Silver comes into play: Henry reaction and domino cycloisomerisation sequence catalysed by [Ag(I)(Pc-L)] complexes

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General experimental details. All of the reactions that involved the use of reagents sensitive to oxygen or hydrolysis were carried out under an inert atmosphere. The glassware was previously dried in an oven at 110 °C and was set with cycles of vacuum and nitrogen. Also syringes, used to transfer reagents and solvents, were previously set under a nitrogen atmosphere. The syntheses of the silver complexes were carried out under a nitrogen atmosphere by employing standard Schlenk techniques. All chemicals and solvents were commercially available and were used after distillation or treatment with drying agents. The chromatographic column separations were performed by a flash technique, using silica gel (pore size 60 Å, particle size 230−400 mesh, Merck grade 9385). For TLC, silica was used on TLC Alu foils with fluorescent indicator (254 nm) and the detection was performed by irradiation with UV light (λ = 254 nm or 366 nm). ^{1}H NMR analyses were performed with 200, 300, 400 or 600 MHz spectrometers at room temperature. The coupling constants (*J*) are expressed in hertz (Hz), and the chemical shifts (δ) in ppm. ^{13}C NMR analyses were performed with the same instruments at 75.5, 100 or 150 MHz, and attached proton test (APT) sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. All ^{13}C NMR spectra were recorded with complete proton decoupling. The ^{1}H NMR signals of the ligand described in the following have been attributed by correlation spectroscopy (COSY) and nuclear Overhauser effect spectroscopy (NOESY) techniques. Assignments of the resonance in ^{13}C NMR were made using the APT pulse sequence and heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlation (HMBC) techniques. Low resolution MS spectra were recorded with instruments equipped with electron ionization (EI), ESI/ion trap (using a syringe pump device to directly inject sample solutions), or fast atom bombardment (FAB) (for Pc-L and metal complexes) sources. The values are expressed as mass−charge ratio and the relative intensities of the most significant peaks are shown in brackets. UV−vis spectra of the ligand and its silver complexes were recorded in CH_2Cl_2. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano. Optical rotations were measured on a Perkin Elmer instruments model 343 plus; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Silver complex **1**[1], *N*-tosyl-aziridine and copper complex **2**[2] and 2,6-pyridinedimethanol 2,6-dimesylate[3] were synthetized as previously reported.

Henry reaction. Yields and ^{1}H spectra of products **4** and **9**

2-nitro-1-(4-nitrophenyl)ethanol **4a**. Yield 90% (62 mg); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.27 (d, J = 8.6 Hz, 2H, H_{Ar}), 7.63 (d, J = 8.5 Hz, 2H, H_{Ar}), 5.60 (dd, J = 7.7, 3.4 Hz, 1H, CH), 4.68 – 4.40 (m, 2H, CH_2), 3.12 (bs, 1H, OH). Spectral data are consistent with literature values.[4]

4-(1-hydroxy-2-nitroethyl)benzonitrile **4b**. Yield 80% (49 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.71 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.56 (d, J = 8.1 Hz, 2H, H_{Ar}), 5.55 (dd, J = 7.9, 3.8 Hz, 1H, CH), 4.68 – 4.43 (m, 2H, CH_2), 3.11 (bs, 1H, OH). Spectral data are consistent with literature values.[4]

2-nitro-1-(4-(trifluoromethyl)phenyl)ethanol **4c**. Yield 92% (69 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.68 (d, J = 8.3 Hz, 2H, H_{Ar}), 7.56 (d, J = 8.2 Hz, 2H, H_{Ar}), 5.56 (d, J = 6.6 Hz, 1H, CH), 4.70 – 4.45 (m, 2H, CH_2), 2.96 (bs, 1H, OH). Spectral data are consistent with literature values.[5]

1-(4-bromophenyl)-2-nitroethanol **4d**. Yield 82% (65 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.54 (d, J = 8.4 Hz, 2H, H_{Ar}), 7.29 (d, J = 8.2 Hz, 2H, H_{Ar}), 5.44 (dd, J = 9.2, 3.3 Hz, 1H, CH), 4.61 – 4.46 (m, 2H, CH_2), 2.88 (bs, 1H, OH). Spectral data are consistent with literature values.[4]

1-(4-chlorophenyl)-2-nitroethanol **4e**. Yield 80% (52 mg); ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.38 (d, J = 8.6 Hz, 2H, H_{Ar}), 7.34 (d, J = 8.5 Hz, 2H, H_{Ar}), 5.44 (d, J = 9.5 Hz, 1H, CH), 4.57 (dd, J = 13.3, 9.5 Hz, 1H, CH_2), 4.49 (dd, J = 13.3, 3.1 Hz, 1H, CH_2), 3.01 (d, J = 3.6 Hz, 1H, OH). Spectral data are consistent with literature values.[4]

1-(4-fluorophenyl)-2-nitroethanol **4f**. Yield 64% (38 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.39 (dd, J = 8.4, 5.2 Hz, 2H, H_{Ar}), 7.10 (pst, J = 8.6 Hz, 2H, H_{Ar}), 5.46 (d, J = 9.1 Hz, 1H, CH), 4.63 – 4.47 (m, 2H, CH_2), 2.82 (bs, 1H, OH). Spectral data are consistent with literature values.[4]

2-nitro-1-phenylethanol **4g**. Yield 55% (29 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.42 – 7.29 (m, 5H, H_{Ar}), 5.48 (dd, J = 9.3, 3.2 Hz, 1H, CH), 4.66 – 4.50 (m, 2H, CH_2), 1.56 (bs, 1H, OH exchanging with water). Spectral data are consistent with literature values.[4]

2-nitro-1-(perfluorophenyl)ethanol **4i**. Yield 68% (56 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.87 (ddd, J = 9.2, 5.8, 3.5 Hz, 1H, CH), 5.02 (dd, J = 13.9, 9.4 Hz, 1H, CH_2), 4.61 (dd, J = 14.0, 3.4 Hz, 1H, CH_2), 3.08 (d, J = 6.0 Hz, 1H, OH). Spectral data are consistent with literature values.[6]

2-nitro-1-(2-nitrophenyl)ethanol **4k**. Yield 95% (65 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.07 (d, J = 8.2 Hz, 1H, H_{Ar}), 7.95 (d, J = 7.9 Hz, 1H, H_{Ar}), 7.75 (pst, J = 7.6 Hz, 1H, H_{Ar}), 7.56 (pst, J = 7.8 Hz, 1H, H_{Ar}), 6.05 (dd, J = 9.0, 2.0 Hz, 1H, CH), 4.87 (dd, J = 13.8, 2.3 Hz, 1H, CH_2), 4.55 (dd, J = 13.8, 9.1 Hz, 1H, CH_2), 3.23 (bs, 1H, OH). Spectral data are consistent with literature values.[4]

1-(2-bromophenyl)-2-nitroethanol **4l**. Yield 65% (51 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.67 (d, J = 7.9 Hz, 1H, H_{Ar}), 7.57 (d, J = 8.0 Hz, 1H, H_{Ar}), 7.41 (pst, J = 7.1 Hz, 1H, H_{Ar}), 7.22 (pst, J = 7.7 Hz, 1H, H_{Ar}), 5.96 – 5.70 (m, 1H, CH), 4.70 (dd, J = 13.7, 2.3 Hz, 1H, CH_2), 4.44 (dd, J = 13.7, 9.6 Hz, 1H, CH_2), 2.94 (d, J = 4.0 Hz, 1H, OH). Spectral data are consistent with literature values.[4]

1-(2,6-dichlorophenyl)-2-nitroethanol **4m**. Yield 68% (51 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.37 (m, 2H, H_{Ar}), 7.32 – 7.20 (m, 2H, H_{Ar}), 6.38 – 6.21 (m, 1H, CH), 5.17 (dd, J = 13.1, 10.1 Hz, 1H, CH_2), 4.56 (dd, J = 13.1, 3.4 Hz, 1H, CH_2), 3.24 (d, J = 8.3 Hz, 1H, OH). Spectral data are consistent with literature values.[5]

1-(furan-2-yl)-2-nitroethanol **4o**. Yield 62% (31 mg); ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.40 (s, 1H, H_{Ar}), 6.55 – 6.23 (m, 2H, H_{Ar}), 5.51 – 5.38 (m, 1H, CH), 4.76 (dd, J = 13.4, 9.0 Hz, 1H, CH_2), 4.65 (dd, J = 13.4, 3.6 Hz, 1H, CH_2), 3.18 (bs, 1H, OH). Spectral data are consistent with literature values.[4]

2-nitro-1-(4-nitrophenyl)propan-1-ol **4q**. Yield 90% (65 mg); Diastereomeric ratio (*syn*/*anti* 60:40) determined by ^{1}H NMR. *Syn* isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.25 – 8.21 (m, 2H, H_{Ar}), 7.60 – 7.56 (m, 2H, H_{Ar}), 5.18 (d, J = 6.6 Hz, 1H, CH), 4.79 – 4.72 (m, 1H, CH), 3.15 (bs, 1H, OH), 1.37 (d, J = 6.6 Hz, 3H, CH_3). *Anti* isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.25 – 8.21 (m, 2H, H_{Ar}), 7.60 – 7.56 (m, 2H, H_{Ar}), 5.55 (m, 1H, CH), 4.79 – 4.72 (m, 1H, CH), 3.15 (bs, 1H, OH), 1.48 (d, J = 6.6 Hz, 3H, CH_3). Spectral data are consistent with literature values.[4]

2-nitro-1-(2-nitrophenyl)propan-1-ol **4r**. Yield 93% (67 mg); Diastereomeric ratio (*syn*/*anti* 45:55) determined by ^{1}H NMR. *Syn* isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.00 (dd, J = 8.2, 0.9 Hz, 1H, H_{Ar}), 7.73 – 7.69 (m, 2H, H_{Ar}), 7.56 – 7.53 (m, 1H, H_{Ar}), 5.71 (d, J = 6.6 Hz, 1H, CH), 5.01 – 4.95 (m, 1H, CH), 3.34 (bs, 1H, OH), 1.56 – 1.51 (m, 3H, CH_3). *Anti* isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 8.08 (dd, J = 8.2, 1.4 Hz, 1H, H_{Ar}), 7.93 (d, J = 7.9 Hz, 1H, H_{Ar}), 7.73 – 7.69 (m, 1H, H_{Ar}), 7.56 – 7.53 (m, 1H, H_{Ar}), 6.09 (d, J = 2.6 Hz, 1H, CH), 4.79 – 4.72 (m, 1H, CH), 3.15 (bs, 1H, OH), 1.56 – 1.51 (d, J = 6.0 Hz, 3H, CH_3). Spectral data are consistent with literature values.[4]

2-nitro-1-(4-(trifluoromethyl)phenyl)propan-1-ol **4s**. Yield 71% (89 mg); Diastereomeric ratio (*syn*/*anti* 51:49) determined by ^{1}H NMR. *Syn* isomer: ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.69 – 7.66 (m, 2H, H_{Ar}), 7.54 – 7.51 (m, 2H, H_{Ar}), 5.13 (d, J = 8.6 Hz, 1H, CH), 4.76 (dq, J = 8.6, 6.9 Hz, 1H, CH), 1.37 (d, J = 6.9 Hz, 3H, CH_3). *Anti* isomer: ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.69 – 7.66 (m, 2H, H_{Ar}), 7.54 – 7.51 (m, 2H, H_{Ar}), 5.50 (d, J = 3.4 Hz, 1H, CH), 4.70 (qd, J = 6.8, 3.4 Hz, 1H, CH), 1.50 (d, J = 6.8 Hz, 3H, CH_3). OH signal appeared as a very broad signal around 3.5 – 1.8 ppm. Spectral data are consistent with literature values.[7]

2-nitro-1-(4-chlorophenyl)propan-1-ol **4t**. Yield 75% (52 mg); Diastereomeric ratio (*syn*/*anti* 61:39) determined by ^{1}H NMR. *Syn* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.39 – 7.35 (m, 2H, H_{Ar}), 7.33 – 7.26 (m, 2H, H_{Ar}), 5.02 (d, J = 8.9 Hz, 1H, CH), 4.76 – 4.70 (m, 1H, CH), 2.67 (br, 1H, OH), 1.33 (dd, J = 6.8, 1.6 Hz, 3H, CH_3). *Anti* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.39 – 7.35 (m, 2H, H_{Ar}), 7.33 – 7.26 (m, 2H, H_{Ar}), 5.37 (br, 1H, CH), 4.68 – 4.62 (m, 1H, CH), 2.77 (br, 1H, OH), 1.49 (dd, J = 6.8, 1.5 Hz, 3H, CH_3). Spectral data are consistent with literature values.[8]

2-nitro-1phenylpropan-1-ol **4u**. Yield 60% (35 mg); Diastereomeric ratio (*syn*/*anti* 55:45) determined by ^{1}H NMR. *Syn* isomer: ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.41 – 7.36 (m, 5H, H_{Ar}), 5.03 (dd, J = 9.0, 3.0 Hz, 1H, CH), 4.77 (dq, J = 9.0, 6.8 Hz, 1H, CH), 2.58 (d, J = 3.0 Hz, 1H, OH), 1.32 (d, J = 6.8 Hz, 3H, CH_3). *Anti* isomer: ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.41 – 7.36 (m, 5H, H_{Ar}), 5.40 (pst, J = 3.5 Hz, 1H, CH), 4.70 (qd, J = 6.8, 3.6 Hz, 1H, CH), 2.70 (d, J = 3.5 Hz, 1H, OH), 1.51 (d, J = 6.8 Hz, 3H, CH_3). Spectral data are consistent with literature values.[8]

3-hydroxy-3-(nitromethyl)indolin-2-one **9a**. Yield 80% (53 mg); ^{1}H NMR (300 MHz, DMSO-d_6, δ) 10.54 (s, 1H, NH), 7.40 (dd, J = 7.3, 1.2 Hz, 1H, H_{Ar}), 7.27 (m, 1H, H_{Ar}), 7.10 – 6.82 (m, 2H, H_{Ar}), 6.74 (d, J = 1.0 Hz, 1H, OH), 5.15 – 4.82 (m, 2H, CH_2). Spectral data are consistent with literature values.[9]

3-hydroxy-3-(nitroethyl)indolin-2-one **9b**. The product was not isolated; the yield and the diastereoisomeric ratio (6:4) were determined by ^{1}H NMR (internal standard 2,4-dinitrotoluene). Major isomer: ^{1}H NMR (300 MHz, DMSO-d_6, δ) 8.12 – 6.75 (m, 4H, H_{Ar}), 5.03 (m, 1H, CH), 1.34 (d, J = 6.8 Hz, 3H, CH_2). Minor isomer: ^{1}H NMR (300 MHz, DMSO-d_6, δ) 8.12 – 6.75 (m, 4H, H_{Ar}), 5.04 (m, 1H, CH), 1.66 (d, J = 6.8 Hz, 3H, CH_2). Spectral data are consistent with literature values.[9]

Henry reaction/cycloisomerisation sequence. Yields and ^{1}H spectra of products **11**, **12** and **13**.

1-(2-((4-methoxyphenyl)ethynyl)phenyl)-2-nitroethanol **11a**. Yield 18% (13 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.62 (d, J = 7.7 Hz, 1H, H_{Ar}), 7.55 – 7.44 (m, 3H, H_{Ar}), 7.37 (td, J = 7.6, 1.3 Hz, 1H, H_{Ar}), 7.31 (td, J = 7.5, 1.3 Hz, 1H, H_{Ar}), 6.88 (d, J = 8.9 Hz, 2H, H_{Ar}), 5.98 (dd, J = 9.8, 1.8 Hz, 1H, CH), 4.79 (dd, J = 13.0, 2.4 Hz, 1H, CH_2), 4.50 (dd, J = 13.0, 9.9 Hz, 1H, CH_2), 3.81 (s, 3H, CH_3). 2.94 (s, 1H, OH). Spectral data are consistent with literature values.[10]

3-(4-methoxyphenyl)-1-(nitromethyl)-1H-isochromene **12a**. Yield 30% (22 mg); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.62 – 7.55 (m, 2H, H_{Ar}), 7.31 (td, J = 7.5, 1.1 Hz, 1H, H_{Ar}), 7.20 (td, J = 7.5, 1.1 Hz, 1H, H_{Ar}), 7.12 (dd, J = 11.4, 7.6 Hz, 2H, H_{Ar}), 6.93 – 6.86 (m, 2H, H_{Ar}), 6.37 (s, 1H, Csp^2-H),

6.11 (dd, J = 10.3, 3.2 Hz, 1H, CH), 4.95 (dd, J = 12.3, 10.3 Hz, 1H, CH_2), 4.35 (dd, J = 12.3, 3.2 Hz, 1H, CH_2), 3.82 (s, 3H, CH_3). Spectral data are consistent with literature values.[10]

2-nitro-1-(2-(p-tolylethynyl)phenyl)ethanol **11c**. Yield 32% (23 mg) Table 5, entry 4; yield 60% (42 mg) Table 5, entry 5; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.59 (d, J = 7.6 Hz, 1H, H_{Ar}), 7.49 (dd, J = 7.6, 1.1 Hz, 1H, H_{Ar}), 7.43 (d, J = 8.1 Hz, 2H, H_{Ar}), 7.35 (td, J = 7.6, 1.3 Hz, 1H, H_{Ar}), 7.28 (td, J = 7.5, 1.2 Hz, 1H, H_{Ar}), 7.14 (d, J = 7.9 Hz, 2H, H_{Ar}), 5.94 (dd, J = 9.8, 2.2 Hz, 1H, CH), 4.74 (dd, J = 13.1, 2.4 Hz, 1H, CH_2), 4.45 (dd, J = 13.1, 9.9 Hz, 1H, CH_2), 2.95 (s, 1H, OH), 2.34 (s, 3H, CH_3). Spectral data are consistent with literature values.[10]

1-(nitromethyl)-3-(p-tolyl)-1H-isochromene **12c**. Yield 31% (22 mg) Table 5, entry 4; yield 5% (4 mg) Table 5, entry 5; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.55 (d, J = 7.9 Hz, 2H, H_{Ar}), 7.32 (t, J = 7.5 Hz, 1H, H_{Ar}), 7.27 – 7.04 (m, 5H, H_{Ar}), 6.45 (s, 1H, Csp^2-H), 6.13 (dd, J = 10.2, 2.7 Hz, 1H, CH), 4.95 (dd, J = 12.3, 7.2 Hz, 1H, CH_2), 4.36 (dd, J = 12.3, 3.0 Hz, 1H, CH_2), 2.37 (s, 3H, CH_3). Spectral data are consistent with literature values.[10]

3-(4-methoxyphenyl)-1H-isochromen-1-one **13**. Yield 29% (18 mg); ^{1}H NMR (200 MHz, $CDCl_3$, δ) 8.29 (d, J = 9.2 Hz, 1H, H_{Ar}), 7.83 (d, J = 8.8 Hz, 2H, H_{Ar}), 7.70 (td, J = 7.7, 1.1 Hz, 1H, H_{Ar}), 7.50 – 7.42 (m, 2H, H_{Ar}), 6.98 (d, J = 8.8 Hz, 2H, H_{Ar}), 6.84 (s, 1H, Csp^2-H), 3.87 (s, 3H, CH_3). Spectral data are consistent with literature values.[11]

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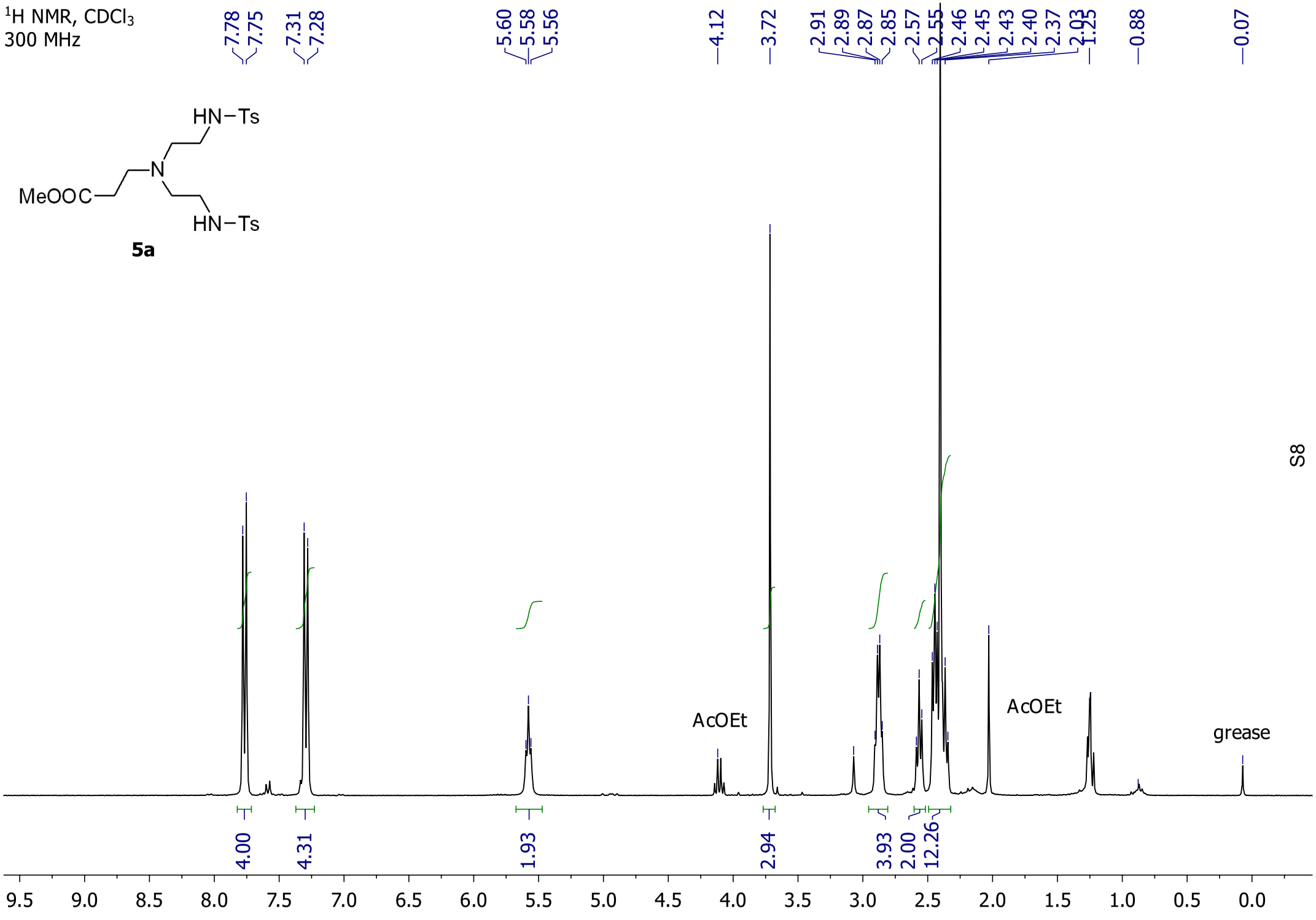
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4.12
3.72
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2.89
2.87
2.85
2.57
2.55
2.46
2.45
2.43
2.40
2.37
2.03
1.25
0.88
0.07
HN−Ts
N
MeOOC
HN−Ts
5a
AcOEt
AcOEt
grease
4.00
4.31
1.93
2.94
3.93
2.00
12.26
9.5
9.0
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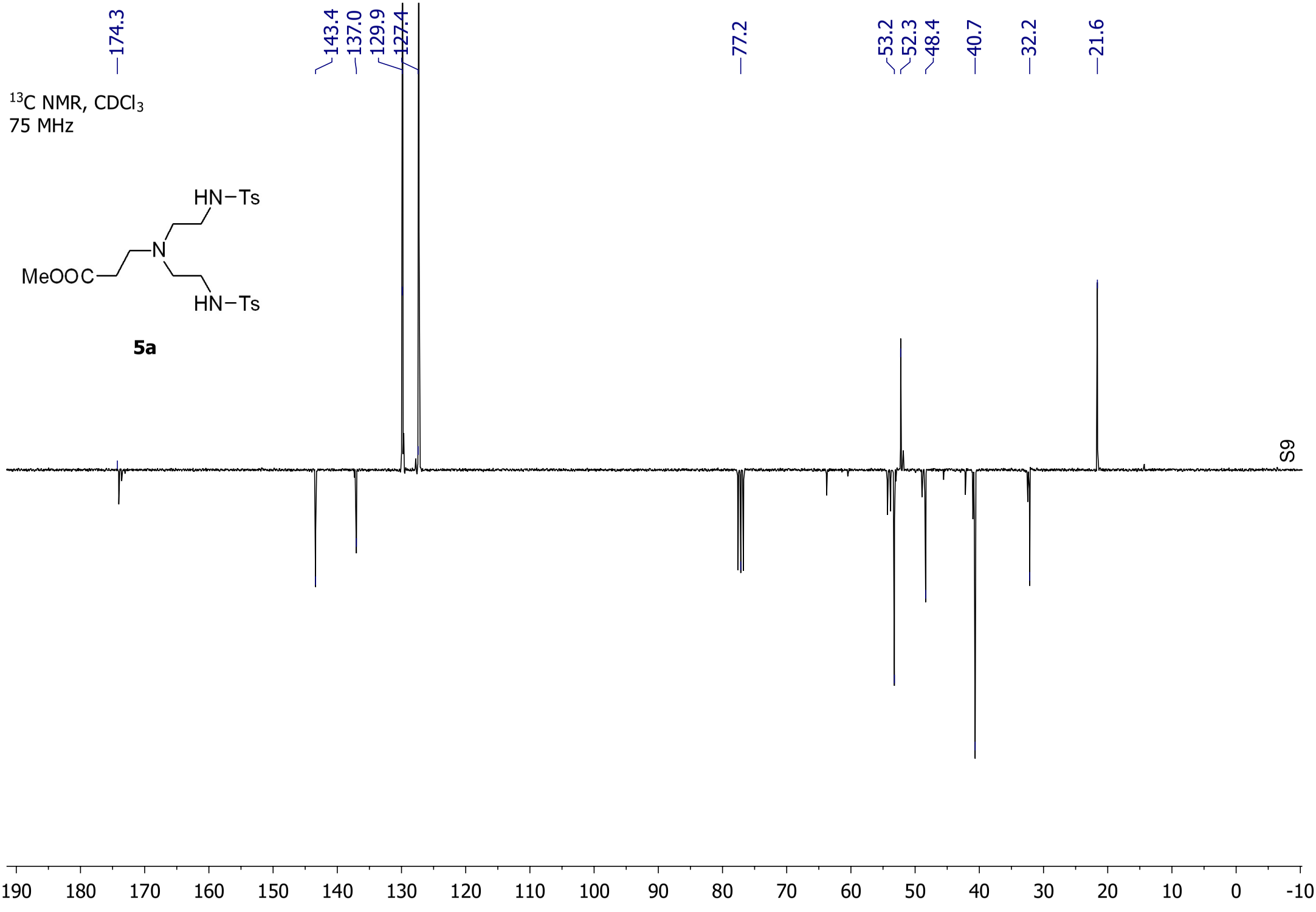
S8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52.3
48.4
40.7
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13C NMR, CDCl3
75 MHz
HN−Ts
N
MeOOC
HN−Ts
5a
S9
190
180
170
160
150
140
130
120
110
100
90
80
70
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40
30
20
10
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-10

^{1}H NMR, $CDCl_3$
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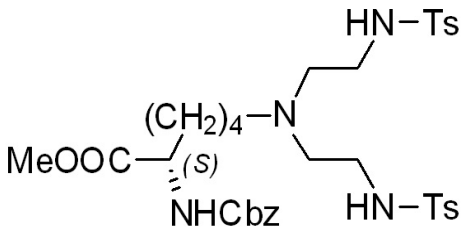
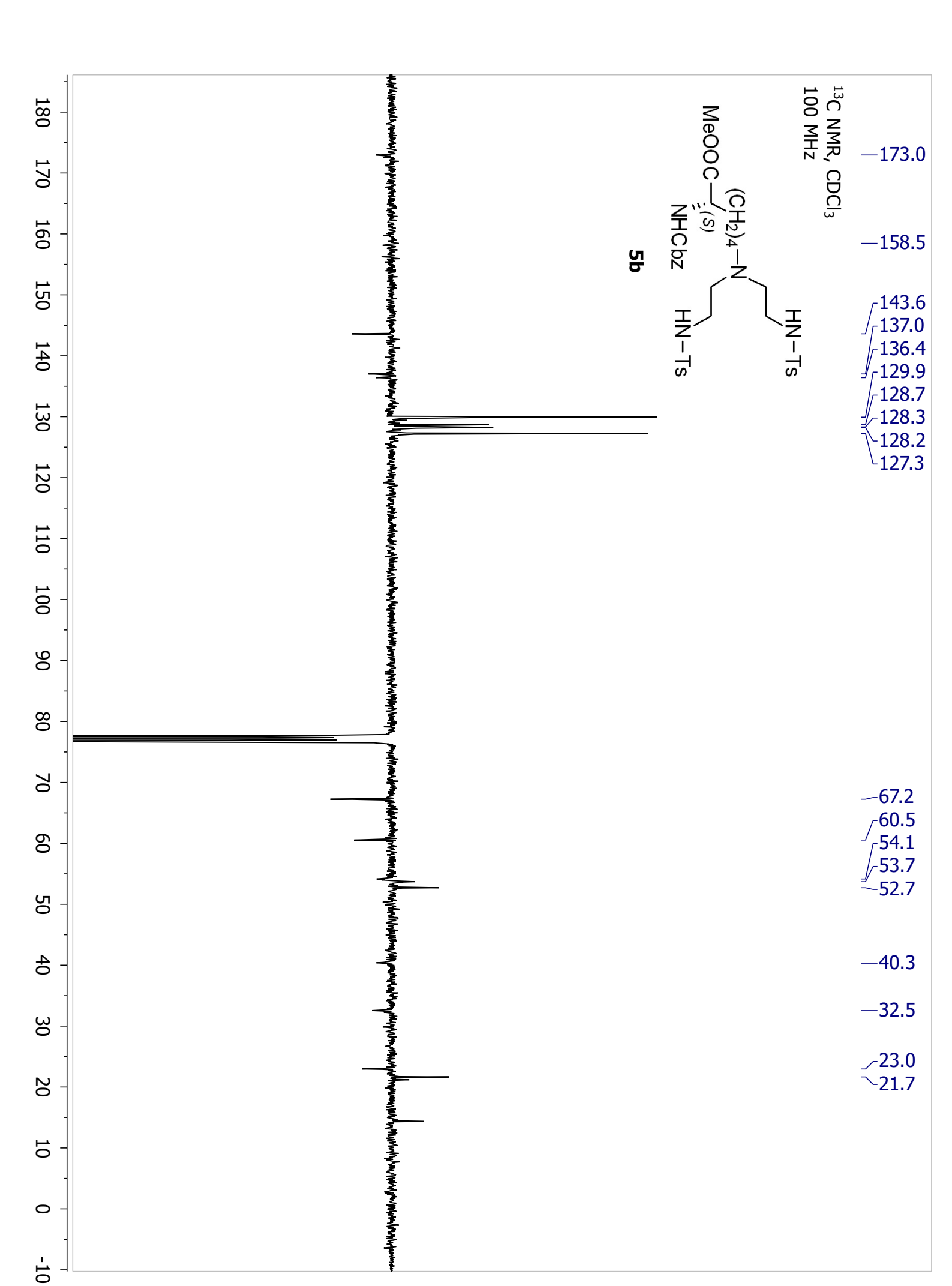


5b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5b
MeOOC
(S)
NHCbz
(CH$_2$)$_4$–N
HN–Ts
HN–Ts
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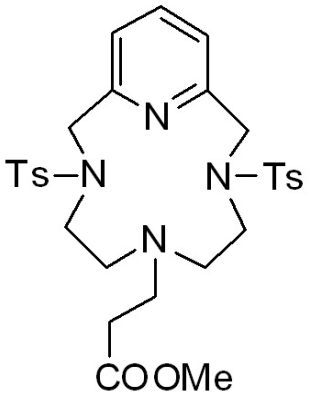
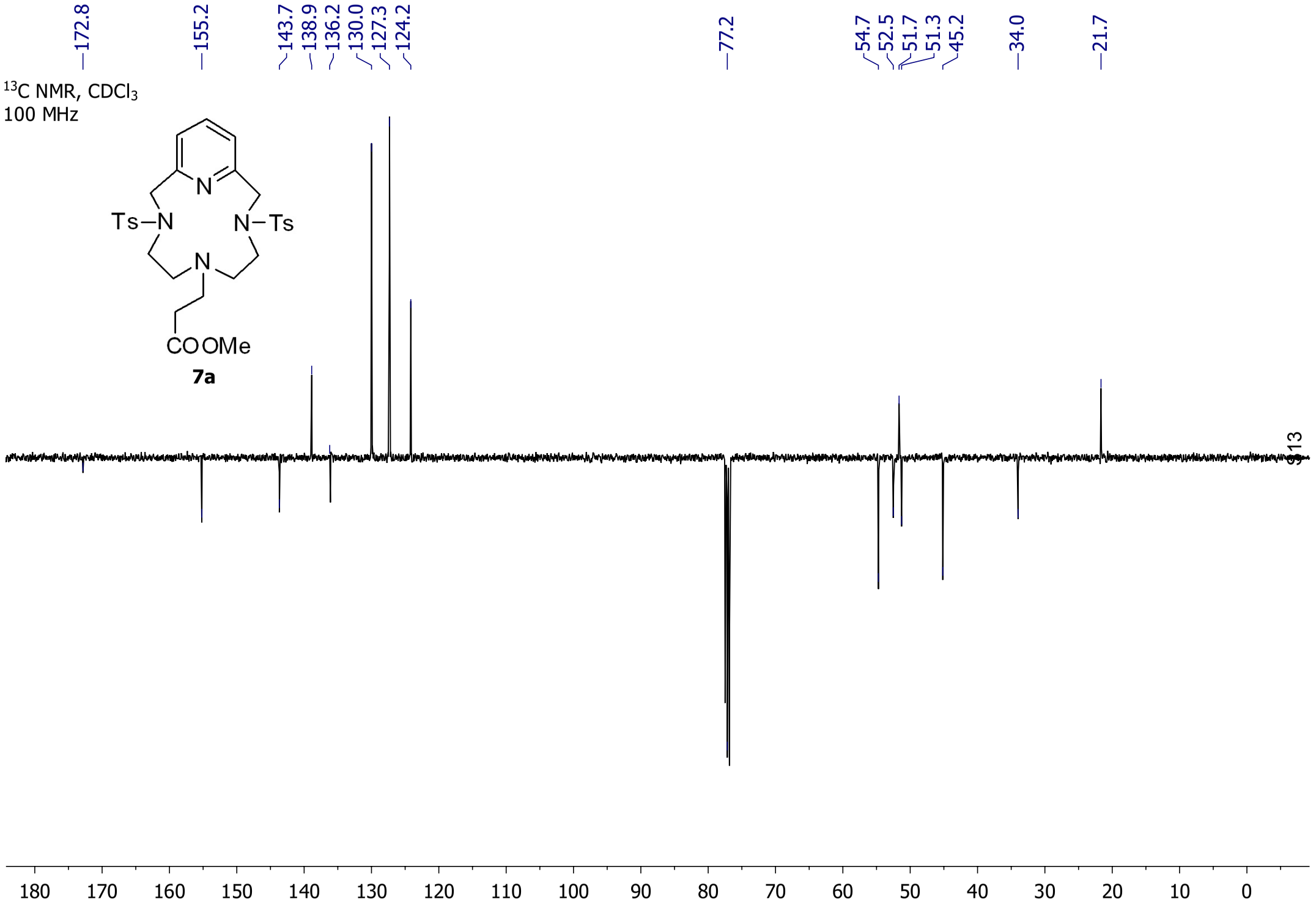
158.5
143.6
137.0
136.4
129.9
128.7
128.3
128.2
127.3
67.2
60.5
54.1
53.7
52.7
40.3
32.5
23.0
21.7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

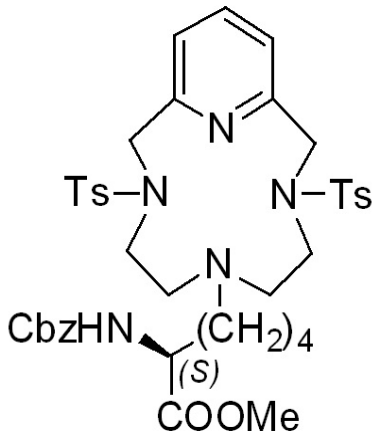
^{1}H NMR, $CDCl_3$
400 MHz



7a

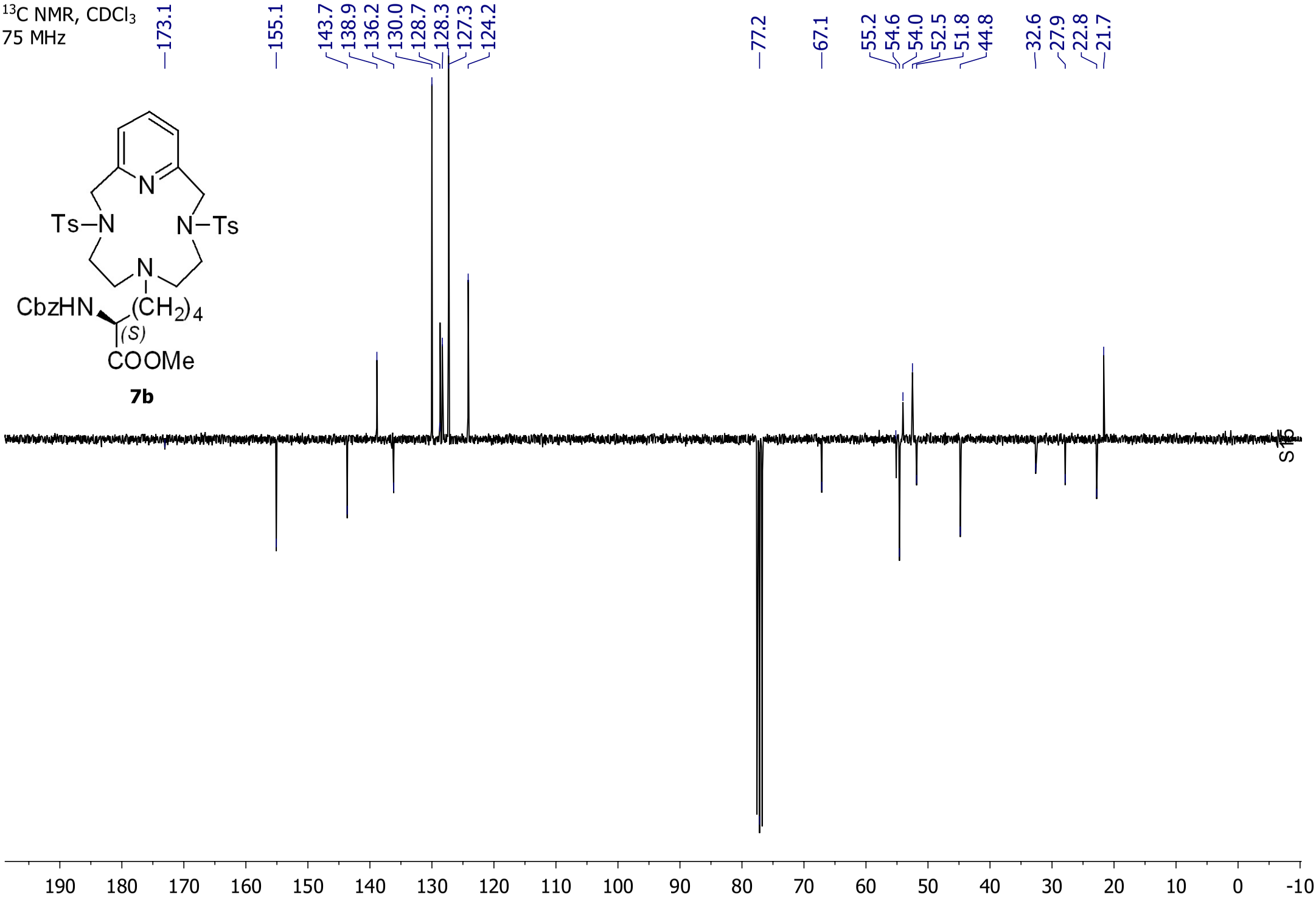

172.8
155.2
143.7
138.9
136.2
130.0
127.3
124.2
77.2
54.7
52.5
51.7
51.3
45.2
34.0
21.7
^{13}C NMR, $CDCl_3$
100 MHz
Ts–N
N–Ts
N
N
CO OMe
7a
913
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR, $CDCl_3$
300 MHz

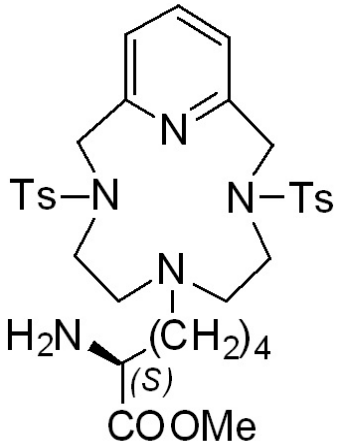


7b

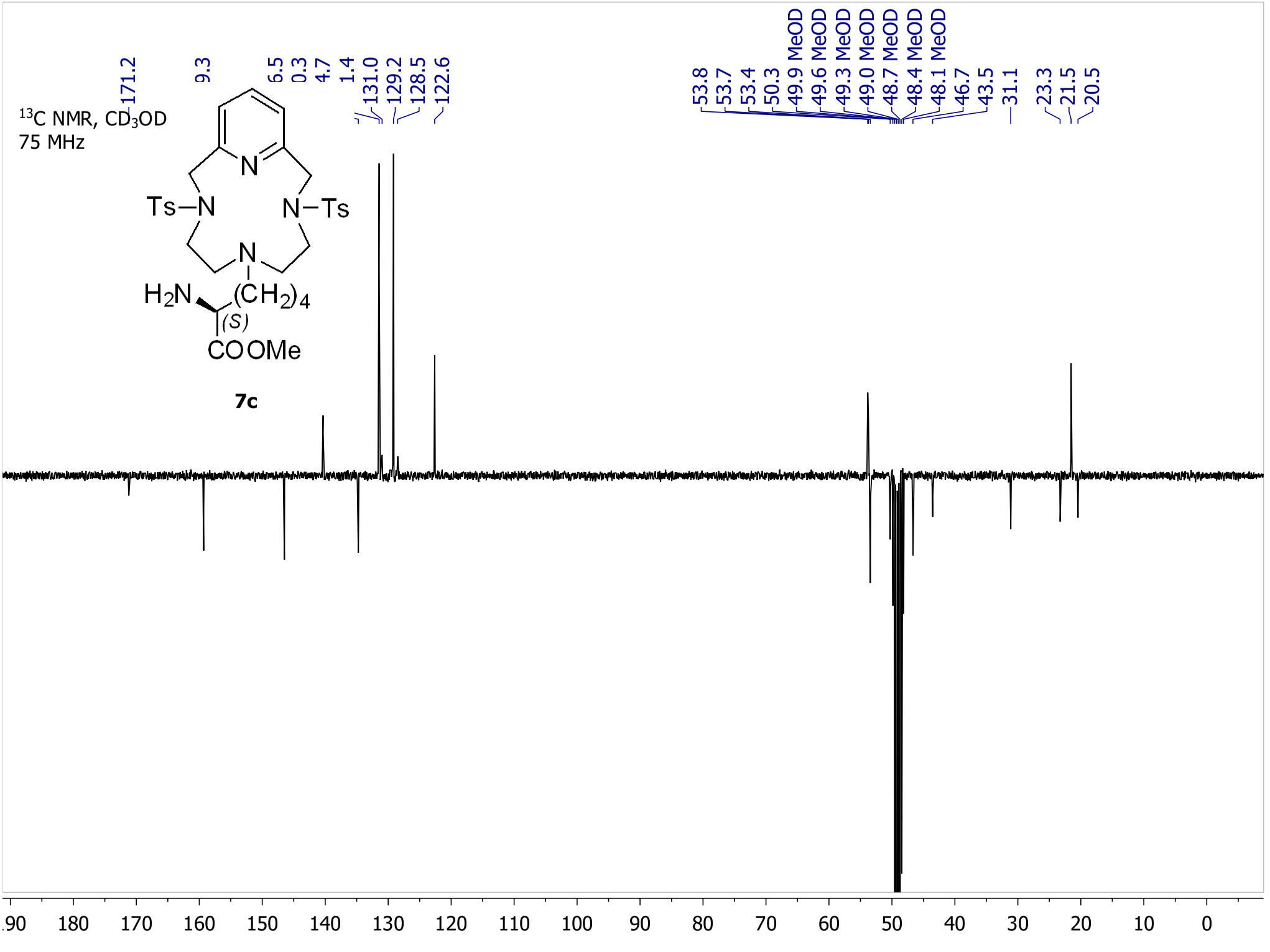
^{13}C NMR, $CDCl_3$
75 MHz



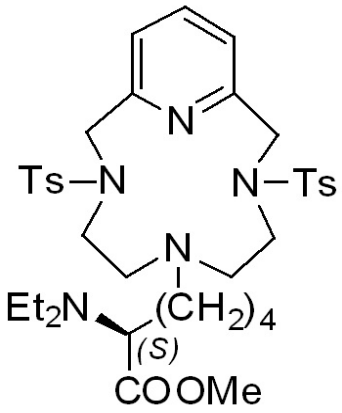
^{1}H NMR, CD_3OD
300 MHz



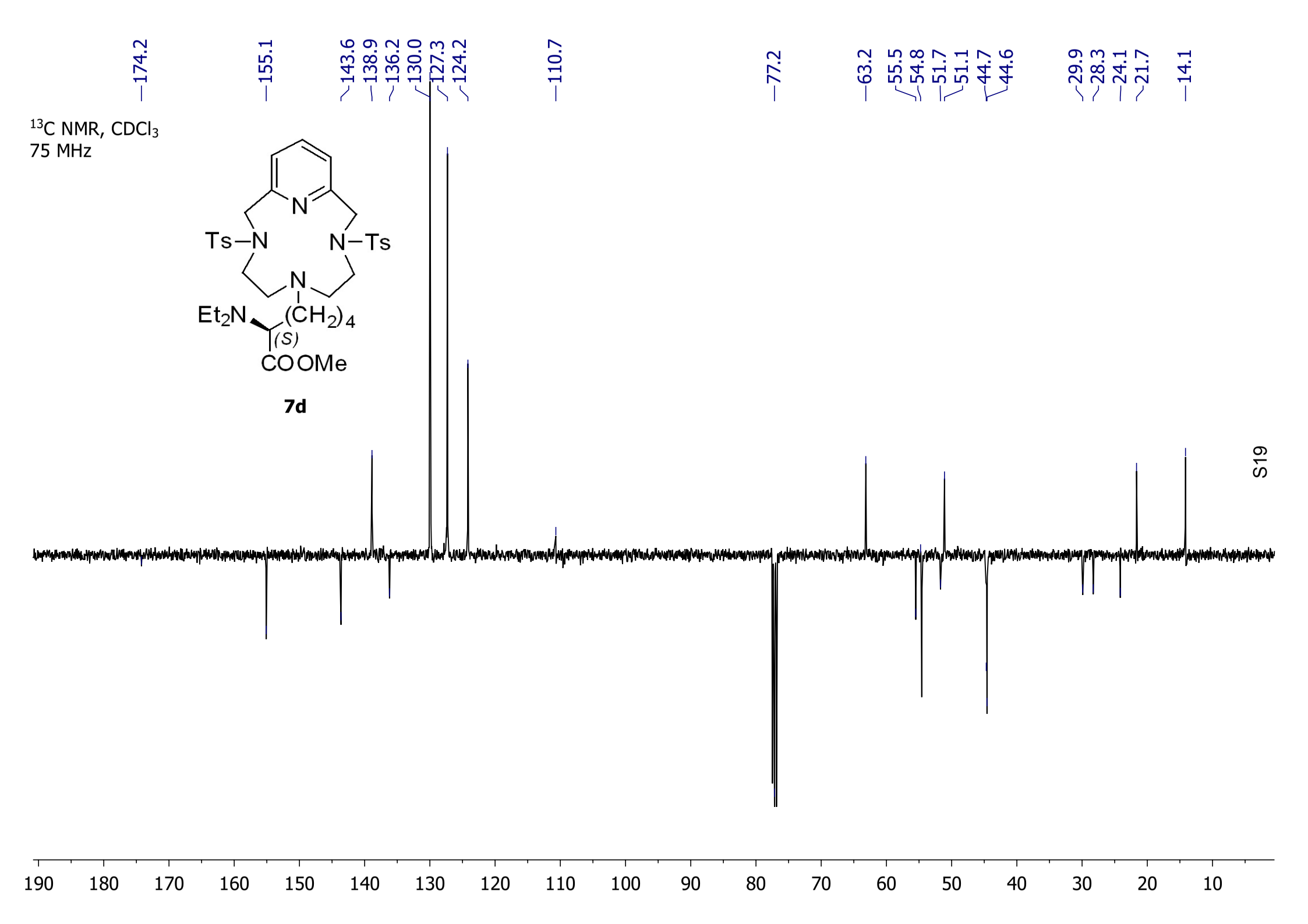
7c

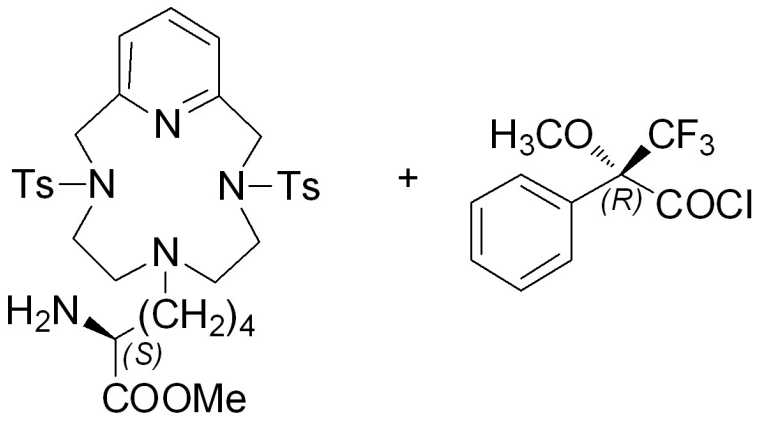

171.2
9.3
6.5
0.3
4.7
1.4
131.0
129.2
128.5
122.6
53.8
53.7
53.4
50.3
49.9 MeOD
49.6 MeOD
49.3 MeOD
49.0 MeOD
48.7 MeOD
48.4 MeOD
48.1 MeOD
46.7
43.5
31.1
23.3
21.5
20.5
13C NMR, CD3OD
75 MHz
Ts–N
N–Ts
H2N
(CH2)4
(S)
COOMe
7c
S17
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

^{1}H NMR, $CDCl_3$
400 MHz



7d


174.2
155.1
143.6
138.9
136.2
130.0
127.3
124.2
110.7
77.2
63.2
55.5
54.8
51.7
51.1
44.7
44.6
29.9
28.3
24.1
21.7
14.1
13C NMR, CDCl3
75 MHz
Ts–N
N–Ts
N
N
Et2N
(CH2)4
(S)
COOMe
7d
S19
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

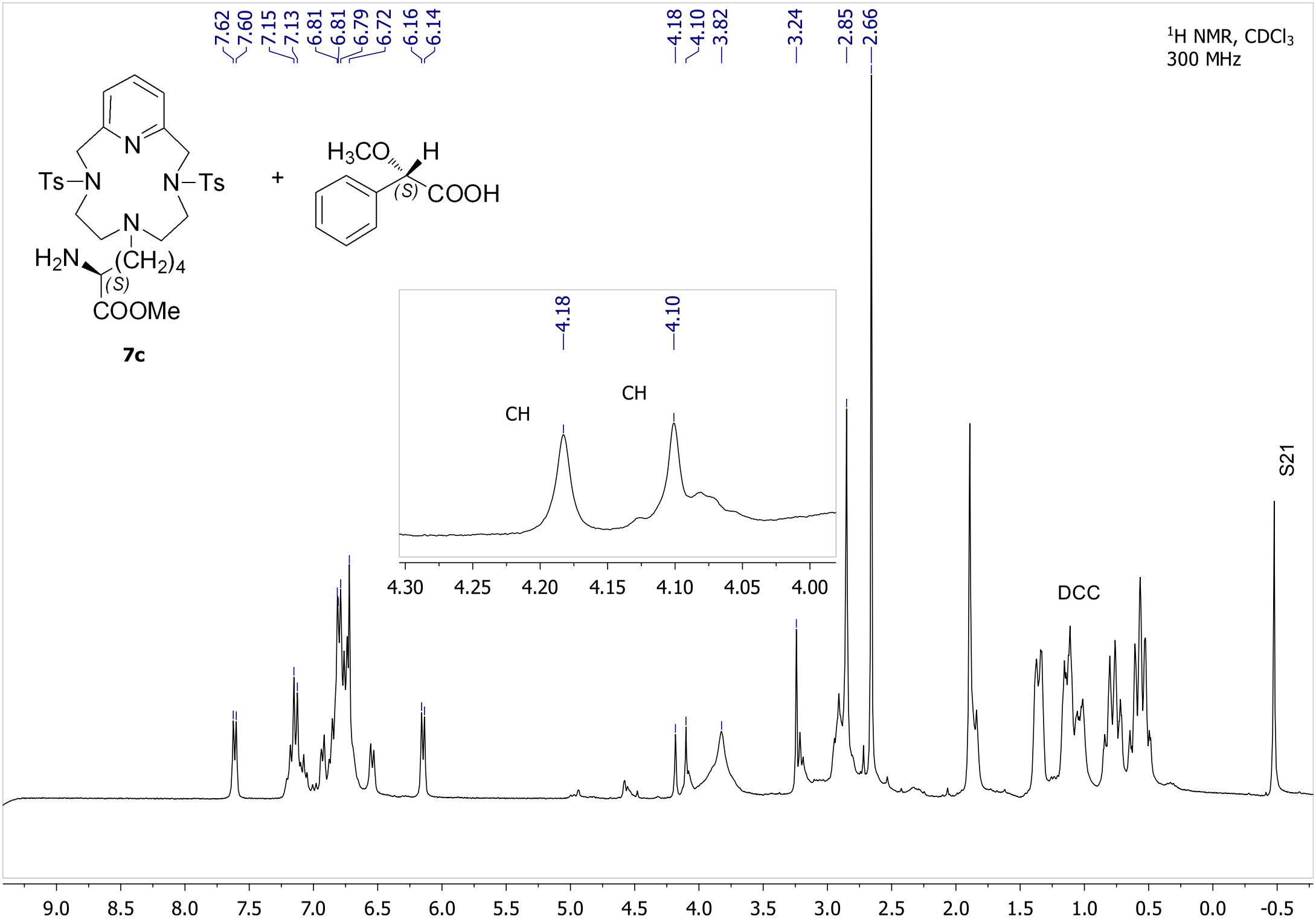

Ts–N
N–Ts
N
N
H2N
(CH2)4
(S)
COOMe

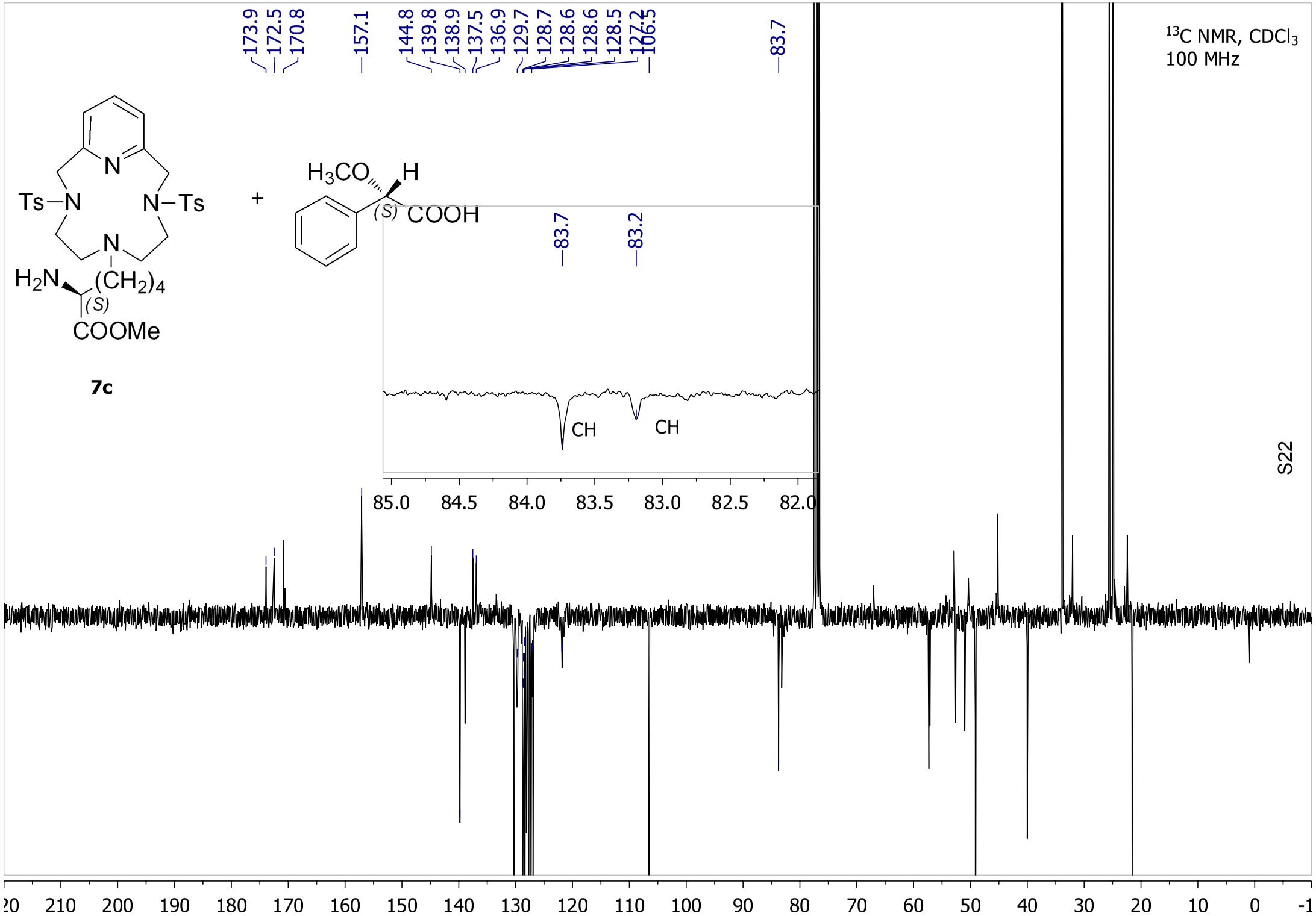
7c

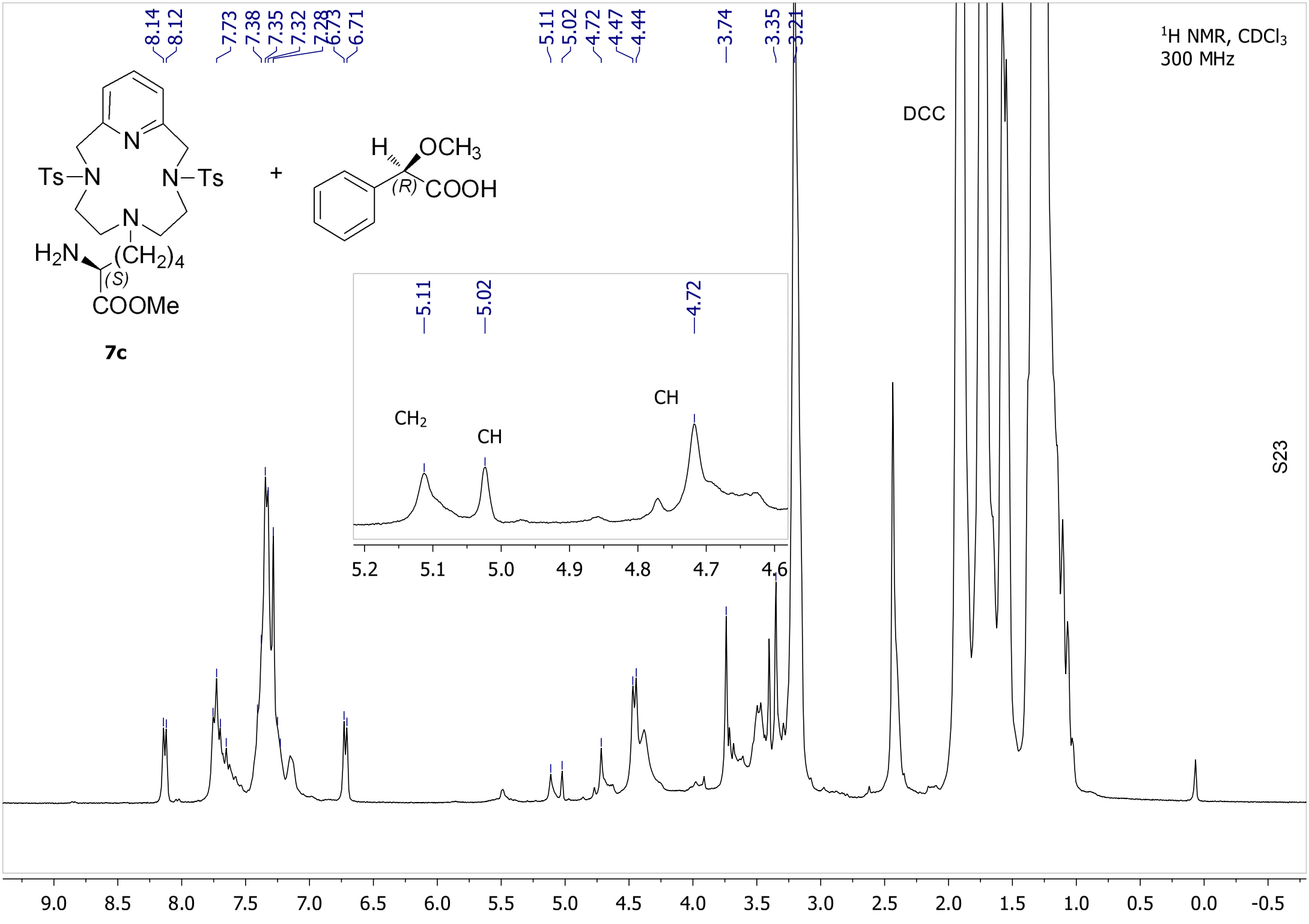
+

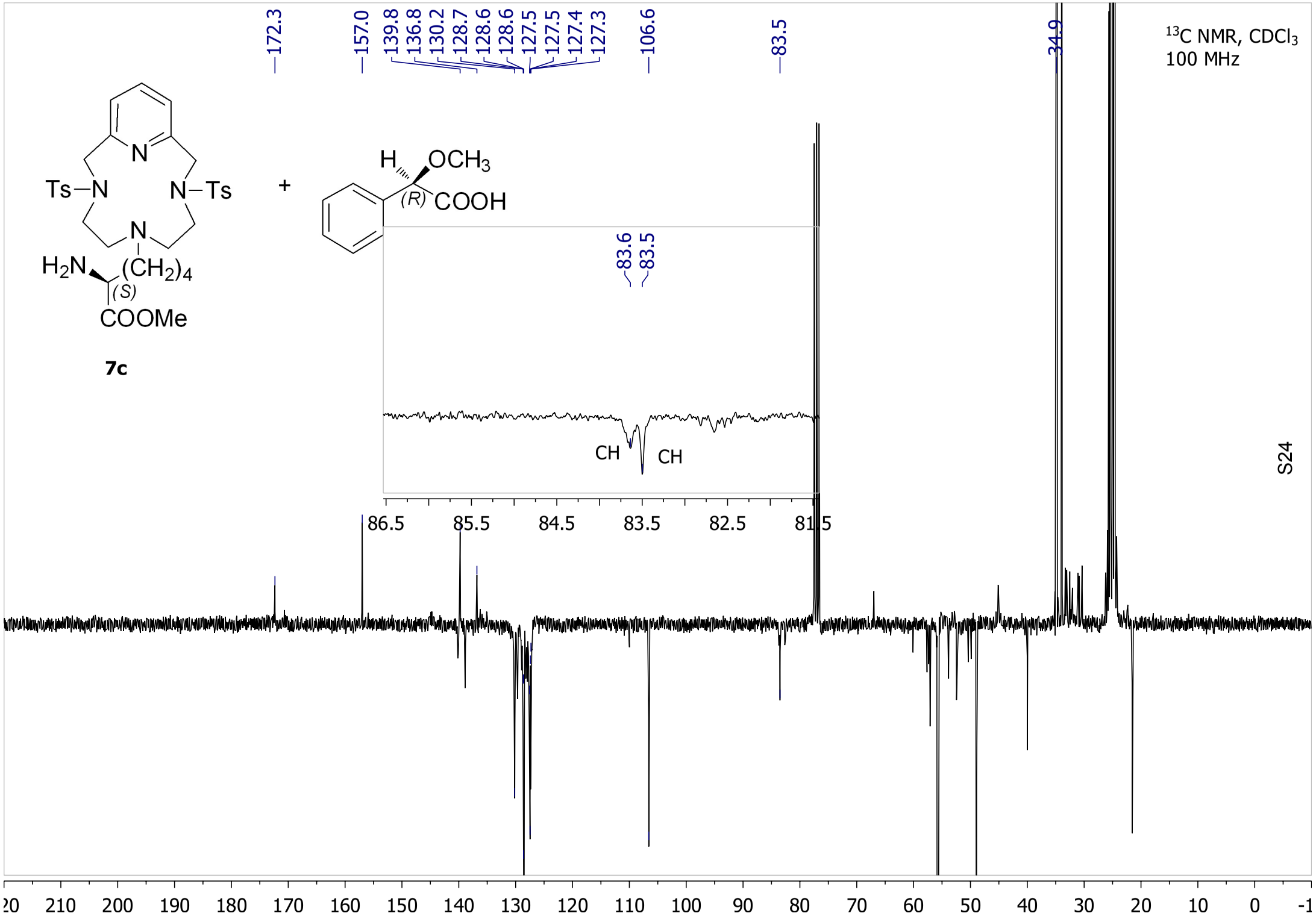
H3CO
CF3
(R)
COCl

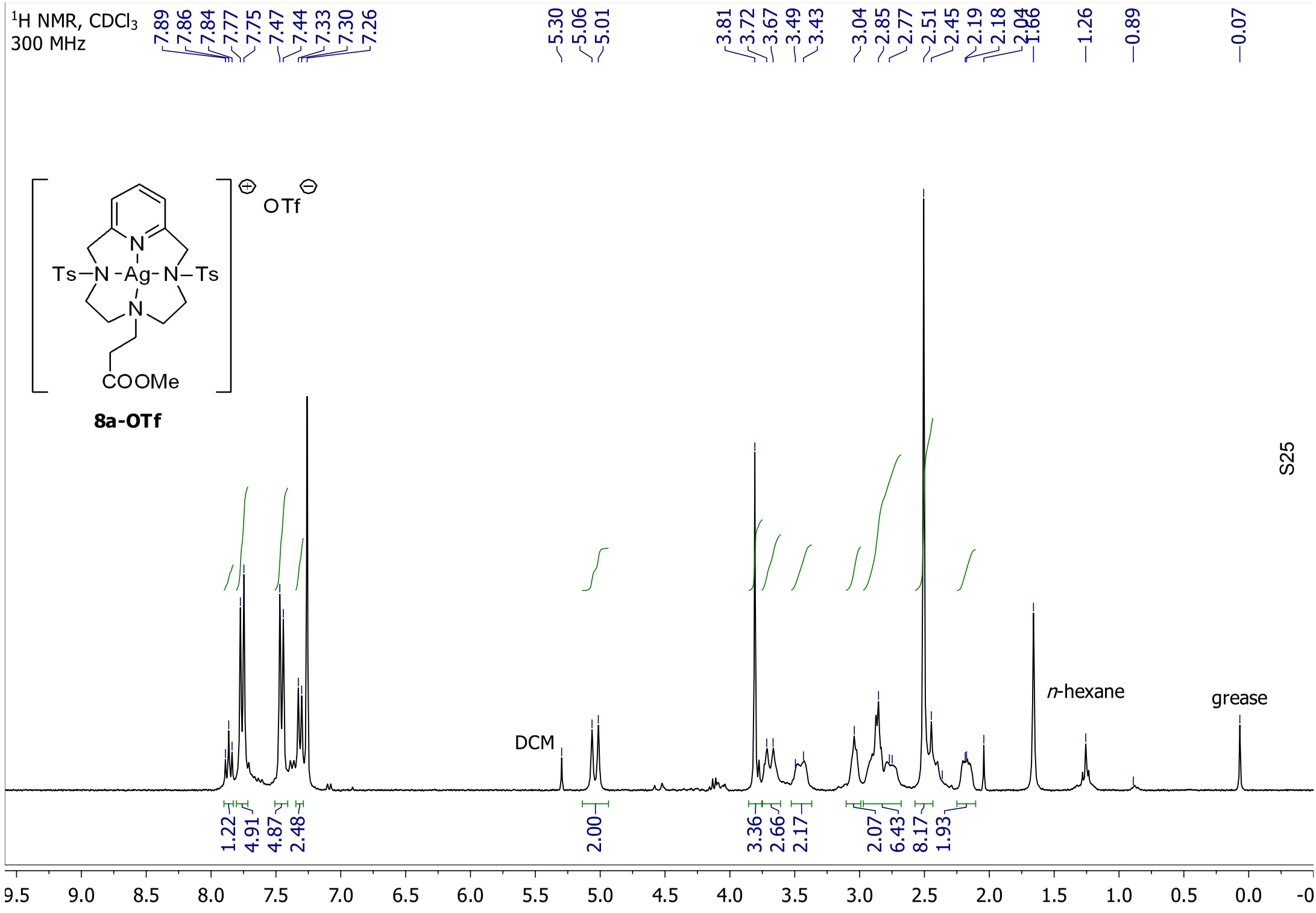
-71.24
19F NMR, CDCl3
282 MHz
S20
-63.5
-64.5
-65.5
-66.5
-67.5
-68.5
-69.5
-70.5
-71.5
-72.5
-73.5
-74.5
-75.5
-76.5
-77.5


7.62
7.60
7.15
7.13
6.81
6.81
6.79
6.72
6.16
6.14
4.18
4.10
3.82
3.24
2.85
2.66
1H NMR, CDCl3
300 MHz
Ts–N
N–Ts
N
N
H2N
(CH2)4
(S)
COOMe
7c
+
H3CO
H
(S)
COOH
4.18
4.10
CH
CH
4.30
4.25
4.20
4.15
4.10
4.05
4.00
DCC
S21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


173.9
172.5
170.8
157.1
144.8
139.8
138.9
137.5
136.9
129.7
128.7
128.6
128.6
128.5
127.2
126.5
83.7
^{13}C NMR, CDCl$_3$
100 MHz
Ts–N
N–Ts
N
N
H$_2$N
(CH$_2$)$_4$
(S)
COOMe
7c
+
H$_3$CO
H
(S)
COOH
83.7
83.2
CH
CH
S22
85.0
84.5
84.0
83.5
83.0
82.5
82.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

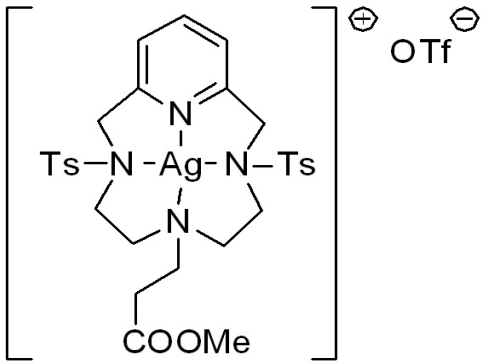

8.14
8.12
7.73
7.38
7.35
7.32
7.28
6.73
6.71
5.11
5.02
4.72
4.47
4.44
3.74
3.35
3.21
^{1}H NMR, $CDCl_3$
300 MHz
DCC
S23
Ts–N
N–Ts
N
H_2N
$(CH_2)_4$
(S)
COOMe
7c
+
H
OCH_3
(R)
COOH
CH_2
CH
CH
5.2
5.1
5.0
4.9
4.8
4.7
4.6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


172.3
157.0
139.8
136.8
130.2
128.7
128.6
128.6
127.5
127.5
127.4
127.3
106.6
83.5
34.9
^{13}C NMR, CDCl$_3$
100 MHz
Ts–N
N–Ts
N
N
H_2N
$(CH_2)_4$
(S)
COOMe
7c
+
H
OCH_3
(R)
COOH
83.6
83.5
CH
CH
86.5
85.5
84.5
83.5
82.5
81.5
S24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


1H NMR, CDCl3
300 MHz
7.89
7.86
7.84
7.77
7.75
7.47
7.44
7.33
7.30
7.26
5.30
5.06
5.01
3.81
3.72
3.67
3.49
3.43
3.04
2.85
2.77
2.51
2.45
2.19
2.18
2.04
1.86
1.26
0.89
0.07
OTf
Ts–N–Ag–N–Ts
N
N
COOMe
8a-OTf
S25
DCM
n-hexane
grease
1.22
4.91
4.87
2.48
2.00
3.36
2.66
2.17
2.07
6.43
8.17
1.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

^{13}C NMR, $CDCl_3$
75 MHz

153.5 145.8 140.9 130.7 128.3 125.5 77.2 56.6 53.4 52.9 48.9 47.0 31.9 21.8

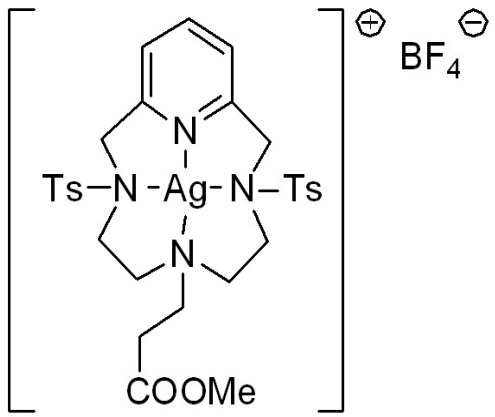


8a-OTf

S26

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

^{1}H NMR, $CDCl_3$
400 MHz



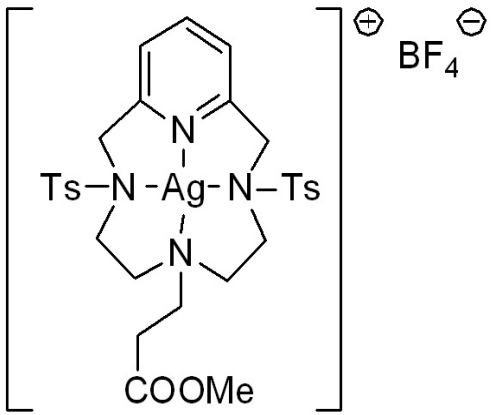
8a-BF_4

coordinated water

grease

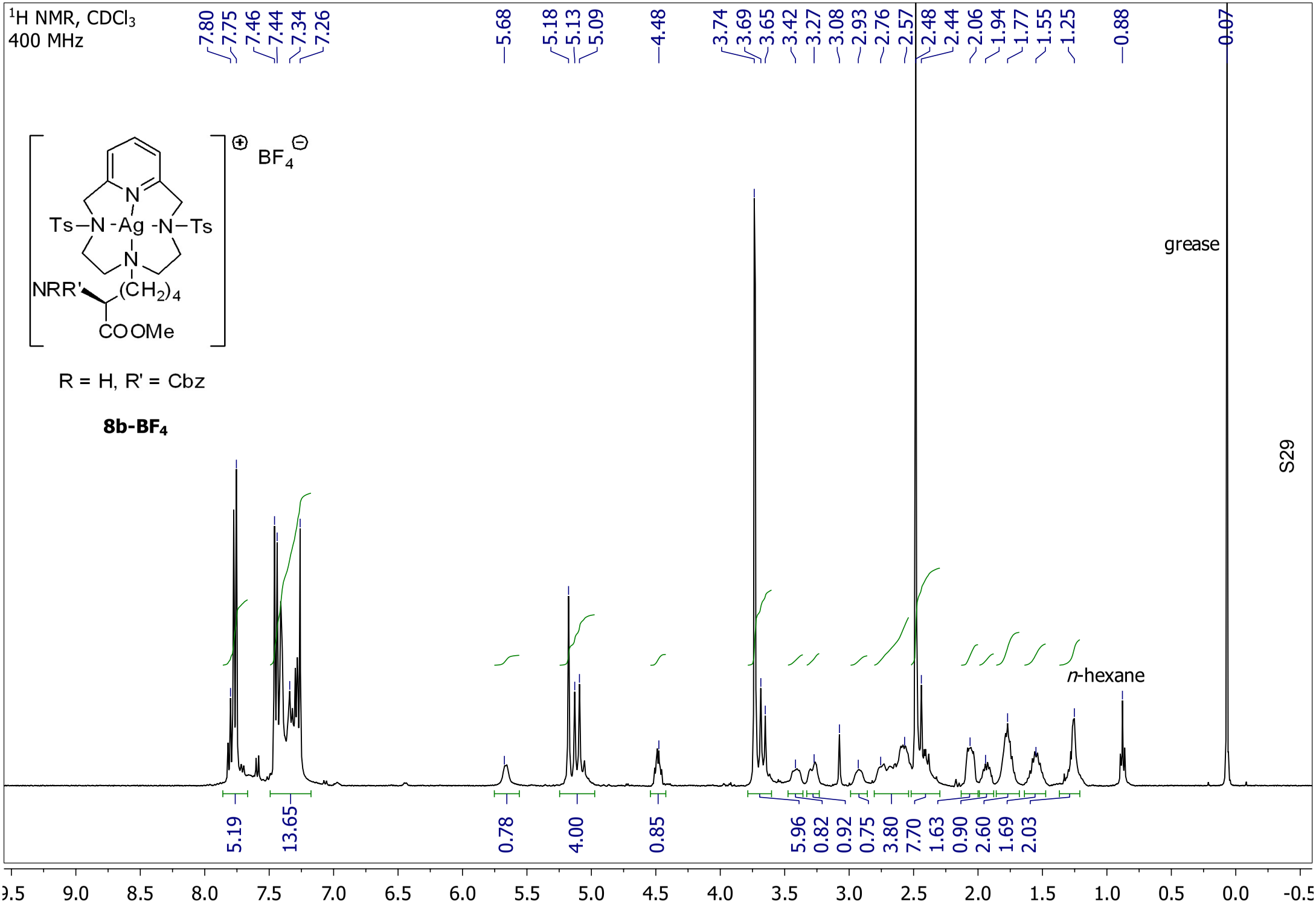
^{13}C NMR, $CDCl_3$
100 MHz

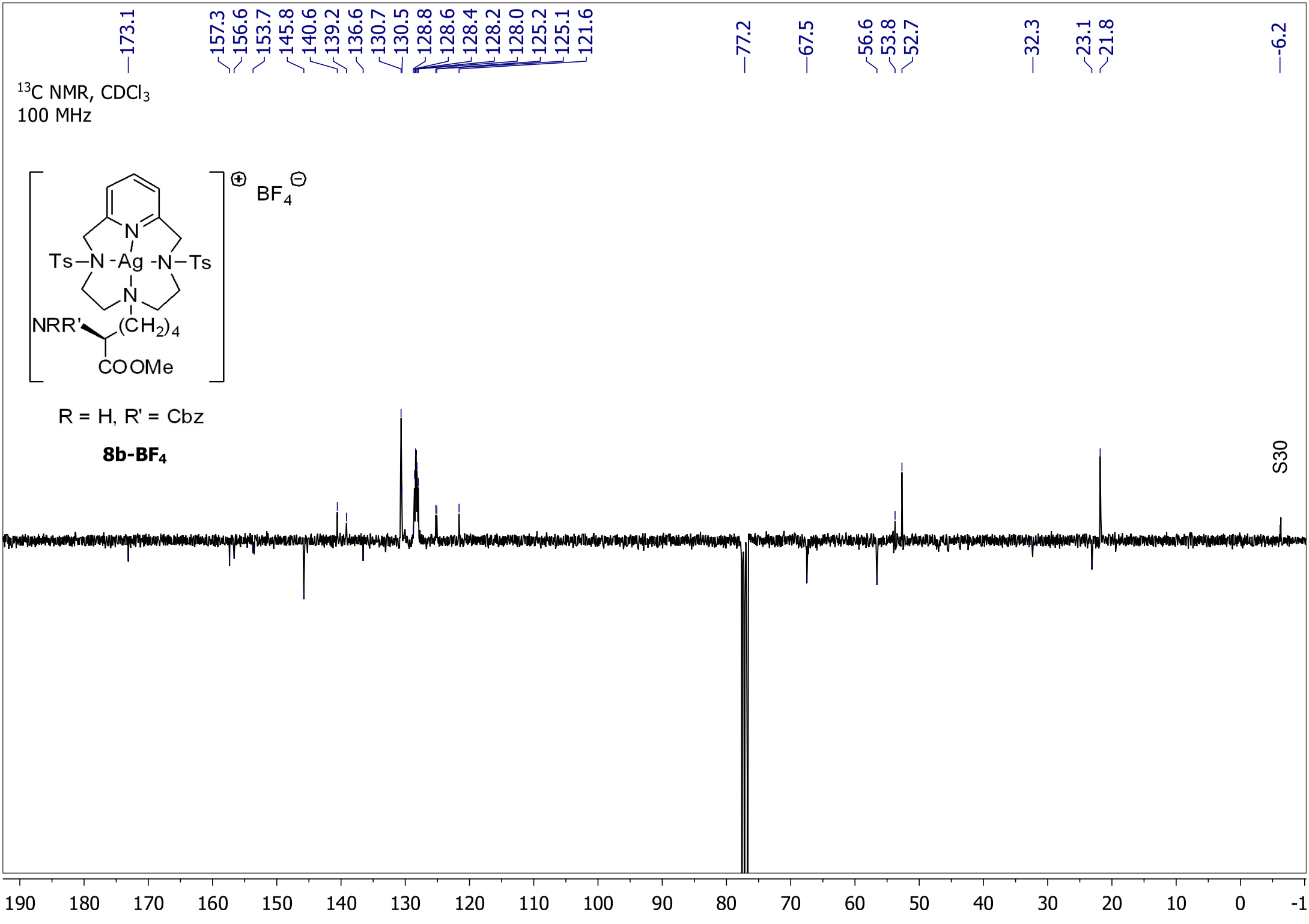
145.8
140.7
130.7
128.3
125.5
77.2
56.6
53.2
52.8
48.9
46.9
45.6
21.8

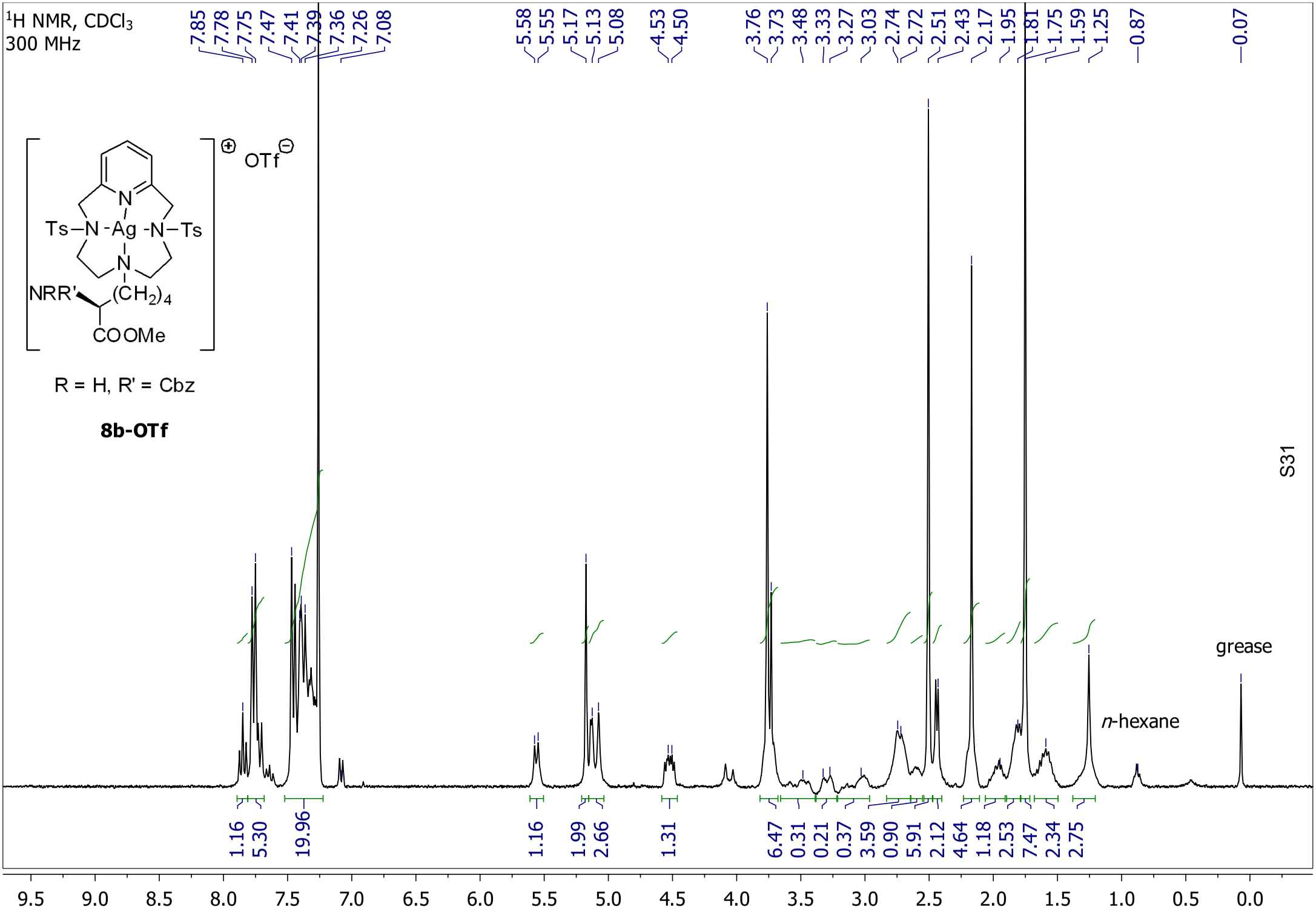


8a-BF_4

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

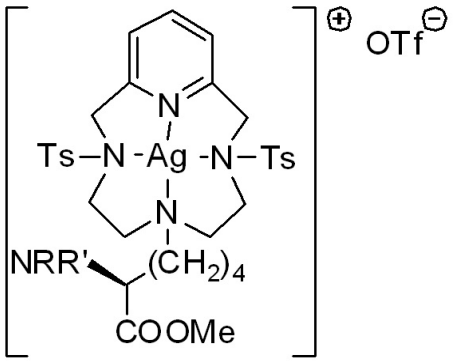

1H NMR, CDCl3
400 MHz
7.80
7.75
7.46
7.44
7.34
7.26
5.68
5.18
5.13
5.09
4.48
3.74
3.69
3.65
3.42
3.27
3.08
2.93
2.76
2.57
2.48
2.44
2.06
1.94
1.77
1.55
1.25
0.88
0.07
BF4
Ts–N -Ag -N–Ts
NRR'
(CH2)4
COOMe
R = H, R' = Cbz
8b-BF4
grease
n-hexane
S29
5.19
13.65
0.78
4.00
0.85
5.96
0.82
0.92
0.75
3.80
7.70
1.63
0.90
2.60
1.69
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


173.1
157.3
156.6
153.7
145.8
140.6
139.2
136.6
130.7
130.5
128.8
128.6
128.4
128.2
128.0
125.2
125.1
121.6
77.2
67.5
56.6
53.8
52.7
32.3
23.1
21.8
-6.2
13C NMR, CDCl3
100 MHz
BF4
Ts–N -Ag -N–Ts
NRR'
(CH2)4
COOMe
R = H, R' = Cbz
8b-BF4
S30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1


1H NMR, CDCl3
300 MHz
7.85
7.78
7.75
7.47
7.41
7.39
7.36
7.26
7.08
5.58
5.55
5.17
5.13
5.08
4.53
4.50
3.76
3.73
3.48
3.33
3.27
3.03
2.74
2.72
2.51
2.43
2.17
1.95
1.81
1.75
1.59
1.25
0.87
0.07
OTf
Ts–N -Ag -N–Ts
NRR'
(CH2)4
COOMe
R = H, R' = Cbz
8b-OTf
S31
grease
n-hexane
1.16
5.30
19.96
1.16
1.99
2.66
1.31
6.47
0.31
0.21
0.37
3.59
0.90
5.91
2.12
4.64
1.18
2.53
7.47
2.34
2.75
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

^{13}C NMR, $CDCl_3$
75 MHz

145.8
130.6
128.3
77.2
53.7
52.7
21.8

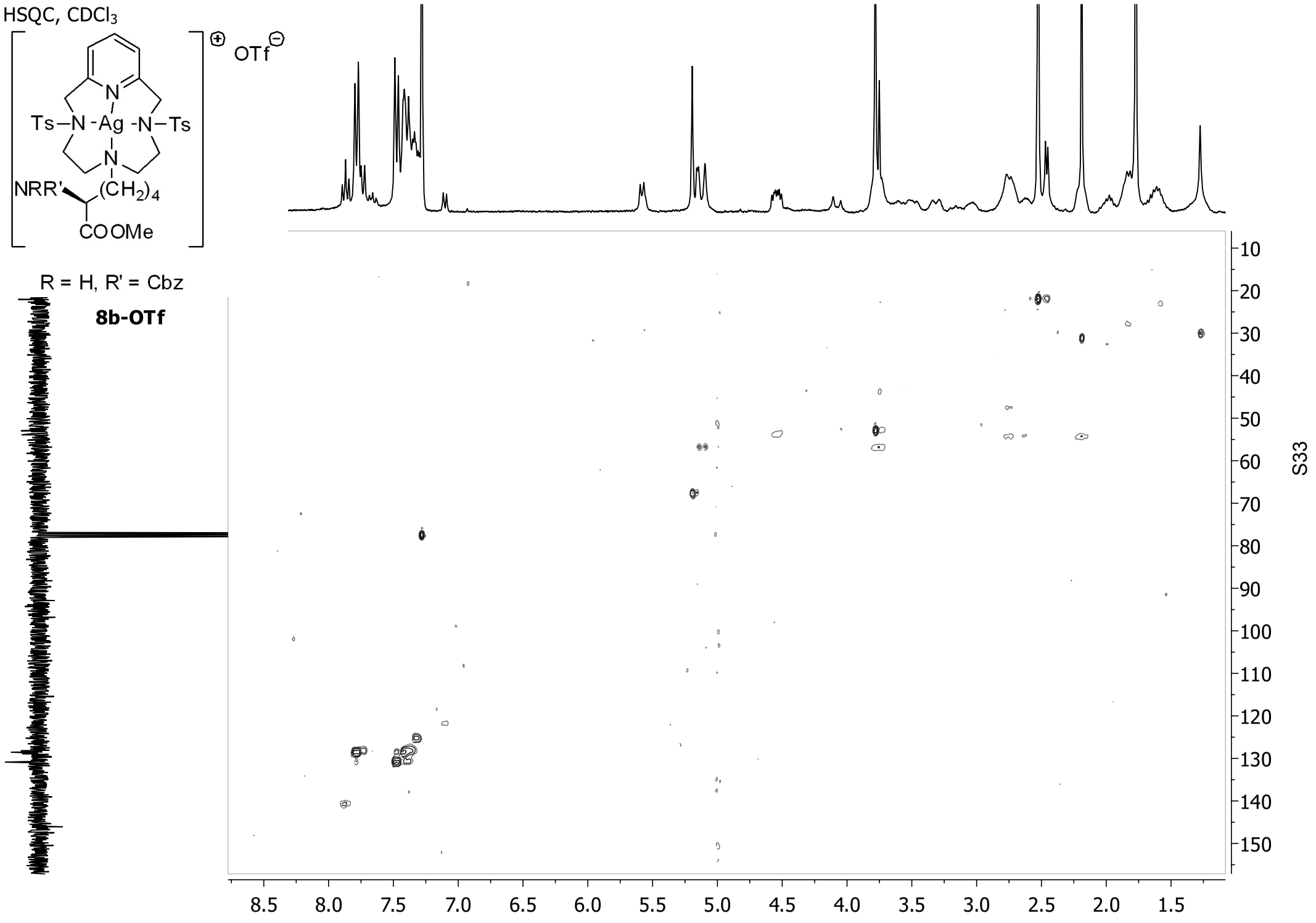


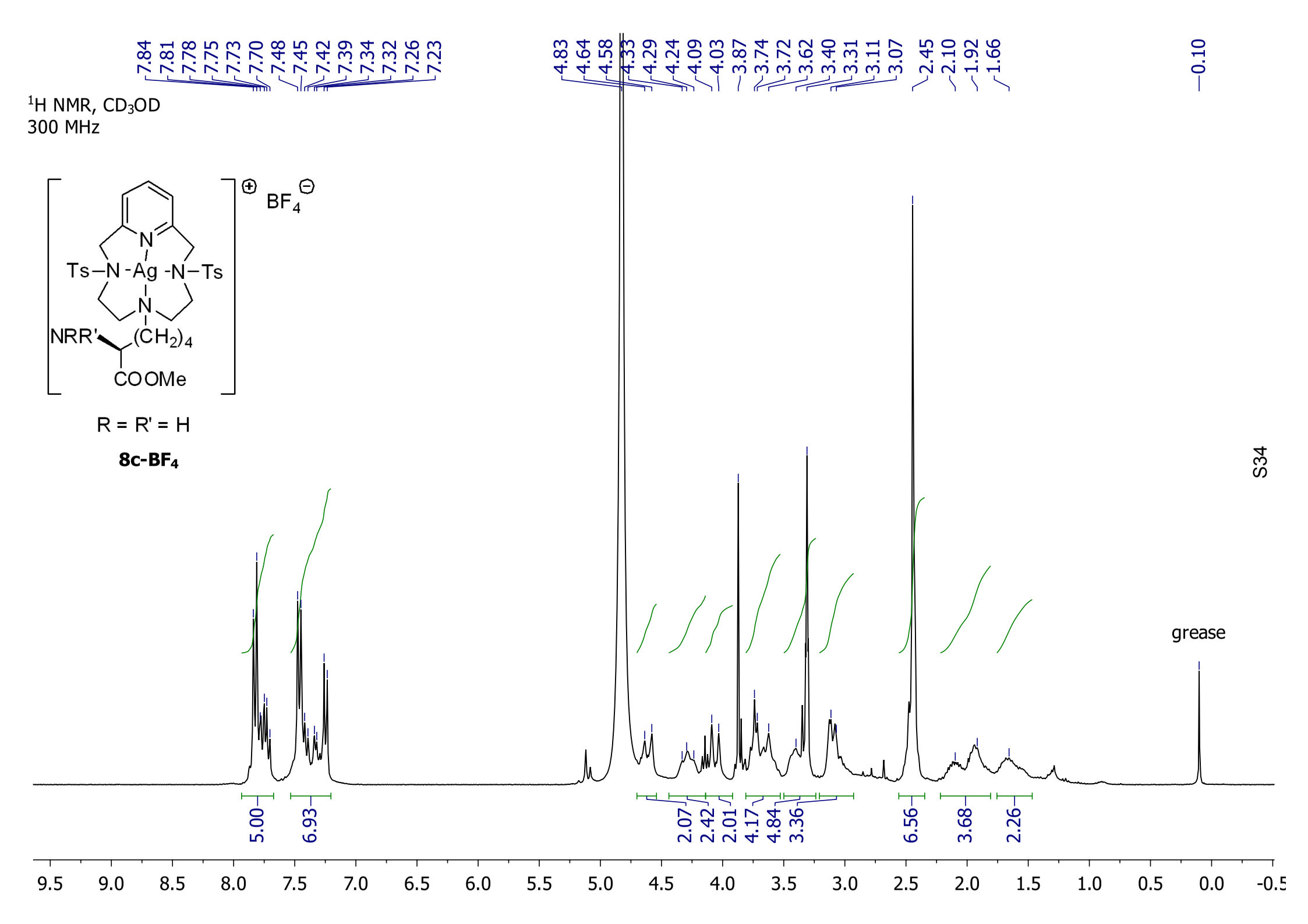
R = H, R' = Cbz

8b-OTf

S32

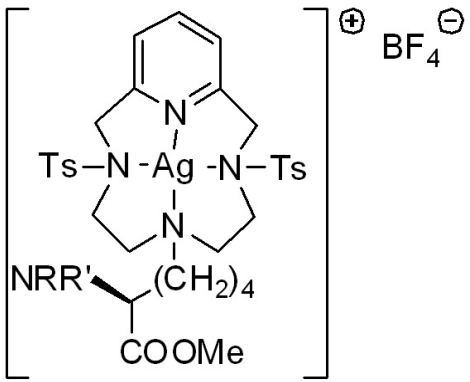
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


HSQC, CDCl3
OTf
Ts–N -Ag -N–Ts
NRR'
(CH2)4
COOMe
R = H, R' = Cbz
8b-OTf
S33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150


7.84
7.81
7.78
7.75
7.73
7.70
7.48
7.45
7.42
7.39
7.34
7.32
7.26
7.23
4.83
4.64
4.58
4.33
4.29
4.24
4.09
4.03
3.87
3.74
3.72
3.62
3.40
3.31
3.11
3.07
2.45
2.10
1.92
1.66
0.10
1H NMR, CD3OD
300 MHz
BF4
Ts–N -Ag -N–Ts
NRR'
(CH2)4
COOMe
R = R' = H
8c-BF4
S34
grease
5.00
6.93
2.07
2.42
2.01
4.17
4.84
3.36
6.56
3.68
2.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

^{13}C NMR, CD_3OD
75 MHz

159.3
146.4
140.3
134.7
131.4
131.0
129.1
128.2
122.6
67.8
53.9
53.7
53.4
49.0
46.7
43.6
31.1
23.2
21.5
20.2



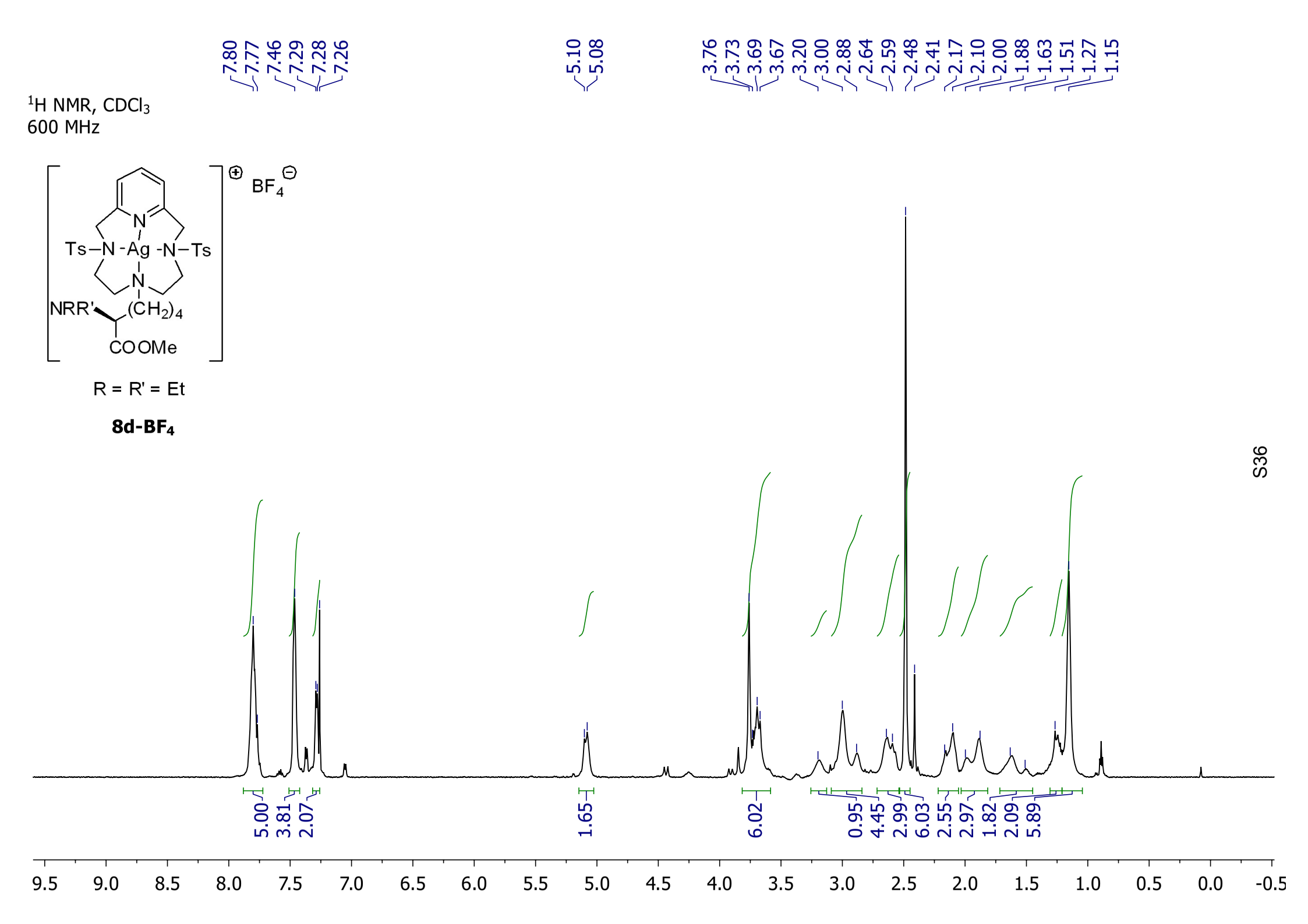
BF_4^-

R = R' = H

8c-BF_4

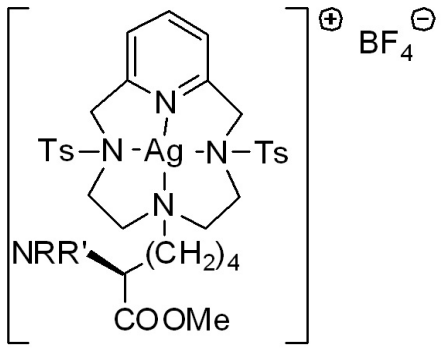
S35

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.80
7.77
7.46
7.29
7.28
7.26
5.10
5.08
3.76
3.73
3.69
3.67
3.20
3.00
2.88
2.64
2.59
2.48
2.41
2.17
2.10
2.00
1.88
1.63
1.51
1.27
1.15
1H NMR, CDCl3
600 MHz
BF4
Ts–N -Ag -N–Ts
NRR'
(CH2)4
COOMe
R = R' = Et
8d-BF4
S36
5.00
3.81
2.07
1.65
6.02
0.95
4.45
2.99
6.03
2.55
2.97
1.82
2.09
5.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

^{13}C NMR, $CDCl_3$
151 MHz

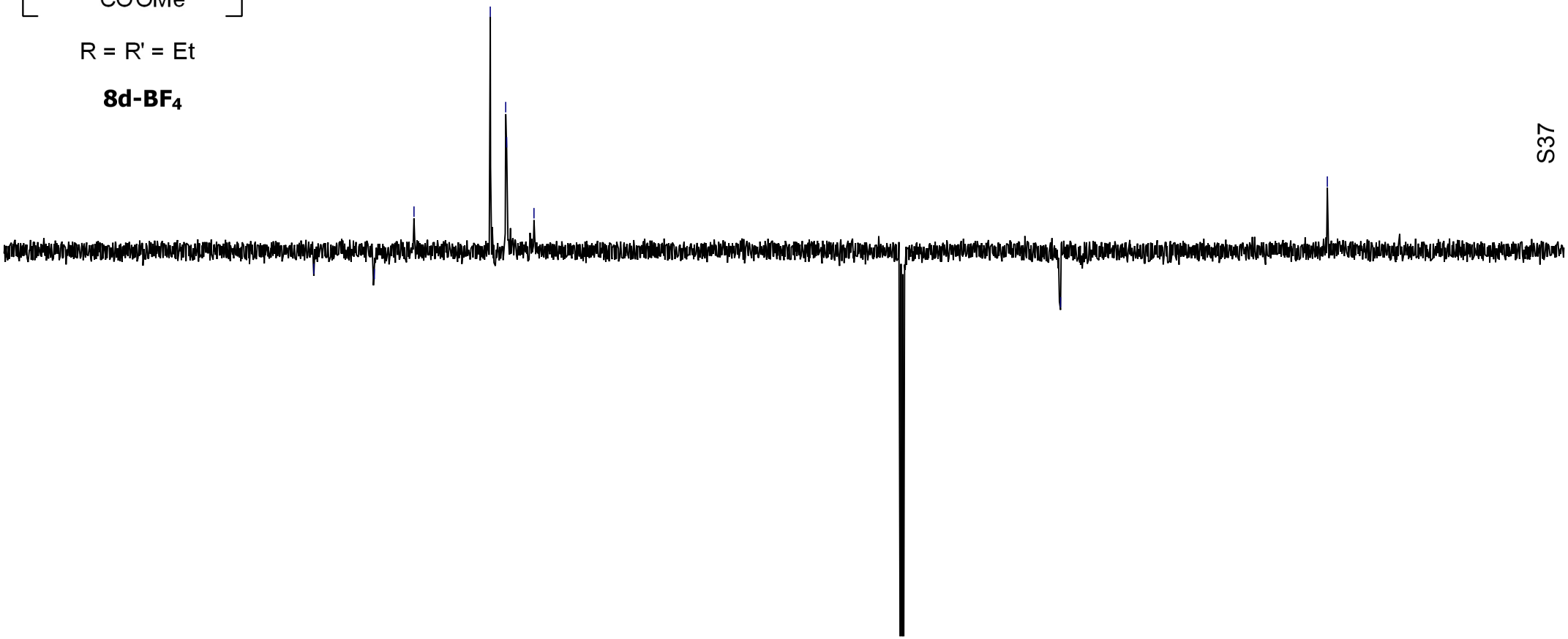
153.7
145.8
140.6
130.7
128.7
128.6
125.0
77.2
56.5
21.8



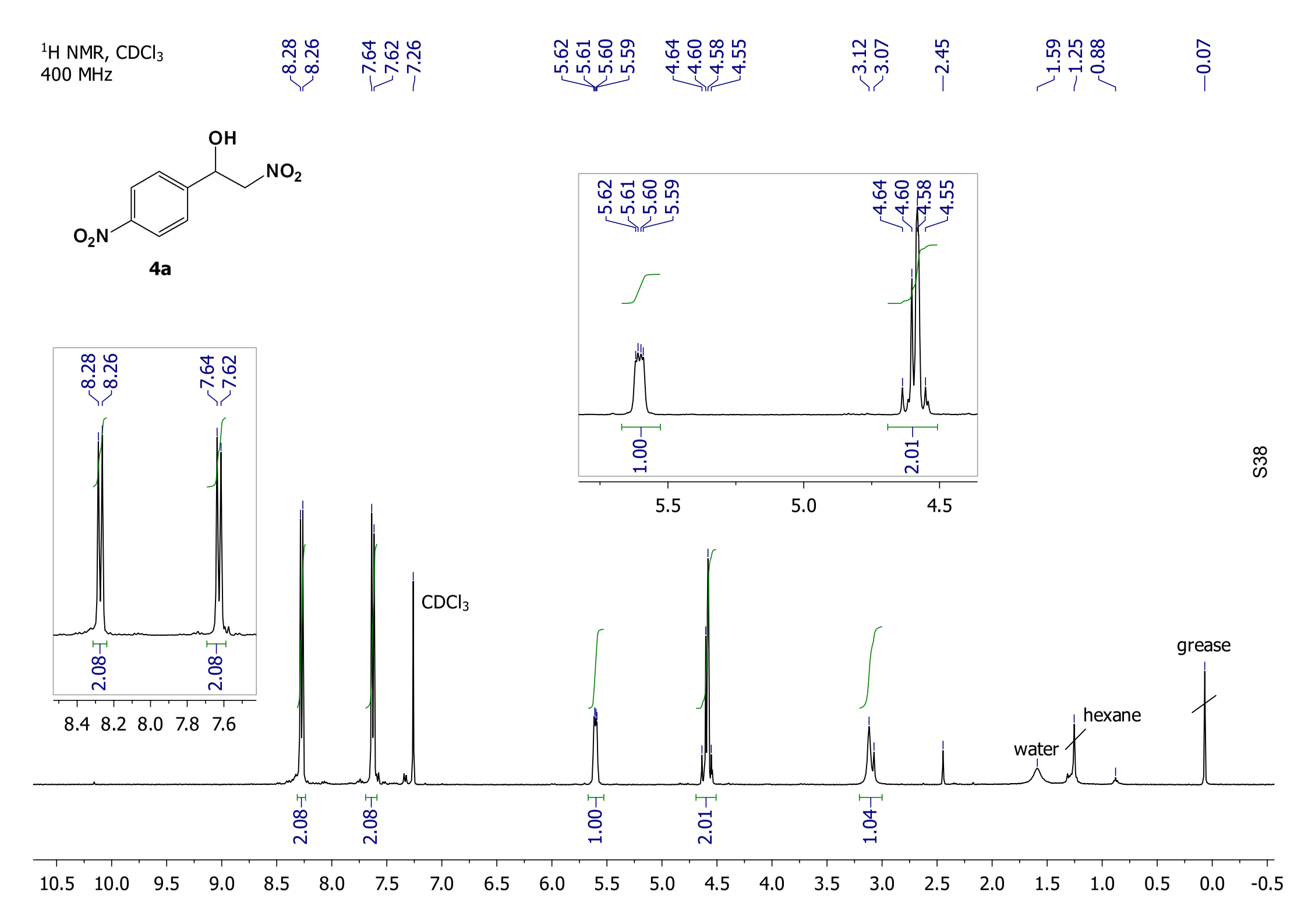
BF_4

R = R' = Et

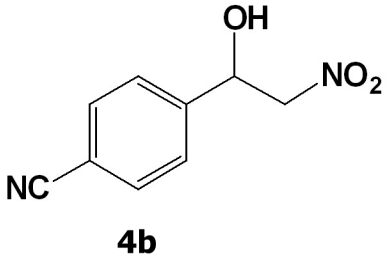
8d-BF_4



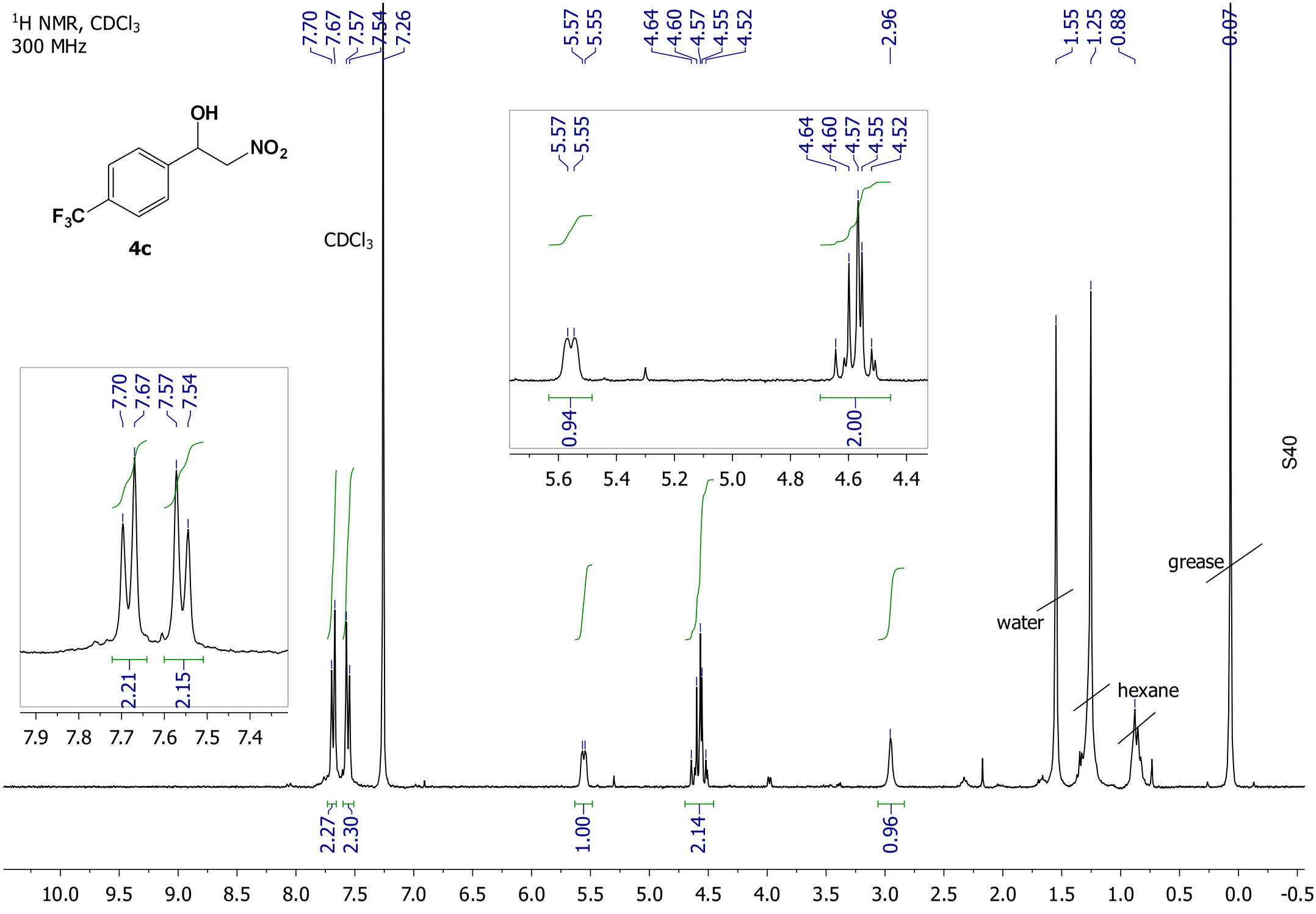
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


^{1}H NMR, $CDCl_3$
400 MHz
8.28
8.26
7.64
7.62
7.26
5.62
5.61
5.60
5.59
4.64
4.60
4.58
4.55
3.12
3.07
2.45
1.59
1.25
0.88
0.07
OH
NO_2
O_2N
4a
1.00
2.01
5.5
5.0
4.5
2.08
2.08
8.4 8.2 8.0 7.8 7.6
$CDCl_3$
grease
hexane
water
2.08
2.08
1.00
2.01
1.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
S38

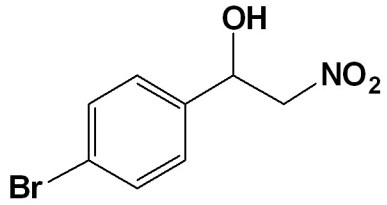
^{1}H NMR, $CDCl_3$
300 MHz



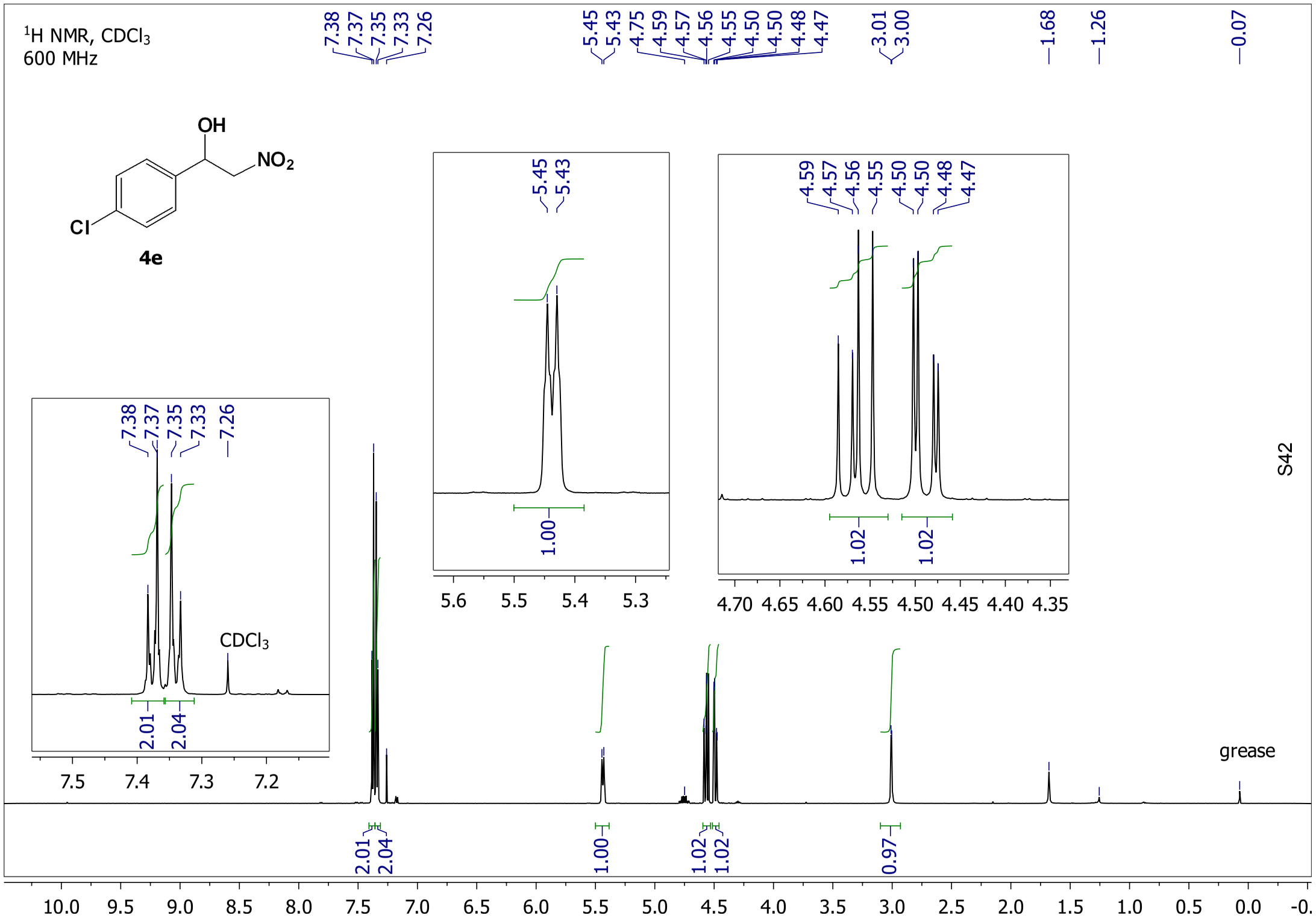
4b

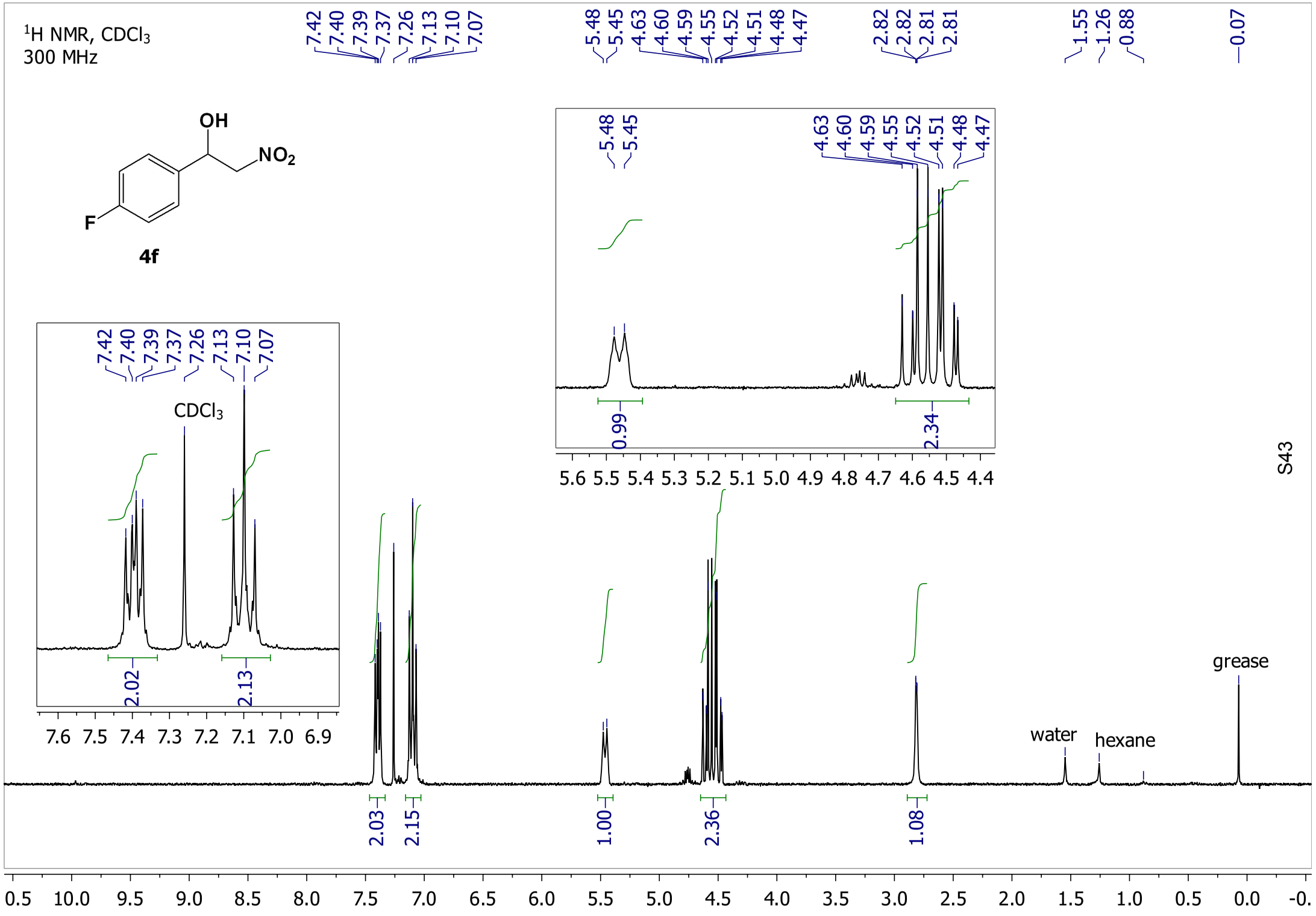

1H NMR, CDCl3
300 MHz
OH
NO2
F3C
4c
CDCl3
7.70
7.67
7.57
7.54
7.26
5.57
5.55
4.64
4.60
4.57
4.55
4.52
2.96
1.55
1.25
0.88
0.07
water
hexane
grease
S40
2.27
2.30
1.00
2.14
0.96
0.94
2.00
2.21
2.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

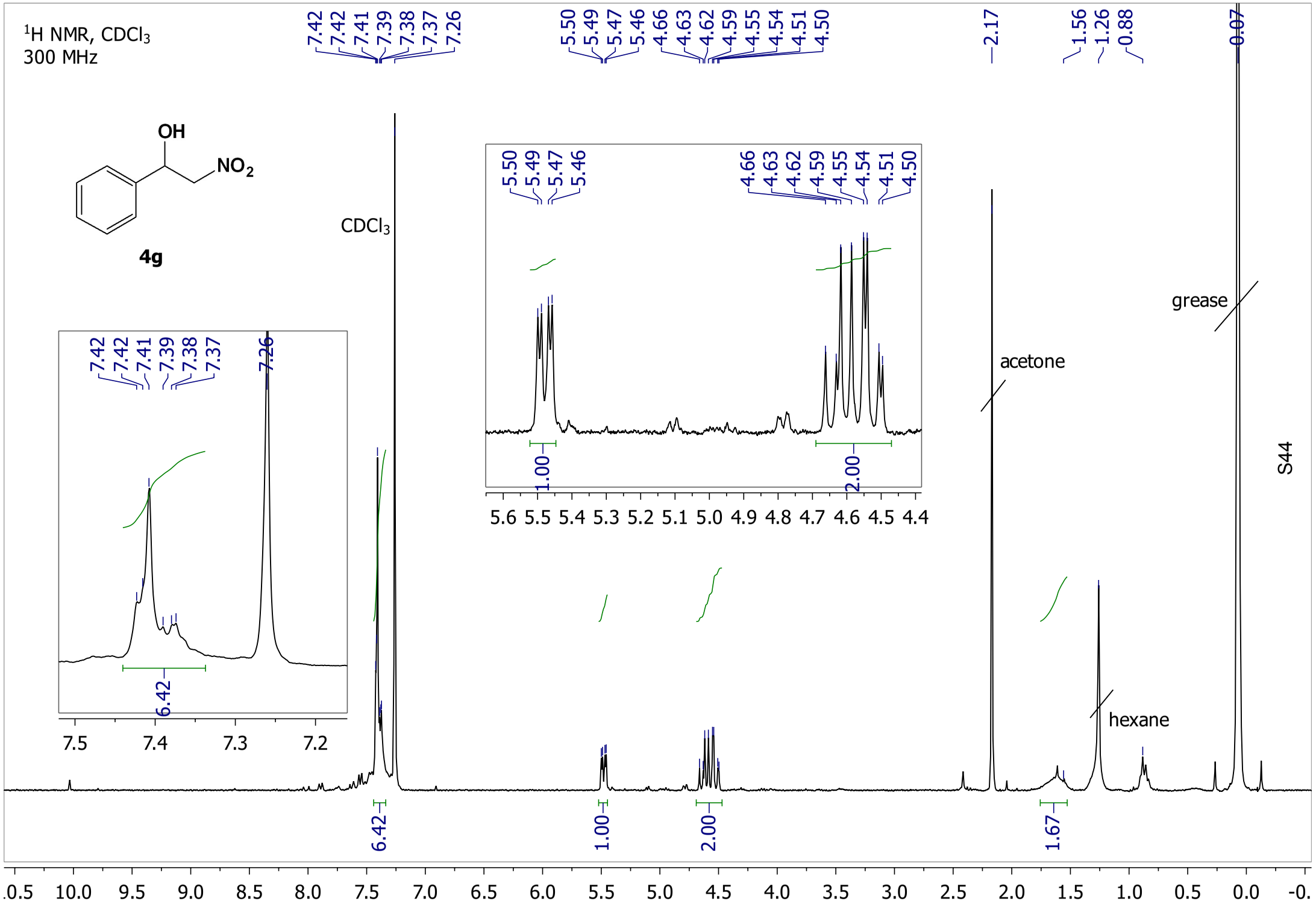
^{1}H NMR, $CDCl_3$
300 MHz



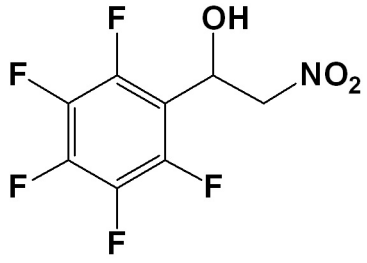
4d


^{1}H NMR, $CDCl_3$
600 MHz
7.38 7.37 7.35 7.33 7.26
5.45 5.43 4.75 4.59 4.57 4.56 4.55 4.50 4.50 4.48 4.47
3.01 3.00
1.68
1.26
0.07
OH
NO2
Cl
4e
5.45 5.43
1.00
5.6 5.5 5.4 5.3
4.59 4.57 4.56 4.55 4.50 4.50 4.48 4.47
1.02 1.02
4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35
7.38 7.37 7.35 7.33 7.26
CDCl3
2.01 2.04
7.5 7.4 7.3 7.2
grease
S42
2.01 2.04 1.00 1.02 1.02 0.97
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

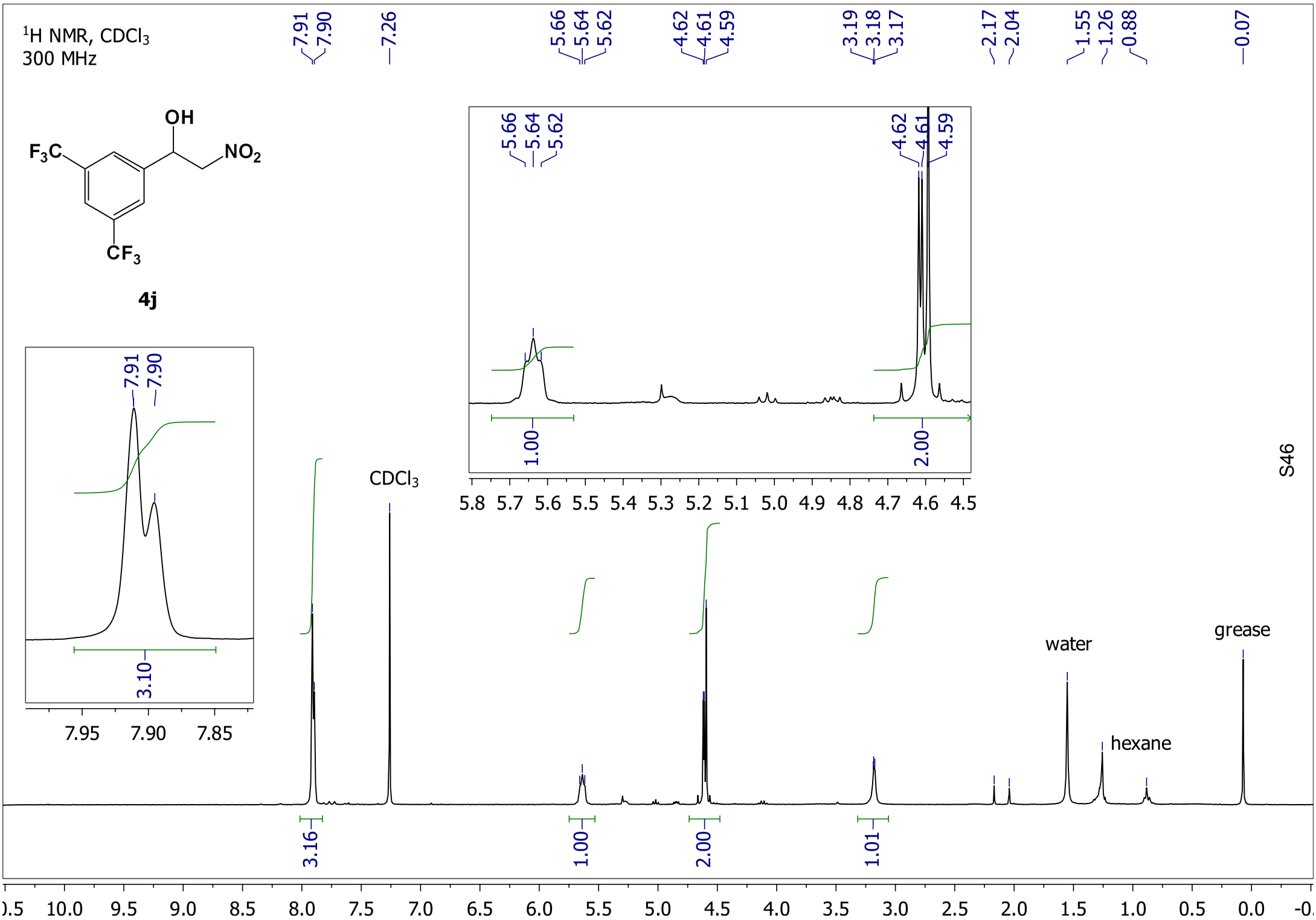

1H NMR, CDCl3
300 MHz
OH
NO2
F
4f
CDCl3
water
hexane
grease
S43


1H NMR, CDCl3
300 MHz
7.42 7.42 7.41 7.39 7.38 7.37 7.26
5.50 5.49 5.47 5.46 4.66 4.63 4.62 4.59 4.55 4.54 4.51 4.50
2.17
1.56 1.26 0.88
0.07
OH
NO2
4g
CDCl3
grease
acetone
hexane
S44
6.42
1.00
2.00
1.67
5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
7.5 7.4 7.3 7.2
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

^{1}H NMR, $CDCl_3$
300 MHz

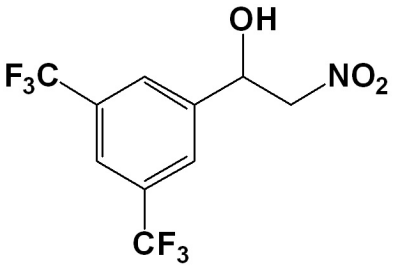


4i


1H NMR, CDCl3
300 MHz
7.91
7.90
7.26
5.66
5.64
5.62
4.62
4.61
4.59
3.19
3.18
3.17
2.17
2.04
1.55
1.26
0.88
0.07
OH
F3C
NO2
CF3
4j
CDCl3
water
hexane
grease
S46
3.16
1.00
2.00
1.01
3.10
1.00
2.00

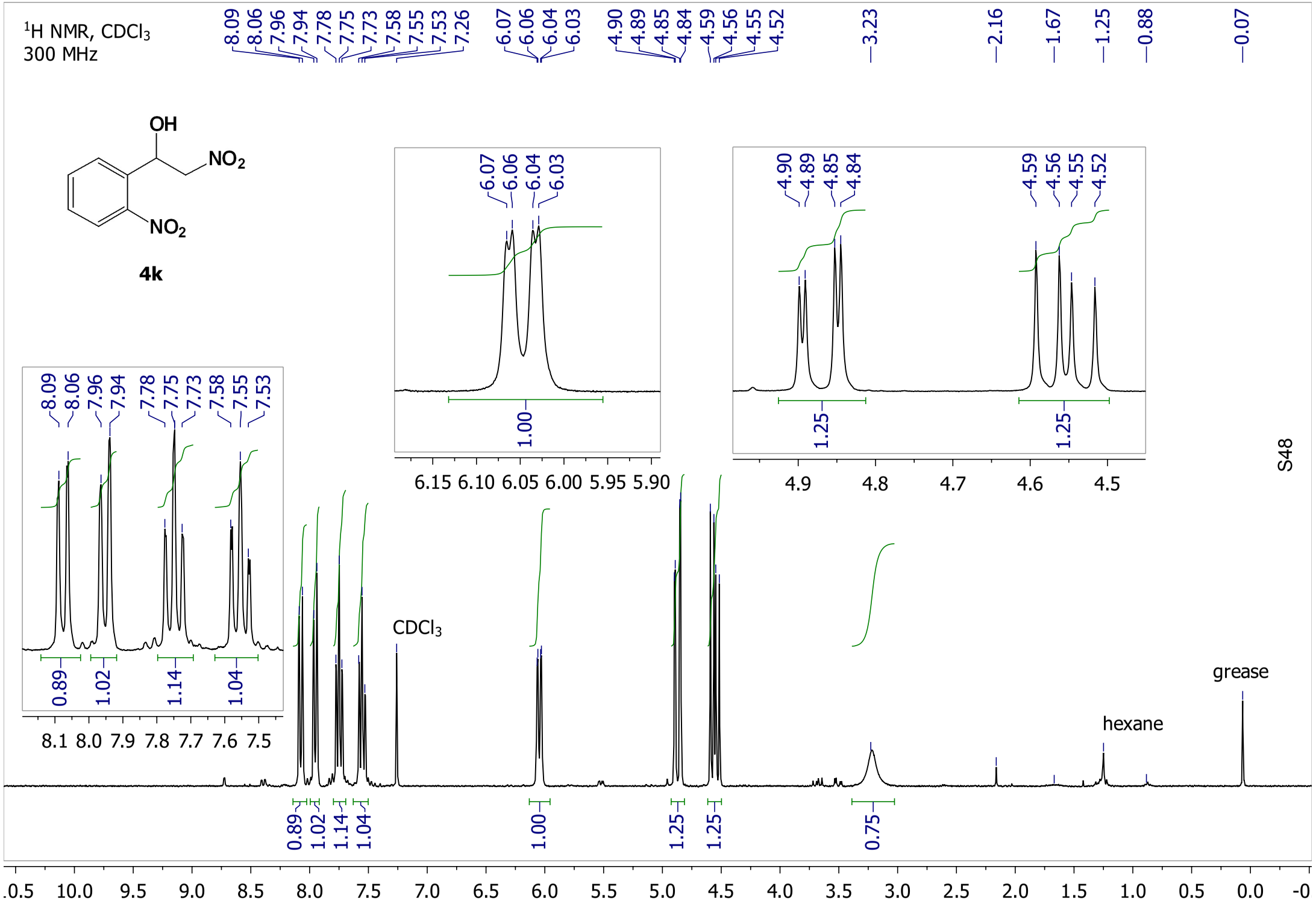
^{13}C NMR, $CDCl_3$
75 MHz

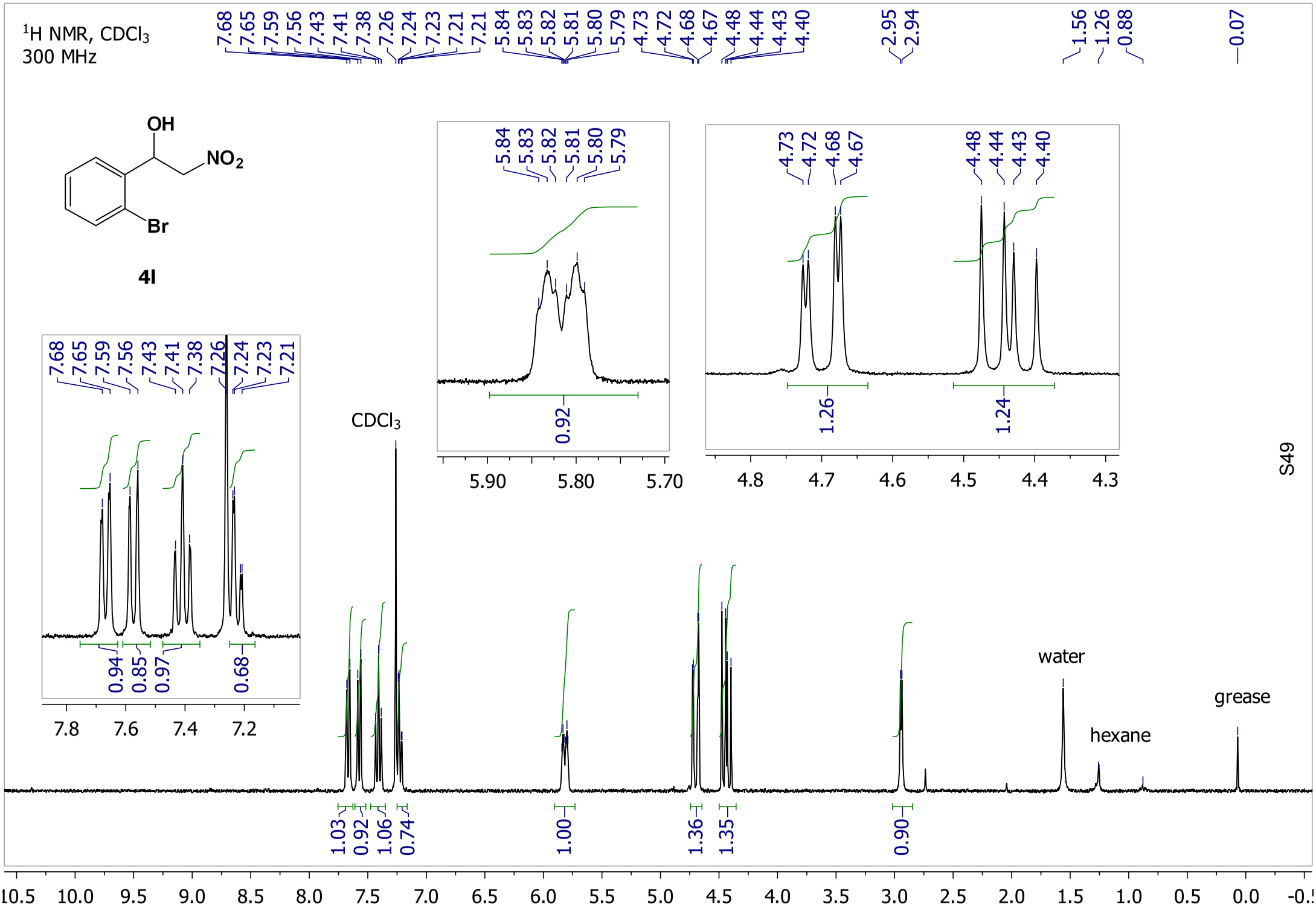
140.7
132.9
132.5
126.4
124.9
123.2
123.1
123.1
123.0
123.0
121.3
95.7
80.6
77.2
71.6
69.8
29.8
14.3
1.2

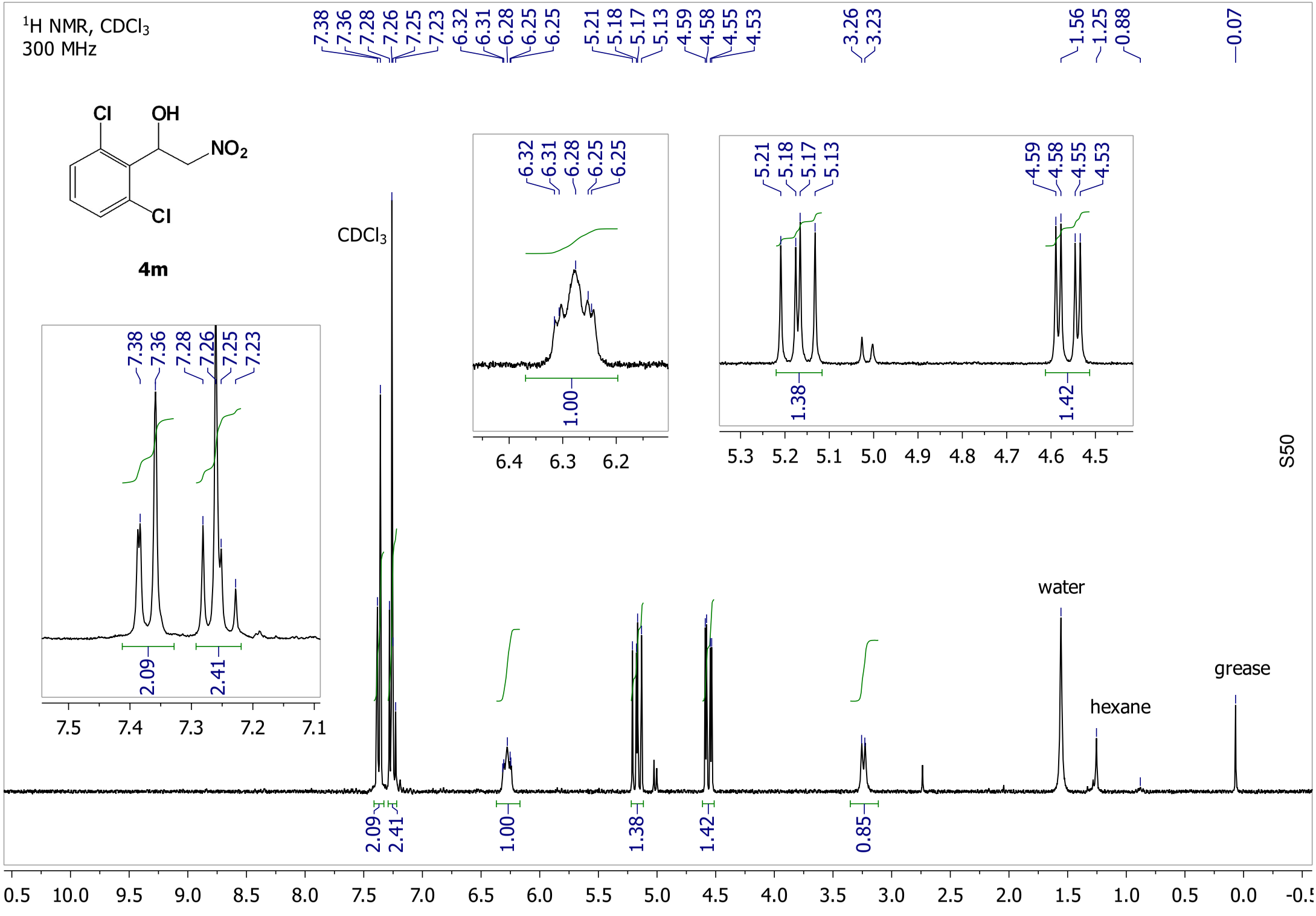


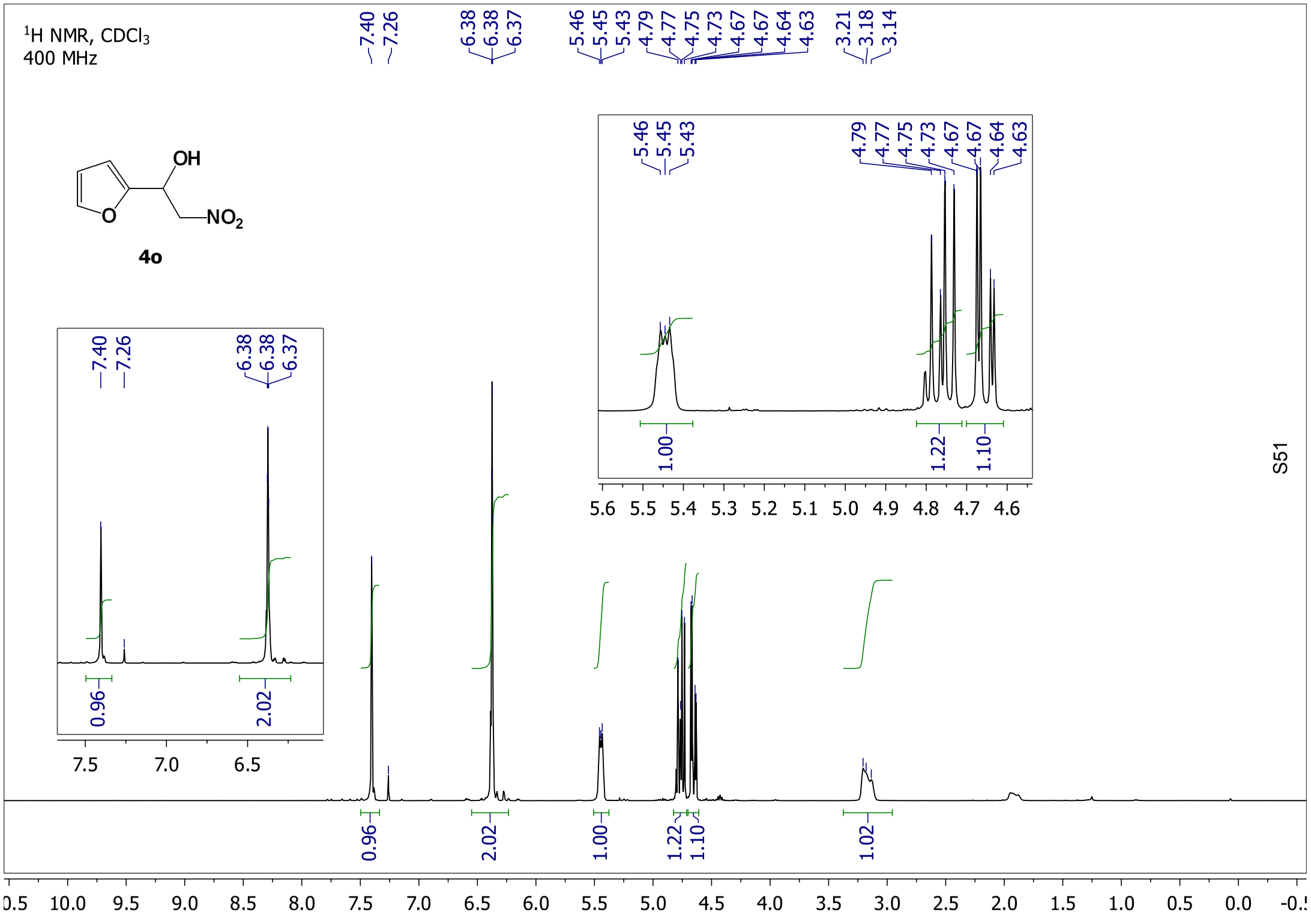
4j

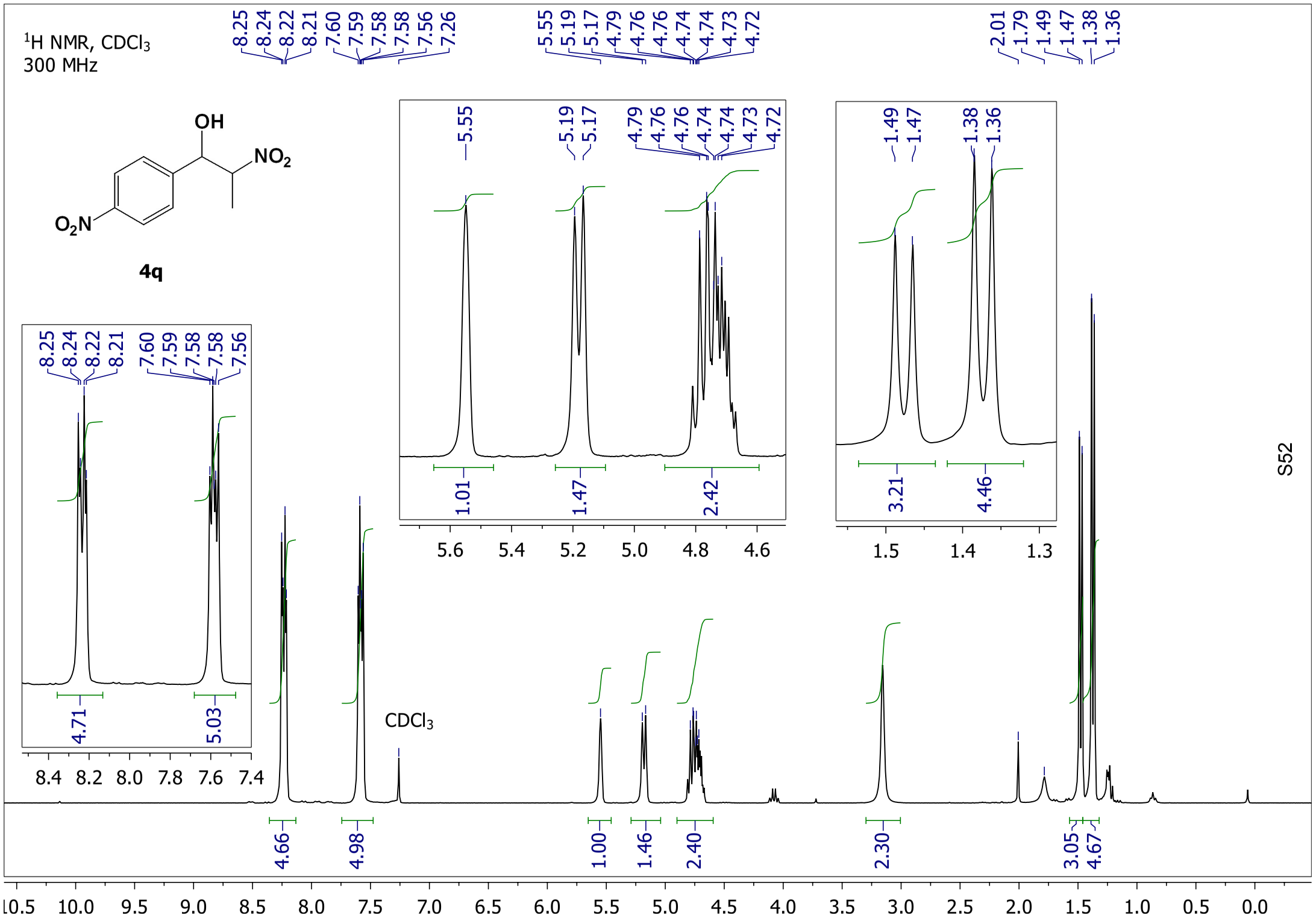
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

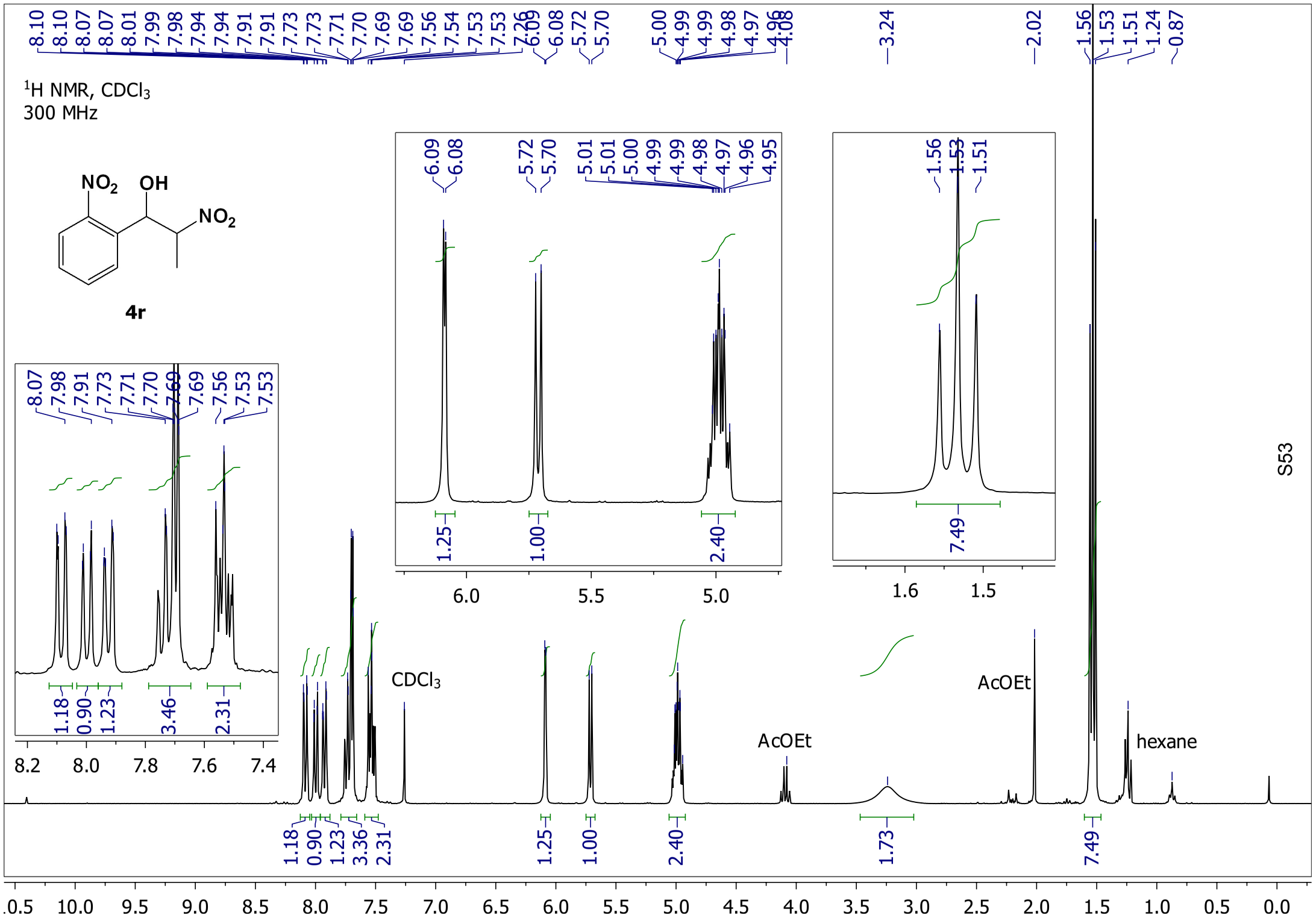

^{1}H NMR, $CDCl_3$
300 MHz
8.09 8.06 7.96 7.94 7.78 7.75 7.73 7.58 7.55 7.53 7.26
6.07 6.06 6.04 6.03
4.90 4.89 4.85 4.84
4.59 4.56 4.55 4.52
3.23
2.16
1.67
1.25
0.88
0.07
OH
NO_2
NO_2
4k
1.00
1.25
1.25
0.89
1.02
1.14
1.04
$CDCl_3$
1.00
1.25
1.25
0.75
hexane
grease
S48

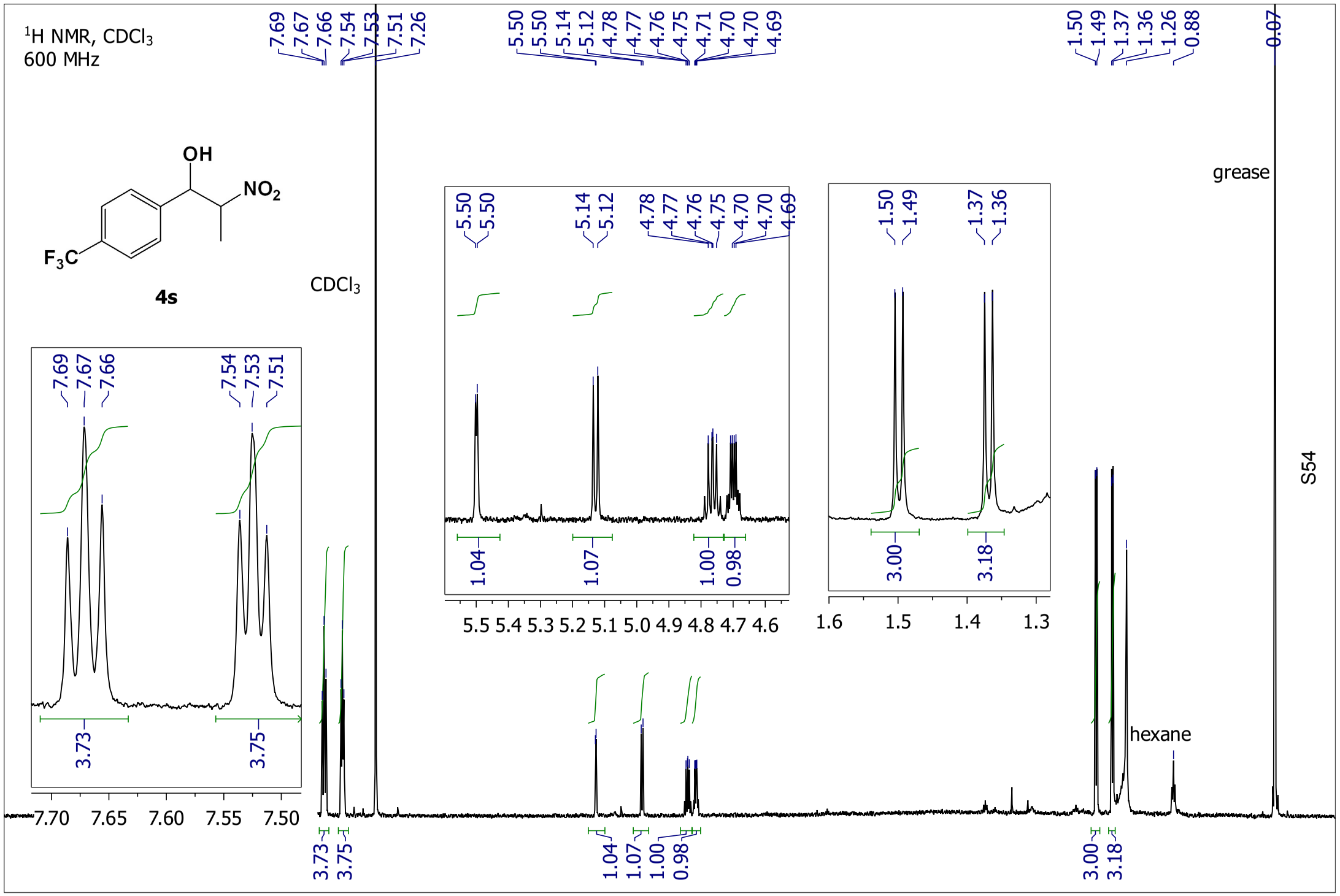

1H NMR, CDCl3
300 MHz
7.68 7.65 7.59 7.56 7.43 7.41 7.38 7.26 7.24 7.23 7.21 7.21 5.84 5.83 5.82 5.81 5.80 5.79 4.73 4.72 4.68 4.67 4.48 4.44 4.43 4.40 2.95 2.94 1.56 1.26 0.88 0.07
OH
NO2
Br
4l
CDCl3
water
hexane
grease
S49
1.03 0.92 1.06 0.74 1.00 1.36 1.35 0.90
0.94 0.85 0.97 0.68
0.92
1.26 1.24

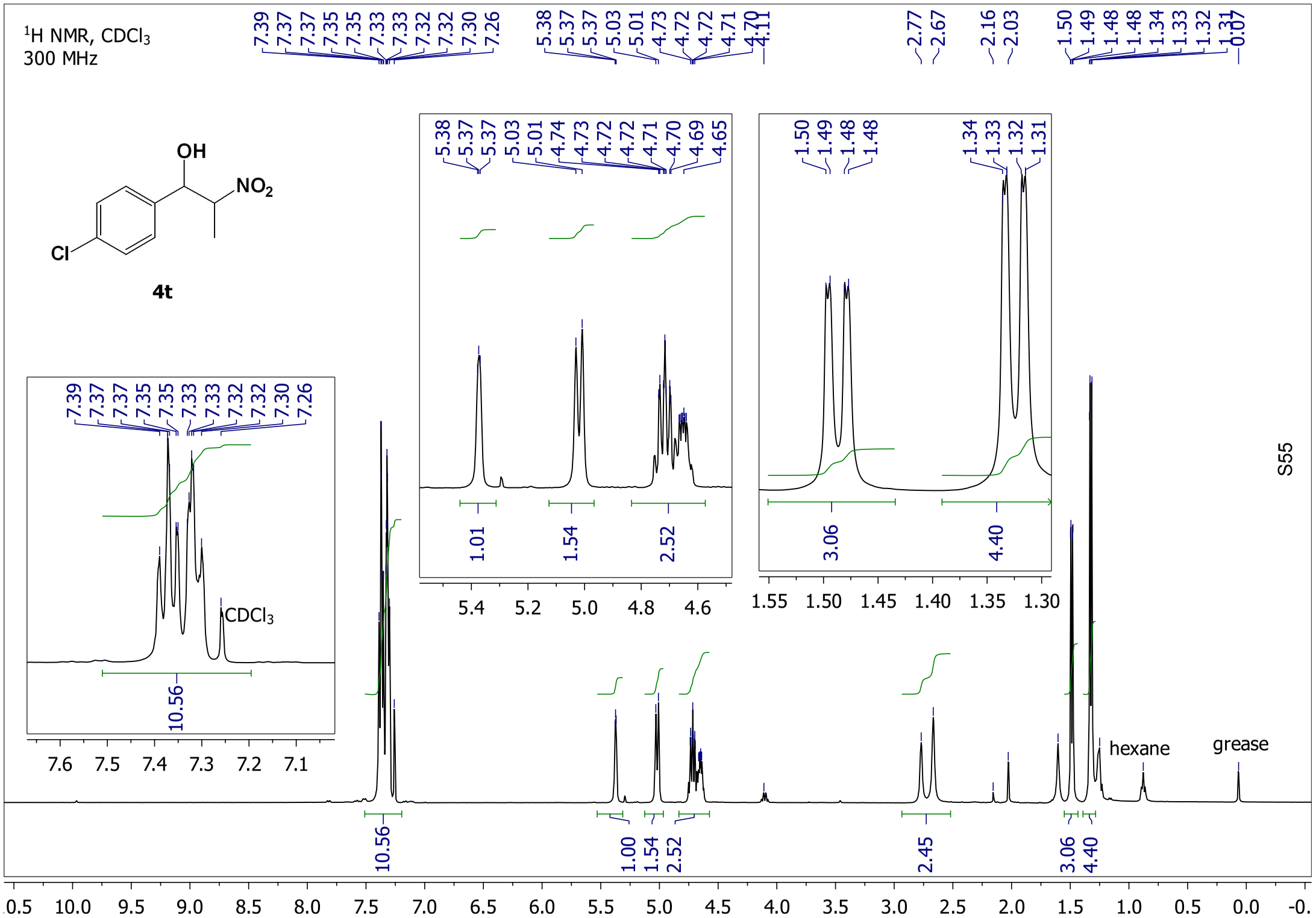

1H NMR, CDCl3
300 MHz
7.38
7.36
7.28
7.26
7.25
7.23
6.32
6.31
6.28
6.25
6.25
5.21
5.18
5.17
5.13
4.59
4.58
4.55
4.53
3.26
3.23
1.56
1.25
0.88
0.07
Cl
OH
NO2
Cl
4m
CDCl3
water
hexane
grease
S50
2.09
2.41
1.00
1.38
1.42
0.85

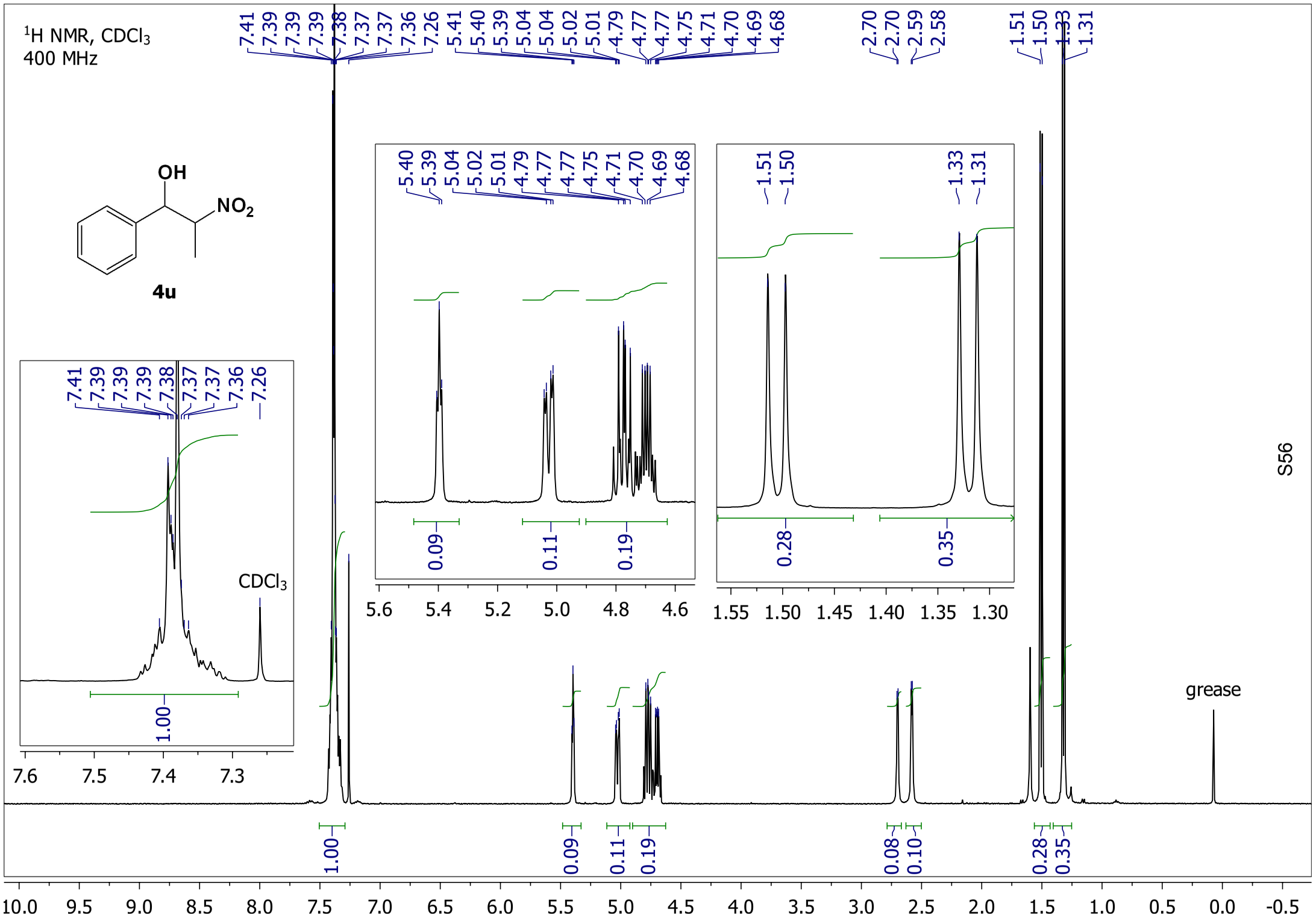

1H NMR, CDCl3
400 MHz
7.40
7.26
6.38
6.38
6.37
5.46
5.45
5.43
4.79
4.77
4.75
4.73
4.67
4.67
4.64
4.63
3.21
3.18
3.14
OH
O
NO2
4o
1.00
1.22
1.10
0.96
2.02
1.02
S51

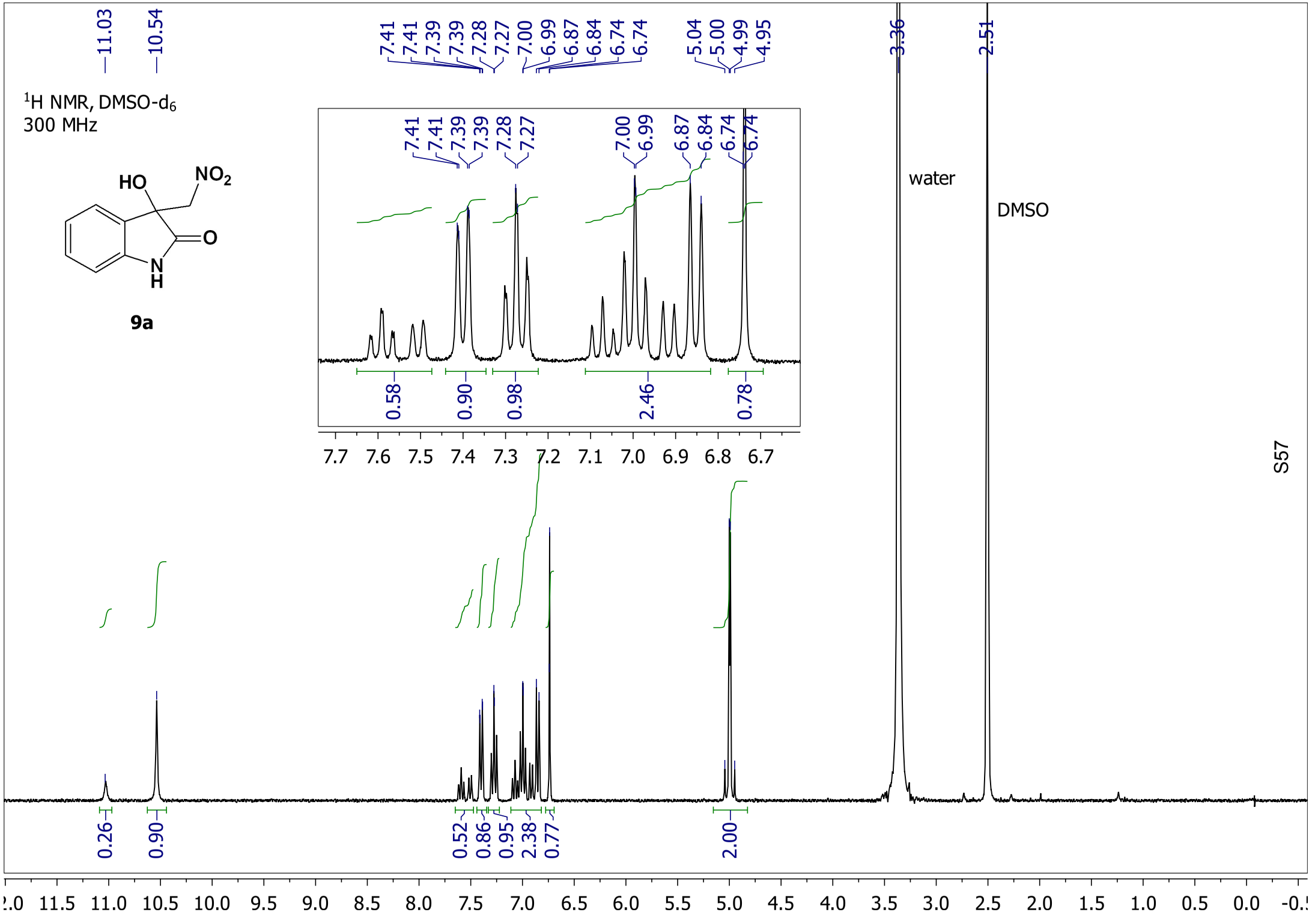

1H NMR, CDCl3
300 MHz
OH
NO2
O2N
4q
CDCl3
S52

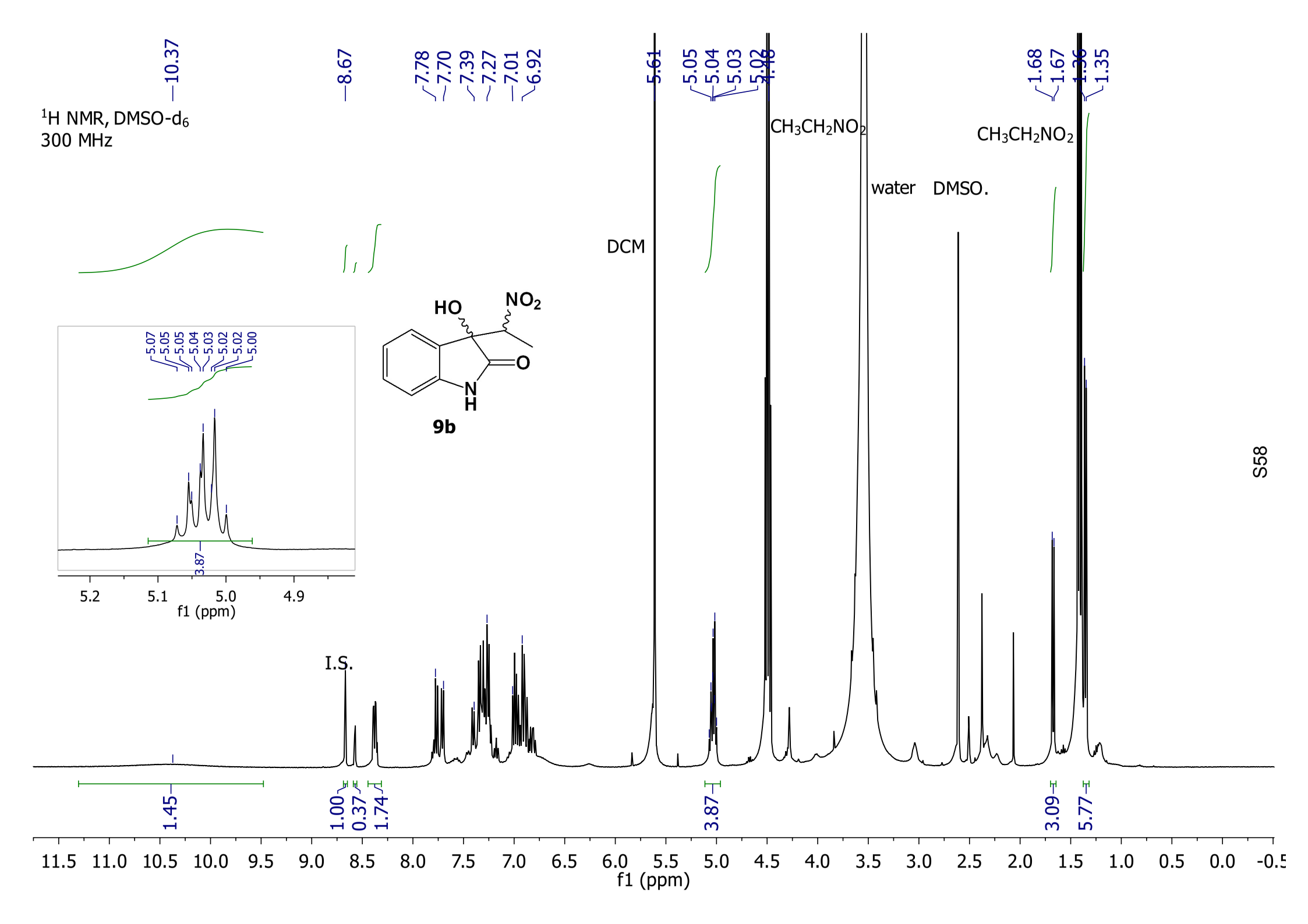

8.10 8.10 8.07 8.07 8.01 7.99 7.98 7.94 7.94 7.91 7.91 7.73 7.73 7.71 7.70 7.69 7.69 7.56 7.54 7.53 7.53 7.26 6.09 6.08 5.72 5.70 5.00 4.99 4.99 4.98 4.97 4.96 4.95 3.24 2.02 1.56 1.53 1.51 1.24 0.87
1H NMR, CDCl3
300 MHz
NO2 OH NO2
4r
6.09 6.08 5.72 5.70 5.01 5.01 5.00 4.99 4.99 4.98 4.97 4.96 4.95
1.25 1.00 2.40
6.0 5.5 5.0
1.56 1.53 1.51
7.49
1.6 1.5
8.07 7.98 7.91 7.73 7.71 7.70 7.69 7.69 7.56 7.53 7.53
1.18 0.90 1.23 3.46 2.31
8.2 8.0 7.8 7.6 7.4
CDCl3
AcOEt
AcOEt
hexane
1.18 0.90 1.23 3.36 2.31 1.25 1.00 2.40 1.73 7.49
S53
.0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

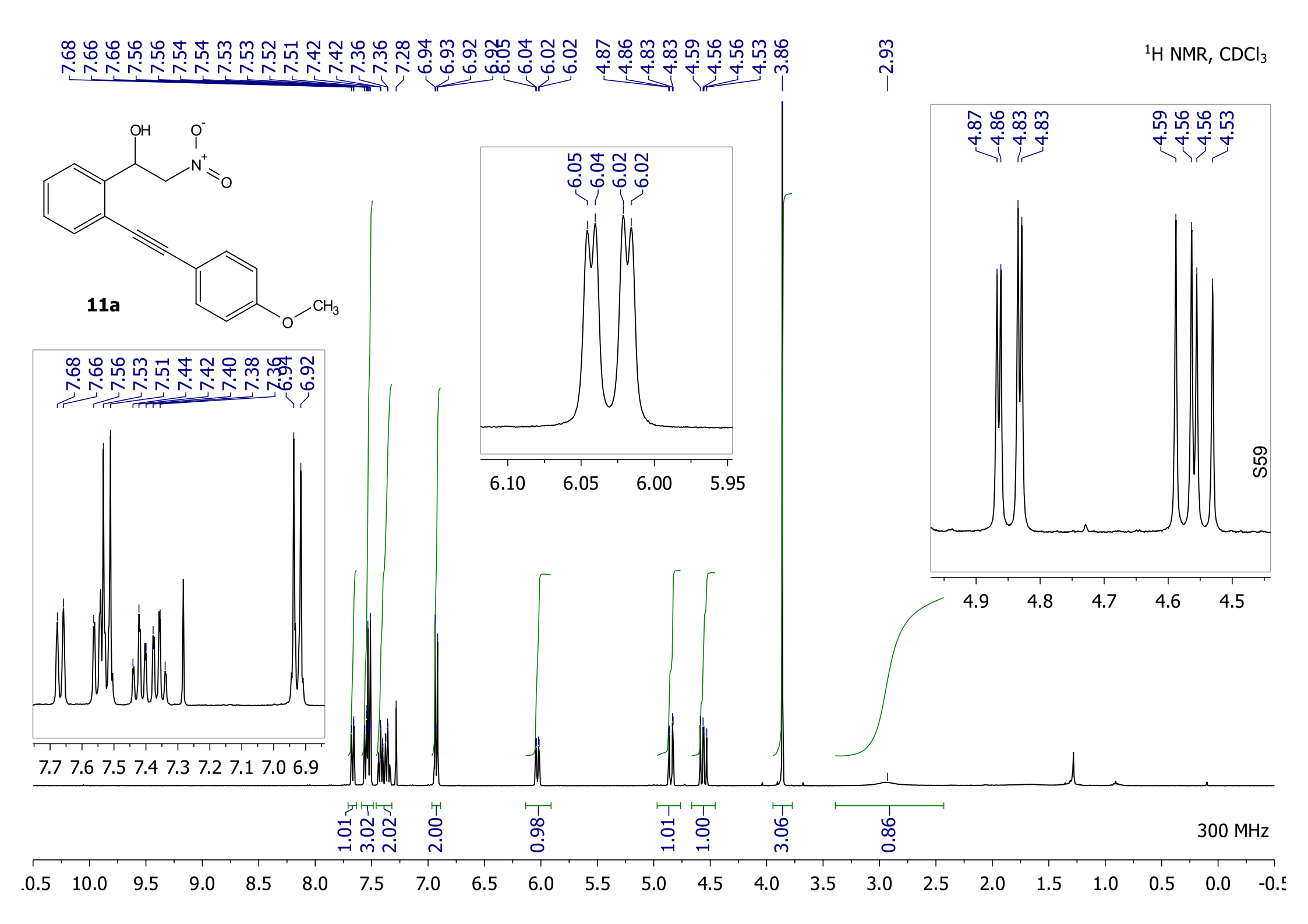

1H NMR, CDCl3
600 MHz
OH
NO2
F3C
4s
CDCl3
grease
hexane
S54
7.69 7.67 7.66 7.54 7.53 7.51 7.26
5.50 5.50 5.14 5.12 4.78 4.77 4.76 4.75 4.71 4.70 4.70 4.69
1.50 1.49 1.37 1.36 1.26 0.88
0.07
3.73 3.75 1.04 1.07 1.00 0.98 3.00 3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

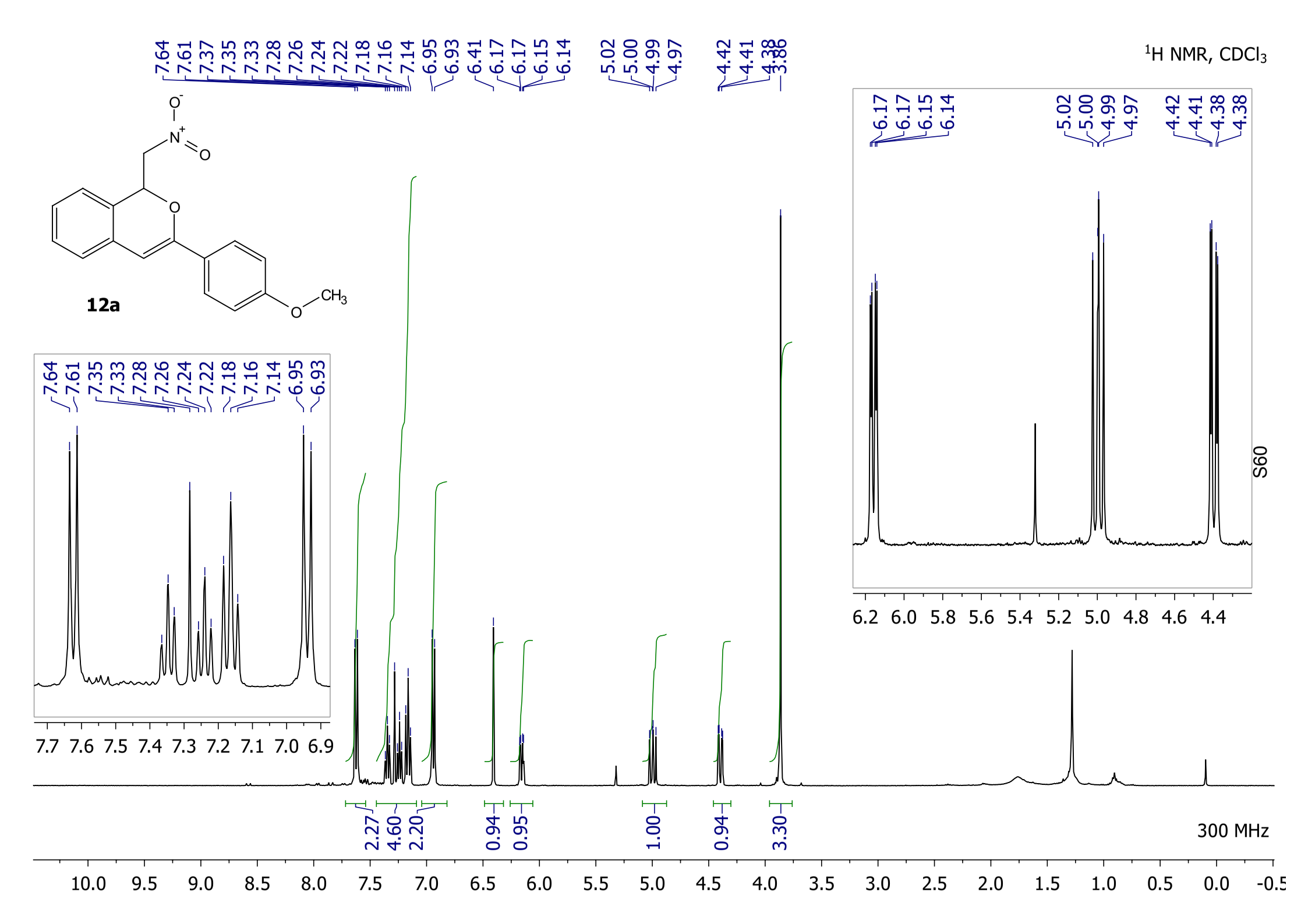

1H NMR, CDCl3
300 MHz
OH
NO2
Cl
4t
CDCl3
hexane
grease
S55

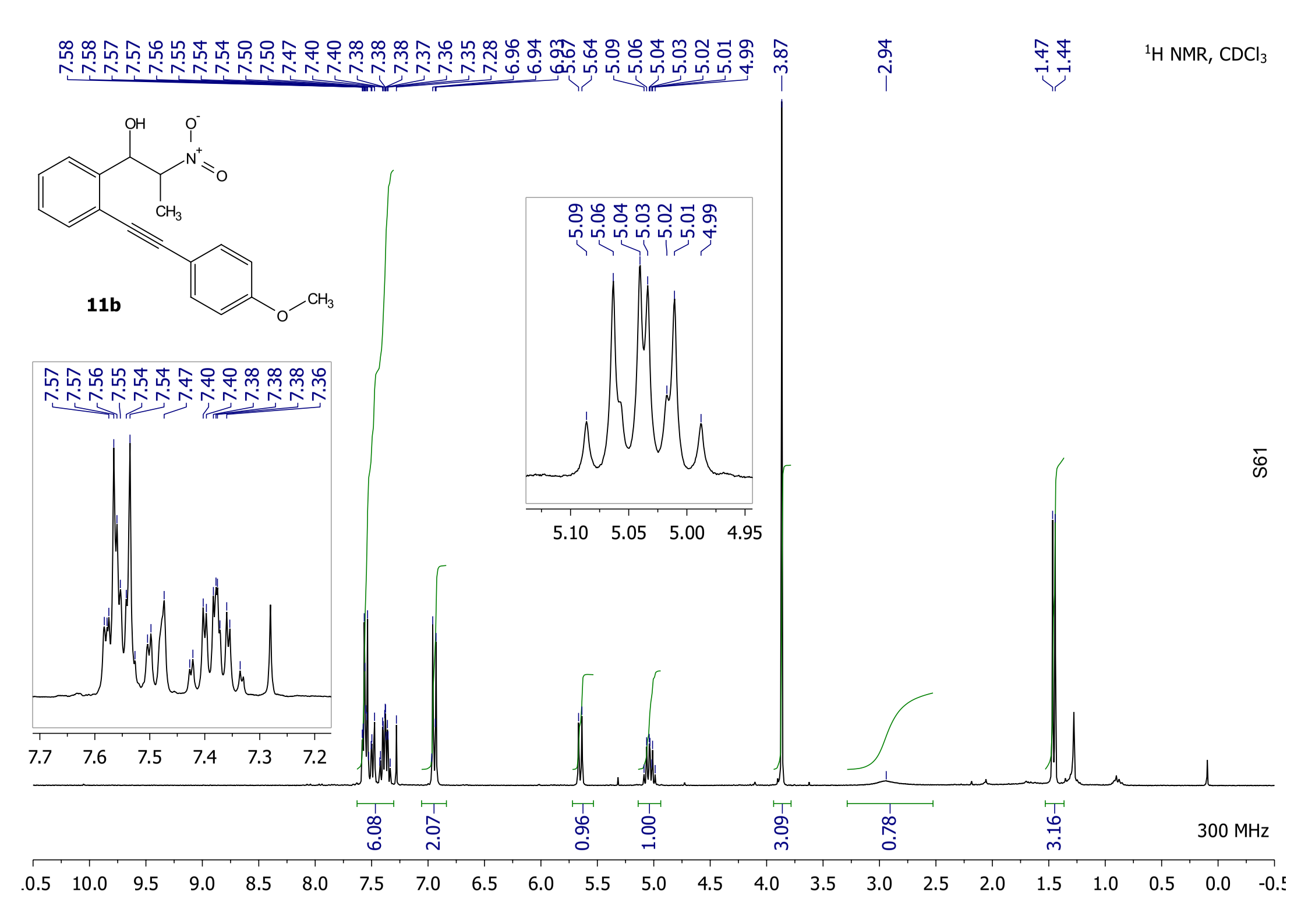

1H NMR, CDCl3
400 MHz
OH
NO2
4u
CDCl3
grease
S56

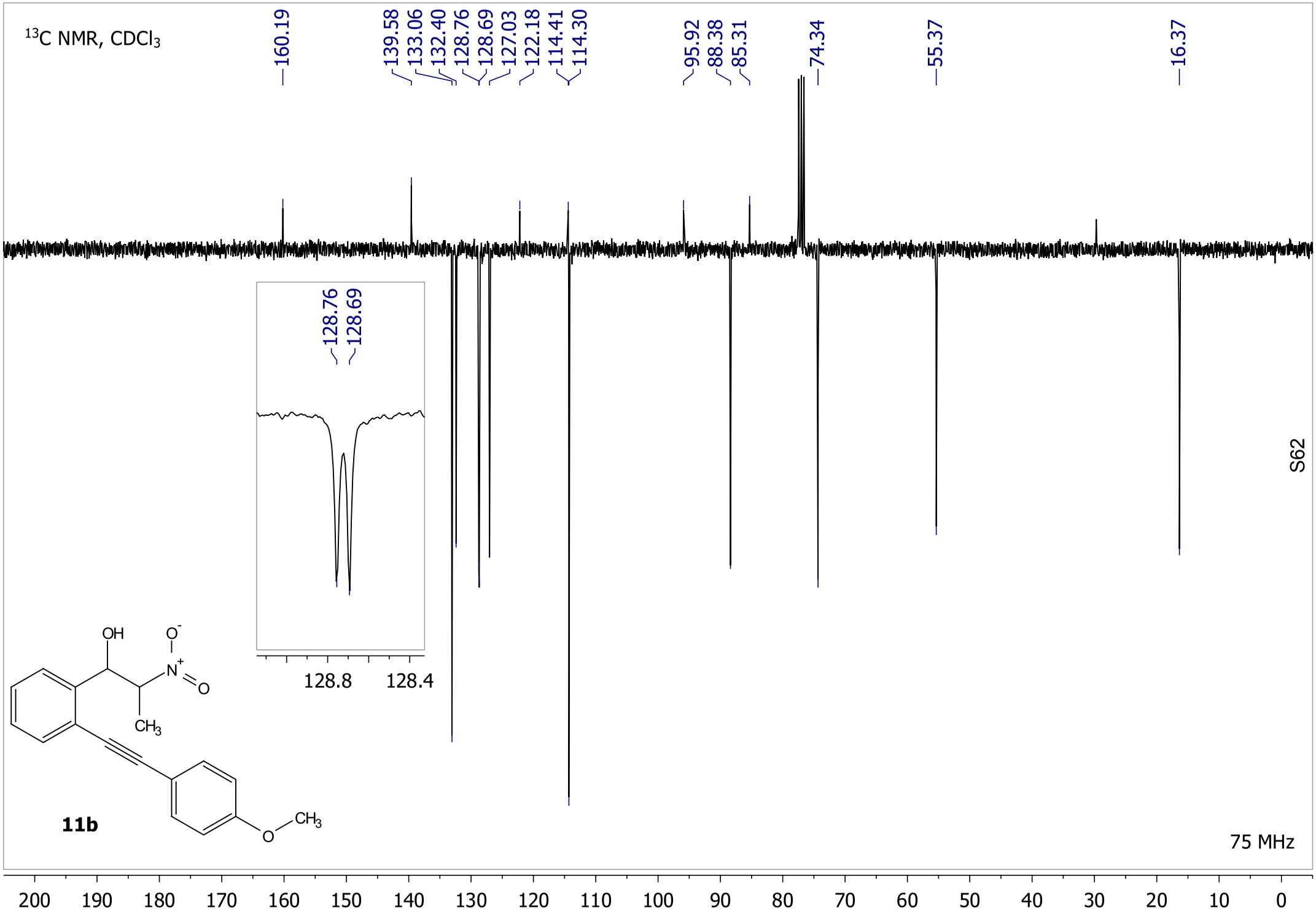

11.03
10.54
7.41
7.41
7.39
7.39
7.28
7.27
7.00
6.99
6.87
6.84
6.74
6.74
5.04
5.00
4.99
4.95
3.36
2.51
1H NMR, DMSO-d6
300 MHz
HO
NO2
O
N
H
9a
water
DMSO
S57
0.58
0.90
0.98
2.46
0.78
0.26
0.90
0.52
0.86
0.95
2.38
0.77
2.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

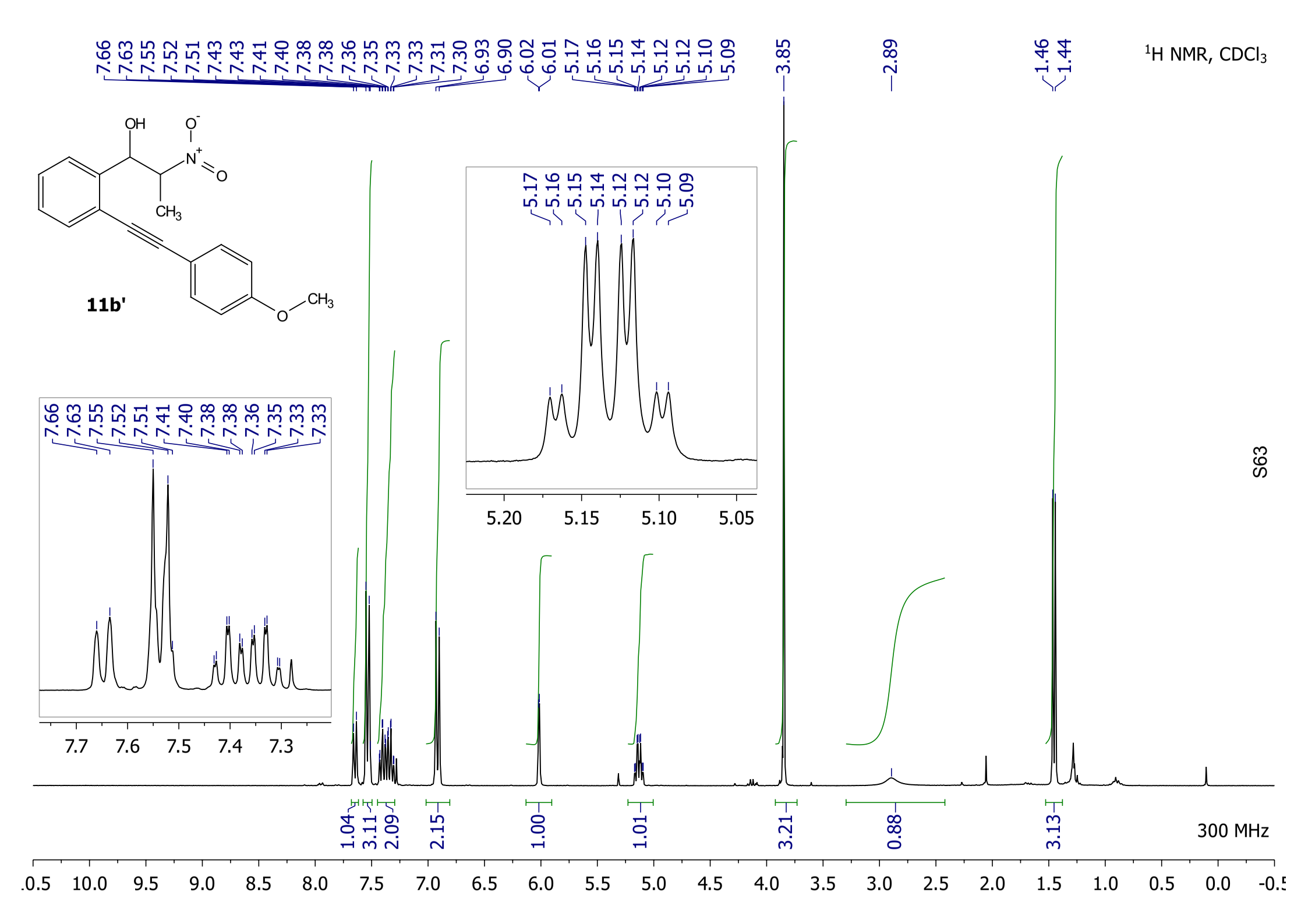

^{1}H NMR, DMSO-d$_6$
300 MHz
10.37
8.67
7.78
7.70
7.39
7.27
7.01
6.92
5.61
5.05
5.04
5.03
5.02
4.98
1.68
1.67
1.36
1.35
DCM
$CH_3CH_2NO_2$
$CH_3CH_2NO_2$
water
DMSO.
HO
NO_2
O
N
H
9b
I.S.
S58
1.45
1.00
0.37
1.74
3.87
3.09
5.77
f1 (ppm)
5.07
5.05
5.05
5.04
5.03
5.02
5.02
5.00
3.87
5.2
5.1
5.0
4.9
f1 (ppm)

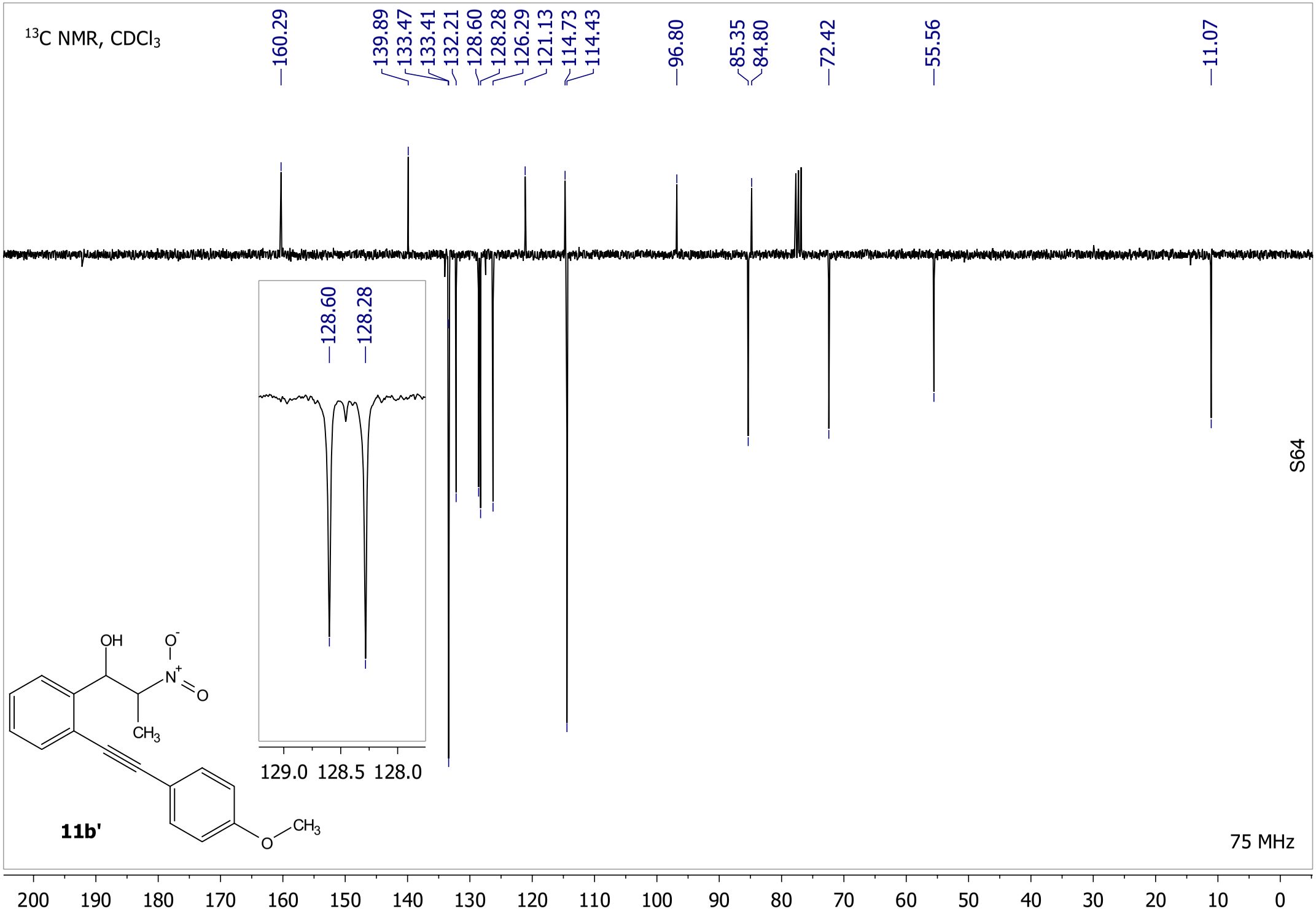

^{1}H NMR, $CDCl_3$
11a
OH
O
N
O
CH3
S59
300 MHz

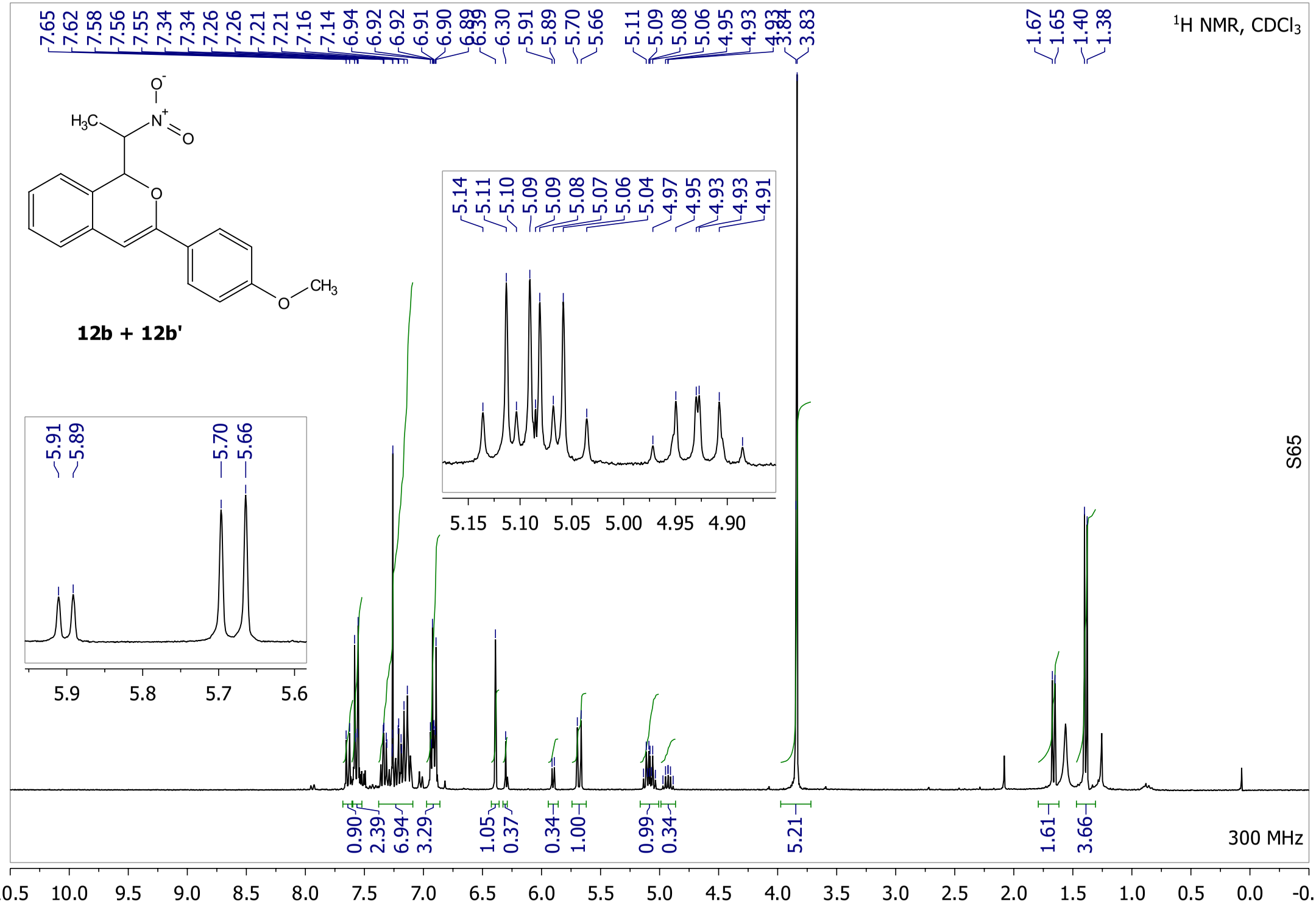

^{1}H NMR, CDCl$_3$
12a
S60
300 MHz

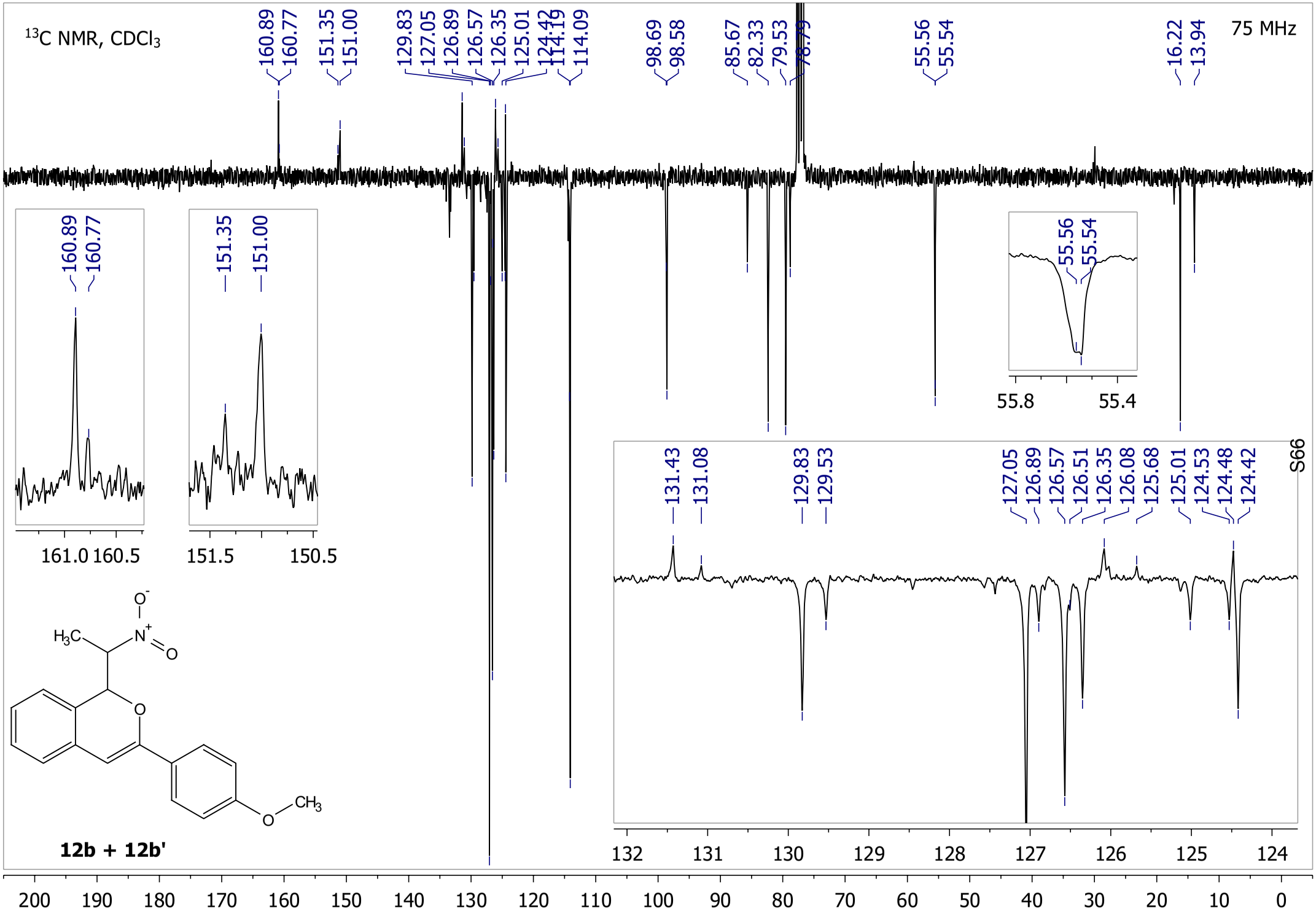

7.58 7.58 7.57 7.57 7.56 7.55 7.54 7.54 7.50 7.50 7.47 7.40 7.40 7.38 7.38 7.38 7.37 7.36 7.35 7.28 6.96 6.94 6.93 5.67 5.64 5.09 5.06 5.04 5.03 5.02 5.01 4.99 3.87 2.94 1.47 1.44
^{1}H NMR, $CDCl_3$
OH
O
N
O
CH3
11b
O
CH3
5.09 5.06 5.04 5.03 5.02 5.01 4.99
5.10 5.05 5.00 4.95
7.57 7.57 7.56 7.55 7.54 7.54 7.47 7.40 7.40 7.38 7.38 7.38 7.36
7.7 7.6 7.5 7.4 7.3 7.2
S61
6.08 2.07 0.96 1.00 3.09 0.78 3.16
300 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

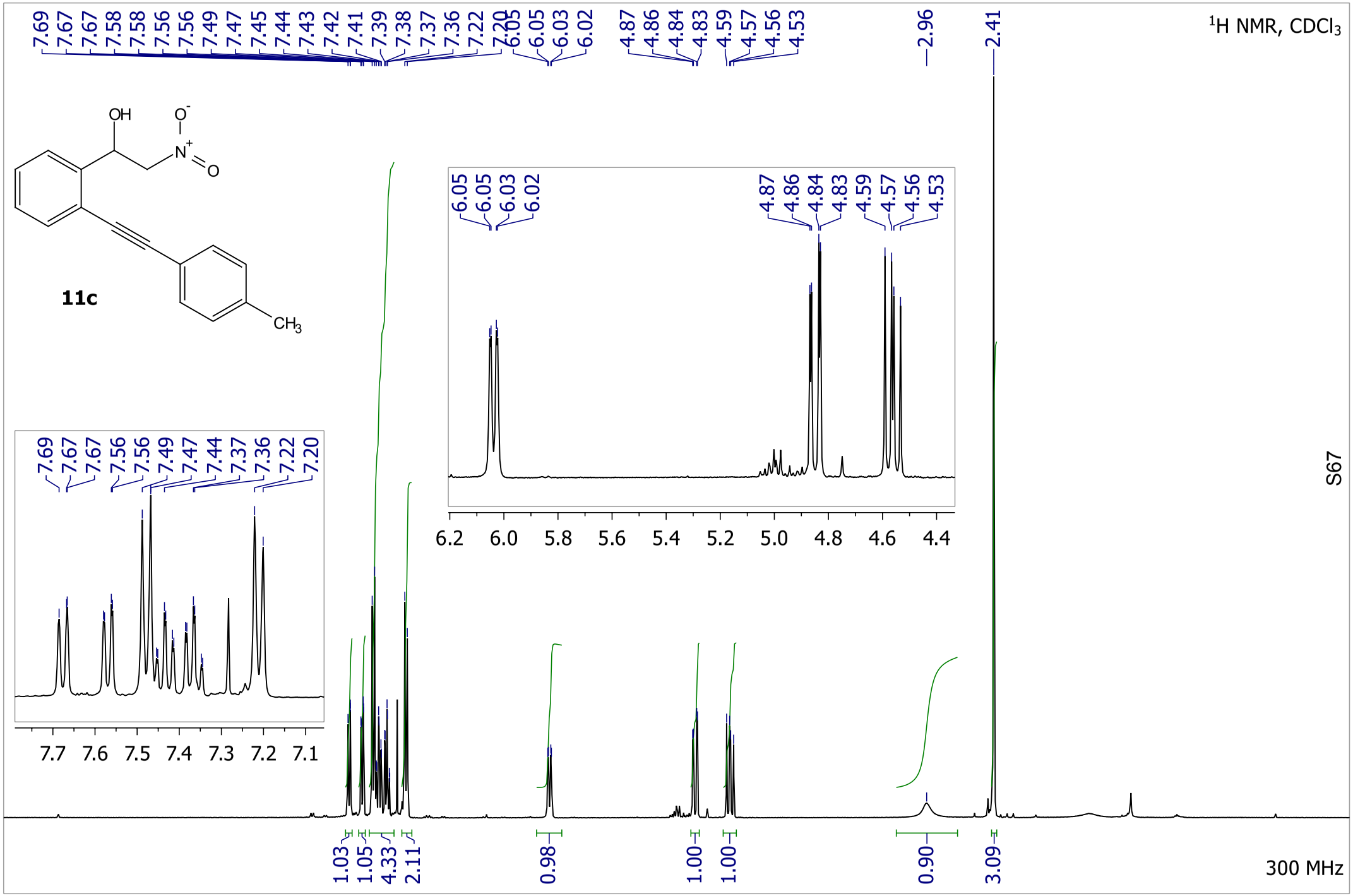

^{13}C NMR, $CDCl_3$
160.19
139.58
133.06
132.40
128.76
128.69
127.03
122.18
114.41
114.30
95.92
88.38
85.31
74.34
55.37
16.37
128.76
128.69
128.8
128.4
OH
O
N
O
CH3
CH3
O
11b
S62
75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

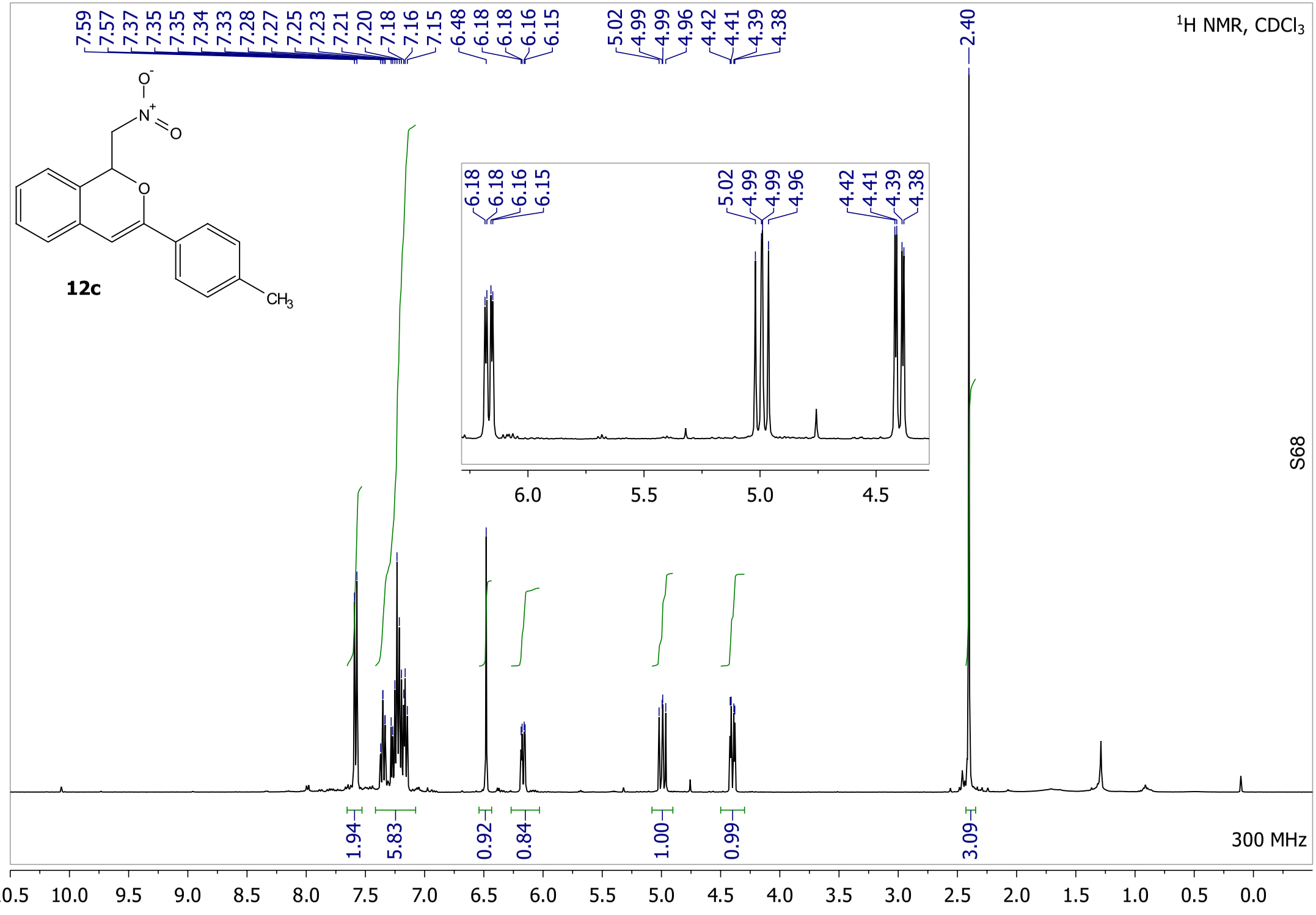

7.66 7.63 7.55 7.52 7.51 7.43 7.43 7.41 7.40 7.38 7.38 7.36 7.35 7.33 7.33 7.31 7.30 6.93 6.90 6.02 6.01 5.17 5.16 5.15 5.14 5.12 5.12 5.10 5.09 3.85 2.89 1.46 1.44
^{1}H NMR, $CDCl_3$
OH
O
N
O
CH3
11b'
O
CH3
5.17 5.16 5.15 5.14 5.12 5.12 5.10 5.09
5.20 5.15 5.10 5.05
7.66 7.63 7.55 7.52 7.51 7.41 7.40 7.38 7.38 7.36 7.35 7.33 7.33
7.7 7.6 7.5 7.4 7.3
1.04 3.11 2.09 2.15 1.00 1.01 3.21 0.88 3.13
300 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
S63

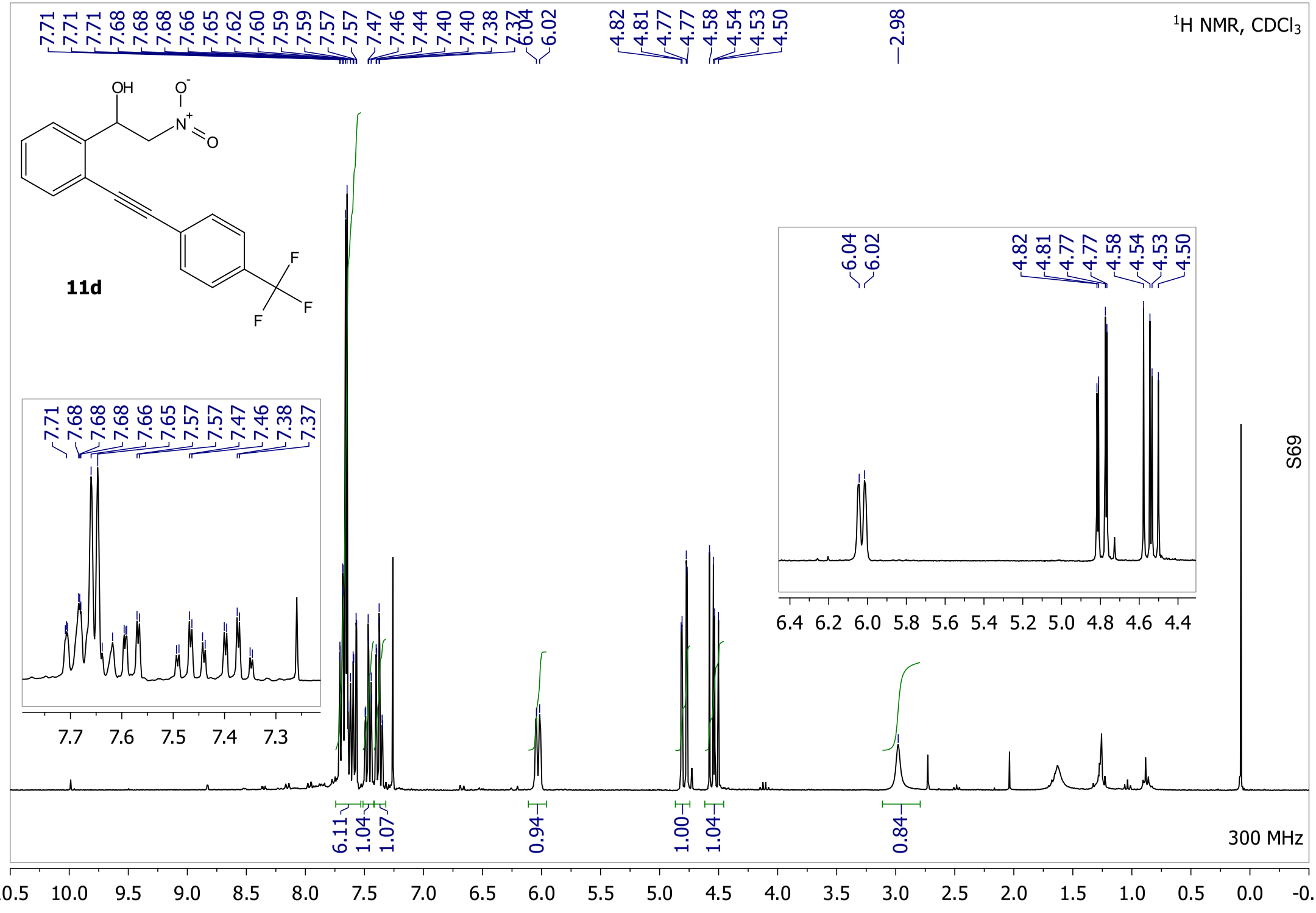

^{13}C NMR, $CDCl_3$
160.29
139.89
133.47
133.41
132.21
128.60
128.28
126.29
121.13
114.73
114.43
96.80
85.35
84.80
72.42
55.56
11.07
128.60
128.28
129.0 128.5 128.0
OH
O
N
O
CH3
CH3
O
11b'
S64
75 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

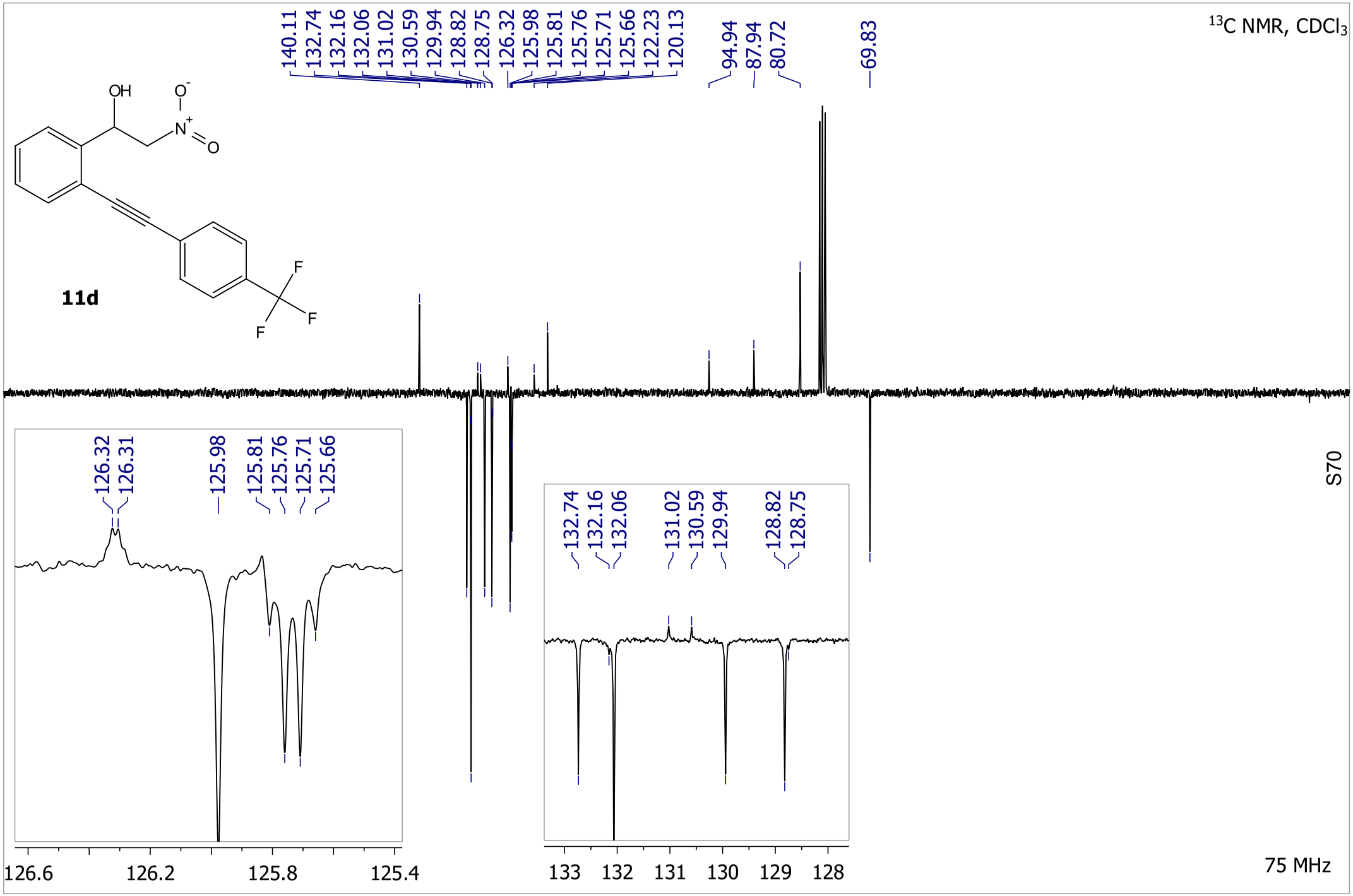

7.65 7.62 7.58 7.56 7.55 7.34 7.34 7.26 7.26 7.21 7.21 7.16 7.14 6.94 6.92 6.92 6.91 6.90 6.89 6.89 6.30 5.91 5.89 5.70 5.66 5.11 5.09 5.08 5.06 4.95 4.93 4.93 3.84 3.83 1.67 1.65 1.40 1.38
^{1}H NMR, $CDCl_3$
12b + 12b'
5.14 5.11 5.10 5.09 5.09 5.08 5.07 5.06 5.04 4.97 4.95 4.93 4.93 4.91
5.15 5.10 5.05 5.00 4.95 4.90
5.91 5.89 5.70 5.66
5.9 5.8 5.7 5.6
0.90 2.39 6.94 3.29 1.05 0.37 0.34 1.00 0.99 0.34 5.21 1.61 3.66
300 MHz
S65
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

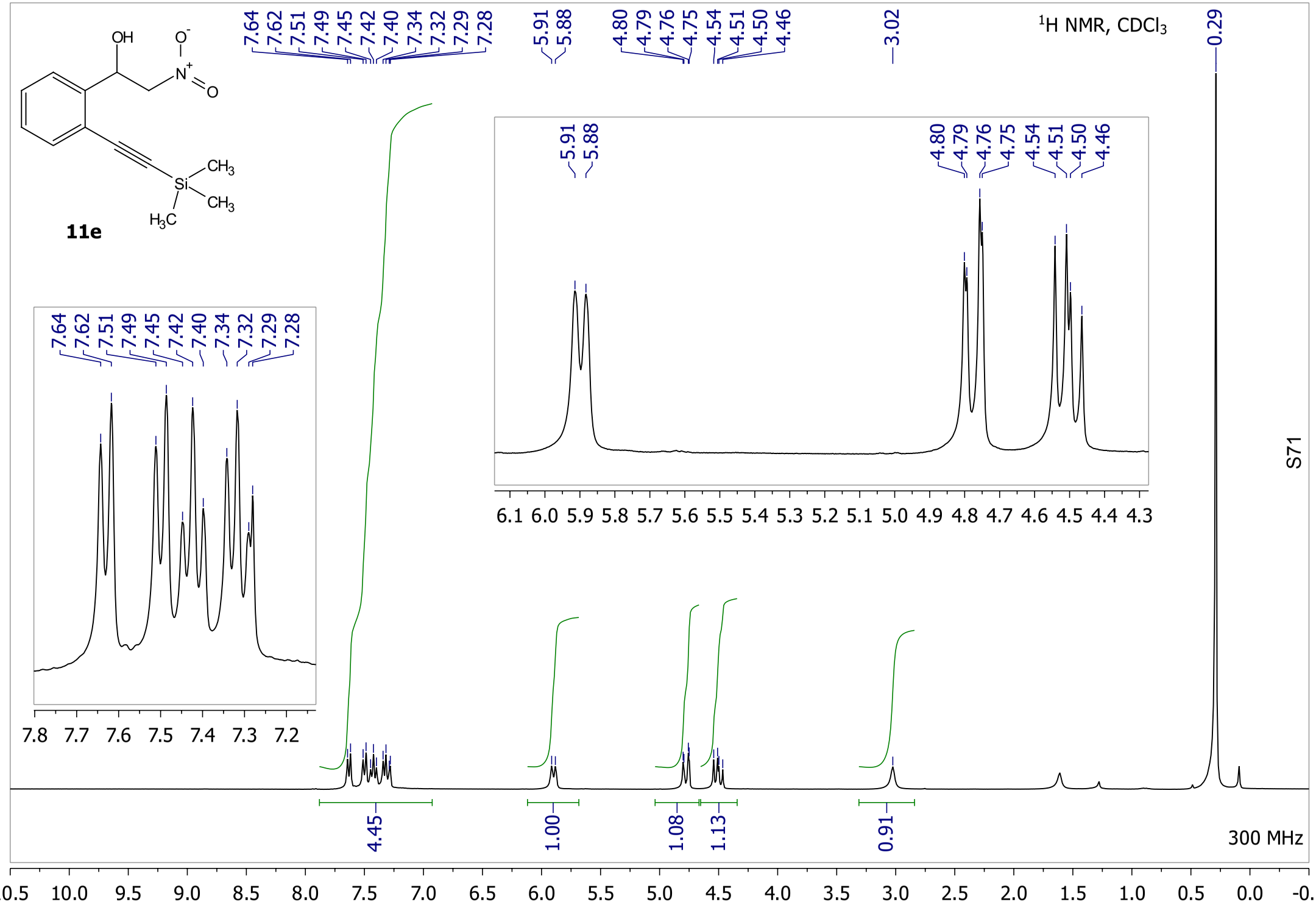

^{13}C NMR, $CDCl_3$
75 MHz
160.89
160.77
151.35
151.00
129.83
127.05
126.89
126.57
126.35
125.01
124.42
114.19
114.09
98.69
98.58
85.67
82.33
79.53
78.79
55.56
55.54
16.22
13.94
161.0 160.5
151.5 150.5
55.8 55.4
131.43
131.08
129.83
129.53
127.05
126.89
126.57
126.51
126.35
126.08
125.68
125.01
124.53
124.48
124.42
S66
132 131 130 129 128 127 126 125 124
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
12b + 12b'

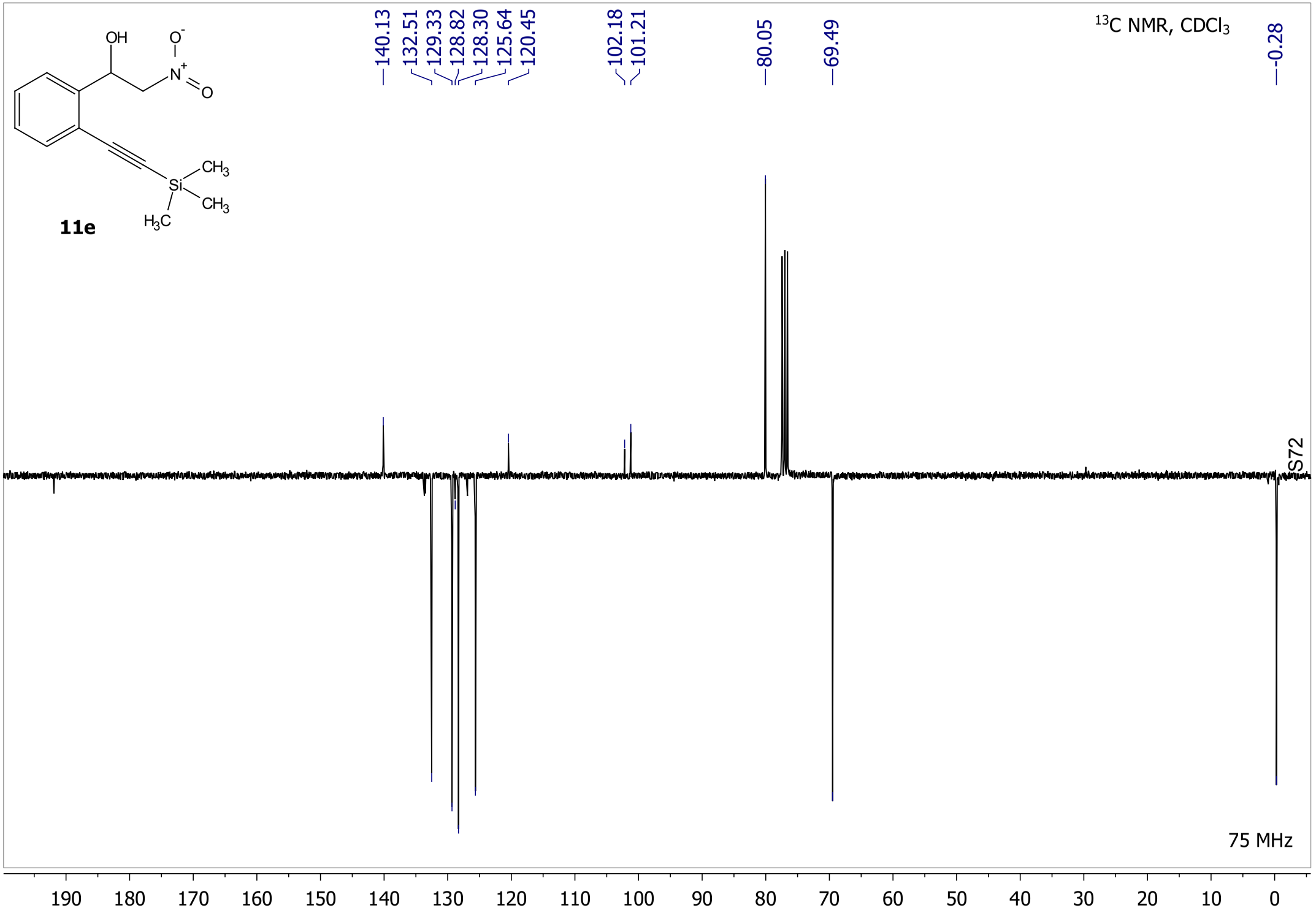

^{1}H NMR, $CDCl_3$
7.69 7.67 7.67 7.58 7.58 7.56 7.56 7.49 7.47 7.45 7.44 7.43 7.42 7.41 7.39 7.38 7.37 7.36 7.22 7.20 6.05 6.05 6.03 6.02 4.87 4.86 4.84 4.83 4.59 4.57 4.56 4.53 2.96 2.41
OH
O
N
O
11c
CH3
6.05 6.05 6.03 6.02 4.87 4.86 4.84 4.83 4.59 4.57 4.56 4.53
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
7.69 7.67 7.67 7.56 7.56 7.49 7.47 7.44 7.37 7.36 7.22 7.20
7.7 7.6 7.5 7.4 7.3 7.2 7.1
1.03 1.05 4.33 2.11 0.98 1.00 1.00 0.90 3.09
S67
300 MHz
.0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

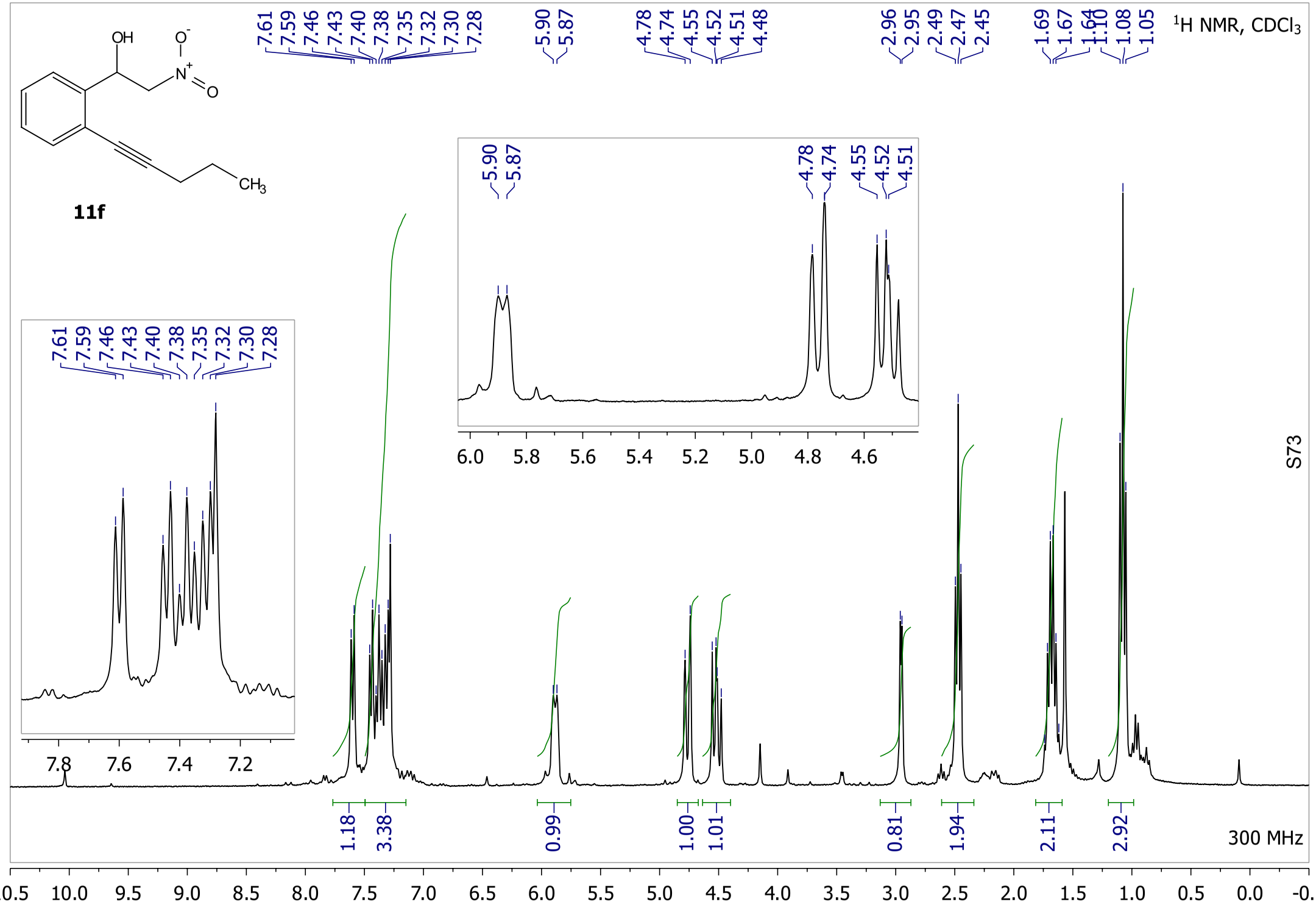

7.59
7.57
7.37
7.35
7.35
7.34
7.33
7.28
7.27
7.25
7.23
7.21
7.20
7.18
7.16
7.15
6.48
6.18
6.18
6.16
6.15
5.02
4.99
4.99
4.96
4.42
4.41
4.39
4.38
2.40
^{1}H NMR, $CDCl_3$
12c
S68
300 MHz
1.94
5.83
0.92
0.84
1.00
0.99
3.09

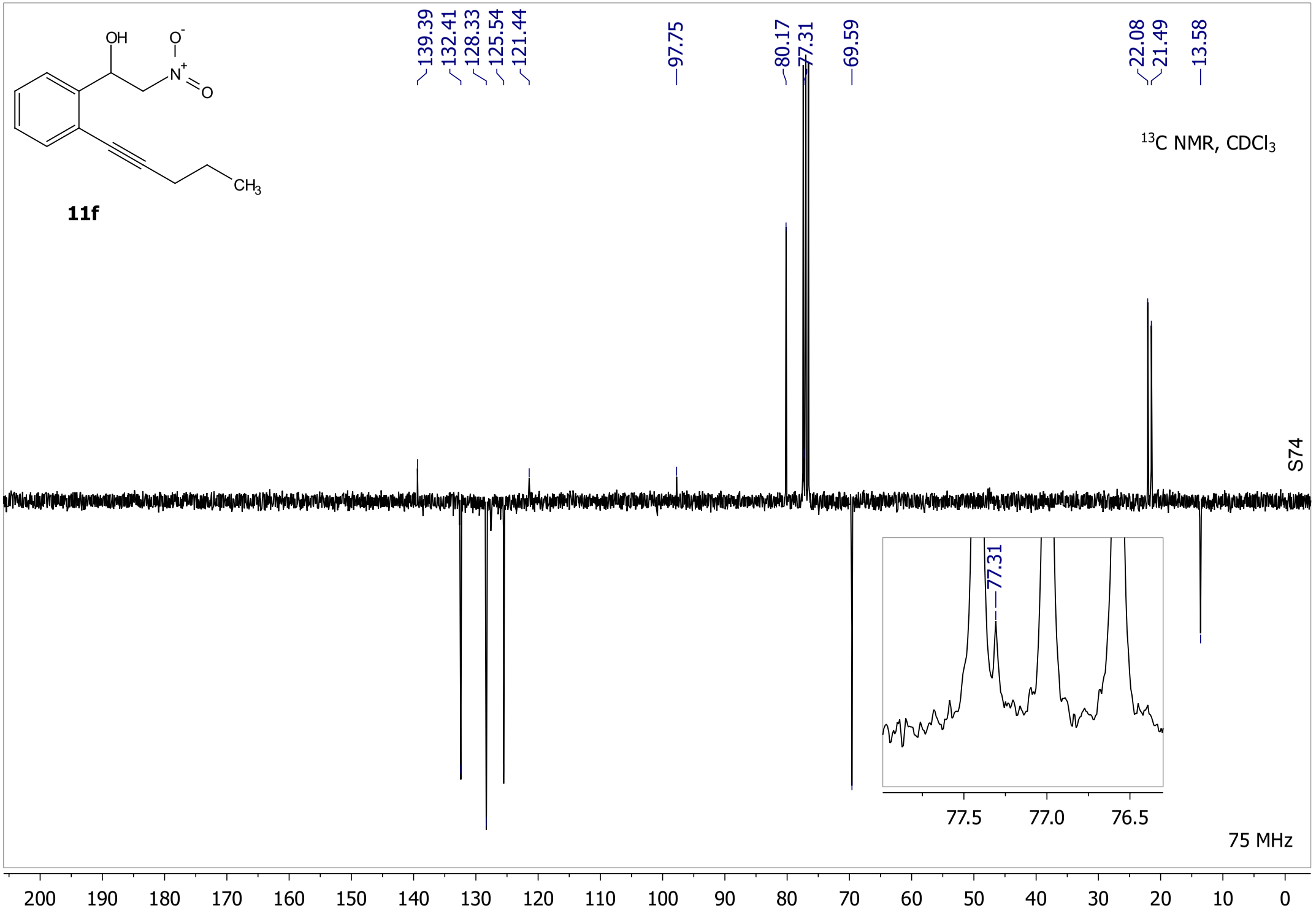

^{1}H NMR, $CDCl_3$
11d
S69
300 MHz

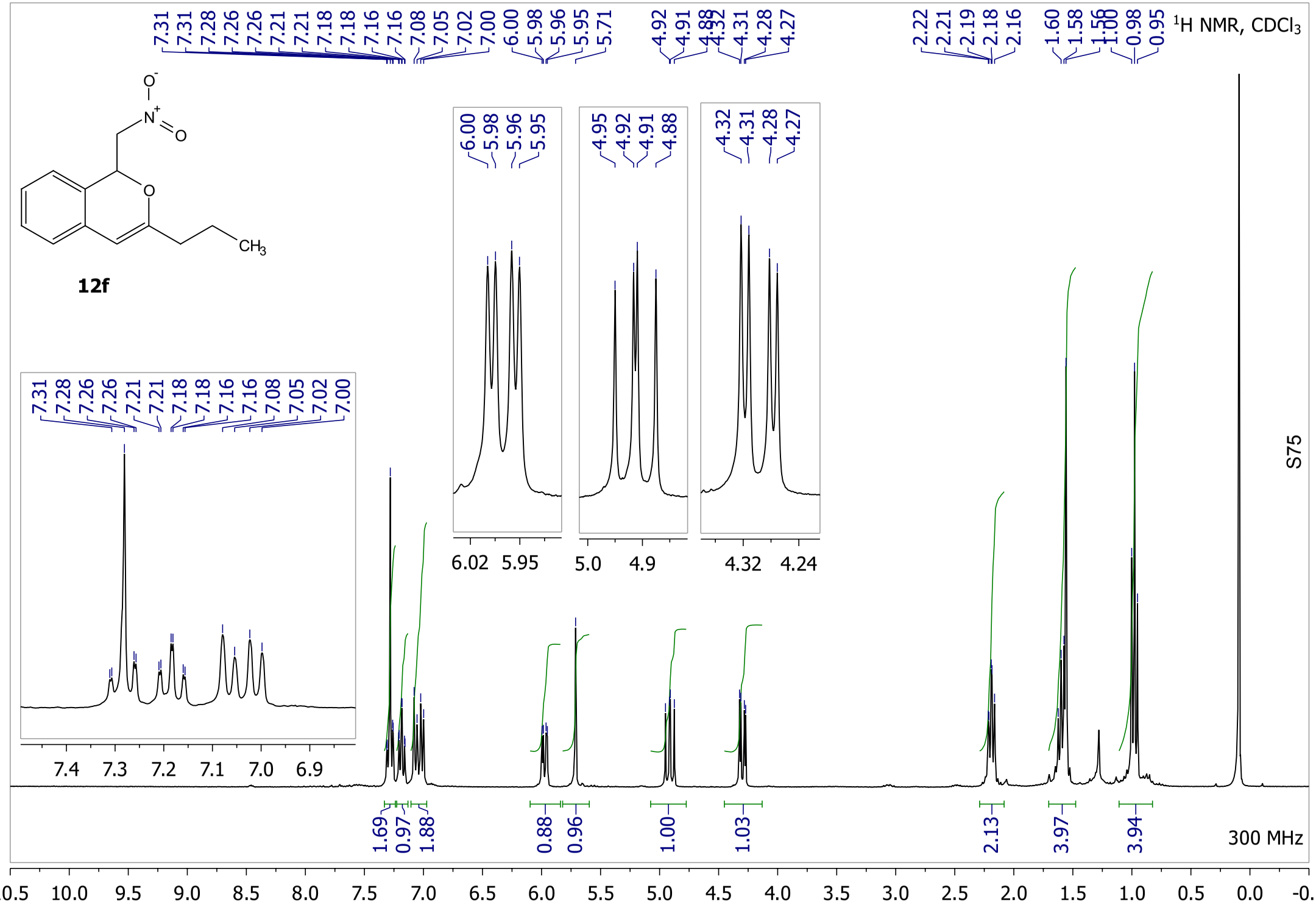

^{13}C NMR, CDCl$_3$
140.11
132.74
132.16
132.06
131.02
130.59
129.94
128.82
128.75
126.32
125.98
125.81
125.76
125.71
125.66
122.23
120.13
94.94
87.94
80.72
69.83
OH
O
N
O
F
F
F
11d
126.32
126.31
125.98
125.81
125.76
125.71
125.66
126.6
126.2
125.8
125.4
132.74
132.16
132.06
131.02
130.59
129.94
128.82
128.75
133
132
131
130
129
128
S70
75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

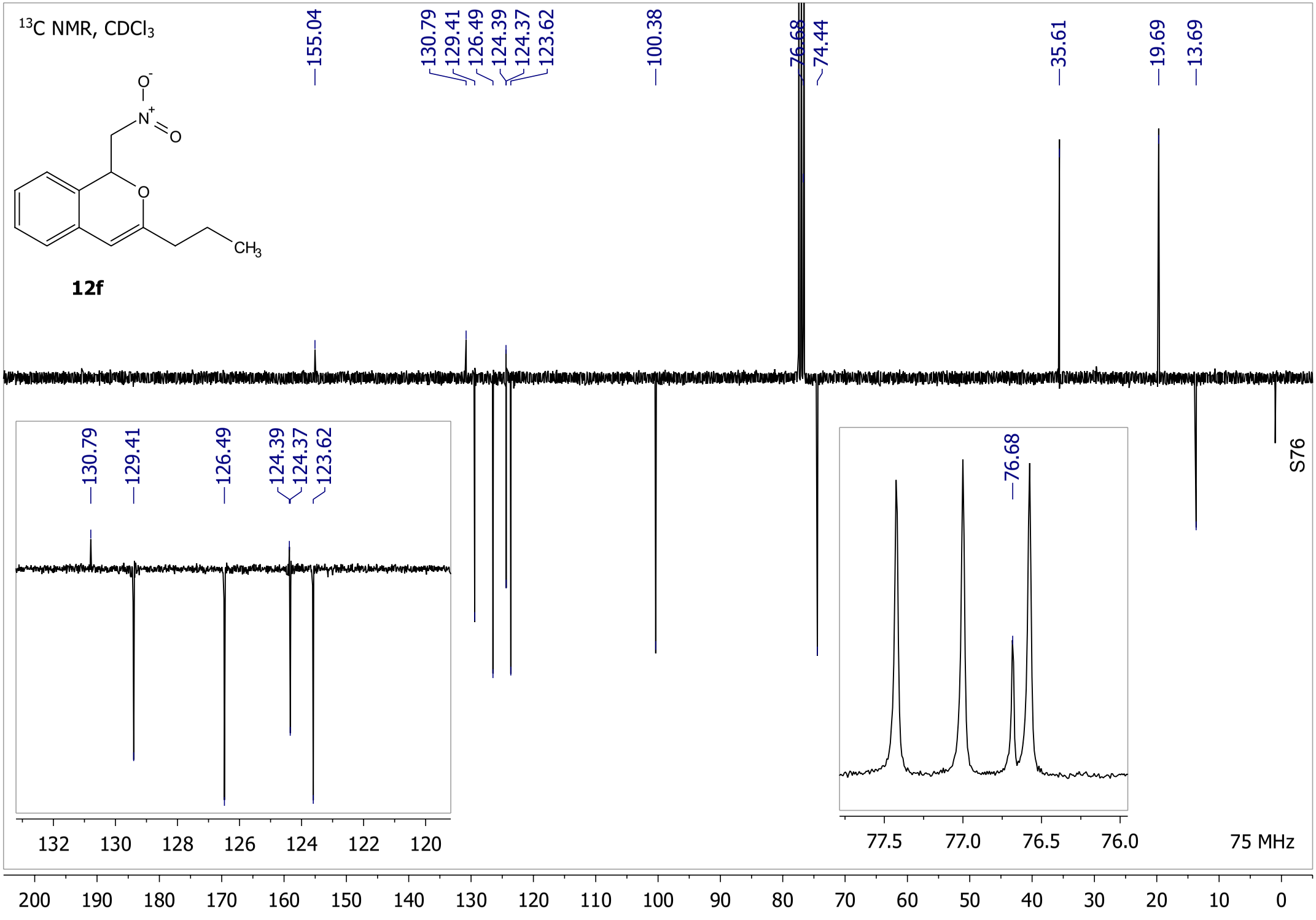

OH
O
N
O
CH3
Si
CH3
H3C
11e
7.64 7.62 7.51 7.49 7.45 7.42 7.40 7.34 7.32 7.29 7.28
5.91 5.88
4.80 4.79 4.76 4.75 4.54 4.51 4.50 4.46
3.02
0.29
1H NMR, CDCl3
S71
7.8 7.7 7.6 7.5 7.4 7.3 7.2
6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3
4.45
1.00
1.08
1.13
0.91
300 MHz
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

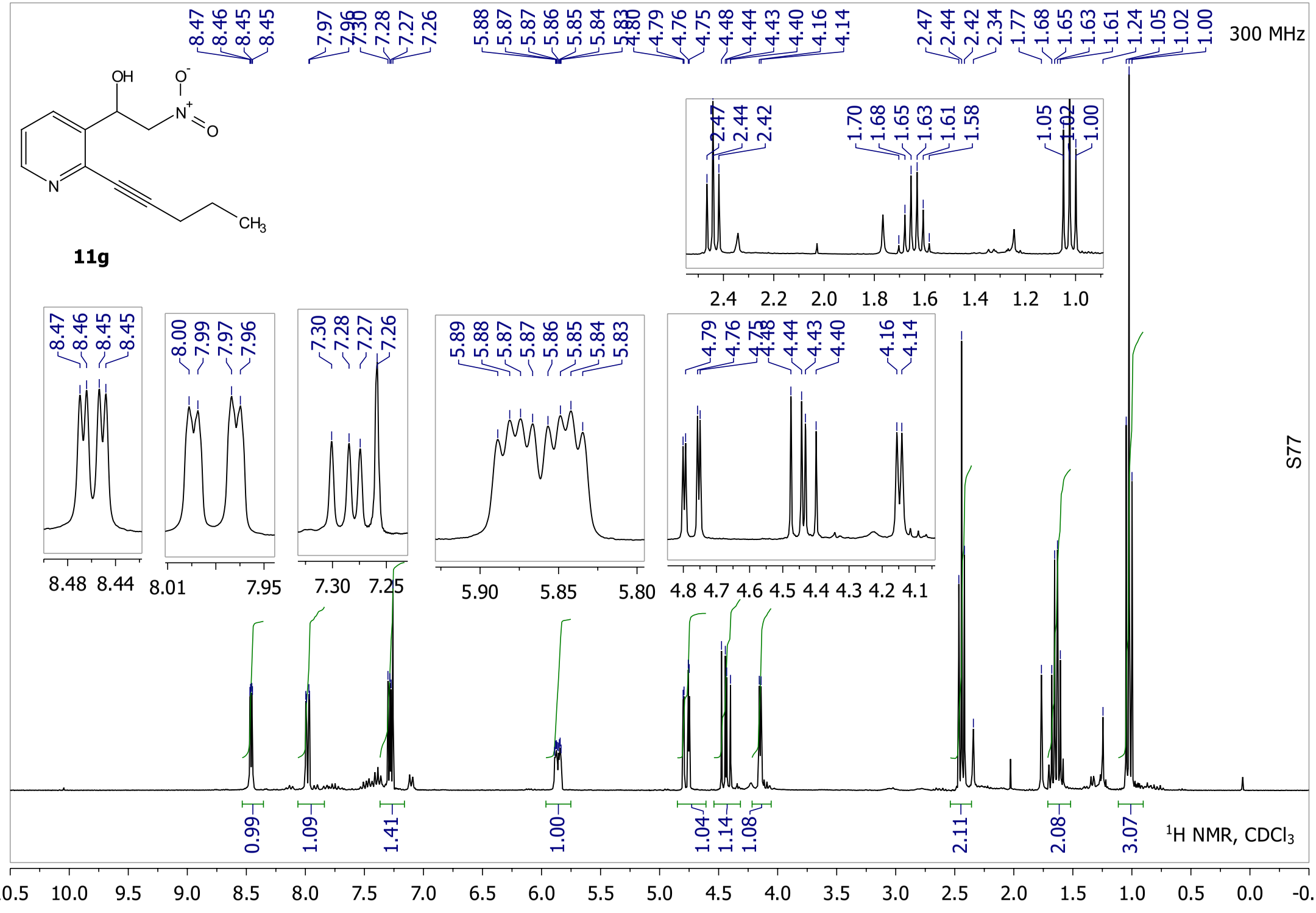

OH
O
N
O
CH3
Si
CH3
H3C
11e
140.13
132.51
129.33
128.82
128.30
125.64
120.45
102.18
101.21
80.05
69.49
-0.28
13C NMR, CDCl3
S72
75 MHz
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

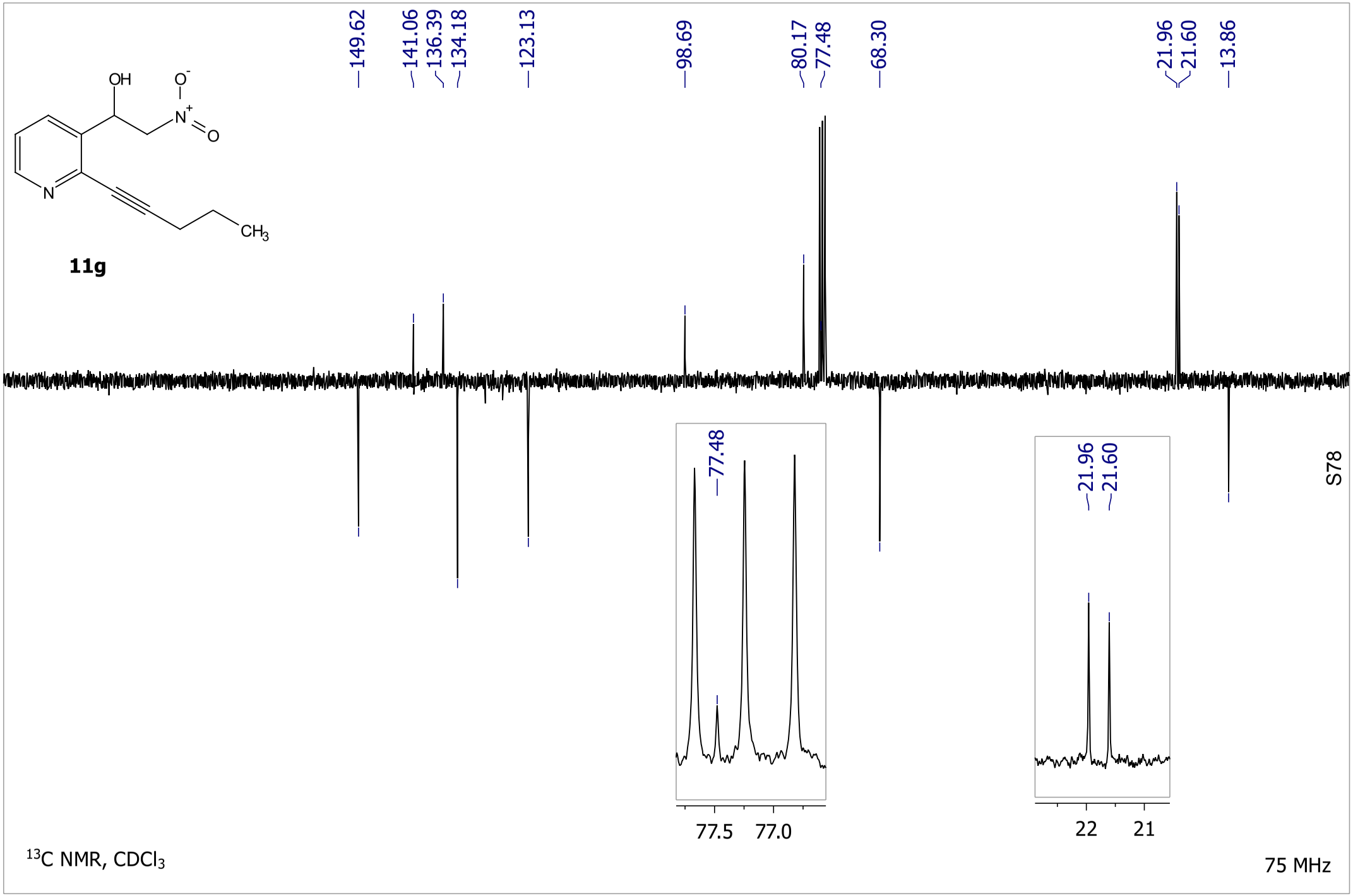

OH
O
N+
O
CH3
11f
7.61 7.59 7.46 7.43 7.40 7.38 7.35 7.32 7.30 7.28
5.90 5.87
4.78 4.74 4.55 4.52 4.51 4.48
2.96 2.95 2.49 2.47 2.45
1.69 1.67 1.64 1.10 1.08 1.05
1H NMR, CDCl3
S73
1.18 3.38 0.99 1.00 1.01 0.81 1.94 2.11 2.92
300 MHz

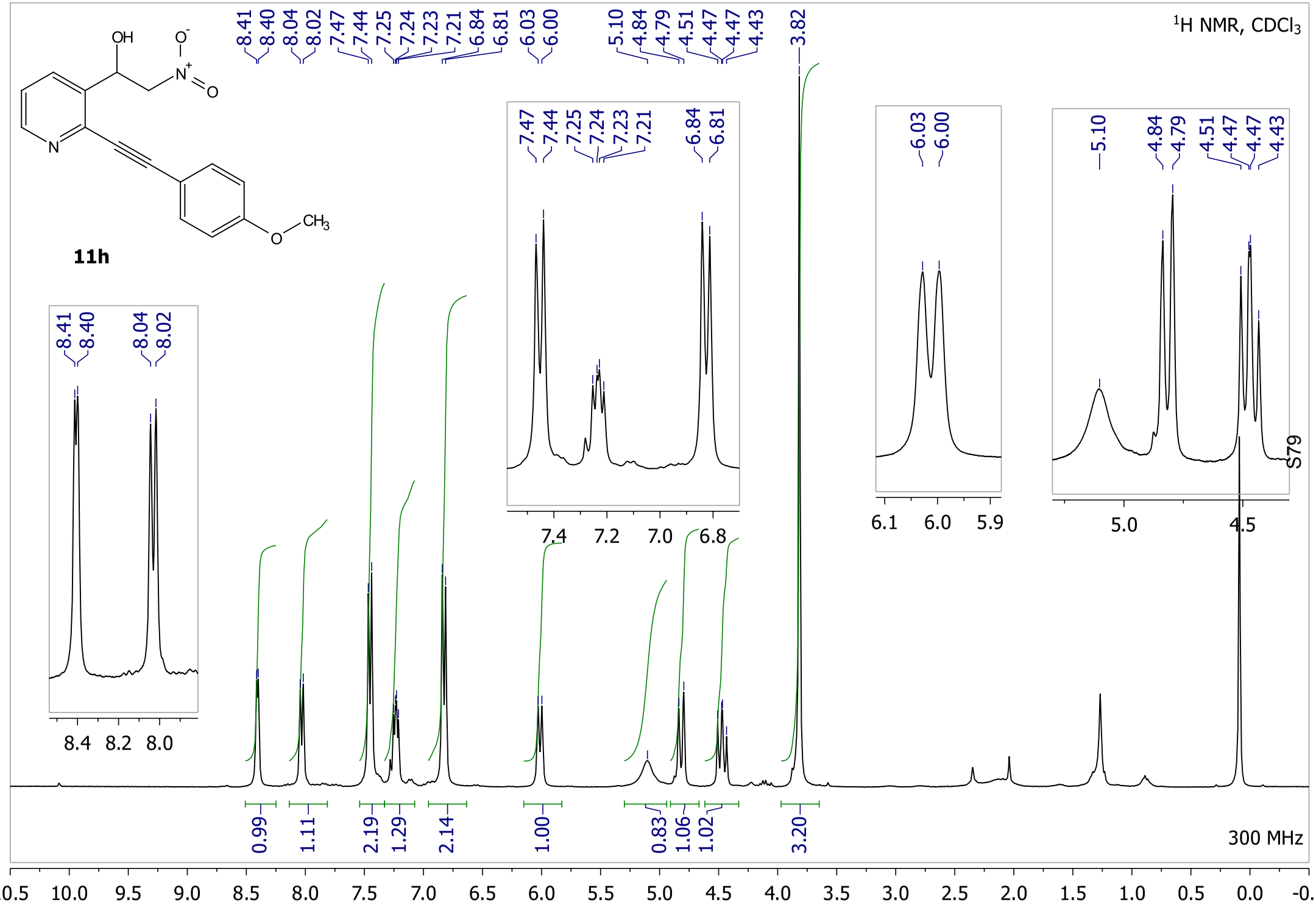

OH
O
N
O
CH3
11f
139.39
132.41
128.33
125.54
121.44
97.75
80.17
77.31
69.59
22.08
21.49
13.58
13C NMR, CDCl3
S74
77.31
77.5
77.0
76.5
75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

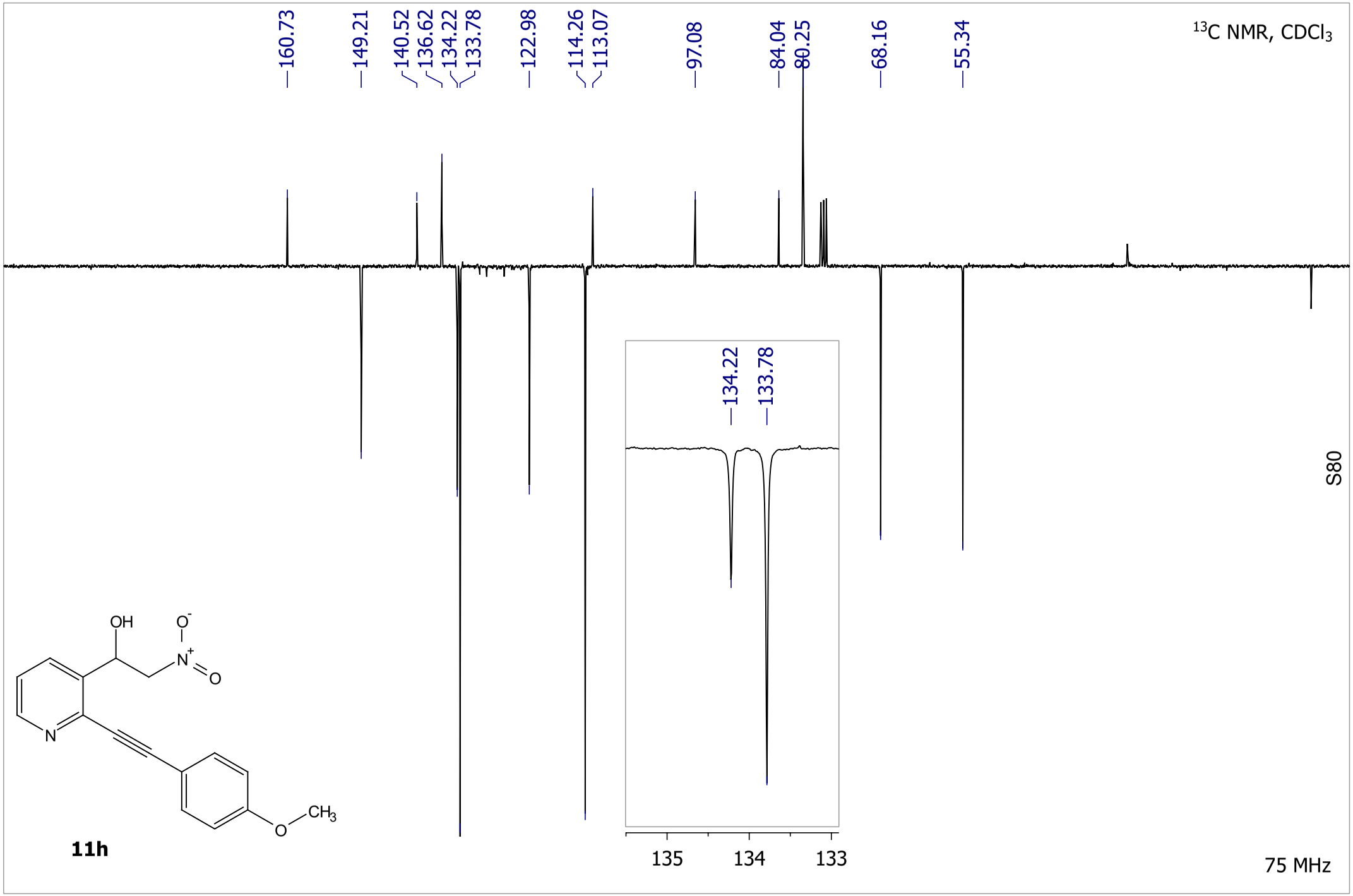

^{1}H NMR, $CDCl_3$
12f
S75
300 MHz
1.69
0.97
1.88
0.88
0.96
1.00
1.03
2.13
3.97
3.94

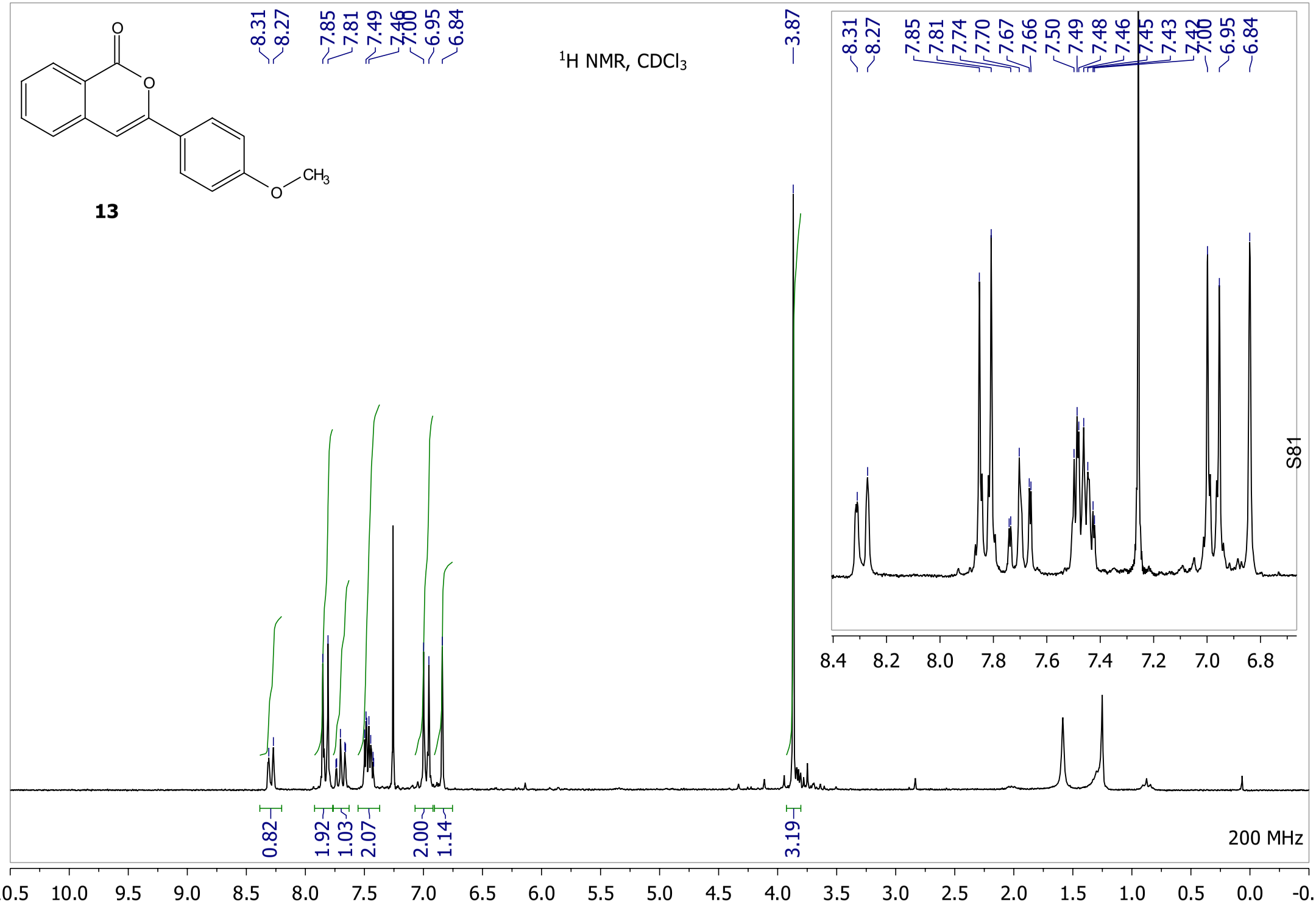

^{13}C NMR, $CDCl_3$
155.04
130.79
129.41
126.49
124.39
124.37
123.62
100.38
76.68
74.44
35.61
19.69
13.69
12f
S76
75 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
132 130 128 126 124 122 120
77.5 77.0 76.5 76.0


300 MHz
11g
S77
1H NMR, CDCl3
0.99
1.09
1.41
1.00
1.04
1.14
1.08
2.11
2.08
3.07


149.62
141.06
136.39
134.18
123.13
98.69
80.17
77.48
68.30
21.96
21.60
13.86
OH
O
N
O
N
CH3
11g
77.48
77.5
77.0
21.96
21.60
22
21
S78
13C NMR, CDCl3
75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


^{1}H NMR, $CDCl_3$
OH
O
N
O
N
O
CH_3
11h
8.41 8.40 8.04 8.02 7.47 7.44 7.25 7.24 7.23 7.21 6.84 6.81 6.03 6.00 5.10 4.84 4.79 4.51 4.47 4.47 4.43 3.82
8.4 8.2 8.0
7.4 7.2 7.0 6.8
6.1 6.0 5.9
5.0 4.5
0.99 1.11 2.19 1.29 2.14 1.00 0.83 1.06 1.02 3.20
300 MHz
S79


160.73
149.21
140.52
136.62
134.22
133.78
122.98
114.26
113.07
97.08
84.04
80.25
68.16
55.34
^{13}C NMR, $CDCl_3$
134.22
133.78
135
134
133
OH
O
N
O
N
O
CH_3
11h
S80
75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


13
^{1}H NMR, $CDCl_3$
8.31
8.27
7.85
7.81
7.49
7.46
7.00
6.95
6.84
3.87
0.82
1.92
1.03
2.07
2.00
1.14
3.19
200 MHz
S81