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S_N2' Addition/1,2-Elimination of Dimethylsulfonium Methylide with Epoxy Vinylsulfones: Synthesis of Exocyclic Cross-conjugated Dienylsulfones.

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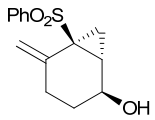
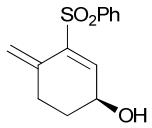
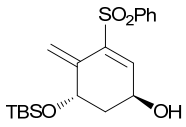
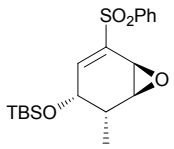
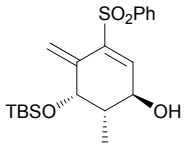
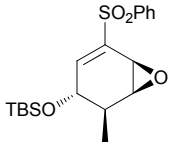
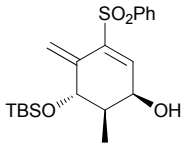
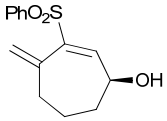
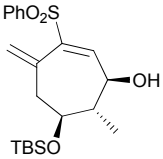
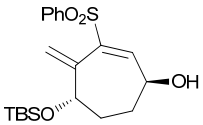
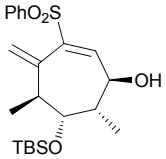
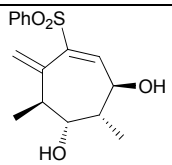
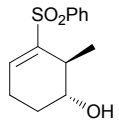
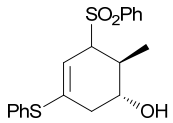
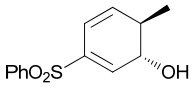
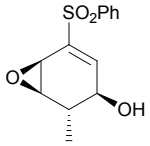
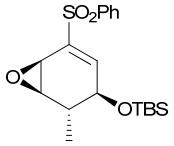
	2
	3
	7
	8

	9
	10
	11
	13
	15
	17
	19
	21

	25
	26
	27
	28
	29

Number in paper	^{1}H NMR	^{13}C NMR	HRMS	MP (^{o}C)	other
2	Y	Y	Y		
5	Y	Y	Y		
7	Y	Y	Y		
8	Y	Y	Y		
9	Y	Y	Y		

10	Y	Y	Y		NOE
11	Y	Y	Y		
13	Y	Y	Y		
15	Y	Y	Y		
17	Y	Y	Y		
19	Y	Y	Y		
21	Y	Y	Y		
25	Y	Y	Y	79.4 - 84.7	
26	Y	Y	Y		
27	Y	Y	Y		
28	Y	Y	Y		
29	Y	Y	Y	63.8 – 65.8	NOE

Supporting Information

GENERAL PROCEDURES

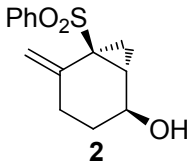
Trimethylsulfonium iodide and trimethylsulfoxonium ioide were purchased from Aldrich. Tetrahydrofuran (THF) was distilled from benzophenone ketyl. Sodium sulfate (Na_2SO_4) was anhydrous. Unless otherwise indicated, all reactions were carried out under in a positive pressure of Argon in anhydrous solvents and the reaction flasks were fitted with rubber septa for the introduction of substrates and reagents via syringe. Progress of reactions was monitored by thin layer chromatography (TLC) using silica gel plates. 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 Inova 300 (300 MHz). The NMR spectra were determined in $CDCl_3$ solution. Peak multiplicities in ^{1}H-NMR spectra, when reported, are abbreviated as s (singlet), d (doublet), t (triplet), m (multiplet), and/or quint (quintet). Mass spectra were run by the Purdue University campus wide mass spectrometry facility.

EXPERIMENTALS

Preparation of **2**:



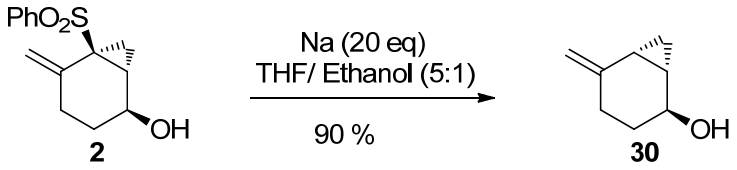
2

To a -10 °C suspension of trimethylsulfonium iodide (4.0 equiv, 1.69 mmol, 346 mg) in THF (6 mL) was added *n*-BuLi (3.7 equiv, 1.55 mmol, 0.62 mL of 2.5 M hexane solution). After 30 min epoxide **1** (1.0 equiv, 0.42 mmol, 100 mg) in THF (3 mL) was introduced and reaction slowly allowed to warm to room temperature over 2 hours and then quenched with water and extracted with diethyl ether or ethyl acetate. The combined extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using 1:3 Ethyl Acetate/Hexane to give the desired alcohol **2** in 87% yield (96 mg).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.89 (2H, d, J=8.4 Hz), 7.46 (3H, m), 5.65 (1H, s), 5.15 (1H, s), 4.26 (1H, s), 2.10-2.19 (2H, m), 1.63-1.78 (3H, m), 0.86 (2H, dd, J=5.1 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 138.79, 138.62, 133.20, 128.77, 128.64, 119.07, 63.44, 43.32, 28.376, 26.932, 26.026, 16.553, HRMS (EI/CI) calculated for $C_{14}H_{16}O_3S$ (M+) 264.0820, found 264.0818

Reductive Desulfonylation of **2**:

The desulfonylation reaction is done to prove the stereochemistry of quaternary sulfone. The ^{1}H and ^{13}C NMR of alcohol **30** is same as the reported NMR.[1]



Alcohol **2** (20 mg, 0.076 mmol) was dissolved in THF/ EtOH (3 mL, 5:1). The solution was cooled to 0 ^{o}C and Na (35 mg, 1.52 mmol) was added. The reaction mixture was stirred for 1 hr and excess sodium was quenched using CH_3OH until the H_2 evolution ceases. The solution is concentrated and loaded on the silica gel column. Flash column chromatography using 30 % ether/ pentane mixture gave alcohol **30** in 90 % yields (8 mg).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.91 (1H, s), 4.79 (1H, d, J= 3 Hz), 4.21 (1H, s), 3.55 (1H, d, J = 6 Hz), 2.29 (1H, m), 1.96 (1H, m), 1.26-1.81 (3H, m), 0.85 (1H, m), 0.37 (1H, dd, J=6 Hz, 12 Hz) ^{13}C NMR ($CDCl_3$, 75 MHz) δ 145.0, 109.1, 66.5, 28.7, 24.3, 20.4, 17.9, 11.0, HRMS (EI/CI) calculated for $C_8H_{12}O$ (M+) 124.0888, found 124.0885.

General Procedure for the reaction of epoxides with dimethylsulfonium methylide:

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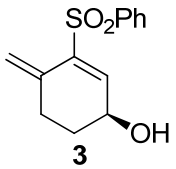
(1) Hodgso, D. M.; Chung, Y. K.; Nuzzo, I.; Freixas, G.; Kulikiewicz, K. K.; Cleator, E.; Paris, J. *J. Am. Chem. Soc.*, **2007**, *129*, 4456–4462.

To a -10 °C suspension of trimethylsulfonium iodide (2.8 equiv, 1.05 mmol, 816 mg) in THF (6 mL) was added *n*-BuLi (2.5 equiv., 3.70 mmol, 1.50 mL of 2.5 M hexane solution). After 30 min, the solution was cooled to -78 ^{o}C and epoxide **1** (1.0 equiv, 0.42 mmol, 100 mg) in THF (3 mL) was introduced. The reaction was left stirring for 5 minutes and then quenched with water and extracted with diethyl ether or ethyl acetate. The combined extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using 1:1 Ethyl Acetate/Hexane to give the desired allylic alcohol **5** in 52 % yield (58 mg).

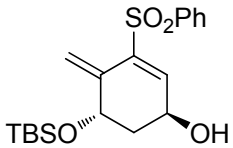
Preparation of **3**:



3

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.86 (2H, d, J= 7.5 Hz), 7.48 (3H, m), 7.19 (1H, s), 5.62 (1H, s), 5.09(s, 1H), 4.55 (1H, br s), 2.24 (1H, m), 2.39 (1H, m), 2.00 (1H, m), 1.61 (1H, m), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 142.76, 139.92, 139.49, 133.66, 133.26, 129.06, 127.43, 116.16, 66.44, 31.09, 30.39, HRMS (EI/CI) calculated for $C_{13}H_{14}O_3S$ (M+) 250.0664, found 250.0662.

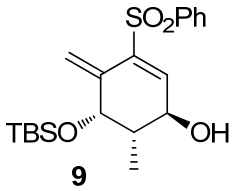
Preparation of **7**



7

^{1}H NMR ($CDCl_3$, 300 MHz): 7.82 (2H, d, J=8.4 Hz), 7.48 (3H, m), 7.23(1H, s), 5.81(1H, s), 5.26 (1H, s), 4.77(1H, s), 4.32 (1H, dd, J=2.1 Hz, 6Hz), 2.36 (1H, 6.6 Hz), 2.15 (1H, m), 1.72 (1H, m), 0.72 (9H, s),-0.04 (3H, s), -0.27 (3H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.7, 139.5, 137.3, 136.7, 133.1, 128.9, 127.6, 116.2, 71.7, 65.1, 39.7, 25.4, 17.8, -5.0, -5.2., HRMS (CI) calculated for $C_{19}H_{28}O_4SSi$ (M+H-H_2O) 363.1450, found 363.1449.

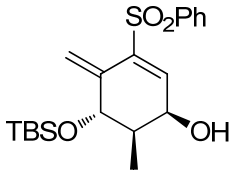
Preparation of **9**



9

^{1}H NMR ($CDCl_3$, 300 MHz): 7.83(2H, d, J = 7.2 Hz), 7.46 (2H, m), 7.22(1H, s), 5.82 (1H, s), 5.22 (1H, s), 4.36 (1H, d, J = 2.4Hz), 4.10 (1H, s), 1.81 (1H, m), 1.06(1H, d, J = 6.9 Hz), 0.69(9H, s,), -0.45(3H, s), -0.04(3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.9, 139.5, 137.1, 136.7, 133.1, 128.9, 127.7, 116.4, 77.1, 70.5, 42.6, 25.5, 17.8, 14.7, -4.7, -5.3. HRMS (CI) calculated for $C_{20}H_{30}O_4S$ (M+H-H_2O) 377.1607 found 377.1611.

Preparation of **11**



11

^{1}H NMR ($CDCl_3$, 300 MHz): 7.82 (2H, d, J=8.4 Hz), 7.47 (3H, m), 7.12 (1H, s), 5.87(1H, s), 5.21 (1H, s), 4.85(1H, t, J=5.4 Hz), 4.02 (1H, d, J=4.8 Hz), 2.32 (1H, d, J=7.2 Hz), 2.2 (1H, m), 0.77 (3H, d, J= 7.2 Hz), 0.71 (9H, s), -0.04 (3H, s), -0.34 (3H, s)

^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.4, 139.9, 136.5, 135.0, 133.0, 128.9, 127.6, 118.0, 78.2, 68.1, 40.3, 25.5, 17.7, 10.3, -4.8, -5.1. HRMS (CI) calculated for $C_{20}H_{30}O_4S$ (M+H-H_2O) 377.1607 found 377.1611.

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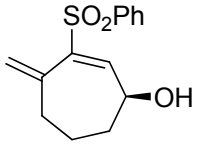

13

^{1}H NMR ($CDCl_3$, 300 MHz): 7.81(2H, d, J=8.1 Hz), 7.50 (3H, m), 7.24 (1H, d, J=3 Hz), 5.83 (1H, s), 5.21 (1H, s), 4.46 (1H, d, J=9.9 Hz), 2.43 (1H, s), 2.05 (1H, m), 1.53-1.89 (4H, m) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.4, 141.0, 139.0, 133.1, 128.8, 128.3, 120.2, 71.1, 35.9, 33.9, 26.8. HRMS (EI/CI) calculated for $C_{14}H_{16}O_3S$ (M+) 264.0820 found 264.0817.

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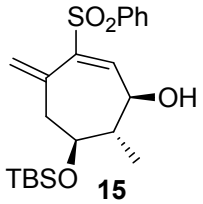
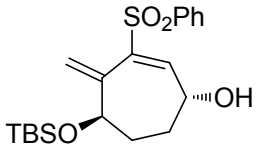


15

^{1}H NMR ($CDCl_3$, 300 MHz): 7.84(2H, d, J=6.6Hz), 7.48 (3H, m), 7.29 (1H, s), 5.48 (1H, s), 5.25 (1H, s), 4.27 (1H, q, J=6.6 Hz, 14.1 Hz), 4.08 (1H, d, J=8.1 Hz), 3.76 (1H, m), 2.02 (3H, m), 0.90 (d, 7.5 Hz), 0.87 (9H, s), 0.09 (3H, s), 0.05 (3H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.0, 142.2, 139.2, 133.5, 133.2, 128.9, 128.4, 75.9, 71.7, 41.3, 40.8, 25.6, 17.9, 14.7, -4.7, -5.0 HRMS (APCI) calculated for $C_{21}H_{32}O_4SSi$ (M+Na) 431.1688, found 431.1689.

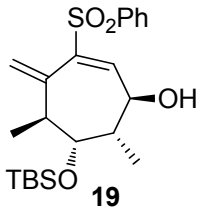
Preparation of **17:**



17

^{1}H NMR ($CDCl_3$, 300 MHz): 7.80(2H, d, J=6.9Hz), 7.48 (3H, m), 7.32 (1H, d, J=2.7 Hz), 5.61 (1H, s), 5.30 (1H, s), 4.43 (1H, d, J=5.1 Hz), 3.53 (1H, dd, J= 3.6 Hz, 8.7 Hz), 2.10-1.80 (4H, m), 0.80 (9H, s), -0.17 (3H, s), -0.27 (3H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.9, 141.8, 138.9, 138.5, 133.2, 128.9, 128.6, 117.7, 71.4, 70.6, 37.8, 34.4, 29.5, 25.5, 17.8, -5.2, -5.4. HRMS (CI) calculated for $C_{20}H_{30}O_4SSi$ (M+H) 395.1712 found 395.1717.

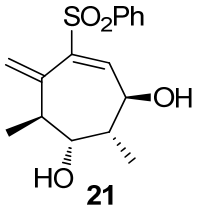
Preparation of **19**:



19

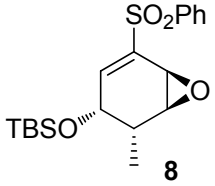
^{1}H NMR ($CDCl_3$, 300 MHz): 7.81(2H, d, J=6.9Hz), 7.48 (3H, m), 7.21 (1H, d, J=3.3 Hz), 5.54 (1H, s), 5.2 (1H, s), 4.50 (1H, m), 3.49 (1H, d, J=4.8 Hz), 2.28 (1H, m), 1.93-2.06 (2H, m), 1.01(3H, d, 6.9 Hz), 0.36 (3H, d, 6.9 Hz), 0.02 (6H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.4, 138.6, 138.4, 133.2, 129.1, 128.6, 121.7, 78.4, 69.1, 47.0, 36.2, 25.8, 18.0, 16.3, 15.0, -3.6, -4.8. HRMS (CI) calculated for $C_{22}H_{34}O_4SSi$ (M+H) = 423.2025, 423.2017.

Preparation of **21:**



^{1}H NMR ($CDCl_3$, 300 MHz): 7.82 (2H, d, J=6.3 Hz), 7.47(3H, m), 7.24 (1H, d, J=2.4 Hz) 5.71 (1H, s), 5.34 (1H, s), 4.41(1H, dd, J =2.4Hz, 10.8 Hz), 3.46(1H, dd, J=2.4 Hz, 6 Hz), 2.21 (1H, t, J=6.6 Hz), 1.97 (1H, m), 1.12 (3H, d, J=6.9 Hz), 0.54 (3H, d, J=6.9 Hz),^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.9, 139.9, 138.8, 138.3, 133.4, 128.9, 128.8, 121.3, 68.9, 47.0, 37.3, 29.6, 15.4. HRMS (EI/CI) calculated for $C_{16}H_{20}O_4S$ (M+) 308.1082 found 308.1085.

Preparation of epoxide 8**:**

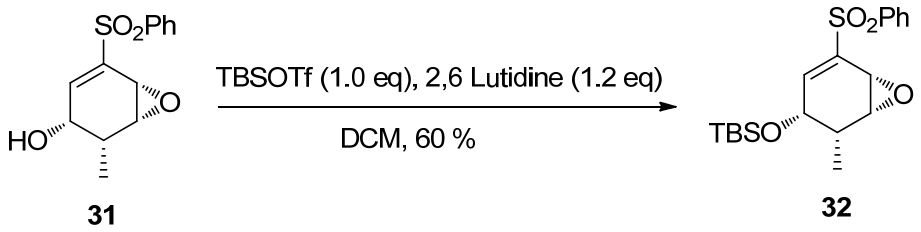


1,1,1 trifluoroacetone (1 mL, 23.7 mmol) was added to a 5 ^{o}C cooled solution of dienyl sulfone **23** (900 mg, 2.37 mmol) in CH_3CN (10 mL) and H_2O (10 mL) mixture. The solution was vigorously stirred and portion wise the mixture of Oxone (4.37 g, 7.11 mmol) and $NaHCO_3$ (1.19 g, 14.21 mmol) is added over 2 hrs. The reaction mixture is diluted with 20 mL water and extracted with dichloromethane (30 mL). The combined extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using Ethyl Acetate/Hexane (1:4) to give epoxide **8** in 84 % yield (750 mg).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.91 (1H, d, J= 7.8 Hz), 7.54 (3H, m), 6.87 (1H, s), 4.42 (1H, d, J= 6.9 Hz), 3.62 (1H, m), 3.38 (1H, m), 2.59 (1H, m), 0.87 (9H, s), 0.78 (3H, d, J= 6.9 Hz), 0.09 (3H, s), 0.07 (3H, s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.8, 139.3, 136.7,

133.6, 129.5, 129.4, 127.9, 66.6, 55.9, 45.2, 31.8, 25.6, 17.9, 9.0, -5.0, HRMS (ESI) calculated for $C_{19}H_{28}O_4SSi$ (M+Na) 403.1375 found 403.1377.

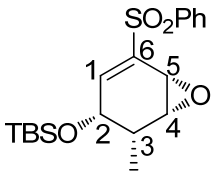
Preparation of **32**



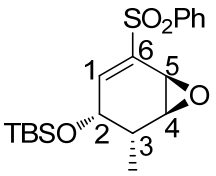
Compound **31** (50 mg, 0.188 mmol) was dissolved in dry DCM (1.5 mL) and cooled to 0 ^{o}C. 2, 6 Lutidine (24.1 mg, 0.23 mmol, 26 μL) was added followed by drop wise addition of TBSOTf (50 mg, 44 μL). The mixture was left stirred for 1 hr at room temperature and then quenched with water and extracted with DCM. The combined extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using Ethyl Acetate/Hexane (1: 4) to give epoxide **32** in 60 % yield (42 mg).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.91 (2H, d, J=6.9 Hz), 7.53 (3H, m), 7.02 (1H, dd, J=1.8 Hz, 4.8 Hz), 4.42 (1H, t, 5.1 Hz), 3.61 (1H, dd, J=1.8 Hz, 4.2 Hz), 3.40 (1H, m), 2.08 (1H, m), 1.11 (3H, d, J= 6.9 Hz), 0.84 (9H, s), 0.06 (3H, s), 0.05 (3H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 142.3, 140.0, 139.2, 133.7, 129.3, 127.8, 66.5, 58.0, 45.2, 33.3, 25.5, 17.9, 12.0, -4.3, -5.0. HRMS (ESI) calculated for $C_{19}H_{28}O_4SSi$ (M+Na) 403.1375 found 403.1377.

Stereochemistry of epoxide **8:**



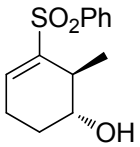
32



8

Compound **32** is obtained after the silyl ether protection of the compound previously prepared.[2] Proton and carbon NMR's of the two epoxides **32** and **8** have distinctly different ppm values confirming their different identity as diasteromers. For example: The proton at C-1 has a ppm value of 7.02 (dd, J=1.8 Hz, 4.8 Hz) for compound **32** wheras 6.87 (s) for compound **8**. For additional details, see reference 2.

Preparation of **25** via epoxide cleavage:



25

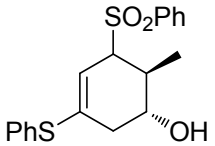
25 % Trimethylaluminum in hexane (127.1 mmol, 51 mL) is dissolved in DCM (200 mL) and cooled to –20 ^{o}C. DI-H_2O (25.4 mmol, 0.5 mL) is added slowly over 30 min so as to avoid an exotherm. After stirring for 1 hr, the solution is brought to rt and epoxide **24** (10 g, 42.4 mmol) dissolved in DCM (50 mL) is added dropwise over 30 min. After 1 hr stirring, the solution is poured to an ice cold solution of 10 % NaOH. The organic phase is separated, washed with brine, dried over sodium sulfate and concentrated to afford a crude product which was purified using 1:1 ethyl acetate and hexane mixture to give a white solid **25** in 98 % yield (10.4 g). MP: 79.4 - 84.7 ^{0}C.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.86 (2H, d, J= 9 Hz), 7.50 (3H, m), 7.09 (1H, t, J= 3 Hz), 3.84 (1H, d, J= 3 Hz), 2.27 (2H, m), 1.72 (2H, m), 1.55 (1H, d, J= 3 Hz), 1.07 (3H, d, J= 9 Hz), ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.8, 139.4, 139.1, 132.9, 132.7, 128.9, 128.6,

2 Chen, Y.; Evarts, J. B.; Torres, E.; Fuchs, P. L. *Org. Let.*, **2002**, 4, 3571-3574.

127.1, 69.2, 35.5, 22.2, 21.1, 18.4, HRMS (EI/CI) calculated for $C_{13}H_{16}O_3S$ (M+) 252.0820 found 252.0824.

Preparation of **26:**



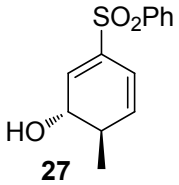
26

To a solution of vinyl sulfone **25** (3 g, 11.9 mmol) in THF (50 mL) was added 2.0 M NaHMDS in THF (38 mmol, 19 mL) at room temperature during which time the reaction color changed to deep red with formation of a red precipitate.[3] After 3 hrs of stirring, PhSSPh (3.1 g, 14.3 mmol) dissolved in THF (20 mL) is added and the reaction quenched after 6 hr by 5 % HCl. The solution is left stirring for 1 hr and then diluted with EtOAc. The combined organic phase is separated and washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using Ethyl Acetate/ Hexane (30 %) to give allylic alcohol **26** in 71 % yield (3 g).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.72 (2H, d, J= 8.4 Hz), 7.59 (1H, t, J= 7.4 Hz), 7.45 (2H, t, J= 7.8 Hz), 7.35-7.29 (5H, m), 5.23 (1H, d, J= 3.3 Hz), 3.54 (2H, m), 3.41 (1H, s), 2.33-2.23 (2H, m), 2.00 (1H, m), 1.16 (3H, d, J= 7.2 Hz) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.5, 136.4, 133.8, 133.7, 130.5, 129.3, 129.1, 129.0, 128.6, 112.8, 69.9, 69.5, 35.6, 34.2, 18.4. HRMS (CI) calculated for $C_{19}H_{21}O_3S_2$ (M+H) 361.0932, found 361.0926.

Preparation of **27:**

3 Torres, E.; Chen, Y.; Kim, I. C.; Fuchs, P. L. *Angew. Chem. Int. Ed.* **2003**, *42*, 3124 – 3131.

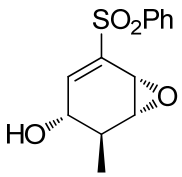


27

Compound **26** (1g, 2.78 mmol) was dissolved in dry DCM (300 mL) and Et_3N (20.8 mmol, 2.9 mL) is added followed by TMSOTf (13.9 mmol, 2.52 mL) at room temperature. The mixture is refluxed for 8 hr and the diluted with 500 mL of water. The organic layer is separated and cooled to 0 ^oC. mCPBA is added over the period of 6 hrs in small portions and reaction mixture stirred for another 4 hr at room temperature. Saturated solution of $NaHSO_3$ is added followed by EtOAc. The organic layer is separated, washed with saturated $NaHCO_3$ followed by brine and dried over magnesium sulfate. The solution is filtered and concentrated under vacuum. The residues were purified on silica gel using Ethyl Acetate/Hexane (1:1) to give dienyl alcohol **27** in 80% yield (550 mg).

^1H NMR ($CDCl_3$, 300 MHz): 7.86 (2H, d, J=8.1 Hz), 7.47 (3H, m), 6.8(1H, d, J=3.3 Hz), 5.99(1H, d, J= 9.9 Hz), 5.86 (1H, dd, J=3.9 Hz, 9.9 Hz), 4.21(1H, dd, J=3.6 Hz, 10.2 Hz), 3.7 (1H, brs), 2.41 (1H, m), 0.98 (1H, d, J=7.2 Hz) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.8, 138.2, 136.7, 135.2, 133.5, 128.1, 127.7, 116.4, 71.1, 36.3, 16.9. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.57; H, 5.67.

<u>Preparation of epoxide **28:**</u>



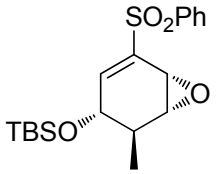
28

Compound **27** (50 mg, 0.18 mmol) was dissolved in benzene (1.5 mL) and $Mo(CO)_6$ (3 mg, 0.009 mmol) was added followed by 65 µL of *t*-BuOOH (0.36 mmol, 5-6 M in decane). The mixture was refluxed for 1 hr at 85 ^oC, brought to room temperature

and then loaded directly on the silica gel column and eluted with CH_2Cl_2/ CH_3CN (10:1). The epoxide **28** was isolated in 85 % yield (39 mg).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.83 (2H, d, J=6.9 Hz), 7.47 (3H, m), 7.16 (1H, dd, J=2.1 Hz, 6.9 Hz), 3.92 (1H, m), 3.74 (1H, dd, J=1.8 Hz, 3.6 Hz), 3.52 (1H, m), 2.55 (1H, dd, J=7.5 Hz, 14.7 Hz), 2.1 (1H, d, J=12.3 Hz), 0.74 (3H, d, J= 7.2 Hz) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.5, 138.8, 138.7, 134.0, 129.5, 127.9, 67.6, 59.7, 46.2, 33.1, 13.1 Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30. Found: C, 58.34; H, 5.30.

Preparation of epoxide **29**:

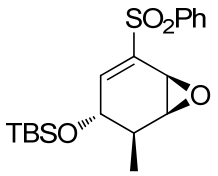


29

Compound **29** (20 mg, 0.075 mmol) was dissolved in dry DCM (1.0 mL) and cooled to 0 ^{o}C. 2, 6-Lutidine (0.09 mmol, 10 μL) was added followed by dropwise addition of TBSOTf (0.075 mmol, 17 μL). The mixture was stirred for 1 hr at room temperature and then quenched with water and extracted with DCM. The combined extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using Ethyl Acetate/Hexane (1: 4) to give epoxide **29** in 90% yield (25 mg). MP: 63.8 – 65.8 ^{o}C.

^{1}H NMR ($CDCl_3$, 300 MHz): 7.90 (2H, d, J=8.7 Hz), 7.53 (3H, m), 6.98 (1H, dd, J=1.5 Hz, 3.9 Hz), 4.22(1H, m), 3.54 (1H, dd, J=1.5 Hz, 4.2 Hz), 3.24 (1H, m), 2.0 (1H, m), 1.04 (3H, d, J=7.5 Hz), 0.87 (9H, s), 0.08 (6H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.8, 139.7, 139.1, 133.7, 129.3, 127.9, 70.7, 58.2, 44.2, 37.2, 25.6, 17.9, 15.8, -4.3, -4.8. HRMS (ESI) calculated for $C_{19}H_{28}O_4SSi$ (M+Na) 403.1375 found 403.1377.

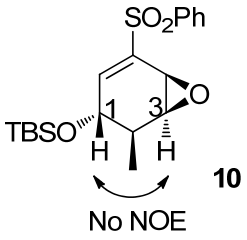
Preparation of epoxide **10:**



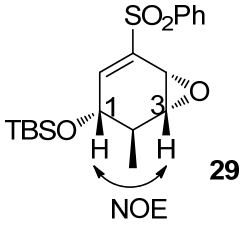
10 Alcohol **27** (500 mg, 2 mmol) was dissolved in dry DCM (50 mL) and cooled to 0 ^{o}C. Et_3N (2.4 mmol, 0.33 mL) was added followed by dropwise addition of TBSOTf (2.2 mmol, 0.51 mL). The mixture was stirred for 1 hr at 0 ^{o}C and then quenched with water (100 mL) and extracted with DCM. The combined extracts were washed with brine, dried over magnesium sulfate, filtered, and concentrated under vacuum. The pale yellow oil is dissolved in 10 mL CH_3CN/ H2O (1:1) and cooled to 8 - 10 ^{o}C. 1,1,1 trifluoroacetone (20 mmol, 1.7 mL) is added followed by mixture of Oxone (6 mmol, 3.7 g) and $NaHCO_3$ (12 mmol, 1 g) in small portions over a period of 3 hr. The reaction mixture is diluted with 20 mL water and extracted with dichloromethane (30 mL). The combined extracts were washed with brine, dried over sodium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel using Ethyl Acetate/Hexane (1:4) to give epoxide **10** in 80% yield (0.6 g).

^{1}H NMR ($CDCl_3$, 300 MHz): 7.87 (2H, d, J=7.8 Hz), 7.50 (3H, m), 6.89 (1H, d, J=1.5 Hz), 3.88 (1H, d, J=9.3 Hz), 3.67 (1H, t, J=2.4 Hz), 3.33 (1H, d, J=3 Hz), 1.72 (1H, m), 1.26 (3H, d, J=6.9 Hz), 0.88 (9H, s), 0.08 (3H, s), 0.05 (3H, s) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.9, 139.1, 137.6, 133.6, 129.3, 127.7, 69.9, 56.2, 46.6, 34.7, 46.6, 34.7, 25.5, 17.7, 16.0, -4.5, -4.9. HRMS (ESI) calculated for $C_{19}H_{28}O_4SSi$ (M+Na) 403.1375 found 403.1377.

<u>Stereochemistry of epoxides **29** and **10:**</u>

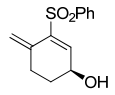


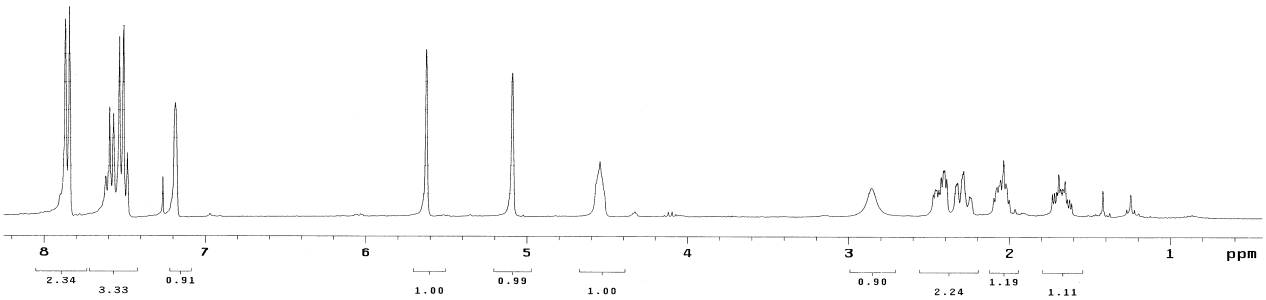
10



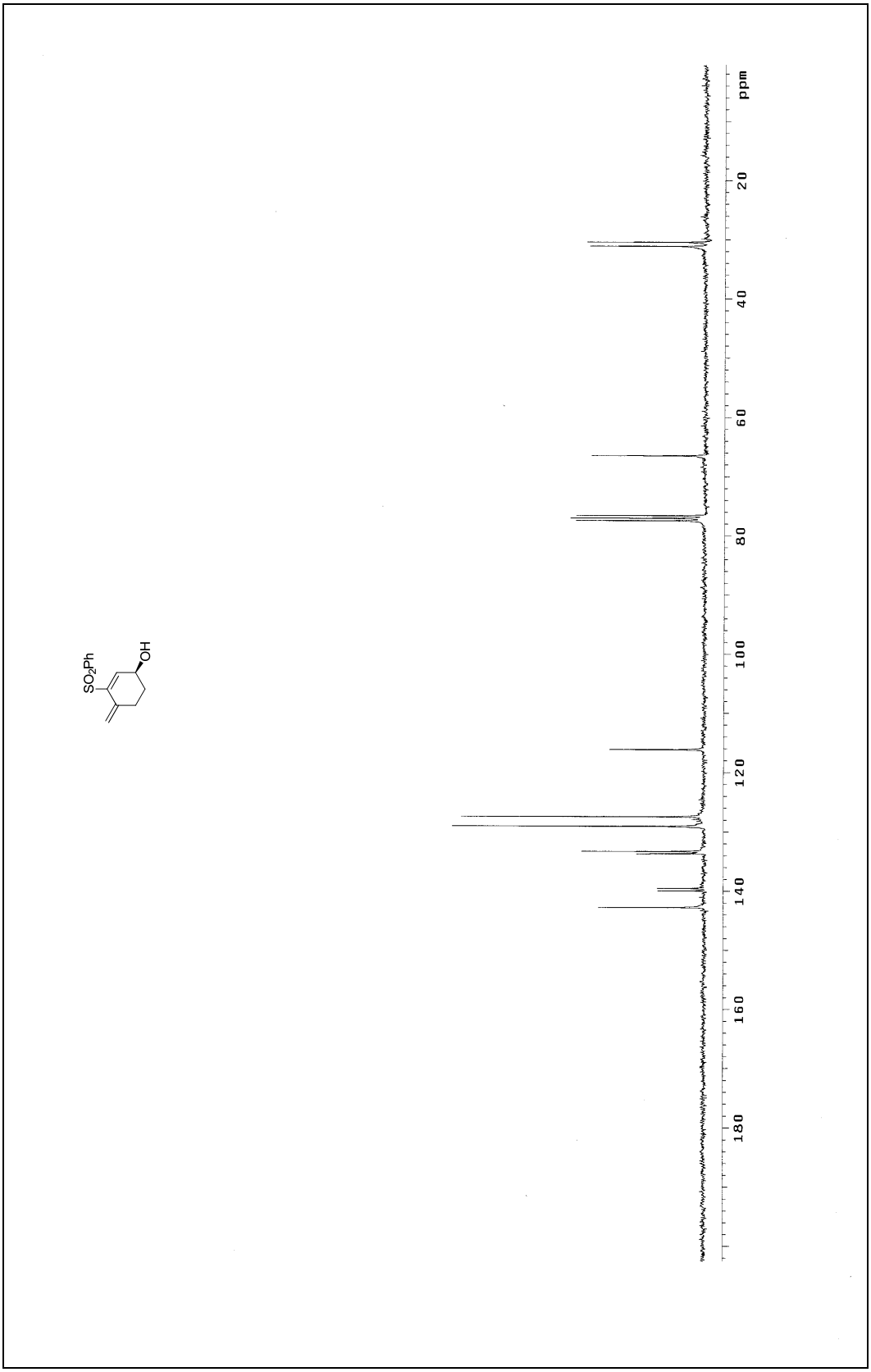
29

Irradiating the proton at C-1 shows the enhancement of 74% in NOE for proton at C-3 in the case of compound **29**. The same NOE experiment done for the compound **10** showed a –22% enhancement. This confirms the stereochemistry on the epoxide **10**. For the details see below.

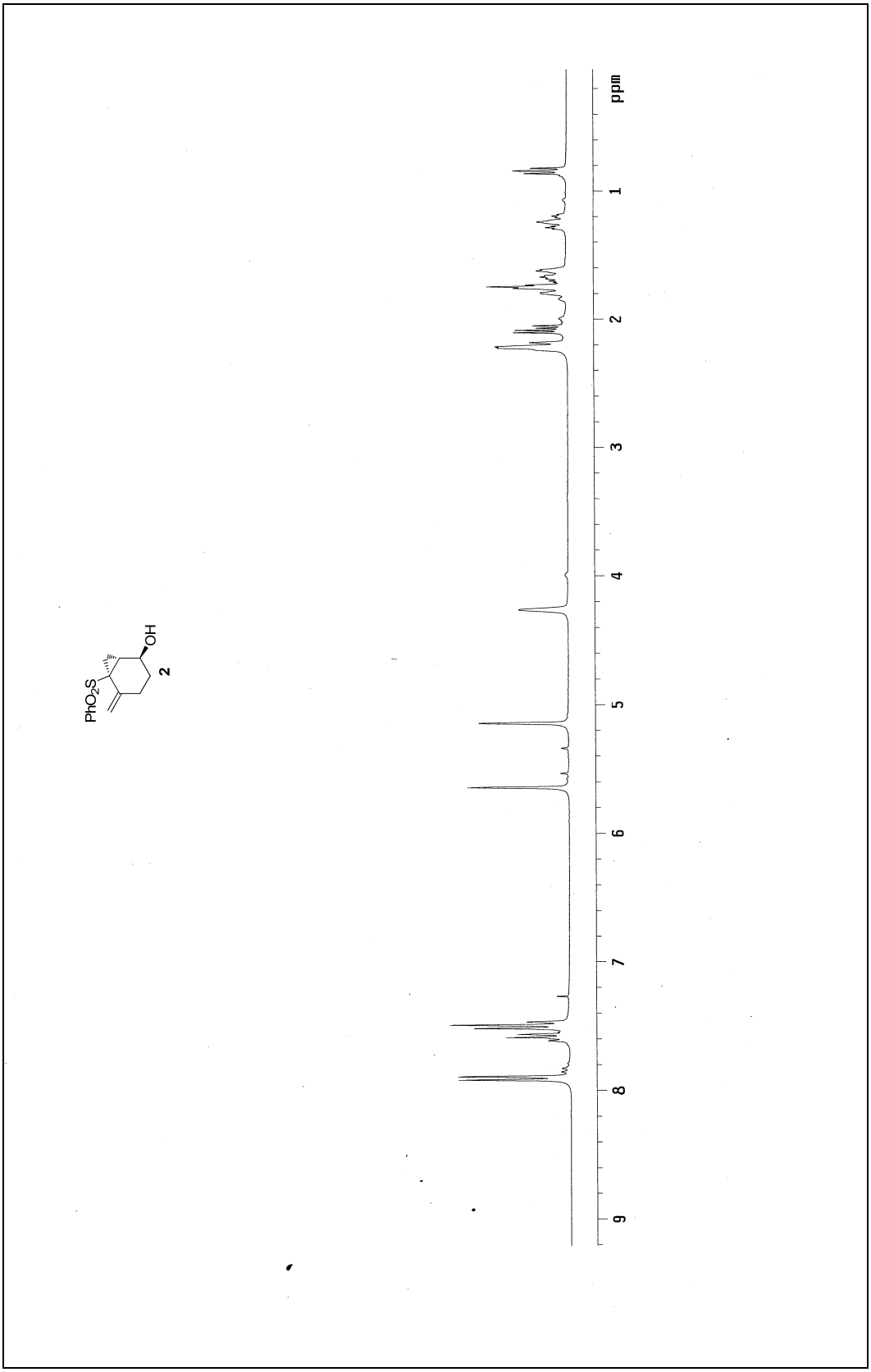




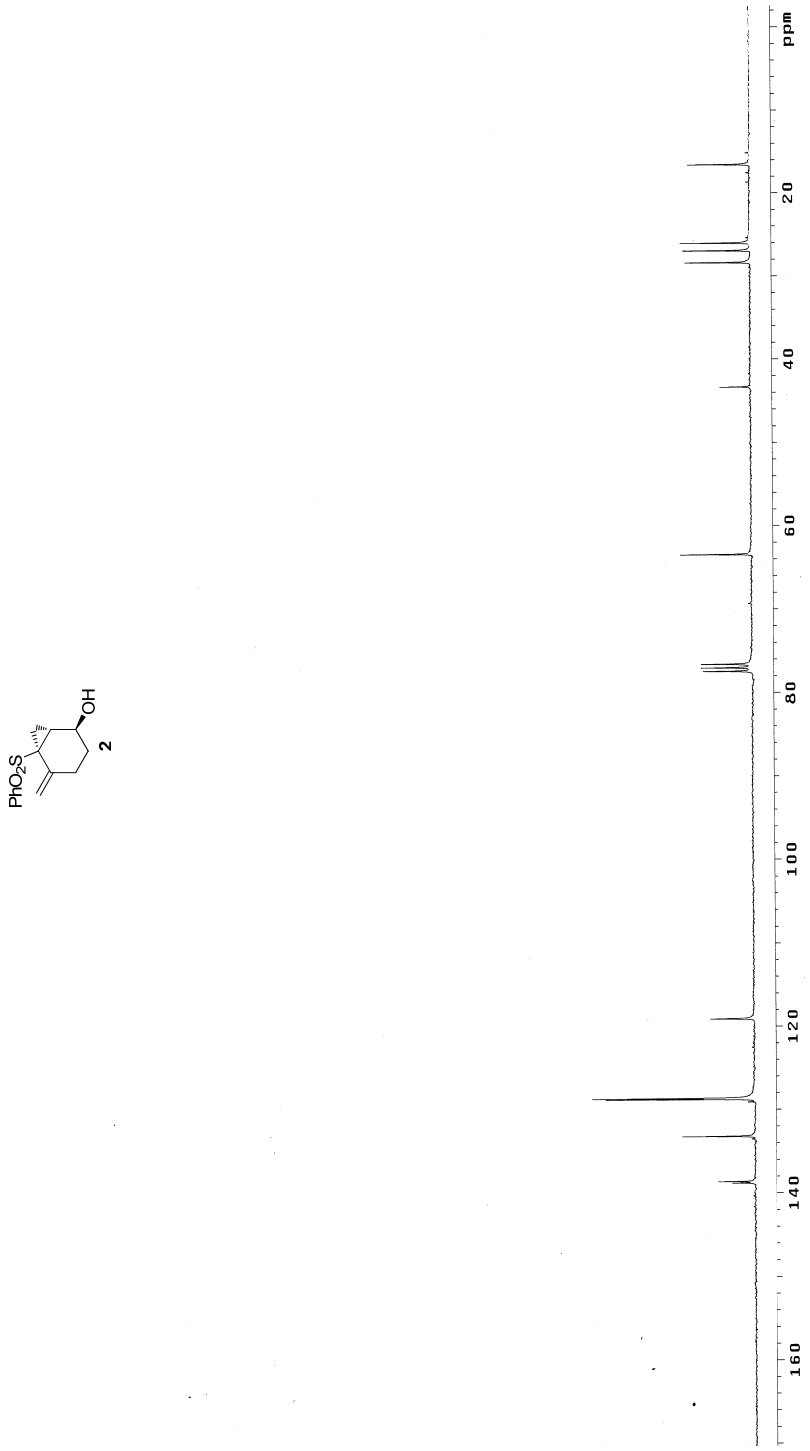
300 MHz ^{1}H NMR of compound **5** in $CDCl_3$



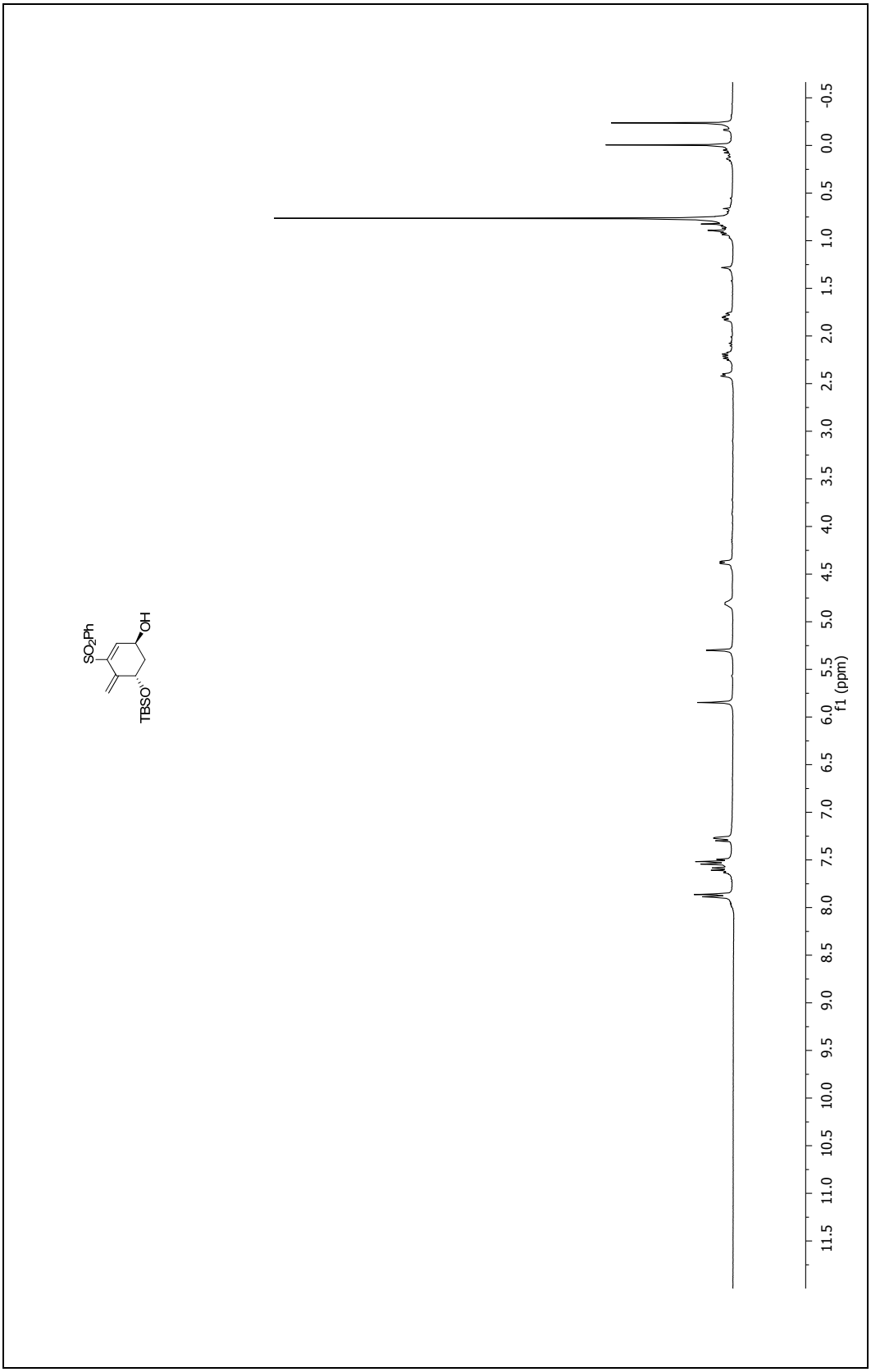
75 MHz ^{13}C NMR of compound **5** in $CDCl_3$



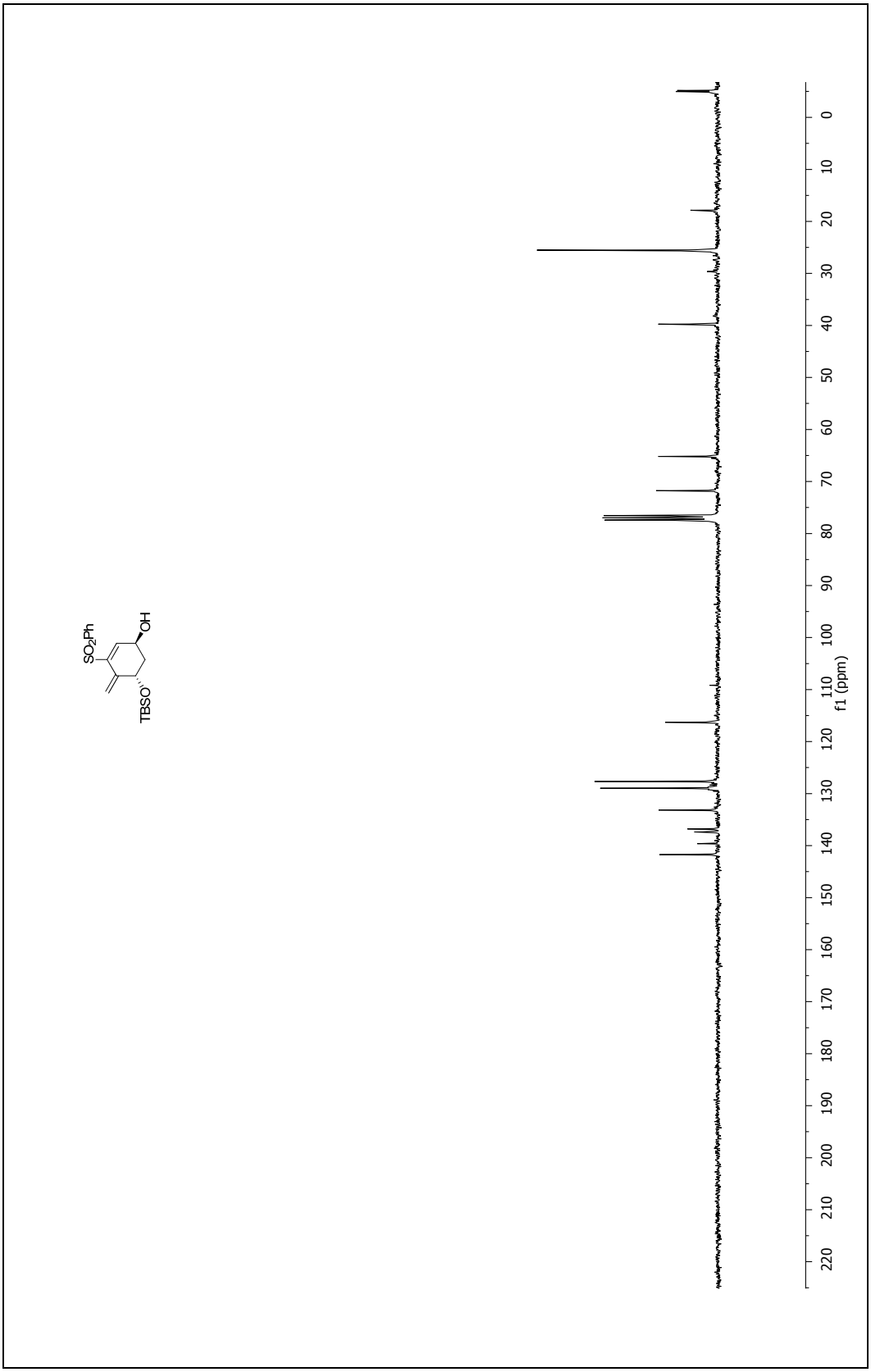
300 MHz ^{1}H NMR of compound **2** in $CDCl_3$



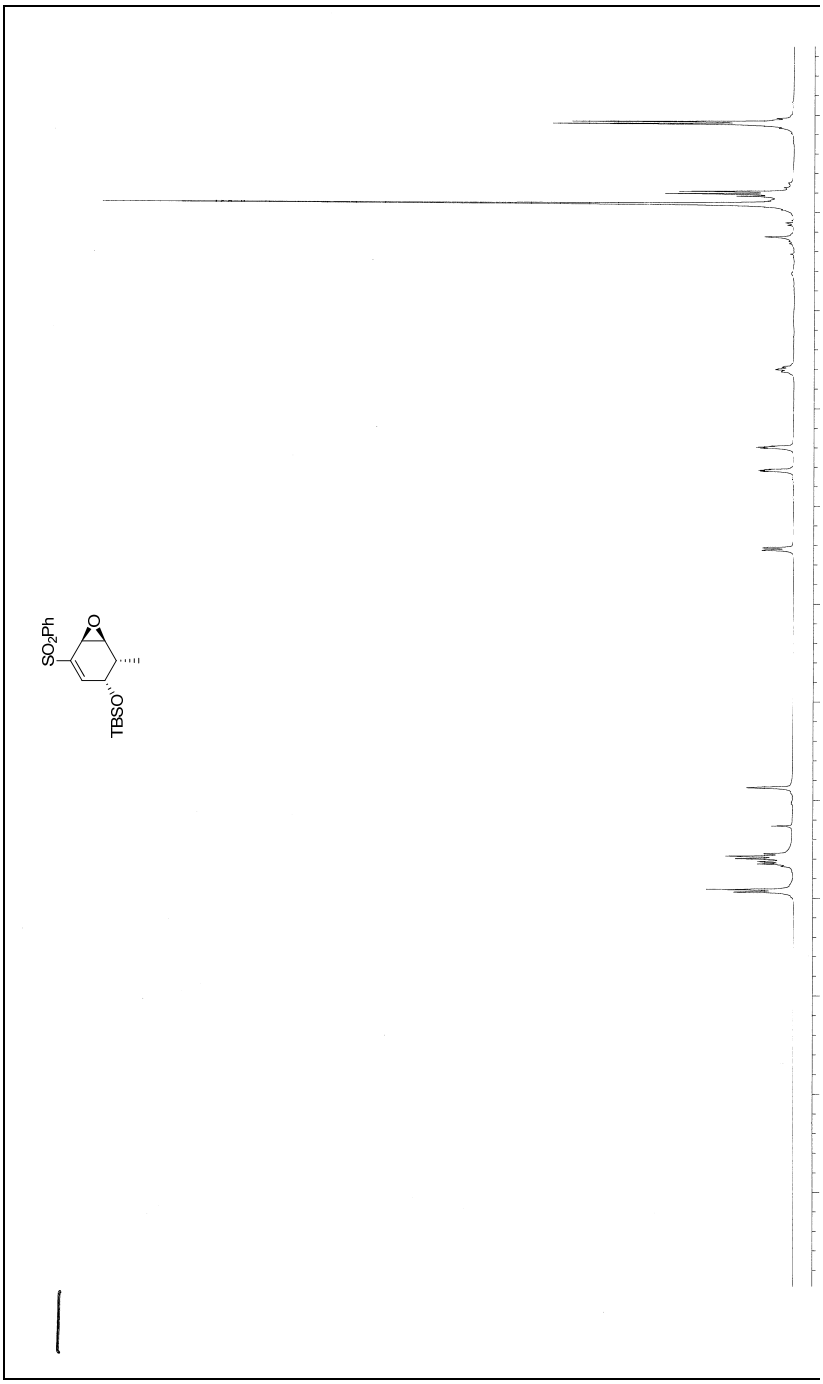
75 MHz ^{13}C NMR of compound **2** in $CDCl_3$



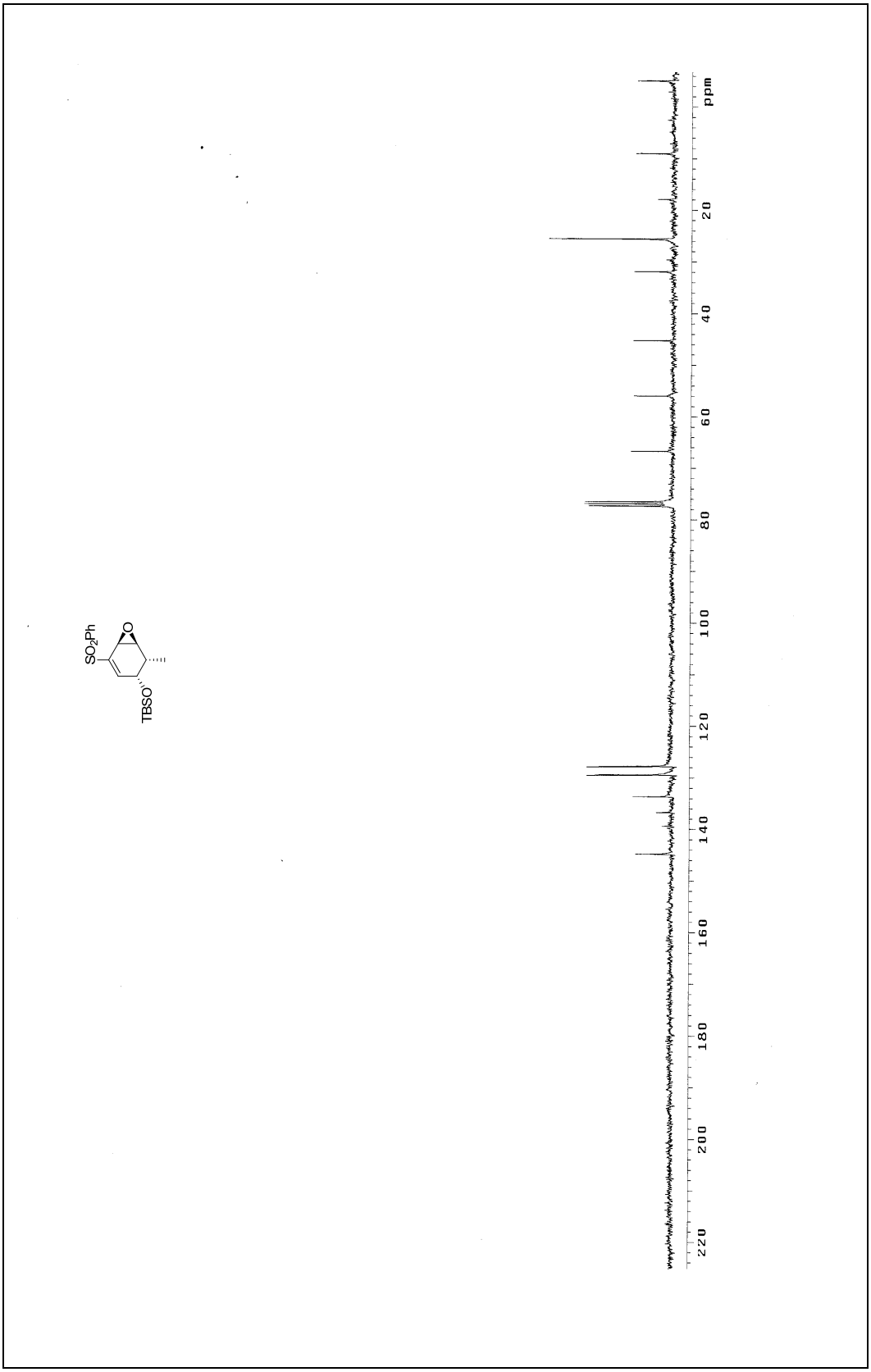
300 MHz ^{1}H NMR of compound **7** in $CDCl_3$



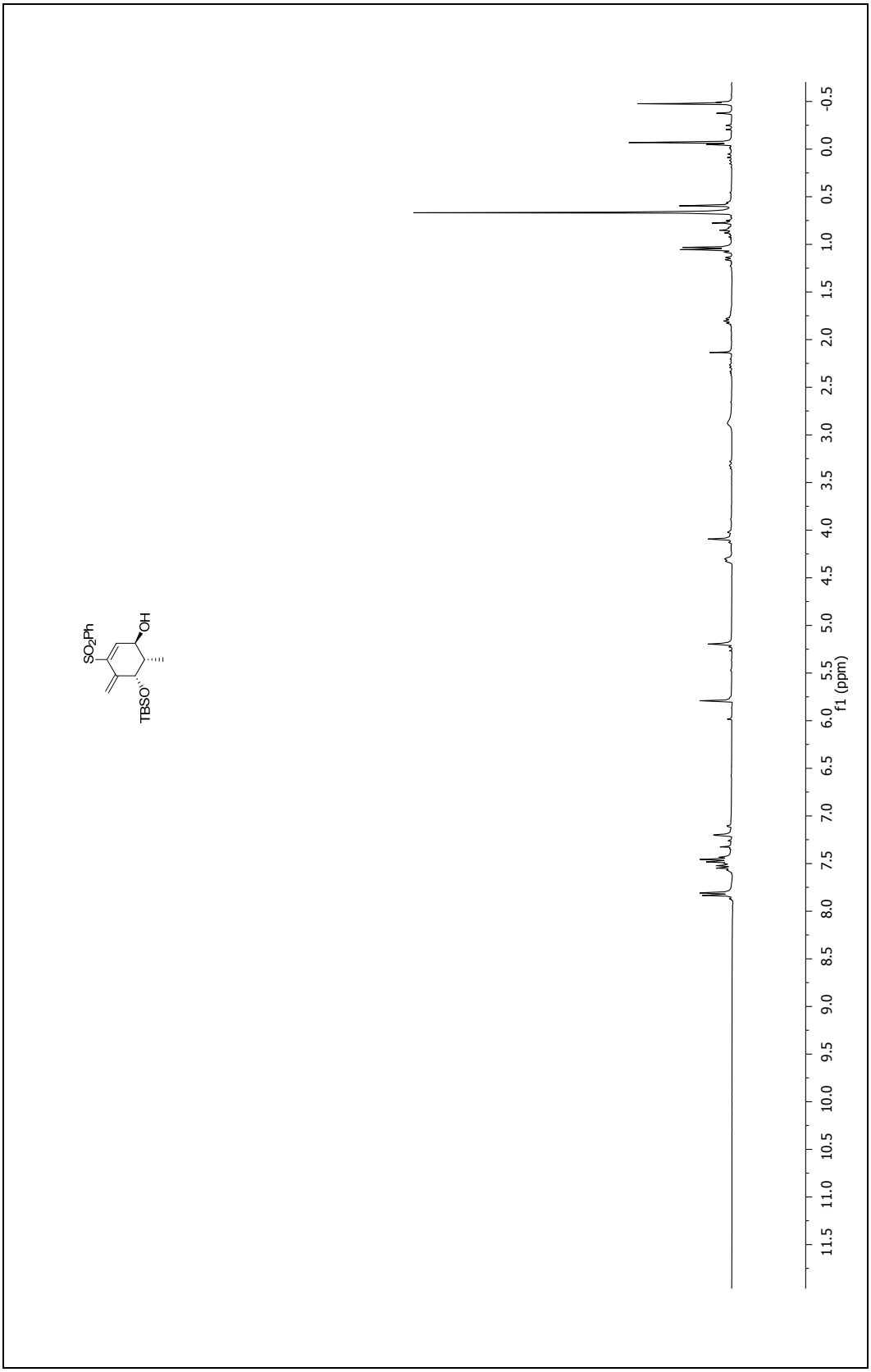
75 MHz ^{13}C NMR of compound **7** in $CDCl_3$



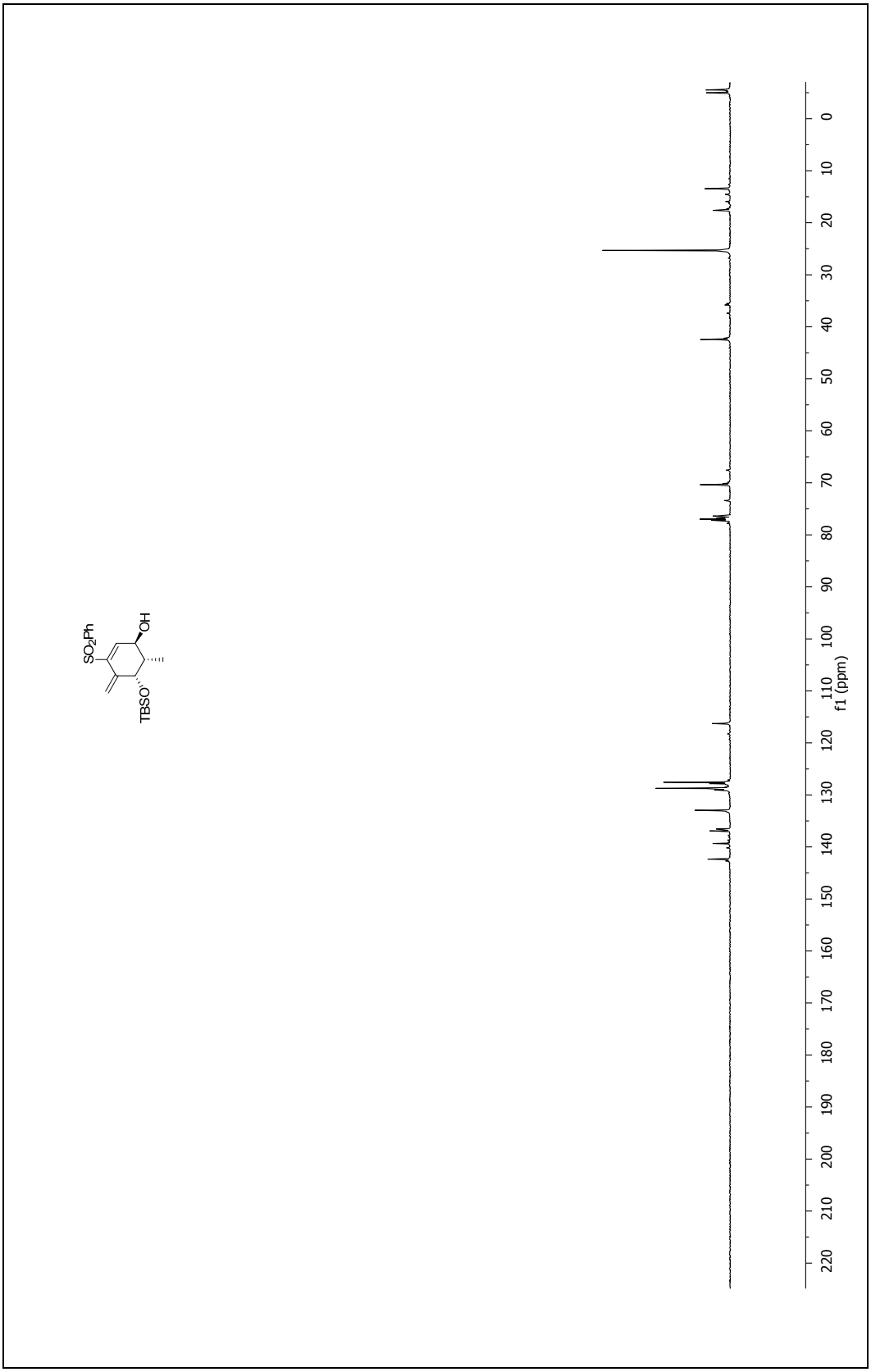
300 MHz ^{1}H NMR of compound **8** in $CDCl_3$



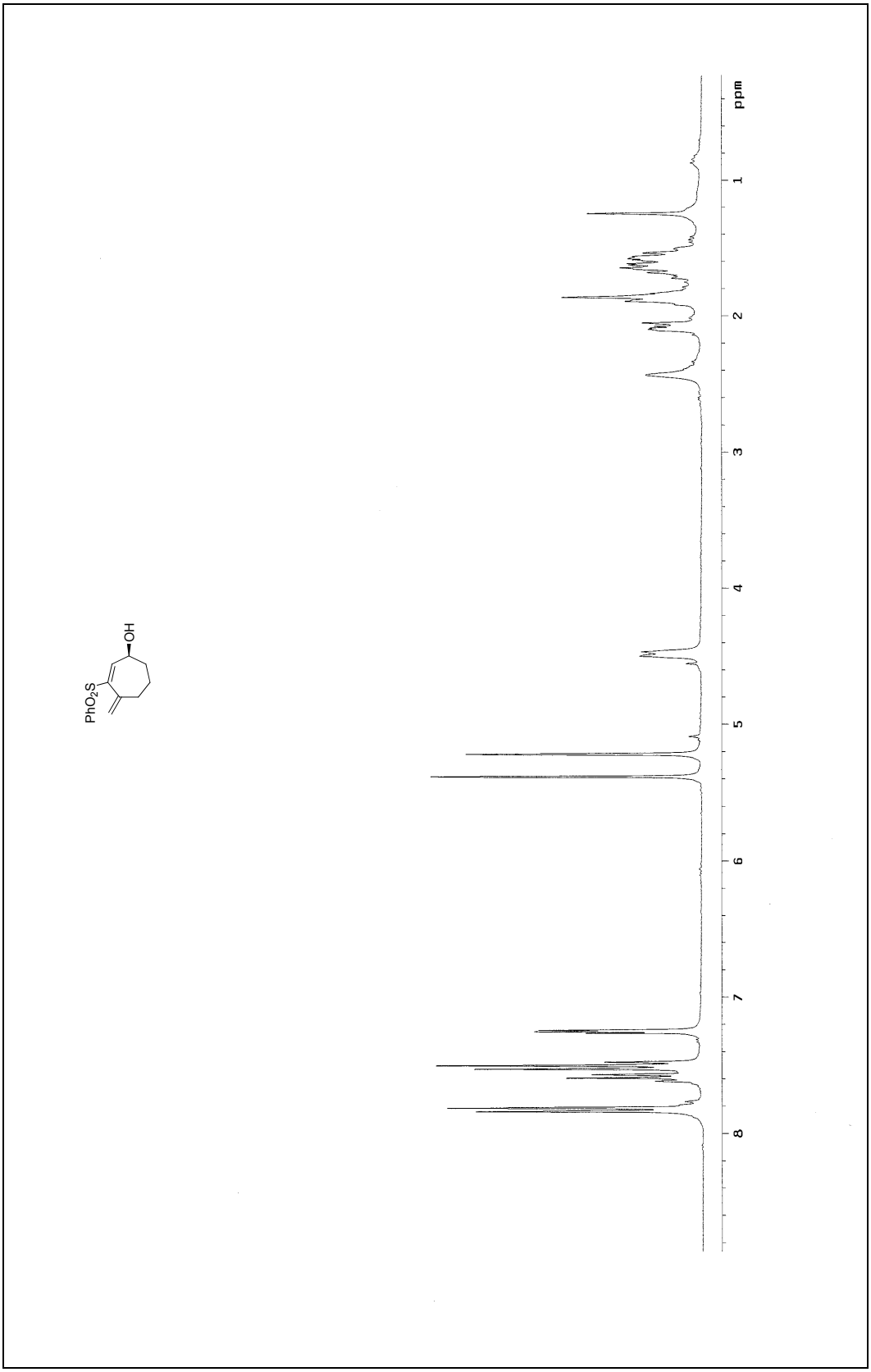
75 MHz ^{13}C NMR of compound **8** in $CDCl_3$



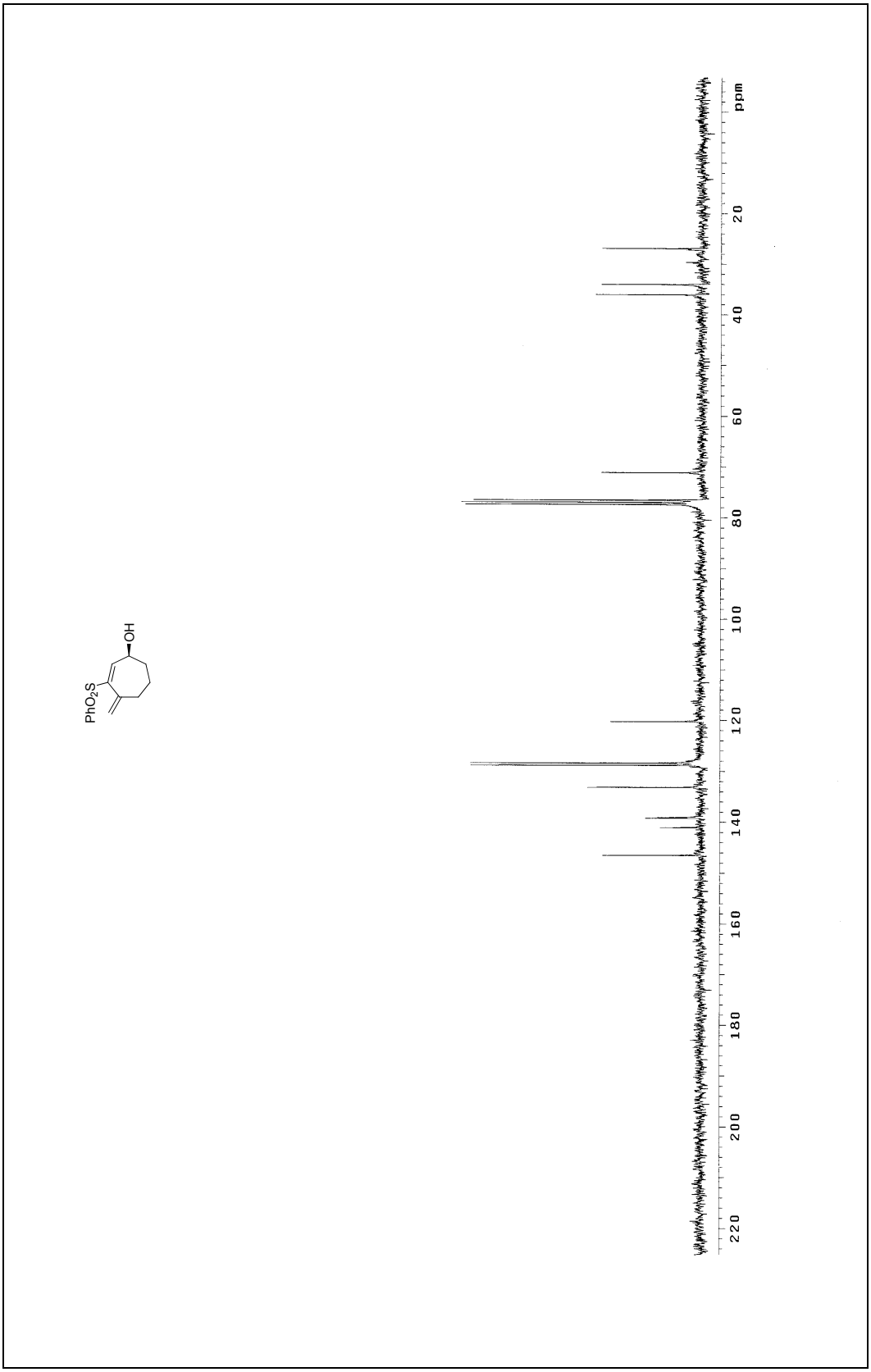
300 MHz ^{1}H NMR of compound **9** in $CDCl_3$



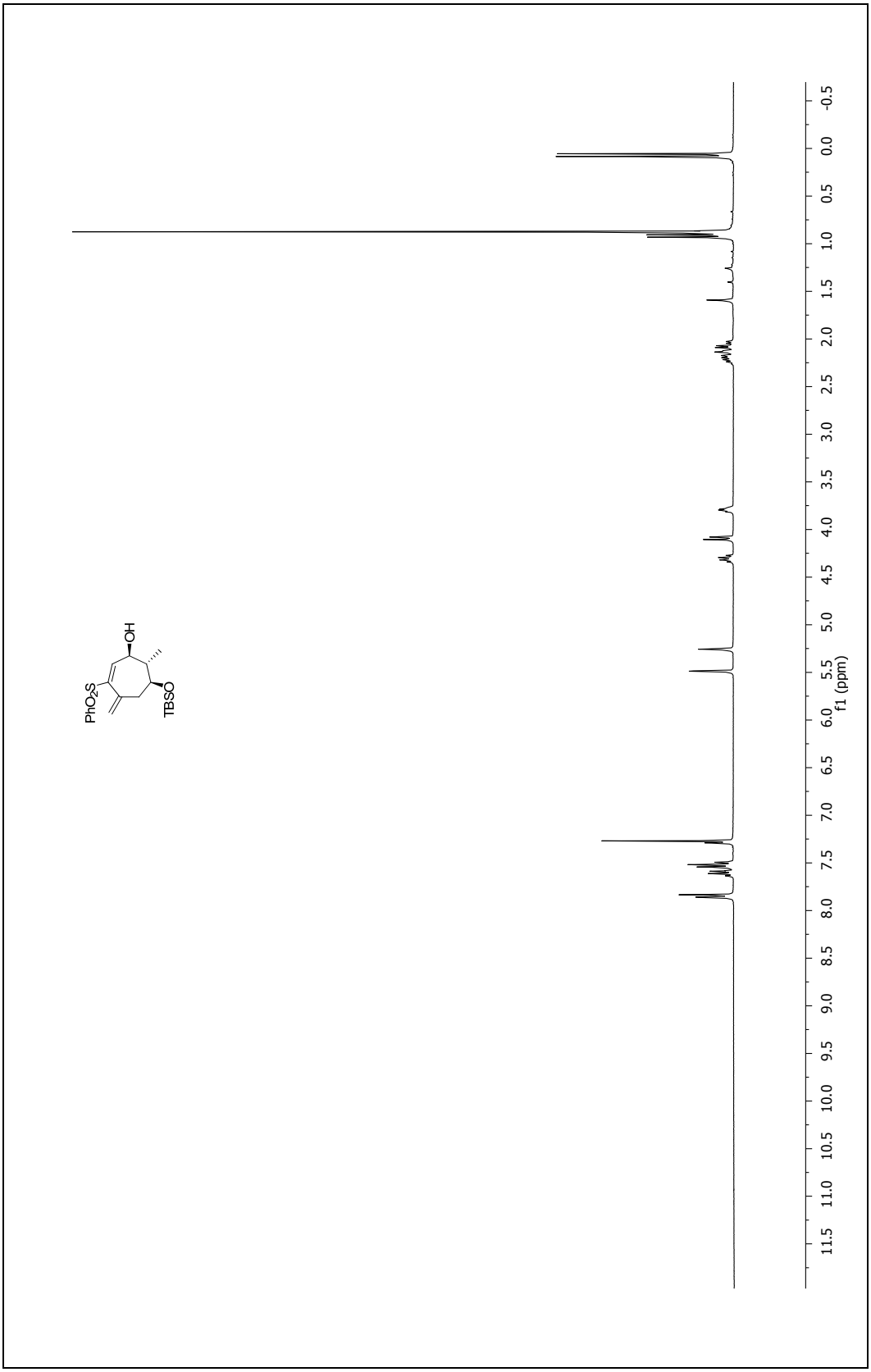
75 MHz ^{13}C NMR of compound **9** in $CDCl_3$



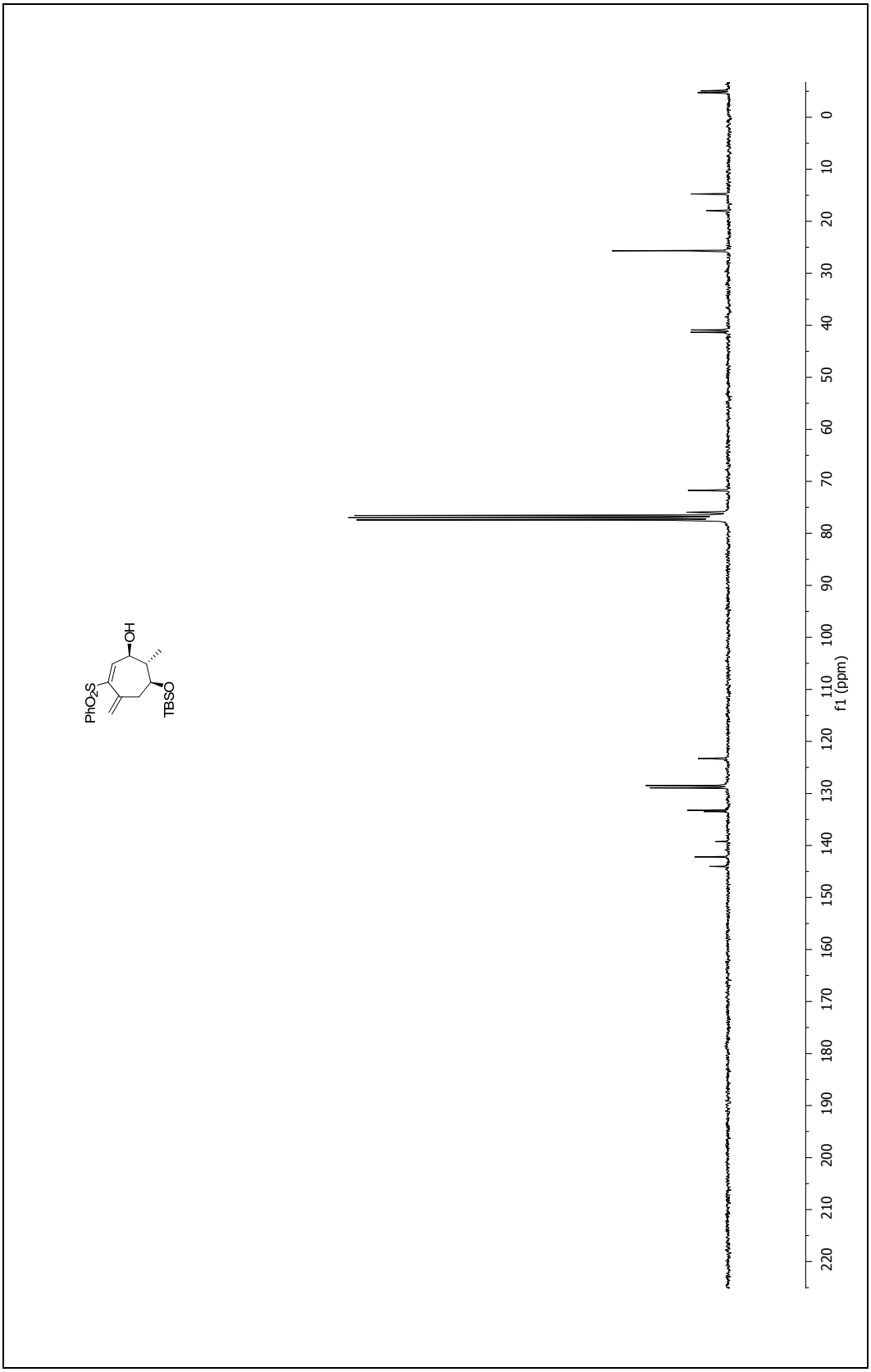
300 MHz ^{1}H NMR of compound **13** in $CDCl_3$



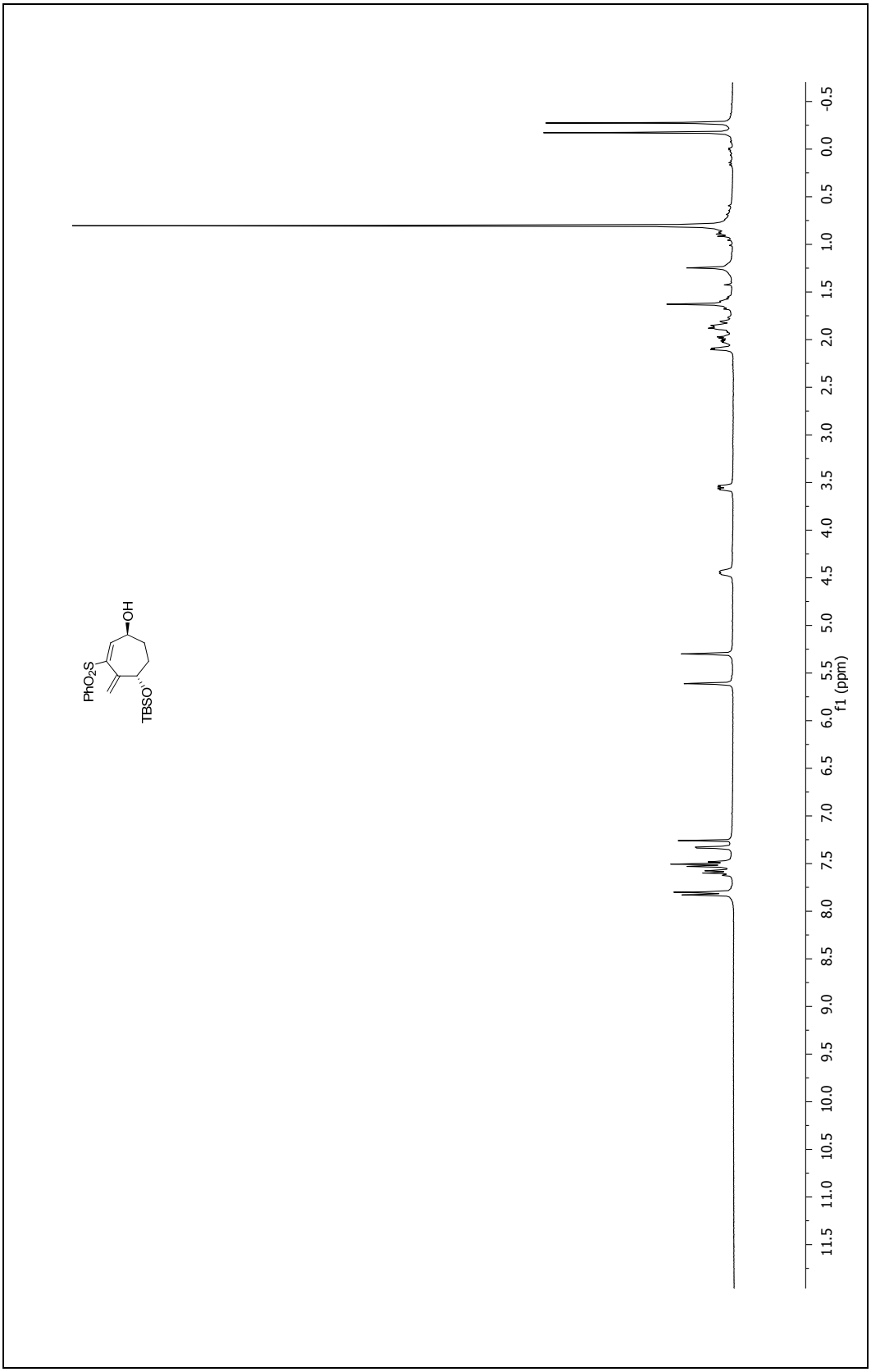
75 MHz ^{13}C NMR of compound **13** in $CDCl_3$



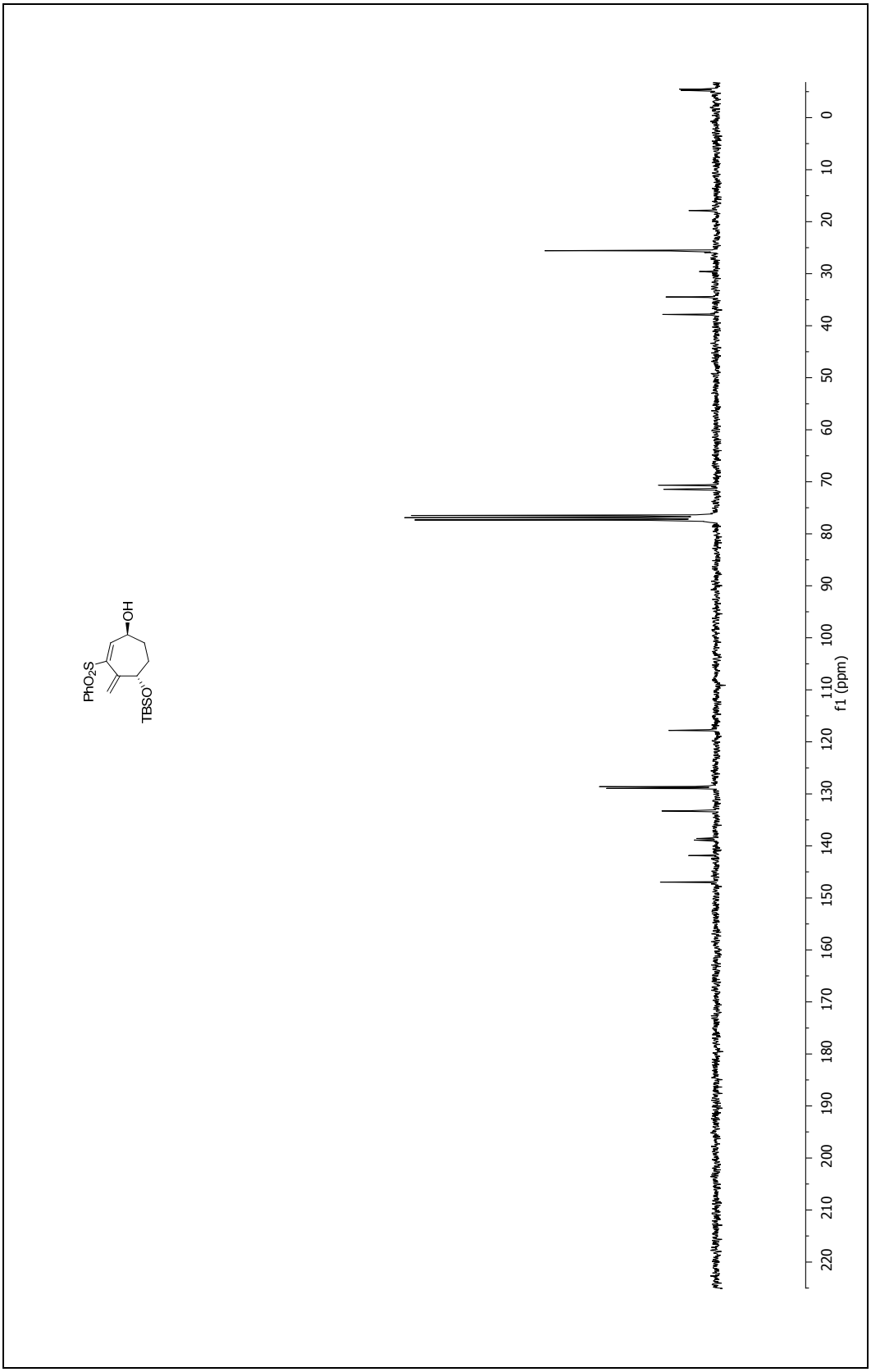
300 MHz ^{1}H NMR of compound **15** in $CDCl_3$



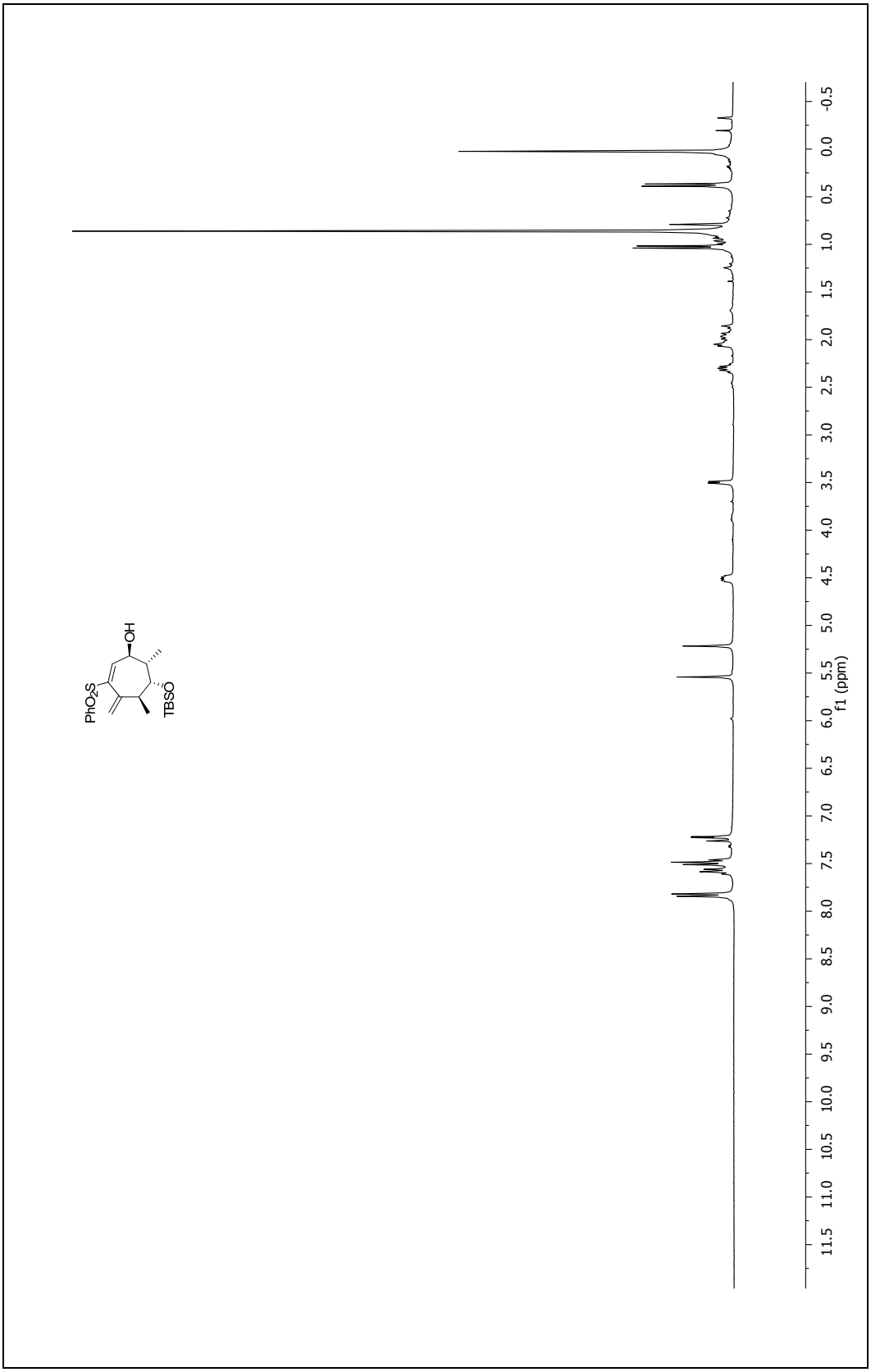
75 MHz ^{13}C NMR of compound **15** in $CDCl_3$



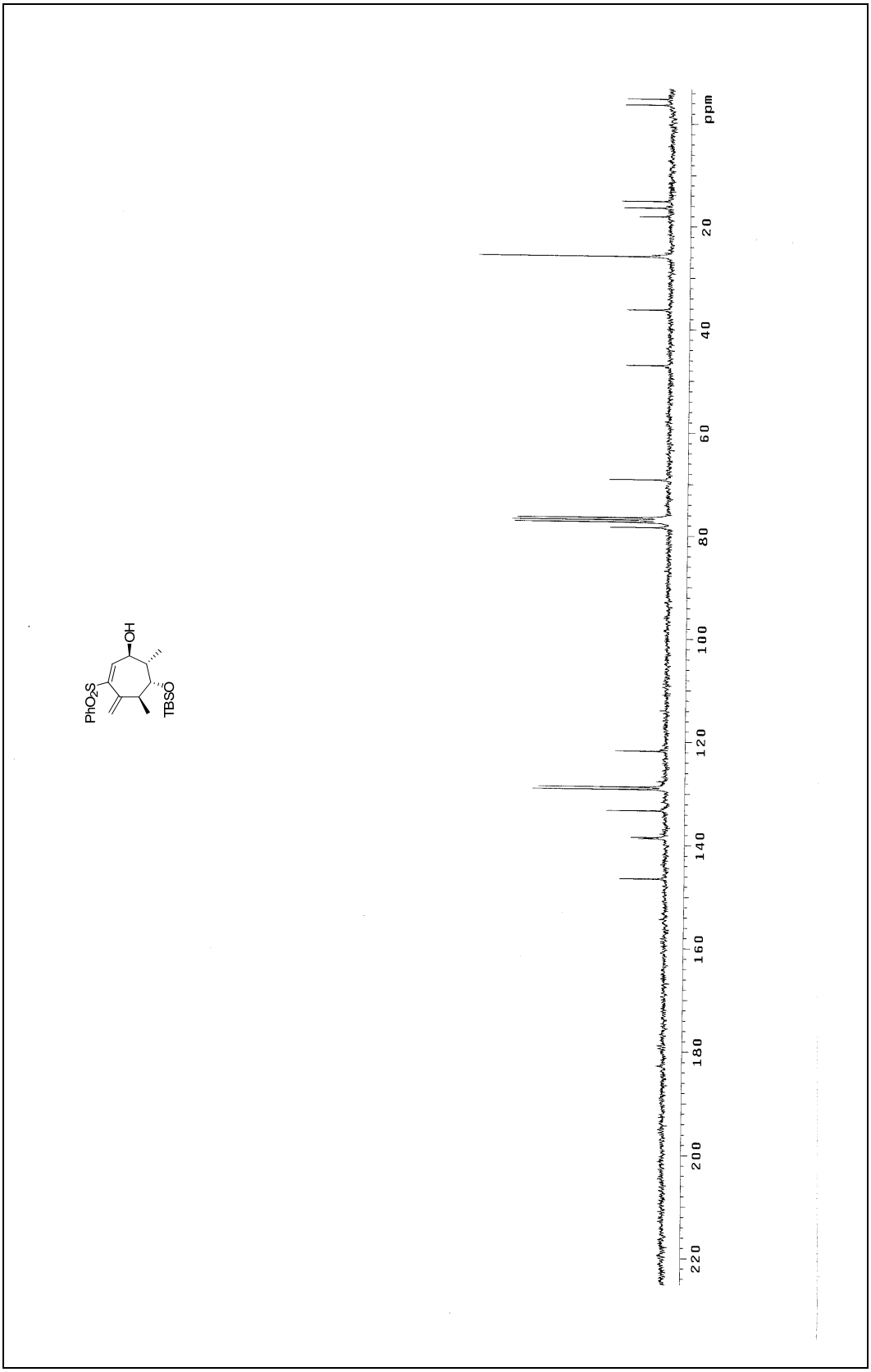
300 MHz ^{1}H NMR of compound **17** in $CDCl_3$



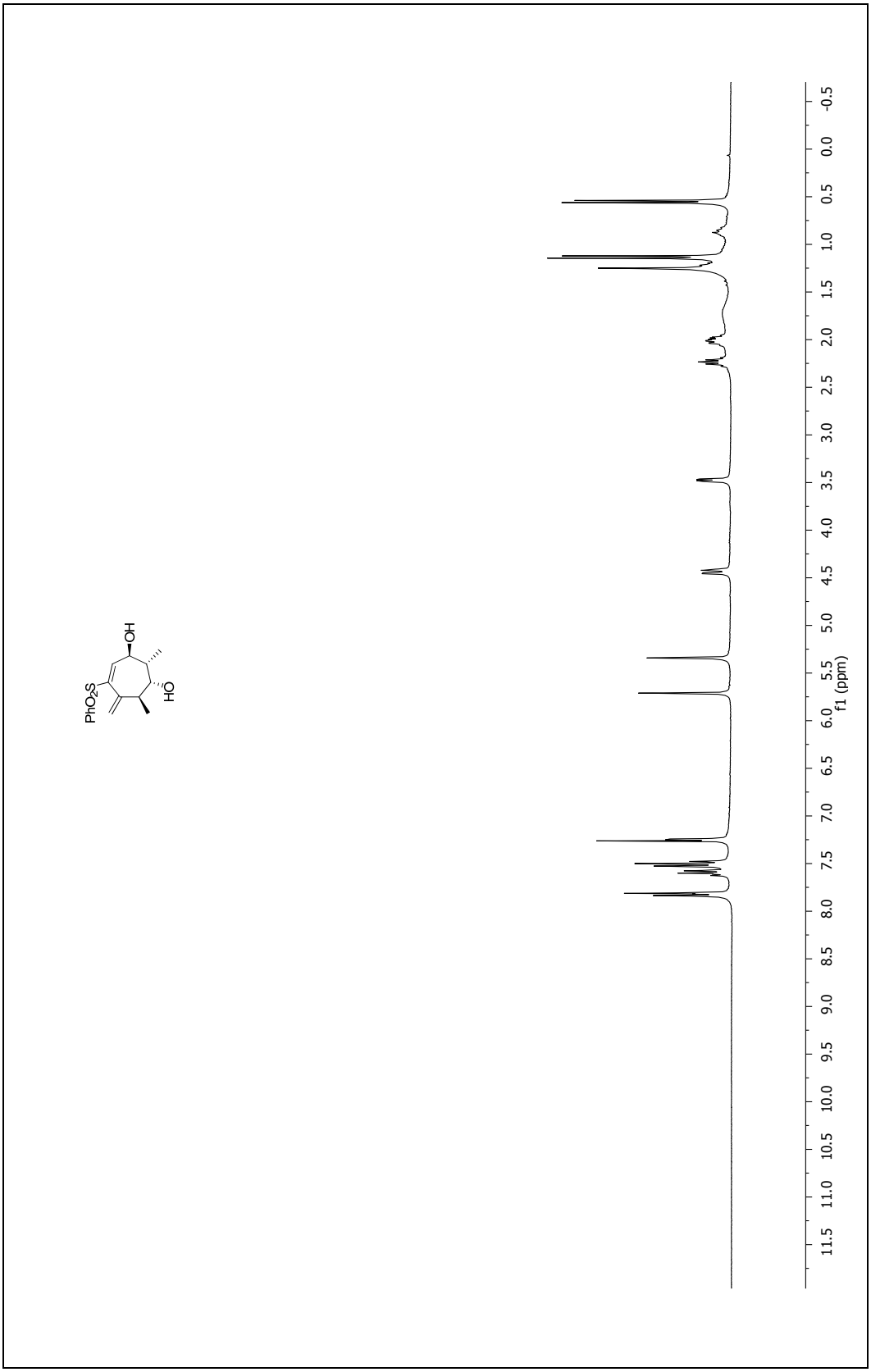
75 MHz ^{13}C NMR of compound **17** in $CDCl_3$



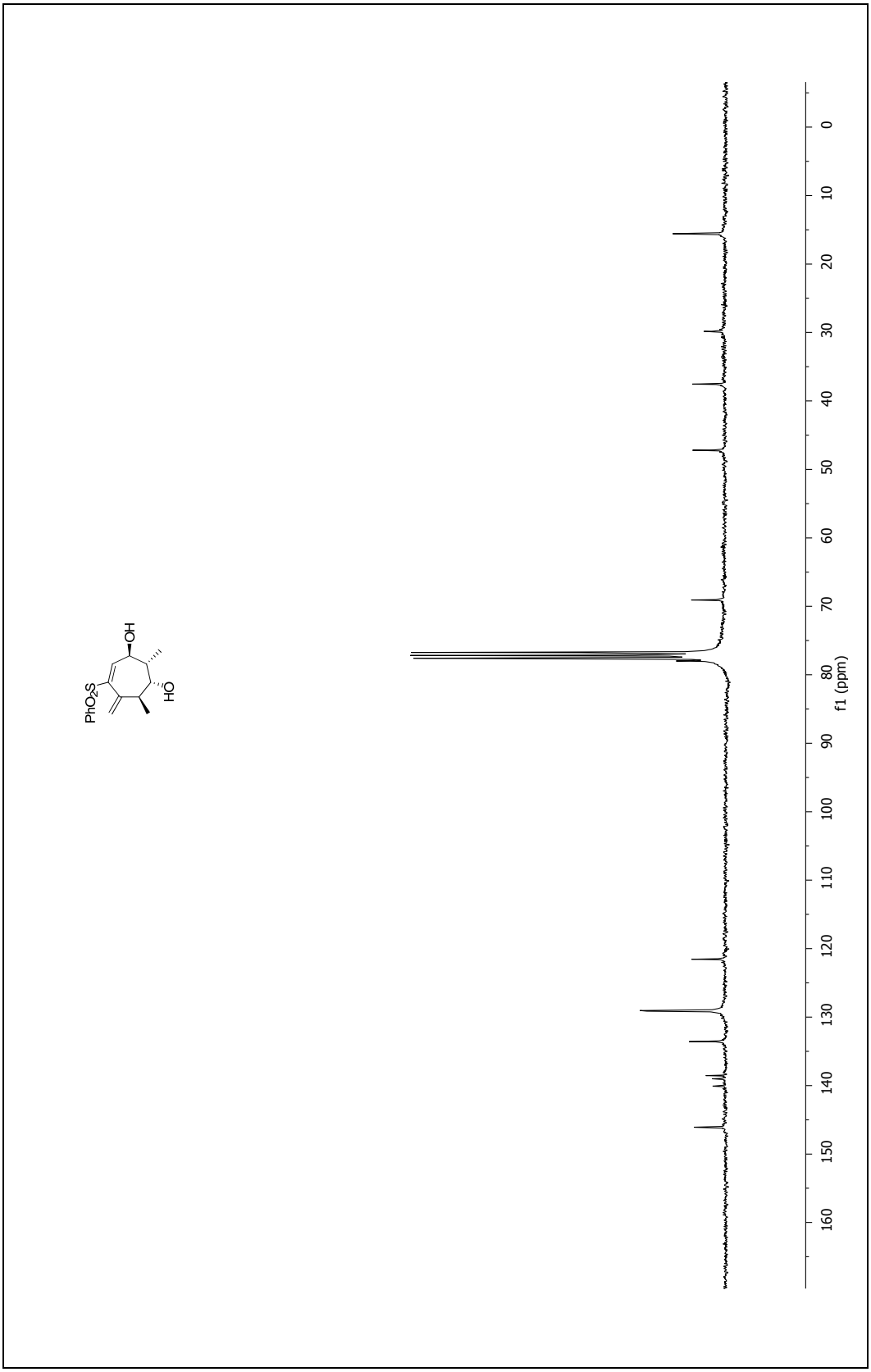
300 MHz ^{1}H NMR of compound **19** in $CDCl_3$



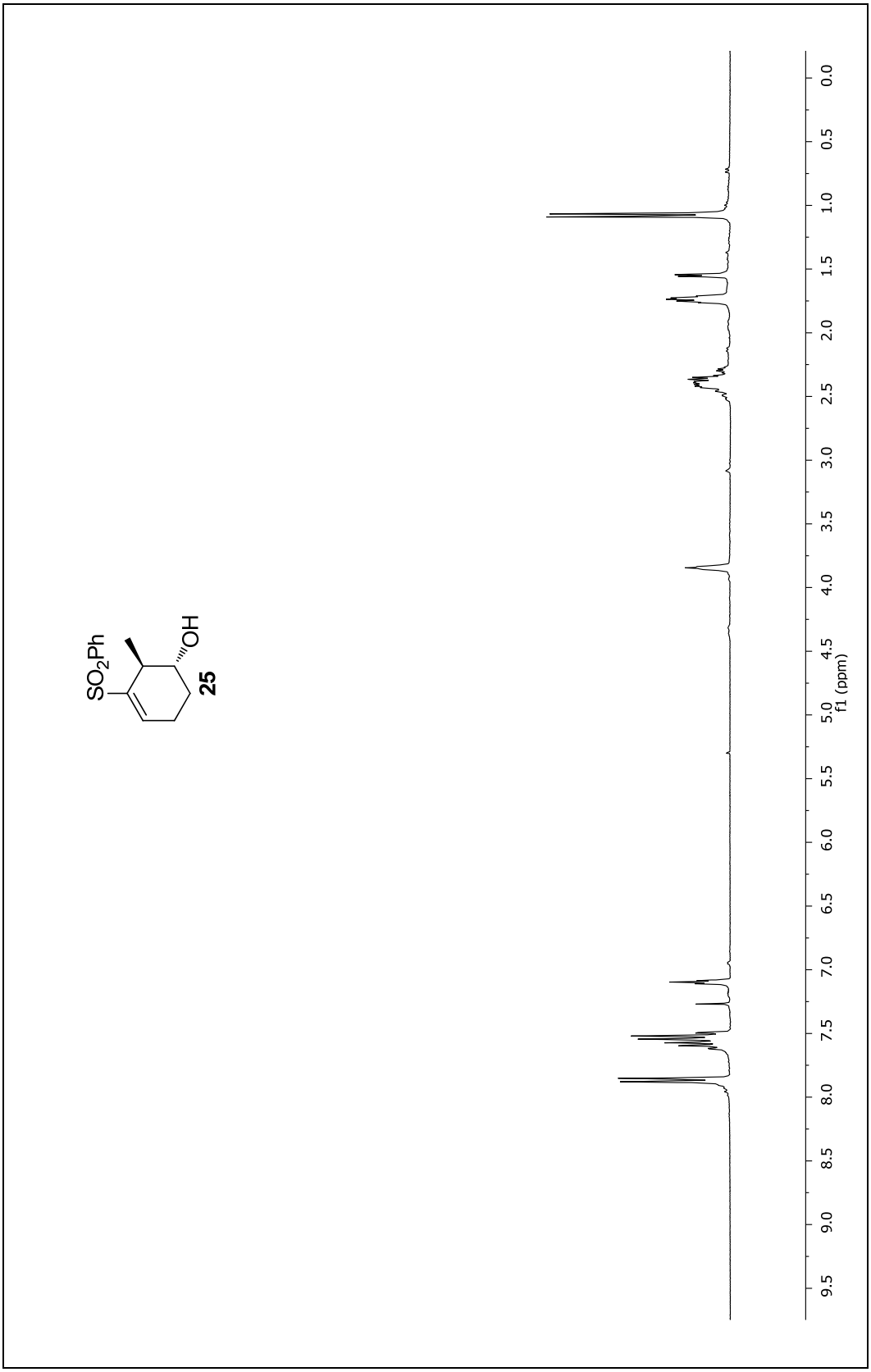
75 MHz ^{13}C NMR of compound **19** in $CDCl_3$



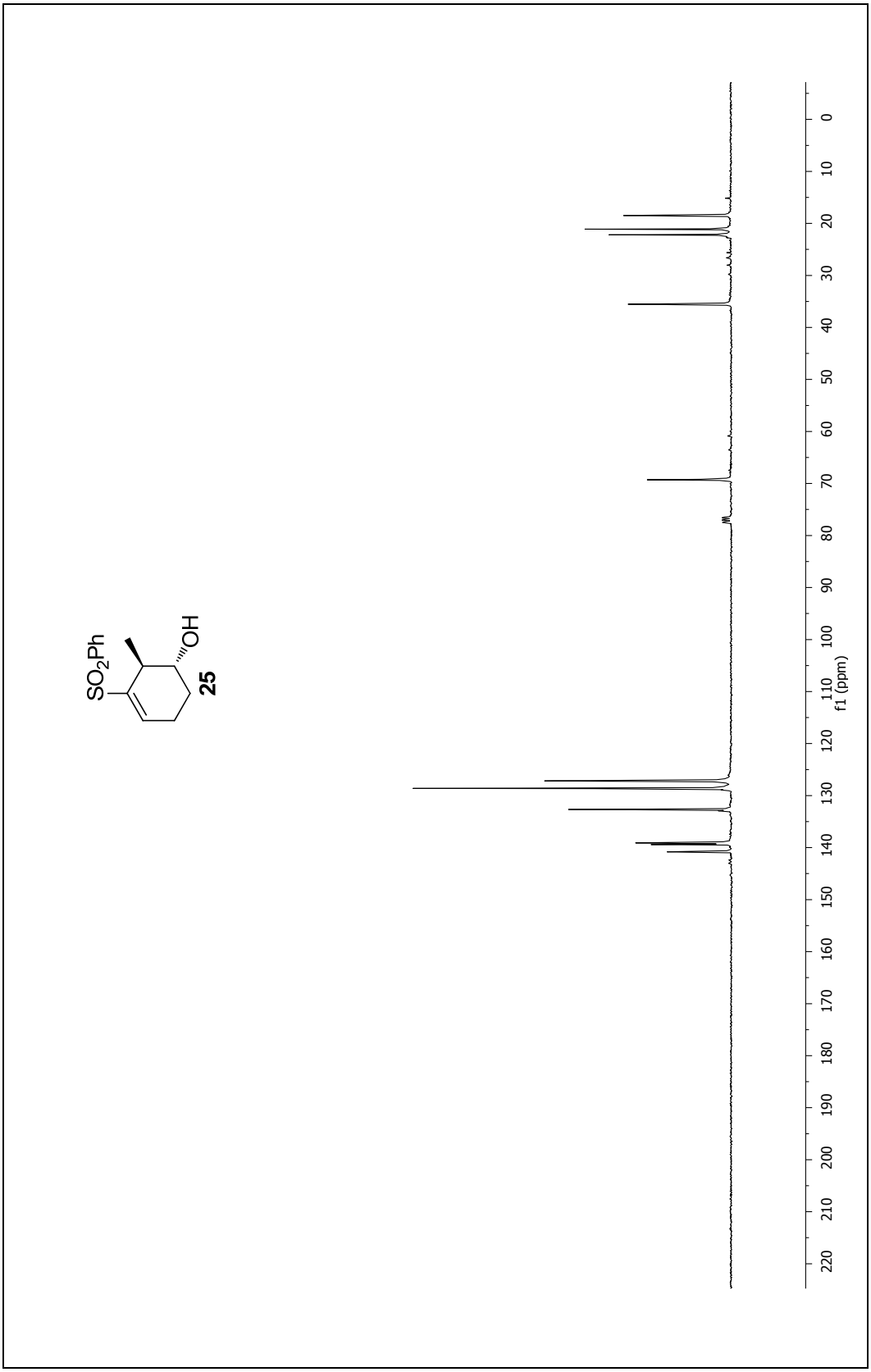
300 MHz ^{1}H NMR of compound **21** in $CDCl_3$



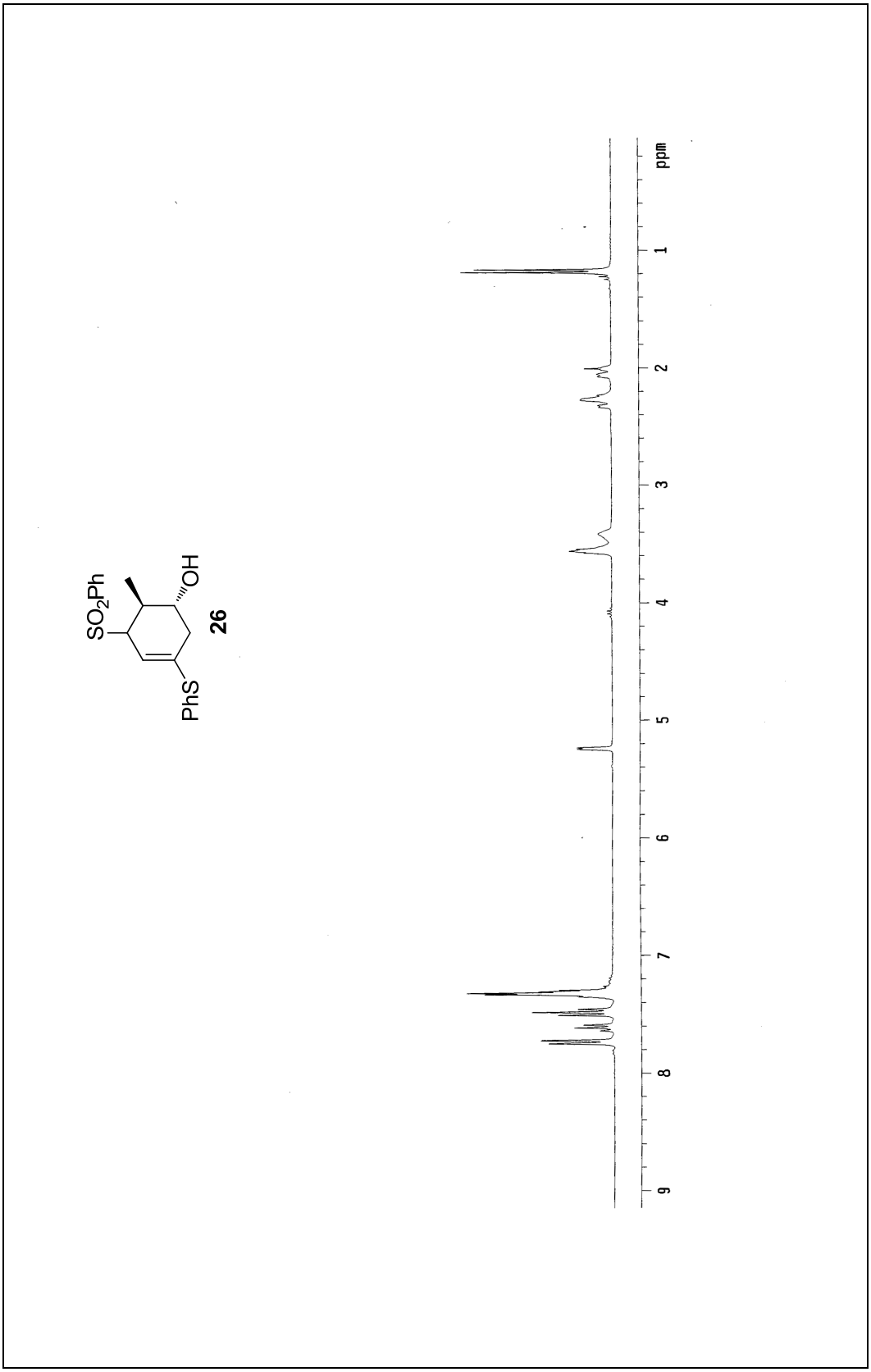
75 MHz ^{13}C NMR of compound **21** in $CDCl_3$



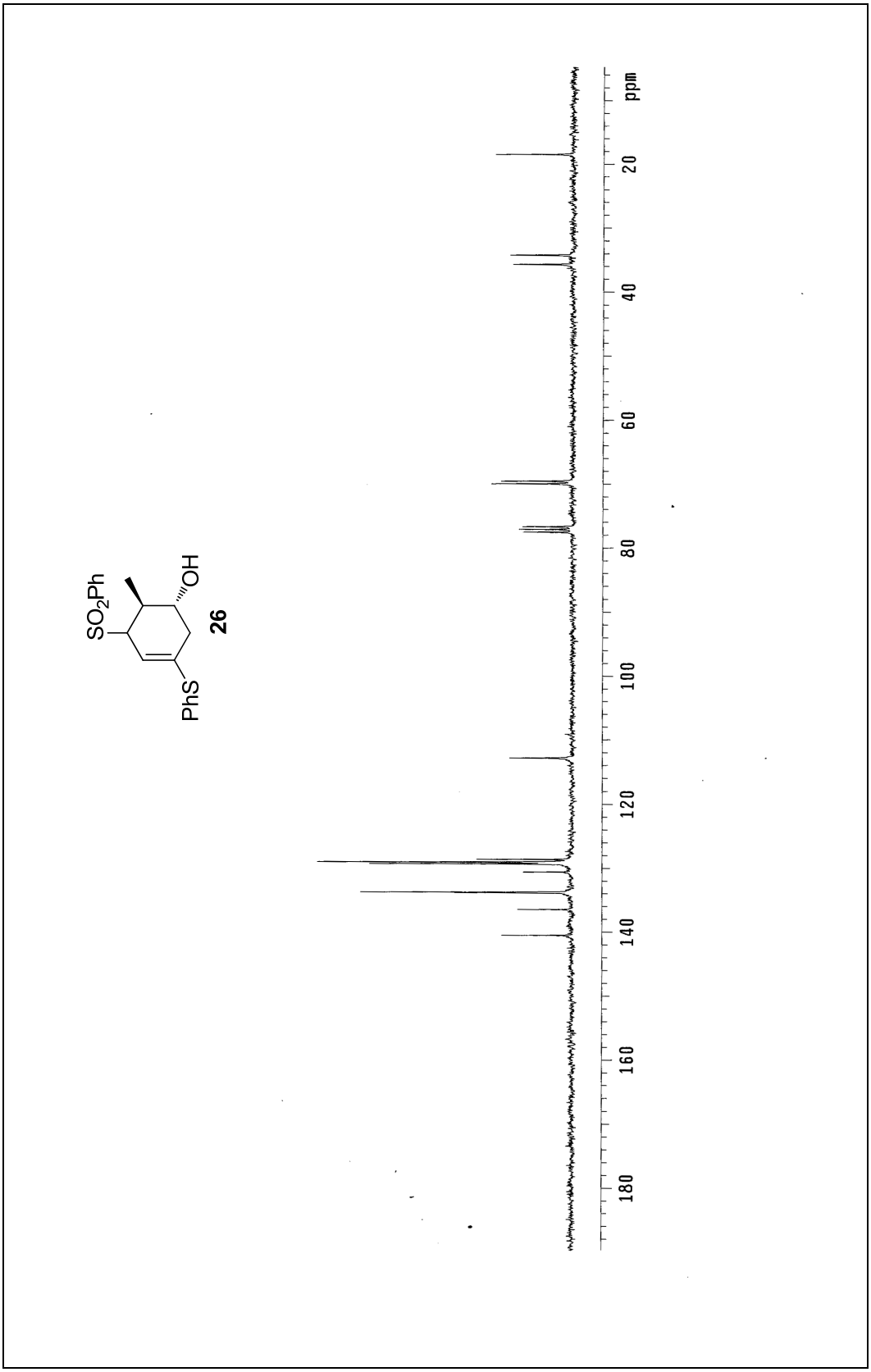
300 MHz ^{1}H NMR of compound **25** in $CDCl_3$



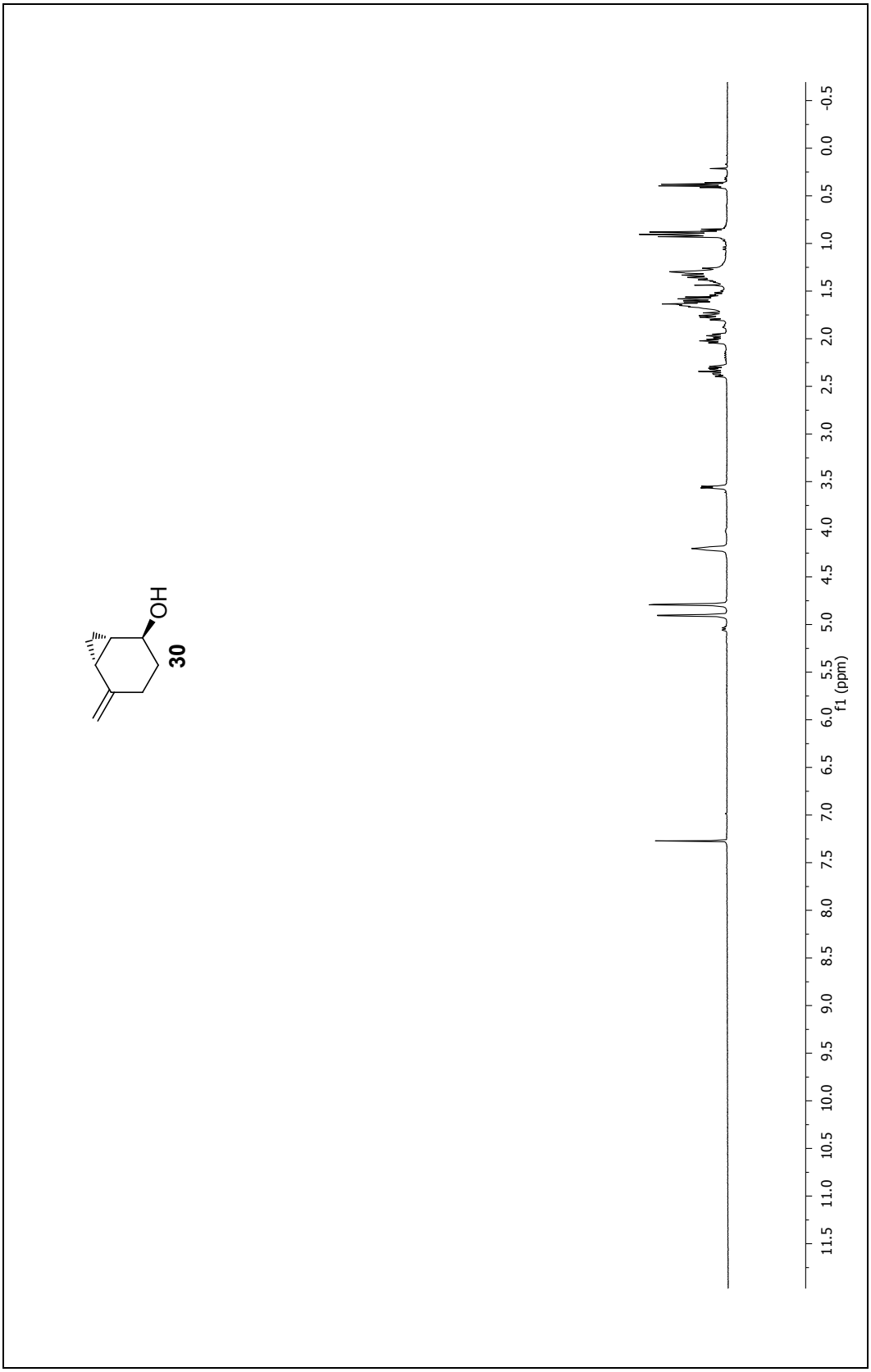
75 MHz ^{13}C NMR of compound **25** in $CDCl_3$



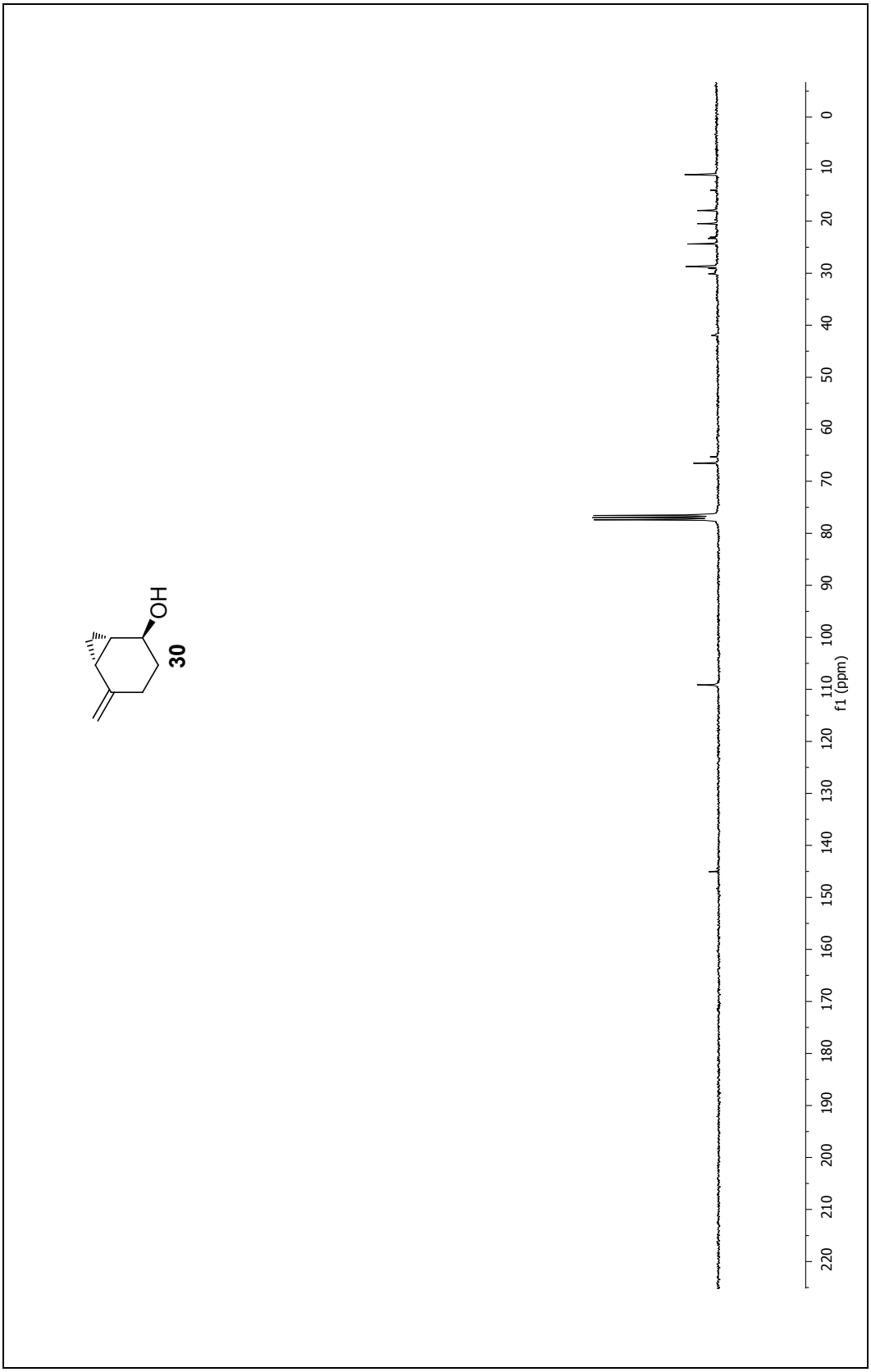
300 MHz ^{1}H NMR of compound **26** in $CDCl_3$



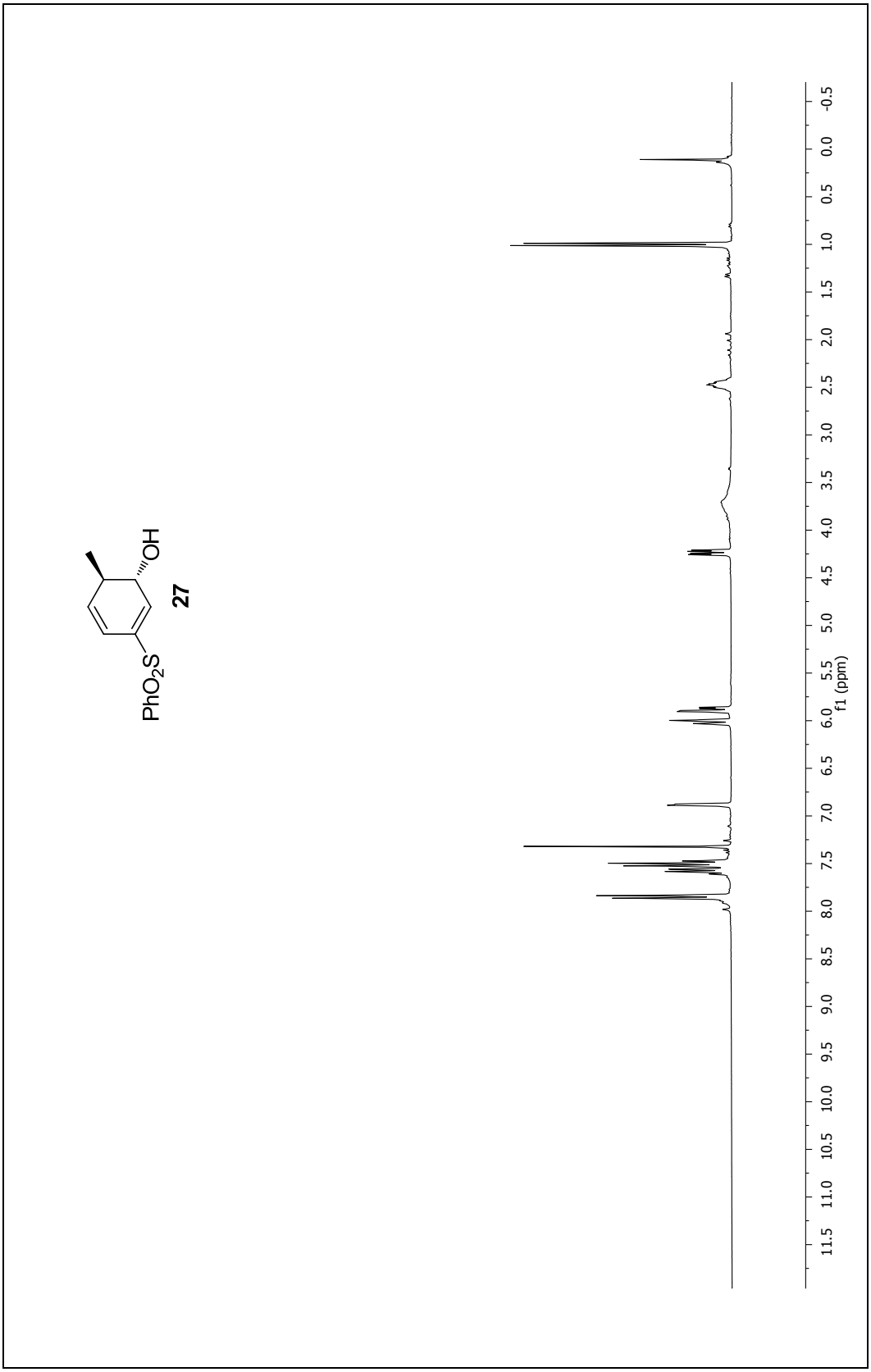
75 MHz ^{13}C NMR of compound **26** in $CDCl_3$



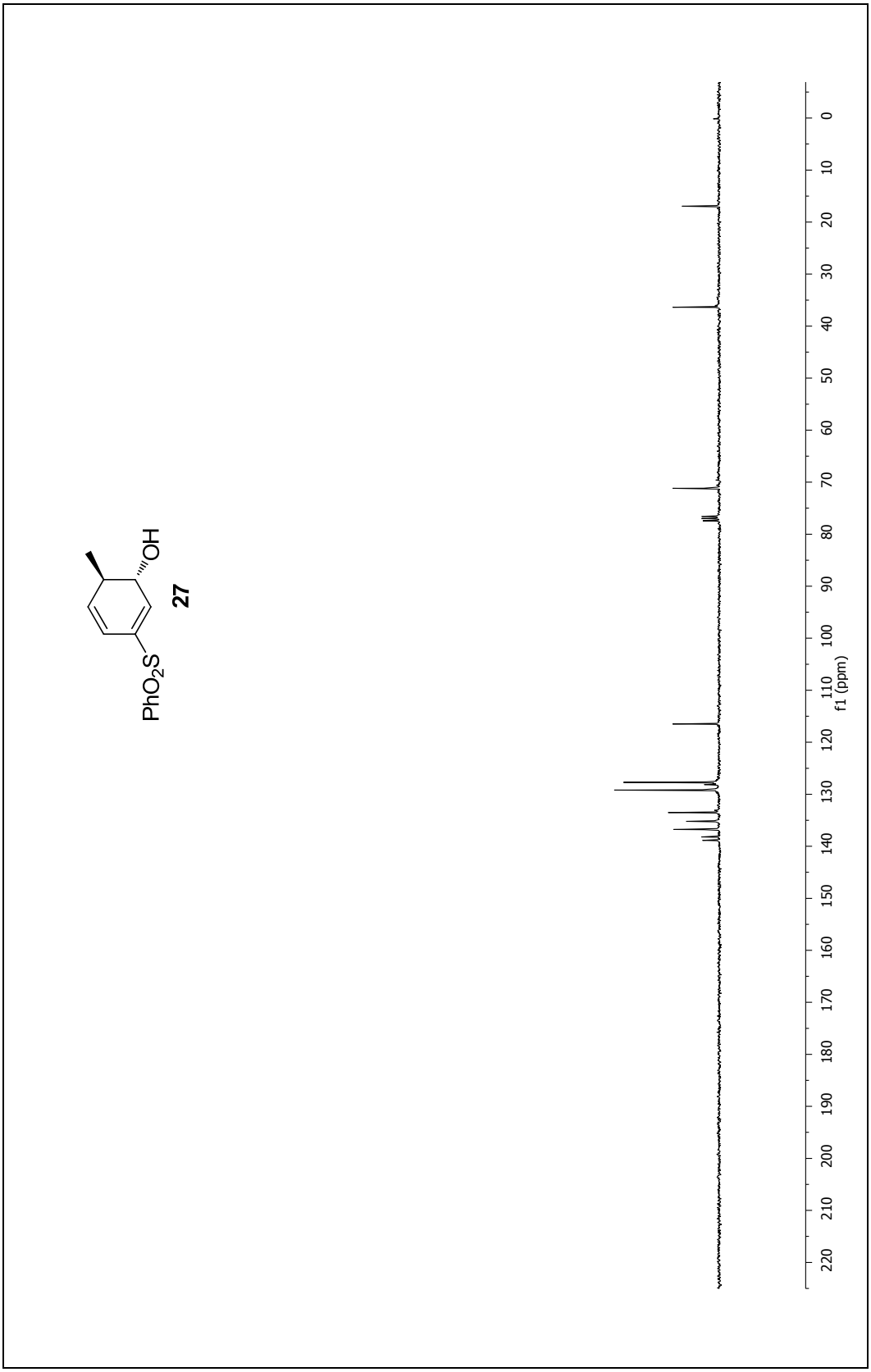
300 MHz ^{1}H NMR of compound **30** in $CDCl_3$



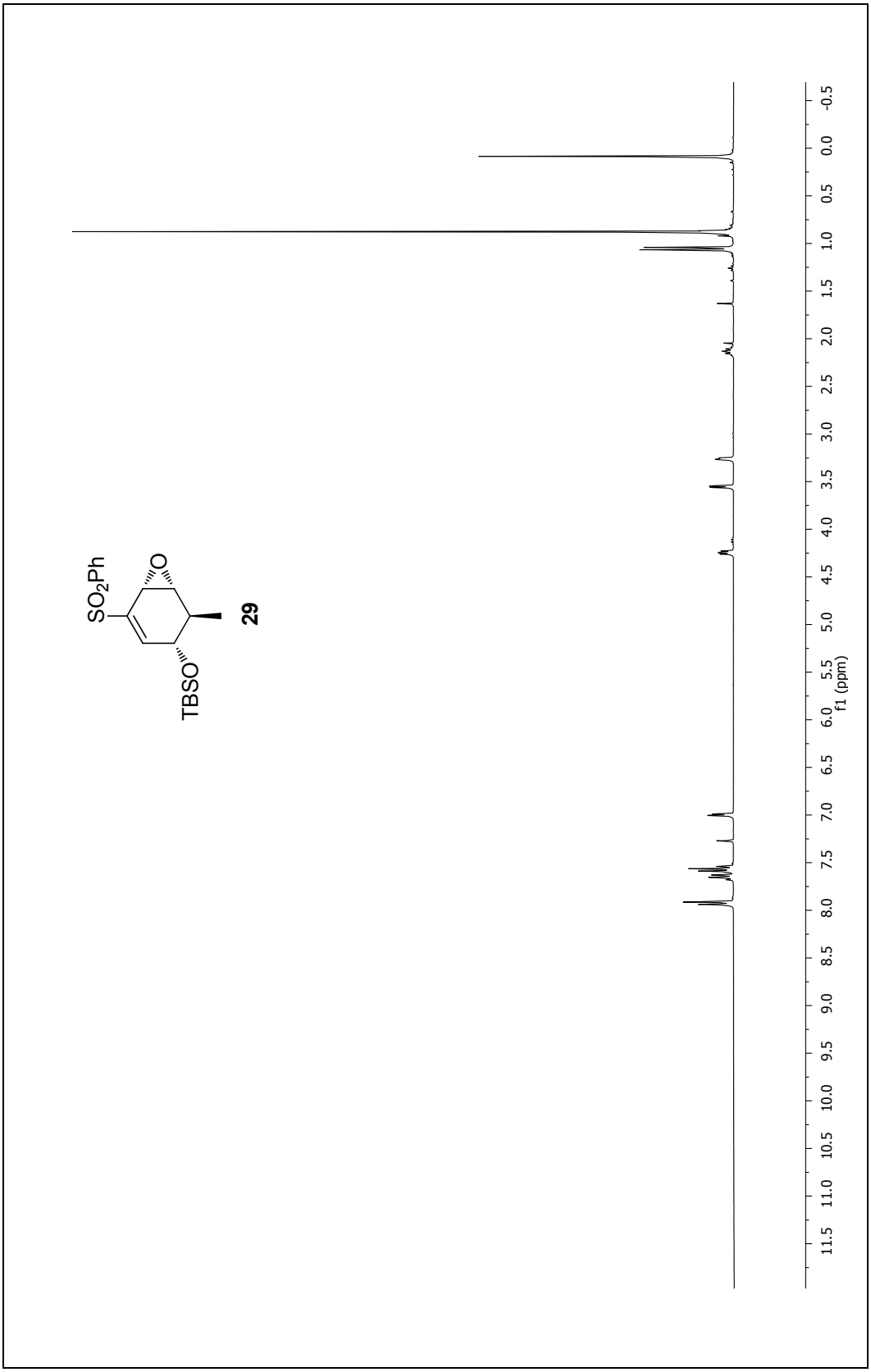
75 MHz ^{13}C NMR of compound **30** in $CDCl_3$



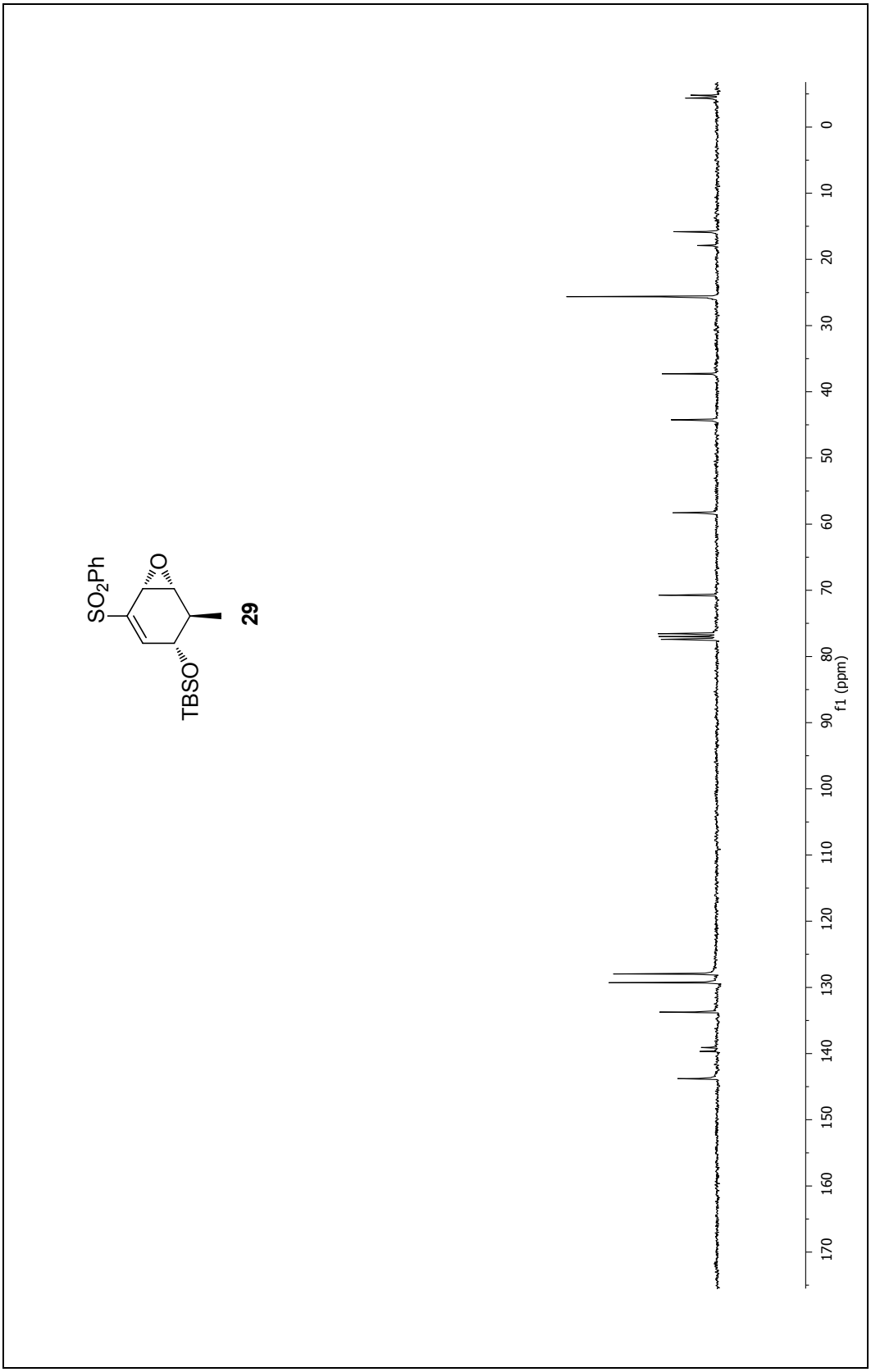
300 MHz ^{1}H NMR of compound **27** in $CDCl_3$



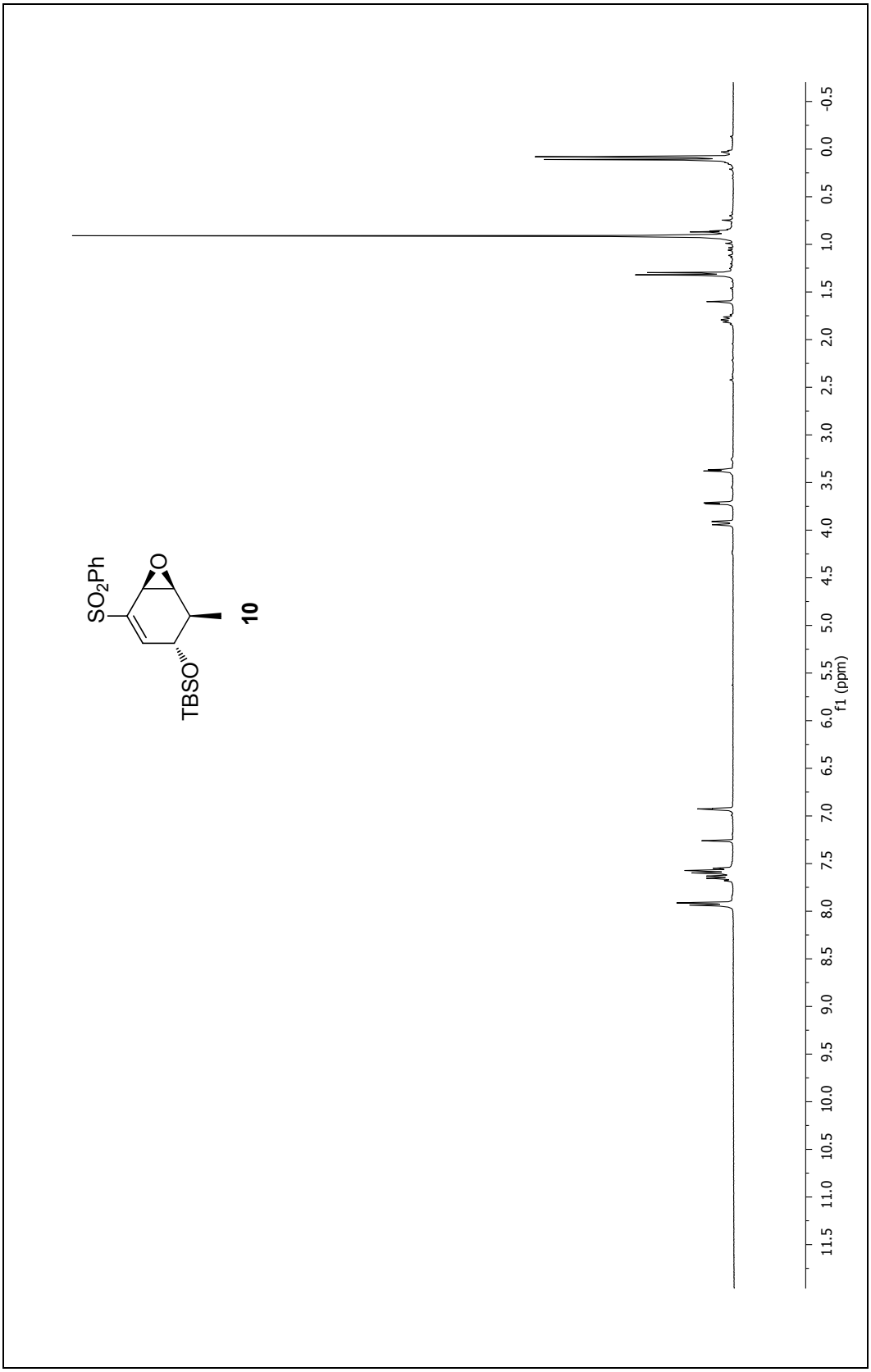
75 MHz ^{13}C NMR of compound **27** in $CDCl_3$



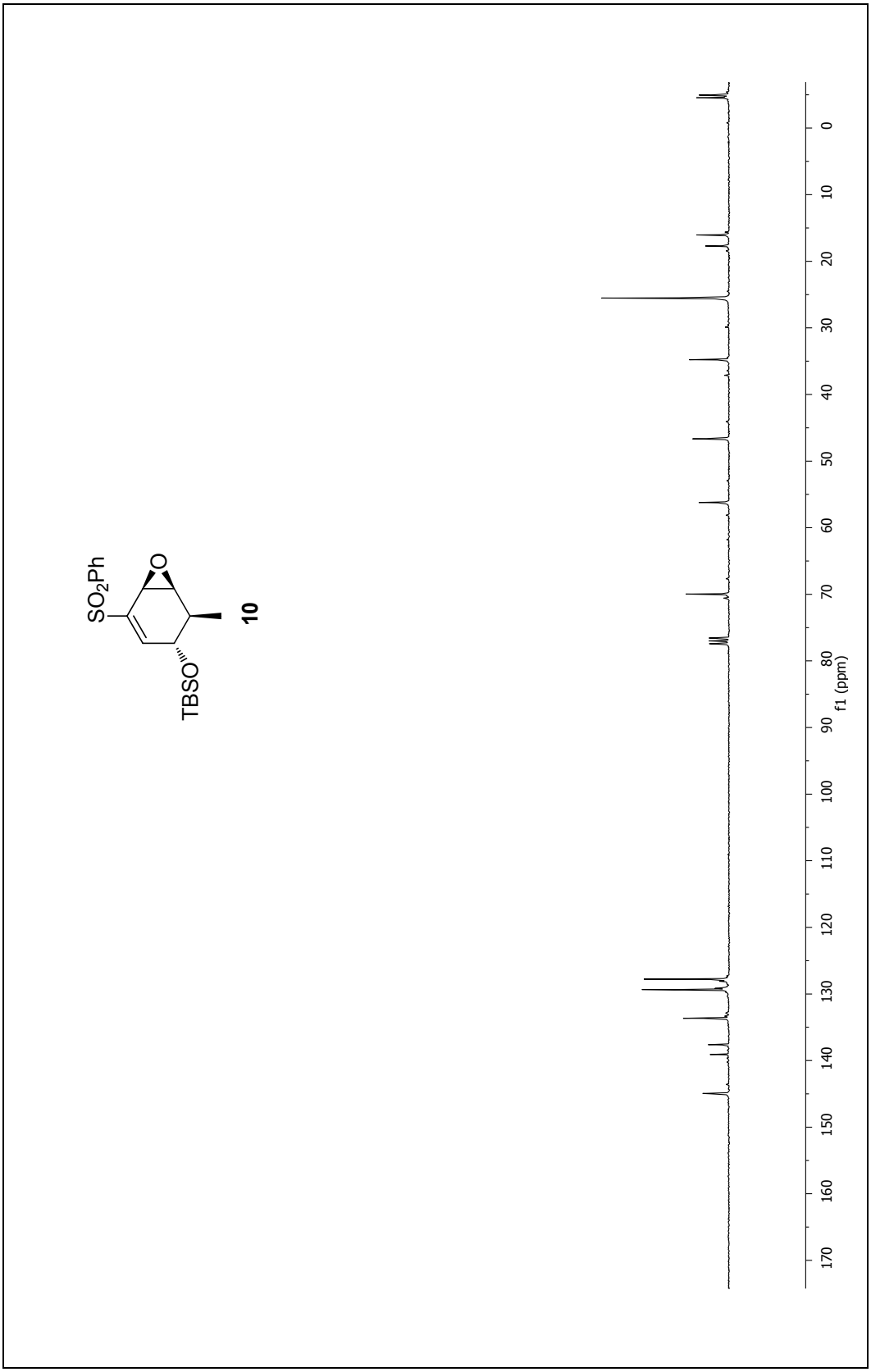
300 MHz ^{1}H NMR of compound **29** in $CDCl_3$



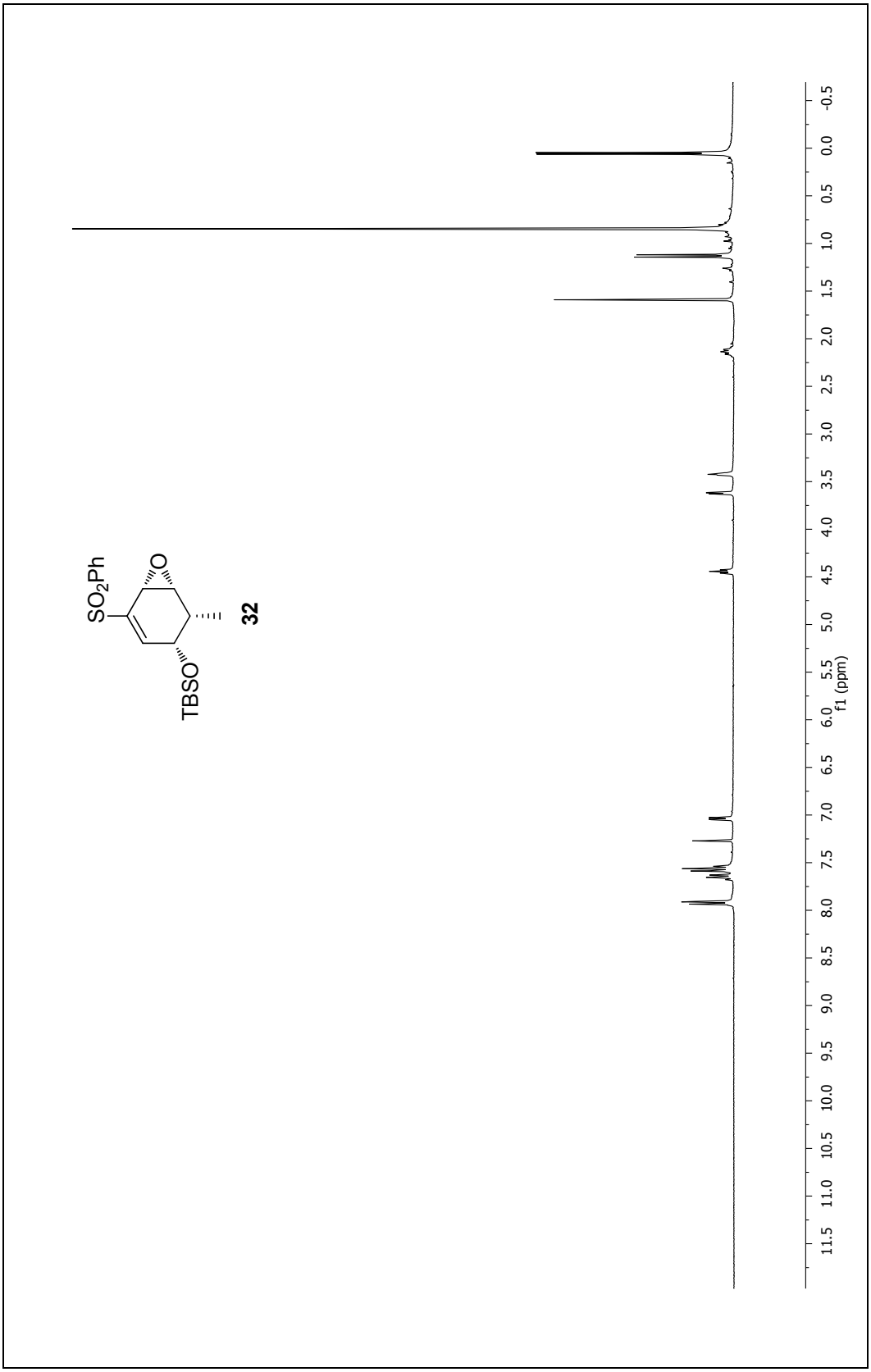
75 MHz ^{13}C NMR of compound **29** in $CDCl_3$



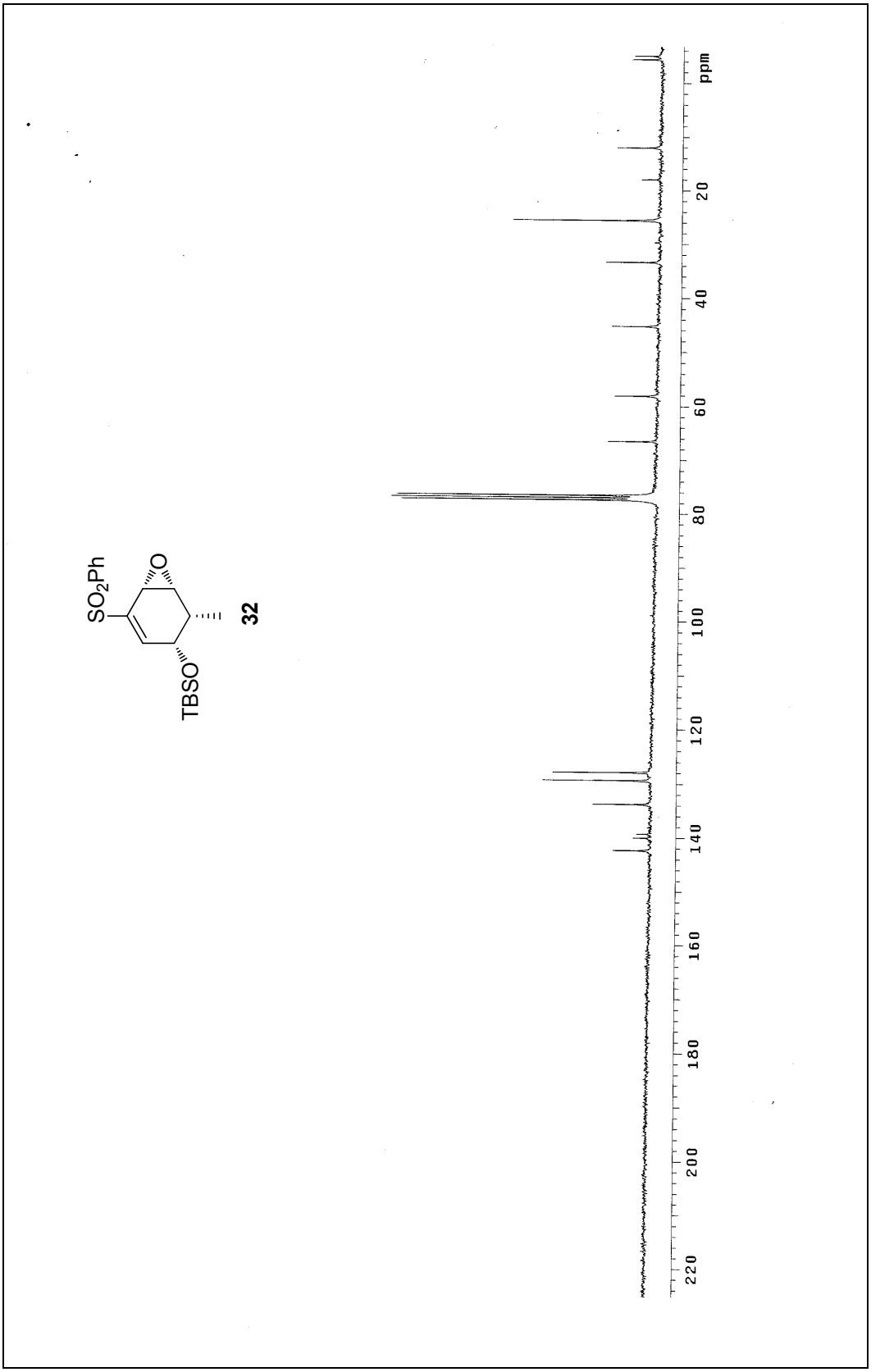
300 MHz ^{1}H NMR of compound **10** in $CDCl_3$



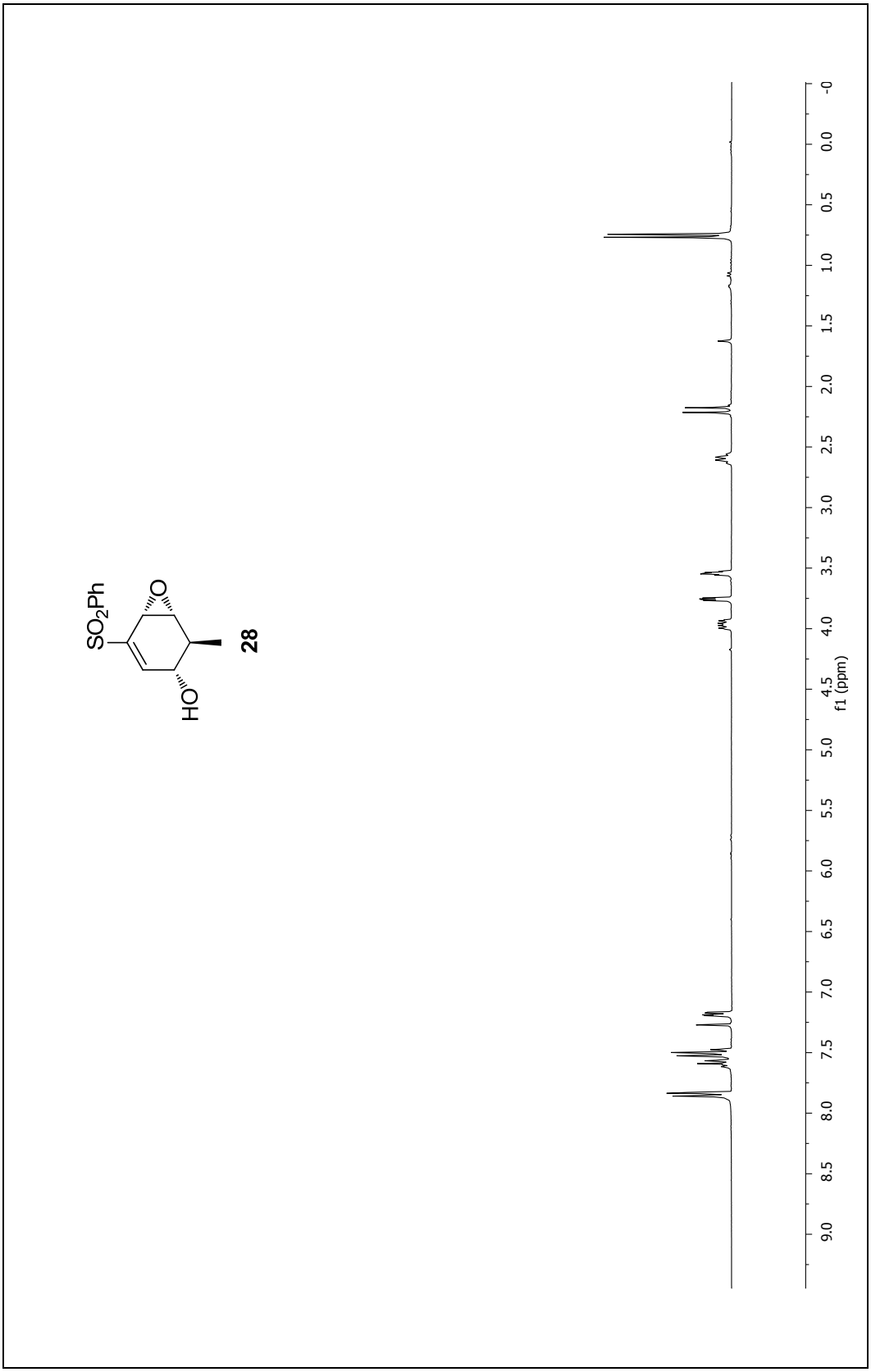
75 MHz ^{13}C NMR of compound **10** in $CDCl_3$



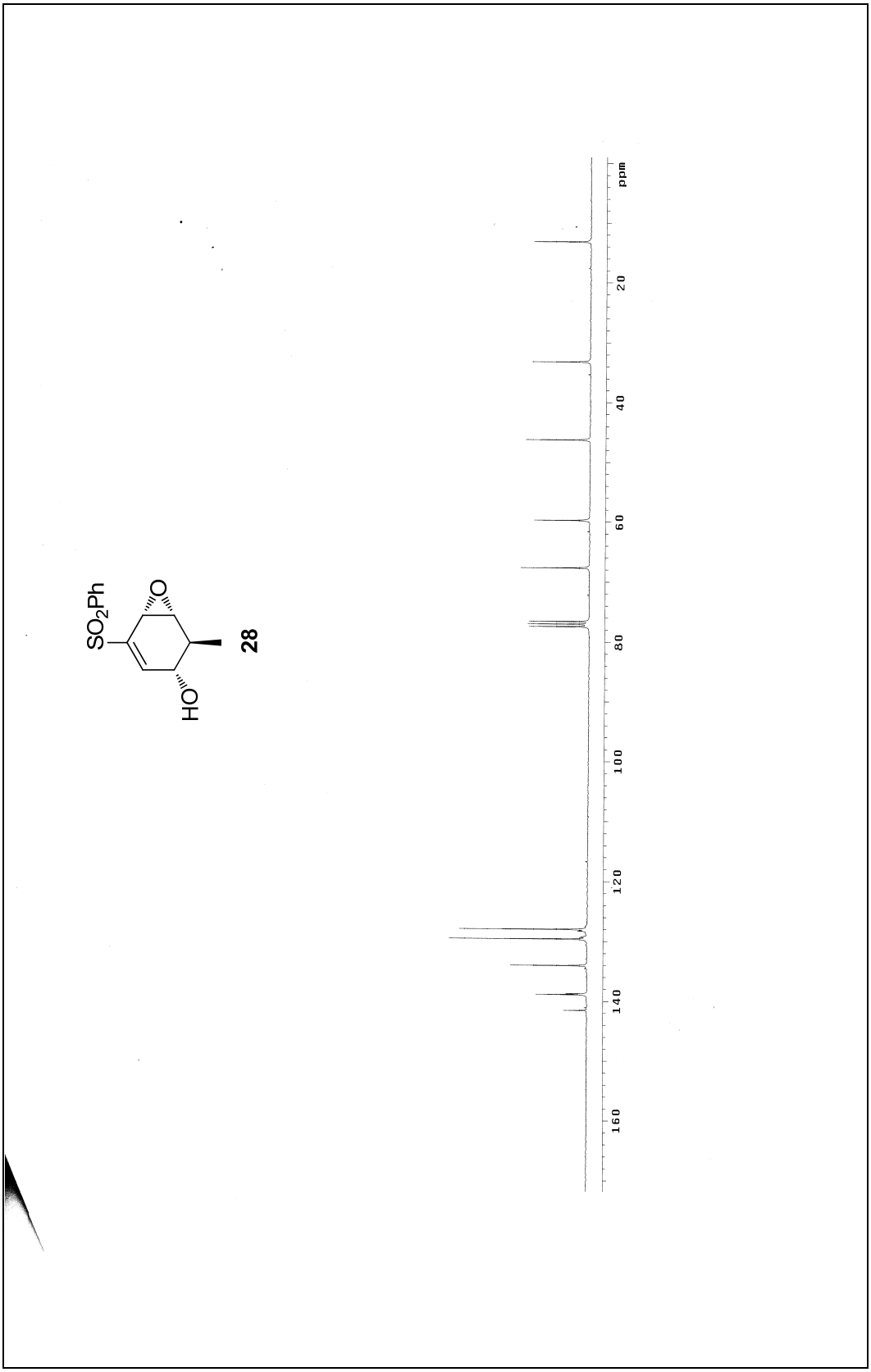
300 MHz ^{1}H NMR of compound **32** in $CDCl_3$



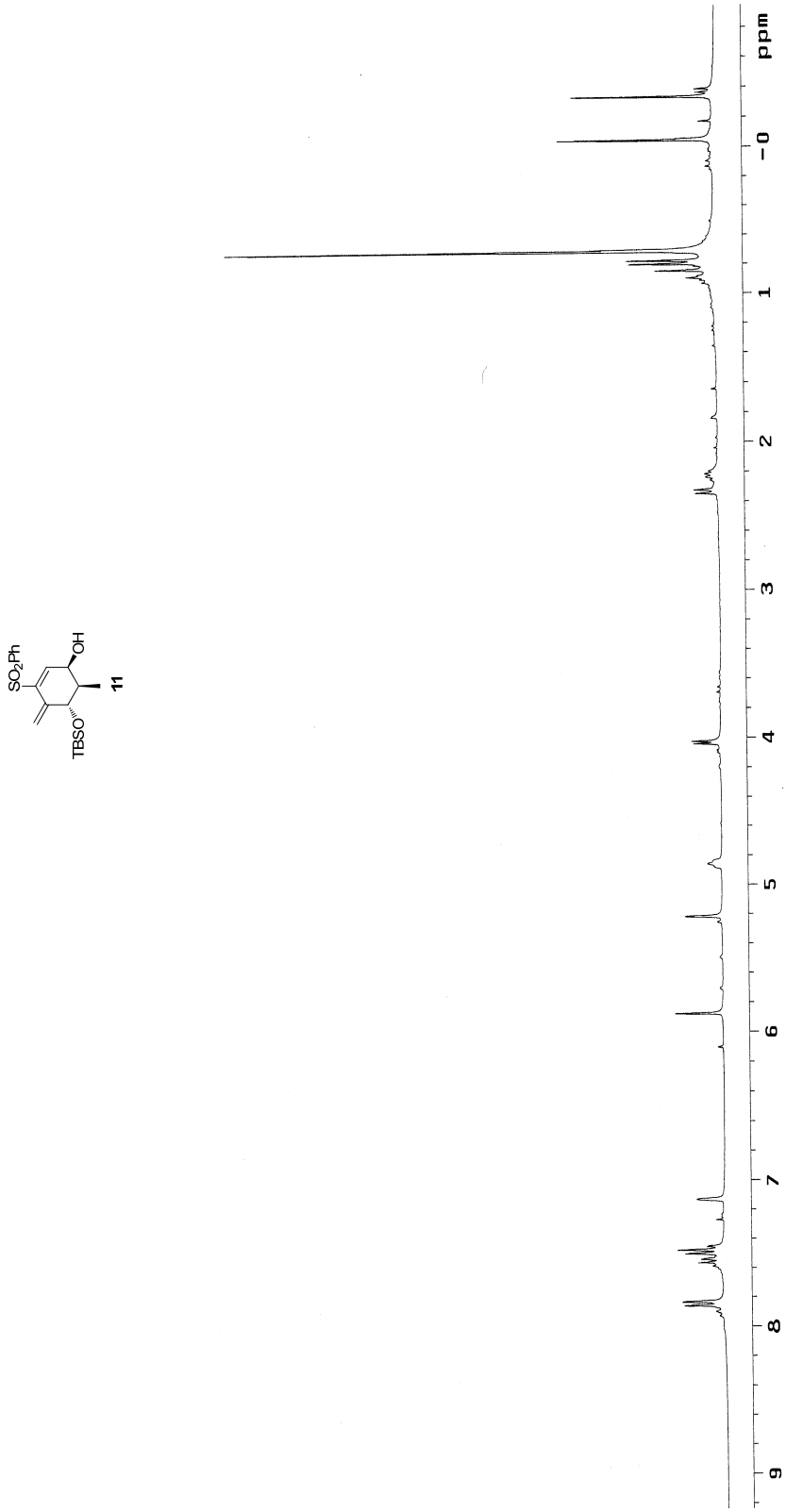
75 MHz ^{13}C NMR of compound **32** in $CDCl_3$



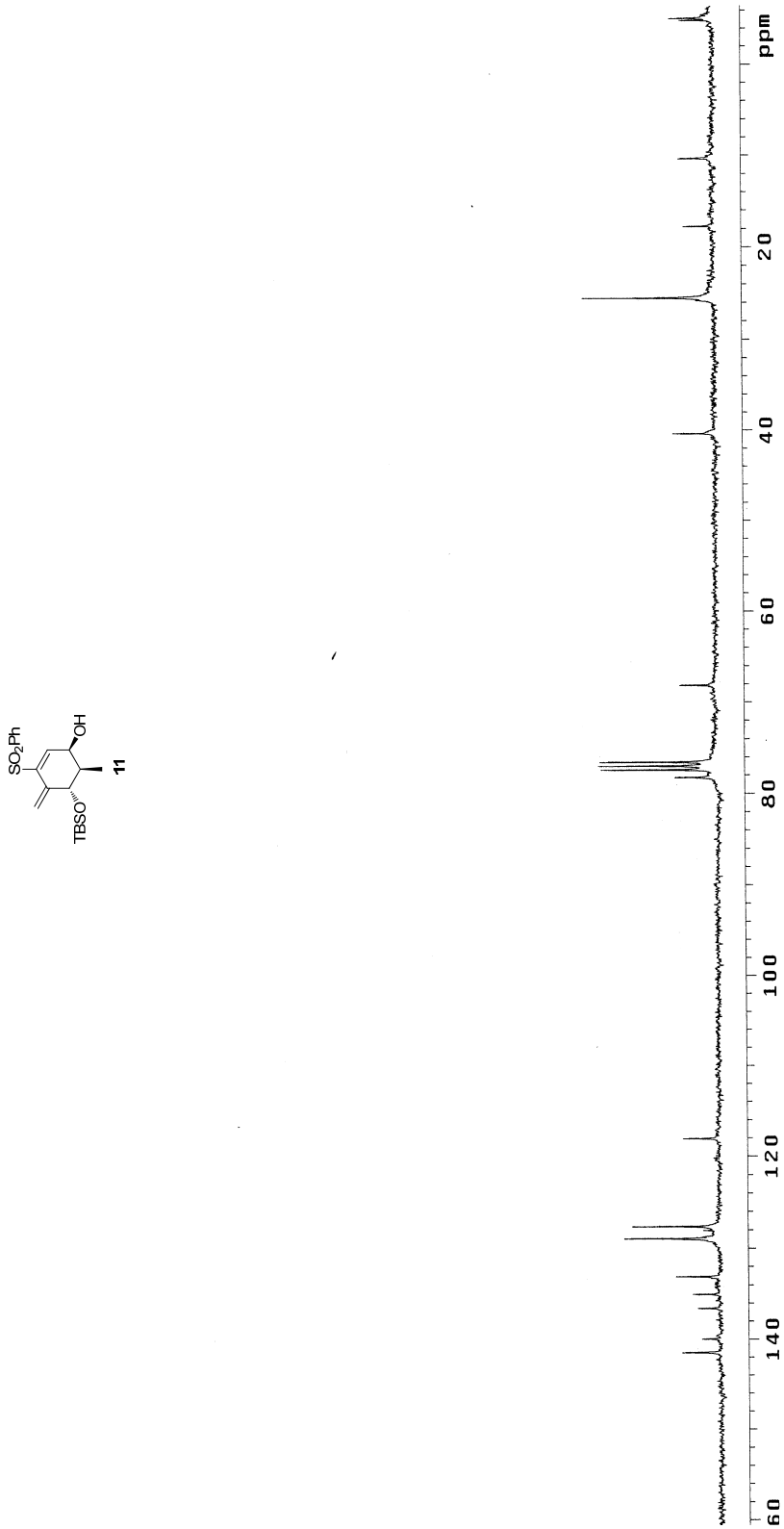
300 MHz ^{1}H NMR of compound **28** in $CDCl_3$



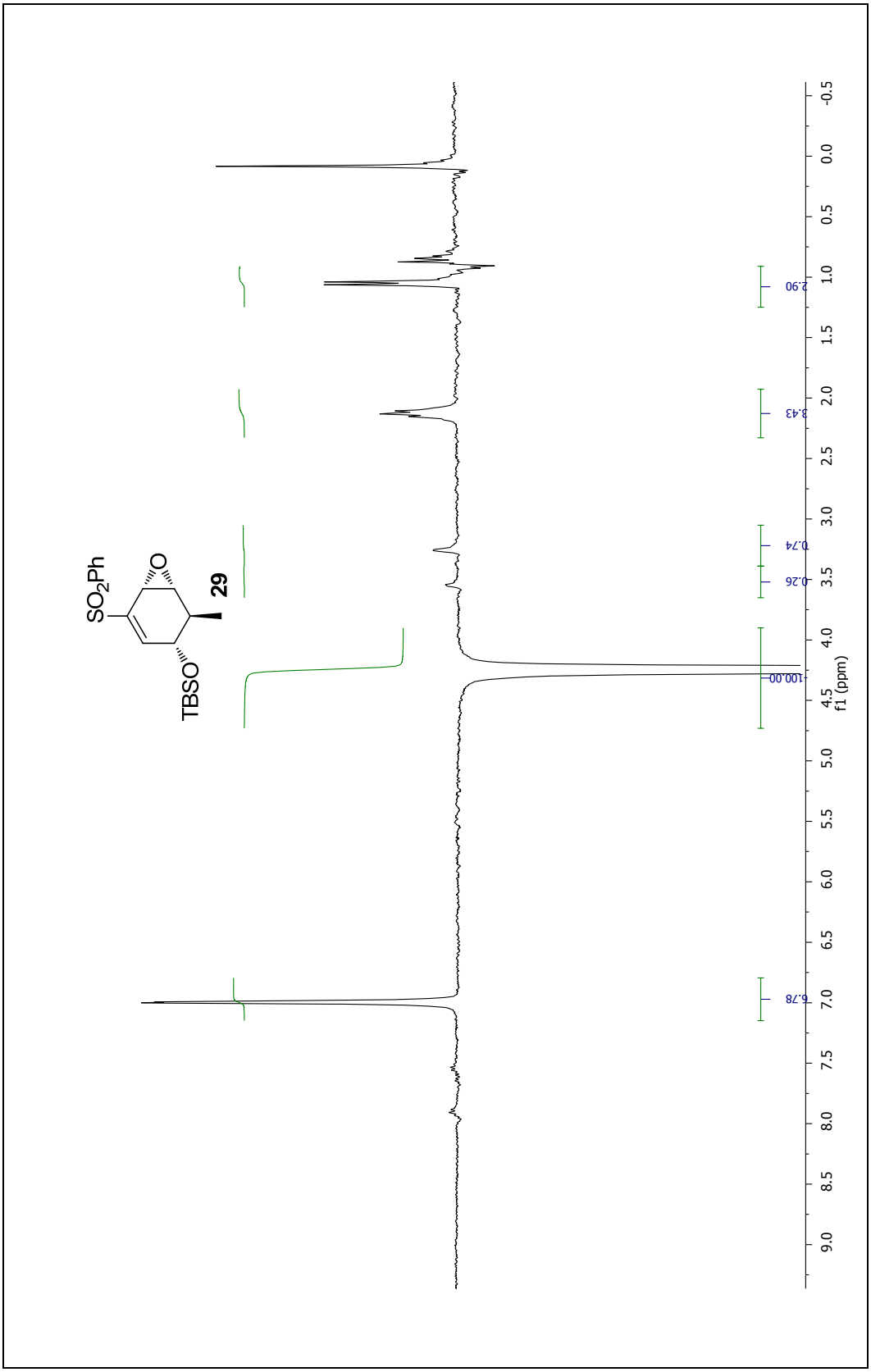
75 MHz ^{13}C NMR of compound **28** in $CDCl_3$



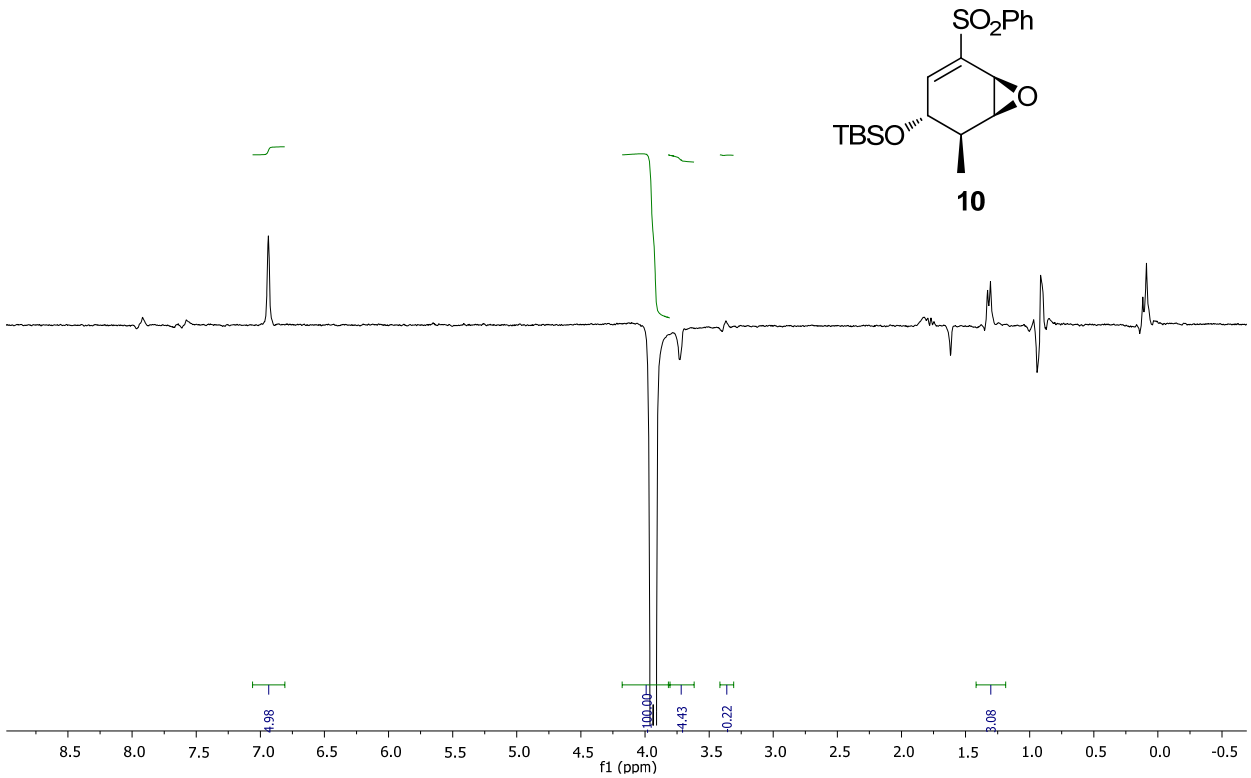
300 MHz ^{1}H NMR of compound **11** in $CDCl_3$



75 MHz ^{13}C NMR of compound **11** in $CDCl_3$



300 MHz NOE NMR of compound **29** in $CDCl_3$



300 MHz NOE NMR of compound **10** in $CDCl_3$