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The corrected version was published April 6, 2007.

SUPPORTING INFORMATION

Catalytic Enantioselective Hetero-Diels-Alder Reaction of an Azo Compound

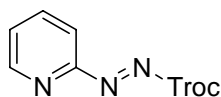
Masanori Kawasaki, Hisashi Yamamoto*

General Methods

All non aqueous reactions were carried out in flame-dried glassware under argon atmosphere unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin-layer chromatography using Whatman pre-coated silica gel flexible plates (0.25 mm) with F₂₅₄ indicator. Visualization was accomplished by UV light (256 nm), potassium permanganate, phosphomolybdic acid, ninhydrin, and iodine. Flash column chromatography was performed using silica gel 60 (mesh 230-400) supplied by E. Merck. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted. Commercial grade reagents and solvents were used without further purification. Propionitrile was dried over activated molecular sieves 4A before use.

Infrared spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 500 (500 MHz ¹H, 125 MHz ¹³C). Chemical shift values are reported in ppm relative to TMS (δ 0.0 ppm). High performance liquid chromatography (HPLC) was performed on Varian ProStar Series equipped with a variable wavelength detector using a Chiralcel OD-H column (0.46 cm x 25 cm) from Daicel. Racemic sample of adducts for HPLC were prepared in the reaction of azopyridine and siloxydienes without catalyst. Optical rotation were measured on a JASCO DIP-1000 polarimeter. Mass spectra were obtained on QSTAR (Applied SCIEX Biochemistry/MDS) spectrometers. X-ray crystallographic data was collected using SMART APEX CCD (BRUKER AXS) based diffraction meter equipped with a low-temperature apparatus.

Preparation of azopyridine

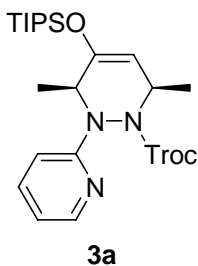


To a solution of 2-hydrazinopyridine (5.00 g, 45.9 mmol) in CH₂Cl₂ (230 mL) was added NEt₃ (7.02 mL, 50.5 mmol) and TrocCl (6.17 mL, 45.9 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under argon for 1 h, quenched with sat. NaHCO₃, and extracted with ethyl acetate (x3). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. To a solution of residue in CH₂Cl₂ (230 mL) was added Pb(OAc)₄ (22.4g, 50.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under

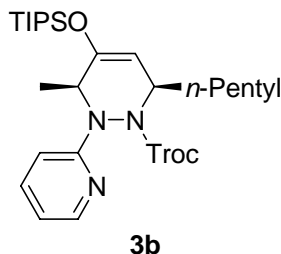
argon for 0.5 h. The reaction mixture was diluted with hexane, filtered through short pad of silica gel (elution with hexane/EtOAc = 7:1), and concentrated under reduced pressure. The residue was crystallized from hexane and Et₂O at -78 °C to give azopyridine **1** (6.8 g, 53%, 2 steps) as orange solids: FTIR (neat) 3055, 3009, 2960, 1774, 1583, 1516, 1433, 1276, 1219, 1184 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.79 (d, *J* = 4.4 Hz, 1H), 8.01 (td, *J* = 7.8, 1.7 Hz, 1H), 7.95-7.97 (m, 1H), 7.55-7.56 (m, 1H), 5.08 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 161.2, 160.8, 150.0, 138.8, 127.8, 119.2, 93.7; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₈H₆Cl₃N₃O₂+H]⁺ 282.0, found 282.0.

General procedure of azo hetero-Diels-Alder reaction

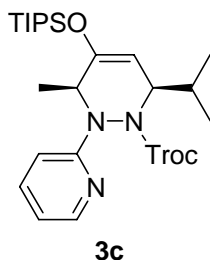
To a Schrenk tube was added AgOTf (6.4 mg, 25 μmol) and (*R*)-BINAP (7.8 mg, 12.5 μmol). The mixture was dried under vacuum for 10 min, anhydrous EtCN (1.5 mL), and stirred for 0.5 h. The clear solution was then cooled to -78 °C and **1** (70 mg, 0.25 mmol) dissolved in anhydrous EtCN (1 mL) was added dropwise. The resulting dark brown solution was stirred for 5 min. To a resulting mixture was added diene (0.5 mmol) dropwise. The reaction mixture was gradually warmed to -40 °C in 3 h and was stirred at -40 °C for additional 1 h. The reaction mixture was diluted with hexane, filtered through short pad of silica gel (elution with hexane/ethyl acetate = 10 : 1), and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give azo hetero-Diels-Alder adduct.



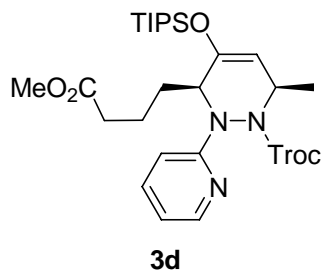
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3a** (116 mg, 87% yield, >99% ee) as colorless oil: [α]_D²⁷ -13.6 (*c* 1.40, CHCl₃); FTIR (neat) 2945, 2892, 2867, 1731, 1664, 1594, 1471, 1434, 1399, 1299, 1218, 1154 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 158.4, 155.0, 152.9, 148.0, 146.5, 137.7, 136.9, 115.5, 112.1, 107.7, 103.3, 95.3, 75.6, 75.0, 53.6, 50.2, 22.0, 17.9, 17.7, 17.0, 12.7, 12.5, 12.3; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₃H₃₆N₃O₃Cl₃Si+H]⁺ 536.1, found 536.1. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.8 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 46.5 min, minor enantiomer *t_r* = 34.3 min).



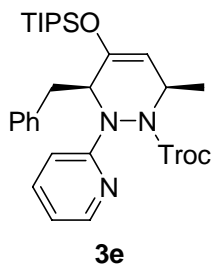
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3b** (124 mg, 84% yield, 95% ee) as colorless oil: $[\alpha]_D^{29} -21.9$ (*c* 1.00, CHCl₃); FTIR (neat) 2945, 2867, 1730, 1665, 1594, 1568, 1472, 1434, 1330, 1211, 1149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.4, 158.5, 157.2, 155.1, 153.3, 152.6, 148.0, 146.6, 137.7, 136.9, 115.4, 115.3, 111.9, 107.7, 104.3, 103.7, 101.1, 95.4, 94.1, 75.7, 74.9, 55.1, 54.6, 53.6, 33.8, 32.8, 31.9, 31.7, 26.6, 24.4, 22.6, 20.0, 17.9, 17.0, 14.0, 12.5; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₇H₄₄N₃O₃Cl₃Si+H]⁺ 592.2, found 592.2. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.7 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 38.2 min, minor enantiomer *t_r* = 23.3 min).



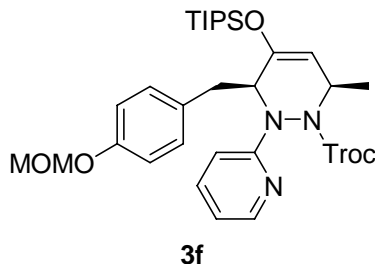
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3c** (91 mg, 65% yield, 84% ee) as colorless oil: $[\alpha]_D^{27} -23.8$ (*c* 1.11, CHCl₃); FTIR (neat) 2946, 2868, 1733, 1668, 1593, 1472, 1435, 1239, 1205 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.3, 158.4, 157.7, 155.3, 154.5, 152.5, 148.0, 146.7, 137.7, 136.9, 115.3, 111.6, 107.5, 103.0, 102.2, 96.0, 94.1, 75.8, 74.8, 61.8, 60.2, 55.0, 54.0, 53.3, 31.2, 27.9, 21.3, 20.2, 20.0, 19.6, 18.0, 17.9, 17.2, 16.4, 12.8, 12.7, 12.6, 12.4, 12.3; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₅H₄₀N₃O₃Cl₃Si+H]⁺ 564.2, found 564.1. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.5 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 33.7 min, minor enantiomer *t_r* = 20.9 min).



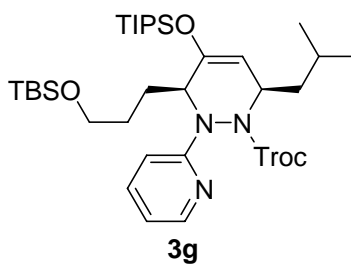
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3d** (114 mg, 74% yield, 98% ee) as colorless oil: $[\alpha]_D^{26}$ -29.5 (*c* 0.90, CHCl₃); FTIR (neat) 2947, 2867, 1735, 1665, 1594, 1472, 1435, 1296, 1214, 1134 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 173.7, 159.3, 158.3, 157.2, 155.1, 153.7, 153.0, 148.0, 146.7, 137.8, 137.0, 115.6, 111.9, 107.7, 103.8, 103.2, 100.8, 95.3, 94.0, 75.8, 74.9, 55.1, 54.8, 54.3, 53.6, 51.6, 51.5, 34.0, 33.8, 33.2, 32.3, 22.4, 20.2, 20.1, 17.9, 17.1, 12.5; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₇H₄₂N₃O₅Cl₃Si+H]⁺ 622.2, found 622.1. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.5 mL/min, hexane/2-Propanol = 97/3, major enantiomer *t_r* = 8.8 min, minor enantiomer *t_r* = 23.3 min).



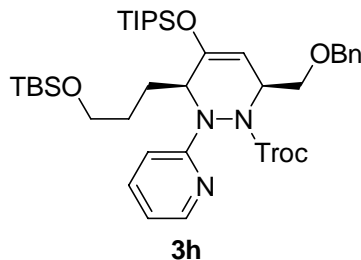
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3e** (113 mg, 74% yield, 92% ee) as colorless oil: $[\alpha]_D^{30}$ -0.95 (*c* 0.46, CHCl₃); FTIR (neat) 2945, 1730, 1666, 1592, 1470, 1433, 1391, 1287, 1210, 1149 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.8, 159.1, 155.9, 150.2, 147.7, 146.6, 139.9, 137.5, 137.2, 130.7, 129.2, 128.3, 127.2, 126.1, 126.0, 116.2, 115.9, 112.8, 109.2, 104.5, 95.0, 75.8, 75.5, 62.8, 50.4, 50.3, 36.9, 33.8, 22.6, 18.1, 18.0, 17.93, 17.89, 12.7, 12.6, 12.5, 12.2; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₉H₄₀N₃O₃Cl₃Si+H]⁺ 612.2, found 612.1. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.5 mL/min, hexane/2-Propanol = 99/1, major enantiomer *t_r* = 10.6 min, minor enantiomer *t_r* = 8.2 min).



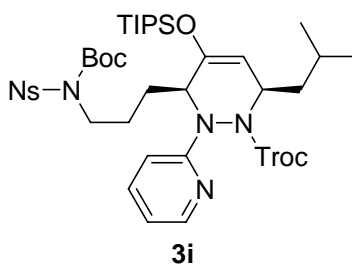
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3f** (143 mg, 85% yield, 90% ee) as colorless oil: $[\alpha]_D^{30}$ 7.83 (*c* 0.60, CH₃OH); FTIR (neat) 2946, 2893, 2867, 1730, 1667, 1591, 1512, 1470, 1433, 1393, 1289, 1257, 1210, 1152 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 159.1, 155.9, 155.7, 155.6, 150.3, 148.3, 147.7, 146.5, 137.5, 137.2, 133.4, 131.6, 130.8, 130.6, 130.2, 129.7, 116.2, 116.1, 116.1, 115.8, 115.2, 112.7, 110.1, 109.2, 104.5, 95.0, 94.54, 94.47, 75.7, 75.5, 62.9, 60.3, 55.9, 55.8, 55.7, 50.4, 50.3, 36.0, 33.0, 22.6, 18.0, 17.91, 17.88, 17.2, 12.6, 12.4, 12.2; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₃₁H₄₄N₃O₅Cl₃Si+H]⁺ 672.2, found 672.1. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.5 mL/min, hexane/2-Propanol = 99.5/0.5, major enantiomer *t_r* = 15.3 min, minor enantiomer *t_r* = 12.6 min).



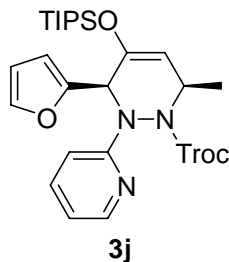
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3g** (150 mg, 82% yield, 95% ee) as colorless oil: $[\alpha]_D^{29}$ -18.0 (*c* 1.10, CHCl₃); FTIR (neat) 2954, 2867, 1730, 1667, 1593, 1470, 1434, 1388, 1255, 1210, 1149, 1100 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.61, 159.55, 157.1, 155.4, 152.1, 149.9, 147.9, 146.6, 137.6, 137.0, 115.8, 112.2, 108.5, 106.0, 101.0, 95.2, 94.2, 75.7, 75.1, 63.7, 63.0, 62.9, 60.0, 58.8, 53.4, 53.1, 44.1, 42.2, 41.7, 29.8, 27.6, 26.7, 25.93, 25.90, 25.7, 25.4, 25.3, 23.9, 22.9, 22.7, 21.7, 18.3, 18.2, 18.0, 17.9, 17.87, 12.6, 12.5, -5.3; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₃₄H₆₀N₃O₄Cl₃Si+H]⁺ 736.3, found 736.2. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.8 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 6.0 min, minor enantiomer *t_r* = 5.1 min).



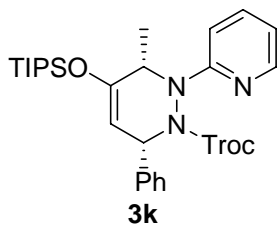
According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3h** (168 mg, 84% yield, 98% ee) as colorless oil: $[\alpha]_D^{30}$ -13.9 (*c* 0.88, CHCl₃); FTIR (neat) 2947, 2866, 1729, 1672, 1592, 1470, 1434, 1400, 1288, 1250, 1211, 1144, 1100 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 159.2, 155.5, 152.6, 147.9, 146.3, 138.5, 138.0, 137.6, 137.1, 128.4, 128.2, 127.8, 127.5, 127.4, 115.9, 108.4, 99.5, 95.1, 75.7, 75.2, 73.3, 72.9, 71.8, 69.7, 63.6, 63.1, 59.6, 58.9, 54.4, 53.9, 29.9, 27.7, 26.5, 26.0, 24.9, 18.3, 17.9, 17.88, 12.6, 12.4, -5.3, -5.33; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₃₈H₆₀N₃O₅Cl₃Si₂+H]⁺ 800.3, found 800.2. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 1 mL/min, hexane/2-Propanol = 98/2, major enantiomer *t_r* = 42.2 min, minor enantiomer *t_r* = 12.9 min) after deprotection of TIPS and TBS groups with TFA in CH₂Cl₂.



According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3i** (175 mg, 77% yield, 98% ee) as colorless oil: $[\alpha]_D^{27}$ -10.1 (*c* 0.78, CHCl₃); FTIR (neat) 2956, 2868, 1733, 1684, 1593, 1544, 1471, 1434, 1369, 1300, 1257, 1212, 1154, 1122 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.5, 159.4, 157.2, 155.3, 151.7, 150.3, 149.8, 147.8, 147.6, 147.5, 146.8, 137.6, 137.1, 134.0, 133.8, 133.7, 133.3, 133.1, 131.62, 131.56, 124.2, 124.1, 116.0, 115.8, 111.9, 108.9, 106.1, 101.2, 95.3, 84.7, 84.1, 75.7, 74.9, 59.8, 58.8, 53.4, 53.1, 48.3, 48.1, 44.1, 42.4, 42.2, 28.2, 27.8, 27.7, 27.5, 26.5, 25.8, 25.5, 24.7, 24.4, 23.9, 22.9, 22.7, 21.7, 18.0, 17.98, 17.9, 17.88, 12.6, 12.5; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₃₉H₅₈N₅O₉Cl₃Si+H]⁺ 906.3, found 906.2. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 0.8 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 11.2 min, minor enantiomer *t_r* = 10.3 min).

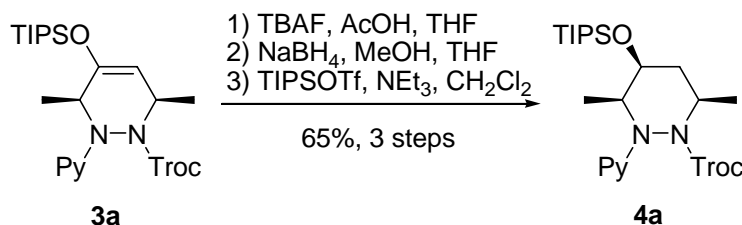


According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3j** (114 mg, 78% yield, 92% ee) as colorless oil: $[\alpha]_D^{27} -54.4$ (*c* 0.85, CHCl₃); FTIR (neat) 2945, 2867, 1734, 1663, 1593, 1568, 1473, 1435, 1386, 1331, 1297, 1273, 1213, 1136 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 159.0, 158.4, 156.5, 155.1, 154.5, 153.8, 152.6, 152.1, 148.1, 146.2, 142.8, 141.5, 138.0, 137.0, 116.0, 115.6, 112.6, 110.7, 110.6, 110.4, 108.0, 107.1, 99.9, 98.7, 95.2, 94.1, 75.6, 75.0, 55.0, 54.1, 52.1, 51.5, 30.3, 19.1, 17.9, 17.8, 12.54, 12.46; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₆H₃₆N₃O₄Cl₃Si+H]⁺ 588.2, found 588.0. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 1 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 11.2 min, minor enantiomer *t_r* = 14.6 min).

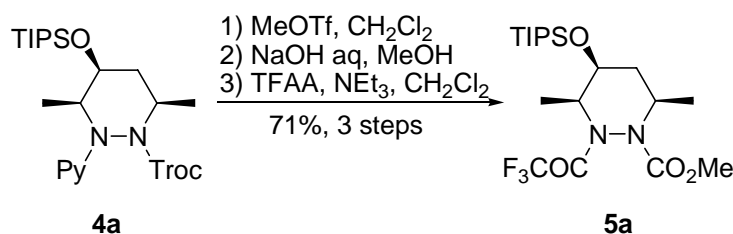


According to a general procedure, the residue was purified by flash column chromatography on silica gel (elution with hexane/ethyl acetate = 10 : 1) to give **3k** (104 mg, 70% yield, 55% ee) as colorless oil: $[\alpha]_D^{25} -21.9$ (*c* 0.9, CHCl₃); FTIR (neat) 2945, 2867, 1736, 1662, 1593, 1471, 1434, 1260, 1218, 1136 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) Broad signals were observed due to a mixture of rotamers. See attached ¹H NMR chart; ¹³C NMR (125 MHz, CDCl₃) δ 158.9, 158.6, 155.1, 151.7, 148.1, 146.2, 141.1, 137.9, 136.8, 129.1, 128.3, 128.0, 127.3, 116.1, 115.7, 112.3, 108.2, 102.4, 101.5, 95.2, 75.8, 75.0, 58.5, 57.8, 55.2, 54.3, 18.0, 17.8, 17.77, 12.6, 12.4; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₈H₃₈N₃O₃Cl₃Si+H]⁺ 598.2, found 598.1. Enantiomeric excess was determined by HPLC analysis with Chiralcel OD-H column (flow rate: 1 mL/min, hexane/2-Propanol = 99.8/0.2, major enantiomer *t_r* = 9.8 min, minor enantiomer *t_r* = 19.0 min).

Cleavage of N-N bond

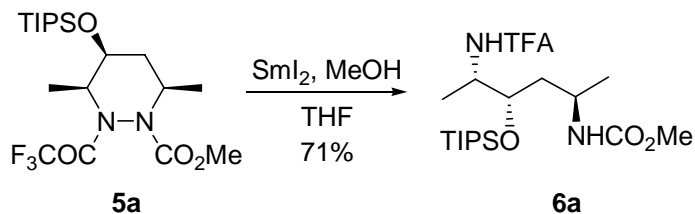


To a solution of **3a** (4.56 g, 8.54 mmol) in THF (43 mL) was added AcOH (2.93 mL, 51.2 mmol) and TBAF (1M solution in THF, 17.1 mL, 17.1 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under argon for 2 h, quenched with sat. NaHCO₃, and extracted with ethyl acetate (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered on silica gel, and concentrated under reduced pressure. To a solution of residue in THF/MeOH (3:1, 40 mL) was added NaBH₄ (487 mg, 12.8 mmol) at -78 °C. The reaction mixture was gradually warmed to -40 °C in 3 h, quenched with sat. NaHCO₃, and extracted with ethyl acetate (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered on silica gel, and concentrated under reduced pressure. To a solution of residue in CH₂Cl₂ (40 mL) was added TIPSOTf (2.3 mL, 8.54 mmol) and NEt₃ (1.3 mL, 9.39 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under argon for 2 h, quenched with sat. NaHCO₃, and extracted with ethyl acetate/hexane (1:10) (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered on silica gel, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **4a** (2.96 g, 65%, 3 steps) as white solid: $[\alpha]_D^{25}$ -39.1 (*c* 0.94, CHCl₃); FTIR (neat) 2944, 2866, 1731, 1593, 1469, 1435, 1300, 1151, 1103 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.17 (dd, *J* = 4.9, 0.86 Hz, 1H), 7.48-7.52, (m, 1H), 6.68 (dd, *J* = 6.9, 5.2 Hz, 1H), 6.34 (d, *J* = 8.5 Hz, 1H), 5.26-5.32 (m, 1H), 4.52-4.58 (br m, 2H), 3.95 (td, *J* = 10.7, 5.1 Hz, 1H), 3.35-3.39 (m, 1H), 1.96 (q, *J* = 12.1 Hz, 1H), 1.67-1.70 (m, 1H), 1.67 (d, *J* = 7.0 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 1H), 1.05-1.10 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 157.7, 148.0, 137.9, 114.7, 107.0, 95.2, 74.9, 67.0, 54.6, 51.7, 37.6, 20.1, 18.0, 17.96, 12.2, 9.6; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₂₃H₃₈N₃O₃Cl₃+H]⁺ 538.2, found 538.0.



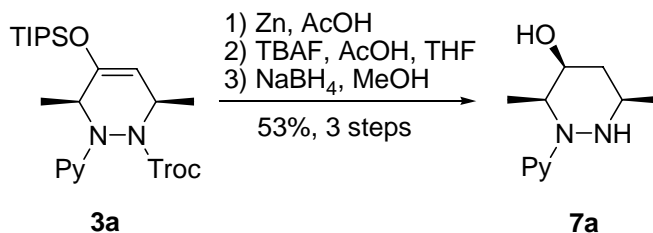
To a solution of **4a** (722 mg, 1.34 mmol) in CH₂Cl₂ (13.4 mL) was added MeOTf (1.52 mL, 13.4 mmol) at room

temperature. The reaction mixture was stirred at room temperature under argon for 3 h, quenched with sat. Na_2CO_3 , and extracted with CH_2Cl_2 (x2). The combined organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. To a solution of residue in MeOH (13.4 mL) was added 2N NaOH aq (6.7 mL, 13.4 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 3 h, diluted with water, extracted with ethyl acetate/ hexane (1:3), dried over anhydrous MgSO_4 , filtered on silica gel, and concentrated under reduced pressure. To a solution of residue in CH_2Cl_2 (13.4 mL) was added TFAA (227 μL , 1.61 mmol) and NEt_3 (224 μL , 1.61 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under argon for 1 h, quenched with sat. NaHCO_3 , and extracted with ethyl acetate (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **5a** (419 mg, 71%, 3 steps) as colorless oil: $[\alpha]_D^{26}$ -16.6 (*c* 1.44, CHCl_3); FTIR (neat) 2946, 2868, 1741, 1716, 1444, 1385, 1292, 1218, 1158, 1104, 1072 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 4.78-4.84 (m, 1H), 3.92-3.98 (m, 1H), 3.69 (s, 3H), 3.28-3.36 (m, 1H), 1.91 (q, *J* = 12.1 Hz, 1H), 1.71-1.76 (m, 1H), 1.62 (d, *J* = 7.1 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H), 1.03-1.11 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.5 (q, *J* = 36.1 Hz), 156.5, 116.0 (q, *J* = 287 Hz), 68.3, 58.5, 52.9, 52.8, 35.7, 19.3, 17.9, 12.1, 9.3; LRMS (CI) *m/z* (M+H)⁺ calcd for $[\text{C}_{19}\text{H}_{35}\text{N}_2\text{O}_4\text{F}_3\text{Si}+\text{H}]^+$ 441.2, found 441.2.

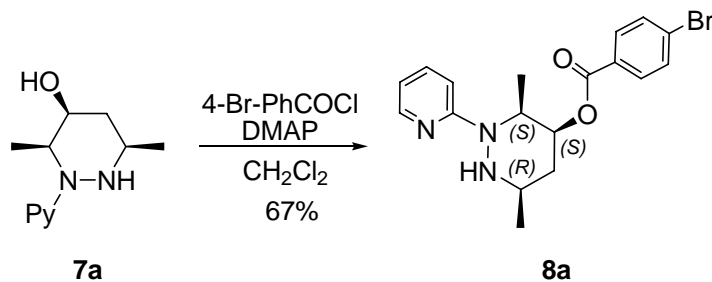


To a solution of **5a** (28 mg, 63.6 μmol) in MeOH (0.2 mL) was added freshly prepared SmI_2 (0.1 M solution in THF, 3.2 mL, 0.32 mmol) at room temperature. The reaction mixture was stirred at room temperature under argon for 0.5 h, quenched with sat. NaHCO_3 , and extracted with AcOEt (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **6a** (20 mg, 71%) as colorless oil: $[\alpha]_D^{25}$ -20.9 (*c* 0.99, CHCl_3); FTIR (neat) 3420, 3323, 2946, 2869, 1716, 1533, 1462, 1359, 1259, 1211, 1165 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.73-6.78 (br m, 1H), 4.95-4.80 (br m, 1H), 4.10-4.12 (br m, 1H), 3.90-3.98 (br m, 1H), 3.70-3.76 (br s, 1H), 3.66 (s, 3H), 1.53-1.75 (m, 2H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H), 1.06-1.13 (m, 21H); ^{13}C NMR (125 MHz, CDCl_3) δ 157.0 (q, *J* = 36.4 Hz), 156.5, 115.9 (q, *J* = 286 Hz), 73.4, 52.0, 49.5, 45.1, 41.6, 22.3, 18.1, 18.0, 12.7; LRMS (CI) *m/z* (M+H)⁺ calcd for $[\text{C}_{19}\text{H}_{37}\text{N}_2\text{O}_4\text{F}_3\text{Si}+\text{H}]^+$ 443.2, found 443.1.

Determination of absolute stereochemistry



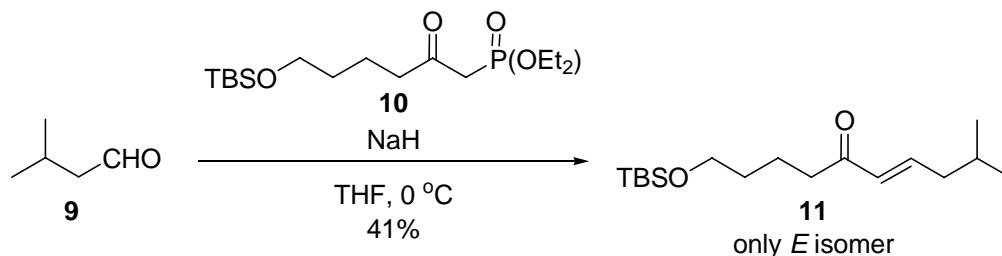
To a solution of **3a** (463 mg, 0.867 mmol) in AcOH (4.3 mL) was added Zn powder (1.13 g, 17.3 mmol) at room temperature. The reaction mixture was stirred at room temperature under argon for 1 h, quenched with sat. NaHCO₃, and extracted with AcOEt (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. To a solution of residue in THF (4.3 mL) was added TBAF (1M solution in THF, 1.3 mL, 1.30 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h, quenched with sat. NaHCO₃, extracted with AcOEt, dried over anhydrous MgSO₄, filtered on silica gel, and concentrated under reduced pressure. To a solution of residue in MeOH (4.3 mL) was added NaBH₄ (49 mg, 1.30 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under argon for 0.5 h, quenched with sat. NaHCO₃, and extracted with ethyl acetate (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **7a** (96 mg, 53%, 3 steps) as colorless oil: [α]_D²⁶ 71.4 (*c* 1.05, CHCl₃); FTIR (neat) 3302, 2962, 2930, 1595, 1559, 1494, 1466, 1426, 1298, 1107, 1051 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.06-8.08 (m, 1H), 7.42-7.46 (m, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 6.54 (t, *J* = 6.2, 1H), 5.06 (quint, *J* = 6.7 Hz, 1H), 3.94 (dt, *J* = 11.9, 4.9 Hz, 1H), 2.89-3.30 (br s, 2H), 2.84-2.90 (m, 1H), 1.81-1.85 (m, 1H), 1.34 (q, *J* = 11.9 Hz, 1H), 1.66 (d, *J* = 6.9 Hz, 3H), 1.58 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 147.0, 137.5, 112.8, 108.7, 67.1, 51.0, 49.1, 36.9, 19.4, 7.5; LRMS (CI) *m/z* (M+H)⁺ calcd for [C₁₁H₁₇N₃O+H]⁺ 208.1, found 208.1.



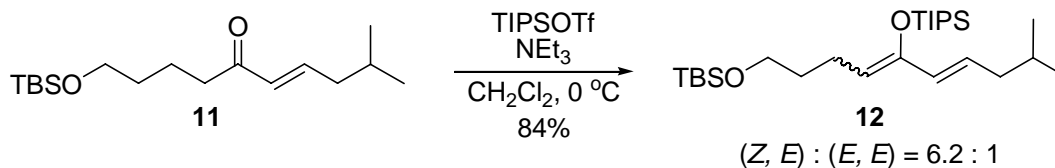
To a solution of **7a** (33 mg, 0.16 mmol) in CH₂Cl₂ (1.6 mL) was added DMAP (58 mg, 0.48 mmol) and 4-bromobenzoyl chloride (105 mg, 0.48 mmol) at 0 °C. The reaction mixture was stirred at room temperature under

argon for 15 h, quenched with sat. NaHCO_3 , and extracted with ethyl acetate (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **8a** (41 mg, 67%) as colorless needle. The sample for X-ray crystallographic analysis was prepared by crystallization from Et_2O : $[\alpha]_D^{28}$ 110.3 (*c* 1.00, CHCl_3); FTIR (neat) 2964, 2936, 1719, 1591, 1427, 1271 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.10-8.14 (m, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.45-7.50 (m, 1H), 7.25-7.27 (m, 1H), 6.58-6.61 (m, 1H), 5.29-5.35 (m, 1H), 5.23 (dt, *J* = 10.4, 5.5 Hz, 1H), 3.00-3.08 (m, 1H), 2.55-2.90 (br s, 1H), 2.04-2.09 (m, 1H), 1.52 (q, *J* = 11.9 Hz), 1.27 (d, *J* = 6.8 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.9, 159.2, 147.3, 137.5, 131.7, 131.0, 129.2, 128.1, 113.3, 108.6, 70.6, 50.7, 46.2, 33.9, 19.4, 8.8; LRMS (CI) *m/z* ($\text{M}+\text{H}$)⁺ calcd for $[\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_2\text{Br}+\text{H}]^+$ 390.0, found 390.0.

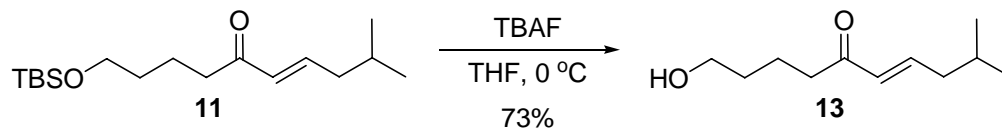
Synthesis of Silyloxydienes



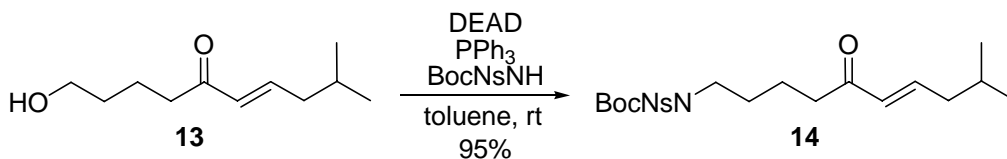
To a solution of NaH (200 mg, 5.0 mmol) in THF (50 mL) was added **11** (1.75 g, 5.0 mmol) at 0 °C. The reaction mixture was stirred at 0 °C under argon for 0.5 h, added **9** (540 μL , 5.0 mmol) at 0 °C, stirred for 1 h at 0 °C, quenched with sat. NH_4Cl , and extracted with Et_2O (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **11** (612 mg, 41%) as colorless oil: FTIR (neat) 2956, 2930, 2856, 1670, 1675, 1472, 1255, 1102 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.80 (dt, *J* = 19.8, 9.3 Hz, 1H), 6.05-6.11 (m, 1H), 3.62 (t, *J* = 7.9 Hz, 2H), 2.56 (t, *J* = 9.0 Hz, 2H), 2.07-2.12 (m, 2H), 1.73-1.82 (m, 1H), 1.63-1.72 (m, 2H), 1.50-1.58 (m, 2H), 0.93 (d, *J* = 8.3 Hz, 6H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.6, 146.1, 131.3, 62.9, 41.7, 39.8, 32.3, 27.9, 25.9, 22.4, 20.8, 18.3, -5.3; LRMS (CI) *m/z* ($\text{M}+\text{H}$)⁺ calcd for $[\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}+\text{H}]^+$ 299.2, found 299.1.



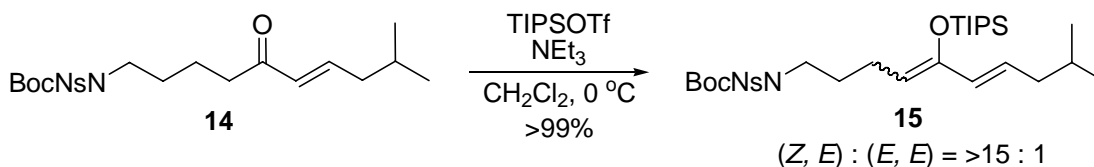
To a solution of **11** (553 mg, 1.86 mmol) in CH_2Cl_2 (10 mL) was added NEt_3 (285 μL , 2.05 mmol) and TIPSOTf (501 μL , 1.86 mmol) at 0 $^\circ\text{C}$. The reaction mixture was stirred at 0 $^\circ\text{C}$ under argon for 1 h, quenched with sat. NaHCO_3 , and extracted with hexane (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **12** (710 mg, 84%) as colorless oil: FTIR (neat) 2953, 2867, 1464, 1367, 1255, 1103 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 5.74-5.83 (m, 2H), 4.62 (t, $J = 7.1$ Hz, 1H), 3.59-3.64 (m, 2H), 2.10-2.19 (m, 2H), 1.94-1.97 (m, 2H), 1.53-1.67 (m, 3H), 1.16-1.22 (m, 3H), 1.07-1.12 (m, 18H), 0.88-0.90 (m, 15H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 149.2, 130.2, 127.7, 111.1, 63.1, 41.8, 33.7, 32.9, 28.6, 26.0, 22.4, 22.3, 18.1, 13.8, -5.34; LRMS (CI) m/z ($\text{M}+\text{H}$) $^+$ calcd for $[\text{C}_{26}\text{H}_{54}\text{O}_2\text{Si}_2+\text{H}]^+$ 455.4, found 455.3.



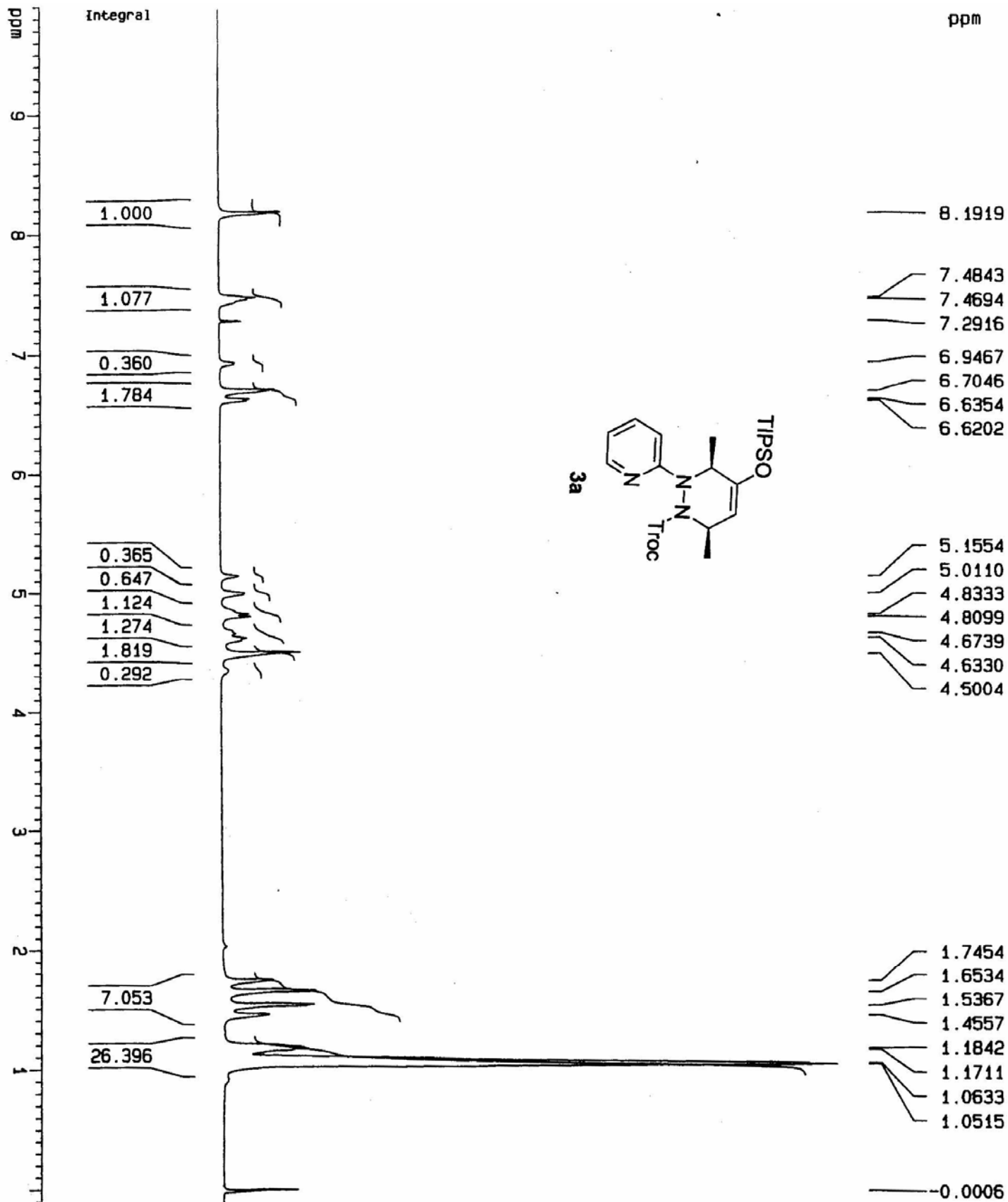
To a solution of **11** (2.05 g, 6.88 mmol) in THF (70 mL) was added TBAF (1M solution in THF, 10.3 mL, 10.3 mmol) at 0 $^\circ\text{C}$. The reaction mixture was stirred at 0 $^\circ\text{C}$ under argon for 2 h, quenched with sat. NH_4Cl , and extracted with Et_2O (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **13** (924 mg, 73%) as colorless oil: FTIR (neat) 3421, 2956, 2870, 1670, 1628, 1465, 1368 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 6.79-6.86 (m, 1H), 6.07-6.12 (m, 1H), 3.63 (t, $J = 6.4$ Hz, 2H), 2.60 (t, $J = 7.2$ Hz, 2H), 2.27 (br s, 1H), 2.09-2.12 (m, 2H), 1.68-1.81 (m, 3H), 1.55-1.62 (m, 2H), 0.93 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.8, 146.6, 131.2, 62.1, 41.7, 39.5, 32.1, 27.8, 22.4, 20.1; LRMS (CI) m/z ($\text{M}+\text{H}$) $^+$ calcd for $[\text{C}_{11}\text{H}_{20}\text{O}_2+\text{H}]^+$ 185.1, found 185.1.

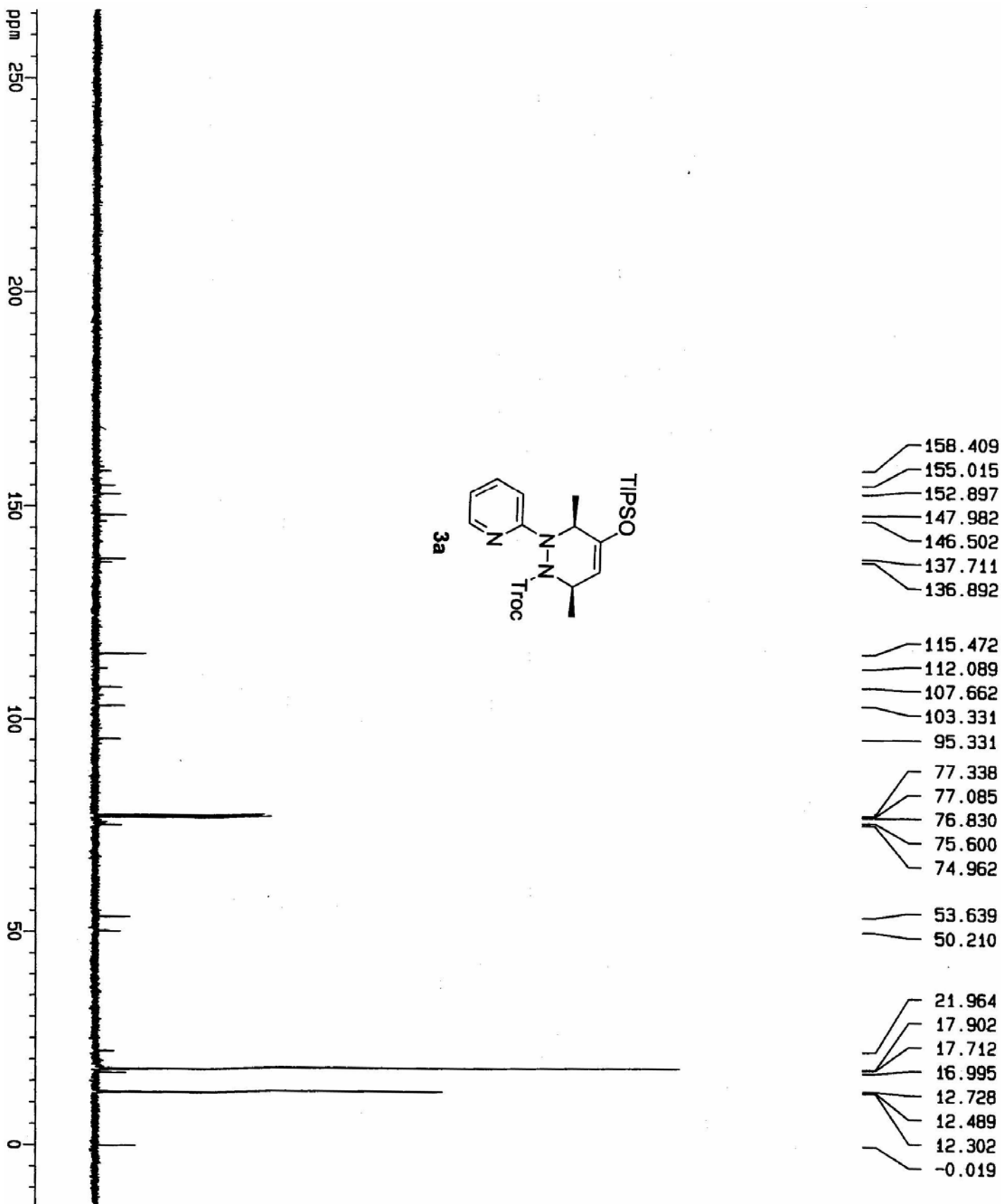


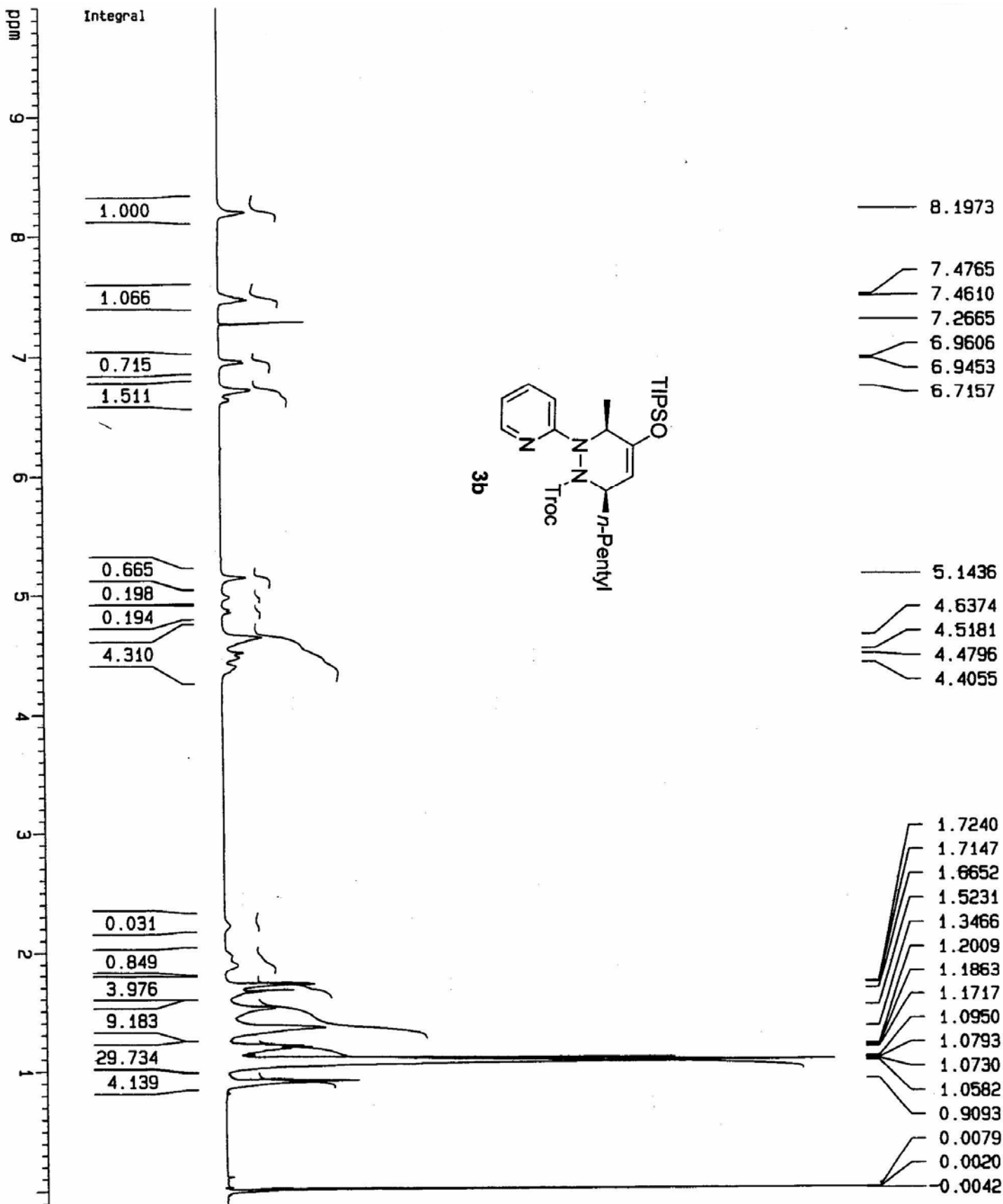
To a solution of **13** (1.04 g, 6.12 mmol) in toluene (30 mL) was added PPh_3 (1.92 g, 7.34 mmol), BocNsNH (2.22 g, 7.34 mmol), and DEAD (1.16 mL, 7.34 mmol) at room temperature. The reaction mixture was stirred at room temperature under argon for 0.5 h and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **14** (2.72 g, 95%) as colorless oil: FTIR (neat) 2957, 1734, 1542, 1367, 1153 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.29-8.32 (m, 1H), 7.72-7.76 (m, 3H), 6.79-6.86 (dt, $J = 15.8, 7.4$ Hz, 1H), 6.09 (d, $J = 15.8$ Hz, 1H), 3.78 (t, $J = 7.0$ Hz, 2H), 2.62 (t, $J = 7.3$ Hz, 2H), 2.09-2.13 (m, 2H), 1.69-1.81 (m, 5H), 1.36 (s, 9H), 0.93 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.0, 150.4, 147.6, 146.4, 134.1, 133.5, 133.3, 131.7, 131.2, 124.3, 84.9, 47.7, 41.7, 39.3, 29.8, 27.9, 27.8, 22.4, 21.2; LRMS (CI) m/z ($\text{M}+\text{H}$)⁺ calcd for $[\text{C}_{22}\text{H}_{32}\text{N}_2\text{O}_7\text{S}+\text{H}-\text{SO}_2]^+$ 405.2, found 405.0.

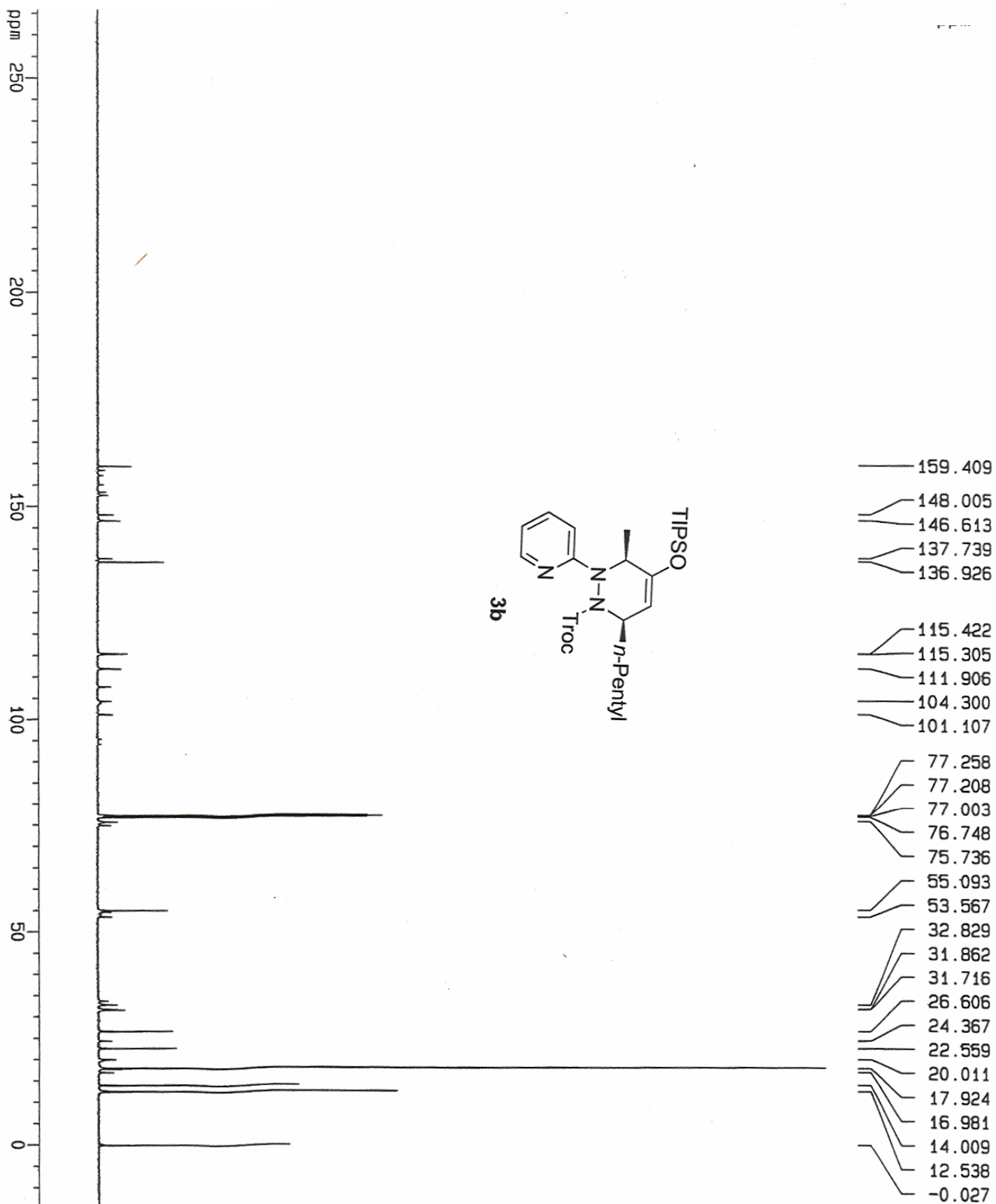


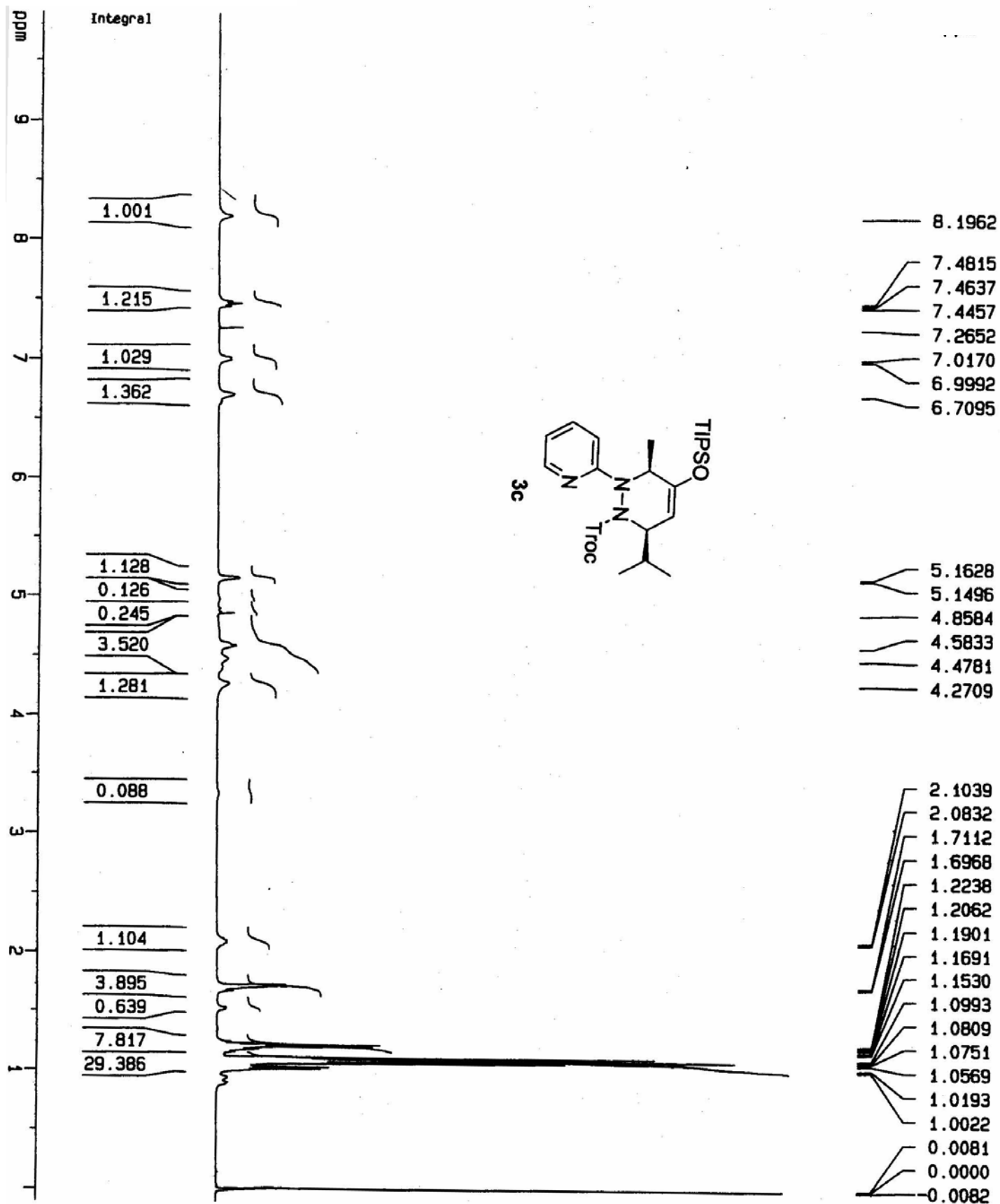
To a solution of **14** (1.72 g, 3.68 mmol) in CH_2Cl_2 (20 mL) was added NEt_3 (563 μL , 4.05 mmol) and TIPSOTf (991 μL , 3.68 mmol) at 0 $^\circ\text{C}$. The reaction mixture was stirred at 0 $^\circ\text{C}$ under argon for 1 h, quenched with sat. NaHCO_3 , and extracted with Et_2O (x2). The combined organic layers were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give **15** (2.3 g, >99%) as colorless oil: FTIR (neat) 2949, 2868, 1733, 1542, 1458, 1368, 1282, 1154 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.15-8.18 (m, 1H), 7.59-7.65 (m, 3H), 5.69-5.74 (m, 2H), 4.54 (t, $J = 7.1$ Hz, 1H), 3.67 (t, $J = 7.5$ Hz, 2H), 2.10 (q, $J = 7.4$ Hz, 2H), 1.84-1.87 (m, 2H), 1.68-1.75 (m, 2H), 1.49-1.56 (m, 1H), 1.24 (s, 9H), 1.06-1.14 (m, 3H), 1.00-1.05 (m, 18H), 0.78 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.3, 149.8, 147.5, 134.1, 133.6, 133.1, 131.7, 130.0, 128.2, 124.3, 109.8, 84.7, 47.9, 41.7, 30.3, 28.5, 27.8, 23.0, 22.3, 18.1, 13.7, ; LRMS (CI) m/z ($\text{M}+\text{H}$)⁺ calcd for $[\text{C}_{31}\text{H}_{52}\text{N}_2\text{O}_7\text{SSi}+\text{H}]^+$ 625.3, found 625.3.

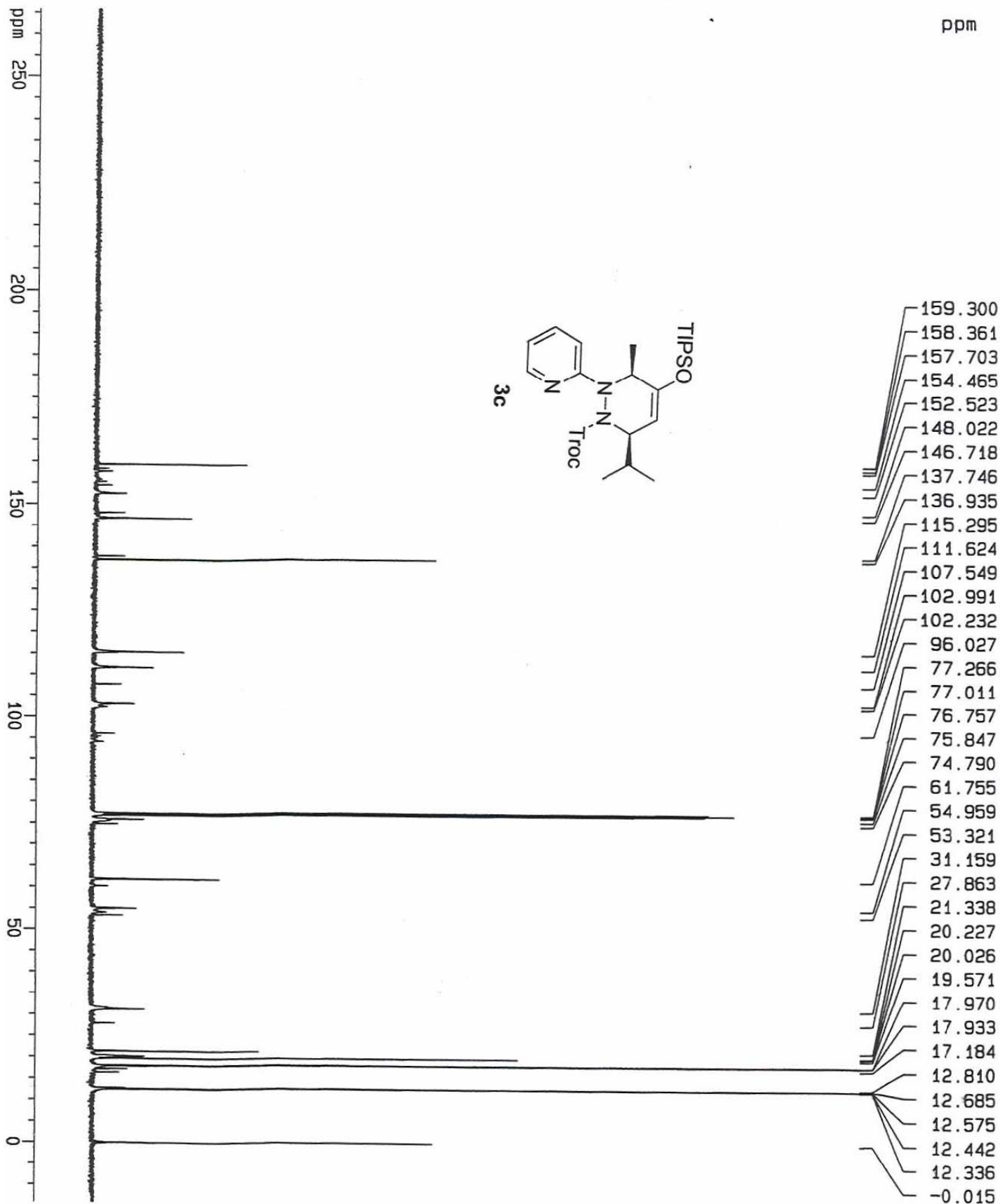


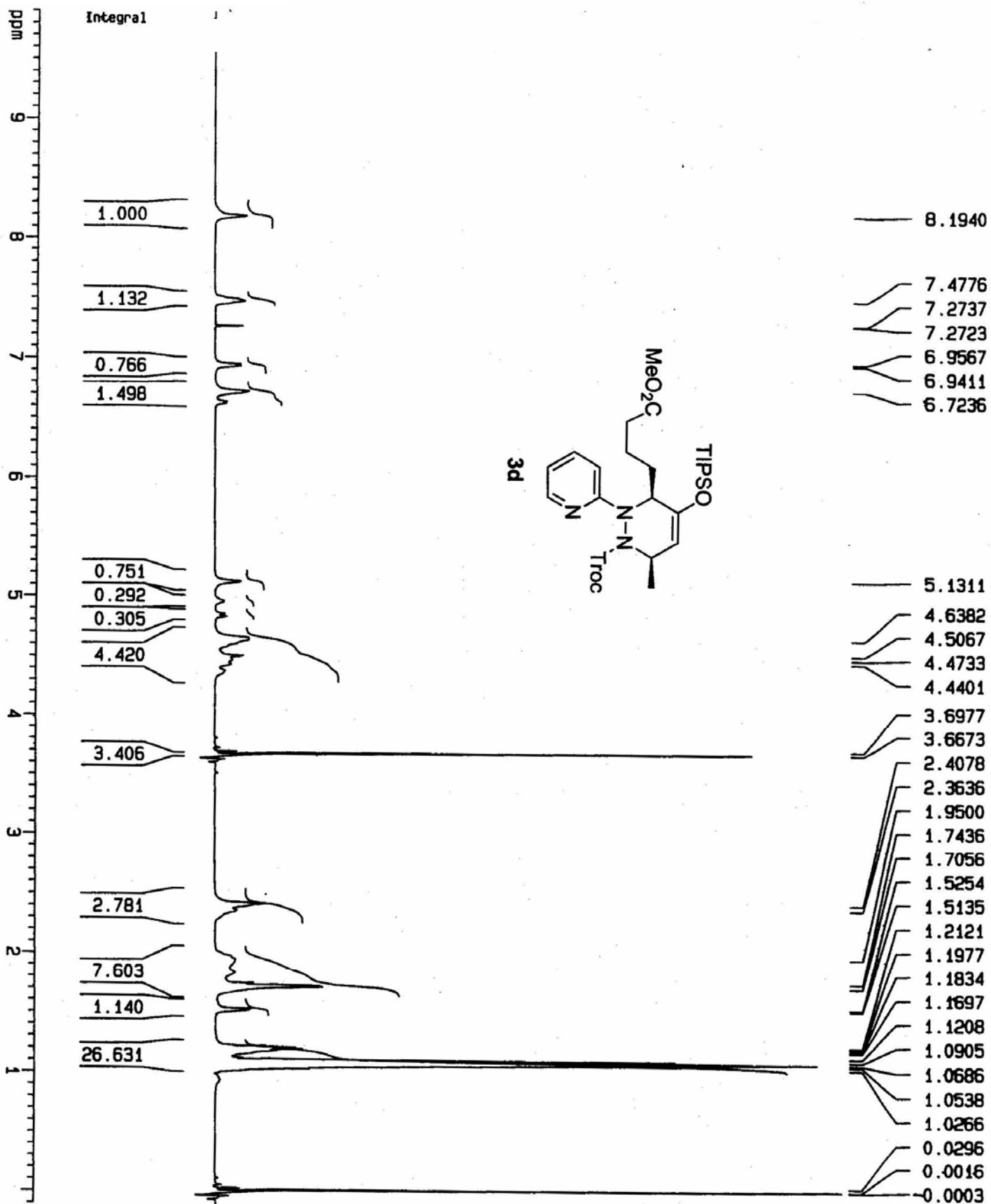


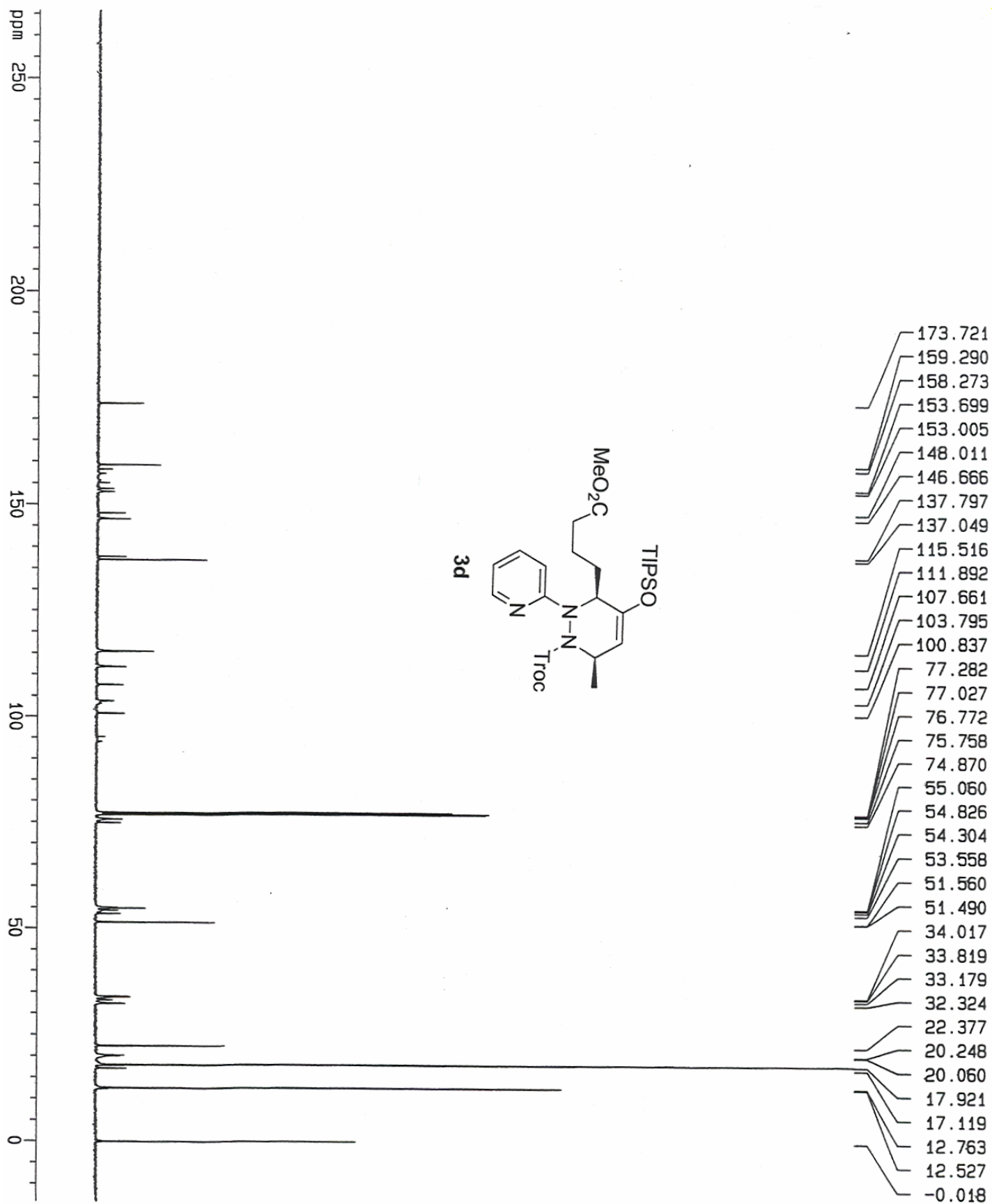


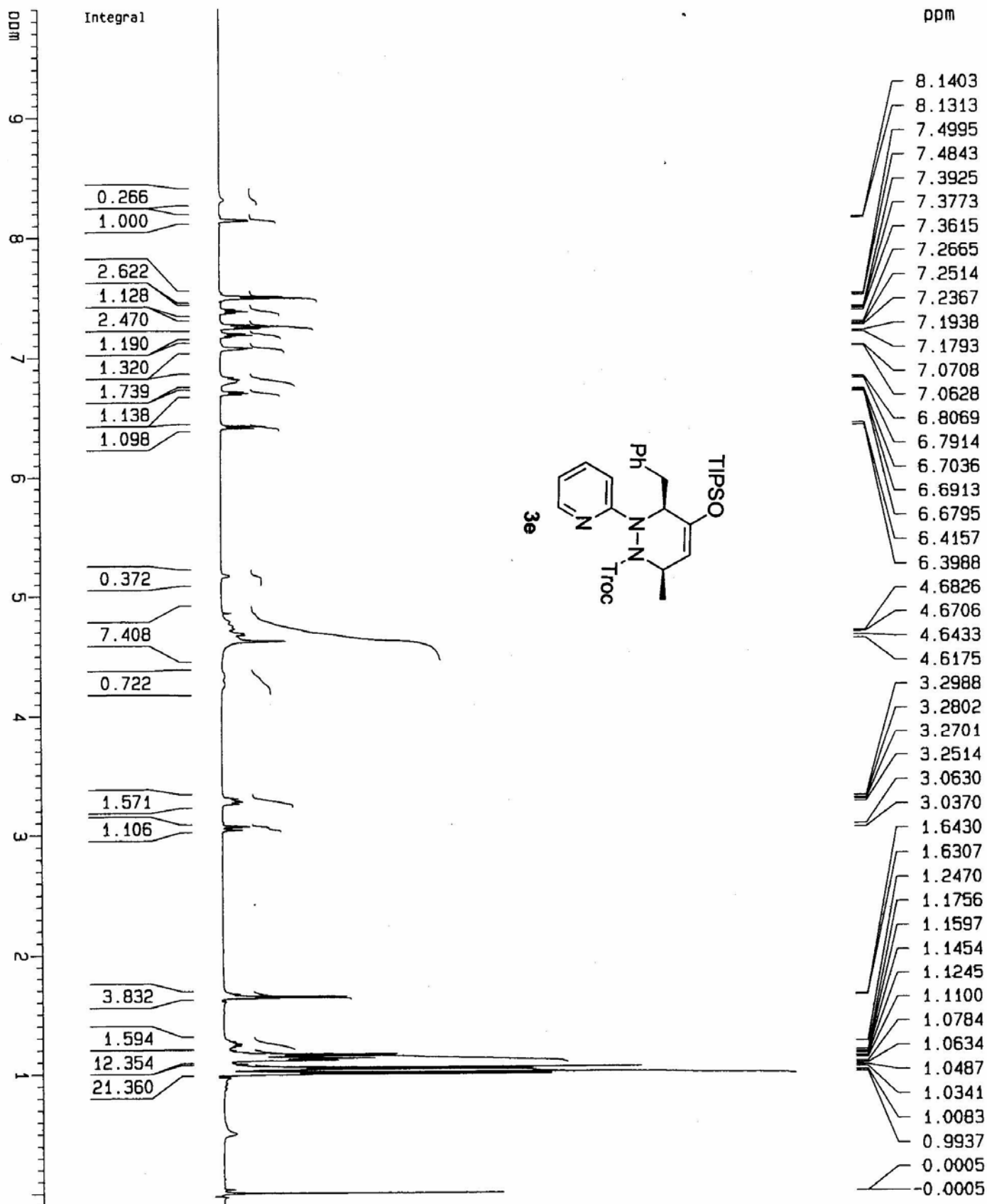


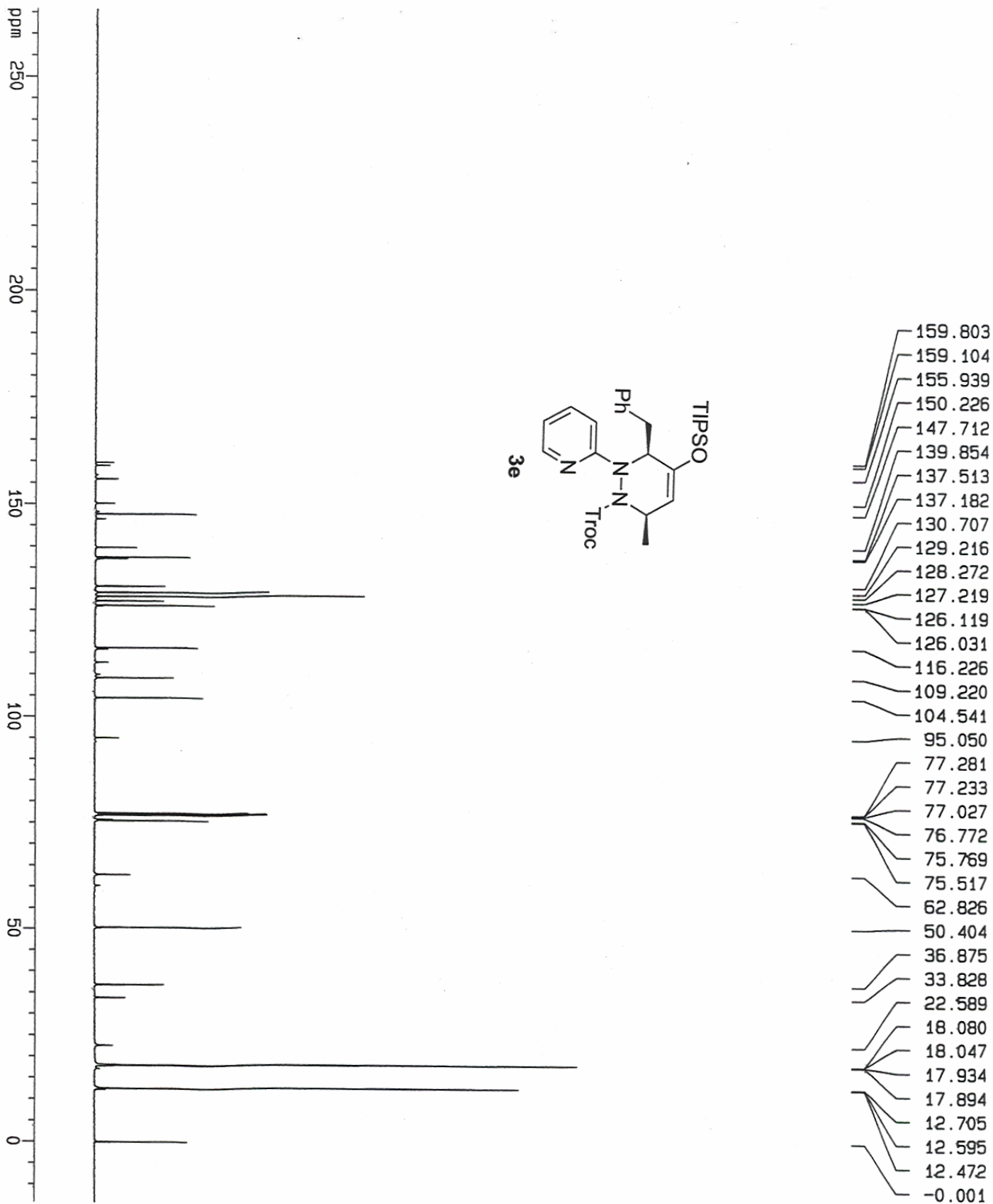


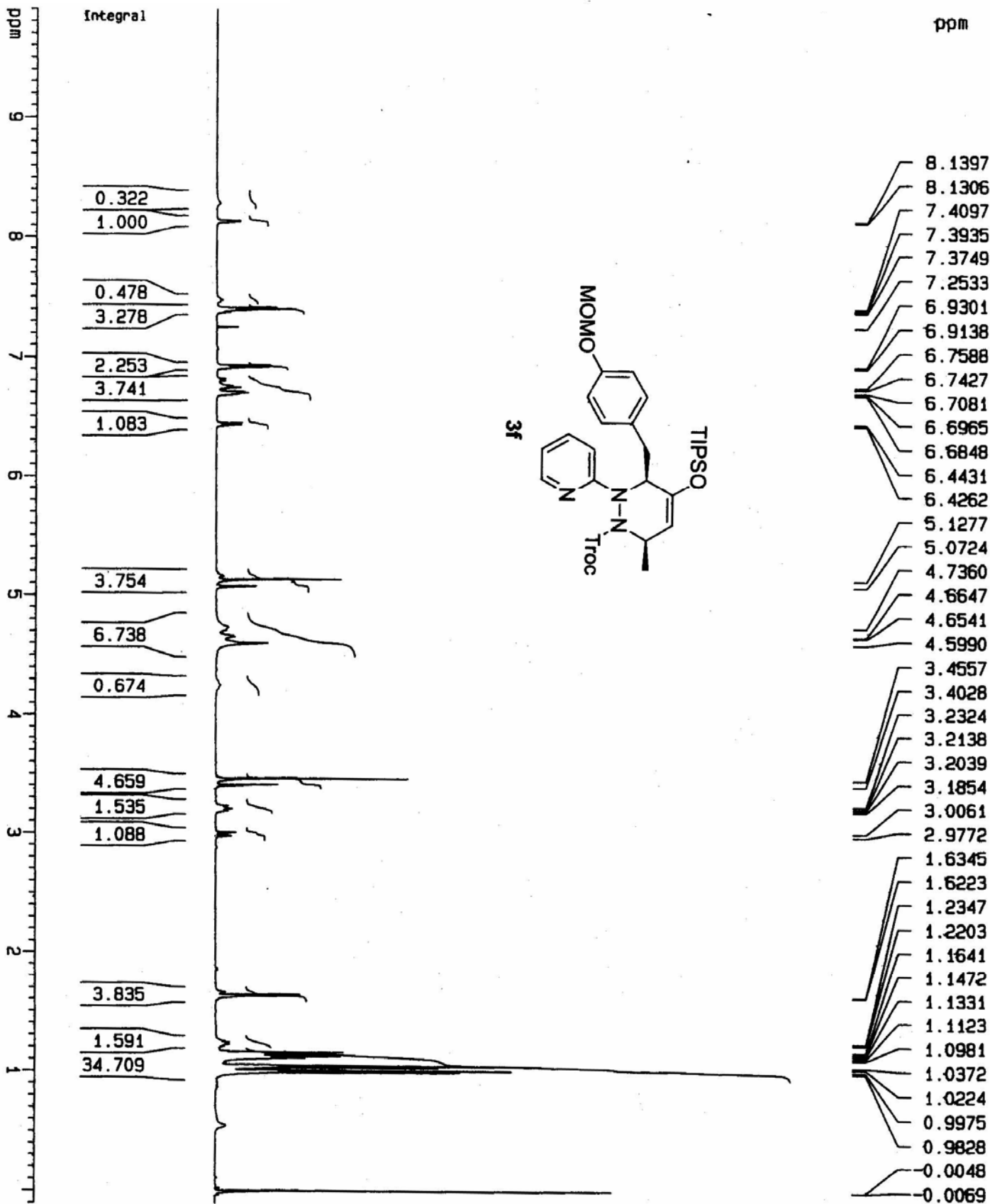




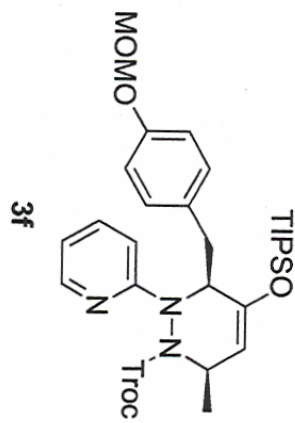






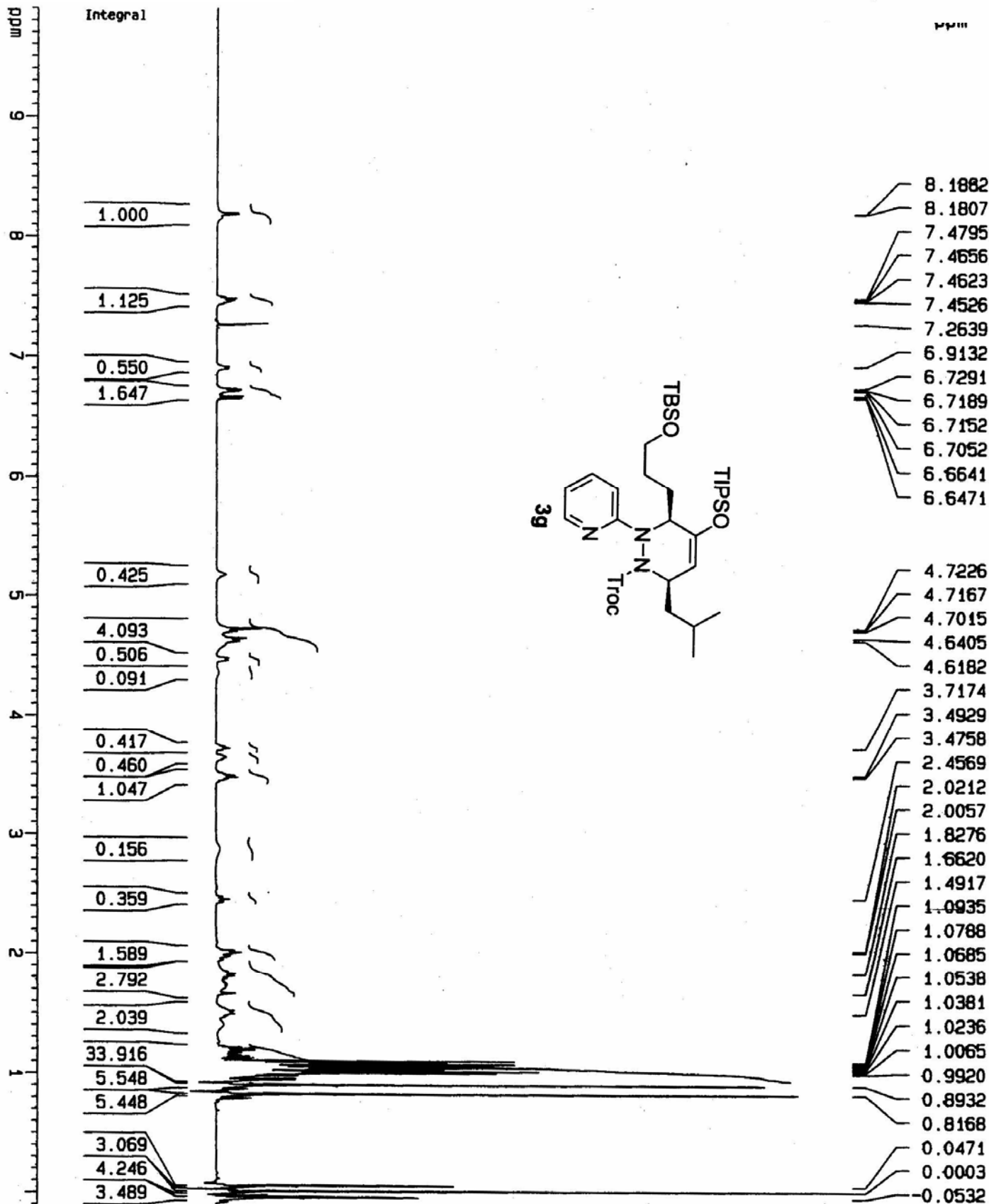


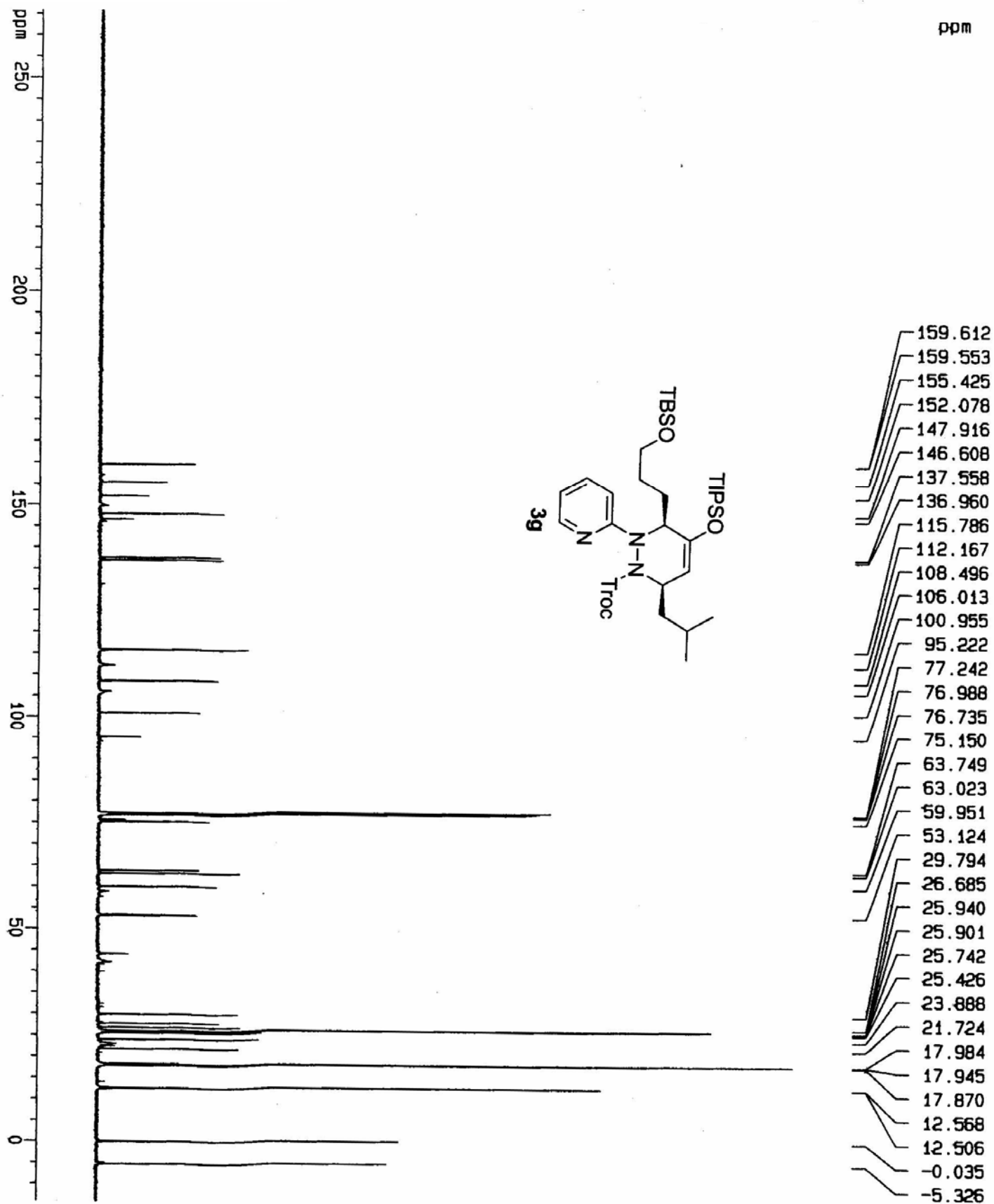
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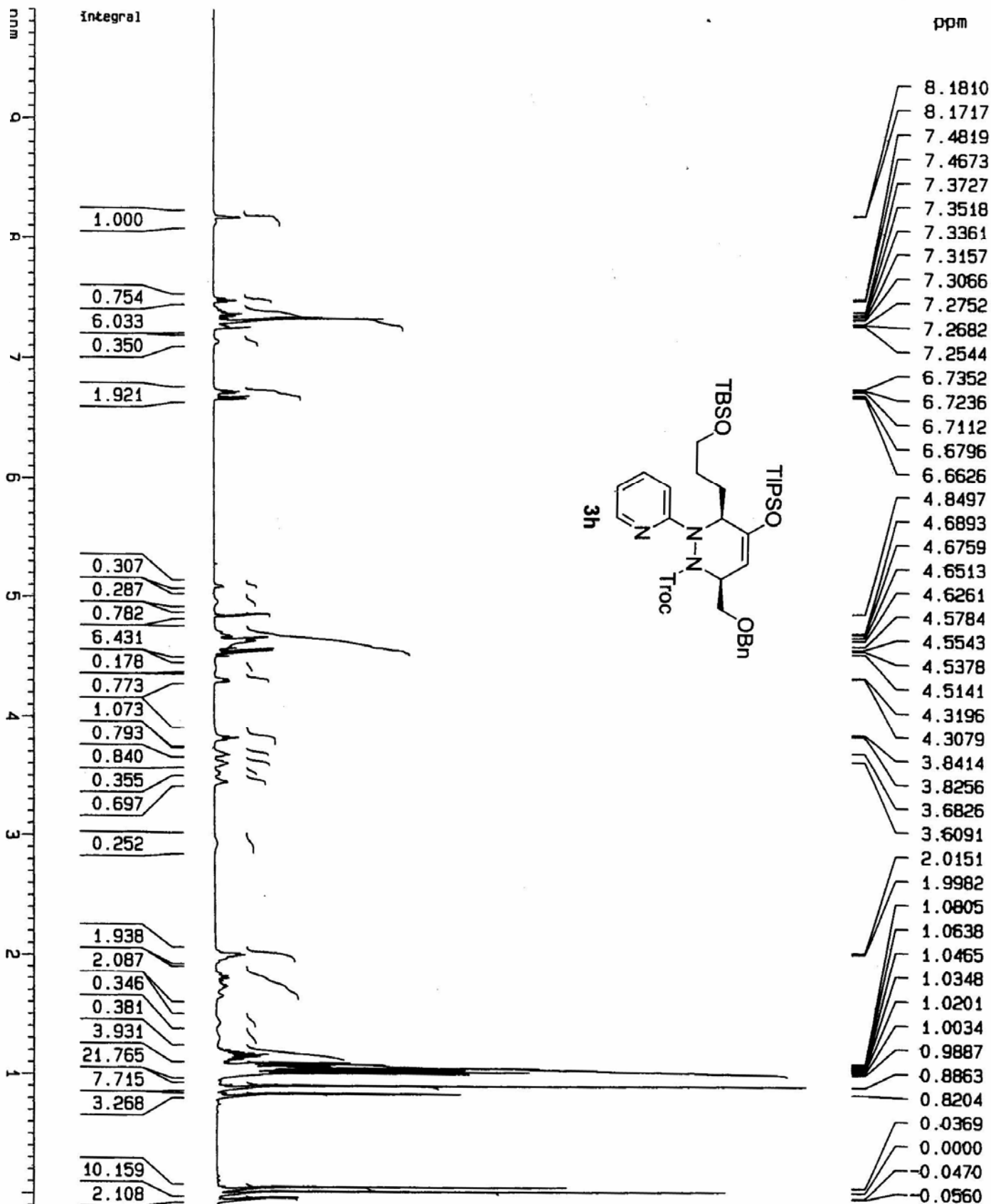


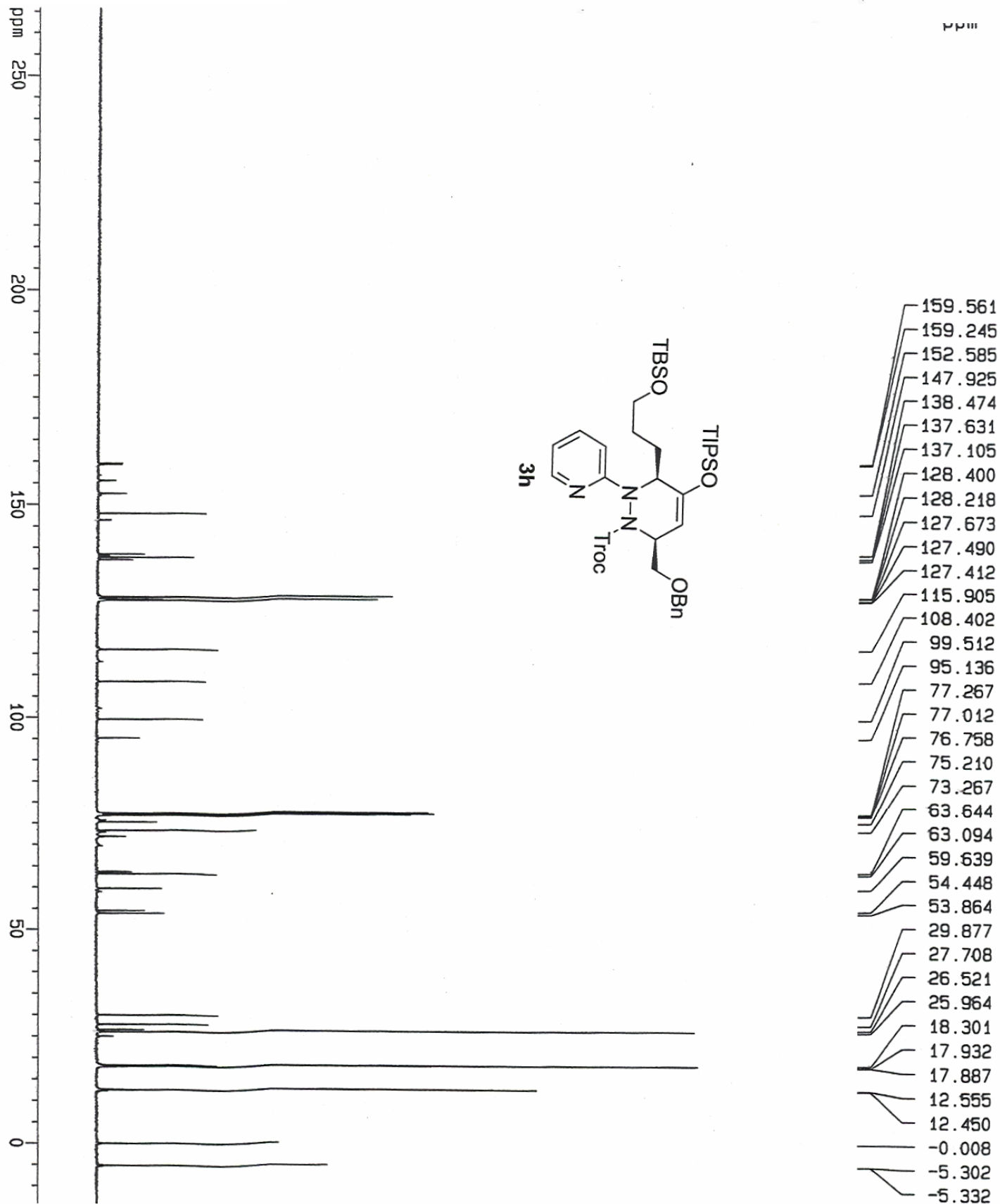
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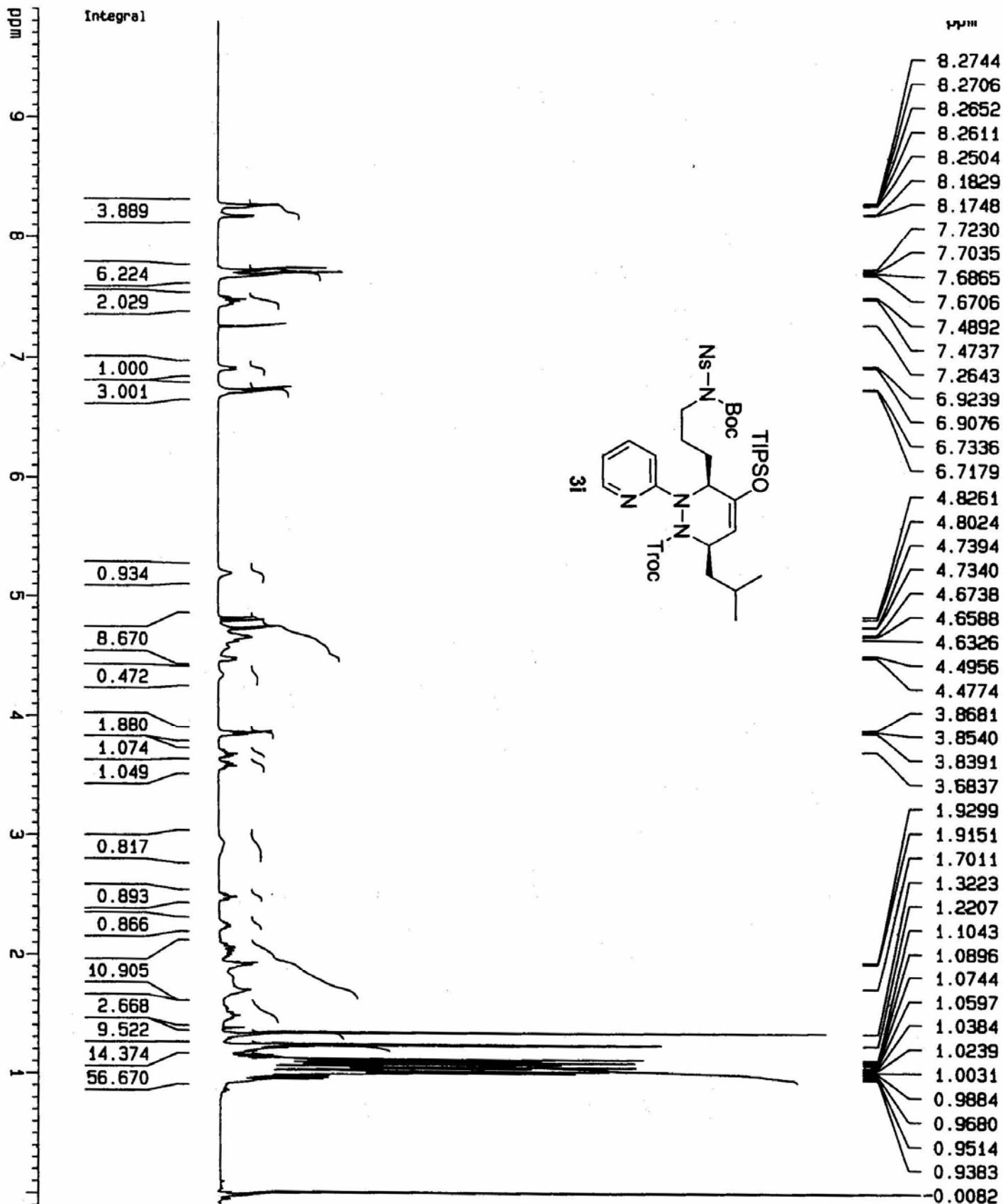
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50.373
50.308
36.021
32.989
18.037
17.916
17.879
17.695
12.568
12.450
-0.013

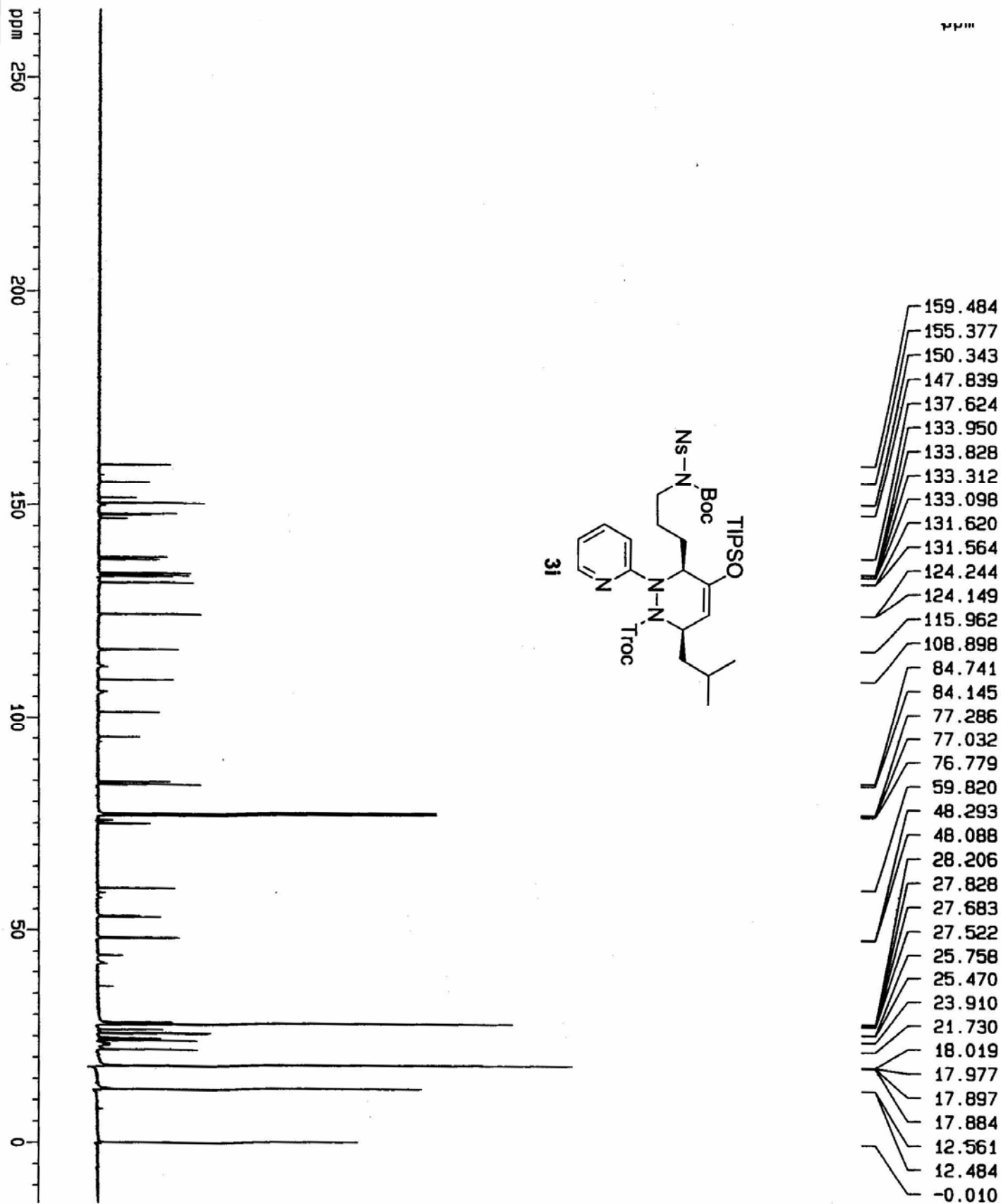


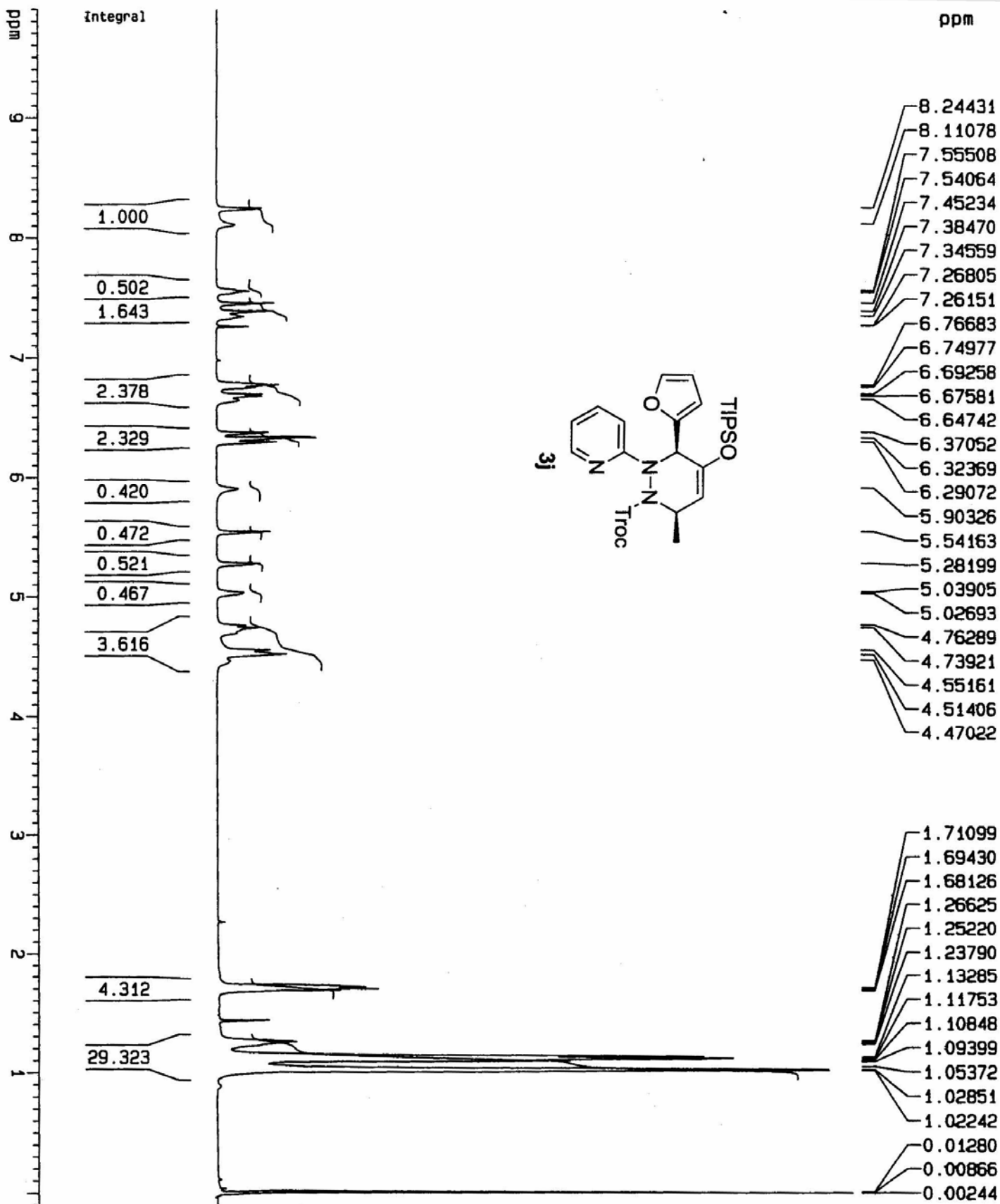


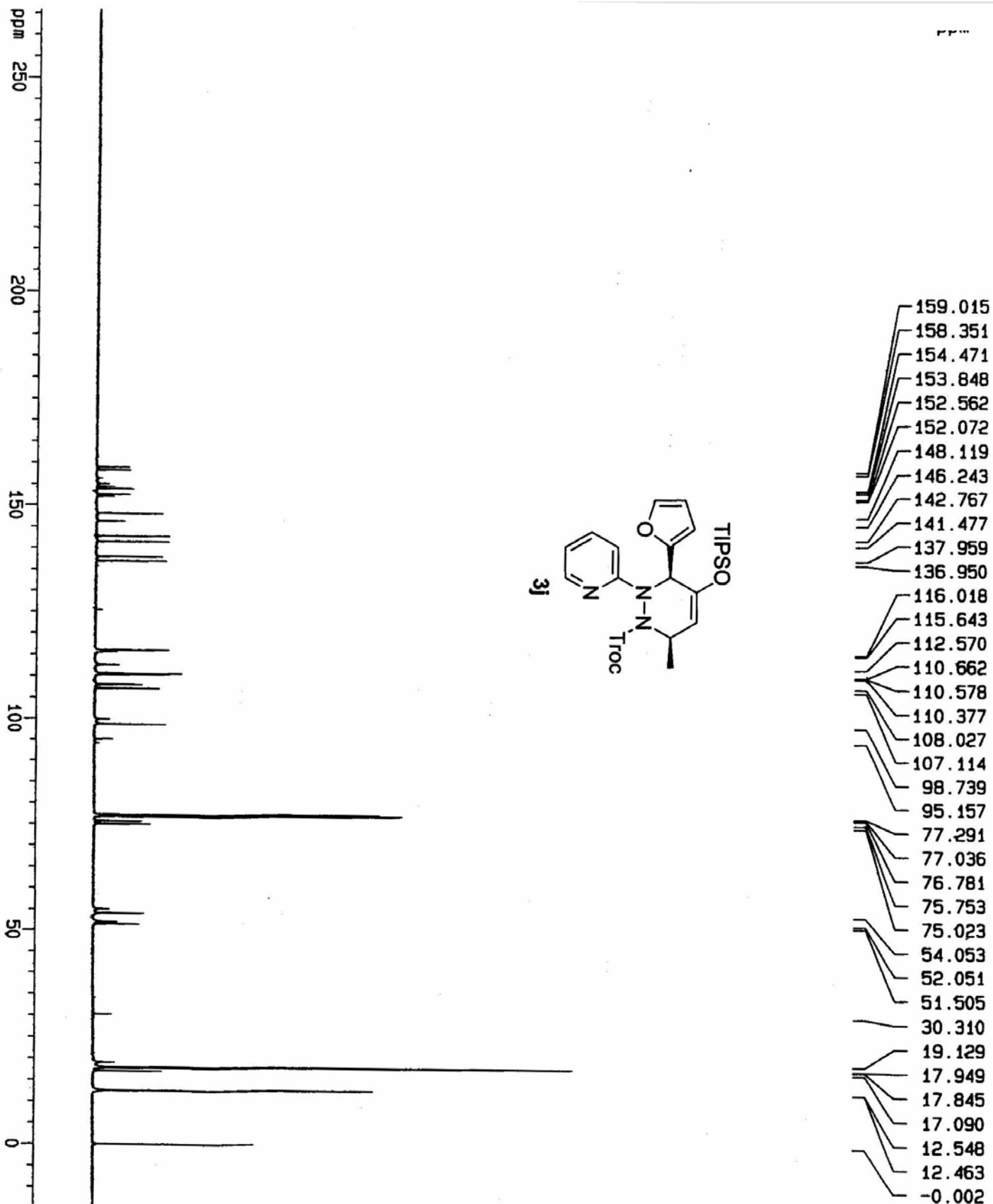


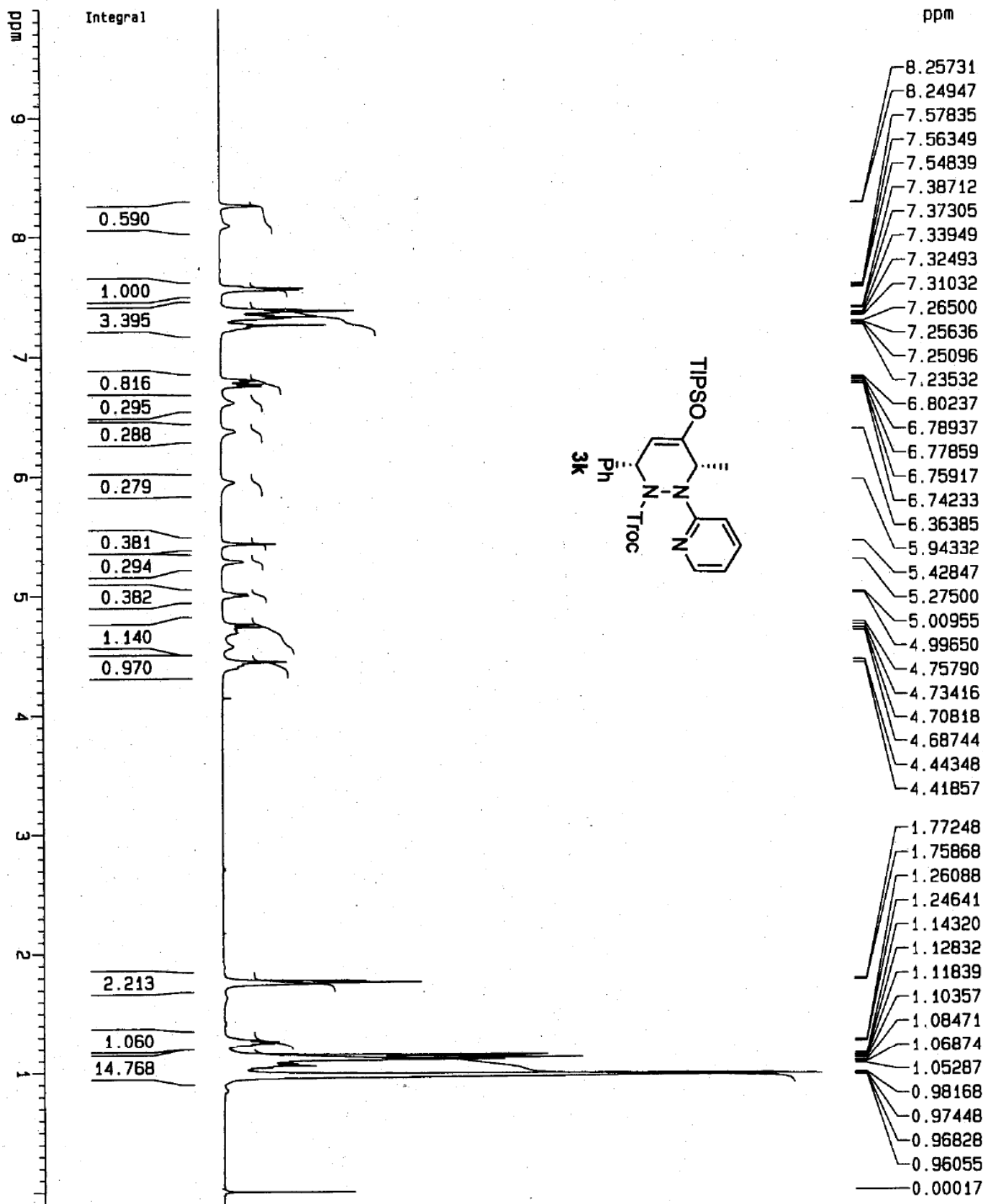


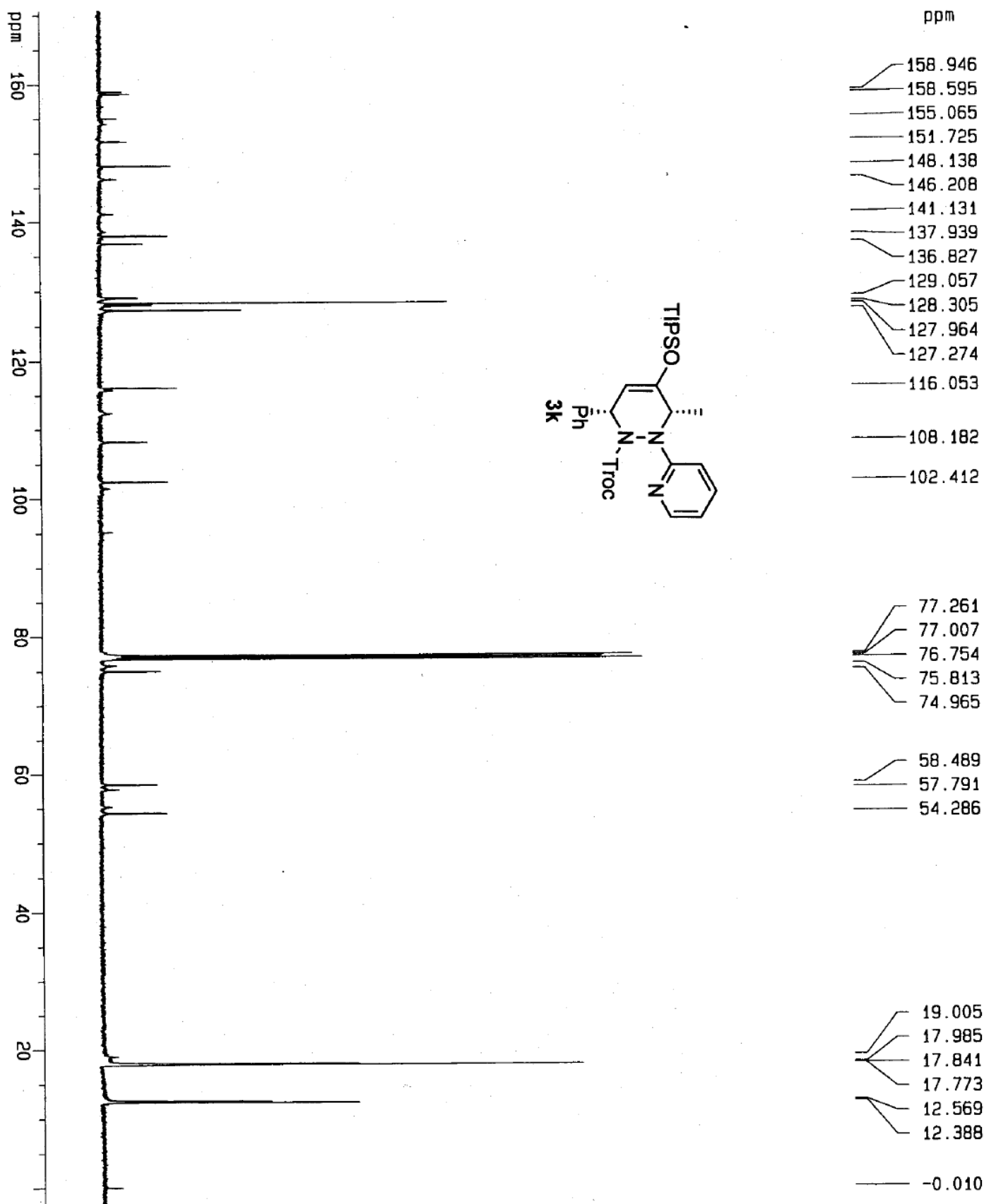












Crystallographic Experimental Section

Data Collection

An irregular broken fragment (05 x 0.12 x 0.10 mm) was selected under a stereomicroscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A “full sphere” data set was obtained which samples approximately all of reciprocal space to a resolution of 0.75 Å using 0.3° steps in ω using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Structure solution and refinement

The space group was determined as $P2_12_12_1$ based on systematic absences and intensity statistics. Direct methods were used to locate most C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C, O and N atoms. Following anisotropic refinement of all non-H atoms, ideal H-atom positions were calculated for most H atoms. Only H19 was located from the difference Fourier map and its position and thermal parameters were refined. Final refinement was anisotropic for all non-H atoms, and isotropic-riding for H atoms except H19. No anomalous bond lengths or thermal parameters were noted. All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Equations of interest:

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$$

$$\text{GooF} = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$$

$$\text{where: } w = q / \sigma^2 (F_o^2) + (aP)^2 + bP;$$

n = number of independent reflections;

q, a, b, P as defined in [1]

p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

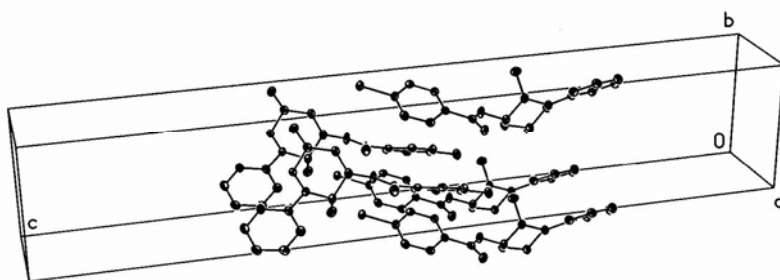
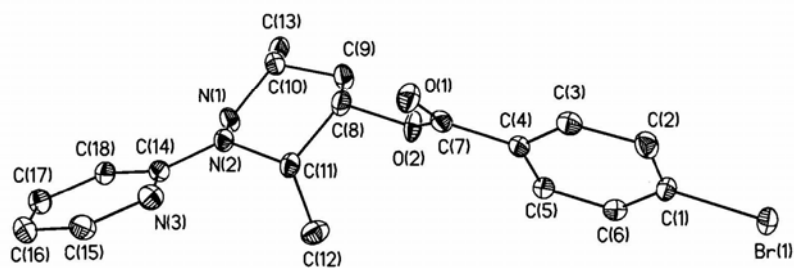
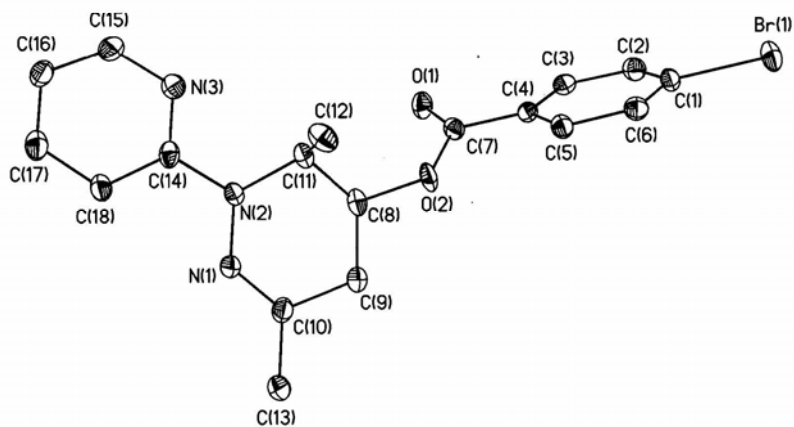


Table 1. Crystal and structure refinement for Kawa01.

Identification Code	Kawa01	
Empirical formula	$C_{18}H_{20}BrN_3O_2$	
Formula weight	390.28	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space Group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 5.5911(11)$ Å	$\alpha = 90.0^\circ$
	$b = 7.3687(15)$ Å	$\beta = 90.0^\circ$
	$c = 41.520(8)$ Å	$\gamma = 90.0^\circ$
Volume	1710.6(6) Å ³	
Z	4	
Density (calculated)	1.515 Mg/m ³	
Absorption coefficient	2.419 mm ⁻¹	
F(000)	800	
Crystal size, color, habit	0.50 x 0.12 x 0.10mm, clear, rod	
Theta range for data collection	1.96 – 28.30 °	
Index ranges	-7 ≤ h ≤ 7, 9 ≤ k ≤ 9, -55 ≤ l ≤ 55	
Reflections collected	20,194	
Independent reflections	4,172 (R _{int} = 0.0440)	
Reflections with I > 4σ(F _o)	3,820	
Flack parameter	0.015(8)	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.568	
Refinement method	Full-matrix least squares on F ²	
Weighting scheme	w = q [σ ² (F _o ²) + (aP) ² + bP] ⁻¹ where: P = (F _o ² + 2F _c ²)/3, a = 0.0402, b = 0.454, q = 1	
Data / restraints / parameters	4172 / 0 / 219	
Goodness-of-fit on F ²	1.068	
Final R indices [I > 2 sigma(I)]	R1 = 0.0323, wR2 = 0.0711	
R indices (all data)	R1 = 0.0372, wR2 = 0.0722	
Largest diff. peak and hole	0.685, -0.359 eÅ ⁻³	

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for Kawa01. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
Br(1)	1731(1)	6355(1)	-746(1)	26(1)	
C(1)	798(5)	5572(3)	-330(1)	20(1)	
C(2)	-1371(5)	4725(3)	-286(1)	21(1)	
C(3)	-2040(5)	4211(3)	23(1)	19(1)	
C(4)	-525(5)	4514(3)	281(1)	17(1)	
C(5)	1702(5)	5332(3)	231(1)	18(1)	
C(6)	2342(4)	5896(3)	-74(1)	19(1)	
C(7)	-1306(4)	3898(3)	606(1)	18(1)	
C(8)	178(5)	3082(3)	1130(1)	21(1)	
C(9)	2405(5)	2019(4)	1213(1)	23(1)	
C(10)	2457(4)	1517(4)	1568(1)	22(1)	
C(11)	-270(5)	4686(3)	1355(1)	19(1)	
C(12)	1435(5)	6278(4)	1310(1)	26(1)	
C(13)	4830(5)	694(4)	1663(1)	24(1)	
C(14)	-1371(5)	4820(3)	1933(1)	19(1)	
C(15)	-4619(5)	6499(4)	2089(1)	23(1)	
C(16)	-3979(4)	6463(4)	2407(1)	25(1)	
C(17)	-1900(5)	5548(3)	2488(1)	24(1)	
C(18)	-567(5)	4714(3)	2253(1)	20(1)	
N(1)	1997(4)	3087(3)	1773(1)	20(1)	
N(2)	-179(4)	3946(3)	1684(1)	19(1)	
N(3)	-3378(4)	5704(3)	1852(1)	21(1)	
O(1)	-3338(3)	3563(3)	680(1)	23(1)	
O(2)	578(3)	3737(3)	804(1)	22(1)	

Table 3. Bond lengths [Å] and angles [°] for Kawa01.

Br(1)-C(1)	1.893(2)	C(9)-C(10)	1.522(3)
C(1)-C(2)	1.376(4)	C(10)-N(1)	1.459(3)
C(1)-C(6)	1.389(3)	C(10)-C(13)	1.511(4)
C(2)-C(3)	1.388(3)	C(11)-N(2)	1.470(3)
C(3)-C(4)	1.384(3)	C(11)-C(12)	1.523(3)
C(4)-C(5)	1.398(4)	C(14)-N(3)	1.340(3)
C(4)-C(7)	1.489(3)	C(14)-N(2)	1.389(3)
C(5)-C(6)	1.383(3)	C(14)-C(18)	1.405(3)
C(7)-O(1)	1.203(3)	C(15)-N(3)	1.340(3)
C(7)-O(2)	1.342(3)	C(15)-C(16)	1.369(4)
C(8)-O(2)	1.454(3)	C(16)-C(17)	1.385(4)
C(8)-C(9)	1.511(4)	C(17)-C(18)	1.372(4)
C(8)-C(11)	1.528(3)	N(1)-N(2)	1.421(3)
C(2)-C(1)-C(6)	121.6(2)	N(1)-C(10)-C(9)	111.7(2)
C(2)-C(1)-Br(1)	120.16(19)	C(13)-C(10)-C(9)	111.5(2)
C(6)-C(1)-Br(1)	118.26(19)	N(2)-C(11)-C(12)	112.2(2)
C(1)-C(2)-C(3)	119.0(2)	N(2)-C(11)-C(8)	106.02(19)
C(4)-C(3)-C(2)	120.4(2)	C(12)-C(11)-C(8)	114.7(2)
C(3)-C(4)-C(5)	120.1(2)	N(3)-C(14)-N(2)	116.1(2)
C(3)-C(4)-C(7)	118.2(2)	N(3)-C(14)-C(18)	122.2(2)
C(5)-C(4)-C(7)	121.7(2)	N(2)-C(14)-C(18)	121.7(2)
C(6)-C(5)-C(4)	119.6(2)	N(3)-C(15)-C(16)	124.5(3)
C(5)-C(6)-C(1)	119.3(2)	C(15)-C(16)-C(17)	117.4(2)
O(1)-C(7)-O(2)	124.4(2)	C(18)-C(17)-C(16)	120.2(2)
O(1)-C(7)-C(4)	124.9(2)	C(17)-C(18)-C(14)	118.2(3)
O(2)-C(7)-C(4)	110.6(2)	N(2)-N(1)-C(10)	110.57(19)
O(2)-C(8)-C(9)	104.9(2)	C(14)-N(2)-N(1)	114.97(19)
O(2)-C(8)-C(11)	109.8(2)	C(14)-N(2)-C(11)	120.2(2)
C(9)-C(8)-C(11)	113.3(2)	N(1)-N(2)-C(11)	115.98(19)
C(8)-C(9)-C(10)	111.3(2)	C(14)-N(3)-C(15)	117.5(2)
N(1)-C(10)-C(13)	108.7(2)	C(7)-O(2)-C(8)	118.62(19)

Table 4. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for Kawa01.
 The anisotropic displacement factor exponent takes the form:
 $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br (1)	37 (1)	25 (1)	14 (1)	2 (1)	2 (1)	-6 (1)
C (1)	27 (1)	19 (1)	14 (1)	2 (1)	3 (1)	2 (1)
C (2)	24 (1)	22 (1)	17 (1)	-2 (1)	-4 (1)	0 (1)
C (3)	18 (1)	17 (1)	21 (1)	-1 (1)	1 (1)	1 (1)
C (4)	22 (1)	14 (1)	15 (1)	-1 (1)	2 (1)	2 (1)
C (5)	23 (1)	16 (1)	16 (1)	0 (1)	0 (1)	0 (1)
C (6)	22 (1)	16 (1)	20 (1)	0 (1)	1 (1)	0 (1)
C (7)	24 (1)	16 (1)	14 (1)	-2 (1)	-3 (1)	1 (1)
C (8)	25 (1)	24 (1)	14 (1)	2 (1)	1 (1)	-3 (1)
C (9)	27 (1)	27 (1)	15 (1)	-2 (1)	0 (1)	4 (1)
C (10)	27 (1)	21 (1)	17 (1)	-2 (1)	2 (1)	2 (1)
C (11)	21 (1)	22 (1)	14 (1)	3 (1)	-1 (1)	0 (1)
C (12)	30 (1)	22 (1)	27 (1)	5 (1)	-6 (1)	-2 (1)
C (13)	28 (1)	24 (1)	19 (1)	5 (1)	3 (1)	3 (1)
C (14)	23 (1)	18 (1)	16 (1)	-2 (1)	1 (1)	-4 (1)
C (15)	23 (1)	20 (1)	25 (1)	-2 (1)	2 (1)	0 (1)
C (16)	30 (1)	22 (1)	21 (1)	-3 (1)	5 (1)	3 (1)
C (17)	31 (1)	23 (1)	17 (1)	-2 (1)	1 (1)	-3 (1)
C (18)	27 (1)	20 (1)	15 (1)	1 (1)	1 (1)	-2 (1)
N (1)	24 (1)	21 (1)	16 (1)	-1 (1)	0 (1)	3 (1)
N (2)	22 (1)	21 (1)	13 (1)	1 (1)	-1 (1)	1 (1)
N (3)	21 (1)	21 (1)	21 (1)	-1 (1)	-2 (1)	-2 (1)
O (1)	21 (1)	30 (1)	19 (1)	2 (1)	3 (1)	-4 (1)
O (2)	21 (1)	36 (1)	10 (1)	4 (1)	-2 (1)	-3 (1)

Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for Kawa01.

	x	y	z	U(eq)
H(2)	-2373	4501	-460	25
H(3)	-3516	3660	56	22
H(5)	2746	5495	403	22
H(6)	3791	6486	-108	23
H(8)	-1211	2272	1132	25
H(9A)	3806	2738	1161	27
H(9B)	2458	922	1084	27
H(10)	1201	616	1608	26
H(11)	-1899	5125	1316	23
H(12A)	982	7248	1452	39
H(12B)	1362	6691	1091	39
H(12C)	3037	5899	1359	39
H(13A)	6089	1545	1620	35
H(13B)	5096	-394	1541	35
H(13C)	4811	408	1889	35
H(15)	-6011	7116	2034	27
H(16)	-4906	7032	2564	29
H(17)	-1404	5499	2701	28
H(18)	831	4094	2304	24
H(19)	3300(50)	3850(40)	1747(6)	20(7)

Table 6. Torsion angles [$^{\circ}$] for Kawa01.

C(6)-C(1)-C(2)-C(3)	1.0(4)
Br(1)-C(1)-C(2)-C(3)	-178.21(19)
C(1)-C(2)-C(3)-C(4)	-1.3(4)
C(2)-C(3)-C(4)-C(5)	-0.4(4)
C(2)-C(3)-C(4)-C(7)	-178.6(2)
C(3)-C(4)-C(5)-C(6)	2.4(3)
C(7)-C(4)-C(5)-C(6)	-179.4(2)
C(4)-C(5)-C(6)-C(1)	-2.6(4)
C(2)-C(1)-C(6)-C(5)	0.9(4)
Br(1)-C(1)-C(6)-C(5)	-179.80(18)
C(3)-C(4)-C(7)-O(1)	-19.1(4)
C(5)-C(4)-C(7)-O(1)	162.7(2)
C(3)-C(4)-C(7)-O(2)	159.9(2)
C(5)-C(4)-C(7)-O(2)	-18.3(3)
O(2)-C(8)-C(9)-C(10)	170.1(2)
C(11)-C(8)-C(9)-C(10)	50.3(3)
C(8)-C(9)-C(10)-N(1)	-49.9(3)
C(8)-C(9)-C(10)-C(13)	-171.8(2)
O(2)-C(8)-C(11)-N(2)	-169.09(19)
C(9)-C(8)-C(11)-N(2)	-52.1(3)
O(2)-C(8)-C(11)-C(12)	-44.7(3)
C(9)-C(8)-C(11)-C(12)	72.3(3)
N(3)-C(15)-C(16)-C(17)	0.3(4)
C(15)-C(16)-C(17)-C(18)	-0.3(4)
C(16)-C(17)-C(18)-C(14)	0.1(4)
N(3)-C(14)-C(18)-C(17)	0.0(4)
N(2)-C(14)-C(18)-C(17)	-177.2(2)
C(13)-C(10)-N(1)-N(2)	177.72(19)
C(9)-C(10)-N(1)-N(2)	54.2(3)
N(3)-C(14)-N(2)-N(1)	177.4(2)
C(18)-C(14)-N(2)-N(1)	-5.2(3)
N(3)-C(14)-N(2)-C(11)	31.3(3)
C(18)-C(14)-N(2)-C(11)	-151.3(2)
C(10)-N(1)-N(2)-C(14)	150.5(2)
C(10)-N(1)-N(2)-C(11)	-62.0(3)
C(12)-C(11)-N(2)-C(14)	78.8(3)
C(8)-C(11)-N(2)-C(14)	-155.3(2)
C(12)-C(11)-N(2)-N(1)	-67.0(3)
C(8)-C(11)-N(2)-N(1)	59.0(3)
N(2)-C(14)-N(3)-C(15)	177.4(2)
C(18)-C(14)-N(3)-C(15)	0.0(4)
C(16)-C(15)-N(3)-C(14)	-0.2(4)
O(1)-C(7)-O(2)-C(8)	1.3(4)
C(4)-C(7)-O(2)-C(8)	-177.7(2)
C(9)-C(8)-O(2)-C(7)	146.7(2)
C(11)-C(8)-O(2)-C(7)	-91.1(3)