Supporting Information

Brønsted acid-induced transannulation of the phytochemical zerumbone

Gengo Kashiwazaki, [a]*‡ Ryo Watanabe,[a]‡ Terutaka Tsuzuki,[a] Chieko Yamamoto,[a] Atsuya Nishikawa,[a] Satoru Ohtomo,[a] Tomomi Yoshikawa,[a] Yuto Kitamura,[a] Yoshimi Utaka,[a] Yasushi Kawai,[b] Noriko Tsuchida,[c] and Takashi Kitayama[a]*

[a]Major in Advanced Bioscience, Graduate School of Agriculture, Kindai University, Nara, Nara 631-8505, Japan

[b]Faculty of Bioscience, Nagahama Institute of Bio-Science and Technology, Nagahama, Shiga 526-0829, Japan

[c]Faculty of Medicine, Saitama Medical University, Moroyama, Saitama 350-0495, Japan

‡These authors contributed equally.

*To whom correspondence should be addressed. E-mail: kashigen@nara.kindai.ac.jp, and kitayama@nara.kindai.ac.jp

Table of contents

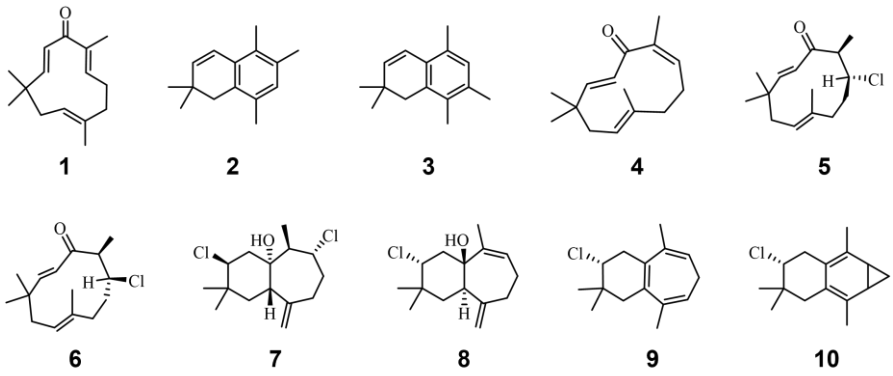


Figure S1. The structures of compounds **1**–**10**.

Table S1. Time-dependent conversion of **1** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	98	0	0	0	0	0	0	0
0.5	24	25	18	11	2	13	0	0
1	14	12	27	8	6	24	1	0
1.5	9	6	32	5	10	27	2	0
2	8	5	32	4	12	27	3	0
2.5	6	4	34	3	13	27	4	0
3	5	3	33	1	14	26	5	0
3.5	4	2	33	1	15	24	6	0
4	4	2	32	1	17	23	6	0
6	3	1	30	1	18	20	10	0
24	2	0	8	0	23	5	28	0
96	0	0	0	0	17	6	22	12
192	0	0	0	0	20	12	17	23
336	0	0	0	0	3	14	3	33

Table S2. Time-dependent conversion of **4** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	0	95	0	0	0	0	0	0
0.5	0	9	4	4	3	56	0	0
6	0	2	12	0	13	46	11	0
24	0	0	0	0	16	21	36	0
72	0	0	0	0	18	0	50	1

Table S3. Time-dependent conversion of **8** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	0	0	0	0	0	97	0	0
1	0	0	0	0	0	76	4	0
2	0	0	0	0	0	61	12	0
4	0	0	0	0	0	20	30	0
8	0	0	0	0	0	15	37	0
24	0	0	0	0	0	0	47	0
48	0	0	0	0	0	0	34	4
72	0	0	0	0	0	0	29	14

Table S4. Time-dependent conversion of **9**, **10** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	0	0	0	0	0	0	96	0
0.5	0	0	0	0	0	0	94	0
4	0	0	0	0	0	0	93	0
6	0	0	0	0	0	0	91	0
8	0	0	0	0	0	0	88	0
24	0	0	0	0	0	0	80	5
168	0	0	0	0	0	0	34	14

Table S5. Time-dependent conversion of **5** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	0	0	97	0	0	0	0	0
1	2	0	82	0	1	1	0	0
2	1	1	72	0	2	5	1	0
4	5	2	61	0	5	8	2	0
8	6	2	52	0	10	12	6	0
24	6	2	28	0	14	11	13	0
48	6	2	15	0	15	4	22	0
72	6	4	12	0	14	4	21	0

Table S6. Time-dependent conversion of **6** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	0	0	0	95	0	0	0	0
0.02	7	2	8	2	43	0	4	0
0.5	0	0	0	1	72	1	8	0
1	0	0	0	0	78	3	10	0

Table S7. Time-dependent conversion of **7** under HCl in ethyl acetate

Time (h)	compound							
	1	**4**	**5**	**6**	**7**	**8**	**9, 10**	**2, 3**
0	0	0	0	0	98	0	0	0
24	0	0	0	0	89	0	0	0

Table S8. ^{1}H and ^{13}C NMR comparison between (2*Z*)-zerumbone (**4**) and (2*Z*,6*Z*)-zerumbone (**1d**)[reference 1]

	4			**1d**[reference 1]		
position	δ_C[a]	δ_H[b]	multiplicity (*J* in Hz)	δ_C[c]	δ_H[d]	multiplicity (*J* in Hz)
1	203.1			203.8		
2	137.5			137.5		
3	131.4	5.53	m	131.5	5.53	m
4a, b	33.5	2.20–2.09	m	33.5	2.18	m
5a	37.1	2.41–2.25	m	37.0	2.31 (2H)	m
5b		1.99–1.77	m			
6	137.6			137.0		
7	123.6	5.13	m	123.8	5.13	t (8.1)
8a	40.1	2.41–2.25	m	40.1	2.05–1.91 (2H)	m
8b		1.99–1.77	m			
9	37.3			42.9		
10	161.4	6.34	d (16.2)	161.7	6.34	d (16.2)
11	127.3	5.88	d (16.2)	127.5	5.88	d (16.2)
C2-Me	21.2	1.90	d (1.1)	21.4	1.91	s
C6-Me	20.3	1.70	d (1.4)	20.7	1.69	s
C9-Me	29.4	1.17	s	29.3	1.15	s
C9-Me	24.2	1.13	s	24.2	1.15	s

[a]Chemical shifts in $CDCl_3$ referenced to TMS (δ_C 0.0) at 100 MHz.
[b]Chemical shifts in $CDCl_3$ referenced to TMS (δ_H 0.0) at 400 MHz.
[c]Chemical shifts referenced to $CDCl_3$ (δ_C 77.0) at 125 MHz.
[d]Chemical shifts referenced to $CDCl_3$ (δ_H 7.26) at 500 MHz.

reference 1

G. Appendino, A. Minassi, J. A. Collado, F. Pollastro, G. Chianese, O. Taglialatela-Scafati, M. Ayyari, V. Garcia and E. Muñoz, *Eur. J. Org. Chem.*, 2015, **2015**, 3721-3726.

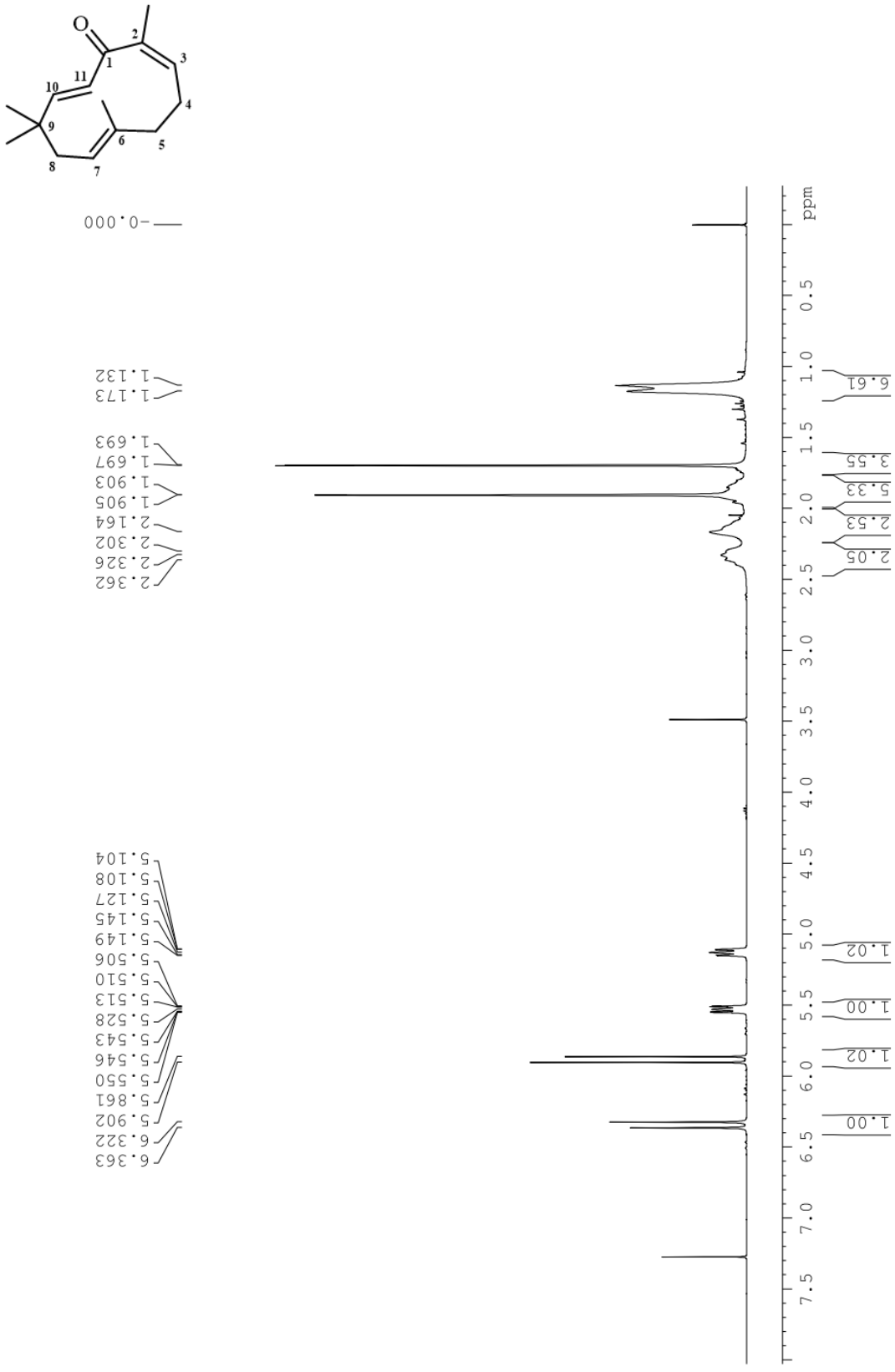


Figure S2. ^{1}H NMR spectrum of **4** ($CDCl_3$, 400 MHz).

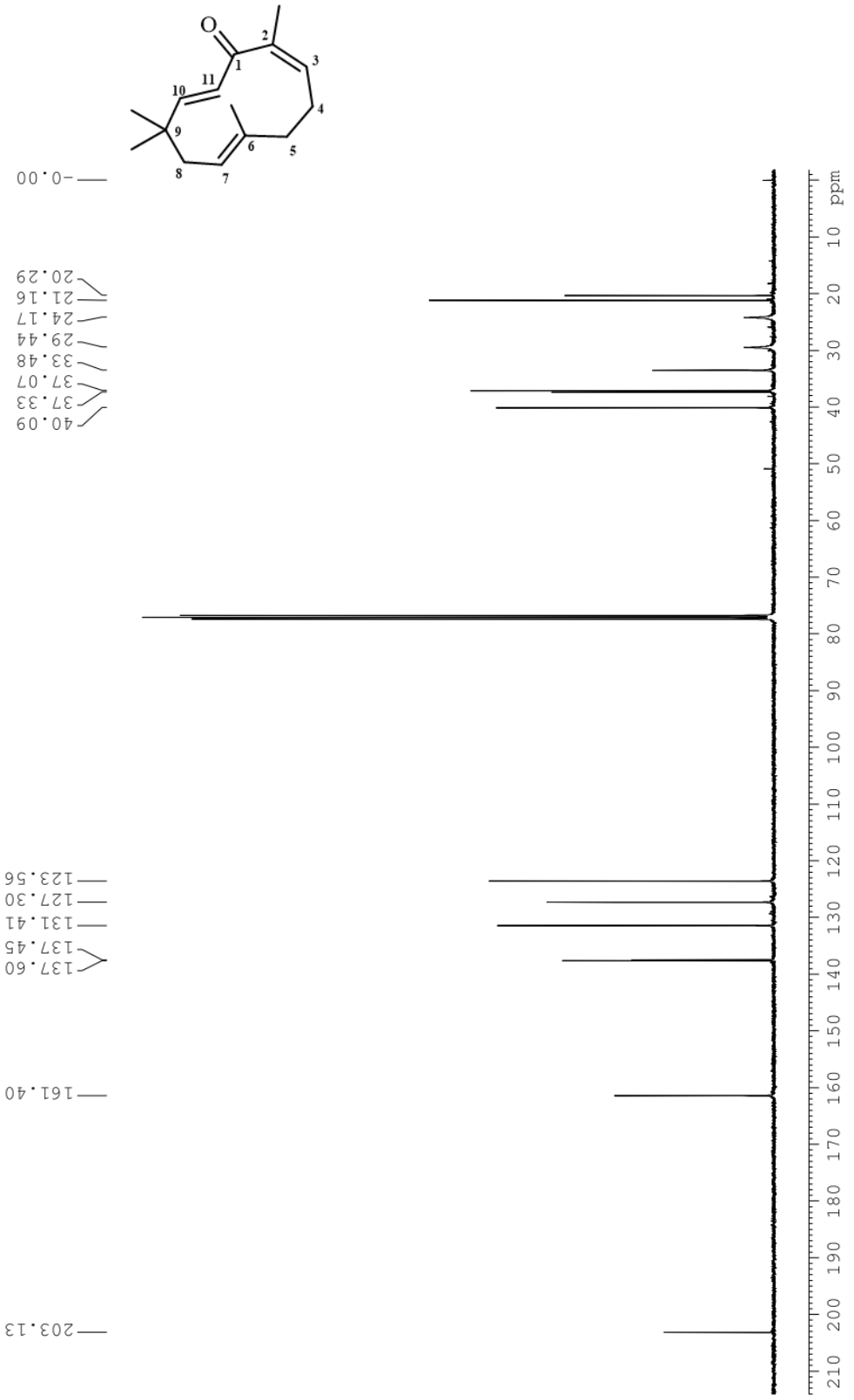


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **4** ($CDCl_3$, 100 MHz).

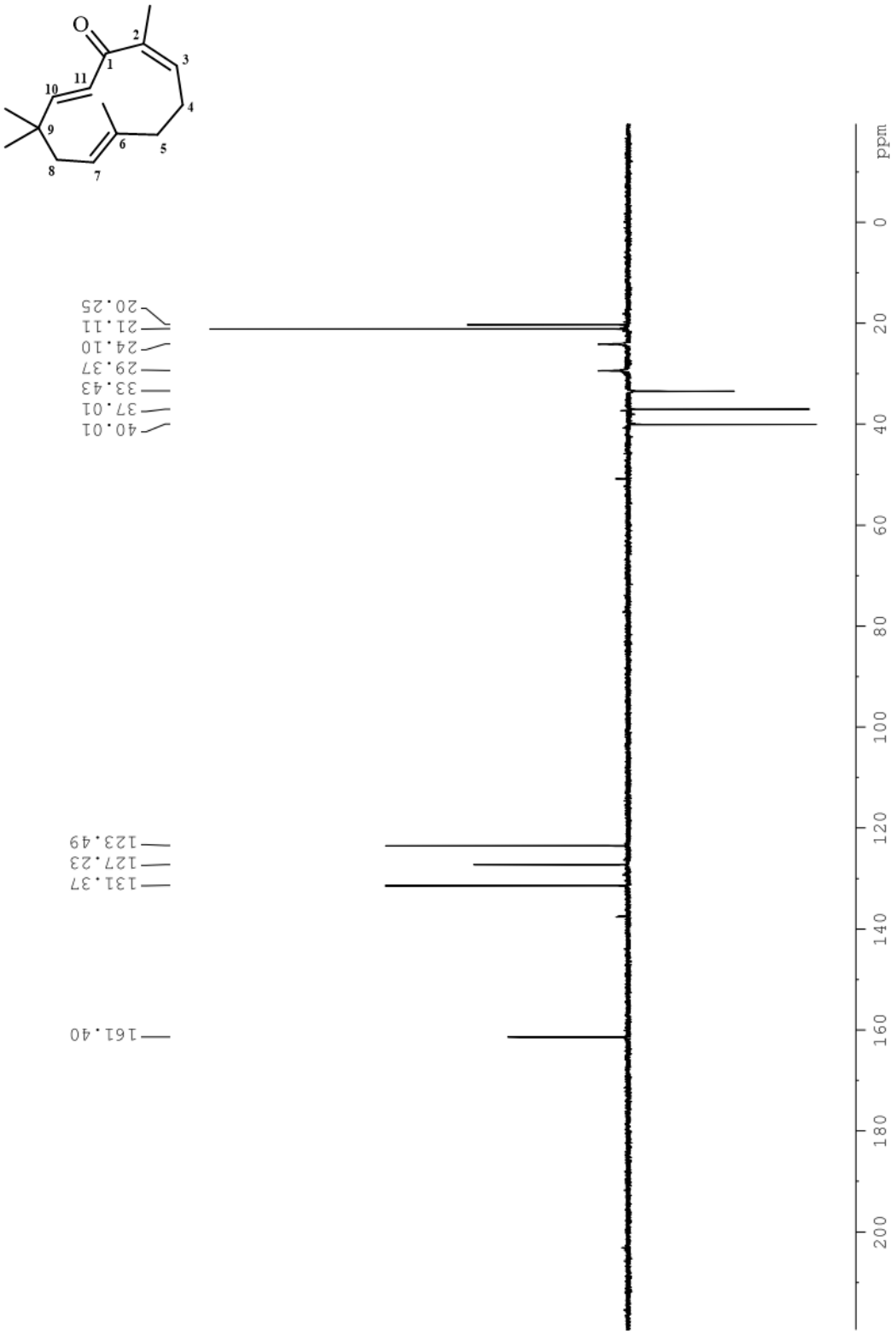


Figure S4. DEPT-135 spectrum of **4** ($CDCl_3$, 100 MHz).

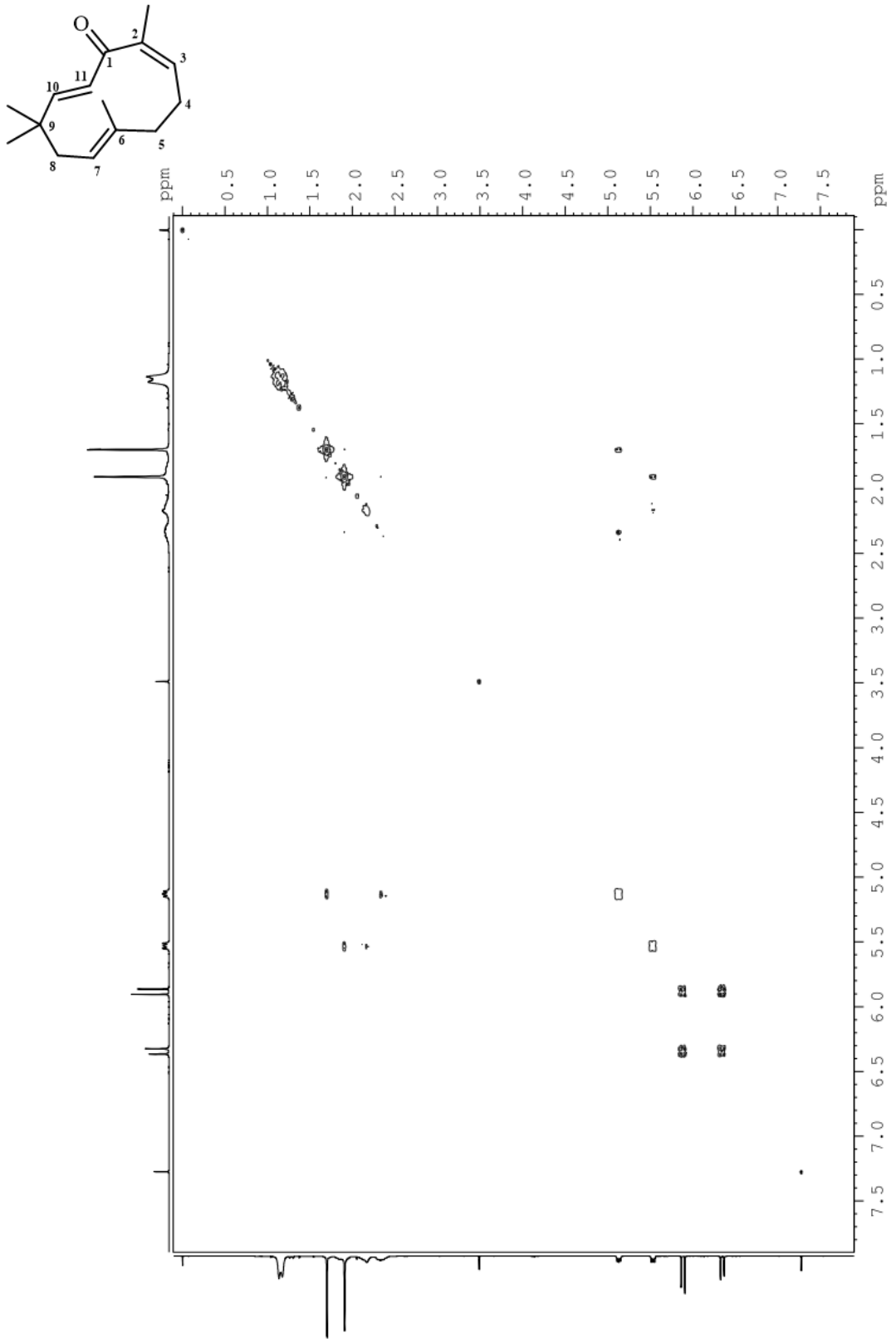


Figure S5. ^{1}H-^{1}H COSY of **4** ($CDCl_3$, 400 MHz).

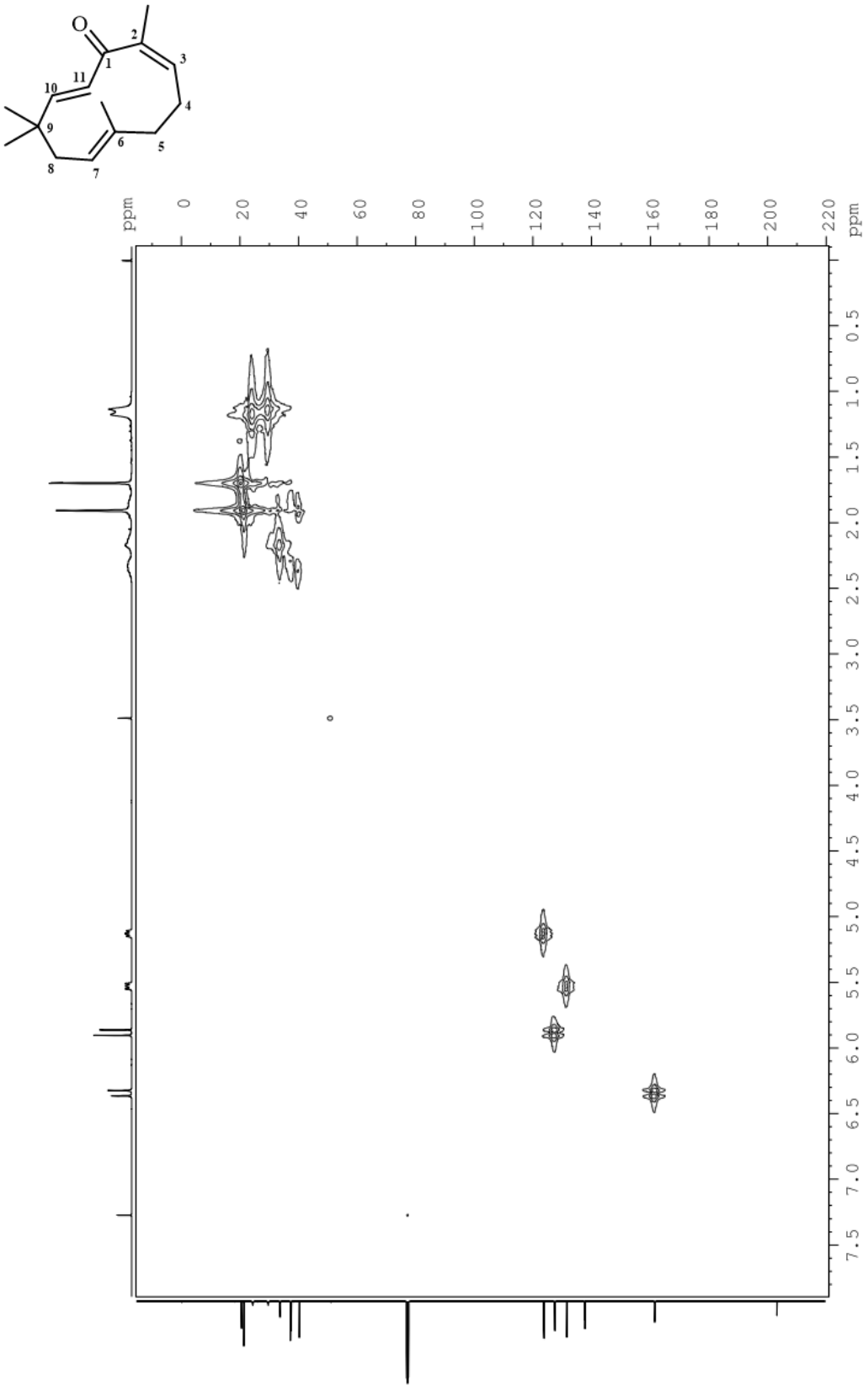


Figure S6. ^{1}H-^{13}C HMQC of **4** ($CDCl_3$, 400 MHz).

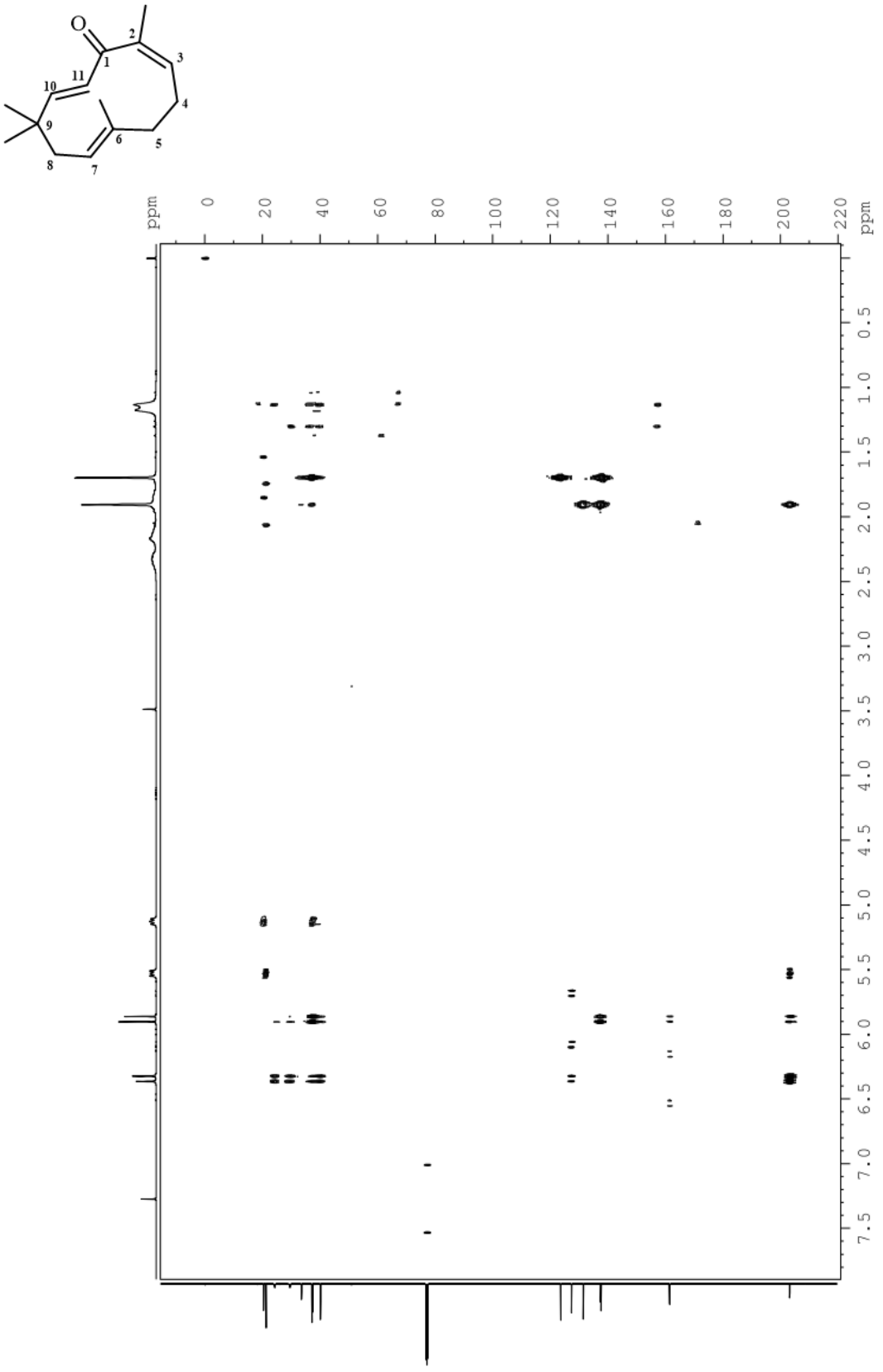


Figure S7. ^{1}H-^{13}C HMBC of **4** ($CDCl_3$, 400 MHz).

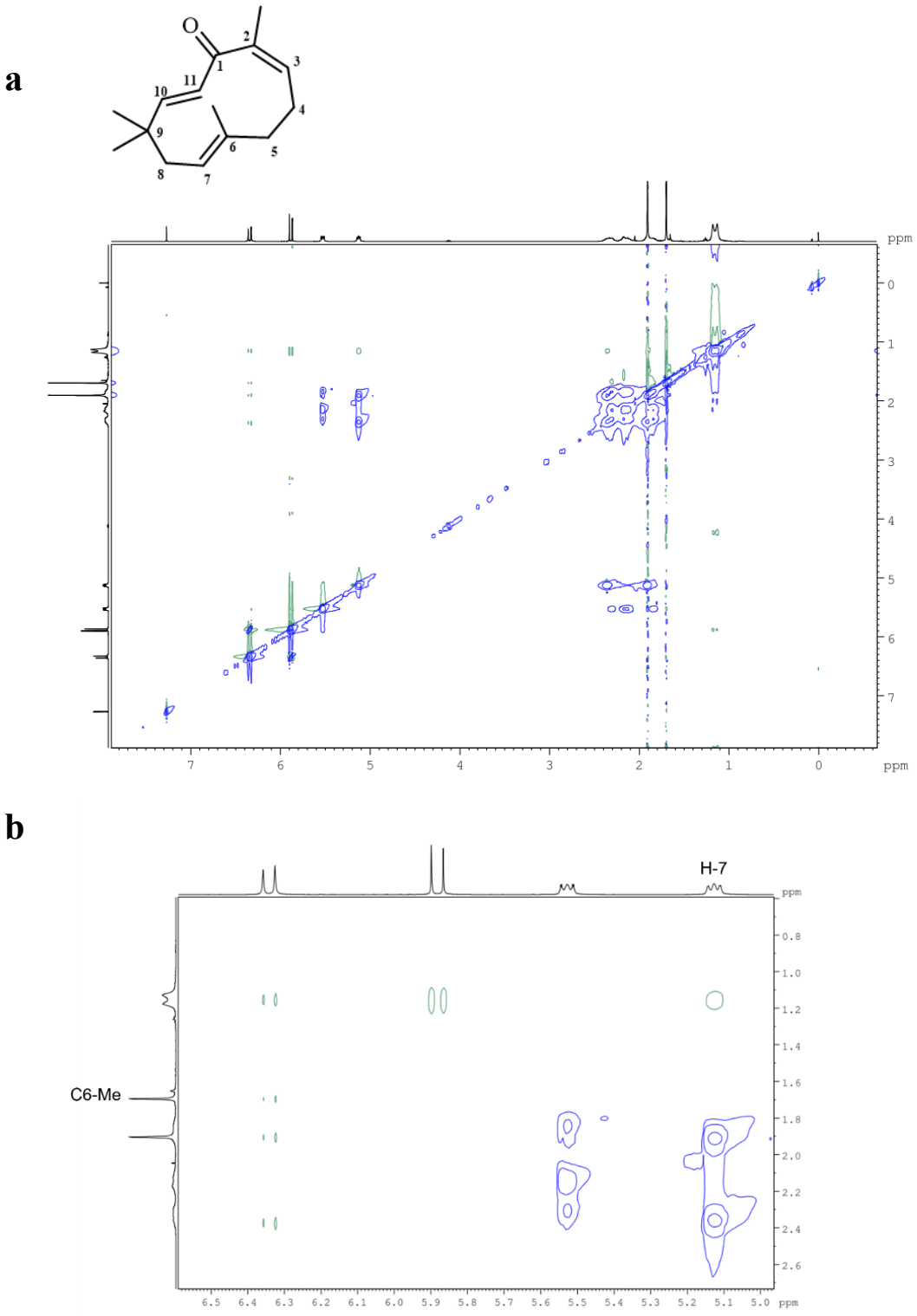


Figure S8. ROESY of **4** ($CDCl_3$, 500 MHz): the overview (a) and the magnified view (b). The positive and negative signals were colored blue and green, respectively. No cross peak between H-7 and C6-Me was observed.

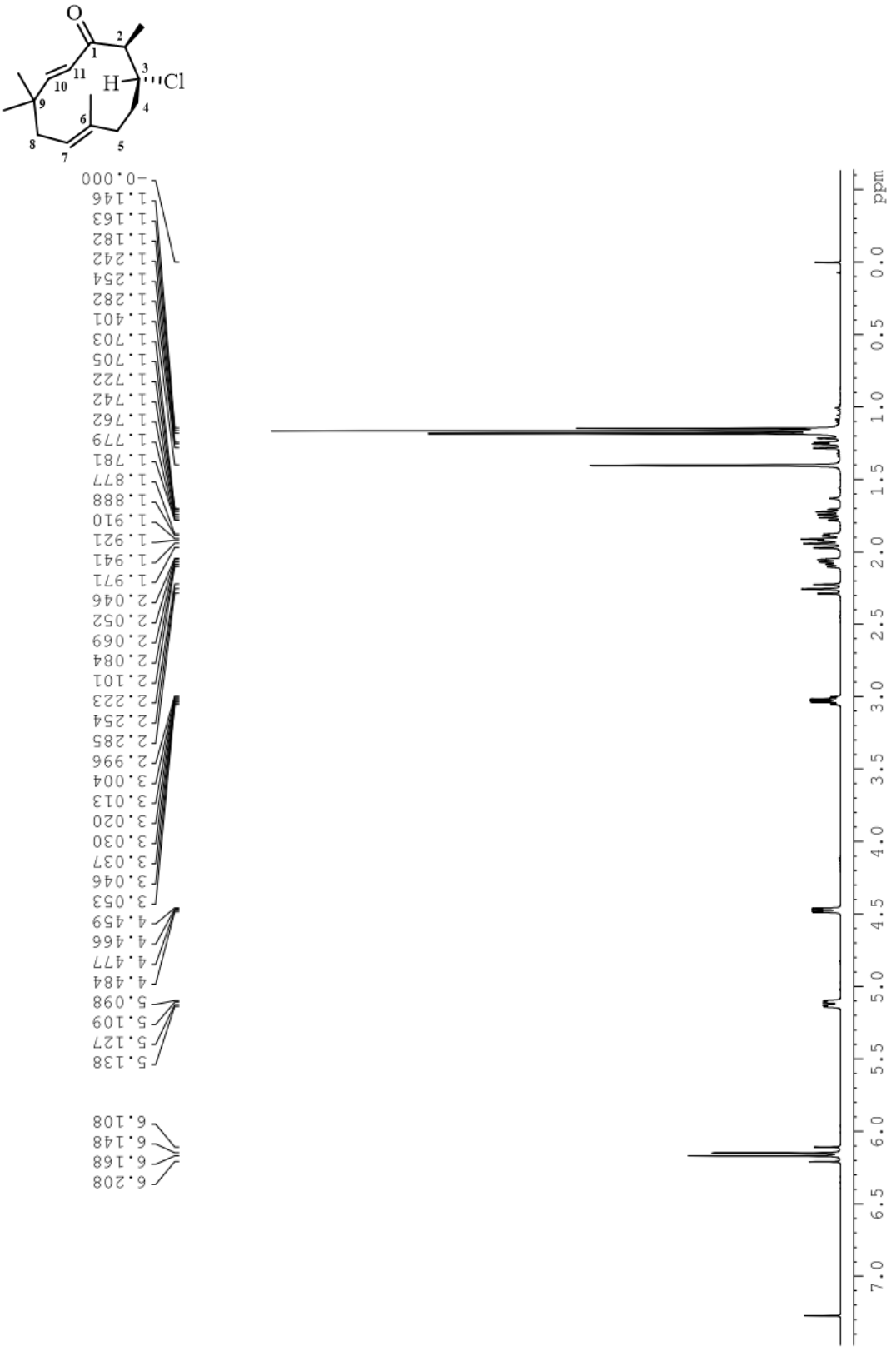


Figure S9. ^{1}H NMR spectrum of **5** ($CDCl_3$, 400 MHz).

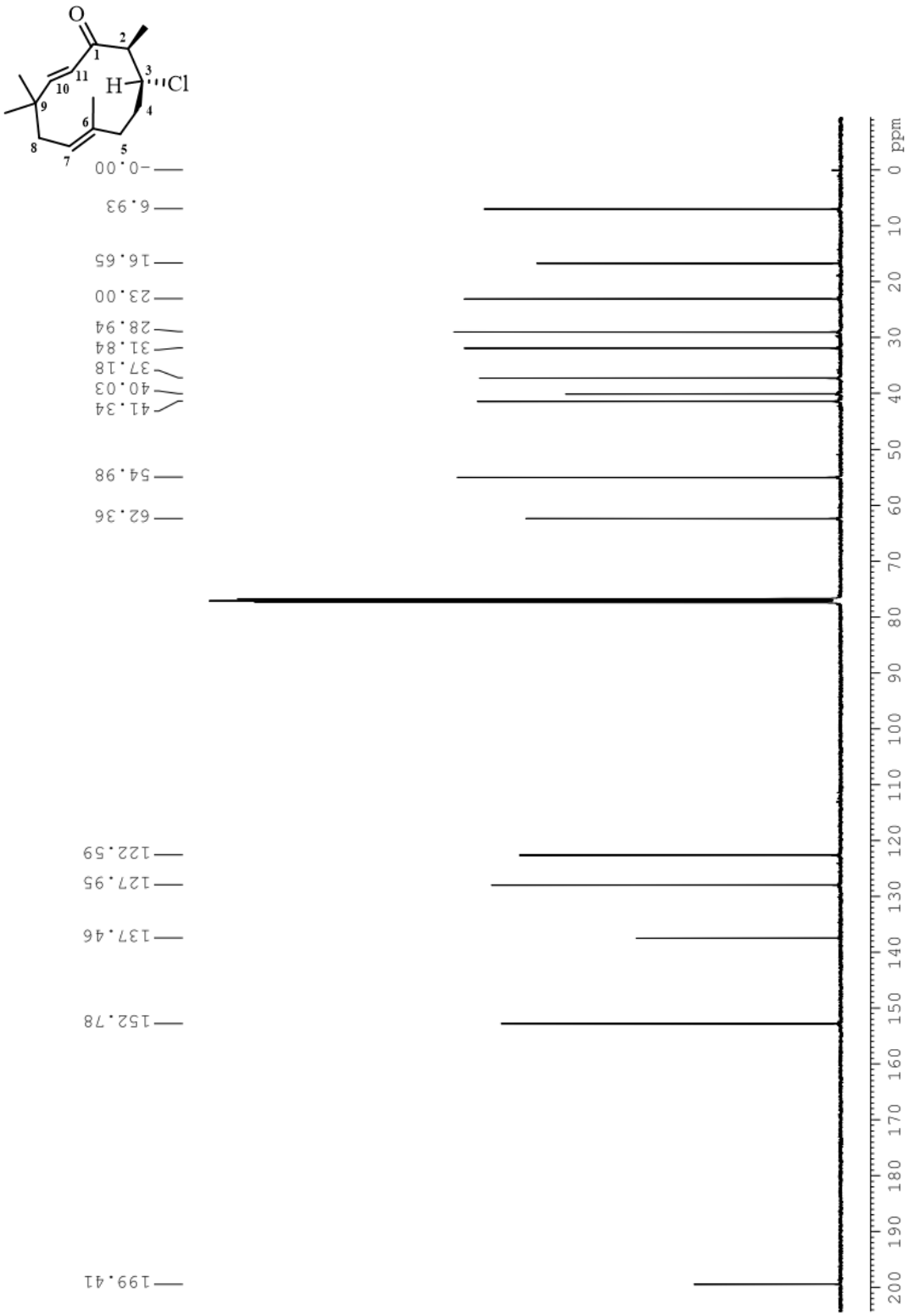


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **5** ($CDCl_3$, 100 MHz).

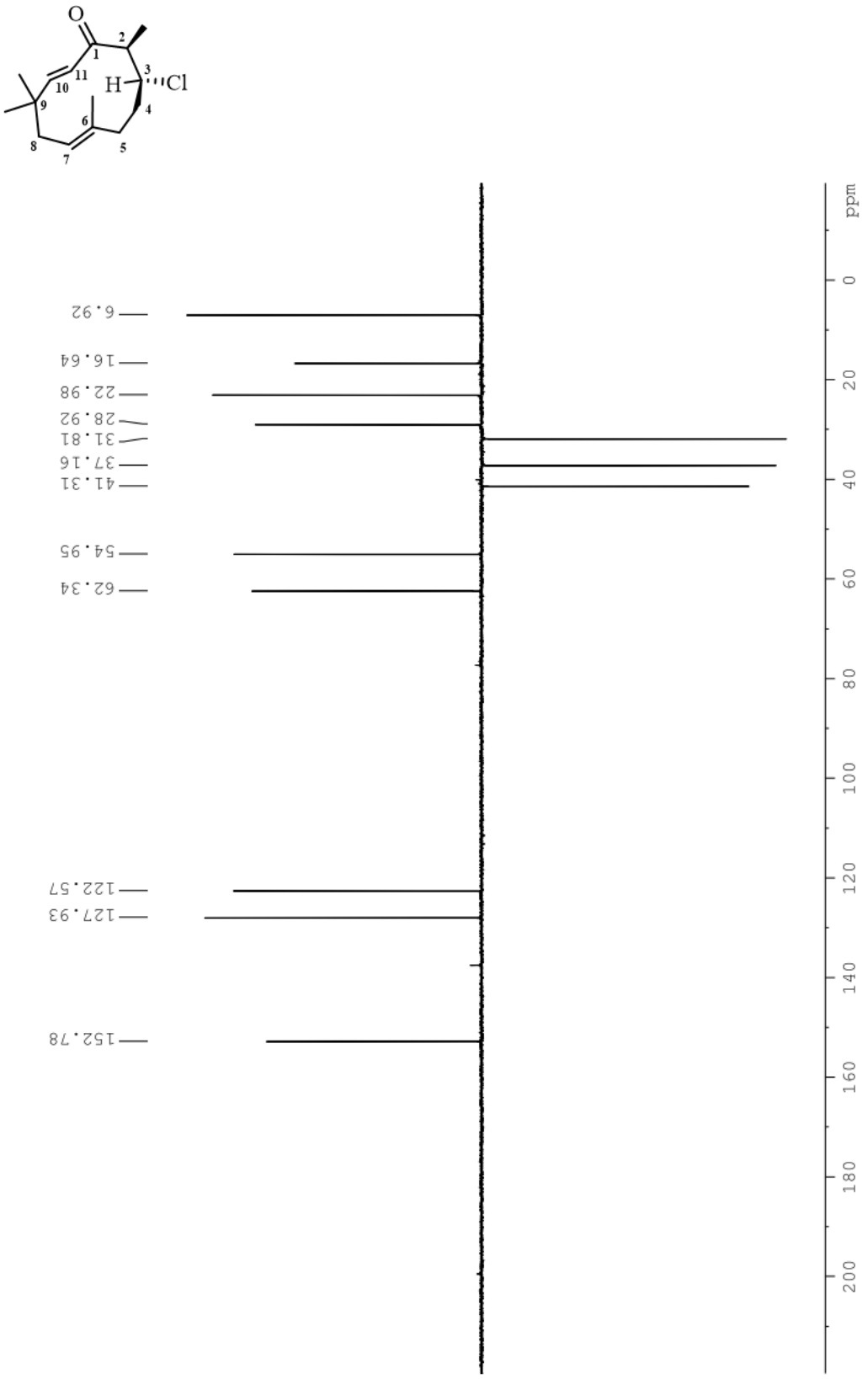


Figure S11. DEPT-135 spectrum of **5** ($CDCl_3$, 100 MHz).

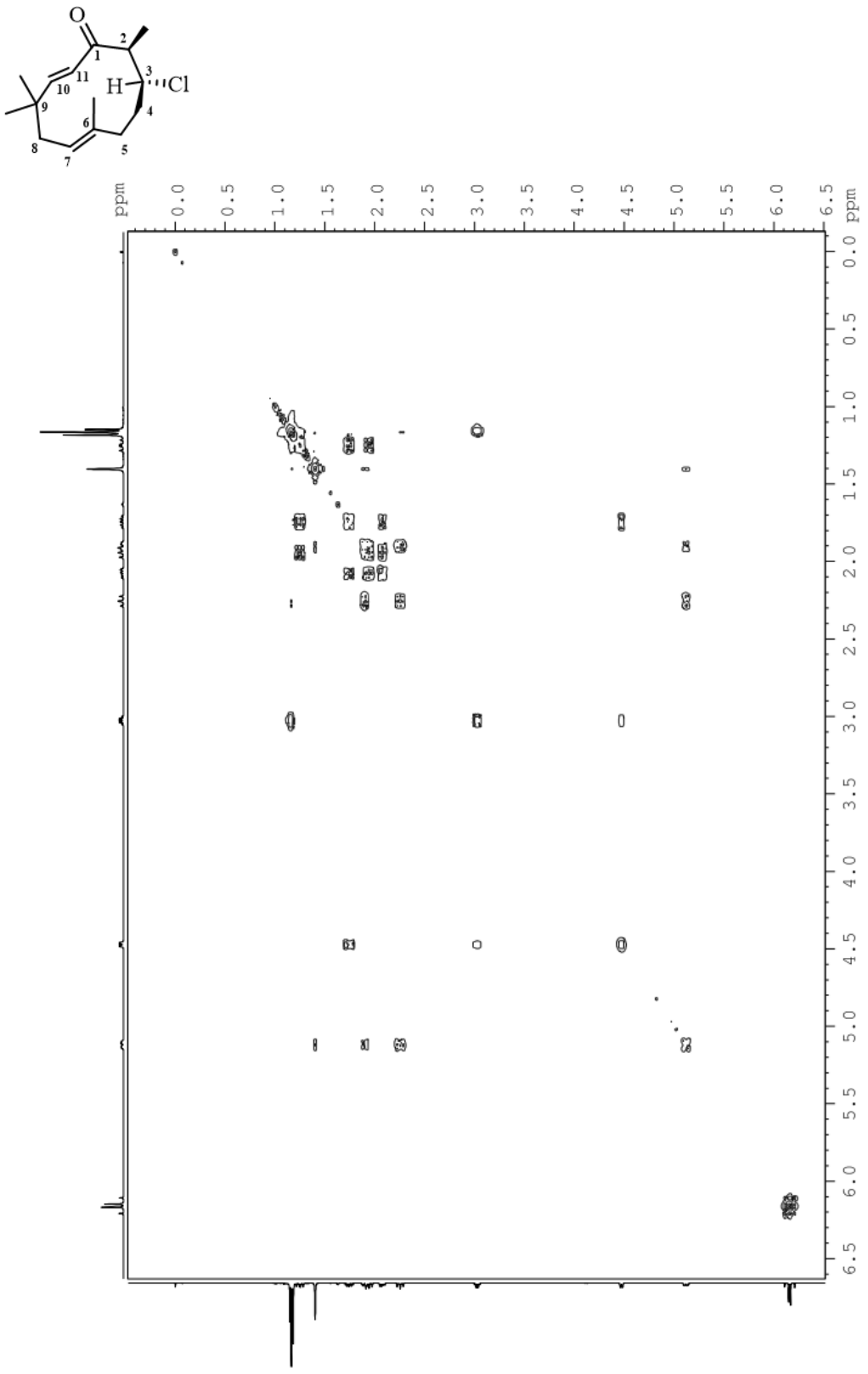


Figure S12. ^{1}H-^{1}H COSY of **5** ($CDCl_3$, 400 MHz).

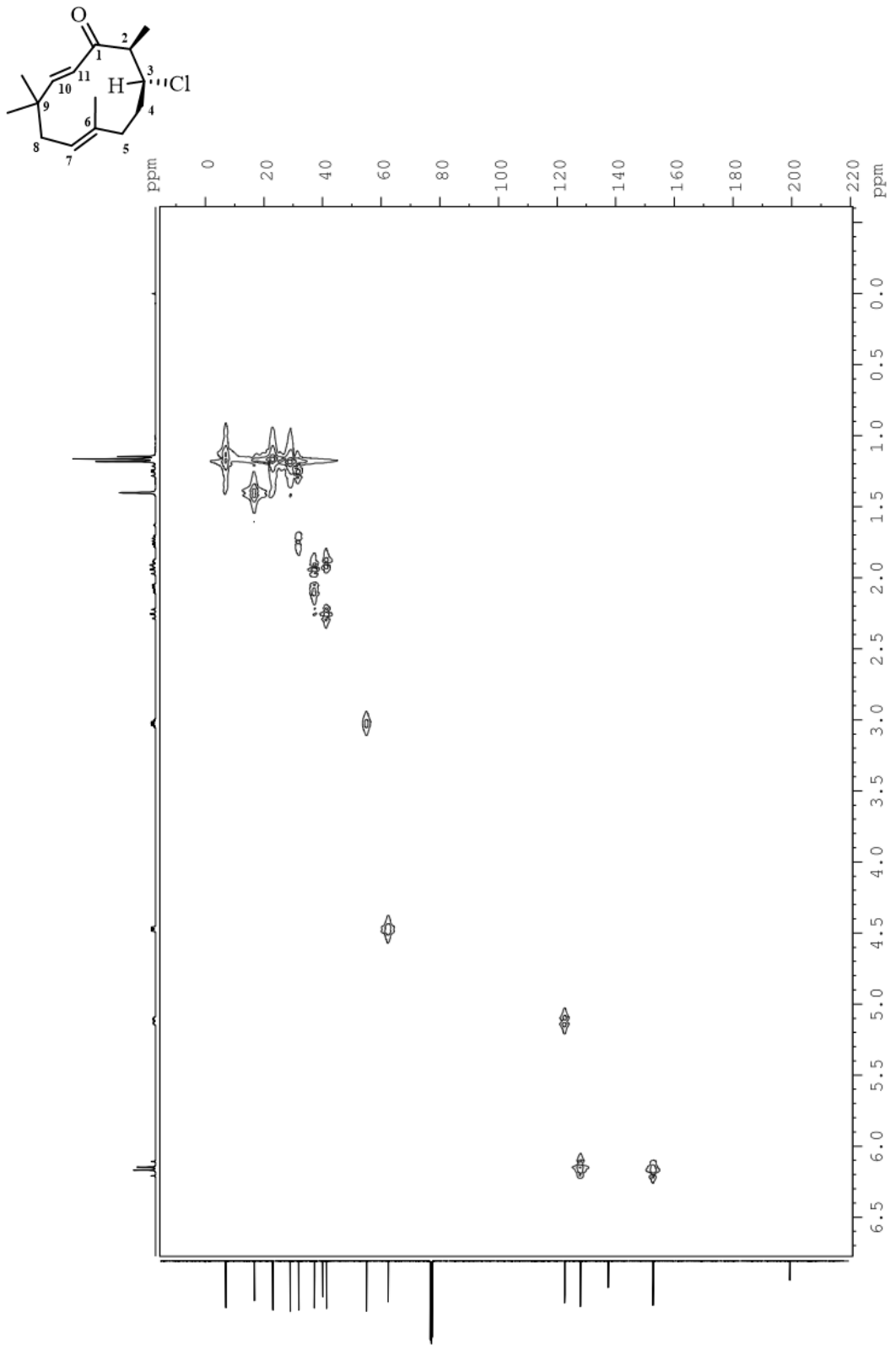


Figure S13. ^{1}H-^{13}C HMQC of **5** ($CDCl_3$, 400 MHz).

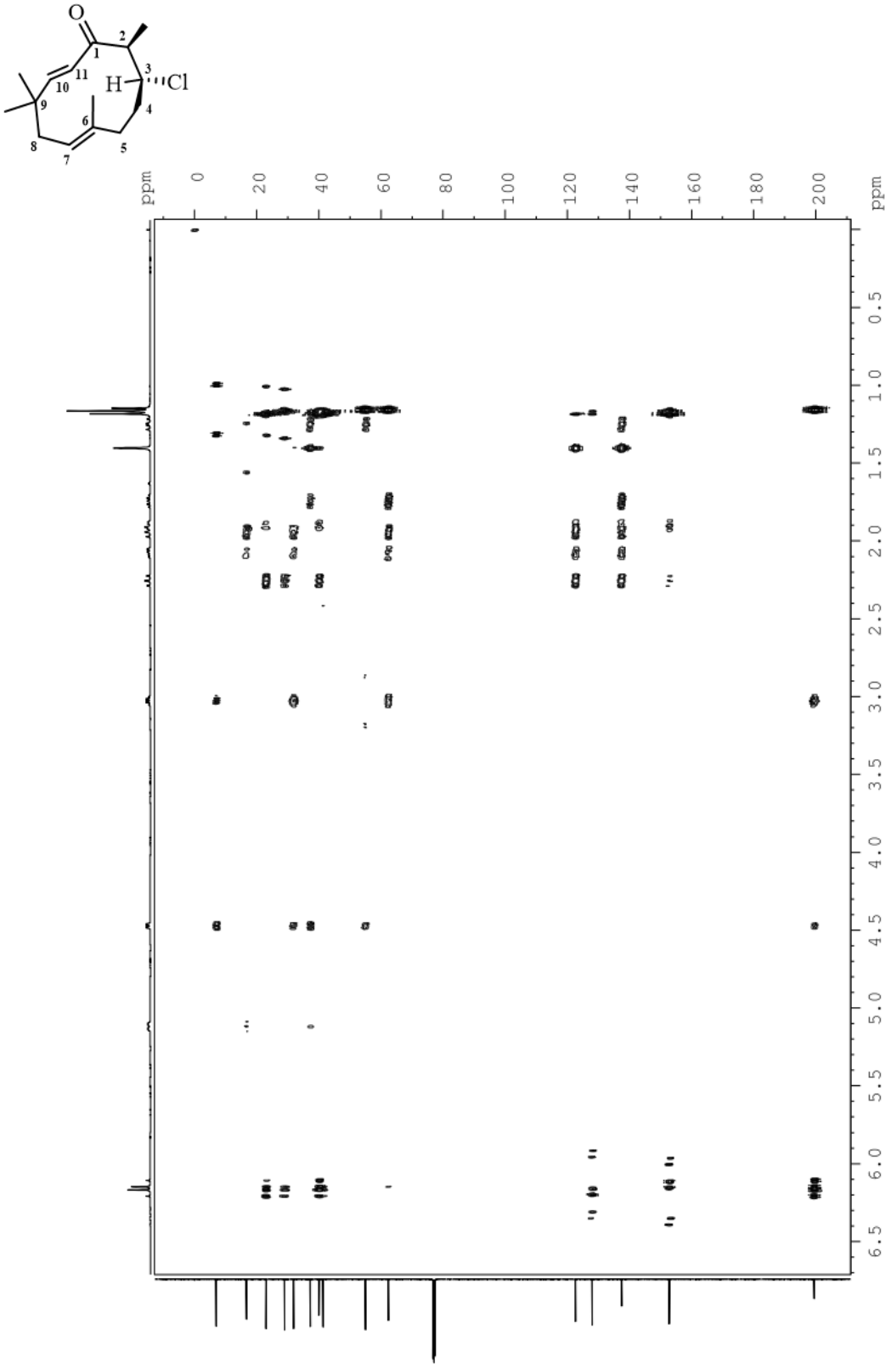


Figure S14. ^{1}H-^{13}C HMBC of **5** ($CDCl_3$, 400 MHz).

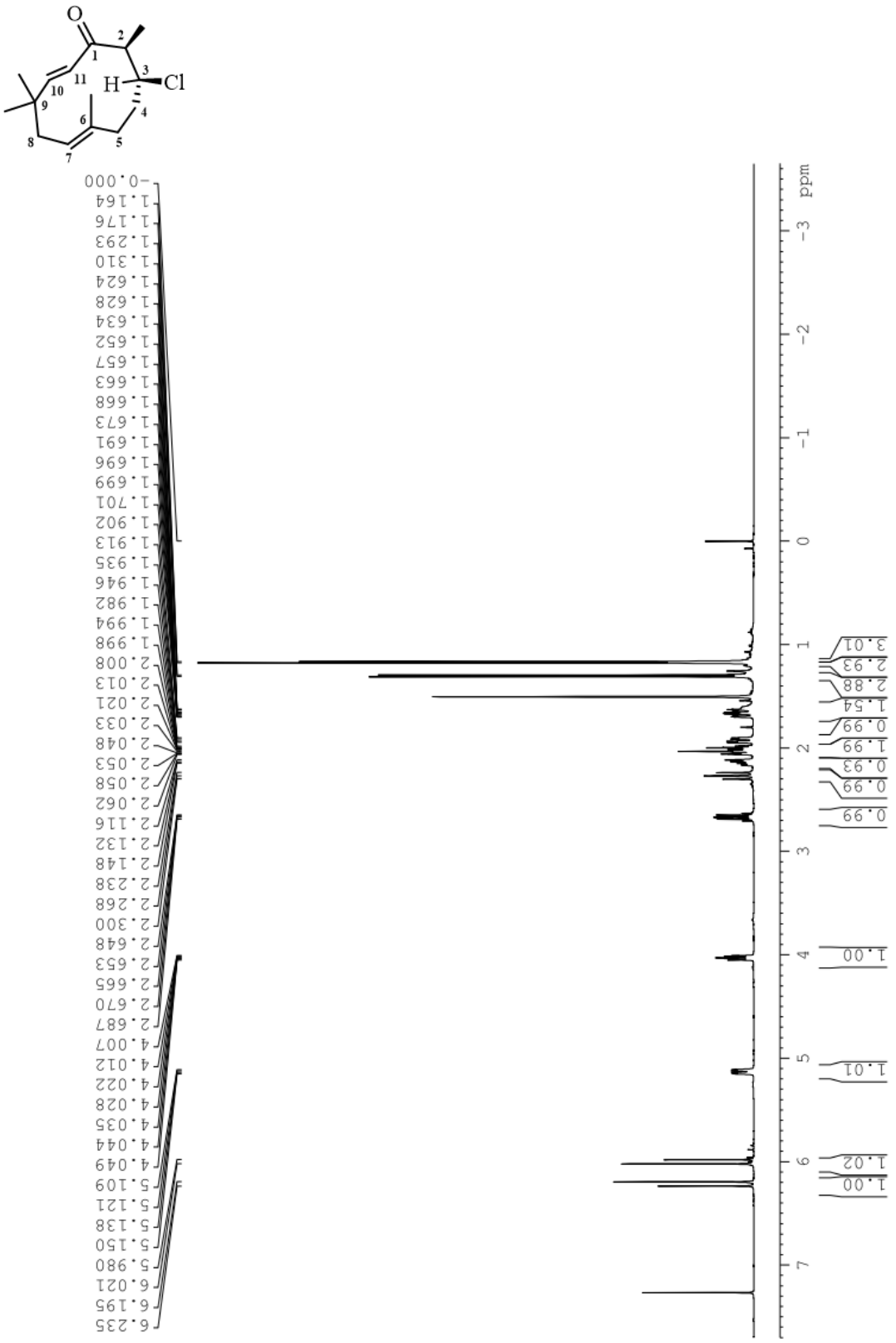


Figure S15. ^{1}H NMR spectrum of **6** ($CDCl_3$, 400 MHz).

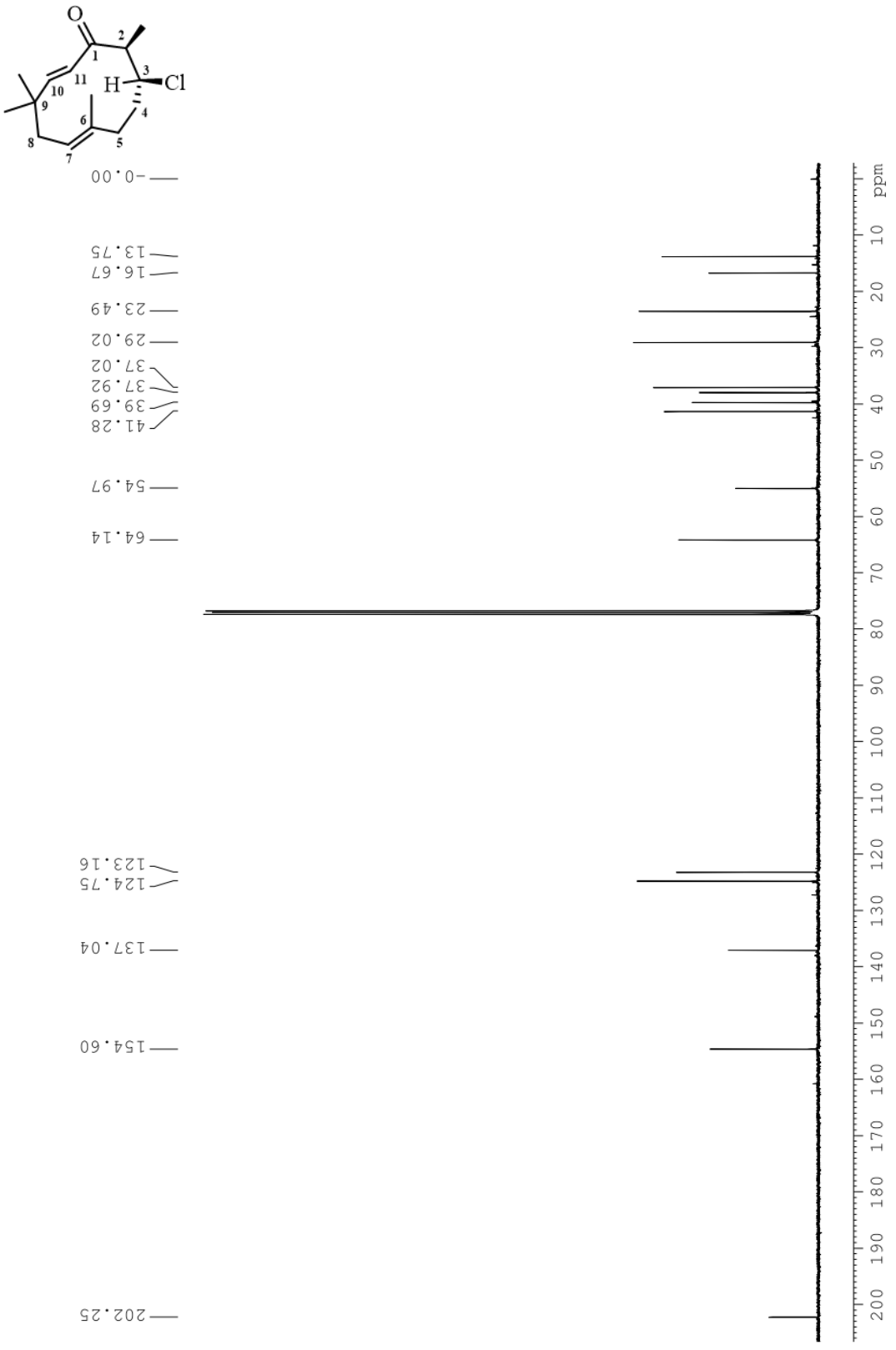


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **6** ($CDCl_3$, 100 MHz).

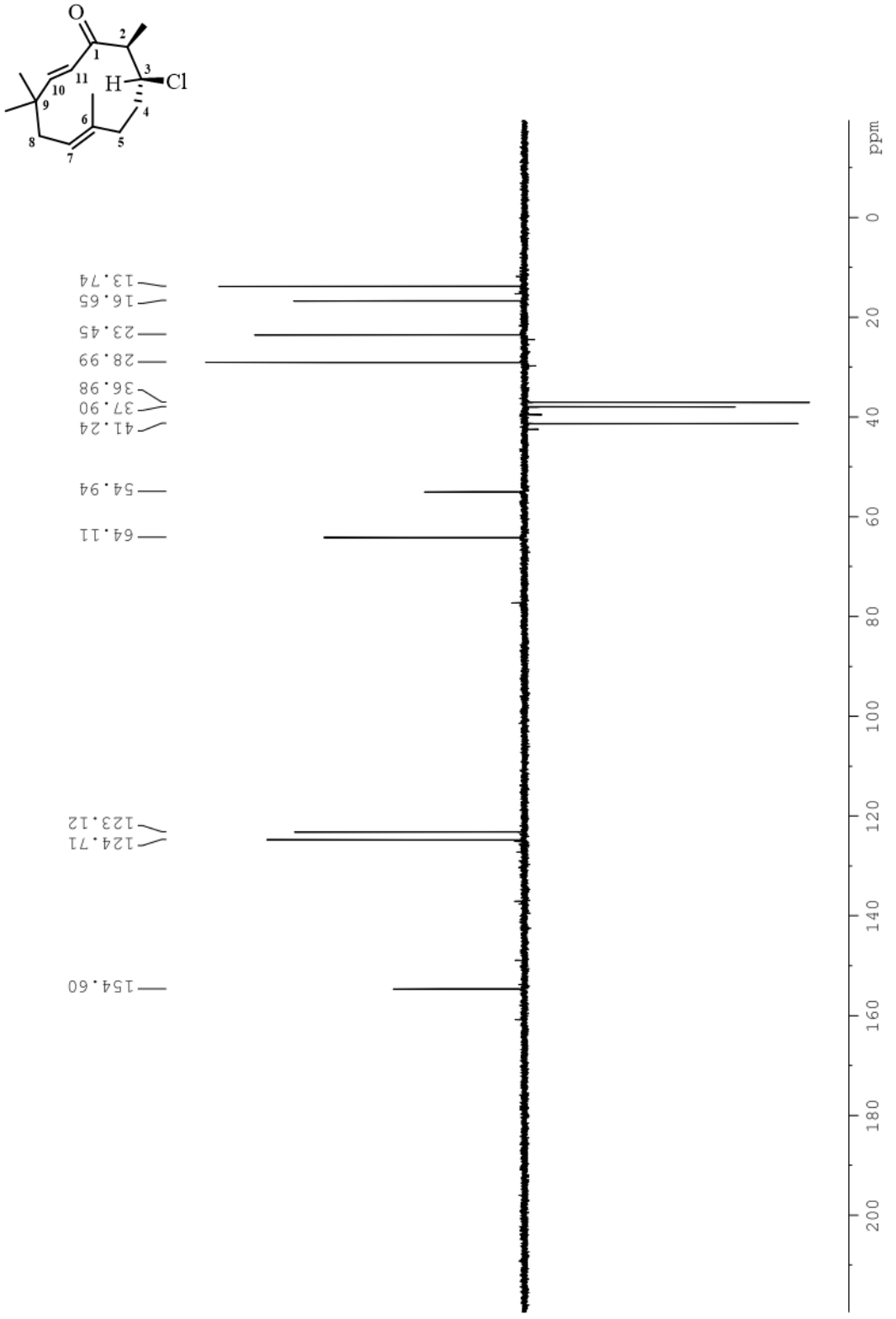


Figure S17. DEPT-135 spectrum of **6** ($CDCl_3$, 100 MHz).

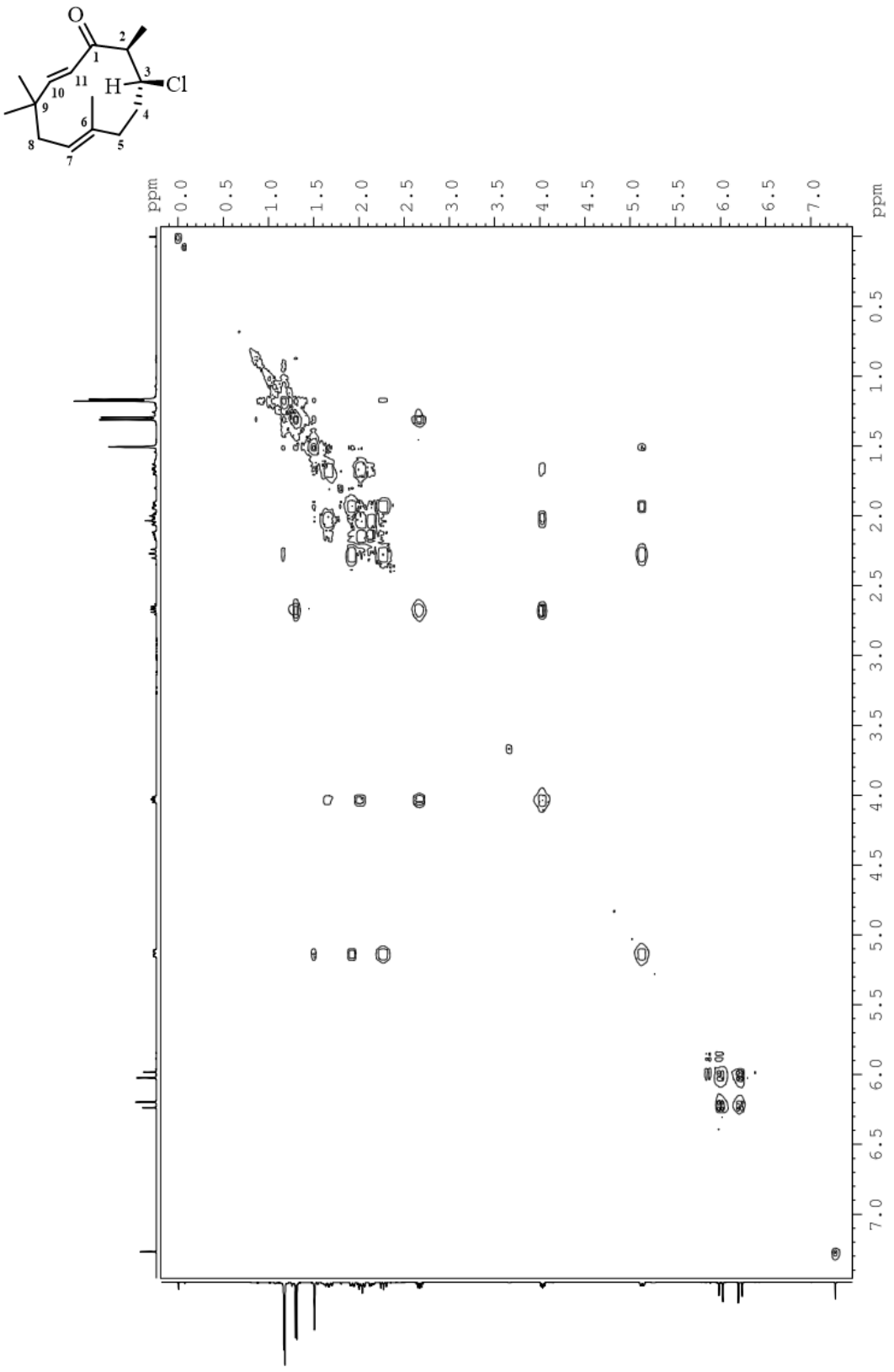


Figure S18. ^{1}H-^{1}H COSY of **6** ($CDCl_3$, 400 MHz).

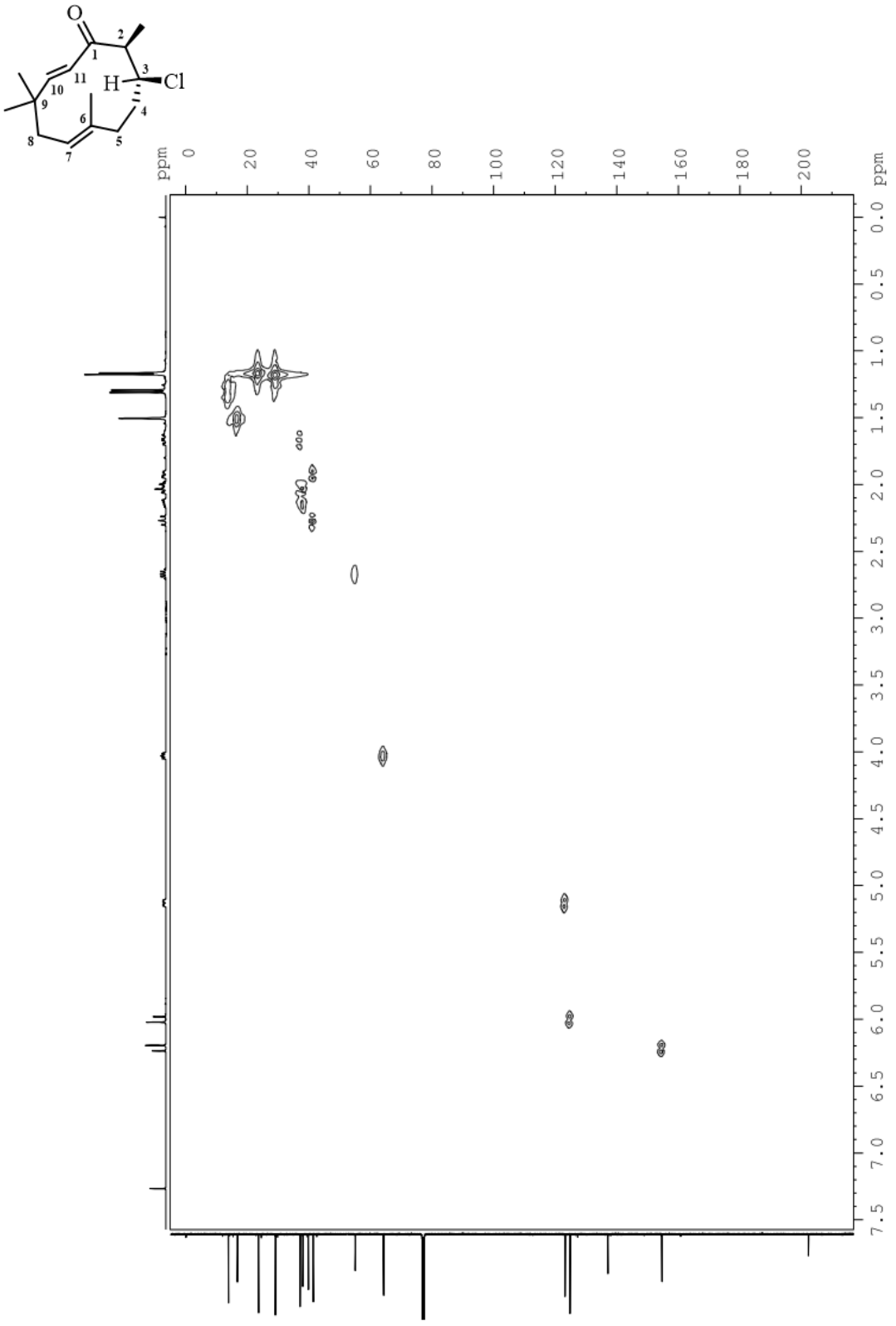


Figure S19. ^{1}H-^{13}C HMQC of **6** ($CDCl_3$, 400 MHz).

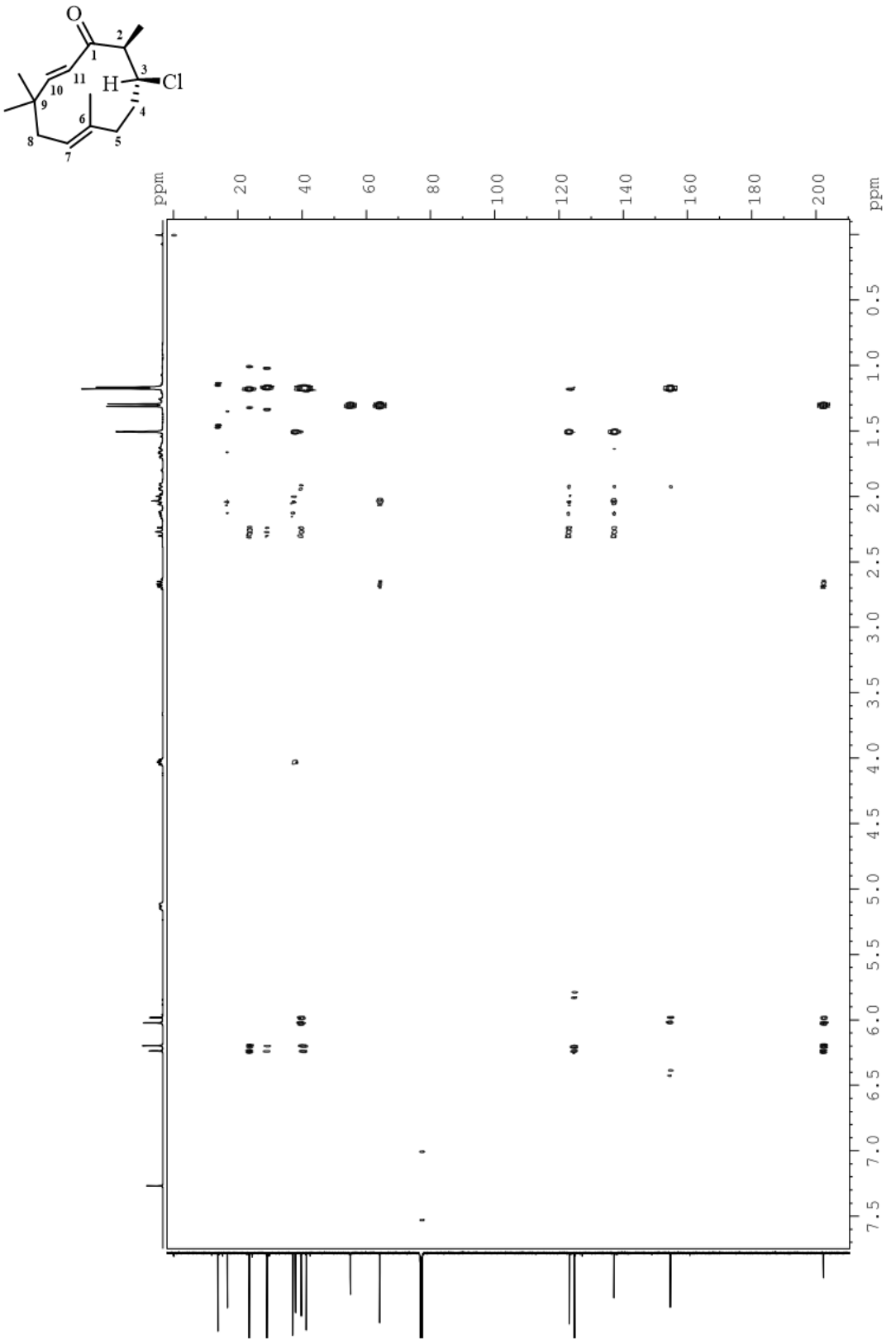


Figure S20. ^{1}H-^{13}C HMBC of **6** ($CDCl_3$, 400 MHz).

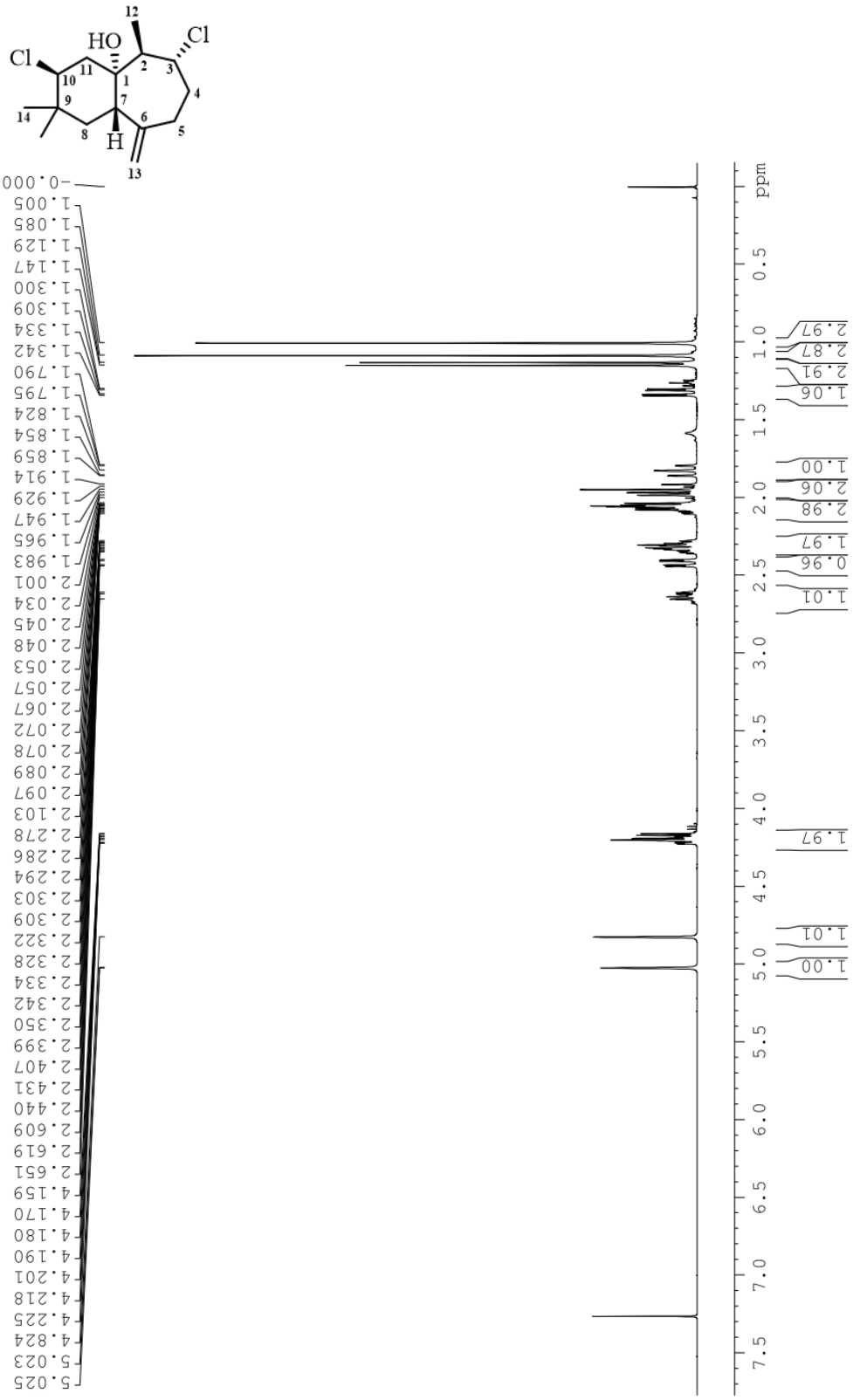


Figure S21. ^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz).

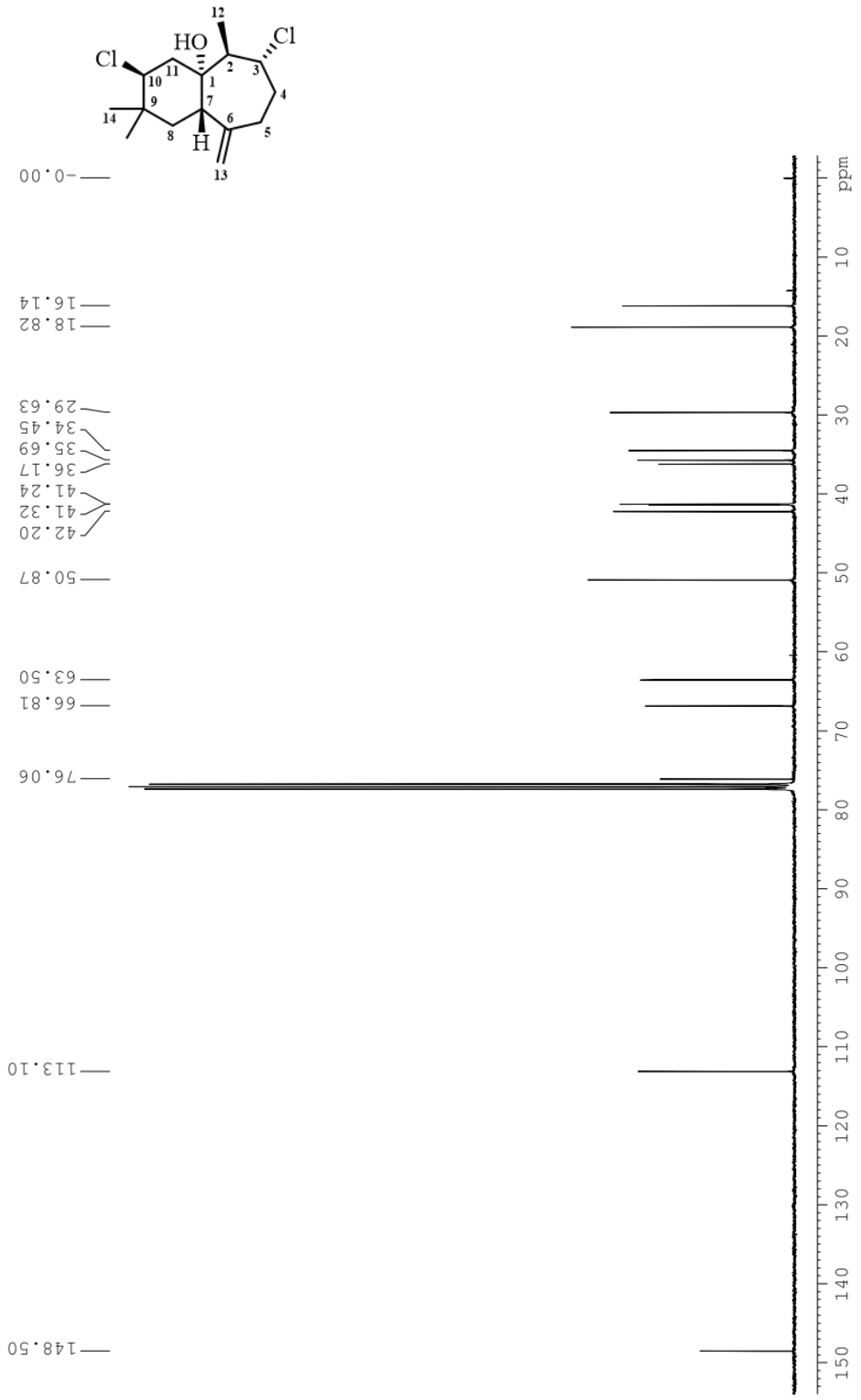


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **7** ($CDCl_3$, 100 MHz).

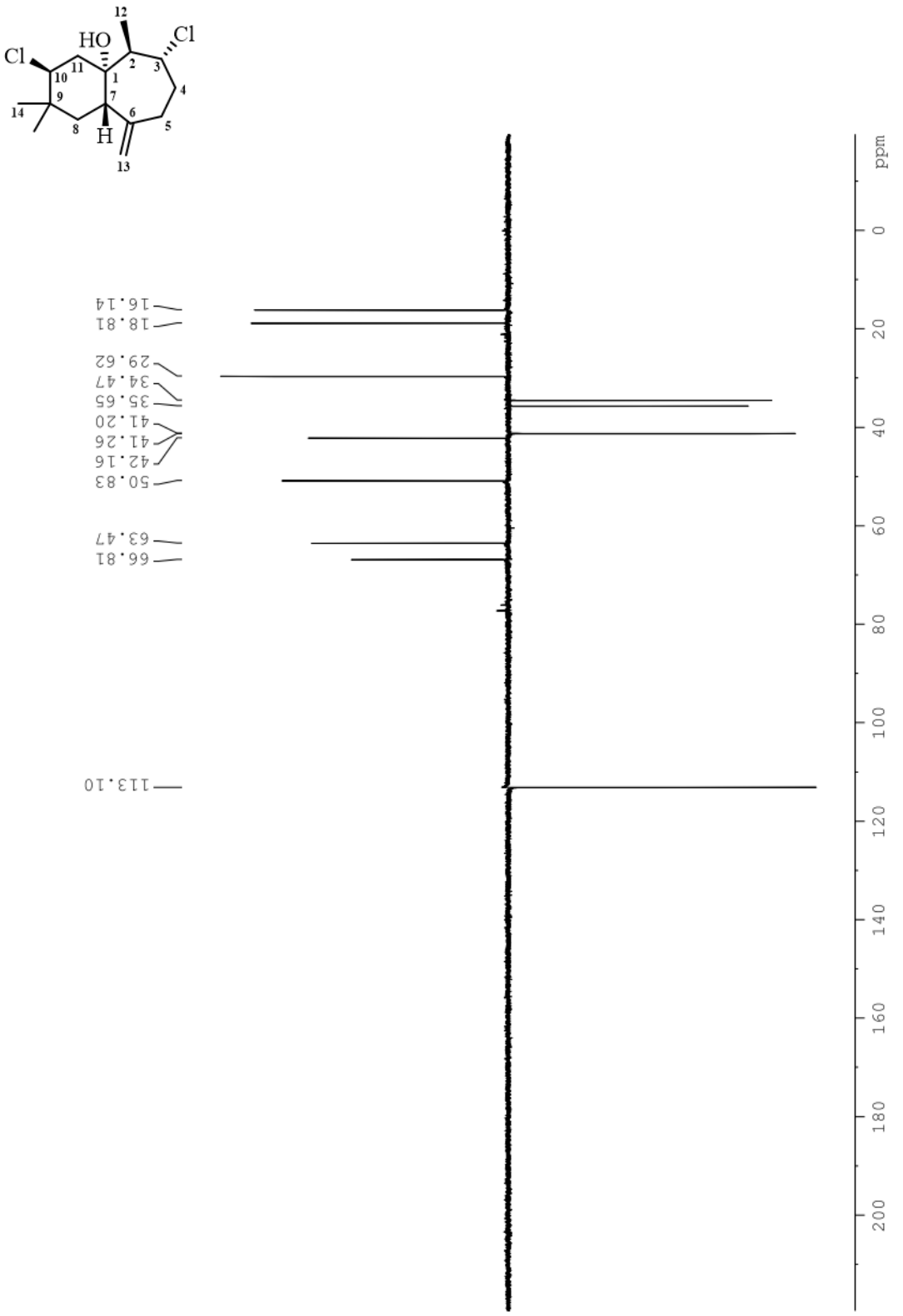


Figure S23. DEPT-135 spectrum of **7** ($CDCl_3$, 100 MHz).

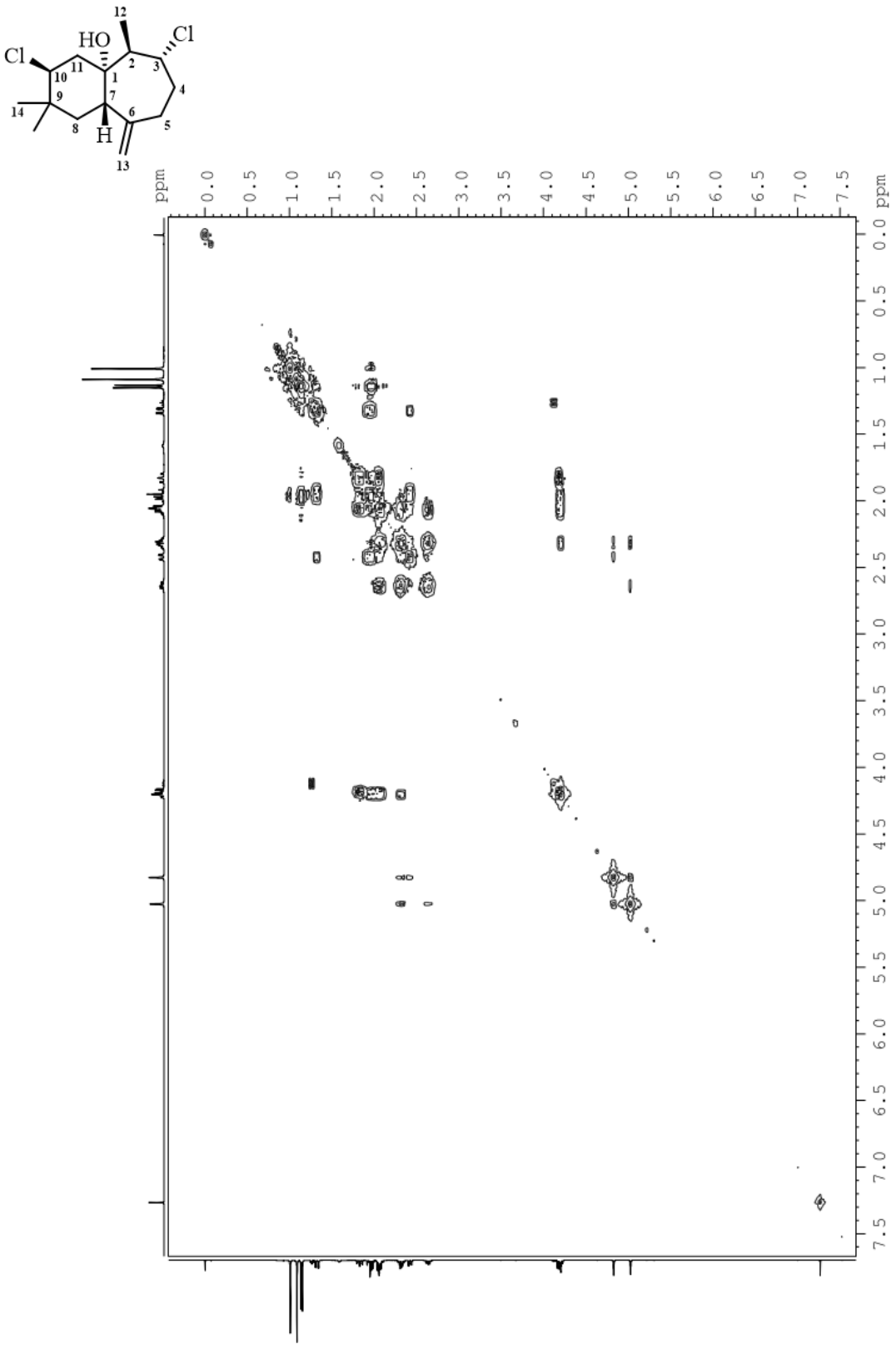


Figure S24. ^{1}H-^{1}H COSY of **7** ($CDCl_3$, 400 MHz).

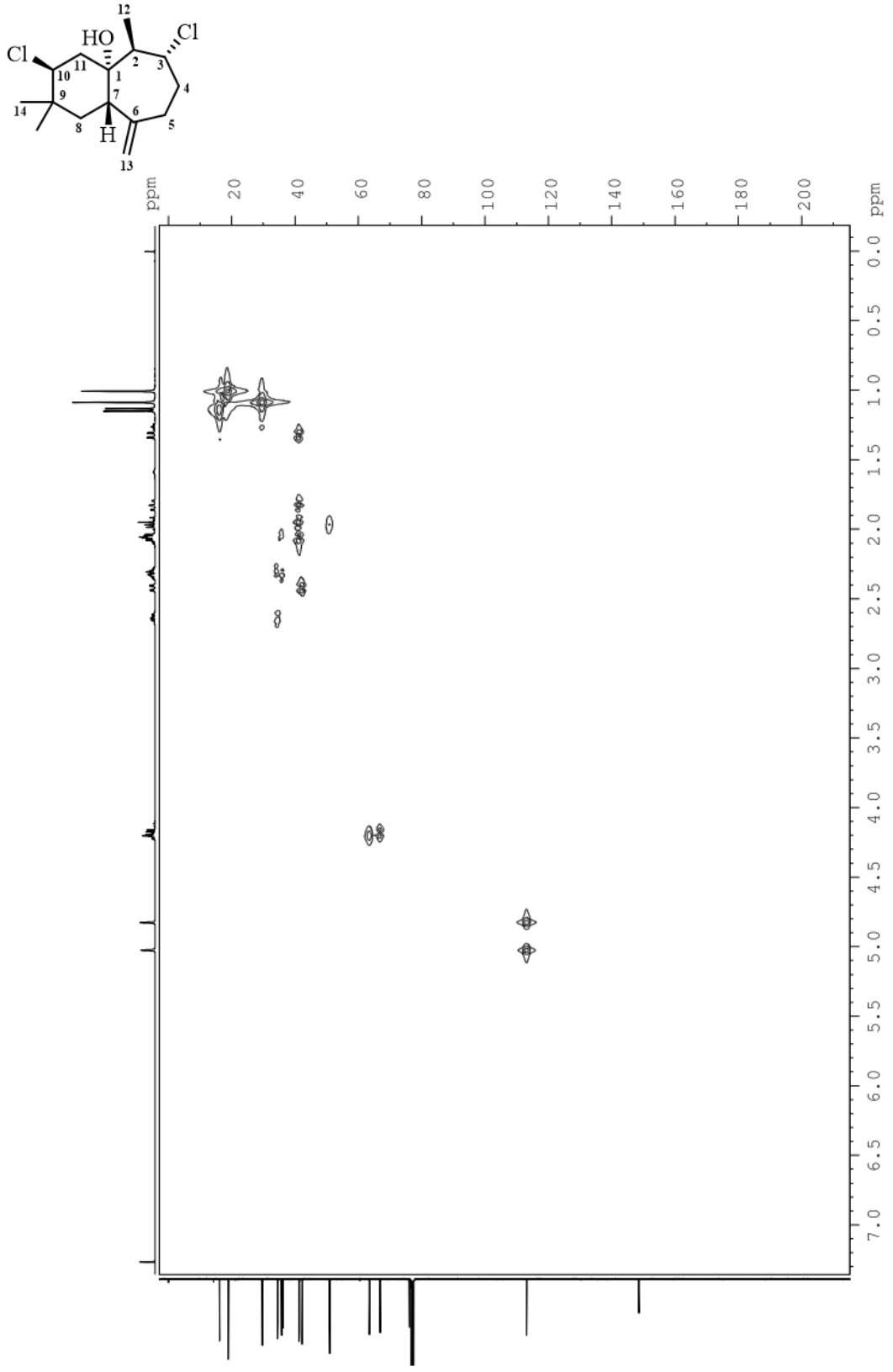


Figure S25. ^{1}H-^{13}C HMQC of **7** ($CDCl_3$, 400 MHz).

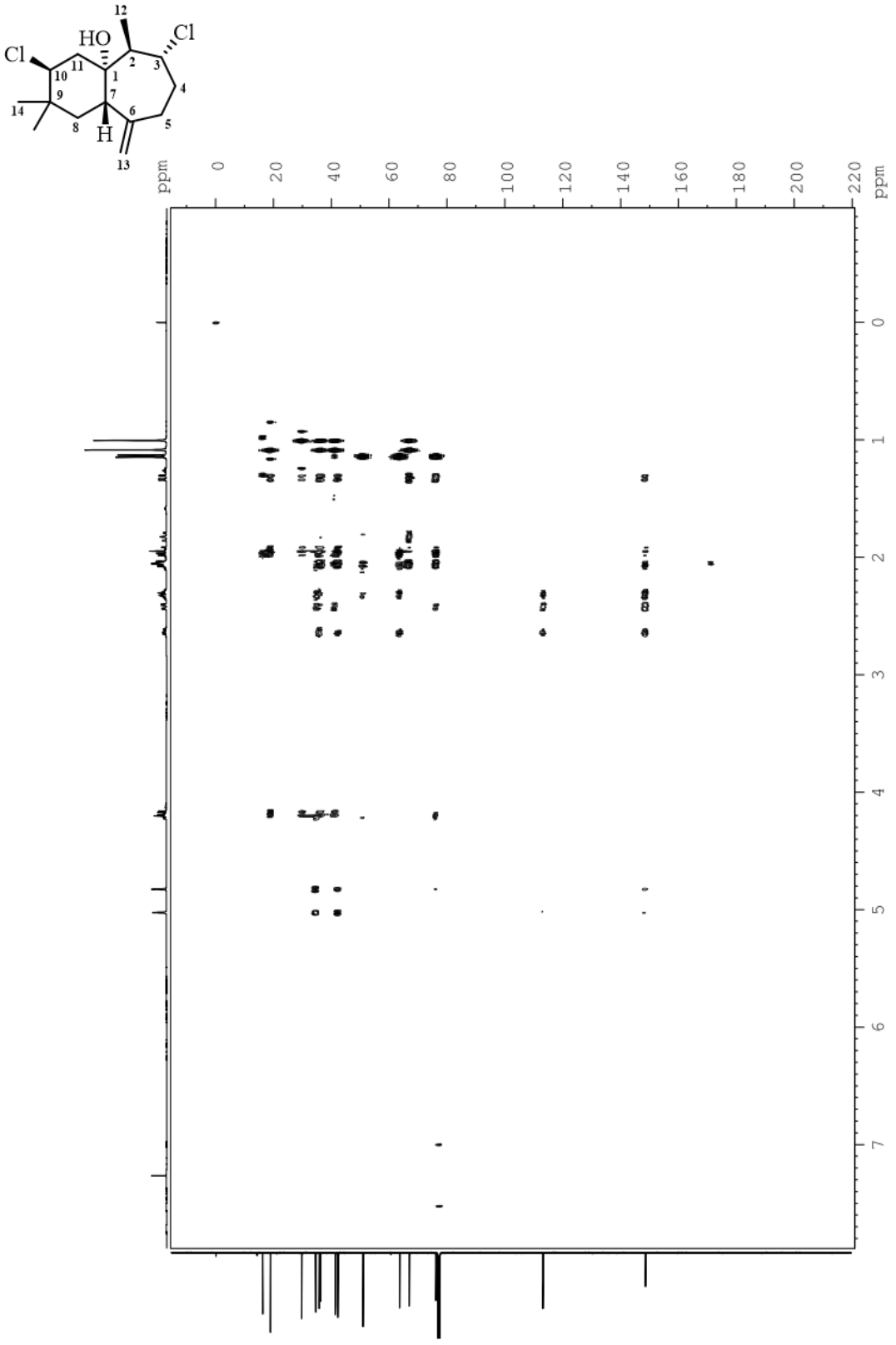


Figure S26. ^{1}H-^{13}C HMBC of **7** ($CDCl_3$, 400 MHz).

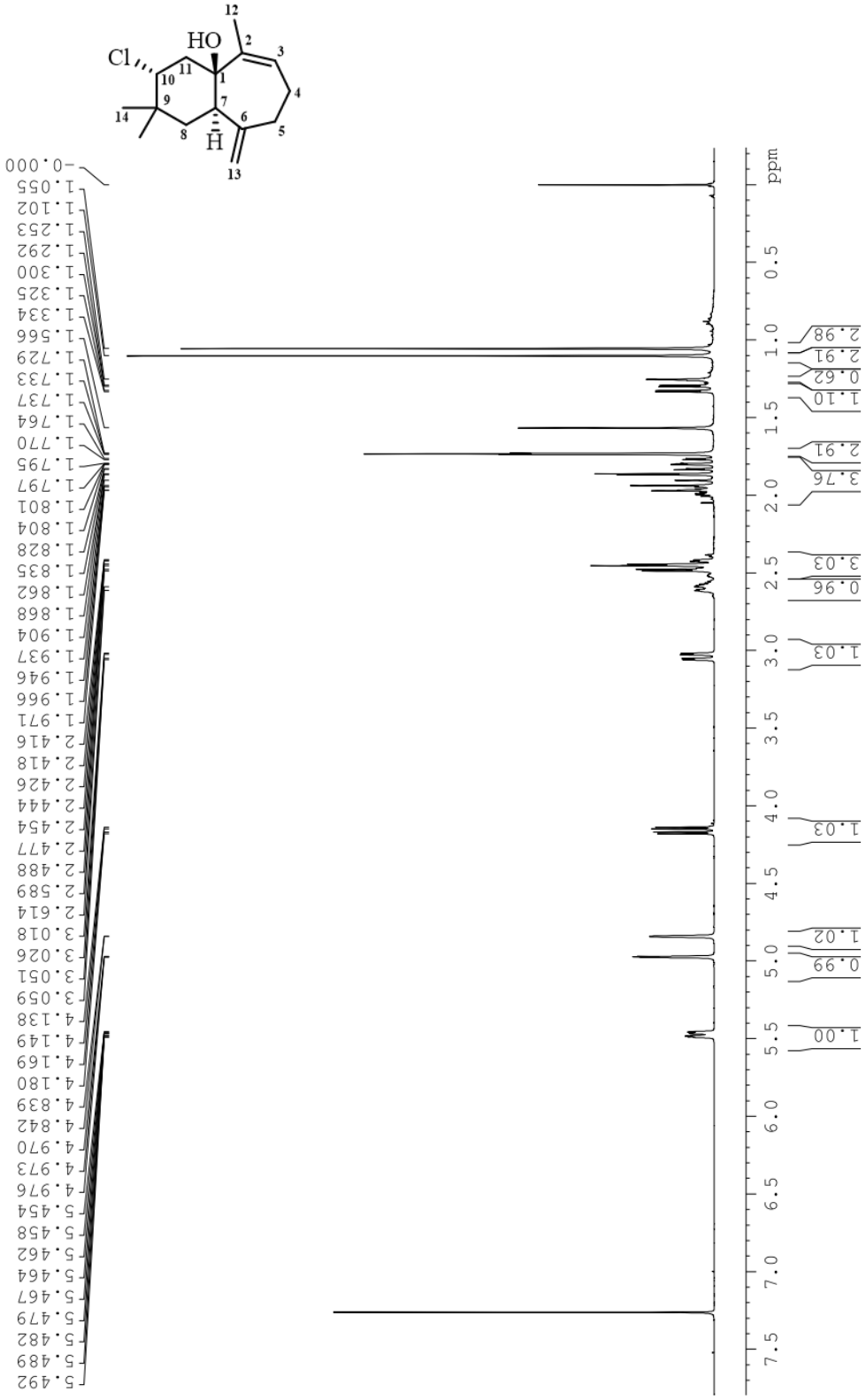


Figure S27. ^{1}H NMR spectrum of **8** ($CDCl_3$, 400 MHz).

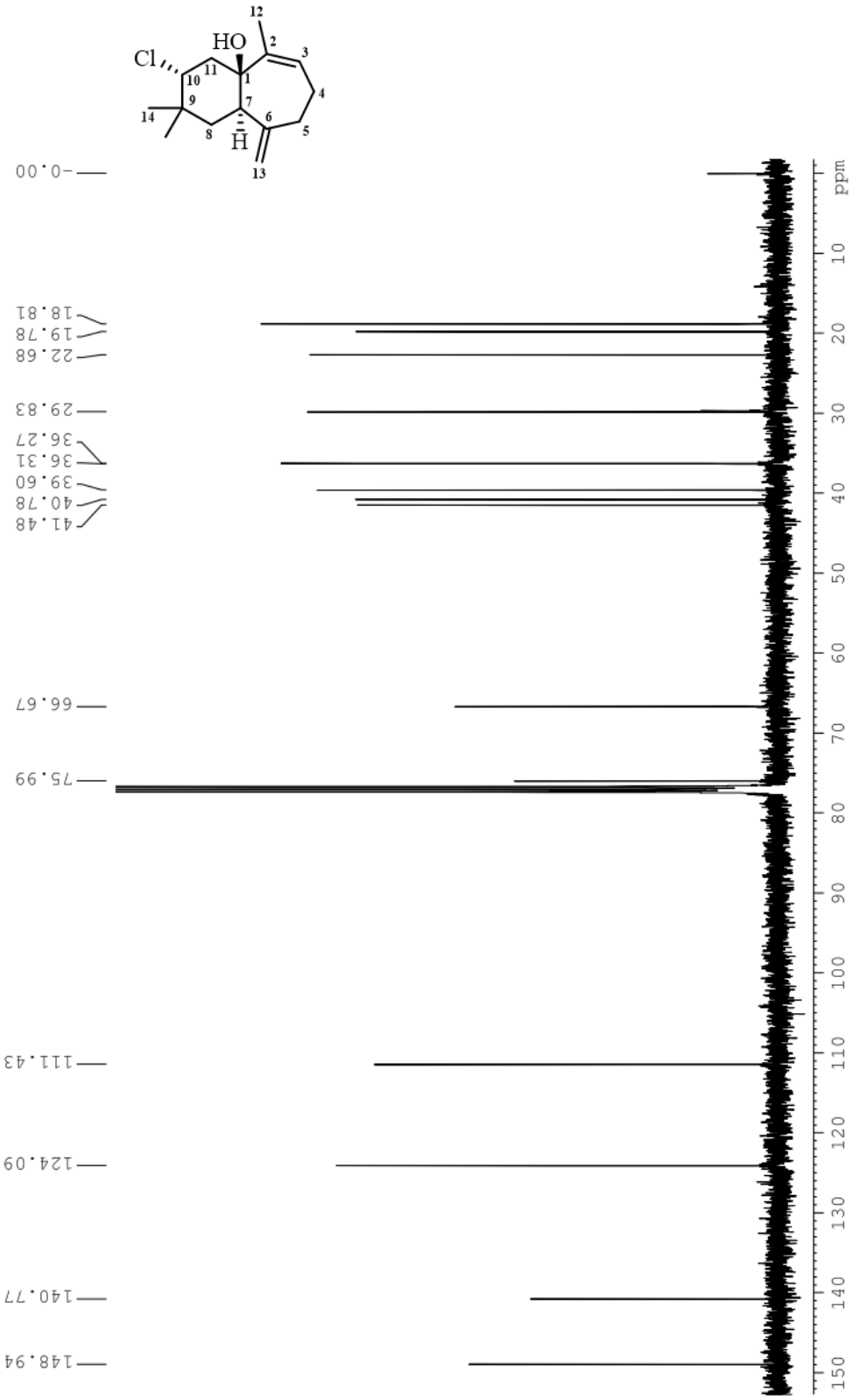


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **8** ($CDCl_3$, 100 MHz).

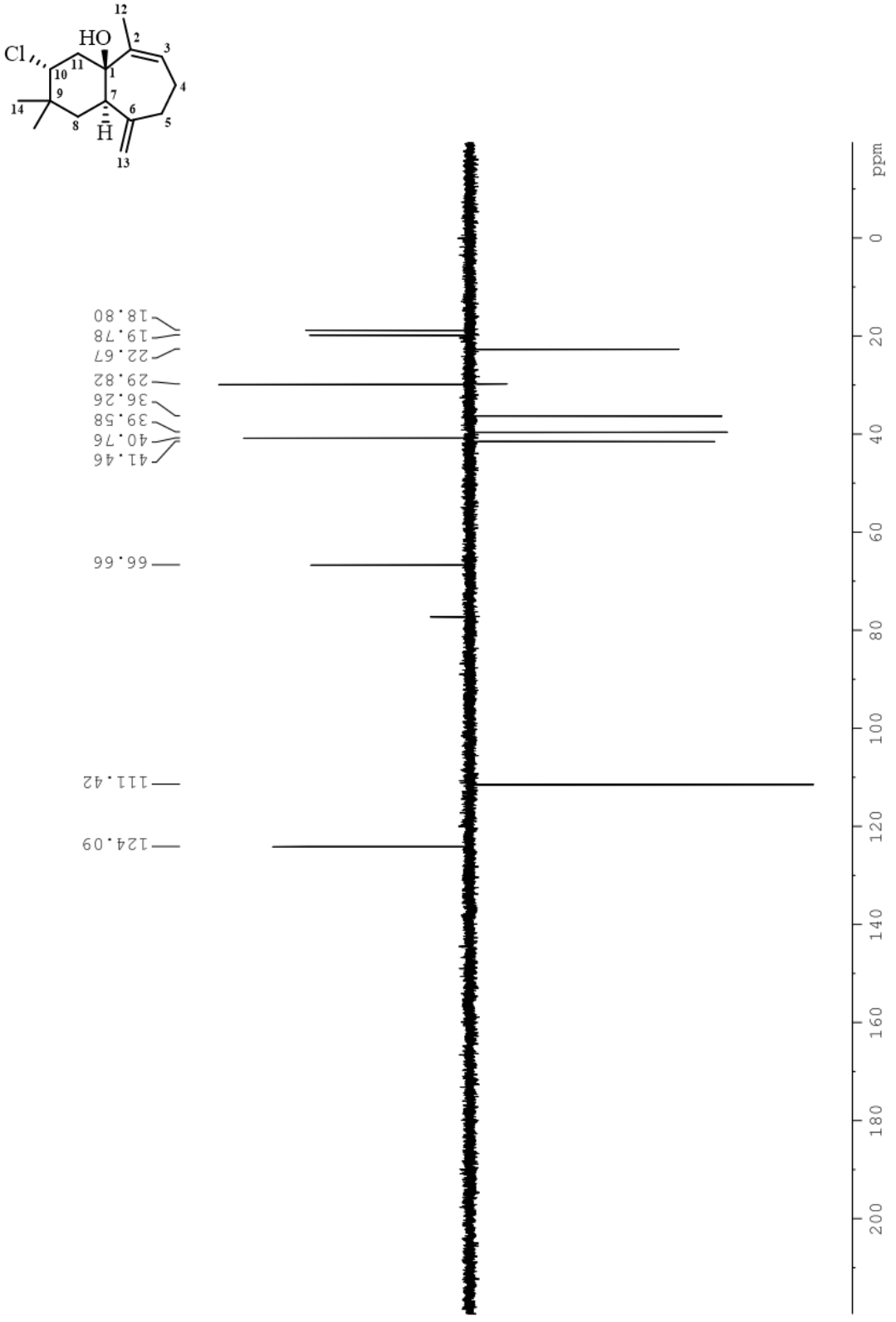


Figure S29. DEPT-135 spectrum of **8** ($CDCl_3$, 100 MHz).

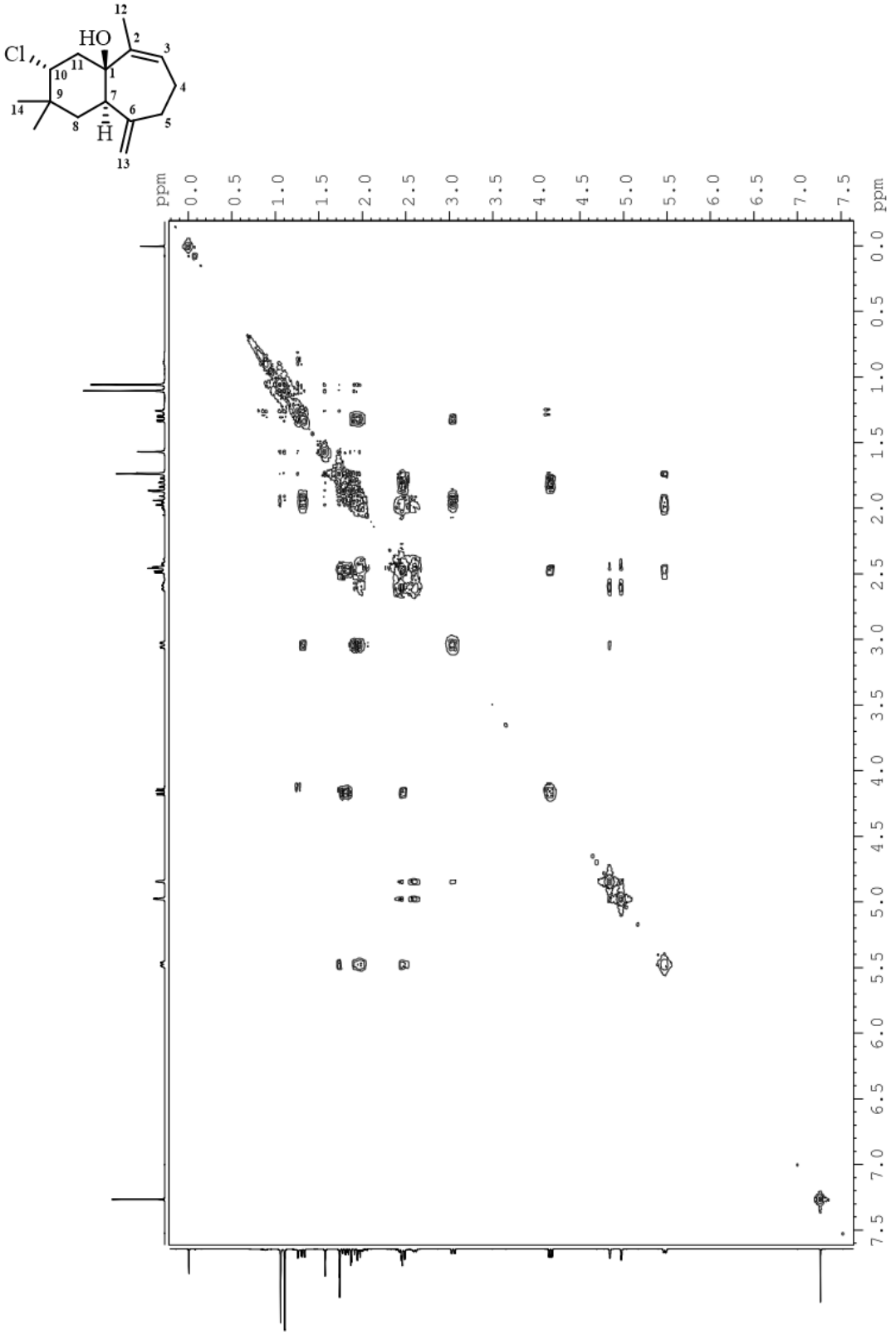


Figure S30. ^{1}H-^{1}H COSY of **8** ($CDCl_3$, 400 MHz).

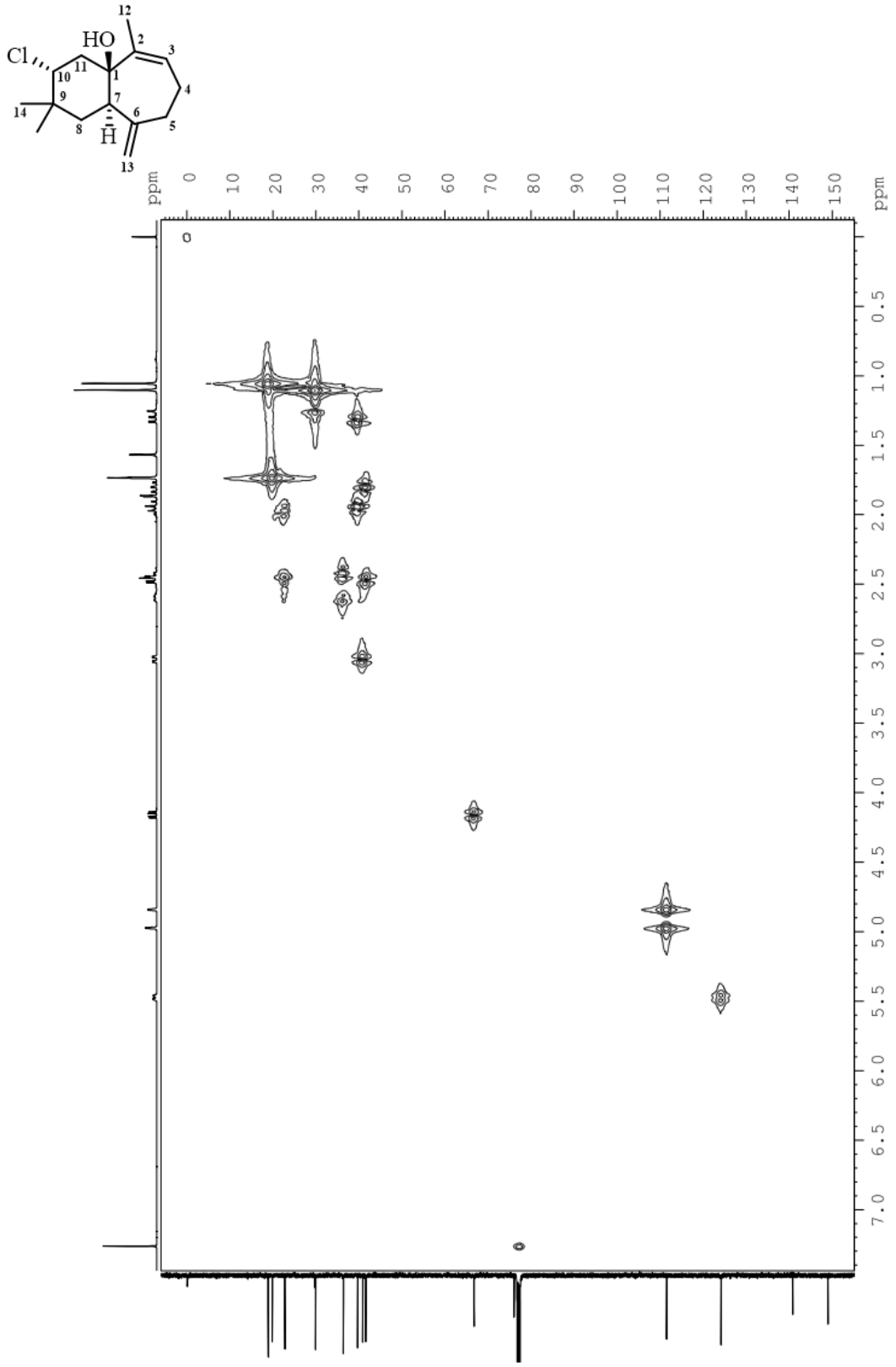


Figure S31. ^{1}H-^{13}C HMQC of **8** ($CDCl_3$, 400 MHz).

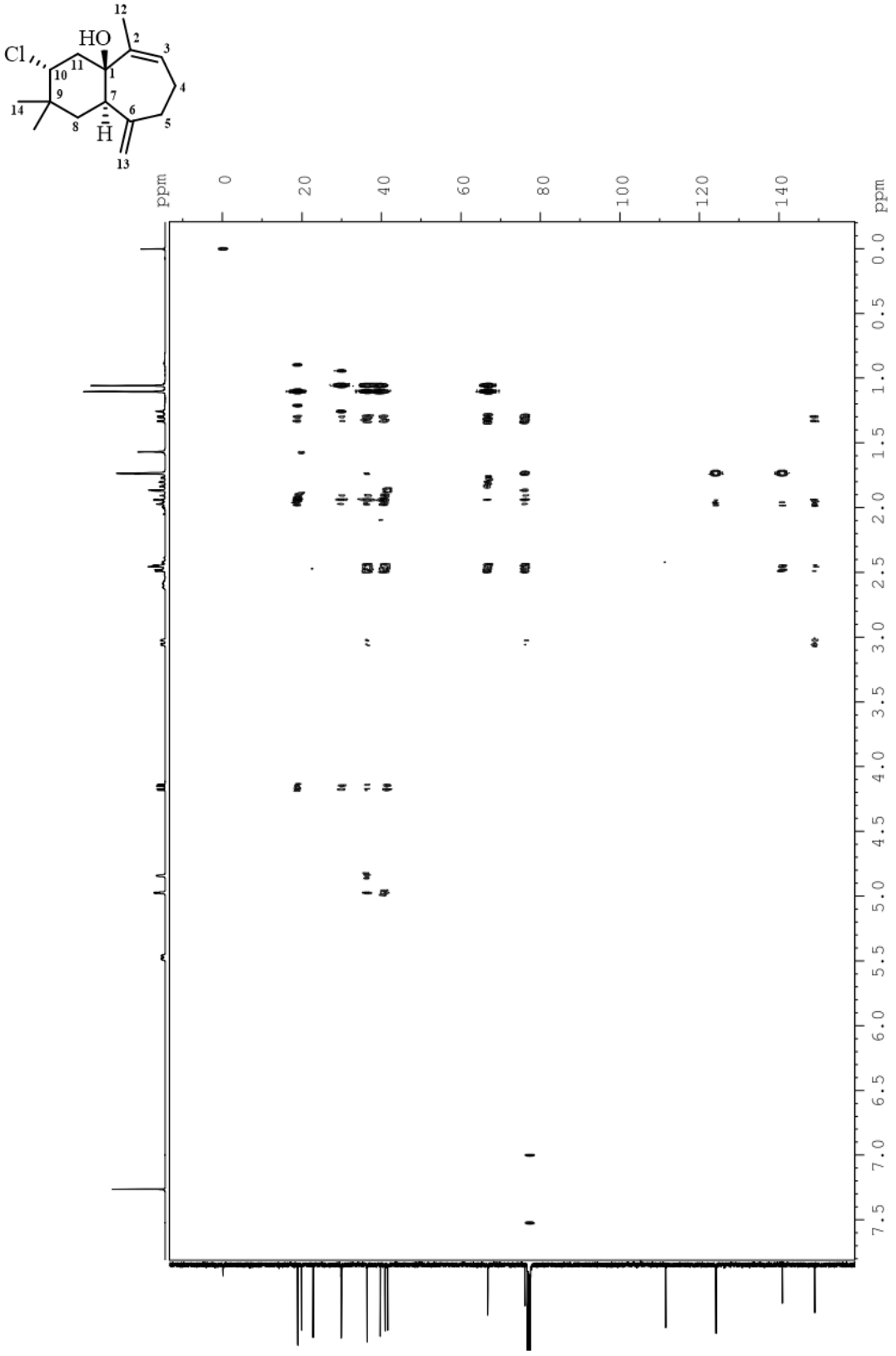


Figure S32. ^{1}H-^{13}C HMBC of **8** ($CDCl_3$, 400 MHz).

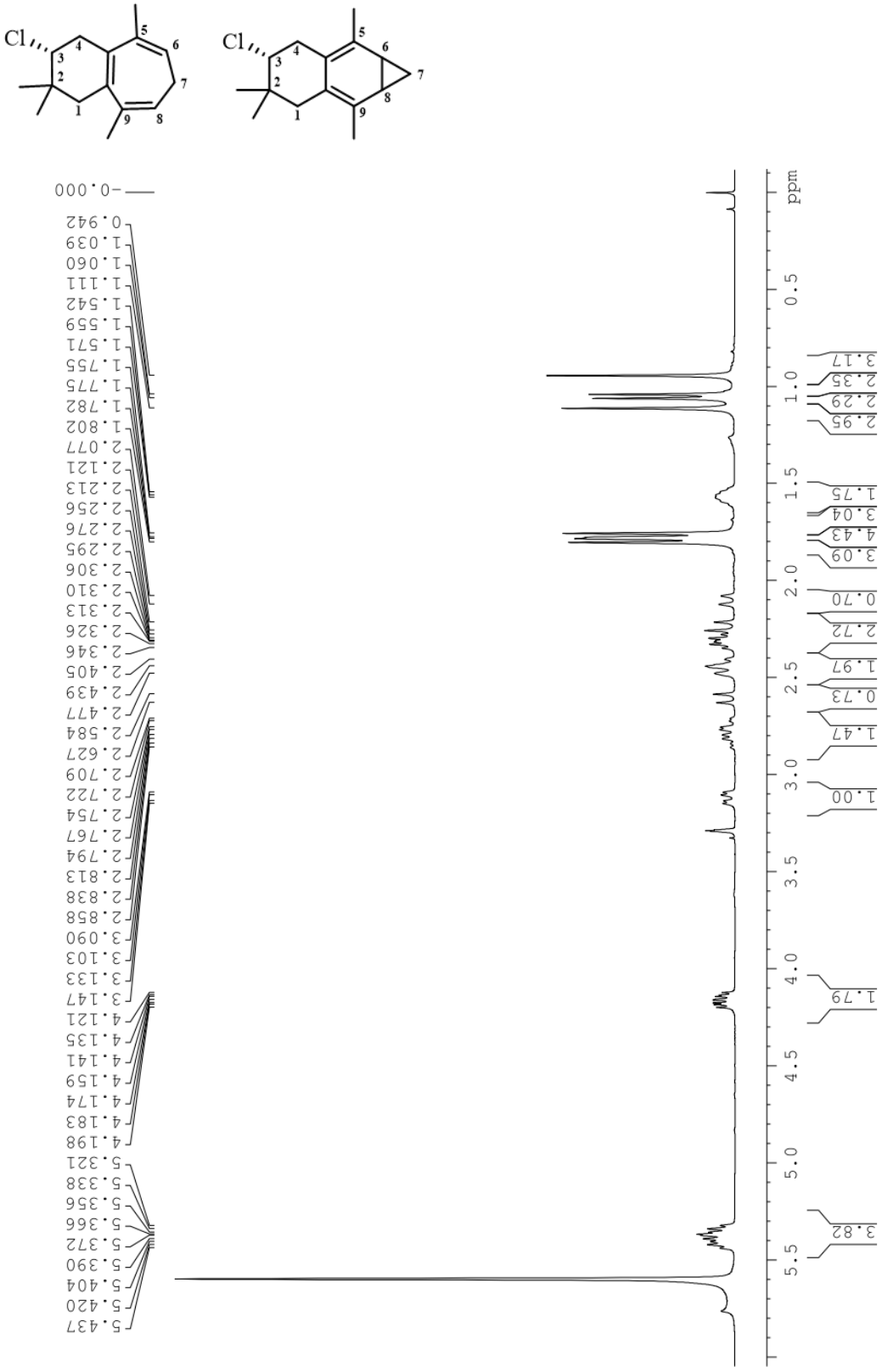


Figure S33. ^{1}H NMR spectrum of isomers **9** and **10** (CD_3OD, 400 MHz, –50 °C).

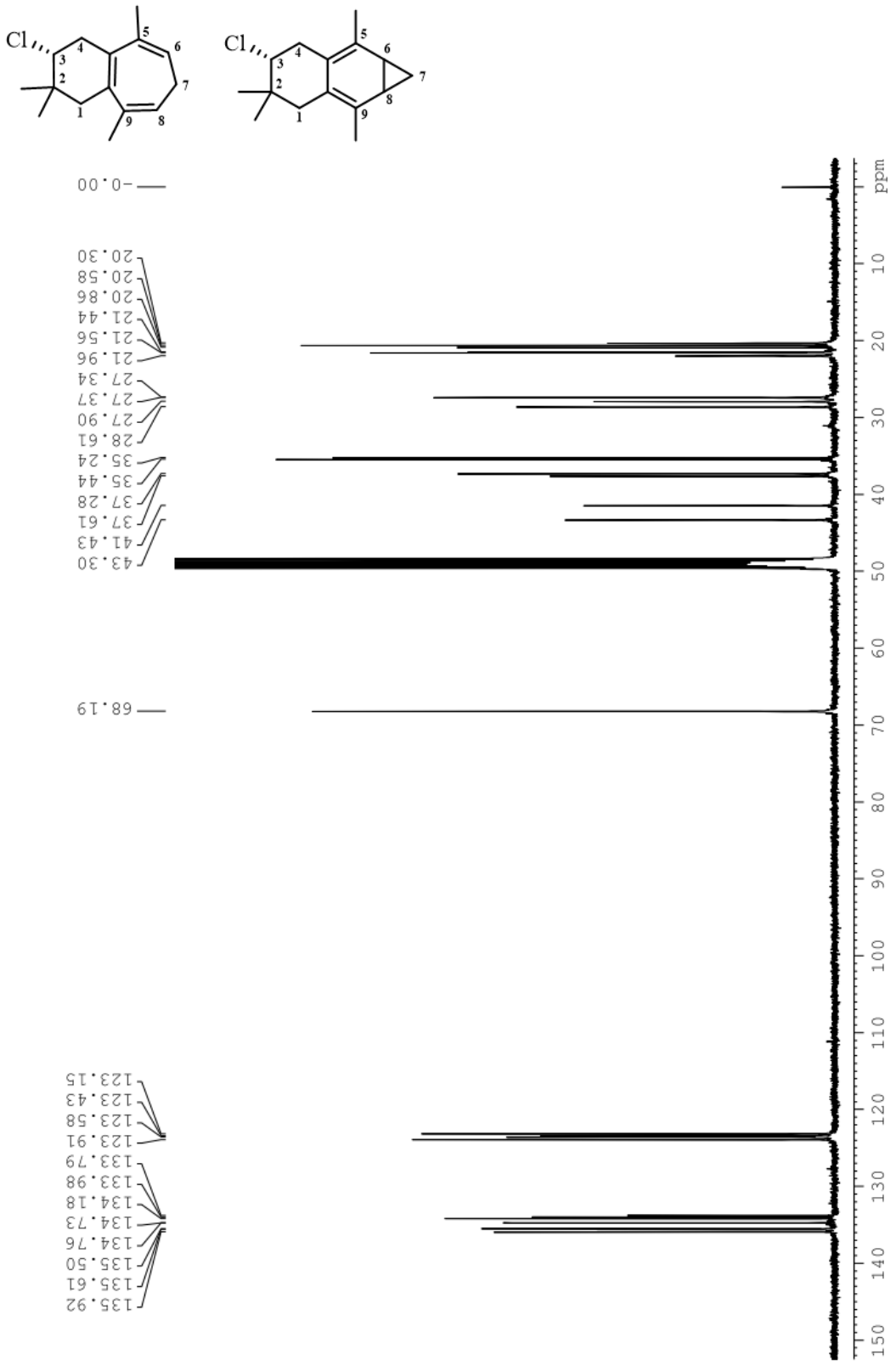


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of iosmers **9** and **10** (CD_3OD, 100 MHz, –50 °C).

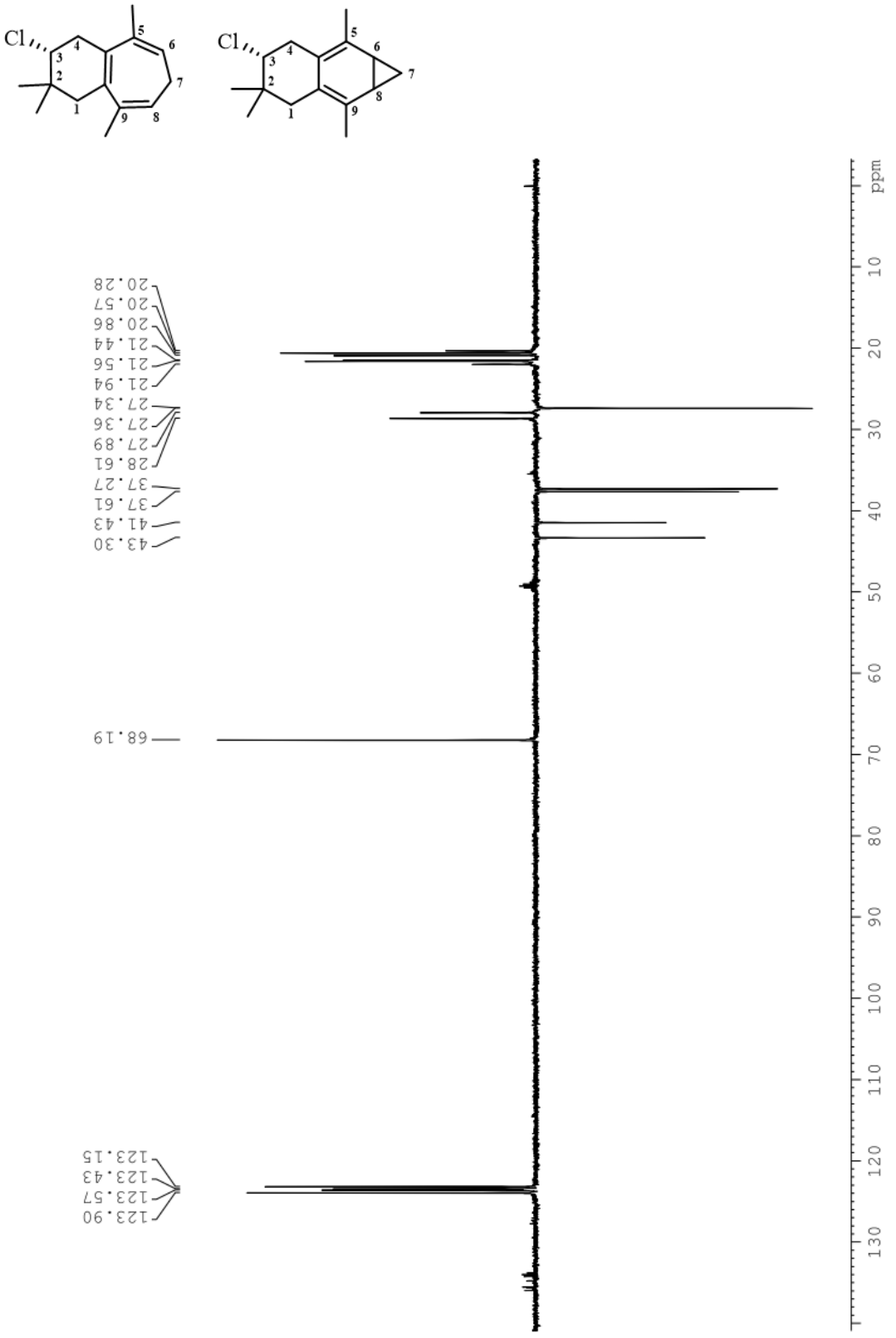


Figure S35. DEPT-135 spectrum of isomers **9** and **10** (CD_3OD, 100 MHz, –50 °C).

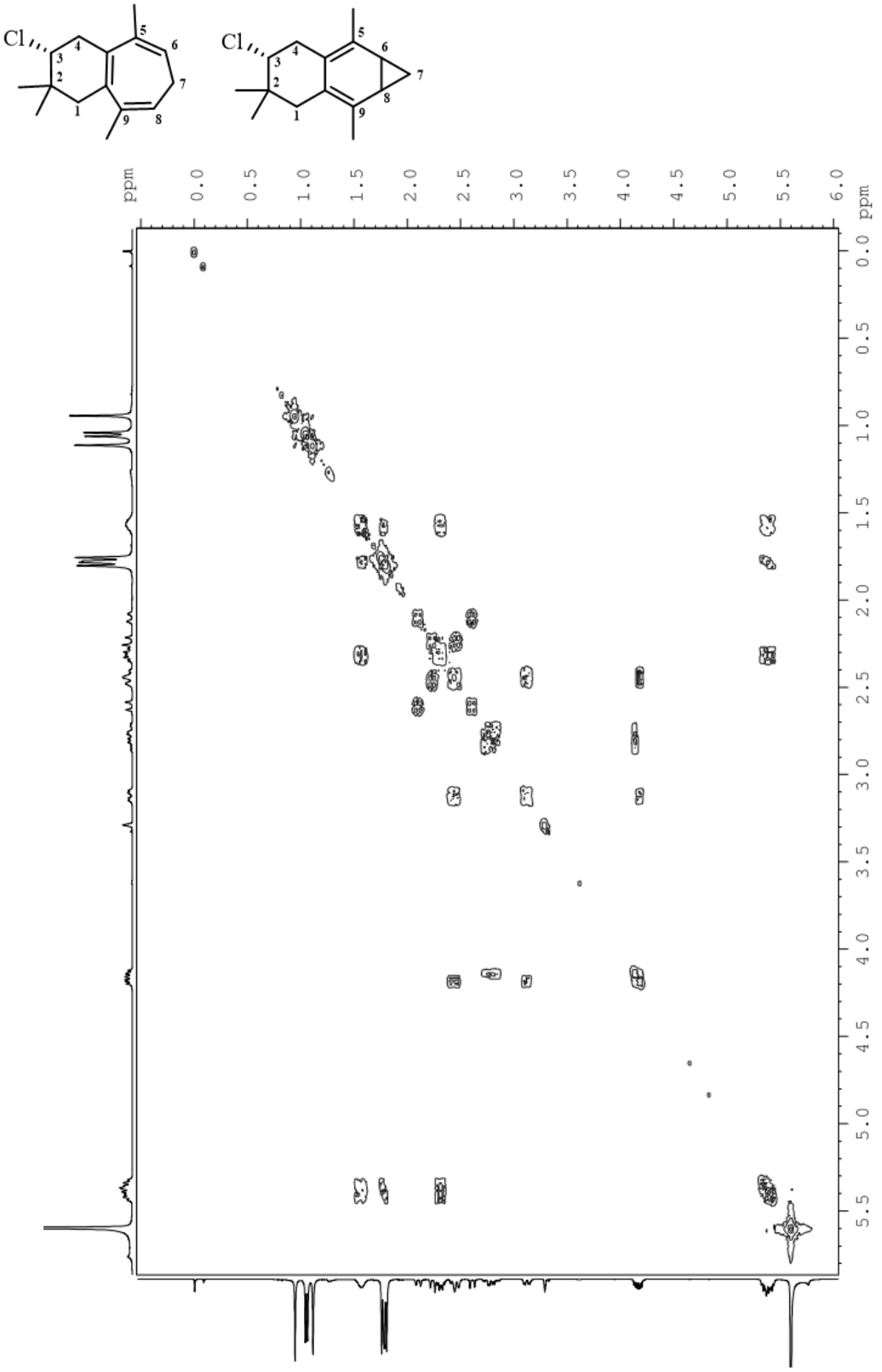


Figure S36. ^{1}H-^{1}H COSY of isomers **9** and **10** (CD_3OD, 400 MHz, –50 °C).

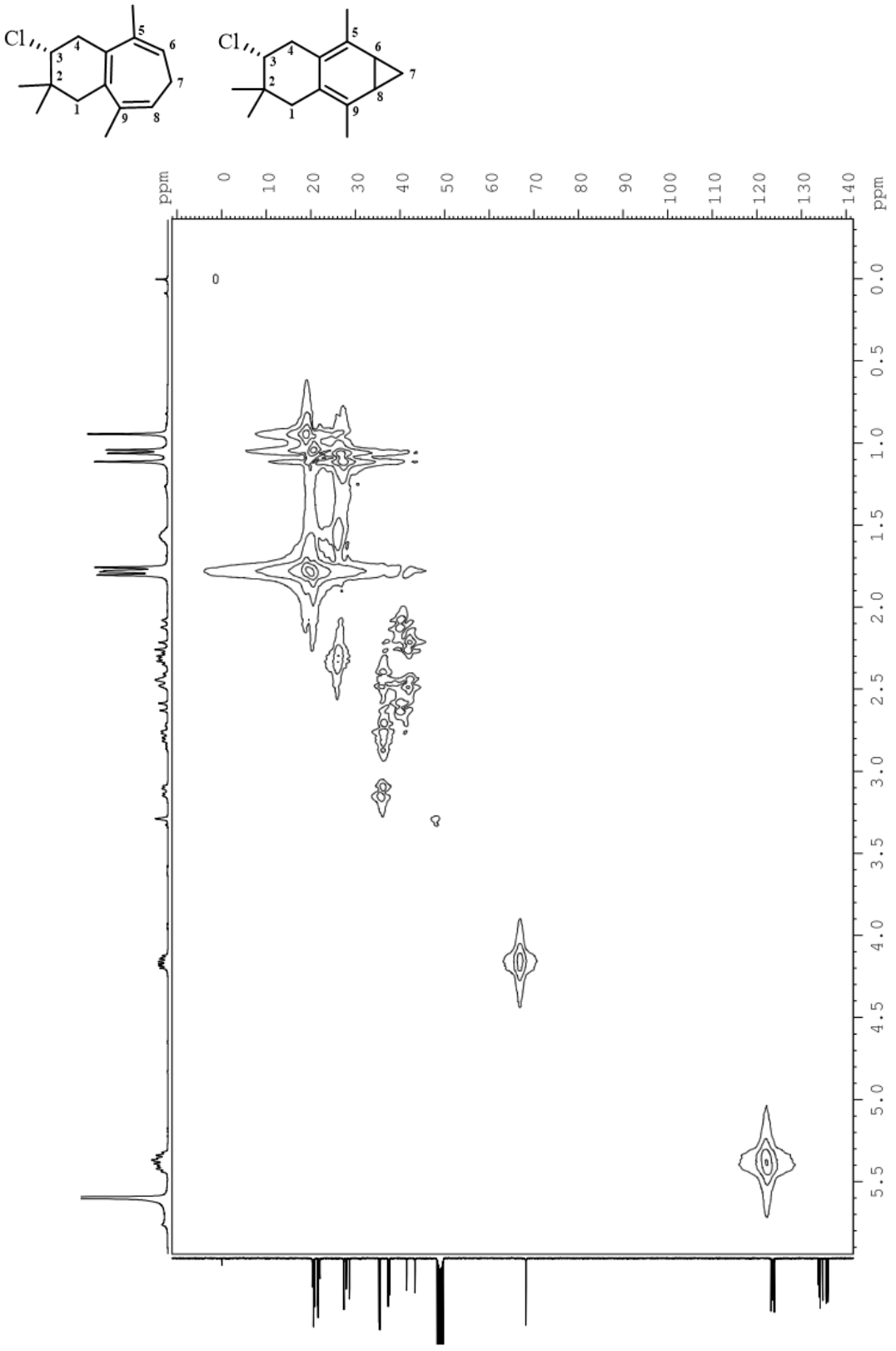


Figure S37. ^{1}H-^{13}C HMQC of isomers **9** and **10** (CD_3OD, 400 MHz, –50 °C).

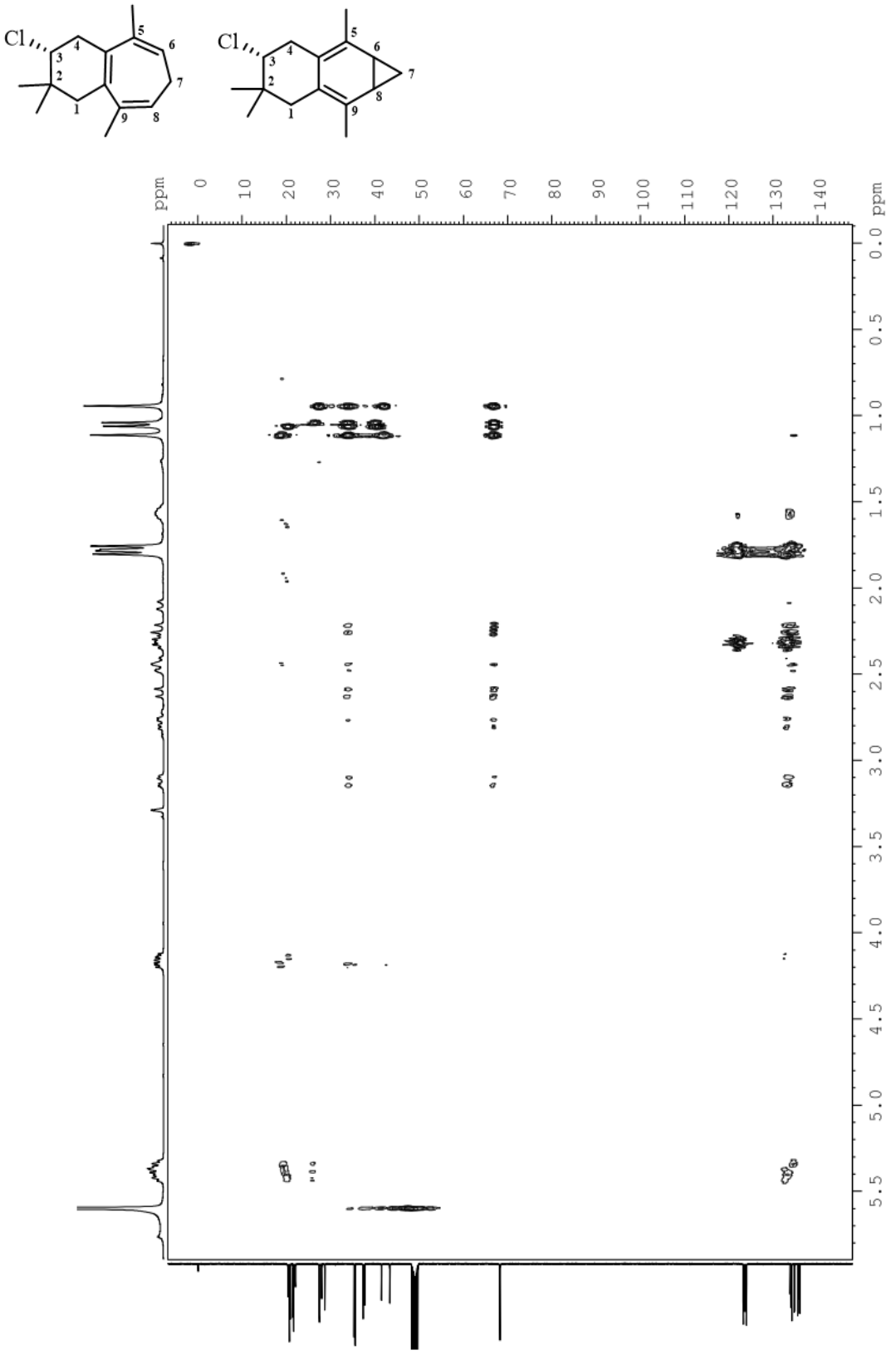


Figure S38. ^{1}H-^{13}C HMBC of isomers **9** and **10** (CD_3OD, 400 MHz, –50 °C).

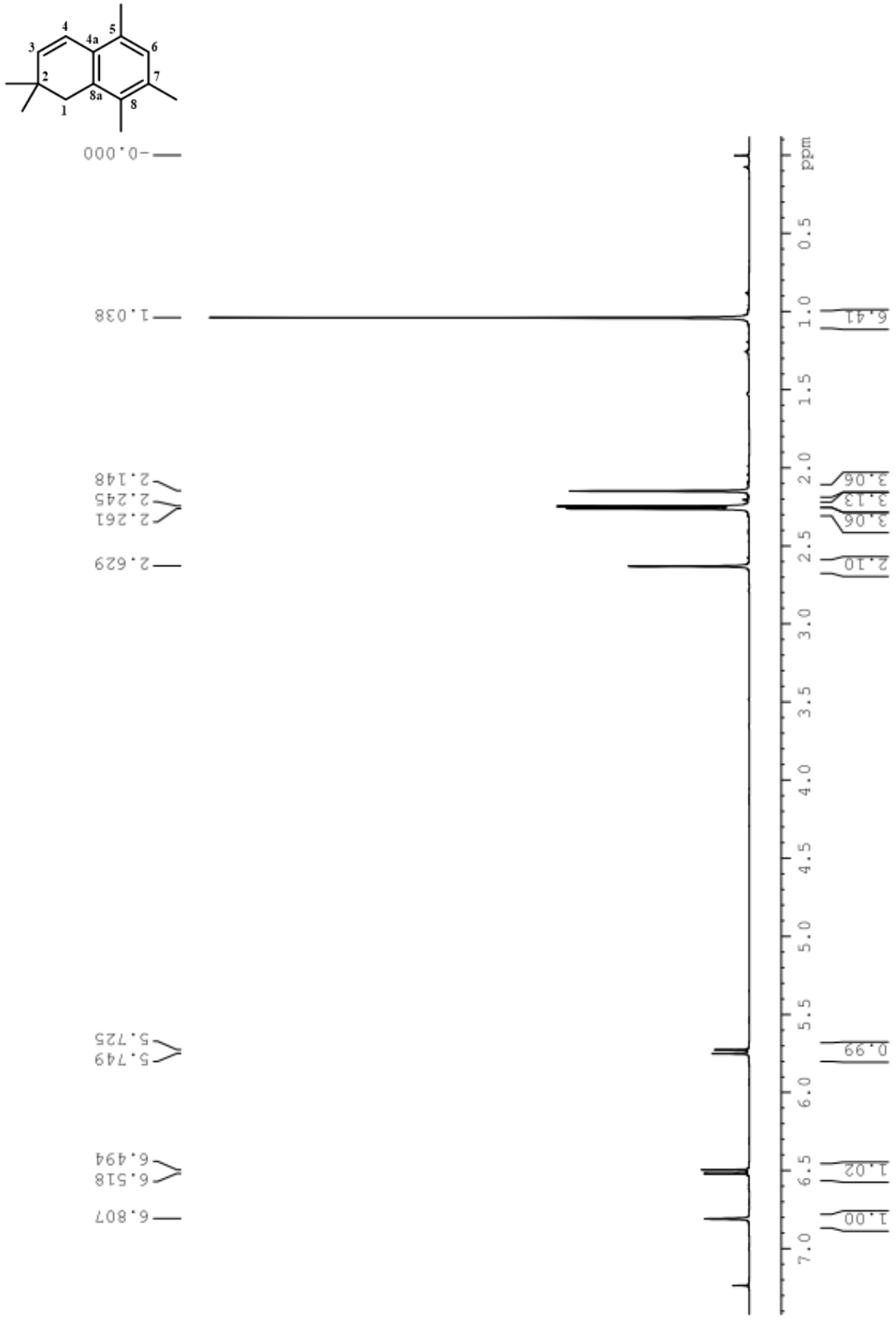


Figure S39. ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz).

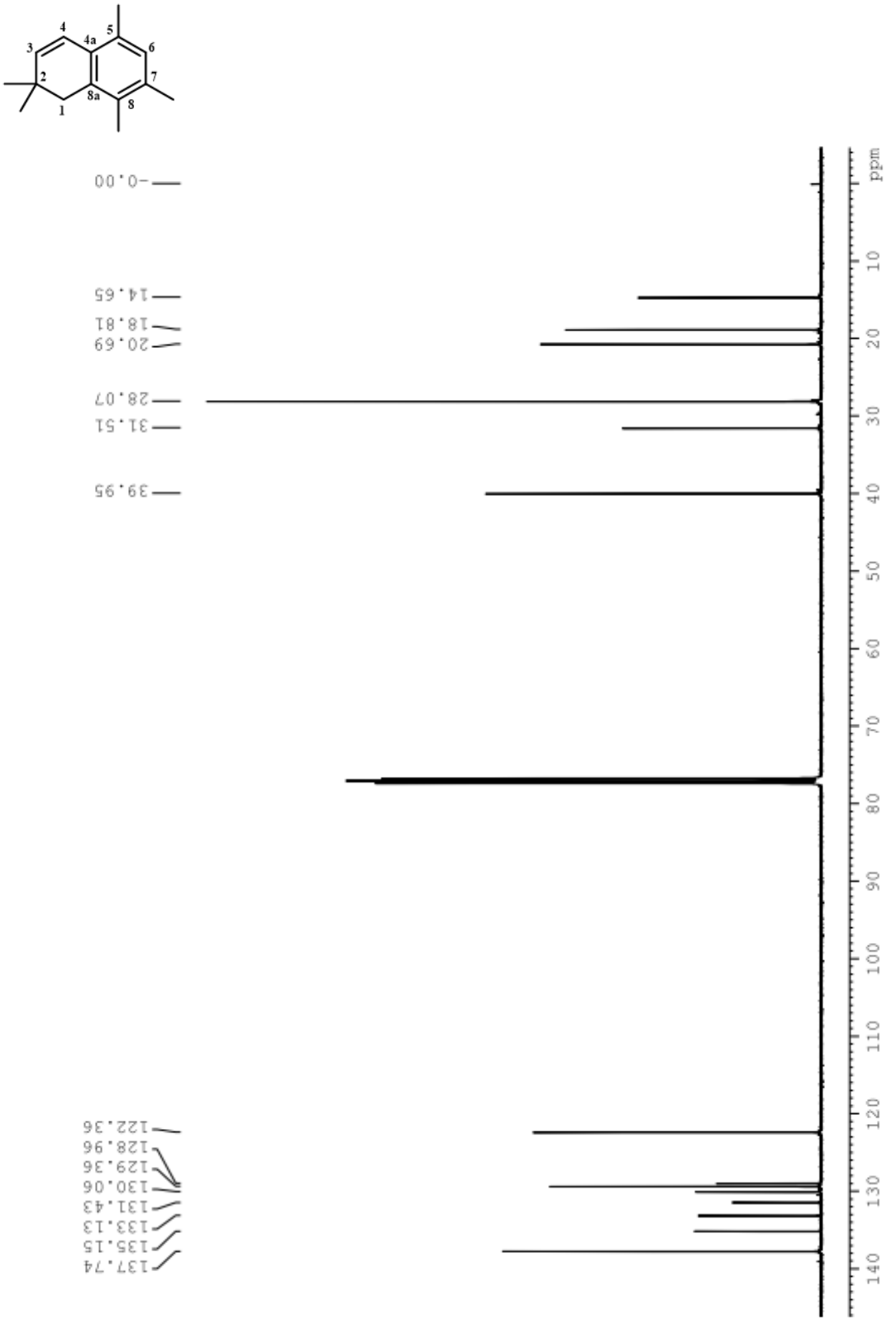


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **2** ($CDCl_3$, 100 MHz).

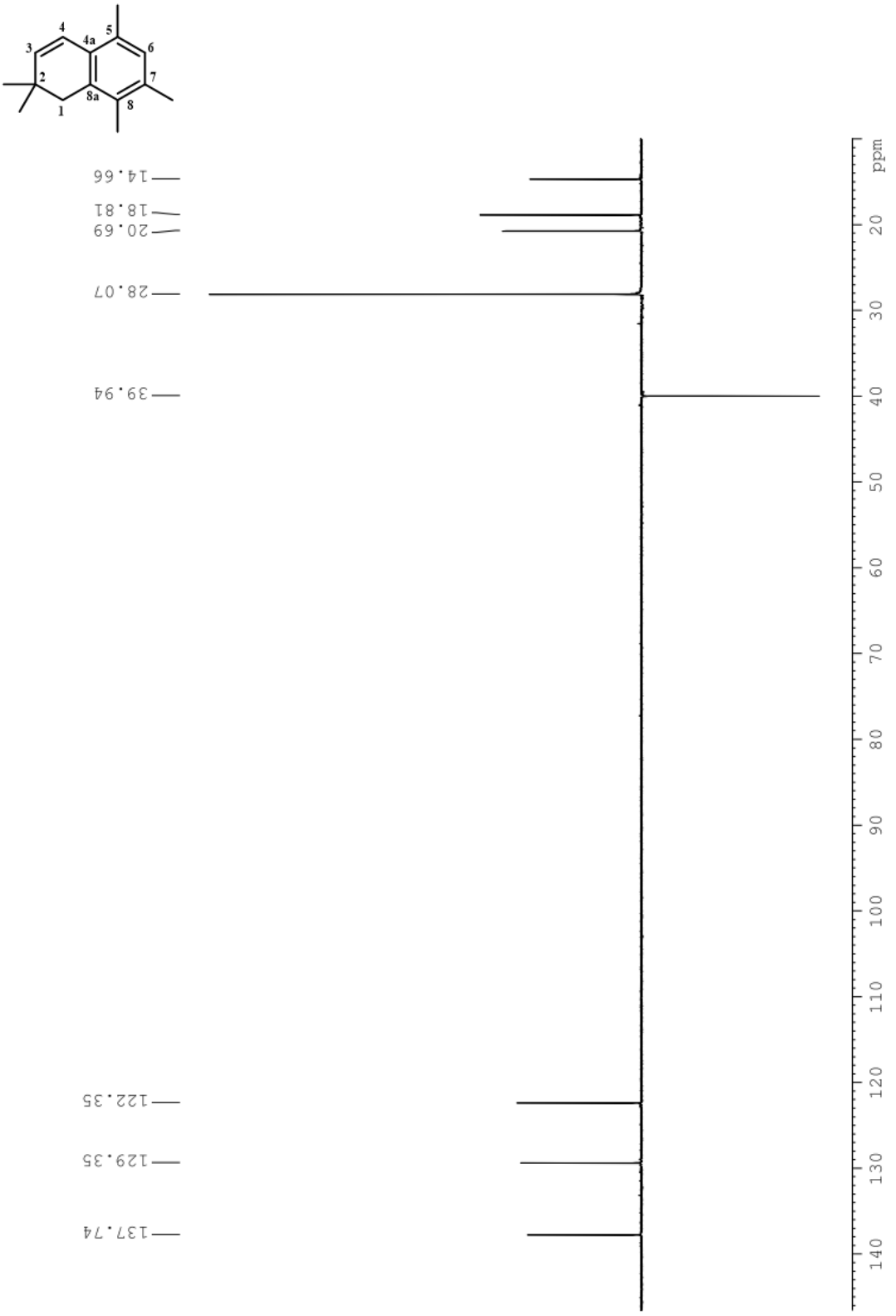


Figure S41. DEPT-135 spectrum of **2** ($CDCl_3$, 100 MHz).

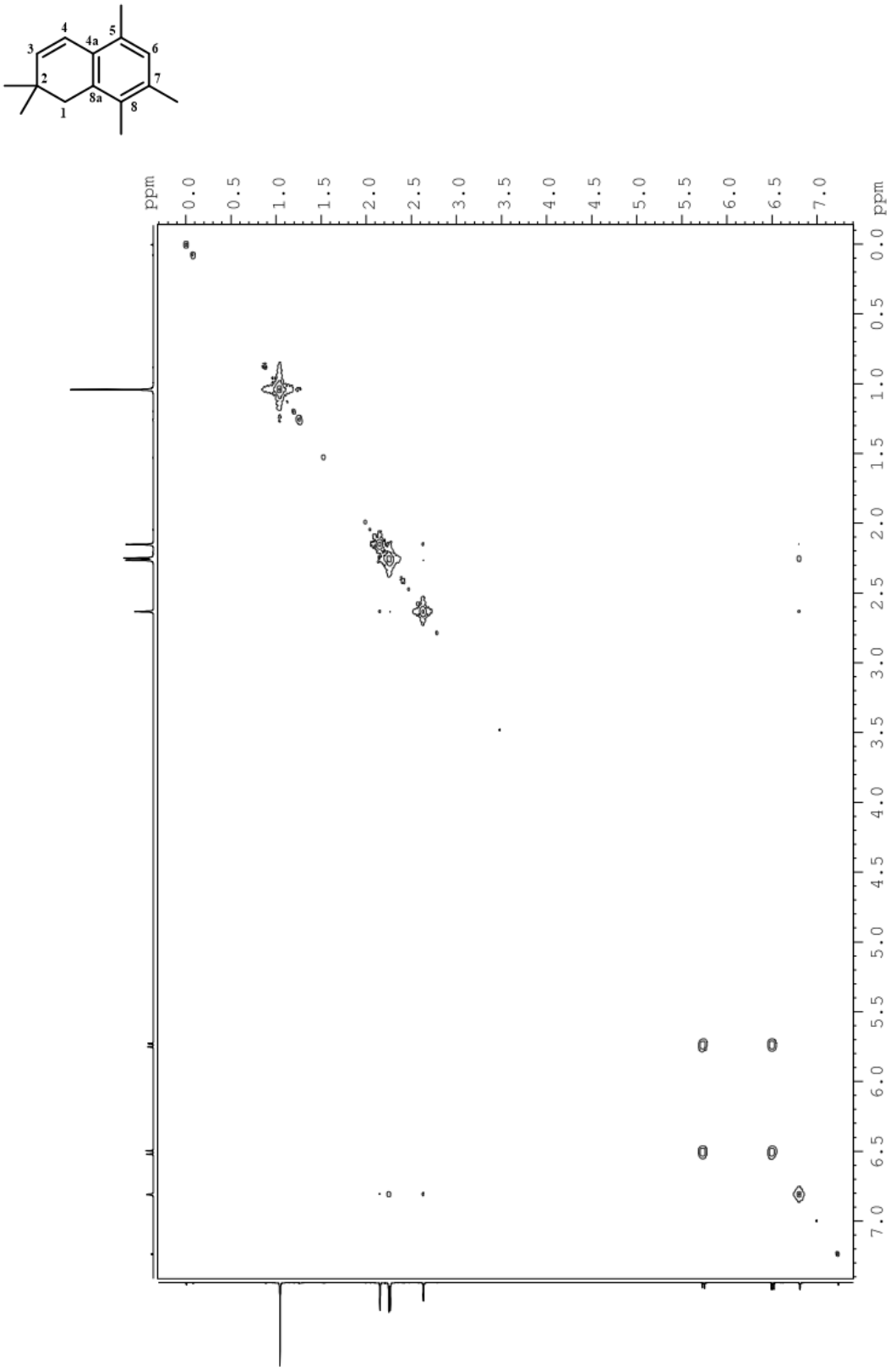


Figure S42. ^{1}H-^{1}H COSY of **2** ($CDCl_3$, 400 MHz).

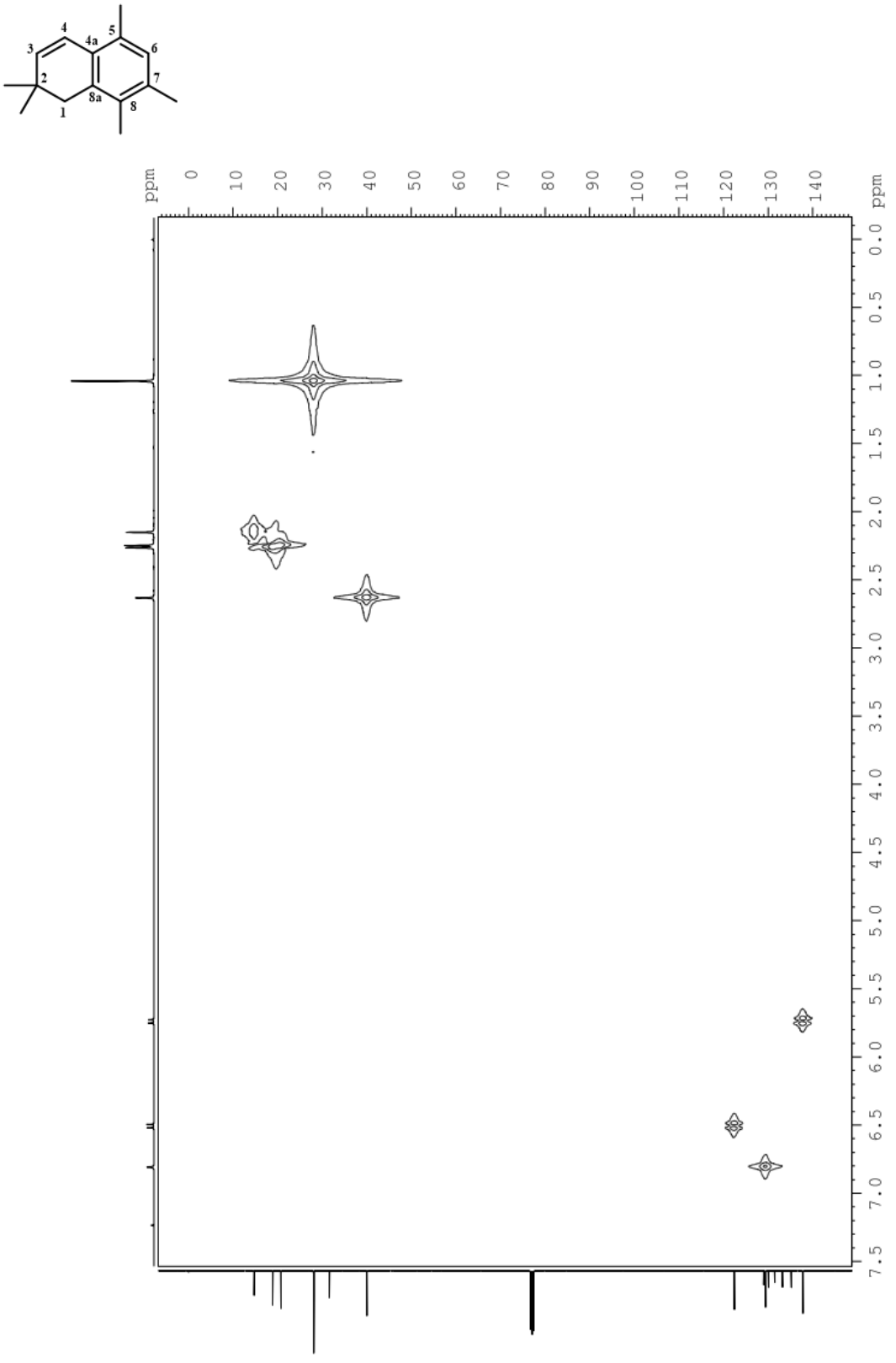


Figure S43. ^{1}H-^{13}C HMQC of **2** ($CDCl_3$, 400 MHz).

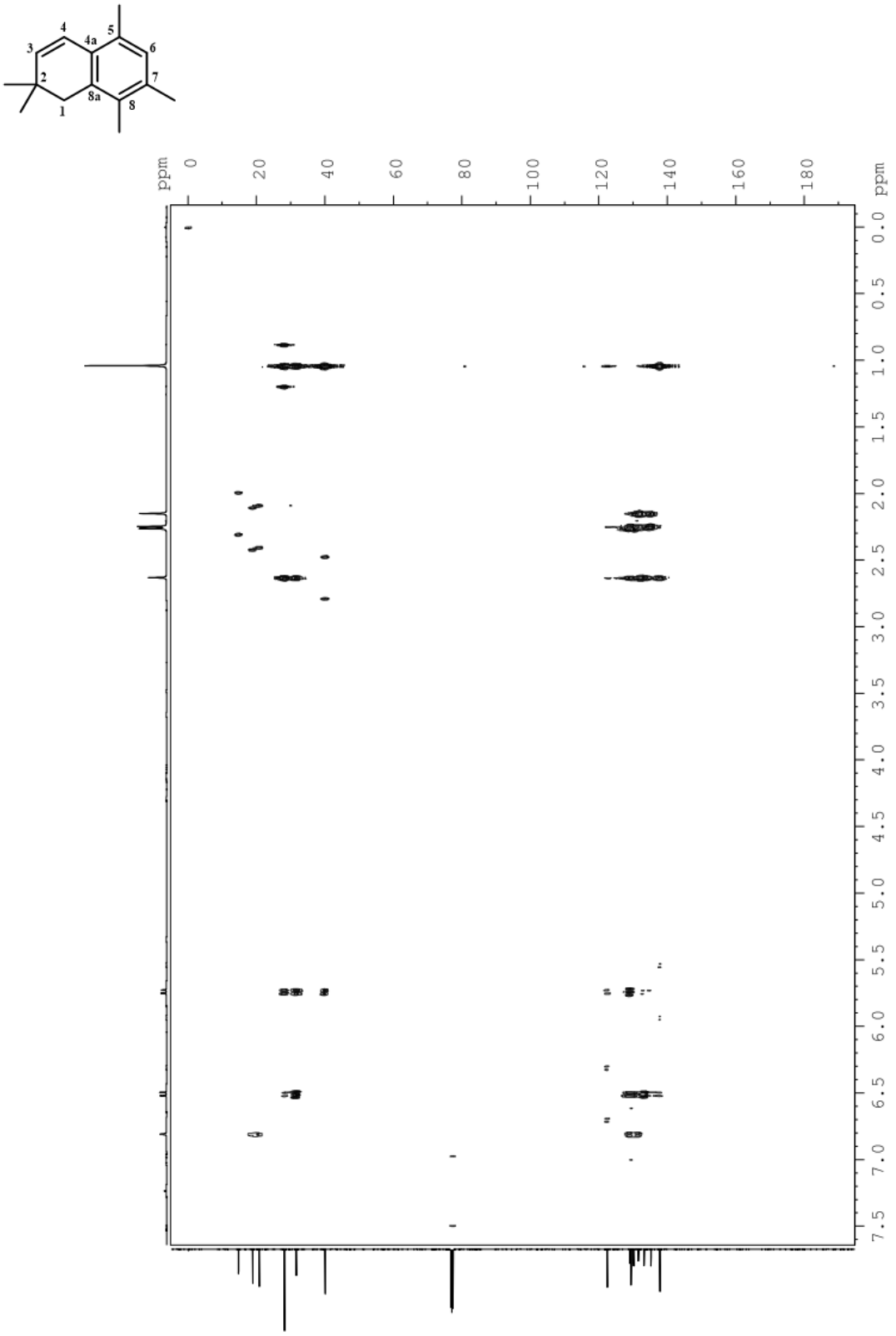


Figure S44. ^{1}H-^{13}C HMBC of **2** ($CDCl_3$, 400 MHz).

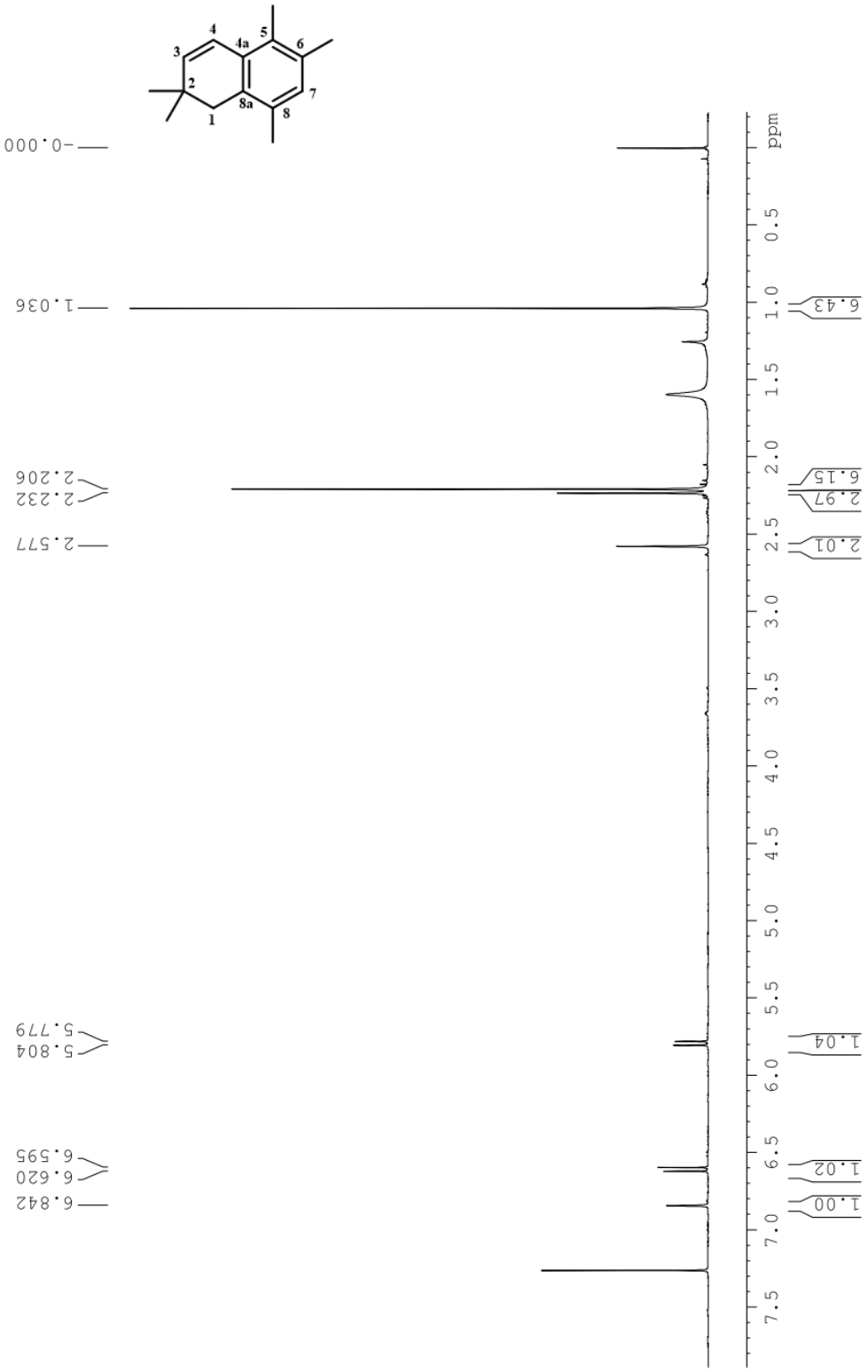


Figure S45. ^{1}H NMR spectrum of **3** ($CDCl_3$, 400 MHz).

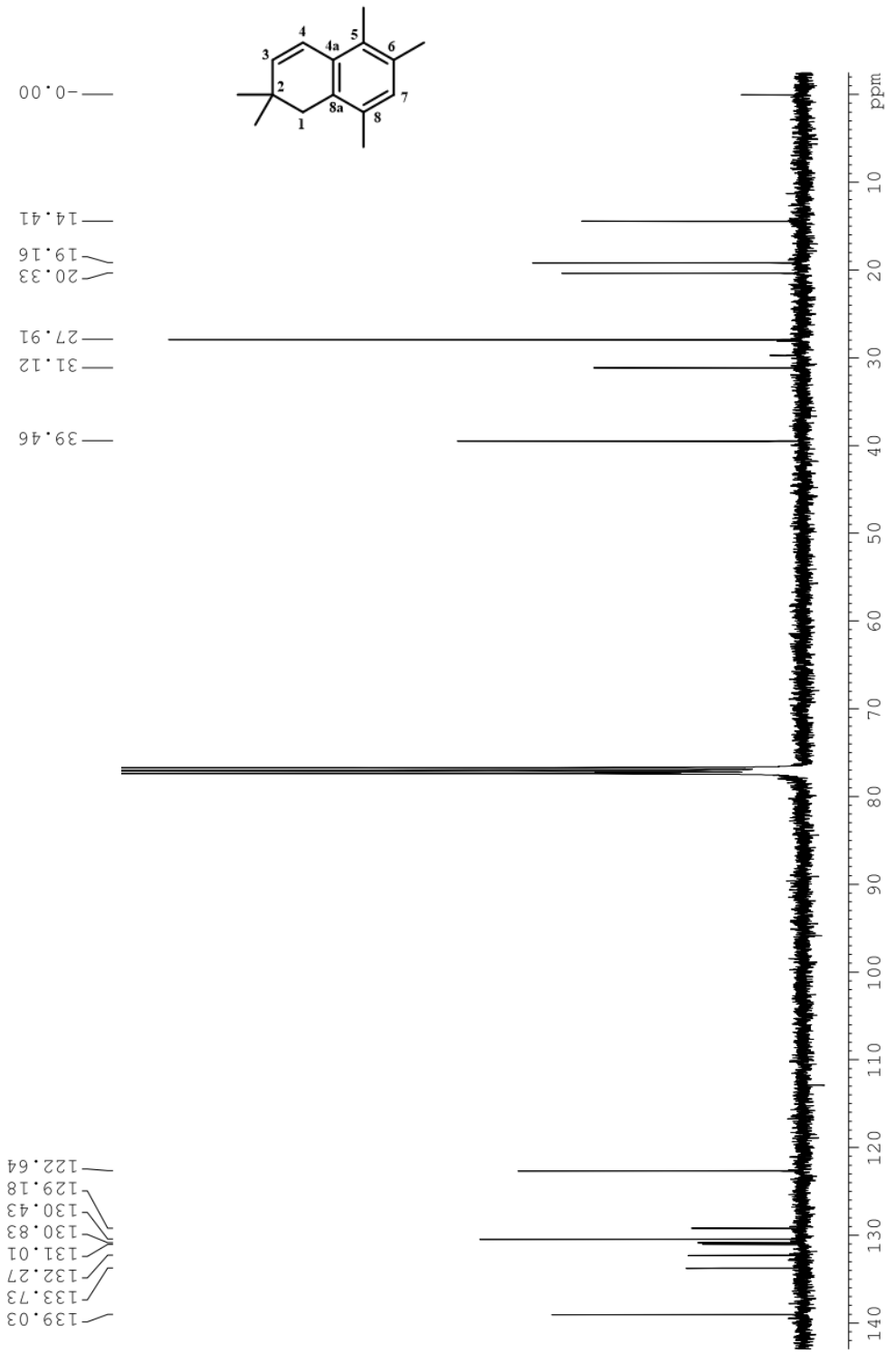


Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum of **3** ($CDCl_3$, 100 MHz).

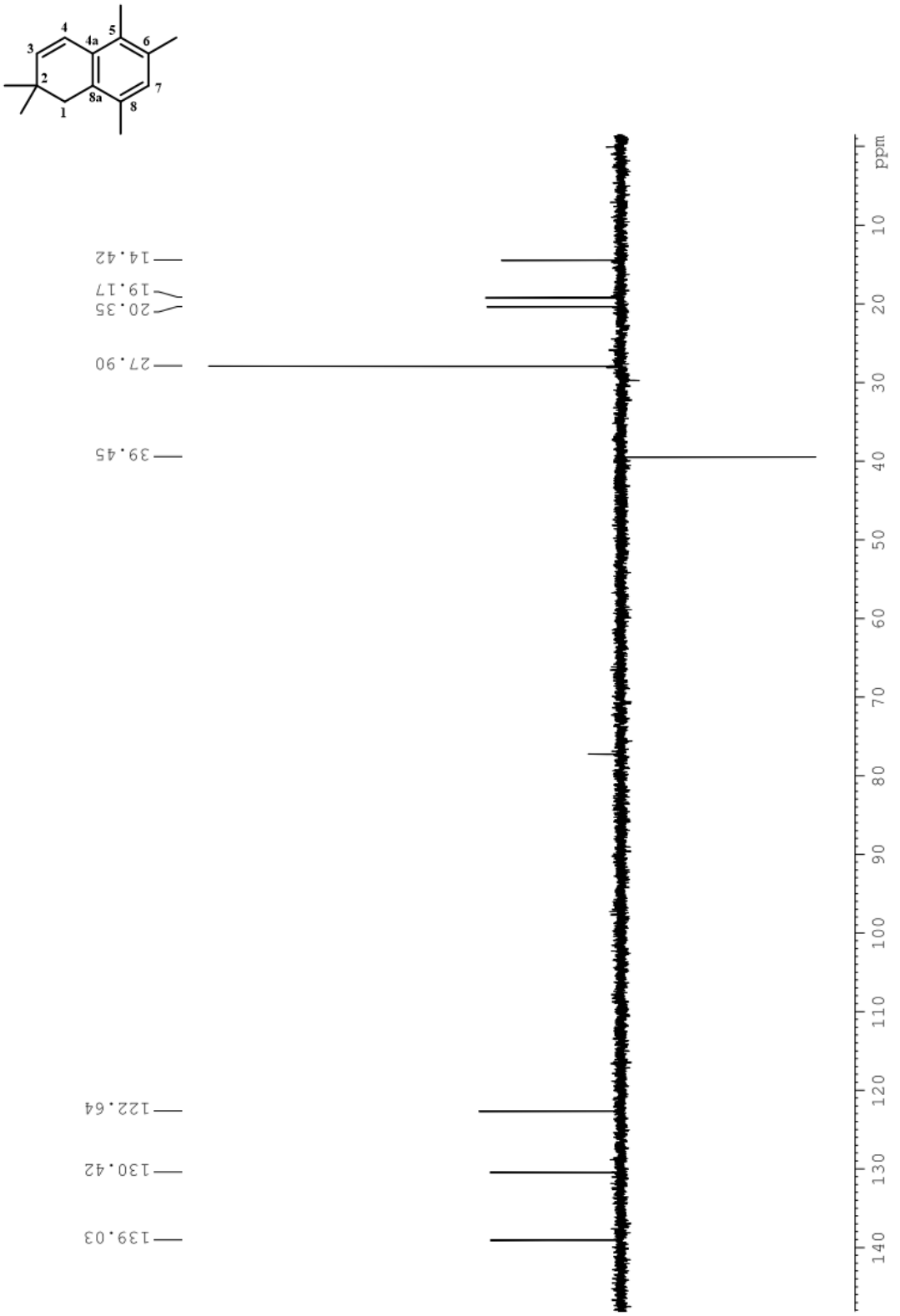


Figure S47. DEPT-135 spectrum of **3** ($CDCl_3$, 100 MHz).

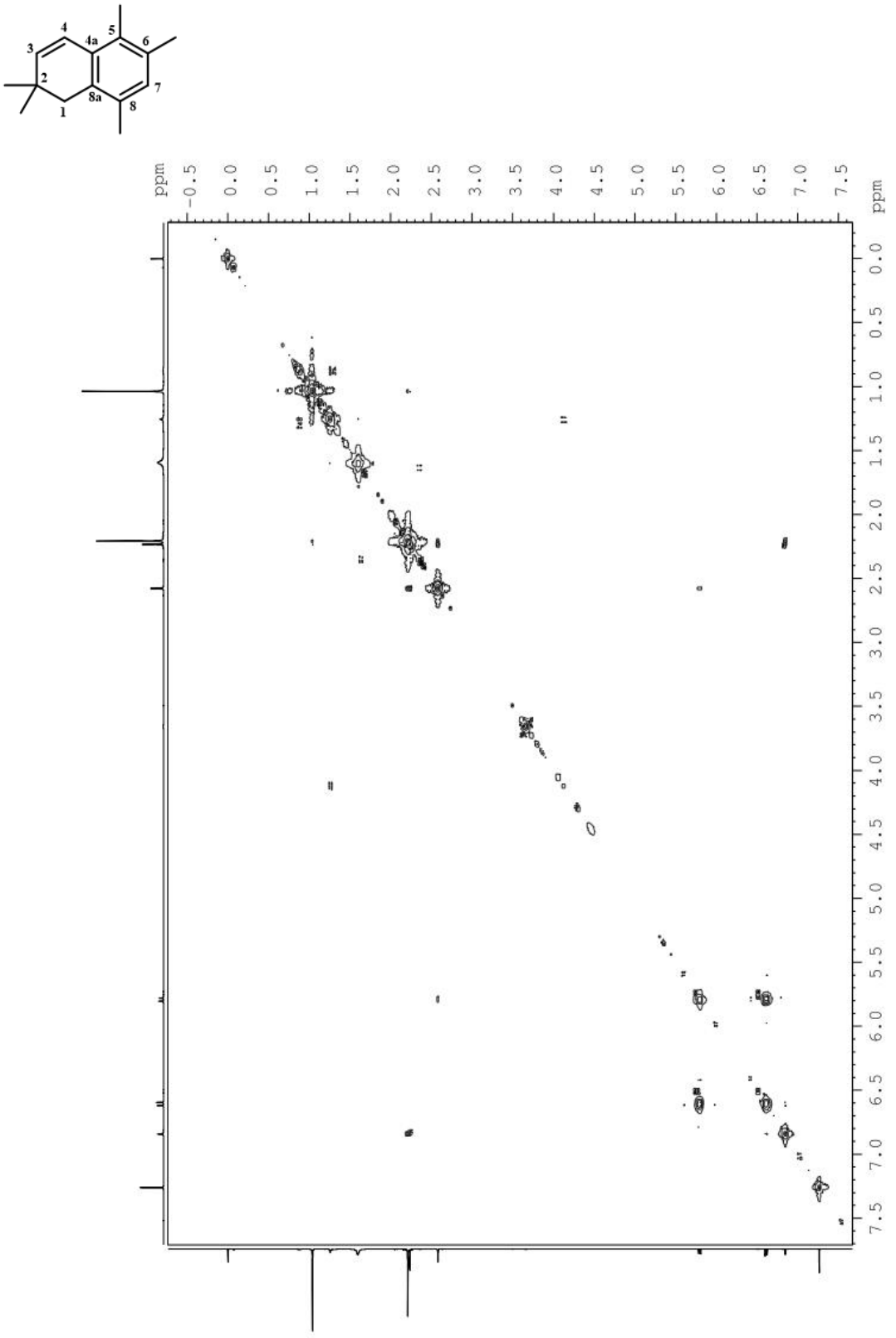


Figure S48. ^{1}H-^{1}H COSY of **3** ($CDCl_3$, 400 MHz).

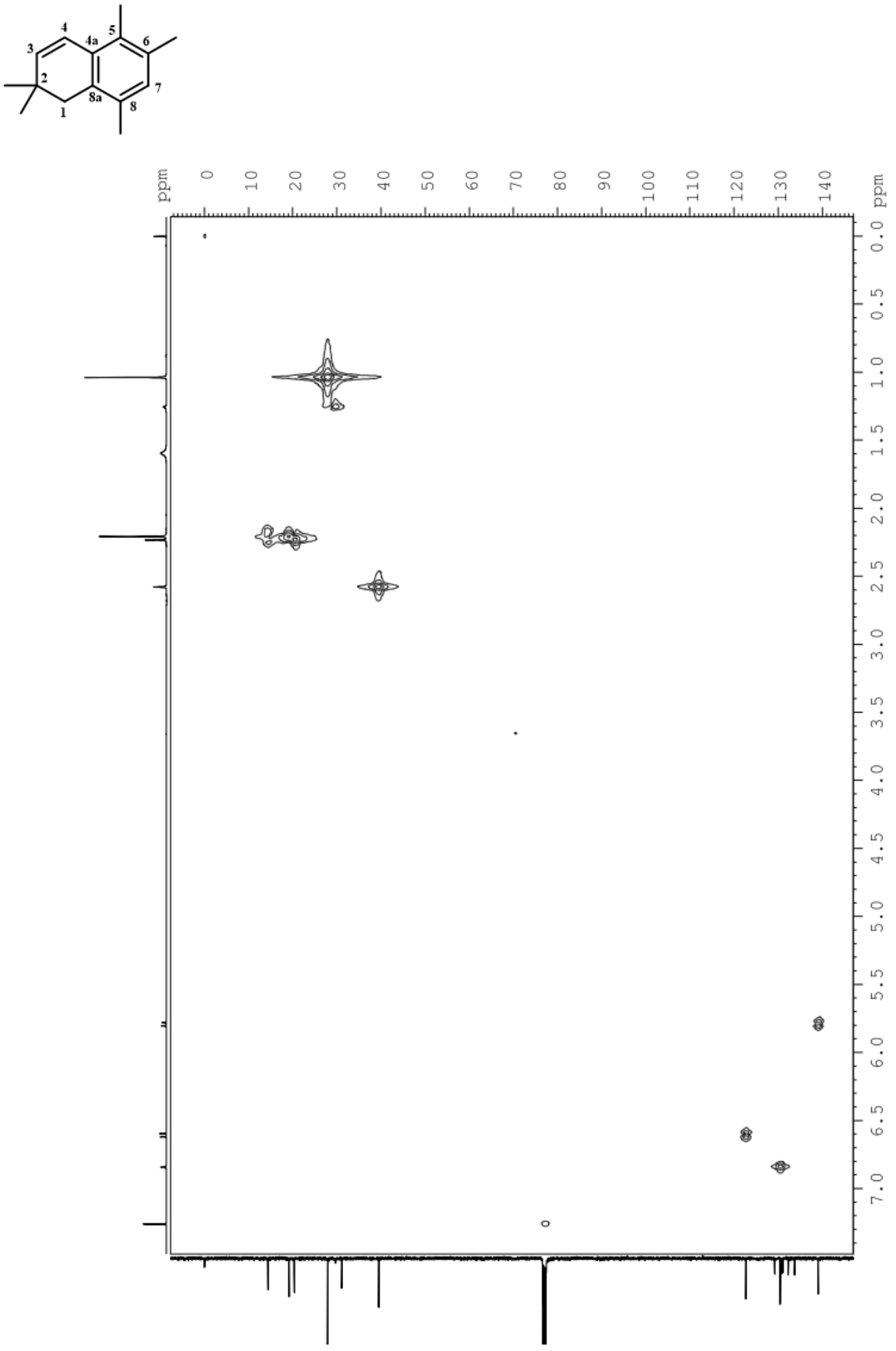


Figure S49. ^{1}H-^{13}C HMQC of **3** ($CDCl_3$, 400 MHz).

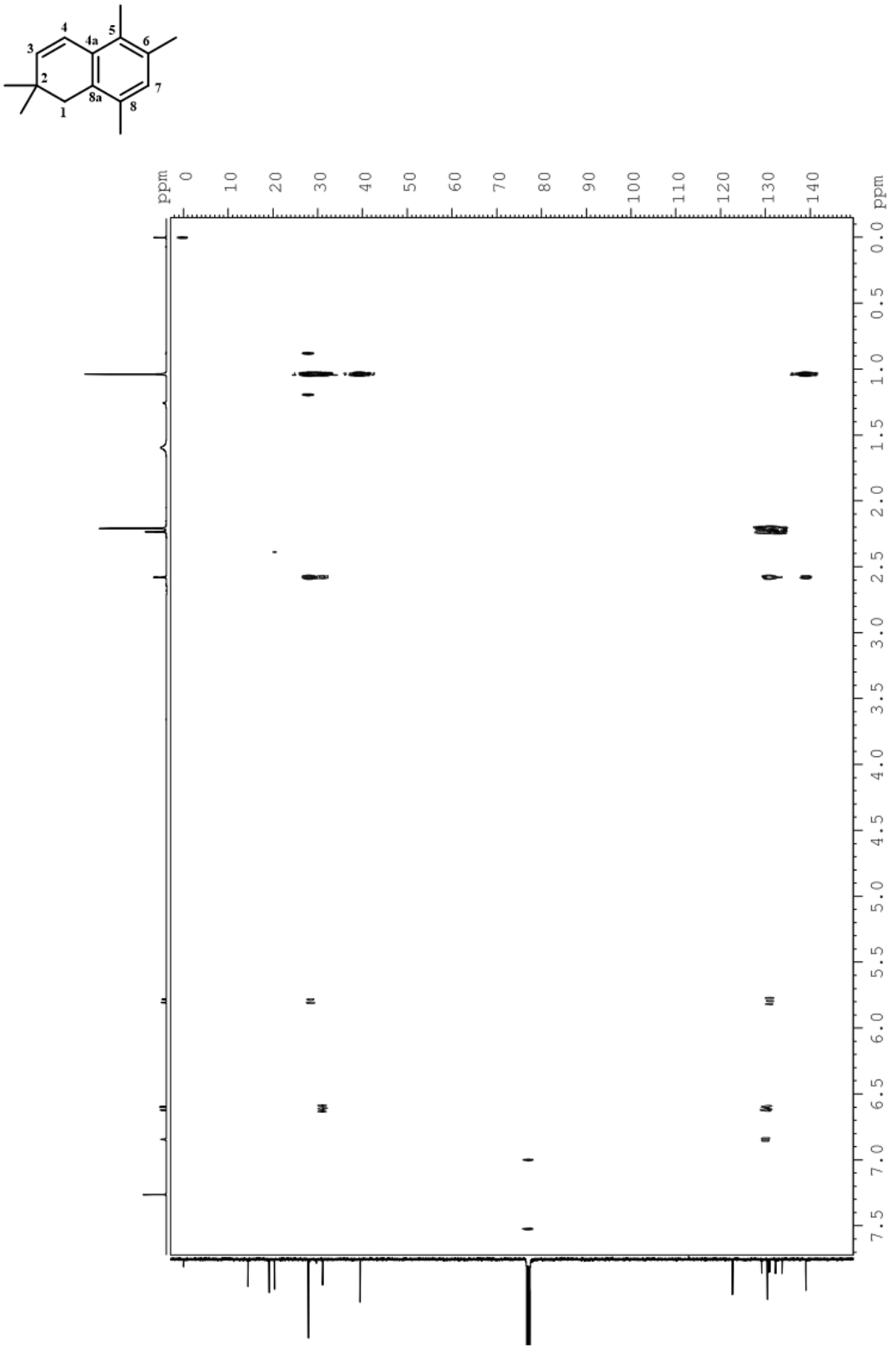


Figure S50. ^{1}H-^{13}C HMBC of **3** ($CDCl_3$, 400 MHz).

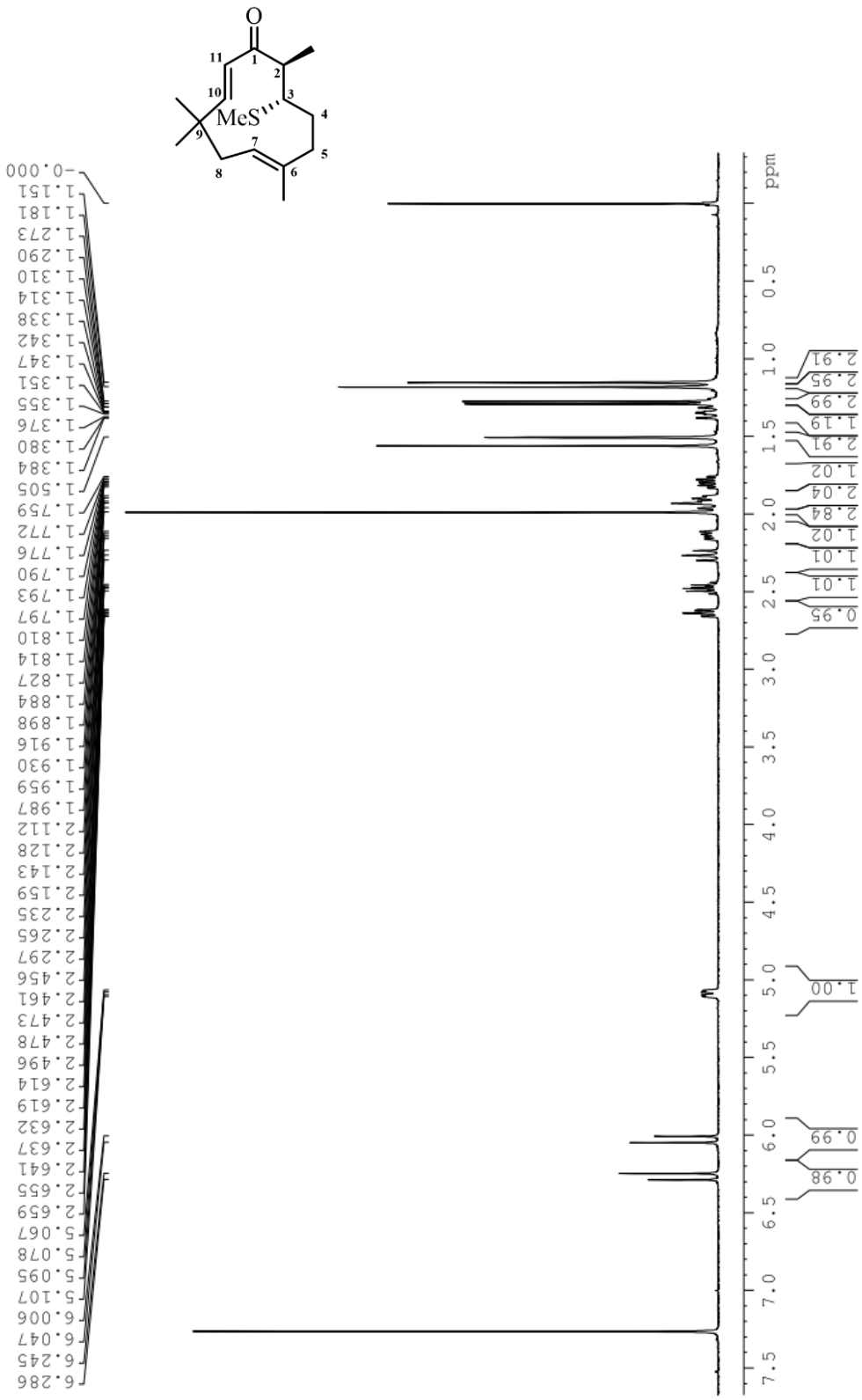


Figure S51. ^{1}H NMR spectrum of **(2*RS*,3*SR*)-11** ($CDCl_3$, 400 MHz).

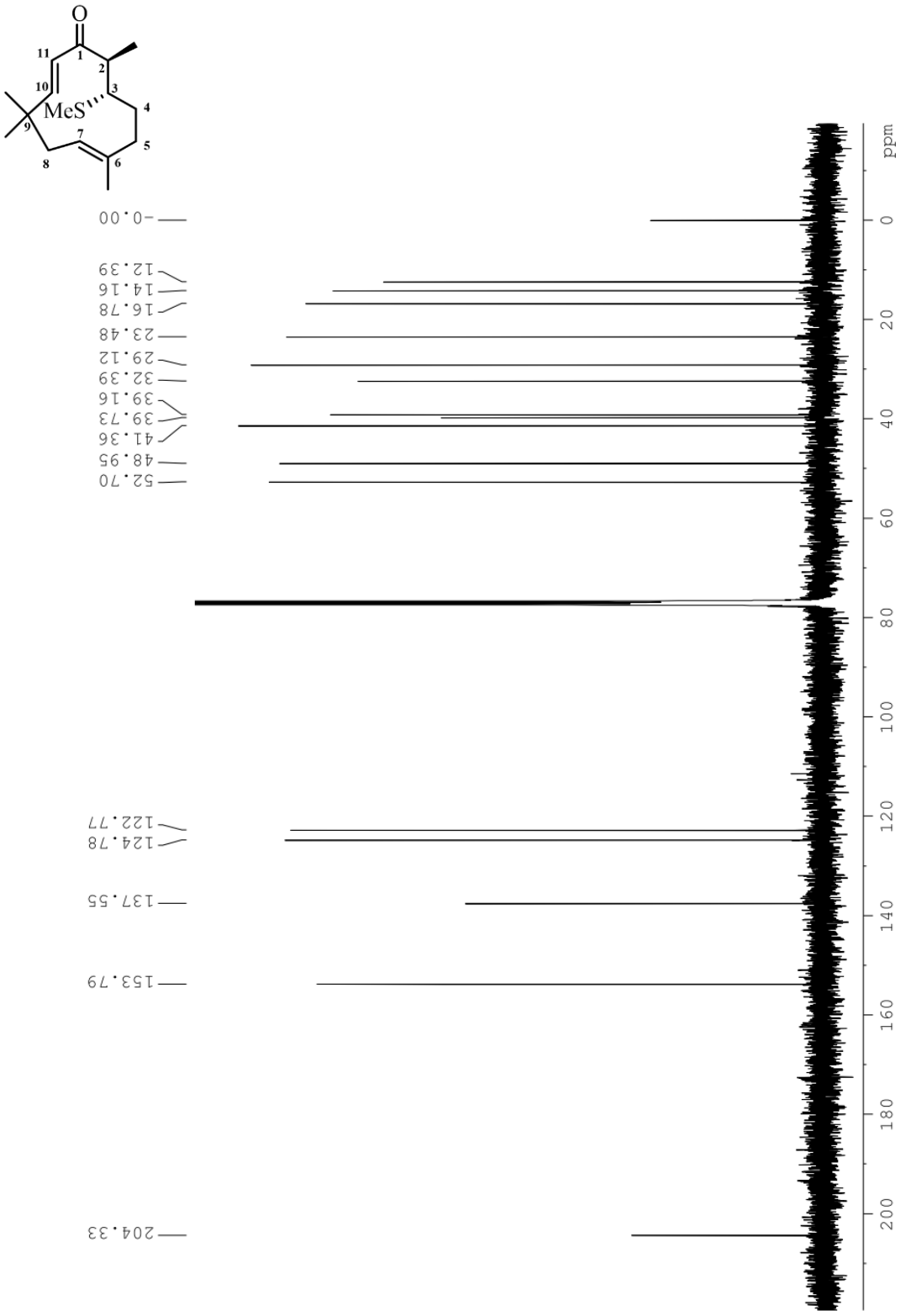


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **(2*RS*,3*SR*)-11** ($CDCl_3$, 100 MHz).

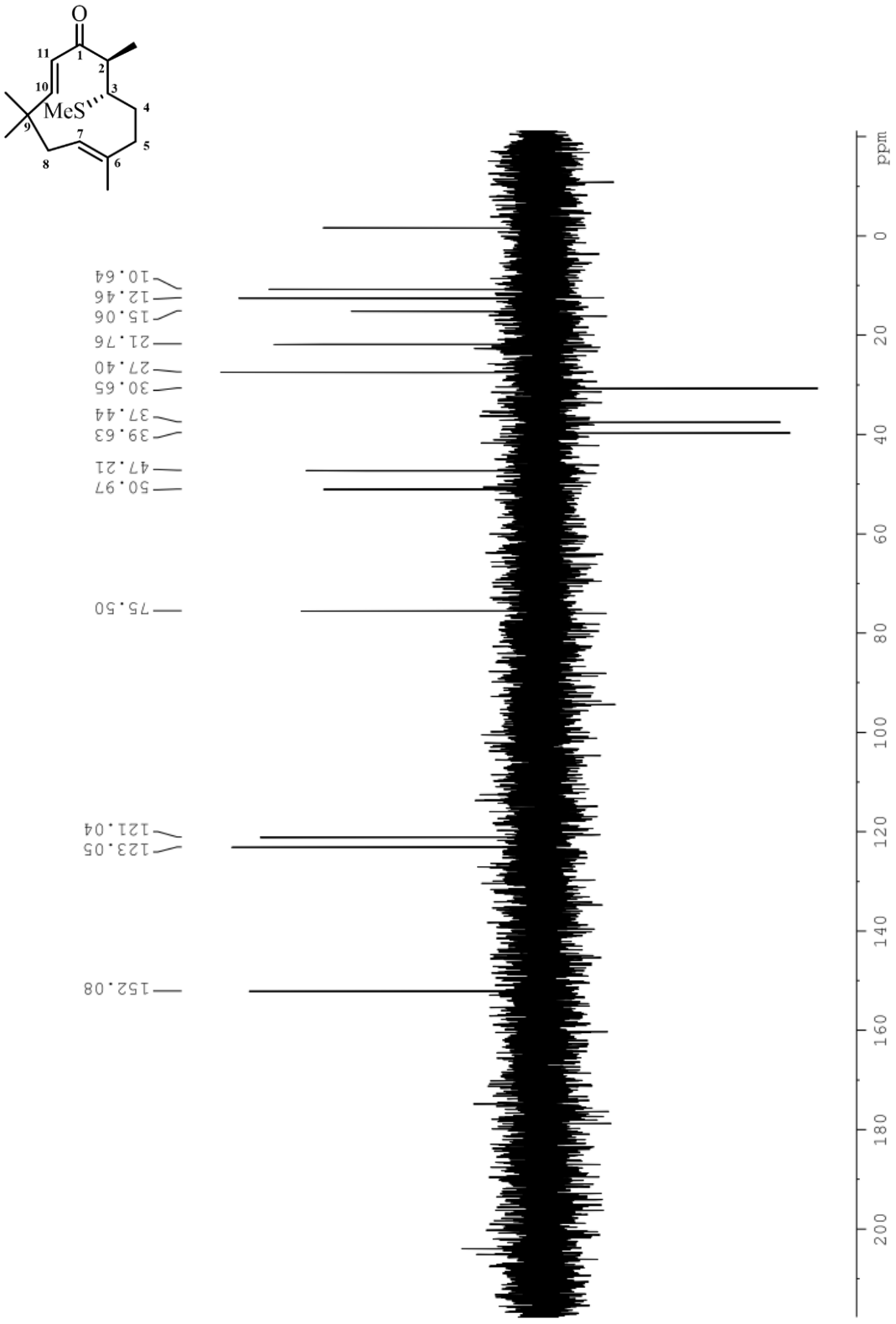


Figure S53. DEPT-135 spectrum of **(2*RS*,3*SR*)-11** ($CDCl_3$, 100 MHz).

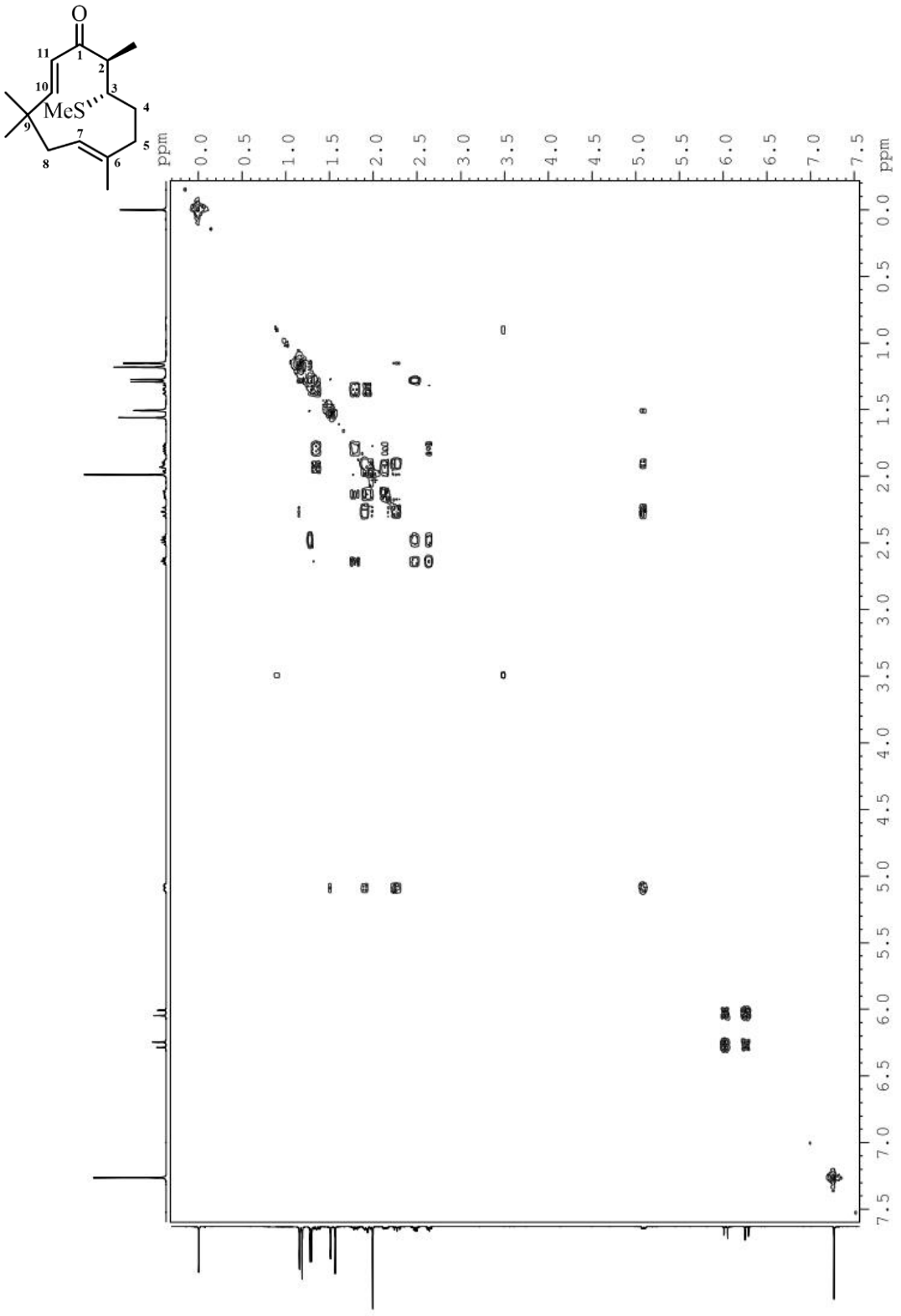


Figure S54. ^{1}H-^{1}H COSY of **(2*RS*,3*SR*)-11** ($CDCl_3$, 400 MHz).

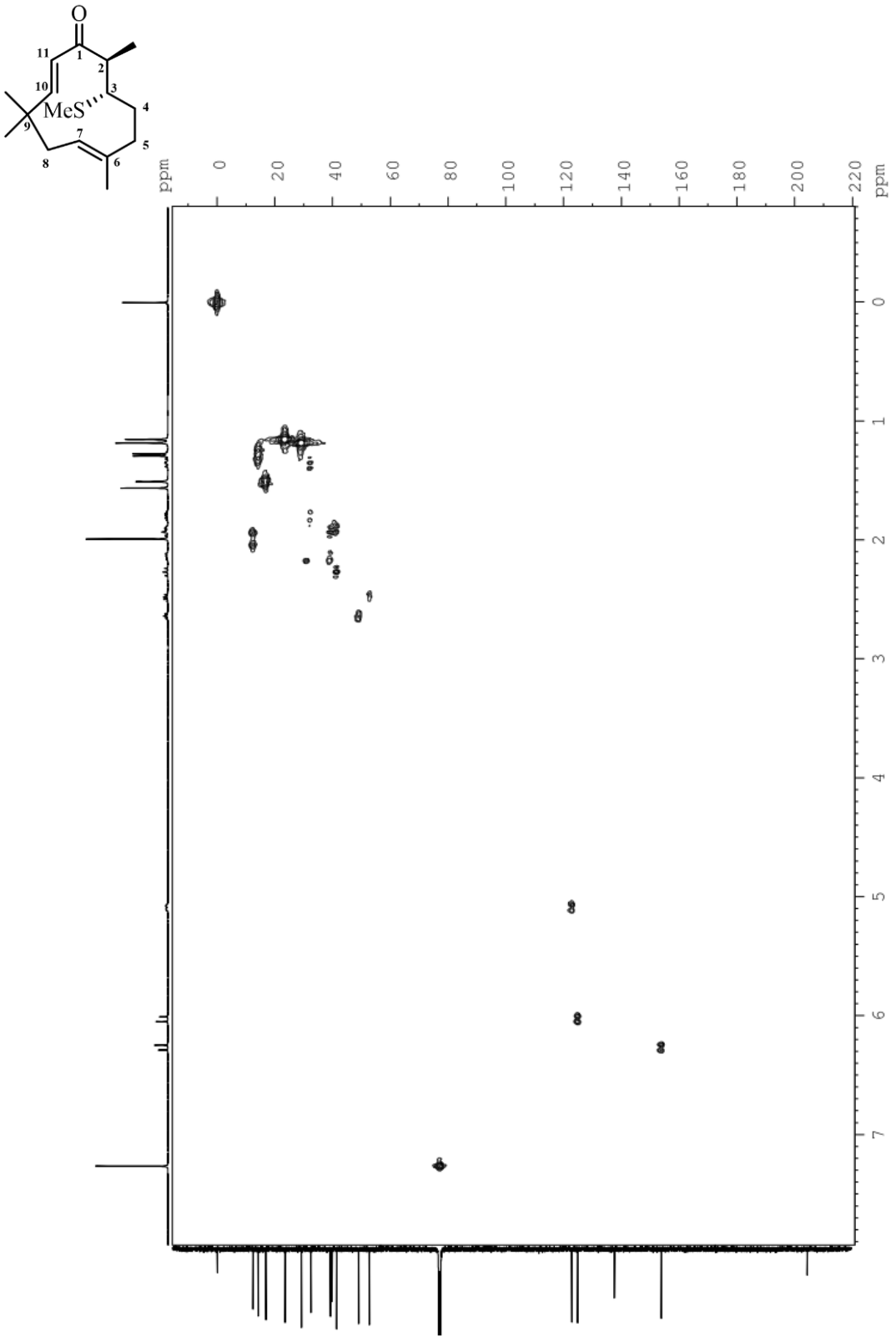


Figure S55. ^{1}H-^{13}C HMQC of **(2*RS*,3*SR*)-11** ($CDCl_3$, 400 MHz).

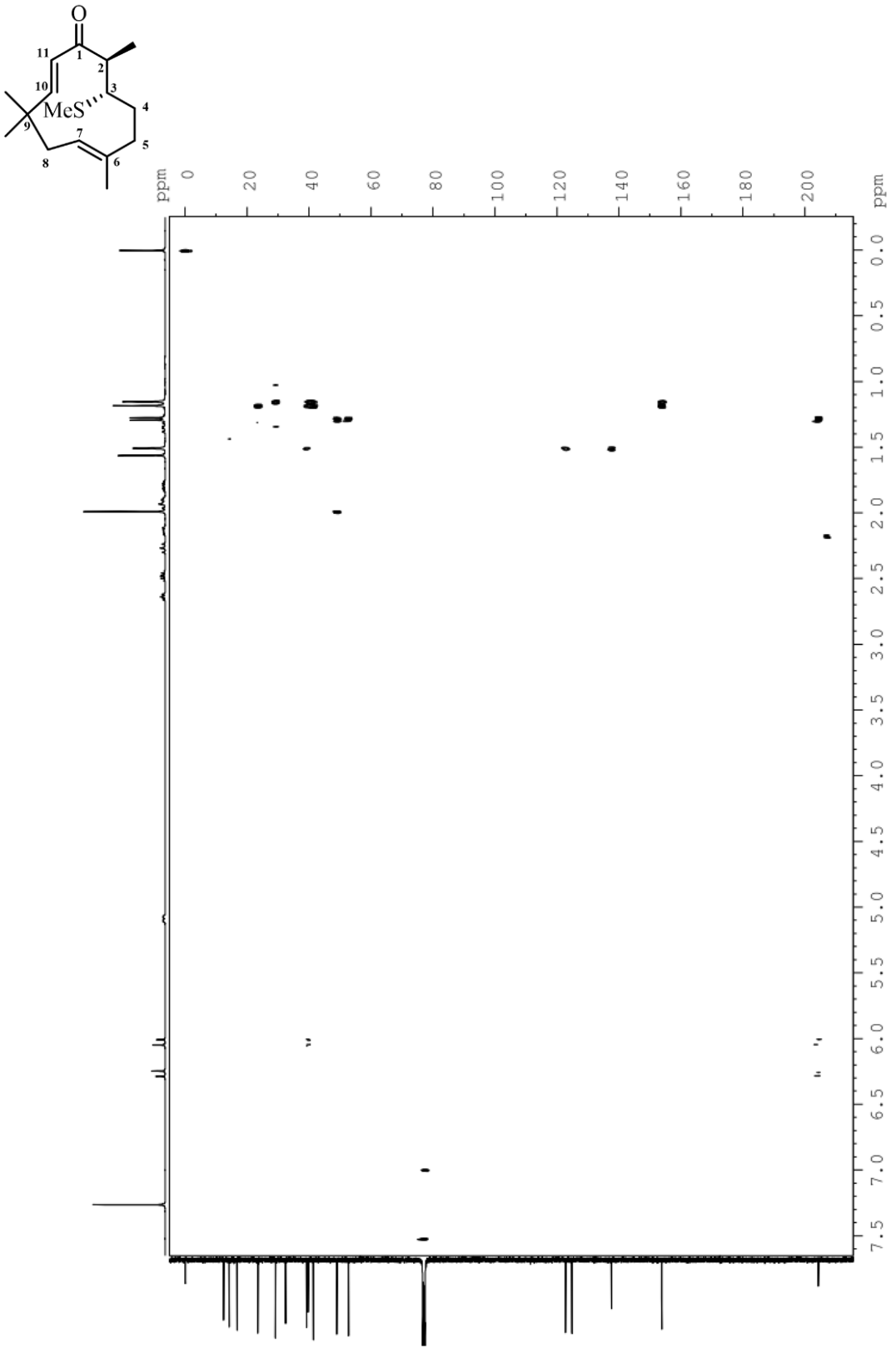


Figure S56. ^{1}H-^{13}C HMBC of **(2*RS*,3*SR*)-11** ($CDCl_3$, 400 MHz).

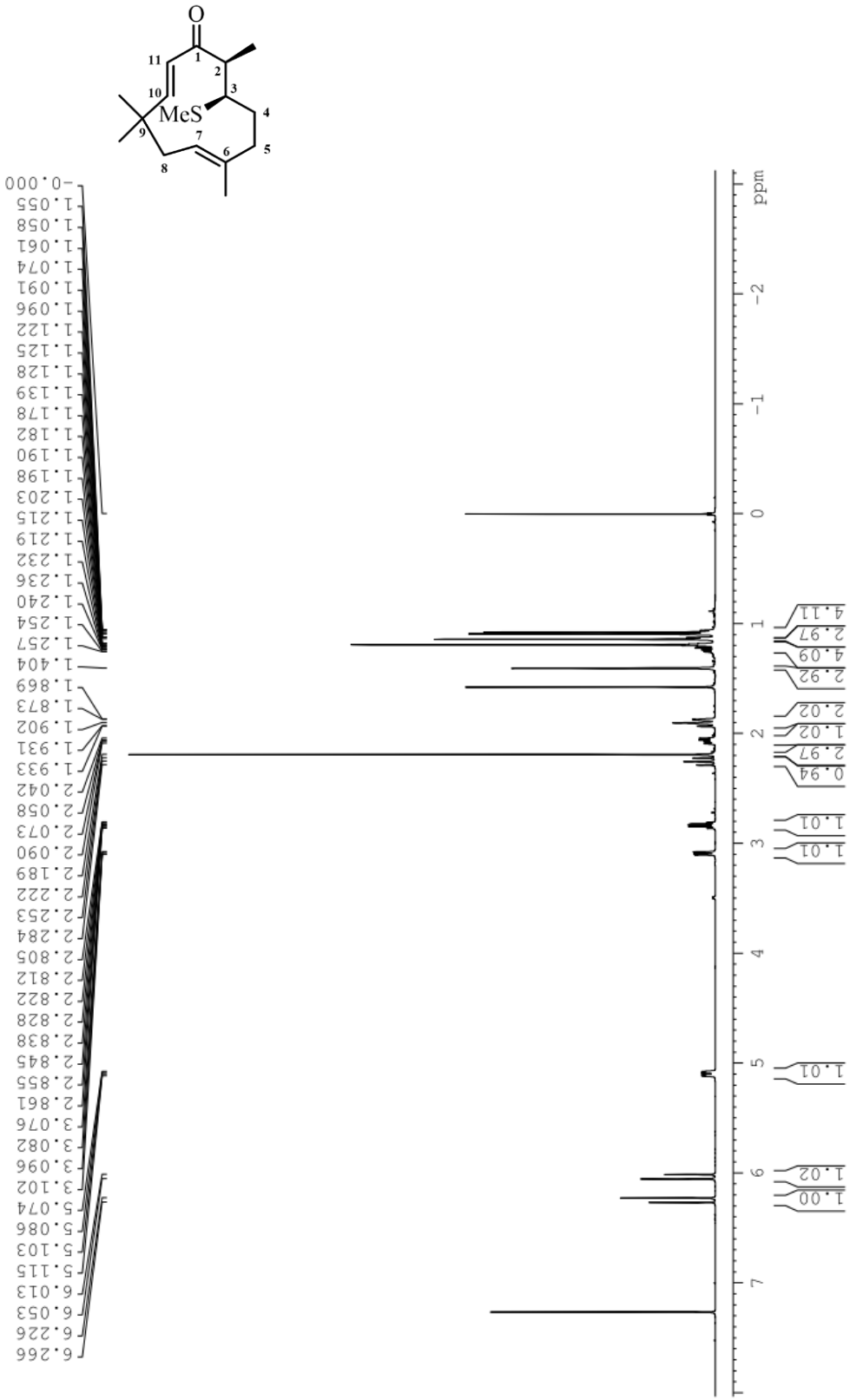


Figure S57. ^{1}H NMR spectrum of **(2*RS*,3*RS*)-11** ($CDCl_3$, 400 MHz).

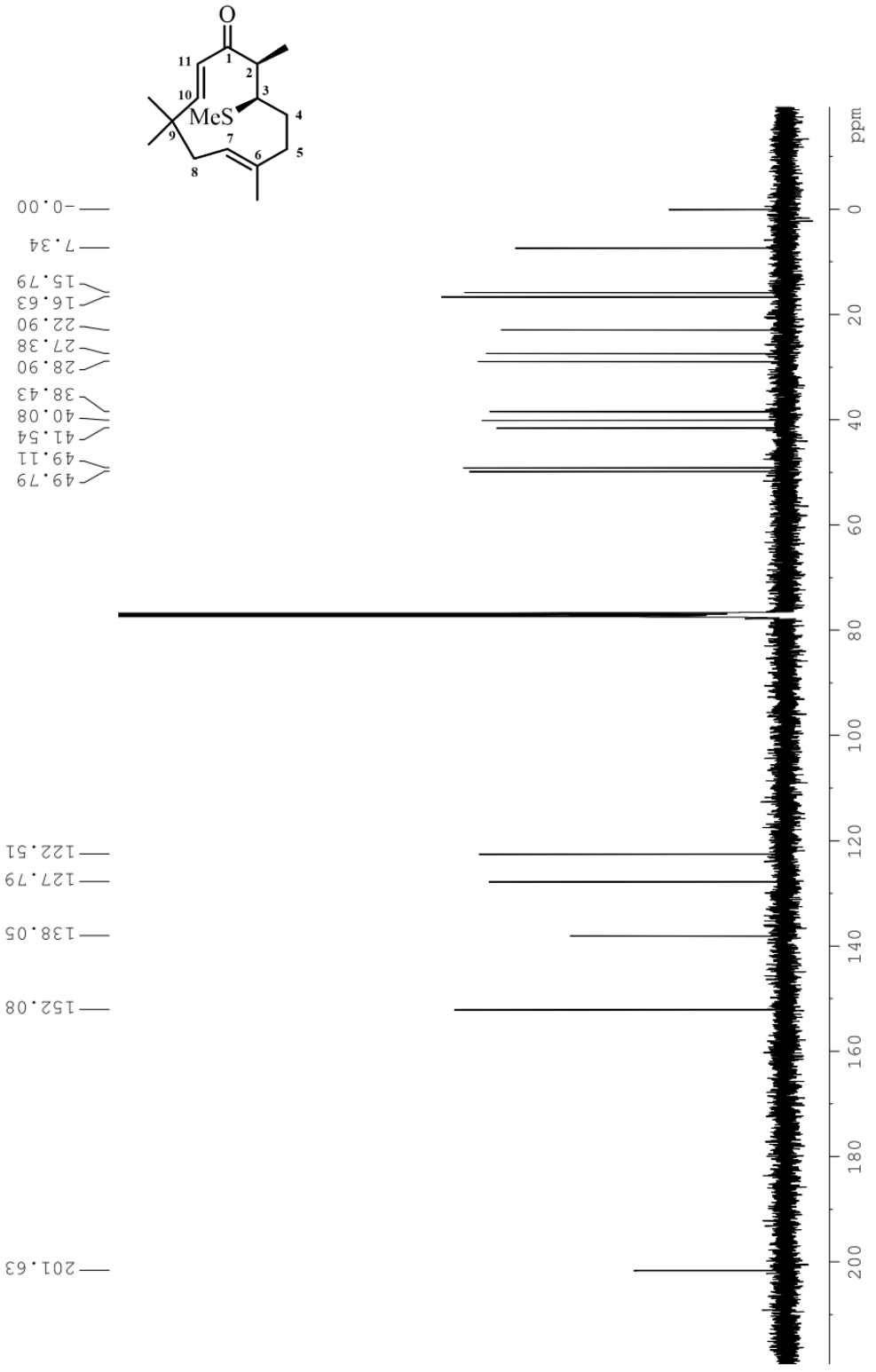


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of **(2*RS*,3*RS*)-11** ($CDCl_3$, 100 MHz).

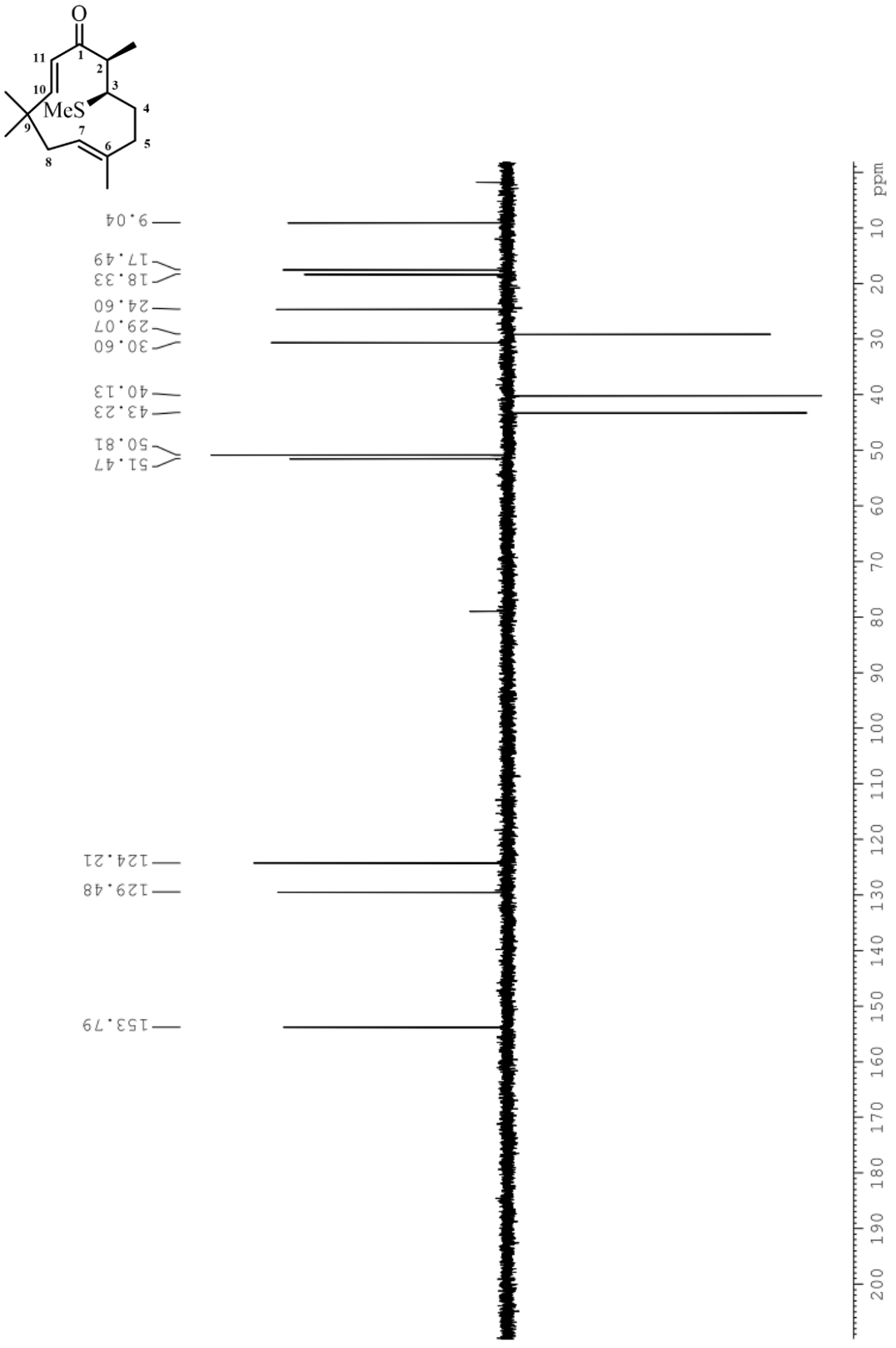


Figure S59. DEPT-135 spectrum of **(2*RS*,3*RS*)-11** ($CDCl_3$, 100 MHz).

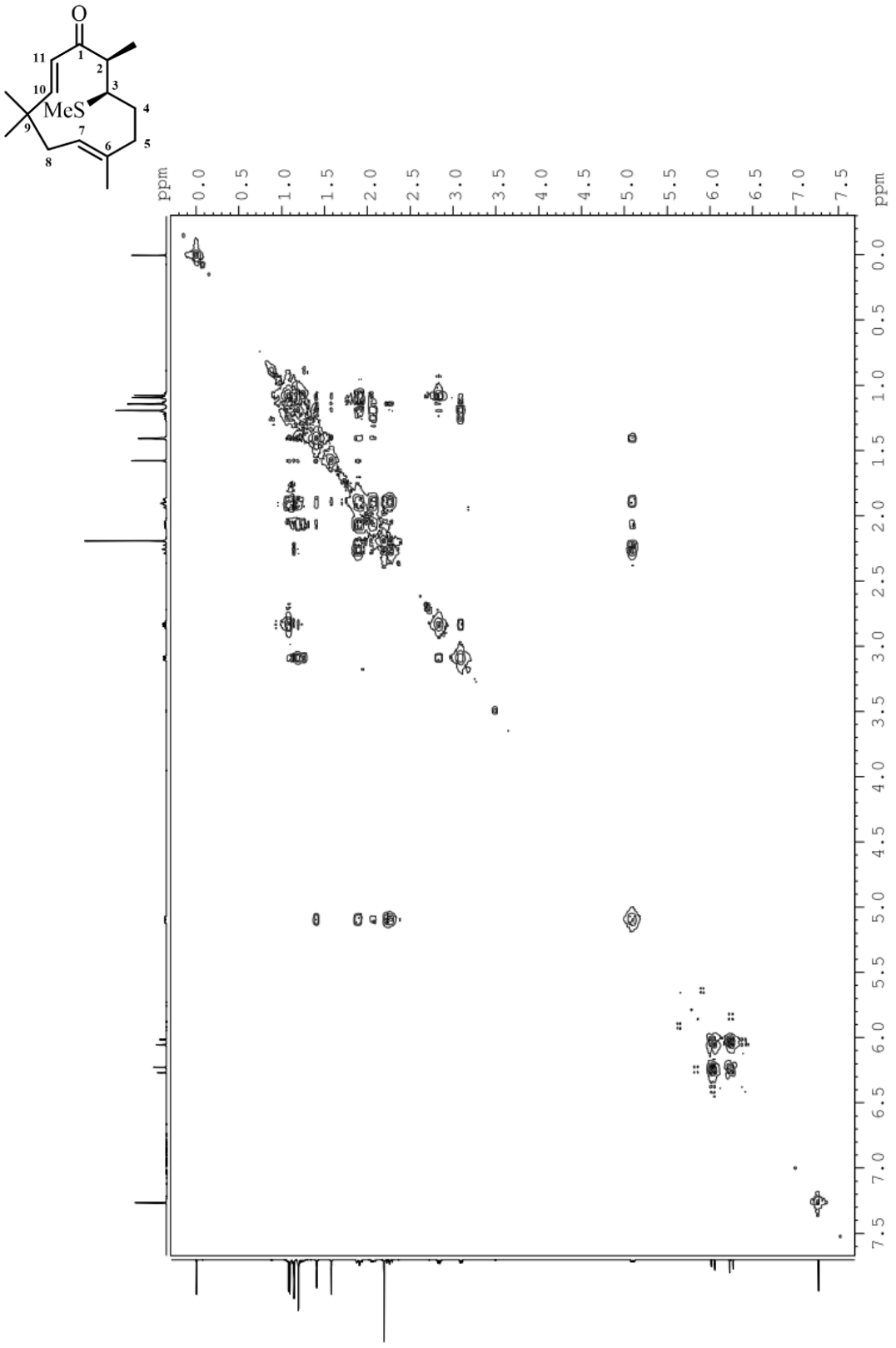


Figure S60. ^{1}H-^{1}H COSY of **(2*RS*,3*RS*)-11** ($CDCl_3$, 400 MHz).

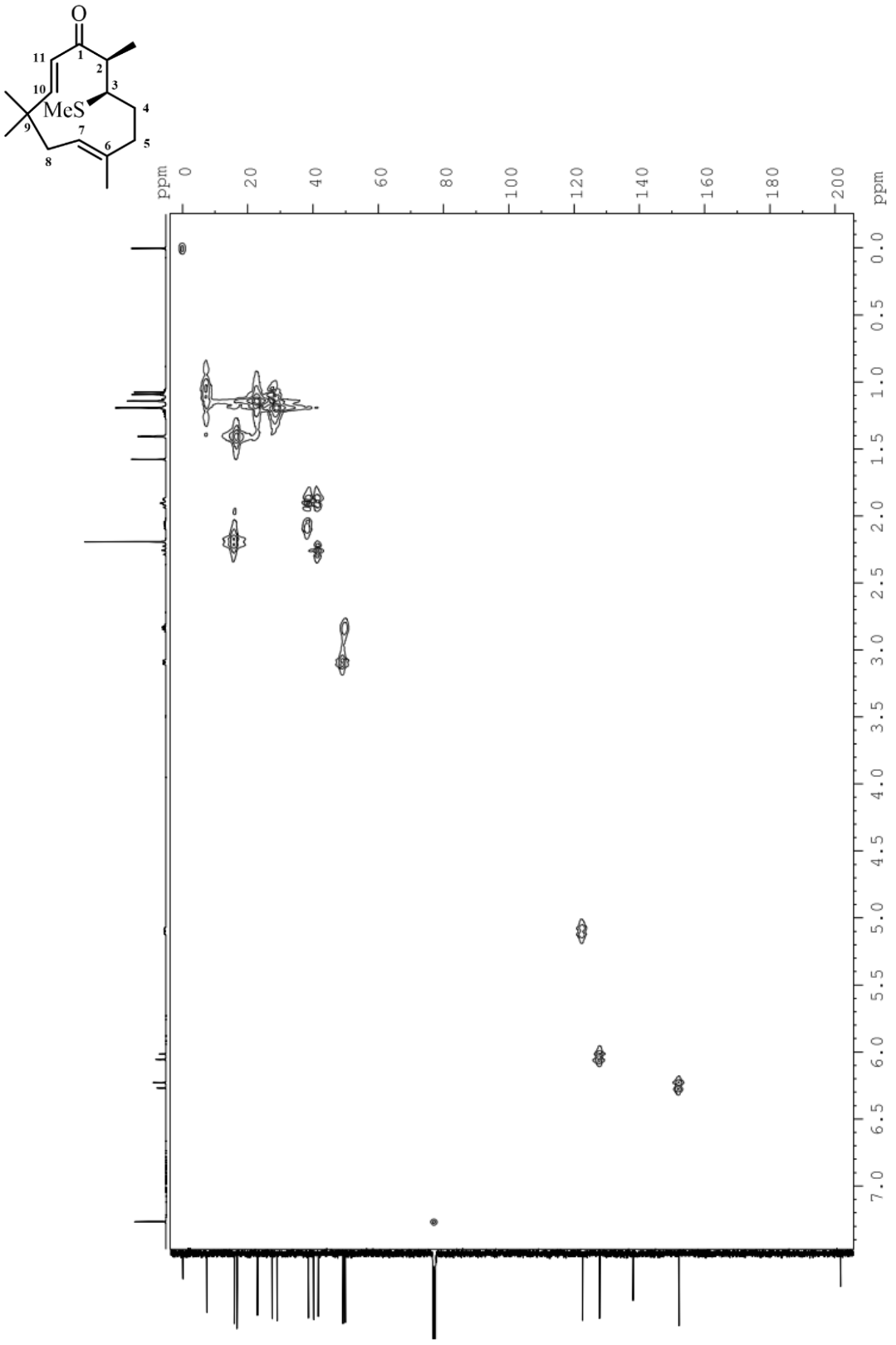


Figure S61. ^{1}H-^{13}C HMQC of **(2*RS*,3*RS*)-11** ($CDCl_3$, 400 MHz).

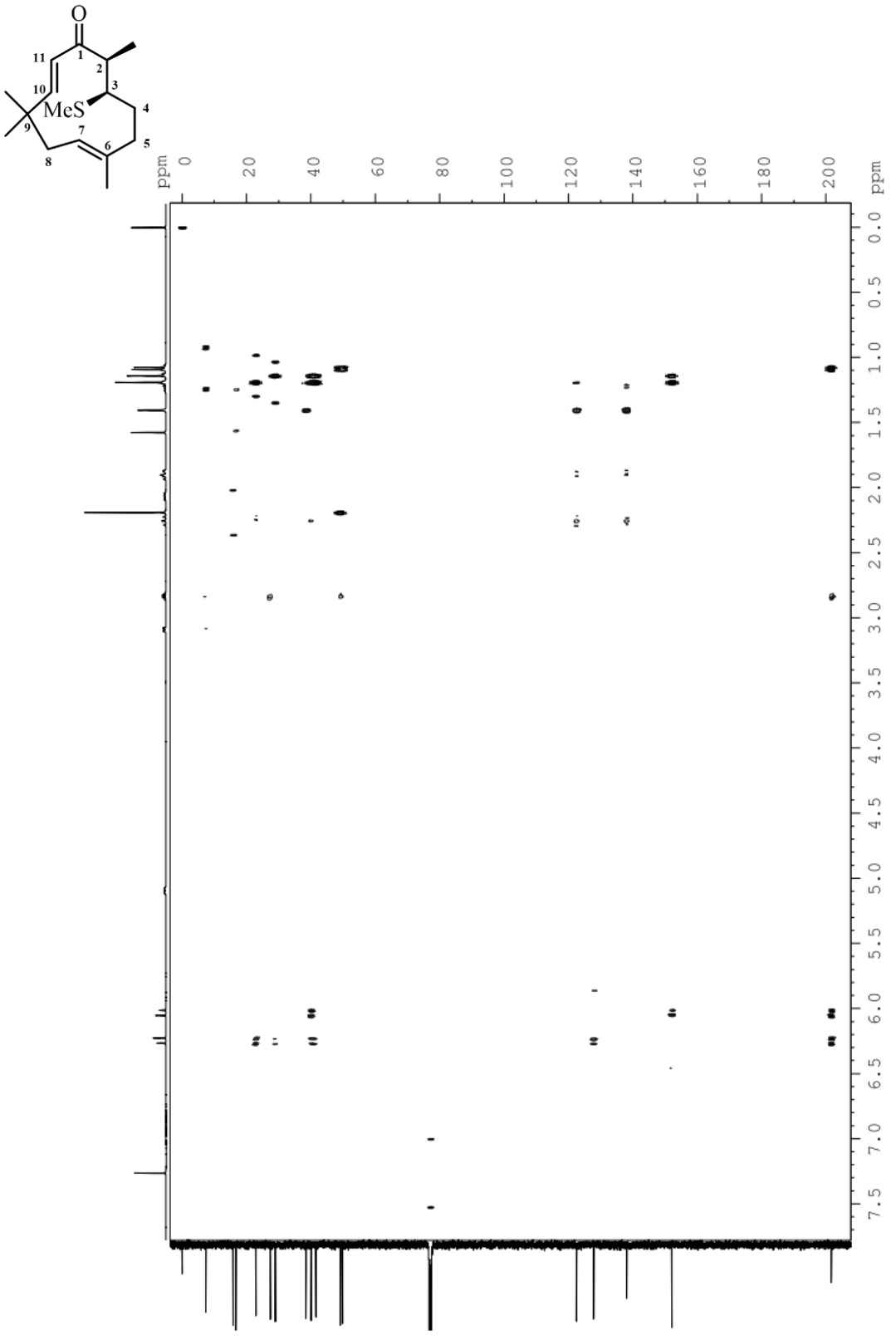


Figure S62. ^{1}H-^{13}C HMBC of **(2*RS*,3*RS*)-11** ($CDCl_3$, 400 MHz).

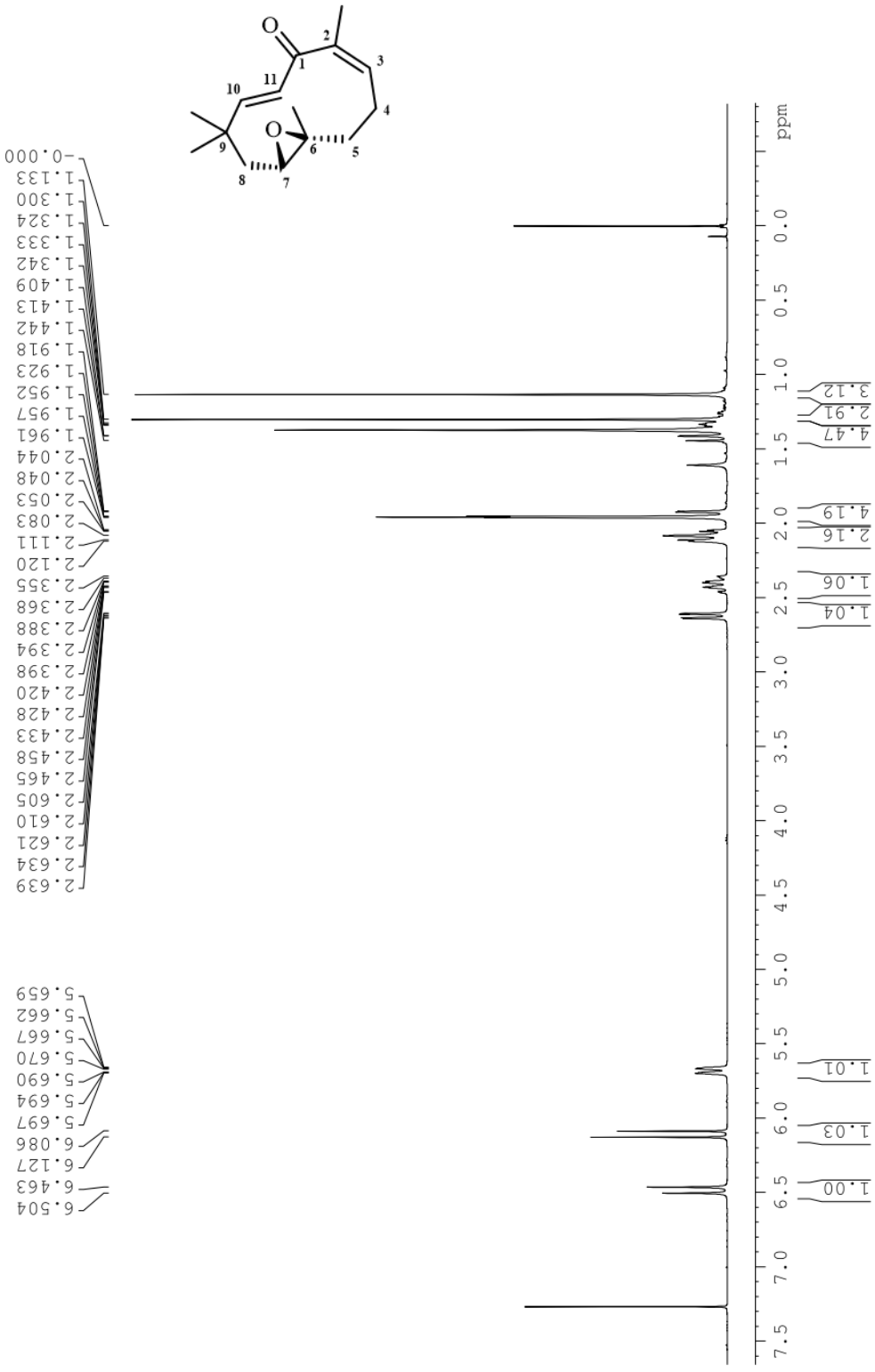


Figure S63. ^{1}H NMR spectrum of **12** ($CDCl_3$, 400 MHz).

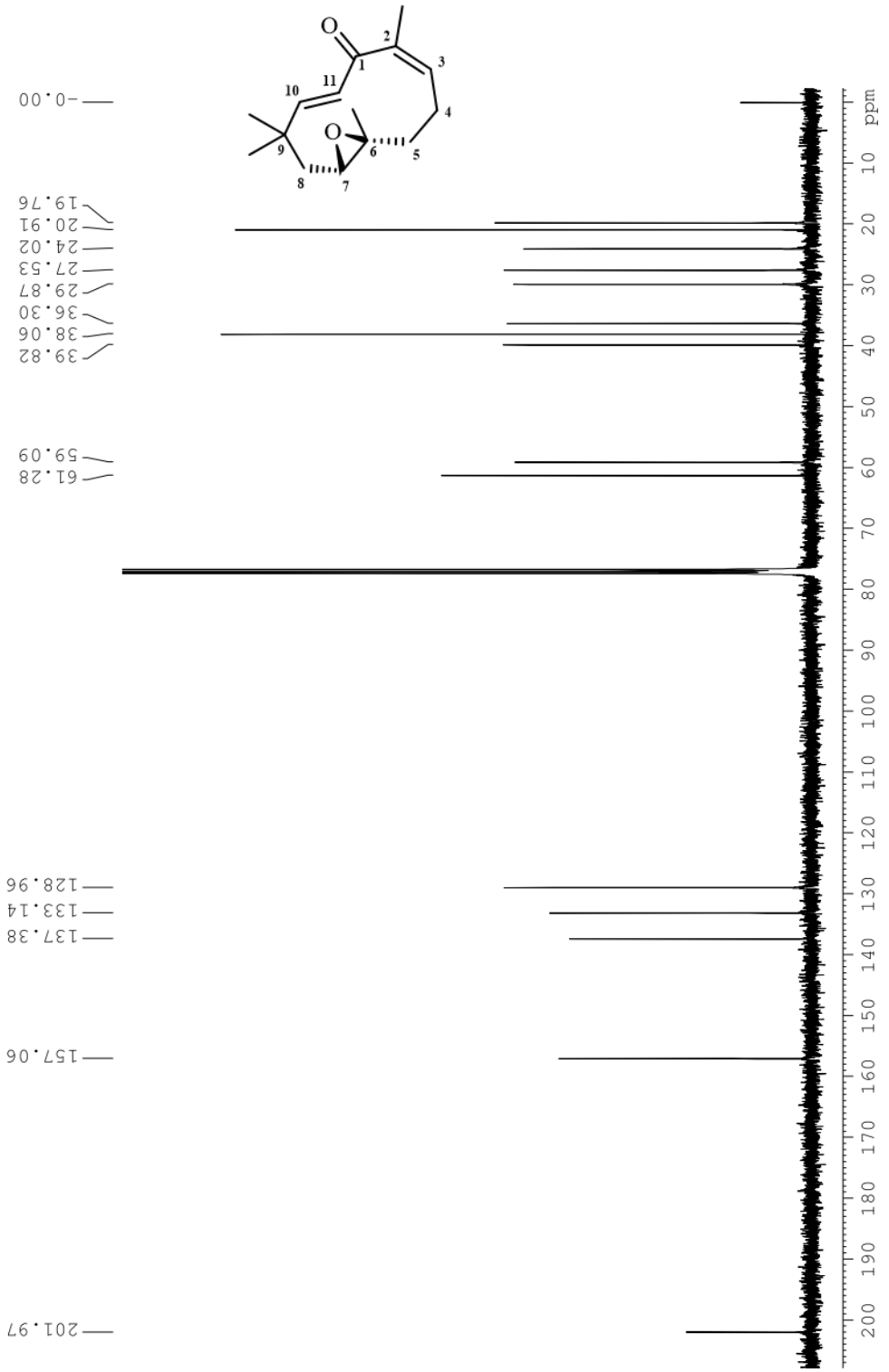


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of **12** ($CDCl_3$, 100 MHz).

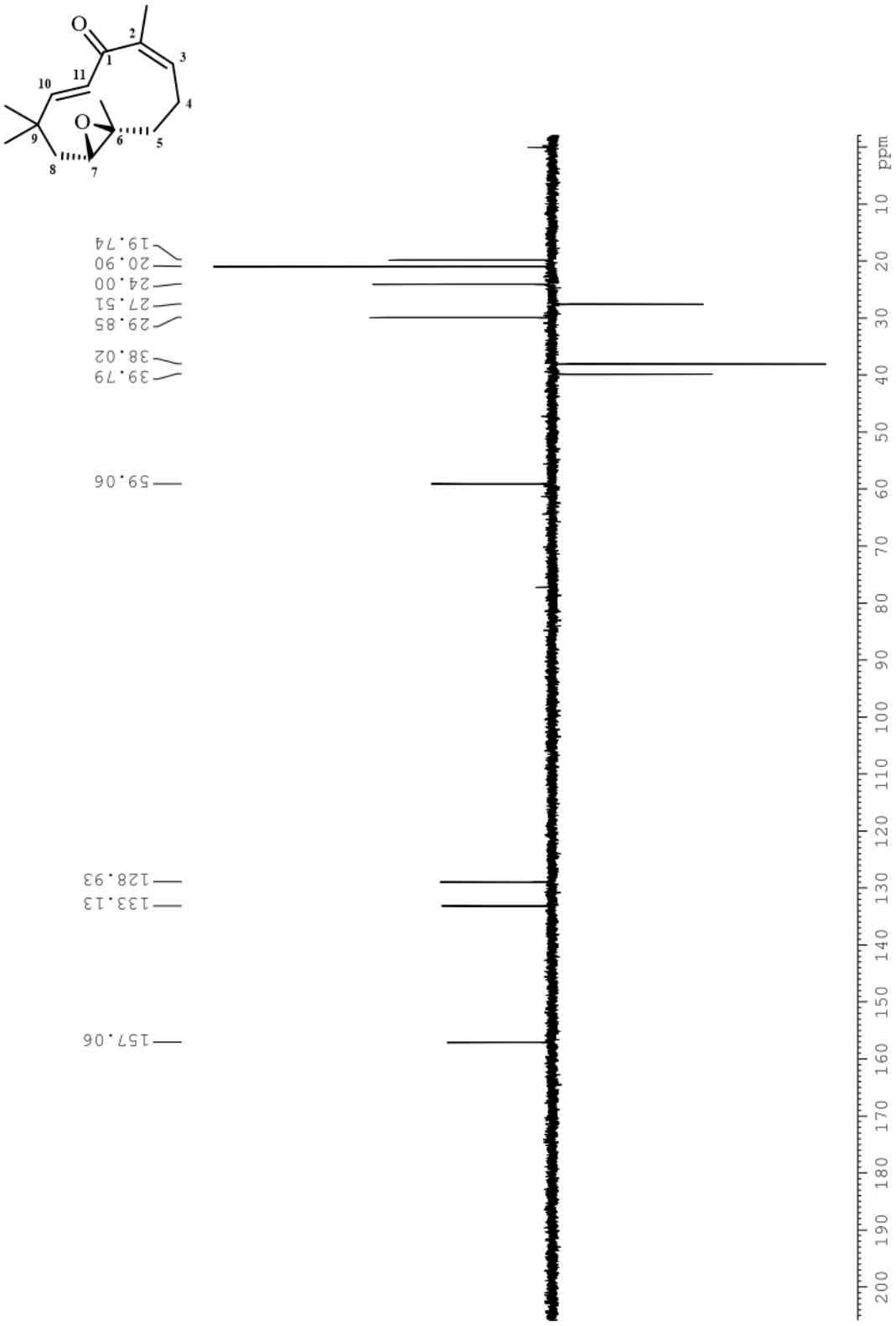


Figure S65. DEPT-135 spectrum of **12** ($CDCl_3$, 100 MHz).

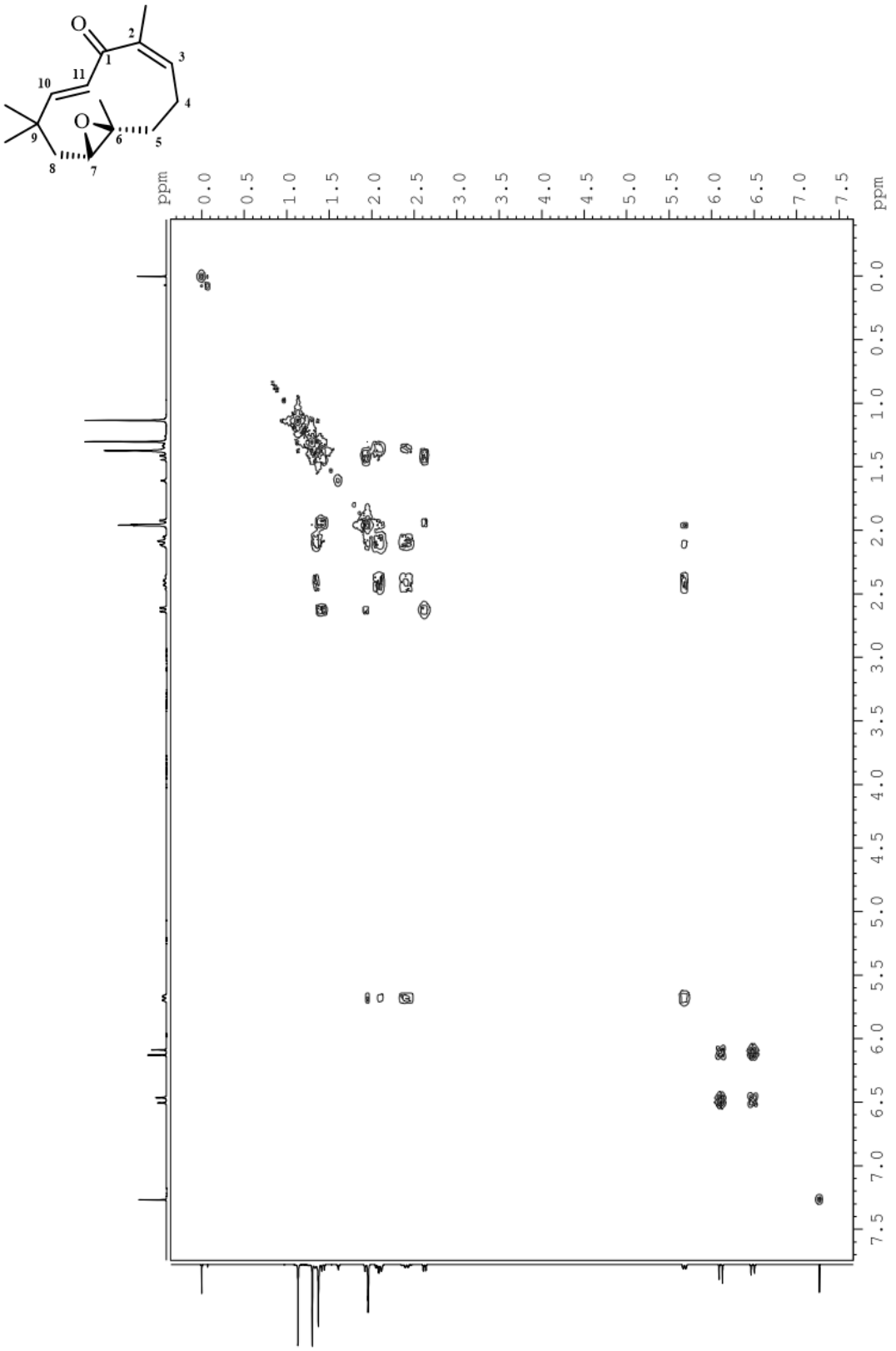


Figure S66. ^{1}H-^{1}H COSY of **12** ($CDCl_3$, 400 MHz).

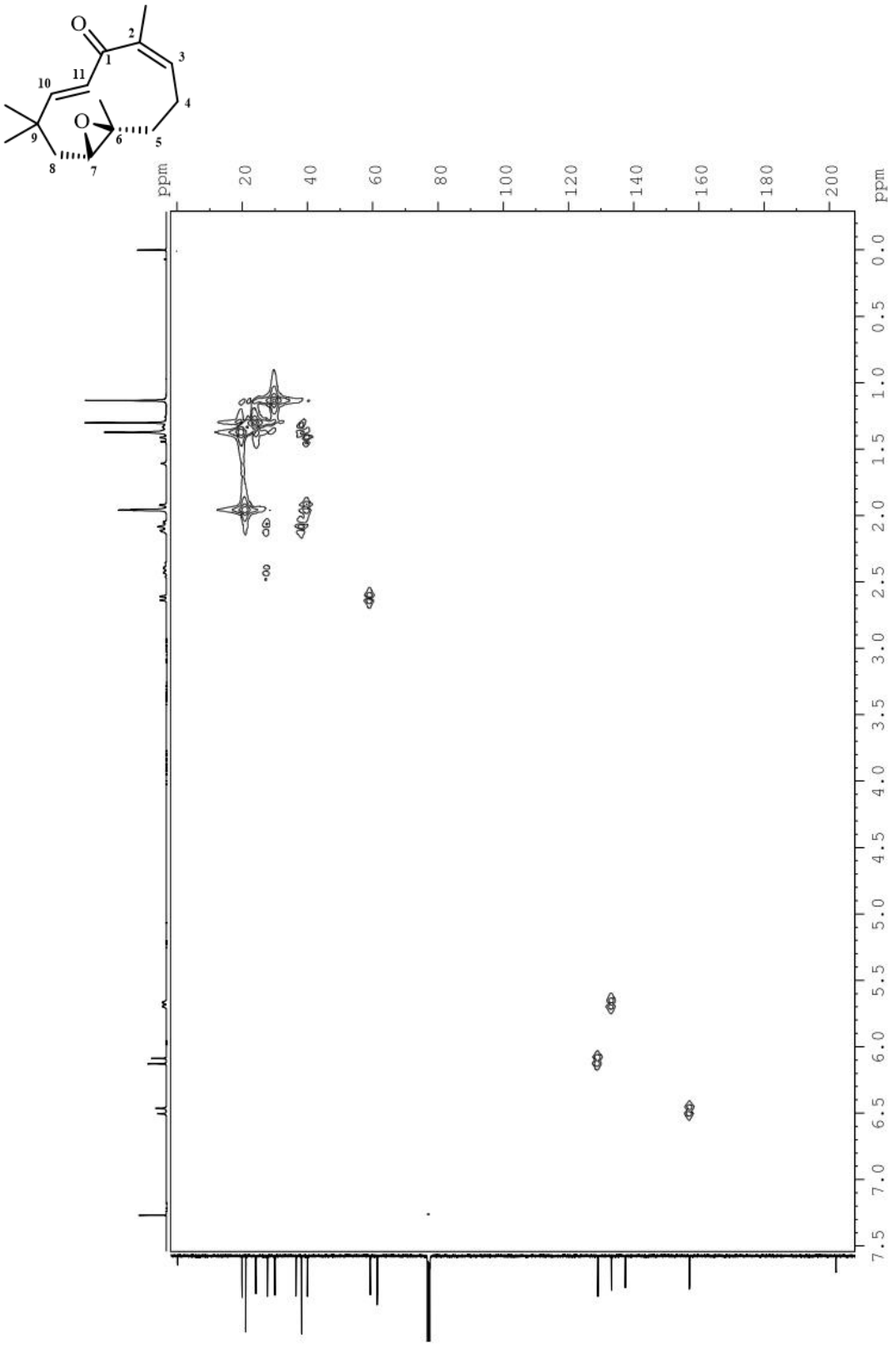


Figure S67. ^{1}H-^{13}C HMQC of **12** ($CDCl_3$, 400 MHz).

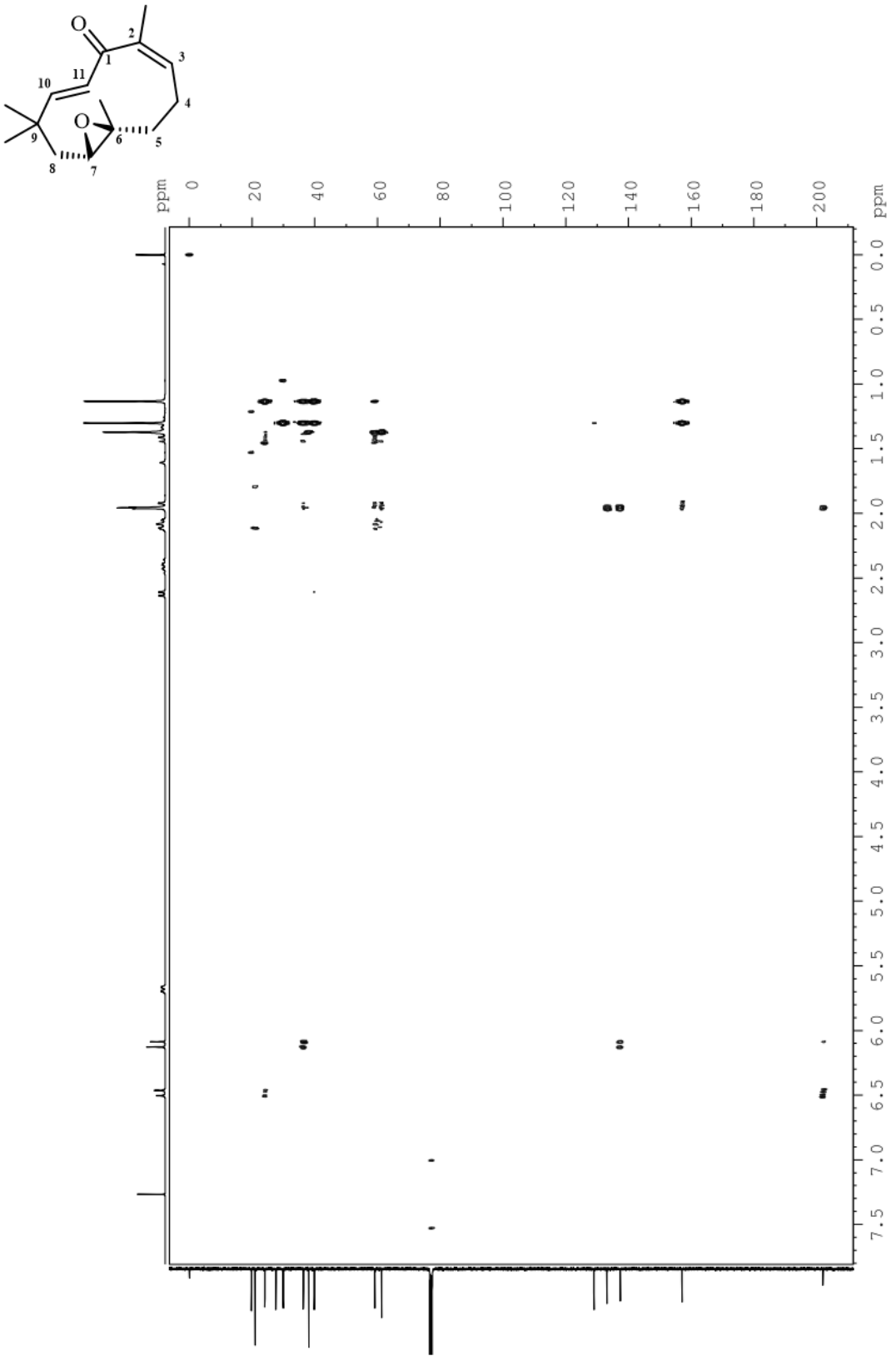


Figure S68. ^{1}H-^{13}C HMBC of **12** ($CDCl_3$, 400 MHz).

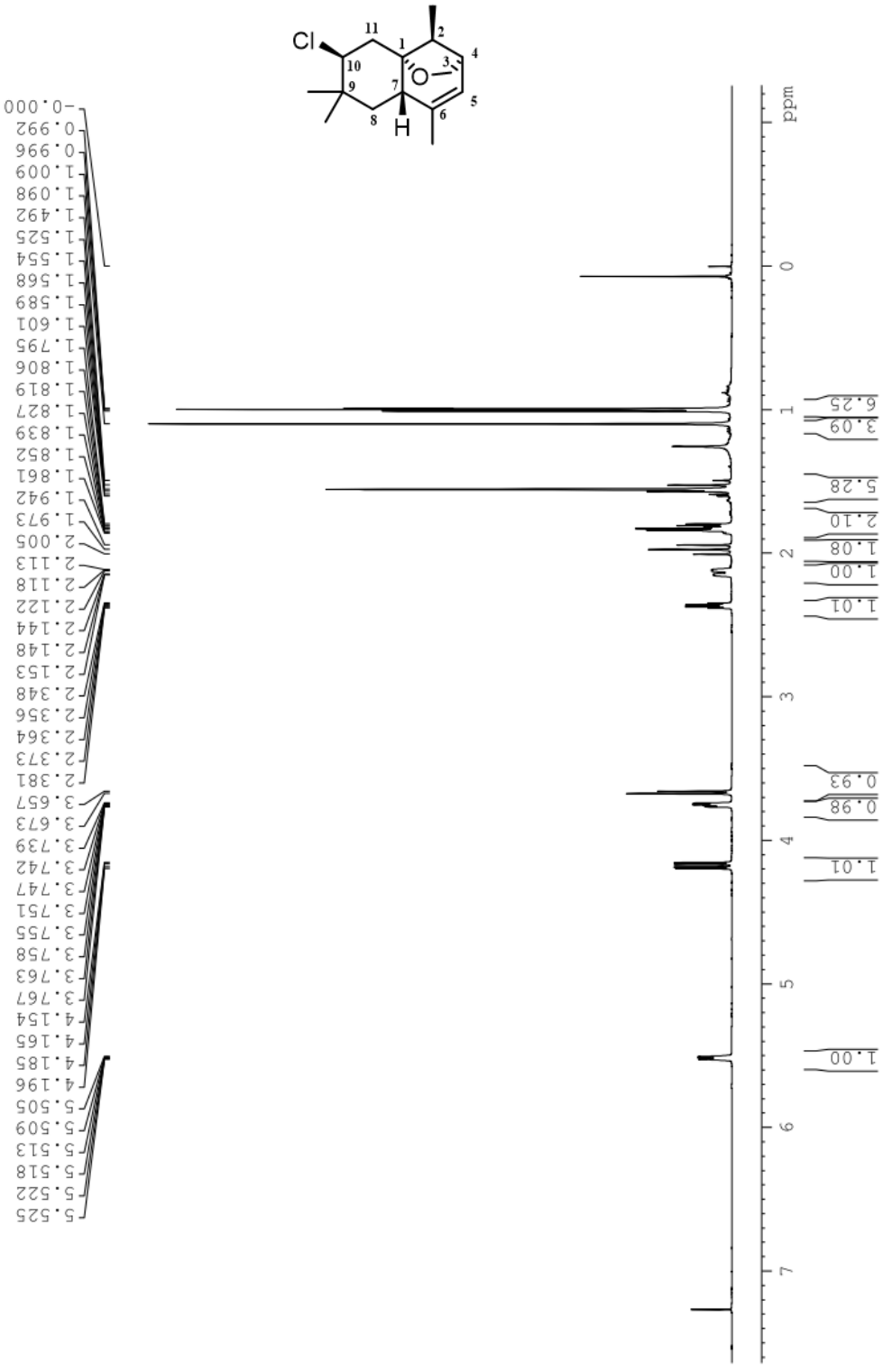


Figure S69. ^{1}H NMR spectrum of **13** ($CDCl_3$, 400 MHz).

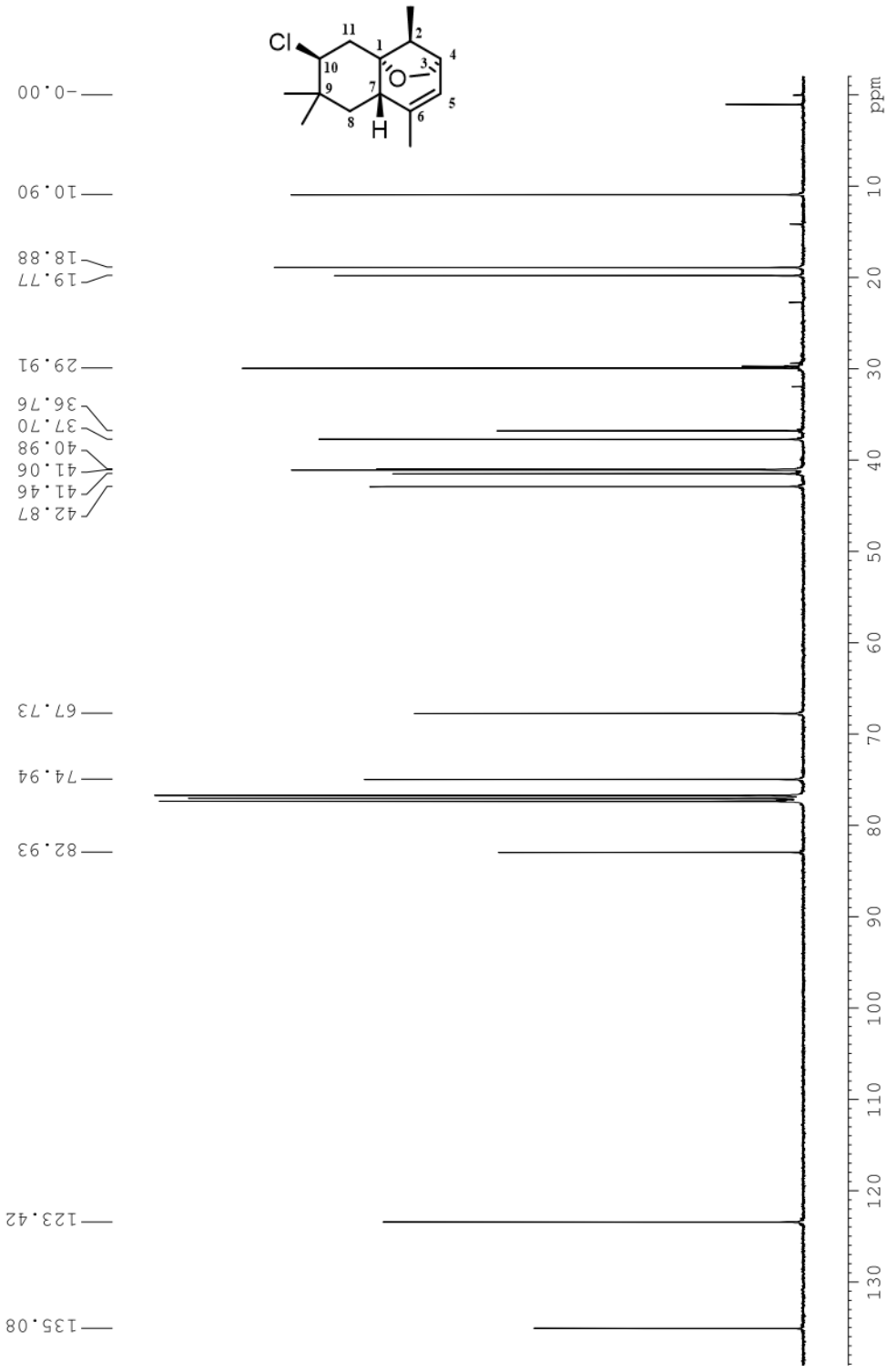


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of **13** ($CDCl_3$, 100 MHz).

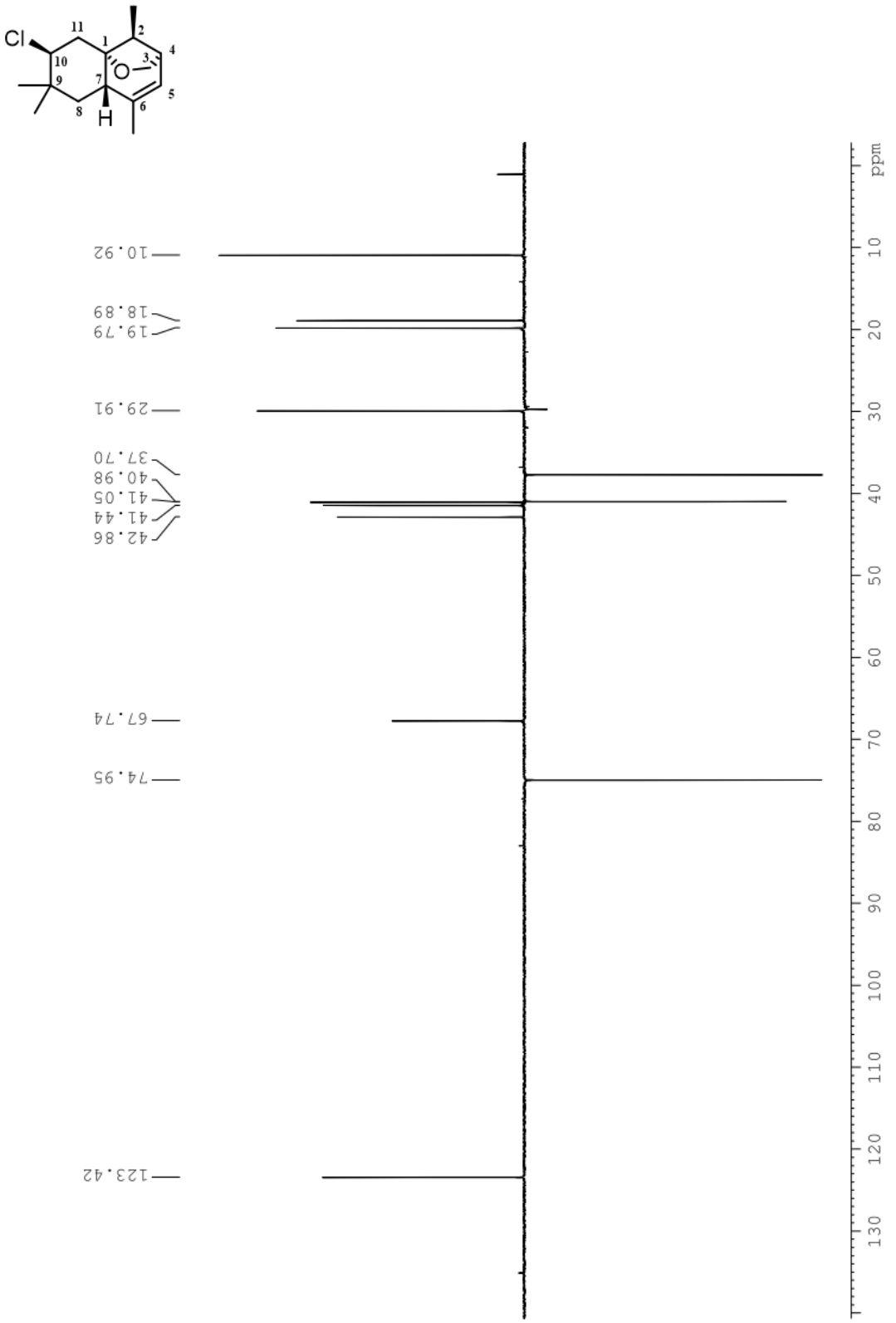


Figure S71. DEPT-135 spectrum of **13** ($CDCl_3$, 100 MHz).

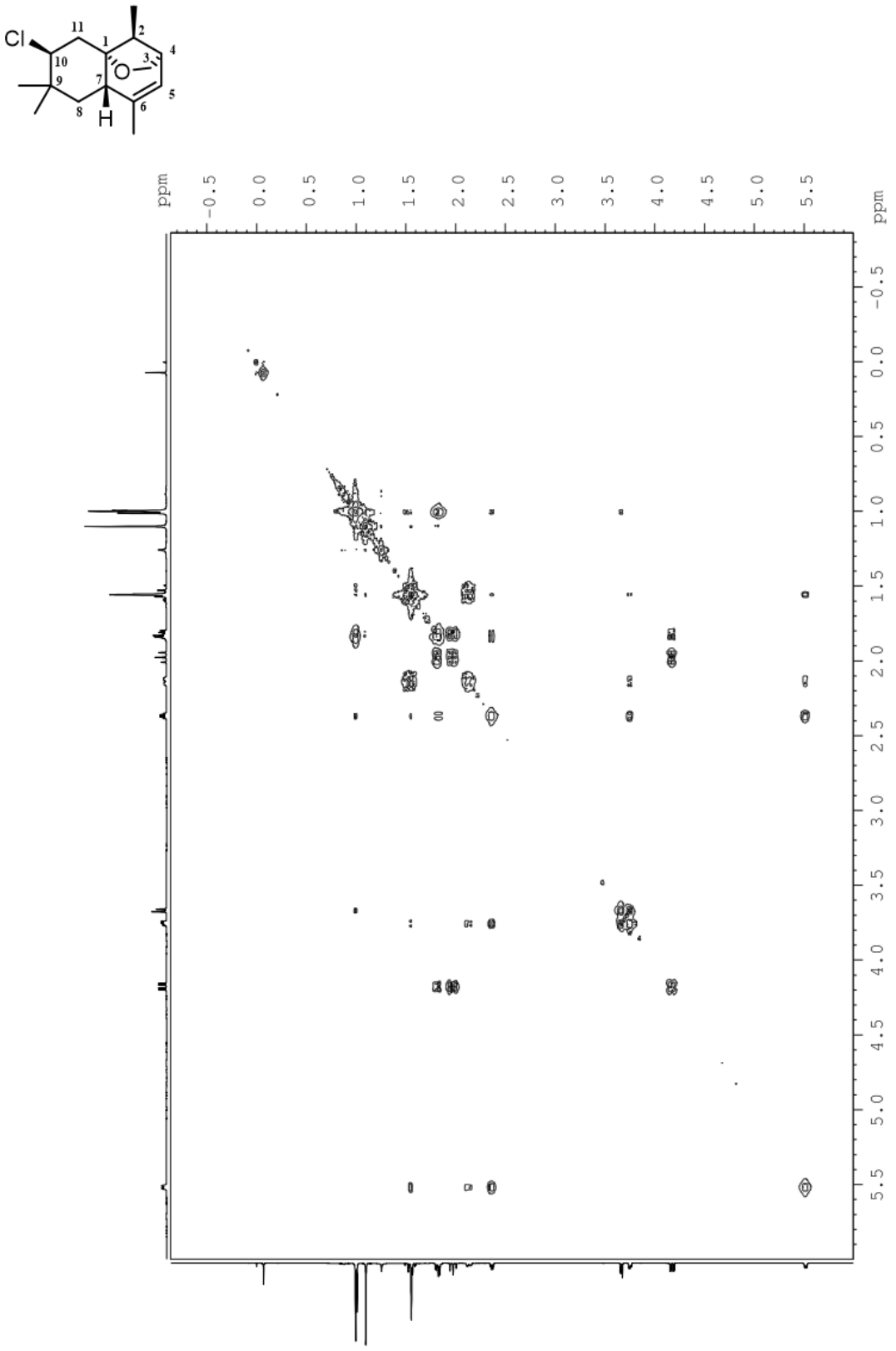
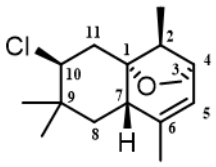


Figure S72. ^{1}H-^{1}H COSY of **13** ($CDCl_3$, 400 MHz).



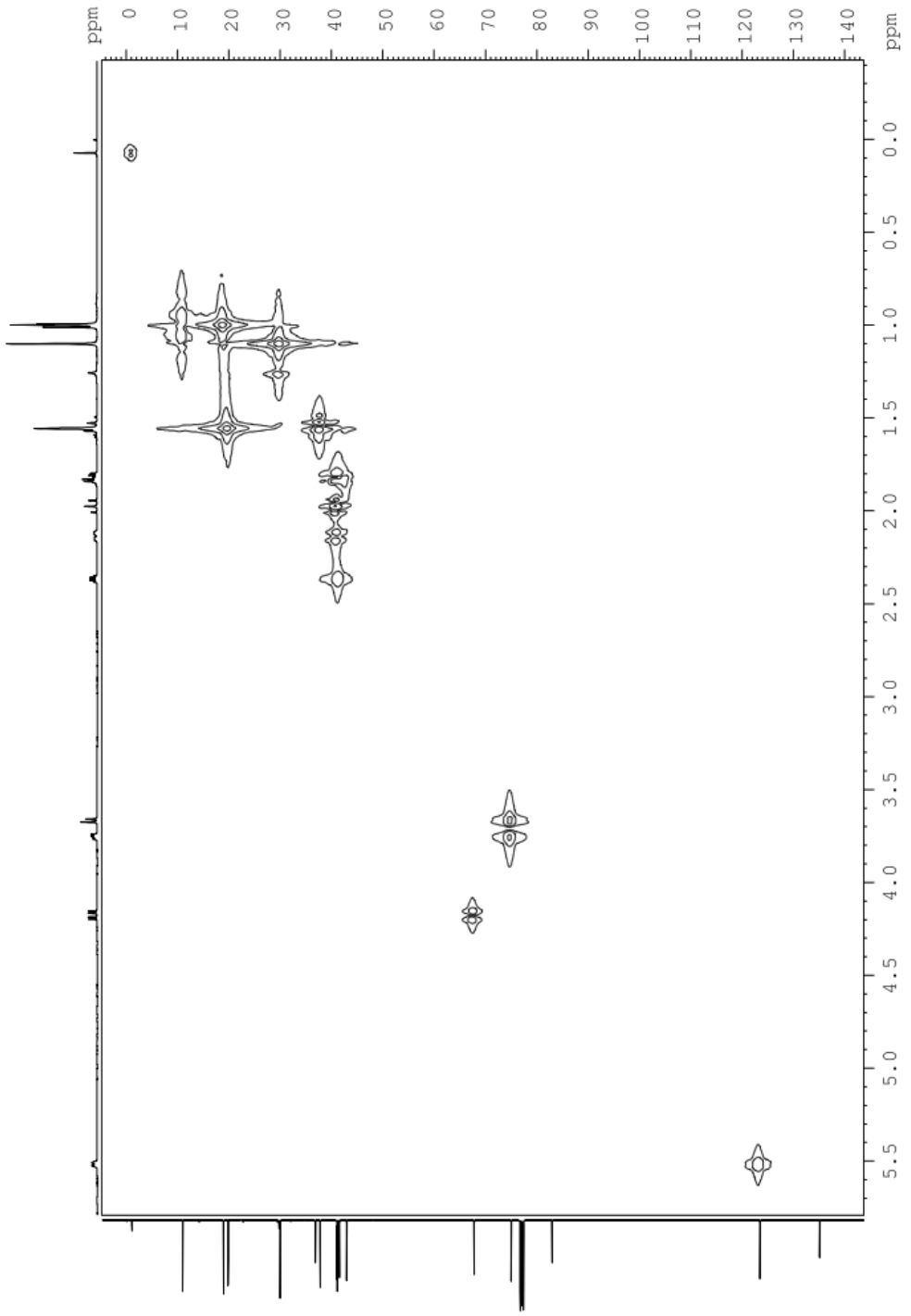


Figure S73. ^{1}H-^{13}C HMQC of **13** ($CDCl_3$, 400 MHz).

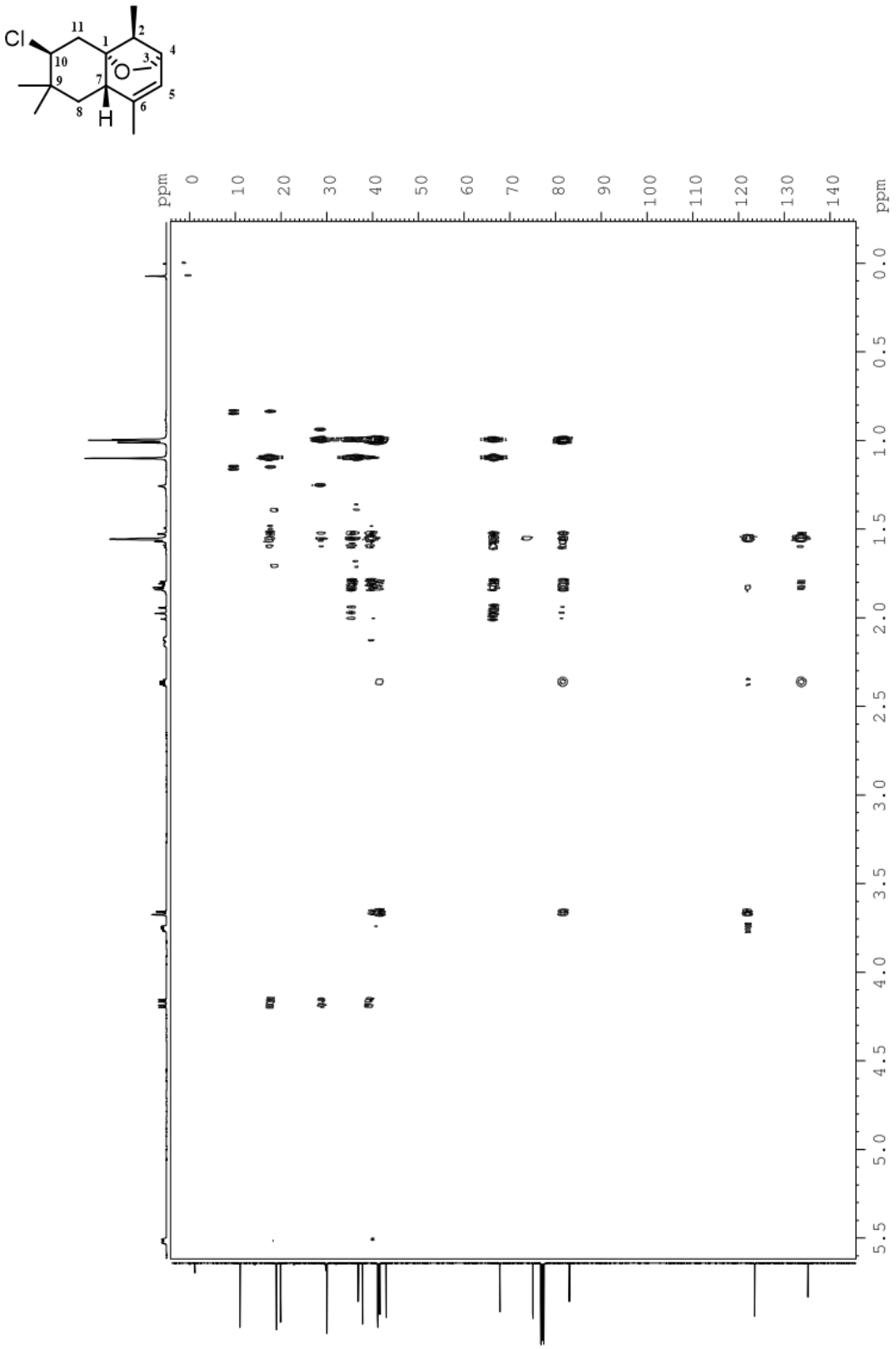


Figure S74. ^{1}H-^{13}C HMBC of **13** ($CDCl_3$, 400 MHz).

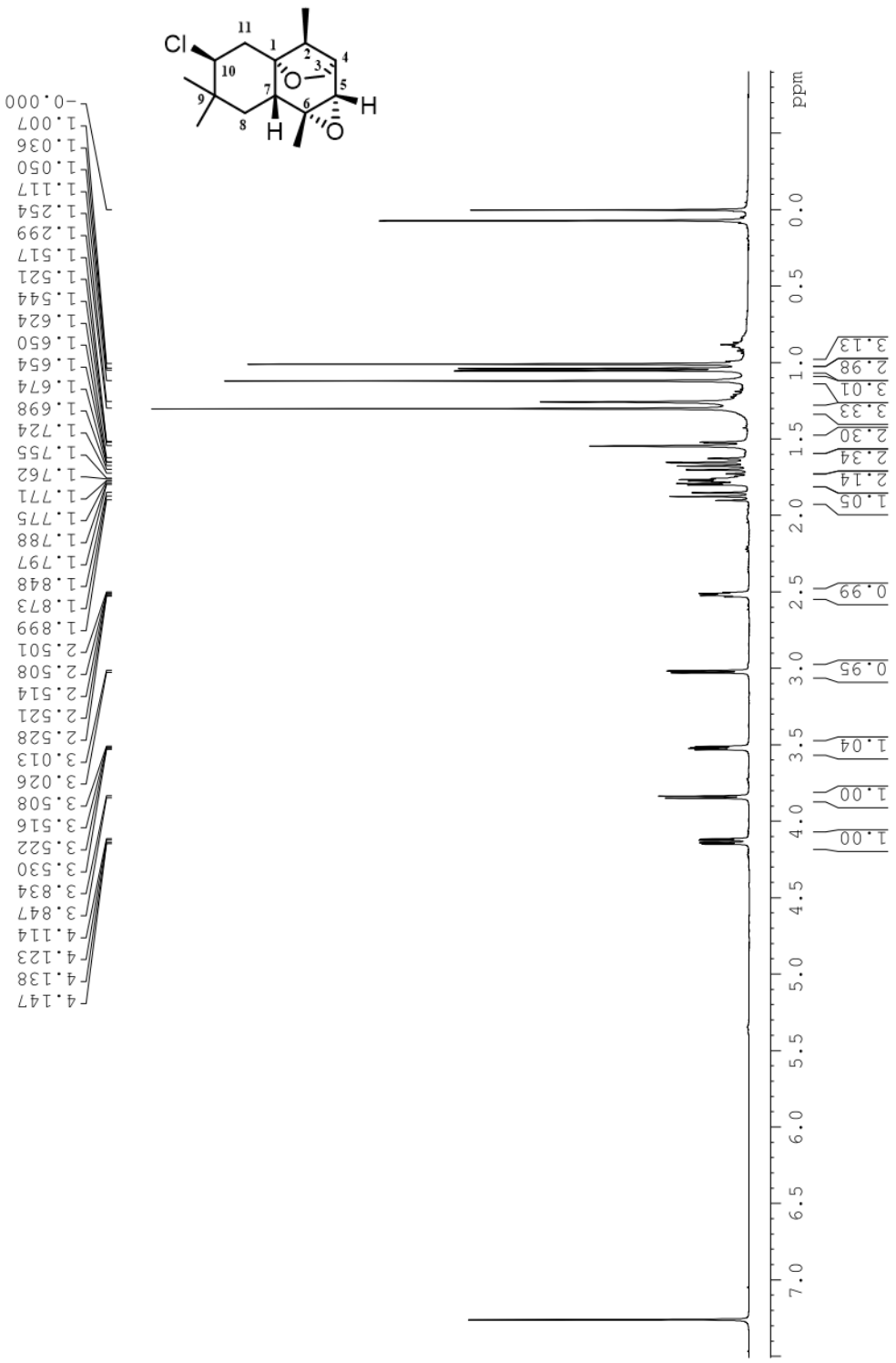


Figure S75. ^{1}H NMR spectrum of **14** ($CDCl_3$, 500 MHz).

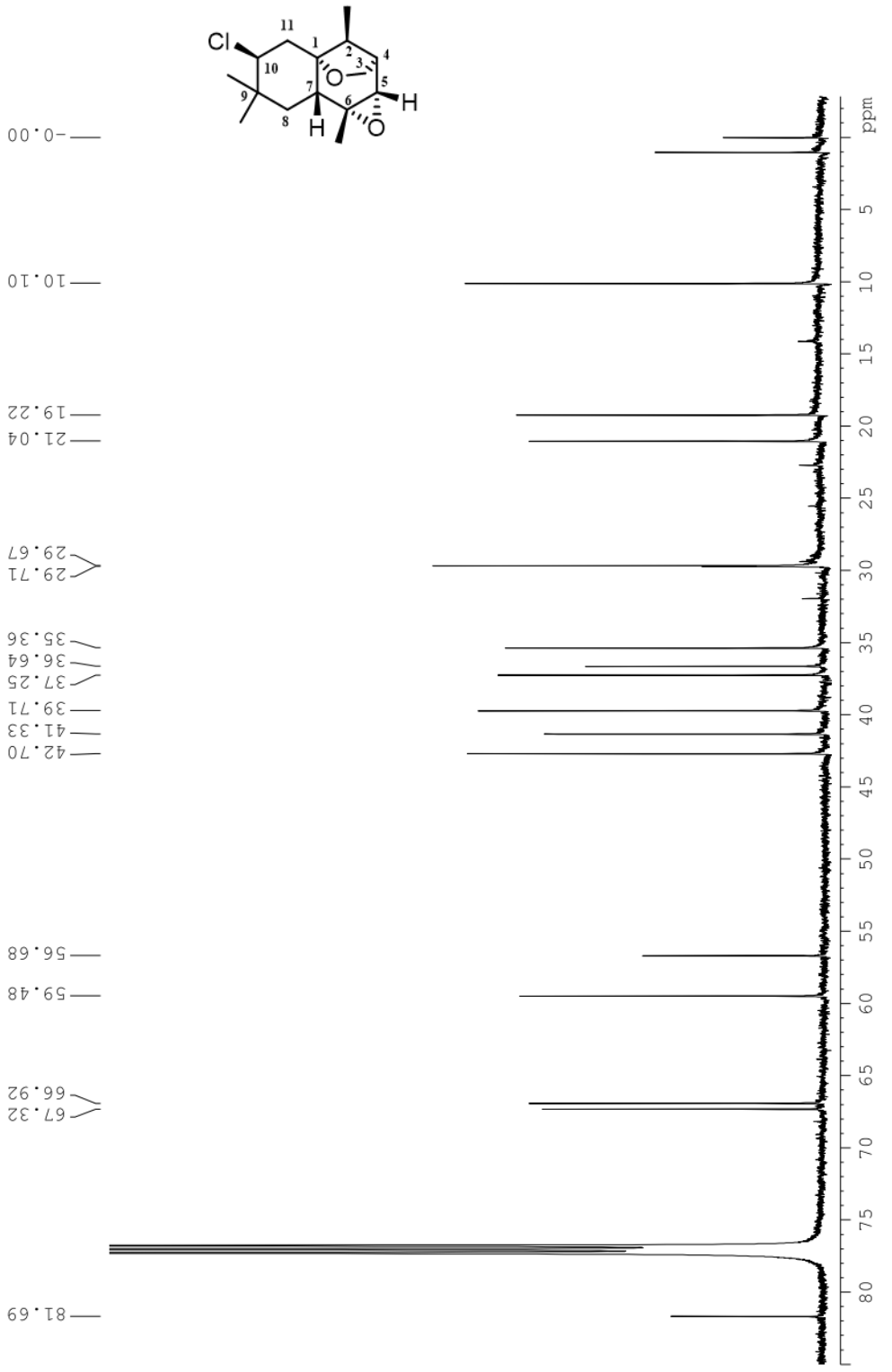


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **14** ($CDCl_3$, 125 MHz).

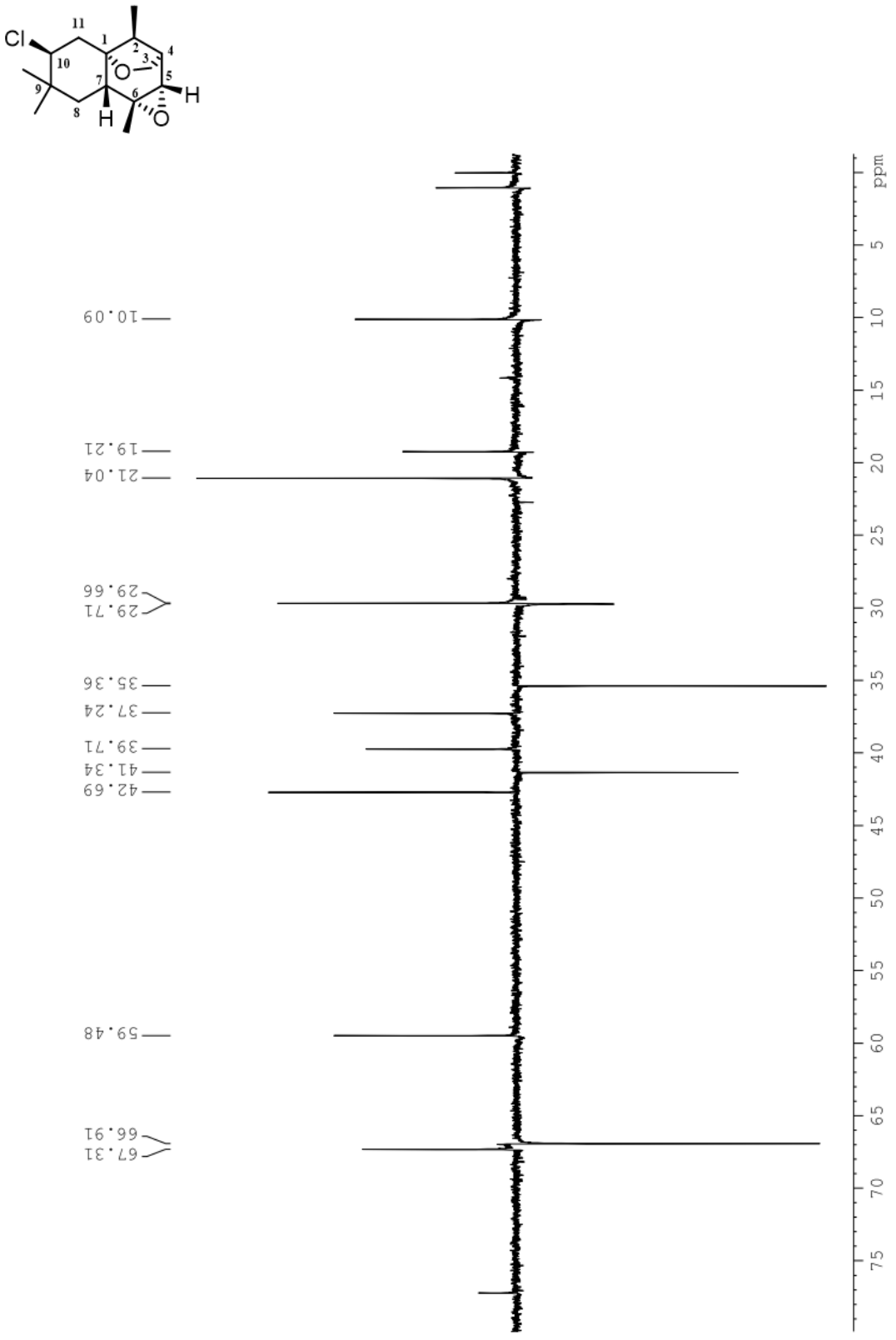


Figure S77. DEPT-135 spectrum of **14** ($CDCl_3$, 125 MHz).

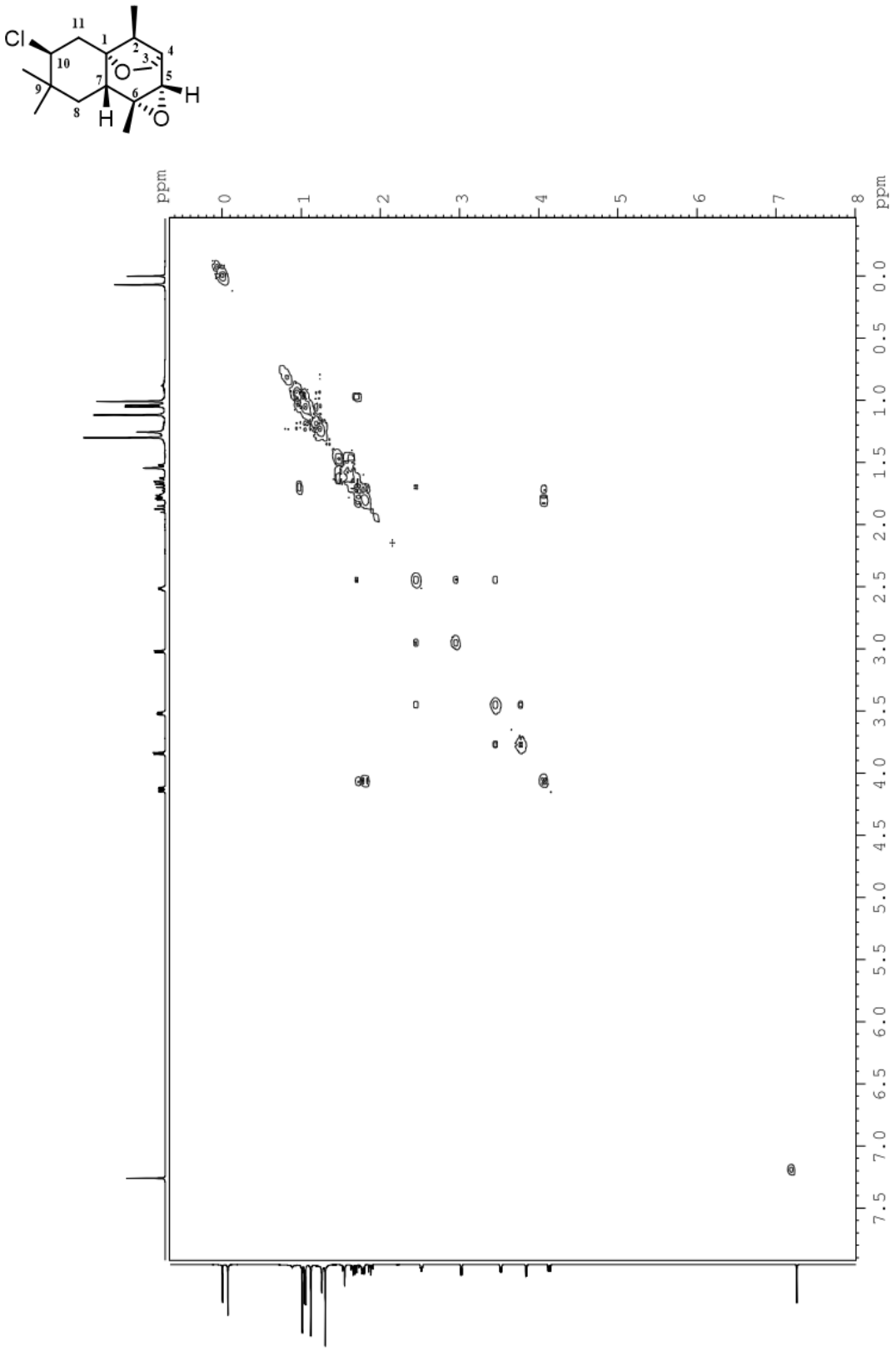


Figure S78. ^{1}H-^{1}H COSY of **14** ($CDCl_3$, 500 MHz).

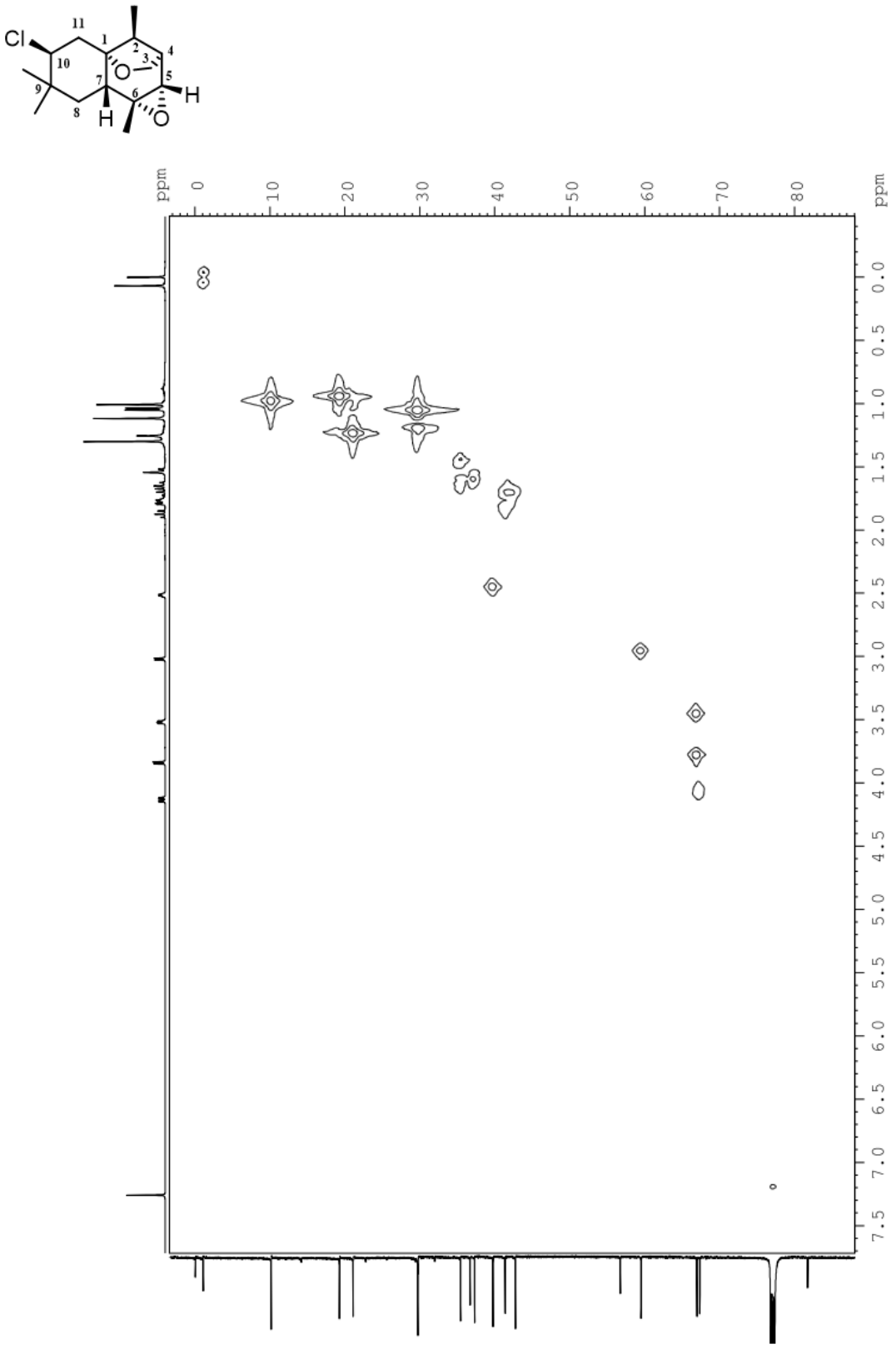


Figure S79. ^{1}H-^{13}C HMQC of **14** ($CDCl_3$, 500 MHz).

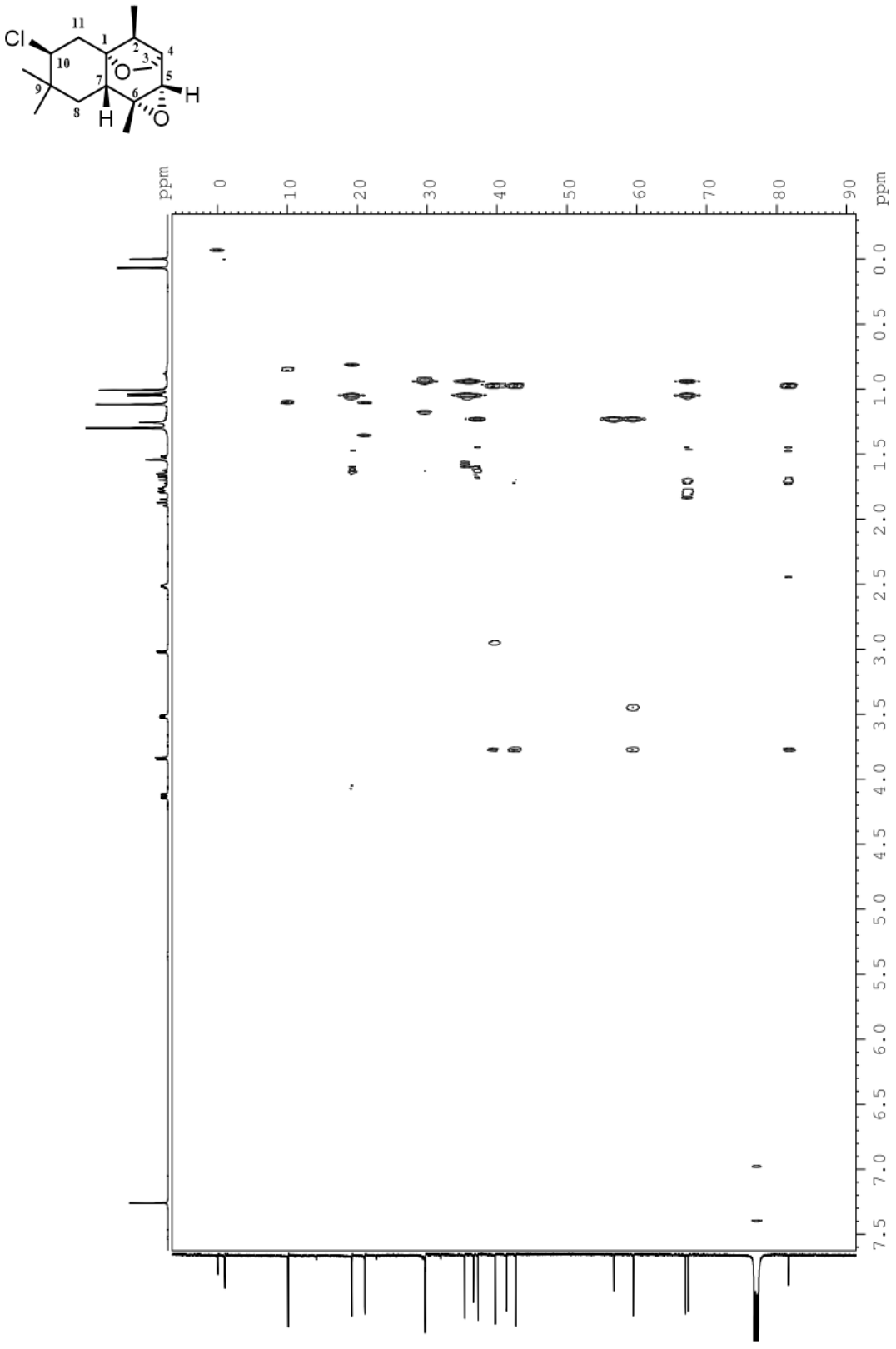


Figure S80. ^{1}H-^{13}C HMBC of **14** ($CDCl_3$, 500 MHz).

X-ray crystal structures of compounds

Data collection and structure solution

The intensity data were measured on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71075 Å). The structure was solved by direct methods (SIR97) and expanded using Fourier techniques (DIRDIF99). All calculations were performed using the Crystal Structure crystallographic software package. Compounds **5**, **6**, **8**, (2*RS*,3*RS*)-**11**, (2*RS*,3*SR*)-**11**, **12**, and **14** were obtained as racemates, and the following diagrams shows one configuration of the two.

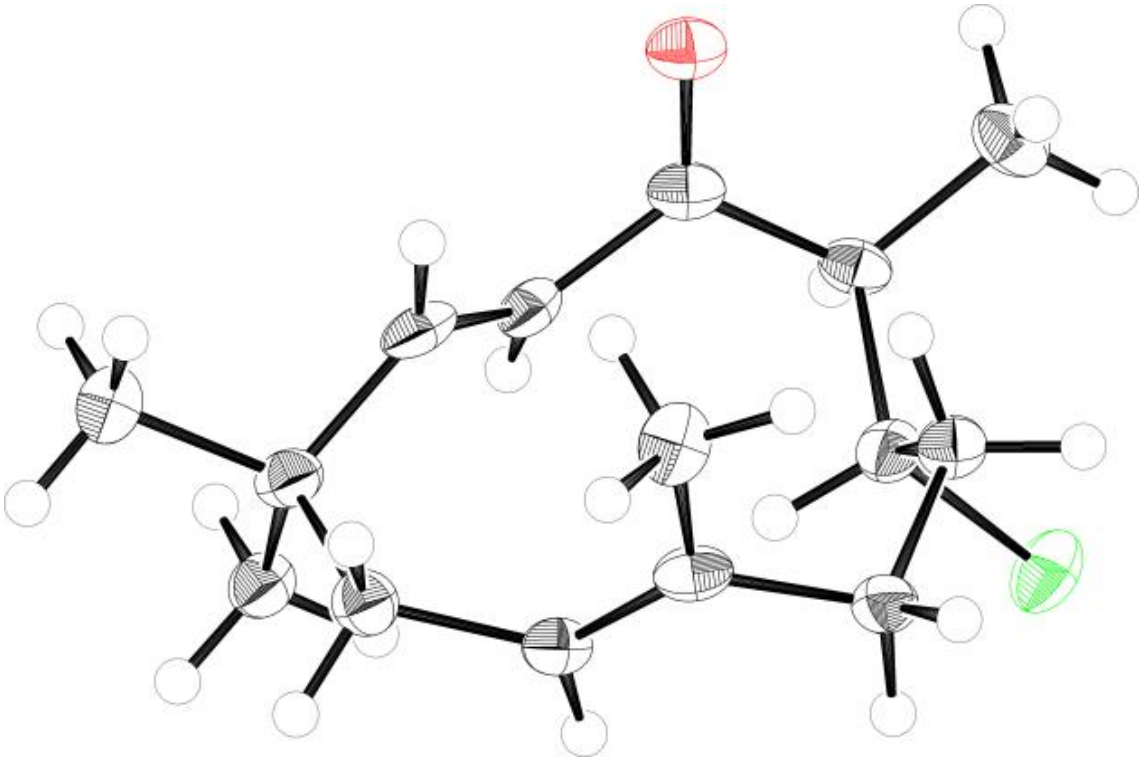


Figure S81. ORTEP diagram of **5**. The ellipsoid contour of probability level is 50%.

Table S9. Crystal data and structure refinement for compound **5**.

CCDC code	2067495	
Chemical formula	$C_{15}H_{23}ClO$	
Formula weight	254.80	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.085(3) Å	α = 79.174(15)°
	b = 10.810(5) Å	β = 85.596(11)°
	c = 19.320(7) Å	γ = 82.452(14)°
Volume	1438.5(10) $Å^3$	
Z	4	
Density (calculated)	1.176 g/cm^3	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	2.491 cm^{-1}	
F(000)	552	
Reflections collected	11704	
Independent reflections	5170 [R(int) = 0.1274]	
Theta range for data collection	3.04 to 27.50°	
Index ranges	$-8 \leq h \leq 8$, $-12 \leq k \leq 12$, $-23 \leq l \leq 20$	
Completeness to theta = 25.24°	99.2%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.990 and 0.416	
Final R indices [I>2sigma(I)]	$R1$ = 0.0839	
R indices (all data)	$R1$ = 0.1820, $wR2$ = 0.2127	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5170 / 0 / 308	
Goodness-of-fit on F^2	1.035	
Largest diff. peak and hole	0.38 and -0.57 $e/Å^{-3}$	

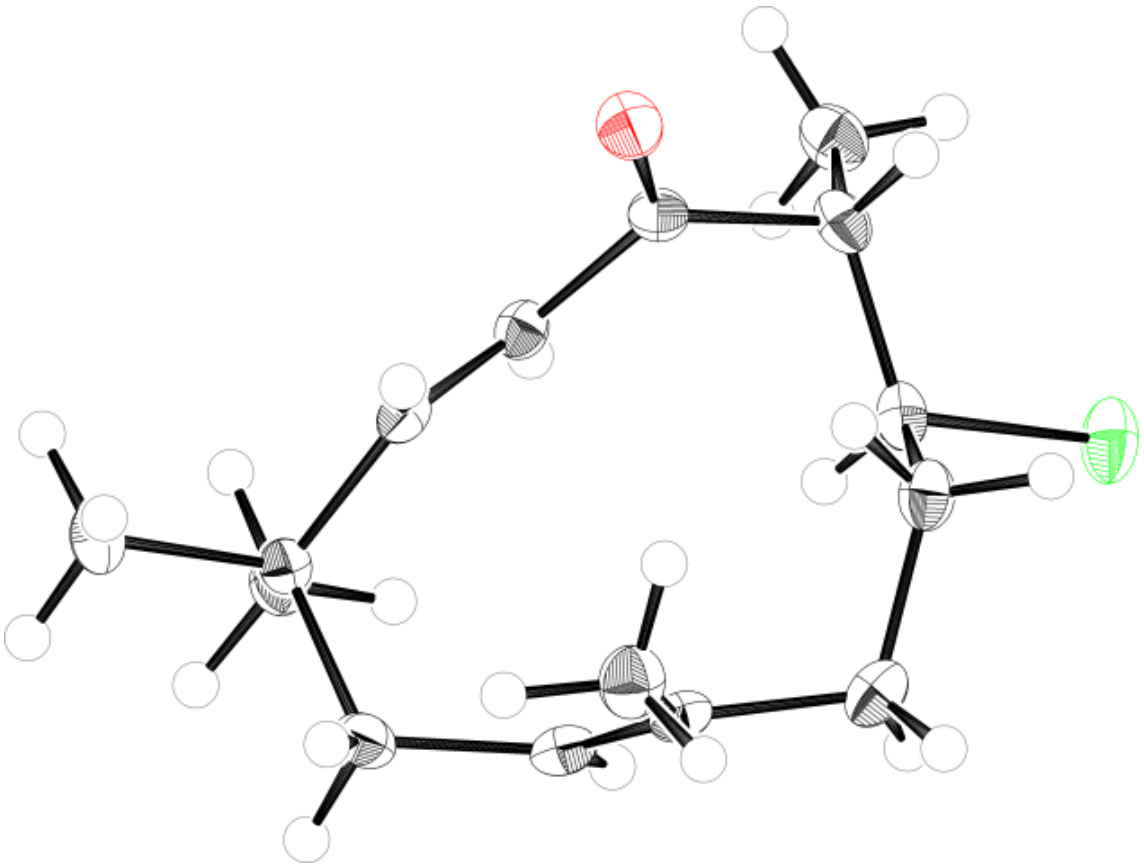


Figure S82. ORTEP diagram of **6**. The ellipsoid contour of probability level is 50%.

Table S10. Crystal data and structure refinement for compound **6**.

CCDC code	2067496	
Chemical formula	$C_{15}H_{23}ClO$	
Formula weight	254.80	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.702(4) Å	α = 90°
	b = 17.711(8) Å	β = 94.834(19)°
	c = 14.235(6) Å	γ = 90°
Volume	1432.5(12) $Å^3$	
Z	4	
Density (calculated)	1.181 g/cm^3	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	2.500 cm^{-1}	
F(000)	552	
Reflections collected	11353	
Independent reflections	2586 [R(int) = 0.0427]	
Theta range for data collection	3.10 to 27.52°	
Index ranges	$-6 \leq h \leq 6$, $-18 \leq k \leq 21$, $-17 \leq l \leq 17$	
Completeness to theta = 25.24°	99.7%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.988 and 0.631	
Final R indices [I>2sigma(I)]	$R1$ = 0.0408	
R indices (all data)	$R1$ = 0.0483, $wR2$ = 0.1136	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2586 / 0 / 246	
Goodness-of-fit on F^2	1.140	
Largest diff. peak and hole	0.34 and -0.21 $e/Å^3$	

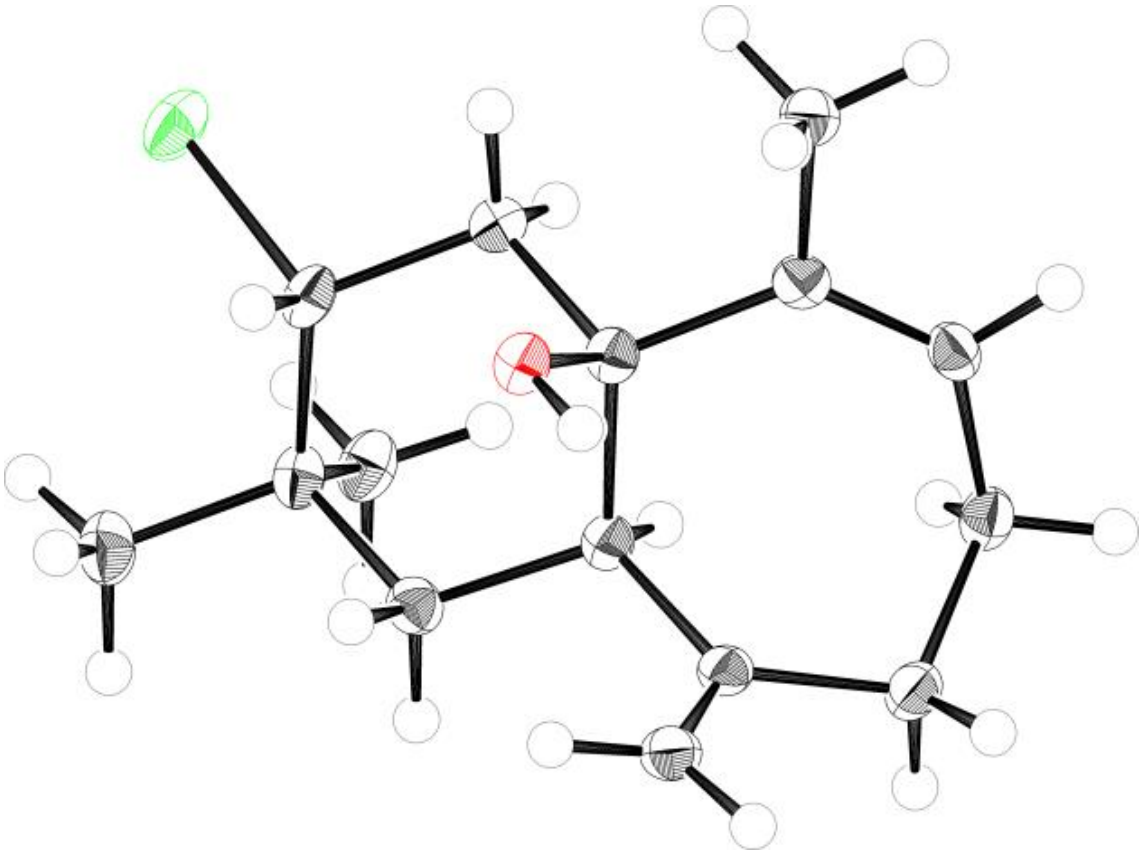


Figure S83. ORTEP diagram of **8**. The ellipsoid contour of probability level is 50%.

Table S11. Crystal data and structure refinement for compound **8**.

CCDC code	2067497	
Chemical formula	$C_{15}H_{23}ClO$	
Formula weight	254.80	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.985(4) Å	α = 90°
	b = 14.486(9) Å	β = 98.454(17)°
	c = 10.592(5) Å	γ = 90°
Volume	1363.5(12) $Å^3$	
Z	4	
Density (calculated)	1.241 g/cm^3	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	2.629 cm^{-1}	
F(000)	552	
Reflections collected	10714	
Independent reflections	2469 [R(int) = 0.0513]	
Theta range for data collection	3.12 to 27.52°	
Index ranges	$-10 \leq h \leq 10$, $-17 \leq k \leq 17$, $-12 \leq l \leq 12$	
Completeness to theta = 25.24°	99.8	
Absorption correction	Multi-scan	
Max. and min. transmission	0.964 and 0.636	
Final R indices [I>2sigma(I)]	$R1$ = 0.0402	
R indices (all data)	$R1$ = 0.0490, $wR2$ = 0.1071	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2469 / 0 / 246	
Goodness-of-fit on F^2	1.079	
Largest diff. peak and hole	0.45 and -0.25 $e/Å^3$	

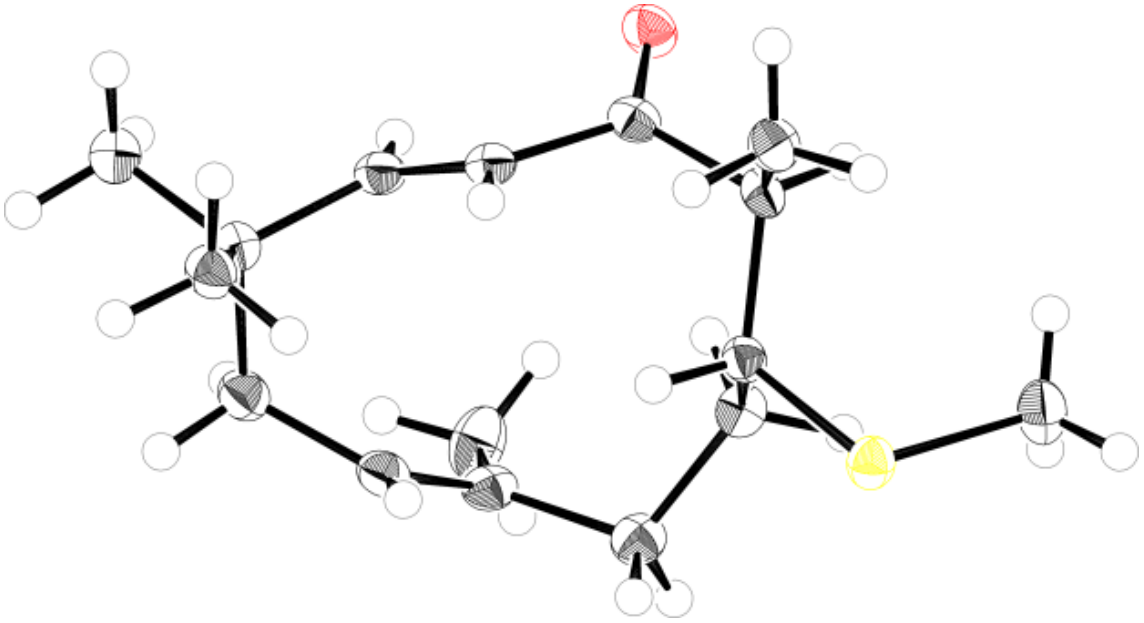


Figure S84. ORTEP diagram of (2*RS*,3*RS*)-**11**. The ellipsoid contour of probability level is 50%.

Table S12. Crystal data and structure refinement for (2*RS*,3*RS*)-**11**.

CCDC code	2067498	
Chemical formula	$C_{16}H_{26}OS$	
Formula weight	266.44	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.525(4) Å	α = 90°
	b = 9.518(4) Å	β = 98.810(15)°
	c = 14.178(6) Å	γ = 90°
Volume	1537.0(11) $Å^3$	
Z	4	
Density (calculated)	1.151 g/cm^3	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	1.989 cm^{-1}	
F(000)	584	
Reflections collected	12048	
Independent reflections	2782 [R(int) = 0.1074]	
Theta range for data collection	3.02 to 27.46°	
Index ranges	$-13 \leq h \leq 13$, $-11 \leq k \leq 11$, $-16 \leq l \leq 16$	
Completeness to theta = 25.24°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.988 and 0.529	
Final R indices [I>2sigma(I)]	$R1$ = 0.0522	
R indices (all data)	$R1$ = 0.0799, $wR2$ = 0.1193	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2782 / 0 / 267	
Goodness-of-fit on F^2	1.044	
Largest diff. peak and hole	0.32 and -0.27 $e/Å^3$	

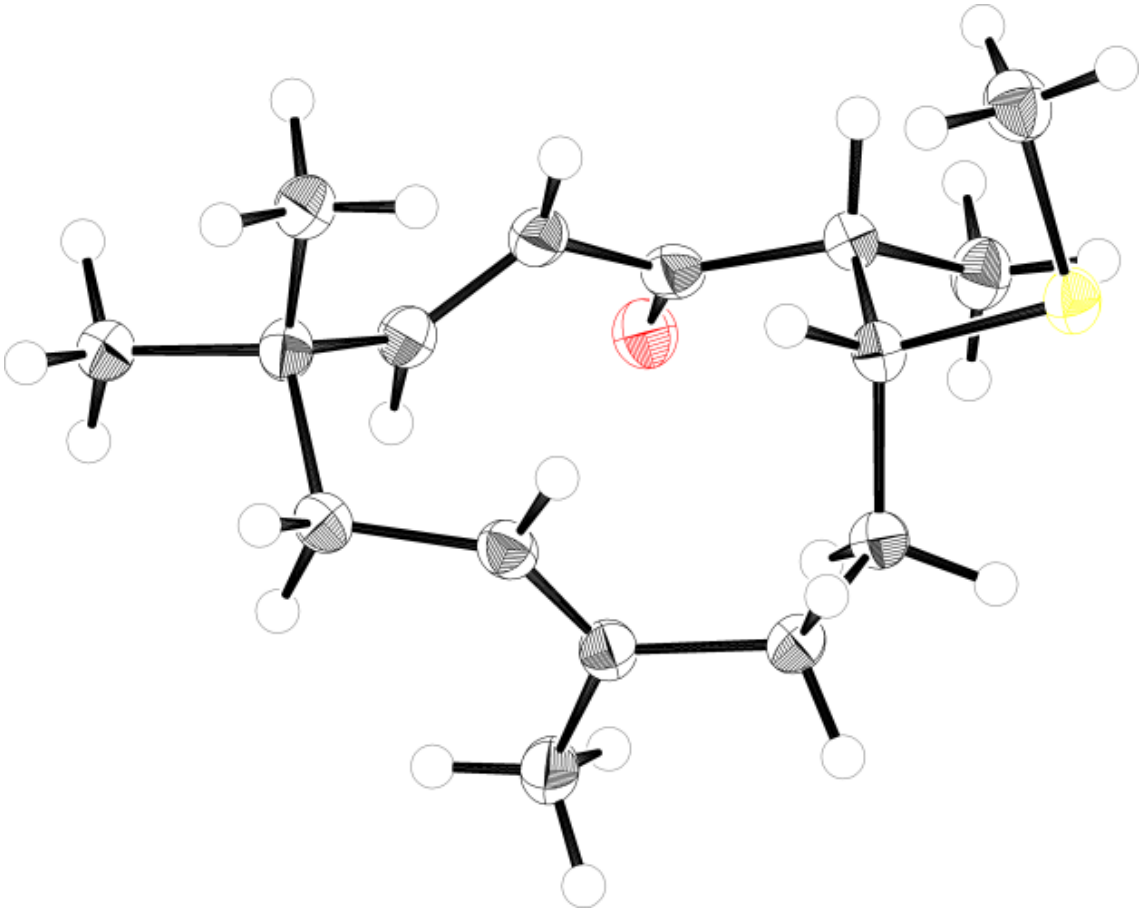


Figure S85. ORTEP diagram of (2*RS*,3*SR*)-**11**. The ellipsoid contour of probability level is 50%.

Table S13. Crystal data and structure refinement for (2*RS*,3*SR*)-**11**.

CCDC code	2067499	
Chemical formula	$C_{16}H_{26}OS$	
Formula weight	266.44	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.686(3) Å	α = 90°
	b = 26.359(13) Å	β = 93.343(17)°
	c = 10.269(5) Å	γ = 90°
Volume	1536.5(12) $Å^3$	
Z	4	
Density (calculated)	1.152 g/cm^3	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	1.990 cm^{-1}	
F(000)	584	
Reflections collected	11689	
Independent reflections	2782 [R(int) = 0.1662]	
Theta range for data collection	3.06 to 28.79°	
Index ranges	$-6 \leq h \leq 6$, $-31 \leq k \leq 31$, $-12 \leq l \leq 12$	
Completeness to theta = 25.24°	99.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.976 and 0.032	
Final R indices [I>2sigma(I)]	$R1$ = 0.0903	
R indices (all data)	$R1$ = 0.1212, $wR2$ = 0.1694	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2781 / 0 / 267	
Goodness-of-fit on F^2	1.082	
Largest diff. peak and hole	0.43 and -0.32 $e/Å^3$	
Flack parameter		

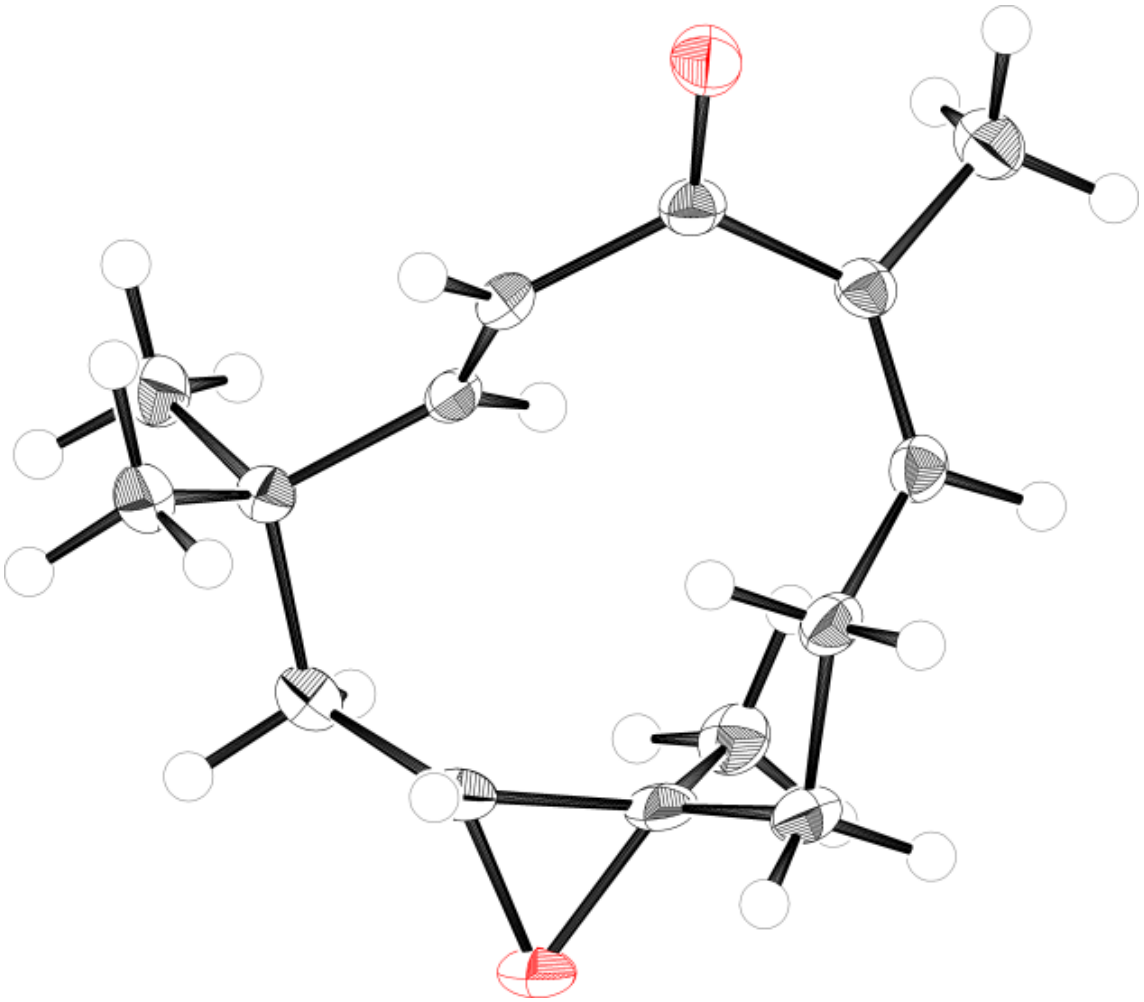


Figure S86. ORTEP diagram of **12**. The ellipsoid contour of probability level is 50%.

Table S14. Crystal data and structure refinement for **12**.

CCDC code	2067501	
Chemical formula	$C_{15}H_{22}O_2$	
Formula weight	234.34	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.183(4) Å	α = 90°
	b = 9.828(3) Å	β = 90°
	c = 16.544(5) Å	γ = 90°
Volume	1330.6(8) $Å^3$	
Z	4	
Density (calculated)	1.170 g/cm^3	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	0.754 cm^{-1}	
F(000)	512	
Reflections collected	11310	
Independent reflections	2536 [R(int) = 0.0560]	
Theta range for data collection	3.22 to 27.48°	
Index ranges	$-10 \leq h \leq 10$, $-12 \leq k \leq 12$, $-19 \leq l \leq 20$	
Completeness to theta = 25.24°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.992 and 0.627	
Final R indices [I>2sigma(I)]	$R1$ = 0.0370, $wR2$ = 0.0721	
R indices (all data)	$R1$ = 0.0457, $wR2$ = 0.0758	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2536 / 0 / 242	
Goodness-of-fit on F^2	1.033	
Largest diff. peak and hole	0.19 and -0.14 e/$Å^{-3}$	
Flack parameter	-0.1(13)	

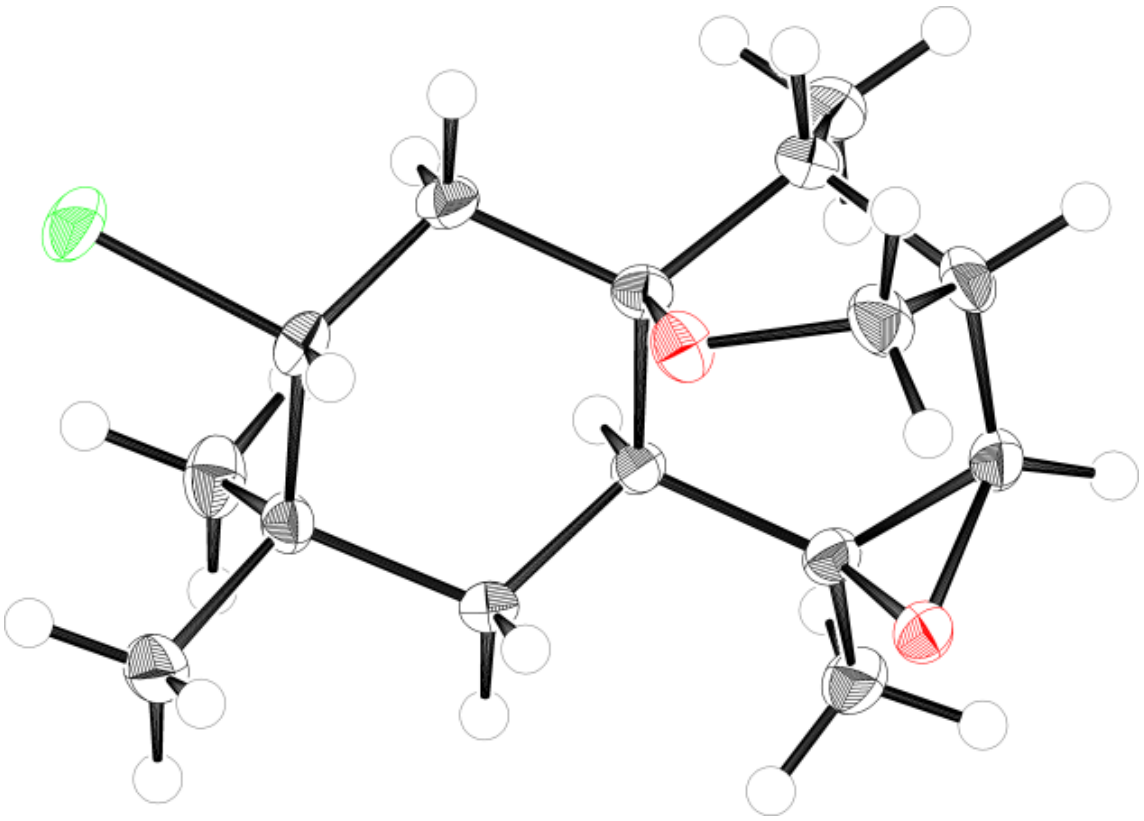


Figure S87. ORTEP diagram of **14**. The ellipsoid contour of probability level is 50%.

Table S15. Crystal data and structure refinement for **14**.

CCDC code	2067500	
Chemical formula	$C_{15}H_{23}ClO_2$	
Formula weight	270.80	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.336(2) Å	α =90°
	b = 12.665(4) Å	β =104.355(14)°
	c = 12.308(4) Å	γ = 90°
Volume	1409.9(8) $Å^3$	
Z	4	
Density (calculated)	1.276 g/cm^3	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Absorption coefficient	2.634 cm^{-1}	
F(000)	584	
Reflections collected	11200	
Independent reflections	2564 [R(int) = 0.0437]	
Theta range for data collection	3.15 to 27.45°	
Index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-14 \leq l \leq 14$	
Completeness to theta = 25.24°	99.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.974 and 0.723	
Final R indices [I>2sigma(I)]	$R1$ = 0.0387, $wR2$ = 0.0904	
R indices (all data)	$R1$ = 0.0466, $wR2$ = 0.0945	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2564 / 0 / 255	
Goodness-of-fit on F^2	1.046	
Largest diff. peak and hole	0.39 and -0.18 $e/Å^3$	

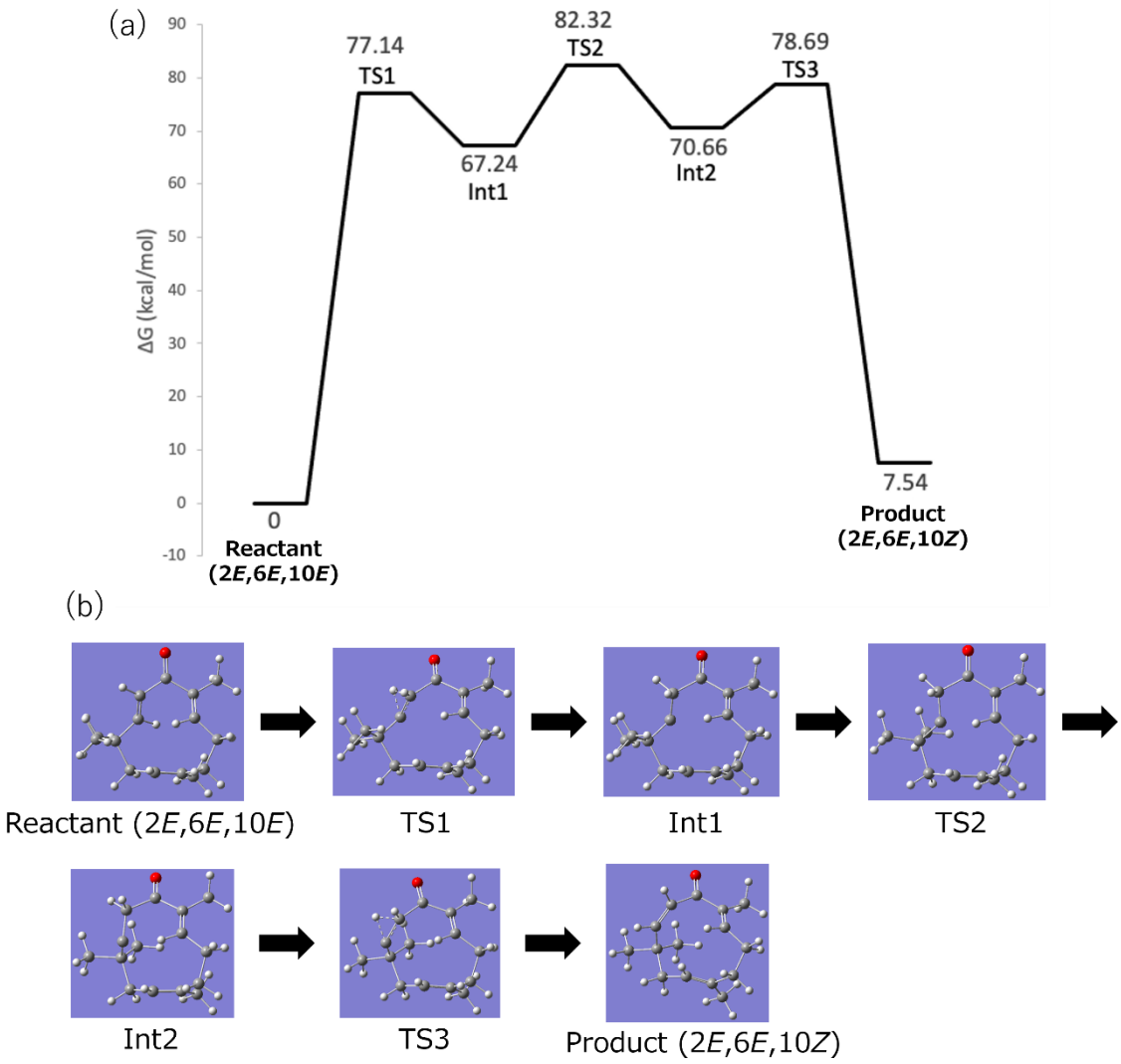


Figure S88. (a) Energy profile for the (2*E*,6*E*,10*E*) to (2*E*,6*E*,10*Z*)-isomer, derived from the B3LYP/6-31G(d) (T =308.15 K) calculation. (b) Optimized geometries along the reaction path for the (2*E*,6*E*,10*E*) to (2*E*,6*E*,10*Z*)-isomer at B3LYP/6-31G(d) level in gas phase.

Table S16. Cartesian coordinates and Gibbs free energies of (2*E*,6*E*,10*E*)-, (2*E*,6*E*,10*Z*)-, (2*Z*,6*E*,10*E*)-, (2*Z*,6*Z*,10*E*)-, and (2*Z*,6*E*,10*Z*)-zerumbone at the B3LYP/6-31G(d) level at 308.15 K in Gas phase (Figure 6).

(2*E*,6*E*,10*E*)-zerumbone

Atom	coordinates (Å) X	Y	Z
C	1.29442	-2.10051	-0.13654
O	1.80836	-3.21153	-0.07238
C	2.10733	-0.84147	0.03893
C	-0.17278	-1.92588	-0.38461
H	-0.62736	-2.6277	-1.08088
C	1.7663	0.23483	-0.69611
H	0.94374	0.09912	-1.39177
C	-0.87954	-0.97999	0.25441
H	-0.34166	-0.3856	0.98993
C	3.28348	-0.94181	0.97436
H	3.89563	-0.03607	0.97235
H	3.91014	-1.78944	0.6753
H	2.96197	-1.14334	2.00453
C	2.27222	1.65058	-0.64874
H	3.0216	1.83375	-1.43312
H	2.76845	1.85982	0.30562
C	-2.31983	-0.54664	0.06901
C	1.08282	2.63948	-0.87765
H	1.43838	3.66251	-0.69344
H	0.79202	2.58679	-1.93396
C	-2.33634	1.03005	0.18264
H	-2.31957	1.29224	1.24572
H	-3.30015	1.38313	-0.21053
C	-0.1182	2.31098	-0.00707
C	-1.1868	1.68842	-0.53893
H	-1.18235	1.53936	-1.62009
C	-3.19379	-1.12416	1.20568
H	-3.25709	-2.21545	1.13259
H	-4.21164	-0.71782	1.15347
H	-2.78212	-0.8764	2.191
C	-2.88818	-0.99433	-1.28834
H	-3.92431	-0.65374	-1.3992
H	-2.88963	-2.08638	-1.37817
H	-2.30592	-0.59208	-2.12452
C	0.05423	2.63074	1.45864
H	-0.84097	2.43374	2.05277
H	0.31254	3.69042	1.58855
H	0.87943	2.05364	1.89866

Sum of electronic and thermal Free Energies
= -659.724081 a.u.

(2*E*,6*E*,10*Z*)-zerumbone

Atom	coordinates (Å) X	Y	Z
C	-0.0176	1.90391	-0.1512
O	0.38354	2.55301	0.81132
C	-1.44698	1.48714	-0.22895
C	0.9499	1.46372	-1.22011
H	0.84536	2.00556	-2.16176
C	-1.77284	0.51253	-1.10357
H	-1.02033	0.25688	-1.84752
C	1.92506	0.5475	-1.13818
H	2.55014	0.45668	-2.02825
C	-2.33594	2.03097	0.85985
H	-3.37148	1.7001	0.74754
H	-1.97526	1.74045	1.85282
H	-2.32285	3.12671	0.8416
C	-2.89659	-0.47825	-1.02242
H	-3.60466	-0.21944	-0.22995
H	-3.46335	-0.5326	-1.96143
C	2.36263	-0.38033	-0.0001
C	-2.26291	-1.89491	-0.74059
H	-1.81893	-2.26433	-1.67276
H	-3.0679	-2.58882	-0.46523
C	1.19784	-1.02131	0.81773
H	1.6517	-1.78676	1.46543
H	0.78458	-0.26688	1.49808
C	-1.19345	-1.78858	0.33061
C	0.08387	-1.5913	-0.03277
H	0.32121	-1.71054	-1.09001
C	3.21395	-1.5134	-0.6164
H	4.06106	-1.10627	-1.18151
H	3.61675	-2.16235	0.16963
H	2.62787	-2.13987	-1.29934
C	3.24713	0.4409	0.96981
H	3.60593	-0.19185	1.79204
H	4.12384	0.84684	0.45159
H	2.6817	1.27984	1.38561
C	-1.68687	-1.69184	1.75242
H	-0.8801	-1.51025	2.46713
H	-2.43014	-0.89191	1.87274
H	-2.18654	-2.62567	2.0463

Sum of electronic and thermal Free Energies
= -659.712062 a.u.

(2*Z*,6*E*,10*E*)-zerumbone

Atom	coordinates (Å) X	Y	Z
C	1.62313	-1.60621	-0.36749
O	2.31002	-2.518	-0.817
C	2.29985	-0.47264	0.37771
C	0.15065	-1.62065	-0.54032
H	-0.1958	-2.25135	-1.35575
C	2.27395	0.80924	-0.03141
H	2.88278	1.5168	0.53759
C	-0.70032	-0.96085	0.2608
H	-0.27438	-0.39965	1.09164
C	3.16921	-0.93004	1.52652
H	3.7121	-0.09274	1.97605
H	2.57618	-1.41732	2.31215
H	3.89336	-1.67153	1.17057
C	1.6014	1.40137	-1.24447
H	2.39069	1.75257	-1.92717
H	1.03886	0.63523	-1.78589
C	-2.2063	-0.83944	0.13556
C	0.65724	2.60555	-0.96078
H	0.28332	2.96695	-1.92696
H	1.23582	3.42802	-0.51961

C	-2.53722	0.70374	0.20625
H	-3.55461	0.85235	-0.18038
H	-2.5541	1.0047	1.25867
C	-0.49899	2.21776	-0.05402
C	-1.52257	1.50997	-0.55969
H	-1.52766	1.35032	-1.63981
C	-2.7366	-1.43592	-1.17867
H	-2.51917	-2.50768	-1.24694
H	-3.82449	-1.31513	-1.23498
H	-2.29659	-0.9485	-2.05542
C	-2.88439	-1.54894	1.32892
H	-3.96563	-1.36395	1.31966
H	-2.72397	-2.63206	1.28526
H	-2.48997	-1.18734	2.28586
C	-0.32155	2.56743	1.40324
H	-1.17043	2.27833	2.02779
H	0.57945	2.09259	1.8149
H	-0.18073	3.65116	1.51582

Sum of electronic and thermal Free Energies
= -659.724964

(2*Z*,6*Z*,10*E*)-zerumbone

Atom	coordinates (Å)		
	X	Y	Z
C	-2.19317	-0.62804	0.78356
O	-3.03228	-0.99711	1.59934
C	-2.59751	0.31621	-0.32623
C	-0.79861	-1.13248	0.87296
H	-0.52663	-1.52395	1.8505
C	-1.94608	1.46309	-0.59563
H	-2.36394	2.09765	-1.38033
C	0.03739	-1.18809	-0.17464
H	-0.34025	-0.83106	-1.13288
C	-3.88938	-0.05575	-1.01497
H	-4.18863	0.70627	-1.74109
H	-4.68552	-0.17208	-0.27166
H	-3.80361	-1.01692	-1.53903
C	-0.72582	2.018	0.09166
H	-0.51043	1.44844	0.99763
H	-0.94615	3.04434	0.41465
C	1.4643	-1.68112	-0.22158
C	0.55156	2.03221	-0.81319
H	0.45983	1.25748	-1.57801
H	0.60096	2.99017	-1.34961
C	2.34072	-0.54104	-0.85482
H	1.90661	-0.28723	-1.83028
H	3.32596	-0.97736	-1.06871
C	1.81549	1.83001	-0.00462
C	2.54619	0.70162	-0.01948
H	3.41107	0.66811	0.64396
C	1.51685	-2.90016	-1.17362
H	0.90713	-3.72456	-0.78788
H	2.54766	-3.25864	-1.28097
H	1.1441	-2.64435	-2.17284
C	2.00667	-2.08021	1.15821
H	3.05198	-2.40103	1.07771
H	1.43571	-2.91373	1.58251
H	1.96307	-1.24364	1.86286
C	2.20154	2.98801	0.88553
H	3.10768	2.77536	1.46138
H	1.40093	3.23419	1.5963
H	2.37995	3.89592	0.29211

Sum of electronic and thermal Free Energies
= -659.729475 a.u.

(2*Z*,6*E*,10*Z*)-zerumbone

Atom	coordinates (Å)		
	X	Y	Z
C	1.6552	-0.89773	0.82092
O	2.29248	-1.90182	1.1202
C	2.23076	0.04514	-0.19593
C	0.33467	-0.68076	1.51621
H	0.4591	-0.36907	2.55449
C	1.9692	1.36348	-0.32356
H	2.51678	1.86666	-1.12432
C	-0.907	-0.97784	1.10967
H	-1.69051	-0.82441	1.85472
C	3.2816	-0.60657	-1.07185
H	3.67305	0.09836	-1.81124
H	4.11185	-0.97656	-0.46155
H	2.87648	-1.47854	-1.59879
C	1.11333	2.31725	0.46195
H	0.7283	1.86583	1.37994
H	1.76371	3.15113	0.76434
C	-1.45369	-1.4806	-0.21743
C	-0.07339	2.89458	-0.37742
H	0.25132	3.02624	-1.41706
H	-0.32577	3.89096	0.00642
C	-2.23154	-0.29927	-0.91563
H	-2.60344	-0.67492	-1.87892
H	-3.11511	-0.06431	-0.31158
C	-1.26779	1.96917	-0.28677
C	-1.3647	0.91222	-1.10789
H	-0.63368	0.84028	-1.91337
C	-0.37911	-2.04023	-1.16556
H	0.18872	-2.84409	-0.68606
H	-0.85395	-2.45094	-2.06494
H	0.3282	-1.27197	-1.48808
C	-2.46872	-2.60603	0.08646
H	-2.95116	-2.94819	-0.83713
H	-1.9732	-3.46706	0.54921
H	-3.25563	-2.26269	0.7691
C	-2.19462	2.26004	0.86879
H	-3.02812	1.55849	0.94627
H	-1.65552	2.24244	1.82627
H	-2.61644	3.26981	0.76893

Sum of electronic and thermal Free Energies
= -659.714591 a.u.

Table S16. Cartesian coordinates and Gibbs free energies of TS1, Int1, TS2, Int2, TS3, TS4, Int4, TS5, Int5, TS6, Int6, and TS7 at the B3LYP/6-31G(d) level at 308.15 K in Gas phase (Figure 7).

TS1

Atom	coordinates (Å)		
	X	Y	Z
C	0.95768	-2.24693	-0.141

O	1.40771	-3.37466	-0.23322
C	1.88903	-1.05093	0.16139
C	-0.47498	-1.88822	-0.40706
H	-0.92742	-2.34795	-1.28226
C	1.85162	-0.07944	-0.85479
H	1.02279	-0.16557	0.21171
C	-1.12706	-0.9953	0.35091
H	-0.62445	-0.63243	1.25169
C	2.87569	-1.25888	1.29922
H	3.52637	-0.39344	1.44597
H	3.49362	-2.12544	1.04068
H	2.36963	-1.49481	2.24213
C	2.57723	1.22564	-0.69748
H	3.35145	1.27055	-1.47642
H	3.09408	1.40206	0.26501
C	-2.42036	-0.25915	0.08058
C	1.54932	2.37726	-0.97174
H	2.04978	3.34417	-0.82281
H	1.2548	2.31257	-2.02348
C	-2.05768	1.27791	0.17734
H	-1.98448	1.5442	1.23785
H	-2.91635	1.83843	-0.22243
C	0.31124	2.27604	-0.08861
C	-0.79093	1.65552	-0.55466
H	-0.74849	1.31597	-1.58849
C	-3.46392	-0.58057	1.17189
H	-3.78299	-1.62706	1.11138
H	-4.35165	0.05322	1.05646
H	-3.05801	-0.40996	2.1762
C	-3.00324	-0.59245	-1.30169
H	-3.92531	-0.02477	-1.47161
H	-3.25173	-1.65729	-1.37833
H	-2.30329	-0.35339	-2.10896
C	0.4697	2.83344	1.3059
H	-0.39495	2.65074	1.94918
H	0.62923	3.91998	1.26738
H	1.35562	2.41377	1.80379

Sum of electronic and thermal Free Energies
= -659.596401 a.u.
Harmonic frequencies = 867.3589*i* (cm^{-1})

Int1

Atom	coordinates (Å)		
	X	Y	Z

C	1.62727	-1.8341	0.07541
O	2.32998	-2.81523	-0.10519
C	2.21922	-0.45535	0.44686
C	0.16301	-1.89113	-0.17385
H	-0.13266	-2.66335	-0.87994
C	1.90231	0.51959	-0.63442
H	1.89477	-0.15874	1.46347
C	-0.73793	-1.06724	0.38242
H	-0.39528	-0.3571	1.13402
C	3.77377	-0.51178	0.43932
H	4.19796	0.35576	0.95162
H	4.15711	-0.54955	-0.58502
H	4.08491	-1.43232	0.93955
C	1.87869	1.94464	-0.20477
H	2.80725	2.35305	-0.64573
H	1.92798	2.14126	0.88446
C	-2.21355	-0.94823	0.05094
C	0.68529	2.71774	-0.8438
H	0.85601	3.79513	-0.71836
H	0.67376	2.49734	-1.91547
C	-2.5226	0.59086	-0.11999
H	-2.75432	1.00887	0.86469
H	-3.43839	0.68523	-0.72054
C	-0.62368	2.30319	-0.19314
C	-1.37367	1.33629	-0.74916
H	-1.048	0.95391	-1.71711
C	-3.05702	-1.49601	1.22431
H	-2.91656	-2.57686	1.33708
H	-4.1236	-1.30652	1.05117
H	-2.78068	-1.019	2.17211
C	-2.58172	-1.70305	-1.23752
H	-3.64989	-1.58212	-1.45085
H	-2.38473	-2.77691	-1.14553
H	-2.01853	-1.33097	-2.10035
C	-0.91573	2.9836	1.12283
H	-1.82824	2.62799	1.6063
H	-1.02362	4.06644	0.97005
H	-0.08698	2.8562	1.83317

Sum of electronic and thermal Free Energies
= -659.613590 a.u.

TS2

Atom	coordinates (Å)		
	X	Y	Z

C	1.87657	-1.71177	0.05976
O	2.71669	-2.56044	-0.19432
C	2.35824	-0.25277	0.4272
C	0.42296	-1.98215	-0.09878
H	0.22181	-2.78065	-0.81005
C	1.40087	0.73714	-0.05466
H	2.06783	-0.1565	1.50284
C	-0.57458	-1.24166	0.42161
H	-0.32777	-0.50765	1.18014
C	3.88697	-0.09903	0.30655
H	4.2055	0.86972	0.70547
H	4.19361	-0.15943	-0.74242
H	4.40972	-0.89575	0.84149
C	1.6001	2.17486	-0.21197
H	2.54074	2.51309	-0.68605
H	1.67021	2.54109	0.83318
C	-2.04487	-1.22588	0.04552
C	0.33632	2.84113	-0.88823
H	0.42475	3.93365	-0.82014
H	0.35857	2.58256	-1.95302
C	-2.50294	0.28947	-0.03689
H	-2.70912	0.64009	0.98073
H	-3.46713	0.29917	-0.56766
C	-0.94387	2.33282	-0.24872
C	-1.49302	1.19207	-0.704
H	-1.06814	0.78468	-1.62069
C	-2.87006	-1.91208	1.15887
H	-2.64324	-2.98283	1.20993
H	-3.94435	-1.79904	0.96702
H	-2.65644	-1.47481	2.14138
C	-2.31103	-1.93276	-1.29419
H	-3.37914	-1.89425	-1.53762
H	-2.02059	-2.98849	-1.25354
H	-1.75747	-1.46562	-2.11577
C	-1.37629	3.05989	1.0008
H	-2.26012	2.61982	1.47006

H	-1.61103	4.10972	0.77728
H	-0.57395	3.07922	1.75465

Sum of electronic and thermal Free Energies
= -659.592489 a.u.
Harmonic frequencies = 232.0587*i* (cm^{-1})

Int2

Atom	coordinates (Å) X	Y	Z
C	1.57662	-1.6029	-0.16918
O	2.28441	-2.22254	-0.95551
C	2.1785	-0.60021	0.82816
C	0.10134	-1.70895	-0.2809
H	-0.21228	-2.3462	-1.10384
C	1.99379	0.86457	0.54109
H	1.78414	-0.79412	1.83646
C	-0.78962	-0.99028	0.42172
H	-0.43139	-0.37355	1.24718
C	3.72504	-0.77051	0.92124
H	4.15062	-0.04472	1.61815
H	4.18668	-0.65239	-0.06152
H	3.94624	-1.78264	1.27051
C	1.76186	1.25188	-0.87472
H	1.46956	0.46251	-1.58559
H	2.77678	1.58269	-1.17779
C	-2.27435	-0.84132	0.14527
C	0.7997	2.47519	-1.02178
H	1.29223	3.37232	-0.63232
H	0.61537	2.63247	-2.09127
C	-2.54481	0.70536	-0.04653
H	-2.68019	1.15785	0.94042
H	-3.50182	0.81467	-0.57545
C	-0.49903	2.21588	-0.26987
C	-1.41679	1.38001	-0.78422
H	-1.24904	1.01935	-1.80088
C	-3.08005	-1.34128	1.36466
H	-2.96765	-2.42373	1.49433
H	-4.147	-1.12377	1.23341
H	-2.74963	-0.85351	2.28938
C	-2.71988	-1.6103	-1.10923
H	-3.79723	-1.48206	-1.26302
H	-2.52432	-2.68413	-1.01209
H	-2.20727	-1.25564	-2.00999
C	-0.5482	2.82938	1.1079
H	-1.45441	2.58537	1.66785
H	-0.48776	3.92404	1.03234
H	0.32834	2.5064	1.68619

Sum of electronic and thermal Free Energies
= -659.612065 a.u.

TS3

Atom	coordinates (Å) X	Y	Z
C	1.51988	-1.64127	-0.38112
O	2.22993	-2.37908	-1.05283
C	2.21096	-0.59326	0.50266
C	0.0454	-1.66338	-0.50142
H	-0.31076	-2.20903	-1.372
C	2.42647	0.7556	0.12411
H	1.53434	0.33768	1.02617
C	-0.796	-1.0081	0.31456
H	-0.38373	-0.52128	1.1991
C	2.96799	-1.18792	1.6793
H	3.42458	-0.38763	2.26739
H	3.76074	-1.82725	1.27577
H	2.33168	-1.81504	2.31544
C	1.78512	1.23919	-1.15983
H	1.20866	0.49678	-1.73535
H	2.65104	1.50466	-1.78704
C	-2.27462	-0.74485	0.12847
C	0.91067	2.51405	-0.99913
H	1.52041	3.31767	-0.57125
H	0.59421	2.83727	-1.9986
C	-2.42858	0.82956	0.15612
H	-2.43587	1.15761	1.20068
H	-3.41693	1.07555	-0.25704
C	-0.3017	2.23805	-0.11902
C	-1.31958	1.508	-0.60679
H	-1.2695	1.24388	-1.66483
C	-3.06888	-1.34606	1.30825
H	-3.02942	-2.44112	1.29276
H	-4.1214	-1.04325	1.25331
H	-2.67246	-1.00668	2.27259
C	-2.81385	-1.31138	-1.19444
H	-3.88355	-1.09286	-1.28782
H	-2.69247	-2.3996	-1.24066
H	-2.3053	-0.87982	-2.06305
C	-0.18586	2.74338	1.29846
H	-0.99421	2.41033	1.955
H	-0.18852	3.8426	1.30274
H	0.77454	2.4426	1.73816

Sum of electronic and thermal Free Energies
= -659.603499 a.u.
Harmonic frequencies = 927.5737*i* (cm^{-1})

TS4

Atom	coordinates (Å) X	Y	Z
C	2.20769	-0.97648	-0.422
O	3.13777	-1.60447	-0.91807
C	2.48585	0.24757	0.41948
C	0.80863	-1.43923	-0.61761
H	0.66531	-2.08688	-1.4799
C	1.96919	1.4627	0.16073
H	2.28933	2.28213	0.80797
C	-0.186	-1.14412	0.23321
H	0.04906	-0.51453	1.08983
C	3.51569	0.02689	1.50371
H	3.74801	0.95875	2.02833
H	4.43726	-0.37357	1.06639
H	3.17102	-0.70698	2.24471
C	1.09049	1.88945	-0.98815
H	0.79554	1.02697	-1.59324
H	1.69176	2.53427	-1.64711
C	-1.65005	-1.52143	0.12273
C	-0.17477	2.69069	-0.58508
H	0.13532	3.62167	-0.0889
H	-0.68355	2.98482	-1.52596
C	-2.4856	-0.22539	0.43699
H	-2.43068	-0.03621	1.51413
H	-3.53357	-0.40657	0.16103

C	-1.01794	1.84292	0.34733
C	-1.89754	0.97176	-0.27885
H	-2.03067	0.94946	-1.37986
C	-1.98544	-2.57302	1.2065
H	-1.46096	-3.51359	1.006
H	-3.06286	-2.7787	1.22447
H	-1.68993	-2.22606	2.20305
C	-2.01953	-2.08426	-1.2603
H	-3.08922	-2.3203	-1.30053
H	-1.47028	-3.0086	-1.46965
H	-1.7978	-1.37538	-2.06548
C	-2.66243	2.45333	0.51915
H	-3.44538	2.45995	-0.26364
H	-2.29346	3.48059	0.55177
H	-3.086	2.15624	1.47416

Sum of electronic and thermal Free Energies
= -659.598629 a.u.
Harmonic frequencies = 556.7423*i* (cm^{-1})

Int4

Atom	coordinates (Å)		
	X	Y	Z
C	2.29826	-0.85635	-0.43689
O	3.23081	-1.4898	-0.92117
C	2.57371	0.37474	0.39153
C	0.9019	-1.32288	-0.63543
H	0.77016	-1.97925	-1.49293
C	1.99342	1.56429	0.15468
H	2.301	2.40445	0.78003
C	-0.09966	-1.05656	0.22027
H	0.1179	-0.42947	1.08583
C	3.65984	0.19991	1.42608
H	3.88489	1.14339	1.93253
H	4.57166	-0.17469	0.94798
H	3.37383	-0.53877	2.18655
C	1.03933	1.92826	-0.95187
H	0.80001	1.06478	-1.57484
H	1.53201	2.66194	-1.60543
C	-1.53748	-1.52268	0.12407
C	-0.2954	2.61055	-0.48423
H	-0.00999	3.53496	0.03854
H	-0.85762	2.88283	-1.39849
C	-2.47106	-0.34742	0.54824
H	-2.39426	-0.21065	1.63428
H	-3.50704	-0.64422	0.33155
C	-0.9773	1.69077	0.46345
C	-2.17331	1.01906	-0.09881
H	-2.20117	0.95303	-1.20367
C	-1.74181	-2.67918	1.1348
H	-1.14654	-3.55448	0.85287
H	-2.79715	-2.9775	1.16564
H	-1.44665	-2.37995	2.14695
C	-1.90409	-2.0202	-1.28606
H	-2.955	-2.33052	-1.31433
H	-1.29956	-2.88621	-1.57685
H	-1.76044	-1.24227	-2.04402
C	-3.28606	2.04561	0.3083
H	-4.25534	1.63556	0.00585
H	-3.15317	3.01155	-0.18813
H	-3.29569	2.20636	1.39064

Sum of electronic and thermal Free Energies
= -659.619102 a.u.

TS5

Atom	coordinates (Å)		
	X	Y	Z
C	2.26645	-0.80603	-0.69683
O	3.09137	-1.36807	-1.411
C	2.70416	0.328	0.19742
C	0.85682	-1.27126	-0.69371
H	0.58505	-1.87423	-1.55683
C	2.0846	1.52242	0.2653
H	2.55869	2.27445	0.90132
C	-0.00039	-1.03926	0.31056
H	0.36619	-0.46951	1.16513
C	4.01077	0.0702	0.91254
H	4.3374	0.94847	1.4775
H	4.78583	-0.19505	0.18568
H	3.92761	-0.77575	1.60761
C	0.86451	2.0264	-0.46166
H	0.4789	1.27647	-1.15216
H	1.18523	2.87449	-1.08346
C	-1.45605	-1.42673	0.40607
C	-0.26273	2.54135	0.49991
H	0.05153	2.44665	1.55396
H	-0.34746	3.63981	0.41324
C	-2.25928	-0.12488	0.69928
H	-1.94711	0.25732	1.68342
H	-3.3207	-0.3724	0.81918
C	-1.69678	2.13022	0.49466
C	-2.1471	1.02202	-0.38563
H	-1.45089	0.69242	-1.17395
C	-1.63298	-2.36709	1.62418
H	-1.09962	-3.31068	1.46595
H	-2.69355	-2.59668	1.78198
H	-1.24673	-1.91002	2.54268
C	-1.98045	-2.13087	-0.85537
H	-3.04145	-2.37817	-0.73679
H	-1.43982	-3.06656	-1.03683
H	-1.87816	-1.50494	-1.74768
C	-3.51392	1.32262	-1.02614
H	-3.91261	0.43335	-1.52948
H	-3.42948	2.12008	-1.77343
H	-4.22551	1.65221	-0.26266

Sum of electronic and thermal Free Energies
= -659.609002 a.u.
Harmonic frequencies = 128.9009*i* (cm^{-1})

Int5

Atom	coordinates (Å)		
	X	Y	Z
C	-2.26198	0.8213	-0.67446
O	-3.07452	1.43121	-1.36353
C	-2.73048	-0.33678	0.17153
C	-0.84153	1.25778	-0.6692
H	-0.5641	1.85654	-1.5334
C	-2.12361	-1.53957	0.22229
H	-2.62595	-2.30727	0.81584
C	0.01897	1.02207	0.3315
H	-0.34781	0.46381	1.19359
C	-4.06112	-0.0956	0.84783

H	-4.40838	-0.98892	1.37556
H	-4.81051	0.19366	0.10371
H	-3.99976	0.72936	1.56976
C	-0.86084	-2.01314	-0.44753
H	-0.47936	-1.26292	-1.13859
H	-1.1044	-2.89821	-1.05157
C	1.47858	1.40607	0.41127
C	0.23688	-2.43728	0.58376
H	0.06553	-1.92117	1.55212
H	0.09808	-3.49007	0.86908
C	2.30279	0.10836	0.67423
H	2.04707	-0.27252	1.67358
H	3.36524	0.3723	0.73728
C	1.69539	-2.17115	0.45868
C	2.14765	-1.04227	-0.40054
H	1.44322	-0.69652	-1.17419
C	1.67301	2.3357	1.63483
H	1.13768	3.28074	1.49275
H	2.7357	2.56394	1.77974
H	1.29991	1.87059	2.55479
C	1.98105	2.12498	-0.85124
H	3.04156	2.37894	-0.74338
H	1.43139	3.05788	-1.0188
H	1.87321	1.50533	-1.74743
C	3.49534	-1.36385	-1.07221
H	3.89187	-0.48226	-1.59083
H	3.38415	-2.16524	-1.81166
H	4.22136	-1.69736	-0.32416

Sum of electronic and thermal Free Energies
= -659.609578 a.u.

TS6

Atom	coordinates (Å)		
	X	Y	Z
C	-2.2298	0.79486	-0.73255
O	-3.01305	1.36681	-1.4843
C	-2.73816	-0.30205	0.17292
C	-0.80214	1.21015	-0.7106
H	-0.4838	1.73676	-1.60722
C	-2.15269	-1.50868	0.30728
H	-2.66424	-2.23403	0.94317
C	0.01759	1.03771	0.33724
H	-0.39604	0.55921	1.22519
C	-4.0737	0.00391	0.811
H	-4.44813	-0.84992	1.38347
H	-4.80429	0.26368	0.0378
H	-4.00664	0.86844	1.48447
C	-0.89355	-2.02468	-0.33475
H	-0.54176	-1.33686	-1.1026
H	-1.1096	-2.97673	-0.8351
C	1.48541	1.38118	0.4411
C	0.23148	-2.29124	0.73383
H	0.1773	-1.48725	1.48539
H	-0.02004	-3.2206	1.25982
C	2.27401	0.05473	0.70694
H	1.97813	-0.3286	1.69169
H	3.33583	0.31299	0.80077
C	1.62295	-2.35854	0.17848
C	2.1441	-1.0676	-0.39072
H	1.41177	-0.70213	-1.13294
C	1.68862	2.30012	1.67008
H	1.17621	3.25816	1.52973
H	2.75456	2.50418	1.8257
H	1.29691	1.83869	2.58432
C	2.02365	2.08953	-0.81216
H	3.08479	2.33046	-0.68369
H	1.48737	3.02749	-0.99394
H	1.92805	1.47027	-1.71028
C	3.48277	-1.29784	-1.11554
H	3.86037	-0.37537	-1.57455
H	3.36933	-2.05247	-1.90065
H	4.23514	-1.67016	-0.41136

Sum of electronic and thermal Free Energies
= -659.602470 a.u.
Harmonic frequencies = 371.7801*i* (cm^{-1})

Int6

Atom	coordinates (Å)		
	X	Y	Z
C	-2.36805	0.64247	-0.6105
O	-3.26792	1.15735	-1.26569
C	-2.68951	-0.47244	0.35866
C	-0.97411	1.14216	-0.74085
H	-0.78183	1.70175	-1.65317
C	-2.0342	-1.64775	0.36334
H	-2.37298	-2.40641	1.0719
C	-0.05175	1.012	0.22529
H	-0.35013	0.48918	1.1336
C	-3.896	-0.21353	1.2283
H	-4.1425	-1.0864	1.84039
H	-4.7579	0.03647	0.60015
H	-3.73364	0.64238	1.89689
C	-0.91331	-2.07209	-0.54807
H	-0.83032	-1.38899	-1.39467
H	-1.14363	-3.05313	-0.97867
C	1.37175	1.51762	0.24688
C	0.48109	-2.16446	0.18099
H	0.44601	-1.6318	1.14646
H	0.67003	-3.22448	0.41044
C	2.31598	0.3386	0.64415
H	1.95874	-0.09273	1.58868
H	3.29961	0.77606	0.86893
C	1.50831	-1.76607	-0.82483
C	2.54205	-0.78172	-0.40042
H	2.9988	-0.33774	-1.29513
C	1.46538	2.58162	1.37094
H	0.8038	3.42933	1.16211
H	2.49123	2.96017	1.45466
H	1.18097	2.16248	2.34348
C	1.7993	2.1556	-1.08502
H	2.85209	2.45829	-1.04193
H	1.206	3.0518	-1.29781
H	1.68006	1.46769	-1.92801
C	3.61333	-1.79389	0.14857
H	4.55787	-1.25649	0.28098
H	3.78073	-2.6222	-0.54582
H	3.30875	-2.20276	1.11757

Sum of electronic and thermal Free Energies
= -659.609836 a.u.

TS7

Atom	coordinates (Å)

	X	Y	Z
C	-2.39004	0.61668	-0.58806
O	-3.3181	1.12878	-1.20684
C	-2.65002	-0.57009	0.30736
C	-1.02536	1.19897	-0.69927
H	-0.86805	1.79934	-1.59227
C	-1.90255	-1.69114	0.29852
H	-2.22961	-2.50279	0.95274
C	-0.09018	1.07864	0.25319
H	-0.35136	0.50708	1.14333
C	-3.92032	-0.46128	1.1187
H	-4.11229	-1.37852	1.68365
H	-4.77005	-0.26658	0.45567
H	-3.87524	0.37697	1.8266
C	-0.69787	-2.0078	-0.54717
H	-0.55254	-1.24449	-1.31286
H	-0.87976	-2.94383	-1.09075
C	1.31539	1.63565	0.2671
C	0.62166	-2.17128	0.27281
H	0.54302	-1.5893	1.20912
H	0.71461	-3.22218	0.57719
C	2.29414	0.4706	0.63464
H	1.95804	0.02201	1.5772
H	3.27842	0.91793	0.82973
C	1.75199	-1.79502	-0.66879
C	2.46172	-0.61469	-0.43313
H	3.14484	-0.29757	-1.22851
C	1.39812	2.68709	1.40161
H	0.71658	3.5218	1.20514
H	2.41588	3.08749	1.48302
H	1.12759	2.25195	2.37092
C	1.71534	2.29129	-1.06483
H	2.75529	2.63605	-1.02372
H	1.08695	3.16333	-1.27626
H	1.61986	1.59727	-1.90631
C	3.41236	-2.09504	-0.00041
H	3.96421	-1.55981	0.79106
H	4.07923	-2.3541	-0.81883
H	3.0129	-2.9877	0.4852

Sum of electronic and thermal Free Energies
= -659.593526 a.u.
Harmonic frequencies = 492.9688*i* (cm^{-1})

Table S17. Cartesian coordinates and Gibbs free energies of TS1, Int1, TS2, Int2, and TS3 at the B3LYP/6-31G(d) level at 308.15 K in Gas phase (Figure 8).

TS1

Atom	coordinates (Å)		
	X	Y	Z
C	0.99134	-2.08822	-0.13293
O	1.16043	-3.19161	0.35992
C	2.06968	-1.05458	-0.18416
C	-0.39396	-1.59098	-0.56146
H	-0.56622	-1.52715	-1.65153
C	1.83321	0.08606	-0.8617
H	0.93734	0.12008	-1.47502
C	-1.19364	-1.01535	0.42341
H	-1.13361	-2.32232	0.20147
C	3.28736	-1.35688	0.64899
H	4.03514	-0.56257	0.58464
H	3.74715	-2.29216	0.31035
H	3.01959	-1.50998	1.701
C	2.51468	1.41969	-0.76264
H	3.14277	1.62627	-1.6412
H	3.17461	1.45364	0.11013
C	-2.45904	-0.27632	0.01055
C	1.41722	2.53308	-0.6676
H	1.8952	3.46365	-0.33222
H	1.02806	2.72007	-1.67577
C	-2.13211	1.21978	0.40297
H	-2.02371	1.26142	1.48957
H	-3.02413	1.80989	0.14372
C	0.26535	2.14646	0.24871
C	-0.92185	1.80149	-0.2834
H	-1.02021	1.90492	-1.36568
C	-3.62589	-0.74737	0.9018
H	-3.91825	-1.77489	0.65143
H	-4.50787	-0.10848	0.7664
H	-3.33404	-0.73112	1.95633
C	-2.88883	-0.35796	-1.4698
H	-3.78332	0.2509	-1.64916
H	-3.13484	-1.38971	-1.75142
H	-2.11227	-0.00464	-2.15751
C	0.59993	2.09598	1.71852
H	-0.25881	1.84494	2.34354
H	0.99608	3.06396	2.05517
H	1.37727	1.34689	1.91885

Sum of electronic and thermal Free Energies
= -659.601156 a.u.
Harmonic frequencies = 1206.1414*i* (cm^{-1})

Int1

Atom	coordinates (Å)		
	X	Y	Z
C	1.09172	-2.1309	-0.1139
O	1.45912	-3.22112	0.29542
C	2.02327	-0.95826	-0.12829
C	-0.37643	-1.88548	-0.50058
H	-0.50327	-1.68967	-1.58014
C	1.70182	0.14357	-0.8336
H	0.81256	0.10022	-1.45683
C	-1.0436	-0.96599	0.46105
H	-0.89857	-2.84257	-0.30627
C	3.26298	-1.13089	0.71141
H	3.93728	-0.27438	0.64161
H	3.80398	-2.02691	0.38907
H	3.00329	-1.29302	1.76433
C	2.34447	1.50282	-0.79663
H	2.9683	1.67313	-1.68639
H	3.0082	1.59009	0.06901
C	-2.33758	-0.33538	0.02477
C	1.24692	2.61414	-0.74586
H	1.7238	3.56121	-0.4589
H	0.84151	2.75283	-1.75537
C	-2.2103	1.18716	0.40641
H	-2.09626	1.25468	1.49055
H	-3.16183	1.67082	0.13892
C	0.11856	2.24998	0.20219
C	-1.05967	1.84791	-0.30644

H	-1.17551	1.91621	-1.38941
C	-3.39836	-0.97458	0.96867
H	-3.54865	-2.03568	0.73803
H	-4.35844	-0.46238	0.82998
H	-3.09498	-0.88984	2.01537
C	-2.80919	-0.49512	-1.43816
H	-3.76122	0.02499	-1.60036
H	-2.96571	-1.54976	-1.69297
H	-2.08728	-0.0871	-2.1545
C	0.46991	2.26064	1.66866
H	-0.38937	2.06753	2.31347
H	0.89663	3.23255	1.9513
H	1.22549	1.49838	1.89788

Sum of electronic and thermal Free Energies
= -659.616931 a.u.

TS2

Atom	coordinates (Å)		
	X	Y	Z
C	1.64405	-1.86599	-0.22442
O	2.2733	-2.86323	0.09358
C	2.21974	-0.49276	-0.09054
C	0.13402	-2.06438	-0.62538
H	0.10616	-2.05892	-1.73688
C	1.68737	0.55688	-0.75694
H	0.9497	0.34268	-1.51751
C	-0.69097	-0.89786	-0.34934
H	-0.14527	-3.09343	-0.32165
C	3.3475	-0.39401	0.91095
H	3.76726	0.61417	0.95515
H	4.14847	-1.08984	0.63802
H	3.02333	-0.67986	1.92021
C	1.8935	2.0332	-0.53075
H	2.65087	2.43548	-1.22149
H	2.27356	2.22087	0.47979
C	-2.10718	-0.85405	0.02132
C	0.57107	2.83905	-0.7714
H	0.77051	3.88622	-0.50132
H	0.35677	2.82484	-1.84741
C	-2.62558	0.65865	-0.11076
H	-2.98289	1.00452	0.86563
H	-3.49756	0.67201	-0.77747
C	-0.6316	2.29813	-0.0152
C	-1.5499	1.56471	-0.66529
H	-1.42535	1.48115	-1.74704
C	-1.96696	-1.20744	1.54822
H	-1.68287	-2.25473	1.68957
H	-2.94169	-1.0418	2.0194
H	-1.23283	-0.57042	2.05108
C	-3.08265	-1.85047	-0.63878
H	-4.0885	-1.75971	-0.2096
H	-2.74856	-2.88536	-0.50383
H	-3.16515	-1.65666	-1.71478
C	-0.60427	2.49002	1.48021
H	-1.54124	2.19455	1.9605
H	-0.41165	3.53967	1.74078
H	0.20171	1.89835	1.93881

Sum of electronic and thermal Free Energies
= -659.592891 a.u.
Harmonic frequencies = 215.8394*i* (cm^{-1})

Int2

Atom	coordinates (Å)		
	X	Y	Z
C	0.66578	2.17047	-0.16092
O	1.13243	3.07846	0.50597
C	-0.79324	1.86098	-0.10415
C	1.6223	1.33096	-1.07134
H	1.54698	1.77511	-2.07523
C	-1.30347	0.84872	-0.83299
H	-0.62463	0.33609	-1.5251
C	1.42063	-0.15555	-1.15097
H	2.6208	1.57595	-0.68227
C	-1.56682	2.73715	0.84984
H	-2.61571	2.44325	0.92534
H	-1.52852	3.78101	0.51786
H	-1.11648	2.71964	1.84811
C	-2.68762	0.25894	-0.7489
H	-3.29849	0.6091	-1.59426
H	-3.1931	0.60506	0.15806
C	1.78705	-0.9488	0.07102
C	-2.65928	-1.30348	-0.77372
H	-3.64383	-1.67111	-0.45494
H	-2.51184	-1.63463	-1.80795
C	1.00224	-2.32171	0.06556
H	0.98525	-2.72228	1.08601
H	1.55442	-3.04164	-0.5505
C	-1.53541	-1.84544	0.09017
C	-0.37477	-2.1442	-0.51549
H	-0.36856	-2.10089	-1.60212
C	1.68471	-0.29221	1.4658
H	2.22276	0.6594	1.51727
H	2.10742	-0.95312	2.23297
H	0.63975	-0.10236	1.73098
C	3.29777	-1.24019	-0.23278
H	3.64128	-2.00879	0.469
H	3.91682	-0.34796	-0.09428
H	3.44114	-1.61426	-1.25147
C	-1.77303	-1.8521	1.57896
H	-0.91746	-2.23789	2.13947
H	-2.64487	-2.47402	1.8254
H	-1.99361	-0.84461	1.95928

Sum of electronic and thermal Free Energies
= -659.611479 a.u.

TS3

Atom	coordinates (Å)		
	X	Y	Z
C	0.35437	2.16508	-0.28355
O	0.89846	3.08975	0.3055
C	-1.05063	1.76105	0.00238
C	1.16372	1.34526	-1.30515
H	1.08269	1.77405	-2.31445
C	-1.61887	0.8154	-0.77156
H	-1.05592	0.48894	-1.64337
C	1.83377	0.10992	-1.22129
H	2.42086	1.34429	-1.27567
C	-1.67309	2.41849	1.2066
H	-2.71038	2.10953	1.35518
H	-1.64953	3.50756	1.0906
H	-1.10345	2.19558	2.11674

C	-2.86839	0.01754	-0.53627
H	-3.66505	0.31341	-1.23442
H	-3.25618	0.18554	0.47357
C	2.01265	-0.66304	0.08167
C	-2.55686	-1.49857	-0.75615
H	-3.42819	-2.08544	-0.43756
H	-2.43338	-1.66928	-1.8324
C	1.284	-2.04365	-0.17034
H	1.32725	-2.60503	0.77061
H	1.87288	-2.60021	-0.90876
C	-1.29469	-1.93236	-0.02682
C	-0.12342	-1.90384	-0.6856
H	-0.16472	-1.6657	-1.74939
C	1.51367	-0.05692	1.41173
H	1.96484	0.92332	1.59788
H	1.78605	-0.70836	2.25223
H	0.42711	0.05971	1.42427
C	3.52465	-0.96241	0.22141
H	3.70336	-1.67759	1.03436
H	4.08305	-0.04769	0.45693
H	3.92672	-1.37287	-0.70936
C	-1.45973	-2.26197	1.43554
H	-0.5189	-2.53952	1.91654
H	-2.16455	-3.09526	1.56352
H	-1.87912	-1.4129	1.99338

Sum of electronic and thermal Free Energies
= -659.598687 a.u.
Harmonic frequencies = 1130.6758*i* (cm^{-1})

Table S18. Cartesian coordinates and Gibbs free energies of protonated (2*E*,6*E*,10*E*)-isomer, TS1, and protonated (2*Z*,6*E*,10*E*)-isomer at the B3LYP/6-31G(d) level with self-consistent reaction field (SCRF) = (polarizable continuum model (PCM), tetrahydrofuran (THF)) at 308.15 K (Figure 9a).

protonated (2*E*,6*E*,10*E*)-isomer

Atom	coordinates (Å) X	Y	Z
C	1.52699	-1.82313	-0.09647
C	2.19167	-0.54945	0.04478
C	0.10861	-1.92979	-0.29409
H	-0.26579	-2.76755	-0.87837
C	1.62542	0.49815	-0.62939
H	0.82308	0.2546	-1.31577
C	-0.73192	-1.01224	0.2619
H	-0.29482	-0.32062	0.97569
C	3.47808	-0.48198	0.83214
H	3.76984	0.55391	1.01544
H	4.28944	-0.96555	0.27598
H	3.38717	-0.998	1.79283
C	1.95202	1.95373	-0.57438
H	2.70822	2.18992	-1.33814
H	2.3967	2.22232	0.3894
C	-2.21105	-0.83538	0.05101
C	0.6697	2.79917	-0.86576
H	0.9088	3.85224	-0.67616
H	0.42921	2.7052	-1.93059
C	-2.49537	0.71881	0.13246
H	-2.56034	0.99976	1.18758
H	-3.48811	0.88825	-0.30333
C	-0.5081	2.33532	-0.02529
C	-1.4417	1.53384	-0.57536
H	-1.37418	1.35823	-1.65044
C	-2.95758	-1.53653	1.21674
H	-2.83549	-2.62316	1.16264
H	-4.02641	-1.30553	1.15141
H	-2.59421	-1.19535	2.19188
C	-2.68775	-1.41219	-1.29334
H	-3.7645	-1.24799	-1.40417
H	-2.51473	-2.49226	-1.35471
H	-2.18321	-0.93812	-2.14203
C	-0.46018	2.74757	1.42612
H	-1.31599	2.39571	2.00576
H	-0.43455	3.8426	1.50027
H	0.45198	2.38491	1.91995
O	2.29476	-2.88896	-0.02482
H	1.77678	-3.71716	-0.04297

Sum of electronic and thermal Free Energies
= -660.138819 a.u.

TS1

Atom	coordinates (Å) X	Y	Z
C	1.88318	-1.48703	0.07221
C	2.27656	-0.21149	0.28604
C	0.49462	-1.8468	-0.25534
H	0.35561	-2.35524	-1.20881
C	1.4474	0.98466	0.30482
H	1.01889	1.29618	1.25954
C	-0.55144	-1.4473	0.47925
H	-0.35684	-0.99649	1.4543
C	3.74819	0.17329	0.49124
H	3.87698	0.93442	1.26829
H	4.19602	0.54839	-0.43591
H	4.28024	-0.72848	0.80399
C	1.45822	2.01138	-0.76473
H	1.41595	1.5259	-1.74719
H	2.45328	2.49428	-0.741
C	-1.99128	-1.37184	0.02781
C	0.33536	3.02286	-0.5199
H	0.62644	3.68367	0.30608
H	0.18359	3.67547	-1.3885
C	-2.32574	0.16602	0.01923
H	-2.58147	0.47191	1.03885
H	-3.2314	0.31751	-0.58681
C	-0.94939	2.31612	-0.1201
C	-1.19857	1.03141	-0.49736
H	-0.58196	0.59306	-1.27746
C	-2.91681	-2.07205	1.04361
H	-2.75064	-3.15479	1.03735
H	-3.9683	-1.88772	0.79526
H	-2.74038	-1.70697	2.06182
C	-2.21332	-1.96778	-1.37177
H	-3.27251	-1.89746	-1.64124
H	-1.93088	-3.02592	-1.40174
H	-1.63917	-1.44285	-2.14369
C	-1.86503	3.12159	0.75531

H	-2.83286	2.6485	0.92563
H	-2.04014	4.10207	0.29277
H	-1.39356	3.32421	1.72724
O	2.83905	-2.45416	-0.00815
H	2.40903	-3.32457	-0.03557

Sum of electronic and thermal Free Energies
= -660.073779 a.u.
Harmonic frequencies = 515.3446*i* (cm^{-1})

protonated (2*Z*,6*E*,10*E*)-isomer

Atom	coordinates (Å) X	Y	Z
C	1.68041	-1.40627	-0.27883
C	2.35101	-0.26275	0.32644
C	0.28125	-1.53523	-0.51059
H	-0.03411	-2.2585	-1.25899
C	2.14073	1.01506	-0.09284
H	2.73324	1.77029	0.42511
C	-0.64129	-0.87693	0.24856
H	-0.27416	-0.2748	1.07503
C	3.43029	-0.59002	1.3433
H	3.80594	0.32818	1.8006
H	4.27163	-1.10528	0.86778
H	3.04869	-1.2434	2.13495
C	1.37437	1.54652	-1.2644
H	0.86416	0.7524	-1.81393
H	2.12819	1.97314	-1.94336
C	-2.14574	-0.97538	0.13657
C	0.3578	2.68257	-0.93573
H	0.88697	3.53027	-0.48587
H	-0.0495	3.0278	-1.89227
C	-2.6608	0.50741	0.22391
H	-2.71917	0.80284	1.2752
H	-3.67942	0.54817	-0.17928
C	-0.74771	2.18567	-0.02629
C	-1.71129	1.39681	-0.54056
H	-1.72125	1.26253	-1.62335
C	-2.67275	-1.79221	1.34291
H	-2.34744	-2.83631	1.28578
H	-3.76812	-1.77491	1.33806
H	-2.33113	-1.37374	2.29566
C	-2.60425	-1.63318	-1.17508
H	-3.69798	-1.64464	-1.21402
H	-2.26461	-2.67229	-1.24763
H	-2.24088	-1.09208	-2.05521
C	-0.58651	2.52921	1.43201
H	-1.38868	2.14573	2.06596
H	-0.55304	3.61948	1.55488
H	0.36845	2.1503	1.82542
O	2.48631	-2.4002	-0.58634
H	1.99857	-3.18122	-0.91608

Sum of electronic and thermal Free Energies
= -660.135496 a.u.

Table S19. Cartesian coordinates and Gibbs free energies of protonated TS1 and protonated (2*E*,6*E*,10*Z*)-isomer at the B3LYP/6-31G(d) level with SCRF = (PCM, THF) at 308.15 K (Figure 9b).

TS1

Atom	coordinates (Å) X	Y	Z
C	1.1183	-2.04455	-0.28957
C	1.81195	-0.75963	0.0244
C	-0.19164	-2.10835	-0.61325
H	-0.70358	-3.06194	-0.74804
C	1.73612	0.26759	-0.84671
H	1.26945	0.07934	-1.81421
C	-1.0135	-0.90787	-0.76357
H	-0.97842	-0.38901	-1.72192
C	2.53649	-0.75428	1.34892
H	2.97888	0.21642	1.57576
H	3.3397	-1.4996	1.33718
H	1.8598	-1.0299	2.16702
C	2.223	1.67836	-0.64786
H	3.00954	1.89853	-1.38202
H	2.67436	1.80175	0.33959
C	-2.03666	-0.43719	0.14292
C	1.08534	2.73047	-0.83845
H	1.48074	3.71227	-0.54926
H	0.82494	2.78378	-1.9016
C	-2.37079	1.0849	-0.05907
H	-2.65902	1.48589	0.9166
H	-3.2443	1.18782	-0.71065
C	-0.14136	2.36635	-0.02867
C	-1.19678	1.82465	-0.66303
H	-1.16402	1.81359	-1.75262
C	-1.89954	-0.84859	1.61093
H	-1.66434	-1.91036	1.71795
H	-2.83534	-0.64349	2.13855
H	-1.10344	-0.26929	2.08812
C	-3.18099	-1.36577	-0.55262
H	-4.09258	-1.00218	-0.06721
H	-3.0424	-2.422	-0.32225
H	-3.2829	-1.2133	-1.62949
C	-0.03205	2.54524	1.46365
H	-0.96814	2.34004	1.98842
H	0.26545	3.57603	1.69472
H	0.7427	1.89624	1.89229
O	1.89999	-3.12854	-0.09118
H	1.40548	-3.95029	-0.25563

Sum of electronic and thermal Free Energies
= -660.074191 a.u.
Harmonic frequencies = 627.0559*i* (cm^{-1})

protonated (2*E*,6*E*,10*Z*)-isomer

Atom	coordinates (Å) X	Y	Z
C	-1.90434	-1.14737	-0.30736
C	-0.72457	-1.85582	0.0818
C	-1.95991	0.03635	-1.15986
H	-2.6201	-0.09356	-2.01855
C	0.40155	-1.61038	-0.65979
H	0.27674	-0.98463	-1.5358
C	-1.39814	1.25798	-0.99795
H	-1.60129	1.93888	-1.82533

C	-0.82415	-2.85538	1.20919
H	0.15653	-3.25204	1.4744
H	-1.45948	-3.69825	0.91573
H	-1.27214	-2.40452	2.10016
C	1.79198	-2.1076	-0.43466
H	1.96372	-2.99459	-1.06395
H	1.93402	-2.42841	0.60146
C	-0.67788	1.94249	0.14573
C	2.80919	-0.99159	-0.8108
H	3.81198	-1.3125	-0.50863
H	2.81799	-0.87367	-1.90002
C	0.79432	2.31919	-0.29716
H	1.26733	2.79215	0.56992
H	0.7283	3.08455	-1.07973
C	2.40356	0.31557	-0.14427
C	1.57989	1.14717	-0.81056
H	1.37268	0.9014	-1.85273
C	-0.65504	1.15899	1.46692
H	-1.65911	0.81285	1.74087
H	-0.30738	1.81495	2.27163
H	0.0116	0.29719	1.43336
C	-1.44526	3.27202	0.38242
H	-0.92786	3.86111	1.14714
H	-2.46559	3.08148	0.73224
H	-1.50146	3.87409	-0.53082
C	2.88705	0.51096	1.26917
H	2.50953	1.42637	1.72984
H	3.98451	0.55286	1.28145
H	2.60437	-0.33347	1.91219
O	-3.03636	-1.66365	0.117
H	-3.80341	-1.10846	-0.12771

Sum of electronic and thermal Free Energies
= -660.128747 a.u.