

Synthesis of Acyloin Natural Products by Mukaiyama Hydration.

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Mark A. Rizzacasa*

Supporting Information

Experimental Section

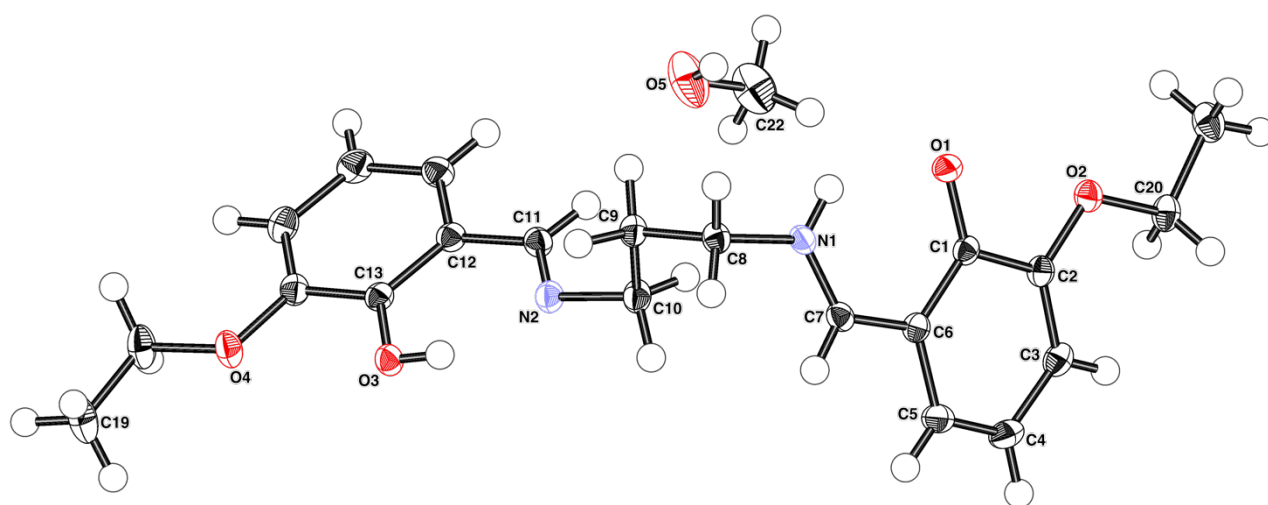
Crystallographic Information	S2
Crystal Data for SALPNligand 13	S2
Crystal Data for Co ^{II} (SALPN)acac 14	S3
Crystal Data for Co ^{II} (SALPN)H ₂ O 15	S4
Crystal Data for soraphinol C diacetate (21)	S5
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¹ H and ¹³ C NMR spectra	S7-S49

Crystallographic Information.

Intensity data for SALPN (**13**), Co^{III} cat.A and Co^{II} cat.B was collected on a Rigaku XtalLAB Synergy at 100.0(1) K. Data for (**25**) was collected on the MX1 beamline¹ at the Australian Synchrotron at 99.96(2) K. The temperature was maintained using an Oxford Cryostream cooling device. The structures were solved by direct methods and difference Fourier synthesis.² Thermal ellipsoid plots were integrated within the WINGX³ suite of programs or Olex2⁴.

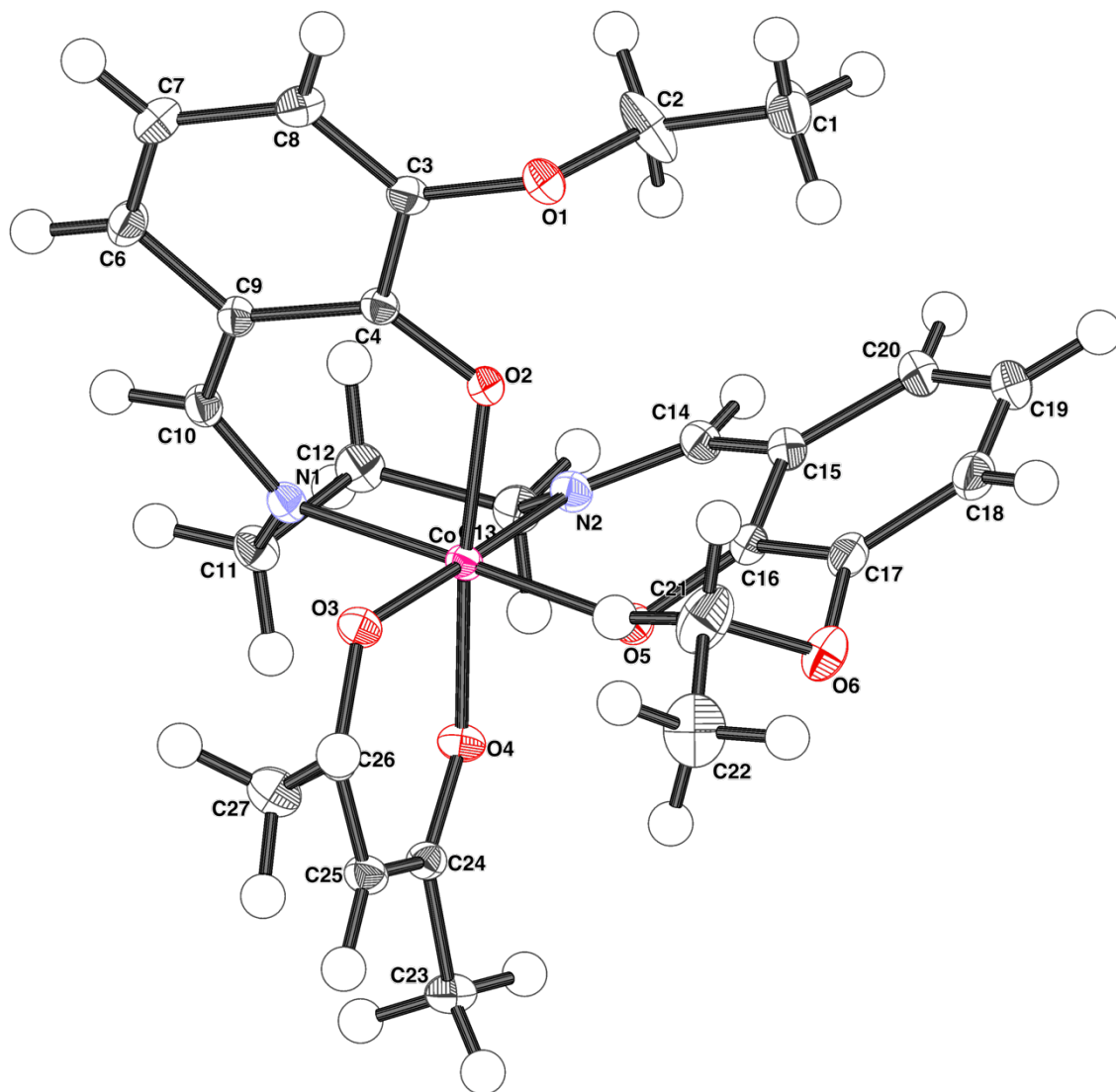
Ortep of SALPN ligand 13.

Synthesised as previously described⁵ and recrystallised from MeOH to give yellow blocks.



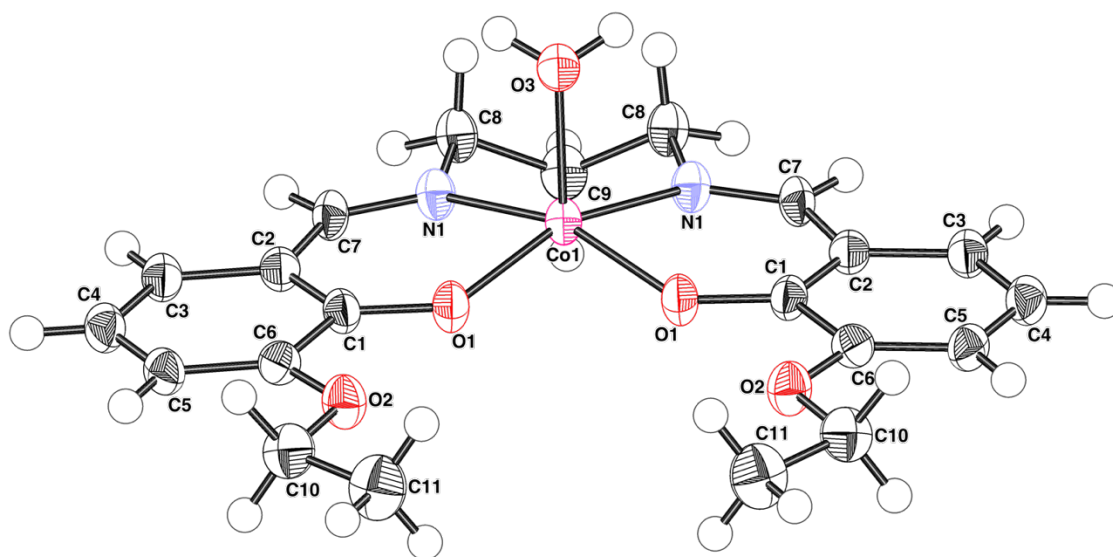
Crystal Data for SALPN ligand 13: C₂₂H₃₀N₂O₅ (*M* = 402.48 g/mol): triclinic, space group P-1 (no. 2), *a* = 8.36320(10) Å, *b* = 10.77980(10) Å, *c* = 12.6342(2) Å, α = 67.3400(10)°, β = 80.5230(10)°, γ = 88.5940(10)°, *V* = 1035.80(2) Å³, *Z* = 2, *T* = 100.00(10) K, μ (Mo K α) = 0.091 mm⁻¹, *D*_{calc} = 1.290 g/cm³, 61757 reflections measured (4.258° ≤ 2 θ ≤ 72.636°), 10019 unique (*R*_{int} = 0.0368, *R*_{sigma} = 0.0242) which were used in all calculations. The final *R*₁ was 0.0408 (*I* > 2 σ (*I*)) and *wR*₂ was 0.1223 (all data).

Ortep of Co^{III}(SALPN)acac 14

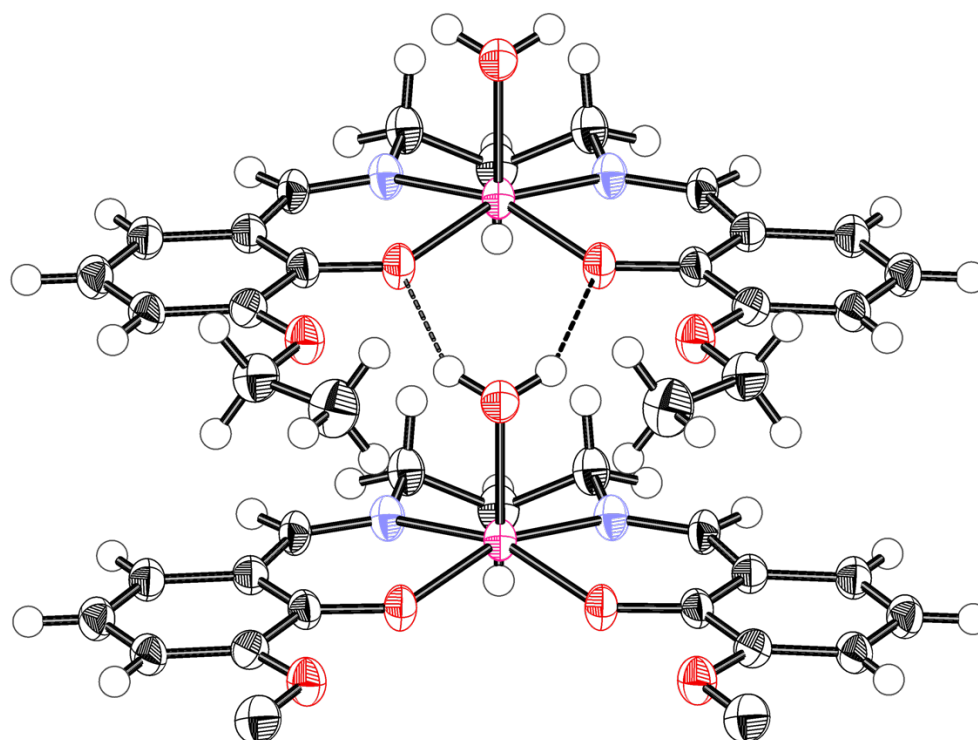


Crystal Data for Co^{III}(SALPN)acac 14 C₂₆H₃₁CoN₂O₆ ($M = 526.46$ g/mol): monoclinic, space group P2₁/c (no. 14), $a = 7.94650(10)$ Å, $b = 26.3631(3)$ Å, $c = 11.4522(2)$ Å, $\beta = 92.6130(10)^\circ$, $V = 2396.68(6)$ Å³, $Z = 4$, $T = 100.0(2)$ K, $\mu(\text{Mo K}\alpha) = 0.761$ mm⁻¹, $D_{\text{calc}} = 1.459$ g/cm³, 176974 reflections measured ($4.714^\circ \leq 2\theta \leq 115.818^\circ$), 33335 unique ($R_{\text{int}} = 0.0839$, $R_{\text{sigma}} = 0.0708$) which were used in all calculations. The final R_1 was 0.0503 ($I > 2\sigma(I)$) and wR_2 was 0.1269 (all data).

Ortep of Co^{II}(SALPN)H₂O (15).

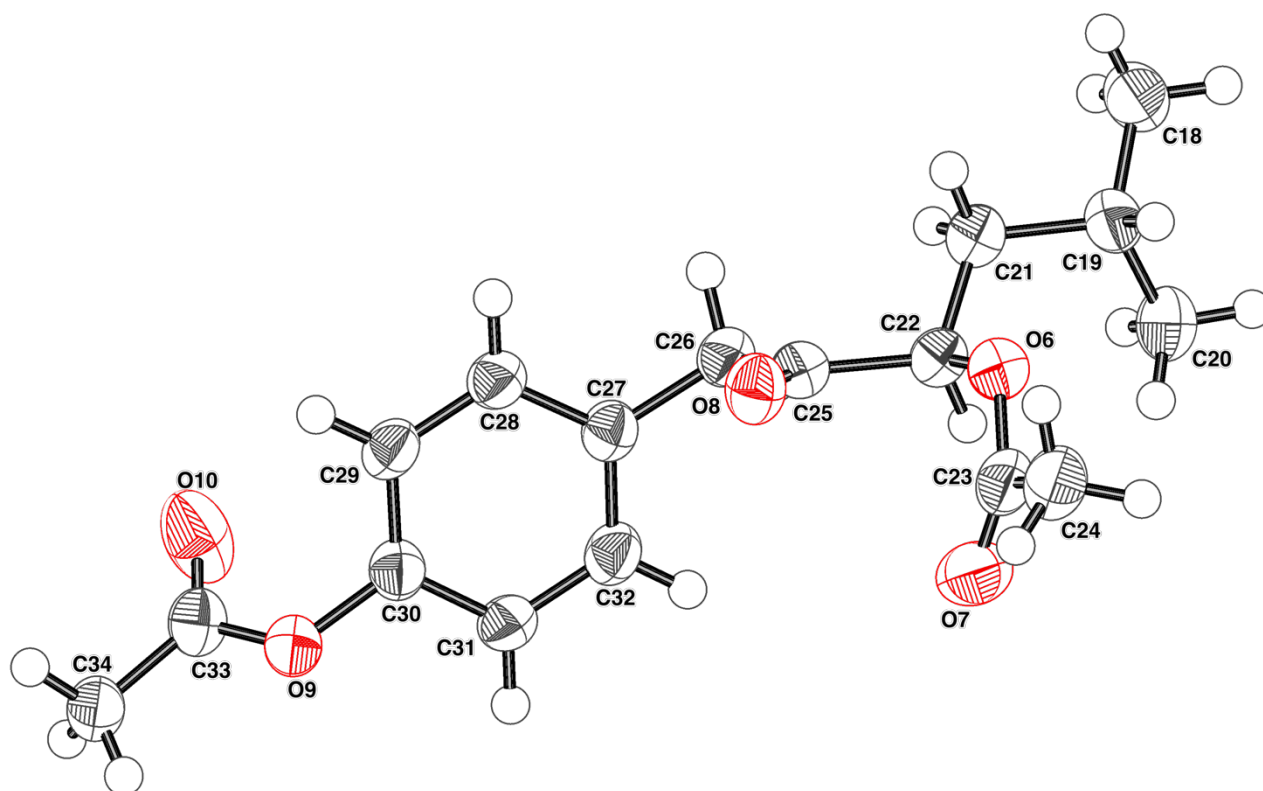


Ortep of CoII(SALPN)H₂O (15) showing close contacts.



Crystal Data for CoII(SALPN)H₂O 15: C₂₁H₂₆N₂O₅Co (*M* = 445.37 g/mol): tetragonal, space group P-42₁m (no. 113), *a* = 20.4662(3) Å, *c* = 5.03150(10) Å, *V* = 2107.52(7) Å³, *Z* = 4, *T* = 100.0(1) K, $\mu(\text{Cu K}\alpha) = 6.675 \text{ mm}^{-1}$, *D*_{calc} = 1.404 g/cm³, 10846 reflections measured ($6.108^\circ \leq 2\theta \leq 154.226^\circ$), 2264 unique (*R*_{int} = 0.0623, *R*_{sigma} = 0.0449) which were used in all calculations. The final *R*₁ was 0.0393 (*I* > 2σ(*I*)) and *wR*₂ was 0.1077 (all data).

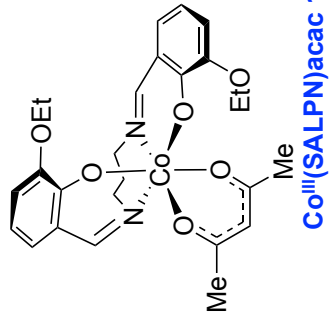
ORTEP of soraphinol C diacetate (21).



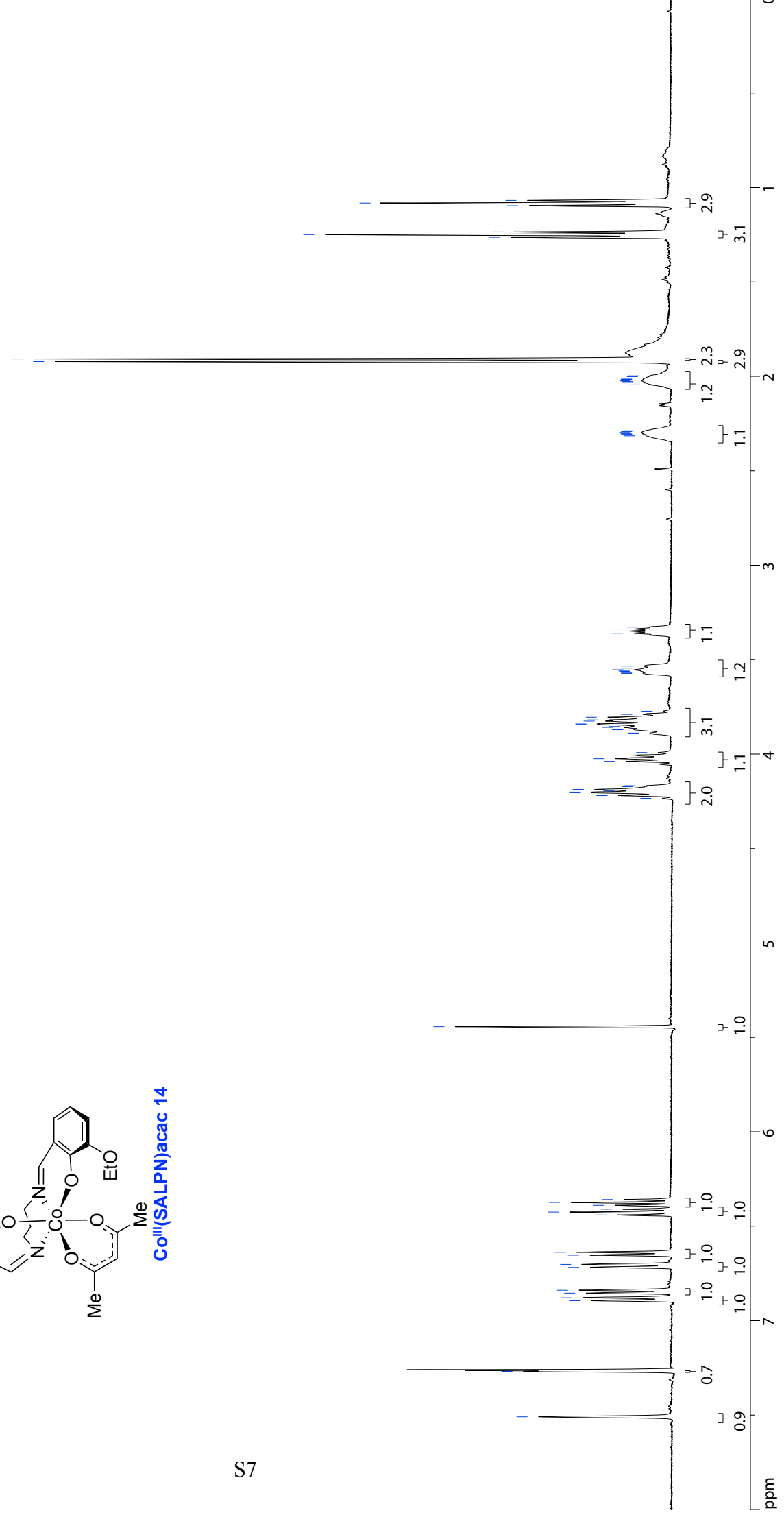
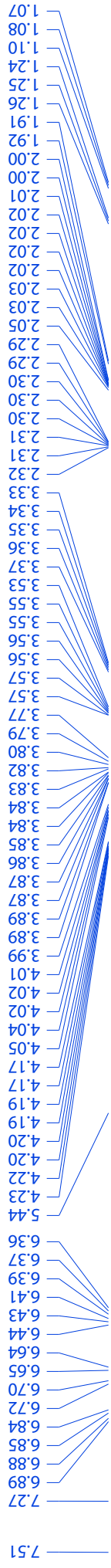
Crystal Data for soraphinol C diacetate (21) $C_{17}H_{22}O_5$ ($M = 306.34$ g/mol): triclinic, space group P-1 (no. 2), $a = 8.78440(10)$ Å, $b = 10.21930(10)$ Å, $c = 18.8935(2)$ Å, $\alpha = 75.4950(10)^\circ$, $\beta = 84.8940(10)^\circ$, $\gamma = 88.4970(10)^\circ$, $V = 1635.49(3)$ Å³, $Z = 4$, $T = 99.96(2)$ K, $\mu(\text{Synchrotron}) = 0.091$ mm⁻¹, $D_{\text{calc}} = 1.244$ g/cm³, 21093 reflections measured ($2.234^\circ \leq 2\theta \leq 58.35^\circ$), 6141 unique ($R_{\text{int}} = 0.0514$, $R_{\text{sigma}} = 0.0492$) which were used in all calculations. The final R_1 was 0.0673 ($I > 2\sigma(I)$) and wR_2 was 0.2120 (all data).

References

1. Cowieson, N.P.; Aragao, D.; Clift, M.; Ericsson, D.J.; Gee, C.; Harrop, S.J.; Mudie, N.; Panjikar, S.; Price, J.R.; Riboldi-Tunncliffe, A.; Williamson, R.; Caradoc-Davies, T. *J. Synchrotron Radiation*, **2015**, *22*, 187-190.
2. Sheldrick, G. *Acta Crystallogr. Section C*, **2015**, *71*, 3-8.
3. Farrugia, L. J.; *J. Appl. Cryst.* **1999**, *32*, 837-838.
4. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* **2009** *42*, 339-341.
5. Donnelly, P. S.; North, A. J.; Radjah, N. C.; Ricca, M.; Robertson, A.; White, J. M.; Rizzacasa, M. A. *Chem. Commun.* **2019**, 7699–7702.



¹H NMR spectrum (CDCl₃, 500 MHz)



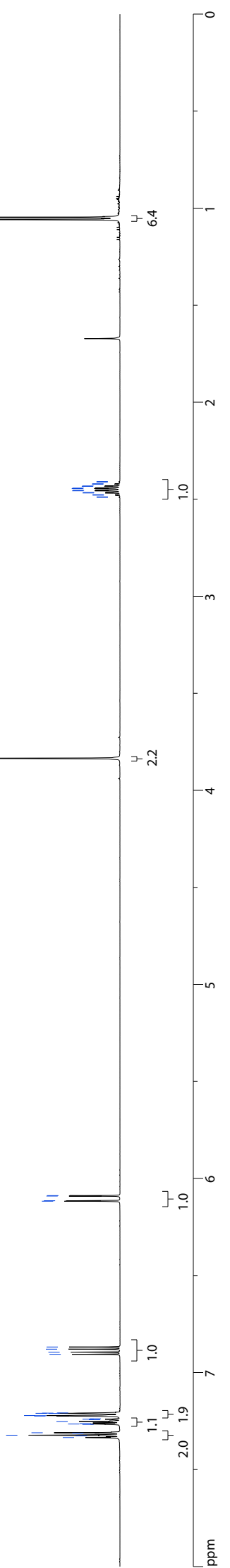
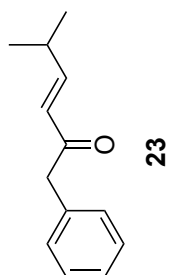
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2.41
2.41
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2.43
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2.46
2.47
2.47
2.48
2.48
2.49
2.49

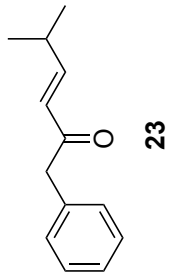
3.84

6.09
6.09
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6.12
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6.88
6.88
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7.21
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7.21
7.22
7.22
7.22
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7.33
7.33

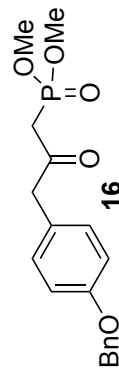
¹H NMR spectrum (CDCl₃, 600 MHz)



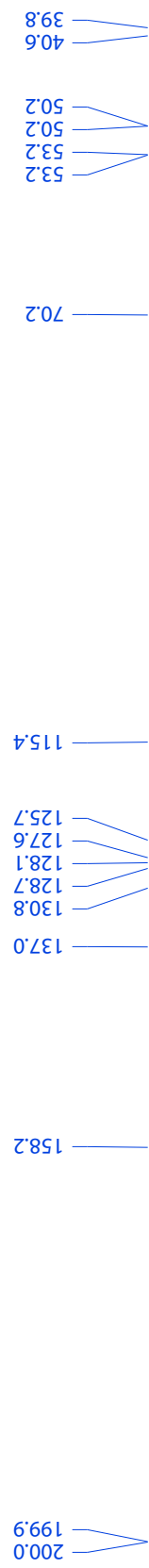
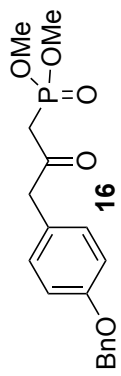
¹³C NMR spectrum (CDCl₃, 151 MHz)



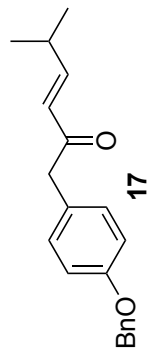
¹H NMR spectrum (CDCl₃, 400 MHz)



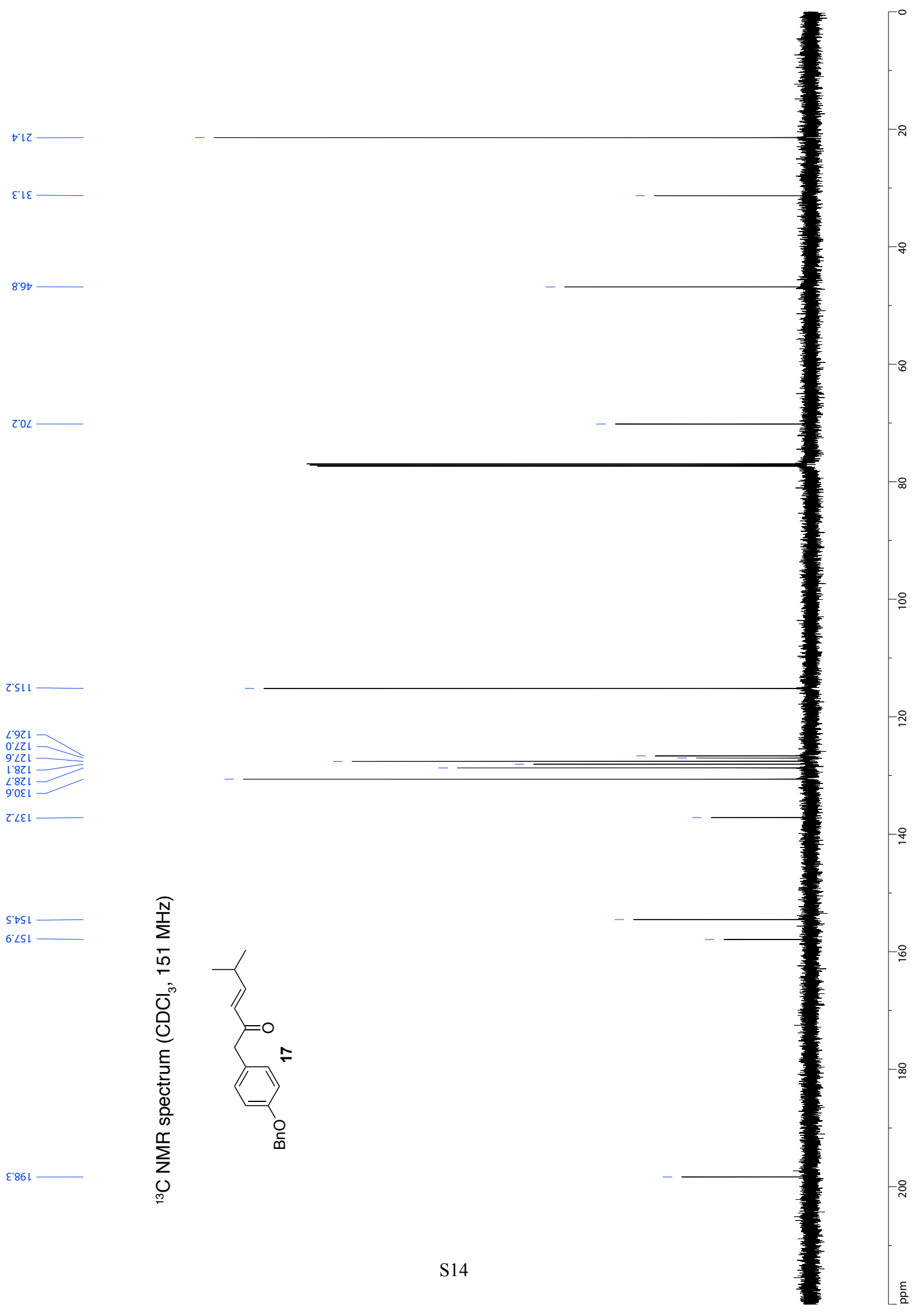
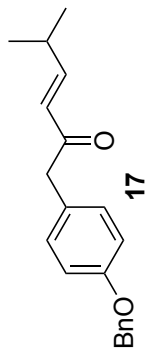
¹³C NMR spectrum (CDCl₃, 151 MHz)

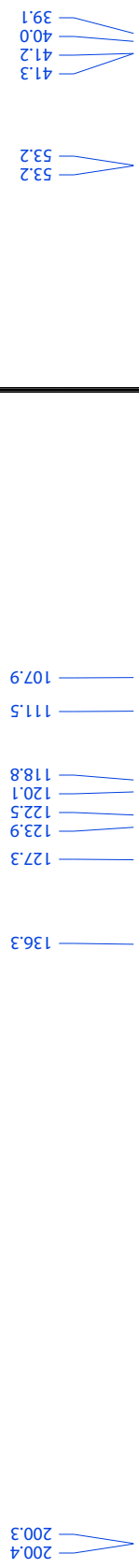
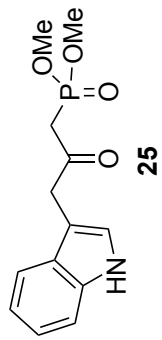


¹H NMR spectrum (CDCl₃, 600 MHz)

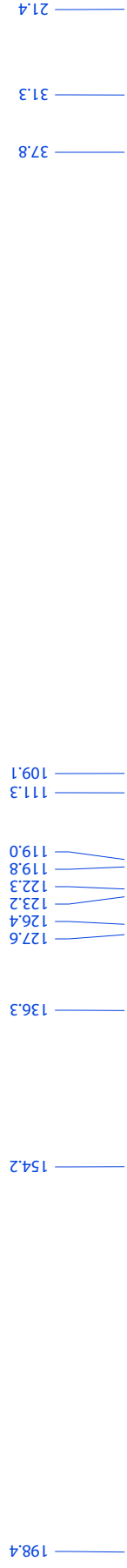
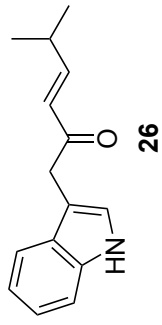


¹³C NMR spectrum (CDCl₃, 151 MHz)

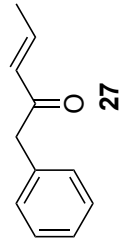


^{13}C NMR spectrum (CDCl_3 , 151 MHz)

¹³C NMR spectrum (CDCl₃, 151 MHz)



¹H NMR spectrum (CDCl₃, 500 MHz)

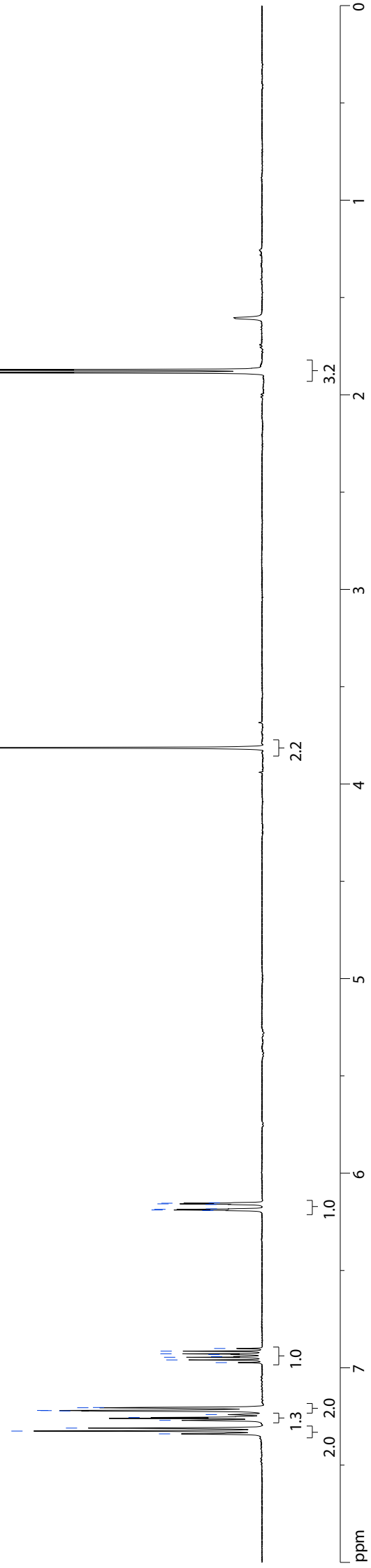


1.89
1.88
1.87
1.87
1.87

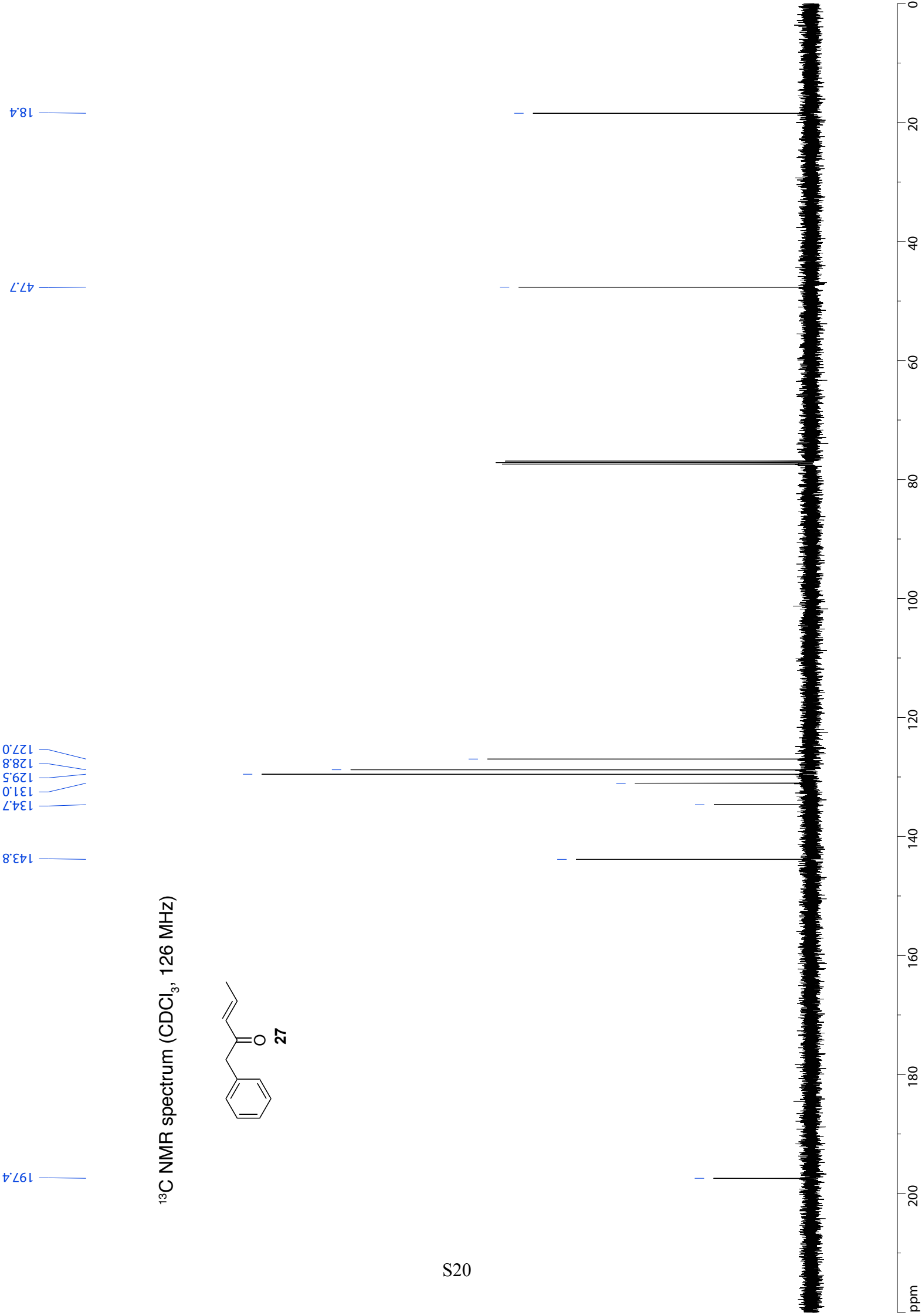
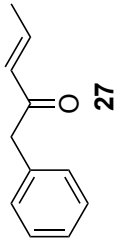
3.81

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6.96
6.95
6.94
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6.15
6.15

619

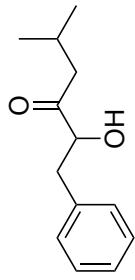


¹³C NMR spectrum (CDCl₃, 126 MHz)



7.33
7.31
7.29
7.25
7.24
7.23

¹H NMR spectrum (CDCl₃, 400 MHz)



Sattabacin (1)

3.43
3.42
3.15
3.14
3.12
3.11
2.85
2.83
2.82
2.80
2.38
2.36
2.23
2.21
2.20
2.18
2.16
2.15
2.13

0.93
0.91

4.40
4.39
4.38
4.38
4.37
4.37
4.36
4.36

1.9
2.7

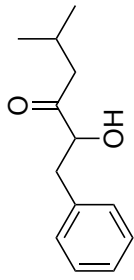
1.4
2.0

1.2
1.1
0.9

6.1

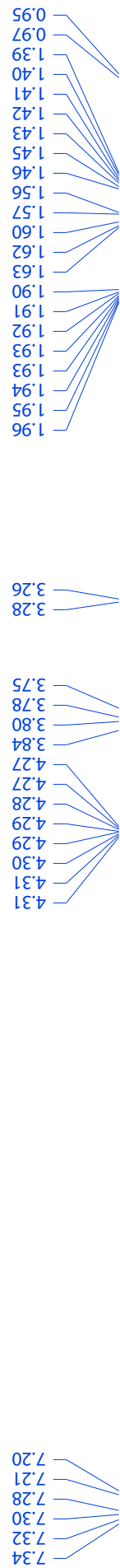
ppm

¹³C NMR spectrum (CDCl₃, 101 MHz)

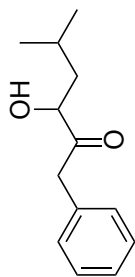


Sattabacin (1)



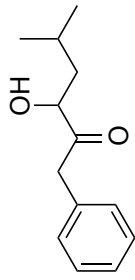


^1H NMR spectrum (CDCl_3 , 400 MHz)



Isosattabacin (**24**)

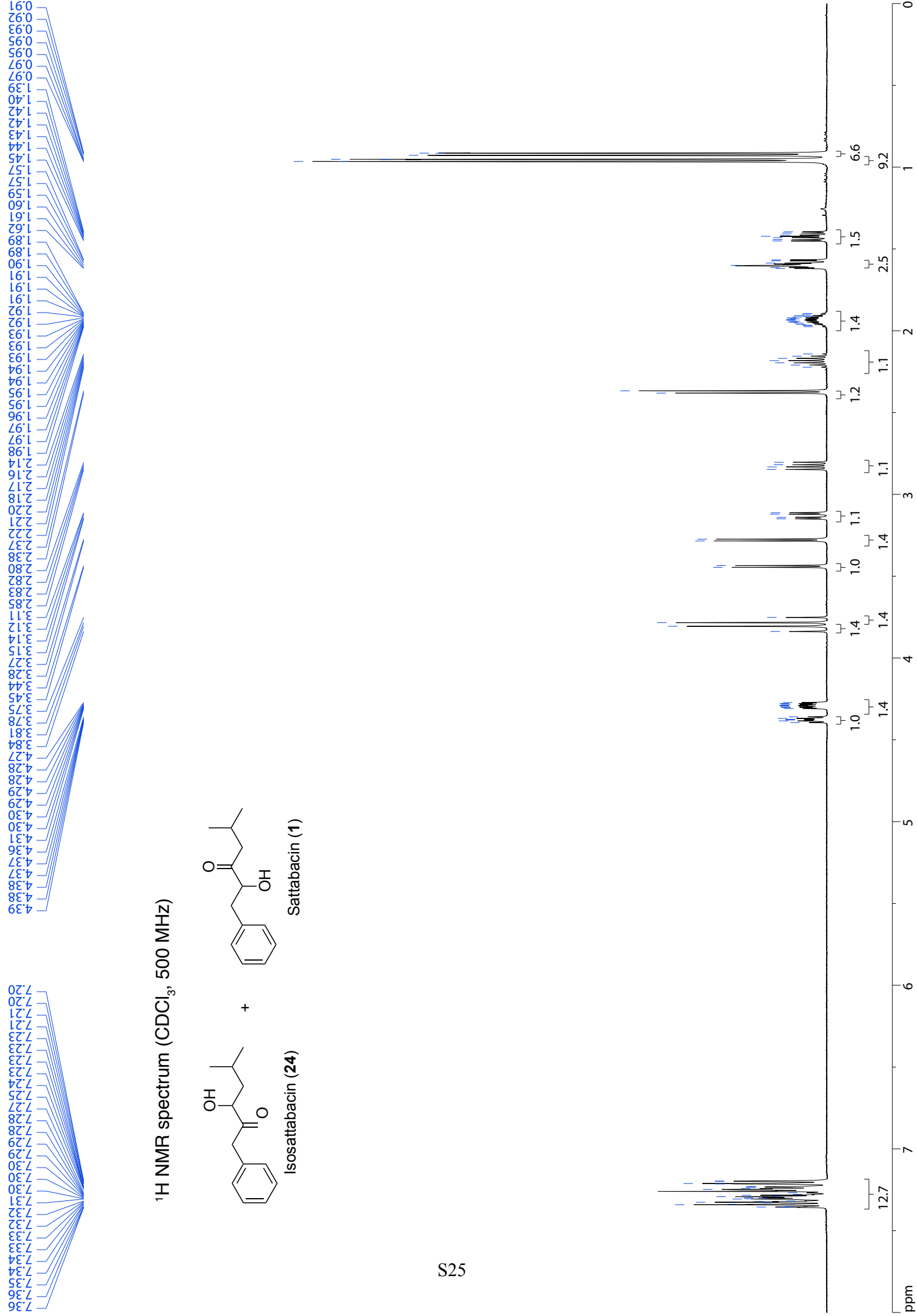
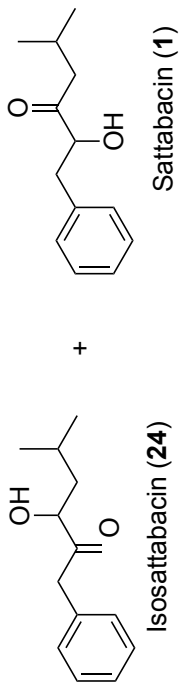
¹³C NMR spectrum (CDCl₃, 151 MHz)



Isosattabacin (**24**)



¹H NMR spectrum (CDCl₃, 500 MHz)



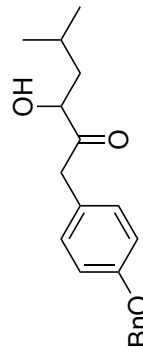
0.91
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0.93
0.94
1.40
1.41
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1.43
1.43
1.44
1.45
1.47
1.48
1.49
1.49
1.50
1.51
1.52
1.78
1.79
1.80
1.81
1.81
1.82
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1.85
1.86
1.87

3.80
4.18
4.18
4.19
4.20

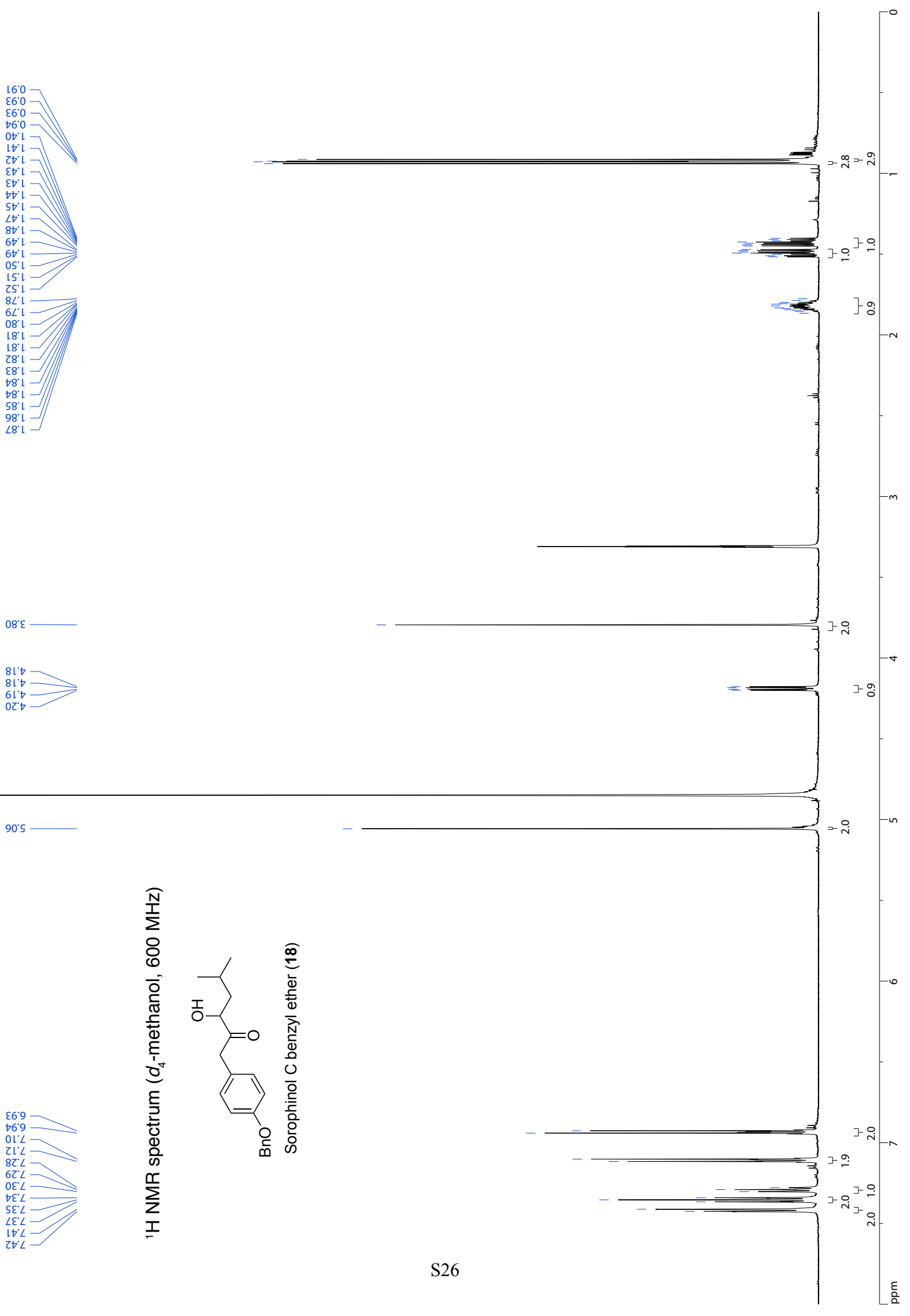
5.06

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7.34
7.35
7.37
7.41
7.42

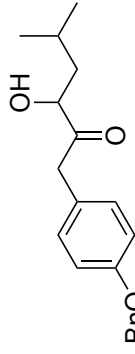
¹H NMR spectrum (d₄-methanol, 600 MHz)



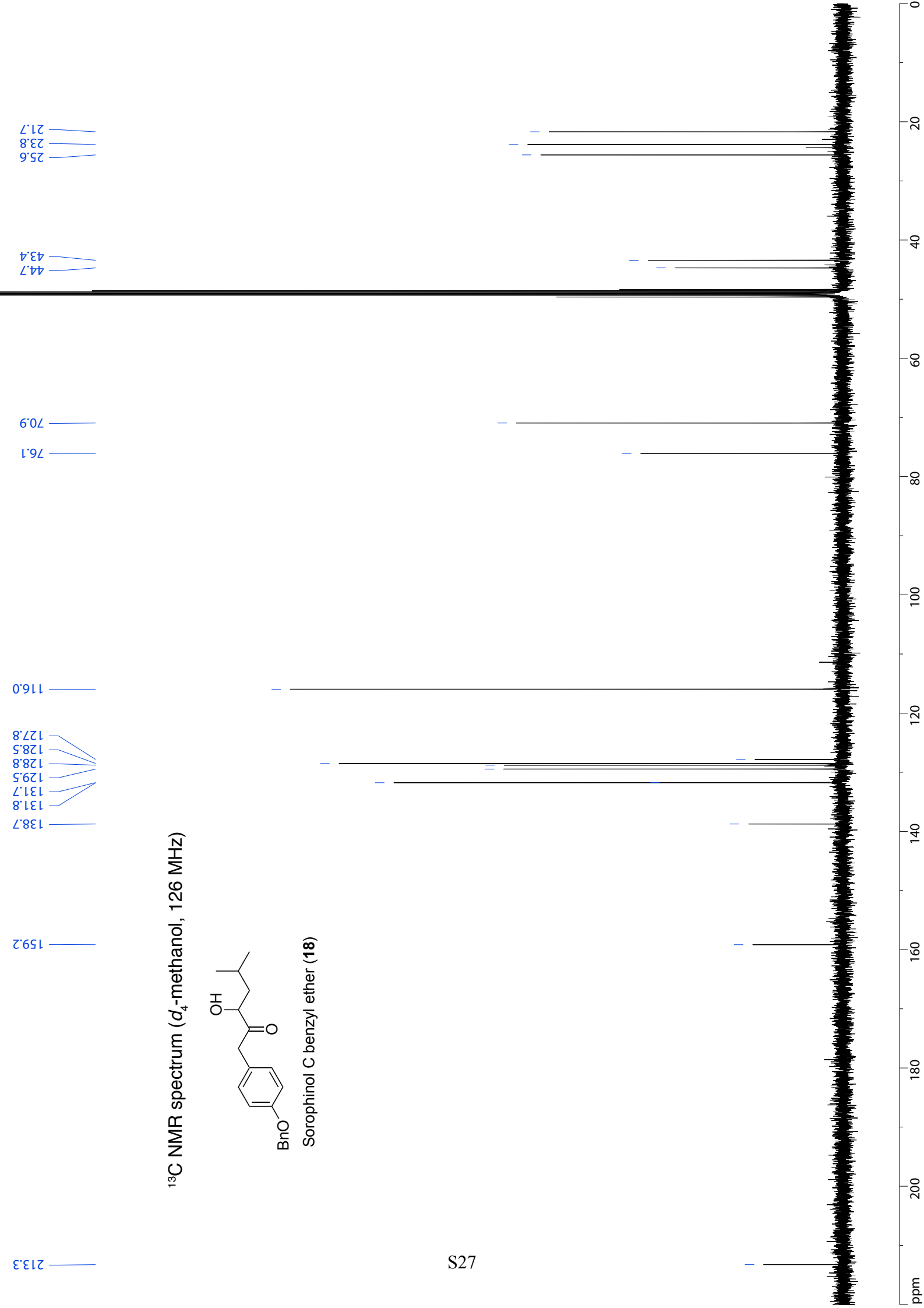
Sorophinol C benzyl ether (**18**)

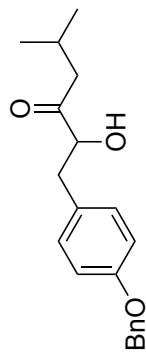


¹³C NMR spectrum (d₄-methanol, 126 MHz)



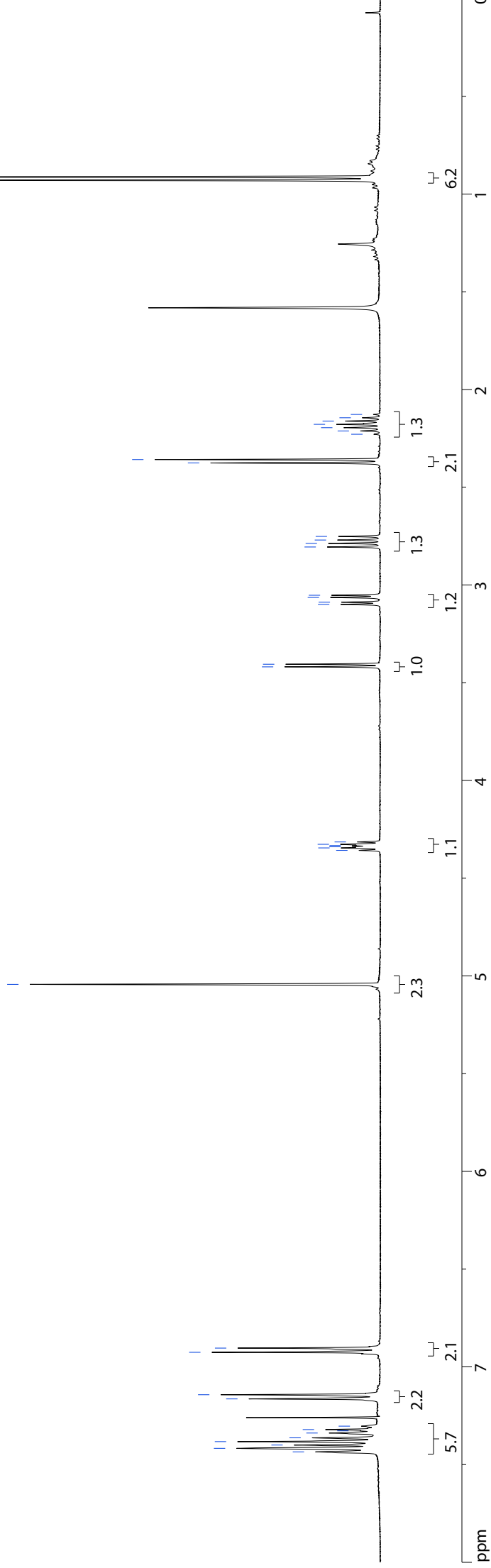
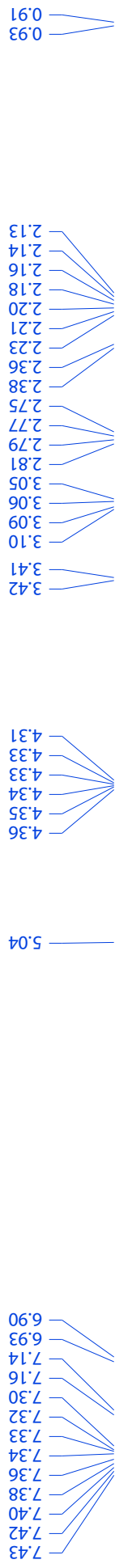
Sorophinol C benzyl ether (**18**)



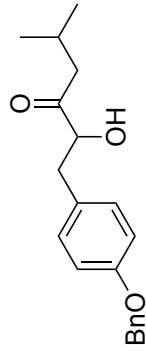


4-Hydroxysattabacin benzyl ether (**19**)

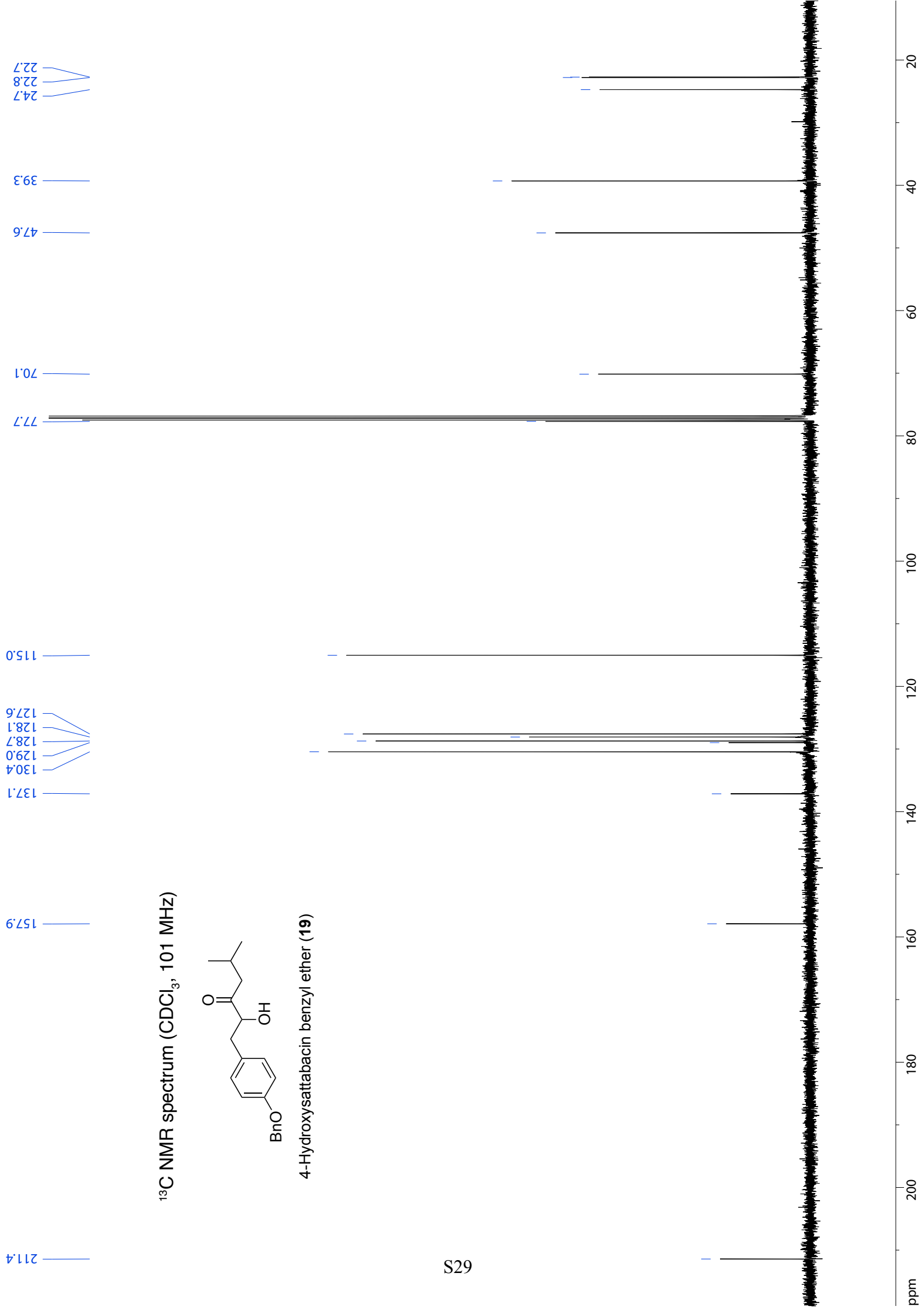
¹H NMR spectrum (CDCl₃, 400 MHz)



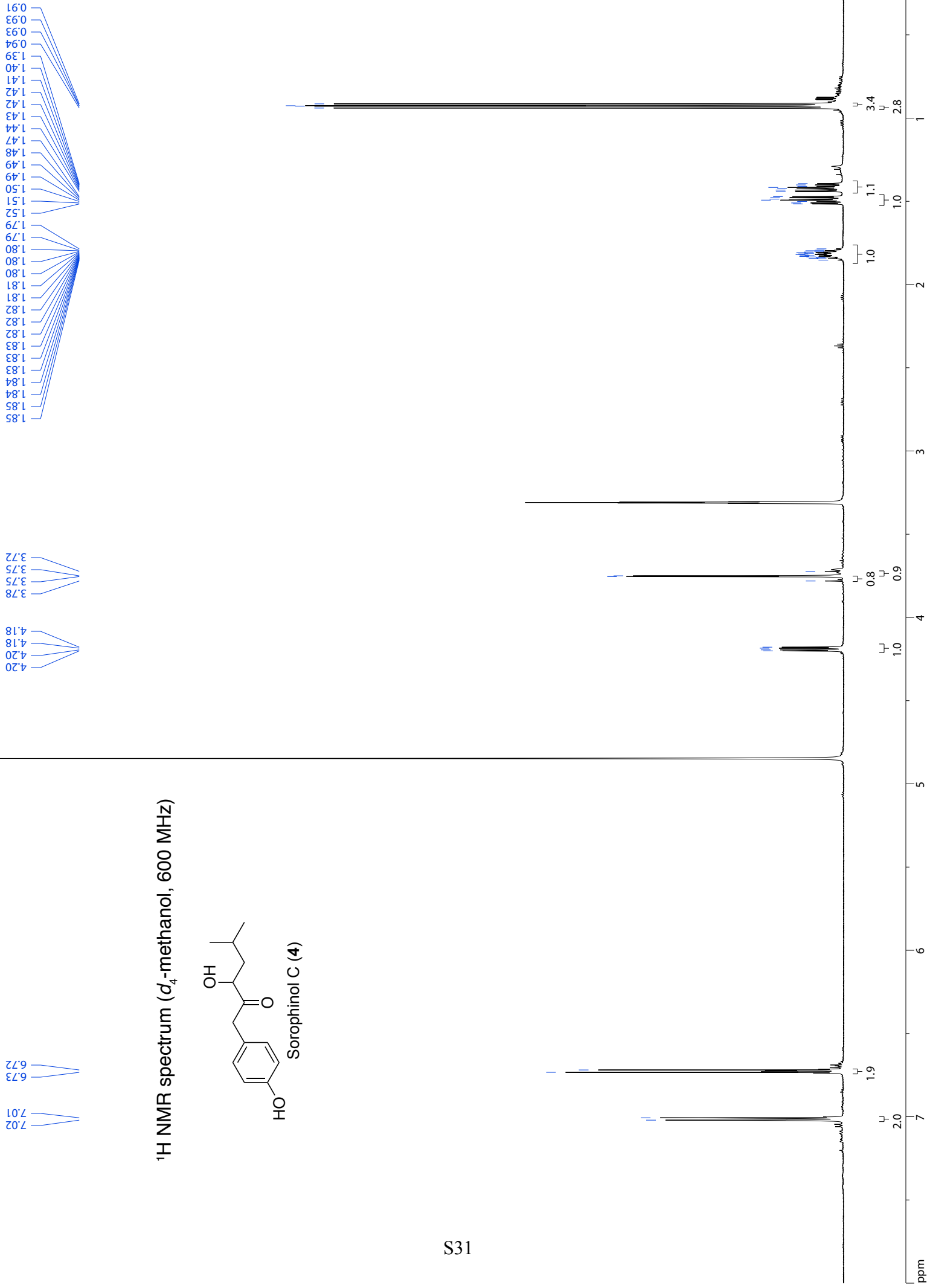
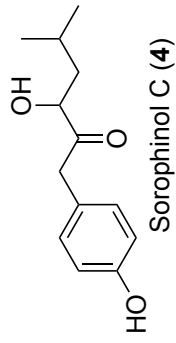
¹³C NMR spectrum (CDCl₃, 101 MHz)



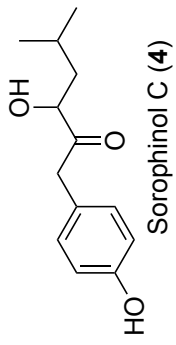
4-Hydroxysattabacin benzyl ether (19)



¹H NMR spectrum (d₄-methanol, 600 MHz)



¹³C NMR spectrum (d₄-methanol, 150 MHz)



25.6
23.8
21.7

43.5
44.9

76.0

116.3

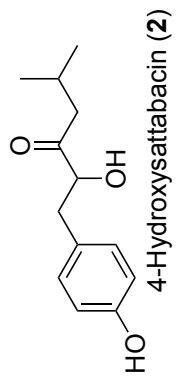
126.2
131.7

157.4

213.5



¹H NMR spectrum (CDCl₃, 400 MHz)



7.08
6.73

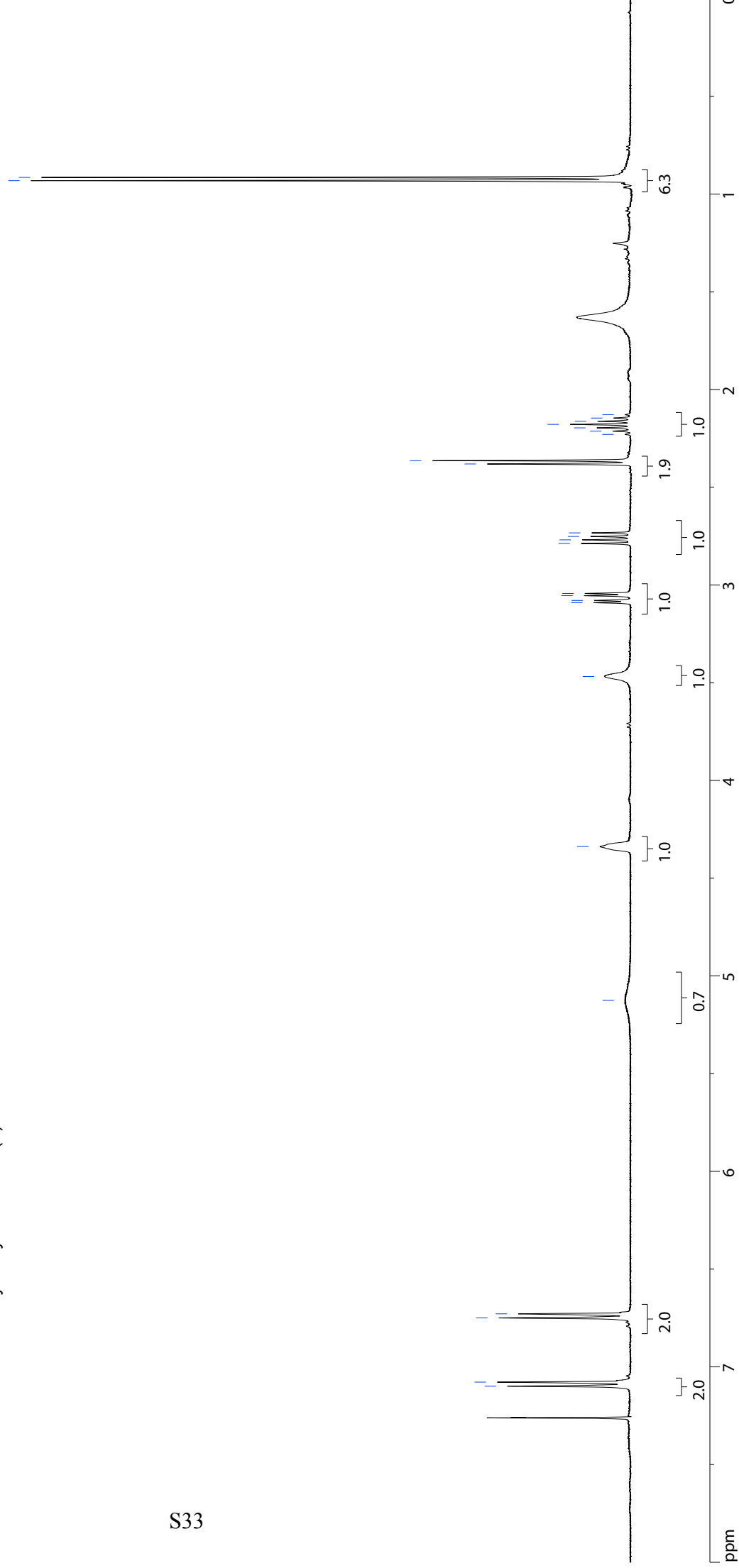
3.09
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2.16
2.15
2.13

3.47

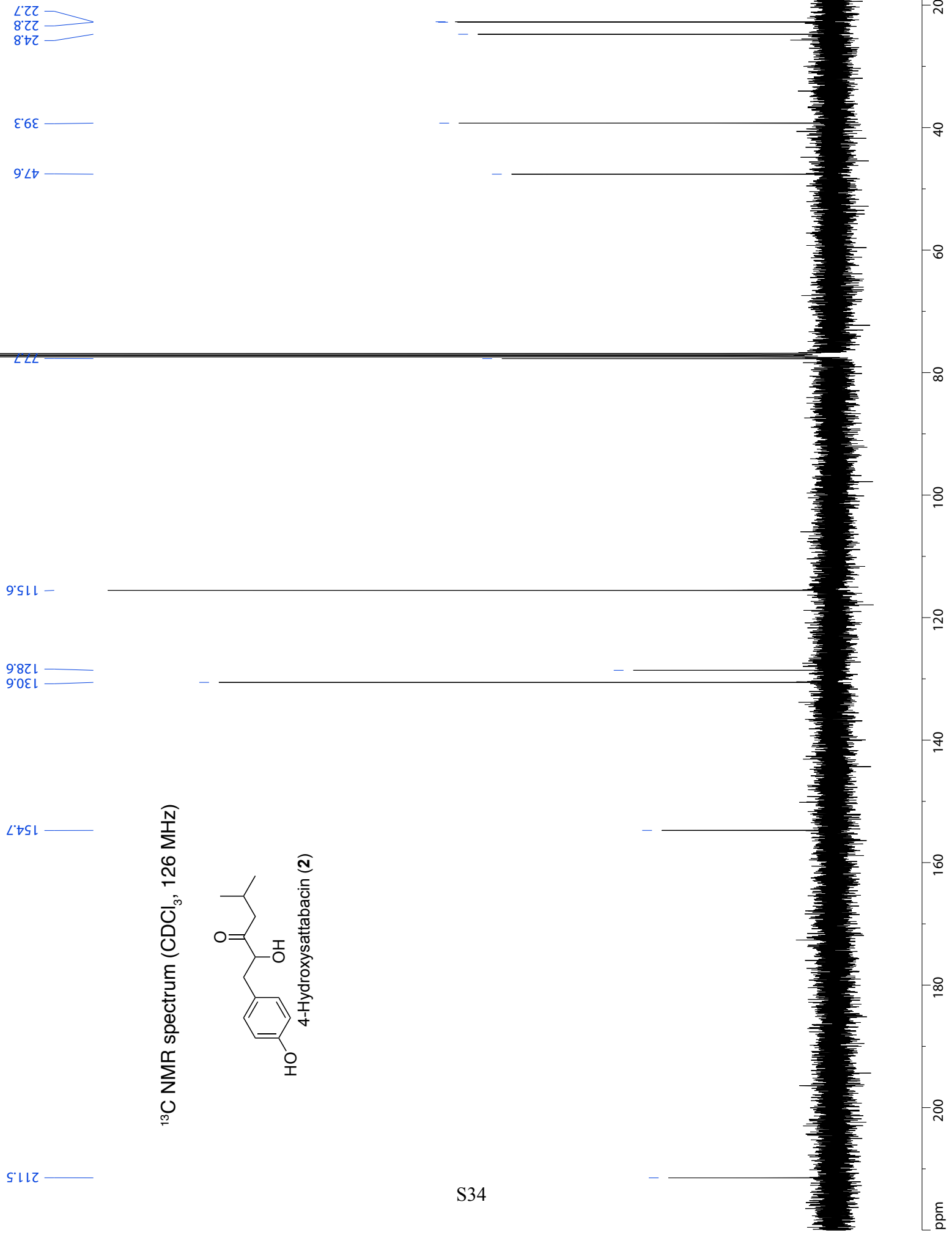
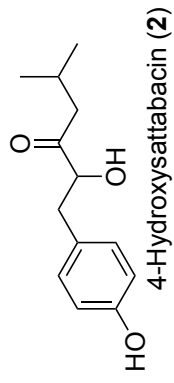
4.34

5.13

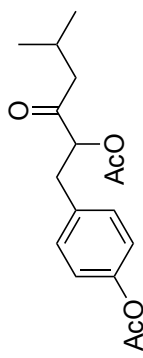
7.10
6.75



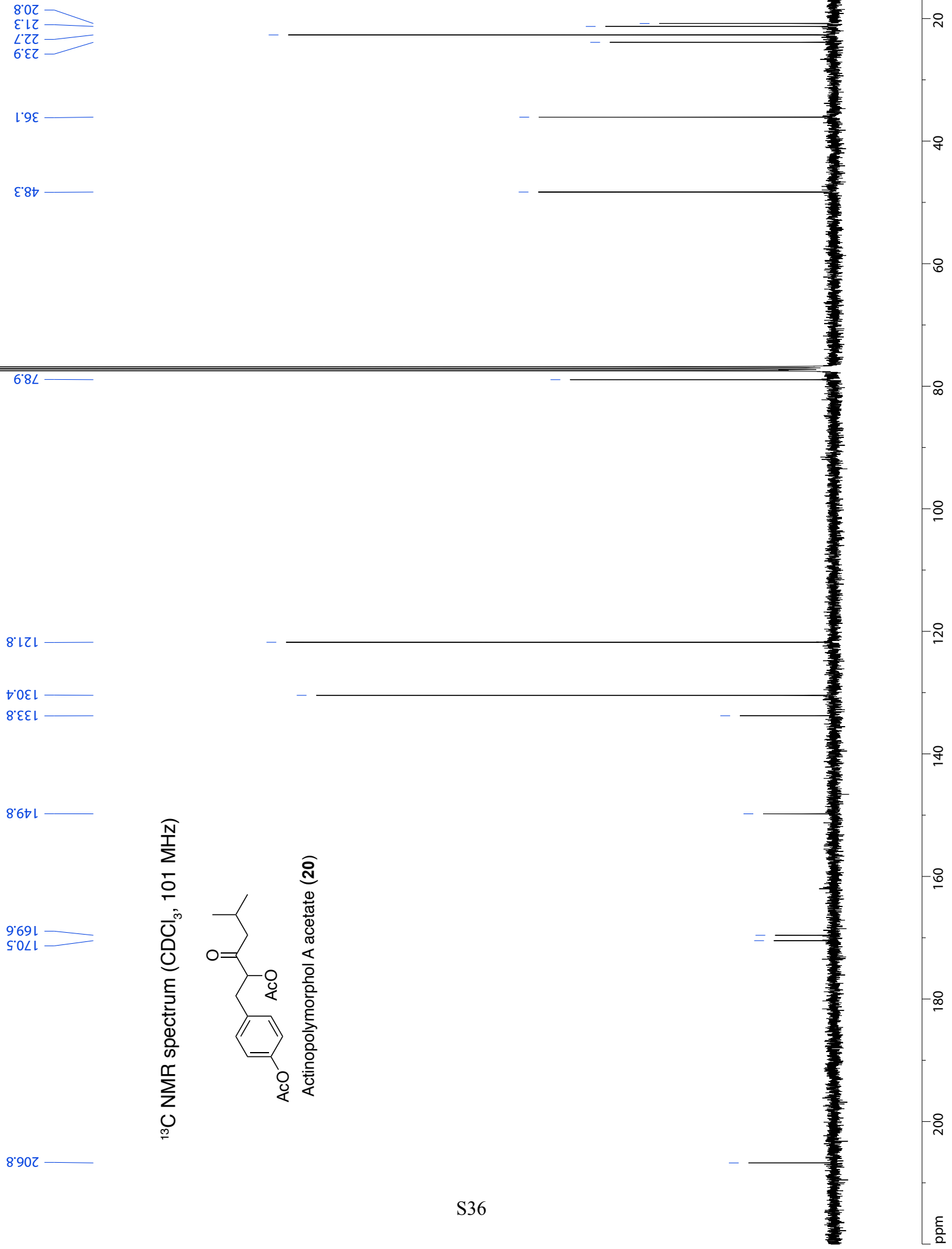
¹³C NMR spectrum (CDCl₃, 126 MHz)

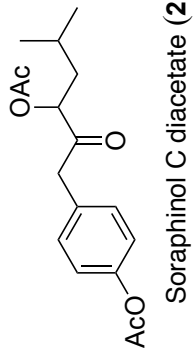


¹³C NMR spectrum (CDCl₃, 101 MHz)

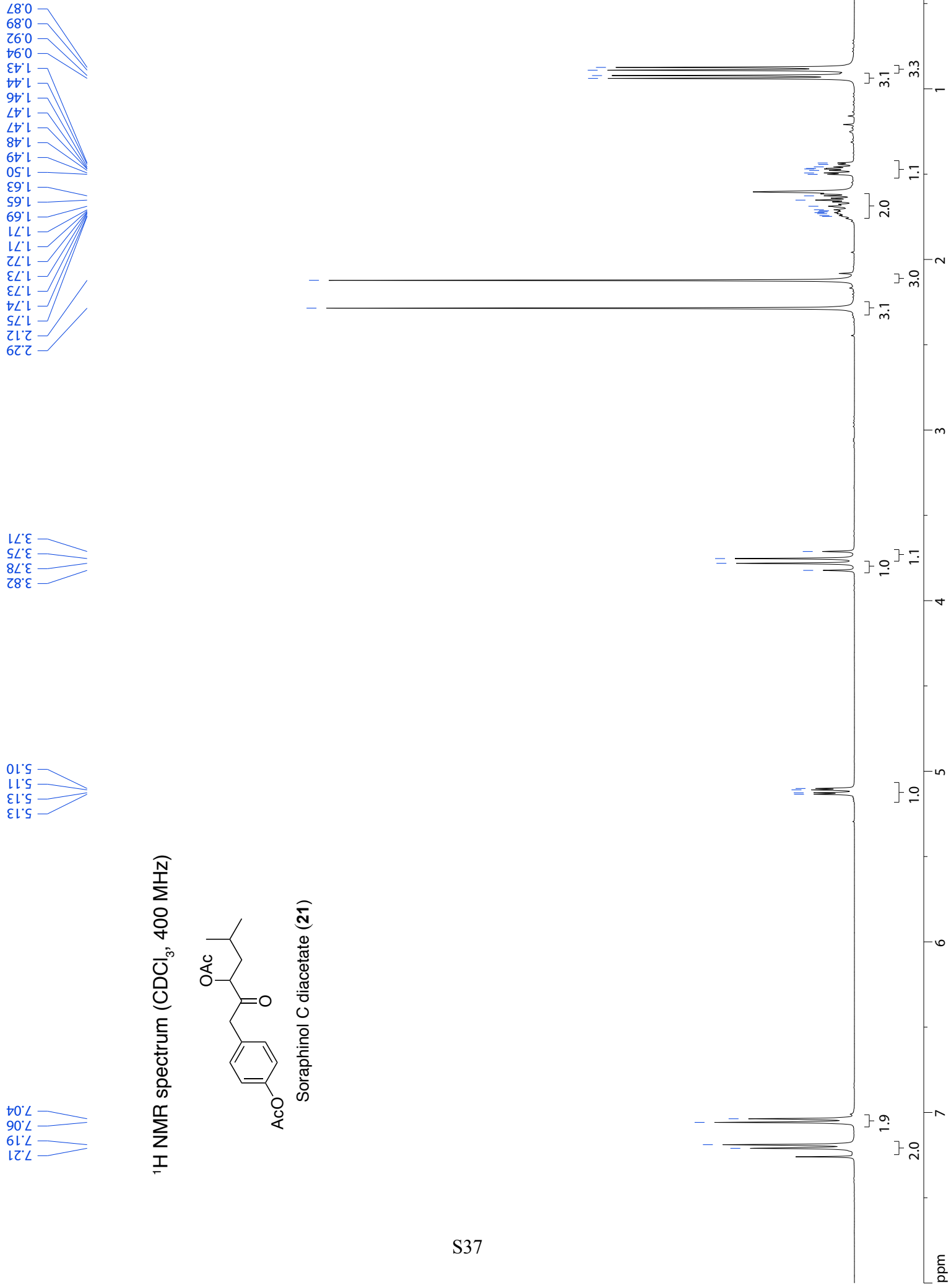


Actinopolymorphol A acetate (**20**)

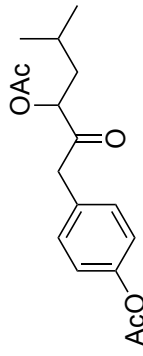




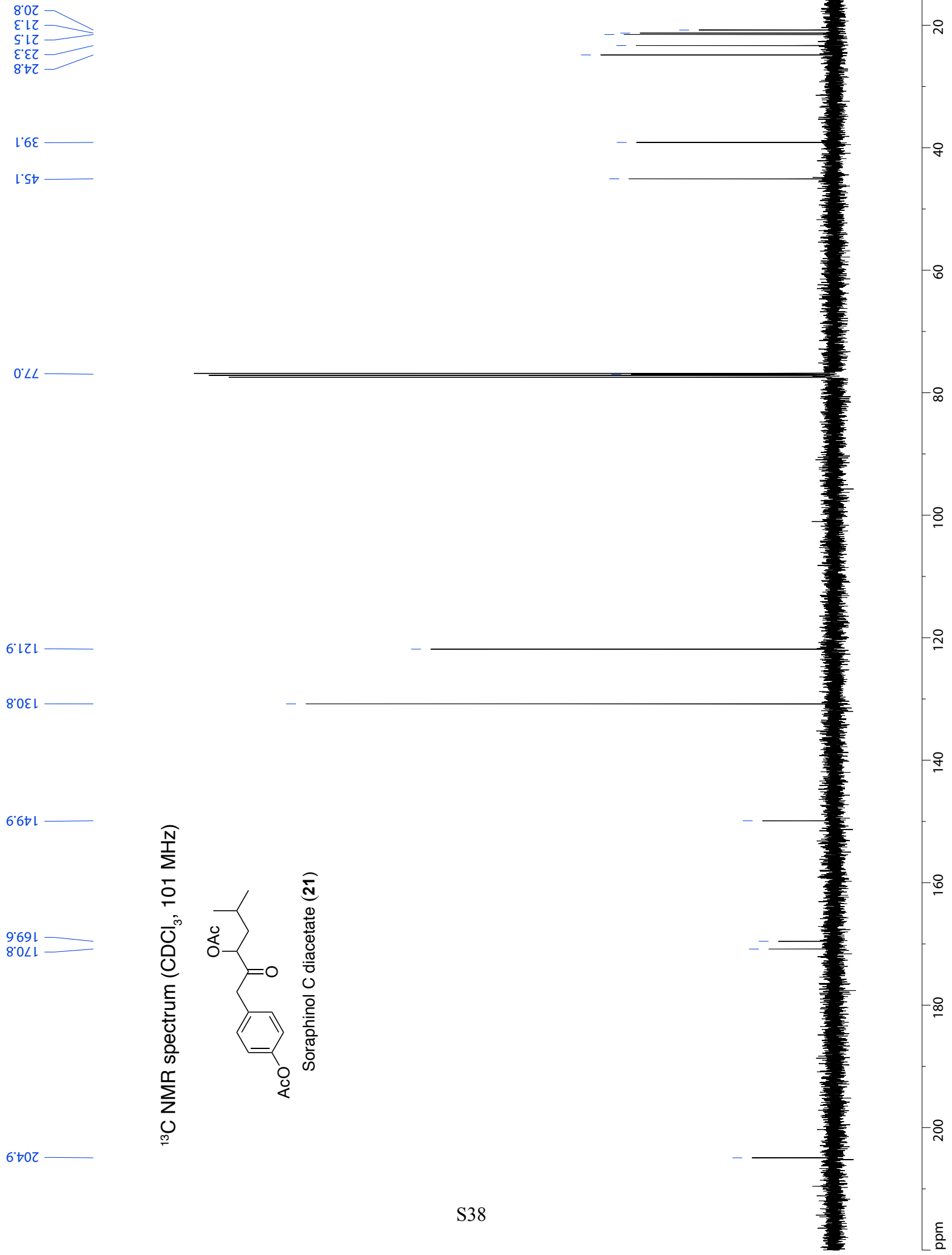
¹H NMR spectrum (CDCl₃, 400 MHz)



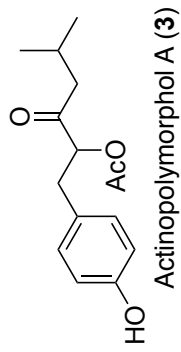
¹³C NMR spectrum (CDCl₃, 101 MHz)



Soraphinol C diacetate (**21**)



¹H NMR spectrum (d₄-methanol, 500 MHz)



0.88
0.87
0.86
0.85

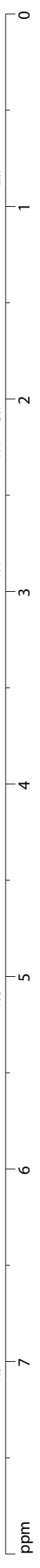
2.01
2.02
2.02
2.03
2.05
2.05
2.08
2.09
2.09
2.16
2.18
2.20
2.21
2.35
2.36
2.39
2.40
2.86
2.87
2.89
2.90
2.99
3.00
3.02
3.03

5.10
5.11
5.12
5.13

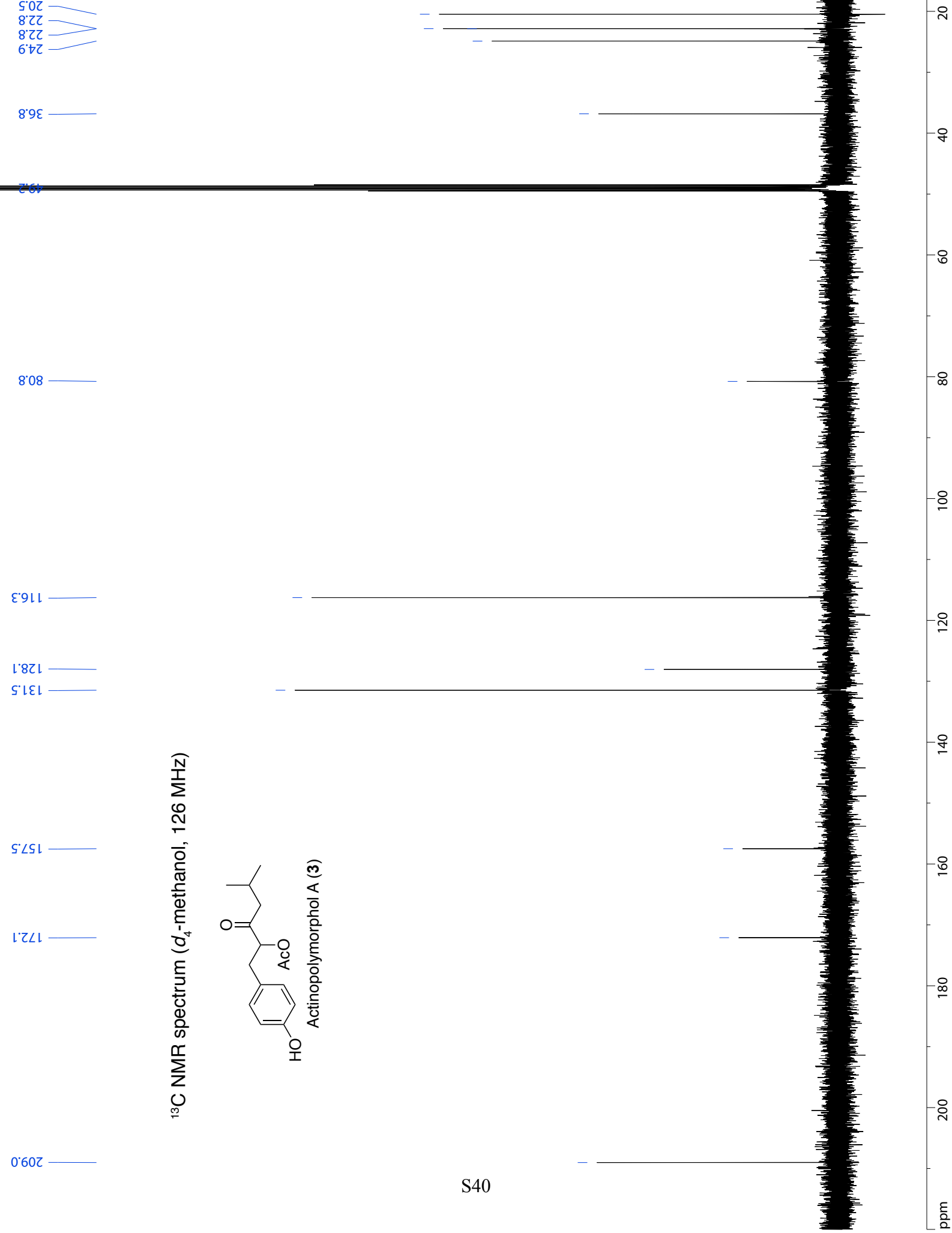
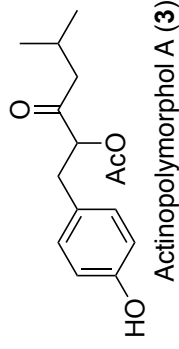
6.72
6.70

7.04
7.06

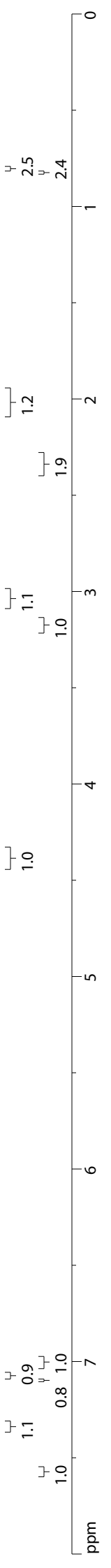
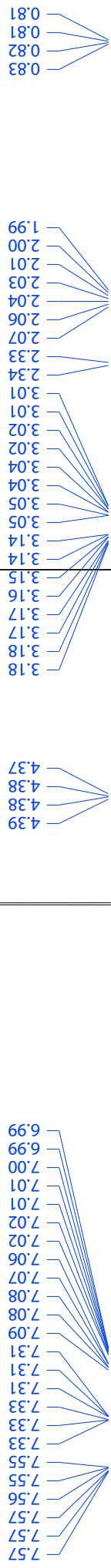
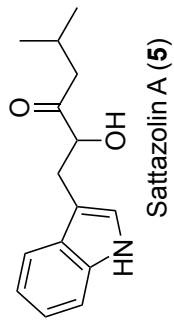
ppm



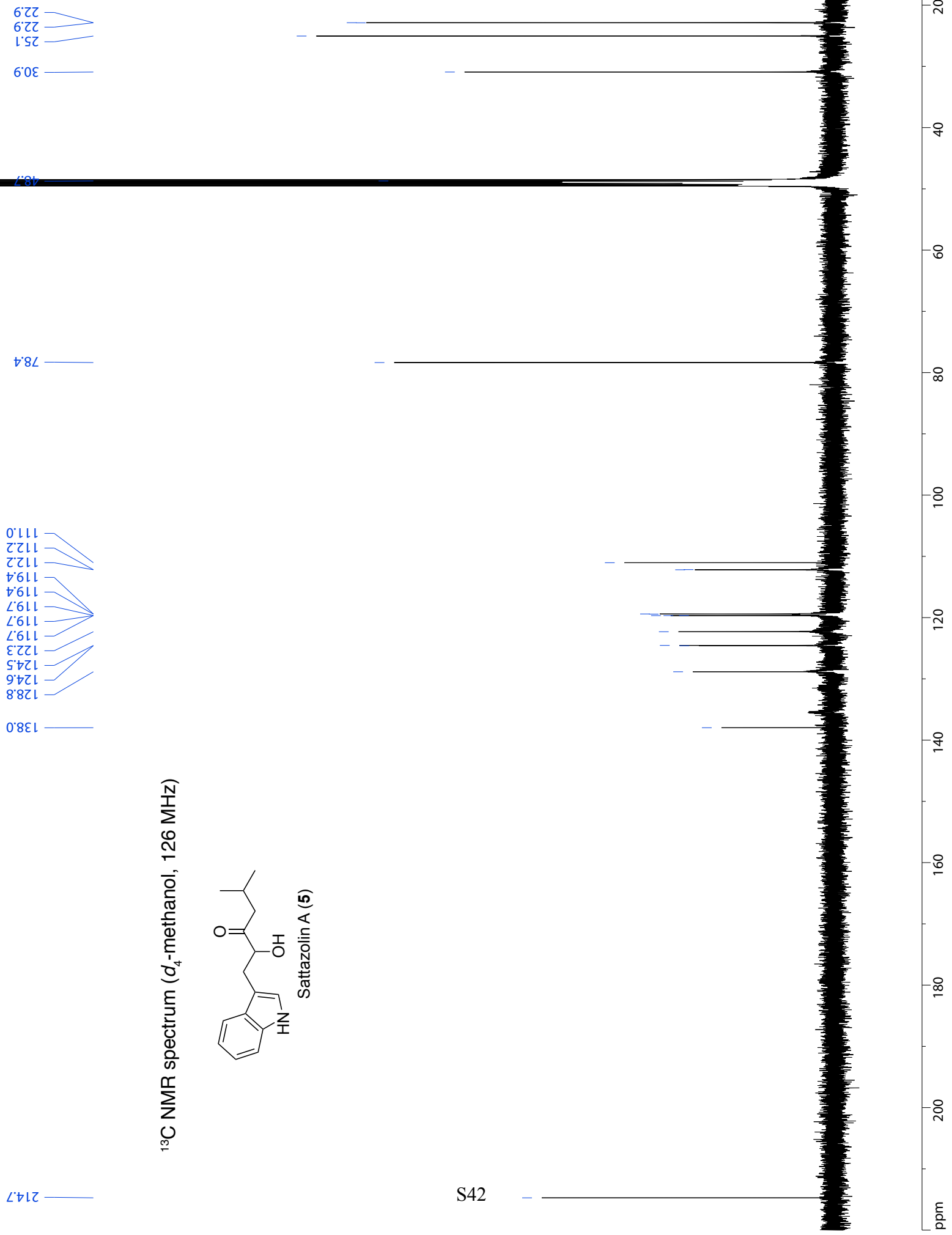
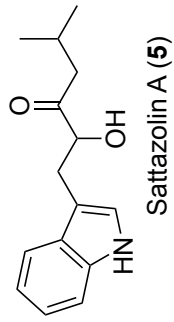
¹³C NMR spectrum (d₄-methanol, 126 MHz)



¹H NMR spectrum (d₄-methanol, 500 MHz)



¹³C NMR spectrum (d₄-methanol, 126 MHz)

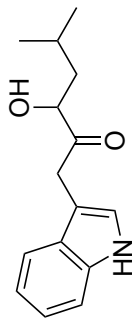


9.21

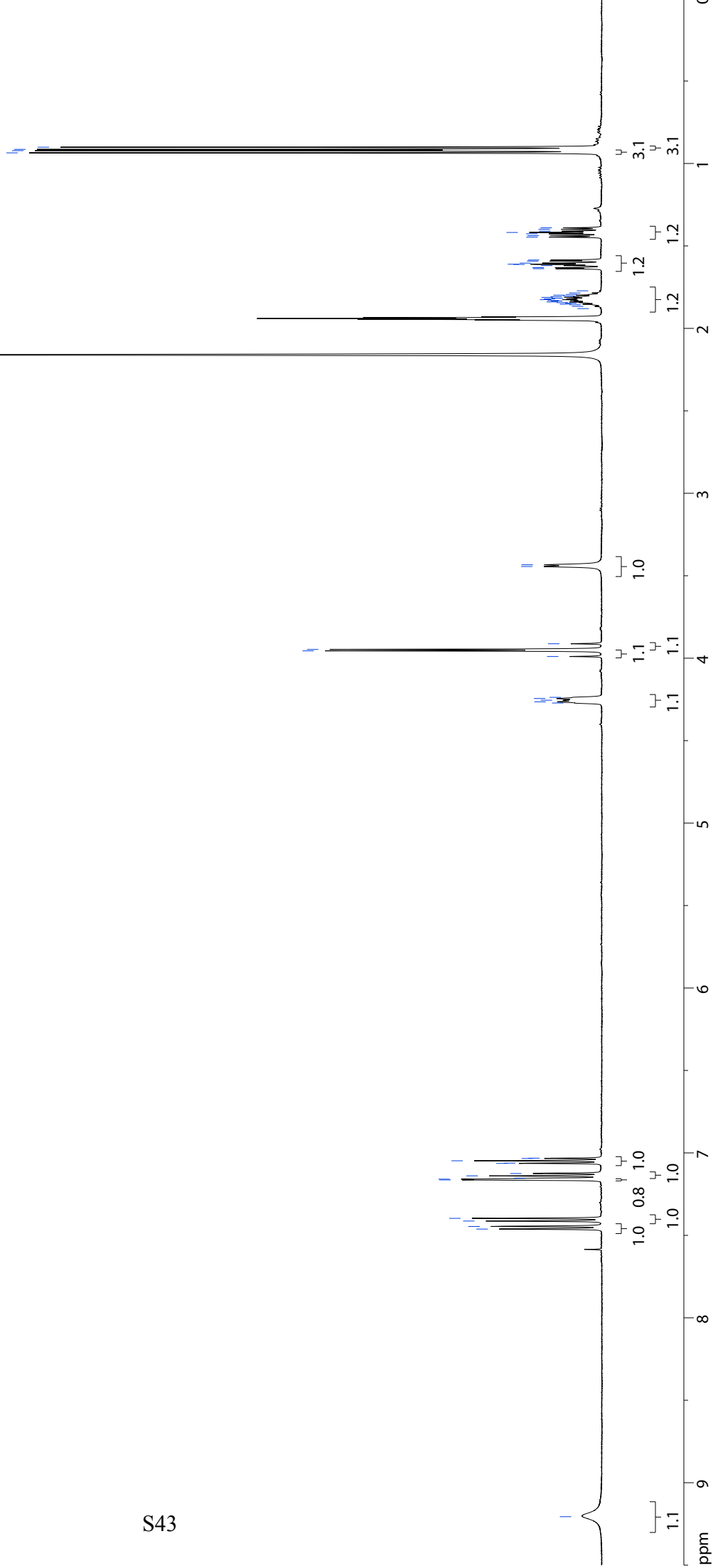
7.46
7.45
7.41
7.40
7.16
7.16
7.15
7.14
7.12
7.06
7.06
7.05
7.03
7.03

4.27
4.26
4.25
4.24
4.24
3.99
3.96
3.95
3.91
3.44
3.43
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.83
1.82
1.82
1.81
1.81
1.80
1.80
1.79
1.79
1.77
1.64
1.63
1.62
1.61
1.61
1.60
1.59
1.59
1.45
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1.42
1.41
1.40
1.39
0.94
0.92
0.91
0.90

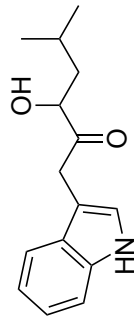
¹H NMR spectrum (d₃-acetonitrile, 500 MHz)



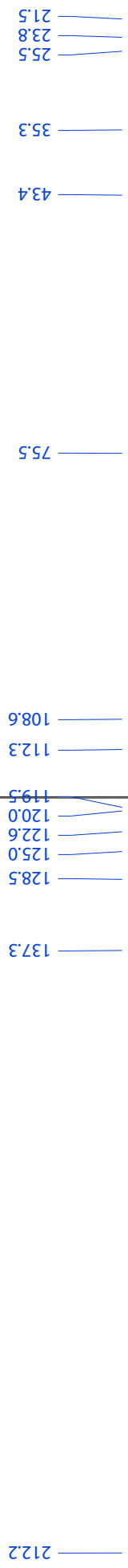
Sattazolin B (**6**)



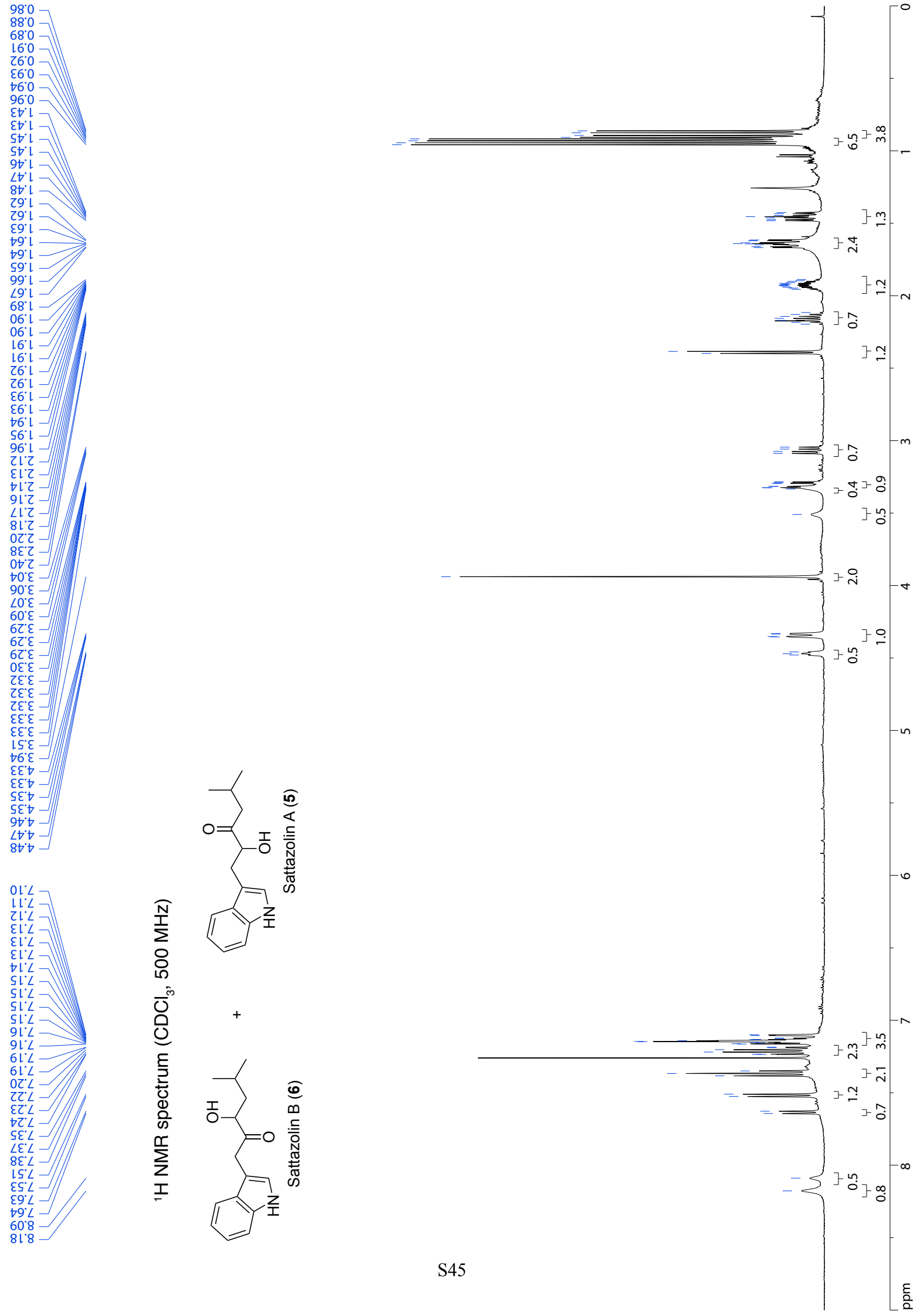
¹³C NMR spectrum (d₃-acetonitrile, 126 MHz)



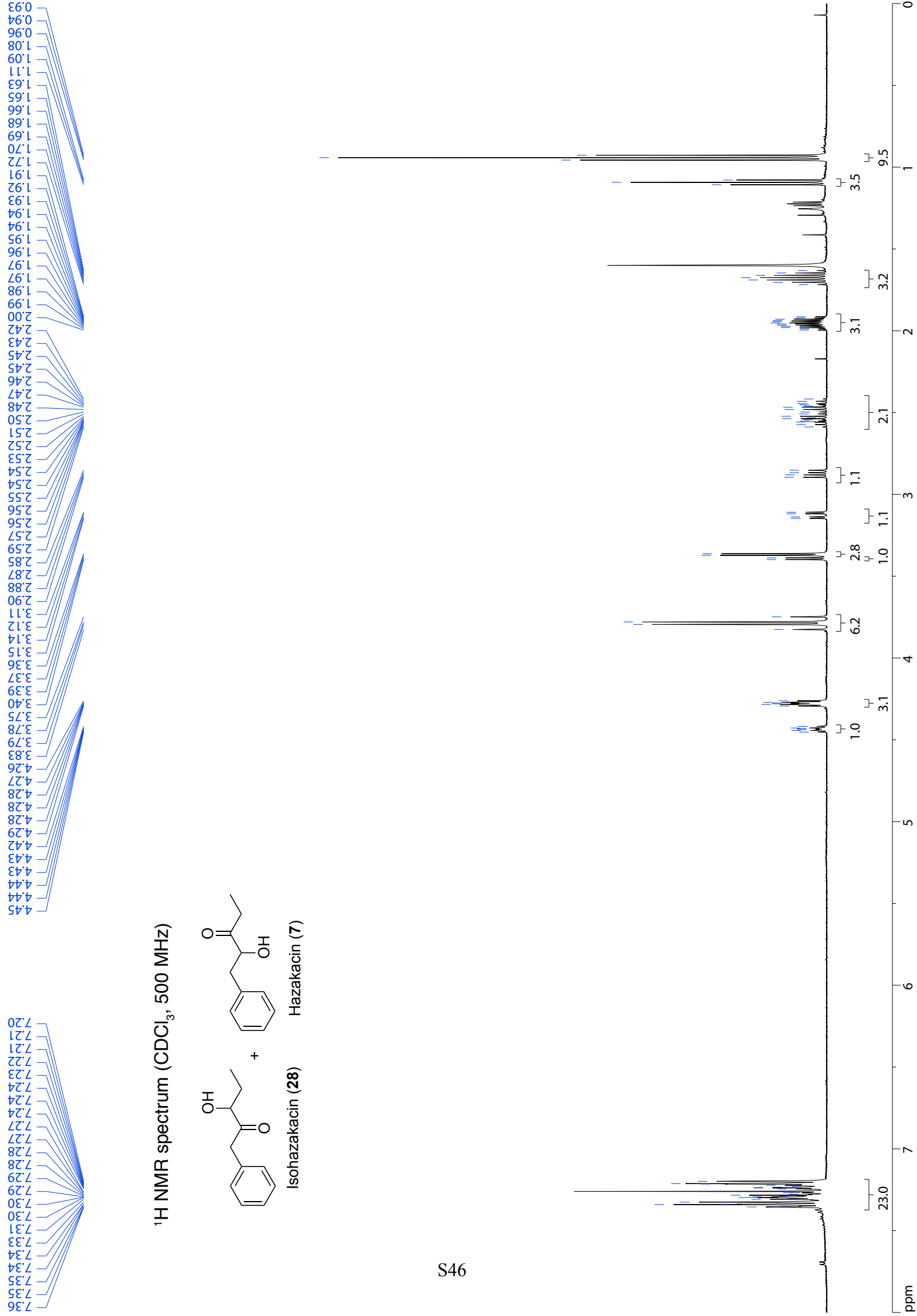
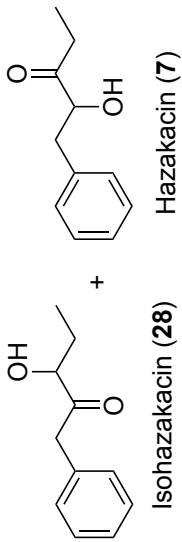
Sattazolin B (**6**)



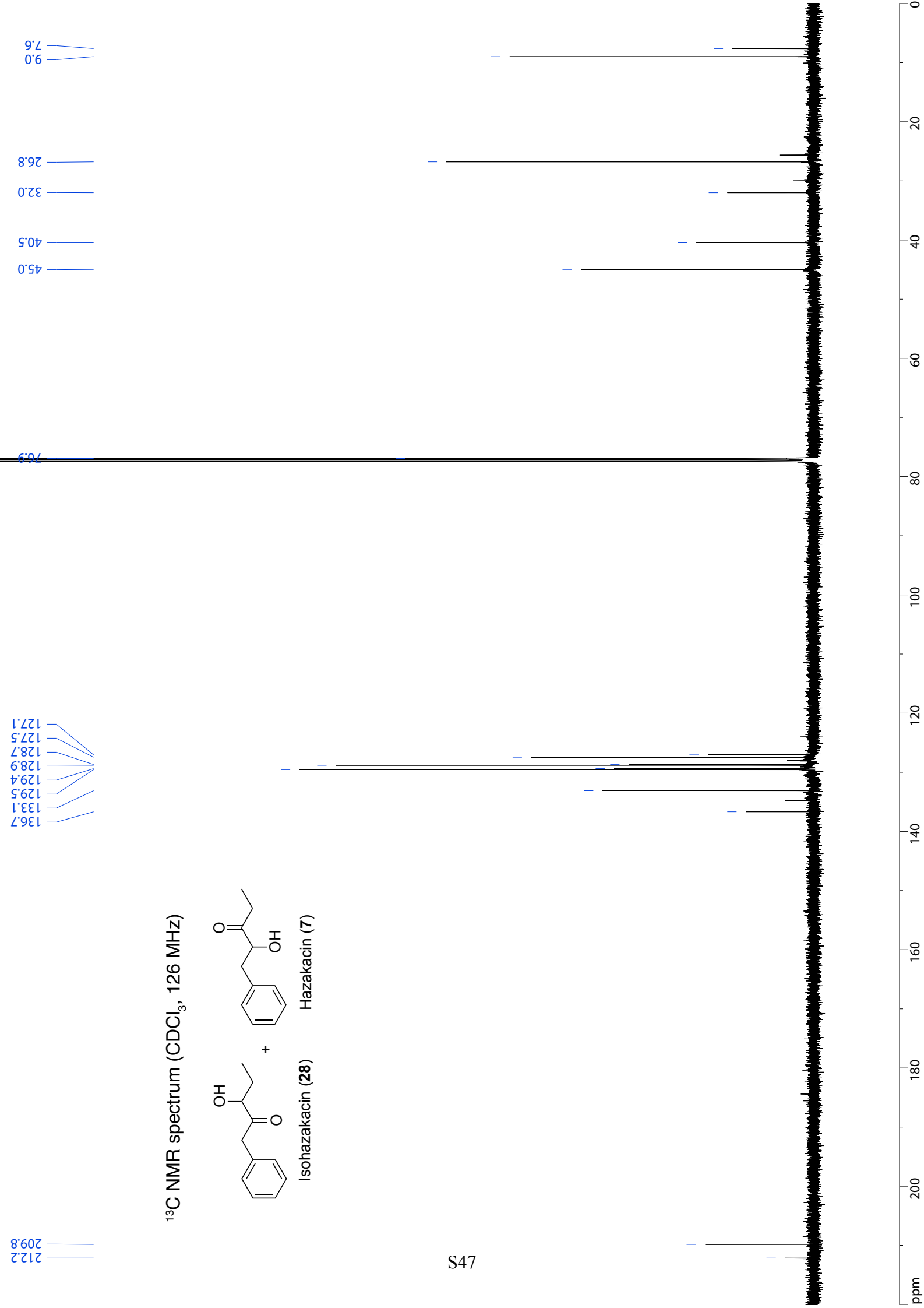
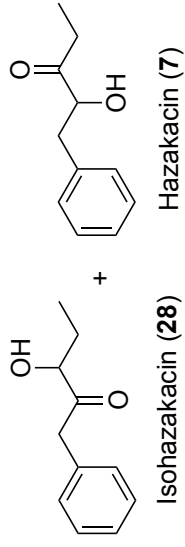
¹H NMR spectrum (CDCl₃, 500 MHz)



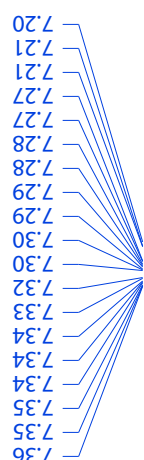
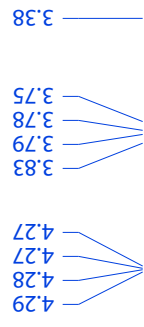
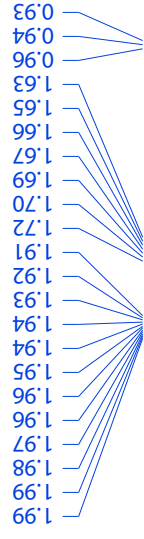
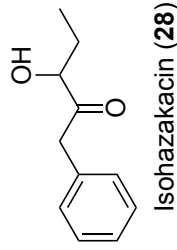
¹H NMR spectrum (CDCl₃, 500 MHz)



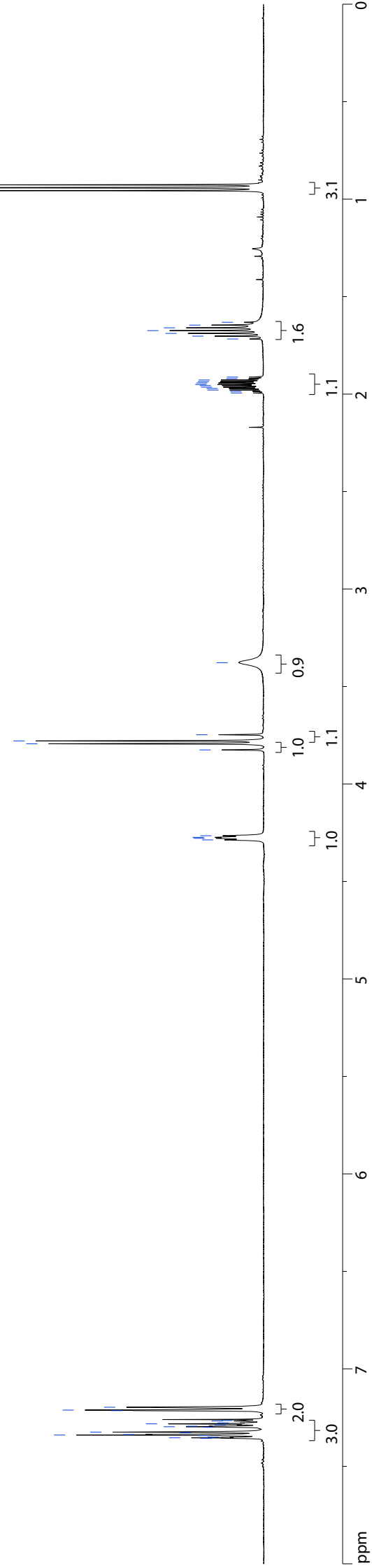
¹³C NMR spectrum (CDCl₃, 126 MHz)



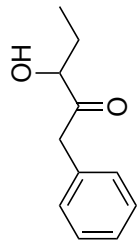
¹H NMR spectrum (CDCl₃, 500 MHz)



S48



¹³C NMR spectrum (CDCl₃, 126 MHz)



Isohazakacin (**28**)

