

## Supporting Information

### One-pot Synthesis of *N*-Sulfonylamidines from *N*-Acylsulfonamides Enabled by a Metal Triflate-Mediated Nonhydrolytic *N*-Deacylation

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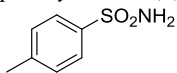
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#### Table of Contents

Experiment-----	S2
References-----	S10
<sup>1</sup> H and <sup>13</sup> C{ <sup>1</sup> H} NMR spectra of compounds-----	S11
ESI HRMS spectra of compounds <b>9s</b> and <b>11</b> -----	S62

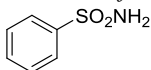
**General Information.** Anhydrous ethanol and methanol were of Extra Dry grade with molecular sieves (water  $\leq$  50 ppm). 95% EtOH was of industrial grade. For reactions conducted at elevated temperatures, an oil bath was used as the heat source (silicone oil). Thin layer chromatography analyses were performed on precoated GF254 silica gel plates and were visualized under UV 254 nm light. NMR spectra were recorded using a Bruker AVANCE-400 FT NMR spectrometer with TMS as the internal standard. ESI HRMS was recorded on a Waters Xevo G2-XS QToF mass spectrometer. Melting points were uncorrected. PE = petroleum ether (60–90).

*p*-Tosylamide (**2**).



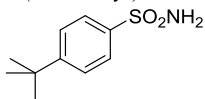
To a solution of *N*-tosylacetamide (**1**, 0.213 g, 1 mmol) in 95% ethanol (20 mL) was added in one portion Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.05 equiv). The mixture was stirred at 75 °C for 18 h. After cooling to room temperature, silica (100 mesh, about 3 g) was added to the mixture. The solvent was removed by a rotary evaporator, and the residue was purified by column chromatography (eluent: PE/EtOAc = 3:1) to afford **2** as a white solid; yield: 0.166 g (97%); mp 135–137 °C (lit.<sup>[1]</sup> 136.5–137.5 °C); *R*<sub>f</sub> = 0.55 (PE/EtOAc = 1:1). From *N*-tosylpropionamide (**3s**, 0.227 g, 1 mmol); yield: 0.165 g (96%). From *N*-tosylisobutyramide (**3t**, 0.242 g, 1 mmol); yield: 0.169 g (98%). From *N*-tosyloctanamide (**3u**, 0.297 g, 1 mmol); yield: 0.169 g (98%). From *N*-tosylcyclopropanecarboxamide (**3v**, 0.239 g, 1 mmol); yield: 0.166 g (97%). From *N*-tosylcyclohexanecarboxamide (**3w**, 0.141 g, 0.5 mmol) and Cu(OTf)<sub>2</sub> (0.009 g, 0.025 mmol, 0.05 equiv); yield: 0.074 g (86%). From *p*-tosylurea (**3x**, 0.214 g, 1 mmol); yield: 0.144 g (84%). From *N*-tosylpivalamide (**3y**, 0.242 g, 1 mmol); yield: 0.092 g (53%). From 2-phenyl-*N*-tosylacetamide (**3aa**, 0.152 g, 0.5 mmol) and Cu(OTf)<sub>2</sub> (0.072 g, 0.2 mmol, 0.4 equiv); yield: 0.081 g (90%). From *N*-tosylbenzamide (**3ab**, 0.137 g, 0.5 mmol) and Cu(OTf)<sub>2</sub> (0.072 g, 0.2 mmol, 0.4 equiv); yield: 0.062 g (72%). From *N*-tosylcinnamamide (**3ac**, 0.151 g, 0.5 mmol) and Cu(OTf)<sub>2</sub> (0.072 g, 0.2 mmol, 0.4 equiv), stirred for 2 days at 75 °C; yield: 0.079 g (92%). From **1** (0.213 g, 1 mmol) using Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.05 equiv) as catalyst, stirred for 18 h at 75 °C in *t*BuOH; yield: 0.009 g (5%). From **1** (0.213 g, 1 mmol) using Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.05 equiv) as catalyst, in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (0.417 g, 2 mmol, 2 equiv), stirred for 18 h at 75 °C; yield: 0.158 g (92%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.71 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (br s, 2H), 2.37 (s, 3H).

Benzenesulfonamide (**4a**).



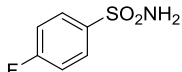
From *N*-(phenylsulfonyl)acetamide (**3a**, 0.199 g, 1 mmol); white solid; yield: 0.148 g (94%); mp 153.5–155.5 °C (lit.<sup>[1]</sup> 150.5–152.5 °C); *R*<sub>f</sub> = 0.35 (PE/EtOAc = 2:1). From *N*-(phenylsulfonyl)pivalamide (**3ad**, 0.241 g, 1 mmol) and Cu(OTf)<sub>2</sub> (0.182 g, 0.5 mmol, 0.5 equiv) stirred in 95% ethanol for 2 days at 75 °C; yield: 0.115 g (73%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.88–7.78 (m, 2H), 7.65–7.53 (m, 3H), 7.36 (s, 2H).

4-(*tert*-Butyl)benzenesulfonamide (**4b**).



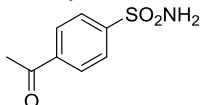
From *N*-(4-(*tert*-butyl)phenylsulfonyl)acetamide (**3b**, 0.255 g, 1 mmol) using Sc(OTf)<sub>3</sub> (0.026 g, 0.05 mmol, 0.05 equiv) as the catalyst; white solid; yield: 0.207 g (97%); mp 136–138 °C (lit.<sup>[2]</sup> 135–138 °C); *R*<sub>f</sub> = 0.79 (PE/EtOAc = 1:1). From **3b** (0.256 g, 1 mmol) using Y(OTf)<sub>3</sub> (0.025 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.198 g (92%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.76 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 2H), 1.31 (s, 9H).

4-Fluorobenzenesulfonamide (**4c**).



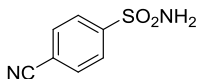
From *N*-((4-fluorophenyl)sulfonyl)acetamide (**3c**, 0.217 g, 1 mmol) using Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.167 g (95%); mp 125–126 °C (lit.<sup>[1]</sup> 125–126 °C); *R*<sub>f</sub> = 0.66 (PE/EtOAc = 1:1). From **3c** (0.221 g, 1.02 mmol) using Sc(OTf)<sub>3</sub> (0.025 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.165 g (92%). From **3c** (0.217 g, 1 mmol) using Y(OTf)<sub>3</sub> (0.026 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.164 g (93%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.97–7.79 (m, 2H), 7.51–7.32 (m, 4H).

4-Acetylbenzenesulfonamide (**4d**).



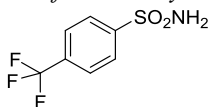
From *N*-((4-acetylphenyl)sulfonyl)acetamide (**3d**, 0.241 g, 1 mmol); white solid; yield: 0.142 g (71%); mp 182–184 °C (lit.<sup>[3]</sup> 176–178 °C); *R*<sub>f</sub> = 0.23 (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.13 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.56 (s, 2H), 2.64 (s, 3H).

4-Cyanobenzenesulfonamide (**4e**).



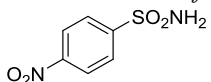
From *N*-((4-cyanophenyl)sulfonyl)acetamide (**3e**, 0.224 g, 1 mmol); white solid; yield: 0.156 g (85%); mp 171–173 °C (lit.<sup>[1]</sup> 168–170 °C);  $R_f = 0.51$  (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.08 (d,  $J = 8.5$  Hz, 1H), 7.98 (d,  $J = 8.4$  Hz, 1H), 7.67 (s, 1H).

*4*-Trifluoromethylbenzenesulfonamide (**4f**).



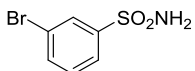
From *N*-((4-trifluoromethylphenyl)sulfonyl)acetamide (**3f**, 0.297 g, 1.11 mmol) using Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.05 equiv) as the catalyst; white solid; yield: 0.235 g (93%); mp 178.5–179.5 °C (lit.<sup>[2]</sup> 175–180 °C);  $R_f = 0.76$  (PE/EtOAc = 1:1). From **3f** (0.298 g, 1.11 mmol) using Sc(OTf)<sub>3</sub> (0.025 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.239 g (95%). From **3f** (0.297 g, 1.11 mmol) using Y(OTf)<sub>3</sub> (0.026 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.239 g (95%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.05 (d,  $J = 8.2$  Hz, 2H), 7.98 (d,  $J = 8.4$  Hz, 2H), 7.64 (s, 2H).

*4*-Nitrobenzenesulfonamide (**4g**).



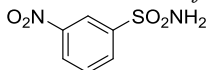
From *N*-((4-nitrophenyl)sulfonyl)acetamide (**3g**, 0.180 g, 0.74 mmol); white solid; yield: 0.102 g (68%); mp 182–184 °C (lit.<sup>[2]</sup> 178–180 °C);  $R_f = 0.43$  (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.42 (d,  $J = 8.8$  Hz, 2H), 8.07 (d,  $J = 8.8$  Hz, 2H), 7.74 (s, 2H).

*3*-Bromobenzenesulfonamide (**4h**).



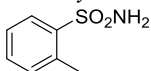
From *N*-((3-bromophenyl)sulfonyl)acetamide (**3h**, 0.278 g, 1 mmol); white solid; yield: 0.223 g (94%); mp 158–160 °C (lit.<sup>[2]</sup> 151–156 °C; lit.<sup>[1]</sup> 155–157 °C);  $R_f = 0.58$  (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.98 (t,  $J = 1.8$  Hz, 1H), 7.85–7.82 (m, 1H), 7.82–7.81 (m, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.52 (br s, 2H).

*3*-Nitrobenzenesulfonamide (**4i**).



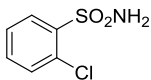
From *N*-((3-nitrophenyl)sulfonyl)acetamide (**3i**, 0.244 g, 1 mmol) using Sc(OTf)<sub>3</sub> (0.024 g, 0.05 mmol, 0.05 equiv) as the catalyst; white solid; yield: 0.188 g (93%); mp 166.5–168.5 °C (lit.<sup>[2]</sup> 166–168 °C);  $R_f = 0.50$  (PE/EtOAc = 1:1). From **3i** (0.244 g, 1 mmol) using Bi(OTf)<sub>3</sub> (0.033 g, 0.05 mmol, 0.05 equiv) as the catalyst; yield: 0.196 g (97%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.60 (t,  $J = 2.1$  Hz, 1H), 8.49–8.42 (m, 1H), 8.25 (d,  $J = 7.8$  Hz, 1H), 7.90 (t,  $J = 8.0$  Hz, 1H), 7.73 (s, 2H).

*2*-Methylbenzenesulfonamide (**4j**).



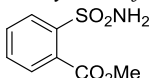
From *N*-(*o*-tolylsulfonyl)acetamide (**3j**, 0.213 g, 1 mmol); white solid; yield: 0.155 g (90%); mp 159–160 °C (lit.<sup>[2]</sup> 156–158 °C);  $R_f = 0.60$  (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.87–7.83 (m, 1H), 7.48 (td,  $J_1 = 7.7$  Hz,  $J_2 = 1.4$  Hz, 1H), 7.41–7.33 (m, 4H), 2.59 (s, 3H).

*2*-Chlorobenzenesulfonamide (**4k**).



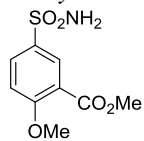
From *N*-((2-chlorophenyl)sulfonyl)acetamide (**3k**, 0.234 g, 1 mmol); white solid; yield: 0.158 g (82%); mp 194–195 °C (lit.<sup>[2]</sup> 189–193 °C);  $R_f = 0.74$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.99 (dd,  $J_1 = 7.8$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.68–7.57 (m, 4H), 7.53 (td,  $J_1 = 7.5$  Hz,  $J_2 = 1.6$  Hz, 1H).

*Methyl 2-sulfamoylbenzoate (4l).*



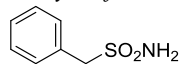
From methyl 2-(*N*-acetylsulfamoyl)benzoate (**3l**, 0.257 g, 1 mmol); white solid; yield: 0.180 g (83%); mp 127–129 °C (lit.<sup>[2]</sup> 126–128 °C);  $R_f = 0.65$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.98 (dd,  $J_1 = 7.3$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.77–7.64 (m, 3H), 7.32 (s, 2H), 3.84 (s, 3H).

**Methyl 2-methoxy-5-sulfamoylbenzoate (4m).**



From methyl 5-(*N*-acetylsulfamoyl)-2-methoxybenzoate (**3m**, 0.287 g, 1 mmol) and Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.05 equiv); off-white solid; yield: 0.199 g (81%); mp 179–181 °C (lit.<sup>[2]</sup> 175–177 °C); *R*<sub>f</sub> = 0.22 (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.11 (d, *J* = 2.5 Hz, 1H), 7.96 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 3H), 3.91 (s, 3H), 3.83 (s, 3H).

**Benzylsulfonamide (4n).**



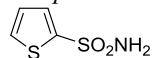
From *N*-(benzylsulfonyl)acetamide (**3n**, 0.213 g, 1 mmol); white solid; yield: 0.168 g (98%); mp 105.5–107.5 °C (lit.<sup>[4]</sup> 102–104 °C); *R*<sub>f</sub> = 0.18 (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.43–7.31 (m, 5H), 6.85 (s, 2H), 4.27 (s, 2H).

**tert-Butylsulfonamide (4o).**



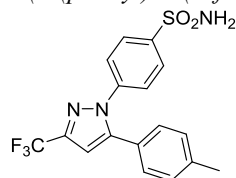
From *N*-(*tert*-butylsulfonyl)acetamide (**3o**, 0.180 g, 1 mmol); purified *via* recrystallization (EtOAc/hexane); white solid; yield: 0.129 g (94%); mp 166–169 °C (lit.<sup>[5]</sup> 162–165 °C). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 6.62 (br s, 2H), 1.27 (s, 9H).

**Thiophene-2-sulfonamide (4p).**



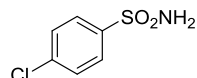
From *N*-(thiophen-2-ylsulfonyl)acetamide (**3p**, 0.410 g, 2 mmol); white solid; yield: 0.301 g (92%); mp 149–150 °C (lit.<sup>[1]</sup> 145–146 °C); *R*<sub>f</sub> = 0.52 (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.84 (dd, *J*<sub>1</sub> = 4.9 Hz, *J*<sub>2</sub> = 1.4 Hz, 1H), 7.65 (s, 2H), 7.56 (dd, *J*<sub>1</sub> = 3.7 Hz, *J*<sub>2</sub> = 1.4 Hz, 1H), 7.14 (dd, *J*<sub>1</sub> = 5.0 Hz, *J*<sub>2</sub> = 3.7 Hz, 1H).

**4-(5-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (4q, celecoxib).**



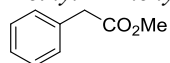
From *N*-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)acetamide (**3q**, 0.213 g, 0.5 mmol); white solid; yield: 0.156 g (81%); mp 164–165.5 °C (lit.<sup>[2]</sup> 157–159 °C); *R*<sub>f</sub> = 0.59 (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.54 (s, 2H), 7.26–7.18 (m, 5H), 2.32 (s, 3H).

**4-Chlorobenzenesulfonamide (4r).**



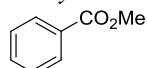
From chlorpropamide (**3r**, 0.275 g, 1.05 mmol); white solid; yield: 0.176 g (87%); mp 146.5–148.5 °C (lit.<sup>[1]</sup> 143.5–145.5 °C); *R*<sub>f</sub> = 0.49 (PE/EtOAc = 2:1). From *N*-((4-chlorophenyl)sulfonyl)pivalamide (**3z**, 0.276 g, 1 mmol) and Cu(OTf)<sub>2</sub> (0.136 g, 0.4 mmol, 0.4 equiv) stirred for 2 days at 75 °C; yield: 0.168 g (87%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.48 (s, 2H).

**Methyl 2-Phenylacetate (5).**<sup>[2]</sup>



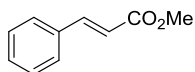
Isolated during deacylation of 2-phenyl-*N*-tosylacetamide (**3aa**); colorless oil; yield: 0.034 g (43%); *R*<sub>f</sub> = 0.60 (PE/EtOAc = 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37–7.23 (m, 5H), 3.68 (s, 3H), 3.63 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 172.1, 134.0, 129.3, 128.6, 127.1, 52.1, 41.2.

**Methyl Benzoate (6).**<sup>[2]</sup>



Obtained during debenzoylation of *N*-tosylbenzamide (**3ab**); colorless oil; yield: 0.015 g (22%); *R*<sub>f</sub> = 0.71 (PE/EtOAc = 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.04 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 3.92 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 167.1, 132.9, 130.1, 129.6, 128.4, 52.1.

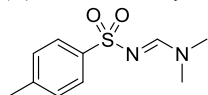
**Methyl Cinnamate (7).**



Obtained during debenzoylation of *N*-tosylcinnamide (**3ac**); white solid; yield: 0.063 g (77%); mp 39–41 °C (lit.<sup>[2]</sup> 34–38 °C);  $R_f$  = 0.91 (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (d,  $J$  = 16.0 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.35 (m, 3H), 6.45 (d,  $J$  = 16.1 Hz, 1H), 3.81 (s, 3H).

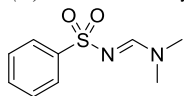
**One-pot Preparation of *N*-Sulfonylformamidines from *N*-Acylsulfonamides in Ethanol (General Procedure B).** A mixture of an *N*-acylsulfonamide (1 mmol) and Ga(OTf)<sub>3</sub> (0.025 g, 0.05 mmol, 0.05 equiv) in anhydrous EtOH was stirred overnight at 75 °C. To the reaction mixture was added DMF-DMA (0.183 g, 1.5 mmol, 1.5 equiv) in one shot. The mixture was allowed to stir overnight. Then silica gel (100 mesh) was added, and the volatiles were removed by a rotary evaporator (*extraction was unnecessary*). The residue was purified by column chromatography (eluent: PE/EtOAc = 3:7) to afford the desired *N*-sulfonylformamidine. Unless otherwise specified, sulfonamides **8** and **9a–9t** were prepared on a 1 mmol scale following this procedure.

(*E*)-*N,N*-Dimethyl-*N'*-tosylformimidamide (**8**).



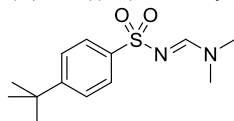
From *N*-tosylacetamide (**1**, 0.213 g, 1 mmol); white solid; yield: 0.220 g (97%); mp 139.5–141.5 °C (lit.<sup>[6]</sup> 137–139 °C);  $R_f$  = 0.18 (PE/EtOAc = 1:1). From *N*-tosylpropionamide (**3s**, 0.228 g, 1 mmol); yield: 0.219 g (96%). From *N*-tosylisobutyramide (**3t**, 0.242 g, 1 mmol); yield: 0.216 g (95%). From *N*-tosyloctanamide (**3u**, 0.298 g, 1 mmol); yield: 0.215 g (94%). From *N*-tosylcyclopropanecarboxamide (**3v**, 0.239 g, 1 mmol); yield: 0.212 g (93%). From *N*-tosylcyclohexanecarboxamide (**3w**, 0.280 g, 1 mmol); yield: 0.212 g (94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (s, 1H), 7.77 (d,  $J$  = 8.3 Hz, 2H), 7.26 (d,  $J$  = 8.3 Hz, 2H), 3.12 (s, 3H), 3.01 (s, 3H), 2.40 (s, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-(phenylsulfonyl)formimidamide (**9a**).



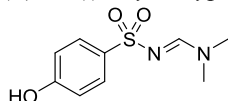
From *N*-(phenylsulfonyl)acetamide (**3a**, 0.199 g, 1 mmol); white solid; yield: 0.200 g (94%); mp 132–134 °C (lit.<sup>[7]</sup> 130–131 °C);  $R_f$  = 0.32 (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.15 (t,  $J$  = 0.7 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.55 – 7.43 (m, 3H), 3.14 (s, 3H), 3.03 (d,  $J$  = 0.7 Hz, 3H).

(*E*)-*N'*-((4-(*tert*-Butyl)phenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9b**).



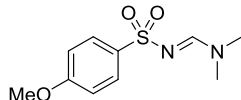
From *N*-(4-(*tert*-butyl)phenyl)sulfonylacetamide (**3b**, 0.255 g, 1 mmol); white solid; yield: 0.257 g (95%); mp 167–169 °C (lit.<sup>[8]</sup> 160–161 °C);  $R_f$  = 0.37 (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.14 (s, 1H), 7.81 (d,  $J$  = 8.6 Hz, 2H), 7.47 (d,  $J$  = 8.6 Hz, 2H), 3.13 (s, 3H), 3.03 (d,  $J$  = 0.6 Hz, 3H), 1.33 (s, 9H).

(*E*)-*N'*-((4-Hydroxyphenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9c**).



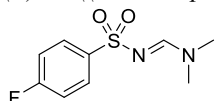
From *N*-((4-hydroxyphenyl)sulfonyl)acetamide (**3ae**, 0.108 g, 0.5 mmol); white solid; yield: 0.107 g (93%); mp 160–162 °C (lit.<sup>[9]</sup> 178 °C);  $R_f$  = 0.10 (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 10.26 (s, 1H), 8.16 (s, 1H), 7.58 (d,  $J$  = 8.7 Hz, 2H), 6.85 (d,  $J$  = 8.8 Hz, 2H), 3.12 (s, 3H), 2.88 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ 160.8, 159.8, 133.7, 128.6, 115.7, 41.2, 35.4.

(*E*)-*N'*-((4-Methoxyphenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9d**).



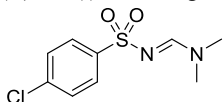
From *N*-((4-methoxyphenyl)sulfonyl)acetamide (**3af**, 0.229 g, 1 mmol); white solid; yield: 0.219 g (90%); mp 157–159 °C (lit.<sup>[8]</sup> 152–153 °C);  $R_f$  = 0.20 (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (s, 1H), 7.82 (d,  $J$  = 8.9 Hz, 2H), 6.94 (d,  $J$  = 8.9 Hz, 2H), 3.85 (s, 3H), 3.12 (s, 3H), 3.01 (d,  $J$  = 0.7 Hz, 3H).

(*E*)-*N'*-((4-Fluorophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9e**).<sup>[10]</sup>



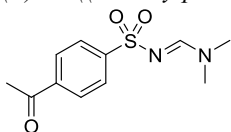
From *N*-((4-fluorophenyl)sulfonyl)acetamide (**3c**, 0.217 g, 1 mmol); white solid; yield: 0.220 g (95%); mp 132.5–133.5 °C;  $R_f = 0.29$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.14 (s, 1H), 7.90 (dd,  $J_1 = 8.9$  Hz,  $J_2 = 5.1$  Hz, 2H), 7.13 (t,  $J = 8.6$  Hz, 2H), 3.15 (s, 3H), 3.03 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N'*-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9f**).



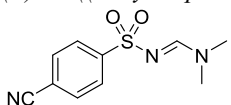
From *N*-((4-chlorophenyl)sulfonyl)acetamide (**3ag**, 0.233 g, 1 mmol); white solid; yield: 0.237 g (96%); mp 125–127 °C (lit.<sup>[6]</sup> 128–130 °C);  $R_f = 0.43$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 – 8.09 (m, 1H), 7.83 (d,  $J = 8.6$  Hz, 2H), 7.43 (d,  $J = 8.6$  Hz, 2H), 3.15 (s, 3H), 3.03 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N'*-((4-Acetylphenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9g**).



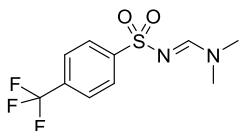
From *N*-((4-acetylphenyl)sulfonyl)acetamide (**3d**, 0.121 g, 0.5 mmol); white solid; yield: 0.095 g (74%); mp 158.5–160.5 °C (lit.<sup>[8]</sup> 154–155 °C);  $R_f = 0.13$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 – 8.14 (m, 1H), 8.03 (d,  $J = 8.7$  Hz, 2H), 7.99 (d,  $J = 8.7$  Hz, 2H), 3.16 (s, 3H), 3.04 (d,  $J = 0.7$  Hz, 3H), 2.64 (s, 3H).

(*E*)-*N'*-((4-Cyanophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9h**).



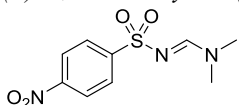
From *N*-((4-cyanophenyl)sulfonyl)acetamide (**3e**, 0.224 g, 1 mmol); white solid; yield: 0.230 g (97%); mp 128.5–130.5 °C (lit.<sup>[11]</sup> 129.6–130.4 °C);  $R_f = 0.22$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 (s, 1H), 8.01 (d,  $J = 8.1$  Hz, 2H), 7.77 (d,  $J = 8.3$  Hz, 2H), 3.18 (s, 3H), 3.05 (s, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-((4-(trifluoromethyl)phenyl)sulfonyl)formimidamide (**9i**).



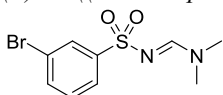
*N*-((4-trifluoromethylphenyl)sulfonyl)acetamide (**3f**, 0.266 g, 1 mmol); white solid; yield: 0.270 g (96%); mp 170.5–172.5 °C (lit.<sup>[12]</sup> 167–168 °C);  $R_f = 0.43$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 – 8.14 (m, 1H), 8.02 (d,  $J = 8.2$  Hz, 2H), 7.73 (d,  $J = 8.2$  Hz, 2H), 3.17 (s, 3H), 3.05 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-((4-nitrophenyl)sulfonyl)formimidamide (**9j**).



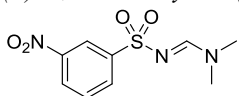
From *N*-((4-nitrophenyl)sulfonyl)acetamide (**3g**, 0.244 g, 1 mmol); white solid; yield: 0.155 g (60%); mp 185–187 °C (lit.<sup>[8]</sup> 186.5–187.5 °C);  $R_f = 0.36$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  8.35 (d,  $J = 8.8$  Hz, 2H), 8.28 (s, 1H), 8.04 (d,  $J = 8.8$  Hz, 2H), 3.18 (s, 3H), 2.94 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  160.7, 149.6, 149.0, 128.0, 124.9, 41.6, 35.7.

(*E*)-*N'*-((3-Bromophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9k**).



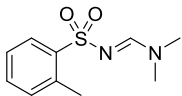
From *N*-((3-bromophenyl)sulfonyl)acetamide (**3h**, 0.278 g, 1 mmol); white solid; yield: 0.280 g (96%); mp 125–127 °C (lit.<sup>[13]</sup> 122 °C);  $R_f = 0.43$  (PE/EtOAc = 1:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.15 – 8.11 (m, 1H), 8.03 (t,  $J = 1.8$  Hz, 1H), 7.84 (ddd,  $J_1 = 7.8$  Hz,  $J_2 = 1.7$  Hz,  $J_3 = 1.0$  Hz, 1H), 7.63 (ddd,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz,  $J_3 = 1.0$  Hz, 1H), 7.34 (t,  $J = 7.9$  Hz, 1H), 3.16 (s, 3H), 3.05 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-((3-nitrophenyl)sulfonyl)formimidamide (**9l**).



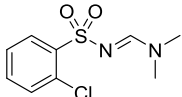
From *N*-((3-nitrophenyl)sulfonyl)acetamide (**3i**, 0.245 g, 1 mmol); white solid; yield: 0.252 g (97%); mp 144–146 °C (lit.<sup>[6]</sup> 140–142 °C);  $R_f = 0.26$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.71 (t,  $J = 2.0$  Hz, 1H), 8.37 (ddd,  $J_1 = 8.3$  Hz,  $J_2 = 2.2$  Hz,  $J_3 = 1.1$  Hz, 1H), 8.25 (ddd,  $J_1 = 7.8$  Hz,  $J_2 = 21.7$  Hz,  $J_3 = 1.1$  Hz, 1H), 8.20–8.16 (m, 1H), 7.68 (t,  $J = 8.0$  Hz, 1H), 3.20 (s, 3H), 3.06 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-(*o*-tolylsulfonyl)formimidamide (**9m**).<sup>[10]</sup>



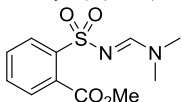
From *N*-(*o*-tolylsulfonyl)acetamide (**3j**, 0.212 g, 1 mmol); white solid; yield: 0.220 g (97%); mp 86.5–88.5 °C;  $R_f = 0.35$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (s, 1H), 8.00 (dd,  $J_1 = 8.2$  Hz,  $J_2 = 1.5$  Hz, 1H), 7.40 (td,  $J_1 = 7.5$  Hz,  $J_2 = 1.4$  Hz, 1H), 7.31–7.24 (m, 2H), 3.12 (s, 3H), 3.04 (d,  $J = 0.7$  Hz, 3H), 2.71 (s, 3H).

(*E*)-*N'*-((2-Chlorophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9n**).<sup>[14]</sup>



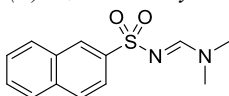
From *N*-((2-chlorophenyl)sulfonyl)acetamide (**3k**, 0.233 g, 1 mmol); white solid; yield: 0.232 g (94%); mp 139–141 °C;  $R_f = 0.45$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.28 (s, 1H), 8.22 (dt,  $J_1 = 7.6$  Hz,  $J_2 = 1.1$  Hz, 1H), 7.47–7.43 (m, 2H), 7.43–7.36 (m, 1H), 3.19 (s, 3H), 3.05 (d,  $J = 0.7$  Hz, 3H).

Methyl (*E*)-2-(*N*-((Dimethylamino)methylene)sulfamoyl)benzoate (**9o**).



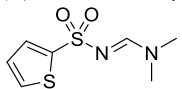
From methyl 2-(*N*-acetylsulfamoyl)benzoate (**3l**, 0.257 g, 1 mmol); white solid; yield: 0.242 g (89%); mp 133–135 °C (lit.<sup>[15]</sup> 128–129 °C);  $R_f = 0.08$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.16–8.12 (m, 1H), 8.12–8.09 (m, 1H), 7.60–7.48 (m, 3H), 3.95 (s, 3H), 3.17 (s, 3H), 3.04 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-(naphthalen-2-ylsulfonyl)formimidamide (**9p**).<sup>[14]</sup>



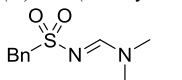
From *N*-(naphthalen-2-ylsulfonyl)acetamide (**3ah**, 0.100 g, 0.4 mmol); white solid; yield: 0.089 g (84%); mp 153.5–155.5 °C;  $R_f = 0.13$  (PE/EtOAc = 2:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.47 (d,  $J = 1.7$  Hz, 1H), 8.20 (s, 1H), 7.97–7.85 (m, 4H), 7.63–7.55 (m, 2H), 3.14 (s, 3H), 3.03 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N,N*-Dimethyl-*N'*-(thiophen-2-ylsulfonyl)formimidamide (**9q**).



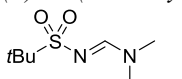
From *N*-(thiophen-2-ylsulfonyl)acetamide (**3p**, 0.205 g, 1 mmol); white solid; yield: 0.209 g (95%); mp 99–100 °C (lit.<sup>[16]</sup> 95–96 °C);  $R_f = 0.33$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.14 (s, 1H), 7.60 (dd,  $J_1 = 3.7$  Hz,  $J_2 = 1.3$  Hz, 1H), 7.50 (dd,  $J_1 = 5.0$  Hz,  $J_2 = 1.4$  Hz, 1H), 7.03 (dd,  $J_1 = 5.0$  Hz,  $J_2 = 3.7$  Hz, 1H), 3.15 (s, 3H), 3.06 (d,  $J = 0.7$  Hz, 3H).

(*E*)-*N'*-(Benzylsulfonyl)-*N,N*-dimethylformimidamide (**9r**).



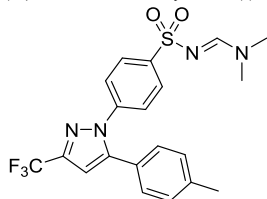
From *N*-(benzylsulfonyl)acetamide (**3n**, 0.213 g, 1 mmol); white solid; yield: 0.220 g (97%); mp 111–113 °C (lit.<sup>[17]</sup> 110–111 °C);  $R_f = 0.27$  (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.50 (s, 1H), 7.40–7.28 (m, 5H), 4.26 (s, 2H), 3.00 (s, 3H), 2.93 (s, 3H).

(*E*)-*N'*-(*tert*-Butylsulfonyl)-*N,N*-dimethylformimidamide (**9s**).



From *N*-(*tert*-butylsulfonyl)acetamide (**3o**, 0.179 g, 1 mmol); the reaction mixture was rotary evaporated to remove volatiles, and the residue was extracted with EtOAc (30 mL×3), dried with MgSO<sub>4</sub>; the product was obtained as a white solid after rotary evaporation of EtOAc; yield: 0.181 g (94%); mp 90–92 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01 (s, 1H), 3.13 (s, 3H), 3.06 (s, 3H), 1.39 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>): δ 160.1, 57.6, 41.3, 35.3, 24.3. ESI HRMS (*m/z*): calcd for C<sub>7</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa (M + Na)<sup>+</sup>, 215.0830; found, 215.0834.

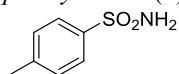
(*E*)-*N,N*-Dimethyl-*N'*-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)formimidamide (**9t**).<sup>[18]</sup>



From *N*-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonyl)acetamide (**3q**, 0.212 g, 0.5 mmol); white solid; yield: 0.211 g (96%); mp 171–173 °C;  $R_f$  = 0.24 (PE/EtOAc = 1:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.12 – 8.10 (m, 1H), 7.88 (d,  $J$  = 8.7 Hz, 2H), 7.41 (d,  $J$  = 8.7 Hz, 2H), 7.17 (d,  $J$  = 7.8 Hz, 2H), 7.11 (d,  $J$  = 8.2 Hz, 2H), 6.73 (s, 1H), 3.15 (s, 3H), 3.03 (d,  $J$  = 0.7 Hz, 3H), 2.38 (s, 3H).

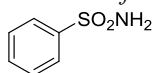
**Depivaloylation of *N*-Sulfonylpivalamides (General Procedure C).** To a 100 mL sealed tube was added an *N*-sulfonylpivalamide (0.5 mmol), Cu(OTf)<sub>2</sub> (0.018 g, 0.05 mmol, 0.1 equiv), and anhydrous methanol (5 mL). The mixture was stirred for 18 hours at 120 °C. Then the volatiles were removed by a rotary evaporator. The residue was purified by column chromatography (eluent: PE/EtOAc = 2:1) on silica gel (200–300 mesh) to afford the resultant sulfonamide as a white solid. Characterization data of amides **2**, **4a–4c**, **4f**, **4r**, and **4s** match those prepared following general procedure A.

*p*-Tosylamide (**2**).



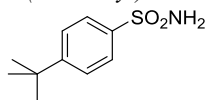
From *N*-tosylpivalamide (**3y**, 0.128 g, 0.5 mmol); yield: 0.084 g (97%).

Benzenesulfonamide (**4a**).



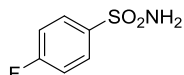
From *N*-(phenylsulfonyl)pivalamide (**3ad**, 0.241 g, 1 mmol); yield: 0.204 g (94%).

4-(*tert*-Butyl)benzenesulfonamide (**4b**).



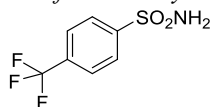
From *N*-((4-(*tert*-butyl)phenyl)sulfonyl)pivalamide (**3ai**, 0.149 g, 0.5 mmol); yield: 0.100 g (93%).

4-Fluorobenzenesulfonamide (**4c**).



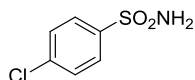
From *N*-((4-fluorophenyl)sulfonyl)pivalamide (**3ak**, 0.130 g, 0.5 mmol); yield: 0.082 g (93%)

4-Trifluoromethylbenzenesulfonamide (**4f**).



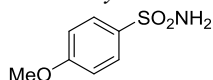
From *N*-((4-trifluoromethylphenyl)sulfonyl)pivalamide (**3al**, 0.155 g, 0.5 mmol); yield: 0.103 g (91%).

4-Chlorobenzenesulfonamide (**4r**).



From *N*-((4-chlorophenyl)sulfonyl)pivalamide (**3z**, 0.137 g, 0.5 mmol); yield: 0.092 g (96%).

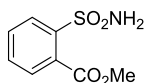
4-Methoxybenzenesulfonamide (**4s**).



From *N*-((4-methoxyphenyl)sulfonyl)pivalamide<sup>[19]</sup> (**3aj**, 0.136 g, 0.5 mmol); white solid; yield: 0.091 g (96%); mp 114.5–116.5 °C (lit.<sup>[2]</sup> 111–115 °C);  $R_f$  = 0.10 (PE/EtOAc = 3:1). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 7.76 (d,  $J$  = 8.9 Hz, 2H), 7.22 (s, 2H), 7.09 (d,  $J$  = 8.9 Hz, 2H), 3.83 (s, 3H).

Methyl 2-sulfamoylbenzoate (**4l**).

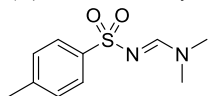




From saccharin (**3an**, 0.183 g, 1 mmol), Ga(OTf)<sub>3</sub> (0.025 g, 0.05 mmol, 0.05 equiv), and anhydrous methanol (5 mL); stirred for 18 h at 120 °C in a sealed tube; yield: 0.021 g (9%).

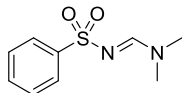
**Alternative One-pot Preparation of *N*-SulfonylAmidines from *N*-Acylsulfonamides (General Procedure D).** To a 100 mL sealed tube was added an *N*-acylsulfonamide (0.5 mmol), Ga(OTf)<sub>3</sub> (0.013 g, 0.025 mmol, 0.05 equiv), and anhydrous methanol (5 mL). The mixture was stirred for 18 hours at 120 °C. To the reaction mixture was added DMF-DMA (0.091 g, 0.75 mmol, 1.5 equiv) in one shot. The mixture was allowed to stir overnight at 75 °C. Then the volatiles were removed by a rotary evaporator. The residue was purified by column chromatography (eluent: PE/EtOAc = 3:7) on silica gel (200–300 mesh) to afford the resultant *N*-sulfonylformamidine as a white solid. The following *N*-sulfonylformamidines were prepared following this general procedure, and the characterization data of **8**, **9a**, **9b**, **9d–9f**, **9i**, and **9s** match those prepared following general procedure B.

(*E*)-*N,N*-Dimethyl-*N'*-tosylformimidamide (**8**).



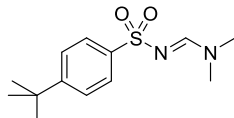
From *N*-tosylpivalamide (**3y**, 0.128 g, 0.5 mmol) and Ga(OTf)<sub>3</sub> (0.013 g, 0.025 mmol, 0.05 equiv); yield: 0.107 g (94%). From *N*-tosylbenzamide (**3ab**, 0.138 g, 0.5 mmol) and Er(OTf)<sub>3</sub> (0.015 g, 0.025 mmol, 0.05 equiv); yield: 0.110 g (96%). From *N*-tosylcinnamamide (**3ac**, 0.151 g, 0.5 mmol) and Y(OTf)<sub>3</sub> (0.014 g, 0.025 mmol, 0.05 equiv); yield: 0.108 g (95%). From *N*-tosylpivalamide (**3y**, 0.127 g, 0.5 mmol) and Ga(OTf)<sub>3</sub> (0.013 g, 0.025 mmol, 0.05 equiv), stirred for 18 h at 120 °C in ethylene glycol (5 mL), then DMF-DMA (0.090 g, 0.75 mmol, 1.5 equiv) was added and the mixture was stirred for another 18 h at 75 °C; yield: 0.104 g (92%).

(*E*)-*N,N*-Dimethyl-*N'*-(phenylsulfonyl)formimidamide (**9a**).



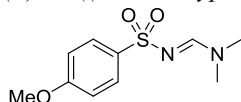
From *N*-(phenylsulfonyl)pivalamide (**3ad**, 0.241 g, 1 mmol); yield: 0.189 g (89%).

(*E*)-*N'*-((4-(*tert*-Butyl)phenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9b**).



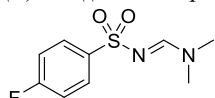
From *N*-((4-(*tert*-butyl)phenyl)sulfonyl)pivalamide (**3ai**, 0.149 g, 0.5 mmol); yield: 0.101 g (75%).

(*E*)-*N'*-((4-Methoxyphenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9d**).



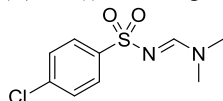
From *N*-((4-methoxyphenyl)sulfonyl)pivalamide<sup>[19]</sup> (**3aj**, 0.271 g, 1 mmol); yield: 0.233 g (96%).

(*E*)-*N'*-((4-Fluorophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9e**).



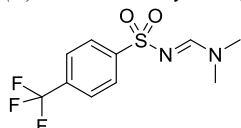
From *N*-((4-fluorophenyl)sulfonyl)pivalamide (**3ak**, 0.130 g, 0.5 mmol); white solid; yield: 0.113 g (97%).

(*E*)-*N'*-((4-Chlorophenyl)sulfonyl)-*N,N*-dimethylformimidamide (**9f**).



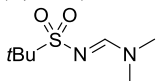
From *N*-((4-chlorophenyl)sulfonyl)pivalamide (**3z**, 0.138 g, 0.5 mmol); yield: 0.112 g (90%).

(*E*)-*N,N*-Dimethyl-*N'*-((4-(trifluoromethyl)phenyl)sulfonyl)formimidamide (**9i**).



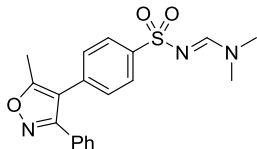
From *N*-((4-(trifluoromethyl)phenyl)sulfonyl)pivalamide (**3a1**, 0.155 g, 0.5 mmol); yield: 0.102 g (72%).

(*E*)-*N'*-(*tert*-Butylsulfonyl)-*N,N*-dimethylformimidamide (**9s**).



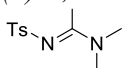
From *N*-(*tert*-butylsulfonyl)pivalamide (**3am**, 0.221 g, 1 mmol); after removal of volatiles by a rotary evaporator, the residue was partitioned between EtOAc and water, and the product was obtained after removal of volatiles; yield: 0.190 g (98%).

(*E*)-*N,N*-Dimethyl-*N'*-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)formimidamide (**11**).



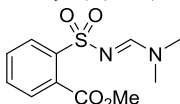
From *N*-((4-(5-methyl-3-phenylisoxazol-4-yl)phenyl)sulfonyl)pivalamide (**10a**, 0.100 g, 0.025 mmol); white solid; yield: 0.067 g (72%); mp 209.5–211.5 °C;  $R_f$  = 0.16 (PE/EtOAc = 1:1). From parecoxib (**10b**, 0.185 g, 0.5 mmol); yield: 0.167 g (90%).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  8.30 (s, 1H), 7.84 (d,  $J$  = 8.4 Hz, 2H), 7.53 – 7.46 (m, 3H), 7.44 – 7.39 (m, 4H), 3.21 (s, 3H), 2.99 (d,  $J$  = 0.7 Hz, 3H), 2.53 (s, 3H).  $^{13}\text{C}$  { $^1\text{H}$ } NMR (101 MHz, DMSO- $d_6$ ):  $\delta$  168.1, 161.2, 160.4, 142.7, 133.6, 130.5, 130.3, 129.3, 128.9, 128.7, 126.8, 114.7, 41.4, 35.6, 11.9. ESI HRMS ( $m/z$ ): calcd for  $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_3\text{SNa}$  ( $\text{M}+\text{Na}$ ) $^+$ , 392.1045; found, 392.1044.

(*E*)-*N,N*-Dimethyl-*N'*-tosylacetimidamide (**12**).



From *N*-tosylpivalamide (**3y**, 0.127 g, 0.5 mmol) using  $\text{Ce}(\text{OTf})_3$  (0.015 g, 0.025 mmol, 0.05 equiv) as the catalyst in anhydrous ethanol in a sealed tube, stirred for 18 h at 120 °C following the General Procedure D to generate sulfonamide (**2**), which was then condensed with DMAc-DMA (85%, 0.112 g, 0.75 mmol, 1.5 equiv); white solid; yield: 0.092 g (76%); mp 123–125 °C (lit.<sup>[12]</sup> 123–124 °C);  $R_f$  = 0.20 (PE/EtOAc = 1:1). From *N*-tosylacetamide (**1**, 0.213 g, 1 mmol) using  $\text{Er}(\text{OTf})_3$  (0.030 g, 0.05 mmol, 0.05 equiv) as the catalyst following the General Procedure B, and the *in situ* generated sulfonamide (**2**) was condensed with DMAc-DMA (85%, 0.235 g, 1.5 mmol, 1.5 equiv); white solid; yield: 0.187 g (77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.82 (d,  $J$  = 8.3 Hz, 2H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 3.09 (s, 3H), 3.07 (s, 3H), 2.49 (s, 3H), 2.40 (s, 3H).

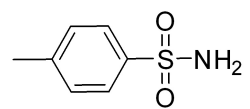
Methyl (*E*)-2-(*N*-((Dimethylamino)methylene)sulfamoyl)benzoate (**9o**).



From saccharin (**3an**, 0.183 g, 1 mmol) and  $\text{Ga}(\text{OTf})_3$  (0.025 g, 0.05 mmol, 0.05 equiv); yield: 0.012 g (4%).

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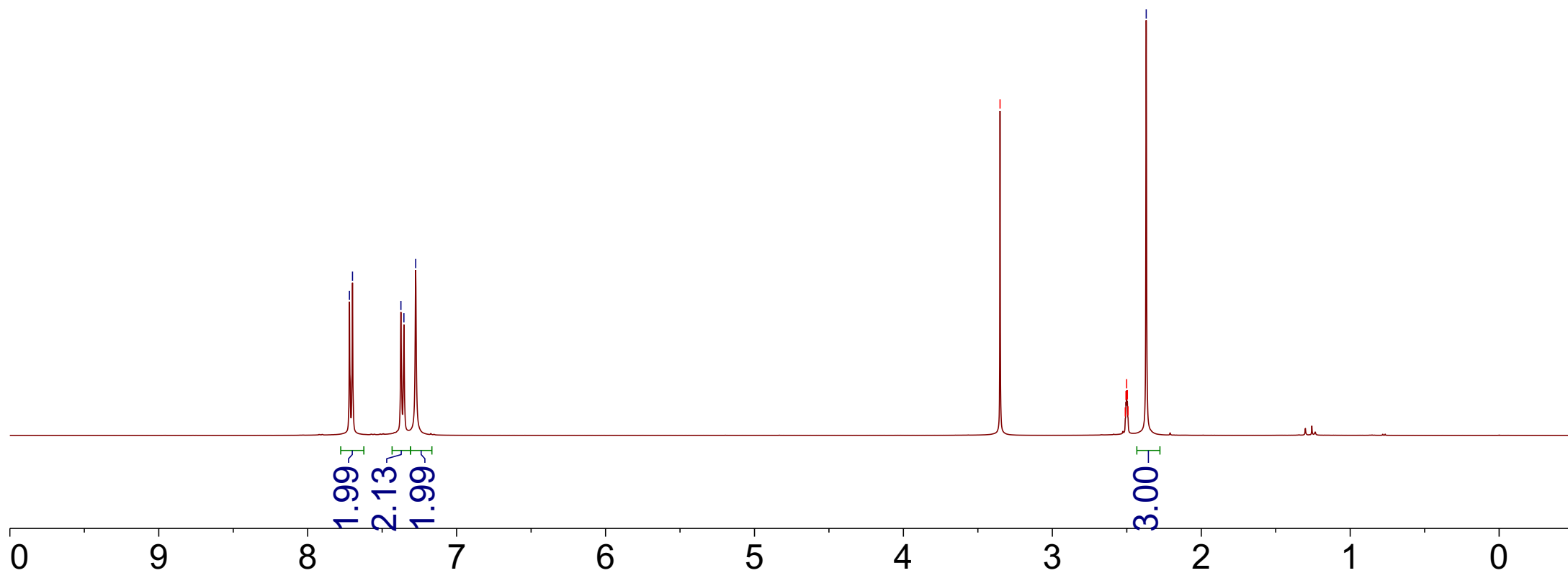


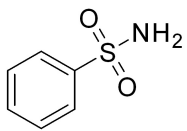
2

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)

7.720  
7.699  
7.374  
7.354  
7.275

3.351 HDO  
2.510 DMSO  
2.506 DMSO  
2.501 DMSO  
2.496 DMSO  
2.492 DMSO  
2.370





**4a**

<sup>1</sup>H NMR

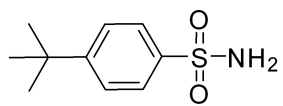
(400MHz, DMSO-*d*<sub>6</sub>)

7.852  
7.845  
7.841  
7.836  
7.831  
7.826  
7.821  
7.628  
7.624  
7.622  
7.611  
7.608  
7.602  
7.598  
7.593  
7.590  
7.582  
7.578  
7.573  
7.563  
7.558  
7.556  
7.551  
7.364

3.364 H<sub>2</sub>O  
2.517 DMSO  
2.513 DMSO  
2.508 DMSO  
2.503 DMSO  
2.499 DMSO

1.99  
3.00  
1.99

0 9 8 7 6 5 4 3 2 1 0 -



**4b**

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)

7.773  
7.751  
7.601  
7.581  
7.279



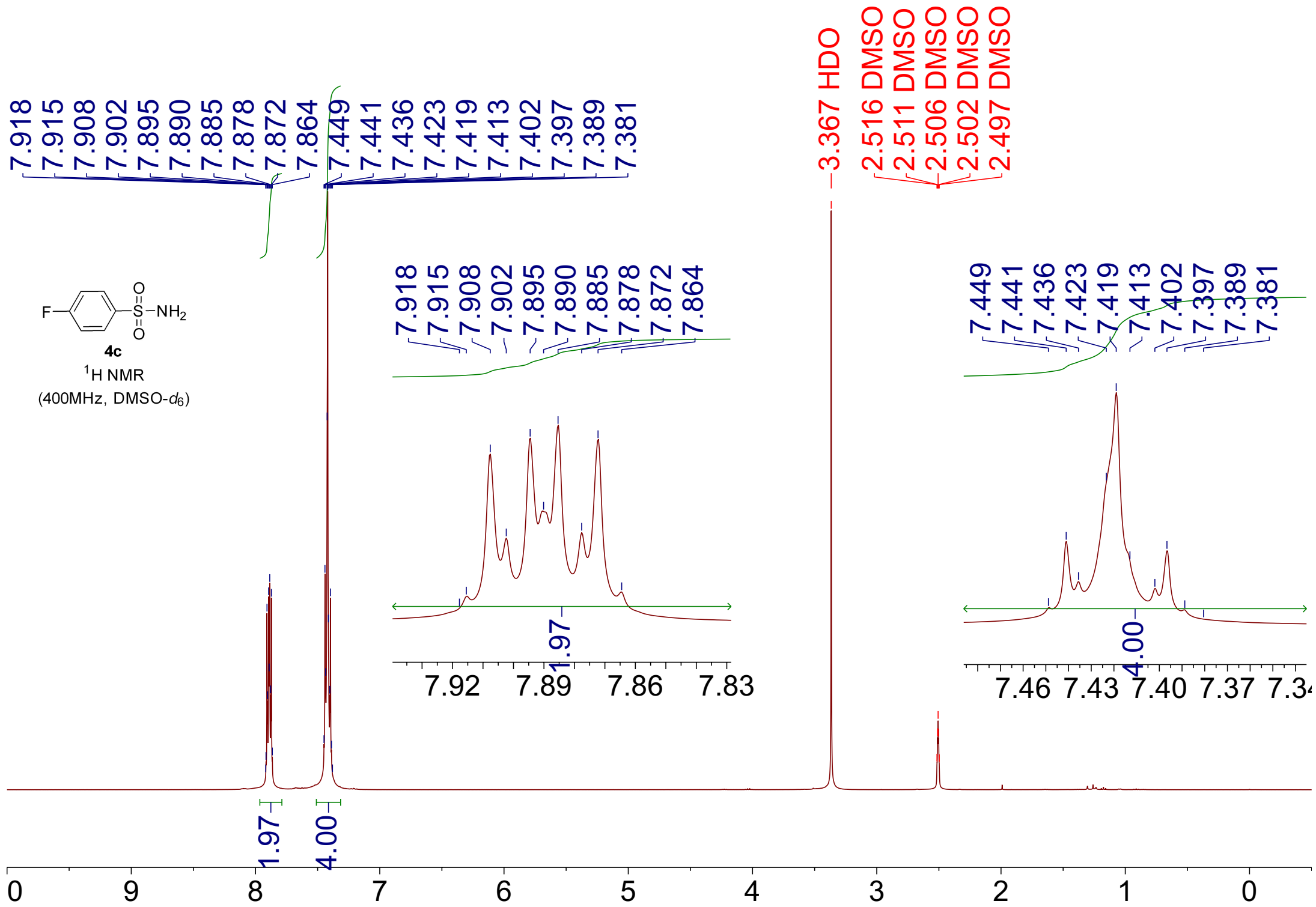
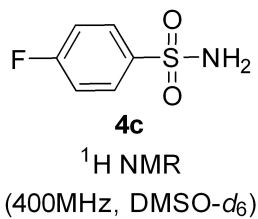
1.96  
1.96  
1.94

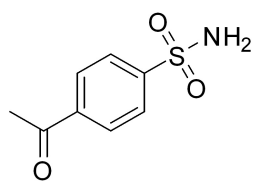
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2.517 DMSO  
2.513 DMSO  
2.508 DMSO  
2.503 DMSO  
2.499 DMSO

1.307

9.00

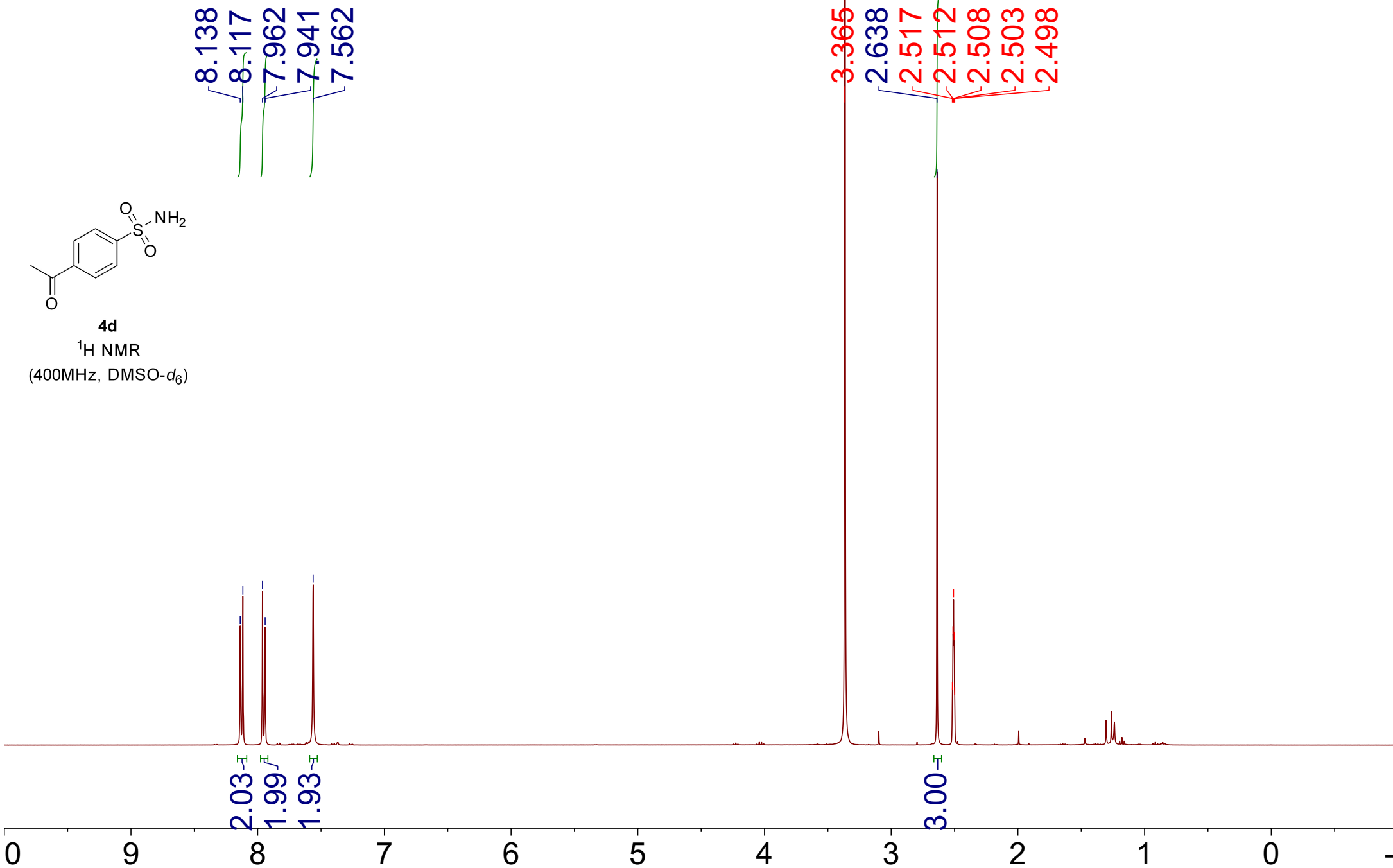
0 9 8 7 6 5 4 3 2 1 0

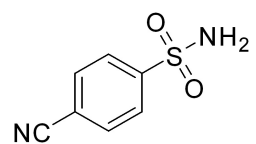




**4d**

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)





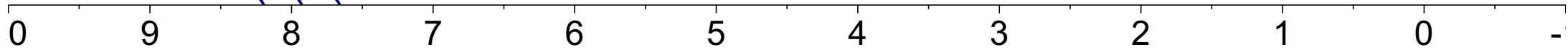
**4e**

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)

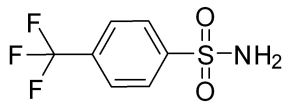
8.095  
8.074  
7.994  
7.973  
7.673

3.364 H<sub>2</sub>O  
2.517 DMSO  
2.513 DMSO  
2.508 DMSO  
2.503 DMSO  
2.499 DMSO

1.00  
1.02  
1.01

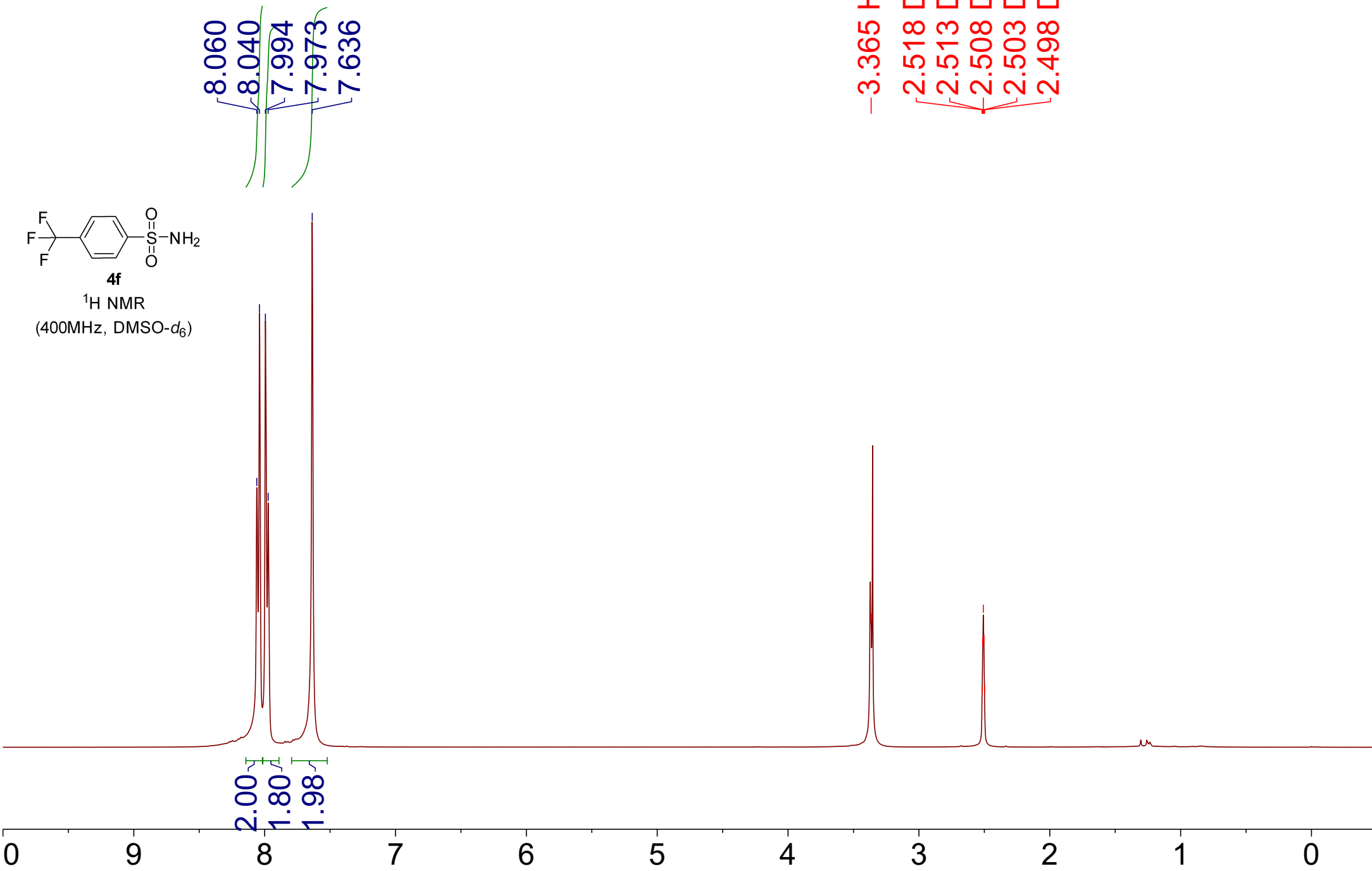


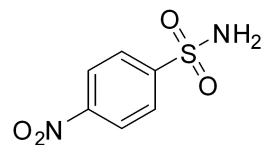




**4f**

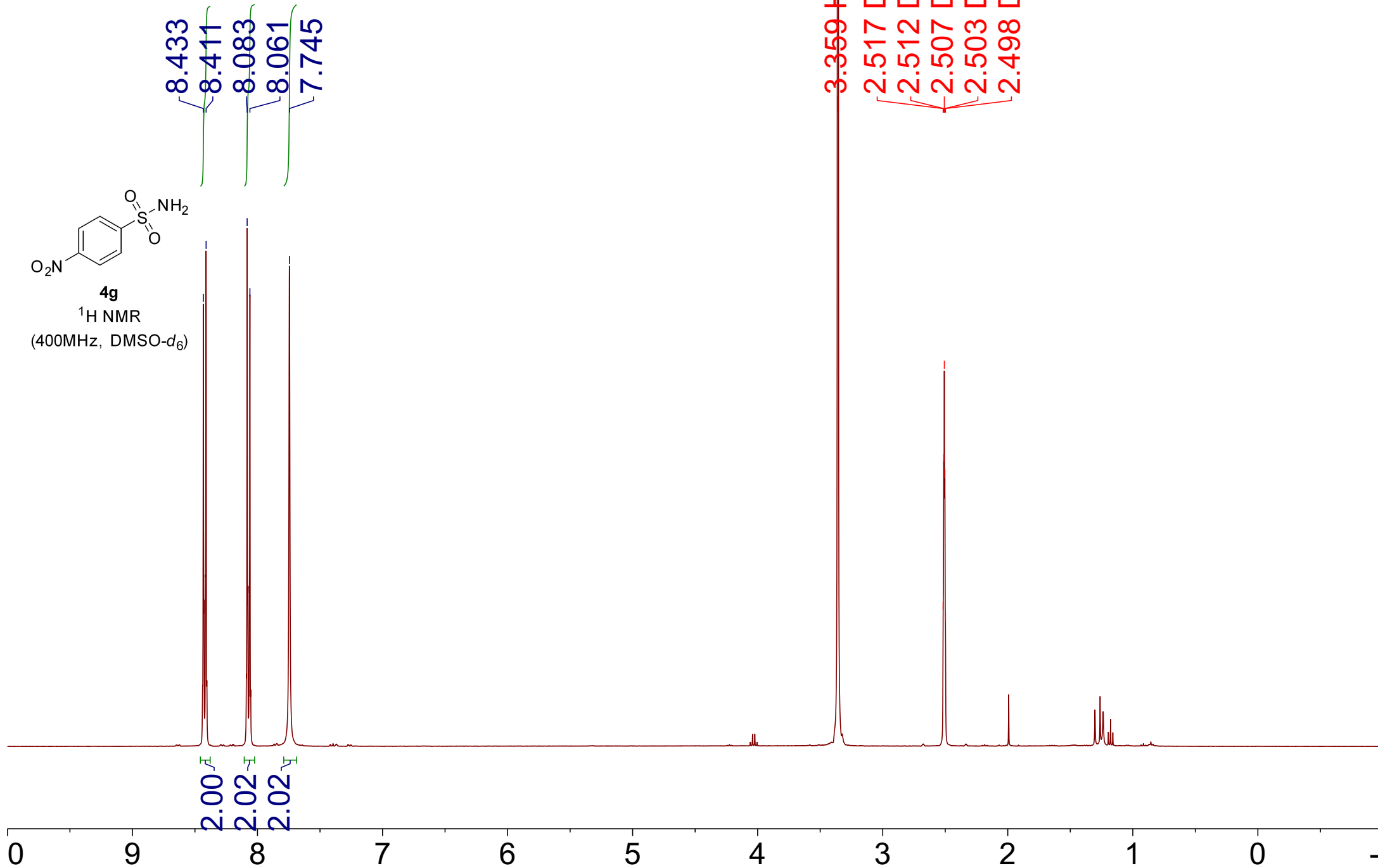
<sup>1</sup>H NMR  
(400MHz, DMSO-*d*<sub>6</sub>)

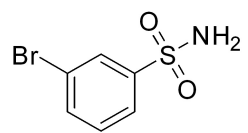




**4g**

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)





4h

<sup>1</sup>H NMR

(400MHz, DMSO-d<sub>6</sub>)

7.986  
7.981  
7.977  
7.846  
7.843  
7.840  
7.838  
7.836  
7.833  
7.832  
7.829  
7.826  
7.823  
7.821  
7.818  
7.816  
7.812  
7.809  
7.574  
7.555  
7.535  
7.523  
7.523  
7.535  
7.555  
7.574

3.362 H<sub>2</sub>O  
2.517 DMSO  
2.513 DMSO  
2.508 DMSO  
2.503 DMSO  
2.499 DMSO

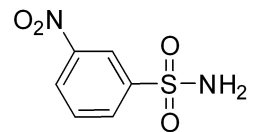
7.574  
7.555  
7.535  
7.523

3.09

1.00  
0.97  
1.04  
3.09

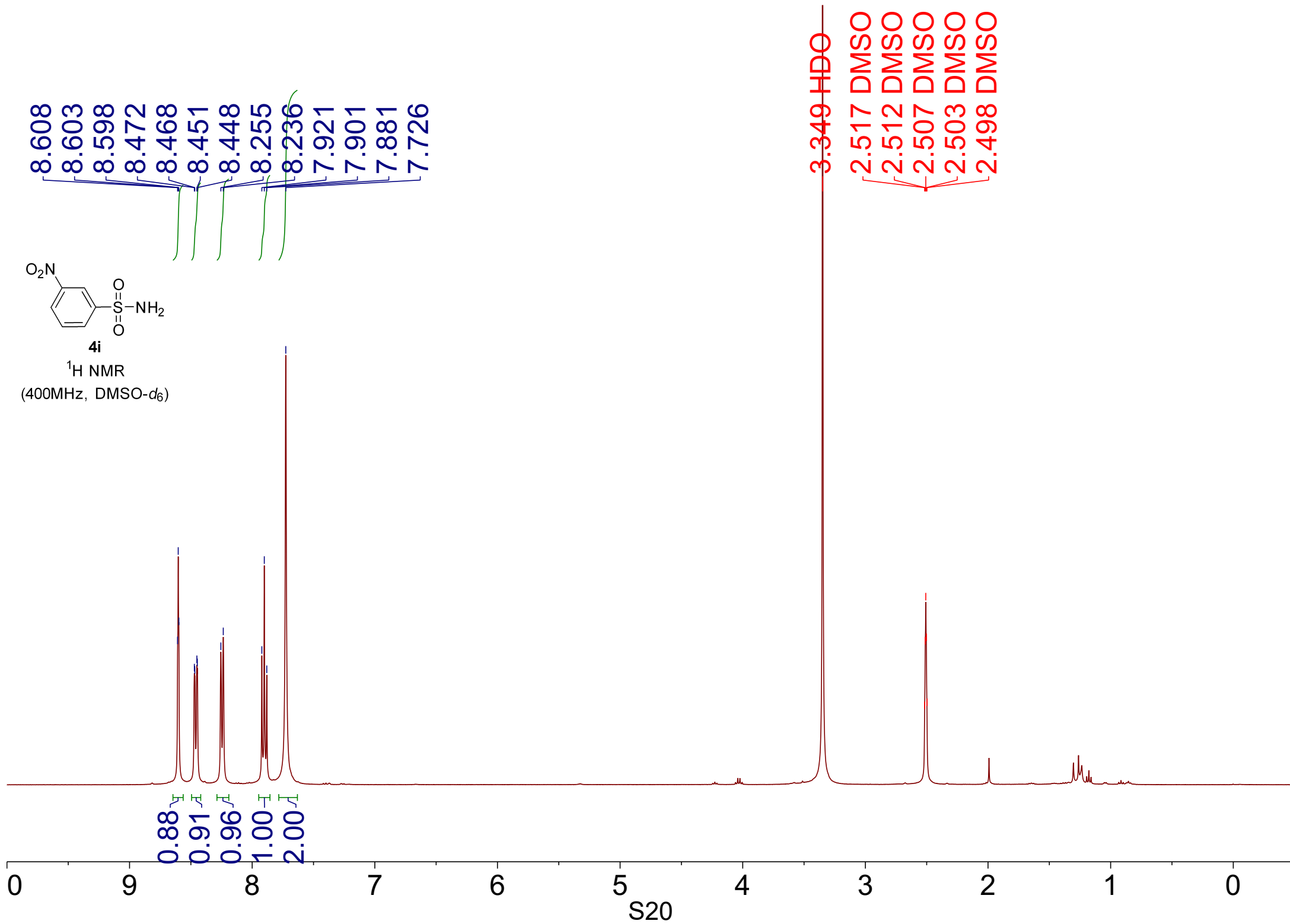
7.64 7.60 7.56 7.52 7.48 7.44

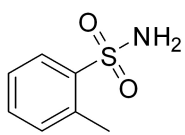
0 9 8 7 6 5 4 3 2 1 0 -



4i

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)

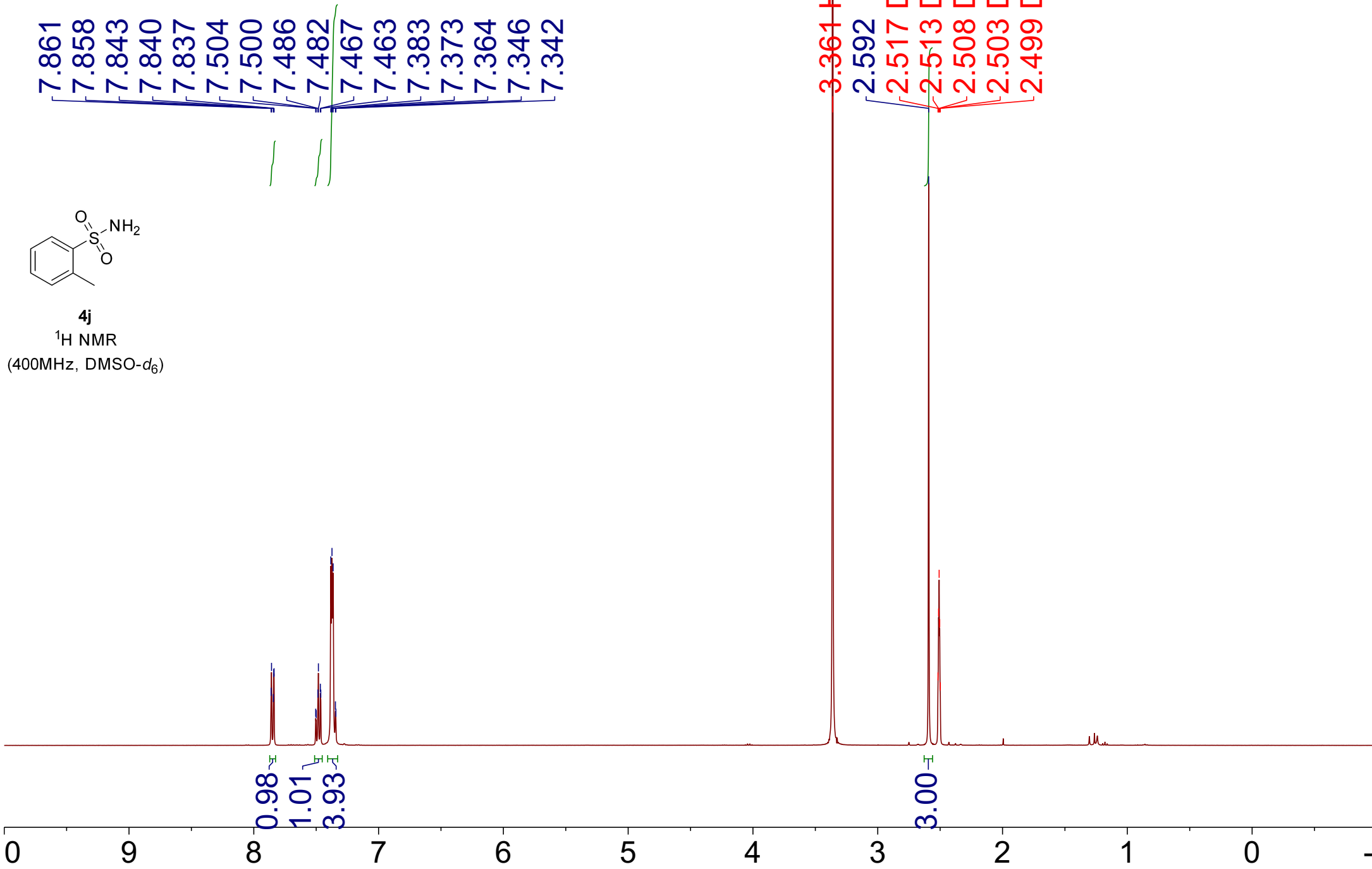




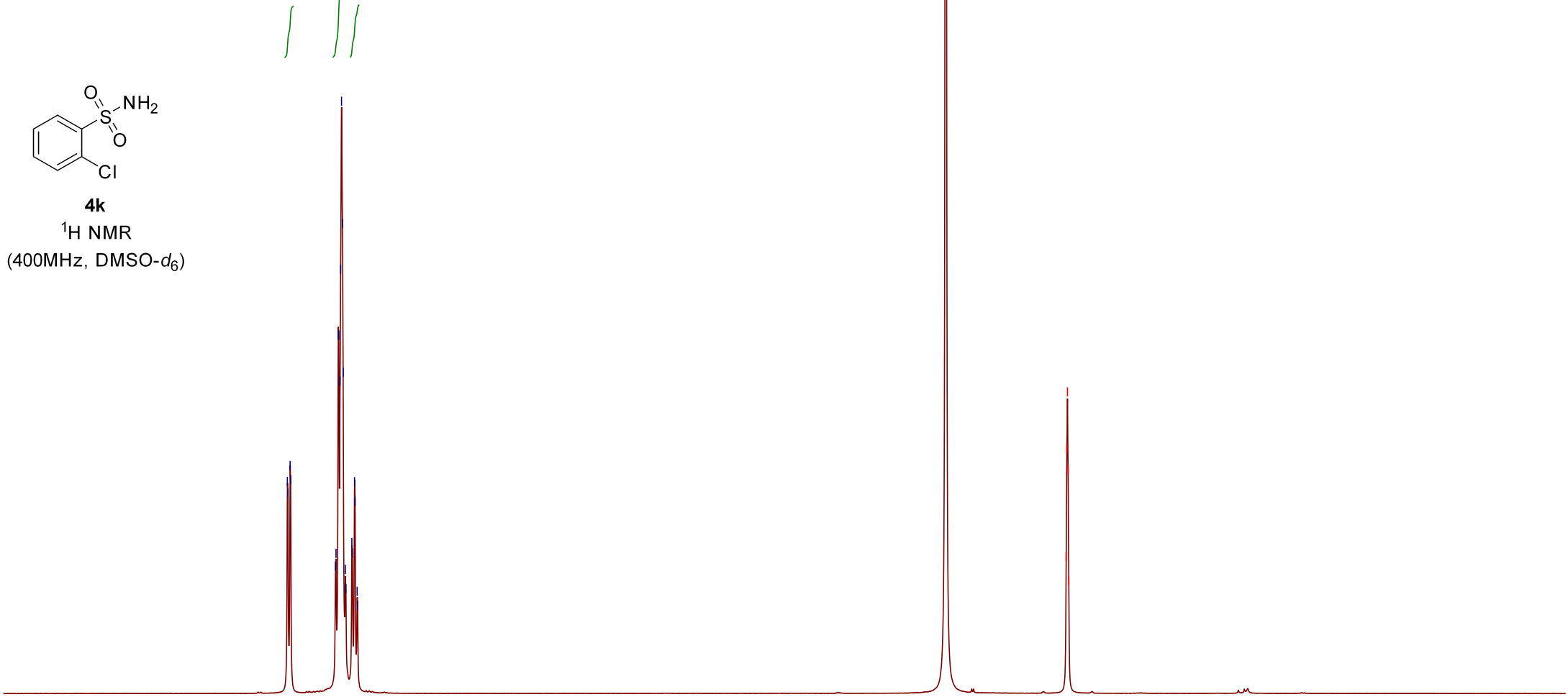
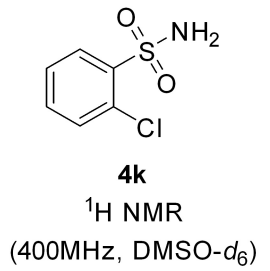
**4j**

<sup>1</sup>H NMR

(400MHz, DMSO-*d*<sub>6</sub>)



8.000  
7.996  
7.981  
7.977  
7.662  
7.658  
7.642  
7.638  
7.630  
7.625  
7.619  
7.612  
7.607  
7.592  
7.588  
7.546  
7.542  
7.528  
7.523  
7.509  
7.505



3.365 H<sub>2</sub>O  
2.517 DMSO  
2.512 DMSO  
2.508 DMSO  
2.503 DMSO  
2.498 DMSO

1.00  
4.00  
1.03

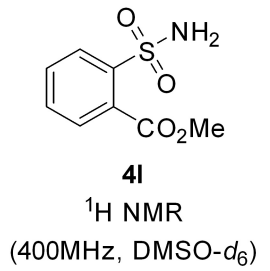
0 9 8 7 6 5 4 3 2 1 0 -

S22

7.992  
7.988  
7.973  
7.969  
7.761  
7.757  
7.743  
7.738  
7.725  
7.719  
7.704  
7.700  
7.686  
7.683  
7.676  
7.672  
7.670  
7.658  
7.653  
7.323

3.844

3.351 HDO  
2.517 DMSO  
2.512 DMSO  
2.508 DMSO  
2.503 DMSO  
2.498 DMSO

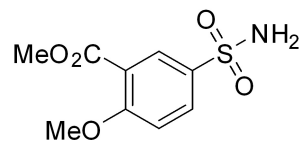


1.01  
3.08  
2.03

3.00

0 9 8 7 6 5 4 3 2 1 0 -

S23



**4m**

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)

8.114  
8.108  
7.977  
7.971  
7.955  
7.949  
7.356  
7.336

3.909  
3.831

3.356 H<sub>2</sub>O

2.517 DMSO  
2.513 DMSO  
2.508 DMSO  
2.503 DMSO  
2.498 DMSO

0.94  
0.98

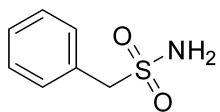
3.02

3.00  
2.94

0 9 8 7 6 5 4 3 2 1 0 -

S24

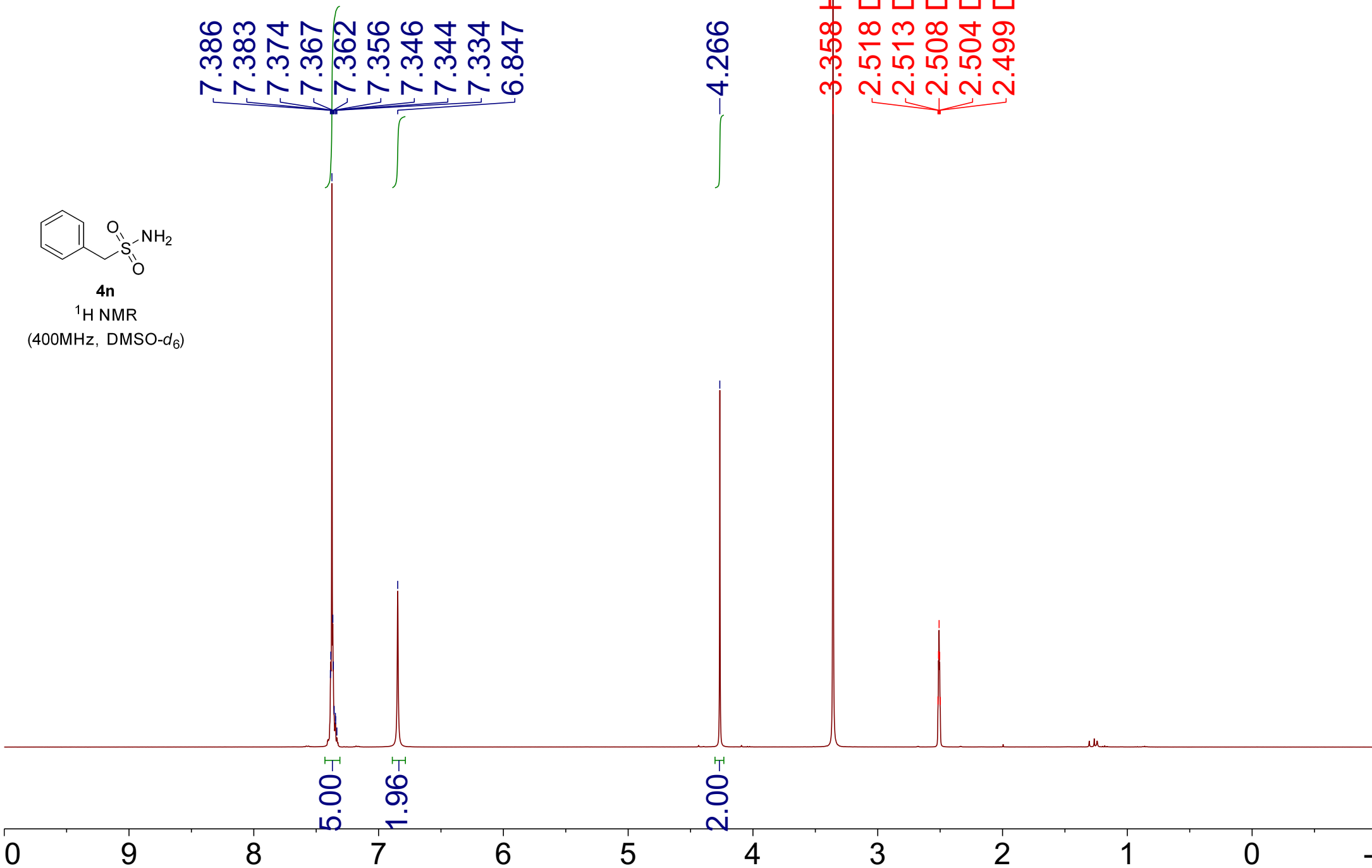


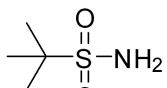


**4n**

<sup>1</sup>H NMR

(400MHz, DMSO-d<sub>6</sub>)

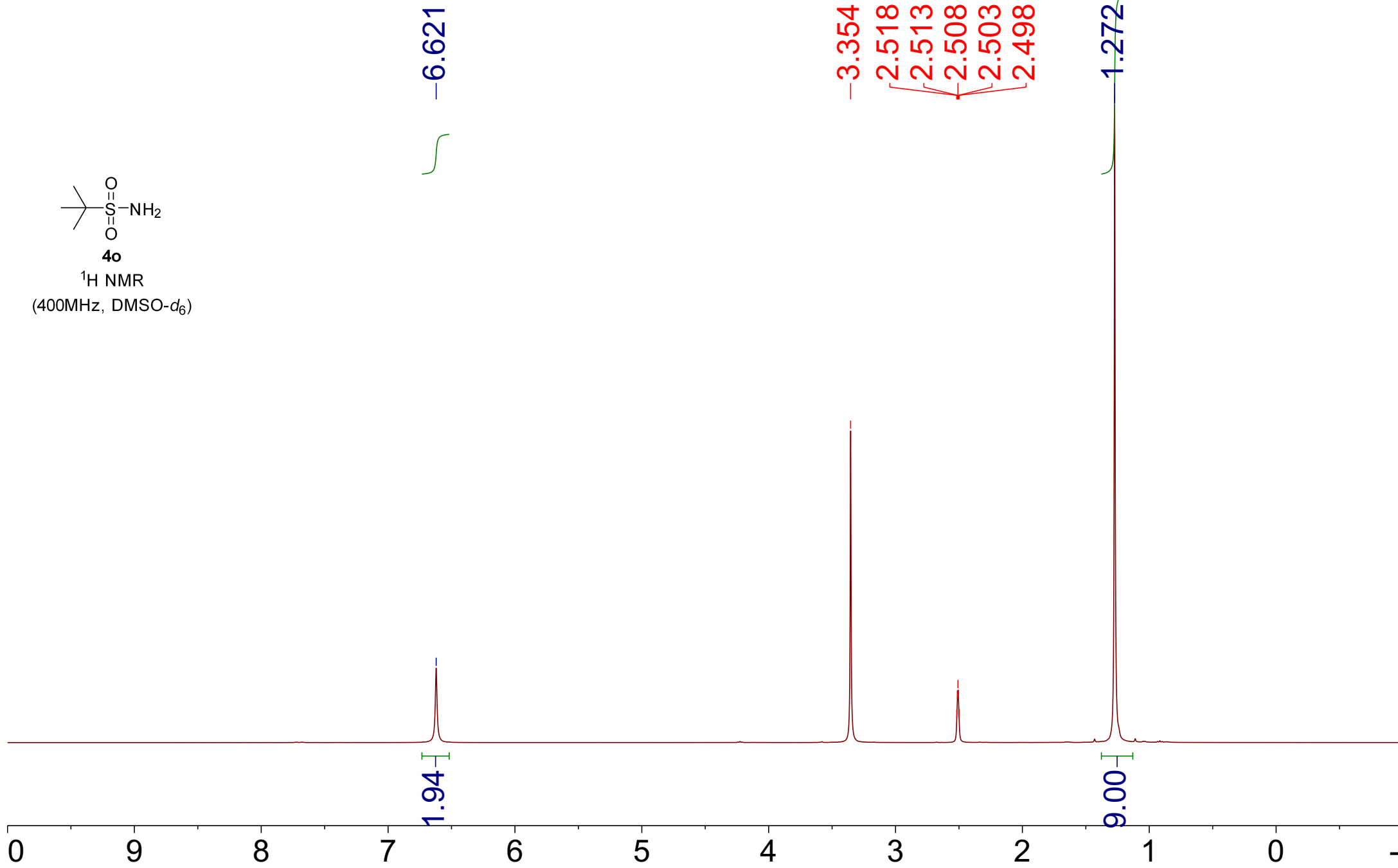


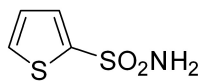


**4o**

<sup>1</sup>H NMR

(400MHz, DMSO-d<sub>6</sub>)

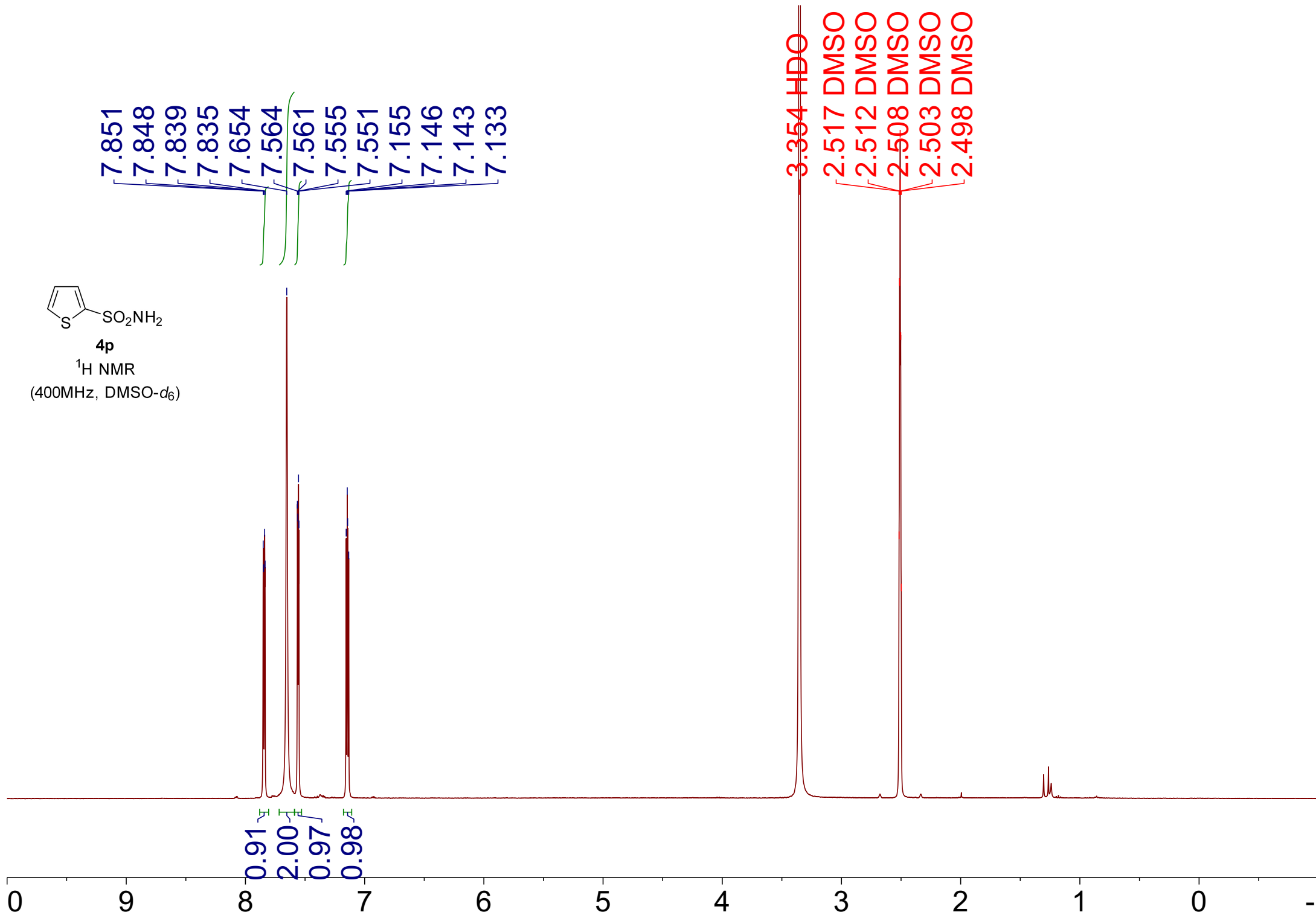


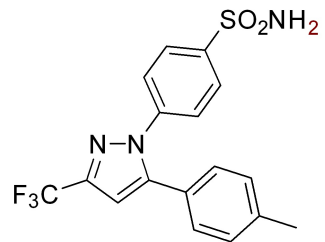


4p

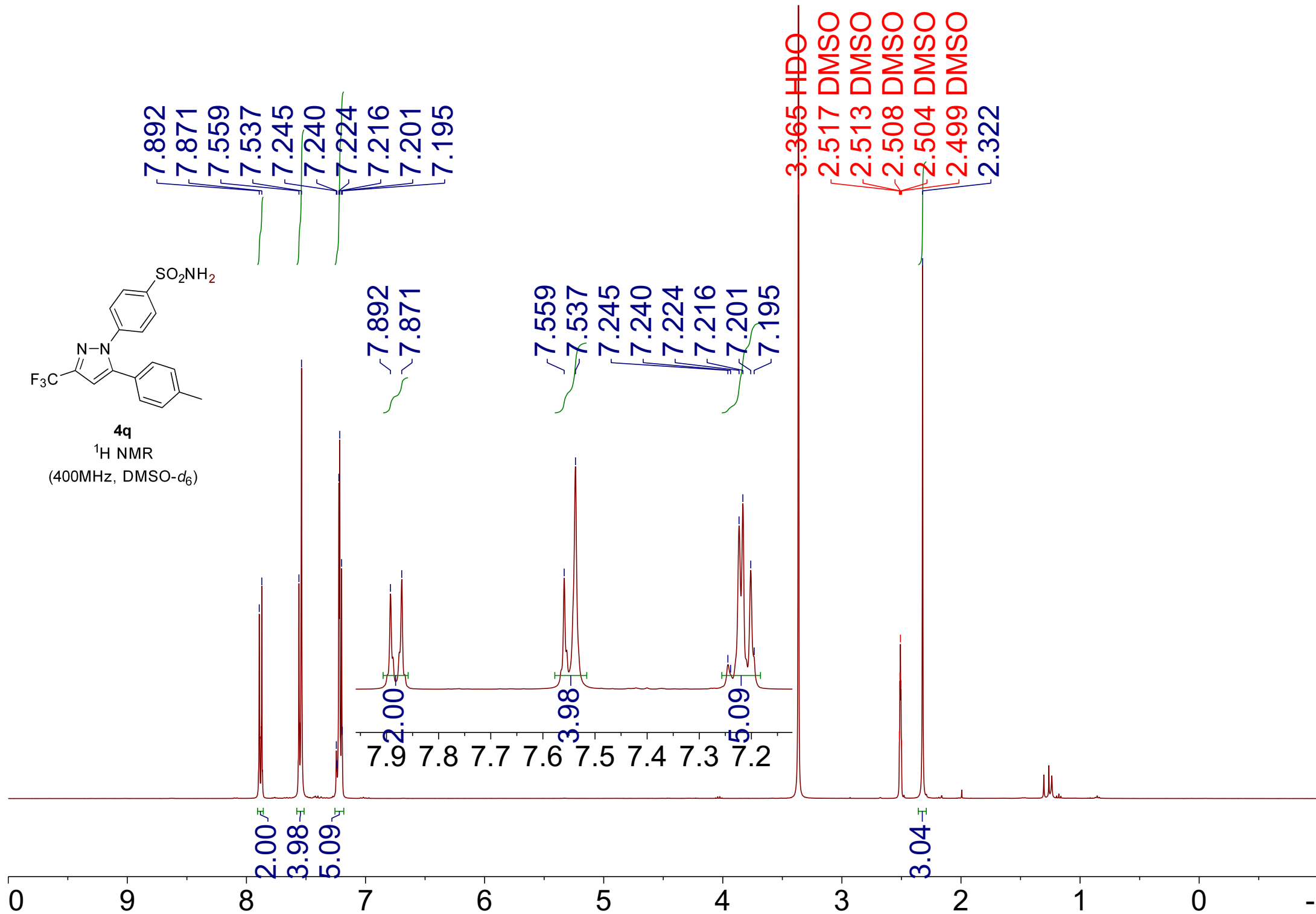
<sup>1</sup>H NMR

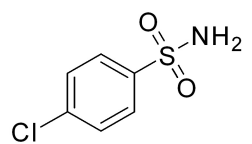
(400MHz, DMSO-d<sub>6</sub>)





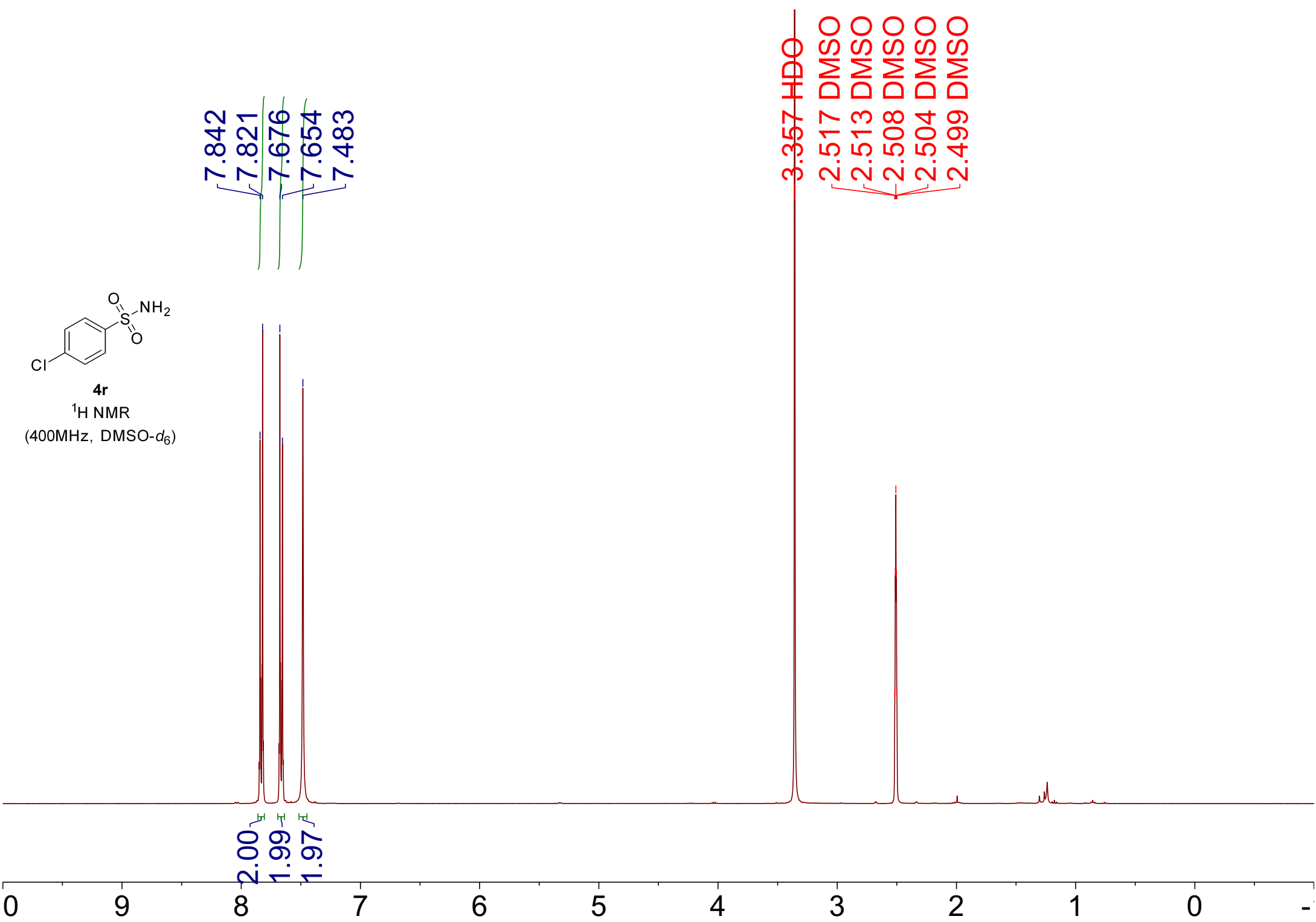
**4q**  
<sup>1</sup>H NMR  
 (400MHz, DMSO-*d*<sub>6</sub>)

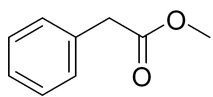




**4r**

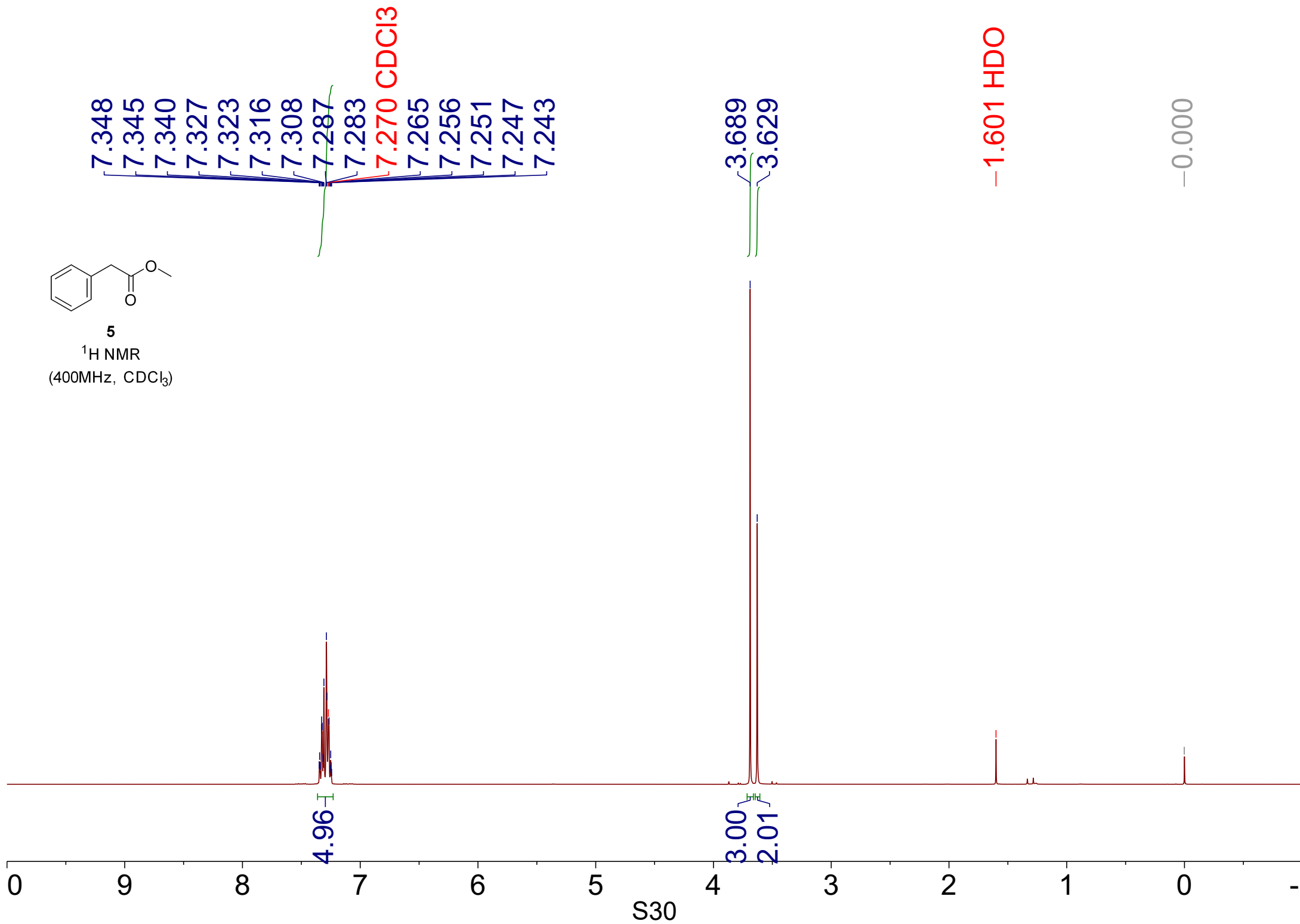
<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)

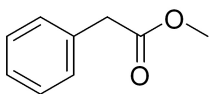




5

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)





**5**

$^{13}\text{C}\{^1\text{H}\}$  NMR  
(101MHz,  $\text{CDCl}_3$ )

172.052

133.973

129.254

128.588

127.115

77.356  $\text{CDCl}_3$

77.038  $\text{CDCl}_3$

76.720  $\text{CDCl}_3$

52.055

41.202

0.000

200

180

160

140

120

100

80

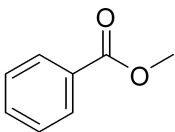
60

40

20

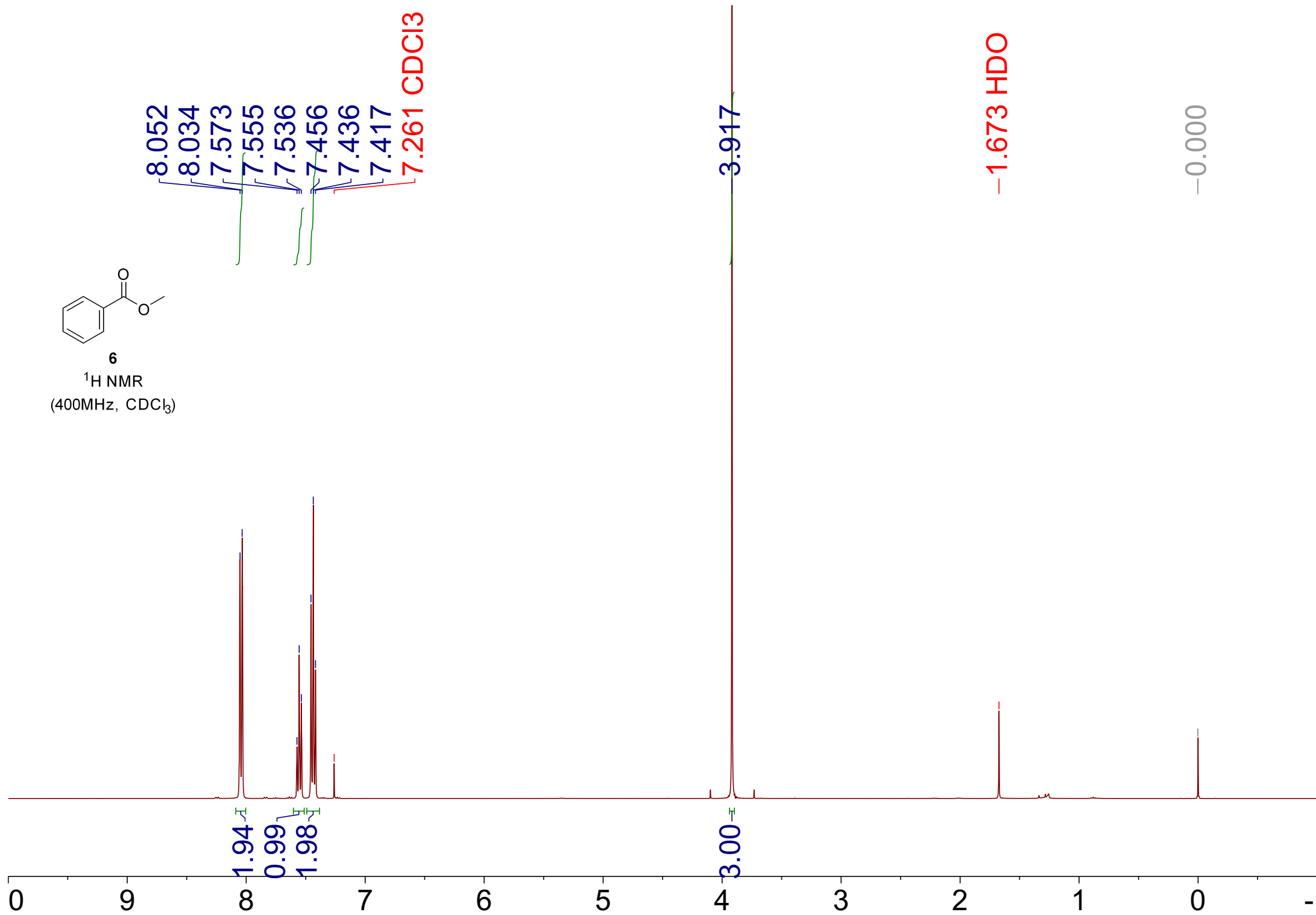
0

S31

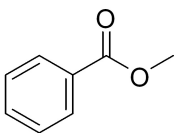


6

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

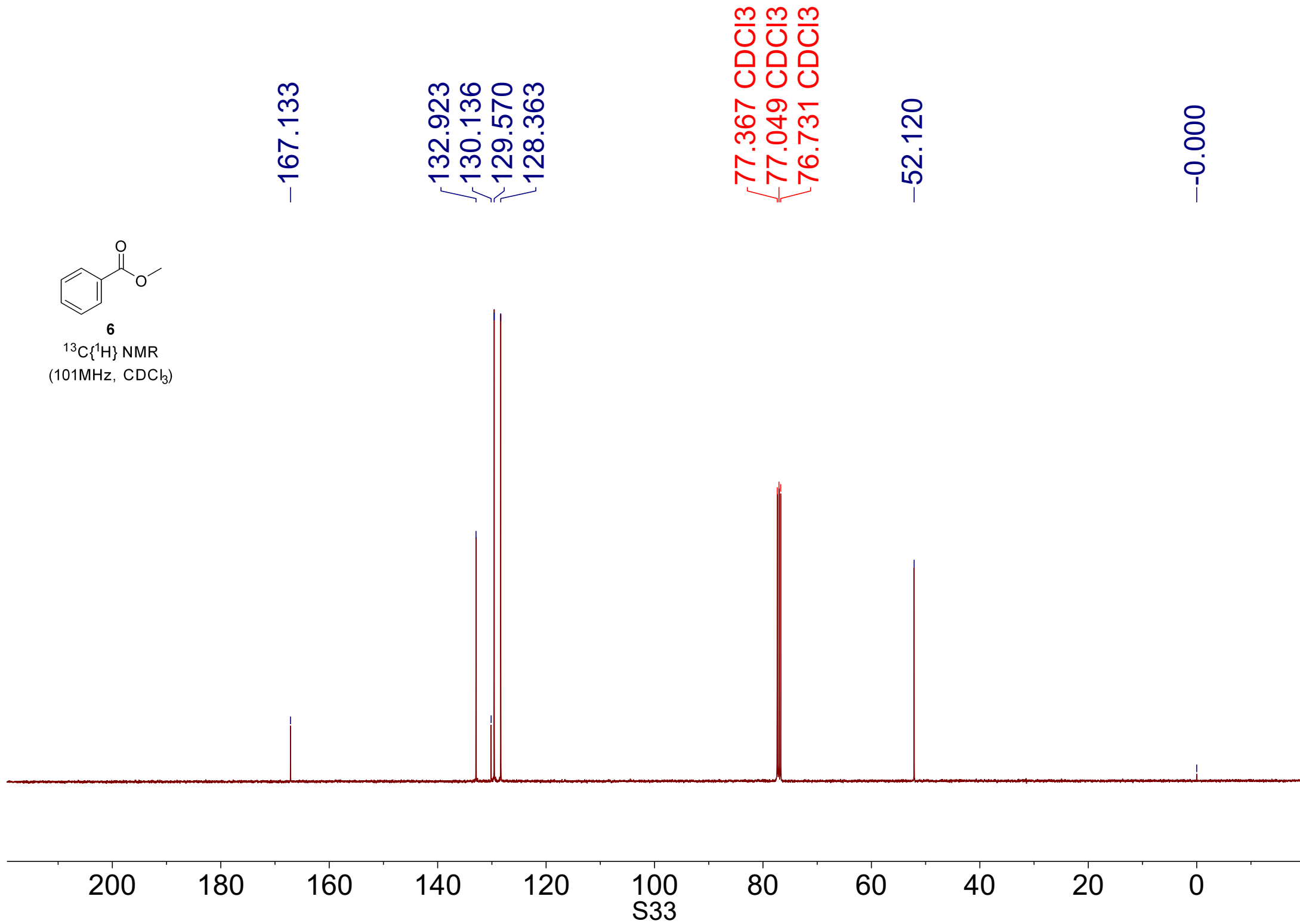


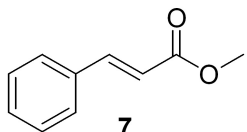




**6**

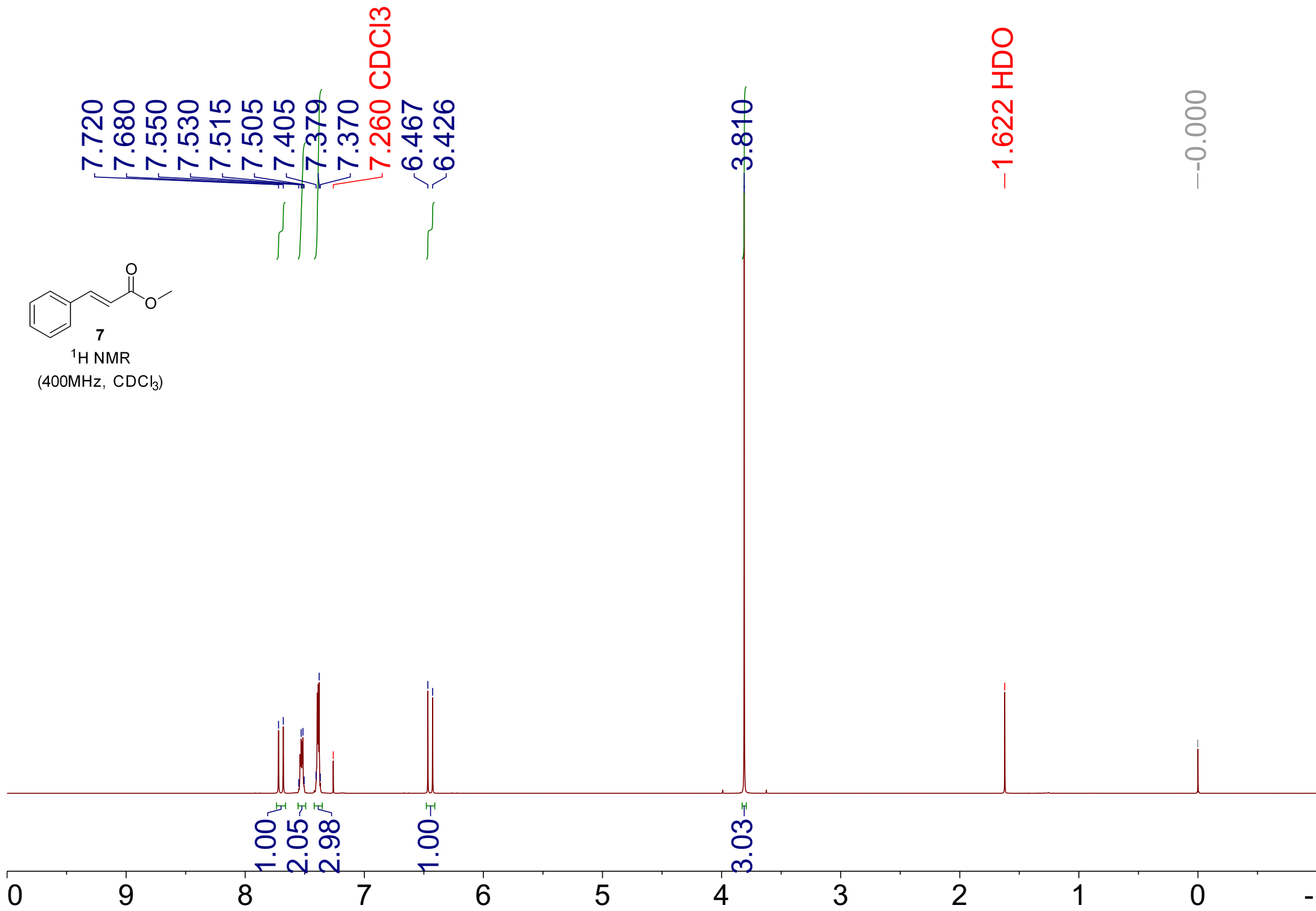
$^{13}\text{C}\{^1\text{H}\}$  NMR  
(101MHz,  $\text{CDCl}_3$ )

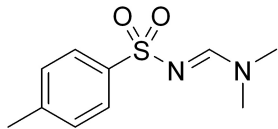




7

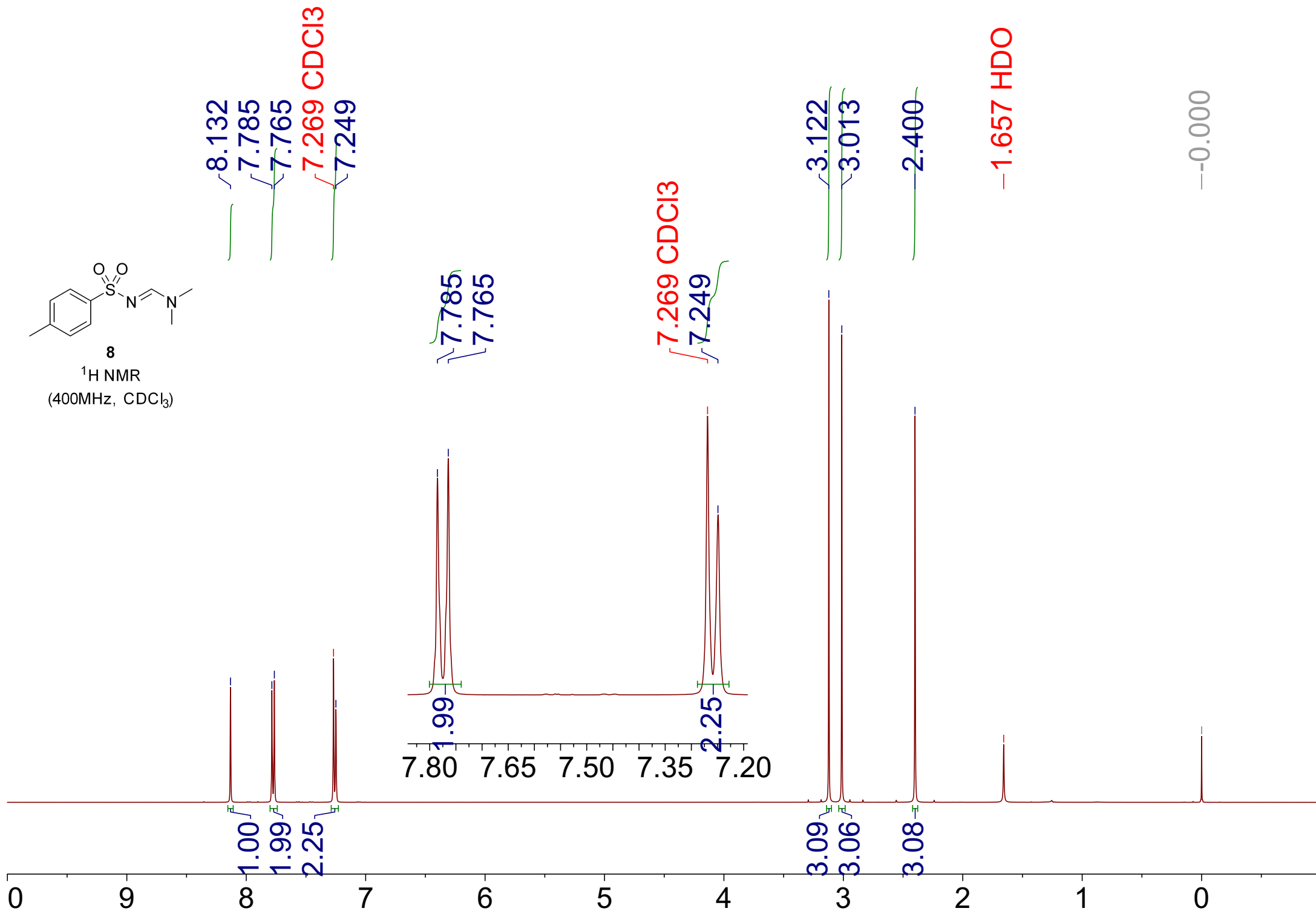
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

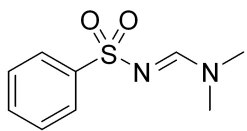




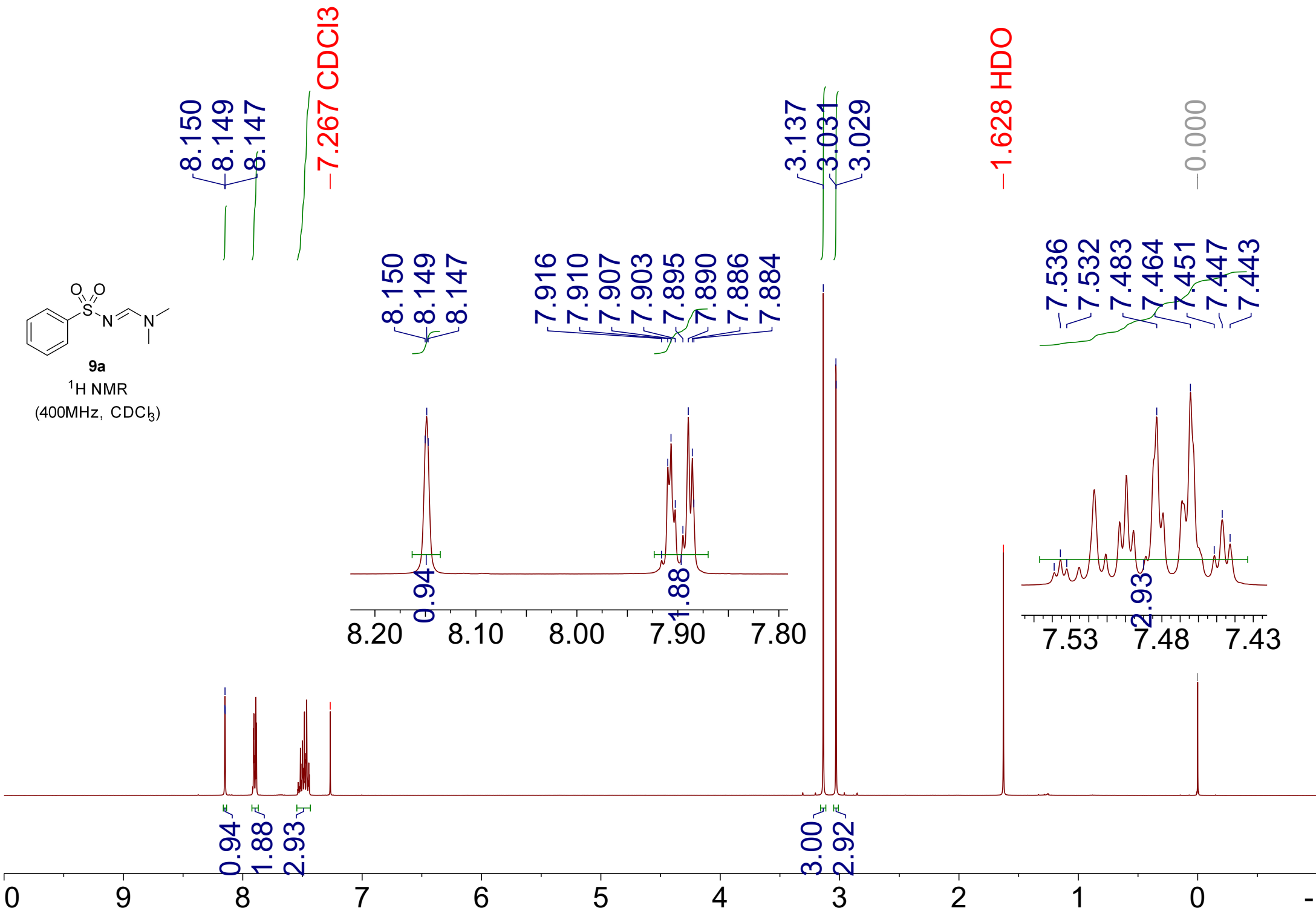
8

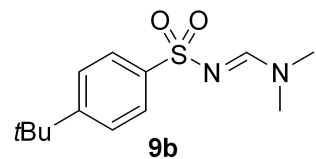
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)



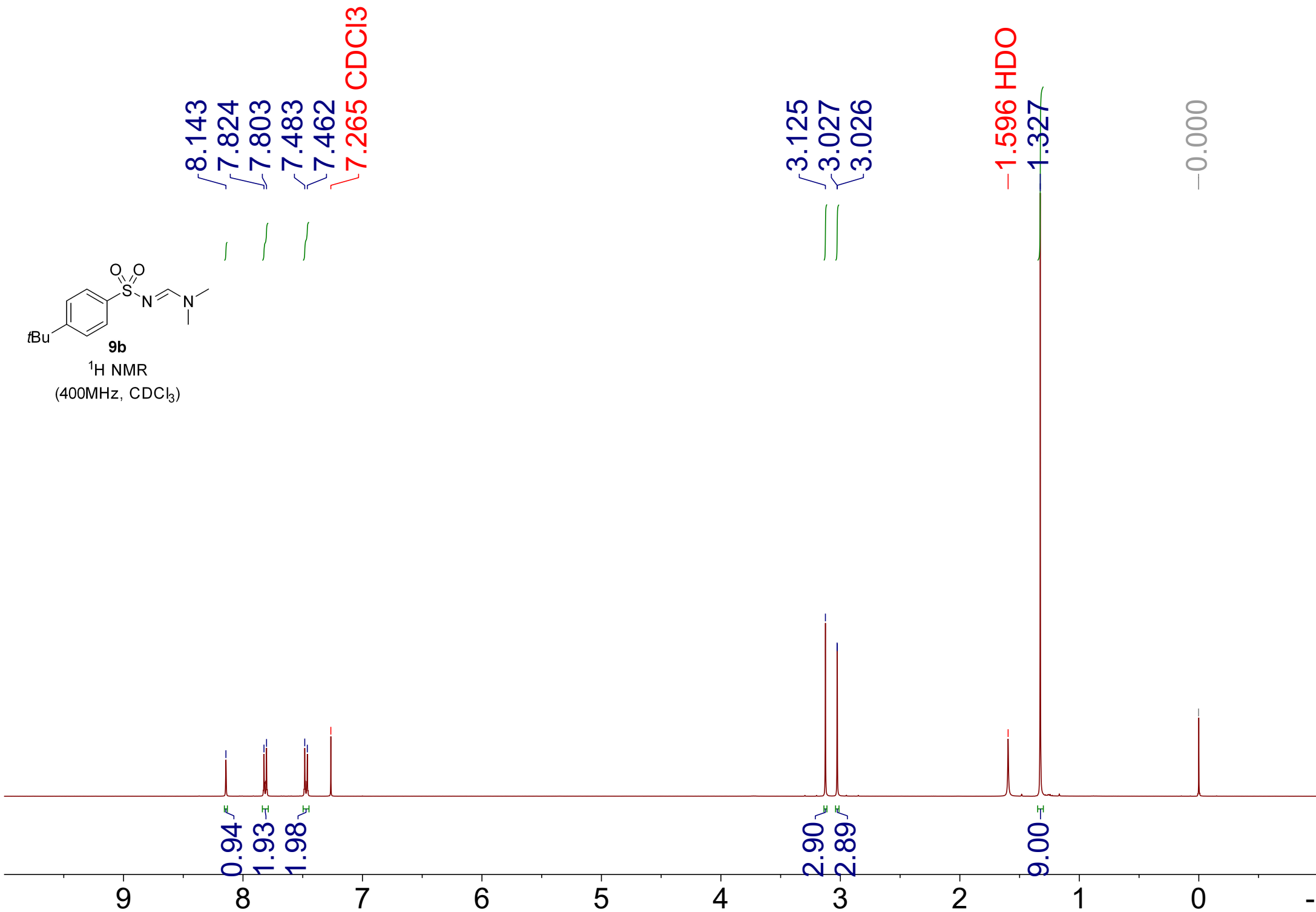


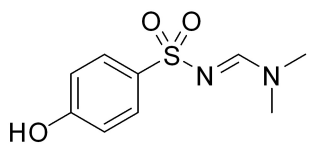
**9a**  
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)





<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

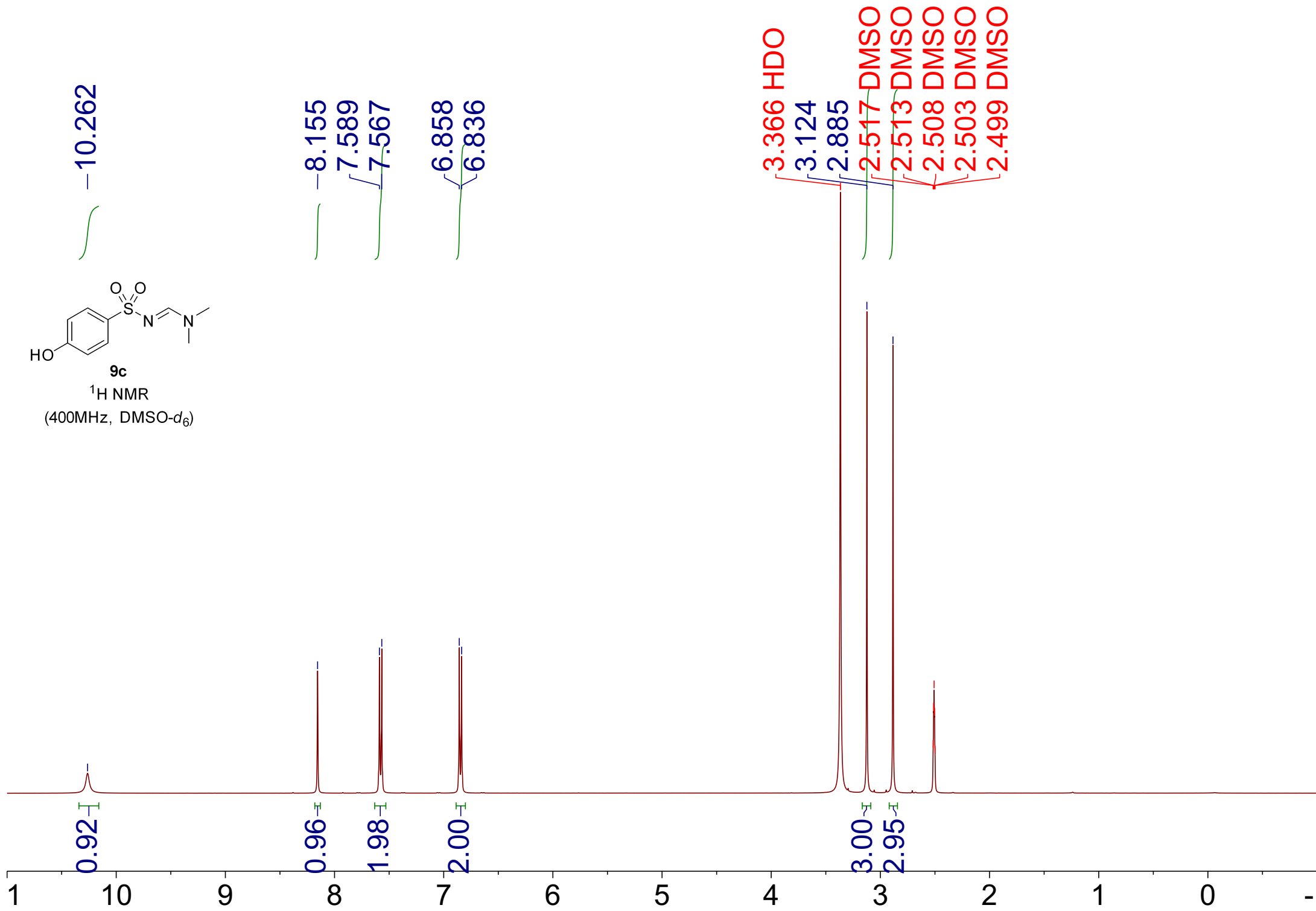


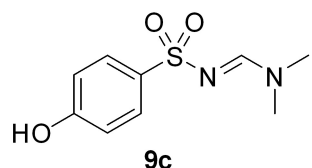


**9c**

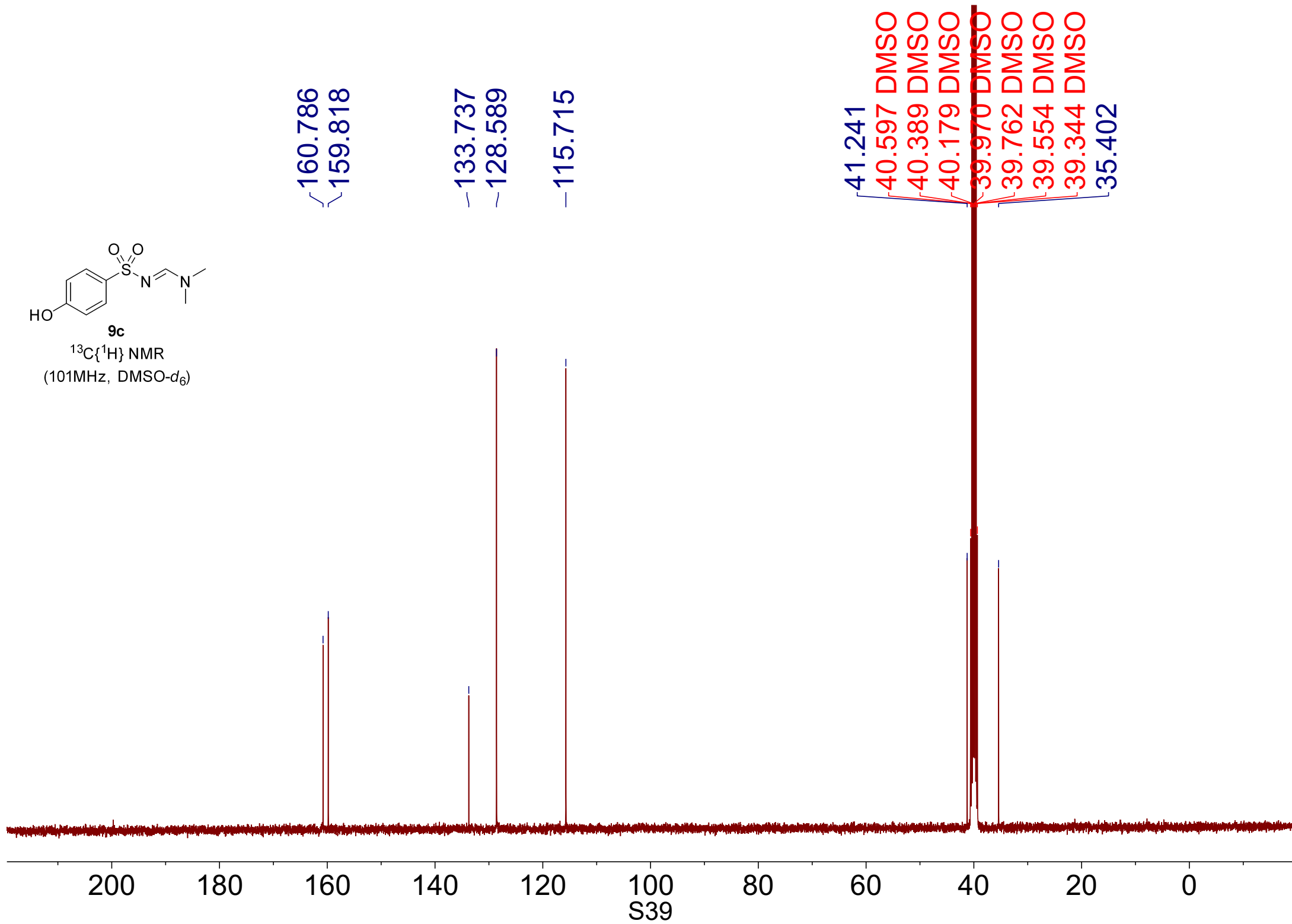
<sup>1</sup>H NMR

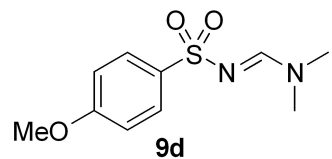
(400MHz, DMSO-d<sub>6</sub>)



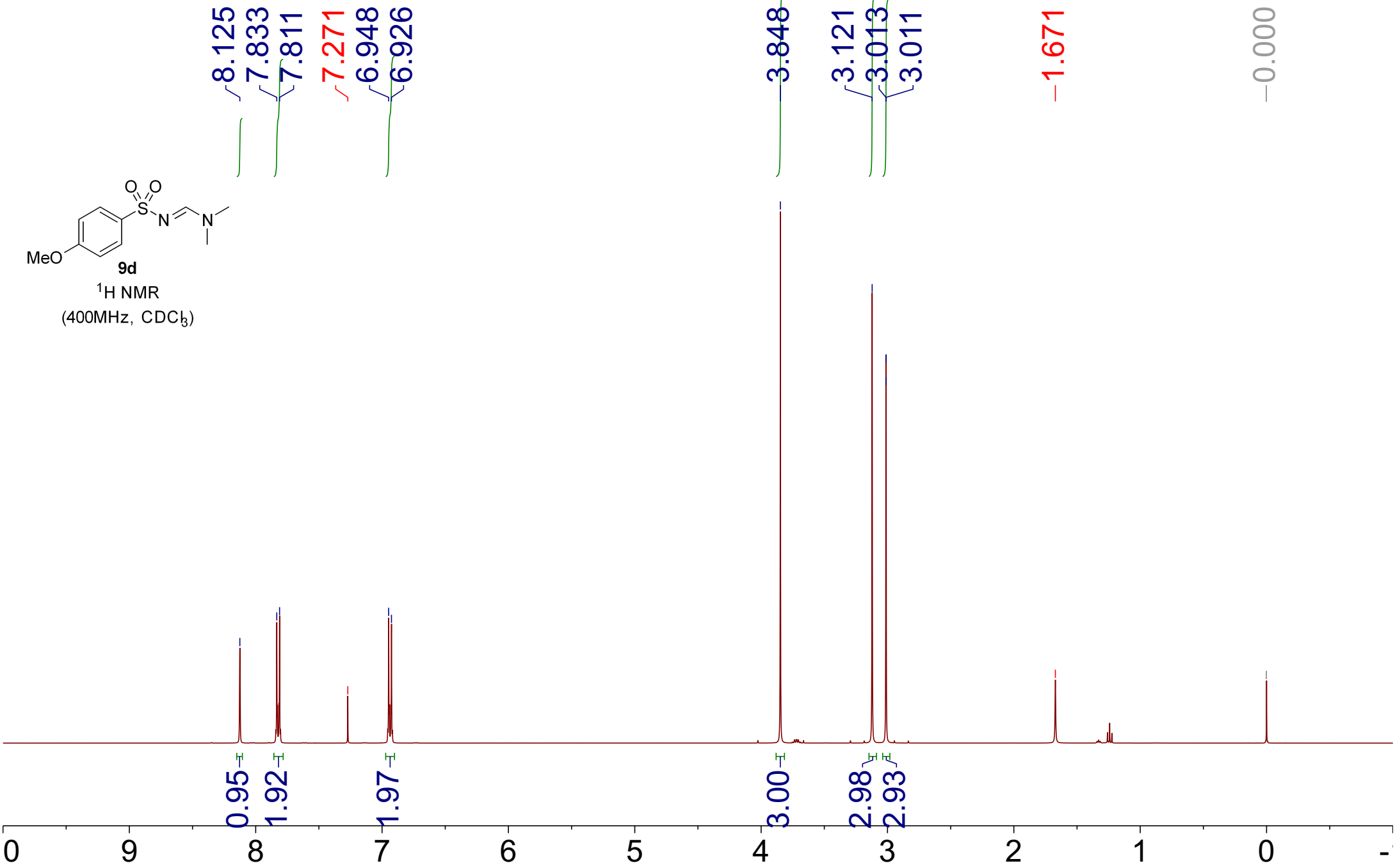


$^{13}\text{C}\{^1\text{H}\}$  NMR  
(101MHz, DMSO- $d_6$ )

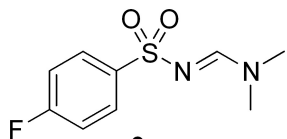




<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

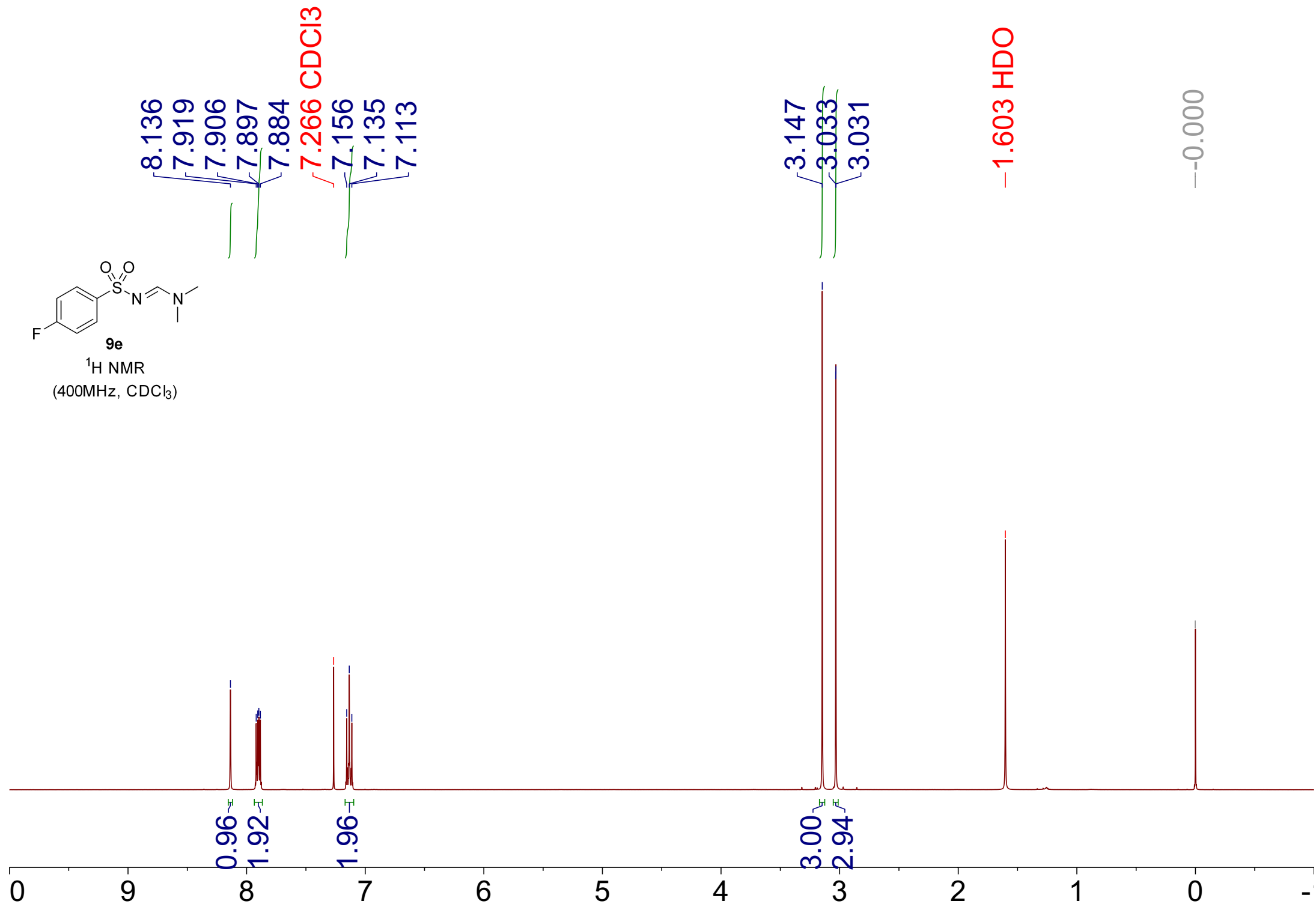


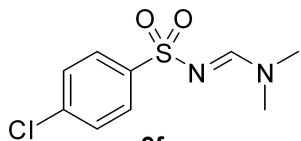




9e

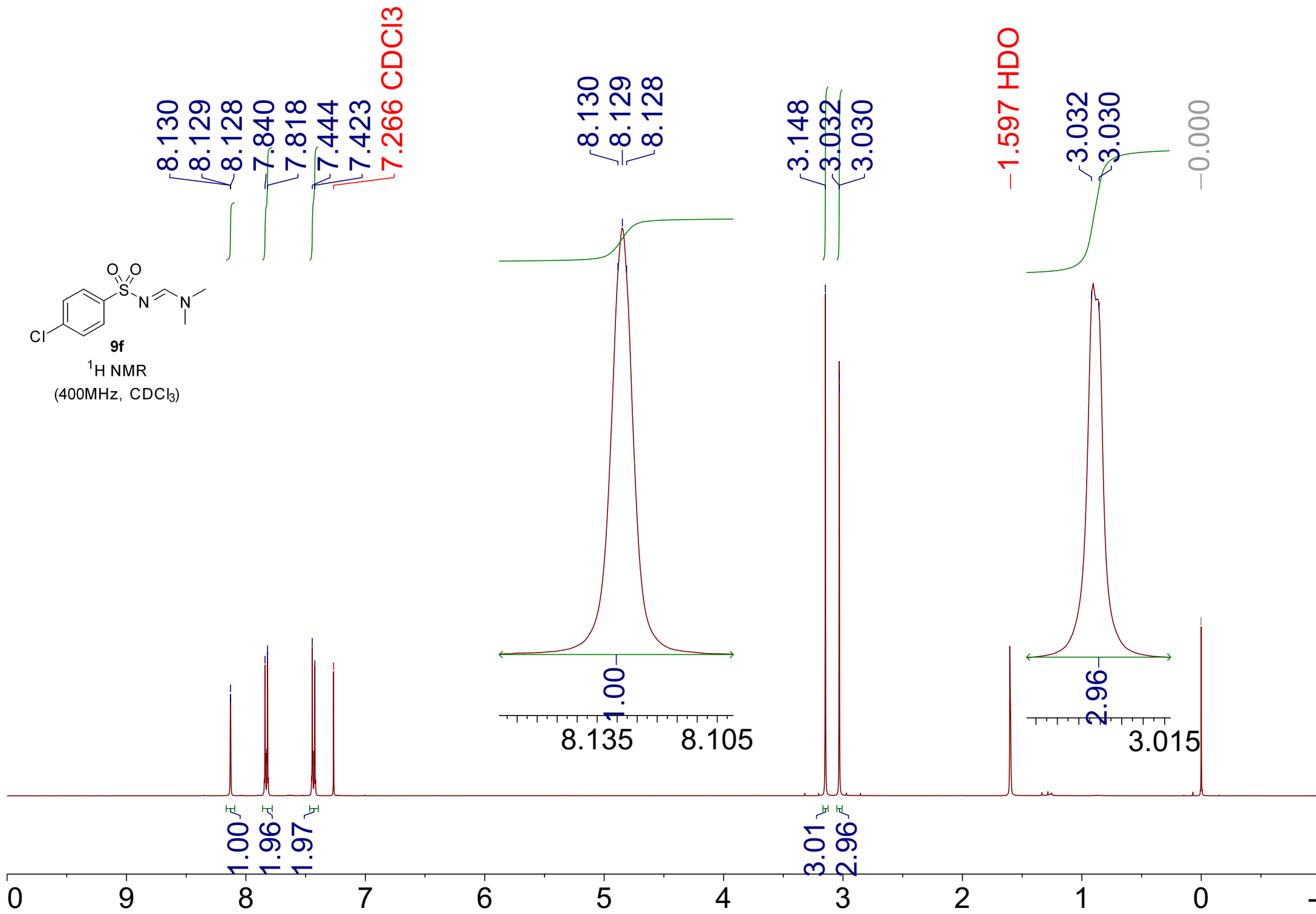
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

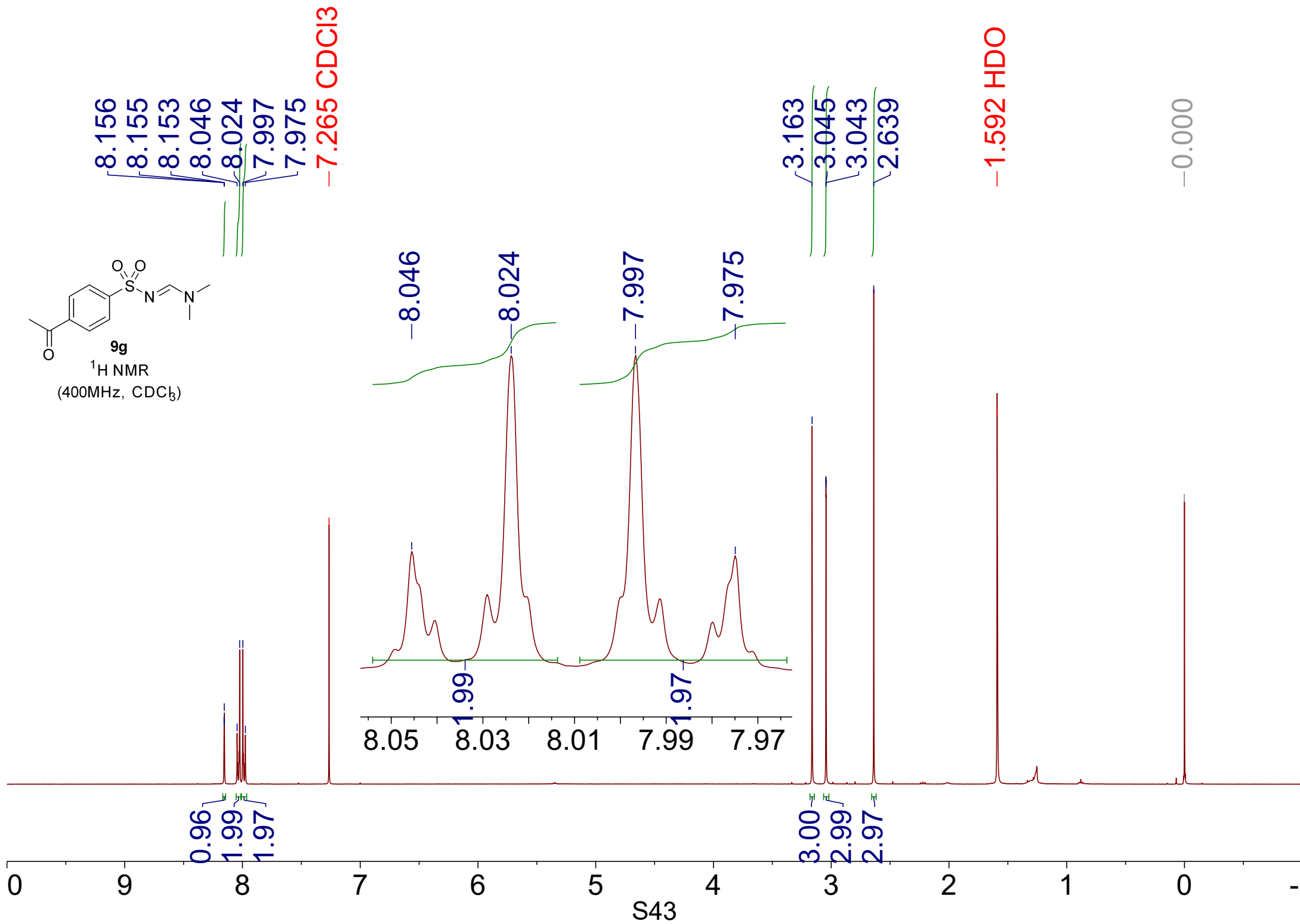
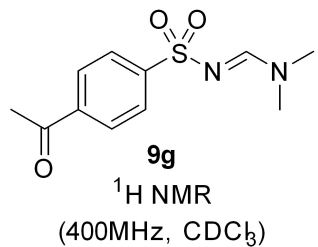


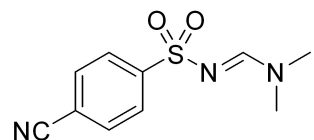


9f

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)







9h

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

8.145  
8.016  
7.995  
7.776  
7.755  
7.274 CDCl<sub>3</sub>

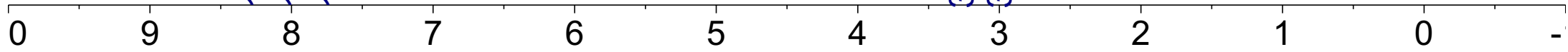
3.179  
3.051

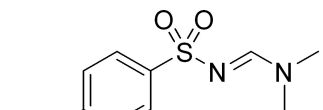
-1.659 H<sub>2</sub>O

-0.000

1.00  
1.93  
1.88

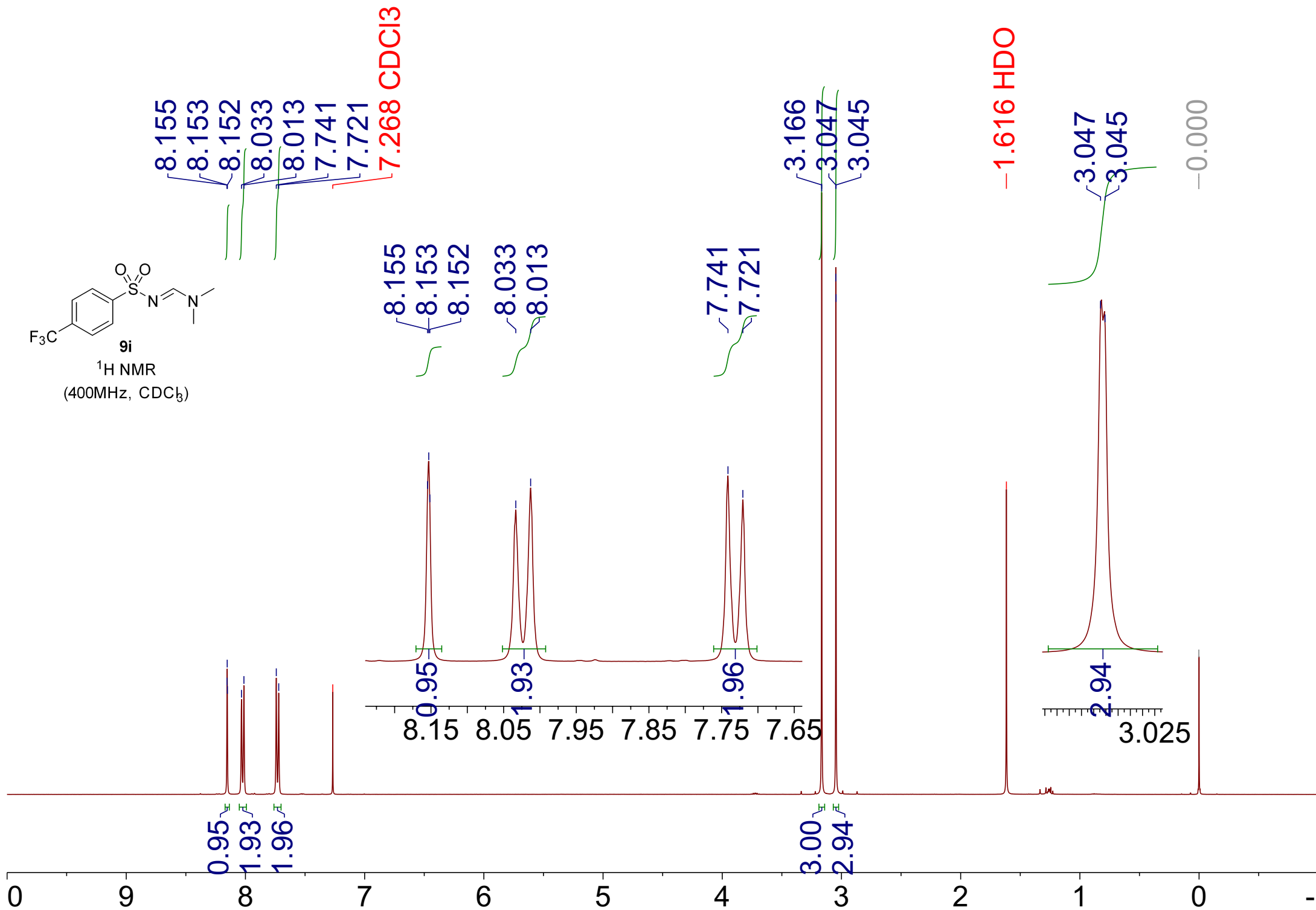
3.00  
3.01

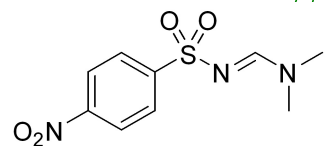




9i

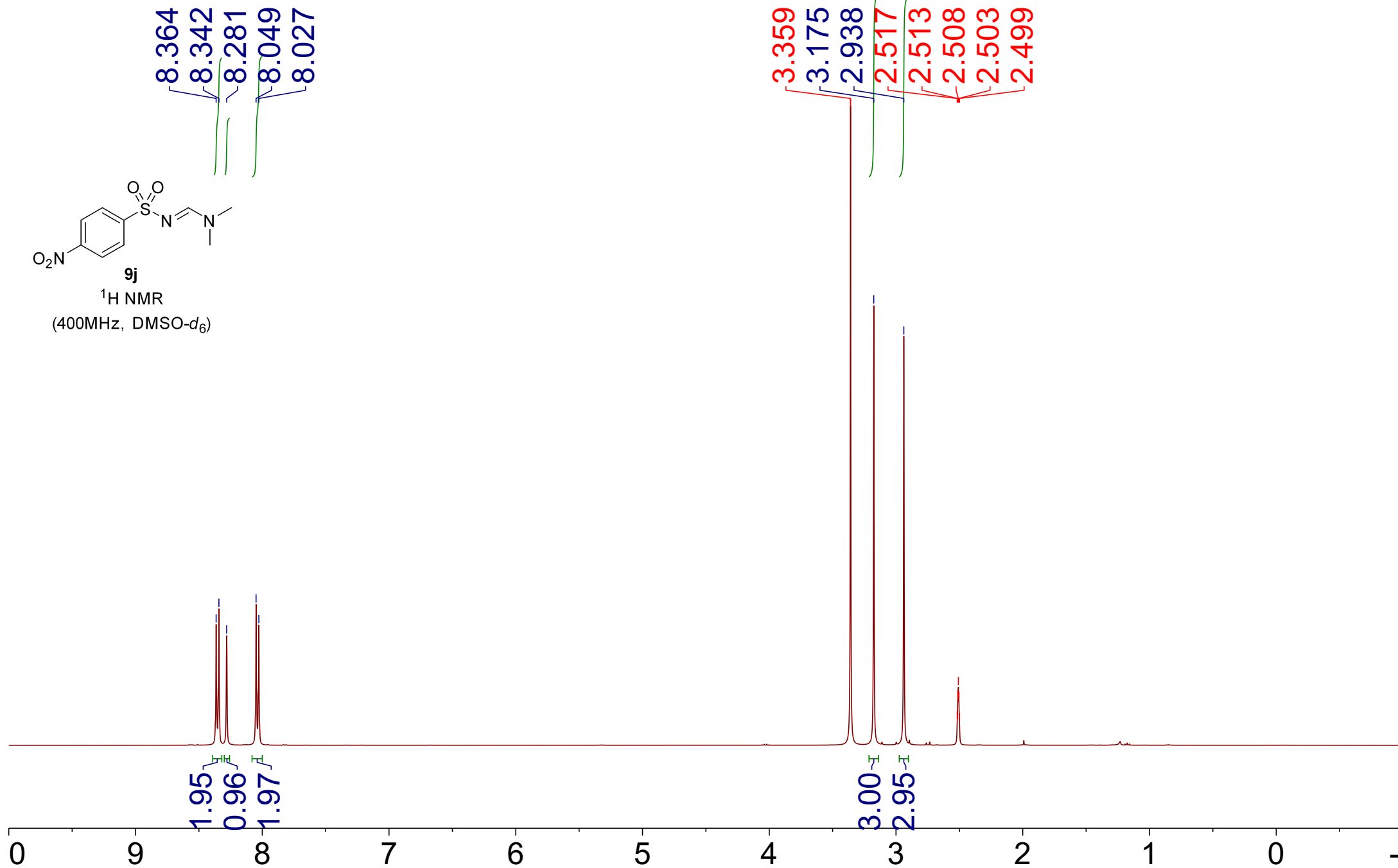
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

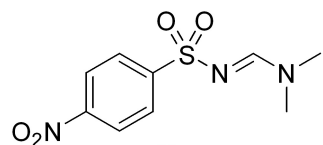




9j

<sup>1</sup>H NMR  
(400MHz, DMSO-d<sub>6</sub>)





$^{13}\text{C}\{^1\text{H}\}$  NMR  
(101MHz, DMSO- $d_6$ )

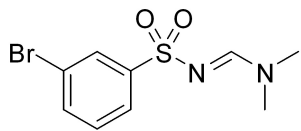
160.713  
149.587  
148.961

127.972  
125.179  
124.863

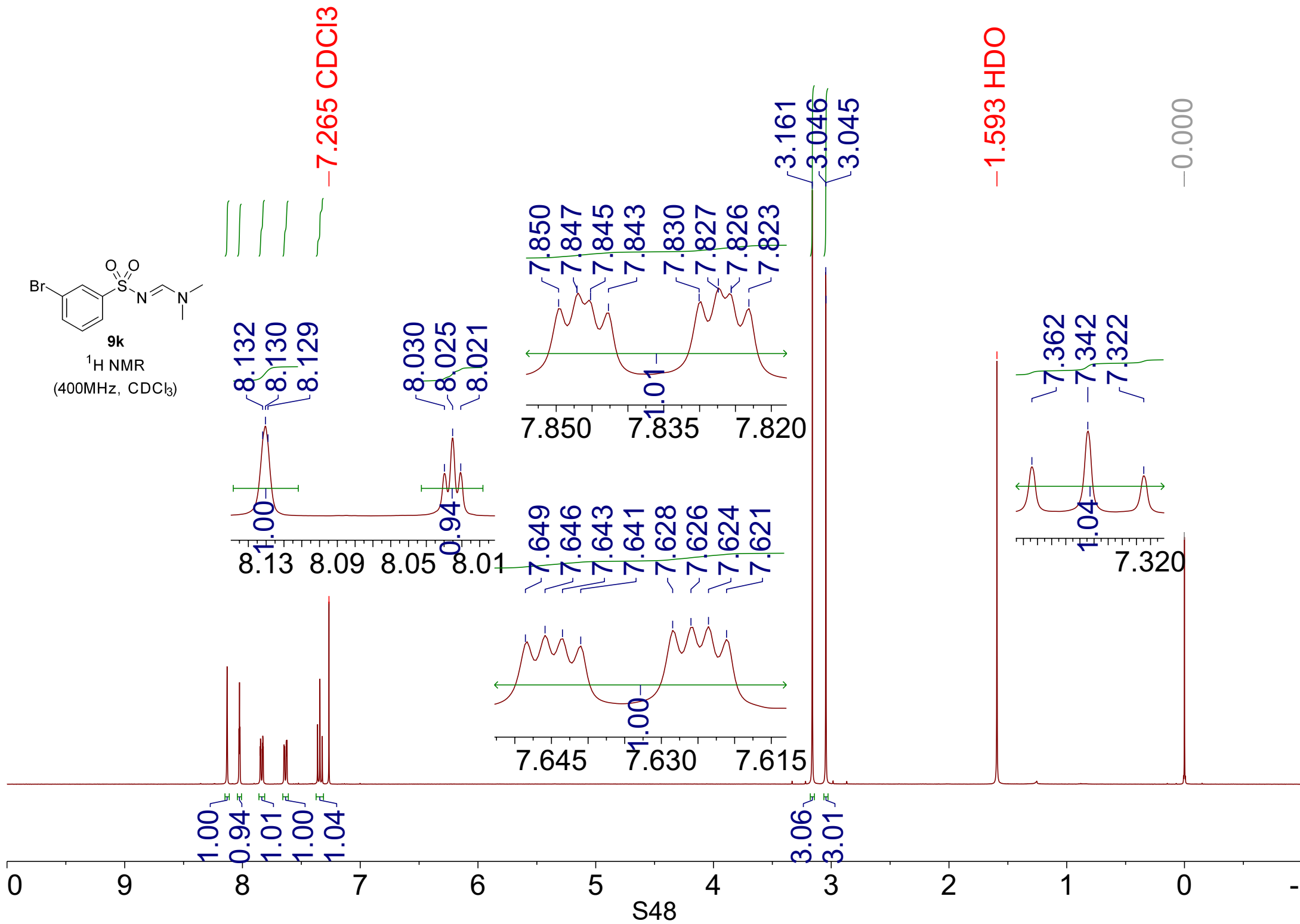
41.576  
40.601 DMSO  
40.392 DMSO  
40.182 DMSO  
39.973 DMSO  
39.766 DMSO  
39.556 DMSO  
39.347 DMSO  
35.716

200 180 160 140 120 100 80 60 40 20 0

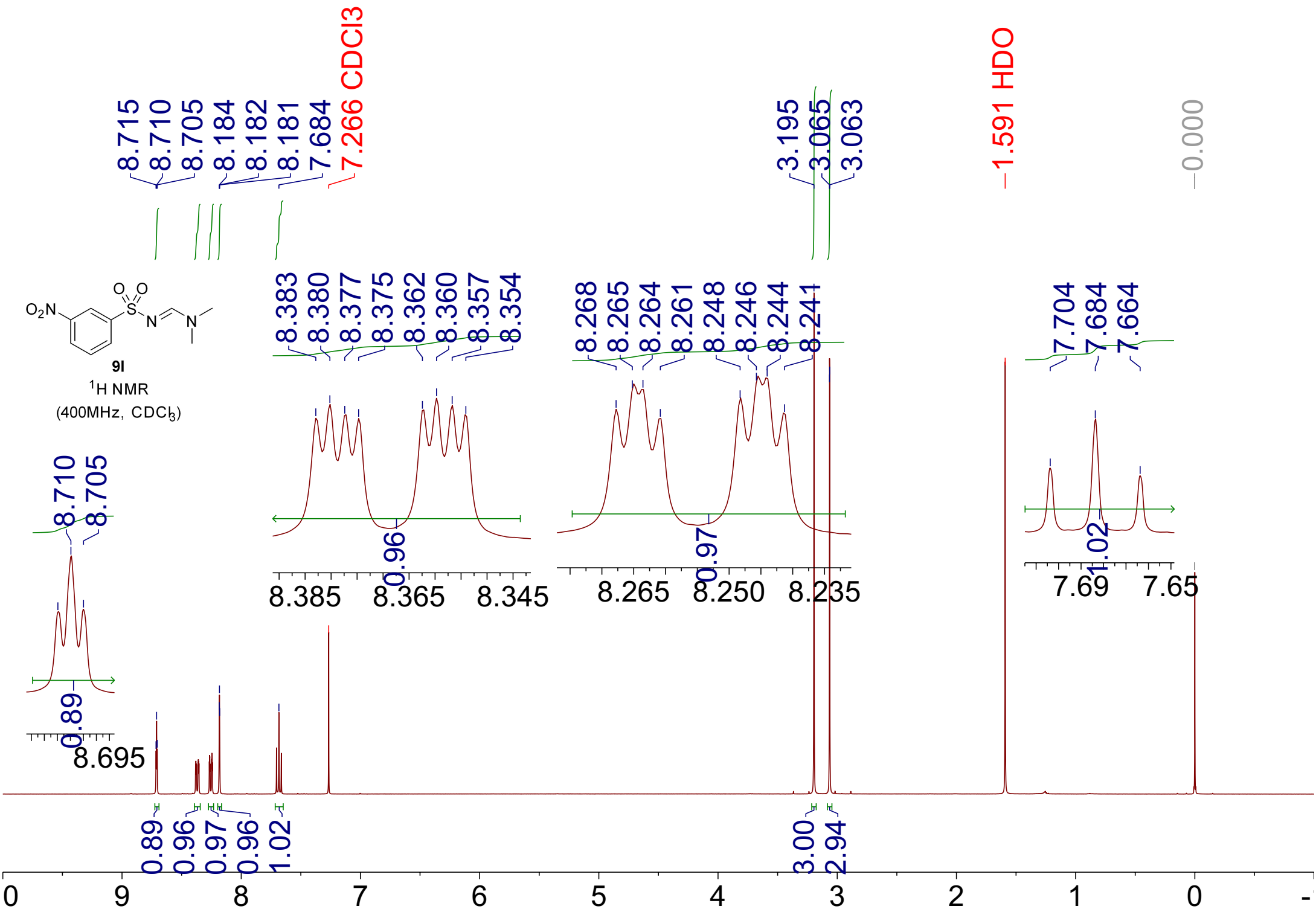
S47

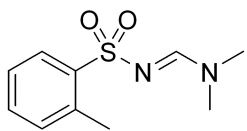


**9k**  
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)



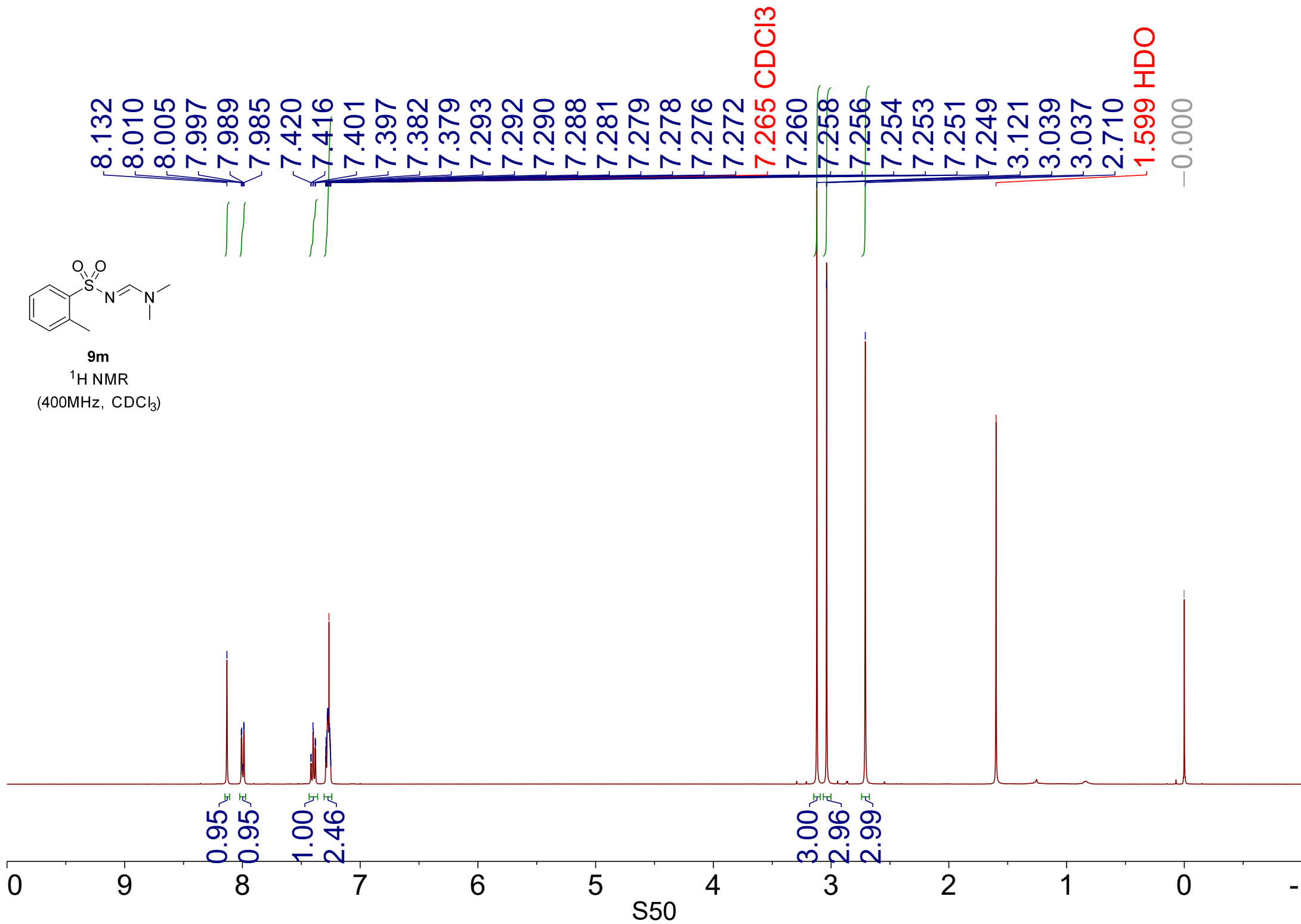


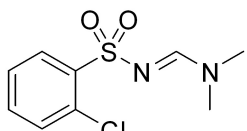




**9m**

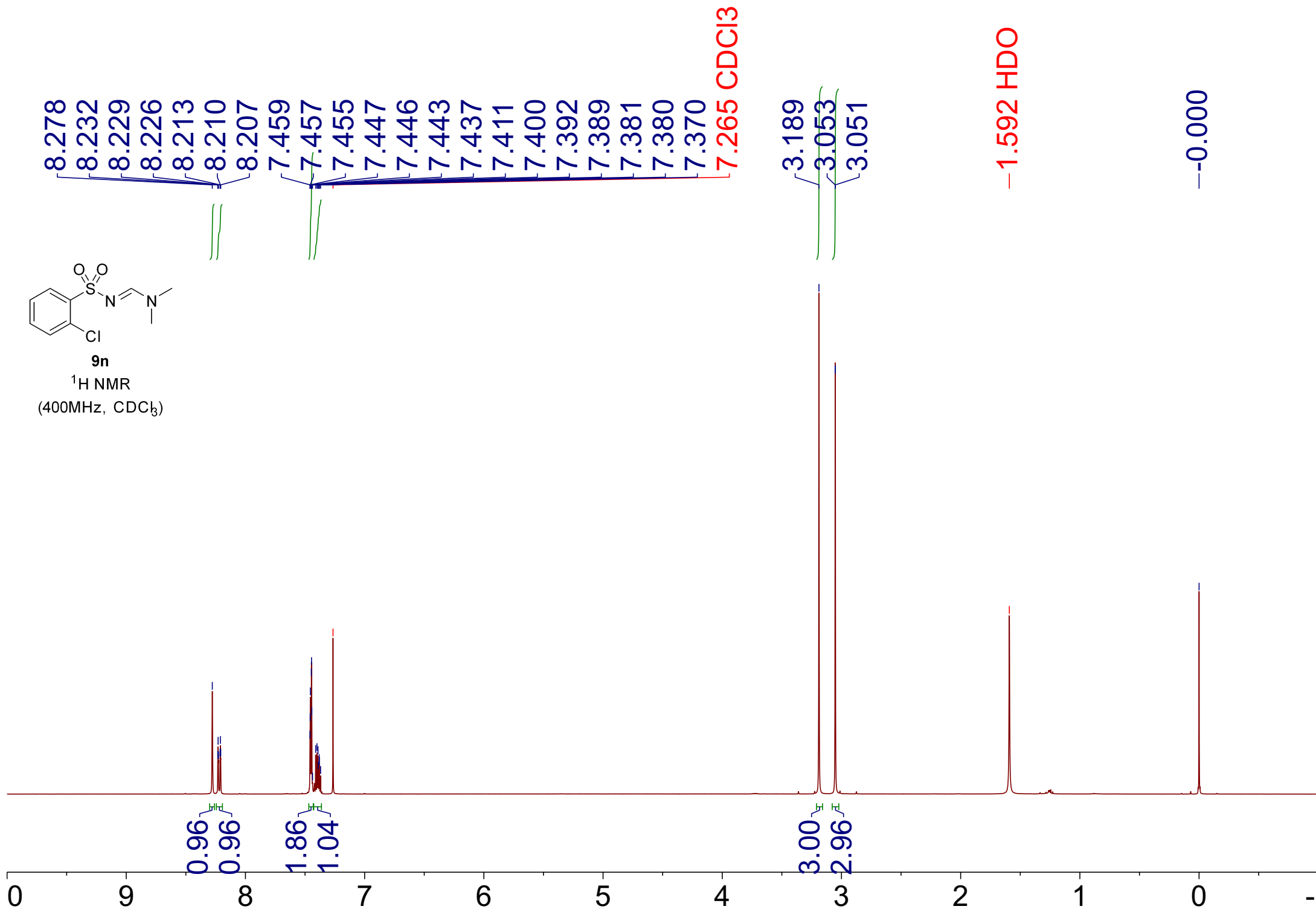
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

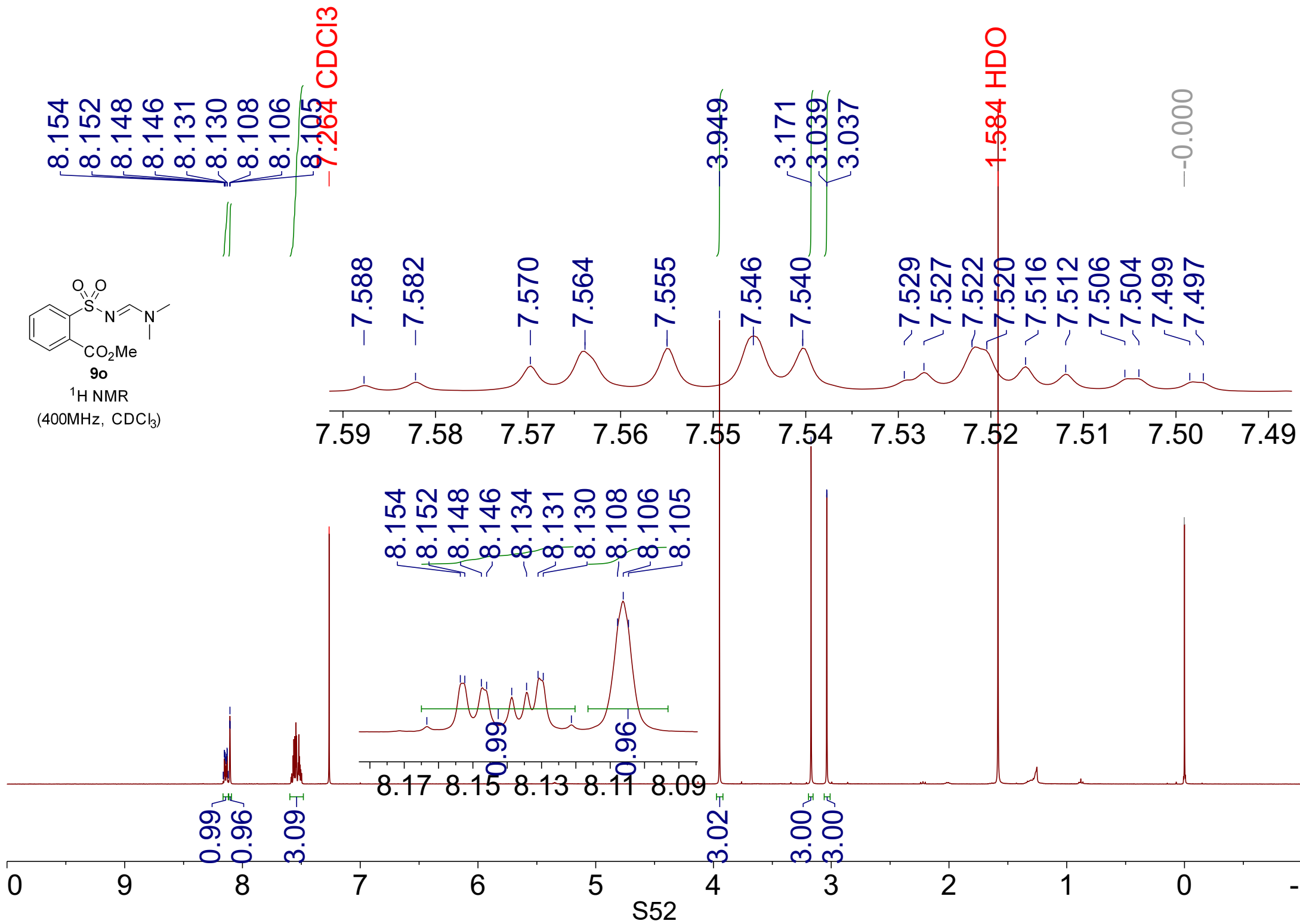
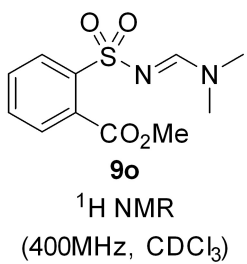


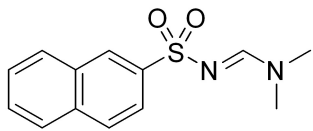


**9n**

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

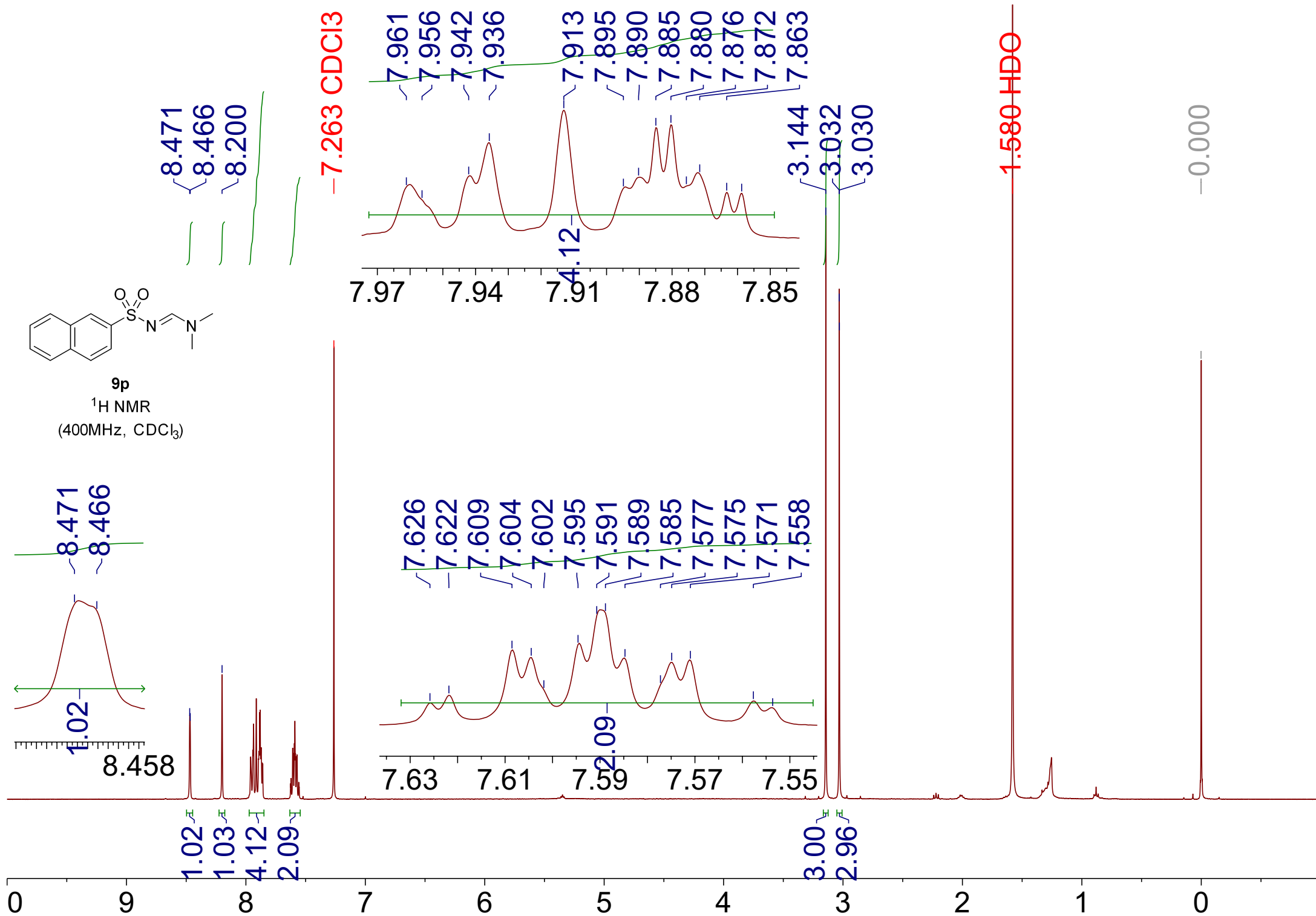


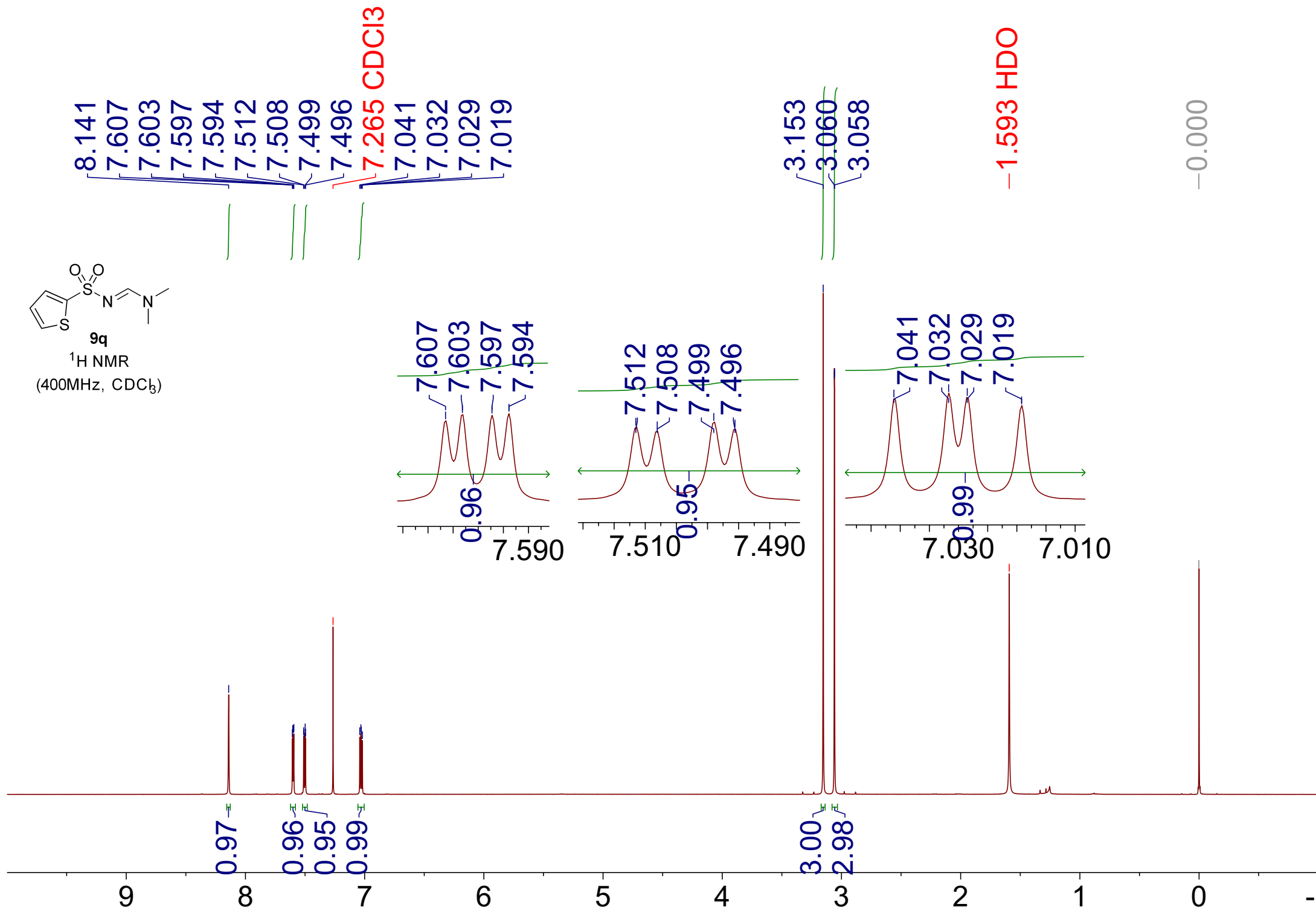
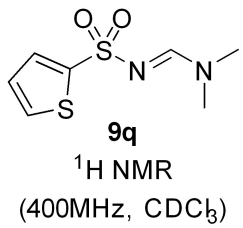


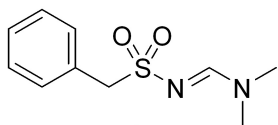


9p

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

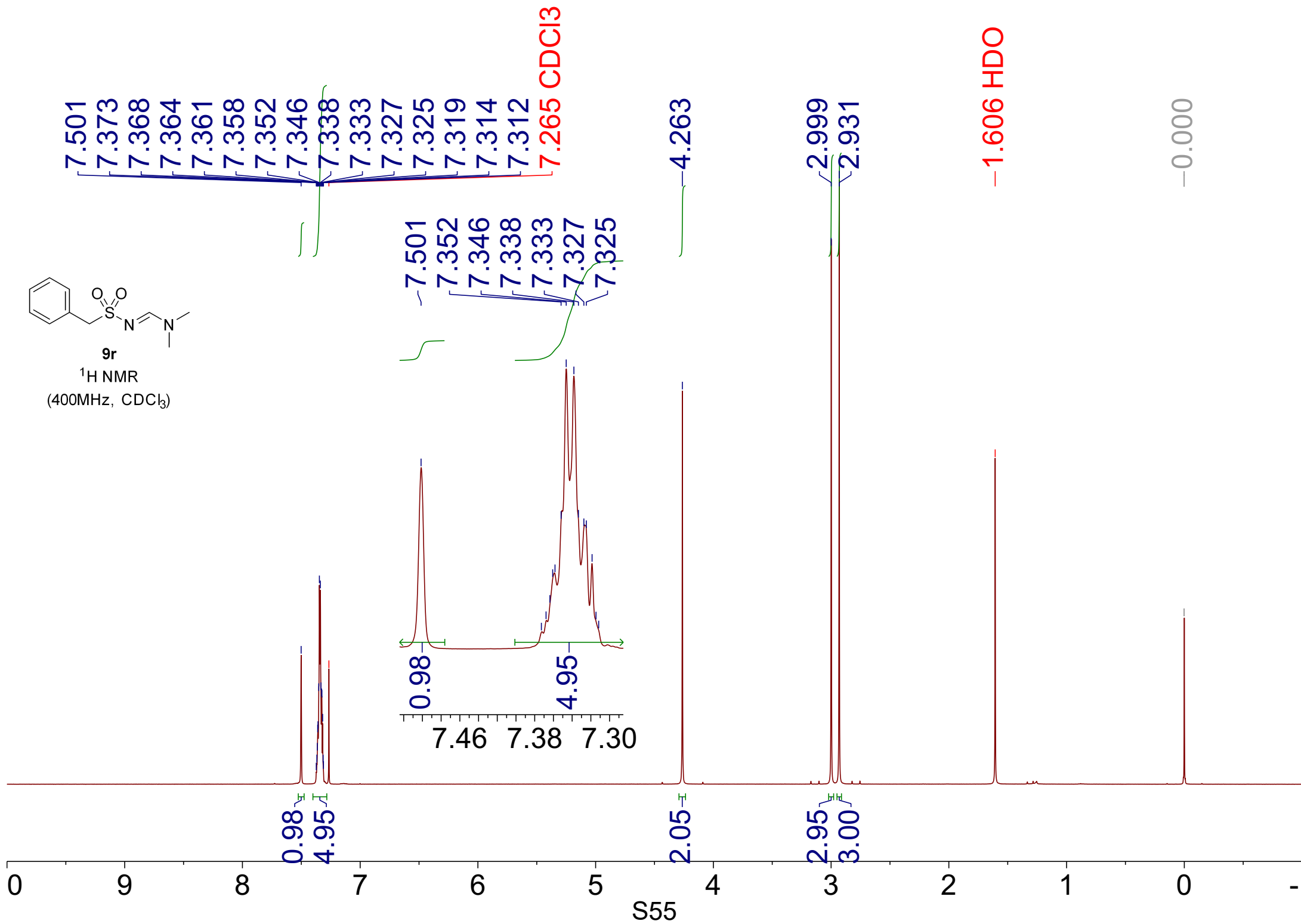


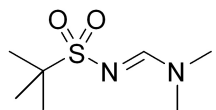




9r

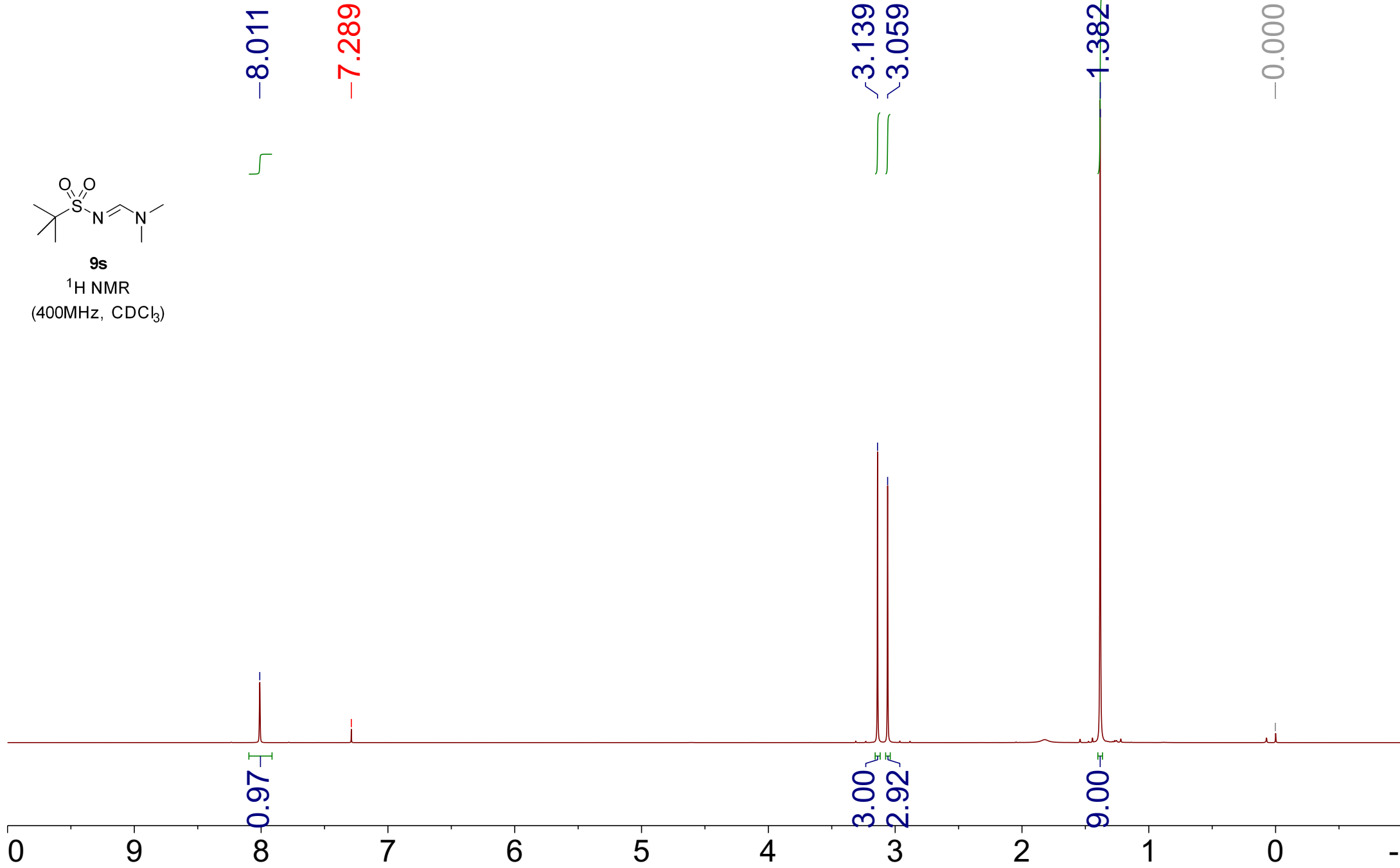
<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)



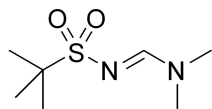


**9s**

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

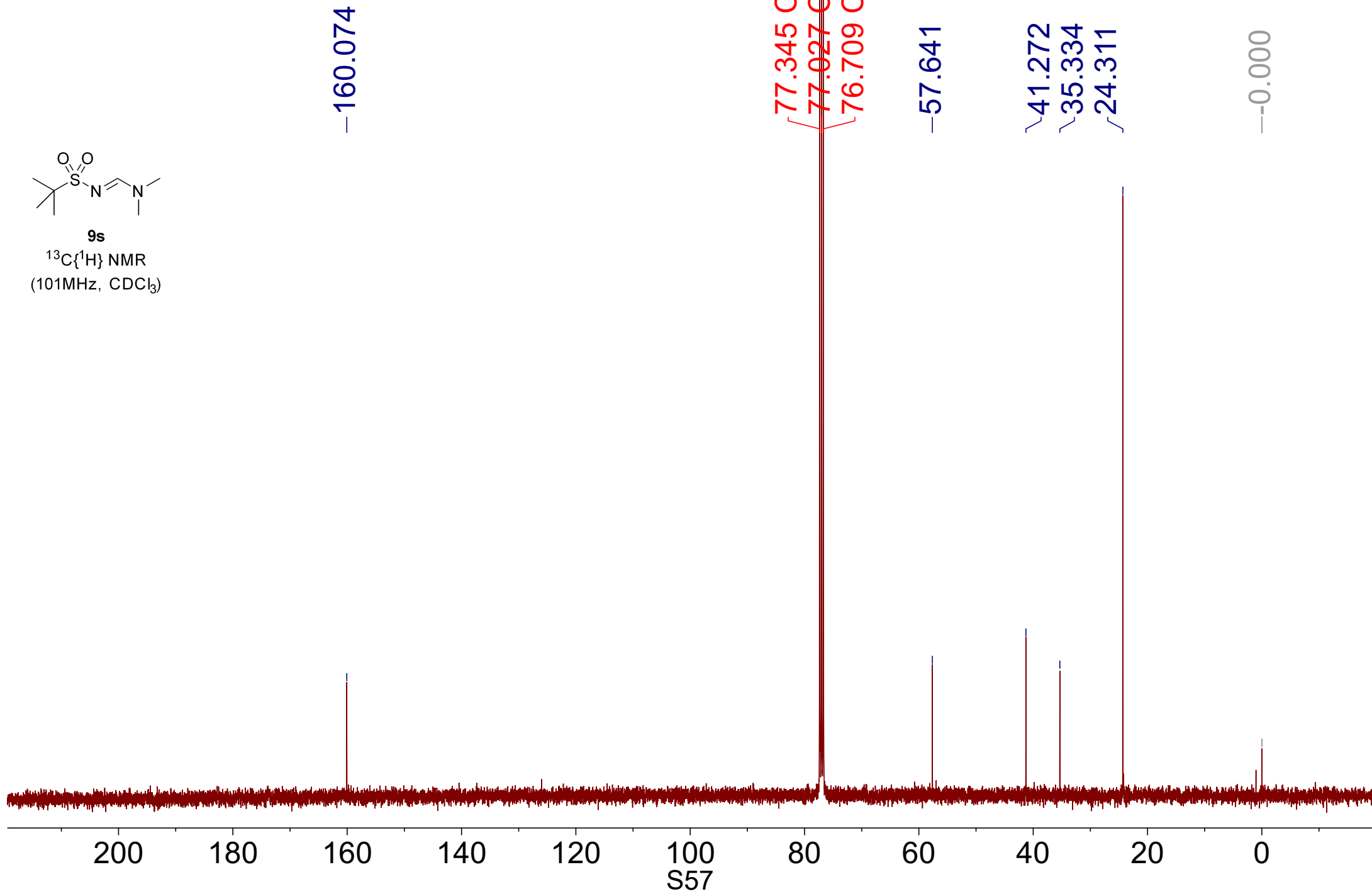


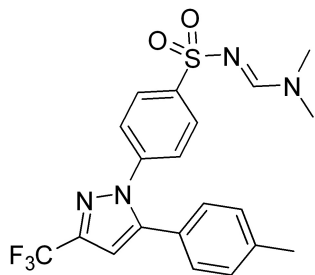




**9s**

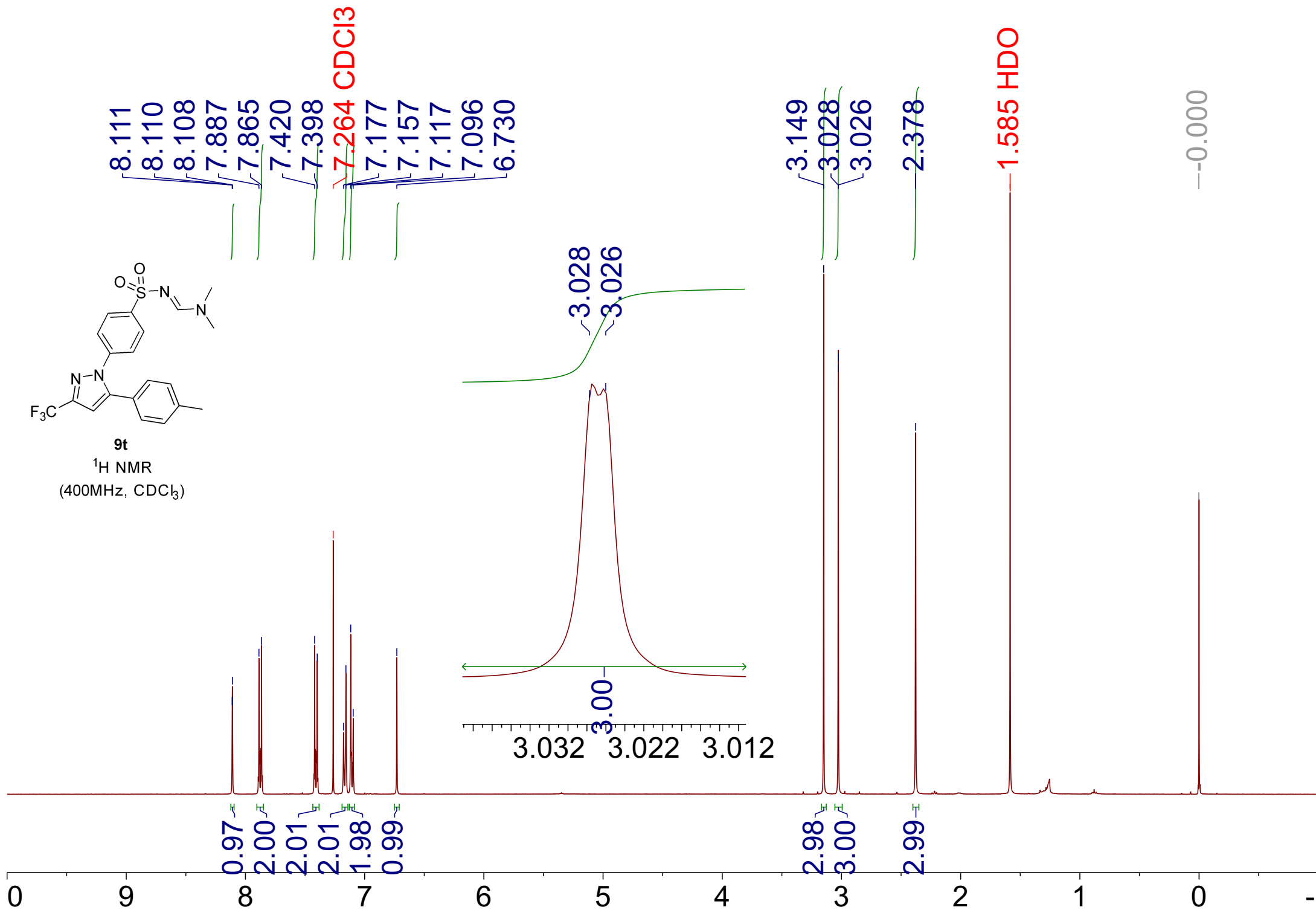
$^{13}\text{C}\{^1\text{H}\}$  NMR  
(101MHz,  $\text{CDCl}_3$ )

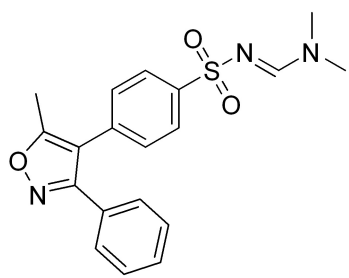




9t

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)

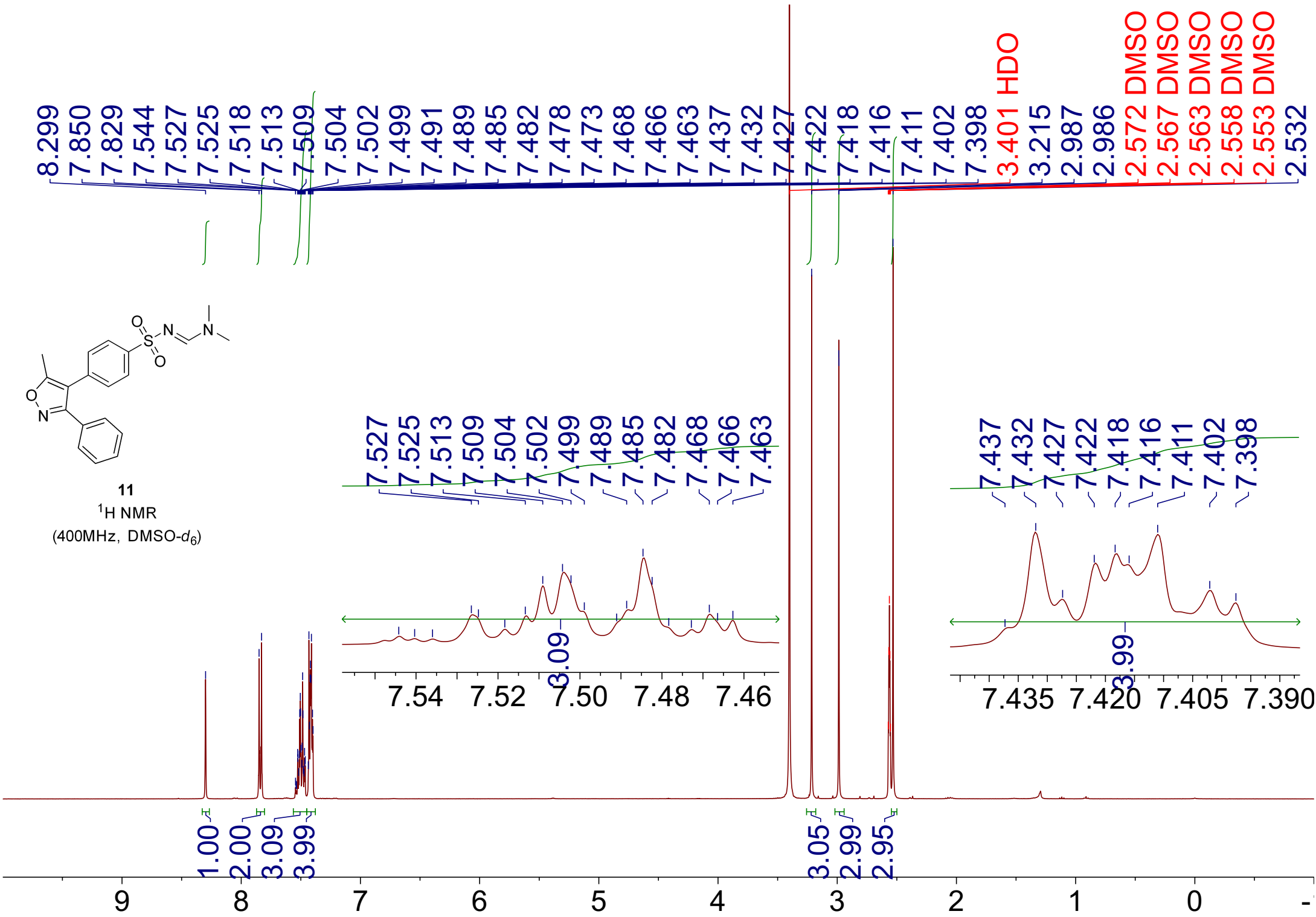


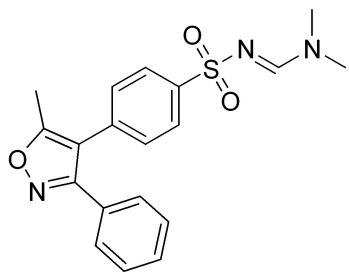


11

<sup>1</sup>H NMR

(400MHz, DMSO-d<sub>6</sub>)



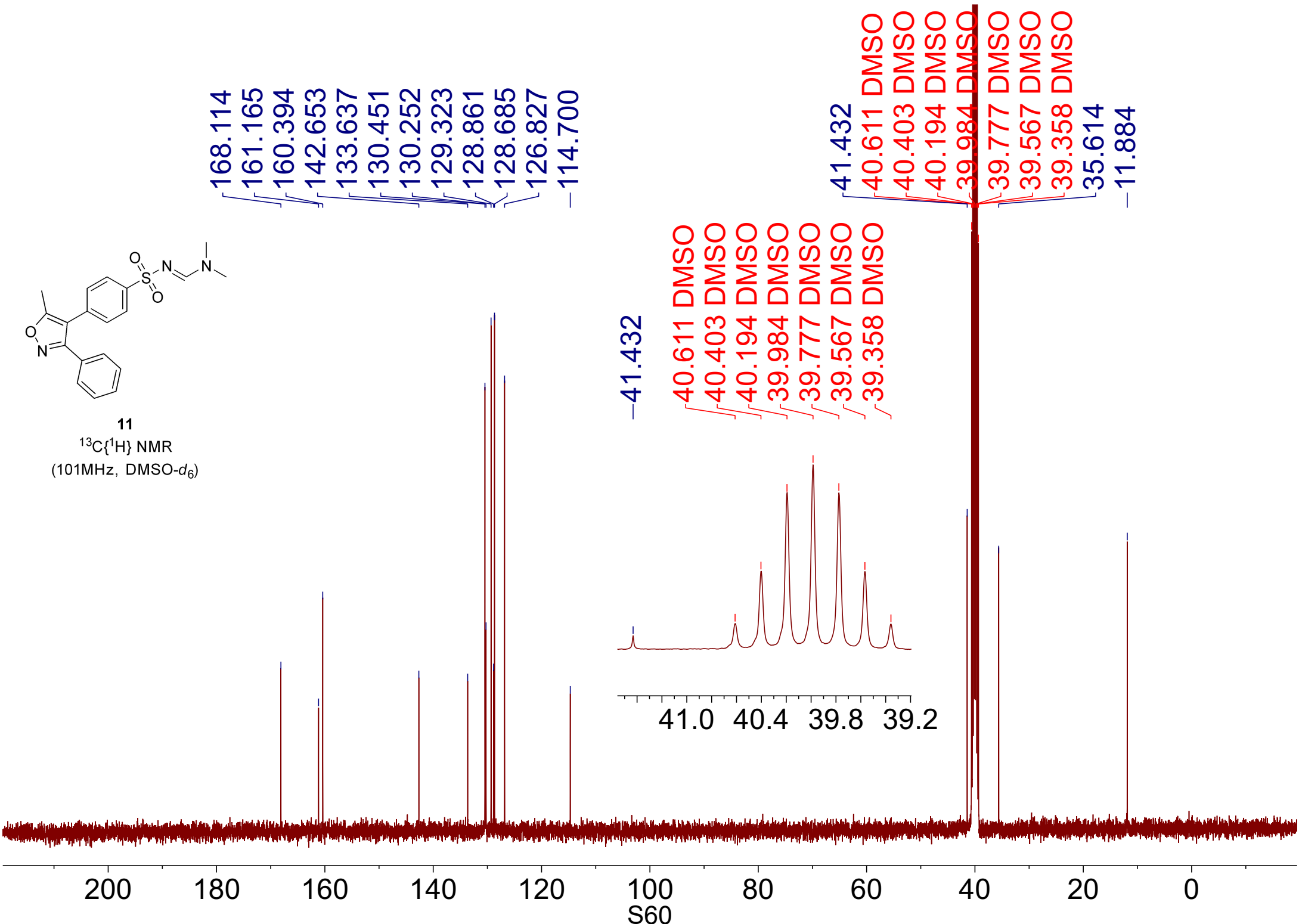


11

$^{13}\text{C}\{^1\text{H}\}$  NMR  
(101MHz, DMSO- $d_6$ )

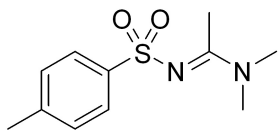
168.114  
161.165  
160.394  
142.653  
133.637  
130.451  
130.252  
129.323  
128.861  
128.685  
126.827  
-114.700

-41.432  
40.611 DMSO  
40.403 DMSO  
40.194 DMSO  
39.984 DMSO  
39.777 DMSO  
39.567 DMSO  
39.358 DMSO  
41.432  
40.611 DMSO  
40.403 DMSO  
40.194 DMSO  
39.984 DMSO  
39.777 DMSO  
39.567 DMSO  
39.358 DMSO  
35.614  
-11.884



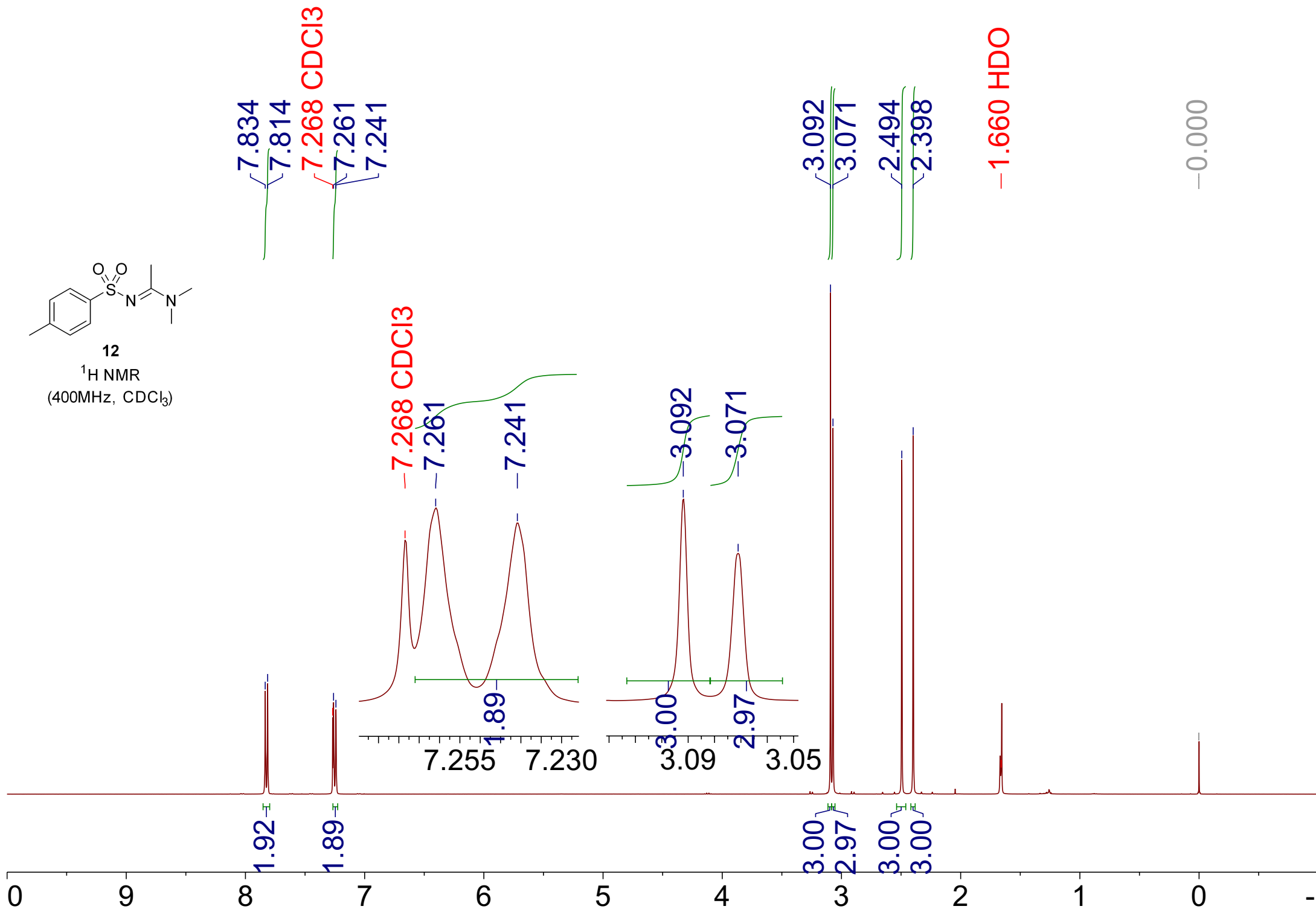
200 180 160 140 120 100 80 60 40 20 0

S60



12

<sup>1</sup>H NMR  
(400MHz, CDCl<sub>3</sub>)



# Elemental Composition Report

## Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

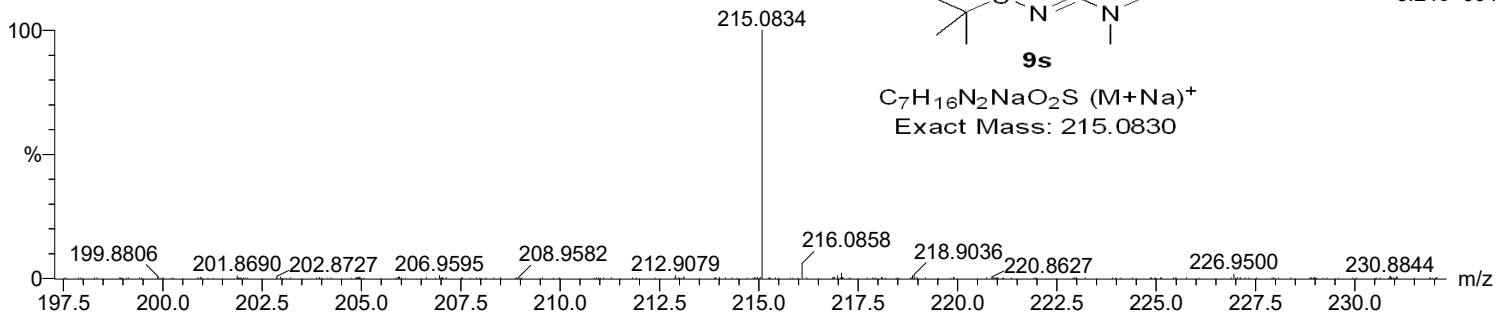
211 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 7-7 H: 16-16 N: 0-100 O: 0-100 Na: 0-1 S: 1-2

11

240414-3-1 58 (0.264)



Minimum: -1.5  
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
215.0834	215.0830	0.4	1.9	0.5	159.6	n/a	n/a	C7 H16 N2 O2 Na S

# Elemental Composition Report

## Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

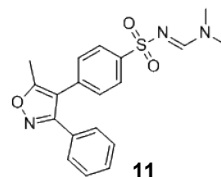
973 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 19-19 H: 19-19 N: 0-100 O: 0-100 Na: 0-1 S: 1-2

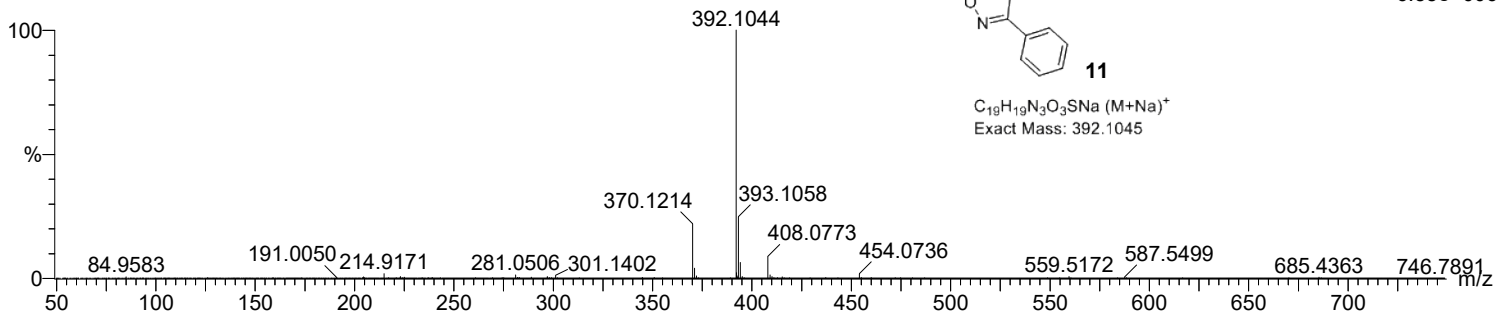
21

240424-12-1 28 (0.297)



C<sub>19</sub>H<sub>19</sub>N<sub>3</sub>O<sub>3</sub>Na (M+Na)<sup>+</sup>  
Exact Mass: 392.1045

1: TOF MS ES+  
6.55e+006



Minimum: -1.5  
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
392.1044	392.1045	-0.1	-0.3	11.5	825.9	n/a	n/a	C <sub>19</sub> H <sub>19</sub> N <sub>3</sub> O <sub>3</sub> Na S