An Effective *cis*-β-Octahedral Mn(III) SALPN Catalyst for the Mukaiyama-Isayama Hydration of α,β-Unsaturated Esters

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Supporting Information

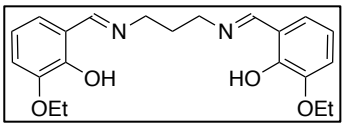
Experimental Section

General Experimental

All commercial reagents and solvents were used as received. Petroleum ether refers petroleum spirits of the fraction boiling between 40 and 60°C. Analytical thin layer chromatography (TLC) was conducted on aluminium backed plates (2 mm silica gel 60 F_{254}) and chromatograms were visualised under UV light (365 nm) and with solutions of 20% w/w phosphomolybdic acid in ethanol (PMA), 20% w/w potassium permanganate in water (PP) or 5% w/v cerium (IV) ammonium molybdate and 1% w/v ceric sulphate in dilute sulphuric acid (CAM). Optical rotations were recorded in a 10.0 cm microcell and units are deg.cm^{2}g^{-1}. Infrared (IR) spectra were recorded using an attenuated total reflectance (ATR) attachment. High-resolution mass spectra (HRMS) were obtained using

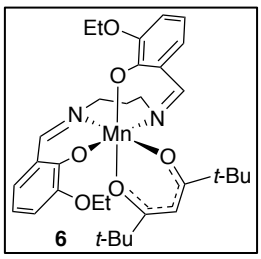
electrospray ionisation (ESI). Nuclear magnetic resonance (NMR) spectra were recorded at 400, 500 or 600 MHz and chemical sifts (δ) were internally referenced to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), CD_3CN and CD_3OD (δ 3.31 ppm).

Preparation of EthoxySALPN



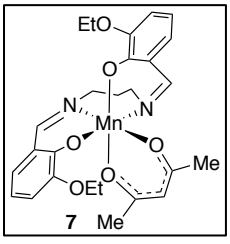
To a solution of the 3-ethoxysalicylaldehyde (3.0 g, 18 mmol) in anhydrous methanol (75mL) at room temperature was added 1,3 diaminopropane (0.753 mL, 0.669 g, 9 mmol) slowly. The mixture was stirred at this temperature overnight, then reduced to approximately half volume. The mixture was cooled in the freezer, and crystallisation induced by scratching the glass/seeding. The crystals were collected and dried to give ethoxySALPN (3.0g, 8.2 mmol 91%) as bright yellow crystals; m.p. 68.6-69.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.47 (t, J = 7.0 Hz, 6H), 2.08 (quint, J = 6.5 Hz, 2H), 3.71 (t, J = 6.4 Hz, 4H), 4.11 (q, J = 7.0 Hz, 4H), 6.78 (t, J = 7.9 Hz, 2H), 6.85 (dd, J = 7.8, 1.3 Hz, 2H), 6.91 (dd, J = 7.9, 1.1 Hz, 2H), 8.35 (s, 2H), 13.91 (br s, 2H). ^{13}C NMR (151 MHz; $CDCl_3$): δ 165.6, 152.0, 147.7, 122.9, 118.6, 117.9, 115.4, 64.5, 56.1, 31.6, 14.9. Calc for $C_{21}H_{27}N_2O_4$ $[M+H]^+$: 371.1971; found 371.1964.

Preparation of Mn(EthoxySALPN)dpm 6



A solution of $Mn(dpm)_3$ (0.114 g, 0.190 mmol) and EthoxySALPN (0.070 g, 0.190 mmol) in MeOH (10 mL) were refluxed for 4 hours. The solution was subsequently concentrated in vacuo to a total volume of 1 mL, water (0.1 mL) was added and solvent was removed by decantation to afford Mn(EthoxySALPN)dpm **6** (0.062 g, 0.102 mmol, 54%) as a green solid. Crystallisation by evaporation from CH_2Cl_2/hexanes afforded **6** as green crystals. HRMS (ESI): Calc. for $C_{21}H_{24}MnN_2O_4$ $[M-(dpm)]^+$: 423.1117; found, 423.1111.

Preparation of Mn(EthoxySALPN)acac 7



A solution of $Mn(acac)_3$ (1.22 g, 3.43 mmol) and EthoxySALPN (1.28 g, 3.43 mmol) in MeOH (50 mL) was refluxed for 4 hours. The solution was subsequently concentrated *in vacuo* to a total volume of 10 mL, cooled to -27°C and the crystalline product collected by vacuum filtration. A second crop of product was collected following cooling of the mother liquor overnight at -27°C to give Mn(EthoxySALPN)acac **7** (1.13 g, 2.16 mmol 62%) as a green solid. Diffraction quality crystals were crystallised from CH_2Cl_2/hexane at -27°C to afford green crystals of **7**. HRMS (ESI): Calc. for $C_{21}H_{24}MnN_2O_4$ $[M-(acac)]^+$: 423.1117; found 423.1113.

General experimental procedure for Mukaiyama-Isayama Hydration

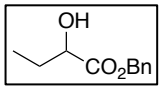
To a solution of ester/lactone (1 equiv.) in iPrOH (0.2 mmol/mL) was added the respective catalyst (20 mol%) and the mixture purged with O_2 for 10 minutes. Phenylsilane (2 equiv.) was then added and the mixture allowed to stir under an atmosphere of O_2 overnight (~16 hours). The reaction mixture was adsorbed onto silica and purified by column chromatography, or preparative normal phase HPLC (Phenomenex Luna 150 x 21.2 mm column, 5µ SiO_2). The catalyst was removed by filtration through a short plug of Florisil®.

Benzyl crotonate

Mn(EthoxySALPN)acac: Conducted as per the general procedure on benzyl crotonate (102 mg, 0.580 mmol). Purification by column chromatography (10-20% EtOAc/petroleum ether) afforded alpha hydroxy ester (79 mg, 0.407 mmol, 70%) as a yellow oil.

Mn(dpm)$_3$: Conducted as per the general procedure on benzyl crotonate (103 mg, 0.585 mmol). Purification by column chromatography (10-20% EtOAc/petroleum ether) afforded benzyl butanoate (56 mg, 0.31 mmol 53%) and alpha hydroxy ester (43 mg, 0.22 mmol, 38%) as yellow oils.

α-Hydroxy ester[1]: ^{1}H NMR (600 MHz; $CDCl_3$) δ 7.39—7.33 (m, 5H), 5.23 and 5.21 (ABq, J_{AB} = 12.2 Hz, 2H), 4.20 (ddd, J = 6.7, 5.8, 4.5 Hz, 1H), 2.75 (d, J = 5.8 Hz, 1H), 1.89—1.82 (m, 1H), 1.70 (dq, J = 14.3, 7.1 Hz, 1H), 0.94 (t, J = 7.4 Hz, 3H).

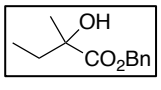


Benzyl tiglate

*Mn(EthoxySALPN)acac **7**:* Conducted as per the general procedure on benzyl tiglate (100 mg, 0.526 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) afforded alpha hydroxy ester (73 mg, 0.35 mmol, 67%) as a yellow oil.

*Mn(dpm)$_3$ **2**:* Conducted as per the general procedure on benzyl tiglate (100 mg, 0.526 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) afforded benzyl 2-methylbutanoate (21 mg, 0.11 mmol, 21%) and alpha hydroxy ester (48 mg, 0.23 mmol, 44%) as a yellow oil.

α-Hydroxy ester[2]: ^{1}H NMR (600 MHz; $CDCl_3$) δ 0.84 (t, J = 7.4 Hz, 3H), 1.42 (s, 3H), 1.65-1.71 (m, 1H), 1.80 (dq, J = 14.1, 7.2 Hz, 1H), 3.13 (s, 1H), 5.20 and 5.21 (ABq, J_{AB} = 12.3 Hz, 2H), 7.33-7.40 (m, 5H).



1. Nakata, K.; Sekiguchi, A.; Shiina, I. *Tetrahedron Asymm*. **2011**, *22*, 1610.

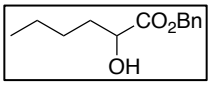
2. Green, J. E.; Bender, D. M.; Jackson, S.; Donnell, M. J. O.; Mccarthy, J. R. *Org. Lett* **2009**, *11*, 807.

Benzyl hexenoate

*Mn(EthoxySALPN)acac **7**:* Conducted as per the general procedure on benzyl hexenoate (101 mg, 0.495 mmol). Purification by column chromatography (5-10% EtOAc/petroleum ether) afforded alpha hydroxy ester (77 mg, 0.35 mmol, 70%) as a yellow oil.

*$Mn(dpm)_3$ **2**:* Conducted as per the general procedure on benzyl hexenoate (101 mg, 0.495 mmol). Purification by column chromatography (5% – 10% EtOAc/Petrol Ether) afforded benzyl hexanoate (32 mg, 0.16 mmol, 30%) and alpha hydroxy ester (56 mg, 0.25 mmol, 51%) as a yellow oil.

α-Hydroxy ester[1]: ^{1}H NMR (600 MHz; $CDCl_3$) δ 0.88 (t, J = 7.1 Hz, 3H), 1.26-1.46 (m, 4H), 1.62-1.68 (m, 1H), 1.78-1.83 (m, 1H), 2.73 (dd, J = 8.2, 5.7 Hz, 1H), 4.23 (ddd, J = 7.1, 5.6, 4.5 Hz, 1H), 5.21 and 5.23 (ABq, J_{AB} = 12.2 Hz, 2H), 7.33-7.39 (m, 4H).

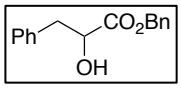


Benzyl cinnamate

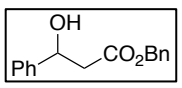
*$Mn((EtO)_2$-SALPN)acac **7**:* Conducted as per the general procedure on benzyl cinnamate (43.4 mg, 0.182 mmol). Purification by preparative HPLC (Phenomenex 21.2 x 150 mm LUNA 5µ Silica (2) 100 Å column, 20% EtOAc/petroleum ether as eluent) afforded alpha hydroxy ester (R_t = 16.5 min, 1.1 mg, 0.0043 mmol, 2%) as a clear oil and beta hydroxy ester (R_t = 19.2 min, 27.6 mg, 0.108 mmol, 59%) as a clear oil.

*$Mn(dpm)_3$ **2**:* Conducted as per the general procedure on benzyl cinnamate (40.6 mg, 0.170 mmol). Purification by column chromatography afforded benzyl 3-phenylpropanate (7.9 mg, 0.033 mmol, 19%) as a clear oil and an inseparable mixture of α and β-hydroxy esters (1 : 3 alpha:beta, 20.6 mg, 0.0804 mmol, 47%) as a yellow oil.

α-Hydroxy ester[3]: ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.70 (d, J = 6.4 Hz, 1H), 2.97 (dd, J = 14.0, 6.5 Hz, 1H), 3.11 (dd, J = 13.9, 4.7 Hz, 1H), 4.48 (td, J = 6.4, 4.7 Hz, 1H), 5.16 and 5.19 (ABq J_{AB} = 15.06 Hz, 2H), 7.13-7.37 (m, 10H). ^{13}C NMR ($CDCl_3$, 151 MHz): 40.5, 67.4, 71.2, 126.8, 128.4, 128.6, 128.6, 128.6, 129.5, 134.9, 136.1, 174.0.



β-Hydroxy ester[4]: ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.78 (dd, J = 16.4, 3.7 Hz, 1H), 2.84 (dd, J = 16.4, 9.2 Hz, 1H), 3.20 (d, J = 3.6 Hz, 1H, OH), 5.15-5.19 (m, 3H) 7.28-7.38 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$): 43.5, 66.8, 70.5, 125.8, 128.0, 128.4, 128.5, 128.7, 128.7, 135.6, 142.5, 172.3.



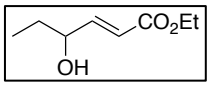
Ethyl sorbate

*Mn(EthoxySALPN)acac **7**:* Conducted as per the general procedure on ethyl sorbate (125.6 mg, 0.896 mmol) 23 mg (0.044 mmol, 0.05 eq) of Mn((EtO_2)-SALPN)(acac) and 145 mg (1.34 mmol, 1.5 eq)

3. Weng, S.; Li, H.; Yang, T. *RSC Adv.* **2013**, *3*, 1976.
4. Shiina, I. Umezaki, Y. Kuroda, N. Iizumi, T. Nagai, S. Katoh, T. *J. Org. Chem.* **2012**, *77*, 4885.

of phenylsilane. Purification by column chromatography (Florisil® with 5-15% EtOAc/pentane as eluent) afforded gamma hydroxy ester (28 mg 0.18 mmol 20%) as a yellow oil.

γ-Hydroxy ester[5]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.96 (t, *J* = 7.46 Hz, 1H), 1.33 (t, *J* = 7.14 Hz, 3H), 1.54-1.69 (m, 2H), 1.98 (d, *J* = 3.49 Hz, 1H), 4.19 (q, *J* = 7.14 Hz, 2H), 4.12-4.27 (m, 1H), 6.02 (dd, *J* = 15.7, 1.58 Hz 1H), 6.93 (dd, *J* = 15.7, 4.97 Hz, 1H). ^{13}C NMR (126 MHz; $CDCl_3$): δ 166.7, 150.0, 120.5, 72.5, 60.6, 29.7, 14.4, 9.6

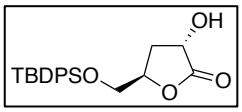


(S)-5-((*t*-Butyldiphenylsilyloxy)methyl)furan-2(5H)-one (TBDPS HBO)

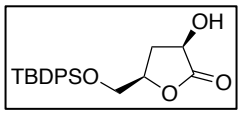
*Mn(EthoxySALPN)acac **7**:* Conducted as per the general procedure on TBDPS HBO (1.43 g, 4.06 mmol). Purification by column chromatography (40% EtOAc/petroleum ether) afforded a mixture of starting material (40.2 mg, 0.114 mmol, 3%) and (S)-5-((*t*-Butyldiphenylsiloxy)-methyl)dihydrofuran-2(3H)-one (80.8 mg, 0.228 mmol, 6%) as clear solid,[6] (2*R*, 4*S*)-5-(*t*-Butyldiphenylsiloxy)-2-hydroxyentan-4-olide (744 mg, 2.00 mmol, 50%) as a clear oil and (2*S*, 4*S*)-5-(*t*-Butyldiphenylsiloxy)-2-hydroxyentan-4-olide (326 mg, 0.88 mmol, 22%) as a yellow oil.

*$Mn(dpm)_3$ **2**:* Conducted as per the general procedure on TBDPS HBO (185 mg, 0.525 mmol). Purification by column chromatography (40% EtOAc/petroleum ether) afforded (S)-5-((*t*-butyldiphenylsiloxy)methyl)dihydrofuran-2(3H)-one (148 mg, 0.412 mmol, 80%) as a colourless crystalline solid.

(2*R*, 4*S*)-5-(*t*-Butyldiphenylsiloxy)-2-hydroxyentan-4-olide: $[\alpha]_D^{23}$ +60.4 (*c* 1.1, $CHCl_3$). Lit.[7] $[\alpha]_D^{25.4}$ +54.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.05 (s, 9H), 2.35 (dt, *J* = 13.0, 9.0 Hz, 1H), 2.63 (ddd, *J* = 13.0, 9.0, 2.0 Hz, 1H), 2.81 (br s, 1H, OH), 3.63 (dd, *J* = 11.6, 2.3 Hz, 1H), 3.90 (dd, *J* = 11.6, 2.6 Hz, 1H), 4.65 (dq, *J* = 8.9 Hz, 1H), 7.40 (ddt, *J* = 8.8, 5.6 1.6 Hz, 4H), 7.43-7.47 (m, 2H), 7.62-7.65 (m, 4H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 19.3, 26.9, 32.9, 65.5, 67.6, 77.7, 128.1, 130.2, 132.2, 132.7, 135.6, 135.7, 178.0. HRMS (ESI): Calc. for $C_{21}H_{26}NaO_4Si^+$ $[M+Na]^+$: 393.1493; found 393.1489.



(2S, 4S)-5-(*t*-Butyldiphenylsiloxy)-2-hydroxyentan-4-olide: $[\alpha]_D^{23}$ +9.88° (*c* 0.98, $CHCl_3$). Lit.[8] $[\alpha]_D^{23}$ +10.2 (*c* 1.38, $CHCl_3$) ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.06 (s, 9H), 2.23 (dt, *J* = 12.8, 9.5 Hz, 1H), 2.60 (ddd, *J* = 12.8, 8.6, 6.0 Hz, 1H), 2.95 (s, 1H, OH), 3.74 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.91 (dd, *J* = 11.7, 3.3 Hz, 1H), 4.49-4.53 (m, 2H), 7.39-7.42 (m, 4H), 7.43-7.46 (m, 2 H) 7.65-7.68 (m, 4 H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 19.4, 26.9, 32.6, 64.6, 68.4, 77.2, 128.0, 130.1, 130.1, 132.6, 132.9, 135.7, 135.8, 176.9. HRMS (ESI): Calc. for $C_{21}H_{26}NaO_4Si^+$ $[M+Na]^+$: 393.1493; found 393.1489.



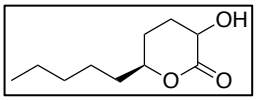
5. Tian, G. Q.; Yang, J.; Rosa-Perez, K. *Org. Lett.* **2010**, *12*, 5072.
6. Yield calculated by ^{1}H NMR spectroscopy.
7. Li, W. Gan, J. Ma, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 8891.
8. Niihata, S. Ebata, T. Kawakami, H. Matsushita, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1509.

6-Pentyl-5,6-dihydropyran-2-one (Massoia lactone)

*Mn(EthoxySALPN)acac **7**:* Conducted as per the general procedure on Massoia lactone (136.7 mg, 0.813 mmol) and Mn(SALPN)acac (42 mg, 0.0813 mmol, 0.1 eq). Purification by column chromatography (40-50% EtOAc/petroleum ether) afforded (*R*)-δ-decalactone (8.3 mg, 0.0488 mmol, 6%) and an inseparable mixture of alpha hydroxy lactones (1:1 dr, 103 mg, 0.553 mmol, 68%) as a yellow gum..

*Mn(dpm)$_3$ **2**:* Conducted as per the general procedure on Massoia lactone (101 mg, 0.601 mmol). Purification by column chromatography (40% EtOAc/petroleum ether) afforded (*R*)-δ-decalactone (72 mg, 0.42 mmol, 71%) as a yellow oil and alpha hydroxy lactone (1:1 dr, 19 mg, 0.10 mmol, 17%) as yellow oils.

α-Hydroxy lactone: ^{1}H NMR (500 MHz; $CDCl_3$): δ 4.39—4.33 (m, 3H), 4.10 (dd, J = 11.9, 6.5 Hz, 1H), 3.29 (s, 2H), 2.46—2.39 (m, 1H), 2.35—2.30 (m, 1H), 2.03—1.96 (m, 2H), 1.85 (qd, J = 12.7, 2.9 Hz, 1H), 1.77—1.45 (m, 13H), 1.40—1.25 (m, 12H), 0.89 (t, J = 6.9 Hz, 7H). ^{13}C NMR (151 MHz; $CDCl_3$): δ 176.4, 174.7, 83.4, 78.1, 68.0, 65.4, 36.1, 35.4, 31.64, 31.62, 28.3, 28.0, 26.3, 25.7, 24.9, 24.6, 22.6, 14.1 HRMS (ESI): Calc. for $C_{10}H_{19}O_3^+$ $[M+H]^+$: 187.1334; found 187.1330.

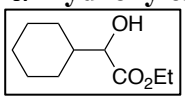


Ethyl cyclohexylidene acetate:

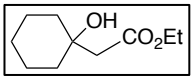
*Mn(EthoxySALPN)acac **7**:* Conducted as per the general procedure on cyclohexilidene acetate (100 mg, 0.600 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) afforded an inseparable mixture of alpha and beta hydroxy ester s (1 : 2.6 alpha:beta, 35 mg, 0.19 mmol, 32%)[9] as a yellow oil and starting material (43 mg, 0.26 mmol, 56% BORSM) as a yellow oil.

*Mn(dpm)$_3$ **2**:* Conducted as per the general procedure on cyclohexilidene acetate (100 mg, 0.600 mmol). Purification by column chromatography (15% EtOAc/petroleum ether) afforded an inseparable mixture of alpha and beta hydroxy esters (3.7 : 1 alpha:beta, 76 mg, 0.41 mmol, 69%) as a yellow oil.

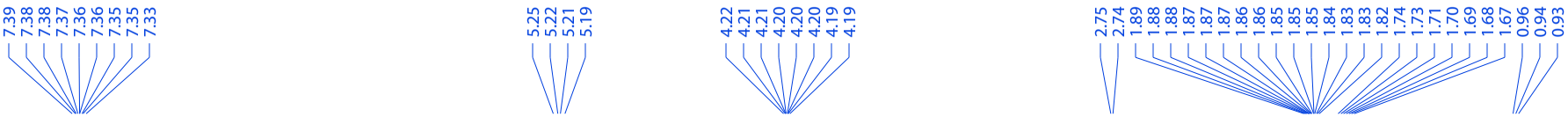
α-Hydroxy ester[10]: ^{1}H NMR (600 MHz; $CDCl_3$) *δ* 1.30 (t, *J* = 7.1 Hz, 4H),1.38-1.46 (m, 5H), 1.50-1.55 (m, 1H), 1.62-1.78 (m, 7H), 2.71 (d, *J* = 6.3 Hz, 1H), 3.99 (dd, *J* = 6.2, 3.5 Hz, 1H), 4.24 (qd, *J* = 7.1, 2.1 Hz, 2H).



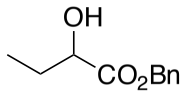
β-Hydroxy ester[11]: ^{1}H NMR (600 MHz; $CDCl_3$) *δ* 1.27 (t, *J* = 7.1 Hz, 4H), 1.38-1.46 (m, 5H), 1.50-1.55 (m, 1H), 1.62-1.78 (m, 7H), 2.46 (s, 2H), 3.42 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H).

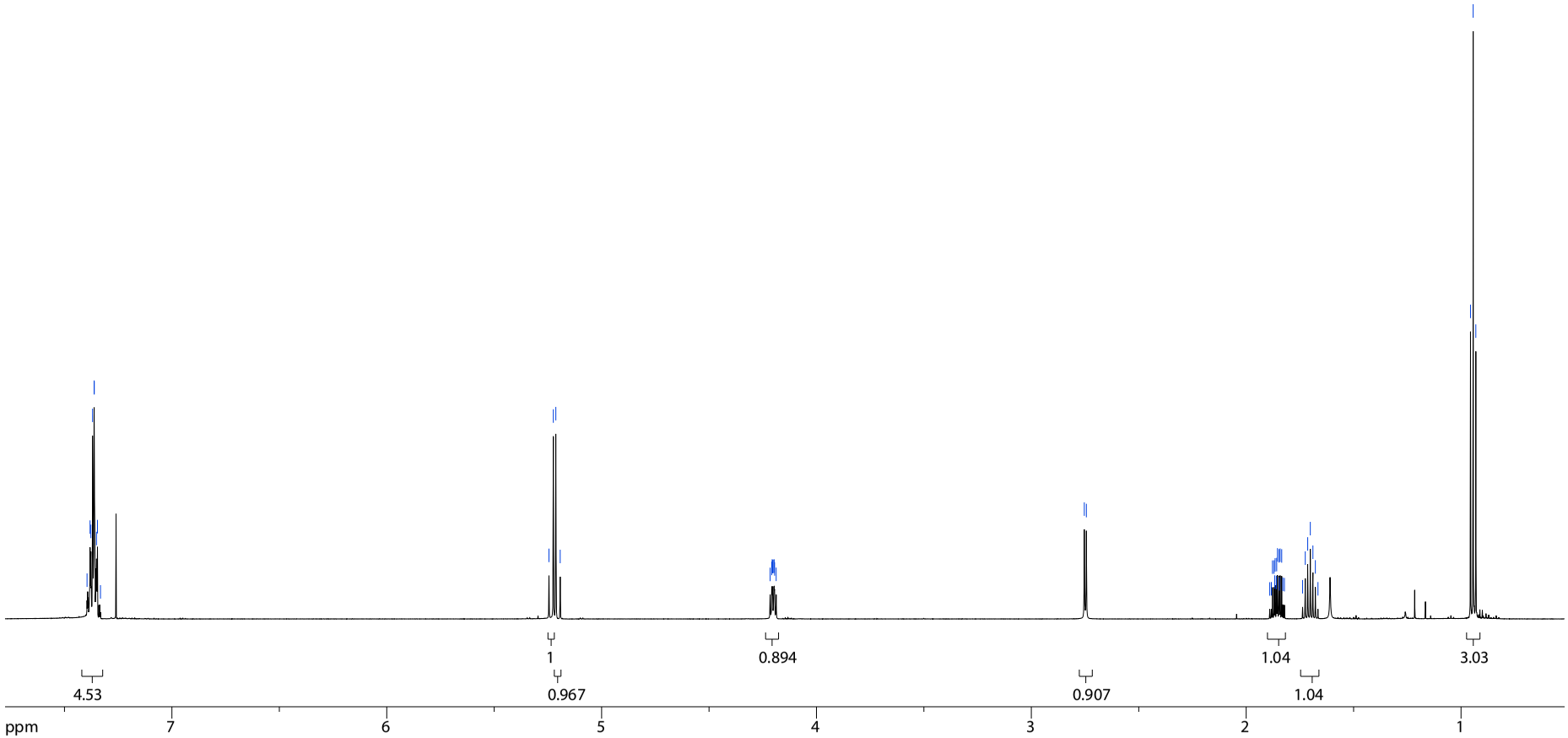


9. The reaction failed to go to completion with a catalyst loading to 50 mol%.
10. Lu, L. Q.; Li, Y.; Junge, K.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 8382.
11. Kaga, A.; Tnay, Y. L.; Chiba, S. *Org. Lett.* **2016**, *18*, 3506.

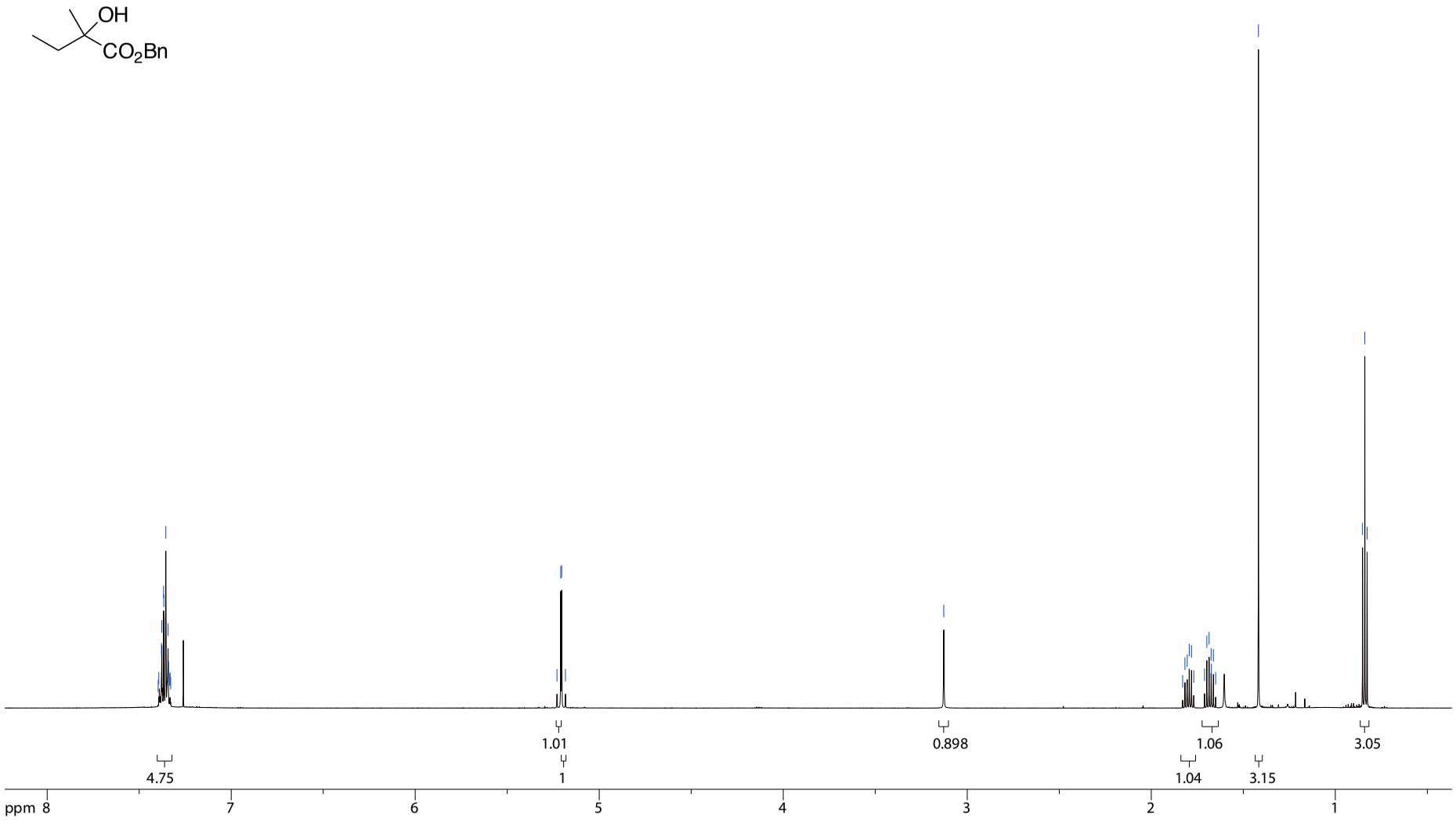


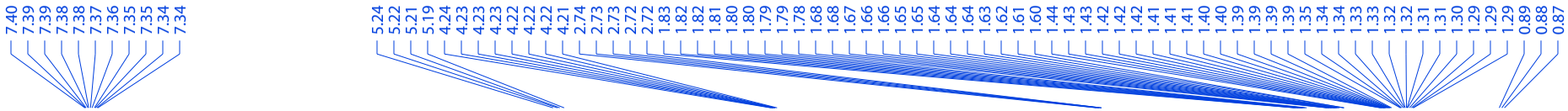
^{1}H NMR Spectrum (600 MHz, $CDCl_3$)



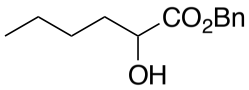


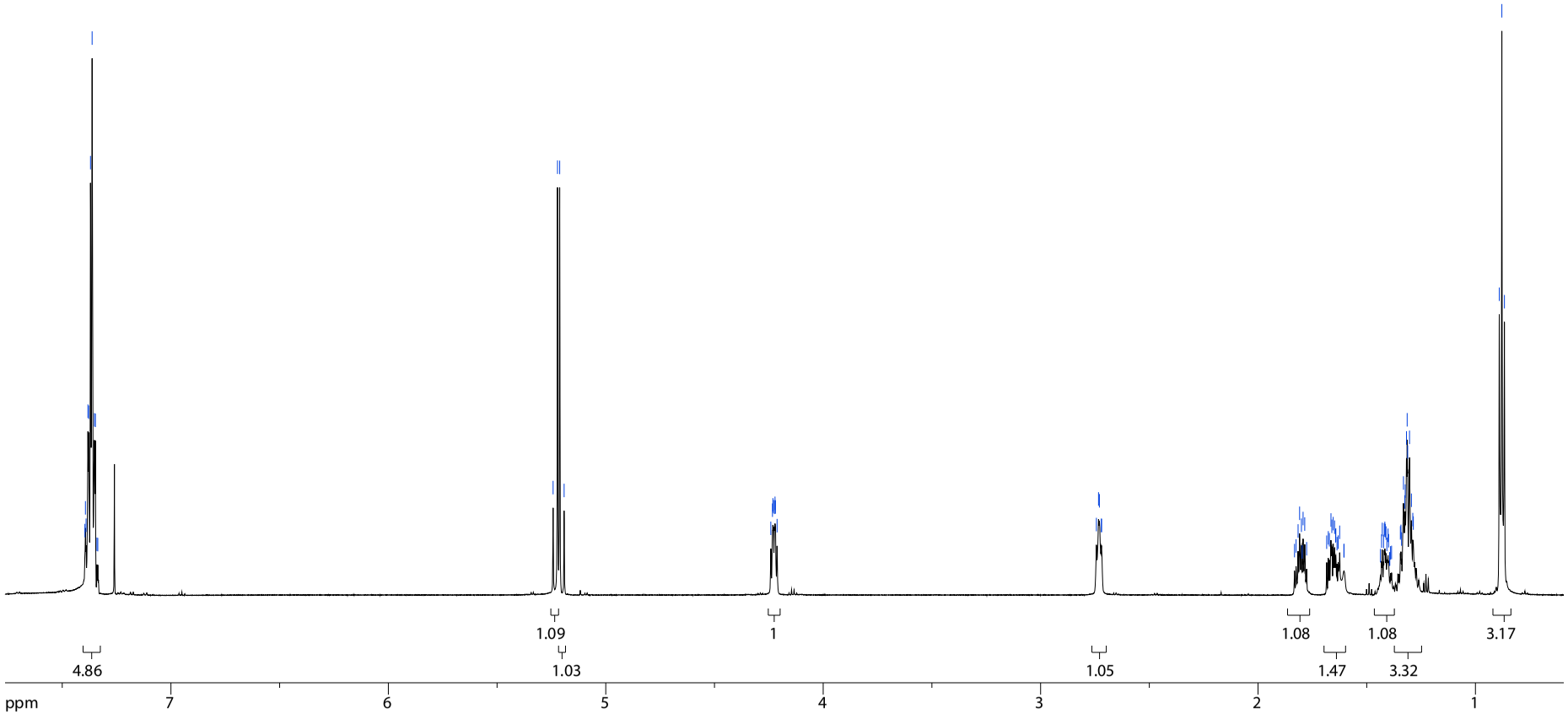
^{1}H NMR Spectrum (600 MHz, $CDCl_3$)

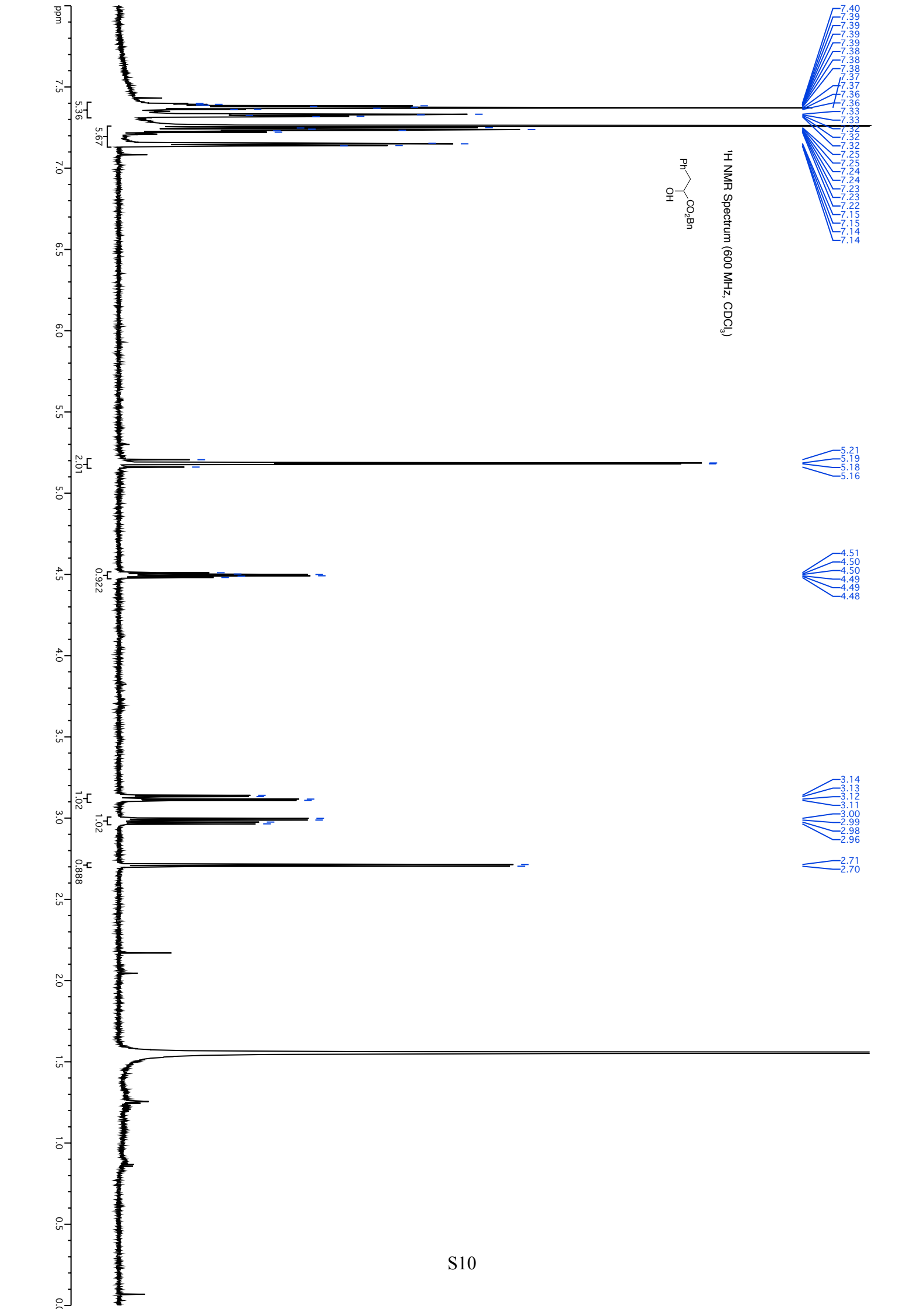


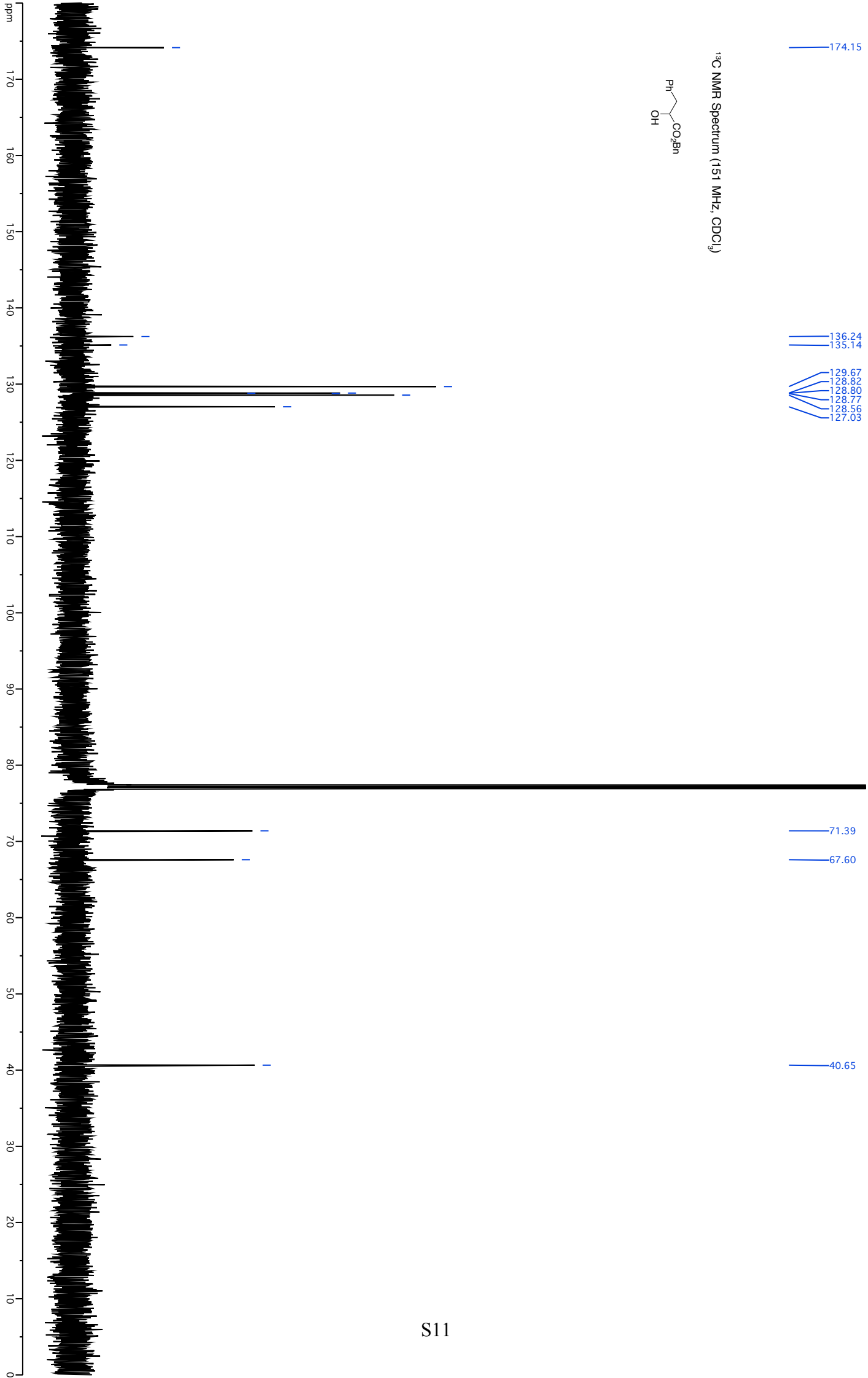


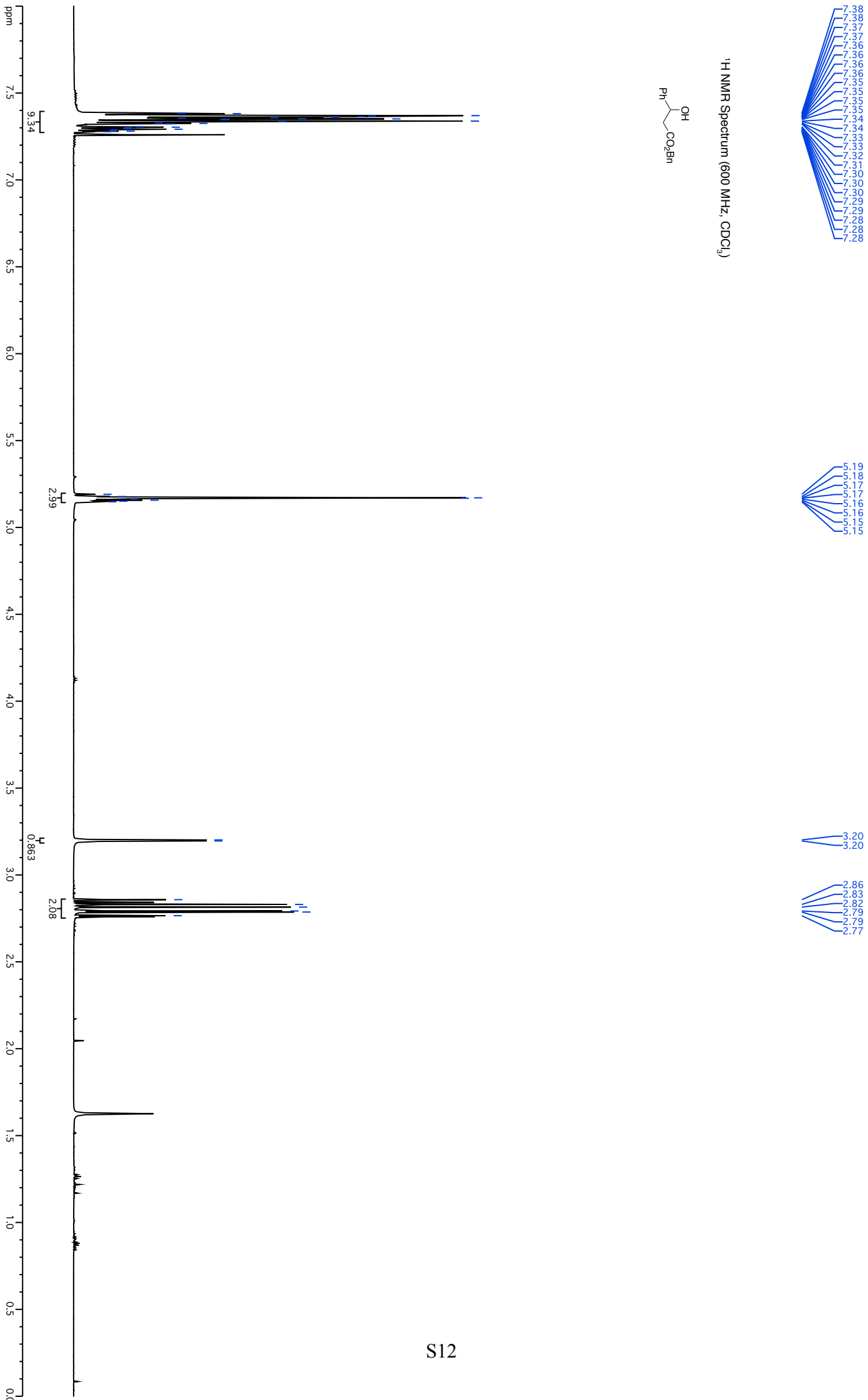
^{1}H NMR Spectrum (600 MHz, $CDCl_3$)

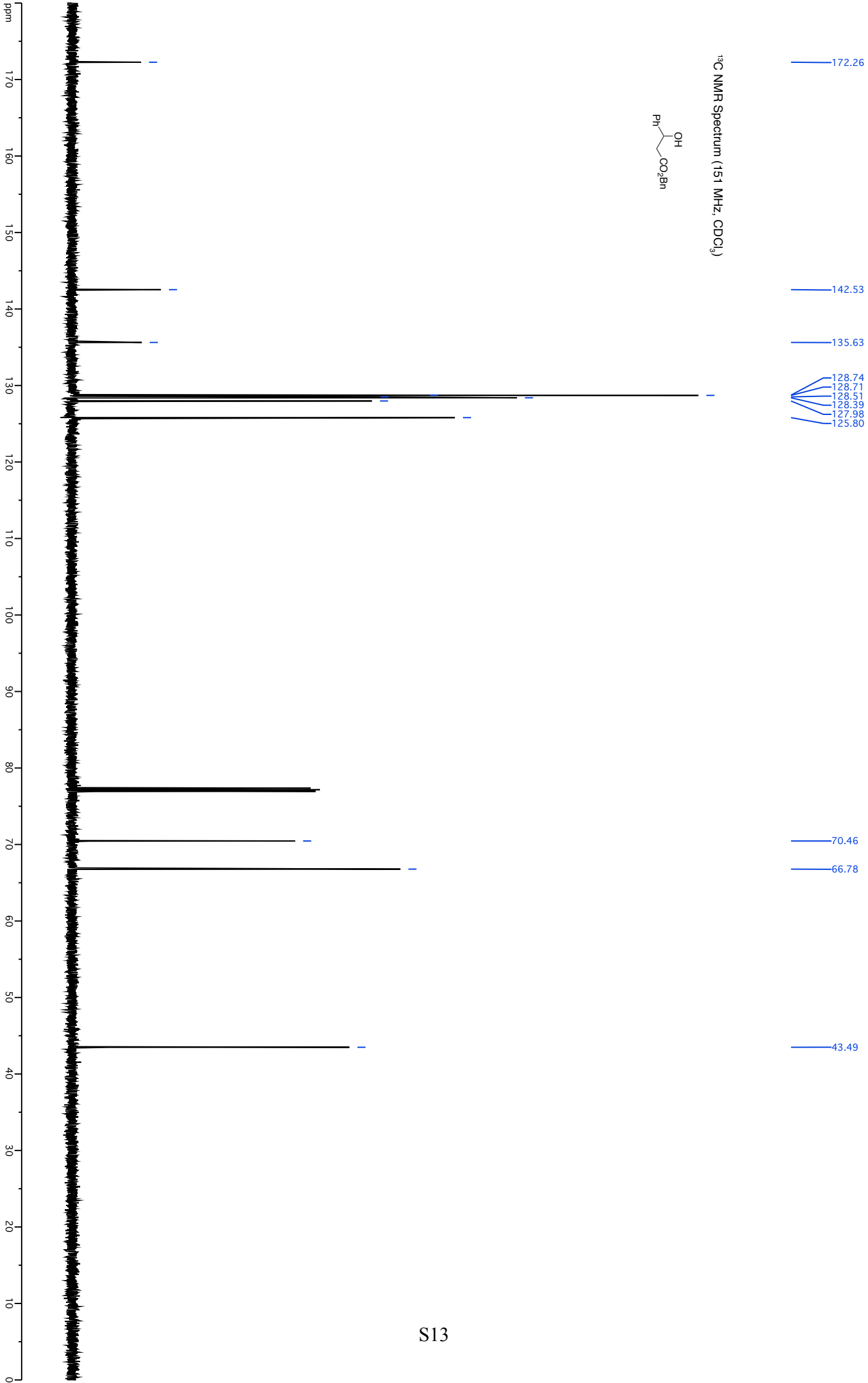


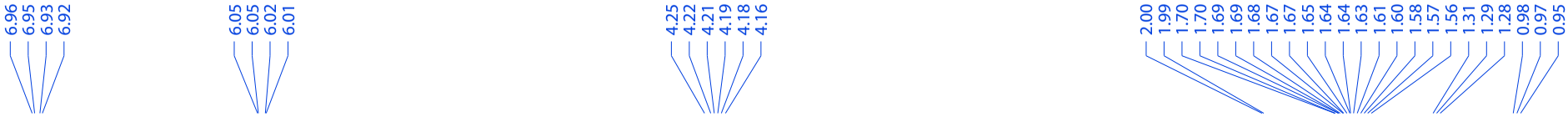



¹H NMR Spectrum (600 MHz, CDCl3)
Ph
OH
CO2Bn
7.40
7.39
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.33
7.33
7.32
7.32
7.32
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.15
7.15
7.14
7.14
5.21
5.19
5.18
5.16
4.51
4.50
4.50
4.49
4.49
4.48
3.14
3.13
3.12
3.11
3.00
2.99
2.98
2.96
2.71
2.70
5.36
5.67
2.01
0.922
1.02
1.02
0.888
ppm

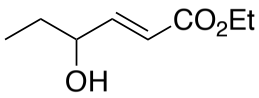

^{13}C NMR Spectrum (151 MHz, $CDCl_3$)
Ph
OH
CO_2Bn
174.15
136.24
135.14
129.67
128.82
128.80
128.77
128.56
127.03
71.39
67.60
40.65
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

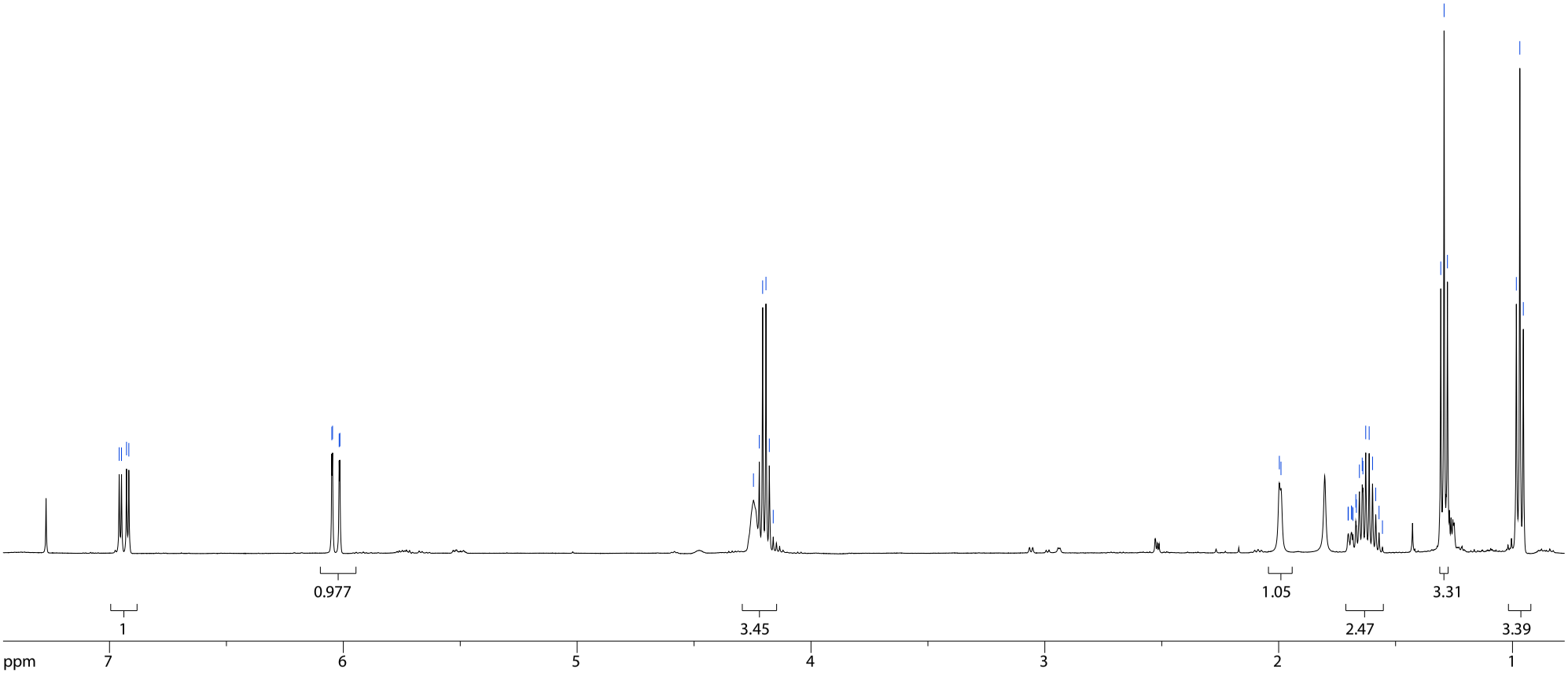

ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
9.34
2.99
0.863
2.08
OH
Ph
CO2Bn
1H NMR Spectrum (600 MHz, CDCl3)
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.36
7.35
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.30
7.29
7.29
7.28
7.28
7.28
5.19
5.18
5.17
5.17
5.16
5.16
5.15
5.15
3.20
3.20
2.86
2.83
2.82
2.79
2.79
2.77

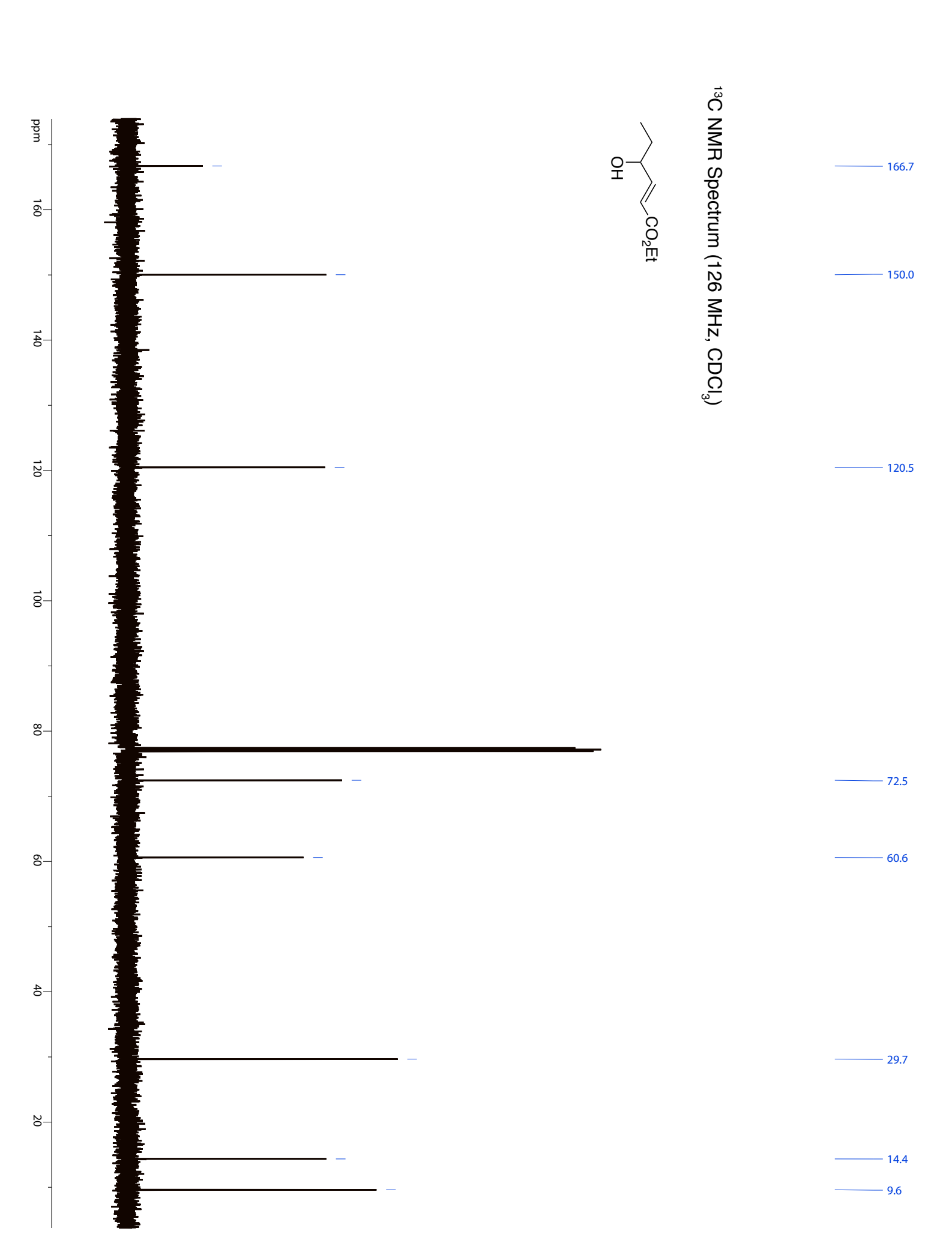

^{13}C NMR Spectrum (151 MHz, $CDCl_3$)
Ph
OH
CO_2Bn
172.26
142.53
135.63
128.74
128.71
128.51
128.39
127.98
125.80
70.46
66.78
43.49
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

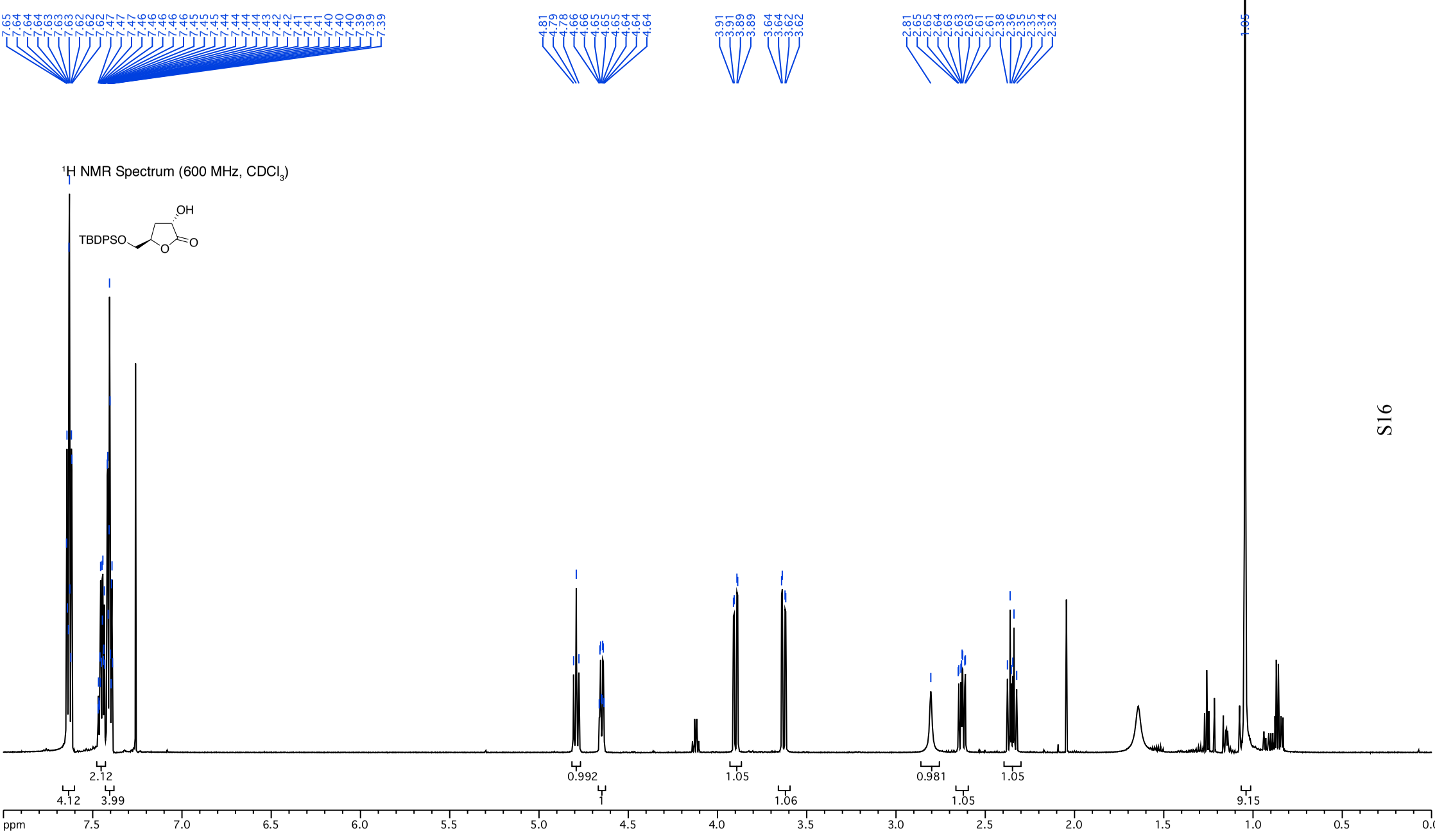


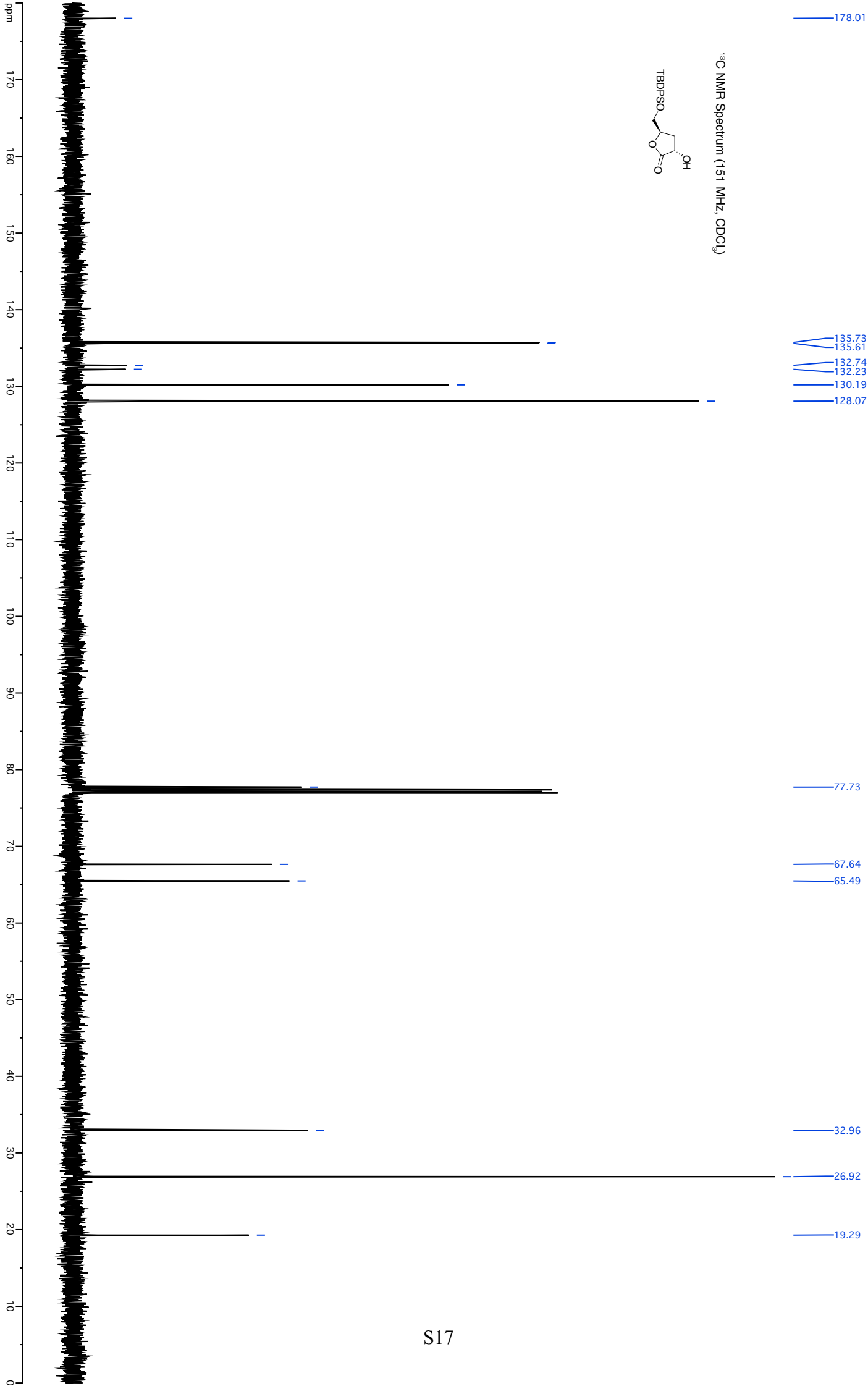
^{1}H NMR Spectrum (500 MHz, $CDCl_3$)

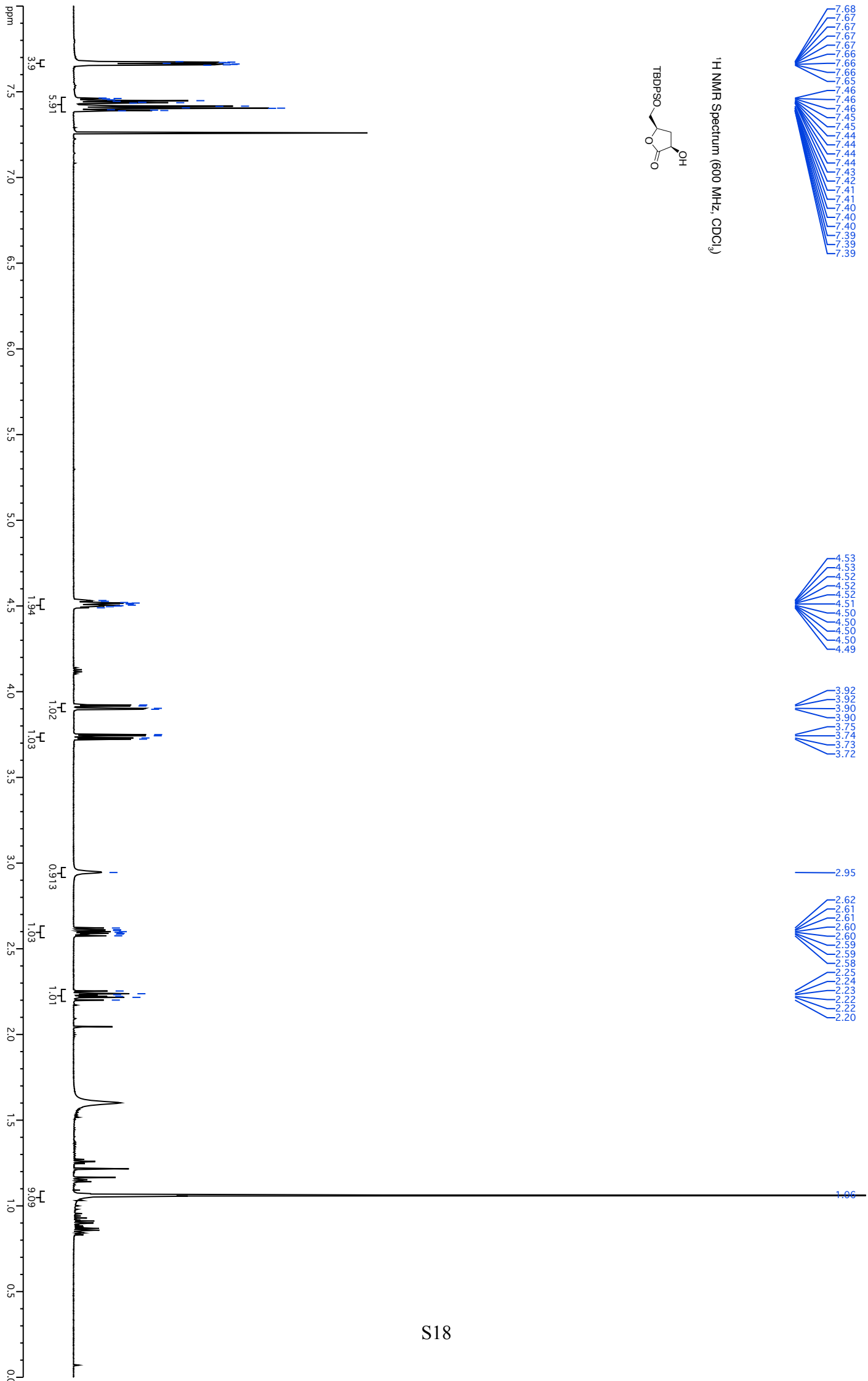


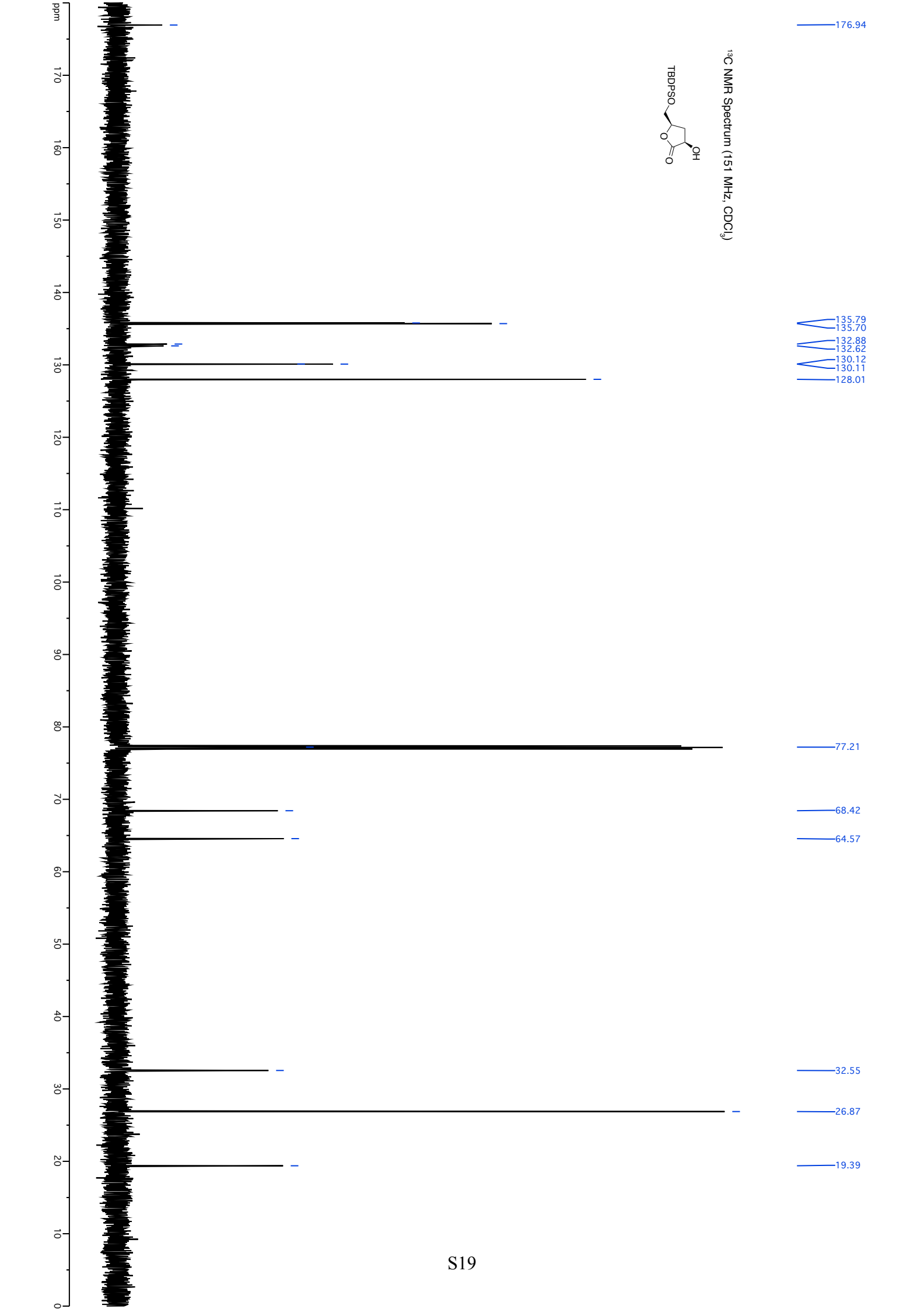


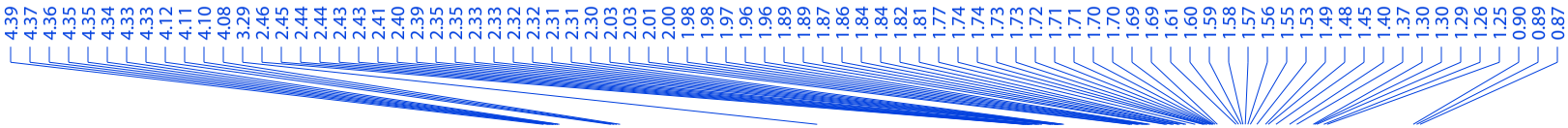

^{13}C NMR Spectrum (126 MHz, $CDCl_3$)
OH
CO_2Et
ppm
160
140
120
100
80
60
40
20
166.7
150.0
120.5
72.5
60.6
29.7
14.4
9.6


7.65 7.64 7.64 7.64 7.63 7.63 7.63 7.62 7.62 7.62 7.47 7.47 7.47 7.46 7.46 7.46 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39
4.81 4.79 4.78 4.66 4.66 4.65 4.65 4.64 4.64 4.64
3.91 3.91 3.89 3.89
3.64 3.64 3.62 3.62
2.81 2.65 2.65 2.64 2.63 2.63 2.63 2.61 2.61 2.38 2.36 2.35 2.34 2.32
1.05
^{1}H NMR Spectrum (600 MHz, $CDCl_3$)
OH
TBDPSO
O
O
2.12
0.992
1.05
0.981
1.05
4.12
3.99
1
1.06
1.05
9.15
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

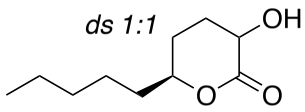

^{13}C NMR Spectrum (151 MHz, $CDCl_3$)
TBDPSO
OH
O
O
178.01
135.73
135.61
132.74
132.23
130.19
128.07
77.73
67.64
65.49
32.96
26.92
19.29
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

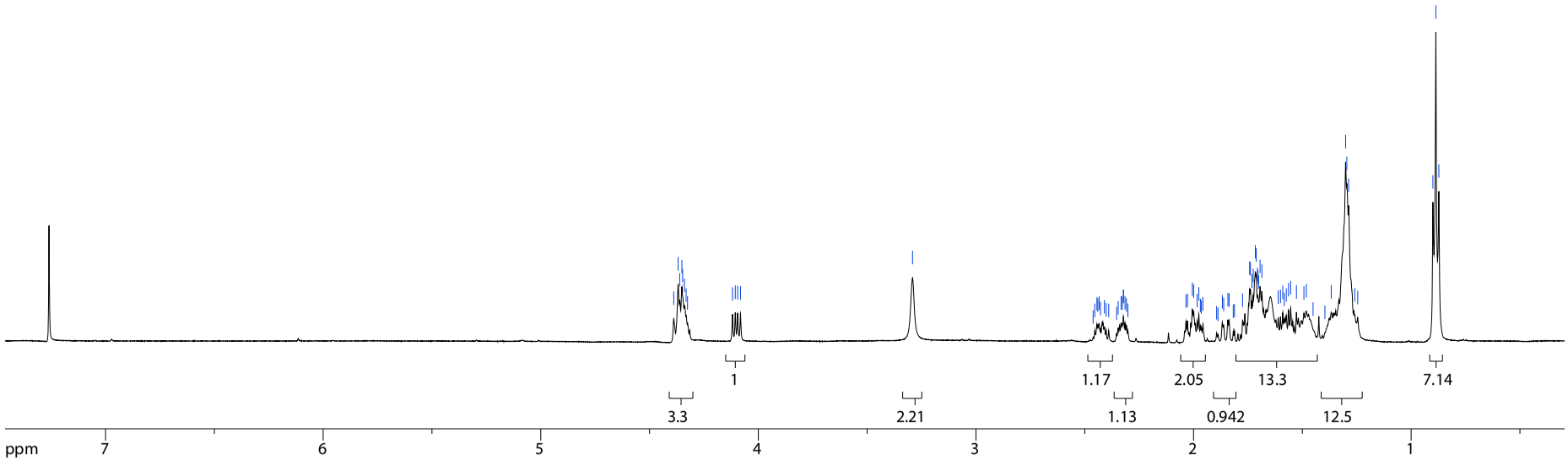

¹H NMR Spectrum (600 MHz, CDCl3)
TBDPSO
OH
O
O
7.68
7.67
7.67
7.67
7.67
7.66
7.66
7.66
7.65
7.46
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.39
4.53
4.53
4.52
4.52
4.52
4.51
4.50
4.50
4.50
4.50
4.49
3.92
3.92
3.90
3.90
3.75
3.74
3.73
3.72
2.95
2.62
2.61
2.61
2.60
2.60
2.59
2.59
2.58
2.25
2.24
2.23
2.22
2.22
2.20
1.06
3.9
5.91
1.94
1.02
1.03
0.913
1.03
1.01
9.09
ppm

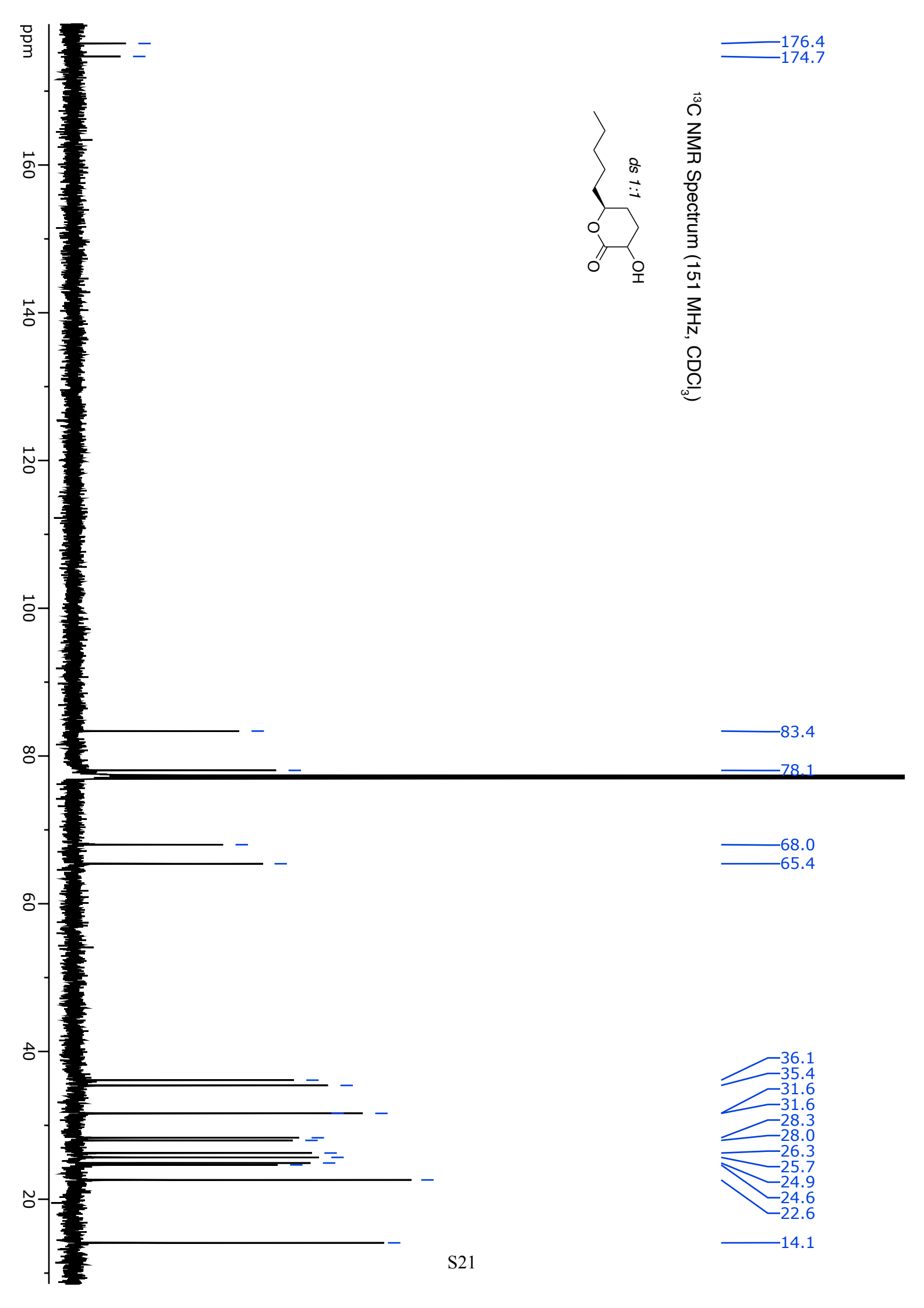

^{13}C NMR Spectrum (151 MHz, $CDCl_3$)
TBDPSO
OH
O
O
ppm
176.94
135.79
135.70
132.88
132.62
130.12
130.11
128.01
77.21
68.42
64.57
32.55
26.87
19.39

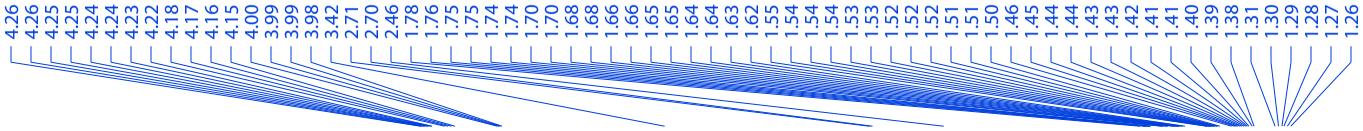


^{1}H NMR Spectrum (500 MHz, $CDCl_3$)






ppm
160
140
120
100
80
60
40
20
176.4
174.7
83.4
78.1
68.0
65.4
36.1
35.4
31.6
31.6
28.3
28.0
26.3
25.7
24.9
24.6
22.6
14.1
ds 1:1
O
O
OH
13C NMR Spectrum (151 MHz, CDCl3)



^{1}H NMR Spectrum (600 MHz, $CDCl_3$)