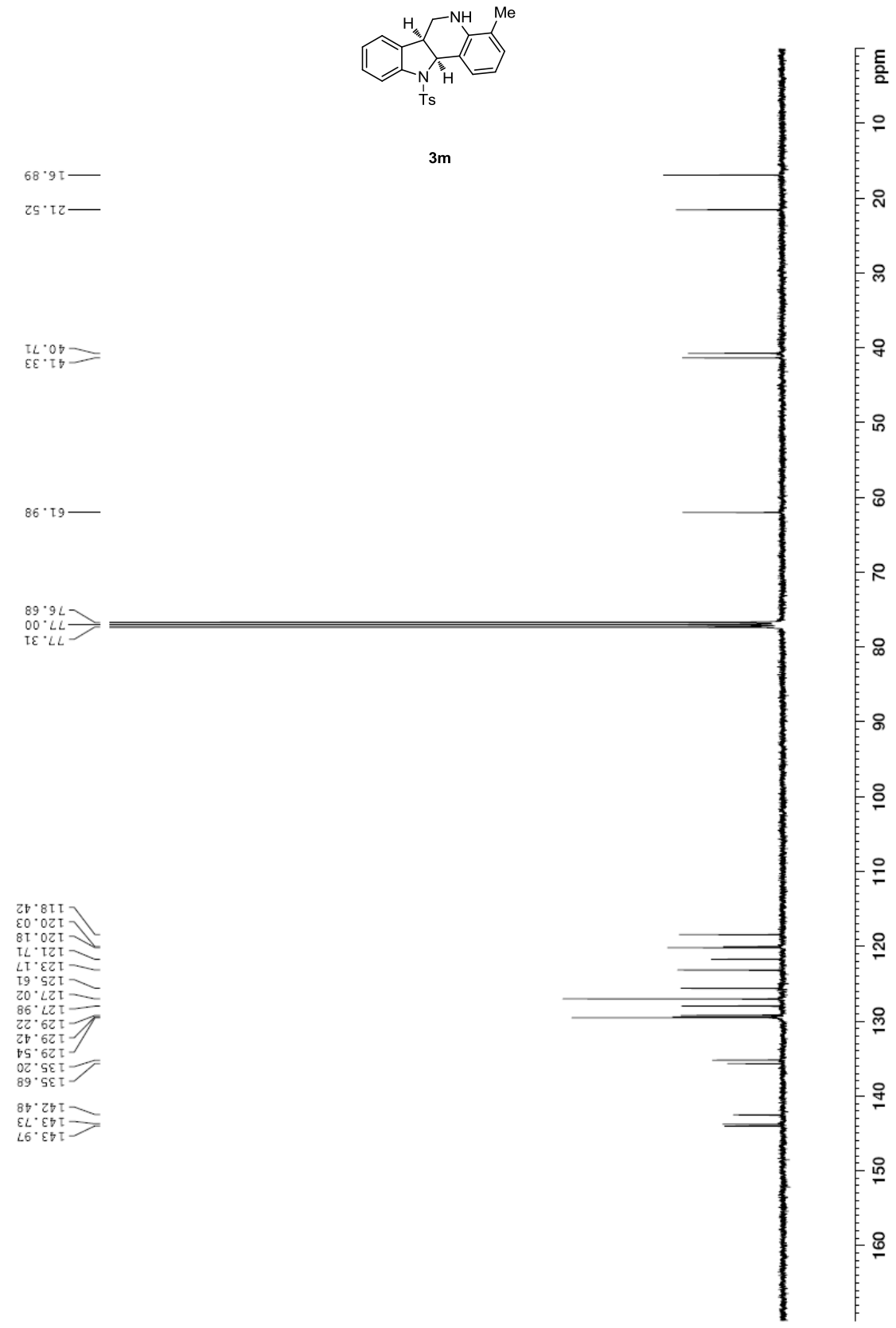


Fig. S23. ^{13}C NMR of 3m (100 MHz, $CDCl_3$)

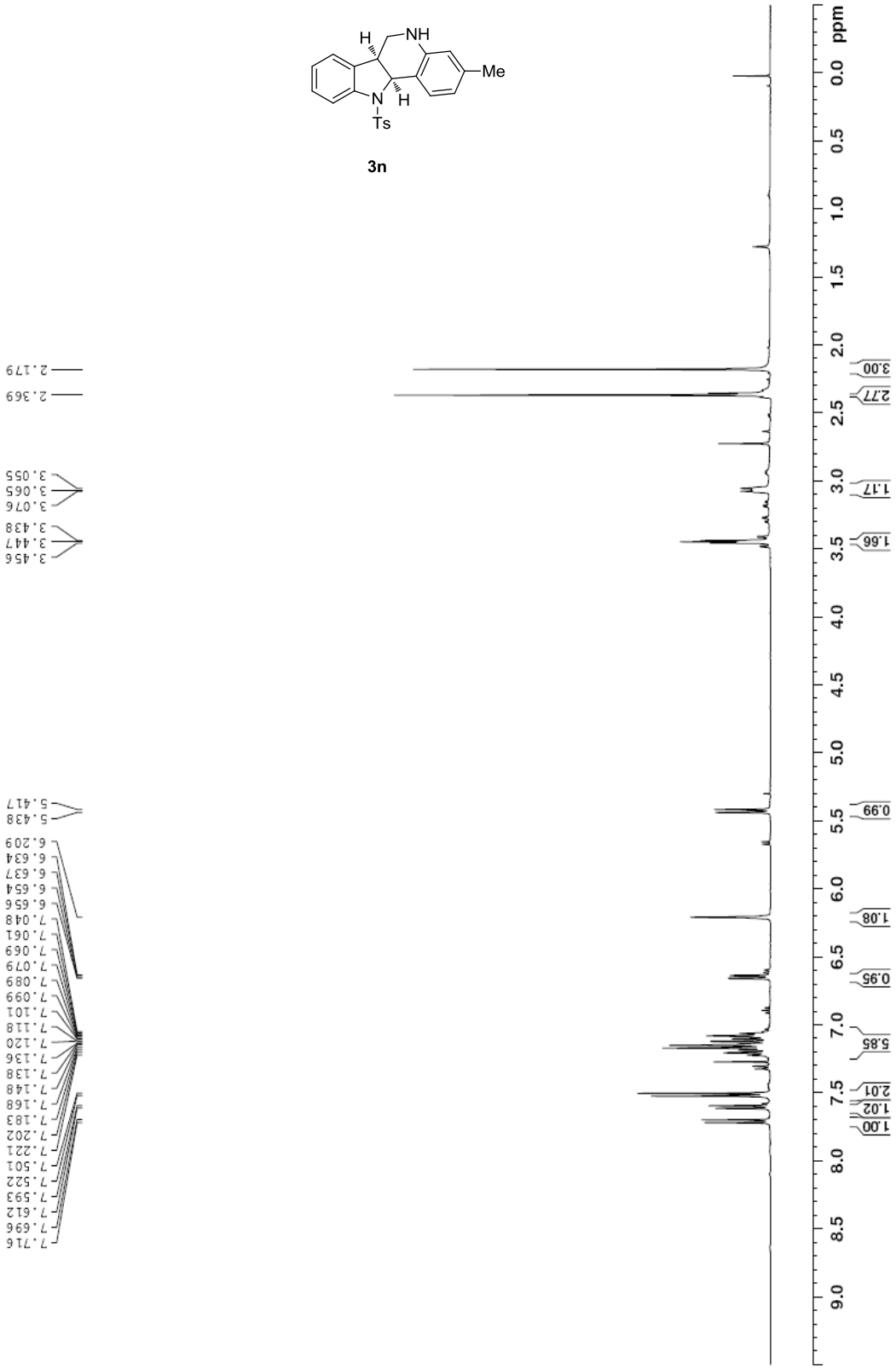


Fig. S24. ^{1}H NMR of 3n (400 MHz, $CDCl_3$)

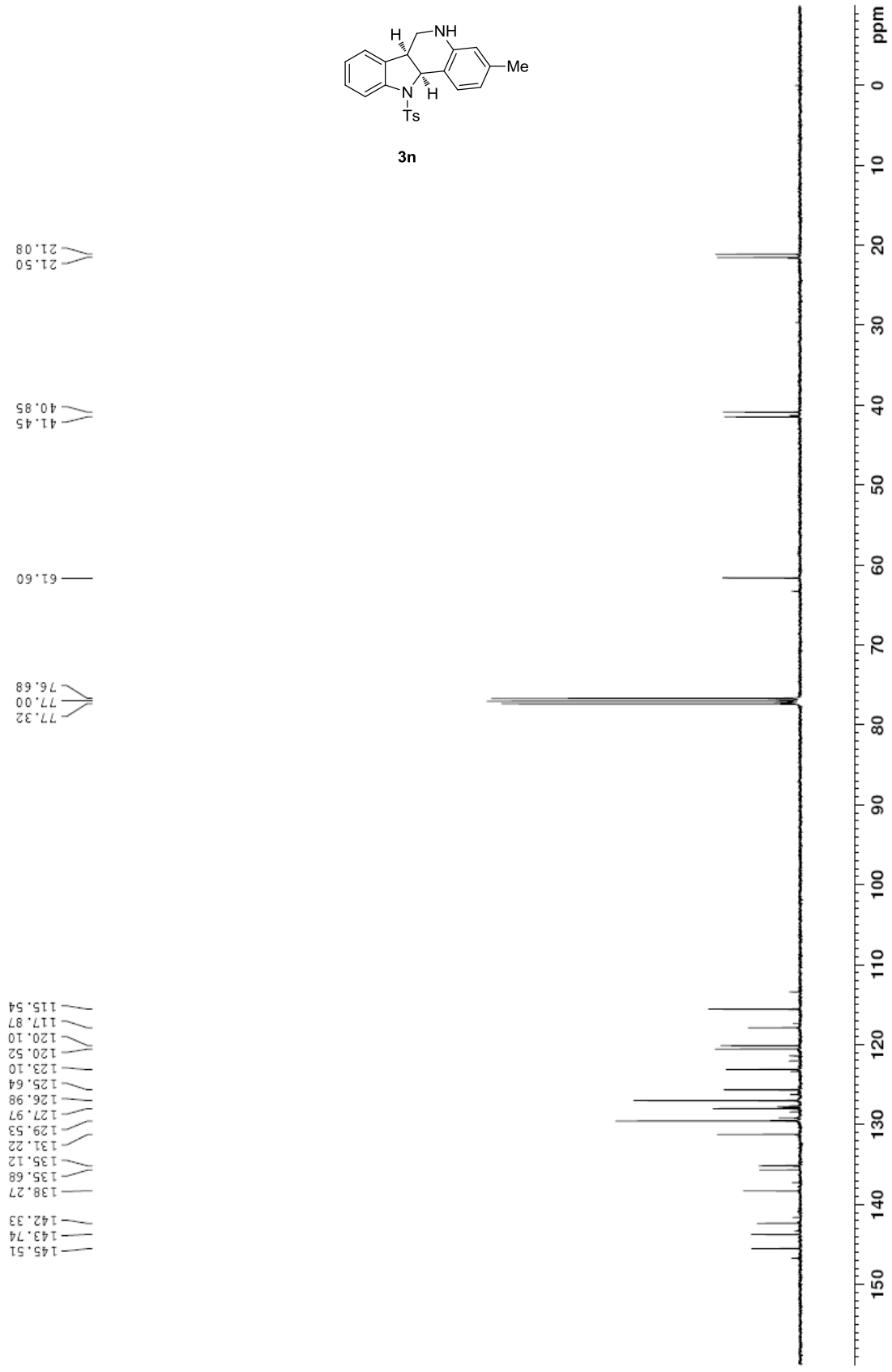


Fig. S25. ^{13}C NMR of 3n (100 MHz, $CDCl_3$)

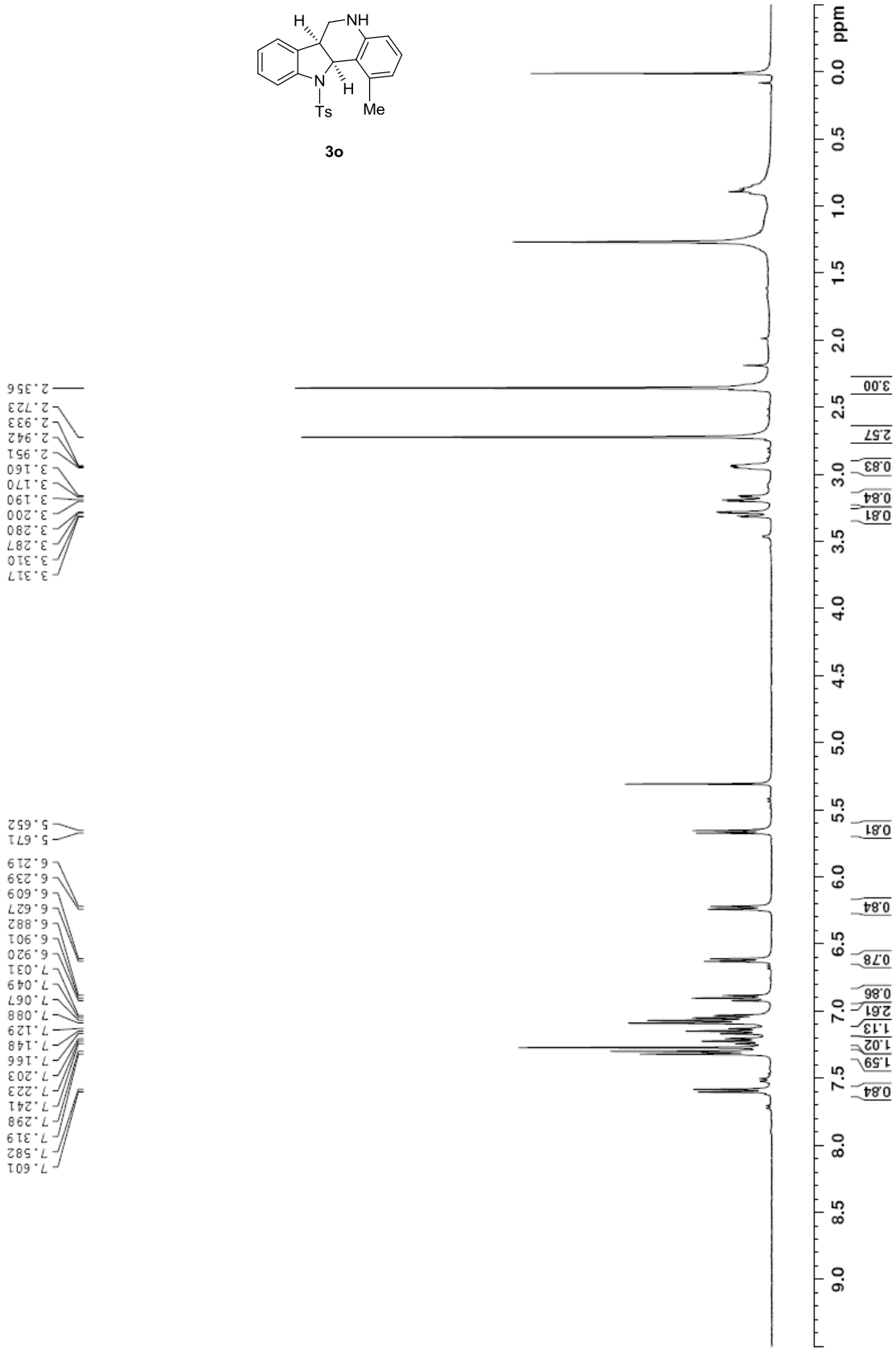


Fig. S26. ^{1}H NMR of 3o (400 MHz, $CDCl_3$)

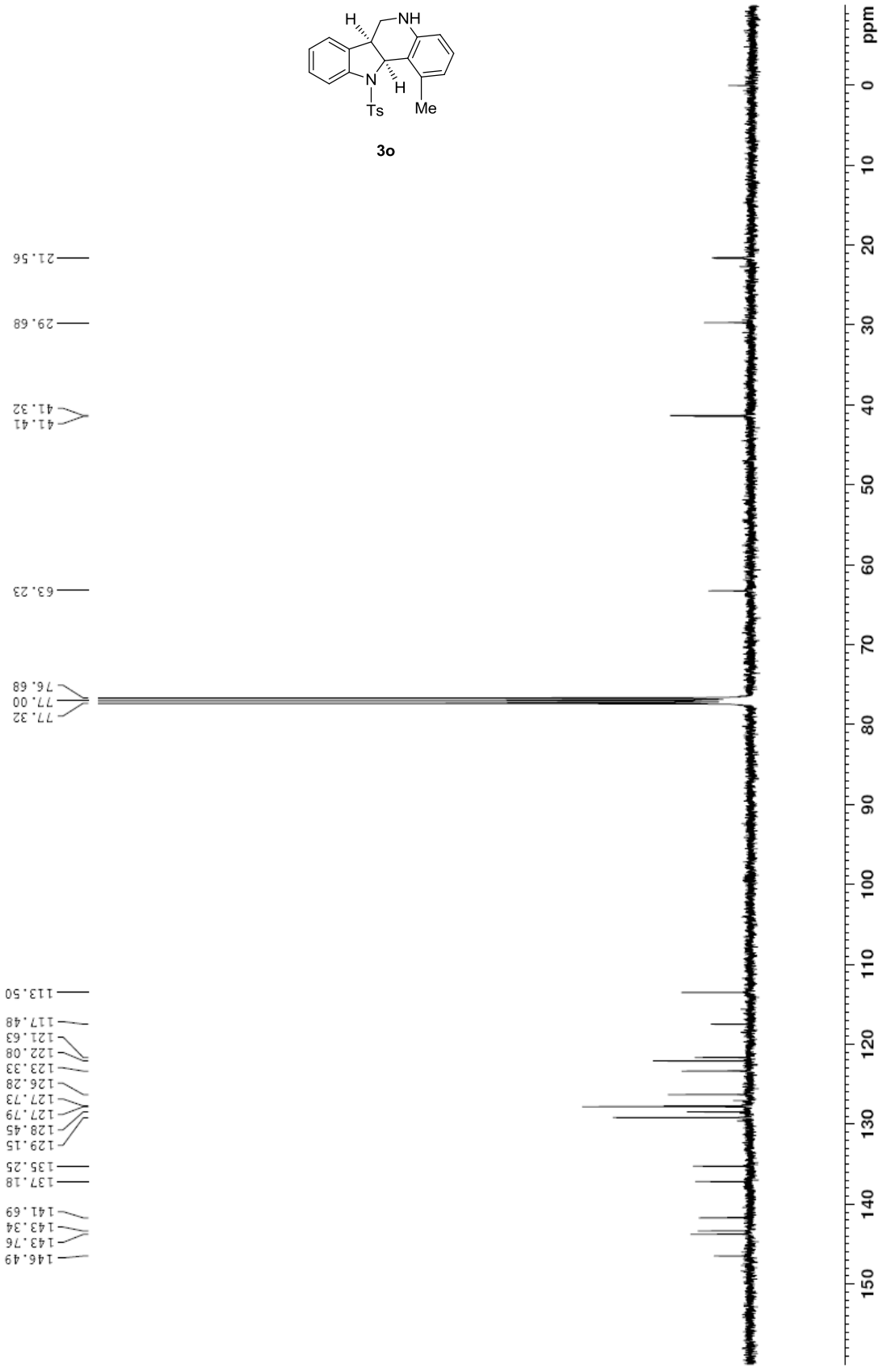


Fig. S27. ^{13}C NMR of 3o (100 MHz, $CDCl_3$)

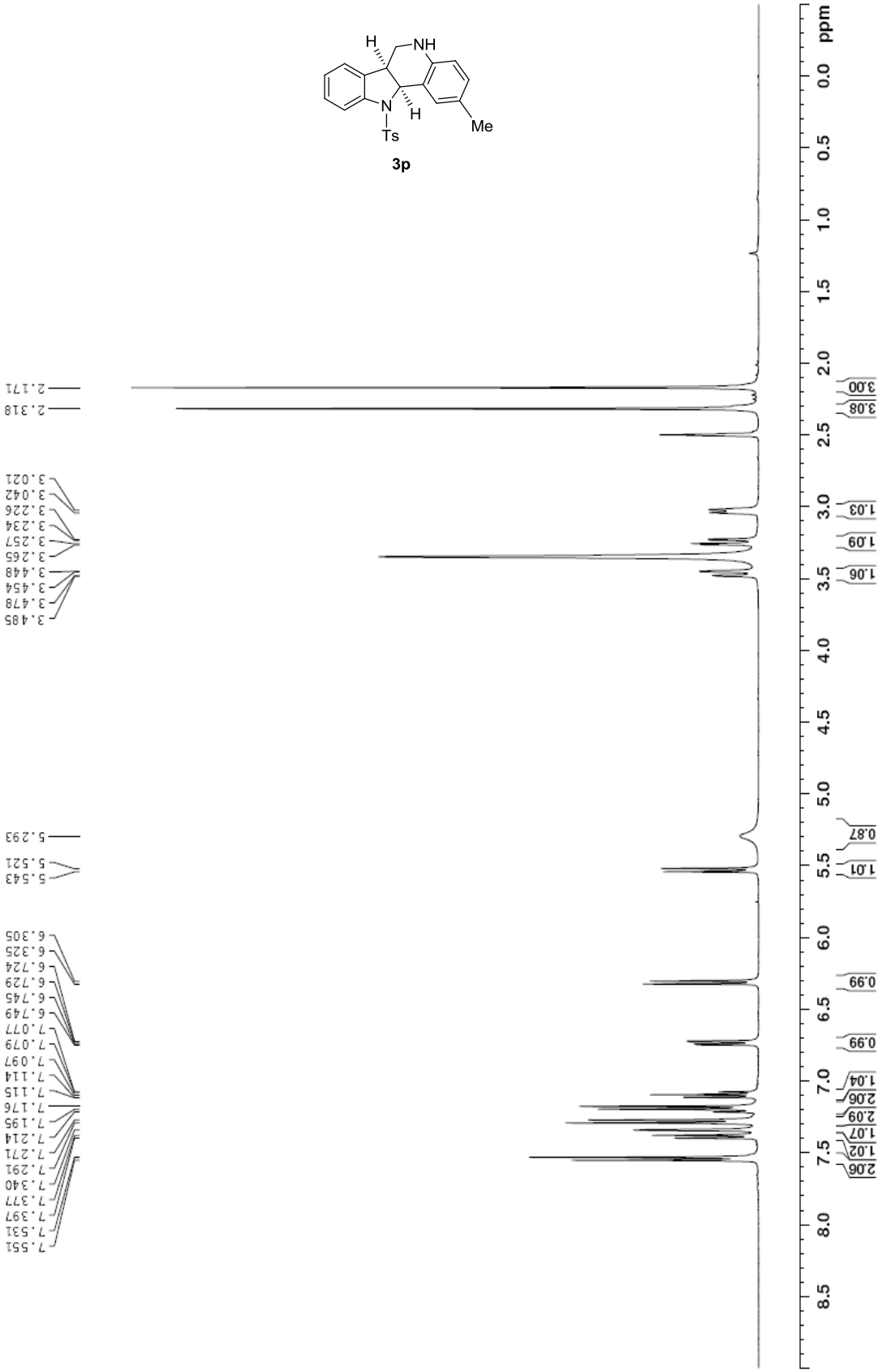


Fig. S28. ^{1}H NMR of 3p (400 MHz, DMSO-d_6)

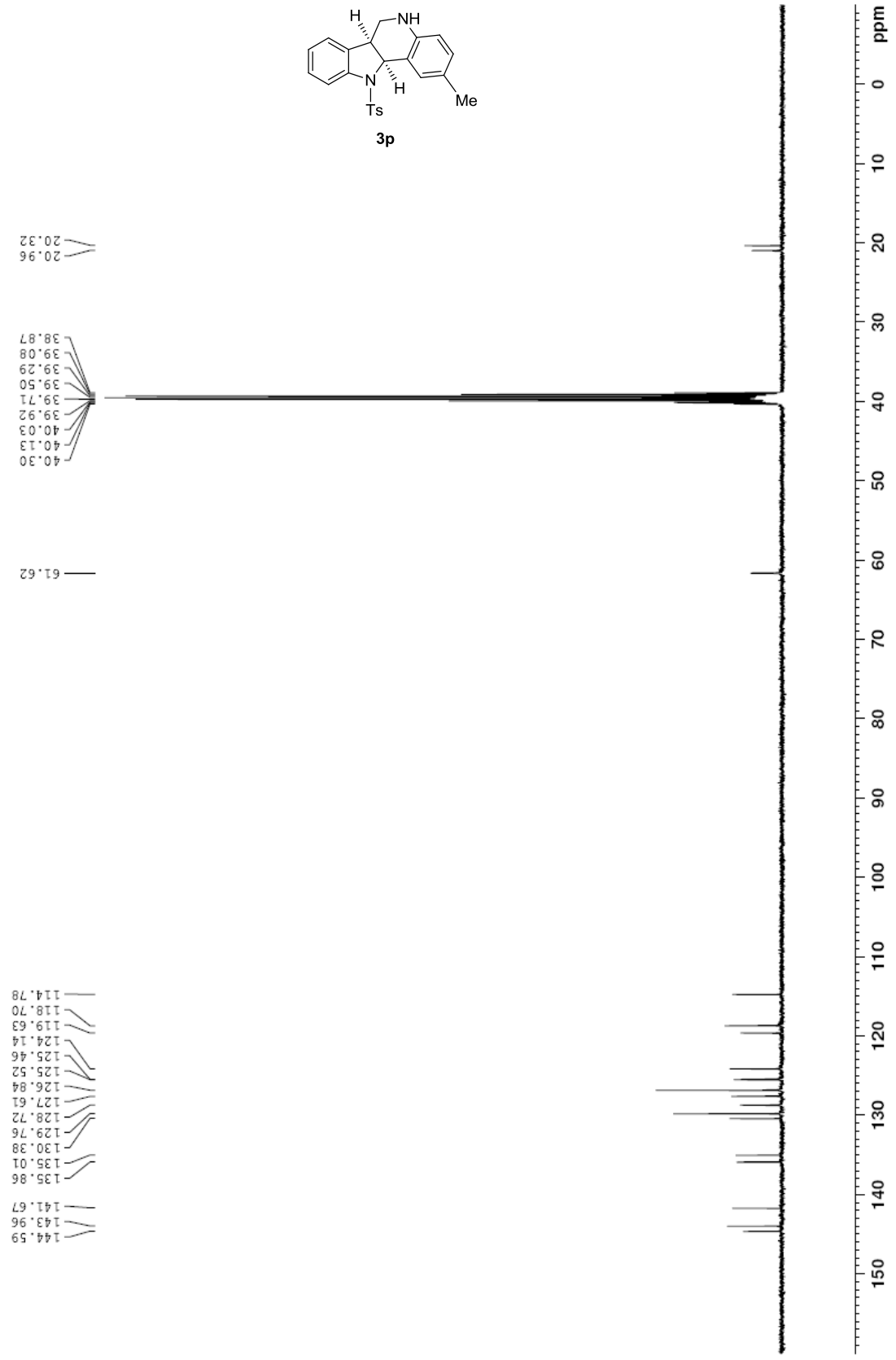


Fig. S29. ^{13}C NMR of 3p (100 MHz, DMSO-d_6)

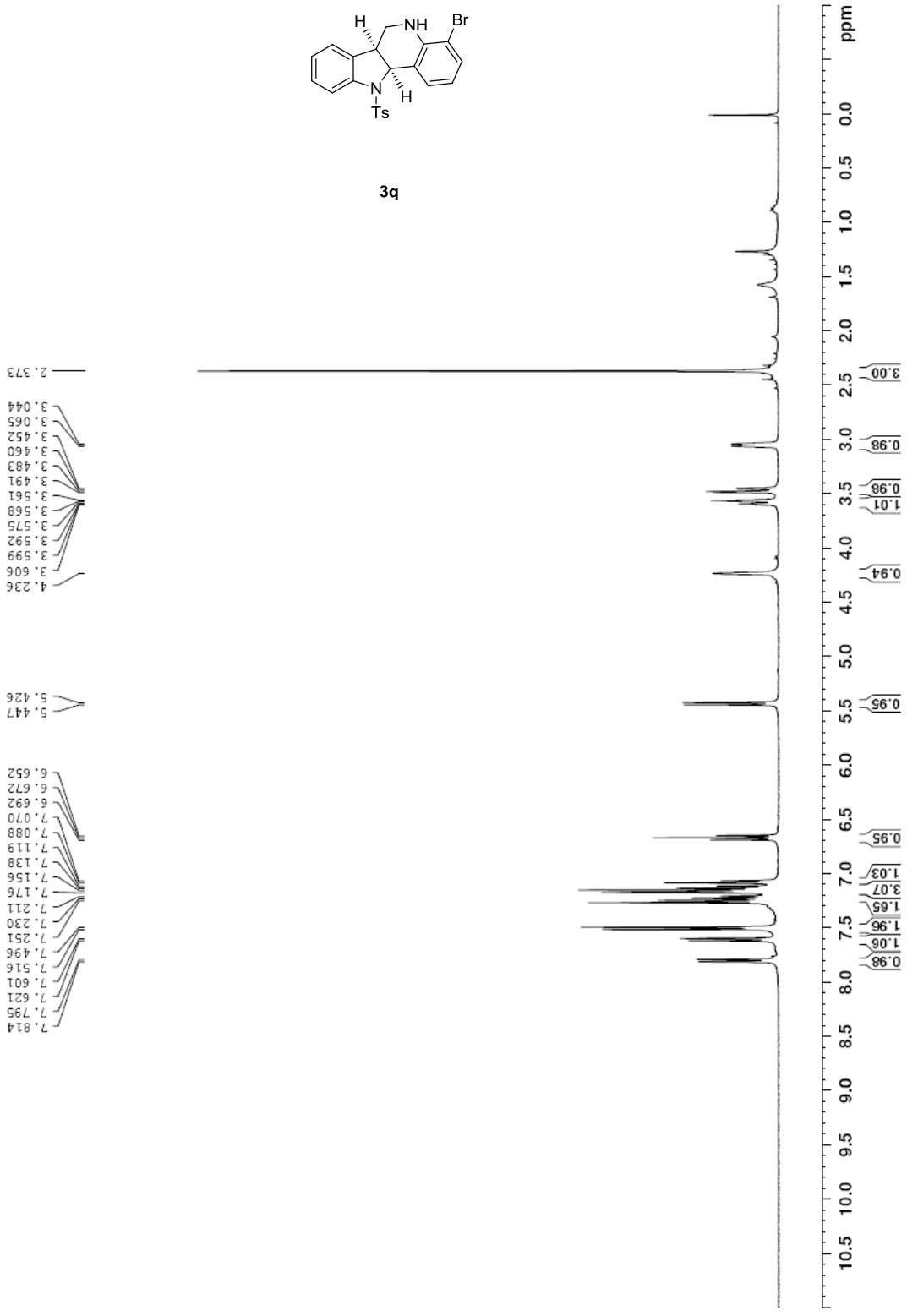


Fig. S30. ^{1}H NMR of 3q (400 MHz, $CDCl_3$)

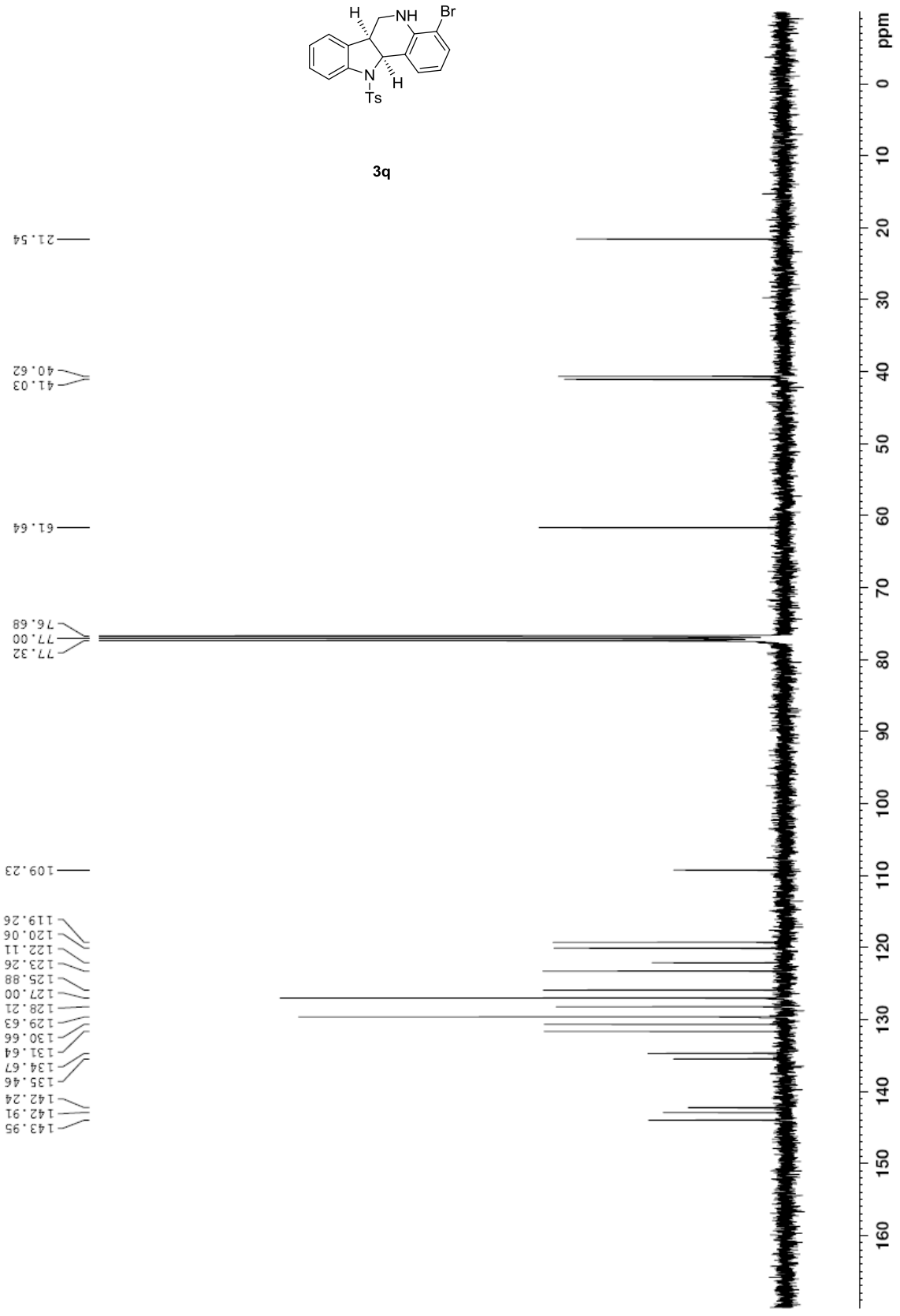


Fig. S31. ^{13}C NMR of 3q (100 MHz, $CDCl_3$)

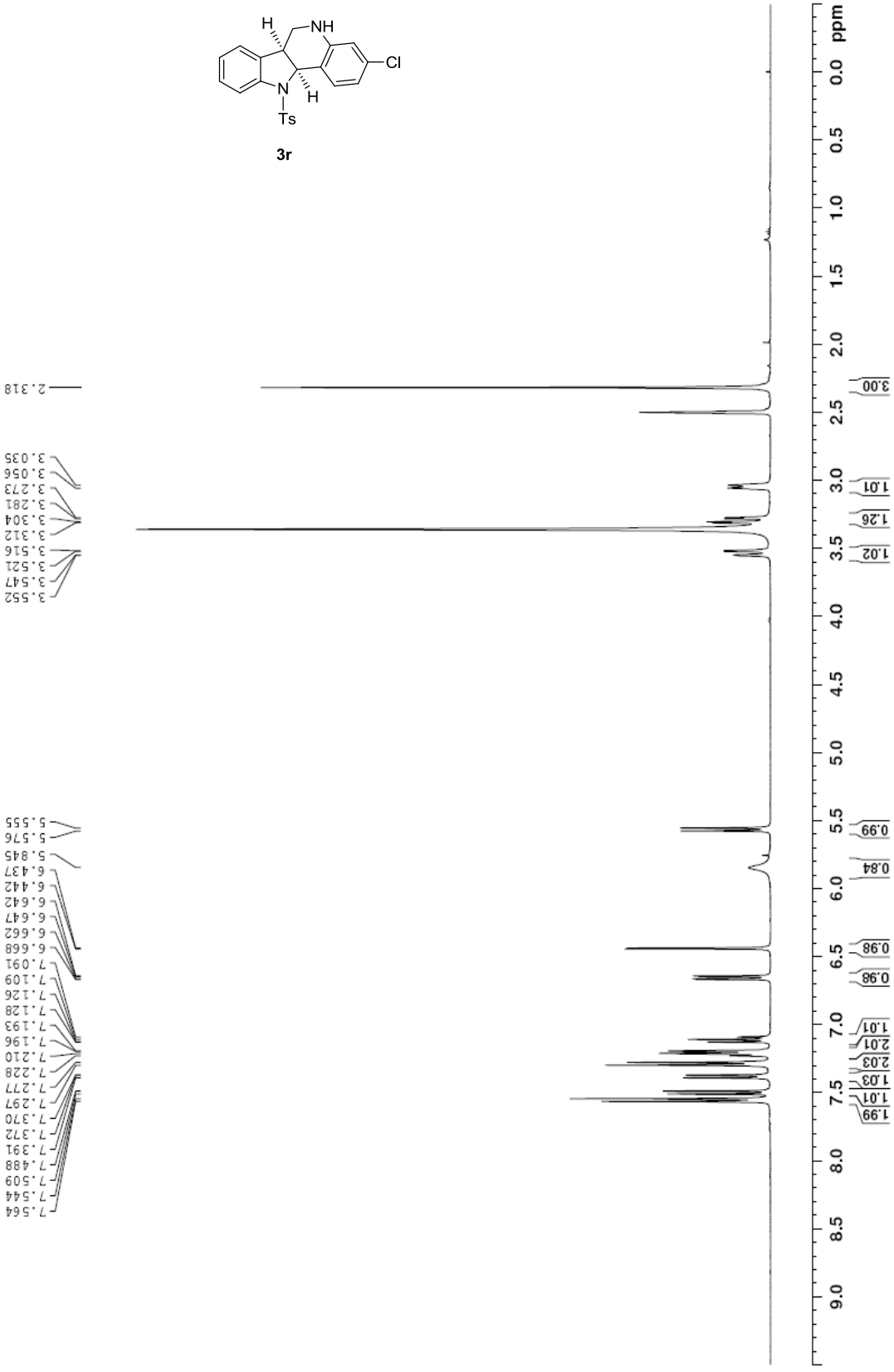


Fig. S32. ^{1}H NMR of 3r (400 MHz, DMSO-d_6)

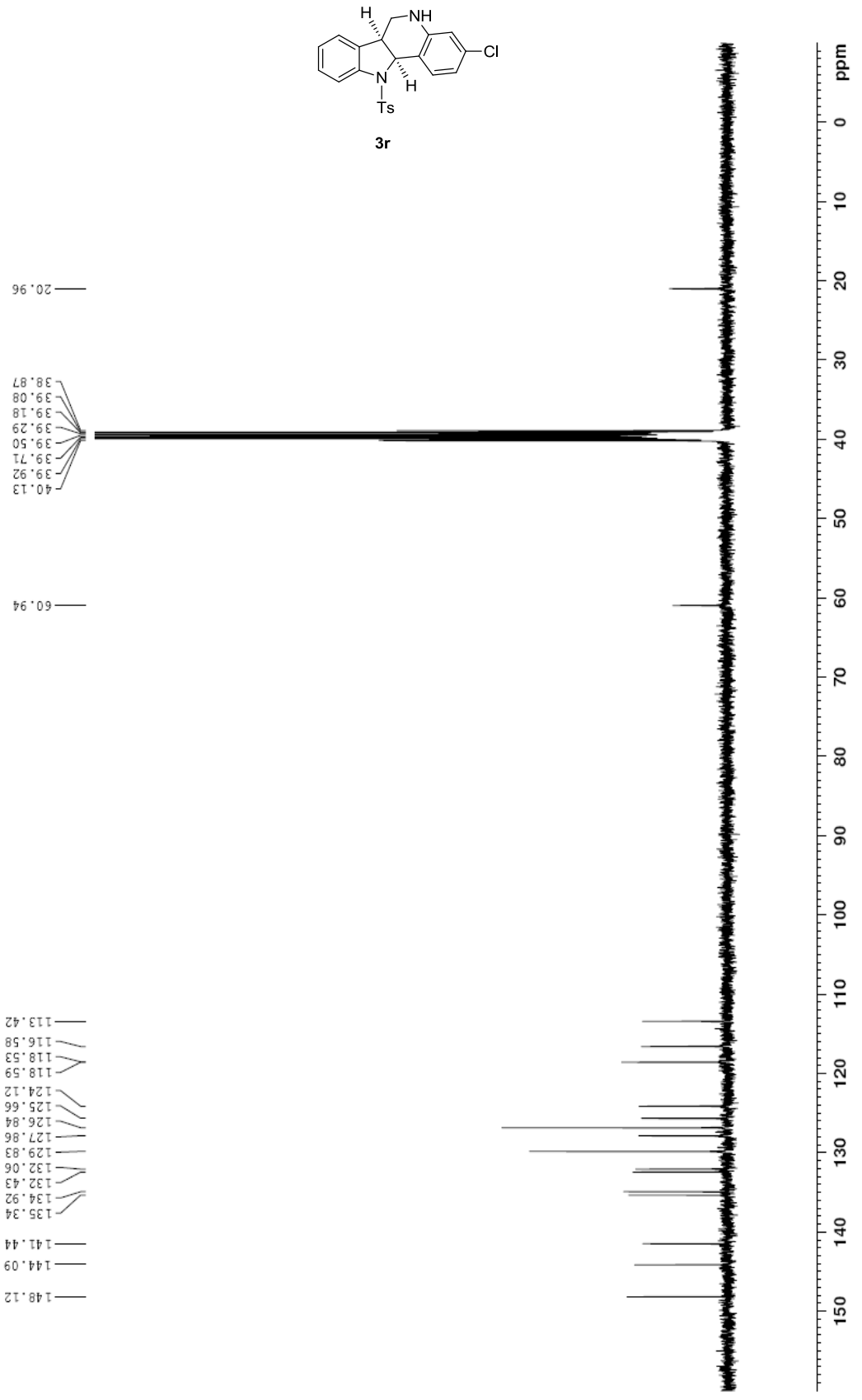


Fig. S33. ^{13}C NMR of 3r (100 MHz, DMSO-d_6)

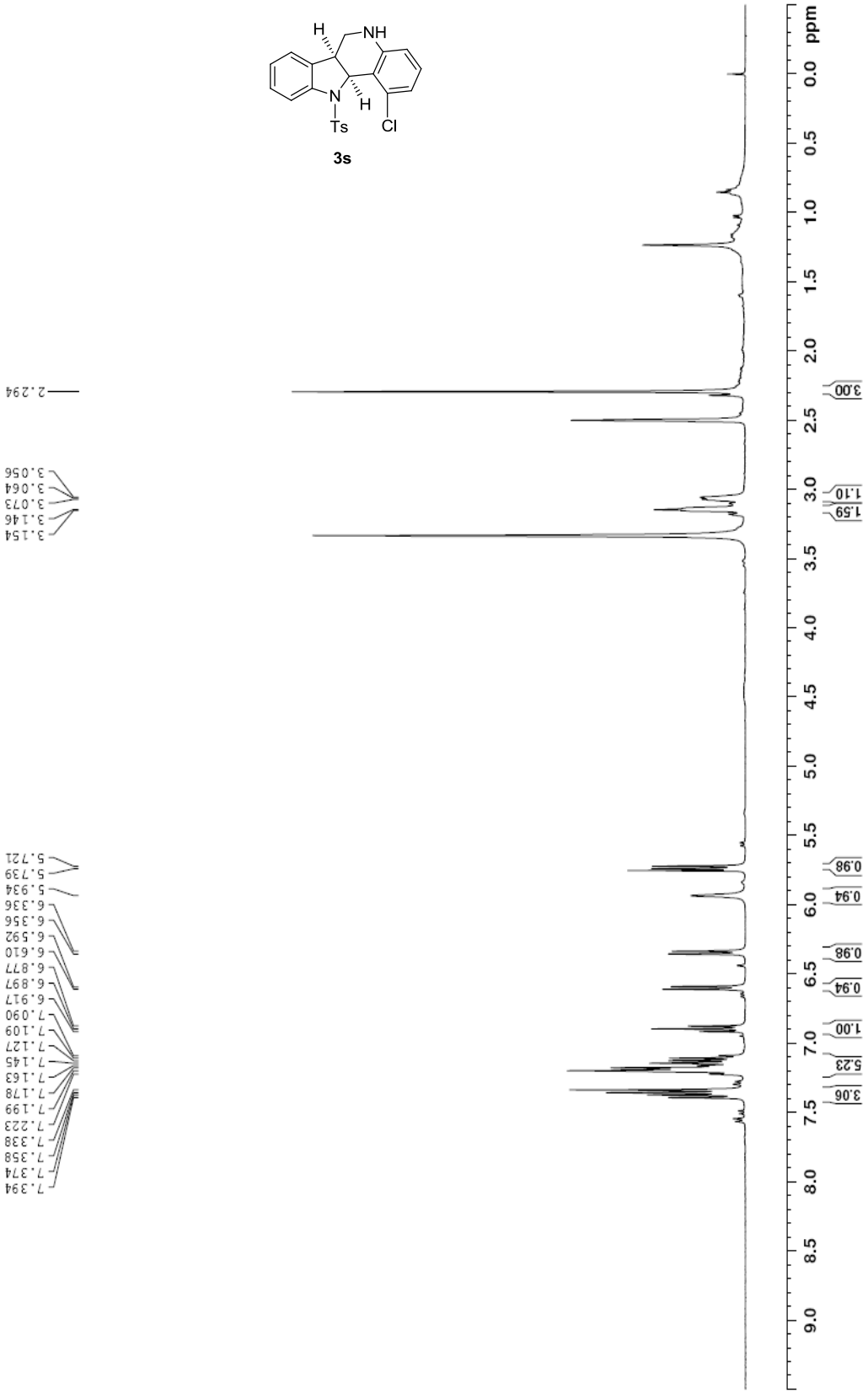


Fig. S34. ^{1}H NMR of 3s (400 MHz, DMSO-d_6)

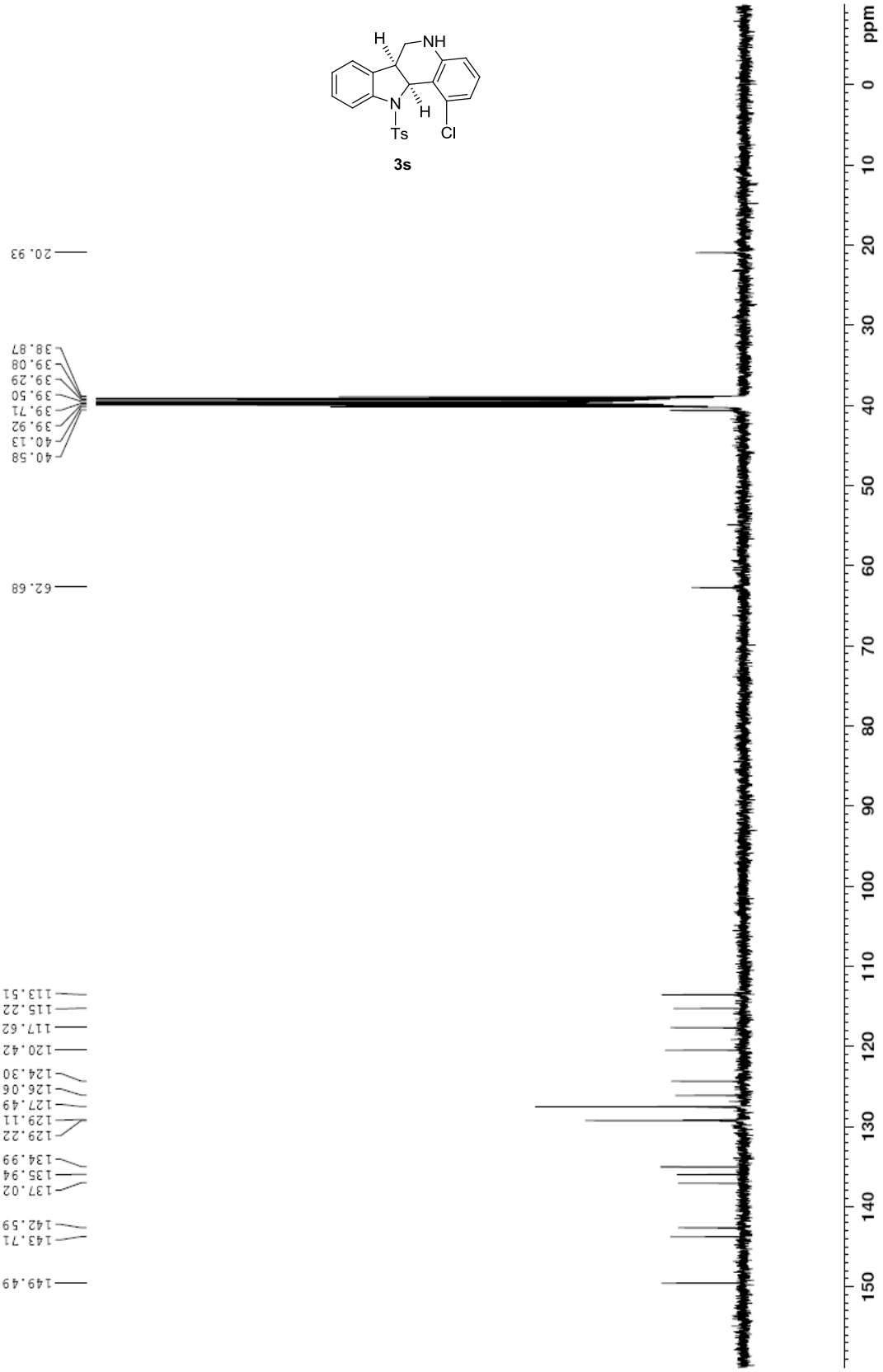


Fig. S35. ^{13}C NMR of 3s (100 MHz, DMSO-d_6)

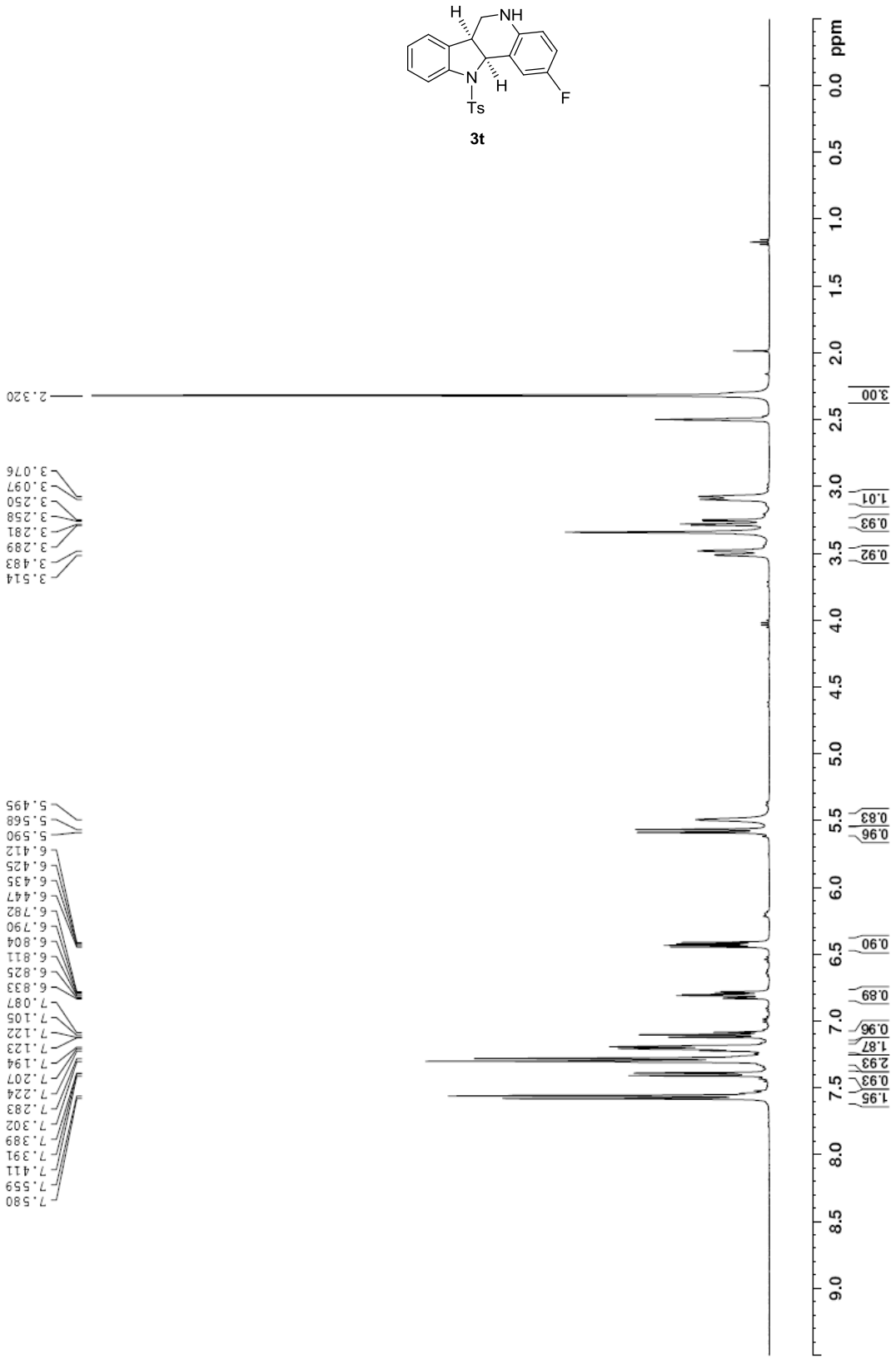


Fig. S36. ^{1}H NMR of 3t (400 MHz, DMSO-d_6)

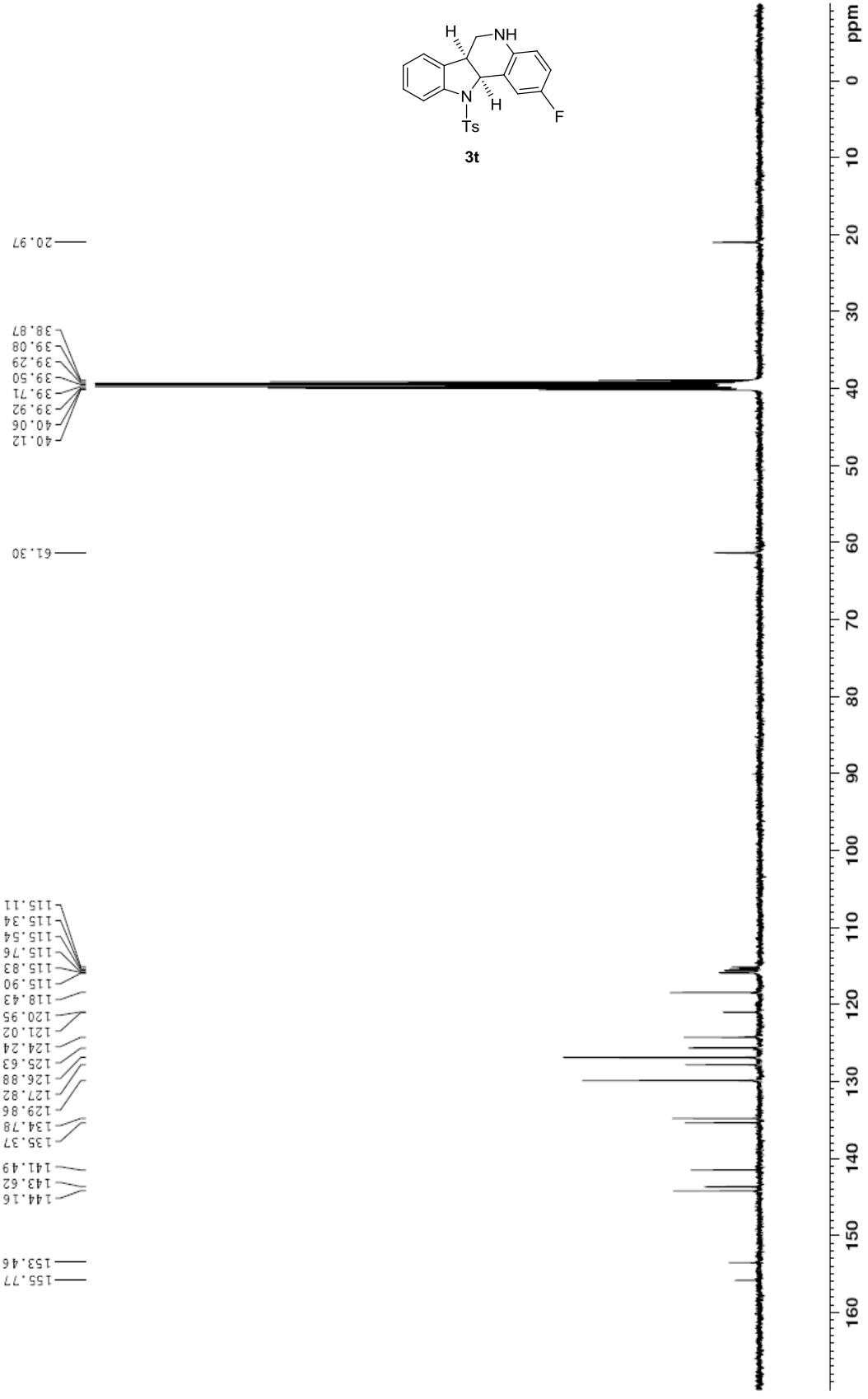


Fig. S37. ^{13}C NMR of 3t (100 MHz, DMSO-d_6)

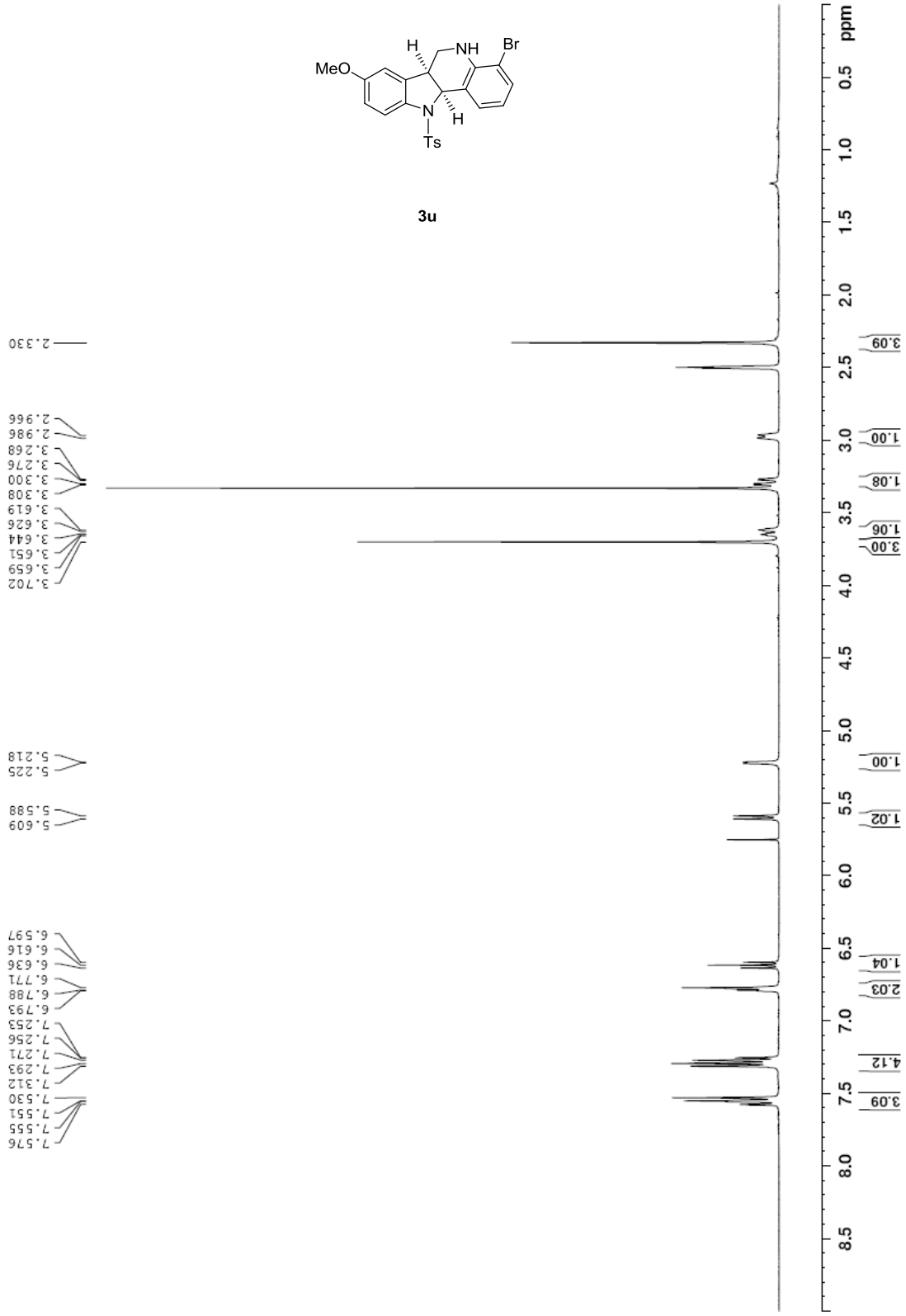


Fig. S38. ^{1}H NMR of 3u (400 MHz, DMSO-d_6)

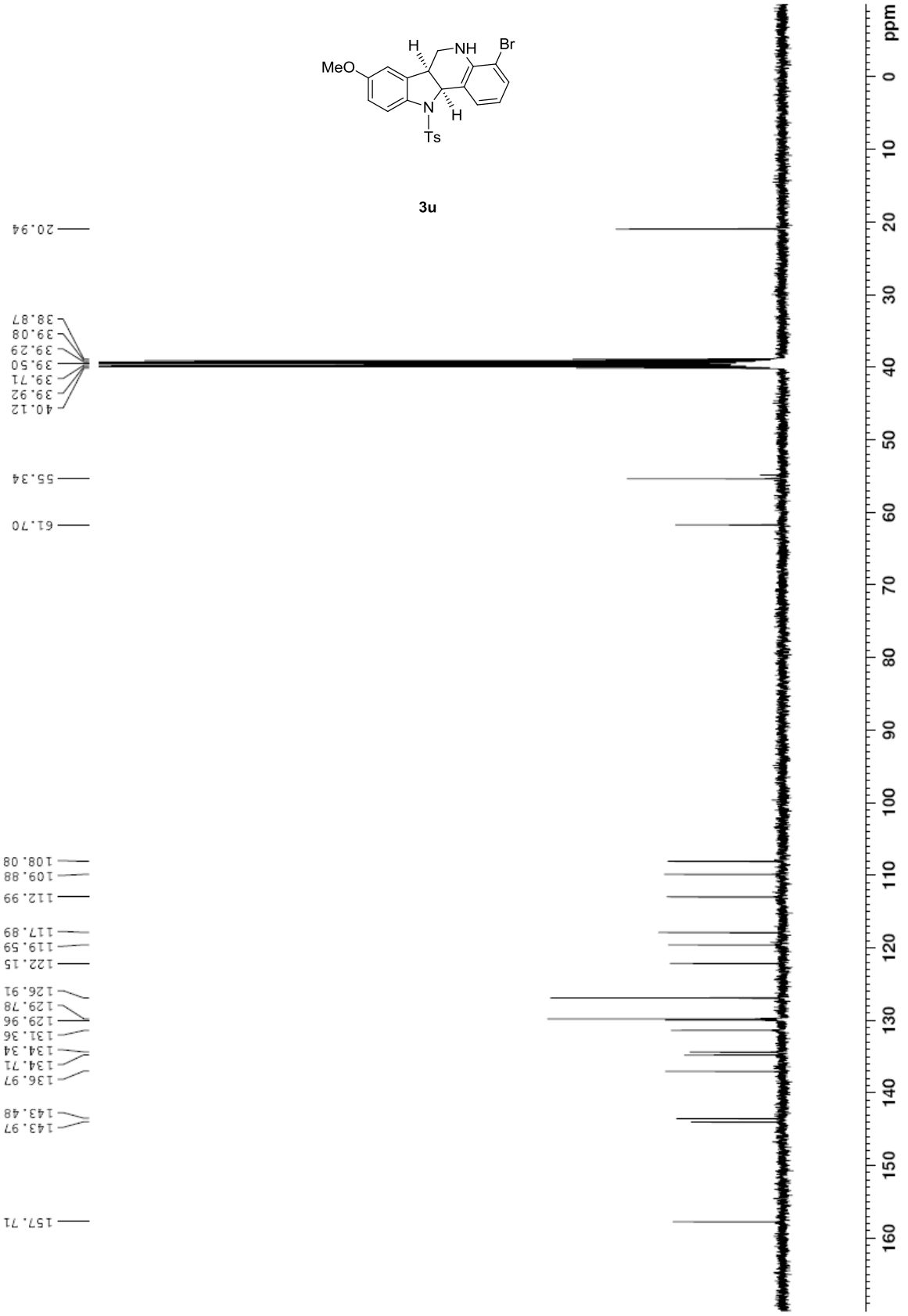


Fig. S39. ^{13}C NMR of 3u (100 MHz, DMSO-d_6)

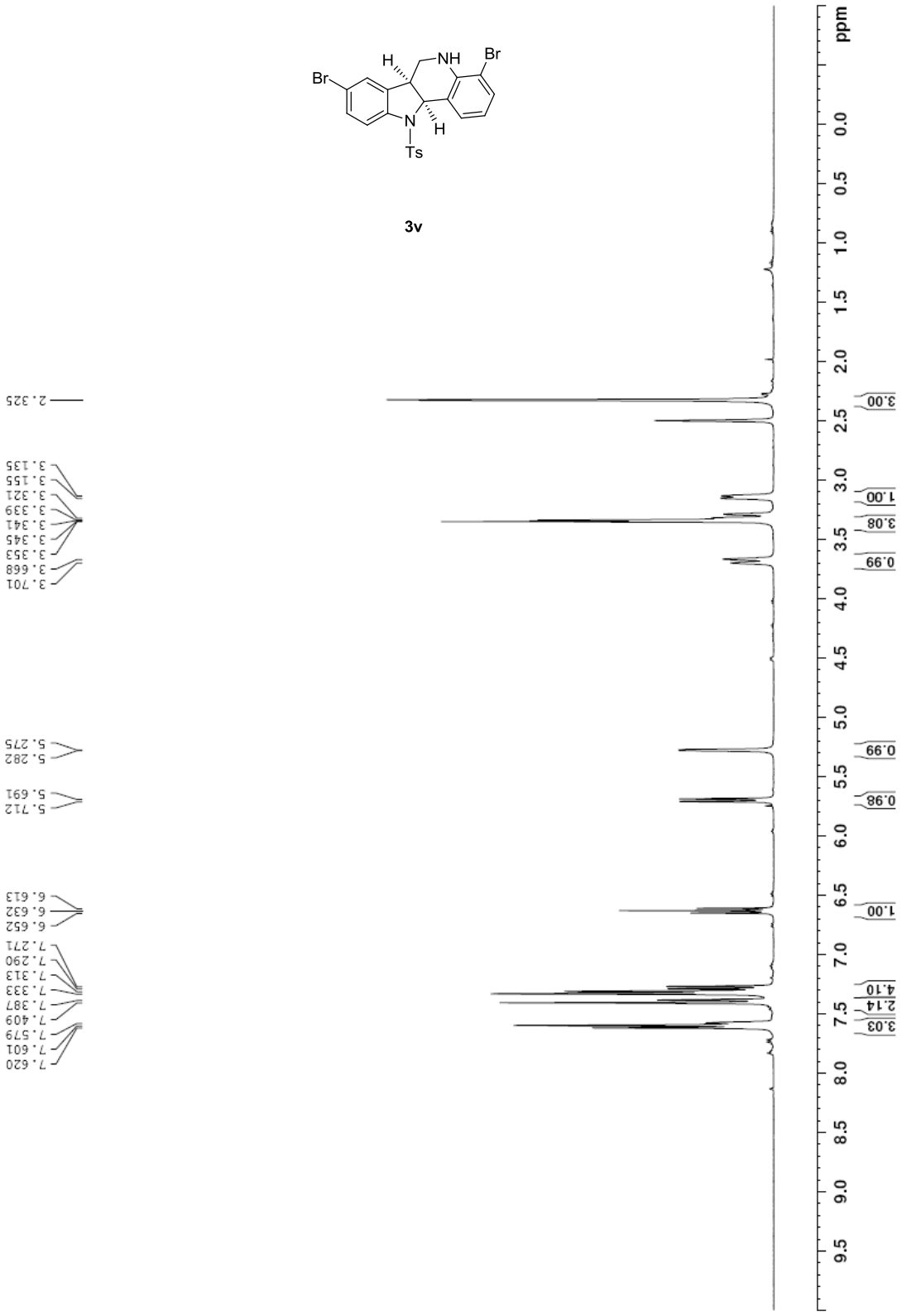


Fig. S40. ^{1}H NMR of 3v (400 MHz, DMSO-d_6)

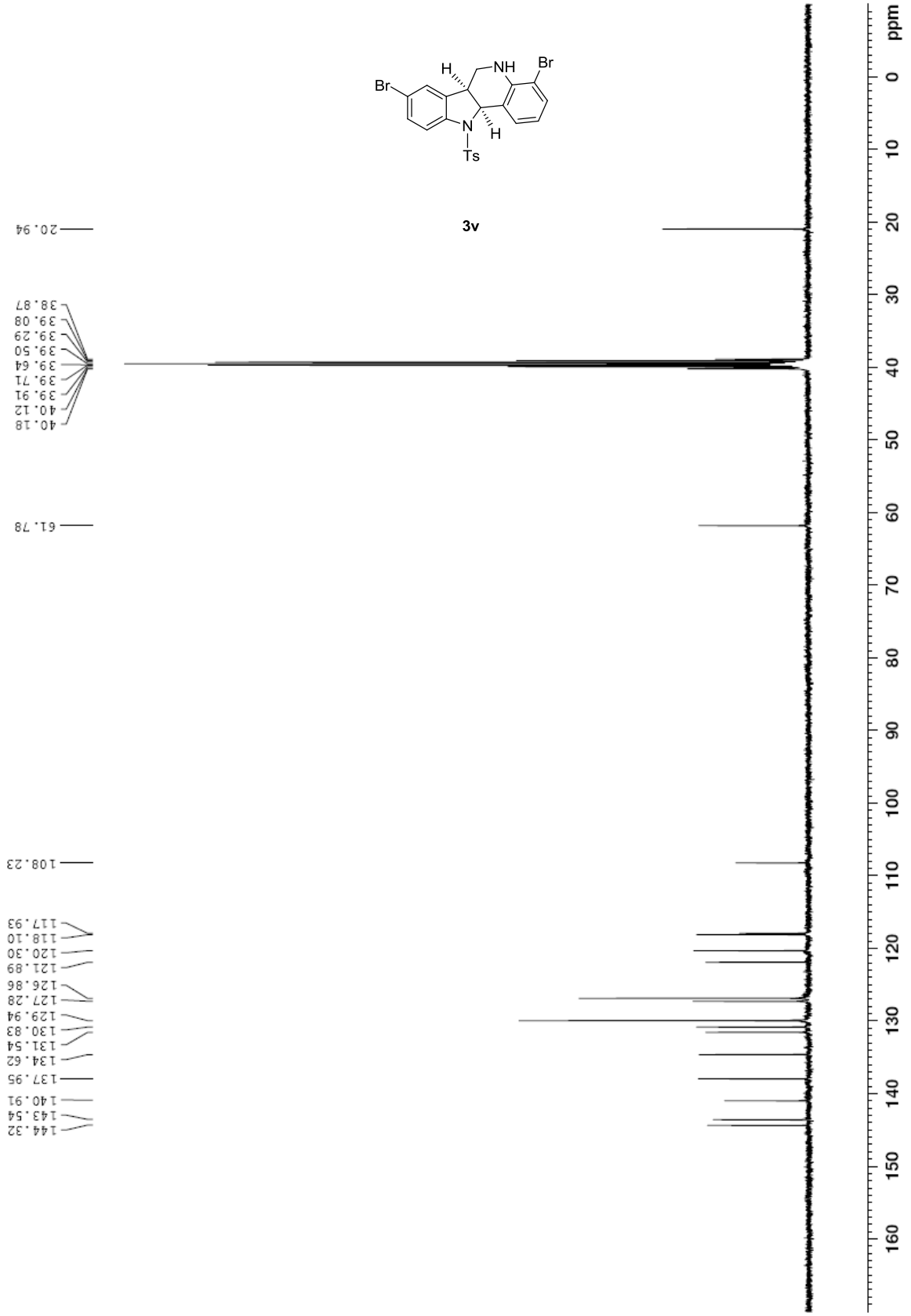


Fig. S41. ^{13}C NMR of 3v (100 MHz, DMSO-d_6)

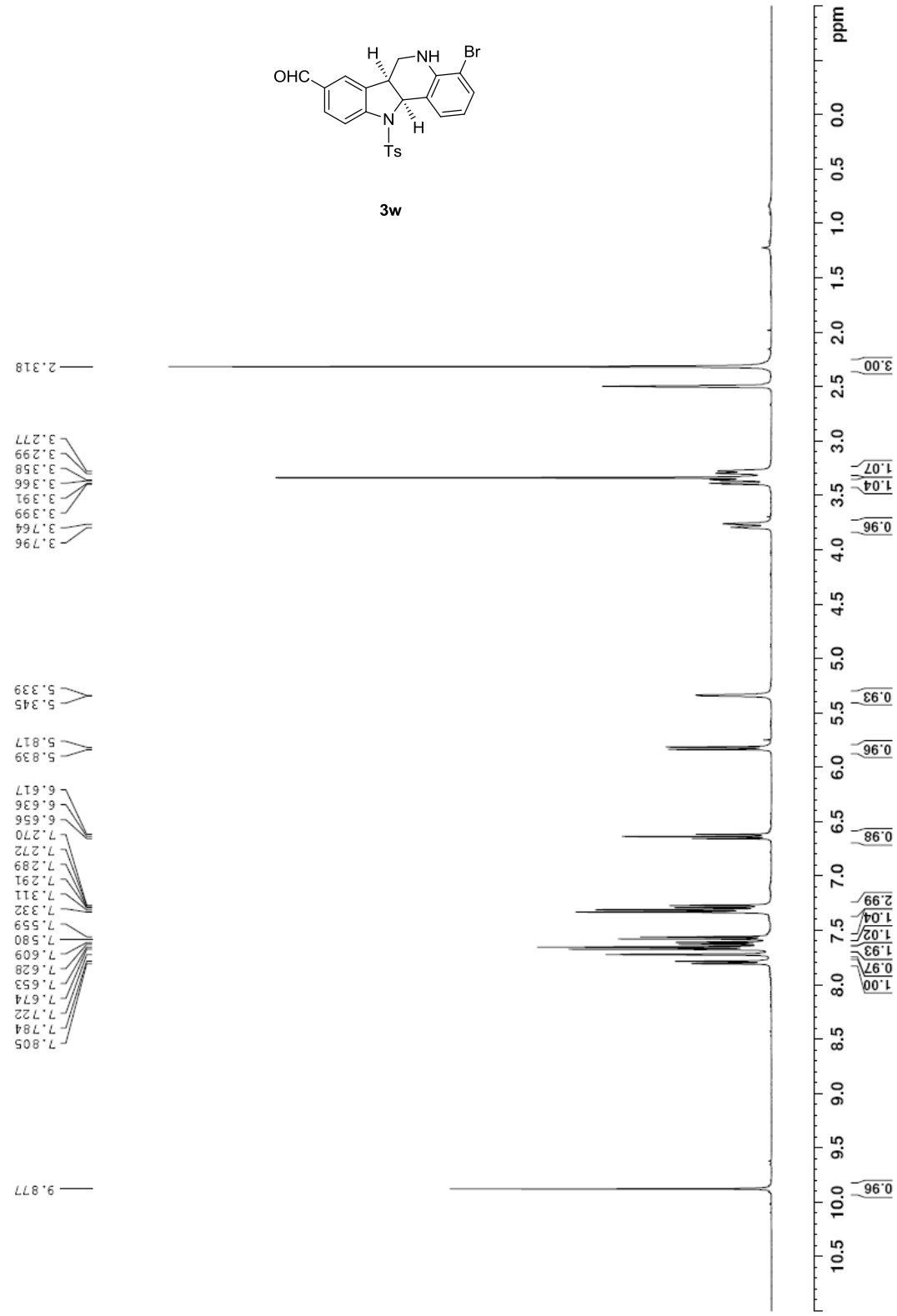


Fig. S42. ^{1}H NMR of 3w (400 MHz, DMSO-d_6)

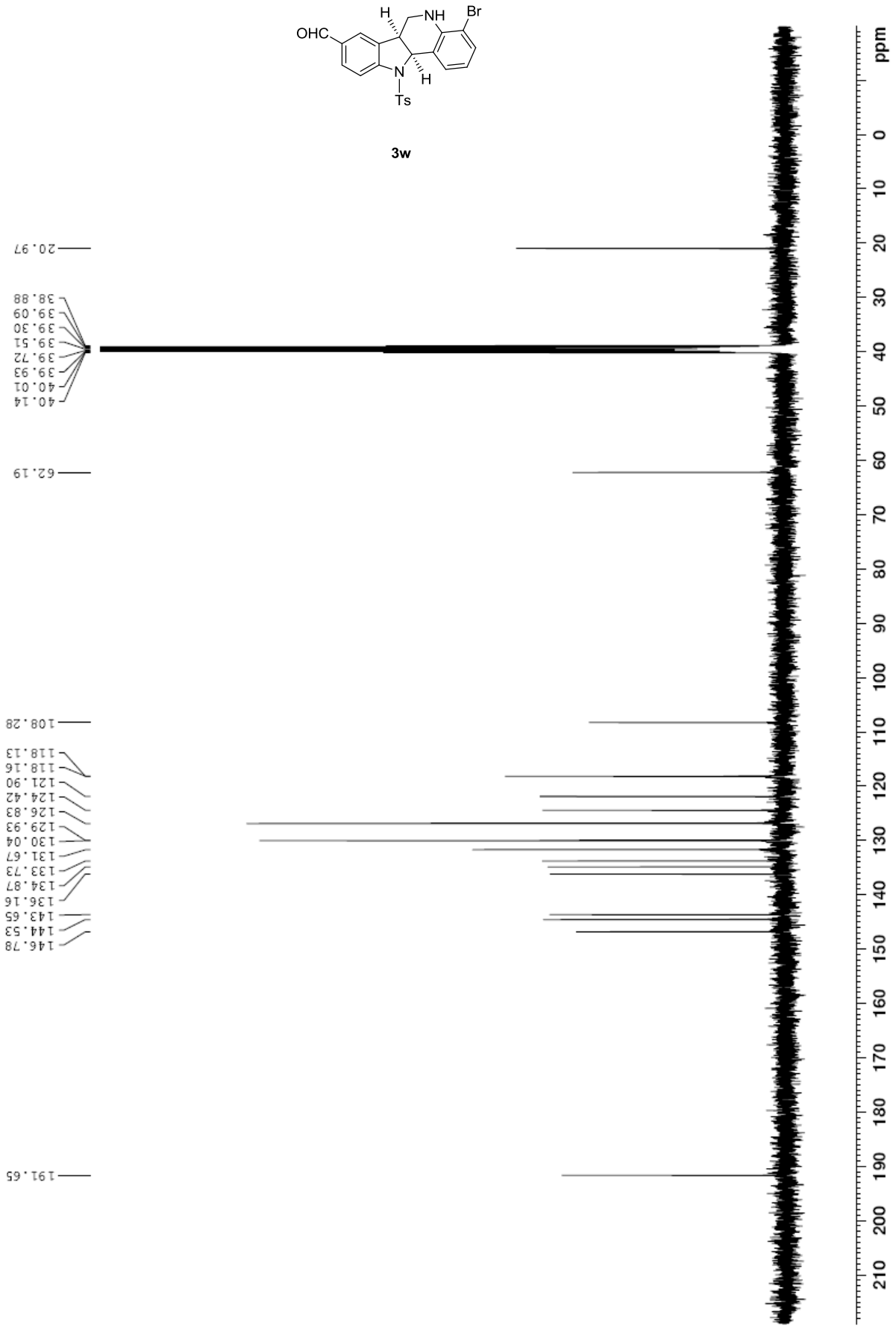


Fig. S43. ^{13}C NMR of 3w (100 MHz, DMSO-d_6)

Part 3. References

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