Supporting Information

Divergent Total Synthesis of (–)-Aspidospermine and (+)-Spegazzinine

James P. Lajiness, Wanlong Jiang, and Dale L. Boger

Contribution from the Department of Chemistry and The Skaggs Institute for Chemical Biology, The Scripps Research Institute, 10650 North Torrey Pines Road, La Jolla, California 92037

boger@scripps.edu

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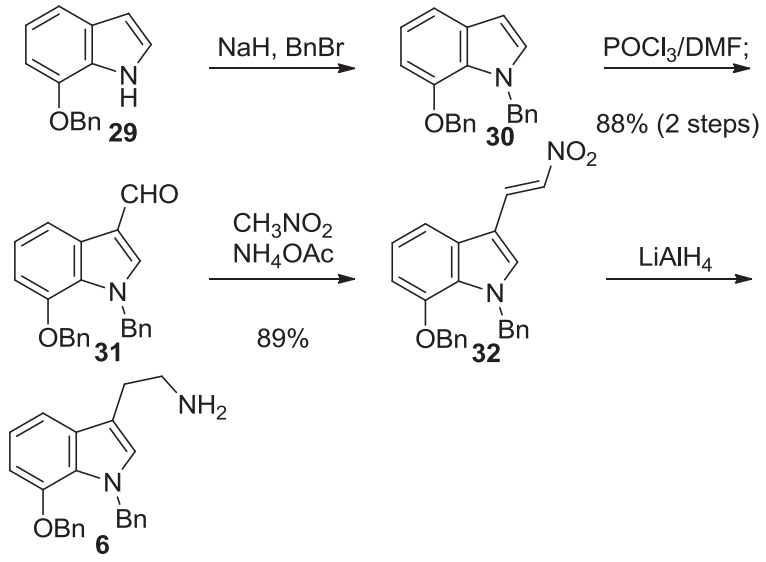
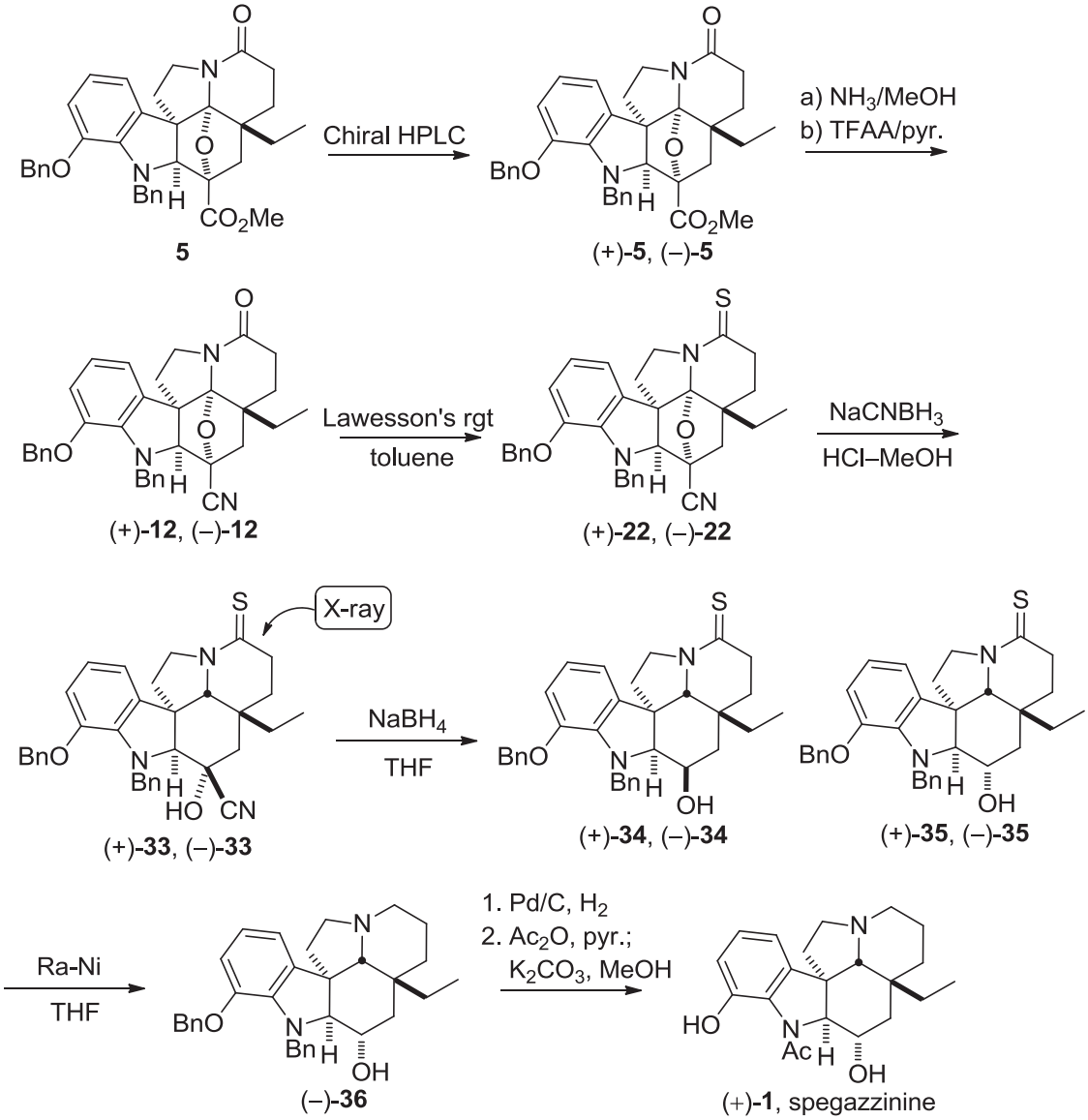
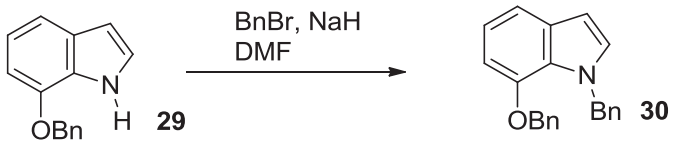
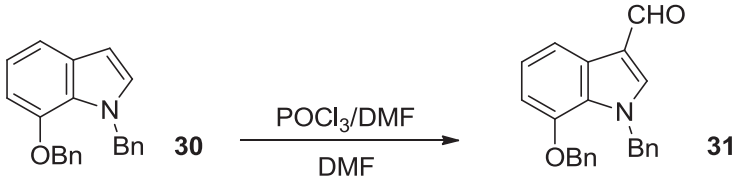


Supporting Information Scheme 2.

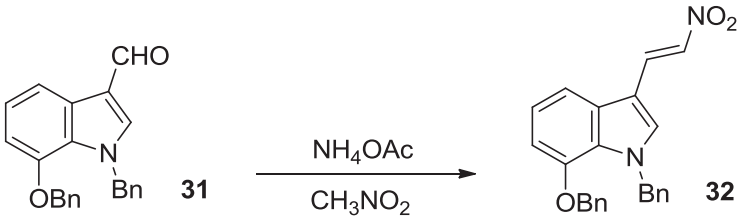




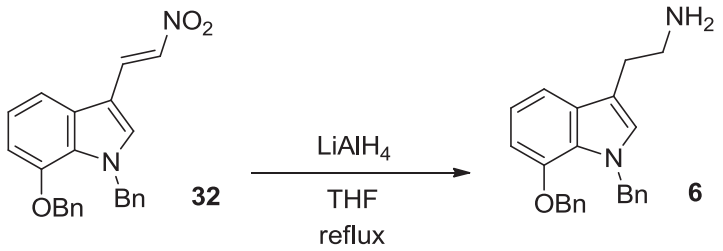
A suspension of NaH (0.367 g, 9.17 mmol, 60% dispersion in mineral oil) in DMF (30 mL) was treated with 7-benzyloxyindole (**29**, 1.02 g, 4.58 mmol) in small portions at room temperature. The reaction mixture was stirred at room temperature for 1 h followed by the addition of BnBr (1.64 mL, 13.8 mmol). The reaction mixture was warmed at 55 °C overnight, cooled to room temperature, and concentrated under reduced pressure to provide **30** as a brown oil that was used in the next step without further purification.



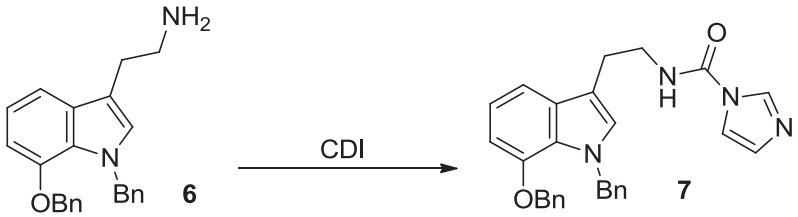
A solution of **30** (1.43 g, 4.58 mmol) in DMF (2 mL) at 0 °C was added slowly to the Vilsmeier reagent, prepared from slow addition of $POCl_3$ (0.47 mL, 5.04 mmol) to DMF (4.3 mL, 55.0 mmol) at 0 °C. The reaction mixture was warmed to 35 °C and stirred for 95 min before it was poured into crushed ice. An aqueous NaOH solution (4.4 mL of aqueous 20% solution, 22.0 mmol) was added dropwise to the reaction mixture and the solution was quickly boiled for 5 min. The reaction mixture was cooled and diluted with CH_2Cl_2, washed with H_2O and saturated aqueous NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by flash chromatography (15–20% EtOAc/hexanes) to provide **31** as a colorless crystalline solid (1.38 g, 88% over two steps): mp 133 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.00 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.63 (s, 1H), 7.30–7.35 (m, 3H), 7.24−7.29 (m, 3H), 7.16–7.24 (m, 3H), 6.91–6.98 (m, 2H), 6.81 (d, J = 7.8 Hz, 1H), 5.63 (s, 2H), 5.08 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.6, 146.5, 139.3, 137.5, 136.2, 128.7, 128.5, 128.1, 127.9, 127.8, 127.6, 127.0, 126.5, 123.7, 118.4, 114.6, 106.2, 70.4, 53.5; IR (film) ν_{max} 3105, 2798, 1649, 1533 cm^{-1}; ESI-TOF HRMS *m/z* 342.1489 (M+H$^+$, $C_{23}H_{20}NO_2$ requires 342.1488).



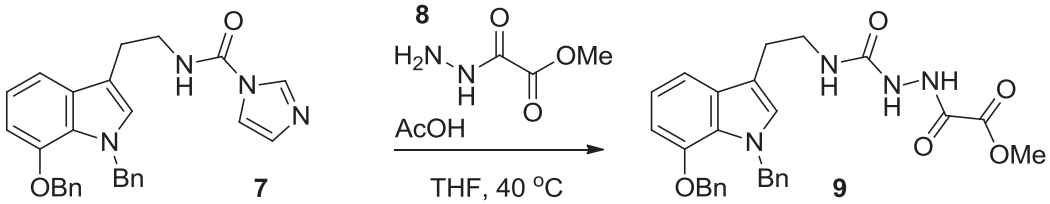
A solution of **31** (2.36 g, 6.91 mmol) in nitromethane (15 mL) was treated with ammonium acetate (586 mg, 7.60 mmol). The reaction mixture was warmed at reflux under nitrogen for 1 h and then cooled to room temperature. The solution was diluted with CH_2Cl_2, washed with H_2O and saturated aqueous NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was recrystallized from 30% EtOAc/hexanes to provide **32** as yellow needle-like crystals (2.36 g, 89%): mp 145–146 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (d, J = 13.4 Hz, 1H), 7.74 (d, J = 13.4 Hz, 1H), 7.46 (s, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.30–7.35 (m, 3H), 7.24−7.29 (m, 3H), 7.16–7.20 (m, 3H), 6.90–6.96 (m, 2H), 6.82 (d, J = 7.8 Hz, 1H), 5.62 (s, 2H), 5.09 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.1, 137.5, 136.7, 136.0, 133.3, 132.2, 128.7, 128.6, 128.2, 128.2, 127.8, 127.6, 127.5, 126.4, 123.4, 113.2, 108.6, 106.1, 70.5, 53.4; IR (film) ν_{max} 3107, 3031, 1611, 1527 cm^{-1}; ESI-TOF HRMS *m/z* 385.1541 (M+H$^+$, $C_{24}H_{21}N_2O_3$ requires 385.1547).



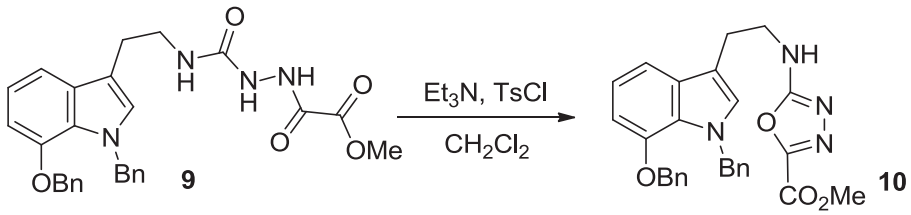
A solution of **32** (2.38 g, 6.18 mmol) in THF (10 mL) was added dropwise to a suspension of $LiAlH_4$ (1.41 g, 37.1 mmol) in anhydrous THF (40 mL) at 0 °C. The reaction mixture was warmed at reflux for 1.5 h and then the excess reagent was destroyed by addition of Na_2SO_4•$10H_2O$ (19.9 g, 61.8 mmol). The resulting mixture was filtered through Celite and washed with CH_2Cl_2. The filtrate was concentrated to provide crude **6** as a colorless oil that was used in the next step without purification.



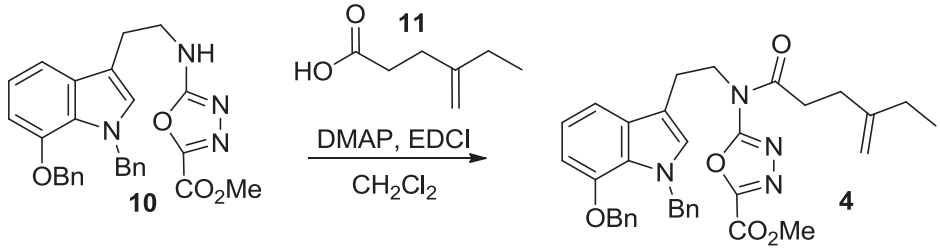
A solution of crude **6** (6.18 mmol) in anhydrous CH_2Cl_2 (20 mL) was added to a solution of 1,1-carbonyldiimidazole (CDI, 2.00 g, 12.4 mmol) in anhydrous THF (50.0 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature slowly and was stirred overnight. The reaction mixture was diluted with CH_2Cl_2, washed with saturated aqueous NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by flash chromatography (60–90% EtOAc/hexanes gradient) to provide **7** as a white colorless crystalline solid (2.14 g, 77% over two steps): mp 129 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (s, 1H), 7.28–7.33 (m, 3H), 7.16–7.25 (m, 6H), 7.07 (s, 1H), 7.01 (t, J = 7.9 Hz, 1H), 6.99 (s, 1H), 6.91–6.95 (m, 2H), 6.91 (s, 1H), 6.71 (d, J = 7.7 Hz, 1H), 5.78 (bs, 1H, NH), 5.57 (s, 2H), 5.10 (s, 2H), 3.71 (q, J = 6.4 Hz, 2H), 3.06 (t, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.7, 146.9, 139.4, 136.6, 130.2, 130.1, 128.5, 128.5, 127.9, 127.6, 127.5, 127.1, 126.5, 126.4, 120.1, 115.7, 111.6, 111.5, 104.2, 70.3, 52.3, 41.3, 25.0; IR (film) ν_{max} 3031, 2928, 1715, 1548 cm^{-1}; ESI-TOF HRMS *m/z* 451.2131 ($M+H^+$, $C_{28}H_{27}N_4O_2$ requires 451.2128).



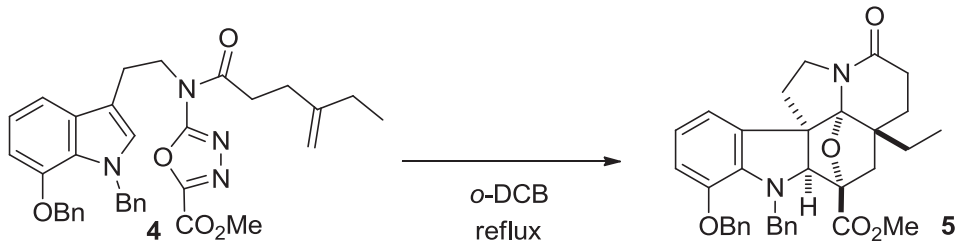
Methyl oxalyl hydrazide (**8**, 204 mg, 1.73 mmol) was added to a solution of **7** (648 mg, 1.44 mmol) and AcOH (91 μL, 1.58 mmol) in THF (15 mL). The mixture was warmed to 40 °C overnight, then cooled to room temperature and concentrated under reduced pressure. The resulting residue was diluted with CH_2Cl_2 and washed with aqueous citric acid (10%, 30 mL). The aqueous layer was extracted quickly with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated to provide **9** as a light brown powder that was used immediately in the next step without purification.



A solution of **9** (1.44 mmol) in CH_2Cl_2 (50 mL) at 0 °C was treated with Et_3N (0.50 mL, 3.60 mmol) and TsCl (302 mg, 1.58 mmol). The reaction mixture was warmed slowly to room temperature over 6 h and poured into saturated aqueous $NaHCO_3$ (20 mL). The mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with water and saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (40–45% EtOAc/hexanes) to provide **10** as a white solid (489 mg, 70% over two steps): mp 132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27–7.33 (m, 3H), 7.16–7.24 (m, 6H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.90–6.93 (m, 2H), 6.90 (s, 1H), 6.70 (d, *J* = 7.7 Hz, 1H), 5.57 (s, 2H), 5.08 (s, 2H), 3.98 (s, 3H), 3.76 (q, *J* = 6.5 Hz, 2H), 3.09 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.6, 155.0, 151.2, 147.0, 139.7, 36.9, 130.3, 128.69, 128.68, 128.1, 128.0, 127.8, 127.2, 126.7, 126.5, 70.5, 53.4, 52.5, 43.8, 25.4; IR (film) ν_{max} 3031, 2927, 1738, 1618, 1572 cm^{-1}; ESI-TOF HRMS *m/z* 483.2014 (M+H$^+$, $C_{28}H_{27}N_4O_4$ requires 483.2027).

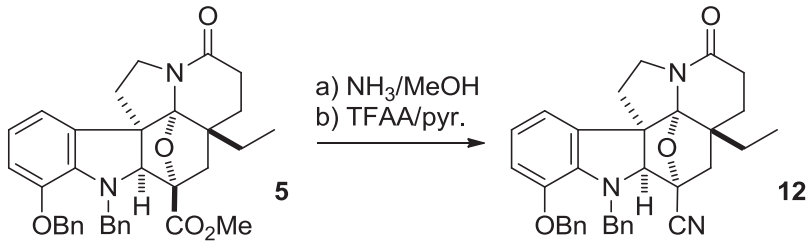


A solution of **10** (458 mg, 0.950 mmol) in CH_2Cl_2 (20 mL) was treated with DMAP (174 mg, 1.43 mmol) and EDCI (273 mg, 1.43 mmol). 4-Ethyl-4-pentenoic acid (**11**, 183 mg, 1.43 mmol) in CH_2Cl_2 (5 mL) was added and the reaction mixture was stirred for 18 h at room temperature. The reaction mixture was treated with saturated aqueous $NaHCO_3$, diluted with EtOAc, washed with water, saturated aqueous NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by flash chromatography (15–20% EtOAc/hexanes) to provide **4** as a white wax-like crystalline solid (489 mg, 87%): mp 102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23–7.32 (m, 4H), 7.14−7.21 (m, 5H), 6.98 (dd, *J* = 7.8 Hz, 1H), 6.87 (dd, *J* = 7.7 Hz, 2.0 Hz, 2H), 6.84 (s, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.51 (s, 2H), 5.03 (s, 2H), 4.73 (s, 1H), 4.67 (s, 1H), 4.18−4.24 (m, 2H), 3.98 (s, 3H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.37 (t, *J* = 7.8 Hz, 2H), 2.01 (q, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.0, 162.0, 154.1, 153.4, 149.4, 146.7, 139.5, 136.8, 130.1, 128.4, 127.9, 127.8, 127.6, 126.9, 126.3, 126.2, 119.8, 111.9, 110.8, 108.3, 103.9, 70.2, 53.6, 52.2, 47.7, 34.8, 30.9, 28.9, 24.2, 12.3; IR (film) ν_{max} 3030, 2962, 1746, 1702, 1559 cm^{-1}; ESI-TOF HRMS *m/z* 593.2756 (M+H$^+$, $C_{35}H_{37}N_4O_5$ requires 593.2758).

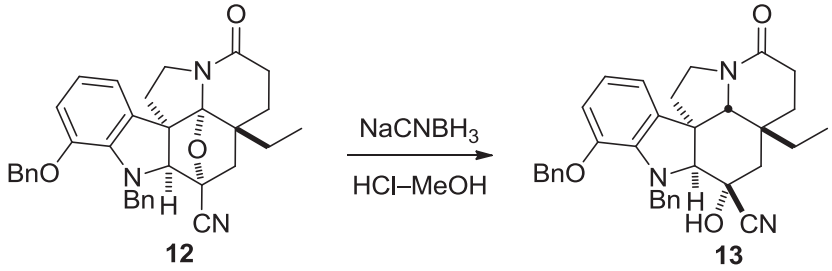


A solution of **4** (268 mg, 0.452 mmol) in anhydrous, degassed 1,2-dichlorobenzene (450 mL) was warmed at reflux for 13 h. The cooled reaction mixture was loaded onto a silica gel column pre-equilibrated in hexanes.

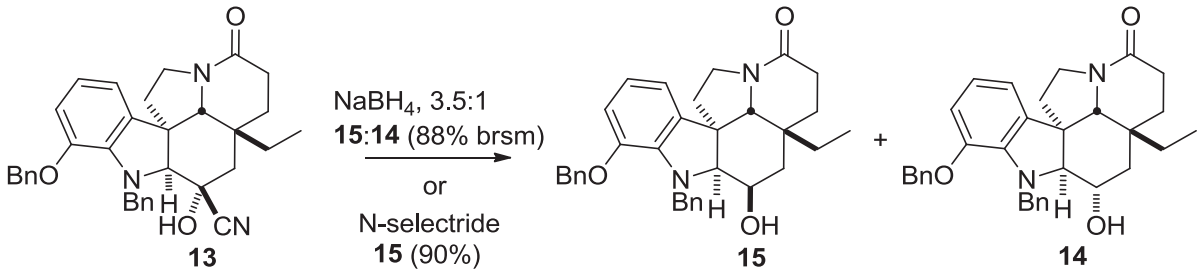
The 1,2-dichlorobenzene was first eluted with hexanes and the product was purified (50–100% EtOAc/hexanes gradient) to provide **5** as a tan oil (181 mg, 71%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27–7.35 (m, 6H), 7.16−7.24 (m, 2H), 7.07−7.12 (m, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.69 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 5.19 (d, *J* = 15.7 Hz, 1H), 5.17 (d, *J* = 11.9 Hz, 1H), 5.07 (d, *J* = 11.9 Hz, 1H), 4.47 (d, *J* = 15.7 Hz, 1H), 4.19 (s, 1H), 3.82−3.98 (m, 2H), 3.74 (s, 3H), 2.02–2.38 (m, 4H), 2.37 (d, *J* = 12.5 Hz, 1H), 1.79 (d, *J* = 12.5 Hz, 1H), 1.68−1.72 (m, 1H), 0.76–0.89 (m, 2H), 0.59 (t, *J* = 7.3 Hz, 3H), 0.10–0.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.1, 170.4, 145.3, 141.0, 138.6, 136.7, 131.5, 128.5, 128.3, 128.1, 127.9, 127.4, 127.0, 120.3, 117.1, 114.2, 106.9, 85.6, 79.9, 70.6, 65.1, 53.3, 52.5, 46.9, 43.9, 38.6, 37.2, 29.2, 27.8, 22.2, 9.8; IR (film) ν_{max} 2932, 1720, 1654, 1560 cm^{-1}; ESI-TOF HRMS *m/z* 565.2698 (M+H$^+$, $C_{35}H_{37}N_2O_5$ requires 565.2697).
Racemic **5** was resolved by chiral phase HPLC (α = 1.40, Chiralcel OD; 20% *i*-PrOH/hexanes; 7 mL/min).
(–)-**5**: $[\alpha]^{23}_D$ –35 (*c* 3.7, CH_2Cl_2).
ent-(+)-**5**: $[\alpha]^{23}_D$ +36 (*c* 3.4, CH_2Cl_2).



A solution of **5** (280 mg, 0.498 mmol) in MeOH (70 mL) in a heavy-wall reaction vessel was cooled to 0 °C. Ammonia gas was bubbled through the solution for 30 min before the vessel was sealed and warmed at 70 °C for 3 h under glass-shield protection. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue containing the primary amide was dissolved in 1,4-dioxane (4 mL) and pyridine (0.167 mL, 2.08 mmol) and cooled to 0 °C. Trifluoroacetic anhydride (133 µL, 1.04 mmol) was added to the mixture, and the solution was allowed to warm to room temperature. After 16 h, the reaction mixture was diluted with EtOAc and quenched with the addition of saturated aqueous $NaHCO_3$. The organic layer was washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by flash chromatography (40–80% EtOAc/hexanes gradient) to provide **12** (224 mg, 85%) as a white solid: mp 170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23–7.38 (m, 8H), 7.15−7.23 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.73 (dd, *J* = 7.7, 7.2 Hz, 1H), 6.52 (d, *J* = 7.2 Hz, 1H), 5.19 (d, *J* = 11.9 Hz, 1H), 5.17 (d, *J* = 11.9 Hz, 1H), 4.98 (d, *J* = 15.3 Hz, 1H), 4.58 (d, *J* = 15.3 Hz, 1H), 4.25 (s, 1H), 3.82−3.97 (m, 2H), 2.39 (d, *J* = 12.5 Hz, 1H), 2.20–2.32 (m, 2H), 2.08–2.20 (m, 2H), 1.85 (d, *J* = 12.5 Hz, 1H), 1.67−1.76 (m, 1H), 0.76–0.91 (m, 2H), 0.59 (t, *J* = 6.8 Hz, 3H), 0.02–0.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.1, 145.5, 140.3, 137.7, 136.5, 130.8, 128.6, 128.6, 128.3, 128.1, 127.6, 127.3, 121.0, 117.9, 117.0, 114.2, 107.8, 82.2, 74.1, 70.6, 64.6, 54.5, 46.9, 43.7, 40.4, 37.1, 29.1, 27.8, 22.1, 9.8; IR (film) ν_{max} 2931, 1665, 1587 cm^{-1}; ESI-TOF HRMS *m/z* 532.2612 (M+H$^+$, $C_{34}H_{34}N_3O_3$ requires 532.2595).
(–)-**12**: $[\alpha]^{23}_D$ –58 (*c* 3.1, CH_2Cl_2).
ent-(+)-**12**: $[\alpha]^{23}_D$ +60 (*c* 2.4, CH_2Cl_2).



A solution of **12** (115 mg, 0.216 mmol) in MeOH (9 mL) was treated with acetyl chloride (9 drops) at 23 °C under argon. After 30 min of stirring (liberation of HCl), $NaCNBH_3$ (128 mg, 1.298 mmol) was added and the reaction mixture was stirred for 2 h at 23 °C. The reaction mixture was quenched with the addition of saturated aqueous $NaHCO_3$, and the organic layer was extracted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash chromatography (5% MeOH/CH_2Cl_2) to provide **13** as a white solid (104 mg, 90%): ^{1}H NMR (CD_3OD, 400 MHz) δ 7.80 (s, 1H), 7.71 (d, *J* = 5.6 Hz, 1H), 7.54−7.61 (m, 3H), 7.47−7.49 (m, 3H), 7.42−7.47 (m, 2H), 7.13 (d, *J* = 6.0 Hz, 1H), 7.01 (t, *J* = 6.0 Hz, 1H), 6.86 (d, *J* = 5.2 Hz, 1H), 5.70 (d, *J* = 12 Hz, 1H), 5.46 (d, *J* = 9.2 Hz, 1H), 5.41 (d, *J* = 9.2 Hz, 1H), 4.68 (d, *J* = 12 Hz, 1H), 3.98 (s, 1H), 3.60−3.63 (m, 1H), 3.42 (s, 1H), 3.28−3.35 (m, 1H), 2.44−2.59 (m, 2H), 2.10−2.15 (m, 1H), 2.05 (d, *J* = 11.6 Hz, 1H), 1.93–1.96 (m, 1H), 1.90 (d, *J* = 11.6 Hz, 1H), 1.77–1.81 (m, 1H), 1.63–1.70 (m, 1H), 1.36−1.40 (m, 1H), 1.09–1.13 (m, 2H), 1.07 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (CD_3OD, 100 MHz) δ 170.9, 146.2, 138.7, 138.6, 137.2, 133.9, 129.2, 128.73, 128.71, 128.1, 127.9, 127.8, 122.0, 121.3, 115.6, 115.1, 77.4, 72.9, 71.5, 70.3, 64.7, 55.4, 53.9, 49.1, 42.8, 38.7, 35.2, 35.0, 31.4, 30.7, 28.3, 7.5; IR (film) ν_{max} 2932, 1680, 1629 cm^{-1}; ESI-TOF HRMS *m/z* 534.2750 ($M+H^+$, $C_{34}H_{36}N_3O_3$ requires 534.2751).



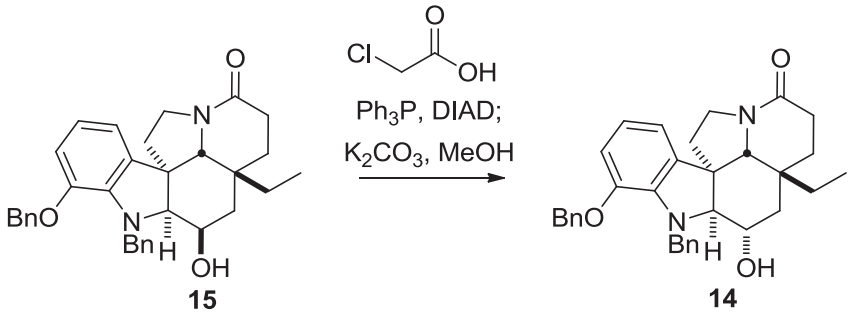
A solution of **13** (31.9 mg, 0.060 mmol) in anhydrous THF (6 mL) was treated with $NaBH_4$ (6.8 mg, 0.18 mmol) at 23 °C. The reaction mixture was stirred for 2 h, after which it was quenched by the addition of aqueous 1 M HCl, diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **15** (15.4 mg, 51%), **14** (4.4 mg, 15%), and recovered ketone (7.6 mg, 25%) as white solids.

A solution of **13** (4.9 mg, 0.0092 mmol) in anhydrous THF (1.0 mL) was treated with N-selectride (1 M in THF, 28 μL, 0.028 mmol) at 23 °C. The reaction mixture was stirred for 2 h, after which it was quenched by the addition of aqueous 1 M HCl, diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **15** (4.2 mg, 90%) as a white solid.

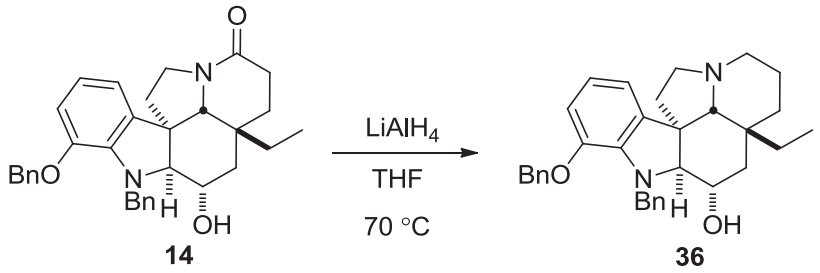
For **15**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.32−7.34 (m, 1H), 7.21−7.25 (m, 3H), 7.10−7.15 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 7.2 Hz, 1H), 5.17−5.22 (m, 2H), 4.97 (d, *J* = 14 Hz, 1H), 4.32 (d, *J* = 14 Hz, 1H), 3.65 (br s, 1H), 3.47−3.52 (m, 2H), 3.30 (d, *J* = 5.4 Hz, 1H), 3.20−3.25 (m, 1H), 2.72 (br s, 1H), 2.27 (t, *J* = 6.6 Hz, 1H), 1.56−1.65 (m, 2H), 1.25–1.35 (m, 3H), 1.16–1.22 (m, 1H), 0.99–1.05 (m, 2H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 146.6, 139.8, 138.1, 136.7, 136.2, 132.0, 129.1, 128.6, 128.5, 128.1, 127.7, 122.0, 115.4, 112.8, 70.7, 67.0, 66.9, 65.6, 56.1, 55.1, 42.4, 39.8, 35.0, 33.0, 32.7, 30.6, 29.2, 7.7; IR (film) ν_{max} 3382, 2931, 2870, 1619 cm^{-1}; ESI-TOF HRMS *m/z* 509.2804 ($M+H^+$, $C_{33}H_{37}N_2O_3$ requires 509.2799).
The structure and relative stereochemistry of **15** were established with a single X-ray structure determination (CCDC850758) conducted on white needles grown from 1:1 hexanes:CH_2Cl_2.

For **14**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.21−7.30 (m, 6H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.81 (t, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 7.2 Hz, 1H), 5.13 (s, 2H), 4.73 (d, *J* = 14 Hz, 1H),

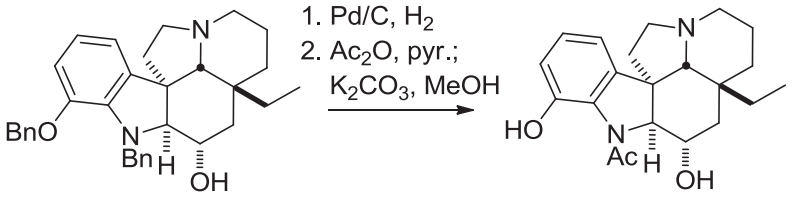
4.39 (d, J = 14 Hz, 1H), 3.66 (s, 1H), 3.37−3.47 (m, 3H), 2.72 (d, J = 7.8 Hz, 1H), 2.34−2.38 (m, 1H), 2.22–2.28 (m, 1H), 1.71−1.75 (m, 1H), 1.48–1.59 (m, 5H), 1.38–1.42 (m, 1H), 1.21–1.33 (m, 1H), 0.68 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.2, 147.5, 140.1, 138.4, 136.9, 136.7, 128.94, 128.92, 128.6, 128.1, 127.8, 127.7, 121.9, 114.8, 112.5, 71.2, 70.6, 69.8, 65.0, 57.0, 56.5, 42.8, 39.2, 36.1, 30.6, 29.2, 29.0, 27.8, 7.2; IR (film) ν_{max} 3326, 2927, 2870, 1612 cm^{-1}; ESI-TOF HRMS *m/z* 509.2799 (M+H$^+$, $C_{33}H_{37}N_2O_3$ requires 509.2799).



A solution of **15** (12.1 mg, 0.0238 mmol), 2-chloroacetic acid (6.8 mg, 0.0715 mmol), and Ph_3P (25.0 mg, 0.0953 mmol) in anhydrous toluene (1.0 mL) at 23 °C was treated dropwise with diisopropyl azodicarboxylate (DIAD, 18.8 μL, 0.0953 mmol). The reaction mixture was stirred for 16 h, after which the solvent was removed under a stream of N_2. The residue was taken up in aqueous MeOH (2 mL) and K_2CO_3 (33 mg, 0.238 mmol) was added. The reaction mixture was stirred for 2 h, after which it was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **14** (6.8 mg, 56%) as a white solid.



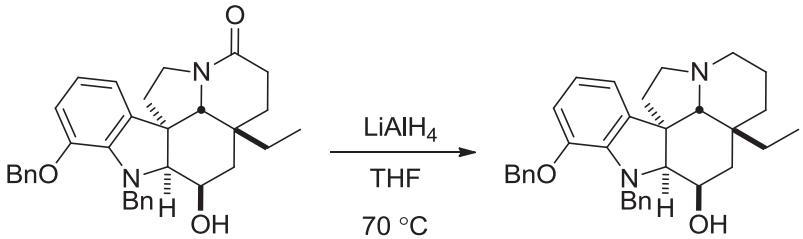
A solution of **14** (7.7 mg, 0.015 mmol) in anhydrous THF (1.5 mL) at 23 °C was treated with $LiAlH_4$ (1 M in THF, 75.3 μL, 0.0753 mmol). The reaction mixture was warmed at 70 °C and stirred for 3 h, after which the reaction was quenched with the addition of H_2O. The resulting mixture was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to afford **36** (4.9 mg, 63%) in addition to a singly debenzylated product (1.4 mg, (22%), which could be carried forward together to the next reaction. For **36**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.74 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.45−7.55 (m, 3H), 7.18−7.30 (m, 5H), 6.78 (dd, J = 6.6, 3.0 Hz, 1H), 6.70−6.72 (m, 2H), 5.10 (d, J = 12 Hz, 1H), 5.02 (d, J = 12 Hz, 1H), 4.83 (d, J = 15 Hz, 1H), 4.57 (d, J = 16 Hz, 1H), 3.79 (m, 1H), 3.47 (s, 1H), 3.11 (t, J = 8.4 Hz, 1H), 3.05 (d, J = 9.6 Hz, 1H), 2.27 (q, J = 12.6, 9.0 Hz, 1H), 2.10 (t, J = 10.8 Hz, 1H), 1.93−2.04 (m, 3H), 1.75−1.80 (m, 1H), 1.59−1.67 (m, 2H), 1.54 (d, J = 13.2 Hz, 1H), 1.47 (d, J = 13.8 Hz, 1H), 1.13−1.18 (m, 1H), 1.06−1.11 (m, 1H), 0.85−0.89 (q, J = 13.8, 7.2 Hz, 2H), 0.55 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) 145.3, 140.2, 137.0, 131.8, 130.5, 128.7, 128.4, 128.2, 127.7, 127.3, 126.8, 119.7, 116.3, 112.9, 73.8, 70.6, 68.1, 54.3, 53.0, 52.7, 52.5, 43.4, 35.4, 34.9, 33.7, 29.7, 21.4, 7.3; IR (film) ν_{max} 3370, 2912, 1640, 1598 cm^{-1}; ESI-TOF HRMS *m/z* 495.3012 (M+H$^+$, $C_{33}H_{38}N_2O_2$ requires 495.3017).
(–)-**36**: $[\alpha]^{23}_D$ –18 (*c* 0.38, CH_2Cl_2).



36 **1**, spegazzinine

A solution of **36** (4.9 mg, 0.0099 mmol) in 2:1 anhydrous MeOH:CH_2Cl_2 (3 mL) at 23 °C was treated with 10% Pd/C (20 mg). H_2 gas was bubbled through the reaction mixture for 10 min and then stirred for 45 min, after which the solution was filtered through a pad of Celite. The catalyst was washed (4 × 5 mL) with 1:1 MeOH:CH_2Cl_2, and then the catalyst was re-suspended in 1:1 MeOH:CH_2Cl_2 (5 mL). The solution was sonicated for 5 min and then was filtered through a pad of Celite. The resulting filtrates were combined and concentrated under reduced pressure to afford the crude product **16**. Crude **16** was dissolved in pyridine (1.5 mL) and treated with Ac_2O (15 drops) at 23 °C. The reaction mixture was stirred for 18 h, after which the solvent was removed under a stream of N_2. The resulting residue was dissolved in aqueous MeOH and K_2CO_3 (20 mg, 0.144 mmol) was added. The reaction mixture was stirred for 2 h, after which it was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **1** (2.0 mg, 57% over 2 steps) as a white solid, which matched a natural sample of spegazzinine in all respects: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.72 (s, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 7.2 Hz, 1H), 4.08 (d, *J* = 7.8 Hz, 1H), 3.67−3.73 (m, 1H), 3.16−3.20 (m, 1H), 3.07−3.09 (m, 1H), 2.50 (s, 3H), 2.29−2.32 (m, 2H), 2.07−2.15 (m, 2H), 2.02 (t, *J* = 11 Hz, 1H), 1.84−1.87 (m, 1H), 1.72−1.79 (m, 1H), 1.68 (d, *J* = 14 Hz, 1H), 1.56–1.63 (m, 2H), 1.41 (dd, *J* = 13, 3.6 Hz, 1H), 1.21–1.26 (m, 1H), 1.13 (dt, *J* = 13, 4.8 Hz, 1H), 0.88–0.92 (m, 2H), 0.68 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 172.4, 147.3, 140.8, 127.9, 127.8, 117.9, 113.2, 75.7, 70.3, 69.4, 54.3, 53.3, 52.1, 38.1, 37.2, 33.9, 32.9, 31.1, 23.7, 21.2, 6.9; IR (film) ν_{max} 3390, 2932, 2787, 1625, 1600, 1572 cm^{-1}; ESI-TOF HRMS *m/z* 357.2179 ($M+H^+$, $C_{21}H_{29}N_2O_3$ requires 357.2173).

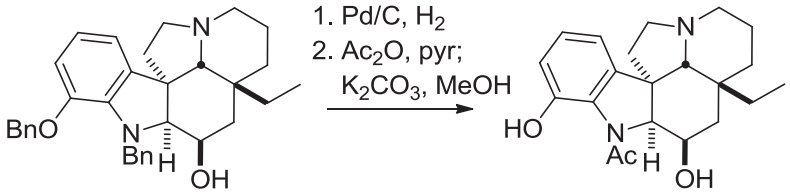
Racemic **1** was resolved by chiral phase HPLC (α = 1.28, Chiralcel OD; 50% *i*-PrOH/hexanes; 7 mL/min; 10.4 min unnatural; 13.3 min natural).
Synthetic sample: (+)-**1**: $[\alpha]^{23}_D$ +125 (*c* 0.11, $CHCl_3$).
Authentic sample: (+)-**1**: $[\alpha]^{23}_D$ +131 (*c* 0.18, $CHCl_3$).
Lit: $[\alpha]^{23}_D$ +176 (*c* 0.65, $CHCl_3$), Reference 1 (*J. Org. Chem.* **1956**, *21*, 979).



15 **37**

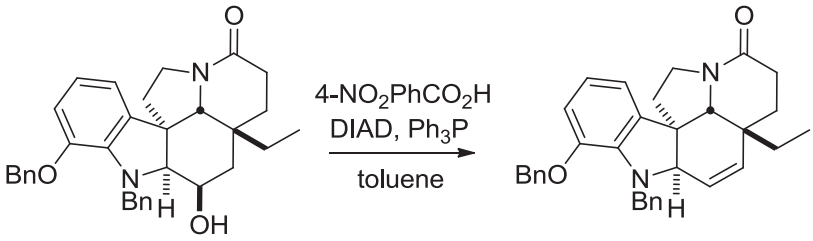
A solution of **15** (1.8 mg, 0.00354 mmol) in anhydrous THF (0.3 mL) at 23 °C was treated with $LiAlH_4$ (1 M in THF, 18.0 μL, 0.0177 mmol). The reaction mixture was warmed at 70 °C and stirred for 3 h, after which the reaction was quenched with the addition of H_2O. The resulting mixture was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to afford **37** (1.2 mg, 69%) in addition to a singly debenzylated product (0.2 mg, (14%), which could be carried forward together to the next reaction. For **37**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.21−7.35 (m, 3H), 7.18−7.30 (m, 8H), 6.79−6.82 (m, 2H), 6.70−6.72 (dd, *J* = 5.6, 2.8 Hz,

1H), 5.10 (dd, *J* = 14, 13 Hz, 1H), 4.83 (d, *J* = 14 Hz, 1H), 4.50 (d, *J* = 14 Hz, 1H), 3.79 (q, *J* = 9.6, 4.8 Hz 1H), 3.39 (d, *J* = 5.6 Hz, 1H), 2.98−3.02 (m, 2H), 2.15 (q, *J* = 18, 9.2 Hz, 1H), 2.08 (s, 1H), 1.90 (t, *J* = 11 Hz, 1H), 1.78 (dd, *J* = 14, 4.0 Hz, 1H), 1.67−1.72 (m, 2H), 1.58−1.63 (m, 2H), 1.45−1.54 (m, 3H), 0.97 (m, 1H), 0.79 (m, 1H), 0.67 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) 146.3, 141.0, 139.5, 139.0, 137.0, 128.7, 128.5, 128.3, 127.8, 127.4, 127.2, 121.5, 115.4, 111.6, 72.8, 72.3, 70.3, 67.5, 56.2, 53.6, 53.5, 52.9, 44.6, 35.2, 34.8, 33.2, 29.5, 21.7, 7.4; IR (film) ν_{max} 3382, 2922, 1641, 1592 cm^{-1}; ESI-TOF HRMS *m/z* 459.3017 (M+H$^+$, $C_{33}H_{38}N_2O_2$ requires 459.3006).



37 **18**

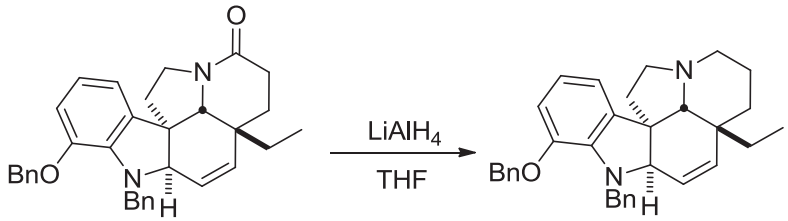
A solution of **37** (9.3 mg, 0.0188 mmol) in 2:1 anhydrous MeOH:CH_2Cl_2 (5.0 mL) at 23 °C was treated with 10% Pd/C (40 mg). H_2 gas was bubbled through the reaction mixture for 10 min and then stirred for 45 min, after which the solution was filtered through a pad of Celite. The catalyst was washed (4 × 5 mL) with 1:1 MeOH:CH_2Cl_2, and then the catalyst was re-suspended in 1:1 MeOH:CH_2Cl_2 (5 mL). The solution was sonicated for 5 min and then was filtered through a pad of Celite. The resulting filtrates were combined and concentrated under reduced pressure to afford the crude product **17**. Crude **17** was dissolved in pyridine (2.5 mL) and treated with Ac_2O (25 drops) at 23 °C. The reaction mixture was stirred for 18 h, after which the solvent was removed under a stream of N_2. The resulting residue was dissolved in aqueous MeOH and K_2CO_3 (30 mg, 0.216 mmol) was added. The reaction mixture was stirred for 2 h, after which it was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **18** (4.2 mg, 63% over 2 steps) as a white solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.55 (s, 1H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 1H), 4.33 (s, 1H), 4.12 (d, *J* = 5.5 Hz, 1H), 3.09−3.13 (m, 1H), 3.04 (d, *J* = 10 Hz, 1H), 2.38 (s, 1H), 2.35 (s, 3H), 2.25−2.32 (m, 1H), 1.99−2.09 (m, 3H), 1.56−1.71 (m, 7H), 1.01−1.05 (m, 1H), 0.91–0.95 (m, 1H), 0.73 (t, *J* = 7.5 Hz, 3H); IR (film) ν_{max} 3350, 2931, 2787, 1629, 1600, 1574 cm^{-1}; ESI-TOF HRMS *m/z* 357.2177 (M+H$^+$, $C_{21}H_{29}N_2O_3$ requires 357.2173).



15 **19**

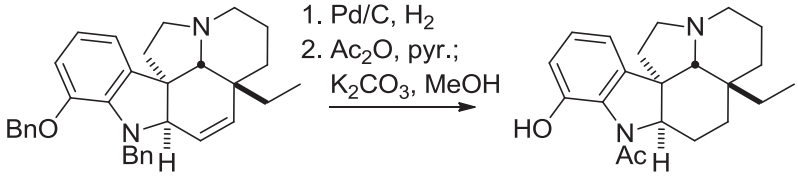
A solution of **15** (22.0 mg, 0.0433 mmol), 4-nitrobenzoic acid (21.7 mg, 0.130 mmol), and Ph_3P (45.4 mg, 0.173) in anhydrous toluene (1.0 mL) at 23 °C was treated dropwise with diisopropyl azodicarboxylate (DIAD, 34.1 µL, 0.173 mmol). The reaction mixture was stirred for 5 h before it was diluted with EtOAc, washed with saturated aqueous $NaHCO_3$, saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The product **19** (>95% conversion by LCMS) was usually taken on crude to the next reaction due to its co-elution with triphenylphosphine oxide. However, a small sample of **19** was purified by PTLC (1:1 EtOAc:hexanes × 2) for characterization purposes: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (d, *J* = 7.0 Hz, 2H), 7.25−7.34 (m, 7H), 7.21 (d, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 7.0 Hz, 1H), 5.62 (dd, *J* = 10, 3.5 Hz, 1H), 5.39 (d, *J* = 10 Hz, 1H), 5.12 (s, 2H), 4.95 (d, *J* = 14.5 Hz, 1H), 4.41 (d,

J = 15 Hz, 1H), 3.78 (s, 1H), 3.50 (d, *J* = 3.0 Hz, 1H), 3.35−3.43 (m, 2H), 2.34 (dd, *J* = 18, 5.5 Hz, 1H), 2.09−2.16 (m, 1H), 1.65−1.74 (m, 2H), 1.25–1.35 (m, 3H), 1.37–1.41 (m, 1H), 1.05–1.11 (m, 1H), 0.86–0.90 (m, 2H), 0.73 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.2, 145.7, 139.0, 138.6, 136.9, 134.0, 129.8, 128.6, 128.5, 128.4, 128.0, 127.9, 127.5, 127.3, 119.9, 115.7, 112.9, 70.5, 64.6, 62.9, 53.8, 52.8, 42.6, 39.7, 36.9, 33.6, 29.6, 28.6, 7.8; IR (film) ν_{max} 3233, 2977, 2787, 2361, 1716, 1618, cm^{-1}; ESI-TOF HRMS *m/z* 491.2685 (M+H$^+$, $C_{33}H_{34}N_2O_2$ requires 491.2693).



19 **38**

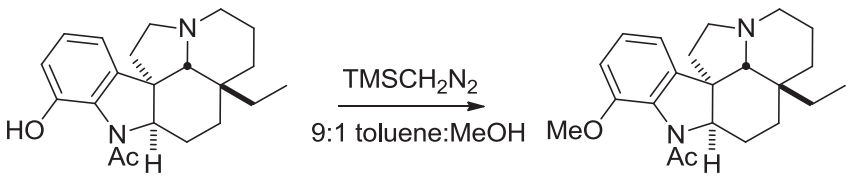
A solution of **19** (0.0755 mmol) in anhydrous THF (5.0 mL) at 23 °C was treated with $LiAlH_4$ (1 M in THF, 0.604 mL, 0.604 mmol). The reaction mixture was warmed at 70 °C and stirred for 5 h, after which the reaction was quenched with the addition of H_2O. The resulting mixture was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **38** (25.0 mg, 70%) as a white solid: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.52 (d, *J* = 6.6 Hz, 4H), 7.32 (m, 2H), 7.21–7.29 (m, 4H), 6.66–6.75 (m, 3H), 5.68–5.71 (m, 1H), 5.60 (d, *J* = 9.0 Hz, 1H), 5.07 (q, *J* = 11 Hz, 2H), 4.93 (d, *J* = 14 Hz, 1H), 4.49 (d, *J* = 14 Hz, 1H), 3.76 (s, 1H), 3.00−3.05 (m, 2H), 2.18−2.24 (m, 2H), 1.93−1.97 (m, 1H), 1.53−1.82 (m, 3H), 1.28−1.35 (m, 1H), 1.09–1.13 (m, 2H), 0.92–0.96 (m, 1H), 0.82–0.87 (m, 1H), 0.64 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 144.9, 138.9, 135.5, 134.3, 133.6, 131.7, 131.0, 128.4, 128.1, 127.7, 127.4, 126.8, 126.1, 119.1, 116.6, 112.4, 73.6, 70.5, 69.0, 53.8, 52.9, 52.6, 44.7, 38.5, 35.3, 34.1, 29.7, 23.0, 7.6; IR (film) ν_{max} 2927, 2854, 1670 cm^{-1}; ESI-TOF HRMS *m/z* 477.2895 (M+H$^+$, $C_{33}H_{37}N_2O$ requires 477.2906).



38 **21**

A solution of **38** (9.7 mg, 0.02035 mmol) in 2:1 anhydrous MeOH:CH_2Cl_2 (5.0 mL) at 23 °C was treated with 10% Pd/C (40 mg). H_2 gas was bubbled through the reaction mixture for 10 min and then stirred for 3 h, after which the solution was filtered through a pad of Celite. The catalyst was washed (4 × 5 mL) with 1:1 MeOH:CH_2Cl_2, and then the catalyst was re-suspended in 1:1 MeOH:CH_2Cl_2 (5 mL). The solution was sonicated for 5 min and then was filtered through a pad of Celite. The resulting filtrates were combined and concentrated under reduced pressure to afford the crude product **20**. Crude **20** was dissolved in pyridine (2.5 mL) and treated with Ac_2O (25 drops) at 23 °C. The reaction mixture was stirred for 18 h, after which the solvent was removed under a stream of N_2. The resulting residue was dissolved in aqueous MeOH and K_2CO_3 (30 mg, 0.216 mmol) was added. The reaction mixture was stirred for 2 h, after which it was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **21** (3.9 mg, 57% over 2 steps) as a white solid: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.88 (s, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 4.06−4.09 (m, 1H), 3.14 (t, *J* = 7.2 Hz, 1H), 3.06 (t, *J* = 10 Hz, 1H), 2.32 (s, 3H), 2.26−2.30 (m, 2H), 2.05−2.07 (m, 1H), 1.95–1.99 (m, 2H), 1.84−1.87 (m, 1H), 1.51−1.71 (m, 4H), 1.33–1.37 (m, 1H), 1.08–1.17 (m, 2H), 0.82–0.89 (m, 2H), 0.63 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 169.2, 147.2, 141.2, 127.8,

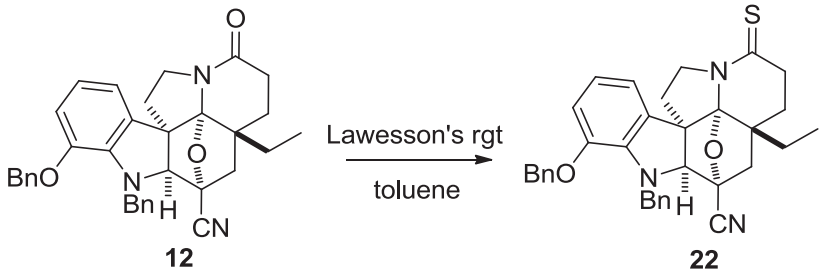
126.9, 117.5, 113.5, 70.9, 69.7, 53.7, 52.8, 52.5, 39.1, 35.5, 34.0, 30.1, 29.7, 25.0, 22.7, 21.5, 6.8; IR (film) ν_{max} 2928, 1630, 1598 cm^{-1}; ESI-TOF HRMS *m/z* 341.2215 ($M+H^+$, $C_{21}H_{29}N_2O_2$ requires 341.2223).



21 **2**, aspidospermine

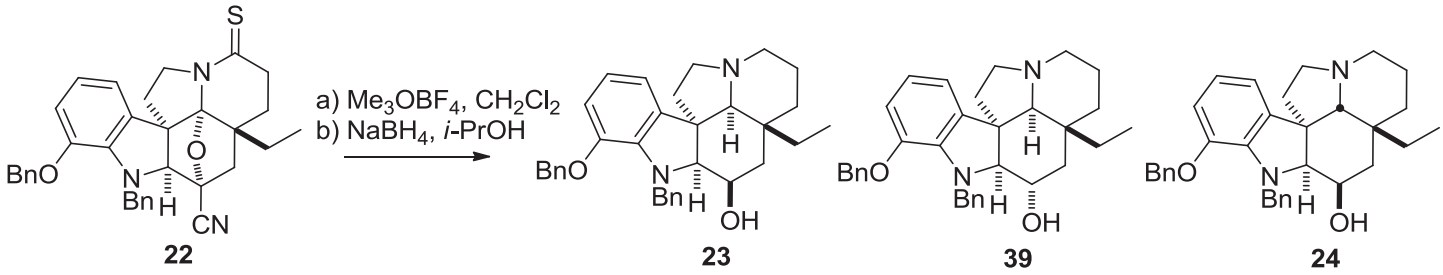
A solution of **21** (2.0 mg, 0.00587 mmol) in 9:1 toluene:MeOH (0.6 mL) at 23 °C was treated with $TMSCH_2N_2$ (14.8 µL, 0.0294 mmol, 2.0 M in Et_2O). The reaction was stirred for 16 h, followed by the addition of 59 µL of 2.0 M $TMSCH_2N_2$. The reaction was stirred for 24 h, and 150 µL of 2.0 M $TMSCH_2N_2$ was added. After 24 h of stirring, the reaction was complete. The solvent was removed under a stream of N_2, and the resulting residue was purified by PTLC (5% MeOH/ CH_2Cl_2) to provide **2** (1.4 mg, 67%) as a clear oil: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.07 (t, *J* = 7.8 Hz, 1H), 6.77−6.84 (m, 2H), 4.65 (br s, 1H), 3.88 (s, 3H), 3.10−3.14 (m, 1H), 3.01−3.05 (m, 1H), 2.16−2.24 (m, 5H), 1.95−2.03 (m, 2H), 1.90 −1.96 (m, 2H), 1.71−1.75 (m, 1H), 1.52−1.62 (m, 3H), 1.14−1.28 (m, 2H), 1.02−1.10 (m, 2H), 0.74−0.81 (m, 1H), 0.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.5, 149.2, 143.9, 129.3, 126.0, 115.5, 110.9, 71.2, 69.5, 55.3, 53.6, 52.5, 38.0, 35.5, 34.2, 30.1, 29.7, 24.7, 23.1, 23.0, 21.6, 6.8; IR (film) ν_{max} 2924, 2854, 1652 cm^{-1}; ESI-TOF HRMS *m/z* 355.2388 ($M+H^+$, $C_{22}H_{30}N_2O_2$ requires 355.2380); data consistent with literature (*Spectroscopy Letters* **1993**, *26*, 707; *Org. Lett.* **2003**, *5*, 749; *Angew. Chem. Int. Ed.* **2007**, *46*, 6159).

Racemic **2** was resolved by chiral phase HPLC (α = 1.17, Chiralcel AD; 10% *i*-PrOH/hexanes; 7 mL/min).
2: $[\alpha]^{23}_D$ –85 (*c* 0.071, $CHCl_3$).
Lit: $[\alpha]^{23}_D$ –90.5 (*c* 0.48, $CHCl_3$), Reference 10m.



12 **22**

Lawesson's reagent (17.0 mg, 0.0421 mmol) was added to a solution of **12** (37.3 mg, 0.0702 mmol) in anhydrous toluene (treated with freshly activated 4 Å MS, 4 mL) at 23 °C under Ar. The reaction mixture was warmed to 80 °C for 1 h under microwave irradiation. The reaction mixture was concentrated under reduced pressure and purified by flash chromatography (10–20% EtOAc/hexanes) to provide **22** (33.8 mg, 88%) as a white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27–7.36 (m, 8H), 7.17−7.23 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.74 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 5.20 (d, *J* = 11.9 Hz, 1H), 5.13 (d, *J* = 11.9 Hz, 1H), 4.97 (d, *J* = 15.2 Hz, 1H), 4.59 (d, *J* = 15.2 Hz, 1H), 4.29 (s, 1H), 4.13−4.30 (m, 2H), 3.08 (dd, *J* = 4.9, 19.8 Hz, 1H), 2.67–2.80 (m, 1H), 2.44 (d, *J* = 12.5 Hz, 1H), 2.18–2.29 (m, 1H), 2.22 (dd, *J* = 12.6, 7.9 Hz, 1H), 2.03–2.14 (m, 1H), 1.87 (d, *J* = 12.5 Hz, 1H), 1.68 (m, 1H), 0.76–0.91 (m, 2H), 0.58 (t, *J* = 7.4 Hz, 3H), 0.05–0.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.4, 145.6, 140.4, 137.6, 136.4, 130.2, 128.7, 128.6, 128.4, 128.1, 127.7, 127.3, 121.2, 117.5, 117.0, 114.3, 105.2, 82.6, 74.8, 70.7, 65.3, 54.5, 44.2, 40.5, 39.0, 36.6, 29.7, 28.0, 22.0, 9.8; ESI-TOF HRMS *m/z* 548.2392 ($M+H^+$, $C_{34}H_{34}N_3O_2S$ requires 548.2366).
(–)-**22**: $[\alpha]^{23}_D$ –124 (*c* 1.00, CH_2Cl_2).
ent-(+)-**22**: $[\alpha]^{23}_D$ +127 (*c* 2.27, CH_2Cl_2).

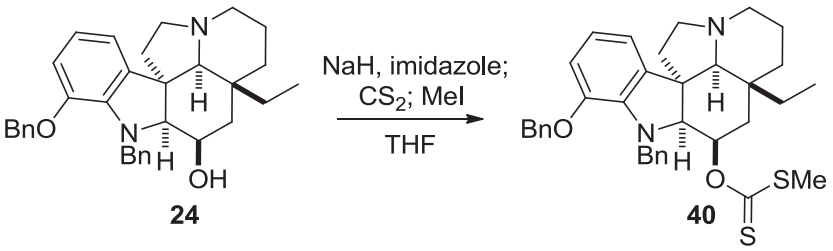


Trimethyloxonium tetrafluoroborate (71.8 mg, 0.485 mmol) was added to a solution of **22** (133.0 mg, 0.243 mmol) in CH_2Cl_2 (5 mL) at 0 °C, and the reaction mixture was warmed to 23 °C and stirred for 1.5 h. The solvent was removed in vacuo and the residue was dissolved in *i*-PrOH (5 mL) and cooled to 0 °C. The reaction mixture was treated with $NaBH_4$ (55.1 mg, 1.46 mmol) in small portions, followed by stirring at 23 °C for 2 h. The reaction mixture was treated with 10% aqueous HCl, stirred for 5 min, and basified with the addition of 10% aqueous NaOH to pH~10. The reaction mixture was diluted with EtOAc, washed with H_2O and saturated aqueous NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide compounds **23** (119 mg, 65%), **39** (9 mg, 5%), and **24** (26 mg, 15%) as colorless oils.

For **23**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, *J* = 7.0 Hz, 2H), 7.28−7.39 (m, 3H), 7.17–7.23 (m, 3H), 7.07–7.13 (m, 2H), 6.92–6.96 (m, 1H), 6.77–6.83 (m, 2H), 5.18 (s, 2H), 4.87 (d, *J* = 14.3 Hz, 1H), 4.24 (d, *J* = 14.3 Hz, 1H), 3.96–4.03 (m, 1H), 3.60 (d, *J* = 5.6 Hz, 1H), 3.18–3.32 (m, 2H), 2.06–2.14 (m, 1H), 2.08 (s, 1H), 1.85–1.93 (m, 1H), 1.56–1.68 (m, 1H), 1.35–1.55 (m, 4H), 1.31 (dd, *J* = 14.0, 4.7 Hz, 1H), 1.17–1.26 (m, 1H), 0.84 (dd, *J* = 13.0, 3.2 Hz, 1H), 0.46–0.56 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5, 141.5, 139.1, 138.3, 137.1, 129.1, 128.5, 128.1, 127.9, 127.6, 127.2, 122.0, 119.6, 111.9, 74.8, 71.7, 70.5, 67.5, 57.3, 56.7, 53.5, 52.9, 41.0, 39.6, 35.3, 34.2, 24.3, 22.3, 7.7; ESI-TOF HRMS *m/z* 495.3017 ($M+H^+$, $C_{33}H_{39}N_2O_2$ requires 495.3006).

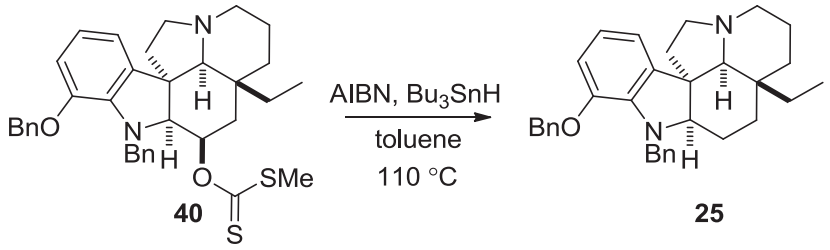
For **39**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.1 Hz, 2H), 7.32−7.39 (m, 5H), 7.22–7.33 (m, 3H), 7.12 (dd, *J* = 6.6, 1.8 Hz, 1H), 6.79–6.86 (m, 2H), 5.13 (dd, *J* = 15.1, 11.6 Hz, 2H), 4.65 (d, *J* = 13.4 Hz, 1H), 4.07 (d, *J* = 13.4 Hz, 1H), 3.36–3.47 (m, 1H), 3.30 (dd, *J* = 9.0, 8.4 Hz, 1H), 3.20–3.25 (m, 1H), 2.83 (d, *J* = 8.0 Hz, 1H), 2.24 (dd, *J* = 10.2, 2.0 Hz, 1H), 2.17 (s, 1H), 1.91–1.99 (m, 1H), 1.80–1.89 (m, 2H), 1.73–1.80 (m, 2H), 1.65–1.72 (m, 1H), 1.41–1.46 (m, 1H), 1.33–1.40 (m, 1H), 0.97–1.07 (m, 1H), 0.81 (t, *J* = 12.6 Hz, 2H), 0.67 (dd, *J* = 13.0, 3.0 Hz, 1H), 0.61 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.5, 142.1, 140.5, 138.9, 137.2, 129.1, 128.7, 128.5, 127.9, 127.6, 127.5, 122.4, 119.4, 111.4, 76.1, 75.9, 71.8, 70.4, 56.8, 56.3, 54.4, 52.1, 41.2, 39.3, 36.3, 34.2, 21.9, 20.0, 7.8.

For **24**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36–7.43 (m, 2H), 7.19−7.36 (m, 8H), 6.77– 6.84 (m, 2H), 6.71 (dd, *J* = 5.6, 2.7 Hz, 1H), 5.13 (dd, *J* = 13.7, 11.8 Hz, 2H), 4.83 (d, *J* = 14.2 Hz, 1H), 4.50 (d, *J* = 14.2 Hz, 1H), 3.84 (d, *J* = 4.6 Hz, 1H), 3.39 (d, *J* = 5.5 Hz, 1H), 2.96–3.05 (m, 2H), 2.15 (d, *J* = 9.1 Hz, 1H), 2.08 (s, 1H), 1.85–1.94 (m, 1H), 1.78 (dd, *J* = 14.3, 4.0 Hz, 2H), 1.65–1.74 (m, 2H), 1.57–1.65 (m, 1H), 0.96 (dd, *J* = 13.5, 4.5 Hz, 1H), 0.73–0.84 (m, 1H), 0.67 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.3, 141.0, 139.5, 139.0, 137.0, 128.7, 128.5, 128.3, 127.8, 127.4, 127.2, 121.5, 115.4, 111.6, 72.8, 72.3, 70.3, 67.5, 56.2, 53.6, 53.5, 52.9, 44.6, 35.2, 34.8, 33.2, 29.5, 21.7, 7.4.



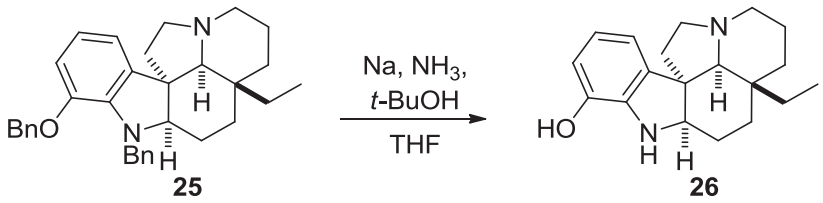
24 **40**

NaH (60% dispersion in mineral oil, 35.0 mg, 1.45 mmol) was added to 2 mL of distilled anhydrous THF and the mixture was stirred for 15 min. The THF was decanted and 2 mL of distilled anhydrous THF was added to the flask at 0 °C followed by addition of imidazole (2.0 mg, 0.0291 mmol) and **24** (72.0 mg, 0.146 mmol) in THF (0.5 mL, rinsed with THF 0.5 mL × 2). The reaction mixture was stirred at 0 °C for 1 h before CS_2 (70 μL, 1.16 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h followed by the addition of MeI (73 μL, 1.16 mmol). The reaction mixture was stirred for 1 h before being quenched by adding saturated aqueous NH_4Cl. The solution was diluted with EtOAc, washed with saturated aqueous NaCl, and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by flash chromatography (25–80% EtOAc/hexane gradient) to provide **40** (70 mg, 83%) as a colorless oil and recovered starting material **24** (10 mg, 14%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39 (d, *J* = 7.0 Hz, 2H), 7.27–7.33 (m, 3H), 7.15−7.22 (m, 5H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 7.9 Hz, 1H), 6.64 (dd, *J* = 7.9, 7.3 Hz, 1H), 6.16–6.22 (m, 1H), 5.35 (d, *J* = 15.3 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 5.06 (d, *J* = 11.9 Hz, 1H), 4.03 (d, *J* = 15.3 Hz, 1H), 3.69 (d, *J* = 4.9 Hz, 1H), 3.32 (dd, *J* = 9.8, 8.2 Hz, 1H), 3.25 (dd, *J* = 9.2, 1.2 Hz, 1H), 2.18–2.25 (m, 1H), 2.20 (s, 3H), 2.19 (s, 1H), 2.04–2.15 (m, 1H), 1.93–2.04 (m, 1H), 1.75–1.83 (m, 1H), 1.55–1.74 (m, 3H), 1.40–1.53 (m, 2H), 1.24–1.32 (m, 2H), 0.96–1.08 (m, 1H), 0.80 (dd, *J* = 13.0, 3.3 Hz, 1H), 0.56 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 214.8, 144.6, 139.5, 138.1, 137.4, 128.4, 128.3, 128.1, 127.7, 127.5, 126.8, 119.7, 119.0, 113.1, 80.8, 74.4, 71.0, 68.1, 57.0, 52.7, 52.6, 52.2, 41.2, 35.9, 34.2, 22.3, 22.1, 17.8, 7.6; ESI-TOF HRMS *m/z* 585.2601 ($M+H^+$, $C_{35}H_{41}N_2O_2S_2$ requires 585.2604).

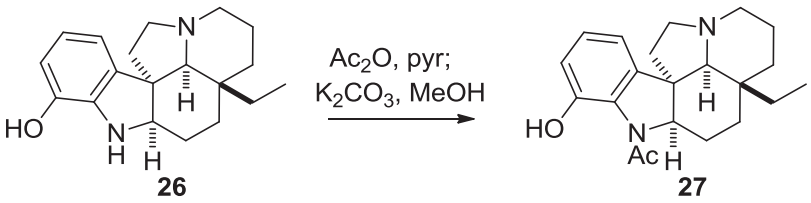


40 **25**

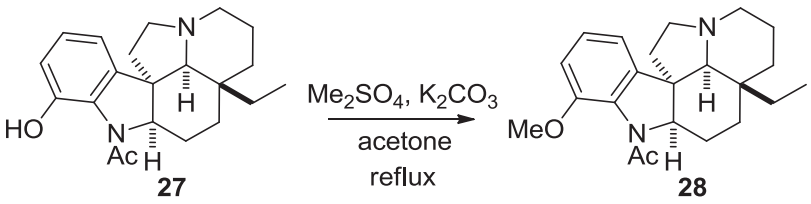
A solution of **40** (54.1 mg, 0.0925 mmol), AIBN (3.0 mg, 0.0185 mmol), and Bu_3SnH (298 μL, 1.11 mmol) in anhydrous toluene (5 mL) was degassed with argon for 30 min. The reaction mixture was warmed at 110 °C for 4 h, cooled to room temperature, and the product purified by flash chromatography (20–40% EtOAc/hexane gradient) to afford **25** (35 mg, 80%) as a clear oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20–7.38 (m, 10H), 7.17 (dd, *J* = 7.4, 1.1 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.66 (dd, *J* = 8.0, 7.4 Hz, 1H), 5.07 (d, *J* = 11.7 Hz, 1H), 5.01 (d, *J* = 11.7 Hz, 1H), 4.97 (d, *J* = 15.9 Hz, 1H), 4.33 (d, *J* = 15.9 Hz, 1H), 3.22−3.30 (m, 2H), 3.08 (dd, *J* = 10.1, 5.8 Hz, 1H), 2.14–2.22 (m, 1H), 1.98 (s, 1H), 1.88–1.98 (m, 1H), 1.66–1.80 (m, 4H), 1.56–1.66 (m, 1H), 1.46–1.56 (m, 2H), 1.32–1.46 (m, 2H), 1.18–1.27 (m, 1H), 0.84–0.94 (m, 1H), 0.63–0.73 (m, 1H), 0.60 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.2, 140.6, 139.6, 138.2, 137.4, 128.3, 128.1, 128.0, 127.6, 127.4, 126.6, 120.5, 119.1, 112.5, 75.6, 70.9, 68.1, 56.9, 52.6, 51.8, 51.7, 36.7, 34.3, 32.5, 27.8, 25.7, 22.3, 19.1, 7.8; ESI-TOF HRMS *m/z* 479.3046 ($M+H^+$, $C_{33}H_{39}N_2O$ requires 479.3057).



In a vial, NH_3 was condensed at –78 °C to a volume of ~1 mL. Na (19 mg, 0.84 mmol), freshly cut and washed with hexanes, was added to the vial and a dark blue color appeared immediately. After 3 to 5 min of stirring, a solution of *t*-BuOH in distilled anhydrous THF (0.041 mL *t*-BuOH in 0.25 mL THF) was added to the blue mixture followed by the addition of a solution of **25** (10 mg, 0.021 mmol) in distilled anhydrous THF (0.5 mL). The reaction mixture was stirred until the dark blue color turned white. Ammonium chloride (0.14 g) was added to quench the reaction and the reaction mixture was uncapped and warmed to room temperature. After evaporation of the NH_3, the reaction product was purified by PTLC (10% MeOH/CH_2Cl_2 × 2) to afford **26** (3.7 mg, 60%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (d, *J* = 6.6 Hz, 1H), 6.64 (dd, *J* = 7.6, 6.6 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 4.55 (br s, 1H), 3.49 (s, 1H), 3.38–3.48 (m, 1H), 3.26–3.38 (m, 2H), 2.33 (t, *J* = 10.0 Hz, 1H), 2.13 (s, 1H), 2.01–2.10 (m, 1H), 1.86–1.96 (m, 1H), 1.72–1.86 (m, 2H), 1.54–1.70 (m, 4H), 1.45–1.53 (m, 1H), 1.30–1.44 (m, 1H), 1.10–1.21 (m, 1H), 0.84 (dd, *J* = 13.7, 3.0 Hz, 1H), 0.61–0.71 (m, 1H), 0.58 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 137.7, 136.2, 120.8, 119.4, 114.6, 75.4, 65.4, 56.9, 53.2, 51.9, 39.5, 36.8, 34.2, 32.5, 28.8, 22.1, 18.9, 7.7; ESI-TOF HRMS *m/z* 299.2111 ($M+H^+$, $C_{19}H_{27}N_2O$ requires 299.2118).

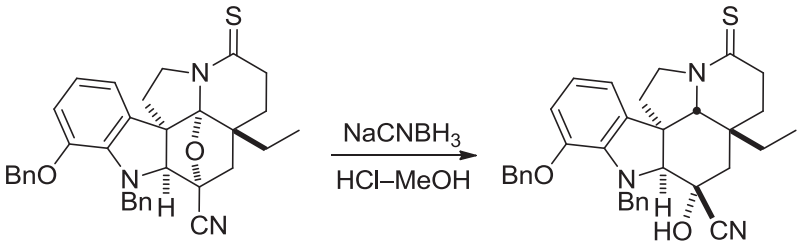


A solution of **26** (5.9 mg, 0.020 mmol) in pyridine (1 mL) at 23 °C was treated with Ac_2O (18.7 μL, 0.198 mmol). The reaction mixture was stirred for 18 h, after which the solvent was removed under a stream of N_2. The resulting residue was dissolved in wet methanol and K_2CO_3 (28 mg, 0.198 mmol) was added. The reaction mixture was stirred for 2 h, after which it was diluted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **27** (5.4 mg, 80%) as a white solid: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 10.83 (s, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 3.90−3.94 (m, 1H), 3.20−3.40 (m, 2H), 2.33 (s, 3H), 2.08−2.12 (m, 2H), 2.00−2.04 (m, 1H), 1.82−1.92 (m, 2H), 1.69−1.73 (m, 2H), 1.61−1.64 (m, 2H), 1.48–1.55 (m, 2H), 0.99–1.02 (m, 1H), 0.86–0.91 (m, 2H), 0.62–0.67 (m, 1H), 0.59 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 168.2, 147.0, 140.5, 127.3, 126.3, 117.9, 117.2, 75.4, 69.0, 56.7, 51.4, 51.3, 39.6, 36.6, 34.1, 32.4, 26.4, 22.8, 22.0, 19.3, 7.7; ESI-TOF HRMS *m/z* 341.2235 ($M+H^+$, $C_{21}H_{29}N_2O_2$ requires 341.2223).



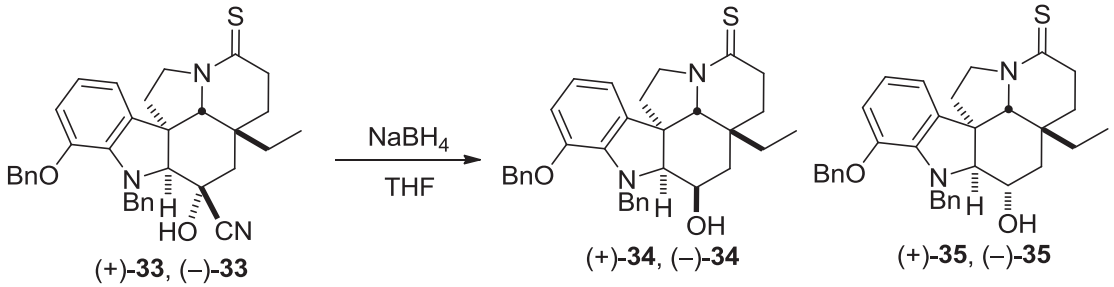
A solution of **27** (2.6 mg, 0.0077 mmol) and K_2CO_3 (10.8 mg, 0.077 mmol) in acetone (1 mL) was treated with Me_2SO_4 (7.3 μL, 0.077 mmol) and the reaction mixture was warmed at reflux for 18 h. The solution was diluted with CH_2Cl_2, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by PTLC (5% MeOH/CH_2Cl_2) to provide **28** (1.4 mg, 52%) as a white solid: ^{1}H NMR

($CDCl_3$, 600 MHz) δ 7.29 (s, 1H), 7.02 (m, 1H), 6.80 (d, *J* = 7.2 Hz, 1H), 4.60 (m, 1H), 3.86 (s, 3H), 3.24−3.33 (m, 2H), 2.31 (t, *J* = 10.8 Hz, 1H), 2.17 (s, 3H), 1.78−1.95 (m, 4H), 1.46−1.71 (m, 5H), 1.25−1.31 (m, 1H), 0.86−0.89 (m, 2H), 0.75−0.82 (m, 1H), 0.61–0.68 (m, 1H), 0.57 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.3, 149.4, 142.9, 128.8, 125.4, 119.7, 110.7, 75.8, 68.2, 56.7, 55.3, 51.4, 38.6, 36.6, 34.1, 32.4, 29.7, 25.9, 23.1, 22.1, 19.3, 7.8; ESI-TOF HRMS *m/z* 355.2393 ($M+H^+$, $C_{22}H_{31}N_2O_2$ requires 355.2380).
The structure and relative stereochemistry of **28** were established with a single crystal X-ray structure determination (CCDC850757) conducted on white needles grown from 1:1 hexanes:CH_2Cl_2.



(+)-**22**, (–)-**22** (+)-**33**, (–)-**33**

A solution of (–)-**22** (60 mg, 0.110 mmol) in MeOH (3 mL) was treated with acetyl chloride (5 drops) at 23 °C under argon. After 30 min of stirring (liberation of HCl), $NaCNBH_3$ (65.1 mg, 0.658 mmol) was added and the reaction mixture was stirred for 2 h at 23 °C. The reaction mixture was quenched with the addition of saturated aqueous $NaHCO_3$, and the organic layer was extracted with EtOAc, washed with saturated aqueous NaCl, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash chromatography (5% MeOH/CH_2Cl_2) to provide (–)-**33** as a white solid (58.0 mg, 96%): ^{1}H NMR (THF-d_8, 600 MHz) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.22−7.27 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.71 (t, *J* = 7.2 Hz, 1H), 5.97 (br s, 1H), 5.54 (d, *J* = 15 Hz, 1H), 5.25 (d, *J* = 12 Hz, 1H), 5.21 (d, *J* = 12 Hz, 1H), 4.38 (d, *J* = 15 Hz, 1H), 3.84−3.87 (m, 1H), 3.74 (s, 1H), 3.30 (s, 1H), 3.23−3.28 (m, 1H), 2.74−2.78 (m, 1H), 2.51−2.57 (m, 2H), 1.77−1.81 (m, 1H), 1.67–1.71 (m, 2H), 1.57–1.63 (m, 2H), 1.17–1.22 (m, 2H), 0.78–0.81 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (THF-d_8, 150 MHz) δ 197.4, 147.1, 140.0, 139.4, 138.6, 135.5, 130.3, 129.4, 129.3, 128.74, 128.72, 128.5, 123.0, 122.0, 116.9, 115.8, 73.2, 72.1, 71.6, 68.1, 56.1, 54.5, 50.5, 40.4, 39.9, 38.2, 36.5, 33.8, 32.0, 7.9; IR (film) ν_{max} 3174, 2939, 1592 cm^{-1}; ESI-TOF HRMS *m/z* 550.2529 ($M+H^+$, $C_{34}H_{35}N_3O_2S$ requires 550.2523).
(–)-**33**: $[\alpha]^{23}_D$ –14 (*c* 1.4, CH_2Cl_2).
ent-(+)-**33**: $[\alpha]^{23}_D$ +14 (*c* 0.9, CH_2Cl_2).
The structure and absolute configuration of (–)-**33** were established with a single crystal X-ray structure determination (CCDC868362) conducted on white needles grown from 1:1 benzene:CH_2Cl_2.

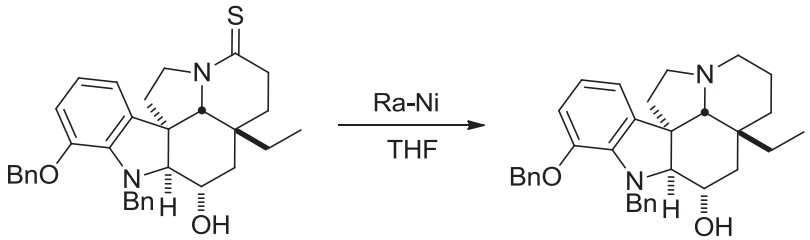


(+)-**33**, (–)-**33** (+)-**34**, (–)-**34** (+)-**35**, (–)-**35**

A solution of (+)-**33** (8.0 mg, 0.015 mmol) in anhydrous THF (1.0 mL) was treated with $NaBH_4$ (2.8 mg, 0.073 mmol) at 23 °C. The reaction mixture was stirred for 18 h, after which it was directly purified by PTLC (5% MeOH/CH_2Cl_2) to provide (+)-**34** (5.4 mg, 71%) and (+)-**35** (1.8 mg, 24%) as white solids:

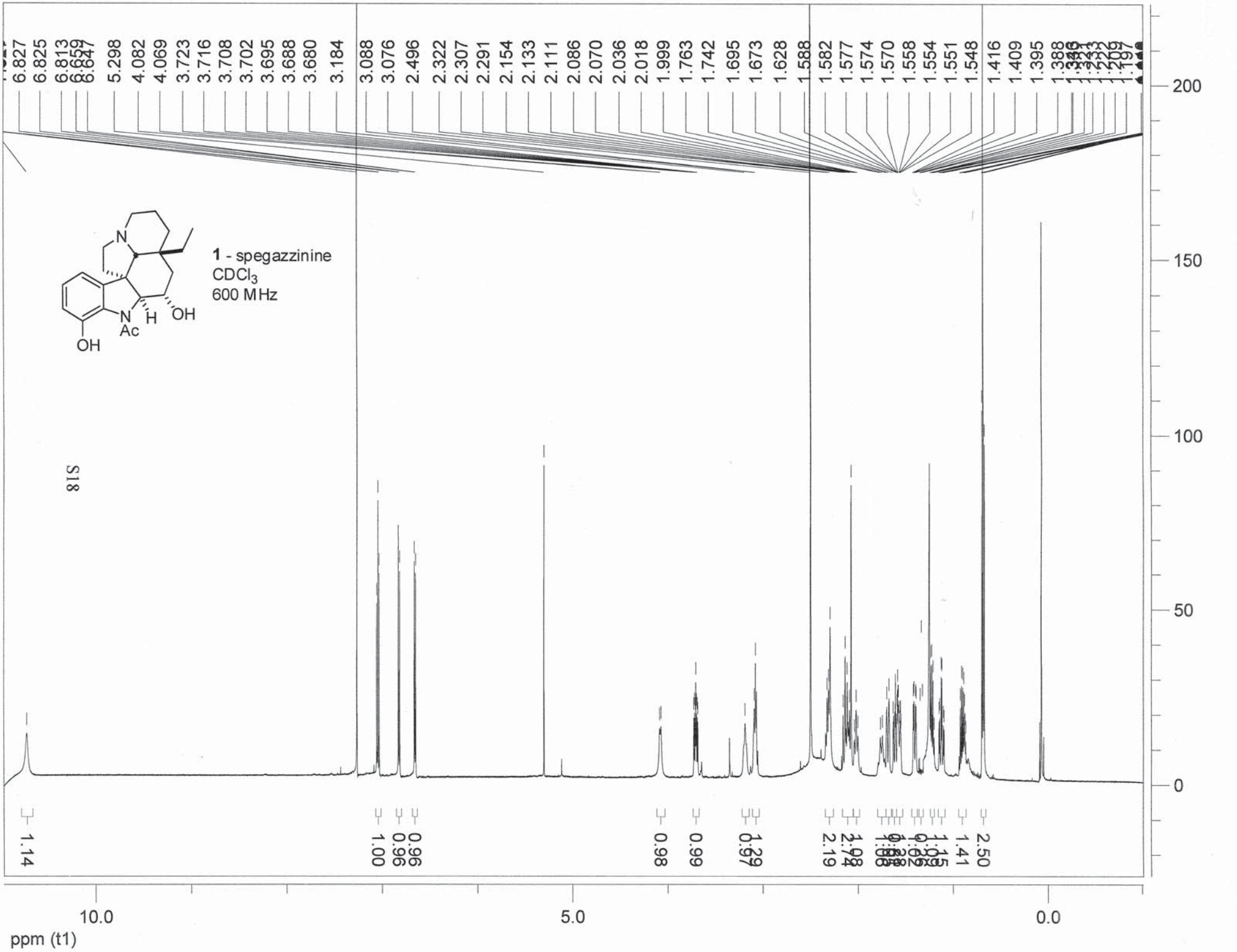
For **34**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.33−7.39 (m, 3H), 7.20−7.24 (m, 3H), 7.09 (d, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.5 Hz, 1H), 5.23 (d, *J* = 12 Hz, 1H), 5.19 (d, *J* = 12 Hz, 1H), 5.13 (d, *J* = 15 Hz, 1H), 4.17 (d, *J* = 15 Hz, 1H), 3.96 (dd, *J* = 14, 9 Hz, 1H), 3.54−3.58 (m, 1H), 3.45 (dd, *J* = 14, 6.0 Hz, 1H), 3.43 (s, 1H), 3.39 (d, *J* = 5.5 Hz, 1H), 2.93 (dt, *J* = 18, 5.0 Hz, 1H), 2.66 (d, *J* = 9.0 Hz, 1H), 2.60−2.65 (m, 1H), 1.61−1.70 (m, 2H), 1.44–1.50 (m, 1H), 1.26–1.28 (m, 1H), 1.15 (sept, *J* = 7.0 Hz, 1H), 1.08 (sept, *J* = 7.0 Hz, 1H), 0.86 (dd, *J* = 13, 6.5 Hz, 1H), 0.70 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 198.9, 146.7, 140.0, 137.7, 136.6, 135.4, 129.3, 128.6, 128.5, 128.2, 127.8, 127.7, 122.1, 115.4, 113.1, 70.8, 68.3, 66.9, 66.7, 56.1, 55.8, 50.1, 39.3, 38.8, 36.1, 34.9, 33.0, 30.0, 7.5; IR (film) ν_{max} 3364, 2931, 2360, 1739, 1592 cm^{-1}; ESI-TOF HRMS *m/z* 525.2576 (M+H$^+$, $C_{33}H_{37}N_2O_2S$ requires 525.2570).
(–)-**34**: $[\alpha]^{23}_D$ –8.5 (*c* 0.90, CH_2Cl_2).
ent-(+)-**34**: $[\alpha]^{23}_D$ +7.4 (*c* 0.92, CH_2Cl_2).

For **35**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, *J* = 7.0 Hz, 2H), 7.27−7.38 (m, 8H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 5.18 (s, 2H), 4.74 (d, *J* = 14 Hz, 1H), 4.53 (d, *J* = 14 Hz, 1H), 3.96 (dd, *J* = 14, 9.5 Hz, 1H), 3.72−3.75 (m, 1H), 3.70 (s, 1H), 3.50−3.52 (m, 1H), 3.03 (dd, *J* = 18, 6.5 Hz, 1H), 2.85−2.92 (m, 1H), 2.80 (d, *J* = 8.5 Hz, 1H), 1.55−1.67 (m, 4H), 1.42 (q, *J* = 8.0 Hz, 2H), 1.20 (t, *J* = 13 Hz, 1H), 1.03 (sept, *J* = 7.0 Hz 1H), 0.73 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 197.0, 147.4, 139.9, 138.1, 136.6, 136.4, 129.0, 128.9, 128.6, 128.2, 127.9, 127.7, 121.9, 114.6, 112.7, 71.3, 70.7, 69.9, 67.7, 57.1, 56.3, 50.6, 38.5, 37.6, 36.5, 30.8, 30.1, 29.3, 6.9; IR (film) ν_{max} 3265, 2361, 1636 cm^{-1}; ESI-TOF HRMS *m/z* 525.2576 (M+H$^+$, $C_{33}H_{37}N_2O_2S$ requires 525.2572).
(–)-**35**: $[\alpha]^{23}_D$ –12 (*c* 0.11, CH_2Cl_2).
ent-(+)-**35**: $[\alpha]^{23}_D$ +11 (*c* 0.92, CH_2Cl_2).



(–)-**35** (–)-**36**

A solution of Raney nickel in H_2O was washed with H_2O (1 mL × 2), MeOH (1 mL × 2), and THF (1 mL × 2) and finally diluted with THF (1 mL). A solution of (–)-**35** (4.2 mg, 0.0080 mmol) in THF (1.0 mL) was treated with the Ra-Ni solution (2 drops) at 23 °C. The mixture was stirred rapidly for 4 h before being filtered through Celite. The Celite was washed with CH_2Cl_2 (10 mL) and the filtrate concentrated under reduced pressure to provide (–)-**36** (3.8 mg, 97%).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5.298
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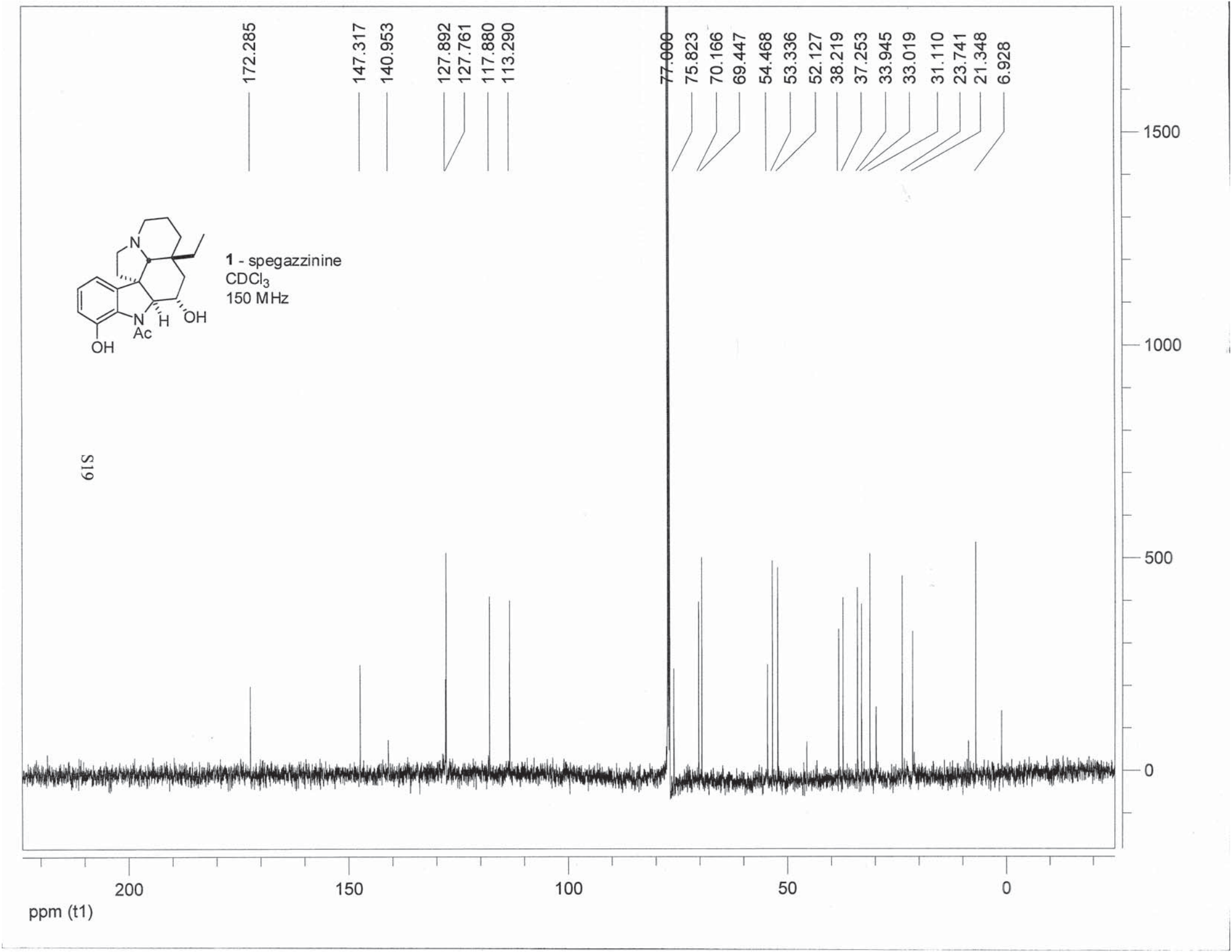
4.069
3.723
3.716
3.708
3.702
3.695
3.688
3.680
3.184
3.088
3.076
2.496
2.322
2.307
2.291
2.154
2.133
2.111
2.086
2.070
2.036
2.018
1.999
1.763
1.742
1.695
1.673
1.628
1.588
1.582
1.577
1.574
1.570
1.558
1.554
1.551
1.548
1.416
1.409
1.395
1.388
1.346
1.331
1.222
1.209
1.197
200
150
100
50
0
1.14
1.00
0.96
0.99
0.98
0.99
0.97
1.29
2.19
2.74
1.98
1.41
2.50
10.0
5.0
0.0
ppm (t1)
N
N
H
Ac
OH
OH
1 - spegazzinine
CDCl3
600 MHz
S18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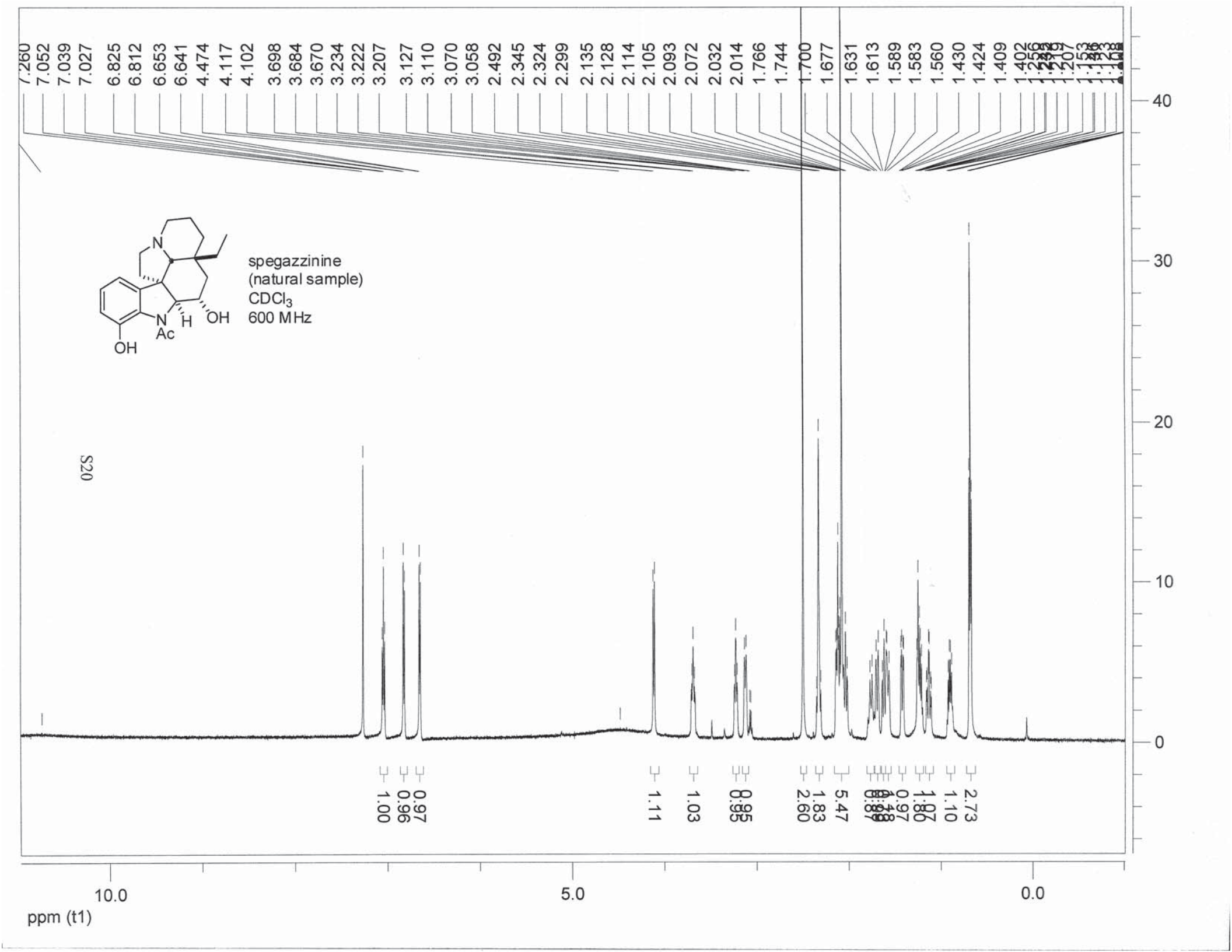
140.953
127.892
127.761
117.880
113.290
77.000
75.823
70.166
69.447
54.468
53.336
52.127
38.219
37.253
33.945
33.019
31.110
23.741
21.348
6.928
1500
1000
500
0
200
150
100
50
0
ppm (t1)
1 - spegazzinine
CDCl3
150 MHz
N
N
H
Ac
OH
OH
S19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7.027
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6.653
6.641
4.474
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4.102
3.698
3.684
3.670
3.234
3.222
3.207
3.127
3.110
3.070
3.058
2.492
2.345
2.324
2.299
2.135
2.128
2.114
2.105
2.093
2.072
2.032
2.014
1.766
1.744
1.700
1.677
1.631
1.613
1.589
1.583
1.560
1.430
1.424
1.409
1.402
spegazzinine
(natural sample)
CDCl3
600 MHz
N
N
H
Ac
OH
OH
S20
1.00
0.96
0.97
1.11
1.03
0.95
2.60
1.83
5.47
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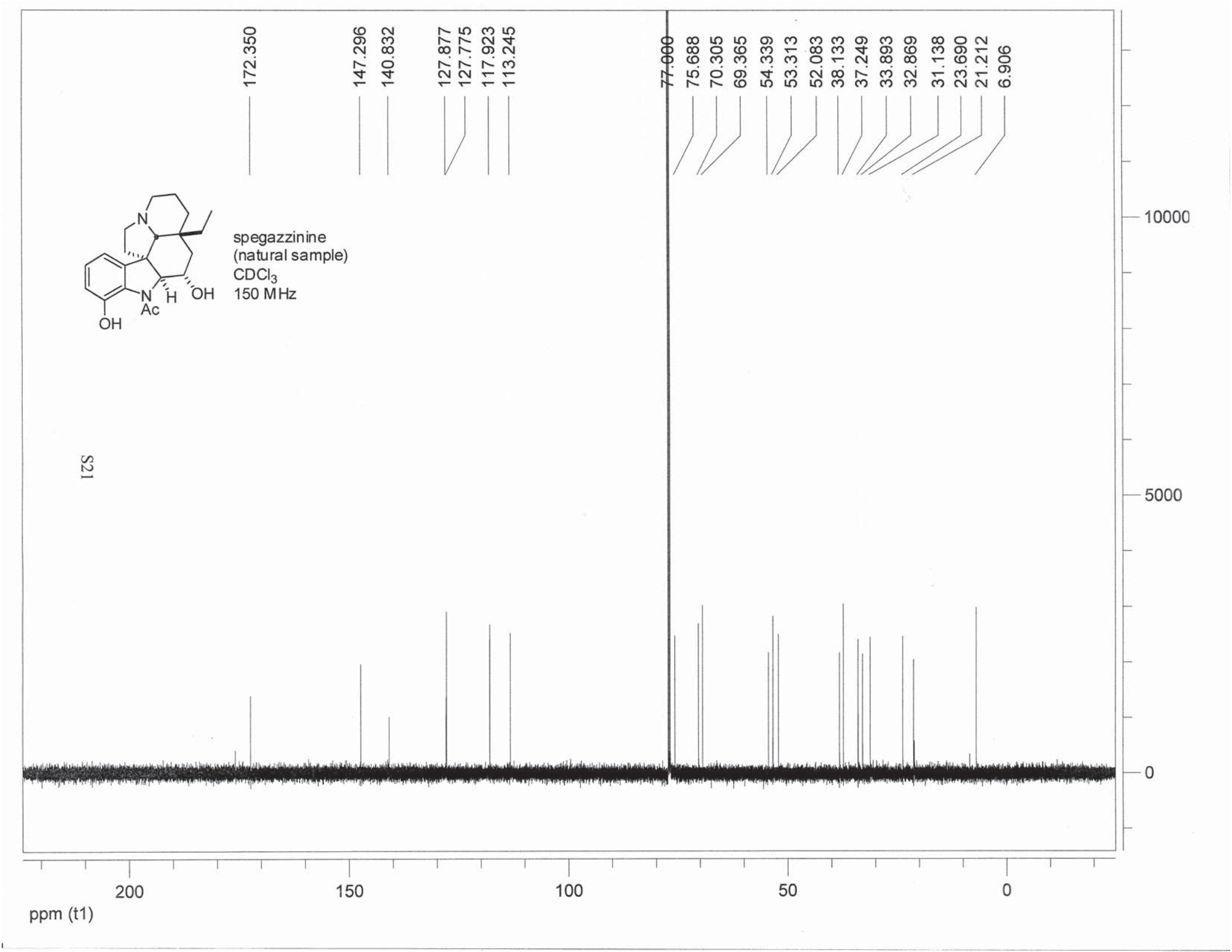
1.10
2.73
40
30
20
10
0
10.0
5.0
0.0
ppm (t1)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127.877
127.775
117.923
113.245
77.000
75.688
70.305
69.365
54.339
53.313
52.083
38.133
37.249
33.893
32.869
31.138
23.690
21.212
6.906
spegazzinine
(natural sample)
CDCl3
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N
N
H
Ac
OH
OH
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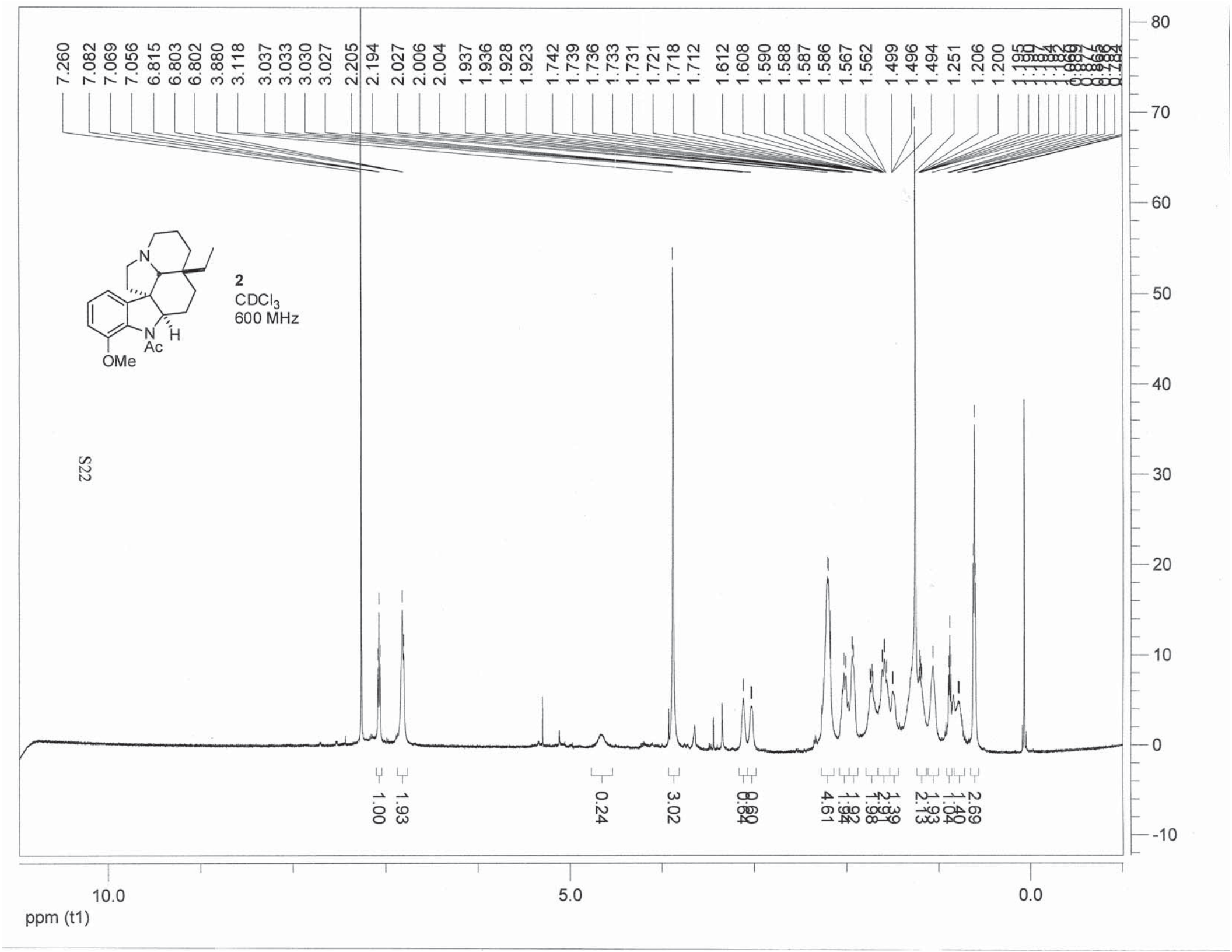
0
200
150
100
50
0
ppm (t1)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3.037
3.033
3.030
3.027
2.205
2.194
2.027
2.006
2.004
1.937
1.936
1.928
1.923
1.742
1.739
1.736
1.733
1.731
1.721
1.718
1.712
1.612
1.608
1.590
1.588
1.587
1.586
1.567
1.562
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1.494
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1.206
1.200
N
N
H
Ac
OMe
2
CDCl3
600 MHz
S22
1.00
1.93
0.24
3.02
0.60
0.64
4.61
1.94
1.92
1.88
1.39
2.13
1.93
1.04
1.40
2.69
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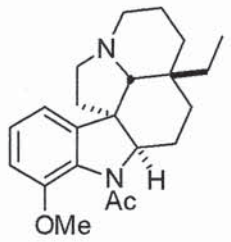
70
60
50
40
30
20
10
0
-10
10.0
5.0
0.0
ppm (t1)



2
$CDCl_3$
150 MHz

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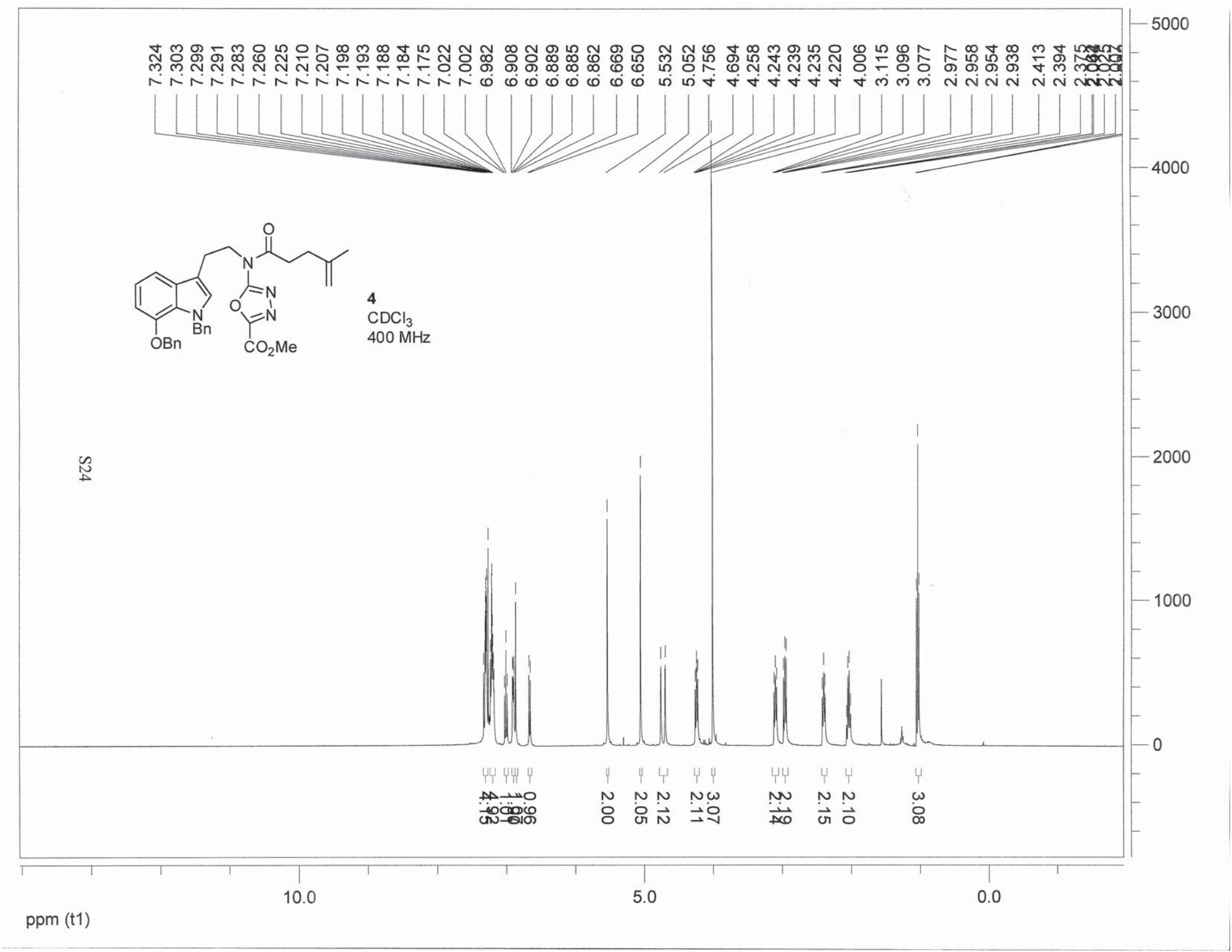
143.86
129.30
125.96
115.52
110.90
77.00
71.17
69.50
55.33
53.64
52.52
38.01
35.55
34.20
30.08
29.70
24.72
23.13
23.01
21.58
6.82

f1 (ppm)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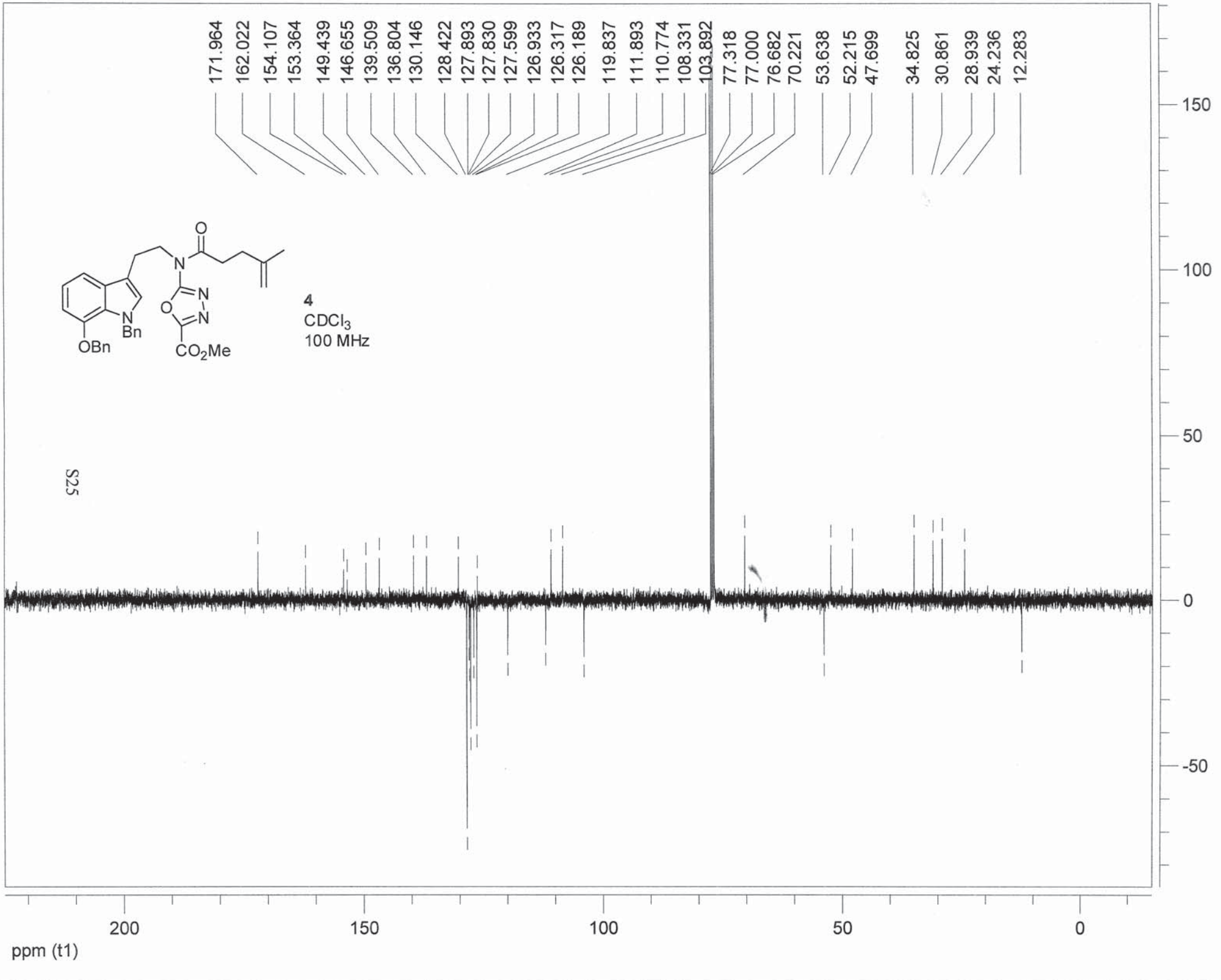
7.210
7.207
7.198
7.193
7.188
7.184
7.175
7.022
7.002
6.982
6.908
6.902
6.889
6.885
6.862
6.669
6.650
5.532
5.052
4.756
4.694
4.258
4.243
4.239
4.235
4.220
4.006
3.115
3.096
3.077
2.977
2.958
2.954
2.938
2.413
2.394
2.375
OBn
N
Bn
O
N
N
O
CO2Me
4
CDCl3
400 MHz
5000
4000
3000
2000
1000
0
4.92
1.00
0.96
2.00
2.05
2.12
2.11
3.07
2.19
2.14
2.15
2.10
3.08
10.0
5.0
0.0
ppm (t1)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136.804
130.146
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127.830
127.599
126.933
126.317
126.189
119.837
111.893
110.774
108.331
103.892
77.318
77.000
76.682
70.221
53.638
52.215
47.699
34.825
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12.283
O
N
N
O
N
N
Bn
OBn
CO2Me
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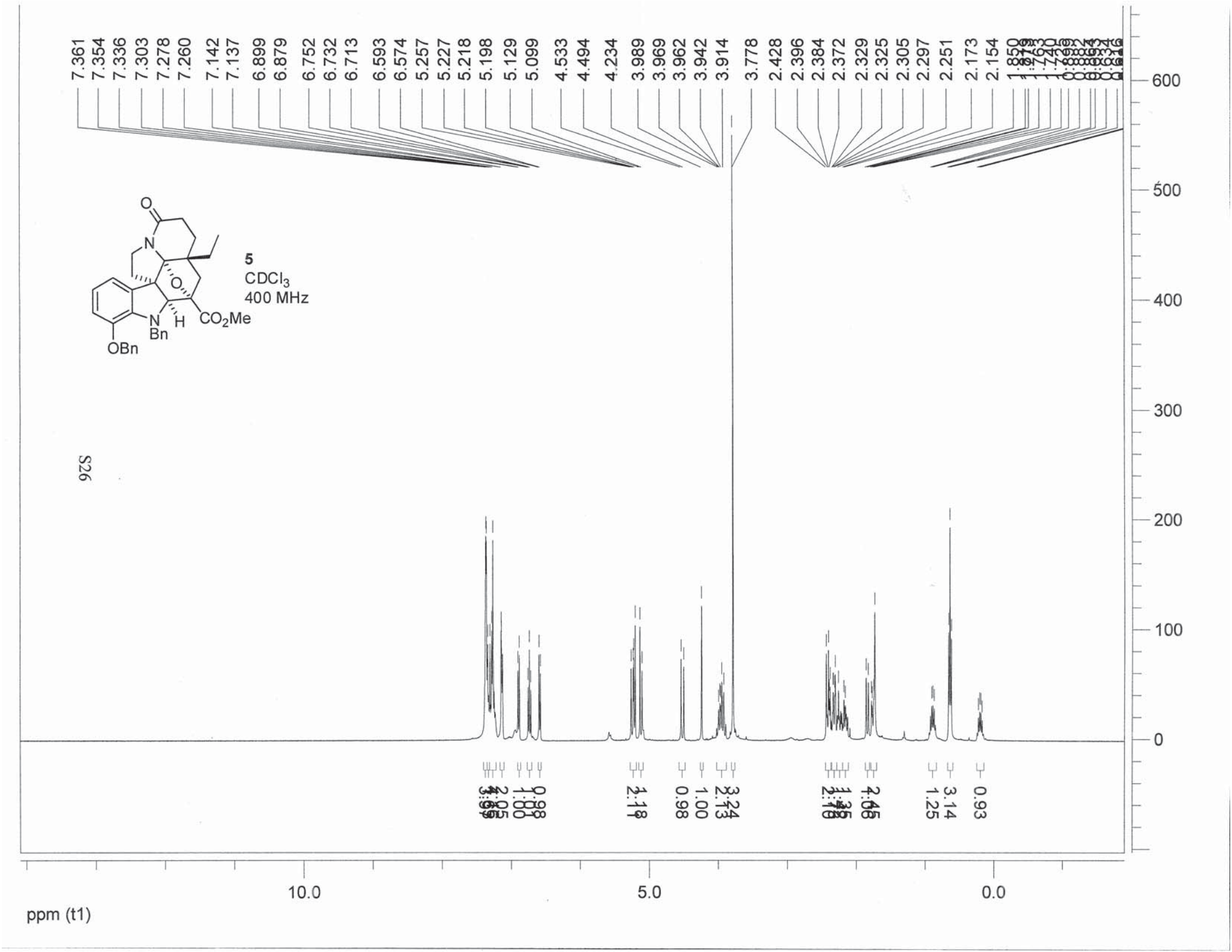
100 MHz
S25
150
100
50
0
-50
200
150
100
50
0
ppm (t1)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6.713
6.593
6.574
5.257
5.227
5.218
5.198
5.129
5.099
4.533
4.494
4.234
3.989
3.969
3.962
3.942
3.914
3.778
2.428
2.396
2.384
2.372
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2.325
2.305
2.297
2.251
2.173
2.154
5
CDCl3
400 MHz
CO2Me
Bn
OBn
S26
0.98
2.18
1.00
2.13
3.24
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1.25
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0.93
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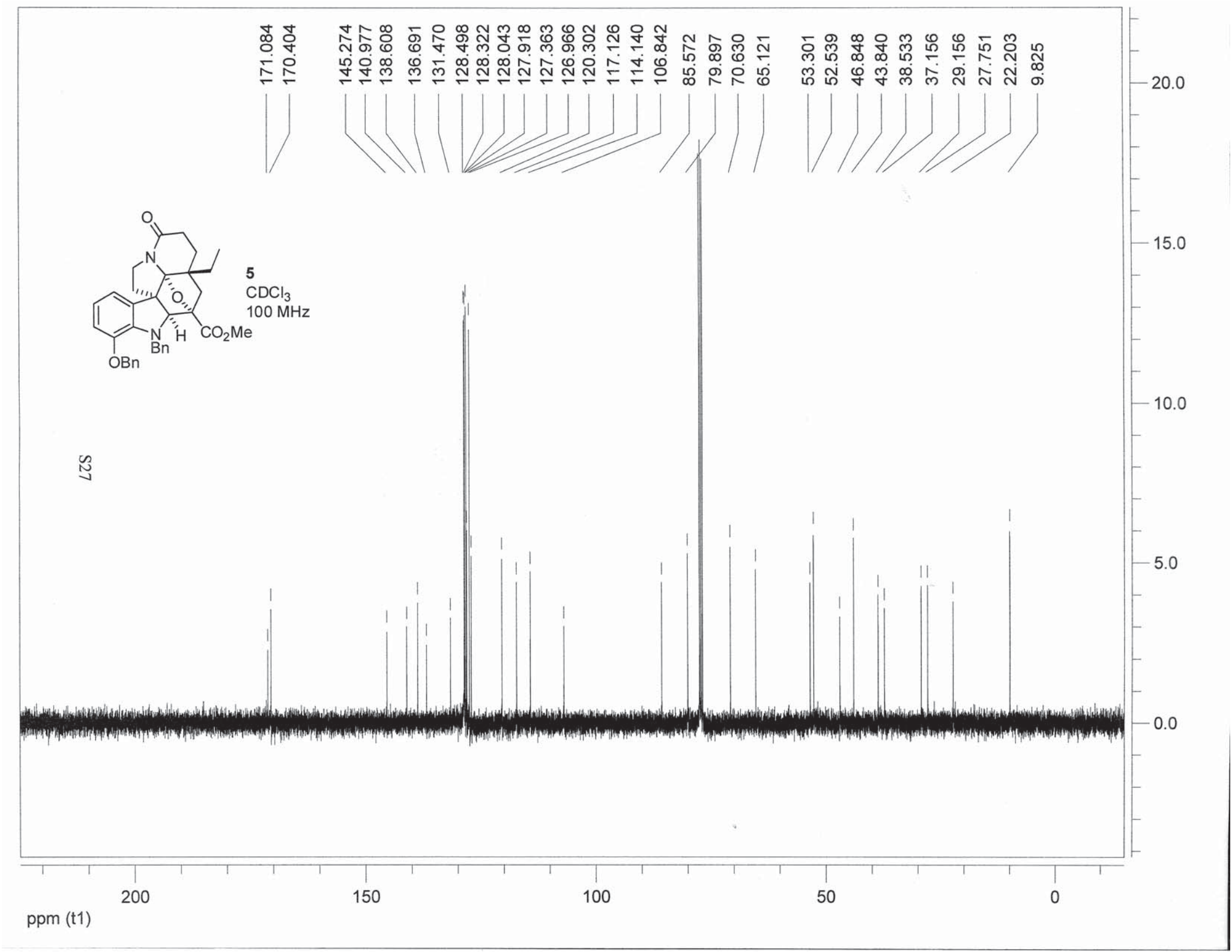
0.0
ppm (t1)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120.302
117.126
114.140
106.842
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79.897
70.630
65.121
53.301
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46.848
43.840
38.533
37.156
29.156
27.751
22.203
9.825
5
CDCl3
100 MHz
CO2Me
N
H
Bn
OBn
O
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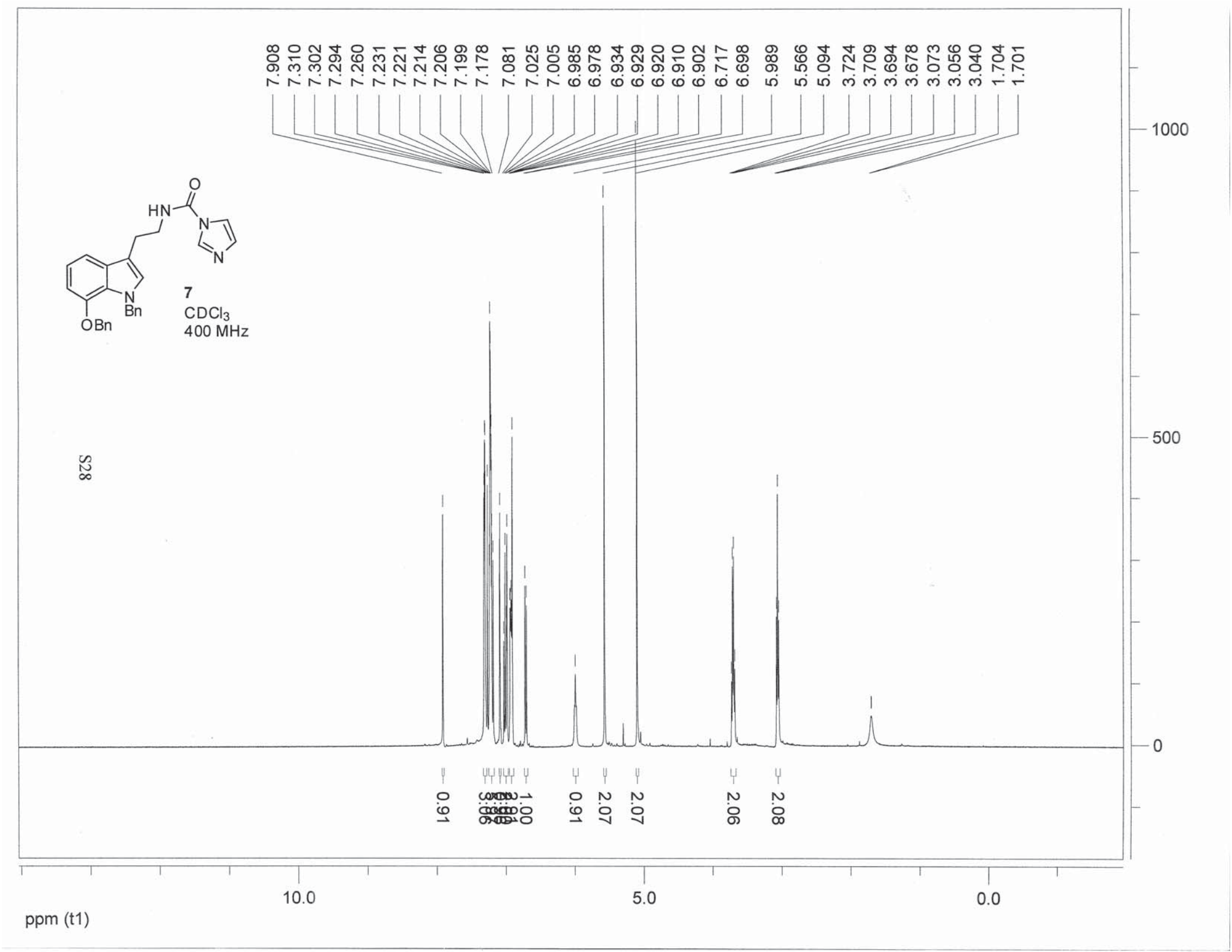
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)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6.929
6.920
6.910
6.902
6.717
6.698
5.989
5.566
5.094
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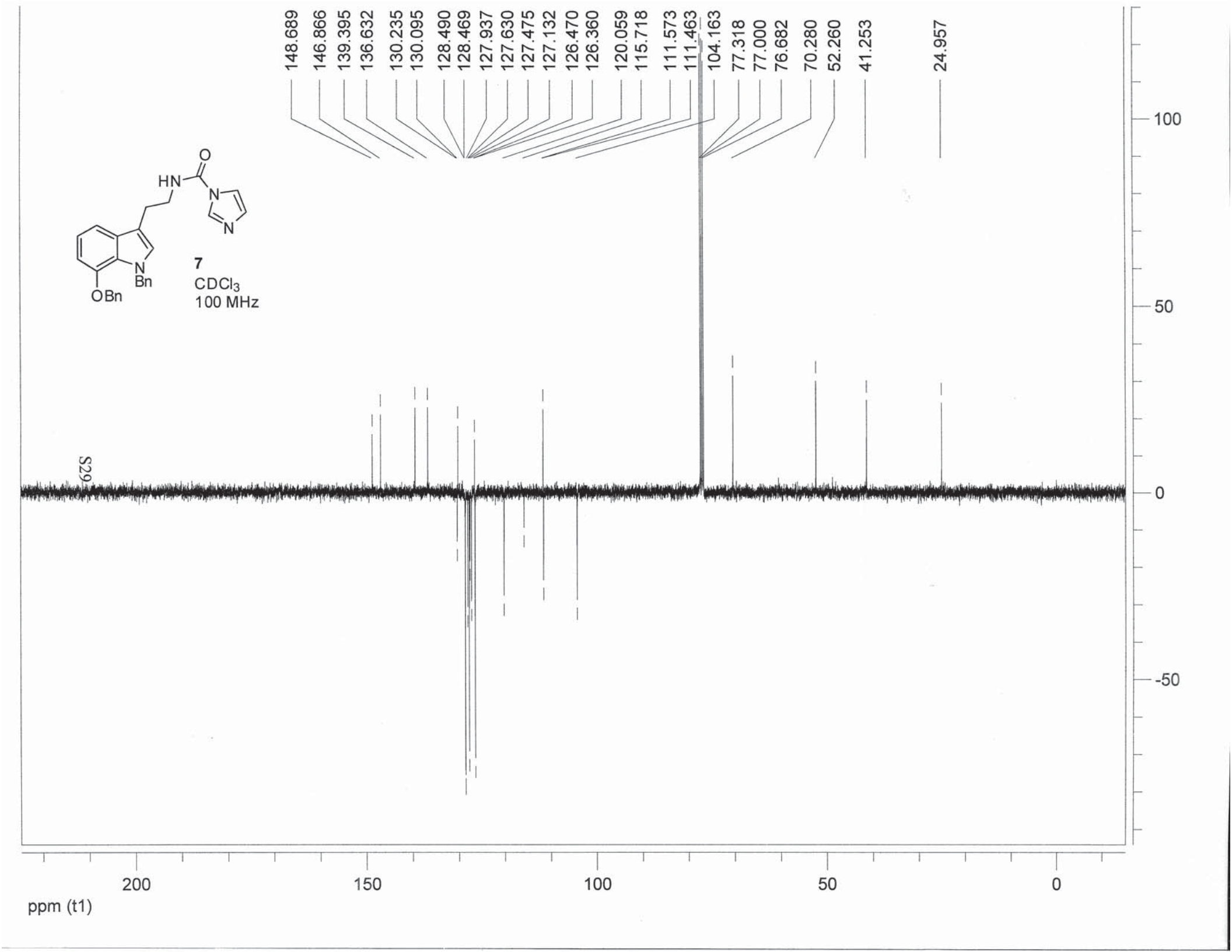
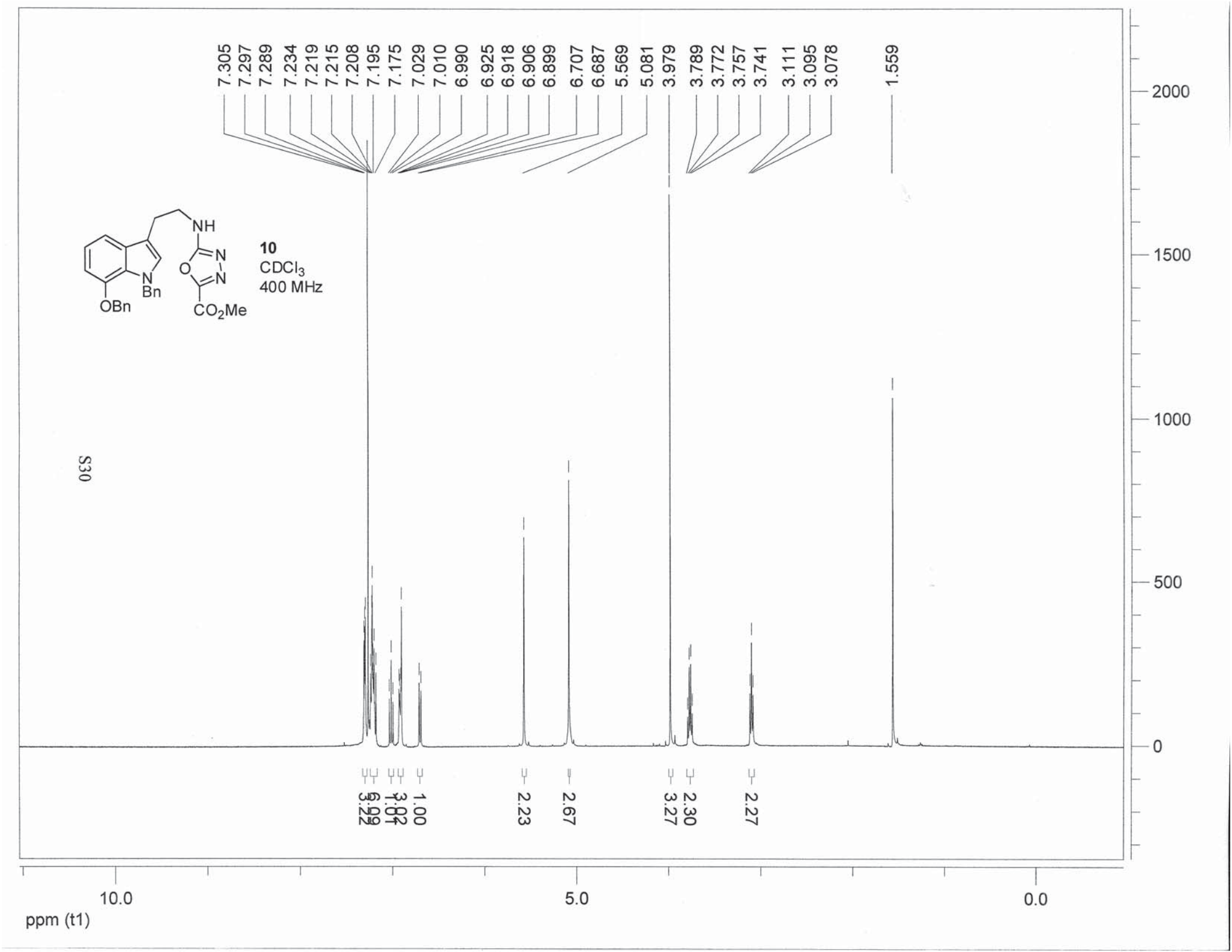
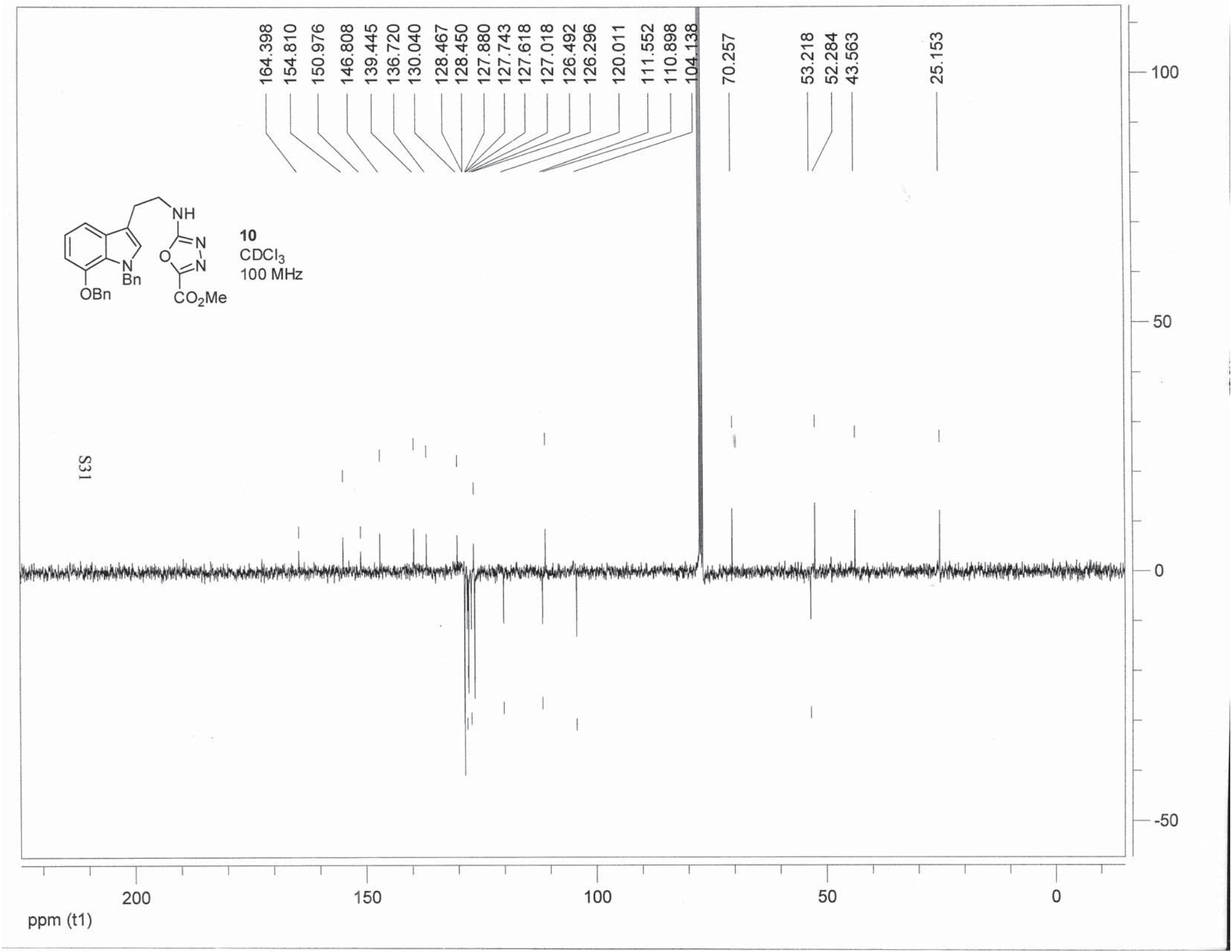
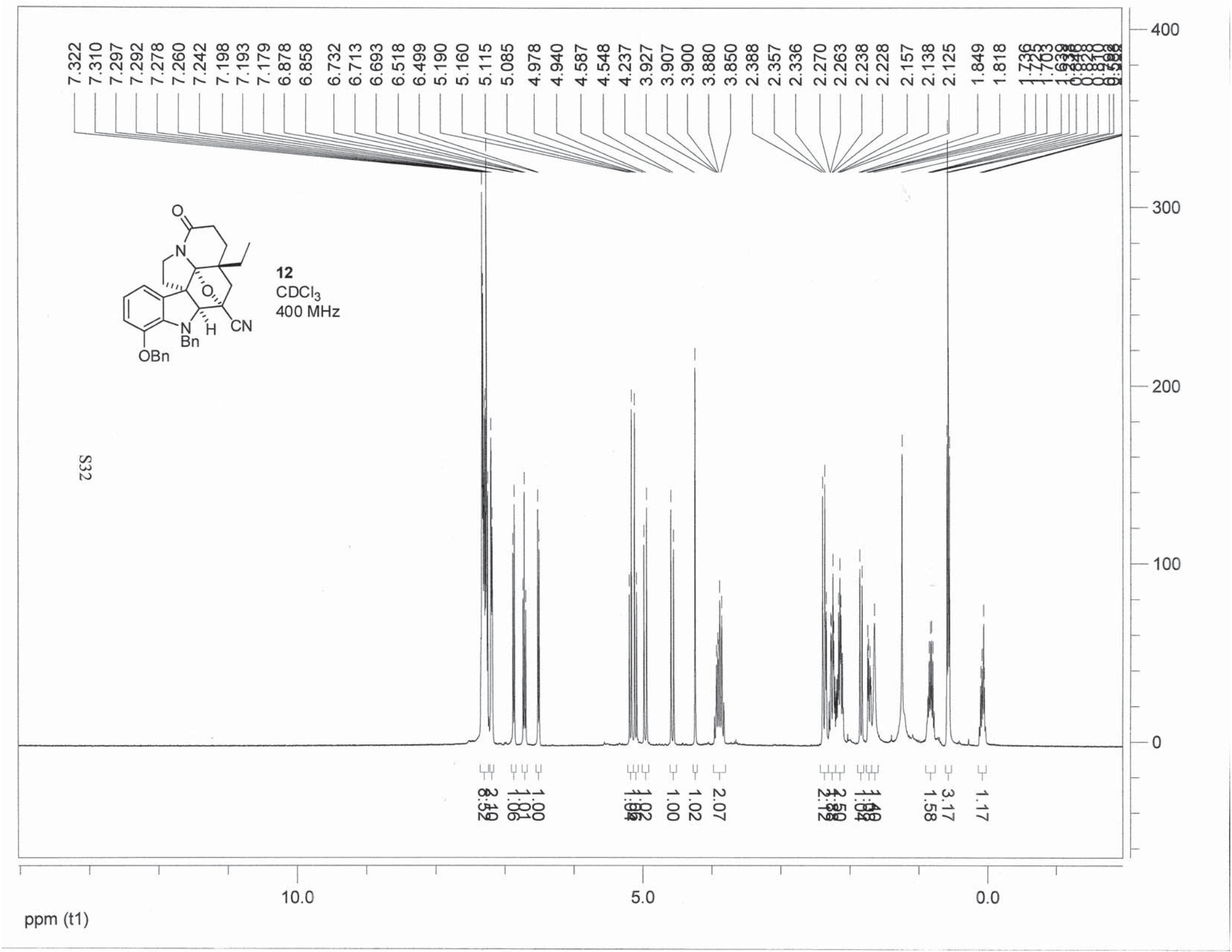
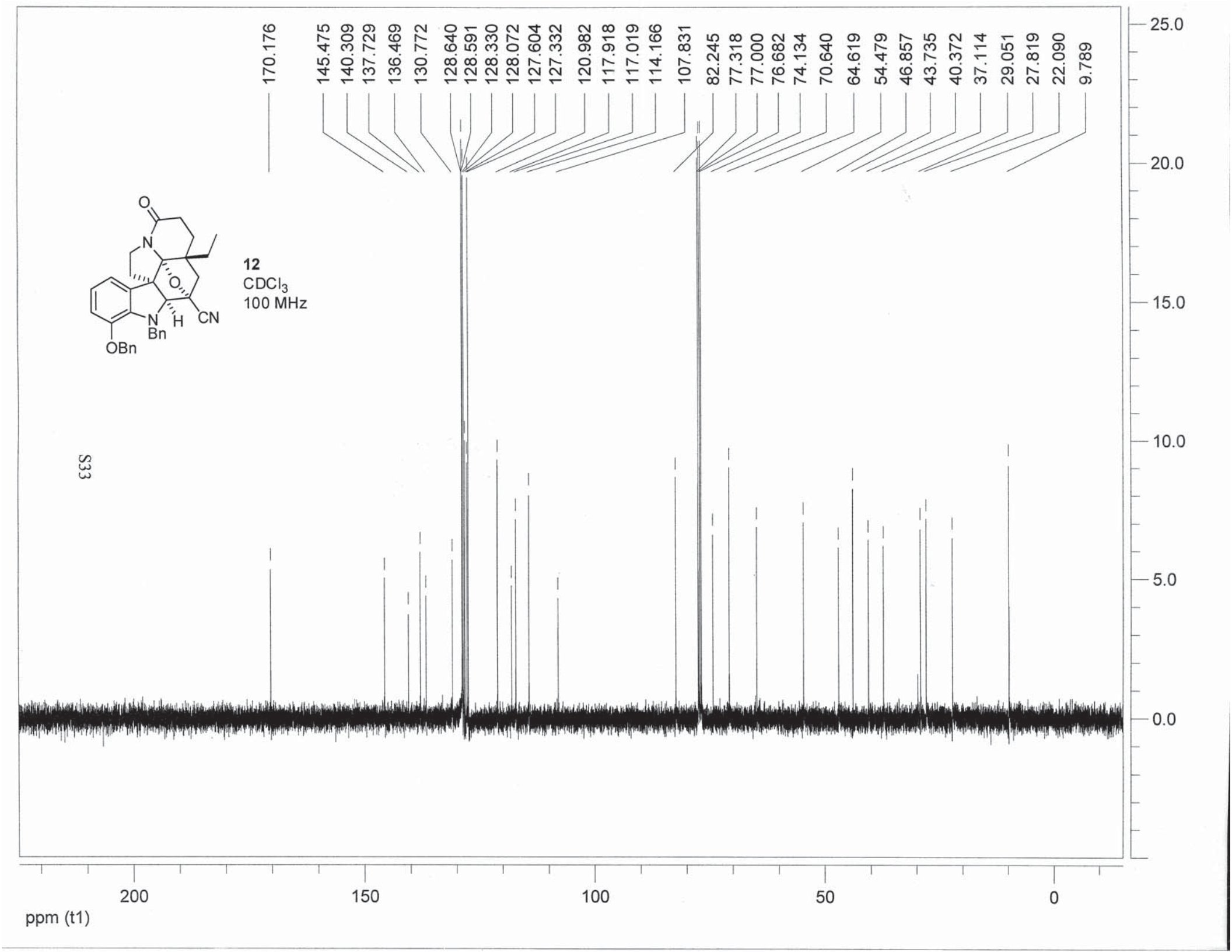
HN
O
N
N
N
Bn
OBn
7
CDCl3
400 MHz
S28
1000
500
0
0.91
1.00
0.91
2.07
2.07
2.06
2.08
10.0
5.0
0.0
ppm (t1)

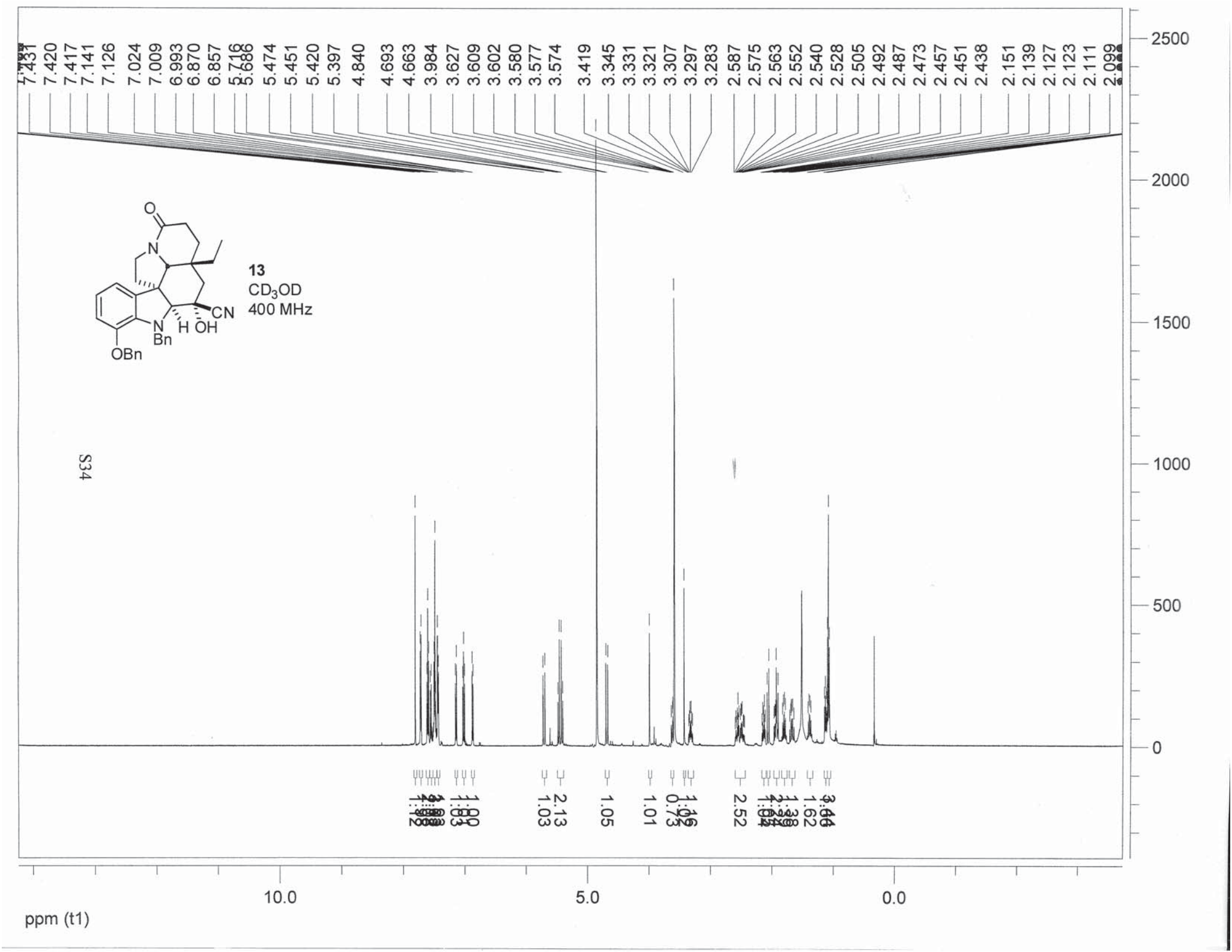

148.689
146.866
139.395
136.632
130.235
130.095
128.490
128.469
127.937
127.630
127.475
127.132
126.470
126.360
120.059
115.718
111.573
111.463
104.163
77.318
77.000
76.682
70.280
52.260
41.253
24.957
HN
O
N
N
N
Bn
OBn
7
CDCl3
100 MHz
100
50
0
-50
200
150
100
50
0
ppm (t1)

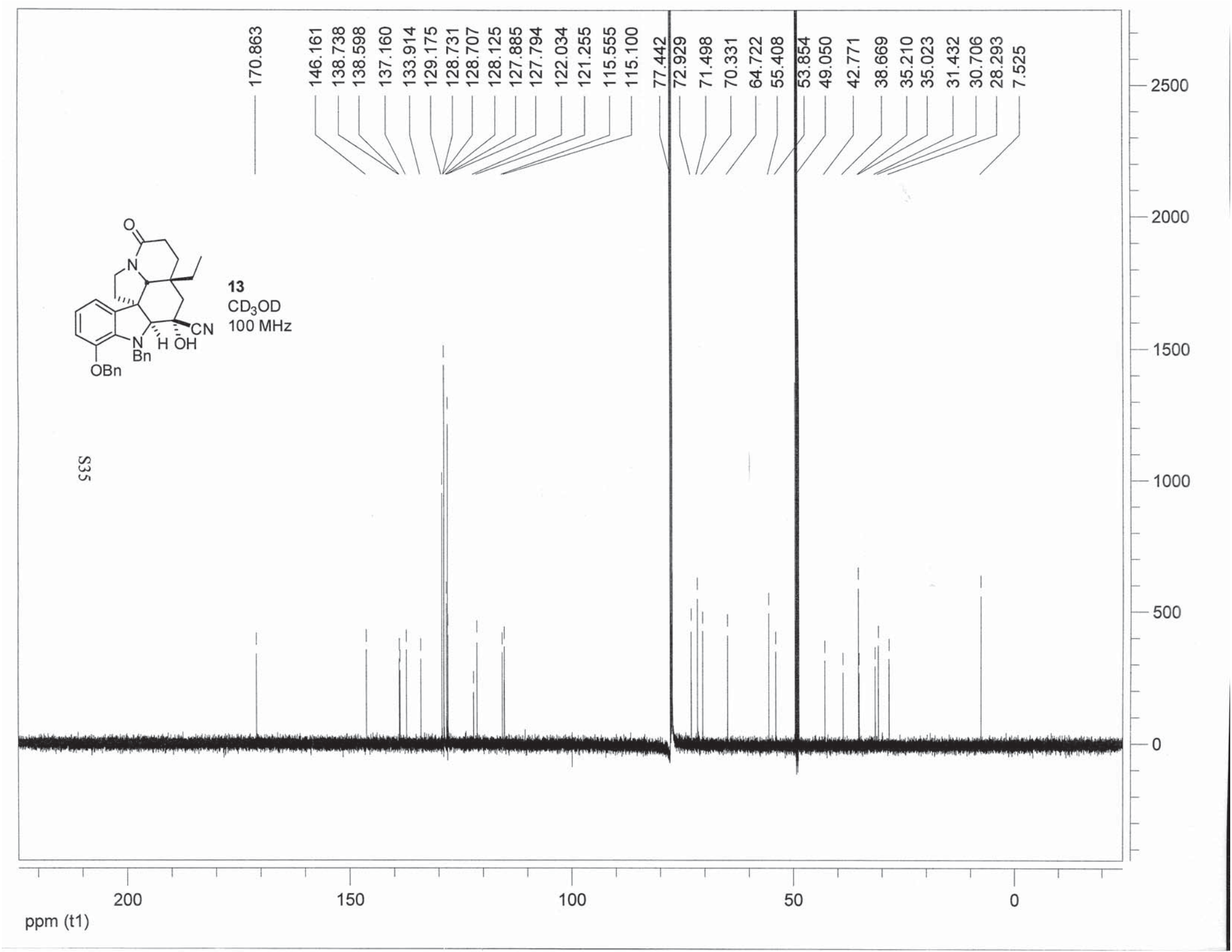

7.305
7.297
7.289
7.234
7.219
7.215
7.208
7.195
7.175
7.029
7.010
6.990
6.925
6.918
6.906
6.899
6.707
6.687
5.569
5.081
3.979
3.789
3.772
3.757
3.741
3.111
3.095
3.078
1.559
NH
N
O
N
N
Bn
OBn
CO2Me
10
CDCl3
400 MHz
S30
3.22
6.09
7.84
3.82
1.00
2.23
2.67
3.27
2.30
2.27
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

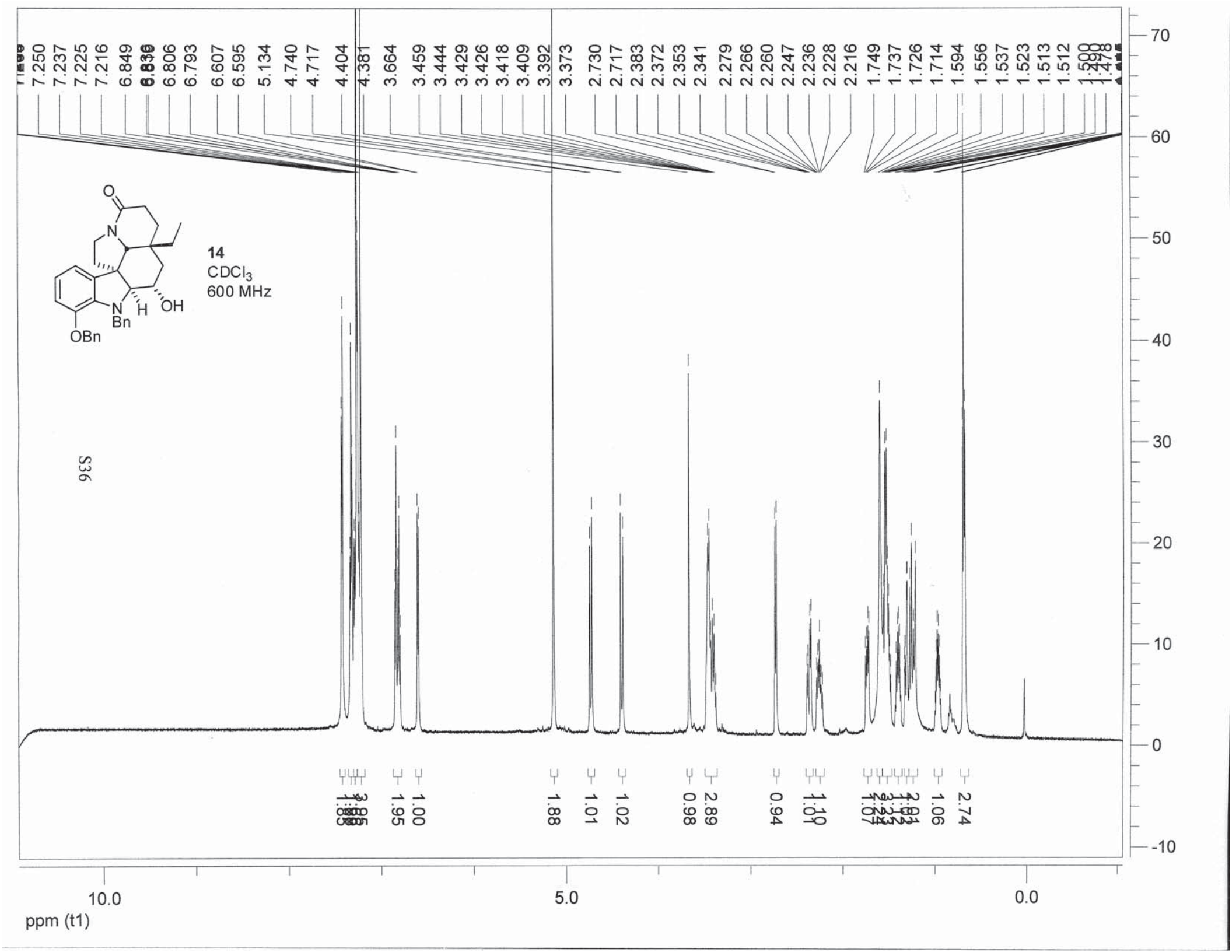

164.398
154.810
150.976
146.808
139.445
136.720
130.040
128.467
128.450
127.880
127.743
127.618
127.018
126.492
126.296
120.011
111.552
110.898
104.138
70.257
53.218
52.284
43.563
25.153
NH
N
O
N
N
Bn
OBn
CO2Me
10
CDCl3
100 MHz
S31
100
50
0
-50
200
150
100
50
0
ppm (t1)

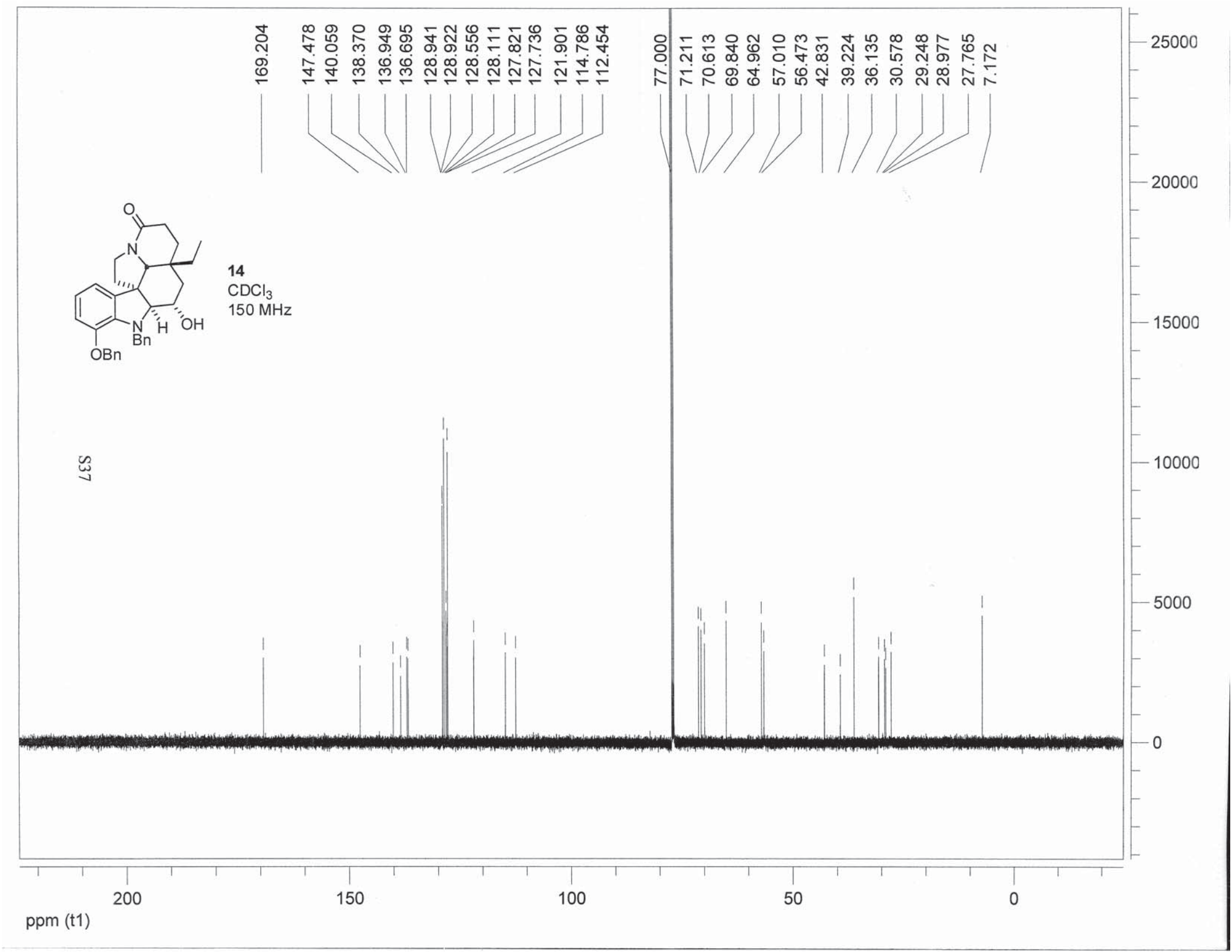

12
CDCl3
400 MHz
S33
ppm (t1)
10.0
5.0
0.0
400
300
200
100
0

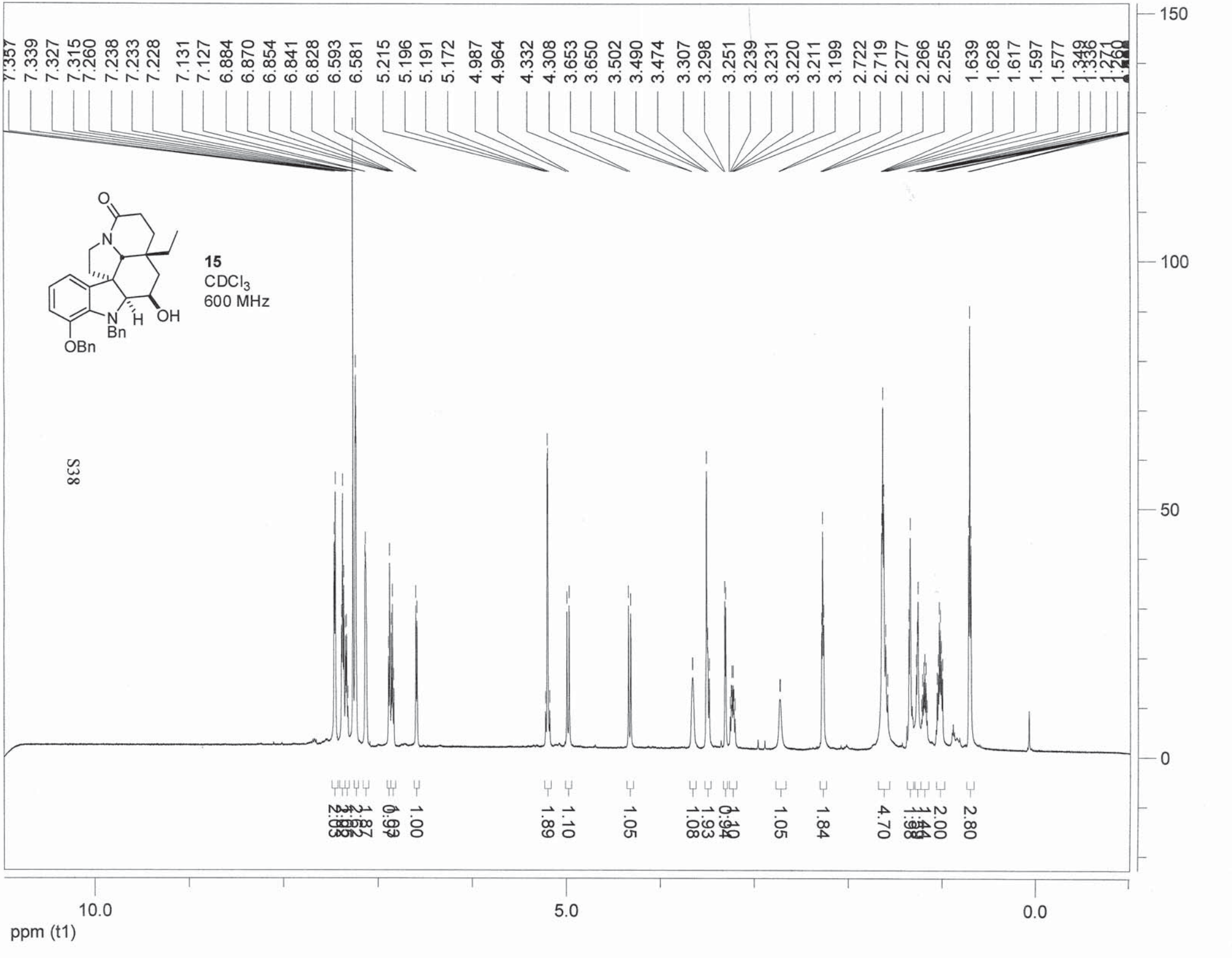

170.176
145.475
140.309
137.729
136.469
130.772
128.640
128.591
128.330
128.072
127.604
127.332
120.982
117.918
117.019
114.166
107.831
82.245
77.318
77.000
76.682
74.134
70.640
64.619
54.479
46.857
43.735
40.372
37.114
29.051
27.819
22.090
9.789
12
CDCl3
100 MHz
S33
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

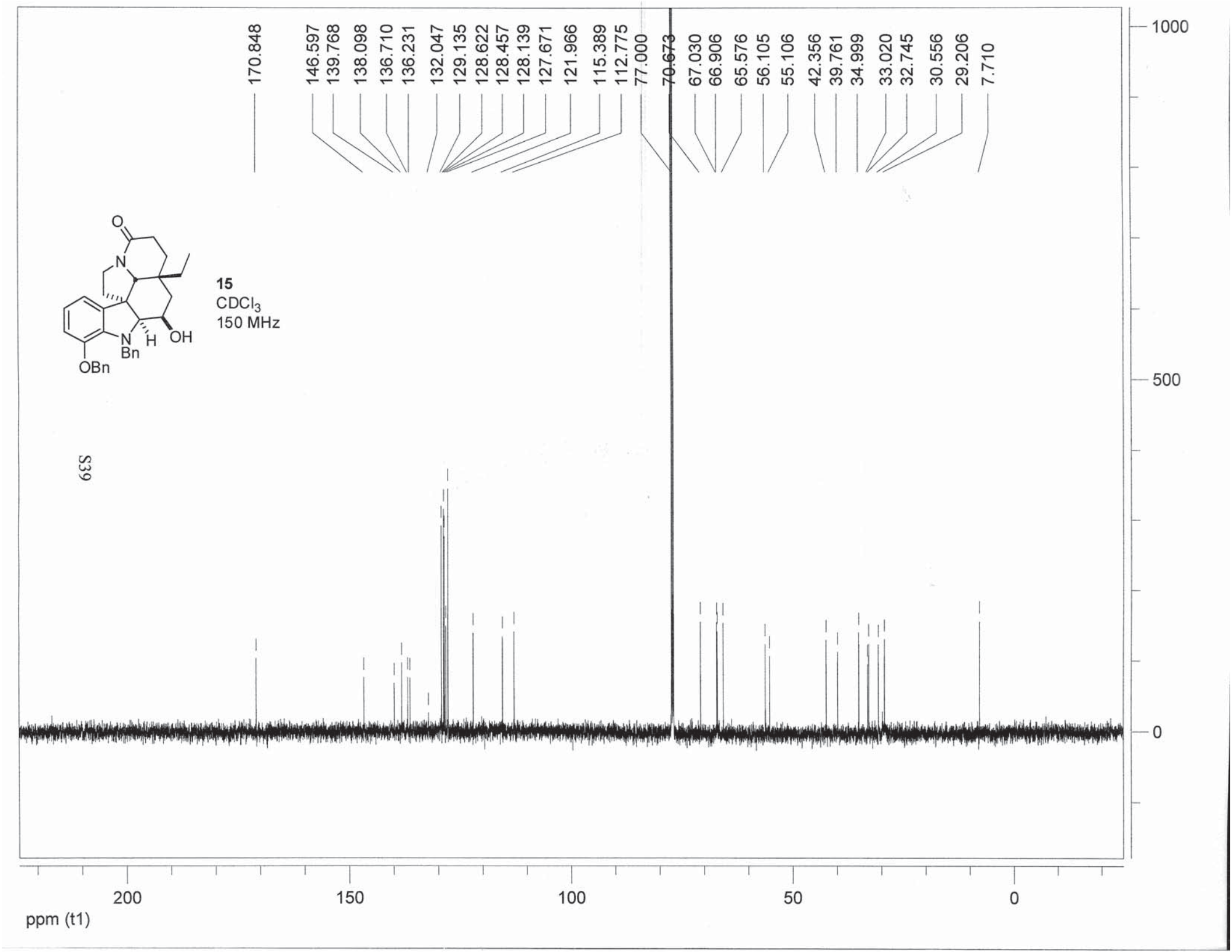

13
CD3OD
400 MHz
CN
H OH
N
Bn
OBn
O
N
S34
7.431
7.420
7.417
7.141
7.126
7.024
7.009
6.993
6.870
6.857
5.716
5.686
5.474
5.451
5.420
5.397
4.840
4.693
4.663
3.984
3.627
3.609
3.602
3.580
3.577
3.574
3.419
3.345
3.331
3.321
3.307
3.297
3.283
2.587
2.575
2.563
2.552
2.540
2.528
2.505
2.492
2.487
2.473
2.457
2.451
2.438
2.151
2.139
2.127
2.123
2.111
2.099
2500
2000
1500
1000
500
0
1.03
2.13
1.05
1.01
0.73
2.52
1.62
10.0
5.0
0.0
ppm (t1)

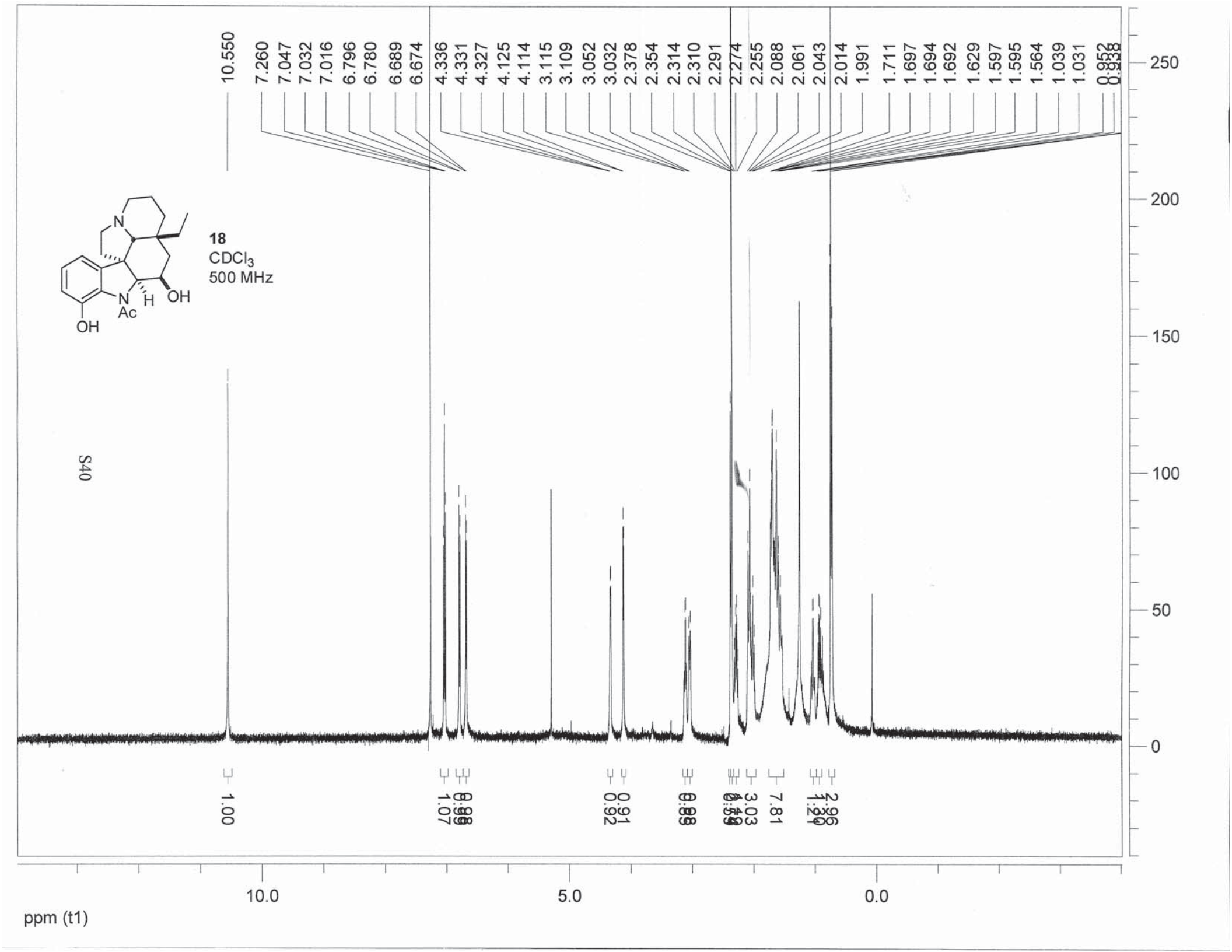

170.863
146.161
138.738
138.598
137.160
133.914
129.175
128.731
128.707
128.125
127.885
127.794
122.034
121.255
115.555
115.100
77.442
72.929
71.498
70.331
64.722
55.408
53.854
49.050
42.771
38.669
35.210
35.023
31.432
30.706
28.293
7.525
13
CD3OD
100 MHz
S33
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

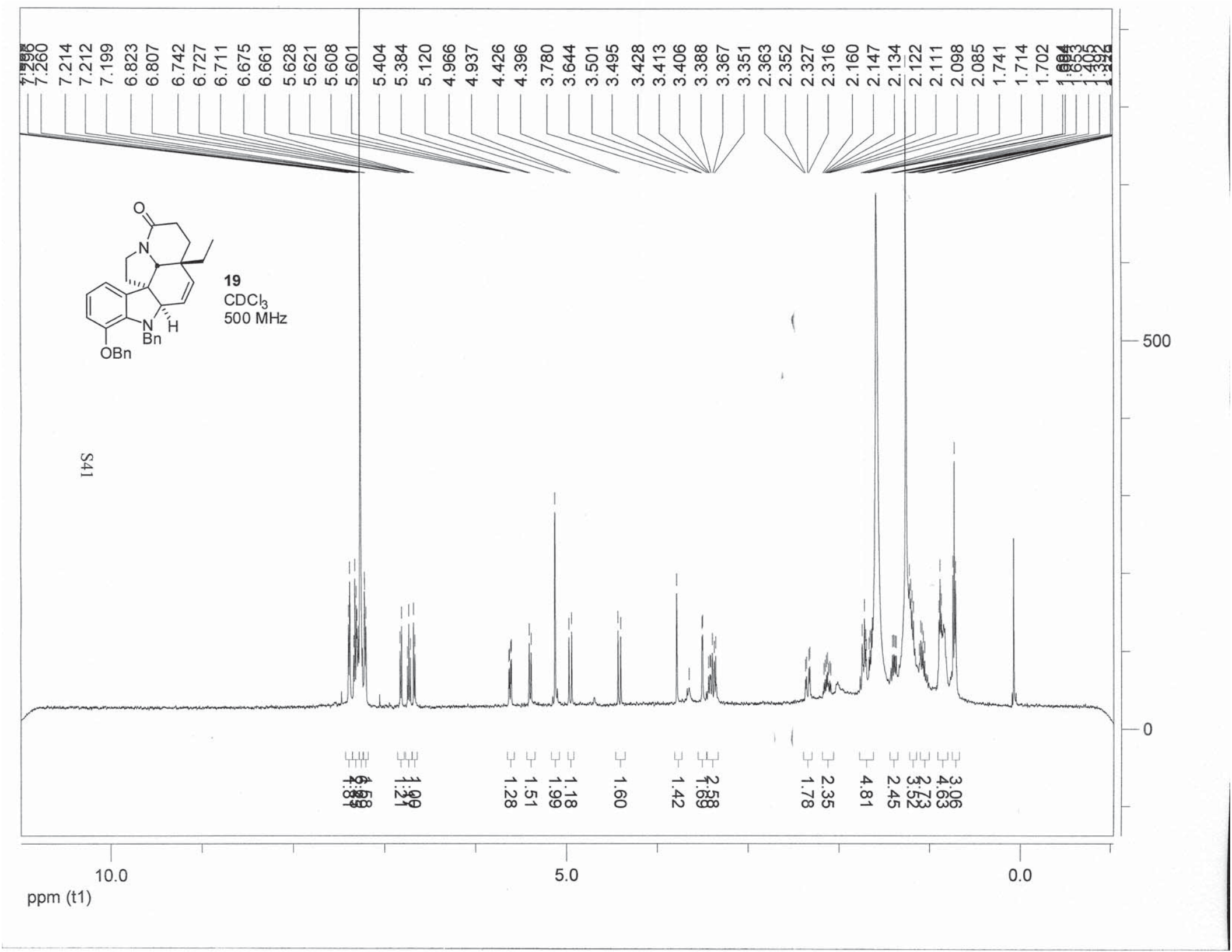

7.250
7.237
7.225
7.216
6.849
6.806
6.793
6.607
6.595
5.134
4.740
4.717
4.404
4.381
3.664
3.459
3.444
3.429
3.426
3.418
3.409
3.392
3.373
2.730
2.717
2.383
2.372
2.353
2.341
2.279
2.266
2.260
2.247
2.236
2.228
2.216
1.749
1.737
1.726
1.714
1.594
1.556
1.537
1.523
1.513
1.512
14
CDCl3
600 MHz
OBn
N
Bn
H
OH
O
S36
1.85
1.95
1.00
1.88
1.01
1.02
0.98
2.89
0.94
1.06
2.74
10.0
5.0
0.0
ppm (t1)

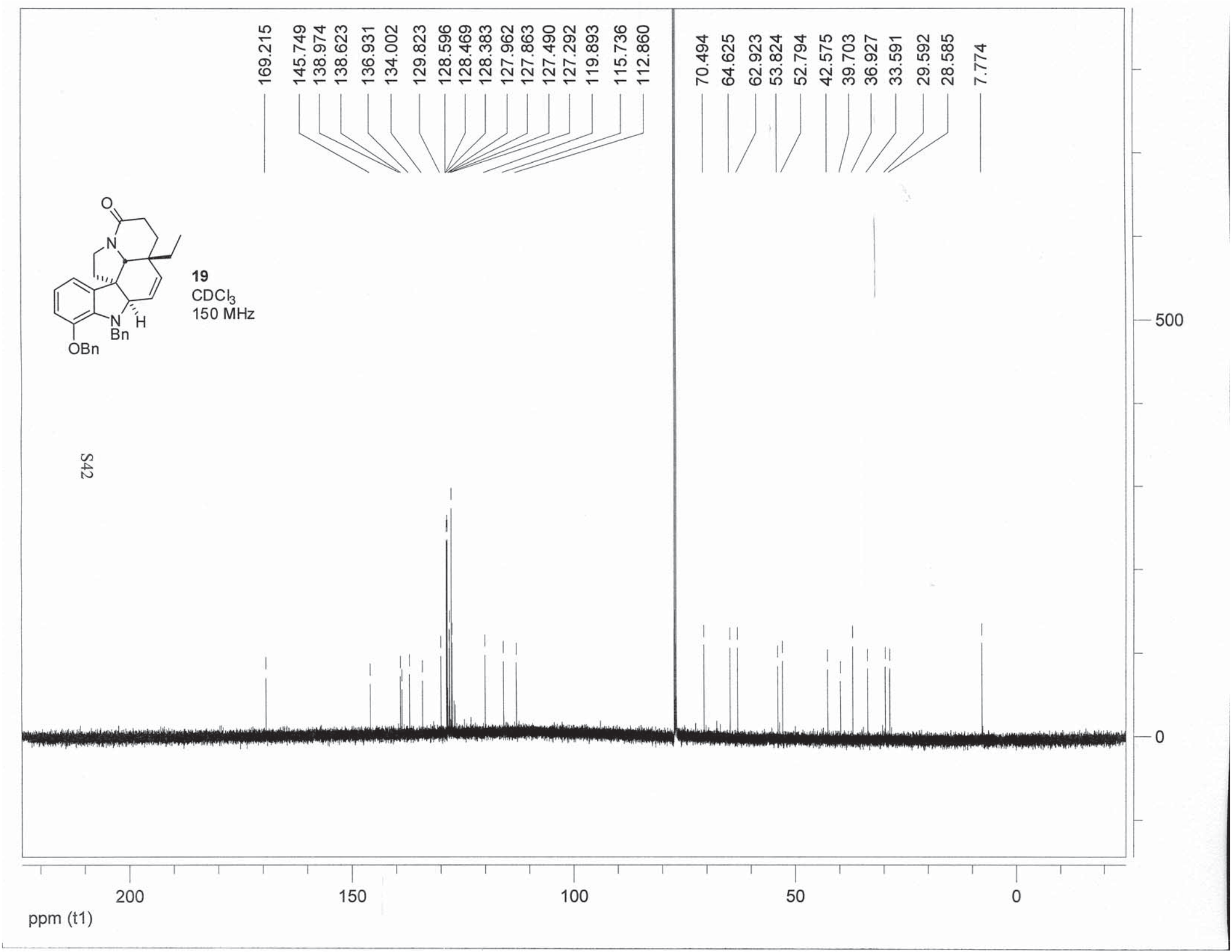

169.204
147.478
140.059
138.370
136.949
136.695
128.941
128.922
128.556
128.111
127.821
127.736
121.901
114.786
112.454
77.000
71.211
70.613
69.840
64.962
57.010
56.473
42.831
39.224
36.135
30.578
29.248
28.977
27.765
7.172
14
CDCl3
150 MHz
S37
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)


7.357
7.339
7.327
7.315
7.260
7.238
7.233
7.228
7.131
7.127
6.884
6.870
6.854
6.841
6.828
6.593
6.581
5.215
5.196
5.191
5.172
4.987
4.964
4.332
4.308
3.653
3.650
3.502
3.490
3.474
3.307
3.298
3.251
3.239
3.231
3.220
3.211
3.199
2.722
2.719
2.277
2.266
2.255
1.639
1.628
1.617
1.597
1.577
1.349
1.338
1.271
1.260
O
N
OH
H
N
Bn
OBn
15
CDCl3
600 MHz
S38
1.00
1.89
1.10
1.05
1.08
1.93
1.05
1.84
4.70
2.00
2.80
150
100
50
0
10.0
5.0
0.0
ppm (t1)

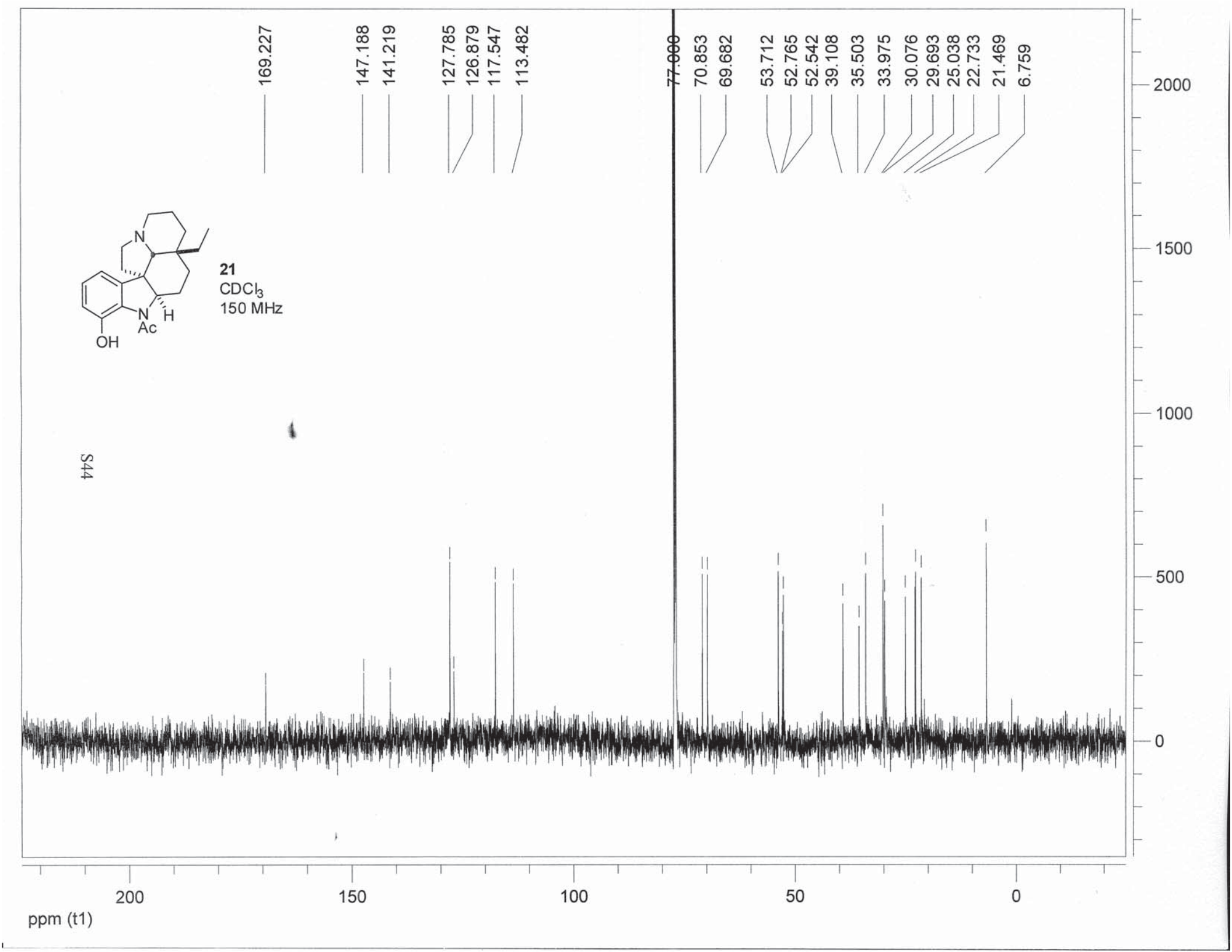

170.848
146.597
139.768
138.098
136.710
136.231
132.047
129.135
128.622
128.457
128.139
127.671
121.966
115.389
112.775
77.000
70.673
67.030
66.906
65.576
56.105
55.106
42.356
39.761
34.999
33.020
32.745
30.556
29.206
7.710
1000
500
0
200
150
100
50
0
ppm (t1)
O
N
N
H
OH
Bn
OBn
15
CDCl3
150 MHz

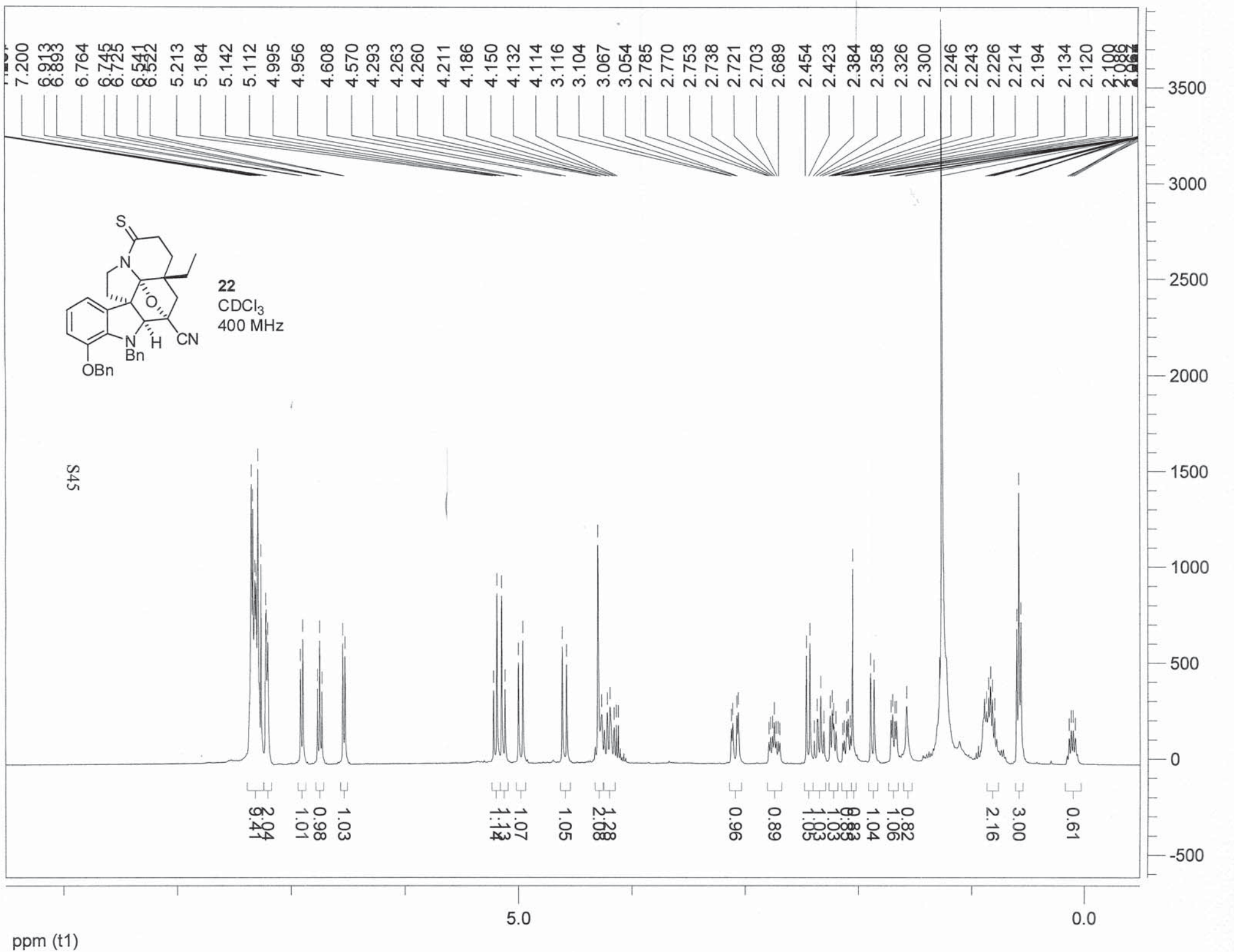

10.550
7.260
7.047
7.032
7.016
6.796
6.780
6.689
6.674
4.336
4.331
4.327
4.125
4.114
3.115
3.109
3.052
3.032
2.378
2.354
2.314
2.310
2.291
2.274
2.255
2.088
2.061
2.043
2.014
1.991
1.711
1.697
1.694
1.692
1.629
1.597
1.595
1.564
1.039
1.031
18
CDCl3
500 MHz
OH
N
H
Ac
OH
S40
1.00
1.07
0.91
0.92
3.03
7.81
1.20
250
200
150
100
50
0
10.0
5.0
0.0
ppm (t1)

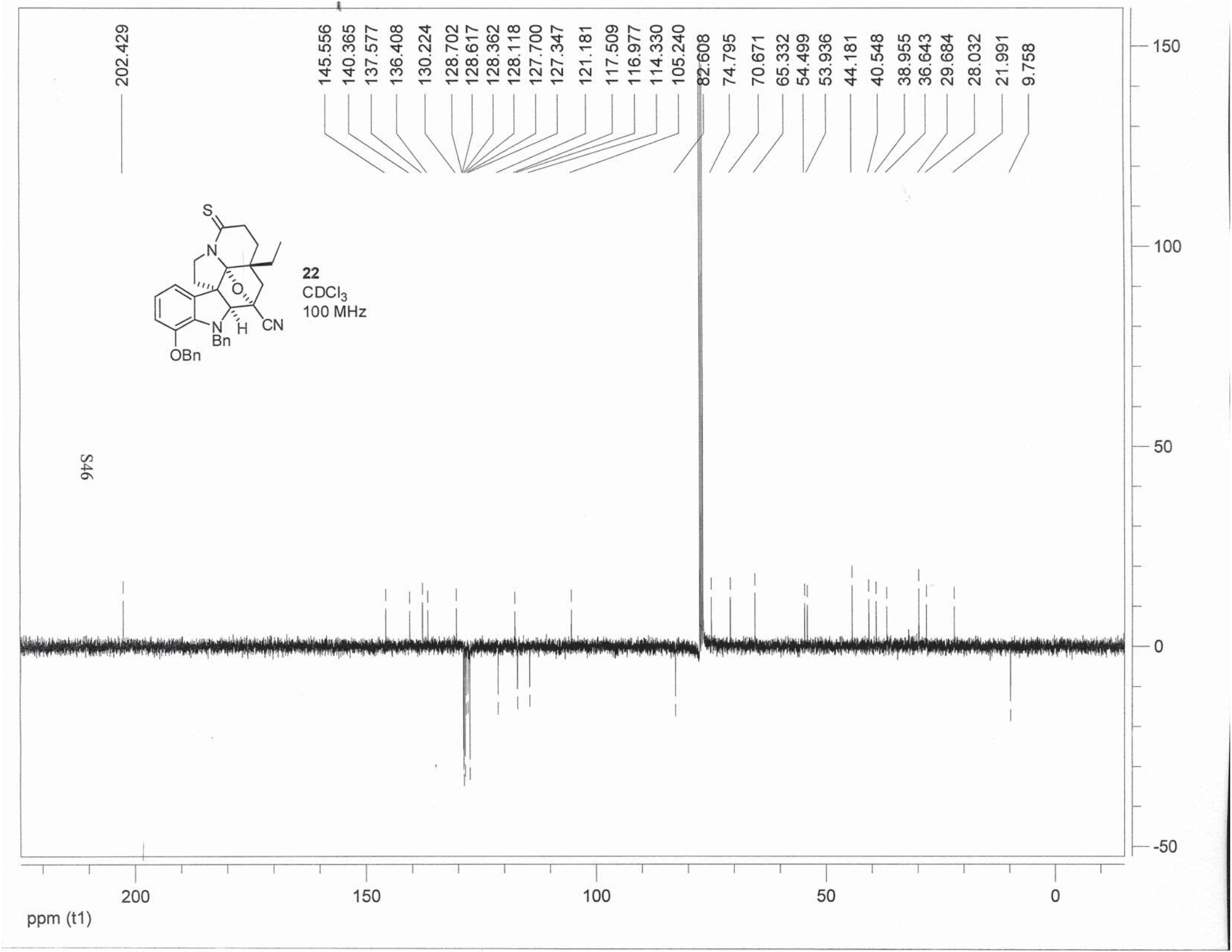

19
CDCl3
500 MHz
OBn
Bn
S41
500
0
10.0
5.0
0.0
ppm (t1)

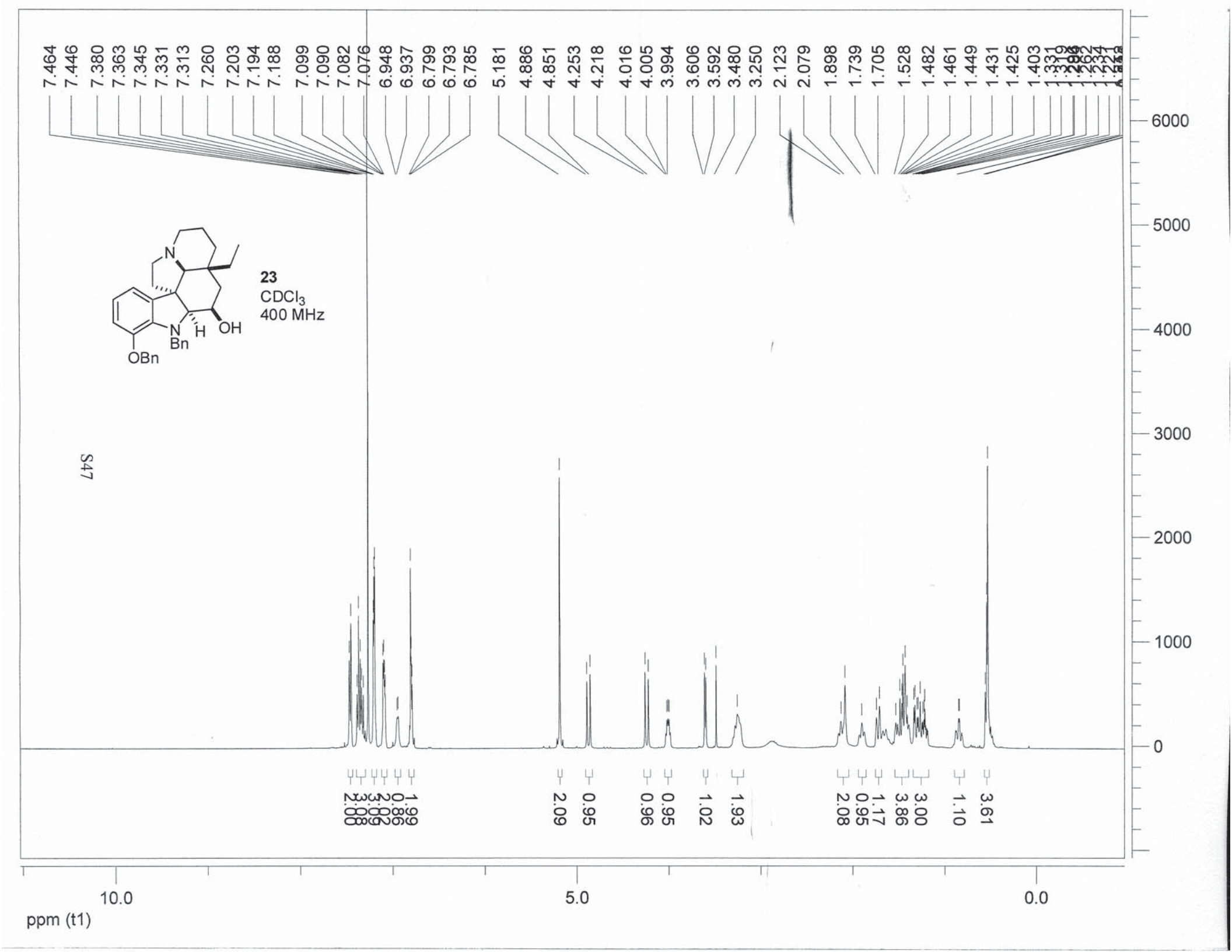

169.215
145.749
138.974
138.623
136.931
134.002
129.823
128.596
128.469
128.383
127.962
127.863
127.490
127.292
119.893
115.736
112.860
70.494
64.625
62.923
53.824
52.794
42.575
39.703
36.927
33.591
29.592
28.585
7.774
O
N
N
H
Bn
OBn
19
CDCl3
150 MHz
S42
500
0
200
150
100
50
0
ppm (t1)

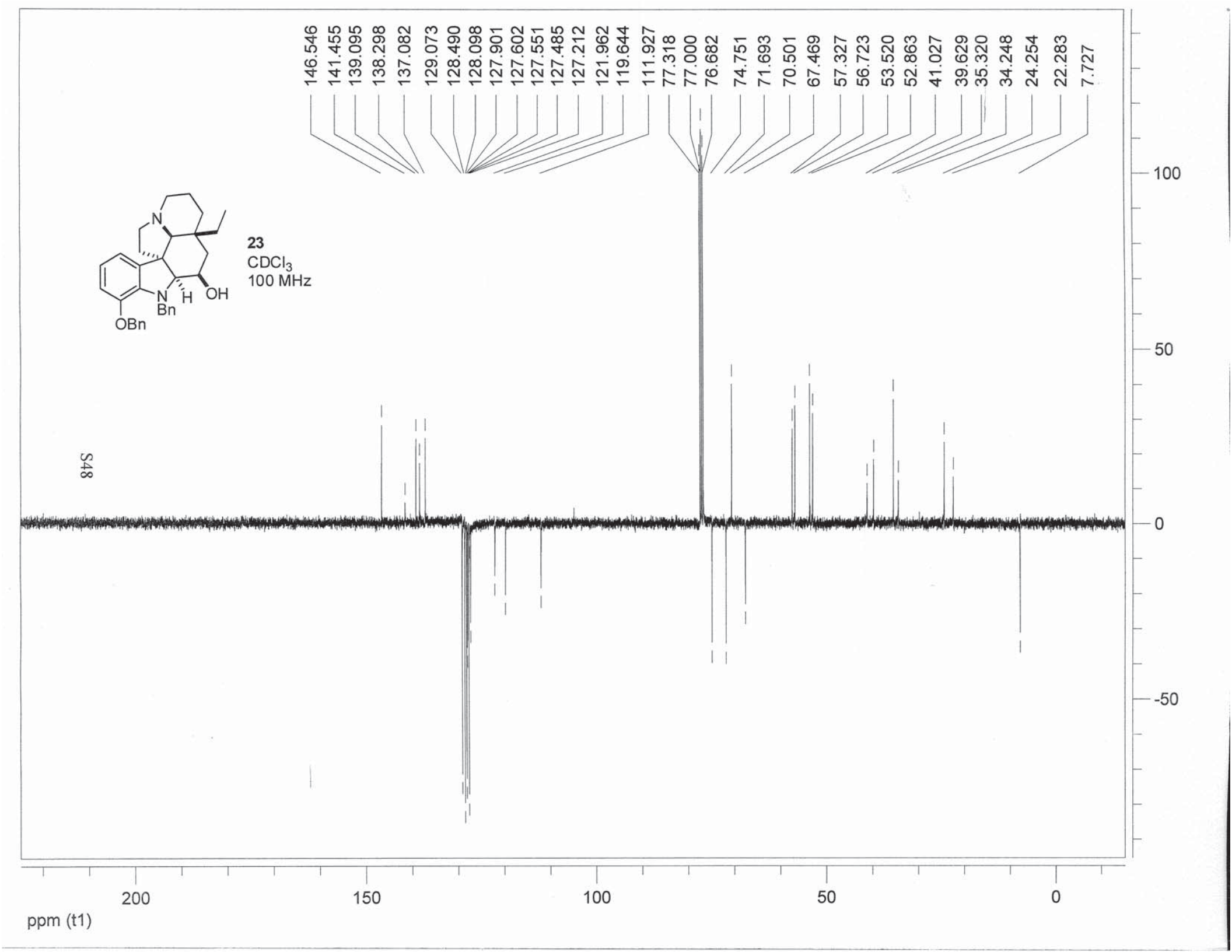
21
CDCl3
600 MHz
N
H
N
Ac
OH
ppm (t1)

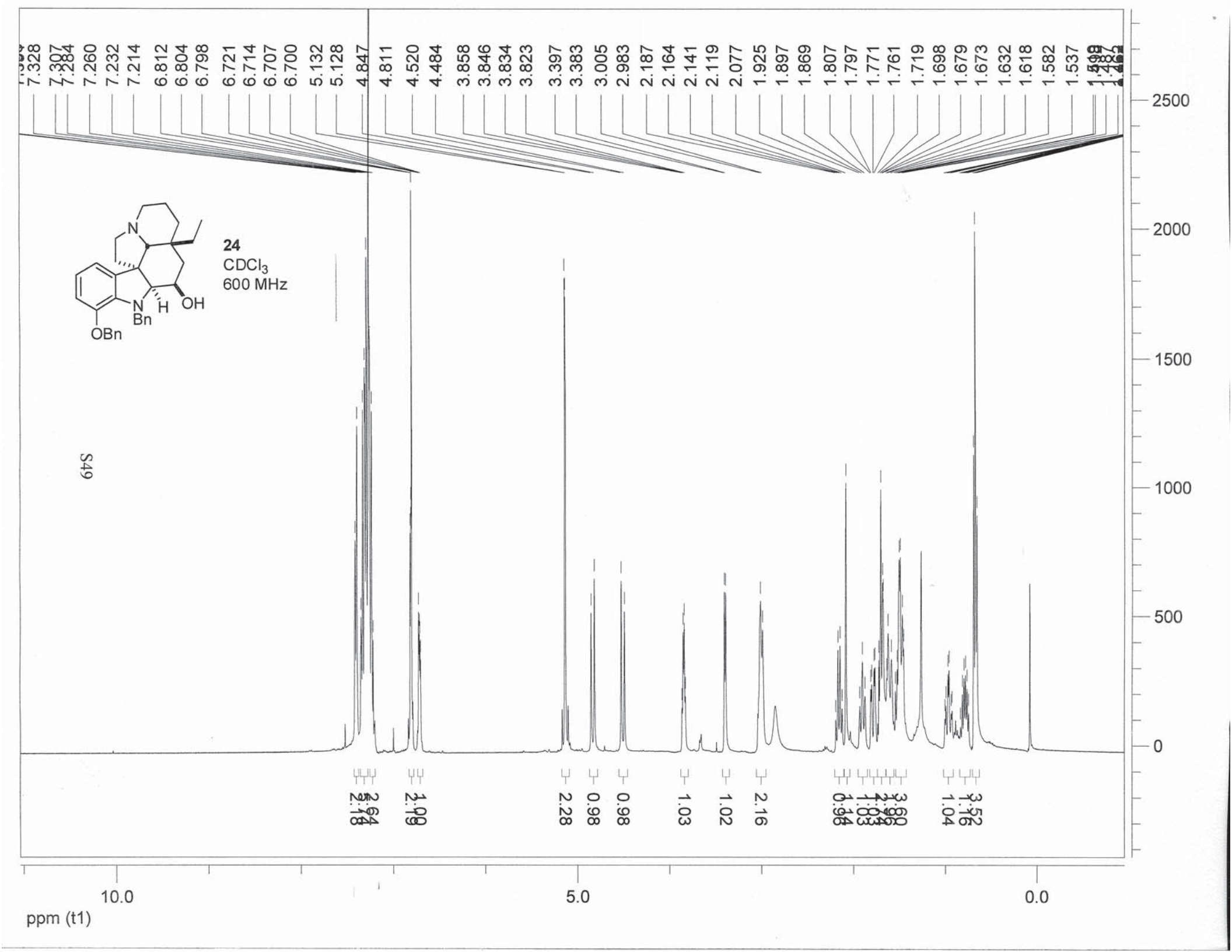

169.227
147.188
141.219
127.785
126.879
117.547
113.482
77.000
70.853
69.682
53.712
52.765
52.542
39.108
35.503
33.975
30.076
29.693
25.038
22.733
21.469
6.759
21
CDCl3
150 MHz
N
N
H
Ac
OH
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

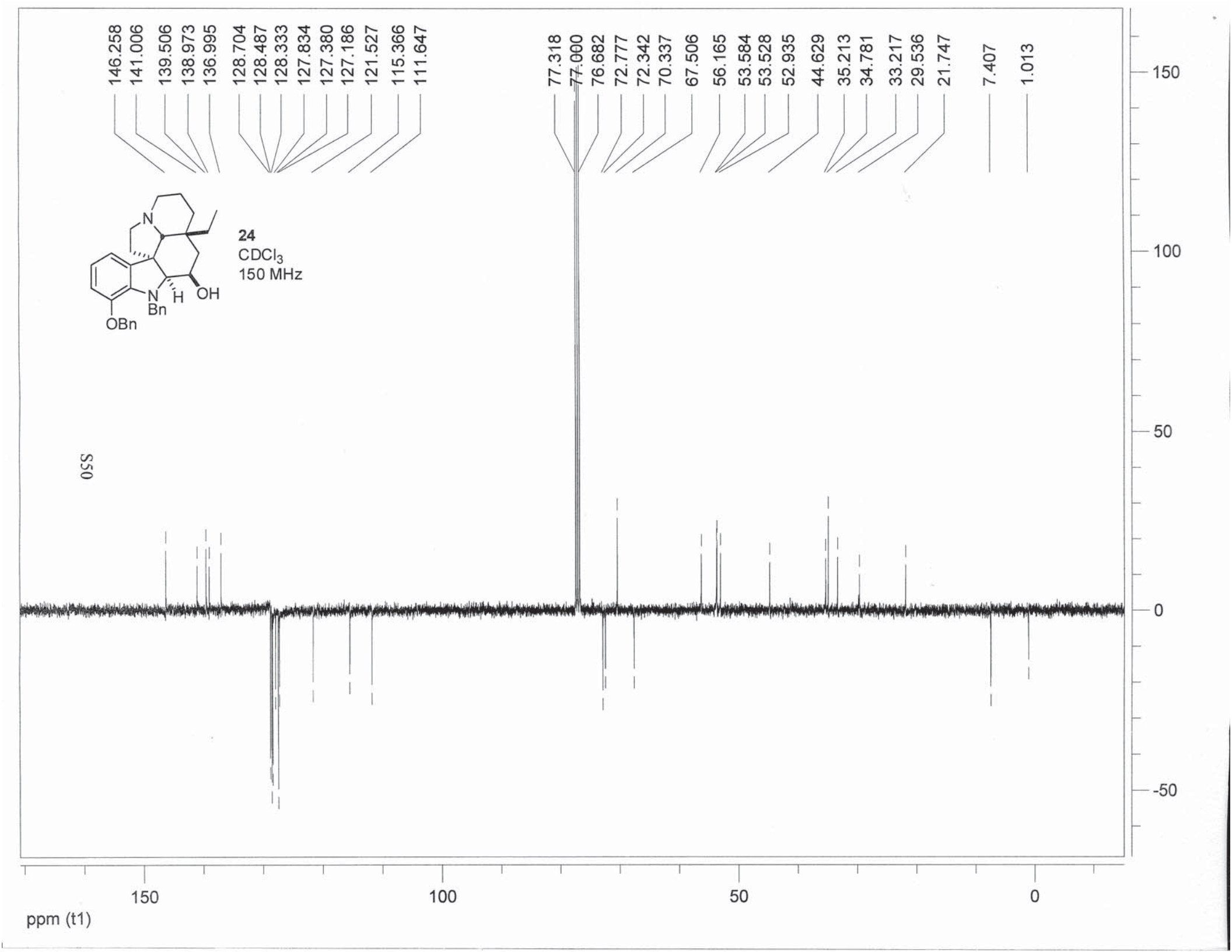

7.200
6.913
6.893
6.764
6.745
6.725
6.541
6.522
5.213
5.184
5.142
5.112
4.995
4.956
4.608
4.570
4.293
4.263
4.260
4.211
4.186
4.150
4.132
4.114
3.116
3.104
3.067
3.054
2.785
2.770
2.753
2.738
2.721
2.703
2.689
2.454
2.423
2.384
2.358
2.326
2.300
2.246
2.243
2.226
2.214
2.194
2.134
2.120
S
N
O
N
H
Bn
CN
OBn
22
CDCl3
400 MHz
S45
3500
3000
2500
2000
1500
1000
500
0
-500
2.04
1.01
0.98
1.03
1.07
1.05
0.96
0.89
1.04
1.06
0.82
2.16
3.00
0.61
5.0
0.0
ppm (t1)

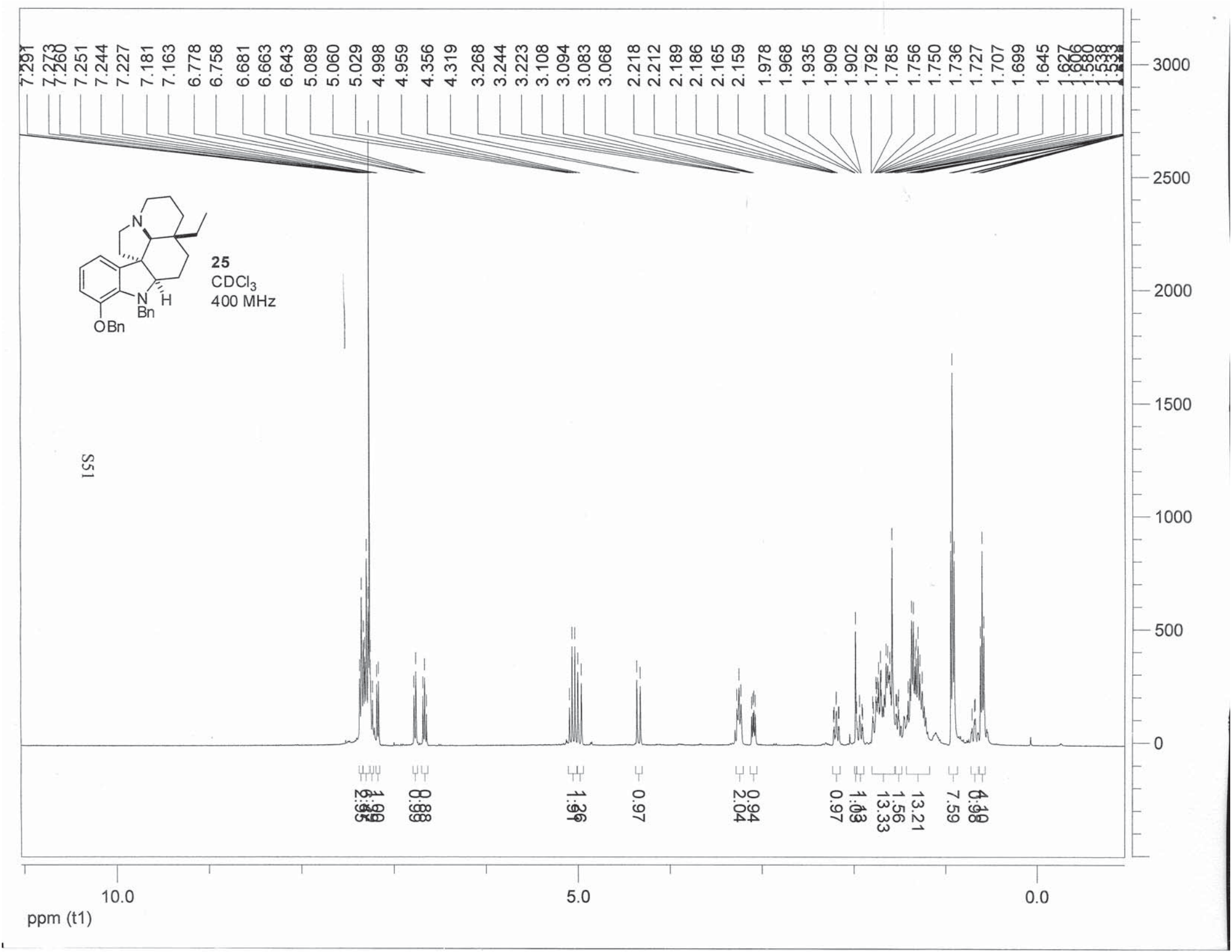

202.429
145.556
140.365
137.577
136.408
130.224
128.702
128.617
128.362
128.118
127.700
127.347
121.181
117.509
116.977
114.330
105.240
82.608
74.795
70.671
65.332
54.499
53.936
44.181
40.548
38.955
36.643
29.684
28.032
21.991
9.758
S
N
O
N
H
CN
Bn
OBn
22
CDCl3
100 MHz
150
100
50
0
-50
200
150
100
50
0
ppm (t1)

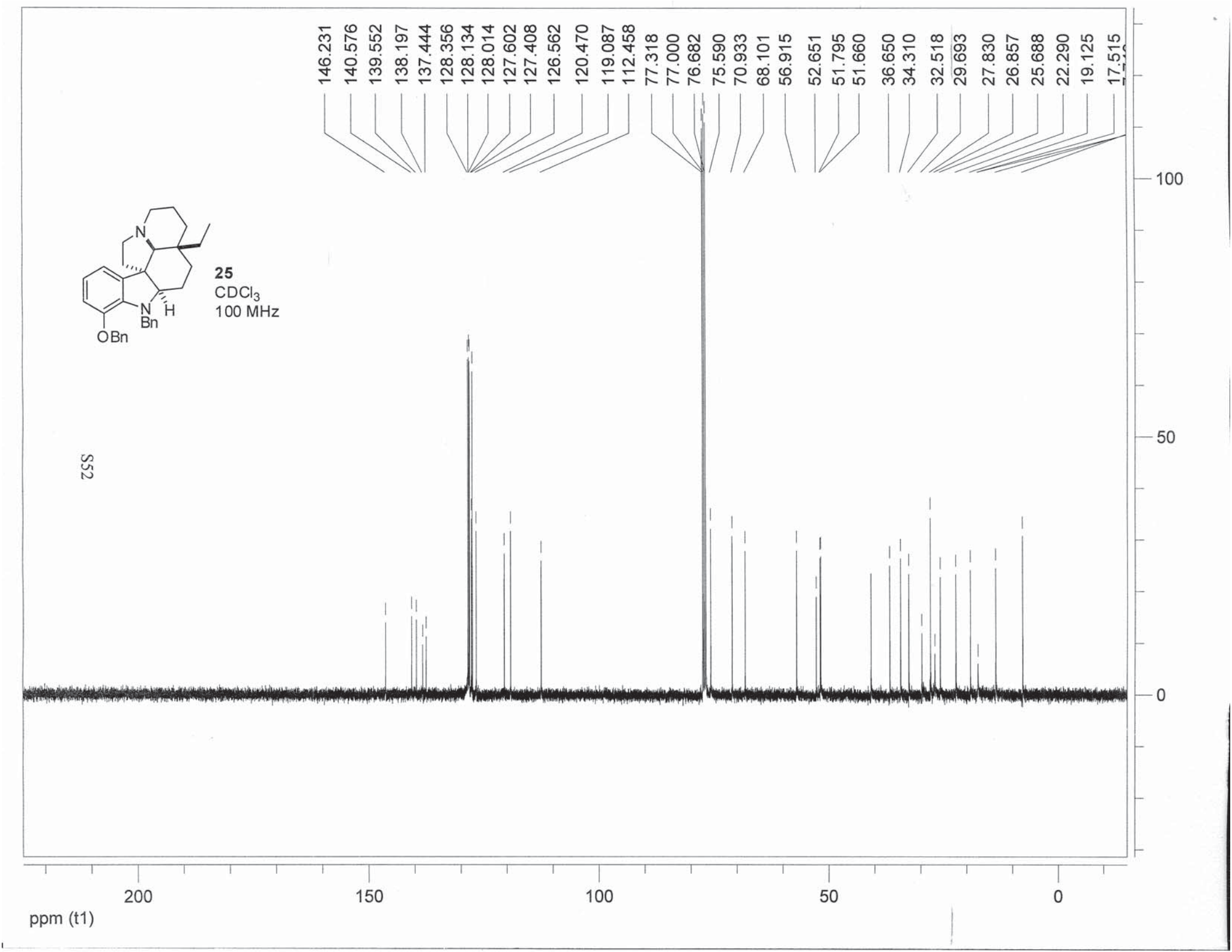

7.464
7.446
7.380
7.363
7.345
7.331
7.313
7.260
7.203
7.194
7.188
7.099
7.090
7.082
7.076
6.948
6.937
6.799
6.793
6.785
5.181
4.886
4.851
4.253
4.218
4.016
4.005
3.994
3.606
3.592
3.480
3.250
2.123
2.079
1.898
1.739
1.705
1.528
1.482
1.461
1.449
1.431
1.425
1.403
1.331
23
CDCl3
400 MHz
OH
N
H
Bn
OBn
S47
2.08
3.09
3.02
0.86
1.99
2.09
0.95
0.96
0.95
1.02
1.93
2.08
0.95
1.17
3.86
3.00
1.10
3.61
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)

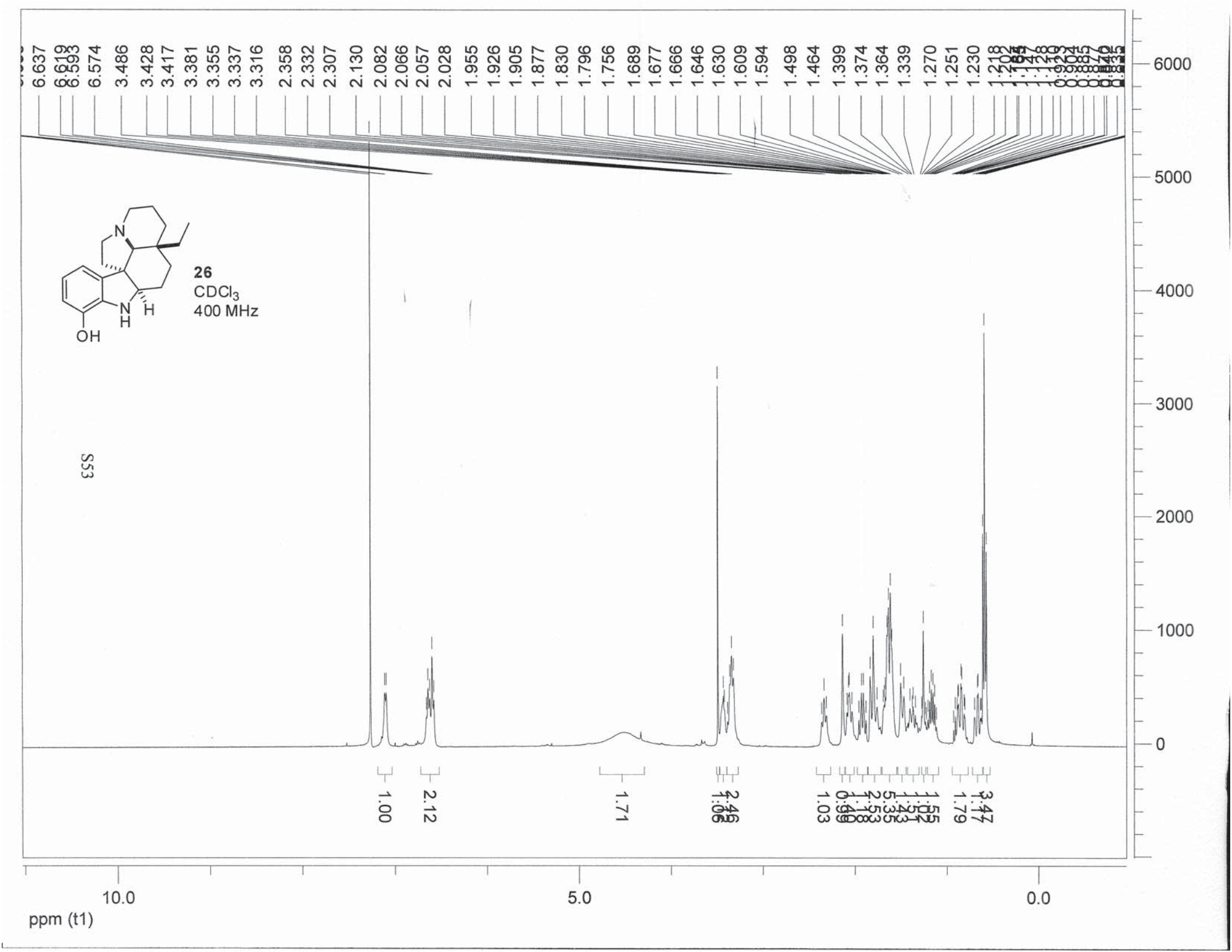

146.546
141.455
139.095
138.298
137.082
129.073
128.490
128.098
127.901
127.602
127.551
127.485
127.212
121.962
119.644
111.927
77.318
77.000
76.682
74.751
71.693
70.501
67.469
57.327
56.723
53.520
52.863
41.027
39.629
35.320
34.248
24.254
22.283
7.727
23
CDCl3
100 MHz
N
N
H
Bn
OH
OBn
S48
100
50
0
-50
200
150
100
50
0
ppm (t1)

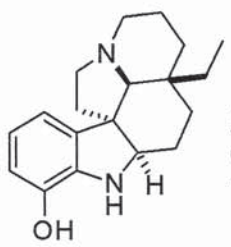

24
CDCl3
600 MHz
OBn
N
Bn
H
OH
S49
7.328
7.307
7.284
7.260
7.232
7.214
6.812
6.804
6.798
6.721
6.714
6.707
6.700
5.132
5.128
4.847
4.811
4.520
4.484
3.858
3.846
3.834
3.823
3.397
3.383
3.005
2.983
2.187
2.164
2.141
2.119
2.077
1.925
1.897
1.869
1.807
1.797
1.771
1.761
1.719
1.698
1.679
1.673
1.632
1.618
1.582
1.537
2.18
2.64
2.14
1.99
2.28
0.98
0.98
1.03
1.02
2.16
0.98
1.04
3.52
1.76
1.04
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)


146.258
141.006
139.506
138.973
136.995
128.704
128.487
128.333
127.834
127.380
127.186
121.527
115.366
111.647
77.318
77.000
76.682
72.777
72.342
70.337
67.506
56.165
53.584
53.528
52.935
44.629
35.213
34.781
33.217
29.536
21.747
7.407
1.013
24
CDCl3
150 MHz
N
N
H
Bn
OH
OBn
SS0
150
100
50
0
-50
150
100
50
0
ppm (t1)


7.291
7.273
7.260
7.251
7.244
7.227
7.181
7.163
6.778
6.758
6.681
6.663
6.643
5.089
5.060
5.029
4.998
4.959
4.356
4.319
3.268
3.244
3.223
3.108
3.094
3.083
3.068
2.218
2.212
2.189
2.186
2.165
2.159
1.978
1.968
1.935
1.909
1.902
1.792
1.785
1.756
1.750
1.736
1.727
1.707
1.699
1.645
1.627
1.606
1.580
1.538
3000
2500
2000
1500
1000
500
0
N
N
H
Bn
OBn
25
CDCl3
400 MHz
SS1
2.95
1.00
0.88
1.96
0.97
2.04
0.97
1.03
13.33
1.56
13.21
7.59
4.10
10.0
5.0
0.0
ppm (t1)


146.231
140.576
139.552
138.197
137.444
128.356
128.134
128.014
127.602
127.408
126.562
120.470
119.087
112.458
77.318
77.000
76.682
75.590
70.933
68.101
56.915
52.651
51.795
51.660
36.650
34.310
32.518
29.693
27.830
26.857
25.688
22.290
19.125
17.515
N
N
H
Bn
OBn
25
CDCl3
100 MHz
S52
100
50
0
200
150
100
50
0
ppm (t1)

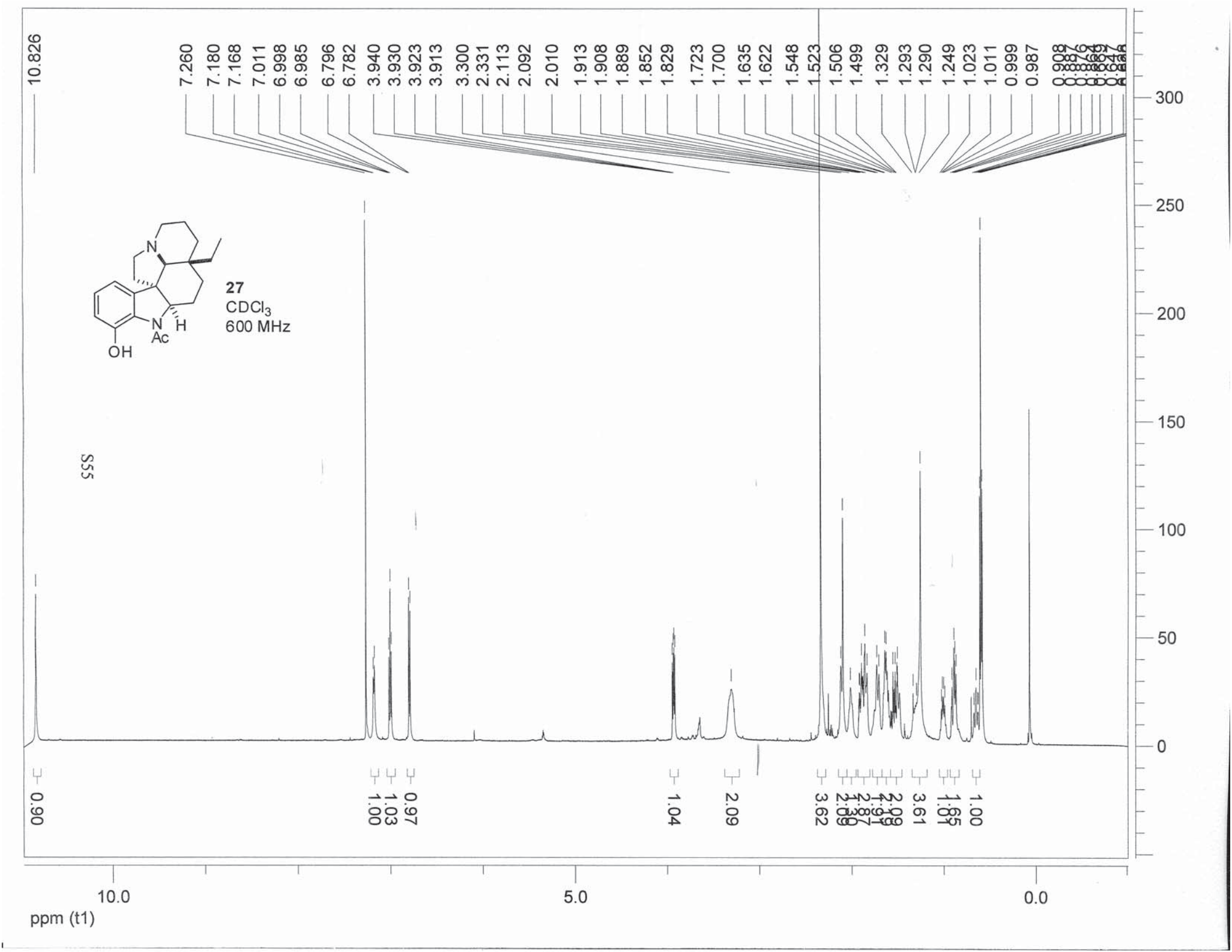

6.637
6.619
6.593
6.574
3.486
3.428
3.417
3.381
3.355
3.337
3.316
2.358
2.332
2.307
2.130
2.082
2.066
2.057
2.028
1.955
1.926
1.905
1.877
1.830
1.796
1.756
1.689
1.677
1.666
1.646
1.630
1.609
1.594
1.498
1.464
1.399
1.374
1.364
1.339
1.270
1.251
1.230
6000
5000
4000
3000
2000
1000
0
N
N
H
H
OH
26
CDCl3
400 MHz
S53
1.00
2.12
1.71
2.46
1.06
1.03
1.79
3.47
10.0
5.0
0.0
ppm (t1)

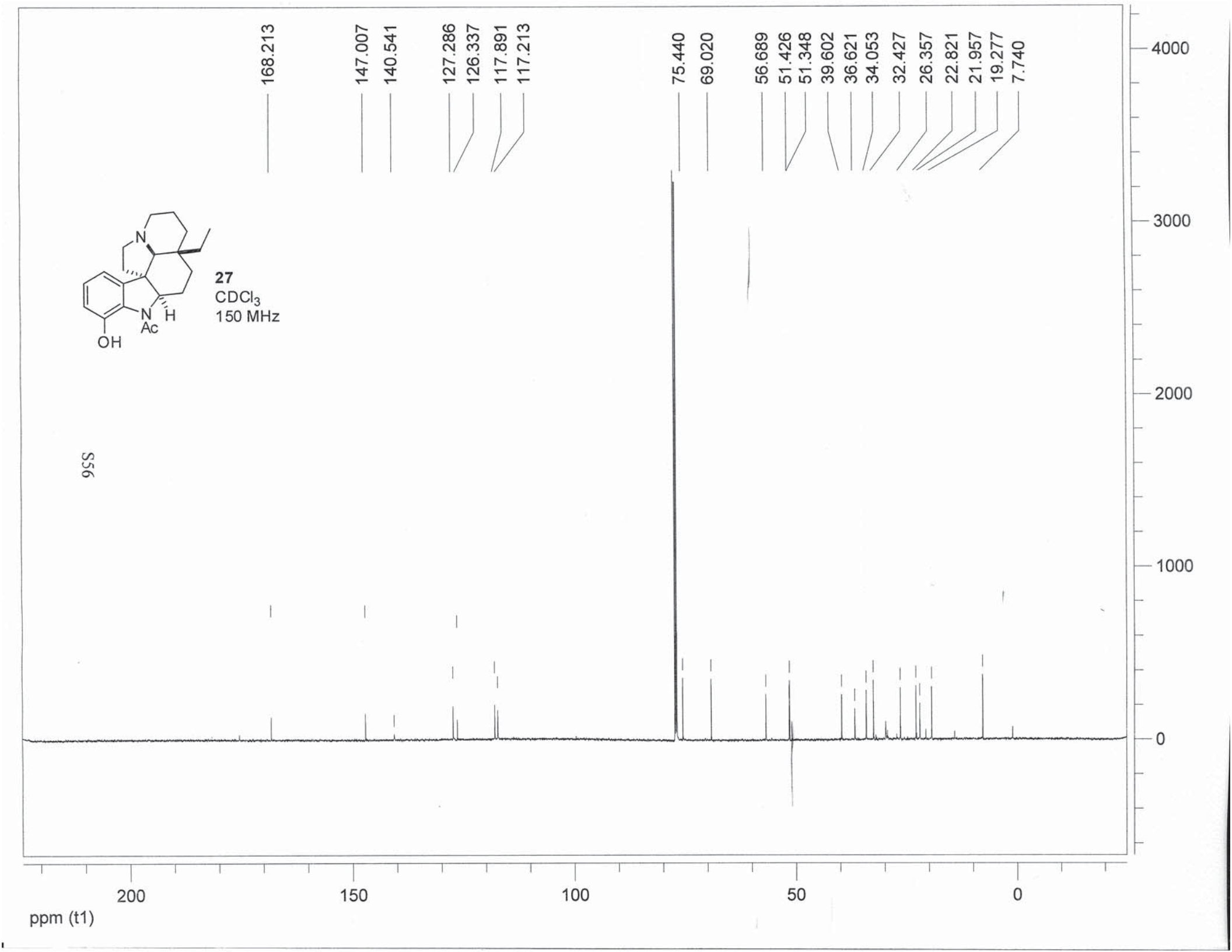


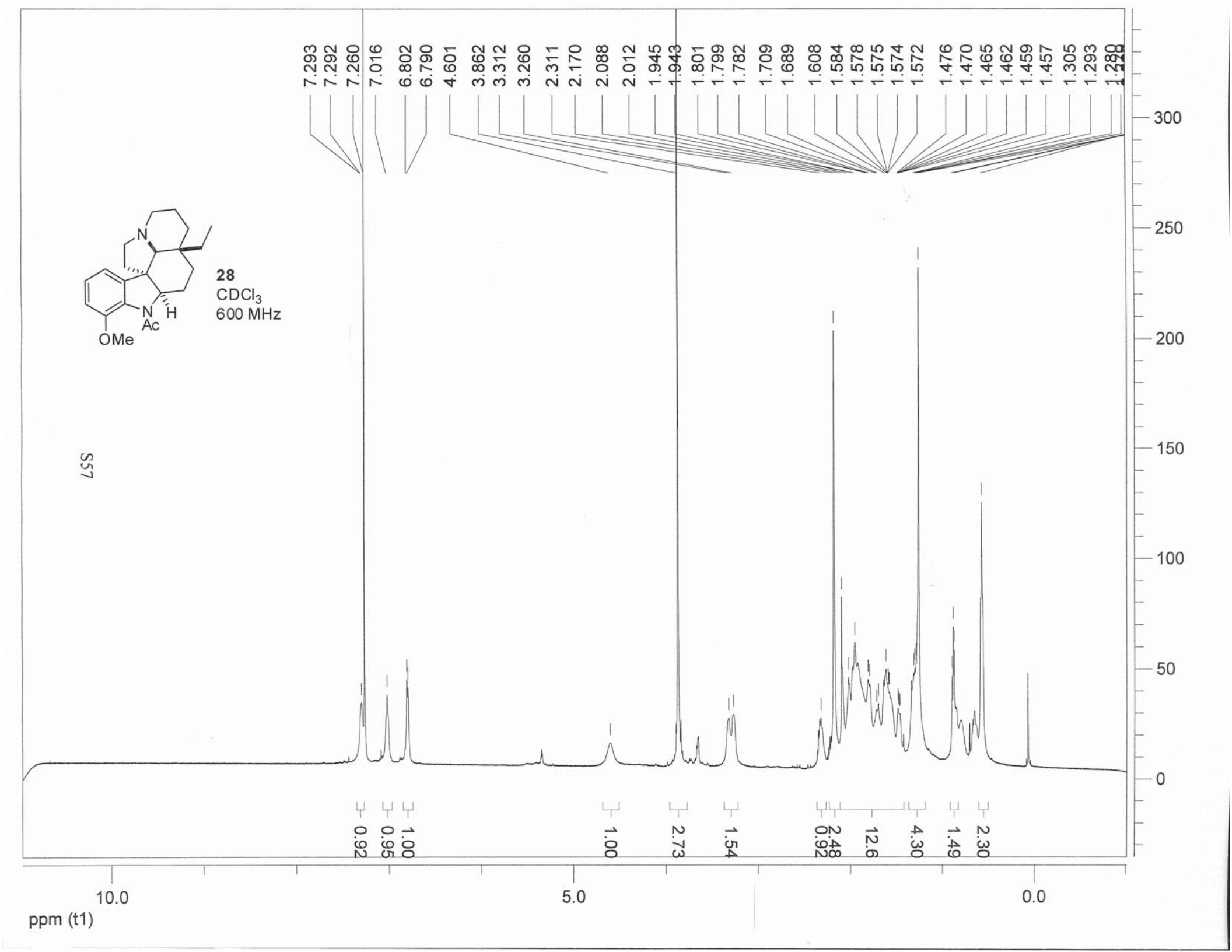
26
$CDCl_3$
100 MHz

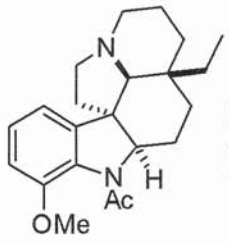
143.19
137.60
136.08
120.86
119.41
114.65
77.32
77.00
76.68
75.35
65.46
56.87
53.20
51.85
39.48
36.78
34.18
32.45
28.80
22.08
18.90
7.71

f1 (ppm)


10.826
7.260
7.180
7.168
7.011
6.998
6.985
6.796
6.782
3.940
3.930
3.923
3.913
3.300
2.331
2.113
2.092
2.010
1.913
1.908
1.889
1.852
1.829
1.723
1.700
1.635
1.622
1.548
1.523
1.506
1.499
1.329
1.293
1.290
1.249
1.023
1.011
0.999
0.987
27
CDCl3
600 MHz
N
N
H
Ac
OH
SSS
0.60
1.00
1.03
0.97
1.04
2.09
3.62
3.61
1.65
1.00
300
250
200
150
100
50
0
10.0
5.0
0.0
ppm (t1)


168.213
147.007
140.541
127.286
126.337
117.891
117.213
75.440
69.020
56.689
51.426
51.348
39.602
36.621
34.053
32.427
26.357
22.821
21.957
19.277
7.740
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)
N
N
H
Ac
OH
27
CDCl3
150 MHz
SS6


7.293
7.292
7.260
7.016
6.802
6.790
4.601
3.862
3.312
3.260
2.311
2.170
2.088
2.012
1.945
1.943
1.801
1.799
1.782
1.709
1.689
1.608
1.584
1.578
1.575
1.574
1.572
1.476
1.470
1.465
1.462
1.459
1.457
1.305
1.293
28
CDCl3
600 MHz
N
N
H
Ac
OMe
S57
0.92
0.95
1.00
1.00
2.73
1.54
0.92
2.48
12.6
4.30
1.49
2.30
300
250
200
150
100
50
0
10.0
5.0
0.0
ppm (t1)

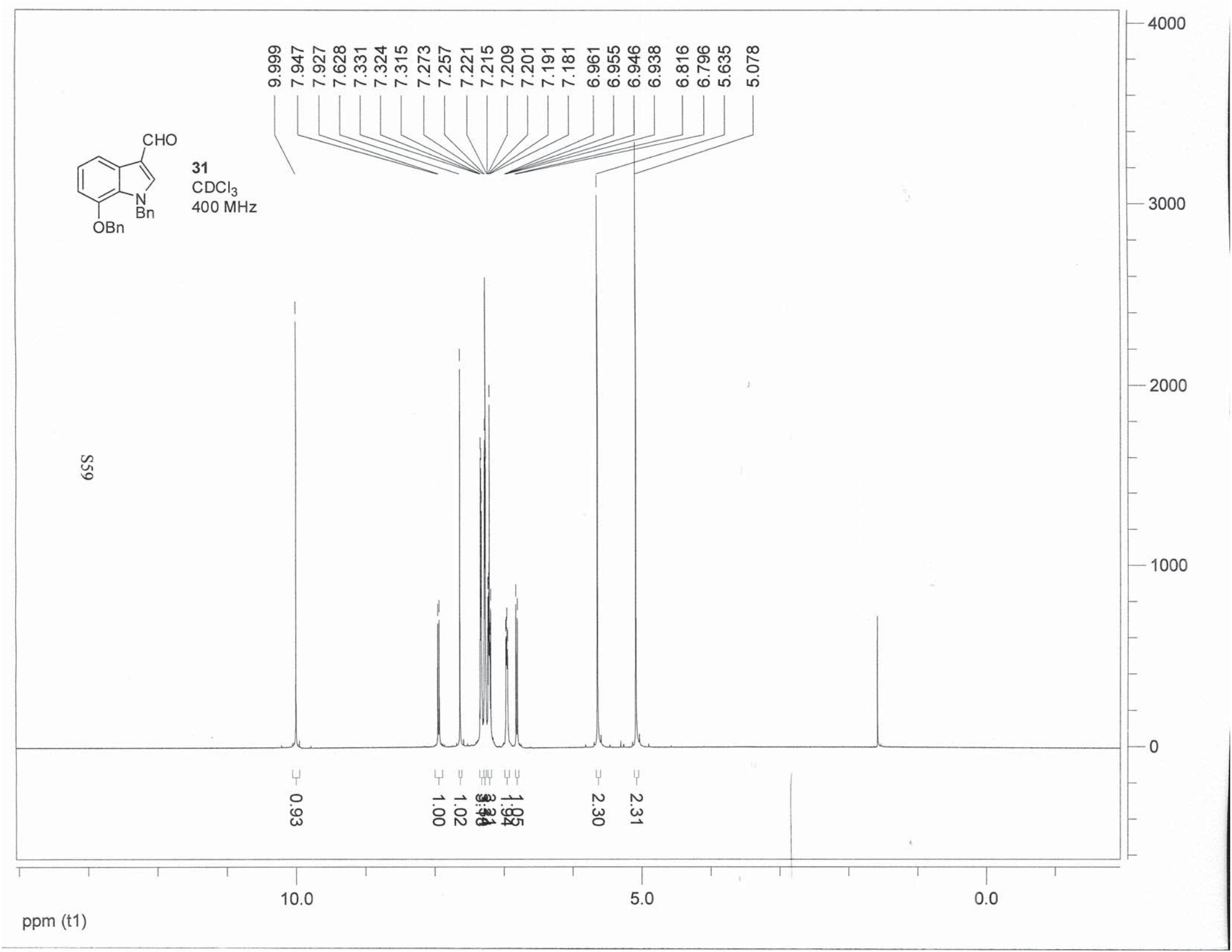


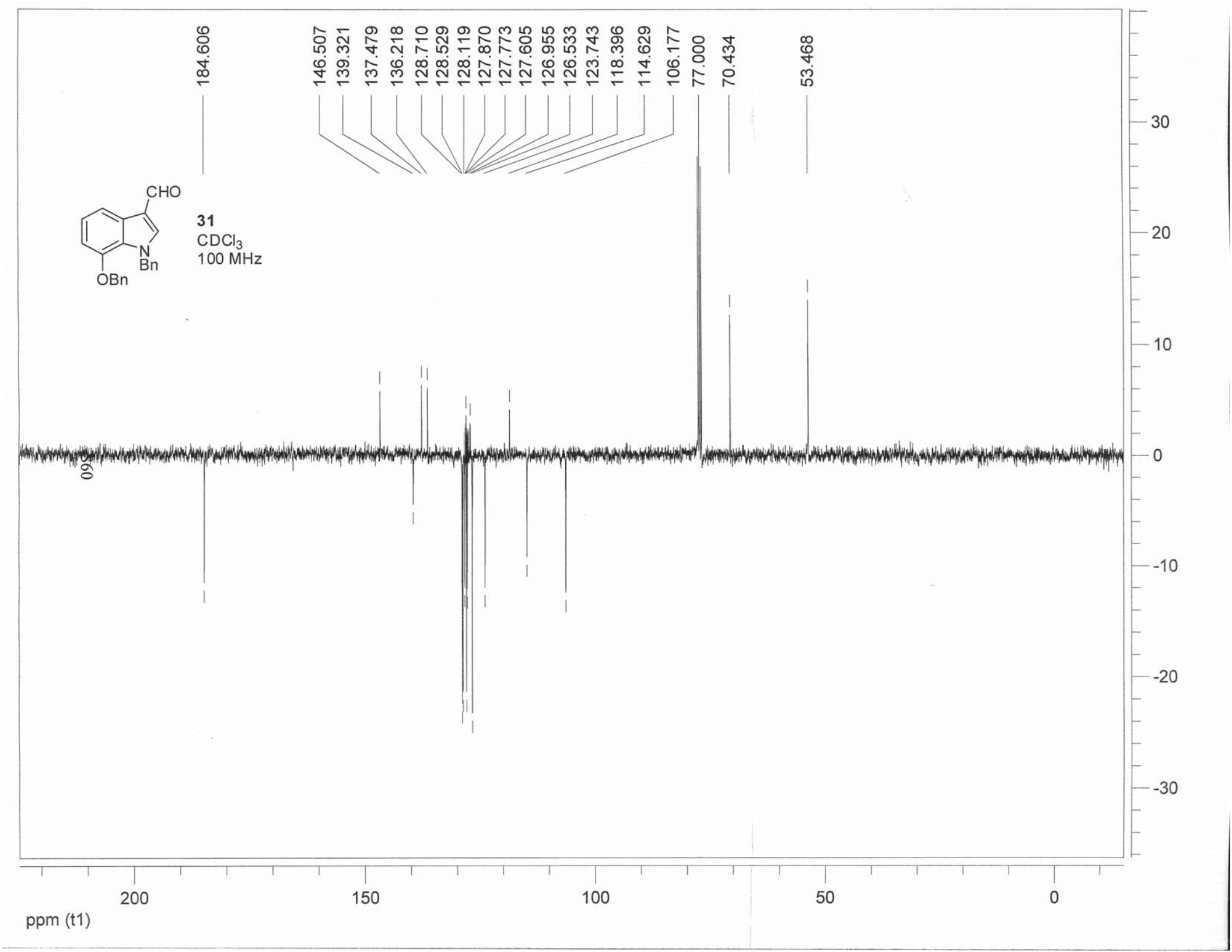
28
$CDCl_3$
150 MHz

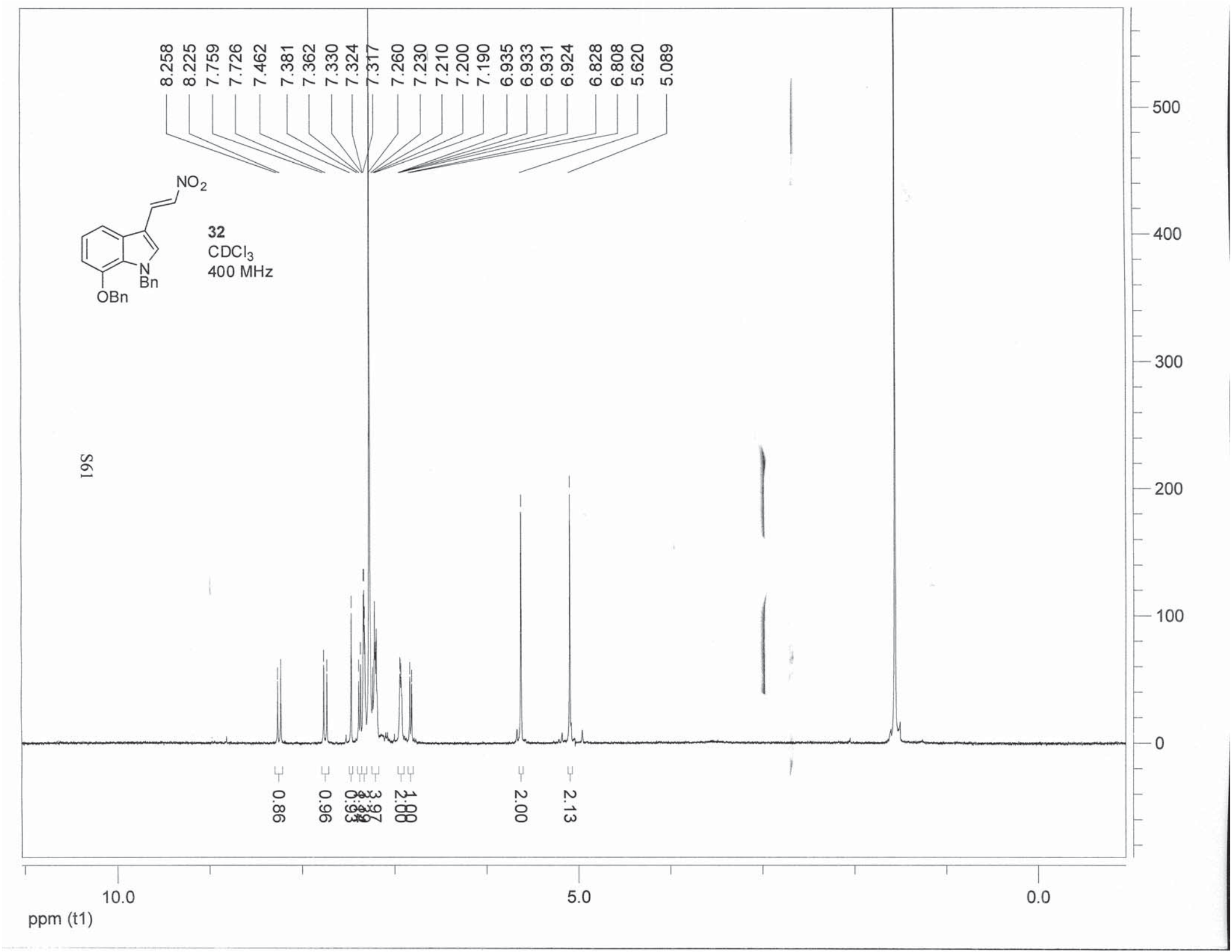
171.27
149.43
142.88
128.79
125.42
119.75
110.69
77.00
75.82
68.23
56.68
55.29
51.44
38.60
36.61
34.07
32.38
29.67
25.86
23.12
22.06
19.33
7.78

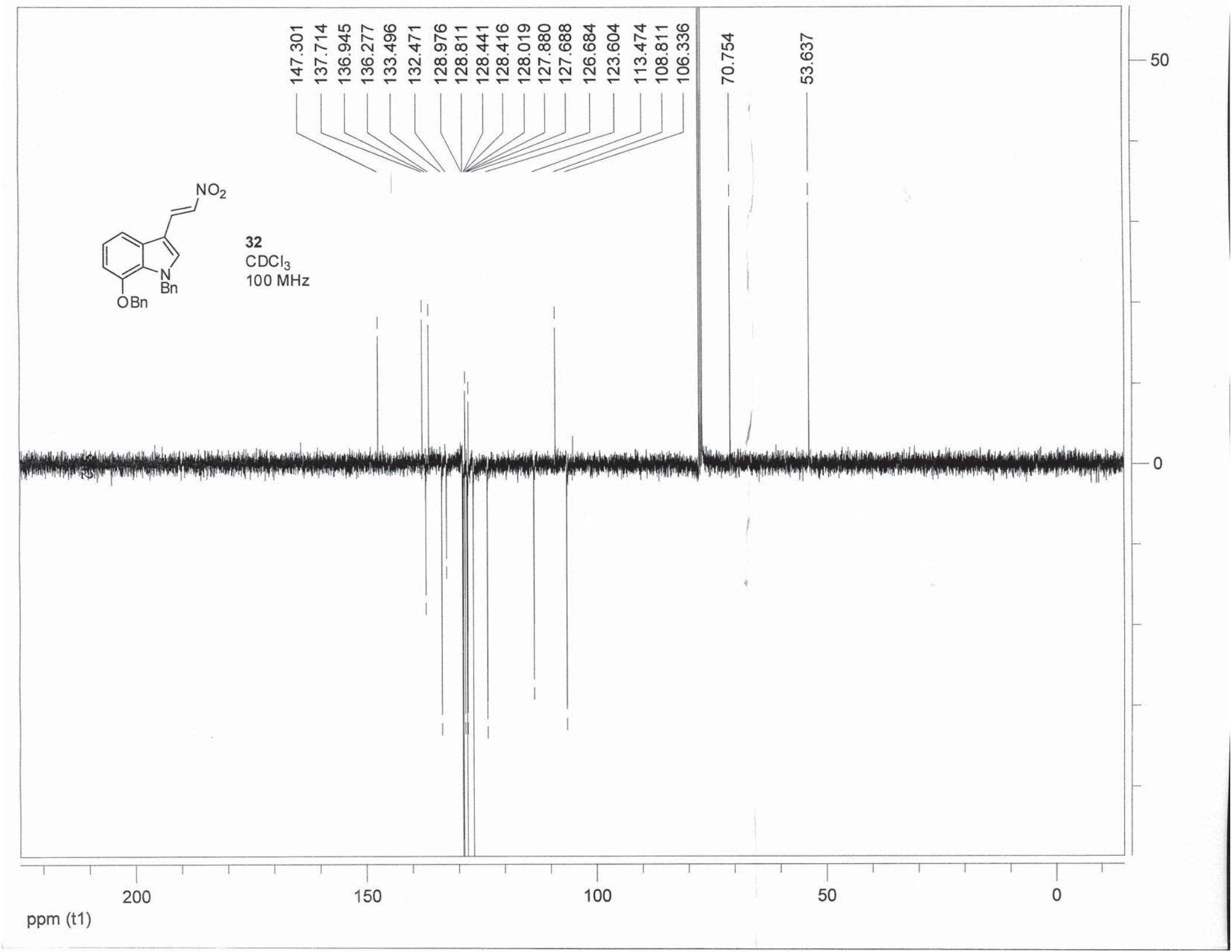
S58

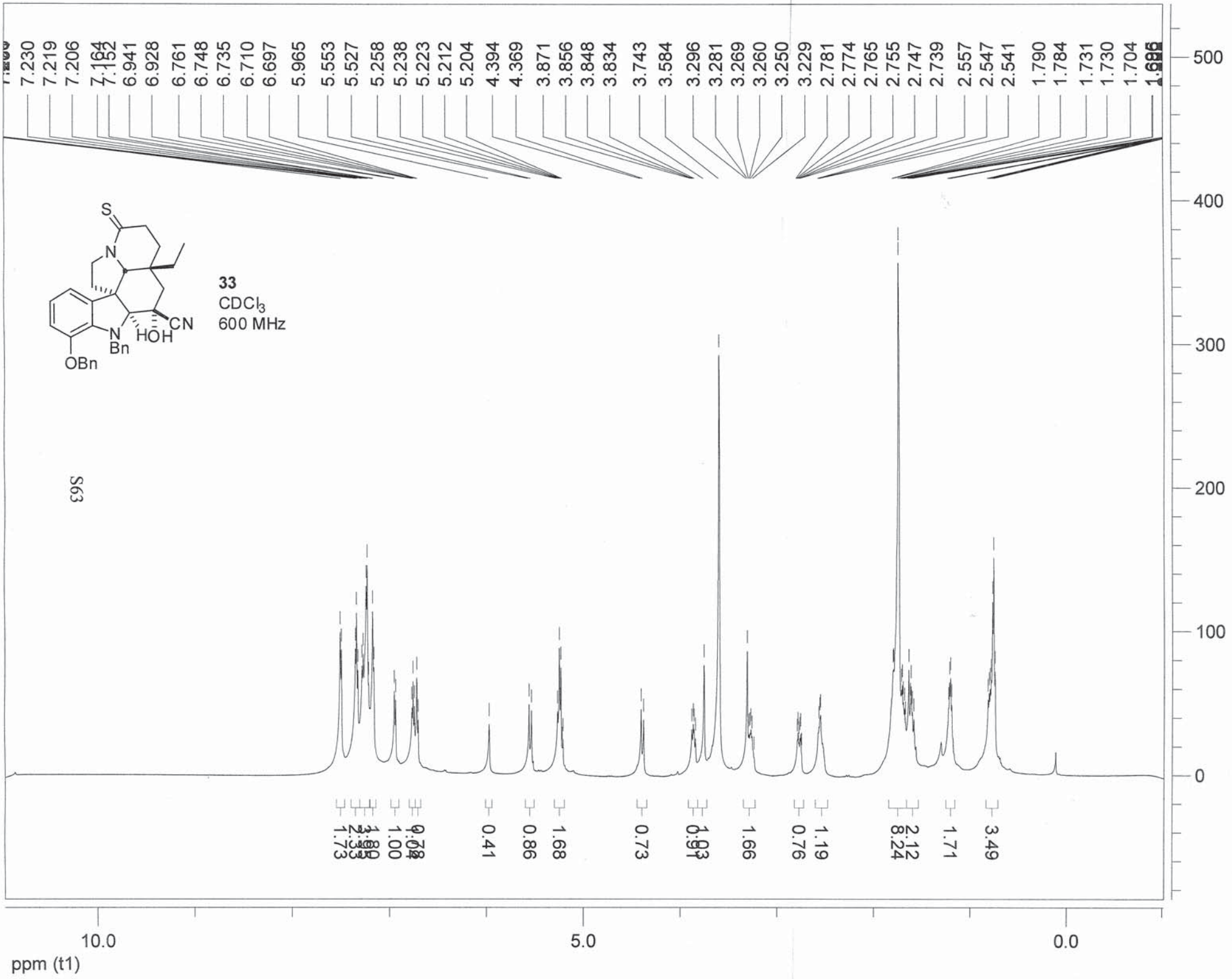
f1 (ppm)

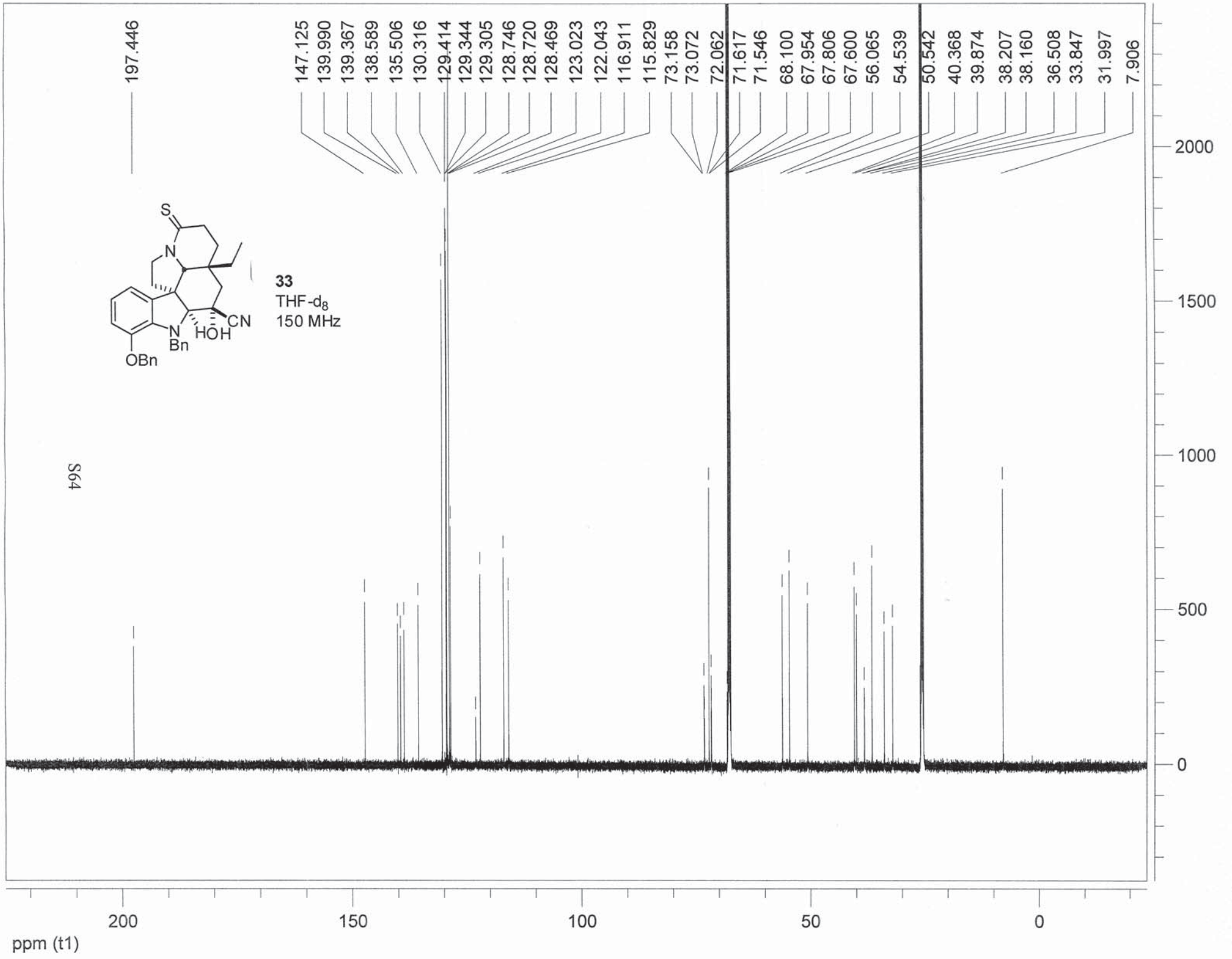

9.999
7.947
7.927
7.628
7.331
7.324
7.315
7.273
7.257
7.221
7.215
7.209
7.201
7.191
7.181
6.961
6.955
6.946
6.938
6.816
6.796
5.635
5.078
CHO
N
Bn
OBn
31
CDCl3
400 MHz
S59
4000
3000
2000
1000
0
0.93
1.00
1.02
2.30
2.31
10.0
5.0
0.0
ppm (t1)

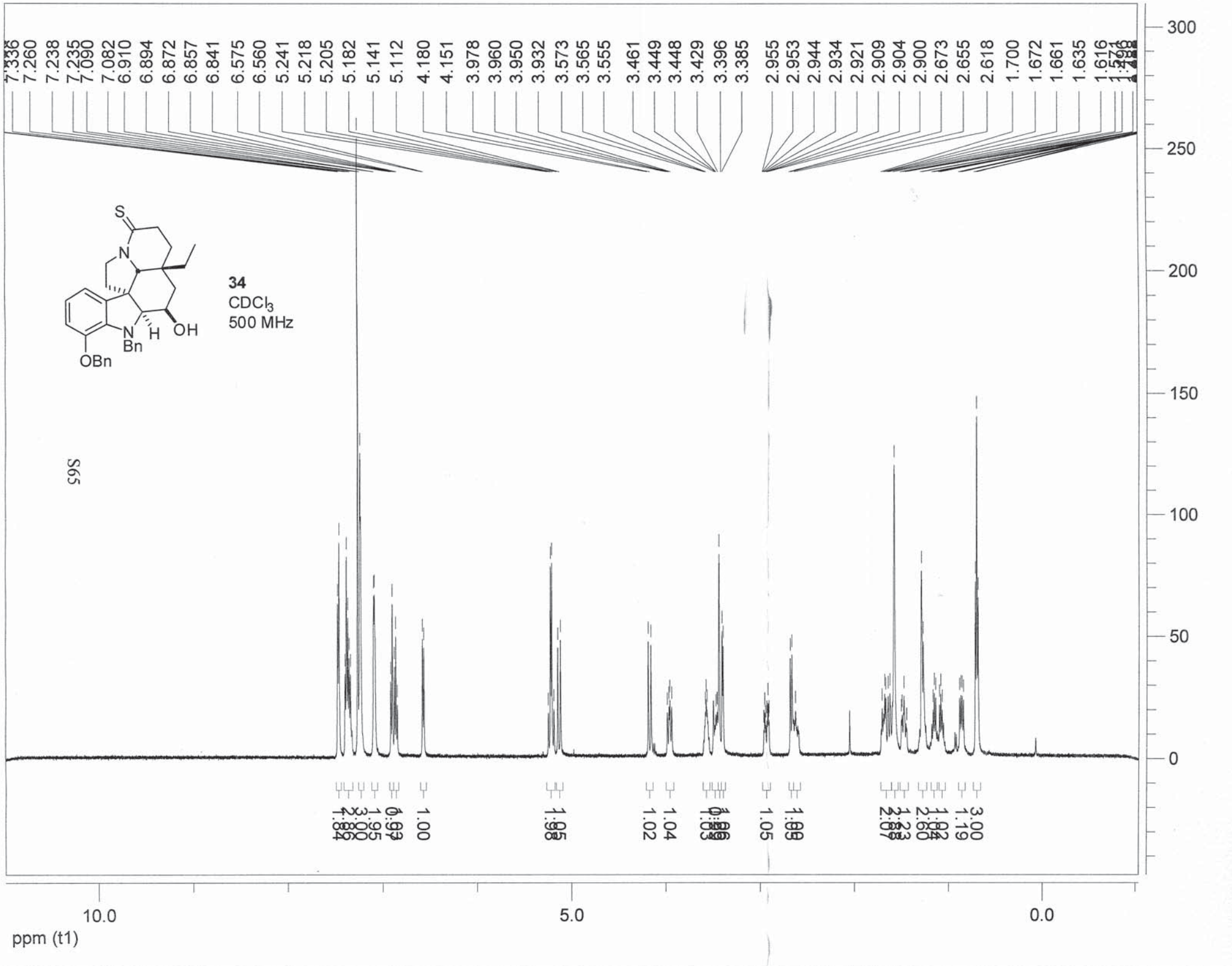

184.606
146.507
139.321
137.479
136.218
128.710
128.529
128.119
127.870
127.773
127.605
126.955
126.533
123.743
118.396
114.629
106.177
77.000
70.434
53.468
CHO
N
Bn
OBn
31
CDCl3
100 MHz
60
30
20
10
0
-10
-20
-30
200
150
100
50
0
ppm (t1)

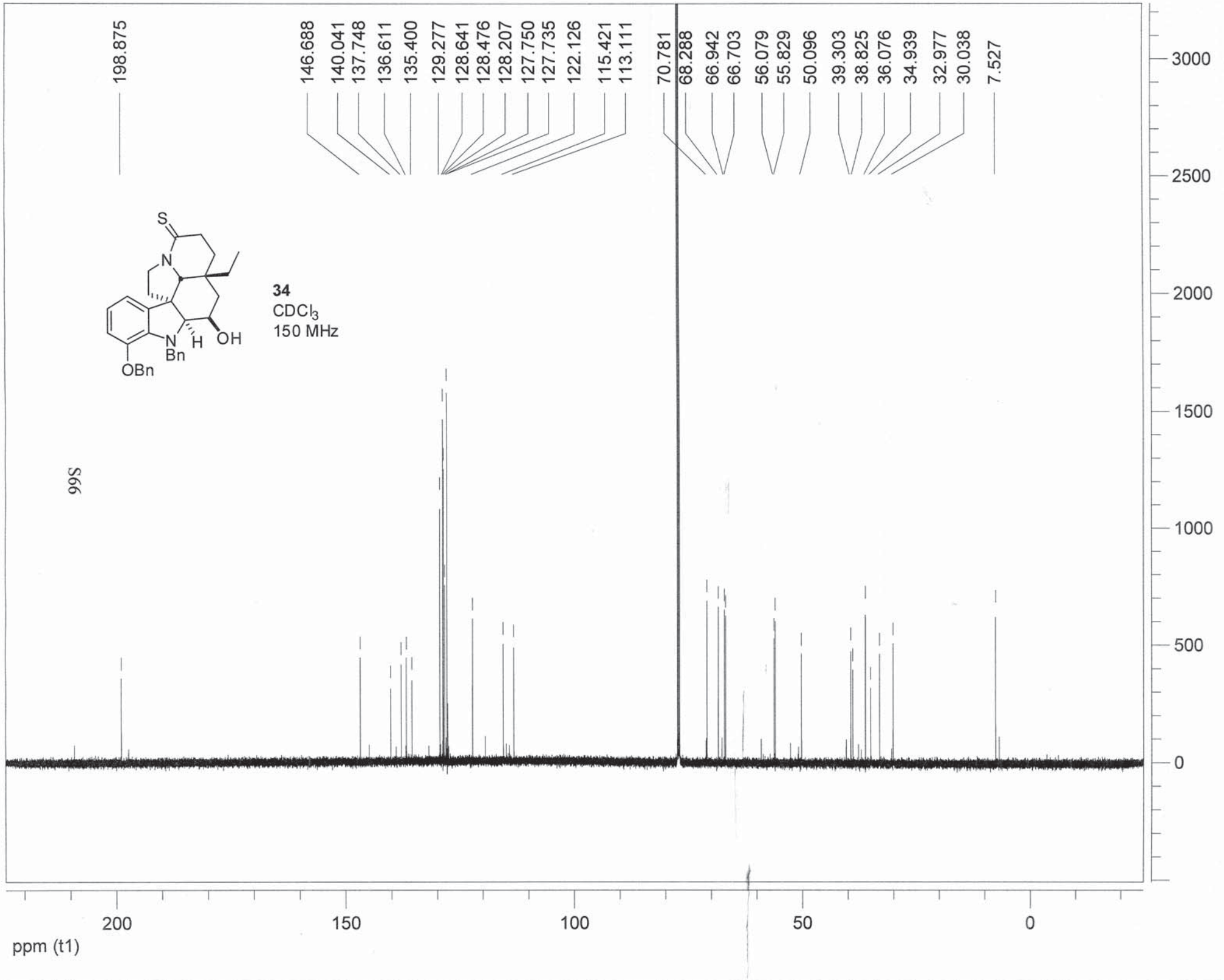

8.258
8.225
7.759
7.726
7.462
7.381
7.362
7.330
7.324
7.317
7.260
7.230
7.210
7.200
7.190
6.935
6.933
6.931
6.924
6.828
6.808
5.620
5.089
NO2
N
Bn
OBn
32
CDCl3
400 MHz
S61
0.86
0.96
2.00
2.13
10.0
5.0
0.0
ppm (t1)

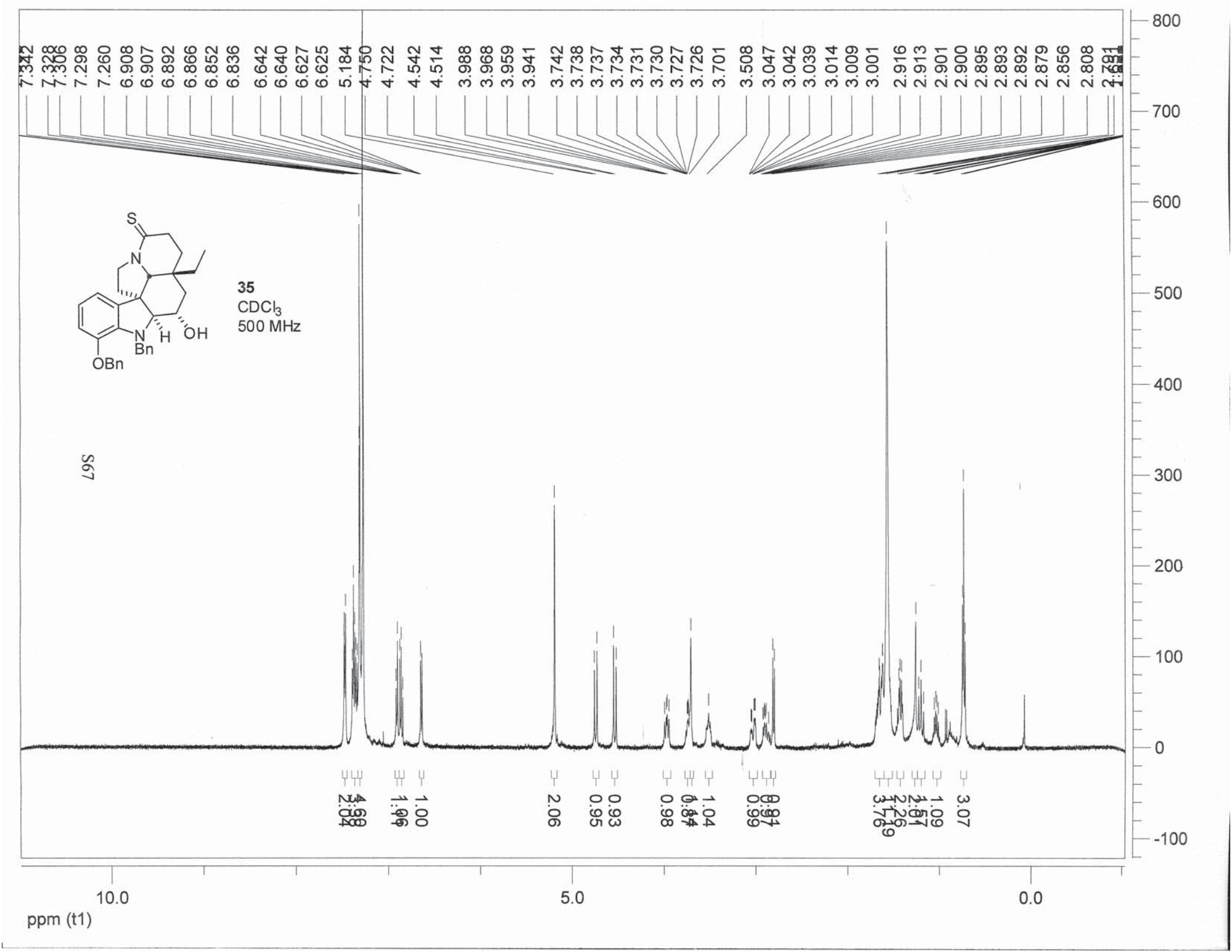

147.301
137.714
136.945
136.277
133.496
132.471
128.976
128.811
128.441
128.416
128.019
127.880
127.688
126.684
123.604
113.474
108.811
106.336
70.754
53.637
NO2
N
Bn
OBn
32
CDCl3
100 MHz
50
0
200
150
100
50
0
ppm (t1)

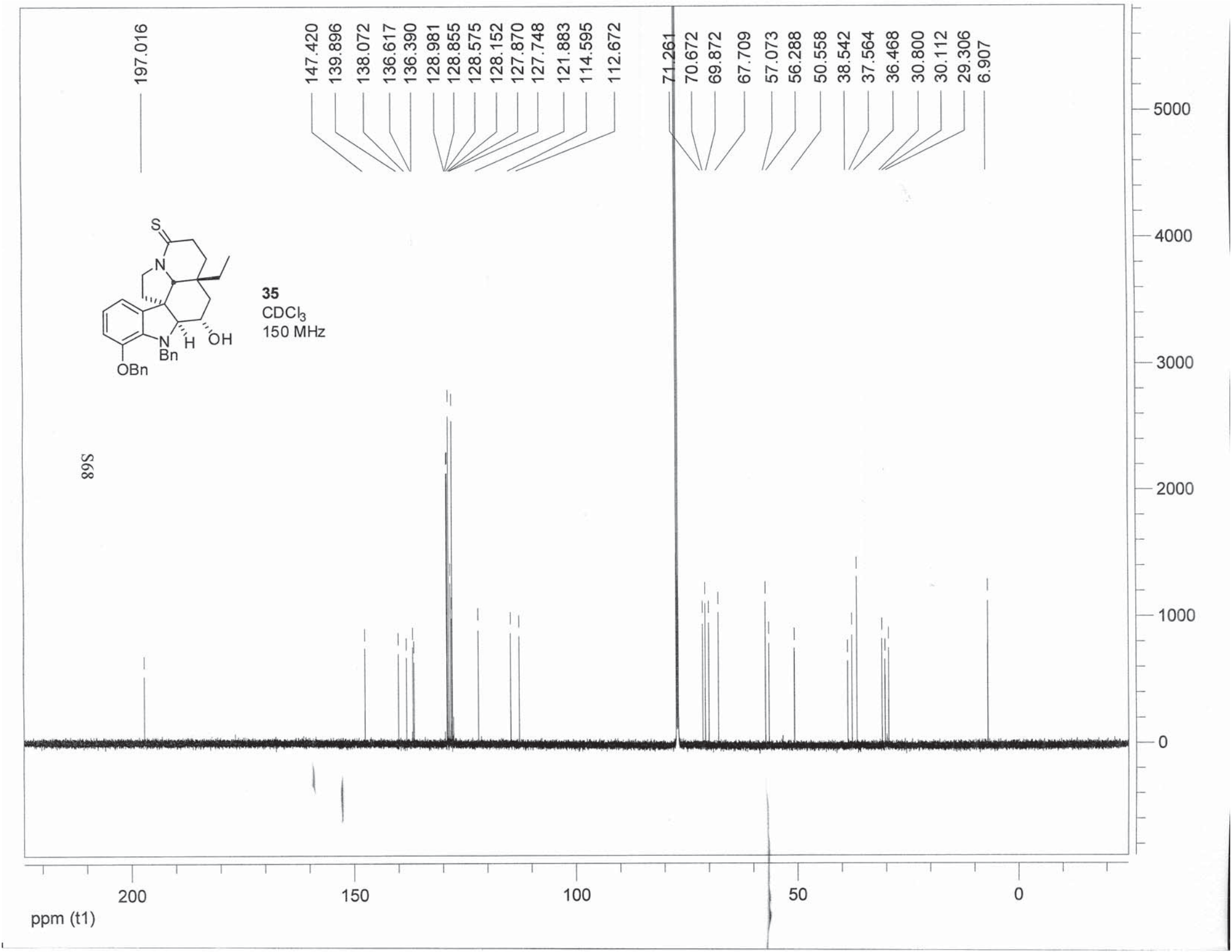

7.230
7.219
7.206
7.164
7.152
6.941
6.928
6.761
6.748
6.735
6.710
6.697
5.965
5.553
5.527
5.258
5.238
5.223
5.212
5.204
4.394
4.369
3.871
3.856
3.848
3.834
3.743
3.584
3.296
3.281
3.269
3.260
3.250
3.229
2.781
2.774
2.765
2.755
2.747
2.739
2.557
2.547
2.541
1.790
1.784
1.731
1.730
1.704
S
N
N
Bn
HO
H
CN
OBn
33
CDCl3
600 MHz
S63
1.73
1.00
0.41
0.89
1.88
0.73
1.99
0.79
1.19
8.24
2.12
1.71
3.49
500
400
300
200
100
0
10.0
5.0
0.0
ppm (t1)

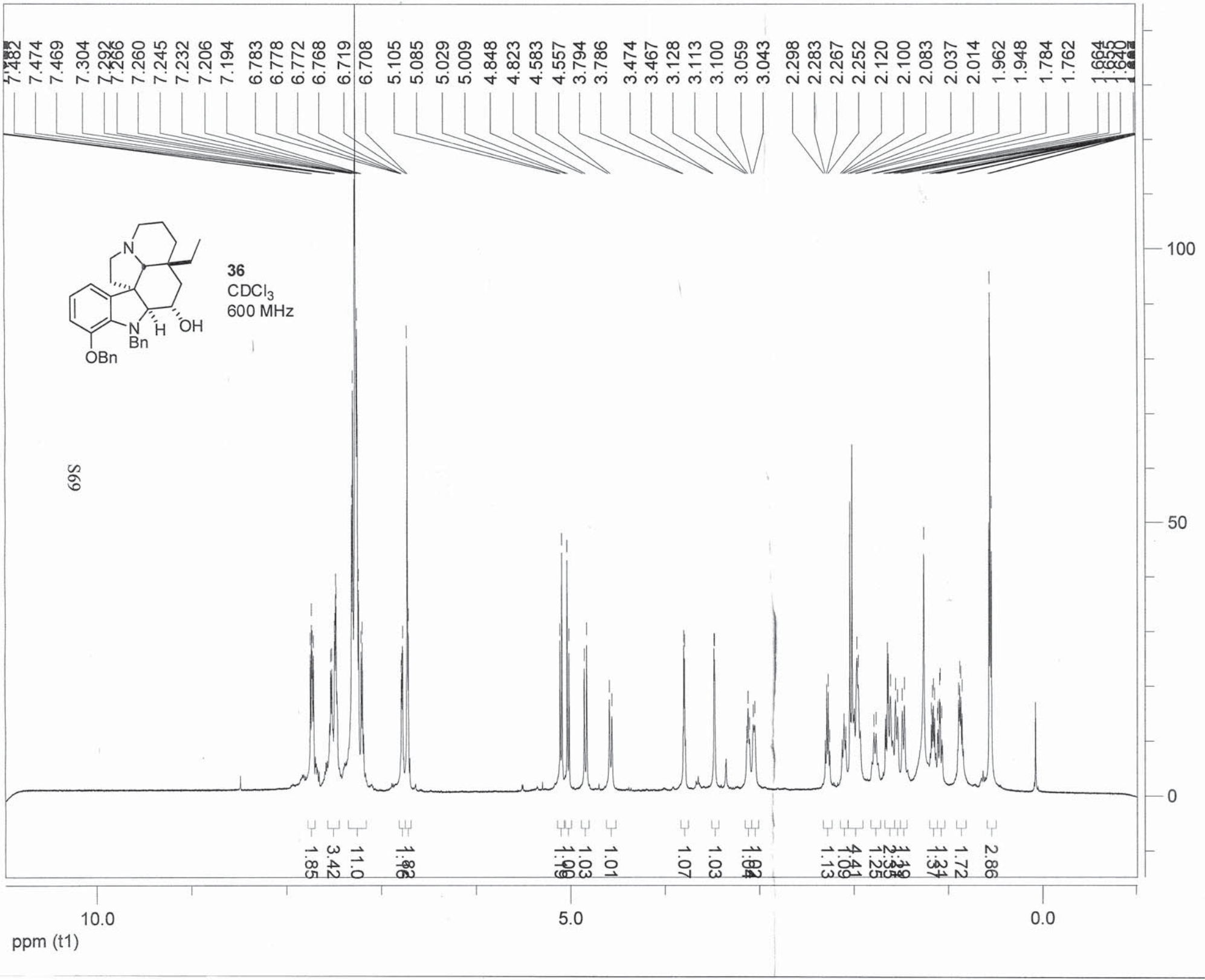

197.446
147.125
139.990
139.367
138.589
135.506
130.316
129.414
129.344
129.305
128.746
128.720
128.469
123.023
122.043
116.911
115.829
73.158
73.072
72.062
71.617
71.546
68.100
67.954
67.806
67.600
56.065
54.539
50.542
40.368
39.874
38.207
38.160
36.508
33.847
31.997
7.906
33
THF-d8
150 MHz
S64
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

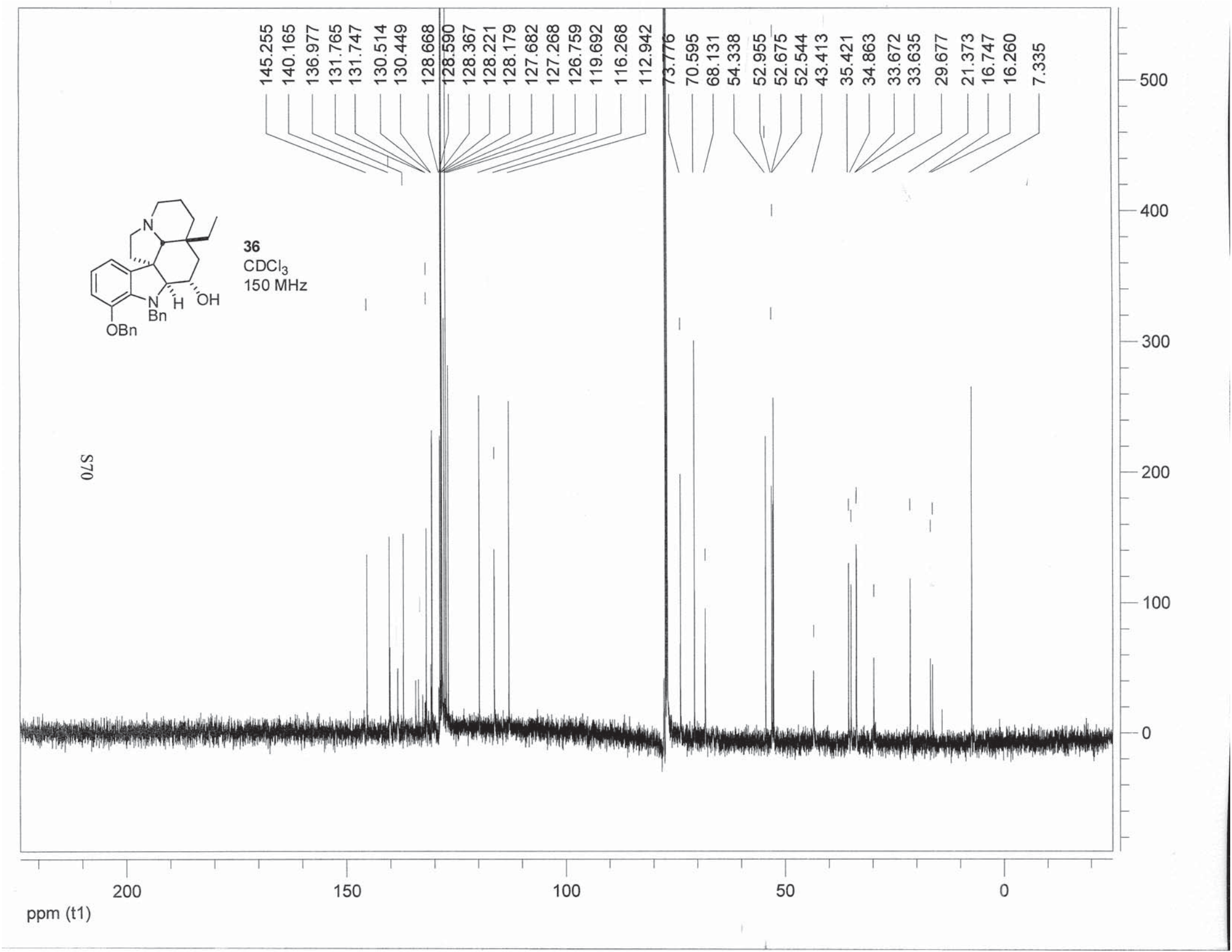

34
CDCl3
500 MHz
OBn
N
Bn
H
OH
S
S65
7.338
7.260
7.238
7.235
7.090
7.082
6.910
6.894
6.872
6.857
6.841
6.575
6.560
5.241
5.218
5.205
5.182
5.141
5.112
4.180
4.151
3.978
3.960
3.950
3.932
3.573
3.565
3.555
3.461
3.449
3.448
3.429
3.396
3.385
2.955
2.953
2.944
2.934
2.921
2.909
2.904
2.900
2.673
2.655
2.618
1.700
1.672
1.661
1.635
1.616
1.84
3.00
1.95
1.00
1.98
1.02
1.04
1.03
1.05
1.09
1.19
300
250
200
150
100
50
0
10.0
5.0
0.0
ppm (t1)

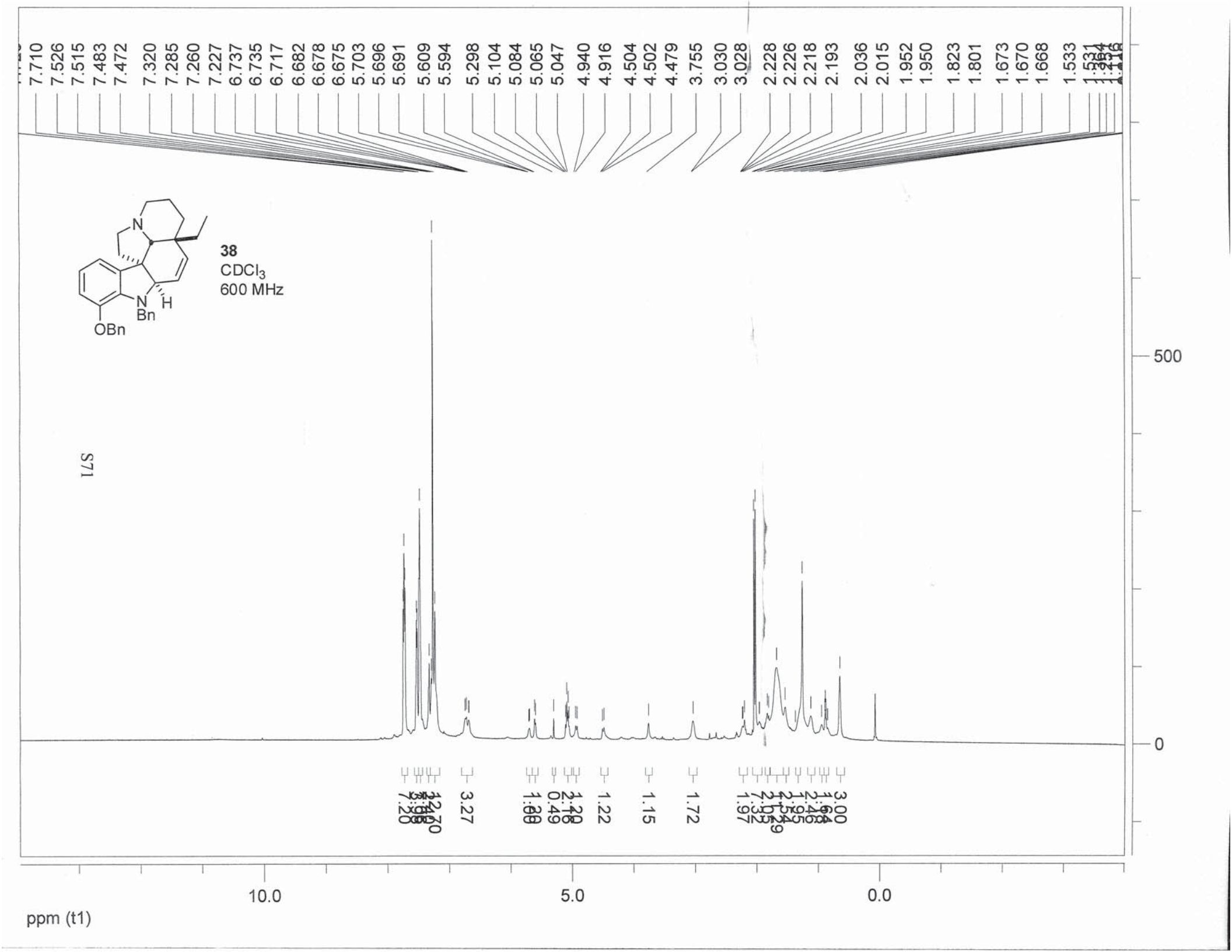

198.875
146.688
140.041
137.748
136.611
135.400
129.277
128.641
128.476
128.207
127.750
127.735
122.126
115.421
113.111
70.781
68.288
66.942
66.703
56.079
55.829
50.096
39.303
38.825
36.076
34.939
32.977
30.038
7.527
34
CDCl3
150 MHz
99S
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

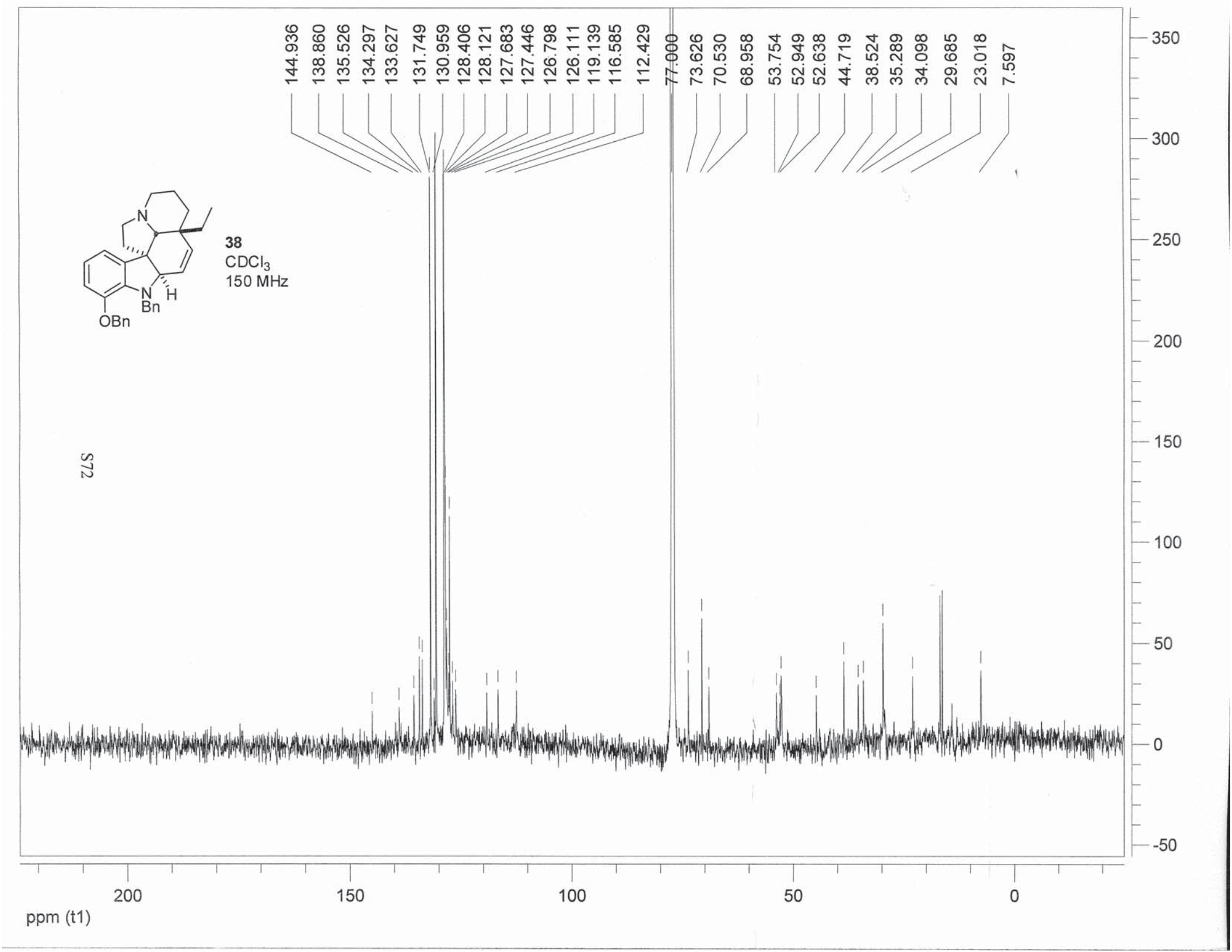

35
CDCl3
500 MHz
OBn
N
Bn
H
OH
S
S67
ppm (t1)
10.0
5.0
0.0

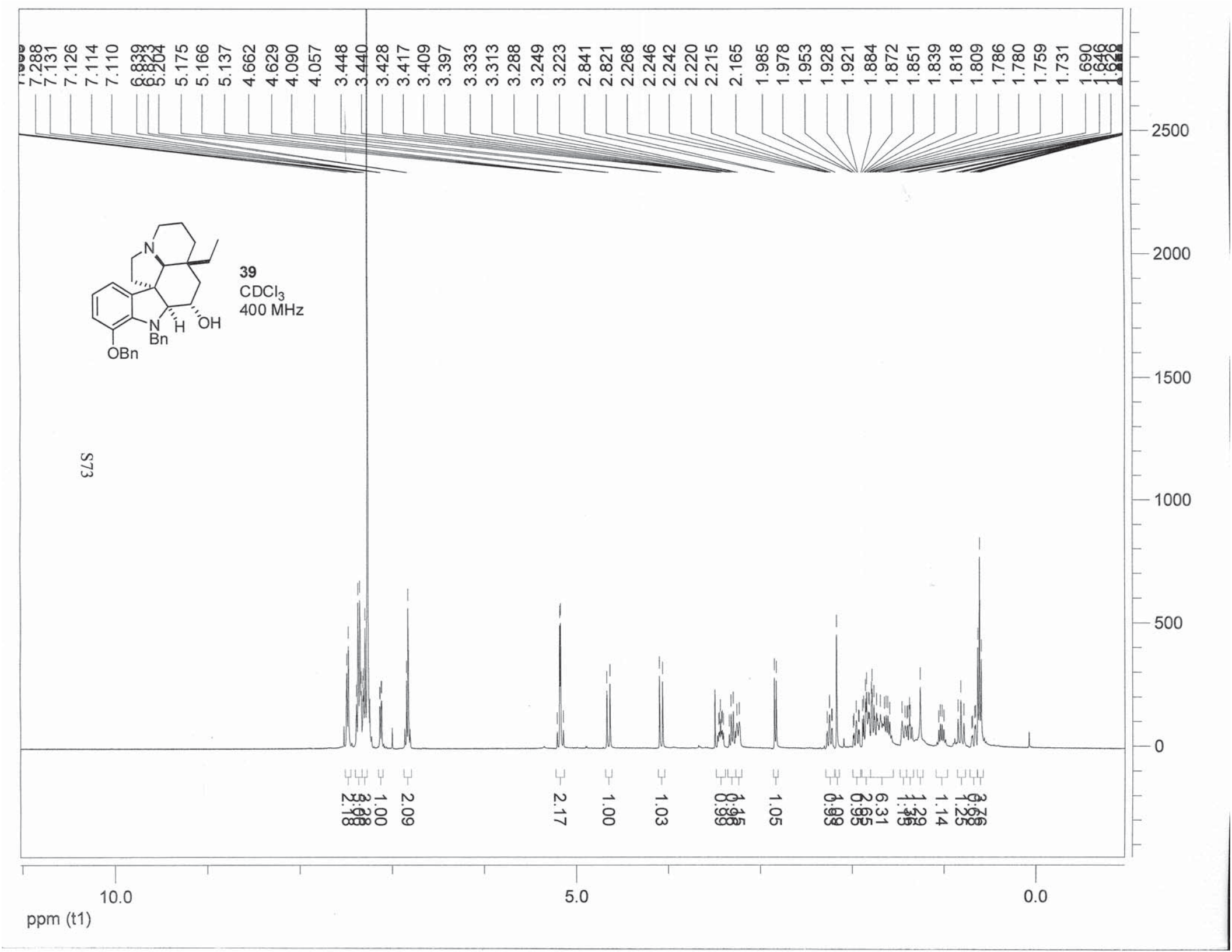

197.016
147.420
139.896
138.072
136.617
136.390
128.981
128.855
128.575
128.152
127.870
127.748
121.883
114.595
112.672
71.261
70.672
69.872
67.709
57.073
56.288
50.558
38.542
37.564
36.468
30.800
30.112
29.306
6.907
S
N
N
Bn
H
OH
OBn
35
CDCl3
150 MHz
89S
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)

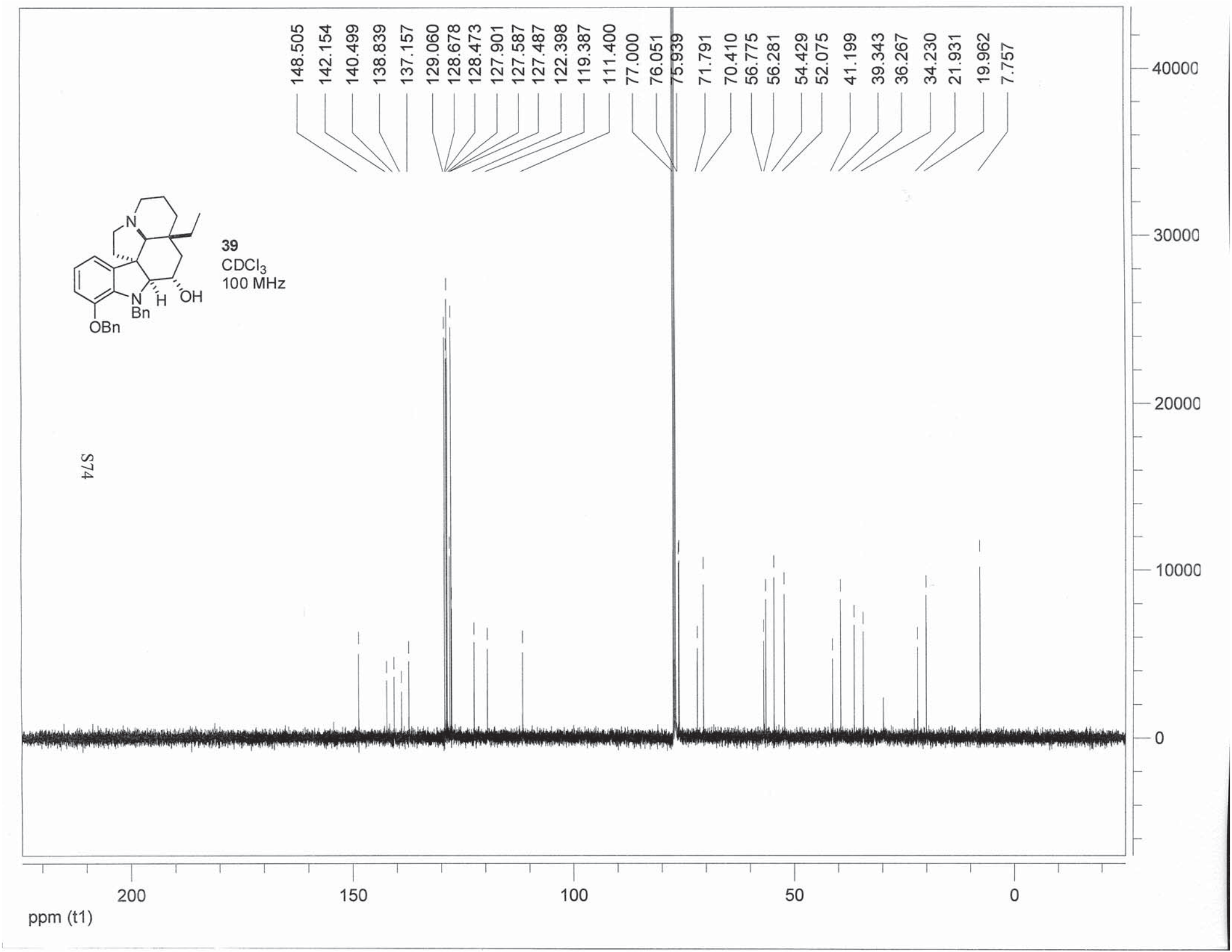

7.482
7.474
7.469
7.304
7.292
7.266
7.260
7.245
7.232
7.206
7.194
6.783
6.778
6.772
6.768
6.719
6.708
5.105
5.085
5.029
5.009
4.848
4.823
4.583
4.557
3.794
3.786
3.474
3.467
3.128
3.113
3.100
3.059
3.043
2.298
2.283
2.267
2.252
2.120
2.100
2.083
2.037
2.014
1.962
1.948
1.784
1.762
1.664
1.655
1.640
36
CDCl3
600 MHz
N
H
OH
Bn
OBn
S69
100
50
0
1.85
3.42
11.0
1.03
1.01
1.07
1.03
1.13
1.09
1.25
1.37
1.72
2.86
10.0
5.0
0.0
ppm (t1)

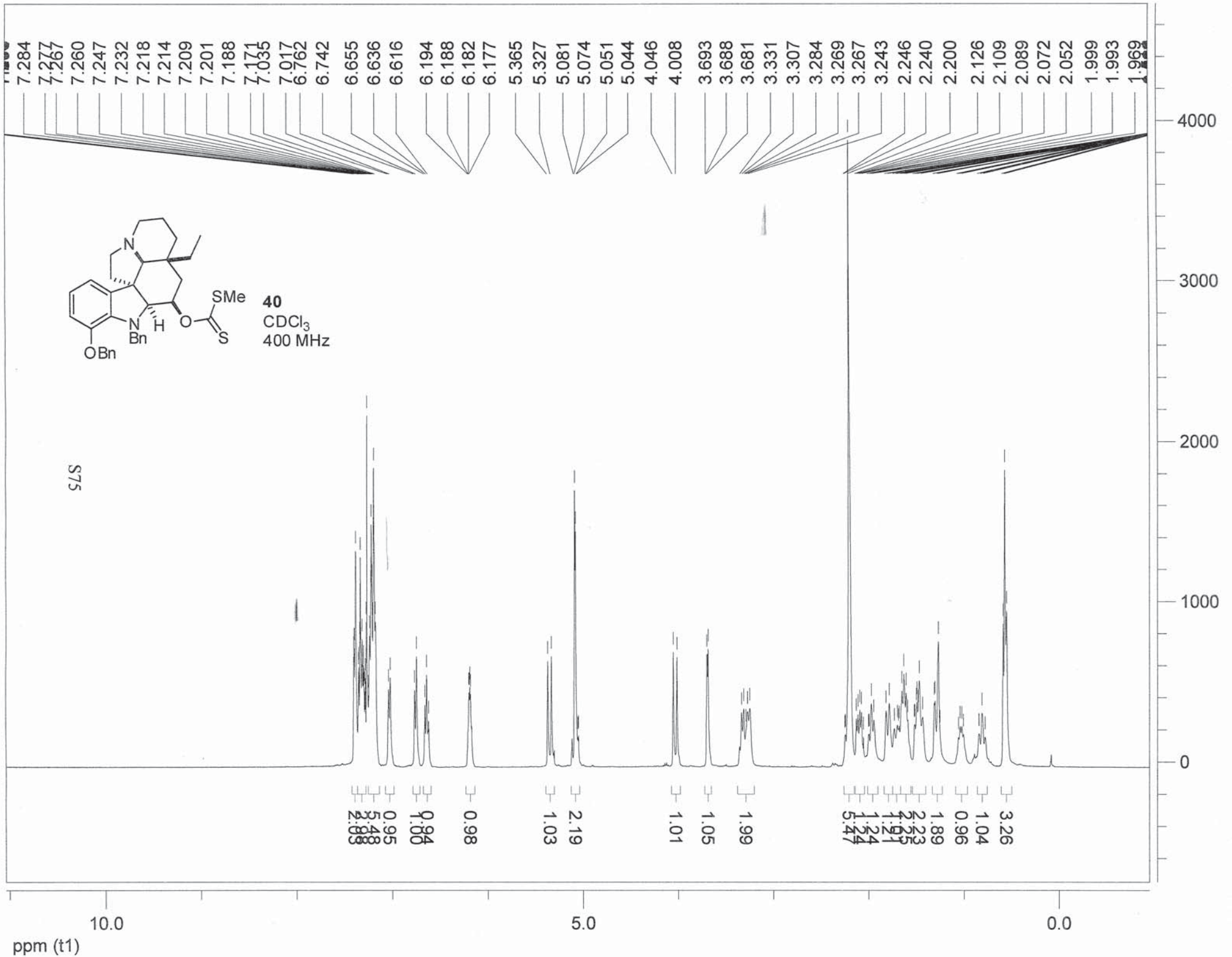

145.255
140.165
136.977
131.765
131.747
130.514
130.449
128.668
128.590
128.367
128.221
128.179
127.682
127.268
126.759
119.692
116.268
112.942
73.776
70.595
68.131
54.338
52.955
52.675
52.544
43.413
35.421
34.863
33.672
33.635
29.677
21.373
16.747
16.260
7.335
36
CDCl3
150 MHz
N
H
OH
Bn
OBn
S70
500
400
300
200
100
0
200
150
100
50
0
ppm (t1)

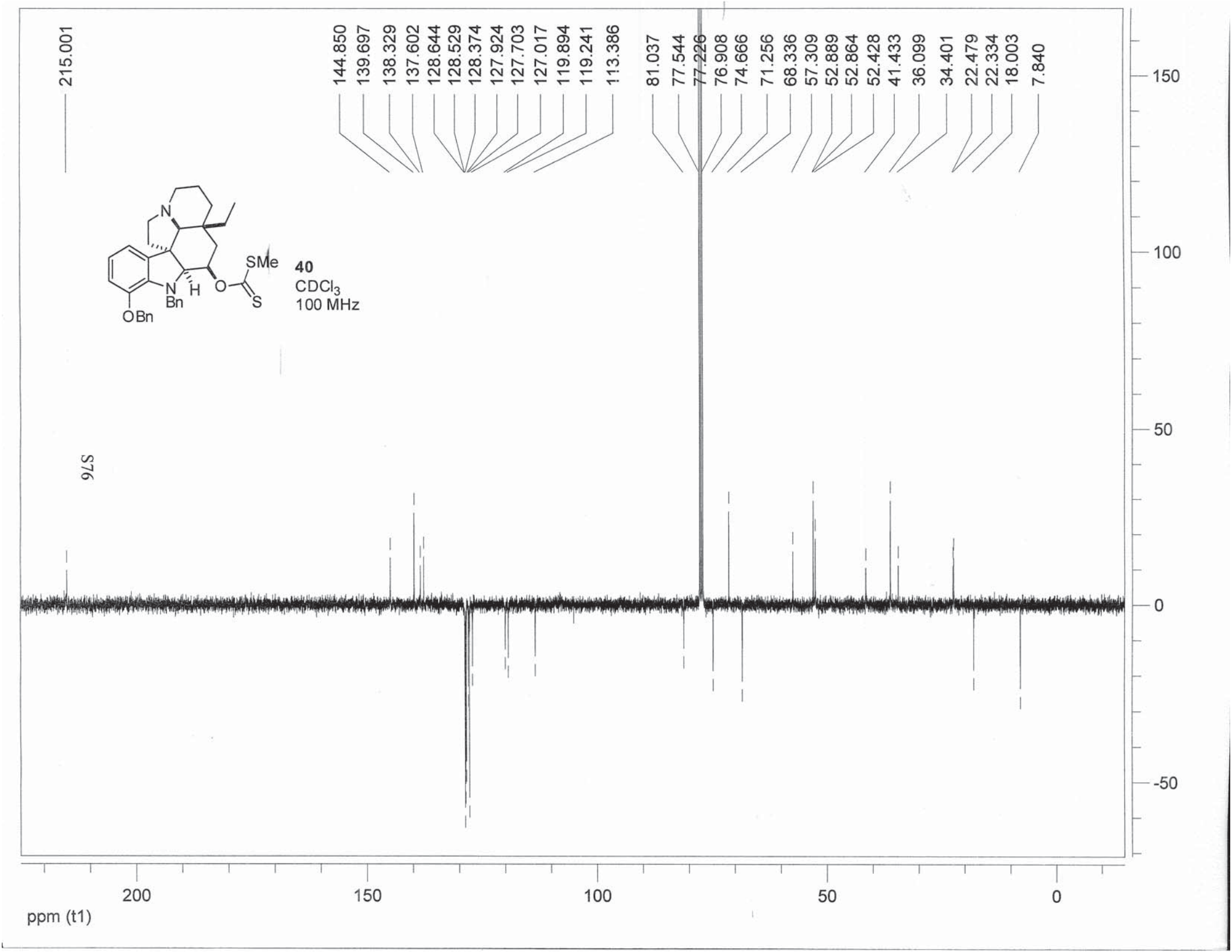

7.710
7.526
7.515
7.483
7.472
7.320
7.285
7.260
7.227
6.737
6.735
6.717
6.682
6.678
6.675
5.703
5.696
5.691
5.609
5.594
5.298
5.104
5.084
5.065
5.047
4.940
4.916
4.504
4.502
4.479
3.755
3.030
3.028
2.228
2.226
2.218
2.193
2.036
2.015
1.952
1.950
1.823
1.801
1.673
1.670
1.668
1.533
N
N
H
Bn
OBn
38
CDCl3
600 MHz
S71
500
0
3.27
1.22
1.15
1.72
3.00
10.0
5.0
0.0
ppm (t1)


144.936
138.860
135.526
134.297
133.627
131.749
130.959
128.406
128.121
127.683
127.446
126.798
126.111
119.139
116.585
112.429
77.000
73.626
70.530
68.958
53.754
52.949
52.638
44.719
38.524
35.289
34.098
29.685
23.018
7.597
38
CDCl3
150 MHz
N
N
Bn
H
OBn
S72
350
300
250
200
150
100
50
0
-50
200
150
100
50
0
ppm (t1)


39
CDCl3
400 MHz
OBn
N
Bn
H
OH
S73
7.288
7.131
7.126
7.114
7.110
6.839
6.804
5.175
5.166
5.137
4.662
4.629
4.090
4.057
3.448
3.440
3.428
3.417
3.409
3.397
3.333
3.313
3.288
3.249
3.223
2.841
2.821
2.268
2.246
2.242
2.220
2.215
2.165
1.985
1.978
1.953
1.928
1.921
1.884
1.872
1.851
1.839
1.818
1.809
1.786
1.780
1.759
1.731
1.690
2.18
1.00
2.09
2.17
1.00
1.03
1.05
6.31
1.14
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)


148.505
142.154
140.499
138.839
137.157
129.060
128.678
128.473
127.901
127.587
127.487
122.398
119.387
111.400
77.000
76.051
75.939
71.791
70.410
56.775
56.281
54.429
52.075
41.199
39.343
36.267
34.230
21.931
19.962
7.757
39
CDCl3
100 MHz
N
N
H
OH
Bn
OBn
S74
40000
30000
20000
10000
0
200
150
100
50
0
ppm (t1)


7.284
7.277
7.267
7.260
7.247
7.232
7.218
7.214
7.209
7.201
7.188
7.171
7.035
7.017
6.762
6.742
6.655
6.636
6.616
6.194
6.188
6.182
6.177
5.365
5.327
5.081
5.074
5.051
5.044
4.046
4.008
3.693
3.688
3.681
3.331
3.307
3.284
3.269
3.267
3.243
2.246
2.240
2.200
2.126
2.109
2.089
2.072
2.052
1.999
1.993
1.969
SMe
O
S
N
H
Bn
OBn
40
CDCl3
400 MHz
S75
4000
3000
2000
1000
0
2.83
0.95
0.84
1.00
0.98
1.03
2.19
1.01
1.05
1.99
1.89
0.96
1.04
3.26
10.0
5.0
0.0
ppm (t1)


215.001
144.850
139.697
138.329
137.602
128.644
128.529
128.374
127.924
127.703
127.017
119.894
119.241
113.386
81.037
77.544
77.226
76.908
74.666
71.256
68.336
57.309
52.889
52.864
52.428
41.433
36.099
34.401
22.479
22.334
18.003
7.840
SMe
O
S
N
H
Bn
OBn
40
CDCl3
100 MHz
S76
150
100
50
0
-50
200
150
100
50
0
ppm (t1)