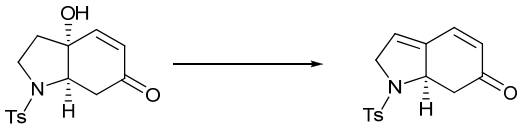
Supporting information for

Flexible Synthesis of Montanine-like Alkaloids: Revisiting the Structure of Montabuphine.

Yifu Guan, Hongbin Zhang,* Chengxue Pan, Jia Wang, Rong Huang, Qilin Li

Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, School of Chemical Science and Technology, Yunnan University, Kunming, Yunnan 650091, P. R. China Fax: 86-871-5035538. E-mail: zhanghb@ynu.edu.cn or zhang_hongbin@hotmail.com

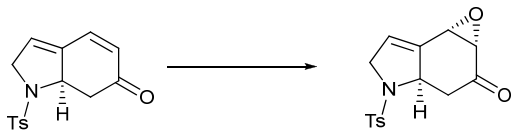
General Experimental: Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz or on a Bruker Avance DRX500 spectrometer at 500 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded on a Bruker Avance 300 spectrometer at 75 MHz or on a Bruker Avance DRX500 spectrometer at 125 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. Low-resolution Mass spectra were recorded on a VG Auto Spec-3000 magnetic sector MS spectrometer. High Resolution Mass spectra were taken on an AB QSTAR Pulsar mass spectrometer. Starting materials and reagents used in reactions were obtained commercially from Acros, Aldrich, Fluka and were used without purification, unless otherwise indicated. THF and dimethyl ether used in the reactions were dried by distillation over metallic sodium and benzophenone; DMF and dichloromethane were distilled over CaH_2. Unless otherwise stated, all reactions were conducted in dried glassware under a positive pressure of dry nitrogen and monitored by thin layer chromatography (TLC). Silica gel (Qingdao, 200-300 mesh) was used for column chromatography.



10 $C_{15}H_{15}NO_3S$ Mol. Wt.: 289.35

To a solution of compound **9a** (2.0 g, 6.5 mmol) in anhydrous pyridine (30 mL) was added dropwise a solution of phosphorous oxychloride ($POCl_3$, 1.51 mL, 1.645 g/mL, 16.2 mmol, 2.5 eq.) at room temperature. The resulting mixture was then stirred at room termperature overnight. This mixture was cooled to 0 ºC, and a saturated aqueous solution of sodium biscarbonate was added (until pH = 8.0). After stirring for 10 minutes, the mixture was extracted with dichloromethane (3×80 mL) and the combined organic phases were washed with water (30 mL) and brine (30 mL). The organic phase was then dried over anhydrous sodium sulfate. After filtration and removal of the solvent, the residue was chromatographed on silica gel (CH_2Cl_2: ethyl acetate = 50:1) to provide enone **10** (1.3 g, 69%).

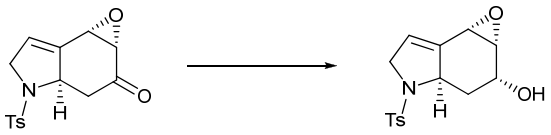
10: white plates, m.p.: 168-169 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.72 (2H, *d*, *J* = 7.8 Hz), 7.36 (2H, *d*, *J* = 7.8 Hz), 7.13 (1H, *d*, *J* = 9.9 Hz), 6.01 (1H, *d*, *J* = 9.9 Hz), 5.89 (1H, *s*), 4.58-4.38 (2H, *m*), 4.14 (1H, *brd*, *J* = 14.7 Hz), 3.36 (1H, *dd*, *J* = 5.1, 15.6 Hz), 2.73 (1H, *dd*, *J* = 12.3, 15.6 Hz), 2.44 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 196.82, 144.23, 137.44, 134.78, 132.86, 130.02, 129.90, 127.85, 124.40, 62.69, 57.04, 46.72, 21.54. **EIMS** *m*/*z* (%) : 289 (M^+, 84%), 261 (1), 224 (2), 155 (36), 134 (79), 116 (13), 106 (49), 91 (100), 77 (46), 65 (54). **HRMS** *m*/*z* Found: 289.0773, Calcd. for $C_{15}H_{15}NO_3S$ $(M)^+$: 289.0773.



10a $C_{15}H_{15}NO_4S$ Mol. Wt.: 305.35

To a solution of enone **10** (2.0 g, 6.9 mmol) in methanol (60 mL) and water (1.4 mL) was added a powder of sodium hydroxide (276 mg, 6.9 mmol, 1.0 eq.) at 0 ºC. Hydrogen peroxide (35% wt. % in H_2O, 1.2 mL, 12.4 mmol, 2.0 eq.) was introduced and the reaction mixture was stirred at 0 ºC for 1.5 hours. The mixture was then extracted with dichloromethane (3×80 mL) and washed with water (30 mL) and brine (30 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, CH_2Cl_2: EtOAc = 40:1) to afford the epoxide as white plates (1.8 g, 86%).

10a: white plates, m.p.: 212-213 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.71 (2H, *d*, *J* = 8.1 Hz), 7.35 (2H, *d*, *J* = 8.1 Hz), 5.92 (1H, *d*, *J* = 1.8 Hz), 4.71-4.58 (1H, *m*), 4.29 (1H, *ddd*, *J* = 2.1, 5.7, 14.8 Hz), 4.14 (1H, *ddd*, *J* = 2.1, 3.0, 14.8 Hz), 3.94 (1H, *d*, *J* = 3.9 Hz), 3.48 (1H, *d*, *J* = 3.9 Hz), 3.30 (1H, *dd*, *J* = 6.9, 18.6 Hz), 2.55 (1H, *dd*, *J* = 9.3, 18.6 Hz), 2.44 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 201.70, 144.16, 134.67, 133.42, 130.04, 127.67, 123.16, 58.92, 57.07, 56.63, 51.83, 47.19, 21.54. **EIMS** *m*/*z* (%) : 305 (M^+, 16%), 289 (5), 276 (22), 263 (11), 247 (4), 234 (2), 216 (1), 155 (37), 150 (35), 139 (12), 122 (52), 108 (18), 94 (40), 91 (100), 80 (28), 67 (17), 65 (46). **HRMS** *m*/*z* Found: 305.0726, Calcd. for $C_{15}H_{15}NO_4S$ $(M)^+$: 305.0722.

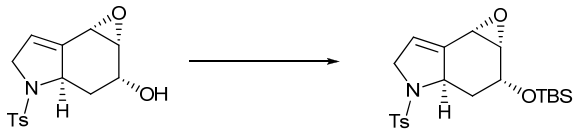


11 $C_{15}H_{17}NO_4S$ Mol. Wt.: 307.36

To a solution of epoxide **10a** (1.99 g, 6.5 mmol) in anhydrous THF (15 mL) and dichloromethane (45 mL) at -78°C was added dropwise a solution of L-selectride (1.0 M in THF, 13 mL, 13.0 mmol, 2.0 eq.) over a period of 15

minutes. The reaction mixture was then stirred at -78°C for 1.5 hours before treated with a saturated aqueous solution of ammonium chloride (2.0 mL). The resulting mixture was allowed to warm gradually to room temperature and diluted with dichloromethane (250 mL). The combined organic phase was washed with water (30 mL) and brine (30 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, CH_2Cl_2: EtOAc = 30: 1) to afford the alcohol **11** (1.91 g, 96%) as white needles.

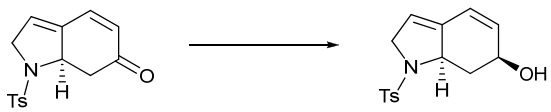
11: colorless crystals, m.p.: 178-180 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.72 (2H, *d*, *J* = 8.1 Hz), 7.33 (2H, *d*, *J* = 8.1 Hz), 5.77 (1H, *s*), 4.42-4.30 (2H, *m*), 4.27 (1H, *ddd*, *J* = 2.1, 5.4, 13.8 Hz), 4.11 (1H, *brd*, *J* = 13.8 Hz), 3.78 (1H, *d*, *J* = 3.9 Hz), 3.62 (1H, *t*, *J* = 3.9 Hz), 2.58 (1H, *dd*, *J* = 3.9, 13.2 Hz), 2.43 (3H, *s*), 2.34 (1H, *d*, *J* = 8.7 Hz), 1.68 (1H, *ddd*, *J* = 5.4, 13.2, 13.2 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 143.79, 137.35, 133.67, 129.93, 127.65, 121.70, 64.67, 59.49, 56.23, 53.47, 41.70, 21.52. **EIMS** *m*/*z* (%) : 307 (M^+, 14%), 290 (6), 278 (4), 263 (8), 235 (3), 222 (1), 170 (6), 155 (33), 152 (35), 139 (9), 134 (38), 124 (12), 122 (12), 108 (26), 106 (49), 91 (100), 85 (63), 83 (81), 65 (49). **HRMS** *m*/*z* Found: 307.0881, Calcd. for $C_{15}H_{17}NO_4S$ $(M)^+$: 307.0878.



11a $C_{21}H_{31}NO_4SSi$ Mol. Wt.: 421.63

To a solution of alcohol **11** (2.43 g, 7.9 mmol) and *tert*-butyldimethylsilyl chloride (1.43 g, 9.5 mmol, 1.2 eq.) in anhydrous DMF (20 mL) was added imidazole (1.35 g, 19.8 mmol, 2.5 eq.). The resulting mixture was then stirred at room temperature overnight. After concentration, the residue was diluted with ethyl acetate (250 mL) and washed with water (2×20 mL) and brine (30 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, Petroleum ether 60-90 ºC: EtOAc = 4:1) to afford the silylether **11a** (3.13 g, 94%).

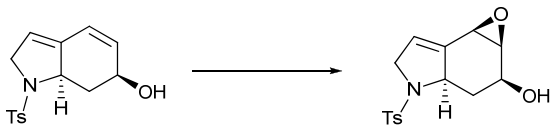
11a: white crystals, m.p.: 76-78 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.52 (2H, *d*, *J* = 8.1 Hz), 7.15 (2H, *d*, *J* = 8.1 Hz), 5.55 (1H, *d*, *J* = 1.2 Hz), 4.27-4.17 (2H, *m*), 4.10 (1H, *ddd*, *J* = 1.8, 5.1, 14.4 Hz), 3.92 (1H, *brd*, *J* = 14.4 Hz), 3.45 (1H, *d*, *J* = 3.6 Hz), 3.24 (1H, *t*, *J* = 3.6 Hz), 2.35-2.23 (1H, *m*), 2.26 (3H, *s*), 1.61-1.48 (1H, *m*), 0.81 (9H, *s*), 0.00 (3H, *s*), -0.02 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 143.67, 138.31, 133.34, 129.84, 127.71, 120.53, 65.62, 59.70, 56.30, 51.45, 42.08, 25.80, 21.50, 18.15, -4.64, -4.79. **EIMS** *m*/*z* (%) : 421 (M^+, 7%), 406 (8), 364 (24), 320 (10), 273 (5), 260 (3), 234 (14), 239 (20), 210 (11), 208 (12), 194 (6), 181 (6), 165 (19), 155 (22), 149 (16), 118 (27), 91 (53), 83 (100), 73 (27). **HRMS** *m*/*z* Found: 421.1754, Calcd. for $C_{21}H_{31}NO_4SSi$ $(M)^+$: 421.1743.



10b $C_{15}H_{17}NO_3S$ Mol. Wt.: 291.37

To a solution of enone **10** (2.1 g, 7.3 mmol) in dichloromethane (33 mL) and methanol (66 mL) was added a powder of $CeCl_3{\bullet}7H_2O$ (2.7 g, 7.3 mmol, 1.0 eq.). Sodium borohydride (0.28 g, 7.3 mmol, 1.0 eq.) was added at 0°C in small portion over a period of 20 minutes. The resulting mixture was then stirred at 0°C for 30 minutes. The mixture was then concentrated and diluted with dichloromethane (200 mL), washed with water (30 mL) and brine (30 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, CH_2Cl_2: EtOAc = 10:1) to afford the alcohol (2.1 g, 99%).

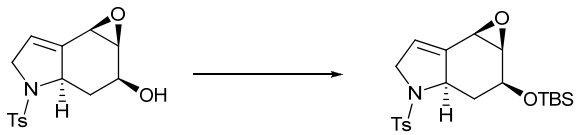
10b: pale white plates, m.p.: 145-147 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.73 (2H, *d*, *J* = 7.8 Hz), 7.34 (2H, *d*, *J* = 7.8 Hz), 6.11 (1H, *d*, *J* = 9.9 Hz), 5.82 (1H, *d*, *J* = 9.9 Hz), 5.35 (1H, *s*), 4.68-4.51 (1H, *m*), 4.27 (1H, *brd*, *J* = 14.7 Hz), 4.19-4.10 (1H, *m*), 4.06 (1H, *brd*, *J* = 14.7 Hz), 2.98 (1H, *ddd*, *J* = 4.5, 4.5, 11.1 Hz), 2.43 (3H, *s*), 2.38 (1H, *d*, *J* = 6.3 Hz), 1.79 (1H, *dd*, *J* = 11.1, 11.4 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 143.83, 136.90, 136.04, 133.30, 129.88, 127.83, 121.50, 116.27, 67.51, 62.92, 56.55, 40.97, 21.53. **EIMS** *m*/*z* (%) : 291 (M^+, 52%), 273 (23), 248 (6), 234 (2), 155 (28), 136 (63), 134 (21), 118 (70), 117 (28), 108 (31), 107 (26), 91 (100), 83 (66), 80 (27), 79 (26), 65 (47). **HRMS** *m*/*z* Found: 291.0923, Calcd. for $C_{15}H_{17}NO_3S$ $(M)^+$: 291.0929.



12 $C_{15}H_{17}NO_4S$ Mol. Wt.: 307.36

Diene **10b** (1.49 g, 5.1 mmol) was dissolved in dichloromethane (30 mL) at 0 ºC. To this mixture, a powder of 3-chloroperbenzoic acide (*m*-CPBA, 77%, 1.49 g, 6.6 mmol, 1.3 eq.) was added. The resulting mixture was then stirred at 0 ºC for 10 hours. The resulting mixture was then diluted with dichloromethane (180 mL) and washed with saturated aqueous solution of sodium biscarbonate (30 mL), water (30 mL) and brine (50 mL), and dried over anhydrous sodium sulfate. After removal of the solvent, the crude products were chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1) to provide epoxide **12** (1.10 g, 70%) as white solid.

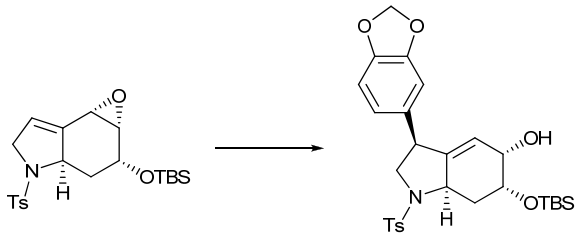
12: white solid, m.p.: 190-192 ºC. **^{1}H-NMR** (300MHz, CD_3SOCD_3), δ (ppm): 7.71 (2H, *d*, *J* = 8.1 Hz), 7.44 (2H, *d*, *J* = 8.1 Hz), 5.98 (1H, *s*), 5.23 (1H, *d*, *J* = 5.7 Hz), 4.17-4.03 (2H, *m*), 3.93-3.73 (2H, *m*), 3.58 (1H, *d*, *J* = 3.9 Hz), 3.27 (1H, *d*, *J* = 3.3 Hz), 2.39 (3H, *s*), 2.28 (1H, *ddd*, *J* = 4.2, 4.3, 11.4 Hz), 1.37 (1H, *dd*, *J* = 11.4, 11.4 Hz). **^{13}C-NMR** (75MHz, CD_3SOCD_3), δ (ppm): 143.76, 134.28, 132.37, 129.99, 127.71, 125.97, 65.42, 62.81, 56.25, 55.71, 47.25, 34.81, 20.95. **EIMS** *m*/*z* (%) : 307 (M^+, 9%), 290 (6), 278 (4), 263 (9), 235 (2), 170 (7), 155 (31), 152 (30), 139 (9), 134 (29), 124 (12), 122 (11), 108 (24), 106 (43), 91 (100), 85 (70), 83 (95), 80 (47), 65 (50). **HRMS** *m*/*z* Found: 307.0869, Calcd. for $C_{15}H_{17}NO_4S$ $(M)^+$: 307.0878.



12a $C_{21}H_{31}NO_4SSi$ Mol. Wt.: 421.63

To a solution of alcohol **12** (0.57 g, 1.9 mmol) and *tert*-butyldimethylsilyl chloride (0.34 g, 2.3 mmol, 1.2 eq.) in anhydrous dichloromethane (15 mL) was added a powder of imidazole (0.33 g, 4.8 mmol, 2.5 eq.) at room temperature. The resulting mixture was then stirred at room temperature for 28 hours. After concentration, the residue was directly chromatographed on silica gel (200-300 mesh, Petroleum ether 60-90 ºC: EtOAc = 4:1) to afford the silylether **12a** (0.48 g, 60%).

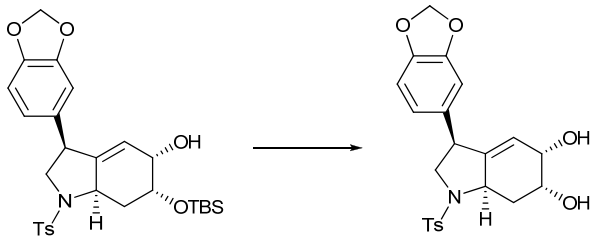
12a: white plates, m.p.: 144-145 ºC. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.59 (2H, *d*, *J* = 8.1 Hz), 7.18 (2H, *d*, *J* = 8.1 Hz), 5.54 (1H, *s*), 4.50 (1H, *d*, *J* = 2.1 Hz), 4.50-4.90 (1H, *m*), 4.15-4.01 (2H, *m*), 3.94 (1H, *brd*, *J* = 14.7 Hz), 3.76 (1H, *s*), 2.29 (3H, *s*), 2.28-2.18 (1H, *m*), 1.70 (1H, *t*, *J* = 11.7 Hz), 0.76 (9H, *s*), 0.00 (6H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 143.71, 135.98, 134.64, 129.83, 127.45, 123.27, 73.62, 66.79, 61.17, 55.35, 54.09, 37.97, 25.72, 21.51, 17.99. **EIMS** *m*/*z* (%) : 422 (M^++1, 12%), 400 (73), 364 (28), 344 (4), 308 (44), 282 (17), 274 (15), 264 (32), 234 (20), 229 (16), 210 (22), 190 (10), 155 (84), 149 (24), 131 (18), 118 (42), 101 (18), 91 (100), 75 (61). **HRMS** *m*/*z* Found: 421.1744, Calcd. for $C_{21}H_{31}NO_4SSi$ $(M)^+$: 421.1743.



14a $C_{28}H_{37}NO_6SSi$ Mol. Wt.: 543.75

A mixture of epoxide **11a** (0.42 g, 1.0 mmol), tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$, FW 915.72, 46 mg, 0.05 mmol, 0.05 eq.], organoboronic acid **13** (0.25 g, 1.5 mmol, 1.5 eq.) and Cs_2CO_3 (0.65 g, 2.0 mmol, 2.0 eq.) in anhydrous tetrahydrofuran (20 mL) was degassed and purged with nitrogen (3 times). The resulting mixture was then stirred at room temperature under nitrogen for 20 hours. After diluted with ethyl acetate (180 mL), the mixture was then washed with water (2 × 15 mL), brine (20 mL) and dried over anhydrous sodium sulfate. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 4:1) to afford the product **14a** (0.46 g, 85%) as colorless syrup.

14a: colorless syrup. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.59 (2H, *d*, *J* = 8.1 Hz), 7.18 (2H, *d*, *J* = 8.1 Hz), 6.56 (1H, *d*, *J* = 7.8 Hz), 6.39 (1H, *d*, *J* = 0.9 Hz), 6.35 (1H, *d*, *J* = 7.8 Hz), 5.77 (2H, *s*), 4.81 (1H, *s*), 4.12-4.02 (1H, *m*), 4.00-3.88 (2H, *m*), 3.62 (1H, *dd*, *J* = 9.0, 11.1 Hz), 3.22 (1H, *t*, *J* = 11.1 Hz), 3.04-2.90 (1H, *m*), 2.66 (1H, *dt*, *J* = 4.5, 11.4 Hz), 2.30 (3H, *s*), 1.99 (1H, *d*, *J* = 11.1 Hz), 1.64 (1H, *dd*, *J* = 11.4, 11.5 Hz), 0.79 (9H, *s*), 0.10 (3H, *s*), 0.00 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.89, 146.85, 144.19, 143.81, 134.05, 130.89, 129.85, 127.71, 123.03, 121.97, 108.51, 108.28, 101.09, 68.83, 67.81, 55.59, 54.75, 46.08, 38.20, 25.87, 21.58, 18.15, -4.37, -5.11. **EIMS** *m*/*z* (%) : 543 (M^+, 8%), 525 (9), 486 (5), 385 (4), 370 (13), 331 (8), 314 (1), 272 (12), 256 (5), 239 (15), 216 (15), 155 (13), 149 (98), 143 (12), 115 (7), 104 (13), 91 (29), 83 (100), 71 (49). **HRMS** *m*/*z* Found: 543.2114, Calcd. for $C_{28}H_{37}NO_6SSi$ $(M)^+$: 543.2111.

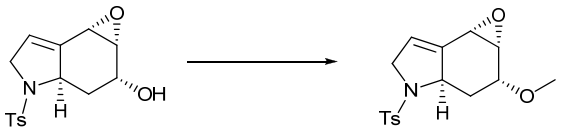


14b $C_{22}H_{23}NO_6S$ Mol. Wt.: 429.49

Compound **14a** (0.42 g, 0.77 mmol) was dissolved in THF (15 mL). A solution of *n*-Bu_4NF (1.0 M in THF, 0.92 mL, 0.92 mmol, 1.2 eq.) was added via syringe. After stirring at room temperature for 1.5 h and concentrated under reduced pressure, the residue was diluted with dichloromethane (100 mL). The resulting mixture was then washed with water (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the diol **14b** (0.27 g, 82%) as white solid.

14b: white needle, m.p.: 184-185 ºC. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.78 (2H, *d*, *J* = 8.1 Hz), 7.36 (2H, *d*, *J* = 8.1 Hz), 6.73 (1H, *d*, *J* = 7.8 Hz), 6.56 (1H, *s*), 6.52 (1H, *d*, *J* = 7.8 Hz), 5.95 (2H, *s*), 4.97 (1H, *brs*), 4.33-4.07 (3H, *m*), 3.73 (1H, *dd*, *J* = 9.3, 10.8 Hz), 3.42 (1H, *dd*, *J* = 10.2, 10.8 Hz), 3.23 (1H, *t*, *J* = 9.3 Hz), 2.95 (1H, *dt*, *J* = 4.5, 12.6 Hz), 2.52 (1H, *s*), 2.46 (3H, *s*), 2.14 (1H, *d*, *J* = 6.6 Hz), 1.82 (1H, *dd*, *J* = 11.4, 12.6 Hz). **^{13}C-NMR**

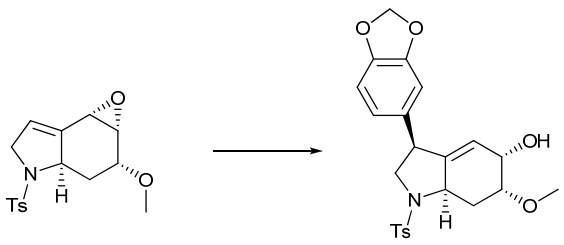
(75MHz, $CDCl_3$), δ (ppm): 147.92, 146.86, 145.45, 143.90, 133.57, 131.21, 129.93, 127.80, 121.91, 121.66, 108.44, 108.32, 101.12, 68.01, 67.41, 55.51, 54.67, 45.95, 36.75, 21.59. **EIMS** *m*/*z* (%) : 429 (M^+, 2%), 411 (9), 318 (13), 300 (29), 285 (14), 275 (15), 257 (7), 238 (5), 231 (9), 216 (9), 201 (8), 189 (10), 174 (20), 165 (43), 153 (30), 149 (20), 135 (13), 111 (15), 105 (15), 91 (33), 83 (100), 77 (17), 69 (40). **HRMS** *m*/*z* Found: 429.1237, Calcd. for $C_{22}H_{23}NO_6S$ $(M)^+$: 429.1246.



11d $C_{16}H_{19}NO_4S$ Mol. Wt.: 321.39

To a mixture of sodium hydride (60% in mineral oil, 78 mg, 1.95 mmol, 1.5 eq.) in anhydrous THF (10 mL) at 0 °C was added a solution of alcohol **11** (0.4 g, 1.3 mmol) in THF (5 mL) via syringe. After stirring at 0 °C for 10 min, methyl iodide (2.28 g/mL, 0.28 g, 1.95 mmol, 1.5 eq.) was added. The resulting mixture was then stirred at room temperature for 5 h under nitrogen. A saturated aqueous solution of NH_4Cl (2 mL) was added and the mixture was diluted with water (50 mL). The resulting mixture was then extracted with ethyl acetate (3 × 25 mL). The combined organic phases were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford ether **11d** (0.35 g, 83%) as white solid.

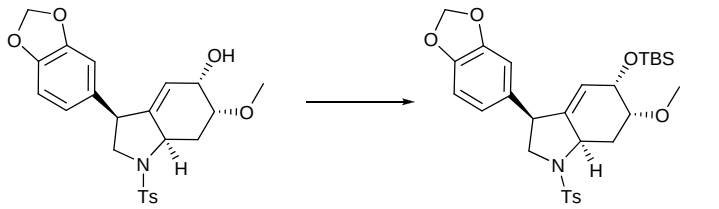
11d: white plates, m.p.: 101-103 ºC. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.70 (2H, *d*, *J* = 7.8 Hz), 7.32 (2H, *d*, *J* = 7.8 Hz), 5.74 (1H, *s*), 4.41-4.21 (2H, *m*), 4.05 (1H, *d*, *J* = 14.4 Hz), 3.93 (1H, *t*, *J* = 4.2 Hz), 3.67 (1H, *d*, *J* = 3.6 Hz), 3.57 (1H, *t*, *J* = 3.6 Hz), 3.50 (3H, *s*), 2.65 (1H, *dd*, *J* = 3.9, 13.8 Hz), 2.42 (3H, *s*), 1.72-1.57 (1H, *m*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 143.73, 137.93, 133.36, 129.93, 127.67, 121.01, 73.66, 60.12, 56.96, 56.23, 54.23, 51.38, 38.08, 21.54. **EIMS** *m*/*z* (%) : 321 (M^+, 16%), 304 (4), 290 (12), 274 (3), 263 (13), 250 (1), 235 (2), 222 (2), 170 (6), 166 (37), 155 (35), 134 (42), 118 (9), 106 (52), 91 (100), 80 (37), 71 (16), 65 (45). **HRMS** *m*/*z* Found: 321.1031, Calcd. for $C_{16}H_{19}NO_4S$ $(M)^+$: 321.1035.



14 $C_{23}H_{25}NO_6S$ Mol. Wt.: 443.51

A mixture of epoxide **11d** (0.16 g, 0.5 mmol), tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$, FW 915.72, 23 mg, 0.025 mmol, 0.05 eq.], organoboronic acid **13** (0.12 g, 0.75 mmol, 1.5 eq.) and Cs_2CO_3 (0.33 g, 1.0 mmol, 2.0 eq.) in anhydrous tetrahydrofuran (12 mL) was degassed and purged with nitrogen (3 times). The resulting mixture was then stirred at room temperature under nitrogen for 20 hours. After diluted with ethyl acetate (100 mL), the mixture was then washed with water (20 mL), brine (20 mL) and dried over anhydrous sodium sulfate. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford the product **14** (0.20 g, 90%) as white syrup.

14: white syrup. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.76 (2H, *d*, *J* = 8.1 Hz), 7.37 (2H, *d*, *J* = 8.1 Hz), 6.72 (1H, *d*, *J* = 7.8 Hz), 6.54 (1H, *d*, *J* = 0.9 Hz), 6.50 (1H, *d*, *J* = 7.8 Hz), 5.94 (2H, *s*), 5.03 (1H, *s*), 4.26-4.13 (1H, *m*), 4.01-3.89 (1H, *m*), 3.77 (2H, *dd*, *J* = 9.0, 11.1 Hz), 3.53 (3H, *s*), 3.40 (1H, *dd*, *J* = 10.5, 10.8 Hz), 3.17 (1H, *t*, *J* = 9.0 Hz), 3.14-3.06 (1H, *m*), 2.57 (1H, *d*, *J* = 10.5 Hz), 2.47 (3H, *s*), 1.70 (1H, *dd*, *J* = 11.1, 13.2 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.91, 146.86, 144.25, 143.97, 133.85, 130.88, 129.94, 127.66, 123.28, 121.86, 108.43, 108.32, 101.10, 77.03, 67.78, 57.14, 55.49, 54.64, 46.00, 33.03, 21.58. **EIMS** *m*/*z* (%) : 443 (M^+, 13%), 425 (38), 385 (11), 369 (3), 321 (1), 288 (5), 272 (16), 256 (9), 238 (19), 230 (16), 208 (12), 201 (13), 166 (7), 155 (15), 149 (16), 135 (18), 115 (13), 91 (37), 83 (100). **HRMS** *m*/*z* Found: 443.1401, Calcd. for $C_{23}H_{25}NO_6S$ $(M)^+$: 443.1403.

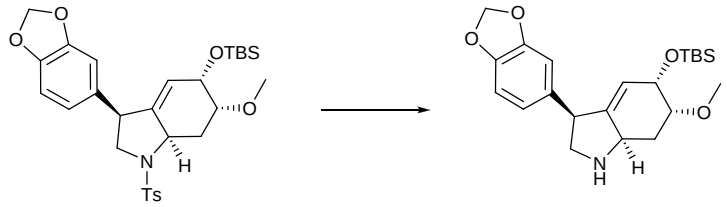


14c $C_{29}H_{39}NO_6SSi$ Mol. Wt.: 557.77

Alcohol **14** (0.15 g, 0.34 mmol), imidazole (58 mg, 0.85 mmol, 2.5 eq.) and *tert*-butyldimethylsilyl chloride (62 mg, 0.41 mmol, 1.2 eq.) were dissolved in anhydrous DMF (5 mL). The resulting mixture was then stirred at room temperature overnight. After concentration, the residue was diluted with ethyl acetate (40 mL) and washed with water (5 mL), brine (5 mL) and dried over anhydrous sodium sulfate. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 8:1) to afford the product **14c** (0.19 g, 92%) as white solid.

14c: white plates, m.p.: 171-172 ºC. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.69 (2H, *d*, *J* = 7.8 Hz), 7.28 (2H, *d*, *J* = 7.8 Hz), 6.67 (1H, *d*, *J* = 7.8 Hz), 6.49 (1H, *s*), 6.44 (1H, *d*, *J* = 7.8 Hz), 5.89 (2H, *s*), 4.80 (1H, *s*), 4.28 (1H, *brs*), 4.13-4.01 (1H, *m*), 3.69 (1H, *dd*, *J* = 9.0, 11.1 Hz), 3.63-3.57 (1H, *m*), 3.47 (3H, *s*), 3.35 (1H, *t*, *J* = 10.8 Hz), 3.09-2.87 (2H, *m*), 2.40 (3H, *s*), 1.66 (1H, *dd*, *J* = 9.3, 11.1 Hz), 0.80 (9H, *s*), 0.00 (3H, *s*), -0.04 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.82, 146.72, 143.96, 133.52, 130.93, 129.83, 127.75, 122.97, 121.89, 108.43, 108.28, 101.05, 77.96, 69.94, 58.01, 56.13, 54.97, 45.95, 33.86, 25.80, 21.55, 18.12, -4.58, -4.74. **EIMS** *m*/*z* (%) : 557 (M^+,

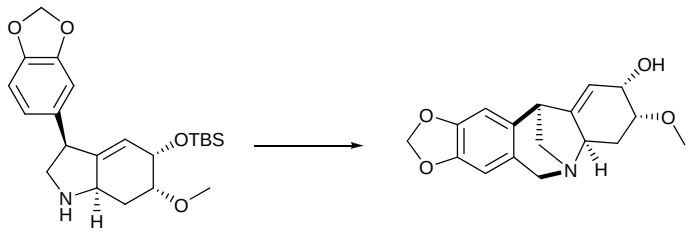
6%), 542 (21), 500 (90), 468 (1), 425 (31), 394 (10), 344 (58), 317 (7), 272 (18), 256 (4), 239 (30), 223 (12), 212 (17), 181 (8), 155 (17), 149 (100), 135 (16), 115 (6), 91 (41), 89 (50), 73 (51). **HRMS** *m*/*z* Found: 557.2228, Calcd. for $C_{29}H_{39}NO_6SSi$ $(M)^+$: 557.2267.



16 $C_{22}H_{33}NO_4Si$ Mol. Wt.: 403.59

A solution of sodium naphthalenide was prepared by adding sodium (0.1 g, 4.16 mmol), in small pieces, to a solution of naphthalene (0.7 g, 5.33 mmol) in deoxygenated DME (6 mL) and by stirring the resulting green mixture at room temperature for 2 h. This solution was then added, dropwise via syringe, to a solution of compound **14c** (0.11 g, 0.2 mmol) in DME (10 mL) at –78 °C under nitrogen, until a light-green colour persisted. Saturated aq. $NaHCO_3$ (0.19 mL) was added to the reaction mixture followed by a powder of anhydrous K_2CO_3 (ca. 0.87 g). The resulting mixture was then stirred at room temperature for 1 h. The mixture was filtered and washed with dichloromethane (30 mL). The organic phases were concentrated under reduced pressure and the residue was chromatographed on silica gel (MeOH: CH_2Cl_2 = 1:20) to afford the product **16** (73 mg, 91%) as colorless oil.

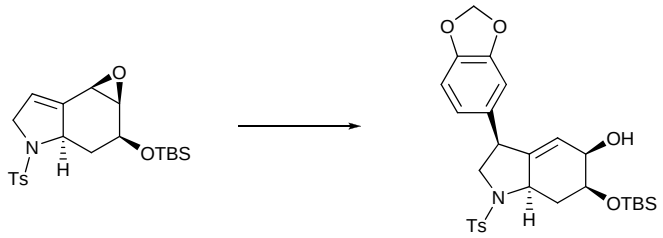
16: colorless syrup. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 6.72 (1H, *s*), 6.71 (1H, *d*, *J* = 8.1 Hz), 6.64 (1H, *d*, *J* = 8.1 Hz), 5.89 (2H, *d*, *J* = 2.7 Hz), 4.98 (1H, *s*), 4.39-4.32 (1H, *m*), 4.12-4.03 (1H, *m*), 3.89-3.77 (1H, *m*), 3.66 (1H, *d*, *J* = 11.1 Hz), 3.59 (1H, *d*, *J* = 4.2 Hz), 3.41 (3H, *s*), 3.26 (1H, *dd*, *J* = 7.5, 11.4 Hz), 2.71-2.58 (1H, *m*), 1.95 (1H, *dd*, *J* = 11.4, 11.7 Hz), 0.81 (9H, *s*), 0.00 (3H, *s*), -0.03 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 148.03, 146.83, 142.71, 132.62, 124.83, 122.09, 108.63, 108.41, 101.08, 77.65, 69.84, 58.62, 55.16, 51.38, 46.24, 30.17, 25.81, 18.14, -4.59, -4.68. **EIMS** *m*/*z* (%) : 403 (M^+, 28%), 388 (8), 372 (11), 346 (73), 317 (6), 271 (78), 256 (14), 240 (100), 228 (13), 215 (37), 211 (29), 200 (16), 181 (15), 148 (29), 135 (18), 118 (23), 91 (20), 89 (63), 83 (30). **HRMS** *m*/*z* Found: 403.2177, Calcd. for $C_{22}H_{33}NO_4Si$ $(M)^+$: 403.2179.



6 $C_{17}H_{19}NO_4$ Mol. Wt.: 301.34

Amine **16** (50 mg, 0.12 mmol) and paraformaldehyde (18 mg, 0.6 mmol, 5.0 eq.) in formic acid (88% in water, 4 mL) was heated at 80 °C (oil bath) for 16 h. The mixture was then cooled to room temperature and concentrated under reduced pressure. The residue was diluted with dichloromethane (5 mL) followed by saturated aqueous solution of $NaHCO_3$ (10 mL). The resulting mixture was stirred at room temperature for 30 min then extracted with dichloromethane (3×10 mL). The combined organic phase was washed with water (10 mL) and brine (10 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure. The residue was then treated with K_2CO_3 (25 mg) in methanol (4 mL) at room temperature for 16 h. The mixture was concentrated and directly chromatographed on silica gel (200-300 mesh, CH_2Cl_2: MeOH = 20:1) to afford compound **6** (26 mg, 72%).

6: white plates, m.p.: 200-202 ºC. **^{1}H-NMR** (500MHz, $CDCl_3$), δ (ppm): 6.50 (1H, *s*), 6.43 (1H, *s*), 5.88 (2H, *s*), 5.25 (1H, *t*, *J* = 2.7 Hz), 4.21 (1H, *d*, *J* = 17.8 Hz), 4.06 (1H, *m*), 3.82 (1H, *m*), 3.78 (1H, *d*, *J* = 17.8 Hz), 3.77 (1H, *m*), 3.47 (3H, *s*), 3.43 (1H, *d*, *J* = 2.8 Hz), 3.20 (1H, *dd*, *J* = 3.3, 11.0 Hz), 3.11 (1H, *d*, *J* = 11.0 Hz), 2.59 (1H, *dt*, *J* = 4.3, 12.6 Hz), 1.49 (1H, *ddd*, *J* = 0.7, 12.0, 12.7 Hz). **^{13}C-NMR** (125MHz, $CDCl_3$), δ (ppm): 150.6, 146.5, 146.2, 138.4, 124.9, 118.4, 106.9, 105.7, 101.1, 77.5, 69.8, 61.0, 58.0, 57.6, 50.8, 43.9, 28.8. **EIMS** *m*/*z* (%) : 301 (M^+, 49%), 286 (10), 270 (11), 252 (7), 243 (18), 241 (16), 223 (17), 214 (18), 199 (22), 185 (21), 173 (6), 153 (7), 141 (8), 128 (11), 115 (13), 91 (6), 83 (100), 77 (10). **HRMS** *m*/*z* Found: 301.1316, Calcd. for $C_{17}H_{19}NO_4$ $(M)^+$: 301.1314.

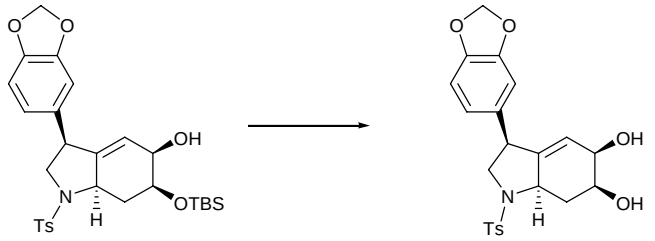


15a $C_{28}H_{37}NO_6SSi$ Mol. Wt.: 543.75

A mixture of epoxide **12a** (0.15 g, 0.36 mmol), tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$, FW 915.72, 16 mg, 0.018 mmol, 0.05 eq.], organoboronic acid **13** (90 mg, 0.54 mmol, 1.5 eq.) and Cs_2CO_3 (0.23 g, 0.72 mmol, 2.0 eq.) in anhydrous tetrahydrofuran (10 mL) was degassed and purged with nitrogen (3 times). The resulting mixture was then stirred at room temperature under nitrogen for 26 hours. After diluted with ethyl acetate (100 mL), the mixture was then washed with water (20 mL), brine (20 mL) and dried over anhydrous sodium sulfate. After removal of the solvents, the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 6:1) to afford the product **15a** (0.17 g, 86%) as white foam.

15a: white foam. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.60 (2H, *d*, *J* = 8.1 Hz), 7.19 (2H, *d*, *J* = 8.1 Hz), 6.57 (1H, *d*, *J* = 7.8 Hz), 6.44 (1H, *d*, *J* = 0.9 Hz), 6.39 (1H, *d*, *J* = 7.8 Hz), 5.77 (2H, *s*), 5.13 (1H, *brs*), 3.82-3.57 (4H, *m*), 3.23-3.06 (2H, *m*), 2.67 (1H, *s*), 2.30 (3H, *s*), 2.23-2.13 (1H, *m*), 1.70 (1H, *dd*, *J* = 11.4, 11.5 Hz), 0.77 (9H, *s*), 0.00

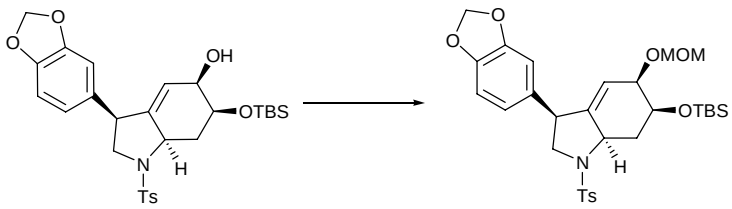
(3H, *s*), -0.03 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.97, 146.96, 145.69, 143.84, 134.96, 130.42, 129.86, 127.59, 122.02, 121.53, 108.71, 108.39, 101.09, 68.92, 65.20, 59.15, 54.50, 46.64, 33.30, 25.78, 21.57, 18.07, -4.45, -4.81. **EIMS** *m*/*z* (%) : 543 (M^+, 7%), 527 (3), 486 (21), 395 (4), 385 (24), 364 (2), 331 (6), 315 (3), 301 (3), 272 (8), 256 (6), 239 (17), 230 (19), 212 (10), 155 (14), 149 (76), 135 (12), 91 (28), 83 (100), 75 (27). **HRMS** *m*/*z* Found: 543.2069, Calcd. for $C_{28}H_{37}NO_6SSi$ $(M)^+$: 543.2111.



15b $C_{22}H_{23}NO_6S$ Mol. Wt.: 429.49

Compound **15a** (50 mg, 0.09 mmol) was dissolved in THF (10 mL). A solution of *n*-Bu_4NF (1.0 M in THF, 0.11 mL, 0.11 mmol, 1.2 eq.) was added via syringe. After stirring at room temperature for 1.5 h and concentrated under reduced pressure, the residue was diluted with ethyl acetate (50 mL). The resulting mixture was then washed with water (10 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1) to afford the diol **15b** (35 mg, 89%) as white solid.

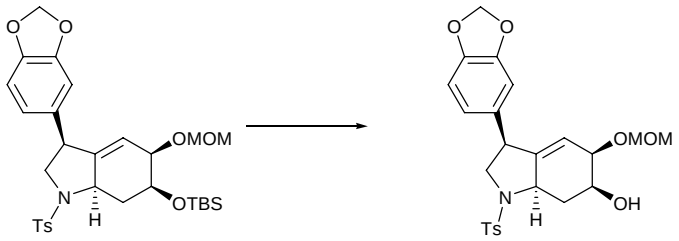
15b: white plates, m.p.: 152-154 ºC. **^{1}H-NMR** (300MHz, CD_3SOCD_3), δ (ppm): 7.79 (2H, *d*, *J* = 8.1 Hz), 7.47 (2H, *d*, *J* = 8.1 Hz), 6.83 (1H, *d*, *J* = 7.8 Hz), 6.74 (1H, *s*), 6.57 (1H, *d*, *J* = 7.8 Hz), 5.99 (2H, *s*), 4.99 (1H, *brs*), 4.56 (1H, *s*), 4.54 (1H, *s*), 3.85-3.66 (3H, *m*), 3.49-3.30 (1H, *m*), 3.29 (1H, *t*, *J* = 10.2 Hz), 3.15 (1H, *brt*, *J* = 9.0 Hz), 2.43 (3H, *s*), 2.24-2.13 (1H, *m*), 1.70 (1H, *dd*, *J* = 11.1, 11.7 Hz). **^{13}C-NMR** (75MHz, CD_3SOCD_3), δ (ppm): 147.32, 146.26, 143.76, 143.66, 133.74, 131.11, 129.99, 127.44, 122.71, 122.09, 108.51, 108.10, 100.88, 66.65, 64.15, 59.21, 54.37, 45.26, 33.40, 21.01. **EIMS** *m*/*z* (%) : 429 (M^+, 9%), 411 (2), 385 (13), 369 (2), 342 (1), 272 (10), 256 (7), 238 (14), 230 (18), 216 (60), 201 (16), 184 (100), 169 (26), 155 (17), 141 (12), 135 (20), 115 (24), 91 (59), 83 (44). **HRMS** *m*/*z* Found: 429.1243, Calcd. for $C_{22}H_{23}NO_6S$ $(M)^+$: 429.1246.



15c $C_{30}H_{41}NO_7SSi$ Mol. Wt.: 587.80

Compound **15a** (0.28 g, 0.51 mmol), *N*,*N*-diisopropylethylamine (Hünig's base, 0.33 g, 2.55 mmol, 5.0 eq.) and 4-dimethylaminopyridine (DMAP, 6 mg, 0.051 mmol, 0.1 eq.) were dissolved in dichloromethane (50 mL) at 0 °C. Methoxymethyl chloride (MOMCl, 0.11 mL, 1.53 mmol, 3.0 eq.) was added dropwise over a period of 5 minutes. The mixture was then stirred at room temperature for 24 hours. Saturated aq. NH_4Cl (3 mL) was added and the resulting mixture was stirred for 15 minutes. Water (50 mL) was added and the mixture was extracted with ethyl acetate (3×30 mL). The combined organic phase was washed with water (20 mL) and brine (20 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (200-300 mesh, Petroleum ether 60-90 ºC: EtOAc = 6:1) to afford the methoxymethyl ether (0.28 g, 93%).

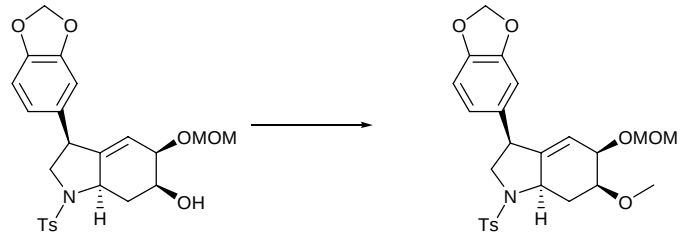
15c: white plates, m.p.: 164-166 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.63 (2H, *d*, *J* = 8.1 Hz), 7.22 (2H, *d*, *J* = 8.1 Hz), 6.60 (1H, *d*, *J* = 7.8 Hz), 6.48 (1H, *s*), 6.44 (1H, *d*, *J* = 7.8 Hz), 5.80 (2H, *s*), 5.12-5.06 (1H, *m*), 4.68 (1H, *d*, *J* = 6.6 Hz), 4.50 (1H, *d*, *J* = 6.6 Hz), 3.82-3.60 (4H, *m*), 3.21 (1H, *d*, *J* = 10.5 Hz), 3.16 (1H, *d*, *J* = 10.5 Hz), 3.14 (3H, *s*), 2.33 (3H, *s*), 2.28-2.14 (1H, *m*), 1.85 (1H, *dd*, *J* = 11.1, 11.7 Hz), 0.79 (9H, *s*), 0.00 (3H, *s*), -0.03 (3H, *s*). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.91, 146.90, 145.18, 143.80, 134.95, 130.89, 129.85, 127.60, 122.06, 121.74, 108.74, 108.30, 101.09, 97.28, 72.05, 69.27, 59.43, 55.24, 54.87, 46.53, 34.33, 25.88, 21.57, 18.25, -4.56, -4.70. **EIMS** *m*/*z* (%) : 587 (M^+, 12%), 530 (8), 526 (9), 500 (45), 470 (3), 429 (100), 394 (47), 384 (60), 376 (16), 342 (16), 330 (29), 318 (42), 286 (10), 274 (59), 239 (53), 229 (20), 212 (56), 211 (25), 155 (44), 135 (35), 115 (11), 91 (71). **HRMS** *m*/*z* Found: 587.2357, Calcd. for $C_{30}H_{41}NO_7SSi$ $(M)^+$: 587.2373.



15d $C_{24}H_{27}NO_7S$ Mol. Wt.: 473.54

Compound **15c** (0.21 g, 0.35 mmol) was dissolved in THF (15 mL). A solution of *n*-Bu_4NF (1.0 M, 0.42 mL, 0.42 mmol, 1.2 eq.) in THF was added via syringe. After stirring at room temperature for 3 h and concentrated under reduced pressure, the residue was diluted with ethyl acetate (80 mL). The resulting mixture was then washed with water (15 mL), brine (15 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 1:1) to afford the diol **15d** (0.16 g, 97%) as white plates.

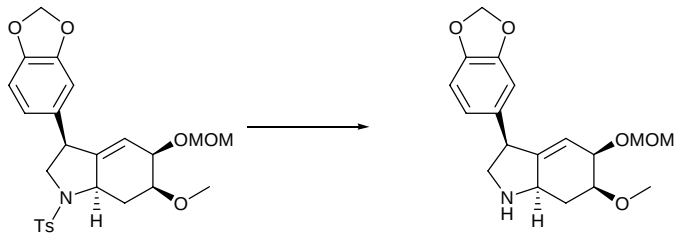
15d: white plates, m.p.: 152-154 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.77 (2H, *d*, *J* = 8.1 Hz), 7.36 (2H, *d*, *J* = 8.1 Hz), 6.73 (1H, *d*, *J* = 7.8 Hz), 6.60 (1H, *d*, *J* = 1.2 Hz), 6.55 (1H, *dd*, *J* = 1.2, 7.8 Hz), 5.93 (2H, *s*), 5.32-5.25 (1H, *m*), 4.71 (1H, *d*, *J* = 6.6 Hz), 4.67 (1H, *d*, *J* = 6.6 Hz), 3.92 (1H, *brs*), 3.84-3.64 (3H, *m*), 3.39 (1H, *t*, *J* = 10.5 Hz), 3.29 (3H, *s*), 3.29-3.23 (1H, *m*), 2.92 (1H, *d*, *J* = 10.5 Hz), 2.67-2.55 (1H, *m*), 2.46 (3H, *s*), 1.83 (1H, *dd*, *J* = 11.4, 11.7 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.93, 146.92, 146.35, 143.88, 134.23, 131.17, 129.90, 127.65, 122.02, 121.19, 108.57, 108.30, 101.11, 97.30, 73.41, 67.14, 59.29, 55.62, 54.90, 46.28, 34.76, 21.56. **EIMS** *m*/*z* (%) : 473 (M^+, 13%), 429 (100), 411 (15), 384 (48), 369 (5), 344 (5), 318 (6), 274 (49), 256 (20), 242 (22), 229 (30), 212 (45), 201 (30), 185 (19), 155 (28), 135 (26), 115 (19), 91 (81). **HRMS** *m*/*z* Found: 473.1506, Calcd. for $C_{24}H_{27}NO_7S$ $(M)^+$: 473.1508.



15e $C_{25}H_{29}NO_7S$ Mol. Wt.: 487.57

To a mixture of sodium hydride (60% in mineral oil, 20 mg, 0.5 mmol, 1.5 eq.) in anhydrous THF (10 mL) at 0 °C was added a solution of alcohol **15d** (0.15 g, 0.32 mmol) in THF (5 mL) via syringe. After stirring at 0 °C for 10 min, methyl iodide (68 mg, 0.48 mmol, 1.5 eq.) was added. The resulting mixture was then stirred at room temperature for 5 h under nitrogen. A saturated aqueous solution of NH_4Cl (2 mL) was added and the mixture was diluted with water (50 mL). The resulting mixture was then extracted with ethyl acetate (3 × 25 mL). The combined organic phases were washed with brine (15 mL) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on silica gel (Petroleum ether 60-90 ºC: ethyl acetate = 2:1) to afford ether **15e** (0.13 g, 83%) as white solid.

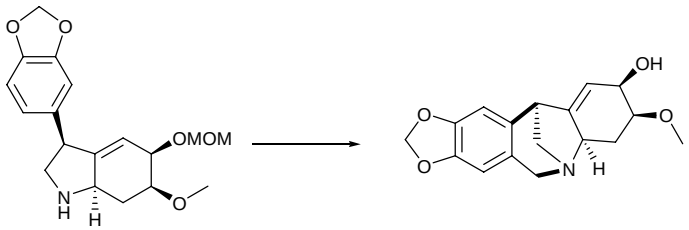
15e: white plates, m.p.: 149-150 °C. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 7.77 (2H, *d*, *J* = 8.1 Hz), 7.35 (2H, *d*, *J* = 8.1 Hz), 6.72 (1H, *d*, *J* = 7.8 Hz), 6.60 (1H, *s*), 6.55 (1H, *d*, *J* = 7.8 Hz), 5.93 (2H, *s*), 5.32-5.23 (1H, *m*), 4.75 (1H, *d*, *J* = 6.9 Hz), 4.65 (1H, *d*, *J* = 6.9 Hz), 4.10 (1H, *brs*), 3.94-3.84 (1H, *m*), 3.84 (1H, *dd*, *J* = 7.8, 9.3 Hz), 3.44 (3H, *s*), 3.40-3.20 (3H, *m*), 3.25 (3H, *s*), 2.71-2.59 (1H, *m*), 2.45 (3H, *s*), 1.91 (1H, *dd*, *J* = 11.4, 11.7 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 147.90, 146.93, 145.53, 143.84, 134.83, 130.59, 129.90, 127.51, 122.09, 121.24, 108.68, 108.29, 101.12, 96.72, 77.04, 69.24, 59.51, 56.63, 55.35, 54.79, 46.47, 30.67, 21.57. **EIMS** *m*/*z* (%) : 487 (M^+, 4%), 429 (100), 400 (7), 384 (53), 368 (1), 331 (2), 274 (54), 242 (34), 229 (31), 212 (46), 201 (47), 185 (13), 169 (9), 155 (28), 149 (12), 135 (20), 115 (16), 91 (76), 83 (90). **HRMS** *m*/*z* Found: 487.1647, Calcd. for $C_{25}H_{29}NO_7S$ $(M)^+$: 487.1665.



17 $C_{18}H_{23}NO_5$ Mol. Wt.: 333.38

A solution of sodium naphthalenide was prepared by adding sodium (0.1 g, 4.16 mmol), in small pieces, to a solution of naphthalene (0.7 g, 5.33 mmol) in deoxygenated DME (6 mL) and by stirring the resulting green mixture at room temperature for 2 h. This solution was then added, dropwise via syringe, to a solution of compound **15e** (0.12 g, 0.25 mmol) in DME (10 mL) at –78 °C under nitrogen, until a light-green colour persisted. Saturated aq. $NaHCO_3$ (0.23 mL) was added to the reaction mixture followed by a powder of anhydrous K_2CO_3 (ca. 1.1 g). The resulting mixture was then stirred at room temperature for 1 h. The mixture was filtered and washed with dichloromethane (30 mL). The organic phases were concentrated under reduced pressure and the residue was chromatographed on silica gel (MeOH: CH_2Cl_2 = 1:10) to afford the product **17** (74 mg, 89%) as colorless oil.

17: white foam. **^{1}H-NMR** (300MHz, $CDCl_3$), δ (ppm): 6.73 (1H, *d*, *J* = 8.1 Hz), 6.70 (1H, *d*, *J* = 1.2 Hz), 6.65 (1H, *dd*, *J* = 1.2, 8.1 Hz), 5.92 (2H, *s*), 5.32-5.28 (1H, *m*), 4.75 (1H, *d*, *J* = 6.9 Hz), 4.67 (1H, *d*, *J* = 6.9 Hz), 4.17 (1H, *brs*), 3.77-3.65 (1H, *m*), 3.52-3.36 (3H, *m*), 3.40 (3H, *s*), 3.25 (3H, *s*), 3.03 (1H, *dd*, *J* = 5.4, 11.4 Hz), 2.39-2.27 (1H, *m*), 2.02 (1H, *brs*), 1.72 (1H, *dd*, *J* = 11.1, 11.4 Hz). **^{13}C-NMR** (75MHz, $CDCl_3$), δ (ppm): 150.84, 147.76, 146.12, 137.04, 121.37, 119.03, 108.39, 108.08, 100.88, 96.44, 78.01, 70.19, 59.57, 56.46, 55.21, 54.86, 48.15, 30.04. **EIMS** *m*/*z* (%) : 333 (M^+, 12%), 331 (6), 302 (2), 286 (7), 271 (100), 256 (9), 242 (36), 240 (30), 230 (51), 211 (72), 201 (21), 185 (15), 181 (30), 172 (9), 150 (59), 148 (26), 135 (34), 115 (29). **HRMS** *m*/*z* Found: 333.1573, Calcd. for $C_{18}H_{23}NO_5$ $(M)^+$: 333.1576.



7 $C_{17}H_{19}NO_4$ Mol. Wt.: 301.34

Amine **17** (56 mg, 0.17 mmol) and paraformaldehyde (26 mg, 0.85 mmol, 5.0 eq.) in formic acid (88% in water, 4 mL) was heated at 80 °C (oil bath) for 16 h. The mixture was then cooled to room temperature and concentrated under reduced pressure. The residue was diluted with dichloromethane (5 mL) followed by saturated aqueous solution of $NaHCO_3$ (10 mL). The resulting mixture was stirred at room temperature for 30 min then extracted with dichloromethane (3×10 mL). The combined organic phase was washed with water (10 mL) and brine (10 mL). After dried over anhydrous sodium sulfate and filtration, the solvent was removed under reduced pressure. The residue was then treated with K_2CO_3 (25 mg) in methanol (4 mL) at room temperature for 16 h. The mixture was concentrated and directly chromatographed on silica gel (200-300 mesh, CH_2Cl_2: MeOH = 10:1) to afford compound **7** (23 mg, 45%) as a white plates.

7: white plates, m.p.: 206-208 °C. **^{1}H-NMR** (500MHz, $CDCl_3$), δ (ppm): 6.50 (1H, *s*), 6.44 (1H, *s*), 5.89 (2H, *s*), 5.27 (1H, *t*, *J* = 2.7 Hz), 4.21 (1H, *d*, *J* = 17.8 Hz), 4.10 (1H, *m*), 3.81 (1H, *d*, *J* = 17.8 Hz), 3.69 (1H, *m*), 3.47 (1H, *m*), 3.46 (3H, *s*), 3.43 (1H, *d*, *J* = 3.1 Hz), 3.19 (1H, *dd*, *J* = 3.2, 11.1 Hz), 3.14 (1H, *d*, *J* = 11.1 Hz), 2.48 (1H, *dt*, *J* = 3.5, 10.8 Hz), 1.41 (1H, *t*, *J* = 11.0 Hz). **^{13}C-NMR** (125MHz, $CDCl_3$), δ (ppm): 151.7, 146.6, 146.3, 138.0, 124.8, 116.8, 106.9, 105.7, 101.2, 84.8, 75.0, 65.6, 58.2, 57.5, 50.9, 43.5, 30.2. **EIMS** *m*/*z* (%) : 301 (M^+, 100%), 300 (M^+-1, 18%), 286 (15), 270 (23), 252 (12), 241 (24), 223 (32), 214 (19), 199 (32), 185 (37), 174 (13), 165 (17), 153 (16), 149 (35), 141 (19), 128 (32), 115 (41), 103 (11), 89 (13), 83 (13), 77 (24). **HRMS** *m*/*z* Found: 301.1318, Calcd. for $C_{17}H_{19}NO_4$ $(M)^+$: 301.1314.

Table 1, Comparison of the ^{13}C-NMR data for natural montabuphine, synthetical compound **6** and **7**

Montabuphine **δ (ppm)**	**Compound 6** **δ (ppm)**	**Compound 7** **δ (ppm)**
150.8	150.6	151.7
146.9	146.5	146.6
146.3	146.2	146.3
130.9	138.4	138.0
122.6	124.9	124.8
117.6	118.4	116.8
107.6	106.9	106.9
106.7	105.7	105.7
100.8	101.1	101.2
77.0	77.5	84.8
67.8	69.8	75.0
60.0	61.0	65.6
58.7	58.0	58.2

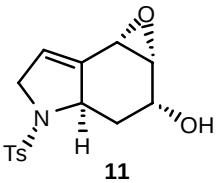
57.4	57.6	57.5
55.1	50.8	50.9
44.8	43.9	43.5
31.6	28.8	30.2

Data reported for montabuphine (*Phytochemistry* **1995**, *40*, 307) were recorded in $CDCl_3$ at 50 MHz. The ^{13}C-NMR data reported in this paper were collected in $CDCl_3$ at 125 MHz.

Table 2, Comparison of the ^{1}H-NMR data for natural montabuphine, synthetical compound **6** and **7**

Montabuphine δ (ppm)	**Compound 6 δ (ppm)**	**Compound 7 δ (ppm)**
6.54 (1H, s)	6.50 (1H, s)	6.50 (1H, s)
6.46 (1H, s)	6.43 (1H, s)	6.44 (1H, s)
5.88 (1H, d, *J* = 1.5 Hz)	5.88 (2H, s)	5.89 (2H, s)
5.86 (1H, d, *J* = 1.5 Hz)		
5.53 (1H, dd, *J* = 2.0, 2.5 Hz)	5.25 (1H, t, *J* = 2.7 Hz)	5.27 (1H, t, *J* = 2.7 Hz)
4.38 (1H, d, *J* = 16.5 Hz)	4.21 (1H, d, *J* = 17.8 Hz)	4.21 (1H, d, *J* = 17.8 Hz)
4.18 (1H, ddd, *J* = 2.5, 3.5, 5.0 Hz)	4.06 (1H, m)	4.10 (1H, m)
3.87 (1H, d, *J* = 16.5 Hz)	3.82 (1H, m)	3.81 (1H, d, *J* = 17.8 Hz)
3.70 (1H, ddd, *J* = 1.5, 4.5, 5.0 Hz)	3.78 (1H, d, *J* = 17.8 Hz)	3.69 (1H, m)
3.54 (1H, brd, *J* = 13.0 Hz)	3.77 (1H, m)	3.47 (1H, m)
3.39 (3H, s)	3.47 (3H, s)	3.46 (3H, s)
3.30 (1H, d, *J* = 2.0 Hz)	3.43 (1H, d, *J* = 2.8 Hz)	3.43 (1H, d, *J* = 3.1 Hz)
3.11 (1H, dd, *J* = 2.0, 11.0 Hz)	3.20 (1H, dd, *J* = 3.3, 11.0 Hz)	3.19 (1H, dd, *J* = 3.2, 11.1 Hz)
3.07 (1H, d, *J* = 11.0 Hz)	3.11 (1H, d, *J* = 11.0 Hz)	3.14 (1H, d, *J* = 11.1 Hz)
2.70 (1H, ddd, *J* = 4.5, 4.5, 13.0 Hz)	2.59 (1H, dt, *J* = 4.3, 12.6 Hz)	2.48 (1H, dt, *J* = 3.5, 10.8 Hz)
1.58 (1H, ddd, *J* = 1.5, 13.0, 13.0 Hz)	1.49 (1H, ddd, *J* = 0.7, 12.0, 12.7 Hz)	1.41 (1H, t, *J* = 11.0 Hz)

Data reported for montabuphine (*Phytochemistry* **1995**, *40*, 307) were recorded in $CDCl_3$ at 500 MHz. The ^{1}H-NMR data reported in this paper were collected in $CDCl_3$ at 500 MHz.



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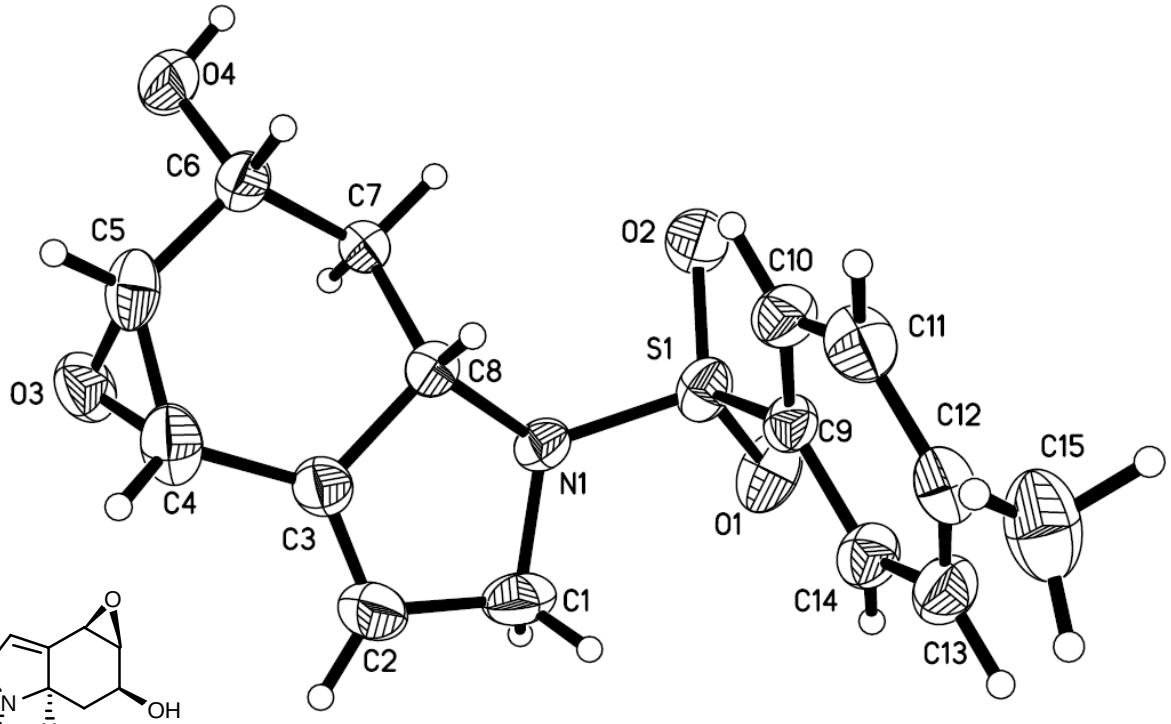

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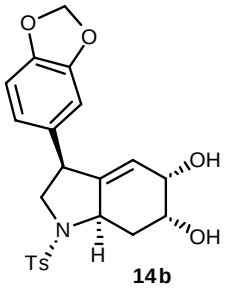

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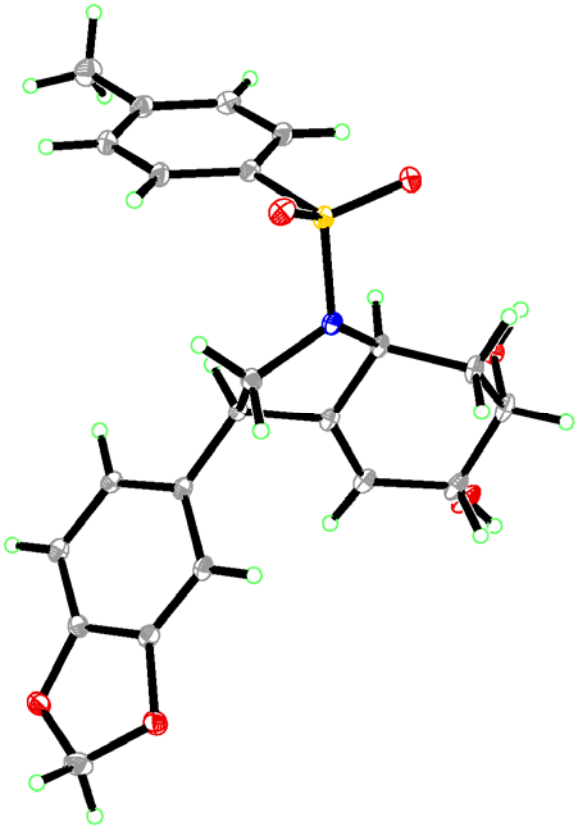

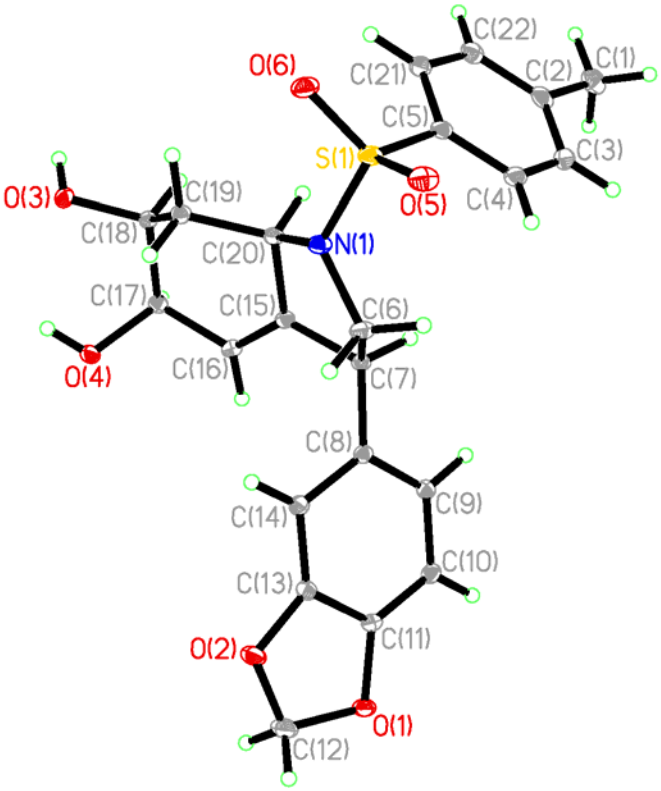

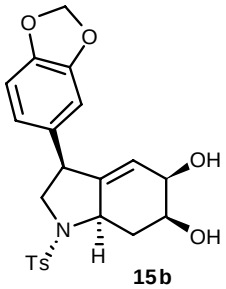

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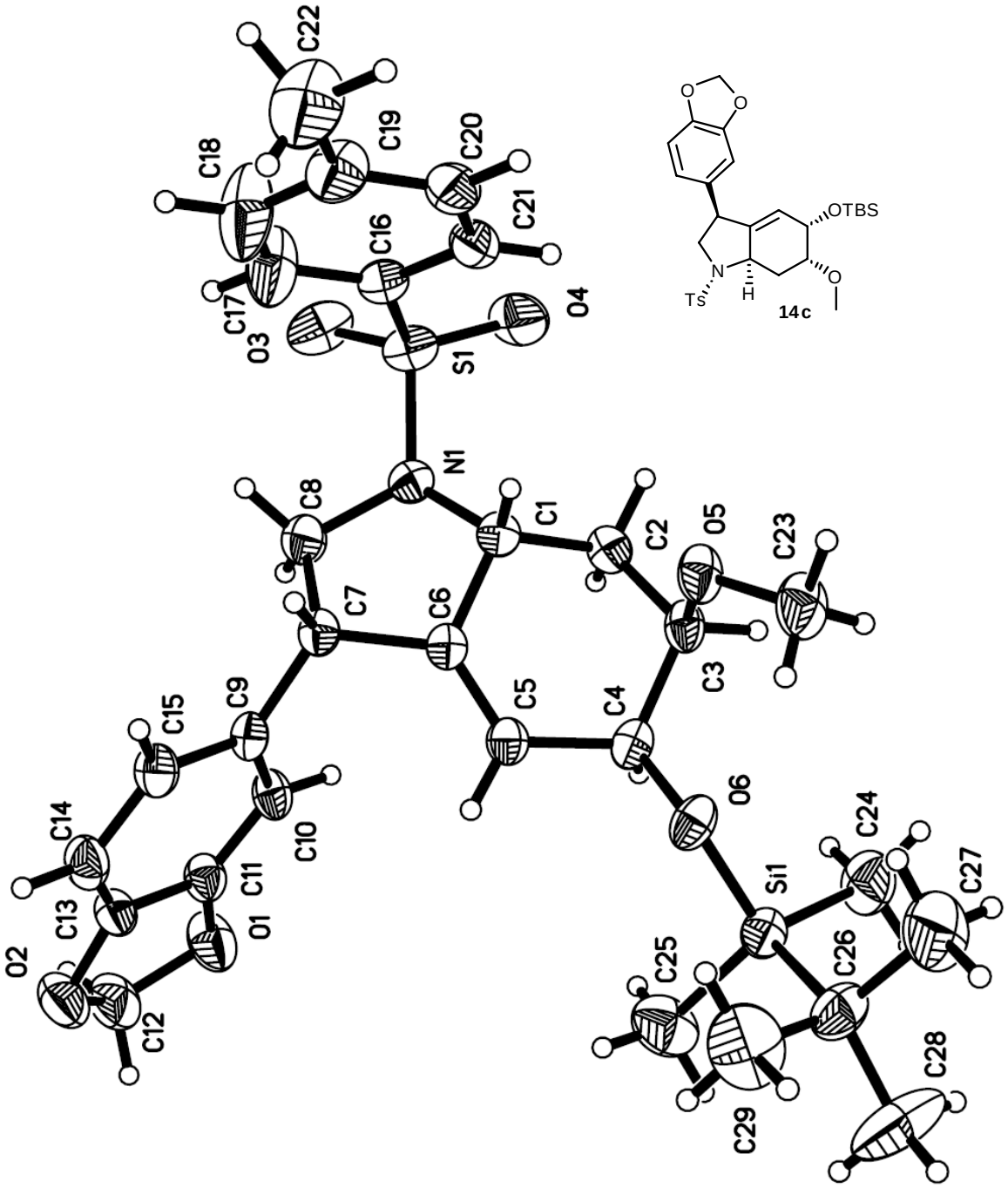

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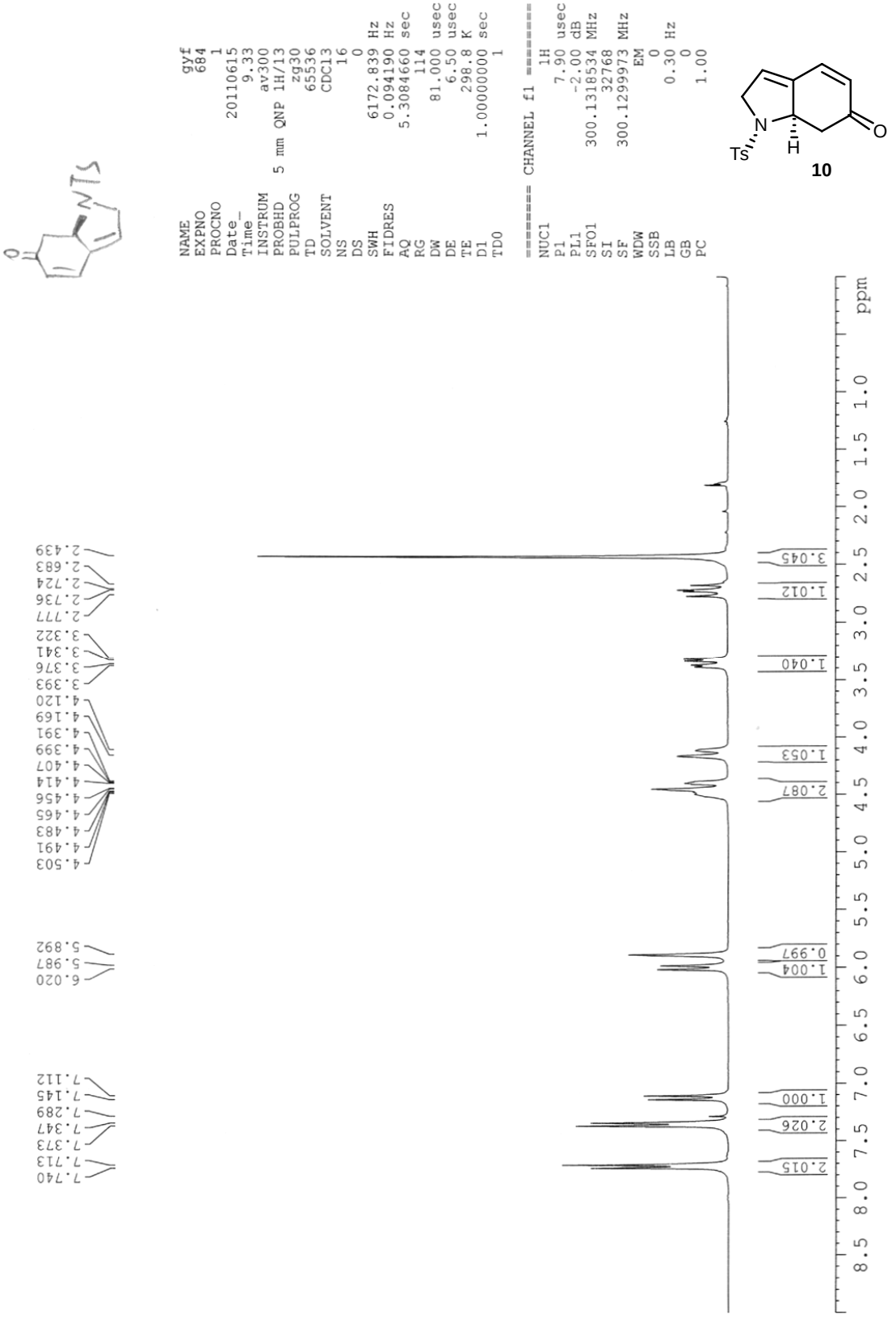

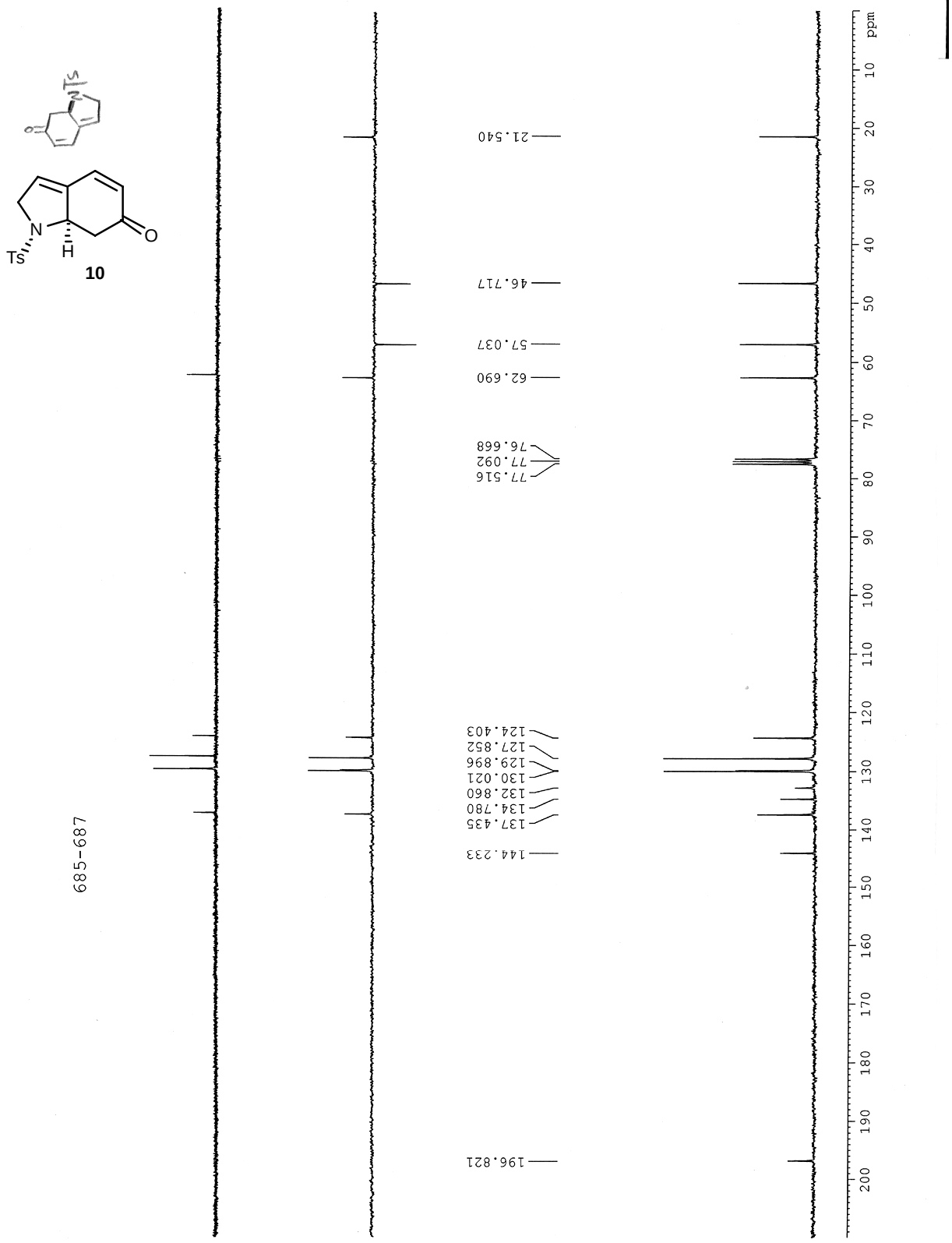

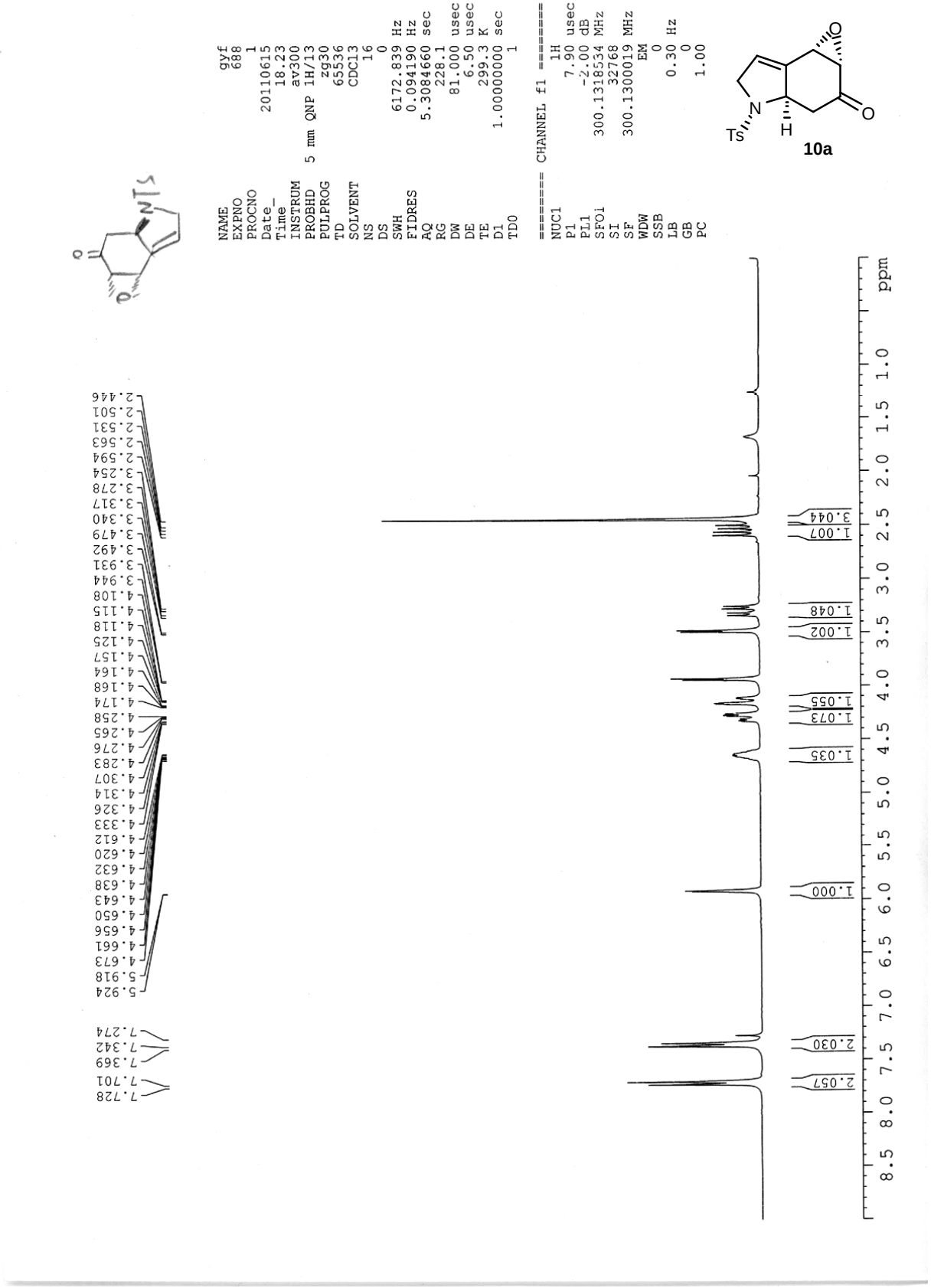

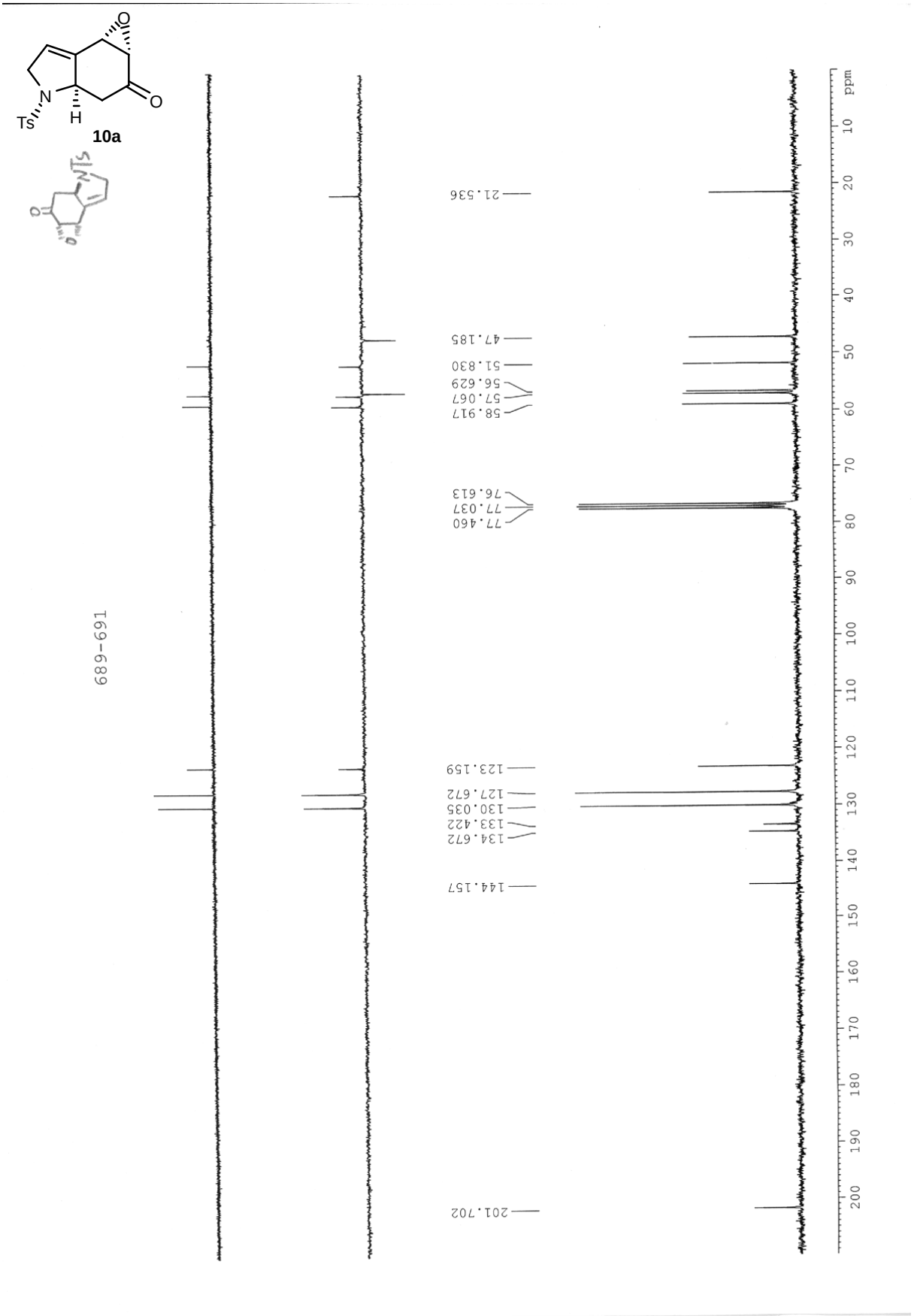

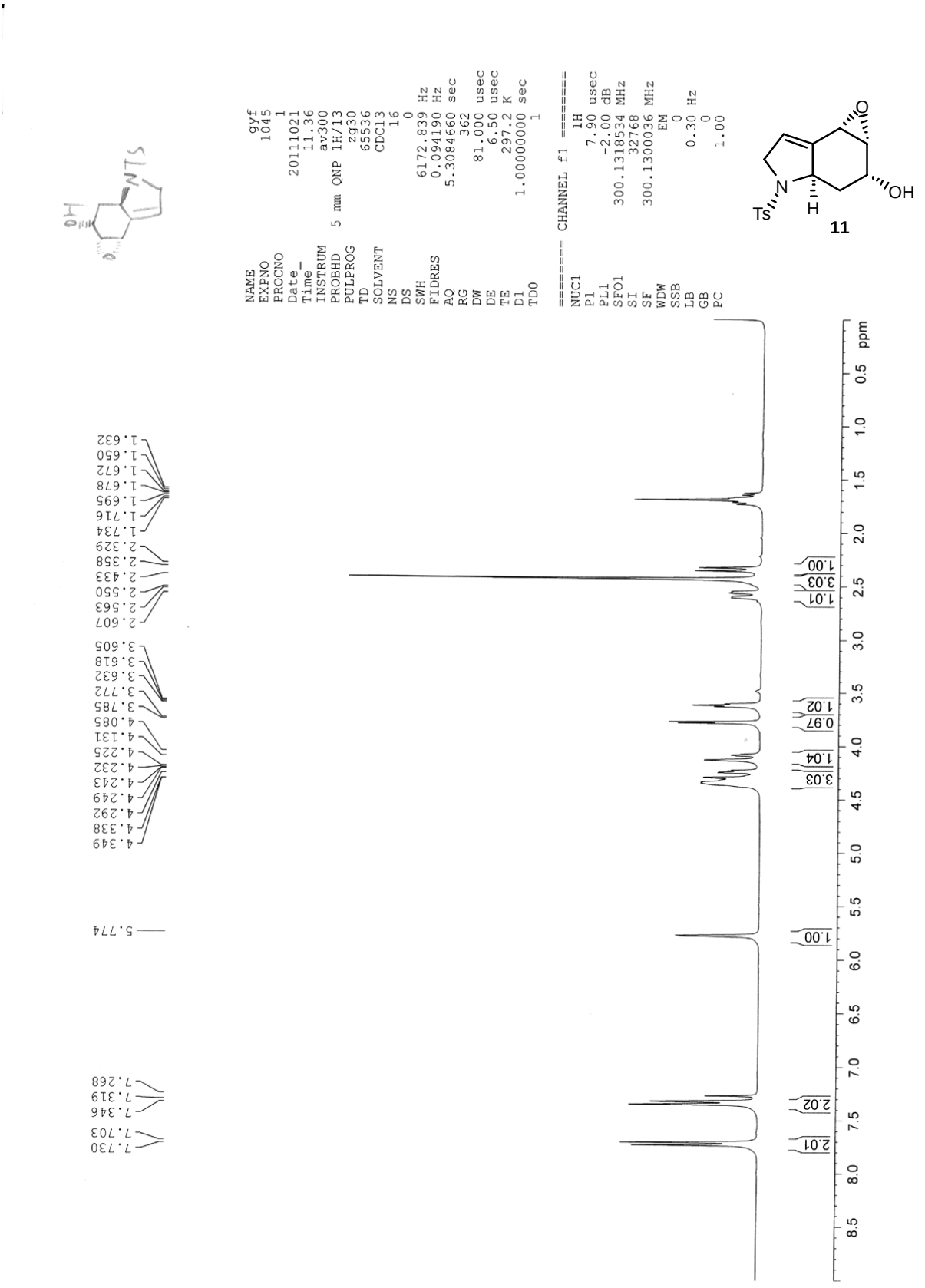
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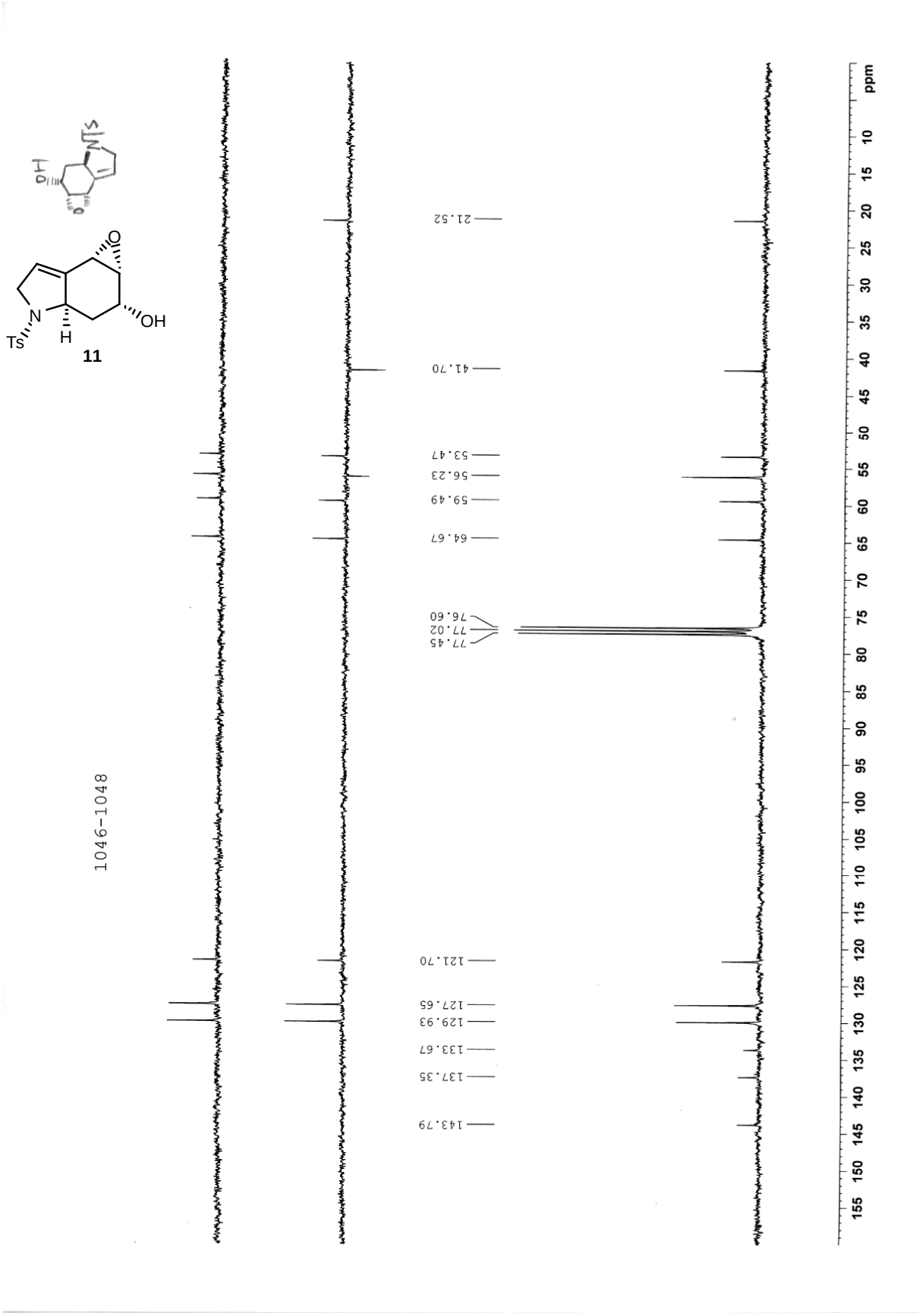

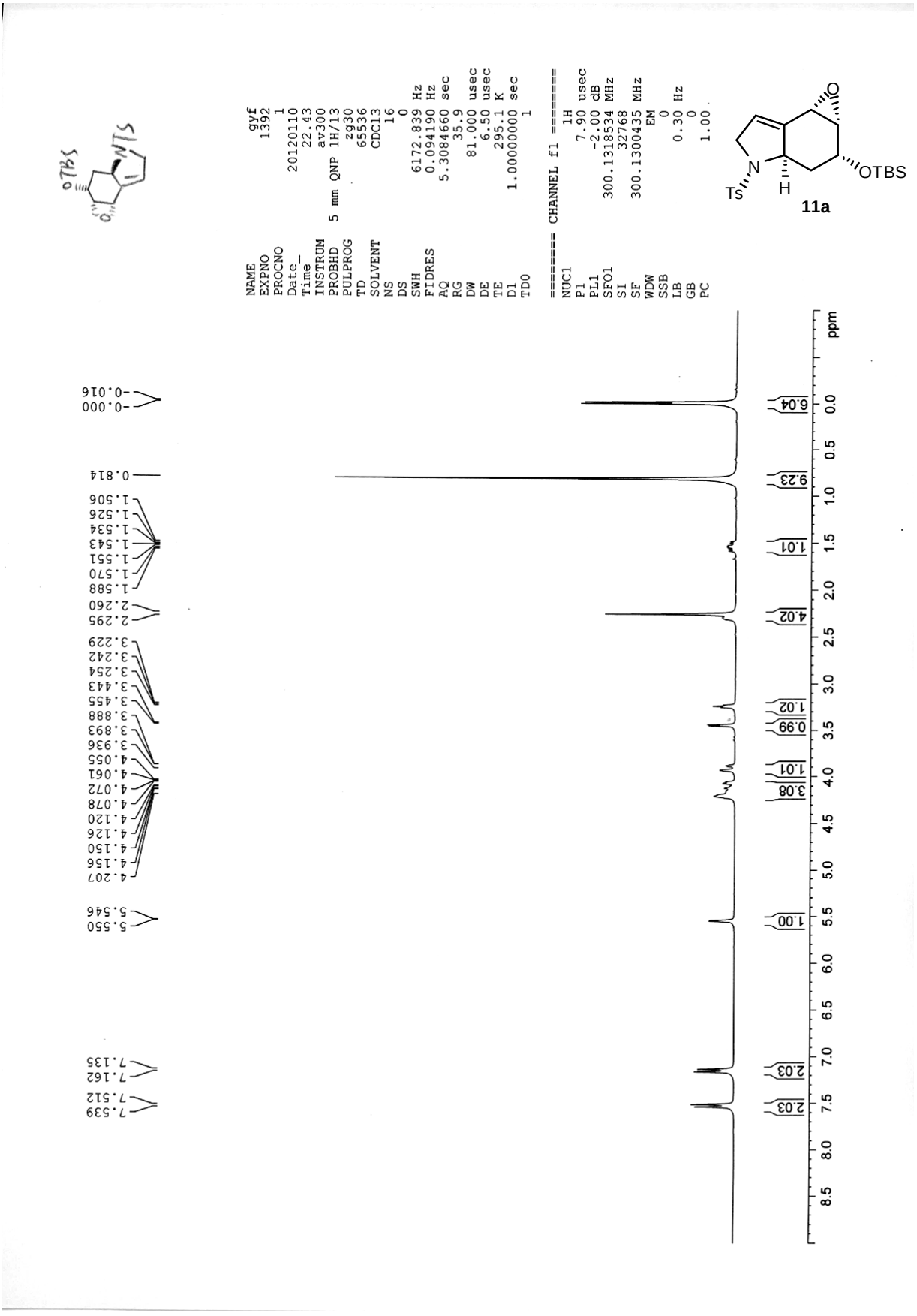
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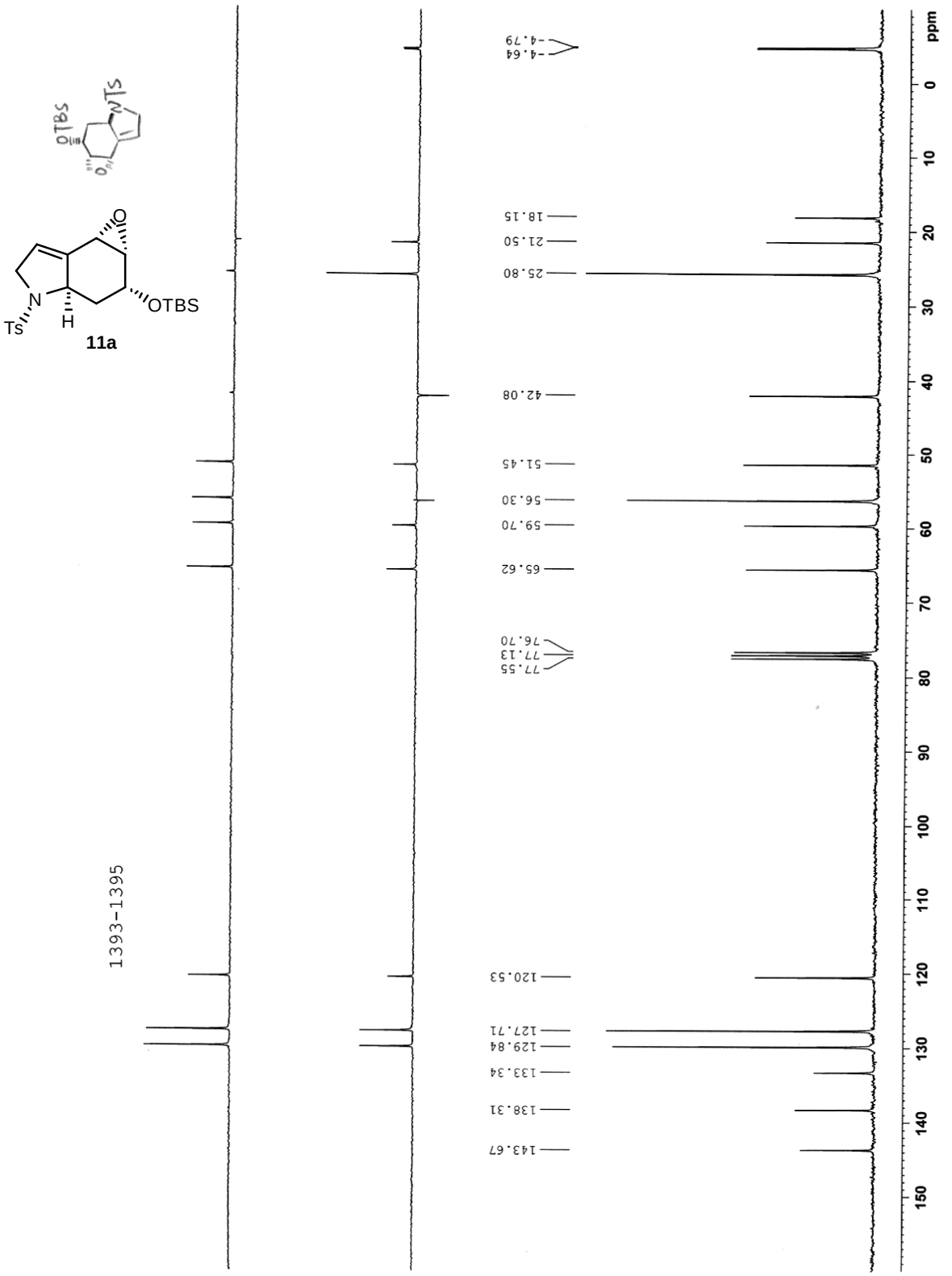
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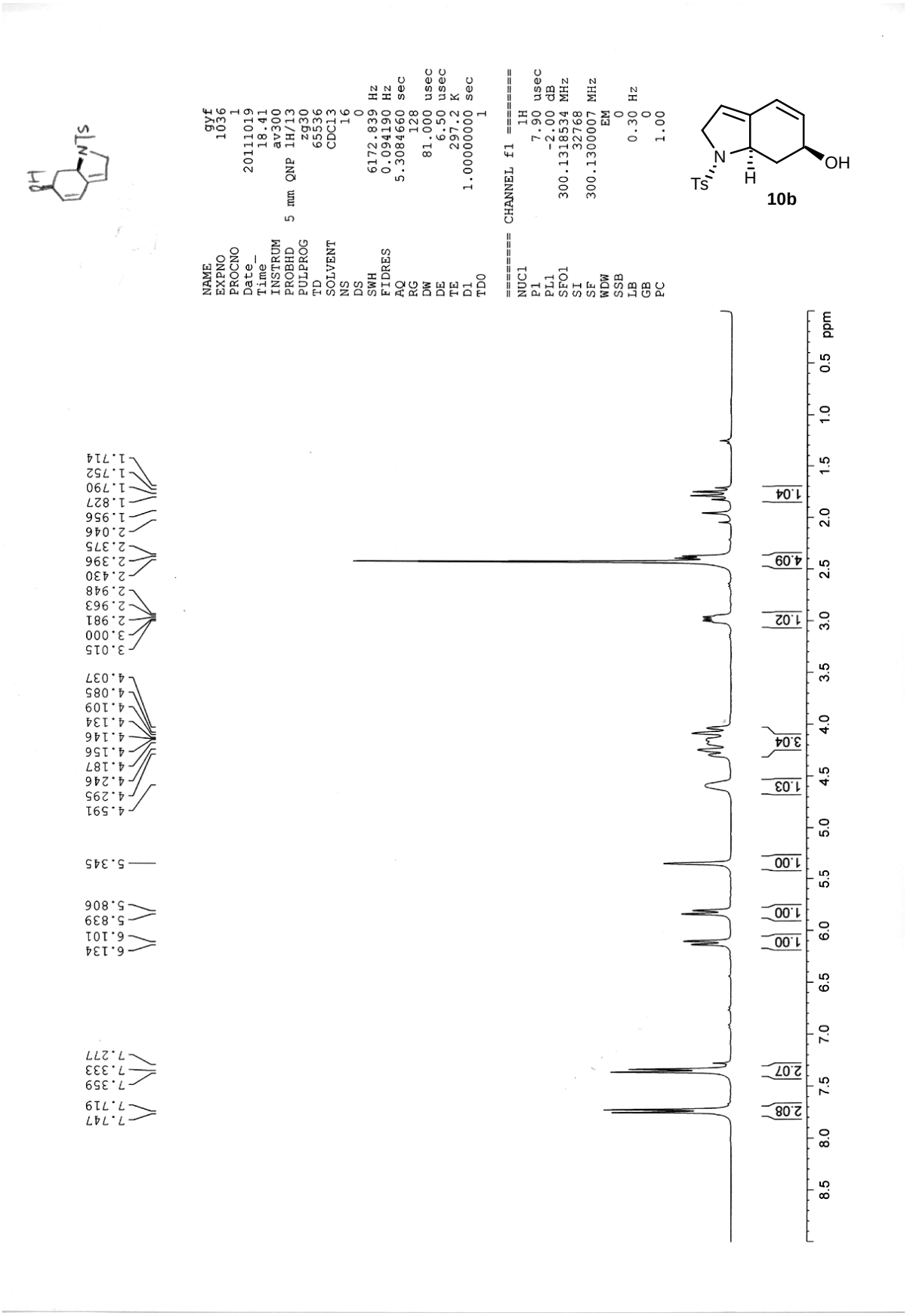

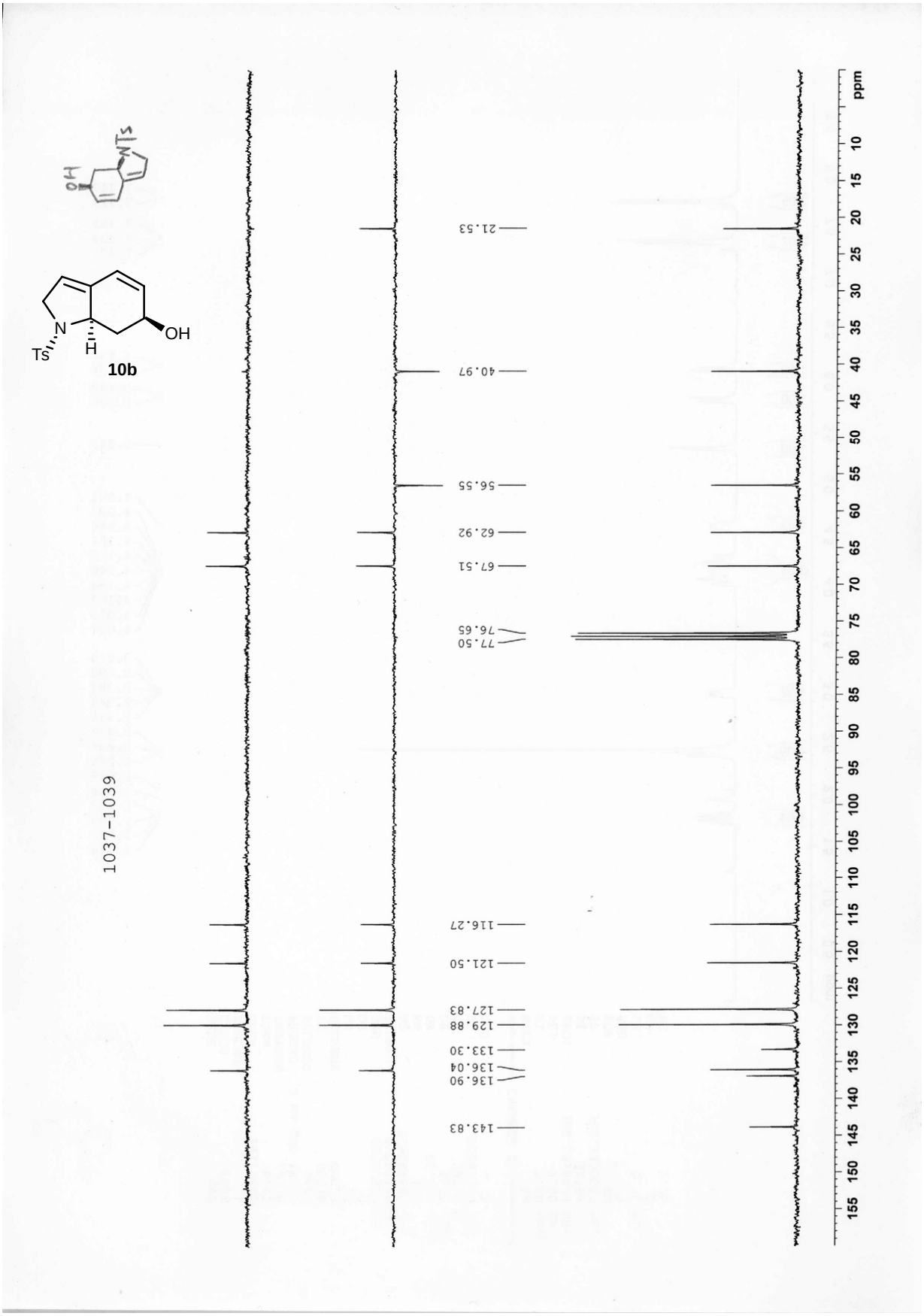

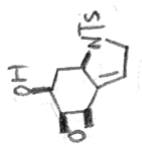

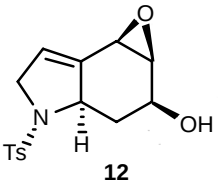

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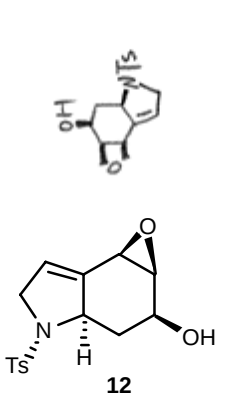
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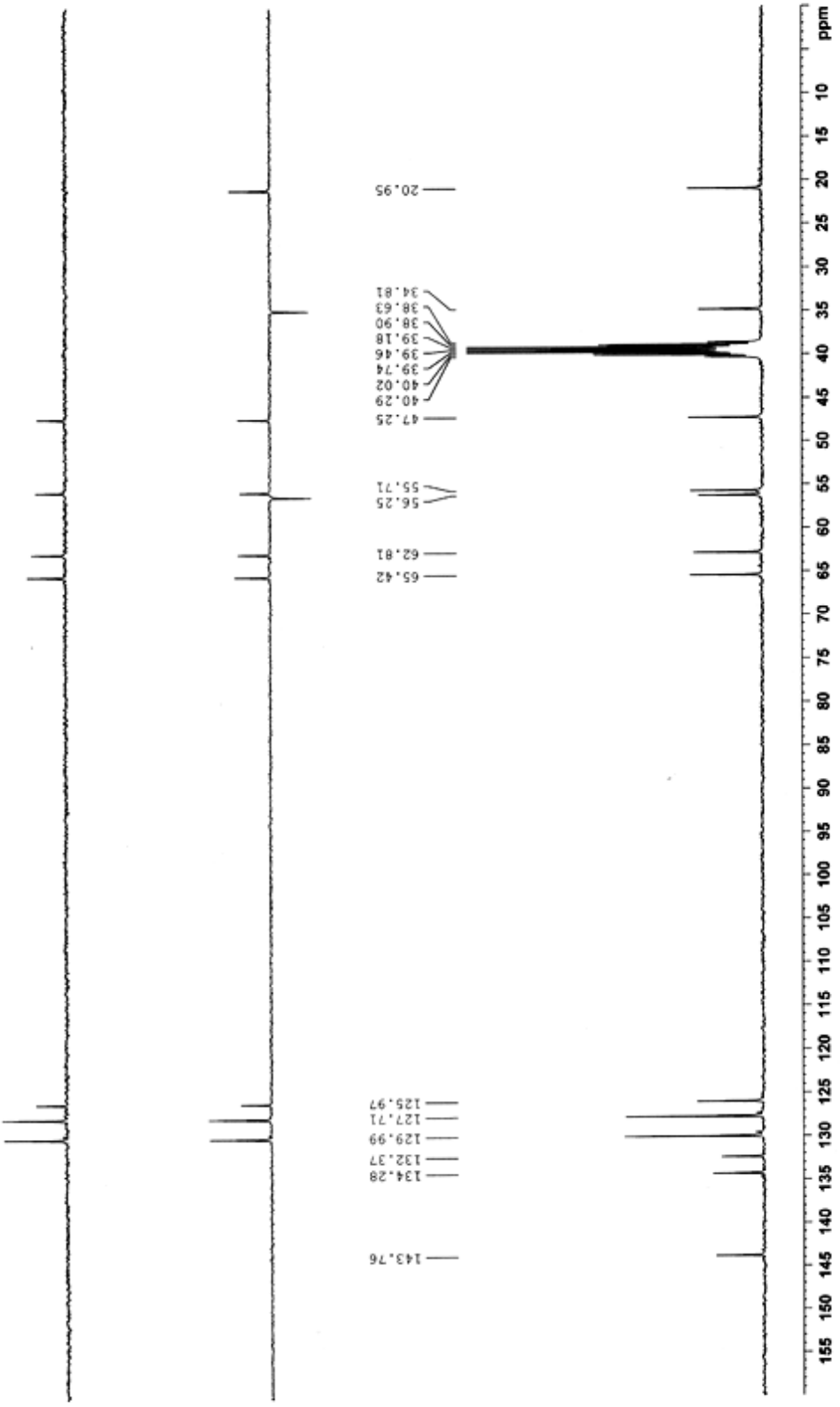
12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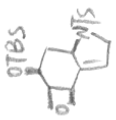

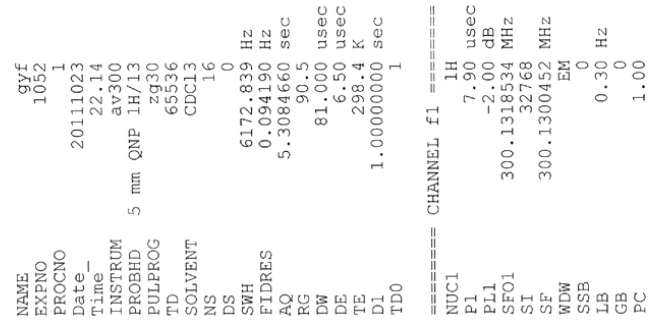

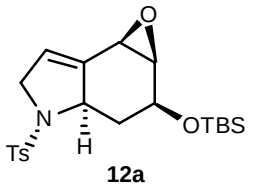

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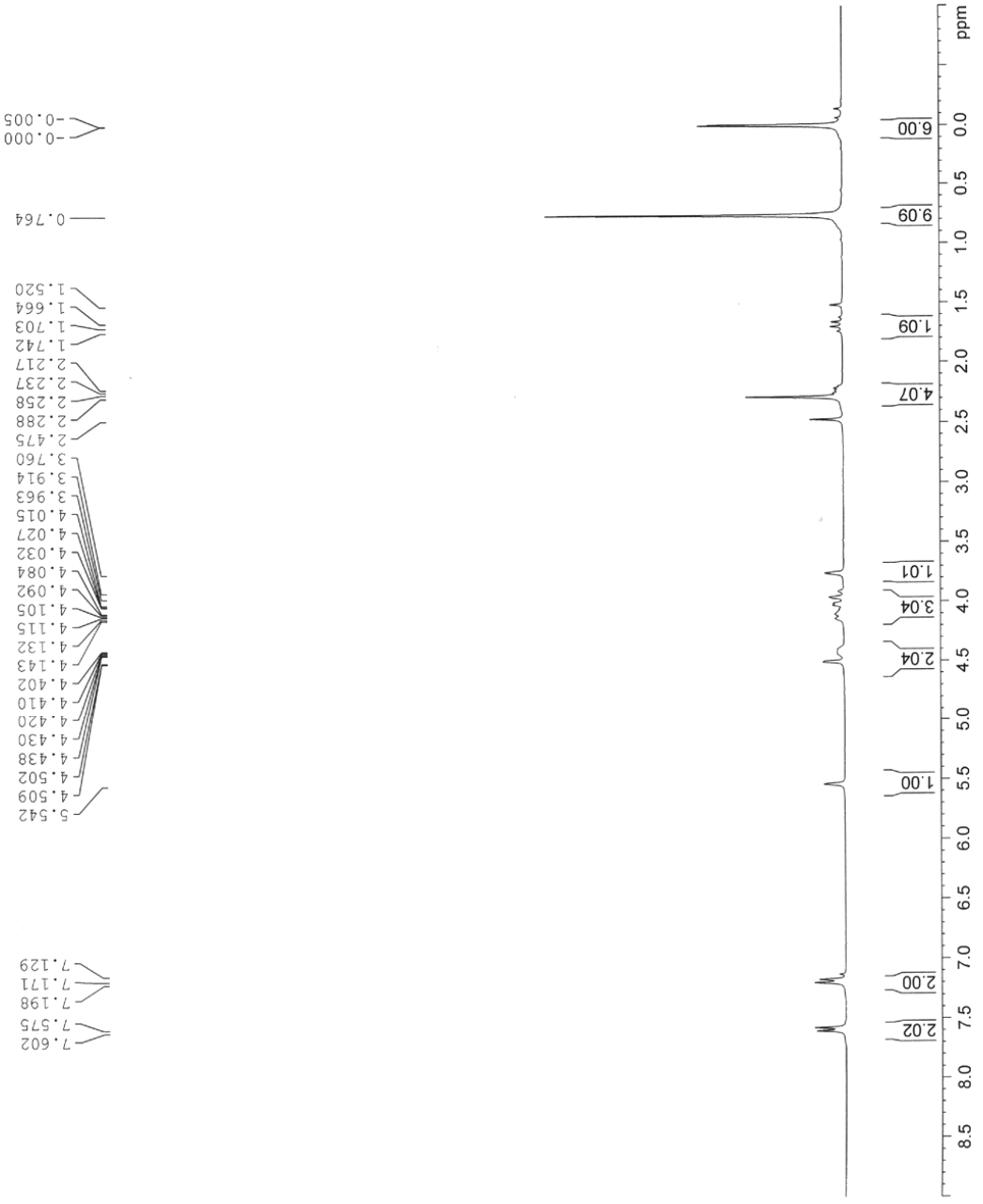

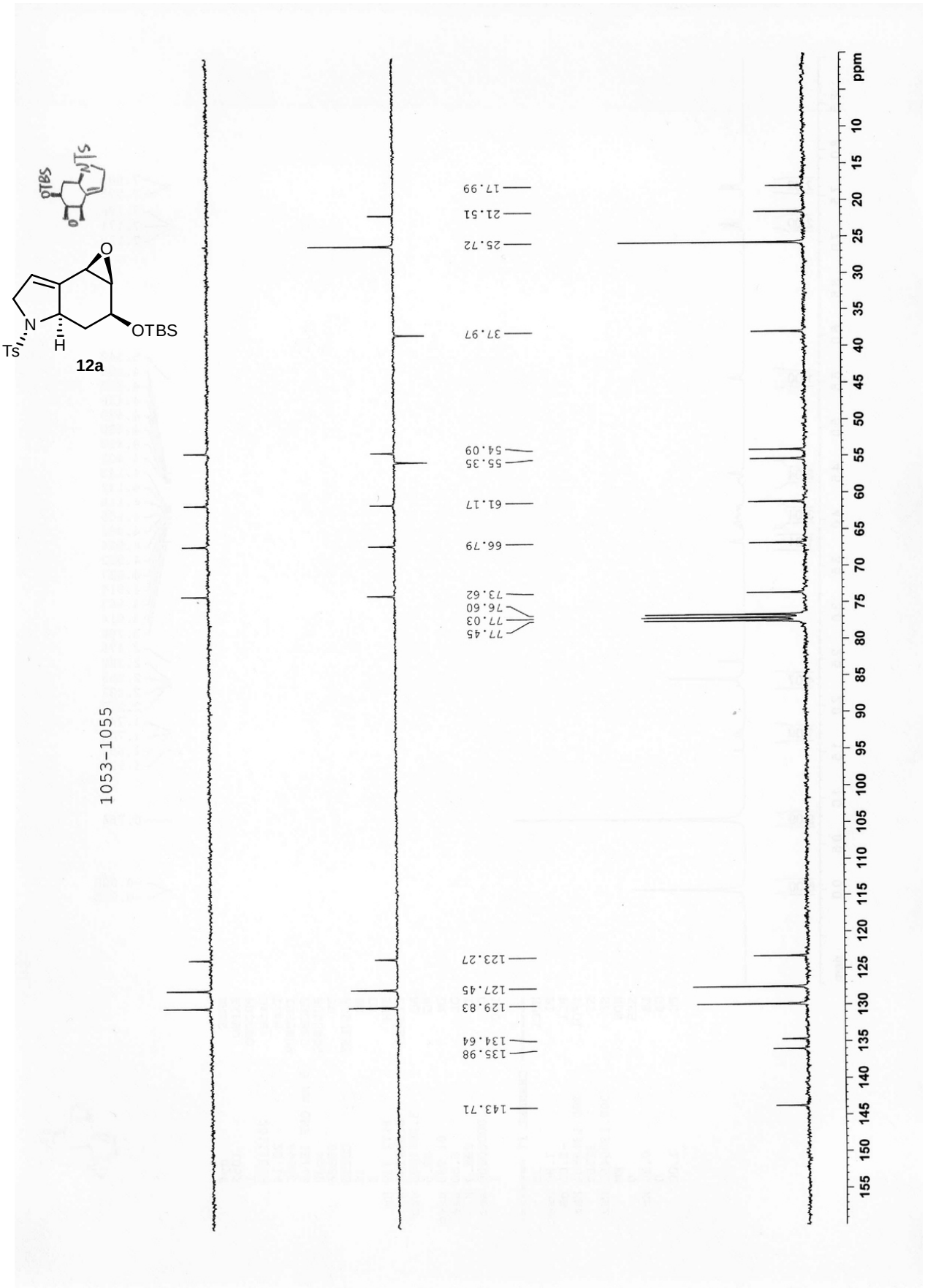

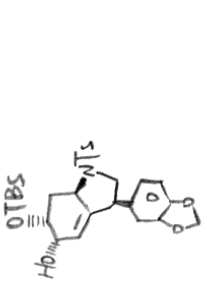


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TD                   65536
SOLVENT              CDCl3
NS                      16
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SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084660 sec
RG                      90.5
DW                 81.000 usec
DE                  6.50 usec
TE                  295.0 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  7.90 usec
PL1                 -2.00 dB
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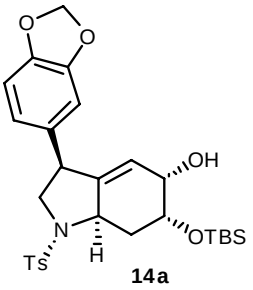

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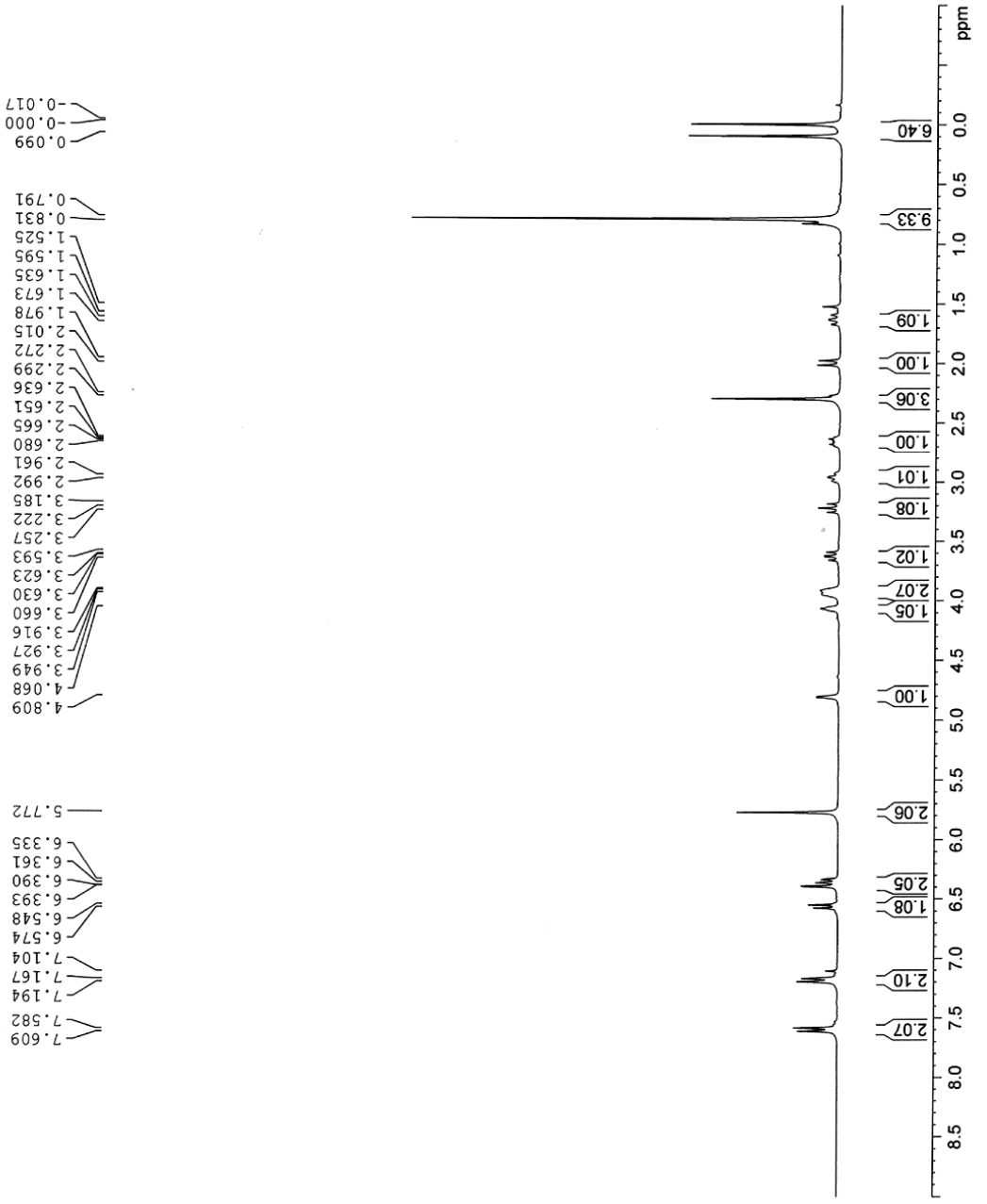

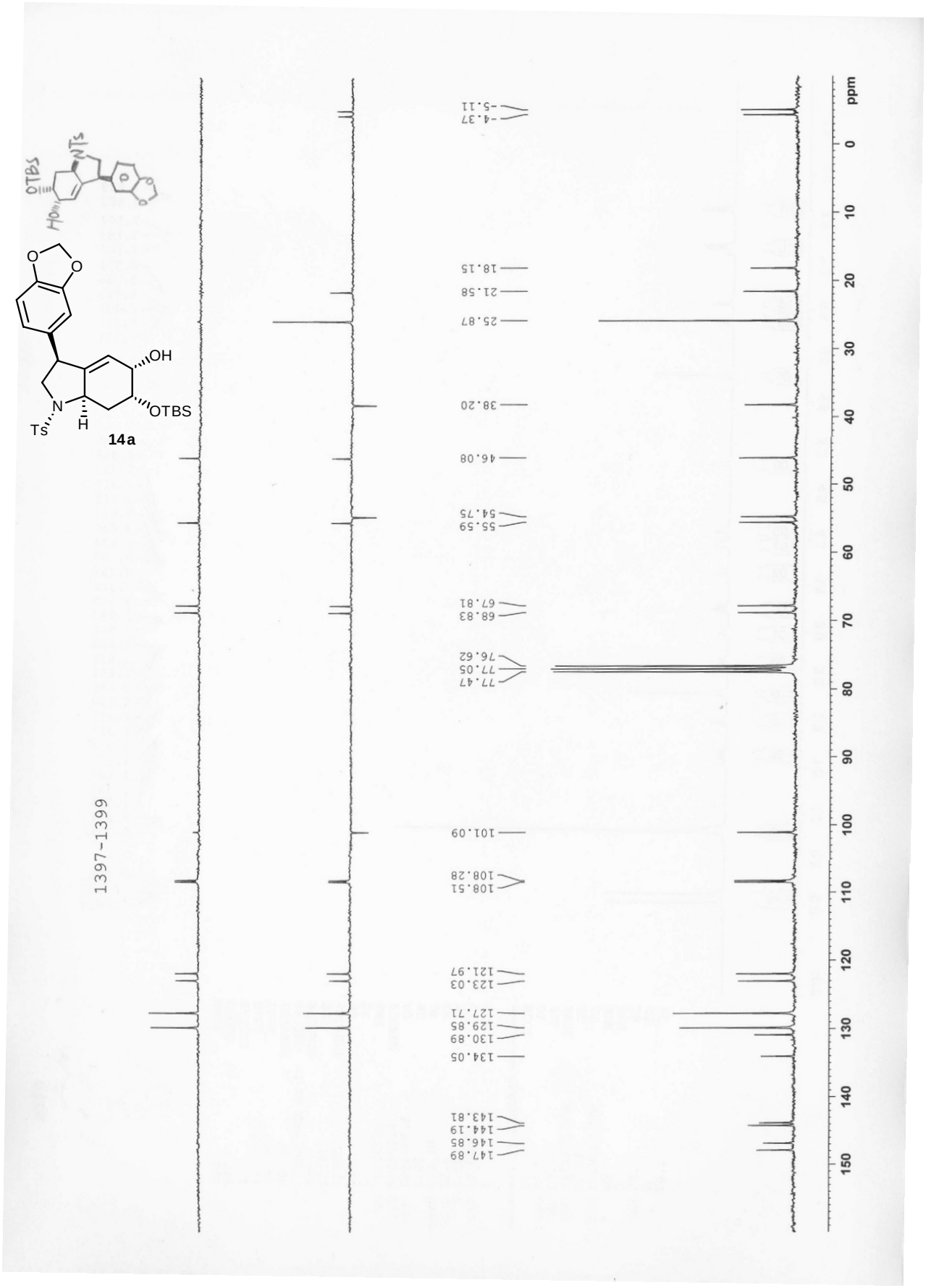

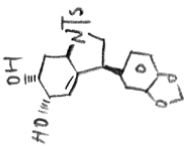

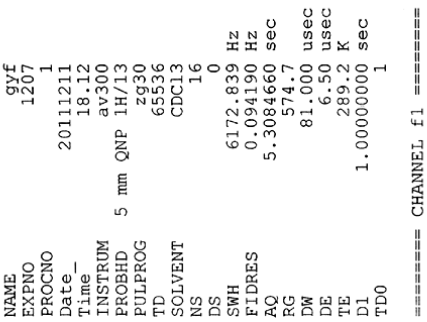

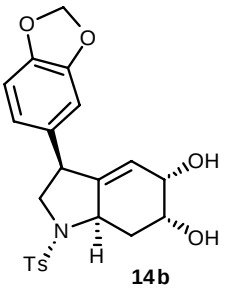

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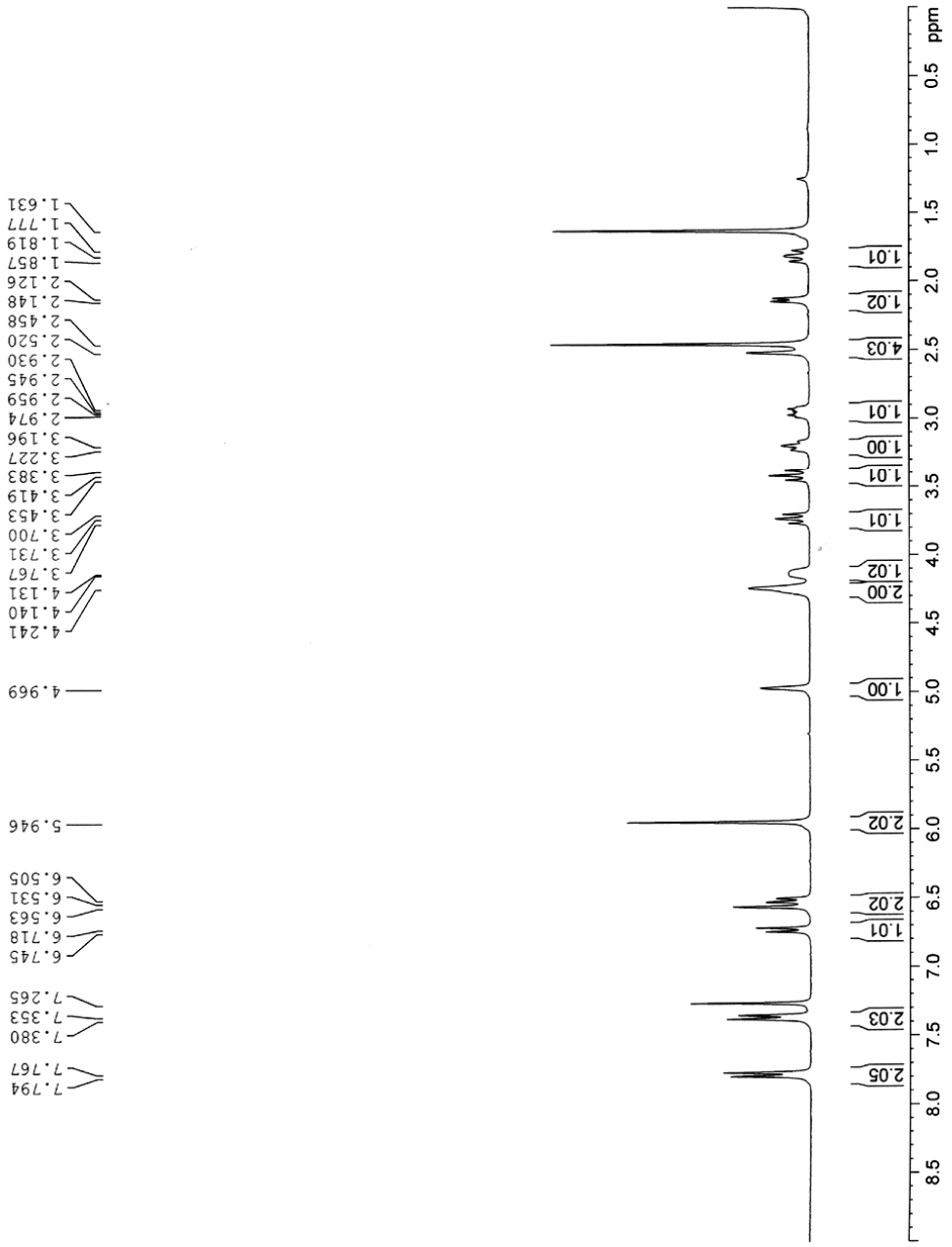

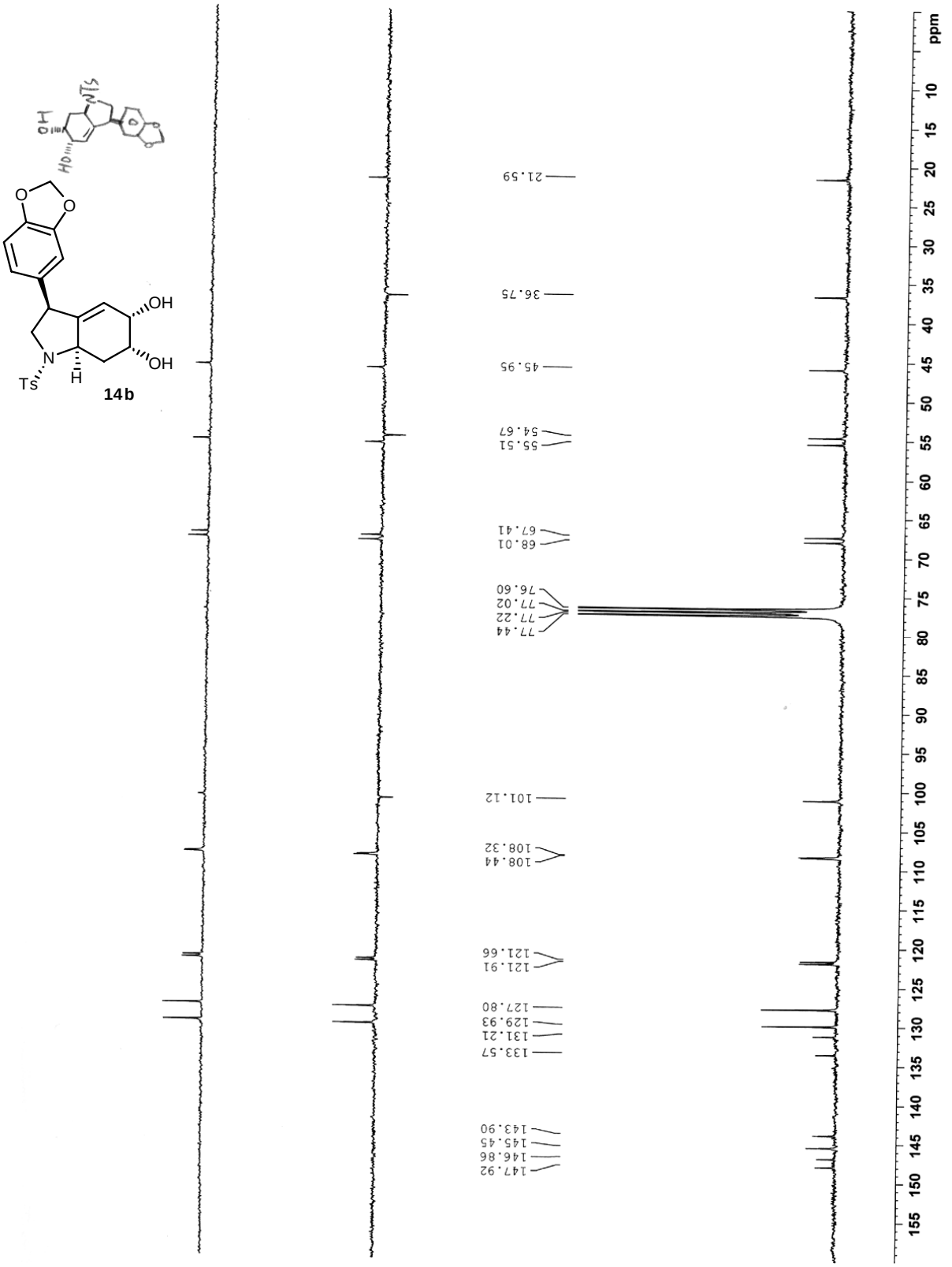

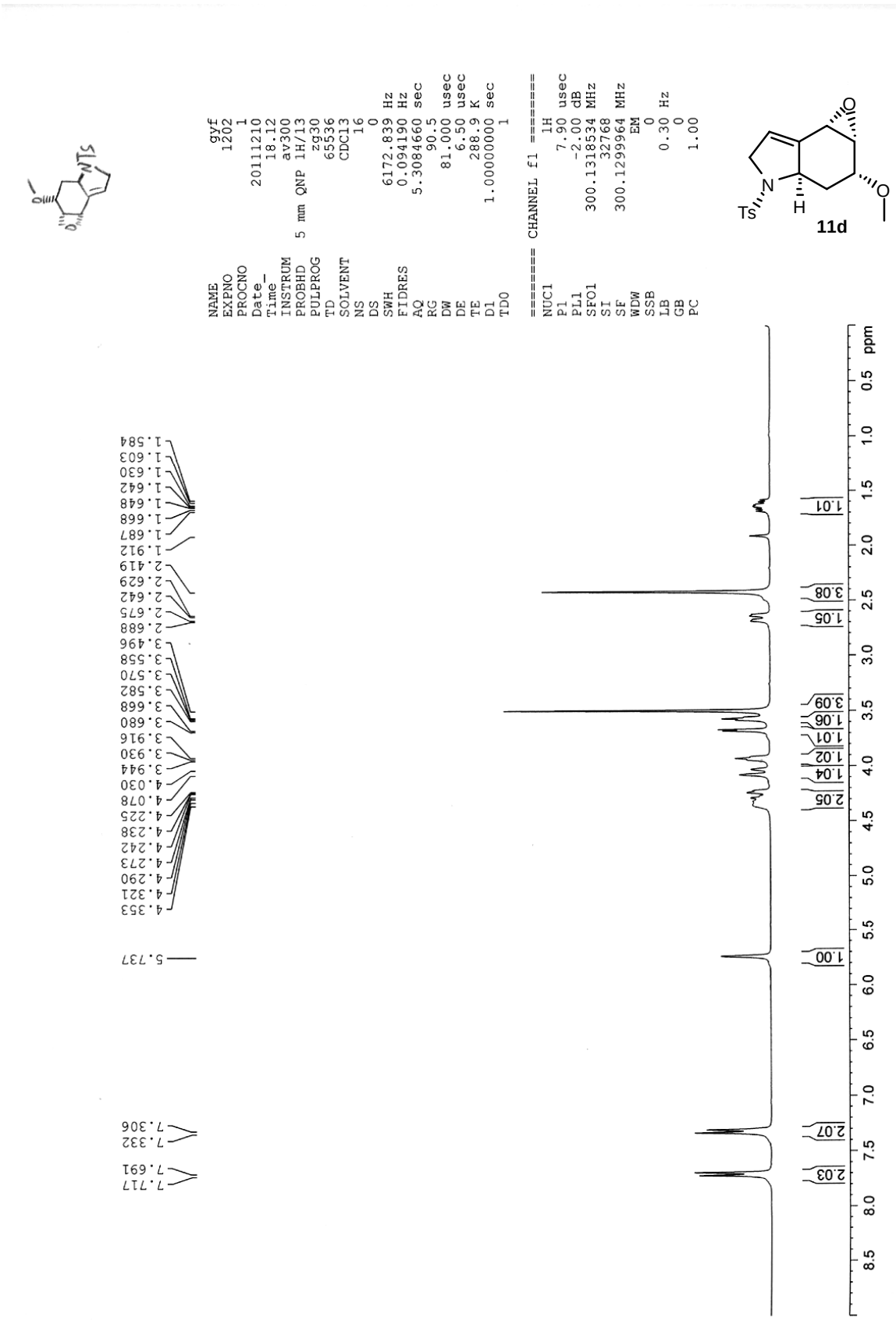
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TD 65536
SOLVENT CDC13
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SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 90.5
DW 81.000 usec
DE 6.50 usec
TE 288.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.90 usec
PL1 -2.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1299964 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
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1.603
1.630
1.642
1.648
1.668
1.687
1.912
2.419
2.629
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3.582
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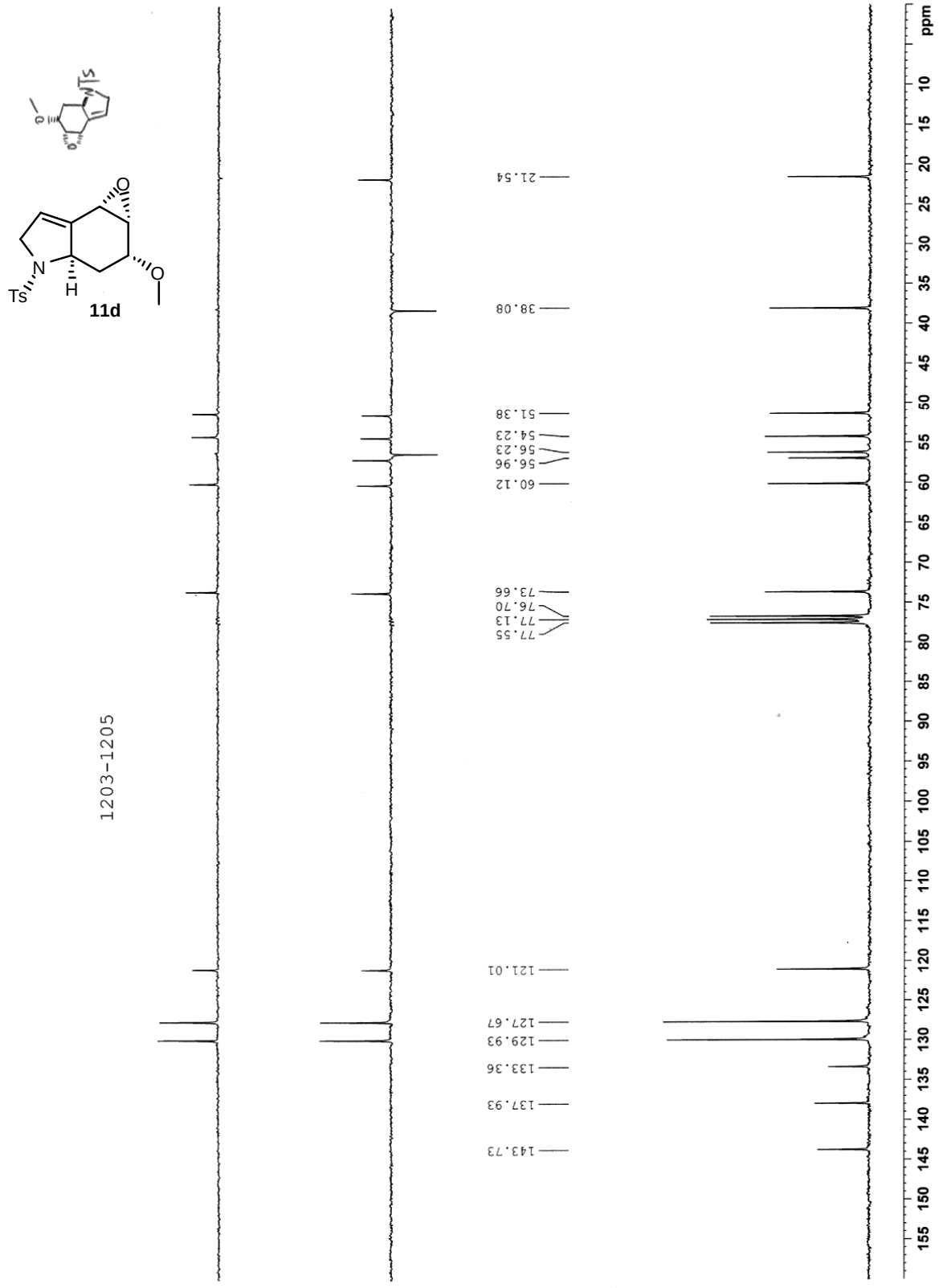

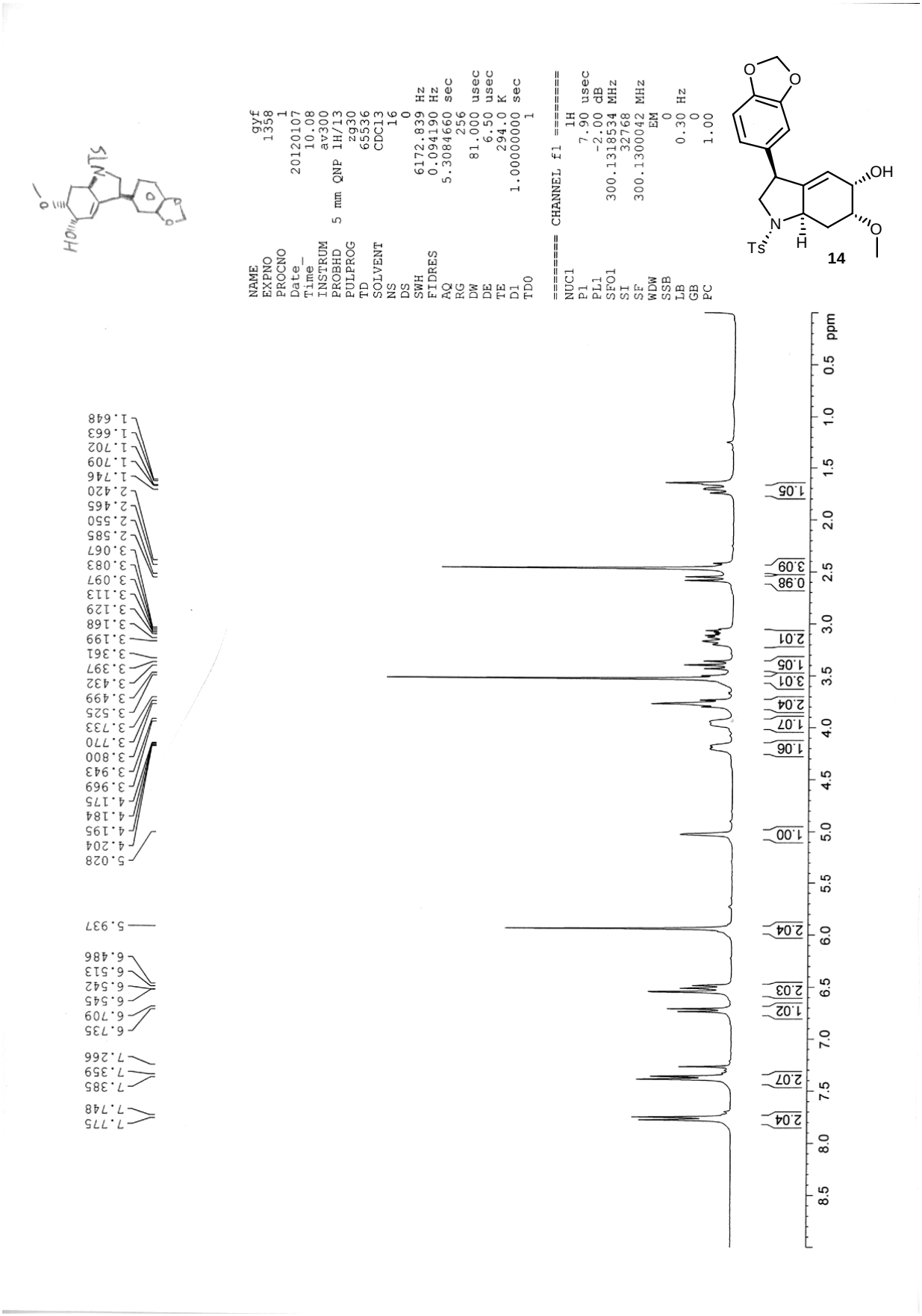

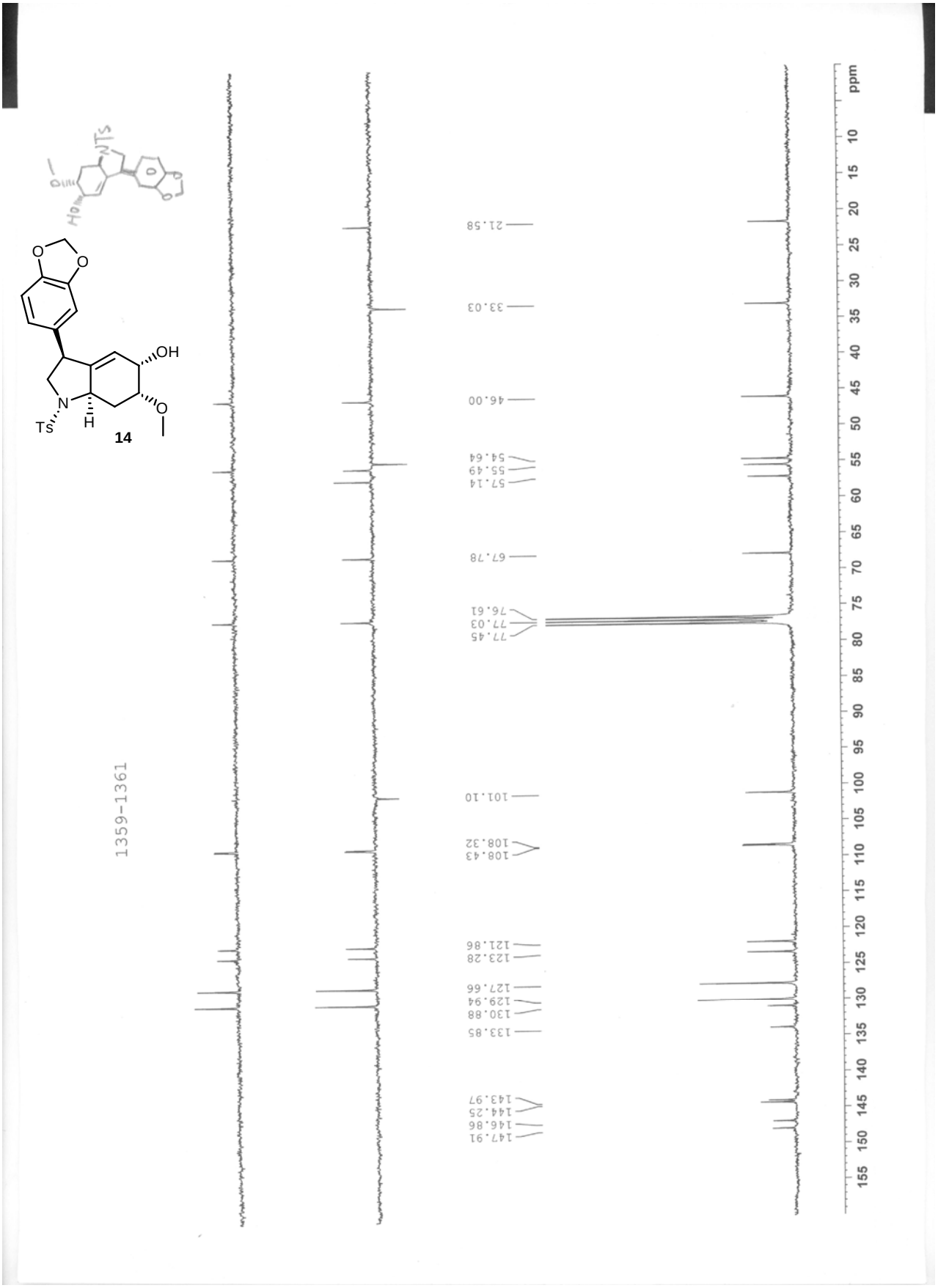

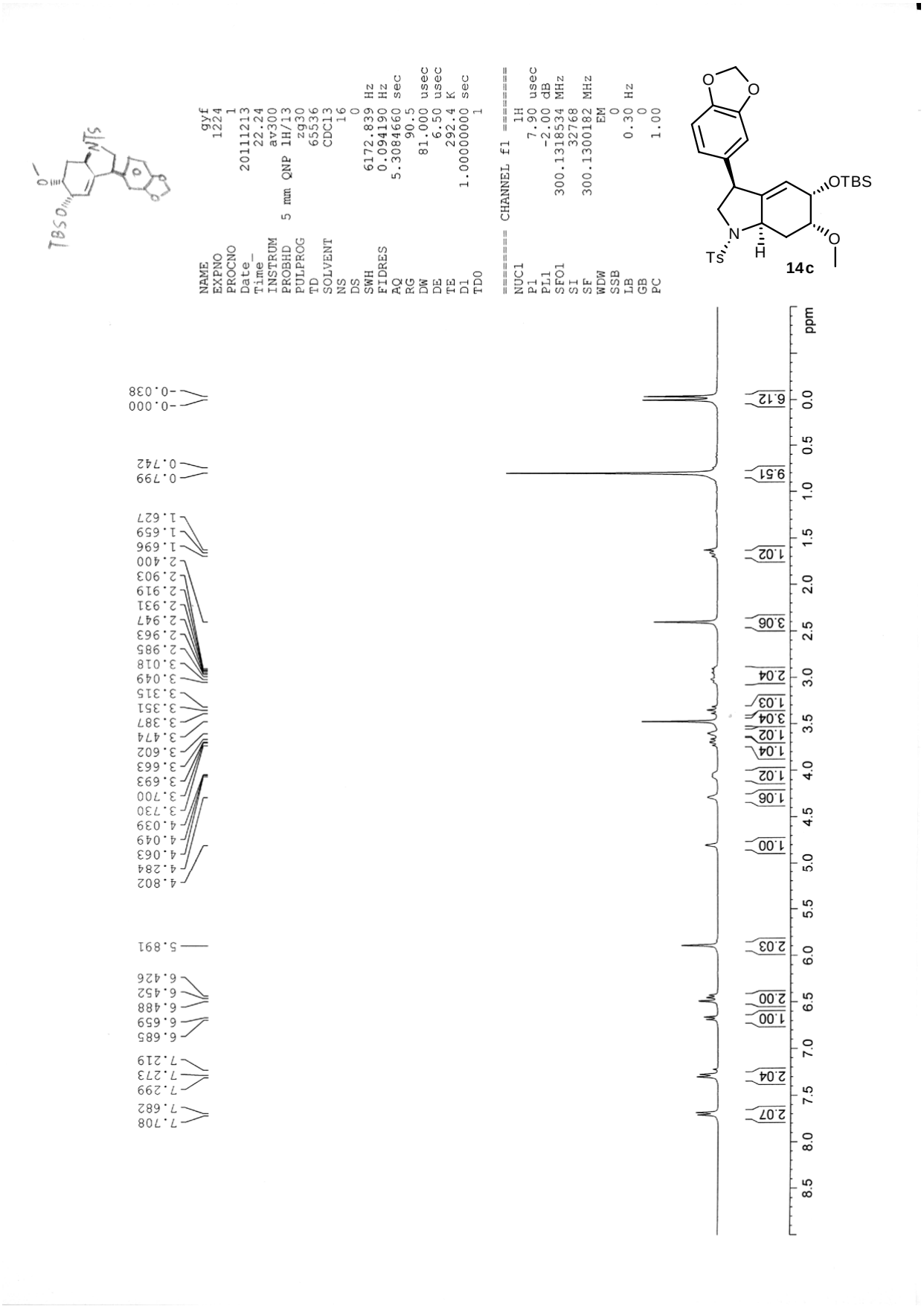

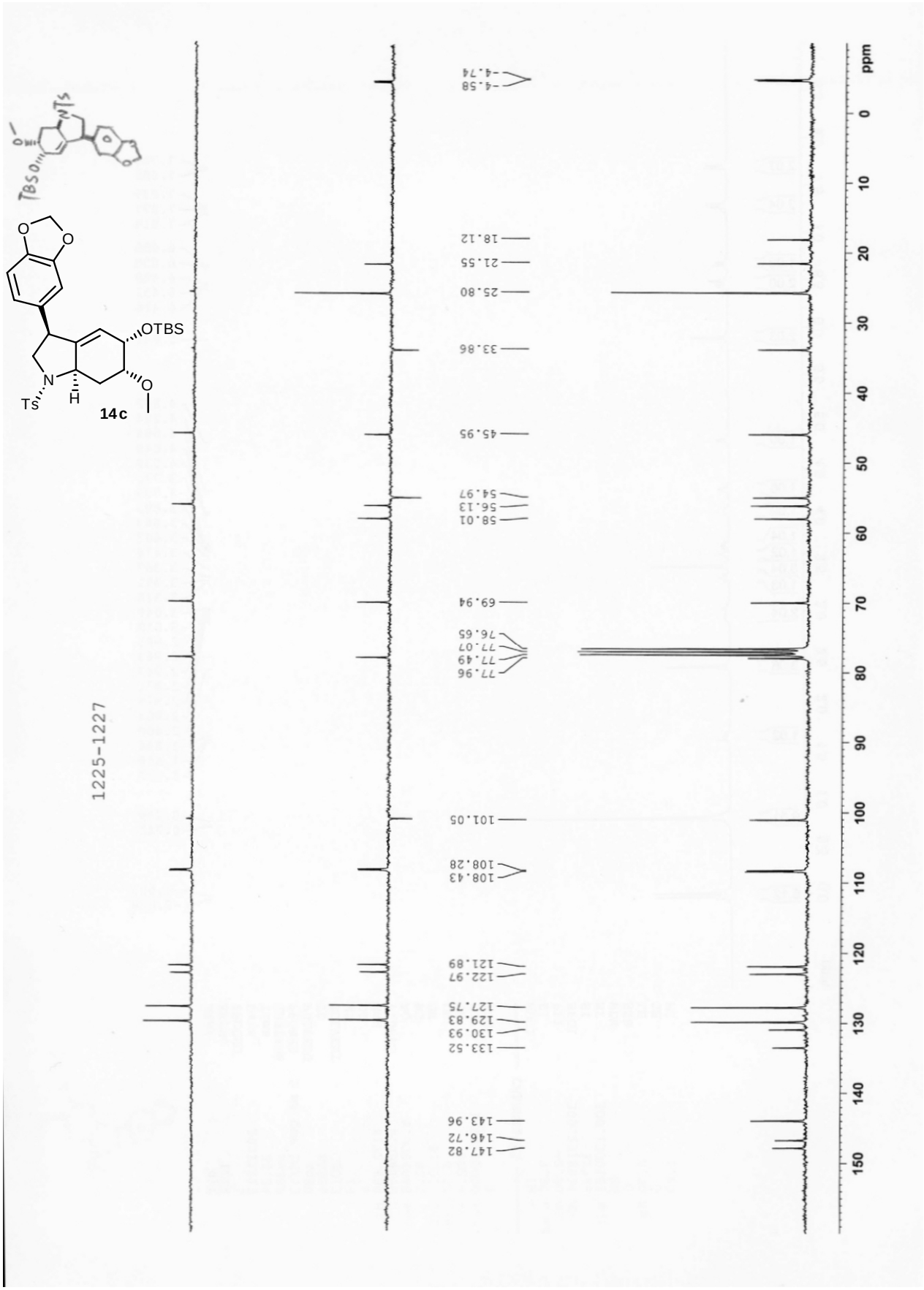

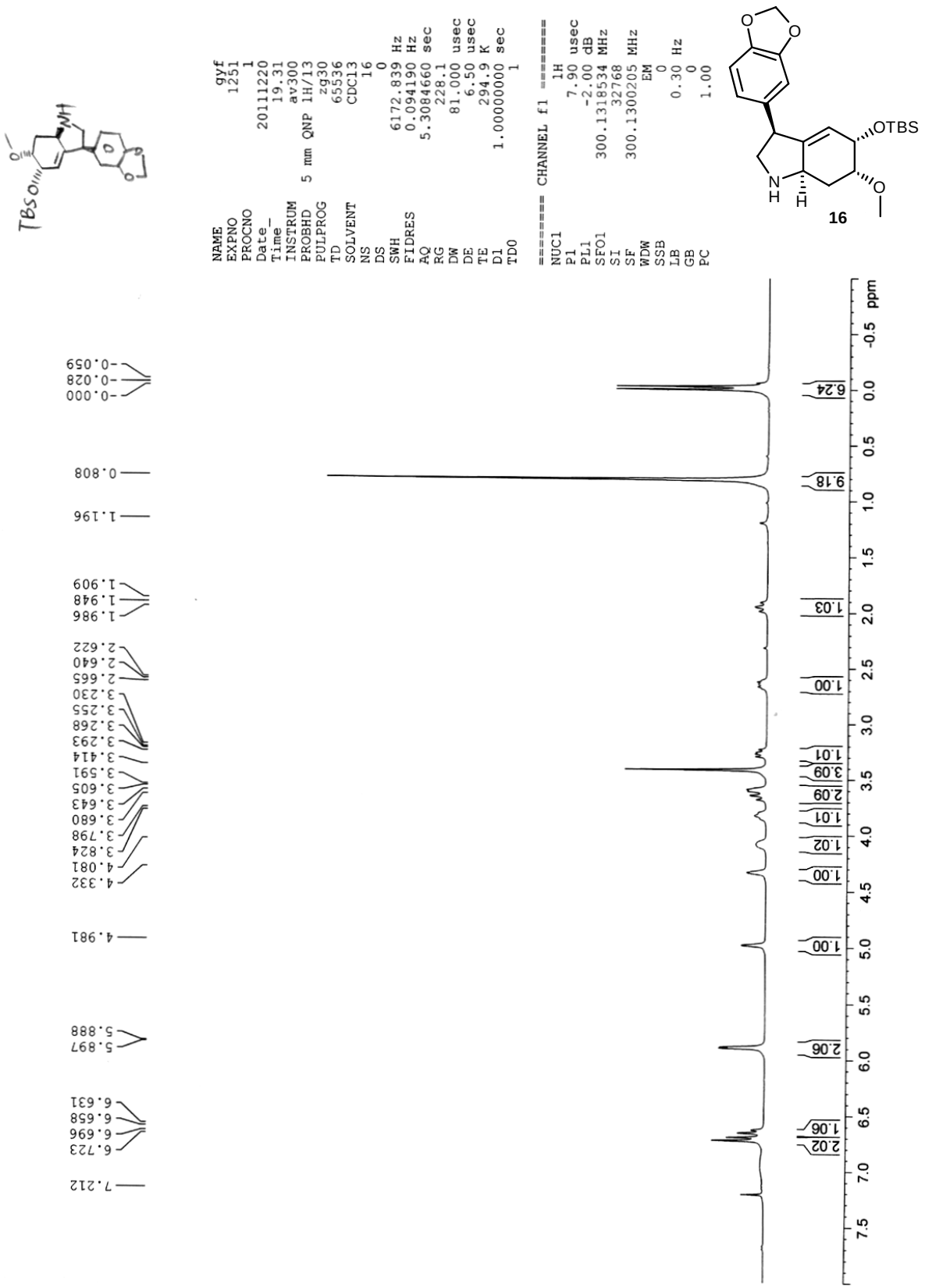

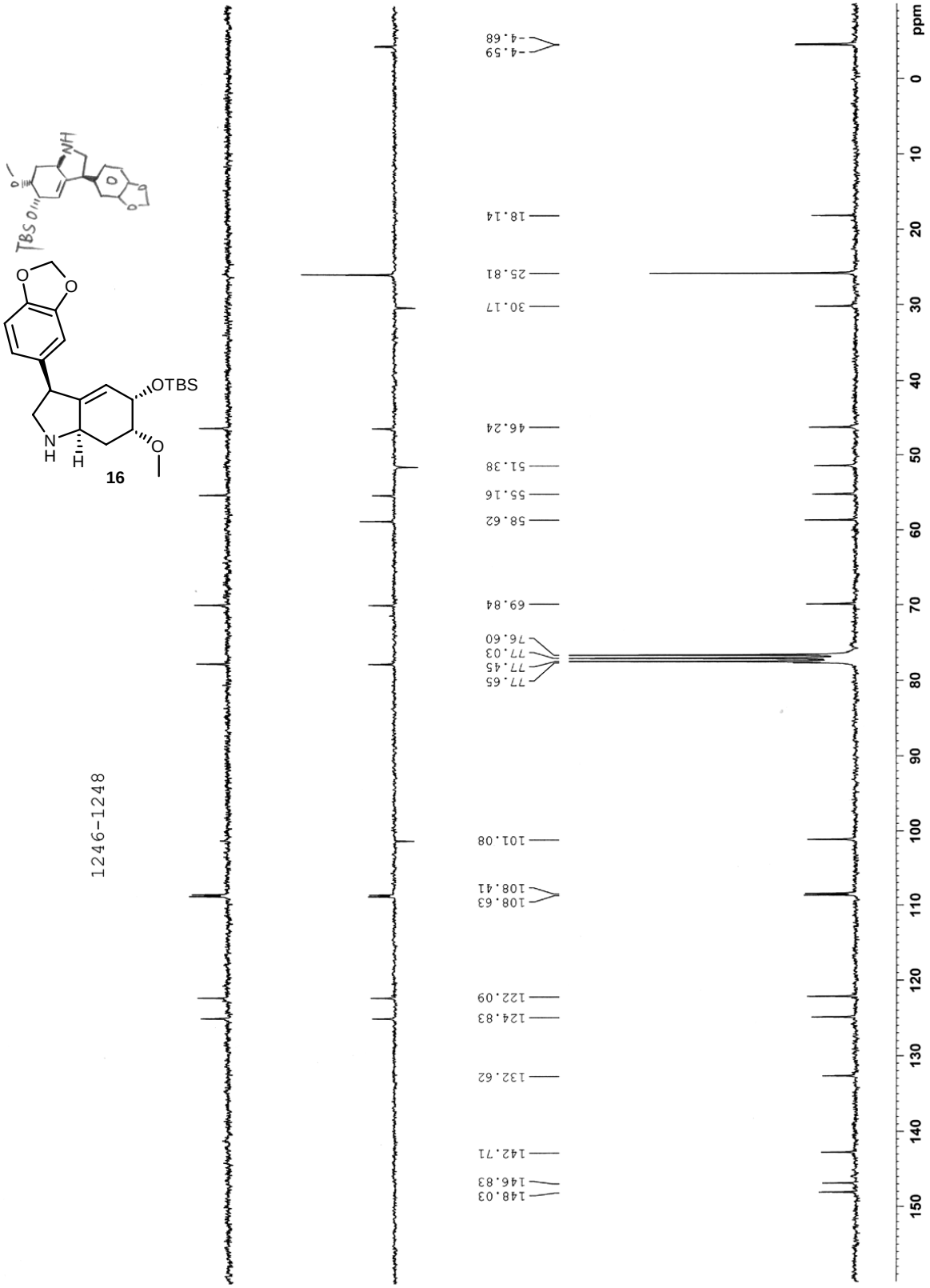

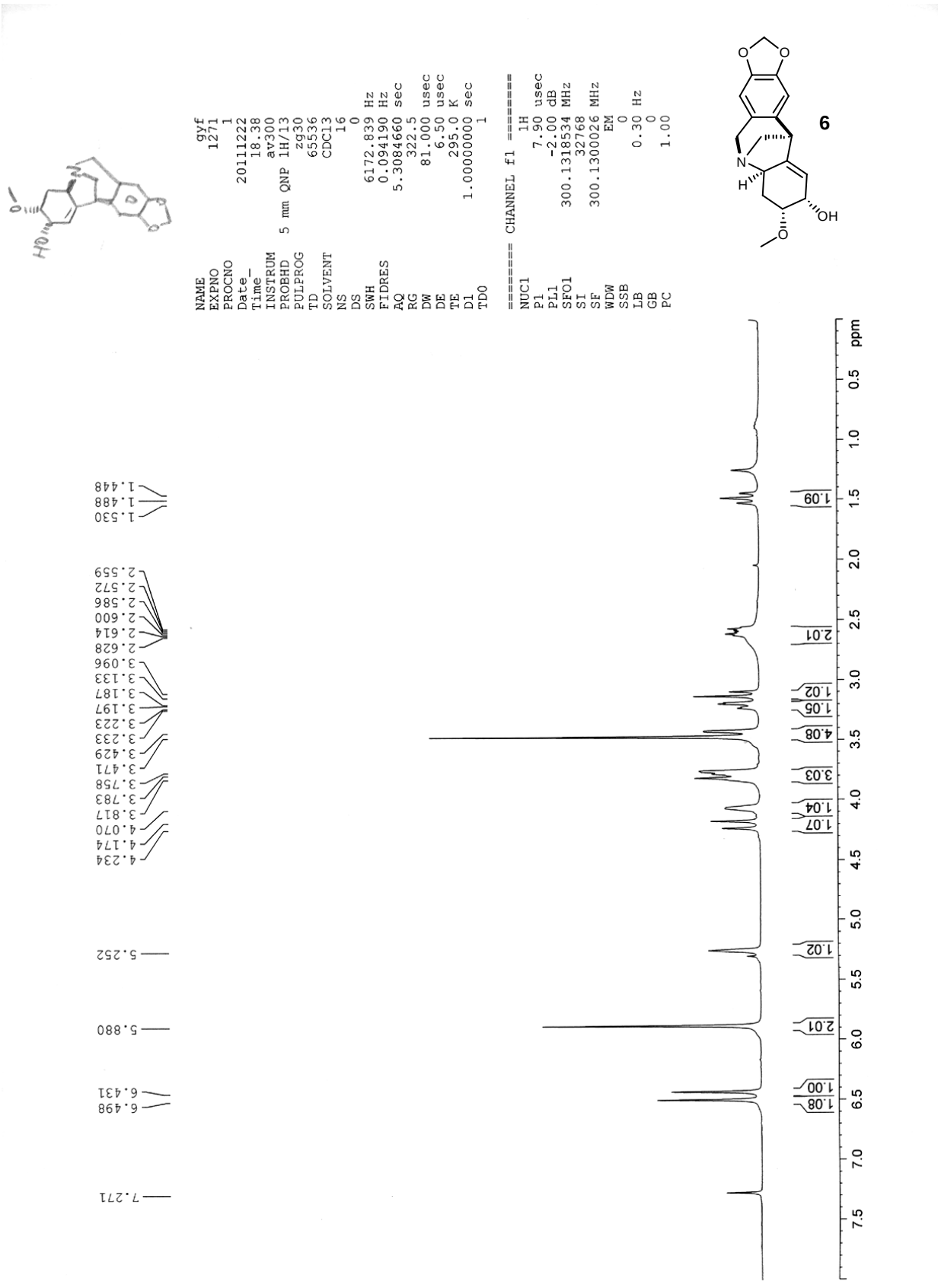

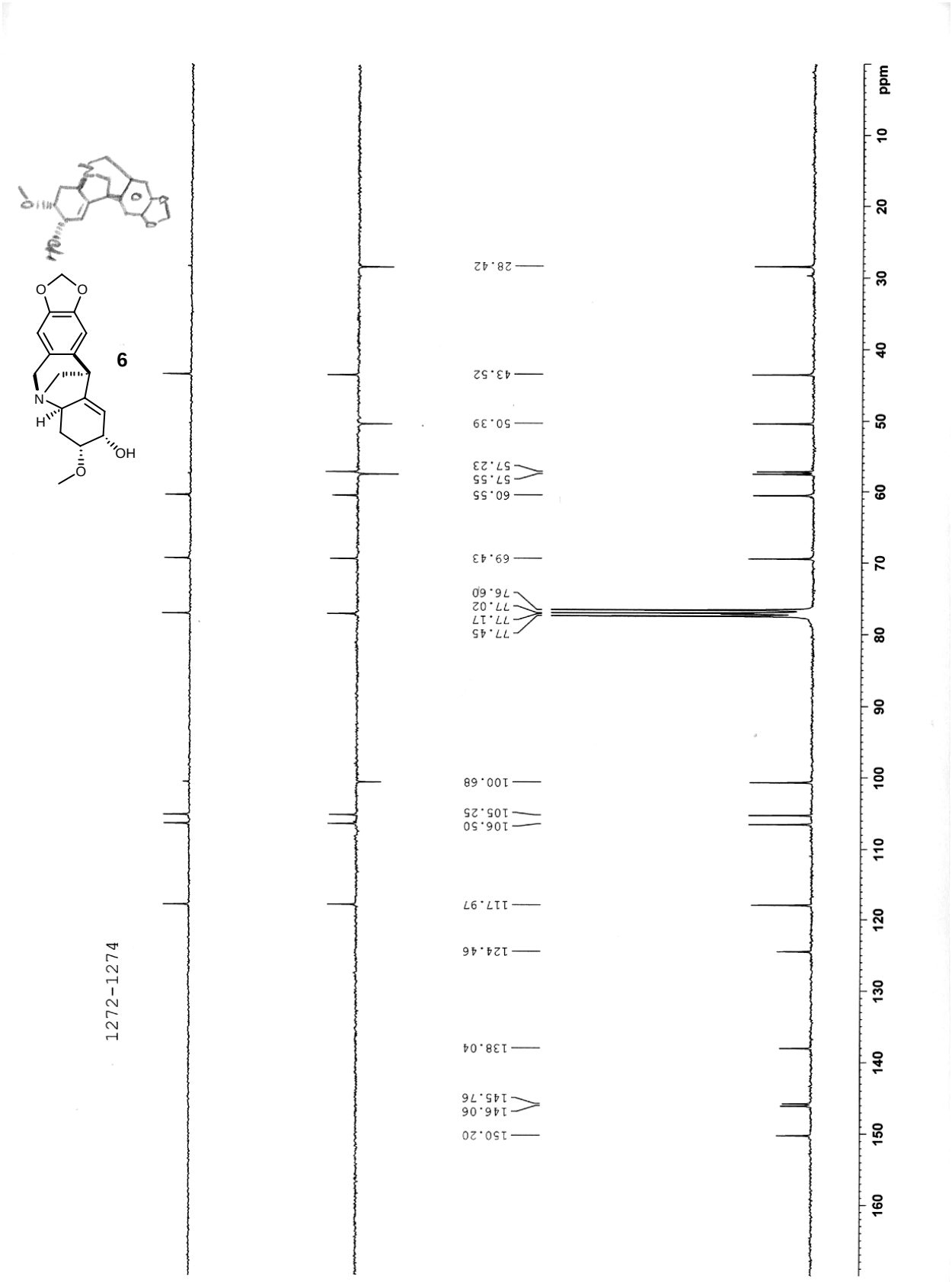

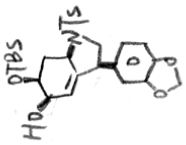

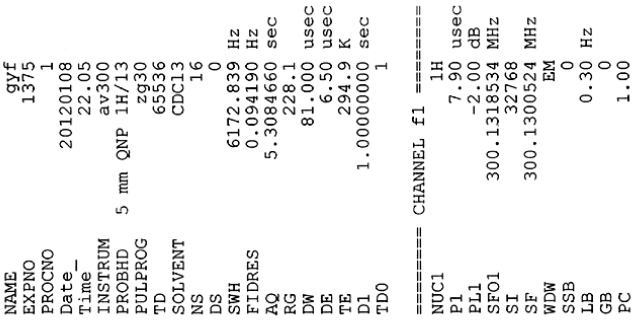

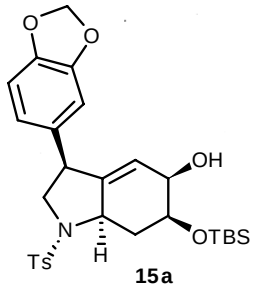

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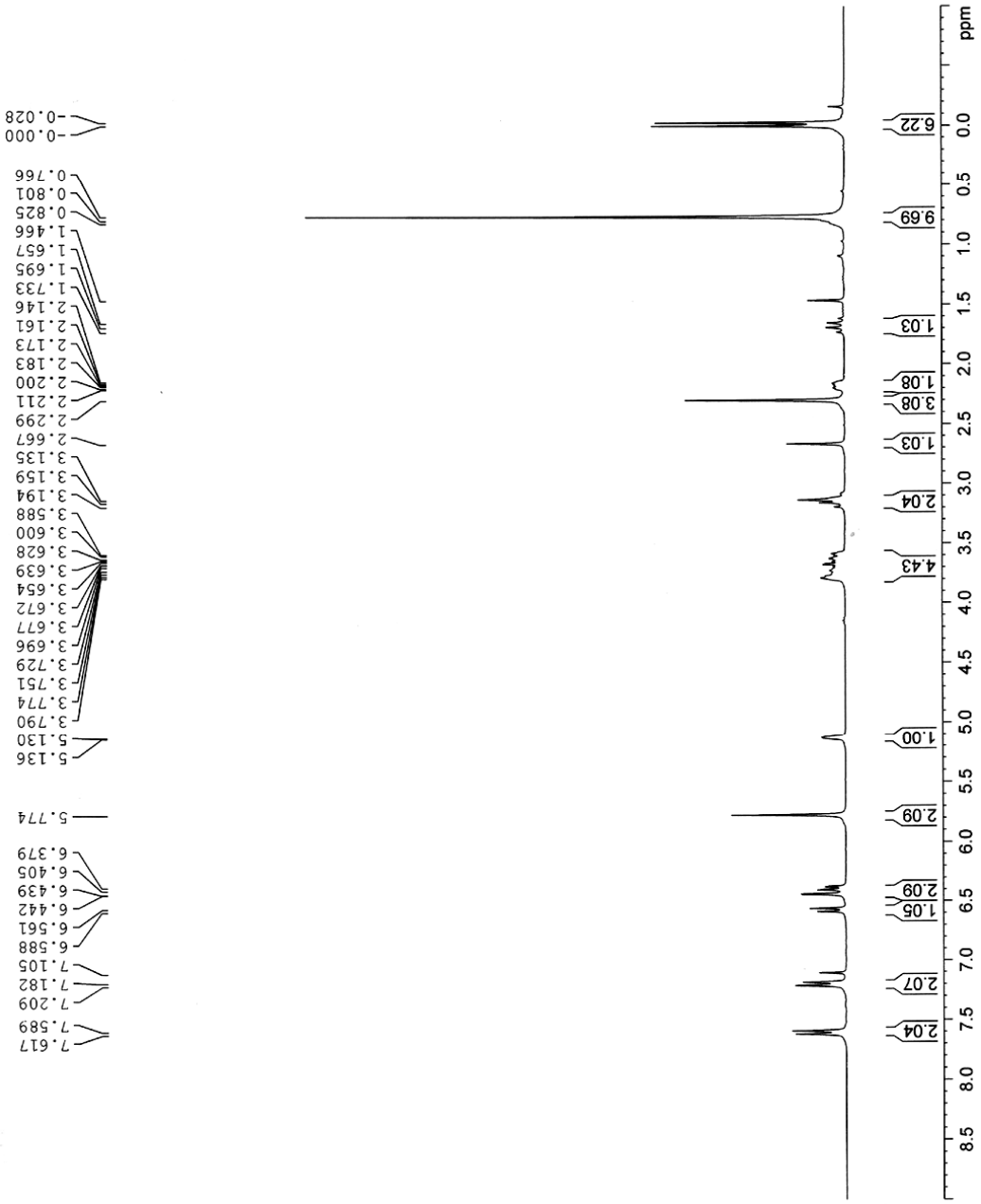

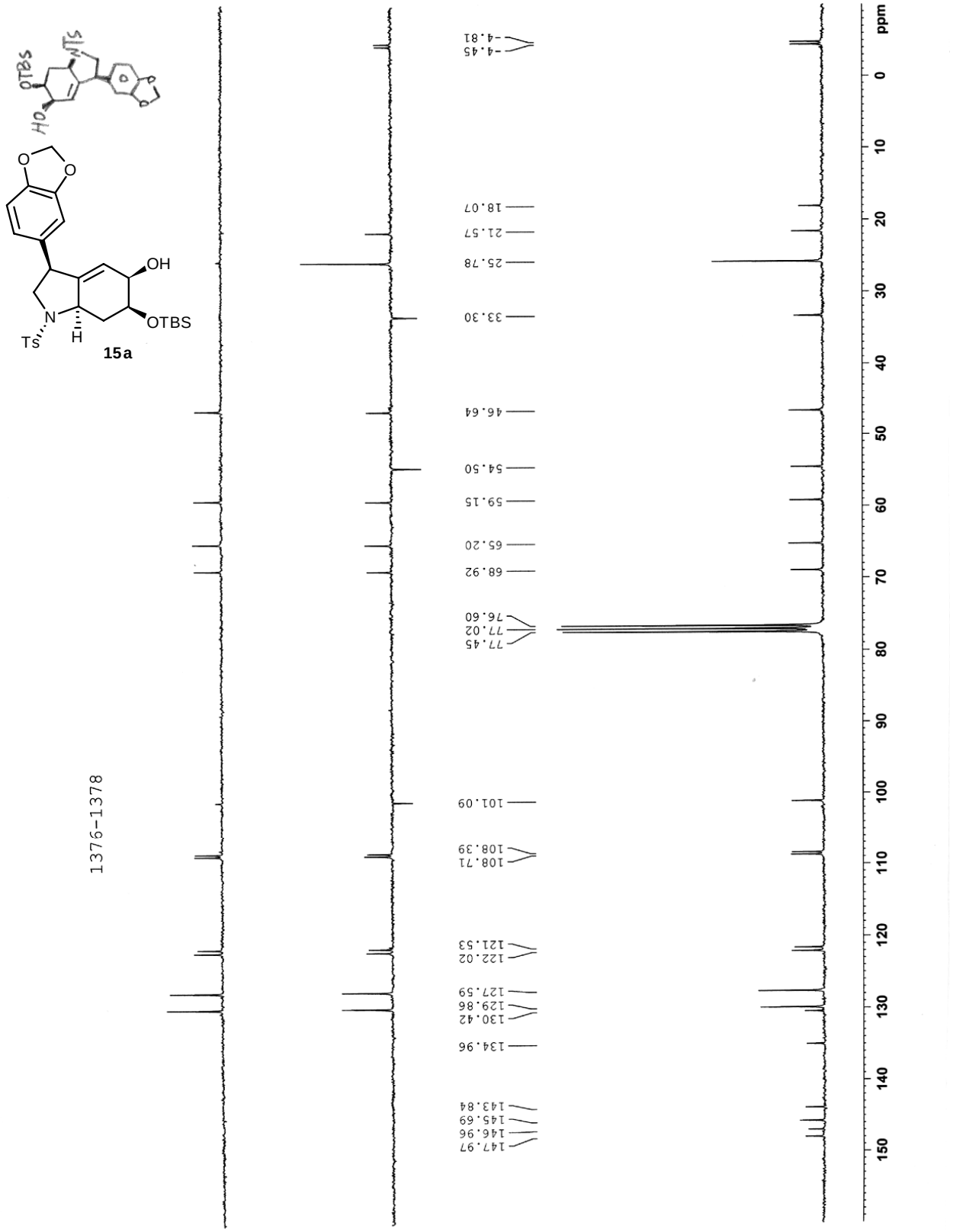

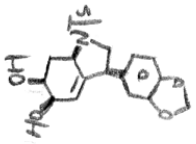

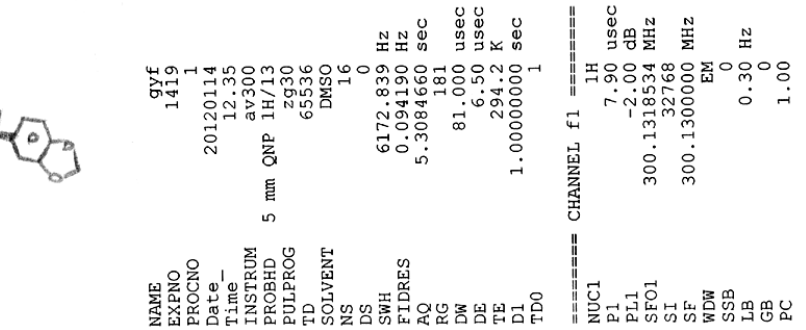

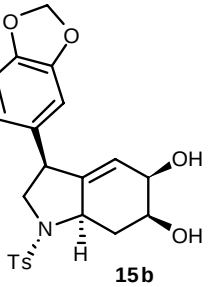

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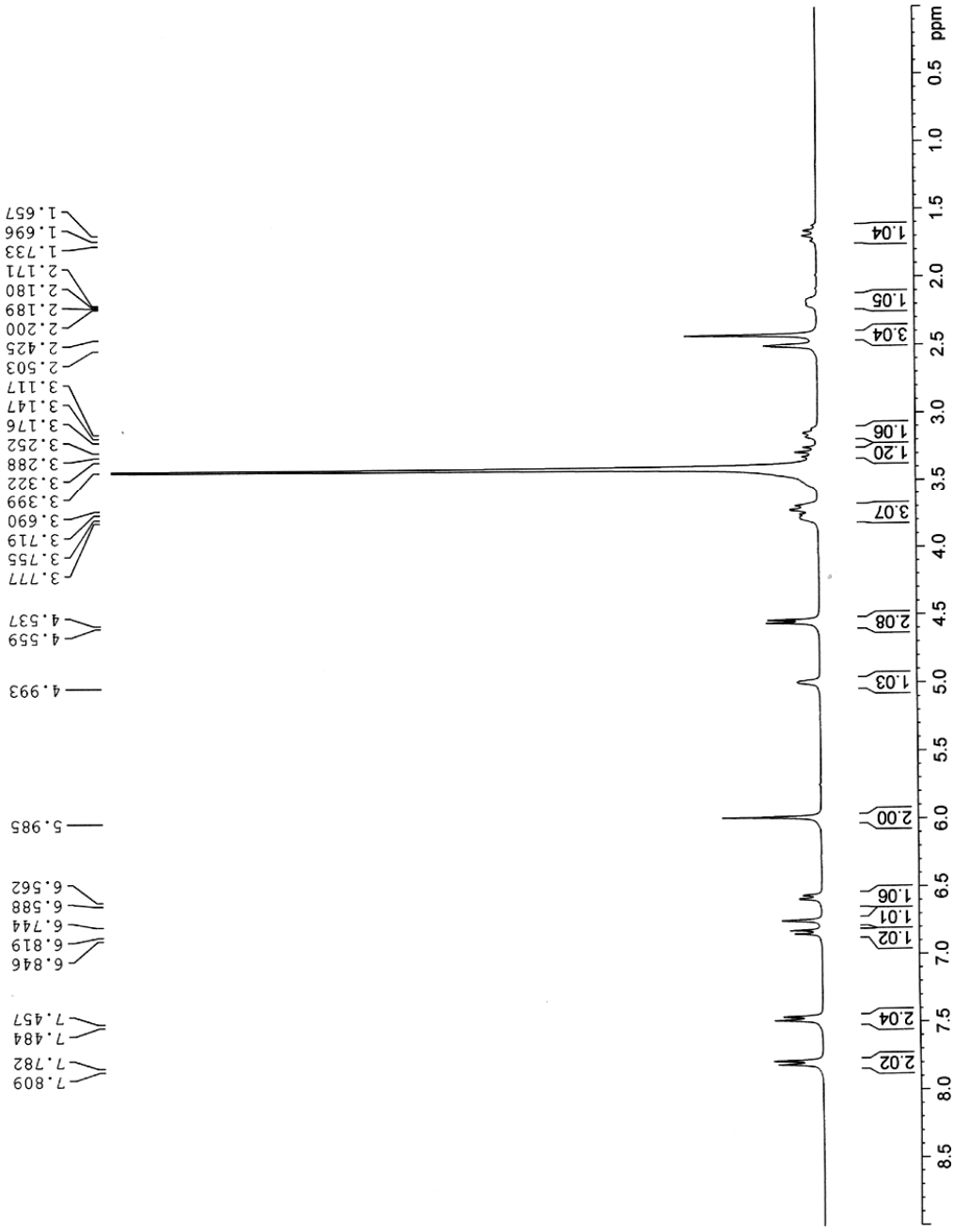

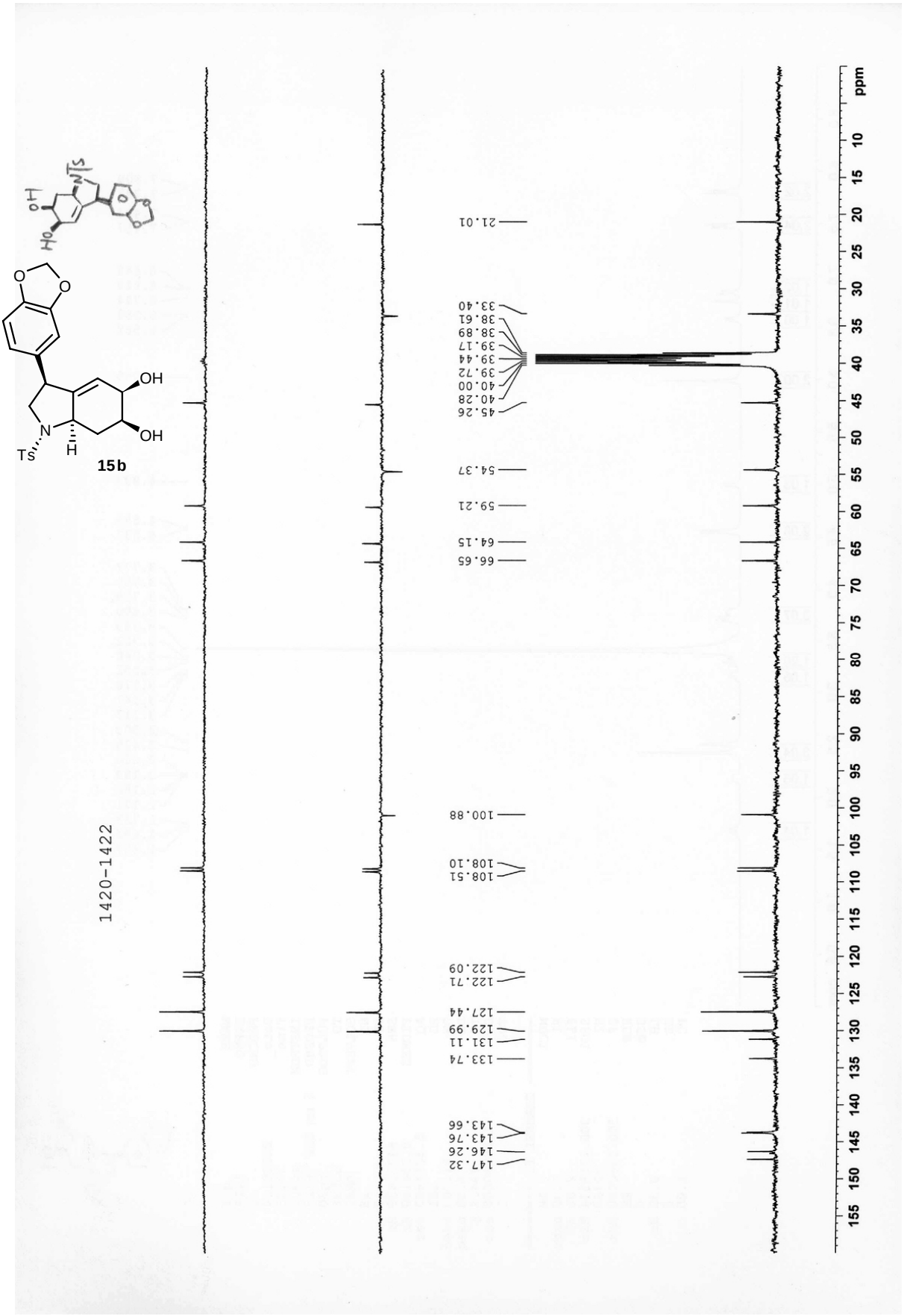

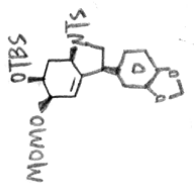

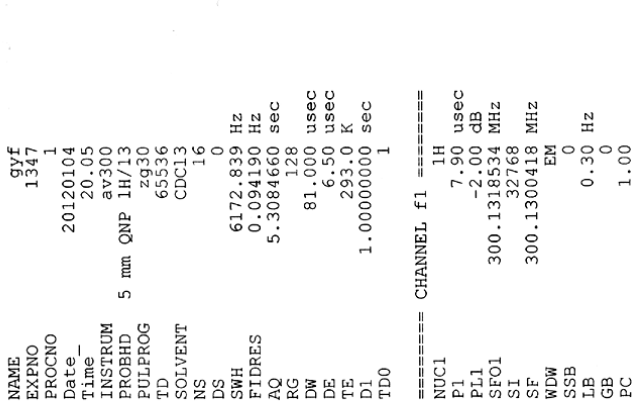

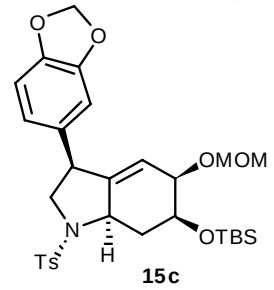

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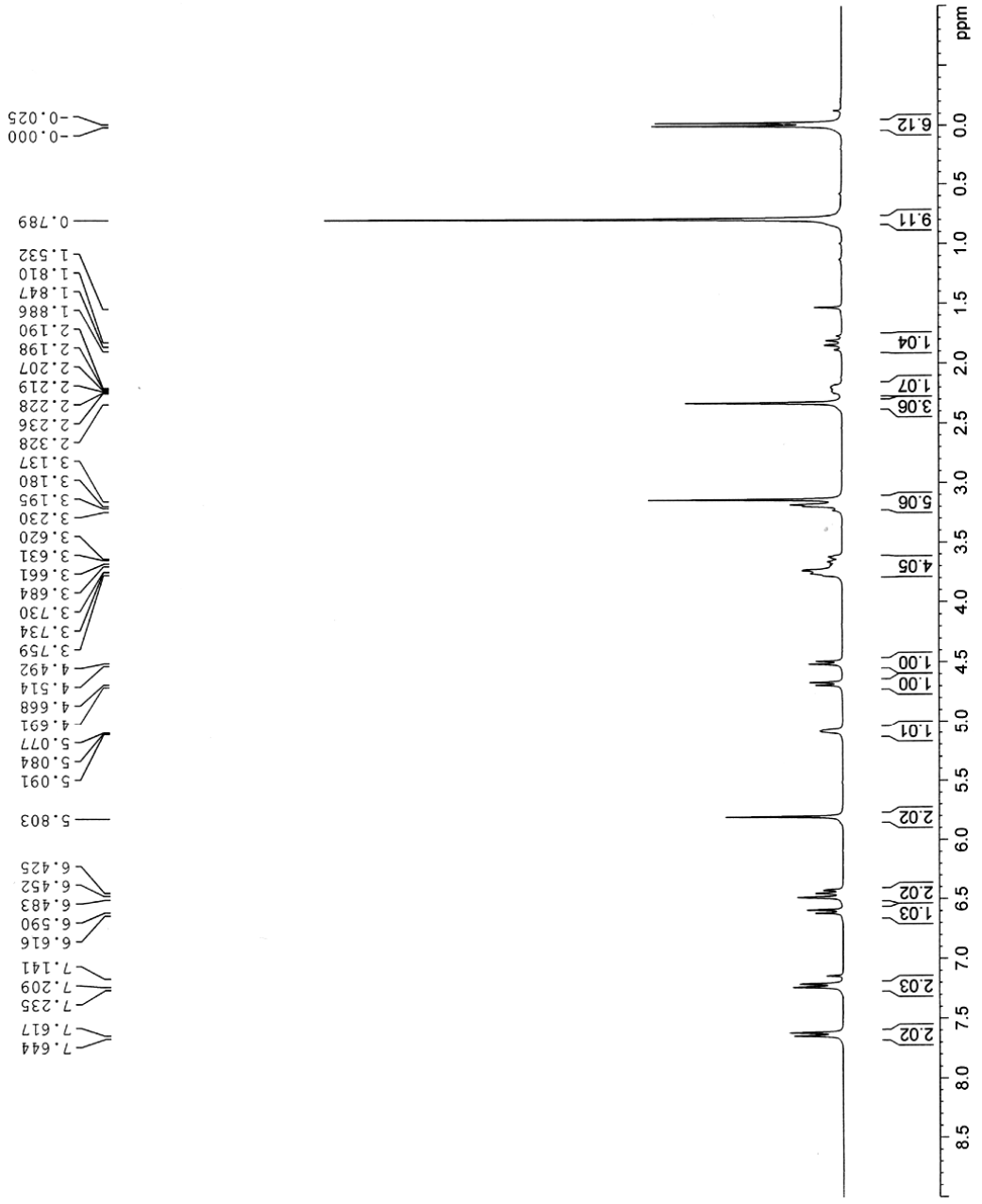

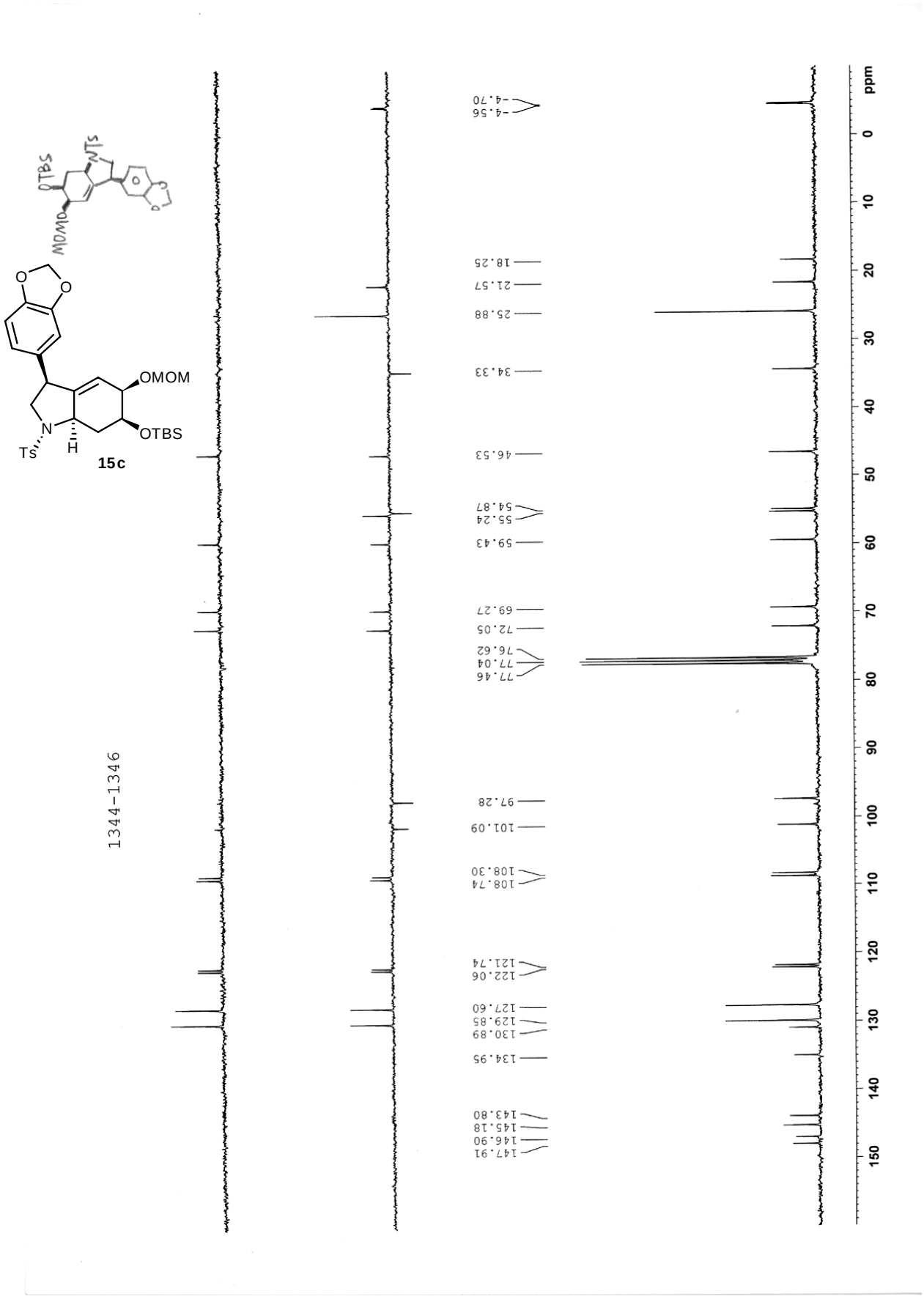

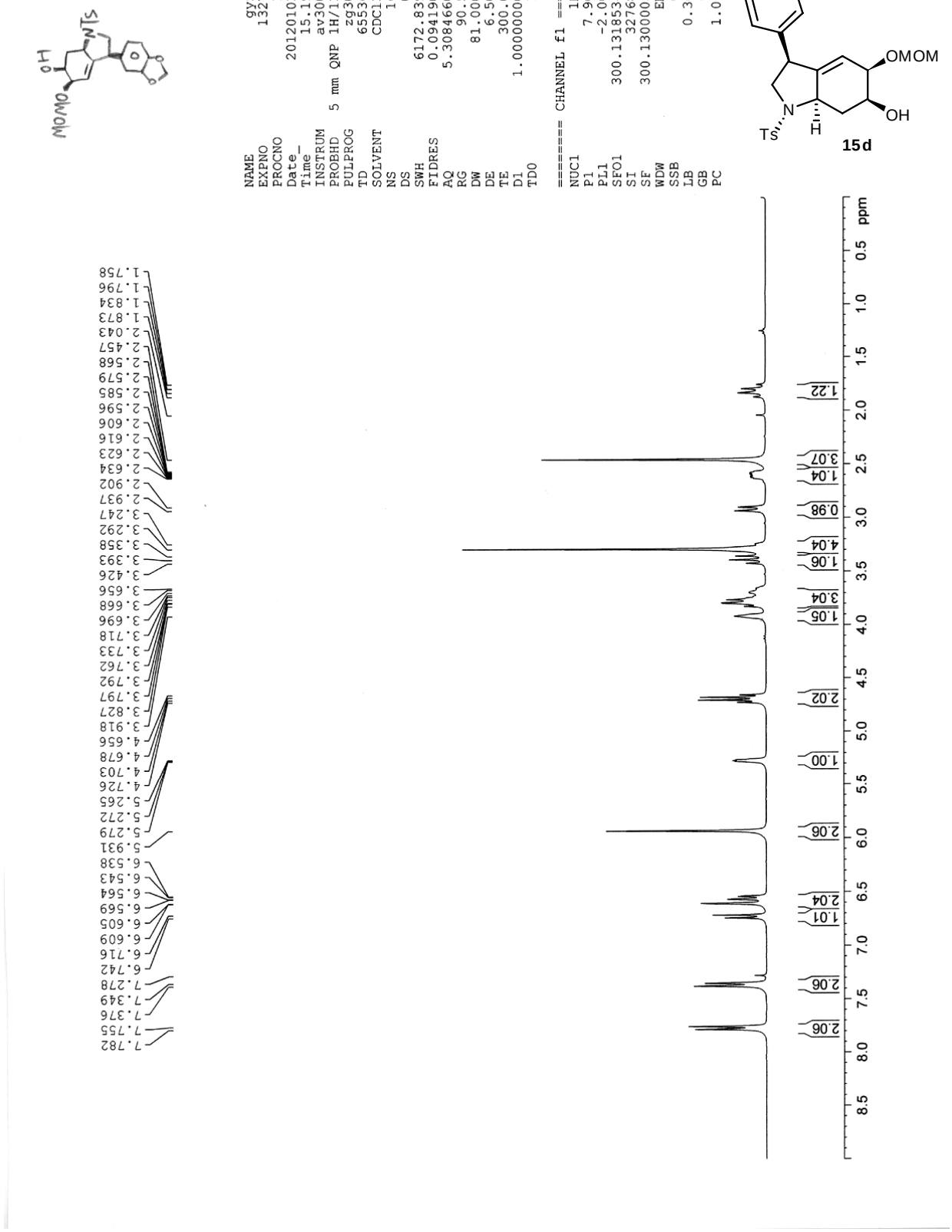

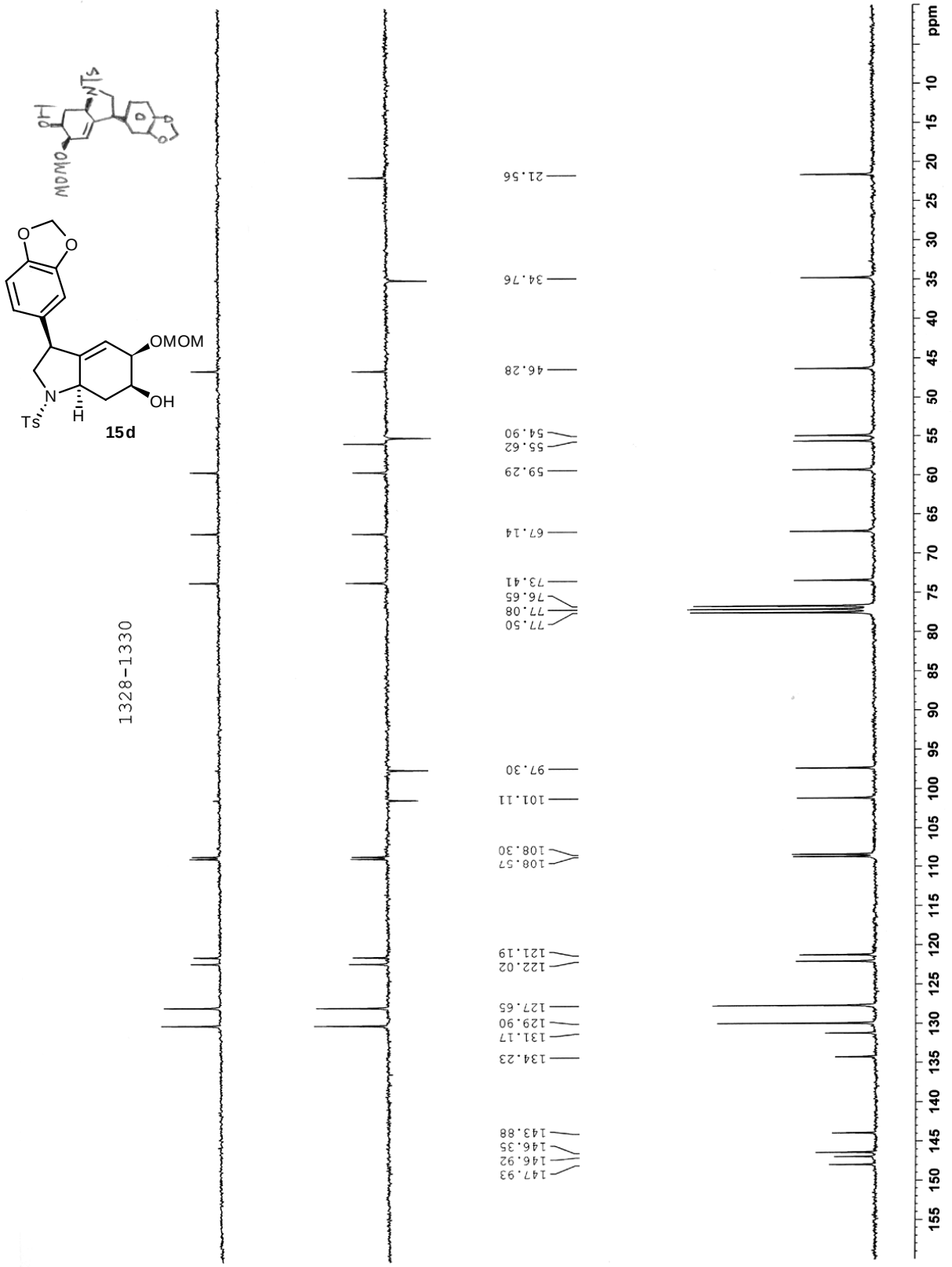

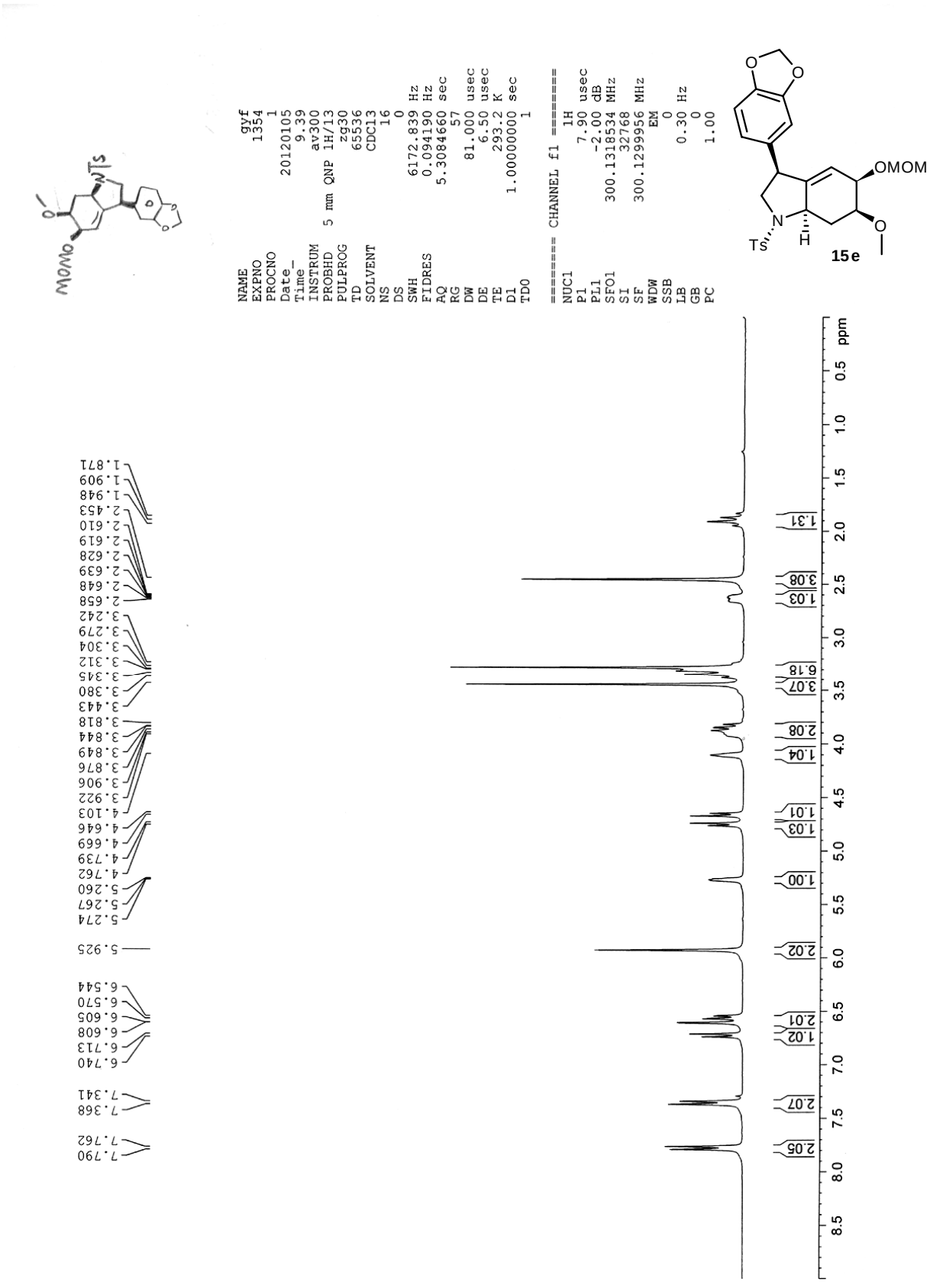

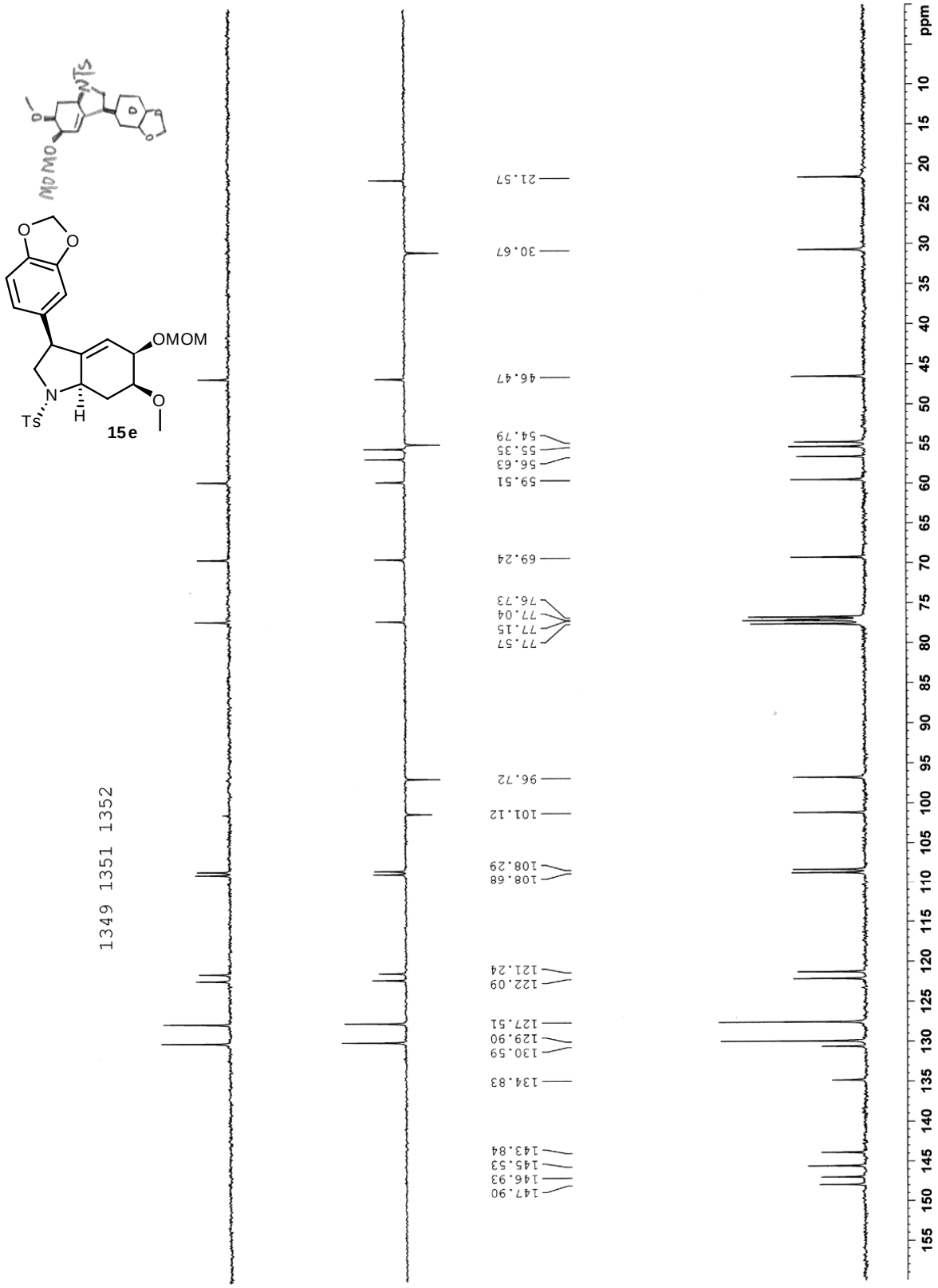

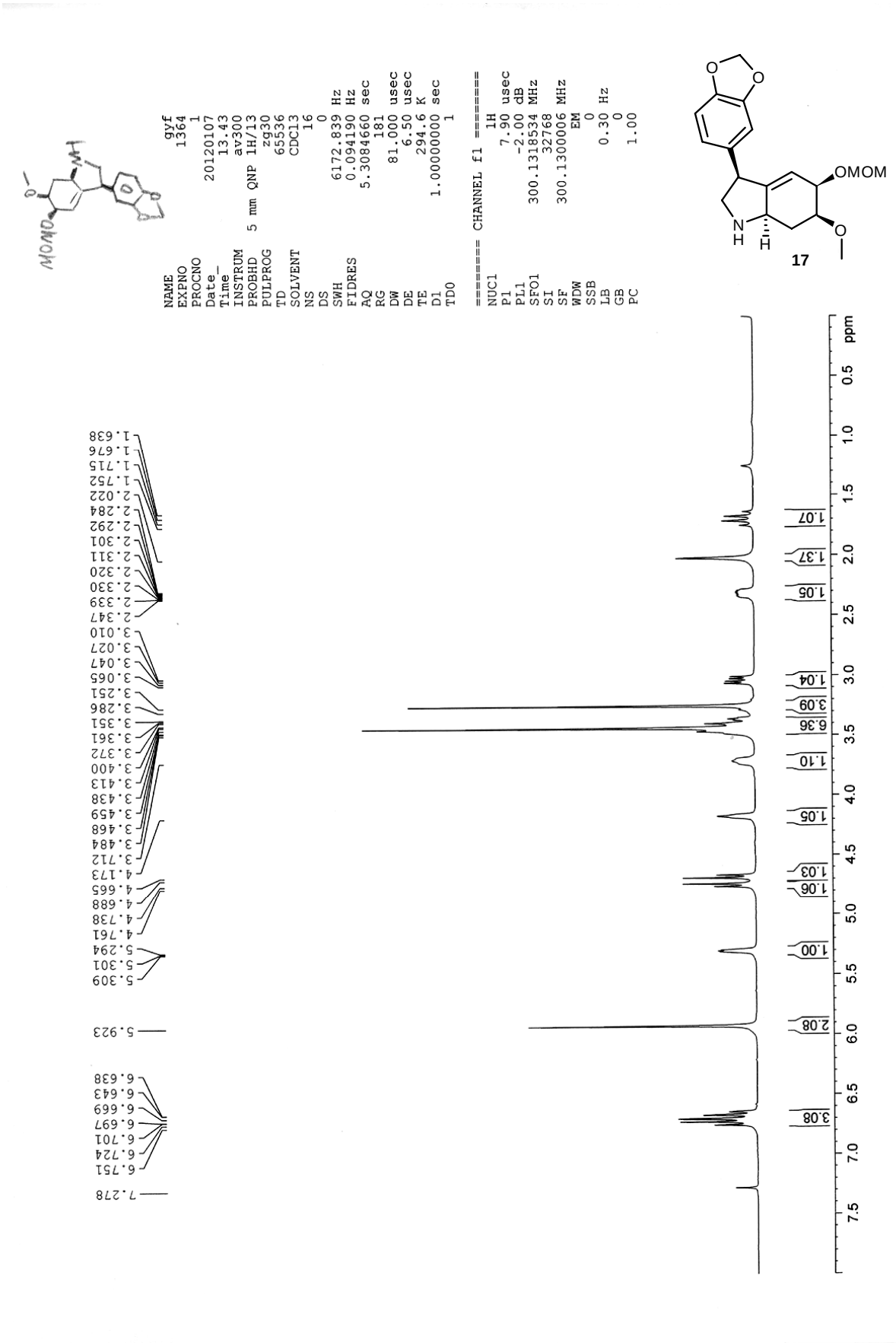

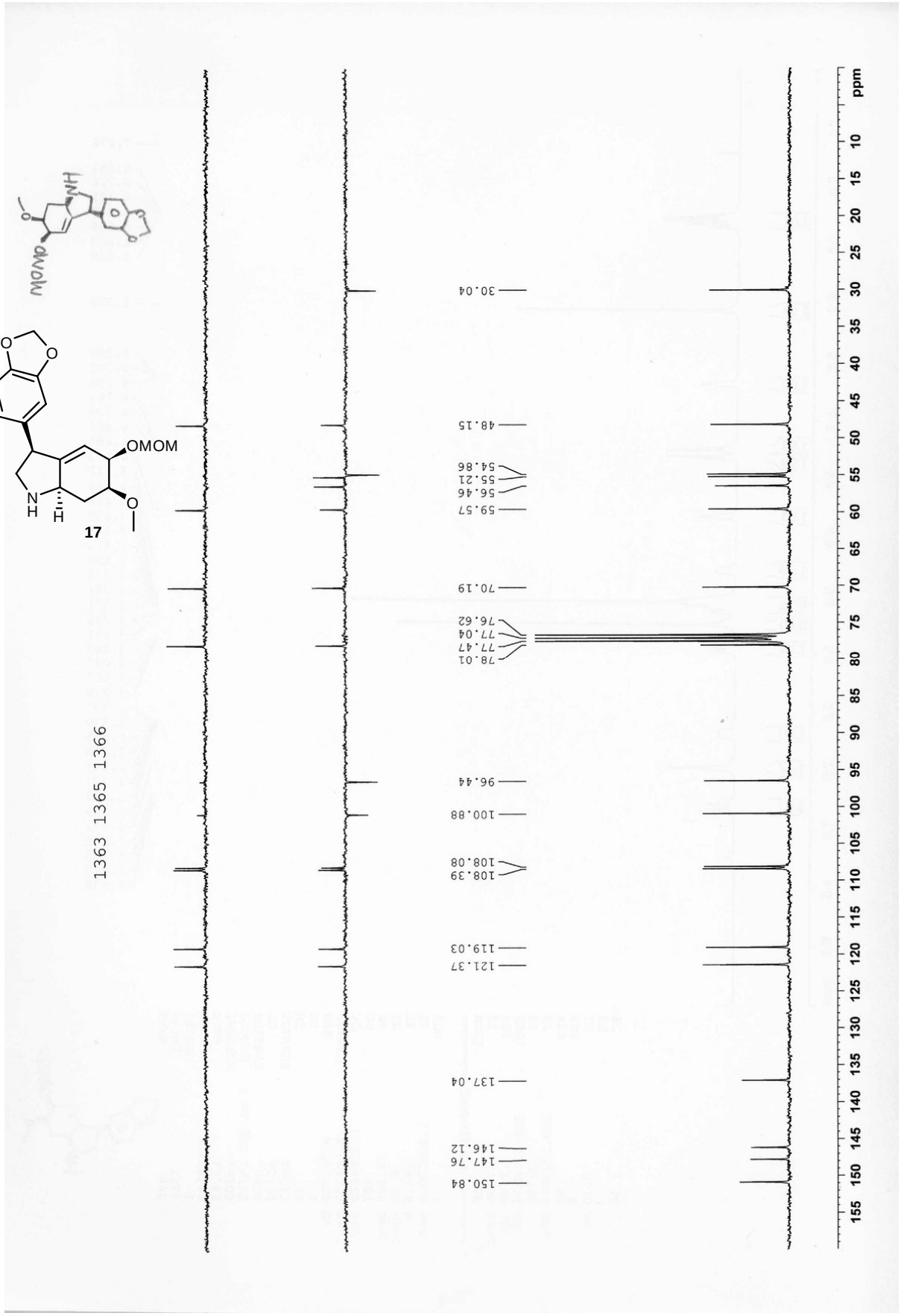
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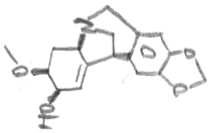
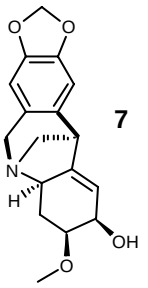
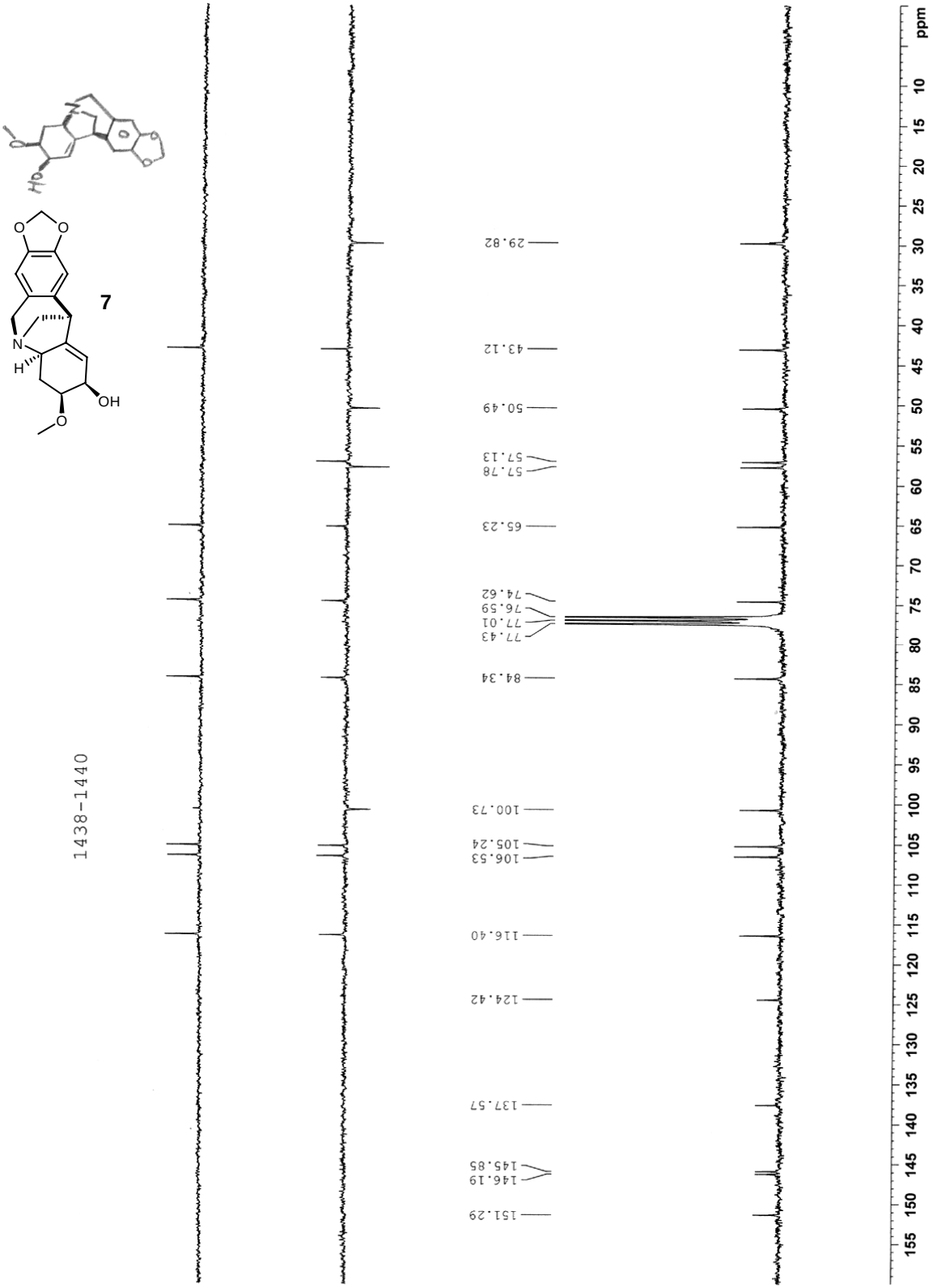
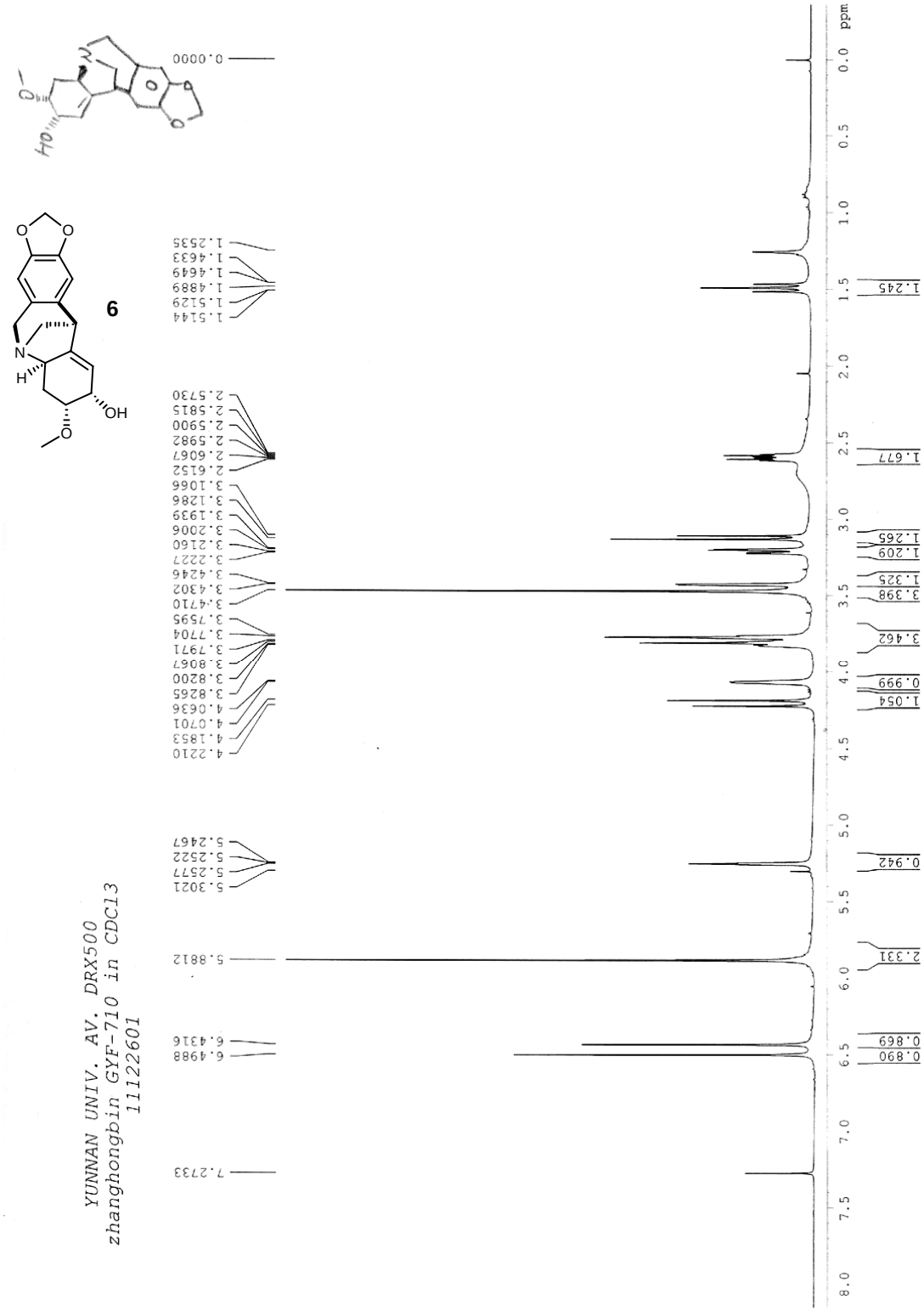
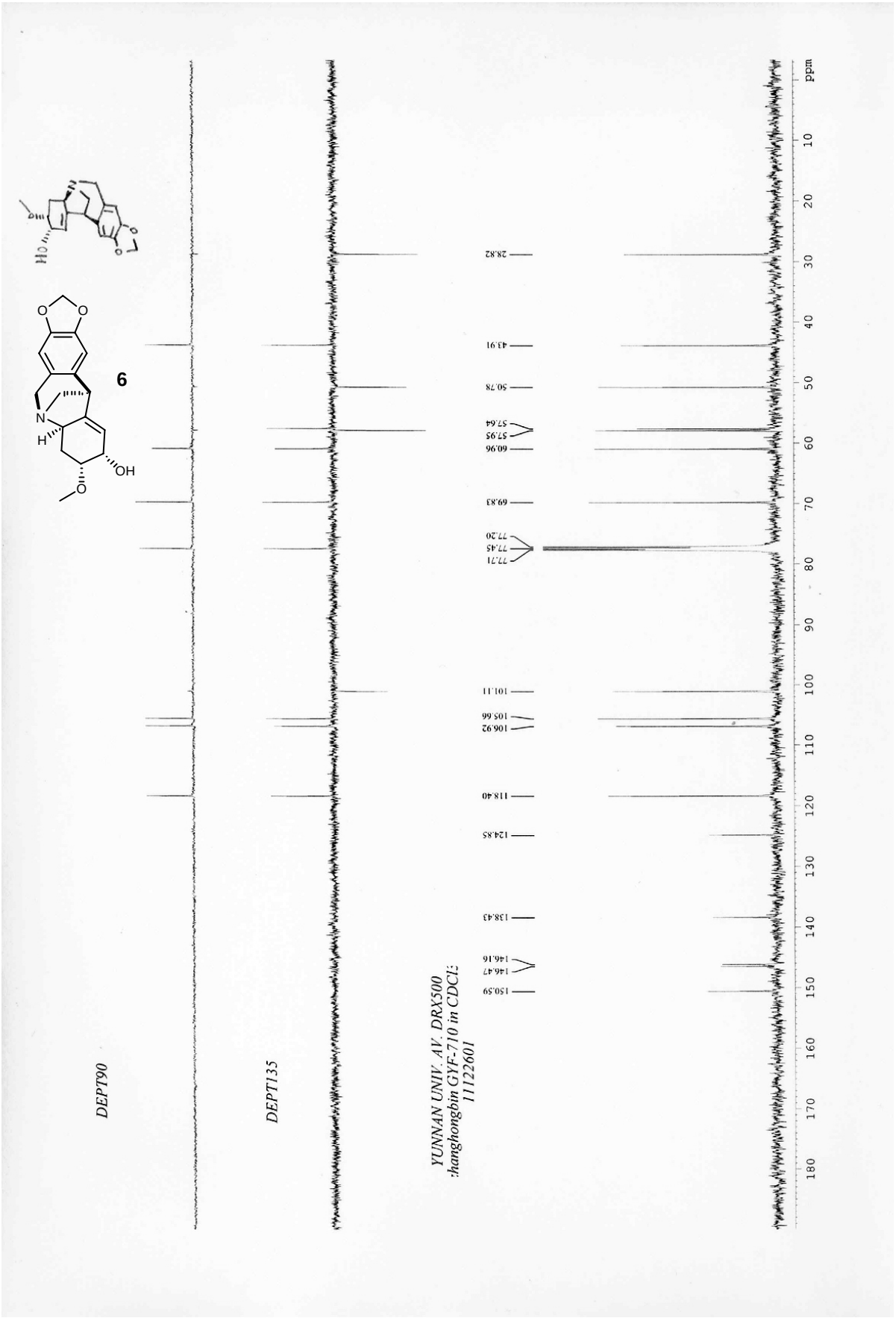
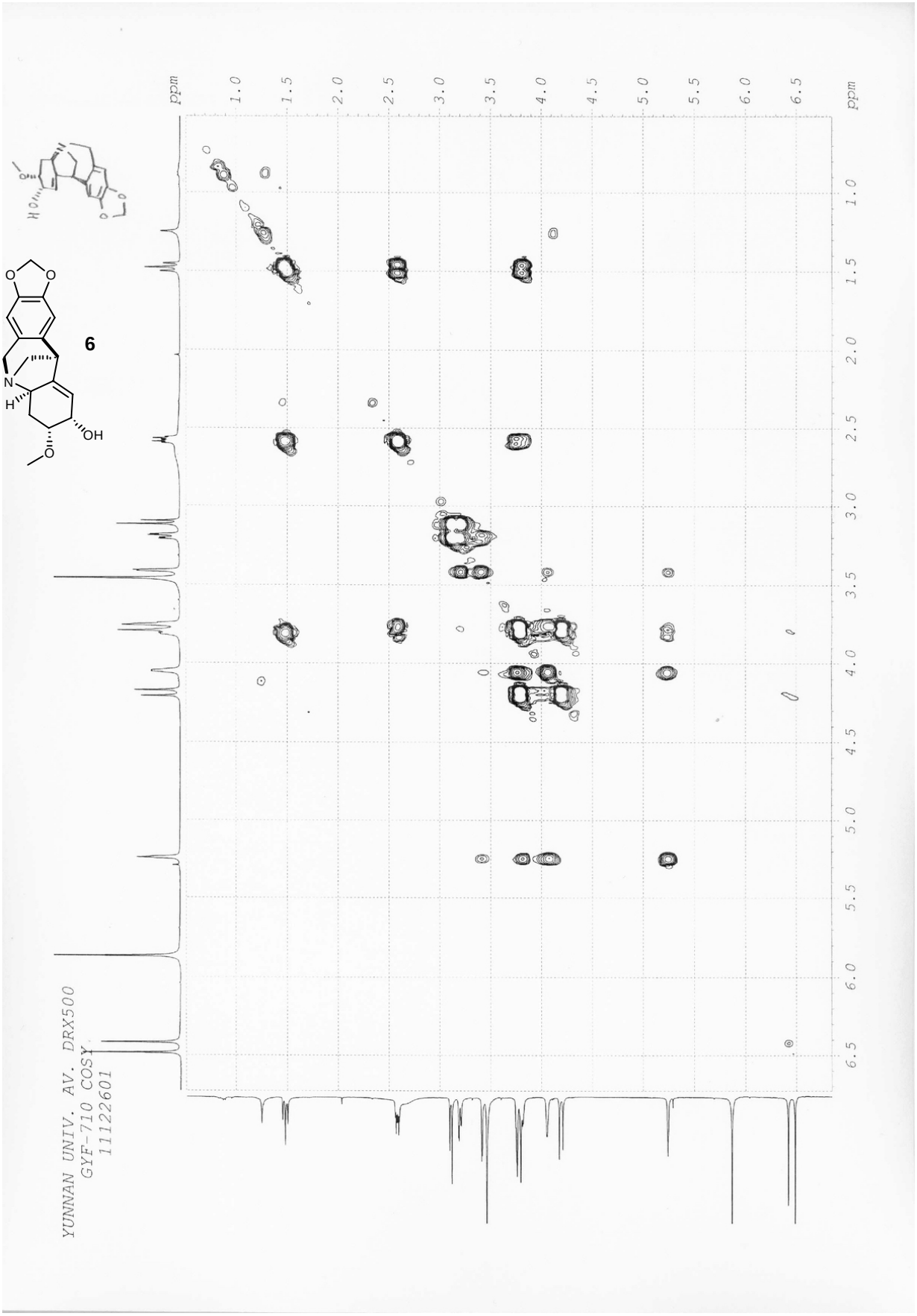


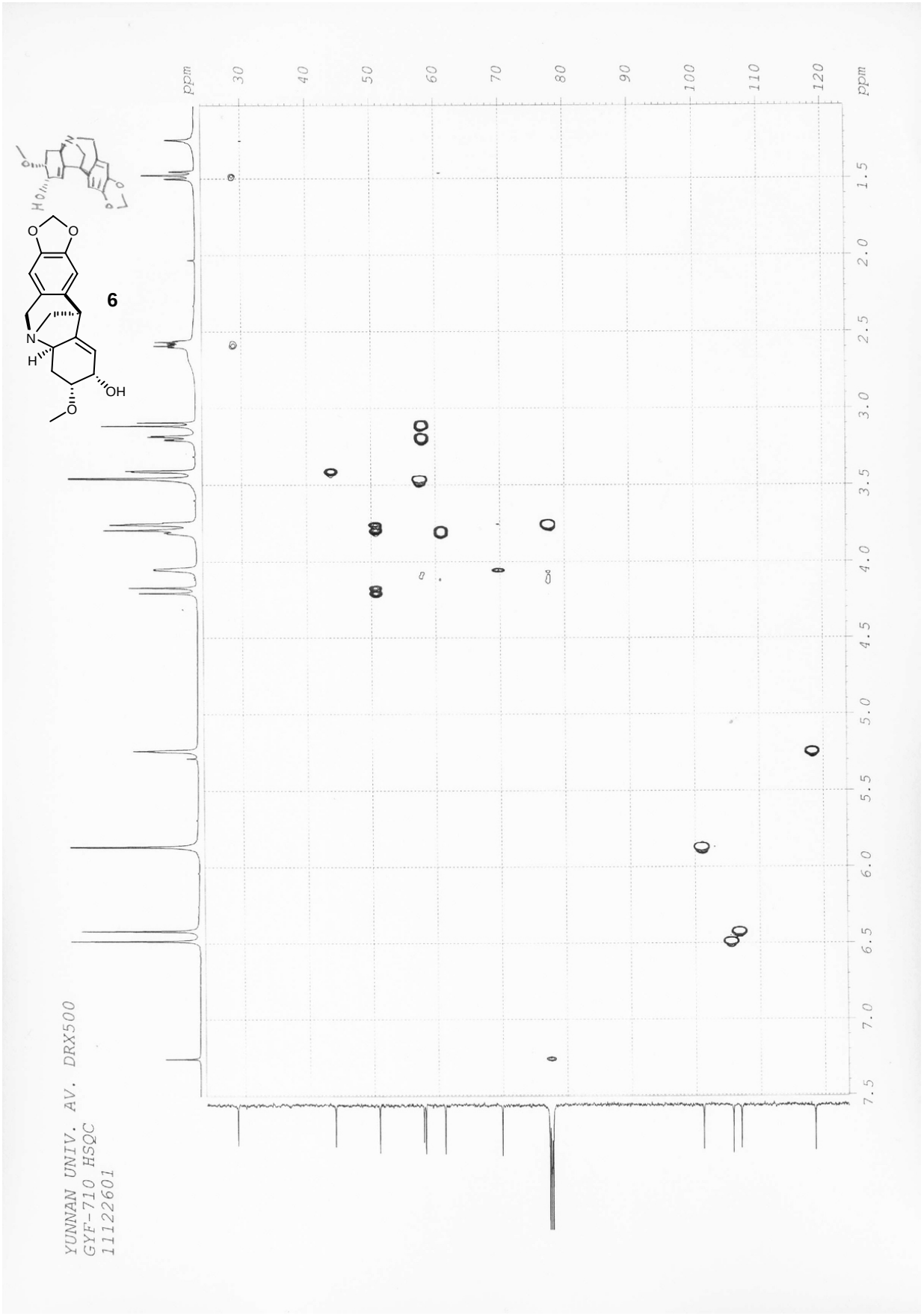


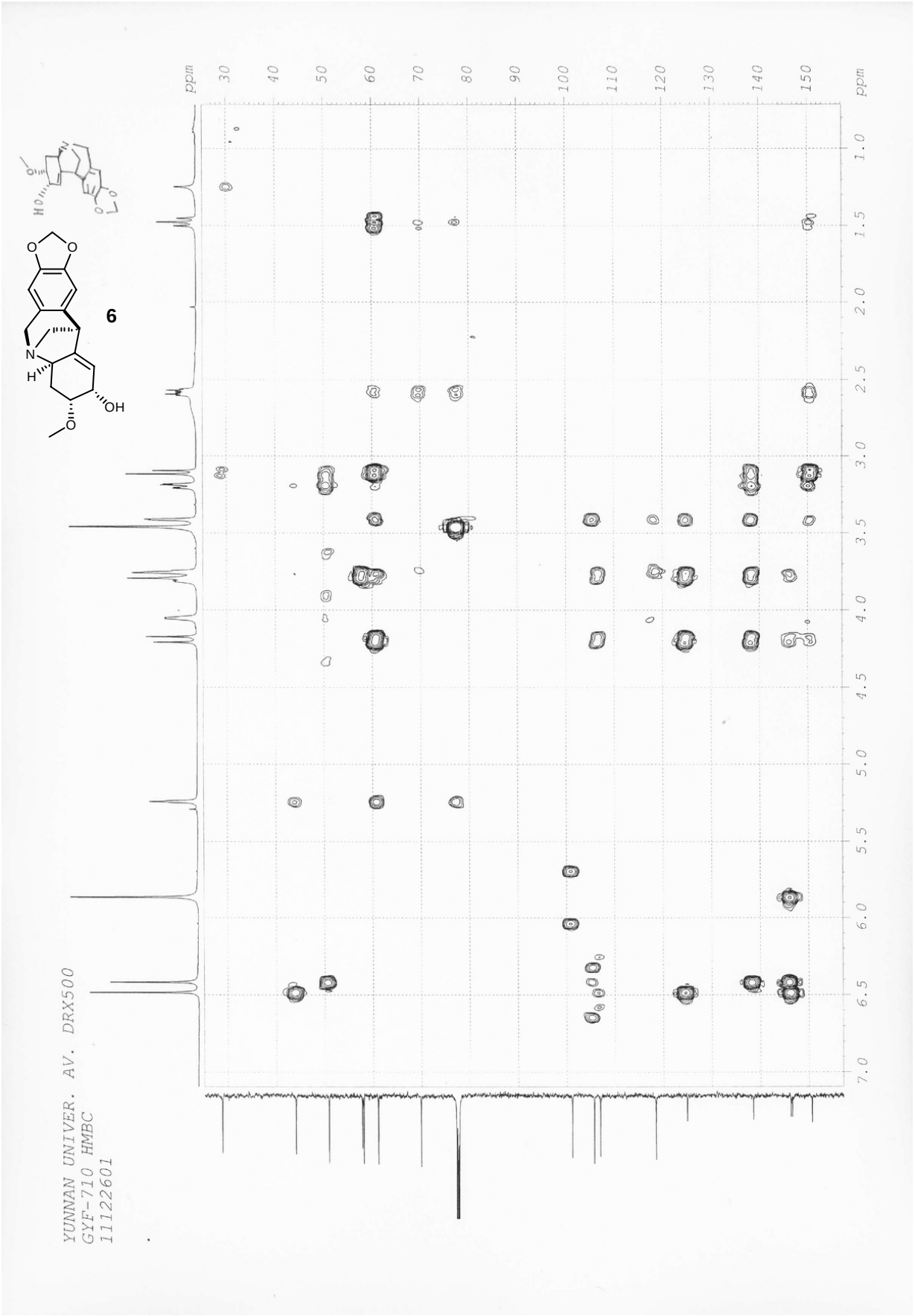


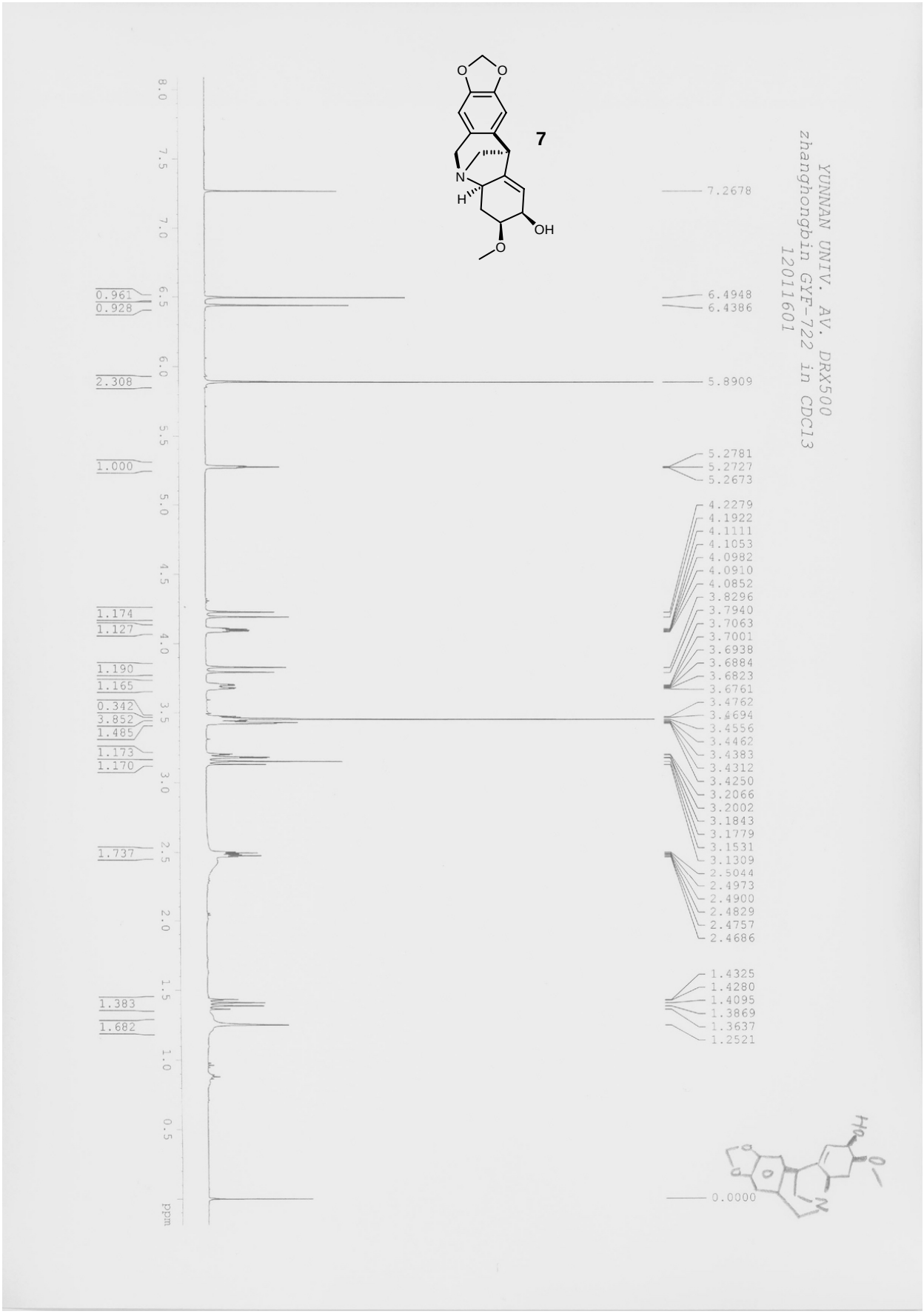

6
YUNNAN UNIV. AV. DRX500
zhanghongbin GYF-710 in CDCl3
11122601
ppm

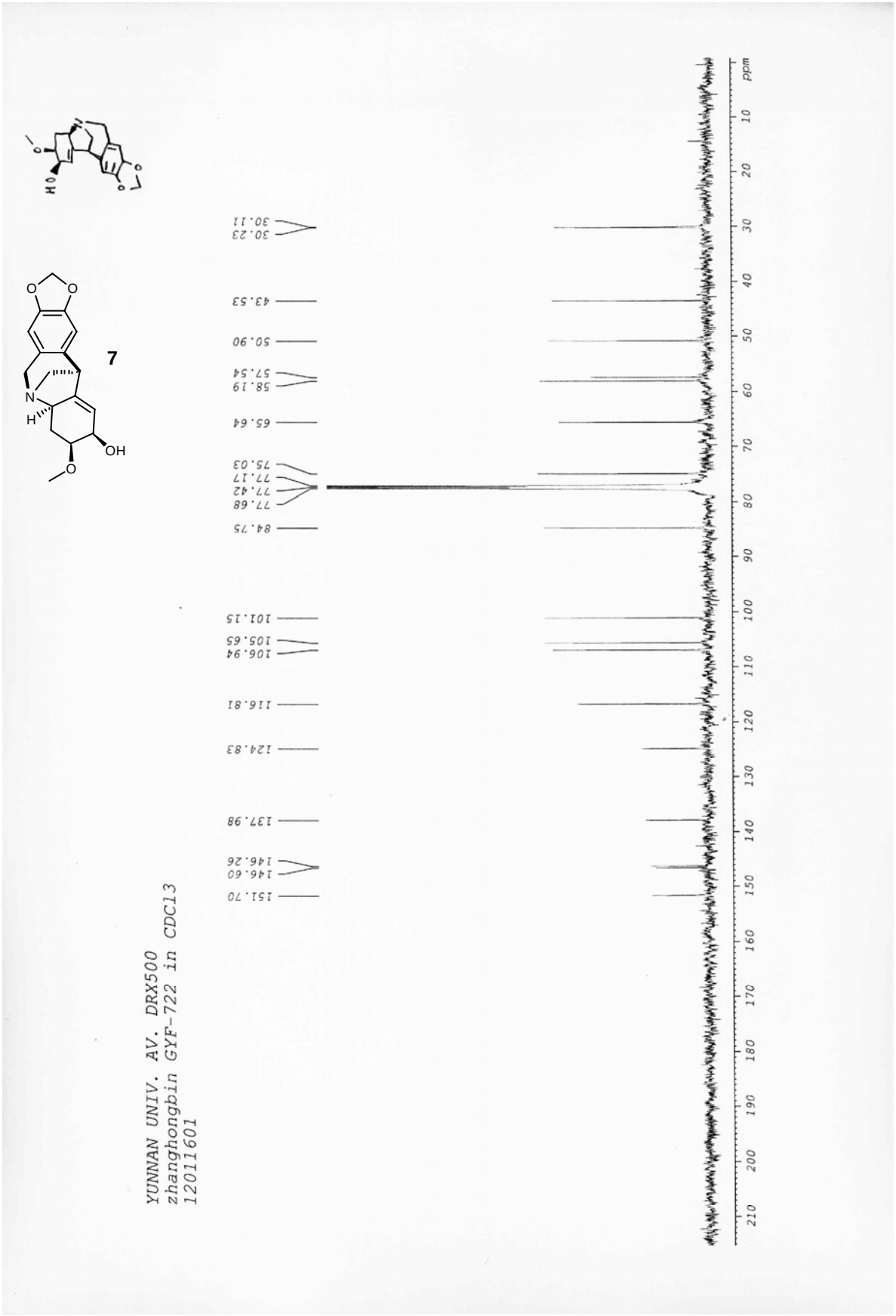


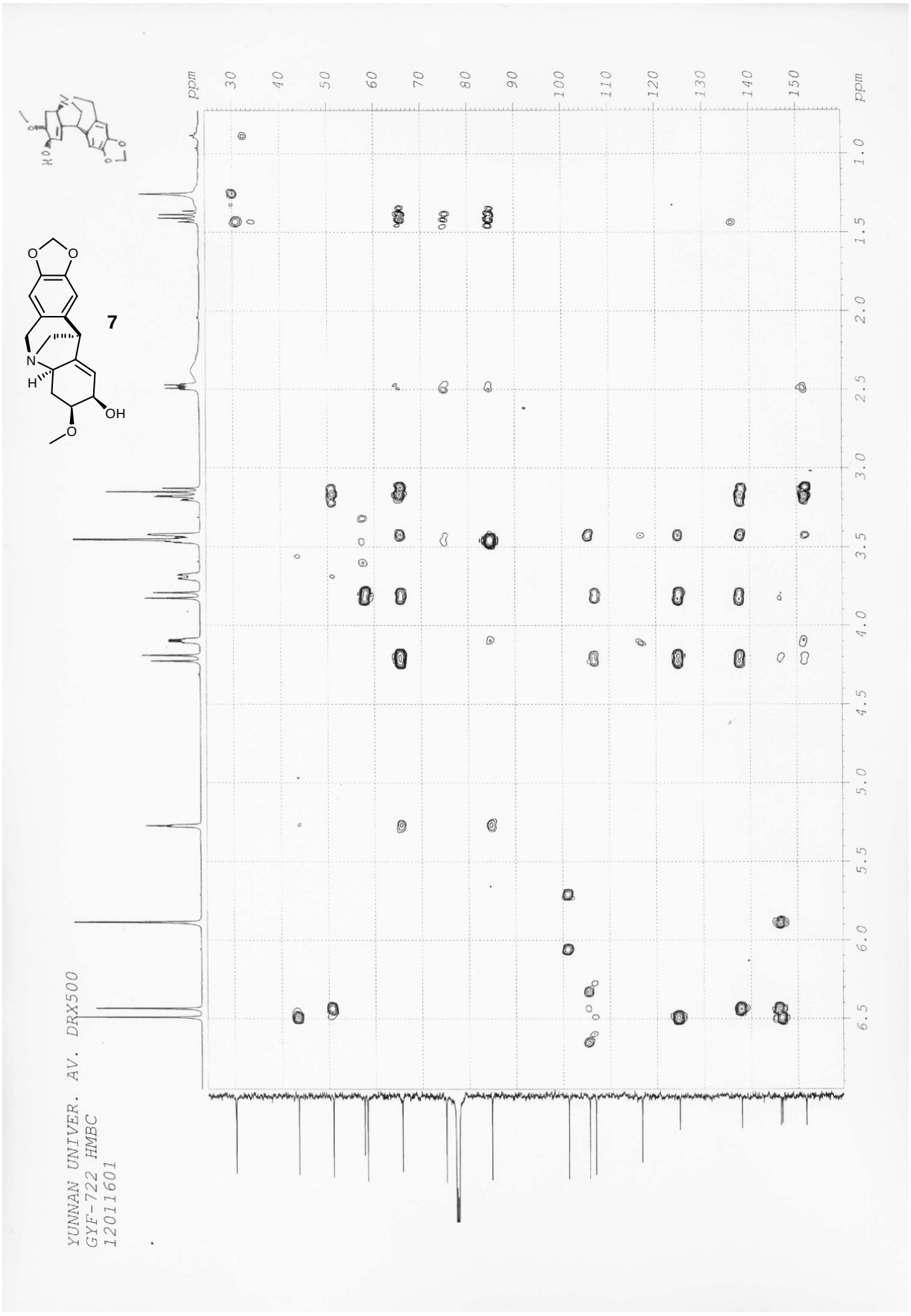

6
N
H
OH
O
O
O
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
YUNNAN UNIV. AV. DRX500
GYF-710 COSY
11122601

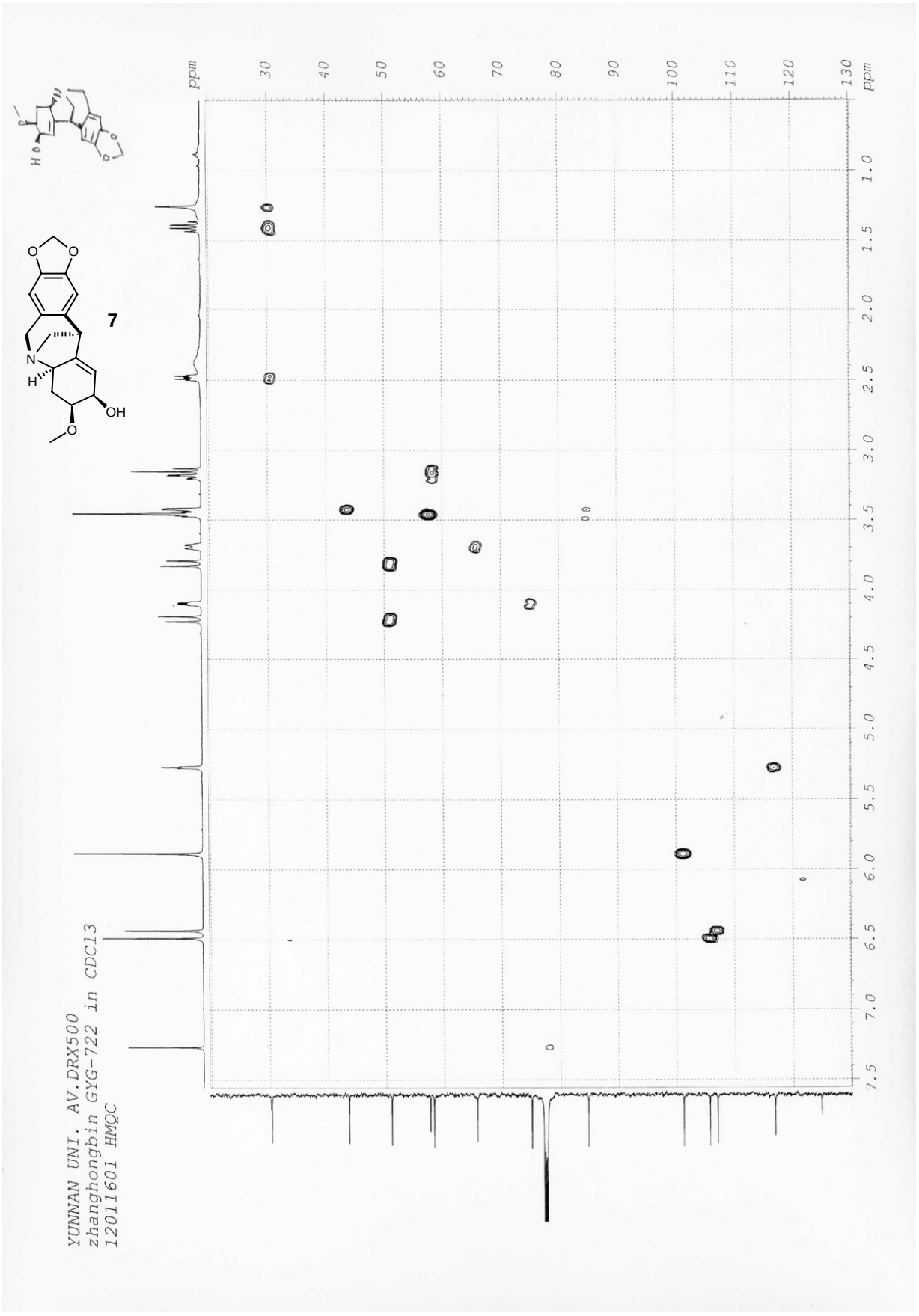



6
N
H
OH
O
O
O
HO
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
YUNNAN UNIVER. AV. DRX500
GYF-710 HMBC
11122601




7
YUNNAN UNIV. AV. DRX500
zhanghongbin GYF-722 in CDCl3
12011601
30.23
30.11
43.53
50.90
57.54
58.19
65.64
75.03
77.17
77.42
77.68
84.75
101.15
105.65
106.94
116.81
124.83
137.98
146.26
146.60
151.70
ppm


7
OH
YUNNAN UNIVER. AV. DRX500
GYF-722 HMBC
12011601
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5


7
OH
YUNNAN UNI. AV.DRX500
zhanghongbin GYG-722 in CDCl3
12011601 HMQC
ppm
ppm