Supporting Information

$LiNTf_2$-*i*Pr_2NEt: A Catalyst for the Acylation of Phenols and Primary Alcohols with Carboxylic Anhydrides

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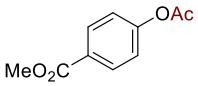
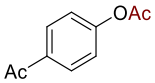
General Information. Unless otherwise stated, all the reagents and solvents were purchased and used as received without further purification. Anhydrous dichloromethane was of Extra Dry grade with molecular sieves (water ≤ 50 ppm). For reactions conducted at elevated temperatures, an oil bath was used as the heat source (silicone oil). Thin-layer chromatography analyses were performed on precoated GF254 silica gel plates and visualized under UV 254 nm light or by iodine staining. NMR spectra were recorded on a Bruker AVANCE-400 FT NMR spectrometer with TMS as internal standard. The melting points were uncorrected. PE = petroleum ether (60−90).

Methyl 4-Acetoxybenzoate (**2**). **General Procedure A**.



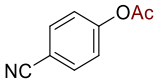
To a 100 mL round-bottom flask was added in sequence methyl 4-hydroxybenzoate (**1**, 0.152 g, 1 mmol), *i*Pr$_2$NEt (0.004 g, 0.03 mmol, 3 mol%), Ac$_2$O (0.153 g, 1.5 mmol, 1.5 equiv), LiNTf$_2$ (0.003 g, 0.01 mmol, 1 mol%), and DCM (2 mL). The mixture was stirring for 18 h at room temperature, then silica gel (100–200 mesh) was added, and the volatiles were removed by a rotary evaporator. *Note: extraction with EtOAc was unnecessary.* The residue was purified by column chromatography on silica gel (200−300 mesh, eluent: PE/EtOAc = 4:1, v/v) to afford **2** as a white solid; yield: 0.193 g (99%); mp 80−82 °C (lit.[1] 79−81 °C); R_f = 0.55 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.08 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H), 2.33 (s, 3H). Unless specified otherwise, the following compounds were prepared following this general procedure.

4-Acetylphenyl Acetate (**4a**)



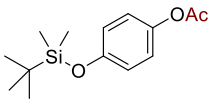
From 4-acetylphenol (**3a**, 0.136 g, 1 mmol); white solid; yield: 0.175 g (98%); mp 44−46 °C (lit.[2] 45−46 °C); R_f = 0.17 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.00 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 2.60 (s, 3H), 2.33 (s, 3H).

4-Cyanophenyl Acetate (**4b**)



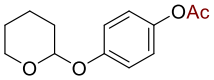
From 4-cyanophenol (**3b**, 0.119 g, 1 mmol); white solid; yield: 0.156 g (96%); mp 54−56 °C (lit.[2] 56−57 °C); R_f = 0.55 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.00 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 2.60 (s, 3H), 2.33 (s, 3H).

4-((*tert*-Butyldimethylsilyl)oxy)phenyl Acetate (**4c**)[3]



From 4-((*tert*-butyldimethylsilyl)oxy)phenol (**3c**, 0.224 g, 1 mmol); colorless liquid; yield: 0.263 g (98%); R_f = 0.56 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 6.93 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 2.27 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ: 169.8, 153.3, 144.6, 122.2, 120.5, 25.6, 21.1, 18.2, -4.5.

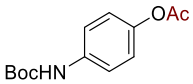
4-((Tetrahydro-2*H*-pyran-2-yl)oxy)phenyl Acetate (**4d**)[4]



From 4-((tetrahydro-2*H*-pyran-2-yl)oxy)phenol (**3d**, 0.194 g, 1 mmol); colorless liquid; yield: 0.219 g (92%); R_f = 0.58 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.05 (d, *J* = 9.2 Hz, 2H), 6.98 (d, *J* = 9.2 Hz, 2H), 5.37 (t, *J* = 3.2 Hz, 1H), 3.90 (ddd, J_1 = 11.4 Hz, J_2 = 9.5 Hz, J_3 = 3.1 Hz, 1H), 3.60 (dtd, J_1 = 11.4 Hz, J_2 = 4.1 Hz, J_3 = 1.5 Hz, 1H), 2.28 (s, 3H), 1.99 (ddtd, J_1 = 11.6 Hz, J_2 = 9.1 Hz, J_3 = 6.9 Hz, J_4 = 3.0 Hz, 1H), 1.85 (ddd, J_1 = 8.2 Hz, J_2 = 4.3 Hz, J_3 = 3.1 Hz, 2H), 1.74 – 1.59 (m, 3H). ^{13}C NMR (101 MHz, CDCl$_3$)

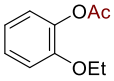
δ: 169.9, 154.8, 144.8, 122.2, 117.2, 96.7, 62.0, 30.4, 25.2, 21.1, 18.7.

4-((*tert*-Butoxycarbonyl)amino)phenyl Acetate (**4e**)[5]



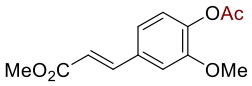
From 4-((*tert*-butoxycarbonyl)amino)phenol (**3e**, 0.209 g, 1 mmol); white solid; yield: 0.248 g (98%); mp 120 °C; R_f = 0.63 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.28 (d, J = 9.2 Hz, 2H), 7.29 (d, J = 9.1 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.7, 152.7, 146.0, 136.0, 122.0, 119.4, 80.7, 28.3, 21.1.

2-Ethoxyphenyl Acetate (**4f**)[6]



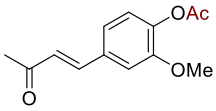
From 2-ethoxyphenol (**3f**, 0.138 g, 1 mmol); colorless liquid; yield: 0.146 g (81%); R_f = 0.41 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (ddd, J_1 = 8.2 Hz, J_2 = 7.4 Hz, J_3 = 1.7 Hz, 1H), 7.03 (dd, J_1 = 7.8 Hz, J_2 = 1.7 Hz, 1H), 6.96 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.93 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 4.05 (q, J = 7.0 Hz, 2H), 2.31 (s, 3H), 1.39 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.1, 150.5, 140.1, 126.8, 122.7, 120.7, 113.5, 64.3, 20.6, 14.8.

Methyl (*E*)-3-(4-Acetoxy-3-methoxyphenyl)acrylate (**4g**)



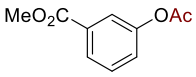
From methyl ferulate (**3g**, 0.208 g, 1 mmol); white solid; yield: 0.249 g (99%); mp 118−120 °C (lit.[7] 118.5–119.5 °C); R_f = 0.41 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, J = 16.0 Hz, 1H), 7.12 (dd, J_1 = 8.1 Hz, J_2 = 1.9 Hz, 1H), 7.10 (d, J = 1.8 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.39 (d, J = 16.0 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.33 (s, 3H).

(*E*)-2-Methoxy-4-(3-oxobut-1-en-1-yl)phenyl Acetate (**4h**)



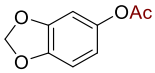
From vanillylidenacetone (**3h**, 0.192 g, 1 mmol); white solid; yield: 0.226 g (96%); mp 111−113 °C (lit.[8] 115–116 °C); R_f = 0.65 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J = 16.2 Hz, 1H), 7.14 (d, J = 8.6 Hz, 1H), 7.13 (s, 1H), 7.06 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 16.3 Hz, 1H), 3.87 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H).

Methyl 3-Acetoxybenzoate (**4i**)



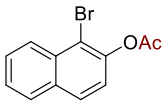
From methyl 3-hydroxybenzoate (**3i**, 0.152 g, 1 mmol); yield: 0.188 g (96%); mp 48−50 °C (lit.[9] 29 °C); R_f = 0.31 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (dt, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.46 (t, J = 7.9 Hz, 1H), 7.29 (ddd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, J_3 = 1.1 Hz, 1H), 3.92 (s, 3H), 2.32 (s, 3H).

Benzo[*d*][1,3]dioxol-5-yl Acetate (**4j**)[10]



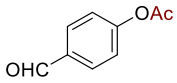
From 3,4-methylendioxyphenol (**3j**, 0.138 g, 1 mmol); colorless liquid; yield: 0.169 g (93%); R_f = 0.41 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.77 (d, J = 8.4 Hz, 1H), 6.60 (d, J = 2.3 Hz, 1H), 6.52 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H), 5.98 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.8, 148.0, 145.4, 145.0, 113.9, 108.0, 103.7, 101.7, 21.0.

1-Bromonaphthalen-2-yl Acetate (**4k**)[11]



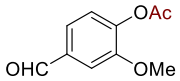
From 1-bromonaphthalen-2-ol (**3k**, 0.223 g, 1 mmol); viscous oil; yield: 0.257 g (96%); R_f = 0.57 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.6 Hz, 1H), 7.84 (dd, J_1 = 8.5 Hz, J_2 = 4.7 Hz, 2H), 7.62 (ddd, J_1 = 8.4 Hz, J_2 = 6.9 Hz, J_3 = 1.3 Hz, 1H), 7.53 (ddd, J_1 = 8.1 Hz, J_2 = 6.9 Hz, J_3 = 1.2 Hz, 1H), 7.26 (d, J = 8.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.8, 146.4, 132.7, 132.5, 128.9, 128.2, 127.9, 127.0, 126.4, 121.9, 115.1, 20.9.

4-Formylphenyl Acetate (**4l**)[12]



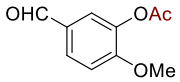
From 4-formylphenol (**3l**, 0.122 g, 1 mmol); colorless liquid; yield: 0.151 g (92%); R_f = 0.65 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.99 (s, 1H), 7.93 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.9, 168.7, 155.4, 134.0, 131.2, 122.4, 21.2. This compound is unstable and undergoes oxidation rapidly even at room temperature.

4-Formyl-2-methoxyphenyl Acetate (**4m**)



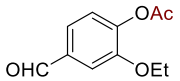
From vanillin (**3m**, 0.152 g, 1 mmol); white solid; yield: 0.182 g (93%); mp 74−76 °C (lit.[13] 74−76 °C); R_f = 0.49 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.95 (s, 1H), 7.50 (d, J = 1.8 Hz, 1H), 7.48 (dd, J_1 = 7.9 Hz, J_2 = 1.8 Hz, 1H), 7.22 (d, J = 7.9 Hz, 1H), 3.91 (s, 3H), 2.35 (s, 3H).

5-Formyl-2-methoxyphenyl Acetate (**4n**)



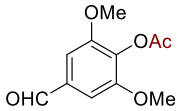
From isovanillin (**3n**, 0.152 g, 1 mmol); white solid; yield: 0.187 g (96%); mp 84−85.5 °C (lit.[14] 84−86 °C); R_f = 0.30 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.87 (s, 1H), 7.77 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.59 (d, J = 2.1 Hz, 1H), 7.08 (d, J = 8.5 Hz, 1H), 3.93 (s, 3H), 2.34 (s, 3H).

2-Ethoxy4-formyl-phenyl Acetate (**4o**)



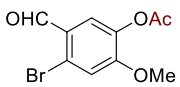
From ethylvanillin (**3o**, 0.166 g, 1 mmol); white solid; yield: 0.199 g (95%); mp 42−44 °C (lit.[15] 48−49 °C); R_f = 0.53 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.93 (s, 1H), 7.47 (d, J = 1.6 Hz 1H), 7.46 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 4.13 (q, J = 7.0 Hz, 2H), 2.34 (s, 3H), 1.42 (t, J = 7.0 Hz, 3H).

4-Formyl-2,6-dimethoxyphenyl Acetate (**4p**)



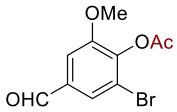
From 4-hydroxy-3,5-dimethoxybenzaldehyde (**3p**, 0.182 g, 1 mmol); white solid; yield: 0.222 g (99%); mp 112−114 °C (lit.[16] 116−117 °C); R_f = 0.46 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.91 (s, 1H), 7.15 (s, 2H), 3.90 (s, 6H), 2.36 (s, 3H).

4-Bromo-5-formyl-2-methoxyphenyl Acetate (**4q**)



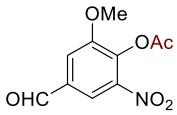
From 2-bromo-5-hydroxy-4-methoxybenzaldehyde (**3q**, 0.231 g, 1 mmol); white solid; yield: 0.175 g (64%); mp 102−104 °C (lit.[17] 106−107 °C); R_f = 0.36 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.18 (s, 1H), 7.63 (s, 1H), 7.17 (s, 1H), 3.92 (s, 3H), 2.32 (s, 3H).

2-Bromo-4-formyl-6-methoxyphenyl Acetate (**4r**)



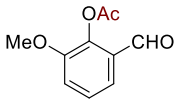
From 5-bromovanillin (**3r**, 0.231 g, 1 mmol); white solid; yield: 0.269 g (98%); mp 81−83 °C (lit[18]. 84 °C); R_f = 0.51 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.89 (s, 1H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 1H), 3.91 (s, 3H), 2.39 (s, 3H).

4-Formyl-2-methoxy-6-nitrophenyl Acetate (**4s**)



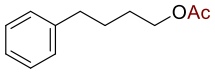
From 5-nitrovanillin (**3s**, 0.197 g, 1 mmol); white solid; yield: 0.201 g (84%); mp 94.5−96.5 °C (lit.[19] 88 °C); R_f = 0.28 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.99 (s, 1H), 8.12 – 8.09 (m, 1H), 7.74 – 7.71 (m, 1H), 3.99 (s, 3H), 2.41 (s, 3H).

2-Formyl-6-methoxyphenyl Acetate (**4t**)



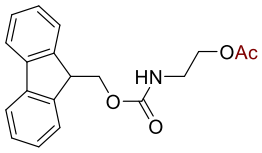
From *o*-vanillin (**3t**, 0.152 g, 1 mmol); white solid; yield: 0.191 g (98%); mp 73−75 °C (lit.[20] 75−77 °C); R_f = 0.36 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.13 (s, 1H), 7.46 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.22 (dd, J_1 = 8.2 Hz, J_2 = 1.5 Hz, 1H), 3.88 (s, 3H), 2.40 (s, 3H).

4-Phenylbutyl Acetate (**4u**)[21]



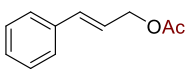
From 4-phenylbutan-1-ol (**3u**, 0.150 g, 1 mmol); colorless liquid; yield: 0.181 g (94%); R_f = 0.72 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 3H), 4.08 (t, *J* = 6.2 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.72 – 1.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.2, 142.0, 128.4, 128.3, 125.8, 64.4, 35.5, 28.2, 27.7, 21.0.

2-((((9*H*-Fluoren-9-yl)methoxy)carbonyl)amino)ethyl Acetate (**4v**)[22]



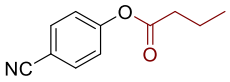
From (9*H*-fluoren-9-yl)methyl (2-hydroxyethyl)carbamate (**3v**, 0.283 g, 1 mmol); white solid; mp 120−121 °C; yield: 0.316 g (97%); R_f = 0.72 (PE/EtOAc = 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ *anti*-**4v** : 7.77 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 2H), 5.04 (br s, 1H), 4.43 (d, *J* = 6.9 Hz, 2H), 4.22 (t, *J* = 6.9 Hz, 1H), 4.15 (t, *J* = 5.3 Hz, 2H), 3.47 (q, *J* = 5.6 Hz, 2H), 2.08 (s, 3H); *syn*-**4v**: 7.77 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (td, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 2H), 4.76 (br s, 1H), 4.46 (br s, 2H), 4.22 (t, *J* = 6.9 Hz, 1H), 3.99 (br s, 2H), 3.34 (br s, 2H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.0, 156.3, 143.9, 141.3, 127.7, 127.1, 125.0, 120.0, 66.8, 63.4, 47.2, 40.2, 20.9.

Cinnamyl Acetate (**4w**)[23]



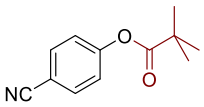
From cinnamyl alcohol (**3w**, 0.134 g, 1 mmol), DTBMP (0.012 g, 0.06 mml, 0.06 equiv), Ac_2O (0.153 g, 1.5 mmol, 1.5 equiv), and $LiNTf_2$ (0.006 g, 0.02 mmol, 0.02 equiv); colorless oil; yield: 0.164 g (93%); R_f = 0.77 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (d, J = 7.0 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.26 (tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 6.66 (d, J = 15.9 Hz, 1H), 6.29 (dt, J_1 = 15.9 Hz, J_2 = 6.4 Hz, 1H), 4.73 (dd, J_1 = 6.5 Hz, J_2 = 1.3 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.9, 136.2, 134.2, 128.6, 128.1, 126.6, 123.2, 65.1, 21.0.

4-Cyanophenyl Butyrate (**4x**)



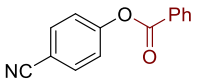
From **3b** (0.119 g, 1 mmol) and (nPrCO)$_2$O (0.227 g, 1.5 mmol, 1.5 equiv); colorless liquid, solidified after standing overnight at bench; yield: 0.188 g (99%); mp 32−34 °C (lit.[2] 32−33 °C); R_f = 0.40 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.8 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 2.57 (t, J = 7.4 Hz, 2H), 1.79 (h, J = 7.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 171.3, 154.0, 133.7, 122.8, 118.3, 109.6, 36.1, 18.3, 13.6.

4-Cyanophenyl Pivalate (**4y**)



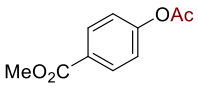
From **3b** (0.119 g, 1 mmol) and Piv_2O (0.279 g, 1.5 mmol, 1.5 equiv); white solid; yield: 0.146 g (71%); mp 32−34 °C (lit.[2] 32−33 °C); R_f = 0.40 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 1.36 (s, 9H).

4-Cyanophenyl Benzoate (**4z**)



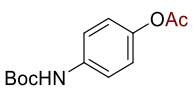
From **3b** (0.119 g, 1 mmol) and Bz_2O (0.339 g, 1.5 mmol, 1.5 equiv); white solid; yield: 0.195 g (87%); mp 91−93 °C (lit.[24] 90−91.8 °C); R_f = 0.34 (PE/EtOAc = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (d, J = 7.4 Hz, 2H), 7.75 (d, J = 8.7 Hz, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H).

Methyl 4-Acetoxybenzoate (**2**). **General Procedure B**.



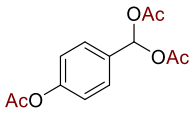
To a 100 mL round-bottom flask was added Ac_2O (0.153 g, 1.5 mmol, 1.5 equiv), methyl 4-hydroxybenzoate (**1**, 0.152 g, 1 mmol), $Cu(NTf_2)_2$ (0.006 g, 0.01 mmol, 1 mol%), and DCM (1.5 mL) in sequence. After stirring for 18 h at room temperature, silica gel (100–200 mesh) was added, and the volatiles were removed by a rotary evaporator. *Note: extraction with EtOAc was unnecessary.* The residue was purified by column chromatography on silica gel (200−300 mesh, eluent: PE/EtOAc = 4:1, v/v) to afford **2** as a white solid, yield: 0.189 g (97%). Unless specified otherwise, the following compounds were prepared following this general procedure, and the characterization data of the following products match those prepared following General Procedure A.

4-((*tert*-Butoxycarbonyl)amino)phenyl Acetate (**4e**)[5]



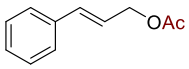
From 4-((*tert*-butoxycarbonyl)amino)phenol (**3e**, 0.209 g, 1 mmol); white solid; yield: 0.099 g (39%).

(4-Acetoxyphenyl)methylene Diacetate (**4l'**)



From 4-hydroxybenzaldehyde (**3l**, 0.122 g, 1 mmol) and Ac_2O (0.510 g, 5 mmol, 5 equiv); white solid; yield: 0.146 g (54%); mp 91−93 °C (lit.[25] 90−92 °C); R_f = 0.47 (PE/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 2.31 (s, 3H), 2.12 (s, 6H).

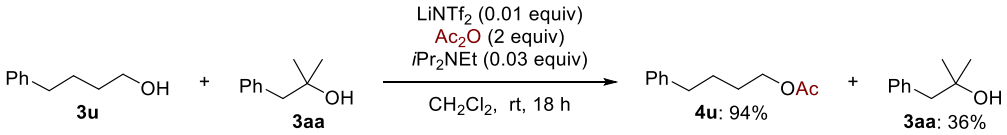
Cinnamyl Acetate (**4w**)[23]



From cinnamyl alcohol (**3w**, 0.134 g, 1 mmol) and $Mn(NTf_2)_2$ (0.006 g, 0.01 mmol, 1 mol%) in neat Ac_2O (0.153 g, 1.5 mmol) for 10 minutes at room temperature. Then Al_2O_3 was added to the reaction mixture, followed by purification with column chromatography on silica gel (200–300 mesh, eluent: PE/EtOAc = 10:1, v/v); colorless oil; yield: 0.159 g (90%).

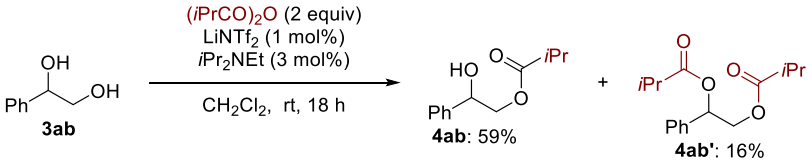
Chemoselective Acylation

4-Phenylbutyl Acetate (**4u**)



A mixture of **3u** (0.151 g, 1 mmol) and **3aa** (0.150 g, 1 mmol, 1 equiv) was treated with $LiNTf_2$ (0.003 g, 0.01 mmol, 1 mol%), *i*Pr_2NEt (0.004 g, 0.03 mmol, 3 mol%), and Ac_2O (0.204 g, 2 mmol, 2 equiv) following General Procedure A to afford **4u**; yield: 0.182 g (94%). Unreacted **3aa** was recovered (0.055 g, 36%). The poor recovery of **3aa** was seemingly due to decomposition.

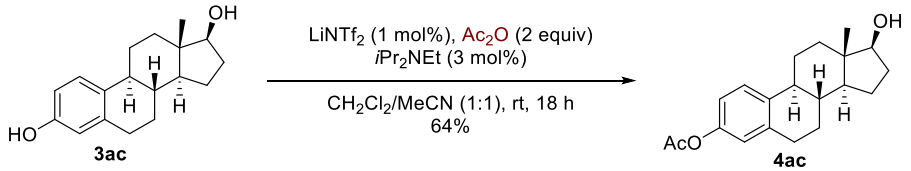
2-Hydroxy-2-phenylethyl isobutyrate (**4ab**)[26]



1-Phenylethane-1,2-diol (**3ab**, 0.138 g, 1 mmol) was treated with $LiNTf_2$ (0.003 g, 0.01 mmol, 1 mol%), *i*Pr_2NEt (0.004 g, 0.03 mmol, 3 mol%), and $(iPr_2CO)_2O$ (0.316 g, 2 mmol, 2 equiv) following General Procedure A to afford **4ab** as a colorless oil, yield: 0.124 g (59%); R_f = 0.46 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 – 7.29 (m, 5H), 4.97 (dd, J_1 = 8.2 Hz, J_2 = 3.5 Hz, 1H), 4.29 (dd, J_1 = 11.6 Hz, J_2 = 3.5 Hz, 1H), 4.18 (dd, J_1 = 11.6 Hz, J_2 = 8.2 Hz, 1H), 2.60 (hept, *J* = 7.1 Hz, 2H), 1.176 (d, *J* = 6.8 Hz, 3H), 1.173 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 177.4, 139.8, 128.6, 128.2, 126.2, 72.5, 69.2, 33.9, 19.0, 19.0.

1-Phenylethane-1,2-diyl Diisobutyrate (**4ab'**)[26] was obtained as a by-product during the preparation of **4ab**; colorless oil; yield: 0.046 g (16%); R_f = 0.75 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 – 7.28 (m, 5H), 6.03 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 1H), 4.35 – 4.26 (m, 2H), 2.62 (hept, *J* = 7.0 Hz, 1H), 2.54 (hept, *J* = 7.0 Hz, 1H),1.20 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.143 (dd, *J* = 7.1, 3H), 1.139 (dd, *J* = 7.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.6, 176.0, 136.8, 128.6, 128.5, 126.6, 73.0, 66.0, 34.1, 33.9, 19.0, 18.9, 18.9.

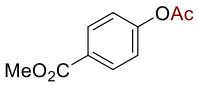
Estrodiol Acetate (**4ac**)



Estrogen (**3ac**, 0.272 g, 1 mmol) was treated with $LiNTf_2$ (0.003 g, 0.01 mmol, 1 mol%), *i*Pr_2NEt (0.004 g, 0.03 mmol, 3 mol%), and Ac_2O (0.153 g, 1.5 mmol, 1.5 equiv) in anhydrous dichloromethane (5 mL) and anhydrous MeCN (5 mL) following General Procedure A to afford **4ac** as a white solid; yield: 0.203 g (64%); mp 138−140 °C (lit.[27] 135−136 °C); R_f = 0.32 (PE/EtOAc = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29 (d, J = 8.4 Hz, 1H), 6.84 (dd, J_1 = 8.5 Hz, J_2 = 2.6 Hz, 1H), 6.79 (d, J = 2.6 Hz, 1H), 3.73 (td, J_1 = 8.5 Hz, J_2 = 4.3 Hz, 1H), 2.86 (dt, J_1 = 7.3 Hz, J_2 = 4.7 Hz, 2H), 2.38– 2.26 (m, 1H), 2.28 (s, 3H), 2.26 – 2.17 (m, 1H), 2.12 (dtd, J_1 = 12.8 Hz, J_2 = 9.3 Hz, J_3 = 5.4 Hz, 1H), 1.95 (ddd, J_1 = 12.6 Hz, J_2 = 3.9 Hz, J_3 = 2.6 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.76 – 1.64 (m, 1H), 1.56 – 1.13 (m, 8H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.9, 148.4, 138.3, 138.0, 126.4, 121.5, 118.6, 81.9, 50.0, 44.1, 43.2, 38.4, 36.7, 30.6, 29.5, 27.0, 26.1, 23.1, 21.1, 11.0.

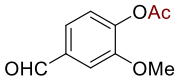
Gram-scale Preparations

Methyl 4-Acetoxybenzoate (**2**)



From **1** (1.521 g, 10 mmol), *i*Pr_2NEt (0.038 g, 0.3 mml, 3 mol%), Ac_2O (1.530 g, 15 mmol, 1.5 equiv), and $LiNTf_2$ (0.029 g, 0.1 mmol, 1 mol%) in CH_2Cl_2 (20 mL), following General Procedure B; yield: 1.905 g (98%).

4-Formyl-2-methoxyphenyl Acetate (**4m**)



From **3m** (1.521 g, 10 mmol), *i*Pr_2NEt (0.038 g, 0.3 mml, 3 mol%), Ac_2O (1.530 g, 15 mmol, 1.5 equiv) and $LiNTf_2$ (0.029 g, 0.1 mmol, 1 mol%) in CH_2Cl_2 (20 mL), following General Procedure B; yield: 1.753 g (90%).

References

(1) Yamamoto, Y. The First General and Selective Palladium(II)-Catalyzed Alkoxycarbonylation of Arylboronates: Interplay among Benzoquinone-Ligated Palladium(0) Complex, Organoboron, and Alcohol Solvent. *Adv. Synth. Catal.* **2010**, *352*, 478-492.

(2) Koh, H. J.; Kim, S. I.; Lee, B. C.; Lee, I. Kinetics and mechanism of aminolysis of phenyl acetates and phenyl trimethylacetates in dimethyl sulfoxide. *J. Chem. Soc. Perkin Trans. 2* **1996**, 1353-1357.

(3) Xu, Z.-Y.; Xu, D.-Q.; Liu, B.-Y.; Luo, S.-P. An Effective Approach for the Silylation of Hydroxyl Compounds in Room Temperature Ionic Liquids. *Synth. Commun.* **2006**, *33*, 4143-4149.

(4) Ouedraogo, A.; Lessard, J. The conformational behaviour of 2-aryloxytetrahydropyrans and 2-acetoxytetrahydropyran, and barrier to ring inversion. *Can. J. Chem.* **1991**, *69*, 474-480.

(5) Kobayashi, S.; Yamaguchi, R.; Yamamoto, F.; Komori, J.; Sakamoto, H.; Kasashima, T.; Adriaenssens, L.; Lear, M. J. One-Pot Conversion of Benzyl Alcohols to N-Protected Anilines and Alkyl Alcohols to Carbamoyl Azides. *Eur. J. Org. Chem.* **2023**, *26*, e202300786.

(6) Wang, H.; Li, Y.; Liu, S.; Makha, M.; Bai, J.-F.; Li, Y. CO2-Promoted Direct Acylation of Amines and Phenols by the Activation of Inert Thioacid Salts. *ChemSusChem* **2022**, *15*, e202200227.

(7) Aoki, T.; Takagi, K.; Hirata, T.; Suga, T. Two naturally occurring acyclic diterpene and norditerpene aldehydes from Tetragonia tetragonoides. *Phytochemistry* **1982**, *21*, 1361-1363.

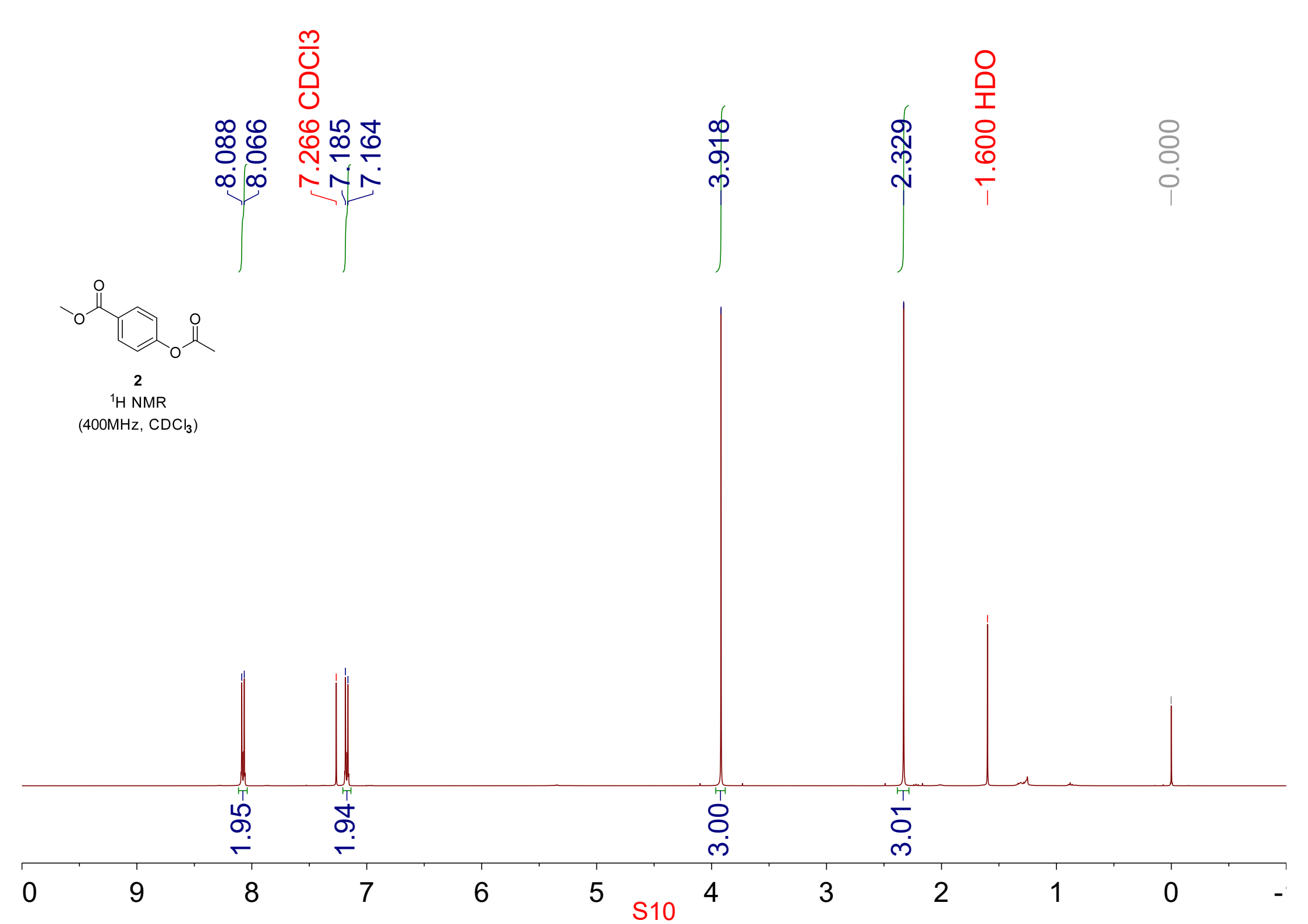
(8) Elias, G.; Rao, M. N. A. Synthesis and anti-inflammatory activity of substituted (E)-4-phenyl-3-buten-2-ones. *Eur. J. Med. Chem.* **1988**, *23*, 379-380.

(9) Anschütz, R.; Aschenberg, H.; Kuckertz, H.; Krone, F.; Riepenkröger, K.; Zerbe, C. Über die wechselseitige Umlagerung der isomeren O- und N-Acoyl-salicylsäure-amide, sowie über die Konstitution der Acoyl-salicoylimid-salze. *Justus Liebigs Ann. Chem.* **1925**, *442*, 18-46.

(10) Kumar, M.; Bagchi, S.; Sharma, A. The first vinyl acetate mediated organocatalytic transesterification of phenols: a step towards sustainability. *New J. Chem.* **2015**, *39*, 8329-8336.

(11) Fort, A. W. Reactions of Some Organic Compounds with Cupric Bromide. *J. Org. Chem.* **1961**, *26*, 765-767.

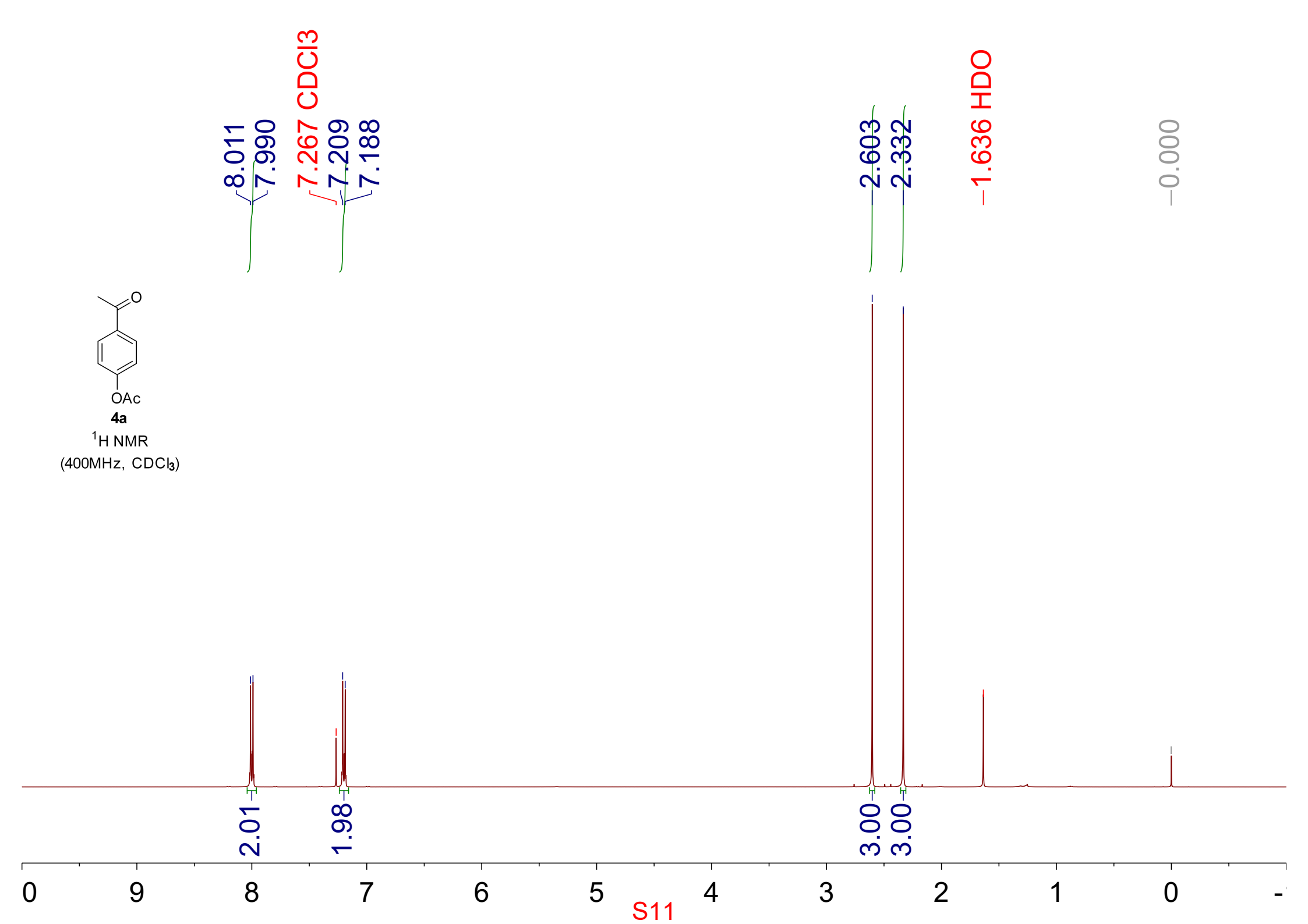
(12) Pathania, V.; Roy, S. R. Phenalenyl-Based Photocatalyst for Bioinspired Oxidative Dehydrogenation of N-Heterocycles and Benzyl Alcohols. *J. Org. Chem.* **2024**, *89*, 4145-4155.
(13) Ahamad, J.; Khan, F. A. Biomimetic total syntheses of renifolin F and antiarone K. *Org. Biomol. Chem.* **2024**, *22*, 4877-4881.
(14) Khan, F. A.; Hussain, M. A. Total Synthesis of (±)-Cassumunins A–C and Curcumin Analogues. *Synthesis* **2020**, *52*, 1561-1575.
(15) King, H. 255. Synthesis of diphenyl ethers containing methoxy- and ethoxy-groups. *J. Chem. Soc.* **1939**, 1165-1168.
(16) Pettit, G. R.; Minardi, M. D.; Hogan, F.; Price, P. M. An Efficient Synthetic Strategy for Obtaining 4-Methoxy Carbon Isotope Labeled Combretastatin A-4 Phosphate and Other Z-Combretastatins. *J. Nat. Prod.* **2009**, *73*, 399-403.
(17) Raiford, L. C.; Ravely, M. F. ACTION OF BROMINE ON VANILLIN, ISOVANILLIN, AND SOME OF THEIR DERIVATIVES, AND MODIFICATION OF THE DIRECTIVE INFLUENCE OF HYDROXYL IN THESE COMPOUNDS. *J. Org. Chem.* **1940**, *05*, 204-211.
(18) Cartwright, N. J.; Haworth, R. D. 147. The constituents of natural phenolic resins. Part XIX. The oxidation of ferulic acid. *J. Chem. Soc.* **1944**.
(19) Vogl, W. Zur Kenntniss des Nitrovanillins. *Monatsh. Chem.* **1901**, *20*, 383-400.
(20) Wu, K.; Song, C.; Cui, D.-M.; Zhang, C. Synthesis of SMND-309, a derivate of salvianolic acid B. *Synth. Commun.* **2017**, *47*, 1387-1391.
(21) Lu, P.; Hou, T.; Gu, X.; Li, P. Visible-light-promoted conversion of alkyl benzyl ether to alkyl ester or alcohol via O-α-sp^3 C-H cleavage. *Org. Lett.* **2015**, *17*, 1954-1957.
(22) Chaubey, S. A.; Mishra, R. Synthesis of task-specific imidazolium ionic liquid as an efficient catalyst in acetylation of alcohols, phenols, and amines. *Chem. Pap.* **2020**, *74*, 3259-3268.
(23) Chakraborti, A. K.; Shivani, S. Magnesium bistrifluoromethanesulfonimide as a new and efficient acylation catalyst. *J. Org. Chem.* **2006**, *71*, 5785-5788.
(24) Zhao, Z.; Li, W.; Shan, Q.; Young, D. J.; Ren, Z.-G.; Li, H.-X. Visible-Light-Induced Synthesis of Esters via a Self-Propagating Radical Reaction. *J. Org. Chem.* **2025**, *90*, 1616-1627.
(25) Zhang, F.; Liu, H.; Zhang, Q.-J.; Zhao, Y.-F.; Yang, F.-L. Silica Phosphoric Acid: An Efficient and Recyclable Catalyst for the Solvent-Free Synthesis of Acylals and Their Deprotection in MeOH. *Synth. Commun.* **2010**, *40*, 3240-3250.
(26) Toda, Y.; Sakamoto, T.; Komiyama, Y.; Kikuchi, A.; Suga, H. A Phosphonium Ylide as an Ionic Nucleophilic Catalyst for Primary Hydroxyl Group Selective Acylation of Diols. *ACS Catal.* **2017**, *7*, 6150-6154.
(27) Grob, C. A.; Goldberg, W. A. Versuche zur Herstellung künstlicher Komplexantigene der Steroidreihe. 2. Mitteilung. Weitere Steroidester der 4-Amino-2-sulfo-benzoesäure. *Helv. Chim. Acta* **2004**, *32*, 184-190.

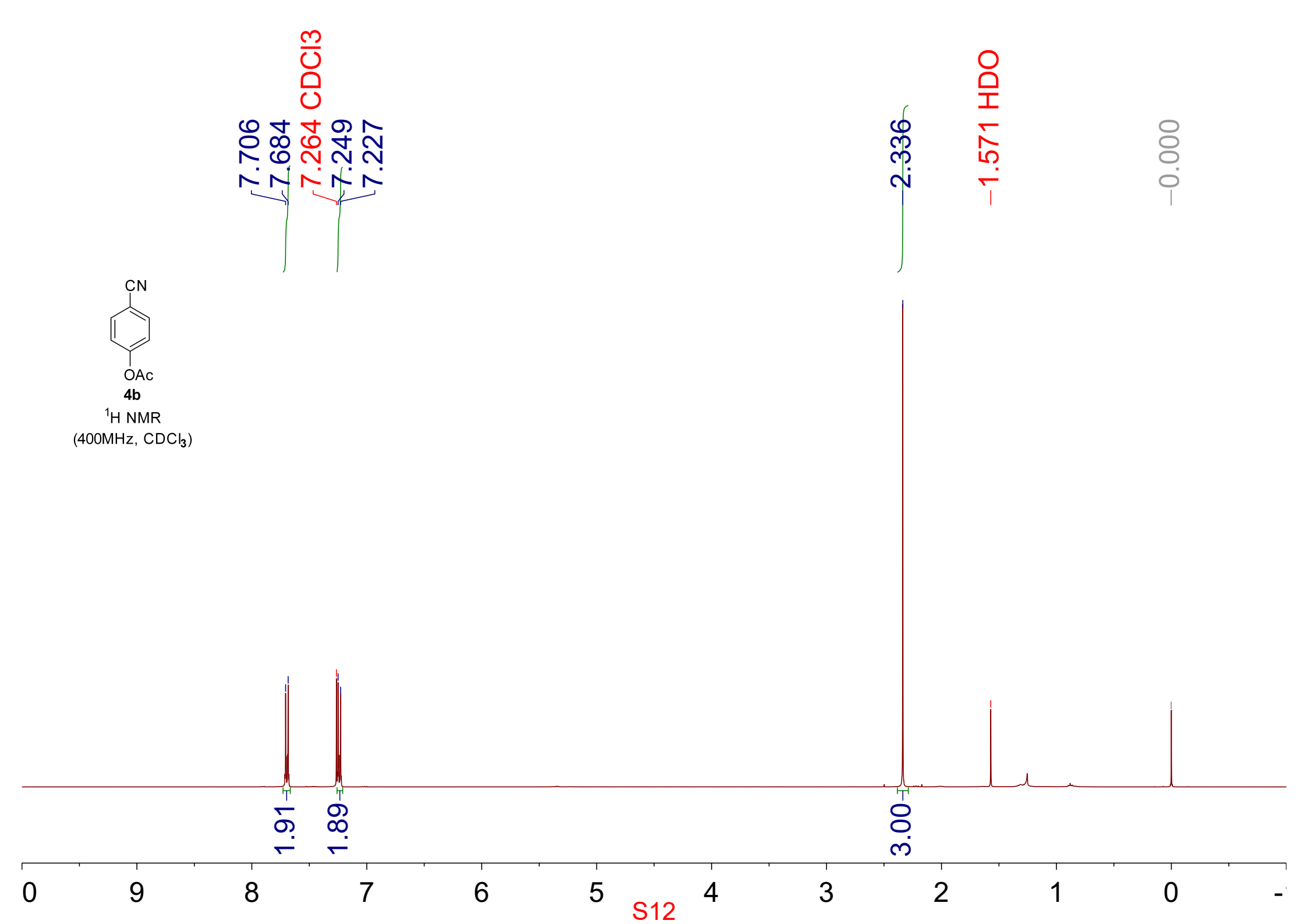


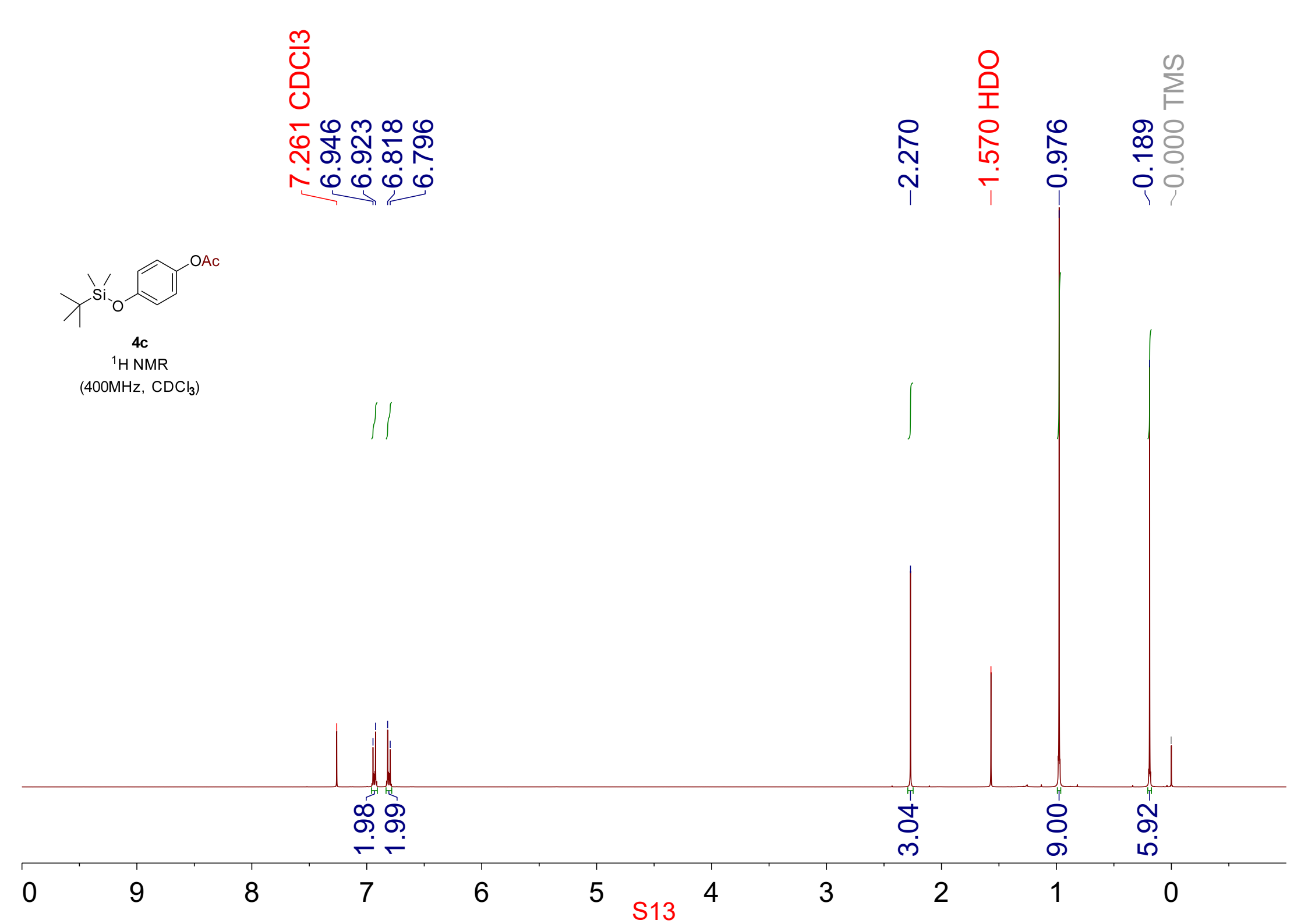
2

^{1}H NMR

(400MHz, $CDCl_3$)


8.011
7.990
7.267 CDCl3
7.209
7.188
2.603
2.332
1.636 HDO
0.000
O
OAc
4a
1H NMR
(400MHz, CDCl3)
2.01
1.98
3.00
3.00
0
9
8
7
6
5
4
3
2
1
0
-


7.706
7.684
7.264 CDCl3
7.249
7.227
2.336
1.571 HDO
0.000
CN
OAc
4b
1H NMR
(400MHz, CDCl3)
1.91
1.89
3.00
0
9
8
7
6
5
4
3
2
1
0
-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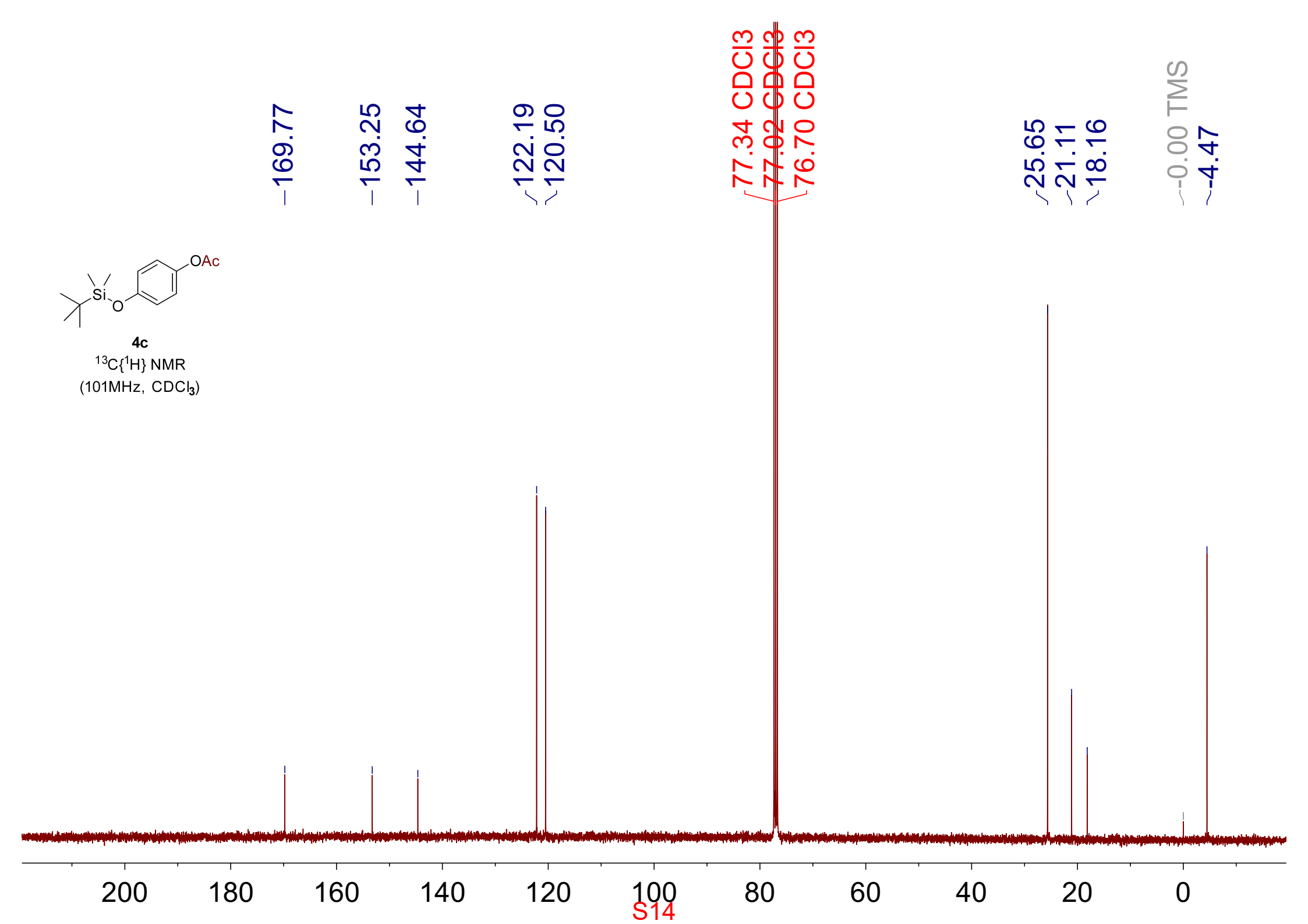
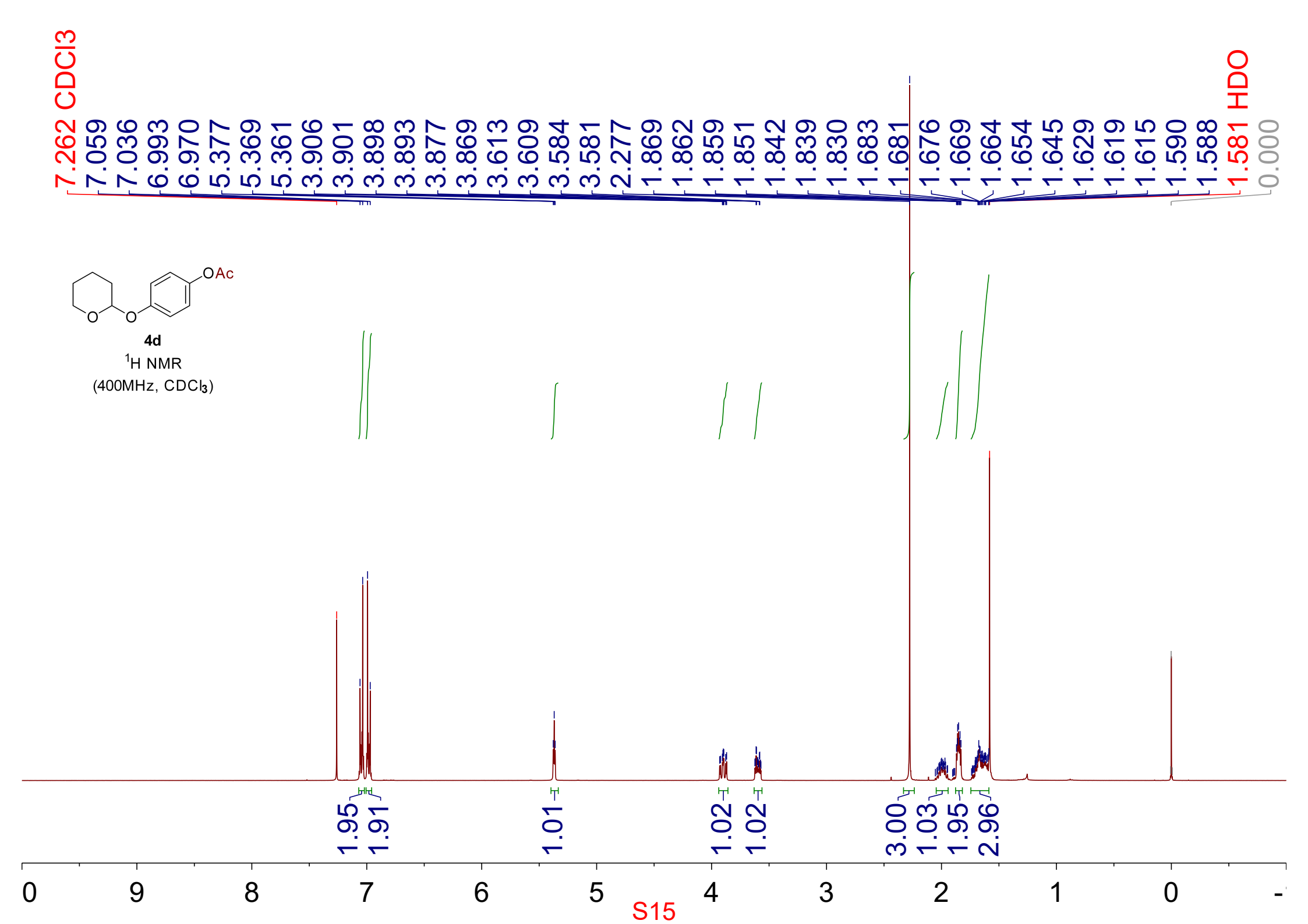
6.946
6.923
6.818
6.796
2.270
1.570 HDO
0.976
0.189
0.000 TMS
OAc
Si
O
4c
1H NMR
(400MHz, CDCl3)
1.98
1.99
3.04
9.00
5.92
0
9
8
7
6
5
4
3
2
1
0


169.77
153.25
144.64
122.19
120.50
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
25.65
21.11
18.16
-0.00 TMS
-4.47
OAc
Si
O
4c
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0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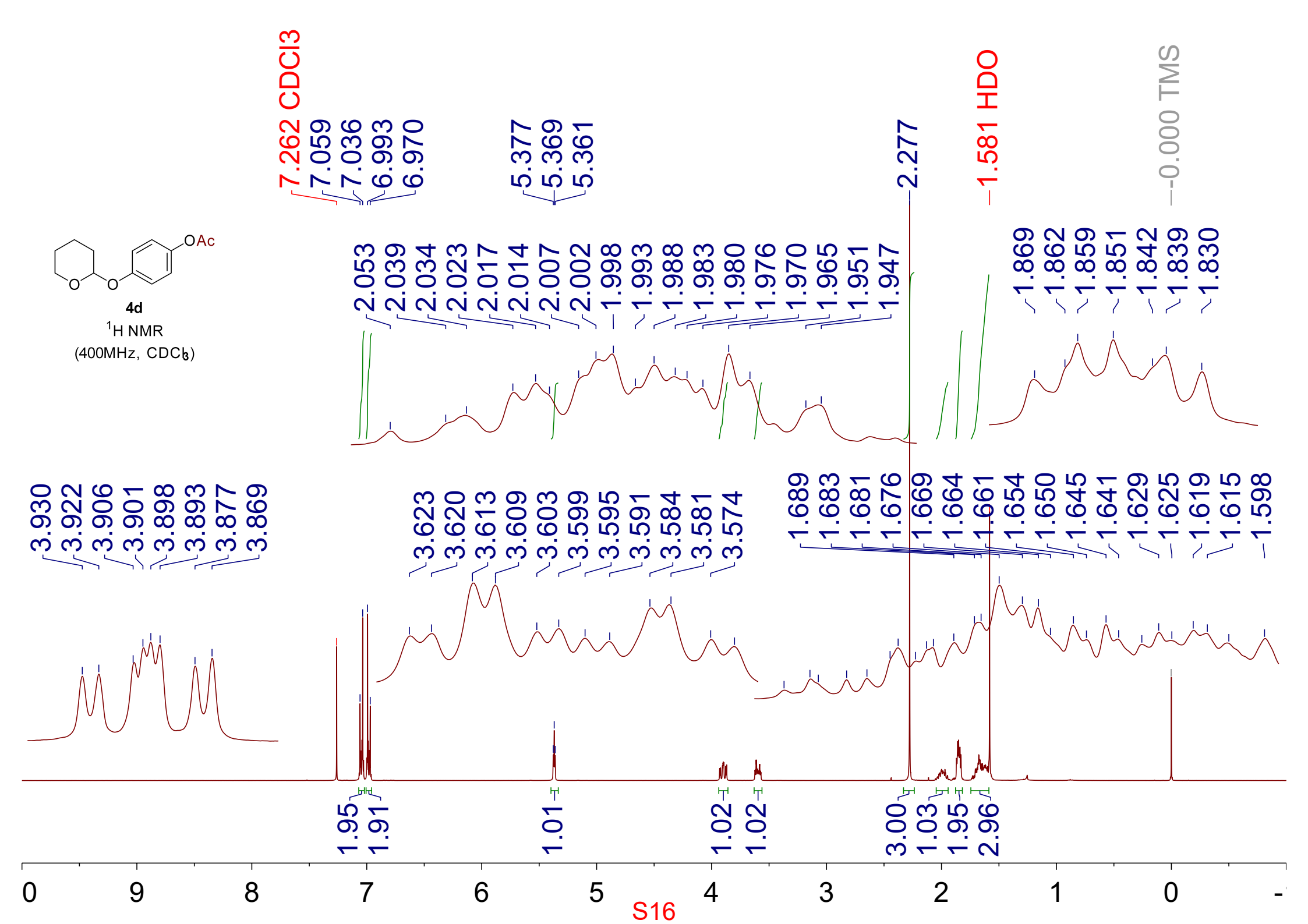
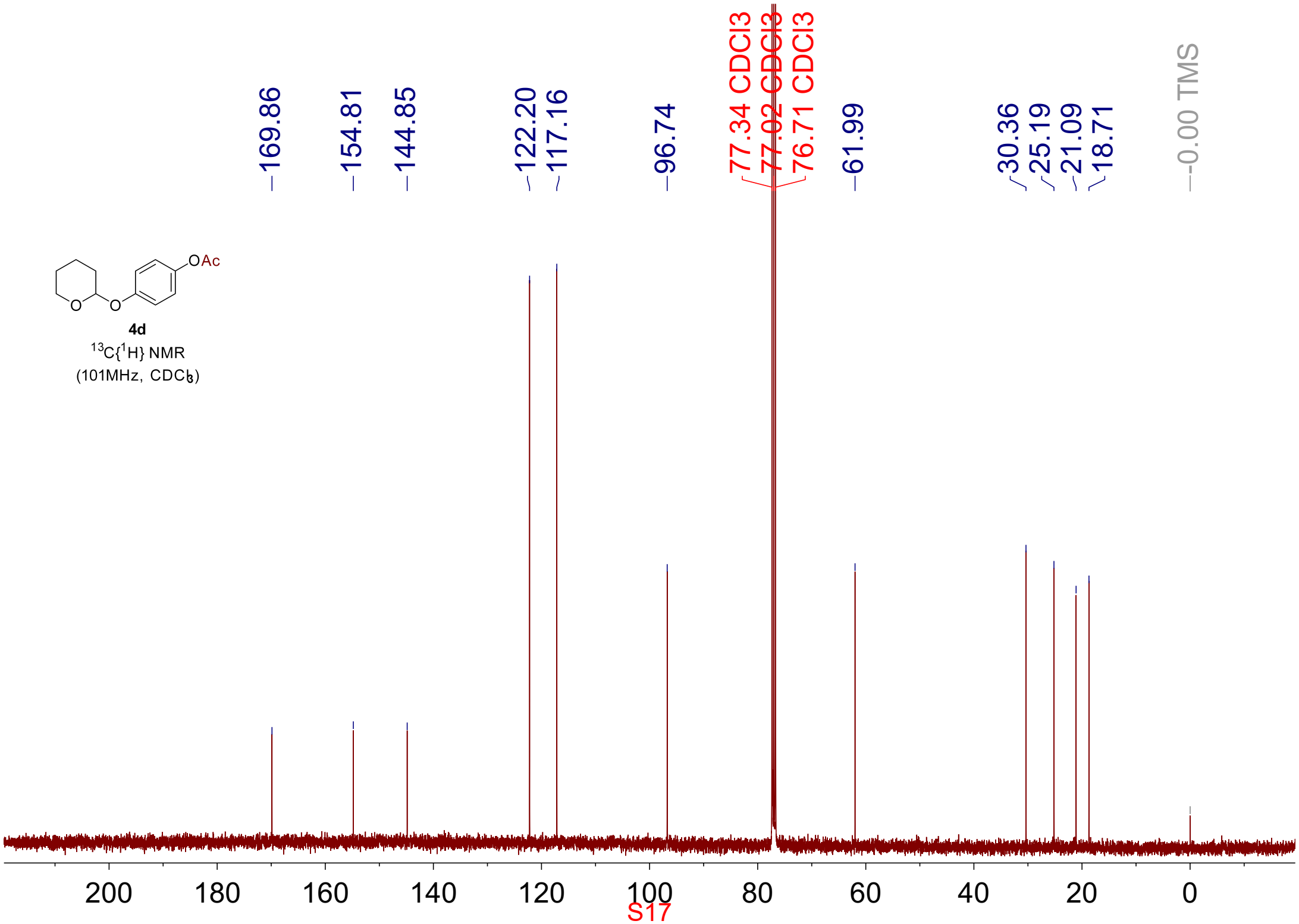
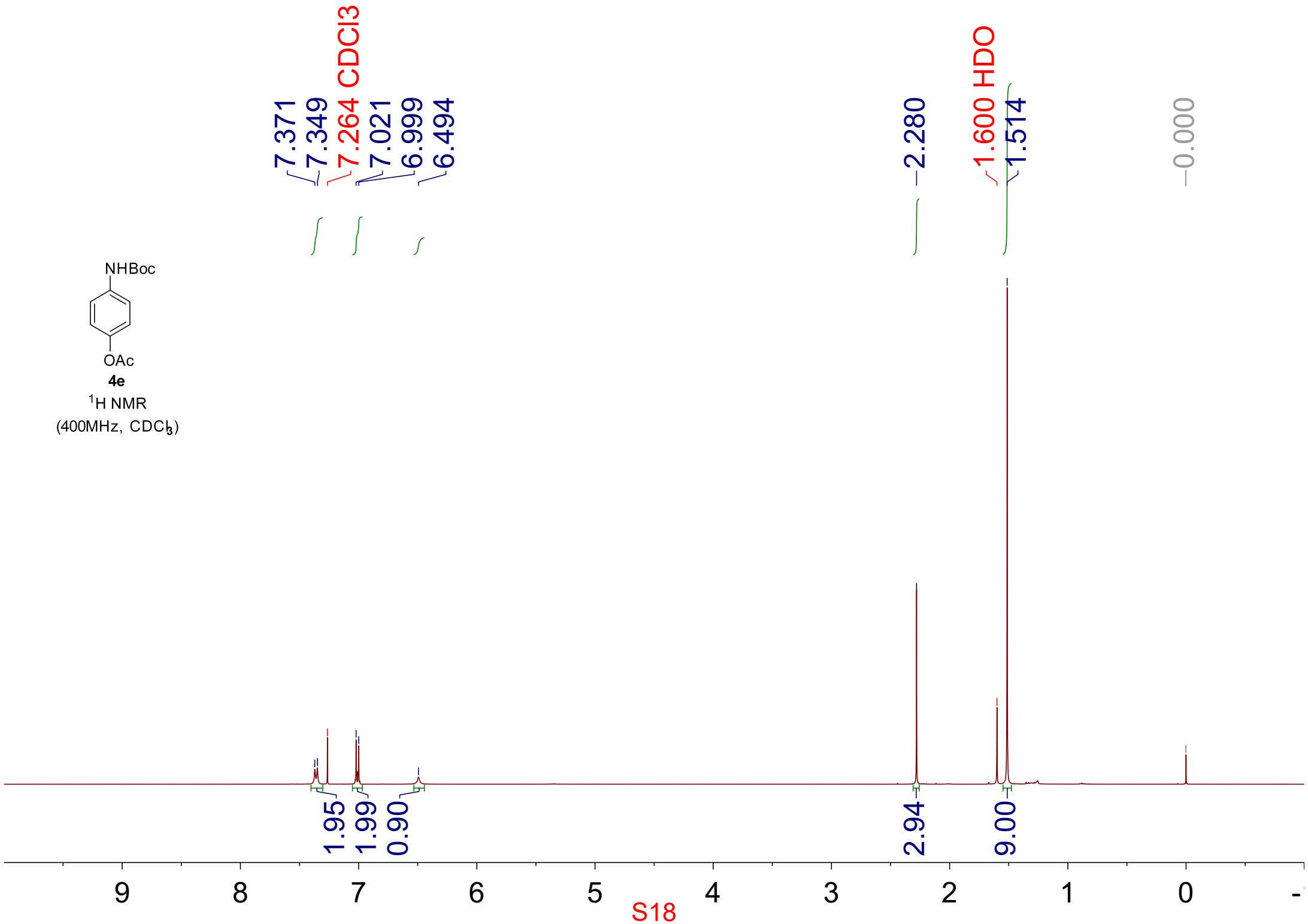
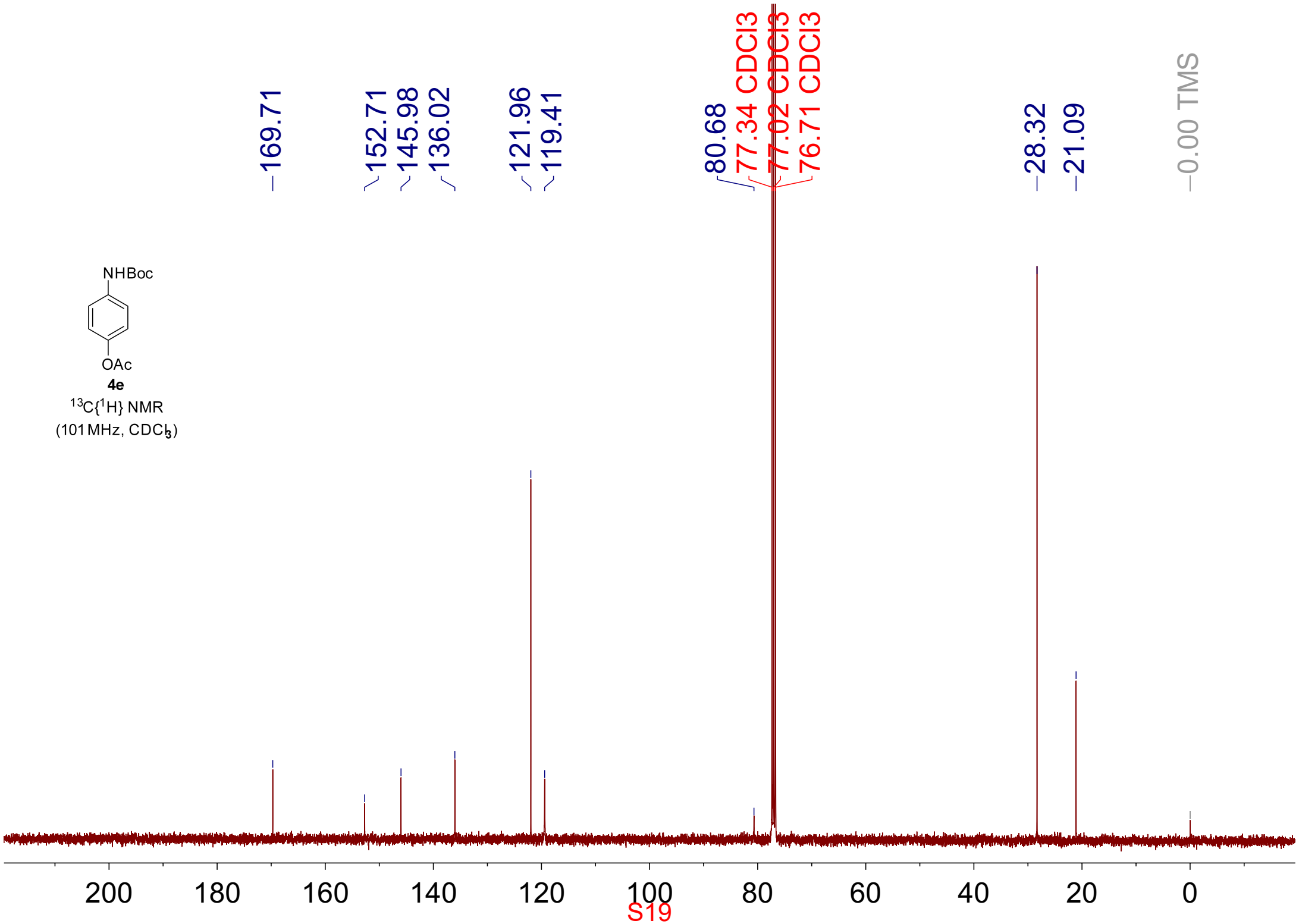
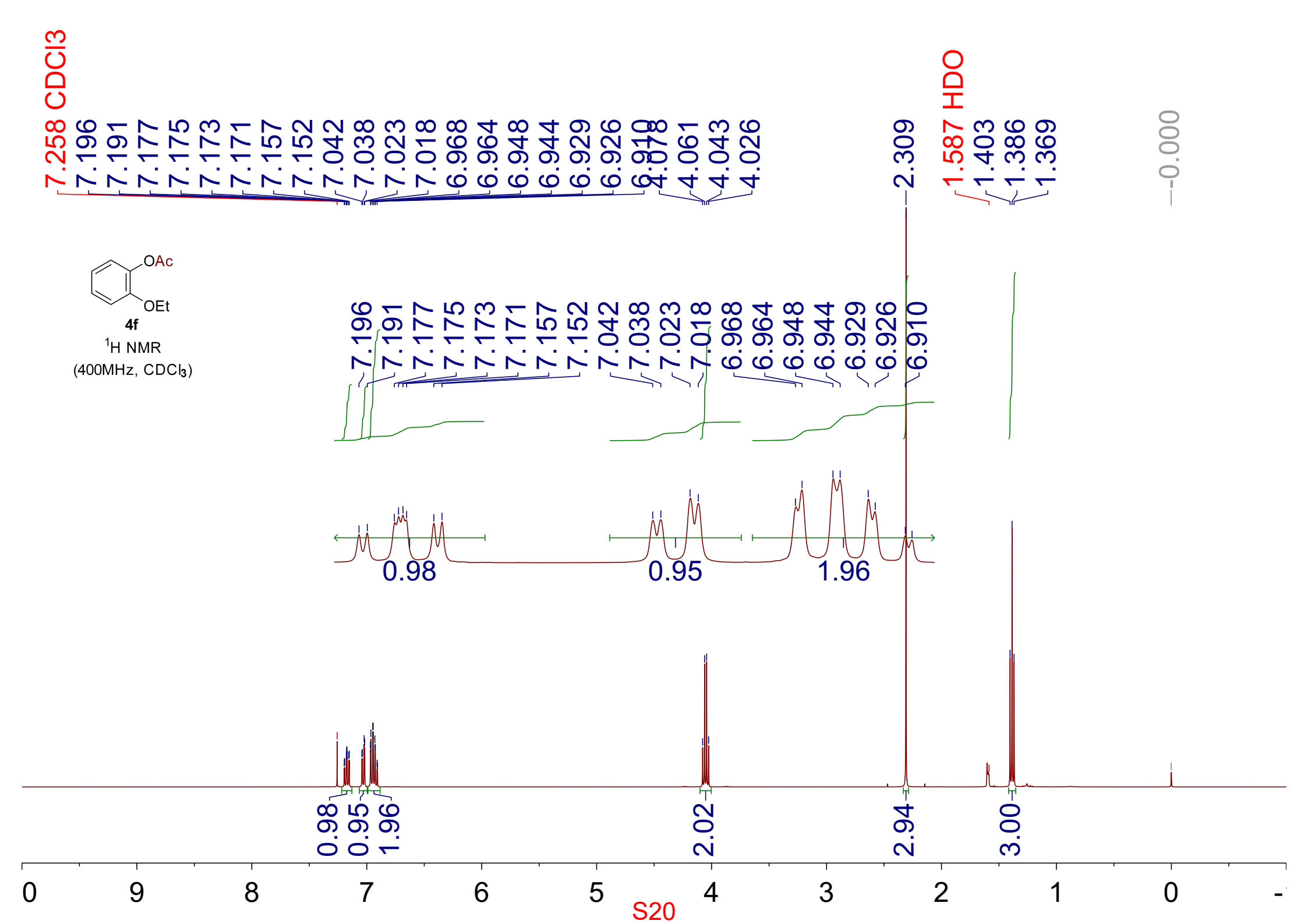
7.059
7.036
6.993
6.970
5.377
5.369
5.361
3.906
3.901
3.898
3.893
3.877
3.869
3.613
3.609
3.584
3.581
2.277
1.869
1.862
1.859
1.851
1.842
1.839
1.830
1.683
1.681
1.676
1.669
1.664
1.654
1.645
1.629
1.619
1.615
1.590
1.588
1.581 HDO
0.000
OAc
O
O
4d
1H NMR
(400MHz, CDCl3)
1.95
1.91
1.01
1.02
1.02
3.00
1.03
1.95
2.96
0
9
8
7
6
5
4
3
2
1
0
-

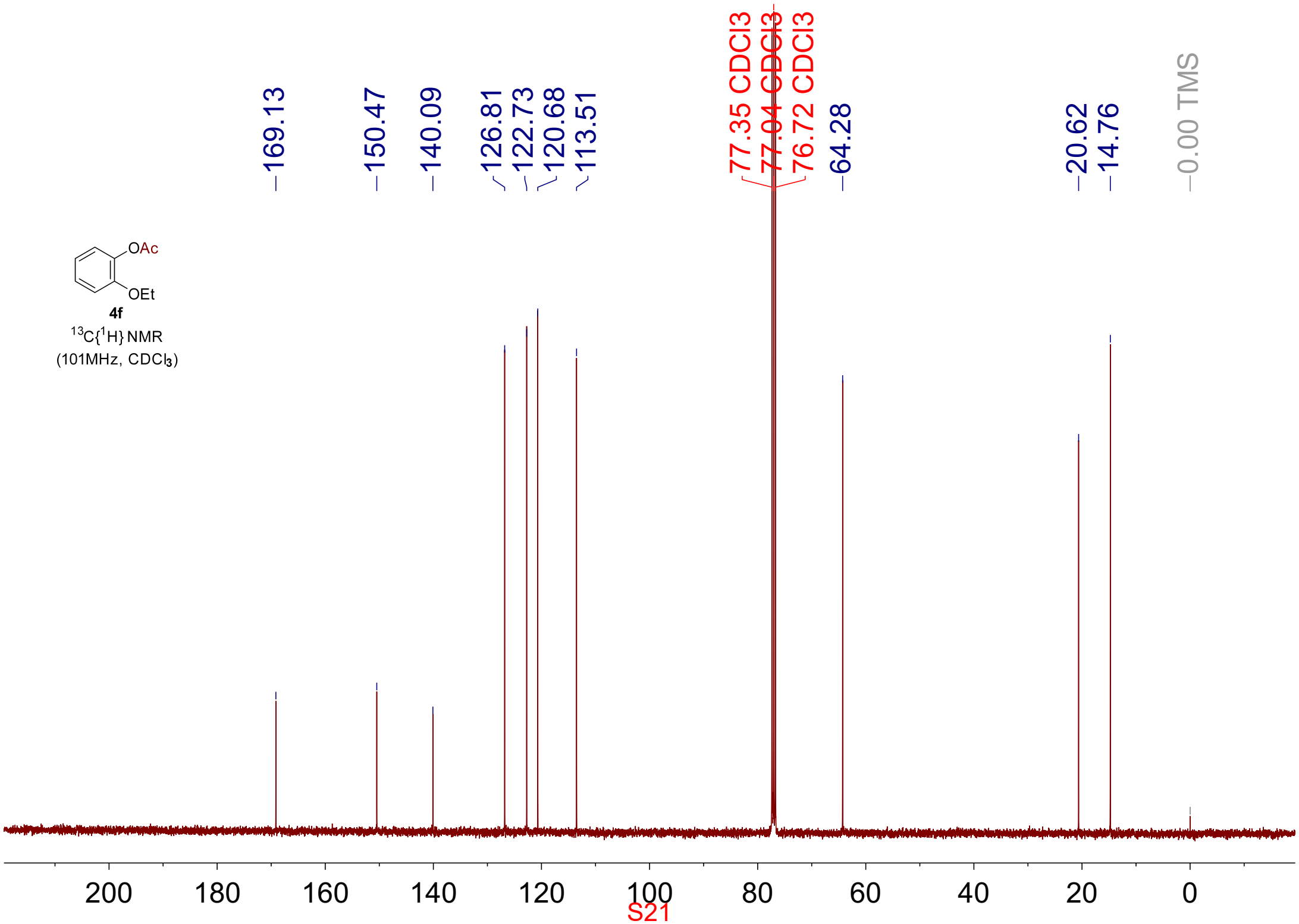

7.262 CDCl3
7.059
7.036
6.993
6.970
5.377
5.369
5.361
2.277
1.581 HDO
0.000 TMS
OAc
O
O
4d
1H NMR
(400MHz, CDCl3)
2.053
2.039
2.034
2.023
2.017
2.014
2.007
2.002
1.998
1.993
1.988
1.983
1.980
1.976
1.970
1.965
1.951
1.947
1.869
1.862
1.859
1.851
1.842
1.839
1.830
3.930
3.922
3.906
3.901
3.898
3.893
3.877
3.869
3.623
3.620
3.613
3.609
3.603
3.599
3.595
3.591
3.584
3.581
3.574
1.689
1.683
1.681
1.676
1.669
1.664
1.661
1.654
1.650
1.645
1.641
1.629
1.625
1.619
1.615
1.598
1.95
1.91
1.01
1.02
1.02
3.00
1.03
1.95
2.96
0
9
8
7
6
5
4
3
2
1
0
-

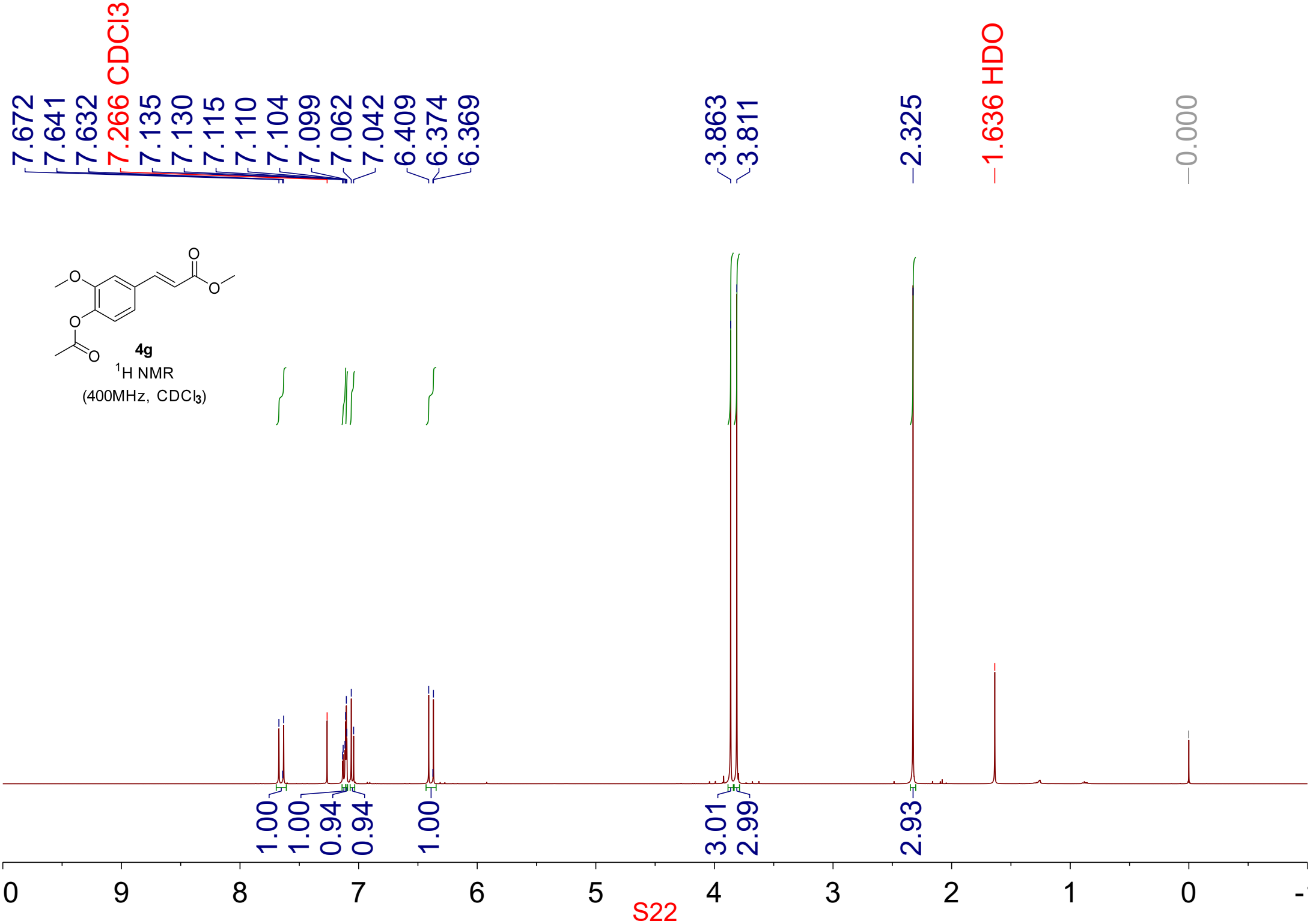

169.86
154.81
144.85
122.20
117.16
96.74
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
61.99
30.36
25.19
21.09
18.71
0.00 TMS
OAc
O
O
4d
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

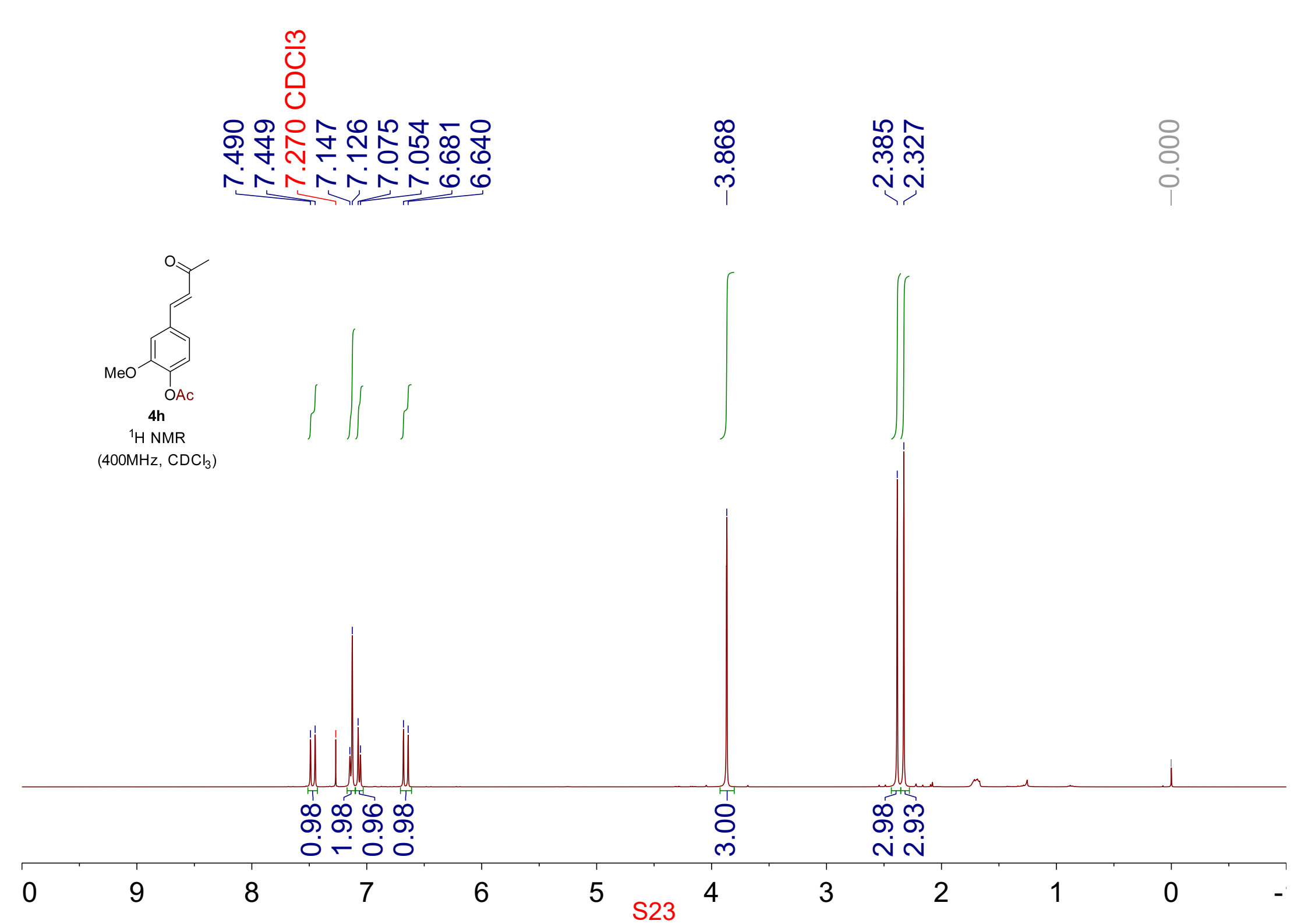

7.371
7.349
7.264 CDCl3
7.021
6.999
6.494
2.280
1.600 HDO
1.514
0.000
NHBoc
OAc
4e
1H NMR
(400MHz, CDCl3)
1.95
1.99
0.90
2.94
9.00
9
8
7
6
5
4
3
2
1
0
-


169.71
152.71
145.98
136.02
121.96
119.41
80.68
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
28.32
21.09
0.00 TMS
NHBoc
OAc
4e
13C{1H} NMR
(101 MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0


7.258 CDCl3
7.196
7.191
7.177
7.175
7.173
7.171
7.157
7.152
7.042
7.038
7.023
7.018
6.968
6.964
6.948
6.944
6.929
6.926
6.910
4.078
4.061
4.043
4.026
2.309
1.587 HDO
1.403
1.386
1.369
0.000
OAc
OEt
4f
1H NMR
(400MHz, CDCl3)
0.98
0.95
1.96
2.02
2.94
3.00
0
9
8
7
6
5
4
3
2
1
0
S20


169.13
150.47
140.09
126.81
122.73
120.68
113.51
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
64.28
20.62
14.76
0.00 TMS
OAc
OEt
4f
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0


7.672
7.641
7.632
7.266 CDCl3
7.135
7.130
7.115
7.110
7.104
7.099
7.062
7.042
6.409
6.374
6.369
3.863
3.811
2.325
1.636 HDO
0.000
4g
1H NMR
(400MHz, CDCl3)
1.00
1.00
0.94
0.94
1.00
3.01
2.99
2.93
0
9
8
7
6
5
4
3
2
1
0
-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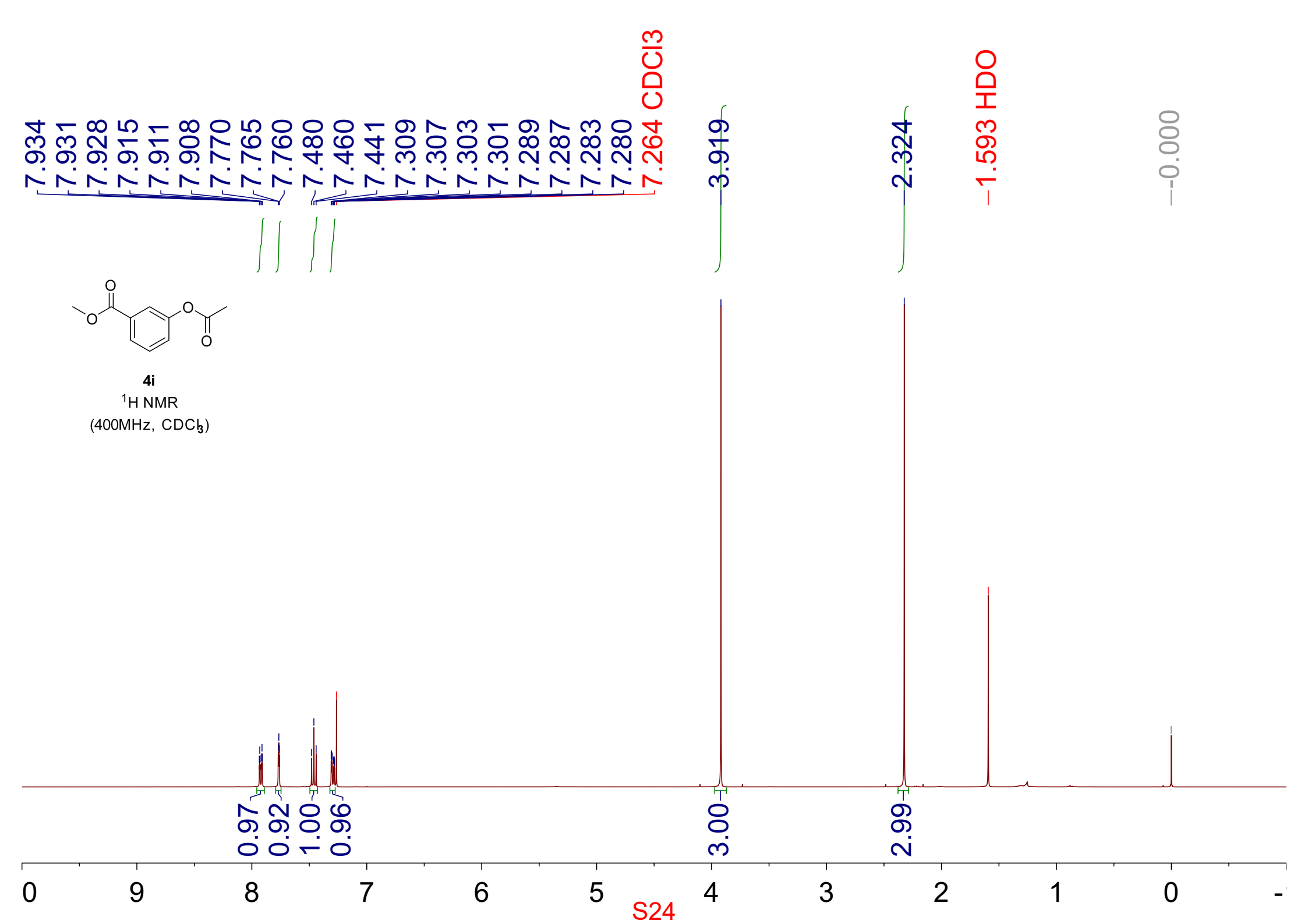
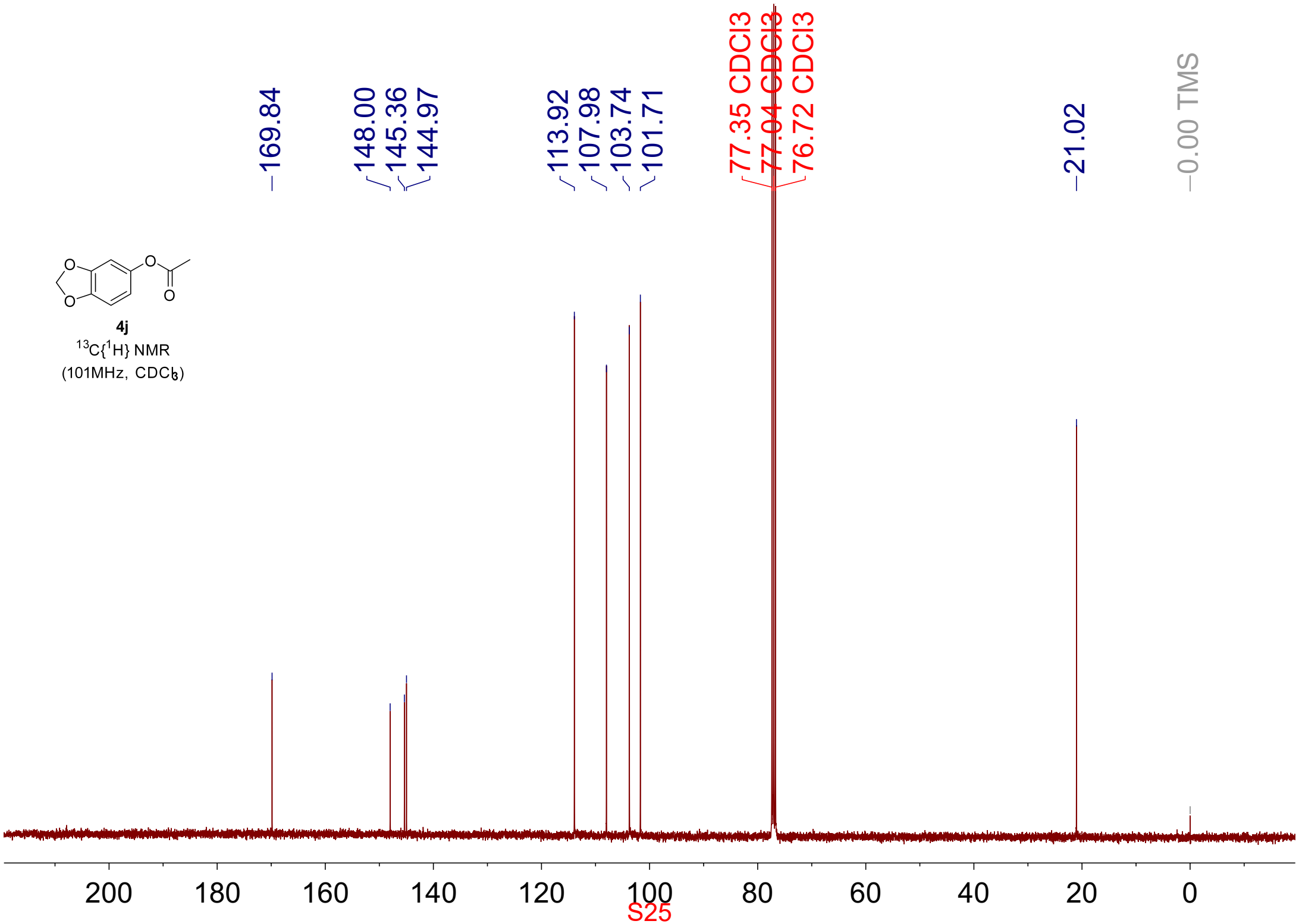
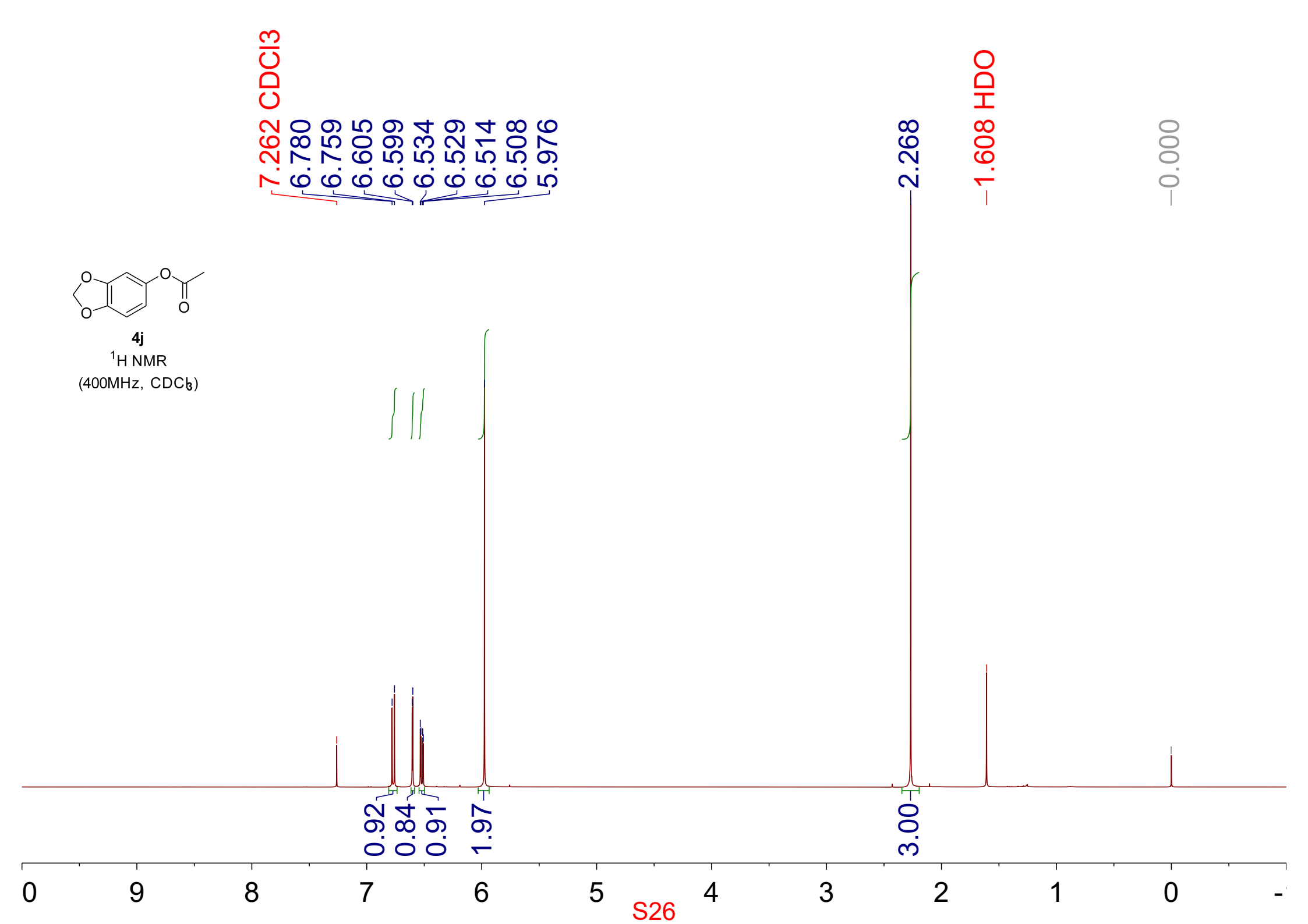
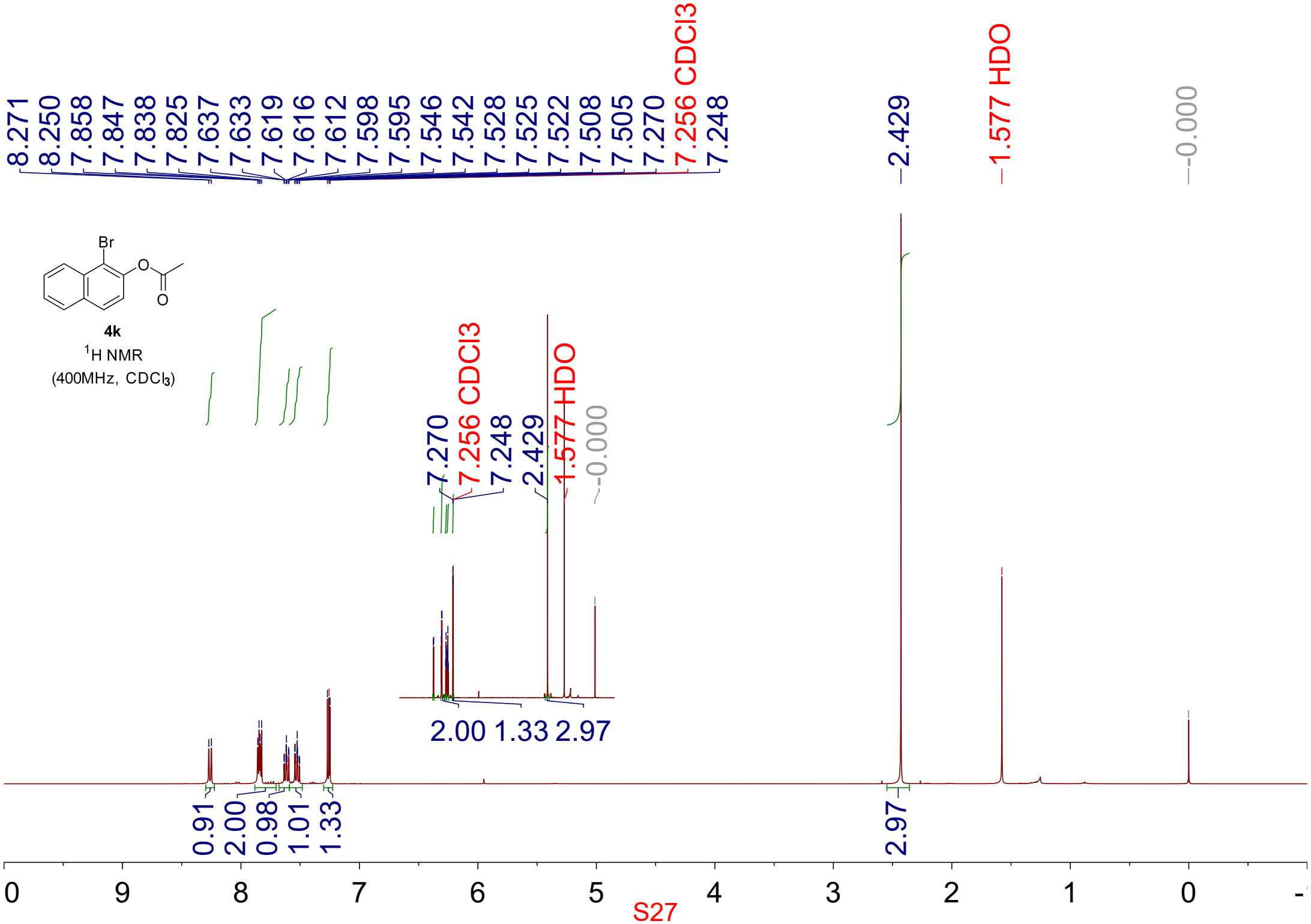
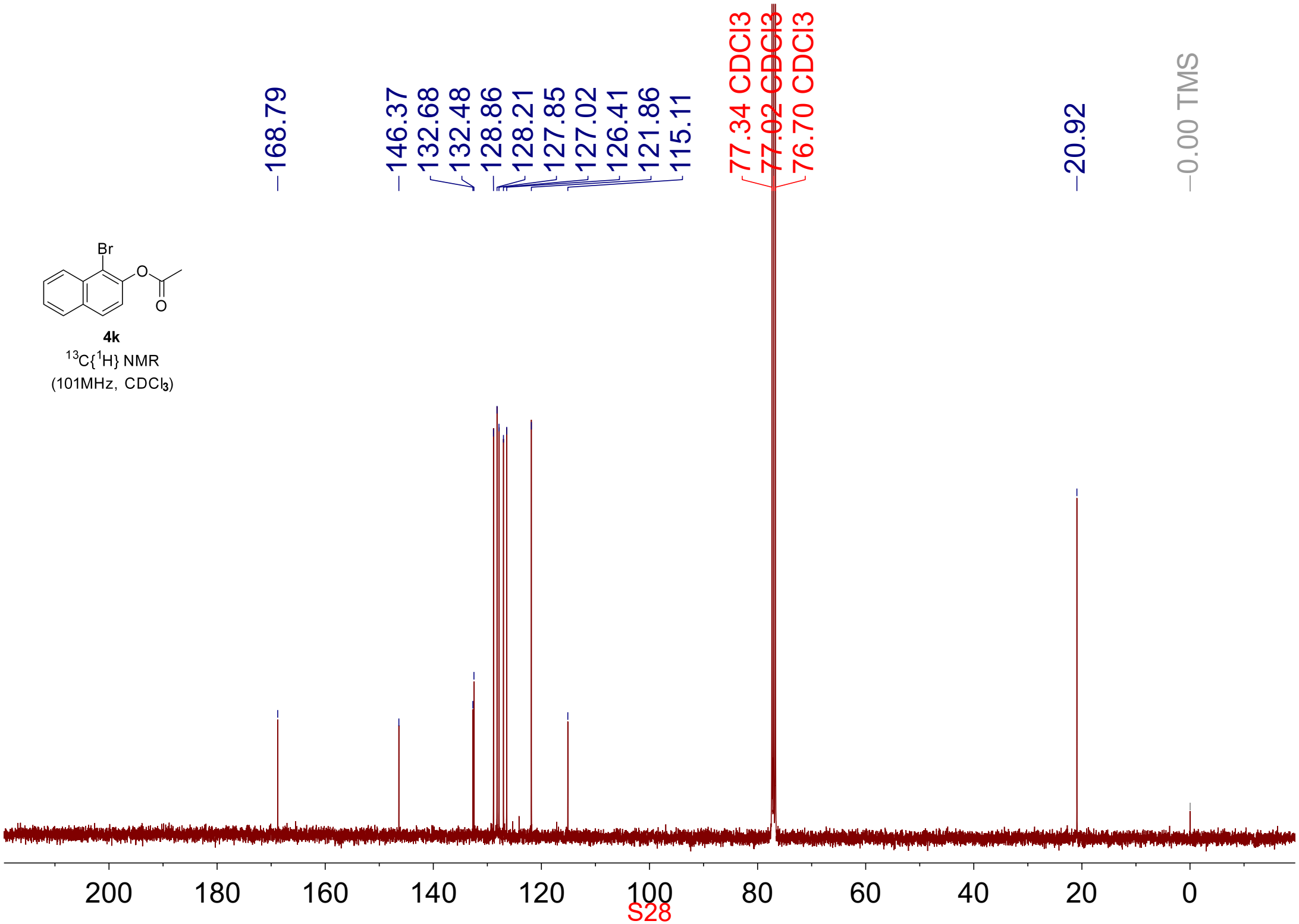
7.449
7.270 CDCl3
7.147
7.126
7.075
7.054
6.681
6.640
3.868
2.385
2.327
0.000
MeO
OAc
4h
1H NMR
(400MHz, CDCl3)
0.98
1.98
0.96
0.98
3.00
2.98
2.93
0
9
8
7
6
5
4
3
2
1
0
-

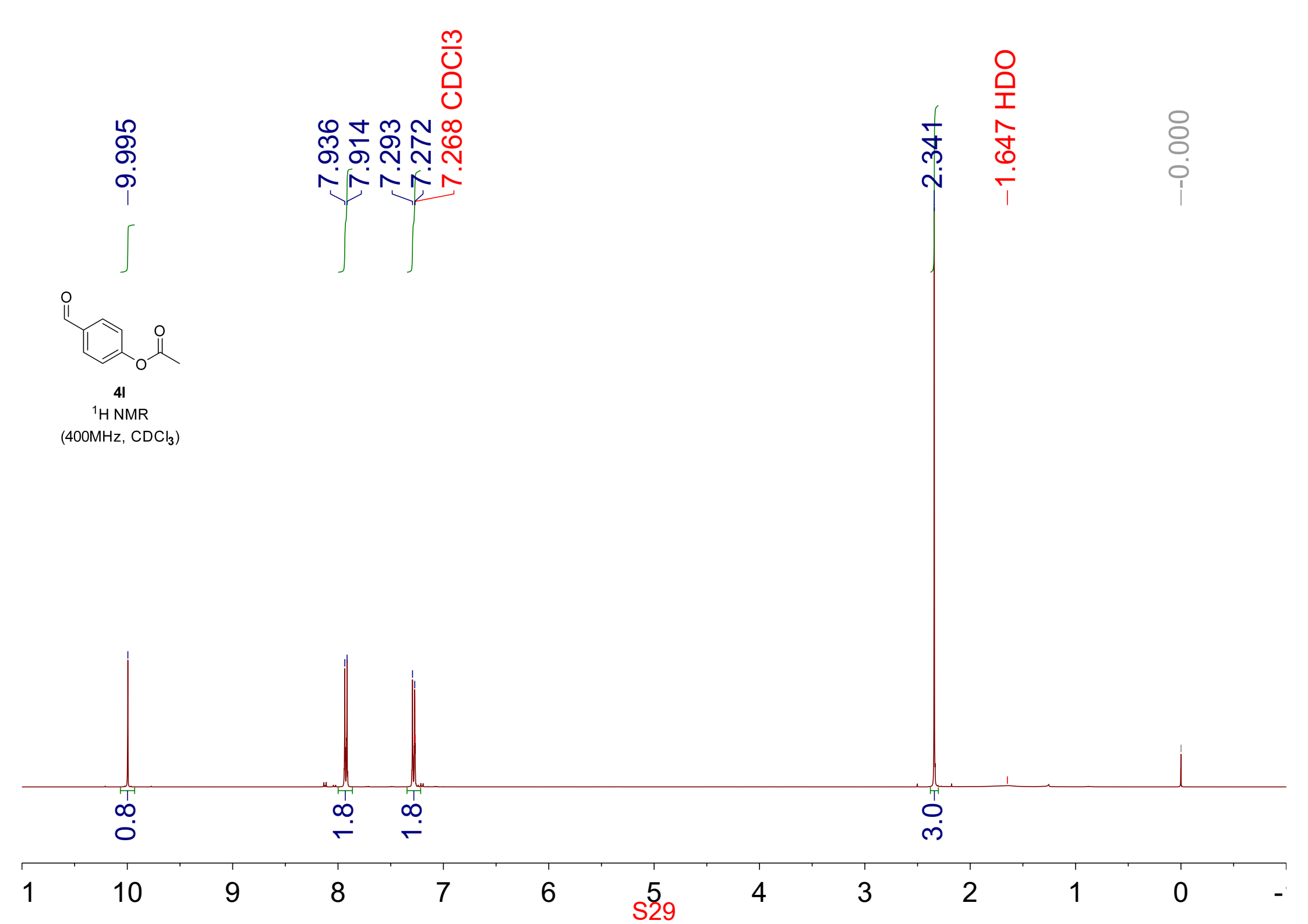

7.934
7.931
7.928
7.915
7.911
7.908
7.770
7.765
7.760
7.480
7.460
7.441
7.309
7.307
7.303
7.301
7.289
7.287
7.283
7.280
7.264 CDCl3
3.919
2.324
1.593 HDO
0.000
4i
1H NMR
(400MHz, CDCl3)
0.97
0.92
1.00
0.96
3.00
2.99
0
9
8
7
6
5
4
3
2
1
0
-

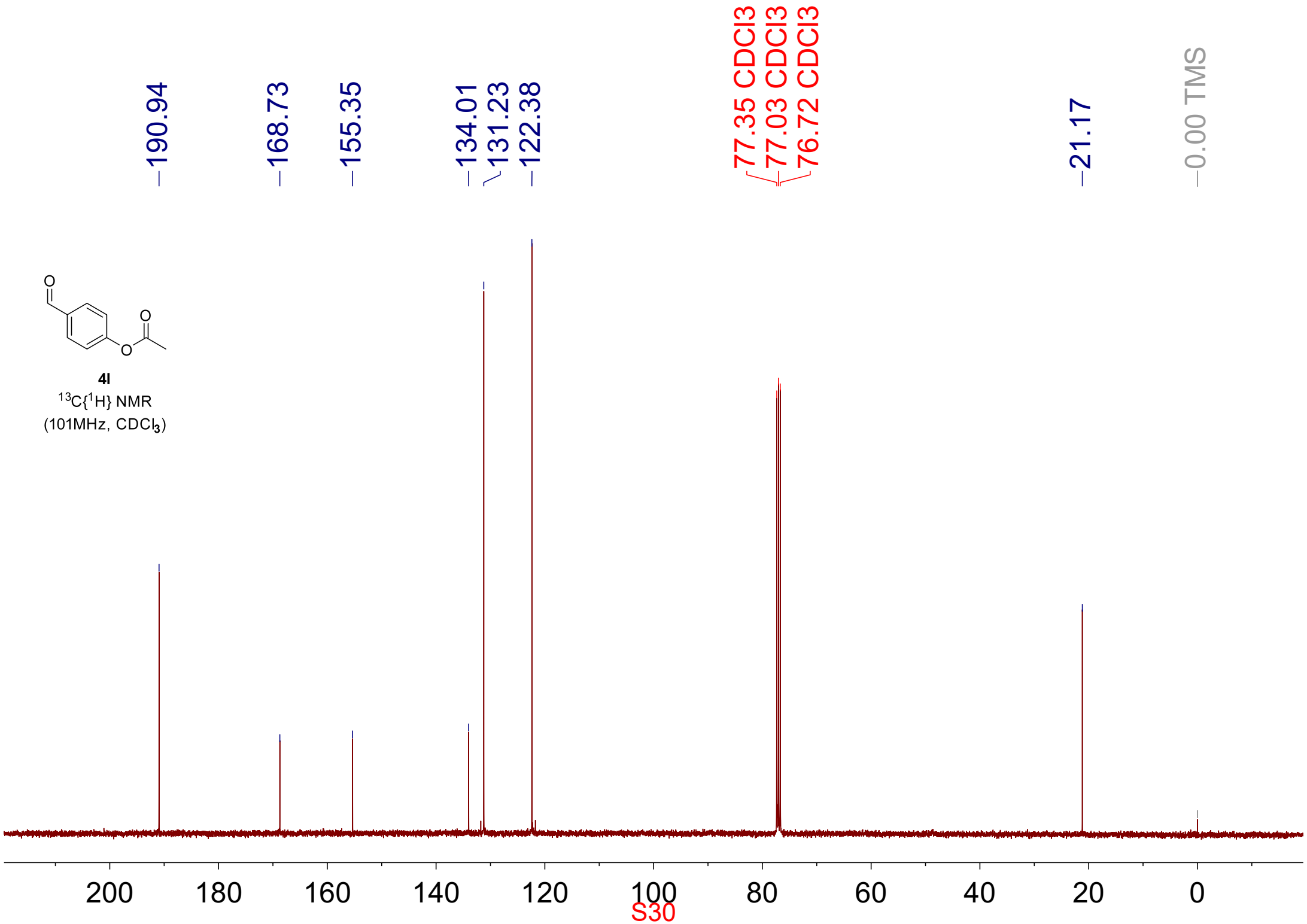

169.84
148.00
145.36
144.97
113.92
107.98
103.74
101.71
77.35 CDCl3
77.04 CDCl3
76.72 CDCl3
21.02
0.00 TMS
4j
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

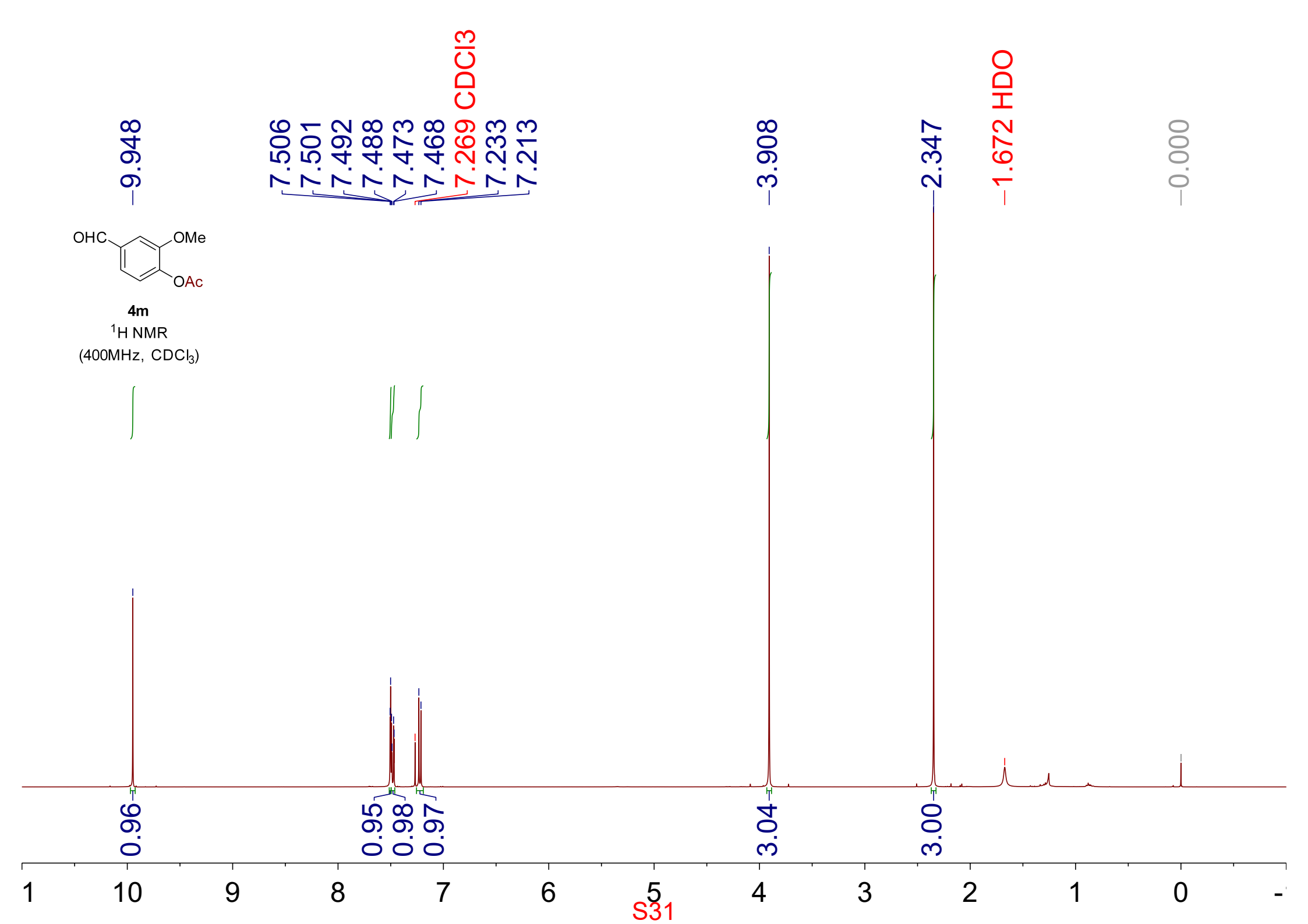

7.262 CDCl3
6.780
6.759
6.605
6.599
6.534
6.529
6.514
6.508
5.976
2.268
1.608 HDO
0.000
4j
1H NMR
(400MHz, CDCl3)
0.92
0.84
0.91
1.97
3.00
0
9
8
7
6
5
4
3
2
1
0
-

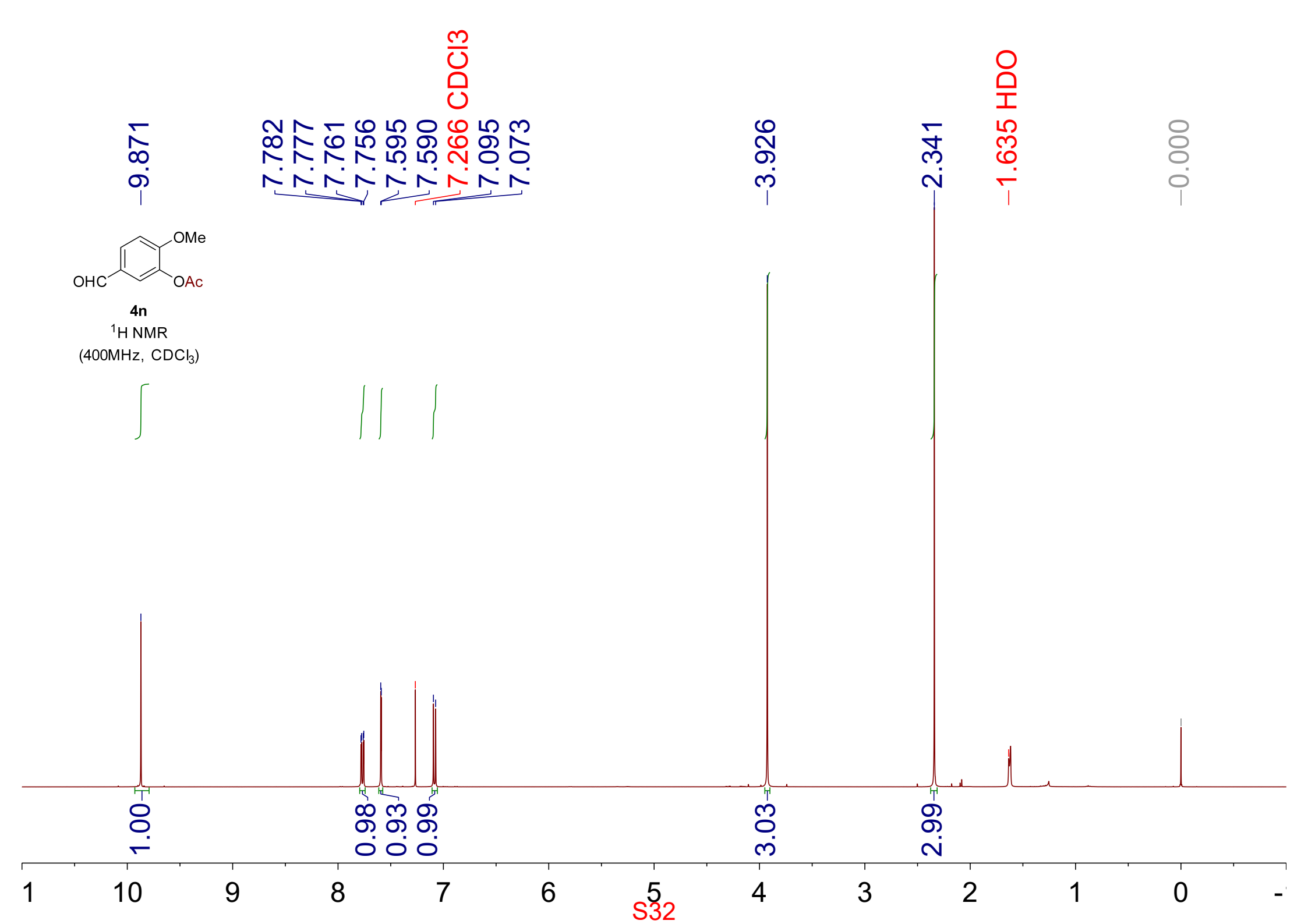

8.271
8.250
7.858
7.847
7.838
7.825
7.637
7.633
7.619
7.616
7.612
7.598
7.595
7.546
7.542
7.528
7.525
7.522
7.508
7.505
7.270
7.256 CDCl3
7.248
2.429
1.577 HDO
0.000
Br
O
O
4k
1H NMR
(400MHz, CDCl3)
2.00 1.33 2.97
0.91
2.00
0.98
1.01
1.33
2.97
0
9
8
7
6
5
4
3
2
1
0

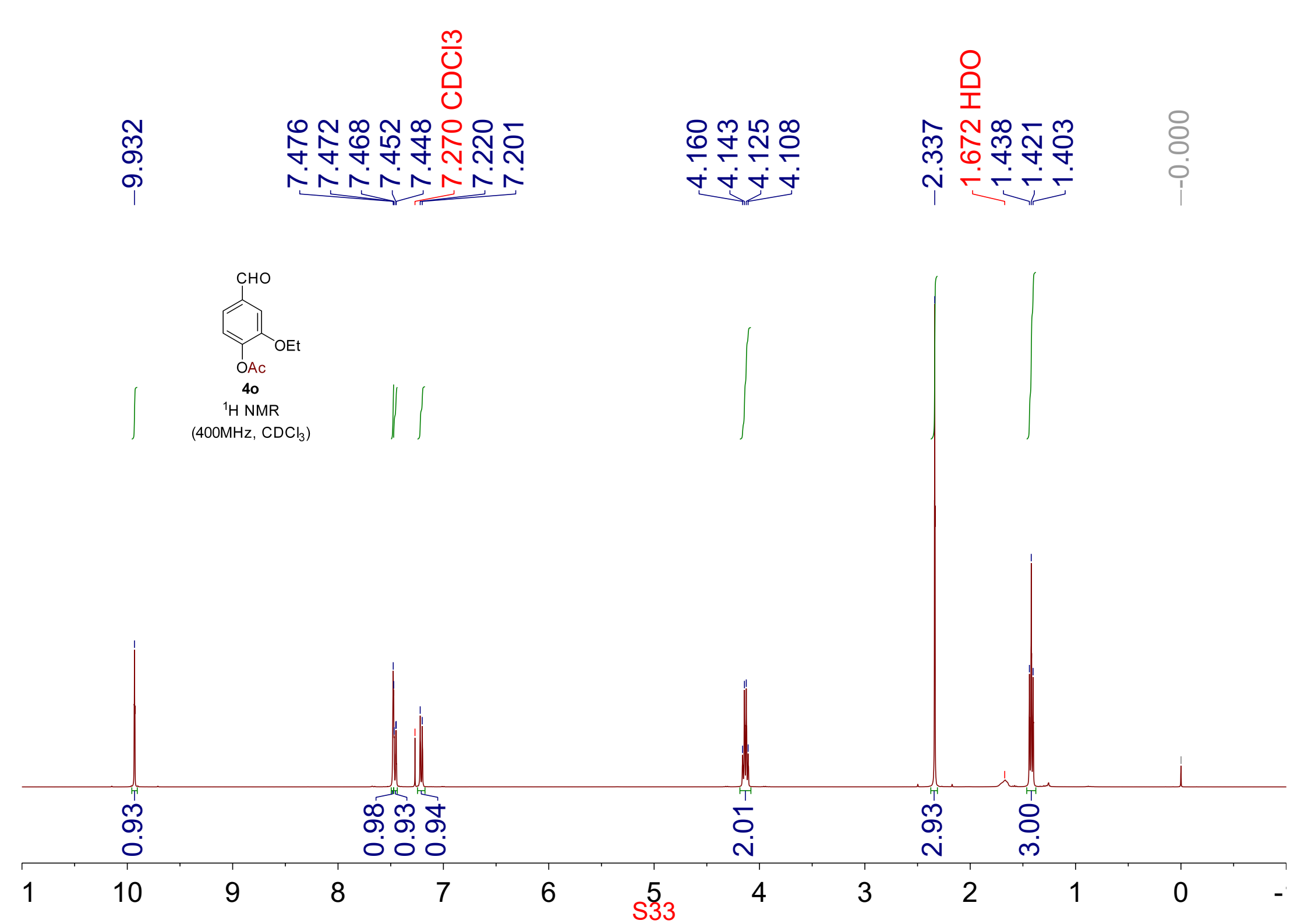

168.79
146.37
132.68
132.48
128.86
128.21
127.85
127.02
126.41
121.86
115.11
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
20.92
0.00 TMS
Br
O
O
4k
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

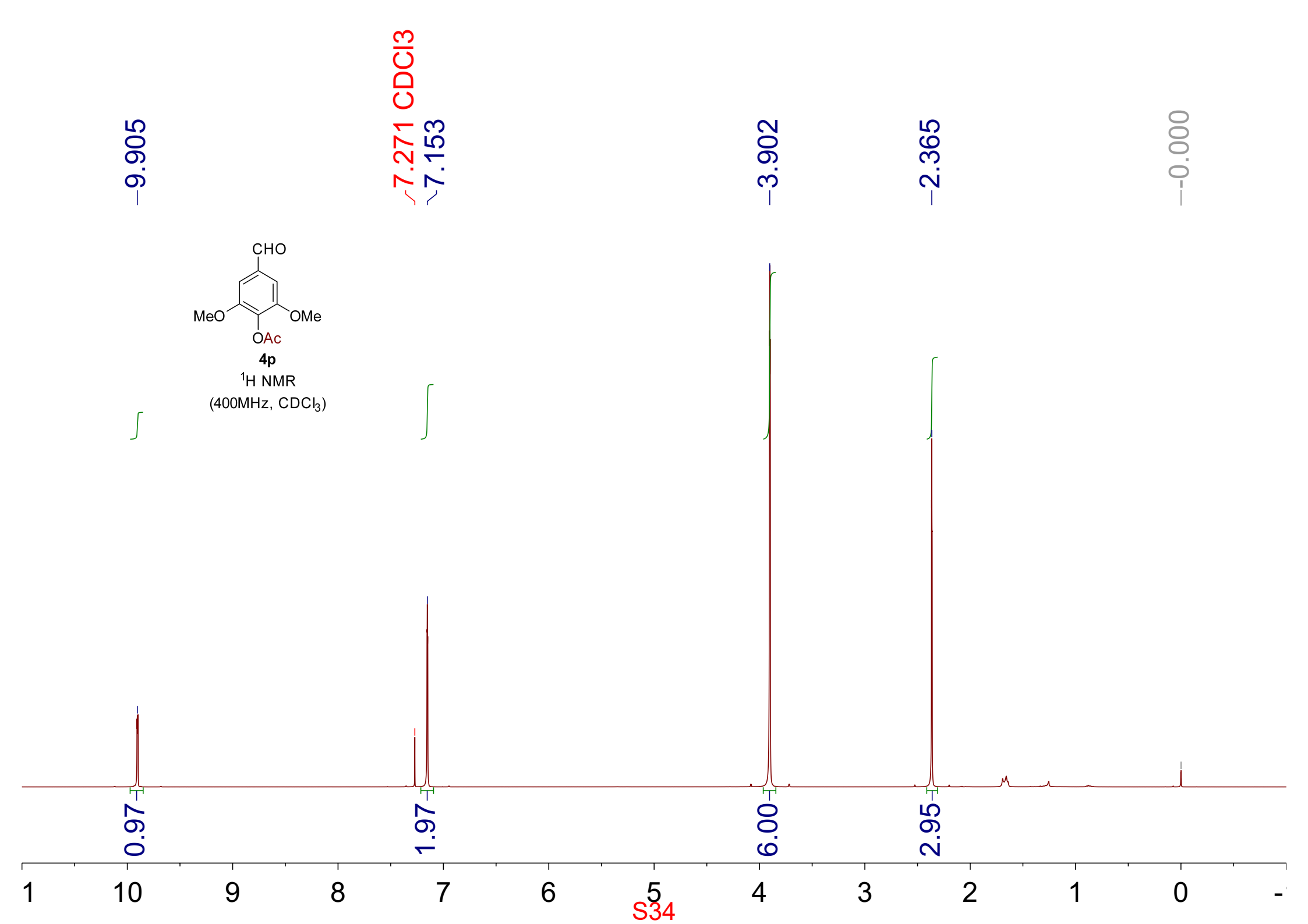

9.995
7.936
7.914
7.293
7.272
7.268 CDCl3
2.341
1.647 HDO
0.000
O
O
O
4l
1H NMR
(400MHz, CDCl3)
0.8
1.8
1.8
3.0
1
10
9
8
7
6
5
4
3
2
1
0
-

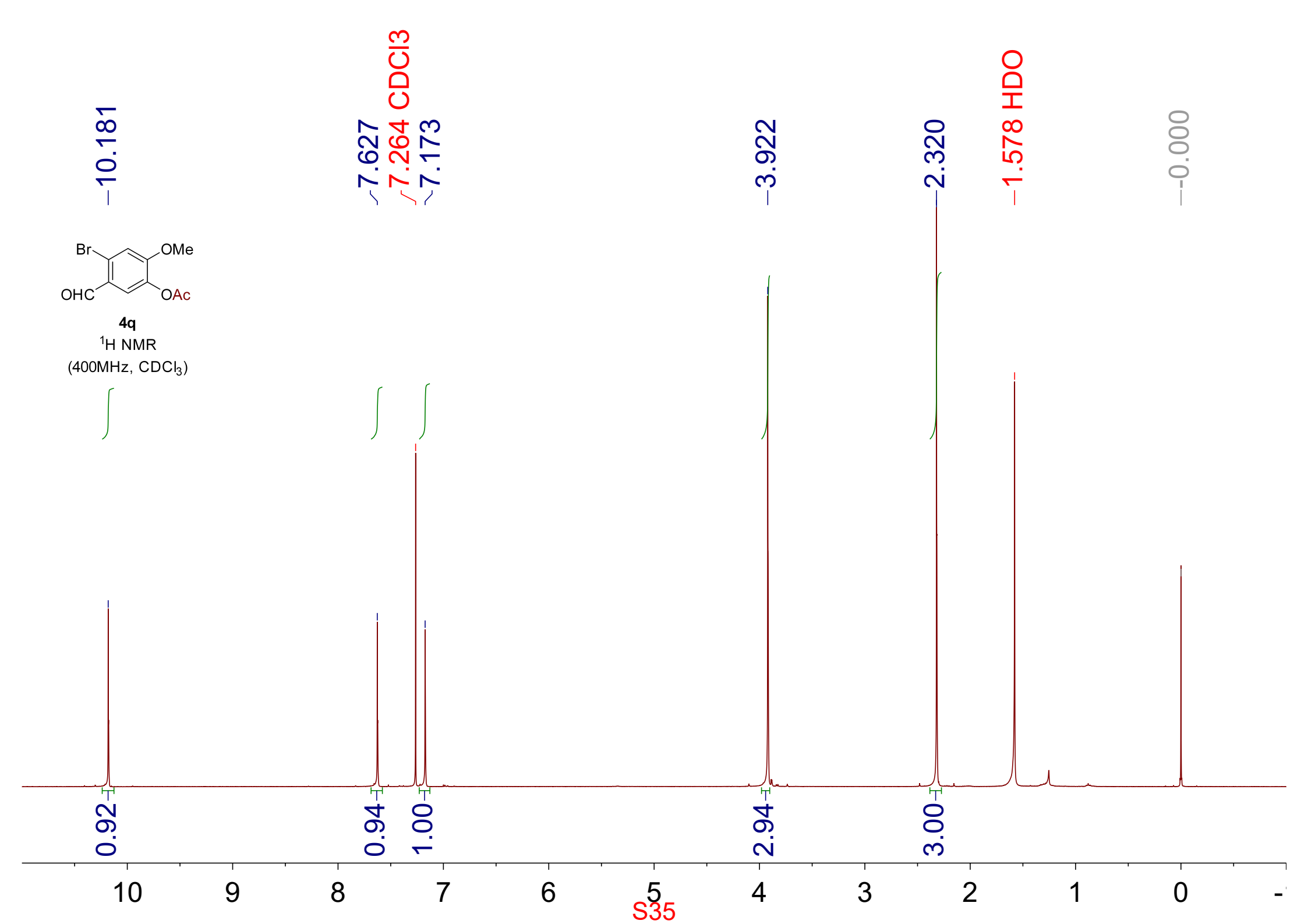

190.94
168.73
155.35
134.01
131.23
122.38
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
21.17
0.00 TMS
4l
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

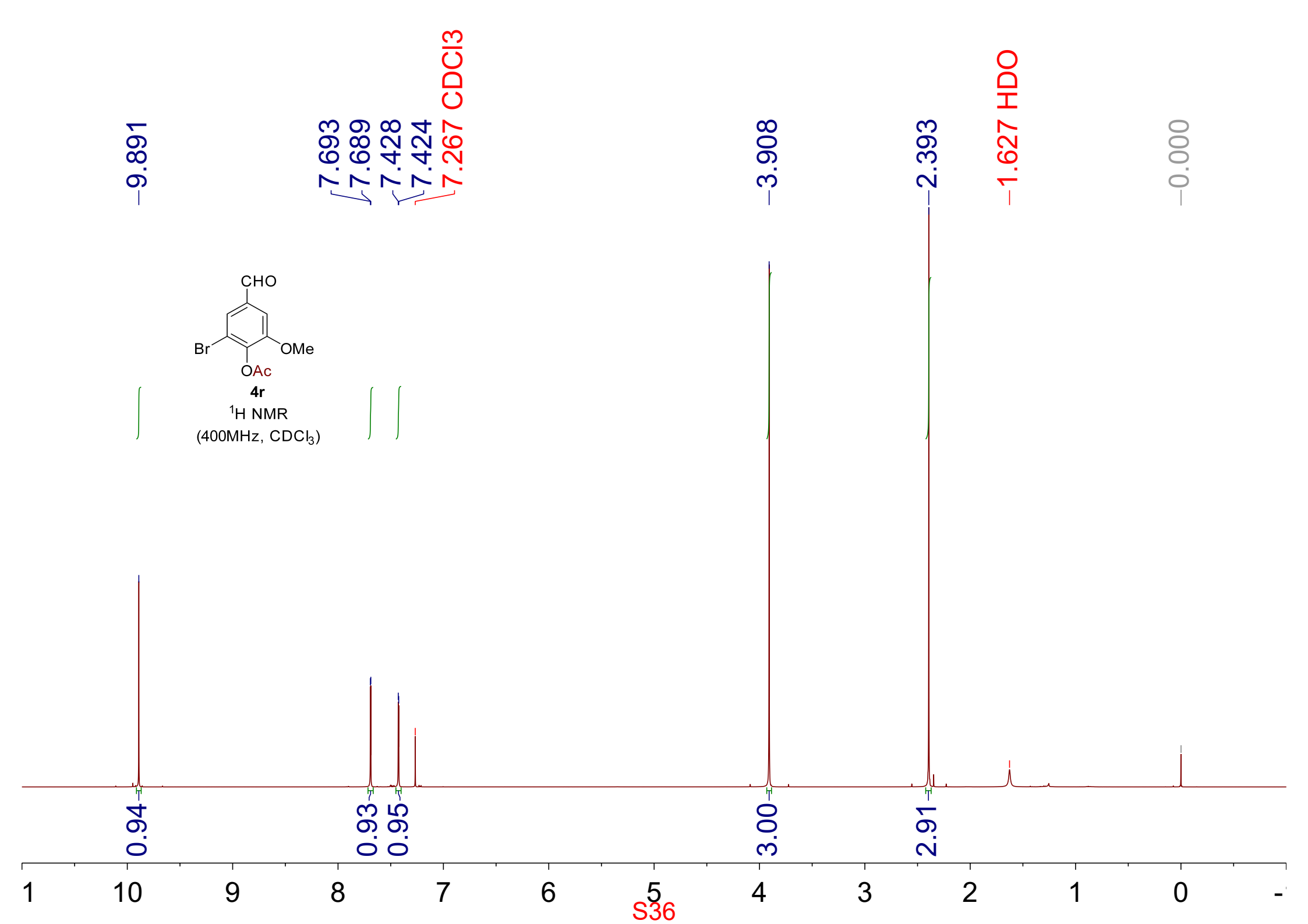

9.948
7.506
7.501
7.492
7.488
7.473
7.468
7.269 CDCl3
7.233
7.213
3.908
2.347
1.672 HDO
0.000
OHC
OMe
OAc
4m
1H NMR
(400MHz, CDCl3)
0.96
0.95
0.98
0.97
3.04
3.00
1
10
9
8
7
6
5
4
3
2
1
0
-

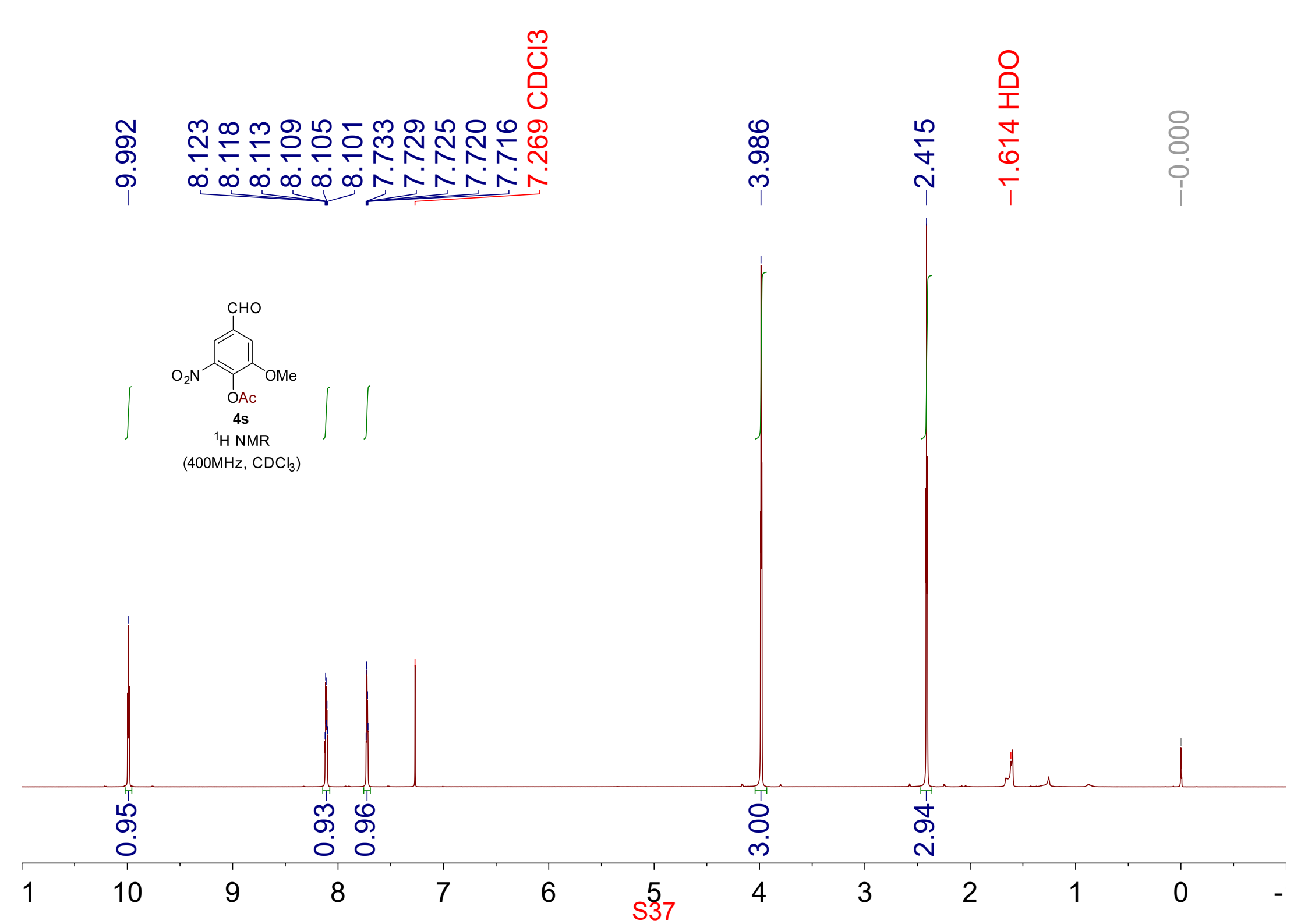

9.871
7.782
7.777
7.761
7.756
7.595
7.590
7.266 CDCl3
7.095
7.073
3.926
2.341
1.635 HDO
0.000
OMe
OHC
OAc
4n
1H NMR
(400MHz, CDCl3)
1.00
0.98
0.93
0.99
3.03
2.99
1
10
9
8
7
6
5
4
3
2
1
0
-

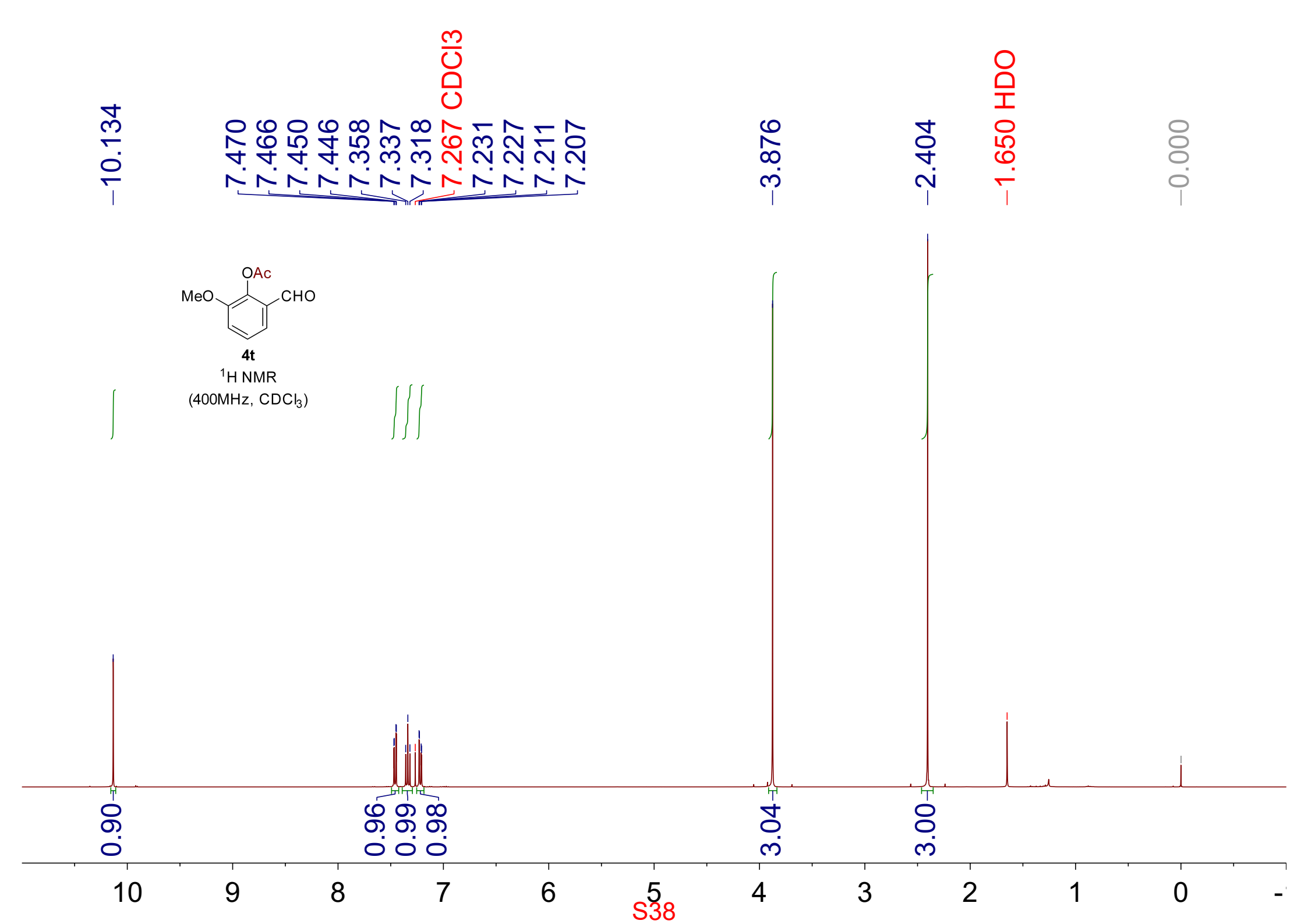

9.932
7.476
7.472
7.468
7.452
7.448
7.270 CDCl3
7.220
7.201
4.160
4.143
4.125
4.108
2.337
1.672 HDO
1.438
1.421
1.403
0.000
CHO
OEt
OAc
4o
1H NMR
(400MHz, CDCl3)
0.93
0.98
0.93
0.94
2.01
2.93
3.00
1
10
9
8
7
6
5
4
3
2
1
0

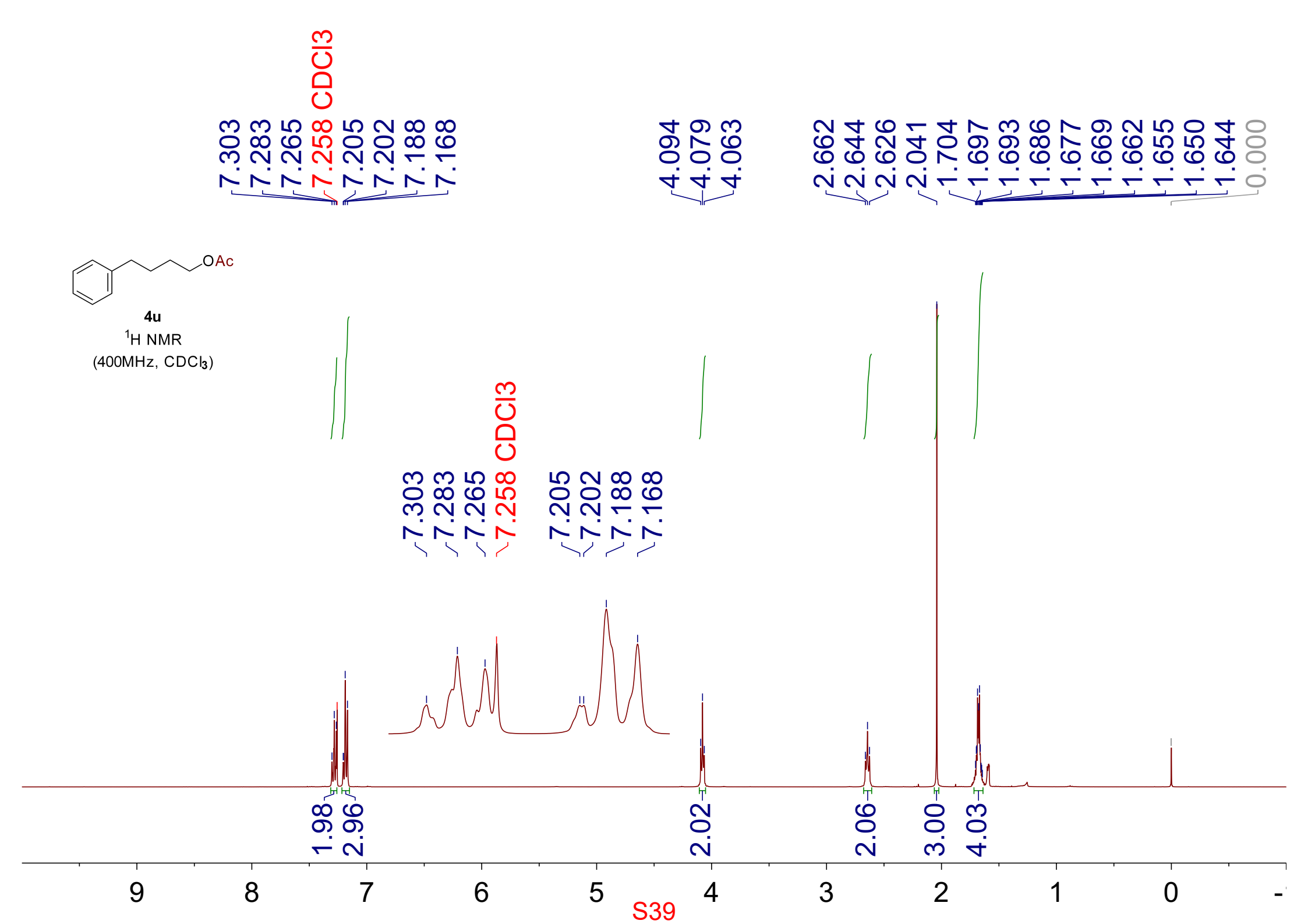

9.905
7.271 CDCl3
7.153
3.902
2.365
0.000
CHO
MeO
OMe
OAc
4p
1H NMR
(400MHz, CDCl3)
0.97
1.97
6.00
2.95
1
10
9
8
7
6
5
4
3
2
1
0

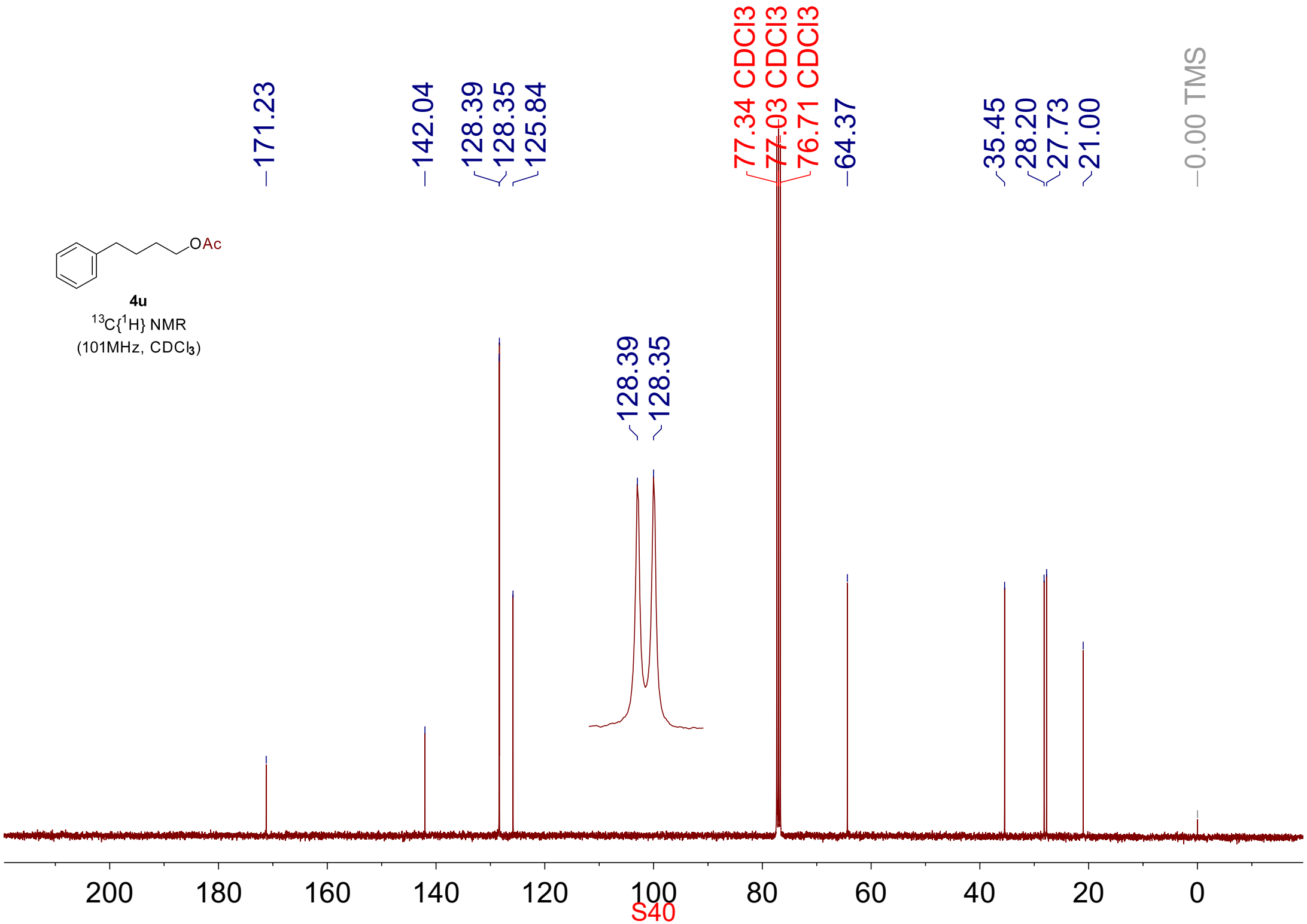

10.181
7.627
7.264 CDCl3
7.173
3.922
2.320
1.578 HDO
0.000
Br
OMe
OHC
OAc
4q
1H NMR
(400MHz, CDCl3)
0.92
0.94
1.00
2.94
3.00
10
9
8
7
6
5
4
3
2
1
0

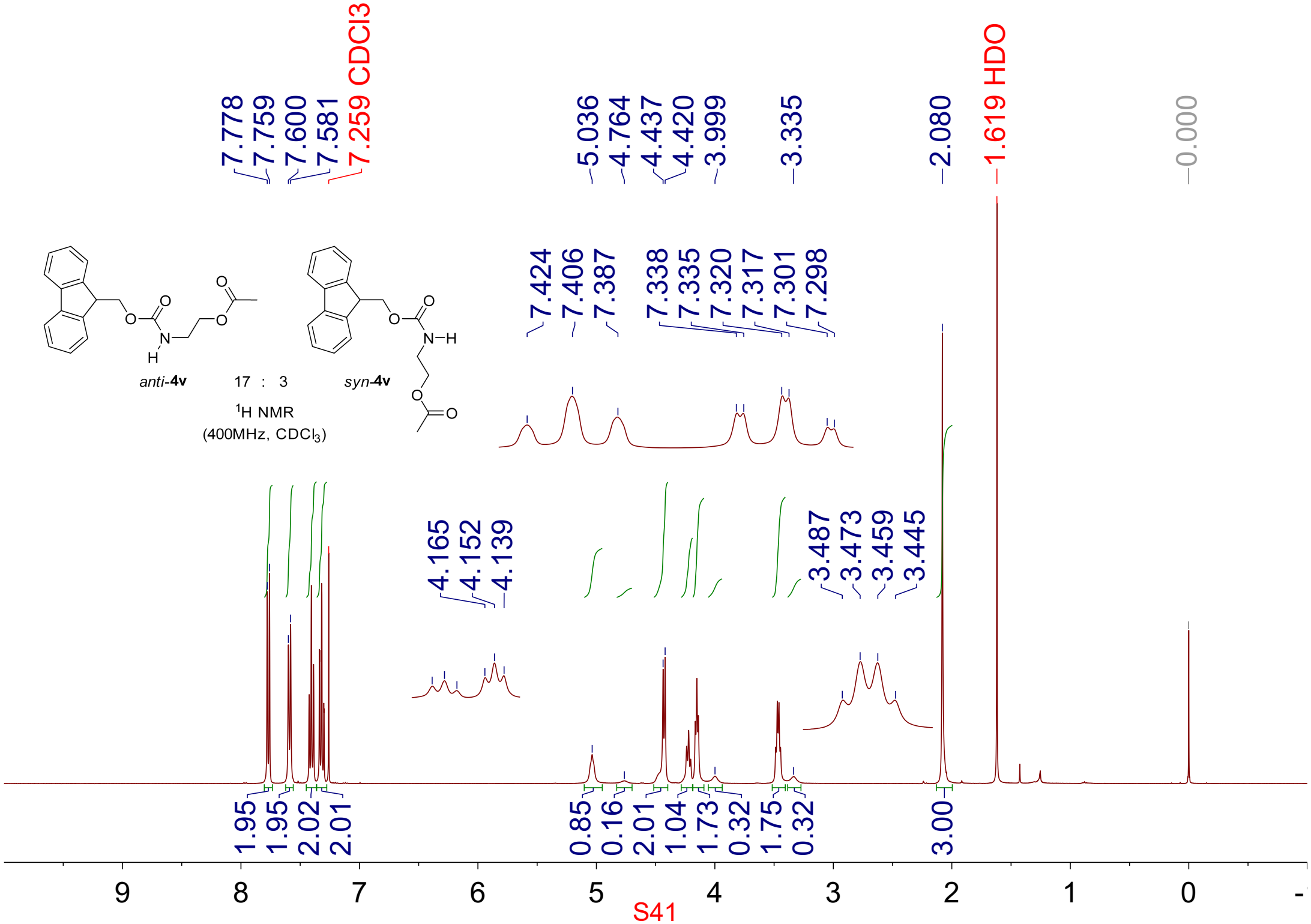

9.891
7.693
7.689
7.428
7.424
7.267 CDCl3
3.908
2.393
1.627 HDO
0.000
CHO
Br
OMe
OAc
4r
1H NMR
(400MHz, CDCl3)
0.94
0.93
0.95
3.00
2.91
1
10
9
8
7
6
5
4
3
2
1
0

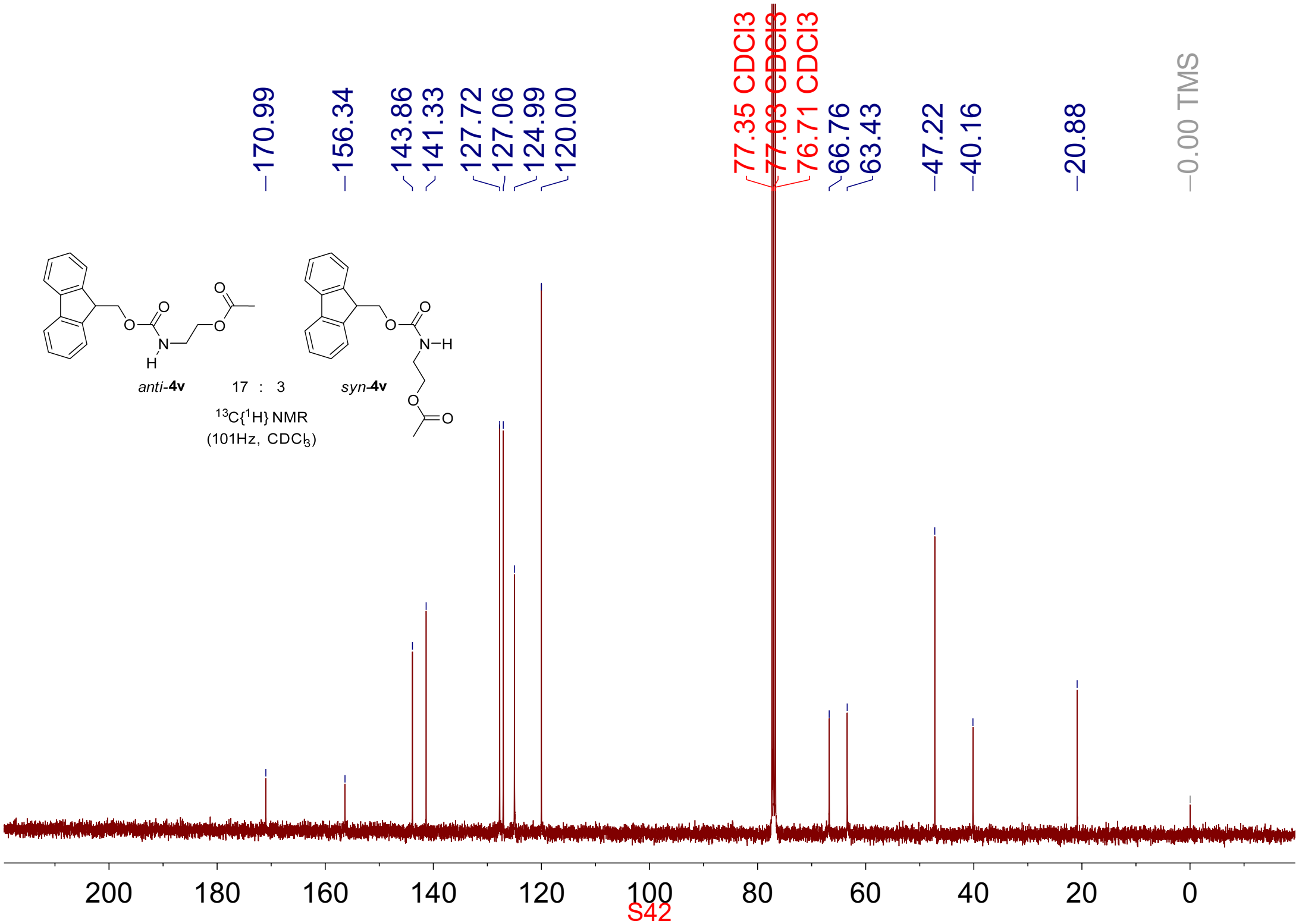

9.992
8.123
8.118
8.113
8.109
8.105
8.101
7.733
7.729
7.725
7.720
7.716
7.269 CDCl3
3.986
2.415
1.614 HDO
0.000
CHO
O2N
OMe
OAc
4s
1H NMR
(400MHz, CDCl3)
0.95
0.93
0.96
3.00
2.94
1
10
9
8
7
6
5
4
3
2
1
0


10.134
7.470
7.466
7.450
7.446
7.358
7.337
7.318
7.267 CDCl3
7.231
7.227
7.211
7.207
3.876
2.404
1.650 HDO
0.000
OAc
MeO
CHO
4t
1H NMR
(400MHz, CDCl3)
0.90
0.96
0.99
0.98
3.04
3.00
10
9
8
7
6
5
4
3
2
1
0


7.303
7.283
7.265
7.258 CDCl3
7.205
7.202
7.188
7.168
4.094
4.079
4.063
2.662
2.644
2.626
2.041
1.704
1.697
1.693
1.686
1.677
1.669
1.662
1.655
1.650
1.644
0.000
OAc
4u
1H NMR
(400MHz, CDCl3)
1.98
2.96
2.02
2.06
3.00
4.03
9
8
7
6
5
4
3
2
1
0
-


171.23
142.04
128.39
128.35
125.84
77.34 CDCl3
77.03 CDCl3
76.71 CDCl3
64.37
35.45
28.20
27.73
21.00
0.00 TMS
OAc
4u
13C{1H} NMR
(101MHz, CDCl3)
128.39
128.35
200
180
160
140
120
100
80
60
40
20
0


7.778
7.759
7.600
7.581
7.259 CDCl3
5.036
4.764
4.437
4.420
3.999
3.335
2.080
1.619 HDO
0.000
7.424
7.406
7.387
7.338
7.335
7.320
7.317
7.301
7.298
4.165
4.152
4.139
3.487
3.473
3.459
3.445
anti-4v
17 : 3
syn-4v
1H NMR
(400MHz, CDCl3)
1.95
1.95
2.02
2.01
0.85
0.16
2.01
1.04
1.73
0.32
1.75
0.32
3.00
9
8
7
6
5
4
3
2
1
0
-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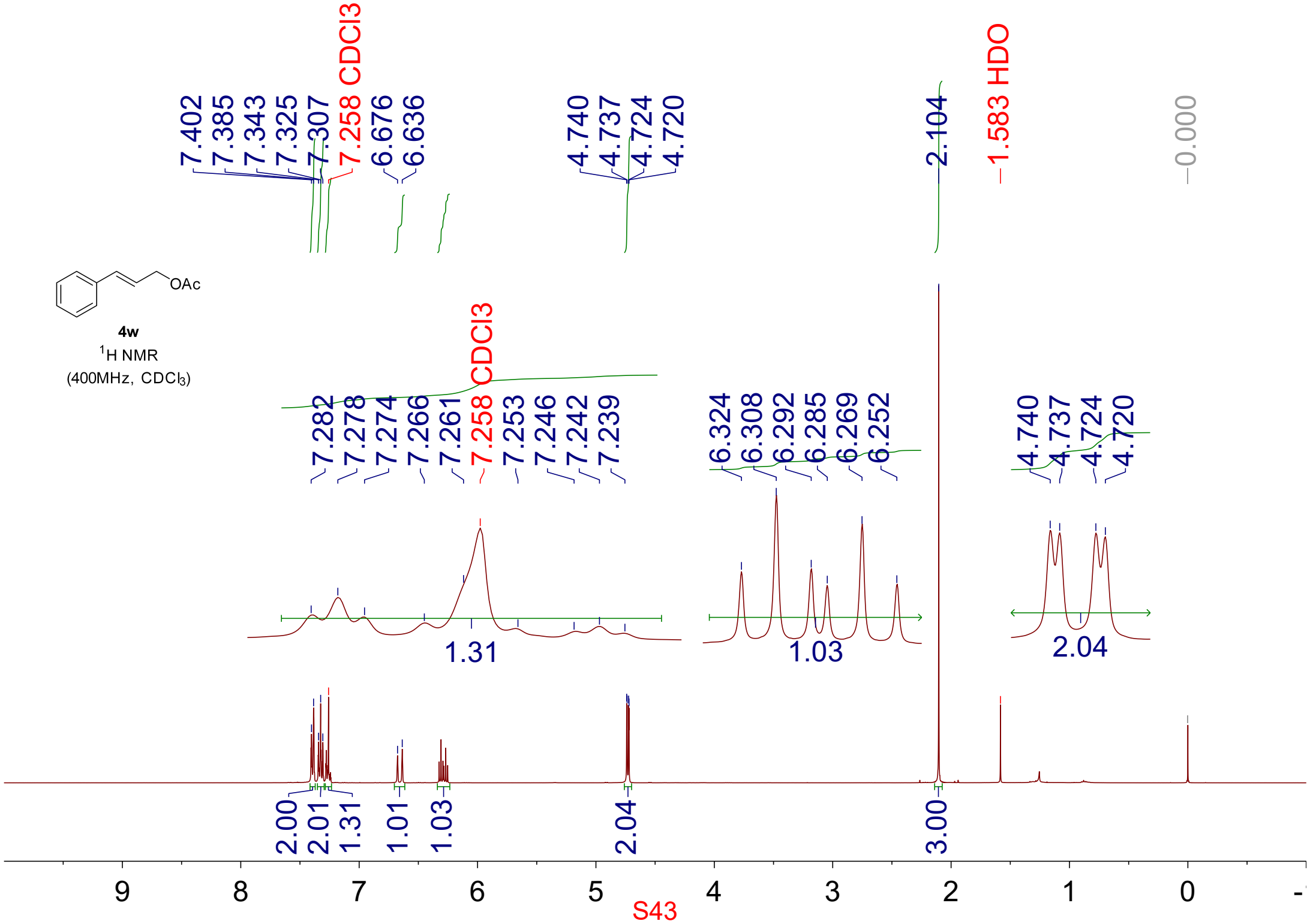
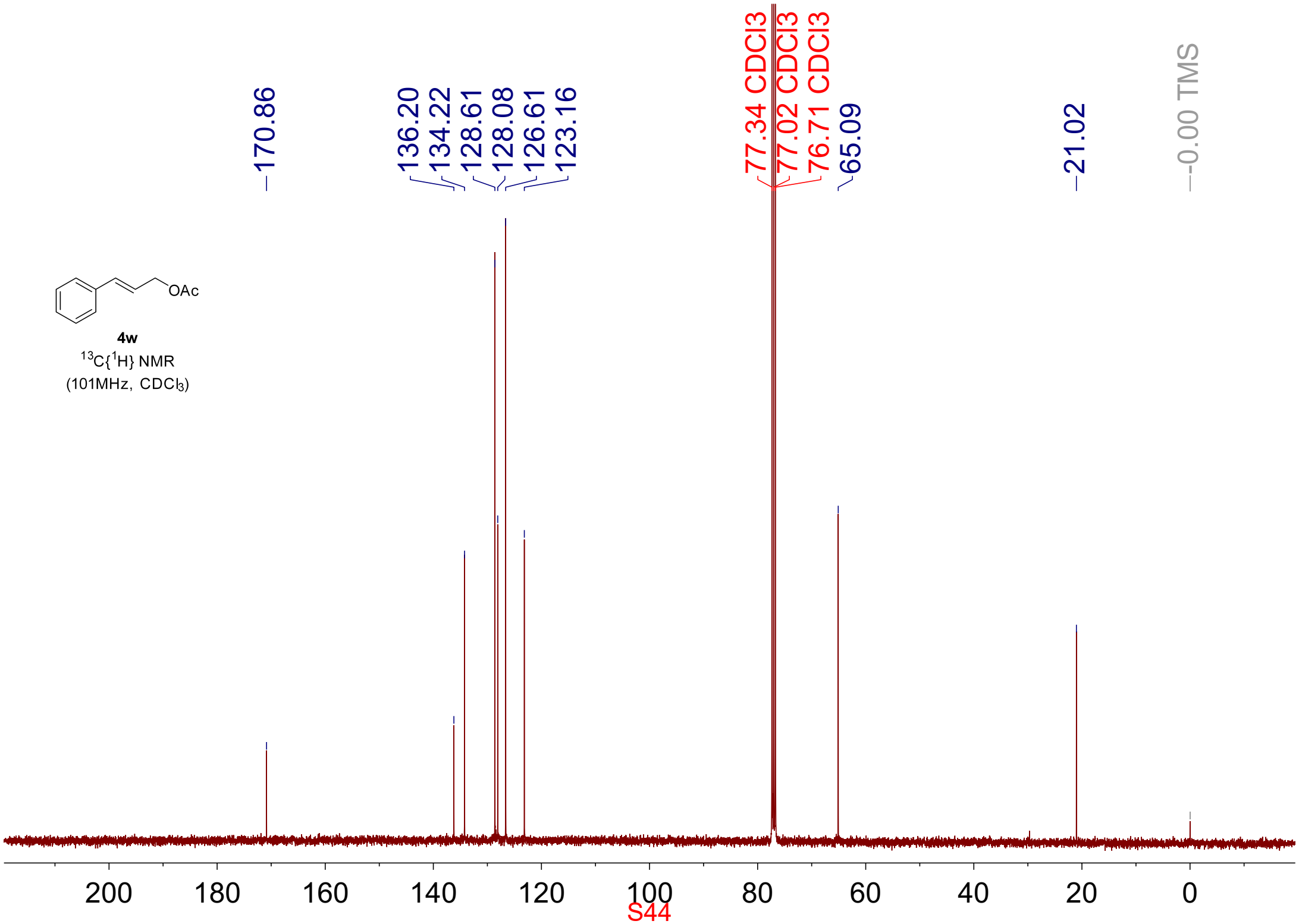
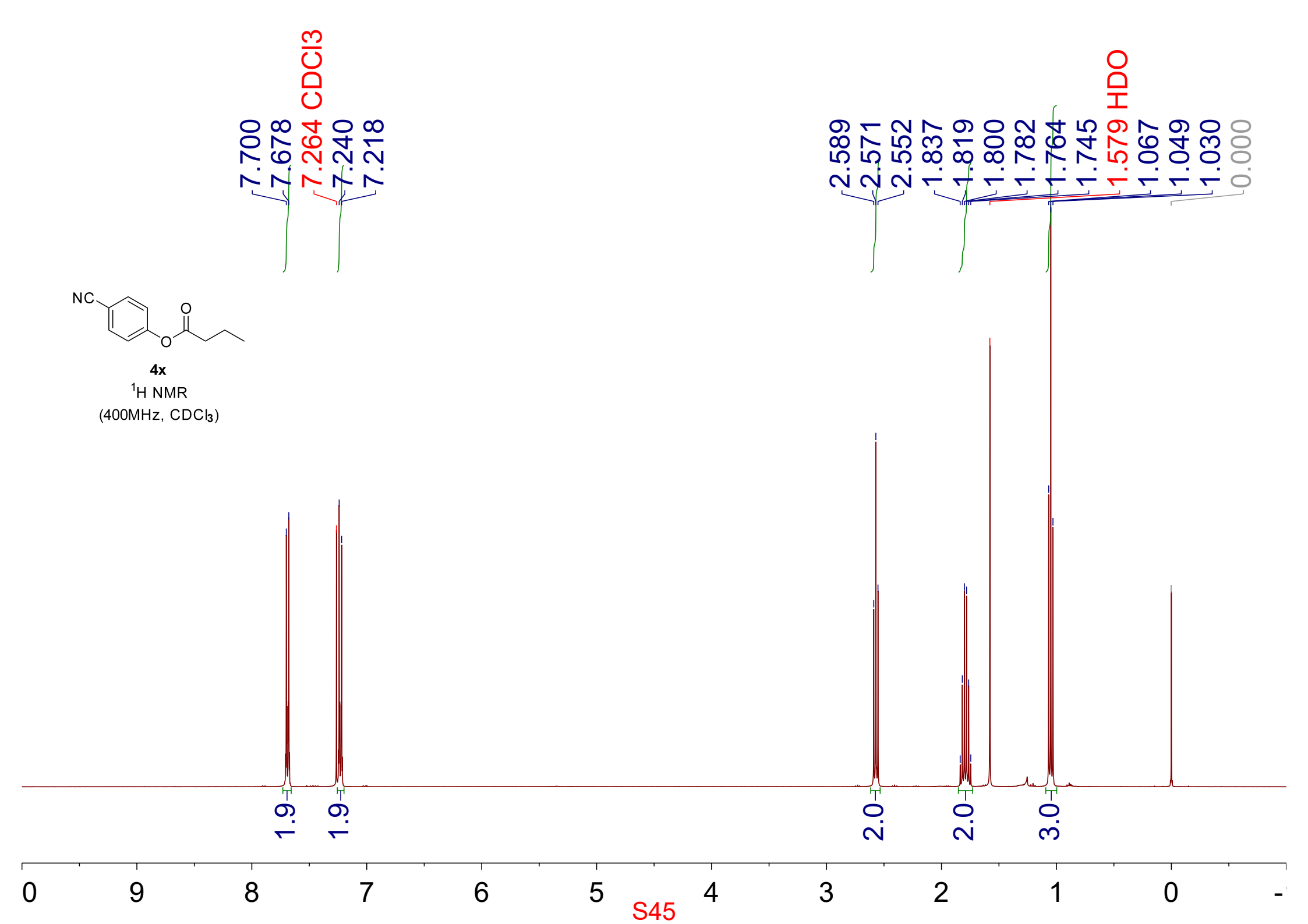
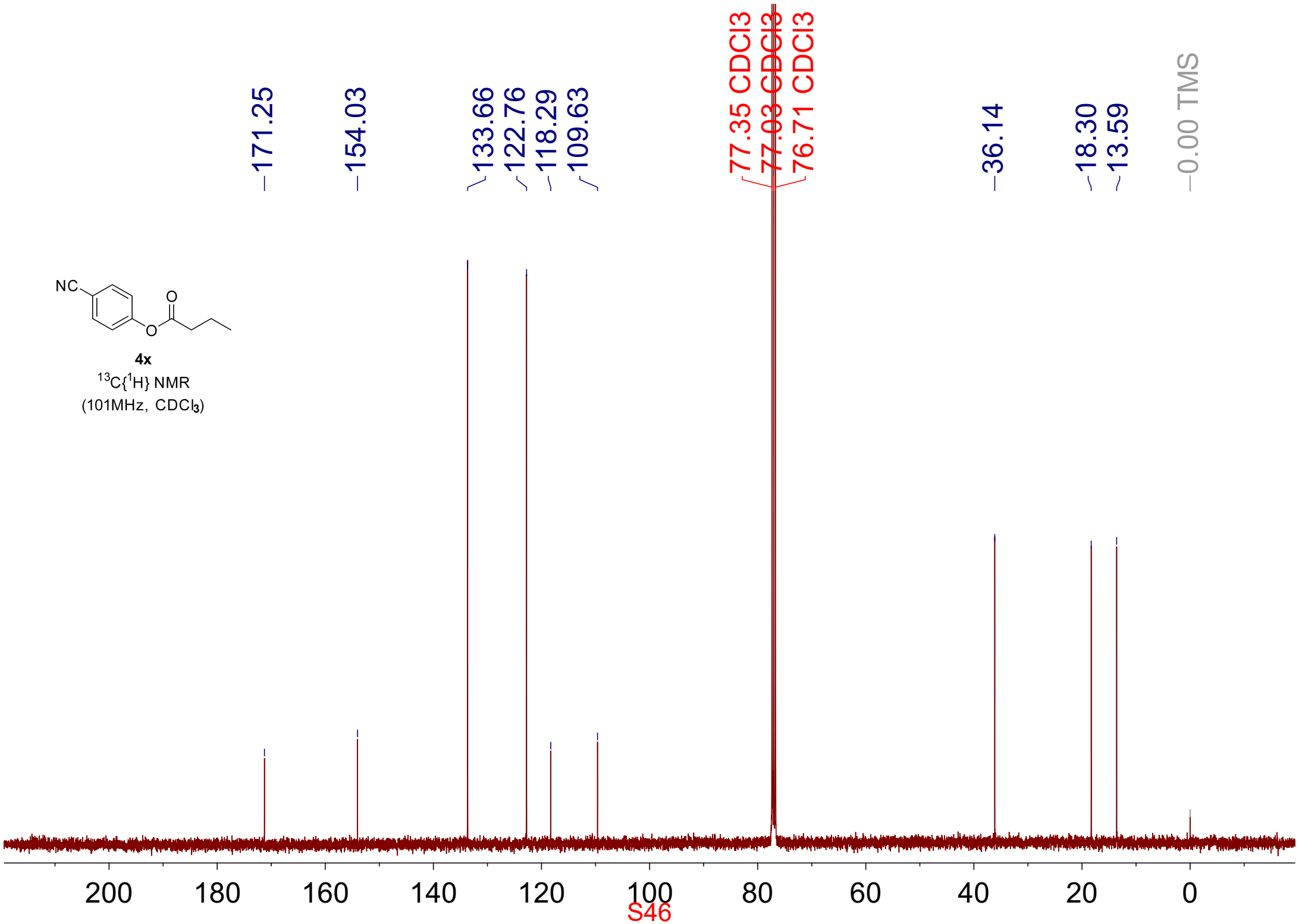
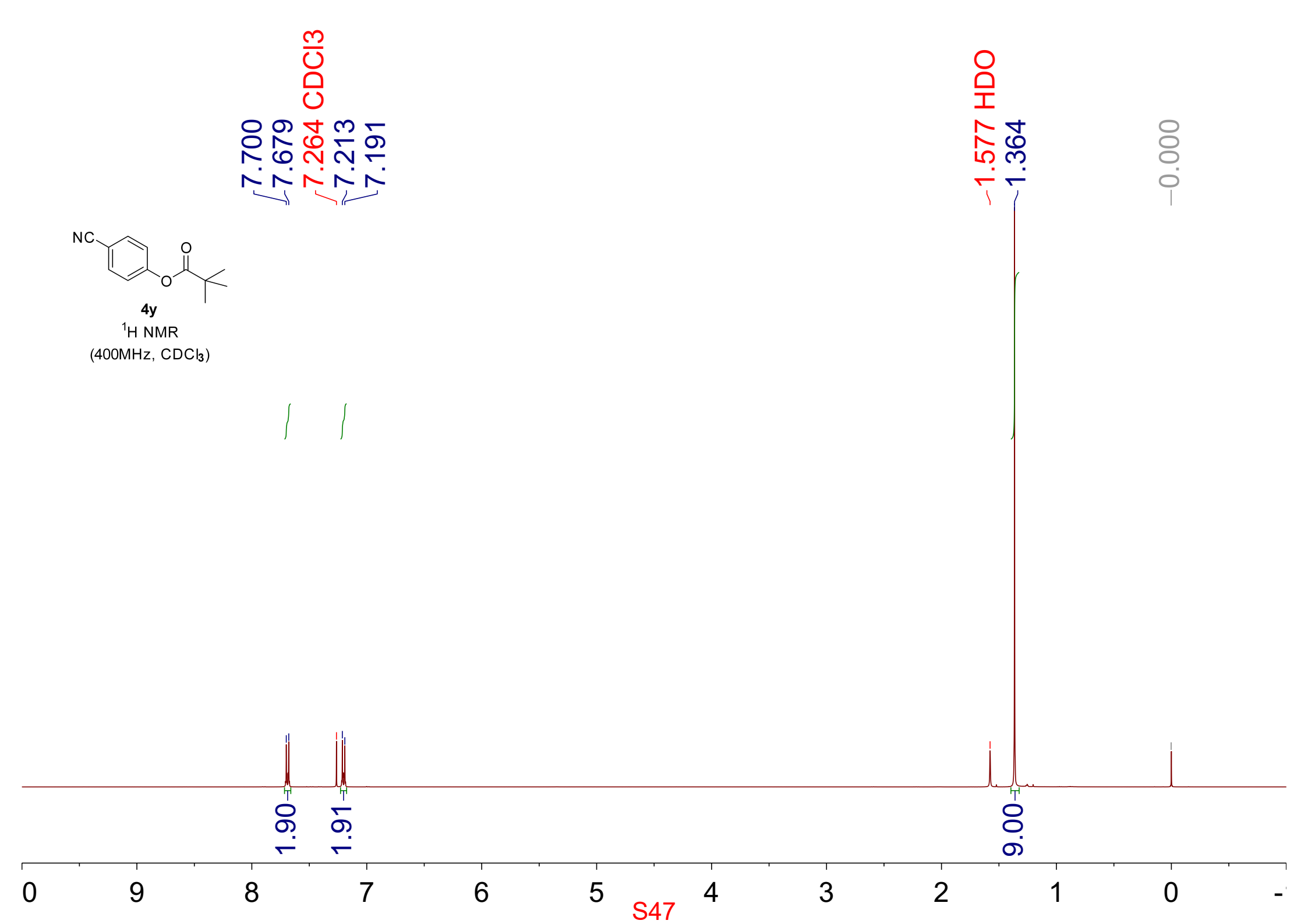
156.34
143.86
141.33
127.72
127.06
124.99
120.00
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
66.76
63.43
47.22
40.16
20.88
0.00 TMS
anti-4v
17 : 3
syn-4v
13C{1H} NMR
(101Hz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

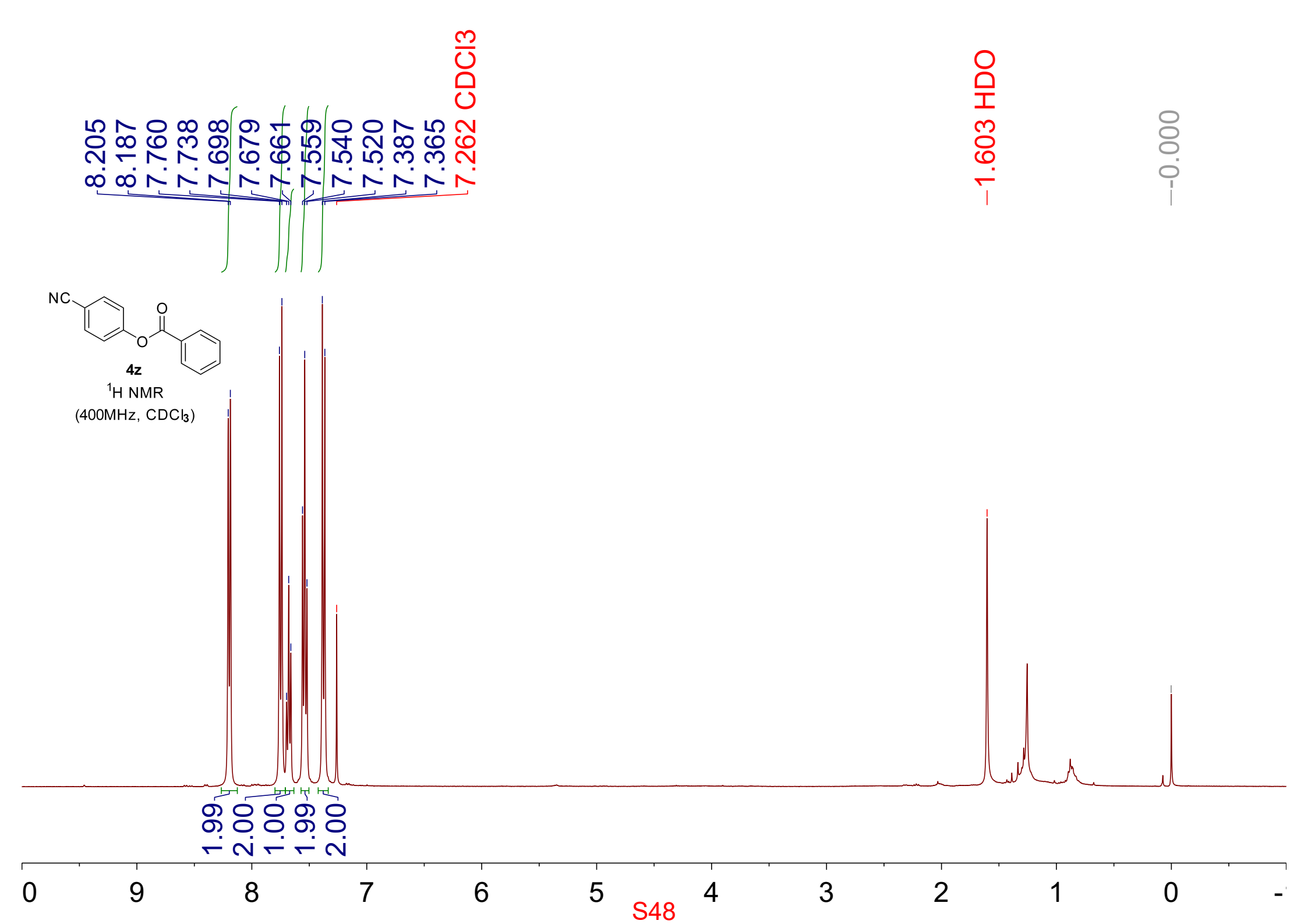

7.402
7.385
7.343
7.325
7.307
7.258 CDCl3
6.676
6.636
4.740
4.737
4.724
4.720
2.104
1.583 HDO
0.000
OAc
4w
1H NMR
(400MHz, CDCl3)
7.282
7.278
7.274
7.266
7.261
7.258 CDCl3
7.253
7.246
7.242
7.239
6.324
6.308
6.292
6.285
6.269
6.252
4.740
4.737
4.724
4.720
1.31
1.03
2.04
2.00
2.01
1.31
1.01
1.03
2.04
3.00
9
8
7
6
5
4
3
2
1
0
-

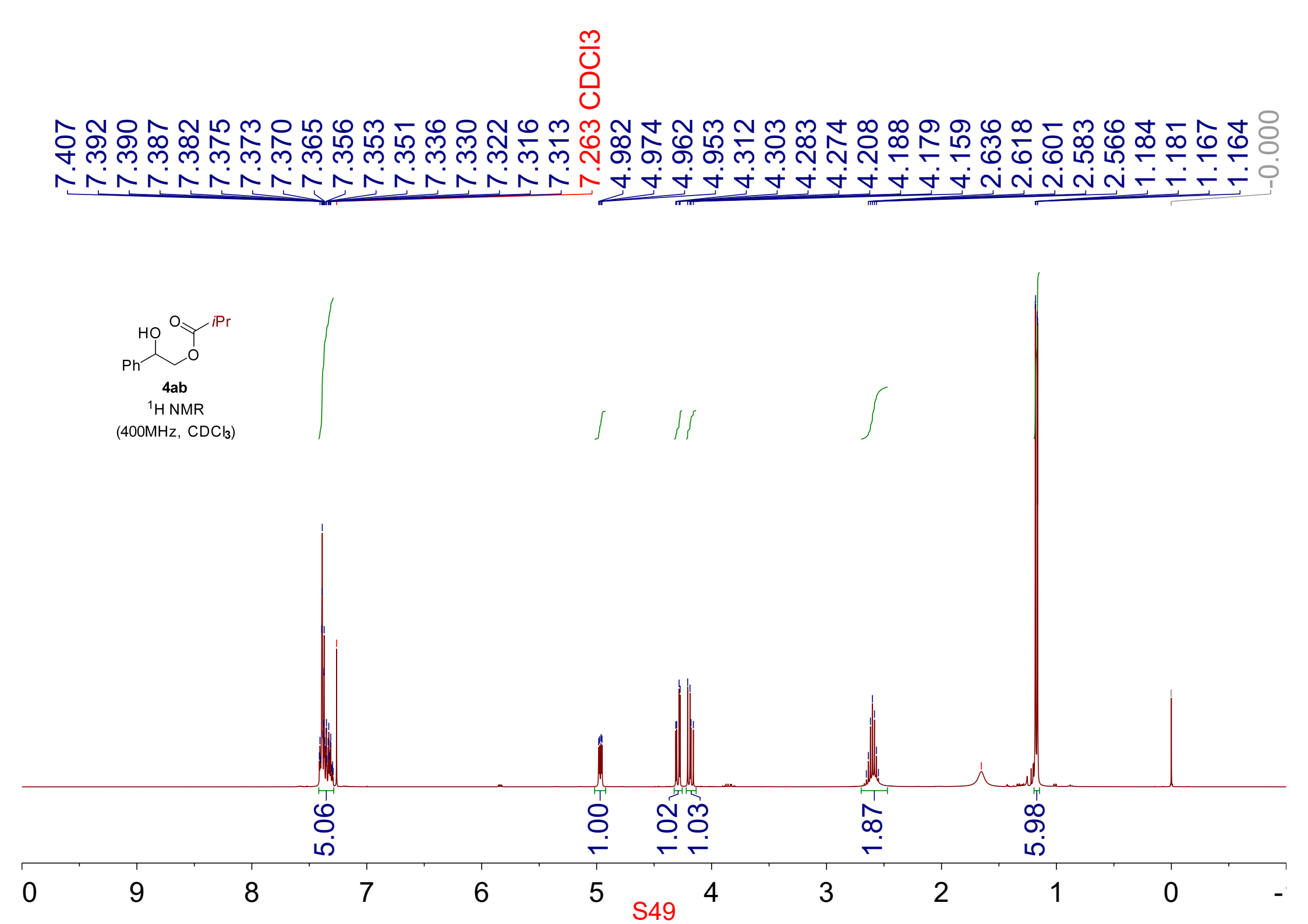

170.86
136.20
134.22
128.61
128.08
126.61
123.16
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
65.09
21.02
0.00 TMS
OAc
4w
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

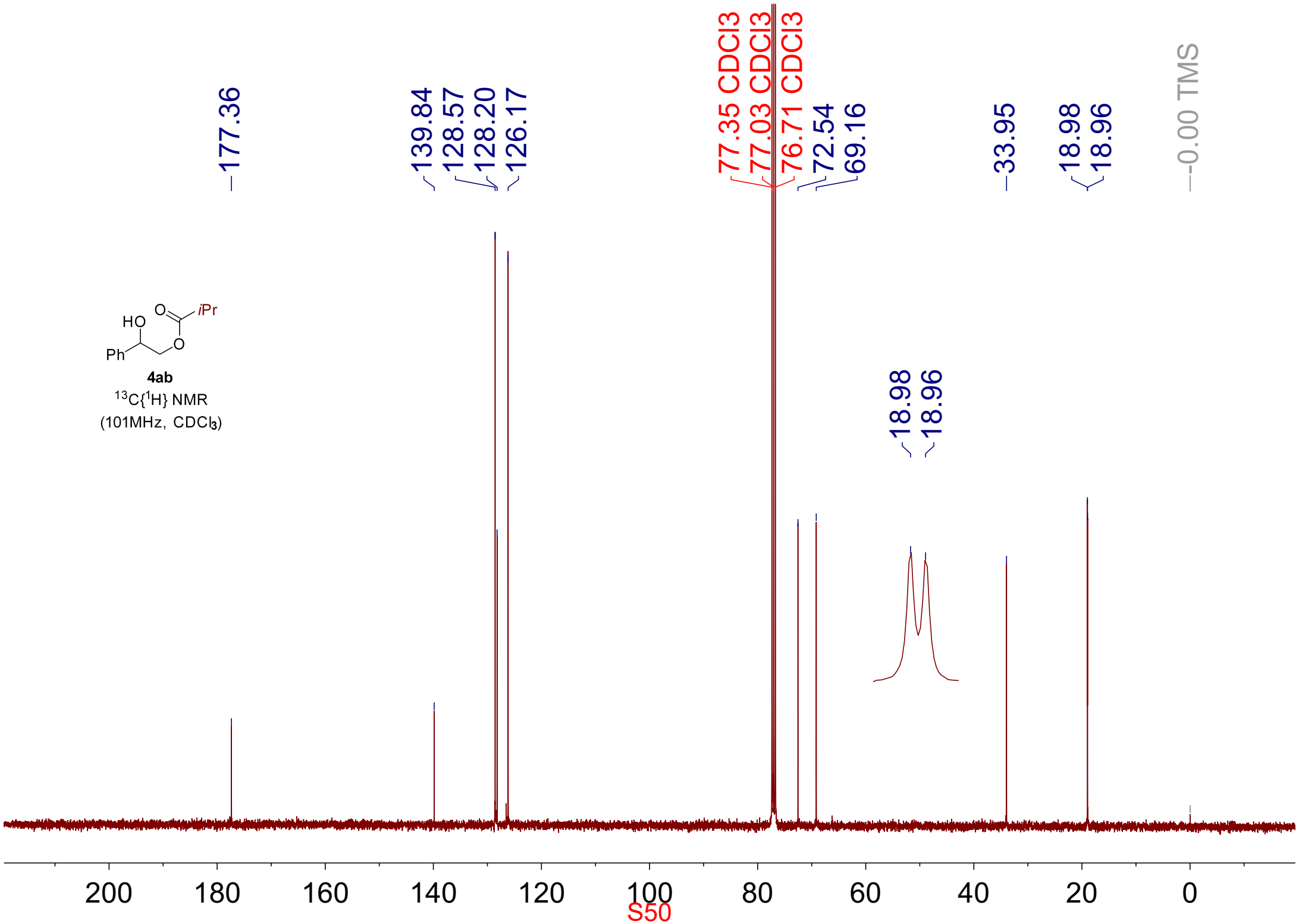

7.700
7.678
7.264 CDCl3
7.240
7.218
2.589
2.571
2.552
1.837
1.819
1.800
1.782
1.764
1.745
1.579 HDO
1.067
1.049
1.030
0.000
NC
O
O
4x
1H NMR
(400MHz, CDCl3)
1.9
1.9
2.0
2.0
3.0
0
9
8
7
6
5
4
3
2
1
0
-

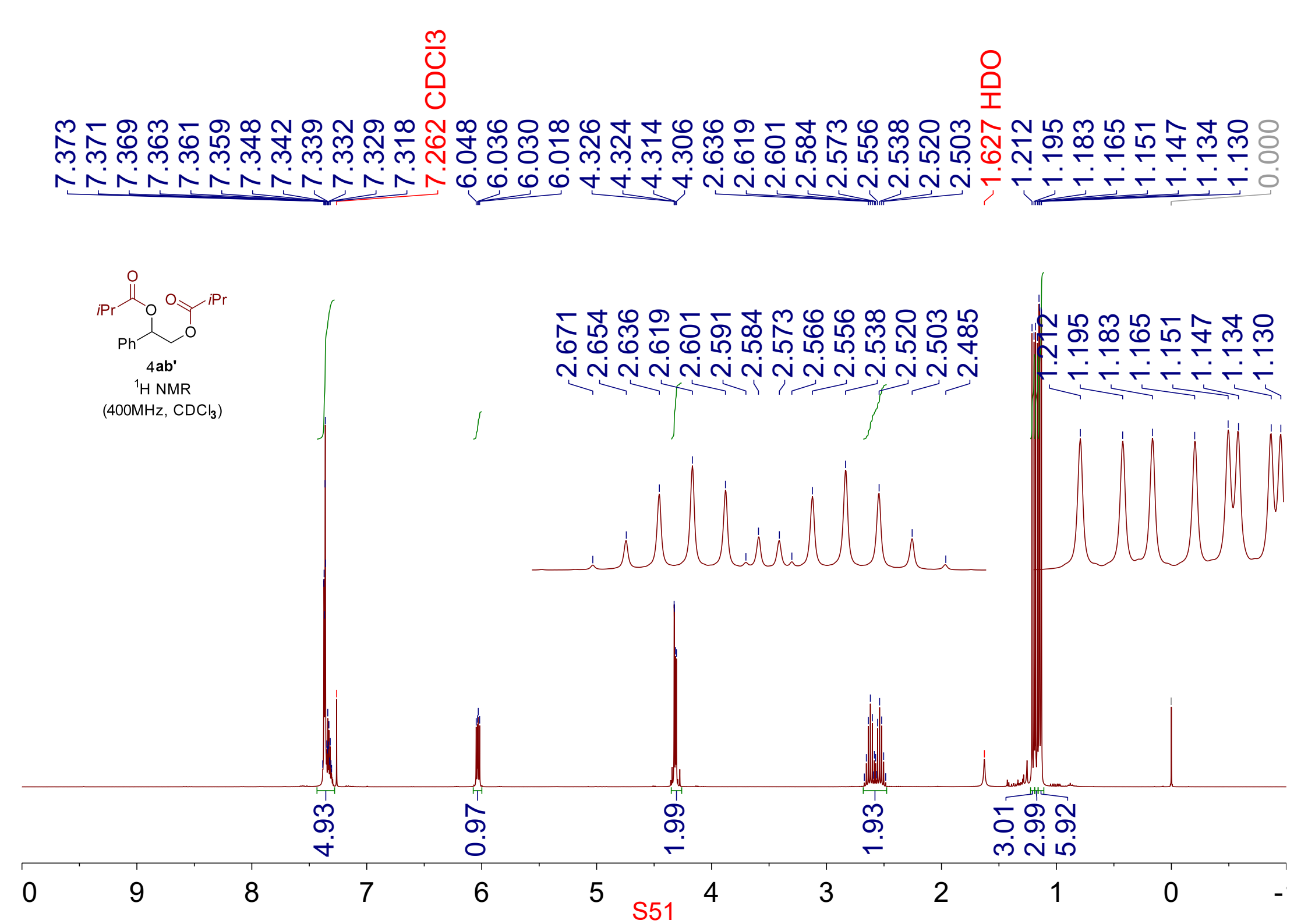

171.25
154.03
133.66
122.76
118.29
109.63
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
36.14
18.30
13.59
0.00 TMS
NC
O
O
4x
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0

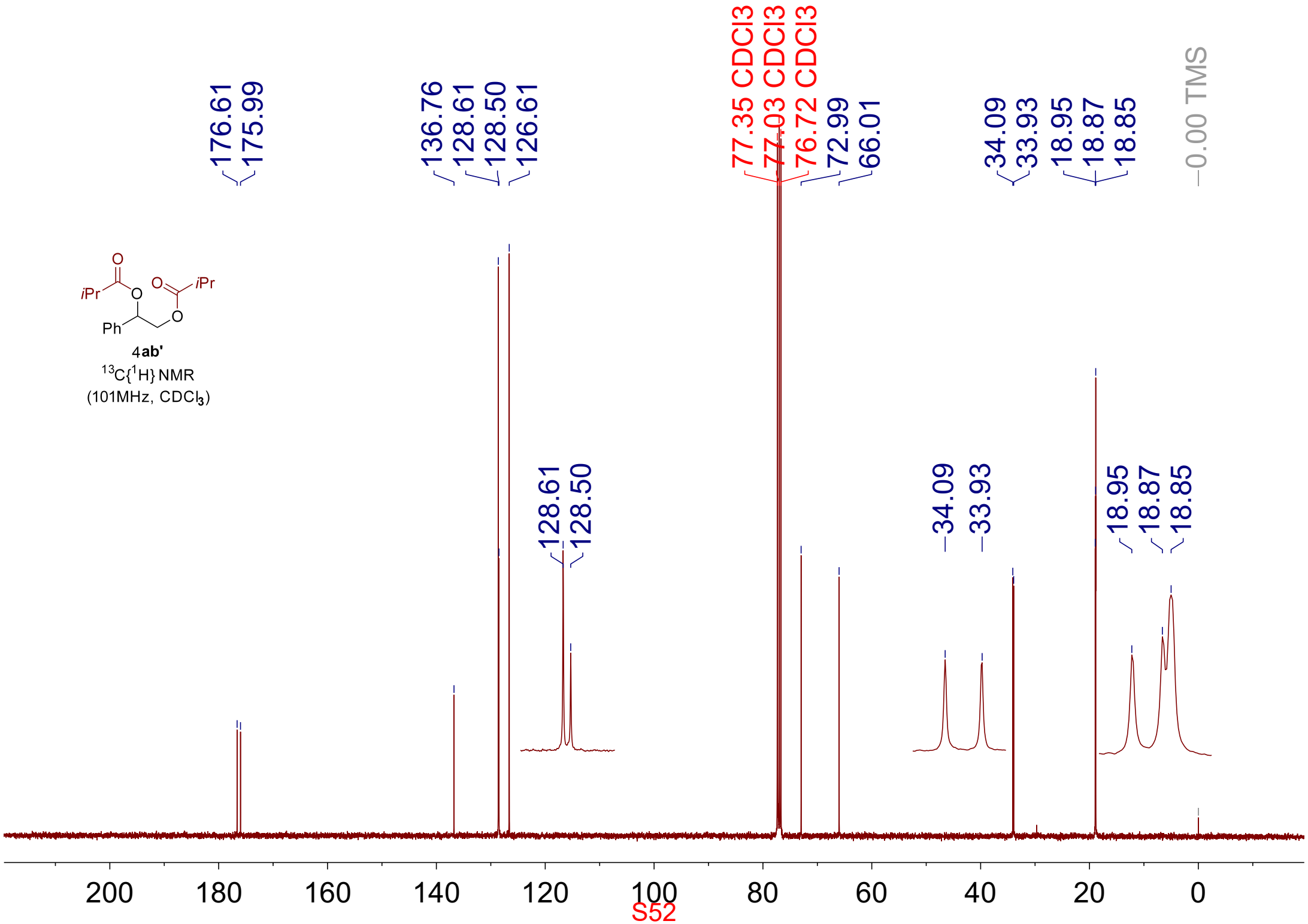

7.700
7.679
7.264 CDCl3
7.213
7.191
1.577 HDO
1.364
0.000
NC
O
O
4y
1H NMR
(400MHz, CDCl3)
1.90
1.91
9.00
0
9
8
7
6
5
4
3
2
1
0
-

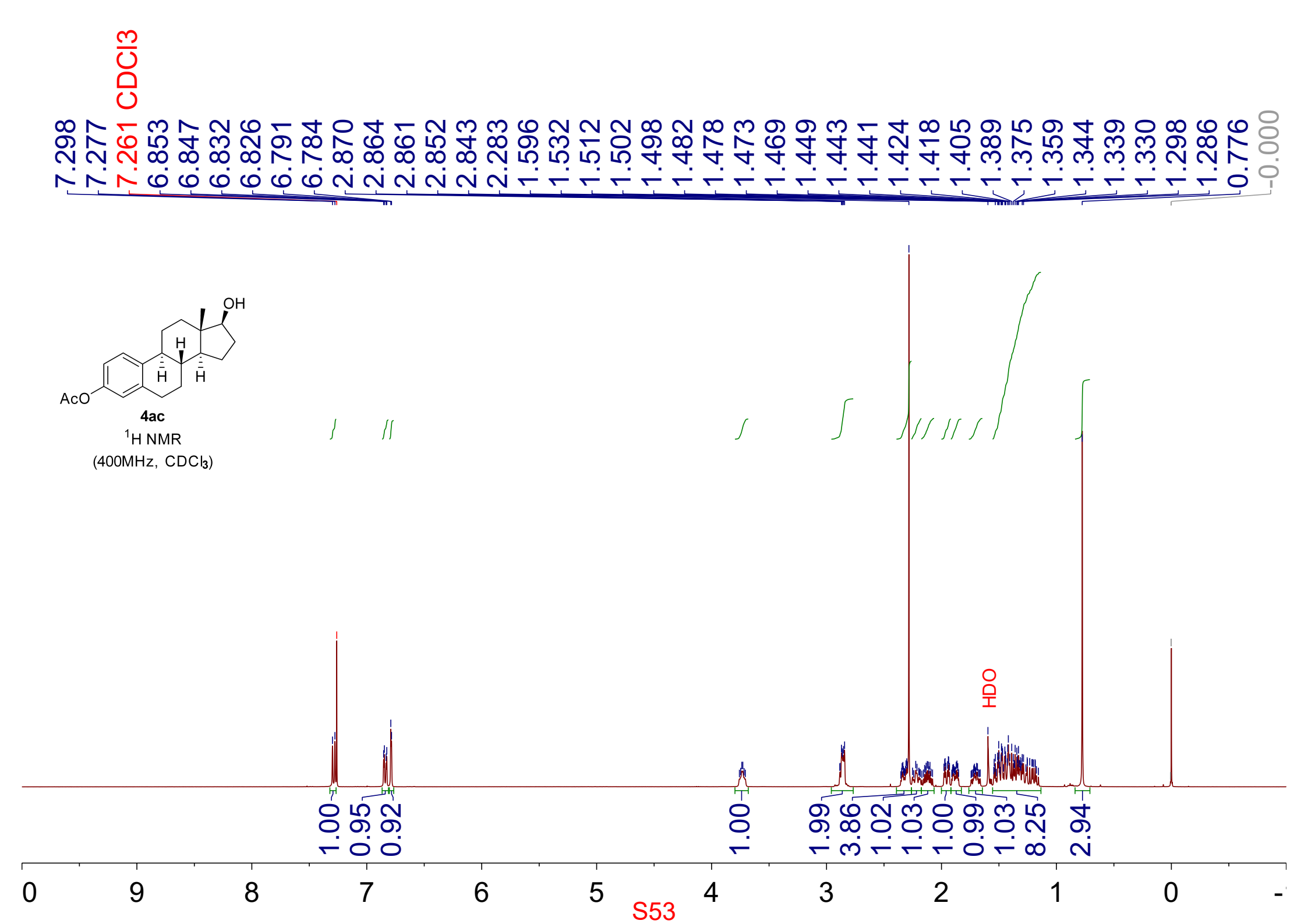

8.205
8.187
7.760
7.738
7.698
7.679
7.661
7.559
7.540
7.520
7.387
7.365
7.262 CDCl3
1.603 HDO
0.000
NC
O
O
4z
1H NMR
(400MHz, CDCl3)
1.99
2.00
1.00
1.99
2.00
0
9
8
7
6
5
4
3
2
1
0


7.407
7.392
7.390
7.387
7.382
7.375
7.373
7.370
7.365
7.356
7.353
7.351
7.336
7.330
7.322
7.316
7.313
7.263 CDCl3
4.982
4.974
4.962
4.953
4.312
4.303
4.283
4.274
4.208
4.188
4.179
4.159
2.636
2.618
2.601
2.583
2.566
1.184
1.181
1.167
1.164
-0.000
HO
O
iPr
Ph
O
4ab
1H NMR
(400MHz, CDCl3)
5.06
1.00
1.02
1.03
1.87
5.98
0
9
8
7
6
5
4
3
2
1
0
-


177.36
139.84
128.57
128.20
126.17
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
72.54
69.16
33.95
18.98
18.96
0.00 TMS
18.98
18.96
HO
O
iPr
Ph
O
4ab
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0


7.373
7.371
7.369
7.363
7.361
7.359
7.348
7.342
7.339
7.332
7.329
7.318
7.262 CDCl3
6.048
6.036
6.030
6.018
4.326
4.324
4.314
4.306
2.636
2.619
2.601
2.584
2.573
2.556
2.538
2.520
2.503
1.627 HDO
1.212
1.195
1.183
1.165
1.151
1.147
1.134
1.130
0.000
iPr
iPr
Ph
4ab'
1H NMR
(400MHz, CDCl3)
2.671
2.654
2.636
2.619
2.601
2.591
2.584
2.573
2.566
2.556
2.538
2.520
2.503
2.485
1.212
1.195
1.183
1.165
1.151
1.147
1.134
1.130
4.93
0.97
1.99
1.93
3.01
2.99
5.92
0
9
8
7
6
5
4
3
2
1
0
-


176.61
175.99
136.76
128.61
128.50
126.61
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
72.99
66.01
34.09
33.93
18.95
18.87
18.85
0.00 TMS
128.61
128.50
34.09
33.93
18.95
18.87
18.85
iPr
iPr
Ph
4ab'
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0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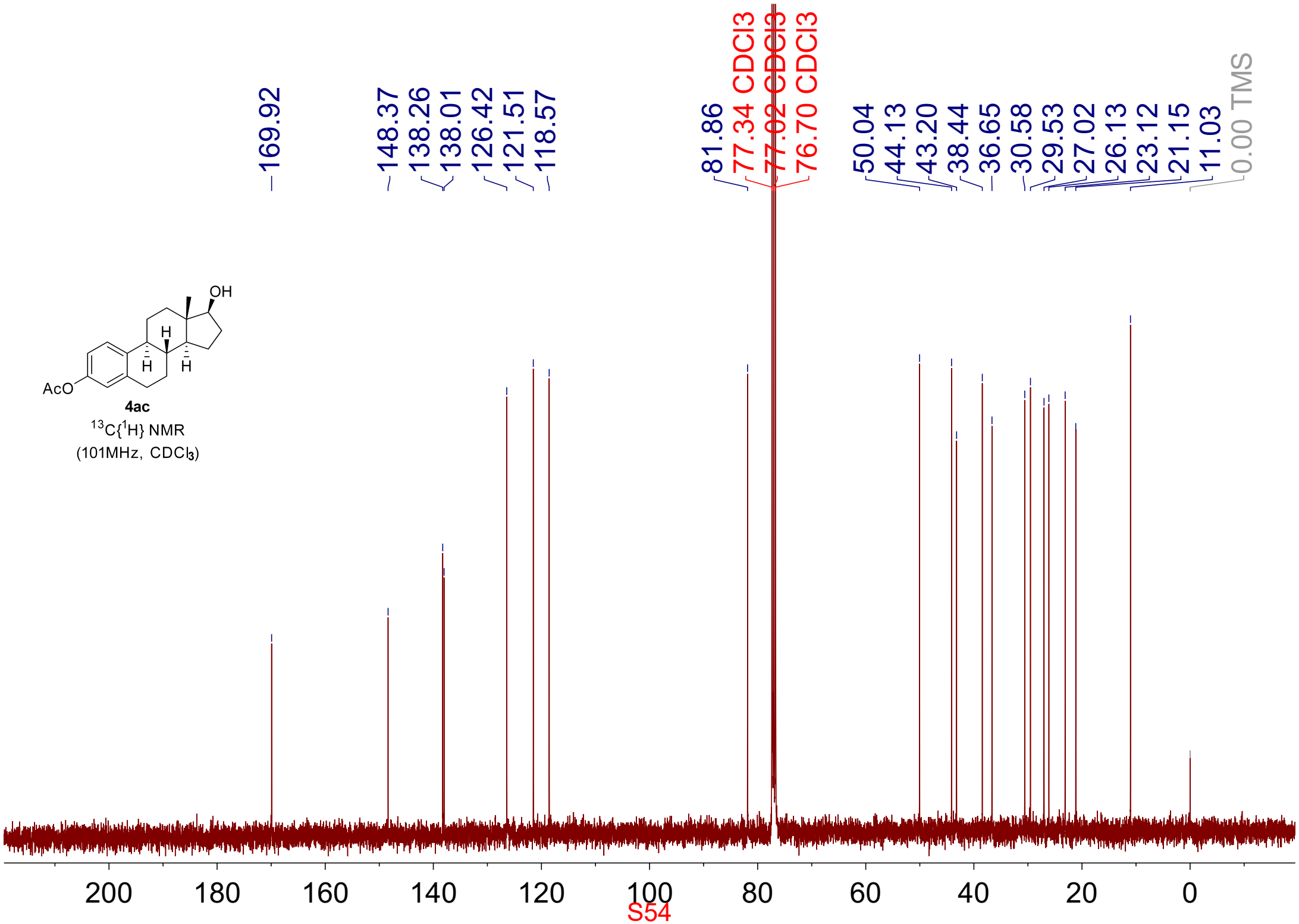
6.847
6.832
6.826
6.791
6.784
2.870
2.864
2.861
2.852
2.843
2.283
1.596
1.532
1.512
1.502
1.498
1.482
1.478
1.473
1.469
1.449
1.443
1.441
1.424
1.418
1.405
1.389
1.375
1.359
1.344
1.339
1.330
1.298
1.286
0.776
-0.000
OH
H
H
H
AcO
4ac
1H NMR
(400MHz, CDCl3)
HDO
1.00
0.95
0.92
1.00
1.99
3.86
1.02
1.03
1.00
0.99
1.03
8.25
2.94
0
9
8
7
6
5
4
3
2
1
0
-


169.92
148.37
138.26
138.01
126.42
121.51
118.57
81.86
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
50.04
44.13
43.20
38.44
36.65
30.58
29.53
27.02
26.13
23.12
21.15
11.03
0.00 TMS
OH
H
H
H
AcO
4ac
13C{1H} NMR
(101MHz, CDCl3)
200
180
160
140
120
100
80
60
40
20
0