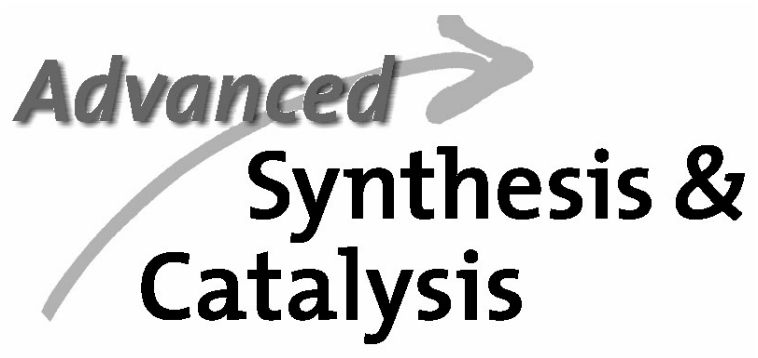

Supporting Information

Supporting Information

Catalytic Synthesis of Peptide-Derived Thiazolines and Oxazolines Using Bis(quinolinolato)dioxomolybdenum(VI) Complexes

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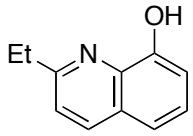
General Method.

IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. ^{1}H spectra were measured on a Varian Gemini-2000 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethysilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; m = multiplet), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a Varian Gemini-2000 spectrometer (75 MHz) or Varian INOVA-500 spectrometer (125 MHz). Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm). Analytical HPLC was performed on a Shimadzu Model LC-6A instrument using a column of Nomura Chemical Develosil 30-5 (4.6 × 250 mm) or a Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP instrument using a chiral column of Daicel CHIRALCEL AD-H (4.6 × 250 mm). All experiments were carried out under an atmosphere of dry nitrogen. For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. For preparative column chromatography, Merck silica gel 60 (0.040–0.063 mm) was used. High-resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Center, Nagoya University. X-ray crystallographic analysis was performed with a Bruker SMART APEX diffractometer (graphite monochromator, MoKα radiation, λ = 0.71073 Å) and the structure was solved by direct methods and expanded using Fourier techniques (Sir97 and SHELXL-97[1]).

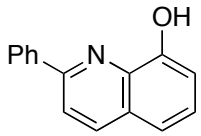
Dry toluene was purchased from Wako as the "anhydrous" and stored under nitrogen. $MoO_2(acac)_2$ (Wako Pure Chemical Industries, Ltd.), $(NH_4)_6Mo_7O_{24}•4H_2O$ (Nacalai tesque), $(NH_4)_2MoO_4$ (Aldrich), 8-quinolinol (Wako Pure Chemical Industries, Ltd.), 2-methyl-8-quinolinol (TCI) and other materials were obtained from commercial supplies and used without further purification.

2-Ethyl-8-quinolinol,[2] 2-phenyl-8-quinolinol,[3] 2,4-dimethyl-8-quinolinol,[4] 5,7-dibromo-2,4-dimethyl-8-quinolinol,[5] *cis*-bis(8-quinolinolato-*N,O*)dioxomolybdenum(VI) (**7**),[6] *cis*-bis(2-methyl-8-quinolinolato-*N,O*)dioxomolybdenum(VI) (**8**),[7] thiazoline **2a**[8] and **2b**,[9] and oxazoline **5a**[8] were reported previously.

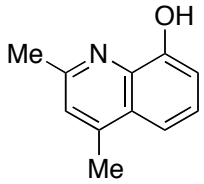
Preparation of dioxobis(quinolinolato)molybdenum(VI) Complexes



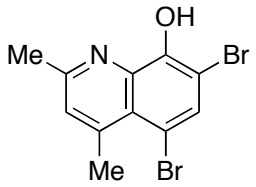
2-Ethyl-8-quinolinol.[2] A mixture of 0.26 M solution of EtLi in hexane–cyclohexane (9:1) (11.5 mL, 3.0 mmol) and 0.21 M solution of EtMgCl in THF (7.0 mL, 1.50 mmol) was stirred at –10 °C for 15 min under nitrogen atmosphere. To this solution was added a solution of 8-quinolinol (72.6 mg, 0.50 mmol) in THF (1 mL) at –78 °C. After being stirred at –10 °C for 5.5 h, the mixture was quenched by saturated aqueous NH_4Cl (5 mL), extracted with ether (15 mL), washed by brine (10 mL), dry over Na_2SO_4 and air was bubbled through the mixture for 2 h at rt. The combined organic layer was evaporated *in vacuo* and the residue was purified by column chromatography using a mixture of hexane–EtOAc (50/1 → 40/1 → 5/1) as an eluent to give the product as pale yellow solid (61.3 mg, 71%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.5 Hz, 3H), 3.00 (q, *J* = 7.5 Hz, 2H), 7.15 (dd, J = 1.2, 7.5 Hz, 1H), 7.29 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 7.5, 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H).



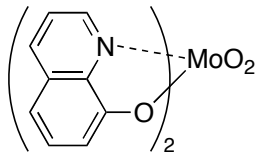
2-Phenyl-8-quinolinol. 2-Phenyl-8-quinolinol was prepared according to the reported procedure.[3] 85% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 1.5, 7.4 Hz, 1H), 7.32 (dd, *J* = 1.5, 8.2 Hz, 1H), 7.43 (dd, *J* = 7.4, 8.2 Hz, 1H), 7.49–7.60 (m, 3H), 7.85 (d, *J* = 8.4 Hz, 1H), 8.12–8.19 (m, 2H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.25–8.50 (s, 1H).



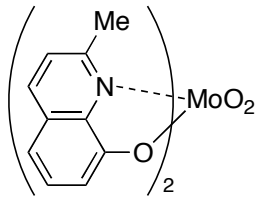
2,4-Dimethyl-8-quinolinol. 2,4-Dimethyl-8-quinolinol was prepared according to the reported procedure.[4] 45% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64 (d, *J* = 0.9 Hz, 3H), 2.67 (s, 3H), 7.13 (dd, *J* = 2.7, 6.0 Hz, 1H), 7.14 (s, 1H), 7.39 (d, *J* = 6.0 Hz, 1H), 7.40 (d, *J* = 2.7 Hz, 1H).



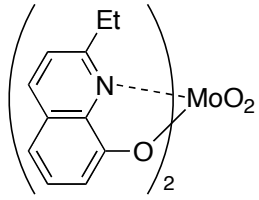
5,7-Dibromo-2,4-dimethyl-8-quinolinol. 5,7-Dibromo-2,4-methyl-8-quinolinol was prepared according to the reported procedure.[5] 92% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (s, 1H), 2.66 (s, 3H), 3.05 (s, 3H), 7.19 (s, 1H), 7.87 (s, 1H)



***cis*-Bis(8-quinolinolato-*N,O*)dioxomolybdenum(VI) (7).** **7** was prepared according to the reported procedure.[6] 98% yield; ^{1}H NMR (300 MHz, DMSO-d_6) d 7.42 (dd, J = 1.2, 7.5 Hz, 1H), 7.53 (dd, *J* = 1.2, 8.4 Hz, 1H), 7.55 (dd, *J* = 5.4, 7.8 Hz, 1H), 7.69 (dd, *J* = 7.5, 8.4 Hz, 1H), 8.52 (d, *J* = 7.8 Hz, 1H), 8.53 (d, *J* = 5.4 Hz, 1H).

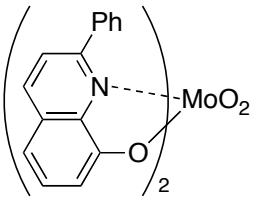


***cis*-Bis(2-methyl-8-quinolinolato-*N,O*)dioxomolybdenum(VI) (8).** **8** was prepared according to the reported procedure.[7] 99% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 0.75H), 2.73 (s, 0.75H), 2.95 (s, 3H), 3.41 (s, 1.5H), 5.30 (d, *J* = 7.5 Hz, 0.25H), 5.76 (d, *J* = 7.5 Hz, 0.25H), 6.20 (dd, *J* = 2.4, 6.3 Hz, 0.25H), 6.49 (m, 0.5H), 6.67 (t, *J* = 8.4 Hz, 0.25H), 7.01 (m, 1H), 7.15 (m, 0.5H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.21 (m, 0.5H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.30 (m, 0.5H), 7.38 (t, *J* = 7.8 Hz, 0.25H), 7.42–7.55 (m, 0.75H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.91 (d, *J* = 8.7 Hz, 0.25H), 8.00 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 0.25H), 8.12 (d, *J* = 8.7 Hz, 0.25H), 8.25 (d, *J* = 8.4 Hz, 0.25H). **8** was a ca. 2:1:1 isomeric mixture in $CDCl_3$.

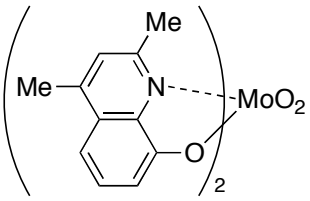


***cis*-Bis(2-ethyl-8-quinolinolato-*N,O*)dioxomolybdenum(VI) (9).** To a solution of $MoO_2(acac)_2$ (44.2 mg, 0.135 mmol) in EtOH (0.50 mL) was added a solution of 2-ethyl-8-quinolinol (47.0 mg,

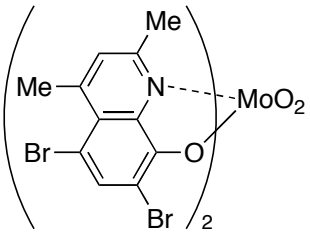
0.27 mmol) in EtOH (1.0 mL). After being stirred at ambient temperature for 12 h, **9** was obtained by filtration (58 mg, 91%). Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2. IR (KBr) 908 (Mo=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.5 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 1.7H), 1.32 (t, *J* = 7.5 Hz, 1.3H), 2.62 (m, 0.8H), 3.14 (m, 1.2H), 3.49 (m, 1.2H), 4.08 (m, 0.8H), 5.18 (d, *J* = 7.5 Hz, 0.4H), 5.74 (d, *J* = 7.5 Hz, 0.4H), 6.21 (dd, *J* = 2.4, 6.3 Hz, 0.4H), 6.46 (m, 0.8H), 6.62 (t, *J* = 7.5 Hz, 0.4H), 6.95–7.05 (m, 2.4H), 7.20–7.30 (m, 1.2H), 7.48 (t, *J* = 8.1 Hz, 1.2H), 7.53 (d, *J* = 8.1 Hz, 0.4H), 7.58 (d, *J* = 8.1 Hz, 0.4H), 7.91 (d, *J* = 8.1 Hz, 0.4H), 8.06 (d, *J* = 8.1 Hz, 0.6H), 8.15 (d, *J* = 8.1 Hz, 0.4H), 8.29 (d, *J* = 8.7 Hz, 0.6H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.0, 14.0, 14.8, 27.4, 29.1, 29.2, 111.7, 113.4, 114.7, 115.9, 116.0, 118.2, 122.2, 123.0, 123.3, 124.7, 126.4, 127.0, 127.7, 127.8, 130.2, 132.8, 136.8, 138.1, 138.5, 140.1, 144.6, 150.3, 156.5, 159.0, 166.4; **9** was a ca. 3:2 isomeric mixture in $CDCl_3$; HRMS (FAB) calcd for $C_{22}H_{21}MoN_2O_4$ $[M+H]^+$ 475.0555, found 475.0563.



***cis*-Bis(2-phenyl-8-quinolinolato-*N,O*)-dioxomolybdenum(VI) (10).** To a solution of $MoO_2(acac)_2$ (65.2 mg, 0.20 mmol) in EtOH (0.50 mL) was added a solution of 2-phenyl-8-quinolinol (88.5 mg, 0.40 mmol) in EtOH (1.0 mL). After being stirred at ambient temperature for 15 min, **10** was obtained by filtration (91 mg, 80%). Single crystals suitable for X-ray analysis were obtained from EtOH. IR (KBr) 900 (Mo=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.50 (d, *J* = 7.5 Hz, 0.2H), 5.75 (d, *J* = 5.1 Hz, 0.1H), 5.76 (d, *J* = 5.1 Hz, 0.1H), 5.96 (dd, *J* = 1.8, 7.2 Hz, 0.9H), 6.24 (d, *J* = 7.8 Hz, 0.2H), 6.48 (s, 0.2H), 6.49 (d, *J* = 2.1 Hz, 0.2H), 6.76 (t, *J* = 7.8 Hz, 0.2H), 6.97 (d, *J* = 7.8 Hz, 0.2H), 7.05 (t, *J* = 6.6 Hz, 0.6H), 7.13–7.25 (m, 4.2H), 7.35 (d, *J* = 6.9 Hz, 0.4H), 7.42–7.64 (m, 6.2H), 7.66–7.82 (m, 3.2H), 7.94 (d, *J* = 8.7 Hz, 0.2H), 8.00 (d, *J* = 8.1 Hz, 0.9H), 8.16 (m, 0.9H), 8.23 (m, 0.9H), 8.43 (d, *J* = 8.4 Hz, 0.2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 115.3, 117.5, 124.8, 127.7, 128.0, 129.5, 130.5, 137.8, 138.0, 138.2, 139.9, 155.0, 158.2, 160.1; **10** was a ca. 9:1 isomeric mixture in $CDCl_3$; HRMS (FAB) calcd for $C_{30}H_{21}MoN_2O_4$ $[M+H]^+$ 571.0555, found 571.0542.



***cis*-Bis(2,4-dimethyl-8-quinolinolato-*N,O*)-dioxomolybdenum(VI) (11).** To a solution of $MoO_2(acac)_2$ (32.6 mg, 0.10 mmol) in EtOH (0.50 mL) was added 2,4-dimethyl-8-quinolinol (34.6 mg, 0.20 mmol). After being stirred at ambient temperature for 12 h, **11** was obtained by filtration (41 mg, 87%). IR (KBr) 903 (Mo=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 0.3H), 2.53 (s, 5.3H), 2.64 (s, 0.3H), 2.67 (s, 0.4H), 2.89 (s, 5.3H), 3.34 (s, 0.4H), 6.97 (s, 2H), 7.18 (dd, *J* = 1.2, 7.5 Hz, 2H), 7.32 (dd, *J* = 1.2, 8.4 Hz, 2H), 7.46 (dd, *J* = 7.5, 8.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 18.5, 23.3, 114.4, 114.5, 125.7, 127.4, 127.7, 140.2, 147.5, 159.3, 160.3; **11** was ca. 88:7:5 isomeric mixture in $CDCl_3$; HRMS (FAB) calcd for $C_{22}H_{21}MoN_2O_4$ $[M+H]^+$ 475.0555, found 475.0550.



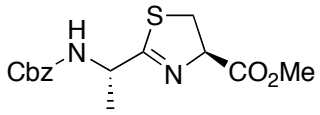
***cis*-Bis(5,7-dibromo-2,4-dimethyl-8-quinolinolato-*N,O*)-dioxomolybdenum(VI) (12).** To a solution of $MoO_2(acac)_2$ (32.6 mg, 0.10 mmol) in EtOH (0.50 mL) was added a solution of 5,7-dibromo-2,4-dimethyl-8-quinolinol (66.2 mg, 0.20 mmol) in EtOH (1.0 mL) and acetone (1.5 mL). After being stirred at reflux for 2 h, **12** was obtained by filtration (54.0 mg, 69%). IR (KBr) 1071, 803 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.92 (s, 5.1H), 2.95 (s, 5.1H), 3.05 (s, 0.45H), 3.07 (s, 0.45H), 3.29 (s, 0.45H), 3.33 (s, 0.45H), 7.05 (s, 1.7H), 7.29 (s, 0.15H), 7.44 (s, 0.15H), 7.75 (s, 0.15H), 7.87 (s, 0.15H), 7.97 (s, 1.7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 24.8 107.9, 109.0,125.6, 129.2, 136.5, 141.7, 149.4, 156.0, 161.7. **12** was ca. 85:15 isomeric mixture in $CDCl_3$; HRMS (FAB) calcd for $C_{22}H_{17}Br_4MoN_2O_4$ $[M+H]^+$ 786.6976, found 786.6948.

X-ray Crystallographic Analysis

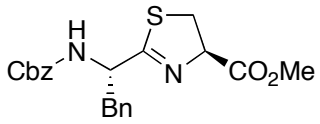
Crystal data for 9. Formula $C_{22}H_{20}MoN_2O_4$, colorless, crystal dimensions 0.40 × 0.40 × 0.30 mm^3, orthorhombic, space group $P2_12_12_1$(#19), a = 9.4211(19) Å, b = 9.4286(18) Å, c = 22.334(4) Å, V = 1983.9(7) $Å^3$, Z = 4, and D_{calc} = 1.581 g cm^{-3}, F(000) = 960, μ = 0.693 mm^{-1}, T = 223(2) K. 14851 reflections collected, 5243 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 29.14°), and 264 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0197 and *wR2* = 0.0528, GOF = 1.143. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Supplementary publication No. CCDC-630883.

Crystal data for 10. Formula $C_{30}H_{20}MoN_2O_4$, colorless, crystal dimensions 0.50 × 0.40 × 0.40 mm^3, monoclinic, space group *Cc*(#7), a = 27.814(5) Å, b = 12.760(2) Å, c = 15.796(3) Å, β = 119.415(3)°, V = 4883.3(14) $Å^3$, Z = 8, and D_{calc} = 1.546 g cm^{-3}, F(000) = 2304, μ = 0.578 mm^{-1}, T = 223(2) K. 17873 reflections collected, 11153 independent reflections with $I > 2\sigma(I)$ ($2\theta_{max}$ = 29.11°), and 667 parameters were used for the solution of the structure. The non-hydrogen atoms were refined anisotropically. R_1 = 0.0236 and *wR2* = 0.0630, GOF = 1.018. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Supplementary publication No. CCDC-630884.

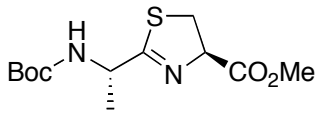
General Procedure for the Dehydrative Cyclization of Dipeptides 1 and 4. A 20-mL, single-necked, round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a 5-mL pressure-equalized addition funnel [containing a cotton plug and ca. 0.1 g of CaH_2] surmounted by a reflux condenser was charged with a dipeptide **1** or **4** (0.10 mmol) and a molybdenum(VI) complex (1 mol %) in toluene (10 mL). The mixture was heated for several hours under azeotropic reflux conditions with the removal of water. The reaction mixture was cooled to ambient temperature, washed with saturated aqueous solution of $NaHCO_3$ (10 mL) and brine (10 mL), and the organic solvent was then removed to give a crude product. The obtained crude product was purified by column chromatography on silica gel using toluene–acetone (for **2**) or hexane–EtOAc (for **5**), to give a corresponding thiazoline **2** or oxazoline **5**.



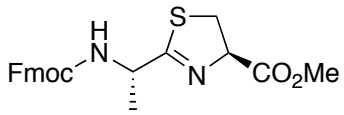
Thiazoline 2a. Spectral data of thiazoline **2a** were identical with those in ref 8. The data did not provide any evidence of the presence of the epimer **3a**. The diastereo ratio was determined by HPLC analysis on Develosil 30-5. **2a:** t_R = 32.2 min, **3a:** t_R = 34.3 min (hexane–EtOAc–MeOH = 64:16:1).



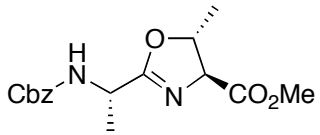
Thiazoline 2b. Spectral data of thiazoline **2b** were identical with those in ref 9. The diastereo ratio was determined by HPLC analysis on Develosil 30-5. **2b:** t_R = 16.1 min, **3b:** t_R = 17.6 min (hexane–EtOAc–MeOH = 32:8:1).



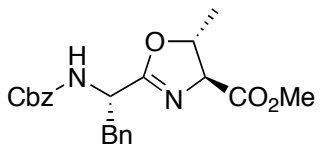
Thiazoline 2c. IR (neat) 3360, 1715, 1621, 1581, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 1.45(m, 3H), 3.53 (dd, *J* = 11.4, 9.6 Hz, 1H), 3.61 (dd, *J* = 11.4, 9.0 Hz, 1H), 3.82 (s, 3H), 4.52-4.65 (m, 1H), 5.11 (t, *J* = 9.6 Hz, 1H), 5.29 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 28.3, 35.4, 49.2, 52.7, 77.8, 79.8, 154.8, 171.0, 177.2; HRMS (FAB) calcd for $C_{12}H_{21}O_4N_2S$ $[M+H]^+$ 289.1222, found 289.1213. The diastereo ratio was determined by HPLC analysis on AD-H. **5b:** t_R = 64.4 min, **6b:** t_R = 58.8 min (hexane–*i*PrOH = 50:1).



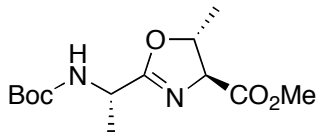
Thiazoline 2d. IR (neat) 3311, 1716, 1522, 1449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.49 (d, *J* = 6.9 Hz, 3H), 3.51-3.65 (m, 2H), 3.82 (s, 3H), 4.23 (t, *J* = 6.9 Hz, 1H), 4.33-4.47 (m, 2H), 4.66 (dq, *J* = 7.5, 6.9 Hz, 1H), 5.11 (t, *J* = 9.0 Hz, 1H), 5.62 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.58–7.63 (m, 2H), 7.76 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 35.6, 47.1, 49.7, 52.8, 66.9, 77.7, 119.9, 125.0, 125.1, 127.0, 127.6, 141.2, 143.7, 143.9, 155.4, 171.0, 176.7; HRMS (FAB) calcd for $C_{22}H_{23}O_4N_2S$ $[M+H]^+$ 411.1379, found 411.1359. The diastereo ratio was determined by HPLC analysis on Develosil 30-5. **5b:** t_R = 25.9 min, **6b:** t_R = 27.1 min (hexane–EtOAc–MeOH = 32:8:1).



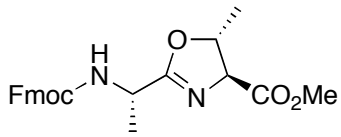
Oxazoline 5a.[8b] IR (KBr) 3326, 1724, 1661, 1531, 1454 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.44 (d, *J* = 7.2 Hz, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 4.27 (d, *J* = 7.5 Hz, 1H), 4.52 (dq, *J* = 7.5, 7.2 Hz, 1H), 4.86 (dq, *J* = 7.5, 7.2 Hz, 1H), 5.08 (d, *J* = 12.3 Hz, 1H), 5.13 (d, *J* = 12.3 Hz, 1H), 5.53 (br d, *J* = 7.5 Hz, 1H), 7.27–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 20.6, 45.2, 52.5, 66.6, 74.0, 79.7, 127.9, 127.9, 128.3, 136.2, 155.3, 169.7, 171.0; HRMS (FAB) calcd for $C_{16}H_{21}O_5N_2$ $[M+H]^+$ 321.1450, found 321.1439. The diastereo ratio was determined by HPLC analysis on Develosil 30-5. **5a:** t_R = 9.7 min, **6a:** t_R = 10.9 min (hexane–EtOAc–MeOH = 16:8:1).



Oxazoline 5b. IR (neat) 3328, 1731, 1660, 1507 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.3 Hz, 3H), 3.06 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.14 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.72 (s, 3H), 4.22 (d, *J* = 6.0 Hz, 1H), 4.74-4.80 (m, 1H), 4.91 (dq, *J* = 6.3, 6.0 Hz, 1H), 5.05 (d, *J* = 12.3 Hz, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.41 (d, *J* = 8.7 Hz, 1H), 7.08-7.11 (m, *2*H), 7.21–7.38 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7, 38.6, 50.1, 52.5, 66.8, 74.2, 79.6, 126.9, 127.9, 128.0, 128.3, 128.4, 129.6, 135.4, 136.3, 155.4, 167.9, 170.8; HRMS (FAB) calcd for $C_{22}H_{25}O_5N_2$ $[M+H]^+$ 397.1763, found 397.1776. The diastereo ratio was determined by HPLC analysis on Develosil 30-5. **5b:** t_R = 18.0 min, **6b:** t_R = 20.8 min (hexane–EtOAc–MeOH = 32:8:1).

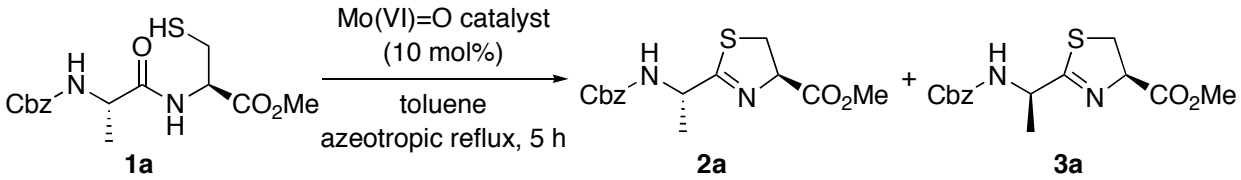


Oxazoline 5c. IR (KBr) 3370, 1715, 1661, 1506, 1454 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.41 (d, *J* = 6.9 Hz, 3H), 1.44 (s, 9H), 1.45 (d, *J* = 6.3 Hz, 3H), 3.79 (s, 3H), 4.27 (d, *J* = 7.5 Hz, 1H), 4.45 (br q, *J* = 6.9 Hz, 1H), 4.86 (dq, *J* = 7.5, 6.3 Hz, 1H), 5.29 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.6, 20.8, 28.2, 44.8, 52.5, 52.6, 74.1, 79.7, 154.8, 170.2, 171; HRMS (FAB) calcd for $C_{13}H_{23}O_5N_2$ $[M+H]^+$ 287.1607, found 287.1617. The diastereo ratio was determined by HPLC analysis on AD-H. **5c:** t_R = 63.6 min, **6c:** t_R = 59.5 min (hexane–*i*PrOH= 50:1).

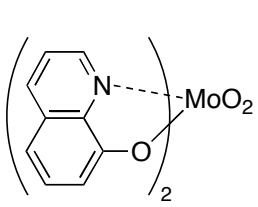


Oxazoline 5c. IR (KBr) 3425, 1618 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45 (d, *J* = 6.6 Hz, 6H), 3.80 (s, 3H), 4.22 (t, *J* = 6.9 Hz, 1H), 4.29 (d, *J* = 7.5 Hz, 1H), 4.39 (d, *J* = 6.9 Hz, 2H), 4.53 (dq, *J* = 7.5, 6.6 Hz, 1H), 4.87 (dq, *J* = 7.5, 6.6 Hz, 1H), 5.61 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.58–7.63 (m, 2H), 7.77 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 20.8, 45.3, 47.1, 52.7, 66.9, 74.1, 79.9, 119.9, 125.1, 127.0, 127.6, 141.2, 143.7, 143.9, 155.5, 169.9, 171.1; HRMS (FAB) calcd for $C_{23}H_{25}O_5N_2$ $[M+H]^+$ 409.1763, found 409.1777. The diastereo ratio was determined by HPLC analysis on Develosil 30-5. **5c:** t_R = 23.2 min, **6c:** t_R = 29.0 min (hexane–EtOAc–MeOH = 32:8:1).

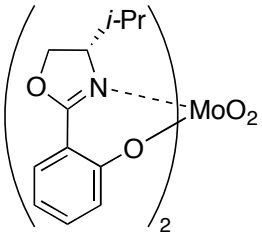
Investigation of Catalytic Activities of Various Molybdenum(VI) Complexes.



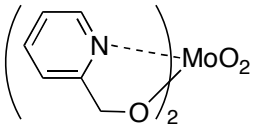
Mo(VI)=O catalyst
yield (%)
dr (**2a**:**3a**)



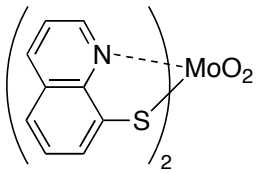
80
96:4



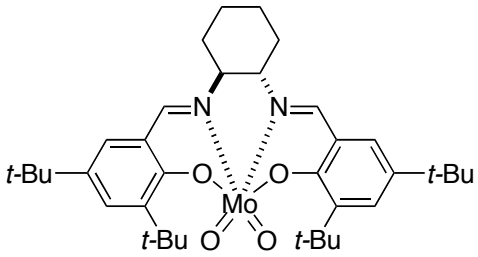
80
92:8



78
96:4



68
96:4



15
93:7

References.

1. Sheldrick, G. M. SHELXL-97, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

2. Kaneko, H.; Ueno, K. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1910.

3. Delapierre, G.; Brunel, J. M.; Constantieux, T; Buono, G. *Tetrahedron: Asymmetry* **2001**, *12*, 1345.

4. Uchiyama, K.; Hayashi, Y.; Narasaka, K. *Synlett* **1997**, 445.

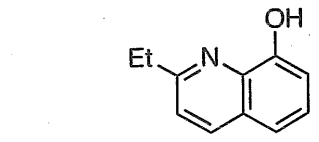
5. Phillips, J. P.; Elbinger, R. L.; Merritt, Jr., L. L. *J. Am. Chem. Soc.* **1949**, *71*, 3986.

6. (a) Dawoodi, Z.; Kelly, R. L. *Polyhedron* **1986**, *5*, 271. (b) Isbell, Jr., A. F.; Sawyer, D. T. *Inorg. Chem.* **1971**, *10*, 2449.

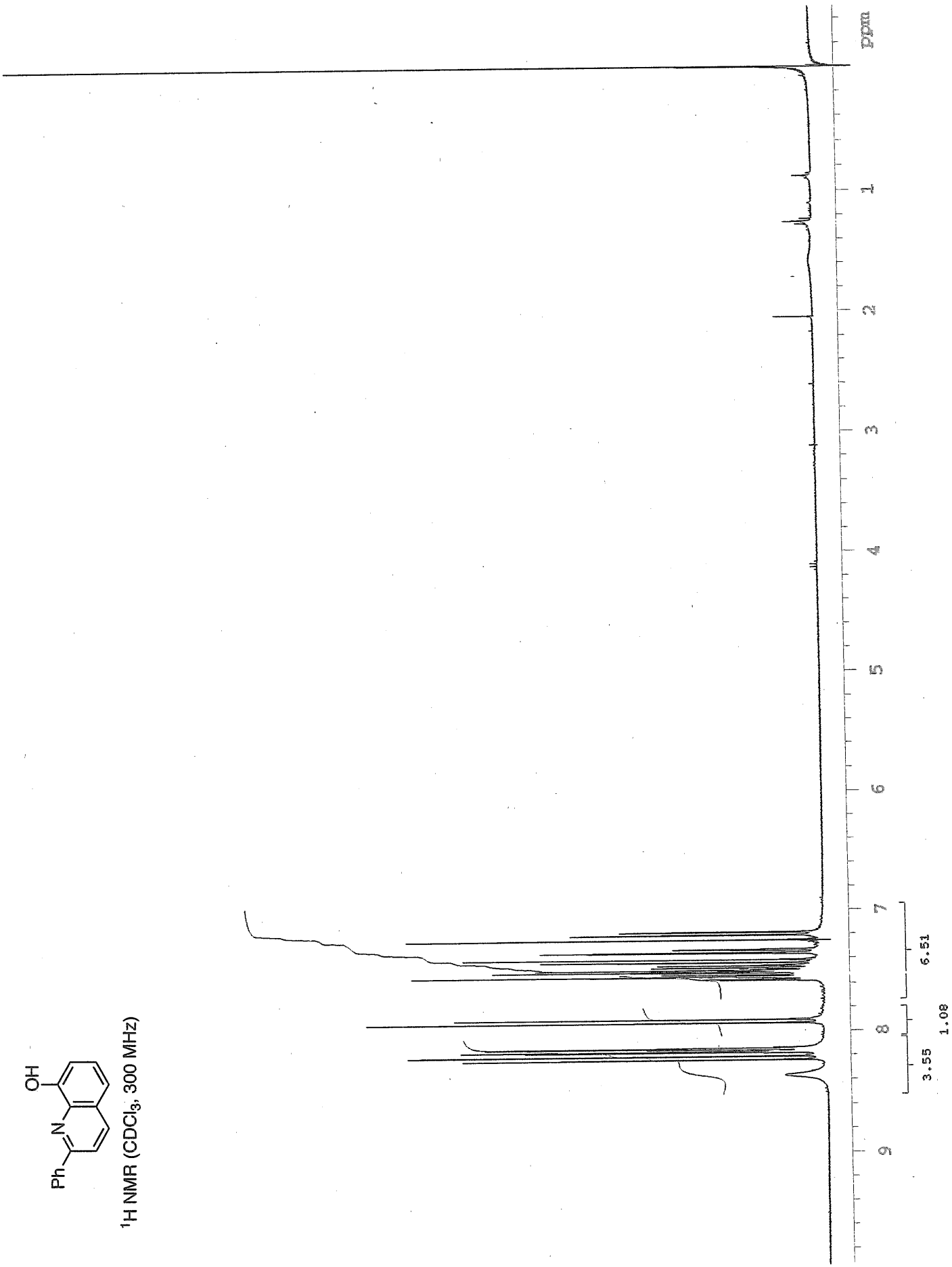
7. Fun, H.-K.; Sivakumar, K.; Niu, J.-Y.; Wang, J.-P.; You, X.-Z. *Acta Cryst.* **1996**, *C52*, 1150.

8. (a) Yonetani, K.; Hirotsu, Y.; Shiba, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3302. (b) Sakakura, A.; Kondo, R.; Ishihara, K. *Org. Lett.* **2005**, *7*, 1971.

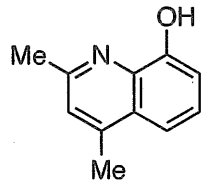
9. Wipf, P.; Fritch, P. C. *Tetrahedron Lett.* **1994**, *35*, 5397.



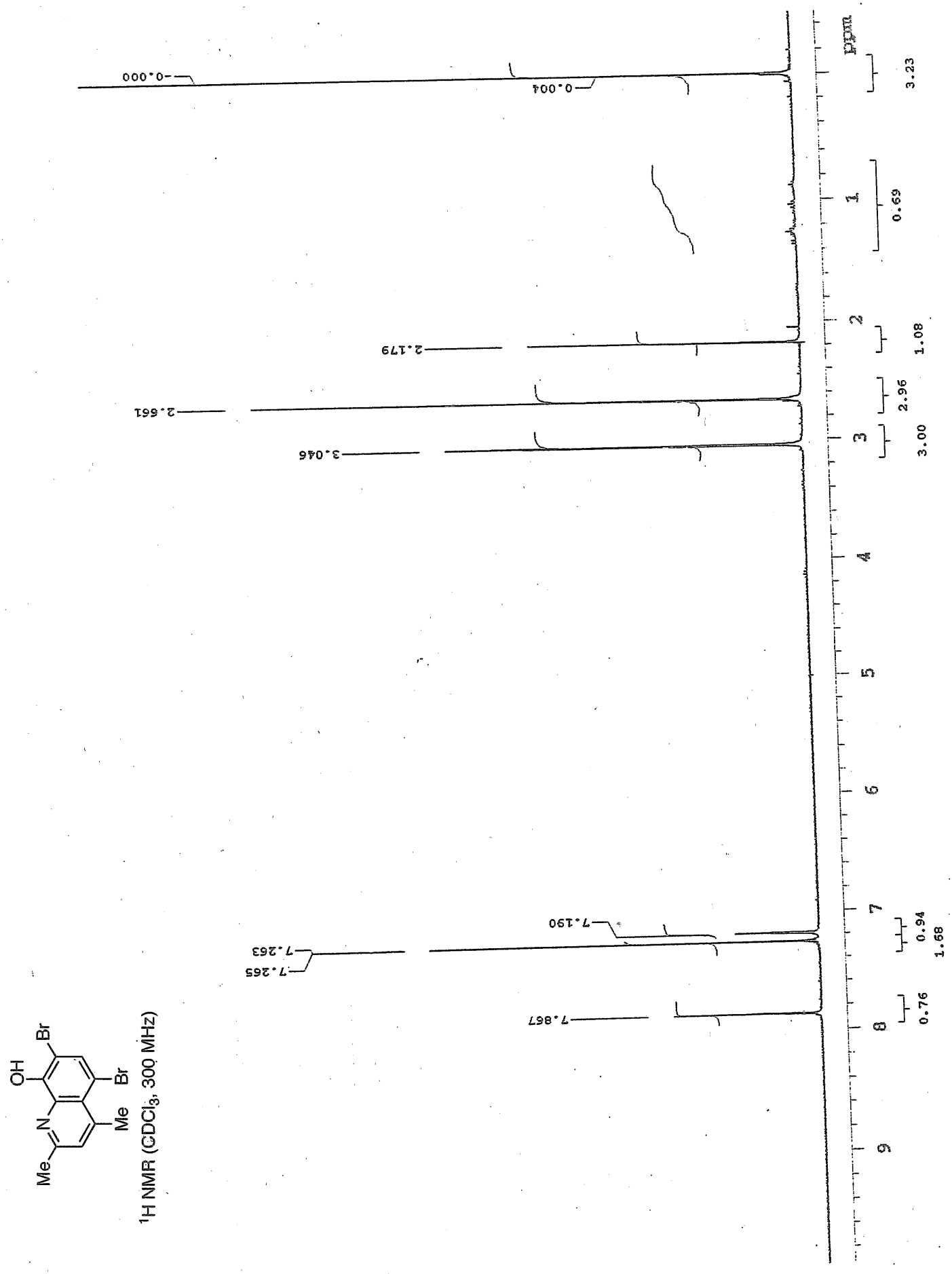
^{1}H NMR ($CDCl_3$, 300 MHz)

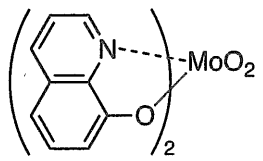


^{1}H NMR ($CDCl_3$, 300 MHz)



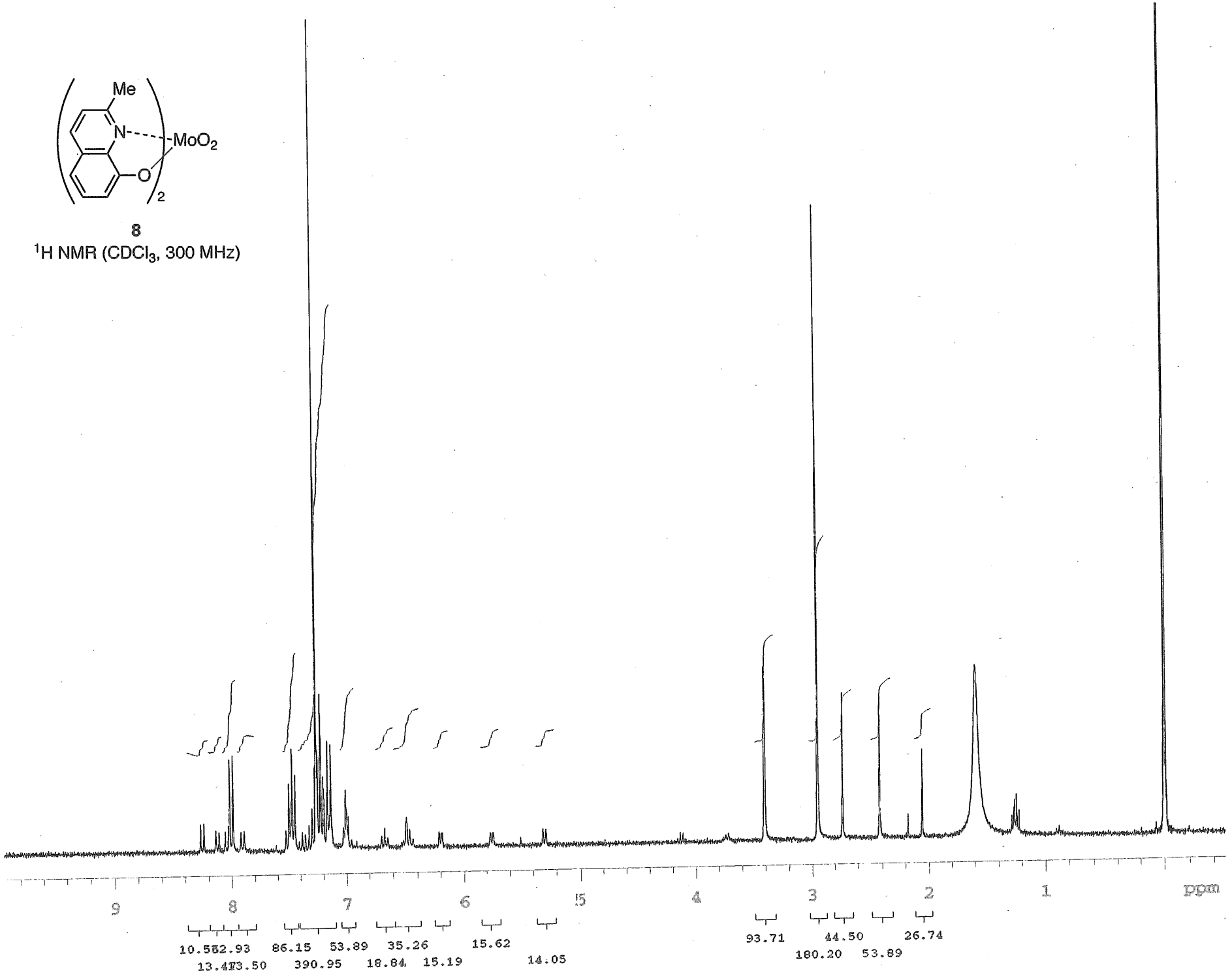
^{1}H NMR ($CDCl_3$, 300 MHz)

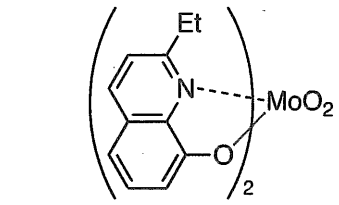

Br
OH
Br
N
Me
Me
^{1}H NMR ($CDCl_3$, 300 MHz)
0.000
0.004
2.179
2.661
3.046
7.190
7.263
7.265
7.867
ppm
3.23
0.69
1.08
2.96
3.00
0.94
1.68
0.76



7

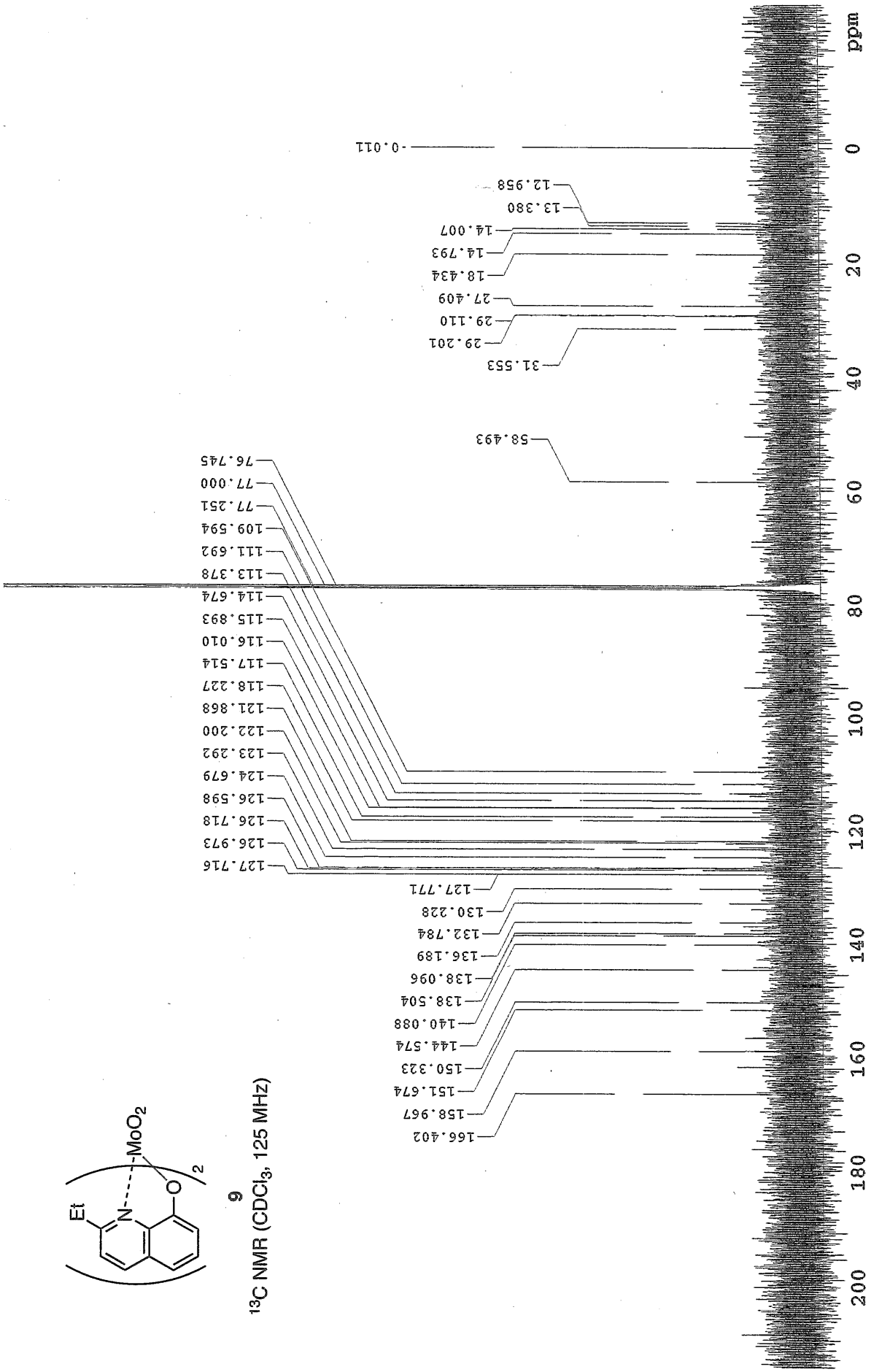
^{1}H NMR (DMSO-d_6, 300 MHz)

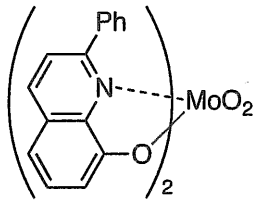

Me
N
MoO2
O
2
8
1H NMR (CDCl3, 300 MHz)
9
8
7
6
5
4
3
2
1
ppm
10.58
2.93
13.47
3.50
86.15
53.89
390.95
35.26
18.84
15.19
15.62
14.05
93.71
44.50
180.20
53.89
26.74



9

^{1}H NMR ($CDCl_3$, 300 MHz)

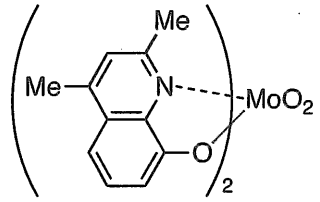

Et
N
O
MoO2
2
9
13C NMR (CDCl3, 125 MHz)
ppm
0
20
40
60
80
100
120
140
160
180
200
-0.011
12.958
13.380
14.007
14.793
18.434
27.409
29.110
29.201
31.553
58.493
76.745
77.000
77.251
109.594
111.692
113.378
114.674
115.893
116.010
117.514
118.227
121.868
122.200
123.292
124.679
126.598
126.718
126.973
127.716
127.771
130.228
132.784
136.189
138.096
138.504
140.088
144.574
150.323
151.674
158.967
166.402



10

^{1}H NMR ($CDCl_3$, 300 MHz)

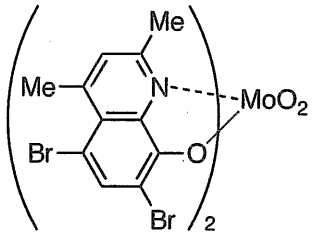
10
^{13}C NMR ($CDCl_3$, 125 MHz)
MoO_2
Ph
N
O
2
ppm
0
20
40
60
80
100
120
140
160
180
200
-0.008
76.749
77.000
77.255
110.152
115.315
117.536
117.619
119.596
124.778
127.377
127.497
127.683
127.960
128.877
129.482
129.587
130.527
136.997
137.802
138.209
139.892
154.954
158.220
160.099



11

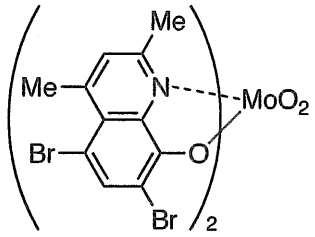
^{1}H NMR ($CDCl_3$, 300 MHz)

11
^{13}C NMR ($CDCl_3$, 125 MHz)
Me
N
MoO_2
O
2
Me
160.256
159.320
147.476
140.208
127.716
127.377
125.699
114.514
114.382
77.251
77.000
76.745
30.941
23.273
18.536
-0.019
ppm
0
20
40
60
80
100
120
140
160
180
200



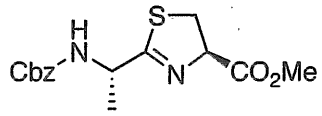
12

^{1}H NMR ($CDCl_3$, 300 MHz)



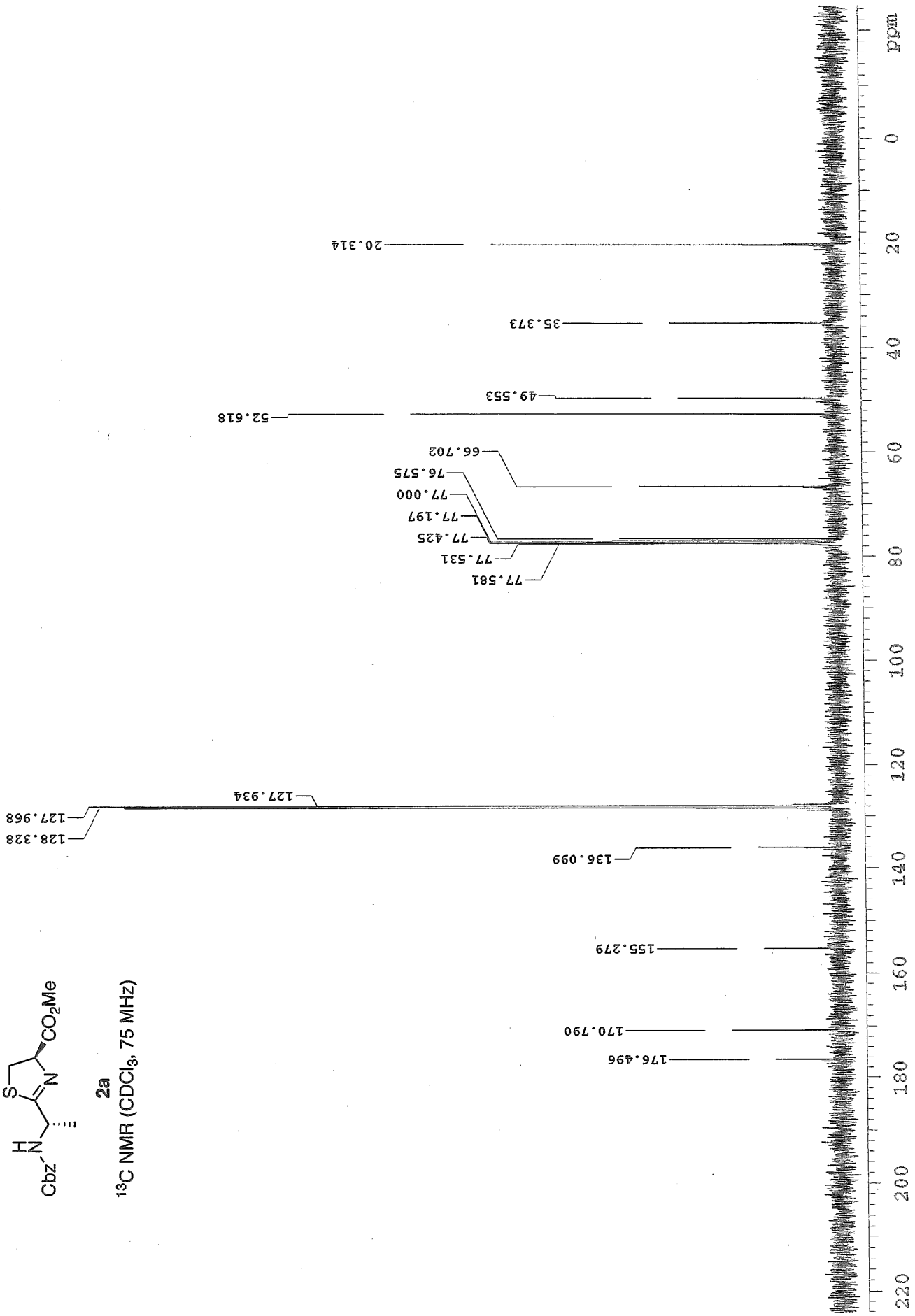
12

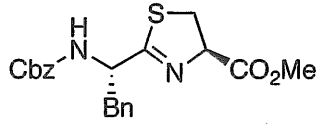
^{13}C NMR ($CDCl_3$, 125 MHz)



2a

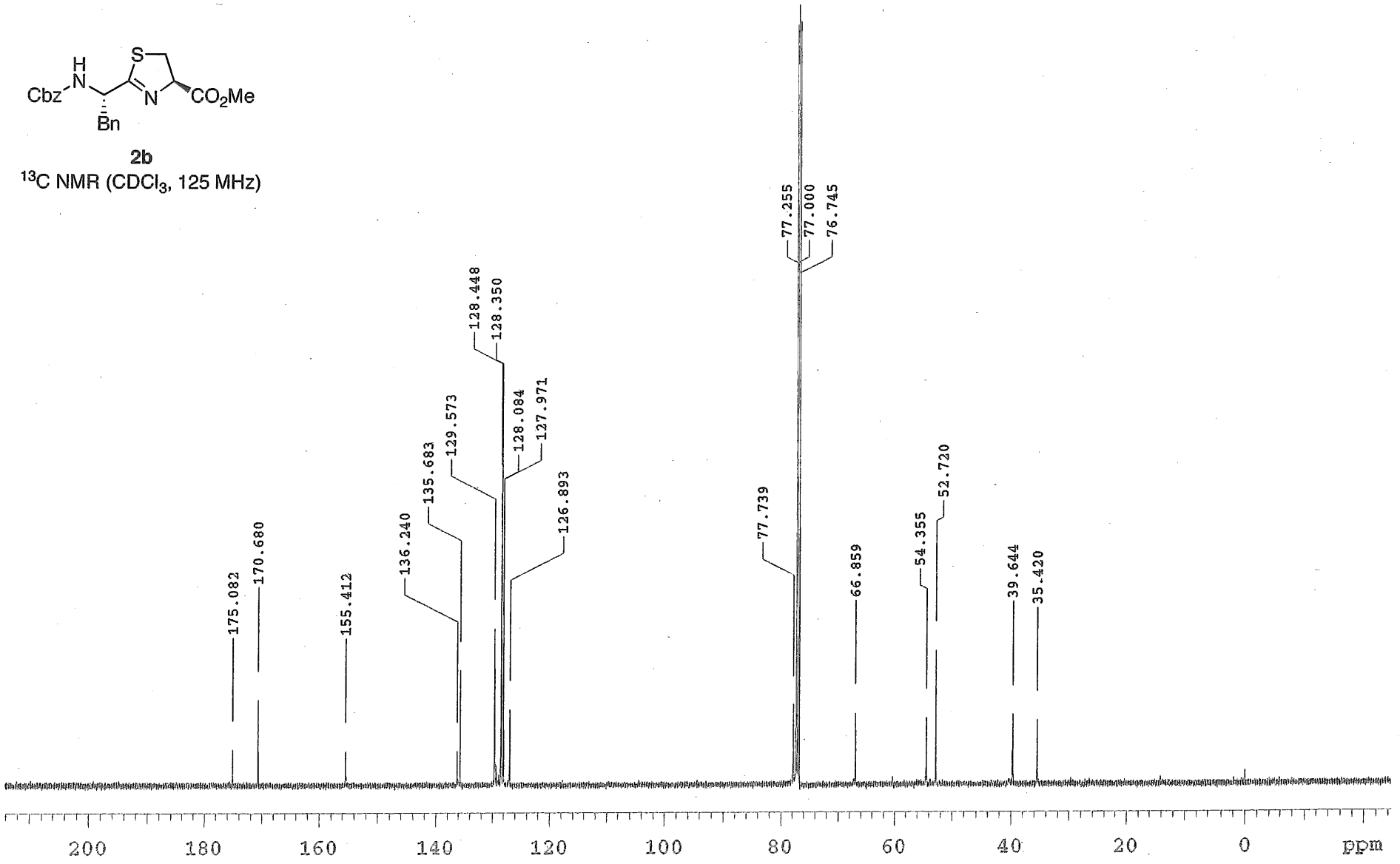
^{1}H NMR ($CDCl_3$, 300 MHz)

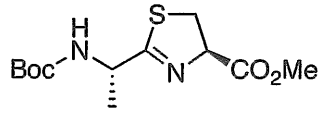

20.314
35.373
49.553
52.618
66.702
76.575
77.000
77.197
77.425
77.531
77.581
127.934
127.968
128.328
136.099
155.279
170.790
176.496
ppm
0
20
40
60
80
100
120
140
160
180
200
220
CO2Me
S
N
H
N
Cbz
2a
13C NMR (CDCl3, 75 MHz)



2b

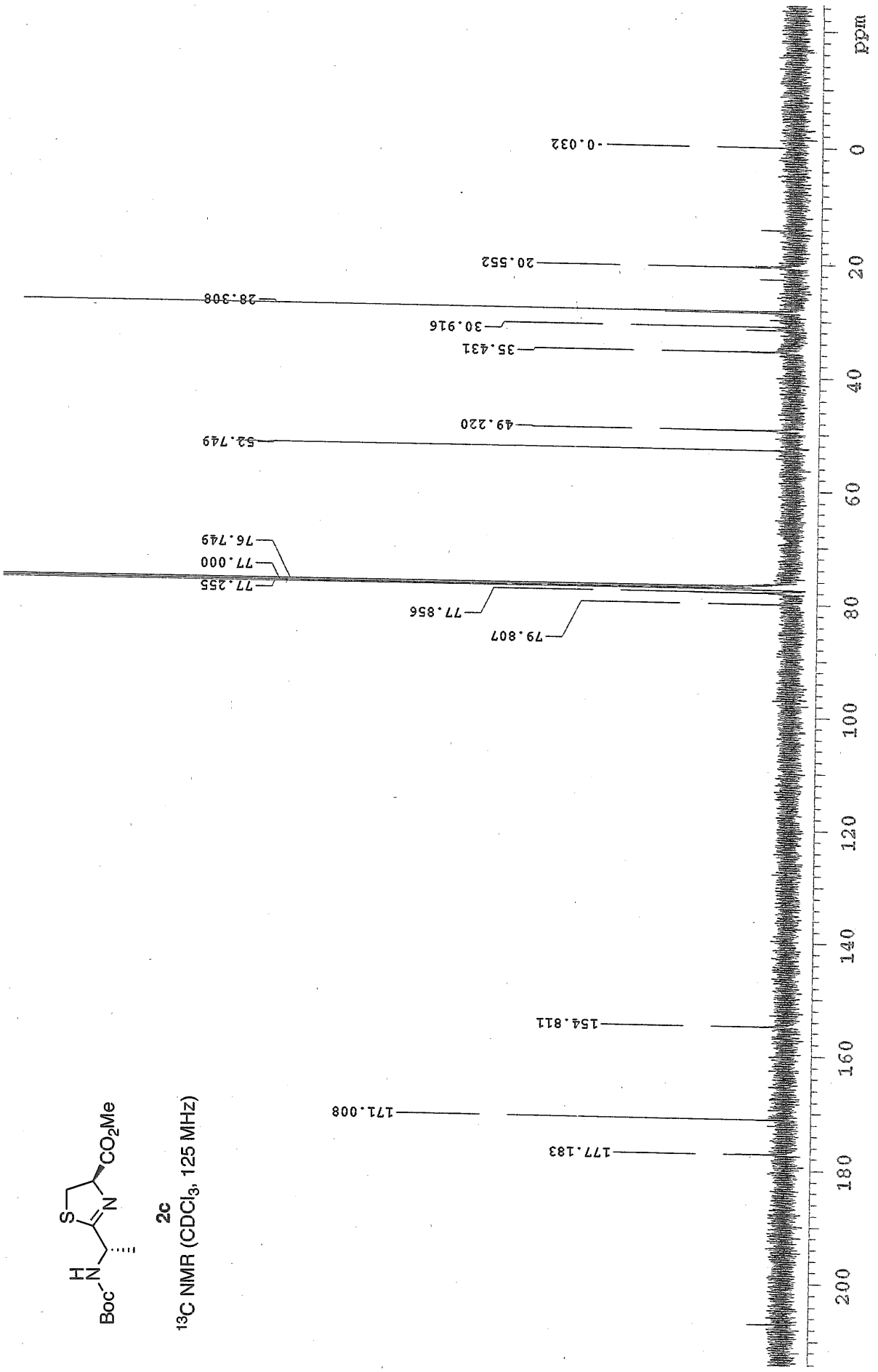
^{1}H NMR ($CDCl_3$, 300 MHz)


Cbz
H
N
S
N
CO2Me
Bn
2b
13C NMR (CDCl3, 125 MHz)
175.082
170.680
155.412
136.240
135.683
129.573
128.448
128.350
128.084
127.971
126.893
77.739
77.255
77.000
76.745
66.859
54.355
52.720
39.644
35.420
200
180
160
140
120
100
80
60
40
20
0
ppm



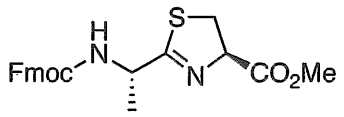
2c

^{1}H NMR ($CDCl_3$, 300 MHz)



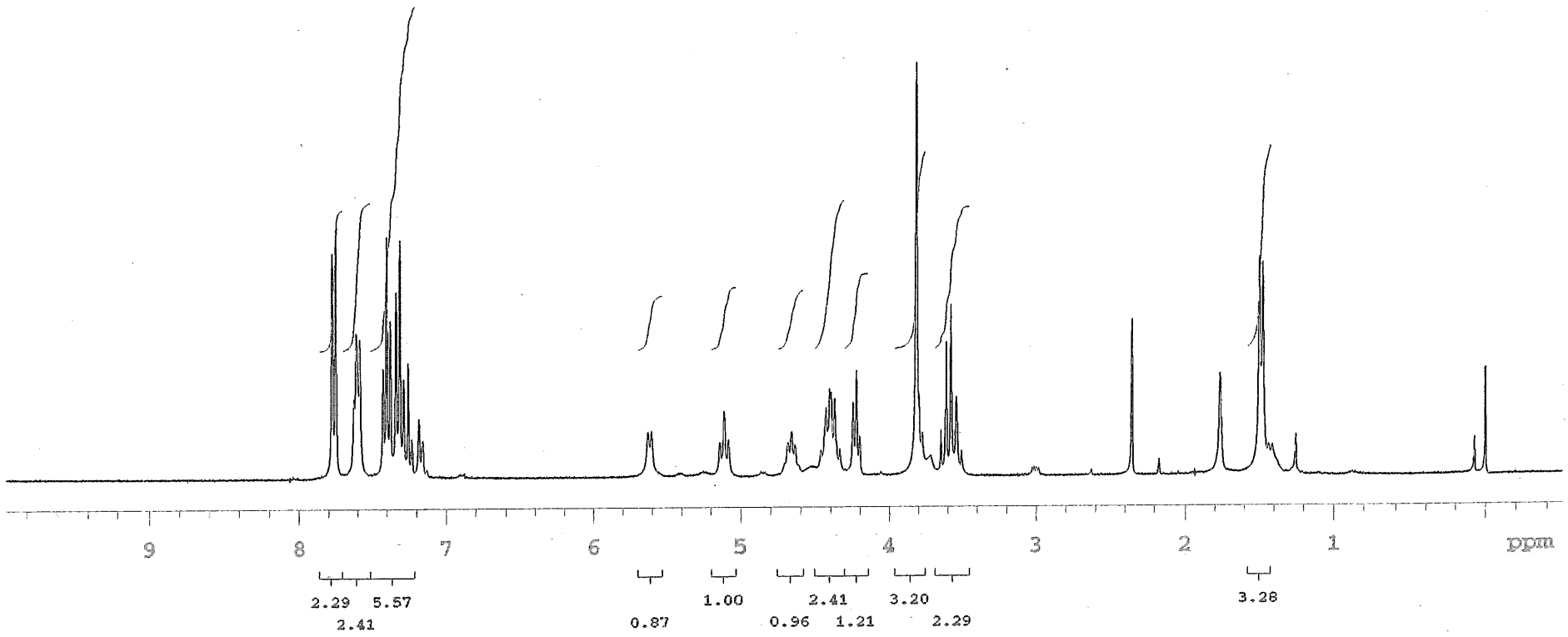
2c

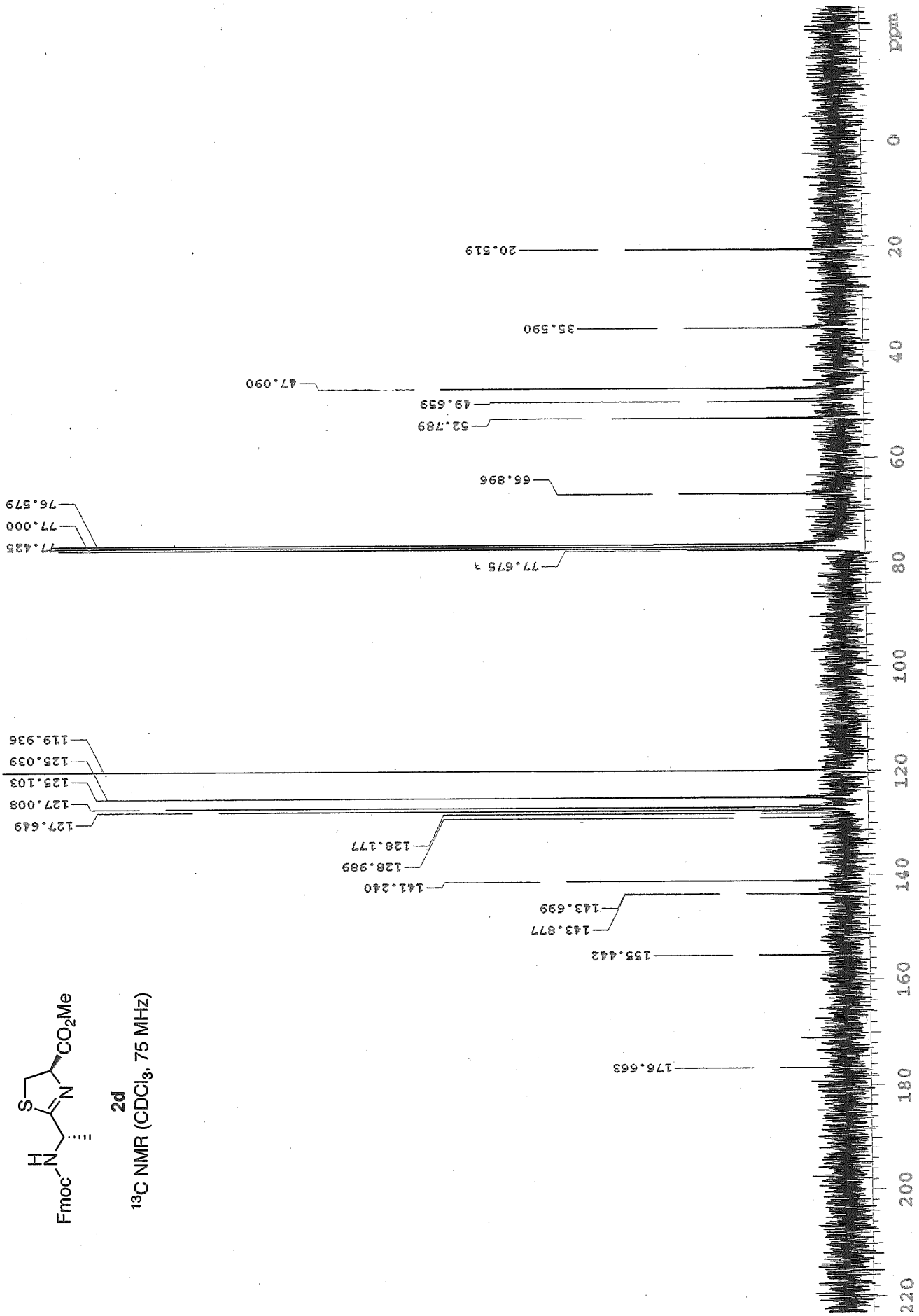
^{13}C NMR ($CDCl_3$, 125 MHz)

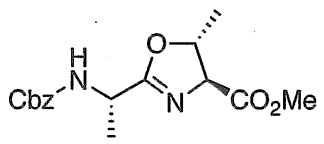


2d

^{1}H NMR ($CDCl_3$, 300 MHz)

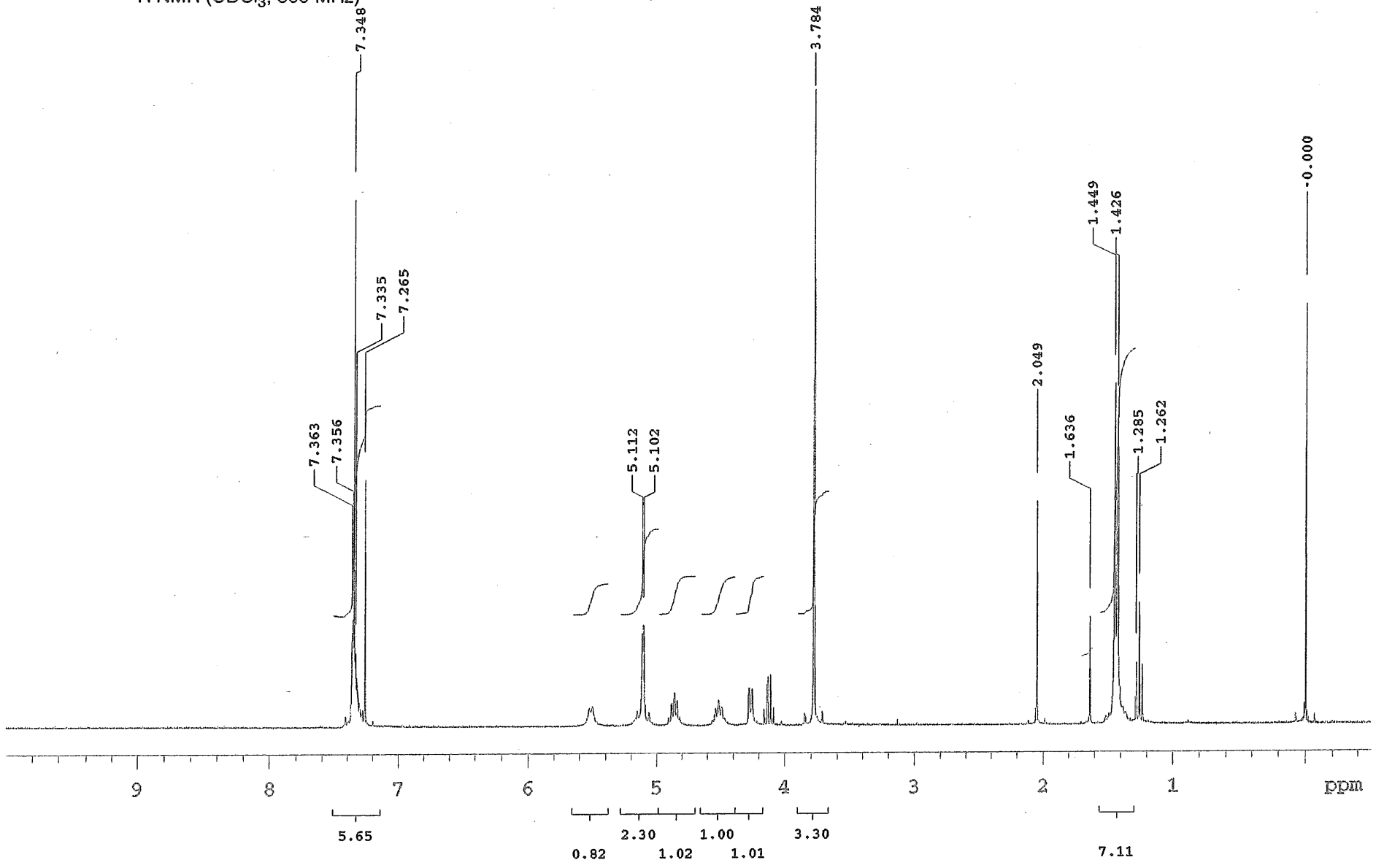


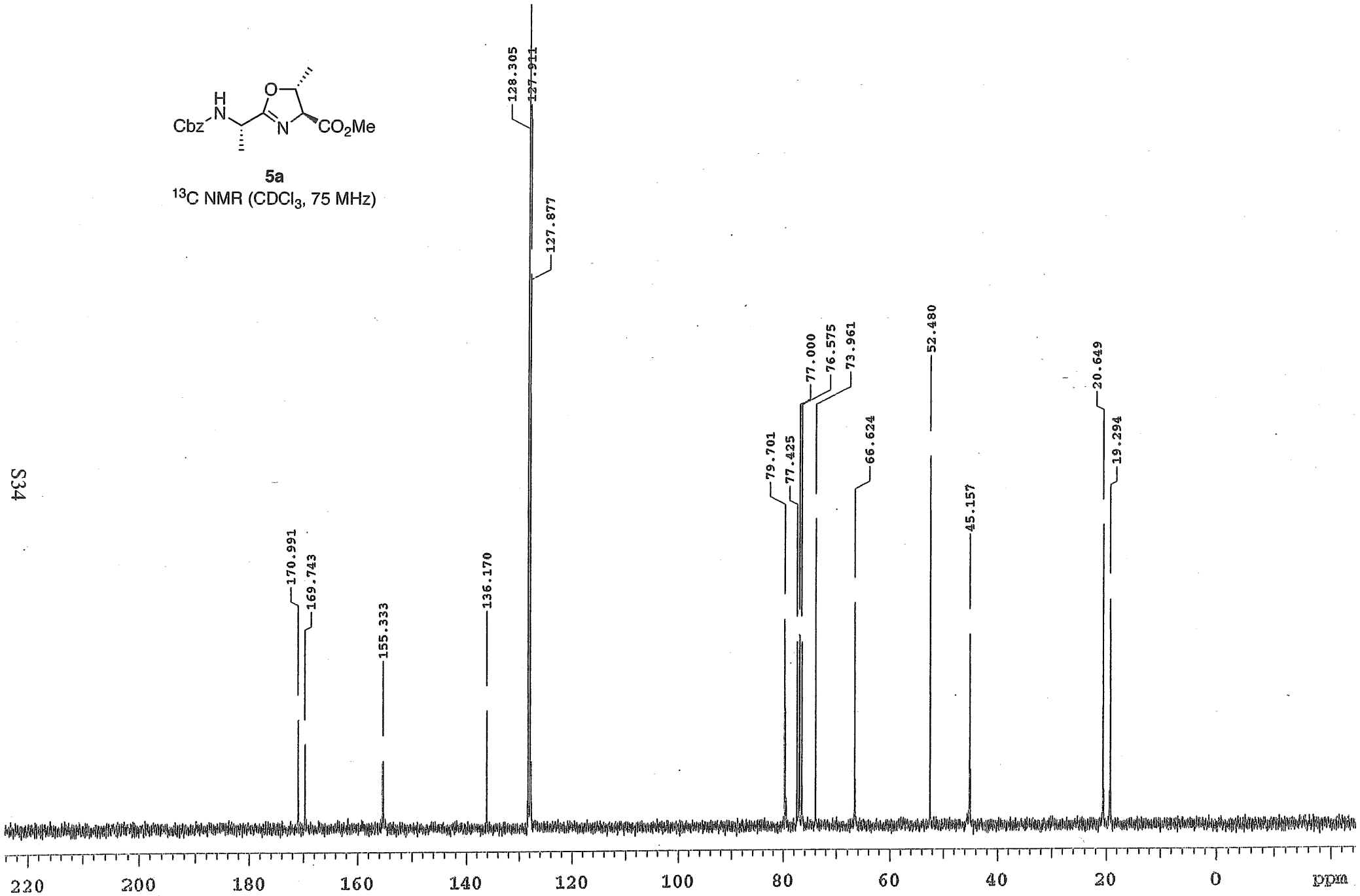

20.519
35.590
47.090
49.659
52.789
66.896
76.579
77.000
77.425
77.675
119.936
125.039
125.103
127.008
127.649
128.177
128.989
141.240
143.699
143.877
155.442
176.663
ppm
0
20
40
60
80
100
120
140
160
180
200
220
Fmoc
N
H
S
N
CO2Me
2d
13C NMR (CDCl3, 75 MHz)

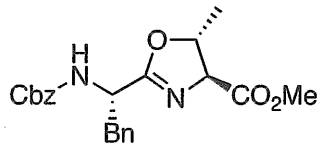


5a

^{1}H NMR ($CDCl_3$, 300 MHz)

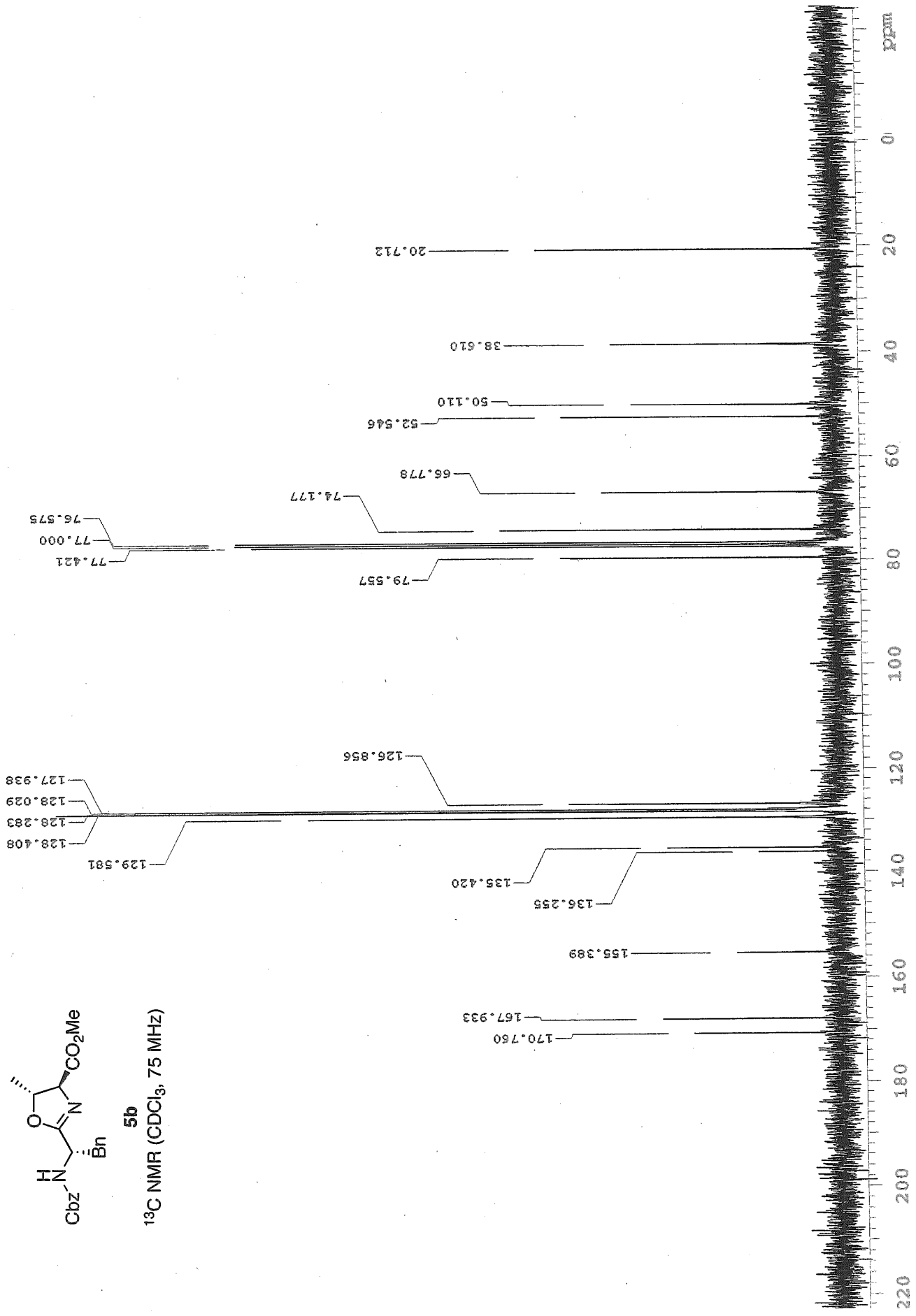


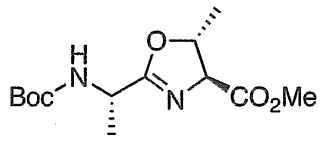

Cbz
N
H
O
N
CO2Me
5a
13C NMR (CDCl3, 75 MHz)
170.991
169.743
155.333
136.170
128.305
127.911
127.877
79.701
77.425
77.000
76.575
73.961
66.624
52.480
45.157
20.649
19.294
220
200
180
160
140
120
100
80
60
40
20
0
ppm



5b

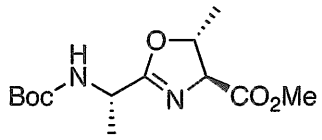
^{1}H NMR ($CDCl_3$, 300 MHz)


5b
^{13}C NMR ($CDCl_3$, 75 MHz)
Cbz
Bn
CO_2Me
ppm
0
20
40
60
80
100
120
140
160
180
200
220
20.712
38.610
50.110
52.546
66.778
74.177
76.575
77.000
77.421
79.557
126.856
127.938
128.029
128.283
128.408
129.581
135.420
136.255
155.389
167.933
170.760



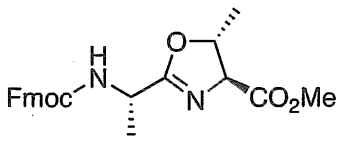
5c

^{1}H NMR ($CDCl_3$, 300 MHz)



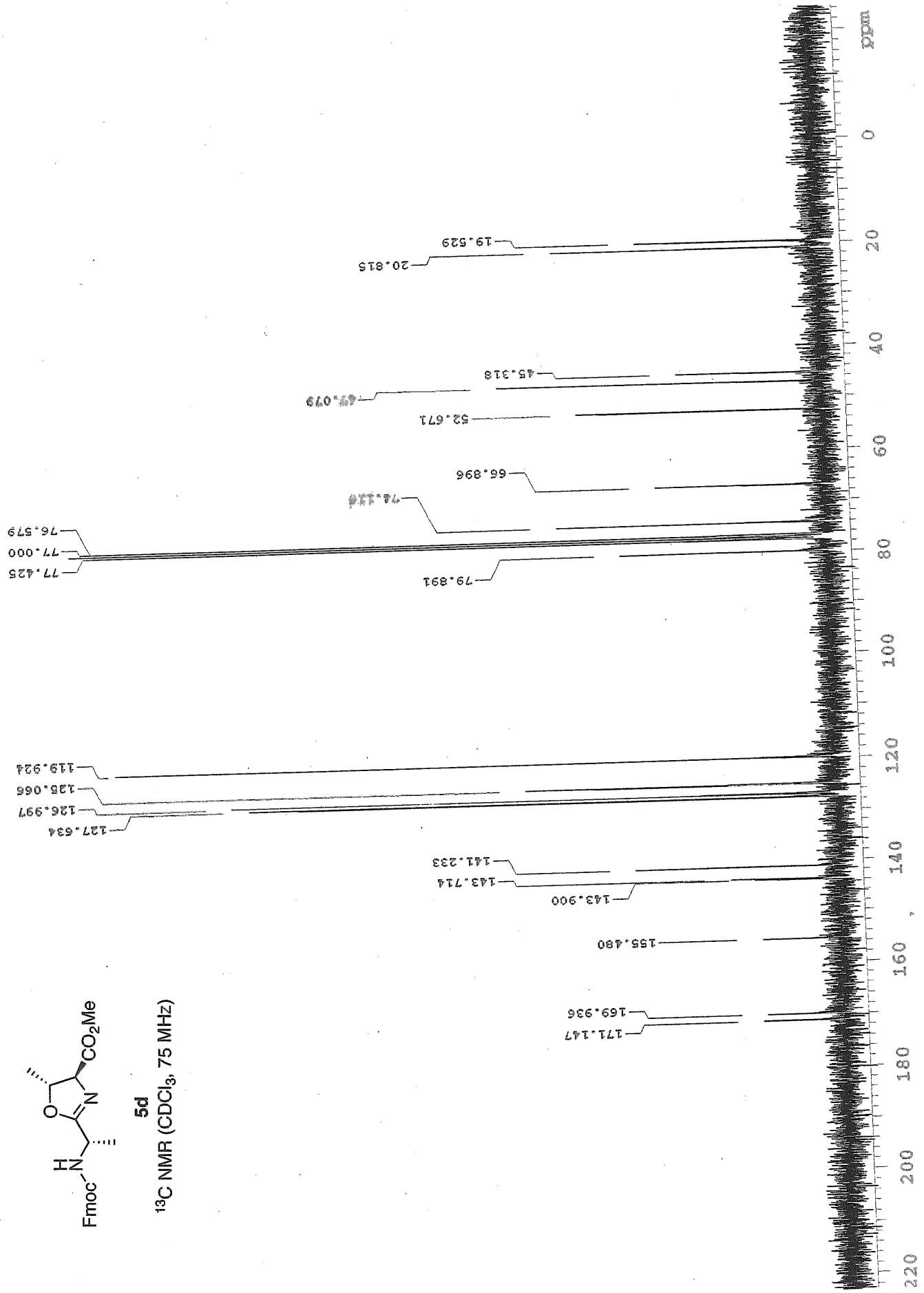
5c

^{13}C NMR ($CDCl_3$, 75 MHz)



5d

^{1}H NMR ($CDCl_3$, 300 MHz)


5d
^{13}C NMR ($CDCl_3$, 75 MHz)
Fmoc
CO_2Me
ppm
0
20
40
60
80
100
120
140
160
180
200
220
19.529
20.815
45.318
49.079
52.671
66.896
74.134
76.579
77.000
77.425
79.891
119.924
125.066
126.997
127.634
141.233
143.714
143.900
155.480
169.936
171.147