Supplemental materials for:

# Total Synthesis of Alkaloid (±)-G. B. 13 Using a Rh(I)-Catalyzed Ketone Hydroarylation and Late-Stage Pyridine Reduction

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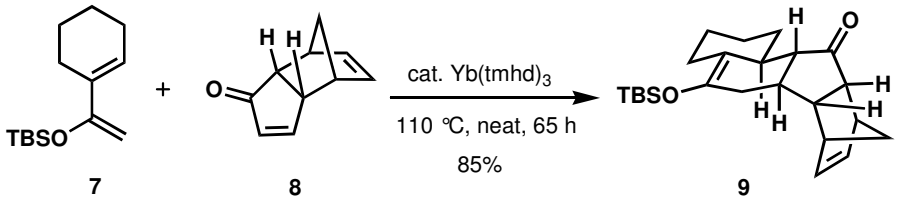
**Materials and Methods.** Unless stated otherwise, reactions were performed in flame-dried glassware sealed with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stir bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled over sodium/benzophenone ketyl. Dichloromethane ($CH_2Cl_2$), toluene, methanol (MeOH), and benzene were distilled over calcium hydride. Potassium acetate (KOAc) was dried at 130 °C under vacuum overnight prior to use. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath or heating block temperatures, which were controlled by an IKAmag® temperature modulator. Thin layer chromatography was performed using SiliCycle silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation and anisaldehyde stain or CAM stain. Sorbent silica gel (particle size 40-63 μm) was used for flash chromatography. $^1$H NMR were recorded on a Bruker AV-600 (at 600 MHz) spectrometer, and $^{13}$C NMR were recorded on a Bruker AV-600 spectrometer (at 150 MHz). $^{19}$F NMR were recorded on a Bruker AVQ-400 spectrometer (at 376 MHz). $^1$H and $^{13}$C chemical shifts (δ) are reported relative to the residual solvent signal, $CHCl_3$ (δ = 7.26 for $^1$H NMR and δ = 77.16 for $^{13}$C NMR) or $C_6H_6$ (δ 7.16 for $^1$H and δ 128.06 for $^{13}$C). $^{19}$F chemical shifts are reported relative to $CFCl_3$ at 0 ppm. Data for $^1$H NMR are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), ddd (doublet of doublet of doublet), m (multiplet), br (broad). IR spectra were recorded on a Nicolet MAGNA-IR 850 spectrometer and are reported in frequency of absorption ($cm^{-1}$). High resolution mass spectral data were obtained from the University of California, Berkeley Mass Spectral Facility.

**Experimental Procedures.**




7 8 9

**Diels-Alder Adduct 9.** Diene **7**[1] (8.21 g, 34.3 mmol, 1 equiv), enone **8**[2] (5.01 g, 34.3 mmol, 1 equiv), and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)-ytterbium (III) ($Yb(tmhd)_3$) (1.24 g, 1.72 mmol, 5 mol %) were placed in a 50 mL Schlenk flask. The flask was evacuated and backfilled with nitrogen, sealed with a Teflon screw cap, and the reaction mixture was then stirred at 110 °C in an oil bath for 65 h. The crude reaction mixture was loaded on to a silica column and purified by flash chromatography (hexanes to 29:1 hexanes/EtOAc) to give **9** (11.2 g, 85%) as a slightly yellow oil. $\mathbf{R_f}$ 0.59 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 5.5, 2.8 MHz, 1H), 5.97 (dd, *J* = 5.5, 3.0 MHz, 1H), 3.09-3.03 (m, 2H), 2.97-2.94 (br, 1H), 2.86-2.80 (m, 1H), 2.66-2.61 (m, 1H), 2.32-2.26 (m, 2H), 2.21-2.13 (m, 1H), 2.05-1.99 (m, 1H), 1.96-1.90 (m, 1H), 1.71-1.63 (m, 3H), 1.50-1.42 (m, 2H), 1.37-1.24 (m, 2H), 1.12-1.03 (m, 1H), 0.95 (s, 9H), 0.71-0.62 (m, 1H), 0.13 (s, 3H), 0.11 (s, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 214.4, 140.9, 137.1, 135.7, 119.2, 60.0, 55.3, 52.9, 45.4, 44.5, 42.9, 39.4, 38.2, 36.0, 33.8, 26.7, 26.3, 26.0, 25.8, 18.3, -3.6, -4.1; **IR** (film) 2954, 2928, 2855, 1738, 1252, 1198, 836 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{24}H_{37}O_2Si]^+$ $(M+H)^+$: *m/z* 385.2557, found 385.2548.

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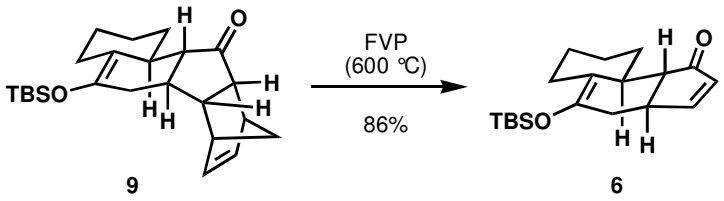
[1] Diene **7** was prepared from 1-acetylcyclohexene and TBSCl, according to the procedure of Ohkata et al.: Ohkata, K.; Lee, Y. G.; Utsumi, Y.; Ishimaru, K.; Akiba, K. *J. Org. Chem.* **1991**, *56*, 5052-5059.

[2] Enone **8** was prepared via the Mihelich-Eickhoff photooxygenation of cyclopentadiene dimer, according to the procedure of Borsato et al.: Borsato, G.; De Lucchi, O.; Fabris, F.; Lucchini, V.; Frascella, P.; Zambon, A. *Tetrahedron Lett.* **2003**, *44*, 3517-3520. Purification was achieved by flash chromatography eluting with a gradient of hexanes to 29:1 hexanes/EtOAc.




**Enone 6.** Diels-Alder adduct **9** (4.02 g, 10.5 mmol) in benzene (10.5 mL, 1.0 M) was injected into a quartz tube (~2 cm in diameter) inside a tube furnace (12 in) at 600 °C under vacuum (~0.02 torr) (see Figure S1). The solution was injected into the system through a 20-guage needle from a gas-tight syringe (fitted with a valve) in small aliquots (~0.3 mL every 30-45 s). The product was collected in a liquid nitrogen-cooled trap. The crude product was purified via flash chromatography (29:1 hexanes/EtOAc) to give **6** (2.85 g, 86% yield) as a colorless oily solid. $\mathbf{R_f}$ 0.59 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 5.8 Hz, 1H), 6.09 (dd, *J* = 5.8, 2.5 Hz), 2.95-2.89 (m, 1H), 2.74-2.65 (m, 2H), 2.38-2.24 (m, 3H), 1.83 (dd, *J* = 10.5, 6.5 Hz, 1H), 1.78-1.72 (m, 2H), 1.61-1.53 (m, 1H), 1.40-1.32 (m, 1H), 1.20-1.11 (m, 1H), 0.96 (s, 9H), 0.93-0.85 (m, 1H), 0.14-0.13 (m, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 207.9, 159.8, 141.5, 134.5, 121.5, 57.3, 42.9, 36.9, 35.6, 33.5, 26.6, 26.5, 26.0, 25.6, 18.4, -3.6, -4.0; **IR** (film) 2928, 2855, 1716, 1256, 1191, 1152, 839, 778cm$^{-1}$; HRMS (ESI$^+$) calc'd for $[C_{19}H_{31}O_2Si]^+$ $(M+H)^+$: *m/z* 319.2088, found 319.2083.

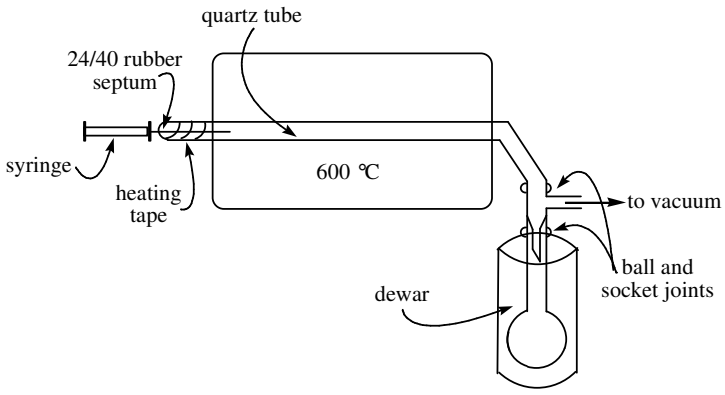
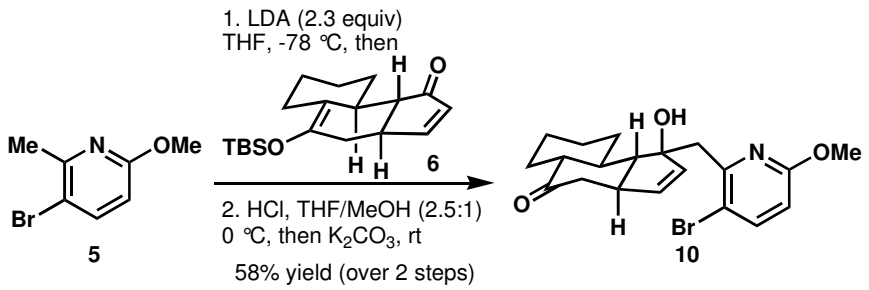



**Figure S1**

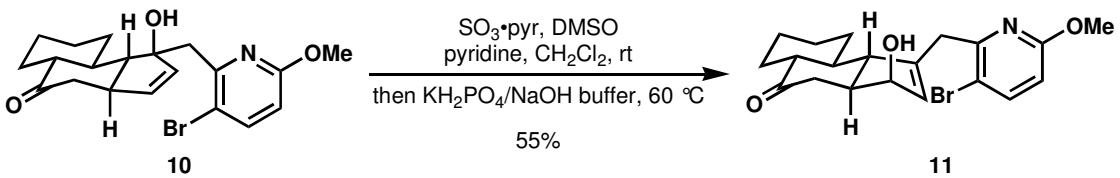



**Tertiary allylic alcohol 10.** Lithium diisopropyl amide was generated by the addition of n-BuLi (10.7 mL of a 2.5 M soln. in hexanes, 27 mmol, 2.3 equiv) to a solution of diisopropyl amine (3.9 mL, 28 mmol, 2.4 equiv) in 50 mL of THF at -78 °C. The solution of LDA was stirred for 1 h at this temperature. Picoline **5**[3] (2.34 g, 11.6 mmol, 1 equiv) in THF (30 mL) at -78 °C was then added to the LDA solution via cannula. The resulting apple-red solution was stirred 30 min at -78 °C. At this time, enone **6** (3.87 g, 12.1 mmol, 1.04 equiv) in THF (30 mL) at -78 °C was transferred to the reaction flask via cannula, and the color of the solution turned to orange. After stirring for 25 min, the reaction mixture was quenched at -78 °C with saturated aqueous $NH_4Cl$ (50 mL) and then allowed to come to rt. The mixture was extracted with $Et_2O$ (2 x 200 mL), and the organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The majority of impurities in the crude product could be removed by flash chromatography (29:1 hexanes/EtOAc). This material was of suitable purity and taken on to the next step. $\mathbf{R_f}$ 0.60 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 5.78 (s, 1H), 5.76 (d, *J* = 5.7 Hz, 1H), 5.60 (dd, *J* = 5.7, 2.5 Hz, 1H), 3.91 (s, 3H), 3.21 (d, *J* = 15.1 Hz, 1H), 2.99-2.94 (m, 2H), 2.48-2.41 (m, 1H), 2.33-2.24 (m, 3H), 2.15-2.08 (m, 1H), 1.76-1.70 (m, 2H), 1.65-1.55 (m, 2H), 1.34-1.24 (m, 1H), 1.23-1.13 (m, 1H), 1.09-1.00 (m, 1H), 0.96 (s, 9H), 0.13 (s, 6H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 162.2, 155.1, 143.3, 141.7, 139.5, 133.7, 120.4, 112.9, 110.9, 84.5, 60.0, 54.0, 43.4, 38.3, 37.3,

[3] Haudrechy, A.; Chassaing, C.; Riche, C.; Langlois, Y. *Tetrahedron* **2000**, *56*, 3181-3187.

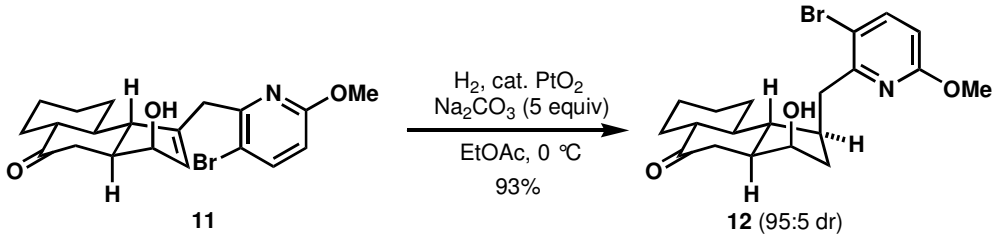
36.5, 34.0, 26.7, 26.5, 26.0, 18.4, -3.6, -4.0; **IR** (film) 3425, 2928, 2854, 1579, 1463, 1293, 854, 839 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{26}H_{39}O_3NBrSi]^+$ $(M+H)^+$: *m/z* 520.1877, found 520.1885.

12 N HCl (0.06 mL, 0.72 mmol) was added to the chromatographed silyl enol ether in THF (25 mL) and MeOH (10 mL) at 0 °C, and the reaction mixture was stirred at this temperature for 2 h. $K_2CO_3$ (2 g, 14.5 mmol) was then added (to epimerize to the trans-decalin isomer), and the reaction mixture was allowed to come to rt and was stirred for 1 h before a second portion of $K_2CO_3$ (1.3 g, 9.4 mmol) was added. After an additional 2.5 h of stirring, the solution was diluted sequentially with $Et_2O$ (100 mL) and saturated aqueous $NH_4Cl$ (75 mL). The layers were separated and the aqueous layer was extracted with additional $Et_2O$ (2 x 100 mL). The combined organic layers were then washed with $H_2O$ (2 x 100 mL) and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (using a gradient of 5:1 to 4:1 hexanes/EtOAc) to give tertiary allylic alcohol **11** as a slightly yellow oily solid (2.72 g, 58% yield over two steps, >95:5 trans/cis decalin isomers). $\mathbf{R_f}$ 0.32 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 8.7 Hz), 5.79 (s, 1H), 5.72 (d, *J* = 5.8 Hz, 1H), 5.62 (dd, *J* = 5.8, 2.6 Hz, 1H), 3.91 (s, 3H), 3.23 (d, *J* = 15.1 Hz, 1H), 2.95 (d, *J* = 15.1 Hz, 1H), 2.68 (dd, *J* = 12.6, 3.5 Hz, 1H), 2.60-2.53 (m, 1H), 2.43-2.36 (m, 1H), 2.33-2.27 (m, 1H), 2.09-1.97 (m, 3H), 1.86-1.81 (m, 1H), 1.78-1.70 (m, 2H), 1.35-1.16 (m, 4H); **$^{13}$C NMR** (150 MHz, CDCl3) δ 210.7, 162.2, 154.5, 143.3, 140.3, 132.9, 112.8, 111.1, 83.8, 61.6, 55.8, 54.0, 47.1, 46.4, 42.8, 37.3, 32.2, 25.8, 25.7, 25.5; **IR** (film) 3408, 2928, 2852, 1709, 1580, 1463, 1413, 1294 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{20}H_{25}O_3NBr]^+$ $(M+H)^+$: *m/z* 406.1012, found 406.1007.



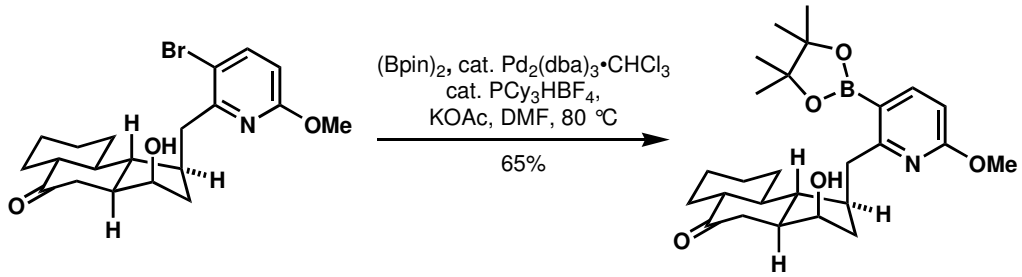

**10** **11**

**Secondary allylic alcohol 11.** Pyridine (1.2 mL, 15 mmol, 30 equiv) was added to $SO_3$•pyridine (396 mg, 2.49 mmol, 5 equiv) in DMSO (1.8 mL, 25 mmol, 50 equiv) at rt, and the solution was stirred for 15 min.[4] Tertiary allylic alcohol **11** (202 mg, 0.497 mmol, 1 equiv) in $CH_2Cl_2$ (5 mL) was then added, and the reaction mixture was stirred at rt for 6 h. At this time, 5 mL of Fisher® pH 7.00 $KH_2PO_4$-NaOH buffer solution concentrate was added, and the biphasic mixture was stirred vigorously at 60 °C for 3.5 h. The reaction mixture was then allowed to cool to rt, the layers were separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered through a fritted funnel, and concentrated under reduced pressure. The crude product was purified by flash chromatography (using a gradient of 4:1 to 1:1 hexanes/EtOAc) to afford 111 mg (55% yield) of secondary allylic acetate **12** as a colorless oil. $\mathbf{R_f}$ 0.13 (2:1 hex/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 1H), 6.53 (d, *J* = 8.6 Hz, 1H), 5.41-5.38 (m, 1H), 4.33-4.30 (m, 1H), 3.88 (s, 3H), 3.79 (d, *J* = 16.9 Hz, 1H), 3.74 (d, *J* = 16.8 Hz, 1H), 2.91-2.85 (m, 1H), 2.76-2.70 (m, 1H), 2.52 (dd, *J* = 13.4, 3.4 Hz, 1H), 2.24-2.18 (m, 1H), 2.09-1.99 (m, 2H), 1.98-1.92 (m, 1H), 1.83-1.78 (m, 1H), 1.72-1.67 (m, 1H), 1.66-1.58 (m, 1H), 1.29-1.11 (m, 5H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 211.6, 162.8, 154.9, 150.4, 142.7, 131.4, 112.2, 110.4, 73.9, 55.8, 53.9, 52.4, 51.7, 46.6, 42.6, 40.2, 32.6, 25.8, 25.7, 25.6; **IR** (film) 3400, 2924, 2855, 1705, 1575, 1460, 1416 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{20}H_{25}O_3NBr]^+$ $(M+H)^+$: *m/z* 406.1012, found 406.1024.




[4] Chen, L. J.; Lee, S.; Renner, M.; Tian, Q. P.; Nayyar, N. *Org. Process Res. Dev.* **2006**, *10*, 163-164.

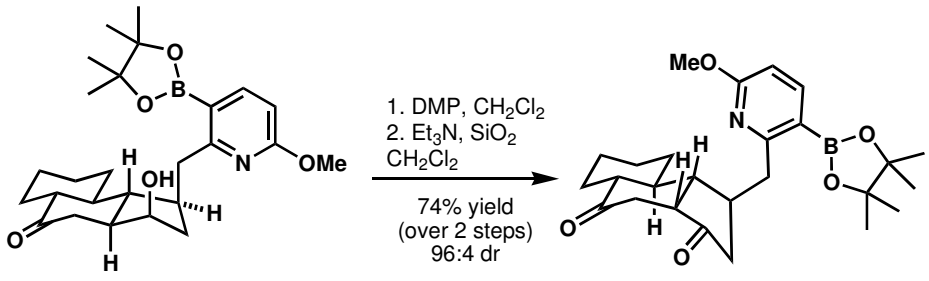
**Secondary alcohol 12.** $Na_2CO_3$ (227 mg, 2.14 mmol, 5 equiv) and $PtO_2$ (9.5 mg, 0.042 mmol, 10 mol %) were added to a solution of **12** (174 mg, 0.428, 1 equiv) in EtOAc (3.6 mL, 0.12 M) at 0 °C. The flask was evacuated and backfilled with $H_2$ (x 3), and the mixture (held at a temperature between 0 and 8 °C) was stirred under a balloon of $H_2$ for 5 h. The reaction mixture was then filtered through a plug of silica, which was rinsed with additional EtOAc. The filtrate was then concentrated under reduced pressure to provide 162 mg (93%) of **13** as a colorless oily solid (95:5 diastereomeric ratio). This product was > 95% pure and used in the ensuing reaction without further purification. $\mathbf{R_f}$ 0.17 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) (major diastereomer) δ 7.64 (d, *J* = 8.6 Hz, 1H), 6.48 (d, *J* = 8.6 Hz, 1H), 4.08-4.03 (m, 1H), 3.90 (s, 3H), 3.27 (dd, *J* = 15.0, 3.2 Hz, 1H), 2.94 (dd, *J* = 15.0, 10.9 Hz, 1H), 2.67-2.60 (m, 1H), 2.51-2.46 (m, 1H), 2.46-2.37 (m, 1H), 2.26-2.21 (m, 1H), 2.20-2.13 (m, 1H), 2.04-1.94 (m, 3H), 1.84-1.74 (m, 2H), 1.73-1.57 (m, 3H), 1.45-1.35 (m, 1H), 1.33-1.15 (m, 4H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 212.9, 162.5, 156.6, 142.4, 112.2, 109.4, 73.5, 54.2, 53.8, 52.0, 50.8, 48.1, 44.4, 42.9, 42.0, 38.7, 32.8, 25.9, 25.6, 25.4. **IR** (film) 3446, 2929, 2854, 1702, 1574, 1459, 1417, 1293 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{20}H_{27}O_3NBr]^+$ $(M+H)^+$: *m/z* 408.1169, found 408.1177.




**12** **13**

**Boronic ester 13.** DMF (3 mL) was added to $Pd_2(dba)_3$•$CHCl_3$ (37 mg, 0.036 mmol, 4.5 mol %) and $PCy_3HBF_4$ (62 mg, 0.18 mmol, 21 mol %) in a 25 mL Schlenk flask under $N_2$. The solution was stirred at rt for 10 min. Bis(pinacolato)diboron (1.01 g, 3.98 mmol, 5 equiv), KOAc (391

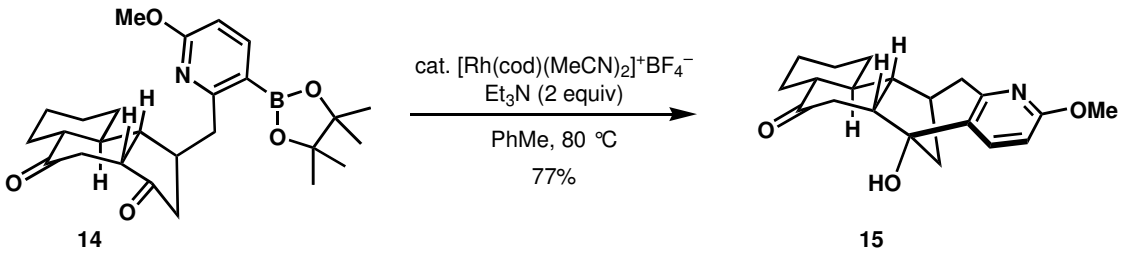
mg, 3.98 mmol, 5 equiv), and a solution aryl bromide **12** (325 mg, 0.796 mmol, 1 equiv) in DMF (5 mL) were added sequentially to the reaction mixture. The Schlenk flask was evacuated and backfilled with $N_2$, and the reaction mixture was stirred at 80 °C for 37 h. At this time, the reaction mixture was allowed to cool to rt and then diluted with $H_2O$ (25 mL) and $Et_2O$ (25 mL). The layers were separated, and the aqueous layer was extracted with $Et_2O$ (2 x 25 mL). The combined ethereal layers were washed with 15% aqueous $NH_4OH$ (2 x 25 mL) and $H_2O$ (2 x 25 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was purified by flash chromatography (3:1 hexanes/EtOAc). The chromatographed product was then washed with 15% aqueous $NH_4OH$ and $H_2O$ (to remove co-eluting pinacol boronic acid) and dried over anhydrous $MgSO_4$ to give **13** (236 mg, 65% yield) as a colorless oil. **$R_f$** 0.19; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 1H), 4.01-3.97 (m, 1H), 3.93 (s, 3H), 3.23 (dd, *J* = 13.1, 4.1 Hz, 1H), 3.12-3.06 (m, 1H), 2.71-2.65 (m, 1H), 2.50 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.41 (d, *J* = 3.7 Hz, 1H), 2.38-2.30 (m, 2H), 2.04-1.91 (m, 3H), 1.89-1.76 (m, 3H), 1.66-1.59 (m, 2H), 1.45-1.37 (m, 1H), 1.35 (s, 12H), 1.27-1.18 (m, 4H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 213.2, 166.4, 165.3, 146.8, 107.0, 84.2, 73.7, 54.6, 53.5, 52.6, 51.6, 48.1, 45.3, 43.2, 40.1, 39.8, 32.7, 26.1, 25.6, 25.6, 25.2, 24.7; **IR** (film) 3502, 2977, 2929, 2855, 1705, 1587, 1345, 1301; **HRMS** ($ESI^+$) calc'd for $[C_{26}H_{39}O_5NB]^+$ $(M+H)^+$: *m/z* 456.2916, found 456.2919.



**Dione 14.** $NaHCO_3$ (77 mg, 0.92 mmol, 2.5 equiv) and Dess-Martin periodinane (DMP) (391 mg, 0.92 mmol, 2.5 equiv) were added to a solution of alcohol **13** (168 mg, 0.369 mmol, 1 equiv) in $CH_2Cl_2$ (3.7 mL, 0.1 M). The reaction mixture was stirred at rt for 11 h. Saturated aqueous $NaHCO_3$ (25 mL) and saturated aqueous $Na_2S_2O_5$ (25 mL) were then added, and the resulting heterogeneous mixture was stirred until the layers became colorless. $Et_2O$ (20 mL) was then added and the layers were separated. The aqueous layer was then extracted with additional $Et_2O$ (2 x 20 mL). The combined organic layers were washed sequentially with saturated aqueous $NaHCO_3$ (2 x 20 mL), $H_2O$ (20 mL), and brine (20 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (4:1 hexanes EtOAc) to provide 141 mg (84% yield) of the trans [6-5] ring-fused ketone as a colorless oily solid. $\mathbf{R_f}$ 0.47 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 3.86 (dd, *J* = 12.9, 3.8 Hz, 1H), 2.83 (dd, *J* = 12.9, 10.8 Hz, 1H), 2.77-2.72 (m, 1H), 2.67-2.62 (m, 1H), 2.60-2.52 (m, 1H), 2.37-2.20 (m, 4H), 2.08-2.04 (m, 1H), 2.03-1.96 (m, 1H), 1.86-1.82 (m, 2H), 1.81-1.75 (m, 1H), 1.66-1.59 (m, 1H). 1.38-1.29 (m, 13H), 1.28-2.21 (m, 3H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 214.7, 210.1, 165.4, 165.0, 147.0, 107.5, 83.8, 55.7, 54.4, 53.5, 52.4, 48.8, 44.7, 43.2, 41.1, 39.8, 32.4, 26.0, 25.7, 25.3, 25.1, 25.0; **IR** (film) 2978, 2928, 2848, 1743, 1710, 1588, 1346, 1297 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{26}H_{37}O_5NB]^+$ $(M+H)^+$: *m/z* 454.2759, found 454.2768.

Triethylamine (0.060 mL, 0.43 mmol, 1.5 equiv) and $SiO_2$ (131 mg) were added to the trans [6-5] ring-fused ketone (131 mg, 0.289 mmol, 1 equiv) in $CH_2Cl_2$ (2.9 mL, 0.1 M). The heterogeneous mixture was stirred at rt for 4 h at which time it was filtered through cotton wool with a short pad of silica. The silica was rinsed with additional $CH_2Cl_2$ and the filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography

(using a gradient of 6:1 to 4:1 hexanes/EtOAc) to give 122 mg (93% yield) of a colorless oily solid. $\mathbf{R_f}$ 0.43 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H), 3.26 (dd, *J* = 12.6, 8.0 Hz, 1H), 3.16-3.11 (m, 1H), 3.01 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.86-2.80 (m, 2H), 2.45-2.40 (m, 1H), 2.27-2.24 (m, 2H), 2.09-2.03 (m, 2H), 1.92-1.85 (m, 2H), 1.81-1.65 (m, 2H), 1.29 (s, 12H), 1.16-1.03 (m, 4H), 0.86-0.78 (m, 1H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 217.2, 210.2, 165.2, 165.1, 146.7, 107.7, 83.9, 53.4, 52.4, 48.0, 46.0, 43.4, 41.9, 40.0, 36.9, 35.9, 32.3, 25.6, 25.4, 25.2, 25.1, 24.9; **IR** (film) 2977, 2930, 2855, 1742, 1713, 1589, 1341, 1305; **HRMS** ($ESI^+$) calc'd for $[C_{26}H_{37}O_5NB]^+$ $(M+H)^+$: *m/z* 454.2759, found 454.2772.

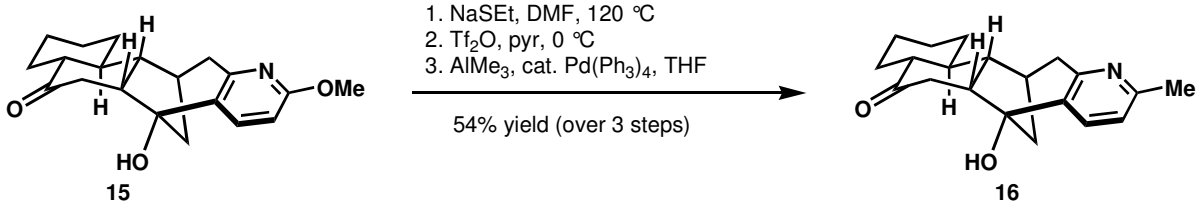



14 15

**Tertiary alcohol 15.** *25 mol % Catalyst loading procedure:* In a glovebox, a solution of ketone **14** (19 mg, 0.042 mmol, 1 equiv) in toluene (0.5 mL, 0.09 M) was added to a vial containing $[Rh(cod)(MeCN)]^+BF_4^-$ (4.1 mg, 0.011 mmol, 25 mol %), and a stir bar. $Et_3N$ (12 μL, 0.084 mmol, 2 equiv) was then added to the vial. The vial was sealed with a Teflon cap, brought outside of the glovebox, and heated in a metal heating block (tall enough to cover ~ 90% of the vial) at 80 °C for 6.5 h. The reaction mixture was then diluted with EtOAc (15 mL) and $H_2O$ (8 mL). The layers were separated and the aqueous layer was extracted with EtOAc (10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (using a gradient of 5:1 to 4:1 hexanes/EtOAc) to give **15** as a yellow oil (0.032 mmol, based on $^1$H NMR integration using 1,2-dichloroethane as an internal standard, 77% yield), contaminated with pinacol boronic

acid. This material was used without further purification in the subsequent reaction. *8 mol % Catalyst loading procedure:* In a glovebox, a solution of ketone **14** (22 mg, 0.049 mmol, 1 equiv) in toluene (0.49 mL, 1.0 M) was added to a vial containing $[Rh(cod)(MeCN)]^+BF_4^-$ (1.5 mg, 0.0039 mmol, 8 mol %), and a stir bar. $Et_3N$ (14 μL, 0.098 mmol, 2 equiv) was then added to the vial. The vial was sealed with a Teflon cap, brought outside of the glovebox, and heated in a metal heating block (tall enough to cover ~ 90% of the vial) at 80 °C for 18 h. The reaction mixture was then diluted with EtOAc (15 mL) and $H_2O$ (8 mL). The layers were separated and the aqueous layer was extracted with EtOAc (10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (5:1 hexanes/EtOAc) to give **15** as a yellow oil (0.035 mmol, based on $^1H$ NMR integration using 1,2-dichloroethane as an internal standard, 71% yield), contaminated with pinacol boronic acid. This material was used without further purification in the subsequent reaction. The majority of the contaminating pinacol boronic acid could be removed to provide an analytically pure sample as follows: The chromatographed material was dissolved in $Et_2O$ (8 mL) and washed with 15% aqueous $NH_4OH$ (5 mL). The layers were separated, and the aqueous phase was extracted with $Et_2O$ (8 mL). The combined organic layers were then washed with 15% aqueous $NH_4OH$ (2 x 5 mL) and brine (5 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to give pure **15**. $\mathbf{R_f}$ 0.20 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 3.14 (dd, *J* = 17.5, 4.2 Hz, 1H), 2.73 (d, *J* = 17.5 Hz, 1H), 2.50-2.45 (m, 1H), 2.41-2.35 (m, 2H), 2.34-2.21 (m, 3H), 2.12-2.07 (m, 1H), 1.84-1.72 (m, 4H), 1.72-1.67 (m, 1H), 1.62-1.56 (m, 1H), 1.47-1.39 (m, 1H), 1.26-1.15 (m, 2H), 1.09-0.92 (m, 2H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 214.3, 163.3, 152.0, 134.8, 133.9, 108.2, 79.2, 53.6, 51.1, 49.1, 47.3, 42.9,

41.4, 38.4, 37.9, 36.7, 33.1, 27.5, 26.0, 25.9; **IR** (film) 3446, 2925, 2854, 1706, 1474, 1307; **HRMS** (ESI$^+$) calc'd for $[C_{20}H_{26}O_3N]^+$ $(M+H)^+$: *m/z* 328.1907, found 328.1902.



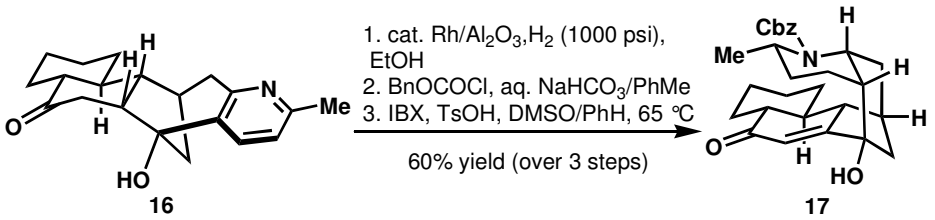

**Methylpyridinyl ketone 16.** EtSH (74 μL, 1.0 mmol, 20 equiv) was added to a suspension of NaH (20 mg of a 60% NaH dispersion in mineral oil, 0.50 mmol, 10 equiv) in DMF (0.2 mL) under $N_2$ in a Schlenk tube. 2-Methoxypyridinyl ketone **15** (0.05 mmol, 1 equiv) in DMF (0.5 mL) was then added. The Schlenk tube was quickly evacuated and backfilled with $N_2$ then sealed, and the reaction mixture was stirred at 120 °C for 15 h. The reaction mixture was allowed to cool to rt and then quenched with $H_2O$ (0.06 mL). The aqueous layer was extracted with $CH_2Cl_2$ (2 x 12 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure via rotary evaporation and then on a high vacuum line (flask at 30 °C). The crude pyridone (containing a trace amount of DMF) was used in the subsequent step.

The pyridone was dissolved in pyridine (0.35 mL) and cooled to 0 °C. Trifluoromethanesulfonic anhydride (20 μL, 0.12 mmol, 2.4 equiv) was then added, and the reaction mixture was stirred at 0 °C for 35 min. The reaction mixture was quenched at 0 °C with saturated aqueous $NaHCO_3$ (2 mL), and the aqueous layer was extracted with $CH_2Cl_2$ (3 x 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (using a gradient of 4:1 to 3:1 hexanes/EtOAc) to give 16.9 mg of the pyridinyl triflate (76% yield over two steps) as a colorless oil. $\mathbf{R_f}$ 0.19 (2:1 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.3 Hz,

1H), 3.20 (dd, *J* = 18.2, 4.2 Hz, 1H), 2.85 (d, *J* = 18.2 Hz, 1H), 2.51-2.43 (m, 2H), 2.42-2.30 (m, 3H), 2.27-2.21 (m, 1H), 2.17-2.12 (br, 1H), 2.11-2.06 (m, 1H), 1.85-1.75 (m, 3H), 1.74-1.69 (m, 1H), 1.64-1.57 (m, 1H), 1.49-1.42 (m, 1H), 1.27-1.14 (m, 2H), 1.09-0.95 (m, 2H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 213.8, 155.1, 154.6, 143.1, 136.3, 118.8 (q, *J* = 320 Hz), 112.7, 79.2, 51.0, 49.0, 47.1, 42.5, 41.2, 38.1, 37.2, 36.3, 33.0, 27.4, 25.9, 25.8; **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -72.3; **IR** (film) 3442, 2927, 2856, 1701, 1419, 1219, 1137 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{20}H_{23}O_5NF_3S]^+$ $(M+H)^+$: *m/z* 446.1244, found 446.1238.

$Pd(PPh_3)_4$ (0.6 mg, 0.0005 mmol, 5 mol %) in THF (0.1 mL) was added to a solution of the pyridinyl triflate described above (4.8 mg, 0.011 mmol, 1 equiv) in THF (0.3 mL) in a Schlenk tube under $N_2$. Trimethyl aluminum (20 μL of a 2.0 M solution in toluene, 0.04 mmol, 4 equiv) was then added to this solution. The Schlenk tube was evacuated and backfilled with $N_2$, sealed, and heated in an oil bath at 80 °C for 12.5 h. The reaction mixture was then allowed to cool to rt; MeOH (0.05 mL) was added and stirring was continued for another 5 min. $NaHCO_3$ (75 mg) and anhydrous $MgSO_4$ (300 mg) were added, and the mixture was diluted with $CH_2Cl_2$ (5 mL) and then stirred for 10 min. This mixture was filtered through Celite, which was rinsed with additional $CH_2Cl_2$ (10 mL). The filtrate was concentrated under reduced pressure to give the crude product, which was purified by flash chromatography (using a gradient from 0.5% MeOH in $CH_2Cl_2$ to 4% MeOH in $CH_2Cl_2$). 2-Methylpyridinyl ketone **16** (2.4 mg, 71% yield) was thus obtained as a yellow oil. $\mathbf{R_f}$ 0.3 (10% MeOH in $CH_2Cl_2$); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 3.21 (dd, *J* = 17.5, 4.2 Hz, 1H), 2.83 (d, *J* = 17.5 Hz, 1H), 2.51-2.46 (m, 4H), 2.43-2.36 (m, 2H), 2.33-2.27 (m, 2H), 2.26-2.21 (m, 1H), 2.12-2.07 (m, 1H), 1.94-1.90 (br, 1H), 1.84-1.74 (m, 3H), 1.72-1.67 (m, 1H), 1.61-1.55 (m, 1H), 1.48-1.40 (m, 1H), 1.24-1.14 (m, 2H), 1.09-1.01 (m, 1H), 1.00-0.92 (m, 1H); **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ

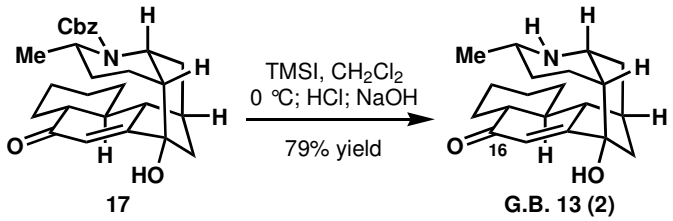
214.2, 157.1, 154.0, 139.2, 131.1, 121.2, 79.3, 51.1, 49.0, 47.2, 43.1, 41.4, 38.3, 37.7, 36.7, 33.0, 27.5, 26.0, 25.8, 24.3; **IR** (film) 3368, 2924, 2853, 1709, 1461, 1101 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{20}H_{26}O_2N]^+$ $(M+H)^+$: *m/z* 312.1958, found 312.1953.




**N-Cbz-G. B. 13 (17).** 5% Rh on alumina (10 mg, 0.005 mmol, 25 mol %) was added to a solution of methylpyridinyl ketone **16** (6.1 mg, 0.020 mmol, 1 equiv) in absolute EtOH (0.3 mL) in a 4 mL vial. The reaction vessel was placed inside a Parr bomb, which was pressurized to 1000 psi with $H_2$. The reaction mixture was stirred at this pressure for 19.5 h. At this time, the Parr bomb was vented. The mixture was filtered through Celite, which was rinsed with $CH_2Cl_2$ (5 mL), and then concentrated under reduced pressure to give the corresponding piperidine as a mixture of ketone and alcohol products. The crude mixture was used immediately without purification.

To the piperidine mixture described above was added toluene (0.25 mL), saturated aqueous $NaHCO_3$ (0.25 mL), and benzylchloroformate (9.1 μL, 0.064 mmol, 3 equiv). The reaction mixture was stirred at rt for 2.5 h at which time it was diluted with $CH_2Cl_2$ (7 mL) and $H_2O$ (2 mL). The layers were separated, and the aqueous layer was extracted with $CH_2Cl_2$ (2 x 7 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluting with 2:1 hexanes/EtOAc to $CH_2Cl_2$ to 9:1 $CH_2Cl_2$/MeOH). The fractions containing Cbz-protected piperidine ketone and alcohol products were combined, concentrated under reduced pressure, and used in the next step.

*p*-Toluenesulfonic acid monohydrate (15 mg, 0.079 mmol, 4 equiv) and IBX (84 mg, 0.30 mmol, 15 equiv) were added to a solution of the Cbz-protected piperidine mixture described above in DMSO (0.20 mL) and benzene (0.15 mL). The mixture was stirred at 65 °C for 18.5 h and then diluted with EtOAc (8 mL) and saturated aqueous $NaHCO_3$ (5 mL). The layers were separated and the aqueous layer was extracted with additional EtOAc (2 x 8 mL). The combined organic layers were then washed sequentially with saturated aqueous $NaHCO_3$ (2 x 5 mL), $H_2O$ (5 mL), and brine (5 mL), dried over $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography (eluting with a gradient of 4:1 to 2:1 hexanes/EtOAc) to give 5.3 mg (60% yield over three steps) of N-Cbz-G. B. 13 (**17**) as a colorless oil. $\mathbf{R_f}$ 0.45 (1:2 hexanes/EtOAc); **$^1$H NMR** (600 MHz, $C_6D_6$) δ 7.32-7.28 (m, 2H), 7.17-7.13 (m, 2H), 7.09-7.05 (m, 1H), 5.96 (d, *J* = 2.0 Hz, 1H), 5.21 (s, 2H), 4.71-4.62 (m, 1H), 4.45-4.35 (m, 1H), 2.64-2.50 (m, 2H), 1.95-1.88 (m, 1H), 1.72-1.62 (m, 4H), 1.53-1.42 (m, 3H), 1.34-1.22 (m, 3H), 1.18-1.12 (m, 1H), 1.12-0.84 (m, 9H), 0.84-0.79 (m, 1H), 0.63-0.54 (m, 1H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) δ 198.7, 172.2, 155.5, 137.8, 119.0, 80.8, 67.2, 56.4, 52.3, 47.10, 47.05, 45.9, 45.0, 35.8, 35.5, 31.4, 30.0, 29.9, 26.6, 26.2, 25.6, 20.0, 19.0; **IR** (film) 3423, 2931, 2852, 1687, 1665, 1414, 1317 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{28}H_{36}O_4N]^+$ $(M+H)^+$: *m/z* 450.2639, found 450.2640.

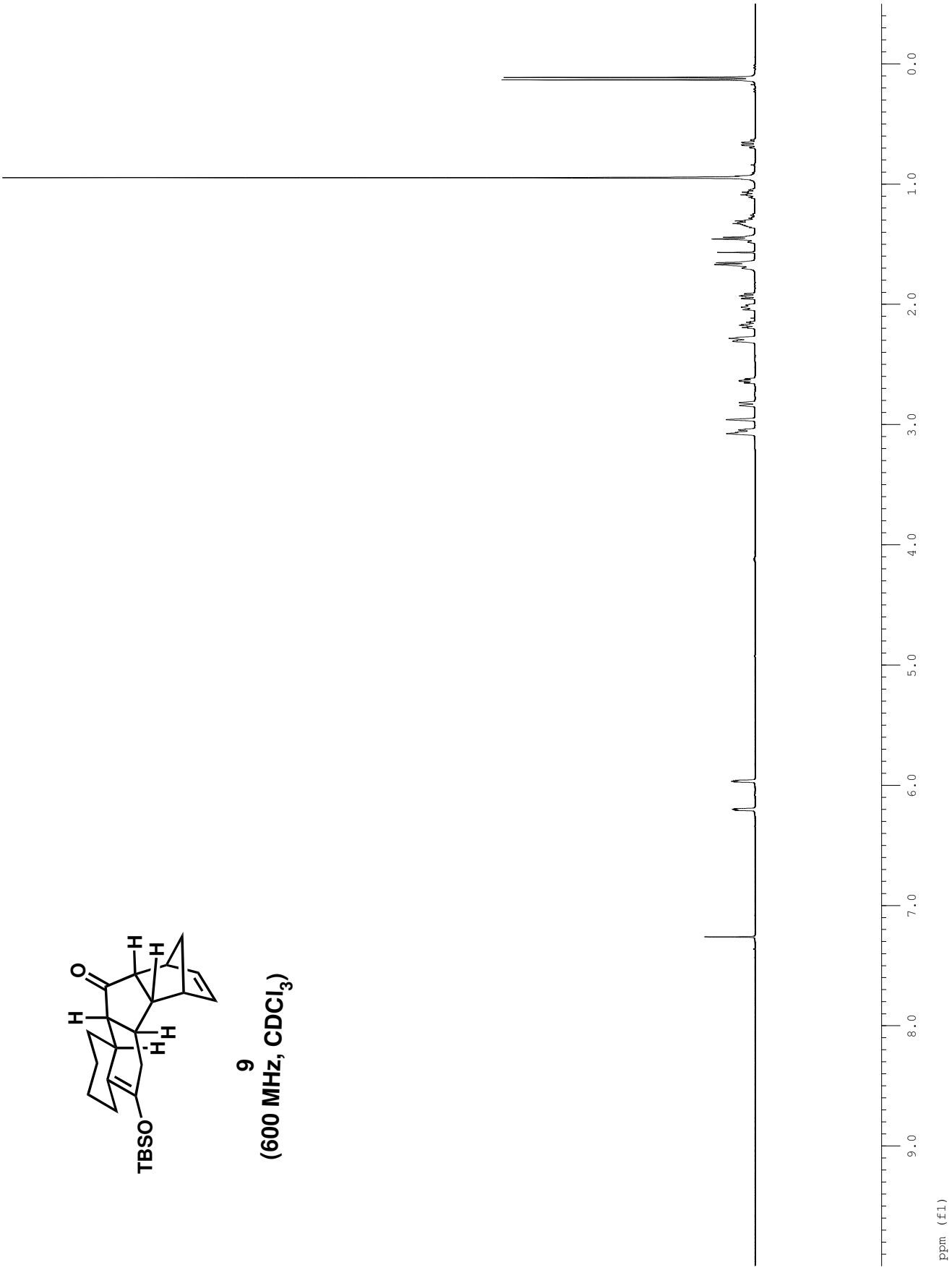



**G. B. 13 (2).** The procedure of Movassaghi, et al.,[5] was followed. Trimethylsilyliodide (1 drop every 25 min for 125 min, ~ 0.06 mL total) was added to a solution of **17** (5.3 mg, 0.012 mmol)

[5] Movassaghi, M.; Hunt, D. K.; Tjandra, M. *J. Am. Chem. Soc.* **2006**, *128*, 8126-8127.

in $CH_2Cl_2$ (1 mL) at 0 °C. After 125 min, TLC analysis indicated the complete consumption of starting material, and 1.5 mL 1 N HCl was added at 0 °C. The reaction mixture was allowed to stir with warming to rt and then was further diluted with 1 N HCl (3.5 mL) and hexanes (10 mL). The layers were separated and the organic phase was extracted with additional 1 N HCl (2 x 5 mL). The combined aqueous layers were washed sequentially with hexanes (2 x 10 mL), $CH_2Cl_2$ (5 mL), and hexanes (10 mL) and then brought to pH 13 with 15% aqueous NaOH (4.5 mL). The basic, aqueous solution was stirred at rt for 1.25 h and then extracted with $CH_2Cl_2$ (5 x 15 mL). The combined $CH_2Cl_2$ layers were dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to give 2.9 mg (79% yield) of a ~ 1:2 mixture of G. B. 13 (**2**) and its N-conjugate addition product, 16-oxo-himgaline, in $C_6D_6$. Stirring this mixture in 15% aqueous NaOH for an additional two hours followed by extraction into $CH_2Cl_2$ then provided a ~ 5:2 mixture of G. B. 13 and 16-oxo-himgaline (in $C_6D_6$), consistent with the observations of Evans.[6] Impurities from solvents could be removed by flash chromatography (eluting with a gradient of 0.1% $Et_3N$ in $CH_2Cl_2$ to 1% $Et_3N$ in $CH_2Cl_2$). **$^1$H NMR** (600 MHz, $C_6D_6$) G. B. 13: δ 6.06 (d, *J* = 2.0 Hz, 1H), 3.31-3.27 (m, 1H), 2.91-2.88 (m, 1H), 2.71-2.65 (m, 1H), 2.60-2.54 (m, 1H), 2.20-2.13 (m, 1H), 1.93-1.89 (m, 1H), 1.85-1.82 (m, 1H), 1.82-1.47 (m, 6H), 1.44-1.40 (ddd, *J* = 10.7, 5.6, 1.9 Hz, 1H), 1.28-0.90 (m, 9H), 0.83-0.74 (m, 1H), 0.76 (d, *J* = 6.1 Hz, 3H); **$^{13}$C NMR** (150 MHz, $C_6D_6$) G. B. 13: δ 199.1, 178.6, 118.9, 79.4, 55.1, 53.0, 52.8, 50.9, 47.9, 47.3, 46.4, 40.7, 32.8, 31.6, 30.3, 27.0, 26.4, 25.8, 24.7, 23.3; **IR** (film) 3391, 2927, 2853, 1706, 1647, 1447, 1317, 1147 $cm^{-1}$; **HRMS** ($ESI^+$) calc'd for $[C_{20}H_{30}O_2N]^+$ $(M+H)^+$: *m/z* 316.2271, found 316.2273.

[6] Evans, D. A.; Adams, D. J. *J. Am. Chem. Soc.* **2007**, *129*, 1048-1049.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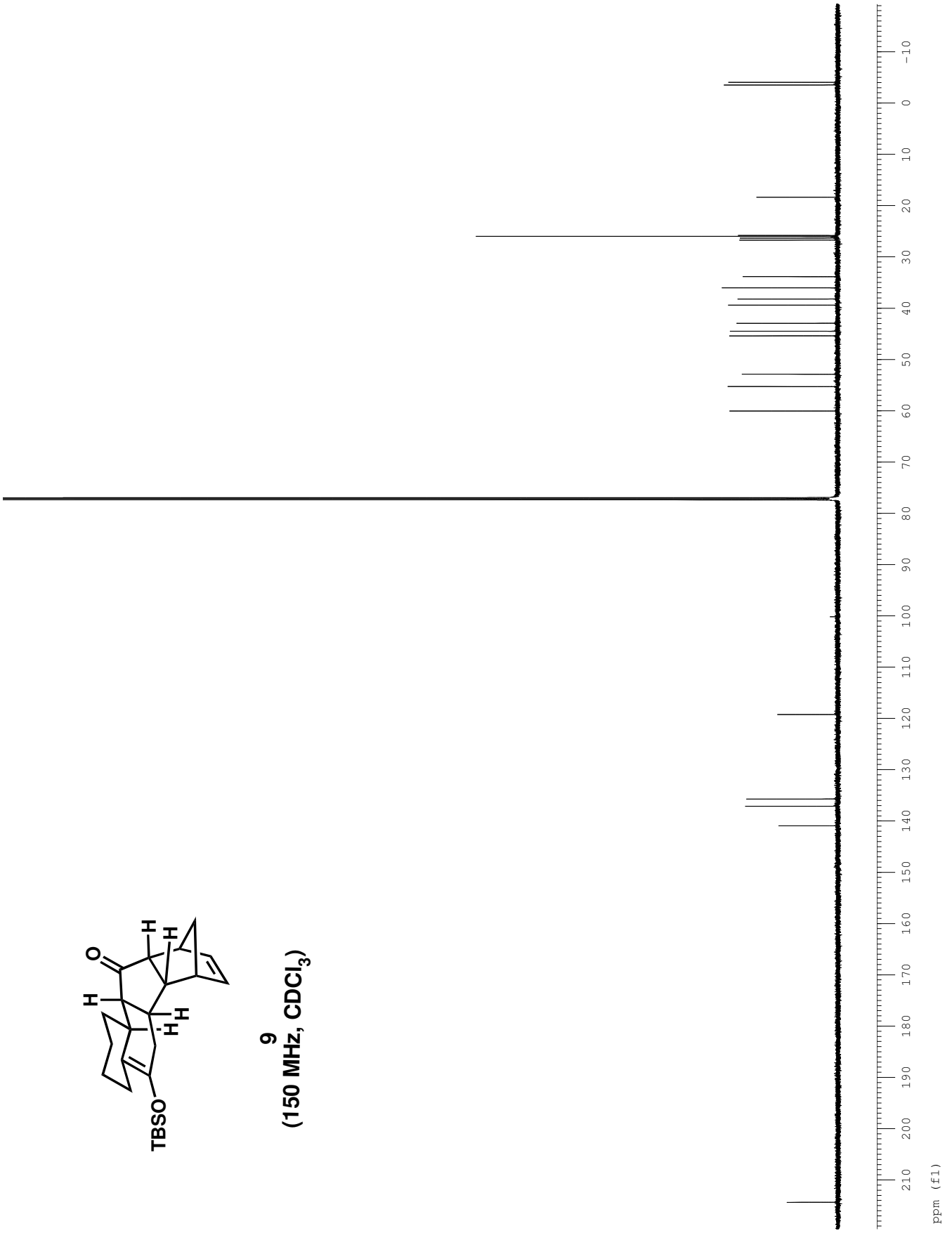
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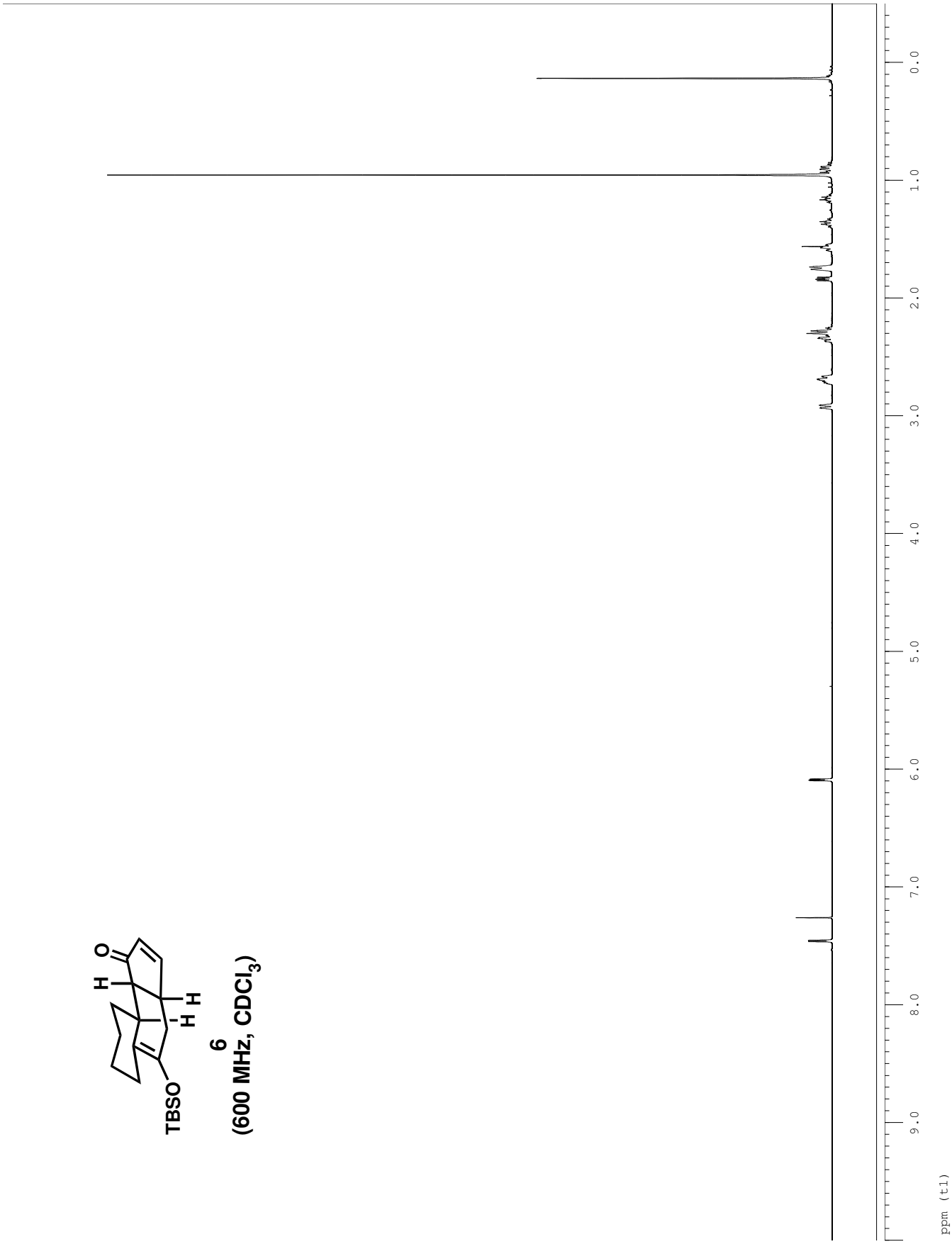
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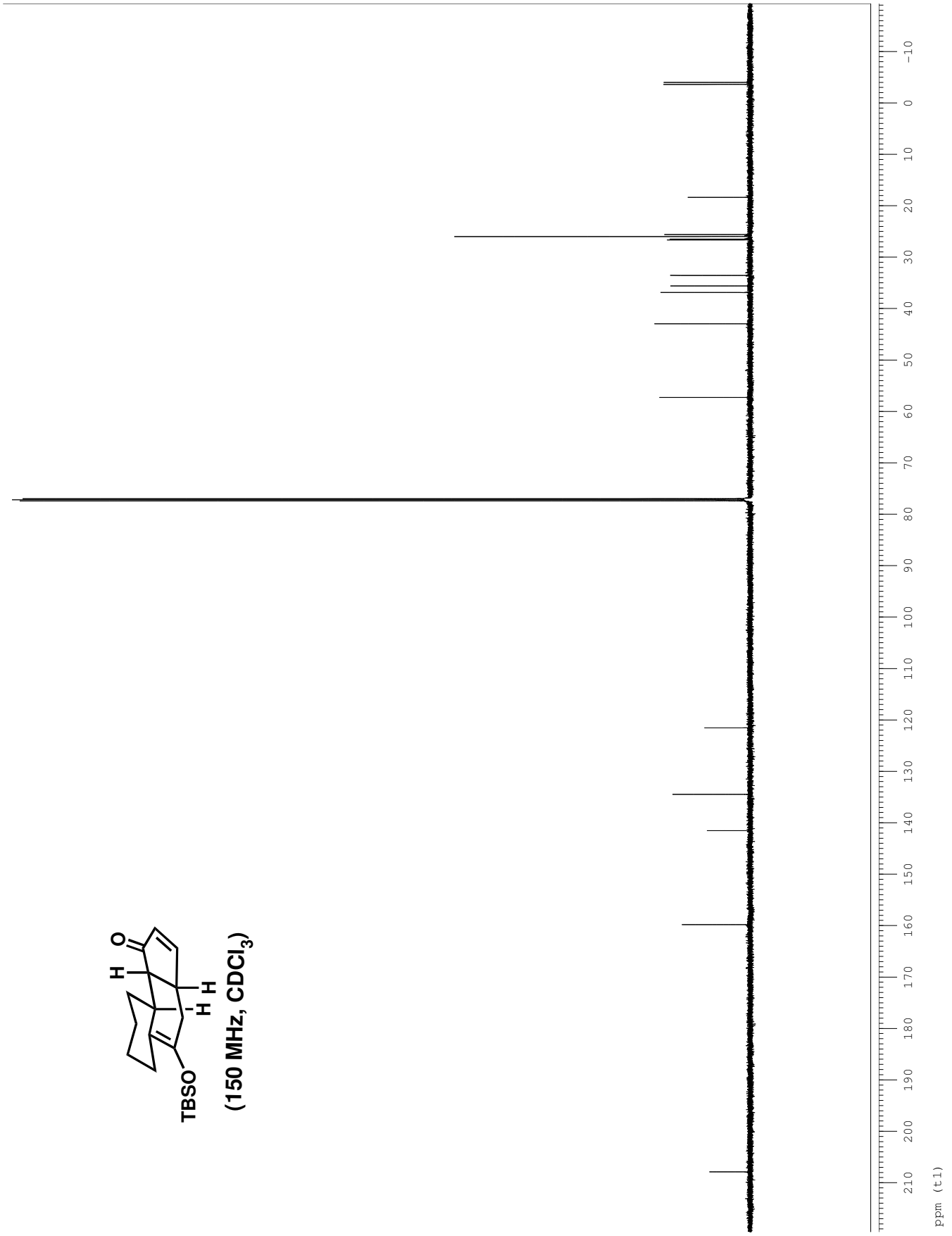
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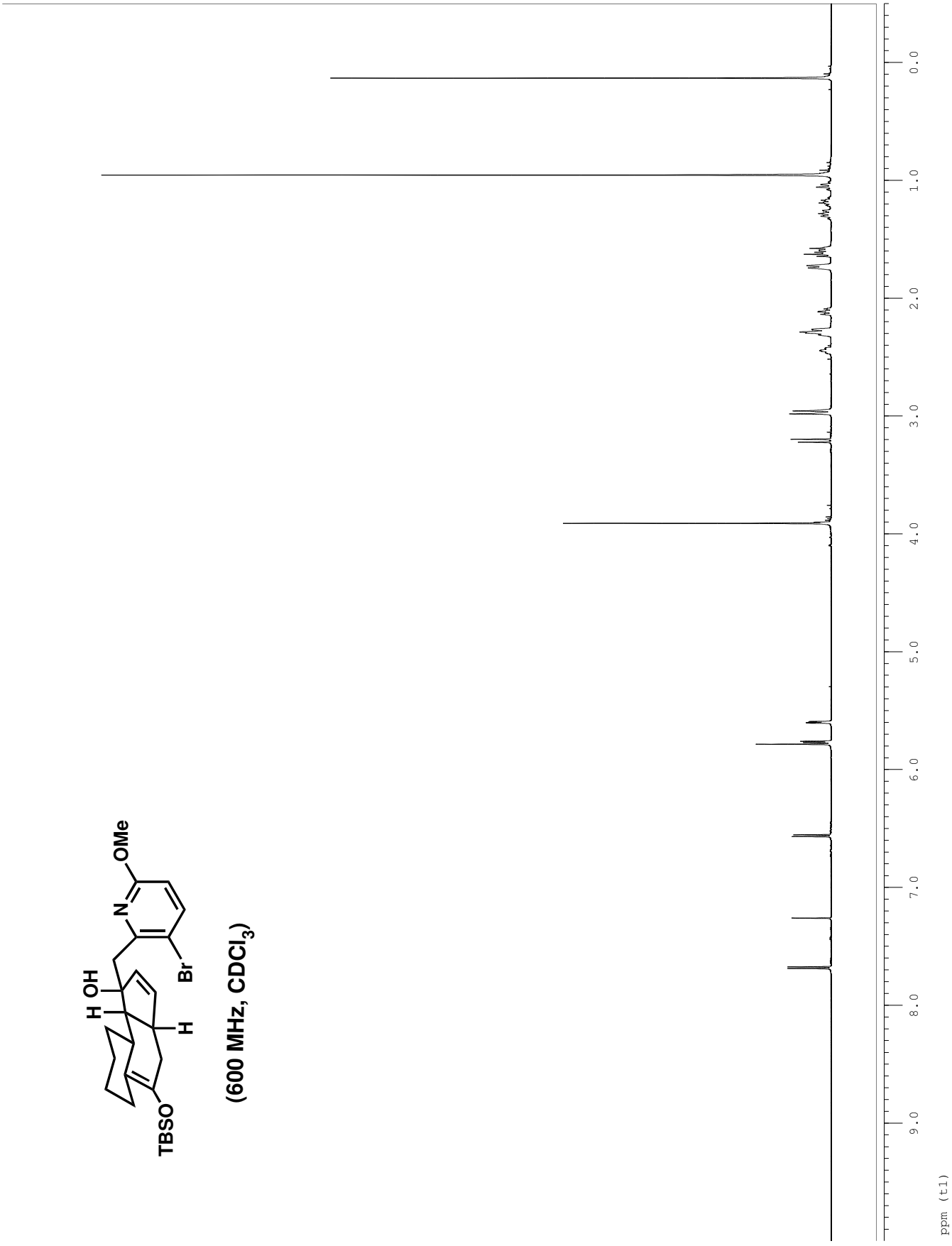
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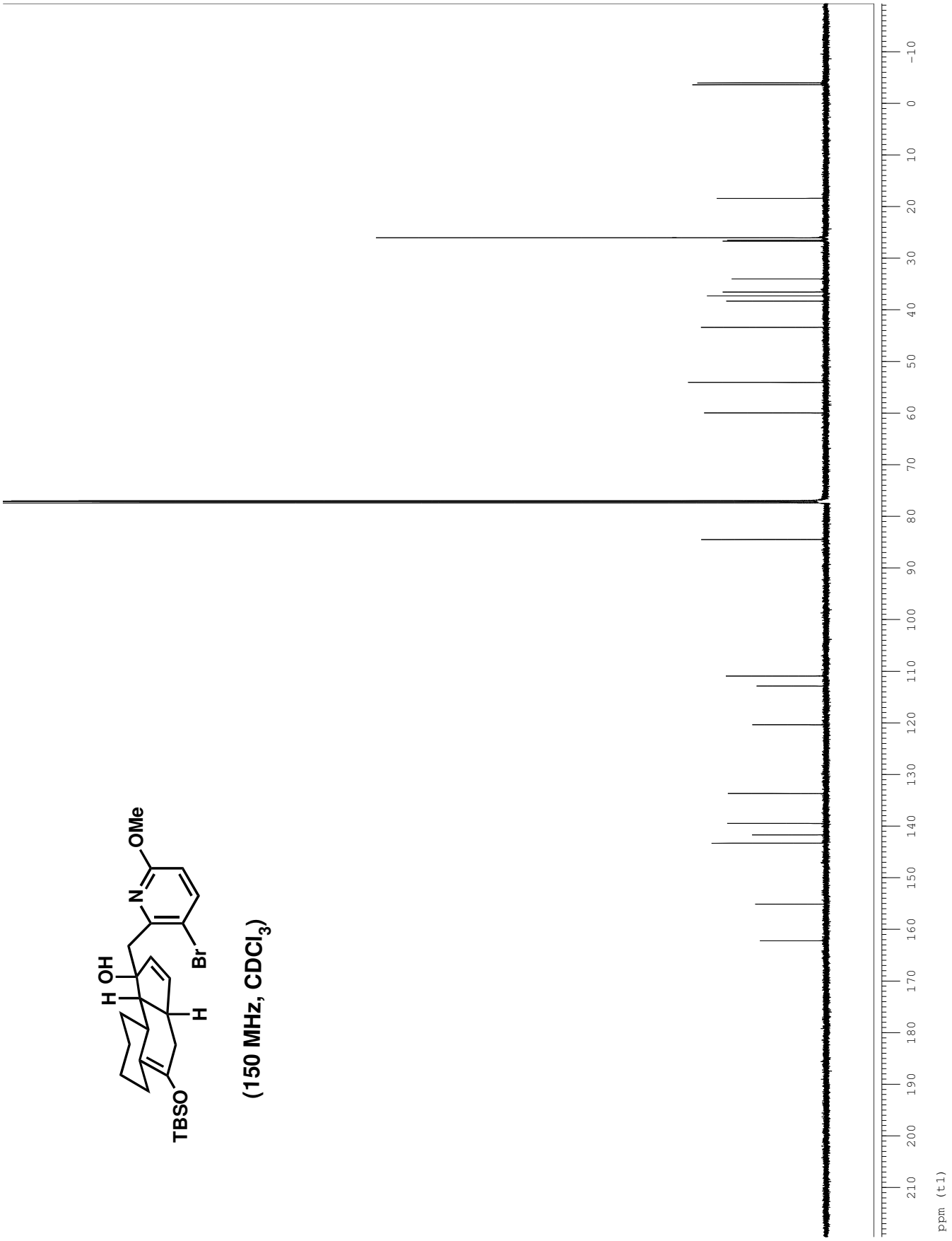
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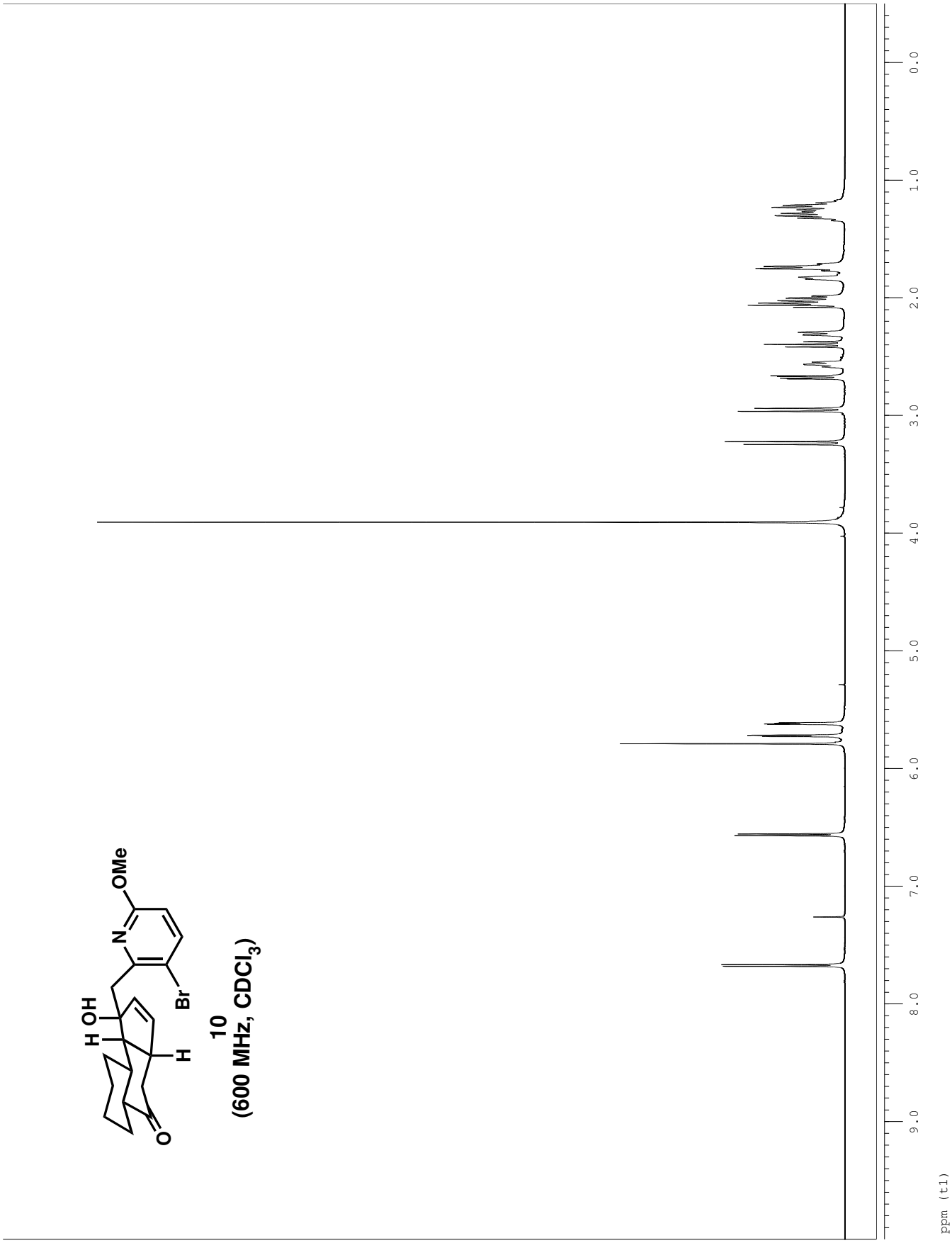
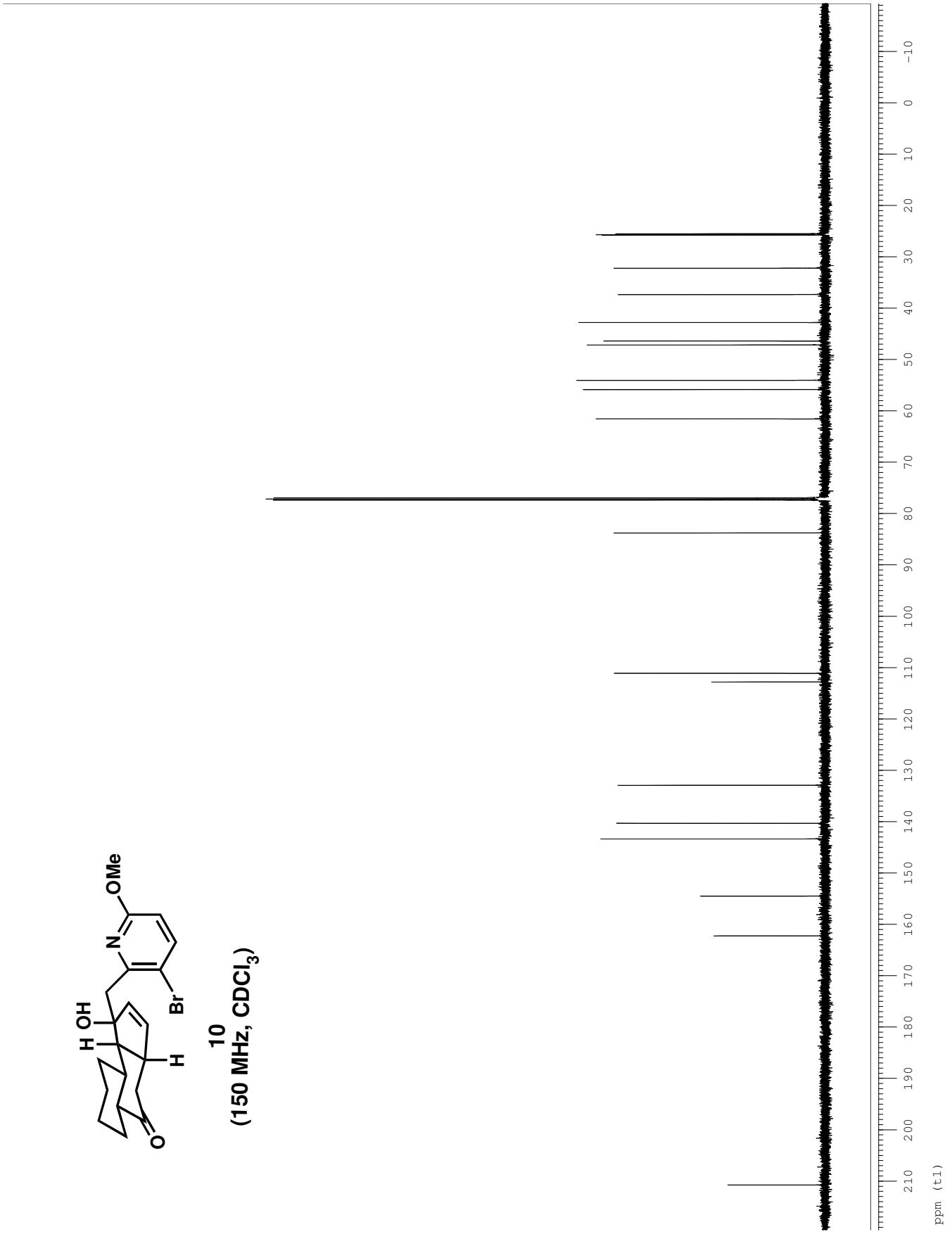
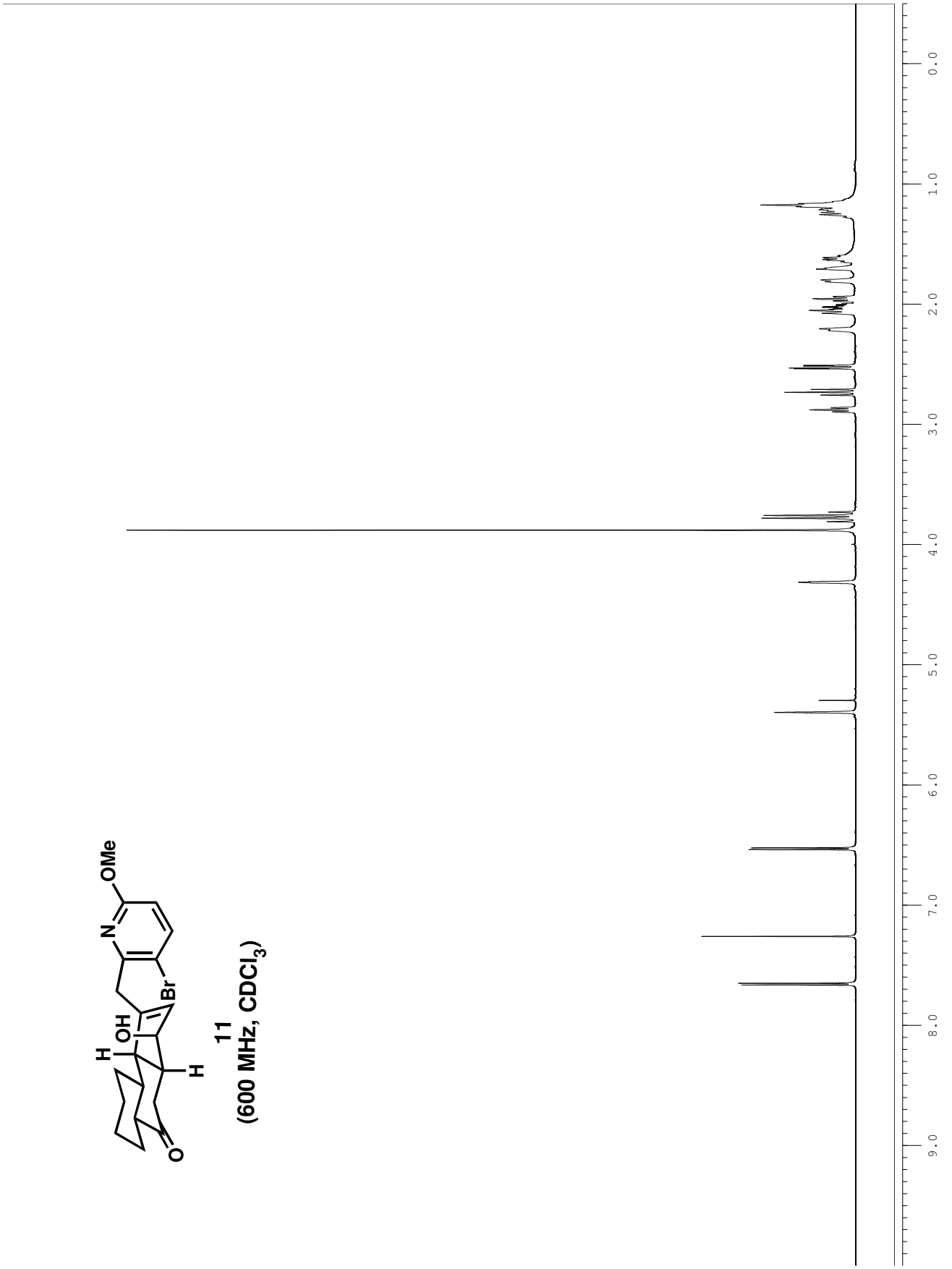
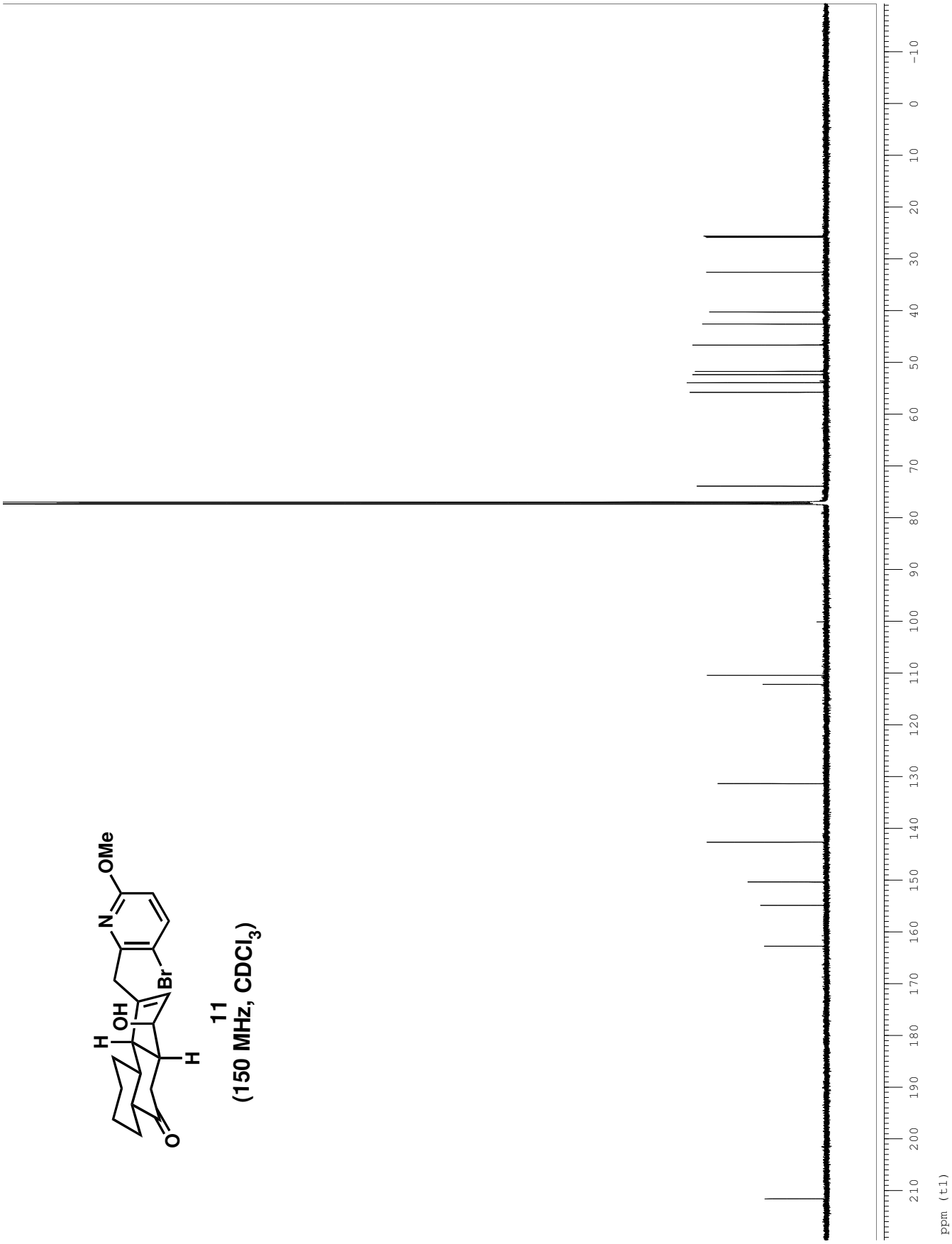
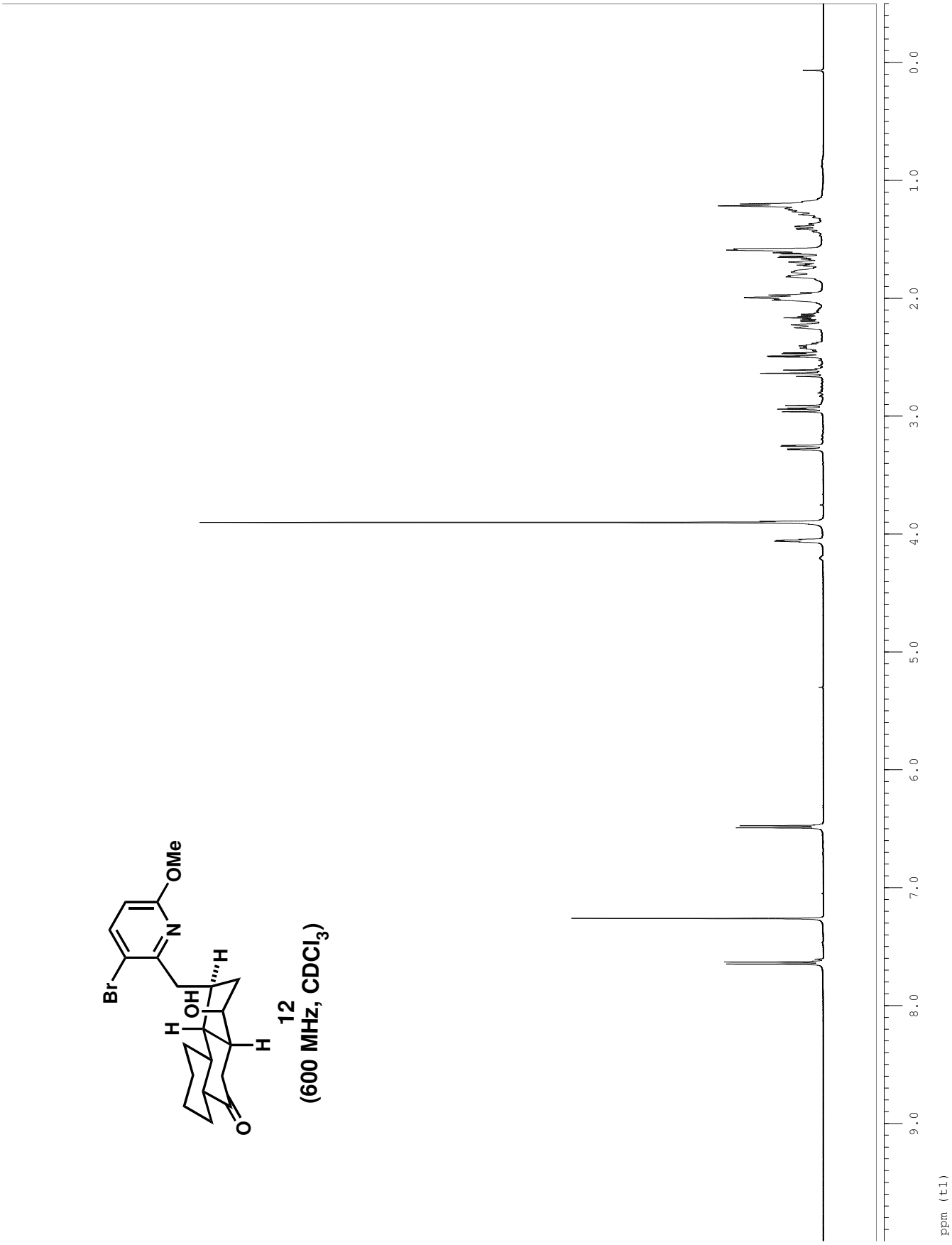
(150 MHz, CDCl3)
ppm (t1)

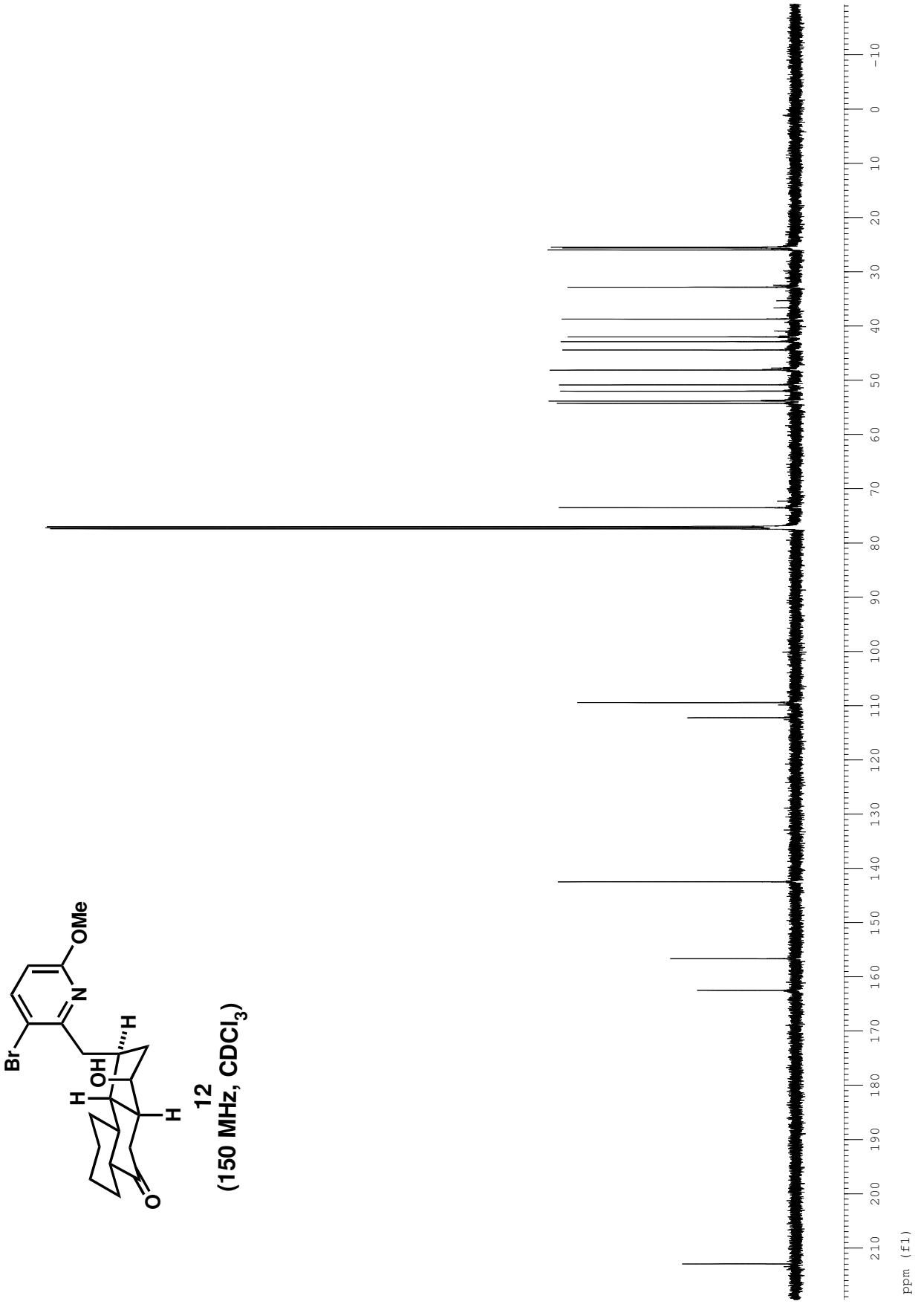

OMe
N
Br
H OH
H
O
10
(600 MHz, $CDCl_3$)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

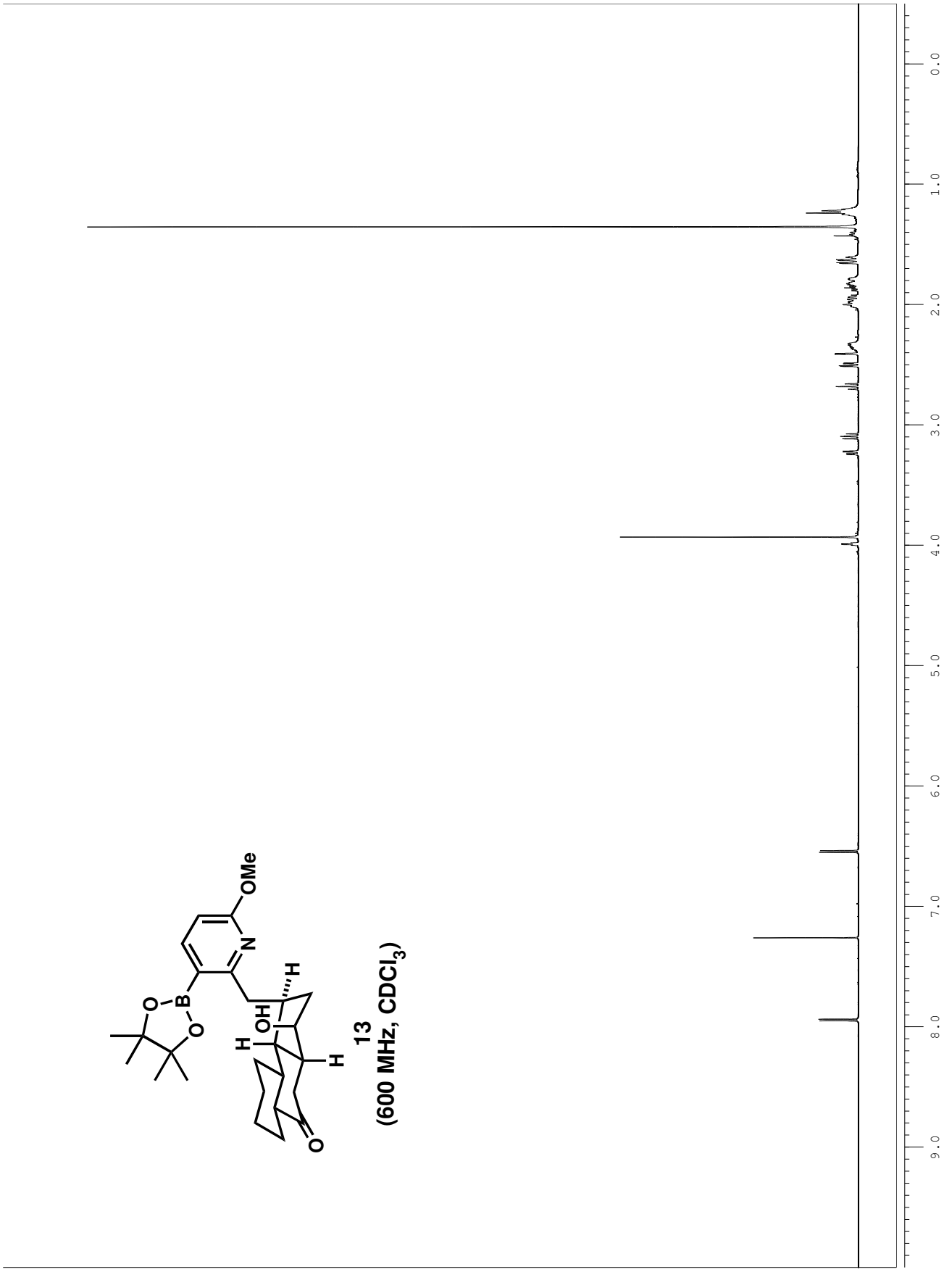

OMe
N
Br
H OH
H
O
10
(150 MHz, CDCl3)
ppm (t1)

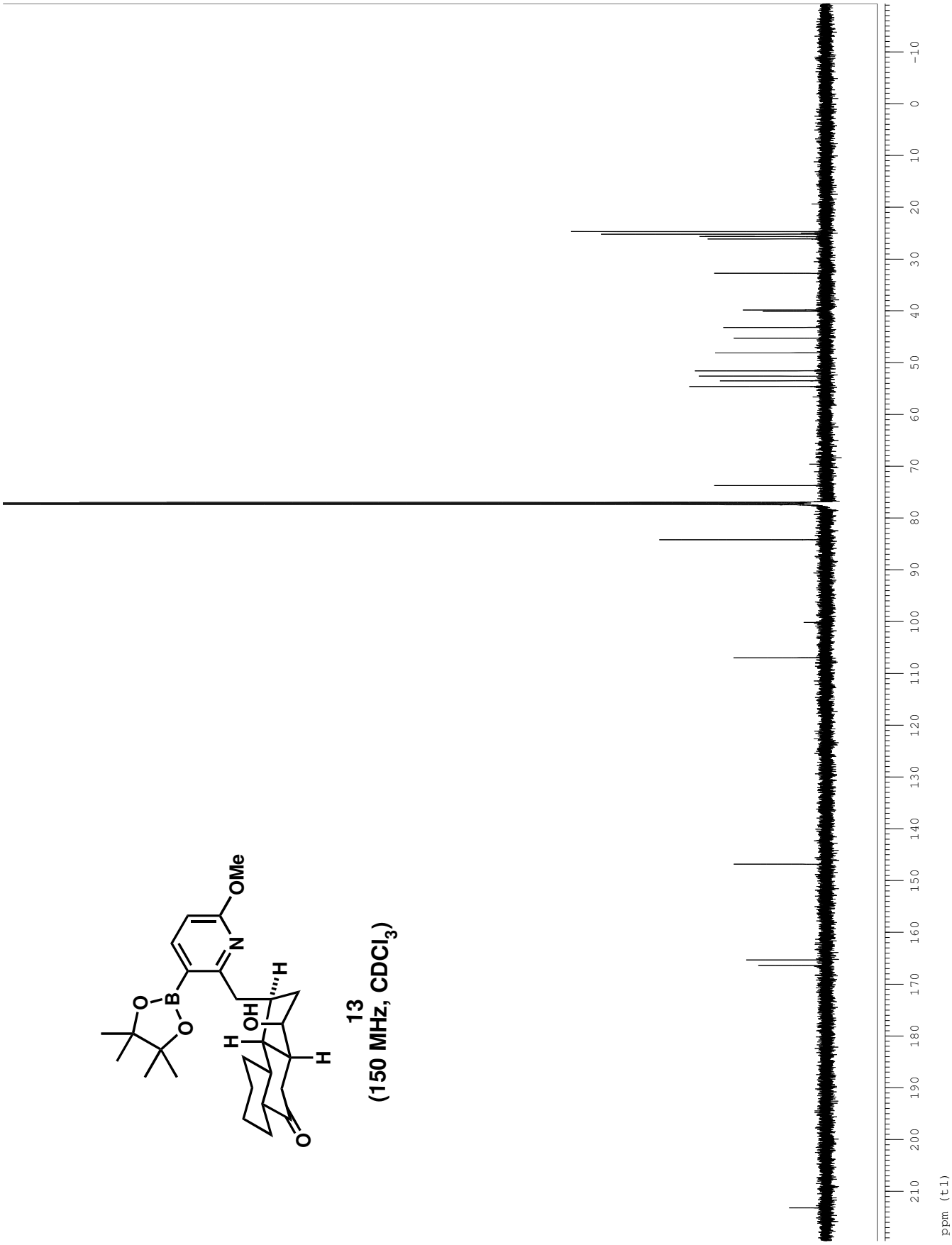

OMe
N
Br
OH
H
H
O
11
(600 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

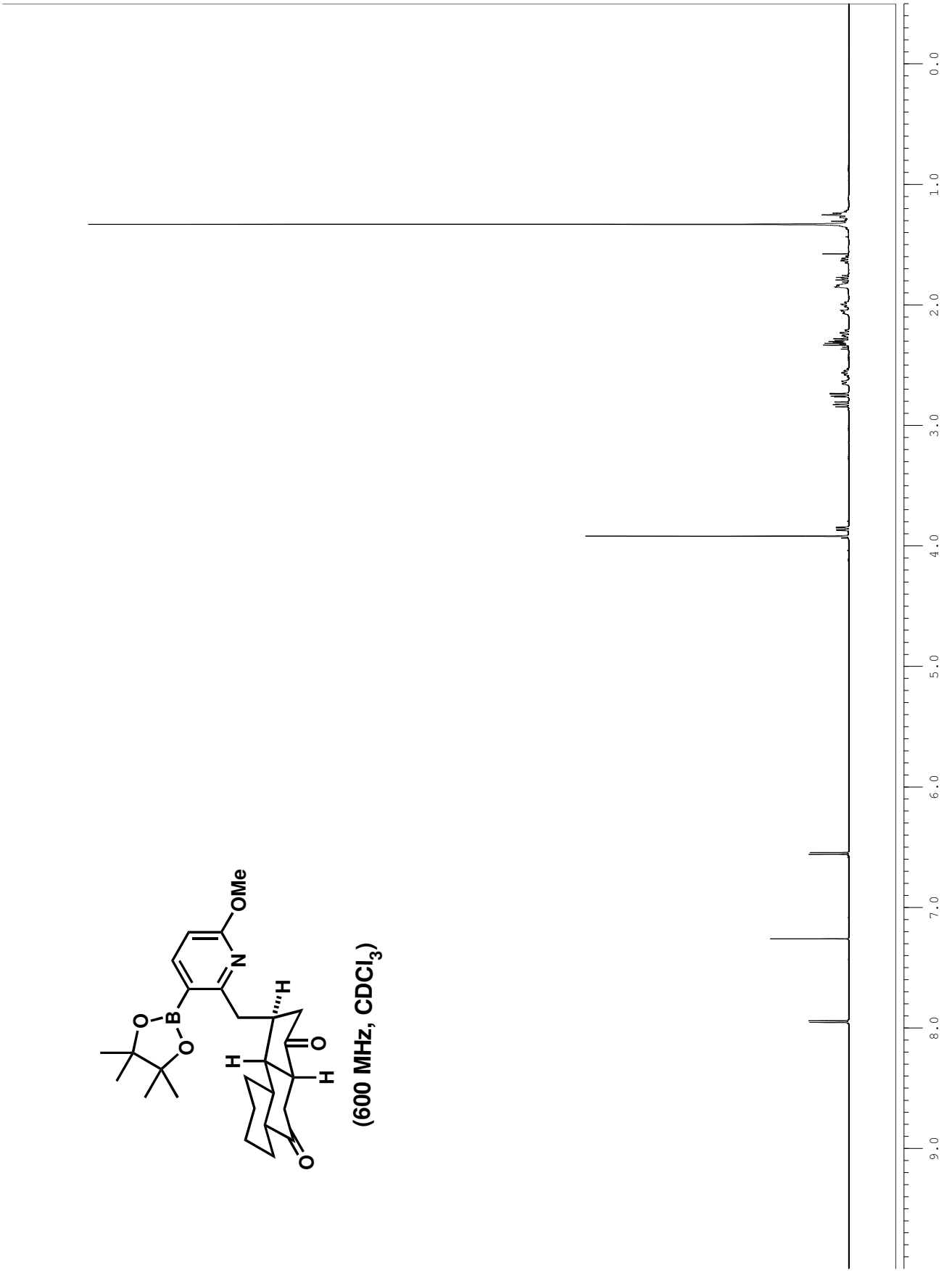

OMe
N
Br
OH
H
H
O
11
(150 MHz, CDCl3)
ppm (t1)

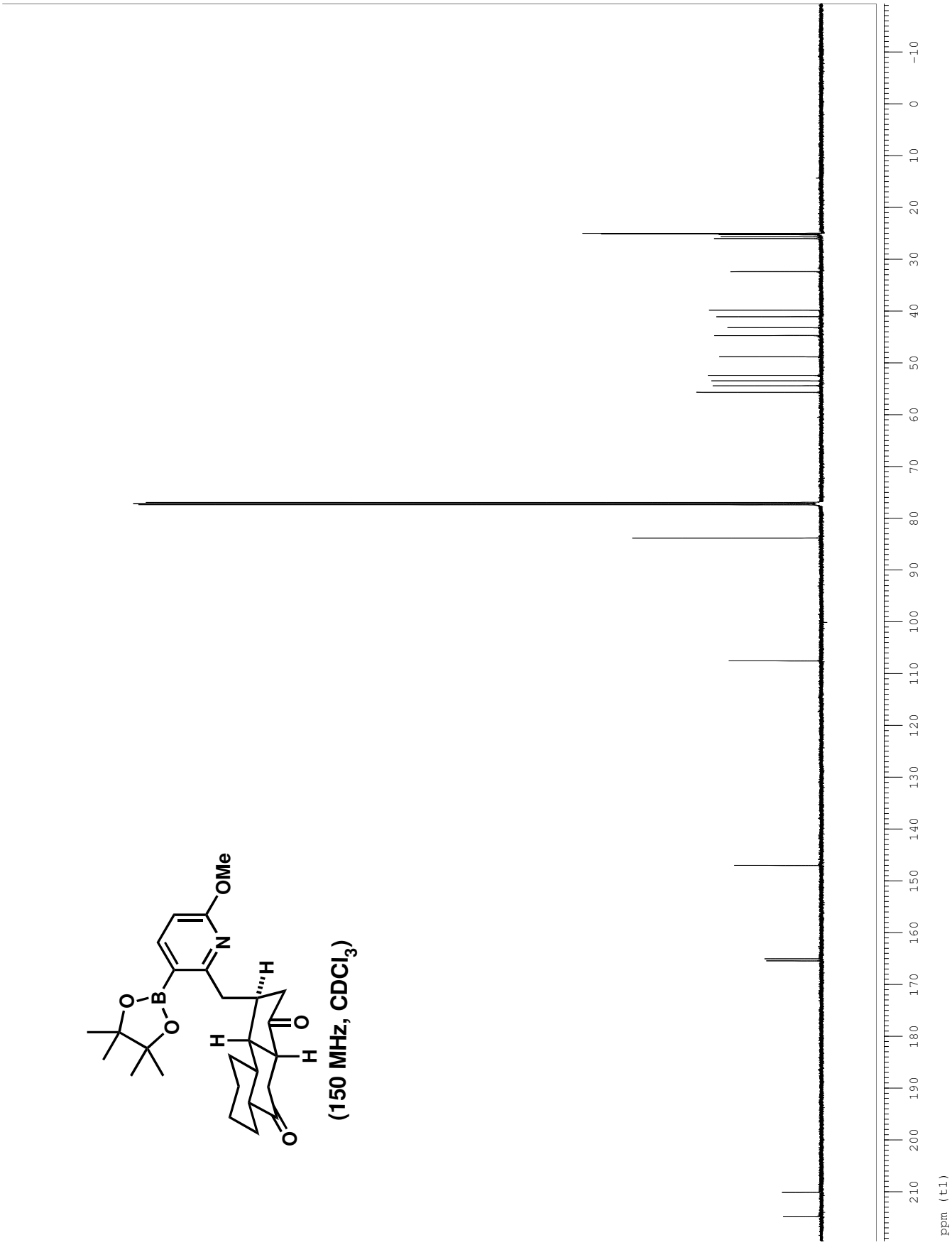

OMe
N
Br
H
OH
H
O
12
(600 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

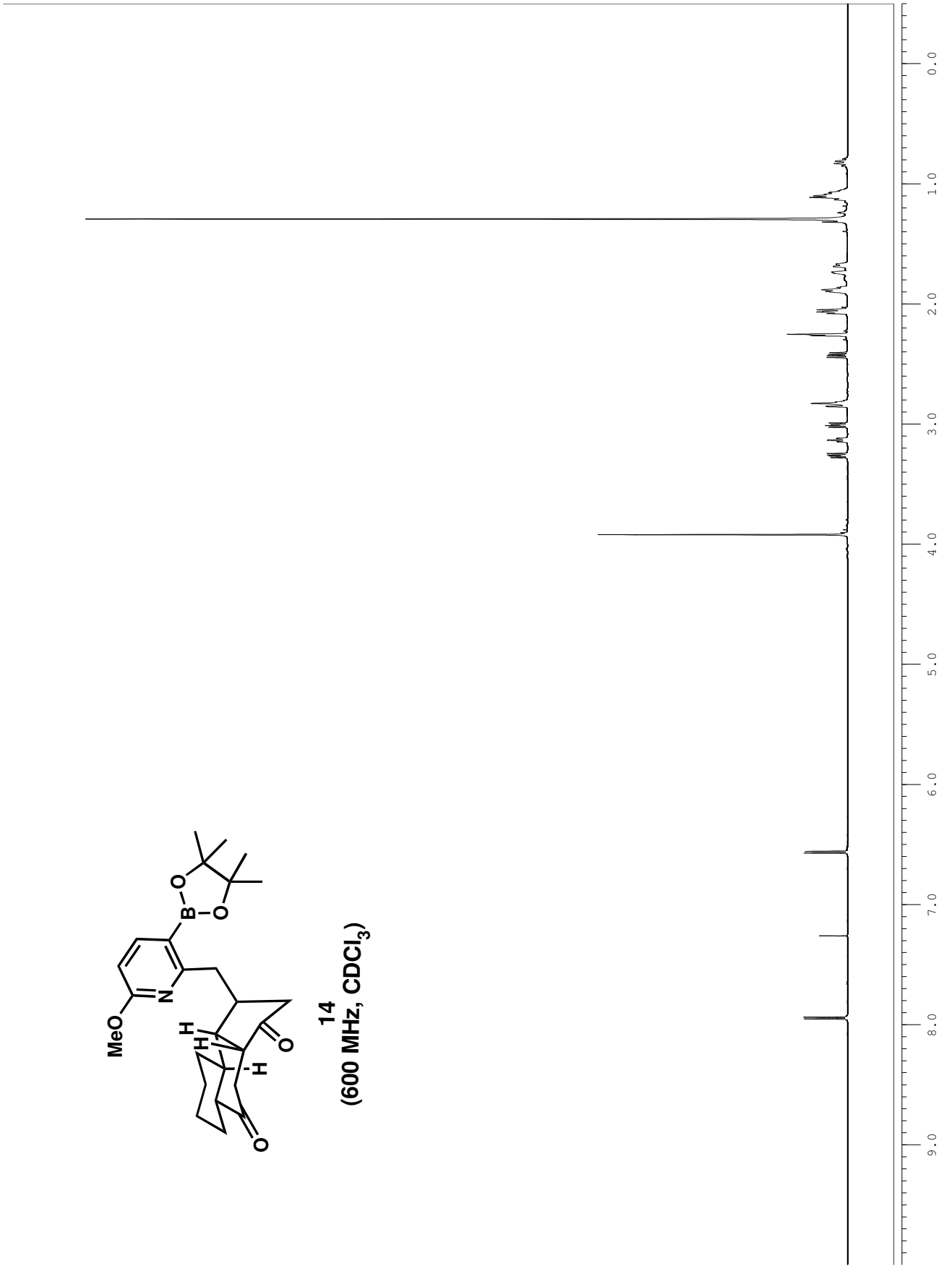

Br
OMe
N
H
OH
H
H
O
12
(150 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (f1)

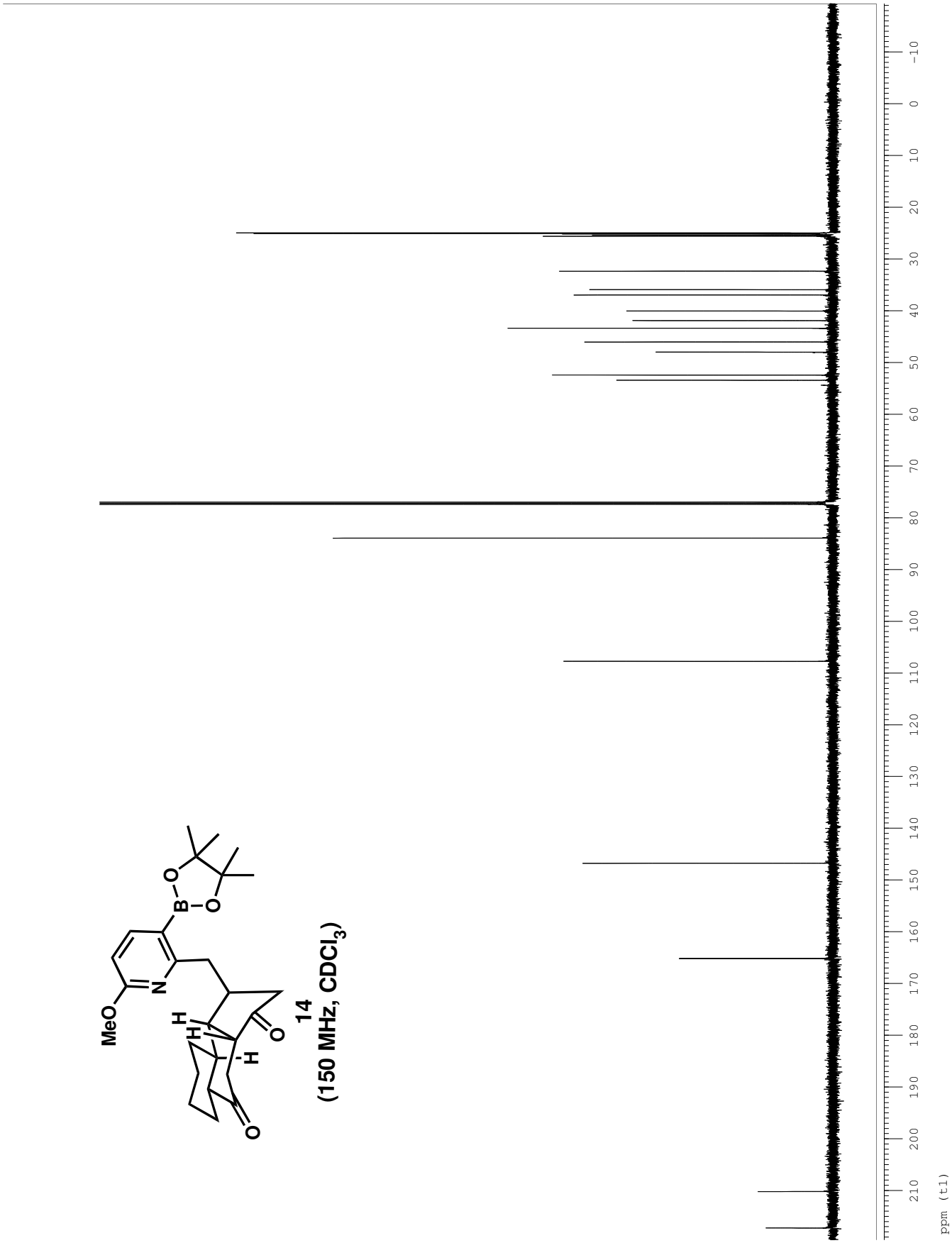

OMe
N
B
O
O
H
OH
H
O
13
(600 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

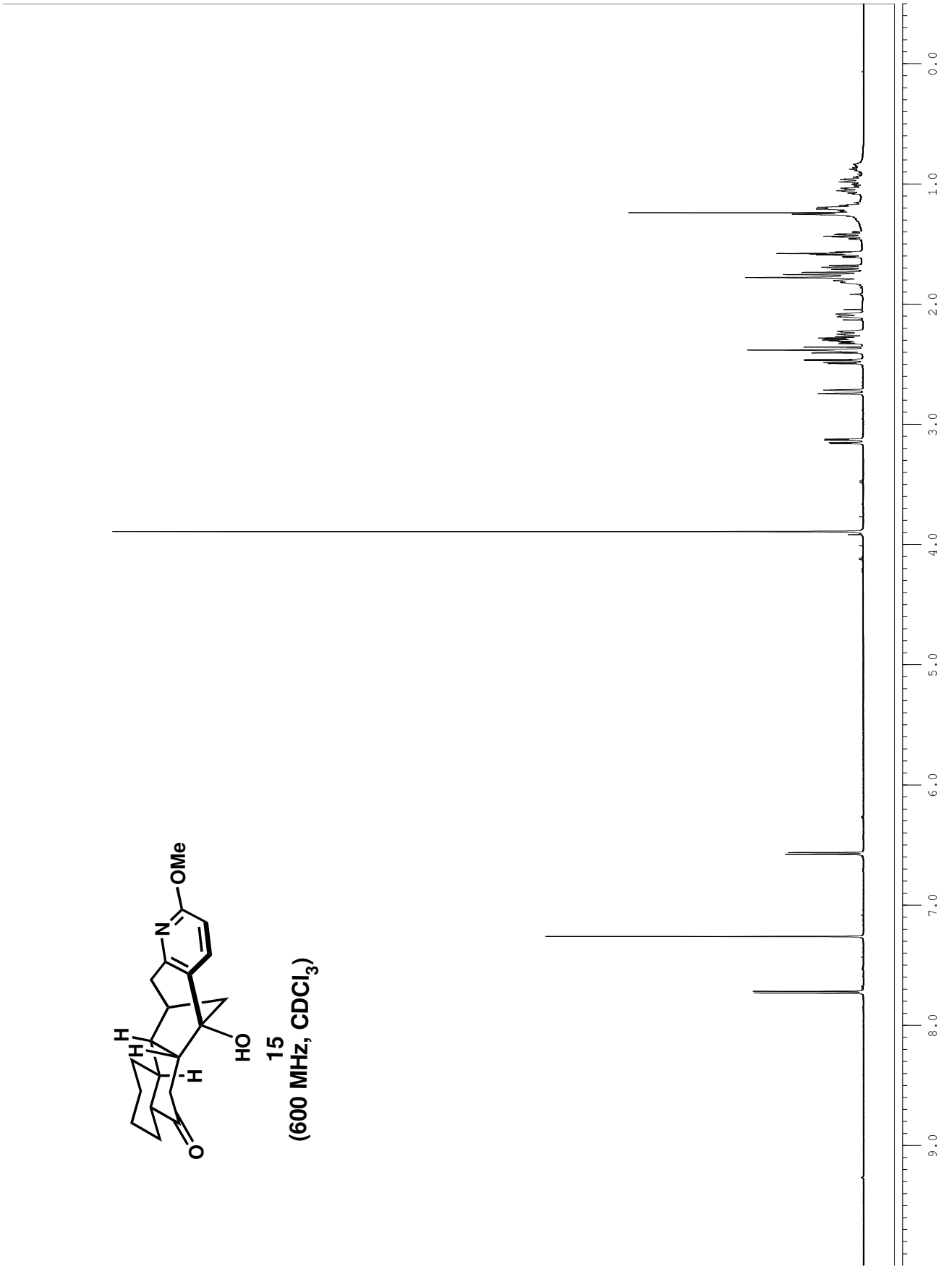

OMe
N
B
O
O
H
OH
H
H
O
13
(150 MHz, CDCl3)
ppm (t1)

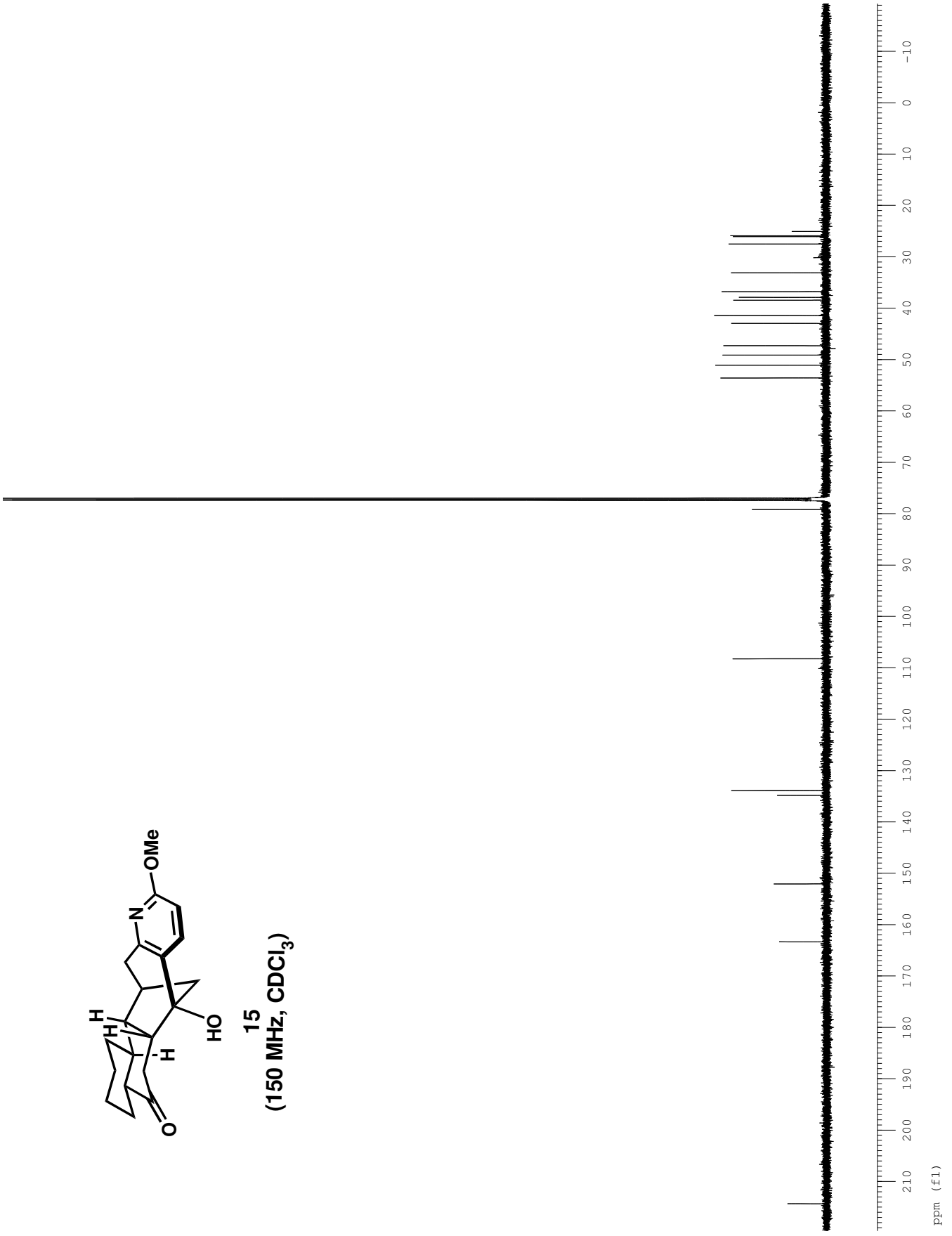

OMe
N
H
O
B
O
O
H
H
O
(600 MHz, CDCl3)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OMe
N
B
O
O
H
H
O
O
(150 MHz, CDCl3)
ppm (t1)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

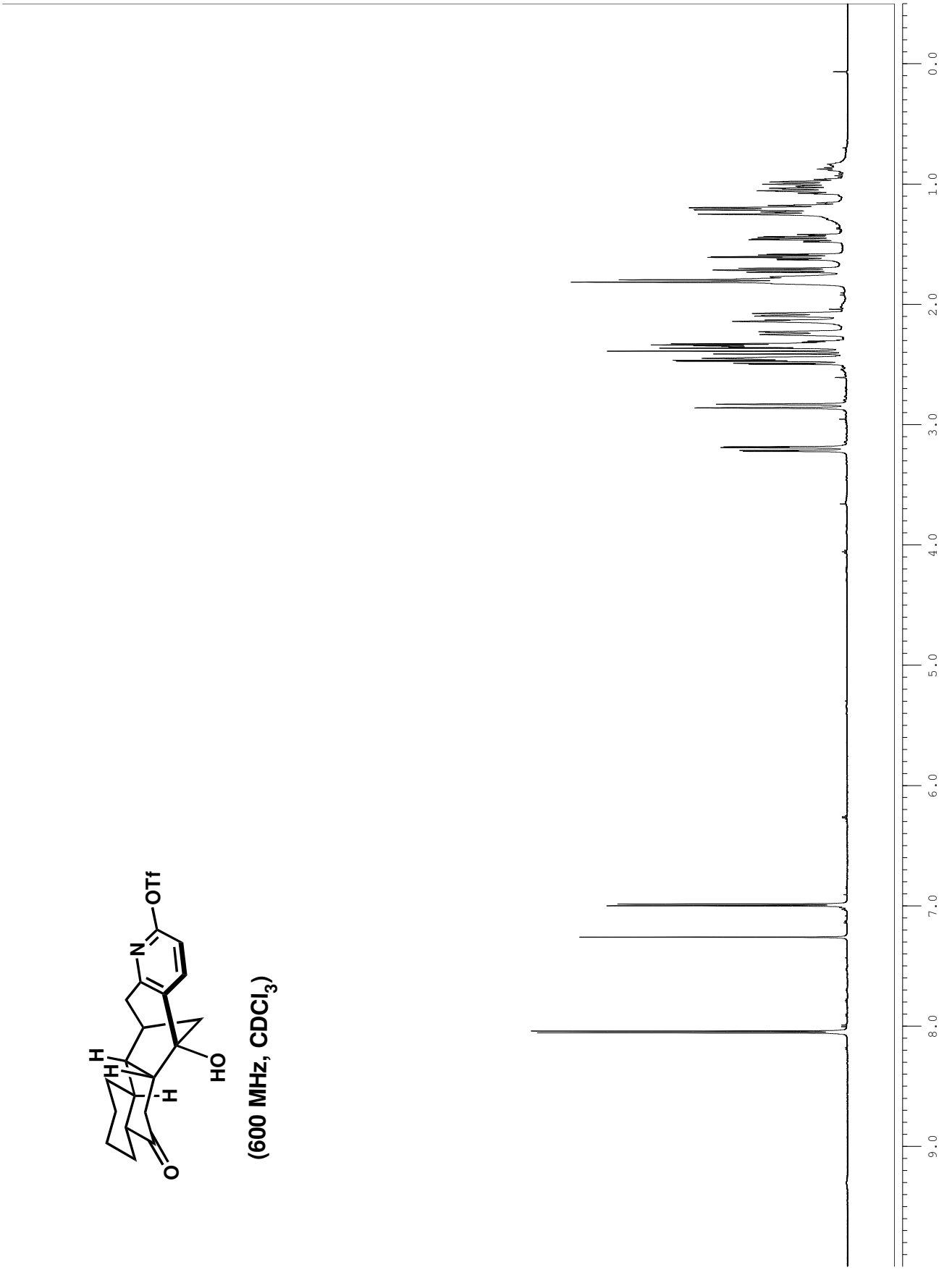

MeO
N
B
O
O
O
H
H
H
O
O
14
(600 MHz, CDCl3)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)

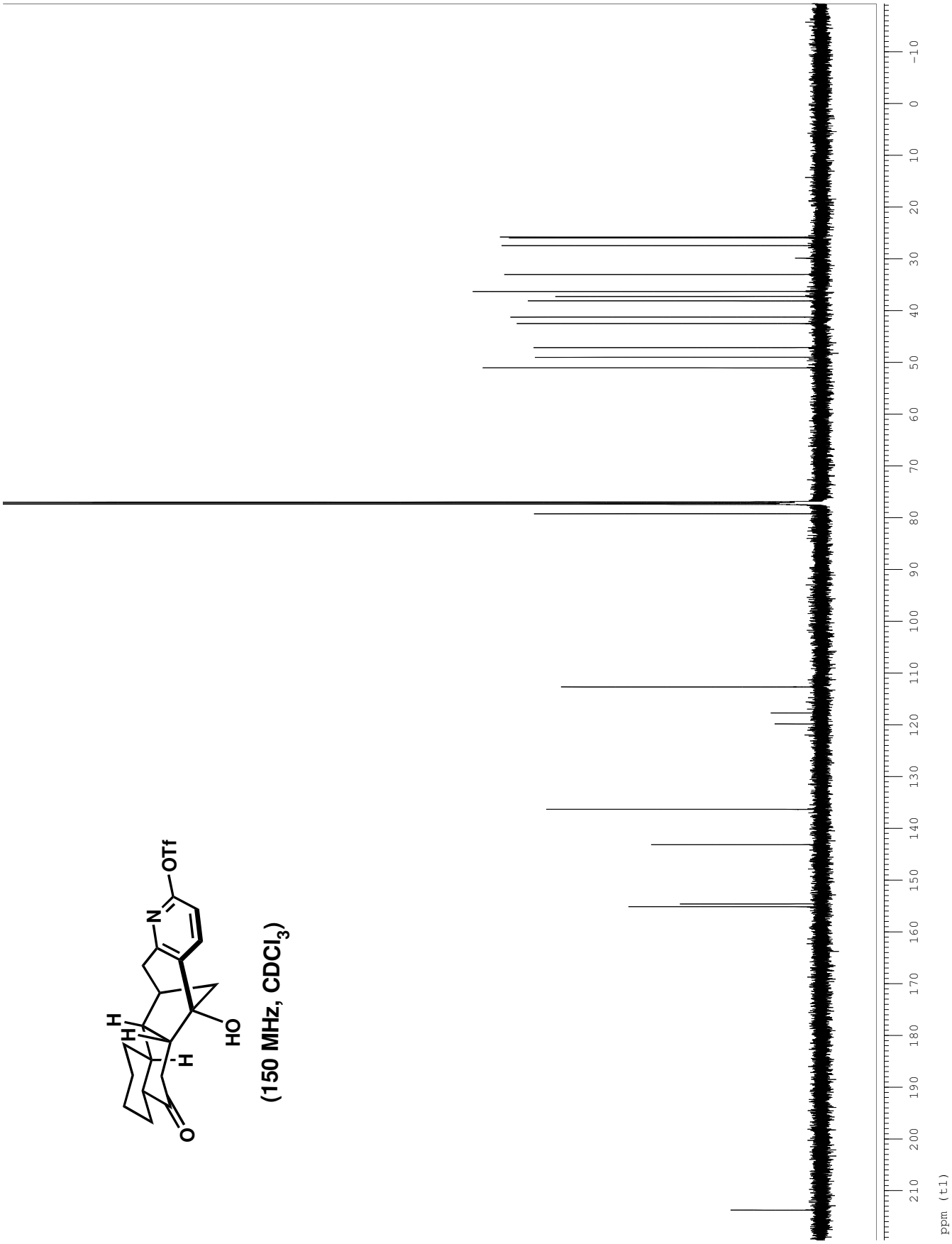

MeO
N
B
O
O
H
H
H
O
O
14
(150 MHz, CDCl3)
ppm (t1)

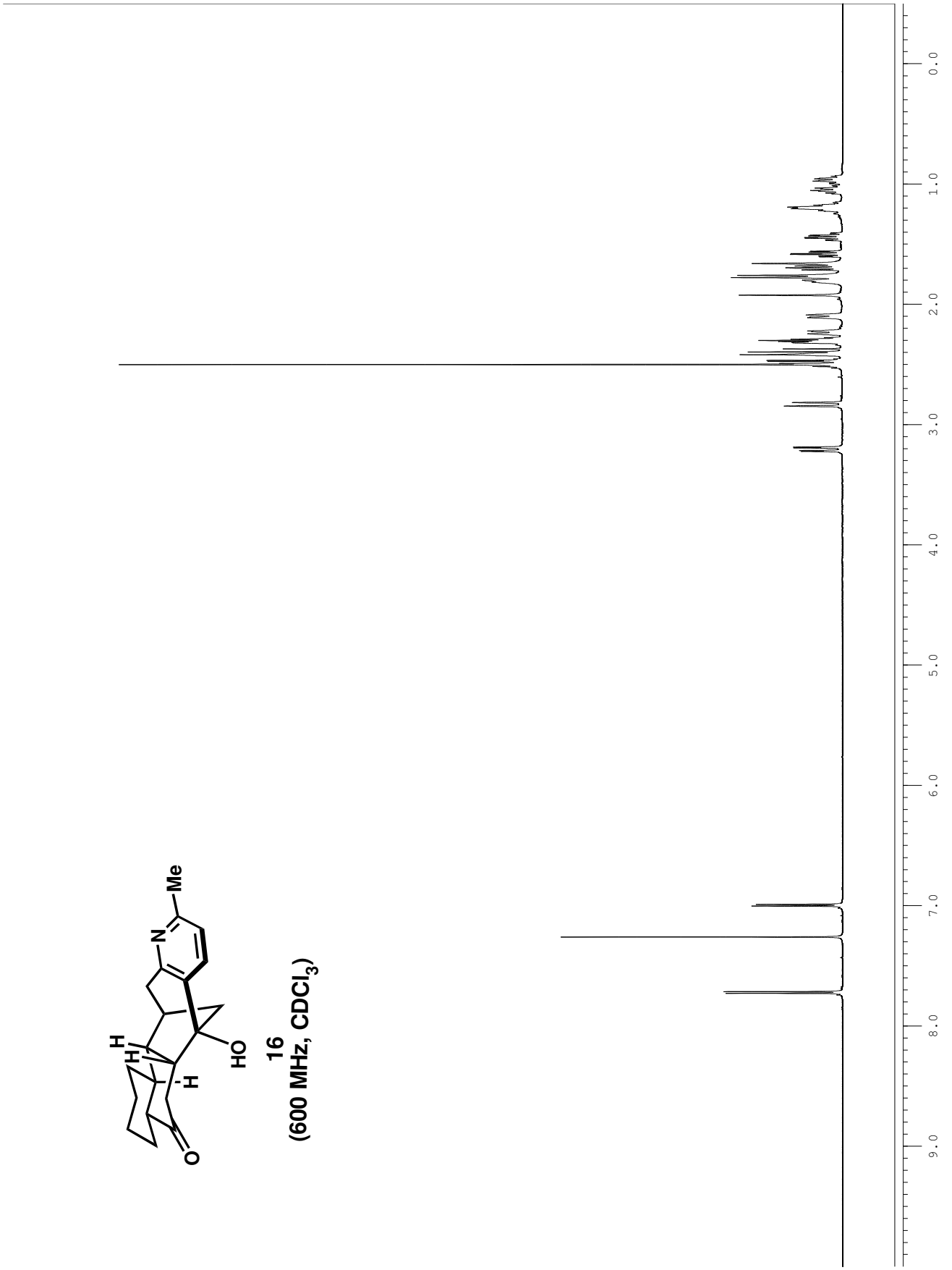

OMe
N
H
H
H
HO
O
15
(600 MHz, $CDCl_3$)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)

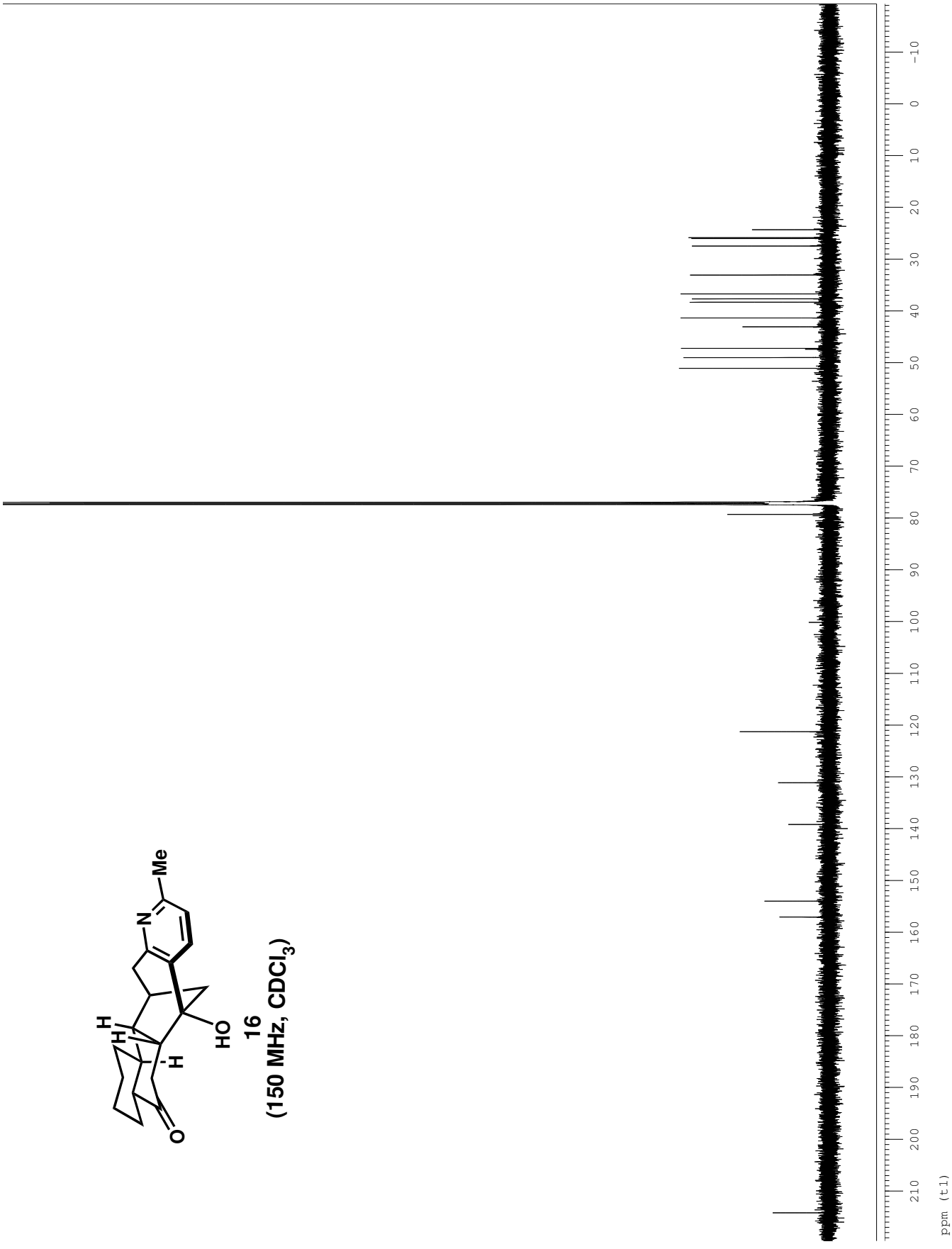


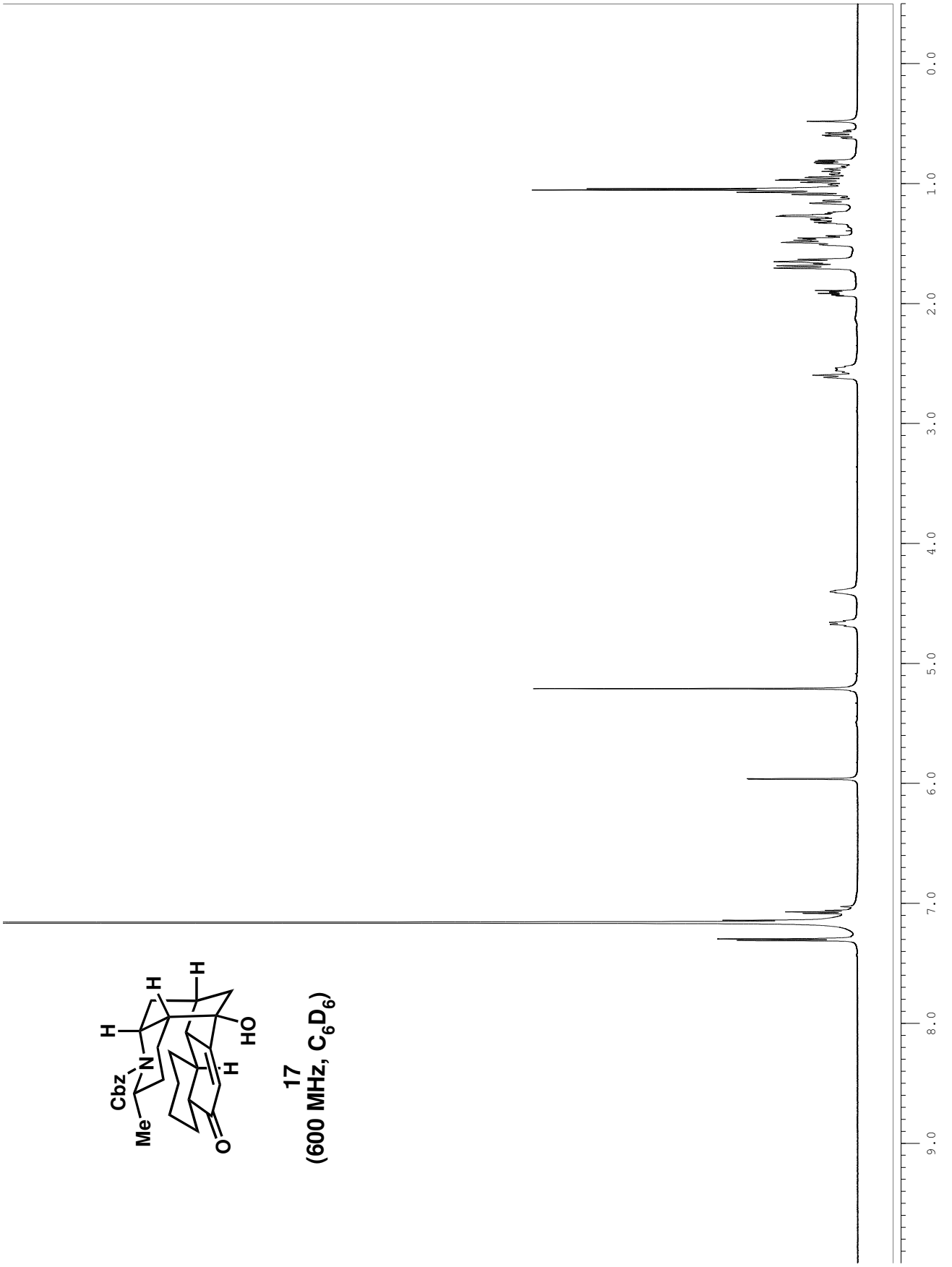

**15**
**(150 MHz, $CDCl_3$)**

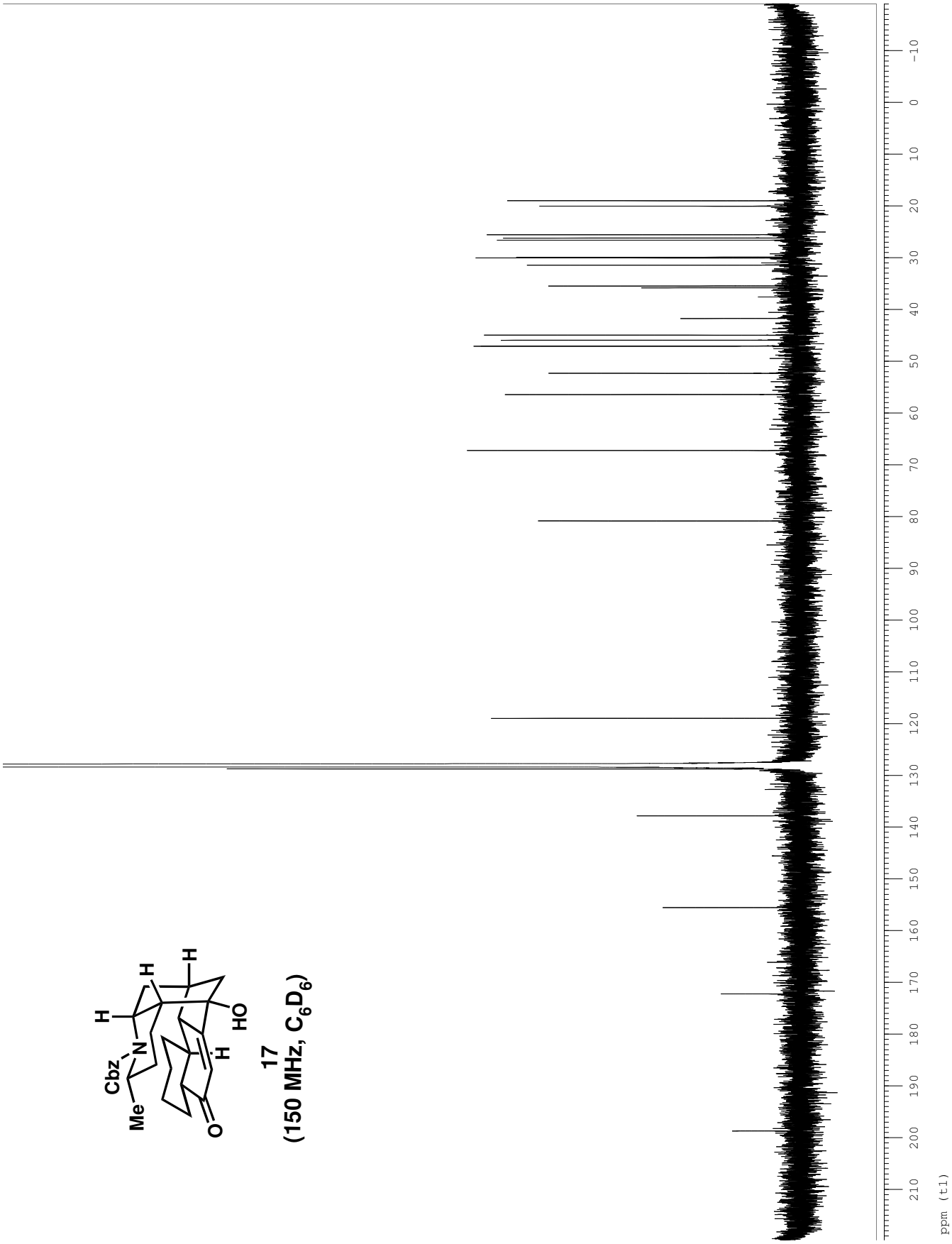

OTf
N
H
H
H
HO
O
(600 MHz, CDCl3)
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (t1)


OTf
N
H
H
H
HO
O
(150 MHz, CDCl3)
ppm (t1)

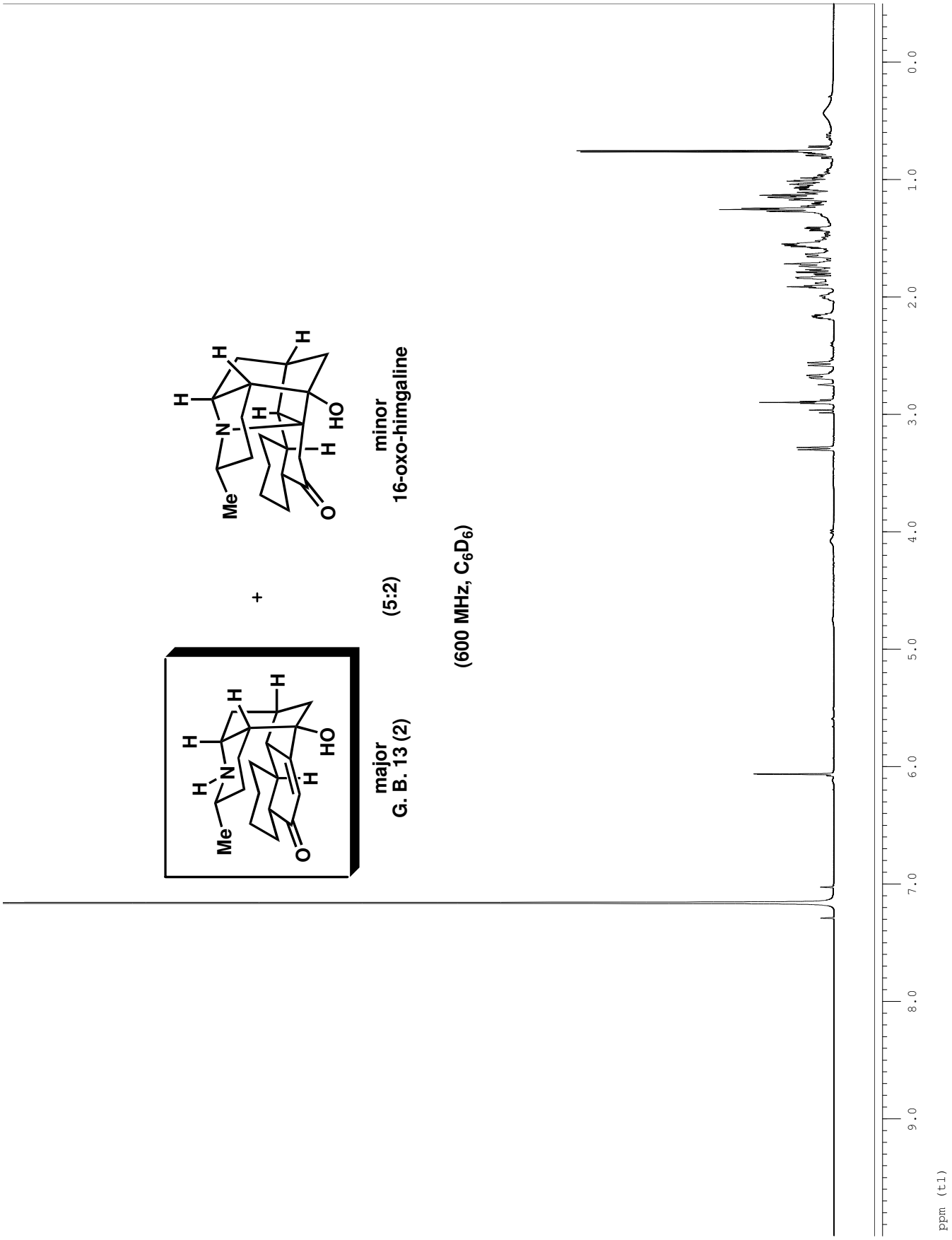

Me
N
H
H
H
HO
O
16
(600 MHz, $CDCl_3$)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

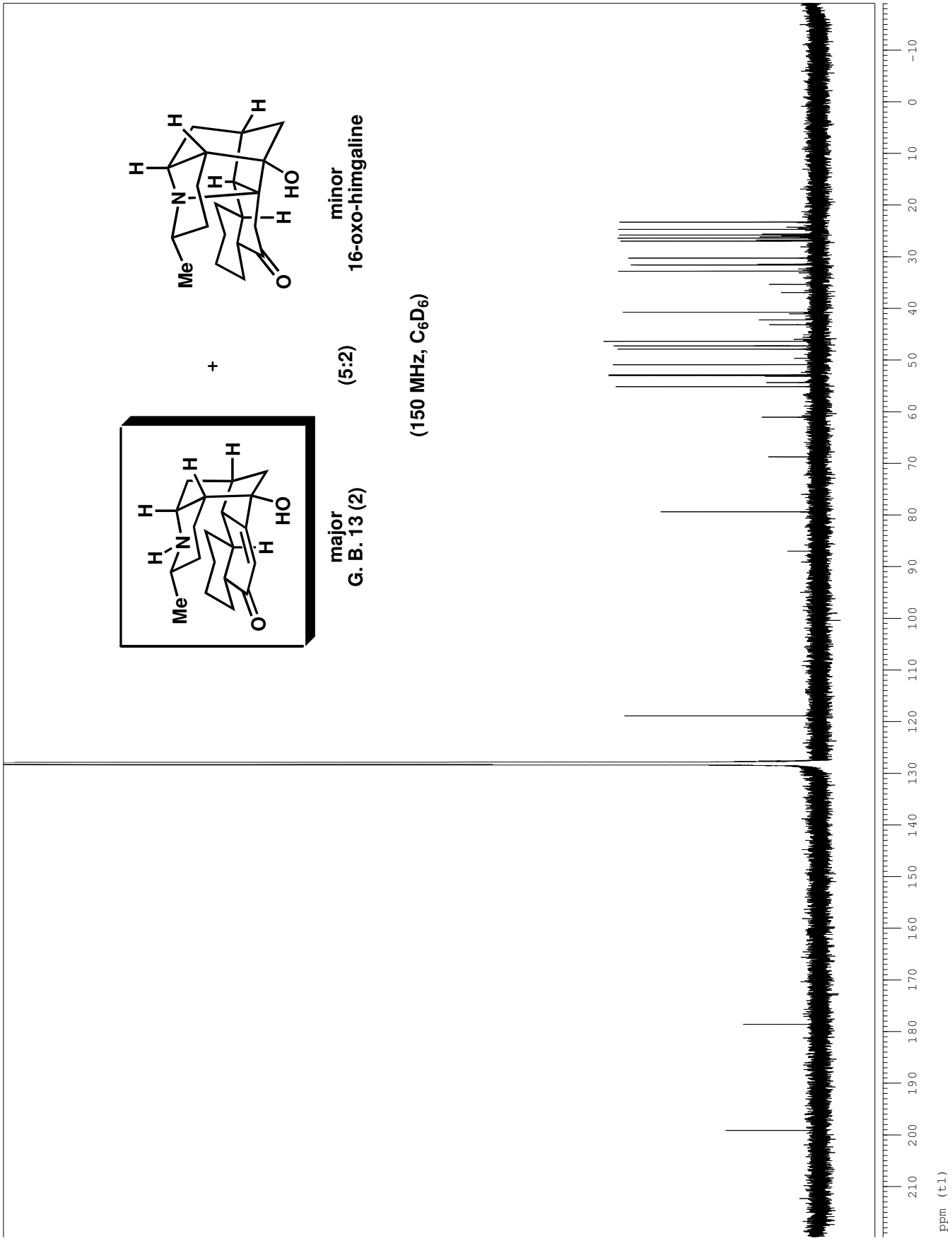

Me
N
H
H
H
HO
O
16
(150 MHz, CDCl3)
ppm (t1)


H
H
H
HO
Cbz
N
Me
H
O
17
(600 MHz, $C_6D_6$)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)




**17**
**(150 MHz, $C_6D_6$)**


major
G. B. 13 (2)
(5:2)
minor
16-oxo-himgaline
(600 MHz, C6D6)
ppm (t1)


major
G. B. 13 (2)
(5:2)
minor
16-oxo-himgaline
(150 MHz, C6D6)
ppm (t1)

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