The Journal of Organic Chemistry

COMPOUND CHARACTERIZATION CHECKLIST

JO 1

Corresponding Author: Philip Fuchs

Title: Asymmetric Synthesis of all Eight Seven-Carbon Dipropionate Stereotetrads

TO DISPLAY INSTRUCTIONS: Double-click HERE (Formula Bar must be visible: Select View>Formula Bar) TO CLOSE: Enter/Return

Compound or structure number (with substituent/ isomer identifier if needed)	IDENTITY												PURITY						COMPUTATIONAL DATA in SI*		
	Known compound [citation given]	IR	UV-Vis	1H NMR	13C NMR	Other NMR	MS	High resolution MS	X-ray [ORTEP and CIF in SI*]	Optical rotation/ORD/CD	er/dr [NMR or chromatography]	COSY	Copy of 1H/13C NMR in SI*	Quant. GC, HPLC, or electrophoresis	Elemental analysis				Cartesian coordinates or Z-matrix	# of imaginary frequencies	Total energy
4	12																				
5	12																				
6	12																				
7	12																				
8	16																				
9				x	x		x				x		x								
10	16										x										
11				x	x			x			x		x								
12				x	x			x	x		x		x								
13				x	x			x			x		x								
14	16										x										
15	16										x										
16				x	x			x			x		x								

* SI = Supporting Information

Compound or structure number (with substituent / isomer identifier if needed)	IDENTITY												PURITY						COMPUTATIONAL DATA in SI*			
	Known compound [citation given]	IR	UV-Vis	1H NMR	13C NMR	Other NMR	MS	High resolution MS	X-ray [ORTEP and CIF in SI*]	Optical rotation/ORD/CD	er/dr [NMR or chromatography]	COSY	Copy of 1H/13C NMR in SI*	Quant. GC, HPLC, or electrophoresis	Elemental analysis				Cartesian coordinates or Z-matrix	# of imaginary frequencies	Total energy	* SI = Supporting Information
17a				x	x		x				x	x	x									
17b				x	x		x				x	x	x									
22				x	x			x	x		x		x									
23				x	x		x				x	x	x									
24				x	x			x	x		x		x									
25				x	x		x				x	x	x									
26				x	x		x				x	x	x									
33	16																					
36				x	x		x				x		x									
38				x	x		x				x		x									
38b				x	x		x		x		x		x									
41				x	x			x			x		x									
42	16																					
43				x	x		x		x		x		x									
44	16																					
45	16																					
46				x	x		x						x									

Compound or structure number (with substituent / isomer identifier if needed)	IDENTITY												PURITY						COMPUTATIONAL DATA in SI*		
	Known compound [citation given]	IR	UV-Vis	1H NMR	13C NMR	Other NMR	MS	High resolution MS	X-ray [ORTEP and CIF in SI*]	Optical rotation / ORD / CD	er / dr [NMR or chromatography]	COSY	Copy of 1H / 13C NMR in SI*	Quant. GC, HPLC, or electrophoresis	Elemental analysis				Cartesian coordinates or Z-matrix	# of imaginary frequencies	Total energy

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	Known compound [citation given]	IR	UV-Vis	1H NMR	13C NMR	Other NMR	MS	High resolution MS	X-ray [ORTEP and CIF in SI*]	Optical rotation / ORD / CD	er / dr [NMR or chromatography]	COSY	Copy of 1H / 13C NMR in SI*	Quant. GC, HPLC, or electrophoresis	Elemental analysis				Cartesian coordinates or Z-matrix	# of imaginary frequencies	Total energy

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	Known compound [citation given]	IR	UV-Vis	1H NMR	13C NMR	Other NMR	MS	High resolution MS	X-ray [ORTEP and CIF in SI*]	Optical rotation / ORD / CD	er / dr [NMR or chromatography]	COSY	Copy of 1H / 13C NMR in SI*	Quant. GC, HPLC, or electrophoresis	Elemental analysis				Cartesian coordinates or Z-matrix	# of imaginary frequencies	Total energy

* SI = Supporting Information

Asymmetric Synthesis of Dipropionate Stereotetrads.

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Supporting Information

GENERAL PROCEDURES

All reagents purchased were used as received. Tetrahydrofuran (THF) and diethyl ether were distilled from benzophenone ketyl. Benzene, toluene, and methylene chloride (CH_2Cl_2) were distilled from calcium hydride. Acetonitrile (CH_3CN) and methanol were spectra-grade. Sodium sulfate (Na_2SO_4) was anhydrous. All recrystallization, chromatographic, and workup solvents were reagent grade.

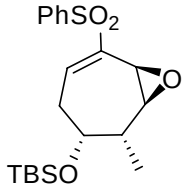
Progress of reactions was monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates (EM reagents, 0.25 mm). The TLC plates were visualized with a UV lamp (254 nm) and/or with TLC visualizing solutions activated with heat. The two commonly employed TLC visualizing solutions were: (i) *p*-anisaldehyde solution (1350mL absolute ethanol, 50mL concentrated H_2SO_4, 37mL *p*-anisaldehyde), and (ii) permanganate solution (weight percents of 1% $KMnO_4$ and 2% Na_2CO_3 in water).

^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Mercury 200 (200 MHz), Varian Inova 300 (300 MHz), Bruker ARX 400 (400 MHz) or Bruker DRX 500 (500 MHz). NMR spectra were determined in chloroform-d_1 ($CDCl_3$) or benzene-d_6 (C_6D_6) solution and are reported in parts per million (ppm) from the residual chloroform (7.27ppm and 77.0ppm) and benzene (7.16ppm and 128.39ppm) standard respectively. Peak multiplicities in ^{1}H-NMR spectra, when reported, are abbreviated as s (singlet), d (doublet), t (triplet), m (multiplet), and/or ap (apparent) and/or br (broad). Melting points were obtained on a MPA100 Optimelt automated melting point system and are uncorrected. Mass spectra were determined by the Purdue University campus wide mass spectrometry facility.

Full characterization of compounds **8**, **14**, **10**, **15**, **44** and **45** in addition to the crystal structure of a derivative of **11** are provided in the supplementary material of the paper cited in footnote 16 of the main text.

EXPERIMENTALS

Preparation of Epoxide **8**[1]:



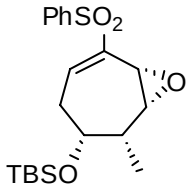
8

Water (8.8 mL) was added to a stirred clear colorless solution of dienyl sulfone **6** (1.014 g, 2.64 mmol) in acetone (17 mL) at room temperature. $NaHCO_3$ (2 g, 0.024 mol) was added to the above mixture to give a fine white suspension. OXONE® (3.24 g, 5.3

[1] For ^{1}H and ^{13}C NMR spectra and HR MS, see reference 16 in the main text.

mmol) was added in 3 portions at five minute intervals with vigorous stirring.[2] After 90 minutes, the reaction was judged complete by TLC and the mixture was transferred to a separatory funnel, followed by addition of 40 mL water and was extracted with ether (2 × 60 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated via rotary evaporation and dried under vacuum over night to afford 1.04 g (100%) of **8**. The ^{1}H NMR shows that **8** is sufficiently pure and needs no further purification. If needed, **8** can be crystallized from ether (1g/ 2 mL) at -10 ^{o}C for 12 hours to give (yield= 64%) of combined first and second crops. mp= 83.8-84.5 ^{o}C.

Preparation of Epoxide **9**:



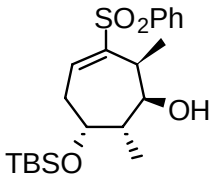
9

To a vigorously stirred mixture of dienyl sulfone **6** (1.05g, 2.64 mmol), Na_2CO_3 (1.75 g, 17 mmol) and urea-hydrogen peroxide complex (2.5 g, 26 mmol) in methylene chloride (13.2 mL) at 10 ^{o}C was slowly added $(CF_3CO)_2O$ (0.93 mL, 6.6 mmol).[3] After 1 minute the reaction was cooled to 0 ^{o}C. After 1.5 hours the reaction was judged complete by TLC (Hexanes: EtOAc= 2:1) and was transferred to a separatory funnel. Water (30 mL) was added and the mixture was extracted with ether (2 ×30 mL). The combined organic layers were dried over Na_2SO_4, and concentrated via rotary evaporation to give a white solid that was crystallized from MeOH (4 mL) to afford 776 mg (71%) of combined first and second crops of **9**; mp= 146.5-148 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92 (m, 2H),

[2] The reaction becomes a heavy white suspension after OXONE® addition is complete.
[3] After addition of $(CF_3CO)_2O$ the suspended solids in the reaction mixture lump together into big masses and hinder stirring. Hence, very efficient stirring is required, preferably with a mechanical stirrer.

7.64 (m, 1H), 7.55 (m, 2H), 7.11 (t, *J* = 3.9 Hz, 1H), 4.02 (m, 1H), 3.68 (d, J = 4.2 Hz, 1H), 3.36 (dd, *J* = 3.9, 6.9 Hz, 1H), 2.57 (m, 2H), 2.45 (m, 1H), 0.86 (s, 9H), 0.76 (d, *J* = 7.5 Hz, 3H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.5, 139.7, 138.0, 133.5, 129.1, 128.1, 68.7, 56.9, 49.7, 37.7, 35.9, 25.7, 17.9, 9.0, -4.8, -5.0. HRMS (CI) calculated for $C_{20}H_{31}O_4SSi$ (M+H) 395.1712, found 395.1711.

Preparation of Tetrad **10**[4,5]:

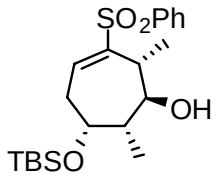


10

Toluene (23 mL) was added to a mixture of 3,5-dimethylpyrazole (547 mg, 5.7 mmol) and epoxide **8** (1.87 g, 4.74 mmol) and stirred at 70 ^{o}C under Ar for 3 hours.[6] The reaction was cooled to room temperature over 1 hour, followed by dropwise addition of MeMgBr (10.2 mL, 14 mmol, 1.4M in Tol: THF=3:1) over 5 minutes.[7] After stirring for 45 minutes at room temperature the reaction was quenched by the addition of cold H_2O (5 mL). The reaction mixture was then transferred to a separatory funnel containing 5% HCl (30 mL) and was extracted with ether (2 ×30 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, concentrated via rotary evaporation, and held at high vacuum for 24 hours to give 1.95 g (100 %) of **10** as orange oil. No further purification was necessary.

[4] This is an improved procedure of the one reported in reference 16 of the main text.
[5] Full characterization data of **10**, including X-ray of a derivative is provided in the reference in footnote 16 of the main text.
[6] After toluene addition the reaction became a clear light yellow solution.
[7] During MeMgBr addition bubbles were seen in the reaction mixture, and the reaction became yellowish orange by the end of its addition.

Preparation of Tetrad **11**[8]:

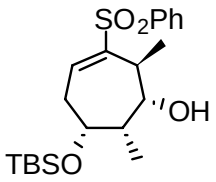


11

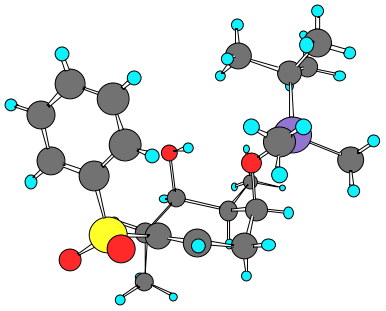
MeMgBr (0.362 mL, 0.5 mmol, 1.4M in Tol: THF=3:1) was added to a stirred colorless solution of MeLi (0.317mL, 0.5mmol, 3M in $(EtO)_2CH_2$) in ether (1 mL) at room temperature under Ar, and stirred for 5 minutes. The resultant turbid white solution was cooled to -45 ^oC and then cannulated to a solution of epoxide **8** (99 mg, 0.253 mmol) in ether (1 mL) with suspended CuI at -45 ^oC under Ar, to instantaneously give a bright yellow suspension. The above suspension was stirred for 45 minutes and then quenched with i-PrOH (0.5 mL) and saturated aqueous NH_4Cl (3 mL). The reaction mixture was transferred to a separatory funnel, brine (15 mL) was added and the mixture is extracted with ether (2 ×15 mL). The combined organic layers were dried over Na_2SO_4, concentrated via rotary evaporation to give a light yellow oil that was purified by flash column chromatography (3.5% EtOAc in DCM) to afford 85 mg (82%) of **11** as a colorless oil; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, *J*= 7.6 Hz, 2H), 7.60 (t, *J*= 7.2 Hz 1H), 7.52 (t, *J*= 7.6 Hz, 2H), 7.15 (dd, *J* = 5.2, 9.2 Hz, 1H), 4.04 (dt, *J*= 3.6, 10.4 Hz, 1H), 3.72 (t, *J*= 5.6 Hz, 1H), 2.80 (m, 1H), 2.63 (m, 1H), 2.36 (m, 1H), 2.13 (m, 1H), 1.72 (bs, 1H), 1.00 (d, *J* = 7.6 Hz, 3H), 0.86 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.1, 138.7, 136.6, 133.3, 129.1, 128.3, 75.0, 67.5, 44.5, 40.9, 31.9, 25.7, 17.9, 17.1, 12.0, -4.8, -5.0. HRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M-H) 409.1869, found 409.1865.

[8] Relative and absolute stereochemistries of **11** were confirmed via X-ray analysis of its diTBS derivative; See reference in footnote 16 of the main text.

Preparation of Tetrad **12**:



12



Enantiomer **12**

H_2O (5.5 μL, 0.3 mmol) was added to a stirred colorless solution of epoxide **9**[9] (115.5 mg, 0.29 mmol) in 1,2-dichloroethane (1.5 mL) at room temperature under Ar. A solution of Me_3Al (0.6 mL, 0.1.2 mmol, 2M in Hexane) was added dropwise to the above mixture.[10] The above mixture was stirred for 20 hours[11] at room temperature and was then quenched by transferring to a separatory funnel containing 5% HCl (30 mL). The quenched reaction mixture was extracted with $CHCl_3$ (2 ×30 mL). The combined organic layers were dried over Na_2SO_4, concentrated via rotary evaporation to give a white solid that was purified by flash column chromatography (3.5% EtOAc in DCM) to afford 105 mg (88 %) of **12** as white crystals (mp=162.8-165.4 ^oC); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.86 (m, 2H), 7.57 (tt, *J*= 1.2, 6.3 Hz, 1H), 7.46 (tt, *J*= 1.8, 7.8 Hz, 2H), 7.13 (dd, *J*= 3.6, 9.3 Hz, 1H), 3.97 (bd, J = 6 Hz, 1H), 3.53 (d, *J*= 9.3, 1H), 3.43 (bt, 1H), 3.08 (m, 1H), 2.78 (m, 1H), 2.46 (ddd, *J*= 1.2, 3.6, 15.9 Hz, 1H), 1.90 (qt, *J*= 1.5, 6.9 Hz, 1H), 1.15 (d, J = 7.8 Hz, 3H), 1.14 (d, J = 7.2 Hz, 3H), 0.83 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.4, 138.7, 136.4, 133.1, 128.7, 128.6, 75.3, 73.9, 40.1, 37.5, 34.5, 25.6, 19.1, 17.7, 14.8, -4.7, -5.3; HRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411.2025, found 411.2030. Relative stereochemistry was confirmed via X-ray analysis of the enantiomer of **12** (See attached cif file).

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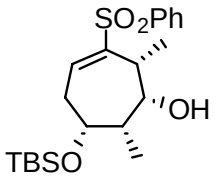
[9] Epoxide **9** was azeotropically dried with toluene before use.
[10] During Me_3Al addition bubbles and white fumes were generated. Five minutes after the addition was complete the reaction was a clear colorless solution.
[11] After ca. 3 hours the reaction became a white suspension.

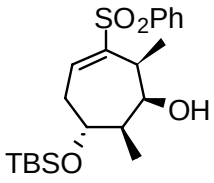
Preparation of Tetrad **13**:



13

Dichloromethane (2.5 mL) was added to a mixture of tetrad **11** (52 mg, 0.13 mmol) and Dess-Martin periodinane (75 mg, 0.18 mmol) and stirred at room temperature under Ar for 3 hours. The above clear colorless solution was cooled to -72 ^{o}C, followed by dropwise addition of DIBAL (0.78 mL, 0.78 mmol) and stirred for 1 hour then quenched with 5% HCl (15 mL). The quenched reaction mixture was transferred to a separatory funnel and extracted with $CHCl_3$ (2 ×15 mL). The combined organic layers were dried over Na_2SO_4, concentrated via rotary evaporation to give a white solid that was purified by flash column chromatography (3.5% EtOAc in CH_2Cl_2) to afford 50 mg (96%) of **13** as a colorless oil.; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (m, 2H), 7.59 (bt, *J*= 7.5 Hz, 1H), 7.50 (bt, *J*= 8 Hz, 2H), 7.29 (t, *J*= 7 Hz, 1H), 3.93 (d, *J* = 7.5 Hz, 1H), 3.47 (s, 1H), 2.87 (m, 2H), 2.41 (dd, *J*= 6, 14 Hz, 1H), 1.86 (bs, 1H), 1.24 (bd, J = 6.5 Hz, 3H), 1.12 (d, J = 7.5 Hz, 3H), 0.93 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 140.2, 138.7, 133.0, 128.7, 128.2, 71.4, 44.9, 40.6, 33.7, 25.7, 17.8, 16.6, -4.7, -5.2; HRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411.2025, found 411.2017. Relative and absolute stereochemistries were confirmed via X-ray analysis of a derivative; **43**, vide infra.

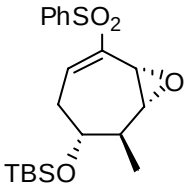
Preparation of Tetrad **15**[12]:



15

Toluene (2.9 mL) was added to a mixture of 3,5-dimethylpyrazole (62 mg, 0.63 mmol) and epoxide **14** (224 mg, 0.57 mmol) and the mixture was stirred under Ar at 65 ^{o}C for 3 hours.[13] The reaction was cooled to 36 ^{o}C over 1 hour, followed by addition of MeMgBr (1 mL, 1.42 mmol, 1.4M in Tol: THF=3:1).[14,15] After stirring for 1 hour, the reaction was quenched by the addition of i-PrOH (2 mL). The reaction mixture was then transferred to a separatory funnel containing 5% HCl (30 mL) and was extracted with ether (2 ×30 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and concentrated via rotary evaporation to give 226 mg (99 %) of **15** as yellow oil. No further purification was necessary.

Preparation of Epoxide **16**:

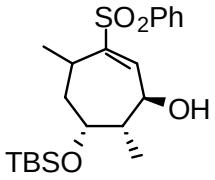


16

[12] Full characterization data of **15**, including X-ray of a derivative is provided in the reference in footnote 16 of the main text.
[13] After toluene addition the reaction became a clear light yellow solution.
[14] During MeMgBr addition bubbles were seen in the reaction mixture, and the reaction became yellowish orange by the end of its addition.
[15] It is important not to use excess of MeMgBr to avoid addition of a third methyl group to the vinylsulfone of **15**. Typically, 2.2-2.4 equivalents are used.

To a vigorously stirred mixture of dienyl sulfone **7** (1.37g, 3.62 mmol), Na_2CO_3 (2.4 g, 20 mmol) and urea-hydrogen peroxide complex (3.4 g, 36.2 mmol) in methylene chloride (18 mL) at 10 ^oC was slowly added $(CF_3CO)_2O$ (0.47 mL, 3.3 mmol). After 1 minute the reaction was cooled to 3 ^oC and run for 1.5 hours. Water (30 mL) was added and the mixture was extracted with ether (2 ×30 mL). The combined organic layers were dried over Na_2SO_4, concentrated via rotary evaporation and dried under vacuum over night to afford 1.43 g (100%) of **16** as a white solid. The ^1H NMR shows that **16** is sufficiently pure and needs no further purification. If needed, **16** can be crystallized from Et_2O (1.5 + 0.5 mL) at -20 ^oC to afford 1.077g (75%) of combined first and second crops of **16**; mp= 98.0-98.8 ^oC; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.92 (m, 2H), 7.63 (tt, *J*= 1.2, 6 Hz 1H), 7.54 (m, 2H), 7.06 (t, *J* = 6 Hz, 1H), 3.68 (m, 2H), 2.84 (dd, *J*= 4.2, 7.2 Hz, 1H), 2.78 (td, *J*= 1.2, 5.7 Hz 1H), 2.46 (dt, *J*= 6.3, 18 Hz, 1H), 1.34 (m, 1H), 1.11 (d, *J* = 6.6 Hz, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.2, 139.8, 138.7, 133.4, 129.0, 128.2, 69.3, 58.7, 49.3, 41.5, 38.8, 25.6, 17.8, 16.4, -4.6, -4.9. HRMS (CI) calculated for $C_{20}H_{31}O_4SSi$ (M+H) 395.1712, found 395.1718.

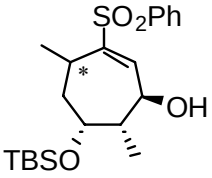
Characterization of **17**:



17a

17a was isolated as a side product in the preparation of tetrad **11** ; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.86 (m, 2H), 7.63 (tt, *J*= 1.2, 6.9 Hz, 1H), 7.54 (m, 2H), 7.23 (d, *J* = 6.6 Hz, 1H), 4.5 (m, 1H), 4.35 (dt, *J*= 3, 10.8 Hz, 1H), 2.76 (m, 1H), 2.22 (m, 1H), 2.08 (d, *J*=

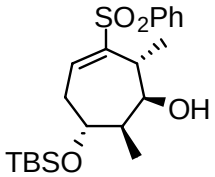
3.9Hz, 1H), 2.40 (m, 2H), 1.23 (d, *J*= 7.2 Hz, 3H), 0.86 (s, 9H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.1, 141.6, 139.3, 133.3, 129.2, 128.0, 68.6, 67.3, 42.8, 37.5, 29.7, 25.8, 19.7, 18.0, 11.1, -4.7, -4.9. LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411.



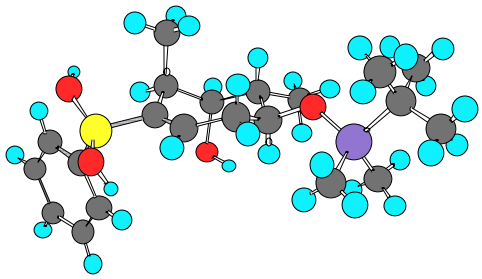
17b

17b was isolated as a side product in the preparation of tetrad **11**, and it is epimeric to **17a** ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (t, *J*= 7.6 Hz, 2H), 7.60 (t, *J*= 6.8 Hz, 1H), 7.53 (t, *J*= 8 Hz, 2H), 7.17 (d, *J* = 3.6 Hz, 1H), 4.7 (m, 1H), 3.82 (bt, *J*= 3.2 Hz, 1H), 2.74 (m, 1H), 2.22 (m, 1H), 2.14 (d, *J*= 5.2 Hz, 1H), 1.75 (m, 2H), 1.46 (ddd, *J*= 1.6, 5.2, 14.8 Hz, 1H), 1.11 (d, *J*= 8 Hz, 3H), 1.06 (d, *J* = 8 Hz, 3H), 0.85 (s, 9H), -0.03 (s, 3H), -0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.6, 143.5, 139.2, 133.2, 129.1, 128.2, 73.4, 69.0, 42.7, 38.2, 31.2, 25.9, 20.1, 18.0, 15.1, -3.8, -5.3. LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411.

Preparation of Tetrad **22**:



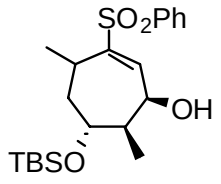
22



Enantiomer **22**

MeLi (0.338 mL, 1 mmol, 3M in $(EtO)_2CH_2$) was added to a stirred suspension of CuI (96 mg, 0.5 mmol) in ether (1.5 mL) at 0 ^oC under Ar, and stirred for 15 minutes to give a clear colorless solution and was then cooled to -70 ^oC. A solution of epoxide **14** (87.5 mg, 0.22 mmol) in ether (1.5 mL) was cannulated to the above solution to instantaneously give a bright yellow suspension. The above suspension was stirred for 45 minutes and then quenched with i-PrOH (0.5 mL). The reaction mixture was transferred to a separatory funnel, brine (5 mL), H_2O (5 mL), and aqueous NH_3 (2 mL) were added and the mixture was extracted with ether (2 ×15 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4, concentrated via rotary evaporation to give a light yellow oil that was purified by flash column chromatography (3.5% EtOAc in DCM) to afford 65 mg (62%) of **22** as white crystals (mp=170.9-172.5 ^oC); ^1H NMR (C_6D_6, 300 MHz) δ 7.85 (m, 2H), 7.29 (dd, 4.8, 9.3 Hz, 1H), 6.97 (m, 3H), 3.73 (td, J = 3.6, 9.9 Hz, 1H), 3.55 (t, 4.2 Hz, 1H), 2.88 (m, 1H), 2.29 (m, 2H), 1.81 (m, 2H), 1.18 (d, J = 6.9 Hz, 3H), 0.95 (s, 9H), 0.63 (d, J = 6.9 Hz, 3H) 0.02 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (C_6D_6, 75 MHz) δ 146.4, 140.0, 135.9, 132.9, 129.0, 128.8, 75.9, 68.2, 43.2, 39.4, 37.0, 26.0, 18.6, 18.1, 14.3, -4.4, -4.6.HRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411.2025, found 411.2029. Relative stereochemistry was confirmed via X-ray analysis of the enantiomer of **22** (See attached cif file).

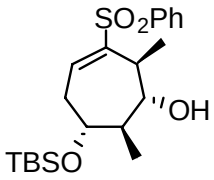
Characterization of **23**:



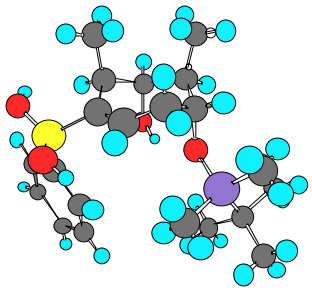
23

23 was isolated as a side product in the preparation of tetrad **22** ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (m, 2H), 7.62 (tt, *J*= 2.4, 7.2 Hz, 1H), 7.54 (m, 2H), 7.02 (dt, *J* = 1.6, 3.6 Hz, 1H), 5.26 (d, *J*= 3.2 Hz,1H), 3.78 (bs, 1H), 2.75 (m, 1H), 2.04 (m, 2H), 1.54 (m, 2H), 1.12 (d, *J*= 7.2 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.86 (s, 9H), 0.02 (s, 3H), -0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.1, 143.2, 139.2, 133.3, 129.1, 128.2, 74.2, 68.0, 44.8, 32.6, 31.7, 25.7, 19.6, 17.9, 11.0, -4.9, -5.2. LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411.

Preparation of Tetrad **24**:



24

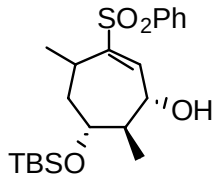


24

MeLi (0.314 mL, 0.94 mmol, 3M in $(EtO)_2CH_2$) was added to a stirred suspension of CuI (90 mg, 0.47 mmol) in ether (0.5 mL) at 0 ^{o}C under Ar, and stirred for 15 minutes to give a clear colorless solution and was then cooled to -22 ^{o}C. A solution of epoxide **16** (57 mg, 0.144 mmol) in ether (1 mL) was cannulated to the above solution to instantaneously give a bright yellow suspension. The above suspension was stirred for 45 minutes during which it warmed up to -10 ^{o}C and was then quenched with aqueous NH_4Cl (2 mL). The reaction mixture was transferred to a separatory funnel, brine (5 mL), H_2O (5 mL), and aqueous NH_3 (2 mL) were added and the mixture is extracted with ether (2 ×15 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4, concentrated via rotary evaporation to give a white solid that was purified by flash column chromatography (3.5% EtOAc in DCM) to afford 42 mg (71%) of **22** as

white crystals (mp=127.9-129.4 ^{o}C); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (m, 2H), 7.54 (m, 1H), 7.45 (t, *J*= 7.5 Hz, 2H), 7.11(dd, *J*= 5.1, 8.7 Hz, 1H), 3.88 (bt, J = 4.2 Hz, 1H), 3.52 (bs, 1H), 3.38 (bs, 1H), 3.00 (m, 1H), 2.70 (m, 2H), 2.25 (m, 1H), 1.24 (d, J = 7.5 Hz, 3H), 1.00 (d, J = 7.5 Hz, 3H), 0.82 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.3, 138.9, 137.6, 133.0, 128.7, 128.2, 75.6, 73.5, 44.9, 41.7, 30.2, 25.5, 17.6, 16.3, -5.1, -5.4; HRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411.2025, found 411.2018. Relative and absolute stereochemistries were confirmed via X-ray analysis (See attached cif file).

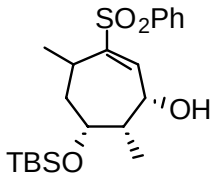
Characterization of **25**:



25

25 was isolated as a side product in the preparation of tetrad **24** ; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (m, 2H), 7.62 (m, 1H), 7.54 (m, 2H), 7.14 (d, *J* = 3.6 Hz, 1H), 4.23 (m,1H), 3.58 (m, 1H), 2.79 (m, 1H), 2.62 (d, *J*= 5.4 Hz, 1H), 1.75 (ddd, *J*= 3,5.4,14.1 Hz, 1H), 1.63 (m, 1H), 1.30 (m, 1H), 1.24 (d, *J*= 6.3 Hz, 3H), 1.02 (d, *J* = 7.8 Hz, 3H), 0.85 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.7, 144.0, 138.9, 133.3, 129.2, 128.1, 71.6, 70.8, 46.7, 41.8, 29.5, 25.8, 18.0, 17.0, 15.0, -4.3, -4.6. LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411.

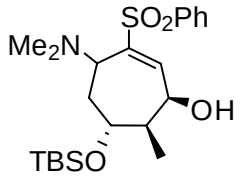
Characterization of **26**:



26

26 was isolated as a side product in the preparation of tetrad **12** ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (m, 2H), 7.63 (tt, *J*= 2.4, 7.2 Hz, 1H), 7.55 (m, 2H), 7.02 (bd, *J* = 1.6 Hz, 1H), 4.70 (m, 1H), 4.04 (m, 1H), 2.76 (m, 1H), 2.58 (d, *J*= 4.4 Hz, 1H), 2.20 (m, 1H), 1.36 (q, *J*= 4 Hz, 1H), 1.05 (d, *J*= 7.6 Hz, 3H), 0.83 (s, 9H), 0.82 (d, *J* = 6 Hz, 3H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.3, 142.3, 138.8, 133.4, 129.2, 128.1, 70.0, 68.4, 45.4, 34.3, 29.5, 25.7, 17.9, 16.7, 5.6, -4.9. LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411.

Preparation of dimethylamine adduct **36**:

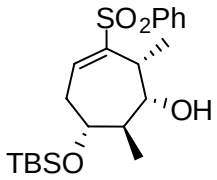


36

To a stirred solution of epoxide **16** (299 mg, 0.76 mmol) in toluene (3.8 mL) at room temperature, was added dimethylamine (190 μL, 1.51 mmol, 40% in water). The above mixture was stirred at room temperature for 45 minutes and then concentrated via rotary evaporation and azeotropically dried with toluene (3×5 mL) to give 330 mg of **36** as a white powder (mp= 149-151 ^{o}C). The crude ^{1}H NMR showed high purity and no purification was necessary.; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (m, 2H), δ 7.60 (m,1H), δ 7.54 (m, 2H), δ 7.44 (dd, *J* = 1.2, 7.8 Hz, 1H), δ 7.36 (bs, 1H), δ 4.23 (dd, *J* = 4.2, 7.8

Hz, 1H), δ 3.52 (dd, *J* = 4.8, 9 Hz, 1H), δ 3.13 (t, *J* = 4.2 Hz, 1H), δ 2.20 (s, 6H), δ 2.13 (m, 2H), δ 1.42 (td, *J* = 3.3, 15 Hz, 1H), δ 0.84 (s, 9H), δ 0.75 (d, *J* = 6.9 Hz, 3H), δ -0.046 (s, 3H), δ -0.099 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.7, 145.0, 139.5, 133.7, 129.4, 128.6, 75.3, 70.8, 61.0, 44.1, 31.9, 25.9, 18.0, 16.4, -4.6, -5.1**;** LRMS (ESI) calculated for $C_{22}H_{38}NO_4SSi$ (M+H) 440, found 440.

Preparation of Tetrad **38**:

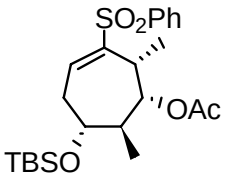


38

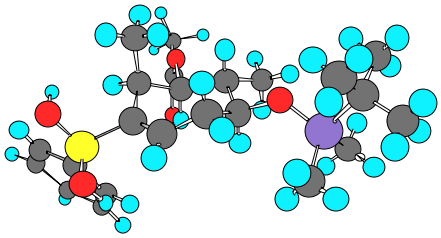
To a stirred solution of **36** (330 mg, 0.75 mmol) in toluene (7.5 mL) under Ar at 0 ^{o}C, was added MeMgBr (1.60 mL, 2.27 mmol, 1.4M in Tol: THF=3:1) dropwise over 5 minutes. The solution was stirred at 0 ^{o}C for 45 min and then warmed up to room temperature. A second portion of MeMgBr (0.80 ml, 1.13 mmol) was added to the solution, followed by stirring at room temperature for 15 minutes and was quenched with 5% HCl (4 mL). The aqueous phase was extracted with diethyl ether (2×4 mL). The combined organic phases were washed with brine (4 mL), dried over Na_2SO_4 and concentrated via rotary evaporation to give a pale yellow oil that was purified by flash chromatography (20% EtOAc in hexanes) to afford 233 mg (75 %) of **38** as a colorless oil.; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85 (m, 2H), δ 7.60 (m,1H), δ 7.54 (m, 2H), δ 7.11 (dd, *J* = 5.7, 8.1 Hz, 1H), δ 3.27 (m, 2H), δ 2.86 (m, 1H), δ 2.54 (m, 2H), δ 1.96 (m, 1H), δ 1.89 (d, *J* = 5.4 Hz, 1H), δ 1.06 (d, *J* = 6.6 Hz, 3H), δ 0.92 (d, *J* = 6.9 Hz, 3H), δ 0.89 (s, 9H), δ 0.077 (s, 3H), δ 0.055 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.9, 139.0,

136.6, 133.3, 129.2, 128.2, 74.1, 72.3, 45.2, 39.1, 35.4, 25.8, 18.0, 16.2, 10.8, -4.5, -4.7; LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411.

Preparation of Tetrad **38b**:



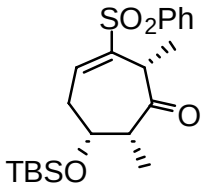
38b



Enantiomer **38b**

To a stirred solution of tetrad **38** (222 mg, 0.54 mmol) in dichloromethane (5.5 mL) under Ar, was added pyridine (131 µL, 1.62 mmol), 4-dimethylaminopyridine (6.5 mg, 0.05 mmol) and acetic anhydride (103 µL, 1.08 mmol) dropwise at room temperature. The solution was stirred for 1.5 hours then quenched with 5% HCl (5 mL). The aqueous phase was transferred to a separatory funnel and extracted wit ether (2× 4 mL). The combined organic phases were washed with brine (5 mL)**,** dried over Na_2SO_4 and concentrated via rotary evaporation to afford 241 mg of **38b** (98 %) as a white solid (mp= 113.4-115.2 ^{o}C). The crude ^{1}H NMR showed high purity and no purification was necessary.; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.85 (m, 2H), δ 7.63 (m, 1H), δ 7.56 (m, 2H), δ 7.12 (dd, *J* = 5.4, 8.1 Hz, 1H), δ 4.35 (dd, *J* = 3.3, 11.1 Hz, 1H), δ 3.27 (dt, *J* = 3.6, 8.7 Hz, 1H), δ 2.82 (m, 1H), δ 2.57 (m, 2H), δ 2.14 (m, 1H), δ 1.98 (s, 3H), δ 1.13 (d, *J* = 7.5 Hz, 3H), δ 0.89 (d, *J* = 5.4 Hz, 3H), δ 0.88 (s, 9H), δ 0.08 (s, 3H), δ 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.4, 145.5, 139.0, 136.9, 133.3, 129.2, 128.0, 74.7, 72.3, 43.0, 36.6, 35.5, 25.8, 20.9, 18.0, 15.8, 11.6, -4.5, -4.8; LRMS (CI) calculated for $C_{23}H_{36}O_5SSi$ (M+H) 453, found 453. Relative stereochemistry was confirmed via X-ray analysis of the enantiomer of **38b** (See attached cif file).

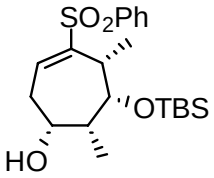
Preparation of **41**(Swern Oxidation):



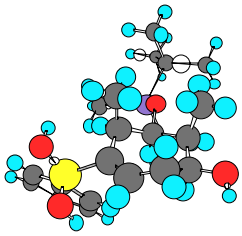
41

To a stirred clear colorless solution of oxalyl chloride (30 μL, 0.35 mmol) in dichloromethane (0.8 mL) under Ar at -70 ^{o}C was dropwise added DMSO (51 μL, 0.72 mmol). After stirring the above solution for 15 minutes, a solution of tetrad **11** (44 mg, 0.11 mmol) in dichloromethane (1.5 mL) at -70 ^{o}C was cannulated to it. The above mixture was allowed to reach -60 ^{o}C over 30 minutes and then Et_3N was dropwise added. The reaction was then allowed to reach room temperature over 2 hours. The reaction mixture was transferred to a separatory funnel followed by addition of H_2O (15 mL) and extracted with Hexane (2×15 mL). The combined organic extracts were washed with brine (15 mL), dried over Na_2SO_4 and concentrated by rotary evaporation to give **41** as a colorless oil (41 mg, 93%) that required no further purification. ^{1}H NMR ($CDCl_3$,400 MHz) δ 7.88 (m, 2H), 7.64 (t, *J*= 6 Hz, 1H), 7.57 (t, *J*= 8 Hz, 2H), 7.24 (t, *J*= 7.2 Hz, 1H), 4.15 (m, 1H), 3.17 (q, J= 7.2 Hz, 1H), 2.99 (m, 1H), 2.67 (m, 1H), 2.37 (m 1H), 1.12 (d, *J*= 7.2 Hz, 3H), 0.96 (d, J= 6.8 Hz, 3H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 208.7, 146.4, 139.1, 136.6, 133.8, 129.5, 128.3, 74.1, 47.4, 46.9, 35.6, 25.7, 18.0, 14.3, 11.9, -4.4, -4.9; HRMS (CI) calculated for $C_{16}H_{22}O_4SSi$ (M-Bu^t) 351.1086, found 351.1093.

Preparation of **43**:



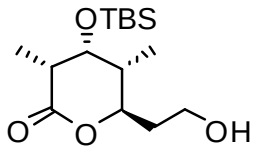
43



Enantiomer **43**

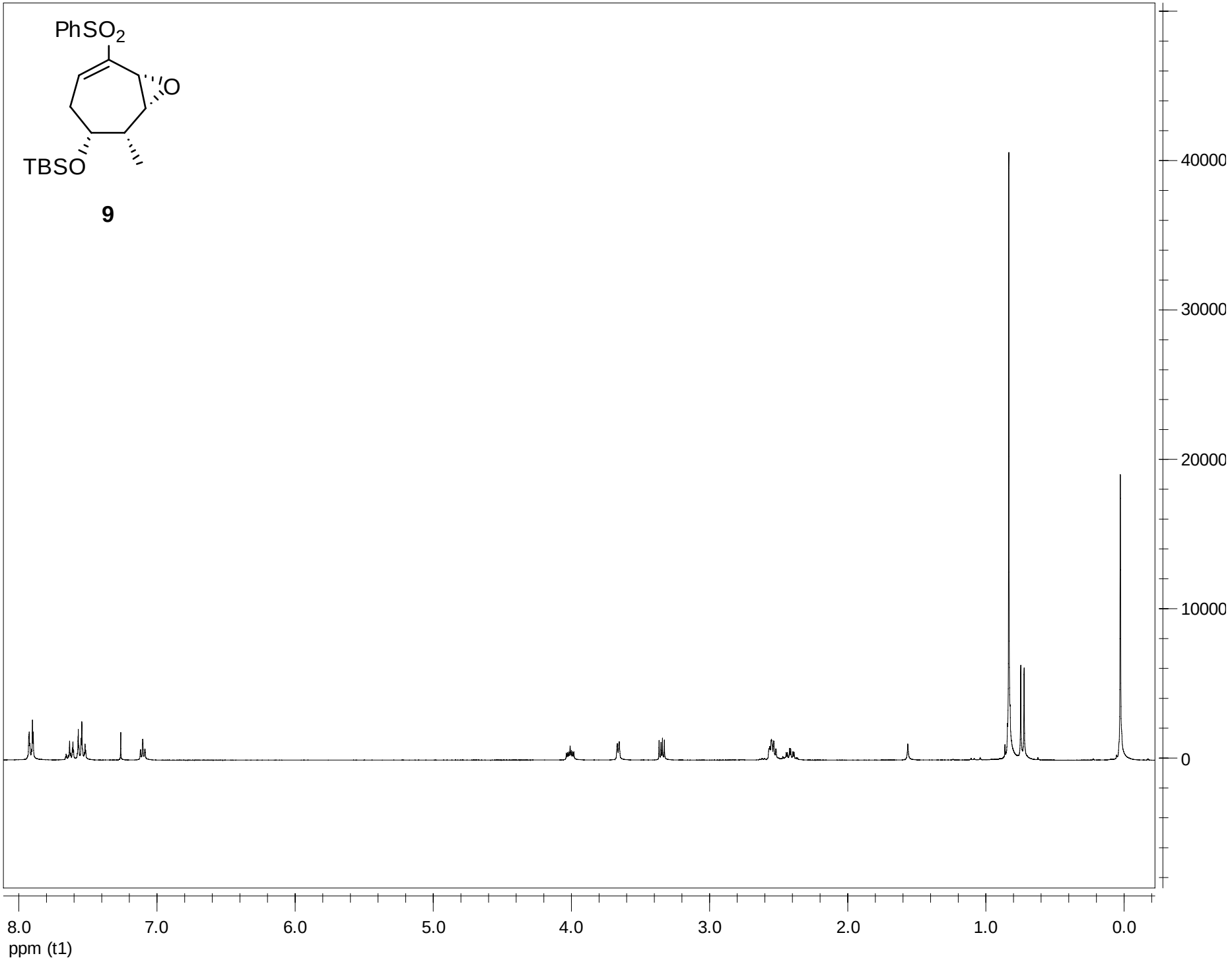
To a stirred clear colorless solution of tetrad **13** (124 mg, 0.3 mmol) and 2,6-lutidine (123 μL, 1.1 mmol) in dichloromethane (3 mL) at room temperature under Ar was added TBSOTf (172 μL, 0.75 mmol). The above solution was stirred for 1 hour then quenched with i-PrOH (1 mL). The quenched reaction mixture was concentrated to yellow oil by rotary evaporation, and then dissolved in THF (5 mL), 6M HCl (3mL) was added and the mixture stirred at room temperature for 40 minutes. The reaction was then transferred to a separatory funnel, H_2O (15 mL) was added and extracted with ether (2×15 mL).The combined organic layers were dried over Na_2SO_4, concentrated via rotary evaporation to give a colorless oil that was purified by flash column chromatography (40% EtOAc in Hexanes) to afford 86 mg (69 %) of **43** as a colorless oil which turned into white crystals upon slow evaporation from MeOH (mp= 105-106.9 ^oC); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, *J*= 4 Hz, 2H), 7.60 (t, *J*= 8 Hz, 1H), 7.52 (bt, *J*= 8 Hz, 2H), 7.17 (dd, *J*= 4,12 Hz, 1H), 3.77 (bd, *J* = 12 Hz, 1H), 3.41 (t, *J*= 4Hz, 1H), 2.77 (m, 1H), 2.56 (m, 1H), 2.31 (m, 3H), 1.09 (d, J = 8 Hz, 3H), 1.05 (d, J = 8 Hz, 3H), 0.80 (s, 9H), -0.17 (s, 3H), -0.25 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.5, 138.8, 137.1, 133.3, 129.2, 128.0, 71.1, 69.4, 47.4, 40.4, 29.9, 25.5, 17.7, 14.9, 7.4, -5.36, -5.38; LRMS (CI) calculated for $C_{21}H_{35}O_4SSi$ (M+H) 411, found 411. Relative stereochemistry was confirmed via X-ray analysis of the enantiomer of **43 (**See attached cif file).

Preparation of **46**:



46

To a stirred clear colorless solution of tetrad **13b** (43 mg, 0.1 mmol) in dichloromethane (12 mL) was added $NaHCO_3$ (26 mg, 0.3 mmol) followed by cooling to -30 ^oC and bubbling of O_3 for 40 minutes. O_2 was then bubbled for 15 minutes followed by addition of Me_2S (0.15 mL, 2 mmol). The above mixture was then stirred at room temperature for 50 minutes followed by addition of BH_3.t-$BuNH_2$ (27 mg, 0.31 mmol), stirring for 15 minutes and was then quenched by addition of 5% HCl (15 mL). The quenched reaction mixture was transferred to a separatory funnel and extracted with Et_2O (2× 20 mL). The combined organic extracts were washed with brine (20 mL), dried with Na_2SO_4 and concentrated by rotary evaporation to give colorless oil. The crude oil was purified by flash column chromatography (Hexane: EtOAc =1:2) to give 27 mg (84%) of **46** as white crystals (mp= 110.8-113.6 ^oC) ^1H NMR ($CDCl_3$, 600 MHz) δ 4.53 (m, 1H), 3.82 (m, 2H), 3.22 (s, 1H), 2.41 (bs, 1H), 2.07 (qd, J= 3, 7.2 Hz, 1H), 1.61 (m, 1H), 1.43 (m 1H), 1.29 (d, *J*= 7.2 Hz, 3H), 0.99 (s, 9H), 0.74 (d, *J* = 6.6 Hz, 3H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.3, 79.9, 74.4, 59.2, 43.7, 40.0, 36.0, 26.0, 18.3, 15.2, 13.9, -3.5, -3.6; LRMS (CI) calculated for $C_{15}H_{31}O_4Si$ (M+H) 303, found 303.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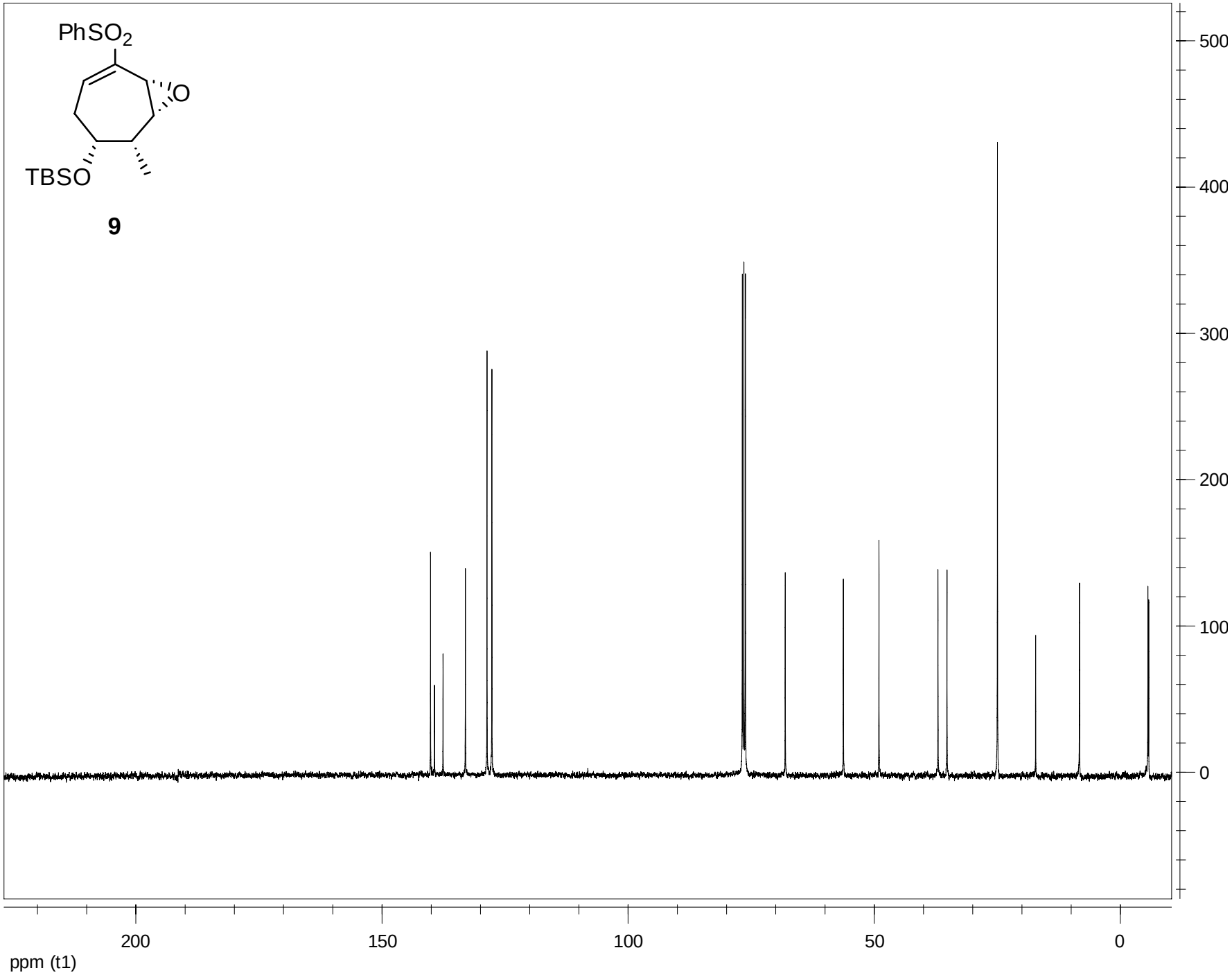
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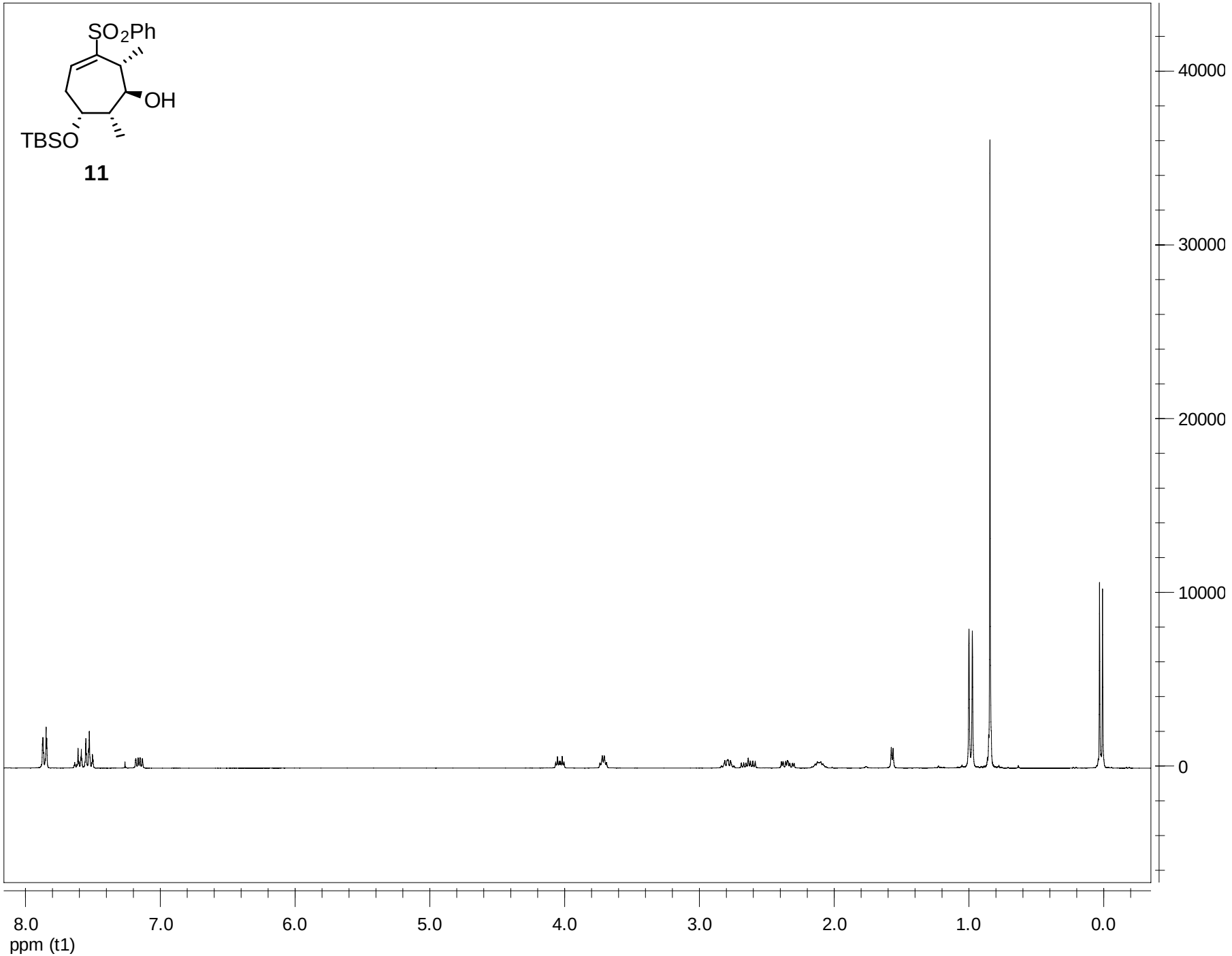
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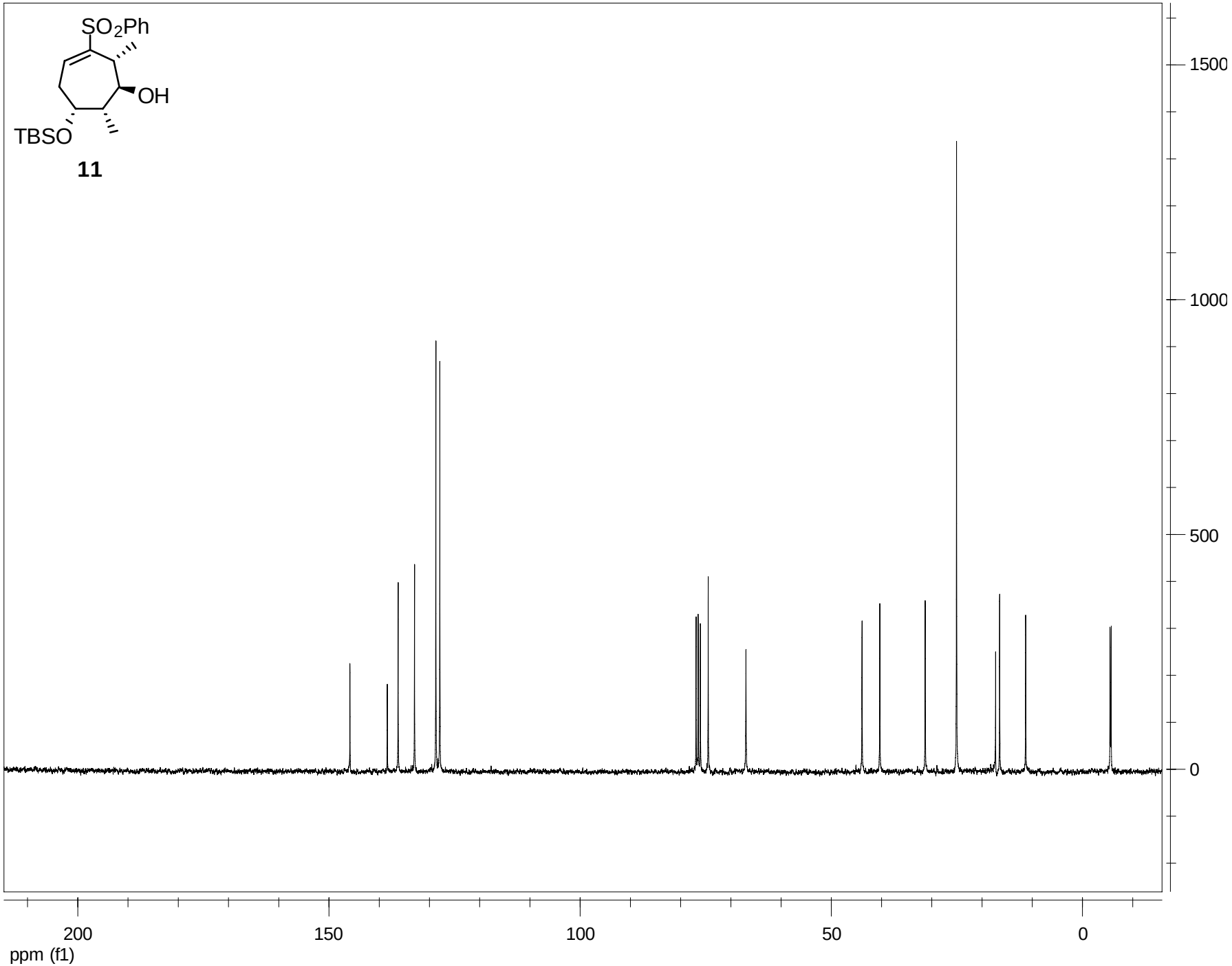
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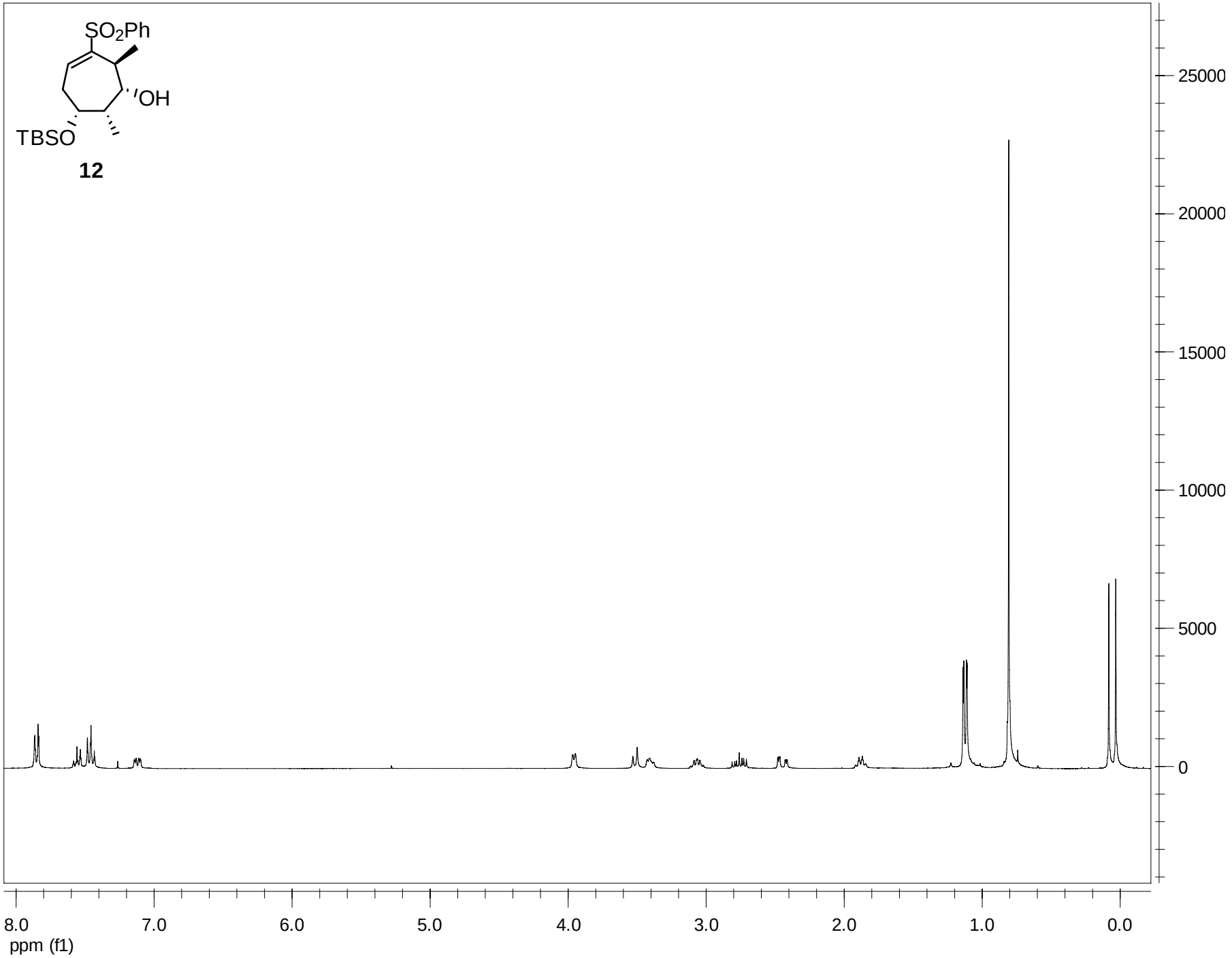
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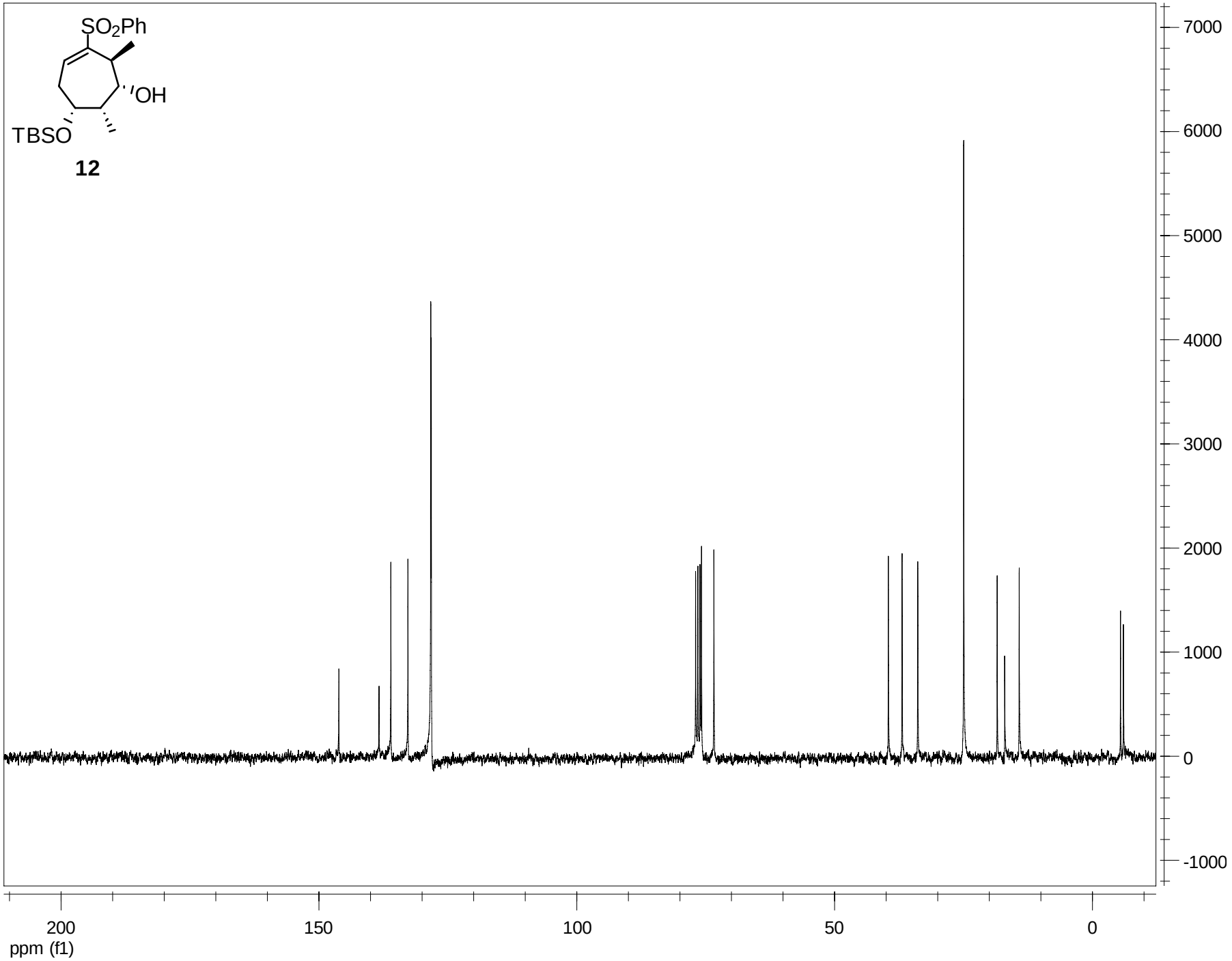
ppm (f1)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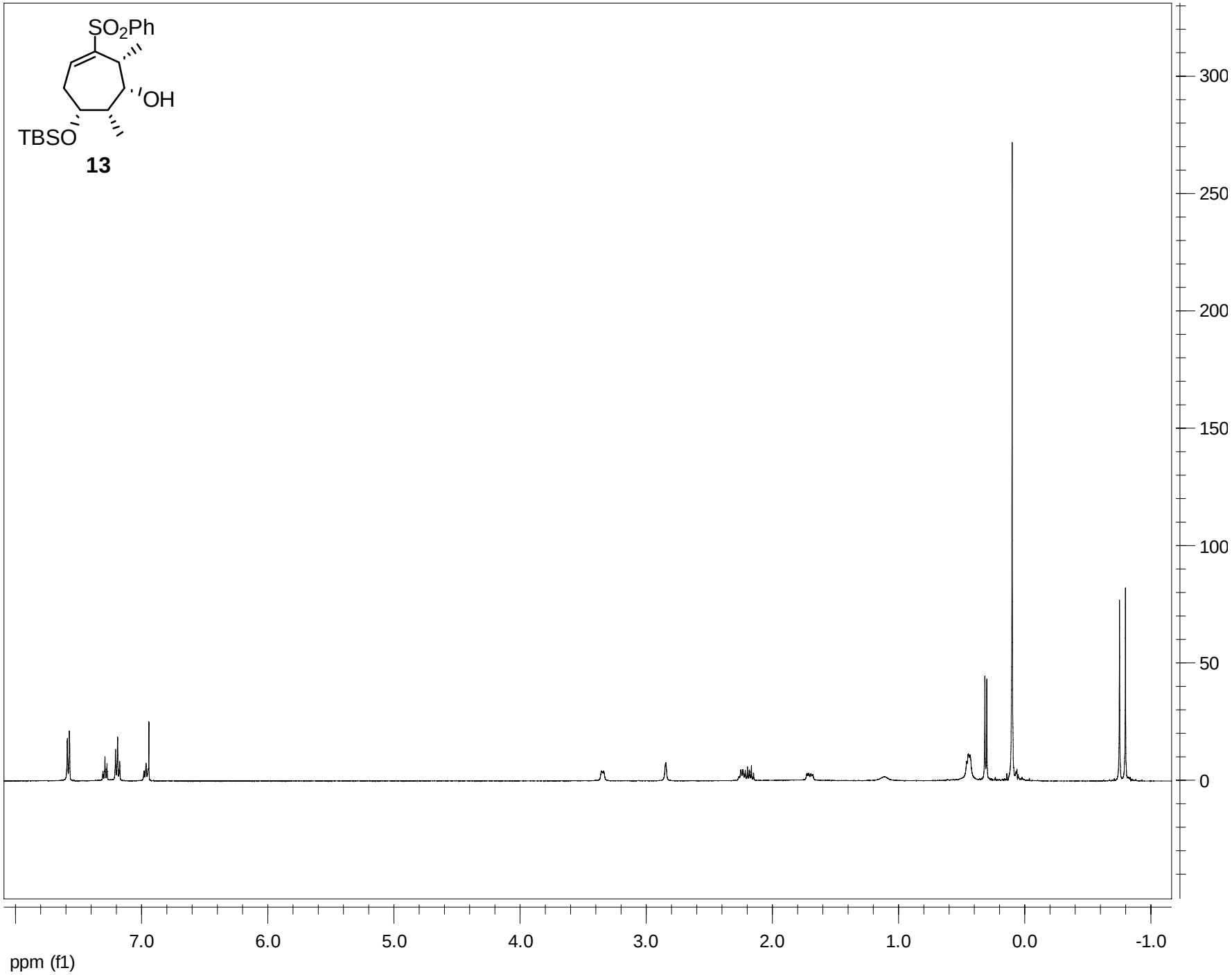
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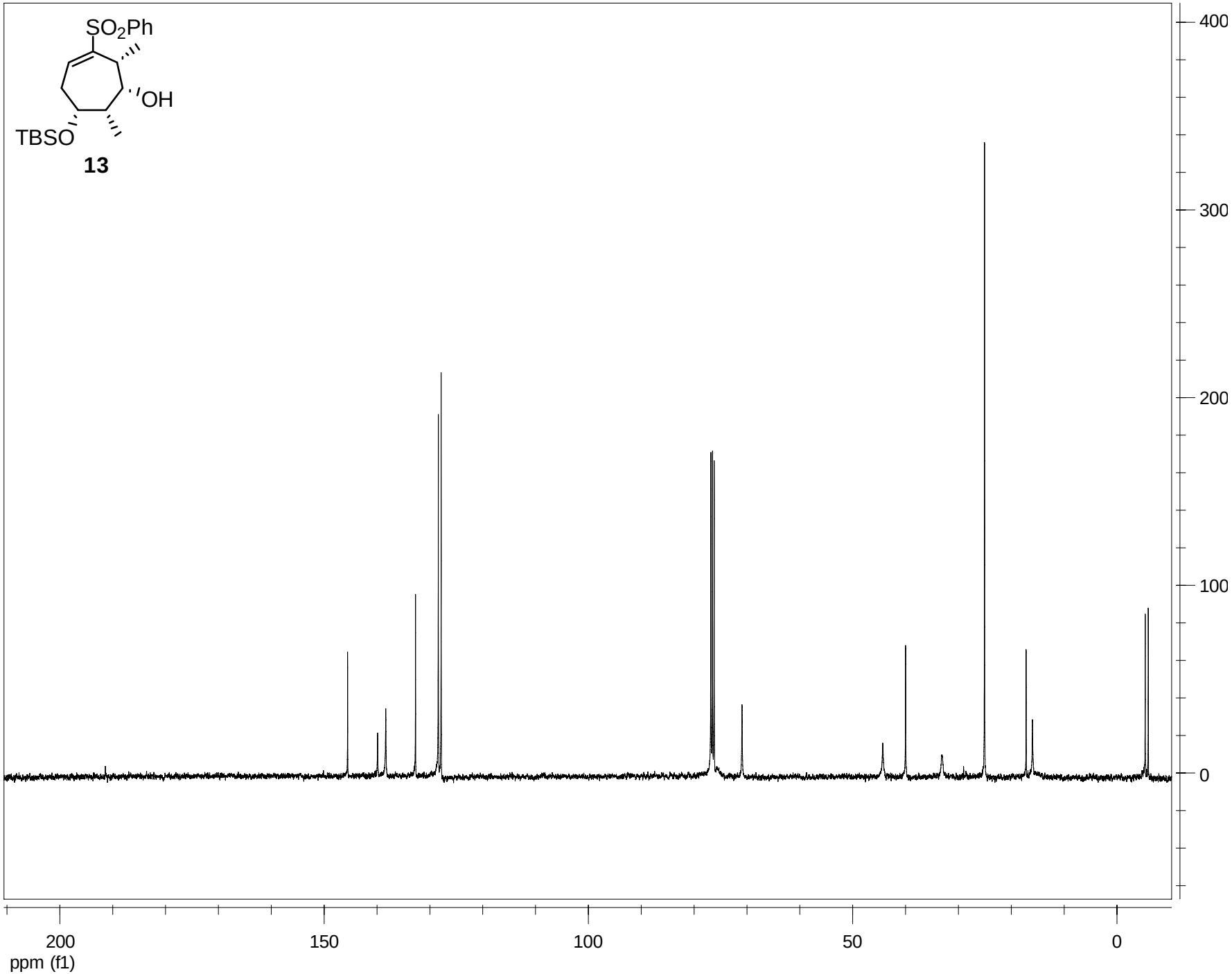
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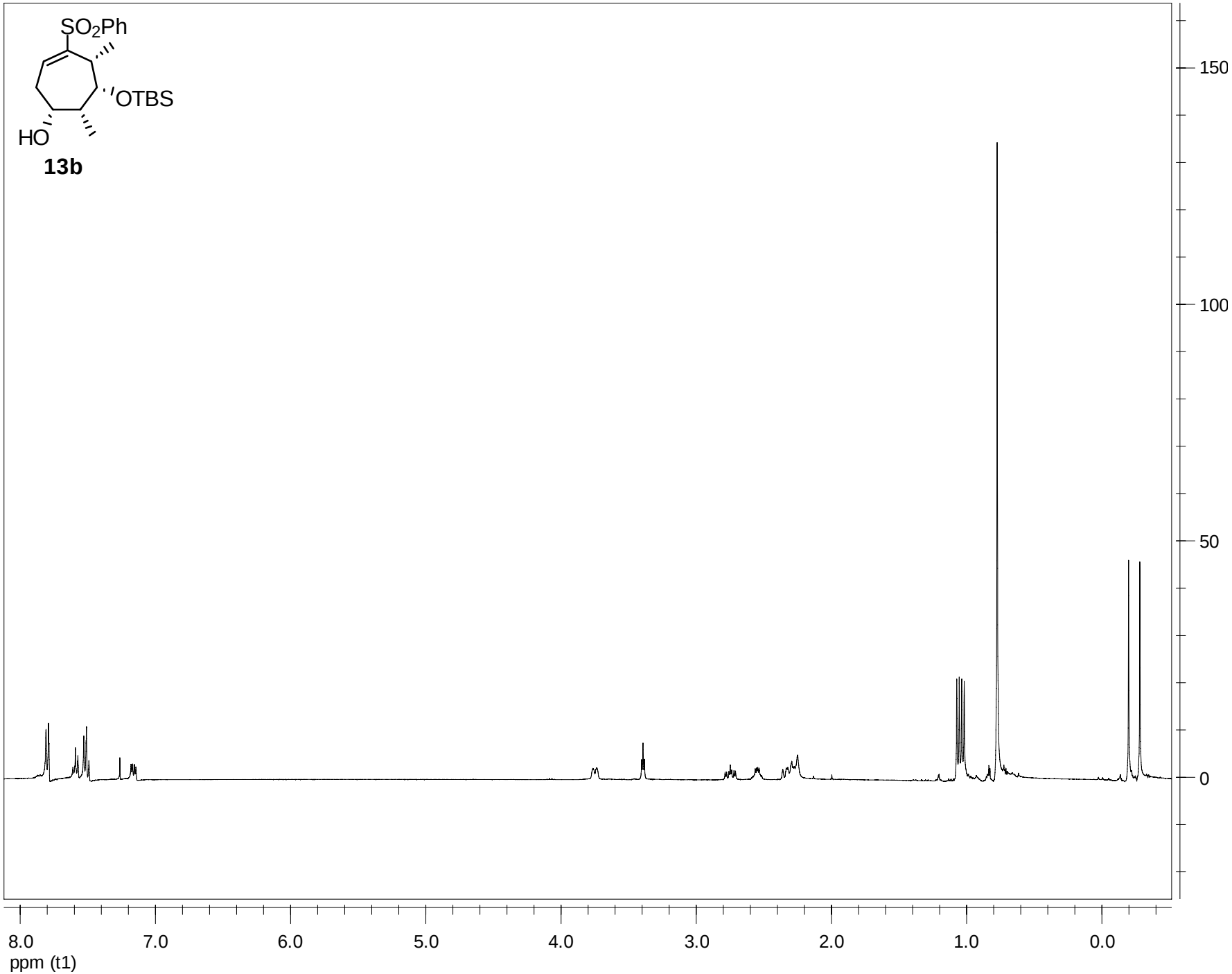
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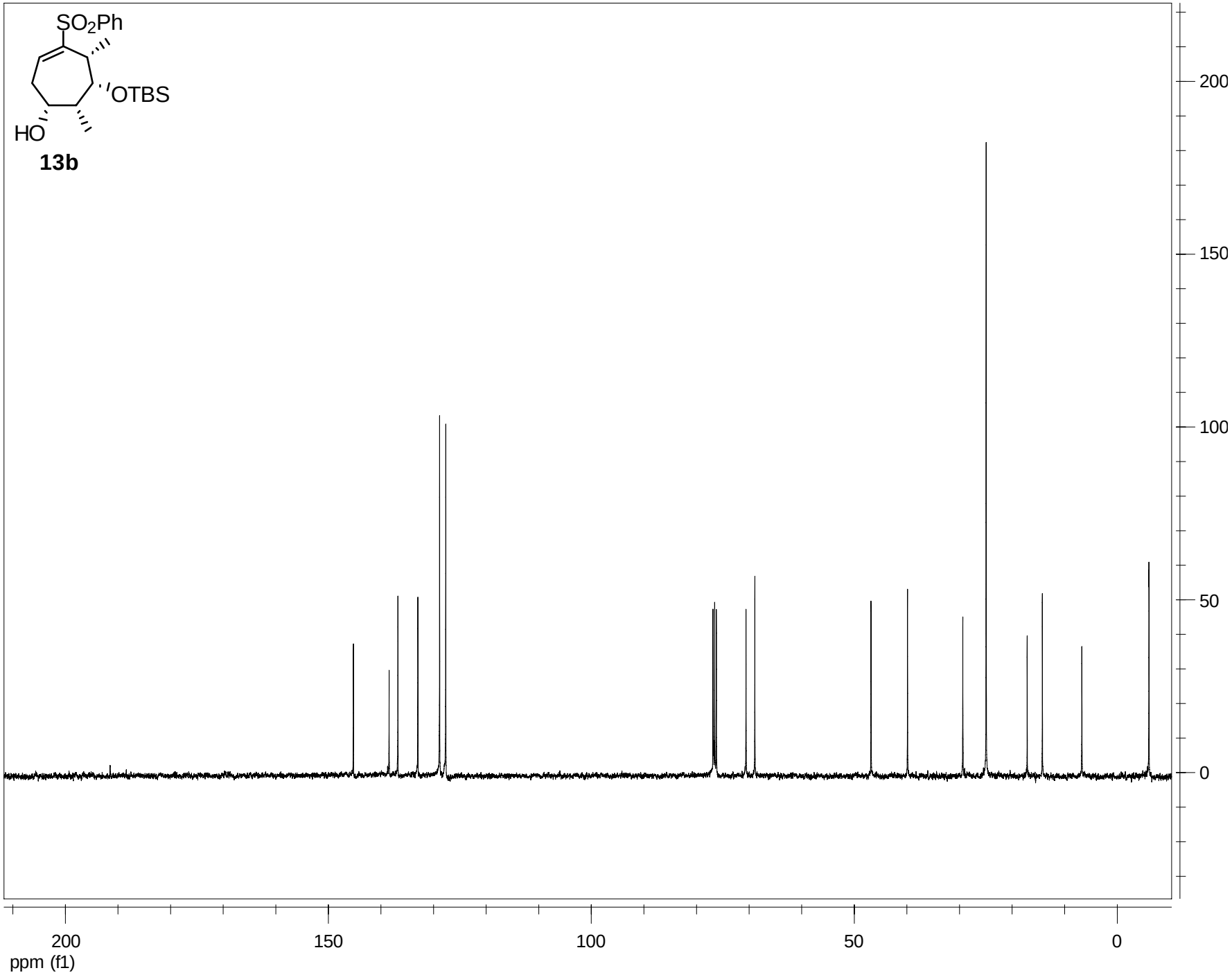
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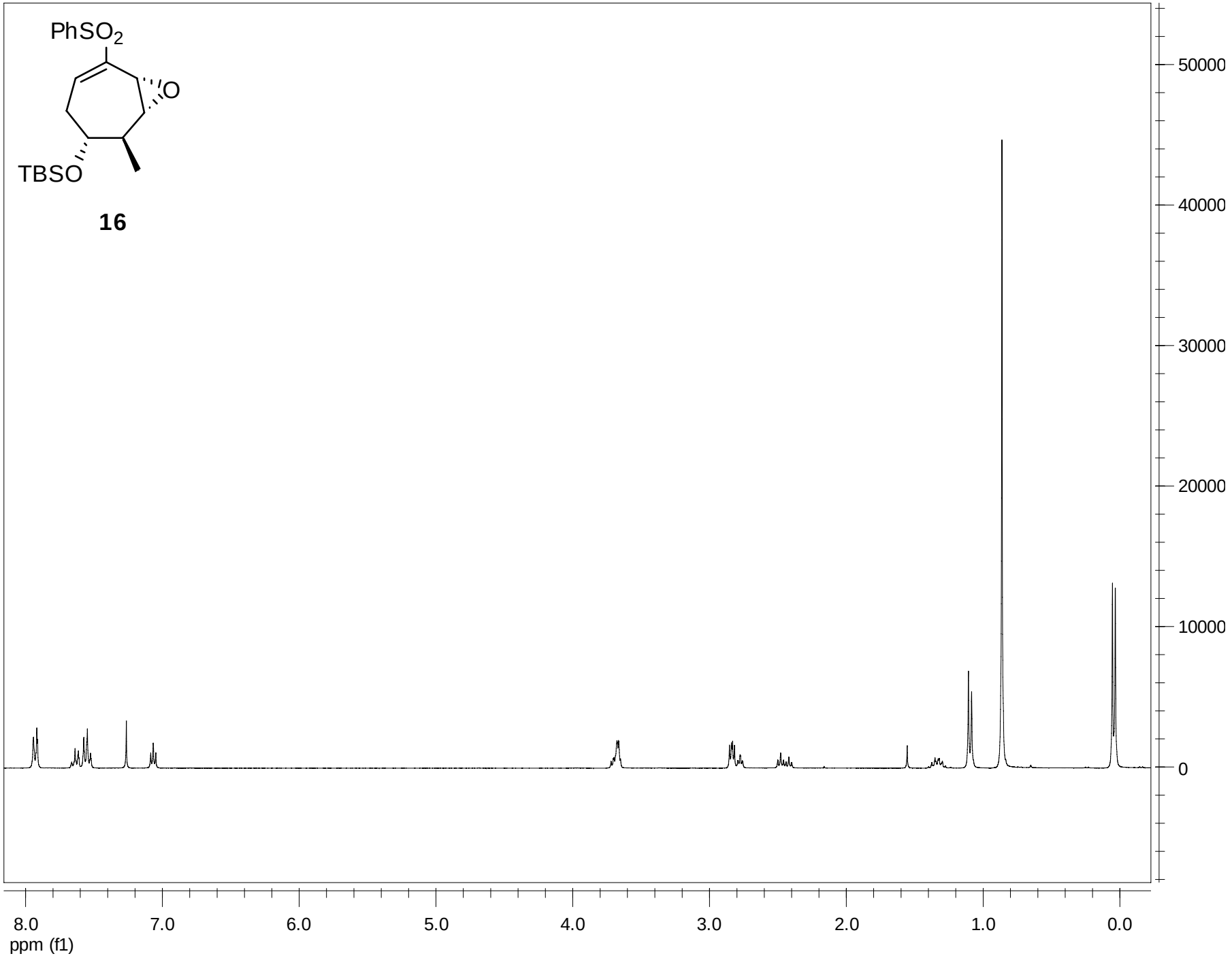
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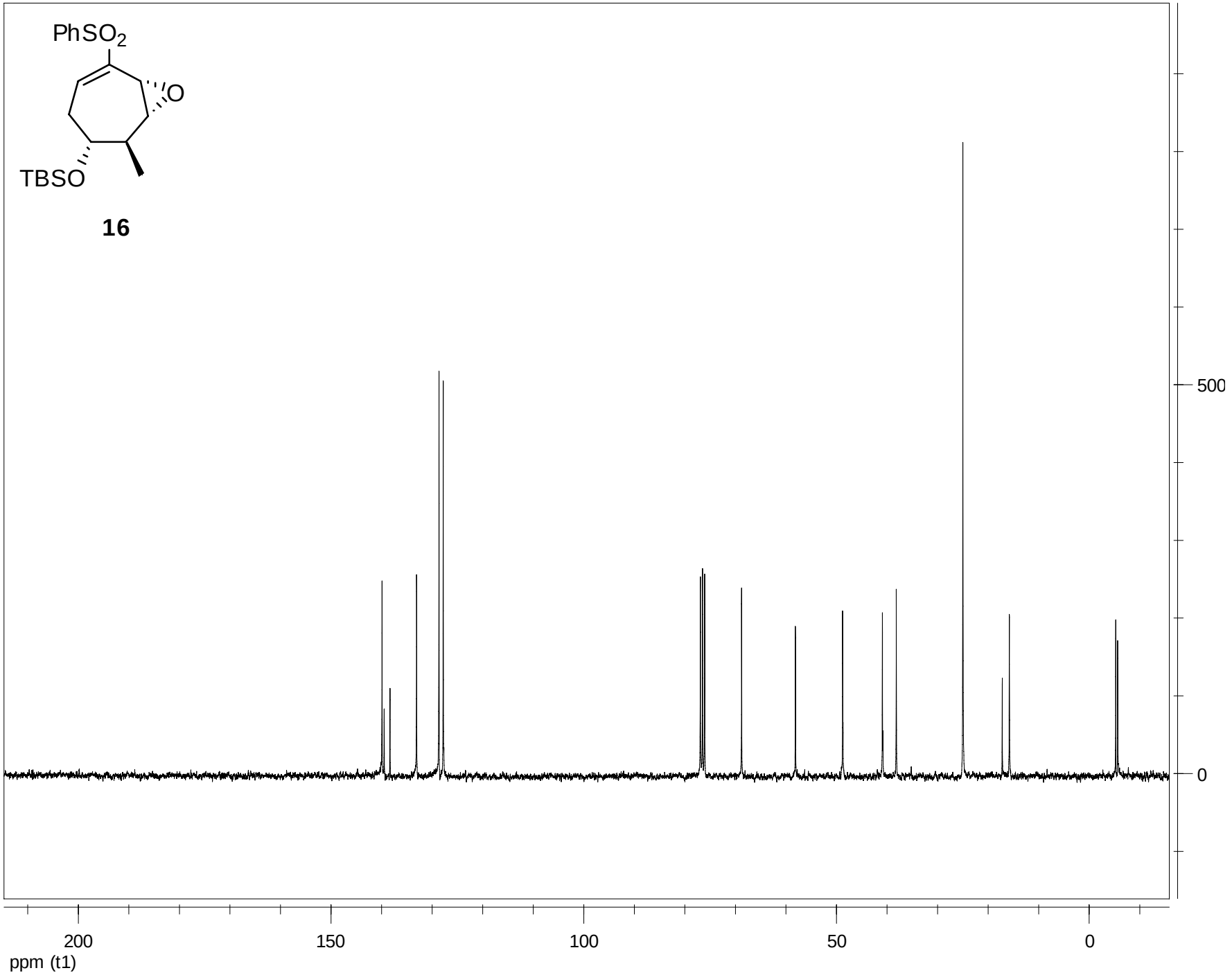
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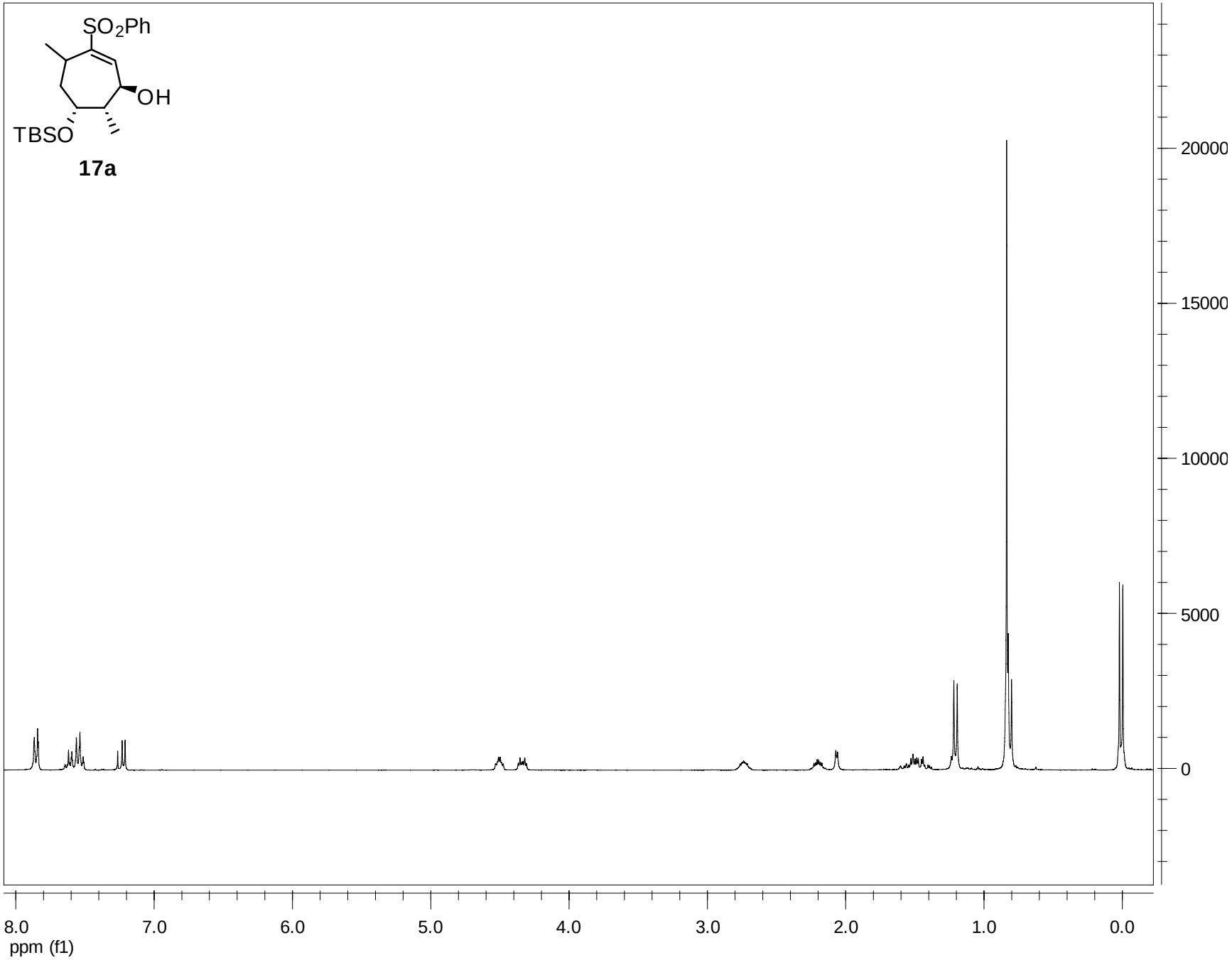
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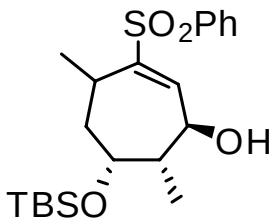

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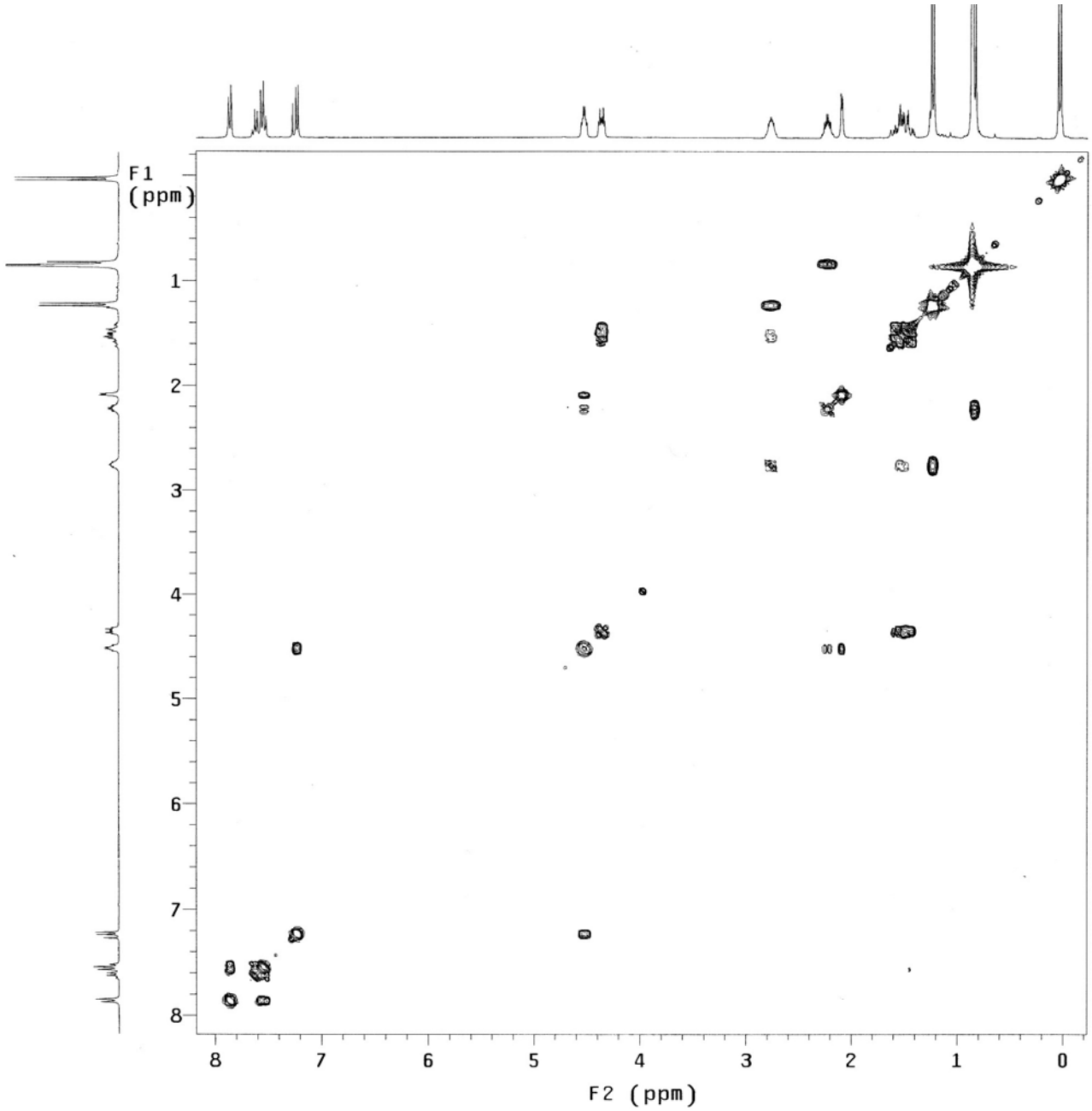

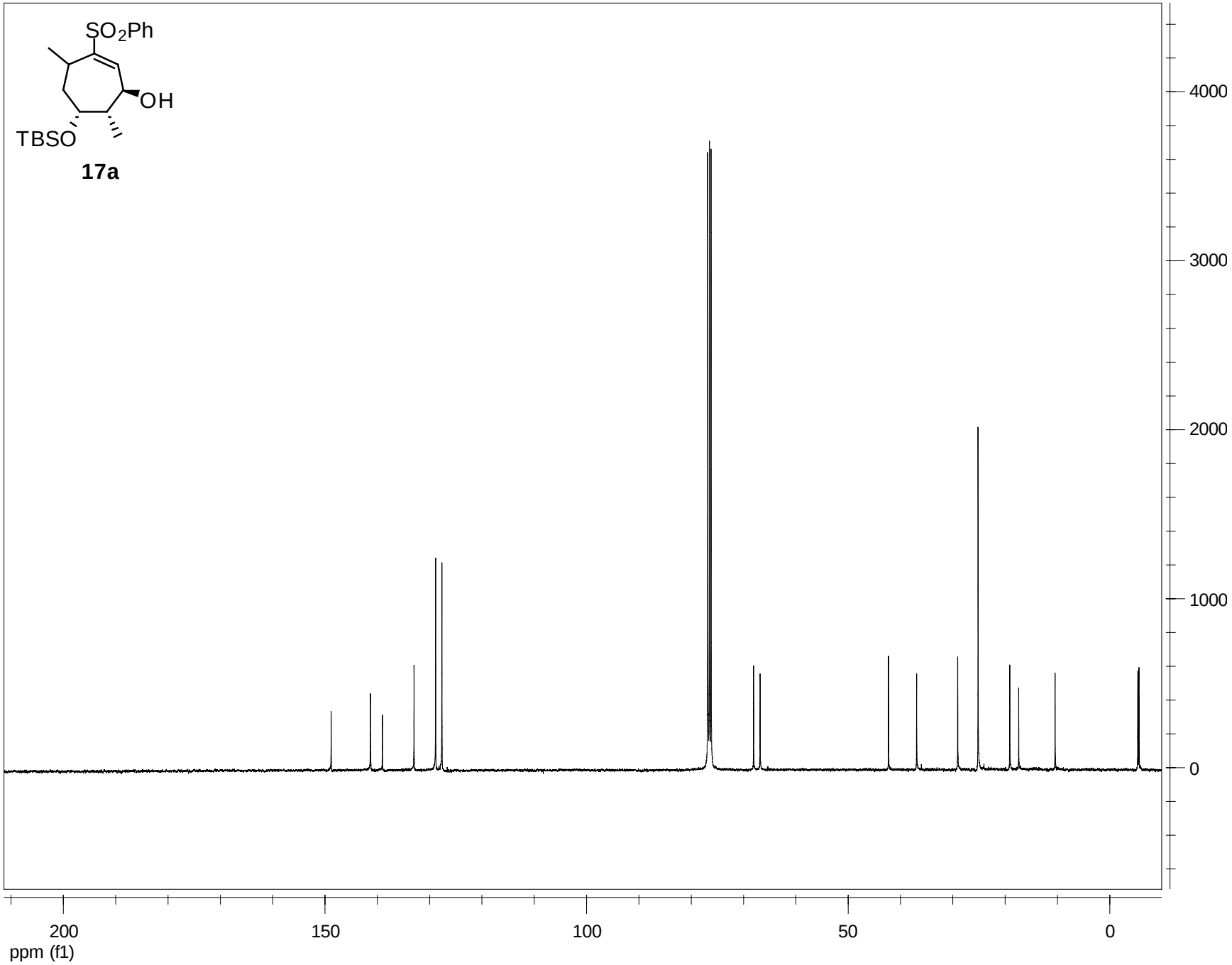
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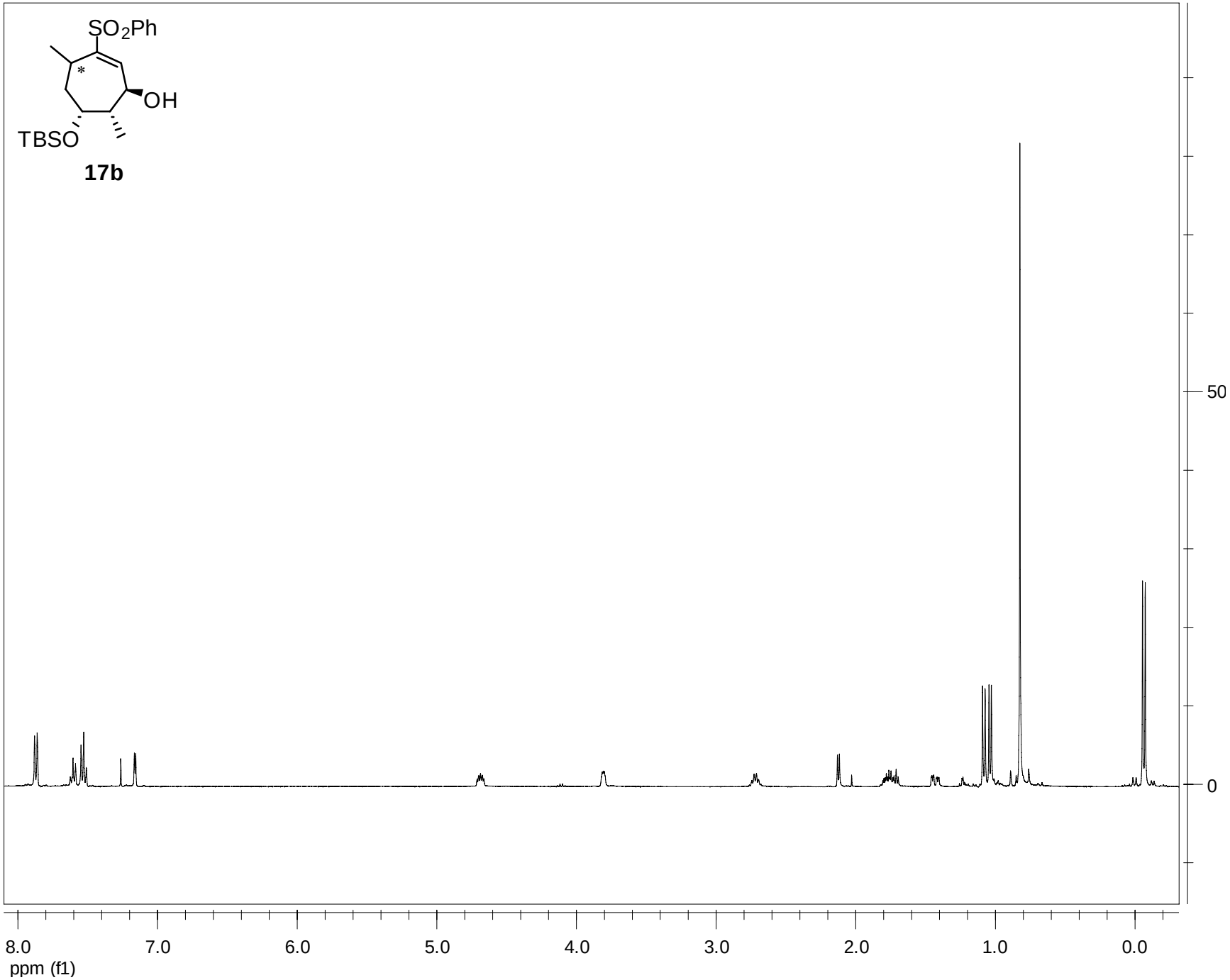
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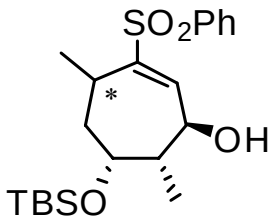

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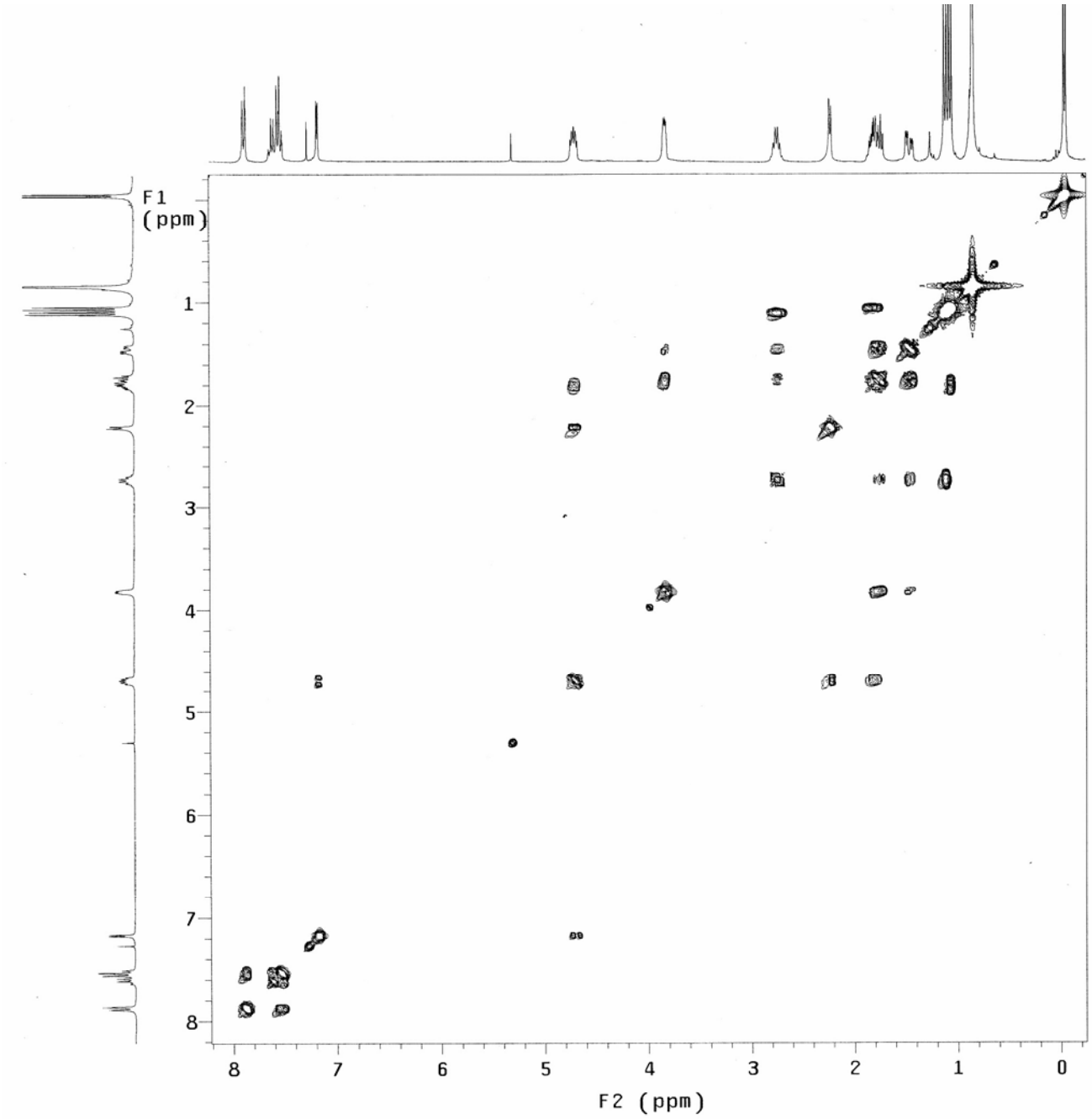

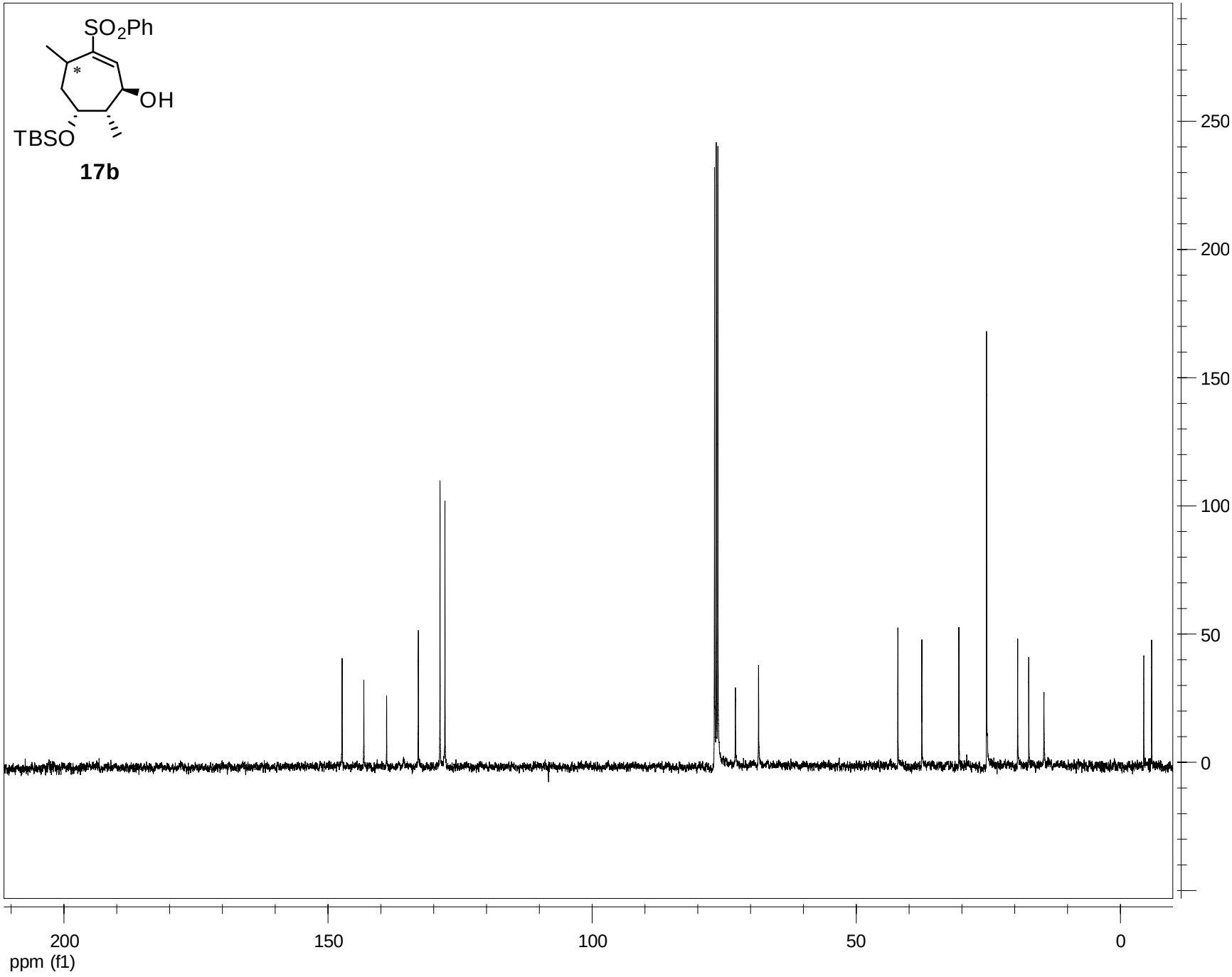
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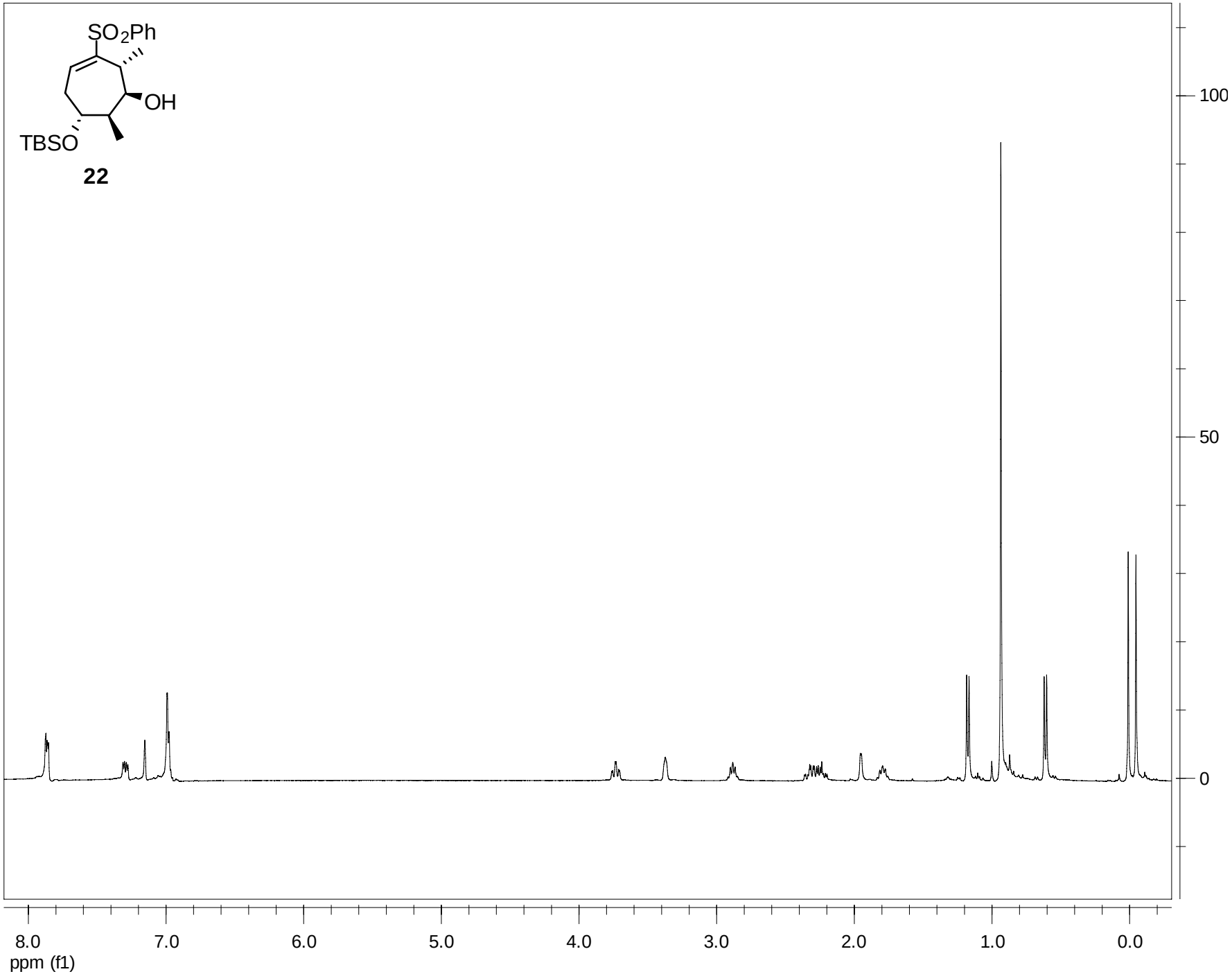
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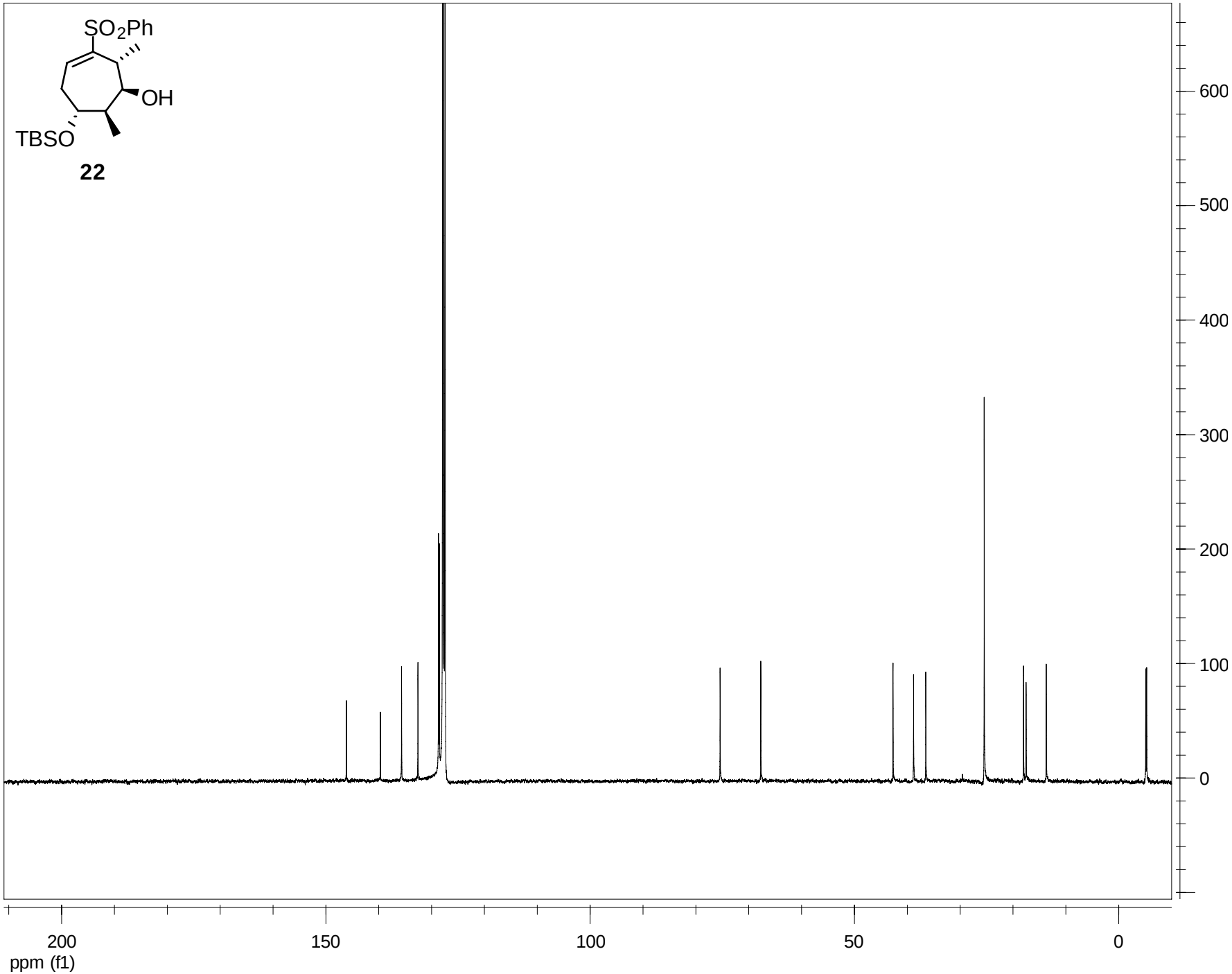
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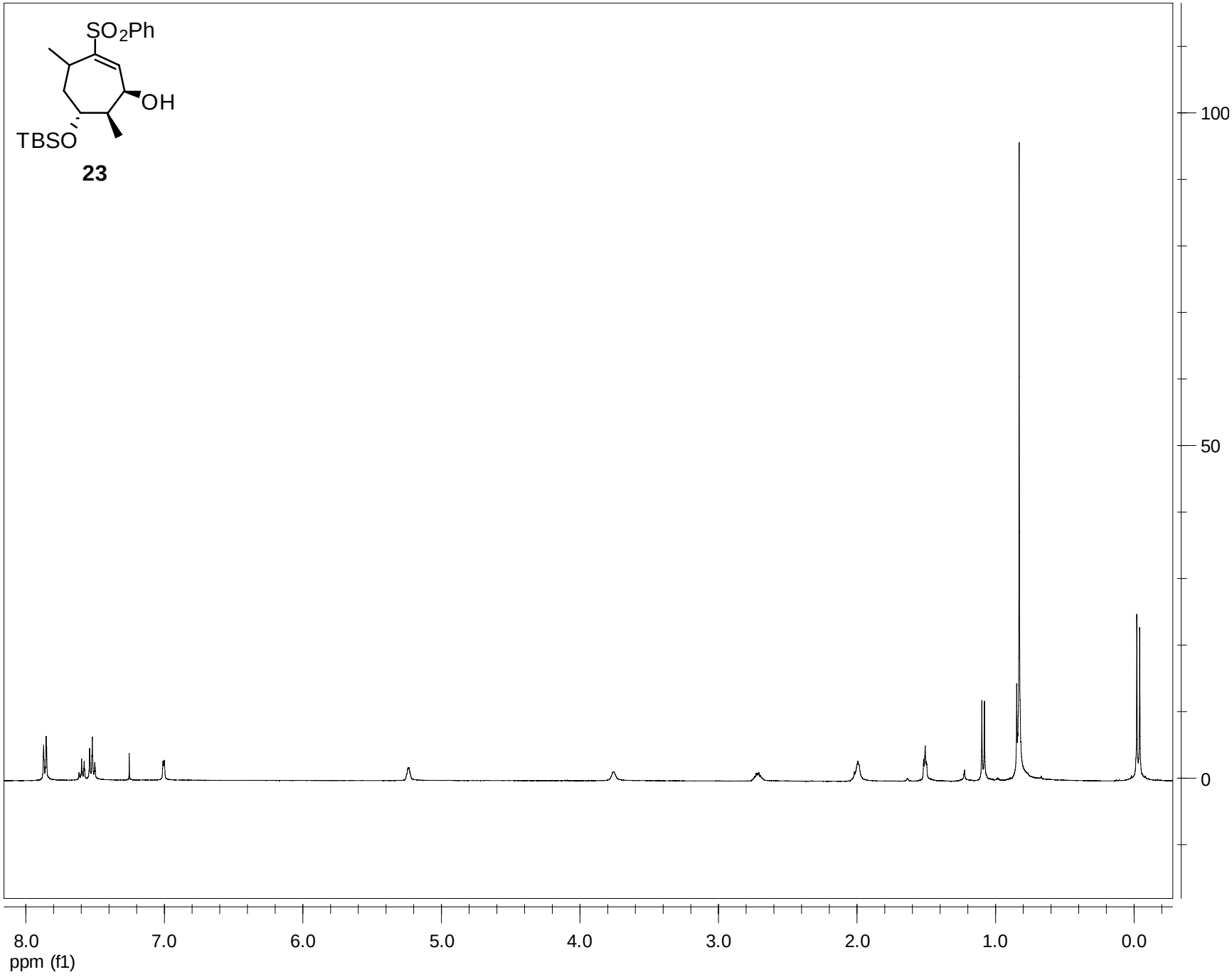
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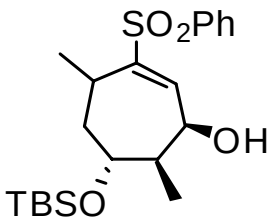

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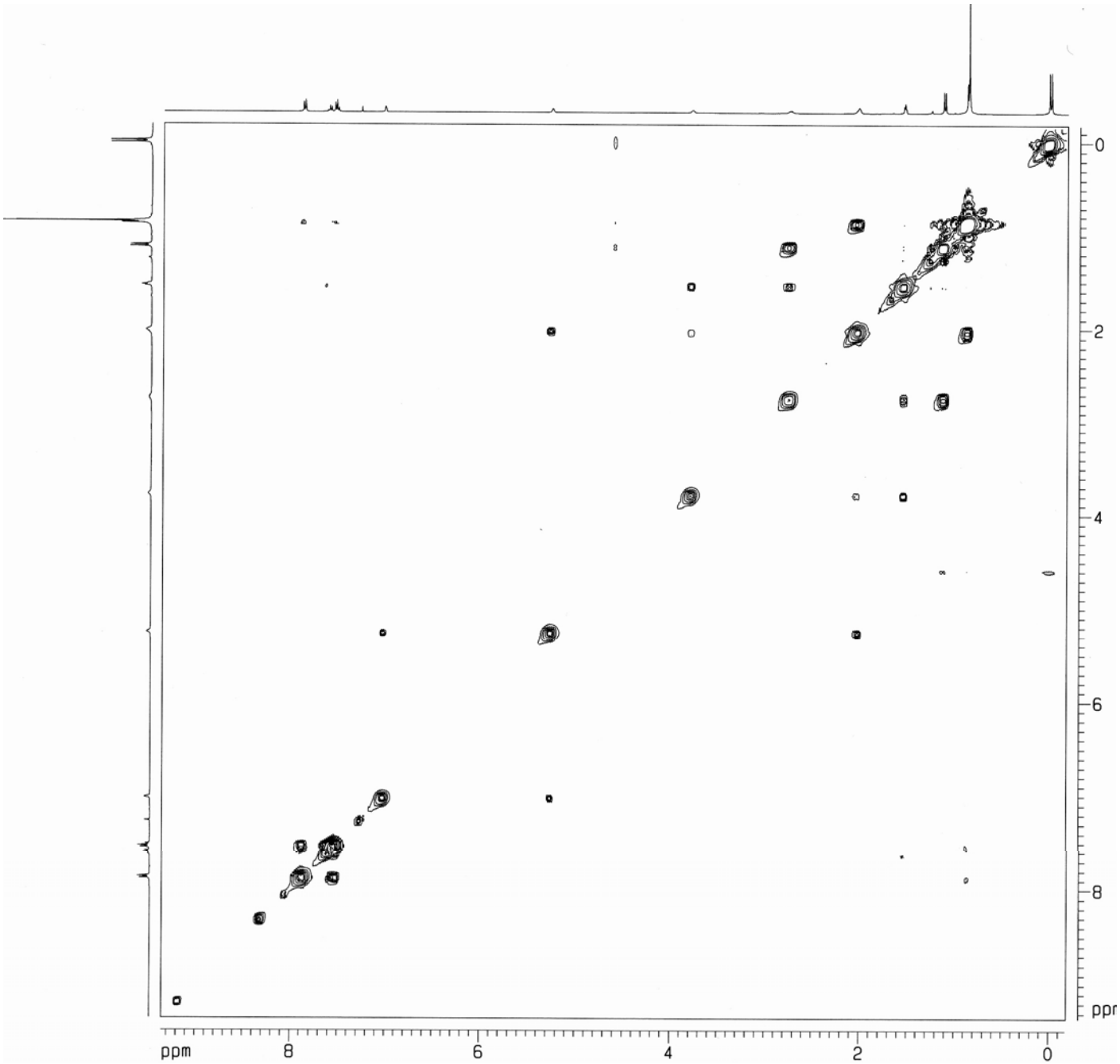

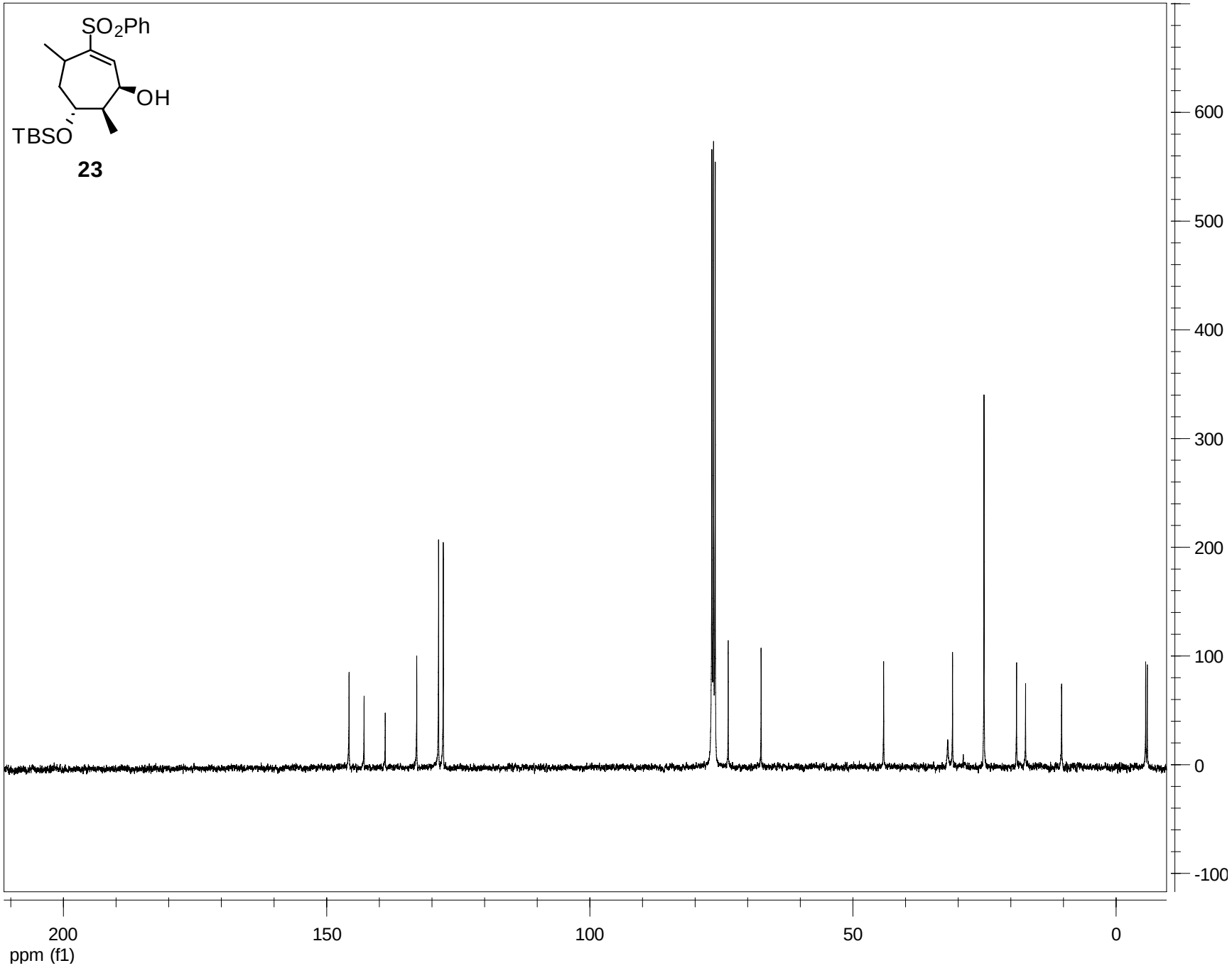
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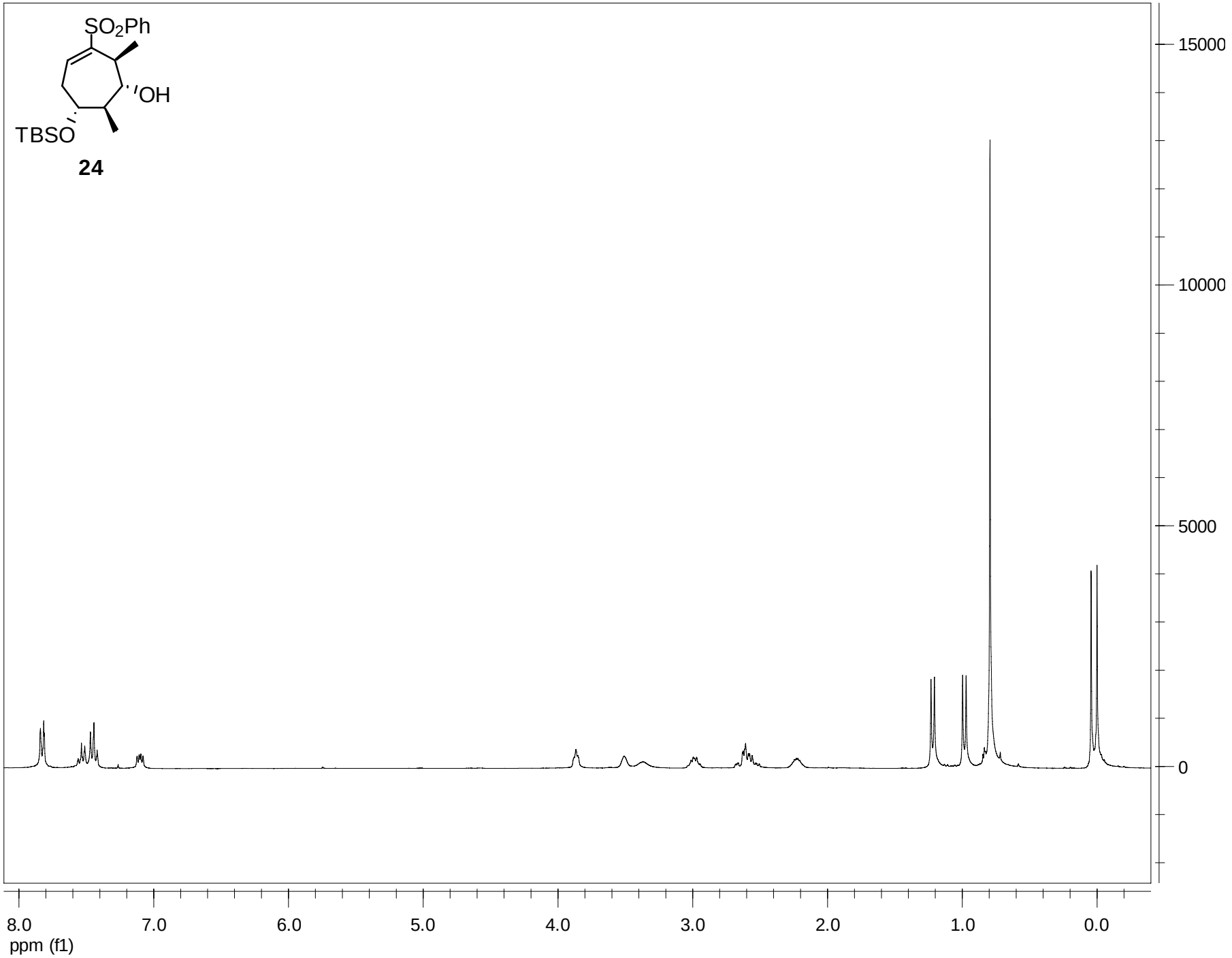
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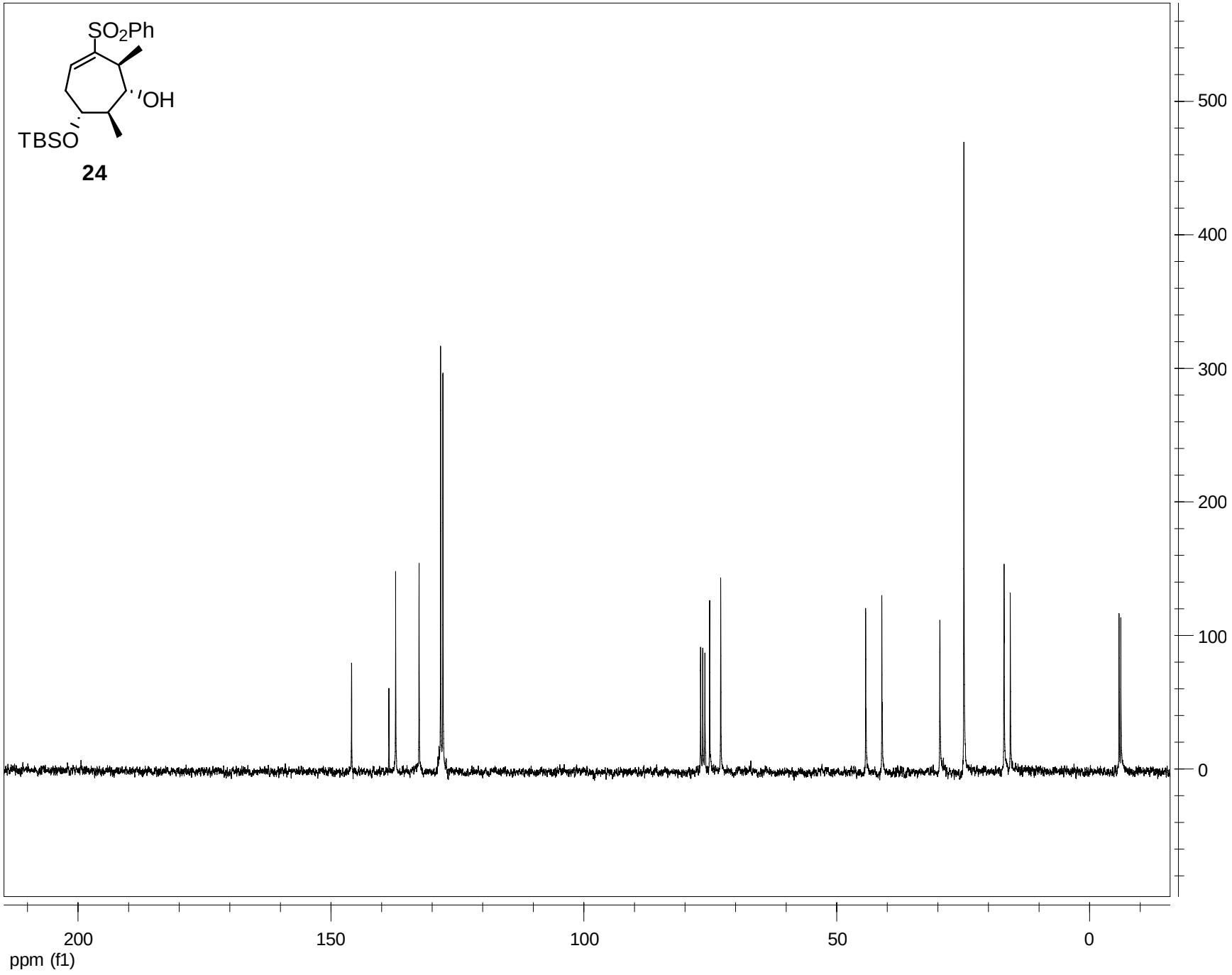
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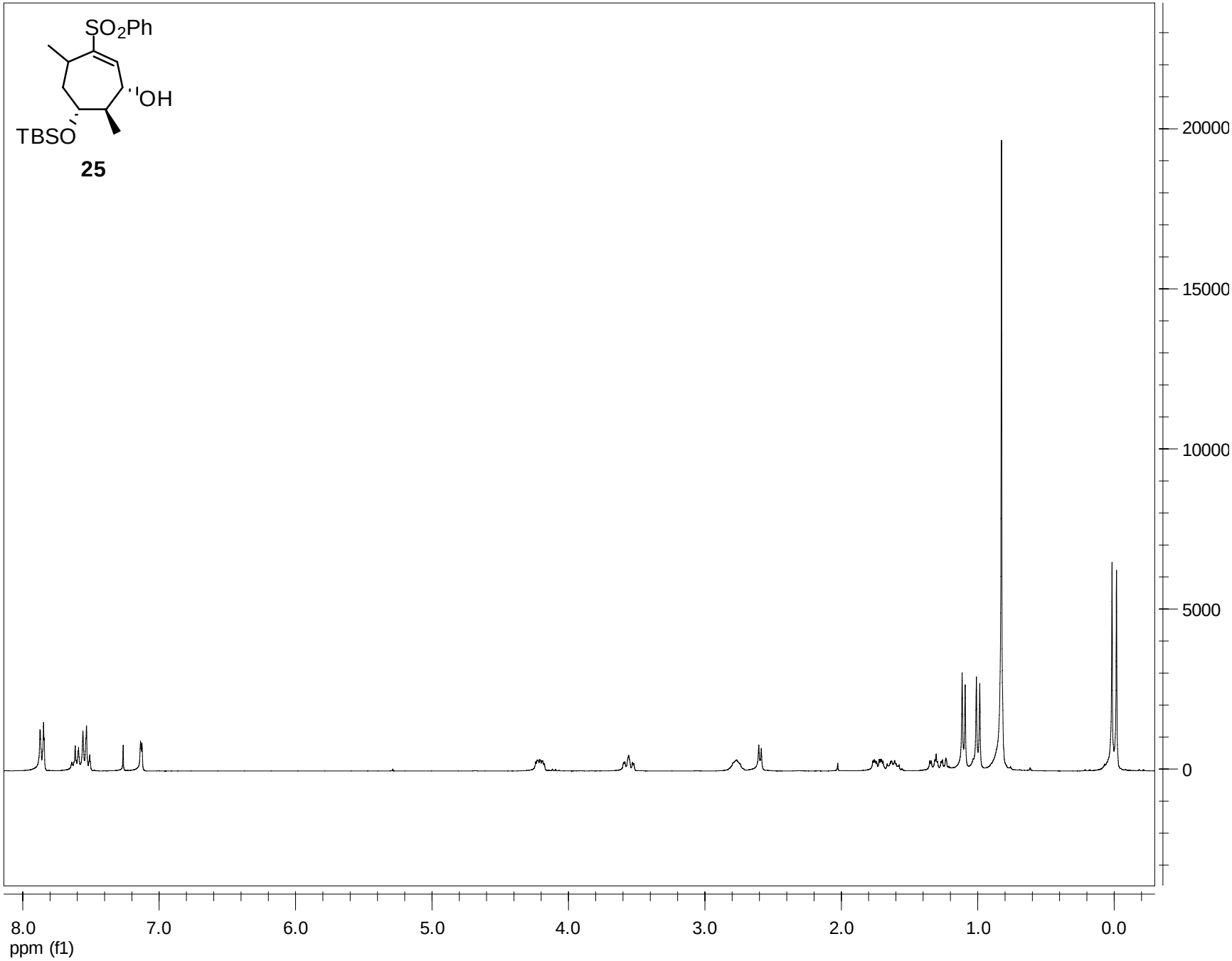
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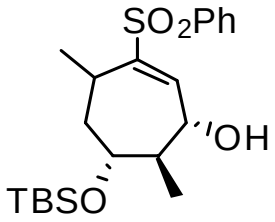

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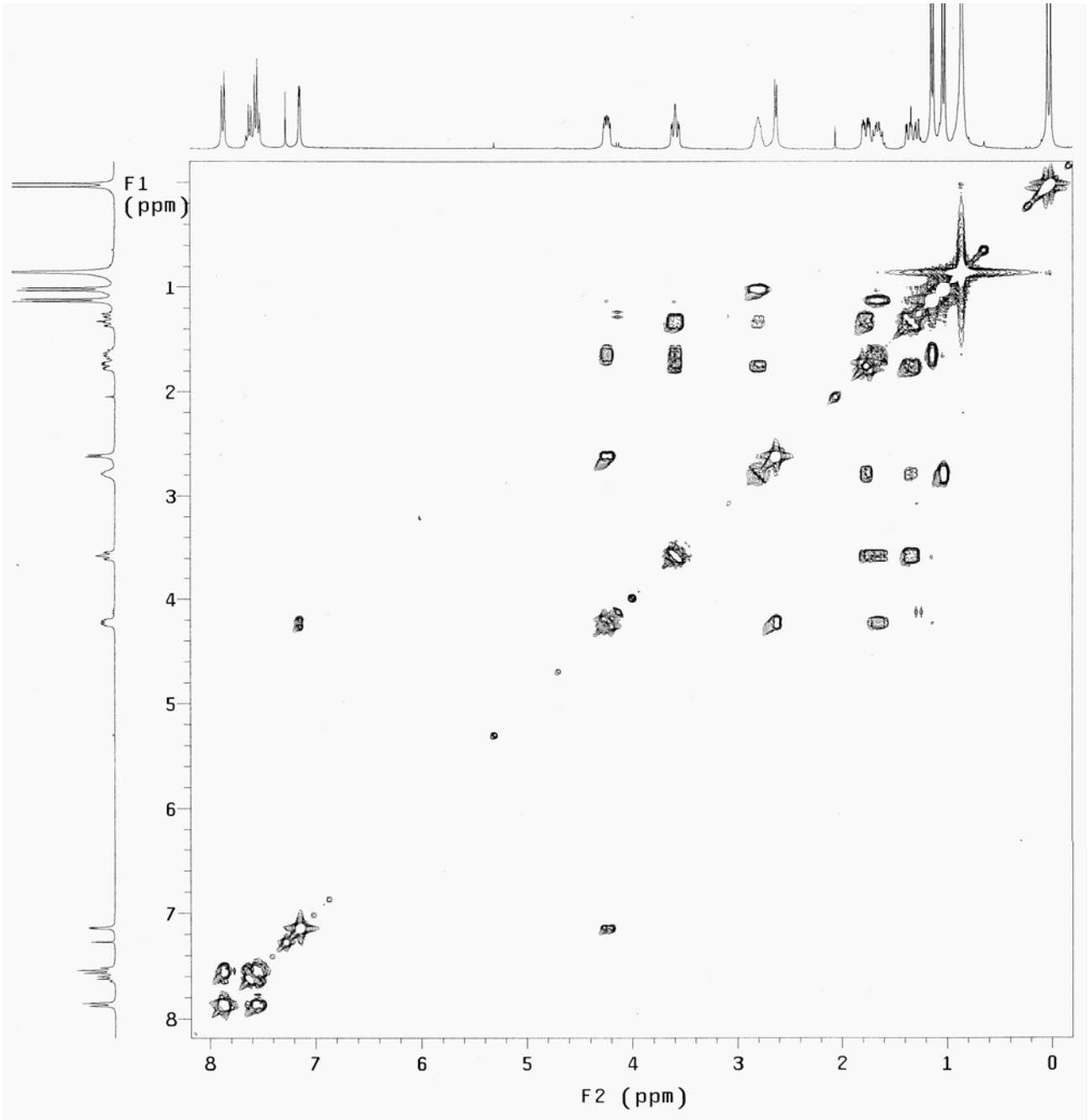

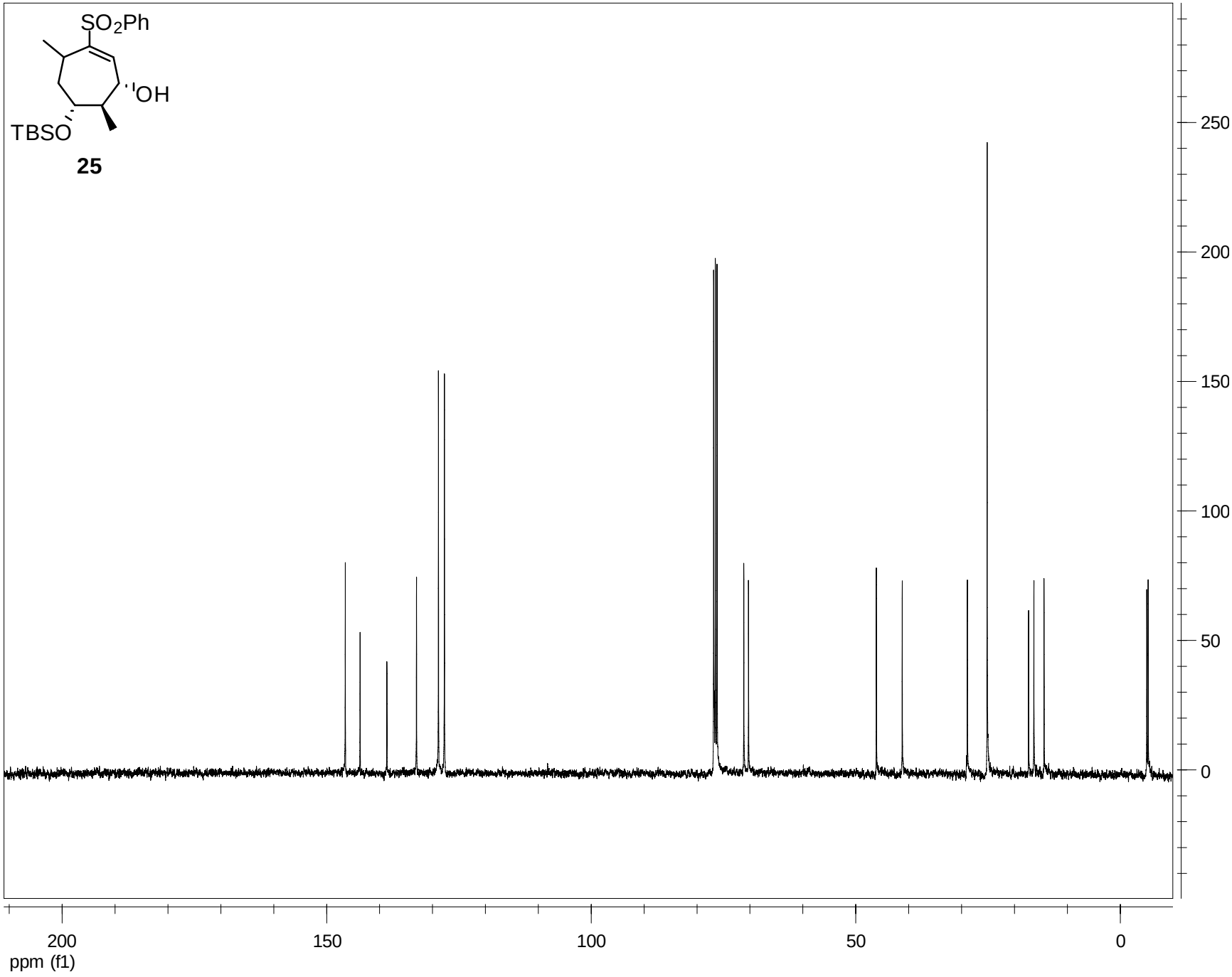
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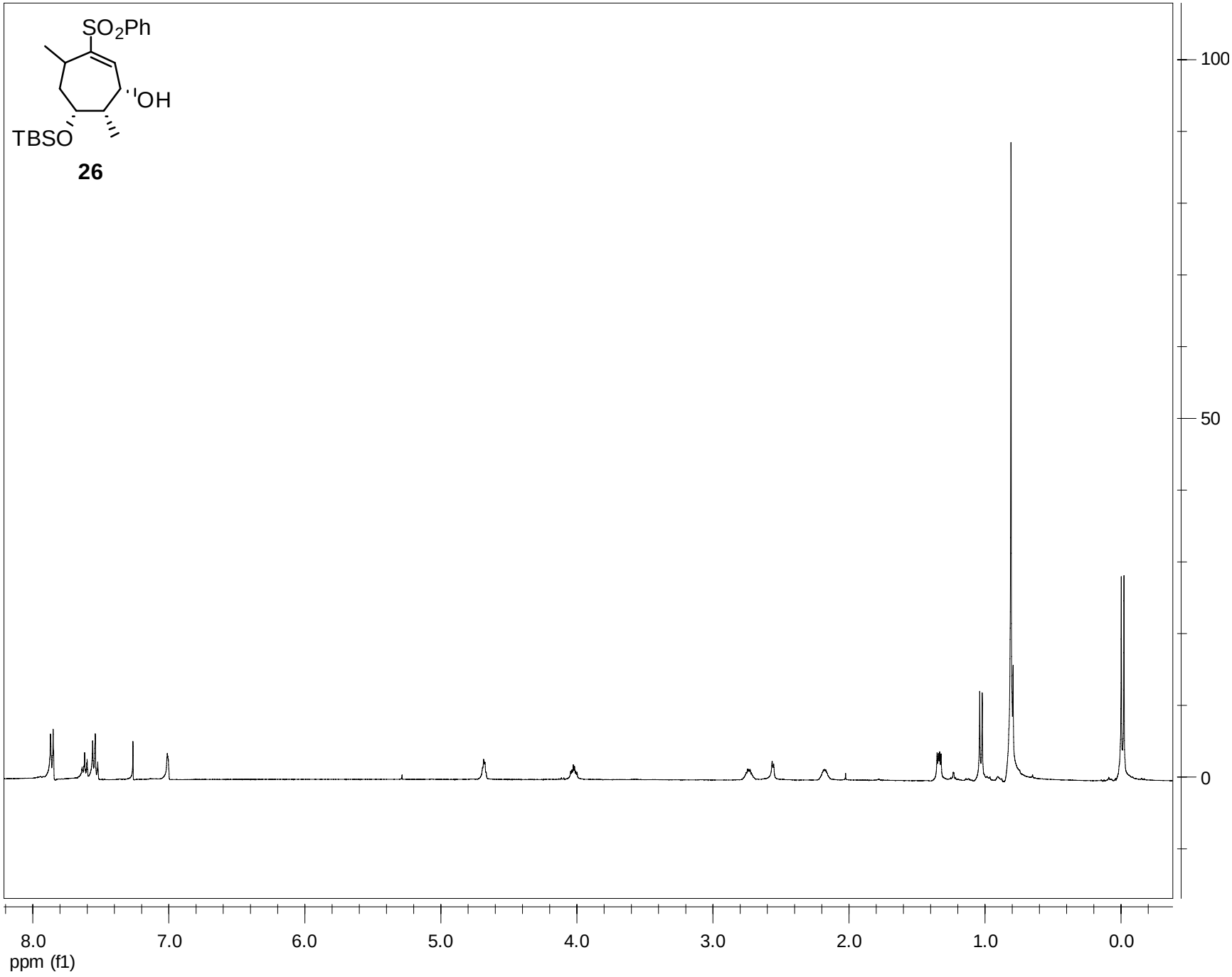
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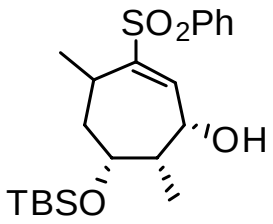

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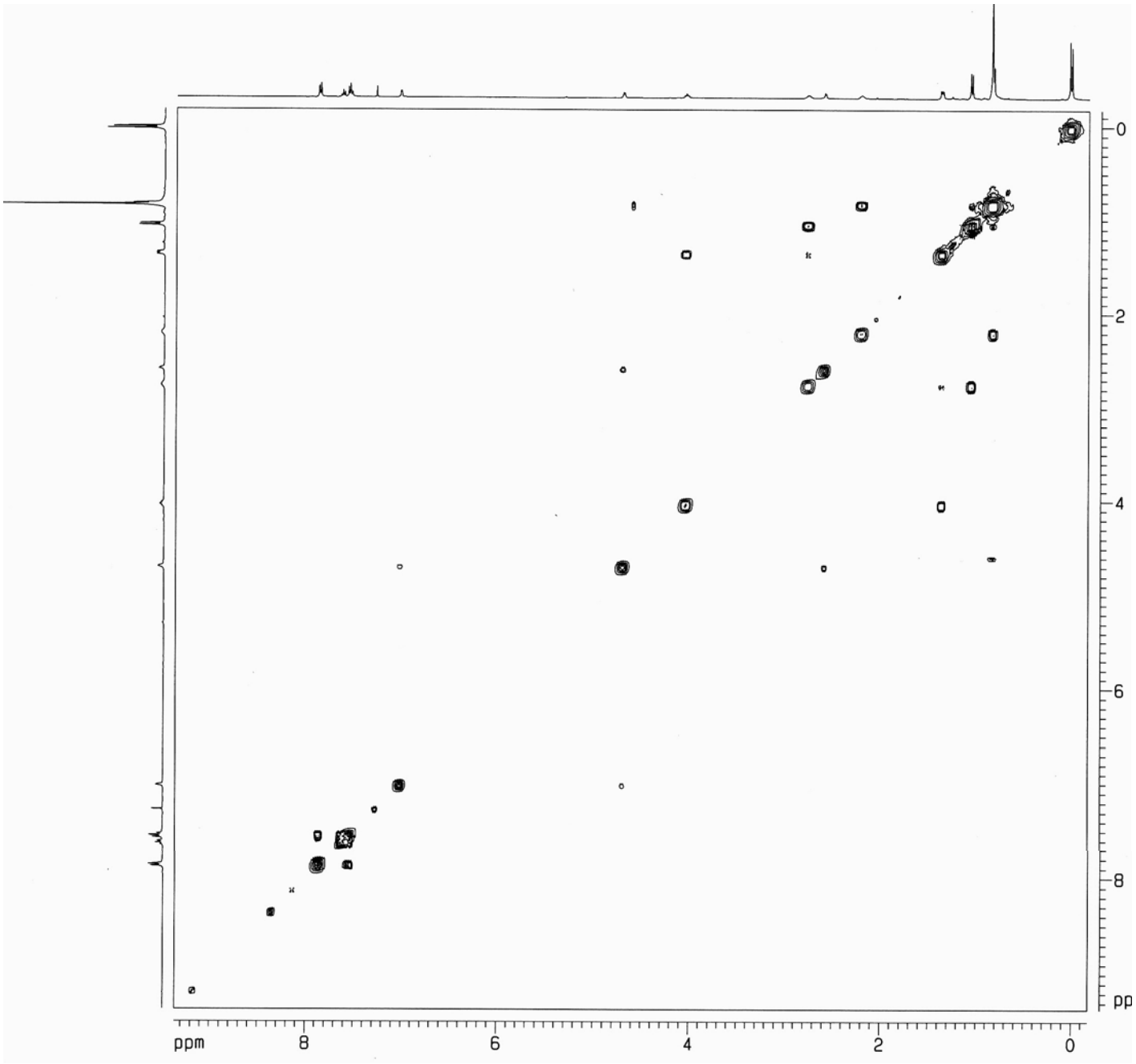

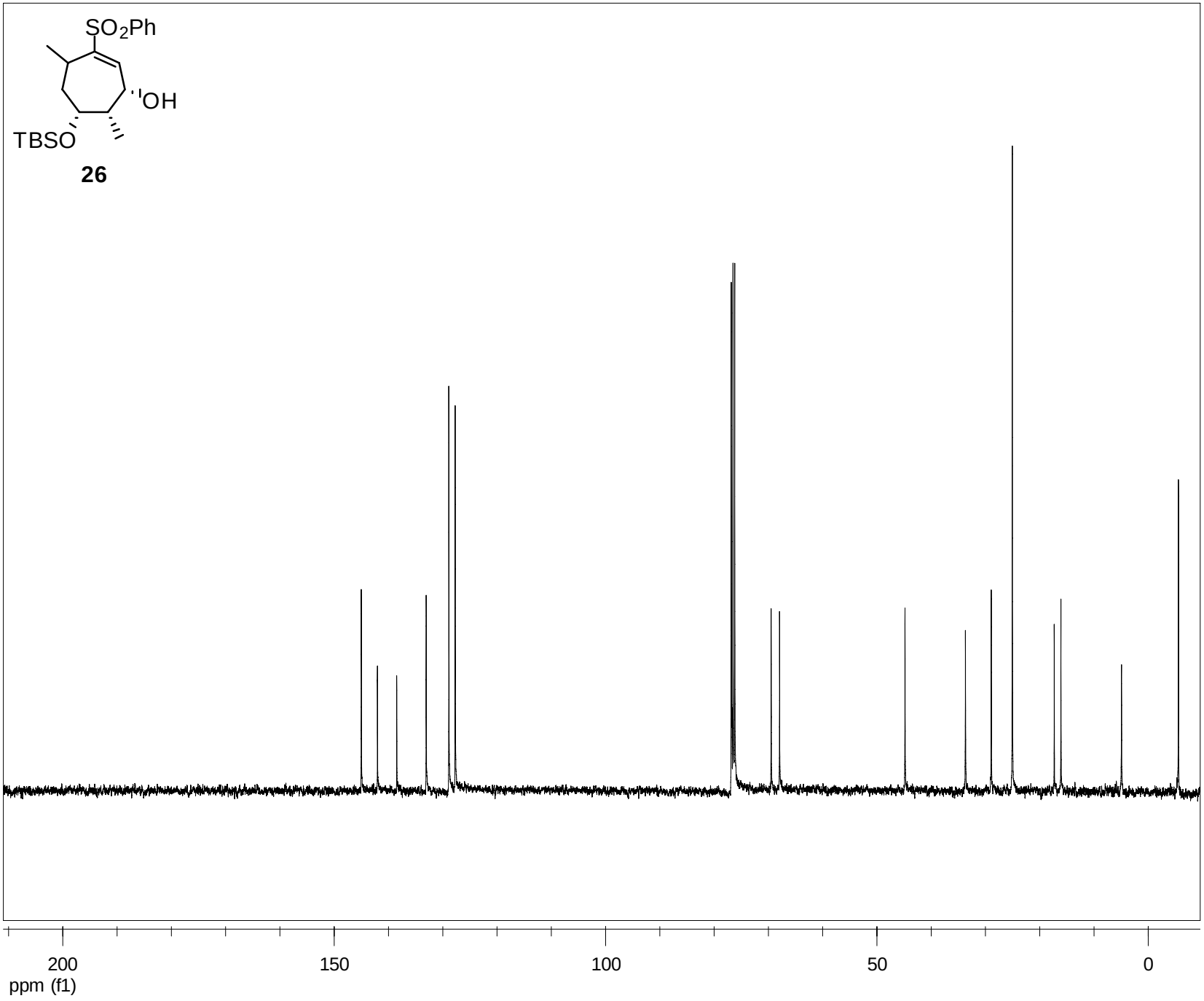
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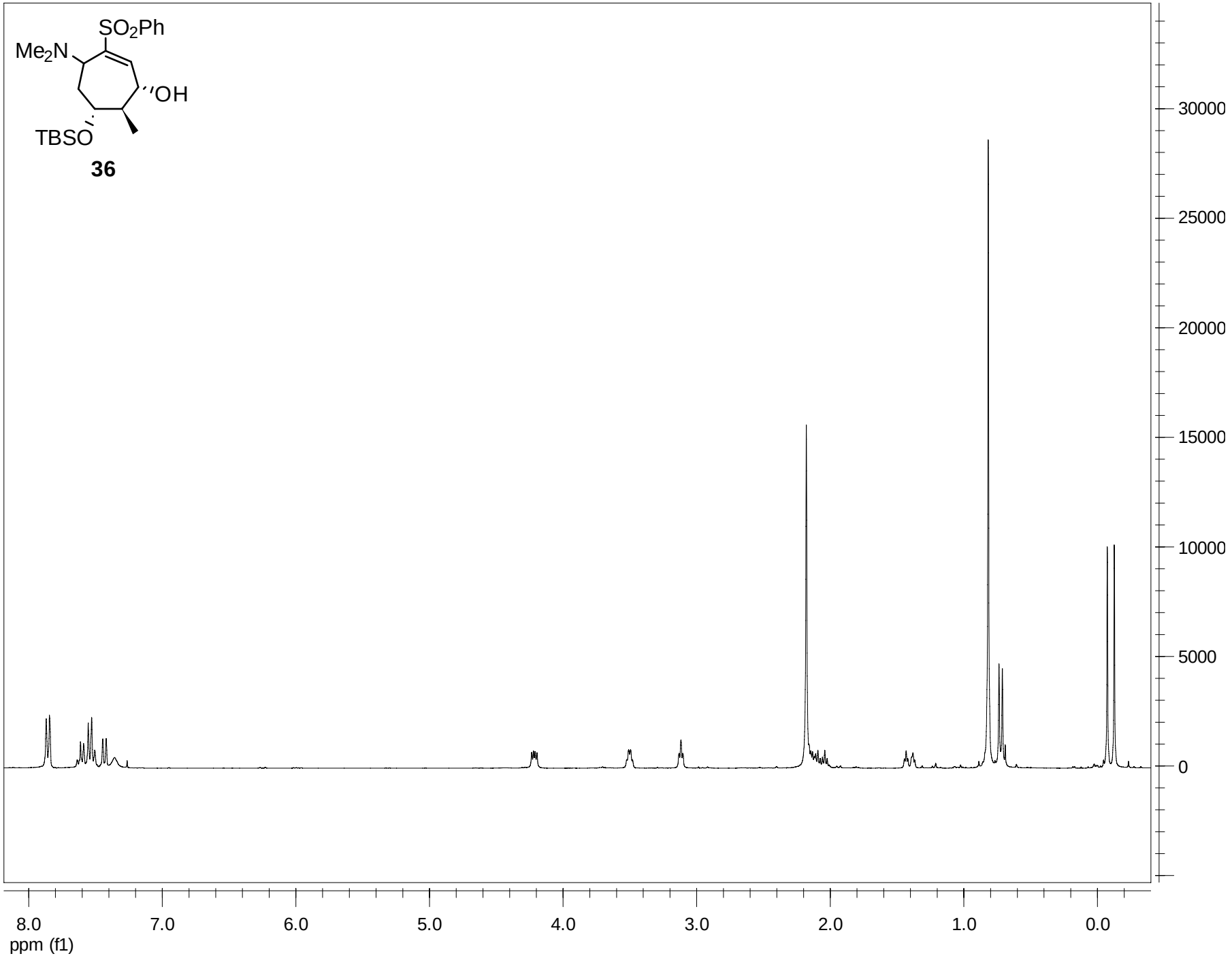
ppm (f1)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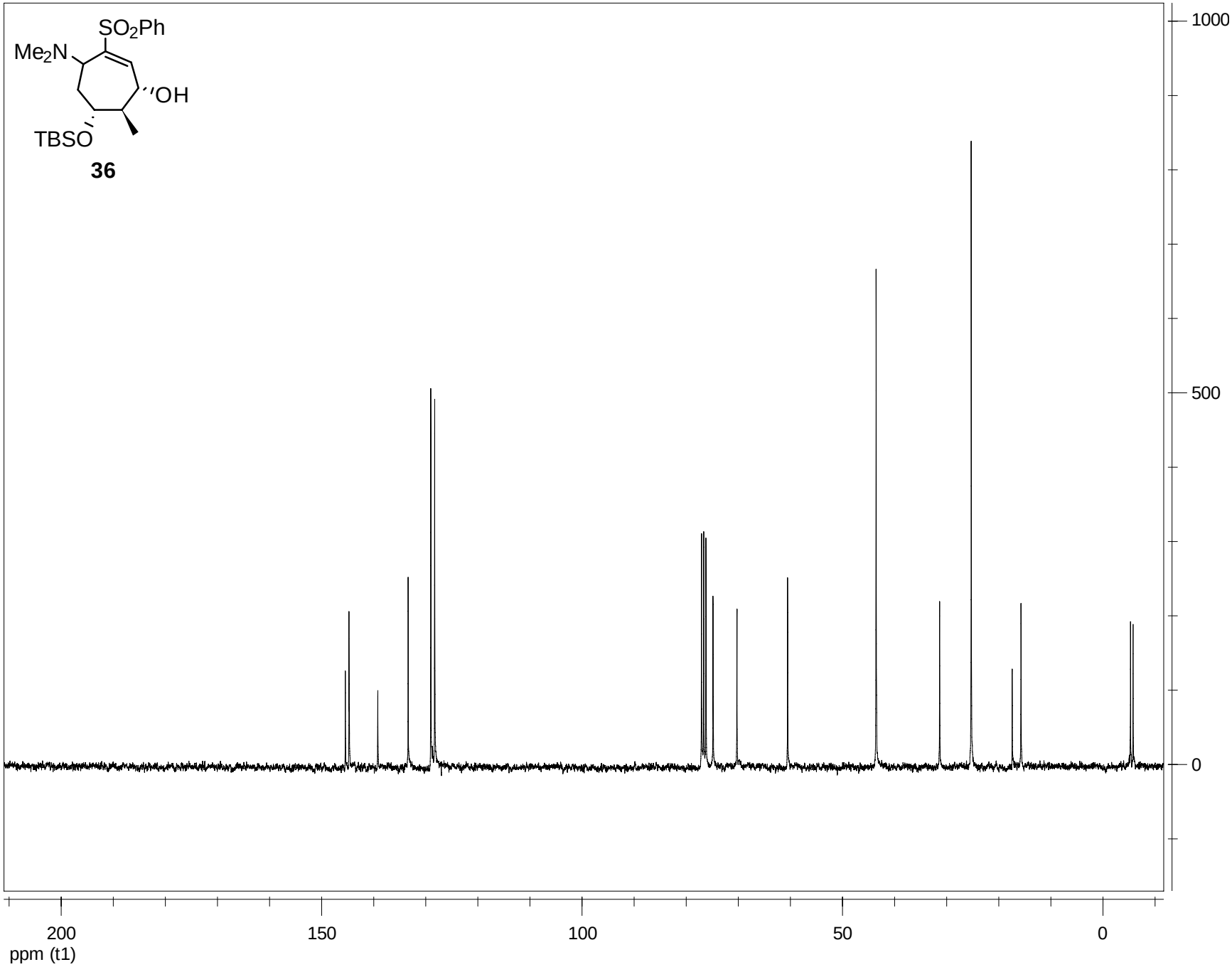
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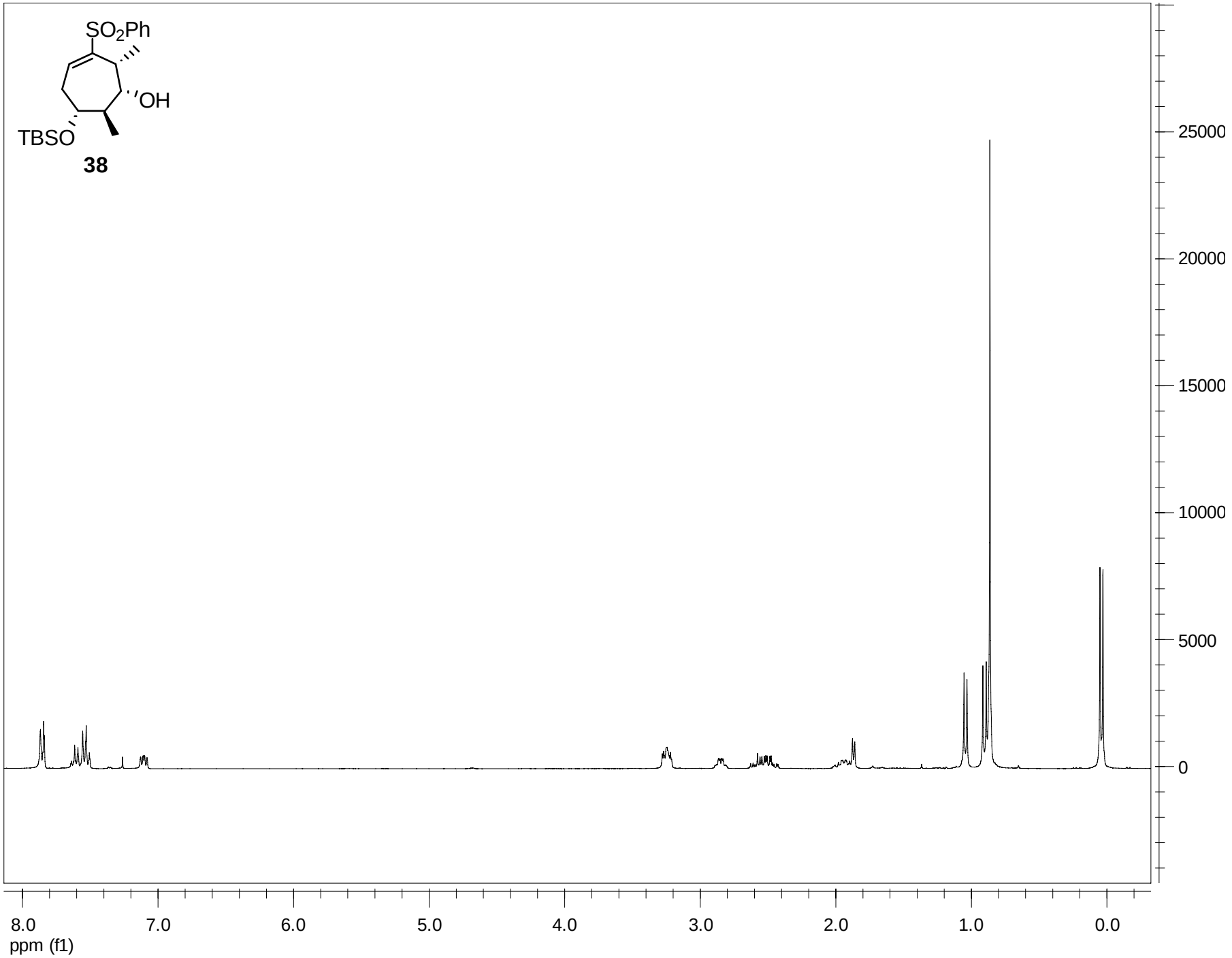
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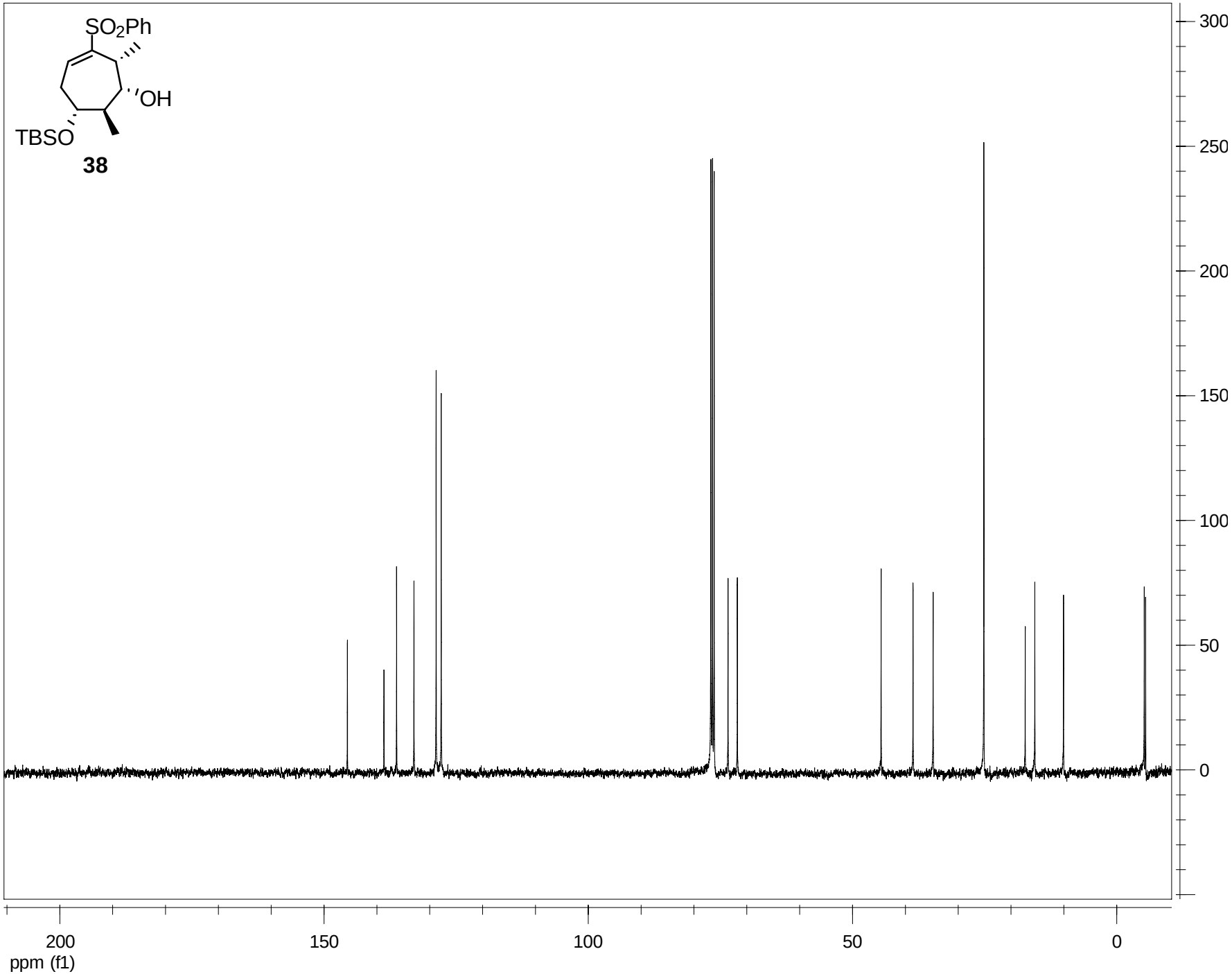
ppm (f1)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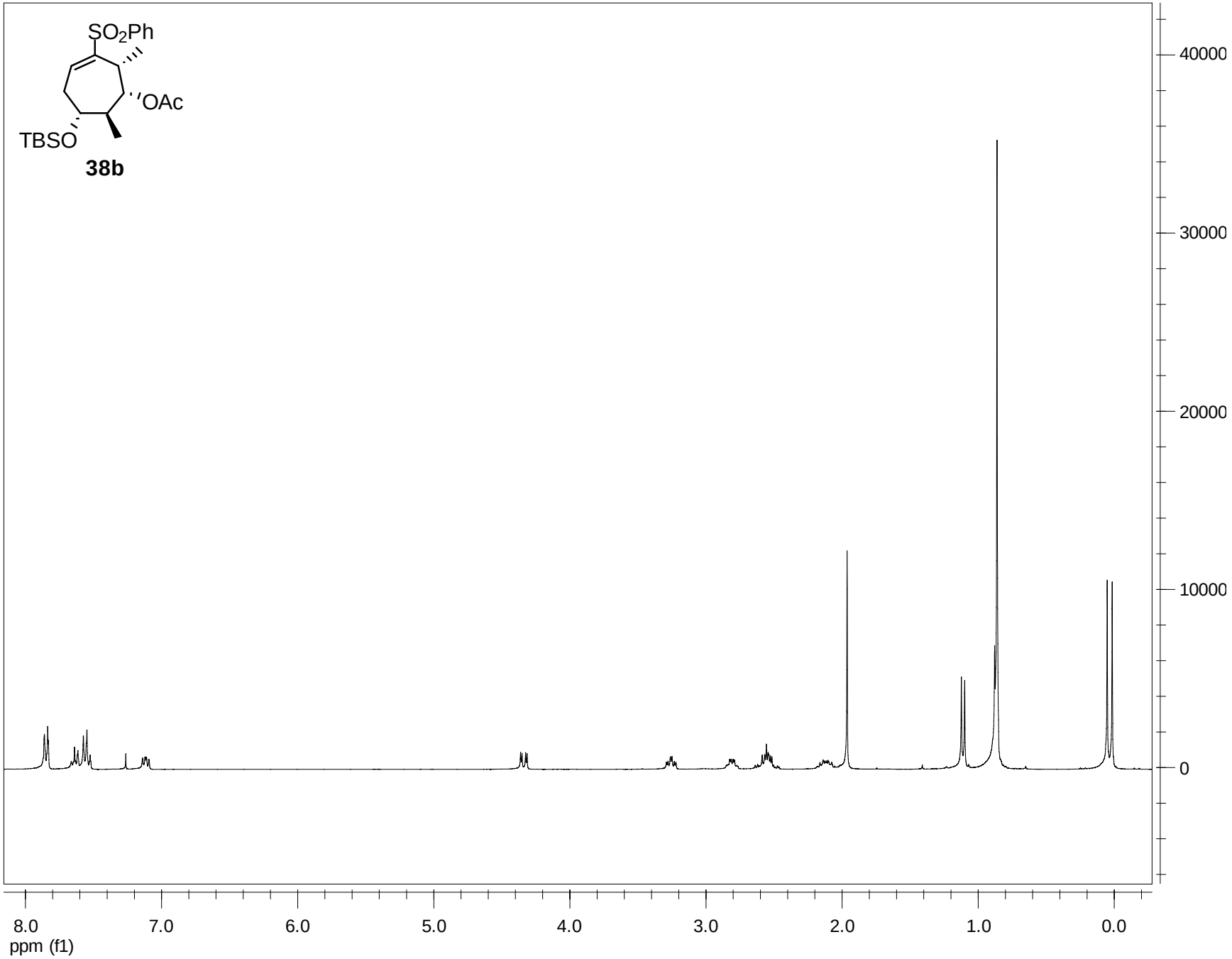
ppm (f1)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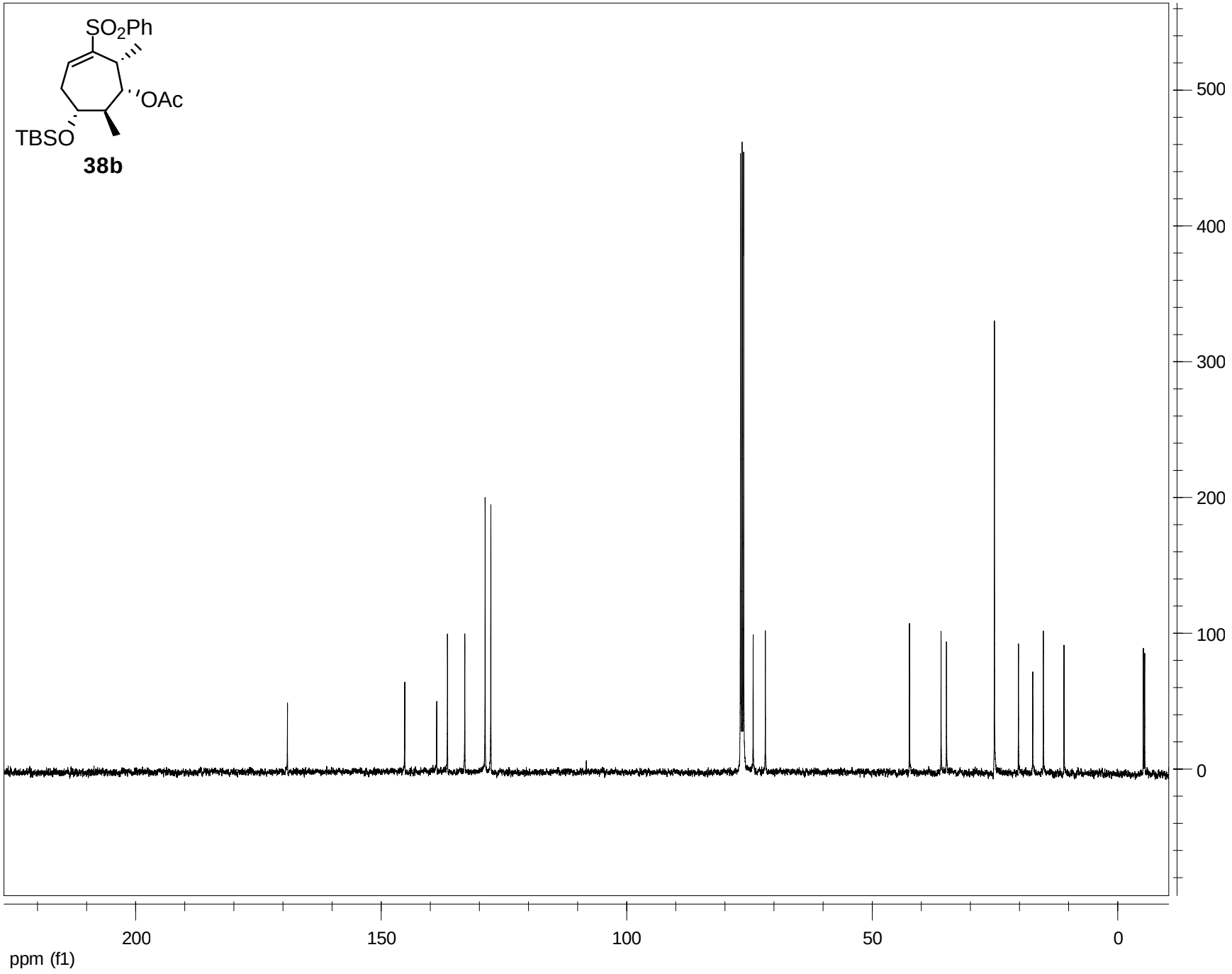
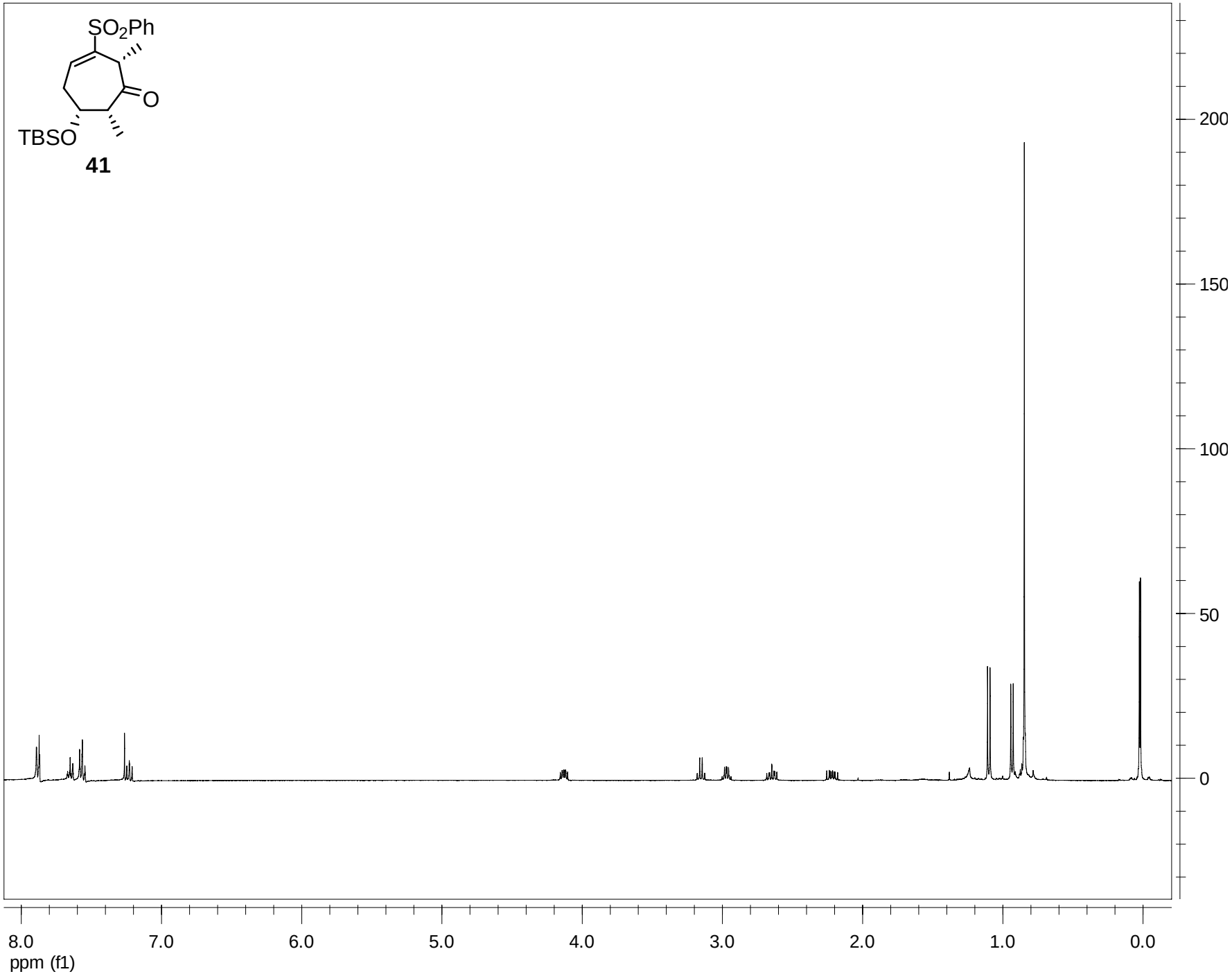
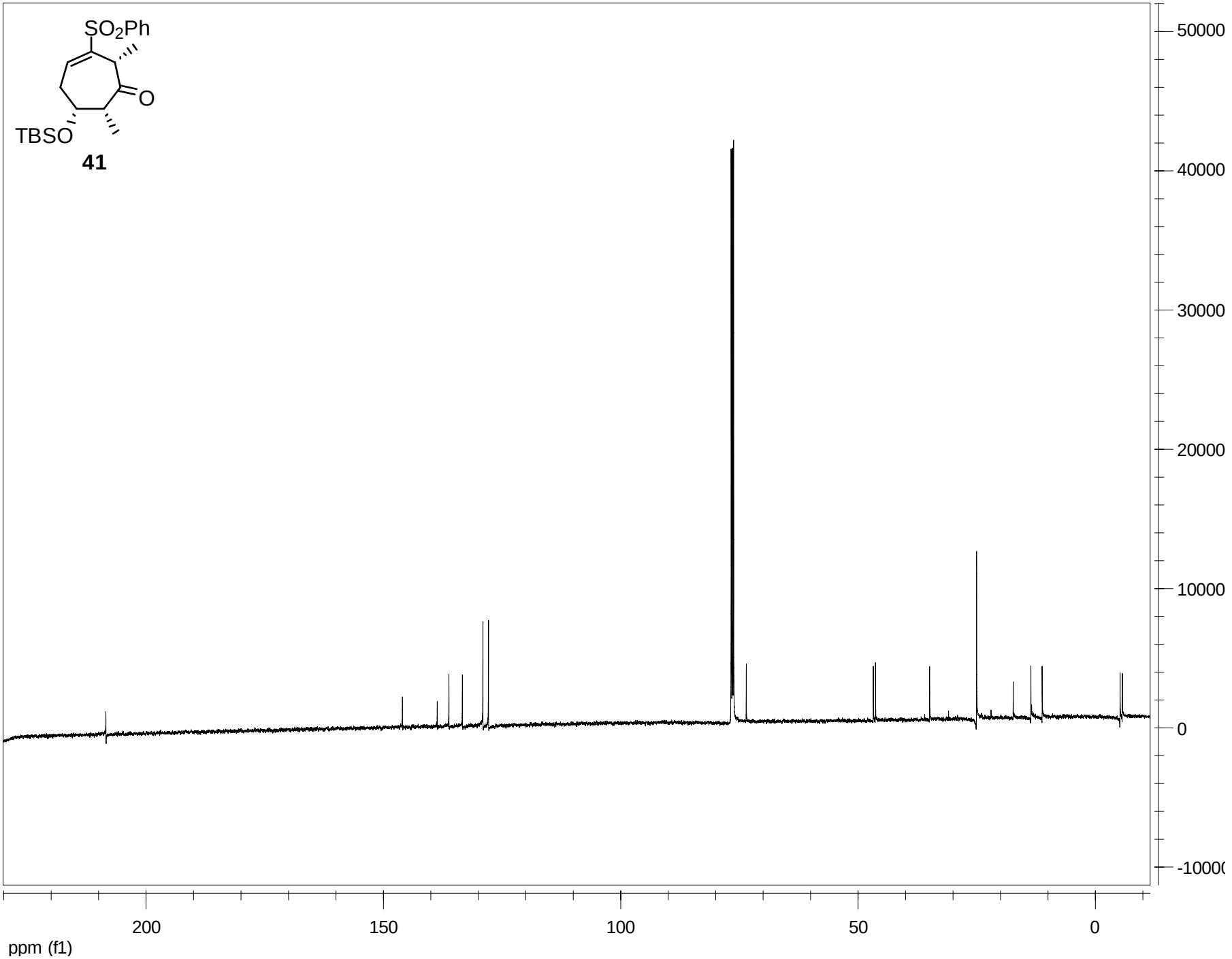
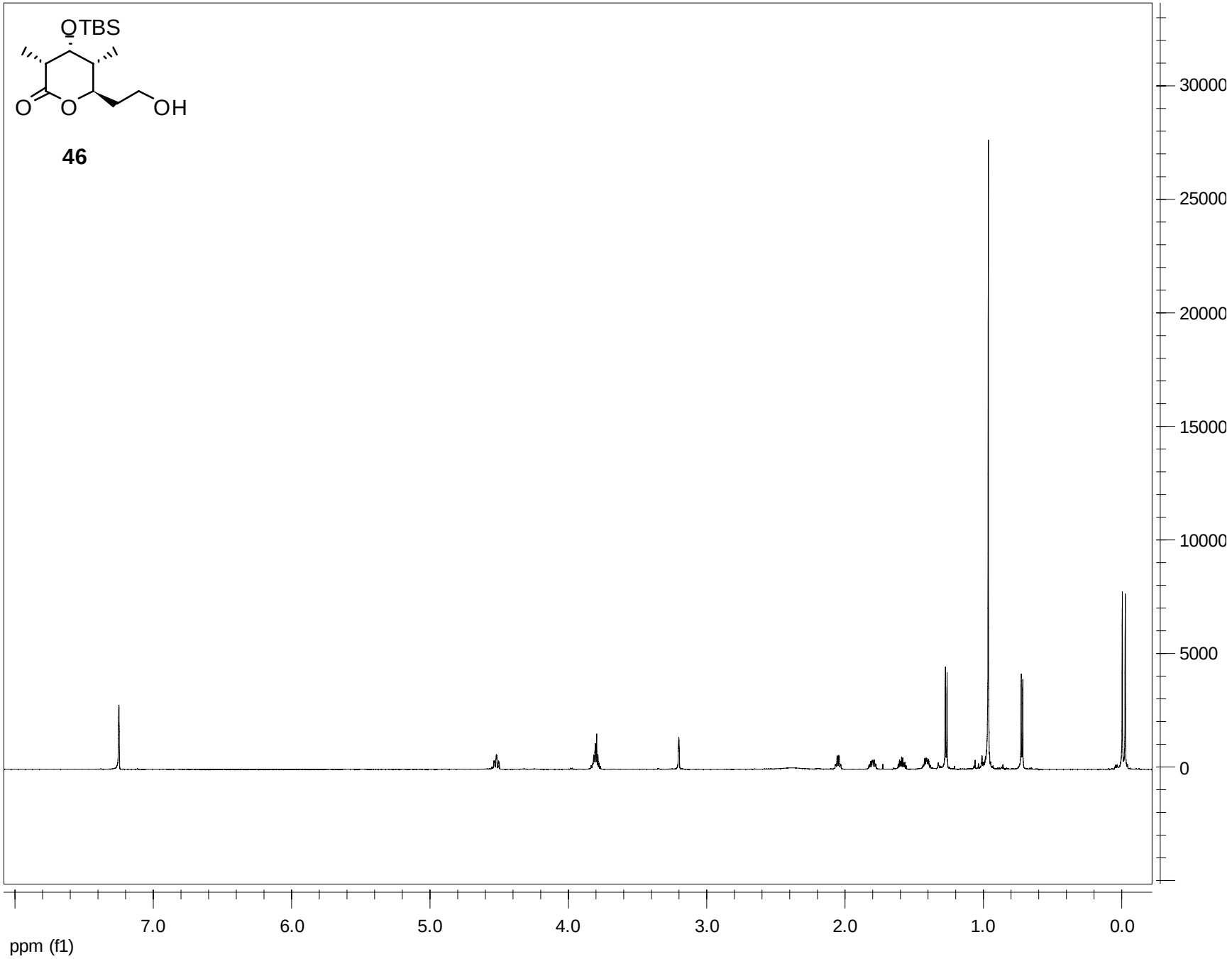
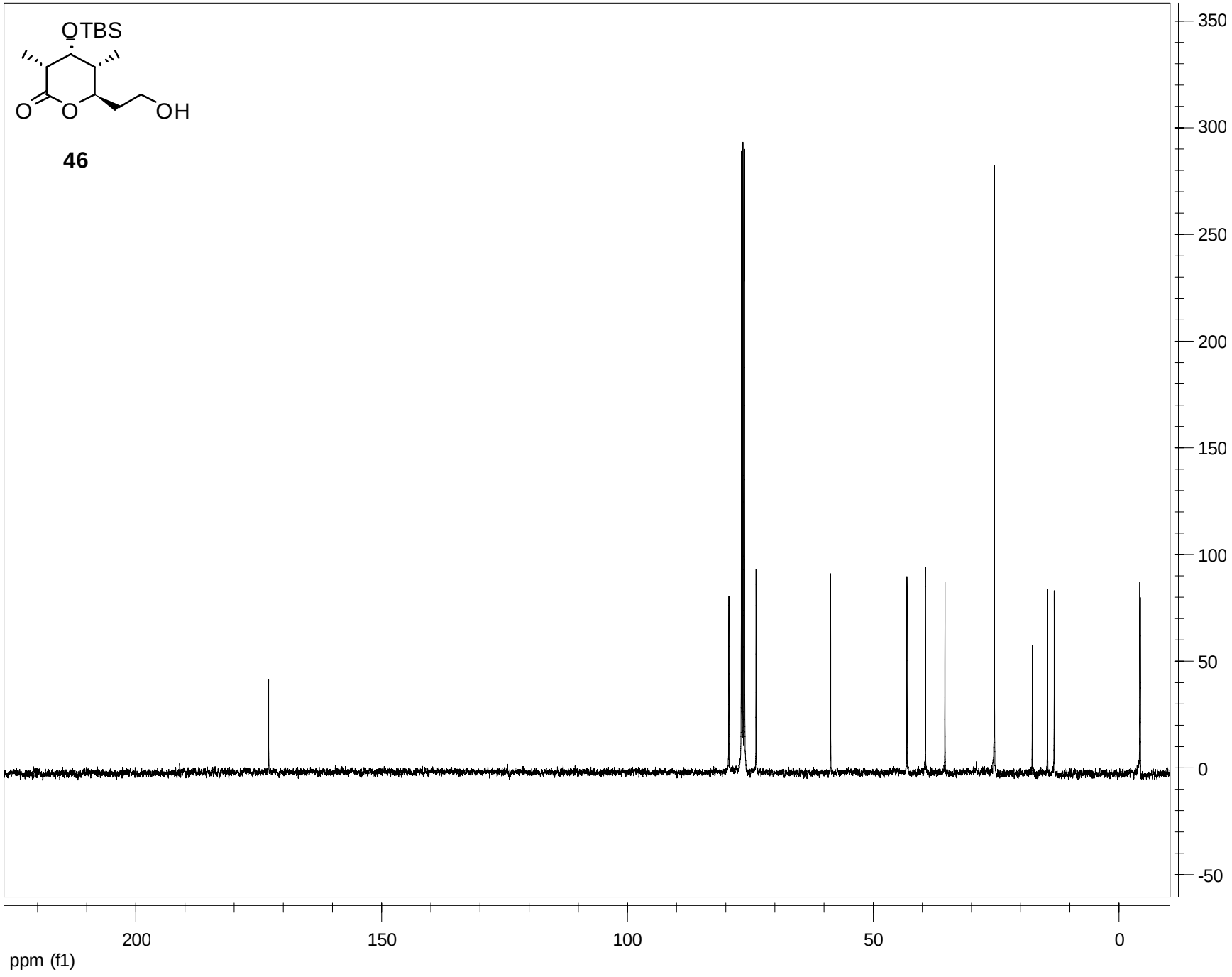
0.0
ppm (f1)


SO2Ph
OAc
TBSO
38b
500
400
300
200
100
0
200
150
100
50
0
ppm (f1)


SO2Ph
O
TBSO
41
200
150
100
50
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


SO2Ph
O
TBSO
41
50000
40000
30000
20000
10000
0
-10000
200
150
100
50
0
ppm (f1)


OTBS
O
O
OH
46
30000
25000
20000
15000
10000
5000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


OTBS
O
O
OH
46
350
300
250
200
150
100
50
0
-50
200
150
100
50
0
ppm (f1)