Supporting Information

An Efficient Total Synthesis of (±)-Lycoramine

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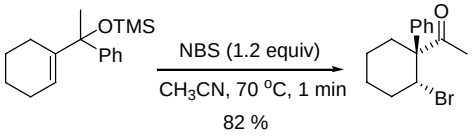
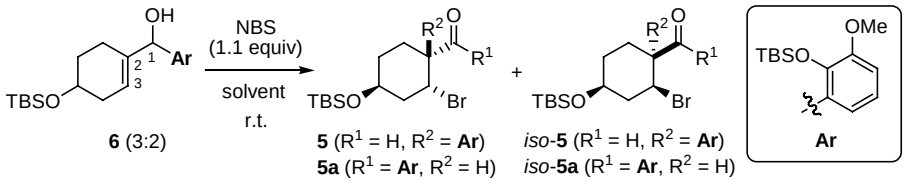
Scheme 1. NBS-Promoted Semipinacol Rearrangement of Tertiary Hydroxy-Protected Allylic Alcohol.



^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41-7.37 (m, 4H), 7.30-7.27 (m, 1H), 5.48 (bs, 1H), 2.51-2.30 (m, 2H), 2.20-2.01 (m, 2H), 2.00 (s, 3H), 1.90-1.70 (m, 1H), 1.65-1.60 (m, 1H), 1.50-1.46 (m, 1H), 1.23-1.13 ppm (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 206.2, 137.5, 129.1, 129.1, 127.4, 127.4, 127.3, 60.3, 56.4, 30.7, 27.1, 24.1, 20.9, 20.8 ppm; **MS** (70 eV): *m*/*z* (%): 239 (0.1) $[M(Br^{81})–CH_3CO]^+$, 237 (0.1) $[M(Br^{79})–CH_3CO]^+$, 201 (0.1) $[M–Br]^+$, 171 (0.8), 169 (0.8), 158 (100) $[M–Br–CH_3CO]^+$, 143 (33), 130 (42), 129 (40), 115 (25), 91 (33), 43 (52); **HRMS** (ESI): *m*/*z* calcd for $C_{14}H_{21}ONBr$: 298.0801; found: 298.0800 $[M+NH_4]^+$.

Note: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Varian Mercury-300 MHz. The MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI technique.

Table 1. NBS-Promoted Semipinacol Rearrangement of Secondary Allylic Alcohol **6**.



6 (3:2)

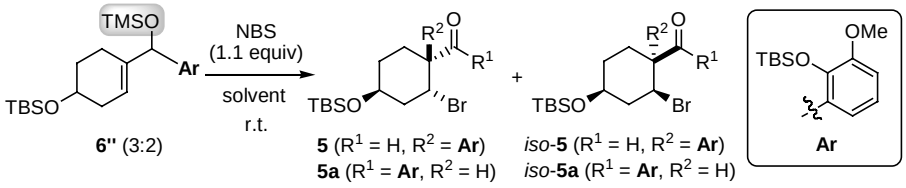
5 (R^1 = H, R^2 = **Ar**)
5a (R^1 = **Ar**, R^2 = H)

iso-**5** (R^1 = H, R^2 = **Ar**)
iso-**5a** (R^1 = **Ar**, R^2 = H)

entry	solvent	**5**:*iso*-**5**:**5a**+*iso*-**5a**[a]	time (min)	yield (%)[b]
1	CH_3CN	91:0:9	50	92
2	acetone	92:0:8	50	93
3	THF	>98:0:2	50	67
4	CH_2Cl_2	97:0:3	30	62
5	$CHCl_3$	>98:0:2	30	53
6	benzene	97:0:3	50	80
7	toluene	97:0:3	50	84
8	MeOH	93:0:7	30	93

[a] The ratios were determined by ^{1}H NMR. [b] Total yield of isolated products **5**/*iso*-**5**/**5a**/*iso*-**5a**.

Table 2. NBS-Mediated Semipinacol Rearrangement of Secondary Hydroxy-Protected Allylic Alcohol **6″**.



6'' (3:2)

5 (R^1 = H, R^2 = **Ar**)
5a (R^1 = **Ar**, R^2 = H)

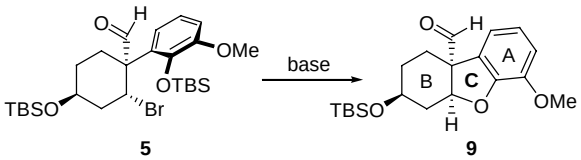
iso-**5** (R^1 = H, R^2 = **Ar**)
iso-**5a** (R^1 = **Ar**, R^2 = H)

entry	solvent	**5**:*iso*-**5**:**5a**+*iso*-**5a**[a]	time (h)	yield (%)[b]
1	acetone	47:50:3	3.5	74
2	*i*-PrOH	98:0:2	2	61

[a] The ratios were established by ^{1}H NMR. [b] Total yield of isolated products **5**/*iso*-**5**/**5a**/*iso*-**5a**.

From the obtained results, we can see when TMS-protected allylic alcohol **6″** was subjected to this NBS-mediated rearrangement in the aprotic reaction medium of acetone (entry 1), the isomeric aldehyde *iso*-**5** could be distinctly observed in the absence of hydrogen bonds. In contrast, we could not find the formation of *iso*-**5** while proceeding in the protic solvent of *i*-PrOH (entry 2) in the presence of the hydrogen bonds between NBS and solvent. Combined with the above Table 1 of Supporting Informatiom, these supporting experiments show that the formation of hydrogen bonds may be the important factor influencing the face-diastereoselectivity of NBS.

Table 3. Base-induced Desilylation/Cyclization Reaction for the Construction of C Ring.

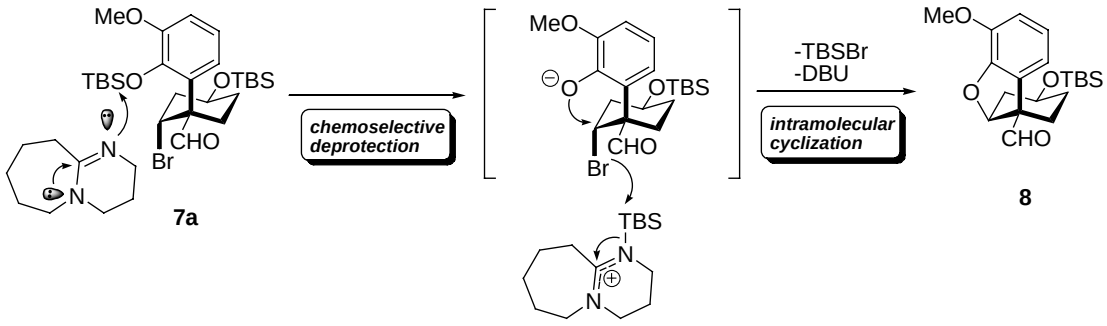


5 **9**

entry	base (equiv)	solvent	*T* (^{o}C)	Time (h)	yield (%)[a]
1	KOH (0.5)	DMF	r.t.	24	[b]
2	KOH (1.5)	DMF	r.t.	24	25
3	Cs_2CO_3 (2.0)	DMF-H_2O	80	48	[b]
4	Et_3N (2.0)	CH_2Cl_2	reflux	12	–[c]
5	*i*-Pr_2NEt (2.0)	CH_2Cl_2	reflux	12	–[c]
6	DMAP (2.0)[d]	CH_2Cl_2	reflux	12	–[c]
7	DBU (2.0)[e]	DMSO	80	0.5	95
8	DBU (0.3)	DMSO	80	1.5	91
9	DBU (0.2)	DMSO	80	8	83
10		DMSO	80	24	–[c]

[a] Isolated yield. [b] Only almost 40 % conversion. [c] No reaction. [d] DMAP = 4-dimethylaminopyridine. [e] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

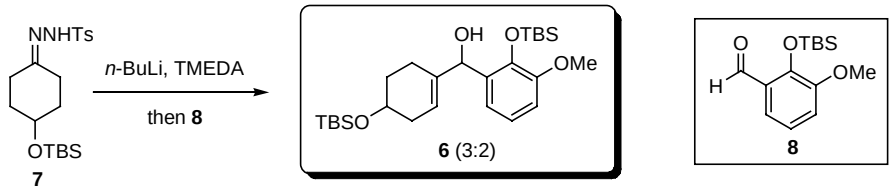
Scheme 2. Proposed Mechanism of The Cyclization Induced by DBU



1. Experimental Procedures and Spectroscopic and Analytical Data of the Products

Note: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Varian Mercury-300 or 400 MHz. The MS data were obtained with EI (70 eV), and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the SIMS or ESI technique.

1.1—— Synthesis of Allylic Alcohol 6

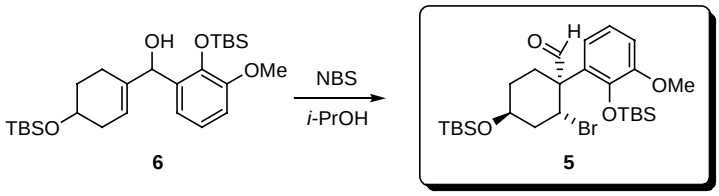


To a cold (-78 °C) suspension of **7** (4.0 g, 10.1 mmol) in dried tetramethylethlenediamine (TMEDA, 30 mL) was added dropwise *n*-BuLi (1.5 M in hexane, 23.6 mL, 35.4 mmol) under an argon atmosphere during 10 min. The reaction mixture stirred at room temperature for 4 h, and then cooled to –78 °C again. The solution of TBS-protected *o*-Vanillin **8** (8.0 g, 30.3 mmol) in dried TMEDA (15 mL) was added dropwise. The mixture was poured into saturated aqueous solution of NH_4C (100 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×100 mL). The combined organic phases were washed with brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by column chromatography on silica gel (petroleum/EtOAc 40:1) provided the allylic alcohol **6** (3:2, 3.6 g, 75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.90-6.86 (m, 2×2H), 6.80-6.77 (m, 2×1H), 5.64 (m, 2×1H), 5.48 (bs, 2×1H), 3.93-3.88 (m, 2×1H), 3.79 (s, 2×3H), 2.36-2.29 (m, 2×1H), 2.17 (d, *J* = 3.9 Hz, 2×1H; OH), 2.09-2.02 (2×3H), 1.82-1.77 (m, 2×1H), 1.62-1.54 (m, 2×1H) 1.00 (s, 2×9H), 0.89 (s, 2×9H), 0.22 (s, 2×3H), 0.20 (s, 2×3H), 0.06 (s, 2×3H), 0.05 ppm (s, 2×3H); **6** (*major*): **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 149.6, 142.7, 138.0, 133.4, 121.0, 120.3, 119.4, 110.5, 71.0,

67.8, 54.6, 34.8, 31.5, 26.1, 26.1, 26.1, 25.8, 25.8, 25.8, 24.8, 18.9, 18.1, -3.8, -3.8, -4.7, -4.7 ppm; **6** (*minor*): **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 149.6, 142.7, 138.0, 133.4, 121.0, 120.3, 119.4, 110.5, 71.5, 68.0, 54.6, 34.8, 31.6, 26.1, 26.1, 26.1, 25.8, 25.8, 25.8, 24.5, 18.9, 18.1, -3.8, -3.8, -3.8, -4.7, -4.7, -4.7 ppm; **MS** (70 eV): *m*/*z* (%): 421 (2) $[M–t\text{-Bu}]^+$, 403 (2) $[M–t\text{-Bu}–H_2O]^+$, 329 (8), 298 (100), 271 (30), 256 (72), 230 (22), 73 (74); **HRMS** (SIMS): *m*/*z* calcd for $C_{26}H_{45}O_3Si_2$: 461.2902; found: 461.2882 $[M–H_2O+H]^+$.

1.2—— Synthesis of Aldehyde 5

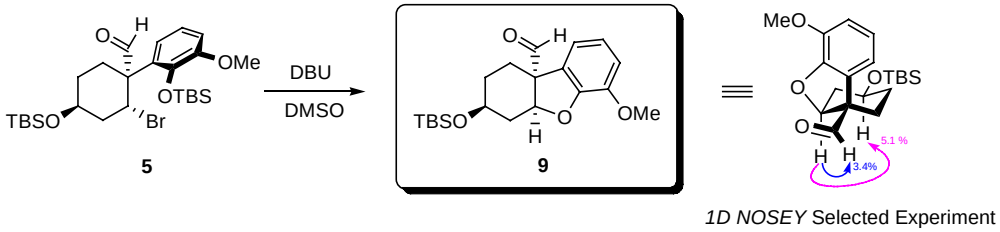


6 **5**

To a solution of **6** (0.2 g, 0.4 mmol) in *i*-PrOH (8 mL) was added *N*-bromosuccinimide (NBS, 81.9 mg, 0.46 mmol) at room temperature. The reaction mixture was stirred for 30 min until allylic alcohol **6** had disappeared completely monitored by TLC. After direct removal of the solvent of *i*-PrOH *in vacuo* at ambient temperature, the residue was rapidly purified by column chromatography on silica gel (petroleum/EtOAc 100:1) to afford the aldehyde **5** (0.22 g, 93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 7.02-6.97 (m, 2H), 6.85-6.83 (m, 1H), 5.27 (bs, 1H), 4.14 (m, 1H), 3.78 (s, 3H), 2.37-2.29 (m, 4H), 2.00-1.96 (m, 1H), 1.61-1.55 (m, 1H), 0.95 (s, 9H), 0.89 (s, 9H), 0.26 (s, 3H), 0.22 (s, 3H), 0.08 (s, 3H), 0.04 ppm (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 202.6, 149.3, 142.8, 130.9, 121.1, 119.1, 110.4, 68.2, 54.5, 54.2, 51.1, 41.1, 30.1, 28.0, 26.7, 26.7, 26.7, 25.8, 25.8, 25.8, 19.7, 18.0, -1.9, -2.2, -4.9, -4.9 ppm; **MS** (70 eV): *m*/*z* (%): 501 (5) $[M(^{81}Br)–t\text{-Bu}]^+$, 499 (5) $[M(^{79}Br)–t\text{-Bu}]^+$, 419 (2) $[M–t\text{-Bu}–HBr]$, 369 (7) $[M(^{81}Br)–t\text{-Bu}–TBSOH]^+$, 367 (7) $[M(^{79}Br)–t\text{-Bu}–TBSOH]^+$, 287 (26) $[M–t\text{-Bu}–TBSOH–HBr]^+$, 209 (16), 171 (26), 135 (21), 73 (100), 57 (17), 41 (17); **HRMS** (SIMS): *m*/*z* calcd for $C_{22}H_{36}{}^{81}BrO_4Si_2$: 501.1317; found: 501.1320 $[M–t\text{-Bu}]^+$.

1.3—— Synthesis of Aldehyde 9



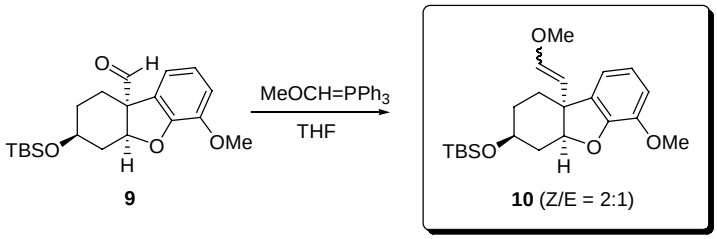
5 **9**

1D NOSEY Selected Experiment

To a solution of **5** (0.50 g, 0.9 mmol) in dried DMSO (10 mL) was added 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU, 0.27 mL, 1.8 mmol) at room temperature under an argon atmosphere. The reaction mixture was heated at 80 ^{o}C for 30 min until aldehyde **5** had disappeared completely monitored by TLC. After cooled to ambient temperature, H_2O (4 mL) was added to the resulting mixture followed by EtOAc (40 mL). The organic phase was separated, and then the aqueous layer was extracted with EtOAc (4×40 mL). The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 30:1) afforded the aldehyde **9** (0.31g, 95%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.48 (s, 1H), 6.93-6.75 (m, 3H), 5.13 (dd, *J* = 6.3, 8.7 Hz, 1H), 3.86 (s, 3H), 3.69-3.61 (m, 1H), 2.30-2.18 (m, 2H), 1.91-1.81 (m, 1H), 1.76-1.65 (m, 2H), 1.47-1.38 (m, 1H), 0.82 (s, 9H), 0.03 (s, 3H), 0.01 ppm (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 197.9, 147.7, 145.7, 127.0, 122.0, 115.6, 113.1, 81.8, 66.0, 59.5, 56.0, 37.4, 30.0, 25.6, 25.6, 25.6, 22.7, 17.9, -4.9, -4.9 ppm; **MS** (70 eV): *m*/*z* (%): 362 (3) $[M]^+$, 305 (62) $[M–t\text{-Bu}]^+$, 287 (37), 201 (76), 73 (100), 57 (54), 41 (46); **HRMS** (SIMS): *m*/*z* calcd for $C_{20}H_{31}O_4Si$: 363.1986; found: 363.1996 $[M+H]^+$.

1.4—— Synthesis of Vinyl Ether 10



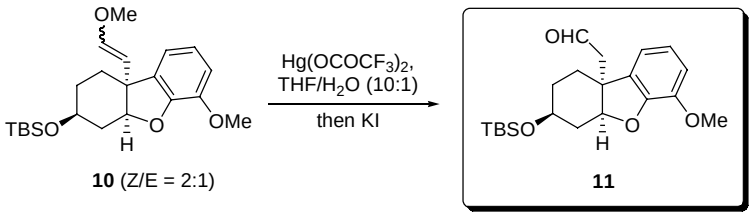
9 **10** (Z/E = 2:1)

Methoxymethyltriphenyl phosphonium chloride ($MeOCH_2–P^+Ph_3•Cl^–$, 2.8 g, 8.2 mmol) was suspended in dried THF (20 mL), and cooled to -10 ^{o}C by ice-salt bath. *n*-BuLi (1.5 M in hexane, 5.5 mL, 8.2 mmol) was added slowly, and then the bright organic resulting mixture was stirred at room temperature for 1 h. Aldehyde **9** (0.49 g, 1.36 mmol) was dissolved in dried THF (15 mL), and added dropwise to the resulting phosphrane solution via syringe at 0 ^{o}C. After stirring at room temperature for 30 min, the reaction mixture was quenched with H_2O (10 mL) followed by addition of EtOAc (80 mL). The organic layer was separated, and the aqueous phase was further extracted with EtOAc (4×80 mL). The combined organic phases were dried over Na_2SO_4. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (petroleum/EtOAc 50:1) to give the vinyl ether **10** (Z/E = 2:1, 0.39 g, 75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.88-6.68 (m, 2×3H), 5.98 (d, *J* = 12.9 Hz, 1H(*E*)), 5.76 (d, *J* = 6.9 Hz, 1H(*Z*)), 4.88 (t, *J* = 6.9 Hz, 1H(*Z*)), 4.82 (d, *J* = 12.9 Hz, 1H(*E*)), 4.54 (dd, *J* = 6.6,

8.1 Hz, 1H(*E*)), 4.33 (d, *J* = 6.9 Hz, 1H(*Z*)), 3.87 (s, 3H(*E*)), 3.85 (s, 3H(*Z*)), 3.79-3.67 (m, 2×1H), 3.56 (s, 3H(*Z*)), 3.43 (s, 3H(*E*)), 2.32-1.26 (m, 2×6H), 0.84 (s, 2×9H), 0.04 (s, 2×3H), 0.02 ppm (s, 2×3H); **10** (*E* isomer): **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 148.2, 146.9, 145.6, 134.4, 121.3, 115.4, 111.7, 109.7, 88.6, 67.0, 56.0, 56.0, 47.6, 37.5, 31.0, 29.4, 25.7, 25.7, 25.7, 18.0, -4.8, -4.8 ppm; **10** (*Z* isomer): **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 146.8, 146.3, 145.3, 136.5, 121.0, 115.0, 111.2, 111.2, 87.6, 66.6, 59.9, 56.0, 48.0, 37.3, 31.0, 28.3, 25.7, 25.7, 25.7, 18.0, -4.8, -4.8 ppm; **MS** (70 eV): *m*/*z* (%): 390 (9) $[M]^+$, 333 (26) $[M–t\text{-Bu}]^+$, 315 (54), 301 (27), 268 (100), 73 (89).

1.5—— Synthesis of Aldehyde 11

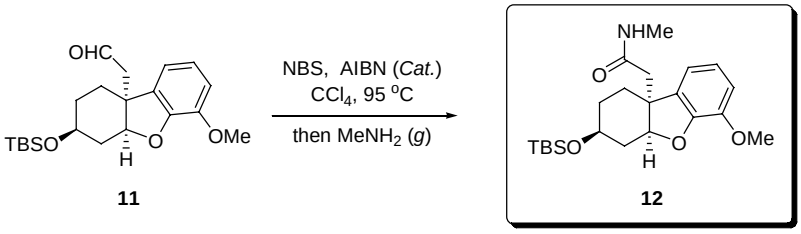


10 (Z/E = 2:1) **11**

To a solution of **10** (0.20 g, 0.51 mmol) in THF/H_2O (10:1, 5 mL) was slowly added $Hg(OCOCF_3)_2$ (0.28 g, 0.67 mmol) at 0 °C under an argon atmosphere. After stirring for 10 min at ambient temperature, excess saturated aqueous solution of KI (1 mL) was added. The resulting reaction mixture was stirred for additional 15 min, and then extracted with EtOAc (3×30 mL). The combined extracts were dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the residue through column chromatography on silica gel (petroleum/EtOAc 20:1) afforded the aldehyde **11** (0.17 g, 91%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.57 (dd, *J* = 2.1, 2.4 Hz, 1H), 6.92-6.87 (m, 1H), 6.81-6.75 (m, 2H), 4.68 (dd, *J* = 6.6, 9.3 Hz, 1H), 3.86 (s, 3H), 3.62-3.59 (m, 1H), 2.64 (dd, *J* = 2.1, 15.6 Hz, 1H), 2.46(dd, *J* = 2.4, 15.6 Hz, 1H), 2.36-2.24 (m, 2H), 1.77-1.68 (m, 2H), 1.50-1.25 (m, 2H), 0.83 (s, 9H), 0.02 ppm (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 201.3, 146.4, 146.0, 132.7, 121.8, 115.0, 112.0, 86.9, 67.2, 55.9, 53.7, 46.6, 38.3, 31.2, 28.4, 25.7, 25.7, 25.7, 18.0, -4.8, -4.8 ppm; **MS** (70 eV): *m*/*z* (%): 376 (4) $[M]^+$, 343 (2), 319 (6) $[M–t\text{-Bu}]^+$, 301 (100), 242 (22), 268 (24), 209 (50), 181 (37), 75 (49); **HRMS** (SIMS): *m*/*z* calcd for $C_{21}H_{33}O_4Si$: 377.2143; found: 377.2152 $[M+H]^+$.

1.6—— Synthesis of Amide 12

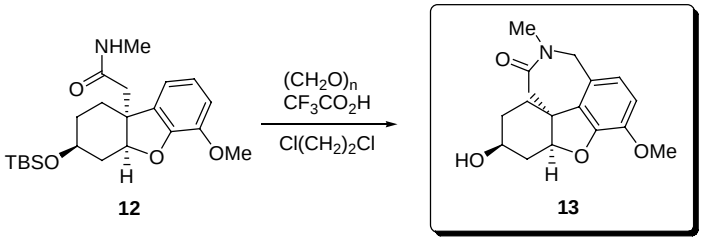


11 **12**

To a solution of **11** (86 mg, 0.23 mmol) in dried CCl_4 (6 mL) was added, sequentially, 2,2′-azobisisobutyronitrile (AIBN, 1.9 mg, 0.01 mmol) and *N*-bromosuccinimide (NBS, 53 mg, 0.30 mmol) under an argon atomosphere. The flask was then placed in an oil-bath ***preheated*** at 95 °C, and the heterogeneous mixture was stirred for 12 min. The crude reaction mixture was cooled to 0 °C, and then bubbled by $MeNH_2$ gas, which was prepared *in situ* from $MeNH_2$•HCl and NaOH and dried by basic drying tower. Keeping on the continuous $MeNH_2$ bubble, the suspension was stirred at room temperature for additional 10 min. After direct removal of CCl_4 *in vacuo* at ambient temperature, the residue was rapidly purified by column chromatography on silica gel (petroleum/EtOAc 2:1) to give the amide **12** (66 mg, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.85-6.81 (m, 1H), 6.76-6.74 (m, 1H), 6.69-6.67 (m, 1H), 5.21 (bs, 1H), 4.84 (dd, *J* = 6.8, 9.6 Hz, 1H), 3.84 (s, 3H), 3.59-3.55 (m, 1H), 2.65 (d, *J* = 4.8 Hz, 3H), 2.36-2.20 (m, 2H), 2.29, 2.23 (ABq, *J* = 14.0 Hz, 2H), 1.90 (td, *J* = 3.6, 14.0 Hz, 1H), 1.73-1.68 (m, 1H), 1.41-1.33 (m, 1H), 1.28-1.19 (m, 1H), 0.80 (s, 9H), 0.01 ppm (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 170.7, 146.4, 145.9, 133.8, 121.4, 115.0, 111.9, 86.6, 67.3, 55.9, 47.4, 46.8, 38.5, 31.4, 27.4, 26.0, 25.7, 25.7, 25.7, 17.9, -4.8, -4.8 ppm; **MS** (70 eV): *m*/*z* (%): 405 (6) $[M]^+$, 372 (3), 348 (19) $[M–t\text{-Bu}]^+$, 303 (100), 275 (60), 174 (16), 73 (40); **HRMS** (ESI): *m*/*z* calcd for $C_{22}H_{35}O_4NSiNa$: 428.2228; found: 428.2238 $[M+Na]^+$.

1.7—— Synthesis of Lactam 13

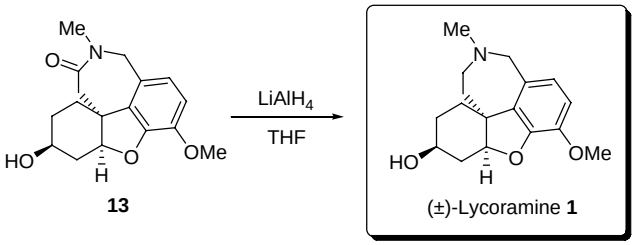


To a solution of **12** (78 mg, 0.19 mmol) in dried $Cl(CH_2)_2Cl$ (6 mL) was added, sequentially, paraformaldehyde (23.1 mg, 0.77 mmol) and CF_3CO_2H (0.19 mL, 2.5 mmol) at room temperature. The reaction mixture was stirred at ambient temperature for 1.5 h, and then quenched with saturated aqueous $NaHCO_3$ (10 mL) followed by addition of CH_2Cl_2 (40 mL). The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (3×40 mL). The combined organic phases were washed by brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 20:1) to give the lactam **13** (47.3 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.66, 6.64 (ABq, *J* = 8.0 Hz, 2H), 4.39, 4.31 (ABq, *J* = 16.4 Hz, 2H), 4.37 (bs, 1H), 4.10-4.08 (m, 1H), 3.85 (s, 3H), 3.01 (s, 3H), 2.84, 2.80 (ABq, *J* = 14.0 Hz, 2H), 2.63 (bs, 1H; OH), 2.56-2.51 (m, 1H), 1.96-1.87 (m, 2H), 1.82-1.77 (m, 1H), 1.69-1.53 ppm (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 171.8, 146.2, 144.8, 136.9, 124.4,

119.6, 111.3, 89.1, 64.6, 56.0, 51.9, 41.6, 39.8, 36.1, 30.8, 27.5, 27.5 ppm; **MS** (70 eV): *m*/*z* (%): 303 (100) $[M]^+$, 272 (3) $[M–MeO]^+$, 260 (5) $[M–MeCO]^+$, 244 (20), 231 (46)$[M–MeCONMe]^+$, 213 (11), 188 (27), 84 (52); **HRMS** (ESI): *m*/*z* calcd for $C_{17}H_{22}O_4N$: 304.1543; found: 304.1544 $[M+H]^+$.

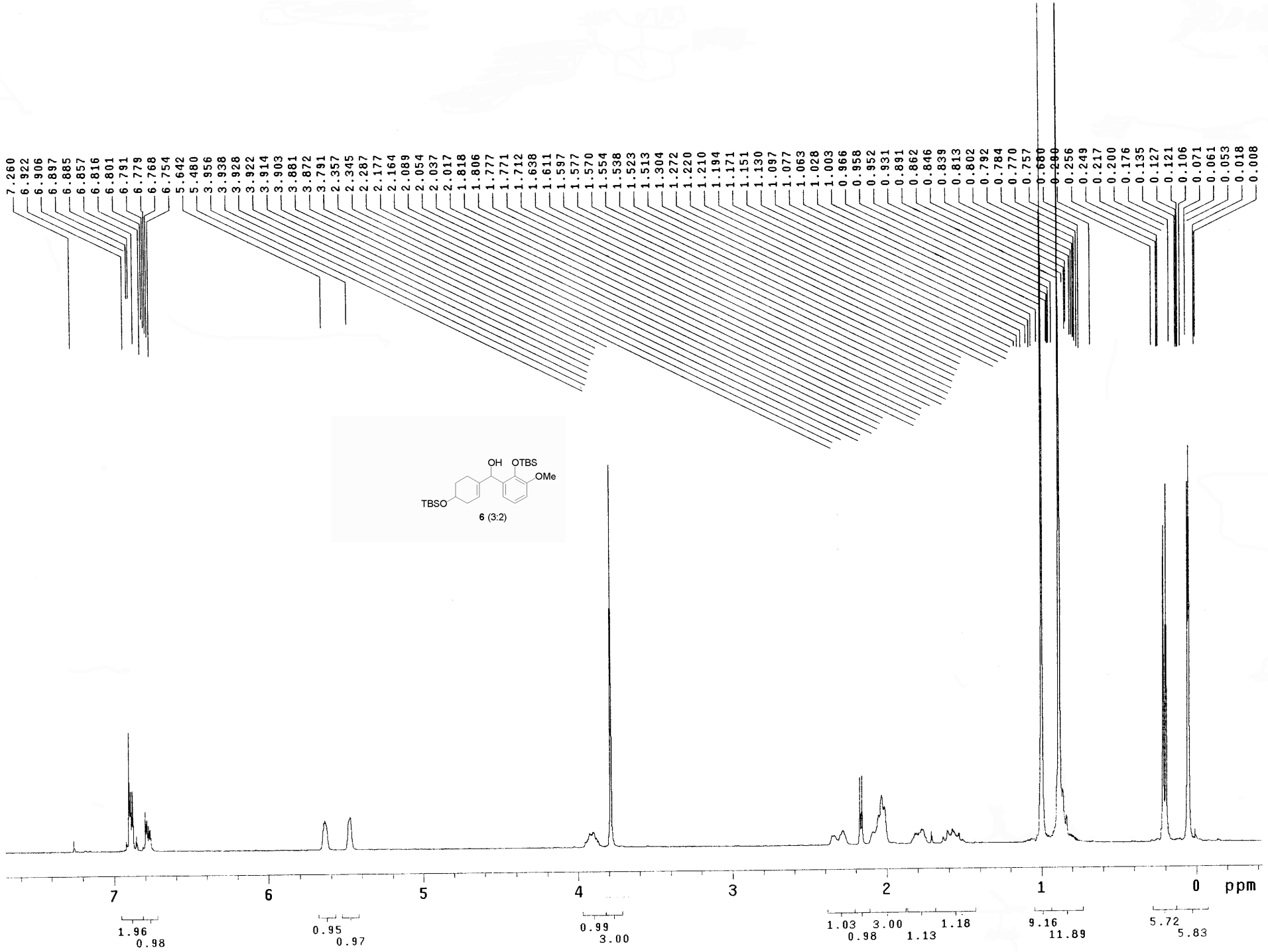
1.8—— Synthesis of (±)-Lycoramine 1



To a suspension of $LiAlH_4$ (34 mg, 0.89 mmol) in dried THF (2 mL) at –78 °C under an argon atmosphere was added slowly a solution of **13** (30 mg, 0.10 mmol) in dried THF (3 mL). The reaction mixture was stirred at reflux for 4 h, cooled to room temperature, and carefully quenched with aqueous NaOH (3*N*, 4 mL) followed by addition of EtOAc (40 mL). The organic layer was separated, and the aqueous phase was carefully extracted with EtOAc (5×30 mL). The combined extracts was dried over K_2CO_3, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel ($CHCl_3$/MeOH 15:1) to afford (±)-Lycoramine **1** (23.7 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64, 6.59 (ABq, *J* = 8.4 Hz, 2H), 4.36 (t, *J* = 2.8 Hz, 1H), 4.08-4.06 (m, 1H), 3.99, 3.62 (ABq, *J* = 15.2 Hz, 2H), 3.84 (s, 3H), 3.24-3.17 (m, 1H), 3.05-3.01 (m, 1H), 2.63 (bs, 1H; OH), 2.52-2.46 (m, 1H), 2.36 (s, 3H), 2.00-1.52 ppm (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 146.0, 144.1, 136.3, 128.8, 121.8, 110.8, 90.0, 65.4, 60.4, 55.9, 54.0, 46.7, 41.8, 31.6, 31.2, 27.7, 23.7 ppm; **MS** (70 eV): *m*/*z* (%): 290 (10) $[M+H]^+$, 289 (57) $[M]^+$, 288 (100) $[M–H]^+$, 232 (8), 202 (10), 115 (13), 84 (50); **HRMS** (ESI): *m*/*z* calcd for $C_{17}H_{24}O_3N$: 290.1751; found: 290.1747 $[M+H]^+$.

2. Copies of NMR Spectra of the Products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6.768
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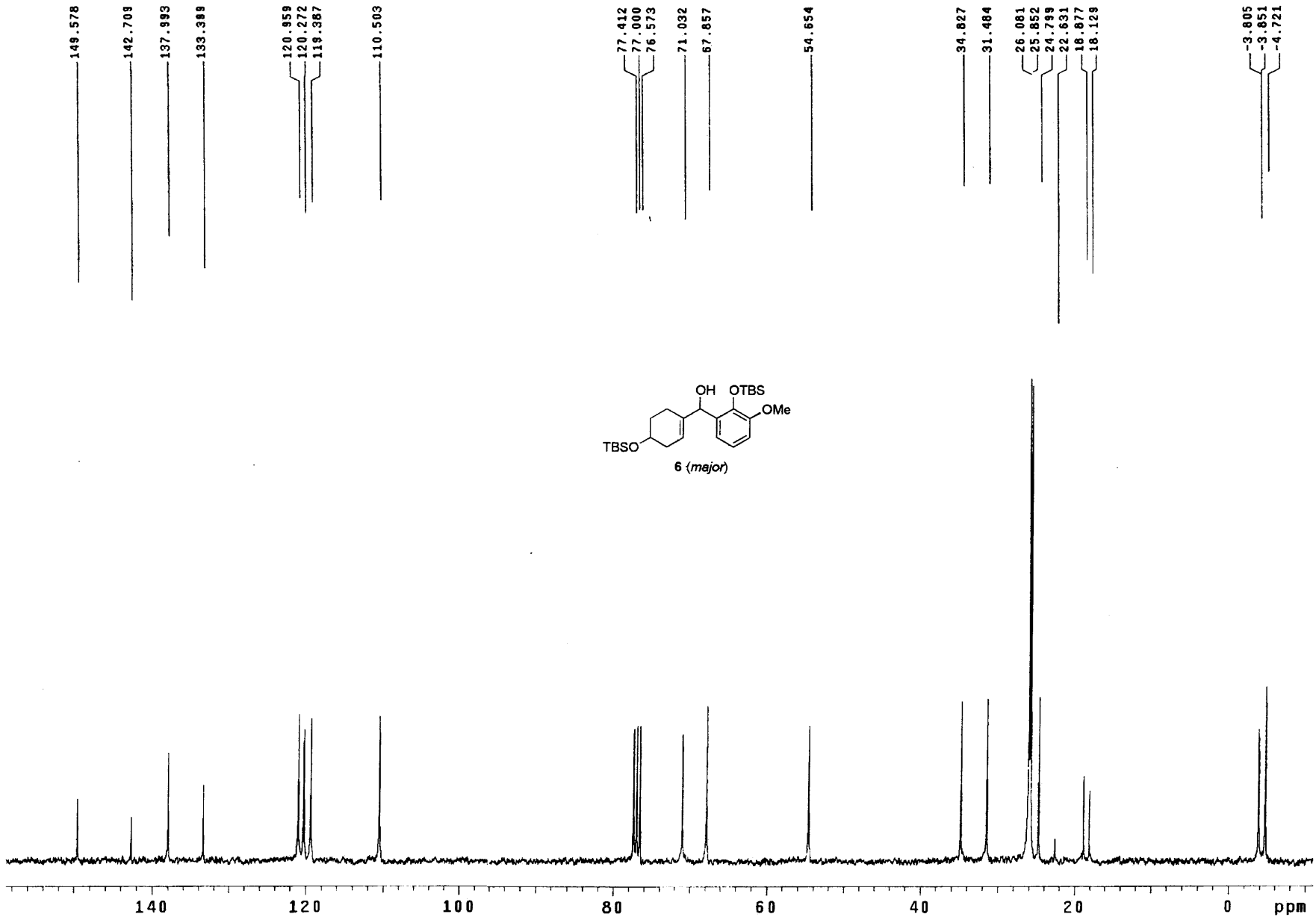
5.642
5.480
3.956
3.938
3.928
3.922
3.914
3.903
3.881
3.872
3.791
2.357
2.345
2.287
2.177
2.164
2.089
2.054
2.037
2.017
1.818
1.806
1.777
1.771
1.712
1.638
1.611
1.597
1.577
1.570
1.554
1.538
1.523
1.513
1.304
1.272
1.220
1.210
1.194
1.171
1.151
1.130
1.097
1.077
1.063
1.028
1.003
0.966
0.958
0.952
0.931
0.891
0.862
0.846
0.839
0.813
0.802
0.792
0.784
0.770
0.757
0.680
0.200
0.256
0.249
0.217
0.200
0.176
0.135
0.127
0.121
0.106
0.071
0.061
0.053
0.018
0.008
OH
OTBS
OMe
TBSO
6 (3:2)
7
6
5
4
3
2
1
0
ppm
1.96
0.98
0.95
0.97
0.99
3.00
1.03
3.00
1.18
0.98
1.13
9.16
11.89
5.72
5.83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120.272
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110.503
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77.000
76.573
71.032
67.857
54.654
34.827
31.484
26.081
25.852
24.799
22.631
18.877
18.129
-3.805
-3.851
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OH
OTBS
OMe
TBSO
6 (major)
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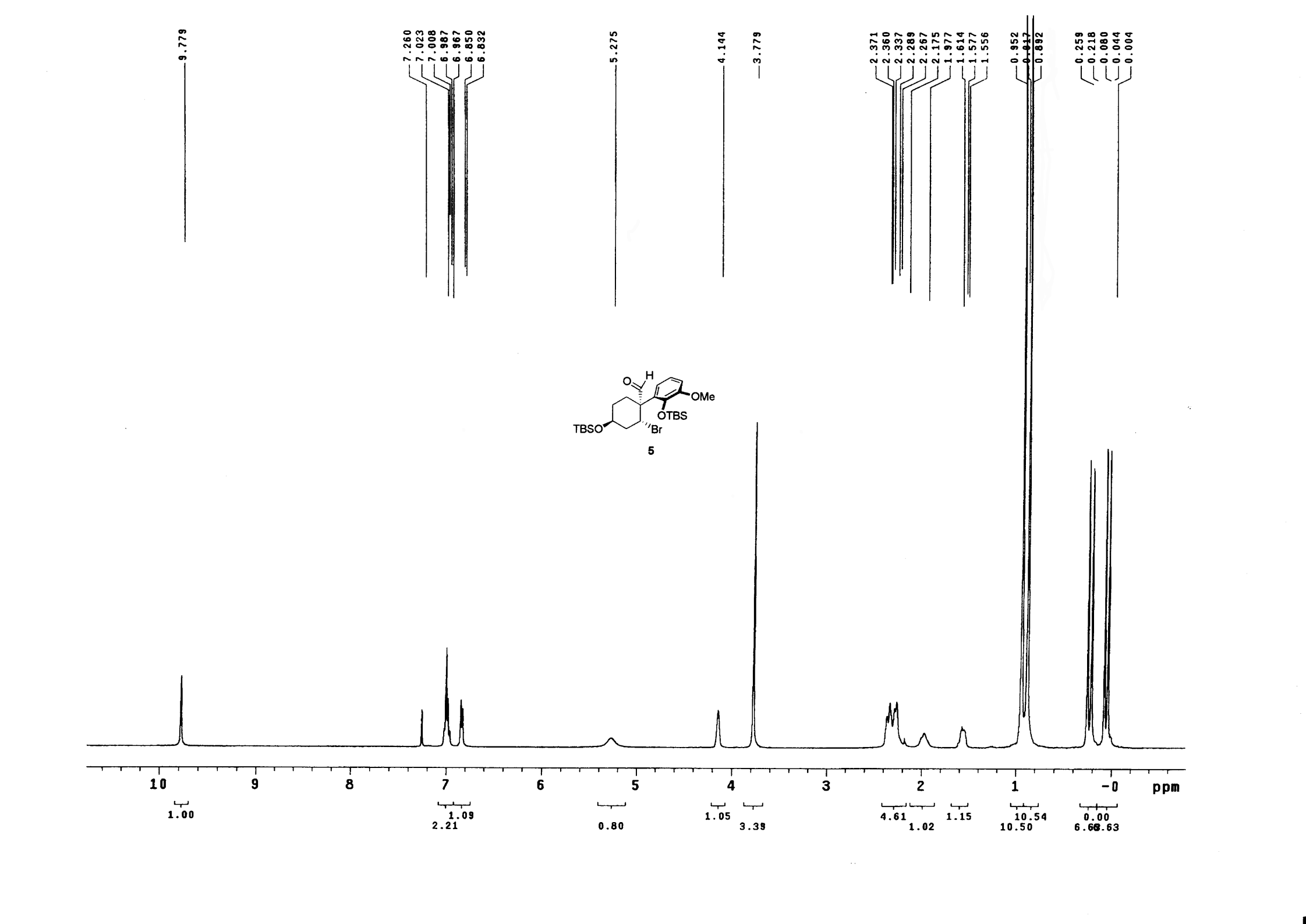
120
100
80
60
40
20
0
ppm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3.779
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2.360
2.337
2.288
2.267
2.175
1.977
1.614
1.577
1.556
0.952
0.892
0.259
0.218
0.080
0.044
0.004
O
H
OMe
OTBS
TBSO
Br
5
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
2.21
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1.05
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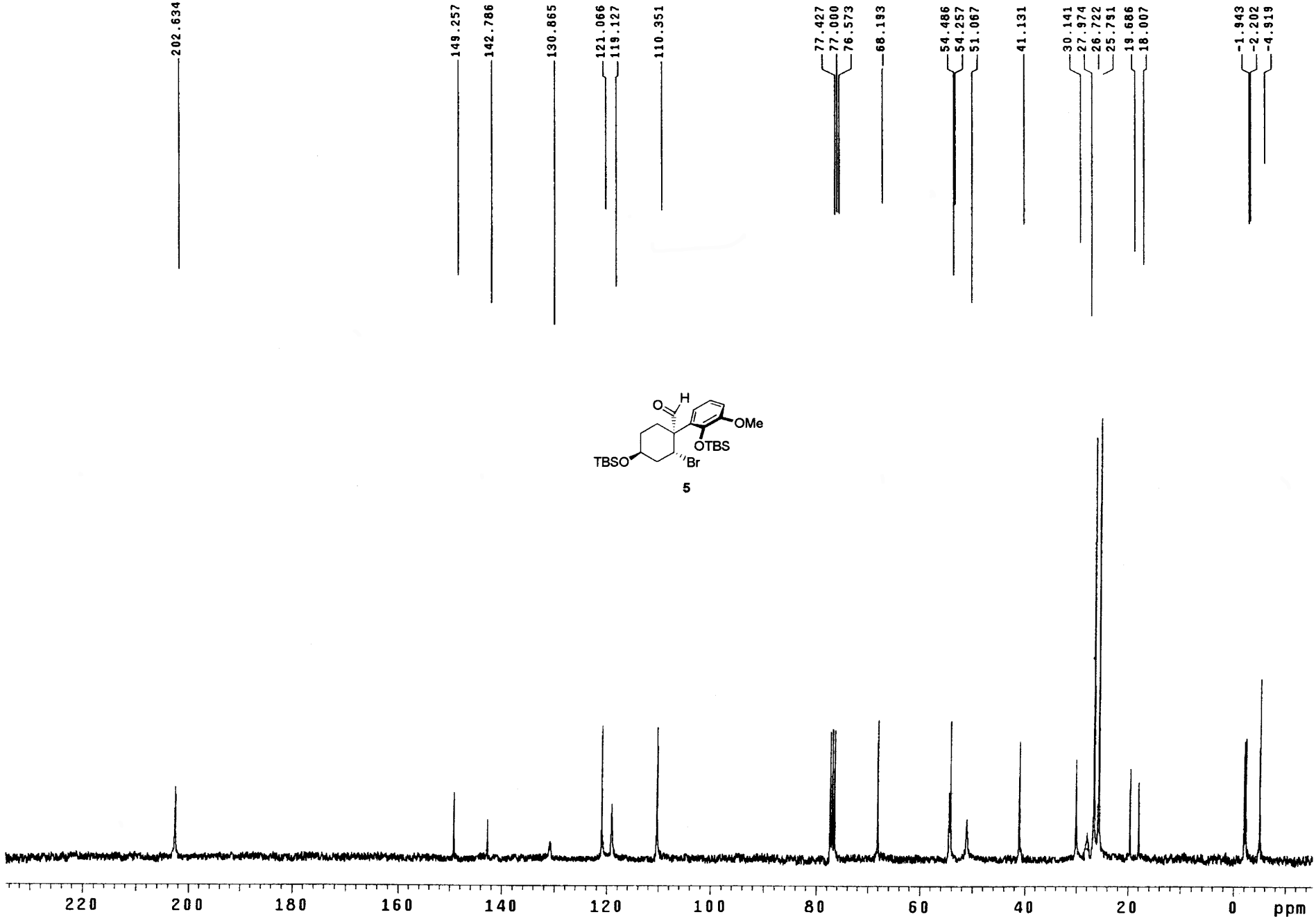
1.02
1.15
10.50
10.54
0.00
6.66
8.63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76.573
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54.257
51.067
41.131
30.141
27.974
26.722
25.791
19.686
18.007
-1.943
-2.202
-4.919
O
H
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OTBS
TBSO
Br
5
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200
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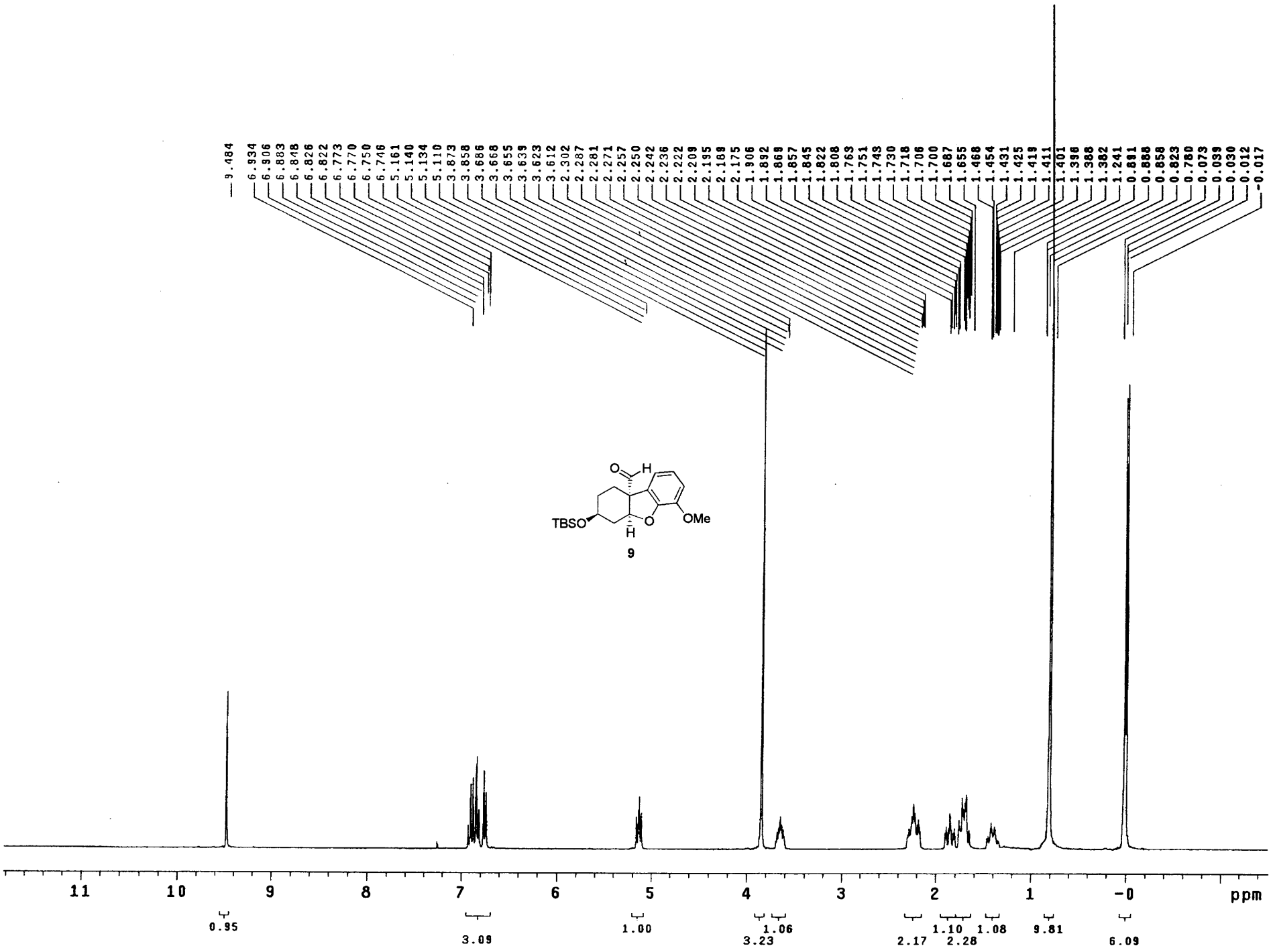
140
120
100
80
60
40
20
0
ppm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5.140
5.134
5.110
3.873
3.858
3.686
3.668
3.655
3.639
3.623
3.612
2.302
2.287
2.281
2.271
2.257
2.250
2.242
2.236
2.222
2.209
2.195
2.189
2.175
1.906
1.892
1.868
1.857
1.845
1.822
1.808
1.763
1.751
1.743
1.730
1.718
1.706
1.700
1.687
1.655
1.468
1.454
1.431
1.425
1.419
1.411
1.401
1.396
1.388
1.382
1.241
0.891
0.886
0.858
0.823
0.780
0.073
0.039
0.030
0.012
-0.017
O
H
TBSO
O
OMe
H
9
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
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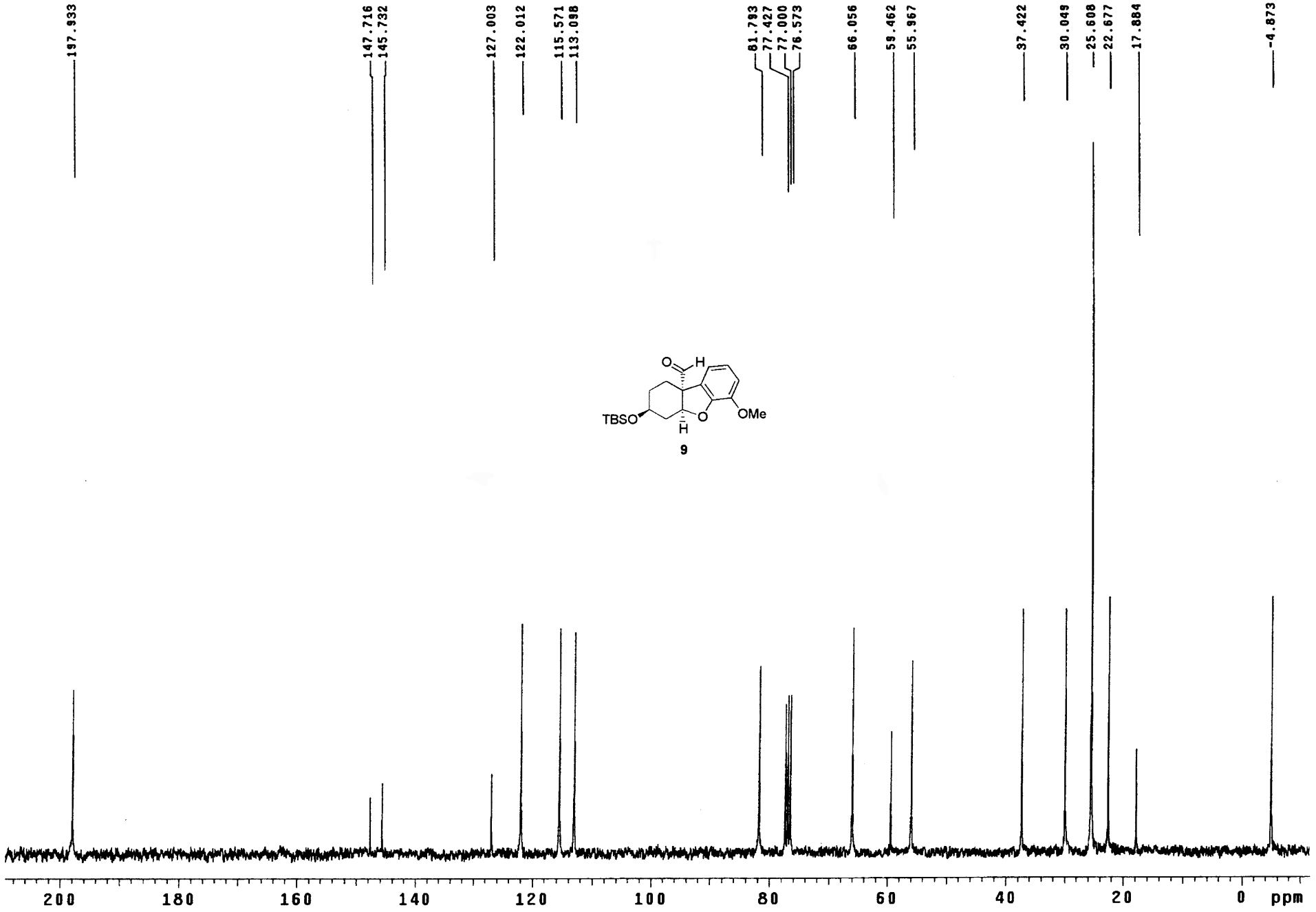
1.00
3.23
1.06
2.17
2.28
1.10
1.08
9.81
6.09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55.967
37.422
30.049
25.608
22.677
17.884
-4.873
O
H
TBSO
O
OMe
H
9
200
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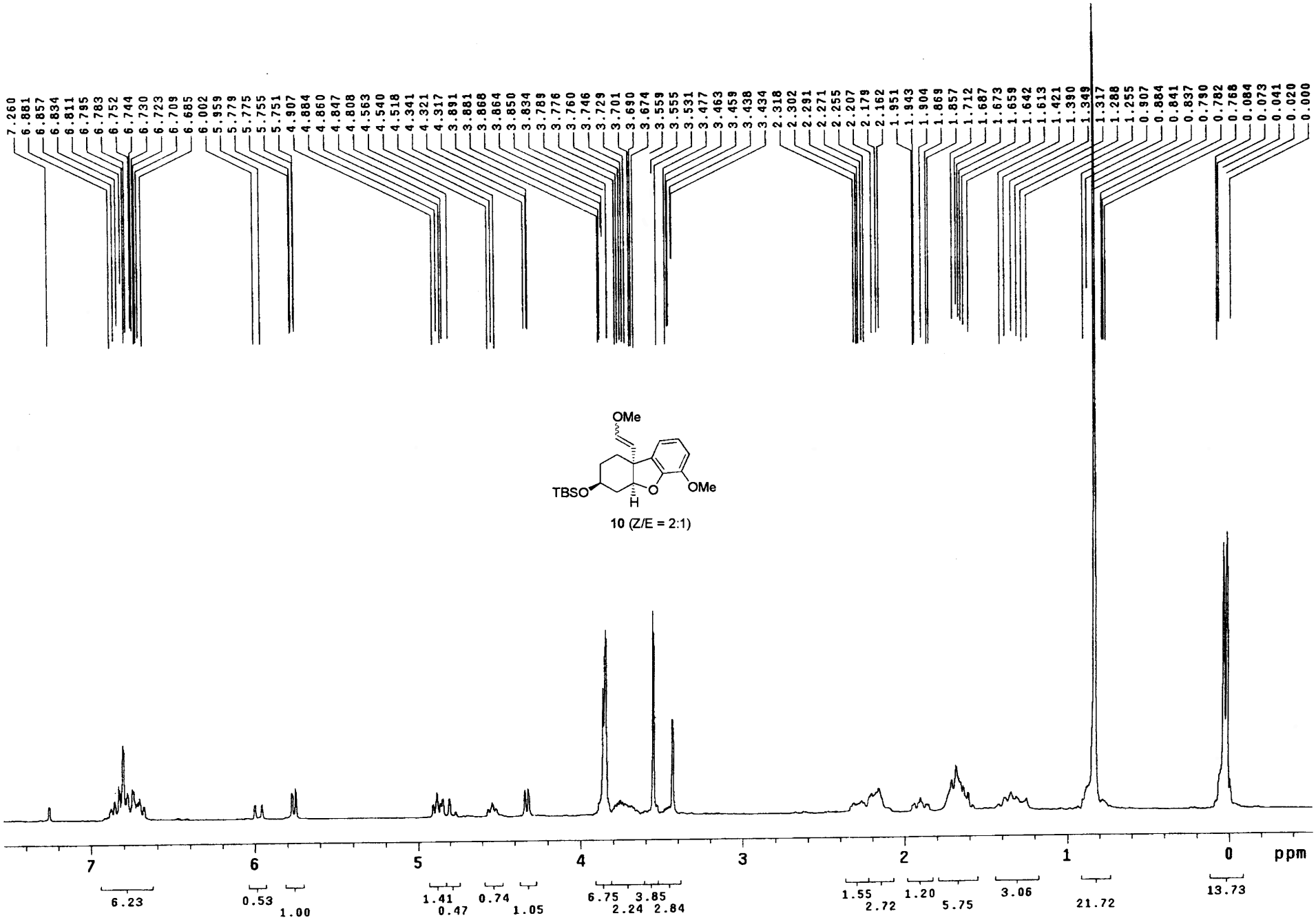
140
120
100
80
60
40
20
0
ppm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6.002
5.959
5.779
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5.755
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4.907
4.884
4.860
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4.808
4.563
4.540
4.518
4.341
4.321
4.317
3.891
3.881
3.868
3.864
3.850
3.834
3.789
3.776
3.760
3.746
3.729
3.701
3.690
3.674
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3.555
3.531
3.477
3.463
3.459
3.438
3.434
2.318
2.302
2.291
2.271
2.255
2.207
2.179
2.162
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1.943
1.904
1.869
1.857
1.712
1.687
1.673
1.659
1.642
1.613
1.421
1.390
1.349
1.317
1.288
1.255
0.907
0.884
0.841
0.837
0.790
0.782
0.768
0.084
0.073
0.041
0.020
0.000
OMe
TBSO
O
OMe
H
10 (Z/E = 2:1)
7
6
5
4
3
2
1
0
ppm
6.23
0.53
1.00
1.41
0.47
0.74
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3.85
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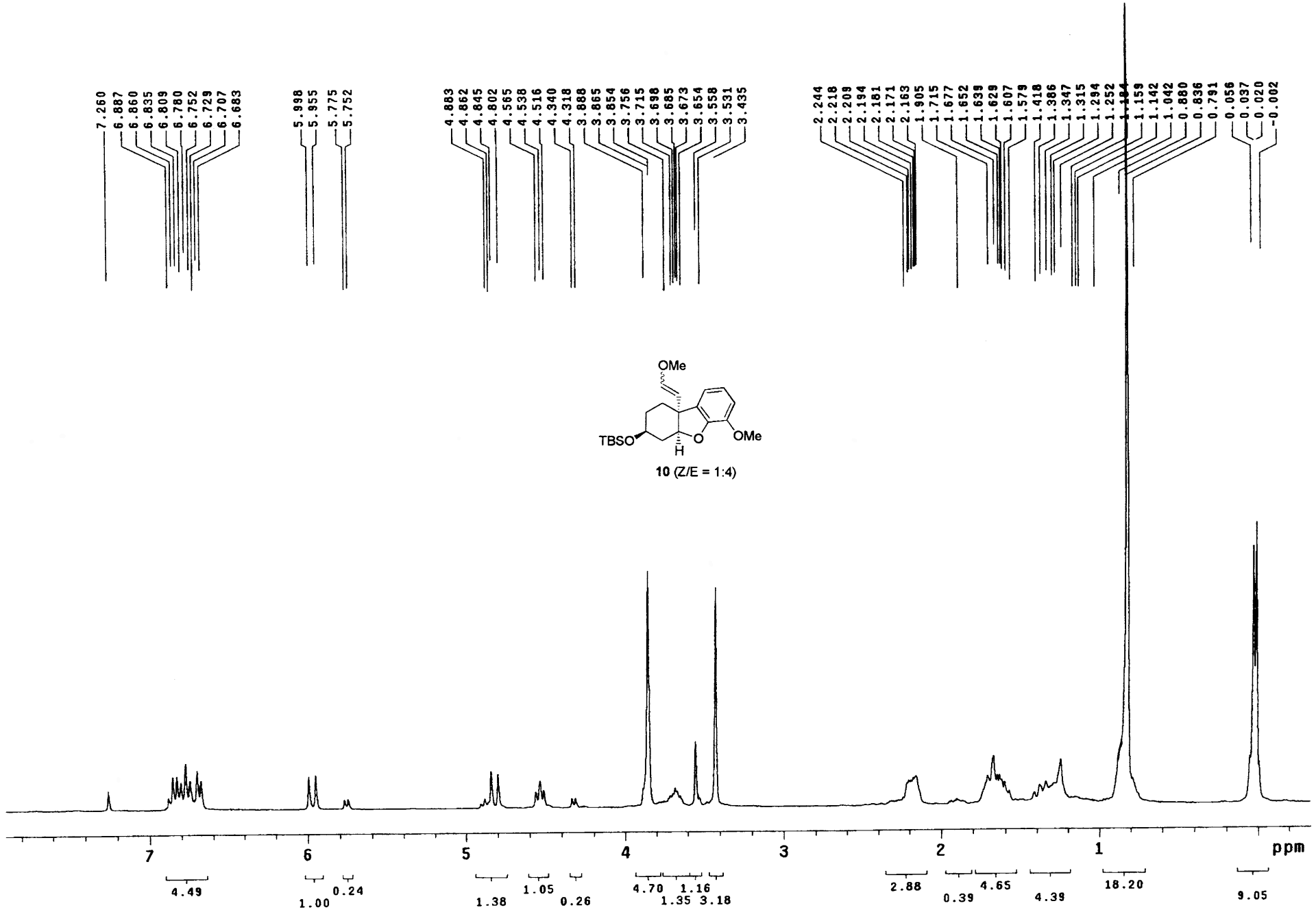
1.20
5.75
3.06
21.72
13.73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5.752
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4.862
4.845
4.802
4.565
4.538
4.516
4.340
4.318
3.888
3.865
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3.715
3.698
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3.435
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2.218
2.209
2.194
2.181
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2.163
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1.715
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1.639
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1.579
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TBSO
O
H
OMe
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6
5
4
3
2
1
ppm
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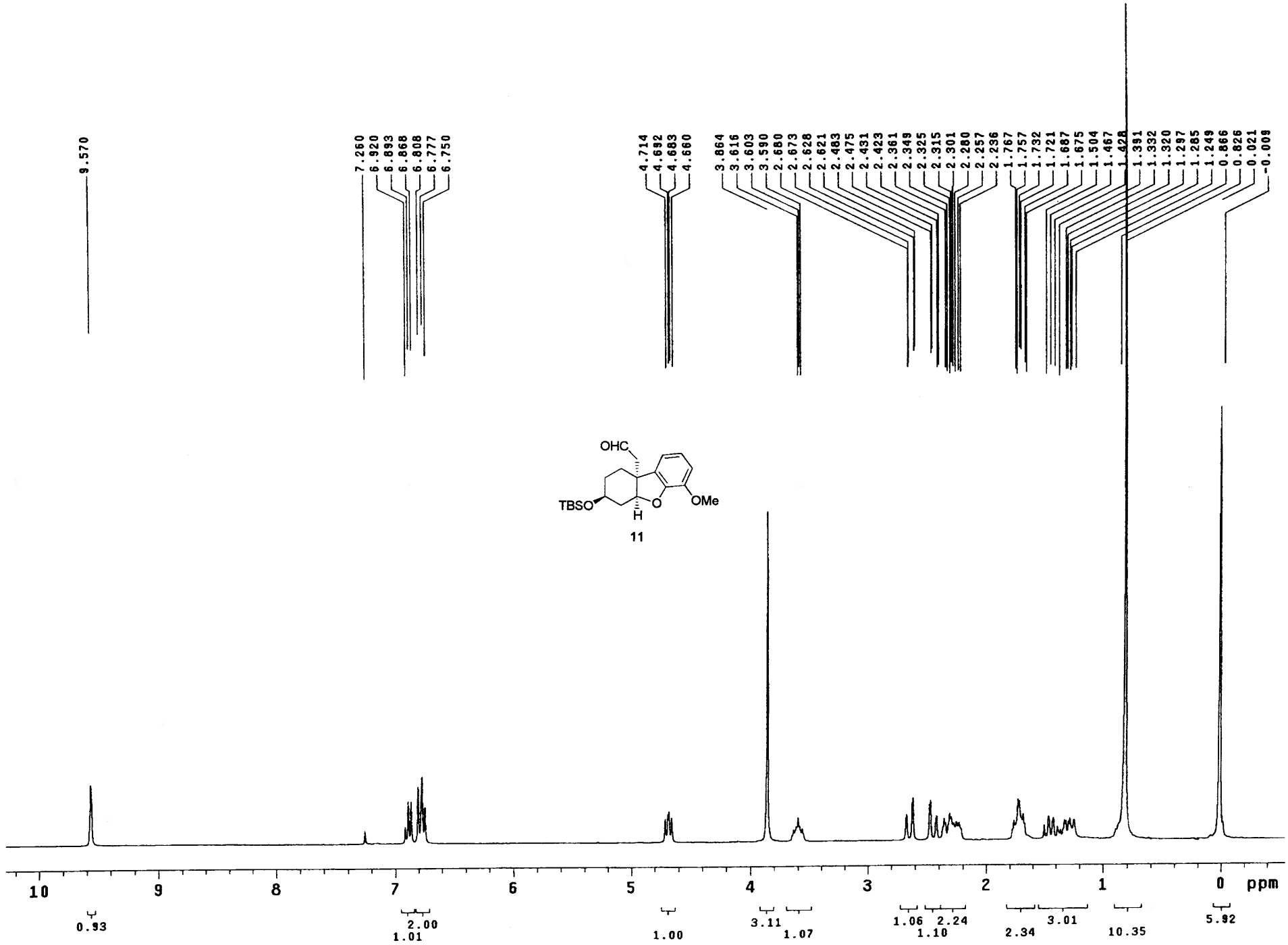
4.39
18.20
9.05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3.616
3.603
3.590
2.680
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2.628
2.621
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2.475
2.431
2.423
2.361
2.349
2.325
2.315
2.301
2.280
2.257
2.236
1.767
1.757
1.732
1.721
1.687
1.675
1.504
1.467
1.428
1.391
1.332
1.320
1.297
1.285
1.249
0.866
0.826
0.021
-0.009
OHC
TBSO
O
H
OMe
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.10
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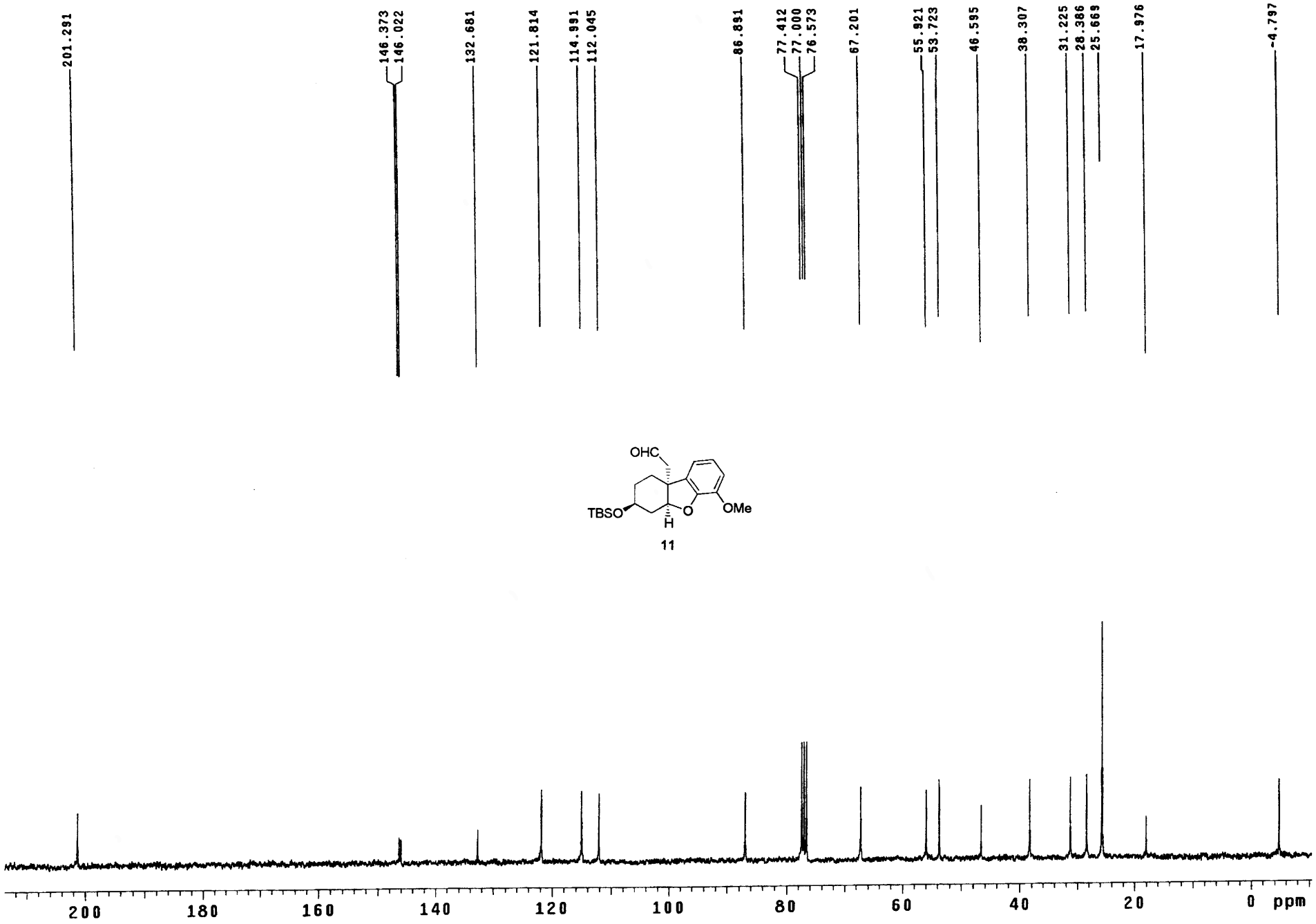
3.01
10.35
5.92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55.921
53.723
46.595
38.307
31.225
28.386
25.669
17.976
-4.797
OHC
TBSO
O
H
OMe
11
200
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120
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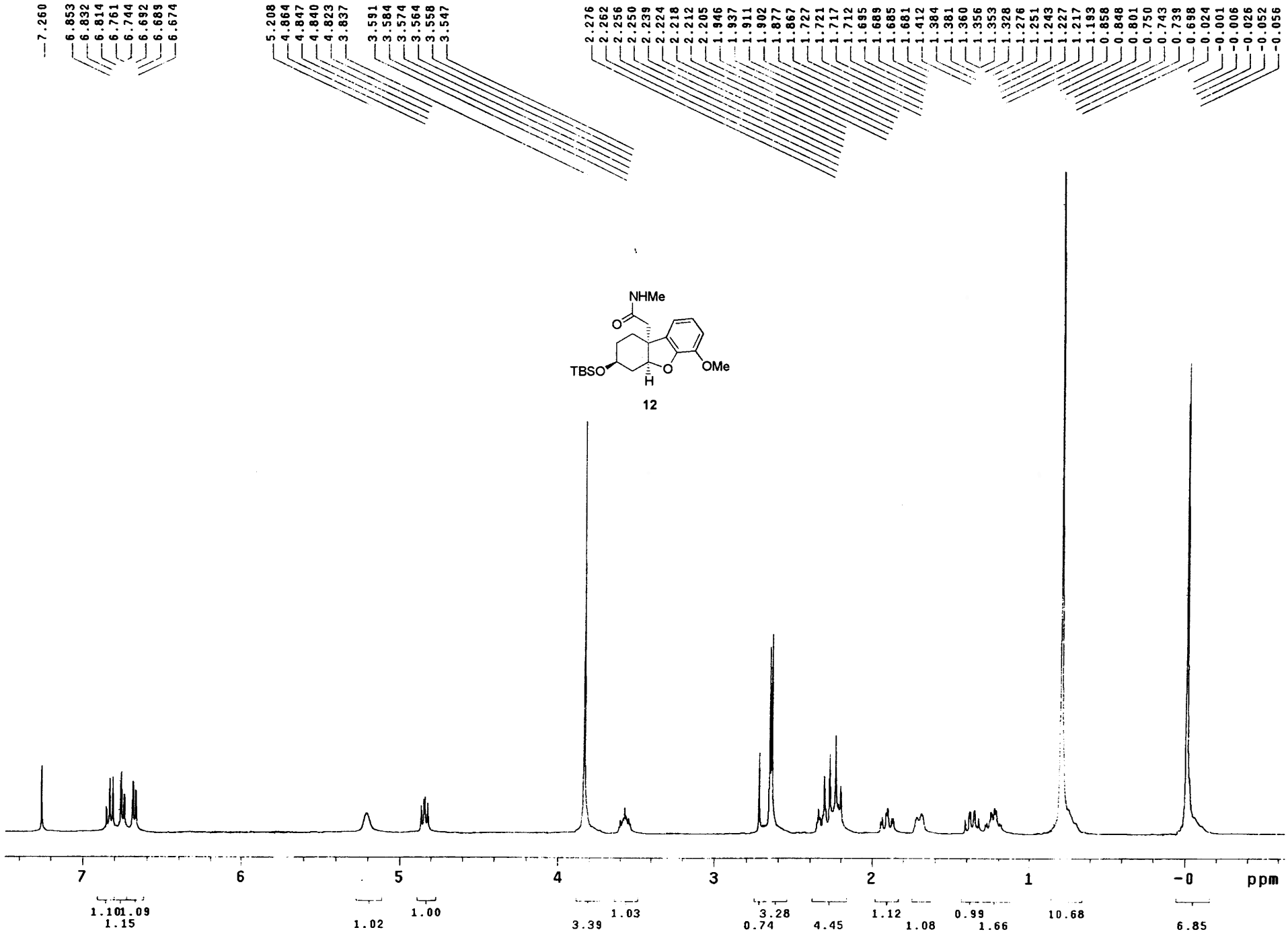
20
0
ppm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3.591
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2.224
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1.937
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1.902
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1.193
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0.801
0.750
0.743
0.739
0.698
0.024
-0.001
-0.006
-0.026
-0.052
-0.056
NHMe
O
TBSO
O
OMe
H
12
7
6
5
4
3
2
1
-0
ppm
1.10
1.09
1.15
1.02
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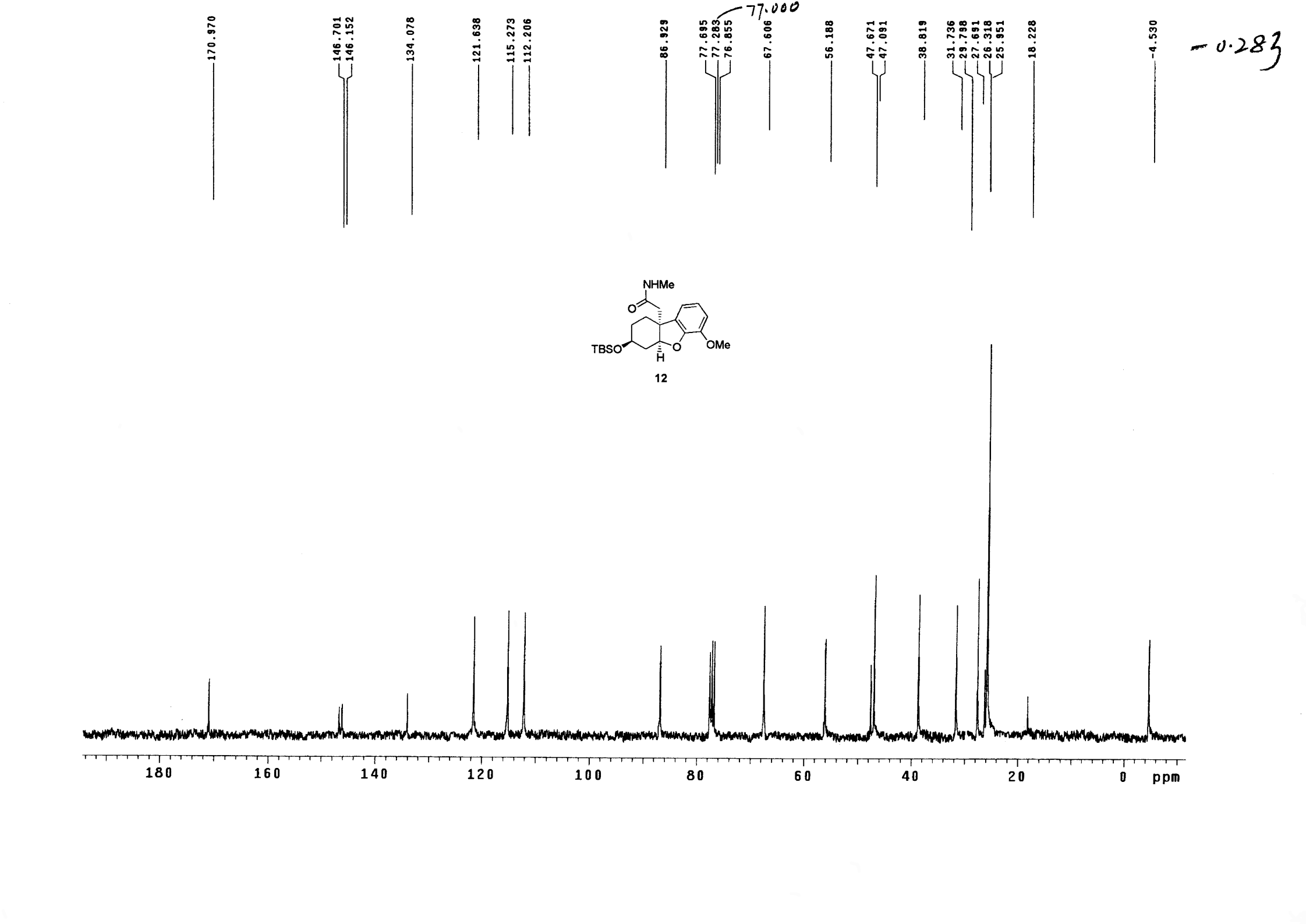
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56.188
47.671
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26.318
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OMe
H
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120
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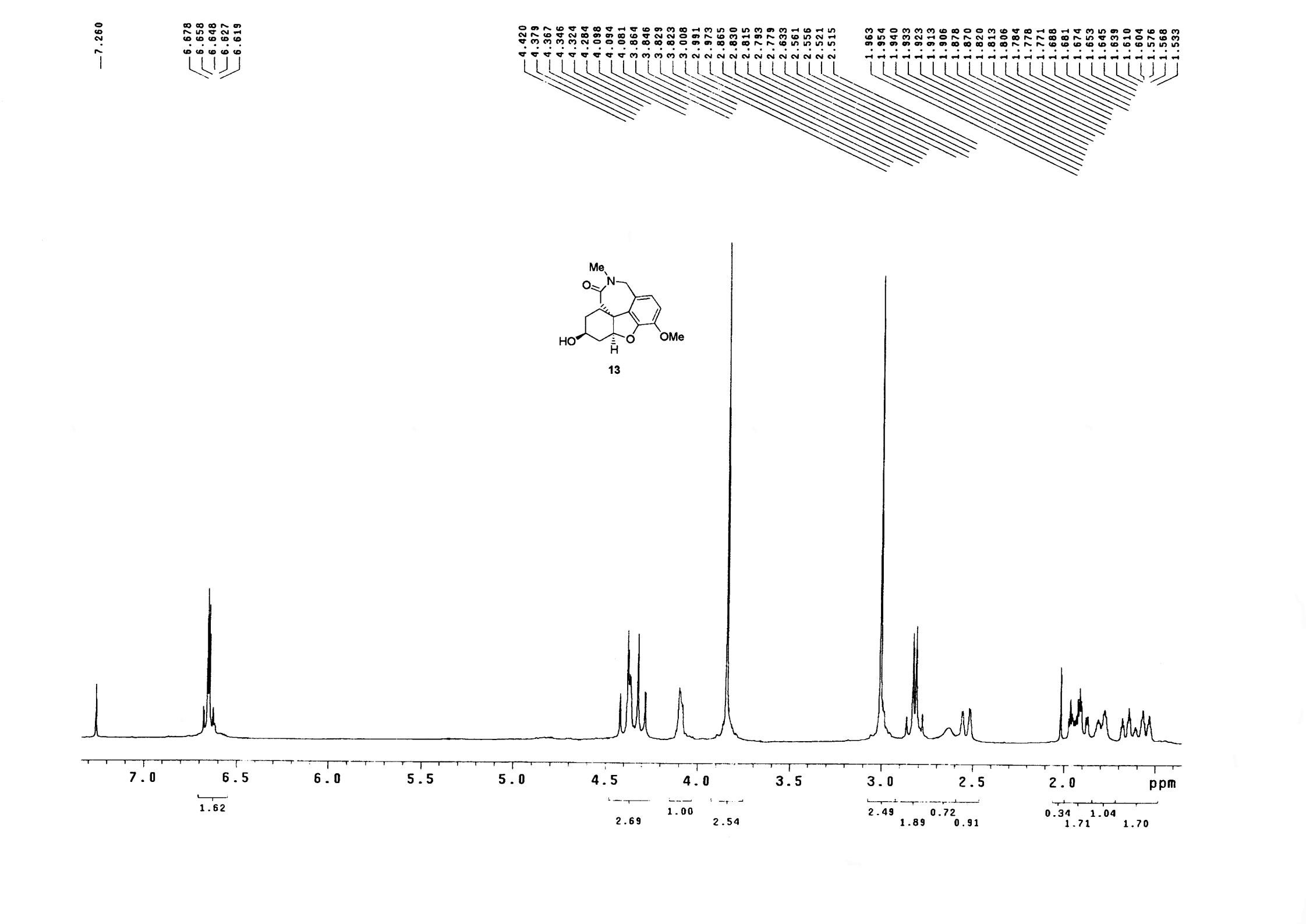
60
40
20
0
ppm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4.094
4.081
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3.846
3.829
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2.865
2.830
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2.779
2.633
2.561
2.556
2.521
2.515
1.963
1.954
1.940
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1.923
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1.878
1.870
1.820
1.813
1.806
1.784
1.778
1.771
1.688
1.681
1.674
1.653
1.645
1.639
1.610
1.604
1.576
1.568
1.533
Me
N
O
HO
OMe
H
13
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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0.91
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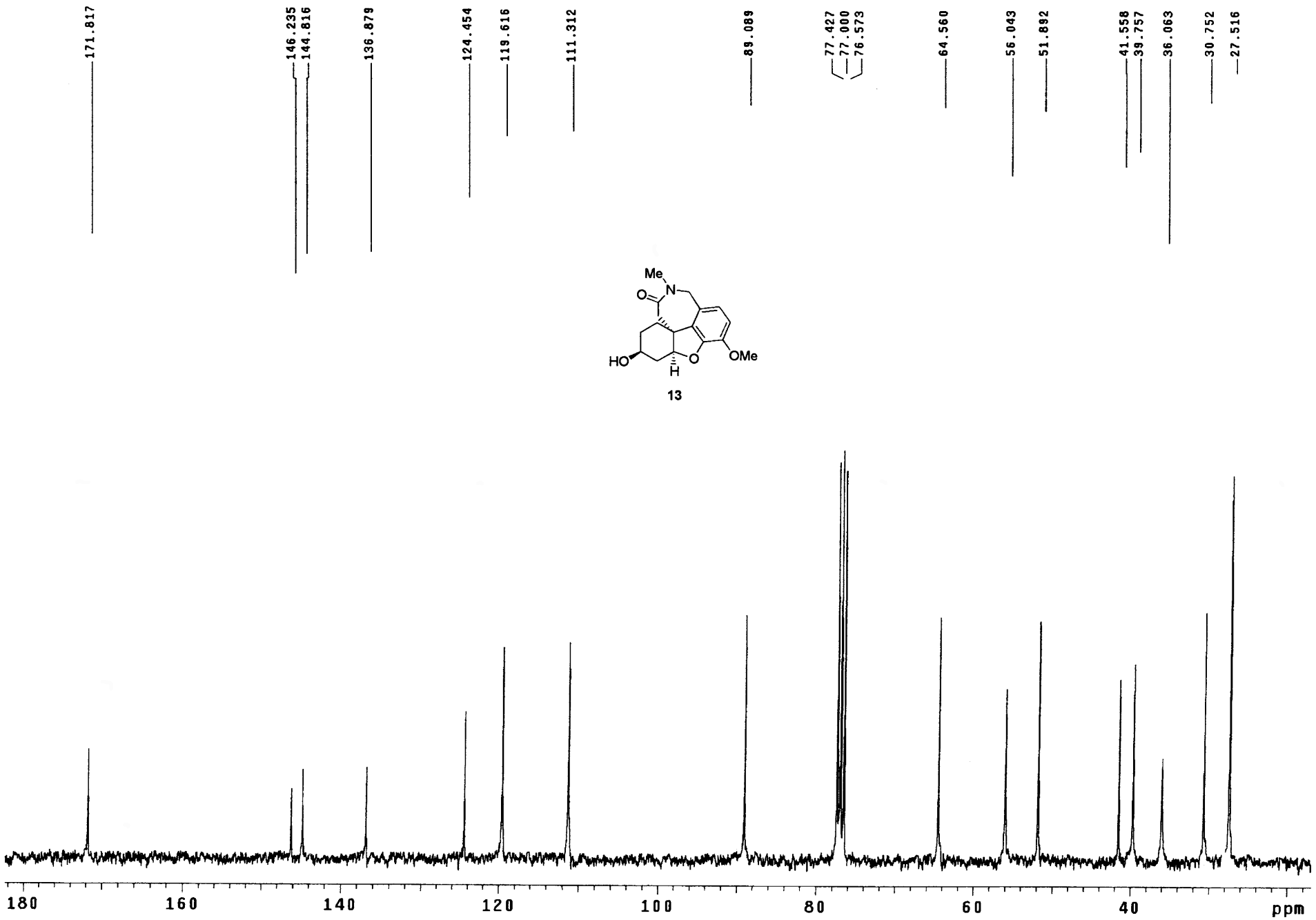
1.04
1.71
1.70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77.000
76.573
64.560
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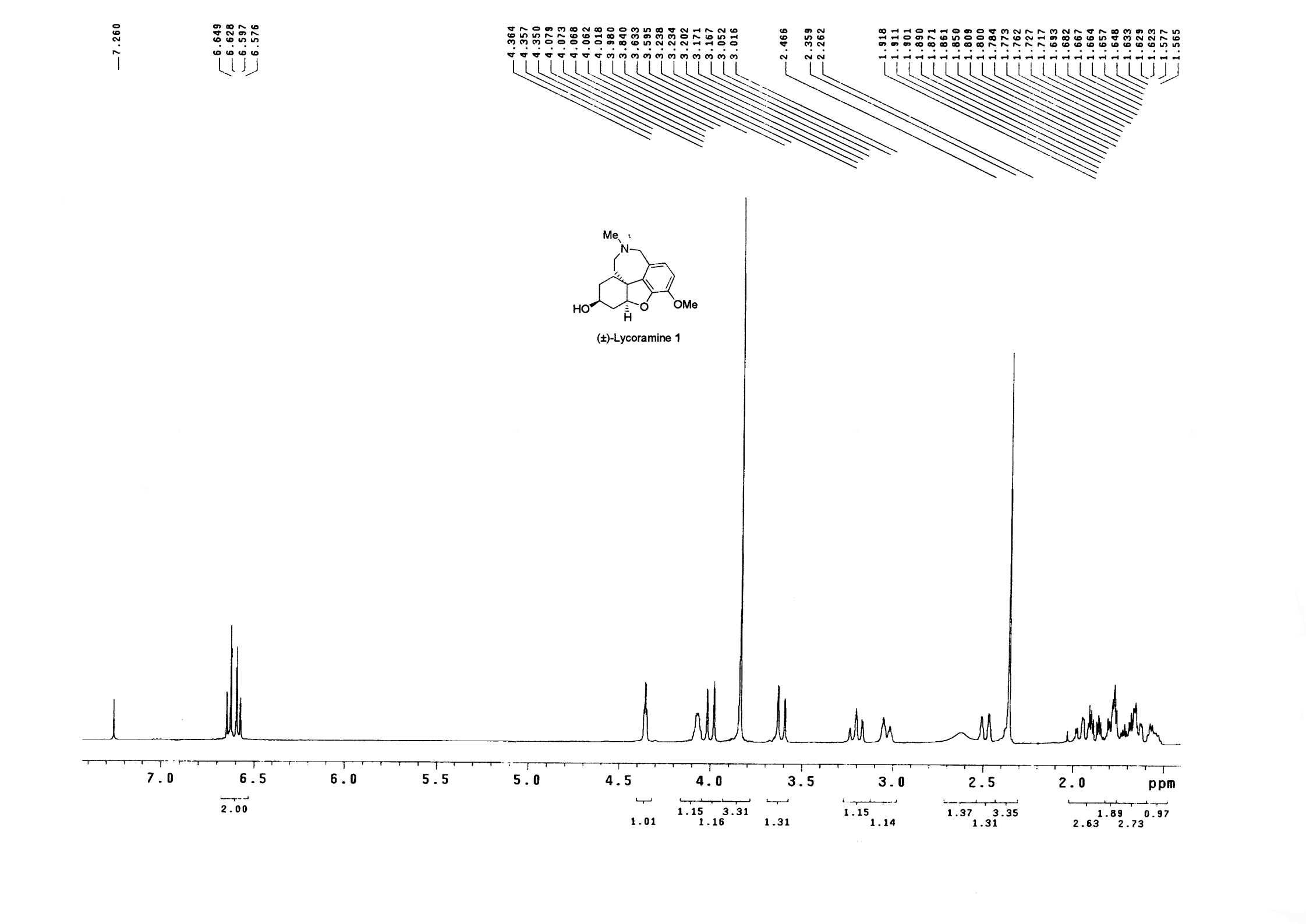
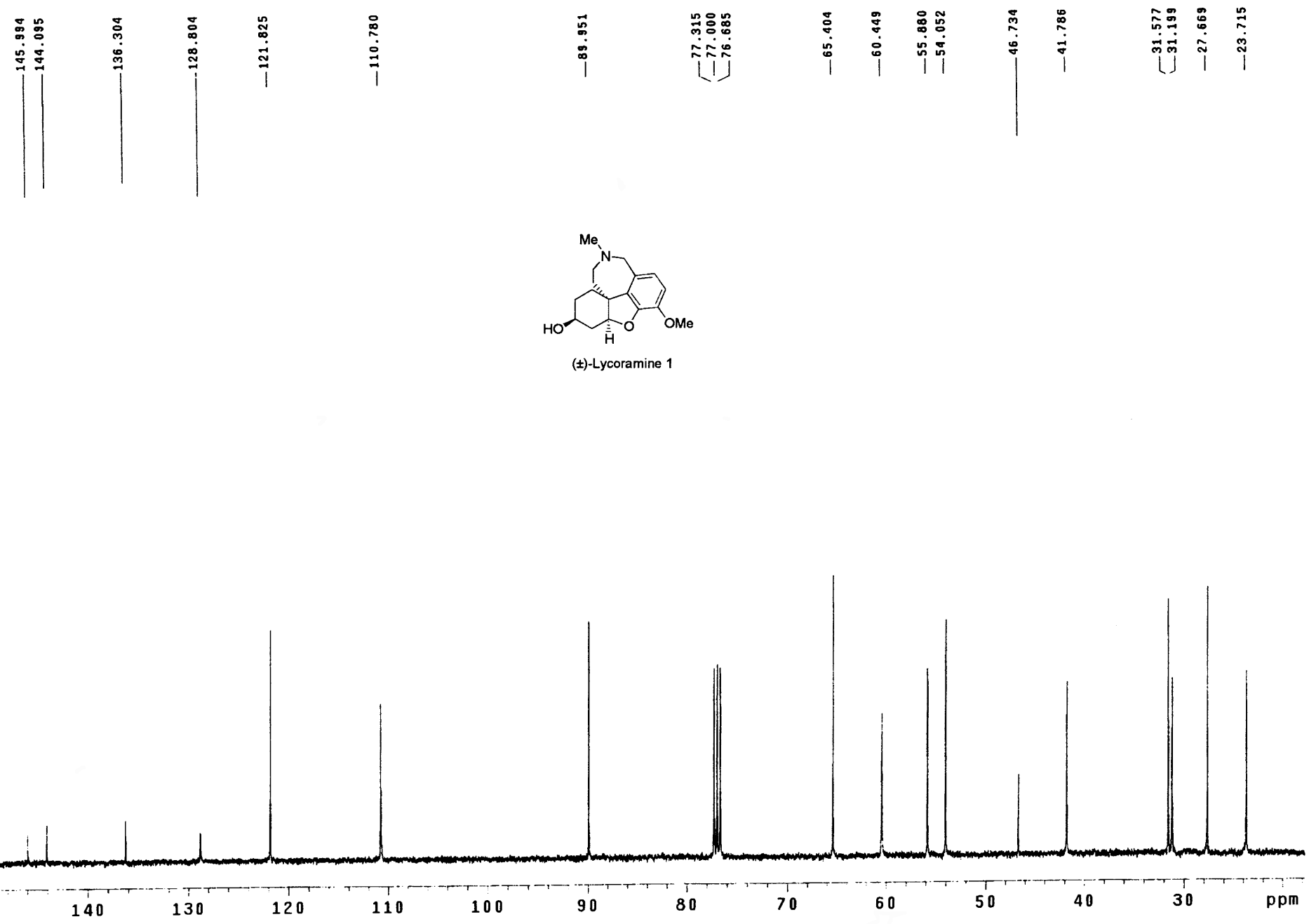
51.892
41.558
39.757
36.063
30.752
27.516
Me
N
O
HO
H
O
OMe
180
160
140
120
100
80
60
40
ppm

13


7.260
6.649
6.628
6.597
6.576
4.364
4.357
4.350
4.079
4.073
4.068
4.062
4.018
3.980
3.840
3.633
3.595
3.238
3.234
3.202
3.171
3.167
3.052
3.016
2.466
2.359
2.262
1.918
1.911
1.901
1.890
1.871
1.861
1.850
1.809
1.800
1.784
1.773
1.762
1.727
1.717
1.693
1.682
1.667
1.664
1.657
1.648
1.633
1.629
1.623
1.577
1.565
Me
N
HO
O
H
OMe
(±)-Lycoramine 1
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
2.00
1.01
1.15
1.16
3.31
1.31
1.15
1.14
1.37
1.31
3.35
2.63
1.89
2.73
0.97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144.095
136.304
128.804
121.825
110.780
89.951
77.315
77.000
76.685
65.404
60.449
55.880
54.052
46.734
41.786
31.577
31.199
27.669
23.715
Me
N
HO
O
H
OMe
(±)-Lycoramine 1
140
130
120
110
100
90
80
70
60
50
40
30
ppm