Supporting Information

Synthesis and Structural Characterization of Natural Benzofuranoids

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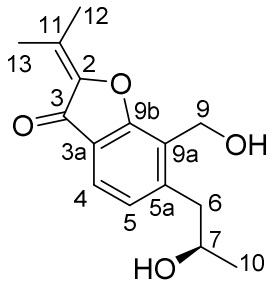
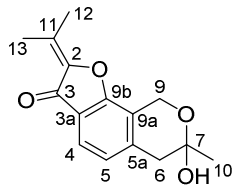
Table S1. NMR Spectroscopic Data ($CDCl_3$) for Natural Ustusorane A (**1**)[S1] (600 MHz) and Synthetic (−)-**1** (400 MHz)



Ustusorane A (**1**)

	Natural **1**		Synthetic (−)-**1**	
position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
2	145.2, C		145.3, C	
3	183.7, C		183.7, C	
3a	121.8, C		121.9, C	
4	123.6, CH	7.55 d (7.8)	123.7, CH	7.58 d (8.0)
5	124.7, CH	6.95 d (7.8)	124.7, CH	6.96 d (8.0)
5a	147.7, C		147.7, C	
6	41.7, CH_2	2.95 dd (13.7, 9.2)	41.8, CH_2	2.96 dd (13.6, 8.8)
		2.90 dd (13.7, 3.0)		2.90 dd (13.6, 3.0)
7	68.9, CH	4.08 m	69.0, C	
9	54.2, CH_2	4.91 br d (12.4)	54.3, CH_2	4.93 d (12.0)
		4.72 dd (12.4, 2.3)		4.74 d (12.0)
9a	124.4, C		124.5, C	
9b	163.3, C		163.4, C	
10	24.2, CH_3	1.37 d (6.4)	24.2, CH_3	1.38 d (6.0)
11	132.4, C		132.3, C	
12	20.2, CH_3	2.11 s	20.3, CH_3	2.12 s
13	17.5, CH_3	2.35 s	17.5, CH_3	2.36 s
7-OH				3.81 brs
9-OH				2.57 brs

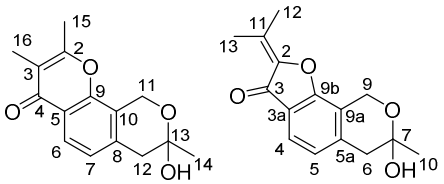
Table S2. NMR Spectroscopic Data (a 1:1 Mixture of $CDCl_3$ and DMSO-d_6) for Natural Pergillin (**4**)[S2] and Synthetic **4** (400 MHz)



Pergillin (**4**)

	Natural **4**		Synthetic **4**	
position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
2	144.7, C		144.5, C	
3	183.7, C		182.4, C	
3a	120.5, C		120.3, C	
4	120.9, CH	7.60 d (8.0)	120.9, CH	7.44 d (8.0)
5	123.1, CH	6.83 d (8.0)	123.3, CH	6.88 d (8.0)
5a	141.7, C		142.1, C	
6	39.2, CH_2	3.00	39.2, CH_2	2.93 d (17.2)
		2.92		2.84 d (17.2)
7	93.8, CH		93.6, C	
9	56.8, CH_2	4.90	56.3, CH_2	4.90 d (15.6)
				4.80 d (15.6)
9a	118.6, C		118.7, C	
9b	159.9, C		159.8, C	
10	28.6, CH_3	1.55 s	28.5, CH_3	1.50 s
11	131.0, C		130.9, C	
12	17.1, CH_3	2.10 s	16.9, CH_3	2.10 s
13	19.9, CH_3	2.33 s	19.8, CH_3	2.32 s
OH		5.72		6.00 s

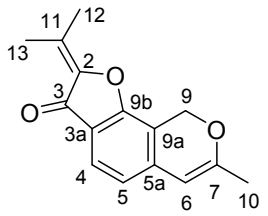
Table S3. NMR Spectroscopic Data (DMSO-d_6) for Natural Aspergione F (**20**)[S3] and Synthetic **4** (400 MHz)



Aspergione F (**20**) Pergillin (**4**)

	Aspergione F (**20**)			Synthetic **4**	
position	δ_C, type	δ_H (*J* in Hz)	position	δ_C, type	δ_H (*J* in Hz)
2	144.3, C		2	144.5, C	
4	182.2, C		3	182.5, C	
5	120.1, C		3a	120.3, C	
7	121.1, CH	7.47 d (7.9)	4	121.3, CH	7.46 d (8.0)
6	123.6, CH	6.94 d (7.9)	5	123.9, CH	6.93 d (8.0)
8	142.5, C		5a	142.7, C	
12	40.1, CH_2	2.92 br d (17.2)	6	39.2, CH_2	2.91 d (17.2)
		2.82 br d (17.2)			2.81 d (17.2)
13	93.6, CH		7	93.8, C	
11	56.1, CH_2	4.85 br d (15.6)	9	56.3, CH_2	4.84 d (15.6)
		4.79 br d (15.6)			4.78 d (15.6)
9	118.7, C		9a	118.9, C	
10	159.6, C		9b	159.8, C	
14	28.5, CH_3	1.46 s	10	28.7, CH_3	1.45 s
3	131.8, C		11	132.0, C	
16	16.8, CH_3	2.08 s	12	17.0, CH_3	2.06 s
15	19.8, CH_3	2.30 s	13	20.0, CH_3	2.29 s
OH		6.08 s	OH		6.09 s

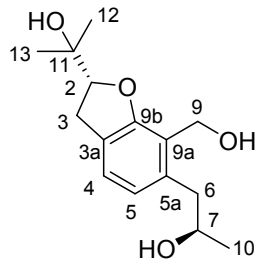
Table S4. NMR Spectroscopic Data (Acetone-d_6) for Natural Ustusorane B (**2**)[S1] (600 MHz) and Synthetic **2** (400 MHz)



Ustusorane B (**2**)

	Natural **2**		Synthetic **2**	
position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
2	145.3, C		145.9, C	
3	182.7, C		182.7, C	
3a	122.3, C		122.3, C	
4	124.4, CH	7.47 d (7.7)	124.4, CH	7.47 d (7.6)
5	118.2, CH	6.77 d (7.7)	118.3, CH	6.77 d (7.6)
5a	141.4, C		141.4, C	
6	102.4, CH	5.85 s	102.4, CH	5.85 s
7	160.4, C		160.4, C	
9	63.0, CH_2	5.28 s	63.0, CH_2	5.28 s
9a	108.9, C		109.6, C	
9b	160.4, C		160.4, C	
10	19.8, CH_3	1.95 s	19.8, CH_3	1.95 s
11	130.6, C		130.6, C	
12	19.8, CH_3	2.07 s	19.8, CH_3	2.07 s
13	17.5, CH_3	2.30 s	16.9, CH_3	2.30 s

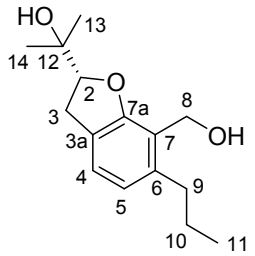
Table S5. NMR Spectroscopic Data (DMSO-d_6) for Natural Ustusorane E (**3**)[S1] (600 MHz) and Synthetic **3** (400 MHz)



Ustusorane E (**3**)

	Natural **3**		Synthetic **3**	
position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
2	88.5, CH	4.50 m	88.7, C	4.50 m
3	30.1, CH_2	3.12 dd (15.8, 7.8)	30.3, CH_2	3.11 dd (15.6, 7.2)
		3.08 dd (15.8, 9.1)		3.05 dd (15.6, 9.6)
3a	124.5, C		124.7, C	
4	123.3, CH	6.98 d (7.7)	123.5, CH	6.98 d (7.6)
5	121.9, CH	6.62 d (7.7)	122.0, CH	6.61 d (7.6)
5a	138.4, C		138.5, C	
6	41.5, CH_2	2.74 dd (13.2, 7.3)	41.6, CH_2	2.74 dd (13.6, 7.2)
		2.60 dd (13.2, 5.5)		2.60 dd (13.6, 5.6)
7	67.6, CH	3.78 m	67.8, CH	3.78 m
9	54.4, CH_2	4.47 dd (11.4, 4.8)	54.6, CH_2	4.51 dd (11.6, 6.4)
		4.42 dd (11.4, 4.0)		4.42 dd (11.6, 4.4)
9a	121.3, C		121.5, C	
9b	158.5, C		158.6, C	
10	23.7, CH_3	1.07 d (7.2)	23.8, CH_3	1.07 d (6.0)
11	70.3, C		70.5, C	
12	25.8, CH_3	1.12 s	26.0, CH_3	1.12 s
13	24.9, CH_3	1.12 s	25.0, CH_3	1.12 s
7-OH		4.78 (5.8)		4.77 d (4.4)
9-OH		4.72 (4.8, 4.0)		4.71 dd (6.4, 4.4)

Table S6. NMR Spectroscopic Data (400 MHz, $CDCl_3$) for Natural Brassicadiol (**7**)[S4] and Synthetic (−)-**7**



Brassicadiol (**7**)

	Natural **7**		Synthetic (−)-**7**	
position	δ_C, type	δ_H (*J* in Hz)	δ_C, type	δ_H (*J* in Hz)
2	89.9, CH	4.64 dd (9, 9)	89.8, CH	4.62 dd (8.8, 8.8)
3	30.6, CH_2	3.17 dd (15.5, 9)	30.5, CH_2	3.16 dd (15.6, 9.2)
		3.11 dd (15.5, 9)		3.09 dd (15.6, 9.6)
3a	124.7, C		124.6, C	
4	122.0, CH	7.02 d (7.5)	121.9, CH	7.00 d (7.6)
5	124.1, CH	6.69 d (7.5)	124.1, CH	6.68 d (7.5)
6	141.0, C		140.9, C	
7	120.6, C		120.3, C	
7a	158.5, C		158.5, C	
8	57.5, CH_2	4.73 s	57.3, CH_2	4.71 s
9	34.7, CH_2	2.62 br t (7.5)	34.6, CH_2	2.62 m
10	25.1, CH_2	1.58 ddd (8, 8, 9.5)	25.1, CH_2	1.58 sextet (7.6)
11	14.1, CH_3	0.97 t (7.5)	14.1, CH_3	0.96 t (7.6)
12	72.0, C		71.7, C	
13	26.3, CH_3	1.28 s	26.2, CH_3	1.34 s
14	24.3, CH_3	1.14 s	24.1, CH_3	1.20 s

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 22

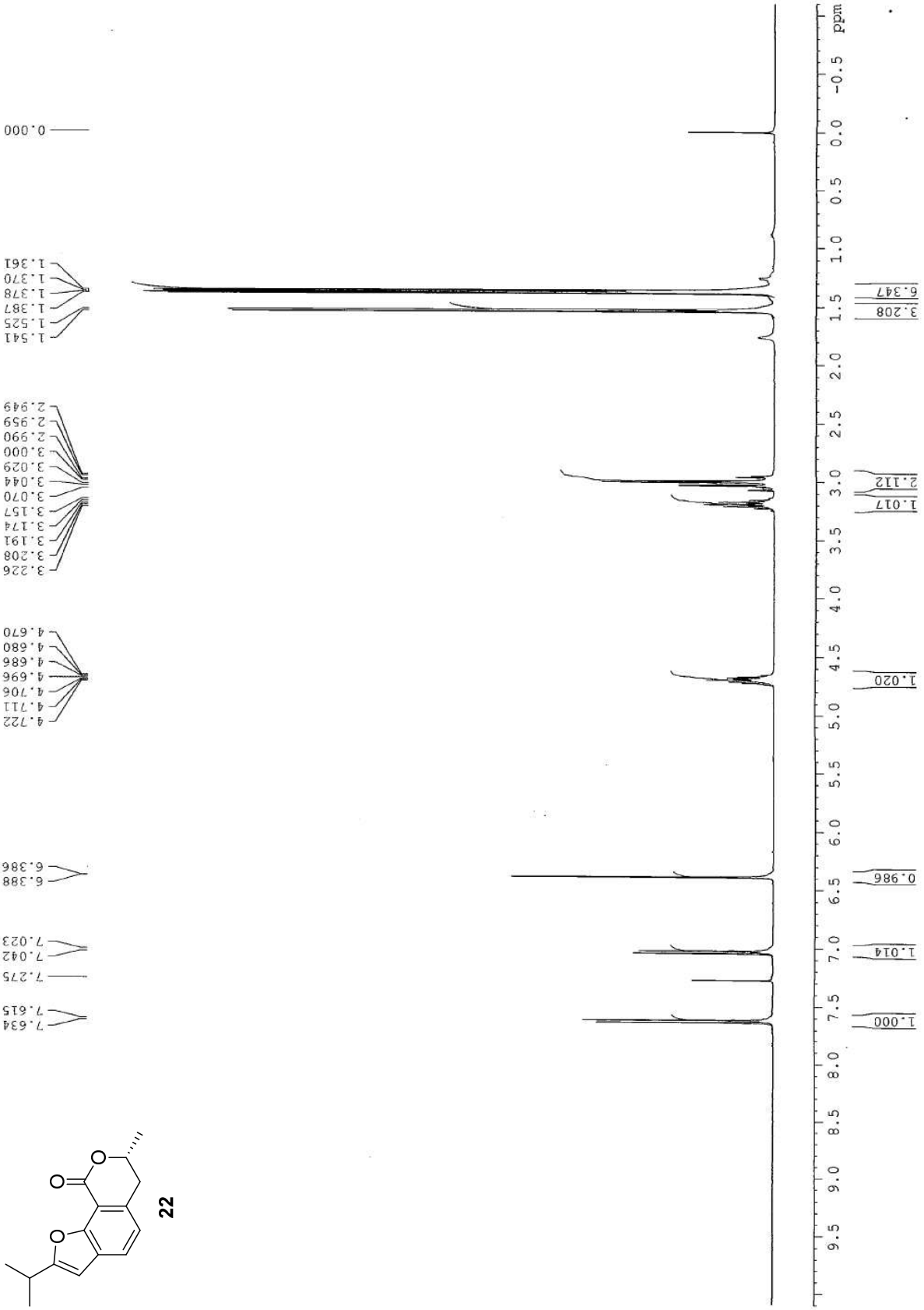


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 22

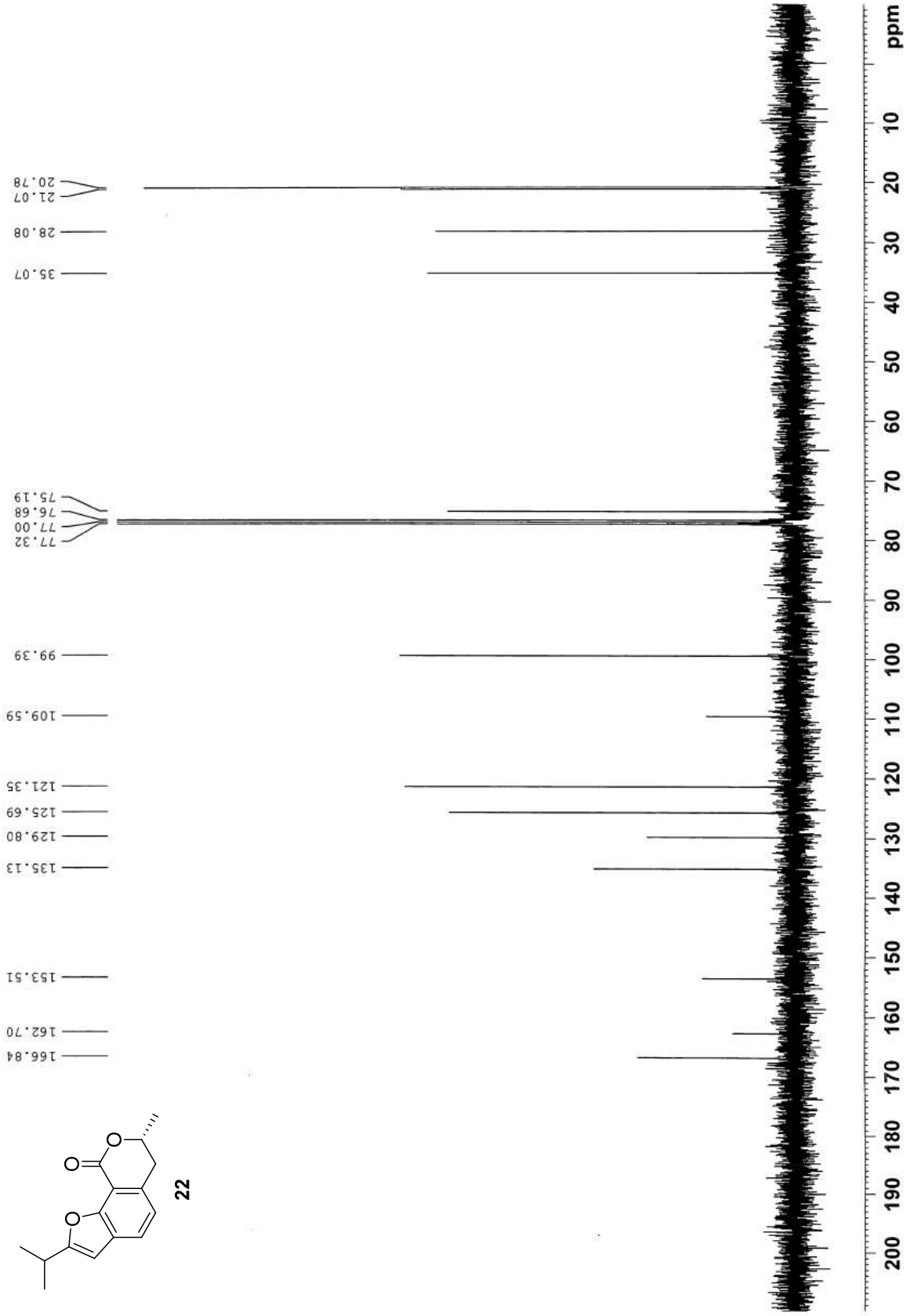


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 23

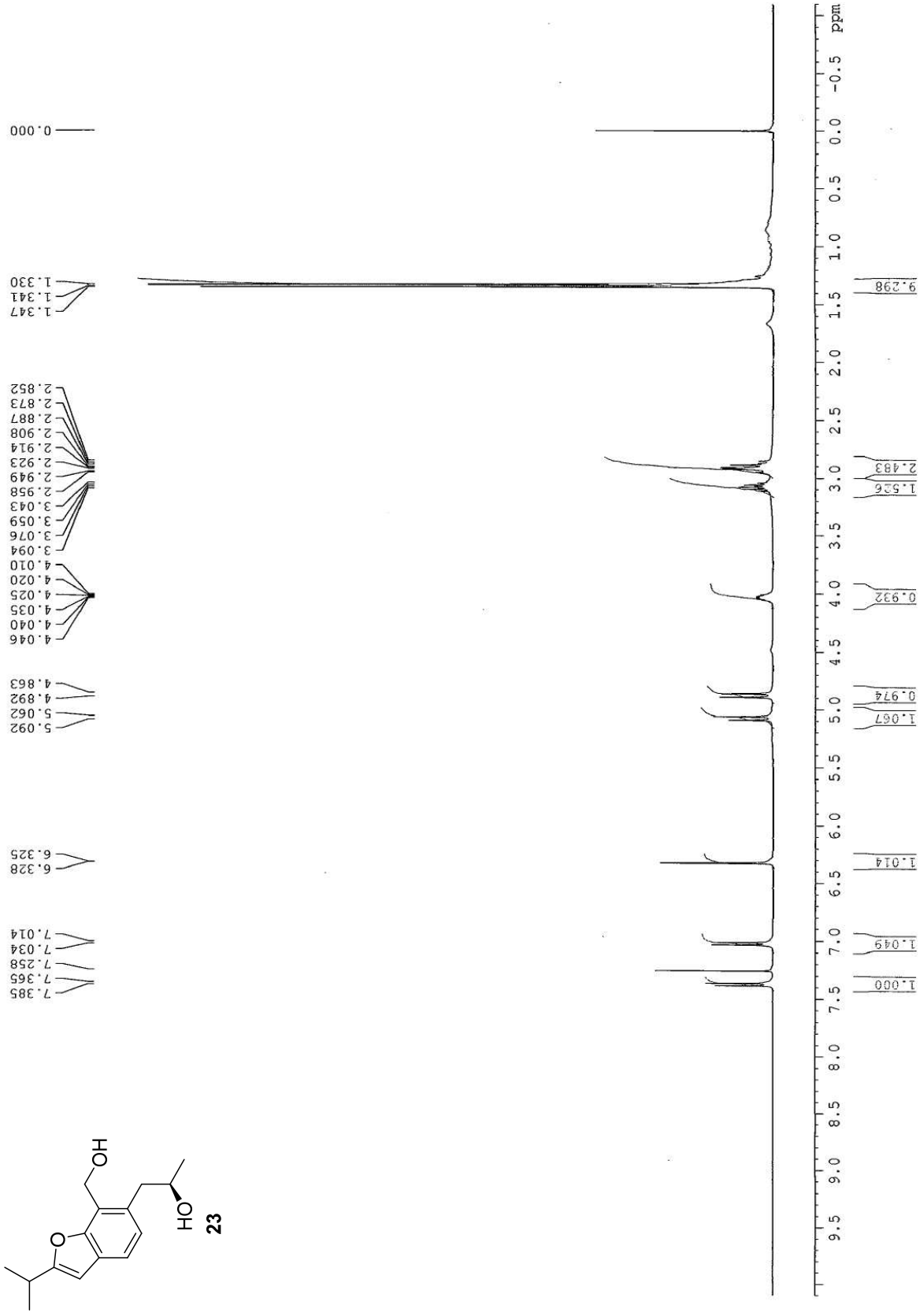


Figure S4. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 23

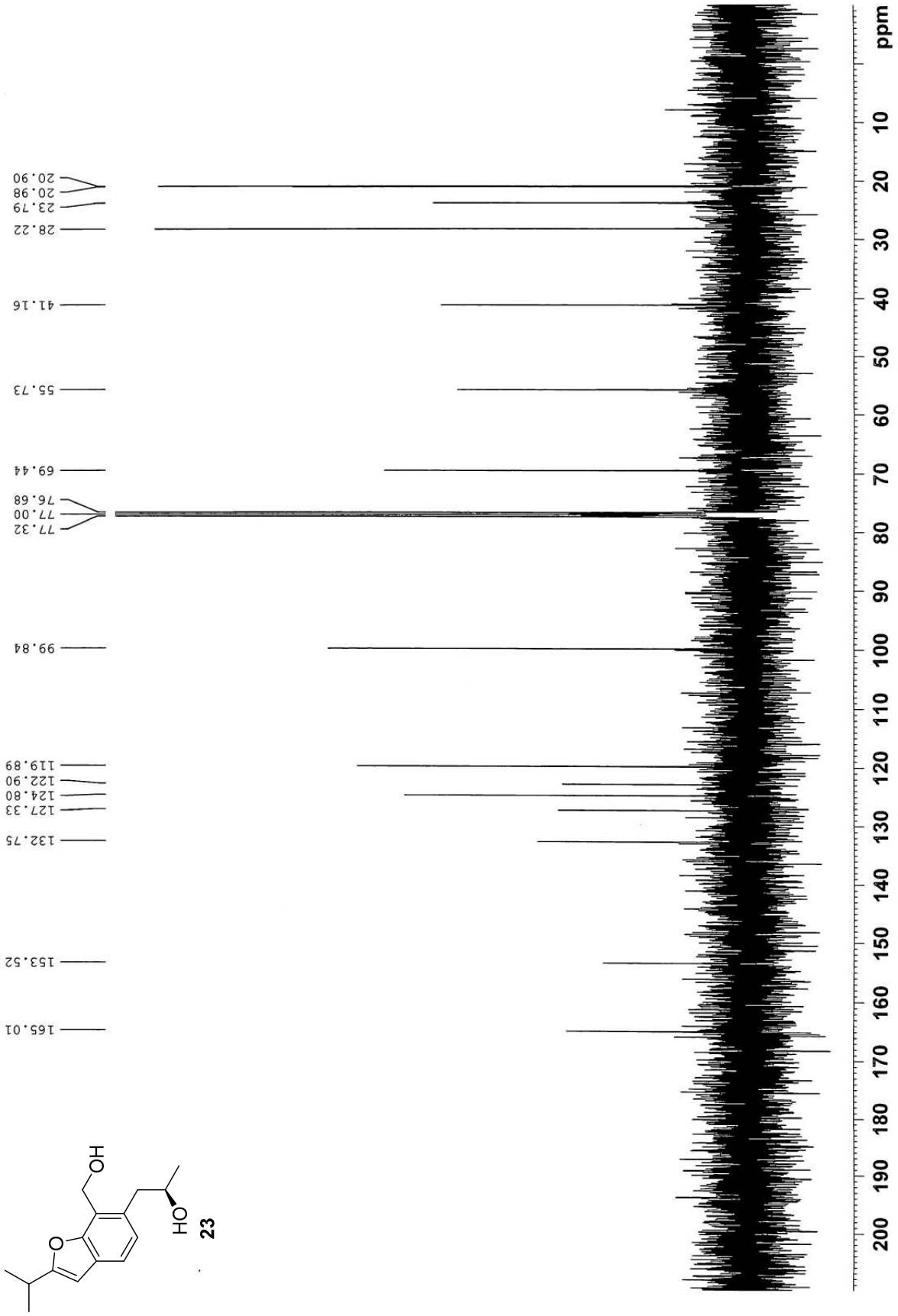


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 24

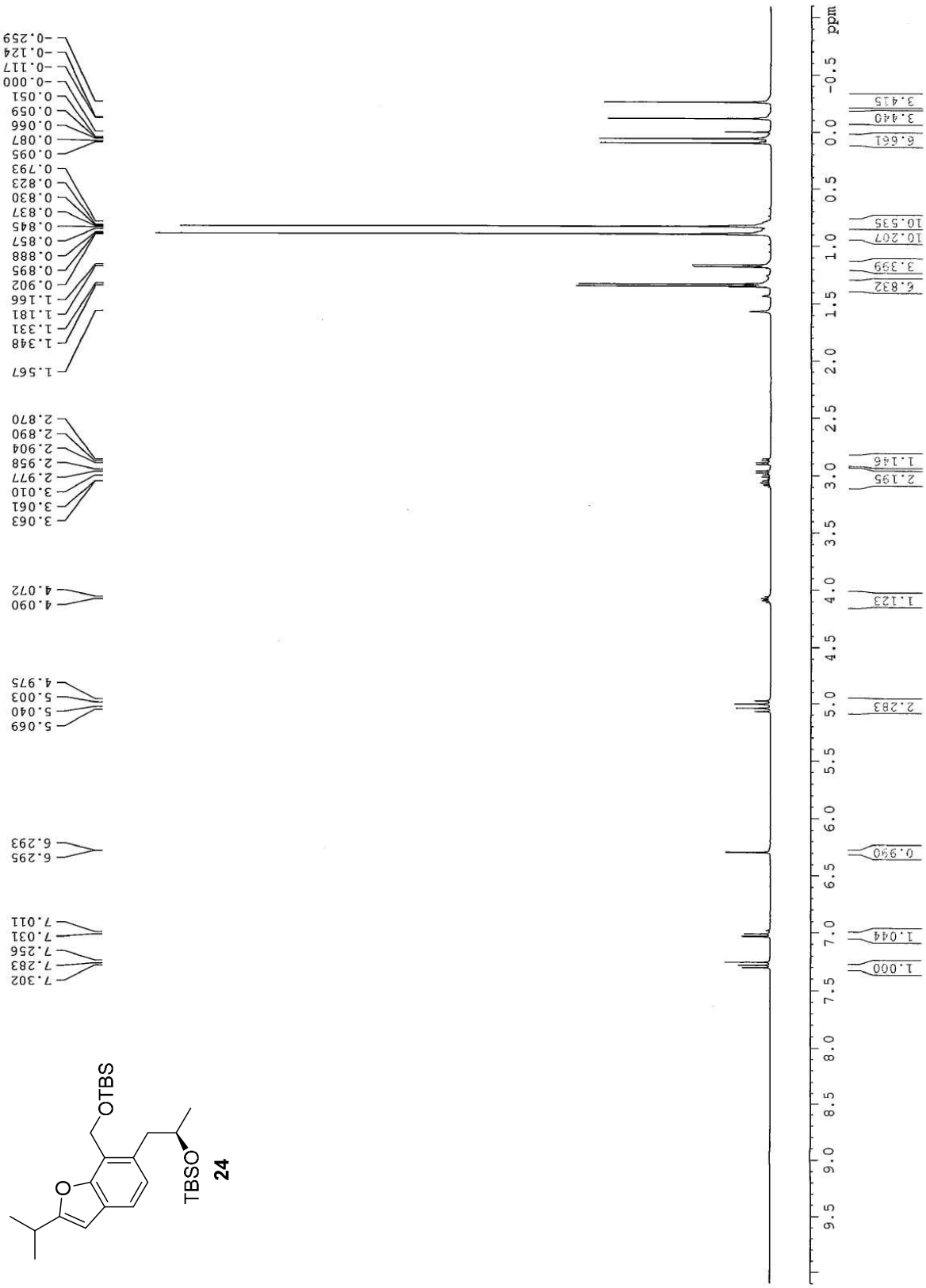


Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 24

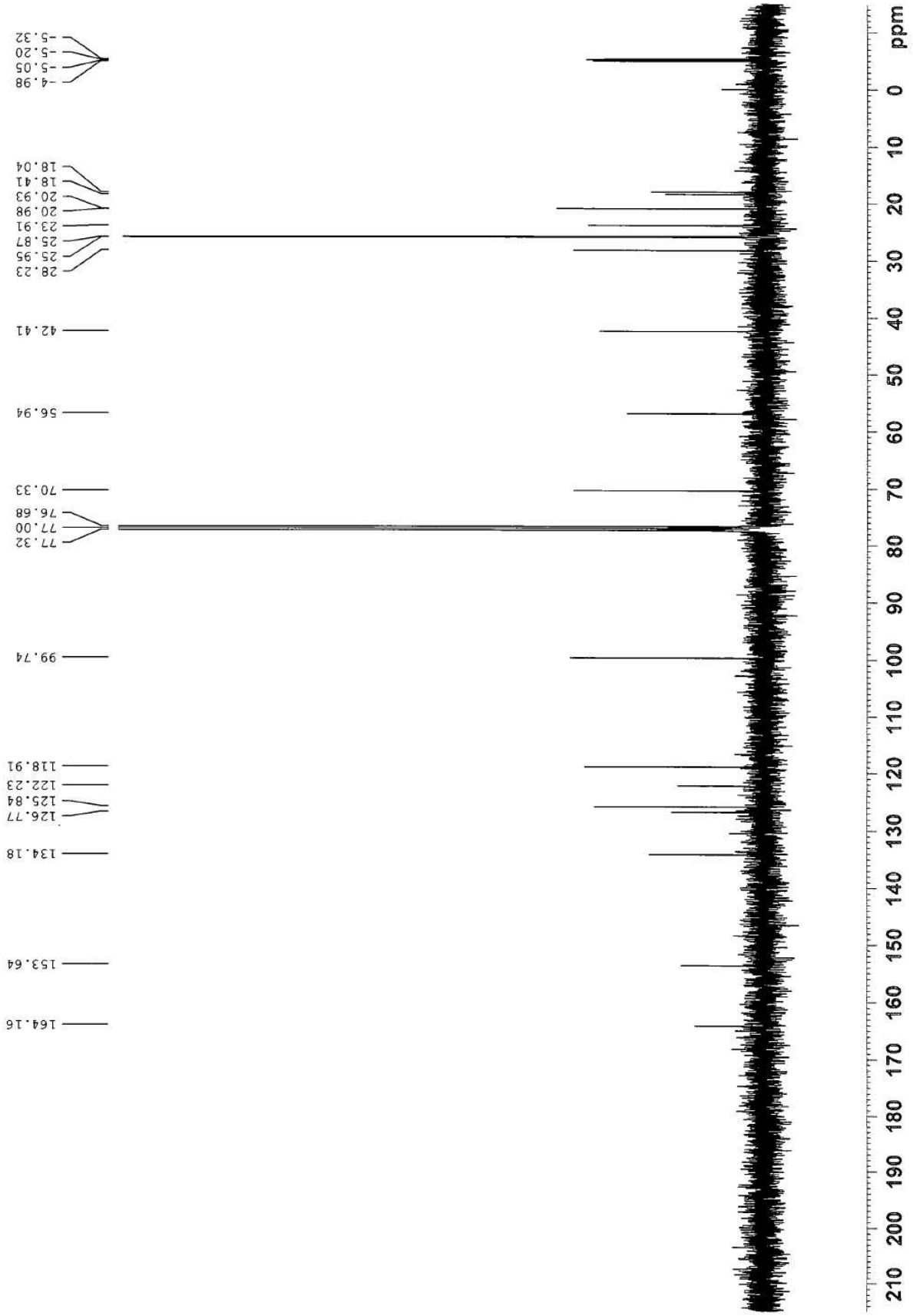


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 25

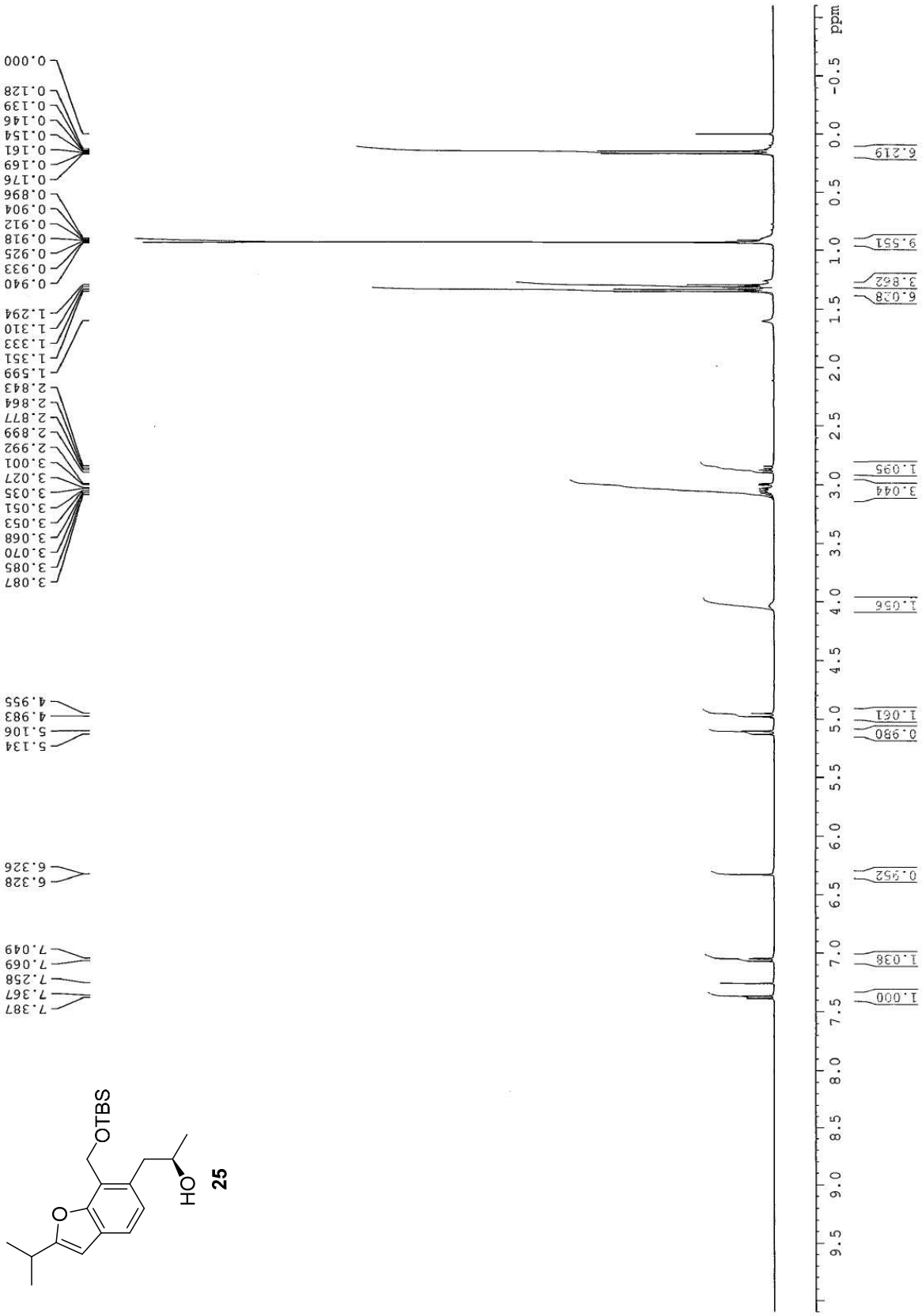


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 25

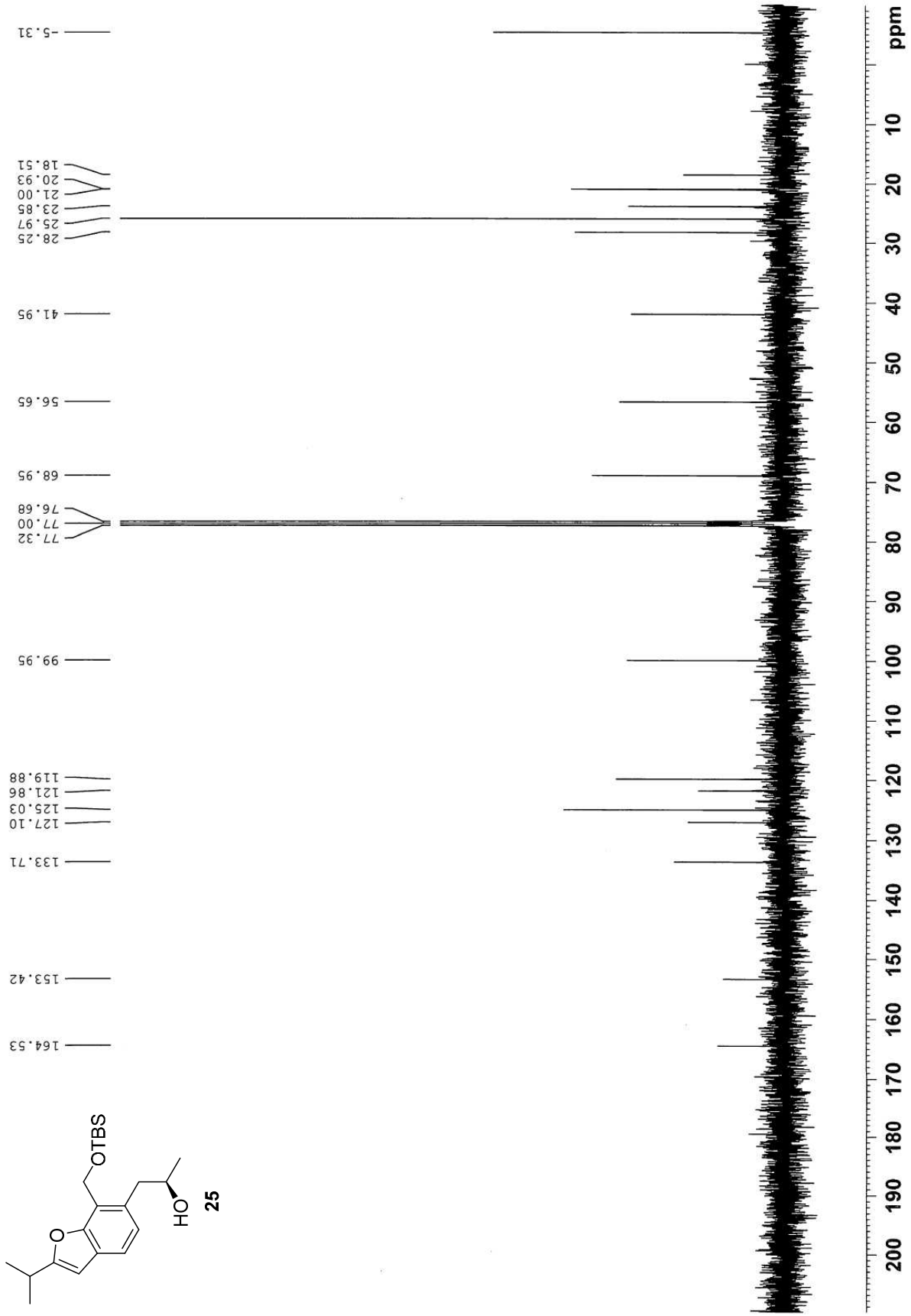


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 26

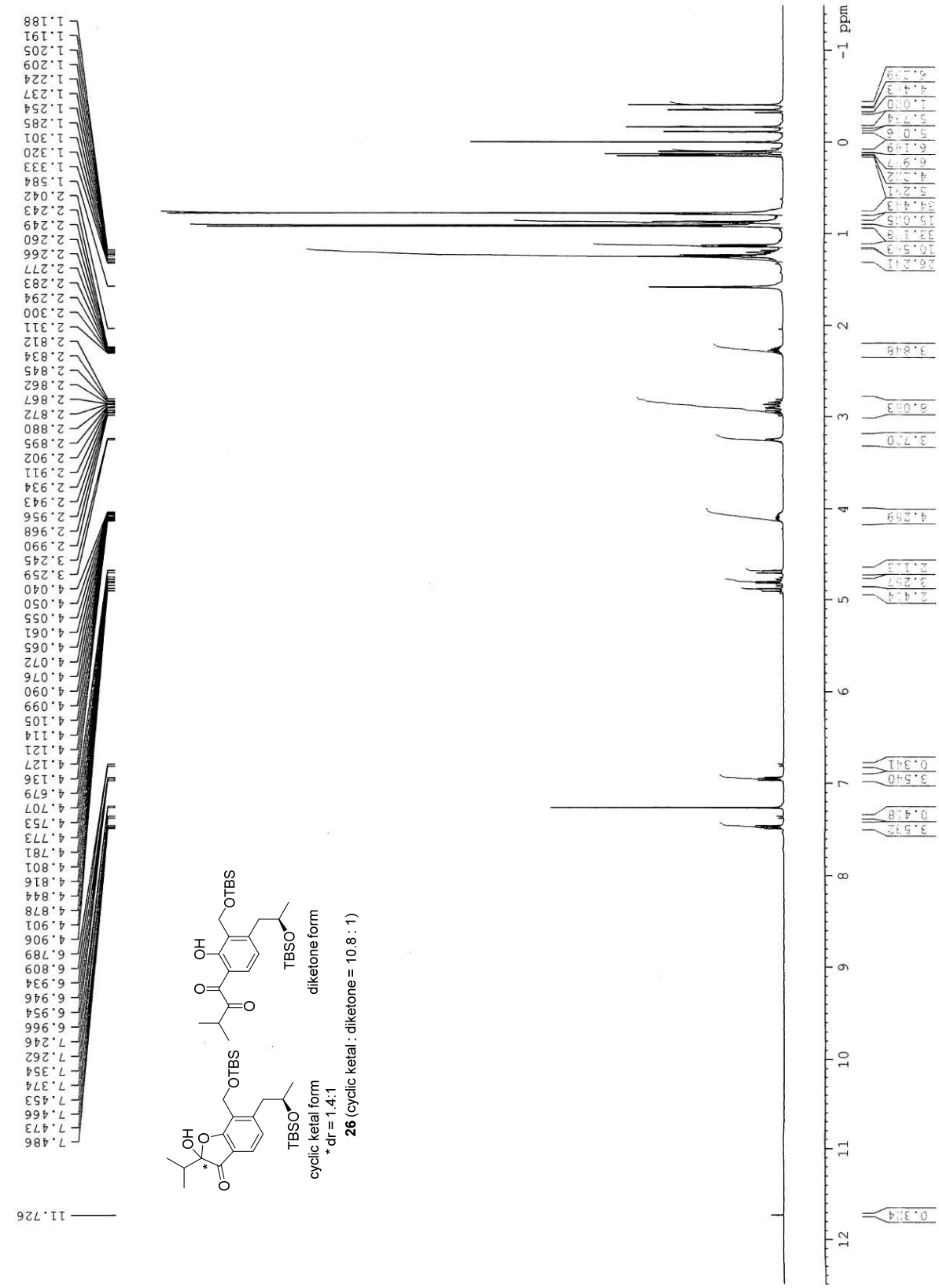


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 26

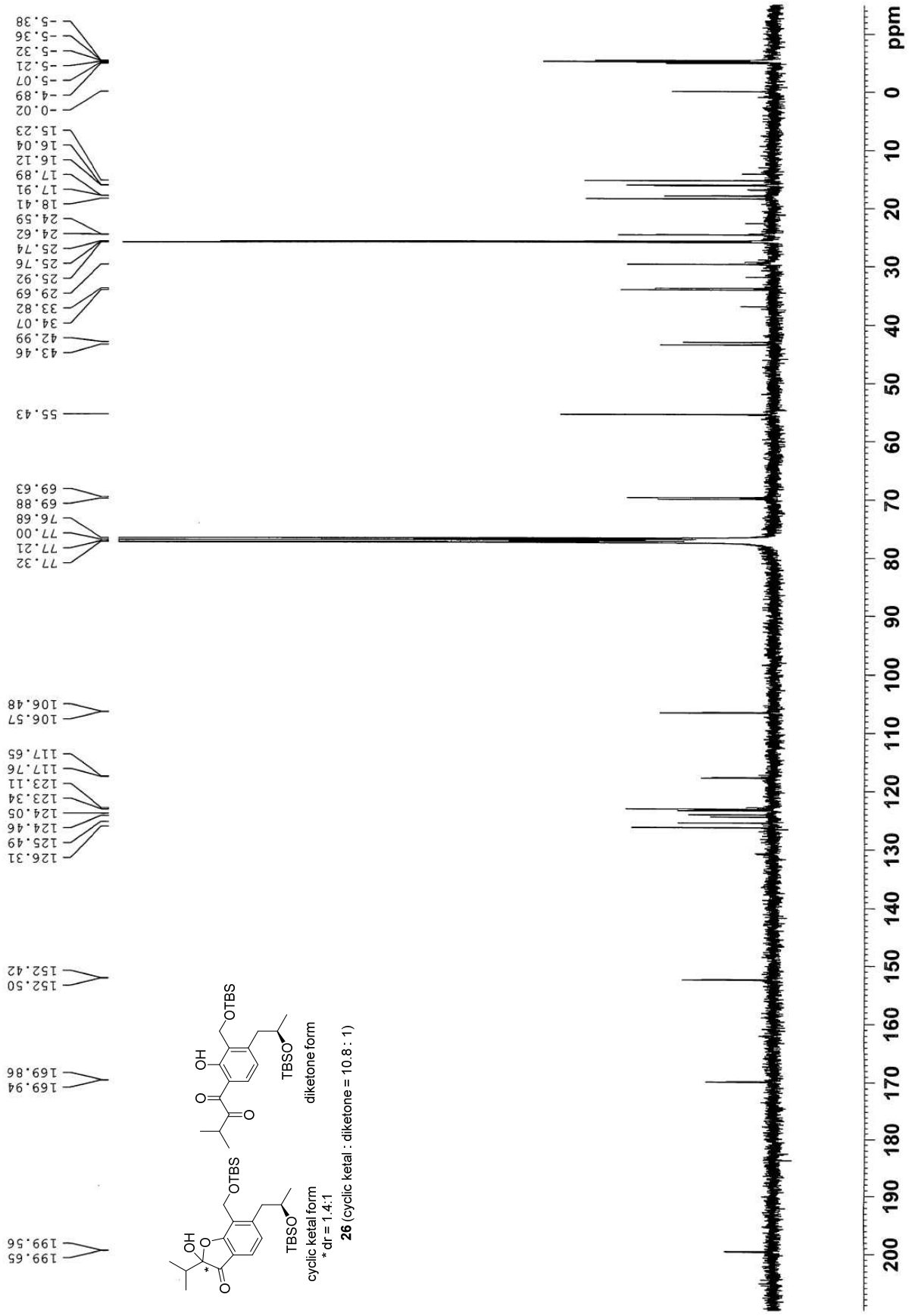


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 27

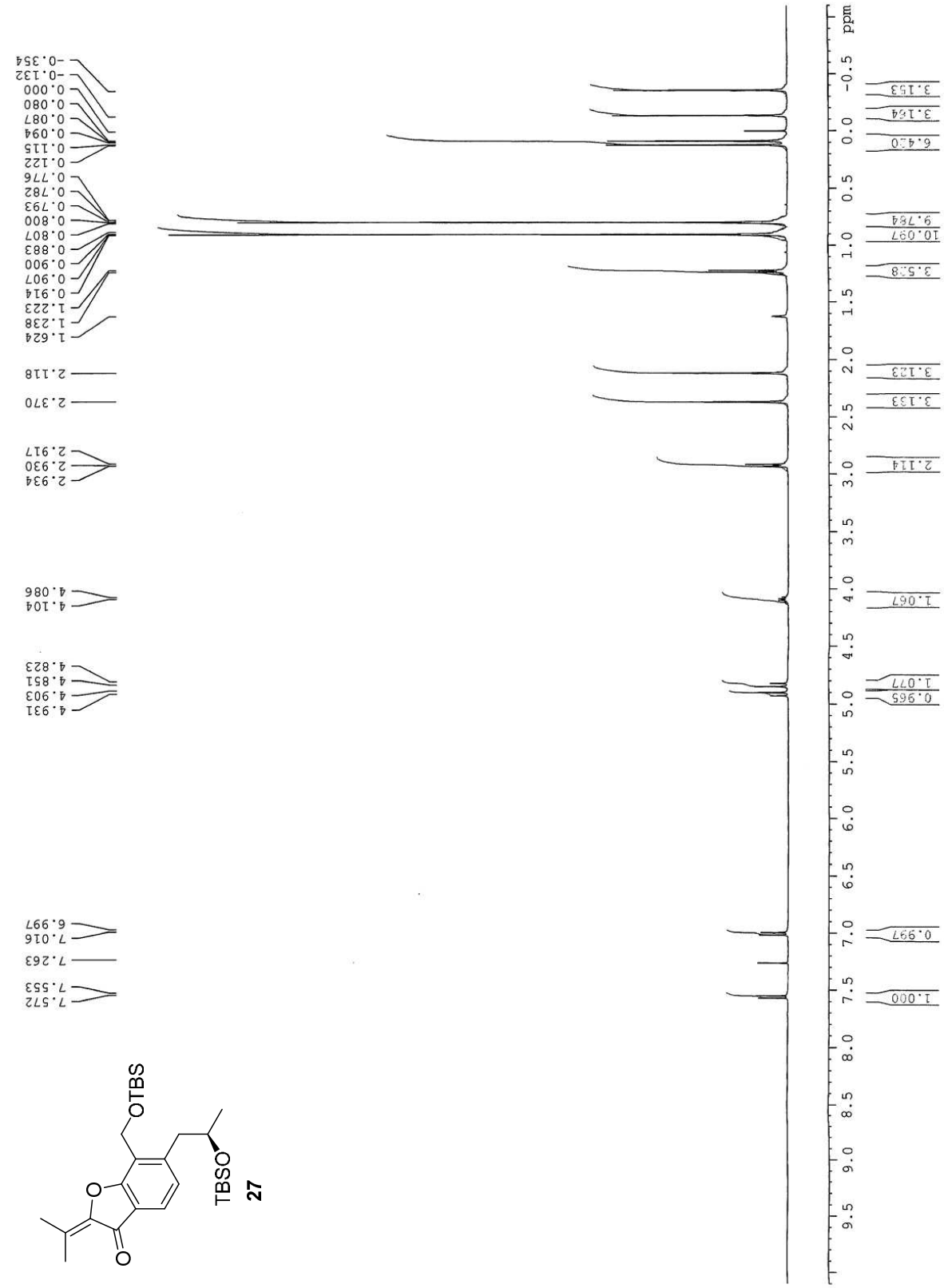


Figure S12. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 27

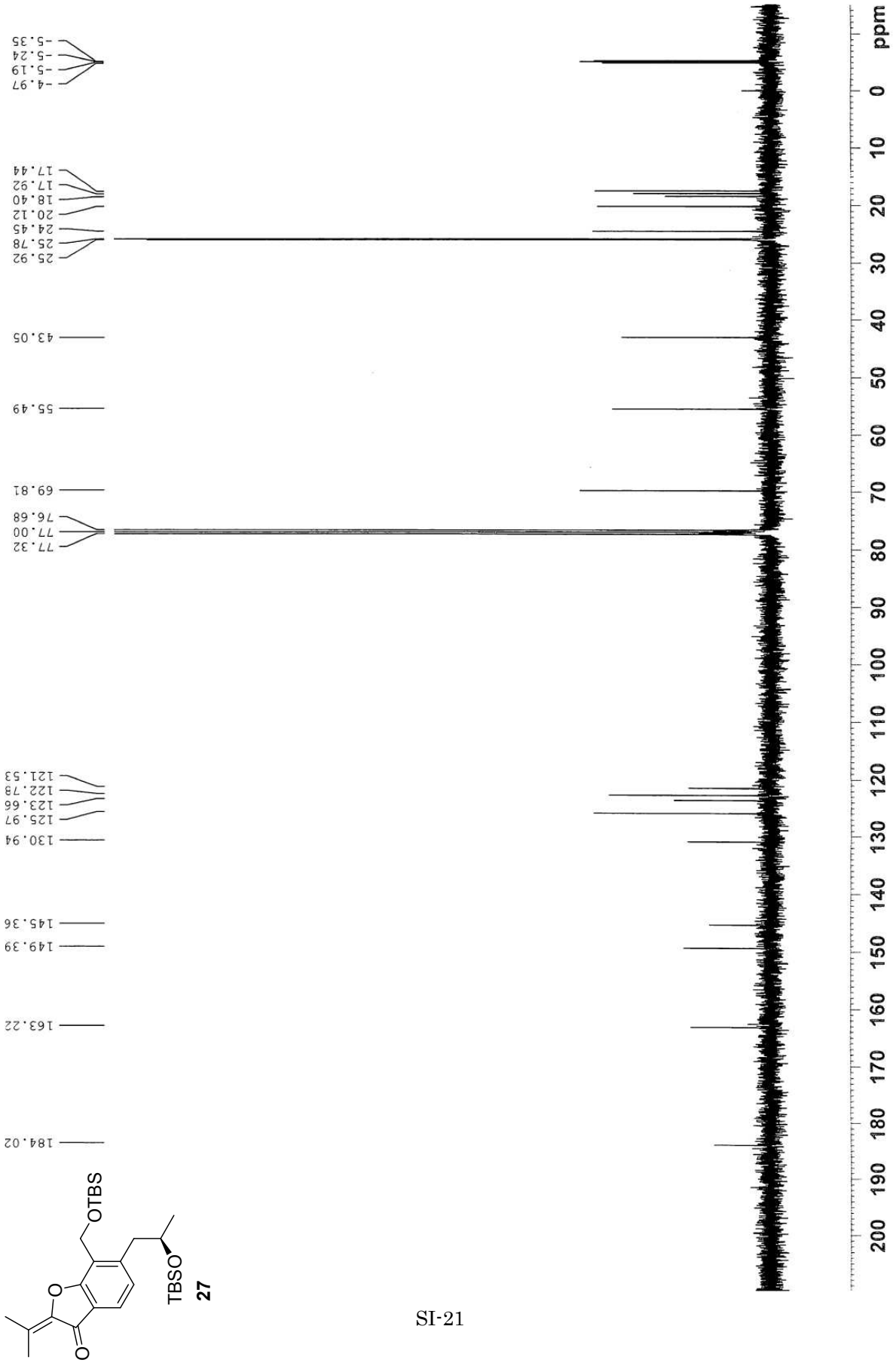


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Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ustusorane A (1)

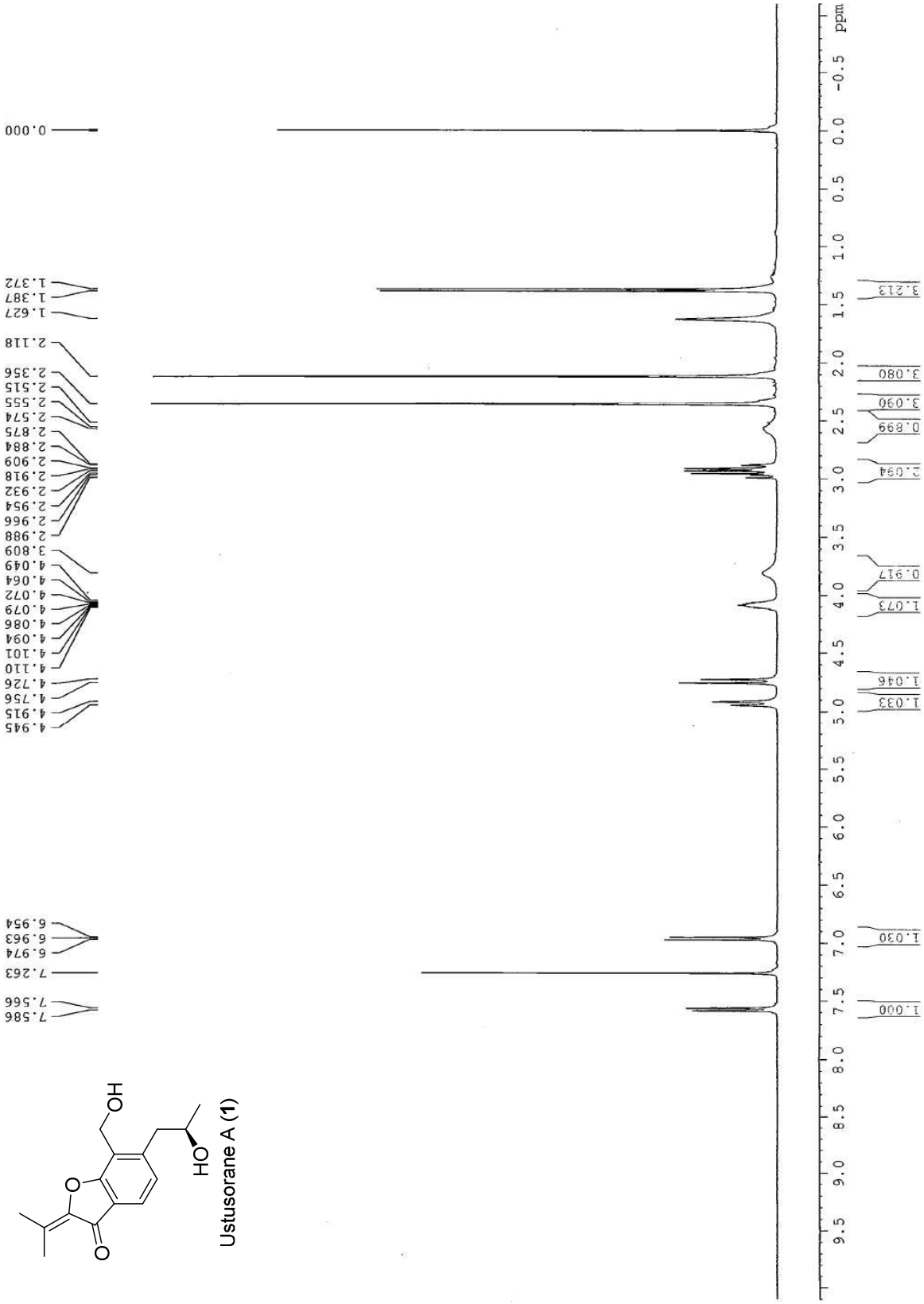


Figure S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of ustusorane A (1)

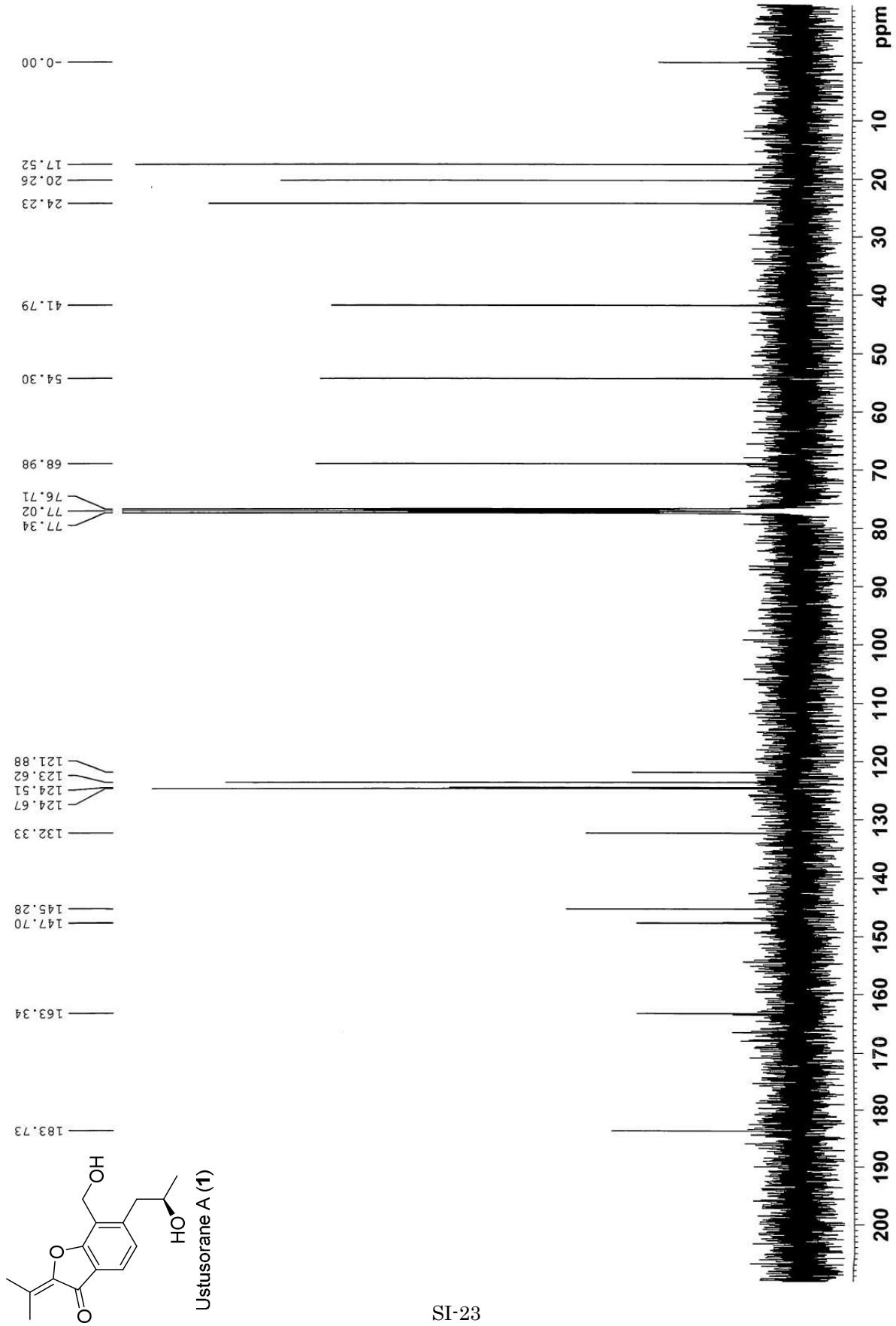


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 28

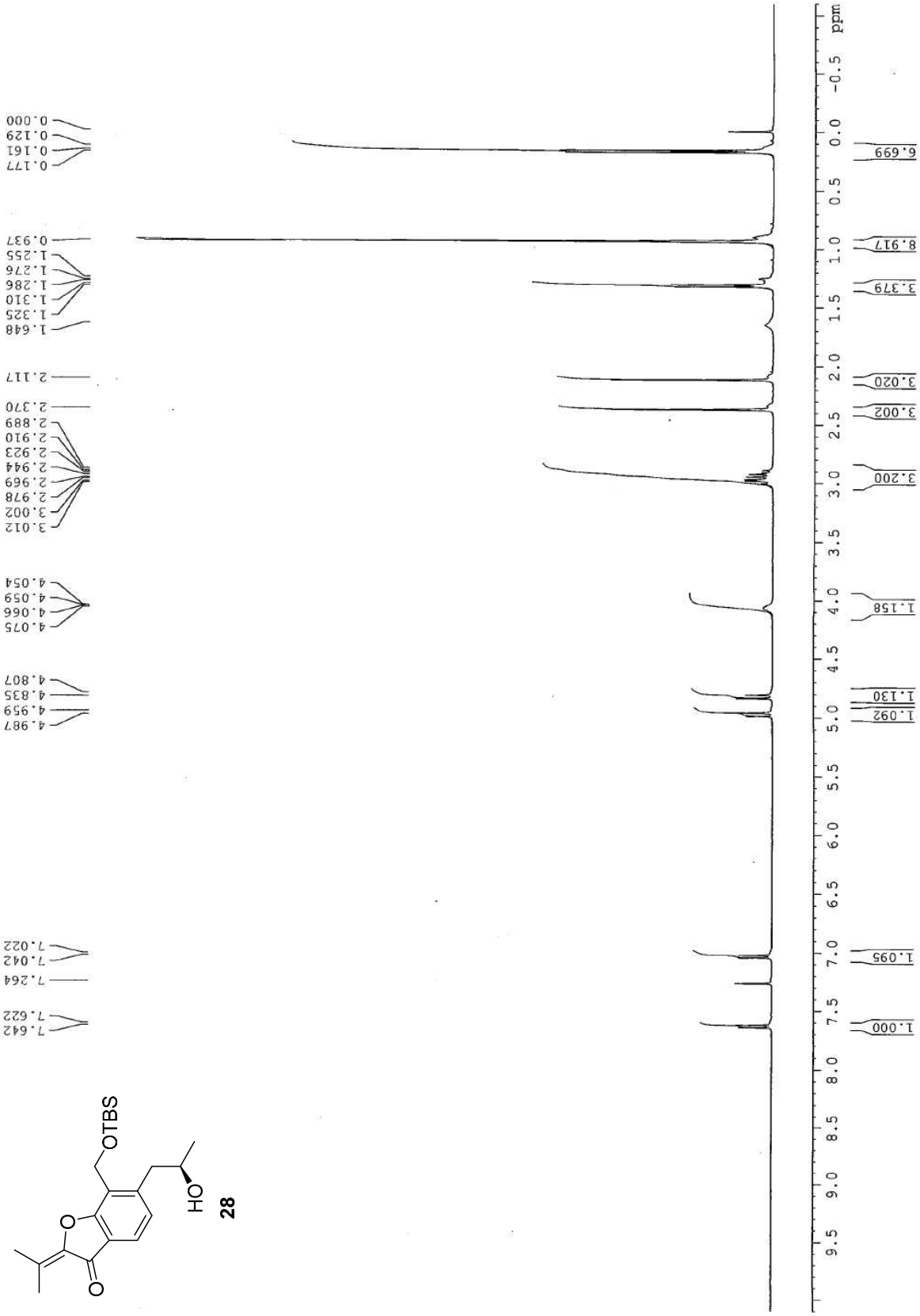


Figure S16. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 28

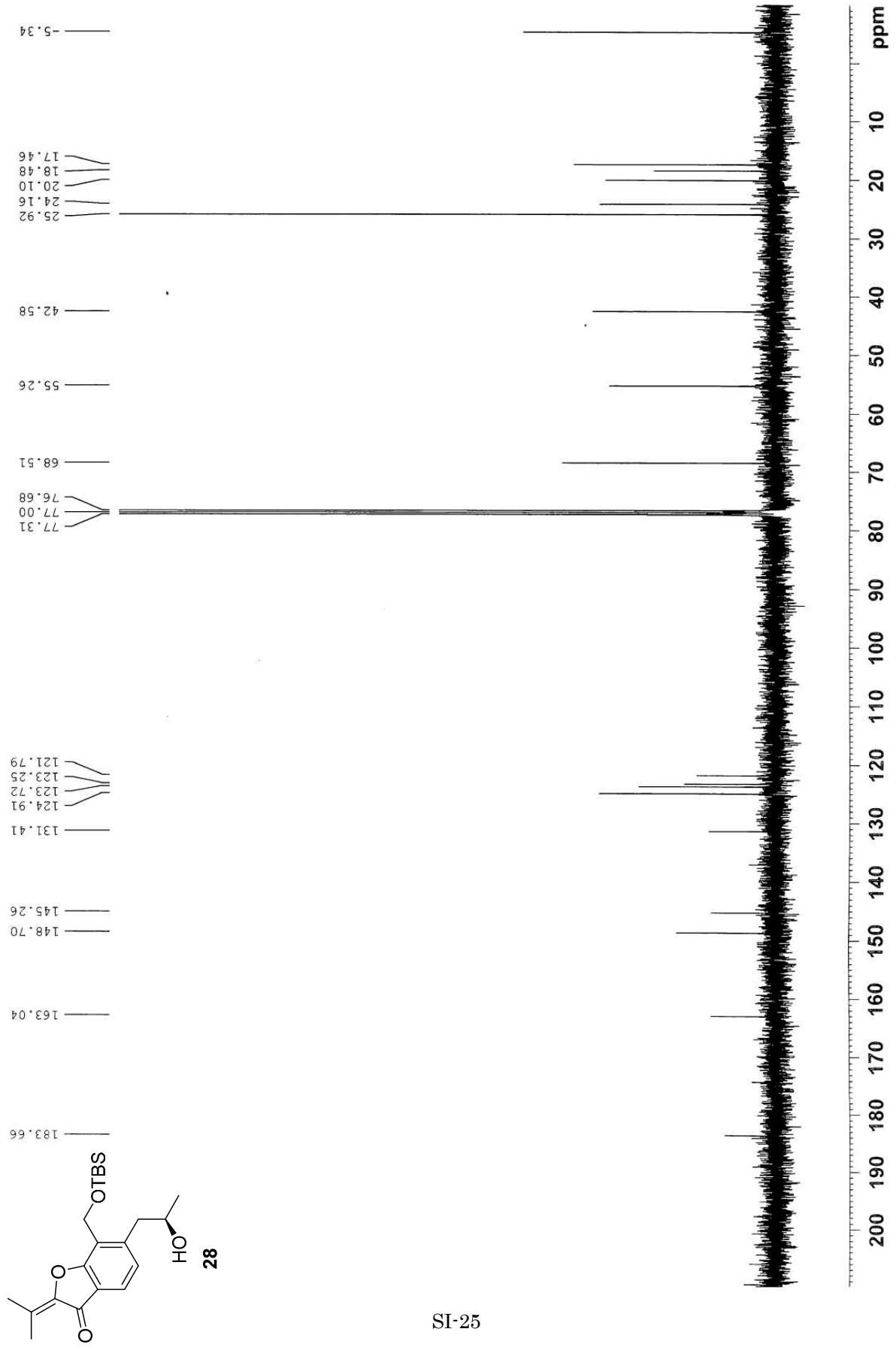


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 29

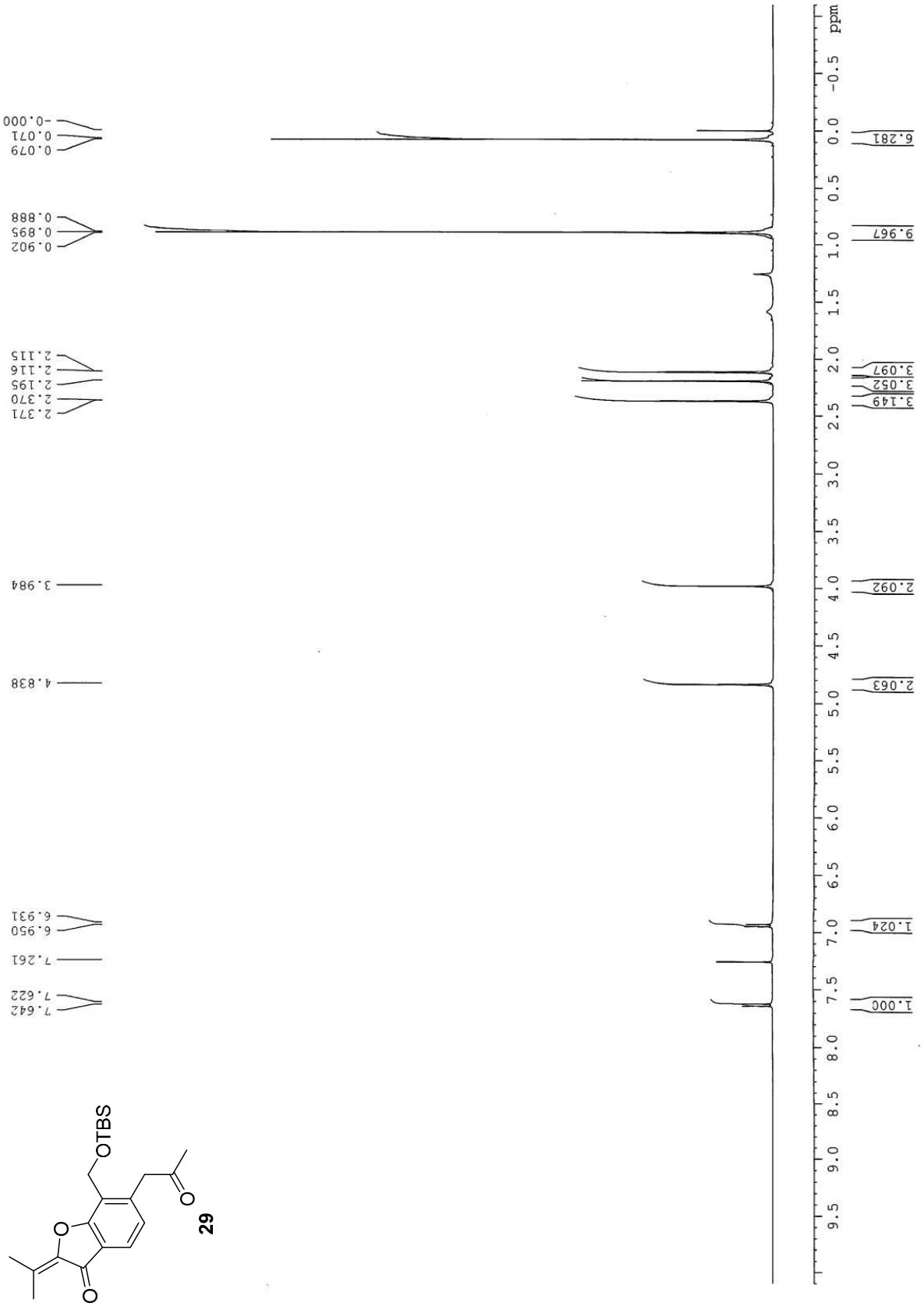


Figure S18. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 29

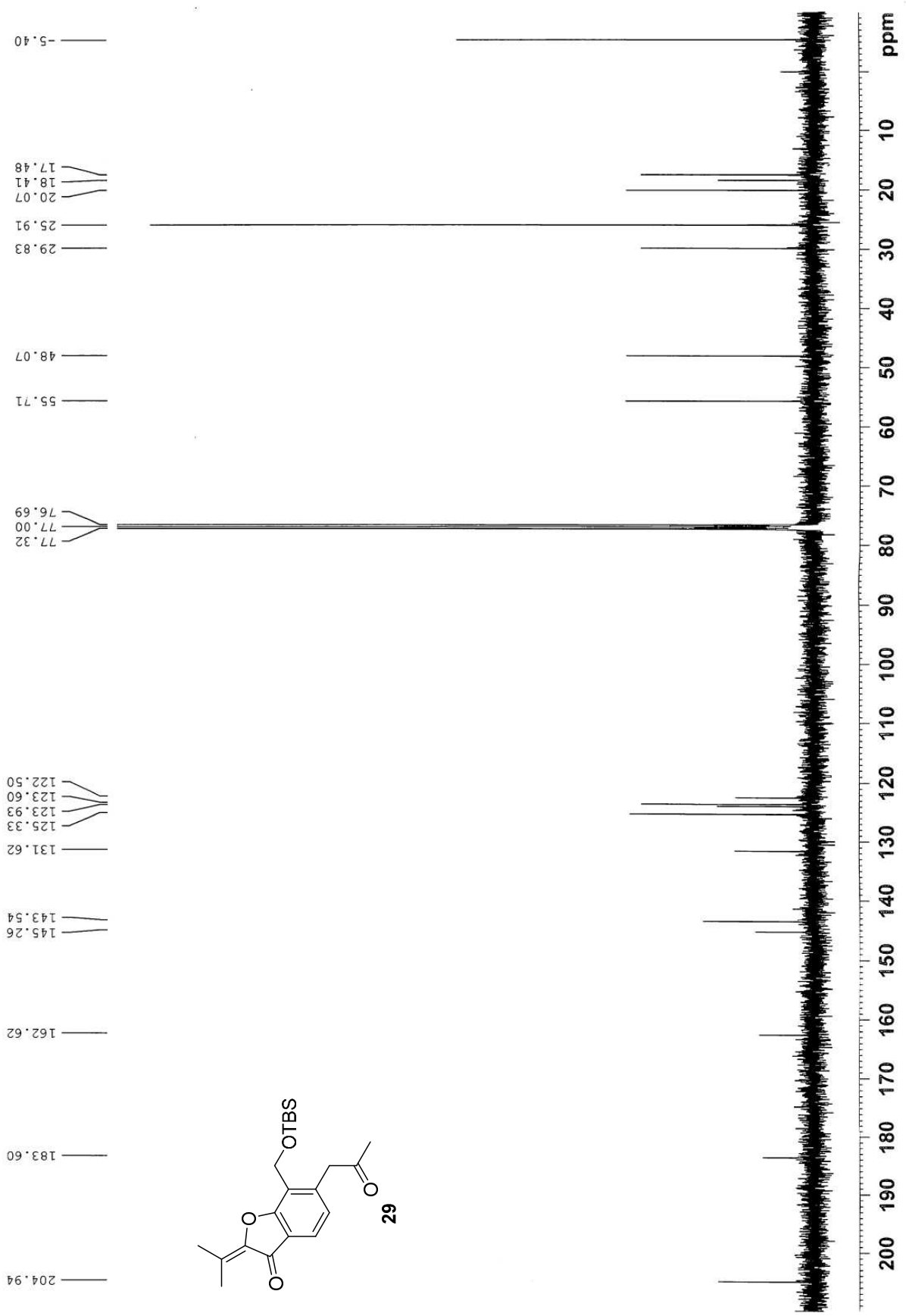


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$:DMSO-d_6 = 1:1) of pergillin (4)

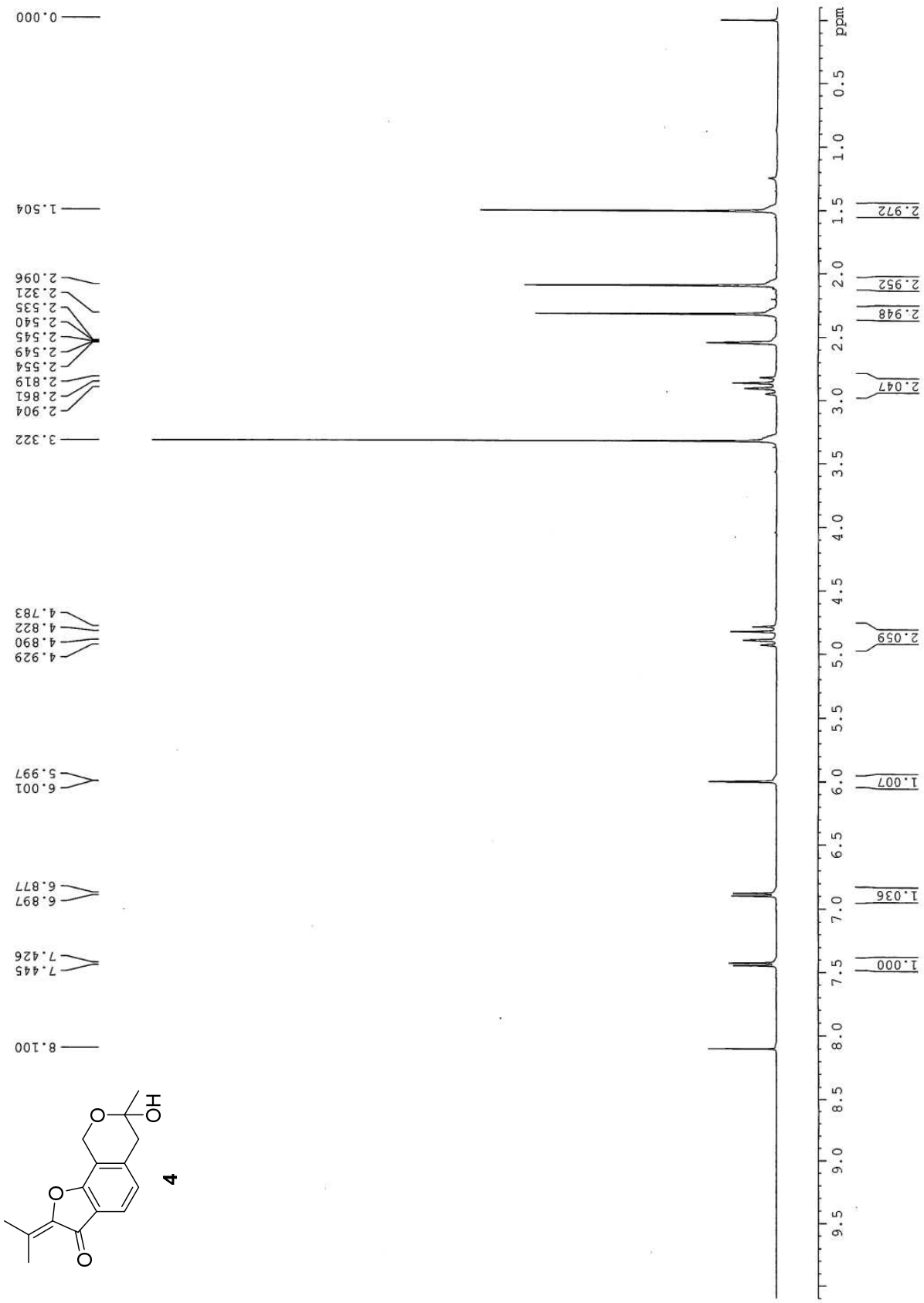


Figure S20. ^{13}C NMR spectrum (100 MHz, $CDCl_3$:DMSO-d_6 = 1:1) of pergillin (4)

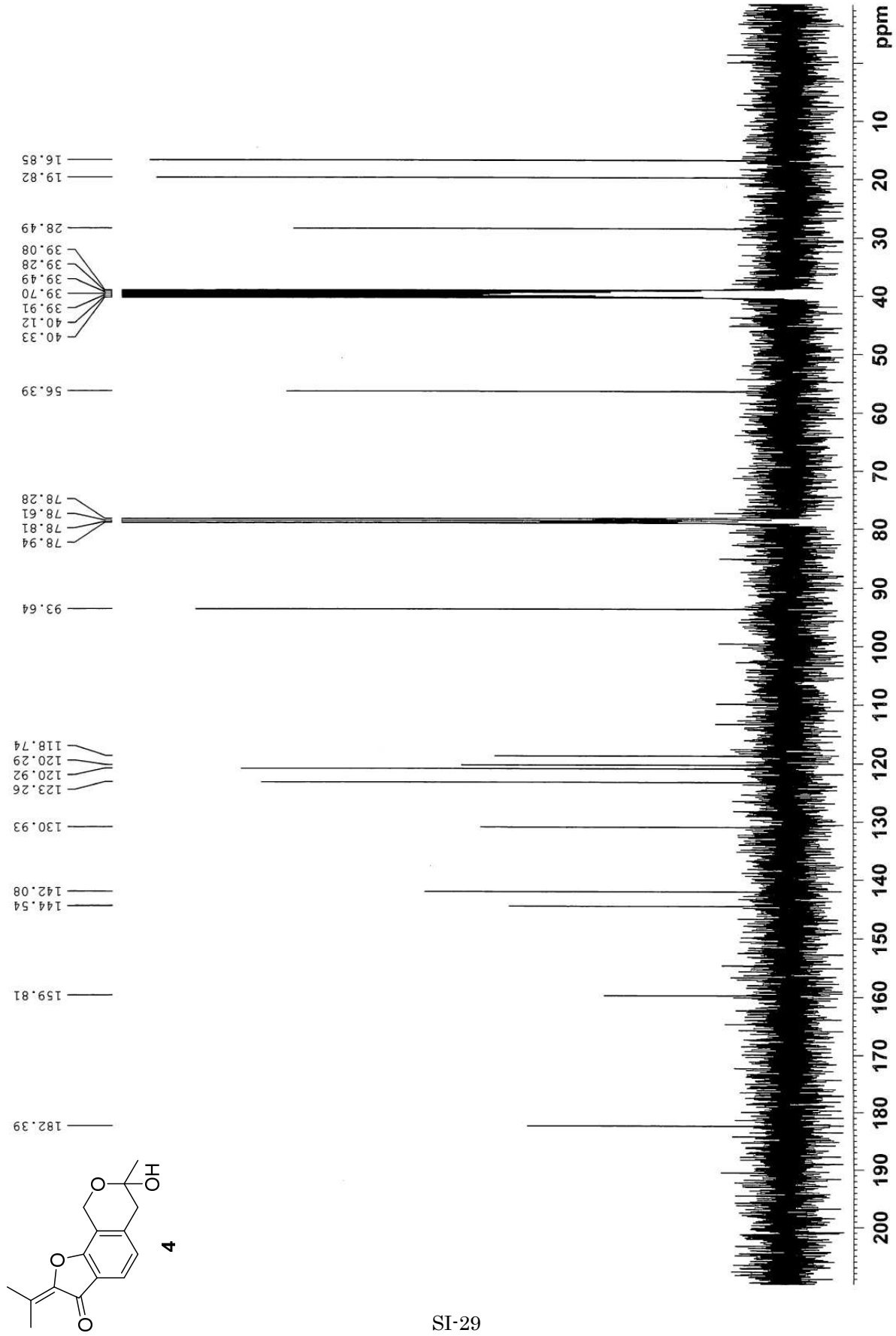


Figure S21. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of pergillin (4)

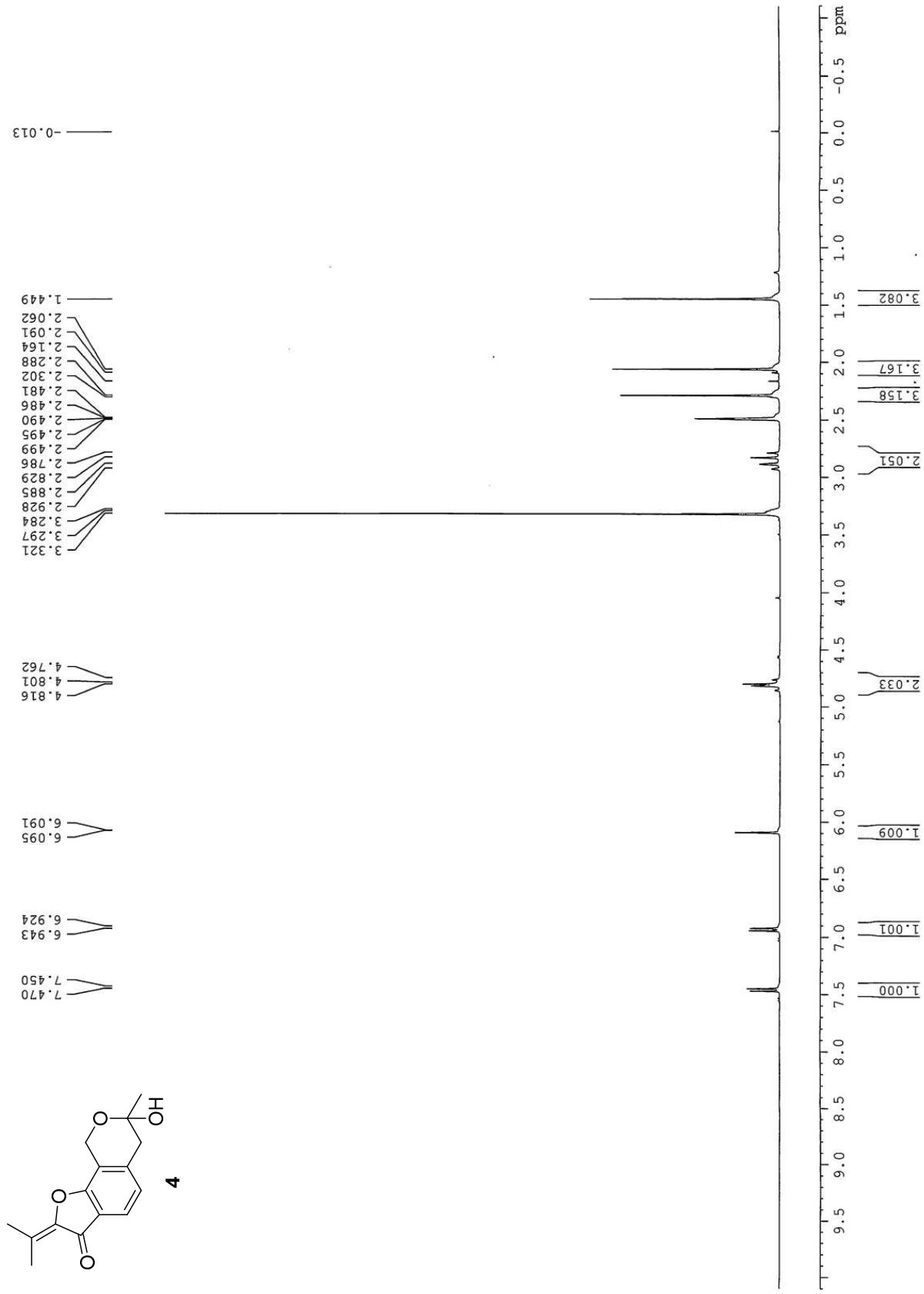


Figure S22. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of pergillin (4)

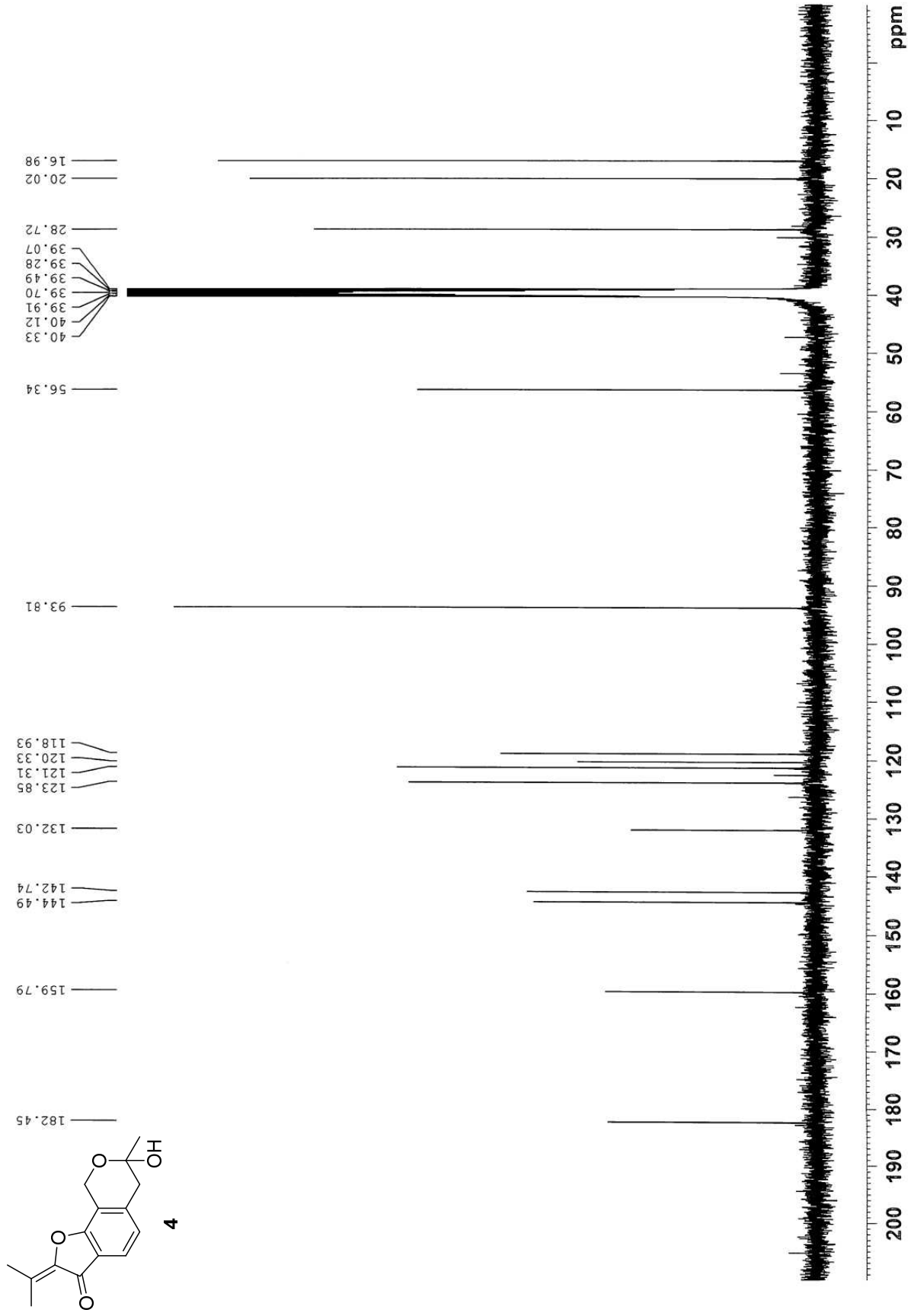


Figure S23. ^{1}H NMR spectrum (400 MHz, CD_3OD) of pergillin (4)

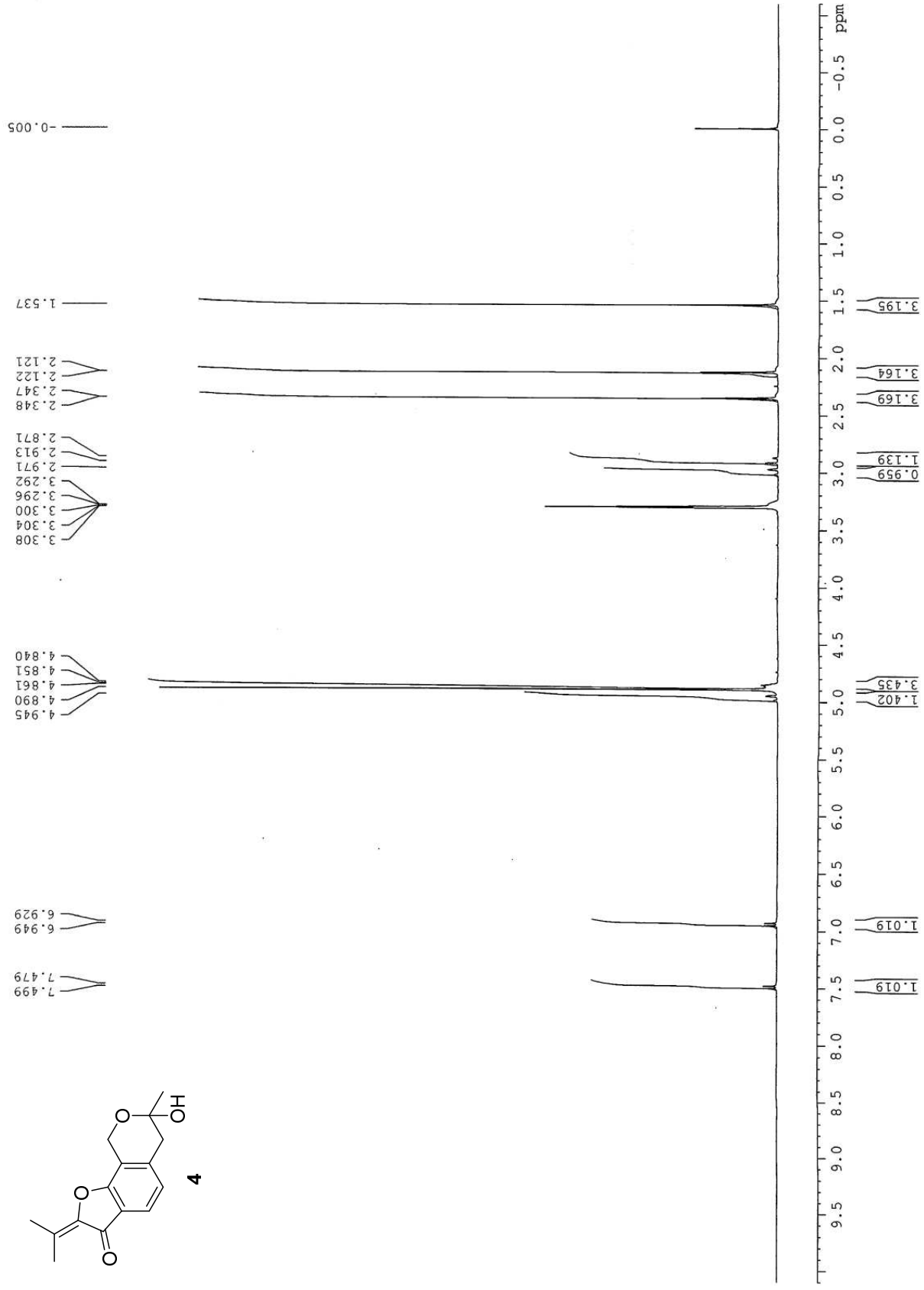


Figure S24. ^{13}C NMR spectrum (100 MHz, CD_3OD) of pergillin (4)

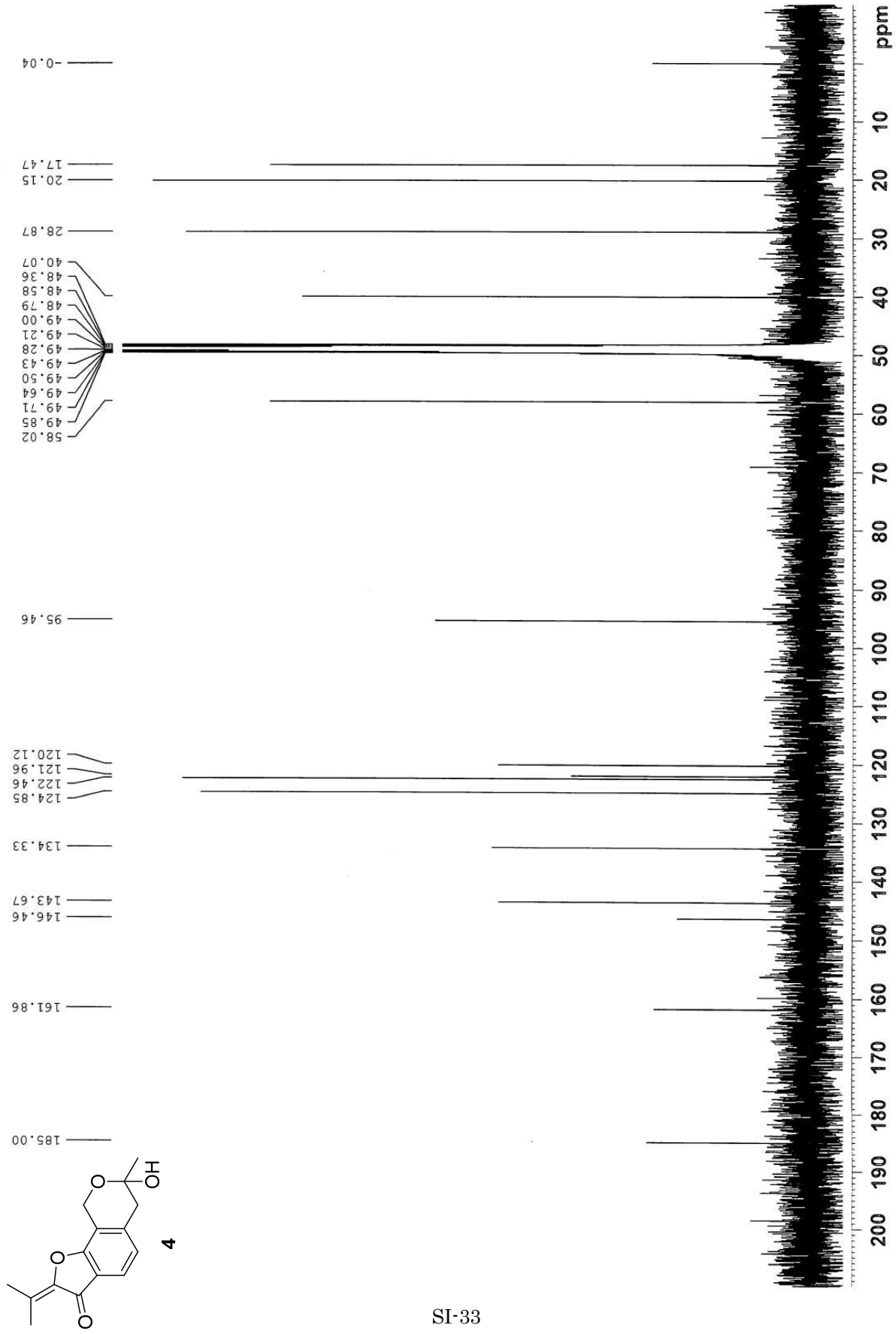


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of dihydropergillin (5) and its 7-epimer (5')

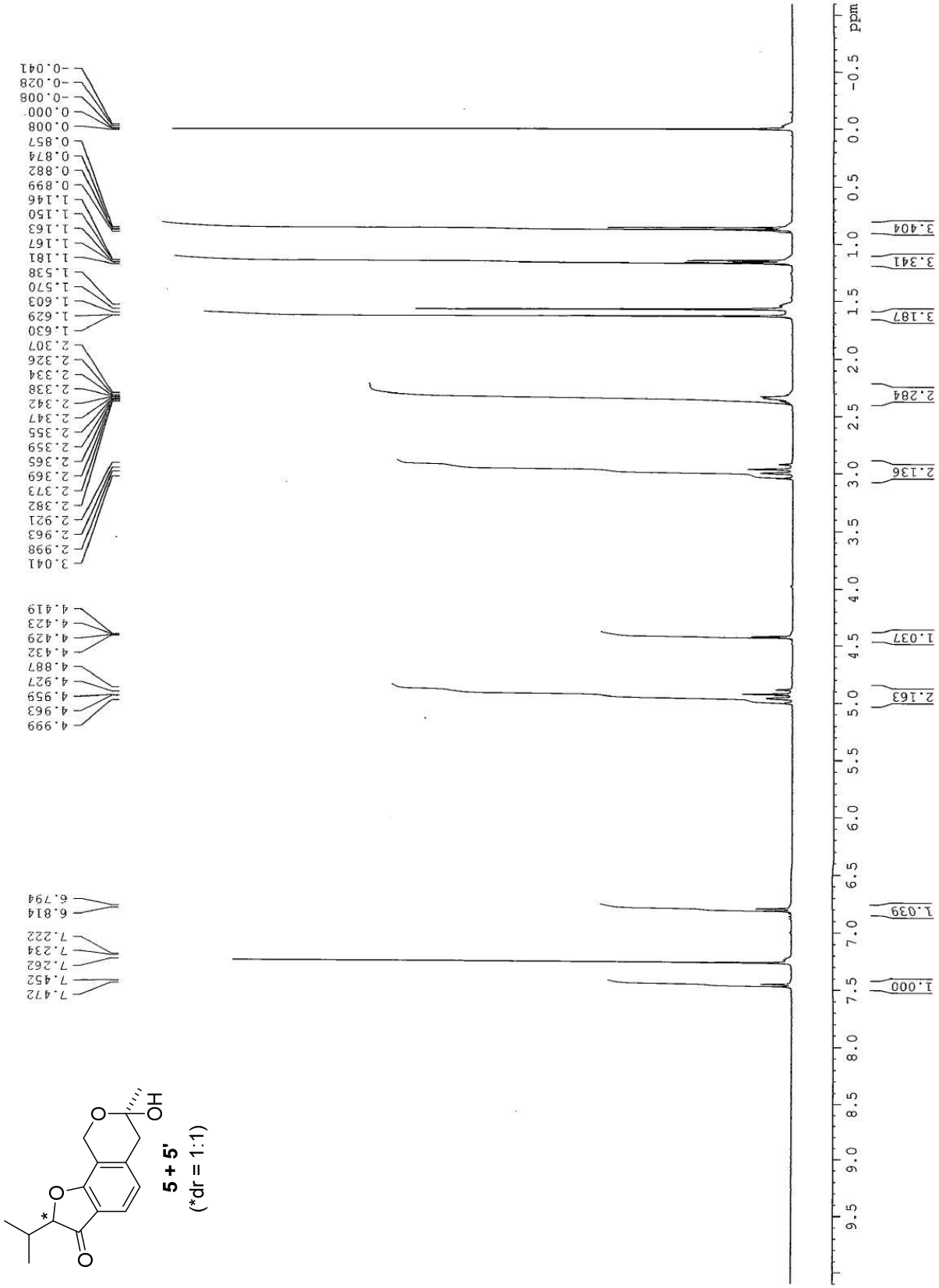


Figure S26. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of dihydropergillin (5) and its 7-epimer (5')

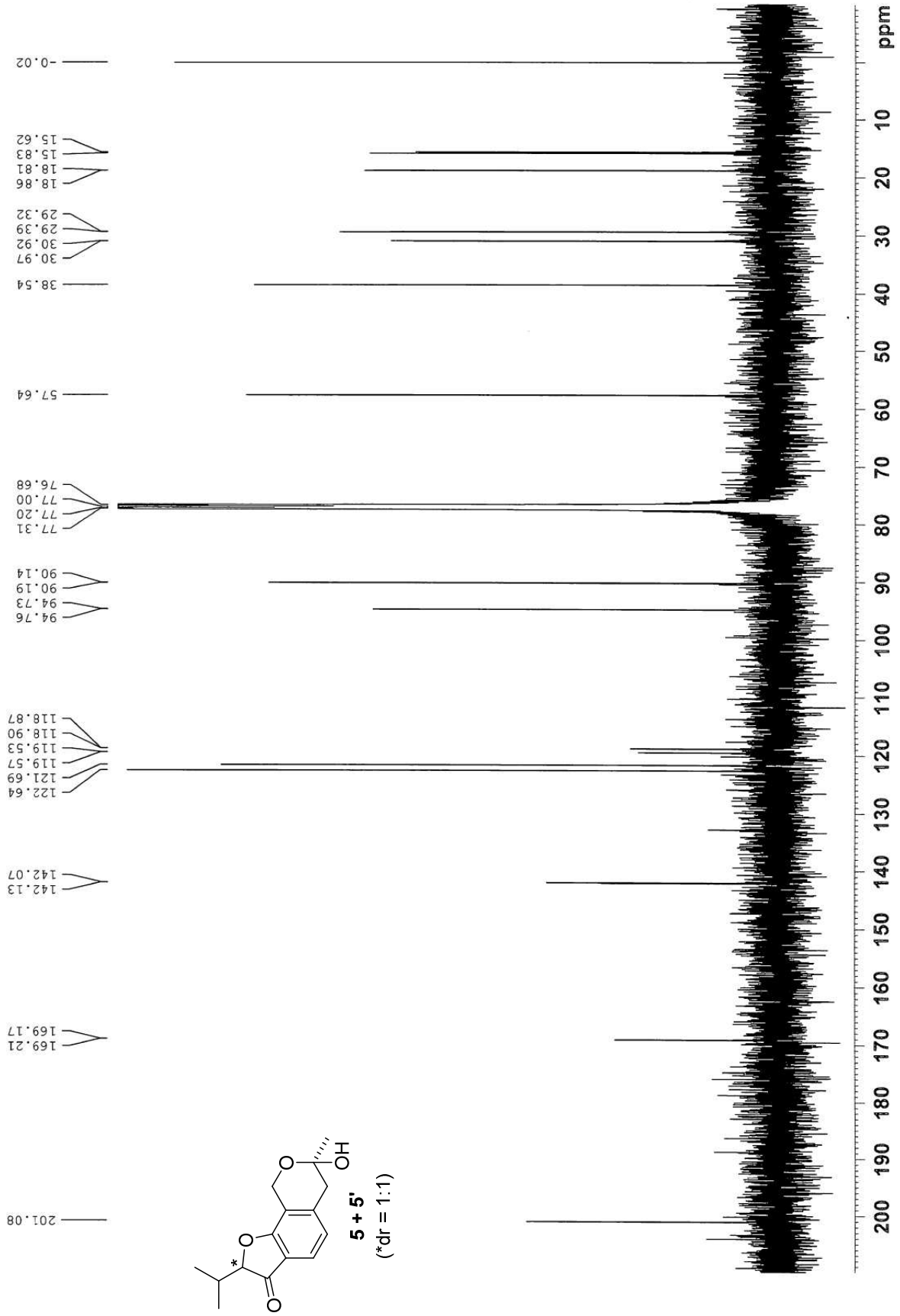


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of penicisochroman A (6)

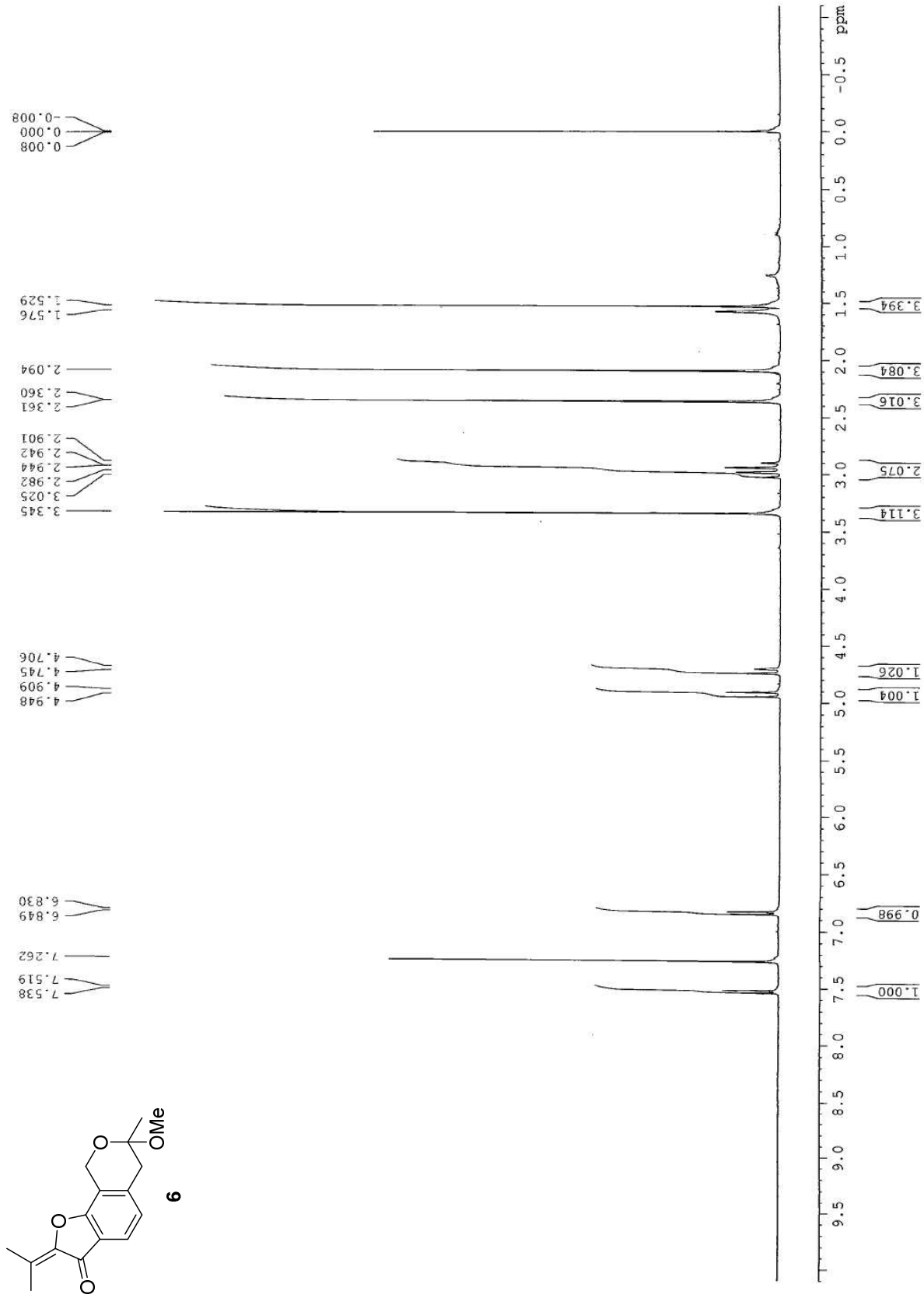


Figure S28. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of penicisochroman A (6)

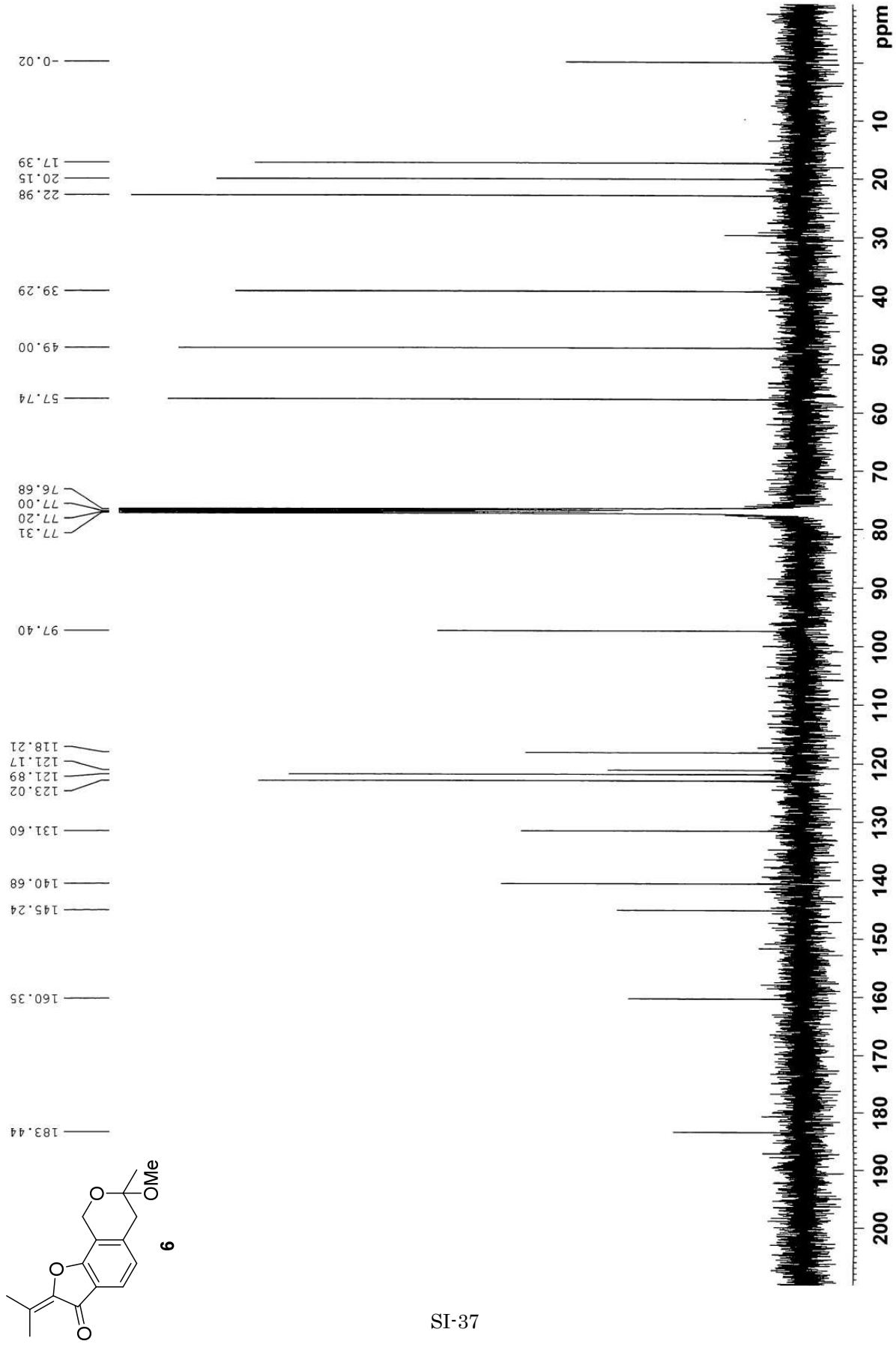


Figure S29. ^{1}H NMR spectrum (400 MHz, CD_3OD) of penicisochroman A (6)

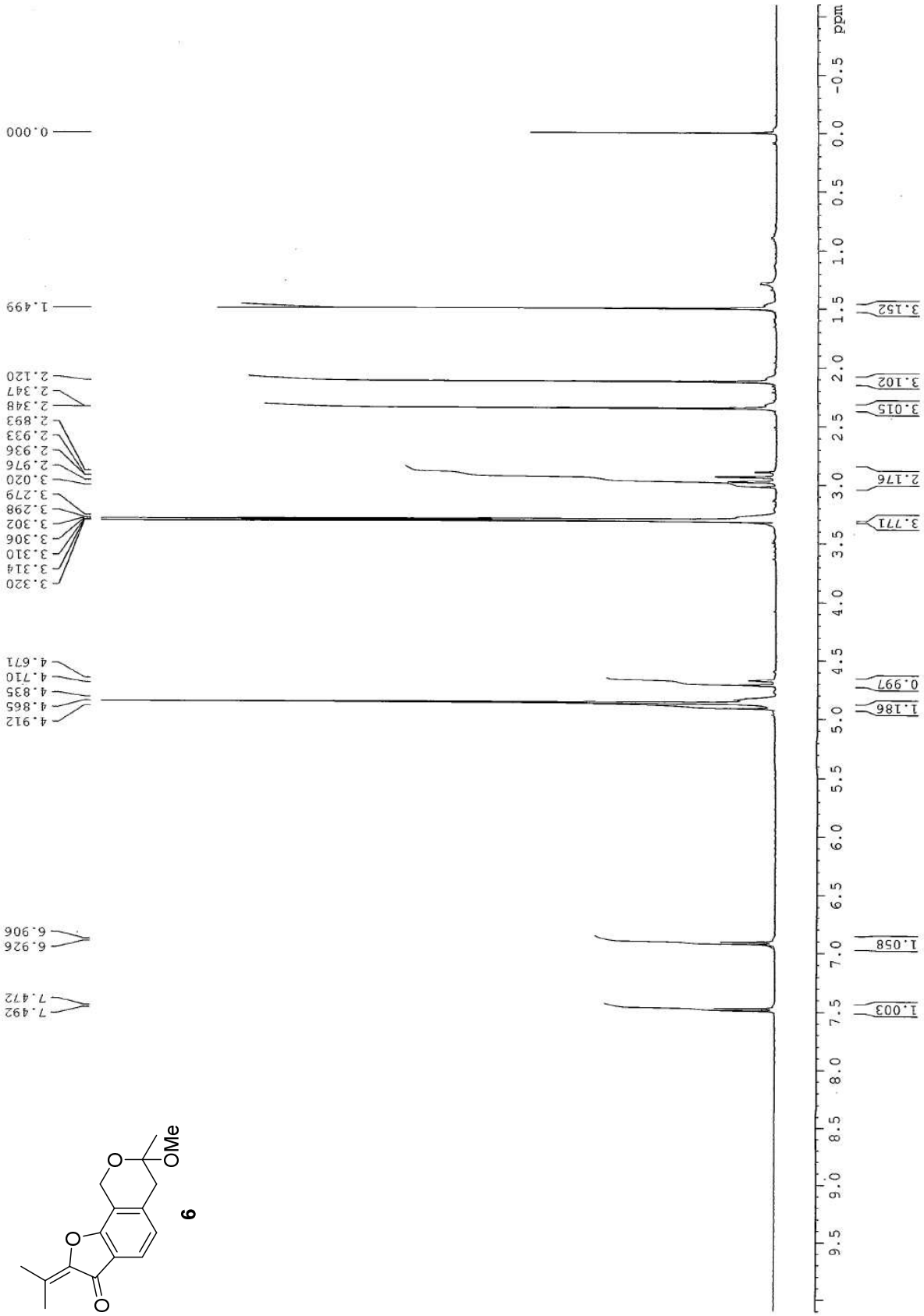


Figure S30. ^{13}C NMR spectrum (100 MHz, CD_3OD) of penicisochroman A (6)

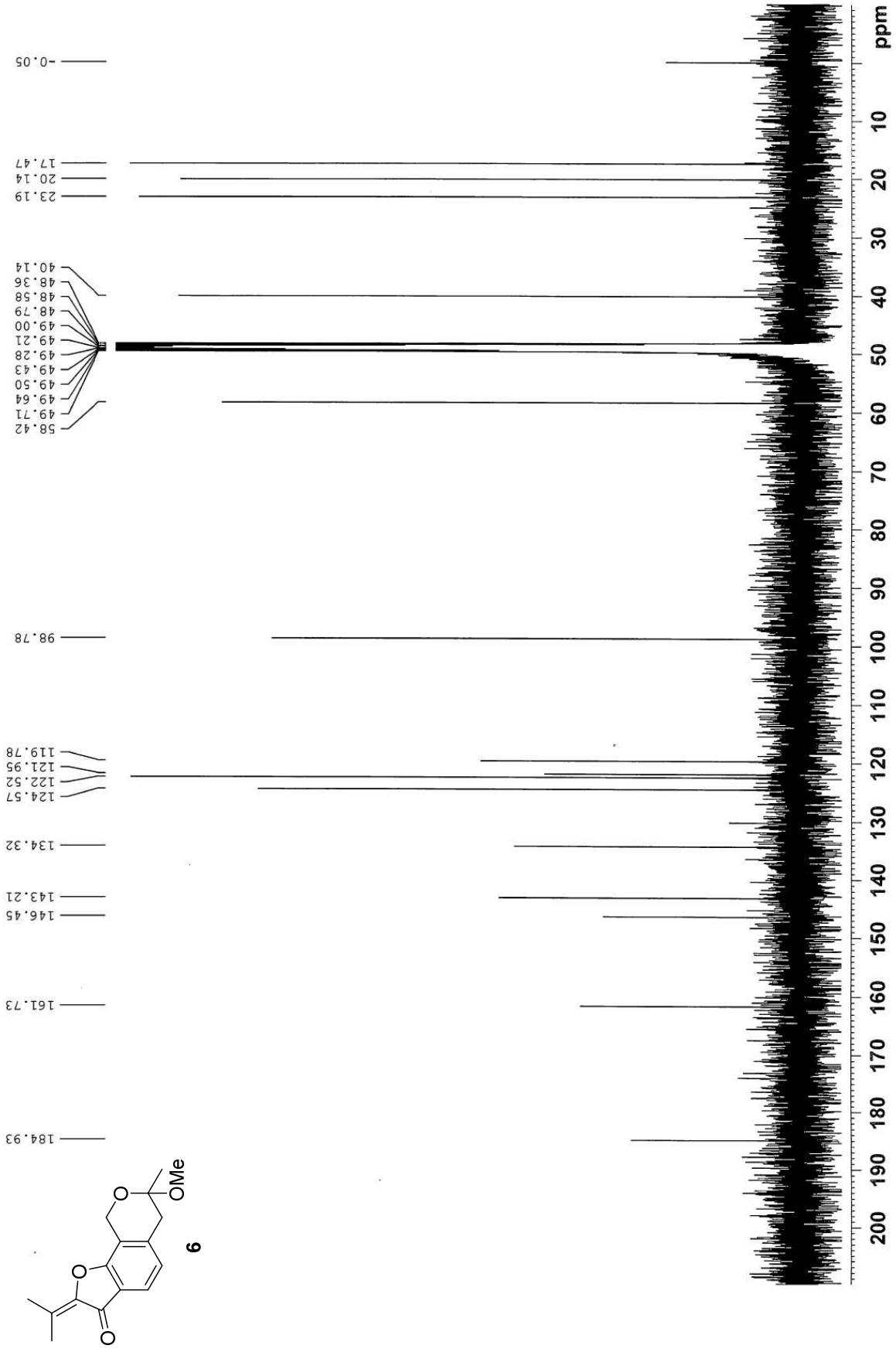


Figure S31. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of ustusorane B (2)

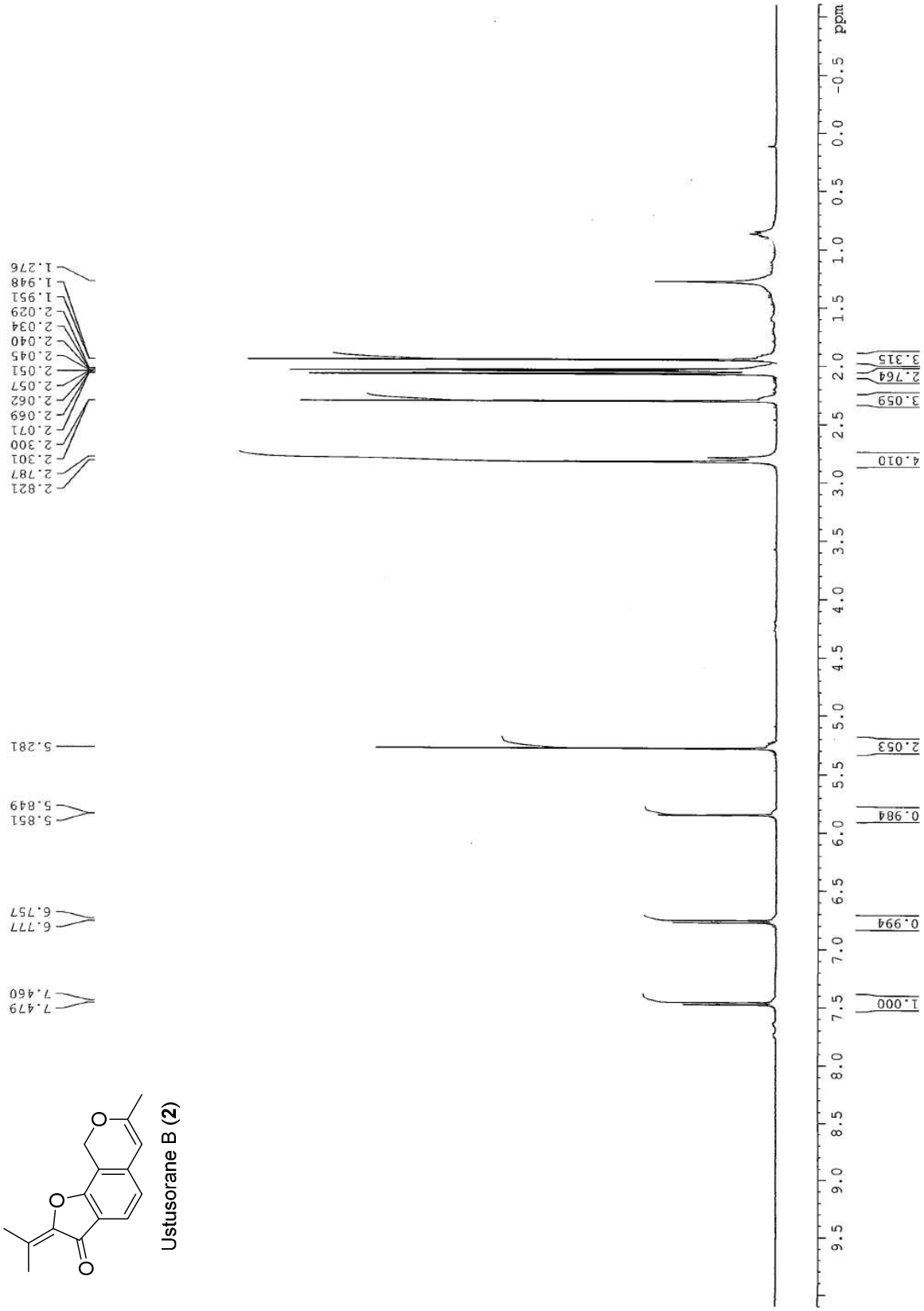


Figure S32. ^{13}C NMR spectrum (100 MHz, acetone-d_6) of ustusorane B (2)

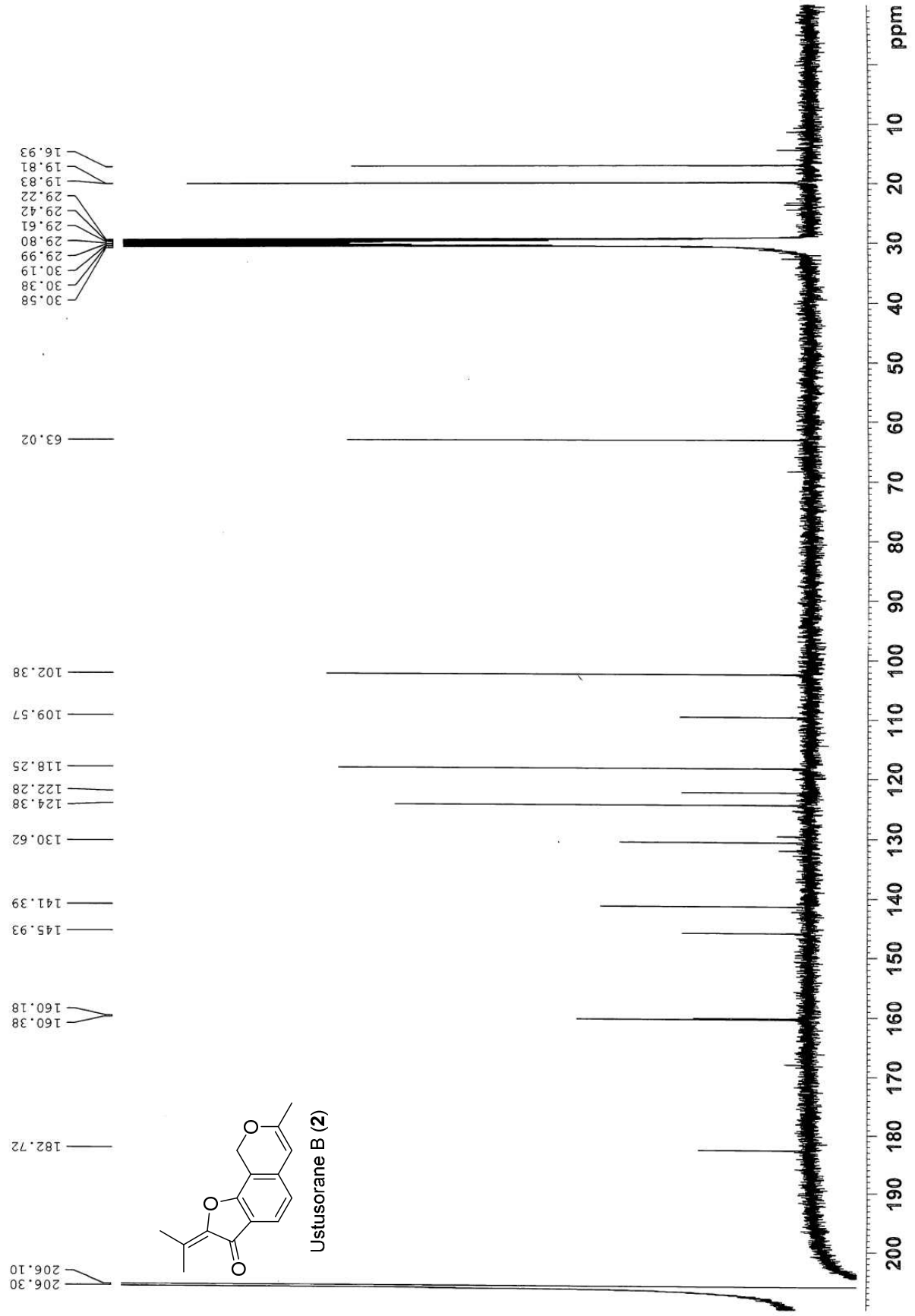


Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 30

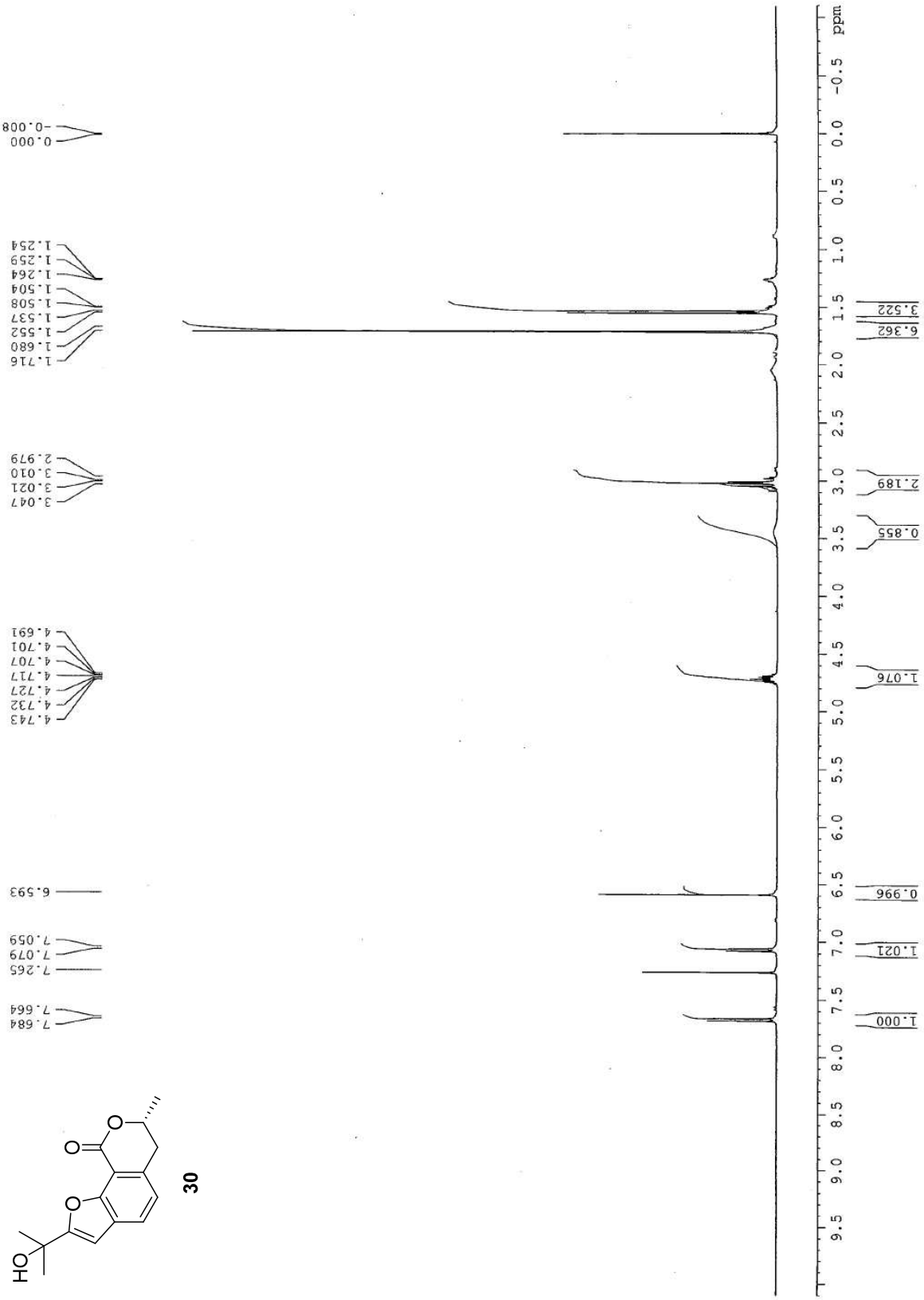


Figure S34. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 30

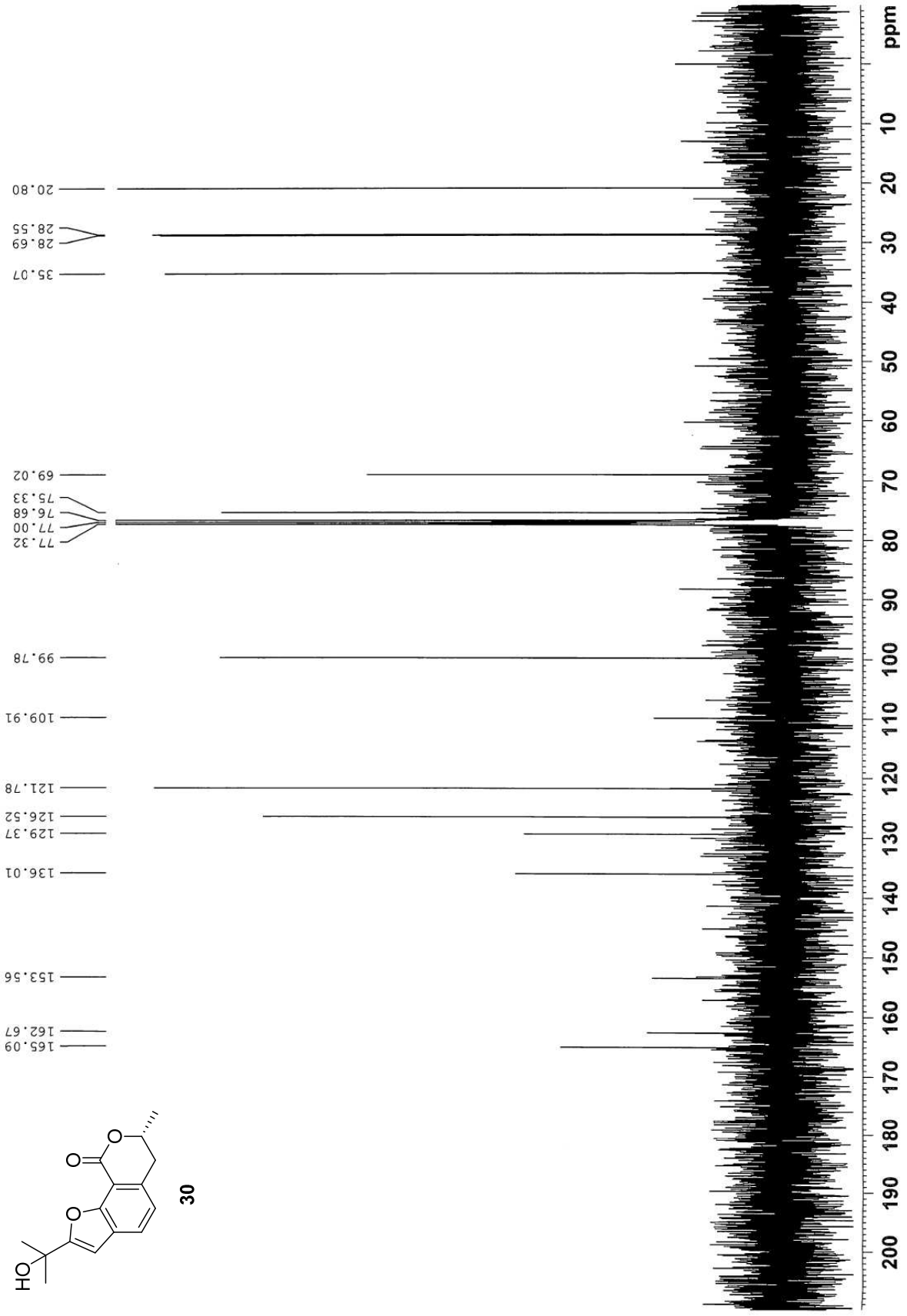


Figure S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 31

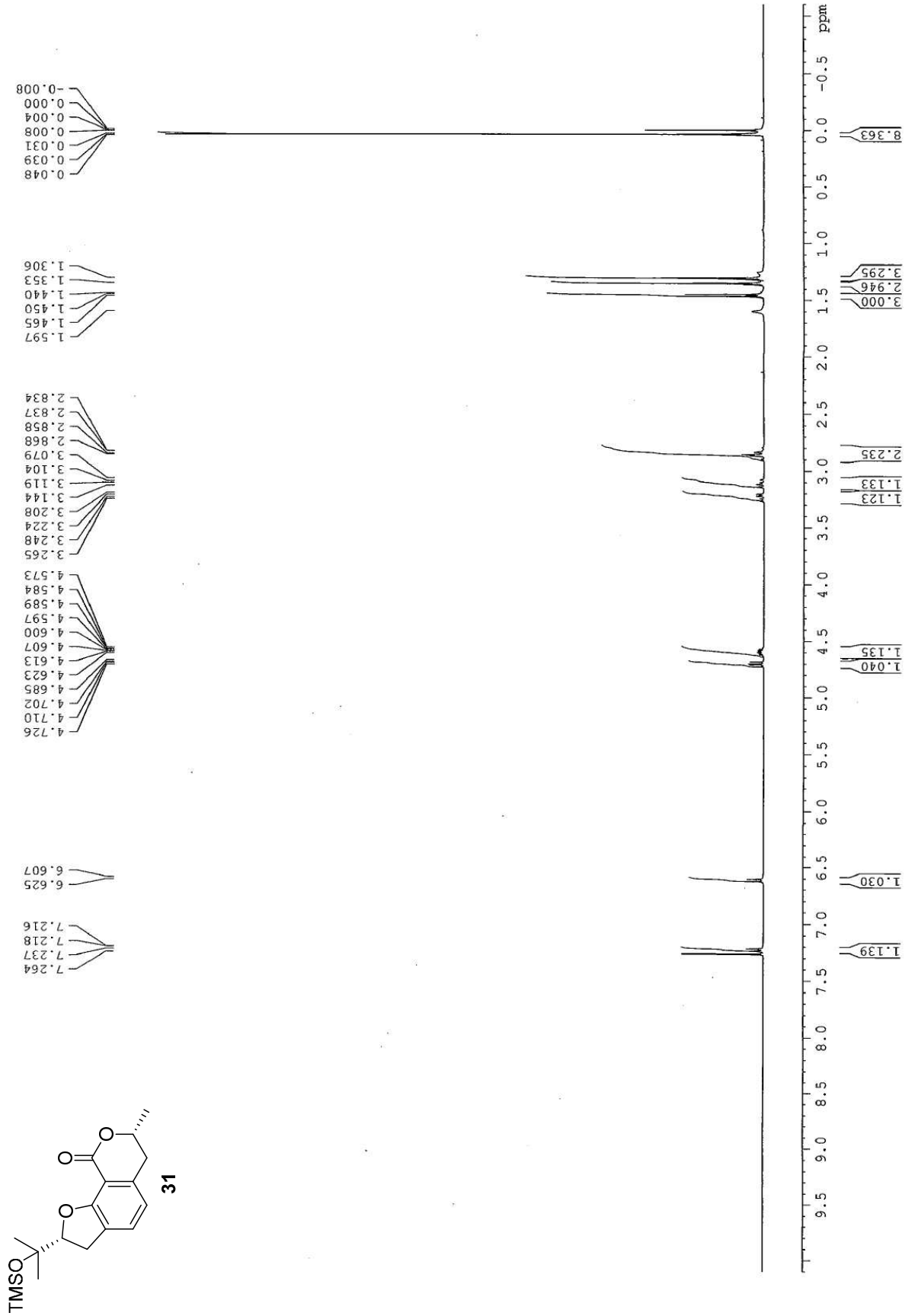


Figure S36. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 31

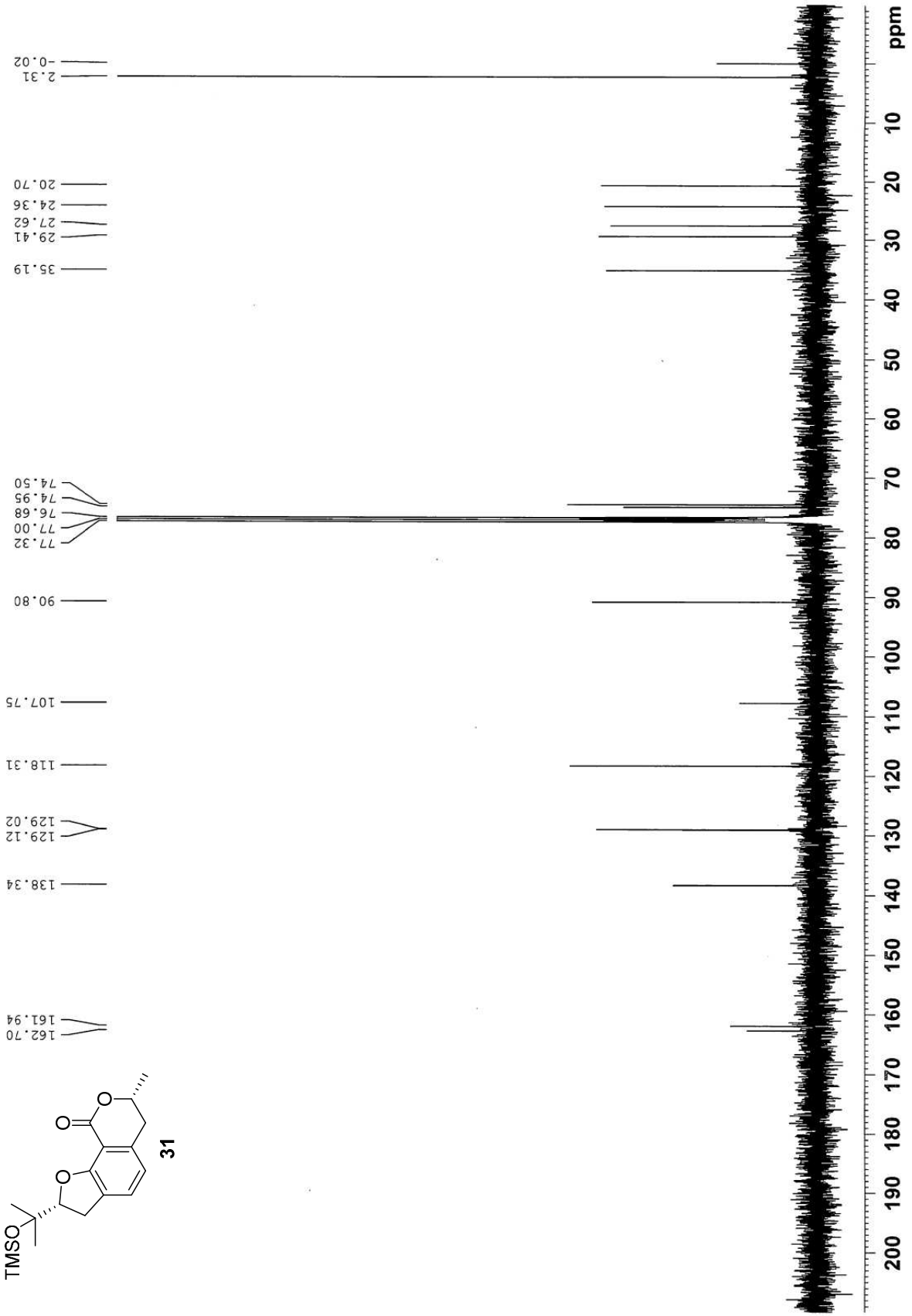


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 32

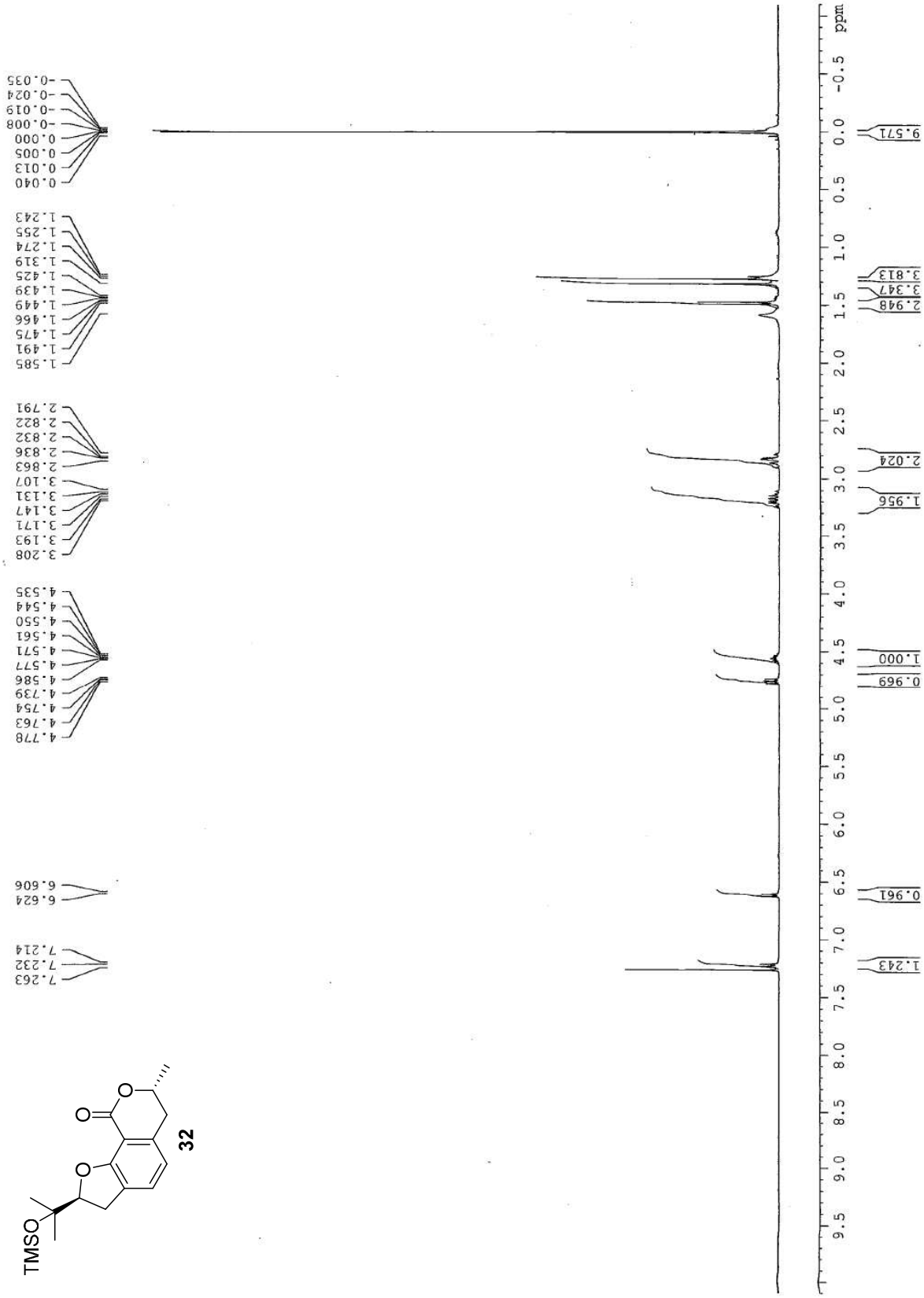
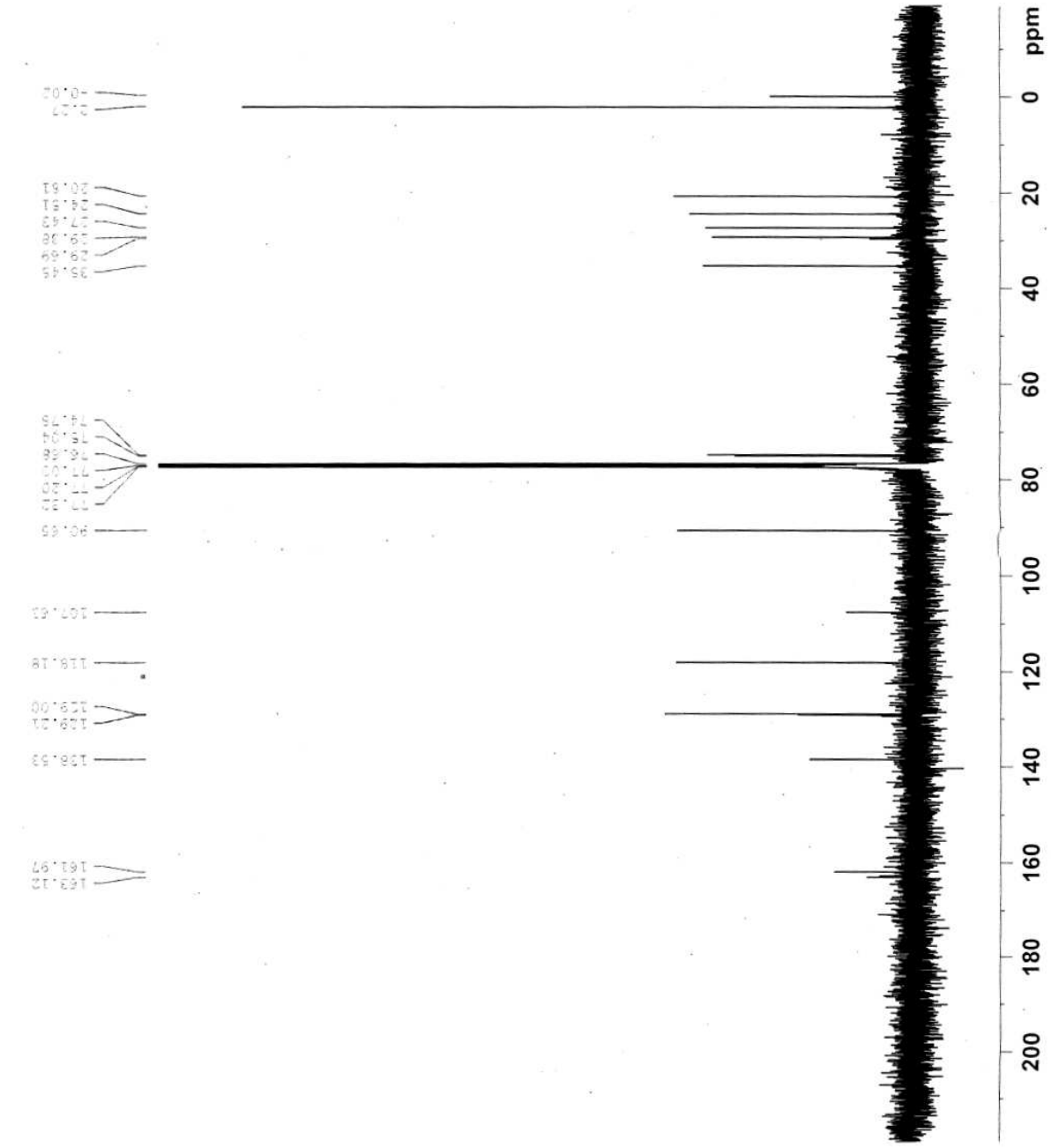


Figure S38. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 32



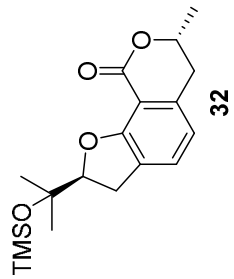


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Figure S39. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of ustusorane E (3)

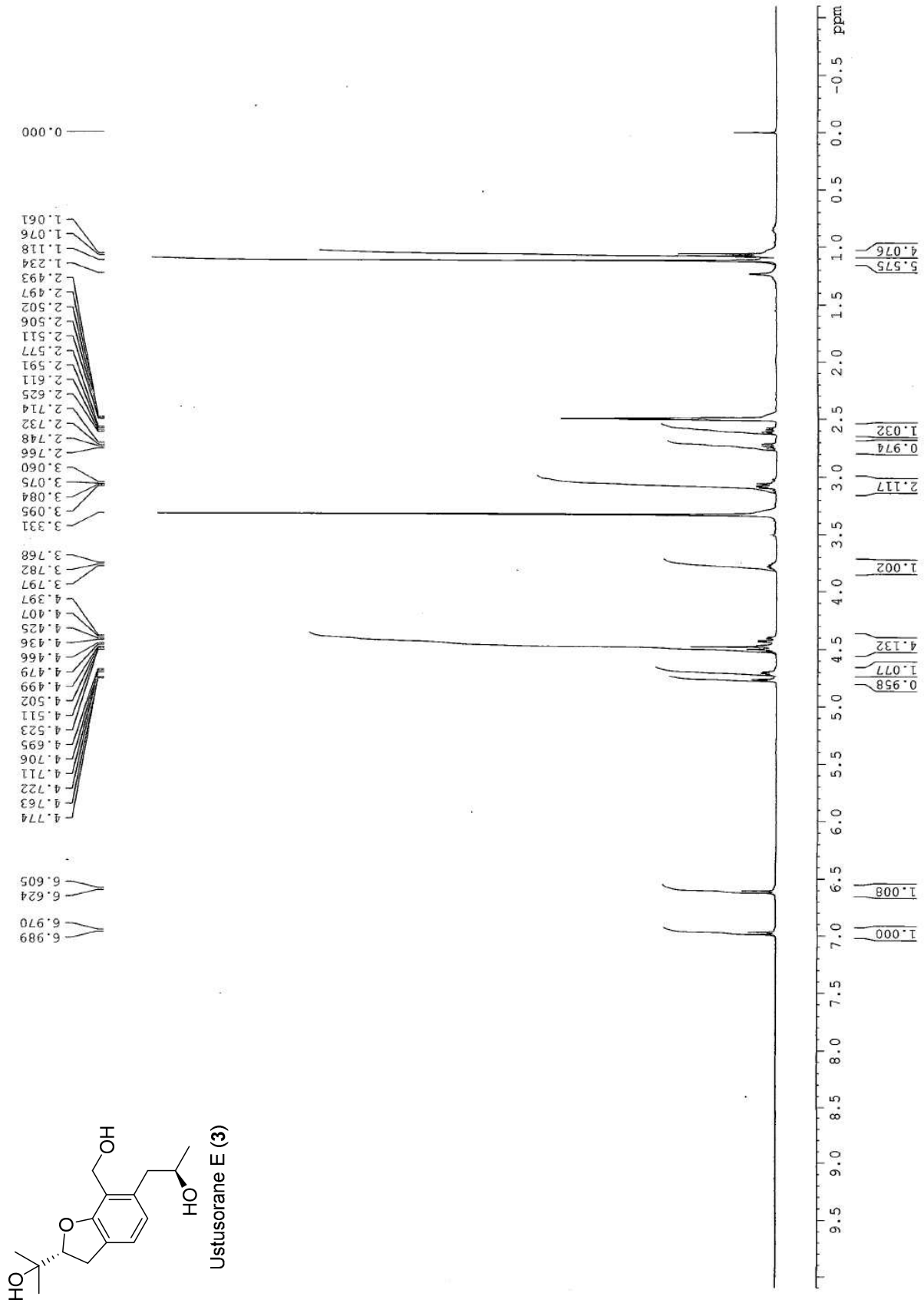
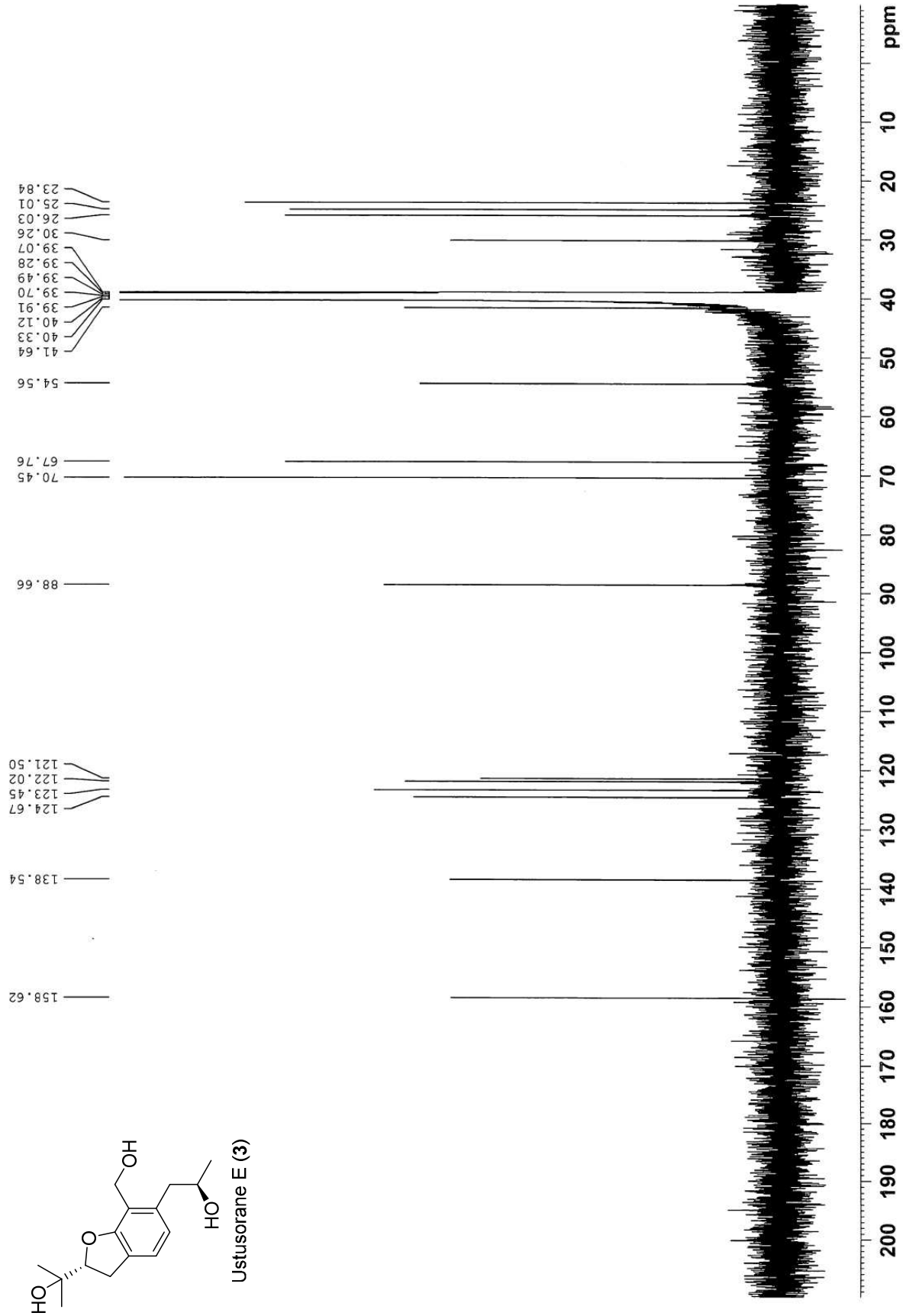


Figure S40. ^{13}C NMR spectrum (100 MHz, DMSO-d_6) of ustusorane E (3)



Preparation and characterization of bis-(*R*)-MTPA ester of synthetic 3. (*S*)-(+)-MTPACl (7 μL, 37.4 μmol) was added to a solution of **3** (4.0 mg, 15.0 μmol), Et_3N (7 μL, 50.2 μL), and DMAP (0.2 mg, 1.6 μmol) in CH_2Cl_2 (3 mL). The mixture was stirred at rt for 3 h. The reaction was then quenched by the addition of H_2O, and the mixture was diluted with EtOAc to give a biphasic solution. The organic layer was then collected and washed with brine before being dried over Na_2SO_4 and concentrated to a residue, which was purified by flash column chromatography (hexane-EtOAc, 4:1, v/v) to give bis-(*R*)-MTPA ester (10.5 mg, quant.) as yellow oil: : $[\alpha]^{24}_D$ +11.1 (c 0.40, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ε) 293 (3.82) nm; IR (neat) ν_{max} 3541, 3064, 2979, 2949, 2850, 1745, 1624, 1597, 1491, 1451, 1381, 1273, 1248, 1182, 1171, 1122, 1082, 1016 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39−7.25 (10H, m, Ph MTPA), 7.09 (1H, d, *J* = 7.6 Hz, H-4), 6.70 (1H, d, *J* = 7.6 Hz, H-5), 5.48 (1H, d, *J* = 12.0 Hz H-9), 5.24 (1H, m, H-7), 5.23 (1H, d, *J* = 12.0 Hz), 4.63 (1H, m, H-2), 3.41 (3H, s, OMe), 3.34 (3H, s, OMe), 3.18 (2H, m, H-3), 3.10 (1H, dd, *J* = 14.4, 8.8 Hz), 2.70 (1H, dd, *J* = 14.4, 5.2 Hz), 2.11 (1H, brs, 11-OH), 1.35 (3H, s, H-12), 1.29 (3H, d, *J* = 6.4 Hz, H-10), 1.14 (3H, s, H-13); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4 (C, CO_2 MTPA), 166.1 (C, CO_2, MTPA), 159.5 (C, C-9b), 136.9 (C, C-5a), 132.2 (2C, Ph MTPA), 129.5 (CH, Ph MTPA), 129.4 (CH, Ph MTPA), 128.33 (2CH, Ph MTPA), 128.28 (2CH, Ph MTPA), 127.30 (CH, Ph MTPA), 127.26 (CH, Ph MTPA), 126.0 (CH, C-4), 125.7 (C, C-3a), 123.3 (q, $J_{C\text{-}F}$ = 287 Hz, C, CF_3), 123.2(q, $J_{C\text{-}F}$ = 287 Hz, C, CF_3), 122.3 (CH, C-5), 115.1 (C, C-9a), 89.6 (CH, C-2), 85.7 (q, $J_{C\text{-}F}$ = 29 Hz, C, $CF_3\underline{C}$), 84.4 (q, $J_{C\text{-}F}$ = 29 Hz, C, $CF_3\underline{C}$), 75.2 (CH, C-7), 71.7 (C, C-11), 60.1 (CH_2, C-9), 55.2 (CH_3, OCH_3), 55.1 (CH_3, OCH_3), 37.8 (CH_2, C-6), 30.5 (CH_2, C-3), 26.2 (CH_3, C-12), 23.6 (CH_3, C-13), 19.5 (CH_3, C-10); HRFABMS m/z 721.2205 (calcd for $C_{35}H_{36}O_8F_6Na$, 721.2207).

Figure S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of bis-(*R*)-MTPA ester of synthetic 3

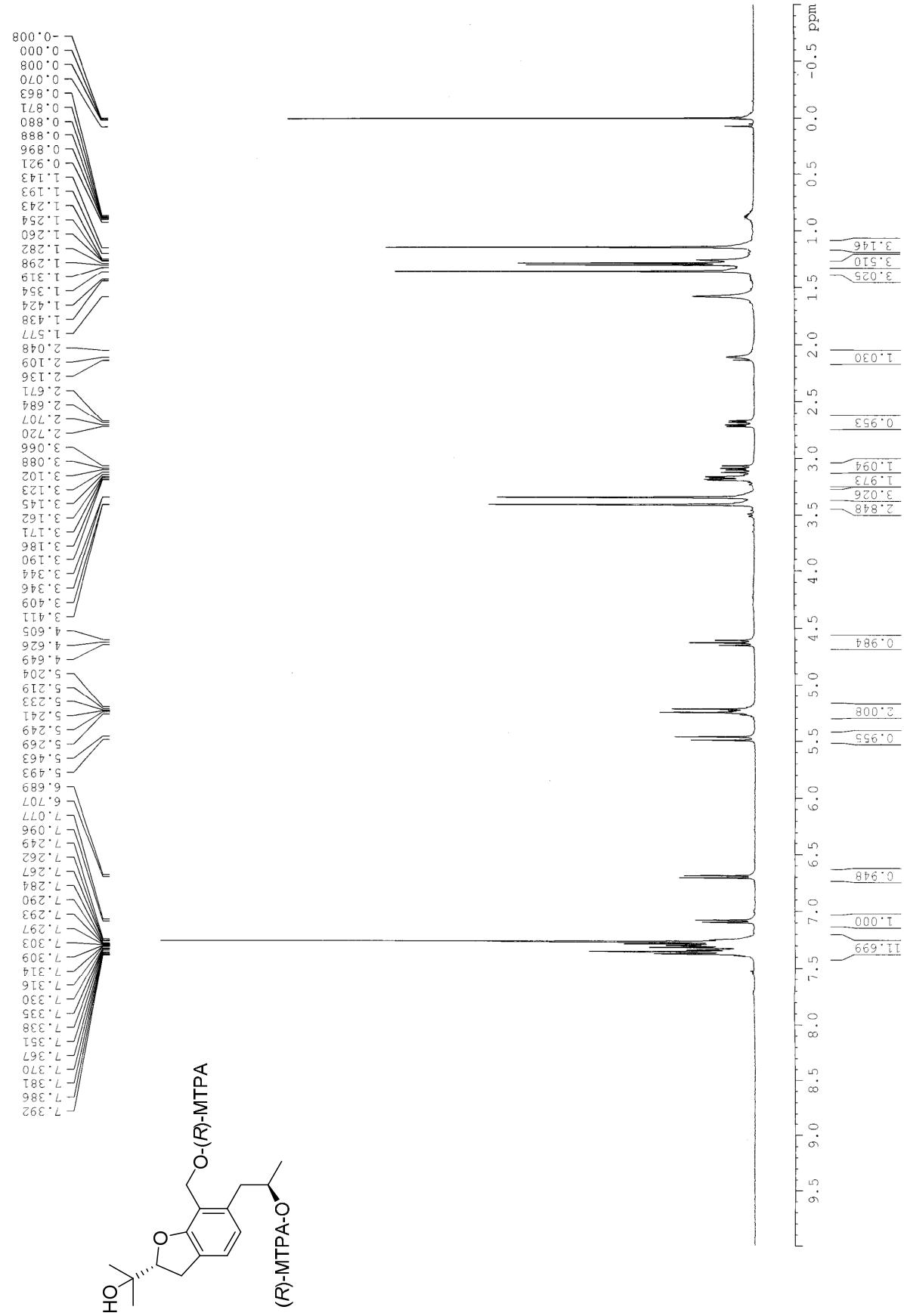


Figure S42. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of bis-(*R*)-MTPA ester of synthetic 3

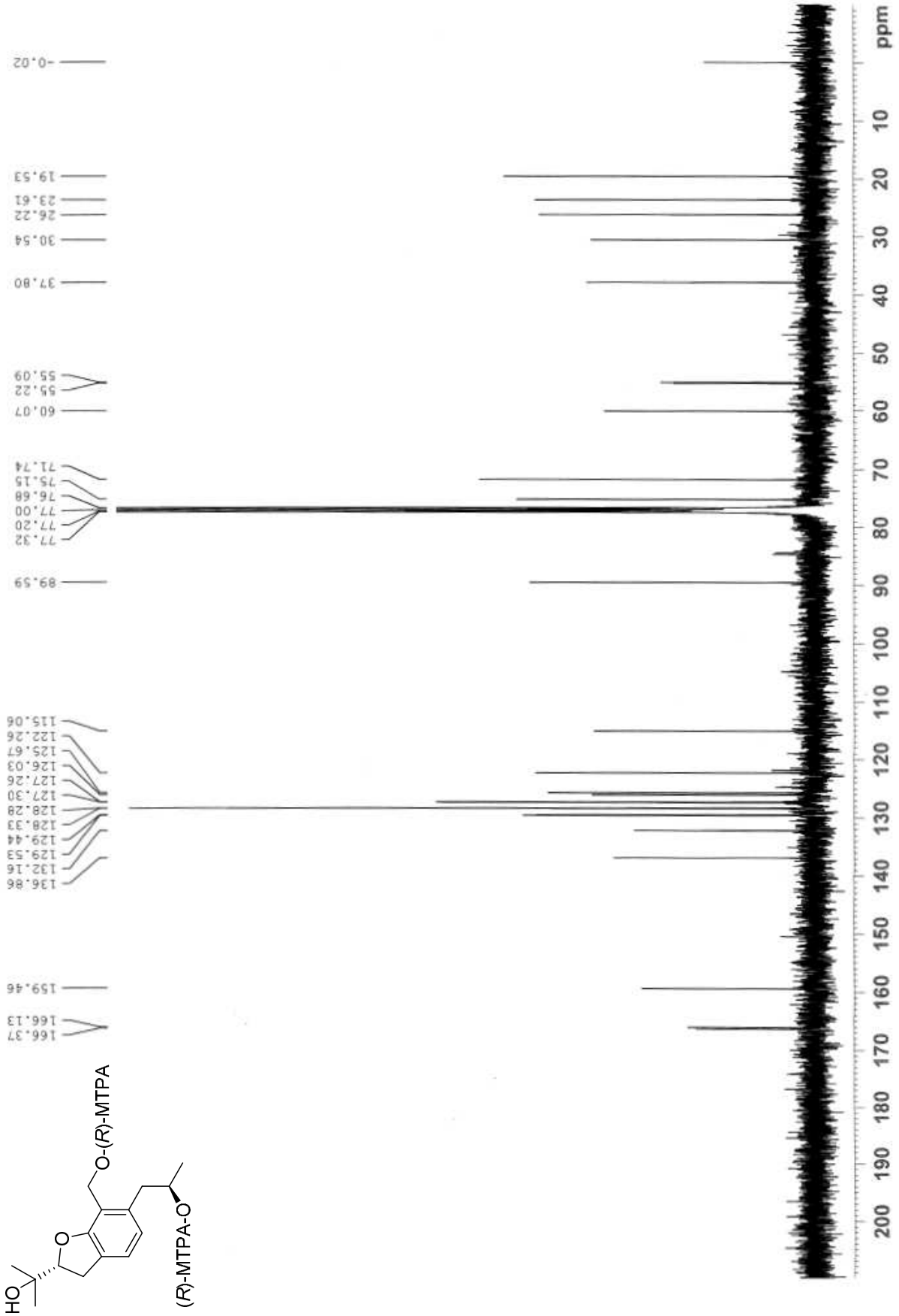


Figure S43. ^{1}H NMR spectrum (400 MHz, DMSO-d$_6$) of 2-*epi*-ustusorane E (2-*epi*-3)

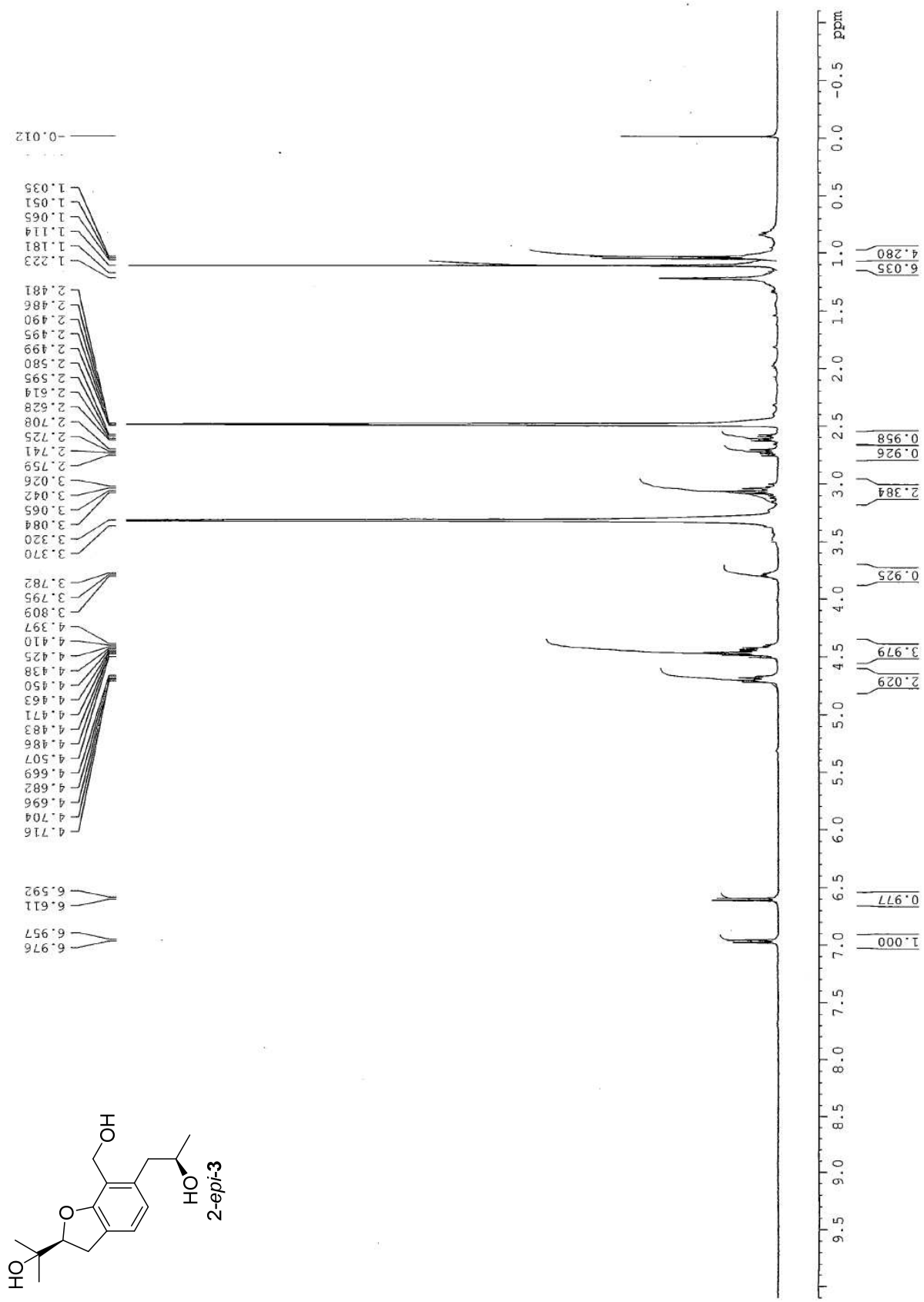


Figure S44. ^{13}C NMR spectrum (100 MHz, DMSO-d$_6$) of 2-*epi*-ustusorane E (2-*epi*-3)

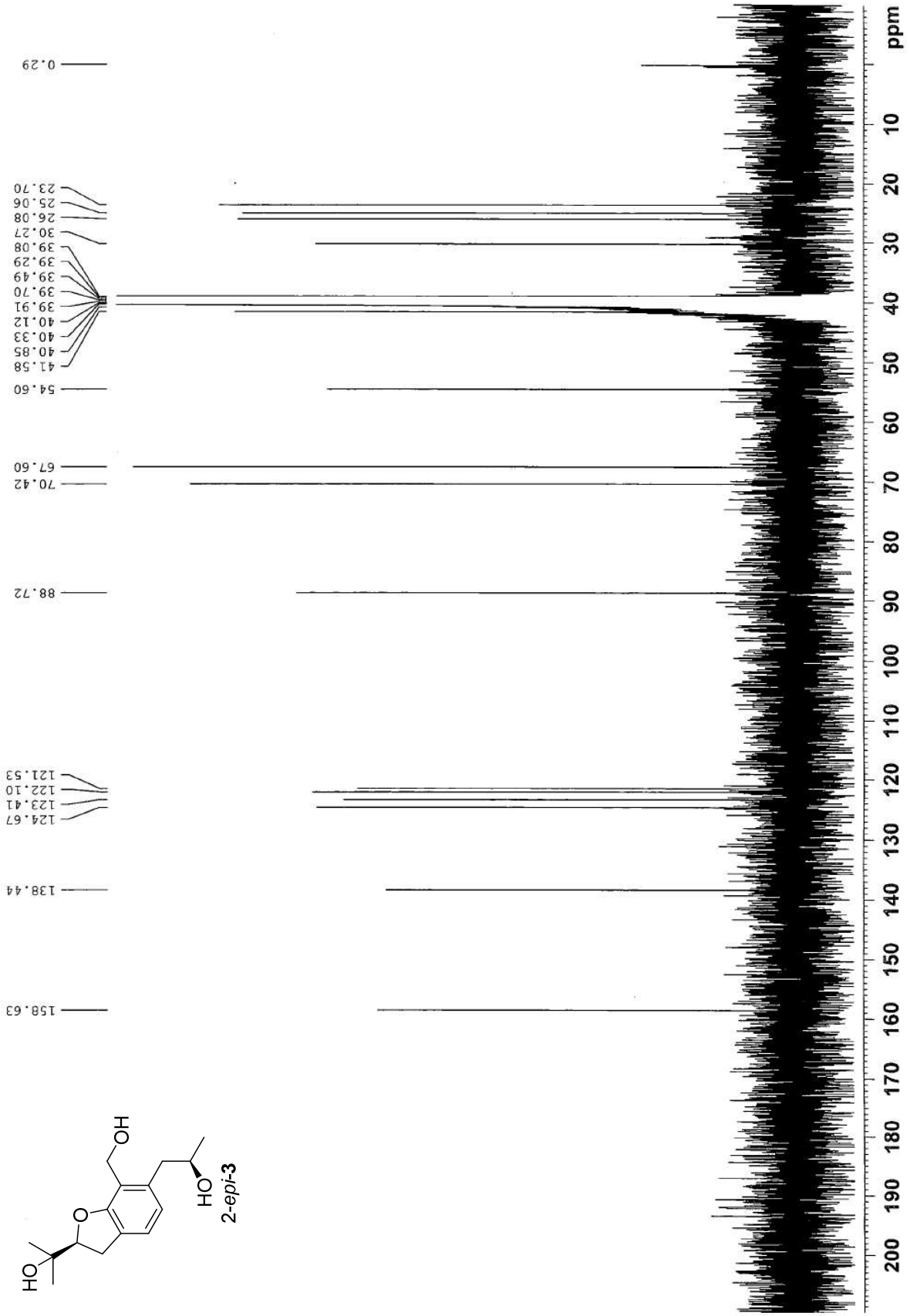


Figure S45. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the new compound 33

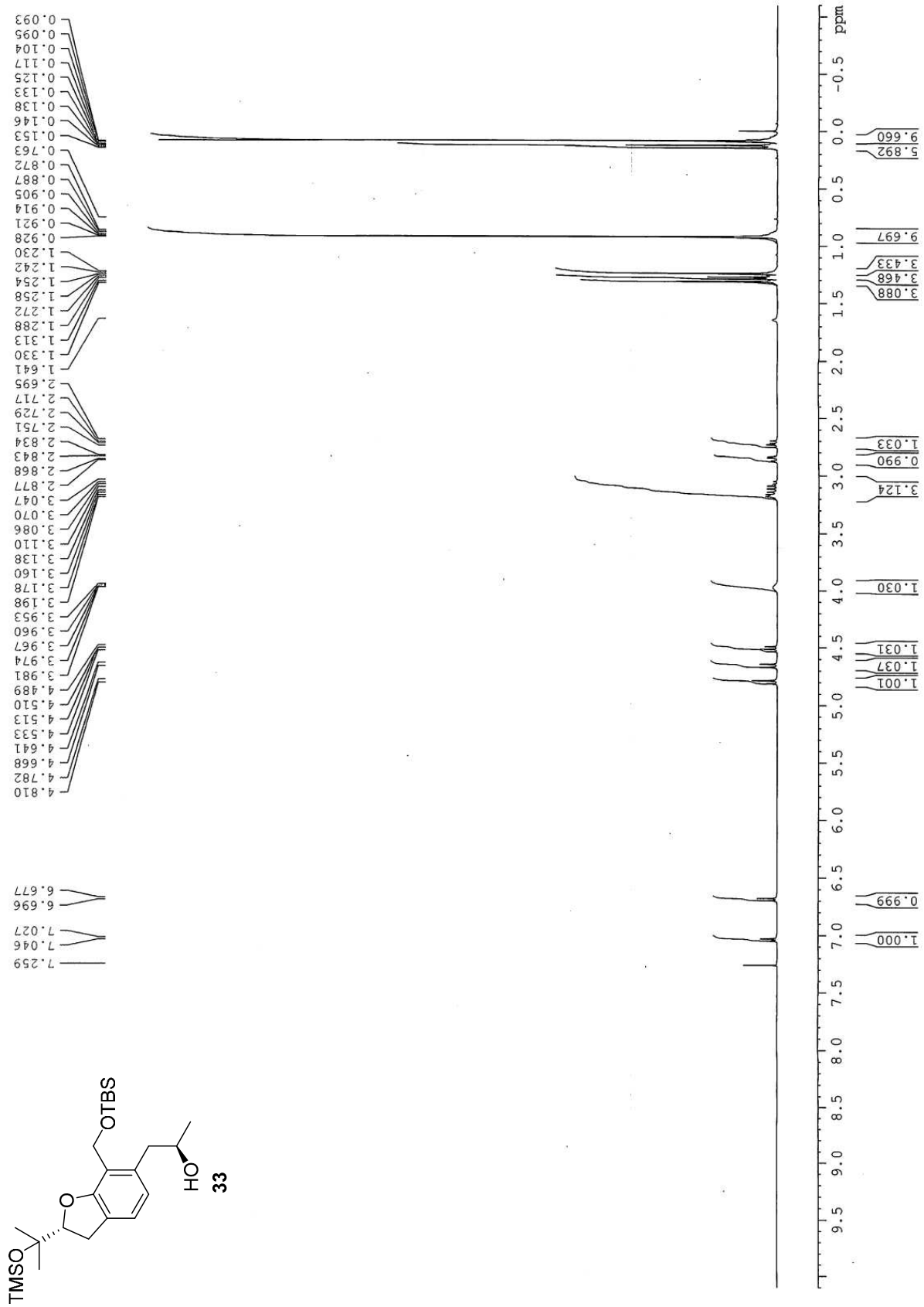


Figure S46. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of the new compound 33

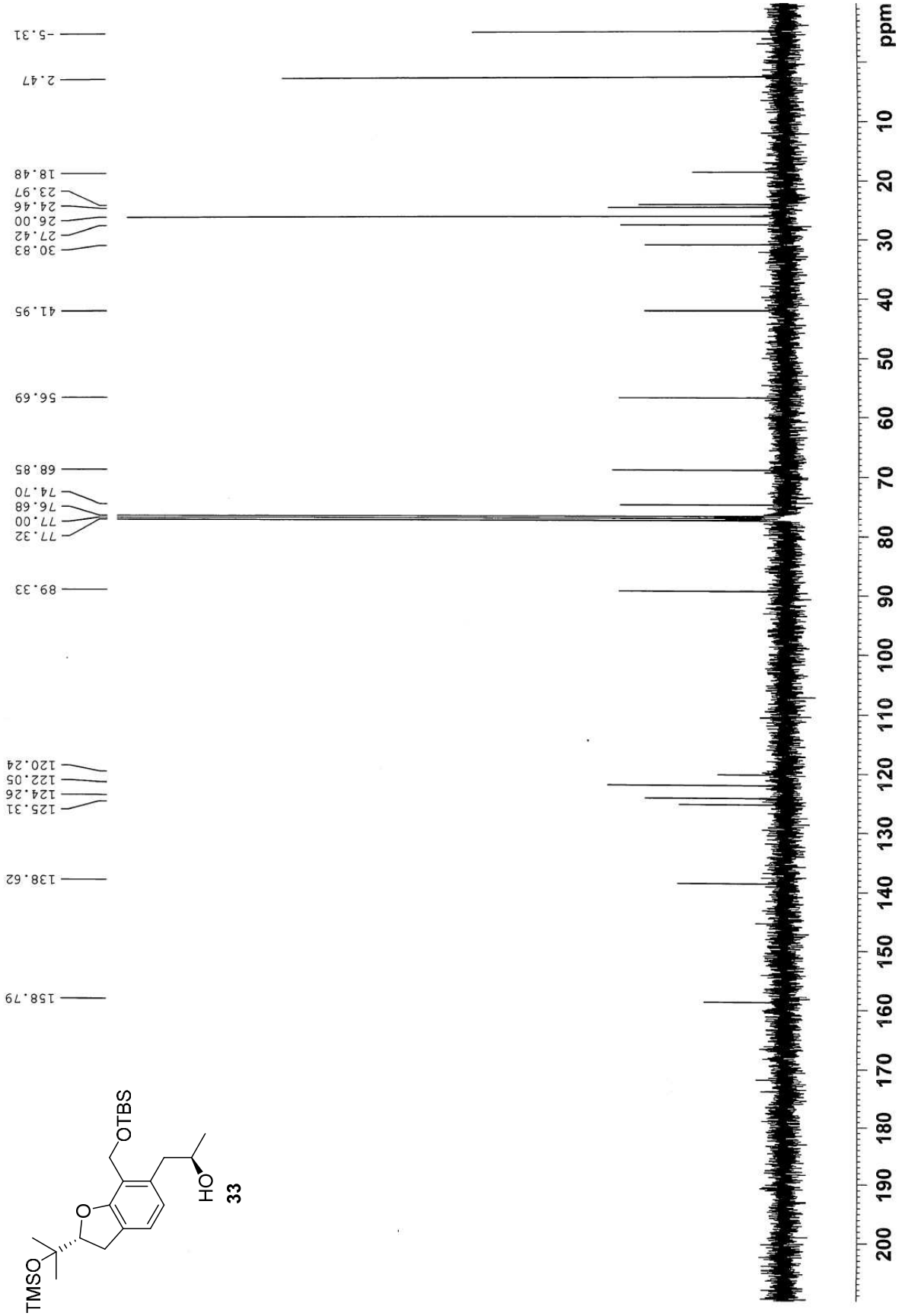


Figure S47. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of (−)-brassicadiol (7)

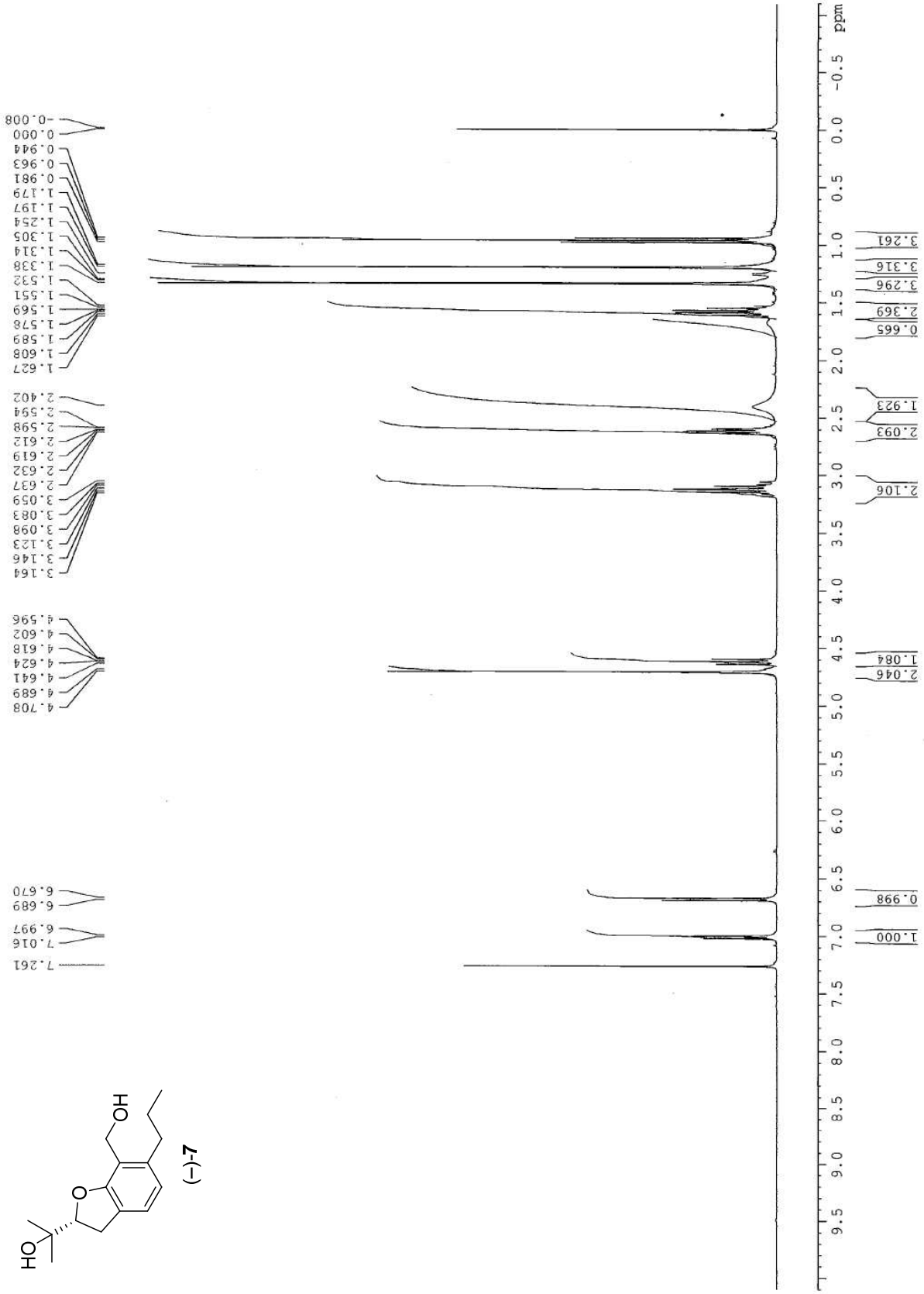
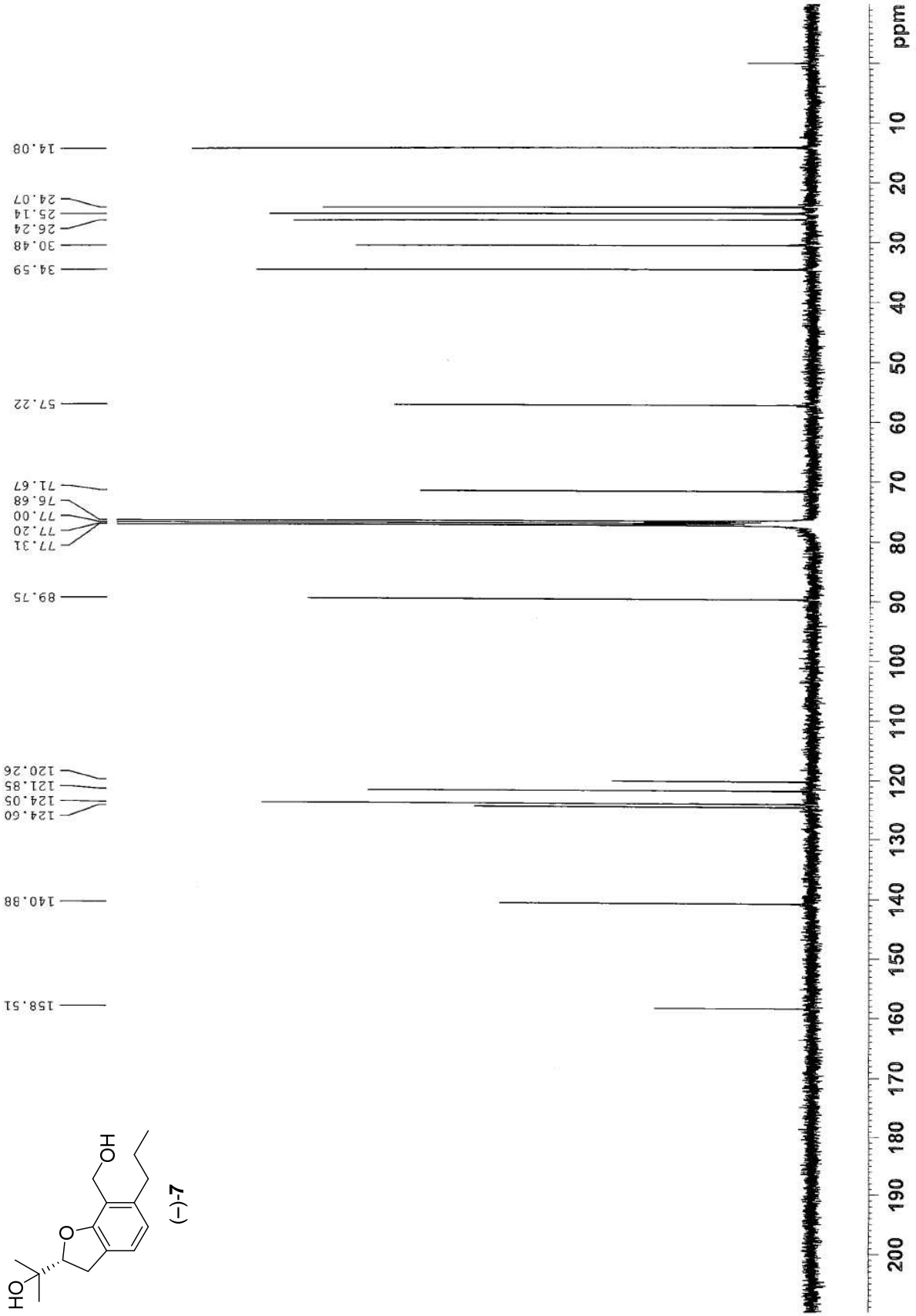


Figure S48. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of (−)-brassicadiol (7)



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