Supporting Information

A Unified Approach towards Syntheses of Juglomycins and Their Derivatives

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‖K.Y. and S.K. contributed equally.

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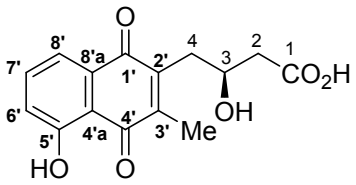
Table S1. NMR Spectroscopic Data for Natural and Synthetic Juglomycin Z (7)



Juglomycin Z (**7**)

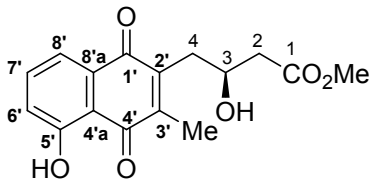
	natural **7**[b]		synthetic **7**[c]			
position[a]	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	$\Delta\delta_C$ (ppm)	$\Delta\delta_H$ (ppm)
1	174.7		176.2	—	−1.5	
2	42.0	2.56, m, 2H	41.2	2.57, m, 2H	+0.8	−0.01
3	67.9	4.28, m	67.5	4.23, m	+0.4	+0.05
		—		—		
4	36.8	3.09, dd (12.6, 7.5)	34.0	2.89, d (6.6), 2H	+2.8	+0.20
		3.27, dd (12.6, 4.0)				+0.38
1'	182.2		184.8		−2.6	
2' or 3'	148.4		144.2		+4.2	
3' or 2'	149.6		145.9		+3.7	
3'-Me	18.5	2.67, s	12.8	2.26, s	+5.7	+0.41
4'	186.6		190.1		−3.5	
4'a	115.8		114.9		+0.9	
5'	161.6		161.2		+0.4	
6'	124.1	7.25, dd (8.0, 2.0)	124.1	7.24, dd (7.0, 2.6)	0	+0.01
7'	136.7	7.64, m	136.1	7.60, m	+0.6	+0.04
8'	119.8	7.63, m	119.2	7.61, m	+0.6	+0.02
8'a	132.3		131.9		+0.4	

[a]Carbon atoms have been labeled using the IUPAC numbering system.

[b]^{1}H NMR (200 MHz, $CDCl_3/CD_3OD$) and ^{13}C NMR (50.3 MHz, $CDCl_3$).[S1]

[c]^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ = 9/1, TMS) and ^{13}C NMR (100 MHz, $CDCl_3$).

Table S2. NMR Spectroscopic Data for Compound 19 Derived from Natural and Synthetic 7[S1]



19

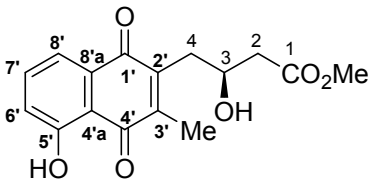
	19 derived from natural **7**[b]		**19** derived from synthetic **7**[c]			
position[a]	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	$\Delta\delta_C$ (ppm)	$\Delta\delta_H$ (ppm)
1	172.6		172.8	—	−0.2	
2	41.2	2.58, dd (15.5, 7.5)	41.3	2.58, dd (16.6, 7.8)	−0.1	0
		2.63, dd (15.5, 5.5)		2.65, dd (16.6, 4.2)		−0.02
3	67.7	4.28, m	67.7	4.24, m	0	+0.04
		—		—		
4	36.0	3.09, dd (12.6, 7.5)	34.0	2.87, m, 2H	+2.0	+0.22
		3.27, dd (12.6, 4.5)				+0.40
1'	182.0		184.6		−2.6	
2' or 3'	147.9		144.4		+3.5	
3' or 2'	149.2		145.7		+3.5	
3'-Me	18.4	2.65, s	12.7	2.25	+5.7	+0.40
4'	186.3		190.2		−3.9	
4'a	115.4		115.0		+0.4	
5'	161.6		161.2		+0.4	
6'	124.0	7.25, dd (8.0, 2.0)	124.0	7.23, dd (7.8, 1.8)	0	+0.02
7'	136.3	7.63, dd (8.0, 7.8)	136.0	7.57, dd (7.8, 7.6)	+0.3	+0.06
8'	119.5	7.61, dd (7.8, 2.0)	119.1	7.61, dd (7.4, 1.8)	+0.4	0
8'a	131.8		132.0		−0.2	
OMe	51.8	3.72, s	51.9	3.72, s	−0.1	0
OH		11.9		12.13		−0.23

[a]Carbon atoms have been labeled using the IUPAC numbering system.

[b]^{1}H NMR (200 MHz, $CDCl_3$) and ^{13}C NMR (50.3 MHz, $CDCl_3$).[S1]

[c]^{1}H NMR (400 MHz, $CDCl_3$, TMS) and ^{13}C NMR (100 MHz, $CDCl_3$).

Table S3. NMR Spectroscopic Data for Compound 19 Derived from Natural Juglomycin Z[S1] and Compound 21



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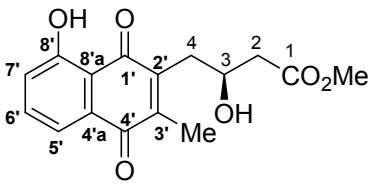


21

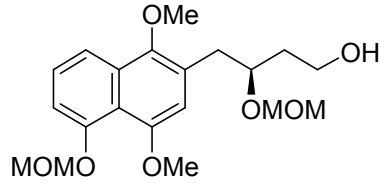
	19 derived from natural **7**[b]			**21**			
position[a]	δ_C	δ_H (*J* in Hz)	position[a]	δ_C	δ_H (*J* in Hz)	$\Delta\delta_C$ (ppm)	$\Delta\delta_H$ (ppm)
1	172.6		1	172.9	—	−0.3	
2	41.2	2.58, dd (15.5, 7.5)	2	41.1	2.59, dd (16.6, 8.0)	−0.1	−0.01
		2.63, dd (15.5, 5.5)			2.66, dd (16.6, 4.0)		−0.03
3	67.7	4.28, m	3	67.6	4.27, m	−0.1	+0.01
		—			—		
4	36.0	3.09, dd (12.6, 7.5)	4	34.0	2.89, m, 2H	+2.0	+0.20
		3.27, dd (12.6, 4.5)					+0.38
1'	182.0		4'	184.2		−2.2	
2' or 3'	147.9		3' or 2'	142.9		+5.0	
3' or 2'	149.2		2' or 3'	147.2		+2.0	
3'-Me	18.4	2.65, s	3'-Me	13.5	2.25	+4.9	+0.40
4'	186.3		1'	190.3		−4.0	
4'a	115.4		8'a	114.8		+0.6	
5'	161.6		8'	161.2		+0.4	
6'	124.0	7.25, dd (8.0, 2.0)	7'	123.9	7.22, dd (8.0, 1.6)	−0.1	+0.03
7'	136.3	7.63, dd (8.0, 7.8)	6'	136.1	7.59, dd (8.0, 7.5)	+0.2	+0.04
8'	119.5	7.61, dd (7.8, 2.0)	5'	119.1	7.61, dd (7.5, 1.6)	+0.4	0
8'a	131.8		4'a	132.0		−0.2	
OMe	51.8	3.72, s		51.9	3.73, s	−0.1	−0.01
OH		11.9			12.11		−0.21

[a]Carbon atoms have been labeled using the IUPAC numbering system.

[b]^{1}H NMR (200 MHz, $CDCl_3$) and ^{13}C NMR (50.3 MHz, $CDCl_3$).[S1]

[c]^{1}H NMR (400 MHz, $CDCl_3$, TMS) and ^{13}C NMR (100 MHz, $CDCl_3$).

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **17**.



17

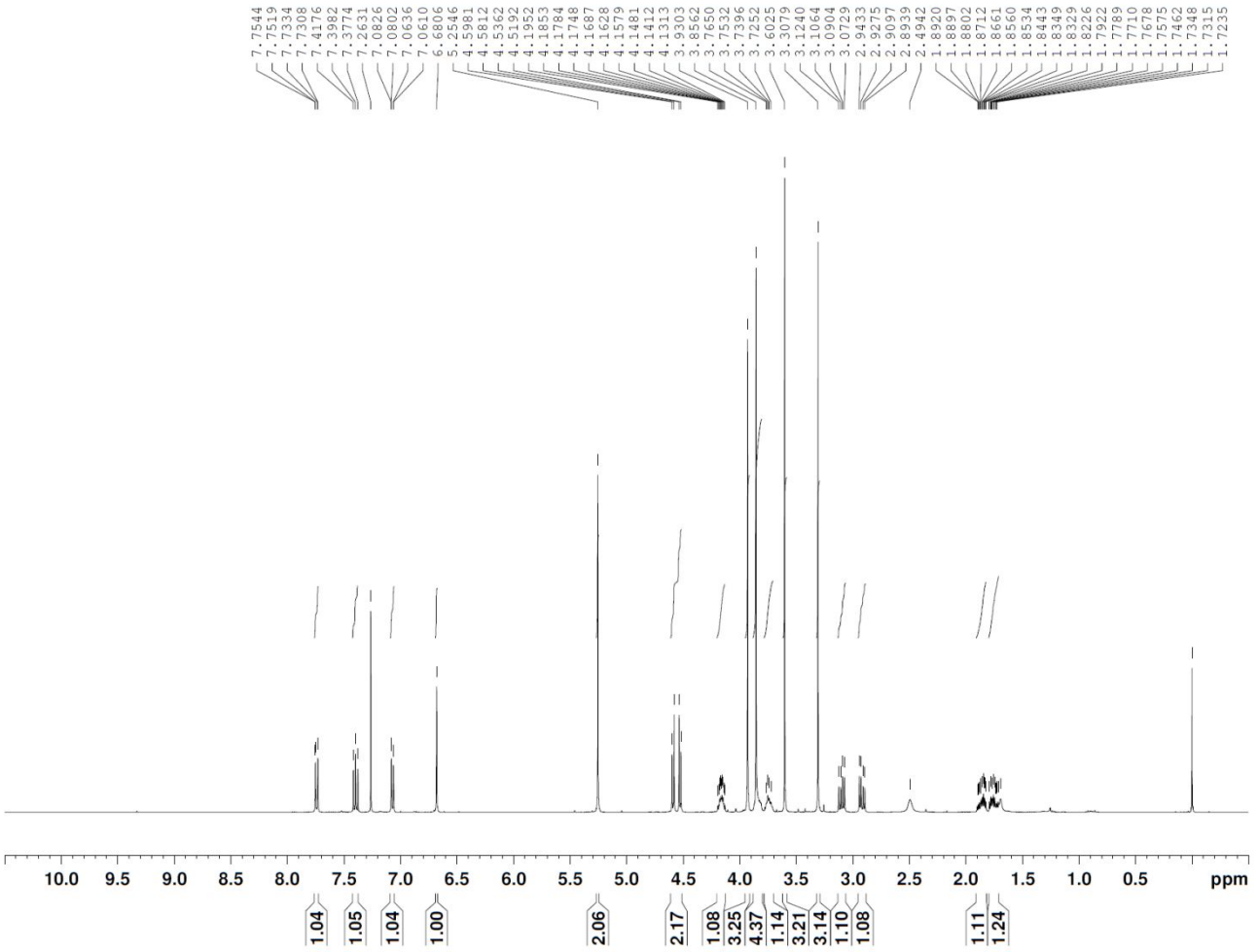
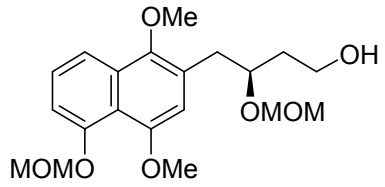


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **17**.



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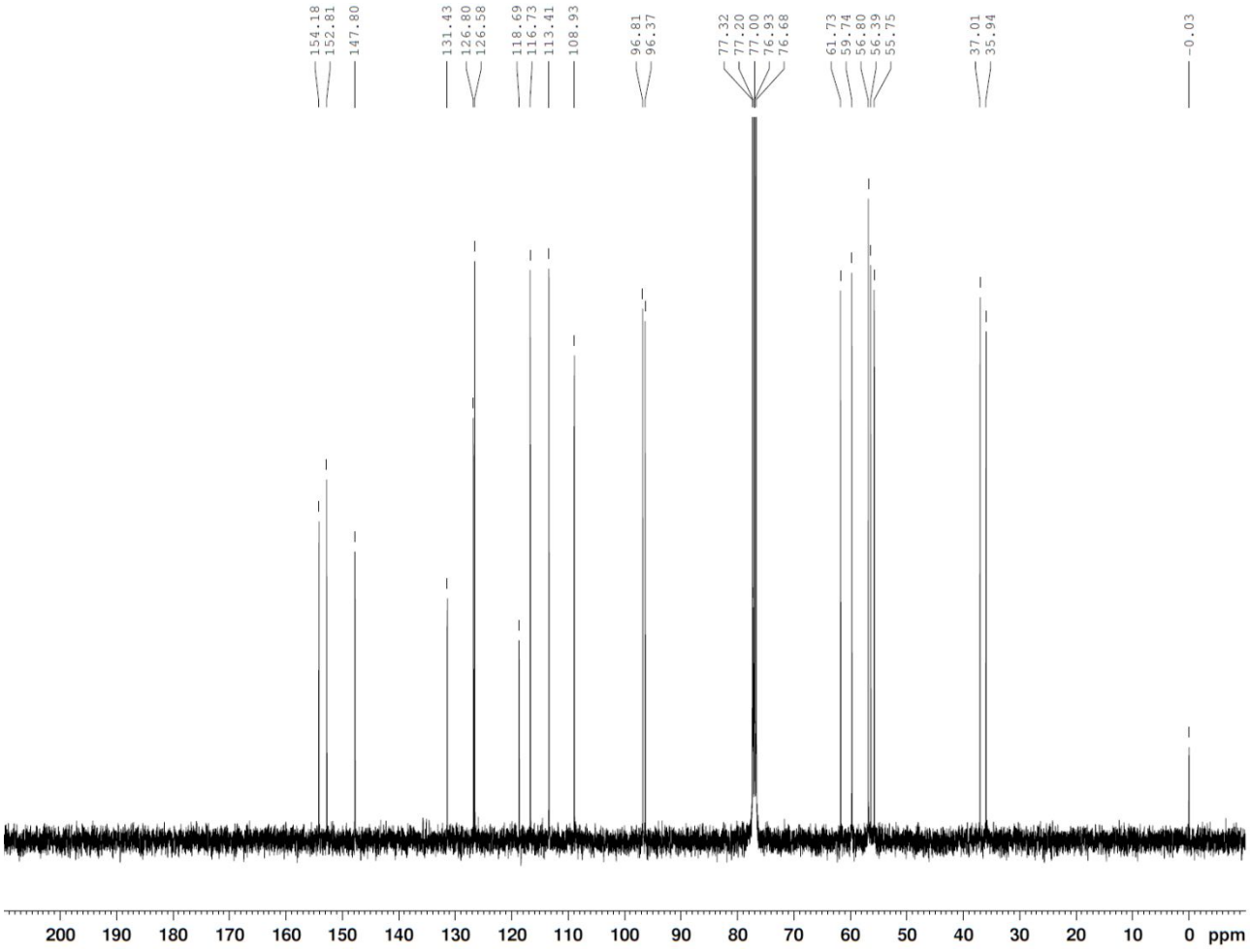


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **10**.

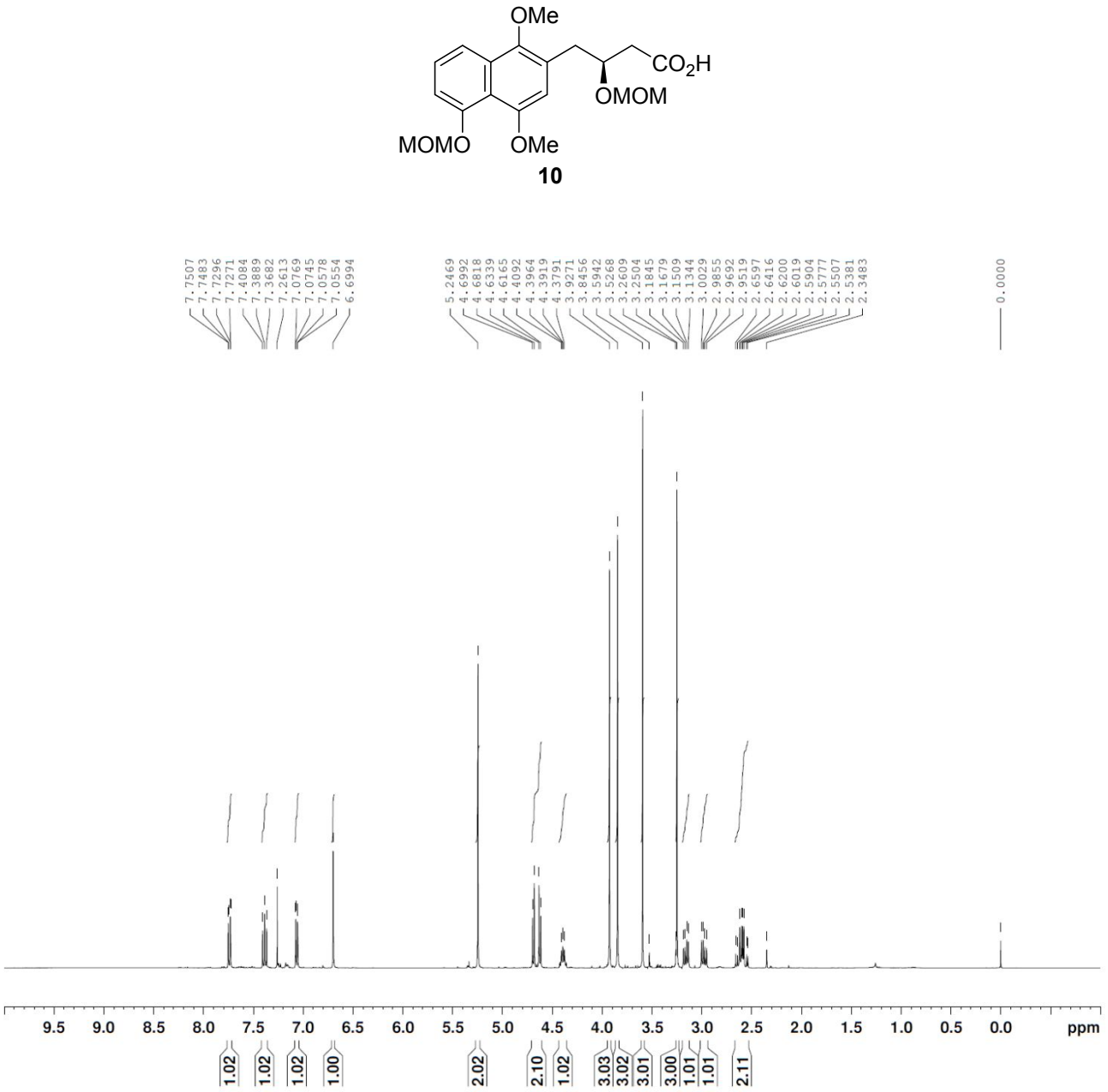


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **10**.

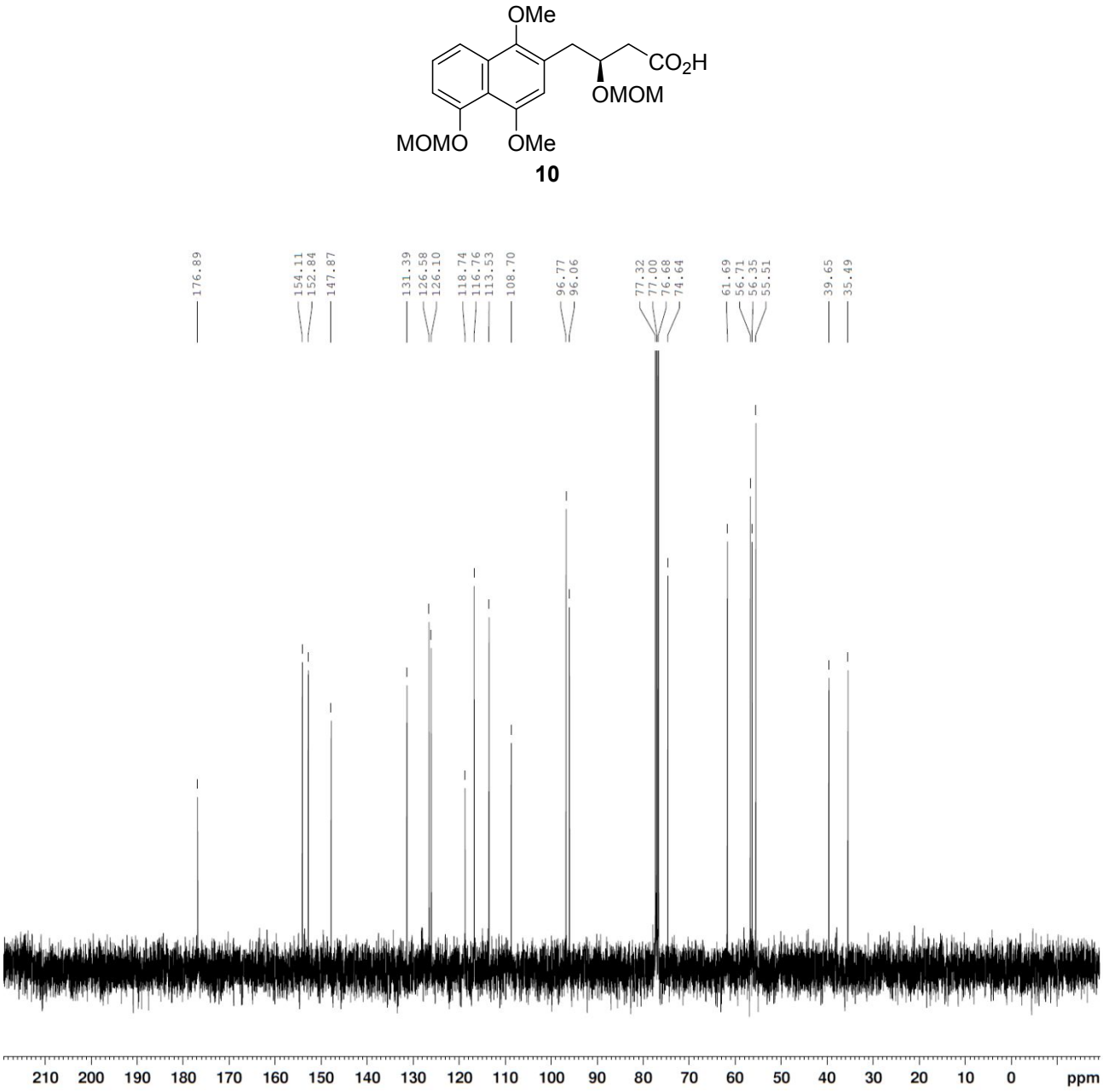
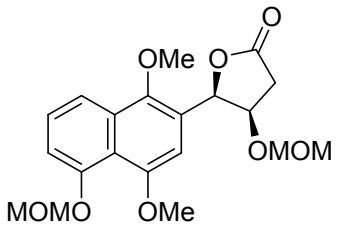


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **11**.



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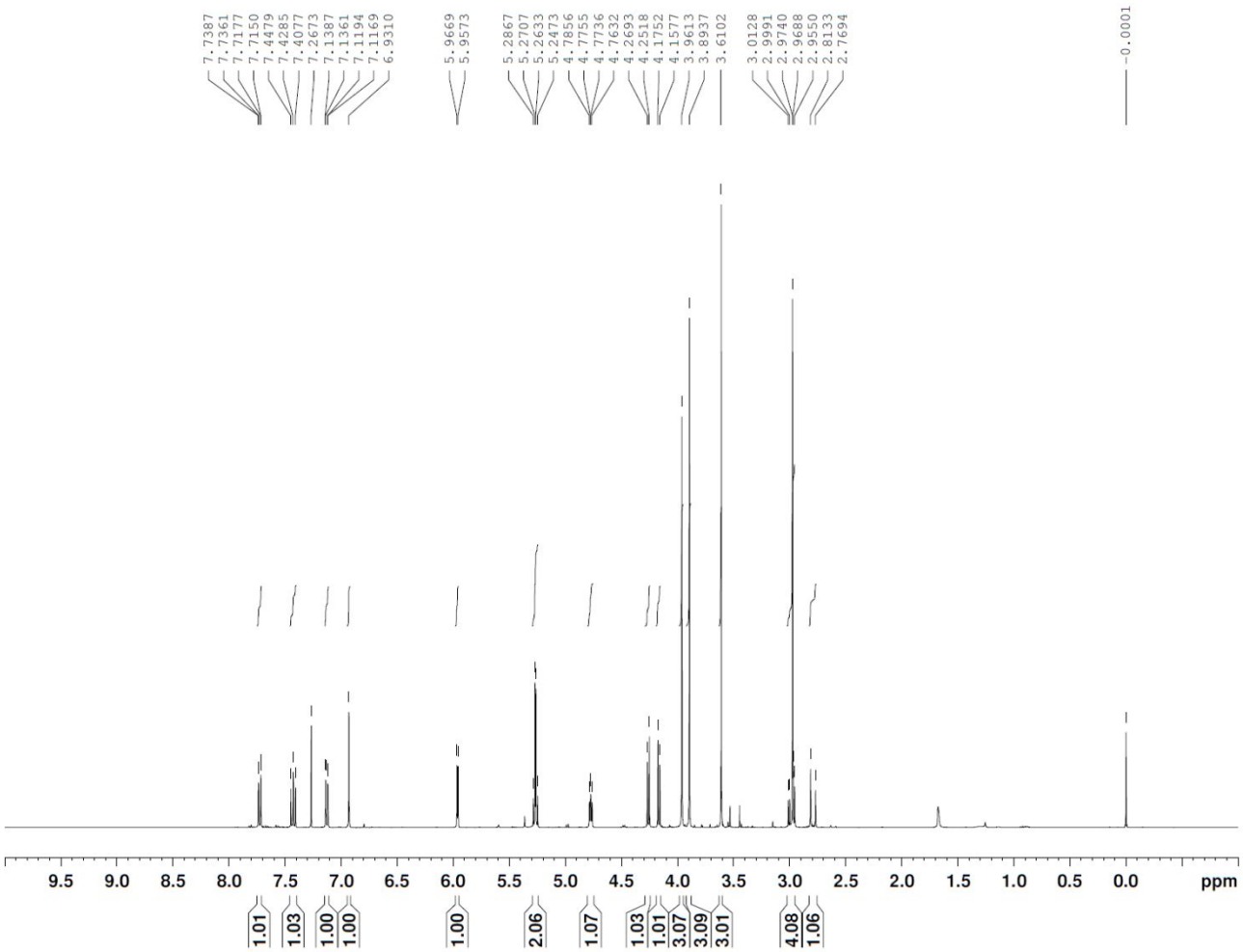
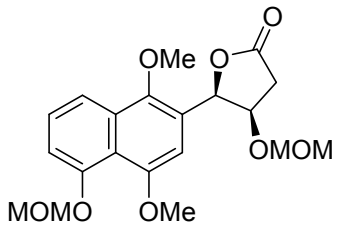


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **11**.



11

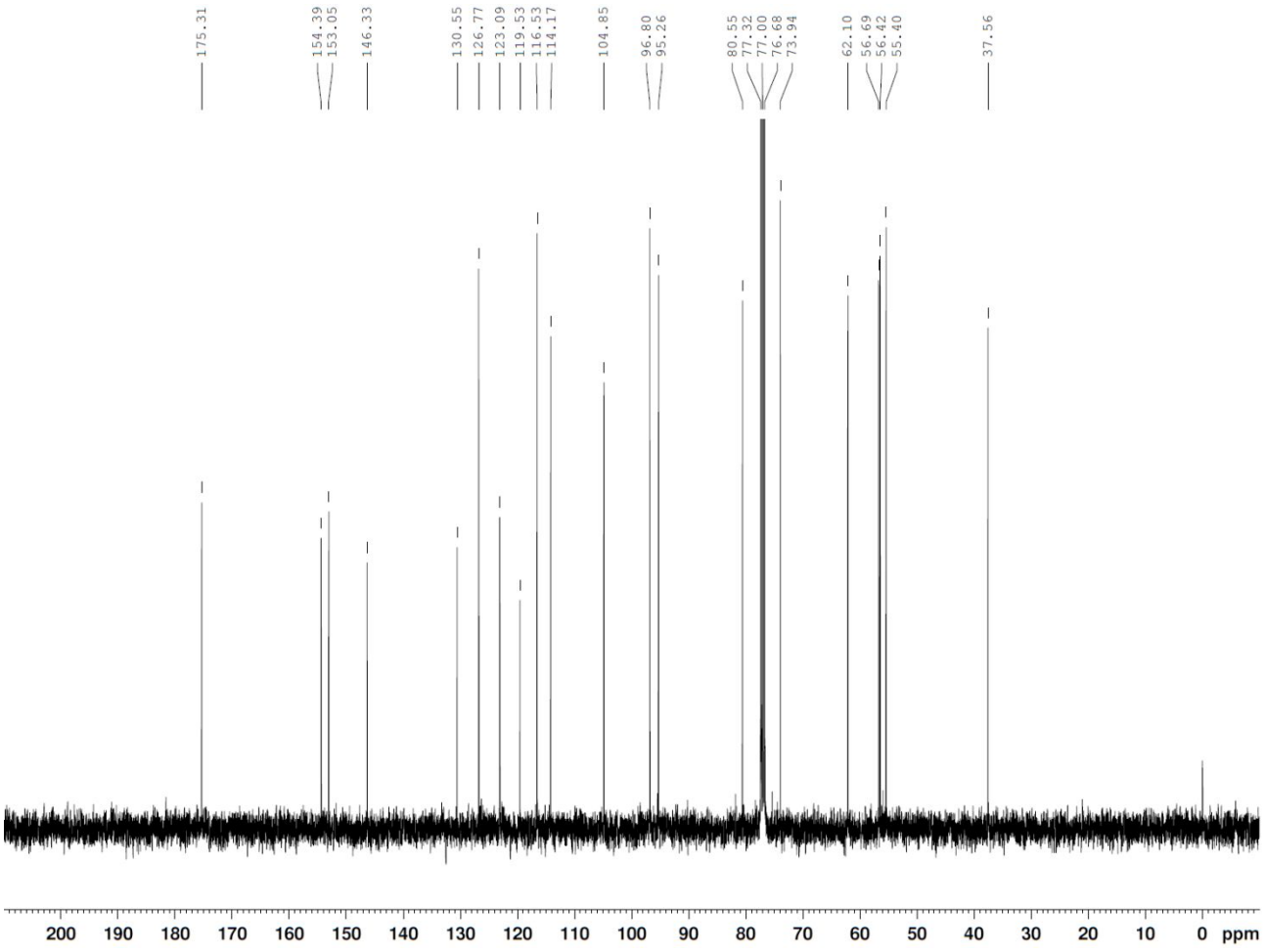
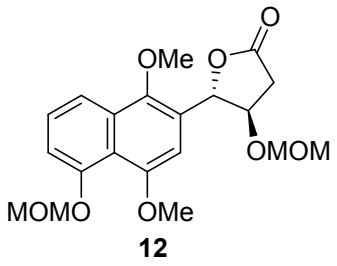


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **12**.



12

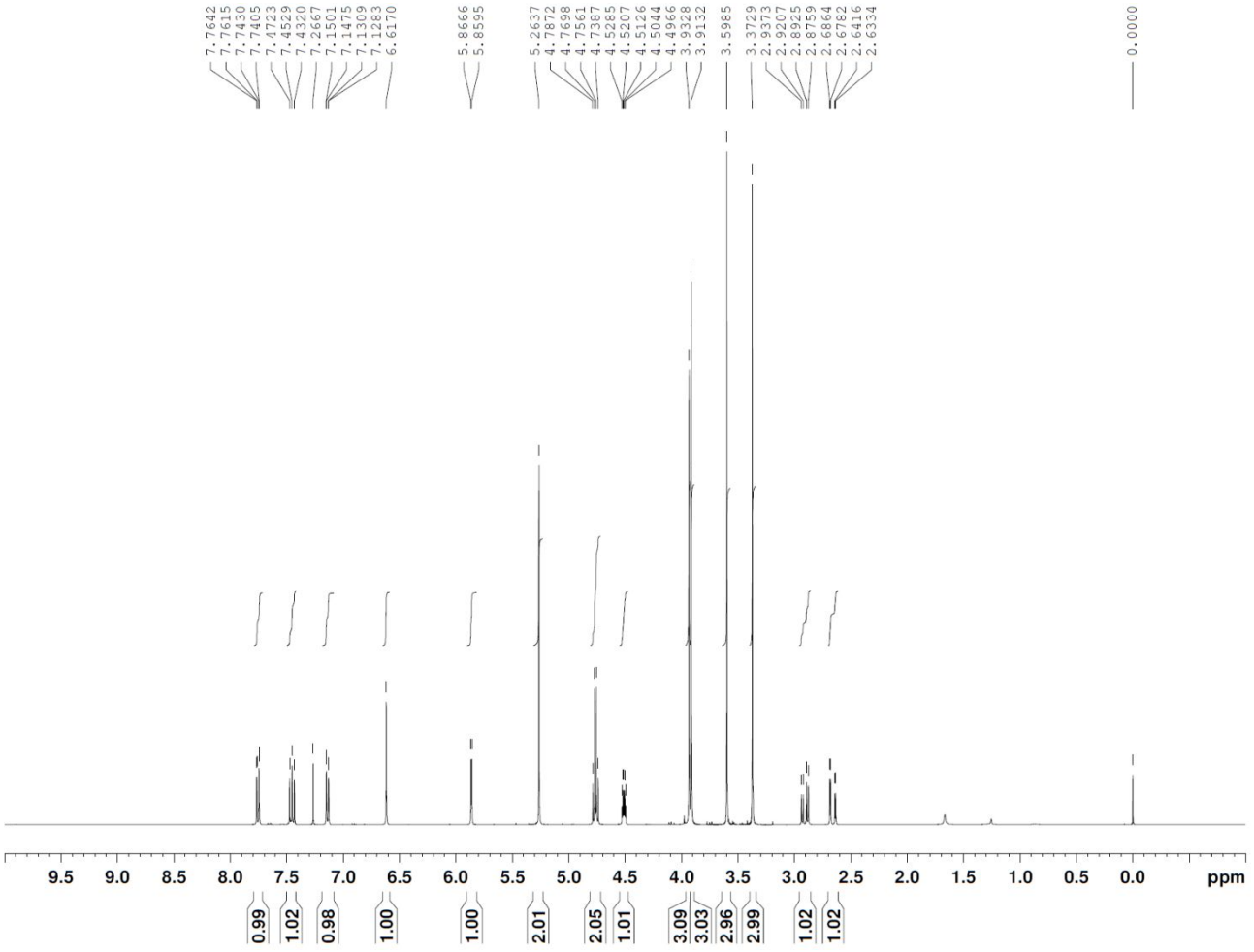


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **12**.

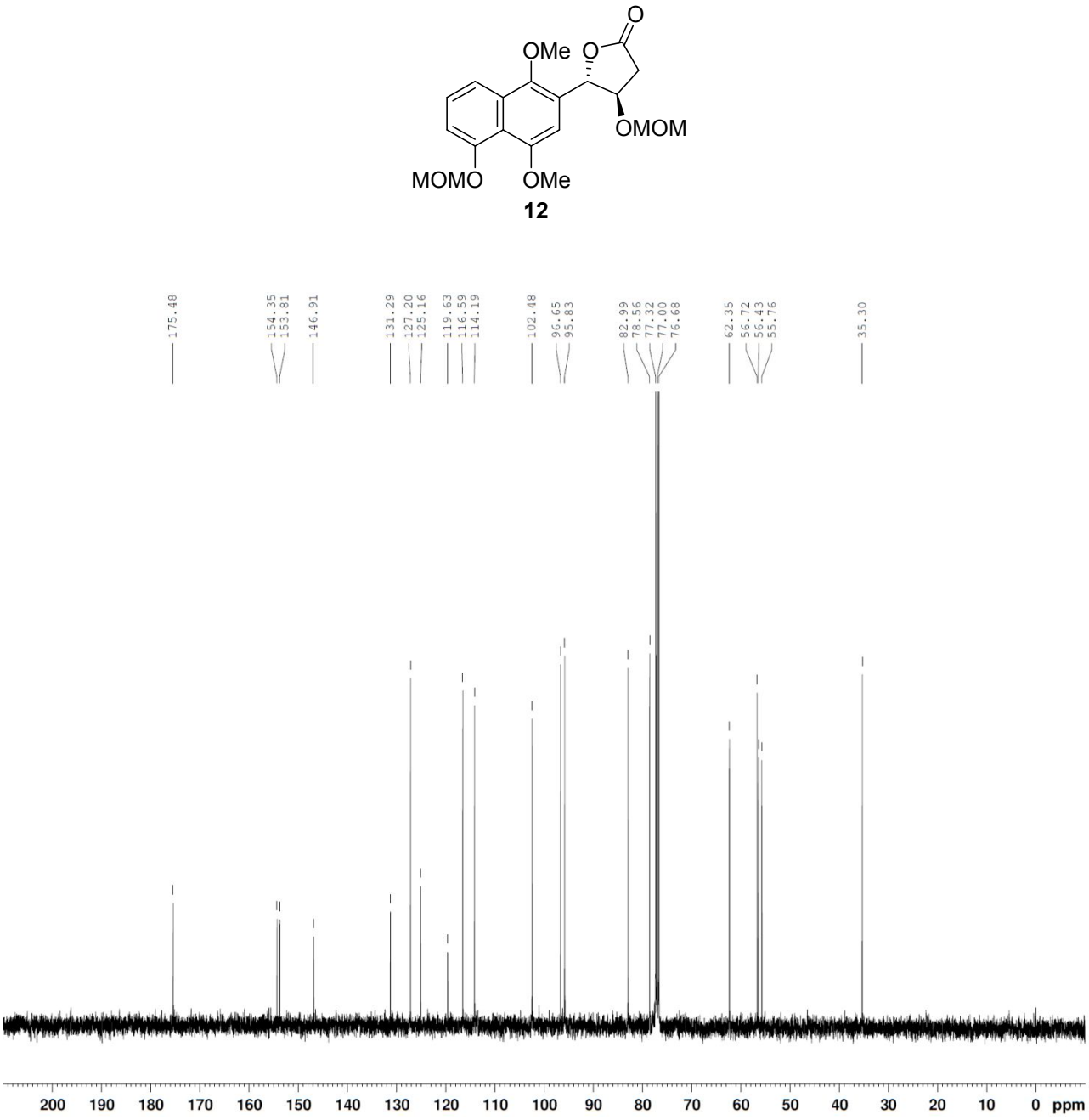


Figure S9. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of compound **1**.

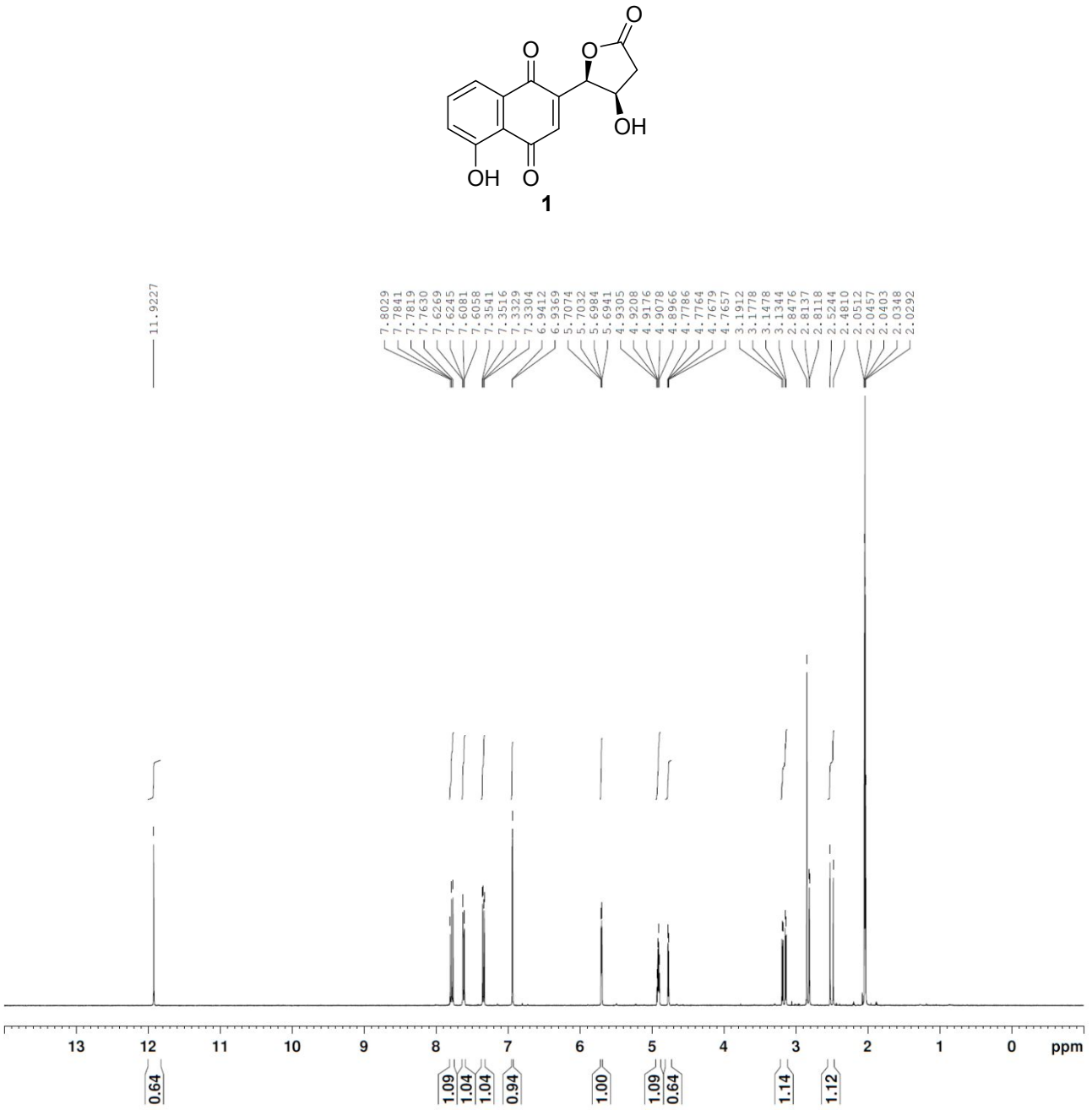
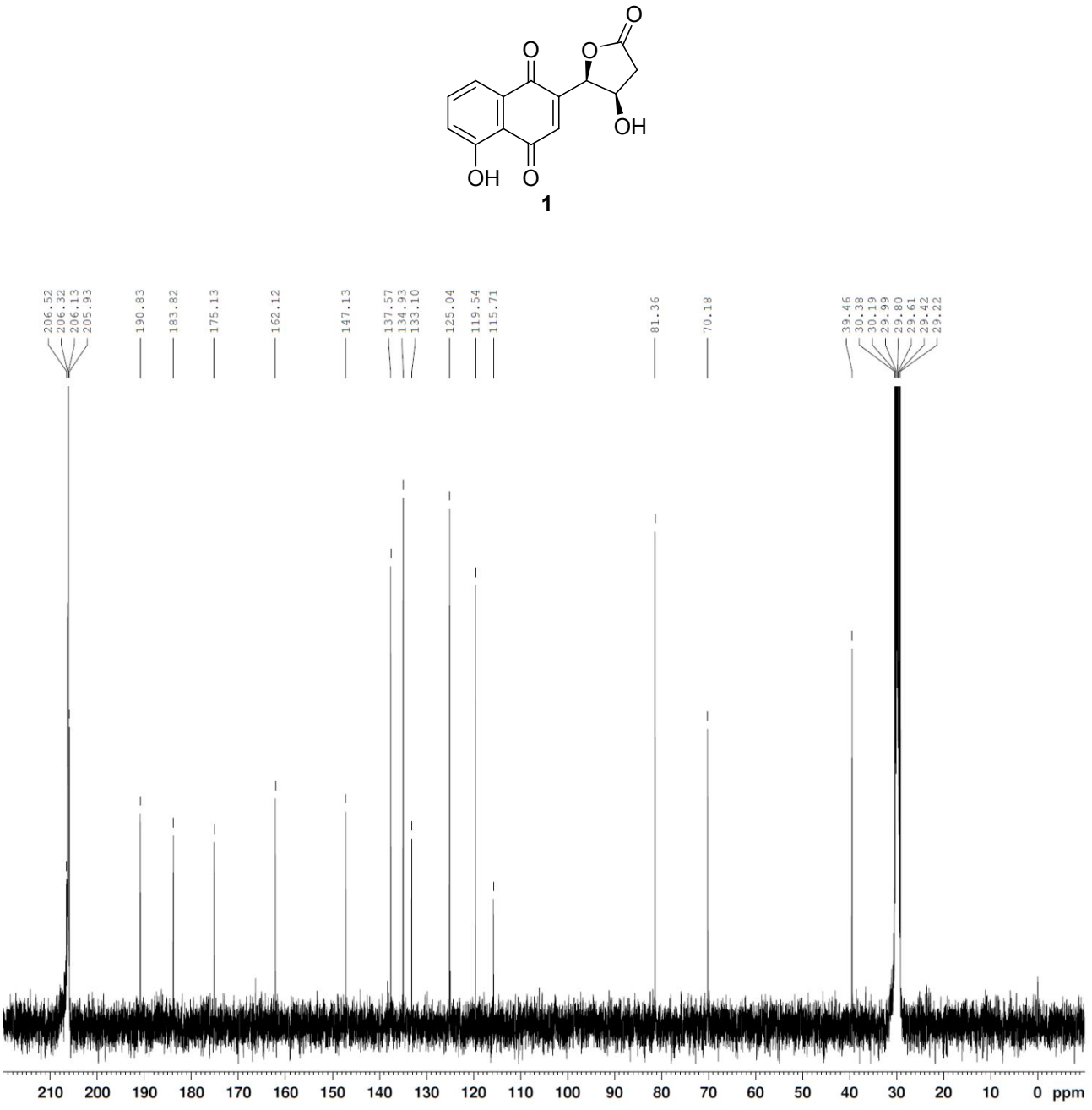


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, acetone-d_6) of compound **1**.



1

Figure S11. ^{1}H NMR spectrum (400 MHz, acetone-d_6, TMS) of compound **2**.

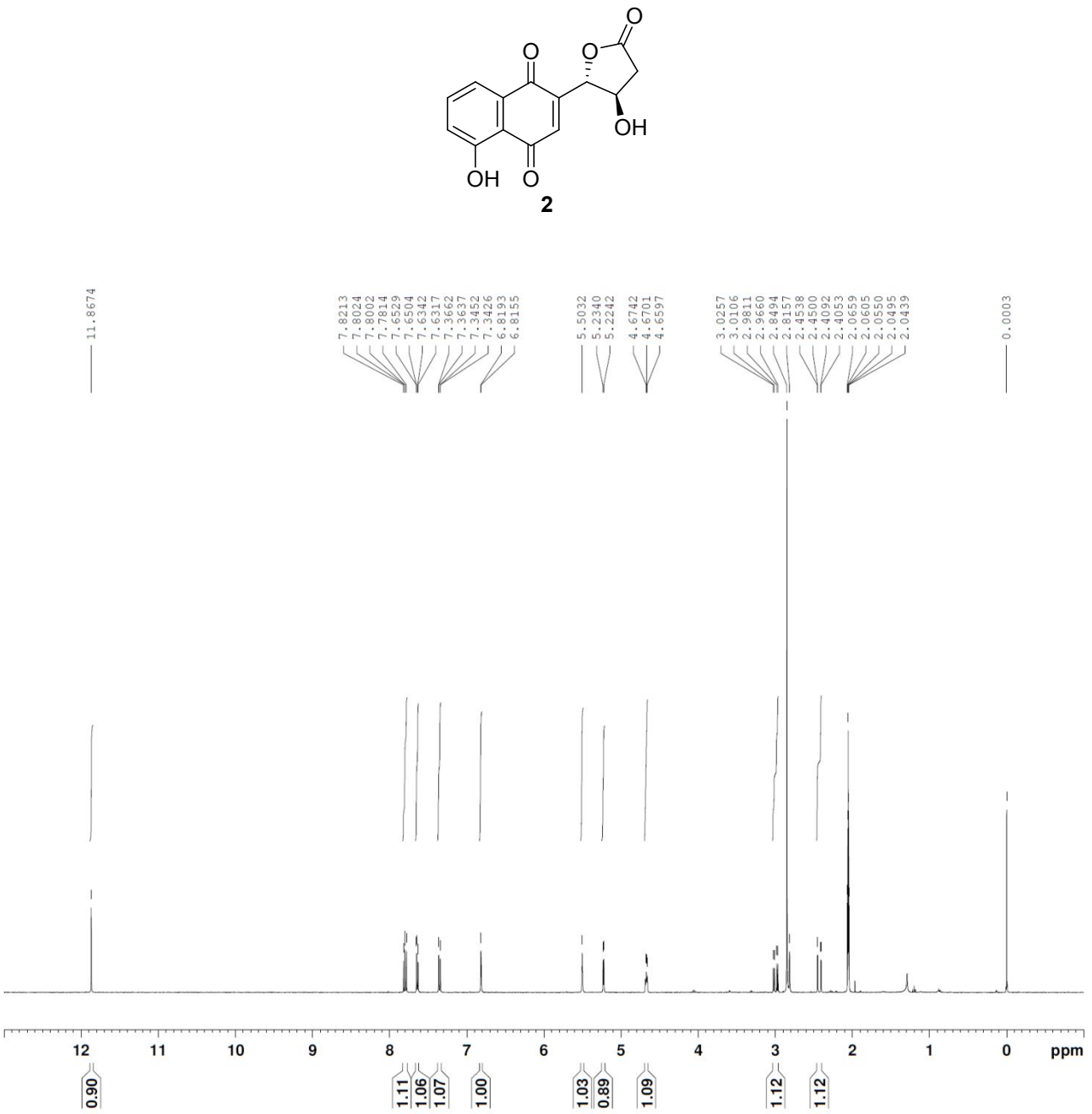
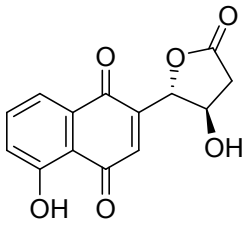


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, acetone-d_6) of compound **2**.



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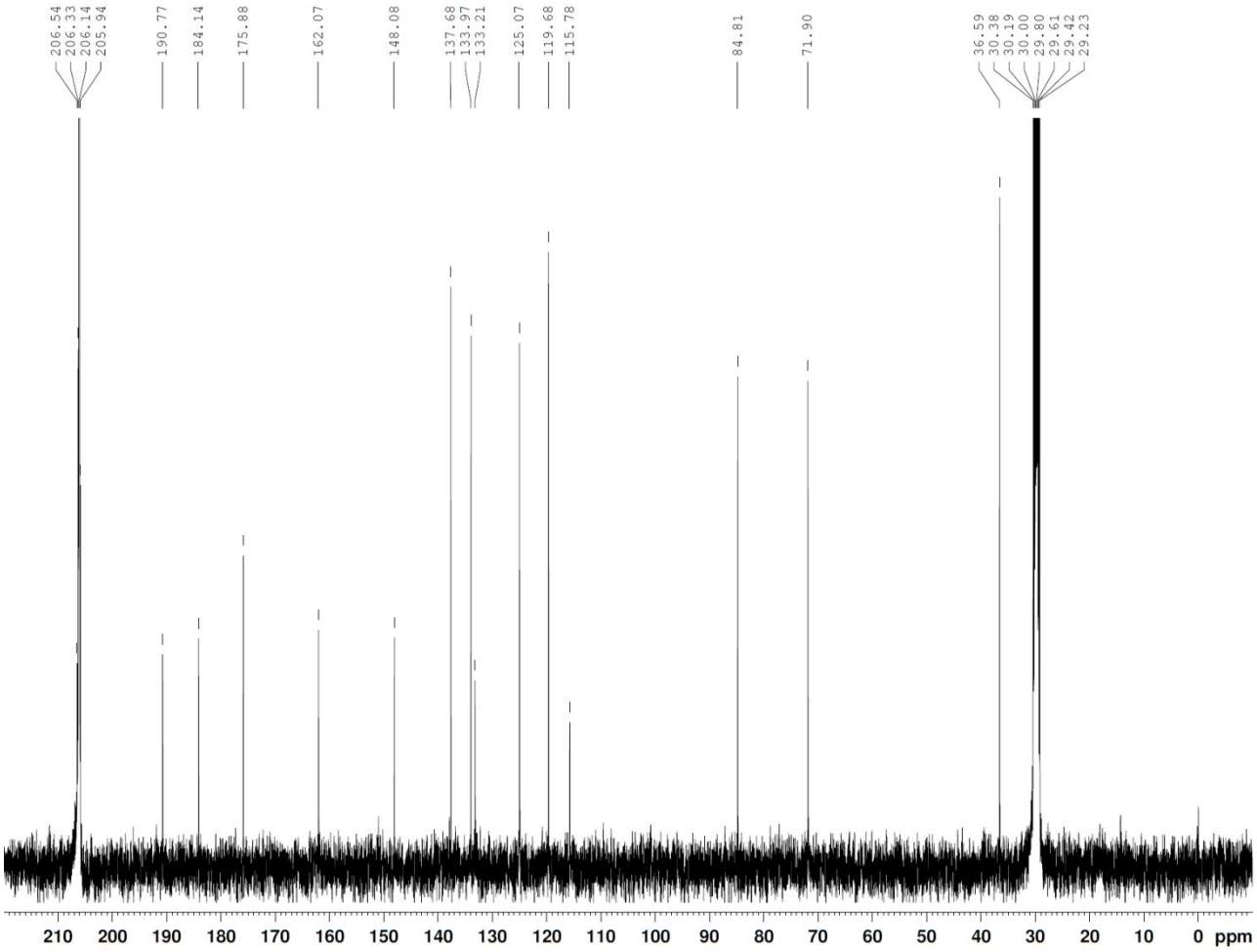
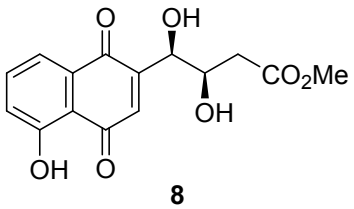


Figure S13. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **8**.



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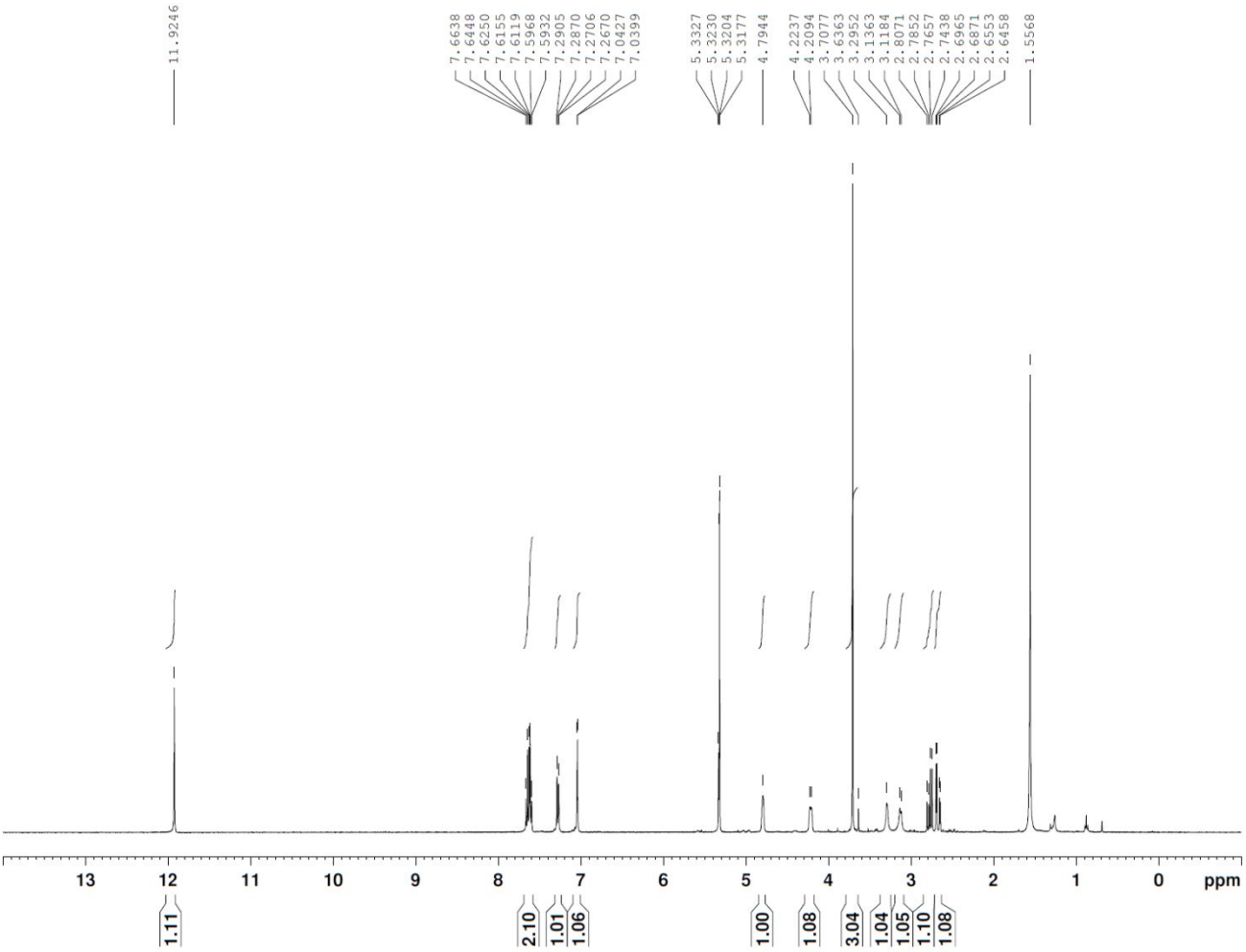
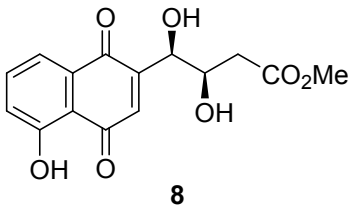


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_2Cl_2) of compound **8**.



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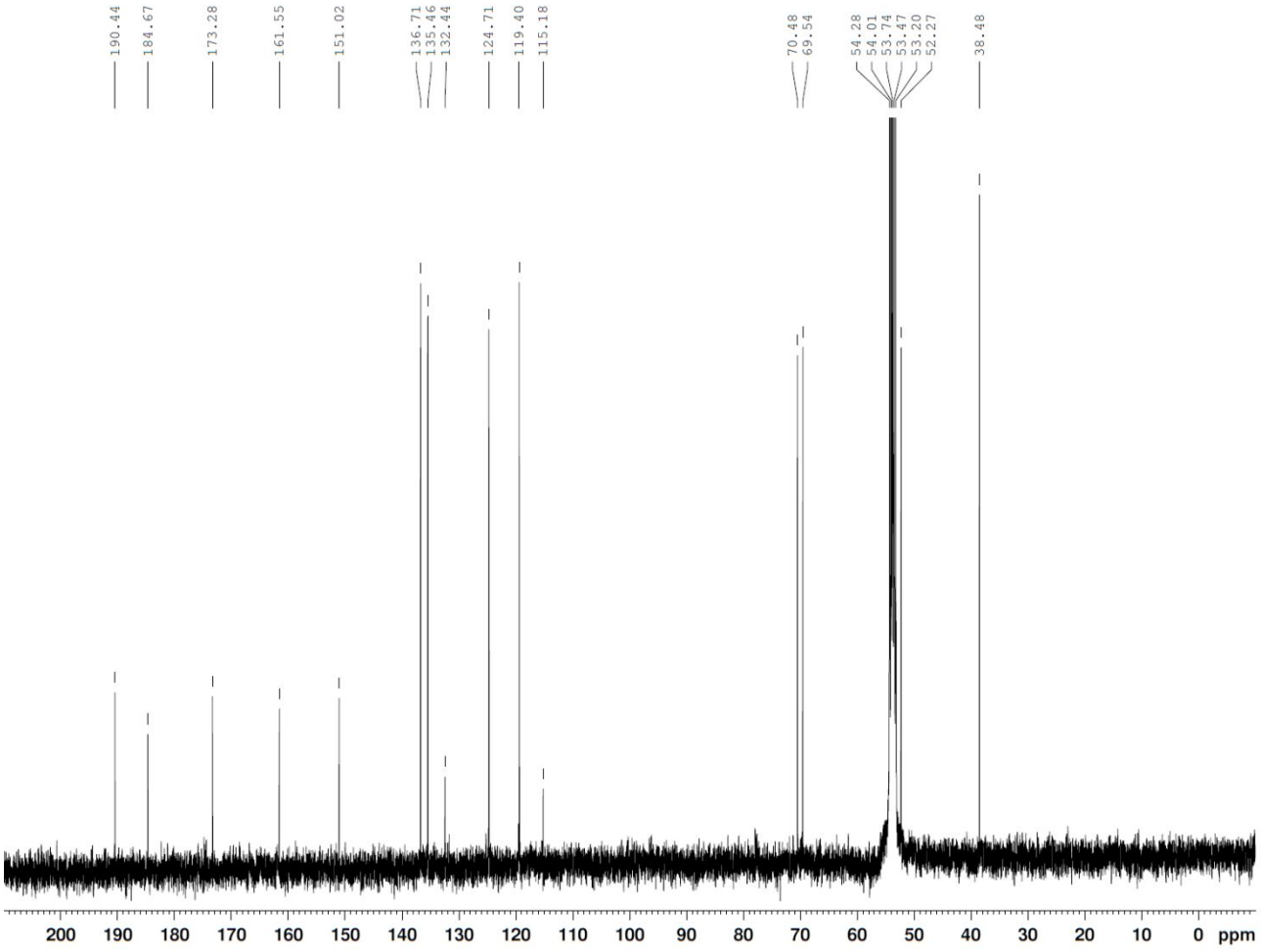


Figure S15. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound 4-*epi*-**8**.

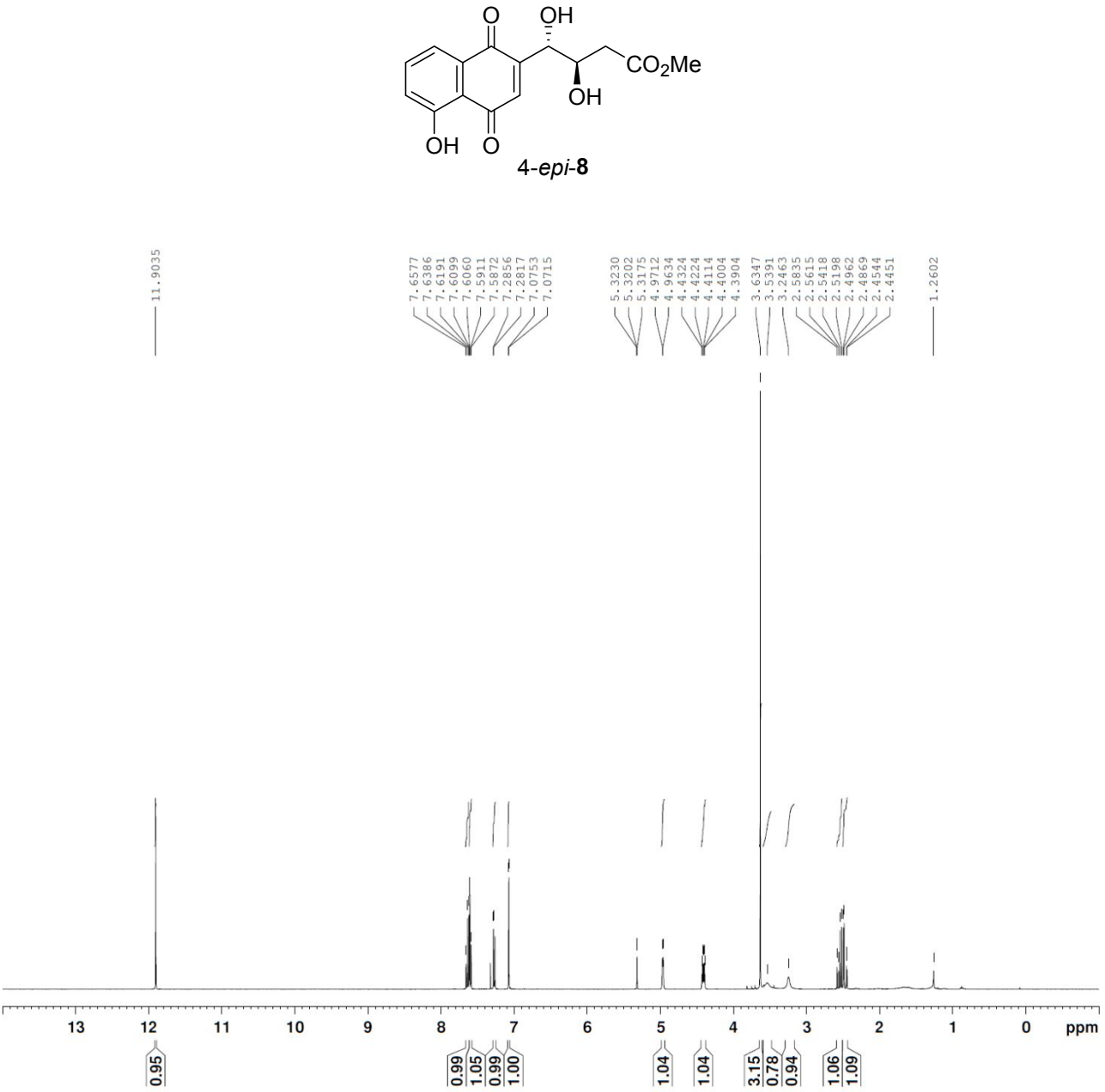
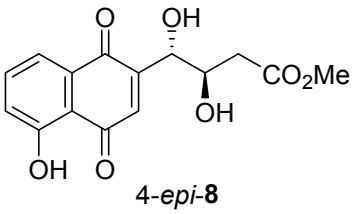


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_2Cl_2) of compound 4-*epi*-**8**.



4-*epi*-**8**

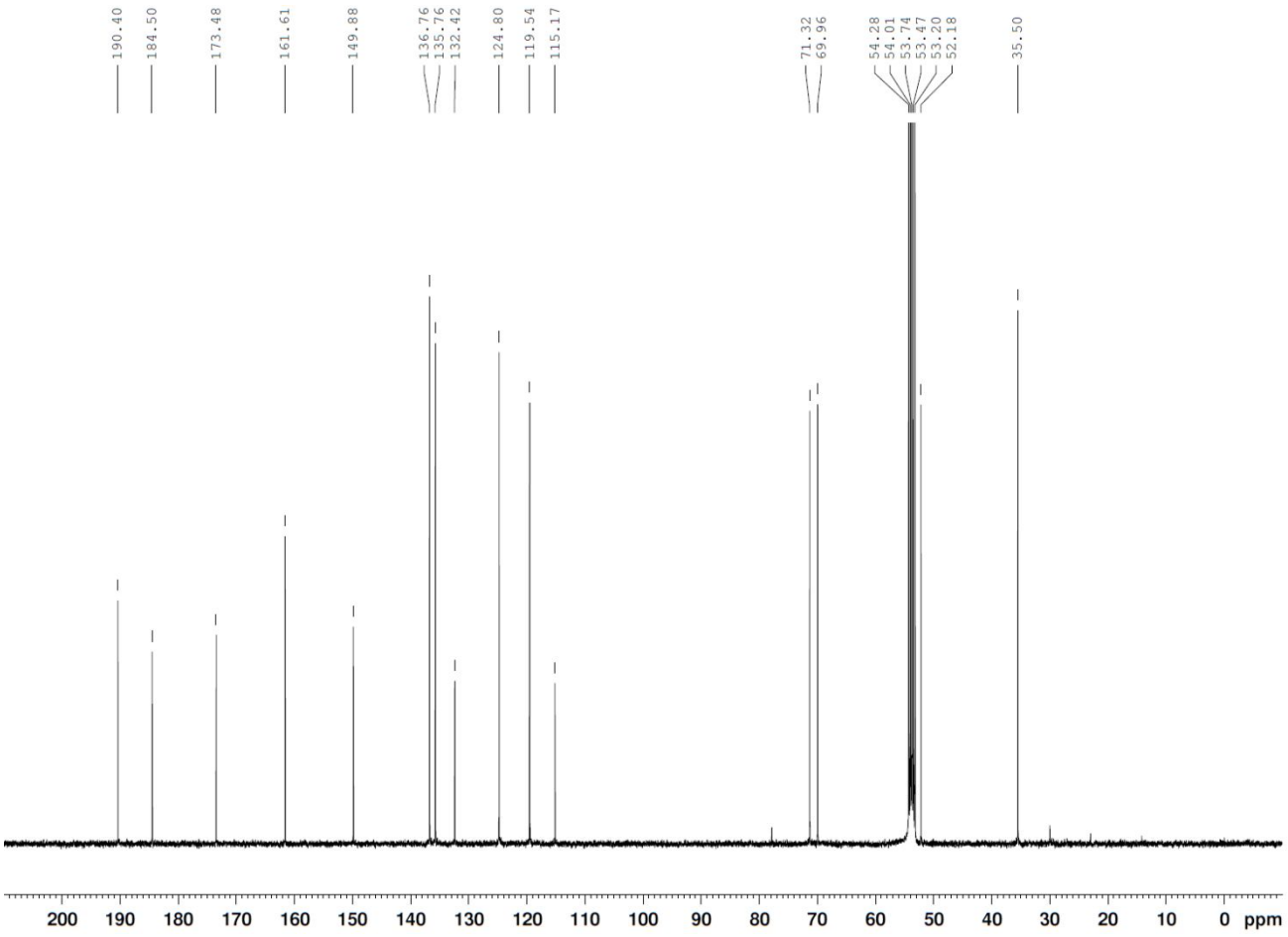
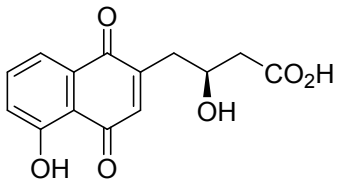


Figure S17. ^{1}H NMR spectrum (400 MHz, acetone-d_6, TMS) of compound **3**.



3

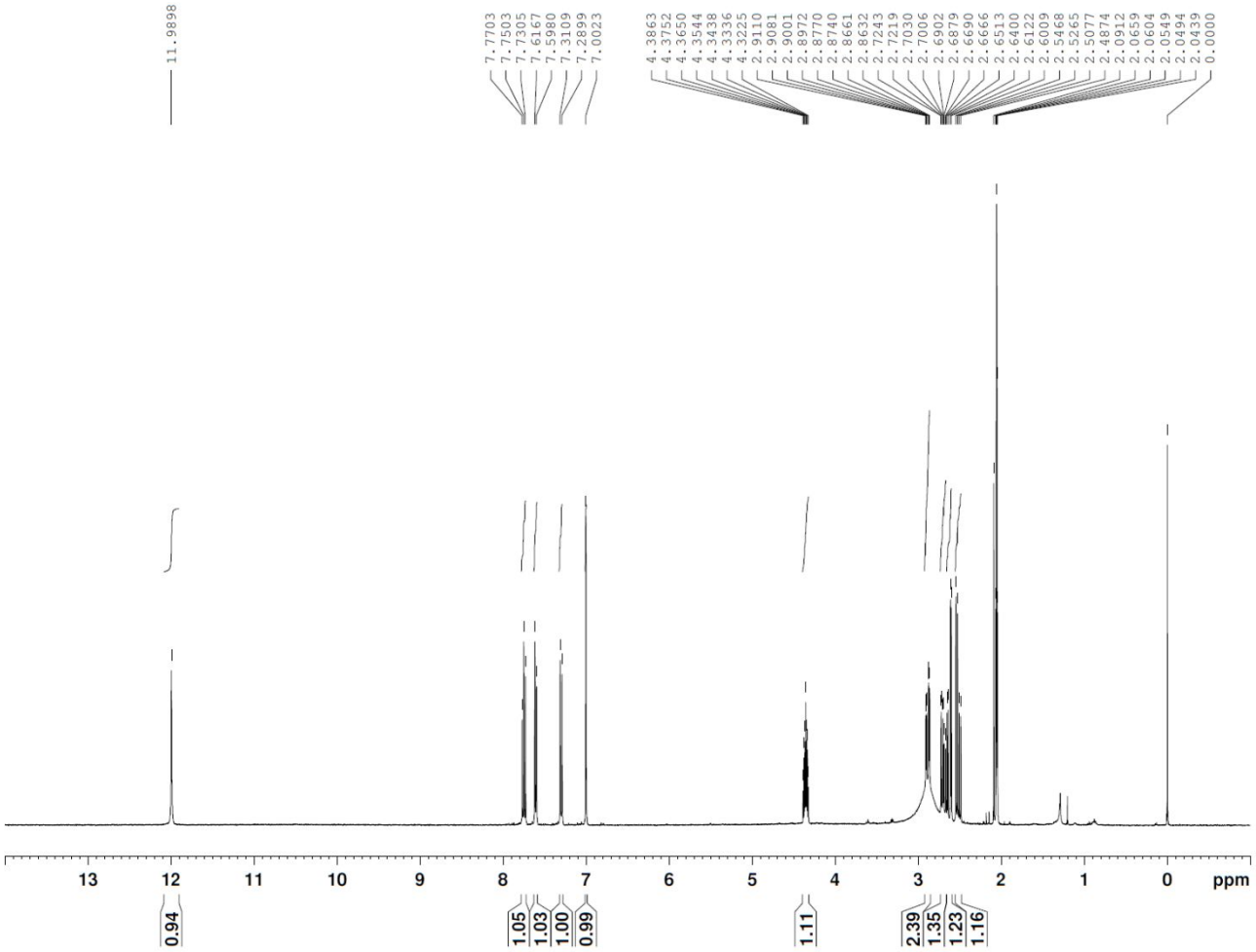
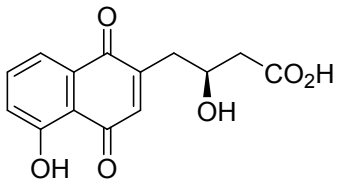
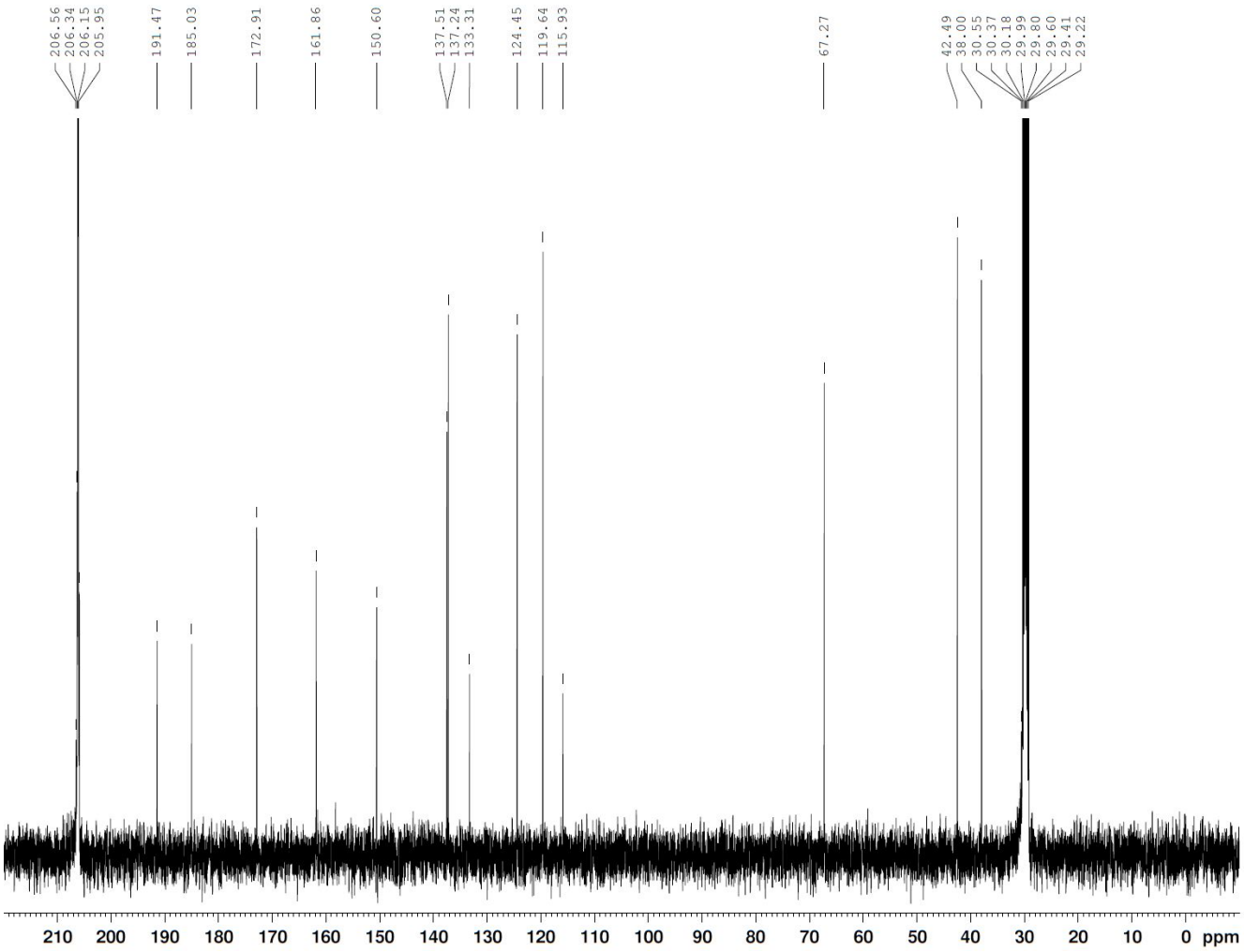


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, acetone-d_6) of compound **3**.



3



CO2H

Figure S19. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of compound **6**.

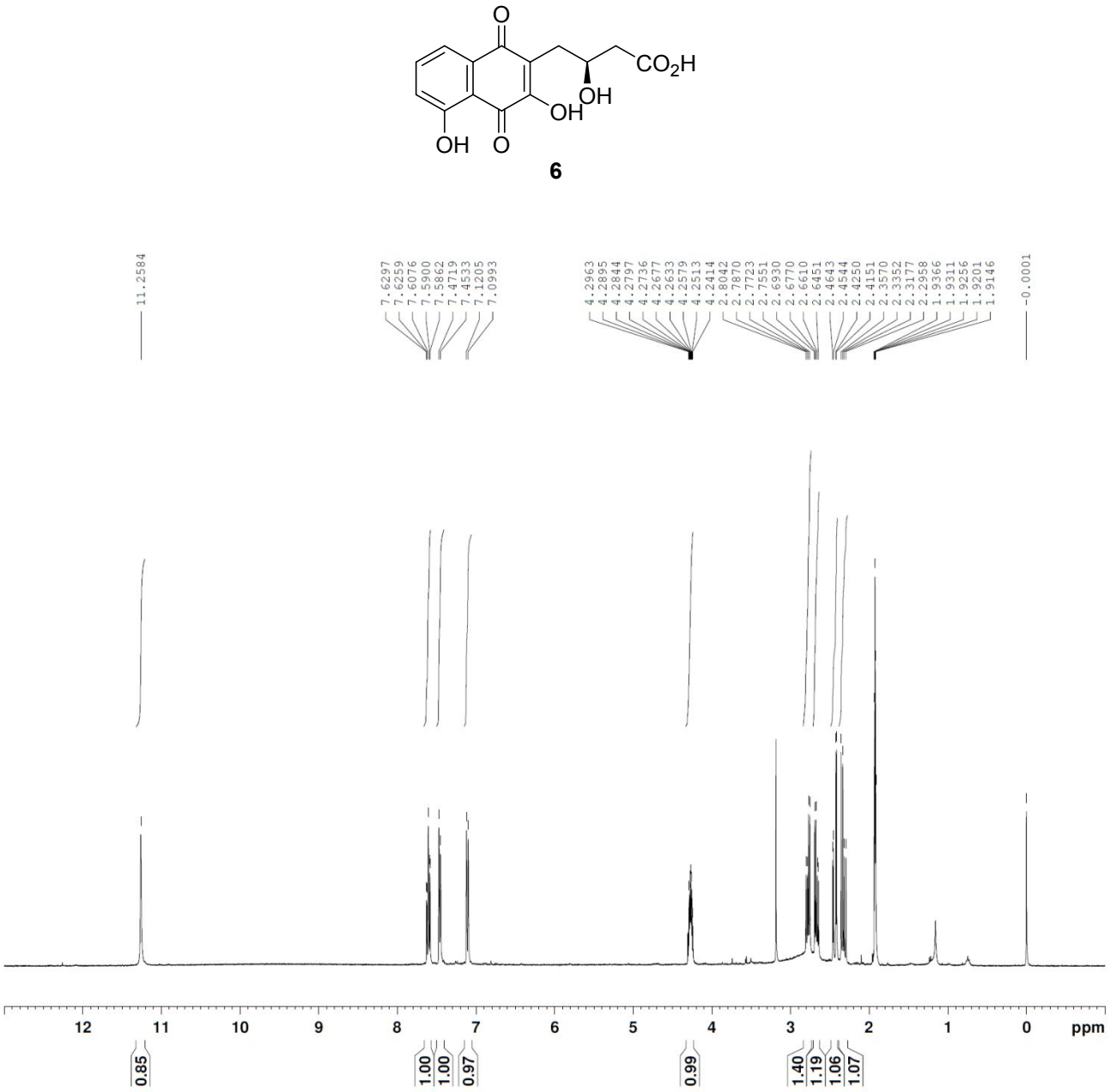
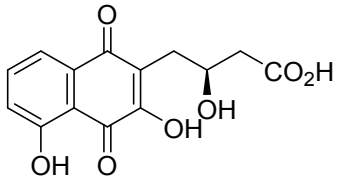


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, acetone-d_6) of compound **6**.



6

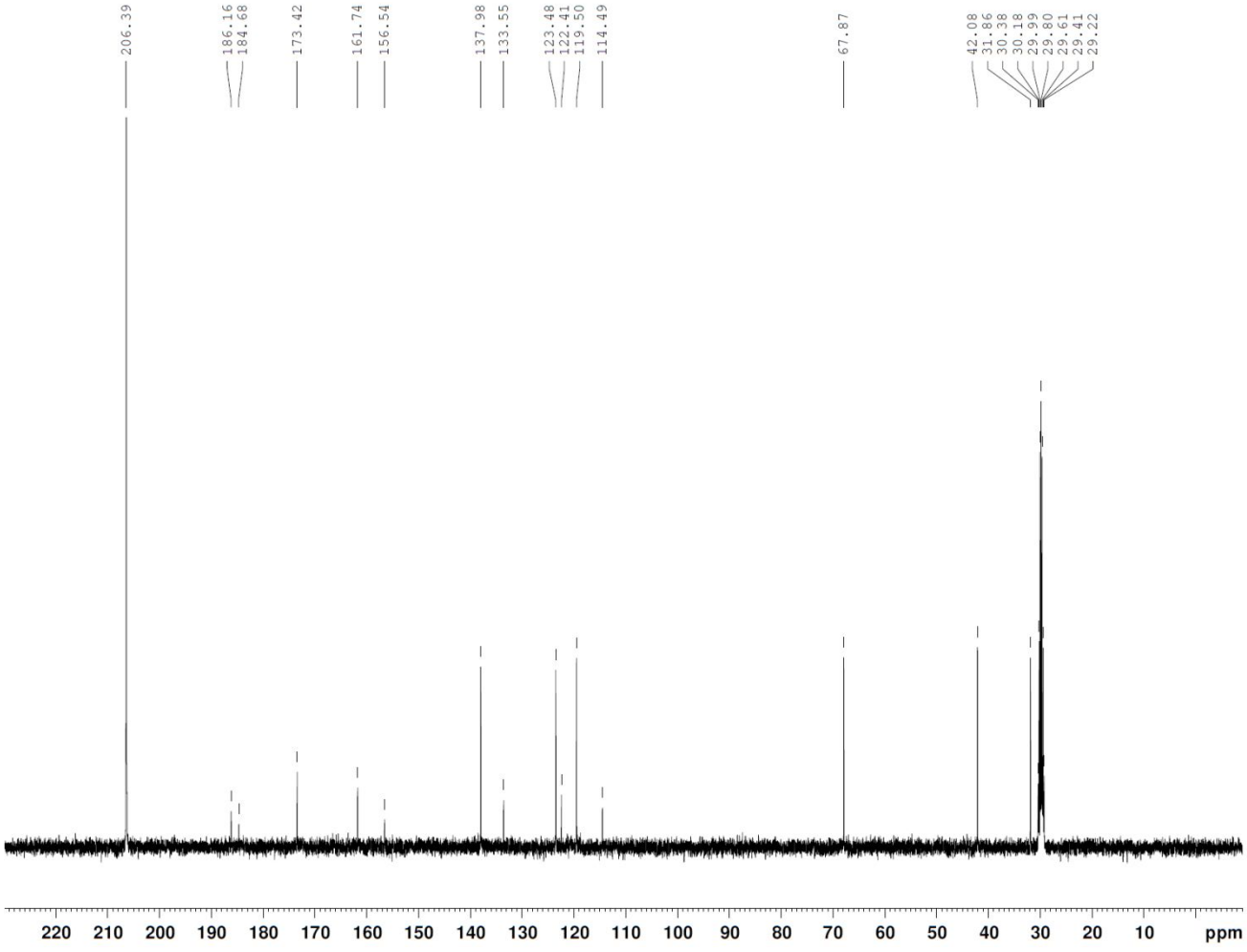
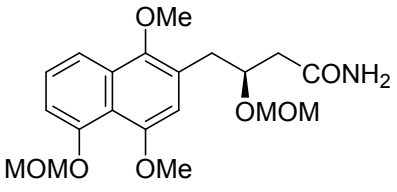


Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **15**.



15

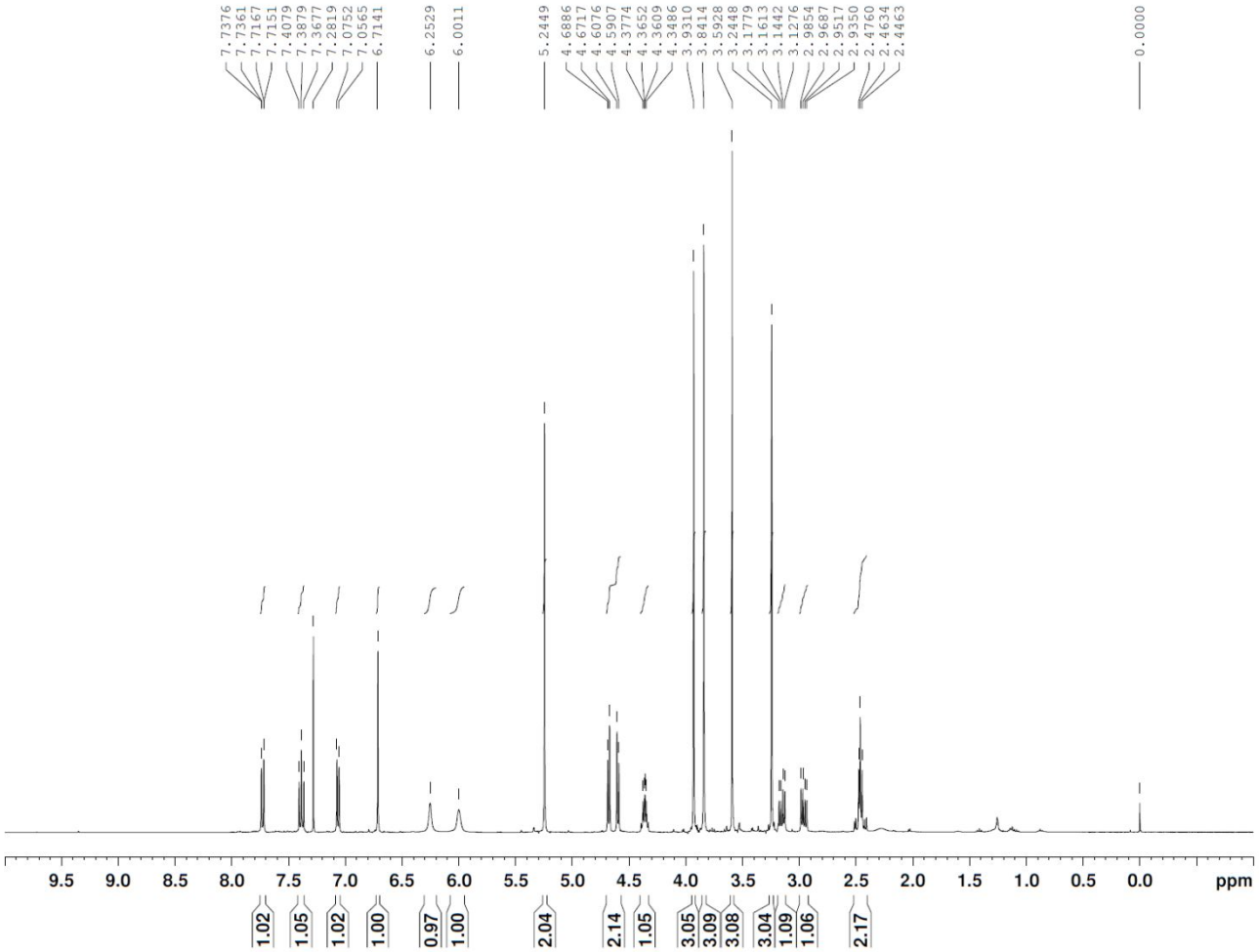
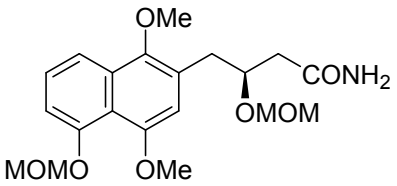


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **15**.



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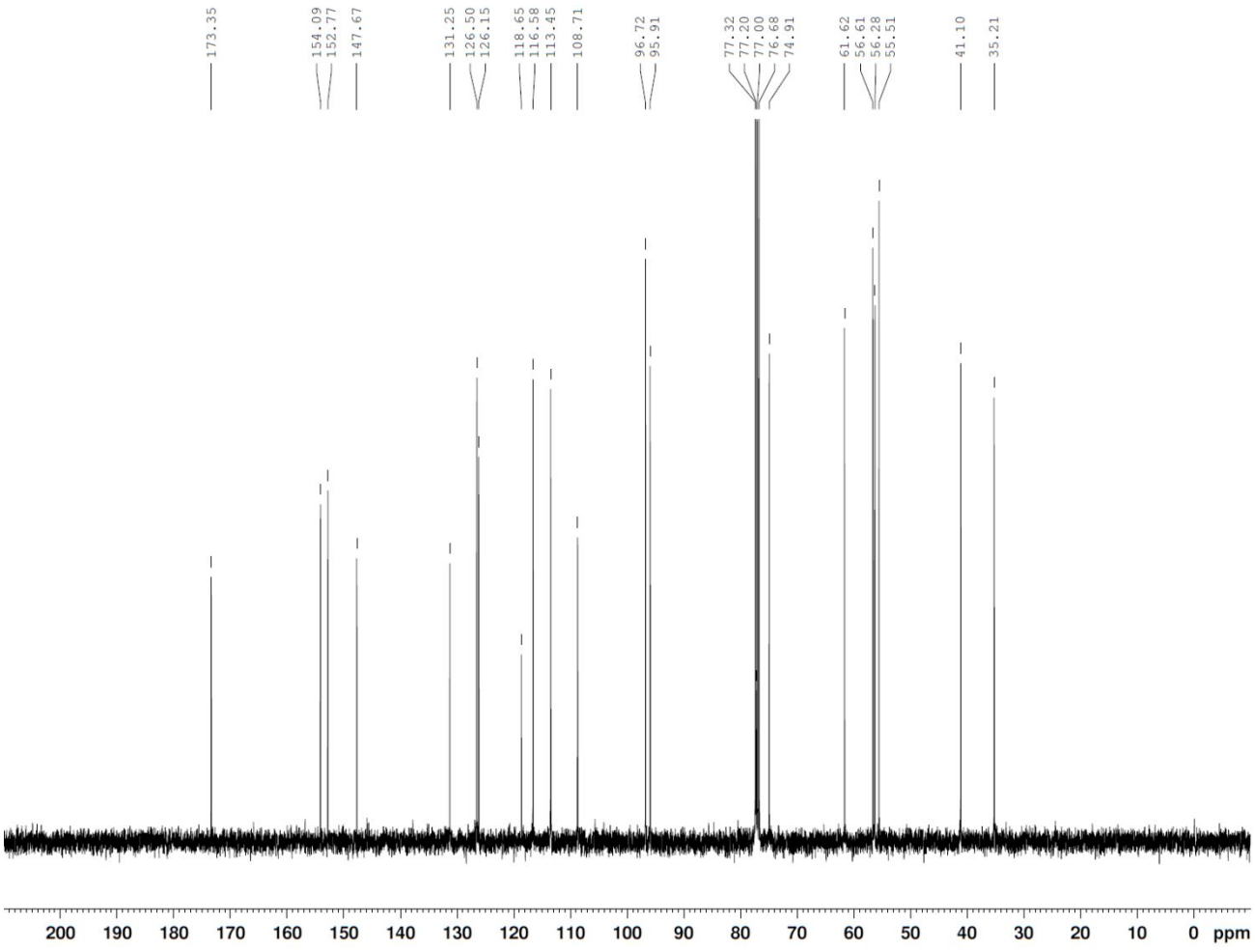
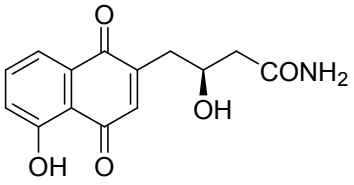


Figure S23. ^{1}H NMR spectrum (400 MHz, CD_3OD, TMS) of compound **5**.



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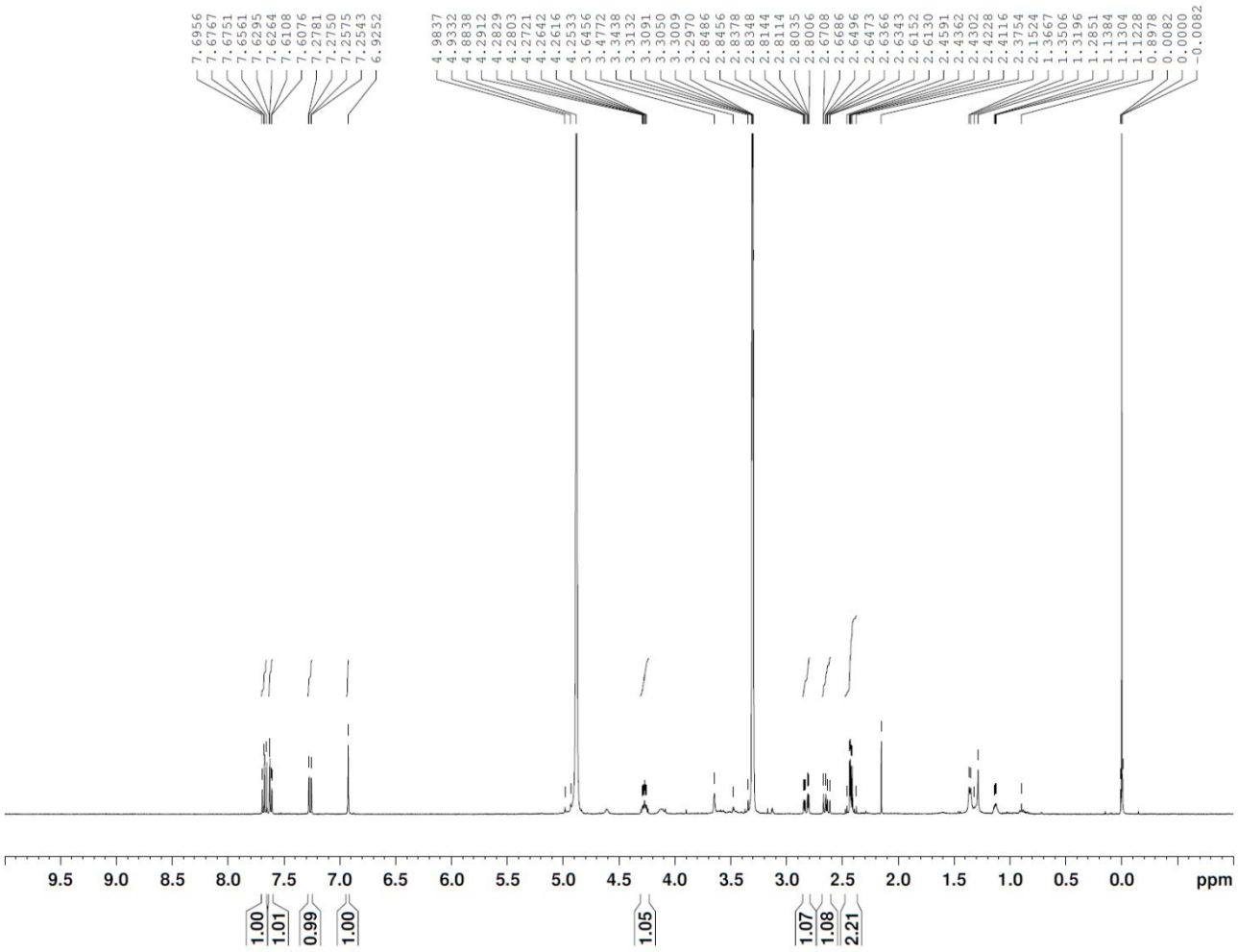
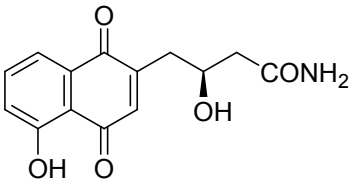


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, CD_3OD) of compound **5**.



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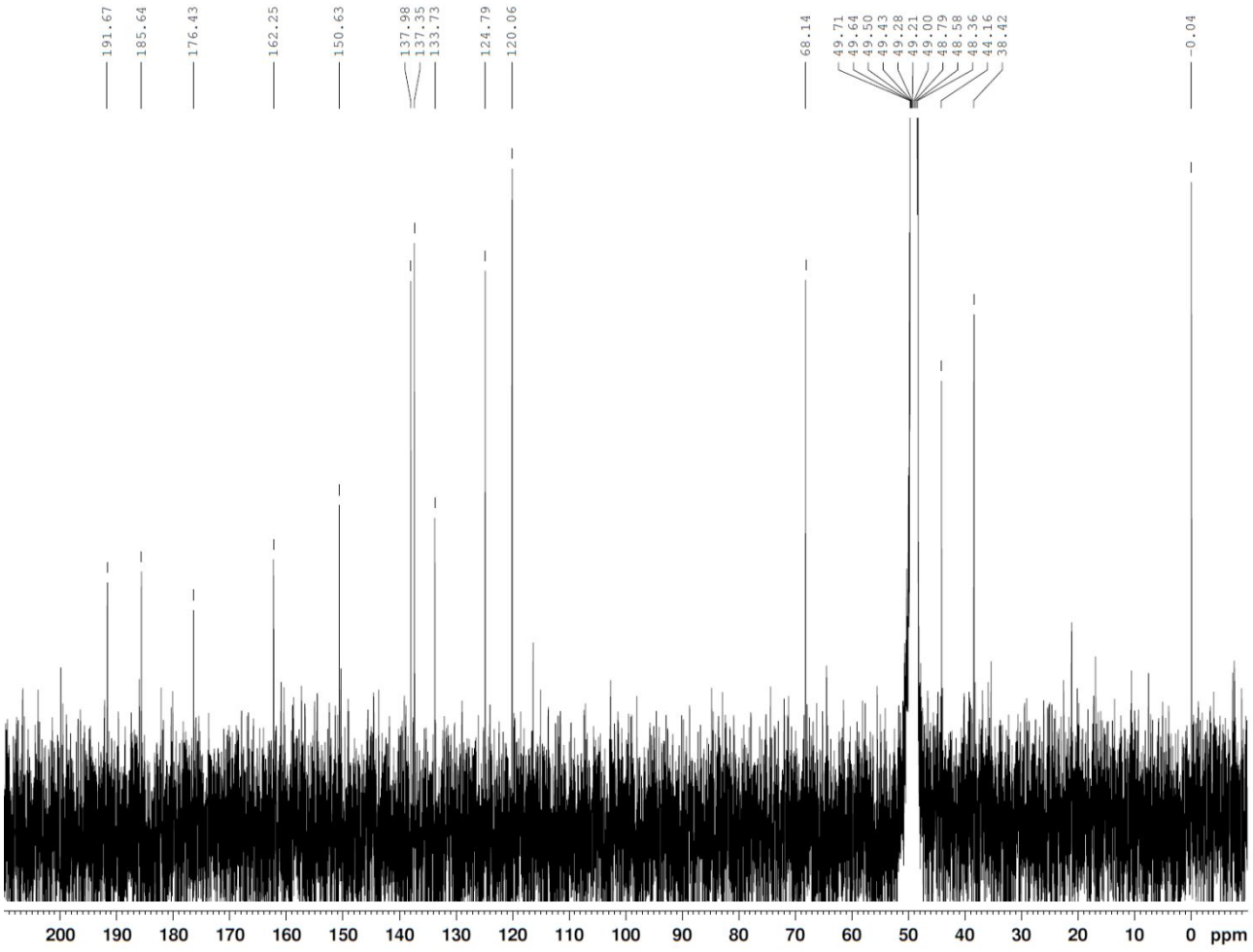
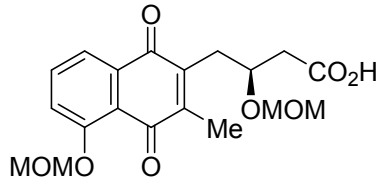


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **16**.



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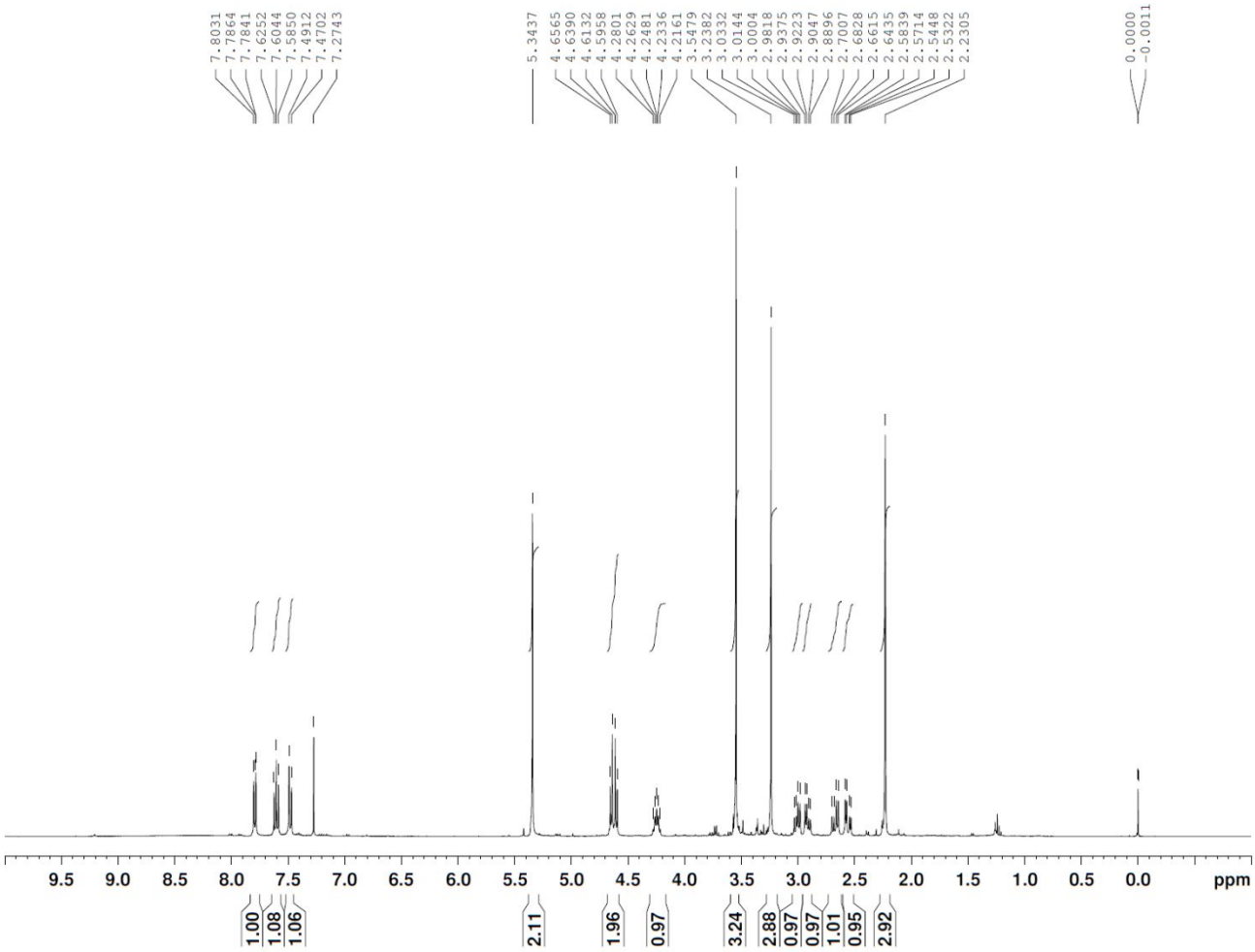
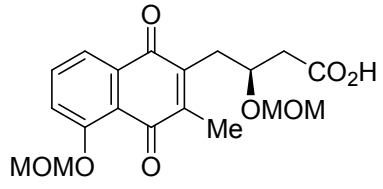


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **16**.



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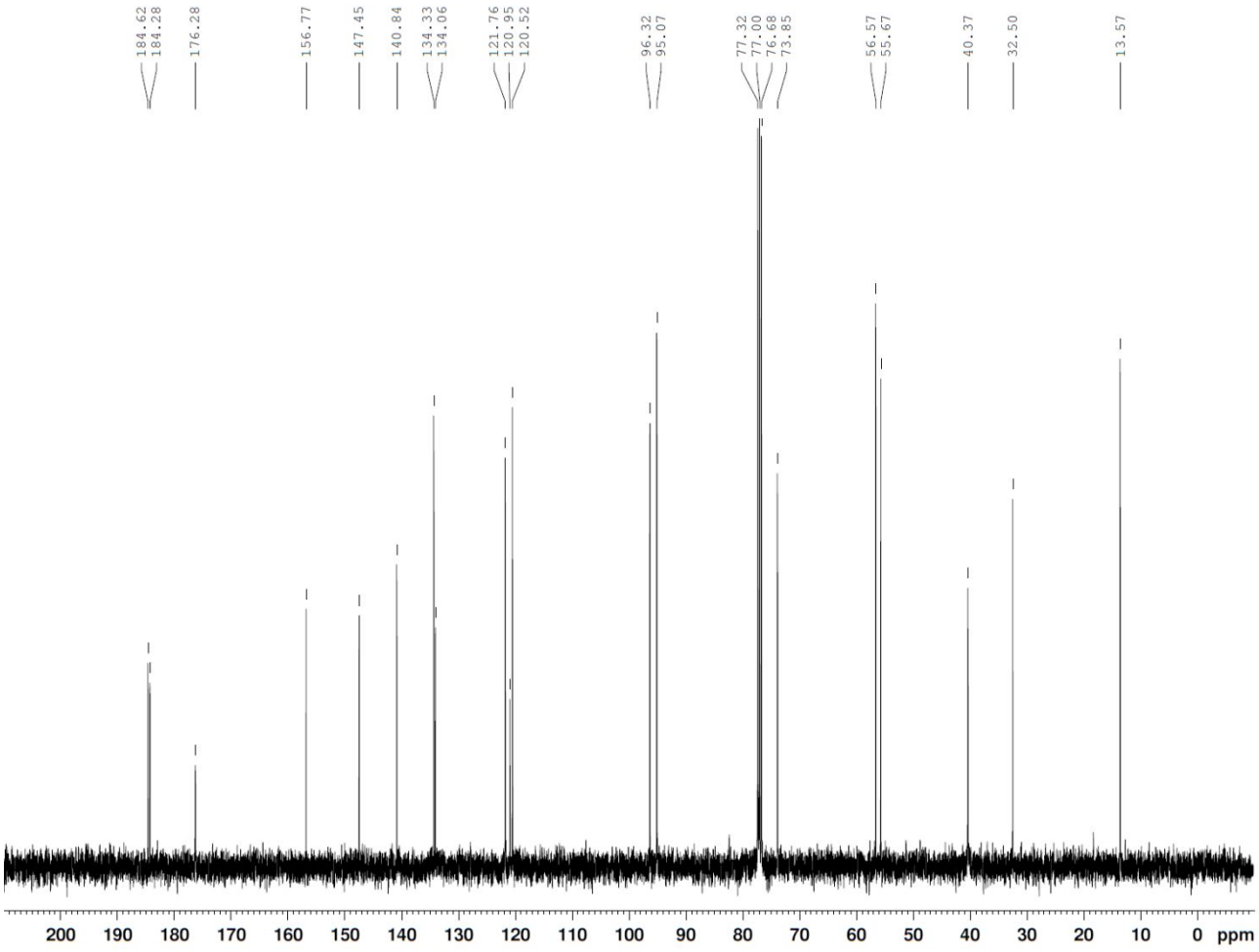
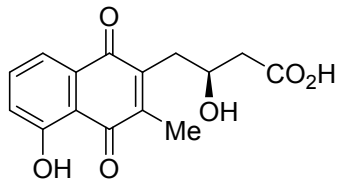


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3/CD_3OD$ = 9/1, TMS) of compound **7**.



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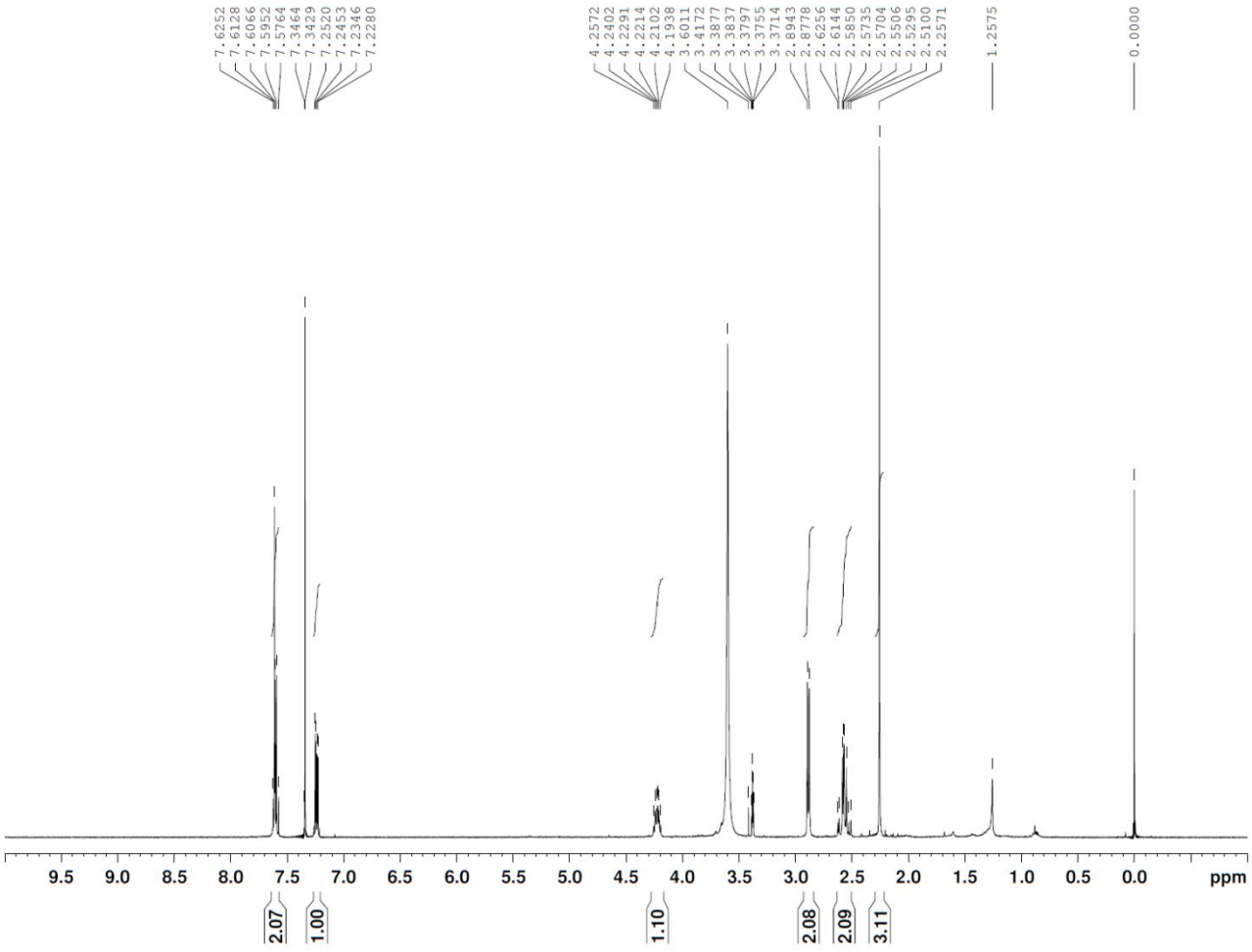
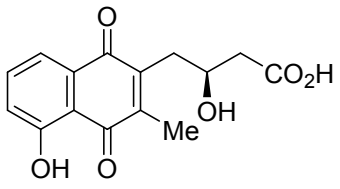


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **7**.



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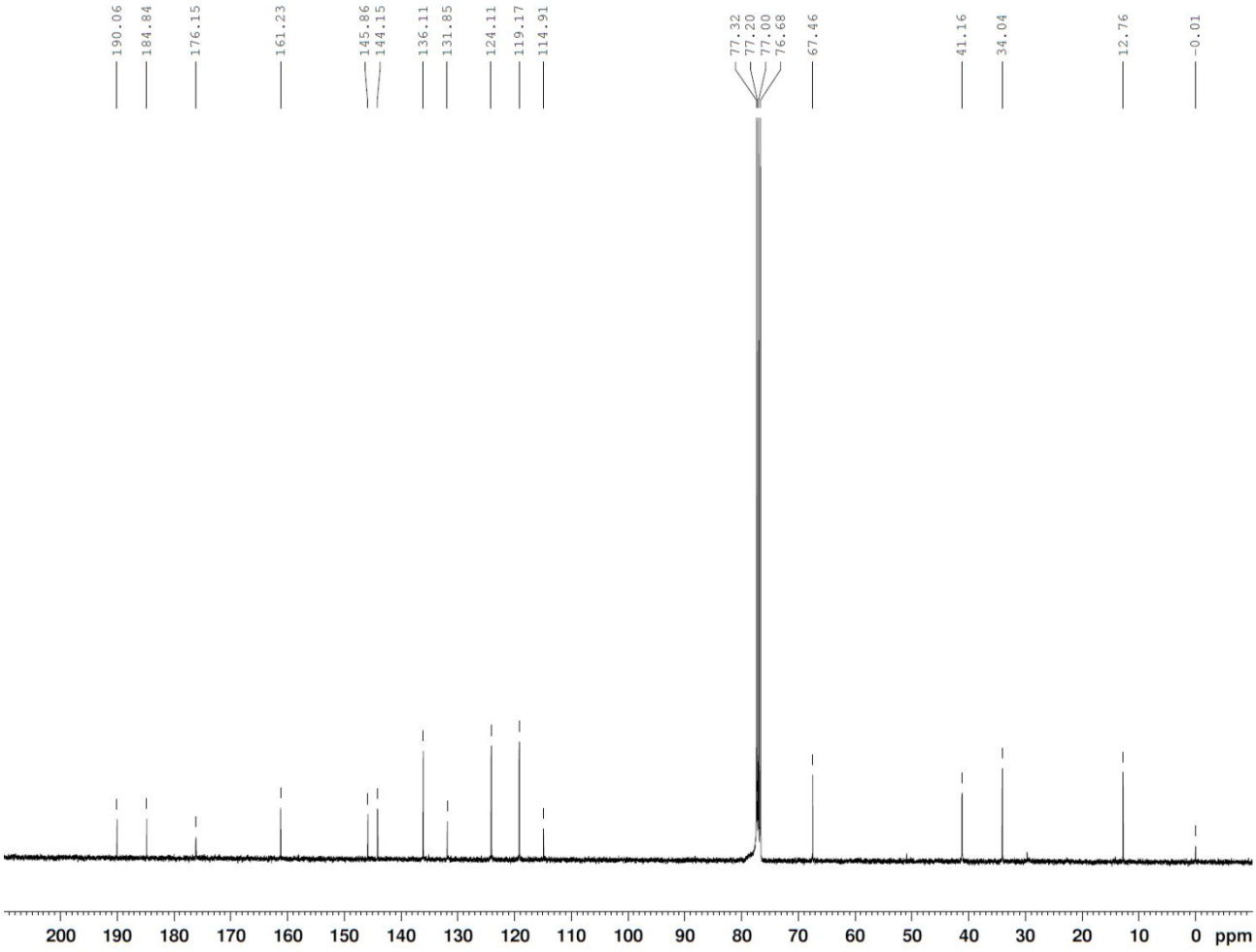
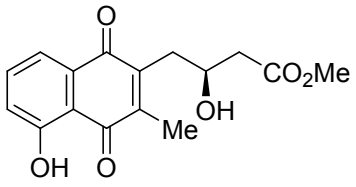


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **19**.



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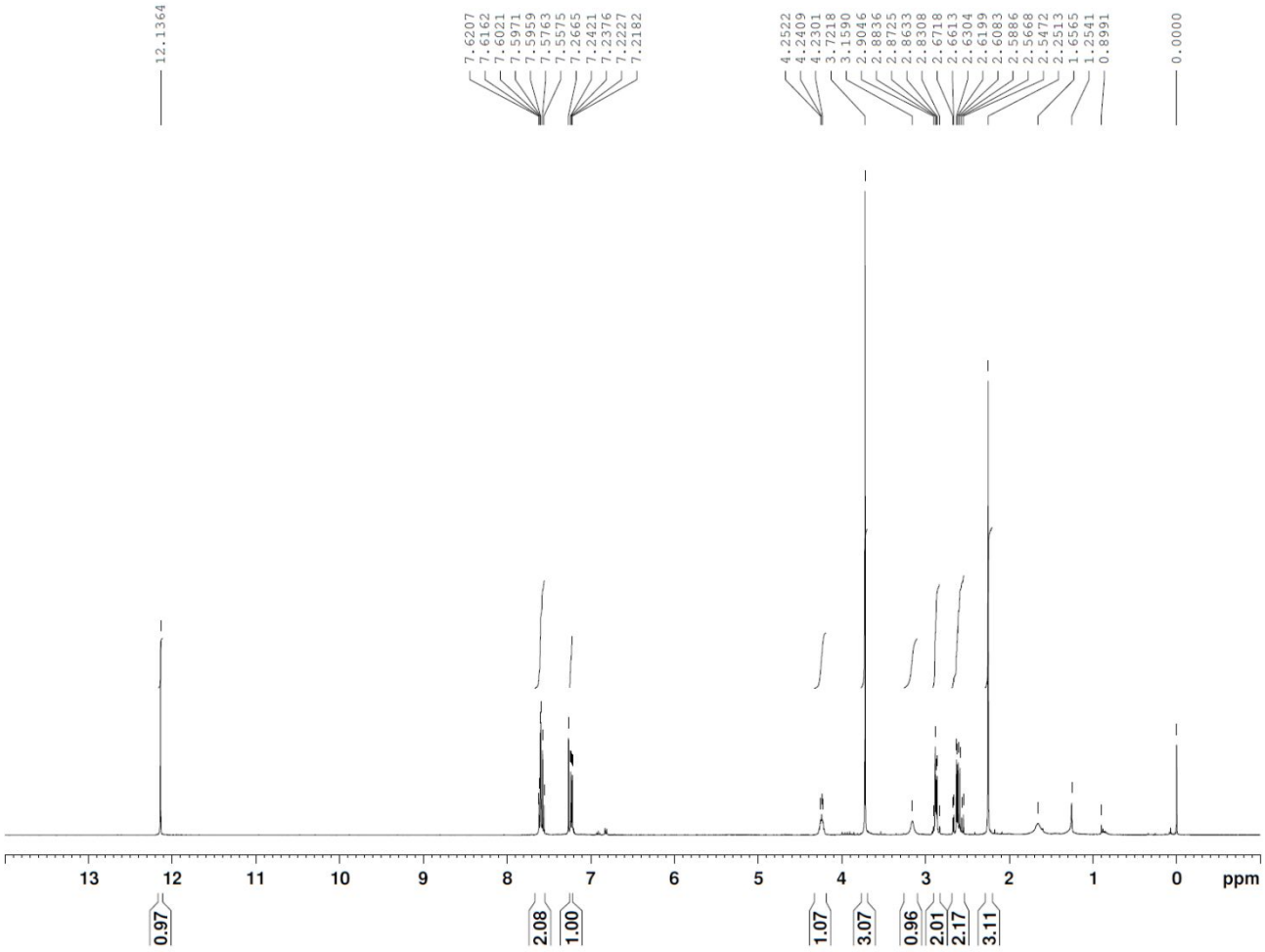
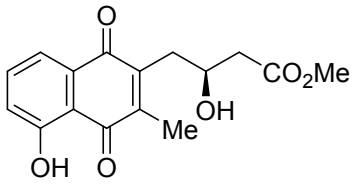


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **19**.



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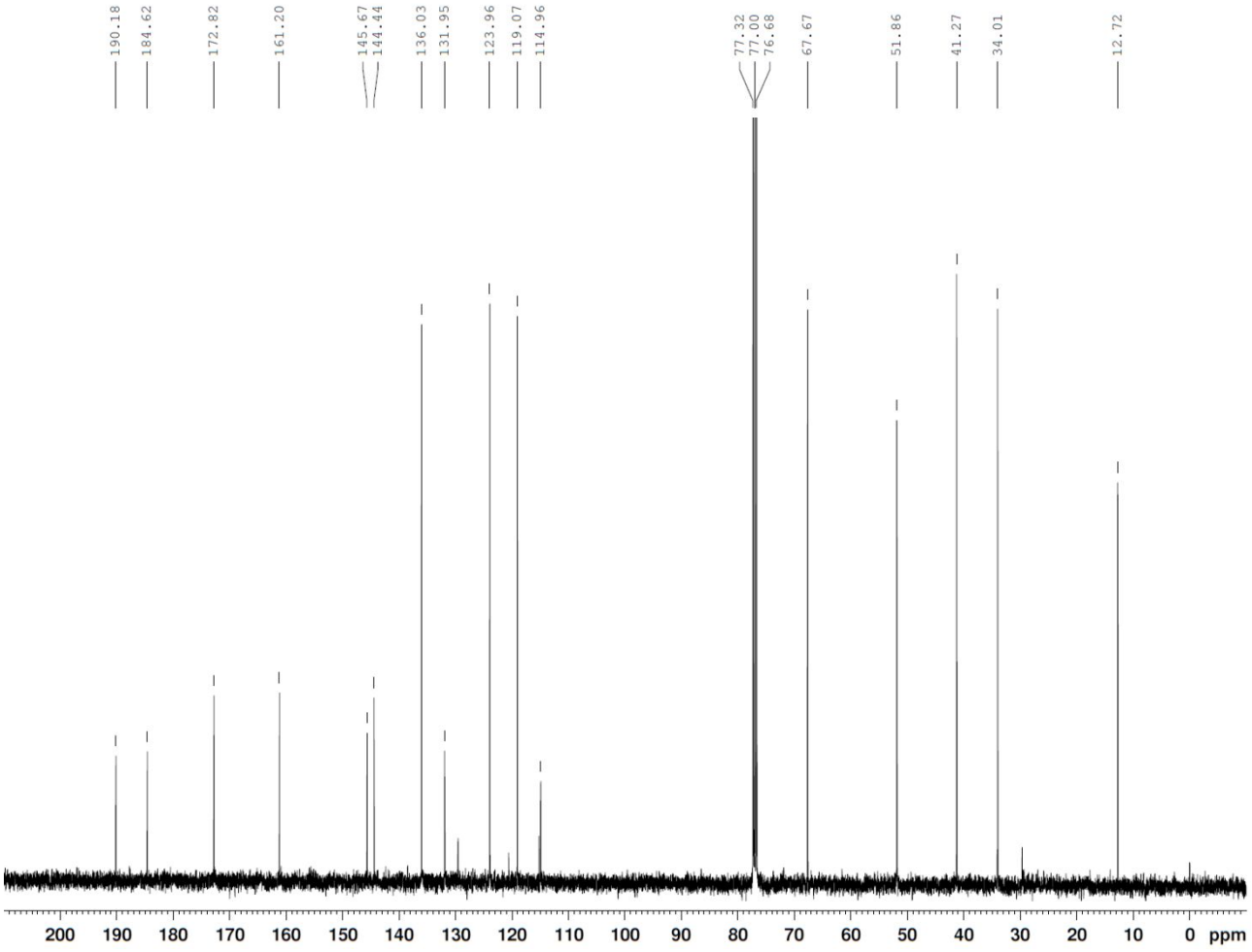


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **24**.

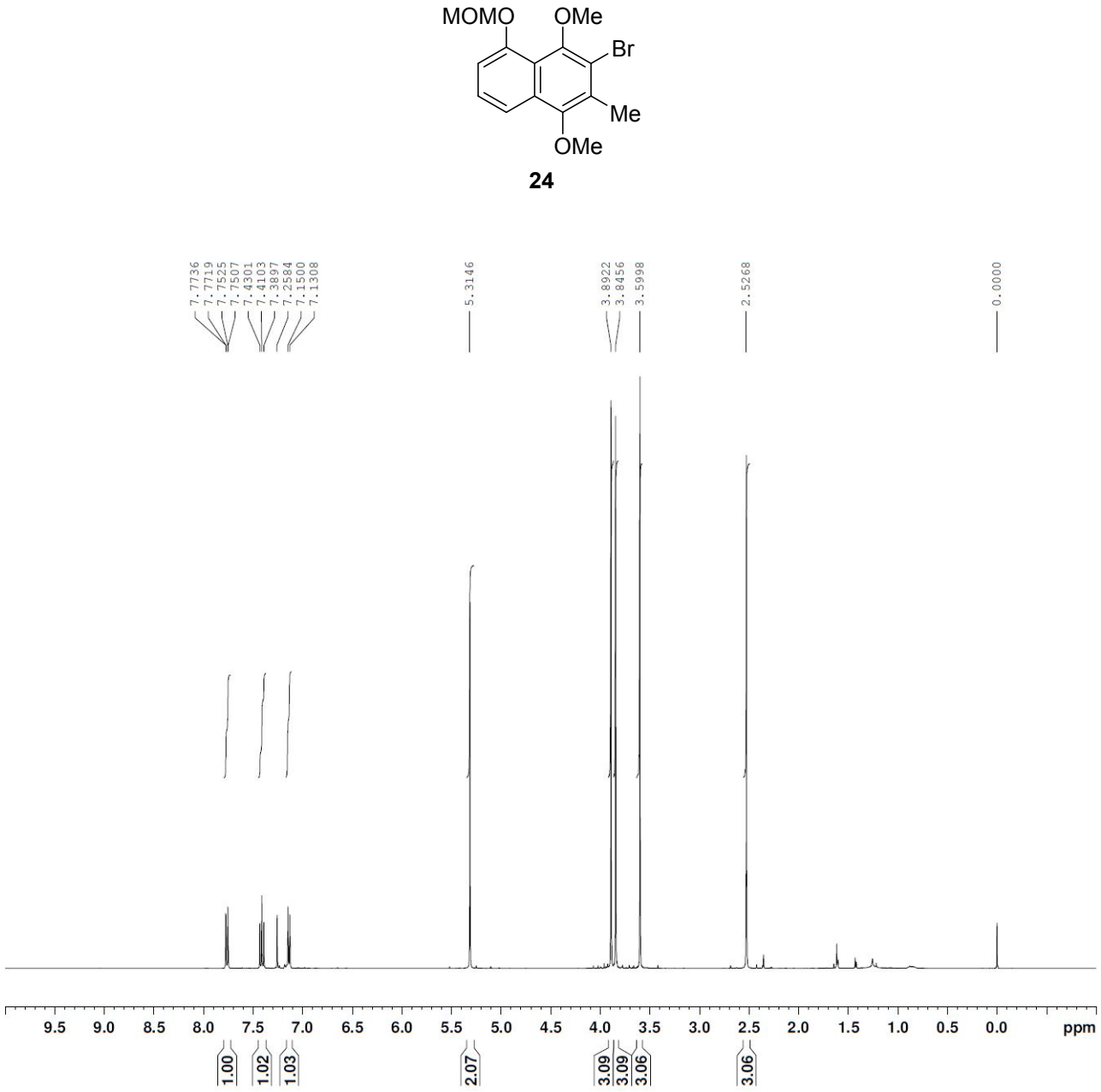


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **24**.

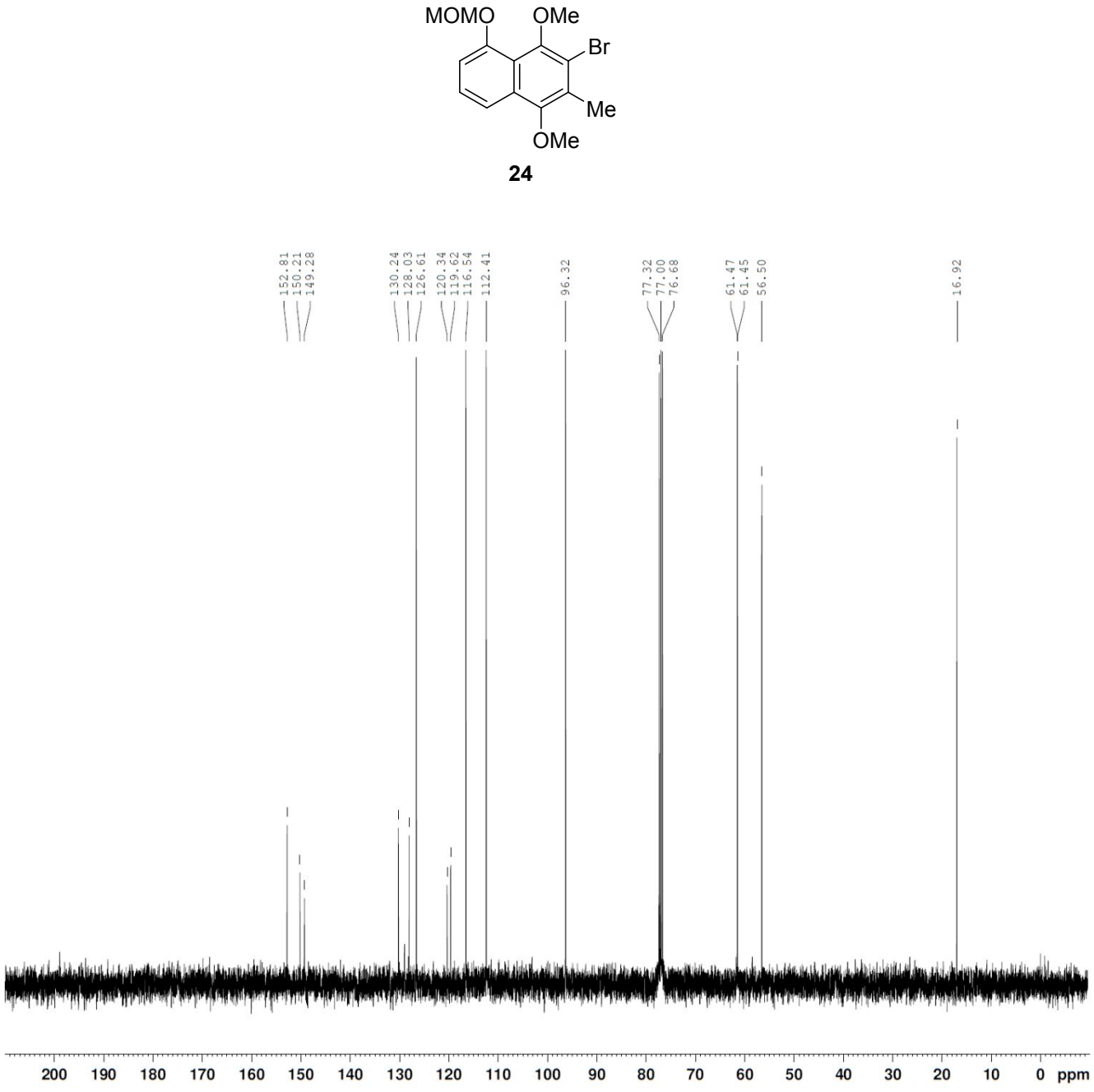
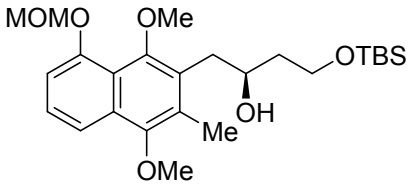


Figure S33. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **26**.



26

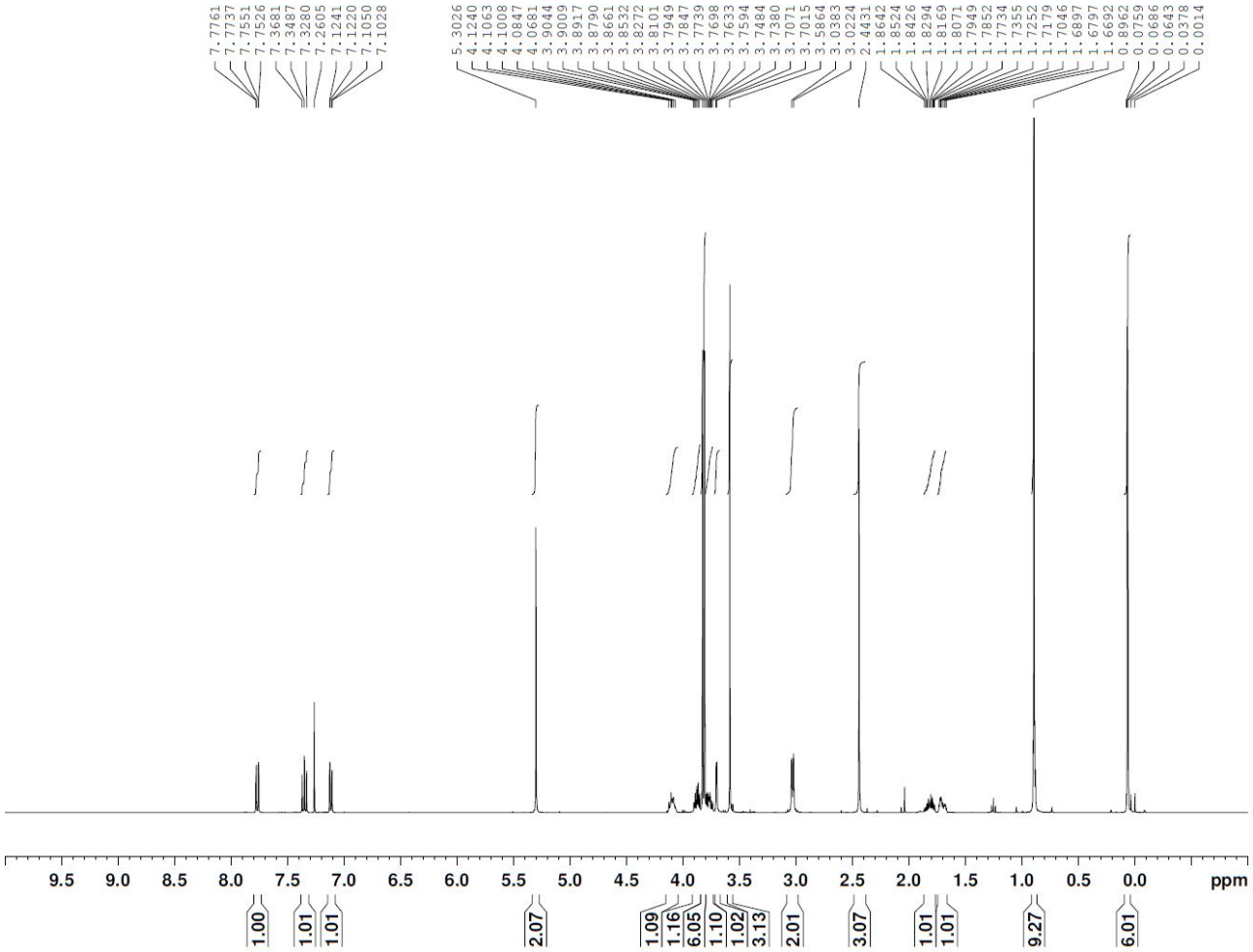


Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **26**.

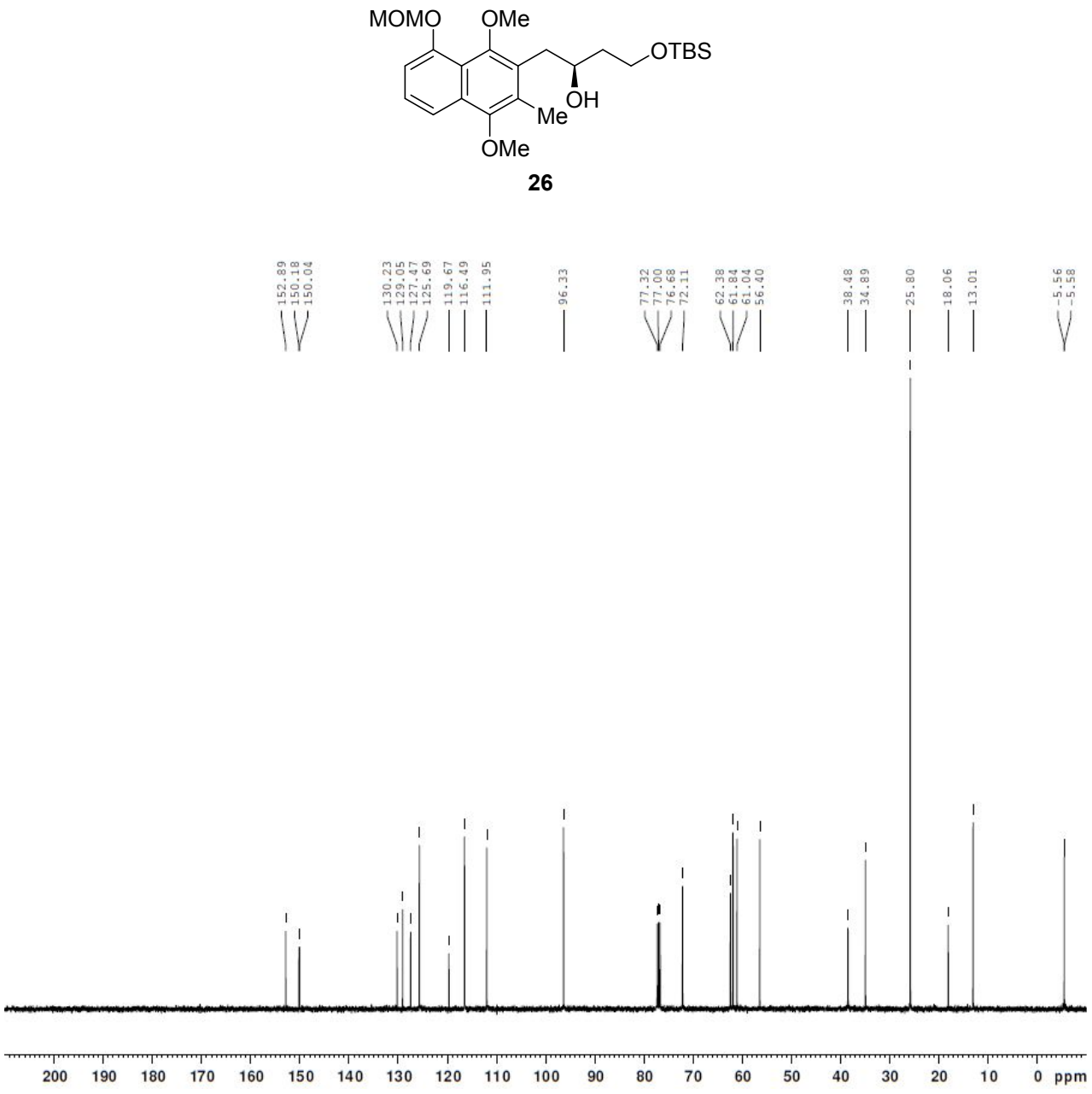
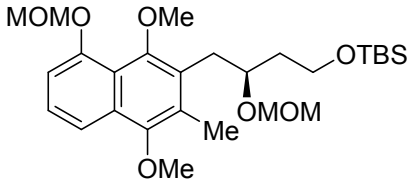


Figure S35. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **27**.



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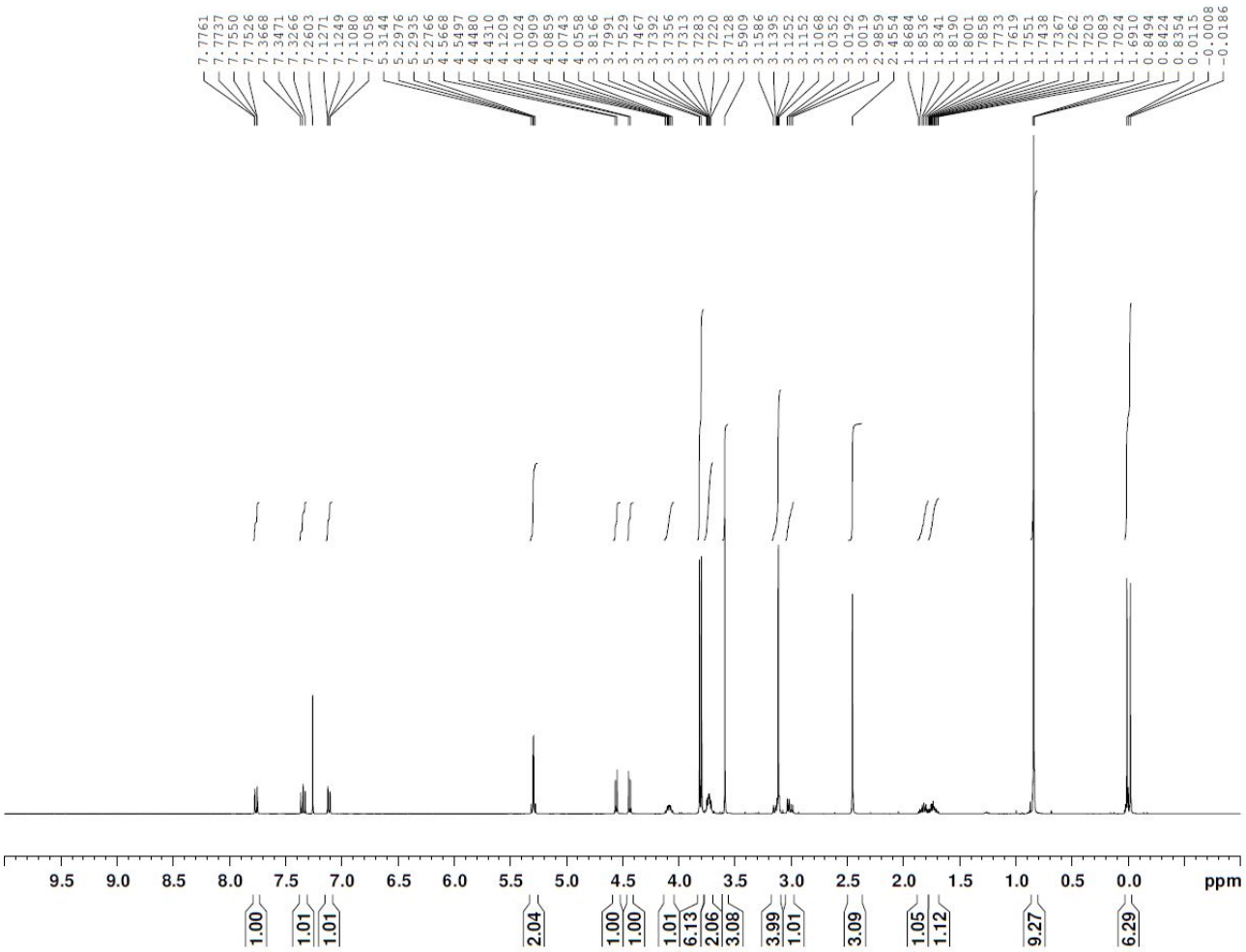
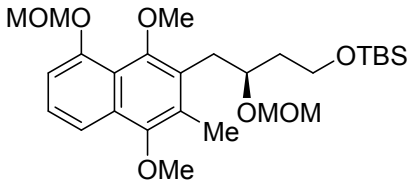


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **27**.



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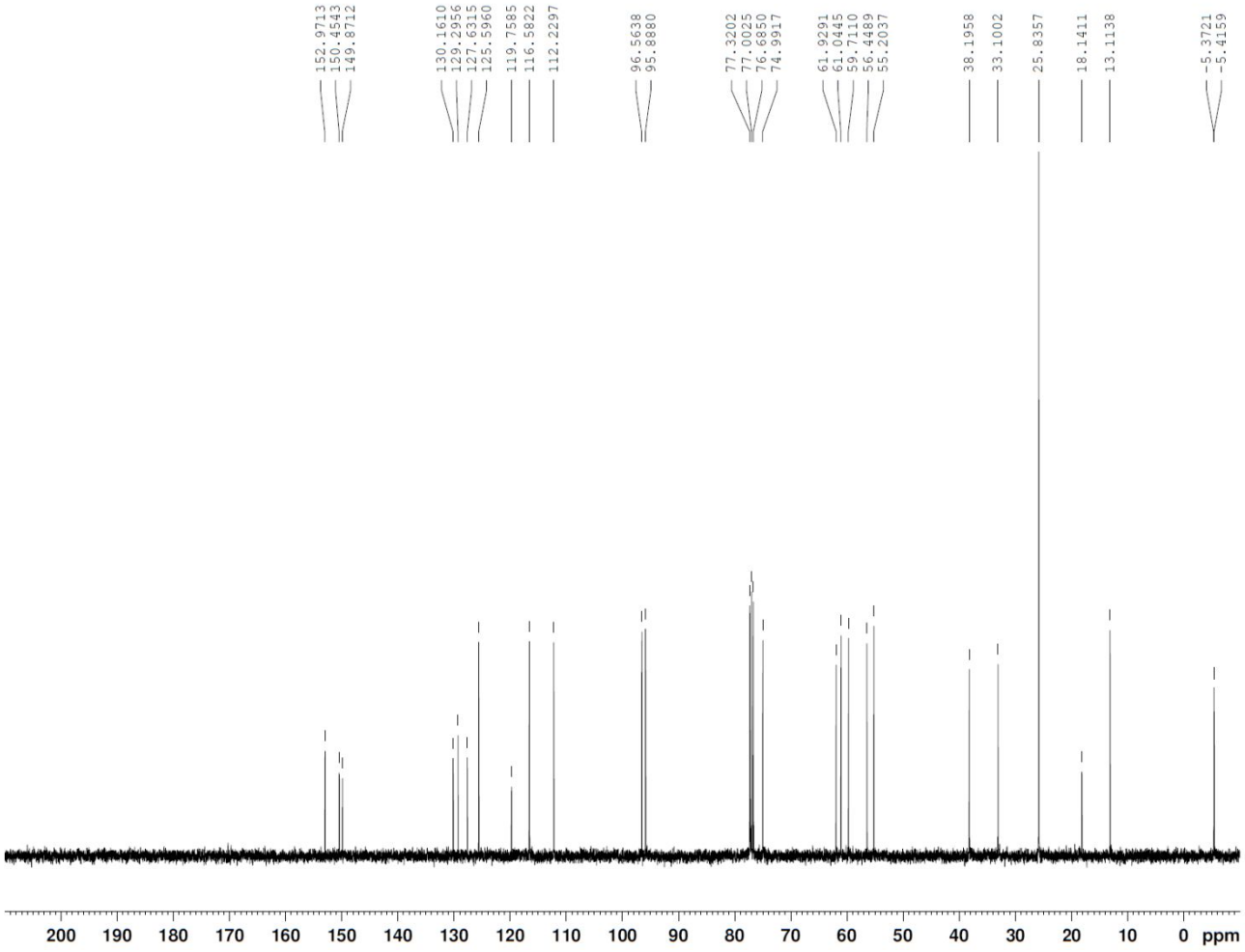
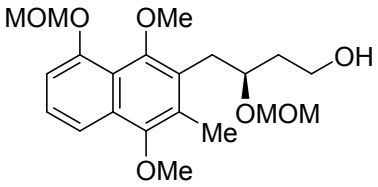


Figure S37. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **28**.



28

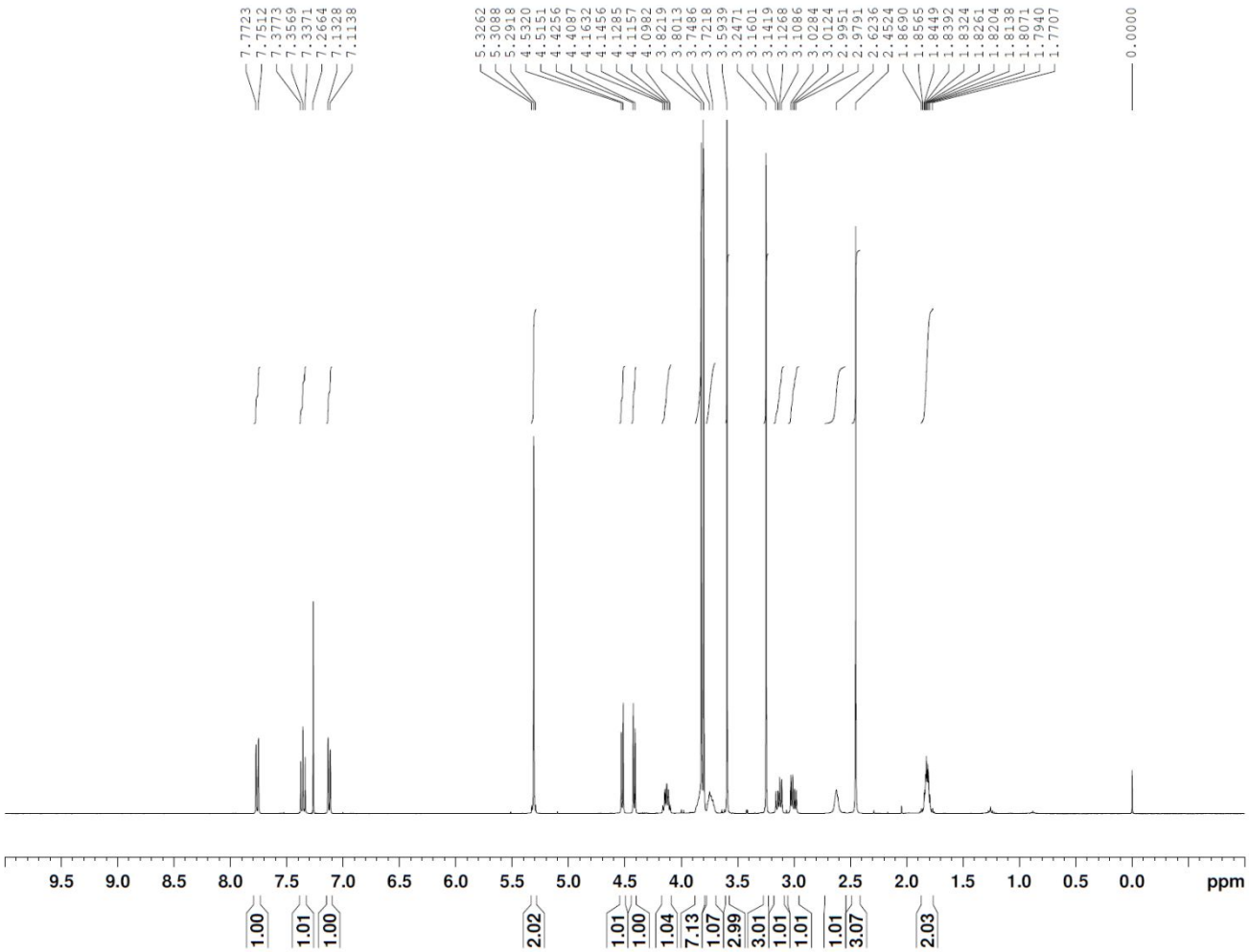


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **28**.

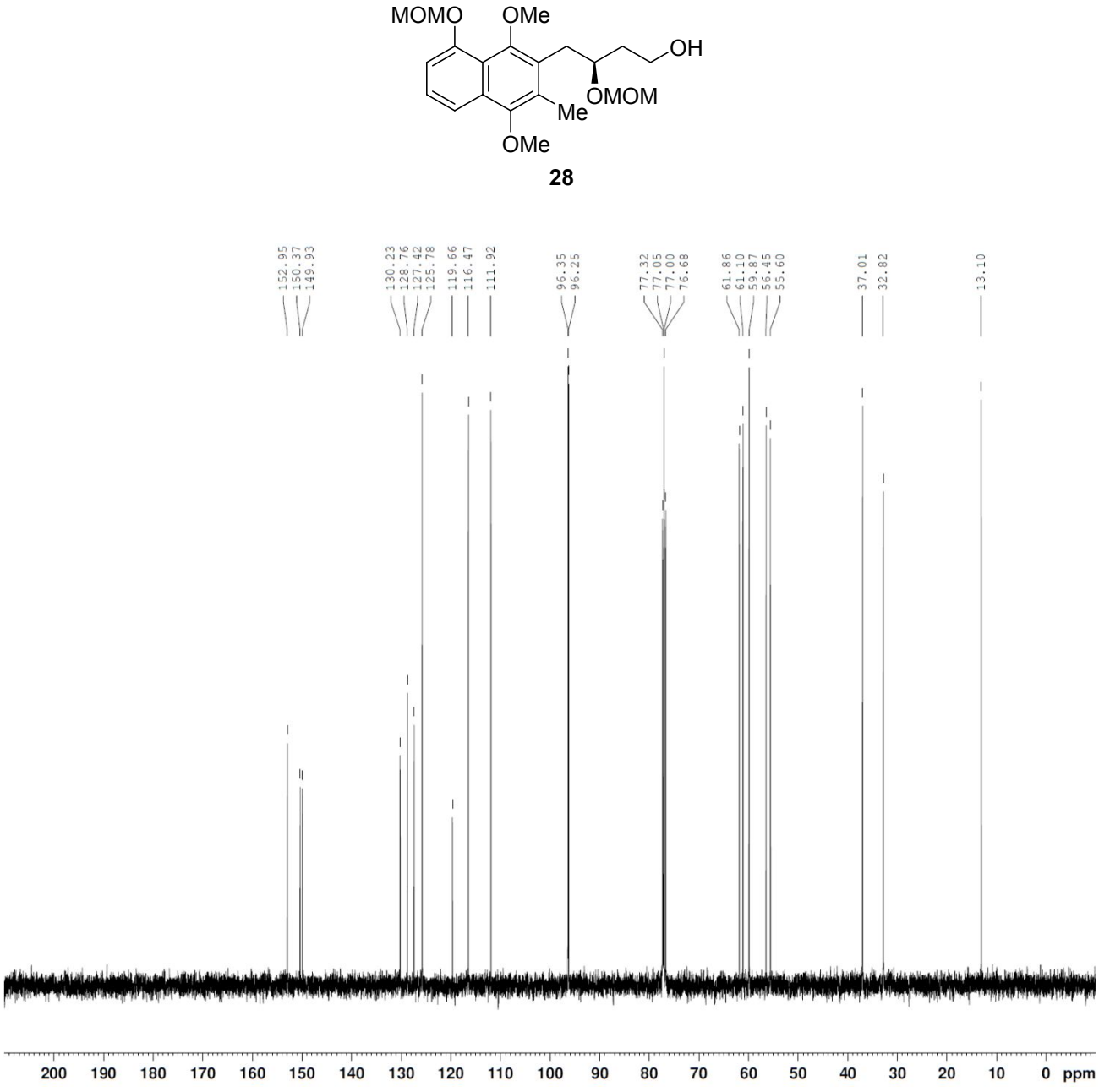
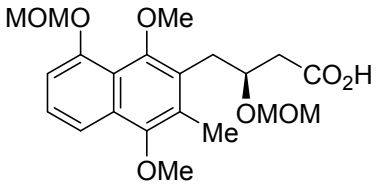


Figure S39. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **29**.



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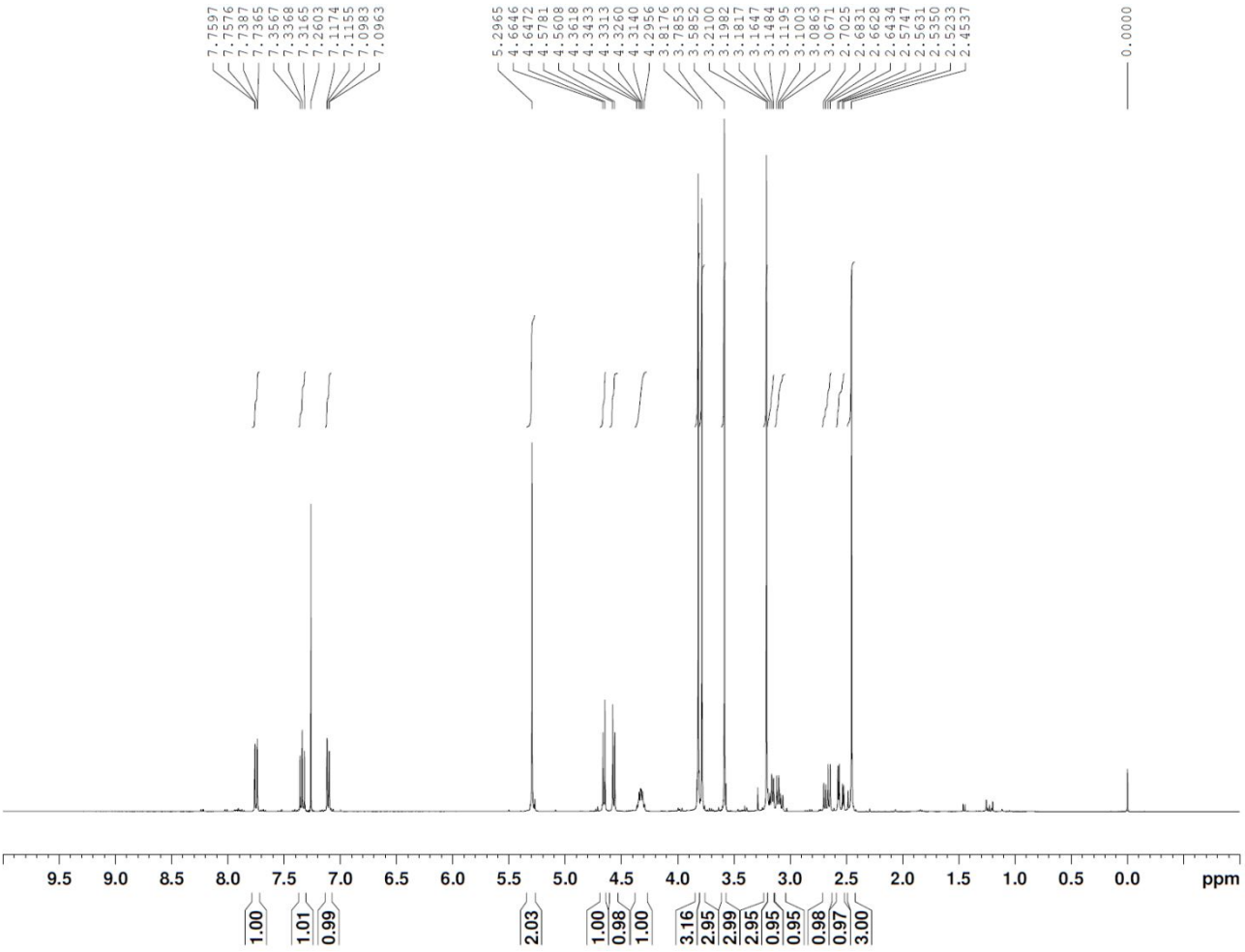
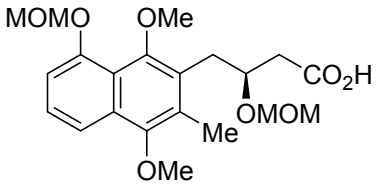


Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **29**.



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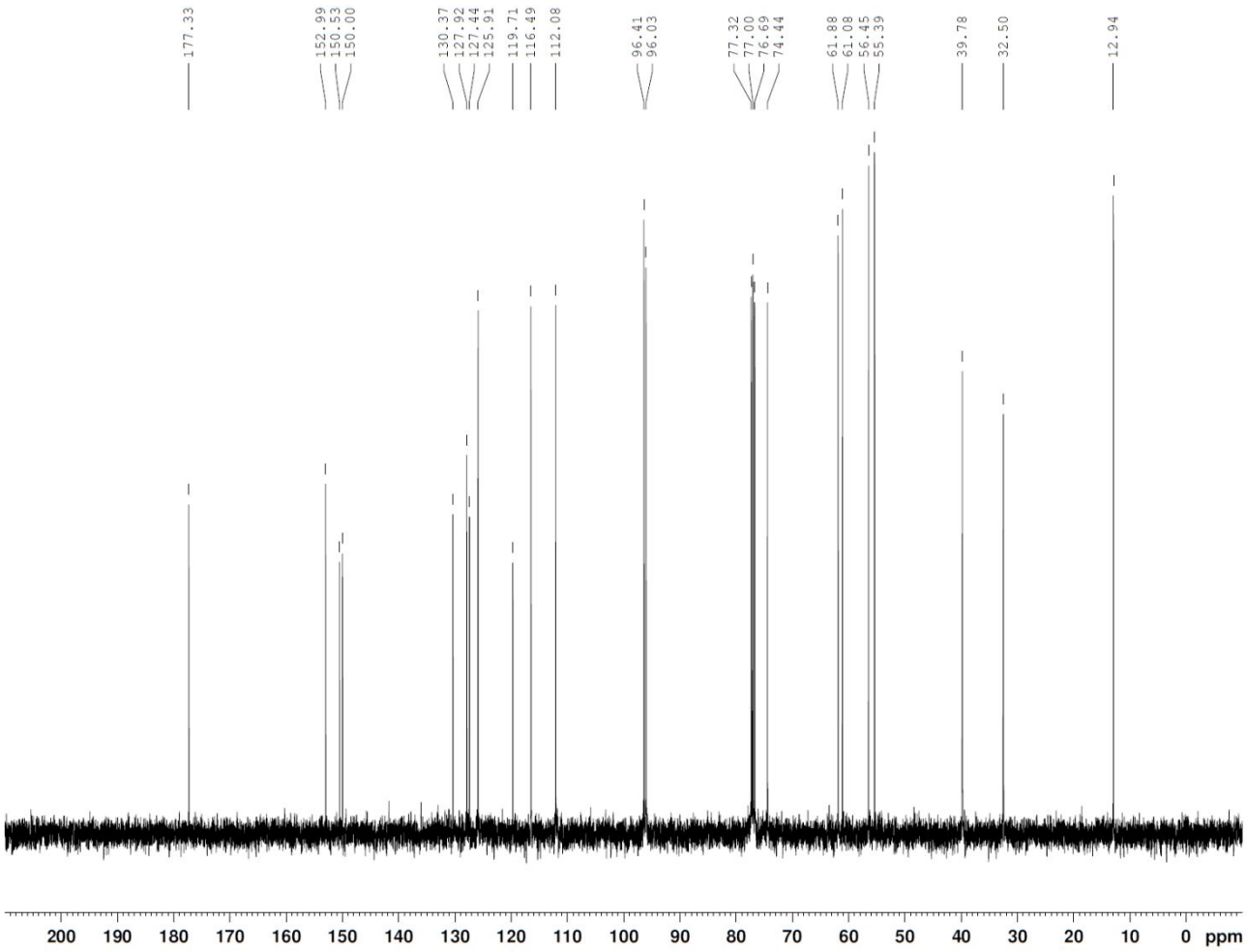
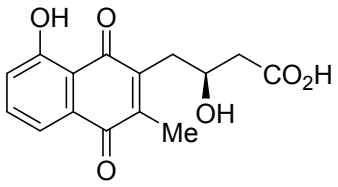


Figure S41. ^{1}H NMR spectrum (400 MHz, acetone-d_6) of compound **20**.



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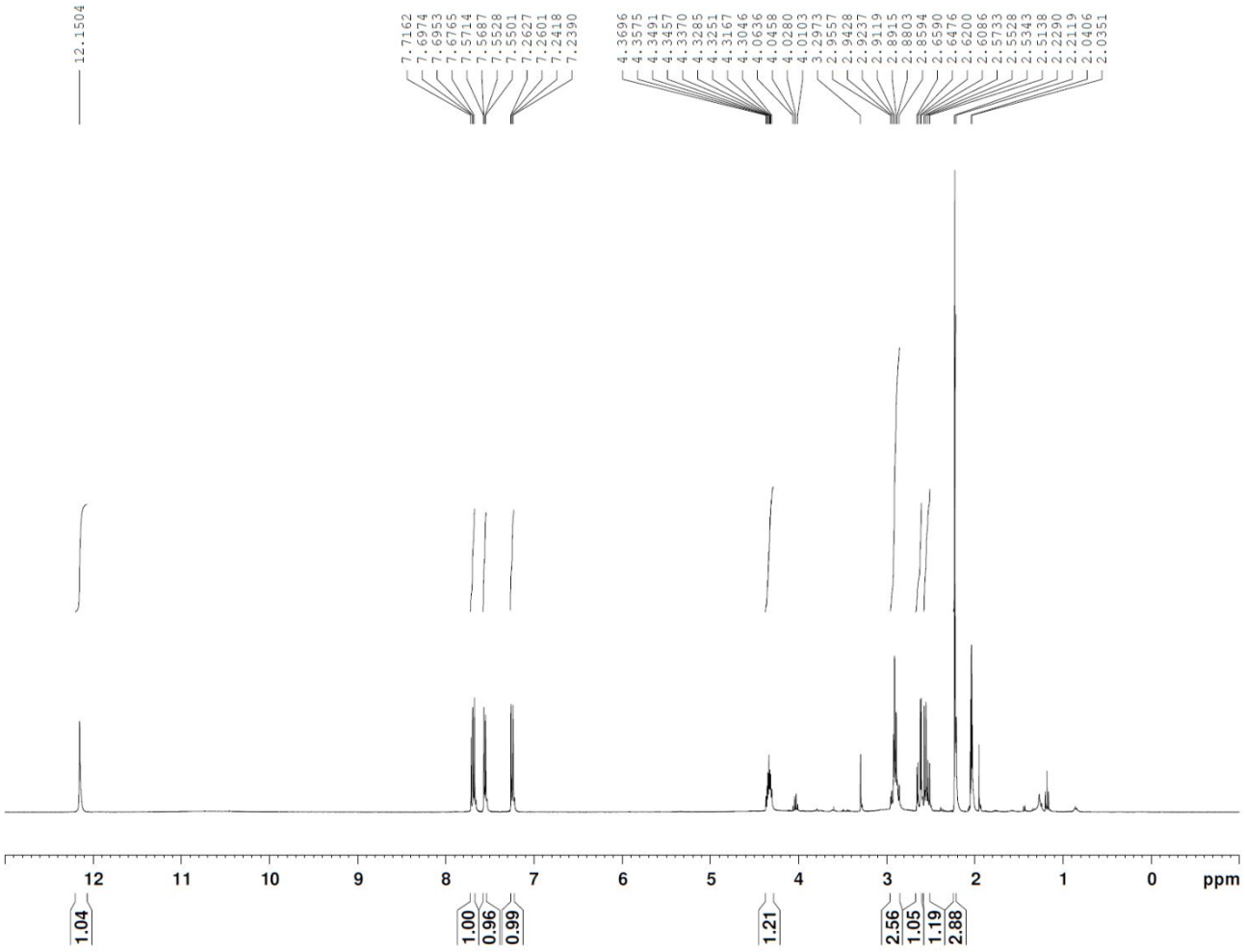
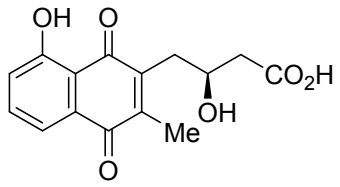


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, acetone-d_6) of compound **20**.



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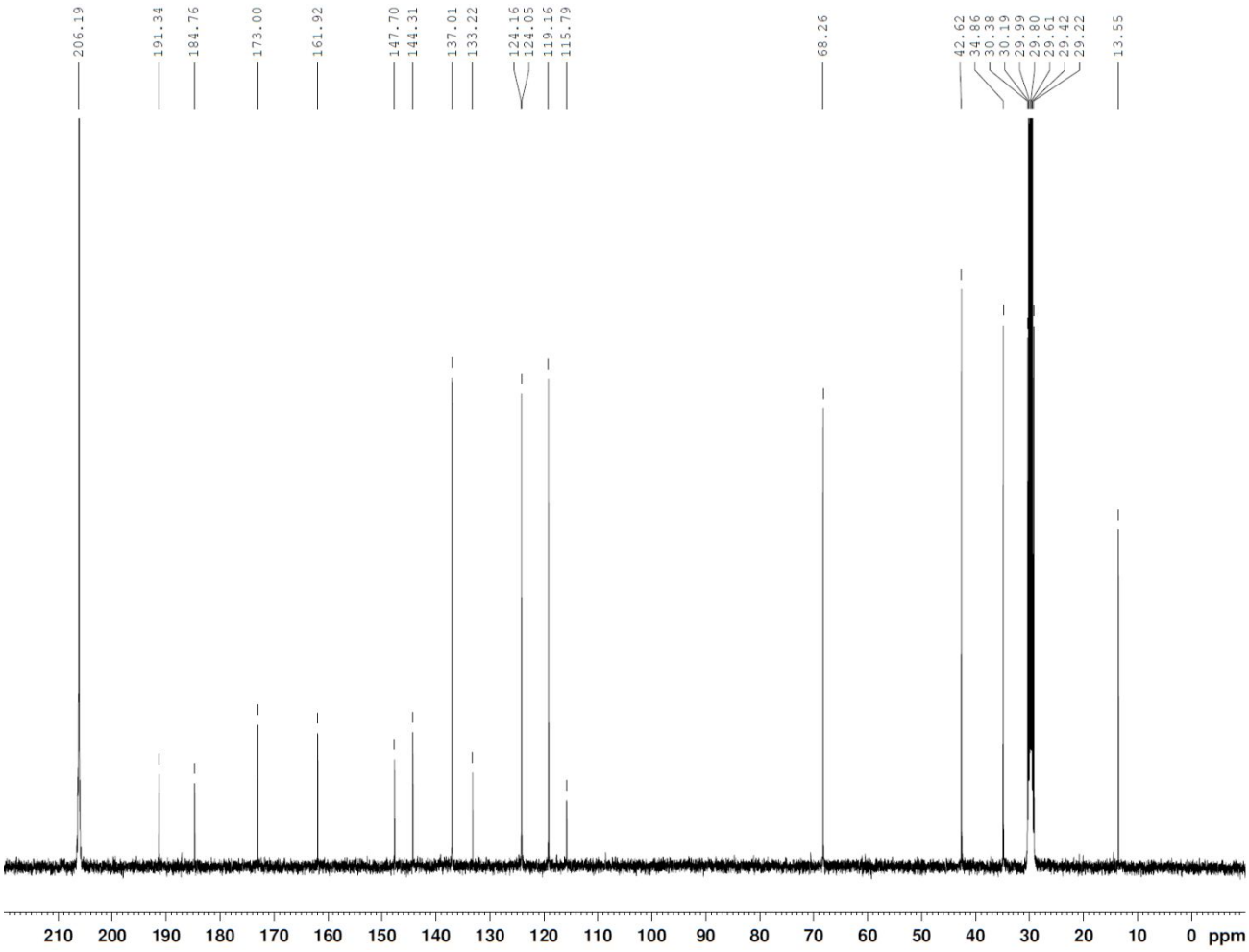
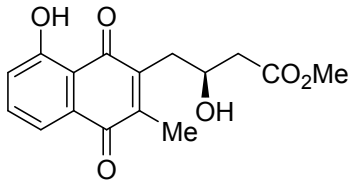


Figure S43. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of compound **21**.



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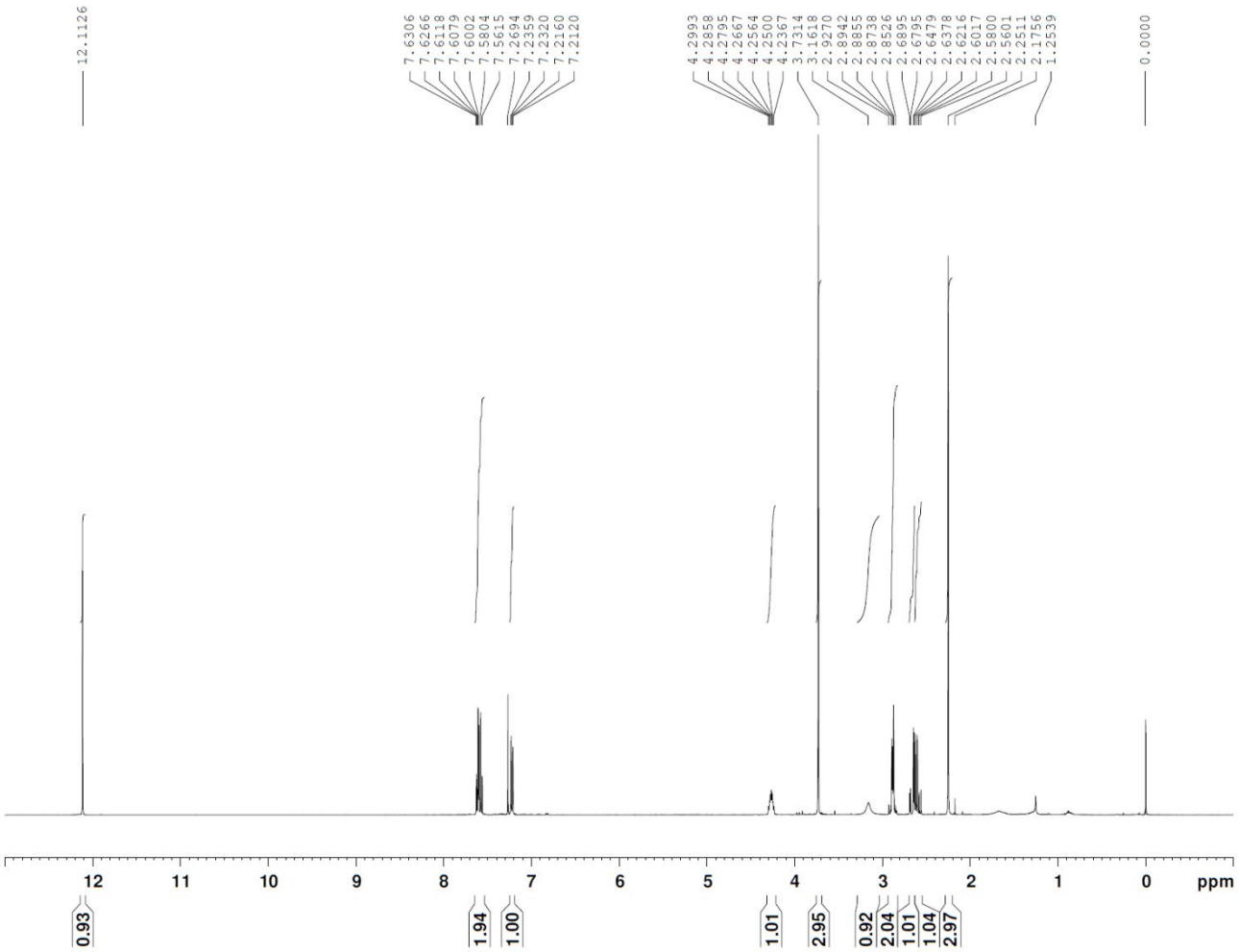
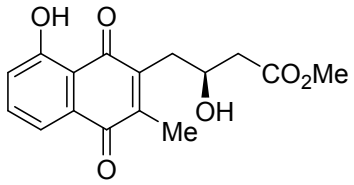


Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **21**.



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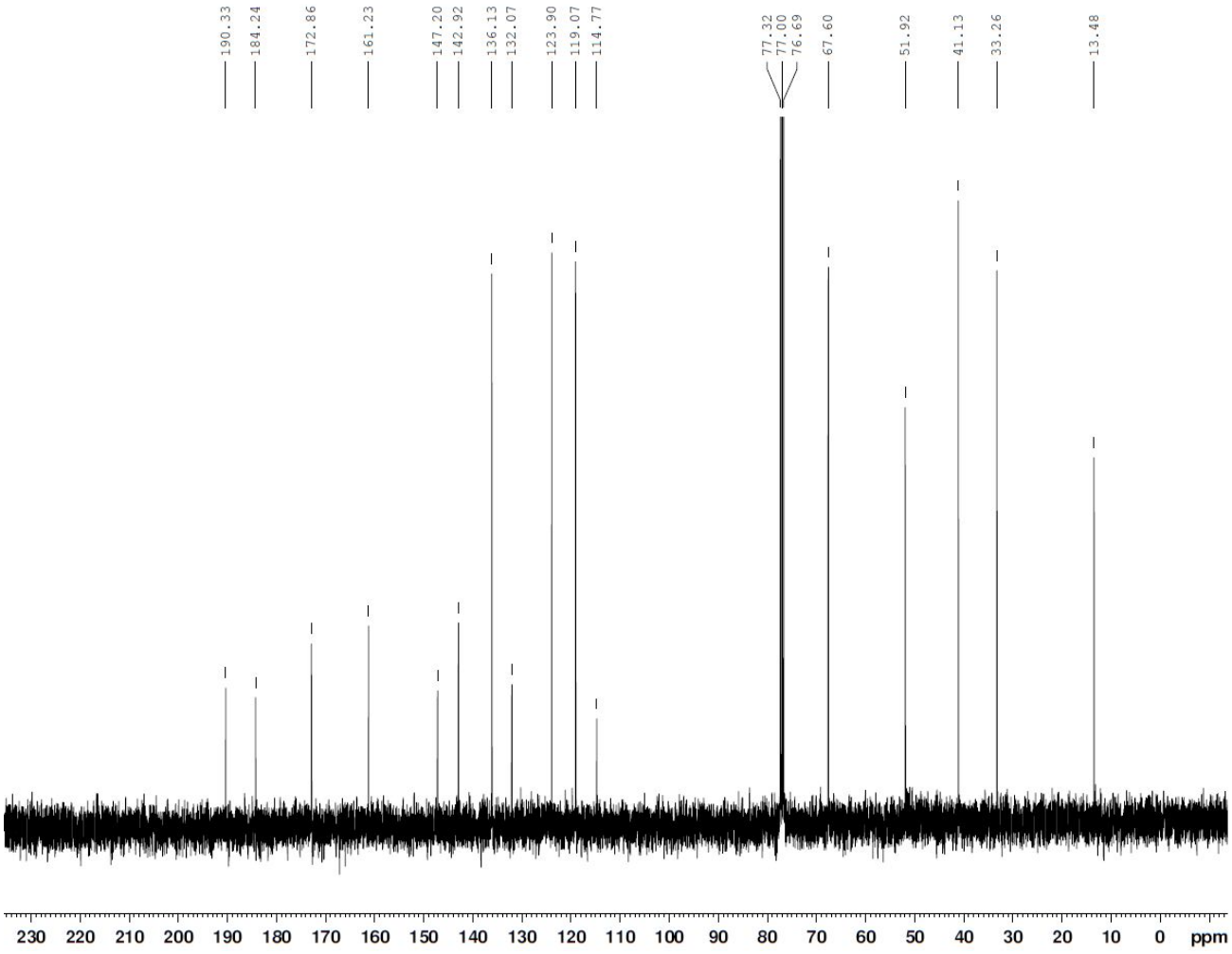

Reference

(S1) Fiedler, H. P.; Kulik, A.; Schüz, T. C.; Volkmann, C.; Zeeck, A. Biosynthetic capacities of Actinomycetes. 2. Juglomycin Z, a new naphthoquinone antibiotic from *Streptomyces tendae*. *J. Antibiot*. **1994**, *47*, 1116–1122.