# Supporting Information

## Tetramate Derivatives by Chemoselective Dieckmann Ring Closure of *allo*-Phenylserines, and their Antibacterial Activity

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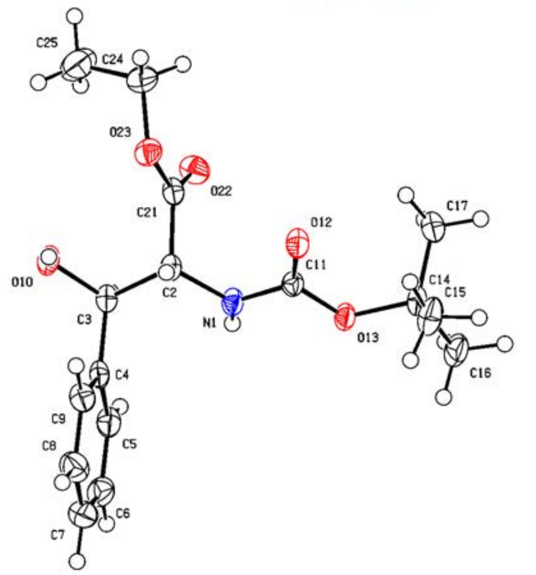
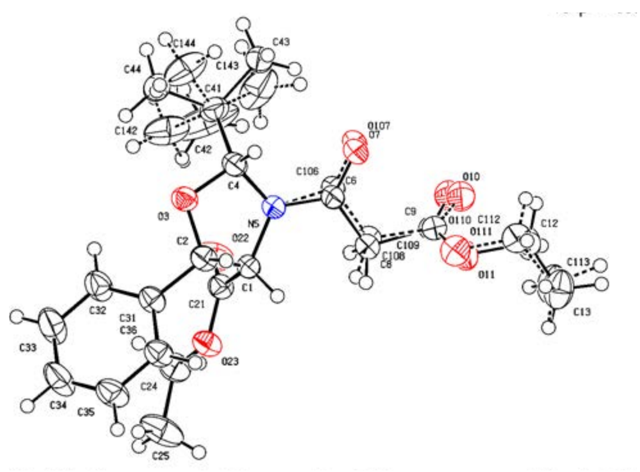


**9a**



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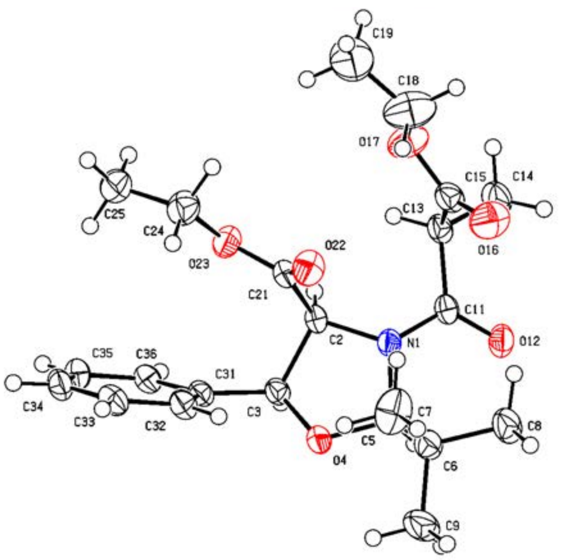

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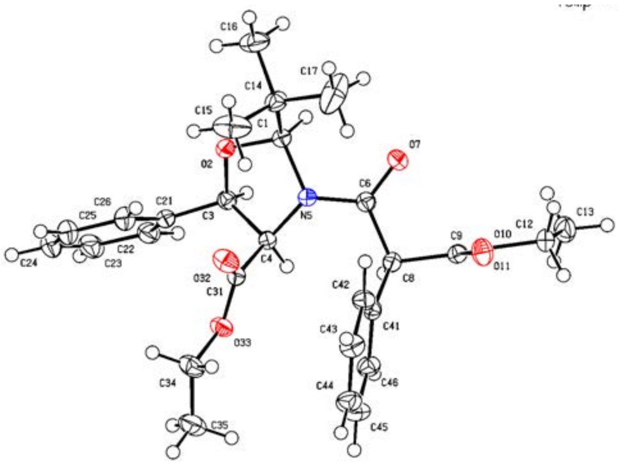

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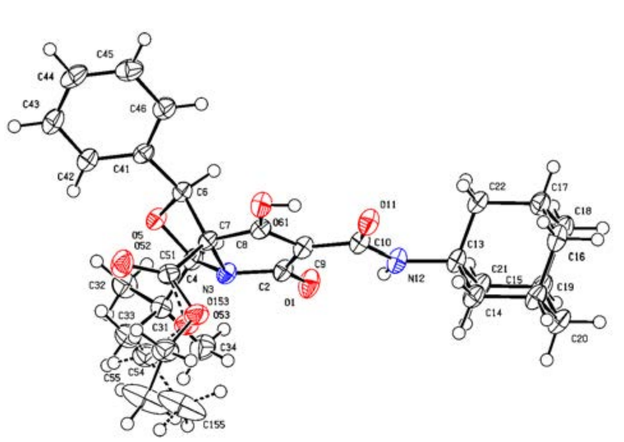
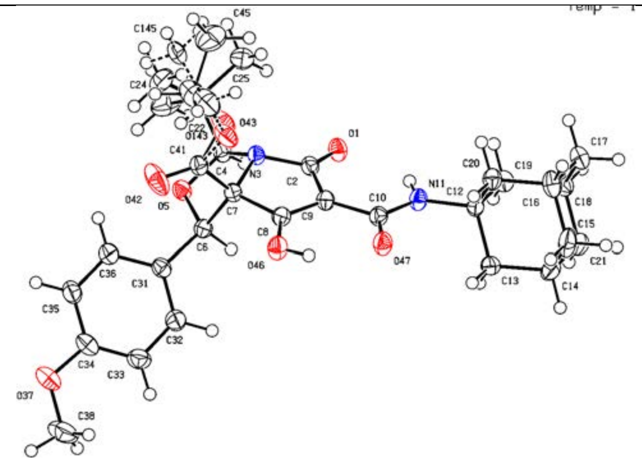


**23a**



**23d**

**Figure S1:** Single-crystal X-ray structure of compounds **9a, 11a, 13a, 13b, 23a, 23d**.

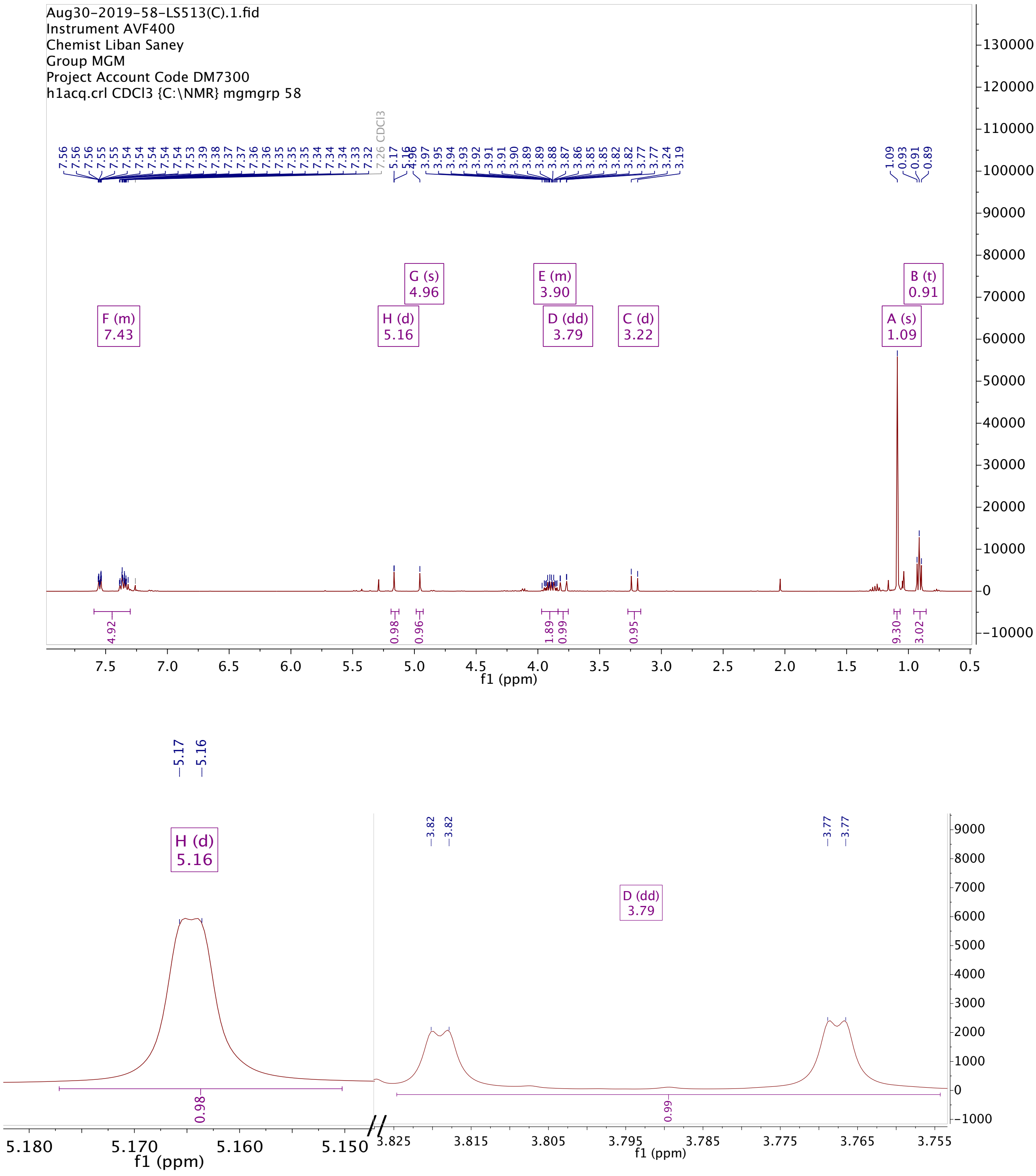
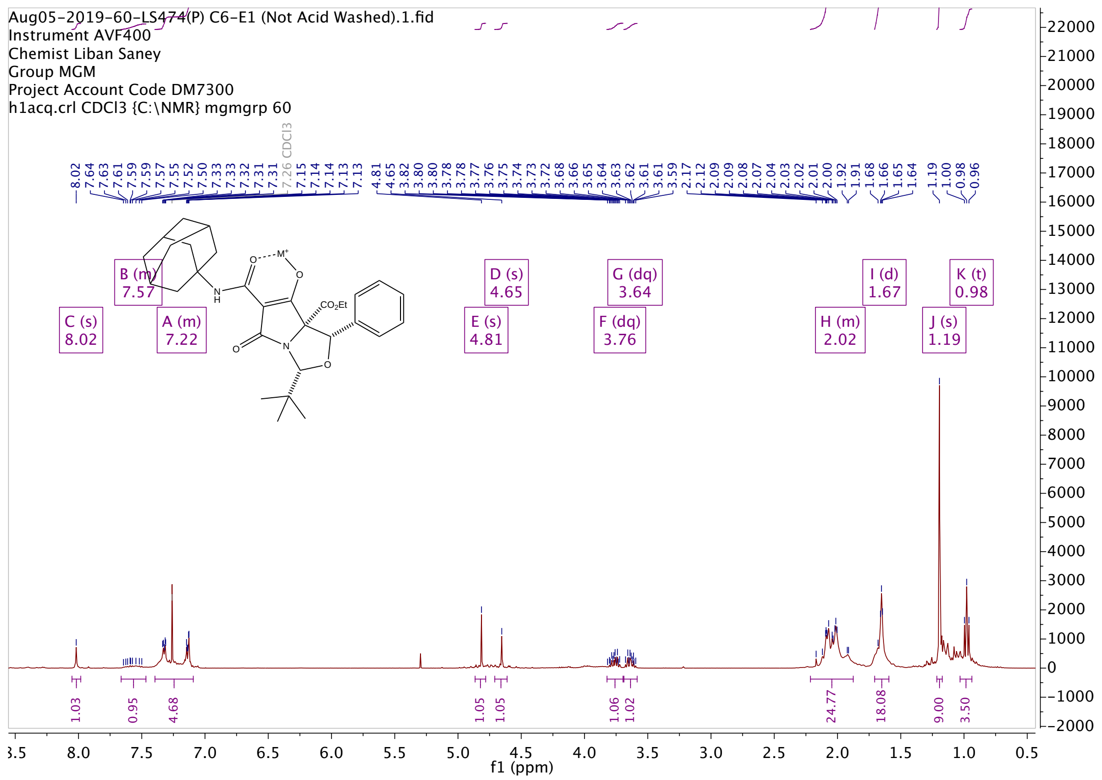



**Figure S2:** $^1$H-NMR spectrum of tetramate **14a**, showing the relative purity of the crude material and the long-range coupling observed between the H2 and H7-protons, with a weak coupling constant of 0.8 Hz observed between these two peaks; $CDCl_3$ solvent, 400 MHz.

**(a)**




**(b)**

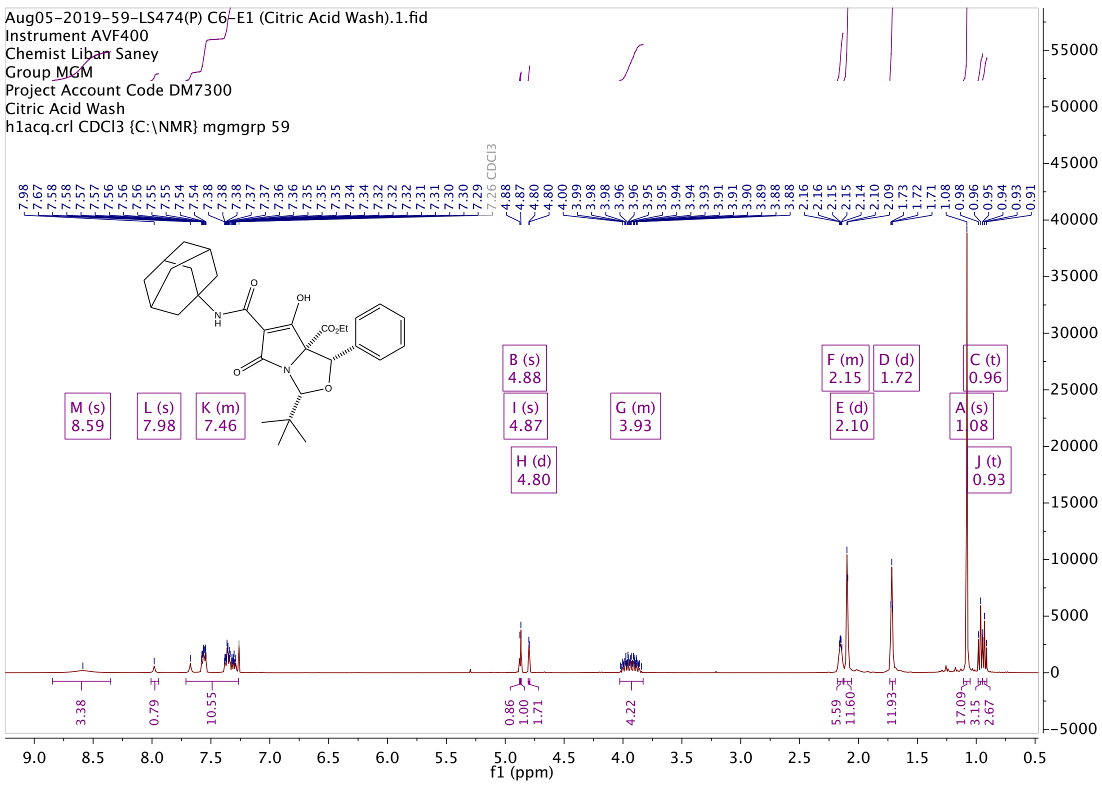



**Figure S3:** $^1$H-NMR spectrum of C7-carboxamide **23a** post-chromatographic purification, before **(a)** acid wash and **(b)** after 10% citric acid (aq.) wash; $CDCl_3$ solution, 400 MHz.

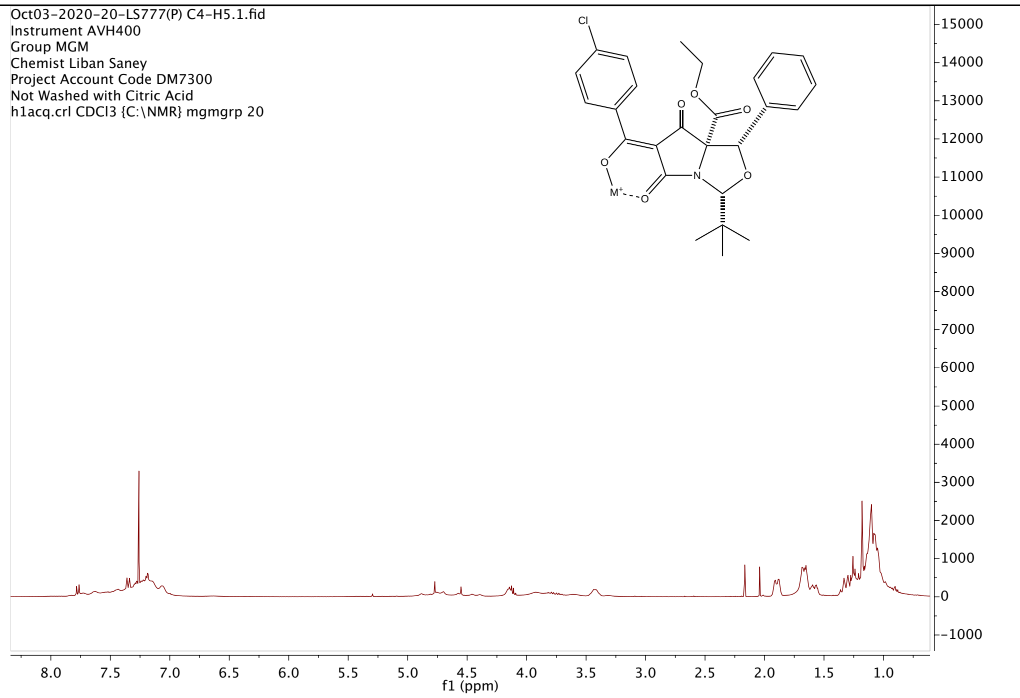
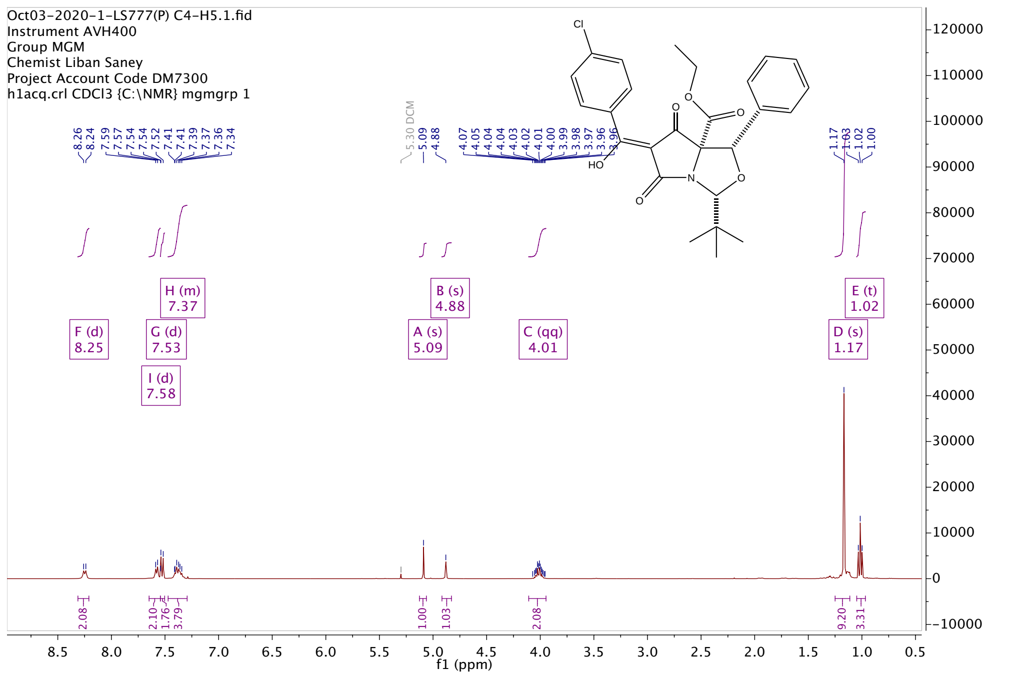
| | |
|---|---|
| **(a)** |  |
| **(b)** |  |



**Figure S4:** $^1$H-NMR spectrum of C7-acyltetramate **25d** post-chromatographic purification, before **(a)** acid wash and **(b)** after 10% citric acid (aq.) wash; [a] $CDCl_3$ solution, 400 MHz.

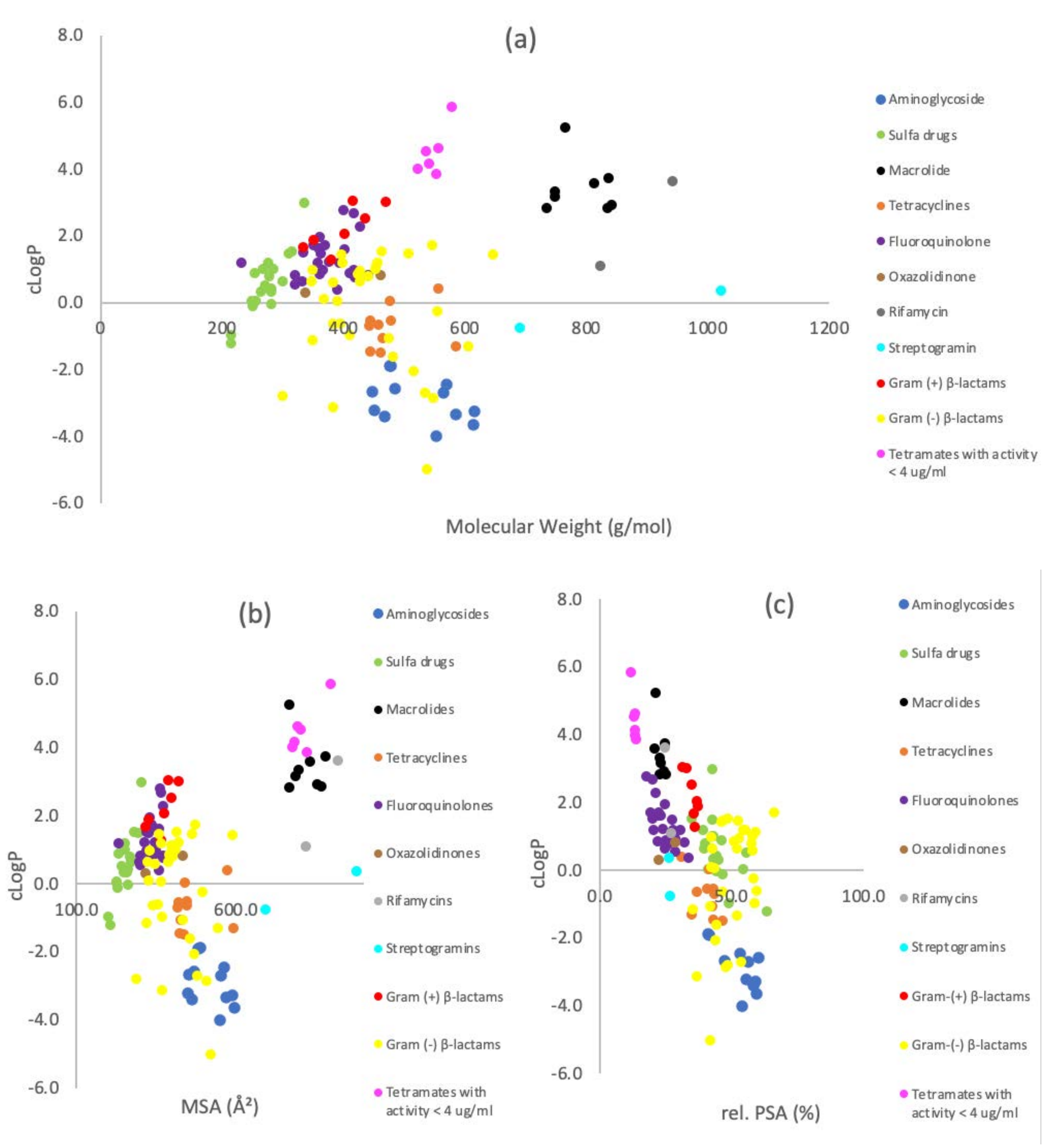



**Figure S5:** Chemical property space of bicyclic tetramates in comparison to known antibiotics. **(a)** cLogP plotted against $M_w$; **(b)** cLogP plotted against MSA and **(c)** cLogP plotted against rel. PSA; cLogP, MSA and PSA for tetramates were calculated using Marvin (19.9.0), 2019, ChemAxon. The remaining data was collected from *J. Med. Chem.*, 2008, **51**, 2871-2878.

| Compound | $\delta_{keto}$ (ppm) | $\delta_{enol}$ (ppm) | Ratio between keto:enol [a] | Yield (%) |
|---|---|---|---|---|
| **5b** | 1.26 (3H, t, *J*=7.1 Hz), 2.42 (3H, s), 3.97 (2H, s), 4.22 (2H, q, *J*=7.2 Hz), 7.28 (2H, d, *J*=8.1 Hz), 7.85 (2H, d, *J*=8.3 Hz) | 1.34 (3H, t, *J*=7.1 Hz), 2.39 (3H, s), 4.27 (2H, m), 5.64 (1H, s), 7.28-8.00 (4H, m), 12.59 (1H, s) | 5.5:1 | Quant. |
| **5c** | 0.94 (3H, m), 1.26 (3H, t, *J*=7.1 Hz), 1.36 (2H, m), 1.62 (2H, m), 2.67 (2H, m), 3.97 (2H, s), 4.22 (2H, q, *J*=7.1 Hz), 7.28 (2H, d, *J*=8.3 Hz), 7.86 (2H, d, *J*=8.3 Hz) | 0.94 (3H, m), 1.26-1.42 (5H, m), 1.62 (2H, m), 2.67 (2H, m), 4.28 (2H, m), 5.64 (1H, s), 7.23-8.04 (4H, m), 12.58 (1H, s) | 2.8:1 | Quant. |
| **5d** | 1.24 (3H, t, *J*=7.1 Hz), 3.86 (3H, s), 3.93 (2H, s), 4.19 (2H, q, *J*=7.1 Hz) 6.93 (2H, d, *J*=8.9 Hz), 7.91 (2H, d, *J*=8.9 Hz) | 1.31 (3H, t, *J*=7.1 Hz), 3.86 (3H, s), 4.25 (2H, m), 5.56 (1H, s), 6.93-8.05 (4H, m), 12.62 (1H, s) | 13:1 | Quant. |
| **5e** | 1.24 (3H, t, *J*=7.1 Hz), 3.95 (2H, s), 4.20 (2H, q, *J*=7.1 Hz), 7.14 (2H, app t, *J*=8.9 Hz), 7.97 (2H, dd, *J*=5.3 Hz, 8.9 Hz) | 1.32 (3H, t, *J*=7.1 Hz), 4.26 (2H, m), 5.59 (1H, s), 7.06-8.10 (4H, m), 12.60 (1H, s) | 4.9:1 | Quant. |
| **5f** | 1.18 (3H, t, *J*=7.1 Hz), 3.88 (2H, s), 4.13 (2H, q, *J*=7.1 Hz), 7.38 (2H, d, *J*=8.6 Hz), 7.81 (2H, d, *J*=8.7 Hz) | 1.26 (3H, t, *J*=7.1 Hz), 4.19 (2H, m), 5.56 (1H, s), 7.31-7.81 (4H, m), 12.50 (1H, s) | 3.2:1 | Quant. |
| **5g** | 1.25 (3H, t, *J*=7.1 Hz), 3.95 (2H, s), 4.20 (2H, q, *J*=7.1 Hz), 7.62 (2H, d, *J*=8.6 Hz), 7.80 (2H, d, *J*=8.6 Hz) | 1.33 (3H, t, *J*=7.1 Hz), 4.26 (2H, m), 5.63 (1H, s), 7.53-7.81 (4H, m), 12.55 (1H, s) | 2.7:1 | 91 |

**Table S1:** $^{1}$H-NMR data and yields of keto-enol tautomeric mixtures of $\beta$-oxoesters **5b-g**; $CDCl_3$ solvent, 400 MHz; [a] Determined from $^{1}$H-NMR studies of the crude material.

| Compound | $R^1$ | $\delta_{keto}$ C2 (ppm) [a] | Compound | Major isomer $\delta$ C2 (ppm) [a] | *E/Z* ratio of isomers [a] | Yield (%) |
|---|---|---|---|---|---|---|
| **5a** | H | 46.1 | **6a** | 149.6 | 21:1 | 71 |
| **5b** | Me | 46.1 | **6b** | 149.8 | 17:1 | 73 |
| **5c** | Bu | 46.1 | **6c** | 149.4 | 3.8:1 | 83 |
| **5d** | OMe | 45.9 | **6d** | 150.0 | 5.7:1 | 93 |
| **5e** | F | 46.1 | **6e** | 149.5 | 3.6:1 | 73 |
| **5f** | Cl | 46.1 | **6f** | 149.4 | 3:1 | 78 |
| **5g** | Br | 46.1 | **6g** | 149.4 | 3.5:1 | 86 |

**Table S2*:*** $^{13}$C-NMR data of **5a-g** and **6a-g** at the C2-position, *E/Z* isomeric ratio and yields of oximes **6a-g**; $CDCl_3$ solvent, 400 MHz; [a] Determined from $^1$H-NMR studies of the crude material.

| Compound | $R^1$ | $\delta$ H2 (ppm) | $\delta$ H3 (ppm) | $J_{H2\text{-}H3}$ (Hz) | Yield (%) |
|---|---|---|---|---|---|
| **7a** [a] | H | 4.44 | 5.36 | 4.2 | 75 |
| **7b** [a] | Me | 4.46 | 5.38 | 4.2 | 27 |
| **7c** [b] | Bu | 4.31 | 5.27 | 3.8 | 72 |
| **7d** [a] | OMe | 4.46 | 5.37 | 4.3 | 67 |
| **7e** [a] | F | 4.50 | 5.43 | 4.1 | 66 |
| **7f** [a] | Cl | 4.51 | 5.42 | 4.0 | 45 |

**Table S3:** Key chemical shifts ($\delta$), coupling constants ($J$) and yields of *allo*-$\beta$-arylserines **7a-f**; [a] $D_2O$ solvent, 400 MHz; [b] $CD_3OD$ solvent, 400 MHz.

| Compound | $\delta$ H4 (ppm) | $\delta$ H5 (ppm) | $J_{H4\text{-}H5}$ (Hz) |
|---|---|---|---|
| **8** [a] | 5.83 | 4.66 | 9.1 |
| Literature data for *threo*-derived oxazolidinone [b] | 5.62 | 4.25 | 5.0 |
| Literature data for *erythro*-derived oxazolidinone [b] | 5.80 | 4.64 | 9.1 |

**Table S4:** Comparison of literature $^1$H-NMR data[1] for oxazolidinone **8**; [a] $CDCl_3$ solvent, 400 MHz; [b] $CDCl_3$ solvent, 300 MHz.

| Compound | 2,5-*cis* oxazolidine | | | | 2,5-*trans* oxazolidine | | | | dr at the C2-position [a] | Yield (%) [b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | δ H2 (ppm) | δ H4 (ppm) | δ H5 (ppm) | $J_{H4-H5}$ (Hz) | δ H2 (ppm) | δ H4 (ppm) | δ H5 (ppm) | $J_{H4-H5}$ (Hz) | | |
| **10a** | 4.15 | 4.98 | 4.09 | 9.0 | 4.94 | 5.23 | 4.22 | 7.4 | 5.6:1 | 81 |
| **10b** | 4.20 | 5.02 | 4.13 | 9.0 | 4.99 | 5.26 | 4.26 | 7.3 | 3.7:1 | 97 |
| **10c** | 4.21 | 5.04 | 4.17 | 9.0 | 4.99 | 5.26 | 4.27 | 7.4 | 5.3:1 | 90 |
| **10d** | 4.19 | 5.02 | 4.13 | 9.0 | 4.99 | 5.26 | 4.25 | 7.3 | 3.9:1 | 97 |
| **10e** | 4.13 | 4.97 | 4.07 | 9.0 | 4.92 | 5.20 | 4.21 | 7.3 | 4.8:1 | 89 |
| **10f** | 4.21 | 5.03 | 4.16 | 9.1 | 4.99 | 5.26 | 4.29 | 7.3 | 5.6:1 | 74 |

**Table S5:** Key chemical shifts (δ), coupling constants (*J*), diastereomeric ratio (dr) and yields of oxazolidines **10a-f**; $CDCl_3$ solvent, 400 MHz; [a] Determined from $^1$H-NMR studies of the crude material; [b] Yields include both diastereomers.

| Compound | $R^1$ | δ (ppm) | | | $J_{H4-H5}$ (Hz) | dr at the C2-position [a] | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | H2 | H4 | H5 | | | |
| **11a** | *p*-H | 5.37 | 5.21 | 4.80 | 6.9 | 11.5:1 | 80 |
| **11b** | *p*-Me | 5.36 | 5.18 | 4.77 | 6.9 | 9:1 | Quant. [b] |
| **11c** | *p*-Bu | 5.37 | 5.19 | 4.77 | 6.9 | 9:1 | 60 |
| **11d** | *p*-OMe | 5.36 | 5.17 | 4.75 | 6.9 | 9:1 | Quant. [b] |
| **11e** | *p*-F | 5.36 | 5.18 | 4.79 | 6.8 | 9:1 | 37 |
| **11f** | *p*-Cl | 5.37 | 5.17 | 4.81 | 6.8 | 9:1 | 76 |

**Table S6:** Key chemical shifts (δ) and coupling constants (*J*) of the major malonamide diastereomer including the diastereomeric ratio (dr) and yields of malonamides **11a-f**; $CDCl_3$ solvent, 400 MHz; [a] Determined from $^1$H-NMR studies of the crude material; [b] Crude yield.

| Compound | $R^1$ | δ (ppm) | | | | $J_{H7-H7}$ (Hz) | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | H2 | H4 | H7 | H7 | | |
| **14a** | *p*-H | 5.16 | 4.96 | 3.79 | 3.22 | 20.5 | 94 |
| **14b** | *p*-Me | 5.15 | 4.92 | 3.78 | 3.22 | 20.6 | 79 |
| **14c** | *p*-Bu | 5.16 | 4.94 | 3.79 | 3.23 | 20.5 | 78 |
| **14d** | *p*-OMe | 5.15 | 4.91 | 3.80 | 3.22 | 20.5 | 80 |
| **14e** | *p*-F | 5.16 | 4.92 | 3.80 | 3.22 | 20.6 | 82 |
| **14f** | *p*-Cl | 5.16 | 4.90 | 3.80 | 3.23 | 20.7 | 86 |

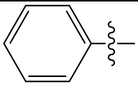
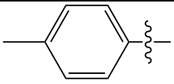
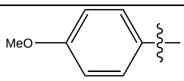
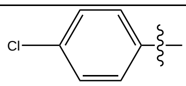
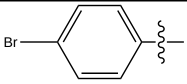
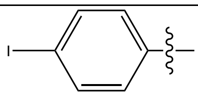
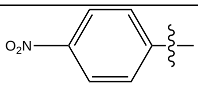
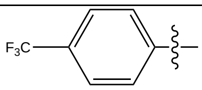
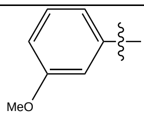
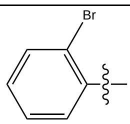
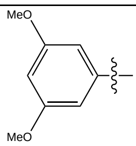
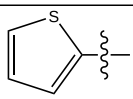
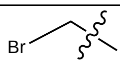
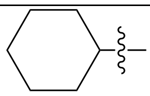
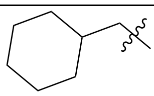
**Table S7:** Key chemical shifts (δ), coupling constants (*J*) and yields of tetramates **14a-f**; $CDCl_3$ solvent, 400 MHz.

| Compound | $R^1$ | δ H2 (ppm) | δ H4 (ppm) | Yield (%) |
|---|---|---|---|---|
| **22a** | *p*-H | 4.91 | 4.81 | 26 |
| **22b** | *p*-Me | 4.90 | 4.77 | 17 |
| **22c** | *p*-Bu | 4.89 | 4.78 | 10 |
| **22d** | *p*-OMe | 4.89 | 4.75 | 19 |
| **22e** | *p*-F | 4.91 | 4.76 | 27 |
| **22f** | *p*-Cl | 4.91 | 4.75 | 11 |

**Table S8:** Key chemical shifts (δ) and yields of tetramates **22a-f**; $CDCl_3$ solvent, 400 MHz.

| Compound | $R^1$ | δ (ppm) | | | | Tautomeric ratio | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | C6 | C8 | C9 | C10 | | |
| **23a** | *p*-H | 188.0<br>189.4 | 176.9<br>182.6 | 166.9<br>167.3 | 165.5<br>166.2 | 54:46 [a] | 42 |
| **23b** | *p*-Me | 187.9<br>189.1 | 176.8<br>182.6 | 166.8<br>167.2 | 165.3<br>166.0 | 58:42 [a] | 49 |
| **23c** | *p*-Bu | 187.9<br>189.2 | 176.9<br>182.6 | 166.8<br>167.2 | 165.4<br>166.1 | 58:42 [a] | 35 |
| **23d** | *p*-OMe | 188.0<br>189.3 | 176.9<br>182.7 | 166.8<br>167.2 | 165.4<br>166.1 | 55:45 [a] | 26 |
| **23e** | *p*-F | 187.9<br>189.7 | 176.9<br>182.5 | 166.9<br>167.2 | 165.5<br>166.1 | 53:47 [b] | 54 |
| **23f** | *p*-Cl | 187.9<br>189.8 | 176.9<br>182.5 | 166.9<br>167.2 | 165.5<br>166.1 | 55:45 [a] | 60 |

**Table S9:** Key $^{13}$C-NMR chemical shift values ($\delta$) of the tautomeric forms of C7-carboxamides **23a-f**; $CDCl_3$ solvent, 400 MHz; [a] Determined from the H2 signal from the $^{1}$H-NMR spectrum; [b] Determined from $^{19}$F-NMR spectrum.

| Compound | $R^1$ | δ (ppm) | | | | | | Yield (%) |
|---|---|---|---|---|---|---|---|---|
| | | H2 | H4 | C6 | C8 | C9 | C10 | |
| **25a** |  | 5.10 | 4.89 | 186.8 | 182.4 | 183.7 | 165.5 | 32 |
| **25b** |  | 5.08 | 4.87 | 186.9 | 182.6 | 183.6 | 165.6 | 26 |
| **25c** |  | 5.05 | 4.84 | 187.0 | 182.8 | 183.0 | 165.7 | 18 |
| **25d** |  | 5.09 | 4.88 | 186.9 | 182.2 | 182.2 | 165.3 | 39 |
| **25e** |  | 5.08 | 4.88 | 187.0 | 182.5 | 182.5 | 165.3 | 35 |
| **25f** [a] |  | 5.06 | 4.85 | 186.9 | 182.2 | 182.7 | 165.4 | 37 |
| **25g** |  | 5.07 | 4.88 | n.d | n.d | n.d | 165.1 | 30 |
| **25h** |  | 5.07 | 4.87 | 186.8 | 182.0 | 182.0 | 165.2 | 41 |
| **25i** |  | 5.06 | 4.84 | 186.7 | 182.5 | 183.5 | 165.5 | 44 |
| **25j** |  | 5.08 | 4.88 | n.d | n.d | n.d | 165.1 | 12 |
| **25k** |  | 5.06 | 4.84 | 186.6 | 182.7 | 183.5 | 165.5 | 17 |
| **25l** |  | 4.97 | 4.78 | 186.6 | 182.8 | 182.8 | 165.5 | 13 |
| **25m** |  | 5.02 | 4.84 | 187.4 | 179.3 | 181.9 | 164.8 | 37 |
| **25n** |  | 5.02 | 4.83 | 187.8 | 180.8 | 196.1 | 165.4 | 57 |
| **25o** [b] |  | 4.99 | 4.79 | 188.3 | 180.2 | 191.7 | 165.3 | 44 |

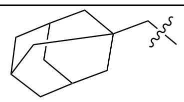
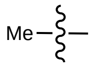
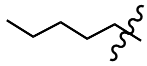
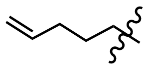
| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **25p** [b] |  | 5.00 | 4.79 | 188.6 | 180.3 | 190.5 | 165.4 | 57 |
| **25q** [b] |  | 4.98 | 4.79 | 188.3 | 179.9 | 188.5 | 165.3 | 51 |
| **25r** |  | 4.99 | 4.79 | 188.1 | 180.3 | 192.6 | 165.4 | 47 |
| **25s** |  | 4.99 | 4.80 | 188.1 | 180.2 | 192.1 | 165.3 | 41 |

**Table S10:** Key chemical shifts ($\delta$) and yields of C7-acyltetramates **25a-s**; $CDCl_3$ solution, 400 MHz; [a] $CDCl_3$ solution, 500 MHz; [b] refers to the major **CD** tautomer; where n.d = not detected.

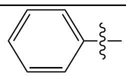
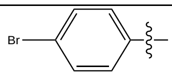
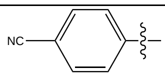
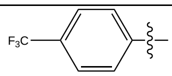
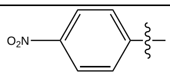
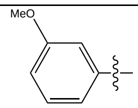
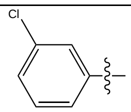
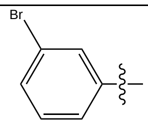
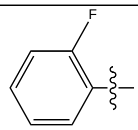
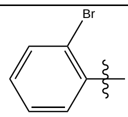
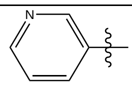
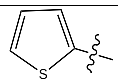
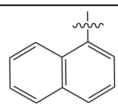
| Compound | $R^1$ | δ (ppm) | | | $J_{H2-H3}$ (Hz) | $J_{H2-NH}$ (Hz) | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | H2 | H3 | NH | | | |
| **9a** |  | 4.61 | 5.12 | 5.25 | 3.9 | 7.6 | 79 |
| **9b** |  | 4.65 | 5.16 | 5.30 | 3.7 | 7.3 | 64 |
| **9c** |  | 4.67 | 5.25 | 5.37 | 3.3 | 6.9 | 69 |
| **9d** |  | 4.69 | 5.25 | 5.36 | 3.7 | 7.2 | 62 |
| **9e** |  | 4.69 | 5.31 | 5.39 | 3.3 | 6.8 | 73 |
| **9f** |  | 4.69 | 5.19 | 5.31 | 3.8 | 7.5 | 69 |
| **9g** |  | 4.66 | 5.19 | 5.37 | 3.6 | 7.2 | 72 |
| **9h** |  | 4.64 | 5.17 | 5.37 | 3.6 | 7.2 | 70 |
| **9i** |  | 4.72 | 5.47 | 5.38 | n.d [a] | n.d [a] | 68 |
| **9j** |  | 4.73 | 5.31-5.48 | 5.31-5.48 | n.d [a] | n.d [a] | 88 |
| **9k** |  | 4.68 | 5.22 | 5.47 | 3.8 | 7.4 | 79 |
| **9l** |  | 4.75 | 5.48 | 5.39 | n.d [a] | n.d [a] | 51 |
| **9m** [b] |  | 4.69 | 6.03 | 5.42 | 2.6 | 9.1 | 15 |

**Table S11:** Yields and key chemical shifts of Boc-protected-*allo*-phenylserines **9a-m**; $CDCl_3$ solvent, 400 MHz; [a] n.d = not determined due to a broad multiplet peak; [b] Data refers to the major rotamer.

| Compound | $R^1$ | δ (ppm) | | | | | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | H2 | H3 | $J_{H2\text{-}H3}$ | C2 | C3 | |
| **28a** | Ph | 4.48 | 5.40 | 4.2 | 58.5 | 71.0 | Quant. |
| **28b** | *p*-Br-$C_6H_4$ | 4.48 | 5.38 | 3.9 | 58.3 | 70.4 | Quant. |
| **28c** | *p*-CN-$C_6H_4$ | 4.56 | 5.48 | 3.6 | 58.1 | 70.5 | Quant. |
| **28d** | *p*-$CF_3$-$C_6H_4$ | 4.57 | 5.51 | 3.7 | 58.3 | 70.5 | Quant. |
| **28e** | *p*-$NO_2$-$C_6H_4$ | 4.60 | 5.53 | 3.5 | 58.1 | 70.4 | Quant. |
| **28f** | *m*-MeO-$C_6H_4$ | 4.49 | 5.40 | 4.1 | 58.4 | 70.7 | Quant. |
| **28g** | *m*-Cl-$C_6H_4$ | 4.49 | 5.39 | 3.9 | 58.3 | 70.3 | Quant. |
| **28h** | *m*-Br-$C_6H_4$ | 4.49 | 5.40 | 3.8 | 58.3 | 70.3 | Quant. |
| **28i** | *o*-F-$C_6H_4$ | 4.54 | 5.59 | 3.7 | 57.0 | 66.3 | Quant. |
| **28j** | *o*-Br-$C_6H_4$ | 4.62 | 5.51 | 3.2 | 55.9 | 70.7 | Quant |
| **28k** | *m*-Pyridyl | 4.69 | 5.64 | 2.7 | 57.5 | 68.2 | Quant. |

**Table S12:** Key chemical shifts, coupling constants and yields of amino esters **28a-k**; $D_2O$ solvent, 400 MHz.

| Compound | $R^1$ | 2,5-*cis* oxazolidine δ (ppm) | | | | 2,5-*trans* oxazolidine δ (ppm) | | | | dr at the C2-position [a] | Yield (%) [b] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | H2 | H4 | H5 | $J_{H4\text{-}H5}$ (Hz) | H2 | H4 | H5 | $J_{H4\text{-}H5}$ (Hz) | | |
| **10a** | Ph | 4.15 | 4.98 | 4.09 | 9.0 | 4.94 | 5.23 | 4.22 | 7.4 | 5.6:1 | 57 |
| **10g** | *p*-Br-$C_6H_4$ | 4.20 | 5.00 | 4.15 | 9.0 | 4.98 | 5.24 | 4.28 | 7.3 | 5.7:1 | 82 |
| **10h** | *p*-CN-$C_6H_4$ | 4.23 | 5.07 | 4.21 | 9.1 | 5.01 | 5.29 | 4.34 | 7.4 | 4.6:1 | 74 |
| **10i** | *p*-$CF_3$-$C_6H_4$ | 4.23 | 5.10 | 4.20 | 9.0 | 5.02 | 5.32 | 4.33 | 7.3 | 5.3:1 | 85 |
| **10j** | *p*-$NO_2$-$C_6H_4$ | 4.25 | 5.13 | 4.24 | 9.1 | 5.03 | 5.35 | 4.37 | 7.4 | 4.6:1 | 61 |
| **10k** | *m*-MeO-$C_6H_4$ | 4.20 | 5.02 | 4.15 | 9.0 | 4.99 | 5.26 | 4.27 | 7.3 | 5.7:1 | 60 |
| **10l** | *m*-Cl-$C_6H_4$ | 4.13 | 4.94 | 4.09 | 9.1 | 4.94 | 5.18 | 4.22 | 7.4 | 4.6:1 | 78 |
| **10m** | *m*-Br-$C_6H_4$ | 4.13 | 4.93 | 4.08 | 8.9 | 4.92 | 5.17 | 4.22 | 7.4 | 3.8:1 | 80 |
| **10n** | *o*-F-$C_6H_4$ | 4.22 | 5.39 | 4.22 | 8.9 | 4.99 | 5.51 | 4.39 | 7.2 | 4.9:1 | 78 |
| **10o** | *o*-Br-$C_6H_4$ | 4.22 | 5.43 | 4.28 | 8.7 | 5.04 | 5.46 | 4.56 | 7.0 | 5.7:1 | 77 |
| **10p** | *m*-Pyridyl | 4.22 | 5.07 | 4.19 | 9.0 | 4.99 | 5.30 | 4.33 | 7.4 | 4.9:1 | 57 |

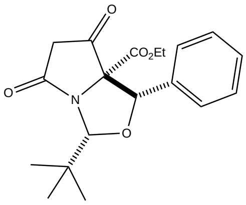
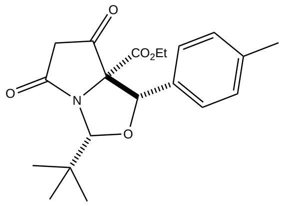
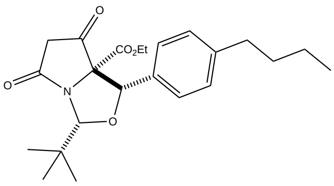
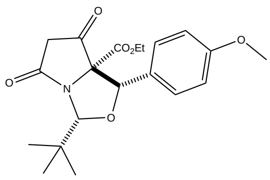
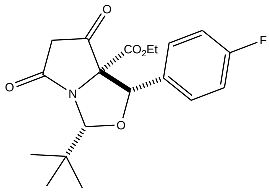
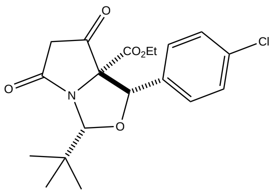
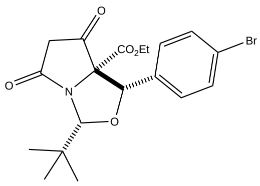
**Table S13:** Key chemical shifts (δ), coupling constants (*J*), diastereomeric ratio (dr) and yields of oxazolidines **10a,g-p**; $CDCl_3$ solvent, 400 MHz; [a] Determined from $^1$H-NMR studies of the crude material where the major diastereomer was the 2,5-*cis* isomer; [b] Yields include both diastereomers.

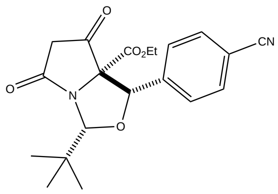
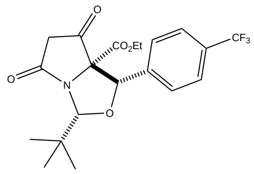
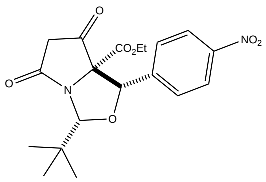
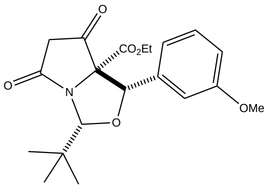
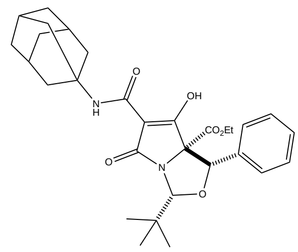
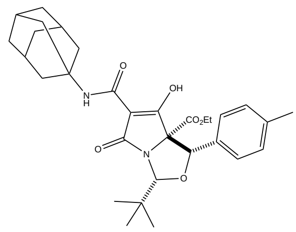
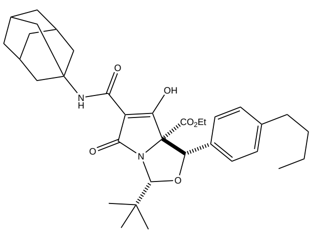
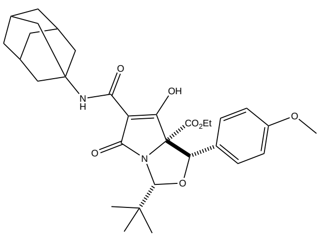
| Compound | $R^1$ | $\delta$ (ppm) | | | $J_{H4-H5}$ (Hz) | Yield (%) |
|---|---|---|---|---|---|---|
| | | H2 | H4 | H5 | | |
| **11a** | Ph | 5.37 | 5.21 | 4.80 | 6.9 | 78 |
| **11g** | *p*-Br-$C_6H_4$ | 5.38 | 5.16 | 4.82 | 6.7 | 69 |
| **11h** | *p*-CN-$C_6H_4$ | 5.40 | 5.22 | 4.93 | 6.5 | 68 |
| **11i** | *p*-$CF_3$-$C_6H_4$ | 5.40 | 5.25 | 4.90 | 6.6 | 59 |
| **11j** | *p*-$NO_2$-$C_6H_4$ | 5.42 | 5.27 | 4.98 | 6.3 | 75 |
| **11k** | *m*-MeO-$C_6H_4$ | 5.38 | 5.18 | 4.80 | 6.9 | 68 |
| **11l** | *m*-Cl-$C_6H_4$ | 5.38 | 5.17 | 4.84 | 6.7 | 72 |
| **11m** | *m*-Br-$C_6H_4$ | 5.38 | 5.17 | 4.84 | 6.7 | 66 |
| **11n** | *o*-F-$C_6H_4$ | 5.39 | 5.33 | 4.93 | 6.3 | 61 |
| **11o** | *o*-Br-$C_6H_4$ | 5.40 | 5.33 | 5.15 | 6.5 | 54 |
| **11p** | *m*-Pyridyl | 5.39 | 5.22 | 4.89 | 6.6 | 68 |

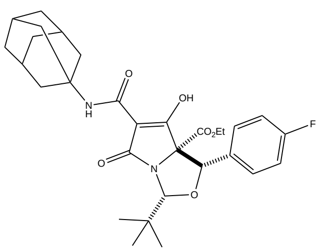
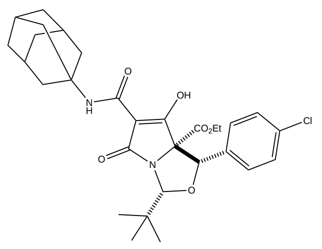
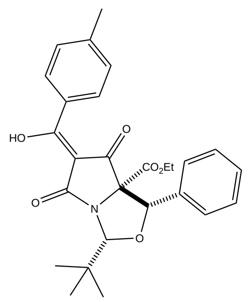
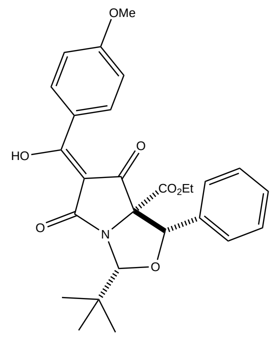
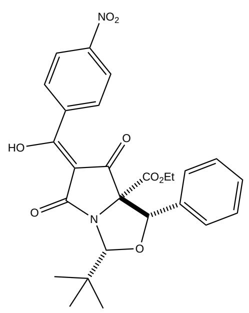
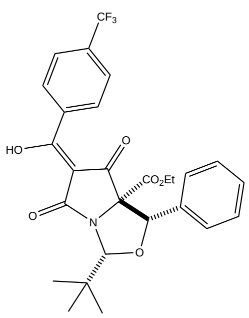
**Table S14:** Key chemical shifts ($\delta$) and coupling constants (*J*) of the major malonamide diastereomer including the yields of malonamides **11a,g-p**; $CDCl_3$ solvent, 400 MHz.

| Compound | $R^1$ | $\delta$ (ppm) | | | | $J_{H7-H7}$ (Hz) | Yield (%) |
|---|---|---|---|---|---|---|---|
| | | H2 | H4 | H7 | H7 | | |
| **14a** | Ph | 5.16 | 4.96 | 3.79 | 3.22 | 20.5 | 81 |
| **14g** | *p*-Br-$C_6H_4$ | 5.16 | 4.88 | 3.81 | 3.23 | 20.7 | 85 |
| **14h** | *p*-CN-$C_6H_4$ | 5.19 | 4.95 | 3.84 | 3.26 | 20.8 | 92 |
| **14i** | *p*-$CF_3$-$C_6H_4$ | 5.20 | 4.97 | 3.84 | 3.26 | 20.7 | 84 |
| **14j** | *p*-$NO_2$-$C_6H_4$ | 5.21 | 4.99 | 3.86 | 3.28 | 20.9 | 86 |
| **14k** | *m*-MeO-$C_6H_4$ | 5.16 | 4.93 | 3.77 | 3.22 | 20.6 | 79 |
| **14l** | *m*-Cl-$C_6H_4$ | 5.16 | 4.90 | 3.82 | 3.23 | 20.7 | 86 |
| **14m** | *m*-Br-$C_6H_4$ | 5.16 | 4.89 | 3.82 | 3.22 | 20.6 | 76 |
| **14n** | *o*-F-$C_6H_4$ | _ | _ | _ | _ | _ | n.d [a] |
| **14o** | *o*-Br-$C_6H_4$ | _ | _ | _ | _ | _ | 0 |
| **14p** | *m*-Pyridyl | _ | _ | _ | _ | _ | 0 |

**Table S15:** Key chemical shifts ($\delta$), coupling constants (*J*) and yields of tetramates **14g-p**; $CDCl_3$ solvent, 400 MHz; [a] n.d = not determined as the compound was discarded.

| Compound | Structure | MW (g/mol) | cLog*P* | PSA (Å²) | MSA (Å²) | rel. PSA (%) | H-donor | H-acceptor | Ro5 | MIC ($\mu$g/ml) |
|---|---|---|---|---|---|---|---|---|---|---|
| **14a** |  | 345.40 | 3.43 | 72.91 | 527.95 | 13.81 | 0 | 4 | 4/4 | 15.6 |
| **14b** |  | 359.42 | 3.94 | 72.91 | 560.84 | 13.00 | 0 | 4 | 4/4 | 7.8 |
| **14c** |  | 401.50 | 5.27 | 72.91 | 652.12 | 11.18 | 0 | 4 | 3/4 | 15.6 |
| **14d** |  | 375.42 | 3.27 | 82.14 | 575.79 | 14.27 | 0 | 5 | 4/4 | 15.6 |
| **14e** |  | 363.39 | 3.57 | 72.91 | 534.55 | 13.64 | 0 | 4 | 4/4 | 15.6 |
| **14f** |  | 379.84 | 4.03 | 72.91 | 544.60 | 13.39 | 0 | 4 | 4/4 | 15.6 |
| **14g** |  | 424.29 | 4.20 | 72.91 | 548.56 | 13.29 | 0 | 4 | 4/4 | 31 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **14h** |  | 370.41 | 3.28 | 96.70 | 545.24 | 17.74 | 0 | 5 | 4/4 | 250 |
| **14i** |  | 413.39 | 4.30 | 72.91 | 577.83 | 12.62 | 0 | 4 | 4/4 | 250 |
| **14j** |  | 390.39 | 3.37 | 116.05 | 566.07 | 20.50 | 0 | 6 | 4/4 | 125 |
| **14k** |  | 375.42 | 3.27 | 82.14 | 576.69 | 14.24 | 0 | 5 | 4/4 | 31 |
| **23a** |  | 522.64 | 4.00 | 105.17 | 777.62 | 13.52 | 2 | 5 | 3/4 | 0.25 |
| **23b** |  | 536.67 | 4.52 | 105.17 | 804.02 | 13.08 | 2 | 5 | 3/4 | 0.25 |
| **23c** |  | 578.75 | 5.85 | 105.17 | 898.42 | 11.71 | 2 | 5 | 2/4 | 3.9 |
| **23d** |  | 552.67 | 3.85 | 114.40 | 823.73 | 13.89 | 2 | 6 | 3/4 | 0.25 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **23e** |  | 540.63 | 4.15 | 105.17 | 784.23 | 13.41 | 2 | 5 | 3/4 | 0.25 |
| **23f** |  | 557.08 | 4.61 | 105.17 | 794.07 | 13.24 | 2 | 5 | 3/4 | 0.25 |
| **25b** |  | 463.53 | 5.24 | 93.14 | 675.92 | 13.78 | 1 | 5 | 3/4 | 125 |
| **25c** |  | 479.53 | 4.57 | 102.37 | 693.57 | 14.76 | 1 | 6 | 4/4 | 125 |
| **25g** |  | 494.50 | 4.67 | 136.28 | 682.43 | 19.97 | 1 | 7 | 4/4 | 125 |
| **25h** |  | 517.50 | 5.61 | 93.14 | 693.63 | 13.43 | 1 | 5 | 2/4 | 125 |

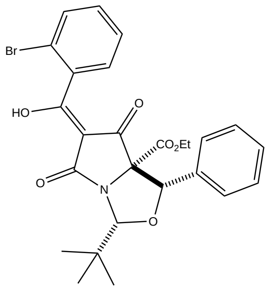
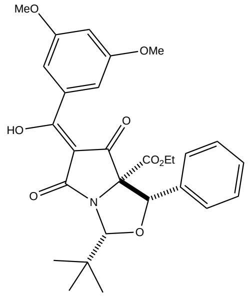
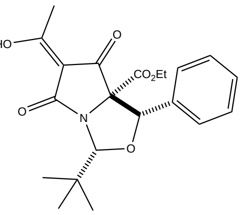
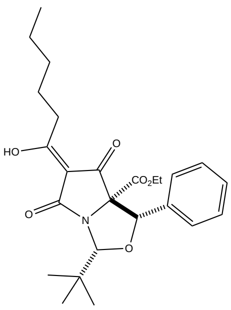
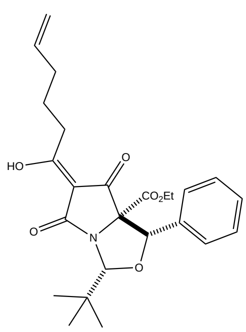
| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **25j** |  | 528.40 | 5.50 | 93.14 | 663.41 | 14.04 | 1 | 5 | 2/4 | 250 |
| **25k** |  | 509.56 | 4.41 | 111.60 | 741.82 | 15.04 | 1 | 7 | 3/4 | 125 |
| **25q** |  | 387.43 | 3.36 | 93.14 | 569.32 | 16.36 | 1 | 5 | 4/4 | 250 |
| **25r** |  | 443.54 | 5.22 | 93.14 | 691.73 | 13.47 | 1 | 5 | 3/4 | 63 |
| **25s** |  | 441.52 | 4.91 | 93.14 | 660.54 | 14.10 | 1 | 5 | 4/4 | 125 |

**Table S16:** Physicochemical properties of bicyclic tetramates; where cLogP, MSA, PSA, H-donors and H-acceptors were calculated using Marvin (19.9.0), 2019, ChemAxon. MIC values indicates potency against *S. aureus*; $M_w$ = molecular weight; cLogP = calculated partition coefficient between octanol and water; PSA = polar surface area; MSA = molecular surface area; rel. PSA = relative polar surface area ((PSA/MSA)x100); H-donor = hydrogen-bond donor count; H-acceptor = hydrogen-bond acceptor count; Ro5 = rule of 5; MIC = minimum inhibitory concentration against *S. aureus*; n.a. = not active.

# Experimental

## General Methods

Overnight reaction refers to reactions occurring between 15-24 h. All reagents were obtained from commercial sources and was used without further purification. Anhydrous solvents were dried by pre-storing them over activated 3 Å molecular sieves before being passed through an activated alumina column on a solvent tower under $N_2$ pressure. Solvents were evaporated at 40°C under reduced pressure on a Büchi R-114 rotatory evaporator attached to a Vacuubrand CVC2 pump and a pressure control system, with the exception of water, which was evaporated between 70-80°C. Analytical thin-layer chromatography (TLC) was carried out on Merck aluminium foil backed sheets precoated with 0.2 mm Kielselgel 60 $F_{254}$. The eluent used is specified in each case. The spots were visualised by UV irradiation ($\lambda$=254 nm) and by staining with $KMnO_4$ solution followed by heating. Retention factors ($R_f$) are quoted to the nearest 0.01. Flash column chromatography was performed on Kielselgel 60 silica gel (230-400 mesh particle size). Melting points were measured using a Stuart Scientific SMP1 melting point instrument and are uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer equipped with an attached Pike Miracle attenuated total reflectance (ATR) module. Absorption maxima ($v_{max}$) are reported in wavenumbers ($cm^{-1}$) and only selected peaks are reported. $^1$H-NMR spectra were recorded at 200 MHz, 400 MHz and 500 MHz, $^{13}$C-NMR spectra were recorded at 101 MHz or 126 MHz and $^{19}$F-NMR spectra were recorded at 377 MHz or 471 MHz using either a Bruker DPX200, AVIIIHD 400 and AVIIIHD 500. Chemical shifts ($\delta_H$, $\delta_F$ and $\delta_C$) are reported in parts per million (ppm) upfield from TMS and are referenced to the residual solvent peak (in some cases, it was not possible to reference the chloroform peak in the $^1$H-NMR spectra due to it being obscured by aromatic protons). Coupling constants (*J*) are quoted in Hertz (Hz). Data is reported in this format: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, dd = double doublet, dt = double triplet, dq = double quartet, m = multiplet, br = broad and app = apparent), coupling constant, and assignment. Two-dimensional COSY, HSQC, HMBC and NOESY experiments were recorded at 400 MHz and 500 MHz and nOe experiments were recorded at 500 MHz. Assignments of the spectra were made with $^1$H, COSY, HSQC, HMBC, $^{13}$C and DEPT-135 experiments and stereochemistry were assigned on the basis of nOe, NOESY or X-ray crystallography. Low resolution mass spectra (*m/z*) were recorded on an Agilent 6120 spectrometer or a Waters LCT Premier XE spectrometer using electrospray ionisation (ESI).

Selected peaks are reported in Daltons and their intensities given as percentages of the base peak. High resolution mass spectra (HRMS) were recorded on a Bruker microTOF (ESI) or on an Agilent 7200 Q-TOF (EI or CI). Crystals for X-ray crystallography were grown from slow vapour diffusion of petroleum ether 40:60 into a solution of compound dissolved in minimal EtOAc at room temperature. Low temperature[2] single-crystal X-ray diffraction data were collected using a Rigaku Oxford SuperNova diffractometer and at the Diamond Light Source Beamline, I19-1. Raw frame data were collected and reduced using CrysAlisPro and the structures were solved using 'Superflip'[3] before refinement with CRYSTALS[4].

**3. Assays / test methods**

**3.1 MIC**

The compounds were tested in a primary 96 well plates screening assay. The substances were diluted in a first step in DMSO (10 mg/mL) and then diluted in cell culture water to its final concentration of 250 µg/mL as stock solution. This solution was serial diluted (1:1) with medium to its final volume of 50 µL per well and overlaid with a microbial solution in the same volume (concentration of $10^5$ CFU/mL). The plates were incubated for 24 h at 37°C for bacteria, 48 h at 27°C for fungi. The MIC represents the lowest compound concentration that totally inhibits microbial growth.

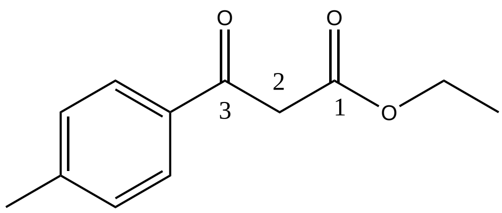
**3.2 Toxicity**

The compounds were tested in a primary 96 well plates screening assay. In a separate dilution plate the prediluted substances (10 mg/mL in 100% DMSO) were diluted in cell culture water to a stock concentration of 250 µg/mL and serial diluted (1:1) with medium. The cells were previously seeded into another 96 well plate and grown to a confluence of 90%. The medium was discarded and cells were overlaid with 100 µL from the dilution plate. Then the 96 well plates were incubated for 48 h under physiological conditions. The toxic concentration displays the lowest compound concentration where all cells are dead.

**General procedure for the synthesis of $\beta$-oxoesters 5:**[5]

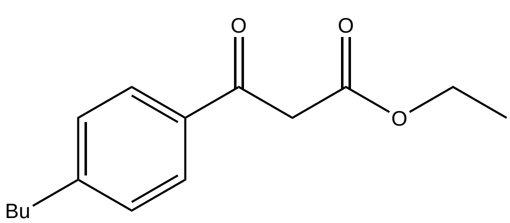
Ethyl potassium malonate (1.9 eq.) was dissolved in MeCN and cooled to 0°C in an ice/water bath. $MgCl_2$ (2.5 eq.) was added and the flask was put under $N_2$ atmosphere. $Et_3N$ (3 eq.) was then added dropwise and the solution was left to stir at rt for 2 h, where a white slurry formed. The flask was re-cooled to 0°C and the acyl chloride (1 eq.) was added dropwise, followed by an additional amount of $Et_3N$ (0.5 eq.) and the solution was stirred overnight at rt. MeCN was then subsequently removed *in-vacuo*. The concentrate was cooled to 0°C and added to it was toluene and 12 % HCl solution (aq.) carefully, and the mixture was left to stir at rt for 20 min. The mixture was then transferred to a separatory funnel, where the organic layer was washed with 12 % HCl solution (aq.), water and brine, dried over $Na_2SO_4$, filtered and the solvent was removed *in-vacuo* to obtain the desired $\beta$-oxoesters **5** as a mixture of keto-enol tautomers and was used without further purification.

**Ethyl 3-oxo-3-(*p*-tolyl)propanoate 5b**



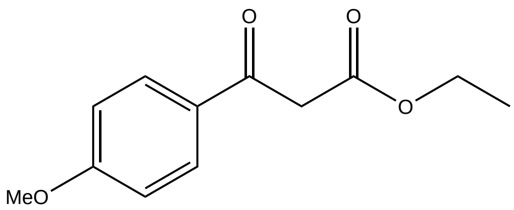
Yield (3.03 g, Quantitative); Red oil; $\nu_{max}/cm^{-1}$ 2983 (C-H), 1738 (C=O), 1682 (C=O); Keto:enol tautomers=5.5:1; $\delta_{H\ (Major\ keto\ tautomer)}$ (400 MHz, $CDCl_3$) 1.26 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 2.42 (3H, s, $CH_3$), 3.97 (2H, s, H2), 4.22 (2H, q, *J*=7.2 Hz, $OCH_2CH_3$), 7.28 (2H, d, *J*=8.1 Hz, Ar-H), 7.85 (2H, d, *J*=8.3 Hz, Ar-H); $\delta_{C\ (Major\ keto\ tautomer)}$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 21.8 ($CH_3$), 46.1 (C2), 61.6 ($OCH_2CH_3$), 128.8 (Ar-C), 129.6 (Ar-C), 133.7 (Ar-C), 144.8 (Ar-C), 167.8 (C1), 192.3 (C3); $\delta_{H\ (Minor\ enol\ tautomer)}$ (400 MHz, $CDCl_3$) 1.34 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 2.39 (3H, s, $CH_3$), 4.27 (2H, m, $OCH_2CH_3$), 5.64 (1H, s, H2), 7.28-8.00 (4H, m, Ar-H), 12.59 (1H, s, OH); $\delta_{C\ (Minor\ enol\ tautomer)}$ (101 MHz, $CDCl_3$) 14.4 ($OCH_2CH_3$), 21.9 ($CH_3$), 60.3 ($OCH_2CH_3$), 86.8 (C2), 129.3 (Ar-C), 130.3 (Ar-C), 133.7 (Ar-C), 144.6 (Ar-C), 171.5 (C=O), 173.4 (C=O); LRMS (ESI$^+$) *m/z*: 229.0 ($[M + Na]^+$ 9%); HRMS (ESI$^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{12}H_{14}O_3Na$, 229.0835, found 229.0837.

**Ethyl 3-(4-butylphenyl)-3-oxopropanoate 5c**



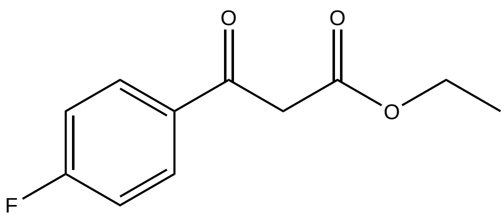
Yield (3.49 g, Quantitative); Orange/red oil that solidified on standing to a semi-solid; $\nu_{max}/cm^{-1}$ 2958 (C-H), 2932 (C-H), 2861 (C-H), 1740 (C=O), 1685 (C=O); Keto:enol tautomers=2.8:1; $\delta_{H\ (Major\ keto\ tautomer)}$ (400 MHz, $CDCl_3$) 0.94 (3H, m, $CH_2CH_3$), 1.26 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.36 (2H, m, $CH_2CH_3$), 1.62 (2H, m, $CH_2CH_2$), 2.67 (2H, m, $CH_2CH_2$), 3.97 (2H, s, H2), 4.22 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.28 (2H, d, *J*=8.3 Hz, Ar-H), 7.86 (2H, d, *J*=8.3 Hz, Ar-H); $\delta_{C\ (Major\ keto\ tautomer)}$ (101 MHz, $CDCl_3$) 14.0 ($CH_2CH_3$), 14.2 ($OCH_2CH_3$), 22.4 ($CH_2CH_3$), 33.3 ($CH_2CH_2$), 35.8 ($CH_2CH_2$), 46.1 (C2), 61.6 ($OCH_2CH_3$), 128.8 (Ar-C), 128.9 (Ar-C), 133.9 (Ar-C), 149.7 (Ar-C), 167.8 (C1), 192.3 (C3); $\delta_{H\ (Minor\ enol\ tautomer)}$ (400 MHz, $CDCl_3$) 0.94 (3H, m, $CH_2CH_3$), 1.26 (3H, m, $OCH_2CH_3$), 1.36 (2H, m, $CH_2CH_3$), 1.62 (2H, m, $CH_2CH_2$), 2.67 (2H, m, $CH_2CH_2$), 4.28 (2H, m, $OCH_2CH_3$), 5.64 (1H, s, H2), 7.23-8.04 (4H, m, Ar-H), 12.58 (1H, s, OH); $\delta_{C\ (Minor\ enol\ tautomer)}$ (101 MHz, $CDCl_3$) 14.0 ($CH_2CH_3$), 14.2 ($OCH_2CH_3$), 22.4 ($CH_2CH_3$), 33.4 ($CH_2CH_2$), 35.9 ($CH_2CH_2$), 60.3 ($OCH_2CH_3$), 86.8 (C2), 128.7 (Ar-C), 130.4 (Ar-C), 133.9 (Ar-C), 149.6 (Ar-C), 171.6 (C=O), 173.4 (C=O); LRMS (ESI$^+$) *m/z*: 271.2 ([M + Na]$^+$ 95%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{15}H_{20}O_3Na$, 271.1305, found 271.1304.

**Ethyl 3-(4-methoxyphenyl)-3-oxopropanoate 5d**



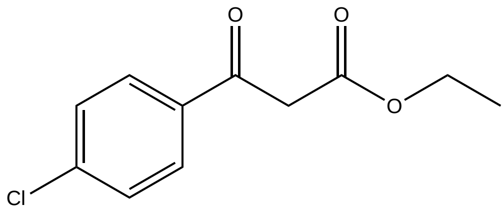

Yield (3.27 g, Quantitative); Orange oil; $\nu_{max}$/cm$^{-1}$ 2981 (C-H), 1736 (C=O), 1676 (C=O); Keto:enol tautomers=13:1; $\delta_{H\ (Major\ keto\ tautomer)}$ (400 MHz, $CDCl_3$) 1.24 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.86 (3H, s, $OCH_3$), 3.93 (2H, s, H2), 4.19 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 6.93 (2H, d, *J*=8.9 Hz, Ar-H), 7.91 (2H, d, *J*=8.9 Hz, Ar-H); $\delta_{C\ (Major\ keto\ tautomer)}$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 45.9 (C2), 55.6 ($OCH_3$), 61.5 ($OCH_2CH_3$), 114.0 (Ar-C), 129.2 (Ar-C), 131.0 (Ar-C), 164.1 (Ar-C), 167.9 (C1), 191.1 (C3); $\delta_{H\ (Minor\ enol\ tautomer)}$ (400 MHz, $CDCl_3$) 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.86 (3H, s, $OCH_3$), 4.25 (2H, m, $OCH_2CH_3$), 5.56 (1H, s, H2), 6.93-8.05 (4H, m, Ar-H), 12.62 (1H, s, OH); $\delta_{C\ (Minor\ enol\ tautomer)}$ (101 MHz, $CDCl_3$) 14.4 ($OCH_2CH_3$), 55.6 ($OCH_3$), 60.3 ($OCH_2CH_3$), 85.8 (C2), 113.8 (Ar-C), 129.2 (Ar-C), 131.2 (Ar-C), 162.2 (Ar-C), 171.5 (C=O), 173.5 (C=O); LRMS (ESI$^+$) *m/z*: 245.0 ([M + Na]$^+$ 72%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{12}H_{14}O_4Na$, 245.0784, found 245.0785.

**Ethyl 3-(4-fluorophenyl)-3-oxopropanoate 5e**



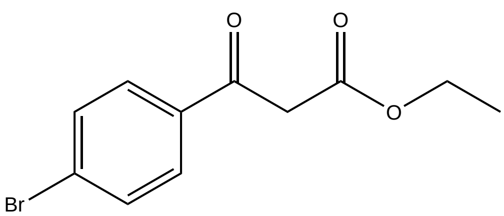

Yield (1.73 g, Quantitative); Orange oil; $\nu_{max}$/cm$^{-1}$ 2985 (C-H), 1736 (C=O), 1686 (C=O); Keto:enol tautomers=4.9:1; $\delta_{H\ (Major\ keto\ tautomer)}$ (400 MHz, $CDCl_3$) 1.24 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.95 (2H, s, H2), 4.20 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.14 (2H, app t, *J*=8.9 Hz, Ar-H), 7.97 (2H, dd, *J*=5.3 Hz, 8.9 Hz, Ar-H); $\delta_{C\ (Major\ keto\ tautomer)}$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 46.1 (C2), 61.7 ($OCH_2CH_3$), 116.1 (d, *J*=21.6 Hz, Ar-C), 131.4 (d, *J*=9.5 Hz, Ar-C), 132.6 (d, *J*=3.1 Hz, Ar-C), 166.4 (d, *J*=255.9 Hz, Ar-C), 167.4 (C1), 191.0 (C3); $\delta_{F\ (Major\ keto\ tautomer)}$ (377 MHz, $CDCl_3$) -103.93; $\delta_{H\ (Minor\ enol\ tautomer)}$ (400 MHz, $CDCl_3$) 1.32 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.26 (2H, m, $OCH_2CH_3$), 5.59 (1H, s, H2), 7.06-8.10 (4H, m, Ar-H), 12.60 (1H, s, OH); $\delta_{C\ (Minor\ enol\ tautomer)}$ (101 MHz, $CDCl_3$) 14.4 ($OCH_2CH_3$), 60.5 ($OCH_2CH_3$), 87.3 (C2), 115.8 (d, *J*=21.6 Hz, Ar-C), 128.3 (d, *J*=8.8 Hz, Ar-C), 132.6 (Ar-C), 166.4 (Ar-C), 170.5 (C=O), 173.2 (C=O); $\delta_{F\ (Minor\ enol\ tautomer)}$ (377 MHz, $CDCl_3$) -108.52; LRMS ($ESI^+$) *m/z*: 233.0 ($[M + Na]^+$ 65%); HRMS ($ESI^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{11}H_{11}O_3FNa$, 233.0584, found 233.0585.

**Ethyl 3-(4-chlorophenyl)-3-oxopropanoate 5f**




Yield (1.78 g, Quantitative); Yellow oil; $\nu_{max}/cm^{-1}$ 2983 (C-H), 1737 (C=O), 1687 (C=O); Keto:enol tautomers=3.2:1; $\delta_{H\ (Major\ keto\ tautomer)}$ (400 MHz, $CDCl_3$) 1.18 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.88 (2H, s, H2), 4.13 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.38 (2H, d, *J*=8.6 Hz, Ar-H), 7.81 (2H, d, *J*=8.7 Hz, Ar-H); $\delta_{C\ (Major\ keto\ tautomer)}$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 46.1 (C2), 61.7 ($OCH_2CH_3$), 129.2 (Ar-C), 130.1 (Ar-C), 134.5 (Ar-C), 140.4 (Ar-C), 167.3 (C1), 191.4 (C3); $\delta_{H\ (Minor\ enol\ tautomer)}$ (400 MHz, $CDCl_3$) 1.26 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.19 (2H, m, $OCH_2CH_3$), 5.56 (1H, s, H2), 7.31-7.81 (4H, m, Ar-H), 12.50 (1H, s, OH); $\delta_{C\ (Minor\ enol\ tautomer)}$ (101 MHz, $CDCl_3$) 14.4 ($OCH_2CH_3$), 60.6 ($OCH_2CH_3$), 87.8 (C2), 127.5 (Ar-C), 128.9 (Ar-C), 134.5 (Ar-C), 140.4 (Ar-C), 170.2 (C=O), 173.2 (C=O); LRMS ($ESI^+$) *m/z*: 249.0 ($[M^{35} + Na]^+$ 82%), 251.0 ($[M^{37} + Na]^+$ 26%); HRMS ($ESI^+$) *m/z*: $[M^{35} + Na]^+$ calcd. for $C_{11}H_{11}O_3ClNa$, 249.0289, found 249.0291; $[M^{37} + Na]^+$ calcd. for $C_{11}H_{11}O_3ClNa$, 251.0259, found 251.0261.

**Ethyl 3-(4-bromophenyl)-3-oxopropanoate 5g**




Yield (2.96 g, 91%); Orange oil; $\nu_{max}/cm^{-1}$ 2983 (C-H), 1739 (C=O), 1687 (C=O); Keto:enol=2.7:1 tautomers; $\delta_{H\ (Major\ keto\ tautomer)}$ (400 MHz, $CDCl_3$) 1.25 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.95 (2H, s, H2), 4.20 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.62 (2H, d, *J*=8.6 Hz, Ar-H), 7.80 (2H, d, *J*=8.6 Hz, Ar-H); $\delta_{C\ (Major\ keto\ tautomer)}$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 46.1 (C2), 61.7 ($OCH_2CH_3$), 129.2 (Ar-C), 130.1 (Ar-C), 132.2 (Ar-C), 134.9 (Ar-C), 167.3 (C1), 191.6 (C3); $\delta_{H\ (Minor\ enol\ tautomer)}$ (400 MHz, $CDCl_3$) 1.33 (3H, t,

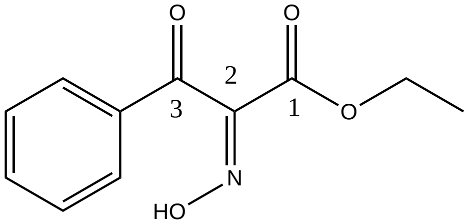
$J$=7.1 Hz, $OCH_2CH_3$), 4.26 (2H, m, $OCH_2CH_3$), 5.63 (1H, s, H2), 7.53-7.81 (4H, m, Ar-H), 12.55 (1H, s, OH); $\delta_{C\ (Minor\ enol\ tautomer)}$ (101 MHz, $CDCl_3$) 14.4 ($OCH_2CH_3$), 60.6 ($OCH_2CH_3$), 87.9 (C2), 127.7 (Ar-C), 129.2 (Ar-C), 131.9 (Ar-C), 134.9 (Ar-C), 170.3 (C=O), 173.2 (C=O); LRMS ($ESI^+$) *m/z*: 293.0 ([$M^{79}$ + Na]$^+$ 30%), 295.0 ([$M^{81}$ + Na]$^+$ 27%); HRMS ($ESI^+$) *m/z*: [$M^{79}$ + Na]$^+$ calcd. for $C_{11}H_{11}O_3BrNa$, 292.9784, found 292.9784; [$M^{81}$ + Na]$^+$ calcd. for $C_{11}H_{11}O_3BrNa$, 294.9763, found 294.9764.

**General procedure for the synthesis of oximes 6:**[6]

**Method A:** To a stirred solution of ethyl benzoylacetate **5a** (1 eq.) dissolved in glacial acetic acid at 0 °C was added a solution of sodium nitrite (1.2-1.3 eq.) in water dropwise to ensure the temperature of the reaction medium did not rise above 10°C. After stirring for 30 minutes at rt, the product started to precipitate out and the solution was poured into water and stirred for a further 10 mins. The product was filtered off via vacuum filtration, washed with water and dried *in-vacuo* to give a white solid **6a** and was used without further purification.

**Method B:** To a stirred solution of substituted $\beta$-oxoesters **5b-g** (1 eq.) dissolved in glacial acetic acid at 0°C was added a solution of sodium nitrite (1.5 eq.) in water dropwise to ensure the temperature of the reaction medium did not rise above 10°C. The reaction was then left to stir at rt for 3 h or left to stir overnight at rt, and then glacial acetic acid was evaporated *in-vacuo*. Then added to the residue was DCM and $H_2O$ and this mixture was left to stir for 10-20 min at rt (where a white/cream suspension might form). The layers were then separated using a separatory funnel, and the organic layer was washed successively with water, $NaHCO_3$ (aq.) (very cautiously) and brine, dried over $Na_2SO_4$, filtered, and the solvent was removed *in-vacuo* to obtain the desired oxime **6b-g** and was used without further purification.

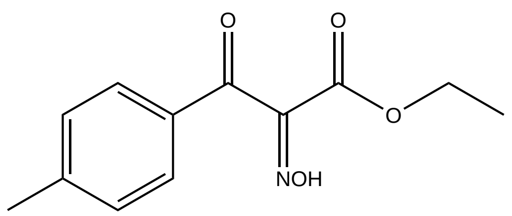
**Ethyl (*E*)-2-(hydroxyimino)-3-oxo-3-phenylpropanoate 6a**




Method A: Yield (16.19 g, 71%); White solid; m.p. 144-147°C (lit.[7] 121-122°C); 21:1 mixture of *E/Z* isomers; $\nu_{max}/cm^{-1}$ 3325 (O-H), 2987 (C-H), 1721 (C=O), 1679 (C=O), 1596 (C=N); $\delta_{H\ (Major\ E\text{-}isomer)}$ (400 MHz, $CDCl_3$) 1.20 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 4.26 (2H, q, $J$=7.1 Hz, $OCH_2CH_3$), 7.41-

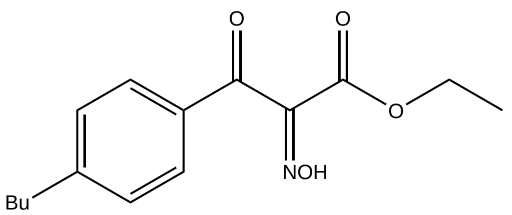
8.00 (5H, m, Ar-H), 10.62 (1H, br s, OH); $\delta_{C\ (Major\ E\text{-isomer})}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 62.8 ($OCH_2CH_3$), 129.2 (Ar-C), 129.3 (Ar-C), 134.3 (Ar-C), 134.9 (Ar-C), 149.6 (C2), 161.0 (C1), 190.3 (C3); LRMS (ESI$^+$) *m/z*: 244.0 ([M + Na]$^+$ 100%); LRMS (ESI$^-$) *m/z*: 220.0 ([M – H]$^-$ 98%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{11}H_{11}NO_4Na$, 244.0580, found 244.0581.

**Ethyl 2-(hydroxyimino)-3-oxo-3-(*p*-tolyl)propanoate 6b**



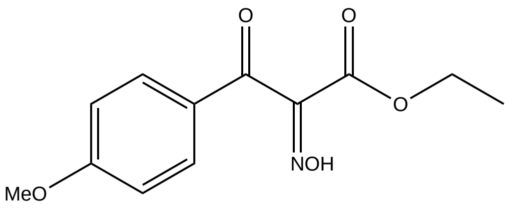

Method B: Yield (2.47 g, 73%); Light brown solid; m.p. 133-136°C; 17:1 mixture of *E/Z* isomers; $\nu_{max}$/cm$^{-1}$ 3312 (O-H), 2985 (C-H), 1721 (C=O), 1678 (C=O), 1605 (C=N); $\delta_{H\ (Major\ isomer)}$ (400 MHz, $CDCl_3$) 1.26 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 2.43 (3H, s, $CH_3$), 4.30 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.31 (2H, d, *J*=8.3 Hz, Ar-H), 7.78 (2H, d, *J*=8.3 Hz, Ar-H); $\delta_{C\ (Major\ isomer)}$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 22.0 ($CH_3$), 62.7 ($OCH_2CH_3$), 129.5 (Ar-C), 129.9 (Ar-C), 132.0 (Ar-C), 146.2 (Ar-C), 149.8 (C2), 160.8 (C1), 189.5 (C3); LRMS (ESI$^-$) *m/z*: 234.1 ([M – H]$^-$ 98%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{12}H_{13}NO_4Na$, 258.0737, found 258.0738.

**Ethyl 3-(4-butylphenyl)-2-(hydroxyimino)-3-oxopropanoate 6c**



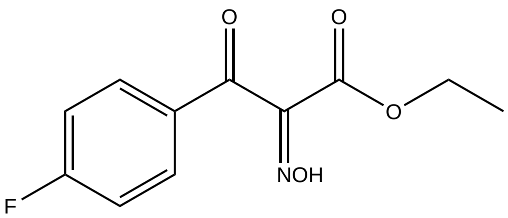

Method B: Yield (3.19 g, 83%); Thick orange oil; $\nu_{max}$/cm$^{-1}$ 3256 (O-H), 2958 (C-H), 2932 (C-H), 2861 (C-H), 1724 (C=O), 1680 (C=O), 1605 (C=N); 3.8:1 mixture of *E/Z* isomers; $\delta_{H\ (Major\ isomer)}$ (400 MHz, $CDCl_3$) 0.94 (3H, m, $CH_2CH_3$), 1.28 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.37 (2H, m, $CH_2CH_3$), 1.62 (2H, m, $CH_2CH_2$), 2.68 (2H, m, $CH_2CH_2$), 4.33 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.30 (2H, d, *J*=8.4 Hz, Ar-H), 7.79 (2H, d, *J*=8.3 Hz, Ar-H); $\delta_{C\ (Major\ isomer)}$ (101 MHz, $CDCl_3$) 14.0 ($CH_2CH_3$), 14.1 ($OCH_2CH_3$), 22.4 ($CH_2CH_3$), 33.2 ($CH_2CH_2$), 36.0 ($CH_2CH_2$), 62.7 ($OCH_2CH_3$), 129.2 (Ar-C), 129.5 (Ar-C), 132.1 (Ar-C), 149.4 (Ar-C), 150.9 (C2), 161.3 (C1), 189.6 (C3); LRMS (ESI$^+$) *m/z*: 300.1 ([M + Na]$^+$ 52%); LRMS (ESI$^-$) *m/z*: 276.1 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{15}H_{18}NO_4$, 276.1241, found 276.1240.

**Ethyl 2-(hydroxyimino)-3-(4-methoxyphenyl)-3-oxopropanoate 6d**



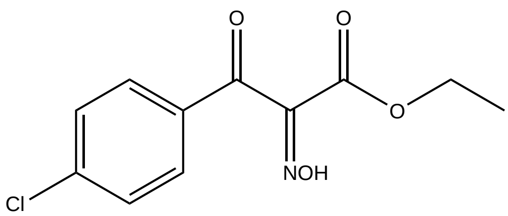
Method B: Yield (3.39 g, 93%); Orange oil; $v_{max}$/cm$^{-1}$ 3307 (O-H), 2984 (C-H), 1719 (C=O), 1668 (C=O), 1594 (C=N); 5.7:1 mixture of *E/Z* isomers; $\delta_{H\ (Major\ isomer)}$ (400 MHz, $CDCl_3$) 1.23 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.87 (3H, s, $OCH_3$), 4.28 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 6.96 (2H, d, *J*=8.9 Hz, Ar-H), 7.83 (2H, d, *J*=8.9 Hz, Ar-H), 9.99 (1H, br s, OH); $\delta_{C\ (Major\ isomer)}$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 55.8 ($OCH_3$), 62.7 ($OCH_2CH_3$), 114.5 (Ar-C), 127.6 (Ar-C), 131.9 (Ar-C), 150.0 (C2), 161.0 (C1), 165.0 (Ar-C), 188.4 (C3); LRMS (ESI$^+$) *m/z*: 274.1 ([M + Na]$^+$ 24%); LRMS (ESI$^-$) *m/z*: 250.1 ([M – H]$^-$ 97%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{12}H_{12}NO_5$, 250.0721, found 250.0722.

**Ethyl 3-(4-fluorophenyl)-2-(hydroxyimino)-3-oxopropanoate 6e**



Method B: Yield (2.72 g, 73%); Yellow solid; m.p. 144-147$^oC$; 3.6:1 mixture of *E/Z* isomers; $v_{max}$/cm$^{-1}$ 3307 (O-H), 2987 (C-H), 1723 (C=O), 1678 (C=O), 1597 (C=N); $\delta_{H\ (Major\ isomer)}$ (400 MHz, $CDCl_3$) 1.23 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.29 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.18 (2H, app t, *J*=8.9 Hz, Ar-H), 7.89 (2H, dd, *J*=5.3 Hz, 8.8 Hz, Ar-H); $\delta_{C\ (Major\ isomer)}$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 62.9 ($OCH_2CH_3$), 116.6 (d, *J*=22.3 Hz, Ar-C), 130.9 (d, *J*=2.6 Hz, Ar-C), 132.1 (d, *J*=10.0 Hz, Ar-C), 149.5 (C2), 160.9 (C1), 166.8 (d, *J*=257.6 Hz, Ar-C), 188.6 (C3); $\delta_{F\ (Major\ isomer)}$ (377 MHz, $CDCl_3$) -101.67; $\delta_{H\ (Minor\ isomer)}$ (400 MHz, $CDCl_3$) 1.35 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.40 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 7.09-8.08 (4H, m, Ar-H); $\delta_{C\ (Minor\ isomer)}$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 62.8 ($OCH_2CH_3$), 115.8 (d, *J*=21.7 Hz, Ar-C), 130.9 (Ar-C), 133.4 (d, *J*=9.5 Hz, Ar-C), 149.8 (C2), 161.6 (C1), 165.5 (d, *J*=256.7 Hz, Ar-C), 185.6 (C3); $\delta_{F\ (Minor\ isomer)}$ (377 MHz, $CDCl_3$) -103.40; LRMS (ESI$^+$) *m/z*: 262.0 ([M + Na]$^+$ 27%); LRMS (ESI$^-$) *m/z*: 238.0 ([M – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{11}H_9NO_4F$, 238.0521, found 238.0521.

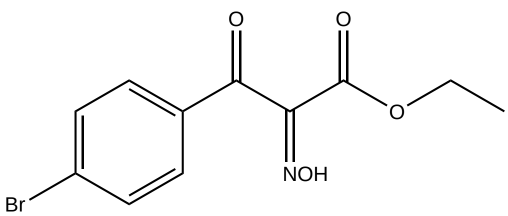
**Ethyl 3-(4-chlorophenyl)-2-(hydroxyimino)-3-oxopropanoate 6f**



Method B: Yield (2.31 g, 78%); Off-white solid; m.p. 148-150$^oC$; 3:1 mixture of *E/Z* isomers; $v_{max}$/cm$^{-1}$ 3291 (O-H), 2986 (C-H), 1725 (C=O), 1681 (C=O), 1588 (C=N); $\delta_{H\ (Major\ isomer)}$ (400 MHz, $CDCl_3$) 1.24

(3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 4.29 (2H, q, $J$=7.1 Hz, $OCH_2CH_3$), 7.48 (2H, d, $J$=8.6 Hz, Ar-H), 7.80 (2H, d, $J$=8.6 Hz, Ar-H); $\delta_{C\ (Major\ isomer)}$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 62.9 ($OCH_2CH_3$), 129.6 (Ar-C), 130.6 (Ar-C), 132.7 (Ar-C), 141.5 (Ar-C), 149.4 (C2), 160.8 (C1), 189.0 (C3); $\delta_{H\ (Minor\ isomer)}$ (400 MHz, $CDCl_3$) 1.35 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 4.40 (2H, q, $J$=7.1 Hz, $OCH_2CH_3$), 7.42 (2H, d, $J$=8.6 Hz, Ar-H), 7.95 (2H, d, $J$=8.7 Hz, Ar-H); $\delta_{C\ (Minor\ isomer)}$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 62.8 ($OCH_2CH_3$), 128.9 (Ar-C), 132.0 (Ar-C), 133.6 (Ar-C), 140.6 (Ar-C), 149.8 (C2), 161.5 (C1), 186.0 (C3); LRMS ($ESI^+$) $m/z$: 278.0 ($[M^{35} + Na]^+$ 32%), 280.0 ($[M^{37} + Na]^+$ 10%); LRMS ($ESI^-$) $m/z$: 254.0 ($[M^{35} – H]^-$ 98%), 255.9 ($[M^{37} – H]^-$ 31%); HRMS ($ESI^-$) $m/z$: $[M^{35} – H]^-$ calcd. for $C_{11}H_9NO_4Cl$, 254.0226, found 254.0226; $[M^{37} – H]^-$ calcd. for $C_{11}H_9NO_4Cl$, 256.0197, found 256.0196.

**Ethyl 3-(4-bromophenyl)-2-(hydroxyimino)-3-oxopropanoate 6g**



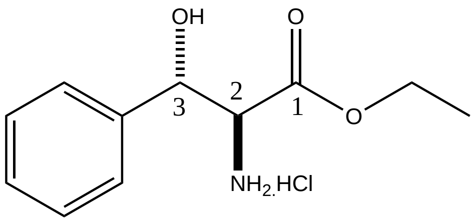

Method B: Yield (2.77 g, 86%); Off-white solid; m.p. 141-144°C; 3.5:1 mixture of $E/Z$ isomers; $\nu_{max}$/$cm^{-1}$ 3336 (O-H), 2986 (C-H), 1721 (C=O), 1682 (C=O), 1585 (C=N); $\delta_{H\ (Major\ isomer)}$ (400 MHz, $CDCl_3$) 1.24 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 4.29 (2H, q, $J$=7.1 Hz, $OCH_2CH_3$), 7.65 (2H, d, $J$=8.6 Hz, Ar-H), 7.72 (2H, d, $J$=8.6 Hz, Ar-H), 10.12 (1H, br s, OH); $\delta_{C\ (Major\ isomer)}$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 62.9 ($OCH_2CH_3$), 130.4 (Ar-C), 130.7 (Ar-C), 132.6 (Ar-C), 133.1 (Ar-C), 149.4 (C2), 160.7 (C1), 189.2 (C3); $\delta_{H\ (Minor\ isomer)}$ (400 MHz, $CDCl_3$) 1.35 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 4.40 (2H, q, $J$=7.2 Hz, $OCH_2CH_3$), 7.58 (2H, d, $J$=8.7 Hz, Ar-H), 7.86 (2H, d, $J$=8.6 Hz, Ar-H); $\delta_{C\ (Minor\ isomer)}$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 62.8 ($OCH_2CH_3$), 130.4 (Ar-C), 131.9 (Ar-C), 132.0 (Ar-C), 133.1 (Ar-C), 149.7 (C2), 161.5 (C1), 186.2 (C3); LRMS ($ESI^-$) $m/z$: 297.9 ($[M^{79} – H]^-$ 92%), 299.9 ($[M^{81} – H]^-$ 96%); HRMS ($ESI^-$) $m/z$: $[M^{79} – H]^-$ calcd. for $C_{11}H_9NO_4Br$, 297.9720, found 297.9719; $[M^{81} – H]^-$ calcd. for $C_{11}H_9NO_4Br$, 299.9699, found 299.9698.

**General procedure for the synthesis of *erythro*-phenylserine 7:**[8-9]

A solution of oxime **6a-g** (1 eq.) dissolved in EtOH and concentrated HCl was hydrogenated in the presence of 10% Pd-C under ambient pressure and temperature for a period of 1-3 d. The reaction mixture was then diluted with water and Pd-C was filtered off x4 under vacuum filtration. The filtrate was then separated between $Et_2O$

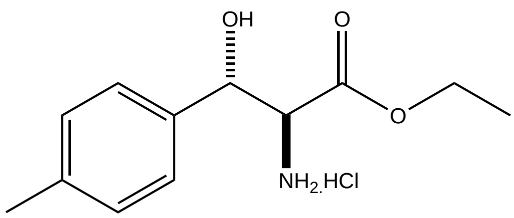
and $H_2O$ and the aqueous layer was concentrated under reduced pressure to give the desired *allo*-phenylserine as a hydrochloride salt **7a-f** and was used without further purification.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-phenylpropanoate hydrochloride salt 7a**



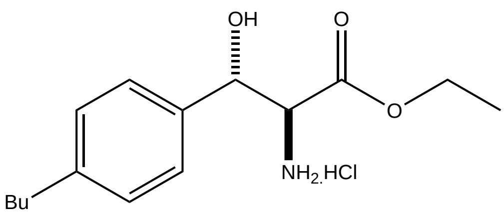

Yield (3.58 g, 75%); Off-white solid; m.p. 197-201°C (lit.[8] 176°C); $\nu_{max}$/cm$^{-1}$ 3311 (N-H/O-H), 3136 (N-H/O-H), 2990 (C-H), 2868 (C-H), 1743 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.12 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.15 (2H, dq, *J*=2.2 Hz, 7.2 Hz, $OCH_2CH_3$), 4.44 (1H, d, *J*=4.2 Hz, H2), 5.36 (1H, d, *J*=4.1 Hz, H3), 7.34-7.46 (5H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.5 (C2), 63.5 ($OCH_2CH_3$), 70.9 (C3), 125.9 (Ar-C), 128.8 (Ar-C), 129.0 (Ar-C), 136.9 (Ar-C), 167.4 (C1); LRMS (ESI$^+$) *m/z*: 210.4 ([M + H]$^+$ 7%), 419.7 ([2M + H]$^+$ 97%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{11}H_{16}NO_3$, 210.1125, found 210.1128.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-(*p*-tolyl)propanoate hydrochloride salt 7b**




Yield (735 mg, 27%); Off-white solid; m.p. 171-173°C; $\nu_{max}$/cm$^{-1}$ 3307 (N-H/O-H), 3134 (N-H/O-H), 2989 (C-H), 2908 (C-H), 2863 (C-H), 1745 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.19 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 2.36 (3H, s, $CH_3$), 4.22 (2H, dq, *J*=2.4 Hz, 7.1 Hz, $OCH_2CH_3$), 4.46 (1H, d, *J*=4.2 Hz, H2), 5.38 (1H, d, *J*=4.1 Hz, H3), 7.29-7.34 (4H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 20.2 ($CH_3$), 58.5 (C2), 63.6 ($OCH_2CH_3$), 70.8 (C3), 126.0 (Ar-C), 129.4 (Ar-C), 133.9 (Ar-C), 139.4 (Ar-C), 167.5 (C1); LRMS (ESI$^+$) *m/z*: 246.0 ([M + Na]$^+$ 15%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{12}H_{18}NO_3$, 224.1281, found 224.1282.

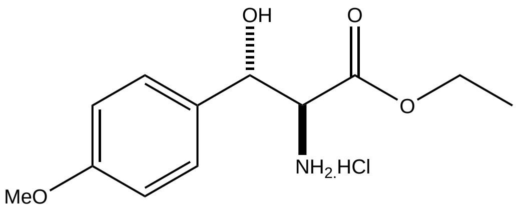
**Ethyl (2*S**,3*S**)-2-amino-3-(4-butylphenyl)-3-hydroxypropanoate hydrochloride salt 7c**




Yield (2.51 g, 72%); Brown gummy semi-solid; $\nu_{max}$/cm$^{-1}$ 3318 (N-H/O-H), 3135 (N-H/O-H), 2954 (C-H), 2927 (C-H), 2859 (C-H), 1747 (C=O); $\delta_H$ (400 MHz, $CD_3OD$) 0.92 (3H, m, $CH_2CH_3$), 1.12 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.35 (2H, m, $CH_2CH_3$), 1.59 (2H, m, $CH_2CH_2$), 2.62

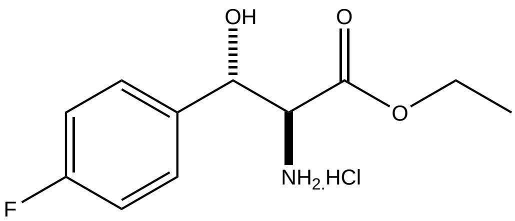
(2H, m, $CH_2CH_2$), 4.12 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 4.31 (1H, d, *J*=3.7 Hz, H2), 5.27 (1H, d, *J*=3.8 Hz, H3), 7.20 (2H, d, *J*=7.9 Hz, Ar-H), 7.30 (2H, d, *J*=8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CD_3OD$) 14.2 ($CH_3CH_2$), 14.2 ($OCH_2CH_3$), 23.2 ($CH_2CH_3$), 34.8 ($CH_2CH_2$), 36.2 ($CH_2CH_2$), 60.0 (C2), 63.3 ($OCH_2CH_3$), 72.1 (C3), 127.2 (Ar-C), 129.5 (Ar-C), 136.9 (Ar-C), 144.3 (Ar-C), 167.9 (C1); LRMS (ESI$^+$) *m/z*: 266.2 ([M + H]$^+$ 15%), 288.2 ([M + Na]$^+$ 9%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{15}H_{24}NO_3$, 266.1751, found 266.1751.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-(4-methoxyphenyl)propanoate hydrochloride salt 7d**



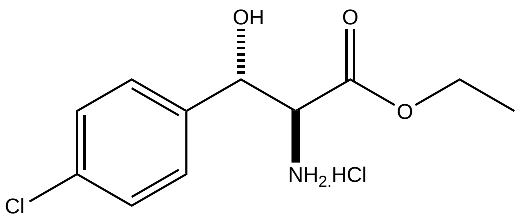

Yield (2.19 g, 67%); Off-white solid; m.p. 172-175°C (lit.[9] 167-170°C); $\nu_{max}/cm^{-1}$ 3325 (N-H/O-H), 3134 (N-H/O-H), 2906 (C-H), 2865 (C-H), 1740 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.19 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.86 (3H, s, $OCH_3$), 4.22 (2H, dq, *J*=1.7 Hz, 7.2 Hz, $OCH_2CH_3$), 4.46 (1H, d, *J*=4.3 Hz, H2), 5.37 (1H, d, *J*=4.4 Hz, H3), 7.07 (2H, d, *J*=8.8 Hz, Ar-H), 7.37 (2H, d, *J*=8.6 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.1 ($OCH_2CH_3$), 55.4 ($OCH_3$), 58.5 (C2), 63.5 ($OCH_2CH_3$), 70.6 (C3), 114.3 (Ar-C), 127.5 (Ar-C), 129.5 (Ar-C), 159.2 (Ar-C), 167.5 (C1); LRMS (ESI$^+$) *m/z*: 240.1 ([M + H]$^+$ 11%), 479.2 ([2M + H]$^+$ 74%), 501.2 ([2M + Na]$^+$ 37%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{12}H_{18}NO_4$, 240.1230, found 240.1232.

**Ethyl (2*S**,3*S**)-2-amino-3-(4-fluorophenyl)-3-hydroxypropanoate hydrochloride salt 7e**



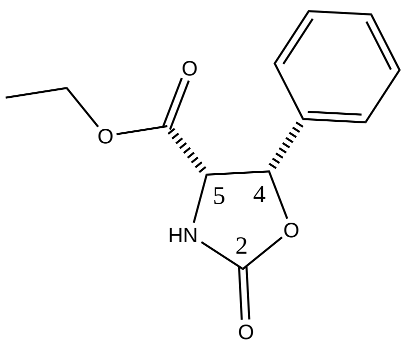

Yield (1.00 g, 66%); Off-white solid; m.p. 155-161°C; $\nu_{max}/cm^{-1}$ 3325 (N-H/O-H), 3138 (N-H/O-H), 2908 (C-H), 2868 (C-H), 1739 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.19 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.23 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 4.50 (1H, d, *J*=4.1 Hz, H2), 5.43 (1H, d, *J*=4.1 Hz, H3), 7.23 (2H, app. t, *J*=8.8 Hz, Ar-H), 7.44 (2H, dd, *J*=5.2 Hz, 8.5 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.5 (C2), 63.6 ($OCH_2CH_3$), 70.4 (C3), 115.7 (d, *J*=21.9 Hz, Ar-C), 128.0 (d, *J*=8.6 Hz, Ar-C), 133.1 (d, *J*=3.0 Hz, Ar-C), 162.7 (d, *J*=244.7 Hz, Ar-C), 167.4 (C1); $\delta_F$ (376 MHz, $D_2O$) -113.80; LRMS (ESI$^+$) *m/z*: 228.1 ([M + H]$^+$ 49%), 250.1 ([M + Na]$^+$ 20%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{11}H_{15}NO_3F$, 228.1030, found 228.1030.

**Ethyl (2*S**,3*S**)-2-amino-3-(4-chlorophenyl)-3-hydroxypropanoate hydrochloride salt 7f**




Yield (728 mg, 45%, contaminated with an unidentified impurity); Off-white solid; m.p. 180-182°C (lit.[10] 168-170°C); $v_{max}$/cm$^{-1}$ 3319 (N-H/O-H), 3140 (N-H/O-H), 2906 (C-H), 2862 (C-H), 1738 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.16 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.21 (2H, m, $OCH_2CH_3$), 4.51 (1H, d, *J*=4.0 Hz, H2), 5.42 (1H, d, *J*=3.8 Hz, H3), 7.40 (2H, d, *J*=8.5 Hz, Ar-H), 7.50 (2H, d, *J*=8.6 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.3 (C2), 63.6 ($OCH_2CH_3$), 70.4 (C3), 127.5 (Ar-C), 128.8 (Ar-C), 134.0 (Ar-C), 136.0 (Ar-C), 167.3 (C1); LRMS (ESI$^+$) *m/z*: 266.1 ([$M^{35}$ + Na]$^+$ 4%); HRMS (ESI$^+$) *m/z*: [$M^{35}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Cl$, 244.0735, found 244.0736; [$M^{37}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Cl$, 246.0705, found 246.0707.

**Synthesis of ethyl (4*S**,5*S**)-2-oxo-5-phenyloxazolidine-4-carboxylate 8:**[1,11]




Ethyl ester hydrochloride **7a** (1.0 eq.) was suspended in THF and triethylamine (1.2 eq.) was added and stirred at rt for 5 mins and 1,1'-carbonyldiimidazole (CDI) (1.8 eq.) was then added and the solution was stirred overnight at rt. The reaction mixture was then quenched with sat. $NH_4Cl$ (aq.), extracted with EtOAc, washed with brine, dried over $Na_2SO_4$, filtered, and concentrated *in-vacuo* to furnish oxazolidinone **8**. Yield (316 mg, Quantitative); Colourless oil; $v_{max}$/cm$^{-1}$ 1747 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.79 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.60 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 3.76 (1H, m, $OCH_2CH_3$), 4.66 (1H, d, *J*=9.1 Hz, H5), 5.83 (1H, d, *J*=9.1 Hz, H4), 6.39 (1H, br s, NH), 7.29-7.42 (5H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 60.0 (C5), 61.8 ($OCH_2CH_3$), 79.4 (C4), 126.5 (Ar-C), 128.5 (Ar-C), 129.4 (Ar-C), 134.2 (Ar-C), 159.1 (C2), 168.7 (C=O); LRMS (ESI$^+$) *m/z*: 258.0 ([M + Na]$^+$ 57%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{12}H_{13}NO_4Na$, 258.0737, found 258.0738.

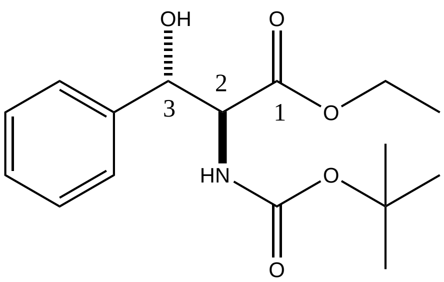
**General procedure for the synthesis of Boc-protected amino esters 9:**

**Method A:** Amino ester **7a** (1 eq.) was suspended in DCM and cooled to 0°C. $Et_3N$ (1.1 eq.) and $Boc_2O$ (1.1-1.2 eq.) was added dropwise at 0°C. The reaction mixture was then heated to reflux overnight. The mixture was then left to cool to rt and then washed with sat. $NH_4Cl$ (aq.), brine, dried over $MgSO_4$, filtered and the solvent was evaporated *in-vacuo*. The reaction mixture was then purified by flash column chromatography to obtain the desired product **9a**.

**Method B:**[12] Boc-protected hemimalonate **27c** (1 eq.), $Et_3N$ (1 eq.) and aldehyde (oil) (4 eq.) was stirred at 50°C for 48 h under an atmosphere of $N_2$ (caution should be taken due to the internal build-up of $CO_2$). The reaction mixture was then directly purified by flash column chromatography to obtain the desired product.

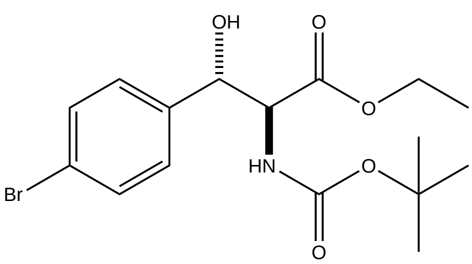
**Method C:**[12] Boc-protected hemimalonate **27c** (1.eq.), $Et_3N$ (1 eq.) and aldehyde (solid) (4 eq.) dissolved in THF (3 M) was stirred at 50°C for 48 h under an atmosphere of $N_2$ (caution should be taken due to the internal build-up of $CO_2$). The reaction mixture was then directly purified by flash column chromatography to obtain the desired product.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-phenylpropanoate 9a**



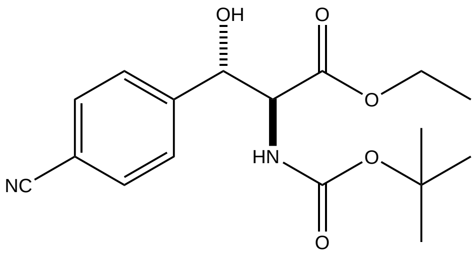

Method A: Yield (1.80 g, 75%); Method B: Yield (3.39 g, 79%); White solid; m.p. 110-115°C (lit.[13] 88-89°C); $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.50; $\nu_{max}$/cm$^{-1}$ 3438 (O-H), 2980 (C-H), 1710 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.11 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.36 (9H, s, $C(CH_3)_3$), 3.98 (1H, br s, OH), 4.06 (2H, q, *J*=7.2 Hz, $OCH_2CH_3$), 4.61 (1H, br dd, *J*=3.9 Hz, 7.9 Hz, H2), 5.12 (1H, br m, H3), 5.25 (1H, br d, *J*=7.6 Hz, NH), 7.19-7.26 (5H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 59.9 (C2), 61.8 ($OCH_2CH_3$), 75.2 (C3), 80.7 ($C(CH_3)_3$), 126.2 (Ar-C), 128.1 (Ar-C), 128.3 (Ar-C), 139.4 (Ar-C), 156.5 (C=O), 169.9 (C1); LRMS (ESI$^+$) *m/z*: 332.2 ([M + Na]$^+$ 95%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{16}H_{23}NO_5Na$, 332.1468, found 332.1468.

**Ethyl (2*S**,3*S**)-3-(4-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxypropanoate 9b**



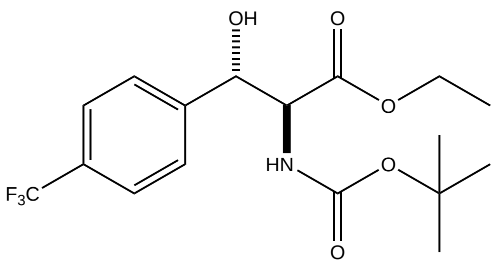

Method C: Yield (1.01 g, 64%); White solid; m.p. 136-140°C (lit.[13] 123-124°C); $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.48; $\nu_{max}$/cm$^{-1}$ 3426 (O-H), 2980 (C-H), 1696 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.22 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.44 (9H, s, $C(CH_3)_3$), 4.16 (2H, m, $OCH_2CH_3$), 4.65 (1H, br dd, *J*=3.7 Hz, 7.3 Hz, H2), 5.16 (1H, br d, *J*=3.7 Hz, H3), 5.30 (1H, br m, NH), 7.15 (2H, d, $J$=8.1 Hz, Ar-H), 7.45 (2H, d, $J$=8.3 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 59.9 (C2), 62.1 ($OCH_2CH_3$), 74.9 (C3), 81.0 ($C(CH_3)_3$), 122.0 (Ar-C), 128.0 (Ar-C), 131.4 (Ar-C), 138.6 (Ar-C), 156.7 (C=O), 169.6 (C1); LRMS (ESI$^+$) *m/z*: 410.0 ([$M^{79}$ + Na]$^+$ 95%), 412.0 ([$M^{81}$ + Na]$^+$ 86%); HRMS (ESI$^+$) *m/z*: [$M^{79}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5BrNa$, 410.0574, found 410.0573; [$M^{81}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5BrNa$, 412.0554, found 412.0551.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-(4-cyanophenyl)-3-hydroxypropanoate 9c**




Method C: Yield (930 mg, 69%); Pale yellow oil that solidified overnight to a white solid; m.p. 109-113°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.40; $\nu_{max}$/cm$^{-1}$ 3432 (O-H), 2981 (C-H), 2229 (C≡N), 1696 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.20 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 1.43 (9H, s, $C(CH_3)_3$), 4.16 (2H, q, $J$=7.1 Hz, $OCH_2CH_3$), 4.40 (1H, br s, OH), 4.67 (1H, br dd, $J$=3.5 Hz, 7.0 Hz, H2), 5.25 (1H, br d, $J$=3.3 Hz, H3), 5.37 (1H, br d, $J$=6.9 Hz, NH), 7.41 (2H, d, $J$=8.0 Hz, Ar-H), 7.62 (2H, d, $J$=8.3 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.3 ($(CH_3)_3$), 60.0 (C2), 62.2 ($OCH_2CH_3$), 74.9 (C3), 81.2 ($C(CH_3)_3$), 111.8 (Ar-C), 118.8 (C≡N), 127.1 (Ar-C), 132.1 (Ar-C), 145.1 (Ar-C), 156.6 (C=O), 169.2 (C1); LRMS (ESI$^+$) *m/z*: 357.2 ([M + Na]$^+$ 10%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{17}H_{22}N_2O_5Na$, 357.1421, found 357.1421.

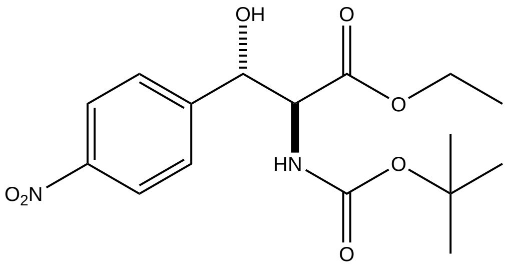
**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-(4-(trifluoromethyl)phenyl)-propanoate 9d**




Method B: Yield (1.09 g, 62%); Pale yellow oil that solidified to a white solid overnight; m.p. 111-115°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.53; $\nu_{max}$/cm$^{-1}$ 3430 (O-H), 2982 (C-H), 1692 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.18 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 1.43 (9H, s, $C(CH_3)_3$), 4.15 (2H, q, $J$=7.1 Hz, $OCH_2CH_3$), 4.69 (1H, br dd, $J$=3.7 Hz, 7.6 Hz, H2), 5.25 (1H, br d, $J$=3.5 Hz, H3), 5.36 (1H, br d, $J$=7.2 Hz, NH), 7.40 (2H, d, $J$=8.1 Hz, Ar-H), 7.58 (2H, d, $J$=8.1 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.3 ($(CH_3)_3$), 59.9 (C2), 62.1 ($OCH_2CH_3$), 74.9 (C3), 81.1 ($C(CH_3)_3$), 124.2 (q, $J$=272.3 Hz, $CF_3$), 125.2 (q, $J$=3.8 Hz, Ar-C), 126.7 (Ar-C), 130.3 (q, $J$=32.4 Hz, Ar-C), 143.7 (Ar-C), 156.6

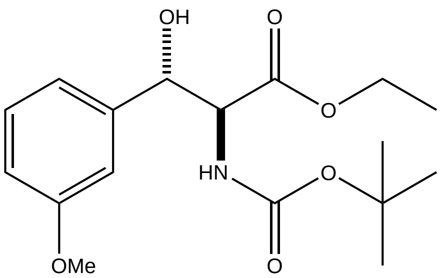
(C=O), 169.5 (C1); $\delta_F$ (376 MHz, $CDCl_3$) -62.57; LRMS (ESI$^+$) *m/z*: 400.2 ([M + Na]$^+$ 52%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{17}H_{22}F_3NO_5Na$, 400.1342, found 400.1343.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-(4-nitrophenyl)propanoate 9e**



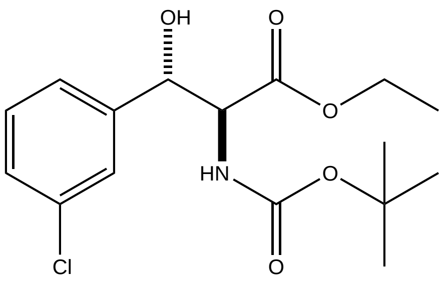

Method C: Yield (1.15 g, 73%); Pale yellow solid; m.p. 117-120°C (lit.[13] 108°C); $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.38; $\nu_{max}$/cm$^{-1}$ 3416 (O-H), 2981 (C-H), 1735 (C=O), 1694 (C=O), 1520 (N-O); $\delta_H$ (400 MHz, $CDCl_3$) 1.21 (3H, t, *J*=6.9 Hz, $OCH_2CH_3$), 1.43 (9H, s, $C(CH_3)_3$), 4.18 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 4.69 (1H, br dd, *J*=3.5 Hz, 7.0 Hz, H2), 5.31 (1H, br d, *J*=3.3 Hz, H3), 5.39 (1H, br d, *J*=6.8 Hz, NH), 7.47 (2H, d, *J*=8.4 Hz, Ar-H), 8.18 (2H, d, *J*=8.8 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 28.3 ($(CH_3)_3$), 60.0 (C2), 62.3 ($OCH_2CH_3$), 74.9 (C3), 81.3 ($C(CH_3)_3$), 123.5 (Ar-C), 127.2 (Ar-C), 147.1 (Ar-C), 147.7 (Ar-C), 156.7 (C=O), 169.1 (C1); LRMS (ESI$^+$) *m/z*: 377.0 ([M + Na]$^+$ 9%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{16}H_{22}N_2O_7Na$, 377.1319, found 377.1318.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-(3-methoxyphenyl)propanoate 9f**



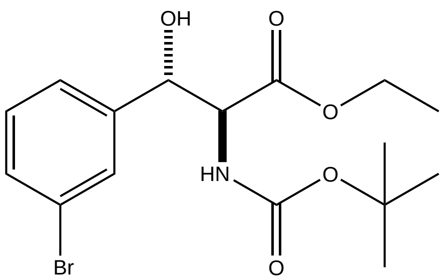

Method B: Yield (995 mg, 69%); White solid; m.p. 108-110°C; $R_f$ (50% EtOAc in Pet. Ether 40:60) 0.70; $\nu_{max}$/cm$^{-1}$ 3435 (O-H), 2979 (C-H), 1701 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.22 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.45 (9H, s, $C(CH_3)_3$), 3.80 (3H, s, $OCH_3$), 4.02 (1H, br s, OH), 4.17 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 4.69 (1H, br dd, *J*=3.8 Hz, 7.9 Hz, H2), 5.19 (1H, br m, H3), 5.31 (1H, br d, *J*=7.5 Hz, NH), 6.81-6.85 (3H, m, Ar-H), 7.22-7.28 (1H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 55.3 ($OCH_3$), 59.9 (C2), 61.9 ($OCH_2CH_3$), 75.1 (C3), 80.8 ($C(CH_3)_3$), 111.8 (Ar-C), 113.7 (Ar-C), 118.5 (Ar-C), 129.4 (Ar-C), 141.1 (Ar-C), 156.6 (C=O), 159.8 (Ar-C), 169.9 (C1); LRMS (ESI$^+$) *m/z*: 362.2 ([M + Na]$^+$ 97%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{17}H_{25}NO_6Na$, 362.1574, found 362.1573.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-(3-chlorophenyl)-3-hydroxypropanoate 9g**



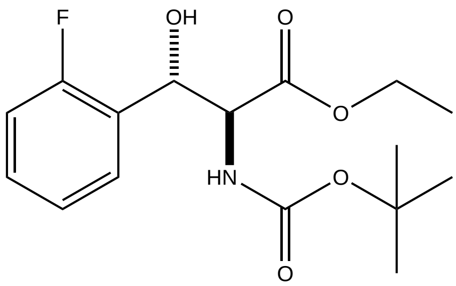
Method B: Yield (1.07 g, 72%); Pale yellow oil that solidified to a white solid overnight; m.p. 56-60°C; $R_f$ (40% EtOAc in Pet. Ether 40:60) 0.75; $\nu_{max}$/cm$^{-1}$ 3427 (O-H), 2980 (C-H), 1694 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.22 (3H, t, *J*=7.0 Hz, $OCH_2CH_3$), 1.45 (9H, s, $C(CH_3)_3$), 4.17 (2H, dq, *J*=1.8 Hz, 7.4 Hz, $OCH_2CH_3$), 4.66 (1H, br dd, *J*=3.6 Hz, 7.4 Hz, H2), 5.19 (1H, br d, *J*=3.6 Hz, H3), 5.37 (1H, br d, *J*=7.2 Hz, NH), 7.15 (1H, m, Ar-H), 7.25-7.27 (2H, m, Ar-H), 7.30 (1H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 60.0 (C2), 62.1 ($OCH_2CH_3$), 74.9 (C3), 81.1 ($C(CH_3)_3$), 124.4 (Ar-C), 126.6 (Ar-C), 128.2 (Ar-C), 129.6 (Ar-C), 134.4 (Ar-C), 141.7 (Ar-C), 156.7 (C=O), 169.5 (C1); LRMS (ESI$^+$) *m/z*: 366.0 ([$M^{35}$ + Na]$^+$ 96%), 368.0 ([$M^{37}$ + Na]$^+$ 39%); HRMS (ESI$^+$) *m/z*: [$M^{35}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5ClNa$, 366.1079, found 366.1079; [$M^{37}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5ClNa$, 368.1050, found 368.1050.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-(3-bromophenyl)-3-hydroxypropanoate 9h**



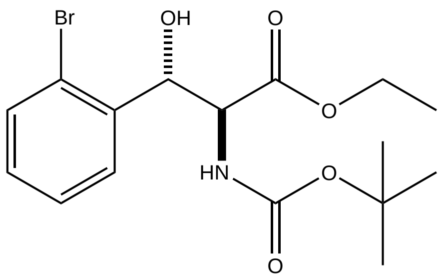
Method B: Yield (1.15 g, 70%); Colourless oil that solidified to a white solid overnight; m.p. 83-87°C; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.28; $\nu_{max}$/cm$^{-1}$ 3424 (O-H), 2979 (C-H), 1692 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.21 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.44 (9H, s, $C(CH_3)_3$), 4.15 (2H, m, $OCH_2CH_3$), 4.64 (1H, br dd, *J*=3.6 Hz, 7.4 Hz, H2), 5.17 (1H, br d, *J*=3.6 Hz, H3), 5.37 (1H, br d, *J*=7.2 Hz, NH), 7.18-7.19 (2H, m, Ar-H), 7.39-7.41 (1H, m, Ar-H), 7.44 (1H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 60.0 (C2), 62.1 ($OCH_2CH_3$), 74.8 (C3), 81.0 ($C(CH_3)_3$), 122.5 (Ar-C), 124.8 (Ar-C), 129.5 (Ar-C), 129.9 (Ar-C), 131.1 (Ar-C), 141.9 (Ar-C), 156.6 (C=O), 169.5 (C1); LRMS (ESI$^+$) *m/z*: 410.0 ([$M^{79}$ + Na]$^+$ 96%), 412.0 ([$M^{81}$ + Na]$^+$ 89%); HRMS (ESI$^+$) *m/z*: [$M^{79}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5BrNa$, 410.0574, found 410.0573; [$M^{81}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5BrNa$, 412.0554, found 412.0551.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-(2-fluorophenyl)-3-hydroxypropanoate 9i**



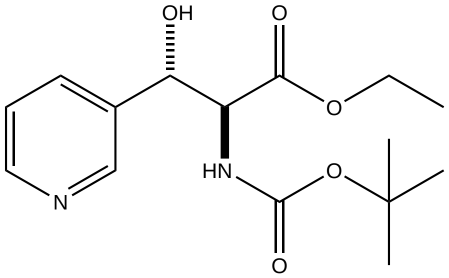
Method B: Yield (933 mg, 68%); Colourless oil; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.25; $\nu_{max}$/cm$^{-1}$ 3430 (O-H), 2980 (C-H), 1716 (C=O), 1696 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.21 (3H, t, *J*=7.0 Hz, $OCH_2CH_3$), 1.43 (9H, s, $C(CH_3)_3$), 4.15 (2H, m, $OCH_2CH_3$), 4.72 (1H, br m, H2), 5.38 (1H, br m, NH), 5.47 (1H, br m, H3), 7.00 (1H, m, Ar-H), 7.15 (1H, dt, *J*=1.2 Hz, 7.6 Hz, Ar-H), 7.27 (1H, m, Ar-H), 7.44 (1H, dt, *J*=1.8 Hz, 7.6 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 28.3 ($(CH_3)_3$), 59.3 (C2), 62.1 ($OCH_2CH_3$), 70.2 (C3), 80.8 ($C(CH_3)_3$), 115.1 (d, *J*=22.0 Hz, Ar-C), 124.2 (d, *J*=3.5 Hz, Ar-C), 126.7 (d, *J*=13.6 Hz, Ar-C), 128.3 (Ar-C), 129.6 (d, *J*=8.3 Hz, Ar-C), 156.7 (C=O), 159.7 (d, *J*=245.0 Hz, Ar-C), 169.8 (C1); $\delta_F$ (376 MHz, $CDCl_3$) -117.84; LRMS (ESI$^+$) *m/z*: 350.2 ([M + Na]$^+$ 96%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{16}H_{22}NO_5FNa$, 350.1374, found 350.1375.

**Ethyl (2*S**,3*S**)-3-(2-bromophenyl)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxypropanoate 9j**



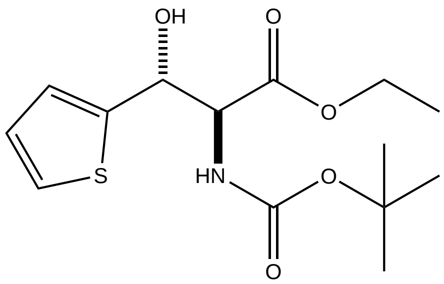
Method B: Yield (1.43 g, 88%); Colourless oil; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.33; $\nu_{max}$/cm$^{-1}$ 3428 (O-H), 2979 (C-H), 1717 (C=O), 1695 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.09 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.41 (9H, s, $C(CH_3)_3$), 3.78 (1H, br s, OH), 3.97-4.30 (2H, m, $OCH_2CH_3$), 4.73 (1H, br m, H2), 5.31-5.48 (2H, br m, NH, H3), 7.15 (1H, dt, *J*=1.8 Hz, 7.7 Hz, Ar-H), 7.32 (1H, dt, *J*=1.3 Hz, 7.6 Hz, Ar-H), 7.49 (1H, dd, *J*=1.7 Hz, 7.8 Hz, Ar-H), 7.52 (1H, dd, *J*=1.3 Hz, 8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 58.1 (C2), 61.7 ($OCH_2CH_3$), 73.9 (C3), 80.6 ($C(CH_3)_3$), 122.4 (Ar-C), 127.5 (Ar-C), 128.5 (Ar-C), 129.6 (Ar-C), 132.8 (Ar-C), 138.9 (Ar-C), 155.7 (C=O), 170.4 (C1); LRMS (ESI$^+$) *m/z*: 410.0 ([M$^{79}$ + Na]$^+$ 97%), 412.0 ([M$^{81}$ + Na]$^+$ 95%); HRMS (ESI$^+$) *m/z*: [M$^{79}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5BrNa$, 410.0574, found 410.0575; [M$^{81}$ + Na]$^+$ calcd. for $C_{16}H_{22}NO_5BrNa$, 412.0554, found 412.0554.

**Ethyl (2*S**,3*S**)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-(pyridin-3-yl)propanoate 9k**



Method B: Yield (2.09 g, 79%); Colourless oil; $R_f$ (100% EtOAc) 0.38; $\nu_{max}$/cm$^{-1}$ 3348 (O-H), 2980 (C-H), 1738 (C=O), 1709 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.20 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.43 (9H, s, $C(CH_3)_3$), 4.16 (2H, m, $OCH_2CH_3$), 4.68 (1H, br dd, *J*=3.9 Hz, 7.4 Hz, H2), 4.95 (1H, br s, OH), 5.22 (1H, br d, *J*=3.8 Hz, H3), 5.47 (1H, br d, *J*=7.4 Hz, NH), 7.27 (1H, m, Ar-H), 7.69 (1H, m, Ar-H), 8.48 (2H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.1 ($OCH_2CH_3$), 28.3 ($(CH_3)_3$), 59.9 (C2), 62.1 ($OCH_2CH_3$), 73.4 (C3), 81.0 ($C(CH_3)_3$), 123.3 (Ar-C), 134.4 (Ar-C), 135.5 (Ar-C), 148.0 (Ar-C), 149.1 (Ar-C), 156.5 (C=O), 169.5 (C1); LRMS (ESI$^+$) *m/z*: 311.2 ($[M + H]^+$ 36%), 333.2 ($[M + Na]^+$ 8%); HRMS (ESI$^+$) *m/z*: $[M + H]^+$ calcd. for $C_{15}H_{23}N_2O_5$, 311.1601, found 311.1600.

**Ethyl (2*S**,3*R**)-2-((*tert*-butoxycarbonyl)amino)-3-hydroxy-3-(thiophen-2-yl)propanoate 9l**



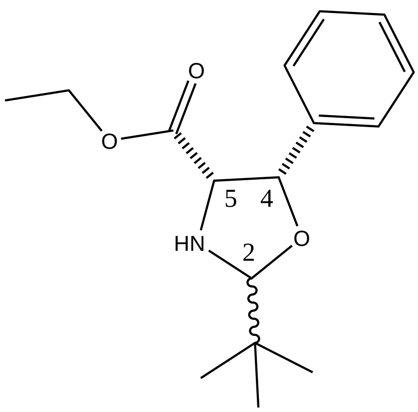
Method B: Yield (651 mg, 51%); White solid; m.p. 79-83°C; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.23; $\nu_{max}$/cm$^{-1}$ 3430 (O-H), 2979 (C-H), 1702 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.25 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.45 (9H, s, $C(CH_3)_3$), 4.20 (2H, q, *J*=7.2 Hz, $OCH_2CH_3$), 4.46 (1H, br d, *J*=5.9 Hz, OH), 4.75 (1H, br m, H2), 5.39 (1H, br m, NH), 5.48 (1H, br m, H3), 6.88 (1H, m, Ar-H), 6.96 (1H, dd, *J*=3.5 Hz, 5.1 Hz, Ar-H), 7.25 (1H, dd, *J*=1.2 Hz, 5.1 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.2 ($OCH_2CH_3$), 28.4 ($(CH_3)_3$), 59.8 (C2), 62.2 ($OCH_2CH_3$), 72.2 (C3), 81.1 ($C(CH_3)_3$), 124.4 (Ar-C), 125.3 (Ar-C), 126.8 (Ar-C), 143.0 (Ar-C), 157.0 (C=O), 169.3 (C1); LRMS (ESI$^+$) *m/z*: 338.2 ($[M + Na]^+$ 98%); HRMS (ESI$^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{14}H_{21}NO_5SNa$, 338.1033, found 338.1035.

**General procedure for the synthesis of oxazolidines 10:**[14-15]

**Method A:** Amino ester **7a-f** (1.0 eq.) was suspended in petroleum ether 40:60 and cooled to 0°C. Triethylamine (1.2 eq.) and trimethylacetaldehyde (1.1 eq.) was added. The reaction mixture was heated overnight to more than 100°C with continuous removal of water using a Dean-Stark apparatus. The white/brown precipitate was then filtered and washed with $Et_2O$. The combined filtrates were concentrated under reduced pressure to furnish a diastereomeric mixture of oxazolidines **10a-f** and was used without further purification.

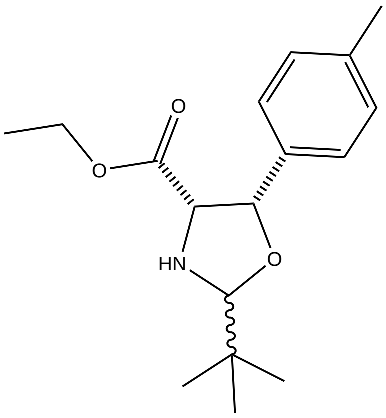
**Method B:** Amino ester **7a,g-k** (1.0 eq.) was suspended in petroleum ether 40:60 and cooled to 0°C. Triethylamine (1.2 eq.) and trimethylacetaldehyde (1.1 eq.) was added. The reaction mixture was heated overnight to more than 100°C with continuous removal of water using a Dean-Stark apparatus. The reaction mixture was then washed with brine, and the organic layer was dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to furnish a diastereomeric mixture of oxazolidines **10a,g-p** and was used without further purification.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-phenyloxazolidine-4-carboxylate 10a**



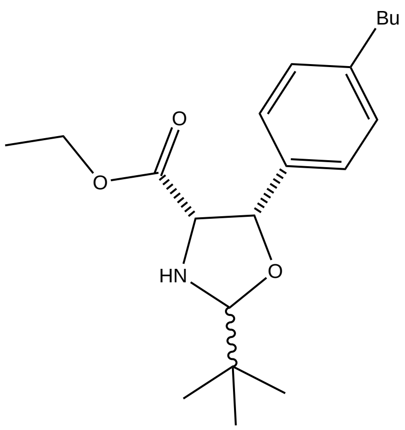

Method A: Yield (1.62 g, 81%); Method B: Yield (1.36 g, 57%); Pale yellow oil; $\nu_{max}$/cm$^{-1}$ 2958 (C-H), 2872 (C-H), 1734 (C=O); 5.6:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.70 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 2.72 (1H, br s, NH), 3.35 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.62 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 4.09 (1H, d, *J*=8.9 Hz, H5), 4.15 (1H, s, H2), 4.98 (1H, d, *J*=9.0 Hz, H4), 7.11-7.29 (5H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.7 (C5), 80.5 (C4), 99.0 (C2), 127.1 (Ar-C), 128.1 (Ar-C), 128.2 (Ar-C), 138.3 (Ar-C), 170.9 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.83 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.91 (9H, s, $C(CH_3)_3$), 2.72 (1H, br s, NH), 3.53 (1H, m, $OCH_2CH_3$), 3.73 (1H, m, $OCH_2CH_3$), 4.22 (1H, d, *J*=7.4 Hz, H5), 4.94 (1H, s, H2), 5.23 (1H, d, *J*=7.3 Hz, H4), 7.11-7.29 (5H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 25.2 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.0 ($OCH_2CH_3$), 65.6 (C5), 81.3 (C4), 101.5 (C2), 126.3-139.2 (Ar-C), 170.3 (C=O); LRMS (ESI$^+$) *m/z*: 278.2 ([M + H]$^+$ 77%), 300.2 ([M + Na]$^+$ 76%); HRMS (ESI$^+$) *m/z:* [M + H]$^+$ calcd. for $C_{16}H_{24}NO_3$, 278.1751, found 278.1749.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(*p*-tolyl)oxazolidine-4-carboxylate 10b**



Method A: Yield (766 mg, 97%); Yellow oil; $v_{max}$/cm$^{-1}$ 3306 (N-H), 2958 (C-H), 2871 (C-H), 1735 (C=O); 3.7:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.78 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 2.29 (3H, s, $CH_3$), 3.47 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.70 (1H, m, $OCH_2CH_3$), 4.13 (1H, d, *J*=9.0 Hz, H5), 4.20 (1H, s, H2), 5.02 (1H, d, *J*=9.0 Hz, H4), 7.08 (2H, m, Ar-H), 7.14 (2H, d, *J*=8.2 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 21.2 ($CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.6 (C5), 80.5 (C4), 98.9 (C2), 127.0 (Ar-C), 128.7 (Ar-C), 135.3 (Ar-C), 137.9 (Ar-C), 171.0 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.93 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.97 (9H, s, $C(CH_3)_3$), 2.29 (3H, s, $CH_3$), 3.65 (1H, m, $OCH_2CH_3$), 3.82 (1H, m, $OCH_2CH_3$), 4.26 (1H, d, *J*=7.3 Hz, H5), 4.99 (1H, s, H2), 5.26 (1H, d, *J*=7.3 Hz, H4), 7.08 (2H, m, Ar-H), 7.14 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 21.2 ($CH_3$), 25.2 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.0 ($OCH_2CH_3$), 65.6 (C5), 81.2 (C4), 101.4 (C2), 126.2 (Ar-C), 128.8 (Ar-C), 136.2 (Ar-C), 137.6 (Ar-C), 170.4 (C=O); LRMS (ESI$^+$) *m/z*: 292.2 ([M + H]$^+$ 20%), 314.2 ([M + Na]$^+$ 20%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{17}H_{26}NO_3$, 292.1907, found 292.1906.

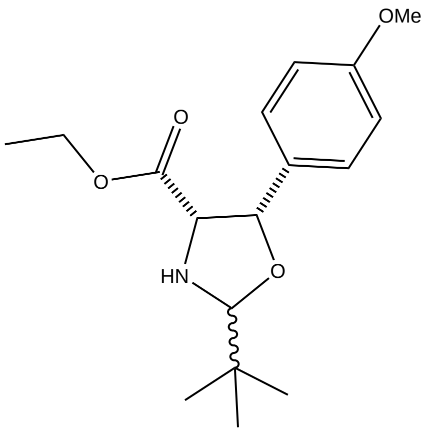
**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-butylphenyl)oxazolidine-4-carboxylate 10c**



Method A: Yield (2.51 g, 90%); Yellow oil; $v_{max}$/cm$^{-1}$ 2957 (C-H), 2931 (C-H), 2871 (C-H), 1735 (C=O); 5.3:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.75 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 0.90 (3H, m, $CH_3CH_2$), 1.14 (9H, s, $C(CH_3)_3$), 1.31 (2H, m, $CH_2CH_3$), 1.56 (2H, m, $CH_2CH_2$), 2.56 (2H, t, *J*=7.6 Hz, $CH_2CH_2$), 3.07 (1H, br s, NH), 3.43 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.69 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 4.17 (1H, d, *J*=9.0 Hz, H5), 4.21 (1H, s, H2), 5.04 (1H, d, *J*=9.0 Hz, H4), 7.09 (2H, d, *J*=8.1 Hz, Ar-H), 7.17 (2H, d, *J*=8.1 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.0 ($CH_3CH_2$), 22.3 ($CH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 33.8 ($CH_2CH_2$), 35.4 ($CH_2CH_2$), 61.2 ($OCH_2CH_3$), 65.4 (C5), 80.6 (C4), 98.7 (C2), 127.0 (Ar-C), 128.1 (Ar-C), 135.4 (Ar-C), 143.0 (Ar-C), 171.0 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.90 (6H, m, $CH_3CH_2$, $OCH_2CH_3$), 0.97 (9H, s, $C(CH_3)_3$), 1.31 (2H, m, $CH_2CH_3$), 1.56 (2H, m, $CH_2CH_2$), 2.56 (2H, m,

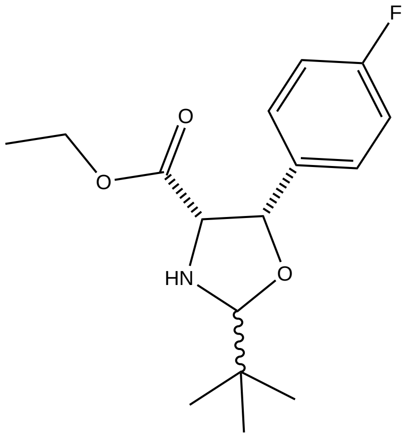
$CH_2CH_2$), 3.07 (1H, br s, NH), 3.69 (1H, m, $OCH_2CH_3$), 3.79 (1H, m, $OCH_2CH_3$), 4.27 (1H, d, *J*=7.4 Hz, H5), 4.99 (1H, s, H2), 5.26 (1H, d, *J*=7.4 Hz, H4), 7.09 (2H, m, Ar-H), 7.17 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.0 ($CH_3CH_2$), 22.4 ($CH_2CH_3$), 25.1 ($(CH_3)_3$), 33.5 ($CH_2CH_2$), 35.8 ($CH_2CH_2$), 36.5 ($C(CH_3)_3$), 60.9 ($OCH_2CH_3$), 65.6 (C5), 81.3 (C4), 101.3 (C2), 126.2 (Ar-C), 128.2 (Ar-C), 136.4 (Ar-C), 142.7 (Ar-C), 170.4 (C=O); LRMS (ESI$^+$) *m/z*: 356.2 ($[M + Na]^+$ 9%); HRMS (ESI$^+$) *m/z*: $[M + H]^+$ calcd. for $C_{20}H_{32}NO_3$, 334.2377, found 334.2376.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-methoxyphenyl)oxazolidine-4-carboxylate 10d**



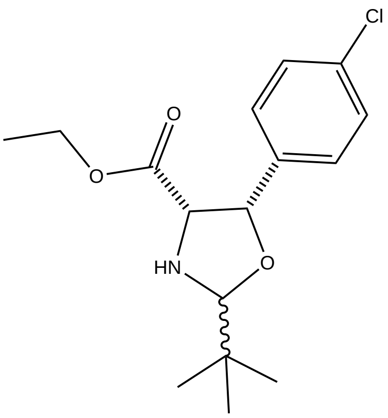

Method A: Yield (2.22 g, 97%); Orange oil; $\nu_{max}$/cm$^{-1}$ 3306 (N-H), 2958 (C-H), 2907 (C-H), 2872 (C-H), 1734 (C=O); 3.9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.82 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 3.50 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.72 (1H, m, $OCH_2CH_3$), 3.77 (3H, s, $OCH_3$), 4.13 (1H, d, *J*=9.0 Hz, H5), 4.19 (1H, s, H2), 5.02 (1H, d, *J*=8.9 Hz, H4), 6.82 (2H, d, *J*=8.8 Hz, Ar-H), 7.19 (2H, d, *J*=8.7 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.3 ($C(CH_3)_3$), 55.4 ($OCH_3$), 61.1 ($OCH_2CH_3$), 65.6 (C5), 80.1 (C4), 98.8 (C2), 113.5 (Ar-C), 128.2 (Ar-C), 130.5 (Ar-C), 159.6 (Ar-C), 171.0 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.95 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.98 (9H, s, $C(CH_3)_3$), 3.50 (1H, m, $OCH_2CH_3$), 3.72 (1H, m, $OCH_2CH_3$), 3.77 (3H, s, $OCH_3$), 4.25 (1H, d, *J*=7.3 Hz, H5), 4.99 (1H, s, H2), 5.26 (1H, d, *J*=7.3 Hz, H4), 6.82 (2H, m, Ar-H), 7.13 (2H, d, *J*=8.6 Hz, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 55.3 ($OCH_3$), 61.0 ($OCH_2CH_3$), 65.6 (C5), 81.0 (C4), 101.3 (C2), 113.5 (Ar-C), 127.5 (Ar-C), 131.3 (Ar-C), 159.4 (Ar-C), 170.4 (C=O); LRMS (ESI$^+$) *m/z*: 330.2 ($[M + Na]^+$ 35%); HRMS (ESI$^+$) *m/z*: $[M + H]^+$ calcd. for $C_{17}H_{26}NO_4$, 308.1856, found 308.1855.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-fluorophenyl)oxazolidine-4-carboxylate 10e**



Method A: Yield (993 mg, 89%); Yellow oil; $v_{max}$/cm$^{-1}$ 2979 (C-H), 2908 (C-H), 2874 (C-H), 1735 (C=O); 4.8:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.76 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 2.81 (1H, br s, NH), 3.43 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 3.68 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 4.07 (1H, d, *J*=9.0 Hz, H5), 4.13 (1H, s, H2), 4.97 (1H, d, *J*=9.0 Hz, H4), 6.91 (2H, app t, *J*=8.6 Hz, Ar-H), 7.18 (2H, dd, *J*=5.5 Hz, 8.7 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.3 ($OCH_2CH_3$), 65.6 (C5), 79.8 (C4), 99.1 (C2), 115.0 (d, *J*=21.5 Hz, Ar-C), 128.7 (d, *J*=8.2 Hz, Ar-C), 134.2 (d, *J*=3.1 Hz, Ar-C), 162.7 (d, *J*=246.2 Hz, Ar-C), 170.8 (C=O); $\delta_{F\ (Major\ diastereomer)}$ (376 MHz, $CDCl_3$) -114.17; $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.87 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.91 (9H, s, $C(CH_3)_3$), 2.81 (1H, br s, NH), 3.58 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 3.76 (1H, m, $OCH_2CH_3$), 4.21 (1H, d, *J*=7.4 Hz, H5), 4.92 (1H, s, H2), 5.20 (1H, d, *J*=7.3 Hz, H4), 6.91 (2H, m, Ar-H), 7.18 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.1 ($OCH_2CH_3$), 65.6 (C5), 80.7 (C4), 101.5 (C2), 115.1 (d, *J*=21.5 Hz, Ar-C), 128.0 (d, *J*=8.1 Hz, Ar-C), 135.1 (d, *J*=3.1 Hz, Ar-C), 162.6 (d, *J*=246.4, Ar-C), 170.3 (C=O); $\delta_{F\ (Minor\ diastereomer)}$ (376 MHz, $CDCl_3$) -114.54; LRMS (ESI$^+$) *m/z*: 296.2 ($[M + H]^+$ 24%); HRMS (ESI$^+$) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{23}NO_3F$, 296.1657, found 296.1656.

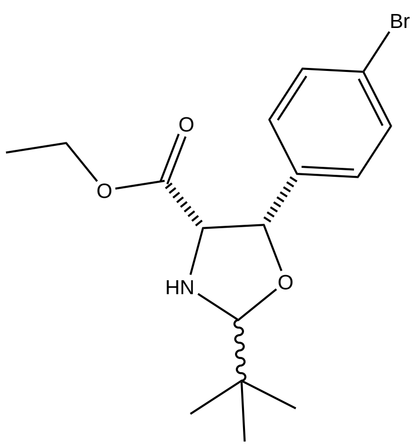
**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-chlorophenyl)oxazolidine-4-carboxylate 10f**



Method A: Yield (1.58 g, 74%); Orange oil; $v_{max}$/cm$^{-1}$ 3306 (N-H), 2960 (C-H), 2907 (C-H), 2872 (C-H), 1735 (C=O); 5.6:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.84 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 3.51 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.76 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 4.16 (1H, d, *J*=9.1 Hz, H5), 4.21 (1H, s, H2), 5.03 (1H, d, *J*=9.1 Hz, H4), 7.22 (2H, m, Ar-H), 7.27 (2H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 65.6 (C5), 79.8 (C4), 99.2 (C2), 128.2 (Ar-C), 128.4 (Ar-C), 134.0 (Ar-C), 137.0 (Ar-C), 170.7 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.95 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 0.98 (9H, s, $C(CH_3)_3$), 3.43 (1H, dq, *J*=7.2 Hz, 10.7

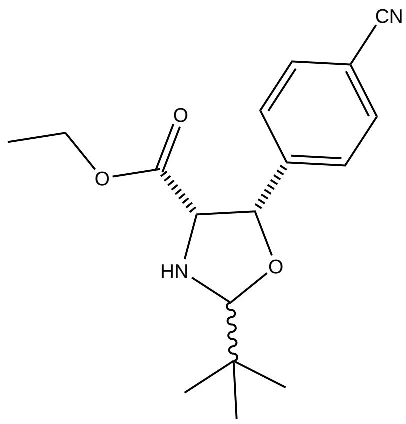
Hz, $OCH_2CH_3$), 3.68 (1H, m, $OCH_2CH_3$), 4.29 (1H, d, *J*=7.4 Hz, H5), 4.99 (1H, s, H2), 5.26 (1H, d, *J*=7.3 Hz, H4), 7.22 (2H, m, Ar-H), 7.27 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.6 (C5), 80.7 (C4), 101.6 (C2), 127.7 (Ar-C), 128.1 (Ar-C), 133.8 (Ar-C), 137.8 (Ar-C), 170.2 (C=O); LRMS (ESI$^+$) *m/z*: 312.2 ($[M^{35} + H]^+$ 34%); HRMS (ESI$^+$) *m/z*: $[M^{35} + H]^+$ calcd. for $C_{16}H_{23}NO_3Cl$, 312.1361, found 312.1361; $[M^{37} + H]^+$ calcd. for $C_{16}H_{23}NO_3Cl$, 314.1332, found 314.1333.

**Ethyl (4*S**,5*S**)-5-(4-bromophenyl)-2-(*tert*-butyl)oxazolidine-4-carboxylate 10g**



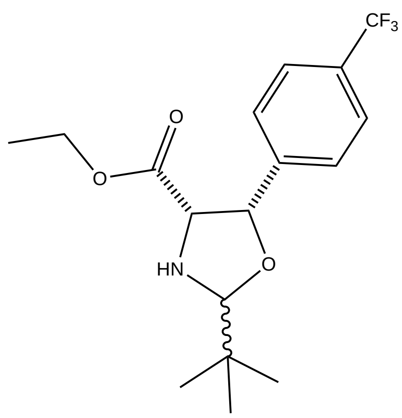

Method B: Yield (735 mg, 82%); Pale yellow oil; $\nu_{max}/cm^{-1}$ 3309 (N-H), 2959 (C-H), 2907 (C-H), 2872 (C-H), 1736 (C=O); 5.7:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.84 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 2.80 (1H, br s, NH), 3.51 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.75 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 4.15 (1H, d, *J*=9.0 Hz, H5), 4.20 (1H, s, H2), 5.00 (1H, d, *J*=9.0 Hz, H4), 7.15 (2H, d, *J*=8.3 Hz, Ar-H), 7.41 (2H, d, *J*=8.5 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 65.6 (C5), 79.9 (C4), 99.2 (C2), 122.1 (Ar-C), 128.8 (Ar-C), 131.2 (Ar-C), 137.5 (Ar-C), 170.7 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.95 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.97 (9H, s, $C(CH_3)_3$), 2.80 (1H, br s, NH), 3.66 (1H, m, $OCH_2CH_3$), 3.84 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.28 (1H, d, *J*=7.3 Hz, H5), 4.98 (1H, s, H2), 5.24 (1H, d, *J*=7.4 Hz, H4), 7.09 (2H, d, *J*=8.2 Hz, Ar-H), 7.41 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.6 (C5), 80.7 (C4), 101.6 (C2), 121.9 (Ar-C), 128.1 (Ar-C), 131.3 (Ar-C), 138.4 (Ar-C), 170.2 (C=O); LRMS (ESI$^+$) *m/z*: 356.0 ($[M^{79} + H]^+$ 46%), 358.0 ($[M^{81} + H]^+$ 42%), 378.2 ($[M^{79} + Na]^+$ 27%), 380.2 ($[M^{81} + Na]^+$ 25%); HRMS (ESI$^+$) *m/z*: $[M^{79} + H]^+$ calcd. for $C_{16}H_{23}NO_3Br$, 356.0856, found 356.0854; $[M^{81} + H]^+$ calcd. for $C_{16}H_{23}NO_3Br$, 358.0835, found 358.0833.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-cyanophenyl)oxazolidine-4-carboxylate 10h**



Method B: Yield (638 mg, 74%); Yellow oil; $v_{max}$/cm$^{-1}$ 3308 (N-H), 2961 (C-H), 2907 (C-H), 2873 (C-H), 2229 (C≡N), 1734 (C=O); 4.6:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.82 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 3.46 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.74 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.21 (1H, d, *J*=9.1 Hz, H5), 4.23 (1H, s, H2), 5.07 (1H, d, *J*=9.0 Hz, H4), 7.40 (2H, d, *J*=8.3 Hz, Ar-H), 7.58 (2H, d, *J*=8.4 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.5 ($OCH_2CH_3$), 65.6 (C5), 79.7 (C4), 99.6 (C2), 112.0 (Ar-C), 118.7 (C≡N), 127.8 (Ar-C), 131.9 (Ar-C), 143.9 (Ar-C), 170.3 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.92 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.98 (9H, s, $C(CH_3)_3$), 3.62 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.82 (1H, m, $OCH_2CH_3$), 4.34 (1H, d, *J*=7.4 Hz, H5), 5.01 (1H, s, H2), 5.29 (1H, d, *J*=7.4 Hz, H4), 7.35 (2H, d, *J*=8.2 Hz, Ar-H), 7.64 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.3 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.6 (C5), 80.6 (C4), 101.9 (C2), 111.8 (Ar-C), 118.7 (C≡N), 127.2 (Ar-C), 132.0 (Ar-C), 144.8 (Ar-C), 169.9 (C=O); LRMS (ESI$^+$) *m/z*: 303.2 ([M + H]$^+$ 95%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{17}H_{23}N_2O_3$ 303.1703, found 303.1703.

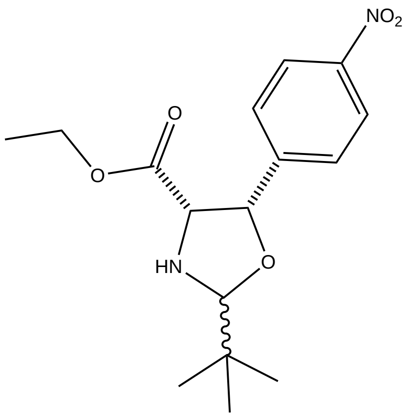
**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-(trifluoromethyl)phenyl)oxazolidine-4-carboxylate 10i**



Method B: Yield (770 mg, 85%); Yellow oil; $v_{max}$/cm$^{-1}$ 3309 (N-H), 2961 (C-H), 2909 (C-H), 2874 (C-H), 1736 (C=O); 5.3:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.76 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.15 (9H, s, $C(CH_3)_3$), 3.46 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.70 (1H, m, $OCH_2CH_3$), 4.20 (1H, d, *J*=9.0 Hz, H5), 4.23 (1H, s, H2), 5.10 (1H, d, *J*=9.0 Hz, H4), 7.40 (2H, d, *J*=8.5 Hz, Ar-H), 7.56 (2H, d, *J*=8.2 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 65.6 (C5), 79.9 (C4), 99.4 (C2), 125.0 (q, *J*=3.7 Hz, Ar-C), 127.5 (Ar-C), 130.5 (q, *J*=32.4 Hz, Ar-C), 142.5 (Ar-C), 170.6 (C=O); $\delta_{F\ (Major\ diastereomer)}$ (376 MHz, $CDCl_3$) -62.70; $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.87 (3H, m, $OCH_2CH_3$), 0.99 (9H, s, $C(CH_3)_3$), 3.61 (1H, m, $OCH_2CH_3$), 3.79 (1H, m, $OCH_2CH_3$), 4.33 (1H, d, *J*=7.3 Hz, H5), 5.02 (1H, s, H2), 5.32 (1H, d, *J*=7.4 Hz, H4), 7.35 (2H, m, Ar-H), 7.47 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101

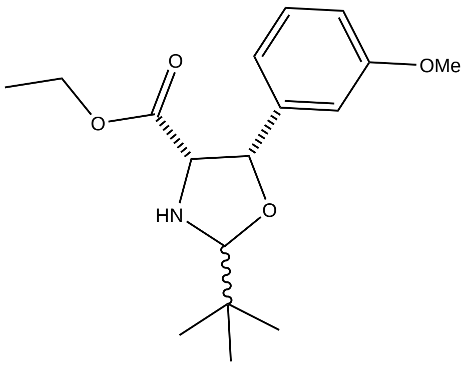
MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.4 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.7 (C5), 80.7 (C4), 101.8 (C2), 126.4 (Ar-C), 126.8 (Ar-C), 130.5 (Ar-C), 143.4 (Ar-C), 170.1 (C=O); $\delta_{F\ (Minor\ diastereomer)}$ (376 MHz, $CDCl_3$) -62.61; LRMS ($ESI^+$) *m/z*: 346.2 ($[M + H]^+$ 82%), 368.2 ($[M + Na]^+$ 24%); HRMS ($ESI^+$) *m/z*: $[M + H]^+$ calcd. for $C_{17}H_{23}NO_3F_3$, 346.1625, found 346.1623.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(4-nitrophenyl)oxazolidine-4-carboxylate 10j**



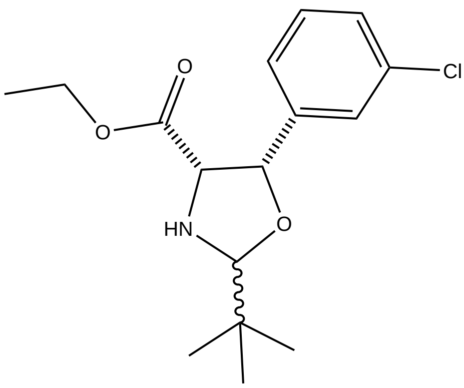

Method B: Yield (602 mg, 61%); Orange oil; $v_{max}/cm^{-1}$ 3305 (N-H), 2961 (C-H), 2908 (C-H), 2873 (C-H), 1736 (C=O), 1523 (N-O); 4.6:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.83 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.15 (9H, s, $C(CH_3)_3$), 3.47 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.75 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.24 (1H, d, *J*=9.1 Hz, H5), 4.25 (1H, s, H2), 5.13 (1H, d, *J*=9.1 Hz, H4), 7.46 (2H, d, *J*=8.6 Hz, Ar-H), 8.16 (2H, d, *J*=8.8 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.5 ($OCH_2CH_3$), 65.7 (C5), 79.5 (C4), 99.7 (C2), 123.3 (Ar-C), 127.9 (Ar-C), 145.9 (Ar-C), 147.8 (Ar-C), 170.3 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.94 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.99 (9H, s, $C(CH_3)_3$), 3.64 (1H, dq, *J*=7.2 Hz, 10.9 Hz, $OCH_2CH_3$), 3.84 (1H, m, $OCH_2CH_3$), 4.37 (1H, d, *J*=7.4 Hz, H5), 5.03 (1H, s, H2), 5.35 (1H, d, *J*=7.4 Hz, H4), 7.41 (2H, d, *J*=8.4 Hz, Ar-H), 8.16 (2H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.4 ($C(CH_3)_3$), 61.3 ($OCH_2CH_3$), 65.7 (C5), 80.4 (C4), 102.0 (C2), 123.4 (Ar-C), 127.3 (Ar-C), 146.8 (Ar-C), 147.7 (Ar-C), 169.9 (C=O); LRMS ($ESI^+$) *m/z*: 323.2 ($[M + H]^+$ 100%); HRMS ($ESI^+$) *m/z*: $[M + H]^+$ calcd. for $C_{16}H_{23}N_2O_5$, 323.1601, found 323.1600.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(3-methoxyphenyl)oxazolidine-4-carboxylate 10k**



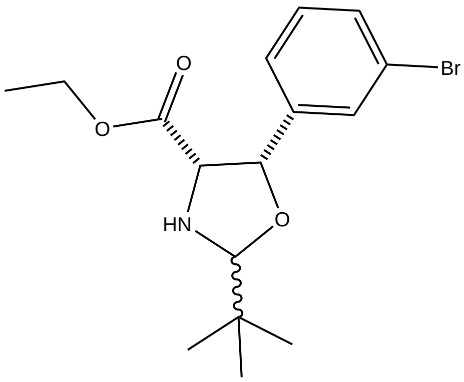

Method B: Yield (568 mg, 60%); Yellow oil; $v_{max}/cm^{-1}$ 3307 (N-H), 2958 (C-H), 2907 (C-H), 2872 (C-H), 1735 (C=O); 5.7:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.81 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 2.76 (1H, br s, NH), 3.50 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 3.72 (1H, m, $OCH_2CH_3$), 3.77 (3H, s, $OCH_3$), 4.15 (1H, d, *J*=9.0 Hz, H5), 4.20 (1H, s, H2), 5.02 (1H, d, *J*=9.0 Hz, H4), 6.78 (1H, m, Ar-H), 6.84 (2H, m, Ar-H), 7.18 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.8 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 55.3 ($OCH_3$), 61.2 ($OCH_2CH_3$), 65.7 (C5), 80.4 (C4), 99.1 (C2), 112.4 (Ar-C), 114.0 (Ar-C), 119.5 (Ar-C), 129.1 (Ar-C), 140.0 (Ar-C), 159.5 (Ar-C), 170.8 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.94 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 0.97 (9H, s, $C(CH_3)_3$), 2.76 (1H, br s, NH), 3.72 (1H, m, $OCH_2CH_3$), 3.77 (3H, s, $OCH_3$), 3.80 (1H, m, $OCH_2CH_3$), 4.27 (1H, d, *J*=7.3 Hz, H5), 4.99 (1H, s, H2), 5.26 (1H, d, *J*=7.3 Hz, H4), 6.78 (1H, m, Ar-H), 6.84 (2H, m, Ar-H), 7.18 (1H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 25.2 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 55.3 ($OCH_3$), 61.0 ($OCH_2CH_3$), 65.6 (C5), 81.2 (C4), 101.5 (C2), 112.1 (Ar-C), 113.3 (Ar-C), 118.7 (Ar-C), 129.2 (Ar-C), 140.9 (Ar-C), 159.6 (Ar-C), 170.3 (C=O); LRMS (ESI$^+$) *m/z*: 308.2 ($[M + H]^+$ 57%), 330.2 ($[M + Na]^+$ 75%); HRMS (ESI$^+$) *m/z*: $[M + H]^+$ calcd. for $C_{17}H_{26}NO_4$, 308.1856, found 308.1856.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(3-chlorophenyl)oxazolidine-4-carboxylate 10l**



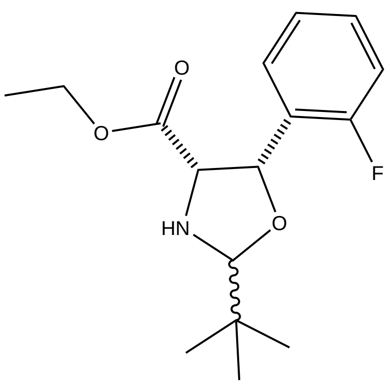

Method B: Yield (689 mg, 78%); Pale yellow oil; $\nu_{max}/cm^{-1}$ 3308 (N-H), 2960 (C-H), 2907 (C-H), 2873 (C-H), 1736 (C=O); 4.6:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.79 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 2.71 (1H, br s, NH), 3.46 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.69 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 4.09 (1H, d, *J*=9.1 Hz, H5), 4.13 (1H, s, H2), 4.94 (1H, d, *J*=9.1 Hz, H4), 7.08-7.24 (4H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.8 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 65.7 (C5), 79.7 (C4), 99.4 (C2), 125.1 (Ar-C), 127.3 (Ar-C), 128.3 (Ar-C), 129.4 (Ar-C), 134.0 (Ar-C), 140.6 (Ar-C), 170.6 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.90 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 0.91 (9H, s, $C(CH_3)_3$), 2.71 (1H, br s, NH), 3.63 (1H, m, $OCH_2CH_3$), 3.78 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.22 (1H, d, *J*=7.4 Hz, H5), 4.94 (1H, s, H2), 5.18 (1H, d, *J*=7.3 Hz, H4), 7.08-7.24 (4H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 25.2 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.2 ($OCH_2CH_3$), 65.6 (C5), 80.6 (C4), 101.7 (C2), 124.5 (Ar-C), 126.5 (Ar-C), 128.1 (Ar-C), 129.5 (Ar-C), 134.2 (Ar-C), 141.4 (Ar-C), 170.1 (C=O); LRMS (ESI$^+$) *m/z*: 312.0 ($[M^{35} + H]^+$ 97%), 314.2 ($[M^{37} + H]^+$ 28%); HRMS (ESI$^+$) *m/z*: $[M^{35} + H]^+$ calcd. for $C_{16}H_{23}NO_3Cl$, 312.1361, found 312.1362; $[M^{37} + H]^+$ calcd. for $C_{16}H_{23}NO_3Cl$, 314.1332, found 314.1334.

**Ethyl (4*S**,5*S**)-5-(3-bromophenyl)-2-(*tert*-butyl)oxazolidine-4-carboxylate 10m**



Method B: Yield (797 mg, 80%); Yellow oil; $\nu_{max}$/cm$^{-1}$ 3307 (N-H), 2959 (C-H), 2906 (C-H), 2872 (C-H), 1734 (C=O); 3.8:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.80 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 2.81 (1H, br s, NH), 3.47 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.69 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.08 (1H, d, *J*=8.9 Hz, H5), 4.13 (1H, s, H2), 4.93 (1H, d, *J*=8.9 Hz, H4), 7.07-7.43 (4H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.8 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 65.7 (C5), 79.7 (C4), 99.4 (C2), 122.1 (Ar-C), 125.6 (Ar-C), 129.7 (Ar-C), 130.2 (Ar-C), 131.2 (Ar-C), 140.9 (Ar-C), 170.5 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.90 (3H, m, $OCH_2CH_3$), 0.91 (9H, s, $C(CH_3)_3$), 2.81 (1H, br s, NH), 3.58 (1H, m, $OCH_2CH_3$), 3.78 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.22 (1H, d, *J*=7.4 Hz, H5), 4.92 (1H, s, H2), 5.17 (1H, d, *J*=7.3 Hz, H4), 7.07-7.43 (4H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.9 ($OCH_2CH_3$), 25.2 ($(CH_3)_3$), 36.5 ($C(CH_3)_3$), 61.3 ($OCH_2CH_3$), 65.7 (C5), 80.5 (C4), 101.7 (C2), 122.1-141.7 (Ar-C), 170.1 (C=O); LRMS (ESI$^+$) *m/z*: 356.0 ([M$^{79}$ + H]$^+$ 83%), 358.0 ([M$^{81}$ + H]$^+$ 77%), 378.0 ([M$^{79}$ + Na]$^+$ 69%), 380.0 ([M$^{81}$ + Na]$^+$ 69%); HRMS (ESI$^+$) *m/z*: [M$^{79}$ + H]$^+$ calcd. for $C_{16}H_{23}NO_3Br$, 356.0856, found 356.0860; [M$^{81}$ + H]$^+$ calcd. for $C_{16}H_{23}NO_3Br$, 358.0836, found 358.0839.

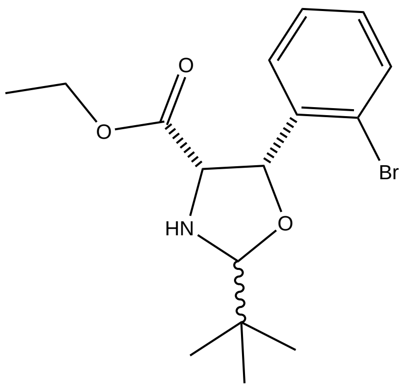
**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(2-fluorophenyl)oxazolidine-4-carboxylate 10n**



Method B: Yield (648 mg, 78%); Yellow oil; $\nu_{max}$/cm$^{-1}$ 3307 (N-H), 2960 (C-H), 2907 (C-H), 2873 (C-H), 1735 (C=O); 4.9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.82 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 3.47 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 3.74 (1H, m, $OCH_2CH_3$), 4.22 (1H, d, *J*=8.9 Hz, H5), 4.22 (1H, s, H2), 5.39 (1H, d, *J*=8.9 Hz, H4), 6.99 (1H, m, Ar-H), 7.08 (1H, m, Ar-H), 7.22 (1H, m, Ar-H), 7.36 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.3 ($OCH_2CH_3$), 64.5 (C5), 73.8 (d, *J*=4.5 Hz, C4), 99.0 (C2), 114.8 (d, *J*=21.3 Hz, Ar-C), 124.1 (d, *J*=3.4 Hz, Ar-C), 125.7

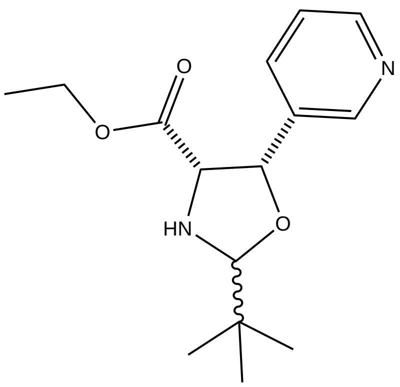
(d, $J$=12.6 Hz, Ar-C), 127.8 (d, $J$=3.7 Hz, Ar-C), 129.4 (d, $J$=8.2 Hz, Ar-C), 160.4 (d, $J$=247.4 Hz, Ar-C), 171.1 (C=O); $\delta_{F\ (Major\ diastereomer)}$ (376 MHz, $CDCl_3$) -118.03; $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.87 (3H, t, $J$=7.2 Hz, $OCH_2CH_3$), 0.99 (9H, s, $C(CH_3)_3$), 3.62 (1H, m, $OCH_2CH_3$), 3.78 (1H, m, $OCH_2CH_3$), 4.39 (1H, d, $J$=7.2 Hz, H5), 4.99 (1H, s, H2), 5.51 (1H, d, $J$=7.2 Hz, H4), 6.99 (1H, m, Ar-H), 7.08 (1H, m, Ar-H), 7.22 (1H, m, Ar-H), 7.36 (1H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 61.0 ($OCH_2CH_3$), 64.8 (C5), 75.4 (d, $J$=4.1 Hz, C4), 101.1 (C2), 114.8 (d, $J$=21.5 Hz, Ar-C), 124.1 (Ar-C), 125.7 (Ar-C), 127.8 (Ar-C), 129.4 (Ar-C), 160.1 (d, $J$=246.2 Hz, Ar-C), 170.7 (C=O); $\delta_{F\ (Minor\ diastereomer)}$ (376 MHz, $CDCl_3$) -117.59; LRMS (ESI$^+$) $m/z$: 296.1 ($[M + H]^+$ 98%), 318.1 ($[M + Na]^+$ 33%); HRMS (ESI$^+$) $m/z$: $[M + H]^+$ calcd. for $C_{16}H_{23}NO_3F$, 296.1656, found 296.1655.

**Ethyl (4*S**,5*S**)-5-(2-bromophenyl)-2-(*tert*-butyl)oxazolidine-4-carboxylate 10o**




Method B: Yield (993 mg, 77%); Yellow oil; $v_{max}/cm^{-1}$ 3305 (N-H), 2959 (C-H), 2906 (C-H), 2872 (C-H), 1733 (C=O); 5.7:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.80 (3H, t, $J$=7.2 Hz, $OCH_2CH_3$), 1.15 (9H, s, $C(CH_3)_3$), 3.24 (1H, br s, NH), 3.43 (1H, dq, $J$=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.71 (1H, dq, $J$=7.2 Hz, 10.6 Hz, $OCH_2CH_3$), 4.22 (1H, s, H2), 4.28 (1H, d, $J$=8.7 Hz, H5), 5.43 (1H, d, $J$=8.6 Hz, H4), 7.11 (1H, m, Ar-H), 7.25 (1H, m, Ar-H), 7.39 (1H, m, Ar-H), 7.49 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 25.8 ($(CH_3)_3$), 33.5 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 63.7 (C5), 79.5 (C4), 99.0 (C2), 123.3 (Ar-C), 127.4 (Ar-C), 128.0 (Ar-C), 129.3 (Ar-C), 132.2 (Ar-C), 137.6 (Ar-C), 171.3 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 1.02 (9H, s, $C(CH_3)_3$), 1.06 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 3.24 (1H, br s, NH), 3.54 (1H, m, $OCH_2CH_3$), 3.71 (1H, m, $OCH_2CH_3$), 4.56 (1H, d, $J$=7.0 Hz, H5), 5.04 (1H, s, H2), 5.46 (1H, d, $J$=7.1 Hz, H4), 7.11 (1H, m, Ar-H), 7.25 (1H, m, Ar-H), 7.39 (1H, m, Ar-H), 7.49 (1H, m, Ar-H); $\delta_{C\ (Minor\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.1 ($(CH_3)_3$), 35.4 ($C(CH_3)_3$), 60.8 ($OCH_2CH_3$), 64.1 (C5), 80.6 (C4), 101.0 (C2), 122.7 (Ar-C), 127.5 (Ar-C), 128.2 (Ar-C), 129.2 (Ar-C), 132.2 (Ar-C), 138.1 (Ar-C), 170.8 (C=O); LRMS (ESI$^+$) $m/z$: 356.0 ($[M^{79} + H]^+$ 7%), 358.0 ($[M^{81} + H]^+$ 7%); HRMS (ESI$^+$) $m/z$: $[M^{79} + H]^+$ calcd. for $C_{16}H_{23}NO_3Br$, 356.0856, found 356.0858; $[M^{81} + H]^+$ calcd. for $C_{16}H_{23}NO_3Br$, 358.0835, found 358.0838.

**Ethyl (4*S**,5*S**)-2-(*tert*-butyl)-5-(pyridin-3-yl)oxazolidine-4-carboxylate 10p**

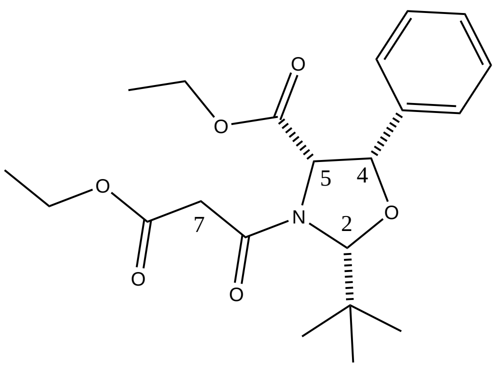


Method B: Yield (1.11 g, 57%); Yellow oil; $v_{max}$/cm$^{-1}$ 3306 (N-H), 2959 (C-H), 2907 (C-H), 2873 (C-H), 1734 (C=O); 4.9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.80 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 3.05 (1H, br s, NH), 3.50 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.73 (1H, dq, *J*=7.0 Hz, 10.7 Hz, $OCH_2CH_3$), 4.19 (1H, d, *J*=9.0 Hz, H5), 4.22 (1H, s, H2), 5.07 (1H, d, *J*=9.0 Hz, H4), 7.22 (1H, m, Ar-H), 7.30 (1H, m, Ar-H), 7.60 (1H, m, Ar-H), 8.52 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 33.4 ($C(CH_3)_3$), 61.4 ($OCH_2CH_3$), 65.7 (C5), 78.1 (C4), 99.5 (C2), 123.2 (Ar-C), 134.3 (Ar-C), 134.5 (Ar-C), 148.8 (Ar-C), 149.5 (Ar-C), 170.5 (C=O); $\delta_{H\ (Minor\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.91 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.97 (9H, s, $C(CH_3)_3$), 3.05 (1H, br s, NH), 3.65 (1H, m, $OCH_2CH_3$), 3.81 (1H, m, $OCH_2CH_3$), 4.33 (1H, d, *J*=7.4 Hz, H5), 4.99 (1H, s, H2), 5.30 (1H, d, *J*=7.6 Hz, H4), 7.10-8.52 (4H, m, Ar-H); LRMS (ESI$^+$) *m/z*: 279.2 ([M + H]$^+$ 96%), 301.2 ([M + Na]$^+$ 78%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{15}H_{23}N_2O_3$, 279.1703, found 279.1704.

**General procedure for the synthesis of malonamides 11:**[14]

To a stirring solution of oxazolidine **10a-p** (1.0 eq.) in anhydrous DCM at 0°C was added ethyl malonyl chloride (1.1 eq.) and pyridine (1.2 eq.) dropwise. The mixture was stirred at 0°C for 10-20 min and then refluxed overnight. The mixture was then left to cool to rt, washed with sat. $NH_4Cl$ (aq.), sat. $NaHCO_3$ (aq.), brine, dried over $Na_2SO_4$, filtered, concentrated under reduced pressure and purified by flash column chromatography to give *N*-acylated oxazolidines **11a-p**.

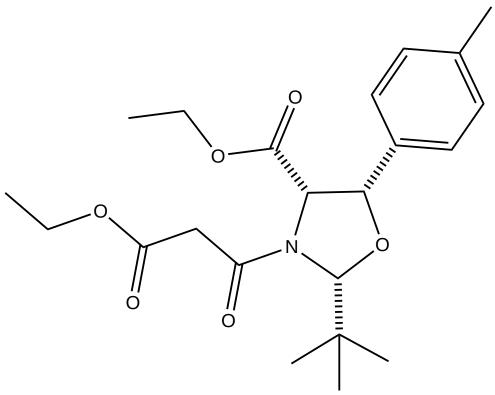
**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-phenyloxazolidine-4-carboxylate 11a**



Yield (2.95 g, 80%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.58; $v_{max}$/cm$^{-1}$ 2981 (C-H), 1739 (C=O), 1679 (C=O); 11.5:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.79 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.41 (1H, d, *J*=15.3 Hz, H7), 3.48 (1H, d,

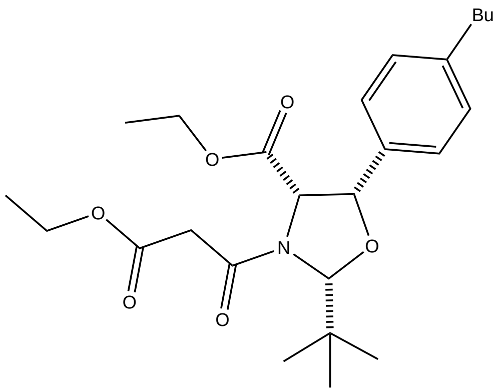
$J$=15.4 Hz, H7), 3.66 (1H, dq, $J$=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.80 (1H, dq, $J$=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 4.21 (2H, m, $OCH_2CH_3$), 4.80 (1H, br d, $J$=6.9 Hz, H5), 5.21 (1H, d, $J$=6.9 Hz, H4), 5.37 (1H, s, H2), 7.31-7.39 (5H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.9 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 44.0 (C7), 61.3 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 64.6 (C5), 80.5 (C4), 97.1 (C2), 126.5 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C), 135.1 (Ar-C), 167.4 (C=O), 168.1 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 414.2 ([M + Na]$^+$ 93%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{21}H_{29}NO_6Na$, 414.1887, found 414.1884.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(*p*-tolyl)oxazolidine-4-carboxylate 11b**



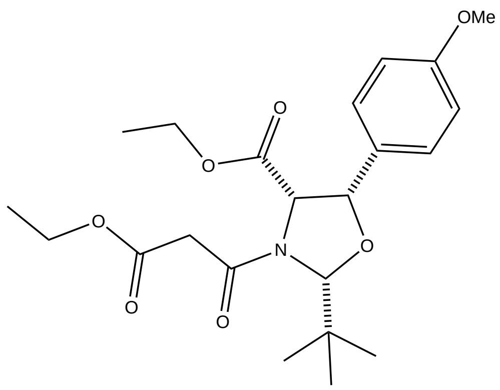

Yield (1.02 g, Quantitative); Red oil; $\nu_{max}$/cm$^{-1}$ 2981 (C-H), 1741 (C=O), 1680 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.82 (3H, t, $J$=7.2 Hz, $OCH_2CH_3$), 1.15 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, $J$=7.2 Hz, $OCH_2CH_3$), 2.35 (3H, s, $CH_3$), 3.42 (1H, d, $J$=15.4 Hz, H7), 3.47 (1H, d, $J$=15.4 Hz, H7), 3.71 (1H, dq, $J$=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.82 (1H, dq, $J$=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.22 (2H, m, $OCH_2CH_3$), 4.77 (1H, br d, $J$=6.9 Hz, H5), 5.18 (1H, d, $J$=6.9 Hz, H4), 5.36 (1H, s, H2), 7.15 (2H, d, $J$=7.9 Hz, Ar-H), 7.26 (2H, d, $J$=8.1 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 21.3 ($CH_3$), 27.0 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 44.0 (C7), 61.2 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 64.6 (C5), 80.5 (C4), 97.1 (C2), 126.5 (Ar-C), 129.0 (Ar-C), 132.0 (Ar-C), 138.4 (Ar-C), 167.4 (C=O), 168.1 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 428.2 ([M + Na]$^+$ 64%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{22}H_{31}NO_6Na$, 428.2044, found 428.2043.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-5-(4-butylphenyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11c**



Yield (1.94 g, 60%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.60; $\nu_{max}$/cm$^{-1}$ 2958 (C-H), 2932 (C-H), 2872 (C-H), 1743 (C=O), 1681 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.79 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.92 (3H, t, *J*=7.3 Hz, $CH_3CH_2$), 1.15 (9H, s, $C(CH_3)_3$), 1.32 (5H, m, $CH_2CH_3$, $OCH_2CH_3$), 1.57 (2H, m, $CH_2CH_2$), 2.60 (2H, m, $CH_2CH_2$), 3.42 (1H, d, *J*=15.4 Hz, H7), 3.46 (1H, d, *J*=15.3 Hz, H7), 3.67 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 3.81 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.77 (1H, br d, *J*=7.0 Hz, H5), 5.19 (1H, d, *J*=6.9 Hz, H4), 5.37 (1H, s, H2), 7.16 (2H, d, *J*=8.2 Hz, Ar-H), 7.28 (2H, d, *J*=8.1 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.0 ($CH_3CH_2$), 14.2 ($OCH_2CH_3$), 22.4 ($CH_2CH_3$), 27.0 ($(CH_3)_3$), 33.8 ($CH_2CH_2$), 35.5 ($CH_2CH_2$), 37.5 ($C(CH_3)_3$), 44.1 (C7), 61.2 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 64.7 (C5), 80.6 (C4), 97.1 (C2), 126.5 (Ar-C), 128.4 (Ar-C), 132.2 (Ar-C), 143.5 (Ar-C), 167.4 (C=O), 168.1 (C=O), 168.2 (C=O); LRMS (ESI$^+$) *m/z*: 470.2 ([M + Na]$^+$ 13%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{25}H_{37}NO_6Na$, 470.2513, found 470.2513.

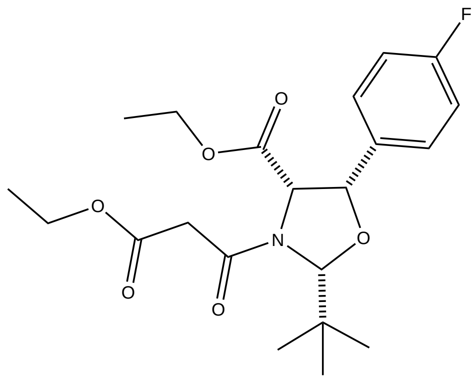
**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(4-methoxyphenyl)oxazolidine-4-carboxylate 11d**



Yield (3.13 g, Quantitative); Red oil; $\nu_{max}$/cm$^{-1}$ 2981 (C-H), 1742 (C=O), 1679 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.86 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.15 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.42 (1H, d, *J*=15.3 Hz, H7), 3.46 (1H, d, *J*=15.3 Hz, H7), 3.72 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.80 (3H, s, $OCH_3$), 3.86 (1H, m, $OCH_2CH_3$), 4.22 (2H, m, $OCH_2CH_3$), 4.75 (1H, br d, *J*=7.0 Hz, H5), 5.17 (1H, d, *J*=6.9 Hz, H4), 5.36 (1H, s, H2), 6.88 (2H, d, *J*=8.7 Hz, Ar-H), 7.30 (2H, d, *J*=8.5 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.9 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 44.0 (C7), 55.4 ($OCH_3$), 61.2 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 64.7 (C5), 80.3 (C4), 97.0 (C2), 113.7 (Ar-C), 127.0 (Ar-C), 127.8 (Ar-C), 159.9 (Ar-C), 167.3 (C=O), 168.1 (C=O), 168.2 (C=O);

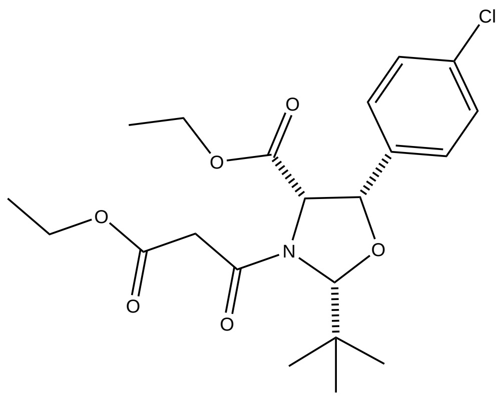
LRMS (ESI+) *m/z*: 444.2 ([M + Na]+ 43%); HRMS (ESI+) *m/z*: [M + Na]+ calcd. for $C_{22}H_{31}NO_7Na$, 444.1993, found 444.1992.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(4-fluorophenyl)oxazolidine-4-carboxylate 11e**



Yield (1.05 g, 37%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.53; $\nu_{max}$/cm$^{-1}$ 2981 (C-H), 1740 (C=O), 1679 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.86 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 1.30 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.42 (1H, d, *J*=15.4 Hz, H7), 3.48 (1H, d, *J*=15.3 Hz, H7), 3.72 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 3.83 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.21 (2H, m, $OCH_2CH_3$), 4.79 (1H, br d, *J*=6.8 Hz, H5), 5.18 (1H, d, *J*=6.8 Hz, H4), 5.36 (1H, s, H2), 7.04 (2H, app t, *J*=8.7 Hz, Ar-H), 7.36 (2H, dd, *J*=5.3 Hz, 8.6 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.9 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 44.0 (C7), 61.4 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 64.4 (C5), 79.9 (C4), 97.1 (C2), 115.3 (d, *J*=22.0 Hz, Ar-C), 128.3 (d, *J*=8.4 Hz, Ar-C), 131.0 (d, *J*=3.2 Hz, Ar-C), 163.2 (d, *J*=247.1 Hz, Ar-C), 167.5 (C=O), 168.0 (C=O), 168.1 (C=O); $\delta_{F\ (Major\ diastereomer)}$ (377 MHz, $CDCl_3$) -113.30; LRMS (ESI+) *m/z*: 432.2 ([M + Na]+ 97%); HRMS (ESI+) *m/z*: [M + Na]+ calcd. for $C_{21}H_{28}NO_6FNa$, 432.1793, found 432.1791.

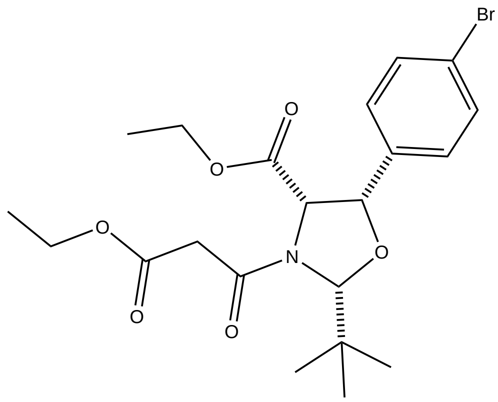
**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-5-(4-chlorophenyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11f**



Yield (1.61 g, 76%); Yellow oil; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.20; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1740 (C=O), 1678 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.86 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.11 (9H, s, $C(CH_3)_3$), 1.30 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.43 (1H, d, *J*=15.3 Hz, H7), 3.50 (1H, d, *J*=15.3 Hz, H7), 3.79 (2H, m, $OCH_2CH_3$), 4.22 (2H, m, $OCH_2CH_3$), 4.81 (1H, br d, *J*=6.8 Hz, H5), 5.17 (1H, d, *J*=6.7 Hz, H4), 5.37 (1H, s, H2), 7.32 (4H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101

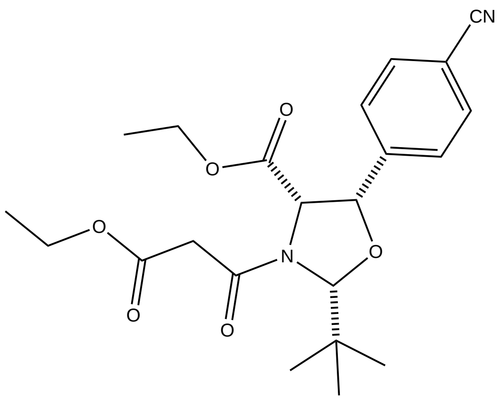
MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.8 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 43.9 (C7), 61.4 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 64.2 (C5), 79.8 (C4), 97.1 (C2), 127.9 (Ar-C), 128.5 (Ar-C), 133.8 (Ar-C), 134.4 (Ar-C), 167.5 (C=O), 167.8 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 448.2 ([$M^{35}$ + Na]$^+$ 65%), 450.2 ([$M^{37}$ + Na]$^+$ 19%); HRMS (ESI$^+$) *m/z*: [$M^{35}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6ClNa$, 448.1497, found 448.1498; [$M^{37}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6ClNa$, 450.1470, found 450.1468.

**Ethyl (2*R**,4*S**,5*S**)-5-(4-bromophenyl)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11g**



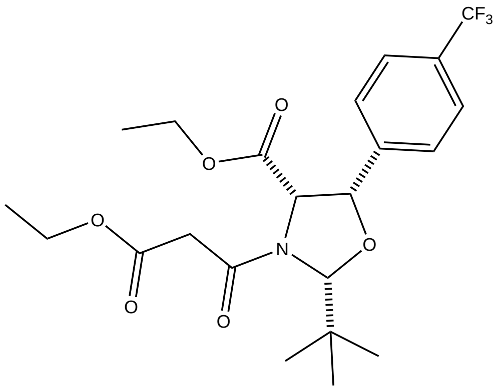

Yield (648 mg, 69%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.55; $v_{max}$/cm$^{-1}$ 2980 (C-H), 1741 (C=O), 1679 (C=O); 91:9 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.88 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.43 (1H, d, *J*=15.3 Hz, H7), 3.52 (1H, d, *J*=15.3 Hz, H7), 3.76 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 3.85 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.82 (1H, br d, *J*=6.7 Hz, H5), 5.16 (1H, d, *J*=6.7 Hz, H4), 5.38 (1H, s, H2), 7.27 (2H, d, *J*=8.4 Hz, Ar-H), 7.49 (2H, d, *J*=8.4 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.8 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 43.9 (C7), 61.4 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 64.1 (C5), 79.8 (C4), 97.1 (C2), 122.5 (Ar-C), 128.2 (Ar-C), 131.5 (Ar-C), 134.3 (Ar-C), 167.5 (C=O), 167.8 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 492.0 ([$M^{79}$ + Na]$^+$ 97%), 494.0 ([$M^{81}$ + Na]$^+$ 81%); HRMS (ESI$^+$) *m/z*: [$M^{79}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6BrNa$, 492.0992, found 492.0994; [$M^{81}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6BrNa$, 494.0973, found 494.0974.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-5-(4-cyanophenyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11h**



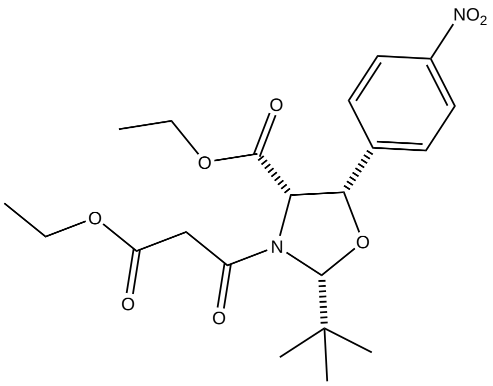
Yield (568 mg, 68%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.28; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 2229 (C≡N), 1740 (C=O), 1678 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.88 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 3.46 (1H, d, $J$=15.3 Hz, H7), 3.59 (1H, d, $J$=15.3 Hz, H7), 3.77 (1H, dq, $J$=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.86 (1H, dq, $J$=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.93 (1H, br d, $J$=6.5 Hz, H5), 5.22 (1H, d, $J$=6.4 Hz, H4), 5.40 (1H, s, H2), 7.51 (2H, d, $J$=8.0 Hz, Ar-H), 7.65 (2H, d, $J$=8.4 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.6 ($(CH_3)_3$), 37.4 ($C(CH_3)_3$), 43.8 (C7), 61.6 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 63.6 (C5), 79.4 (C4), 97.1 (C2), 112.2 (Ar-C), 118.6 (C≡N), 127.2 (Ar-C), 132.1 (Ar-C), 140.8 (Ar-C), 167.5 (C=O), 167.6 (C=O), 168.1 (C=O); LRMS (ESI$^+$) $m/z$: 439.0 ($[M + Na]^+$ 100%); HRMS (ESI$^+$) $m/z$: $[M + Na]^+$ calcd. for $C_{22}H_{28}N_2O_6Na$, 439.1840, found 439.1837.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(4-(trifluoromethyl)phenyl)oxazolidine-4-carboxylate 11i**



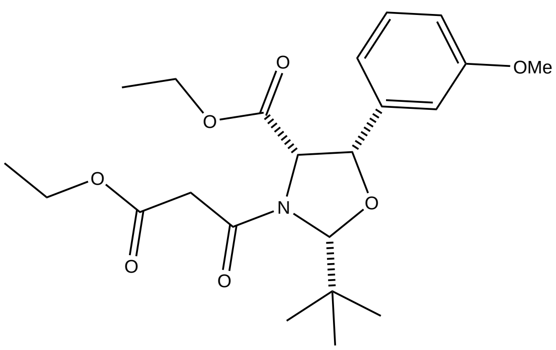
Yield (562 mg, 59%); Pale yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.50; $\nu_{max}$/cm$^{-1}$ 2982 (C-H), 1741 (C=O), 1679 (C=O); 93:7 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.80 (3H, t, $J$=7.2 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 3.45 (1H, d, $J$=15.3 Hz, H7), 3.55 (1H, d, $J$=15.3 Hz, H7), 3.72 (1H, dq, $J$=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 3.82 (1H, dq, $J$=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.90 (1H, d, $J$=6.6 Hz, H5), 5.25 (1H, d, $J$=6.6 Hz, H4), 5.40 (1H, s, H2), 7.52 (2H, d, $J$=8.5 Hz, Ar-H), 7.63 (2H, d, $J$=8.2 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.8 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 43.9 (C7), 61.5 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 64.0 (C5), 79.7 (C4), 97.2 (C2), 125.3 (q, $J$=3.8 Hz, Ar-C), 126.9 (Ar-C), 130.8 (d, $J$=32.6 Hz, Ar-C), 139.4 (Ar-C), 167.6 (C=O), 167.7 (C=O), 168.1 (C=O); $\delta_{F\ (Major\ diastereomer)}$ (376 MHz, $CDCl_3$) -62.68; LRMS (ESI$^+$) $m/z$: 482.2 ($[M + Na]^+$ 97%); HRMS (ESI$^+$) $m/z$: $[M + Na]^+$ calcd. for $C_{22}H_{28}NO_6F_3Na$, 482.1761, found 482.1758.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(4-nitrophenyl)oxazolidine-4-carboxylate 11j**



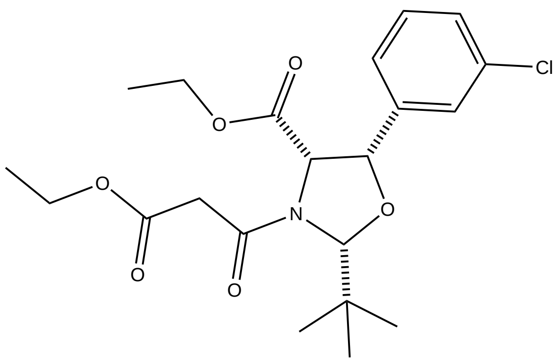

Yield (582 mg, 75%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.33; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1739 (C=O), 1678 (C=O), 1524 (N-O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.90 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.47 (1H, d, *J*=15.3 Hz, H7), 3.63 (1H, d, *J*=15.3 Hz, H7), 3.78 (1H, dq, *J*=7.2 Hz, 10.9 Hz, $OCH_2CH_3$), 3.87 (1H, m, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.98 (1H, br d, *J*=6.3 Hz, H5), 5.27 (1H, d, *J*=6.3 Hz, H4), 5.42 (1H, s, H2), 7.57 (2H, d, *J*=8.5 Hz, Ar-H), 8.22 (2H, d, *J*=8.7 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.6 ($(CH_3)_3$), 37.4 ($C(CH_3)_3$), 43.7 (C7), 61.6 ($OCH_2CH_3$), 62.1 ($OCH_2CH_3$), 63.5 (C5), 79.2 (C4), 97.1 (C2), 123.5 (Ar-C), 127.3 (Ar-C), 142.8 (Ar-C), 147.9 (Ar-C), 167.4 (C=O), 167.7 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 459.2 ([M + Na]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{21}H_{28}N_2O_8Na$, 459.1738, found 459.1736.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(3-methoxyphenyl)oxazolidine-4-carboxylate 11k**



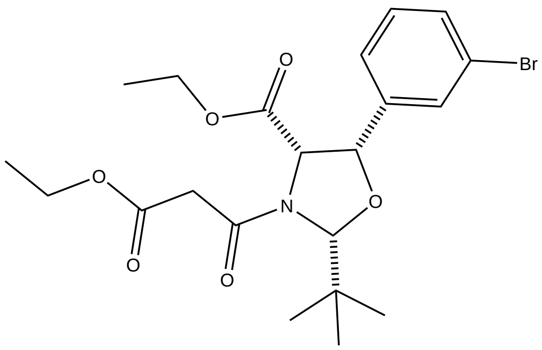

Yield (533 mg, 68%); Yellow oil; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.55; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1741 (C=O), 1679 (C=O); 89:11 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.84 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.15 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.42 (1H, d, *J*=15.3 Hz, H7), 3.49 (1H, d, *J*=15.3 Hz, H7), 3.72 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.80 (3H, s, $OCH_3$), 3.82 (1H, m, $OCH_2CH_3$), 4.22 (2H, m, $OCH_2CH_3$), 4.80 (1H, br d, *J*=6.9 Hz, H5), 5.18 (1H, d, *J*=6.8 Hz, H4), 5.38 (1H, s, H2), 6.86 (1H, m, Ar-H), 6.96 (2H, m, Ar-H), 7.26 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 27.0 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 44.0 (C7), 55.4 ($OCH_3$), 61.3 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 64.5 (C5), 80.4 (C4), 97.1 (C2), 112.2 (Ar-C), 114.0 (Ar-C), 118.9 (Ar-C), 129.4 (Ar-C), 136.7 (Ar-C), 159.7 (Ar-C), 167.4 (C=O), 168.1 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 422.2 ([M + H]$^+$ 75%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{22}H_{31}NO_7Na$, 444.1993, found 444.1991.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-5-(3-chlorophenyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11l**



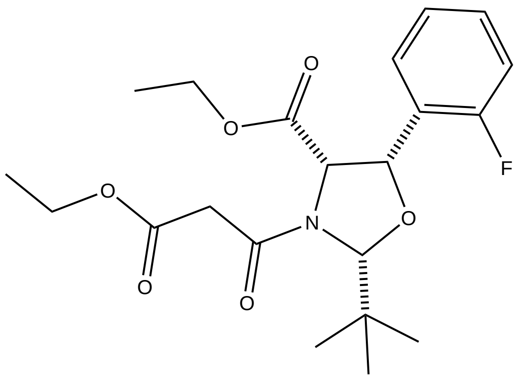

Yield (650 mg, 72%); Off-white solid; m.p. 118-121°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.63; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1740 (C=O), 1678 (C=O); 9:1 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.87 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.43 (1H, d, *J*=15.4 Hz, H7), 3.53 (1H, d, *J*=15.3 Hz, H7), 3.77 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 3.86 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.24 (2H, m, $OCH_2CH_3$), 4.84 (1H, br d, *J*=6.7 Hz, H5), 5.17 (1H, d, *J*=6.7 Hz, H4), 5.38 (1H, s, H2), 7.26-7.31 (3H, m, Ar-H), 7.38 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.8 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 43.9 (C7), 61.4 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 64.2 (C5), 79.7 (C4), 97.1 (C2), 124.7 (Ar-C), 126.7 (Ar-C), 128.7 (Ar-C), 129.6 (Ar-C), 134.4 (Ar-C), 137.3 (Ar-C), 167.5 (C=O), 167.8 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 448.2 ([$M^{35}$ + Na]$^+$ 96%), 450.2 ([$M^{37}$ + Na]$^+$ 30%); HRMS (ESI$^+$) *m/z*: [$M^{35}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6ClNa$, 448.1497, found 448.1498; [$M^{37}$ + Na]$^+$ $C_{21}H_{28}NO_6ClNa$, 450.1470, found 450.1468.

**Ethyl (2*R**,4*S**,5*S**)-5-(3-bromophenyl)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11m**



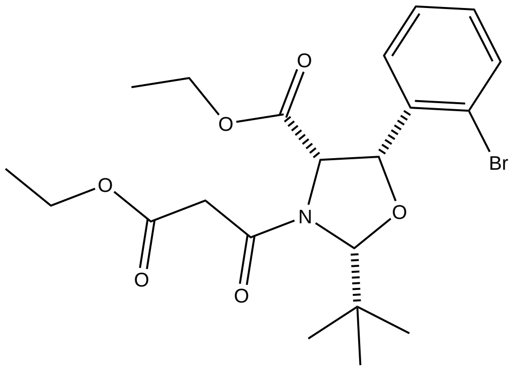

Yield (698 mg, 66%); Off-white solid; m.p. 121-124°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.58; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1738 (C=O), 1678 (C=O); 89:11 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.88 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 1.32 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.44 (1H, d, $J$=15.3 Hz, H7), 3.53 (1H, d, $J$=15.3 Hz, H7), 3.77 (1H, dq, $J$=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.86 (1H, dq, $J$=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.84 (1H, d, $J$=6.7 Hz, H5), 5.17 (1H, d, $J$=6.7 Hz, H4), 5.38 (1H, s, H2), 7.23 (1H, m, Ar-H), 7.32 (1H, m, Ar-H), 7.46 (1H, m, Ar-H), 7.53 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.8 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 43.9 (C7), 61.4 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 64.2 (C5), 79.6 (C4), 97.1 (C2), 122.4 (Ar-C), 125.2 (Ar-C), 129.6 (Ar-C), 129.9 (Ar-C), 131.6 (Ar-C), 137.6 (Ar-C), 167.5 (C=O), 167.8 (C=O), 168.1 (C=O); LRMS (ESI$^+$) $m/z$: 492.0 ([$M^{79}$ + Na]$^+$ 91%), 494.0 ([$M^{81}$ + Na]$^+$ 94%); HRMS (ESI$^+$) $m/z$: [$M^{79}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6BrNa$, 492.0992, found 492.0992; [$M^{81}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6BrNa$, 494.0971, found 494.0971.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(2-fluorophenyl)oxazolidine-4-carboxylate 11n**



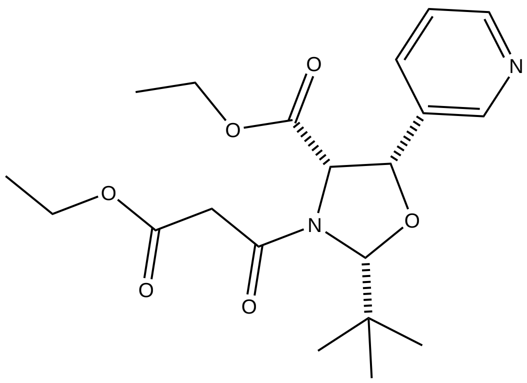

Yield (512 mg, 61%); Off-white solid; m.p. 66-69°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.80; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1743 (C=O), 1680 (C=O); 92:8 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.85 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 1.10 (9H, s, $C(CH_3)_3$), 1.30 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 3.46 (1H, d, $J$=15.4 Hz, H7), 3.60 (1H, d, $J$=15.4 Hz, H7), 3.81 (2H, m, $OCH_2CH_3$), 4.23 (2H, dq, $J$=4.2 Hz, 7.1 Hz, $OCH_2CH_3$), 4.93 (1H, br d, $J$=6.3 Hz, H5), 5.33 (1H, d, $J$=6.3 Hz, H4), 5.39 (1H, s, H2), 7.03 (1H, m, Ar-H), 7.17 (1H, dt, $J$=1.2 Hz, 7.6 Hz, Ar-H), 7.31 (1H, m, Ar-H), 7.57 (1H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.7 ($(CH_3)_3$), 37.4 ($C(CH_3)_3$), 43.9 (C7), 61.3 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 62.6 (d, $J$=1.7 Hz, C5), 74.8 (d, $J$=3.8 Hz, C4), 96.5 (C2), 114.7 (d, $J$=20.5 Hz, Ar-C), 123.3 (d, $J$=13.6 Hz, Ar-C), 124.3 (d, $J$=3.3 Hz, Ar-C), 127.3 (d, $J$=3.9 Hz, Ar-C), 129.7 (d, $J$=8.2 Hz, Ar-C), 159.8 (d, $J$=245.4 Hz, Ar-C), 167.2 (C=O), 167.8 (C=O), 168.2 (C=O); $\delta_{F\ (Major\ diastereomer)}$ (377 MHz, $CDCl_3$) -117.95; LRMS (ESI$^+$) $m/z$: 432.2 ([M + Na]$^+$ 96%); HRMS (ESI$^+$) $m/z$: [M + Na]$^+$ calcd. for $C_{21}H_{28}NO_6FNa$, 432.1793, found 432.1792.

**Ethyl (2*R**,4*S**,5*S**)-5-(2-bromophenyl)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)oxazolidine-4-carboxylate 11o**



Yield (707 mg, 54%); White solid; m.p. 135-139°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.73; $v_{max}$/cm$^{-1}$ 2979 (C-H), 1743 (C=O), 1680 (C=O); >95:5 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.81 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.46 (1H, d, *J*=15.5 Hz, H7), 3.56 (1H, d, *J*=15.4 Hz, H7), 3.72 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.81 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.23 (2H, dq, *J*=1.0 Hz, 7.2 Hz, $OCH_2CH_3$), 5.15 (1H, br d, *J*=6.5 Hz, H5), 5.33 (1H, d, *J*=6.5 Hz, H4), 5.40 (1H, s, H2), 7.20 (1H, dt, *J*=1.7 Hz, 7.7 Hz, Ar-H), 7.34 (1H, dt, *J*=1.3 Hz, 7.6 Hz, Ar-H), 7.54 (1H, dd, *J*=1.2 Hz, 8.0 Hz, Ar-H), 7.63 (1H, ddd, *J*=0.7 Hz, 1.7 Hz, 7.8 Hz, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 14.3 ($OCH_2CH_3$), 26.8 ($(CH_3)_3$), 37.5 ($C(CH_3)_3$), 44.0 (C7), 61.3 ($OCH_2CH_3$), 61.8 (C5), 62.0 ($OCH_2CH_3$), 79.6 (C4), 96.5 (C2), 122.2 (Ar-C), 127.5 (Ar-C), 128.1 (Ar-C), 129.8 (Ar-C), 132.3 (Ar-C), 135.4 (Ar-C), 167.2 (C=O), 167.8 (C=O), 168.3 (C=O); LRMS (ESI$^+$) *m/z*: 492.0 ([M$^{79}$ + Na]$^+$ 89%), 494.0 ([M$^{81}$ + Na]$^+$ 96%); HRMS (ESI$^+$) *m/z*: [M$^{79}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6BrNa$, 492.0992, found 492.0992; [M$^{81}$ + Na]$^+$ calcd. for $C_{21}H_{28}NO_6BrNa$, 494.0973, found 494.0971.

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxopropanoyl)-5-(pyridin-3-yl)oxazolidine-4-carboxylate 11p**

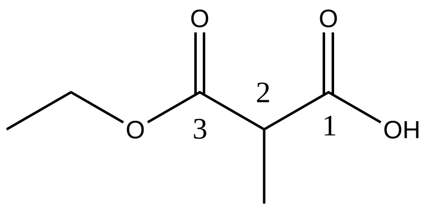


Yield (1.05 g, 68%); Yellow oil; $R_f$ (70% EtOAc in Pet. Ether 40:60) 0.23; $v_{max}$/cm$^{-1}$ 2979 (C-H), 1739 (C=O), 1676 (C=O); 82:18 mixture of diastereomers at the C2-position; $\delta_{H\ (Major\ diastereomer)}$ (400 MHz, $CDCl_3$) 0.85 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.10 (9H, s, $C(CH_3)_3$), 1.30 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.44 (1H, d, *J*=15.4 Hz, H7), 3.56 (1H, d, *J*=15.4 Hz, H7), 3.76 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.85 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.21 (2H, m, $OCH_2CH_3$), 4.89 (1H, br d, *J*=6.6 Hz, H5), 5.22 (1H, d, *J*=6.6 Hz, H4), 5.39 (1H, s, H2), 7.30 (1H, m, Ar-H), 7.74 (1H, m, Ar-H), 8.58 (2H, m, Ar-H); $\delta_{C\ (Major\ diastereomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 14.2 ($OCH_2CH_3$), 26.7 ($(CH_3)_3$), 37.4 ($C(CH_3)_3$), 43.9 (C7), 61.5 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 63.9 (C5), 78.3 (C4), 97.1 (C2), 123.3 (Ar-C), 131.3 (Ar-C), 134.3 (Ar-C), 148.1 (Ar-C), 149.6 (Ar-C), 167.5 (C=O), 167.7 (C=O), 168.1 (C=O); LRMS (ESI$^+$) *m/z*: 393.2 ([M + H]$^+$ 96%), 415.2 ([M + Na]$^+$ 96%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{20}H_{29}N_2O_6$, 393.2020, found 393.2020.

**General procedure for the monosaponification of diethyl methyl malonate 12a and the formation of the acyl chloride 12c:**[16]

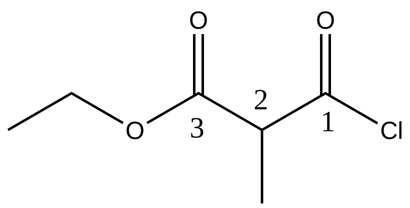
Added dropwise to a stirring 1 M KOH solution (1 eq.) (eth.) at 0°C was diethyl methyl malonate **12a** (1 eq.) and this reaction mixture was refluxed for 2 h. The reaction mixture was then filtered and concentrated to give a white solid. Water was then added to the concentrate and acidified to pH 3 using 3 M HCl solution (aq.) and extracted with $Et_2O$. The organic layer was washed with brine, dried over $Na_2SO_4$, filtered and evaporated *in-vacuo* to obtain the carboxylic acid **12'** as a colourless oil and was used without further purification. $SOCl_2$ (2 eq.) was added dropwise to a solution of monoethyl methyl malonate **12'** (1 eq.) at 0°C and this solution was then stirred for 3.5 h at 50°C. This solution was then concentrated *in-vacuo* to obtain the acyl chloride **12c** as a yellow/orange oil and was used without further purification.

**3-Ethoxy-2-methyl-3-oxopropanoic acid 12'**



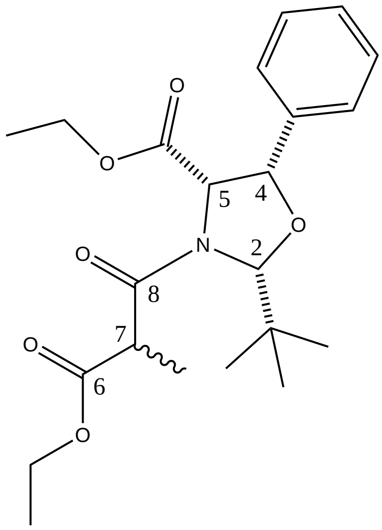

Yield (5.38 g, 71%); Colourless oil; $\nu_{max}$/cm$^{-1}$ 3187 (O-H), 2988 (C-H), 1714 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.26 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.43 (3H, d, *J*=7.3 Hz, $CH_3$), 3.46 (1H, q, *J*=7.3 Hz, H2), 4.20 (2H, dq, *J*=0.8 Hz, 7.2 Hz, $OCH_2CH_3$), 9.52 (1H, br s, OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($CH_3$), 14.1 ($OCH_2CH_3$), 46.1 (C2), 61.9 ($OCH_2CH_3$), 170.0 (C=O), 175.8 (C=O); LRMS (ESI$^+$) *m/z*: 147.0 ([M + H]$^+$ 14%), 168.9 ([M + Na]$^+$ 22%), 185.0 ([M + K]$^+$ 64%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_6H_{10}O_4Na$, 169.0471, found 169.0472.

**Ethyl 3-chloro-2-methyl-3-oxopropanoate 12c**




Yield (5.64 g, 93%); Yellow oil; $\delta_H$ (400 MHz, $CDCl_3$) 1.30 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.52 (3H, d, *J*=7.2 Hz, $CH_3$), 3.84 (1H, q, *J*=7.2 Hz, H2), 4.25 (2H, dq, *J*=2.8 Hz, 7.1 Hz, $OCH_2CH_3$); $\delta_C$ (101 MHz, $CDCl_3$) 14.0 ($CH_3$), 14.2 ($OCH_2CH_3$), 57.2 (C2), 62.4 ($OCH_2CH_3$), 167.6 (C=O), 170.8 (C=O).

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-2-methyl-3-oxopropanoyl)-5-phenyloxazolidine-4-carboxylate 13a**



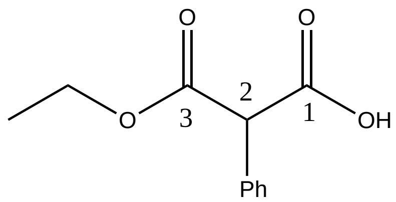
Yield (1.79 g, 76%); Pale green oil that crystallised overnight; $R_f$ (20% EtOAc in Pet. Ether 40:60) $0.58_{(\text{Minor diastereomer})}$, $0.35_{(\text{Major diastereomer})}$; $\nu_{max}$/$cm^{-1}$ 2982 (C-H), 1740 (C=O), 1682 (C=O); 1.8:1 mixture of diastereomers at the C7-position; $\delta_{H\ (\text{Major diastereomer})}$ (400 MHz, $CDCl_3$) 0.79 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 1.32 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.43 (3H, d, *J*=7.0 Hz, $CH_3$), 3.50 (1H, q, *J*=7.0 Hz, H7), 3.68 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.80 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_3$), 4.23 (2H, dq, *J*=4.7 Hz, 7.1 Hz, $OCH_2CH_3$), 4.99 (1H, d, *J*=6.8 Hz, H5), 5.19 (1H, d, *J*=6.8 Hz, H4), 5.41 (1H, s, H2), 7.31-7.39 (5H, m, Ar-H); $\delta_{C\ (\text{Major diastereomer})}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.3 ($CH_3$), 14.7 ($OCH_2CH_3$), 26.9 ($(CH_3)_3$), 37.4 ($C(CH_3)_3$), 46.8 (C7), 61.2 ($OCH_2CH_3$), 61.8 ($OCH_2CH_3$), 64.4 (C5), 80.5 (C4), 96.7 (C2), 126.5 (Ar-C), 128.3 (Ar-C), 128.6 (Ar-C), 135.2 (Ar-C), 168.4 (C=O), 170.1 (C=O), 172.7 (C=O); $\delta_{H\ (\text{Minor diastereomer})}$ (400 MHz, $CDCl_3$) 0.77 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.16 (9H, s, $C(CH_3)_3$), 1.24 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.42 (3H, d, *J*=7.0 Hz, $CH_3$), 3.49 (1H, br s, H7), 3.60 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 3.76 (1H, dq, *J*=7.1 Hz, 10.7 Hz, $OCH_2CH_3$), 4.12 (2H, dq, *J*=5.5 Hz, 7.2 Hz, $OCH_2CH_3$), 4.63 (1H, br s, H5), 5.17 (1H, d, *J*=7.0 Hz, H4), 5.39 (1H, s, H2), 7.30-7.39 (5H, m, Ar-H); $\delta_{C\ (\text{Minor diastereomer})}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 13.5 ($OCH_2CH_3$), 14.1 ($CH_3$), 27.0 ($(CH_3)_3$), 37.7 ($C(CH_3)_3$), 47.3 (C7), 61.0 ($OCH_2CH_3$), 61.7 ($OCH_2CH_3$), 65.0 (C5), 80.8 (C4), 97.2 (C2), 126.6 (Ar-C), 128.4 (Ar-C), 128.7 (Ar-C), 134.9 (Ar-C), 167.7 (C=O), 170.0 (C=O), 172.0 (C=O); LRMS ($ESI^+$ $_{(\text{Major diastereomer})}$) *m/z*: 428.2 ($[M + Na]^+$ 83%); LRMS ($ESI^+$ $_{(\text{Minor diastereomer})}$) *m/z*: 428.2 ($[M + Na]^+$ 95%); HRMS ($ESI^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{22}H_{31}NO_6Na$, 428.2044, found 428.2041.

**General procedure for the monosaponification of diethyl phenyl malonate 12b and the formation of the acyl chloride malonate 12d:**[17]

A solution of diethyl phenyl malonate **12b** (1 eq.) in EtOH (0.7 M) was cooled to 0°C and KOH (1 eq.) was added and left to stir at this temperature for 30 mins. The mixture was then stirred at rt for 5 h and then left in the fridge overnight. The reaction mixture was then concentrated *in-vacuo* and the residue was dissolved in $H_2O$

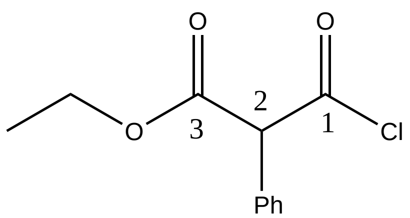
and extracted with $Et_2O$. The aqueous layer was then acidified to pH 1-2, extracted with $Et_2O$ and the organic layer was washed with brine, dried over $Na_2SO_4$, filtered and evaporated *in-vacuo* to obtain carboxylic acid **12''** as a white solid and was used without further purification. To a solution of monoethyl phenyl malonate **12''** (1 eq.) in DCM (0.34 M) was added $SOCl_2$ (2 eq.) dropwise at 0°C and this solution was then refluxed for 3 h. This solution was then concentrated *in-vacuo* to obtain acyl chloride **12d** as a crude yellow oil and was used without further purification.

**3-Ethoxy-3-oxo-2-phenylpropanoic acid 12''**



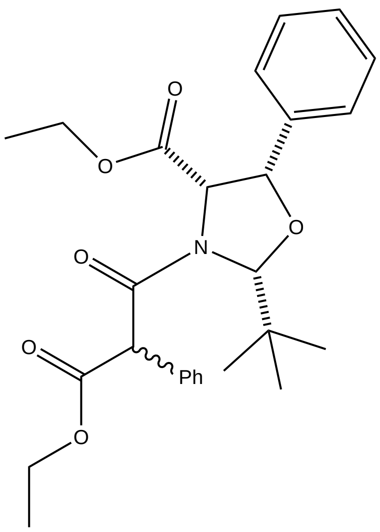
Yield (1.54 g, 35%); Colourless oil that solidified on standing; m.p. 80-85°C (lit.[18] 76-77°C); $\nu_{max}$/cm$^{-1}$ 3172 (O-H), 2985 (C-H), 1715 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.26 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.65 (1H, s, H2), 7.34-7.42 (5H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 57.7 (C2), 62.3 ($OCH_2CH_3$), 128.5 (Ar-C), 128.8 (Ar-C), 129.3 (Ar-C), 132.4 (Ar-C), 168.4 (C=O), 172.8 (C=O); LRMS (ESI$^+$) *m/z*: 231.0 ([M + Na] 100%); HRMS (ESI$^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{11}H_{12}O_4Na$, 231.0628, found 231.0629.

**Ethyl 3-chloro-3-oxo-2-phenylpropanoate 12d**



Yield (1.42 g, 93%); Yellow oil; $\delta_H$ (400 MHz, $CDCl_3$) 1.30 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.27 (2H, m, $OCH_2CH_3$), 5.02 (1H, s, H2), 7.36-7.43 (5H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 14.0 ($OCH_2CH_3$), 62.8 ($OCH_2CH_3$), 68.4 (C2), 129.2 (Ar-C), 129.3 (Ar-C), 129.5 (Ar-C), 130.8 (Ar-C), 165.9 (C=O), 168.7 (C=O).

**Ethyl (2*R**,4*S**,5*S**)-2-(*tert*-butyl)-3-(3-ethoxy-3-oxo-2-phenylpropanoyl)-5-phenyloxazolidine-4-carboxylate 13b**

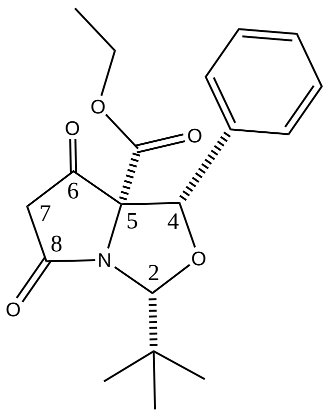



Yield (2.00 g, 70%); Pale green oil that crystallised overnight; $R_f$ (20% EtOAc in Pet. Ether 40:60) $0.58_{(\text{Minor diastereomer})}$ and $0.45_{(\text{Major diastereomer})}$; $\nu_{max}$/cm$^{-1}$ 2980 (C-H), 1753 (C=O), 1675 (C=O); 1.7:1 mixture of diastereomers at the C7-position; $\delta_{H\ (\text{Major diastereomer})}$ (400 MHz, $CDCl_3$) 0.72 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.45 (1H, m, $OCH_2CH_3$), 3.59 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 4.26 (2H, m, $OCH_2CH_3$), 4.77 (1H, s, H7), 4.84 (1H, d, *J*=6.9 Hz, H5), 5.22 (1H, br d, *J*=6.9 Hz, H4), 5.44 (1H, s, H2), 7.26-7.36 (10H, m, Ar-H); $\delta_{C\ (\text{Major diastereomer})}$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.3 ($OCH_2CH_3$), 27.1 ($(CH_3)_3$), 37.6 ($C(CH_3)_3$), 59.6 (C7), 61.0 ($OCH_2CH_3$), 62.1 ($OCH_2CH_3$), 65.1 (C5), 80.8 (C4), 97.3 (C2), 126.5 (Ar-C), 128.3 (Ar-C), 128.4 (Ar-C), 128.5 (Ar-C), 128.7 (Ar-C), 129.9 (Ar-C), 133.0 (Ar-C), 134.9 (Ar-C), 167.5 (C=O), 168.4 (C=O), 171.0 (C=O); $\delta_{H\ (\text{Minor diastereomer})}$ (400 MHz, $CDCl_3$) 0.86 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.19 (9H, s, $C(CH_3)_3$), 1.27 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 3.72 (1H, dq, *J*=7.2 Hz, 10.8 Hz, $OCH_2CH_3$), 3.86 (1H, dq, *J*=7.2 Hz, 10.7 Hz, $OCH_2CH_3$), 4.17 (2H, m, $OCH_2CH_3$), 4.59 (1H, d, *J*=6.9 Hz, H5), 4.66 (1H, s, H7) 4.89 (1H, d, *J*=6.9 Hz, H4), 5.36 (1H, s, H2), 7.19-7.50 (10H, m, Ar-H); $\delta_{C\ (\text{Minor diastereomer})}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 14.1 ($OCH_2CH_3$), 27.0 ($(CH_3)_3$), 37.7 ($C(CH_3)_3$), 59.4 (C7), 61.2 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 63.8 (C5), 80.4 (C4), 97.2 (C2), 126.5-134.9 (Ar-C), 167.9 (C=O), 168.2 (C=O), 169.6 (C=O); LRMS ($ESI^+{}_{(\text{Major diastereomer})}$) *m/z*: 490.2 ($[M + Na]^+$ 96%); LRMS ($ESI^+{}_{(\text{Minor diastereomer})}$) *m/z*: 490.2 ($[M + Na]^+$ 94%); HRMS ($ESI^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{27}H_{33}NO_6Na$, 490.2200, found 490.2197.

**General procedure for the synthesis of C7-unfunctionalised tetramates 14, 21:**[19]

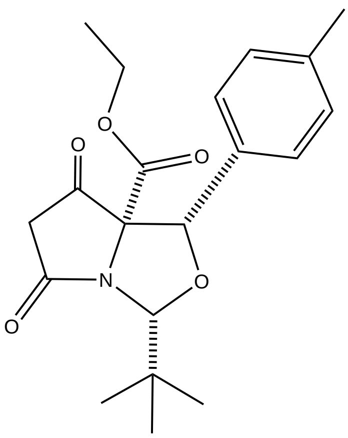
To a solution of *N*-acylated oxazolidine **11a-p**, **13a** and **13b** (1.0 eq.) in anhydrous THF was added DBU (1.1-1.2 eq.). The mixture was stirred overnight at rt. The reaction mixture was then cooled to 0$^o$C, diluted with water, and partitioned between $Et_2O$ and water and the aqueous layer was acidified to pH 1-2 using 3 M HCl solution (aq.) and extracted with EtOAc. The organic layer was washed with brine, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to yield the desired tetramates **14a-m**, **21a** and **21b** and was used without further purification.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14a**



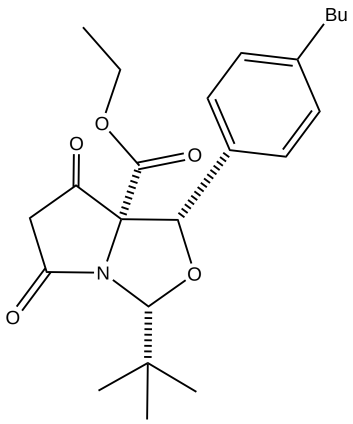
Yield (2.45 g, 94%); Red oil; $v_{max}$/cm$^{-1}$ 2962 (C-H), 1720 (C=O), 1622 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.91 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 3.22 (1H, d, *J*=20.5 Hz, H7), 3.79 (1H, dd, *J*=0.9 Hz, 20.5 Hz, H7), 3.90 (2H, m, $OCH_2CH_3$), 4.96 (1H, s, H4), 5.16 (1H, d, *J*=0.9 Hz, H2), 7.32-7.56 (5H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.1 (C7), 62.4 ($OCH_2CH_3$), 80.4 (C4), 81.7 (C5), 96.9 (C2), 126.5 (Ar-C), 128.1 (Ar-C), 128.3 (Ar-C), 134.4 (Ar-C), 165.0 (C=O), 172.0 (C8), 198.1 (C6); LRMS (ESI$^-$) *m/z*: 344.1 ([M – H]$^-$ 97%); LRMS (ESI$^+$) *m/z*: 368.2 ([M + Na]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{19}H_{23}NO_5Na$, 368.1468, found 368.1470.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-5,7-dioxo-1-(*p*-tolyl)dihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14b**



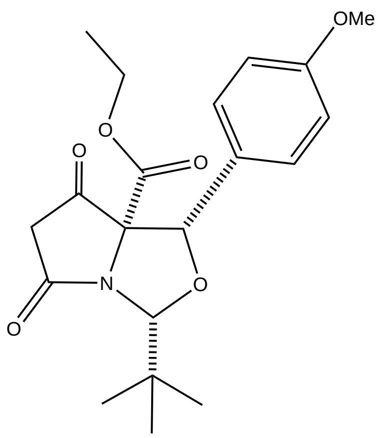
Yield (663 mg, 79%); Red oil; $v_{max}$/cm$^{-1}$ 2976 (C-H), 1722 (C=O), 1620 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.95 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 2.35 (3H, s, $CH_3$), 3.22 (1H, d, *J*=20.6 Hz, H7), 3.78 (1H, dd, *J*=0.9 Hz, 20.6 Hz, H7), 3.91 (2H, m, $OCH_2CH_3$), 4.92 (1H, s, H4), 5.15 (1H, d, *J*=0.8 Hz, H2), 7.17 (2H, d, *J*=7.9 Hz, Ar-H), 7.42 (2H, d, *J*=8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 21.4 ($CH_3$), 25.7 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.1 (C7), 62.4 ($OCH_2CH_3$), 80.6 (C4), 81.6 (C5), 96.9 (C2), 126.5 (Ar-C), 128.7 (Ar-C), 131.3 (Ar-C), 138.1 (Ar-C), 164.9 (C=O), 172.3 (C8), 198.1 (C6); LRMS (ESI$^-$) *m/z*: 358.1 ([M – H]$^-$ 100%); LRMS (ESI$^+$) *m/z*: 382.2 ([M + Na]$^+$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{20}H_{24}NO_5$, 358.1660, found 358.1658.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-butylphenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14c**



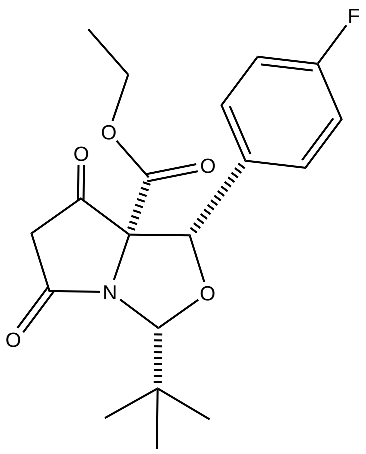
Yield (1.05 g, 78%); Yellow oil; $\nu_{max}$/cm$^{-1}$ 2958 (C-H), 2931 (C-H), 2872 (C-H), 1721 (C=O), 1614 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.93 (6H, m, $CH_3CH_2$, $OCH_2CH_3$), 1.10 (9H, s, $C(CH_3)_3$), 1.34 (2H, m, $CH_2CH_3$), 1.60 (2H, m, $CH_2CH_2$), 2.62 (2H, m, $CH_2CH_2$), 3.23 (1H, d, *J*=20.6 Hz, H7), 3.79 (1H, dd, *J*=1.0 Hz, 20.5 Hz, H7), 3.91 (2H, m, $OCH_2CH_3$), 4.94 (1H, s, H4), 5.16 (1H, d, *J*=0.9 Hz, H2), 7.18 (2H, d, *J*=8.2 Hz, Ar-H), 7.45 (2H, d, *J*=8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 14.1 ($CH_3CH_2$), 22.4 ($CH_2CH_2$), 25.7 ($(CH_3)_3$), 33.7 ($CH_2CH_2$), 35.5 ($CH_2CH_2$), 36.0 ($C(CH_3)_3$), 46.2 (C7), 62.3 ($OCH_2CH_3$), 80.7 (C4), 81.8 (C5), 97.0 (C2), 126.5 (Ar-C), 128.1 (Ar-C), 131.5 (Ar-C), 143.1 (Ar-C), 165.0 (C=O), 172.1 (C8), 198.1 (C6); LRMS (ESI$^-$) *m/z*: 400.2 ([M – H]$^-$ 100%); LRMS (ESI$^+$) *m/z*: 424.2 ([M + Na]$^+$ 51%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{23}H_{30}NO_5$, 400.2129, found 400.2125.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-methoxyphenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14d**



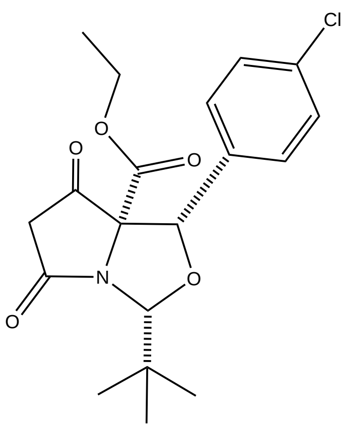
Yield (2.18 g, 80%); Red oil; $\nu_{max}$/cm$^{-1}$ 2962 (C-H), 1722 (C=O), 1615 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 3.22 (1H, d, *J*=20.5 Hz, H7), 3.80 (1H, dd, *J*=0.9 Hz, 20.5 Hz, H7), 3.82 (3H, s, $OCH_3$), 3.93 (2H, m, $OCH_2CH_3$), 4.91 (1H, s, H4), 5.15 (1H, d, *J*=0.8 Hz, H2), 6.91 (2H, d, *J*=8.8 Hz, Ar-H), 7.46 (2H, d, *J*=8.8 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.1 (C7), 55.4 ($OCH_3$), 62.4 ($OCH_2CH_3$), 80.5 (C4), 81.6 (C5), 96.9 (C2), 113.5 (Ar-C), 126.2 (Ar-C), 127.9 (Ar-C), 159.7 (Ar-C), 164.9 (C=O), 172.1 (C8), 198.2 (C6); LRMS (ESI$^-$) *m/z*: 374.1 ([M – H]$^-$ 100%); LRMS (ESI$^+$) *m/z*: 398.2 ([M + Na]$^+$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{20}H_{24}NO_6$, 374.1609, found 374.1606.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-fluorophenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14e**



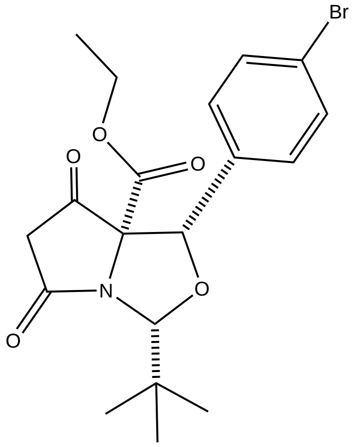
Yield (723 mg, 82%); Orange oil; $\nu_{max}$/cm$^{-1}$ 2963 (C-H), 1720 (C=O), 1606 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 3.22 (1H, d, *J*=20.6 Hz, H7), 3.80 (1H, d, *J*=20.6 Hz, H7), 3.94 (2H, m, $OCH_2CH_3$), 4.92 (1H, s, H4), 5.16 (1H, s, H2), 7.06 (2H, app t, *J*=8.6 Hz, Ar-H), 7.53 (2H, dd, *J*=5.4 Hz, 8.4 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.6 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.1 (C7), 62.5 ($OCH_2CH_3$), 79.9 (C4), 81.4 (C5), 96.9 (C2), 115.0 (d, *J*=21.6 Hz, Ar-C), 128.3 (d, *J*=8.2 Hz, Ar-C), 130.1 (d, *J*=3.3 Hz, Ar-C), 163.1 (d, *J*=246.7 Hz, Ar-C), 164.9 (C=O), 172.1 (C8), 198.2 (C6); $\delta_F$ (377 MHz, $CDCl_3$) -113.84; LRMS (ESI$^-$) *m/z*: 362.1 ([M – H]$^-$ 98%); LRMS (ESI$^+$) *m/z*: 386.0 ([M + Na]$^+$ 38%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{19}H_{21}NO_5F$, 362.1409, found 362.1408.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-chlorophenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14f**



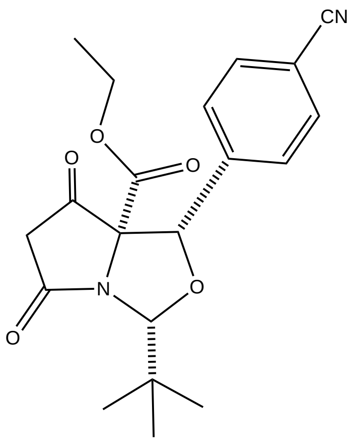
Yield (1.19 g, 86%); Orange oil; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1720 (C=O), 1622 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.06 (9H, s, $C(CH_3)_3$), 3.23 (1H, d, *J*=20.7 Hz, H7), 3.80 (1H, dd, *J*=0.9 Hz, 20.7 Hz, H7), 3.95 (2H, m, $OCH_2CH_3$), 4.90 (1H, s, H4), 5.16 (1H, d, *J*=0.9 Hz, H2), 7.34 (2H, d, *J*=8.5 Hz, Ar-H), 7.49 (2H, d, *J*=8.5 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.6 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.0 (C7), 62.6 ($OCH_2CH_3$), 79.7 (C4), 81.3 (C5), 96.9 (C2), 127.9 (Ar-C), 128.3 (Ar-C), 133.0 (Ar-C), 134.1 (Ar-C), 164.8 (C=O), 172.0 (C8), 198.2 (C6); LRMS (ESI$^-$) *m/z*: 378.0 ([M$^{35}$ – H]$^-$ 100%), 380.1 ([M$^{37}$ – H]$^-$ 36%); LRMS (ESI$^+$) *m/z*: 402.0 ([M$^{35}$ + Na]$^+$ 40%), 404.0 ([M$^{37}$ + Na]$^+$ 7%); HRMS (ESI$^-$) *m/z*: [M$^{35}$ – H]$^-$ calcd. for $C_{19}H_{21}NO_5Cl$, 378.1114, found 378.1112; [M$^{37}$ – H]$^-$ calcd. for $C_{19}H_{21}NO_5Cl$, 380.1085, found 380.1083.

**Ethyl (1*S**,3*R**,7a*R**)-1-(4-bromophenyl)-3-(*tert*-butyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14g**



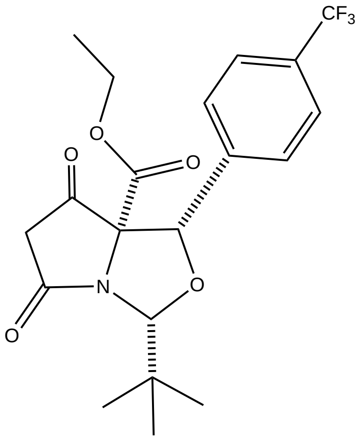
Yield (468 mg, 85%); Yellow oil; $\nu_{max}$/cm$^{-1}$ 2973 (C-H), 1721 (C=O), 1623 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.99 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.06 (9H, s, $C(CH_3)_3$), 3.23 (1H, d, *J*=20.7 Hz, H7), 3.81 (1H, dd, *J*=0.8 Hz, 20.7 Hz, H7), 3.95 (2H, m, $OCH_2CH_3$), 4.88 (1H, s, H4), 5.16 (1H, d, *J*=0.8 Hz, H2), 7.44 (2H, d, *J*=8.6 Hz, Ar-H), 7.50 (2H, d, *J*=8.6 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.6 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.0 (C7), 62.6 ($OCH_2CH_3$), 79.8 (C4), 81.2 (C5), 96.9 (C2), 122.3 (Ar-C), 128.3 (Ar-C), 131.2 (Ar-C), 133.5 (Ar-C), 164.9 (C=O), 172.0 (C8), 198.2 (C6); LRMS (ESI$^-$) *m/z*: 422.0 ([M$^{79}$ – H]$^-$ 100%), 424.0 ([M$^{81}$ – H]$^-$ 100%); HRMS (ESI$^-$) *m/z*: [M$^{79}$ – H]$^-$ calcd. for $C_{19}H_{21}NO_5Br$, 422.0609, found 422.0604; [M$^{81}$ – H]$^-$ calcd. for $C_{19}H_{21}NO_5Br$, 424.0589, found 424.0584.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-cyanophenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14h**



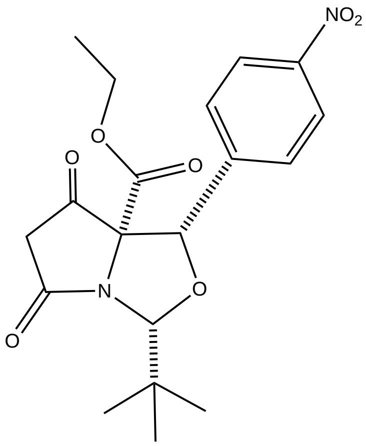
Yield (405 mg, 92%); Yellow oil that solidified overnight; m.p. 164-168°C; $\nu_{max}$/cm$^{-1}$ 2973 (C-H), 2229 (C≡N), 1722 (C=O), 1612 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.00 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.04 (9H, s, $C(CH_3)_3$), 3.26 (1H, d, *J*=20.9 Hz, H7), 3.84 (1H, dd, *J*=0.7 Hz, 20.8 Hz, H7), 3.97 (2H, dq, *J*=4.1 Hz, 7.1 Hz, $OCH_2CH_3$), 4.95 (1H, s, H4), 5.19 (1H, d, *J*=0.8 Hz, H2), 7.66 (2H, d, *J*=8.8 Hz, Ar-H), 7.70 (2H, d, *J*=8.3 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 45.8 (C7), 62.8 ($OCH_2CH_3$), 79.1 (C4), 80.9 (C5), 96.8 (C2), 111.9 (Ar-C), 118.8 (C≡N), 127.2 (Ar-C), 131.9 (Ar-C), 139.9 (Ar-C), 164.7 (C=O), 171.9 (C8), 198.2 (C6); LRMS (ESI$^-$) *m/z*: 369.1 ([M – H]$^-$ 97%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{20}H_{21}N_2O_5$, 369.1456, found 369.1451.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-5,7-dioxo-1-(4-(trifluoromethyl)phenyl)dihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14i**



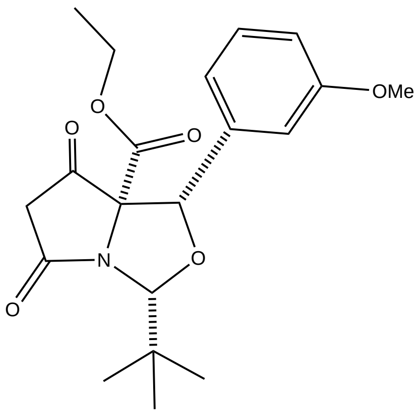
Yield (401 mg, 84%); Yellow oil; $v_{max}$/cm$^{-1}$ 2974 (C-H), 1724 (C=O), 1622 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.95 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 3.26 (1H, d, *J*=20.7 Hz, H7), 3.84 (1H, dd, *J*=0.7 Hz, 20.7 Hz, H7), 3.93 (2H, m, $OCH_2CH_3$), 4.97 (1H, s, H4), 5.20 (1H, d, *J*=0.8 Hz, H2), 7.63 (2H, d, *J*=8.3 Hz, Ar-H), 7.70 (2H, d, *J*=8.5 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.0 (C7), 62.7 ($OCH_2CH_3$), 79.5 (C4), 81.2 (C5), 96.9 (C2), 125.0 (q, *J*=3.8 Hz, Ar-C), 126.9 (Ar-C), 130.4 (d, *J*=32.6 Hz, Ar-C), 138.6 (Ar-C), 164.9 (C=O), 171.9 (C8), 198.2 (C6); $\delta_F$ (376 MHz, $CDCl_3$) -62.61; LRMS (ESI$^-$) *m/z*: 412.1 ([M – H]$^-$ 100%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{20}H_{23}NO_5F_3$, 414.1523, found 414.1522.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-nitrophenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14j**



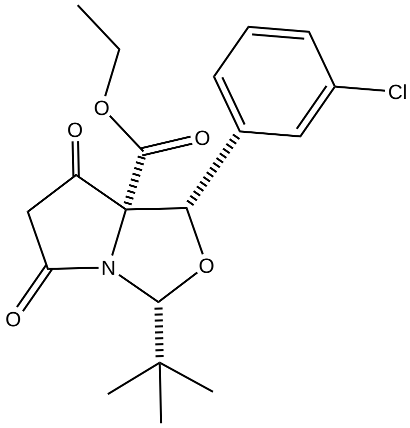
Yield (410 mg, 86%); Orange foamy solid; m.p. 182-185°C; $v_{max}$/cm$^{-1}$ 2974 (C-H), 1723 (C=O), 1606 (C=O), 1523 (N-O); $\delta_H$ (400 MHz, $CDCl_3$) 1.02 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.05 (9H, s, $C(CH_3)_3$), 3.28 (1H, d, *J*=20.9 Hz, H7), 3.86 (1H, dd, *J*=0.6 Hz, 20.9 Hz, H7), 3.98 (2H, dq, *J*=2.2 Hz, 7.1 Hz, $OCH_2CH_3$), 4.99 (1H, s, H4), 5.21 (1H, d, *J*=0.8 Hz, H2), 7.76 (2H, d, *J*=9.0 Hz, Ar-H), 8.23 (2H, d, *J*=9.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 45.8 (C7), 62.8 ($OCH_2CH_3$), 79.0 (C4), 80.9 (C5), 96.9 (C2), 123.3 (Ar-C), 127.4 (Ar-C), 141.9 (Ar-C), 147.7 (Ar-C), 164.7 (C=O), 172.0 (C8), 198.2 (C6); LRMS (ESI$^-$) *m/z*: 389.1 ([M – H]$^-$ 98%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{19}H_{23}N_2O_7$, 391.1500, found 391.1501.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(3-methoxyphenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14k**



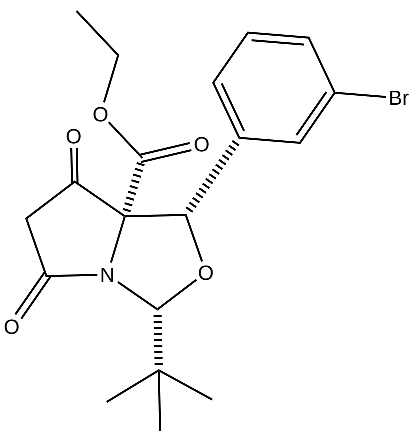
Yield (355 mg, 79%); Orange oil; $v_{max}$/cm$^{-1}$ 2962 (C-H), 1721 (C=O), 1606 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.94 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 3.22 (1H, d, *J*=20.6 Hz, H7), 3.77 (1H, m, H7), 3.82 (3H, s, $OCH_3$), 3.92 (2H, m, $OCH_2CH_3$), 4.93 (1H, s, H4), 5.16 (1H, d, *J*=0.8 Hz, H2), 6.86 (1H, m, Ar-H), 7.14 (2H, m, Ar-H), 7.29 (1H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.7 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.2 (C7), 55.3 ($OCH_3$), 62.4 ($OCH_2CH_3$), 80.2 (C4), 81.7 (C5), 96.9 (C2), 112.3 (Ar-C), 113.7 (Ar-C), 118.9 (Ar-C), 129.2 (Ar-C), 136.0 (Ar-C), 159.4 (Ar-C), 165.0 (C=O), 172.0 (C8), 198.0 (C6); LRMS (ESI$^-$) *m/z*: 374.1 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{20}H_{24}NO_6$, 374.1609, found 374.1605.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(3-chlorophenyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14l**



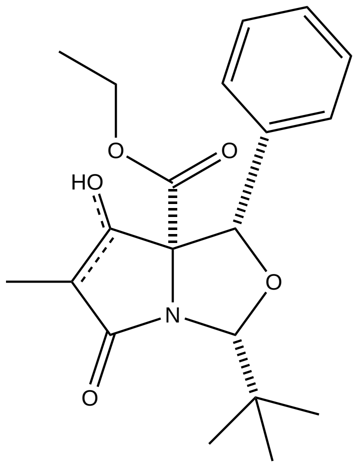
Yield (446 mg, 86%); Yellow oil; $v_{max}$/cm$^{-1}$ 2962 (C-H), 2909 (C-H), 2874 (C-H), 1719 (C=O), 1657 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 3.23 (1H, d, *J*=20.6 Hz, H7), 3.82 (1H, dd, *J*=0.8 Hz, 20.7 Hz, H7), 3.95 (2H, m, $OCH_2CH_3$), 4.90 (1H, s, H4), 5.16 (1H, d, *J*=0.9 Hz, H2), 7.30 (2H, m, Ar-H), 7.45 (1H, m, Ar-H), 7.55 (1H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.6 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.0 (C7), 62.6 ($OCH_2CH_3$), 79.5 (C4), 81.3 (C5), 96.9 (C2), 124.8 (Ar-C), 126.7 (Ar-C), 128.4 (Ar-C), 129.4 (Ar-C), 134.1 (Ar-C), 136.6 (Ar-C), 164.9 (C=O), 171.9 (C8), 198.1 (C6); LRMS (ESI$^-$) *m/z*: 378.1 ([M$^{35}$ – H]$^-$ 47%), 380.1 ([M$^{37}$ – H]$^-$ 15%); HRMS (ESI$^-$) *m/z*: [M$^{35}$ – H]$^-$ calcd. for $C_{19}H_{21}NO_5Cl$, 378.1114, found 378.1106; [M$^{37}$ – H]$^-$ calcd. for $C_{19}H_{21}NO_5Cl$, 380.1085, found 380.1076.

**Ethyl (1*S**,3*R**,7a*R**)-1-(3-bromophenyl)-3-(*tert*-butyl)-5,7-dioxodihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 14m**



Yield (432 mg, 76%); Orange oil; $\nu_{max}$/cm$^{-1}$ 2962 (C-H), 2908 (C-H), 2873 (C-H), 1718 (C=O), 1657 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 3.22 (1H, d, *J*=20.6 Hz, H7), 3.82 (1H, dd, *J*=0.6 Hz, 20.5 Hz, H7), 3.95 (2H, m, $OCH_2CH_3$), 4.89 (1H, s, H4), 5.16 (1H, d, *J*=0.8 Hz, H2), 7.24 (1H, m, Ar-H), 7.47 (2H, m, Ar-H), 7.70 (1H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.6 ($(CH_3)_3$), 36.0 ($C(CH_3)_3$), 46.0 (C7), 62.6 ($OCH_2CH_3$), 79.4 (C4), 81.3 (C5), 96.9 (C2), 122.2 (Ar-C), 125.2 (Ar-C), 129.6 (Ar-C), 129.6 (Ar-C), 131.3 (Ar-C), 136.8 (Ar-C), 164.9 (C=O), 171.9 (C8), 198.0 (C6); LRMS (ESI$^-$) *m/z*: 422.1 ($[M^{79} – H]^-$ 31%), 424.1 ($[M^{81} – H]^-$ 35%); HRMS (ESI$^-$) *m/z*: $[M^{79} – H]^-$ calcd. for $C_{19}H_{21}NO_5Br$, 422.0609, found 422.0606; $[M^{81} – H]^-$ calcd. for $C_{19}H_{21}NO_5Br$, 424.0589, found 424.0585.

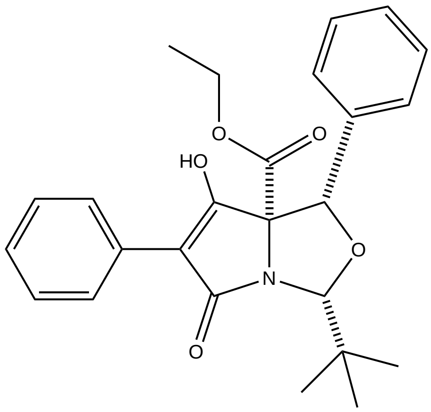
**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-7-hydroxy-6-methyl-5-oxo-1-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 21a**



Yield (1.57 g, 62%); Off-white solid; $\nu_{max}$/cm$^{-1}$ 2963 (C-H), 1758 (C=O), 1658 (C=O), 1623 (C=C); 38:35:27 enol:keto$_{(major)}$:keto$_{(minor)}$ tautomers; $\delta_H$ (400 MHz, $CDCl_3$) 0.85 (3H, t, *J*=7.1Hz, $OCH_2CH_{3\text{-keto(minor)}}$), 1.11 (9H, s, $C(CH_3)_{3\text{-keto(minor+major)}}$), 1.14 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$, underneath $C(CH_3)_3$) peak$_{\text{-keto(major)}}$), 1.16 (9H, s, $C(CH_3)_{3\text{-enol}}$), 1.28 (3H, t, *J*=7.1 Hz, $OCH_2CH_{3\text{-enol}}$), 1.32 (3H, d, *J*=7.2 Hz, $CH_{3\text{-keto(minor)}}$), 1.44 (3H, d, *J*=7.3 Hz, $CH_{3\text{-keto(major)}}$), 1.74 (3H, s, $CH_{3\text{-enol}}$), 3.46 (1H, q, *J*=7.3 Hz, H7$_{\text{-keto(major)}}$), 3.69 (1H, dq, *J*=1.0 Hz, 7.2 Hz, H7$_{\text{-keto(minor)}}$), 3.81 (1H, m, $OCH_2CH_{3\text{-keto(minor)}}$), 3.88 (1H, m, $OCH_2CH_{3\text{-keto(minor)}}$), 3.96 (1H, dq, *J*=7.2 Hz, 10.9 Hz, $OCH_2CH_{3\text{-keto(major)}}$), 4.07 (1H, dq, *J*=7.1 Hz, 10.8 Hz, $OCH_2CH_{3\text{-keto(major)}}$), 4.21 (2H, dq, *J*=0.6 Hz, 7.1 Hz, $OCH_2CH_3$), 4.69 (1H, s, H4$_{\text{-keto(major)}}$), 4.80 (1H, s, H2$_{\text{-keto(major)}}$), 4.89 (1H, s, H4$_{\text{-keto(minor)}}$), 5.12 (1H, d, *J*=1.0 Hz, H2$_{\text{-keto(minor)}}$), 7.28-7.60 (10H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 6.3 ($CH_{3\text{-enol}}$), 7.3 ($CH_{3\text{-keto(minor)}}$), 13.5 ($OCH_2CH_3$), 13.7 ($CH_{3\text{-keto(major)}}$), 13.8 ($OCH_2CH_3$), 14.1 ($OCH_2CH_3$), 25.8 ($(CH_3)_3$), 26.2 ($(CH_3)_3$), 35.5 ($C(CH_3)_3$), 36.1 ($C(CH_3)_3$), 45.9 (C7$_{\text{-keto(major)}}$), 50.5 (C7$_{\text{-keto(minor)}}$), 61.8 ($OCH_2CH_3$), 62.3 ($OCH_2CH_3$), 62.9 ($OCH_2CH_3$), 76.0 (C5), 80.7 (C5), 81.0 (C4$_{\text{-keto(minor)}}$), 86.1 (C4$_{\text{-keto(major)}}$), 97.0 (C2$_{\text{-keto(minor)}}$), 97.8 (C2$_{\text{-keto(major)}}$), 105.6 (C7$_{\text{-enol}}$), 126.3 (Ar-C), 126.6 (Ar-C), 128.1 (Ar-C), 128.4 (Ar-C), 128.6 (Ar-C), 129.0 (Ar-

C), 134.5 (Ar-C), 134.8 (Ar-C), 165.1 (C=O), 166.3 (C=O), 168.7 (C=O), 170.2 (C=O), 174.6 (C=O), 174.9 (C=O), 180.9 ($C6_{-enol}$), 200.6 ($C6_{-keto}$); LRMS (ESI$^+$) *m/z*: 382.2 ([M + Na]$^+$ 77%); LRMS (ESI$^-$) *m/z*: 358.1 ([M – H]$^-$ 100%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{20}H_{26}NO_5$, 360.1805, found 360.1806.

**Ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-7-hydroxy-5-oxo-1,6-diphenyl-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 21b**

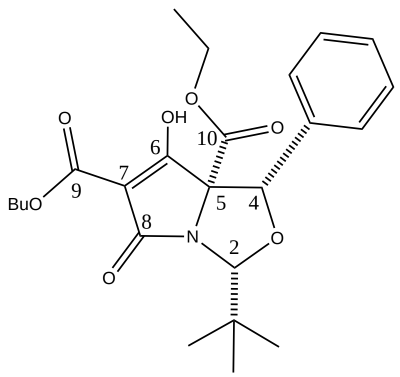


Yield (103 mg, 10%); Pale-yellow oil; $v_{max}$/cm$^{-1}$ 2976 (C-H), 1703 (C=O), 1648 (C=O), 1600 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.22 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.26 (9H, s, $C(CH_3)_3$), 4.14 (2H, m, $OCH_2CH_3$), 4.84 (1H, s, H4), 4.93 (1H, s, H2), 7.30-7.47 (8H, m, Ar-H), 8.00 (2H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 26.4 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 63.3 ($OCH_2CH_3$), 75.4 (C5), 86.6 (C4), 98.6 (C2), 107.7 (C7), 126.2 (Ar-C), 127.7 (Ar-C), 128.0 (Ar-C), 128.3 (Ar-C), 128.8 (Ar-C), 129.4 (Ar-C), 134.5 (Ar-C), 165.7 (C=O), 169.1 (C8), 178.4 (C6); LRMS (ESI$^-$) *m/z*: 420.1 ([M – H]$^-$ 94%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{25}H_{26}NO_5$, 420.1816, found 420.1820.

**General procedure for the synthesis of C7-butyl ester tetramic acids 22:**[20]

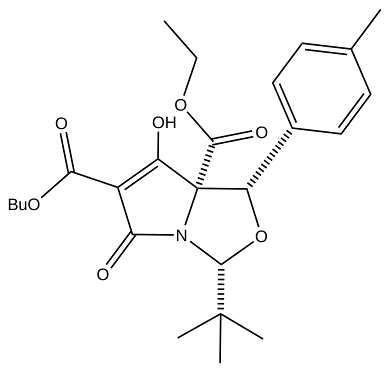
To a solution of tetramate **14a-f** (1.0 eq.) in anhydrous DCM was added DMAP (1.2 eq.) and butyl chloroformate (1.2 eq.) and the reaction mixture was refluxed overnight. The reaction mixture was then washed with 2 M HCl (aq.), brine, dried over $Na_2SO_4$, filtered and concentrated *in-vacuo* and subsequently purified by flash column chromatography to obtain metal-chelated tetramic acids. The tetramic acids were then re-dissolved in EtOAc, washed with 10% citric acid solution (aq.), dried over $Na_2SO_4$, filtered, and concentrated *in-vacuo* to obtain C7-butyl ester tetramic acids **22a-f**.

**6-Butyl 7a-ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-7-hydroxy-5-oxo-1-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-6,7a(5*H*)-dicarboxylate 22a**



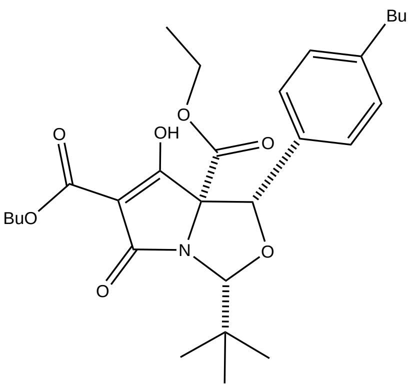

Yield (603 mg, 26%); Red oil; $R_f$ (100% EtOAc) 0.48; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1730 (C=O), 1626 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (6H, m, $CH_2CH_3$, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 1.47 (2H, m, $CH_2CH_3$), 1.78 (2H, m, $OCH_2CH_2$), 3.96 (2H, m, $OCH_2CH_3$), 4.37 (2H, m, $OCH_2CH_2$), 4.81 (1H, s, H4), 4.91 (1H, s, H2), 7.33-7.55 (5H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 13.8 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 25.5 ($(CH_3)_3$), 30.6 ($OCH_2CH_2$), 35.6 ($C(CH_3)_3$), 62.2 ($OCH_2CH_3$), 66.0 ($OCH_2CH_2$), 74.9 (C5), 82.9 (C4), 97.1 (C2), 100.4 (C7), 126.5 (Ar-C), 128.0 (Ar-C), 128.3 (Ar-C), 134.6 (Ar-C), 164.5 (C10), 167.5 (C9), 172.1 (C8), 184.9 (C6); LRMS (ESI$^-$) *m/z*: 444.1 ([M – H]$^-$ 100%); LRMS (ESI$^+$) *m/z*: 468.2 ([M + Na]$^+$ 95%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{24}H_{30}NO_7$, 444.2028, found 444.2027.

**6-Butyl 7a-ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-7-hydroxy-5-oxo-1-(*p*-tolyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-6,7a(5*H*)-dicarboxylate 22b**



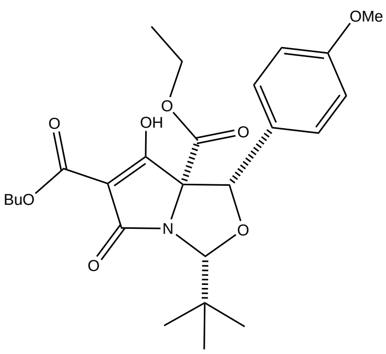

Yield (138 mg, 17%); Orange oil; $R_f$ (100% EtOAc) 0.50; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1732 (C=O), 1657 (C=O), 1626 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.4 Hz, $OCH_2CH_3$), 1.03 (3H, m, $CH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 1.47 (2H, m, $CH_2CH_3$), 1.78 (2H, m, $OCH_2CH_2$), 2.36 (3H, s, $CH_3$), 3.98 (2H, m, $OCH_2CH_3$), 4.37 (2H, m, $OCH_2CH_2$), 4.77 (1H, s, H4), 4.90 (1H, s, H2), 7.18 (2H, d, *J*=7.9 Hz, Ar-H), 7.41 (2H, d, *J*=8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 13.8 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 21.4 ($CH_3$), 25.6 ($(CH_3)_3$), 30.6 ($OCH_2CH_2$), 35.6 ($C(CH_3)_3$), 62.2 ($OCH_2CH_3$), 66.0 ($OCH_2CH_2$), 83.1 (C4), 97.0 (C2), 126.5 (Ar-C), 128.7 (Ar-C), 131.4 (Ar-C), 138.0 (Ar-C), 164.5 (C10), 167.6 (C9), 172.2 (C8), 185.0 (C6); LRMS (ESI$^-$) *m/z*: 458.1 ([M – H]$^-$ 94%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{25}H_{32}NO_7$, 458.2184, found 458.2185.

**6-Butyl 7a-ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-butylphenyl)-7-hydroxy-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-6,7a(5*H*)-dicarboxylate 22c**



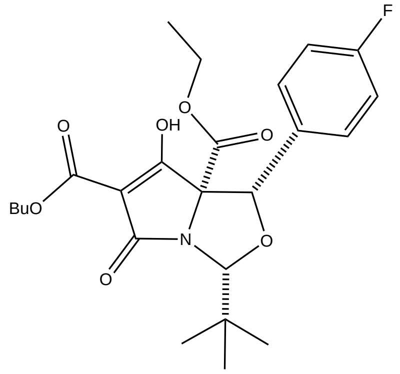
Yield (117 mg, 10%); Orange oil; $R_f$ (70% EtOAc in Pet. Ether 40:60) 0.25; $\nu_{max}$/cm$^{-1}$ 2959 (C-H), 2932 (C-H), 2872 (C-H), 1732 (C=O), 1657 (C=O), 1627 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.90-1.02 (9H, m, $CH_2CH_3$, $CH_2CH_3$, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 1.35 (2H, m, $CH_2CH_3$), 1.47 (2H, m, $CH_2CH_3$), 1.60 (2H, m, $CH_2CH_3$), 1.77 (2H, m, $OCH_2CH_2$), 2.62 (2H, m, $CH_2CH_2$), 3.95 (2H, m, $OCH_2CH_3$), 4.36 (2H, m, $OCH_2CH_2$), 4.78 (1H, s, H4), 4.89 (1H, s, H2), 7.18 (2H, d, *J*=8.2 Hz, Ar-H), 7.43 (2H, d, *J*=8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($CH_2CH_3$), 13.8 ($OCH_2CH_3$), 14.0 ($CH_2CH_3$), 19.1 ($CH_2CH_3$), 22.4 ($CH_2CH_3$), 25.5 ($(CH_3)_3$), 30.6 ($OCH_2CH_2$), 33.6 ($CH_2CH_2$), 35.5 ($CH_2CH_2$), 35.5 ($C(CH_3)_3$), 62.1 ($OCH_2CH_3$), 65.9 ($OCH_2CH_2$), 82.9 (C4), 97.0 (C2), 126.4 (Ar-C), 128.0 (Ar-C), 131.6 (Ar-C), 143.0 (Ar-C), 164.5 (C10), 167.6 (C9), 172.1 (C8), 184.9 (C6); LRMS (ESI$^-$) *m/z*: 500.2 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{28}H_{38}NO_7$, 500.2654, found 500.2655.

**6-Butyl 7a-ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-7-hydroxy-1-(4-methoxyphenyl)-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-6,7a(5*H*)-dicarboxylate 22d**



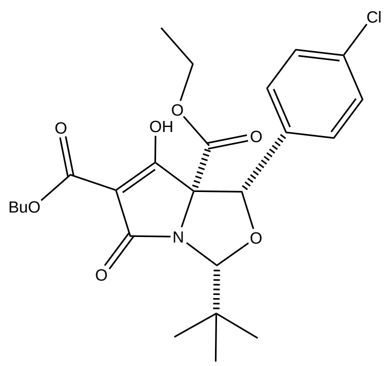
Yield (490 mg, 19%); Red oil; $R_f$ (100% EtOAc) 0.40; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1731 (C=O), 1658 (C=O), 1617 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.4 Hz, $OCH_2CH_3$), 1.03 (3H, m, $CH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 1.46 (2H, m, $CH_2CH_3$), 1.77 (2H, m, $OCH_2CH_2$), 3.81 (3H, s, $OCH_3$), 3.98 (2H, m, $OCH_2CH_3$), 4.36 (2H, m, $OCH_2CH_2$), 4.75 (1H, s, H4), 4.89 (1H, s, H2), 6.90 (2H, d, *J*=8.8 Hz, Ar-H), 7.44 (2H, d, *J*=8.7 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 13.8 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 25.6 ($(CH_3)_3$), 30.6 ($OCH_2CH_2$), 35.6 ($C(CH_3)_3$), 55.4 ($OCH_3$), 62.2 ($OCH_2CH_3$), 66.0 ($OCH_2CH_2$), 80.5 (C5), 83.0 (C4), 97.1 (C2), 113.4 (Ar-C), 126.4 (Ar-C), 127.9 (Ar-C), 159.6 (Ar-C), 164.5 (C10), 167.5 (C9), 172.2 (C8), 185.0 (C6); LRMS (ESI$^-$) *m/z*: 474.2 ([M – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{25}H_{32}NO_8$, 474.2133, found 474.2134.

**6-Butyl 7a-ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-fluorophenyl)-7-hydroxy-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-6,7a(5*H*)-dicarboxylate 22e**



Yield (238 mg, 27%); Red oil; $R_f$ (70% EtOAc in Pet. Ether 40:60) 0.23; $\nu_{max}$/cm$^{-1}$ 2962 (C-H), 1733 (C=O), 1658 (C=O), 1628 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, $J$=7.4 Hz, $OCH_2CH_3$), 1.04 (3H, t, $J$=7.2 Hz, $CH_2CH_3$), 1.06 (9H, s, $C(CH_3)_3$), 1.47 (2H, m, $CH_2CH_3$), 1.77 (2H, m, $OCH_2CH_2$), 3.99 (2H, m, $OCH_2CH_3$), 4.36 (2H, m, $OCH_2CH_2$), 4.76 (1H, s, H4), 4.91 (1H, s, H2), 7.06 (2H, app t, $J$=8.7 Hz, Ar-H), 7.51 (2H, dd, $J$=5.4 Hz, 8.4 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 13.8 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 25.5 ($(CH_3)_3$), 30.6 ($OCH_2CH_2$), 35.6 ($C(CH_3)_3$), 62.3 ($OCH_2CH_3$), 66.0 ($OCH_2CH_2$), 82.2 (C4), 97.1 (C2), 115.0 (d, $J$=21.7 Hz, Ar-C), 128.3 (d, $J$=8.1 Hz, Ar-C), 130.4 (d, $J$=3.2 Hz, Ar-C), 162.7 (d, $J$=246.6 Hz, Ar-C), 164.6 (C10), 167.7 (C9), 172.0 (C8), 184.8 (C6); $\delta_F$ (377 MHz, $CDCl_3$) -113.88; LRMS (ESI$^-$) $m/z$: 462.1 ([M – H]$^-$ 95%).

**6-Butyl 7a-ethyl (1*S**,3*R**,7a*R**)-3-(*tert*-butyl)-1-(4-chlorophenyl)-7-hydroxy-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-6,7a(5*H*)-dicarboxylate 22f**

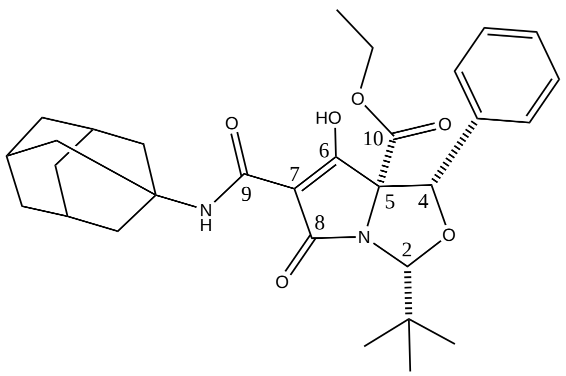


Yield (151 mg, 11%); Orange oil; $R_f$ (70% EtOAc in Pet. Ether 40:60) 0.25; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1733 (C=O), 1658 (C=O), 1628 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, $J$=7.4 Hz, $OCH_2CH_3$), 1.03 (3H, m, $CH_2CH_3$), 1.06 (9H, s, $C(CH_3)_3$), 1.47 (2H, m, $CH_2CH_3$), 1.78 (2H, m, $OCH_2CH_2$), 4.00 (2H, m, $OCH_2CH_3$), 4.37 (2H, m, $OCH_2CH_2$), 4.75 (1H, s, H4), 4.91 (1H, s, H2), 7.35 (2H, d, $J$=8.6 Hz, Ar-H), 7.48 (2H, d, $J$=8.3 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 13.8 ($CH_2CH_3$), 19.2 ($CH_2CH_3$), 25.5 ($(CH_3)_3$), 30.6 ($OCH_2CH_2$), 35.6 ($C(CH_3)_3$), 62.4 ($OCH_2CH_3$), 66.1 ($OCH_2CH_2$), 82.2 (C4), 97.1 (C2), 127.9 (Ar-C), 128.2 (Ar-C), 133.1 (Ar-C), 134.1 (Ar-C), 164.4 (C10), 170.9 (C8), 184.6 (C6); LRMS (ESI$^-$) $m/z$: 478.0 ([M$^{35}$ – H]$^-$ 88%), 480.0 ([M$^{37}$ – H]$^-$ 32%); HRMS (ESI$^-$) $m/z$: [M$^{35}$ – H]$^-$ calcd. for $C_{24}H_{29}NO_7Cl$, 478.1638, found 478.1638; [M$^{37}$ – H]$^-$ calcd. for $C_{24}H_{29}NO_7Cl$, 480.1613, found 480.1603.

**General procedure for the synthesis of C7-carboxamidotetramic acids 23:**[20-21]

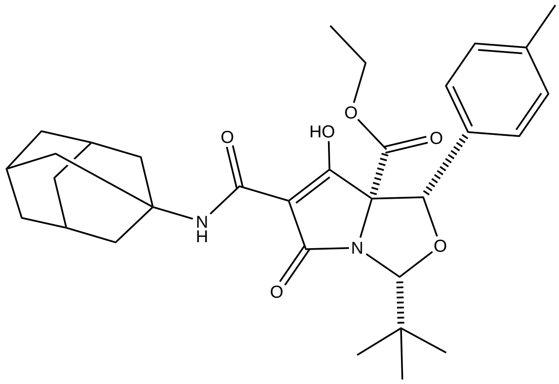
To a solution of C7-butyl ester tetramic acids **22a-f** (1.0 eq.) in anhydrous toluene was added 1-adamantylamine (1.2 eq.). The mixture was heated at reflux overnight. Then the reaction mixture was left to cool to rt, and the solvent was evaporated *in-vacuo* and the concentrate was purified by flash column chromatography to yield tetramates that where chelated with metals. The tetramates were then redissolved in DCM, washed with 10% citric acid solution (aq.), dried over $Na_2SO_4$, filtered and concentrated under reduced pressure to yield the desired carboxamides **23a-f**.

**Ethyl (1*S**,3*R**,7a*R**)-6-(adamantan-1-ylcarbamoyl)-3-(*tert*-butyl)-7-hydroxy-5-oxo-1-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 23a**



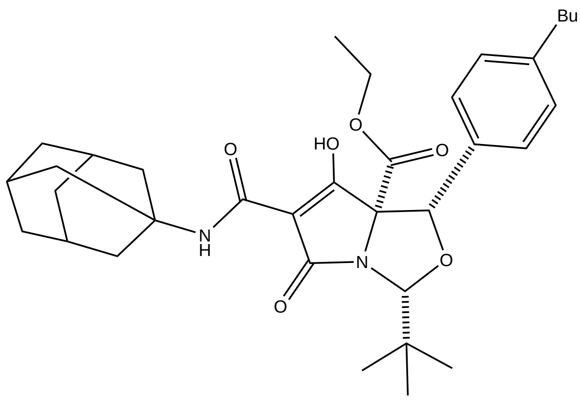

Yield (242 mg, 42%); Brown foamy solid; m.p. 108-111°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.40; $\nu_{max}$/cm$^{-1}$ 3307 (O-H), 2910 (C-H), 2853 (C-H), 1738 (C=O), 1697 (C=O), 1652 (C=O), 1627 (C=C); AB:CD 54:46 by $\delta_H$-NMR; $\delta_H$ (400 MHz, $CDCl_3$) 0.93 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 0.96 (3H, t, *J*=6.5 Hz, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 1.72 (6H, br s, Adamantyl-$CH_2$), 2.10 (6H, m, Adamantyl-$CH_2$), 2.15 (3H, br s, Adamantyl-CH), 3.93 (2H, m, $OCH_2CH_3$), 4.80 (1H, s, H4), 4.80 (1H, s, H4), 4.87 (1H, s, H2), 4.88 (1H, s, H2), 7.29-7.38 (3H, m, Ar-H), 7.54-7.58 (2H, m, Ar-H), 7.67 (1H, br s, NH/OH), 7.98 (1H, br s, NH/OH), 8.59 (2H, br s, NH/OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 25.5 ($(CH_3)_3$), 29.5 (Adamantyl-C), 35.5 ($C(CH_3)_3$), 35.6 ($C(CH_3)_3$), 36.0 (Adamantyl-C), 36.1 (Adamantyl-C), 41.7 (Adamantyl-C), 41.8 (Adamantyl-C), 54.1 (Adamantyl-C), 54.9 (Adamantyl-C), 61.6 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 77.3 (C5), 79.1 (C5), 81.1 (C4), 82.0 (C4), 85.7 (C7), 92.5 (C7), 96.5 (C2), 96.7 (C2), 126.4 (Ar-C), 126.4 (Ar-C), 127.7 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 127.9 (Ar-C), 135.3 (Ar-C), 135.8 (Ar-C), 165.5 (C10), 166.2 (C10), 166.9 (C9), 167.3 (C9), 176.9 (C8), 182.6 (C8), 188.0 (C6), 189.4 (C6); LRMS (ESI$^-$) *m/z*: 521.2 ([M – H]$^-$ 100%); LRMS (ESI$^+$) *m/z*: 545.2 ([M + Na]$^+$ 94%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{30}H_{37}N_2O_6$, 521.2657, found 521.2655.

**Ethyl (1*S**,3*R**,7a*R**)-6-(adamantan-1-ylcarbamoyl)-3-(*tert*-butyl)-7-hydroxy-5-oxo-1-(*p*-tolyl)-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 23b**



Yield (76 mg, 49%); Brown foamy solid; m.p. 115-120°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.68; $v_{max}$/cm$^{-1}$ 3309 (O-H), 2910 (C-H), 2853 (C-H), 1738 (C=O), 1694 (C=O), 1651 (C=O), 1625 (C=C); AB:CD 58:42 by $\delta_H$-NMR; $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.00 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 1.72 (6H, br s, Adamantyl-$CH_2$), 2.09 (6H, m, Adamantyl-$CH_2$), 2.15 (3H, br s, Adamantyl-CH), 2.35 (3H, s, $CH_3$), 3.95 (2H, m, $OCH_2CH_3$), 4.75 (1H, s, H4), 4.85 (1H, s, H2), 4.86 (1H, s, H2), 7.15-7.18 (2H, m, Ar-H), 7.42-7.45 (2H, m, Ar-H), 7.66 (1H, br s, NH/OH), 7.97 (1H, br s, NH/OH), 9.96 (2H, br s, NH/OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 21.4 ($CH_3$), 25.4 ($(CH_3)_3$), 25.5 ($(CH_3)_3$), 29.4 (Adamantyl-C), 35.4 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 36.0 (Adamantyl-C), 36.1 (Adamantyl-C), 41.6 (Adamantyl-C), 41.7 (Adamantyl-C), 54.0 (Adamantyl-C), 54.8 (Adamantyl-C), 61.5 ($OCH_2CH_3$), 61.8 ($OCH_2CH_3$), 79.0 (C5), 81.1 (C4), 82.1 (C4), 85.6 (C7), 92.7 (C7), 96.4 (C2), 96.6 (C2), 126.3 (Ar-C), 128.5 (Ar-C), 128.6 (Ar-C), 132.1 (Ar-C), 132.7 (Ar-C), 137.2 (Ar-C), 137.5 (Ar-C), 165.3 (C10), 166.0 (C10), 166.8 (C9), 167.2 (C9), 176.8 (C8), 182.6 (C8), 187.9 (C6), 189.1 (C6); LRMS (ESI$^-$) *m/z*: 535.2 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{31}H_{39}N_2O_6$, 535.2814, found 535.2816.

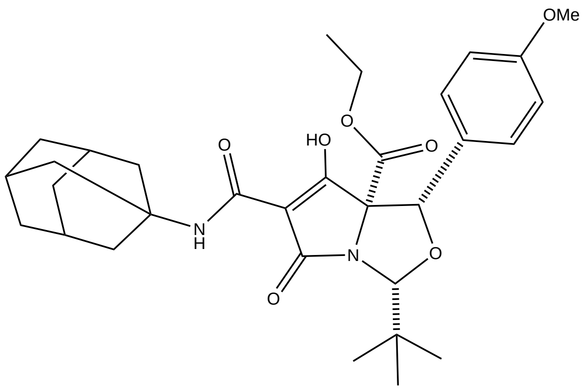
**Ethyl (1*S**,3*R**,7a*R**)-6-(adamantan-1-ylcarbamoyl)-3-(*tert*-butyl)-1-(4-butylphenyl)-7-hydroxy-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 23c**



Yield (47 mg, 35%); Brown foamy solid; m.p. 84-90°C; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.65; $v_{max}$/cm$^{-1}$ 3309 (O-H), 2956 (C-H), 2911 (C-H), 2854 (C-H), 1738 (C=O), 1698 (C=O), 1651 (C=O), 1627 (C=C); AB:CD 58:42 by $\delta_H$-NMR; $\delta_H$ (400 MHz, $CDCl_3$) 0.90-0.98 (6H, m, $CH_2CH_3$, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 1.33 (2H, m, $CH_2CH_3$), 1.59 (2H, m, $CH_2CH_2$), 1.72 (6H, br s, Adamantyl-$CH_2$), 2.09 (6H, m, Adamantyl-$CH_2$), 2.15 (3H, br s, Adamantyl-CH), 2.61 (2H, t, *J*=7.7 Hz, $CH_2CH_2$), 3.94 (2H, m, $OCH_2CH_3$), 4.76 (1H, s, H4), 4.77 (1H, s, H4), 4.85 (1H, s, H2), 4.85 (1H, s, H2), 7.15-7.18 (2H, m, Ar-H), 7.43-7.46 (2H, m, Ar-H), 7.65 (1H, br s, NH/OH), 7.98 (1H, br s, NH/OH), 9.78 (2H, br s, NH/OH);

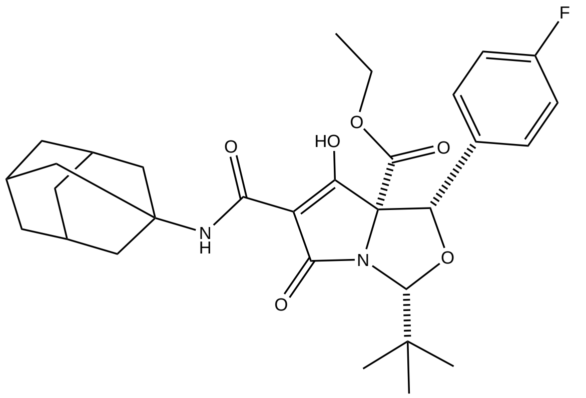
$\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 13.7 ($OCH_2CH_3$), 14.1 ($CH_2CH_3$), 22.4 ($CH_2CH_3$), 25.5 ($(CH_3)_3$), 25.6 ($(CH_3)_3$), 29.5 (Adamantyl-C), 33.7 ($CH_2CH_2$), 33.8 ($CH_2CH_2$), 35.5 ($C(CH_3)_3$), 35.5 ($CH_2CH_2$), 36.0 (Adamantyl-C), 36.1 (Adamantyl-C), 41.7 (Adamantyl-C), 41.7 (Adamantyl-C), 54.0 (Adamantyl-C), 54.8 (Adamantyl-C), 61.5 ($OCH_2CH_3$), 61.8 ($OCH_2CH_3$), 77.3 (C5), 79.2 (C5), 81.3 (C4), 82.2 (C4), 85.6 (C7), 92.8 (C7), 96.5 (C2), 96.7 (C2), 126.3 (Ar-C), 126.4 (Ar-C), 127.9 (Ar-C), 128.0 (Ar-C), 132.4 (Ar-C), 132.9 (Ar-C), 142.4 (Ar-C), 142.6 (Ar-C), 165.4 (C10), 166.1 (C10), 166.8 (C9), 167.2 (C9), 176.9 (C8), 182.6 (C8), 187.9 (C6), 189.2 (C6); LRMS (ESI$^-$) *m/z*: 577.3 ([M – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{34}H_{45}N_2O_6$, 577.3283, found 577.3279.

**Ethyl (1*S**,3*R**,7a*R**)-6-(adamantan-1-ylcarbamoyl)-3-(*tert*-butyl)-7-hydroxy-1-(4-methoxyphenyl)-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 23d**



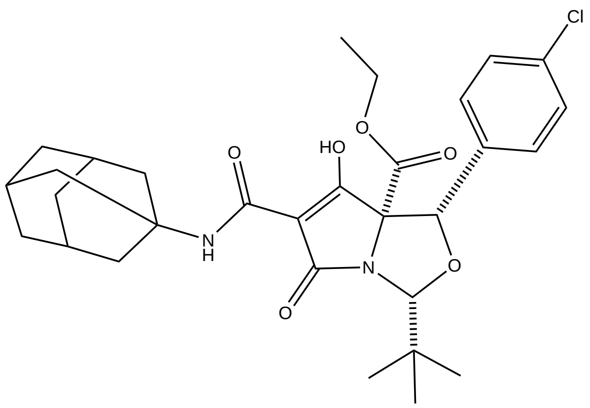

Yield (142 mg, 26%); Brown foamy solid; m.p. 108-111°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.45; $\nu_{max}$/cm$^{-1}$ 3310 (O-H), 2910 (C-H), 2853 (C-H), 1736 (C=O), 1696 (C=O), 1651 (C=O), 1624 (C=C); AB:CD 55:45 by $\delta_H$-NMR; $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.01 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.07 (9H, s, $C(CH_3)_3$), 1.71 (6H, br s, Adamantyl-$CH_2$), 2.09 (6H, m, Adamantyl-$CH_2$), 2.15 (3H, br s, Adamantyl-CH), 3.81 (3H, s, $OCH_3$), 3.81 (3H, s, $OCH_3$), 3.96 (2H, m, $OCH_2CH_3$), 4.73 (1H, s, H4), 4.74 (1H, s, H4), 4.84 (1H, s, H2), 4.85 (1H, s, H2), 6.88-6.91 (2H, m, Ar-H), 7.08 (2H, br s, NH/OH), 7.44-7.48 (2H, m, Ar-H), 7.65 (1H, br s, NH/OH), 7.96 (1H, br s, NH/OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.8 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 25.6 ($(CH_3)_3$), 29.5 (Adamantyl-C), 35.5 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 36.0 (Adamantyl-C), 36.1 (Adamantyl-C), 41.7 (Adamantyl-C), 41.7 (Adamantyl-C), 54.1 (Adamantyl-C), 54.9 (Adamantyl-C), 55.4 ($OCH_3$), 61.6 ($OCH_2CH_3$), 61.9 ($OCH_2CH_3$), 79.0 (C5), 81.1 (C4), 82.0 (C4), 85.6 (C7), 92.7 (C7), 96.5 (C2), 96.7 (C2), 113.3 (Ar-C), 113.4 (Ar-C), 127.2 (Ar-C), 127.7 (Ar-C), 159.2 (Ar-C), 159.4 (Ar-C), 165.4 (C10), 166.1 (C10), 166.8 (C9), 167.2 (C9), 176.9 (C8), 182.7 (C8), 188.0 (C6), 189.3 (C6); LRMS (ESI$^-$) *m/z*: 551.2 ([M – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{31}H_{39}N_2O_7$, 551.2763, found 551.2768.

**Ethyl (1*S**,3*R**,7a*R**)-6-(adamantan-1-ylcarbamoyl)-3-(*tert*-butyl)-1-(4-fluorophenyl)-7-hydroxy-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 23e**



Yield (151 mg, 54%); Brown foamy solid; m.p. 98-102°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.68; $v_{max}$/cm$^{-1}$ 3305 (O-H), 2911 (C-H), 2854 (C-H), 1739 (C=O), 1697 (C=O), 1653 (C=O), 1628 (C=C); AB:CD 53:47 by $\delta_F$-NMR; $\delta_H$ (400 MHz, CDCl$_3$) 1.00 (3H, m, OCH$_2$CH$_3$), 1.06 (9H, s, C(CH$_3$)$_3$), 1.72 (6H, br s, Adamantyl-CH$_2$), 2.09 (6H, m, Adamantyl-CH$_2$), 2.15 (3H, br s, Adamantyl-CH), 3.95 (2H, m, OCH$_2$CH$_3$), 4.75 (1H, s, H4), 4.86 (1H, s, H2), 7.05 (2H, app t, *J*=8.6 Hz, Ar-H), 7.53 (2H, m, Ar-H), 7.70 (1H, br s, NH/OH), 7.98 (1H, br s, NH/OH); $\delta_C$ (101 MHz, CDCl$_3$) 13.8 (OCH$_2$CH$_3$), 25.4 ((CH$_3$)$_3$), 29.5 (Adamantyl-C), 35.5 (C(CH$_3$)$_3$), 35.5 (C(CH$_3$)$_3$), 36.0 (Adamantyl-C), 36.1 (Adamantyl-C), 41.7 (Adamantyl-C), 54.3 (Adamantyl-C), 55.0 (Adamantyl-C), 61.7 (OCH$_2$CH$_3$), 61.9 (OCH$_2$CH$_3$), 78.8 (C5), 80.5 (C4), 81.3 (C4), 85.6 (C7), 91.9 (C7), 96.5 (C2), 96.7 (C2), 114.7 (d, *J*=21.0 Hz, Ar-C), 114.9 (d, *J*=21.5 Hz, Ar-C), 128.1 (d, *J*=8.2 Hz, Ar-C), 131.1 (d, *J*=3.0 Hz, Ar-C), 131.6 (d, *J*=3.0 Hz, Ar-C), 162.5 (d, *J*=245.8 Hz, Ar-C), 165.5 (C10), 166.1 (C10), 166.9 (C9), 167.2 (C9), 176.9 (C8), 182.5 (C8), 187.9 (C6), 189.7 (C6); $\delta_F$ (377 MHz, CDCl$_3$) -114.56, -114.97; LRMS (ESI$^-$) *m/z*: 539.2 ([M – H]$^-$ 83%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{30}H_{38}N_2O_6F$, 541.2708, found 541.2707.

**Ethyl (1*S**,3*R**,7a*R**)-6-(adamantan-1-ylcarbamoyl)-3-(*tert*-butyl)-1-(4-chlorophenyl)-7-hydroxy-5-oxo-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 23f**



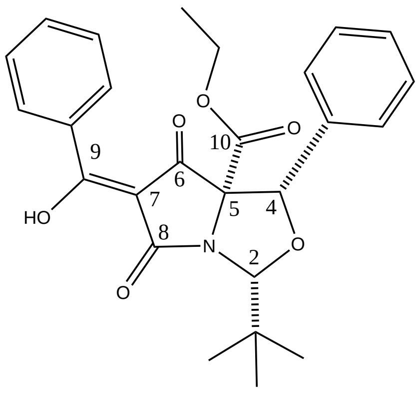
Yield (93 mg, 60%); Brown foamy solid; m.p. 131-135°C; $R_f$ (30% EtOAc in Pet. Ether 40:60) 0.63; $v_{max}$/cm$^{-1}$ 3309 (O-H), 2911 (C-H), 2853 (C-H), 1757 (C=O), 1740 (C=O), 1697 (C=O), 1628 (C=C); AB:CD 55:45 by $\delta_H$-NMR; $\delta_H$ (400 MHz, CDCl$_3$) 0.97-1.03 (6H, m, OCH$_2$CH$_3$), 1.05 (9H, s, C(CH$_3$)$_3$), 1.72 (6H, br s, Adamantyl-CH$_2$), 2.09 (6H, m, Adamantyl-CH$_2$), 2.16 (3H, br s, Adamantyl-CH), 3.96 (2H, m, OCH$_2$CH$_3$), 4.74 (1H, s, H4), 4.86 (1H, s, H2), 4.87 (1H, s, H2), 7.31-7.34 (2H, m, Ar-H), 7.49-7.53 (2H, m, Ar-H), 7.71 (1H, br s, NH/OH), 7.95 (1H, br s, NH/OH); $\delta_C$ (101 MHz, CDCl$_3$) 13.8

($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 25.4 ($(CH_3)_3$), 29.4 (Adamantyl-C), 35.5 ($C(CH_3)_3$), 35.5 ($C(CH_3)_3$), 36.0 (Adamantyl-C), 36.1 (Adamantyl-C), 41.7 (Adamantyl-C), 41.7 (Adamantyl-C), 54.3 (Adamantyl-C), 55.0 (Adamantyl-C), 61.8 ($OCH_2CH_3$), 62.0 ($OCH_2CH_3$), 77.1 (C5), 78.7 (C5), 80.4 (C4), 81.2 (C4), 85.6 (C7), 91.7 (C7), 96.5 (C2), 96.6 (C2), 127.8 (Ar-C), 127.8 (Ar-C), 128.0 (Ar-C), 128.1 (Ar-C), 133.4 (Ar-C), 133.7 (Ar-C), 134.0 (Ar-C), 134.4 (Ar-C), 165.5 (C10), 166.1 (C10), 166.9 (C9), 167.2 (C9), 176.9 (C8), 182.5 (C8), 187.9 (C6), 189.8 (C6); LRMS ($ESI^-$) *m/z*: 555.2 ($[M^{35} - H]^-$ 97%), 557.2 ($[M^{37} - H]^-$ 36%); HRMS ($ESI^-$) *m/z*: $[M^{35} - H]^-$ calcd. for $C_{30}H_{36}N_2O_6Cl$, 555.2267, found 555.2275; $[M^{37} - H]^-$ calcd. for $C_{30}H_{36}N_2O_6Cl$, 557.2247, found 557.2241.

**General procedure for the synthesis of C7-acyltetramates 25:**[20,22-23]

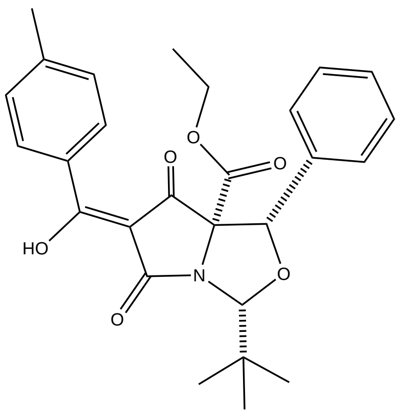
To a stirring solution of tetramic acid **14a** (1 eq.) in DCM was added DCC (1.1 eq.) and DMAP (1.3 eq.). The solution was cooled to 0°C and the respective carboxylic acid (1.1 eq.) was added portion wise. The reaction mixture was then left to stir at rt overnight. The suspension was then filtered, and the filtrate was concentrated *in-vacuo*. The concentrate was then purified by flash column chromatography to obtain metal-chelated tetramic acids which were then re-dissolved in DCM, washed with 10% citric acid solution (aq.), dried over $Na_2SO_4$, filtered, and then concentrated *in-vacuo* to obtain the desired product **25a-s**.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(phenyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25a**



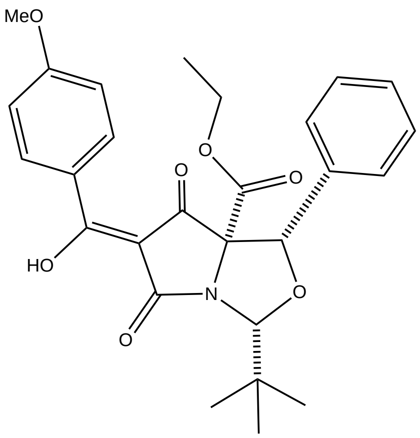

Yield (131 mg, 32%); Red oil; $R_f$ (100% EtOAc) 0.48; $\nu_{max}/cm^{-1}$ 2961 (C-H), 1760 (C=O), 1712 (C=O), 1652 (C=O), 1592 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.02 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.17 (9H, s, $C(CH_3)_3$), 4.02 (2H, q, *J*=7.2 Hz, $OCH_2CH_3$), 4.89 (1H, s, H4), 5.10 (1H, s, H2), 7.36 (3H, m, Ar-H), 7.57 (4H, m, Ar-H), 7.68 (1H, m, Ar-H), 8.24 (2H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 61.9 ($OCH_2CH_3$), 78.0 (C5), 80.9 (C4), 97.2 (C2), 100.3 (C7), 126.5 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 128.5 (Ar-C), 130.3 (Ar-C), 131.1 (Ar-C), 134.8 (Ar-C), 134.9 (Ar-C), 165.5 (C10), 182.4 (C8), 183.7 (C9), 186.8 (C6); LRMS ($ESI^-$) *m/z*: 448.1 ($[M - H]^-$ 94%); HRMS ($ESI^-$) *m/z*: $[M - H]^-$ calcd. for $C_{26}H_{26}NO_6$, 448.1766, found 448.1758.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(*p*-tolyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25b**



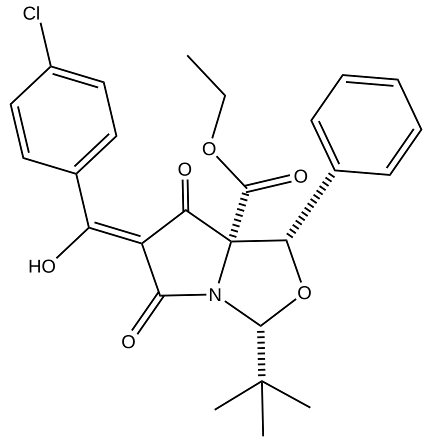
Yield (112 mg, 26%); Orange oil; $R_f$ (100% EtOAc) 0.58; $\nu_{max}/cm^{-1}$ 2960 (C-H), 1761 (C=O), 1737 (C=O), 1710 (C=O), 1651 (C=O), 1588 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.02 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.16 (9H, s, $C(CH_3)_3$), 2.48 (3H, s, $CH_3$), 4.01 (2H, dq, *J*=2.0 Hz, 7.2 Hz, $OCH_2CH_3$), 4.87 (1H, s, H4), 5.08 (1H, s, H2), 7.31-7.42 (5H, m, Ar-H), 7.58 (2H, d, *J*=7.4 Hz, Ar-H), 8.18 (2H, d, *J*=7.9 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 22.1 ($CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 61.9 ($OCH_2CH_3$), 77.9 (C5), 81.0 (C4), 97.2 (C2), 99.9 (C7), 126.5 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 128.4 (Ar-C), 129.2 (Ar-C), 130.5 (Ar-C), 135.0 (Ar-C), 146.4 (Ar-C), 165.6 (C10), 182.6 (C8), 183.6 (C9), 186.9 (C6); LRMS (ESI$^-$) *m/z*: 462.1 ($[M-H]^-$ 100%); HRMS (ESI$^-$) *m/z*: $[M-H]^-$ calcd. for $C_{27}H_{28}NO_6$, 462.1922, found 462.1914.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(4-methoxyphenyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25c**



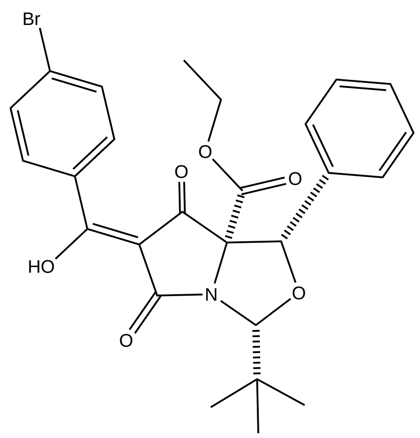
Yield (89 mg, 18%); Orange solid/oil; $R_f$ (100% EtOAc) 0.53; $\nu_{max}/cm^{-1}$ 2961 (C-H), 1759 (C=O), 1736 (C=O), 1705 (C=O), 1650 (C=O), 1584 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.99 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 3.90 (3H, s, $OCH_3$), 3.98 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 4.84 (1H, s, H4), 5.05 (1H, s, H2), 7.00 (2H, d, *J*=9.0 Hz, Ar-H), 7.28-7.37 (3H, m, Ar-H), 7.57 (2H, m, Ar-H), 8.35 (2H, d, *J*=9.0 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 55.7 ($OCH_3$), 61.9 ($OCH_2CH_3$), 77.8 (C5), 81.1 (C4), 97.2 (C2), 99.2 (C7), 114.0 (Ar-C), 126.6 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 133.2 (Ar-C), 135.1 (Ar-C), 165.4 (Ar-C), 165.7 (C10), 182.8 (C8), 183.0 (C9), 187.0 (C6); LRMS (ESI$^-$) *m/z*: 478.1 ($[M-H]^-$ 51%); HRMS (ESI$^-$) *m/z*: $[M-H]^-$ calcd. for $C_{27}H_{28}NO_7$, 478.1871, found 478.1861.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-((4-chlorophenyl)(hydroxy)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25d**



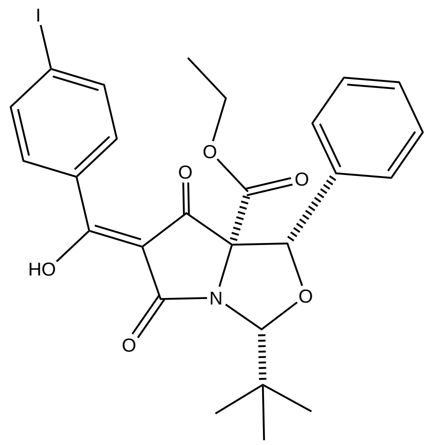
Yield (206 mg, 39%); Red solid; m.p. 42-47°C; $R_f$ (100% EtOAc) 0.45; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1710 (C=O), 1652 (C=O), 1588 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.02 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 1.17 (9H, s, $C(CH_3)_3$), 4.01 (2H, m, $OCH_2CH_3$), 4.88 (1H, s, H4), 5.09 (1H, s, H2), 7.33-7.41 (3H, m, Ar-H), 7.53 (2H, d, $J$=8.7 Hz, Ar-H), 7.58 (2H, d, $J$=7.4 Hz, Ar-H), 8.25 (2H, d, $J$=8.2 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 62.0 ($OCH_2CH_3$), 77.9 (C5), 81.0 (C4), 97.3 (C2), 100.4 (C7), 126.5 (Ar-C), 127.8 (Ar-C), 128.0 (Ar-C), 128.9 (Ar-C), 129.4 (Ar-C), 131.7 (Ar-C), 134.8 (Ar-C), 141.3 (Ar-C), 165.3 (C10), 182.2 (C8), 182.2 (C9), 186.9 (C6); LRMS (ESI$^-$) $m/z$: 482.1 ([$M^{35}$ – H]$^-$ 100%), 484.1 ([$M^{37}$ – H]$^-$ 36%); HRMS (ESI$^-$) $m/z$: [$M^{35}$ – H]$^-$ calcd. for $C_{26}H_{25}NO_6Cl$, 482.1376, found 482.1369; [$M^{37}$ – H]$^-$ calcd. for $C_{26}H_{25}NO_6Cl$, 484.1347, found 484.1344.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-6-((4-bromophenyl)(hydroxy)methylene)-3-(*tert*-butyl)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25e**



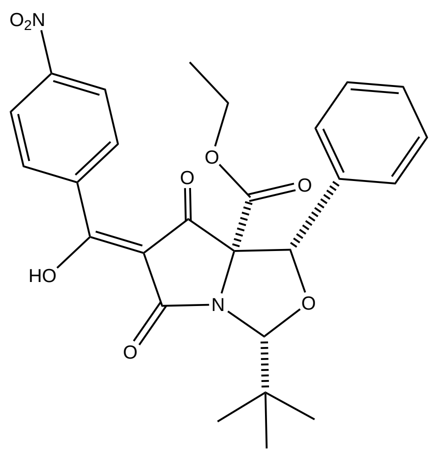
Yield (181 mg, 35%); Orange solid; m.p. 43-48°C; $R_f$ (100% EtOAc) 0.55; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1759 (C=O), 1735 (C=O), 1711 (C=O), 1651 (C=O), 1586 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.01 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 1.16 (9H, s, $C(CH_3)_3$), 4.01 (2H, m, $OCH_2CH_3$), 4.88 (1H, s, H4), 5.08 (1H, s, H2), 7.34-7.41 (3H, m, Ar-H), 7.57 (2H, d, $J$=7.3 Hz, Ar-H), 7.69 (2H, d, $J$=8.7 Hz, Ar-H), 8.15 (2H, d, $J$=8.5 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 62.0 ($OCH_2CH_3$), 77.9 (C5), 81.0 (C4), 97.3 (C2), 126.5 (Ar-C), 127.8 (Ar-C), 128.0 (Ar-C), 129.9 (Ar-C), 130.2 (Ar-C), 131.8 (Ar-C), 131.9 (Ar-C), 134.8 (Ar-C), 165.3 (C10), 182.5 (C8), 182.5 (C9), 187.0 (C6); LRMS (ESI$^-$) $m/z$: 526.0 ([$M^{79}$ – H]$^-$ 95%), 528.0 ([$M^{81}$ – H]$^-$ 97%); HRMS (ESI$^-$) $m/z$: [$M^{79}$ – H]$^-$ calcd. for $C_{26}H_{25}NO_6Br$, 526.0871, found 526.0863; [$M^{81}$ – H]$^-$ calcd. for $C_{26}H_{25}NO_6Br$, 528.0851, found 528.0844.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(4-iodophenyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25f**



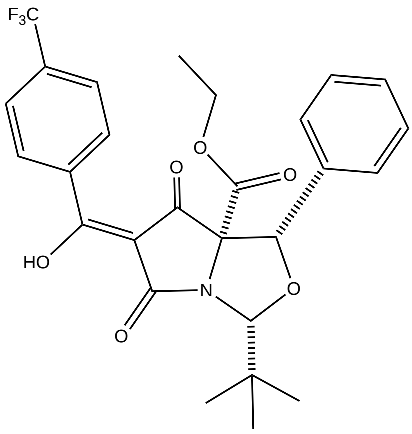
Yield (224 mg, 37%); Pink foamy solid/oil; $R_f$ (100% EtOAc) 0.65; $\nu_{max}/cm^{-1}$ 3320 (O-H), 2932 (C-H), 2855 (C-H), 1760 (C=O), 1713 (C=O), 1653 (C=O), 1584 (C=C); $\delta_H$ (500 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 3.97 (2H, dq, *J*=2.5 Hz, 7.2 Hz, $OCH_2CH_3$), 4.85 (1H, s, H4), 5.06 (1H, s, H2), 7.29-7.39 (3H, m, Ar-H), 7.52 (2H, d, *J*=8.6 Hz, Ar-H), 7.89 (2H, d, *J*=8.5 Hz, Ar-H), 7.94 (2H, d, *J*=8.5 Hz, Ar-H); $\delta_C$ (126 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.7 ($C(CH_3)_3$), 62.1 ($OCH_2CH_3$), 78.1 (C5), 81.0 (C4), 97.3 (C2), 100.6 (Ar-C), 103.3 (C7), 126.5 (Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 131.4 (Ar-C), 134.8 (Ar-C), 138.0 (Ar-C), 165.4 (C10), 182.2 (C8), 182.7 (C9), 186.9 (C6); LRMS ($ESI^-$) *m/z*: 574.0 ($[M-H]^-$ 96%); HRMS ($ESI^-$) *m/z*: $[M-H]^-$ calcd. for $C_{26}H_{25}NO_6I$, 574.0732, found 574.0723.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(4-nitrophenyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25g**



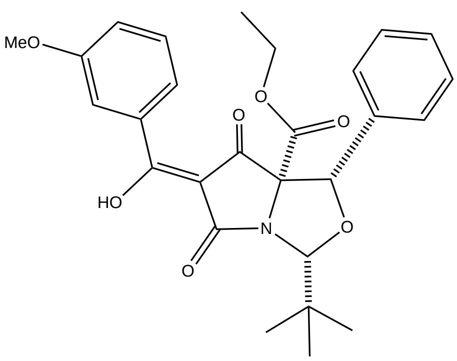
Yield (159 mg, 30%); Red oil/solid; m.p. 160-164°C; $R_f$ (100% EtOAc) 0.60; $\nu_{max}/cm^{-1}$ 2962 (C-H), 1716 (C=O), 1654 (C=O), 1612 (C=O), 1568 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 3.98 (2H, dq, *J*=3.9 Hz, 7.1 Hz, $OCH_2CH_3$), 4.88 (1H, s, H4), 5.07 (1H, s, H2), 7.31-7.37 (3H, m, Ar-H), 7.52 (2H, d, *J*=7.2 Hz, Ar-H), 8.34 (4H, s, Ar-H), 11.38 (1H, br s, OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 62.2 ($OCH_2CH_3$), 78.1 (C5), 81.0 (C4), 97.5 (C2), 123.4 (Ar-C), 126.4 (Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 131.3 (Ar-C), 134.5 (Ar-C), 136.5 (Ar-C), 150.9 (Ar-C), 165.1 (C10); LRMS ($ESI^-$) *m/z*: 493.1 ($[M-H]^-$ 94%); HRMS ($ESI^-$) *m/z*: $[M-H]^-$ calcd. for $C_{26}H_{25}N_2O_8$, 493.1616, found 493.1609.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(4-(trifluoromethyl)phenyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25h**



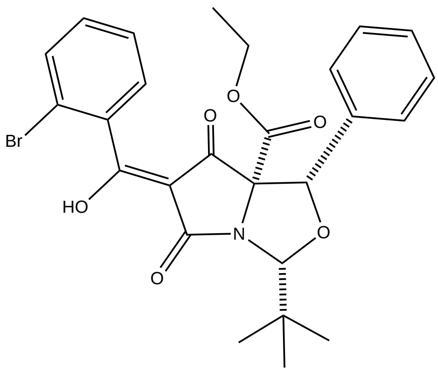

Yield (190 mg, 41%); Orange oil; $R_f$ (100% EtOAc) 0.63; $\nu_{max}$/cm$^{-1}$ 2963 (C-H), 1715 (C=O), 1653 (C=O), 1596 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 3.99 (2H, m, $OCH_2CH_3$), 4.87 (1H, s, H4), 5.07 (1H, s, H2), 7.32-7.38 (3H, m, Ar-H), 7.54 (2H, d, *J*=8.0 Hz, Ar-H), 7.79 (2H, d, *J*=8.3 Hz, Ar-H), 8.30 (2H, d, *J*=8.2 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 62.1 ($OCH_2CH_3$), 78.1 (C5), 81.0 (C4), 97.4 (C2), 125.4 (q, *J*=3.7 Hz, Ar-C), 126.5 (Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 130.6 (Ar-C), 134.7 (Ar-C), 165.2 (C10), 182.0 (C8), 182.0 (C9), 186.8 (C6); $\delta_F$ (376 MHz, $CDCl_3$) -63.36; LRMS (ESI$^-$) *m/z*: 516.1 ([M – H]$^-$ 98%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{27}H_{25}NO_6F_3$, 516.1639, found 516.1628.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(3-methoxyphenyl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25i**



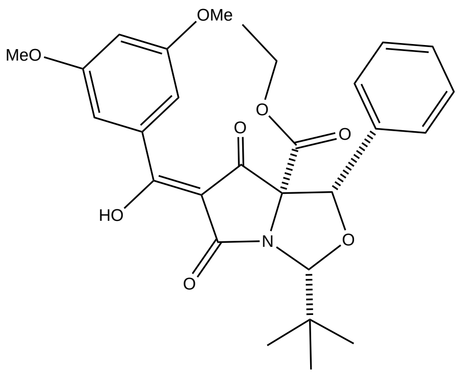

Yield (198 mg, 44%); Orange oil; $R_f$ (100% EtOAc) 0.45; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1760 (C=O), 1734 (C=O), 1711 (C=O), 1653 (C=O), 1592 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.00 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.13 (9H, s, $C(CH_3)_3$), 3.88 (3H, s, $OCH_3$), 3.99 (2H, q, *J*=7.1 Hz, $OCH_2CH_3$), 4.84 (1H, s, H4), 5.06 (1H, s, H2), 7.20 (1H, ddd, *J*=1.0 Hz, 2.6 Hz, 8.3 Hz, Ar-H), 7.28-7.39 (3H, m, Ar-H), 7.43 (1H, t, *J*=8.0 Hz, Ar-H), 7.55 (2H, d, *J*=7.3 Hz, Ar-H), 7.80 (1H, m, Ar-H), 7.85 (1H, d, *J*=7.8 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 55.6 ($OCH_3$), 61.9 ($OCH_2CH_3$), 77.9 (C5), 80.9 (C4), 97.2 (C2), 100.3 (C7), 114.6 (Ar-C), 121.4 (Ar-C), 122.8 (Ar-C), 126.6 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 129.5 (Ar-C), 132.3 (Ar-C), 134.9 (Ar-C), 159.5 (Ar-C), 165.5 (C10), 182.5 (C8), 183.5 (C9), 186.7 (C6); LRMS (ESI$^-$) *m/z*: 478.1 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{27}H_{28}NO_7$, 478.1871, found 478.1867.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-6-((2-bromophenyl)(hydroxy)methylene)-3-(*tert*-butyl)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25j**



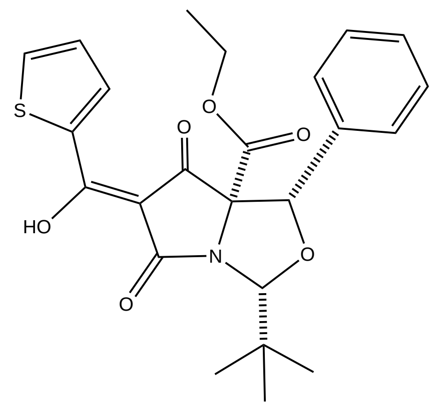
Yield (84 mg, 12%); Orange oil; $R_f$ (100% EtOAc) 0.70; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1761 (C=O), 1725 (C=O), 1656 (C=O), 1606 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.96 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 3.94 (2H, dq, *J*=1.2 Hz, 7.1 Hz, $OCH_2CH_3$), 4.88 (1H, s, H4), 5.08 (1H, s, H2), 7.29-7.53 (8H, m, Ar-H), 7.70 (1H, dd, *J*=1.3 Hz, 7.8 Hz, Ar-H), 11.40 (1H, br s, OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.7 ($C(CH_3)_3$), 62.0 ($OCH_2CH_3$), 80.7 (C4), 97.2 (C2), 126.4 (Ar-C), 127.4 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 130.4 (Ar-C), 133.0 (Ar-C), 133.6 (Ar-C), 134.8 (Ar-C), 165.1 (C10); LRMS (ESI$^-$) *m/z*: 526.0 ([M$^{79}$ – H]$^-$ 93%), 528.0 ([M$^{81}$ – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M$^{79}$ – H]$^-$ calcd. for $C_{26}H_{25}NO_6Br$, 526.0871, found 526.0863; [M$^{81}$ – H]$^-$ calcd. for $C_{26}H_{25}NO_6Br$, 528.0851, found 528.0844.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-((3,5-dimethoxyphenyl)(hydroxy)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25k**



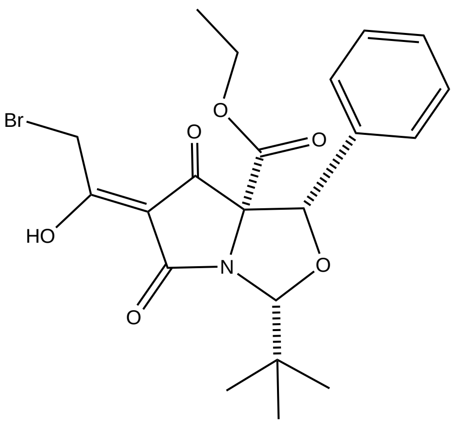
Yield (77 mg, 17%); Orange oil; $R_f$ (100% EtOAc) 0.45; $\nu_{max}$/cm$^{-1}$ 2961 (C-H), 1760 (C=O), 1736 (C=O), 1711 (C=O), 1653 (C=O), 1562 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 1.01 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.12 (9H, s, $C(CH_3)_3$), 3.86 (6H, s, $OCH_3$, $OCH_3$), 3.99 (2H, q, *J*=7.2 Hz, $OCH_2CH_3$), 4.84 (1H, s, H4), 5.06 (1H, s, H2), 6.75 (1H, t, *J*=2.3 Hz, Ar-H), 7.28-7.60 (7H, m, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.7 ($C(CH_3)_3$), 55.8 ($OCH_3$), 61.9 ($OCH_2CH_3$), 77.8 (C5), 81.0 (C4), 97.2 (C2), 100.4 (C7), 107.8 (Ar-C), 107.9 (Ar-C), 126.6 (Ar-C), 127.8 (Ar-C), 128.0 (Ar-C), 132.8 (Ar-C), 134.9 (Ar-C), 160.6 (Ar-C), 165.5 (C10), 182.7 (C8), 183.5 (C9), 186.6 (C6); LRMS (ESI$^-$) *m/z*: 508.1 ([M – H]$^-$ 45%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{28}H_{30}NO_8$, 508.1977, found 508.1968.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(hydroxy(thiophen-2-yl)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25l**



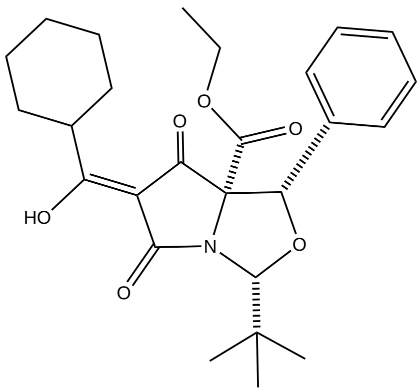
Yield (57 mg, 13%); Yellow foamy solid; m.p. 80-84°C; $R_f$ (100% EtOAc) 0.60; $\nu_{max}$/cm$^{-1}$ 3400 (O-H), 2974 (C-H), 2934 (C-H), 1758 (C=O), 1736 (C=O), 1704 (C=O), 1652 (C=O), 1558 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.90 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.04 (9H, s, $C(CH_3)_3$), 3.89 (2H, m, $OCH_2CH_3$), 4.78 (1H, s, H4), 4.97 (1H, s, H2), 7.20 (1H, dd, *J*=4.1 Hz, 4.9 Hz, Ar-H), 7.22-7.32 (3H, m, Ar-H), 7.49 (2H, m, Ar-H), 7.82 (1H, dd, *J*=1.1 Hz, 4.9 Hz, Ar-H), 9.19 (1H, dd, *J*=1.2 Hz, 4.1 Hz, Ar-H); $\delta_C$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.5 ($(CH_3)_3$), 35.7 ($C(CH_3)_3$), 62.0 ($OCH_2CH_3$), 81.2 (C4), 97.3 (C2), 126.5 (Ar-C), 126.6 (Ar-C), 127.9 (Ar-C), 128.0 (Ar-C), 129.3 (Ar-C), 135.0 (Ar-C), 137.6 (Ar-C), 138.6 (Ar-C), 165.5 (C10), 182.8 (C8), 182.8 (C9), 186.6 (C6); LRMS (ESI$^-$) *m/z*: 454.1 ([M – H]$^-$ 26%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{24}H_{24}NO_6S$, 454.1330, found 454.1320.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-6-(2-bromo-1-hydroxyethylidene)-3-(*tert*-butyl)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25m**



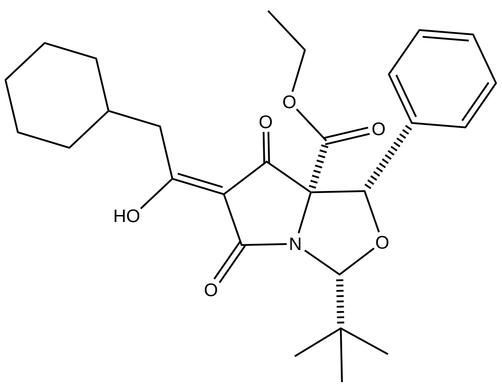
Yield (1.45 g, 37%); Orange semi-solid; $R_f$ (100% EtOAc) 0.70; $\nu_{max}$/cm$^{-1}$ 3305 (O-H), 2962 (C-H), 1721 (C=O), 1664 (C=O), 1606 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.10 (9H, s, $C(CH_3)_3$), 3.95 (2H, dq, *J*=4.3 Hz, 6.8 Hz, $OCH_2CH_3$), 4.41 (1H, d, *J*=10.8 Hz, $CH_2Br$), 4.50 (1H, d, *J*=10.9 Hz, $CH_2Br$), 4.84 (1H, s, H4), 5.02 (1H, s, H2), 7.31-7.40 (3H, m, Ar-H), 7.52 (2H, d, *J*=7.1 Hz, Ar-H), 9.10 (1H, br s, OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 23.5 ($CH_2Br$), 25.4 ($(CH_3)_3$), 35.6 ($C(CH_3)_3$), 62.2 ($OCH_2CH_3$), 79.1 (C5), 80.7 (C4), 97.3 (C2), 102.1 (C7), 126.4 (Ar-C), 128.0 (Ar-C), 128.2 (Ar-C), 134.5 (Ar-C), 164.8 (C10), 179.3 (C8), 181.9 (C9), 187.4 (C6); LRMS (ESI$^-$) *m/z*: 464.0 ([M$^{79}$ – H]$^-$ 93%), 466.0 ([M$^{81}$ – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M$^{79}$ – H]$^-$ calcd. for $C_{21}H_{23}NO_6Br$, 464.0714, found 464.0706; [M$^{81}$ – H]$^-$ calcd. for $C_{21}H_{23}NO_6Br$, 466.0693, found 466.0686.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(cyclohexyl(hydroxy)methylene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25n**



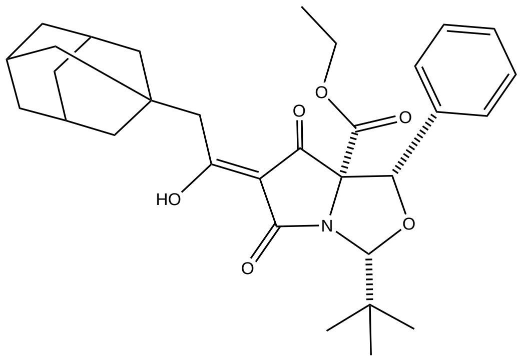
Yield (295 mg, 57%); Orange oil; $R_f$ (100% EtOAc) 0.55; $\nu_{max}$/cm$^{-1}$ 2934 (C-H), 1760 (C=O), 1711 (C=O), 1653 (C=O), 1591 (C=C); $\delta_H$ (400 MHz, $CDCl_3$) 0.98 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.14 (9H, s, $C(CH_3)_3$), 1.25-1.98 (10H, m, Cyclohexyl-$CH_2$), 3.50 (1H, m, Cyclohexyl-H), 3.98 (2H, m, $OCH_2CH_3$), 4.83 (1H, s, H4), 5.02 (1H, s, H2), 7.33-7.42 (3H, m, Ar-H), 7.58 (2H, d, *J*=7.1 Hz, Ar-H), 11.99 (1H, br s, OH); $\delta_C$ (101 MHz, $CDCl_3$) 13.5 ($OCH_2CH_3$), 25.3 ($(CH_3)_3$), 25.3 (Cyclohexyl-C), 25.6 (Cyclohexyl-C), 28.4 (Cyclohexyl-C), 35.4 ($C(CH_3)_3$), 41.3 (Cyclohexyl-C), 61.7 ($OCH_2CH_3$), 78.6 (C5), 80.6 (C4), 96.8 (C2), 100.1 (C7), 126.3 (Ar-C), 127.7 (Ar-C), 127.8 (Ar-C), 135.0 (Ar-C), 165.4 (C10), 180.8 (C8), 187.8 (C6), 196.1 (C9); LRMS (ESI$^-$) *m/z*: 454.2 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{26}H_{32}NO_6$, 454.2235, found 454.2227.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(2-cyclohexyl-1-hydroxyethylidene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25o**



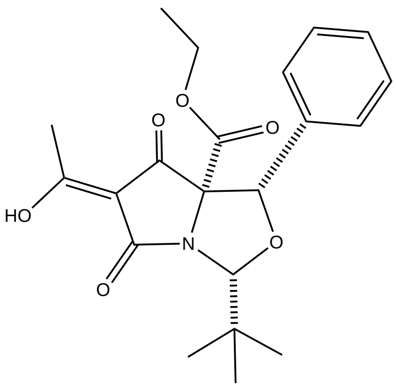
Yield (219 mg, 44%); Orange oil; $R_f$ (100% EtOAc) 0.43; $\nu_{max}$/cm$^{-1}$ 2926 (C-H), 2853 (C-H), 1763 (C=O), 1717 (C=O), 1655 (C=O), 1598 (C=C); AB:CD 22:78 by $\delta_H$-NMR; $\delta_{H\ (Major\ Tautomer)}$ (400 MHz, $CDCl_3$) 0.96 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 1.11-1.33 (6H, m, Cyclohexyl-$CH_2$), 1.60-1.93 (5H, m, Cyclohexyl-$CH_2$, CH), 2.71 (1H, dd, *J*=6.9 Hz, 13.0 Hz, $CH_2$-Cyclohexyl), 2.96 (1H, dd, *J*=7.3 Hz, 13.0 Hz, $CH_2$-Cyclohexyl), 3.94 (2H, dq, *J*=2.6 Hz, 7.1 Hz, $OCH_2CH_3$), 4.79 (1H, s, H4), 4.99 (1H, s, H2), 7.29-7.39 (3H, m, Ar-H), 7.54 (2H, m, Ar-H); $\delta_{C\ (Major\ Tautomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 26.1 (Cyclohexyl-C), 26.1 (Cyclohexyl-C), 32.9 (Cyclohexyl-C), 33.2 (Cyclohexyl-C), 33.8 (Cyclohexyl-C), 35.5 ($C(CH_3)_3$), 36.9 (Cyclohexyl-C), 40.4 ($CH_2$-Cyclohexyl), 61.8 ($OCH_2CH_3$), 78.7 (C5), 80.6 (C4), 96.9 (C2), 102.5 (C7), 126.4 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 134.9 (Ar-C), 165.3 (C10), 180.2 (C8), 188.3 (C6), 191.7 (C9); LRMS (ESI$^-$) *m/z*: 468.2 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{27}H_{34}NO_6$, 468.2392, found 468.2383.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-6-(2-(adamantan-1-yl)-1-hydroxyethylidene)-3-(*tert*-butyl)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25p**



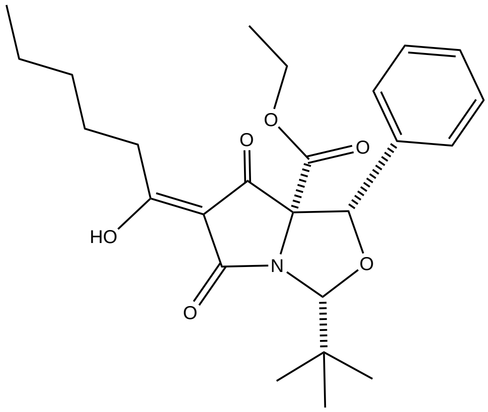
Yield (276 mg, 57%); Yellow foamy solid; m.p. 68-72°C; $R_f$ (100% EtOAc) 0.30; $v_{max}$/cm$^{-1}$ 3400 (O-H), 2904 (C-H), 2850 (C-H), 1763 (C=O), 1717 (C=O), 1653 (C=O), 1598 (C=C); AB:CD 15:85 by $\delta_H$-NMR; $\delta_{H\ (Major\ Tautomer)}$ (400 MHz, $CDCl_3$) 0.97 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.08 (9H, s, $C(CH_3)_3$), 1.65-1.70 (12H, m, Adamantyl-$CH_2$), 1.95-1.98 (3H, m, Adamantyl-CH), 2.48 (1H, d, *J*=11.7 Hz, $CH_2$-Adamantyl), 3.00 (1H, d, *J*=11.7 Hz, $CH_2$-Adamantyl), 3.94 (2H, m, $OCH_2CH_3$), 4.79 (1H, s, H4), 5.00 (1H, s, H2), 7.29-7.39 (3H, m, Ar-H), 7.53 (2H, m, Ar-H); $\delta_{C\ (Major\ Tautomer)}$ (101 MHz, $CDCl_3$) 13.7 ($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 29.0 (Adamantyl-C), 35.6 ($C(CH_3)_3$), 36.7 (Adamantyl-C), 42.6 (Adamantyl-C), 46.5 ($CH_2$-Adamantyl), 49.4 (Adamantyl-C), 61.8 ($OCH_2CH_3$), 78.5 (C5), 80.7 (C4), 96.9 (C2), 103.5 (C7), 126.4 (Ar-C), 127.9 (Ar-C), 128.0 (Ar-C), 134.9 (Ar-C), 165.4 (C10), 180.3 (C8), 188.6 (C6), 190.5 (C9); LRMS (ESI$^-$) *m/z*: 520.2 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{31}H_{38}NO_6$, 520.2705, found 520.2695.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(1-hydroxyethylidene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25q**



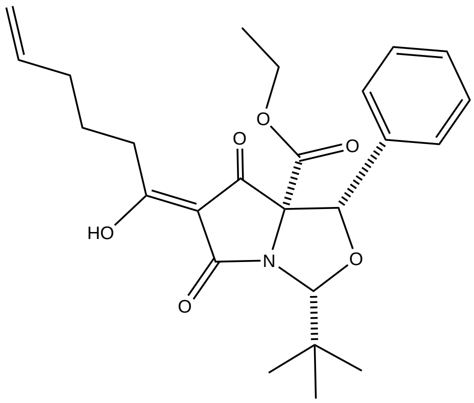
Yield (174 mg, 51%); Yellow oil; $R_f$ (100% EtOAc) 0.18; $v_{max}$/cm$^{-1}$ 2961 (C-H), 1762 (C=O), 1718 (C=O), 1656 (C=O), 1602 (C=C); AB:CD 21:79 by $\delta_H$-NMR; $\delta_{H\ (Major\ Tautomer)}$ (400 MHz, $CDCl_3$) 0.96 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 2.54 (3H, s, $CH_3$), 3.94 (2H, m, $OCH_2CH_3$), 4.79 (1H, s, H4), 4.98 (1H, s, H2), 7.29-7.38 (3H, m, Ar-H), 7.52 (2H, m, Ar-H), 12.22 (1H, br s, OH); $\delta_{C\ (Major\ Tautomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 20.1 ($CH_3$), 25.4 ($(CH_3)_3$), 35.5 ($C(CH_3)_3$), 61.9 ($OCH_2CH_3$), 78.9 (C5), 80.7 (C4), 96.9 (C2), 102.3 (C7), 126.4 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 134.9 (Ar-C), 165.3 (C10), 179.9 (C8), 188.3 (C6), 188.5 (C9); LRMS (ESI$^-$) *m/z*: 386.1 ([M – H]$^-$ 96%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{21}H_{24}NO_6$, 386.1609, found 386.1602.

**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(1-hydroxyhexylidene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25r**



Yield (227 mg, 47%); Orange oil; $R_f$ (100% EtOAc) 0.48; $\nu_{max}$/cm$^{-1}$ 2959 (C-H), 2934 (C-H), 2872 (C-H), 1763 (C=O), 1738 (C=O), 1718 (C=O), 1656 (C=O), 1600 (C=C); $\delta_{H\ (Major\ Tautomer)}$ (400 MHz, $CDCl_3$) 0.91 (3H, t, *J*=7.0 Hz, Hexyl-$CH_3$), 0.96 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 1.32-1.42 (4H, m, Hexyl-$CH_2$), 1.73 (2H, qn, *J*=7.4 Hz, Hexyl-$CH_2$), 2.86 (1H, dt, *J*=7.6 Hz, 14.3 Hz, Hexyl-$CH_2$), 2.98 (1H, dt, *J*=7.6 Hz, 13.8 Hz, Hexyl-$CH_2$), 3.94 (2H, dq, *J*=2.4 Hz, 7.2 Hz, $OCH_2CH_3$), 4.79 (1H, s, H4), 4.99 (1H, s, H2), 7.31-7.39 (3H, m, Ar-H), 7.53 (2H, m, Ar-H); $\delta_{C\ (Major\ Tautomer)}$ (101 MHz, $CDCl_3$) 13.6 (Hexyl-$CH_3$), 13.9 ($OCH_2CH_3$), 22.4 (Hexyl-$CH_2$), 25.4 ($(CH_3)_3$), 25.7 (Hexyl-$CH_2$), 31.4 (Hexyl-$CH_2$), 33.1 (Hexyl-$CH_2$), 35.5 ($C(CH_3)_3$), 61.8 ($OCH_2CH_3$), 78.7 (C5), 80.7 (C4), 96.9 (C2), 101.7 (C7), 126.4 (Ar-C), 127.8 (Ar-C), 127.9 (Ar-C), 134.9 (Ar-C), 165.4 (C10), 180.3 (C8), 188.1 (C6), 192.6 (C9); LRMS (ESI$^-$) *m/z*: 442.1 ([M – H]$^-$ 95%); HRMS (ESI$^-$) *m/z*: [M – H]$^-$ calcd. for $C_{25}H_{32}NO_6$, 442.2235, found 442.2230.

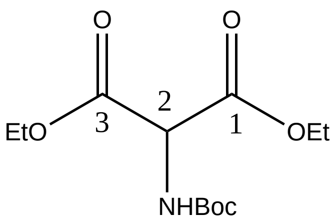
**Ethyl (1*S**,3*R**,7a*R**,*Z*)-3-(*tert*-butyl)-6-(1-hydroxyhex-5-en-1-ylidene)-5,7-dioxo-1-phenyldihydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-7a(5*H*)-carboxylate 25s**



Yield (188 mg, 41%); Red oil; $R_f$ (100% EtOAc) 0.38; $\nu_{max}$/cm$^{-1}$ 2974 (C-H), 2960 (C-H), 2935 (C-H), 1762 (C=O), 1718 (C=O), 1656 (C=O), 1600 (C=C); $\delta_{H\ (Major\ Tautomer)}$ (400 MHz, $CDCl_3$) 0.96 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.09 (9H, s, $C(CH_3)_3$), 1.83 (2H, qn, *J*=7.5 Hz, Hexenyl-$CH_2$), 2.18 (2H, q, *J*=7.4 Hz, Hexenyl-$CH_2$), 2.89 (1H, dt, *J*=7.6 Hz, 14.4 Hz, Hexenyl-$CH_2$), 2.99 (1H, dt, *J*=7.6 Hz, 15.0 Hz, Hexenyl-$CH_2$), 3.94 (2H, dq, *J*=3.2 Hz, 7.1 Hz, $OCH_2CH_3$), 4.80 (1H, s, H4), 4.99 (1H, s, H2), 5.04 (2H, m, $CH_2$=CH), 5.81 (1H, ddt, *J*=6.7 Hz, 10.2 Hz, 17.0 Hz, $CH_2$=CH), 7.30-7.39 (3H, m, Ar-H), 7.53 (2H, m, Ar-H); $\delta_{C\ (Major\ Tautomer)}$ (101 MHz, $CDCl_3$) 13.6 ($OCH_2CH_3$), 25.4 ($(CH_3)_3$), 25.4 (Hexenyl-$CH_2$), 32.6 (Hexenyl-$CH_2$), 33.2 (Hexenyl-$CH_2$), 35.5 ($C(CH_3)_3$), 61.9 ($OCH_2CH_3$), 78.7

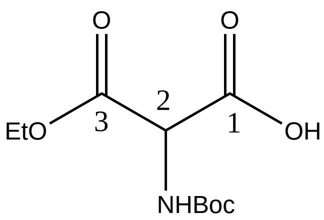
(C5), 80.7 (C4), 96.9 (C2), 101.8 (C7), 115.9 ($CH_2$=CH), 126.4 (Ar-C), 127.9 (Ar-C), 127.9 (Ar-C), 134.9 (Ar-C), 137.3 ($CH_2$=CH), 165.3 (C10), 180.2 (C8), 188.1 (C6), 192.1 (C9); LRMS ($ESI^-$) *m/z*: 440.1 ($[M - H]^-$ 100%); HRMS ($ESI^-$) *m/z*: $[M - H]^-$ calcd. for $C_{25}H_{30}NO_6$, 440.2079, found 440.2075.

**Diethyl 2-((*tert*-butoxycarbonyl)amino)malonate 27b:**[24]




Diethyl aminomalonate.HCl **27a** (1 eq.) was dissolved in 1,4-dioxane (1.2 M) and cooled to 0°C. 1 M NaOH solution (aq.) (1 eq.) was added to this reaction mixture dropwise. $Boc_2O$ (1.1 eq.) in 1,4-dioxane (2.4 M) was subsequently added dropwise at 0°C and the mixture was left to stir at rt overnight. 1,4-Dioxane was then evaporated *in-vacuo* and added to this reaction mixture was EtOAc. After phase separation, the organic layer was washed with 1 M HCl solution (aq.), dried over $Na_2SO_4$, filtered and the solvent was removed *in-vacuo* and the crude product was purified by flash column chromatography to yield the desired Boc-protected malonate **27b** as a colourless oil. Yield (5.11 g, 79%); Colourless oil; $R_f$ (20% EtOAc in Pet. Ether 40:60) 0.45; $\nu_{max}/cm^{-1}$ 2981 (C-H), 1742 (C=O), 1715 (C=O); $\delta_H$ (400 MHz, $CDCl_3$) 1.27 (6H, t, *J*=7.1 Hz, $OCH_2CH_3$, $OCH_2CH_3$), 1.43 (9H, s, $(CH_3)_3$), 4.24 (4H, m, $OCH_2CH_3$, $OCH_2CH_3$), 4.92 (1H, d, *J*=7.7 Hz, H2), 5.54 (1H, br s, NH); LRMS ($ESI^+$) *m/z*: 298.0 ($[M + Na]^+$ 75%); HRMS ($ESI^+$) *m/z*: $[M + Na]^+$ calcd. for $C_{12}H_{21}NO_6Na$, 298.1261, found 298.1263.

**2-((*tert*-butoxycarbonyl)amino)-3-ethoxy-3-oxopropanoic acid 27c:**[12]



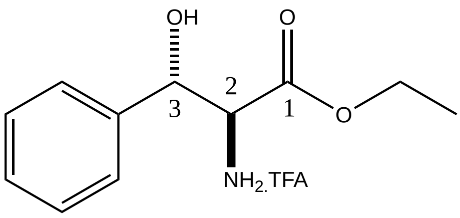

A solution of 4.5 M KOH (1 eq.) (aq.) was added dropwise to a solution of diethyl (Boc-amino)malonate **27b** (1 eq.) in ethanol (0.45 M) at 0°C. The reaction mixture was allowed to warm up to rt and stirred for 15 h. Ethanol was then evaporated *in-vacuo*, and $Et_2O$ was added to the reaction mixture and this was transferred to a separatory funnel. The aqueous layer was then acidified to pH 1 with 1 M HCl solution (aq.), then extracted with EtOAc. The organic layer was then washed with brine, dried over $Na_2SO_4$, filtered and the solvent was removed *in-vacuo* to obtain the carboxylic acid **27c** as a colourless oil and was used without further purification. Yield (3.89 g, 86%); Colourless oil that solidified to a white solid; m.p 83-86°C (lit.[25] 98-99°C); $\nu_{max}/cm^{-1}$ 3309 (O-H), 2981 (C-H), 1720 (C=O), 1669 (C=O); 54:46 mixture of rotamers; $\delta_H$ (400 MHz, $CDCl_3$) 1.31 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 1.43/1.44 (9H, s, $C(CH_3)_3$), 4.26/4.26 (2H, m, $OCH_2CH_3$), 4.77 (1H, d, *J*=5.0 Hz, H2)/4.98 (1H, d, *J*=7.5

Hz, H2), 5.65 (1H, d, $J$=7.5 Hz, NH)/7.59 (1H, d, $J$=5.1 Hz, NH), 8.73 (1H, br s, OH); $\delta_C$ (101 MHz, $CDCl_3$) 14.1/14.2 ($OCH_2CH_3$), 28.3/28.3 ($(CH_3)_3$), 57.5/58.8 (C2), 62.5/63.0 ($OCH_2CH_3$), 81.4/82.8 ($C(CH_3)_3$), 155.4/156.6 (C=O), 166.7/166.7 (C=O), 168.4/169.6 (C=O); LRMS (ESI$^+$) *m/z*: 270.0 ([M + Na]$^+$ 29%); HRMS (ESI$^+$) *m/z*: [M + Na]$^+$ calcd. for $C_{10}H_{17}NO_6Na$, 270.0948, found 270.0948.

**General procedure for the deprotection of Boc-protected amino esters:**

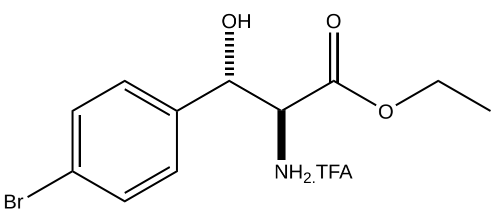
To a solution of Boc-protected amino ester **9a-m** (1 eq.) dissolved in DCM was added TFA (4 eq.) at 0°C under an atmosphere of $N_2$. The reaction mixture was then stirred at rt for 2 h, and then concentrated *in-vacuo* to obtain the deprotected amino ester as a trifluoroacetate ammonium salt **28a-k** and was used without further purification.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-phenylpropanoate trifluoroacetic acid 28a**



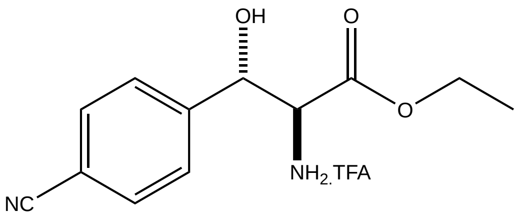

Yield (2.82 g, Quantitative); Thick orange oil; $\delta_H$ (400 MHz, $D_2O$) 1.16 (3H, t, $J$=7.1 Hz, $OCH_2CH_3$), 4.20 (2H, dq, $J$=2.0 Hz, 7.2 Hz, $OCH_2CH_3$), 4.48 (1H, d, $J$=4.2 Hz, H2), 5.40 (1H, d, $J$=4.2 Hz, H3), 7.39-7.50 (5H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.5 (C2), 63.6 ($OCH_2CH_3$), 71.0 (C3), 126.0 (Ar-C), 128.9 (Ar-C), 129.1 (Ar-C), 137.1 (Ar-C), 167.5 (C1); LRMS (ESI$^+$) *m/z*: 210.2 ([M + H]$^+$ 6%), 232.2 ([M + Na]$^+$ 13%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{11}H_{16}NO_3$, 210.1125, found 210.1127.

**Ethyl (2*S**,3*S**)-2-amino-3-(4-bromophenyl)-3-hydroxypropanoate trifluoroacetic acid 28b**



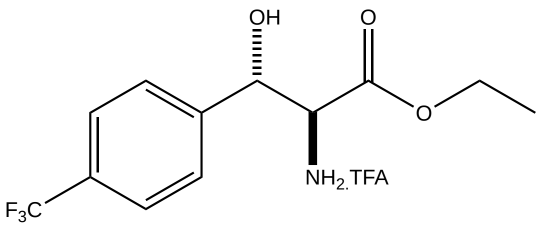

Yield (1.22 g, Quantitative); Pale yellow oil that solidified to a beige solid; m.p. 130-134°C; $\nu_{max}$/cm$^{-1}$ 3140 (O-H), 2902 (N-H), 1741 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.13 (3H, t, $J$=7.2 Hz, $OCH_2CH_3$), 4.18 (2H, dq, $J$=2.5 Hz, 7.1 Hz, $OCH_2CH_3$), 4.48 (1H, d, $J$=3.9 Hz, H2), 5.38 (1H, d, $J$=4.0 Hz, H3), 7.32 (2H, d, $J$=8.4 Hz, Ar-H), 7.64 (2H, d, $J$=8.5 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.3 (C2), 63.6 ($OCH_2CH_3$), 70.4 (C3), 122.2 (Ar-C), 127.8 (Ar-C), 131.8 (Ar-C), 136.6 (Ar-C), 167.3 (C1); LRMS (ESI$^+$) *m/z*: 288.1 ([M$^{79}$ + H]$^+$ 95%), 290.1 ([M$^{81}$ + H]$^+$ 92%); HRMS (ESI$^+$) *m/z*: [M$^{79}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Br$, 288.0230, found 288.0231; [M$^{81}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Br$, 290.0209, found 290.0210.

**Ethyl (2*S**,3*S**)-2-amino-3-(4-cyanophenyl)-3-hydroxypropanoate trifluoroacetic acid 28c**



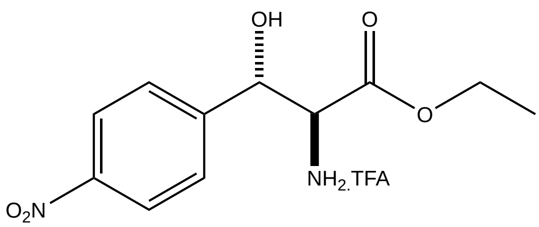

Yield (1.11 g, Quantitative); Light brown oil that solidified to a beige solid; m.p. 150-153°C; $\nu_{max}$/cm$^{-1}$ 3342 (O-H), 2988 (N-H), 2233 (C≡N), 1748 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.07 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.15 (2H, dq, *J*=3.3 Hz, 7.2 Hz, $OCH_2CH_3$), 4.56 (1H, d, *J*=3.6 Hz, H2), 5.48 (1H, d, *J*=3.6 Hz, H3), 7.59 (2H, d, *J*=8.1 Hz, Ar-H), 7.85 (2H, d, *J*=8.5 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 12.9 ($OCH_2CH_3$), 58.1 (C2), 63.5 ($OCH_2CH_3$), 70.5 (C3), 111.2 (Ar-C), 119.4 (C≡N), 126.6 (Ar-C), 132.8 (Ar-C), 143.5 (Ar-C), 167.1 (C1); LRMS (ESI$^+$) *m/z*: 235.1 ([M + H]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{12}H_{15}N_2O_3$, 235.1077, found 235.1078.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-(4-(trifluoromethyl)phenyl)propanoate trifluoroacetic acid 28d**




Yield (1.17 g, Quantitative); Yellow oil that solidified to a beige solid; m.p. 124-127°C; $\nu_{max}$/cm$^{-1}$ 3130 (O-H), 2910 (N-H), 1740 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.10 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.17 (2H, dq, *J*=4.0 Hz, 7.2 Hz, $OCH_2CH_3$), 4.57 (1H, d, *J*=3.7 Hz, H2), 5.51 (1H, d, *J*=3.7 Hz, H3), 7.61 (2H, d, *J*=8.1 Hz, Ar-H), 7.81 (2H, d, *J*=8.3 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 12.9 ($OCH_2CH_3$), 58.3 (C2), 63.5 ($OCH_2CH_3$), 70.5 (C3), 125.7 (q, *J*=3.6 Hz, Ar-C), 126.4 (Ar-C), 130.2 (q, *J*=32.2 Hz, Ar-C), 141.8 (Ar-C), 167.2 (C1); $\delta_F$ (376 MHz, $D_2O$) -62.39; LRMS (ESI$^+$) *m/z*: 278.1 ([M + H]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{12}H_{15}NO_3F_3$, 278.0999, found 278.0998.

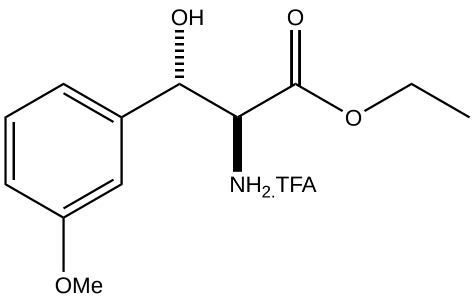
**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-(4-nitrophenyl)propanoate trifluoroacetic acid 28e**




Yield (1.35 g, Quantitative); Yellow oil that solidified to a brown solid; m.p. 142-145°C; $\nu_{max}$/cm$^{-1}$ 3336 (O-H), 2946 (N-H), 1747 (C=O), 1518 (N-O); $\delta_H$ (400 MHz, $D_2O$) 1.06 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.15 (2H, m, $OCH_2CH_3$), 4.60 (1H, d, *J*=3.5 Hz, H2), 5.53 (1H, d, *J*=3.5 Hz, H3), 7.66 (2H, d, *J*=9.0 Hz, Ar-H), 8.31 (2H, d, *J*=8.9 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 12.9

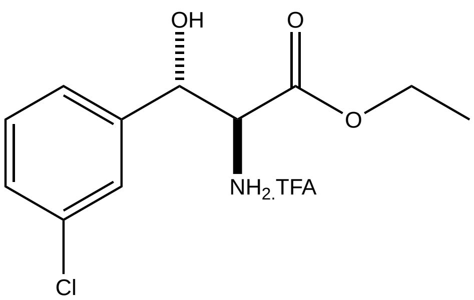
($OCH_2CH_3$), 58.1 (C2), 63.6 ($OCH_2CH_3$), 70.4 (C3), 123.9 (Ar-C), 127.0 (Ar-C), 145.5 (Ar-C), 147.7 (Ar-C), 167.0 (C1); LRMS (ESI$^+$) *m/z*: 255.1 ([M + H]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{11}H_{15}N_2O_5$, 255.0975, found 255.0975.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-(3-methoxyphenyl)propanoate trifluoroacetic acid 28f**



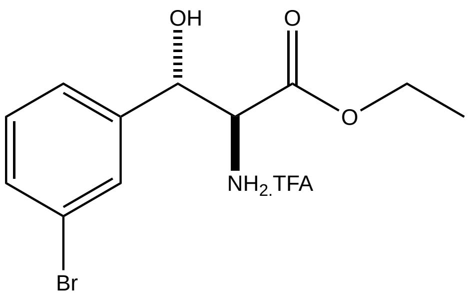
Yield (1.19 g, Quantitative); Yellow oil; $v_{max}$/cm$^{-1}$ 3424 (O-H), 2943 (N-H), 1738 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.16 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 3.86 (3H, s, $OCH_3$), 4.21 (2H, m, $OCH_2CH_3$), 4.49 (1H, d, *J*=4.1 Hz, H2), 5.40 (1H, d, *J*=4.0 Hz, H3), 7.00-7.06 (3H, m, Ar-H), 7.43 (1H, t, *J*=7.9 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 55.4 ($OCH_3$), 58.4 (C2), 63.5 ($OCH_2CH_3$), 70.7 (C3), 111.7 (Ar-C), 114.3 (Ar-C), 118.6 (Ar-C), 130.3 (Ar-C), 139.0 (Ar-C), 159.2 (Ar-C), 167.4 (C1); LRMS (ESI$^+$) *m/z*: 262.0 ([M + Na]$^+$ 21%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{12}H_{18}NO_4$, 240.1230, found 240.1232.

**Ethyl (2*S**,3*S**)-2-amino-3-(3-chlorophenyl)-3-hydroxypropanoate trifluoroacetic acid 28g**



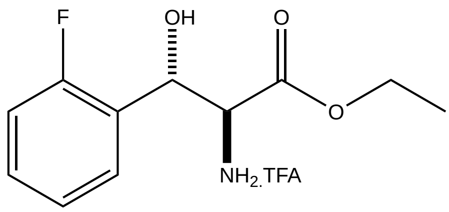
Yield (1.19 g, Quantitative); Yellow oil that solidified to an off-white solid; m.p. 80-83°C; $v_{max}$/cm$^{-1}$ 3450 (O-H), 2989 (N-H), 1741 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.13 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.18 (2H, m, $OCH_2CH_3$), 4.49 (1H, d, *J*=3.9 Hz, H2), 5.39 (1H, d, *J*=3.9 Hz, H3), 7.30-7.45 (4H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.3 (d, *J*=4.8 Hz, C2), 63.6 ($OCH_2CH_3$), 70.3 (d, *J*=5.6 Hz, C3), 124.3 (Ar-C), 125.9 (Ar-C), 128.8 (Ar-C), 130.3 (Ar-C), 134.1 (Ar-C), 139.6 (Ar-C), 167.2 (C1); LRMS (ESI$^+$) *m/z*: 244.1 ([M$^{35}$ + H]$^+$ 75%), 246.1 ([M$^{37}$ + H]$^+$ 67%); HRMS (ESI$^+$) *m/z*: [M$^{35}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Cl$, 244.0735, found 244.0736; [M$^{37}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Cl$, 246.0705, found 246.0707.

**Ethyl (2*S**,3*S**)-2-amino-3-(3-bromophenyl)-3-hydroxypropanoate trifluoroacetic acid 28h**



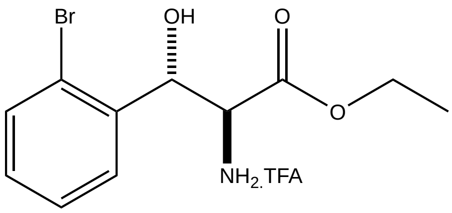
Yield (1.19 g, Quantitative); Off-white semi-solid; $\nu_{max}/cm^{-1}$ 3163 (O-H), 2871 (N-H), 1749 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.14 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.19 (2H, m, $OCH_2CH_3$), 4.49 (1H, d, *J*=3.8 Hz, H2), 5.40 (1H, d, *J*=3.8 Hz, H3), 7.34-7.41 (2H, m, Ar-H), 7.56-7.63 (2H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 13.0 ($OCH_2CH_3$), 58.3 (C2), 63.6 ($OCH_2CH_3$), 70.3 (C3), 122.2 (Ar-C), 124.8 (Ar-C), 128.9 (Ar-C), 130.6 (Ar-C), 131.8 (Ar-C), 139.9 (Ar-C), 167.2 (C1); LRMS (ESI$^+$) *m/z*: 288.0 ([$M^{79}$ + H]$^+$ 100%), 290.1 ([$M^{81}$ + H]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [$M^{79}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Br$, 288.0230, found 288.0230; [$M^{81}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Br$, 290.0209, found 290.0209.

**Ethyl (2*S**,3*S**)-2-amino-3-(2-fluorophenyl)-3-hydroxypropanoate trifluoroacetic acid 28i**



Yield (1.12 g, Quantitative); Yellow oil that solidified to a light orange solid; m.p. 127-130°C; $\nu_{max}/cm^{-1}$ 3558 (O-H), 2907 (N-H), 1733 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.10 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.16 (2H, dq, *J*=0.8 Hz, 7.2 Hz, $OCH_2CH_3$), 4.54 (1H, d, *J*=3.7 Hz, H2), 5.59 (1H, d, *J*=3.7 Hz, H3), 7.21 (1H, m, Ar-H), 7.32 (1H, dt, *J*=1.2 Hz, 7.6 Hz, Ar-H), 7.48 (1H, m, Ar-H), 7.54 (1H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 12.9 ($OCH_2CH_3$), 57.0 (d, *J*=2.1 Hz, C2), 63.5 ($OCH_2CH_3$), 66.3 (d, *J*=2.0 Hz, C3), 115.4 (d, *J*=21.1 Hz, Ar-C), 124.7 (d, *J*=8.0 Hz, Ar-C), 124.7 (d, *J*=8.8 Hz, Ar-C), 127.6 (d, *J*=3.9 Hz, Ar-C), 130.8 (d, *J*=8.6 Hz, Ar-C), 159.4 (d, *J*=244.2 Hz, Ar-C), 167.4 (C1); $\delta_F$ (376 MHz, $D_2O$) -118.29; LRMS (ESI$^+$) *m/z*: 228.1 ([M + H]$^+$ 100%), 250.1 ([M + Na]$^+$ 59%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{11}H_{15}NO_3F$, 228.1030, found 228.1030.

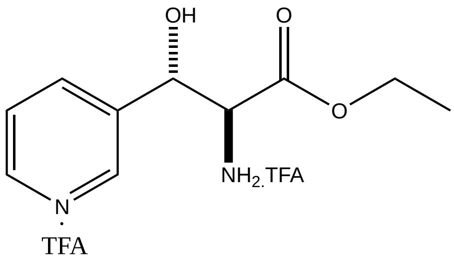
**Ethyl (2*S**,3*S**)-2-amino-3-(2-bromophenyl)-3-hydroxypropanoate trifluoroacetic acid 28j**



Yield (1.61 g, Quantitative); Yellow oil that solidified to an off-white solid; m.p. 65-70°C; $\nu_{max}/cm^{-1}$ 3502 (O-H), 2982 (N-H), 1732 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.02 (3H, t, *J*=7.2 Hz, $OCH_2CH_3$), 4.09 (2H, q, *J*=7.2 Hz, $OCH_2CH_3$), 4.62 (1H, d, *J*=3.2 Hz, H2), 5.51 (1H, d, *J*=3.2 Hz, H3), 7.33 (1H, dt, *J*=1.9 Hz, 7.7 Hz, Ar-H), 7.48 (1H, dt, *J*=1.3 Hz, 7.6 Hz, Ar-H), 7.55 (1H, dd, *J*=1.8 Hz, 7.9 Hz, Ar-H), 7.68 (1H, dd, *J*=1.2 Hz, 8.0 Hz, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 12.9 ($OCH_2CH_3$), 55.9 (C2), 63.4 ($OCH_2CH_3$), 70.7 (C3), 120.8

(Ar-C), 127.9 (Ar-C), 128.1 (Ar-C), 130.4 (Ar-C), 132.8 (Ar-C), 137.0 (Ar-C), 167.3 (C1); LRMS (ESI$^+$) *m/z*: 288.0 ([M$^{79}$ + H]$^+$ 63%), 290.0 ([M$^{81}$ + H]$^+$ 63%); HRMS (ESI$^+$) *m/z*: [M$^{79}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Br$, 288.0230, found 288.0229; [M$^{81}$ + H]$^+$ calcd. for $C_{11}H_{15}NO_3Br$, 290.0209, found 290.0208.

**Ethyl (2*S**,3*S**)-2-amino-3-hydroxy-3-(pyridin-3-yl)propanoate trifluoroacetic acid 28k**




Yield (3.30 g, Quantitative); Yellow semi-solid; $\nu_{max}$/cm$^{-1}$ 3076 (O-H), 2988 (N-H), 1742 (C=O); $\delta_H$ (400 MHz, $D_2O$) 1.02 (3H, t, *J*=7.1 Hz, $OCH_2CH_3$), 4.14 (2H, m, $OCH_2CH_3$), 4.69 (1H, d, *J*=2.7 Hz, H2), 5.64 (1H, d, *J*=2.7 Hz, H3), 8.16 (1H, m, Ar-H), 8.68 (1H, m, Ar-H), 8.82 (1H, m, Ar-H), 8.91 (1H, m, Ar-H); $\delta_C$ (101 MHz, $D_2O$) 12.9 ($OCH_2CH_3$), 57.5 (C2), 63.7 ($OCH_2CH_3$), 68.2 (C3), 127.2 (Ar-C), 139.0 (Ar-C), 140.1 (Ar-C), 140.9 (Ar-C), 144.5 (Ar-C), 166.4 (C1); LRMS (ESI$^+$) *m/z*: 211.1 ([M + H]$^+$ 100%); HRMS (ESI$^+$) *m/z*: [M + H]$^+$ calcd. for $C_{10}H_{15}N_2O_3$, 211.1077, found 211.1079.

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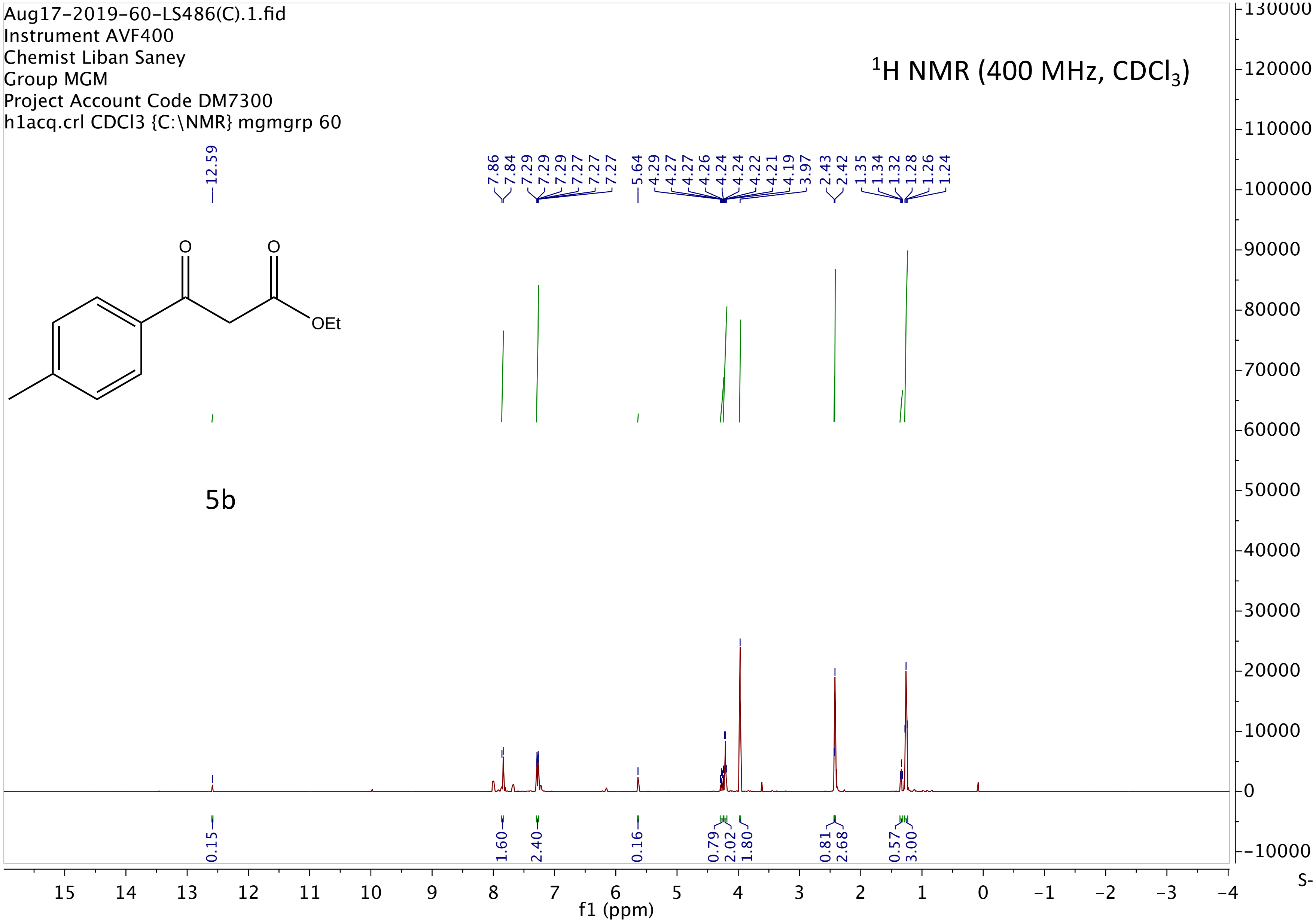


5b

$^1$H NMR (400 MHz, $CDCl_3$)

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Chemist Liban Saney
Group MGM
Project Account Code DM7300
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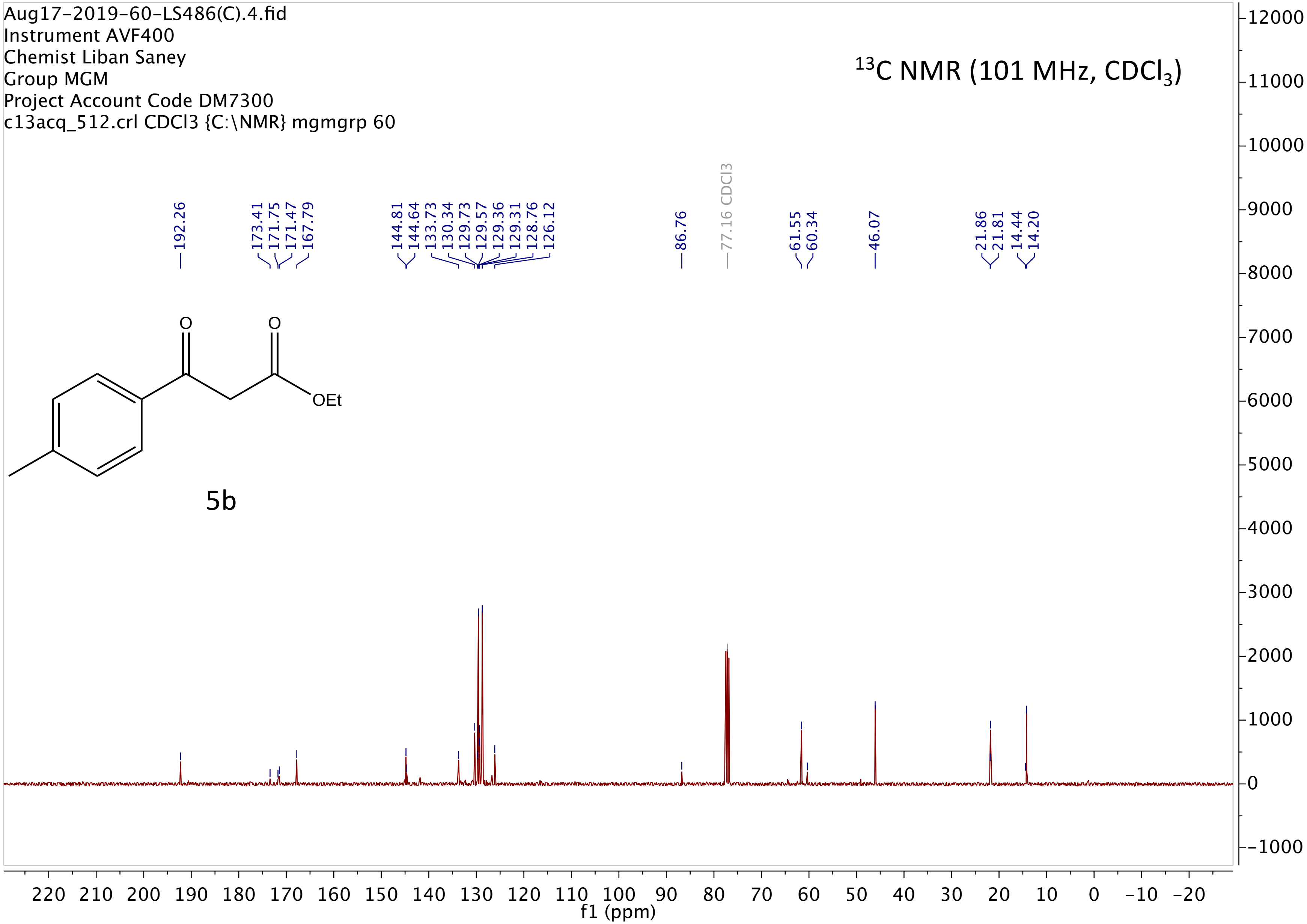
$^{13}C$ NMR (101 MHz, $CDCl_3$)



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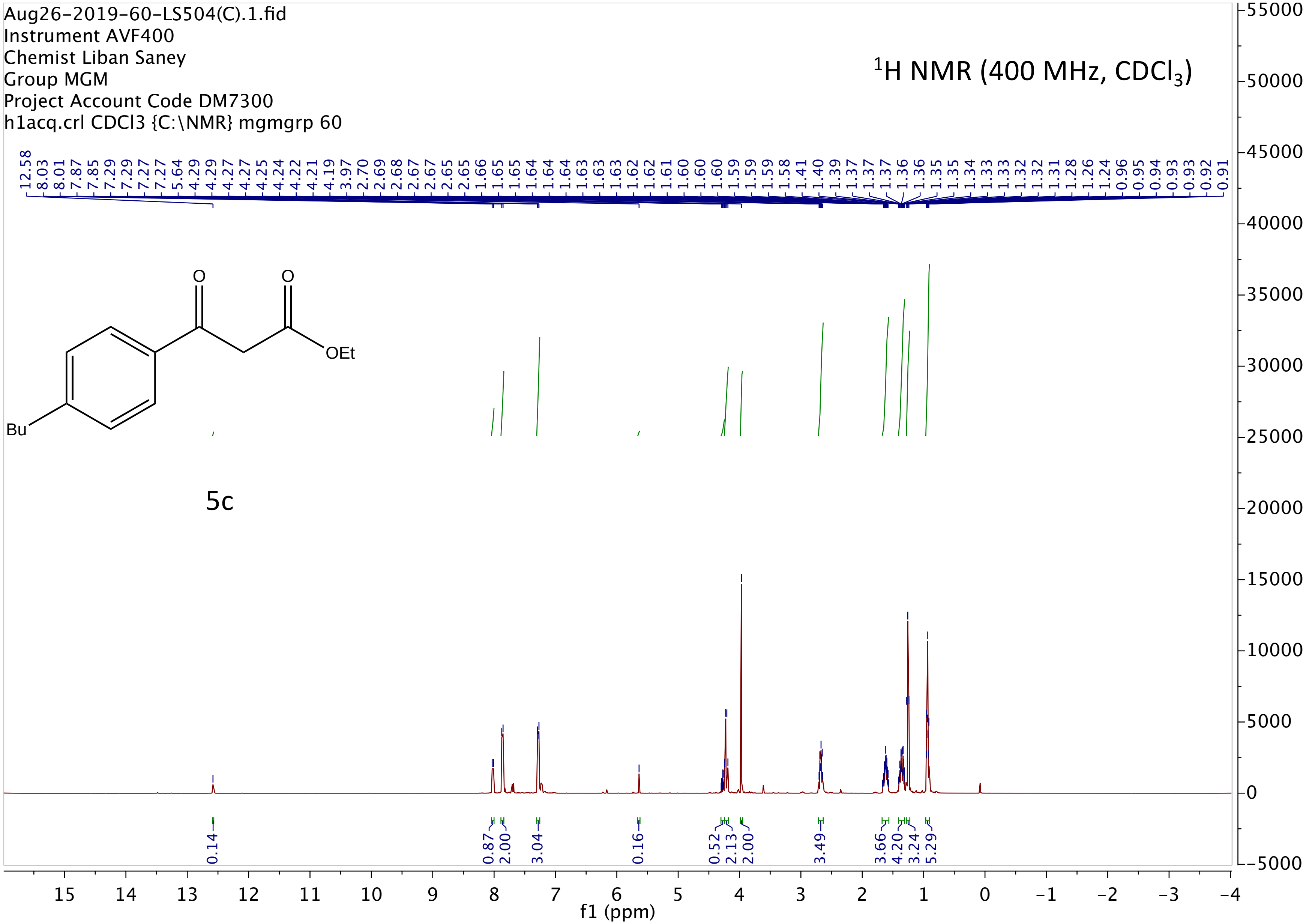
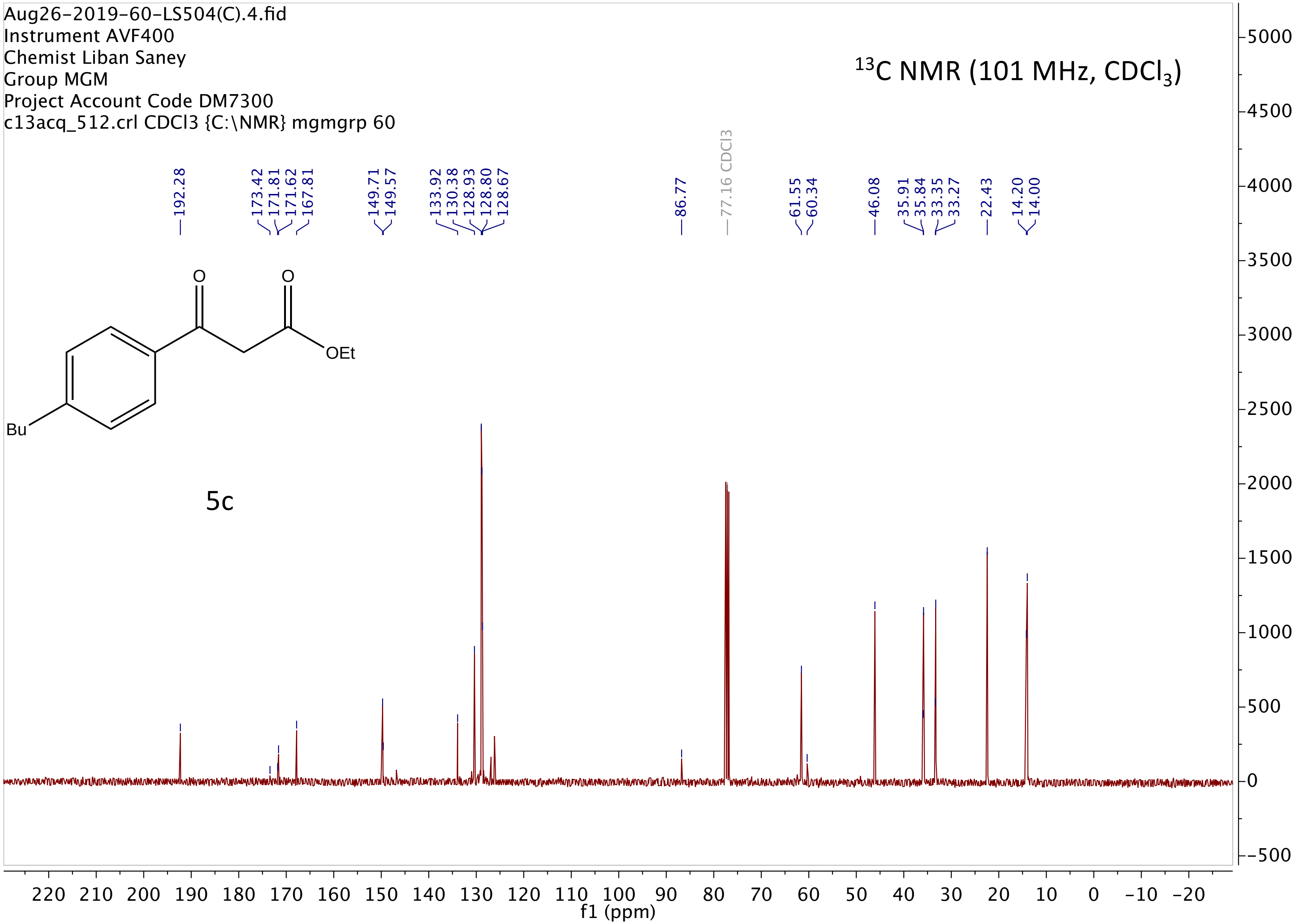
$^{1}$H NMR (400 MHz, $CDCl_3$)

5c

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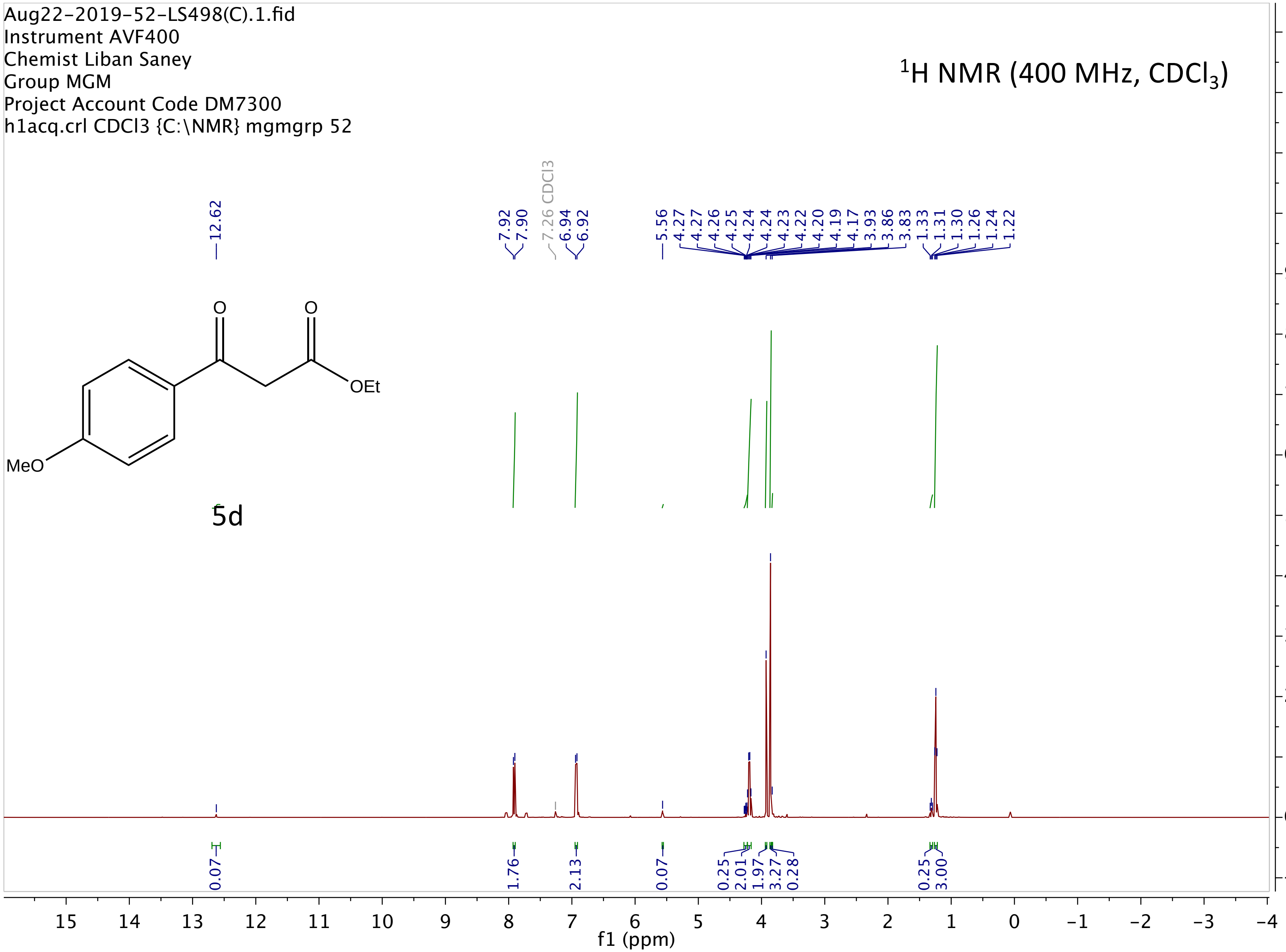
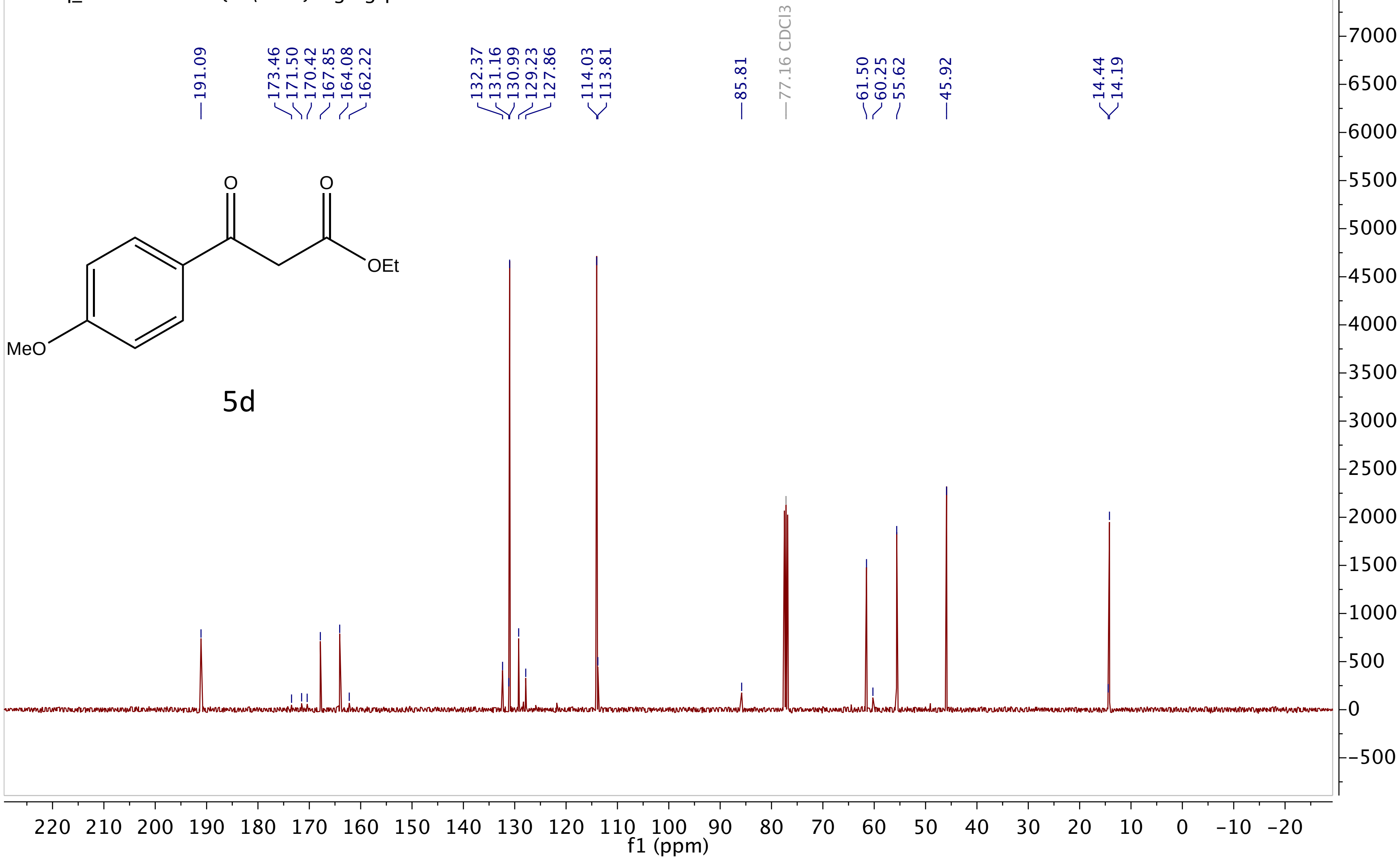
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, CDCl$_3$)
192.28
173.42
171.81
171.62
167.81
149.71
149.57
133.92
130.38
128.93
128.80
128.67
86.77
77.16 CDCl3
61.55
60.34
46.08
35.91
35.84
33.35
33.27
22.43
14.20
14.00
O
O
OEt
Bu
5c
f1 (ppm)


Aug22-2019-52-LS498(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 52
¹H NMR (400 MHz, CDCl₃)
12.62
7.92
7.90
7.26 CDCl3
6.94
6.92
5.56
4.27
4.27
4.26
4.25
4.24
4.24
4.24
4.23
4.22
4.20
4.19
4.17
3.93
3.86
3.83
1.33
1.31
1.30
1.26
1.24
1.22
O
O
OEt
MeO
5d
0.07
1.76
2.13
0.07
0.25
2.01
1.97
3.27
0.28
0.25
3.00
f1 (ppm)

Aug22-2019-52-LS498(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 52

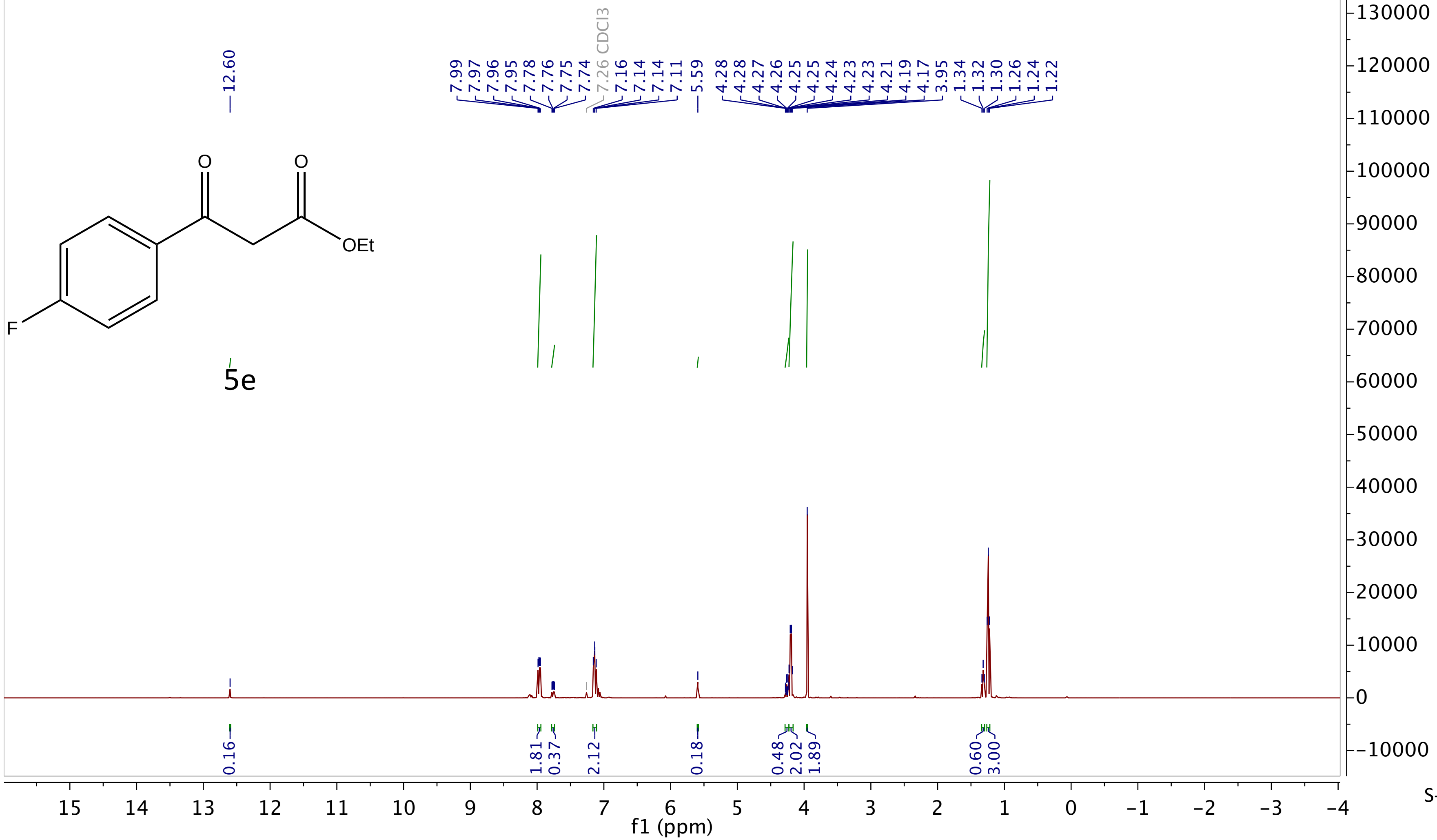
$^{13}$C NMR (101 MHz, $CDCl_3$)




5d

Sep08-2019-60-LS526(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

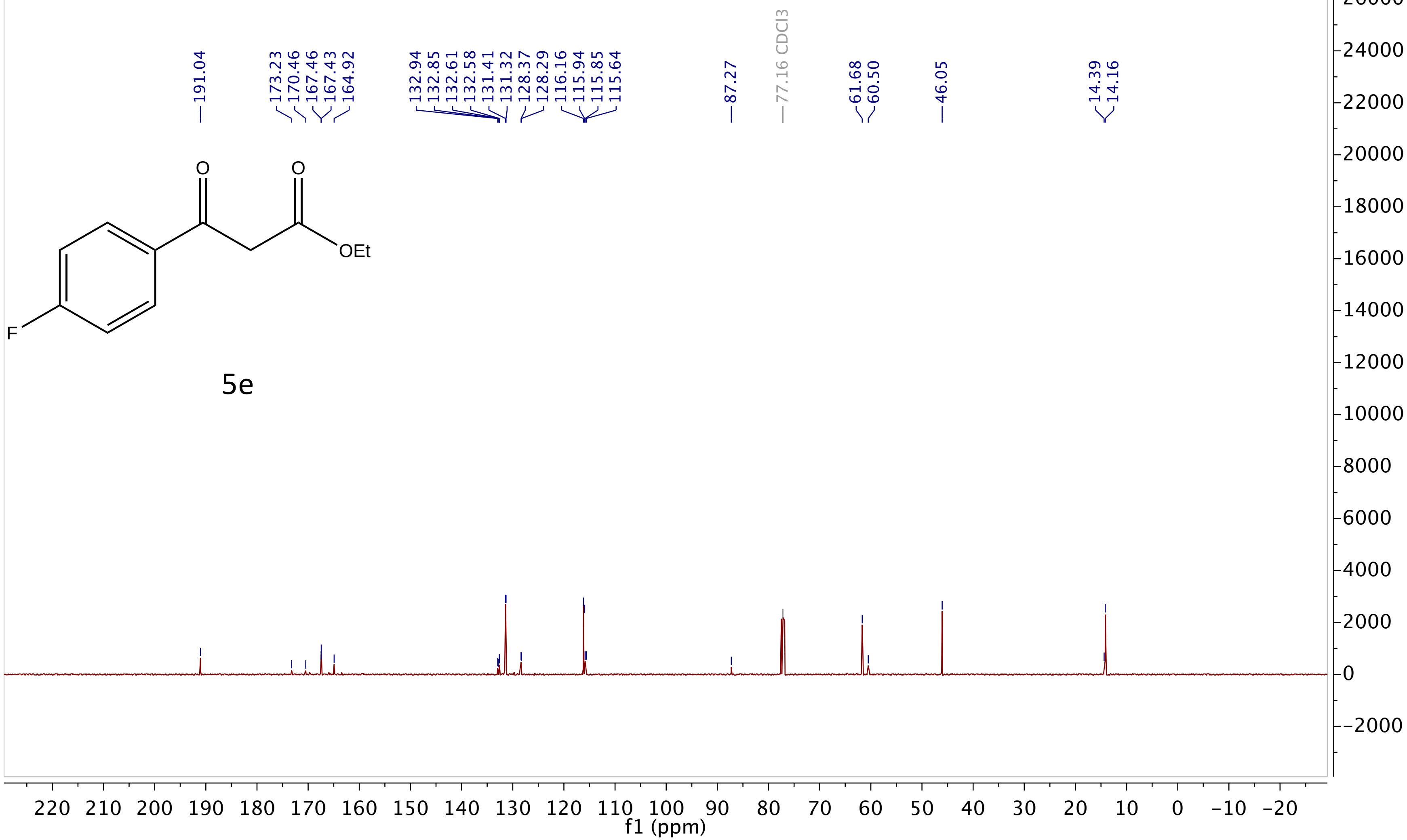
$^1$H NMR (400 MHz, $CDCl_3$)



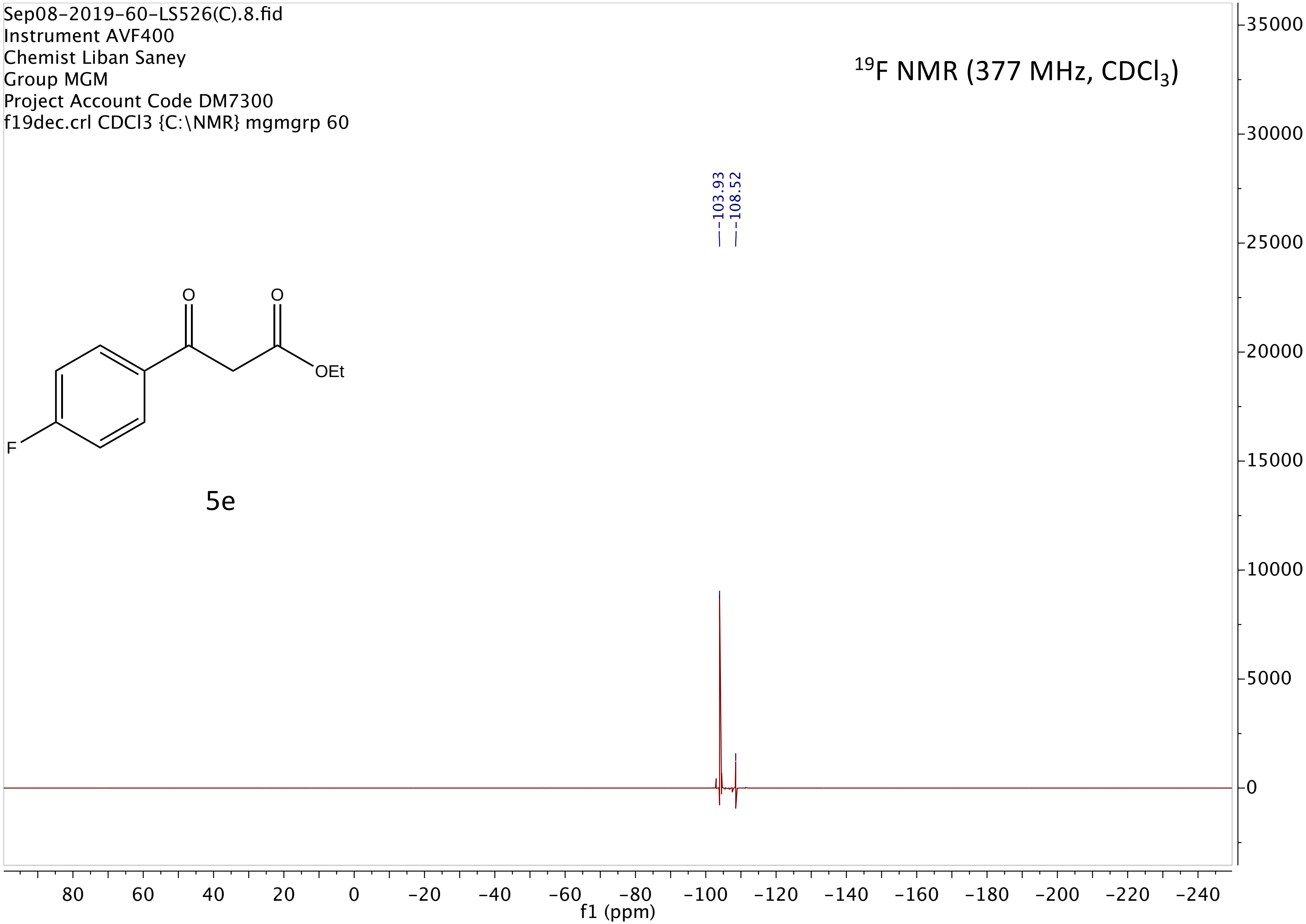
5e

Sep08-2019-60-LS526(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)

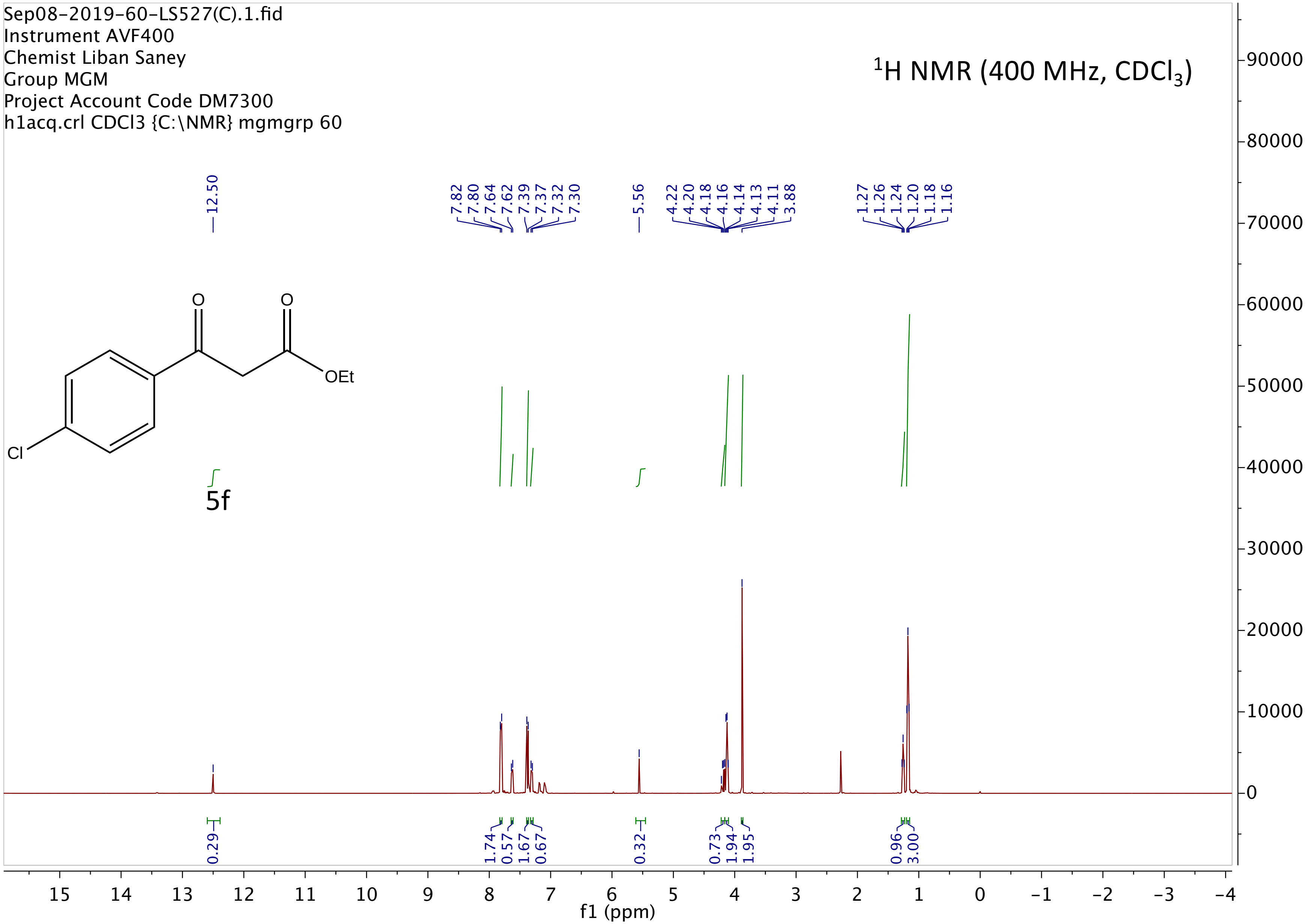



5e

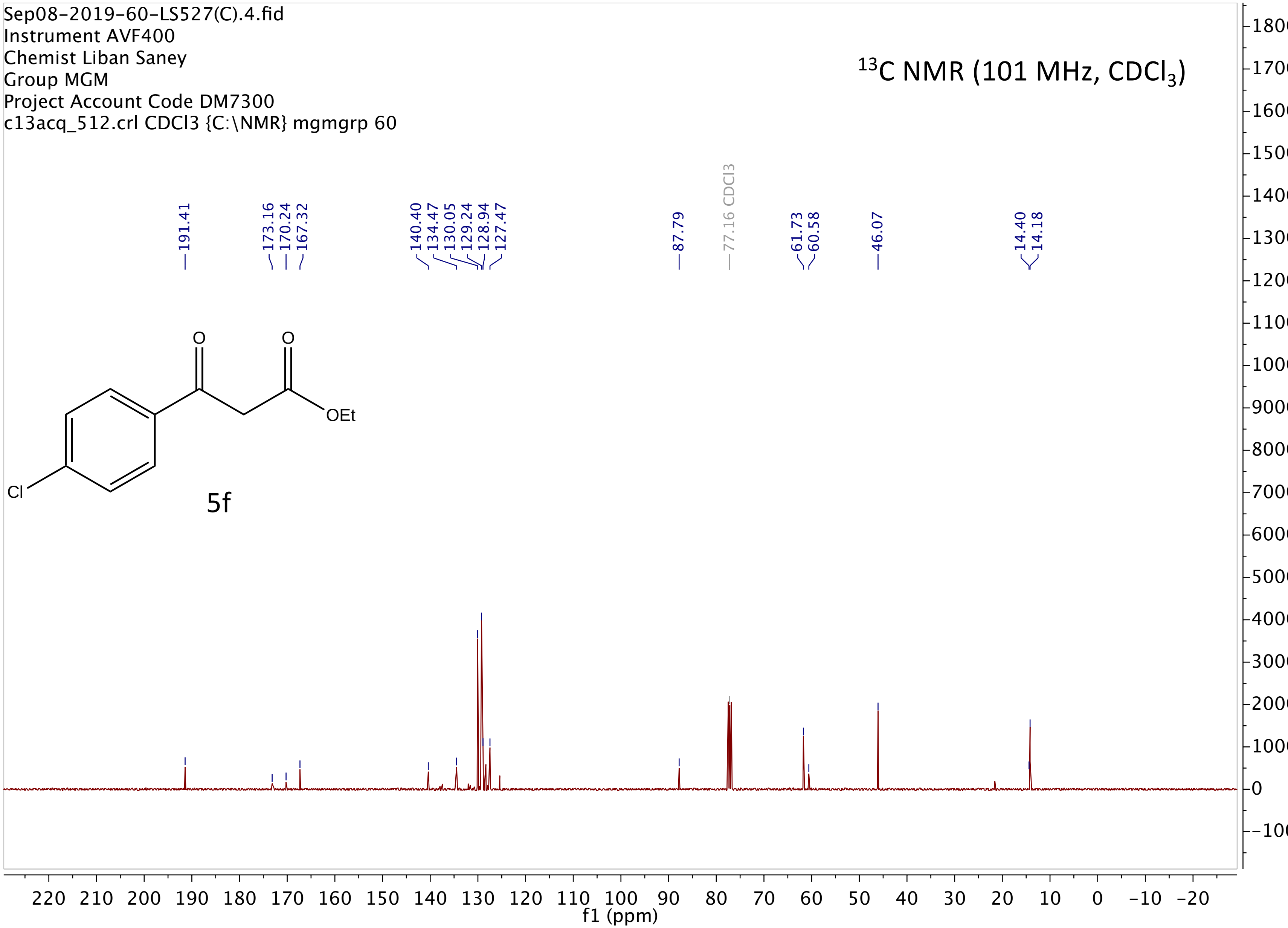

Sep08-2019-60-LS526(C).8.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
f19dec.crl CDCl3 {C:\NMR} mgmgrp 60
$^{19}$F NMR (377 MHz, $CDCl_3$)
-103.93
-108.52
O
O
OEt
F
5e
35000
30000
25000
20000
15000
10000
5000
0
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

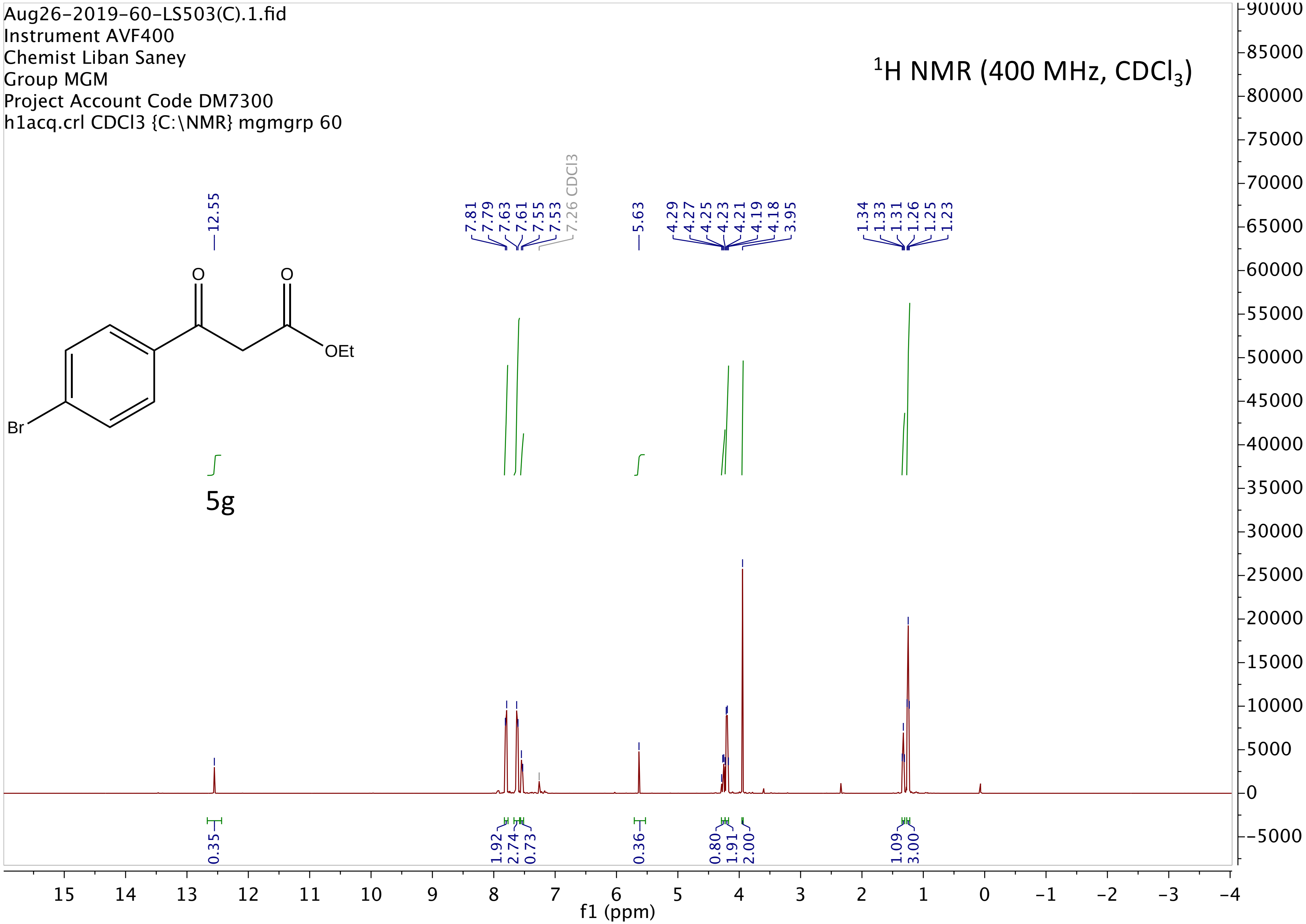
Sep08-2019-60-LS527(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

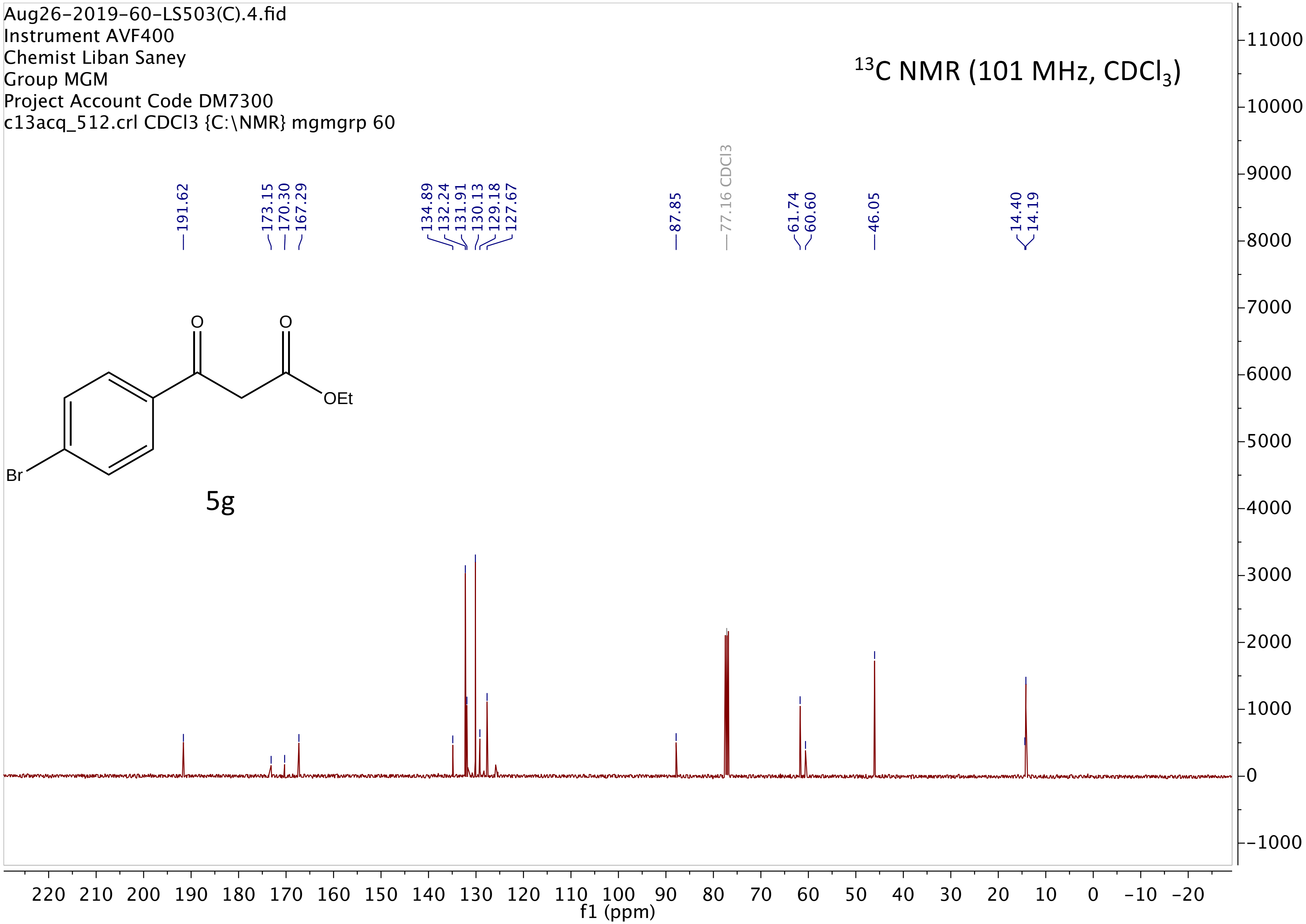
$^{1}H$ NMR (400 MHz, $CDCl_3$)

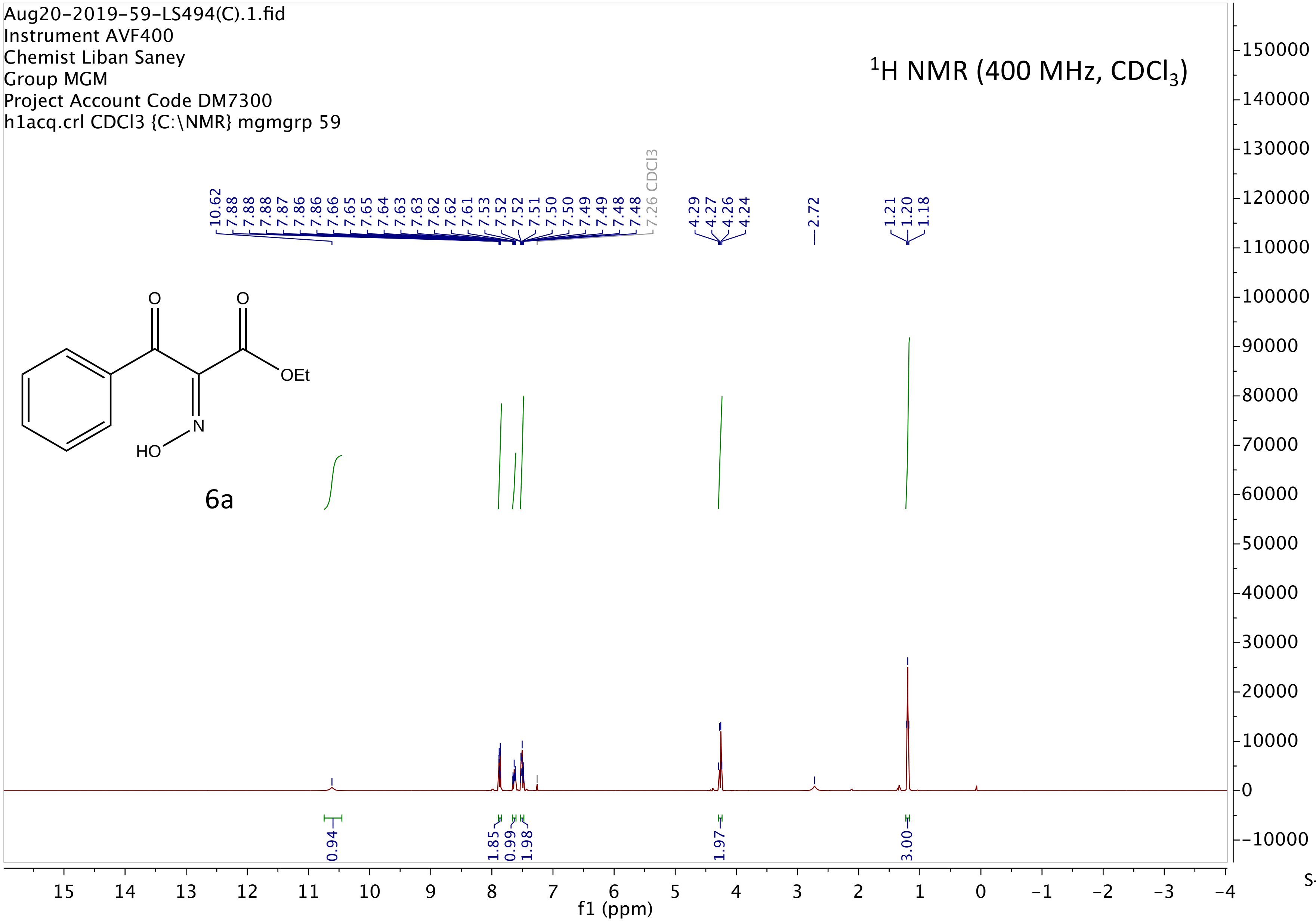



5f


Sep08-2019-60-LS527(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CDCl_3$)
191.41
173.16
170.24
167.32
140.40
134.47
130.05
129.24
128.94
127.47
87.79
77.16 CDCl3
61.73
60.58
46.07
14.40
14.18
O
O
OEt
Cl
5f
f1 (ppm)

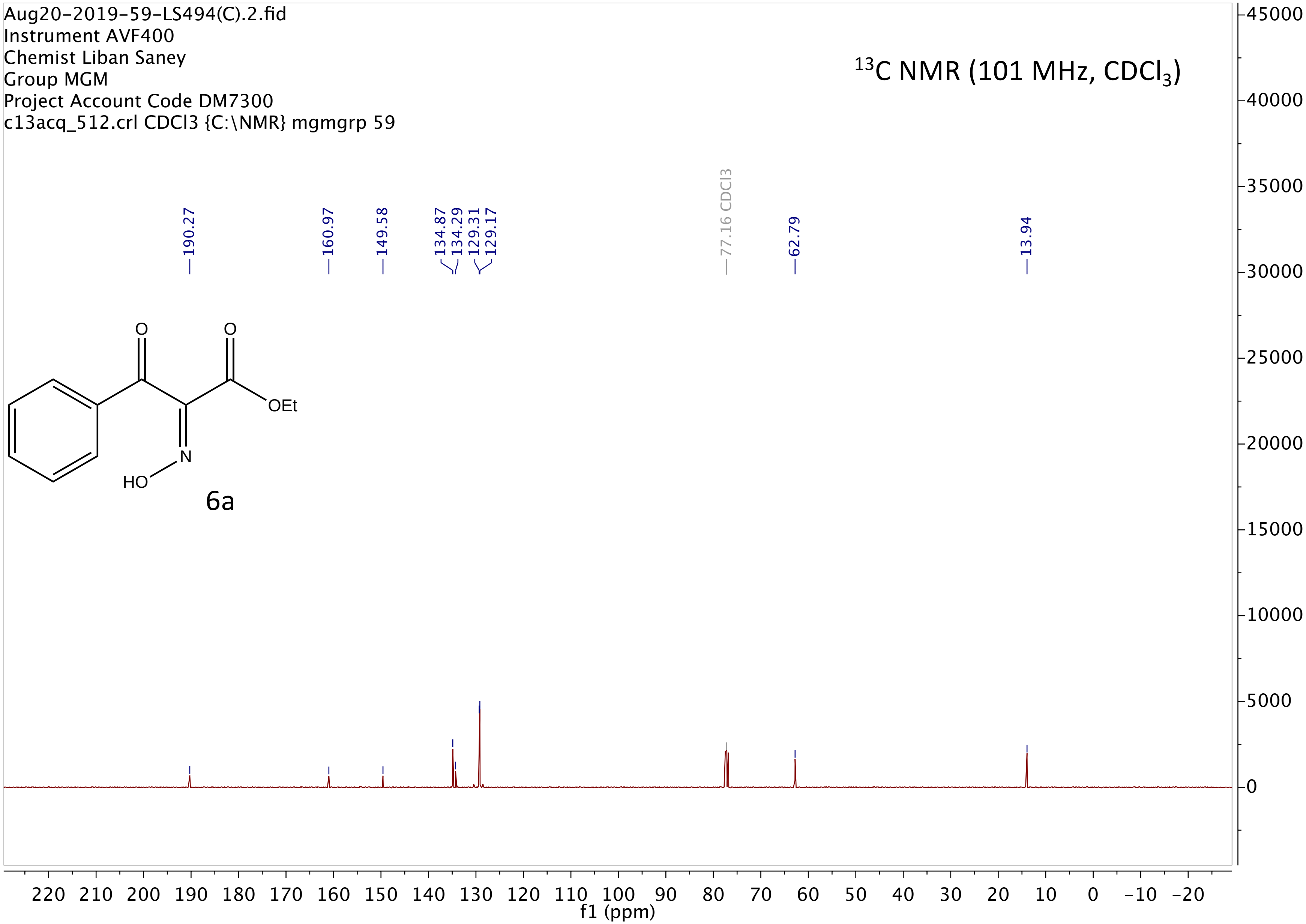

Aug26-2019-60-LS503(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
O
O
OEt
Br
5g
12.55
7.81
7.79
7.63
7.61
7.55
7.53
7.26 CDCl3
5.63
4.29
4.27
4.25
4.23
4.21
4.19
4.18
3.95
1.34
1.33
1.31
1.26
1.25
1.23
0.35
1.92
2.74
0.73
0.36
0.80
1.91
2.00
1.09
3.00
f1 (ppm)

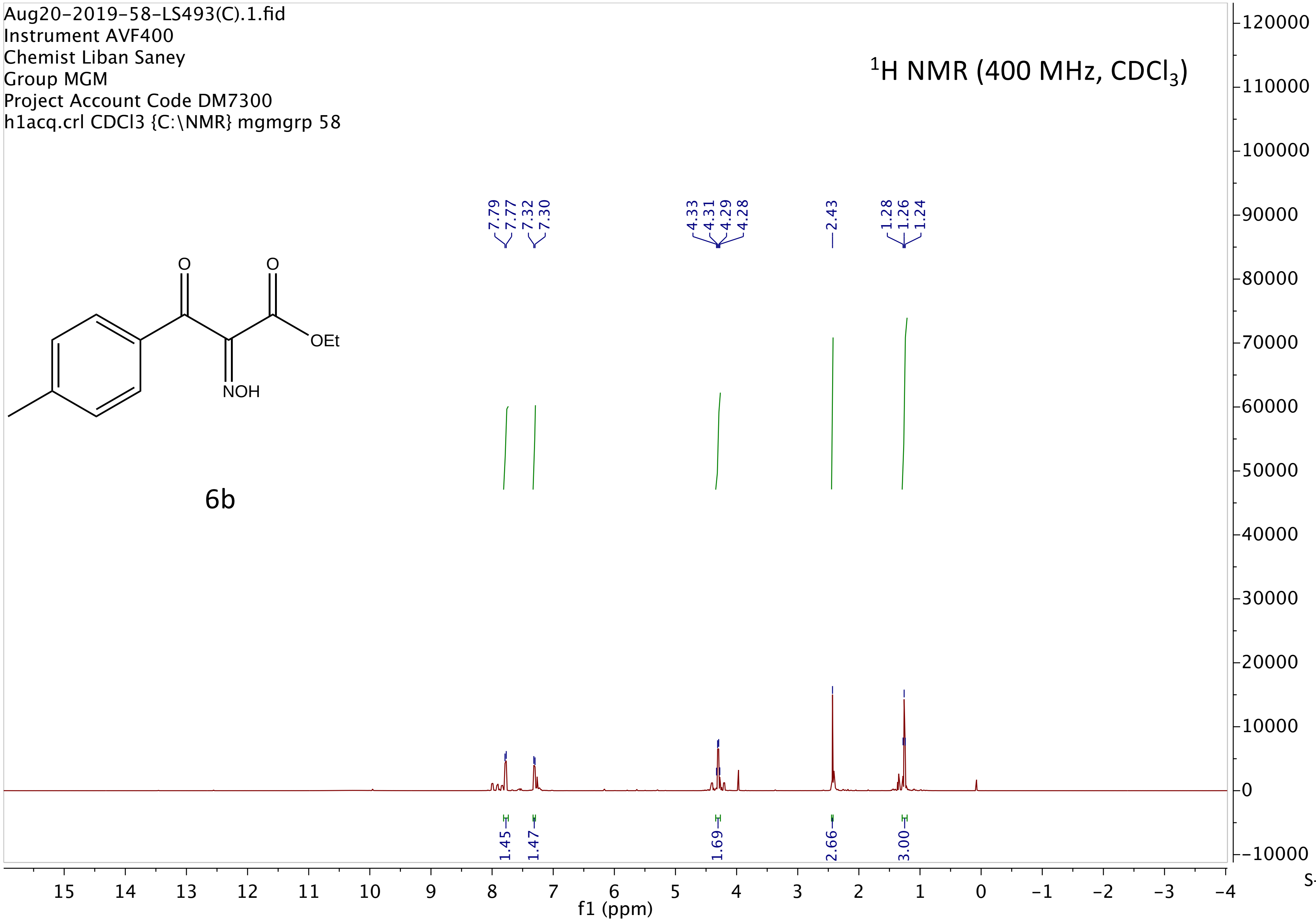

Aug26-2019-60-LS503(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
13C NMR (101 MHz, CDCl3)
191.62
173.15
170.30
167.29
134.89
132.24
131.91
130.13
129.18
127.67
87.85
77.16 CDCl3
61.74
60.60
46.05
14.40
14.19
O
O
OEt
Br
5g
f1 (ppm)



Aug20-2019-59-LS494(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59
$^1$H NMR (400 MHz, $CDCl_3$)
10.62
7.88
7.88
7.88
7.87
7.86
7.86
7.66
7.65
7.65
7.64
7.63
7.63
7.62
7.62
7.61
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.26 CDCl3
4.29
4.27
4.26
4.24
2.72
1.21
1.20
1.18
0.94
1.85
0.99
1.98
1.97
3.00
f1 (ppm)

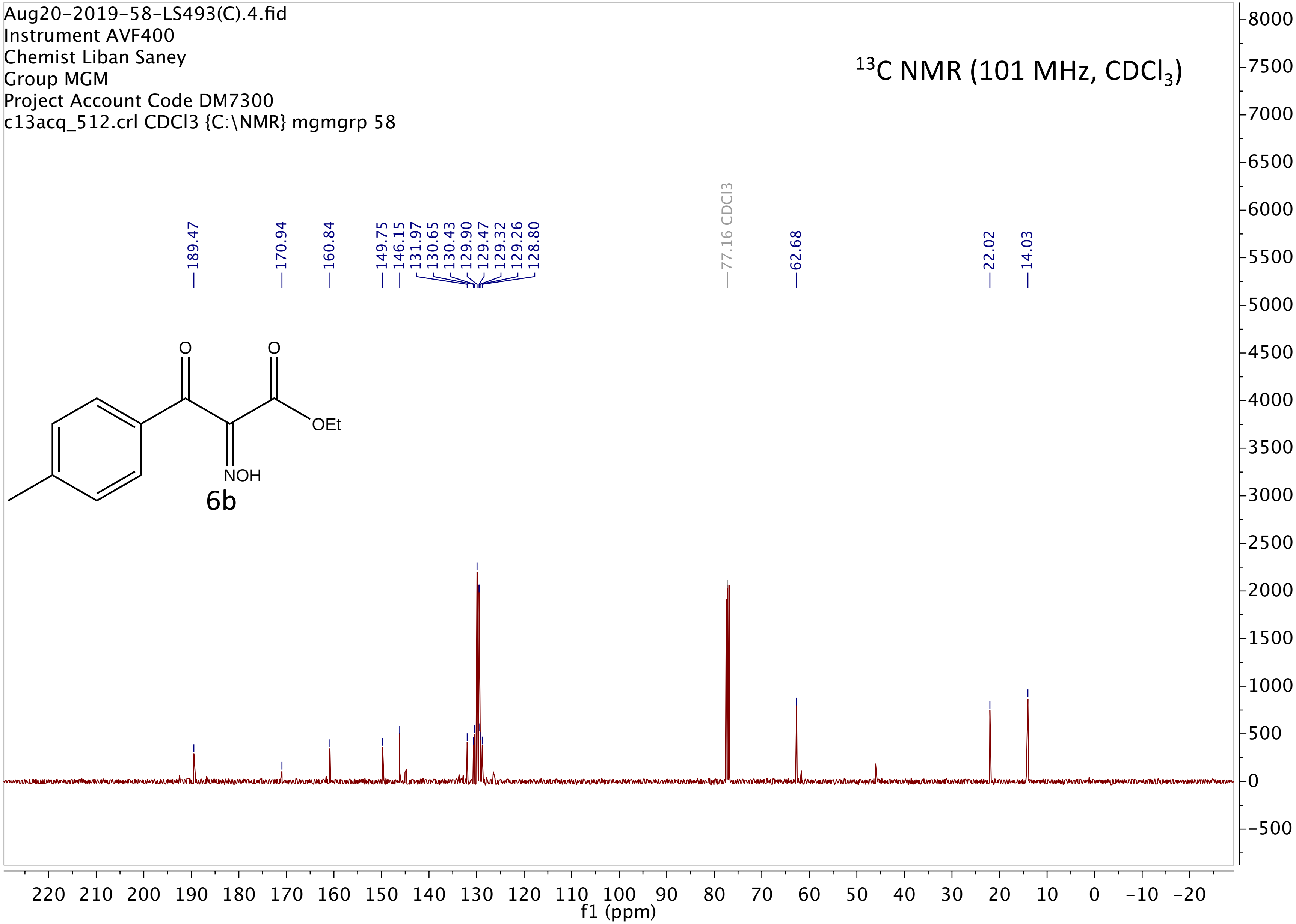

6a


Aug20-2019-59-LS494(C).2.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59
$^{13}$C NMR (101 MHz, $CDCl_3$)
190.27
160.97
149.58
134.87
134.29
129.31
129.17
77.16 CDCl3
62.79
13.94
O
O
OEt
N
HO
6a
f1 (ppm)



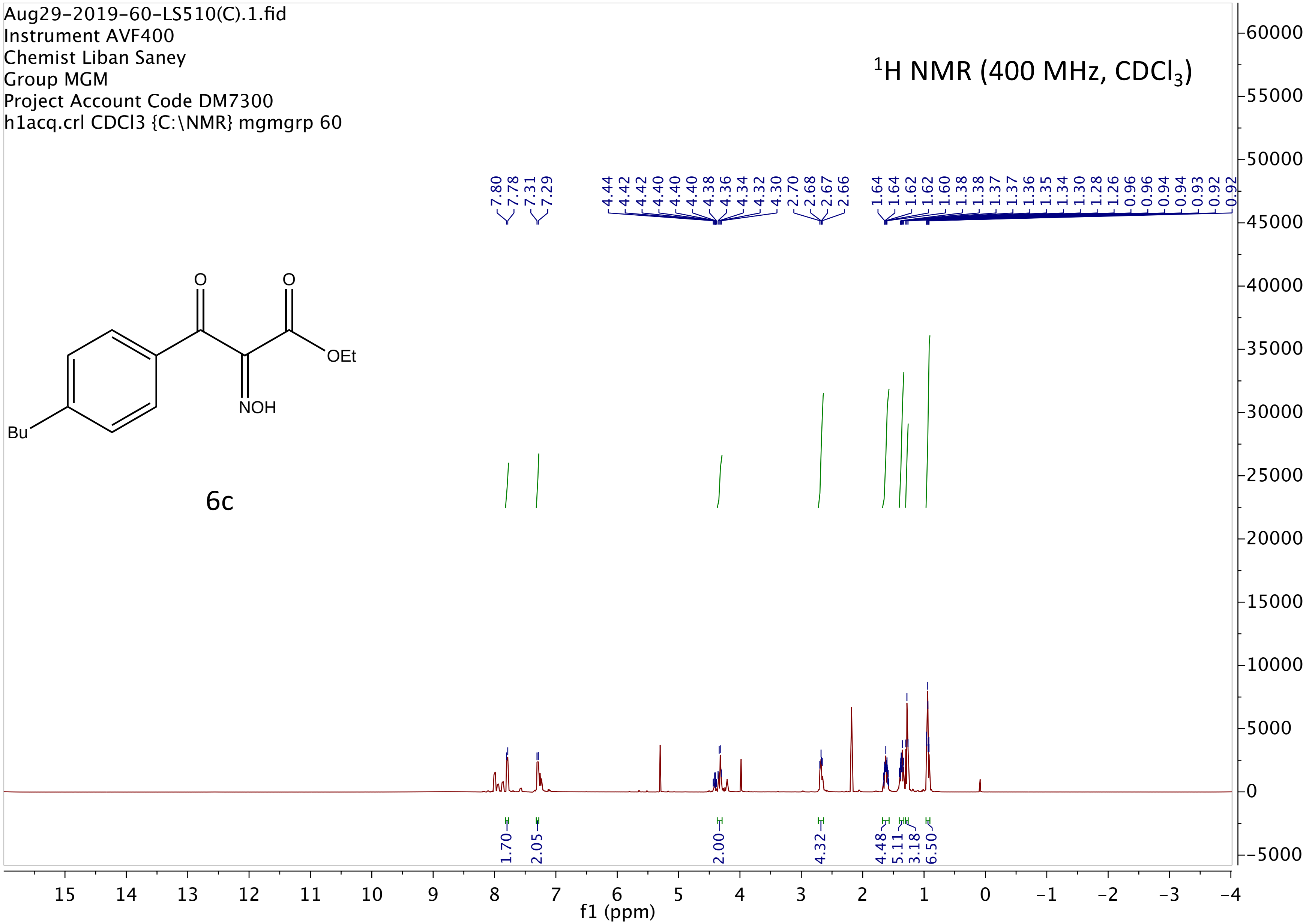
Aug20-2019-58-LS493(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 58
$^1$H NMR (400 MHz, $CDCl_3$)
O
O
OEt
NOH
6b
7.79
7.77
7.32
7.30
4.33
4.31
4.29
4.28
2.43
1.28
1.26
1.24
1.45
1.47
1.69
2.66
3.00
f1 (ppm)

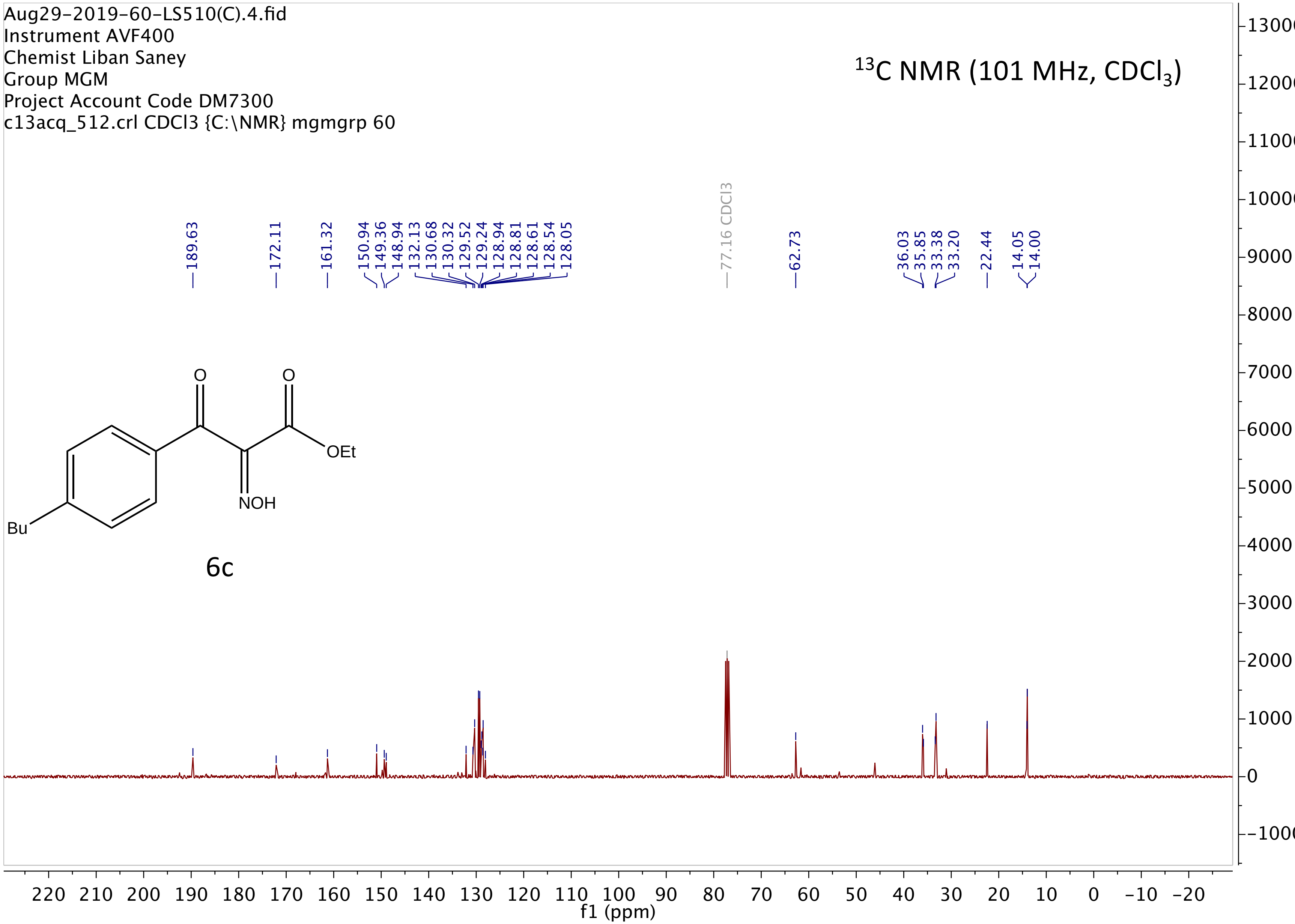
Aug20-2019-58-LS493(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 58

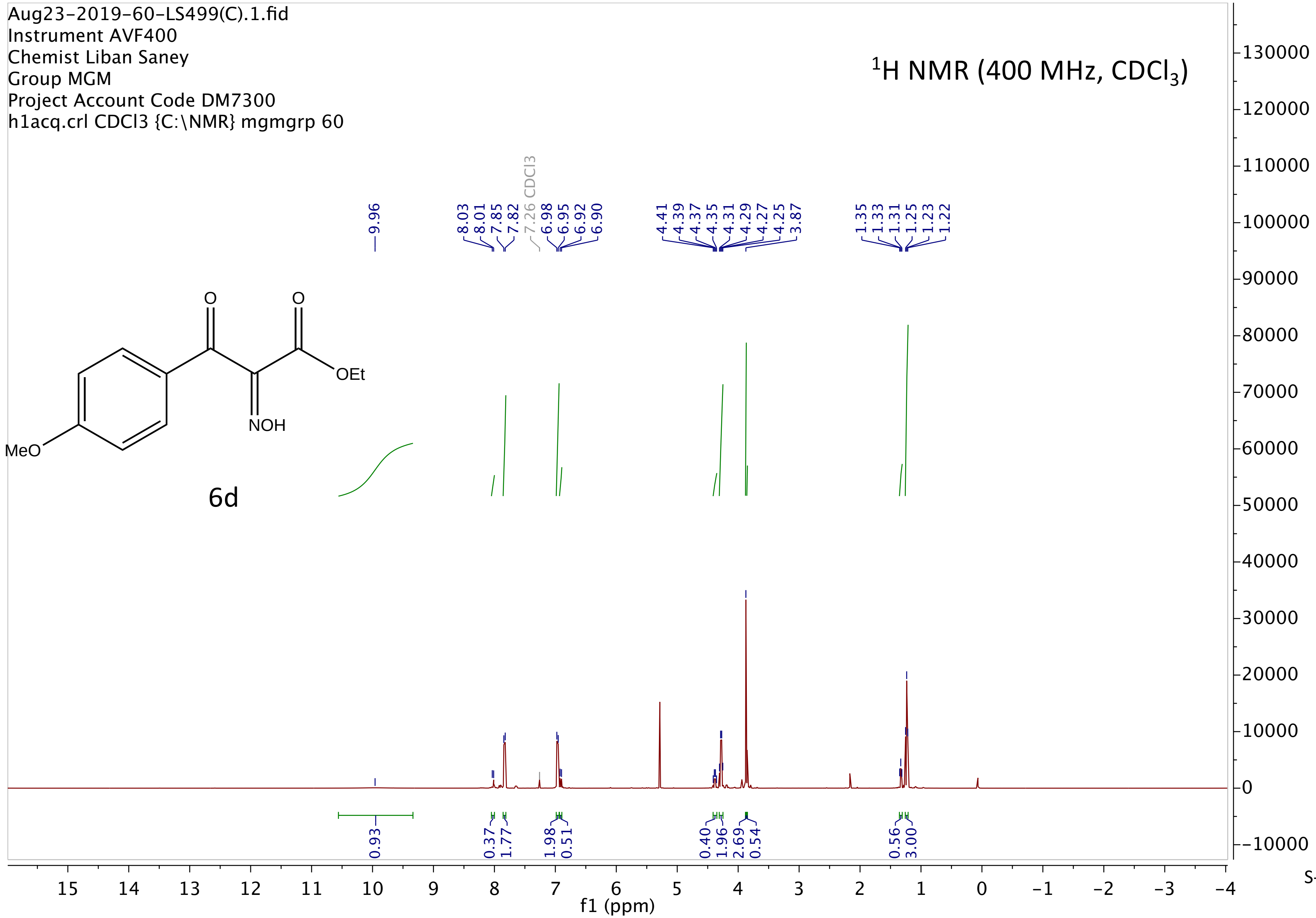


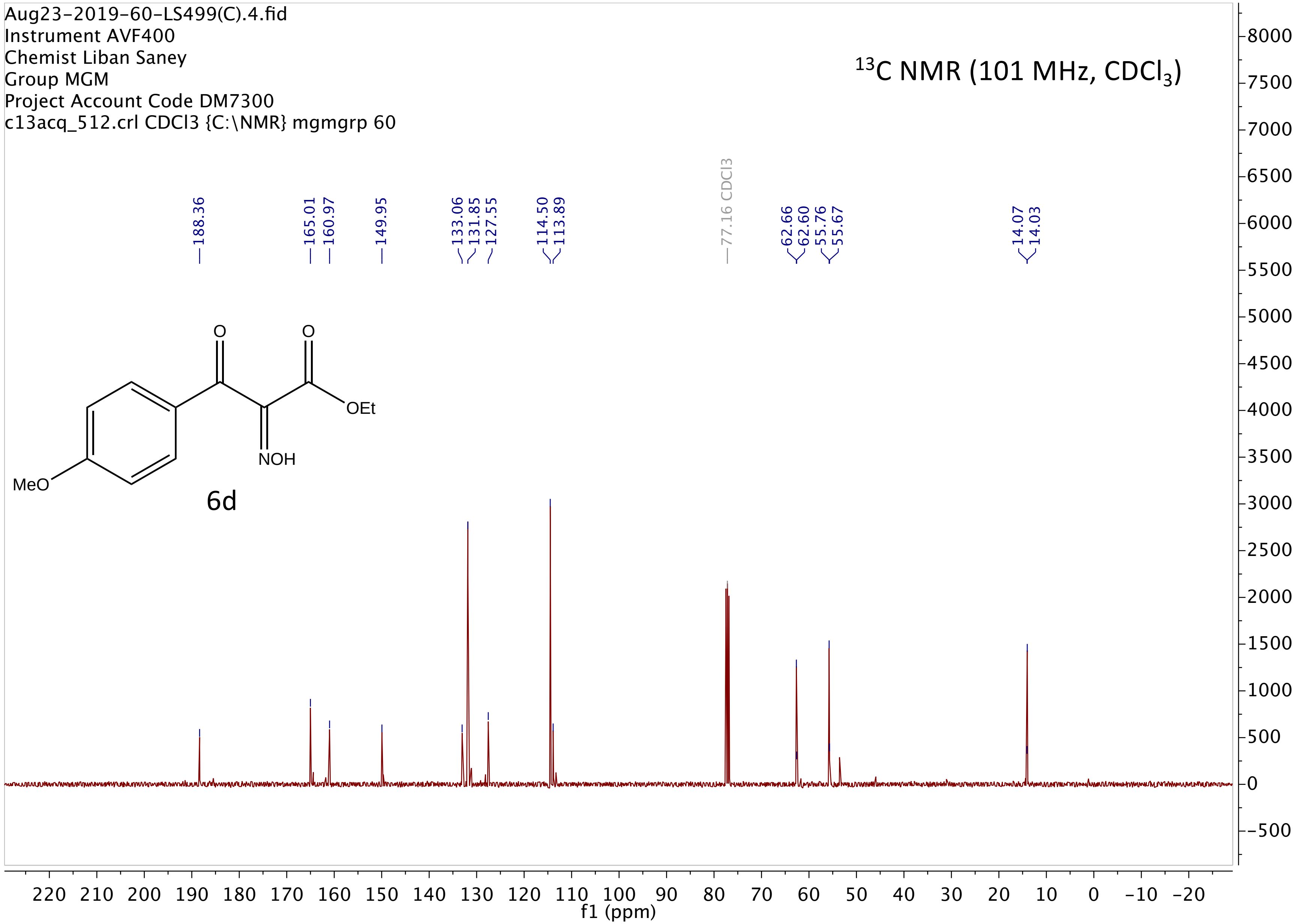
Aug29-2019-60-LS510(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

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

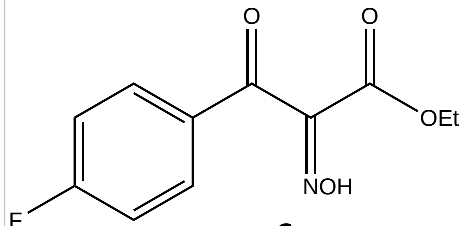



Aug29-2019-60-LS510(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CDCl_3$)
189.63
172.11
161.32
150.94
149.36
148.94
132.13
130.68
130.32
129.52
129.24
128.94
128.81
128.61
128.54
128.05
77.16 CDCl3
62.73
36.03
35.85
33.38
33.20
22.44
14.05
14.00
O
O
OEt
NOH
Bu
6c
f1 (ppm)


Aug23-2019-60-LS499(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
9.96
8.03
8.01
7.85
7.82
7.26 CDCl3
6.98
6.95
6.92
6.90
4.41
4.39
4.37
4.35
4.31
4.29
4.27
4.25
3.87
1.35
1.33
1.31
1.25
1.23
1.22
O
O
OEt
NOH
MeO
6d
0.93
0.37
1.77
1.98
0.51
0.40
1.96
2.69
0.54
0.56
3.00
f1 (ppm)

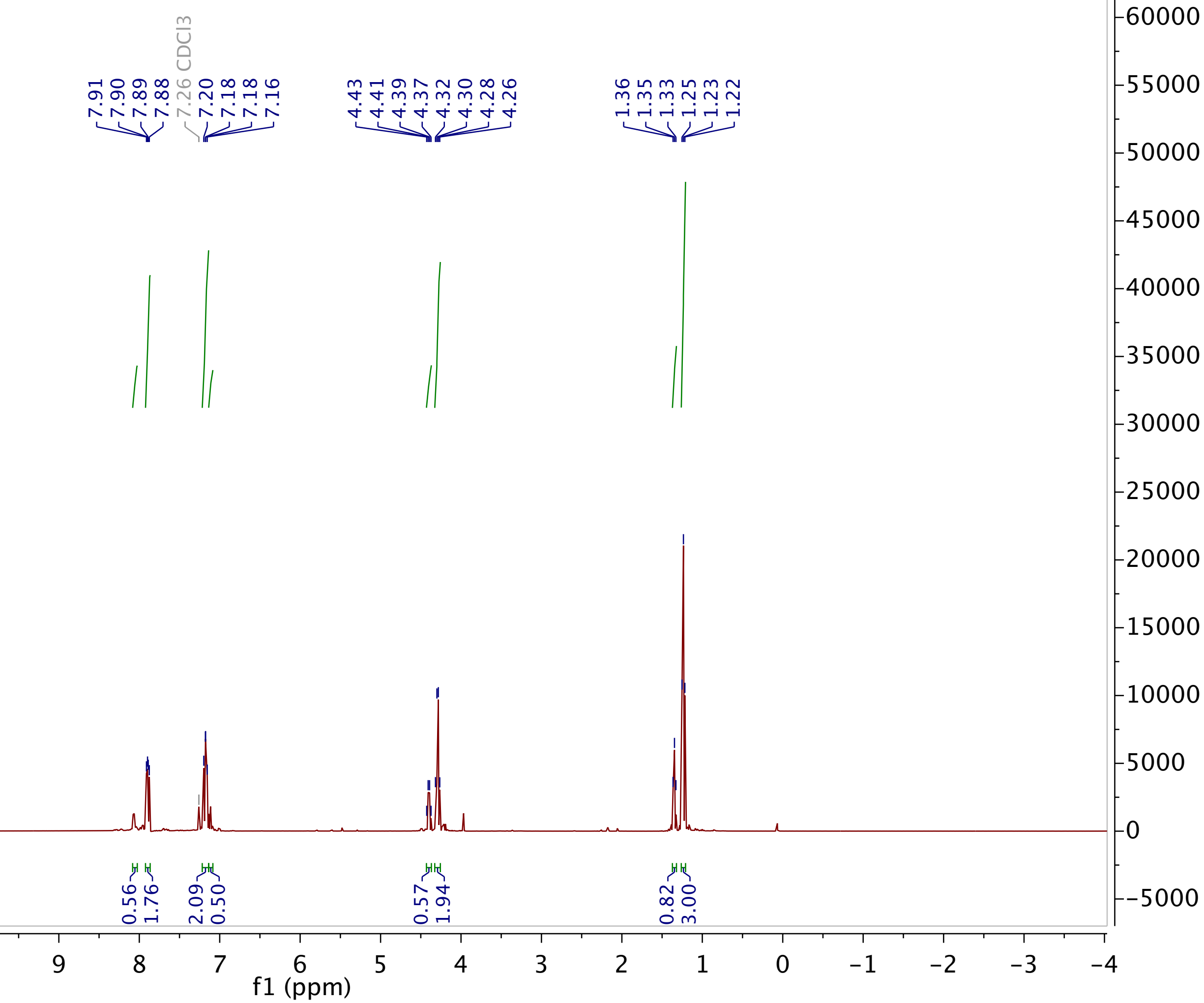

Aug23-2019-60-LS499(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CDCl_3$)
188.36
165.01
160.97
149.95
133.06
131.85
127.55
114.50
113.89
77.16 CDCl3
62.66
62.60
55.76
55.67
14.07
14.03
O
O
OEt
NOH
MeO
6d
f1 (ppm)

Sep11-2019-54-LS528(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 54



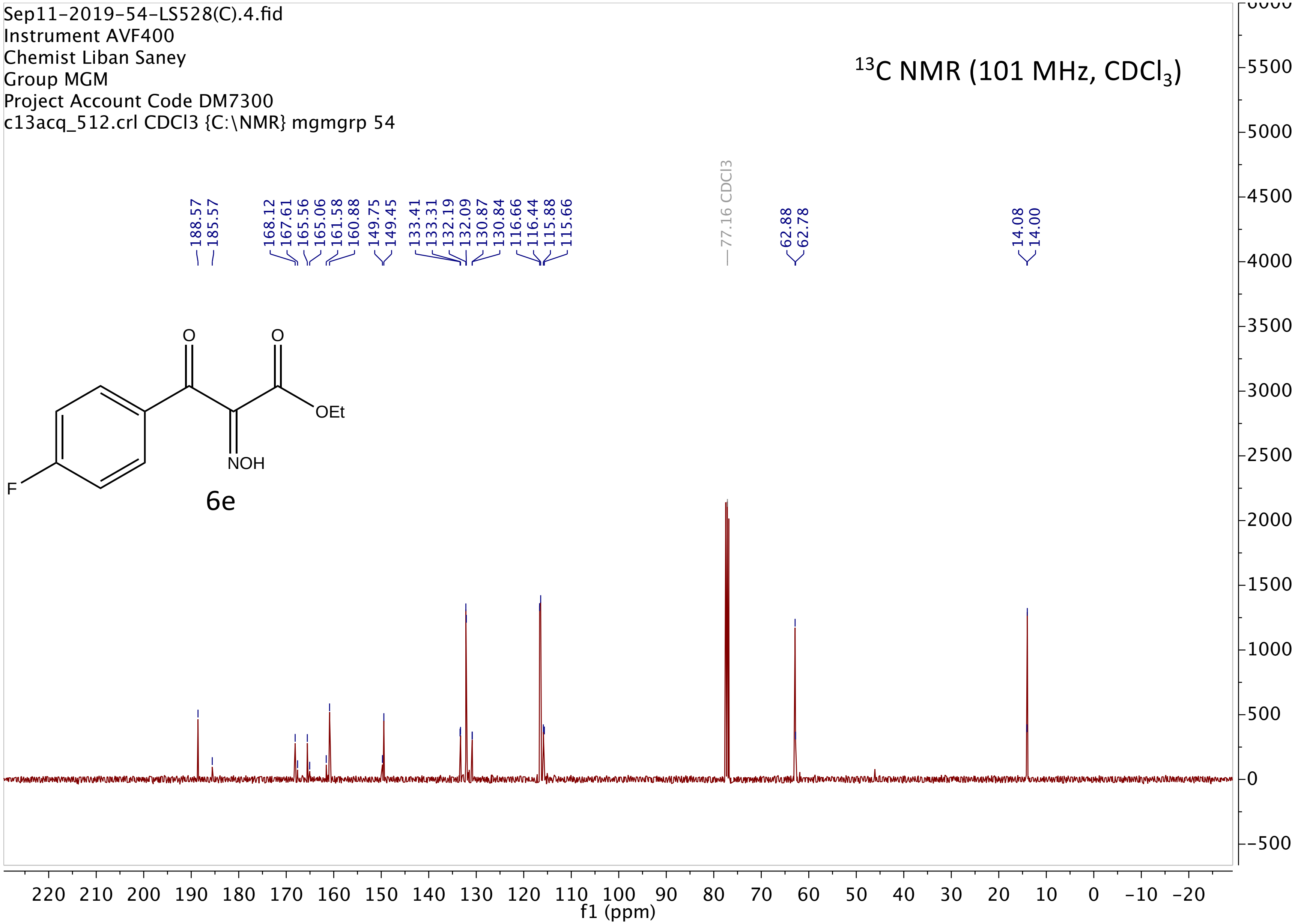

6e

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



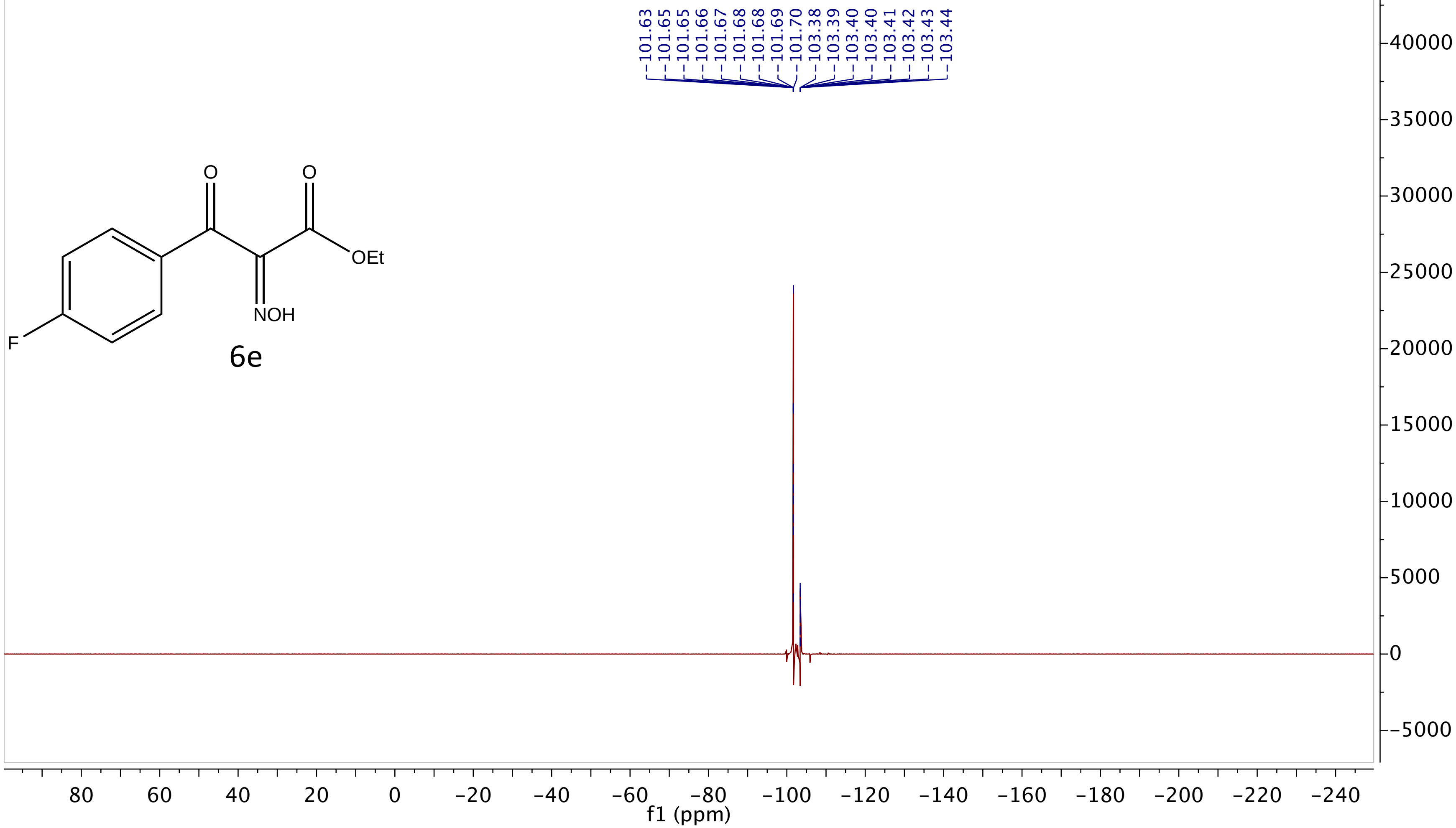
Sep11-2019-54-LS528(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 54

$^{13}C$ NMR (101 MHz, $CDCl_3$)



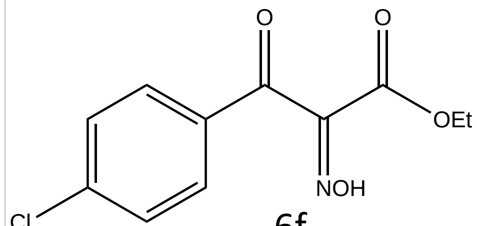
Sep11-2019-54-LS528(C).7.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
f19acq_256.crl CDCl3 {C:\NMR} mgmgrp 54

$^{19}$F NMR (377 MHz, $CDCl_3$)

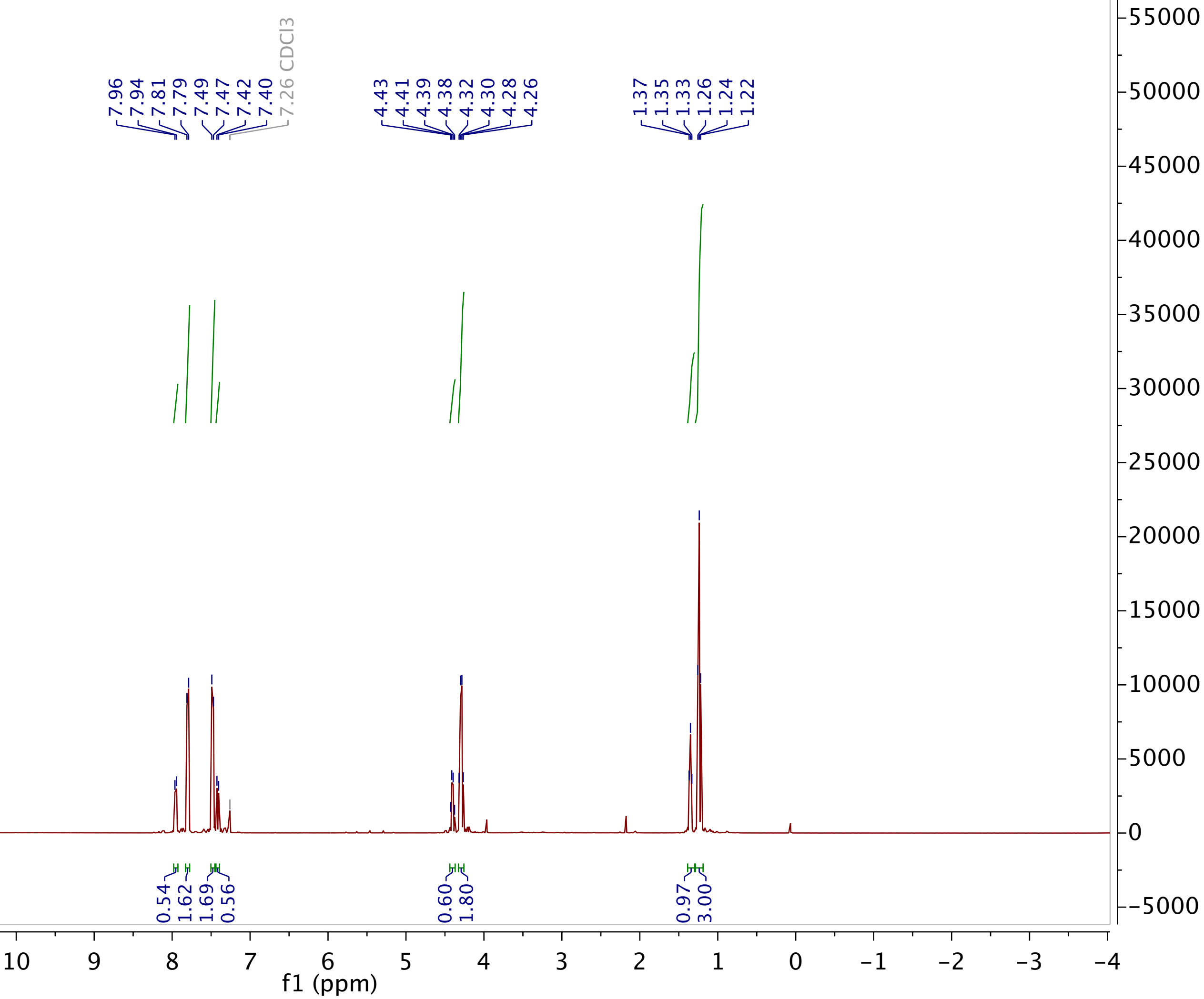


Sep11-2019-58-LS529(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 58

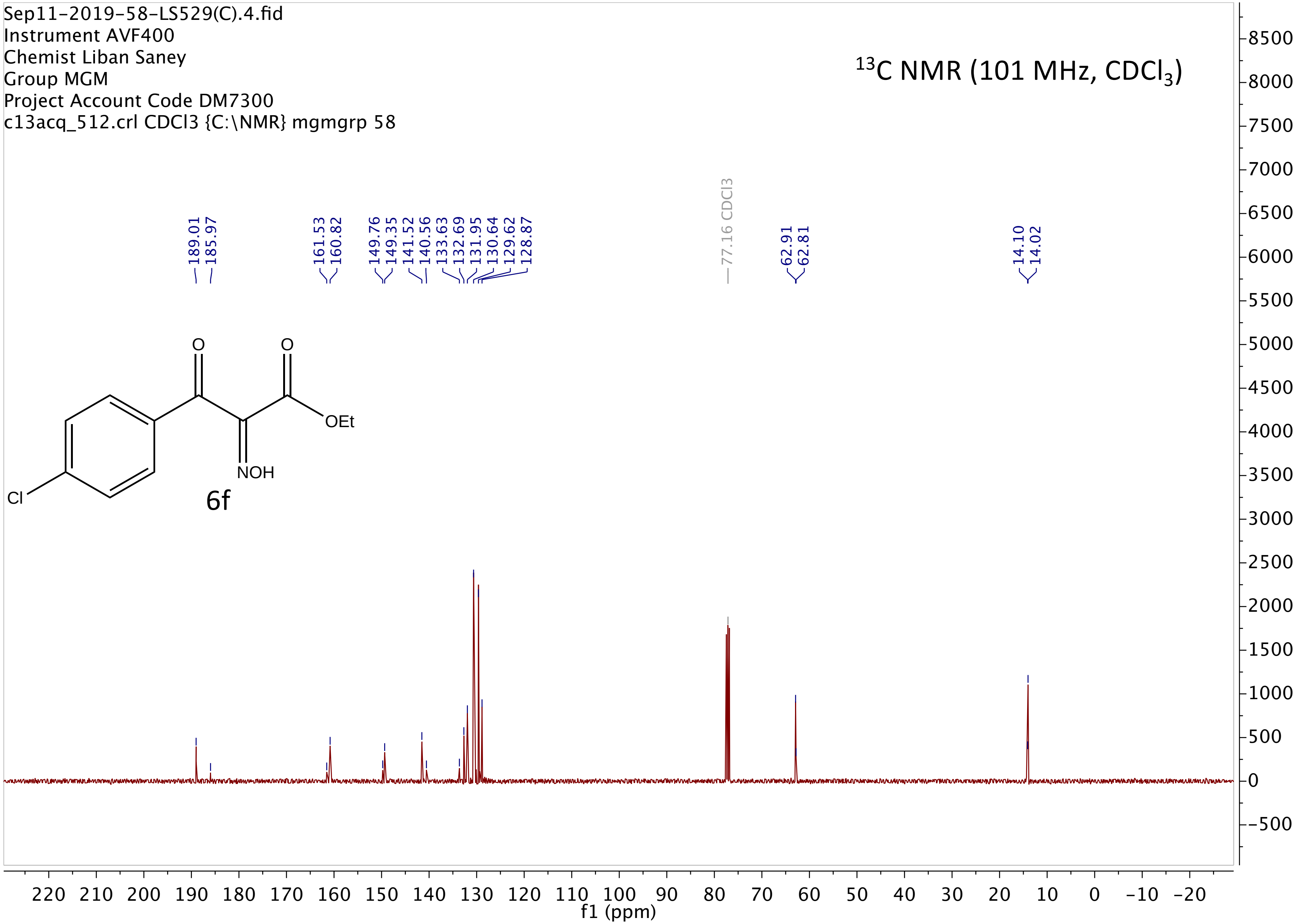
$^1$H NMR (400 MHz, $CDCl_3$)

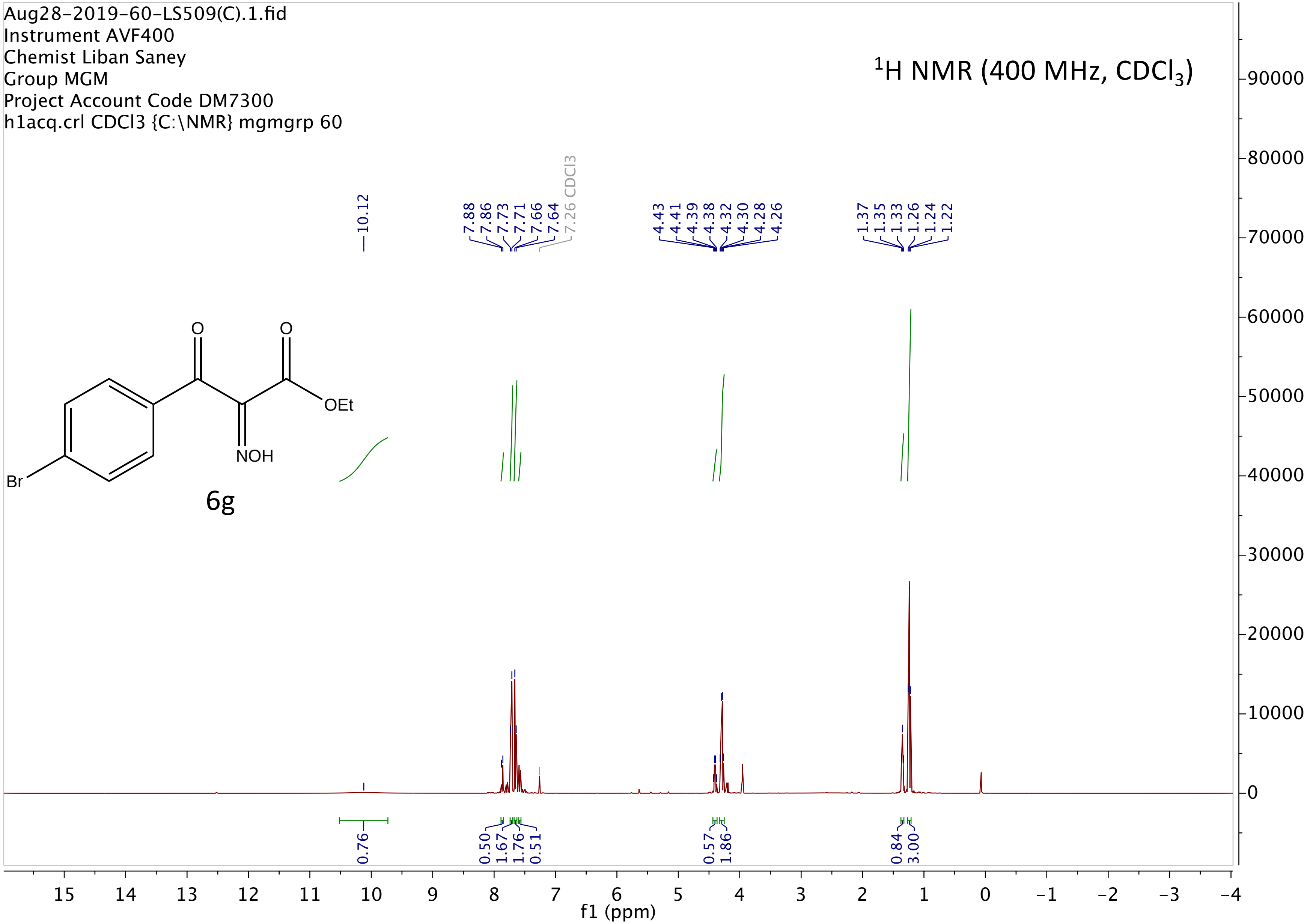


6f



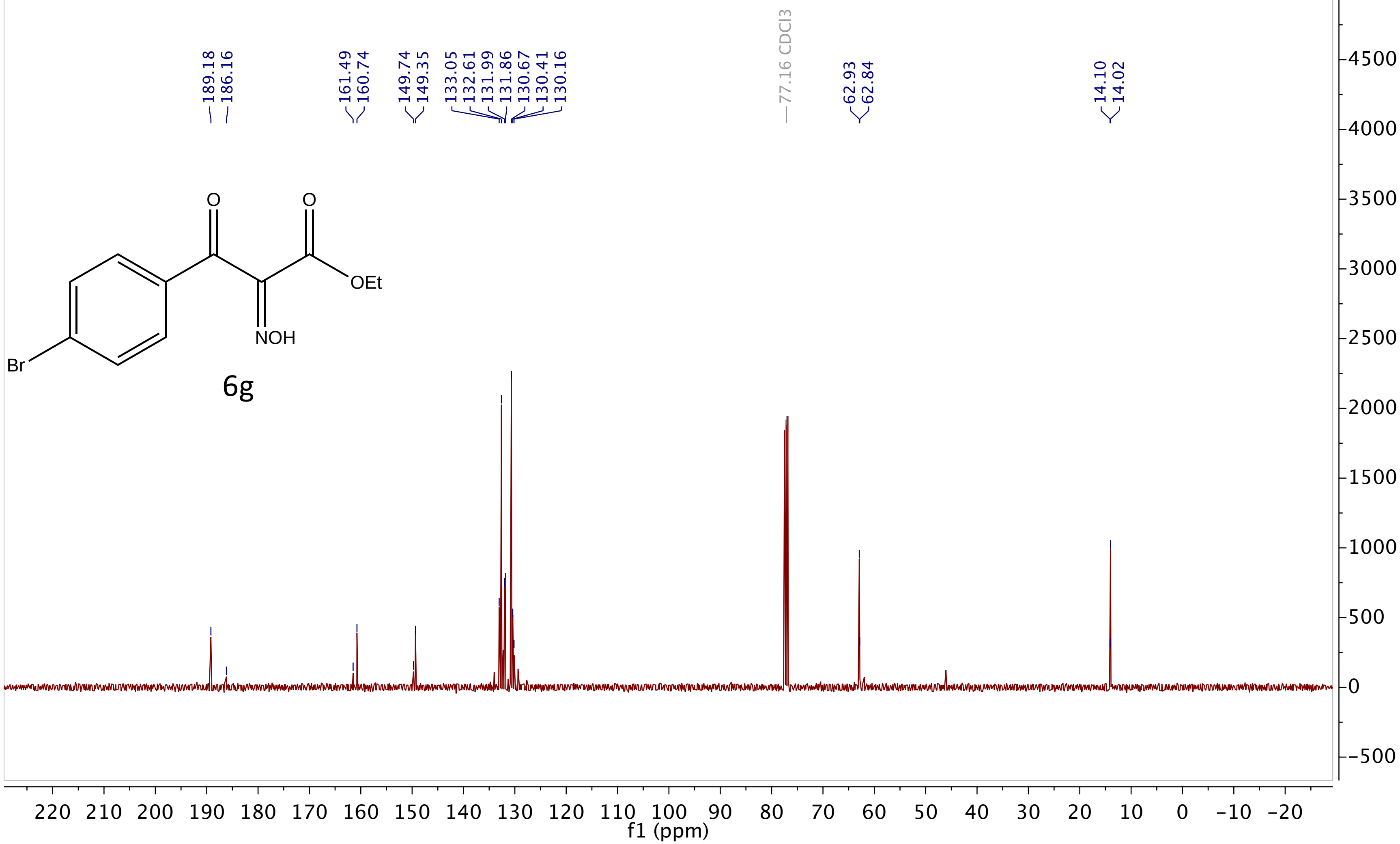
Sep11-2019-58-LS529(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 58




Aug28-2019-60-LS509(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
10.12
7.88
7.86
7.73
7.71
7.66
7.64
7.26 CDCl3
4.43
4.41
4.39
4.38
4.32
4.30
4.28
4.26
1.37
1.35
1.33
1.26
1.24
1.22
O
O
OEt
NOH
Br
6g
0.76
0.50
1.67
1.76
0.51
0.57
1.86
0.84
3.00
f1 (ppm)

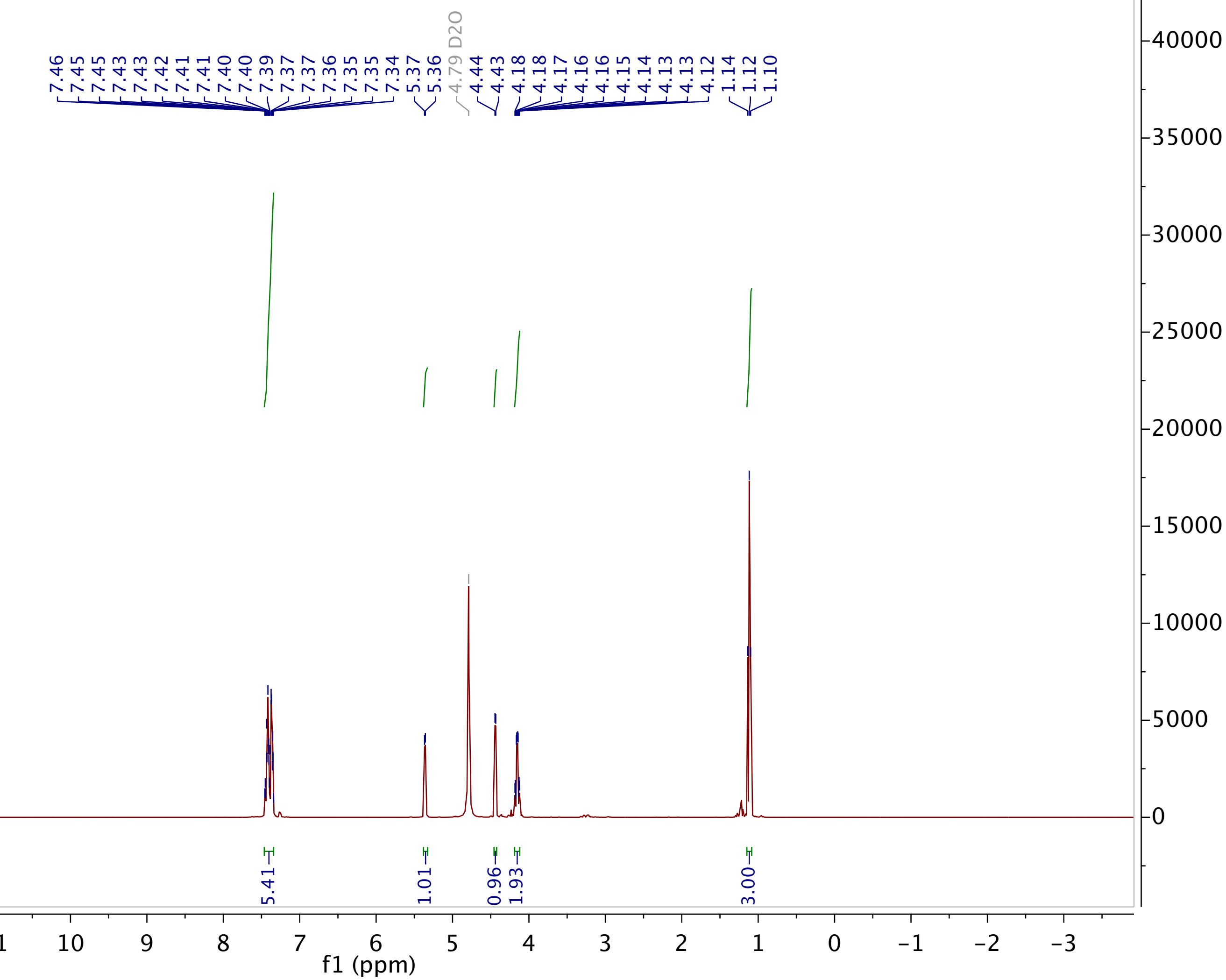
Aug28-2019-60-LS509(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

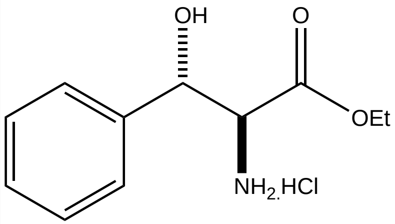
$^{13}$C NMR (101 MHz, $CDCl_3$)



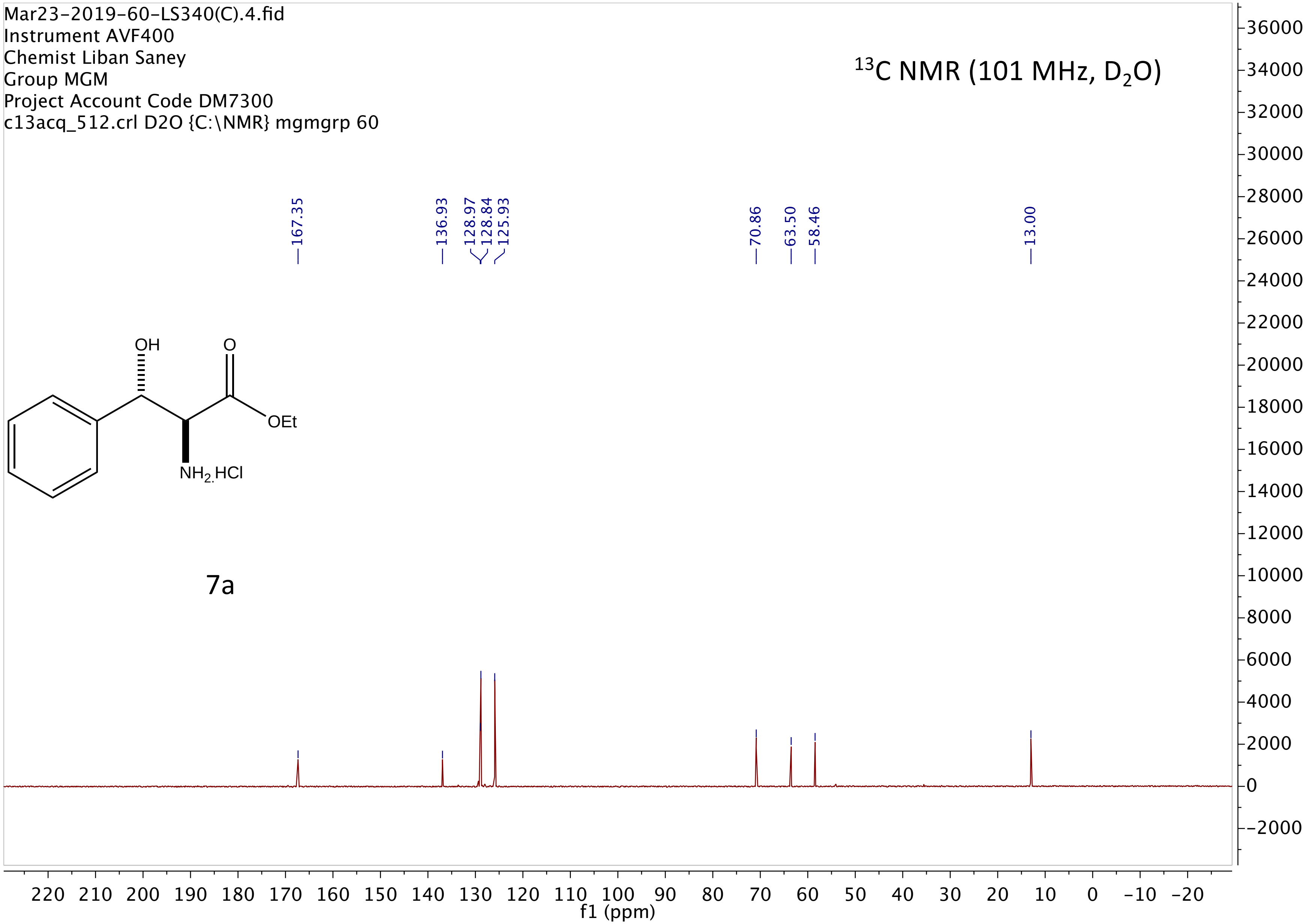
Mar23-2019-60-LS340(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 60

$^{1}$H NMR (400 MHz, $D_2O$)



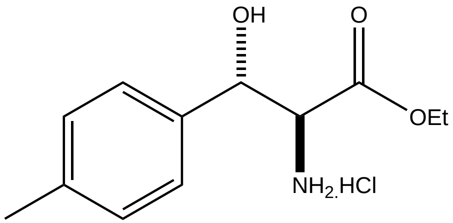

7a



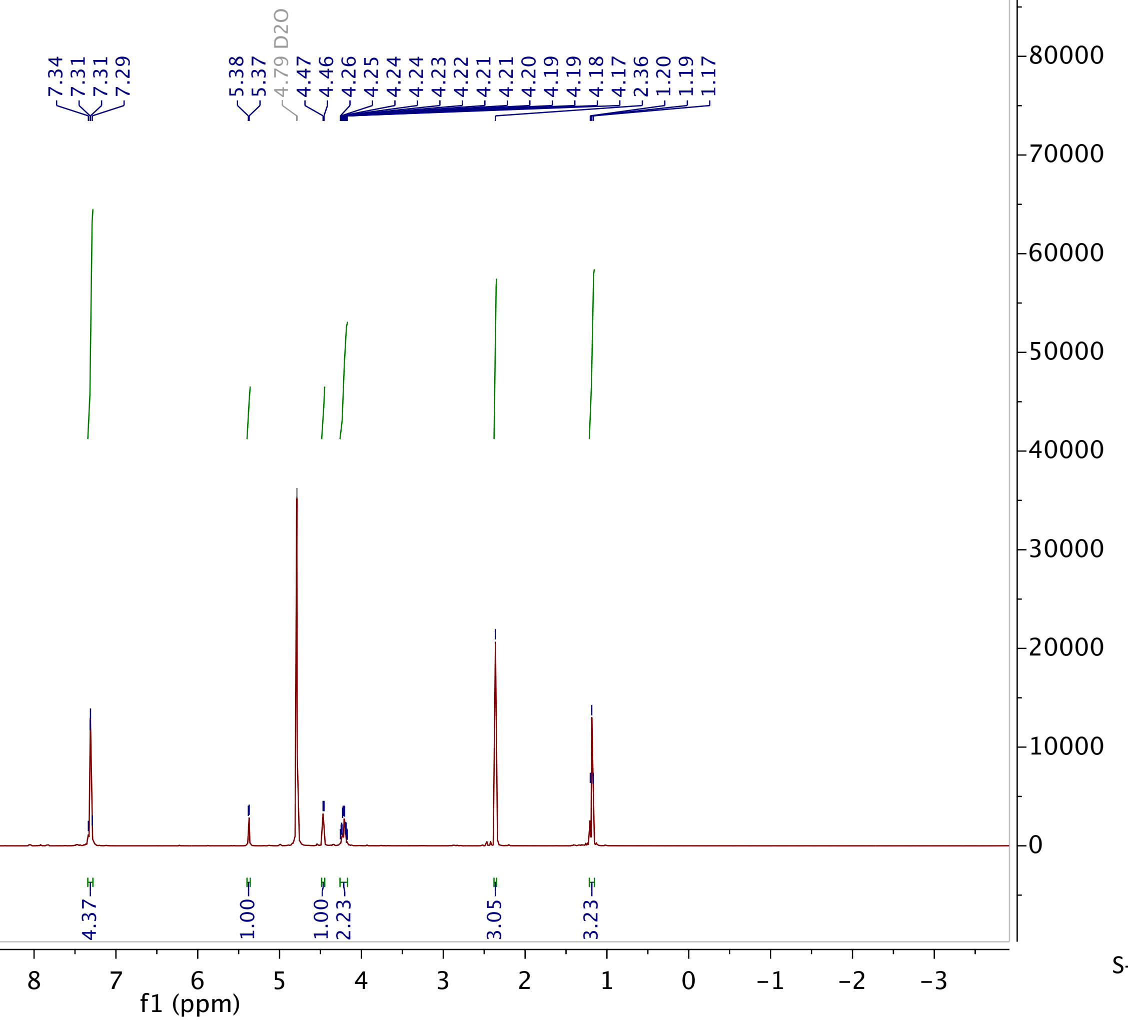
Mar23-2019-60-LS340(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $D_2O$)
167.35
136.93
128.97
128.84
125.93
70.86
63.50
58.46
13.00
OH
O
OEt
NH2.HCl
7a
f1 (ppm)

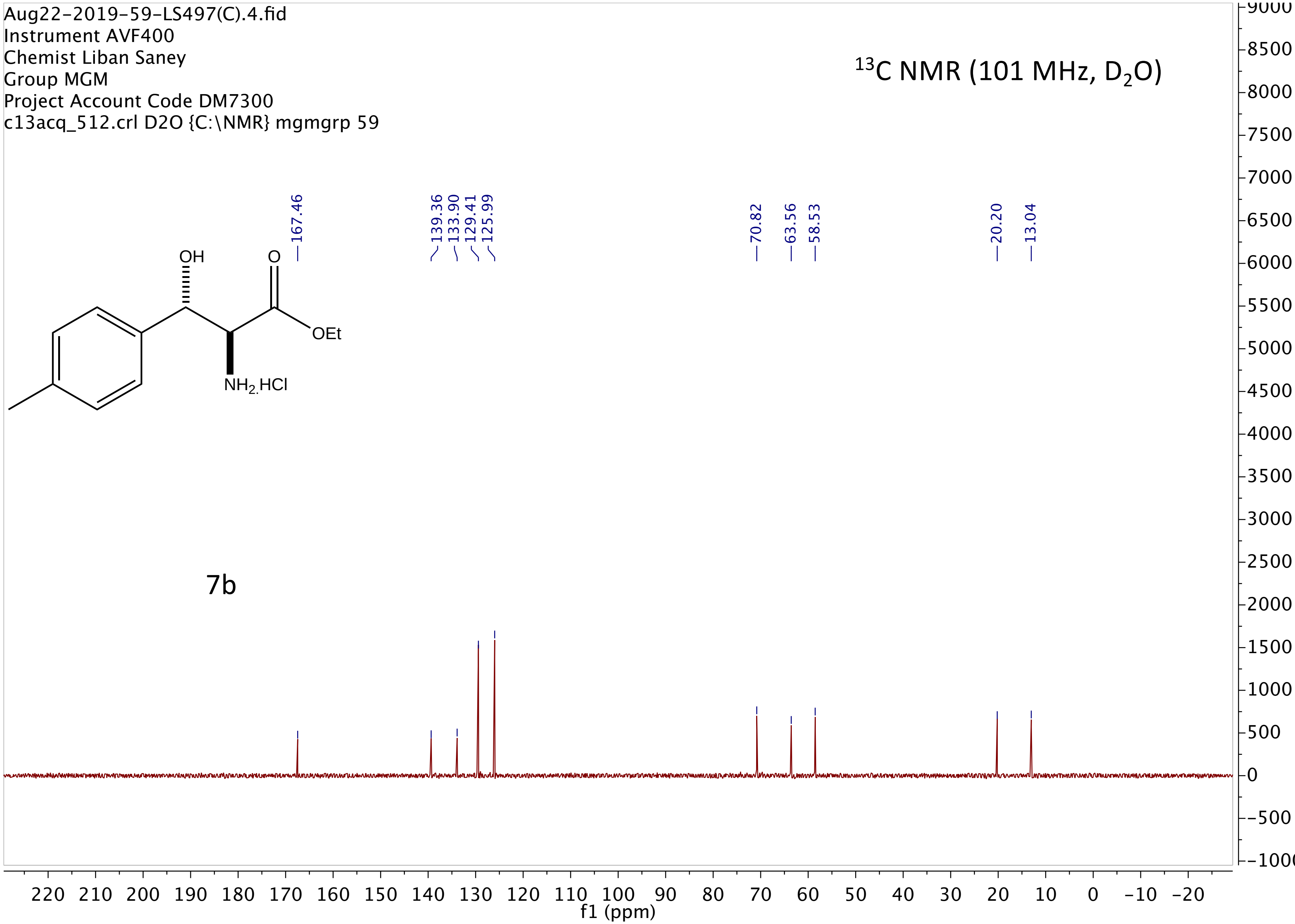
Aug22-2019-59-LS497(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 59

$^1H$ NMR (400 MHz, $D_2O$)



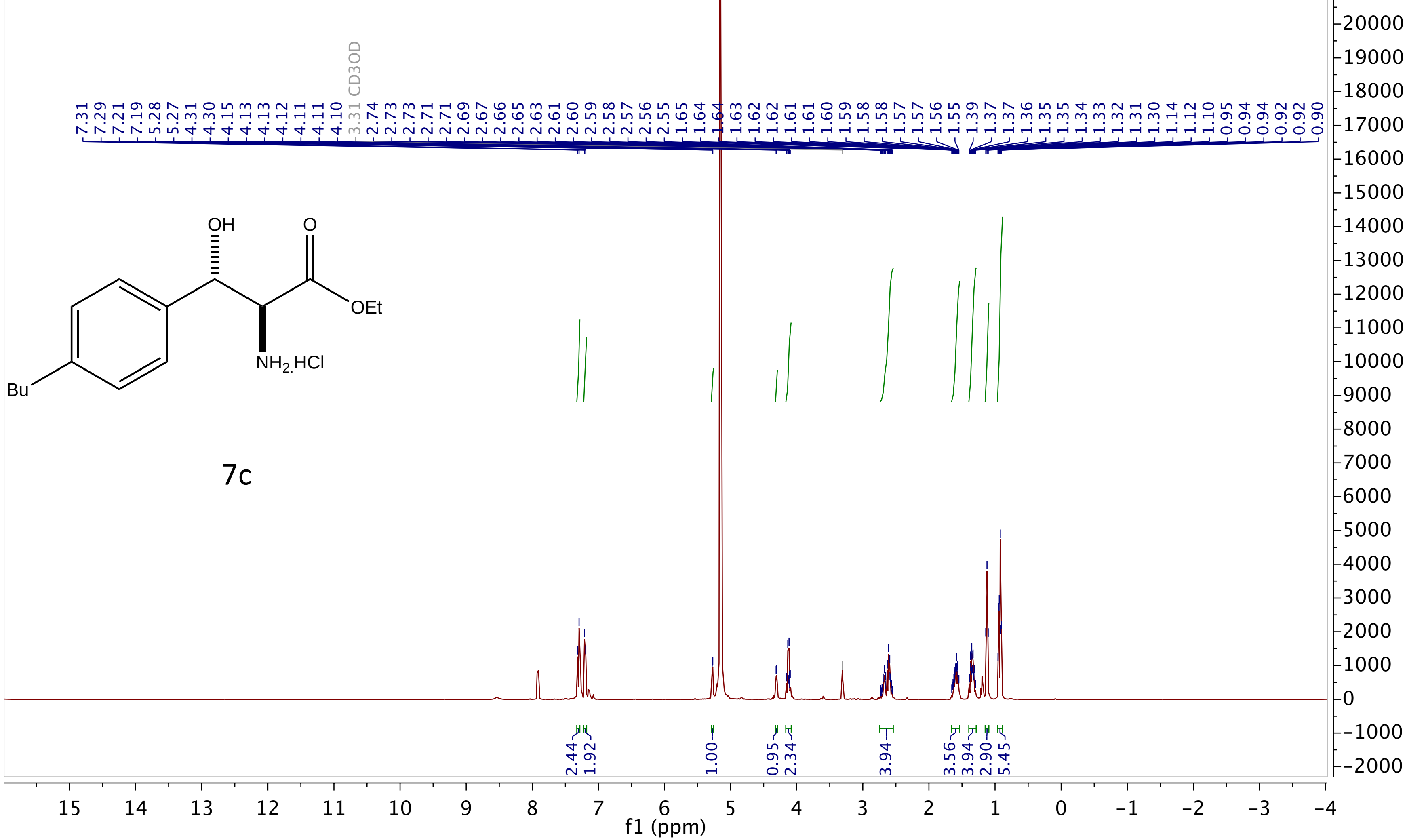
7b

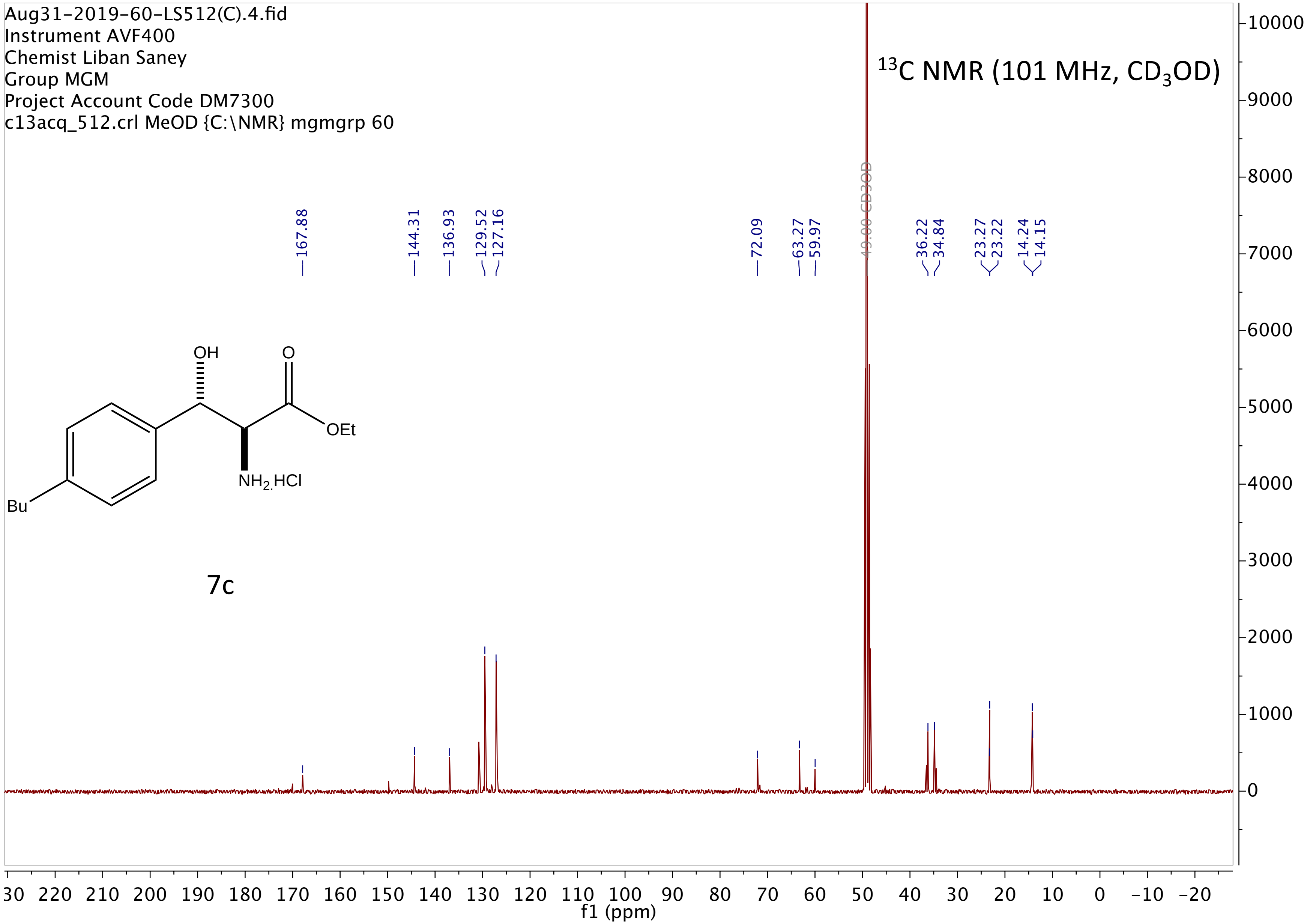


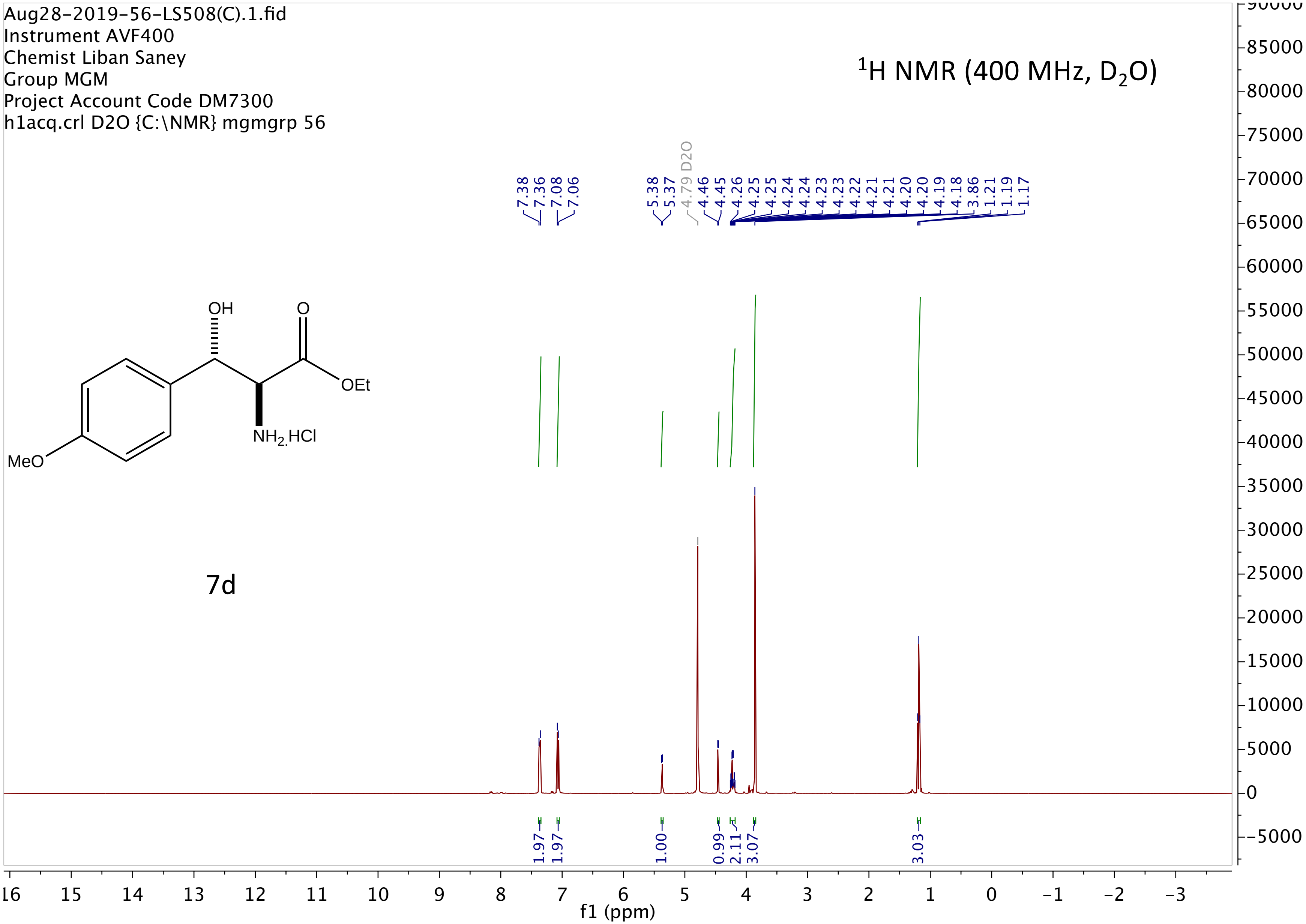

Aug22-2019-59-LS497(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 59
$^{13}$C NMR (101 MHz, $D_2O$)
167.46
139.36
133.90
129.41
125.99
70.82
63.56
58.53
20.20
13.04
OH
O
OEt
NH2.HCl
7b
f1 (ppm)

Aug31-2019-60-LS512(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl MeOD {C:\NMR} mgmgrp 60

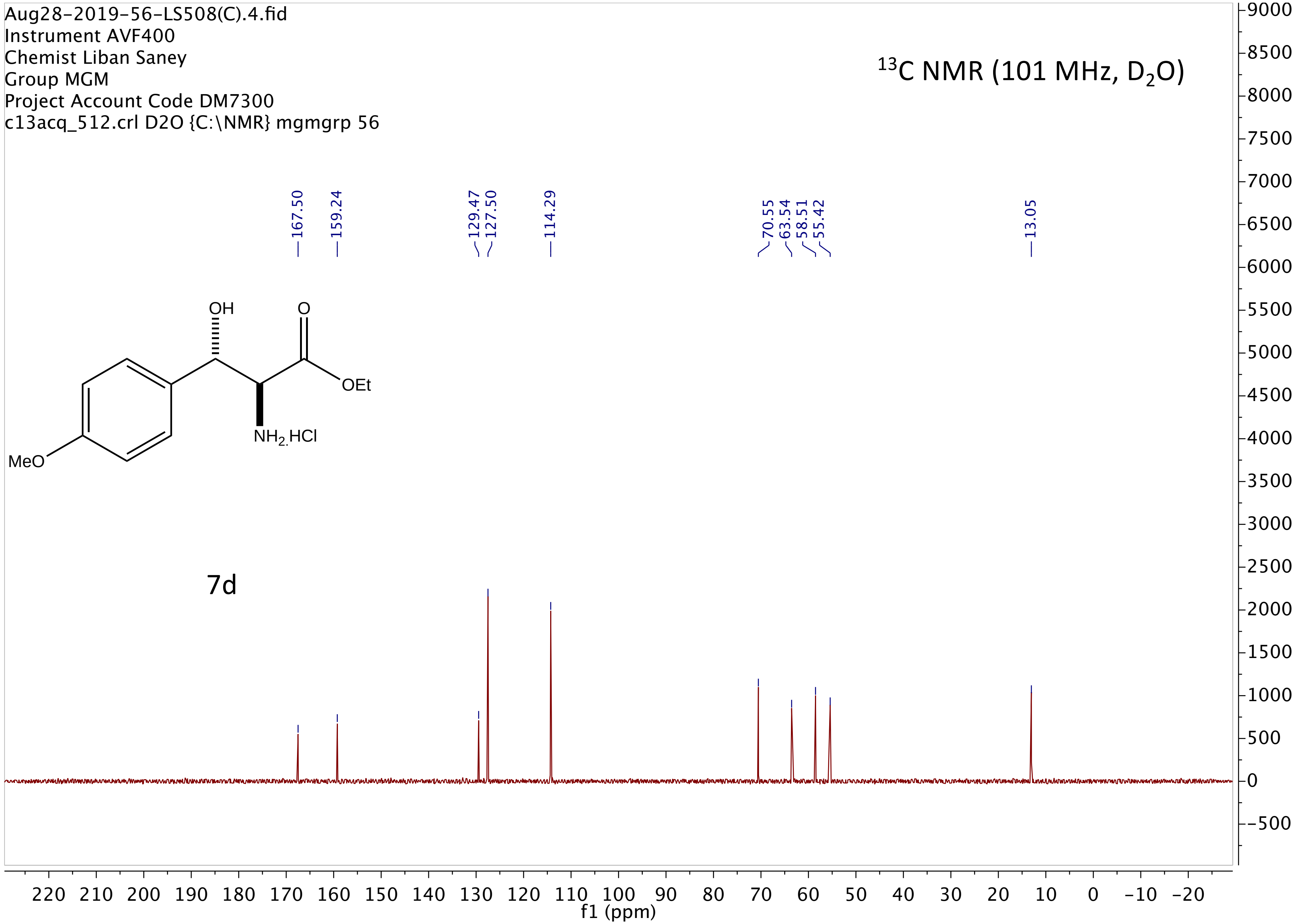
$^1$H NMR (400 MHz, $CD_3OD$)

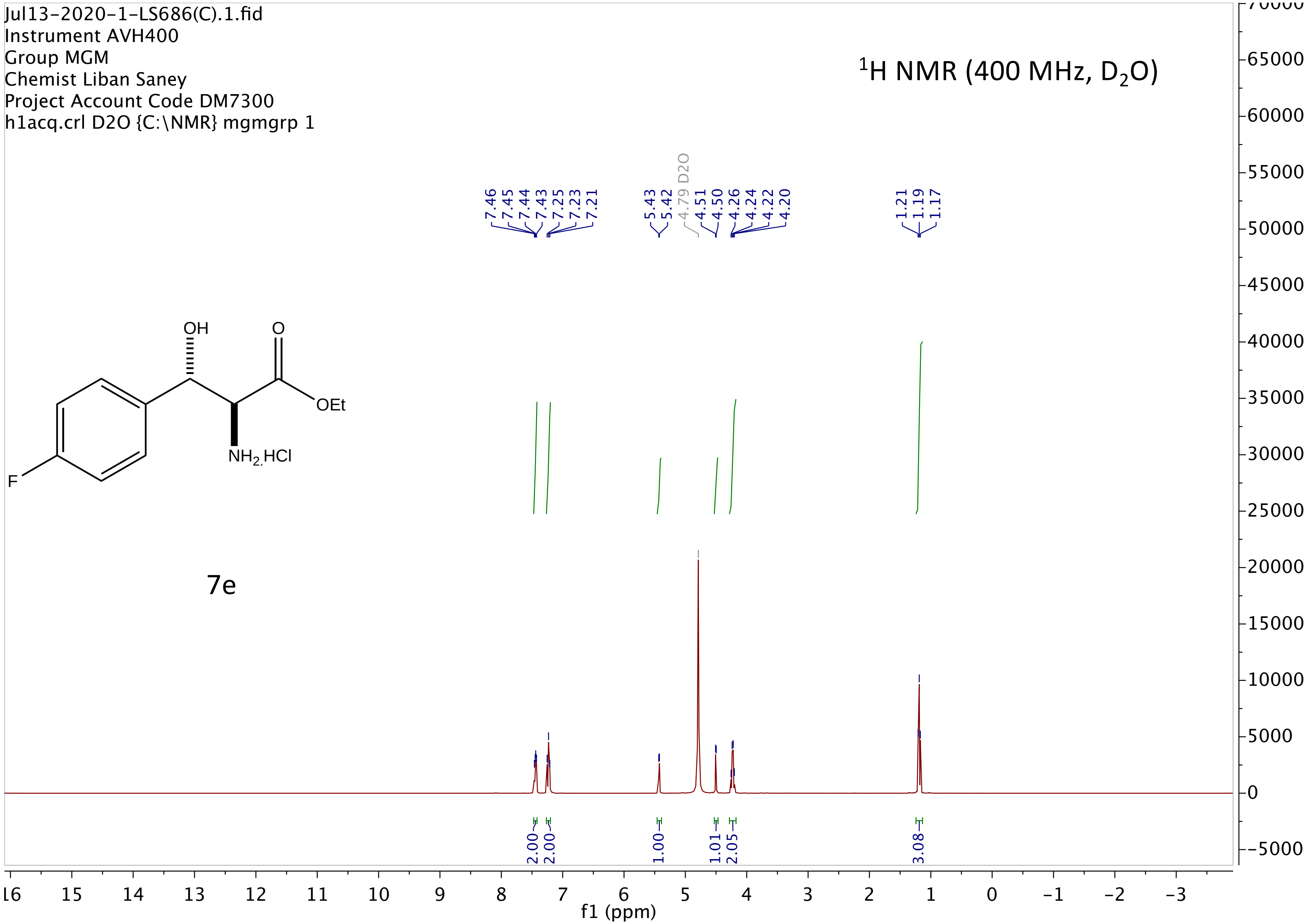



Aug31-2019-60-LS512(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl MeOD {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CD_3OD$)
167.88
144.31
136.93
129.52
127.16
72.09
63.27
59.97
49.00 CD3OD
36.22
34.84
23.27
23.22
14.24
14.15
OH
O
OEt
$NH_2$.HCl
Bu
7c
f1 (ppm)



Aug28-2019-56-LS508(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 56
1H NMR (400 MHz, D2O)
7.38
7.36
7.08
7.06
5.38
5.37
4.79 D2O
4.46
4.45
4.26
4.25
4.25
4.24
4.24
4.23
4.23
4.22
4.21
4.21
4.20
4.20
4.19
4.18
3.86
1.21
1.19
1.17
OH
O
OEt
NH2.HCl
MeO
7d
1.97
1.97
1.00
0.99
2.11
3.07
3.03
f1 (ppm)

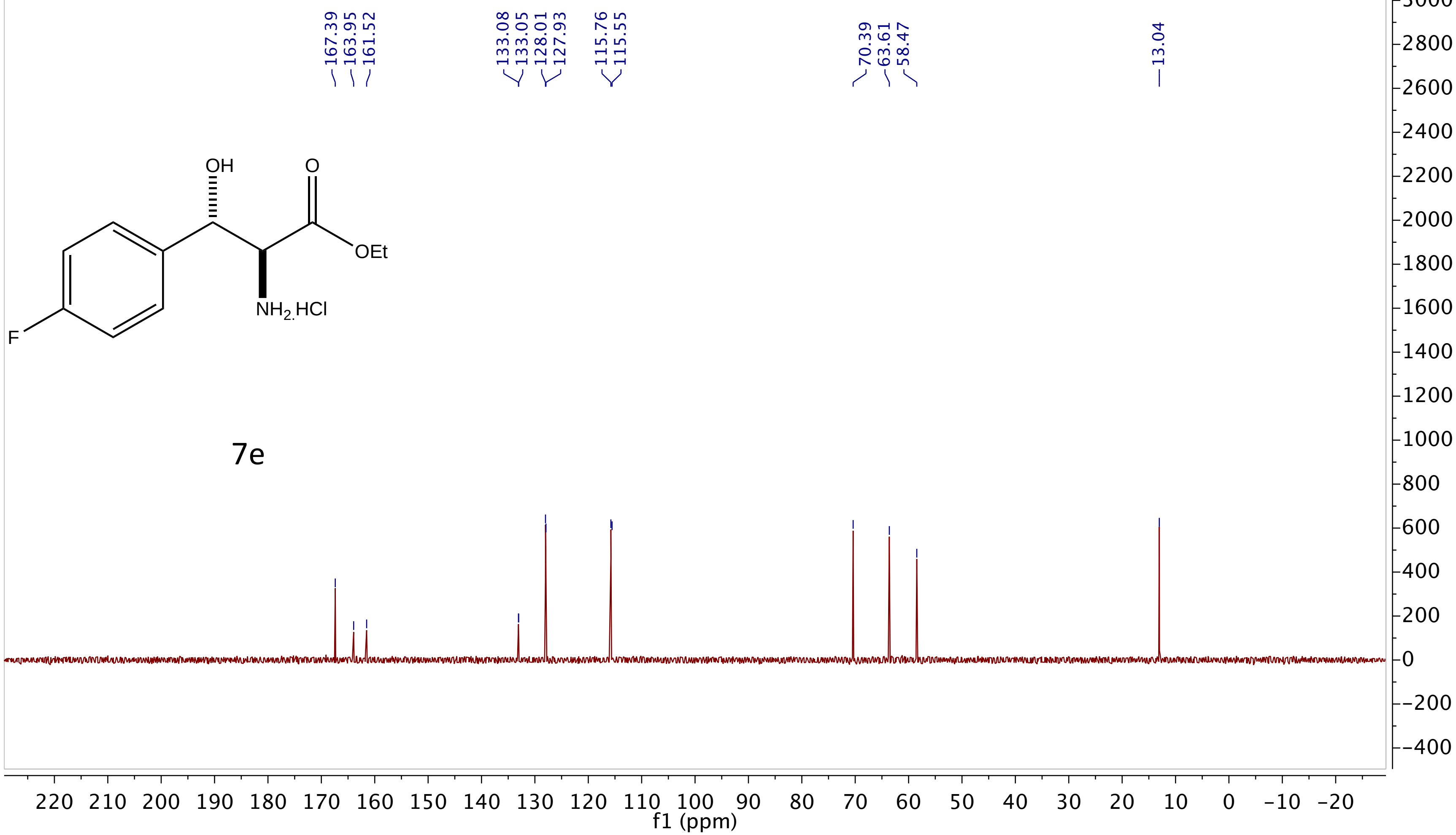

Aug28-2019-56-LS508(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 56
13C NMR (101 MHz, D2O)
167.50
159.24
129.47
127.50
114.29
70.55
63.54
58.51
55.42
13.05
OH
O
OEt
NH2.HCl
MeO
7d
f1 (ppm)



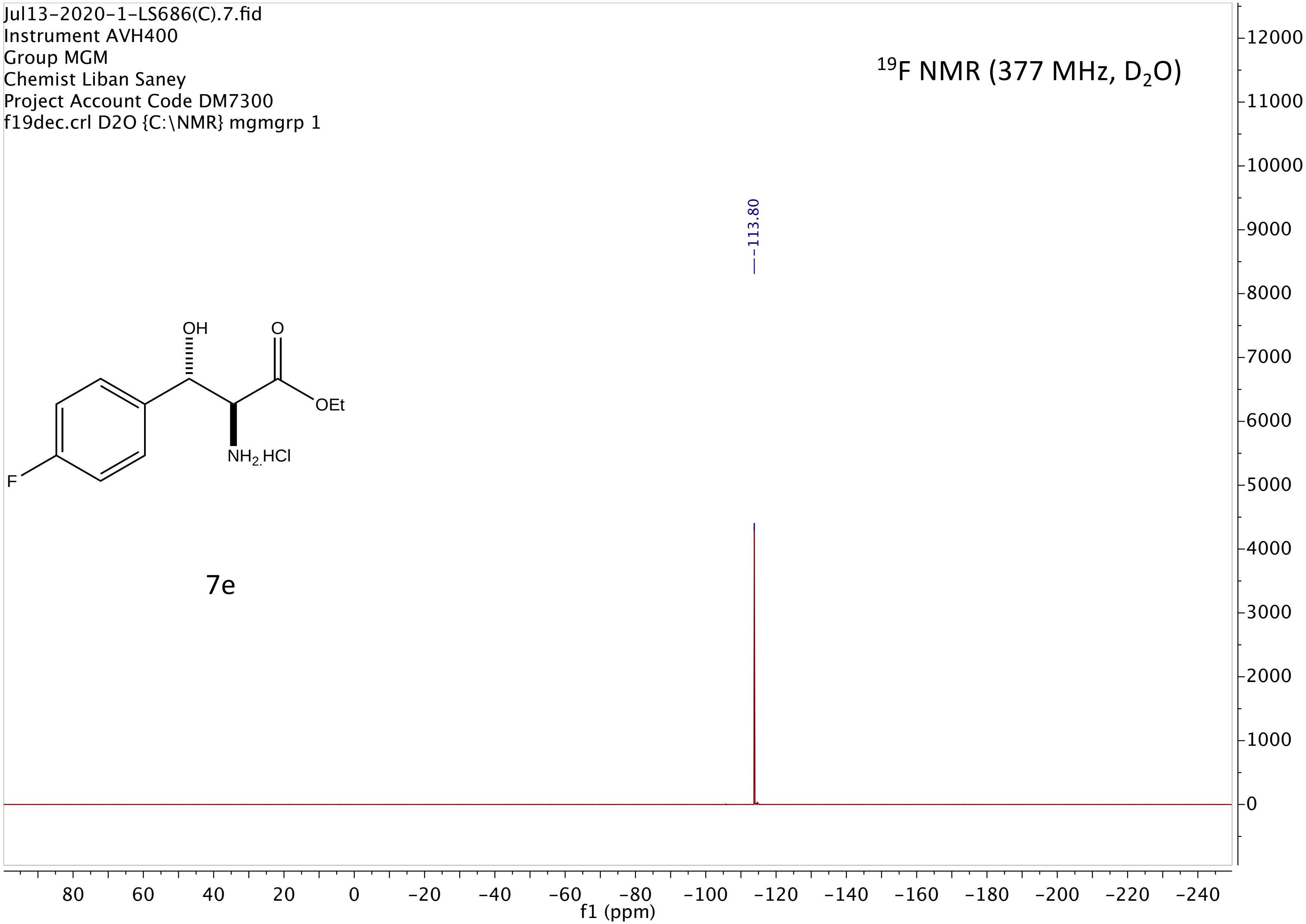
Jul13-2020-1-LS686(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 1
$^1$H NMR (400 MHz, $D_2O$)
7e
7.46
7.45
7.44
7.43
7.25
7.23
7.21
5.43
5.42
4.79 D2O
4.51
4.50
4.26
4.24
4.22
4.20
1.21
1.19
1.17
2.00
2.00
1.00
1.01
2.05
3.08
f1 (ppm)

Jul13-2020-1-LS686(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 1

$^{13}C$ NMR (101 MHz, $D_2O$)

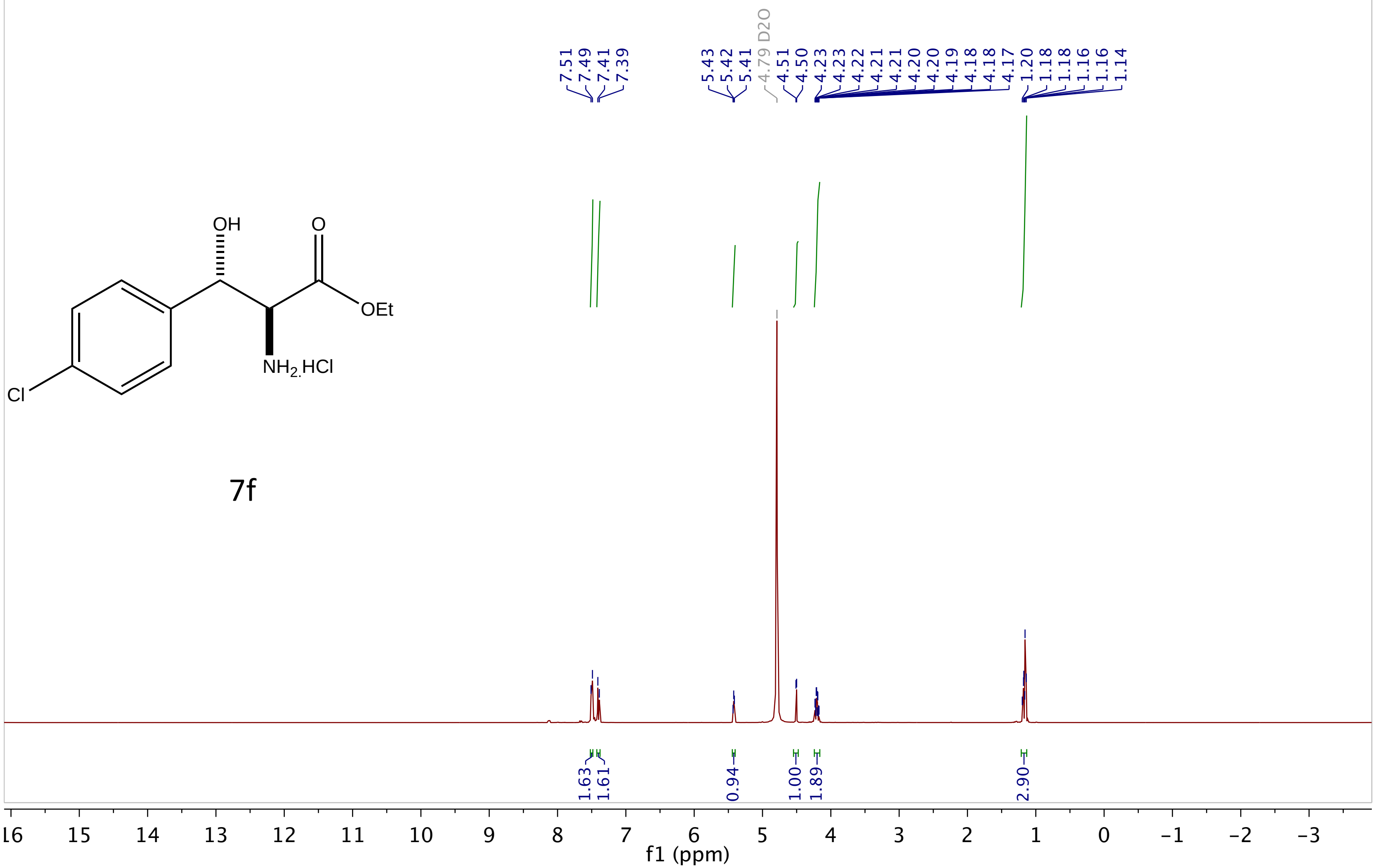



7e

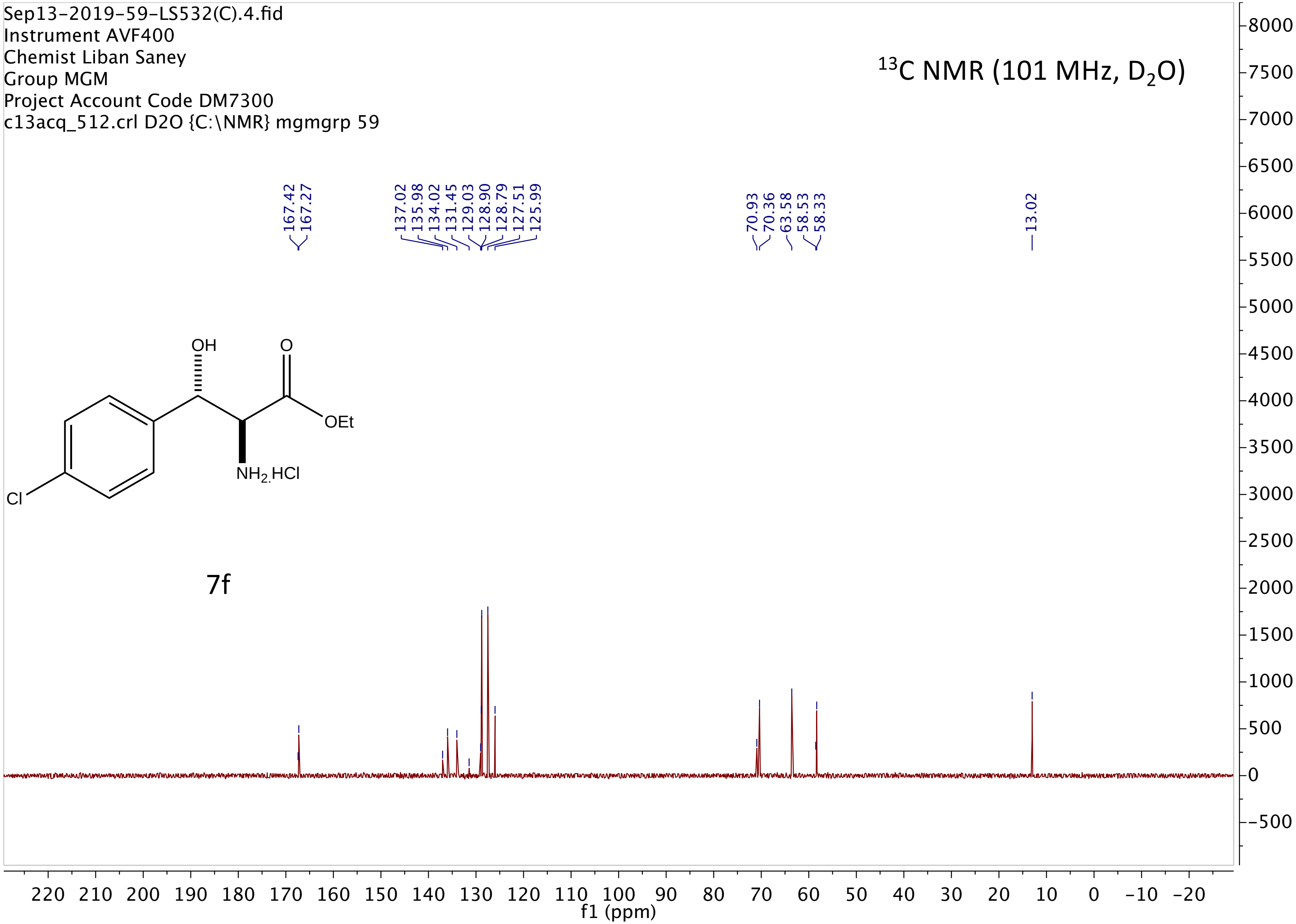

Jul13-2020-1-LS686(C).7.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec.crl D2O {C:\NMR} mgmgrp 1
$^{19}$F NMR (377 MHz, $D_2O$)
-113.80
OH
O
OEt
$NH_2$.HCl
F
7e
f1 (ppm)

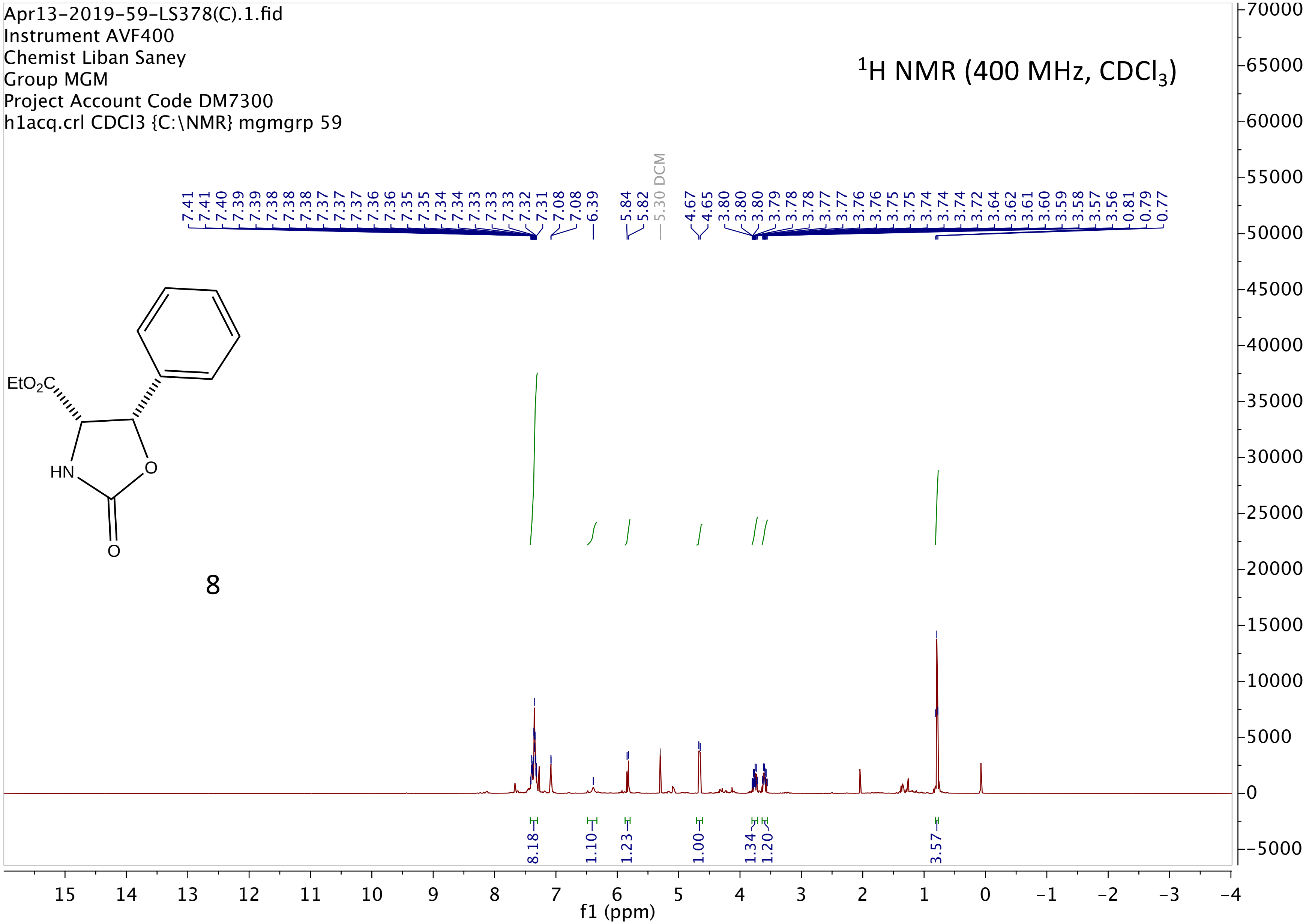
Sep13-2019-59-LS532(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 59

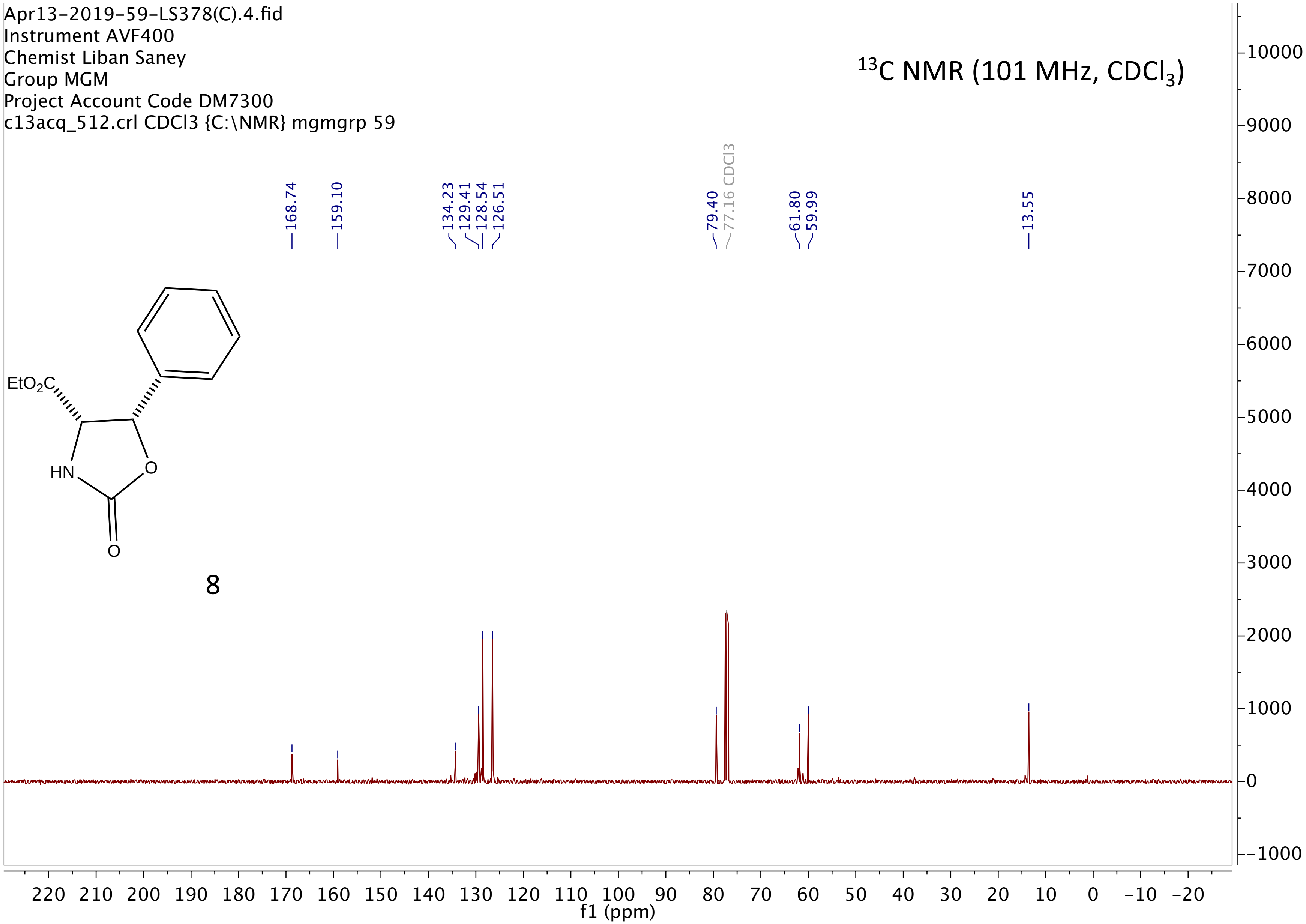
$^1$H NMR (400 MHz, $D_2O$)



Sep13-2019-59-LS532(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 59



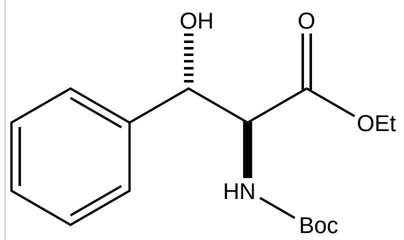

Apr13-2019-59-LS378(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59
$^{1}$H NMR (400 MHz, $CDCl_3$)
7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.08 7.08 6.39 5.84 5.82 5.30 DCM 4.67 4.65 3.80 3.80 3.80 3.79 3.78 3.78 3.77 3.77 3.76 3.76 3.75 3.75 3.74 3.74 3.74 3.72 3.64 3.62 3.61 3.60 3.59 3.58 3.57 3.56 0.81 0.79 0.77
$EtO_2C$
HN
O
O
8
8.18 1.10 1.23 1.00 1.34 1.20 3.57
f1 (ppm)


Apr13-2019-59-LS378(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59
13C NMR (101 MHz, CDCl3)
168.74
159.10
134.23
129.41
128.54
126.51
79.40
77.16 CDCl3
61.80
59.99
13.55
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)
EtO2C
HN
O
O

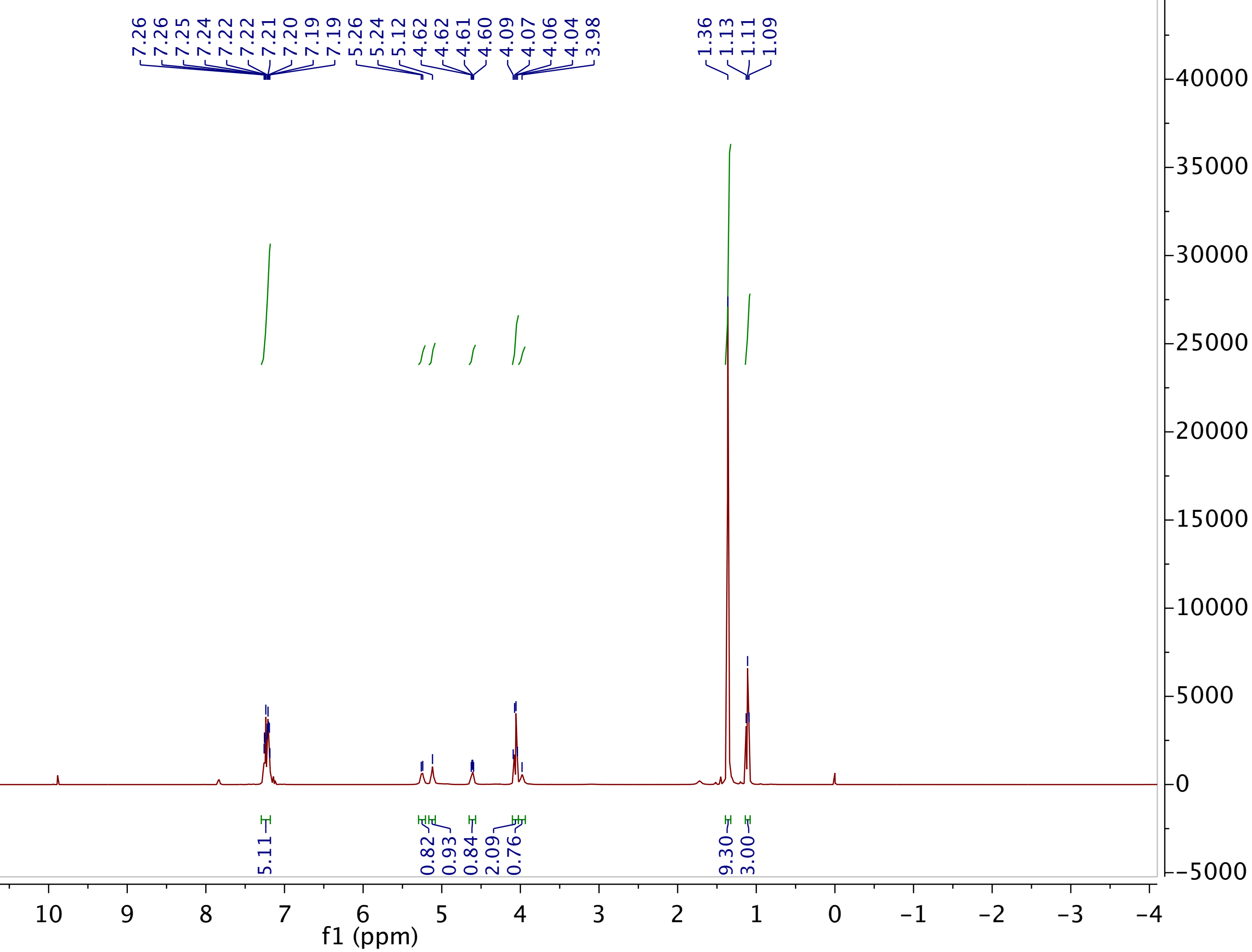
8

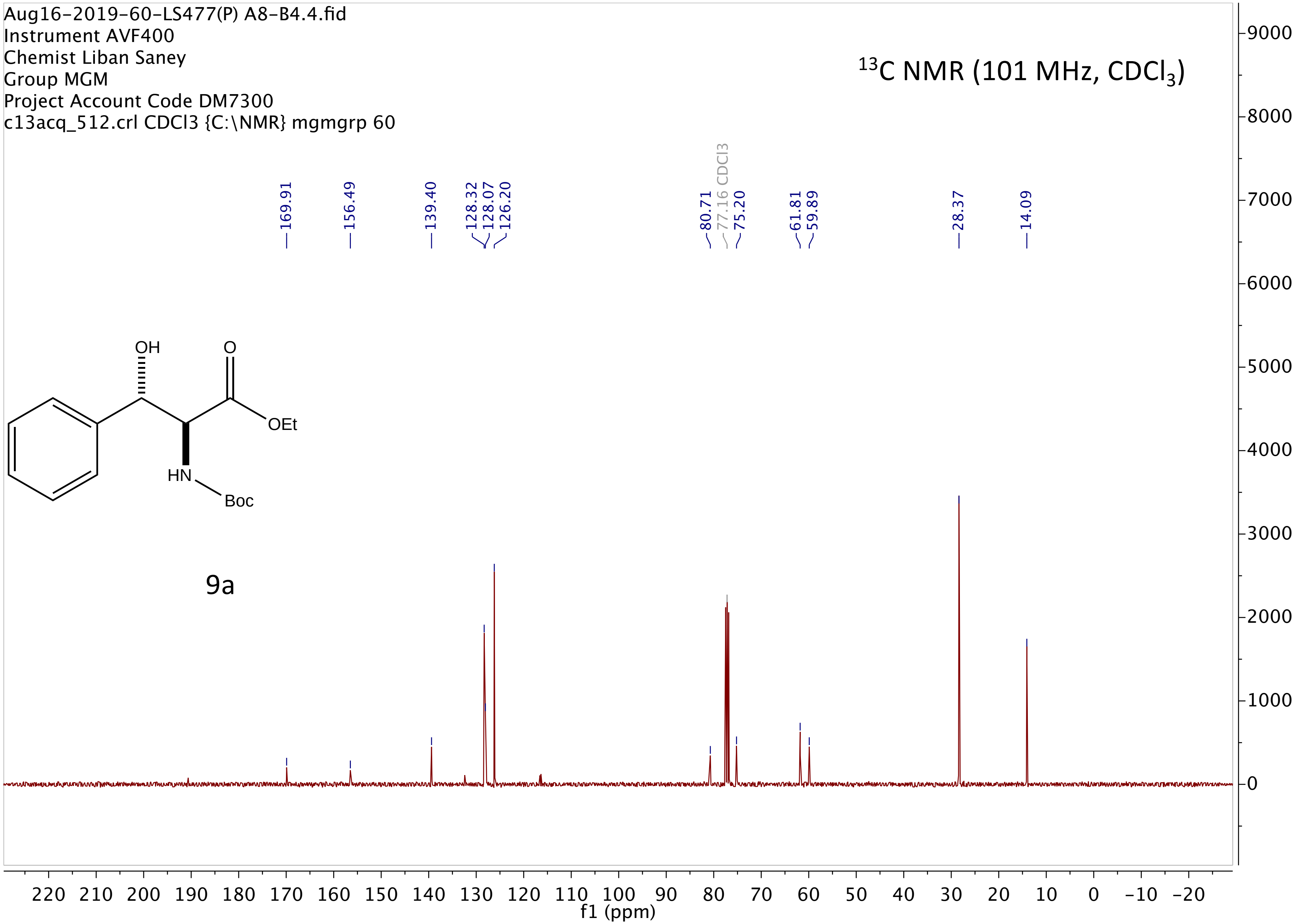
Aug16-2019-60-LS477(P) A8-B4.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

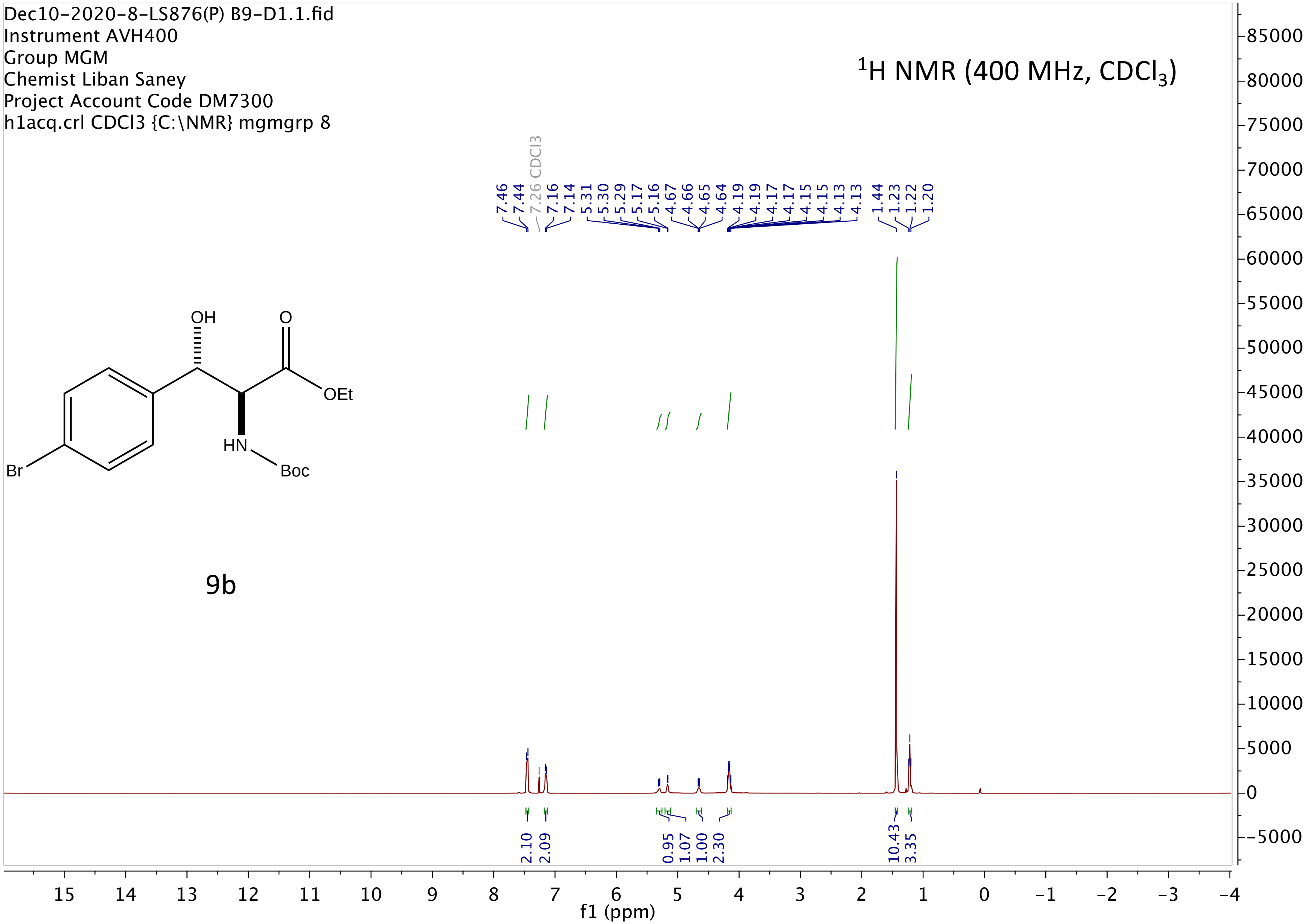
$^{1}$H NMR (400 MHz, $CDCl_3$)

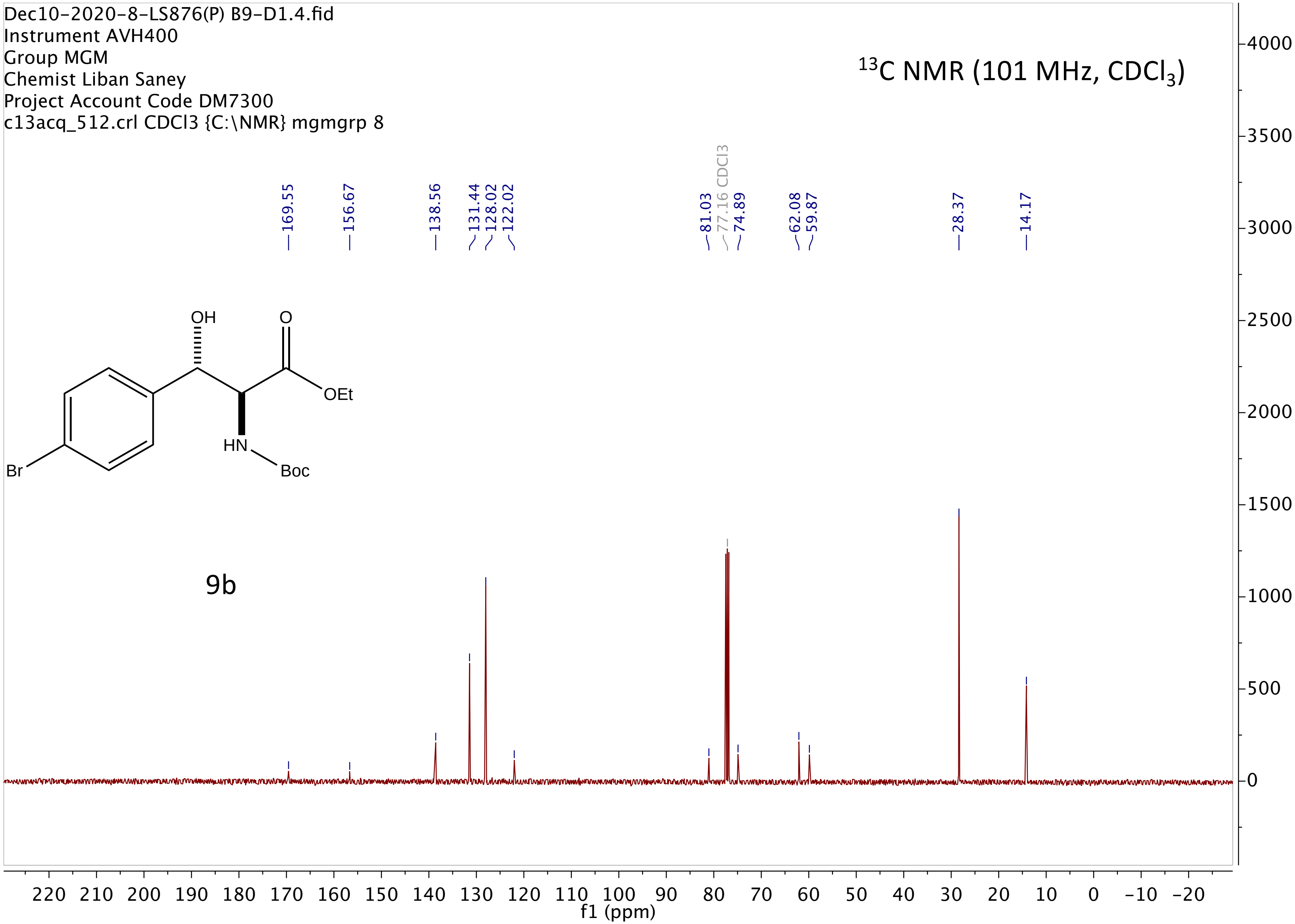


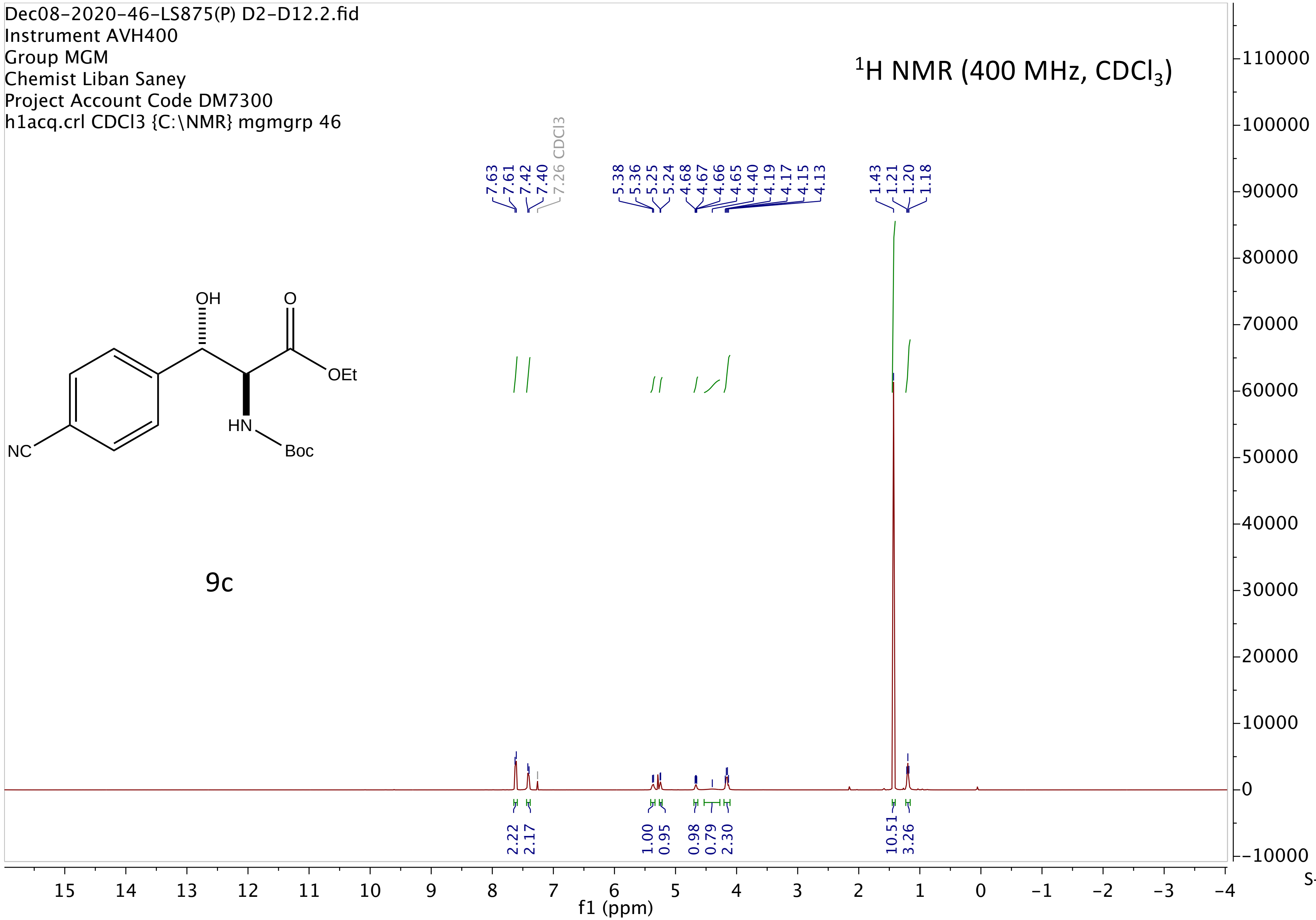

9a




Aug16-2019-60-LS477(P) A8-B4.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CDCl_3$)
169.91
156.49
139.40
128.32
128.07
126.20
80.71
77.16 CDCl3
75.20
61.81
59.89
28.37
14.09
OH
O
OEt
HN
Boc
9a
f1 (ppm)


Dec10-2020-8-LS876(P) B9-D1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 8
1H NMR (400 MHz, CDCl3)
OH
O
OEt
HN
Boc
Br
9b
7.46
7.44
7.26 CDCl3
7.16
7.14
5.31
5.30
5.29
5.17
5.16
4.67
4.66
4.65
4.64
4.19
4.19
4.17
4.17
4.15
4.15
4.13
4.13
1.44
1.23
1.22
1.20
2.10
2.09
0.95
1.07
1.00
2.30
10.43
3.35
f1 (ppm)

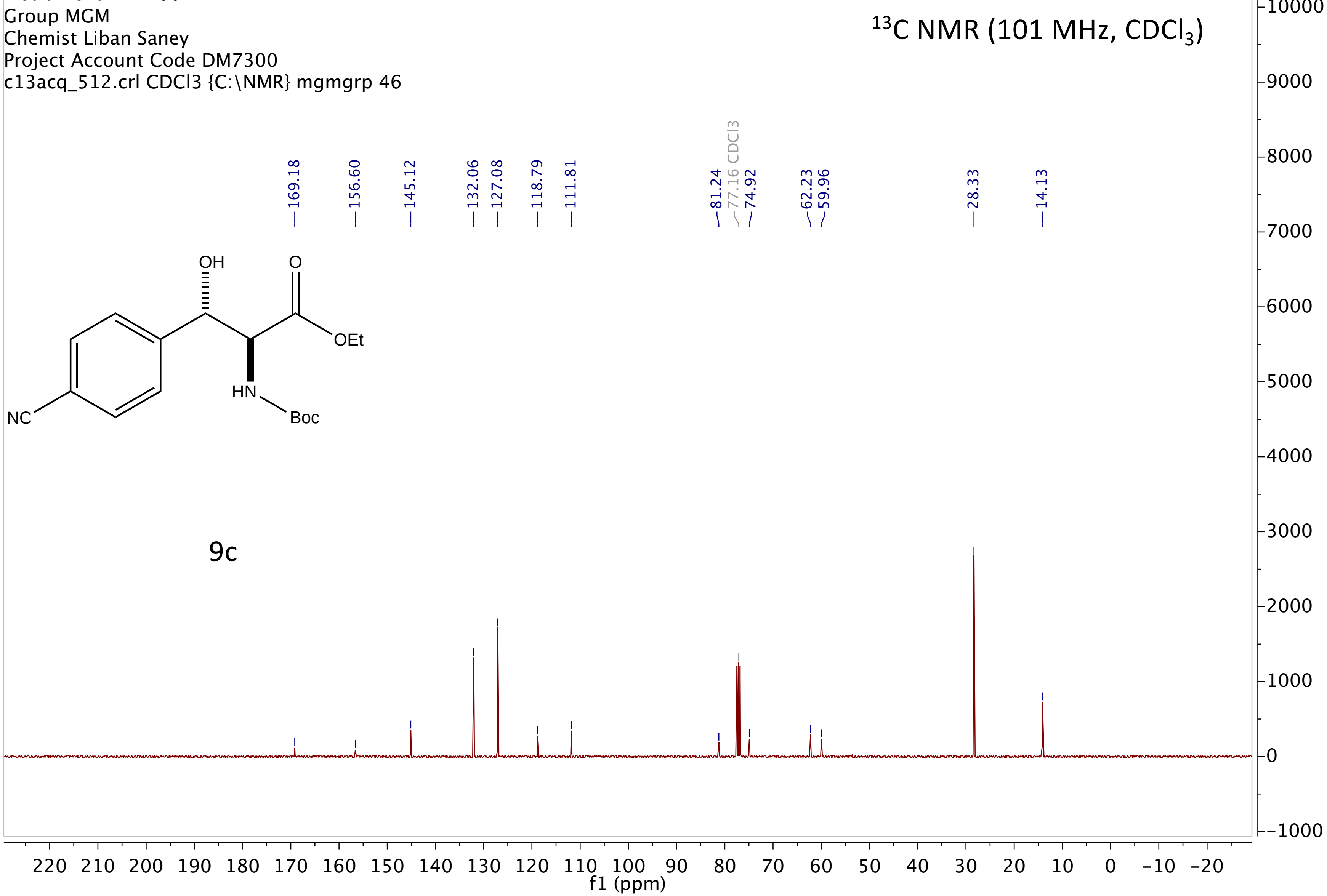

Dec10-2020-8-LS876(P) B9-D1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 8
$^{13}$C NMR (101 MHz, $CDCl_3$)
169.55
156.67
138.56
131.44
128.02
122.02
81.03
77.16 CDCl3
74.89
62.08
59.87
28.37
14.17
OH
O
OEt
HN
Boc
Br
9b
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

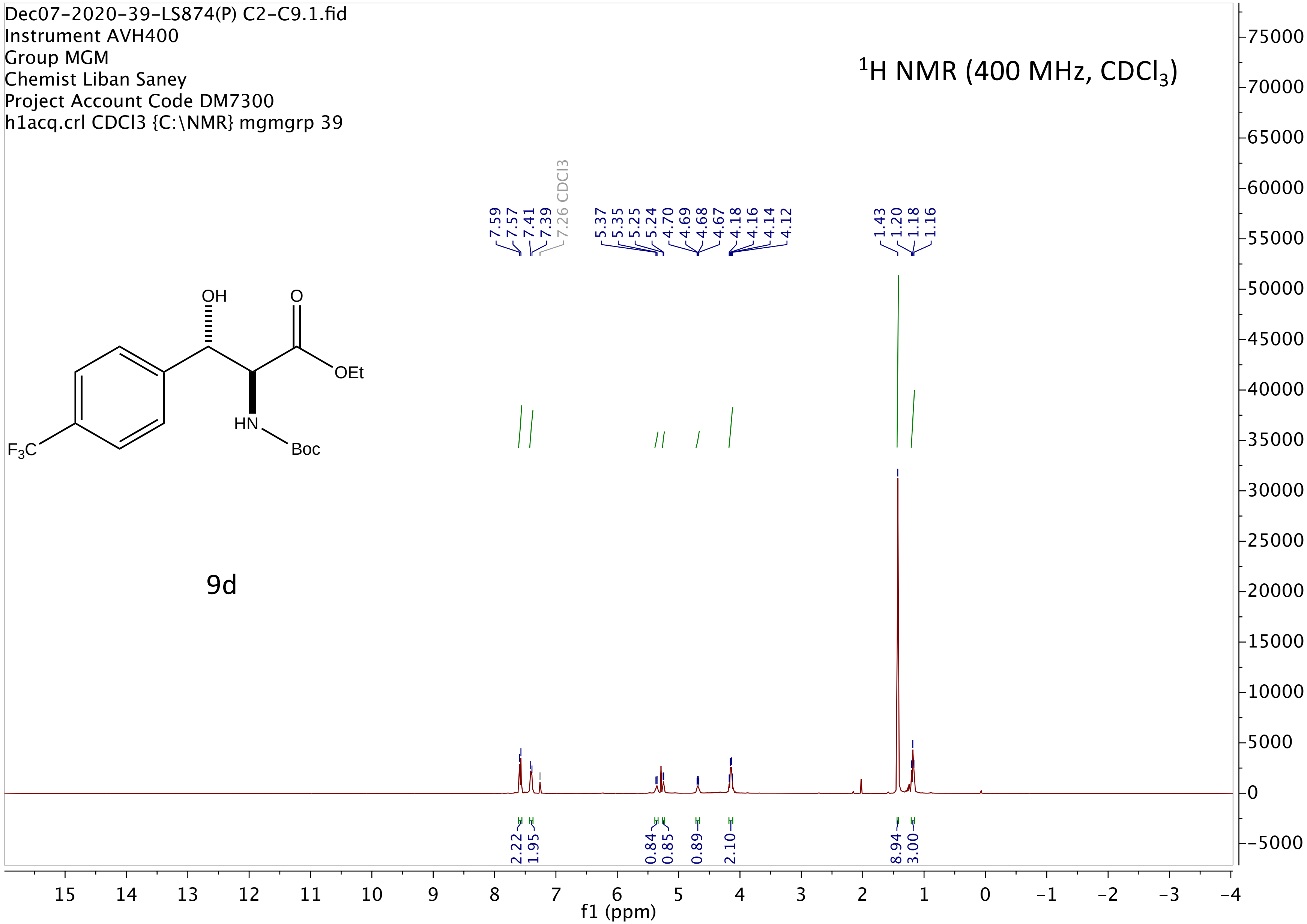


Dec08-2020-46-LS875(P) D2-D12.2.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 46
$^{1}$H NMR (400 MHz, $CDCl_3$)
7.63 7.61 7.42 7.40 7.26 CDCl3
5.38 5.36 5.25 5.24 4.68 4.67 4.66 4.65 4.40 4.19 4.17 4.15 4.13
1.43 1.21 1.20 1.18
2.22 2.17 1.00 0.95 0.98 0.79 2.30 10.51 3.26
OH
O
OEt
HN
Boc
NC
f1 (ppm)


9c

Dec08-2020-46-LS875(P) D2-D12.5.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 46

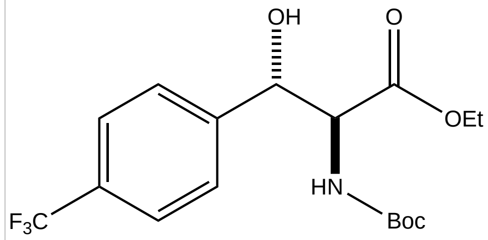



Dec07-2020-39-LS874(P) C2-C9.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 39
$^{1}$H NMR (400 MHz, $CDCl_3$)
7.59
7.57
7.41
7.39
7.26 CDCl3
5.37
5.35
5.25
5.24
4.70
4.69
4.68
4.67
4.18
4.16
4.14
4.12
1.43
1.20
1.18
1.16
OH
O
OEt
HN
Boc
$F_3C$
9d
2.22
1.95
0.84
0.85
0.89
2.10
8.94
3.00
f1 (ppm)

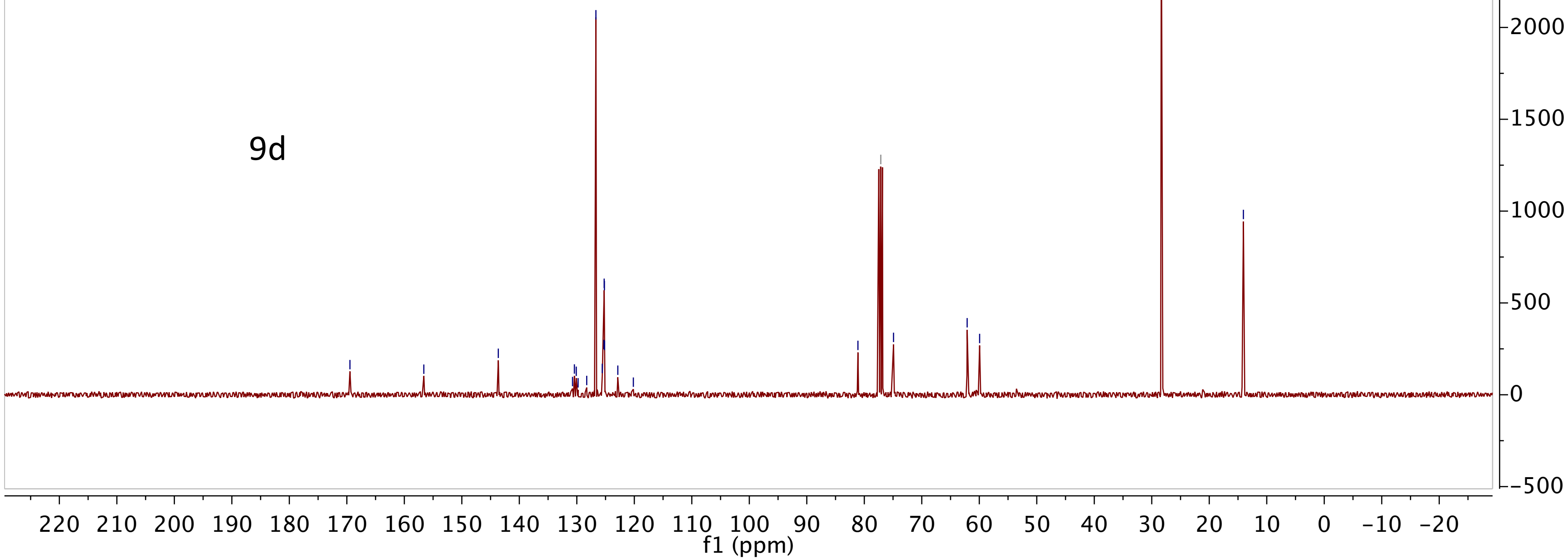
S-144

Dec07-2020-39-LS874(P) C2-C9.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 39

$^{13}$C NMR (101 MHz, $CDCl_3$)

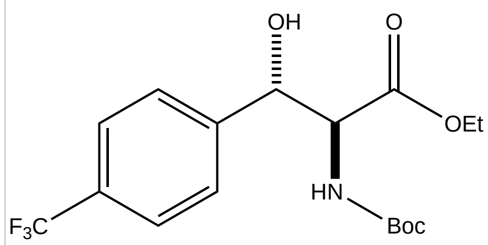


9d

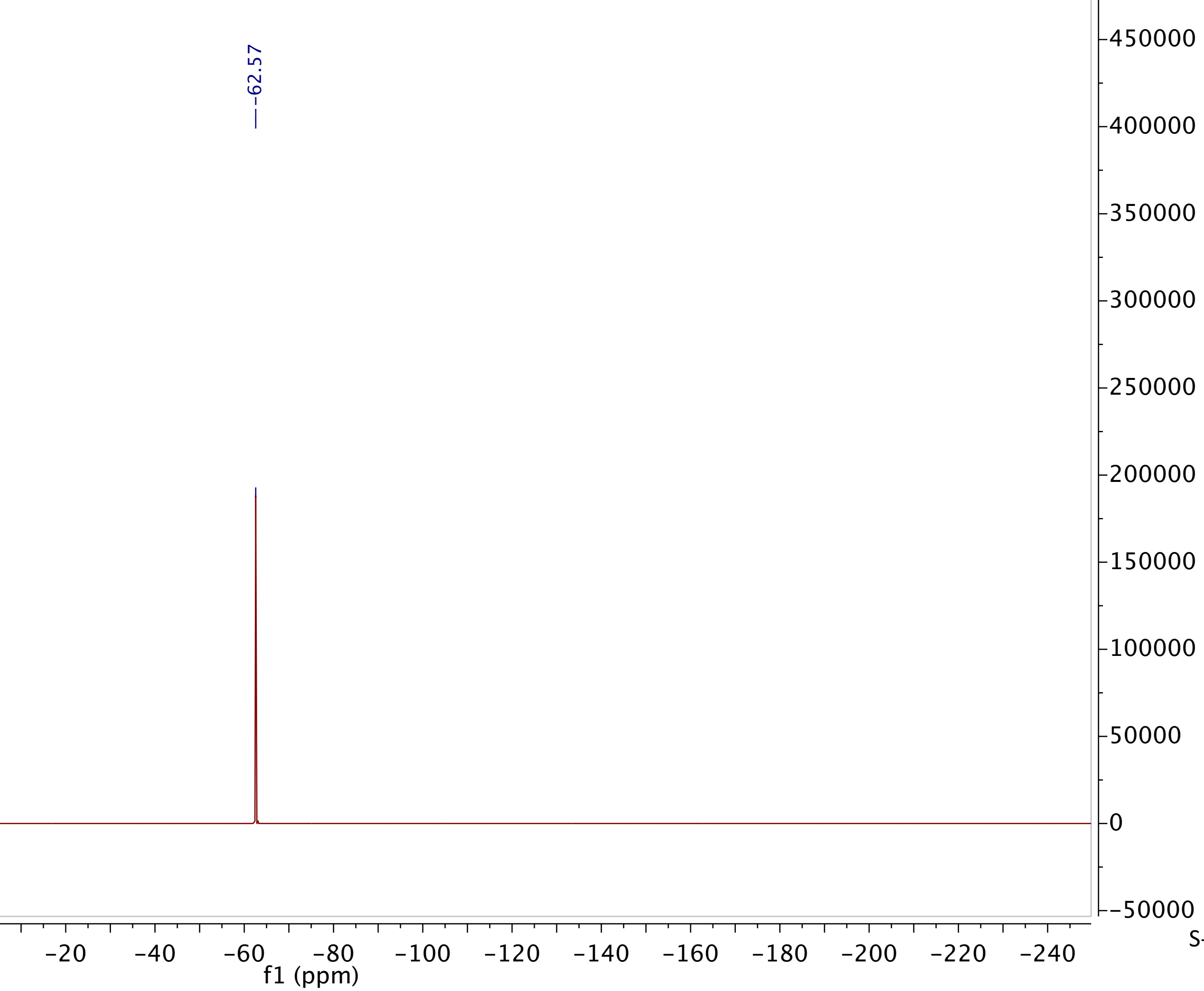


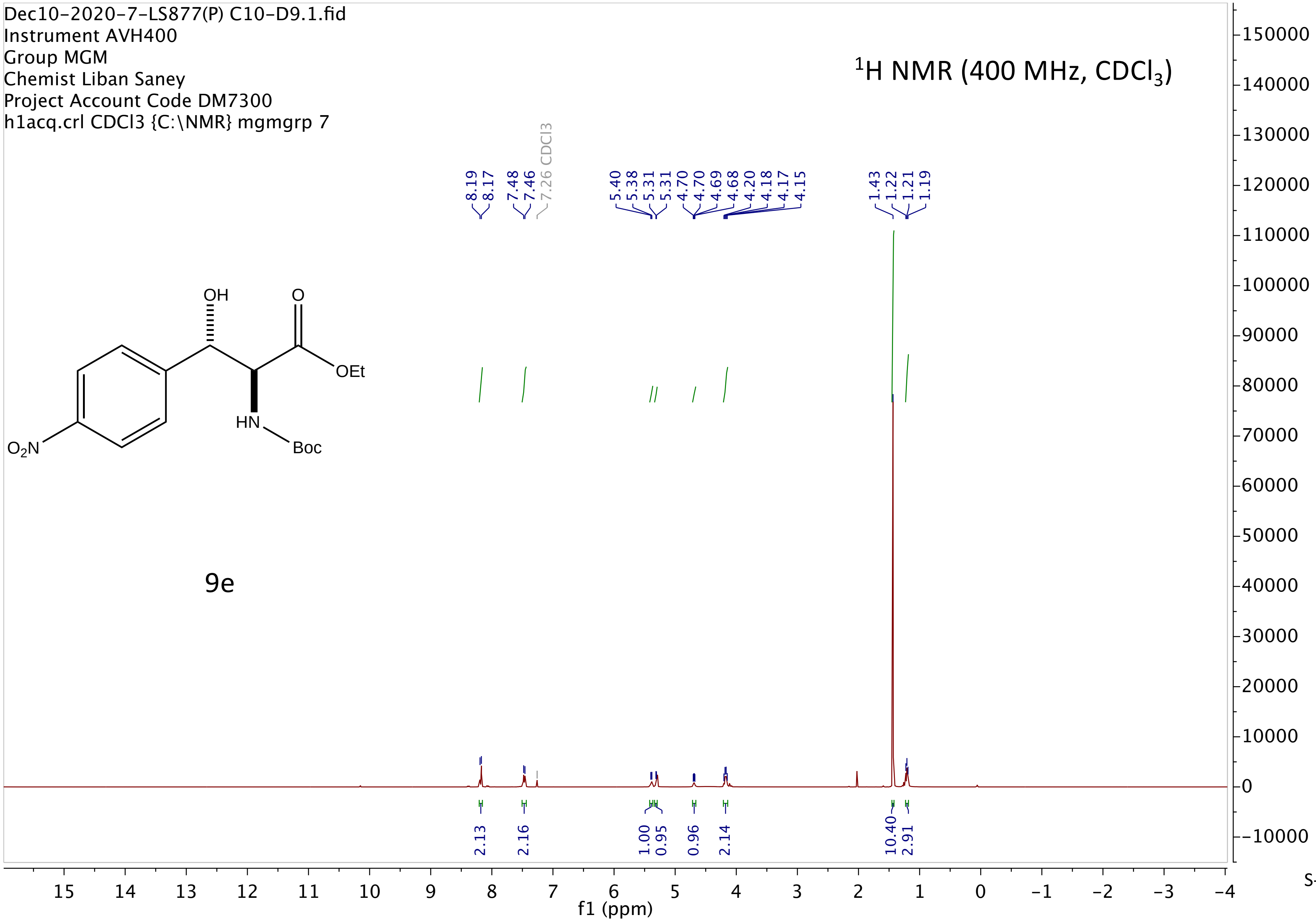
Dec07-2020-39-LS874(P) C2-C9.6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 39

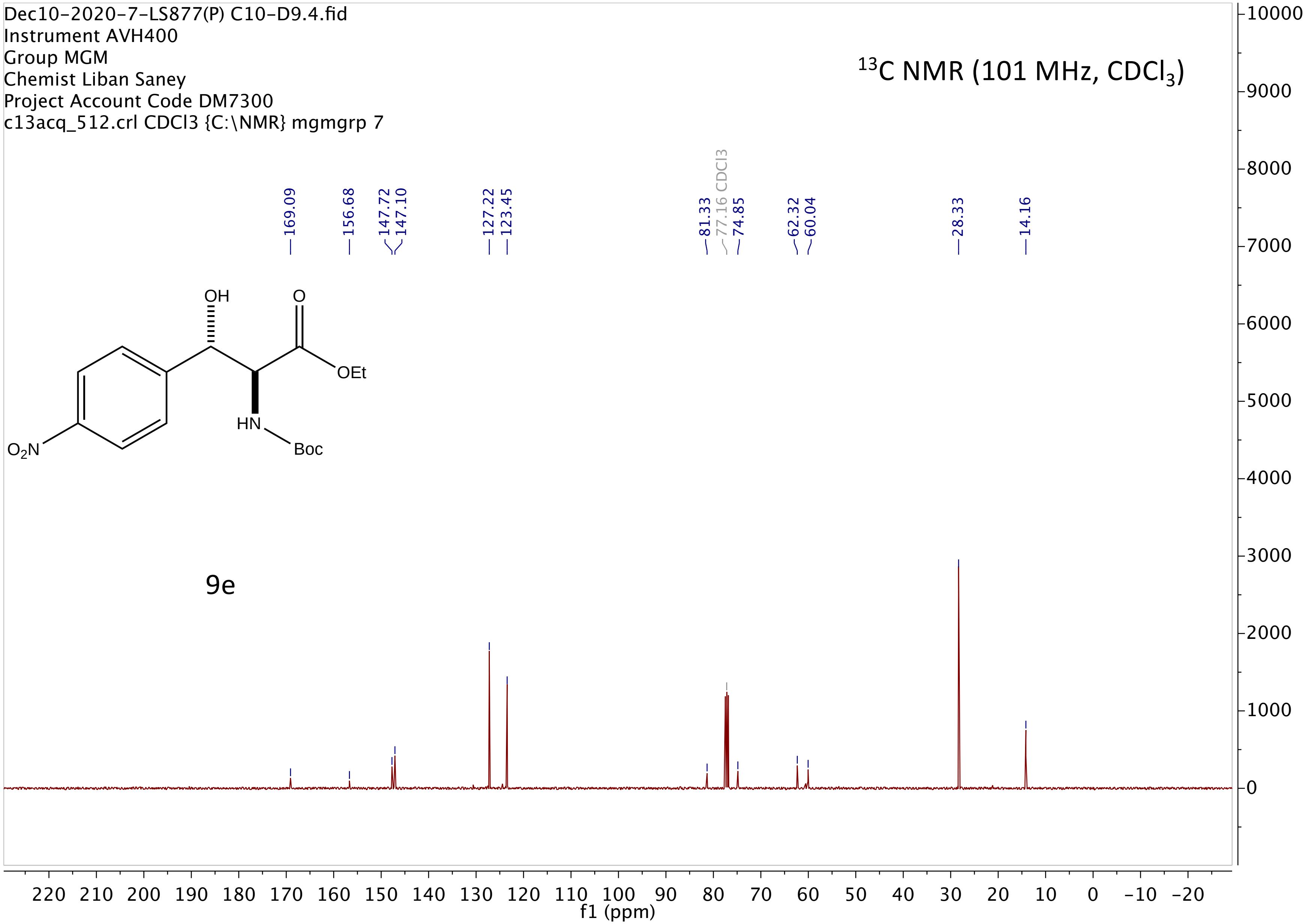
$^{19}$F NMR (377 MHz, $CDCl_3$)



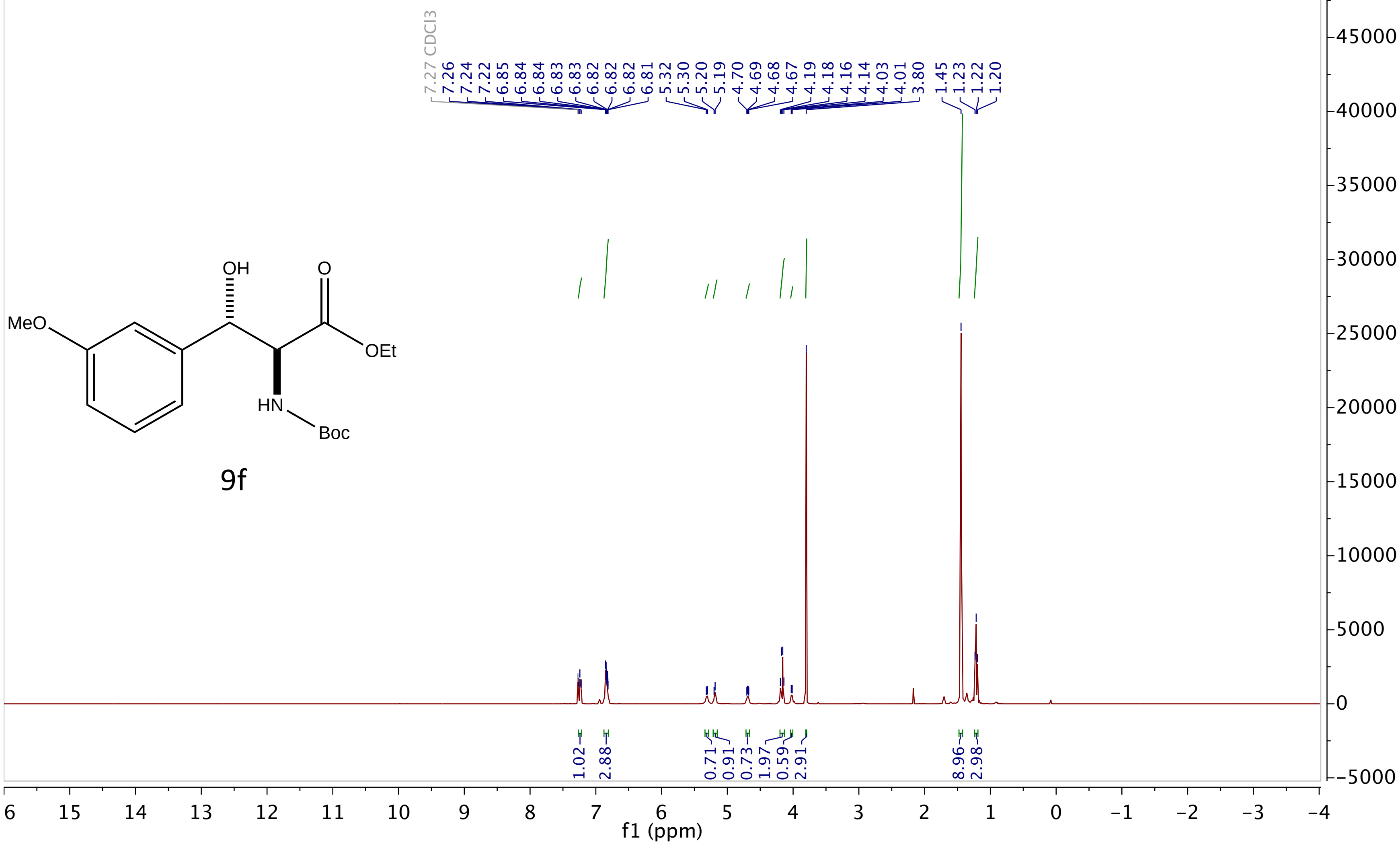
9d

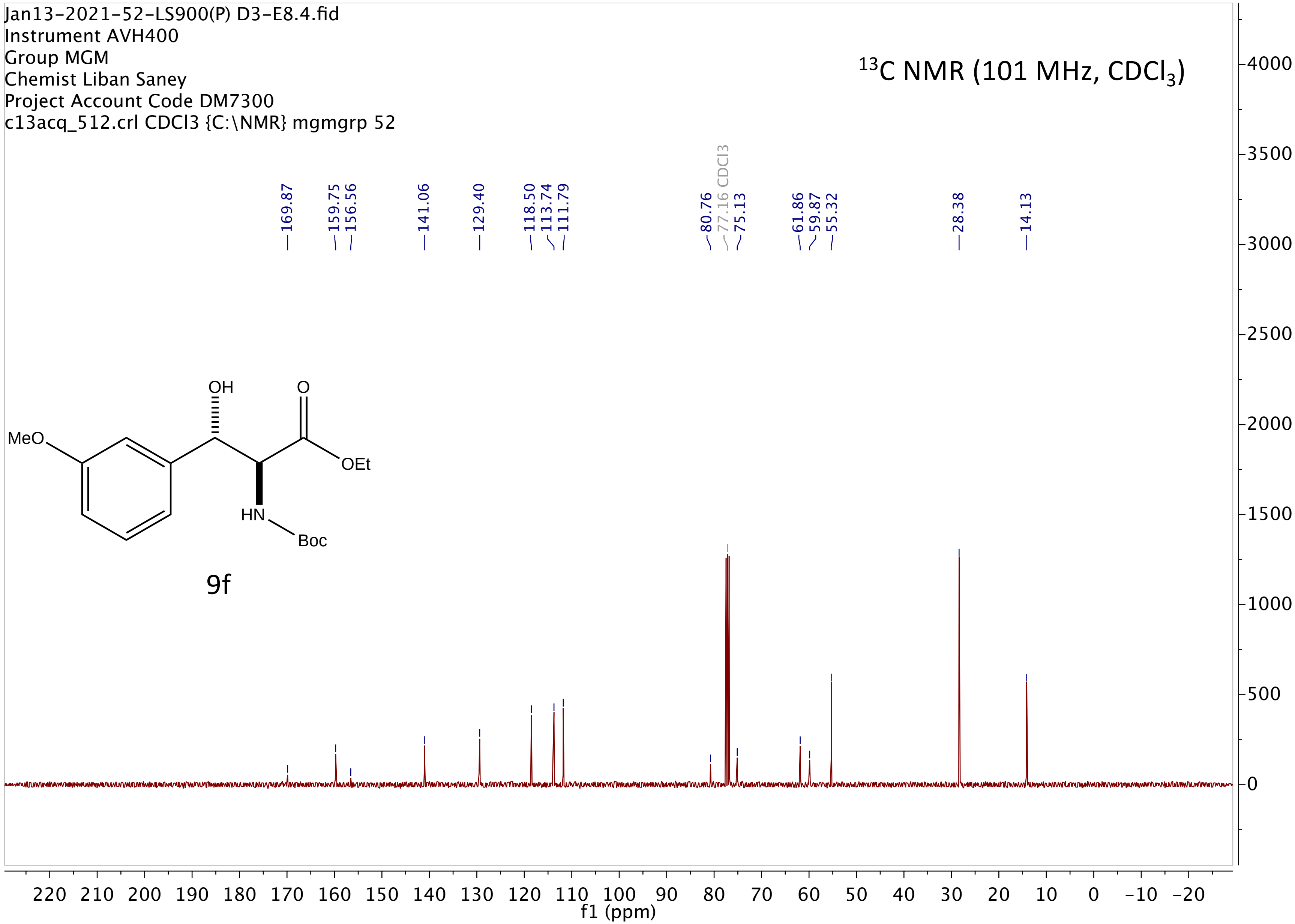


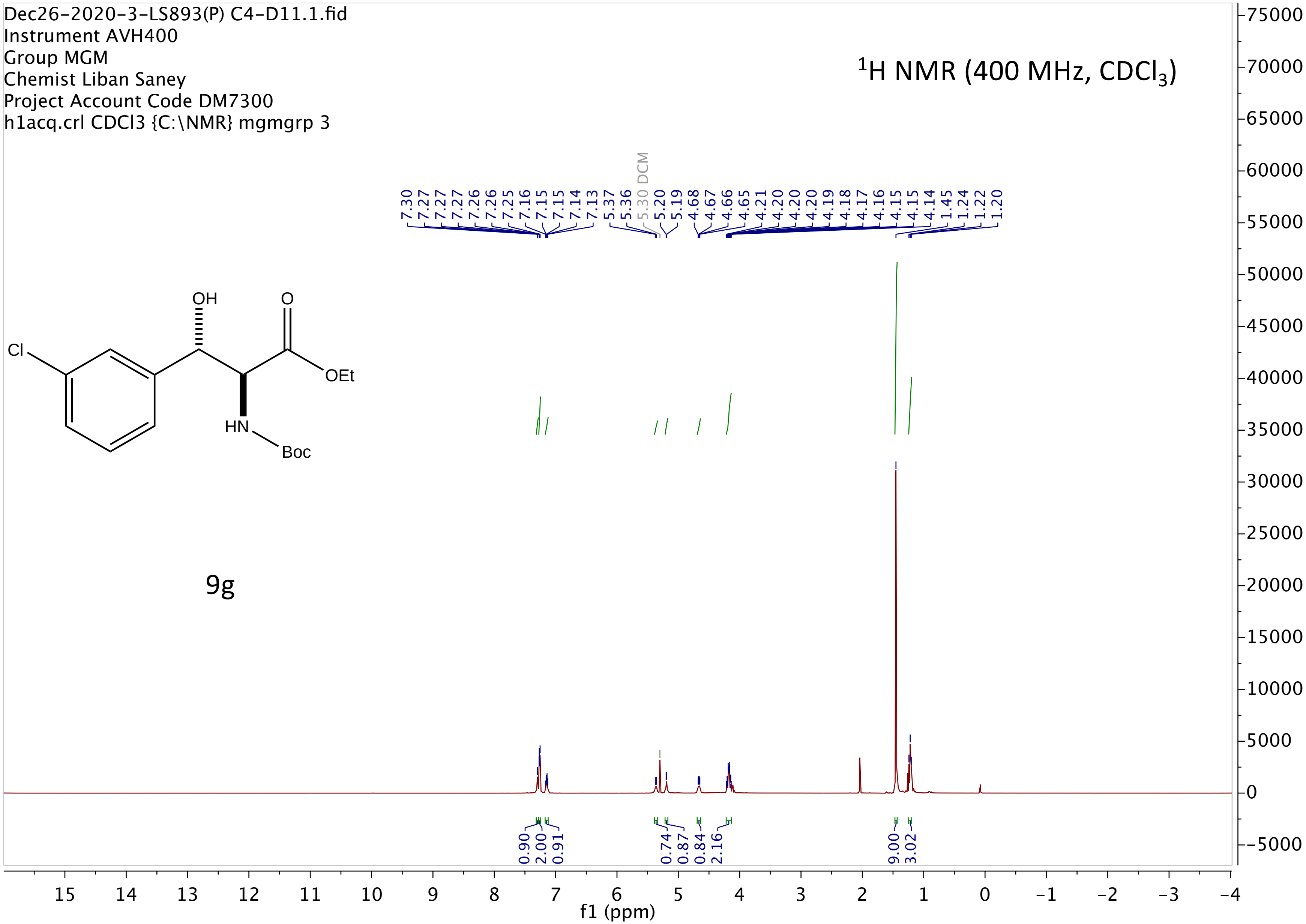

OH
O
OEt
HN
Boc
O2N
9e
Dec10-2020-7-LS877(P) C10-D9.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 7
1H NMR (400 MHz, CDCl3)
8.19
8.17
7.48
7.46
7.26 CDCl3
5.40
5.38
5.31
5.31
4.70
4.70
4.69
4.68
4.20
4.18
4.17
4.15
1.43
1.22
1.21
1.19
2.13
2.16
1.00
0.95
0.96
2.14
10.40
2.91
f1 (ppm)

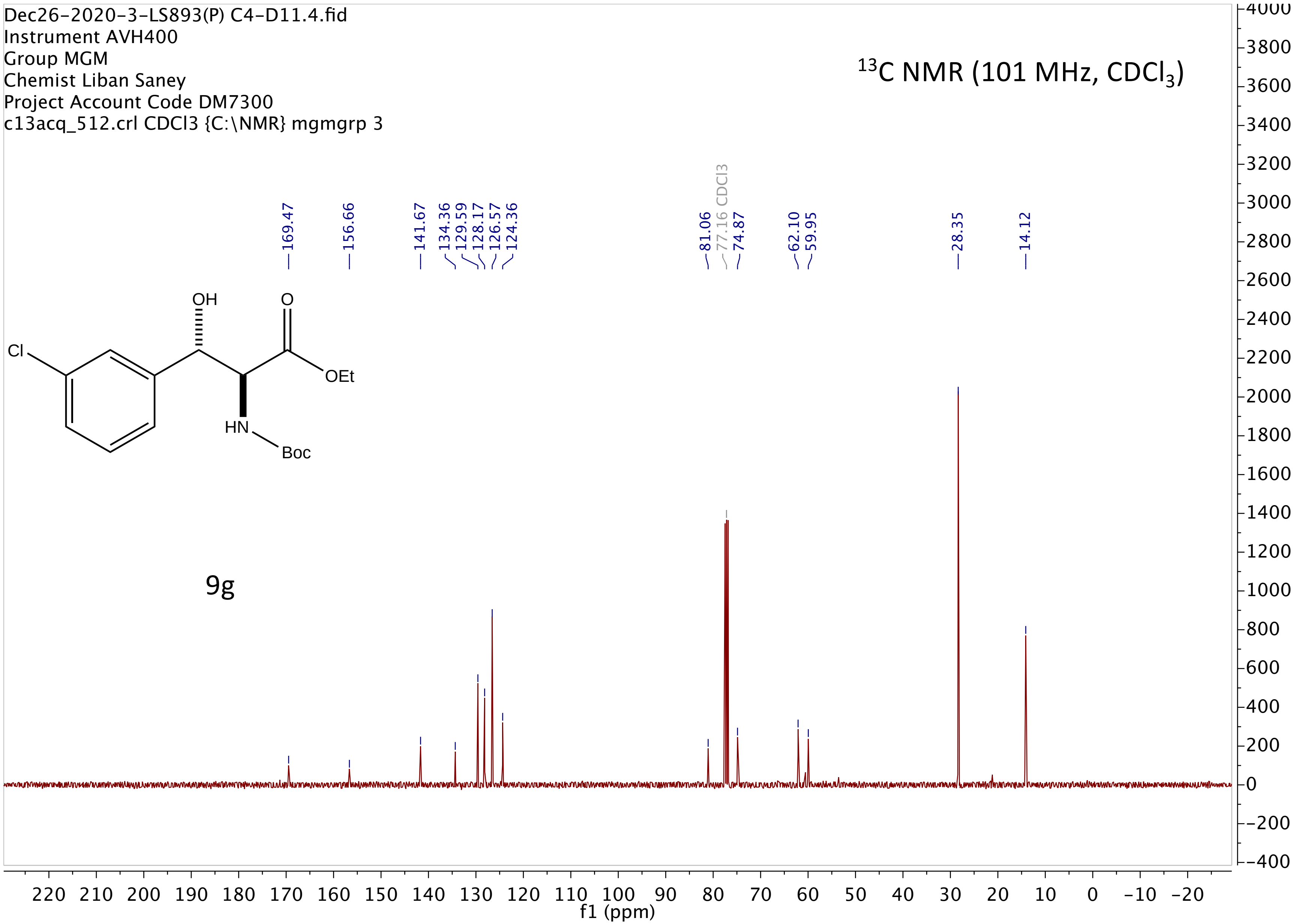

Dec10-2020-7-LS877(P) C10-D9.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 7
13C NMR (101 MHz, CDCl3)
169.09
156.68
147.72
147.10
127.22
123.45
81.33
77.16 CDCl3
74.85
62.32
60.04
28.33
14.16
OH
O
OEt
HN
Boc
O2N
9e
f1 (ppm)

Jan13-2021-52-LS900(P) D3-E8.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 52



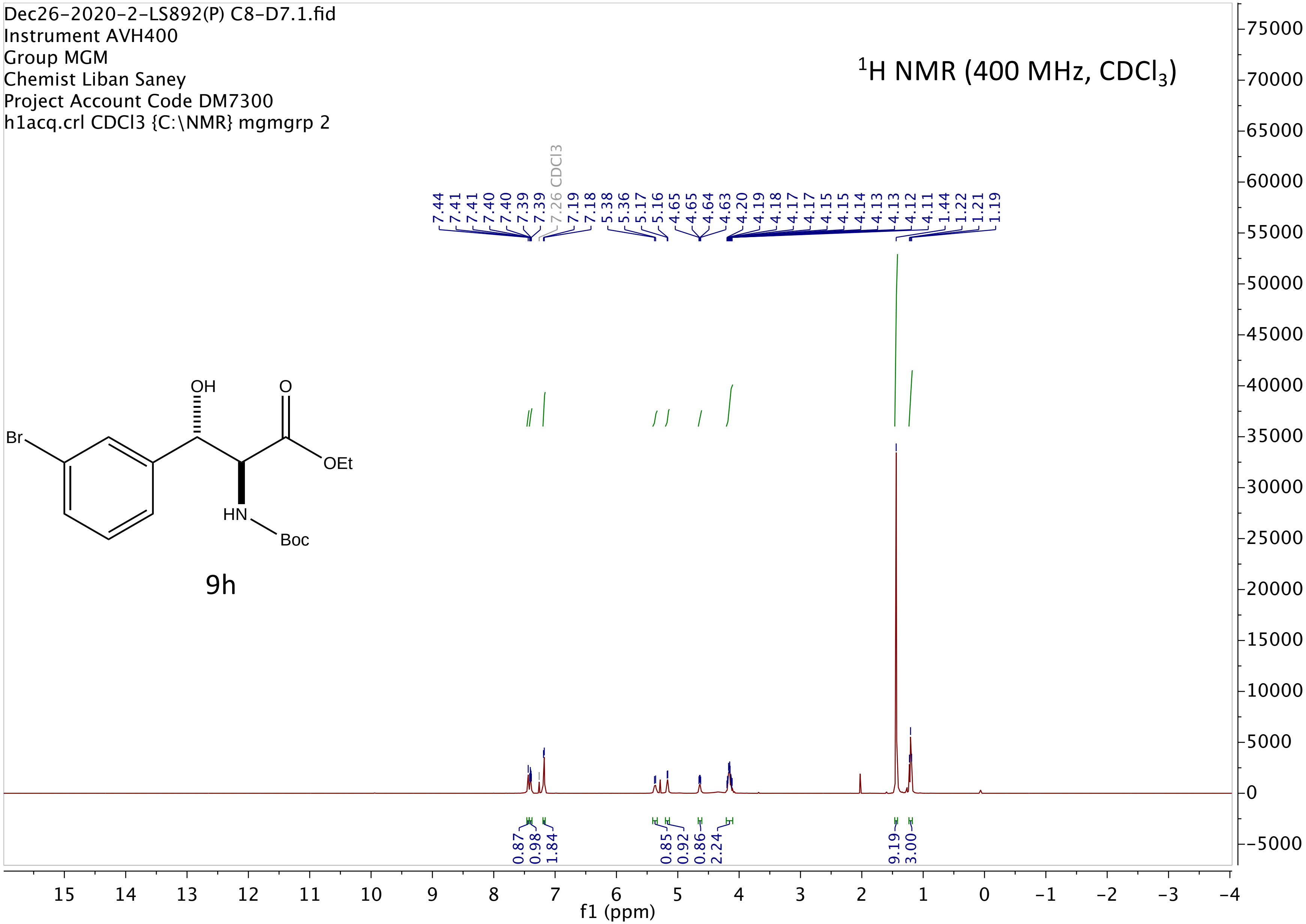

Jan13-2021-52-LS900(P) D3-E8.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 52
$^{13}$C NMR (101 MHz, $CDCl_3$)
169.87
159.75
156.56
141.06
129.40
118.50
113.74
111.79
80.76
77.16 CDCl3
75.13
61.86
59.87
55.32
28.38
14.13
OH
O
MeO
OEt
HN
Boc
9f
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Dec26-2020-3-LS893(P) C4-D11.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 3
$^1$H NMR (400 MHz, $CDCl_3$)
7.30 7.27 7.27 7.27 7.26 7.26 7.25 7.16 7.15 7.15 7.14 7.13 5.37 5.36 5.30 DCM 5.20 5.19 4.68 4.67 4.66 4.65 4.21 4.20 4.20 4.20 4.19 4.18 4.17 4.16 4.15 4.15 4.14 1.45 1.24 1.22 1.20
OH
O
Cl
OEt
HN
Boc
9g
0.90 2.00 0.91 0.74 0.87 0.84 2.16 9.00 3.02
f1 (ppm)


Dec26-2020-3-LS893(P) C4-D11.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 3
13C NMR (101 MHz, CDCl3)
169.47
156.66
141.67
134.36
129.59
128.17
126.57
124.36
81.06
77.16 CDCl3
74.87
62.10
59.95
28.35
14.12
OH
O
Cl
OEt
HN
Boc
9g
f1 (ppm)

Dec26-2020-2-LS892(P) C8-D7.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 2

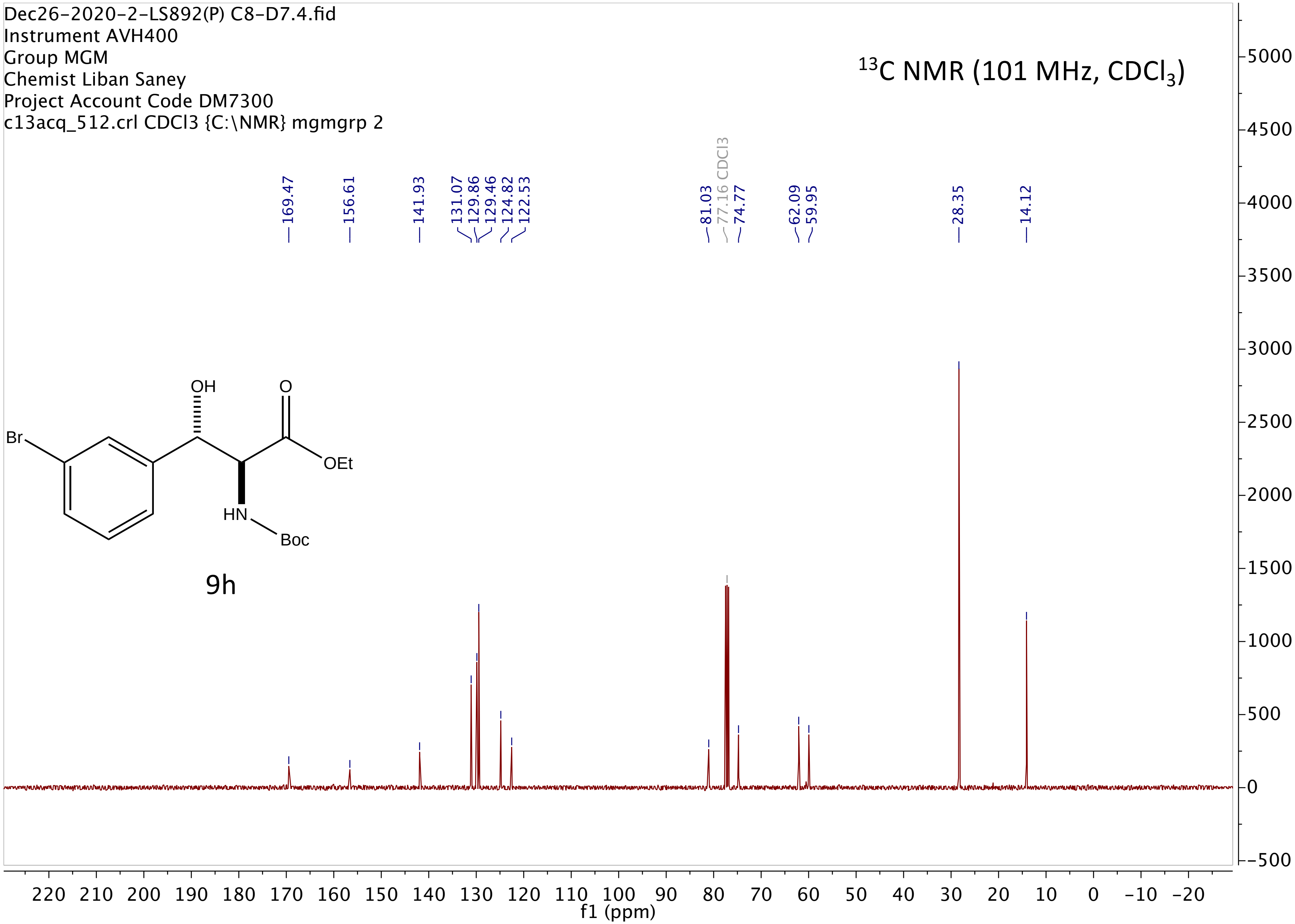
$^{1}$H NMR (400 MHz, $CDCl_3$)



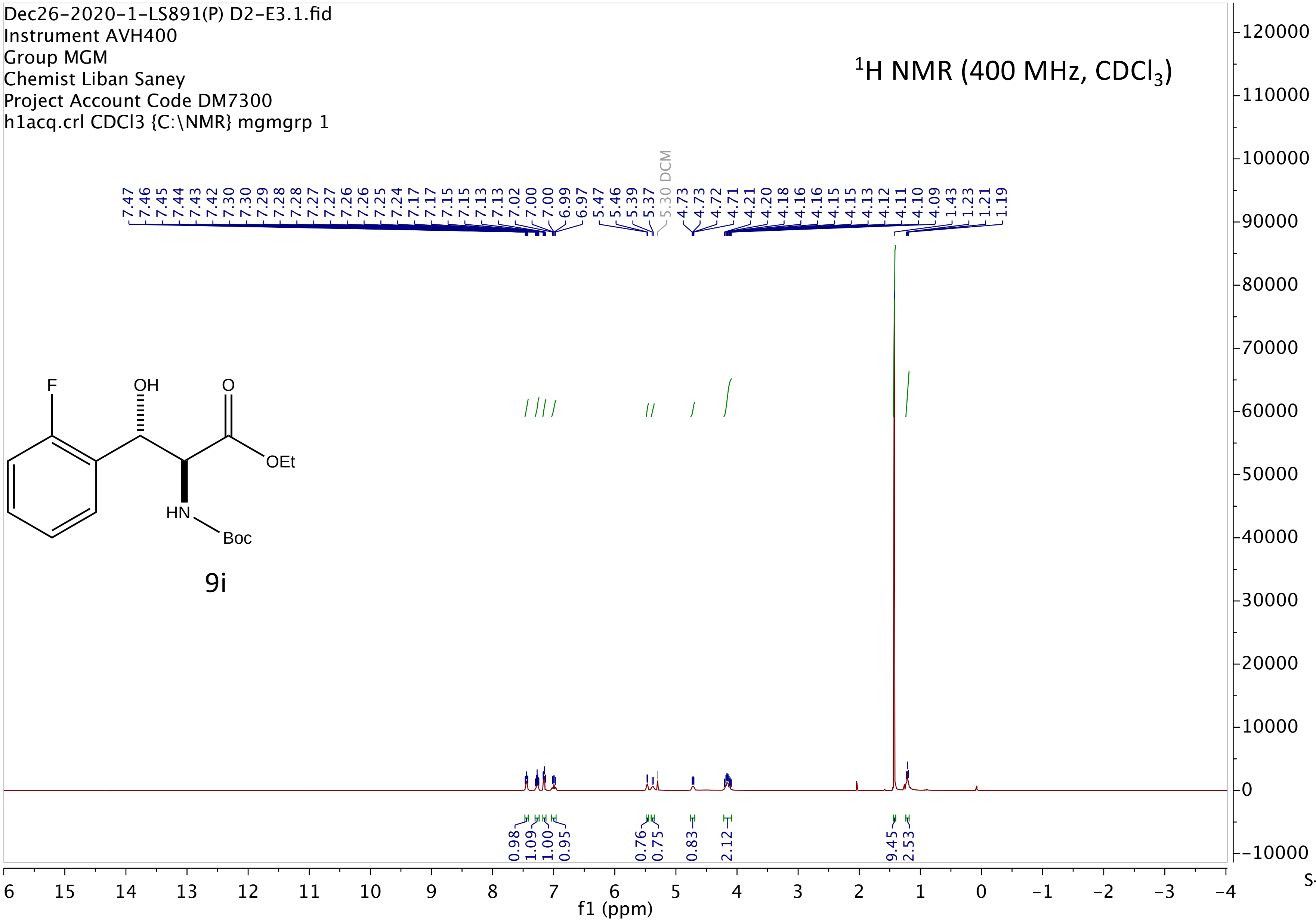

9h

Dec26-2020-2-LS892(P) C8-D7.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 2

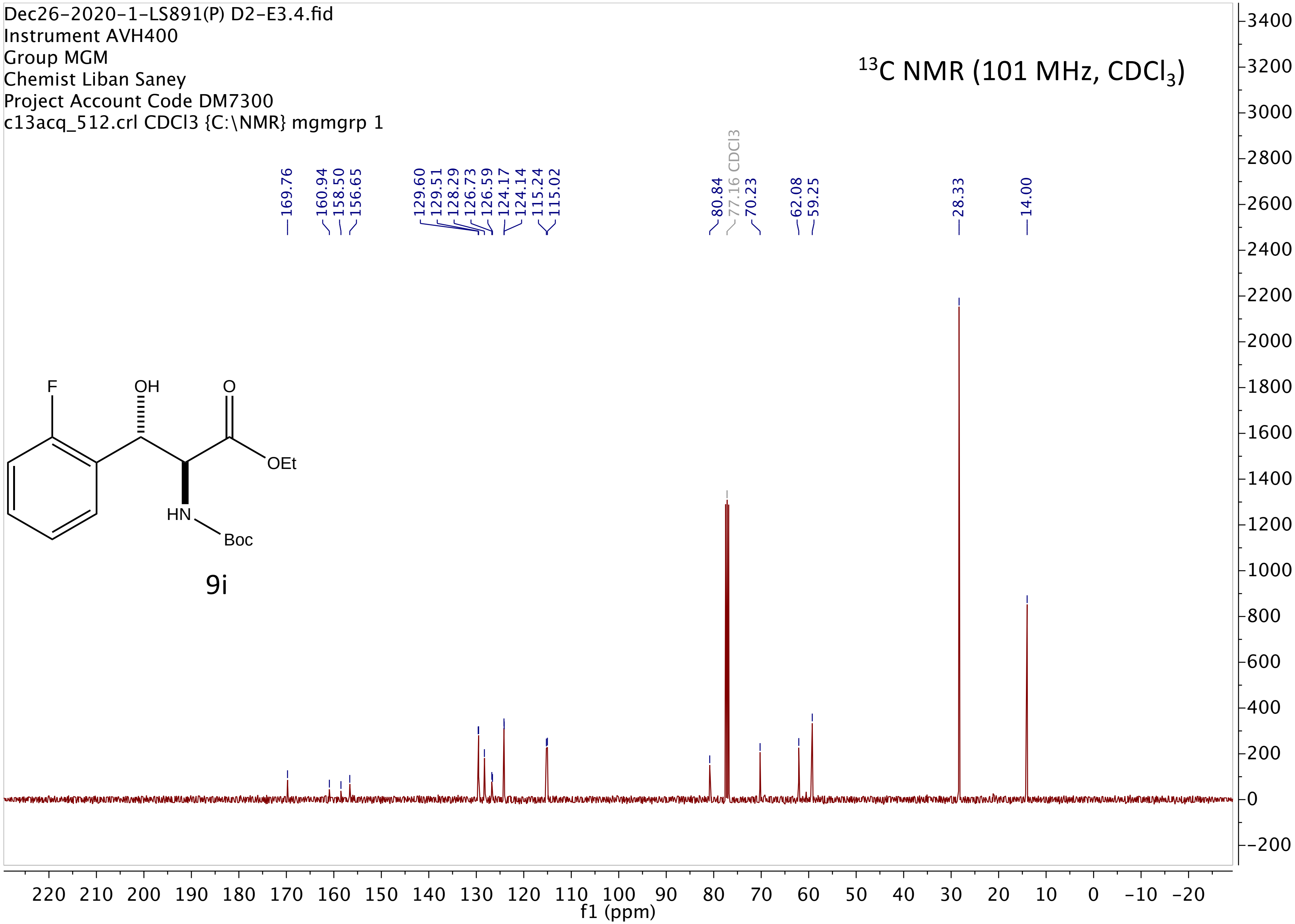
$^{13}C$ NMR (101 MHz, $CDCl_3$)




9h

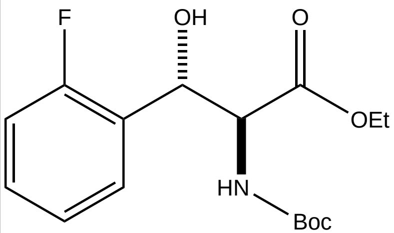

Dec26-2020-1-LS891(P) D2-E3.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1
1H NMR (400 MHz, CDCl3)
7.47 7.46 7.45 7.44 7.43 7.42 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.17 7.17 7.15 7.15 7.13 7.13 7.02 7.00 7.00 6.99 6.97 5.47 5.46 5.39 5.37 5.30 DCM 4.73 4.73 4.72 4.71 4.21 4.20 4.18 4.16 4.16 4.15 4.15 4.13 4.12 4.11 4.10 4.09 1.43 1.23 1.21 1.19
F
OH
O
OEt
HN
Boc
9i
0.98 1.09 1.00 0.95 0.76 0.75 0.83 2.12 9.45 2.53
f1 (ppm)

Dec26-2020-1-LS891(P) D2-E3.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1

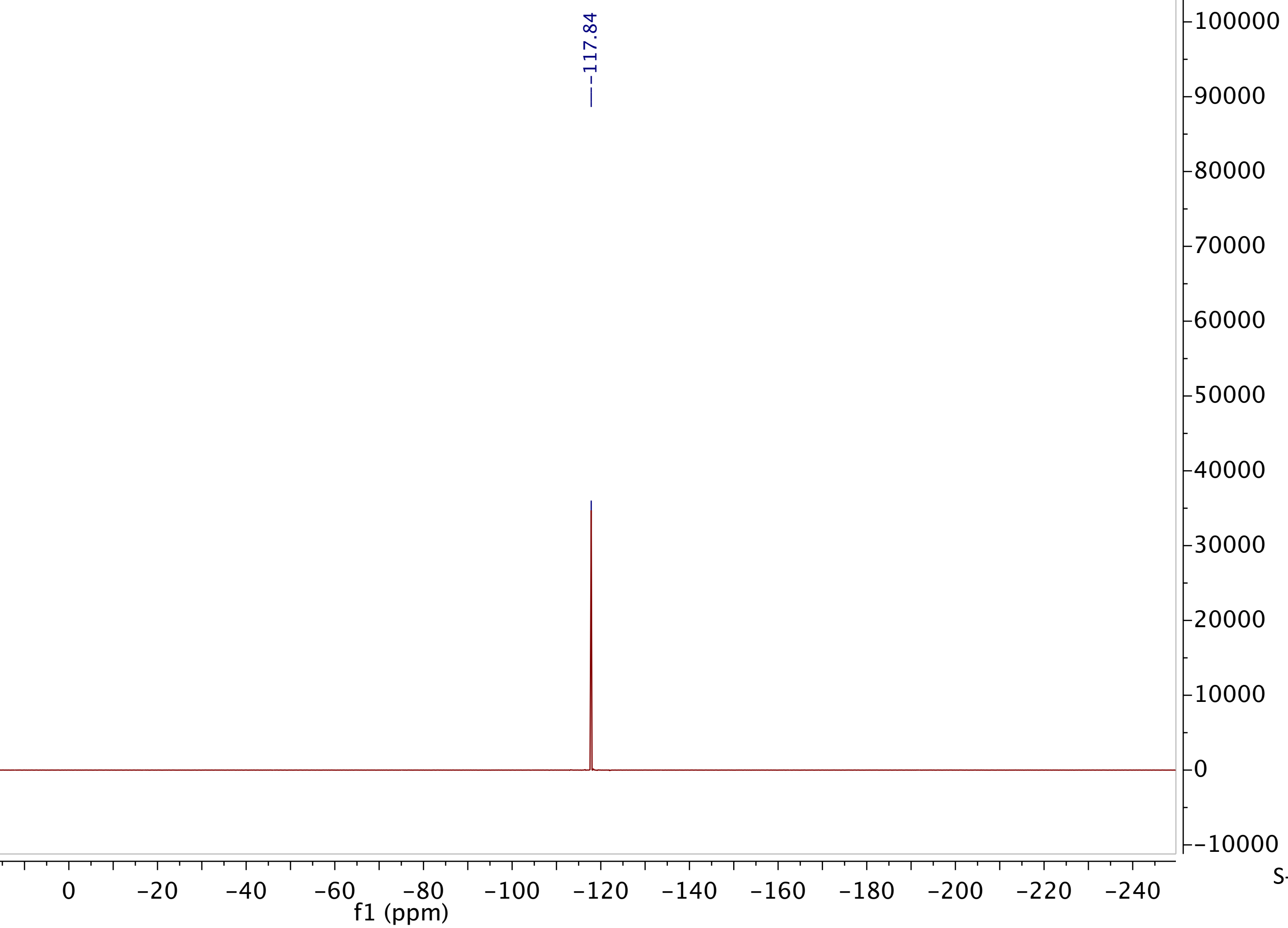


Dec26-2020-1-LS891(P) D2-E3.7.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 1

$^{19}F$ NMR (377 MHz, $CDCl_3$)

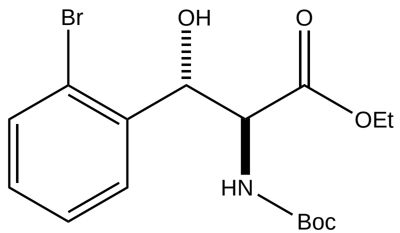



9i

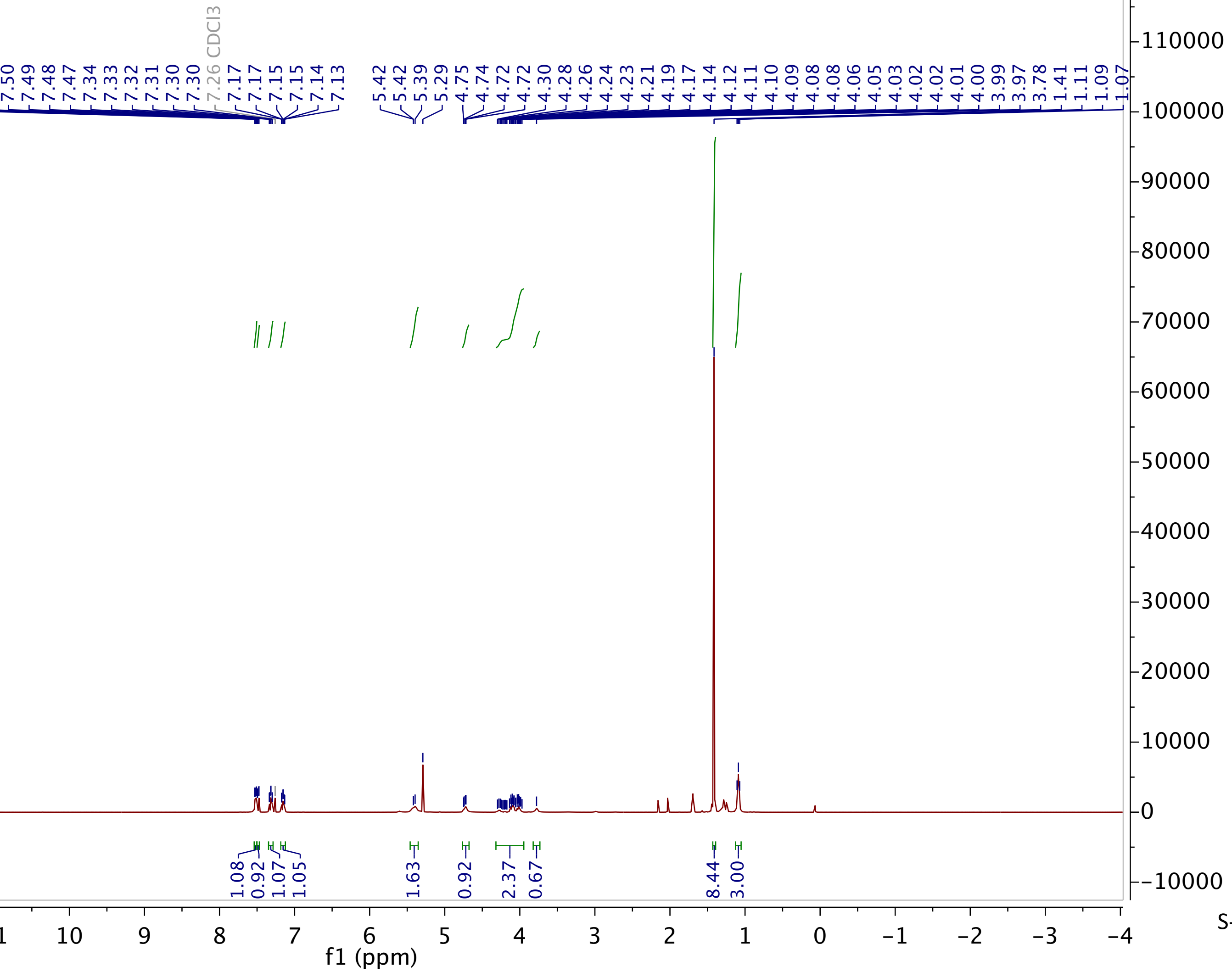


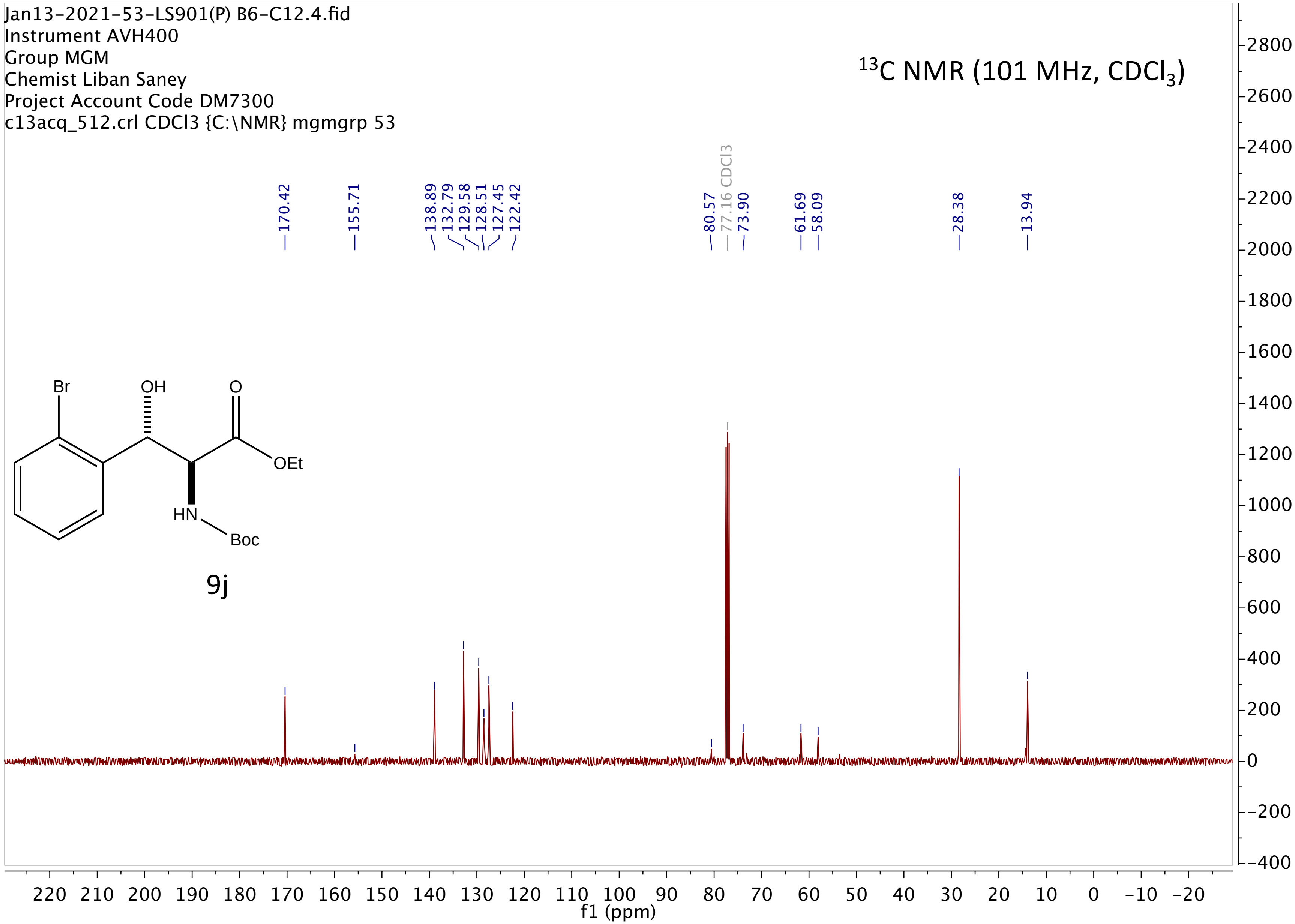
Jan13-2021-53-LS901(P) B6-C12.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 53

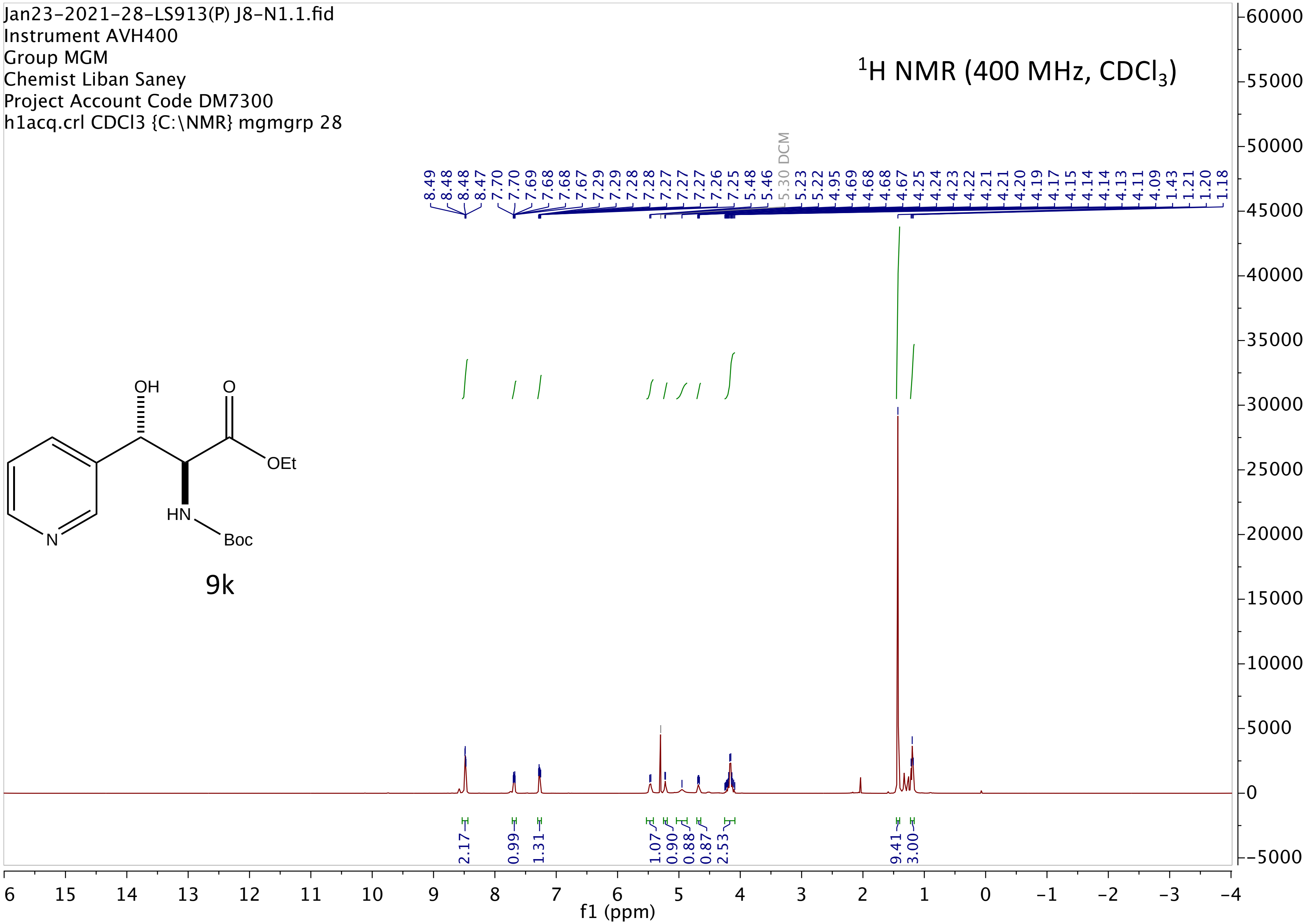
$^1$H NMR (400 MHz, $CDCl_3$)

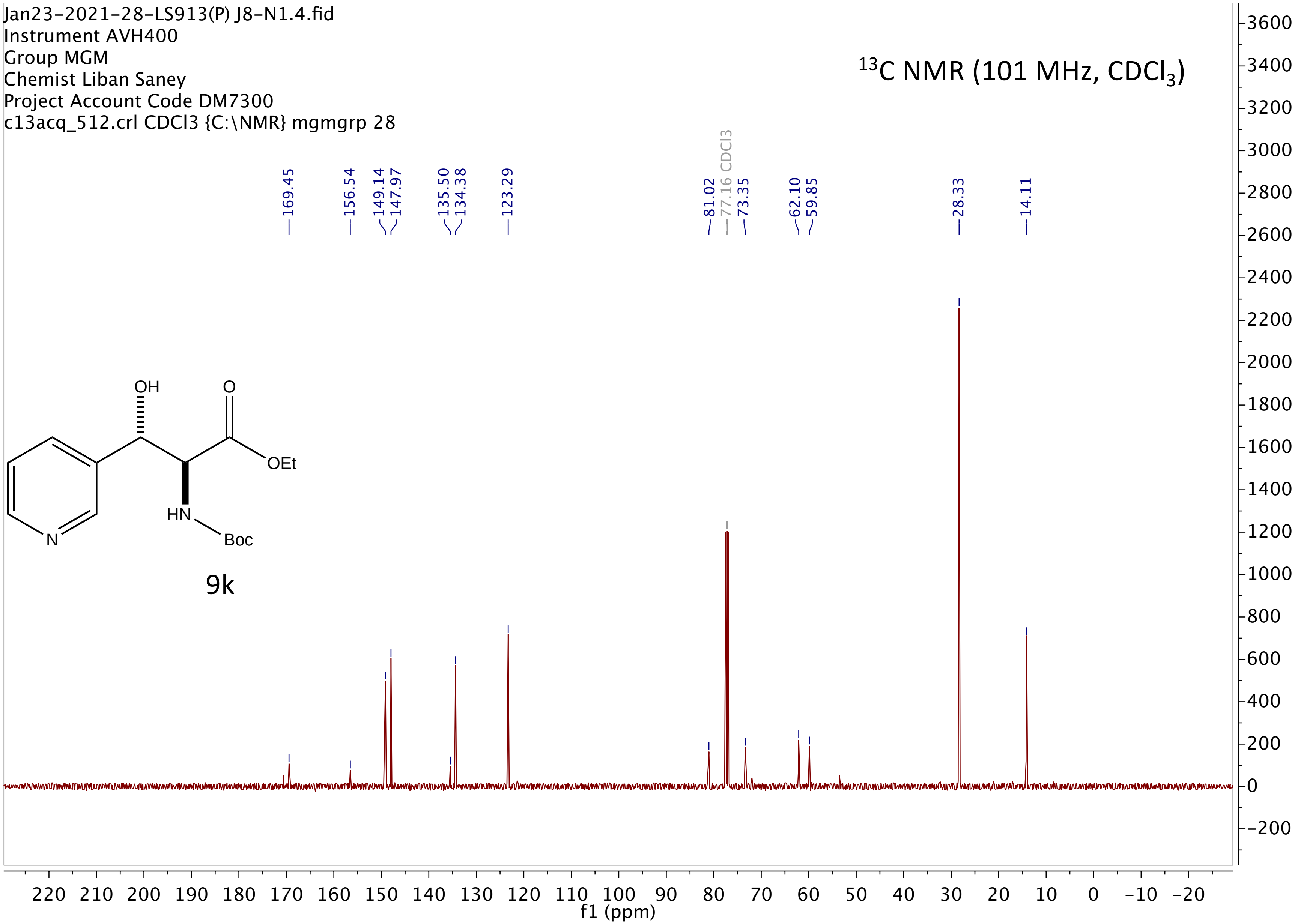



9j




Jan13-2021-53-LS901(P) B6-C12.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 53
13C NMR (101 MHz, CDCl3)
170.42
155.71
138.89
132.79
129.58
128.51
127.45
122.42
80.57
77.16 CDCl3
73.90
61.69
58.09
28.38
13.94
Br
OH
O
OEt
HN
Boc
9j
f1 (ppm)

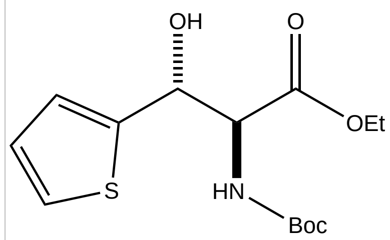

Jan23-2021-28-LS913(P) J8-N1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 28
1H NMR (400 MHz, CDCl3)
5.30 DCM
OH
O
OEt
HN
Boc
N
9k
f1 (ppm)



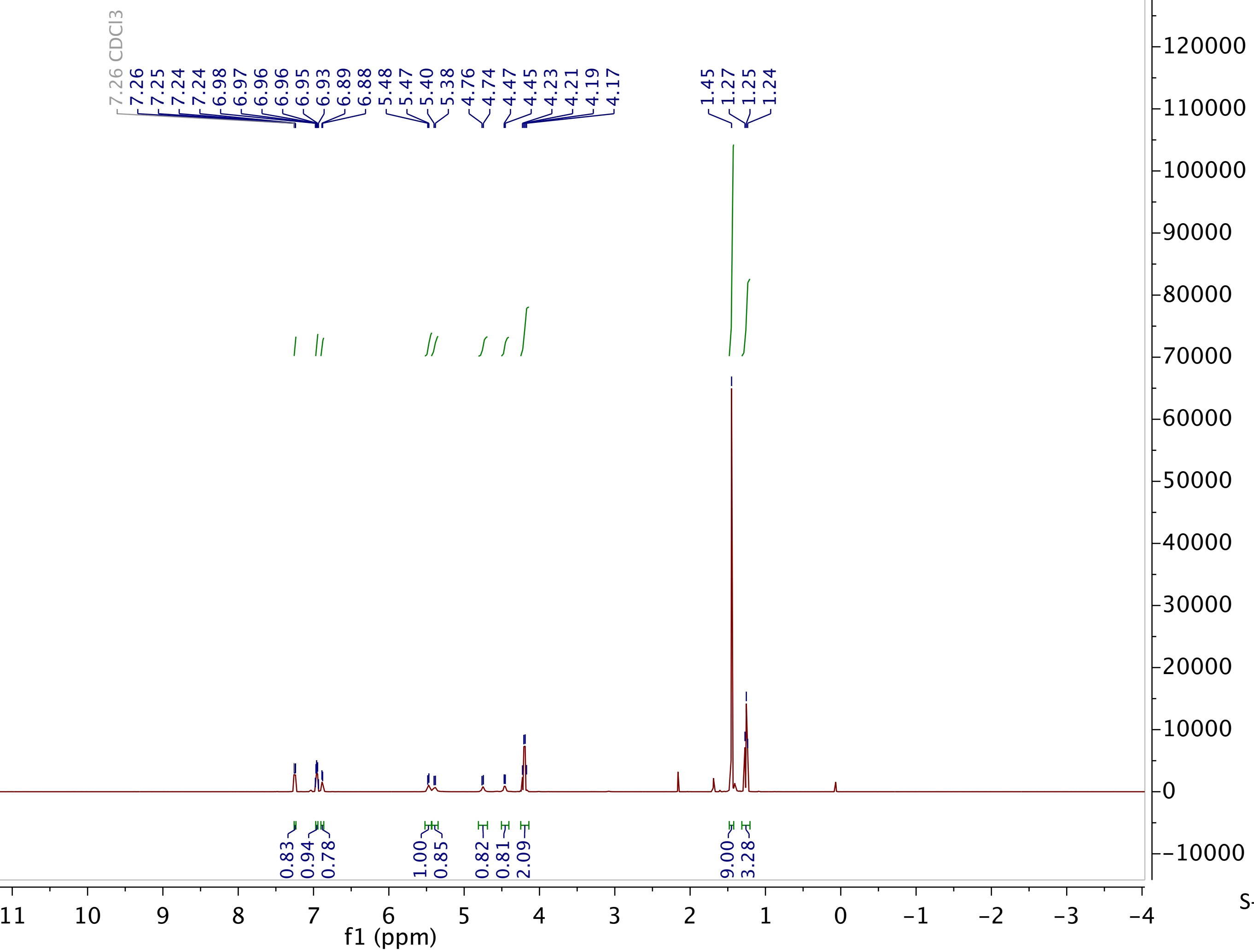
Jan23-2021-28-LS913(P) J8-N1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 28
13C NMR (101 MHz, CDCl3)
169.45
156.54
149.14
147.97
135.50
134.38
123.29
81.02
77.16 CDCl3
73.35
62.10
59.85
28.33
14.11
OH
O
OEt
HN
Boc
N
9k
f1 (ppm)

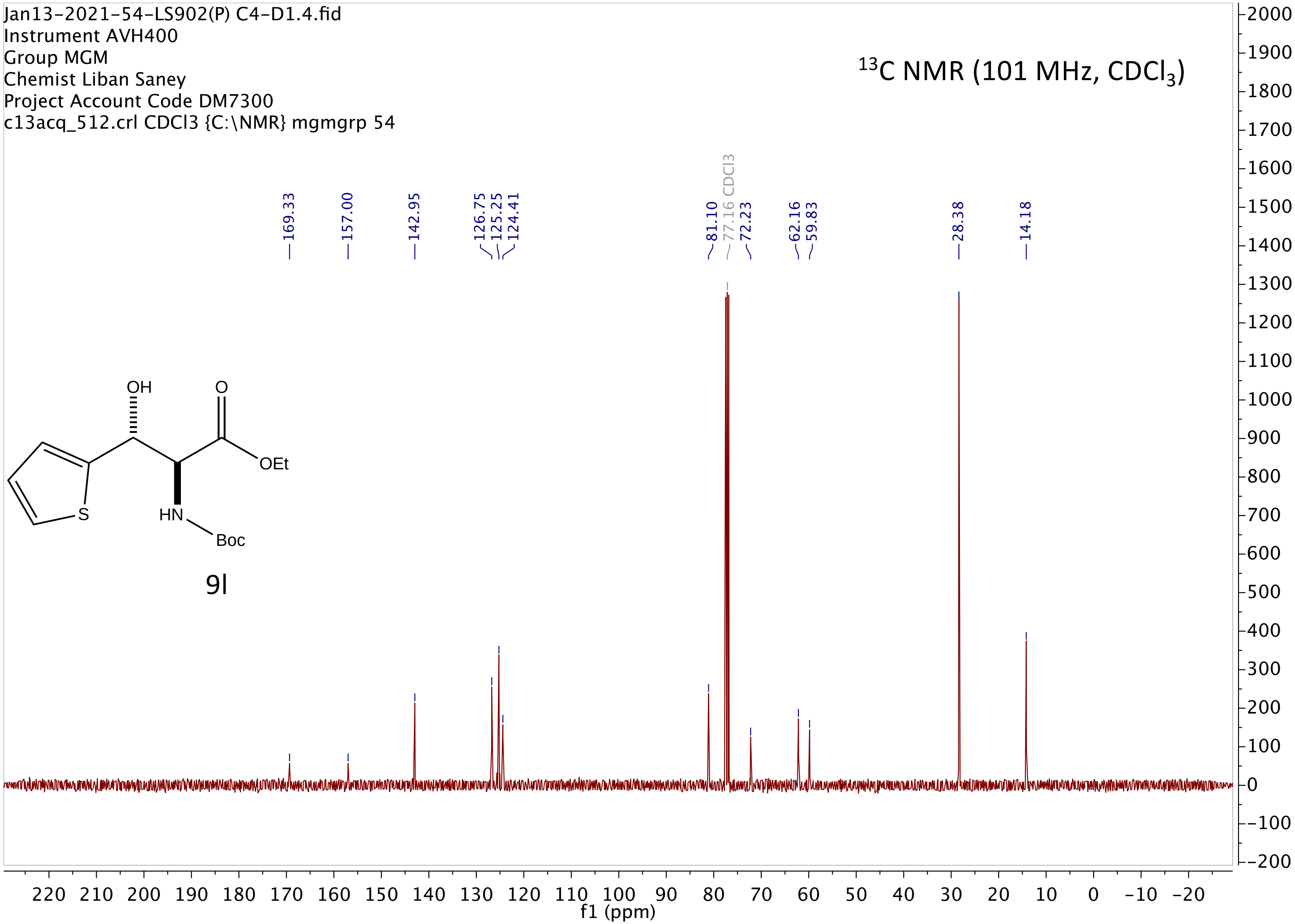
Jan13-2021-54-LS902(P) C4-D1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 54

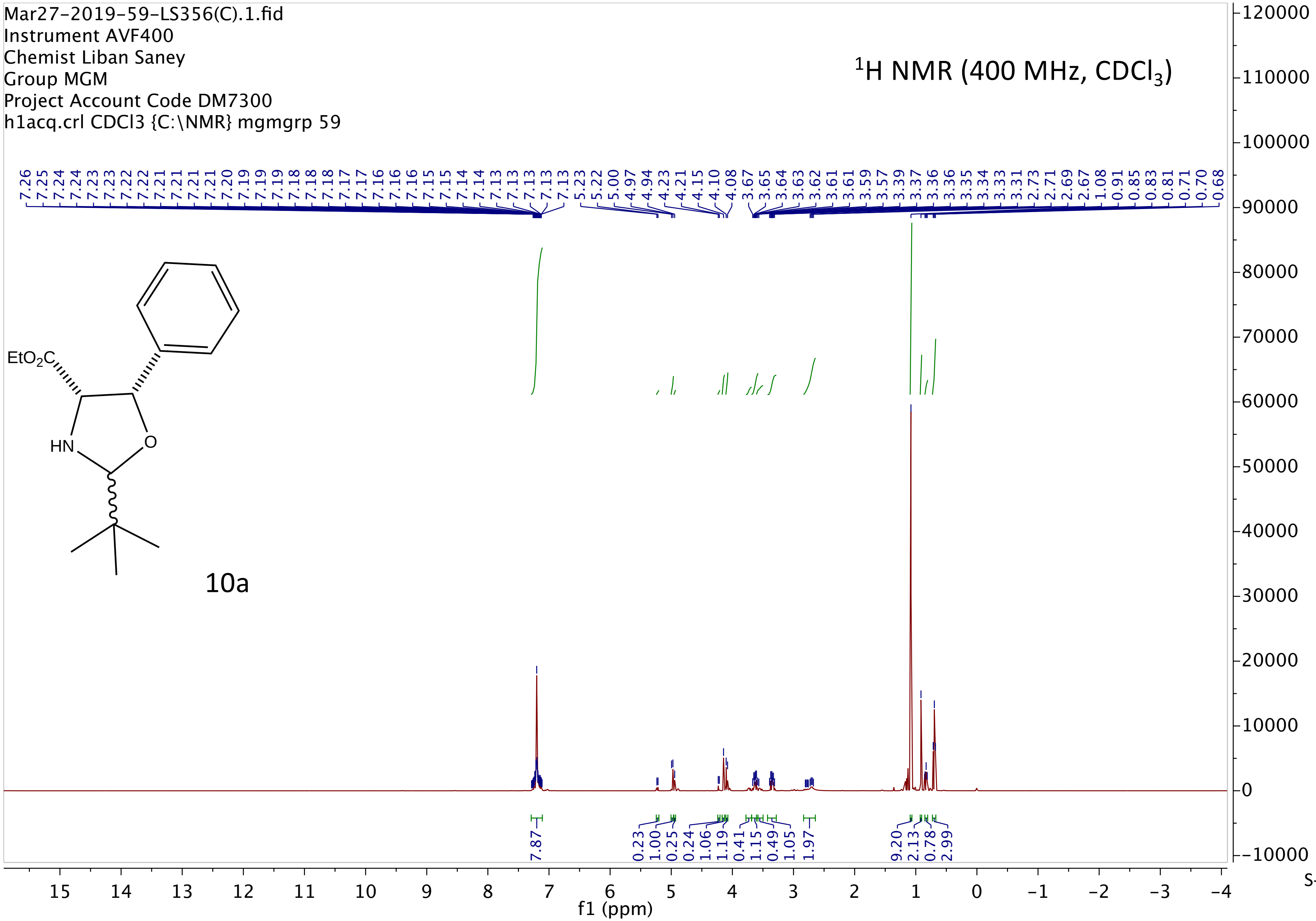
$^{1}$H NMR (400 MHz, $CDCl_3$)

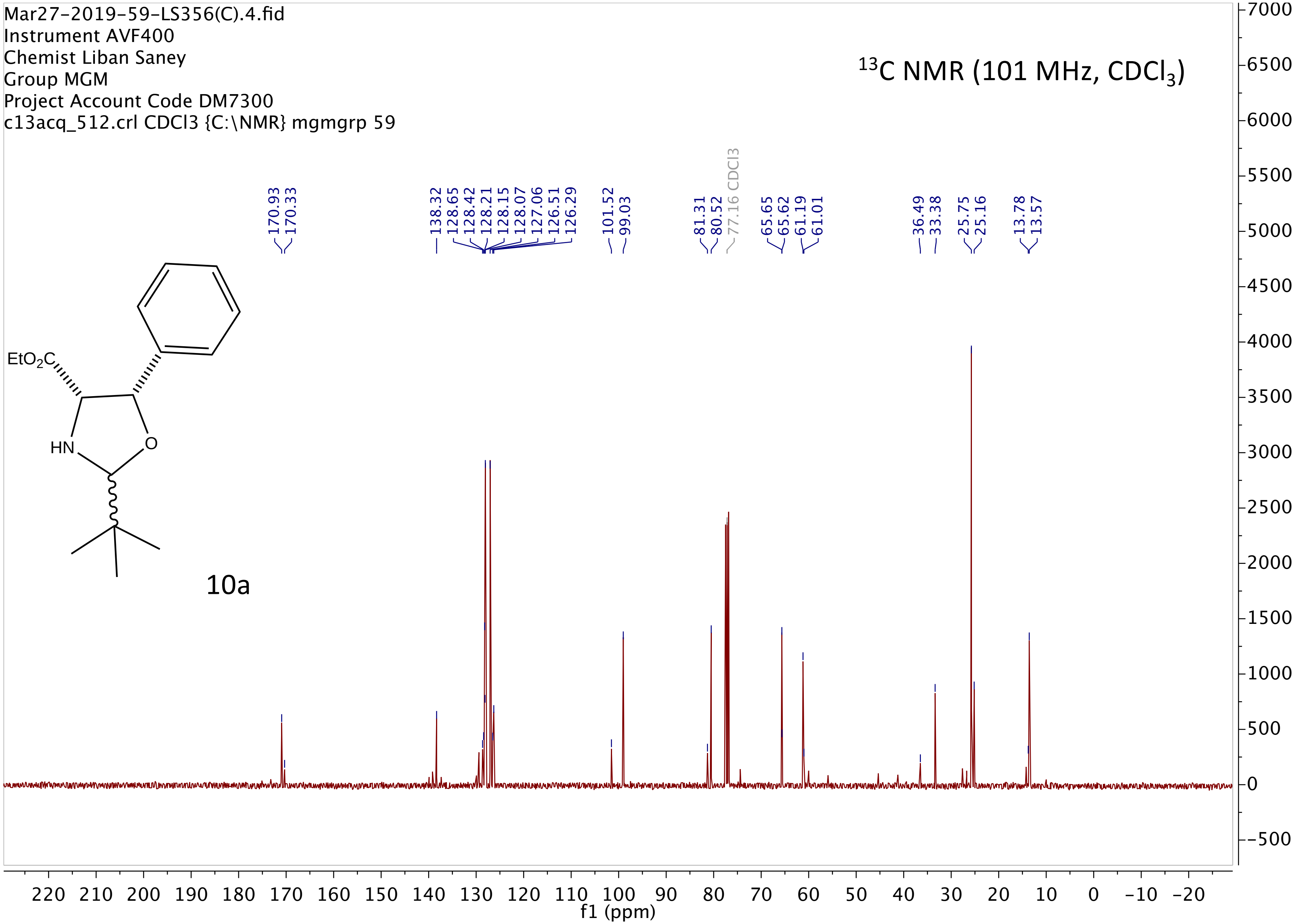


9l

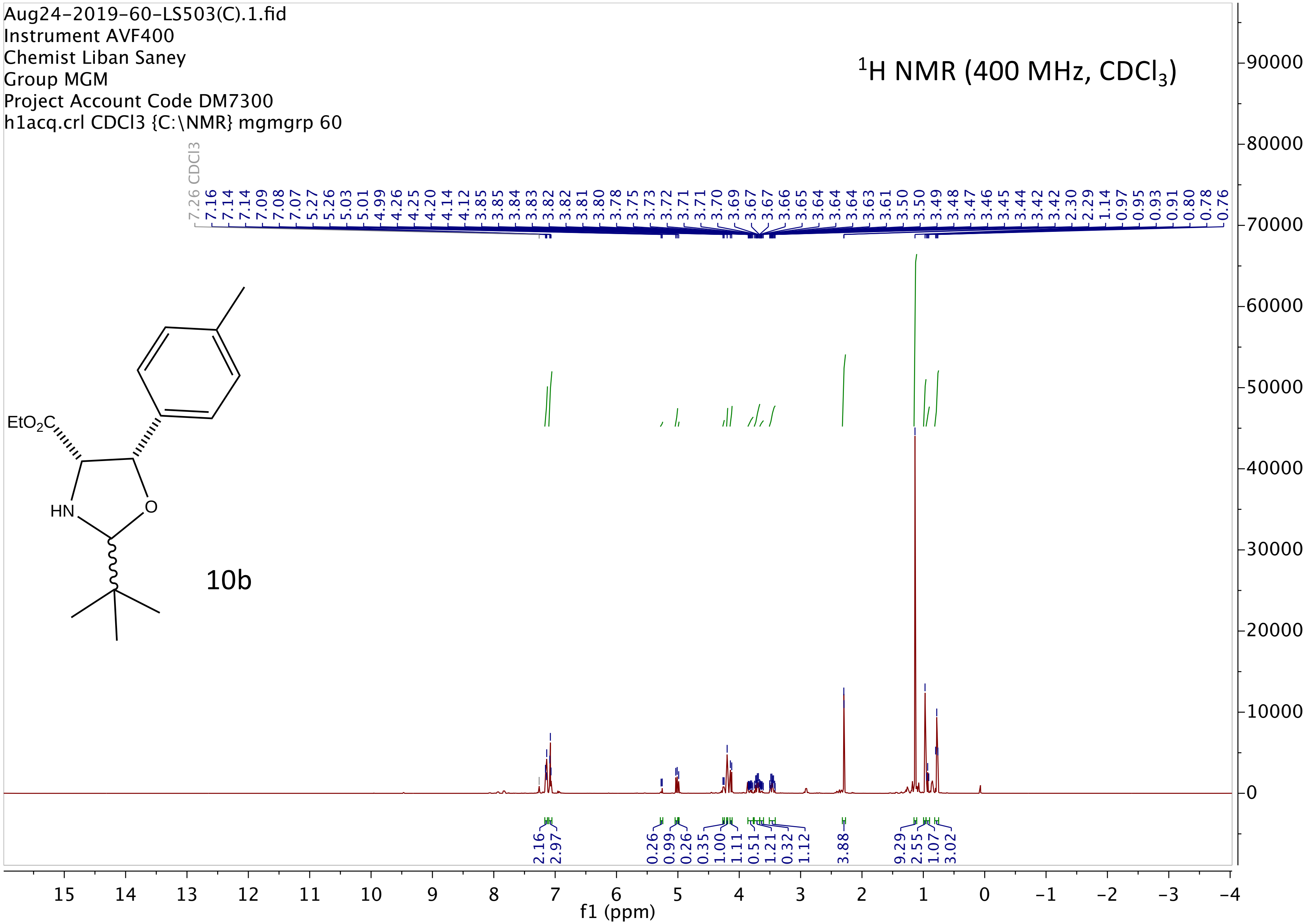



Jan13-2021-54-LS902(P) C4-D1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 54
13C NMR (101 MHz, CDCl3)
169.33
157.00
142.95
126.75
125.25
124.41
81.10
77.16 CDCl3
72.23
62.16
59.83
28.38
14.18
OH
O
OEt
S
HN
Boc
9l
f1 (ppm)


Mar27-2019-59-LS356(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59
1H NMR (400 MHz, CDCl3)
EtO2C
HN
O
10a
f1 (ppm)


Mar27-2019-59-LS356(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59
$^{13}$C NMR (101 MHz, $CDCl_3$)
170.93
170.33
138.32
128.65
128.42
128.21
128.15
128.07
127.06
126.51
126.29
101.52
99.03
81.31
80.52
77.16 CDCl3
65.65
65.62
61.19
61.01
36.49
33.38
25.75
25.16
13.78
13.57
$EtO_2C$
HN
O
10a
f1 (ppm)

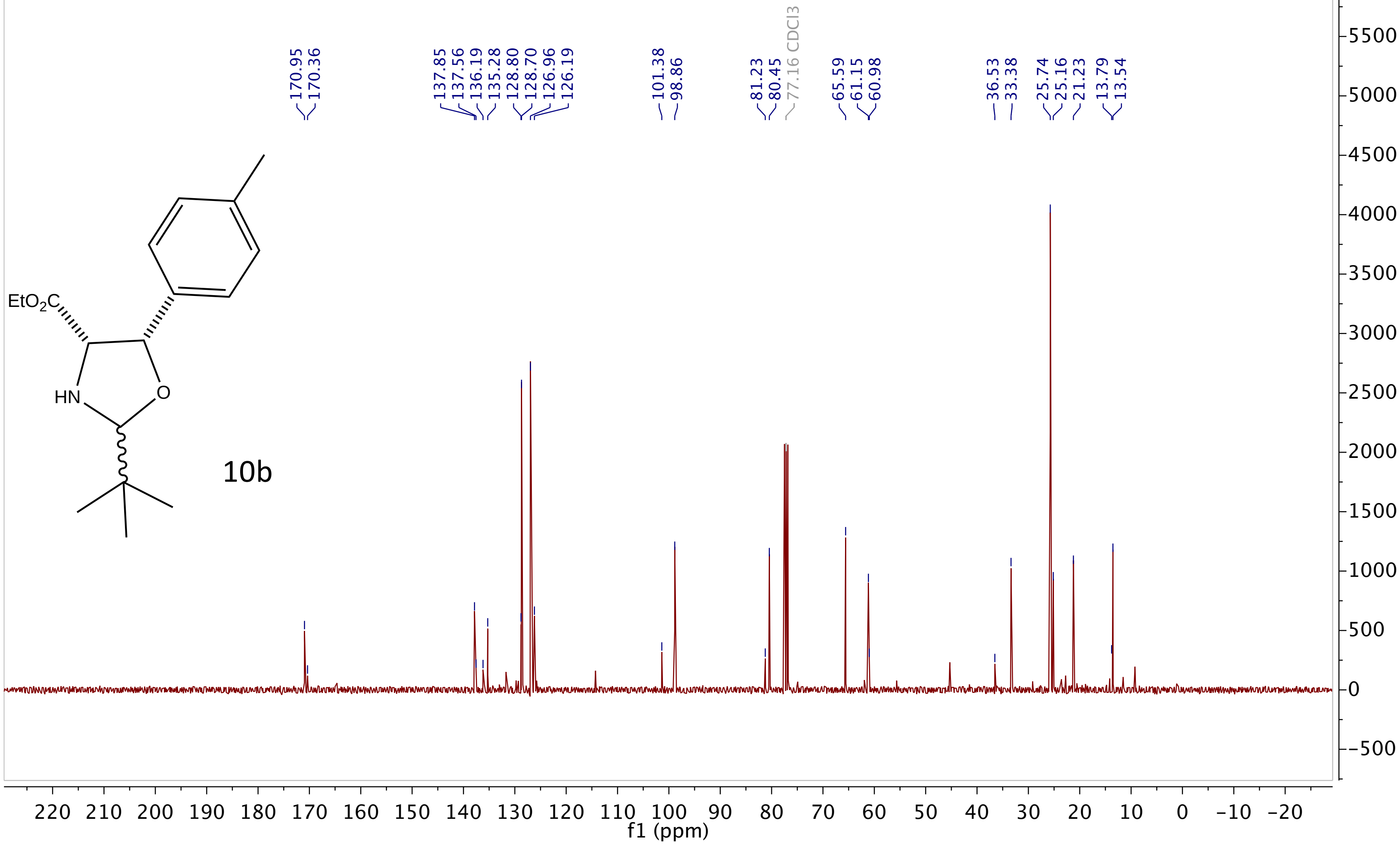
Aug24-2019-60-LS503(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60



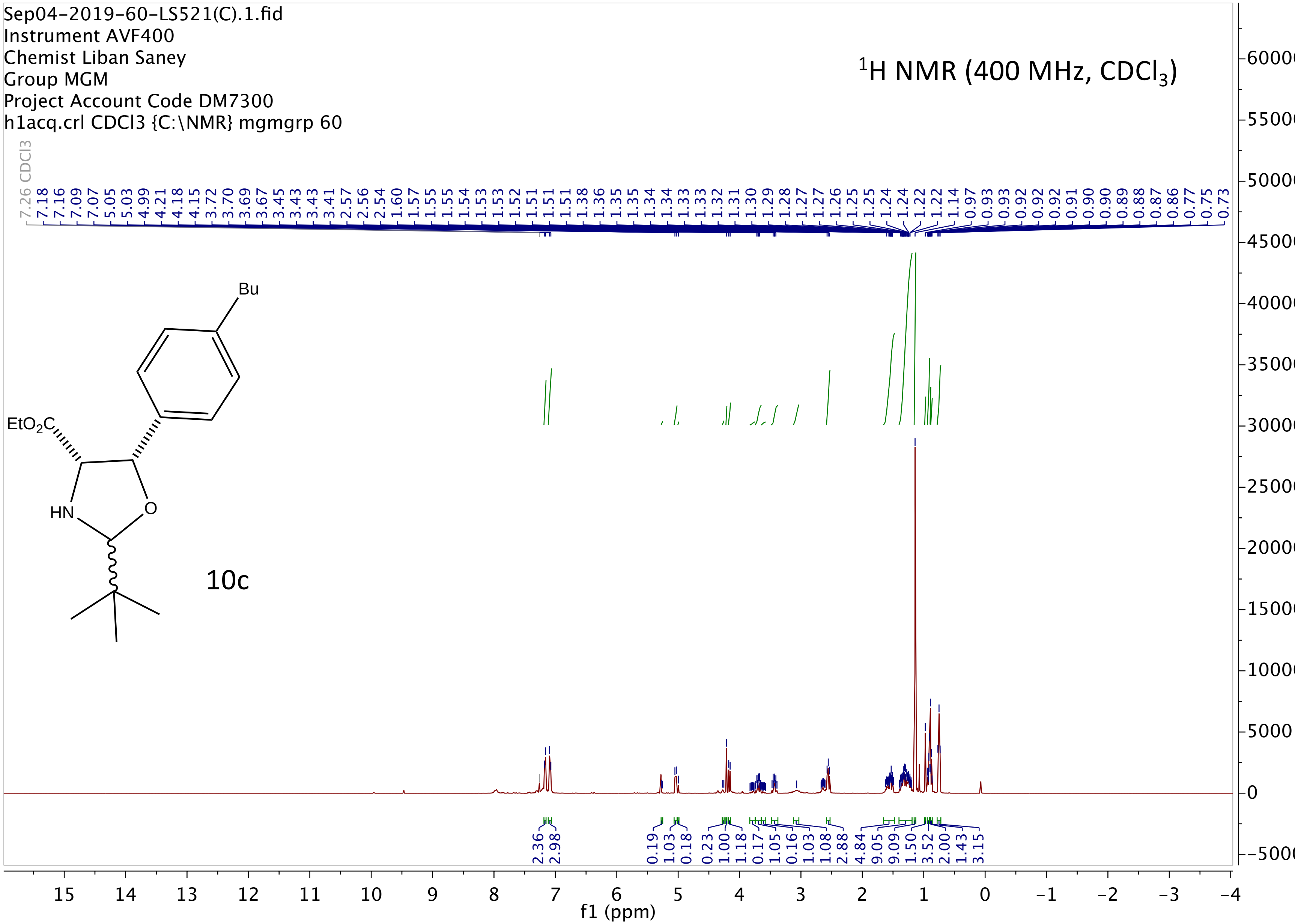

10b

Aug24-2019-60-LS503(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)

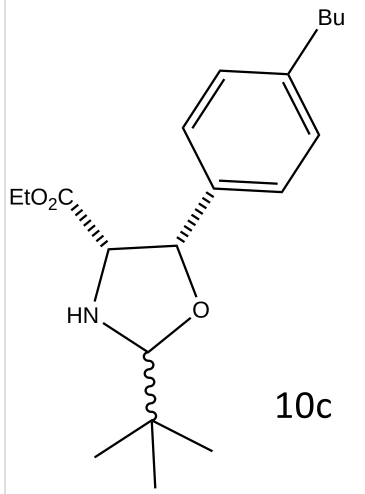



10b

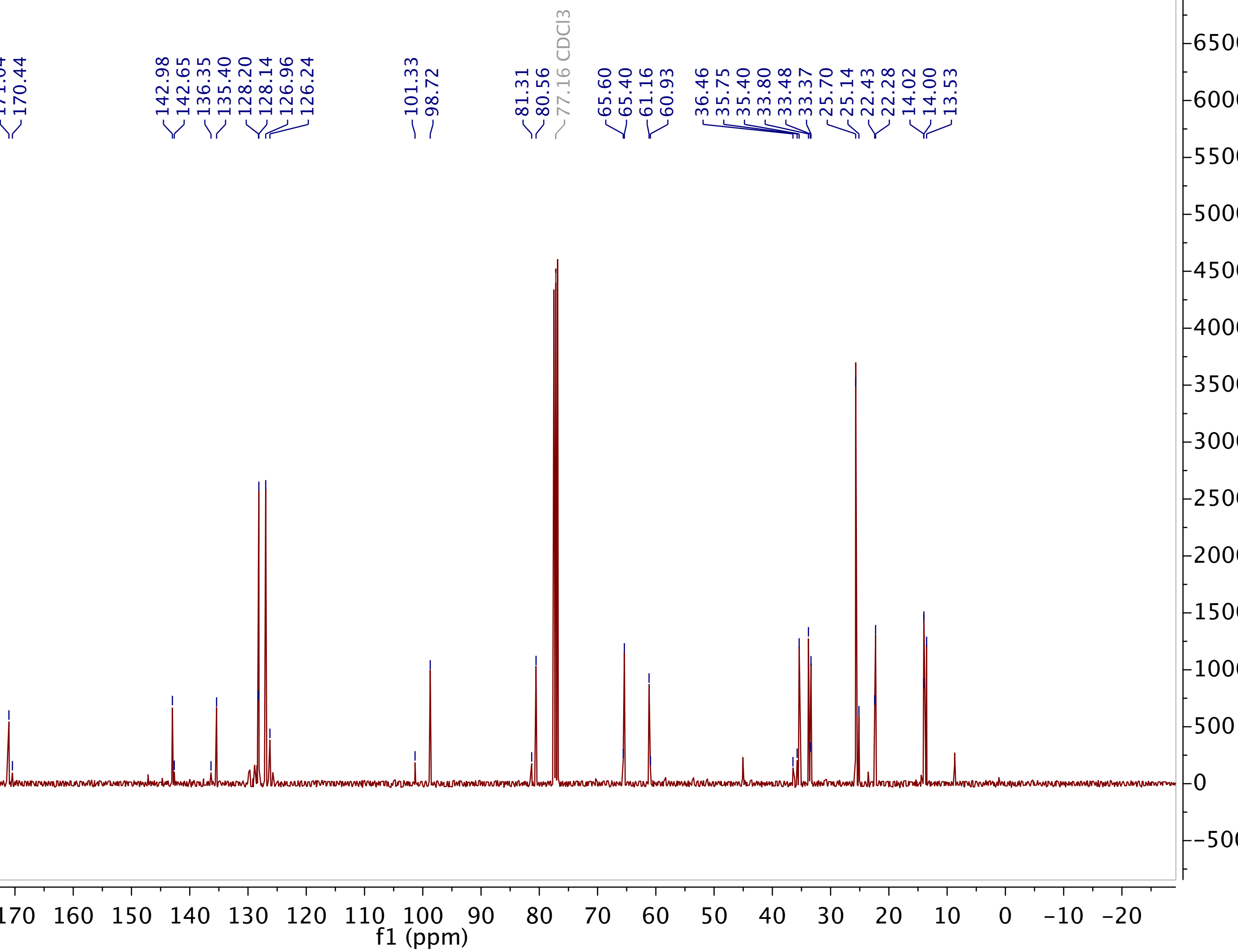

Sep04-2019-60-LS521(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
Bu
EtO2C
HN
O
10c
f1 (ppm)

Sep04-2019-60-LS521(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

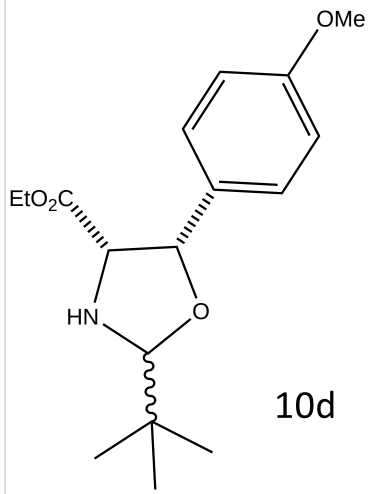
$^{13}C$ NMR (101 MHz, $CDCl_3$)



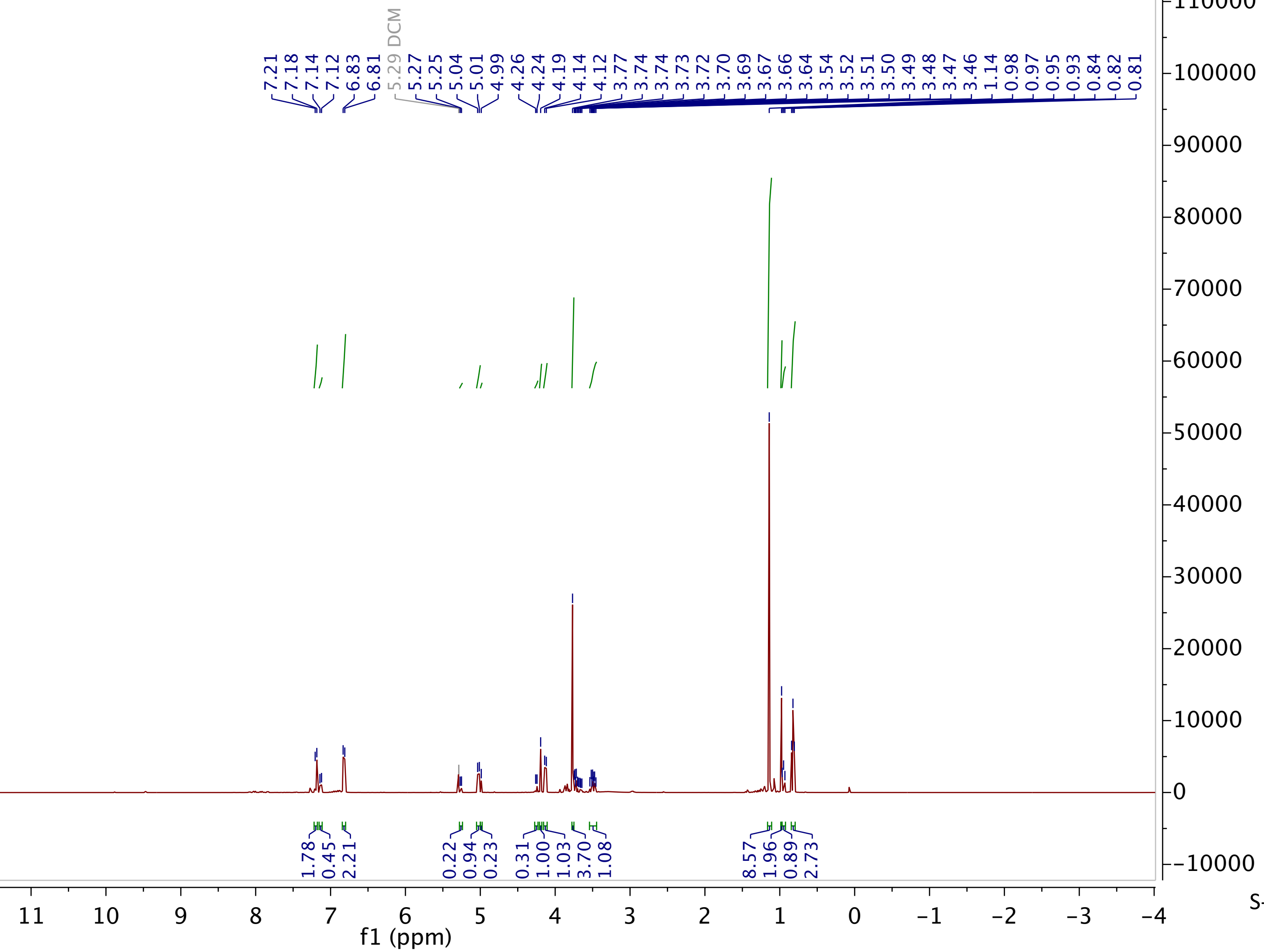
10c



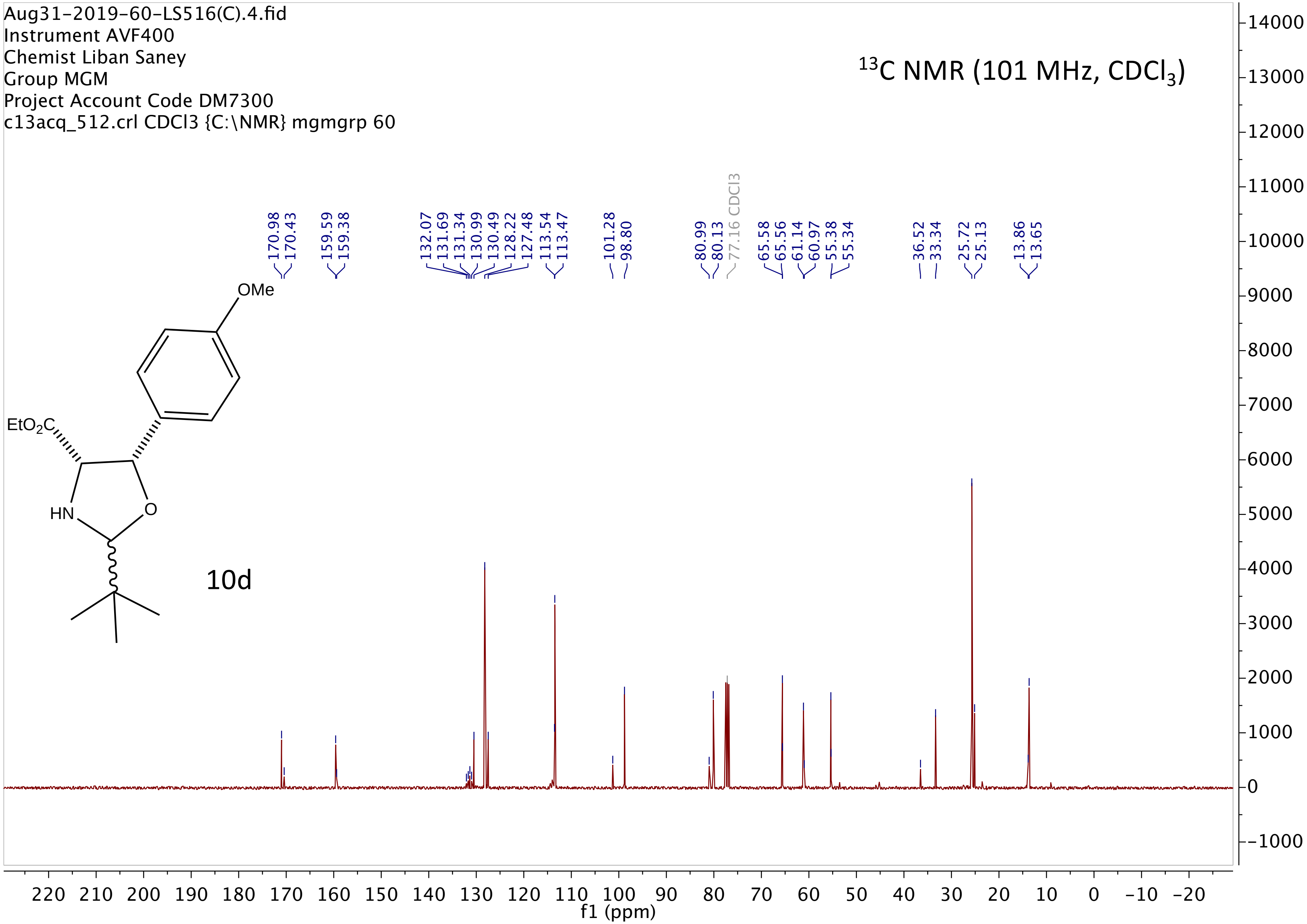
Aug31-2019-60-LS516(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60




10d



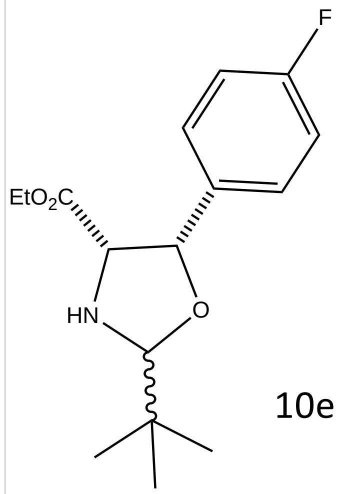
Aug31-2019-60-LS516(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60



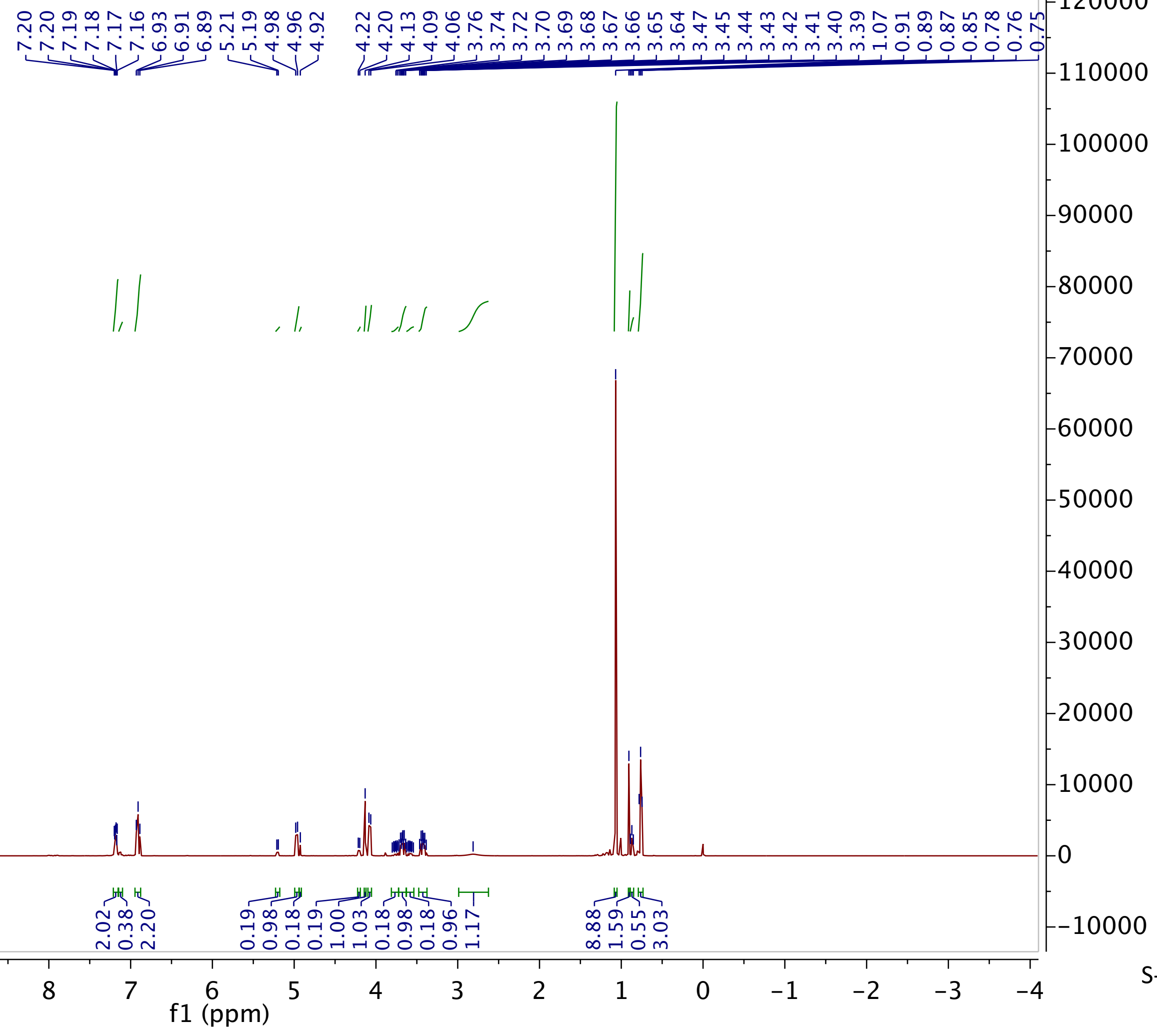

10d

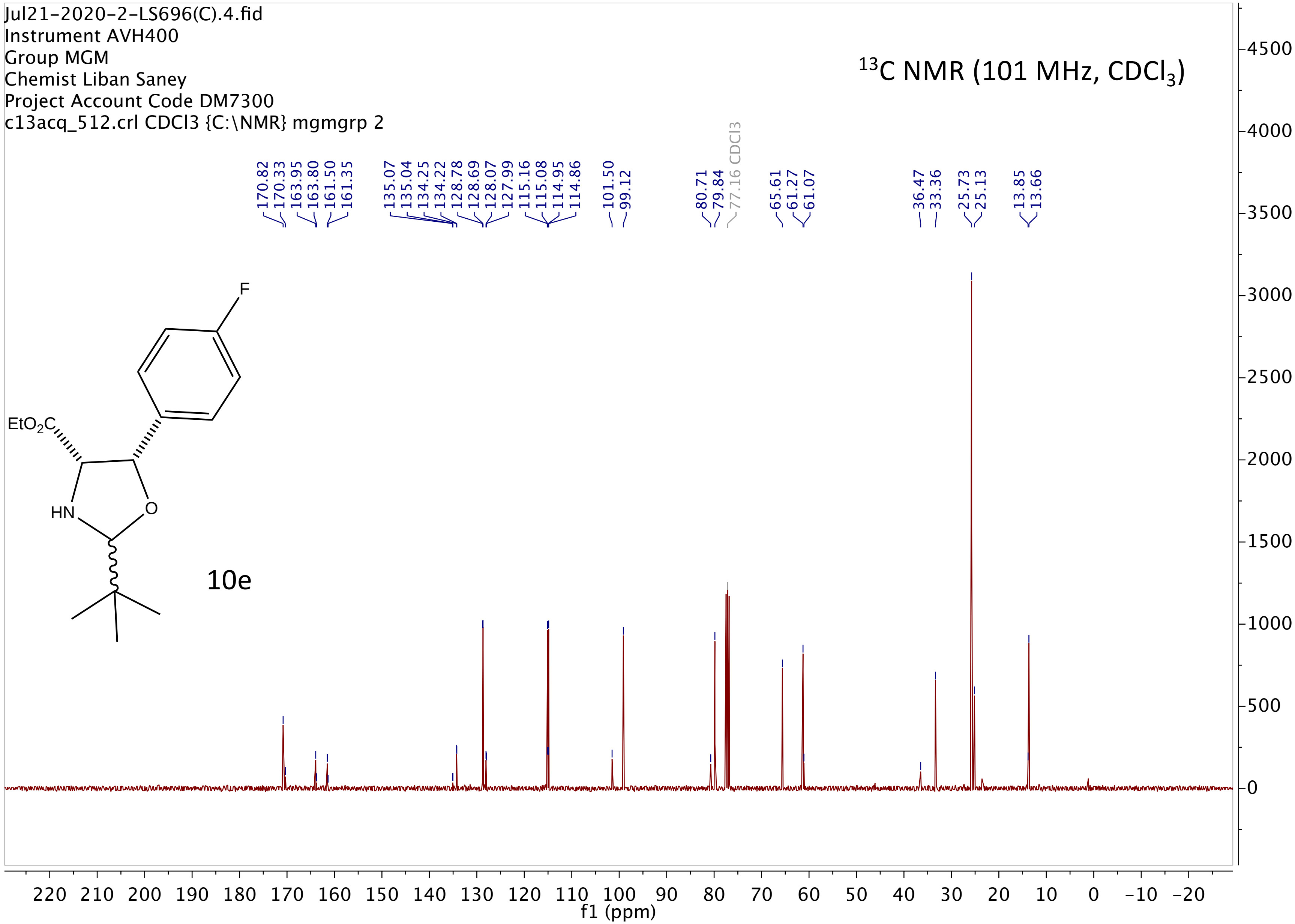
Jul21-2020-2-LS696(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 2

$^1H$ NMR (400 MHz, $CDCl_3$)

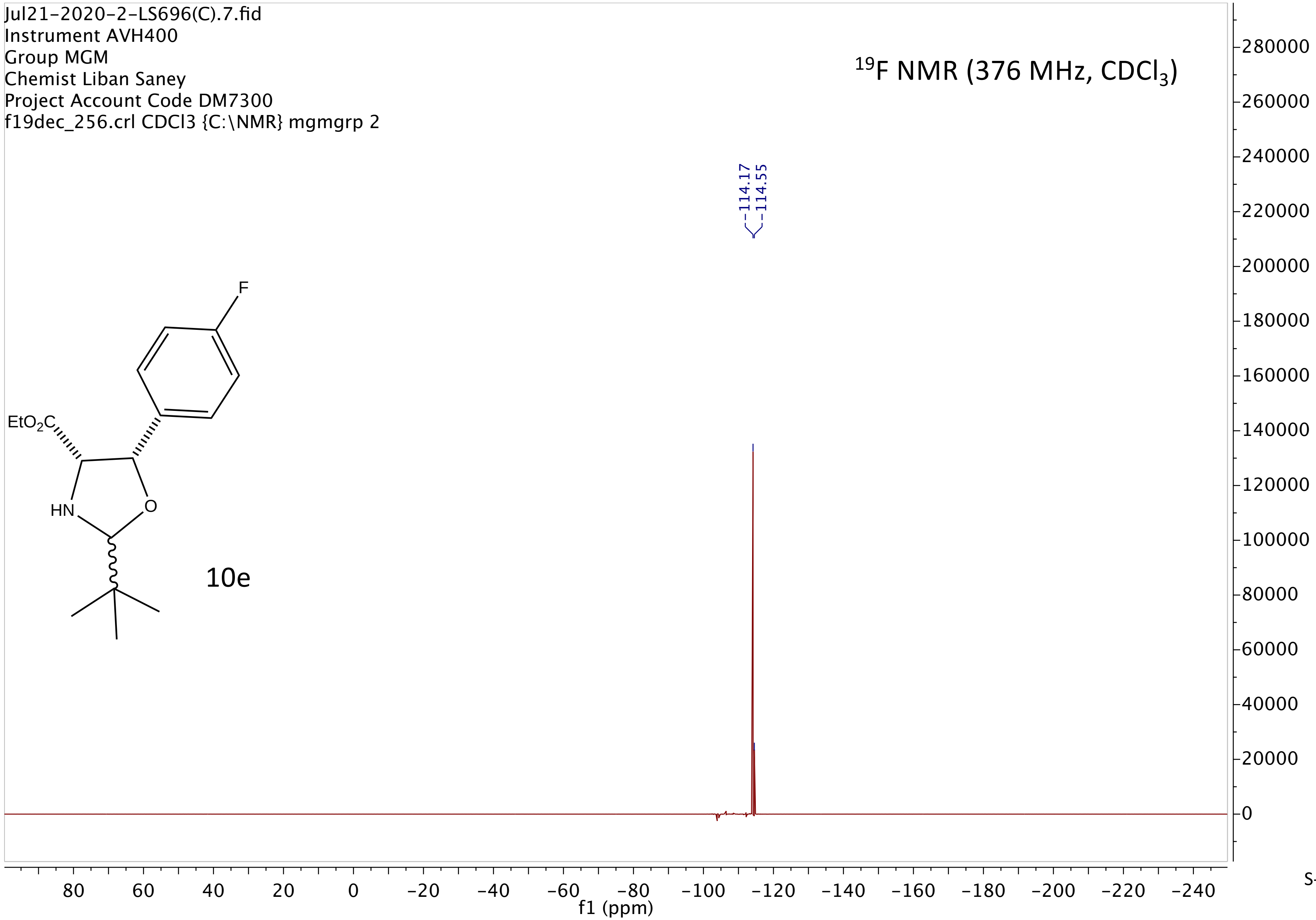


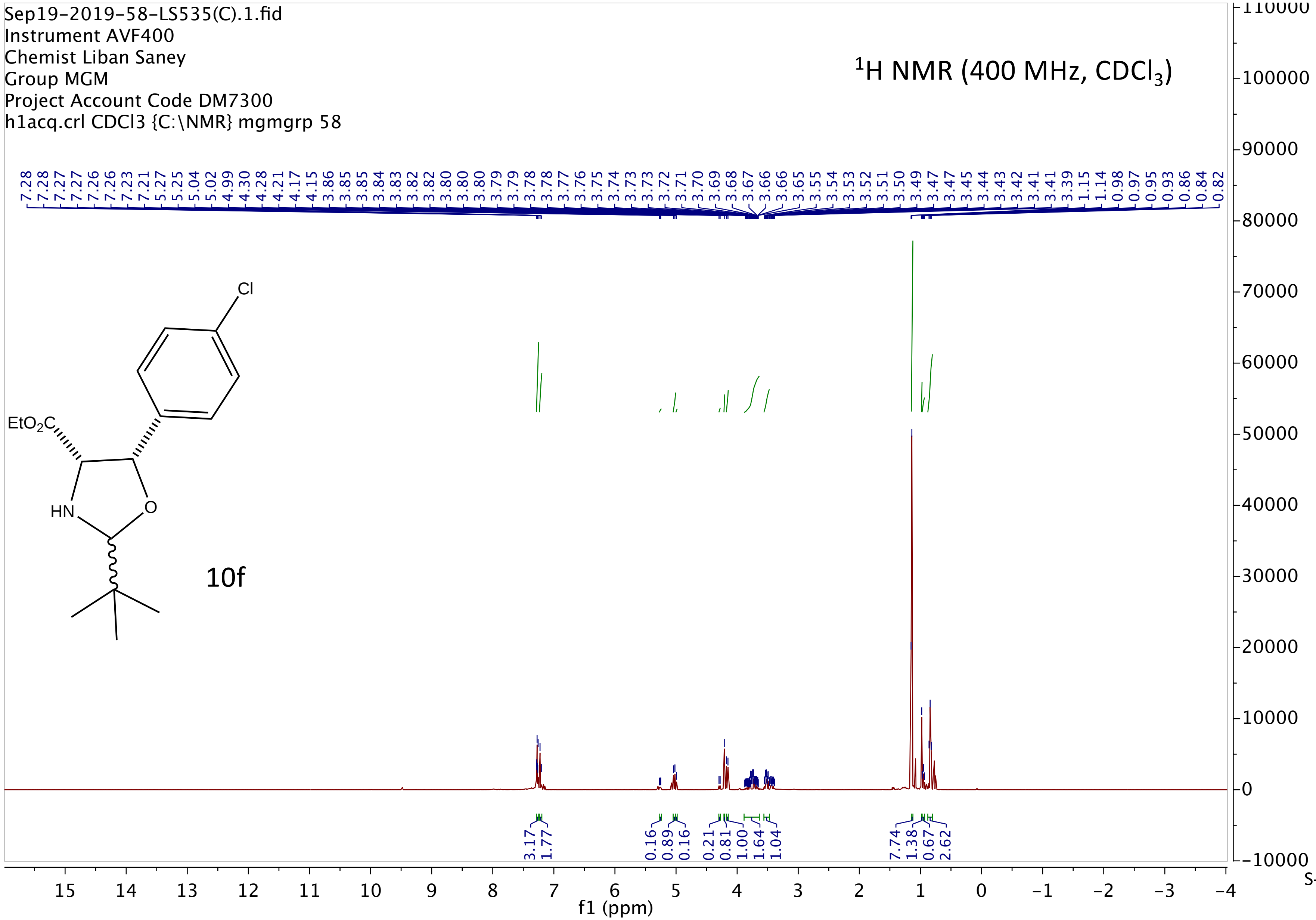
10e





Jul21-2020-2-LS696(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 2
13C NMR (101 MHz, CDCl3)
170.82
170.33
163.95
163.80
161.50
161.35
135.07
135.04
134.25
134.22
128.78
128.69
128.07
127.99
115.16
115.08
114.95
114.86
101.50
99.12
80.71
79.84
77.16 CDCl3
65.61
61.27
61.07
36.47
33.36
25.73
25.13
13.85
13.66
F
EtO2C
HN
O
10e
4500
4000
3500
3000
2500
2000
1500
1000
500
0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

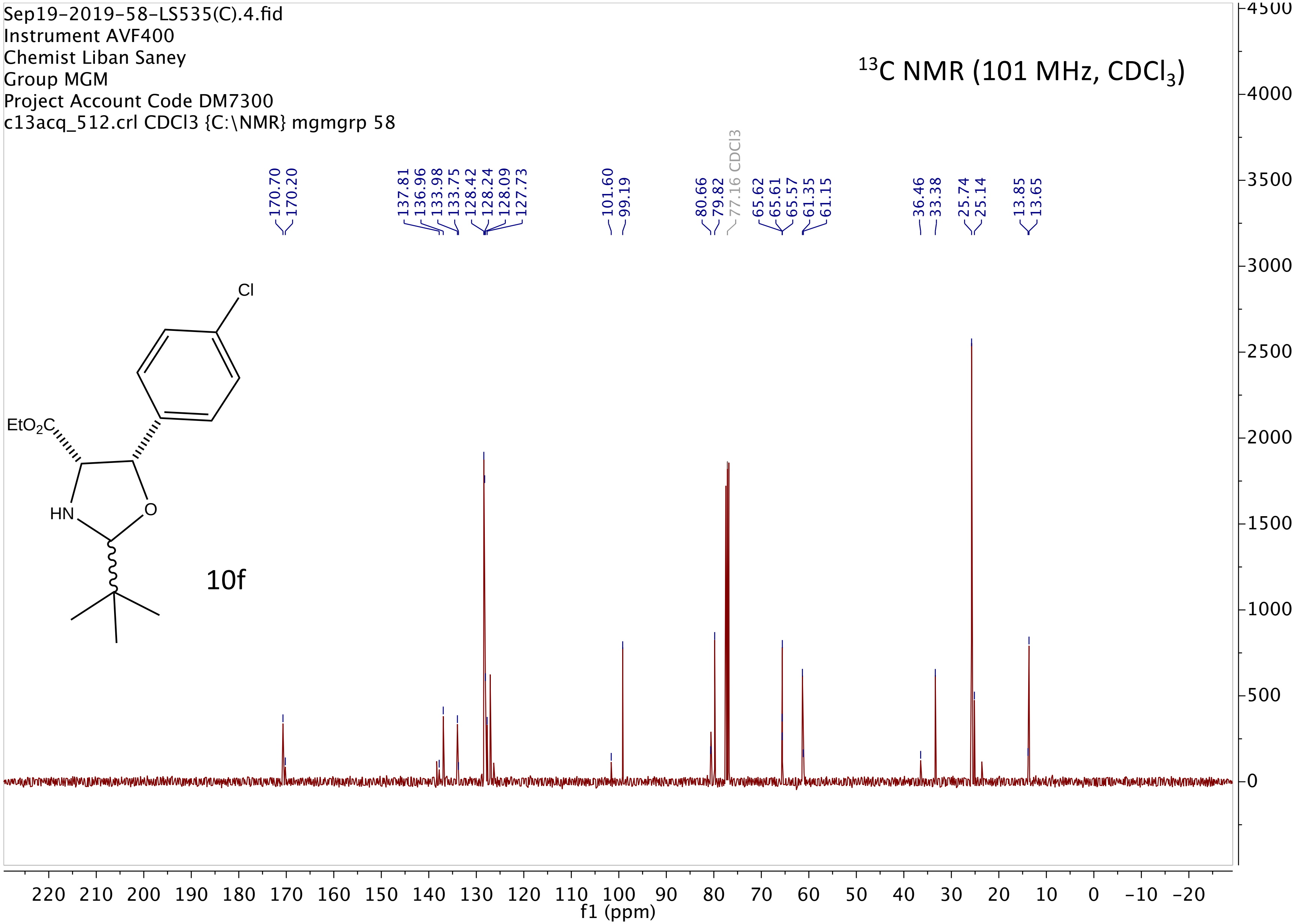

Jul21-2020-2-LS696(C).7.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 2
$^{19}$F NMR (376 MHz, $CDCl_3$)
-114.17
-114.55
F
$EtO_2C$
HN
O
10e
f1 (ppm)


Sep19-2019-58-LS535(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 58
1H NMR (400 MHz, CDCl3)
Cl
EtO2C
HN
O
f1 (ppm)

10f

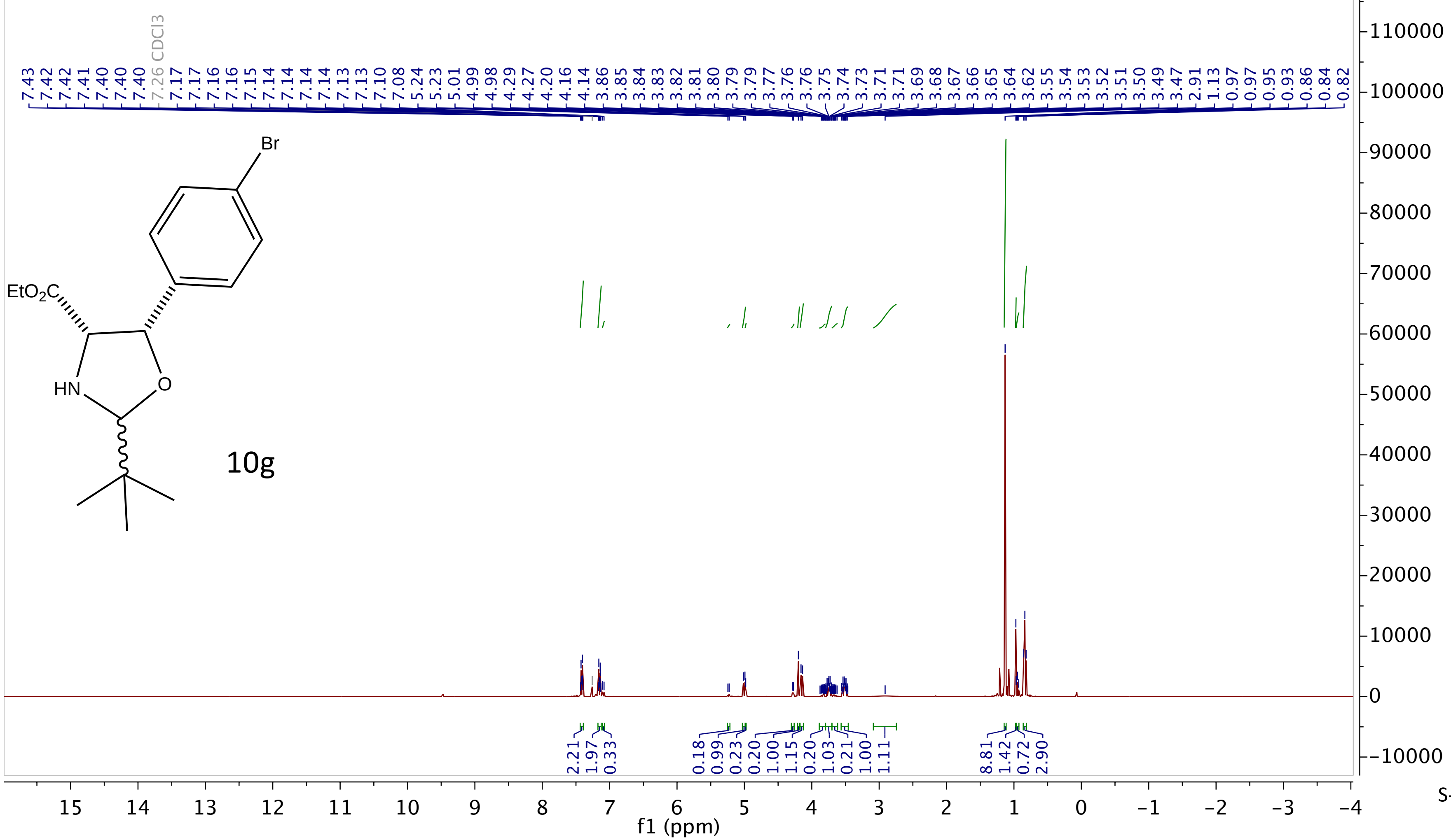
Sep19-2019-58-LS535(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 58

$^{13}$C NMR (101 MHz, $CDCl_3$)



Jan31-2021-1-LS929(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1

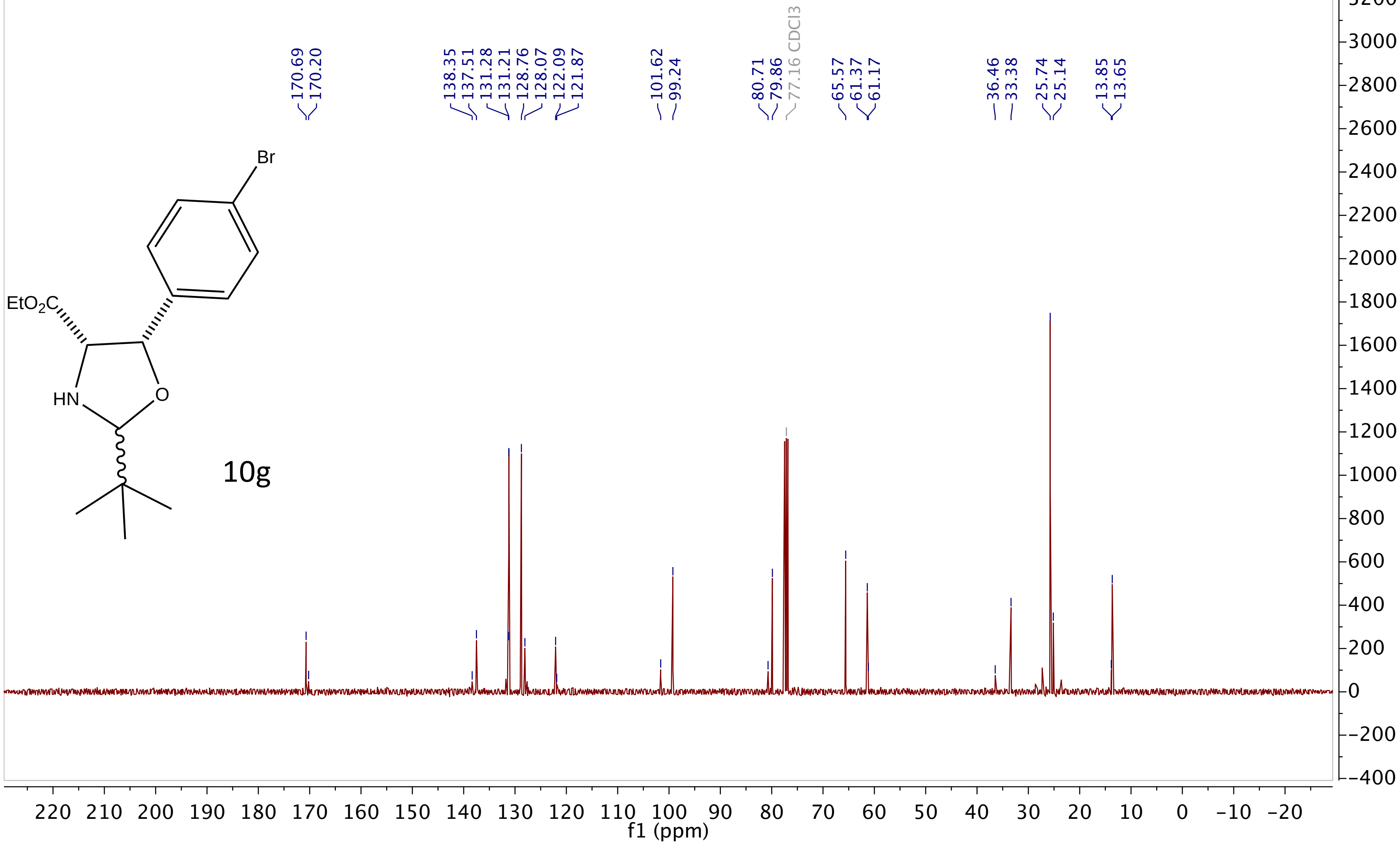
$^1H$ NMR (400 MHz, $CDCl_3$)



10g

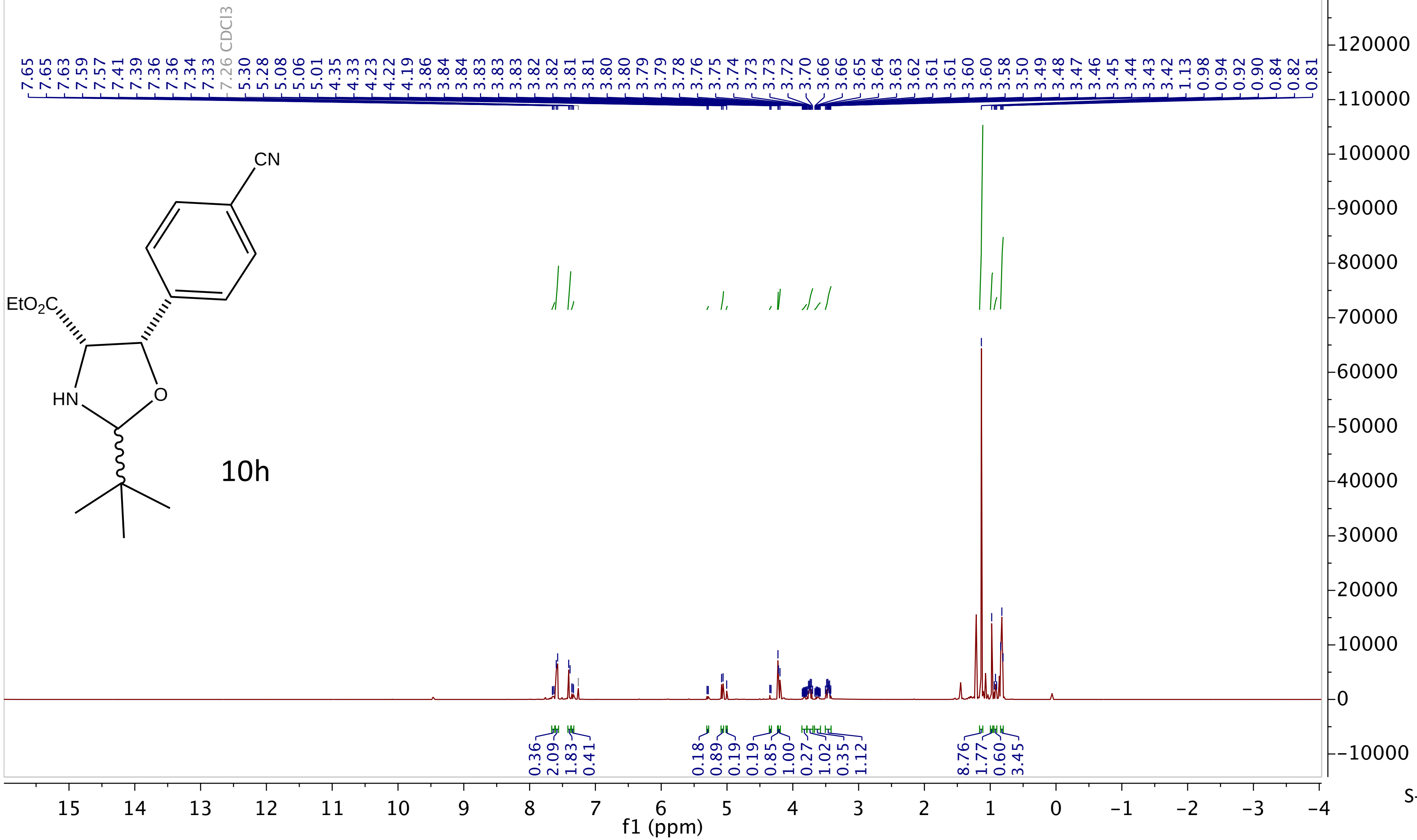
Jan31-2021-1-LS929(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1

$^{13}C$ NMR (101 MHz, $CDCl_3$)



Jan26-2021-6-LS928(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 6

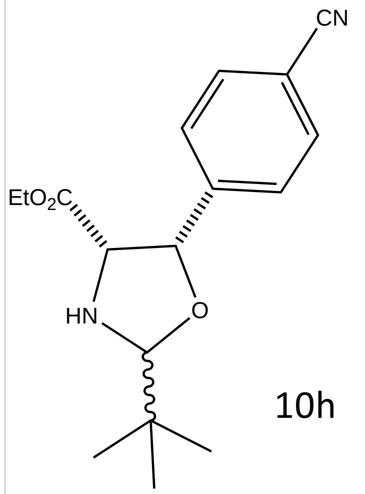
$^{1}$H NMR (400 MHz, $CDCl_3$)



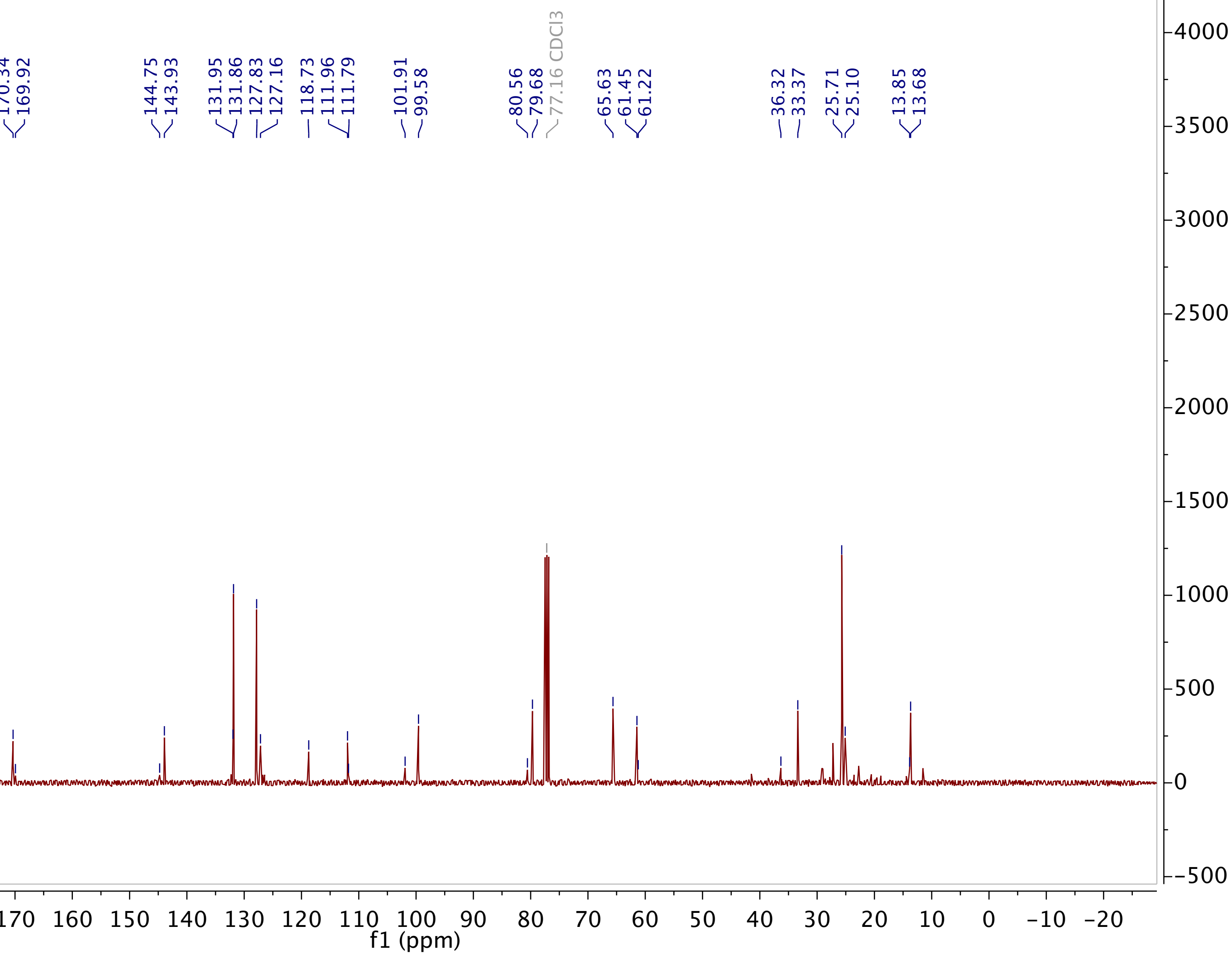

10h

Jan26-2021-6-LS928(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 6

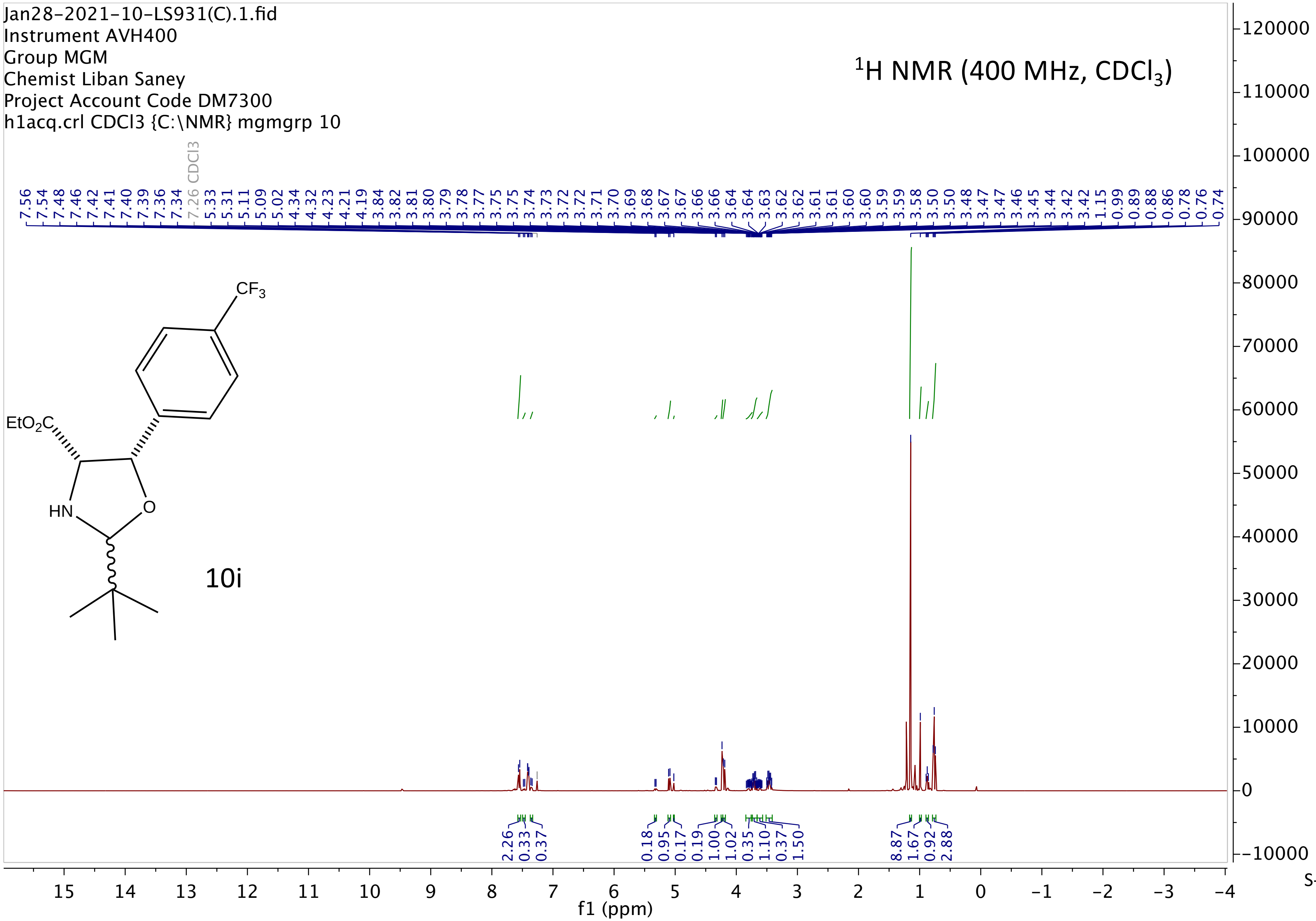
$^{13}C$ NMR (101 MHz, $CDCl_3$)



10h

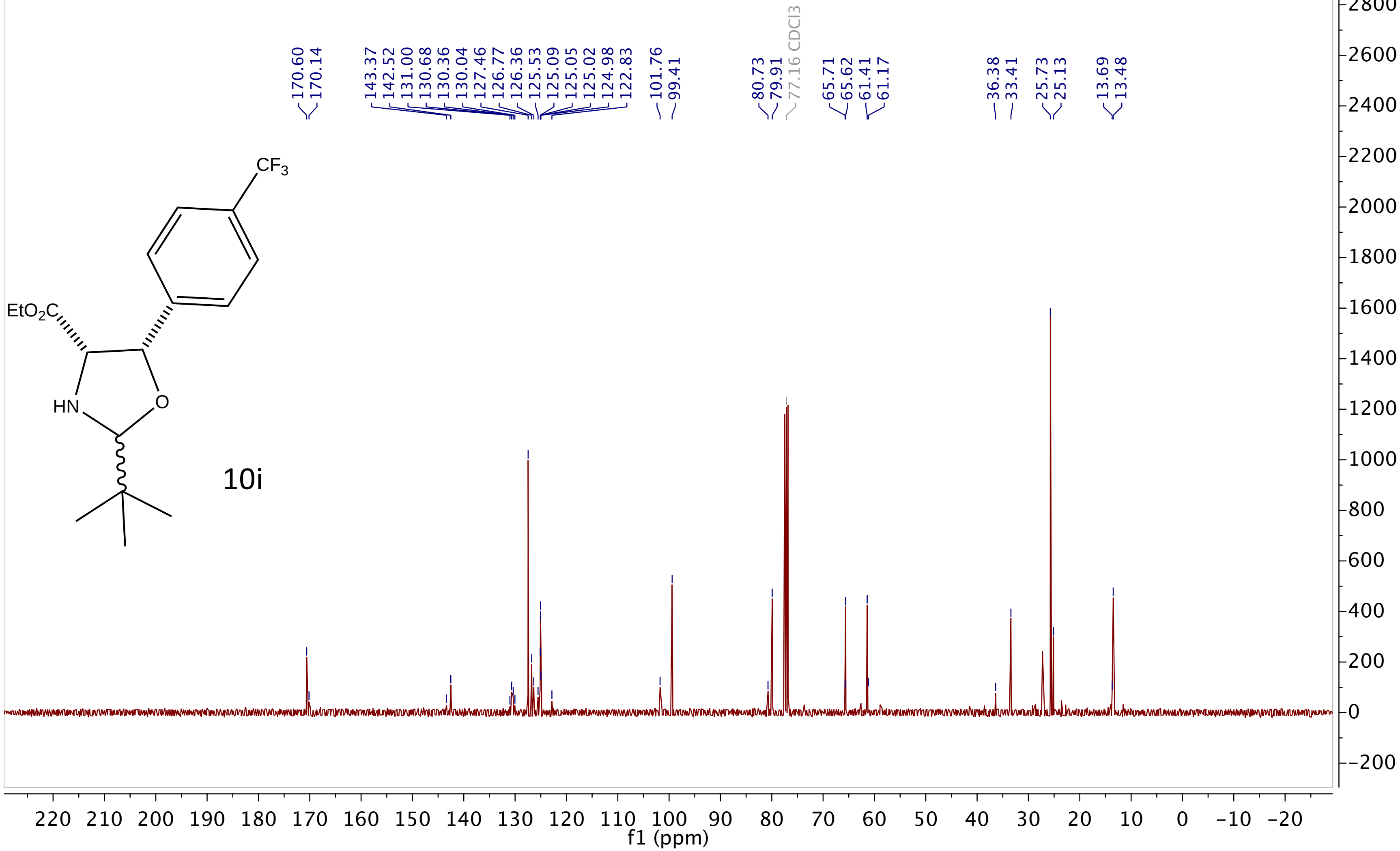


Jan28-2021-10-LS931(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 10



Jan28-2021-10-LS931(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 10

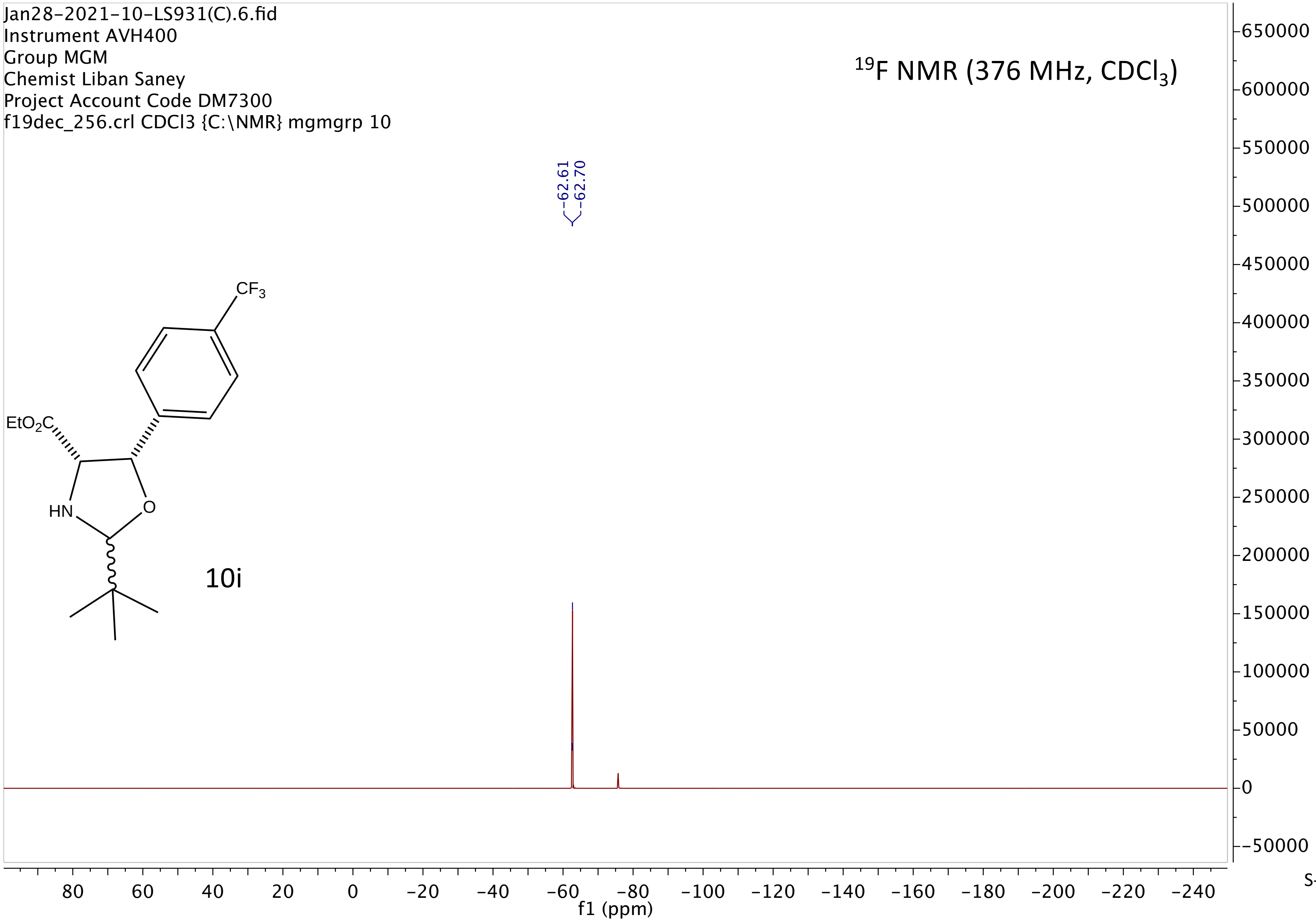
$^{13}C$ NMR (101 MHz, $CDCl_3$)



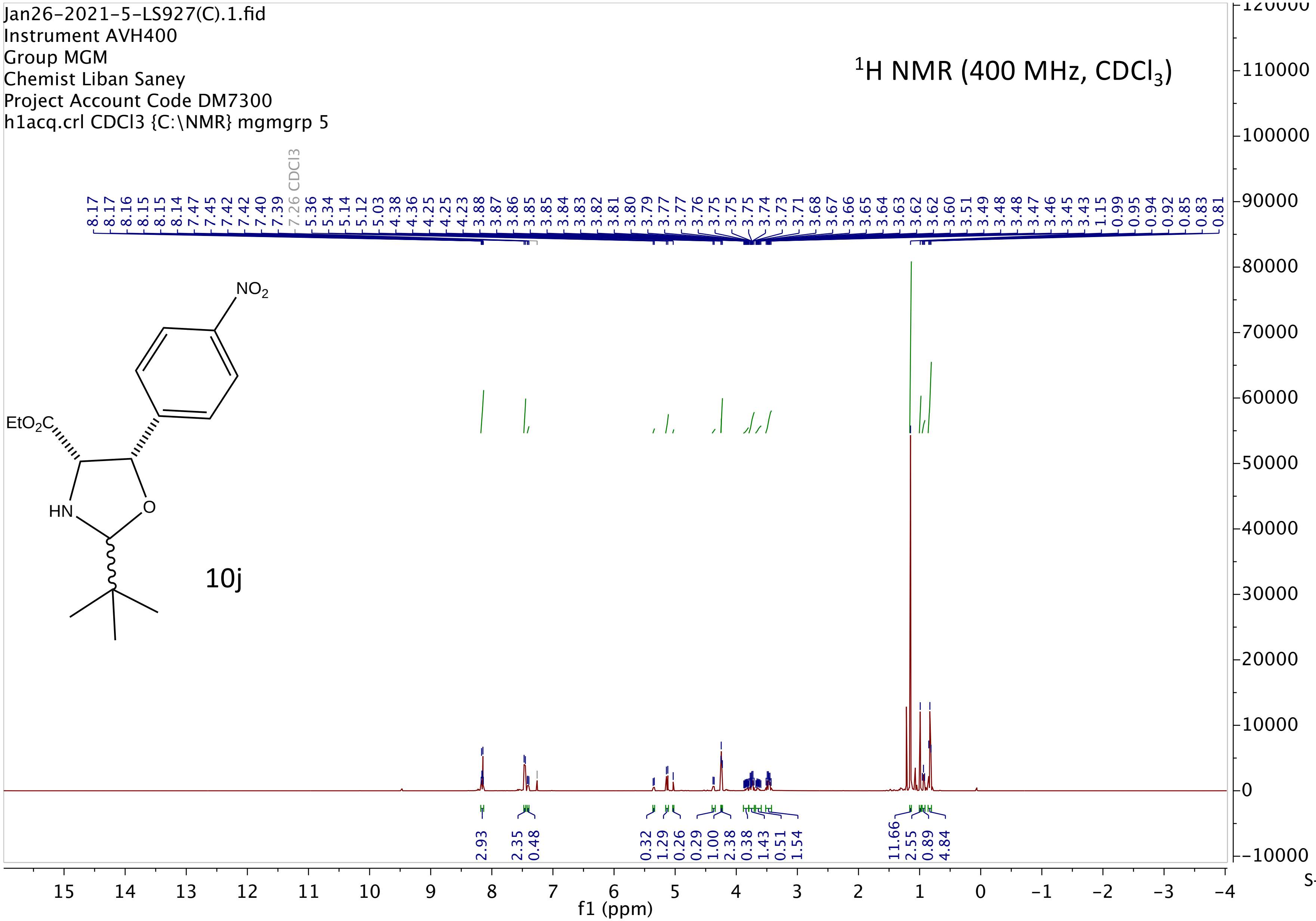

10i

Jan28-2021-10-LS931(C).6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 10

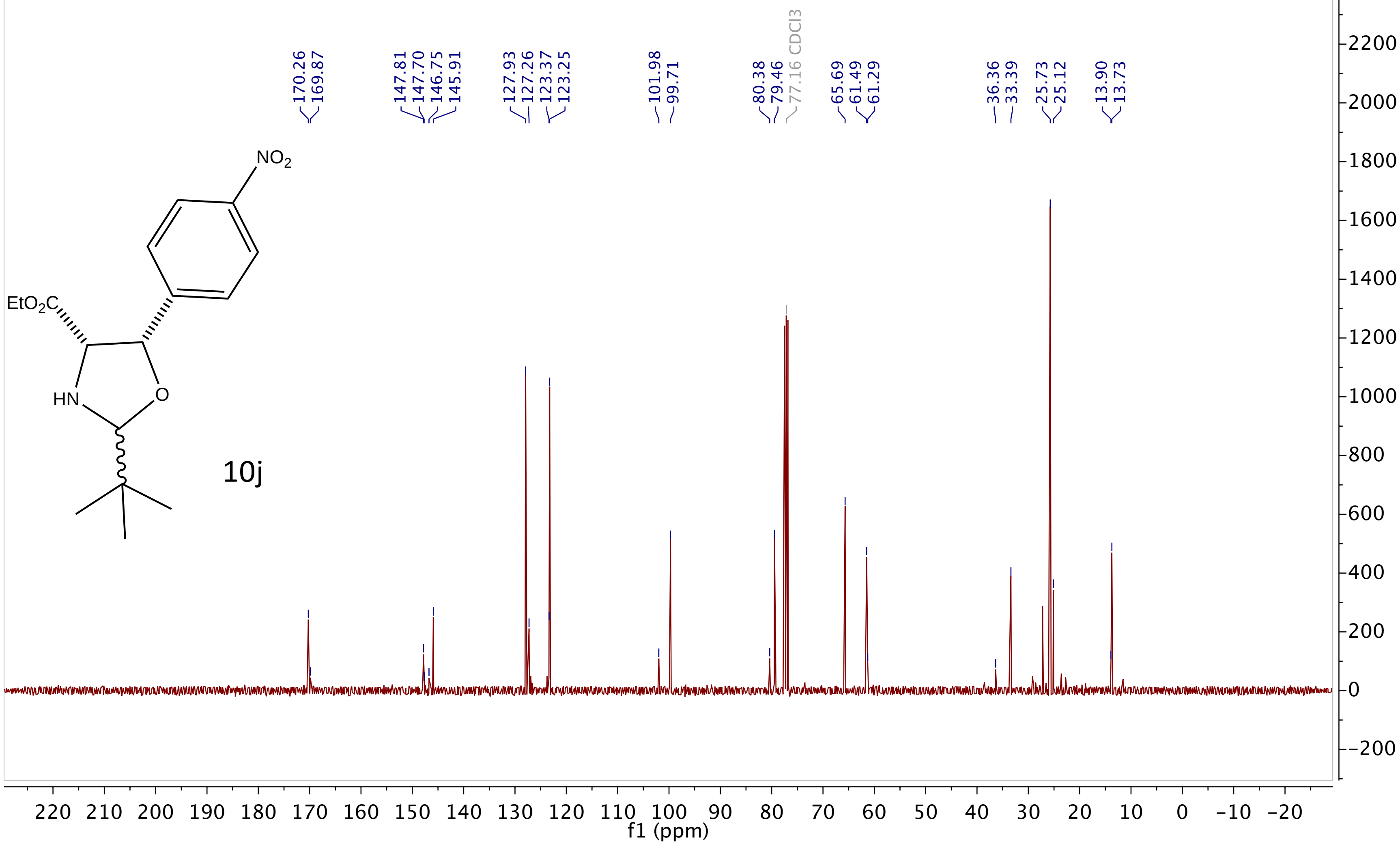
$^{19}$F NMR (376 MHz, $CDCl_3$)



10i

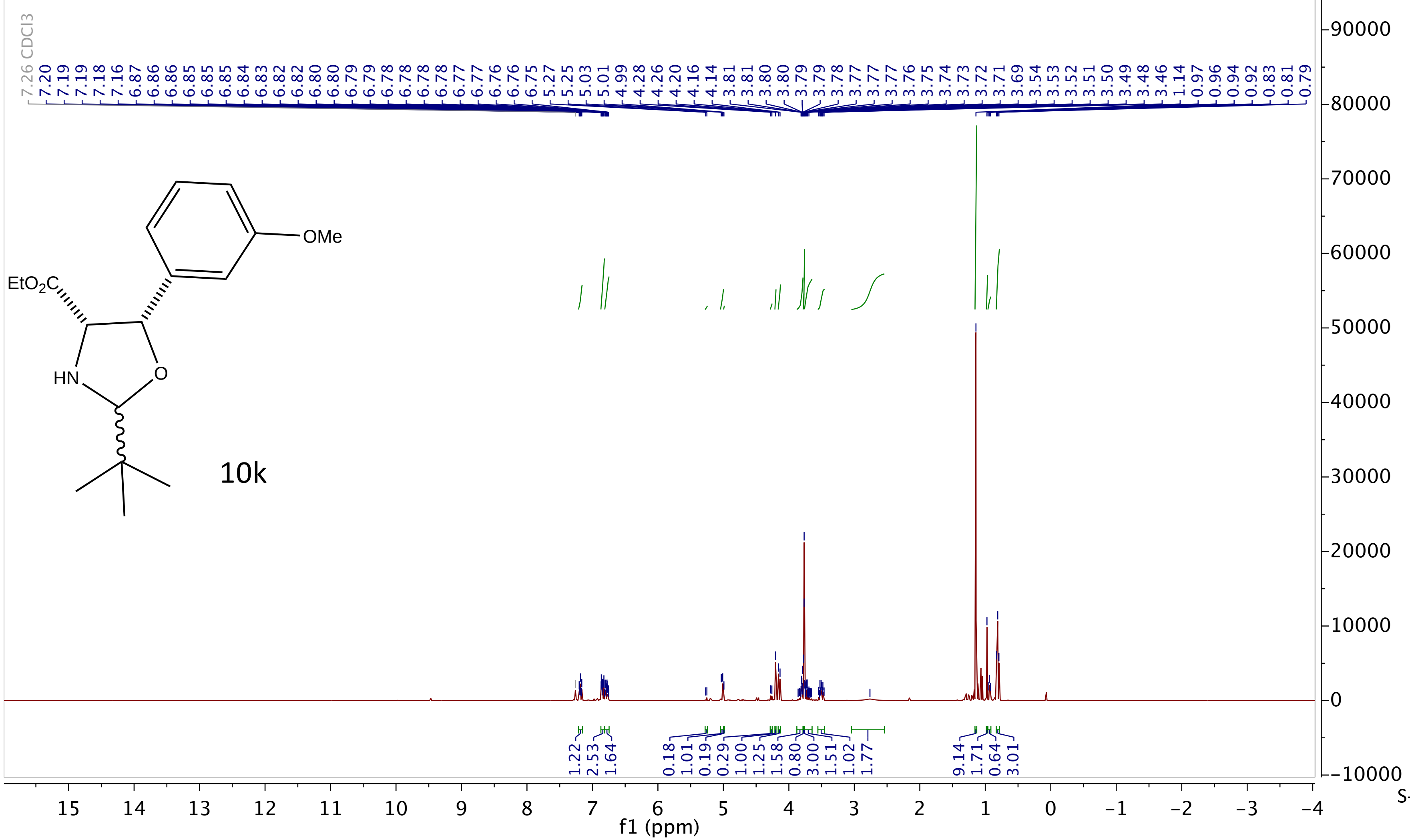

Jan26-2021-5-LS927(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 5
$^1$H NMR (400 MHz, $CDCl_3$)
10j
f1 (ppm)

Jan26-2021-5-LS927(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 5



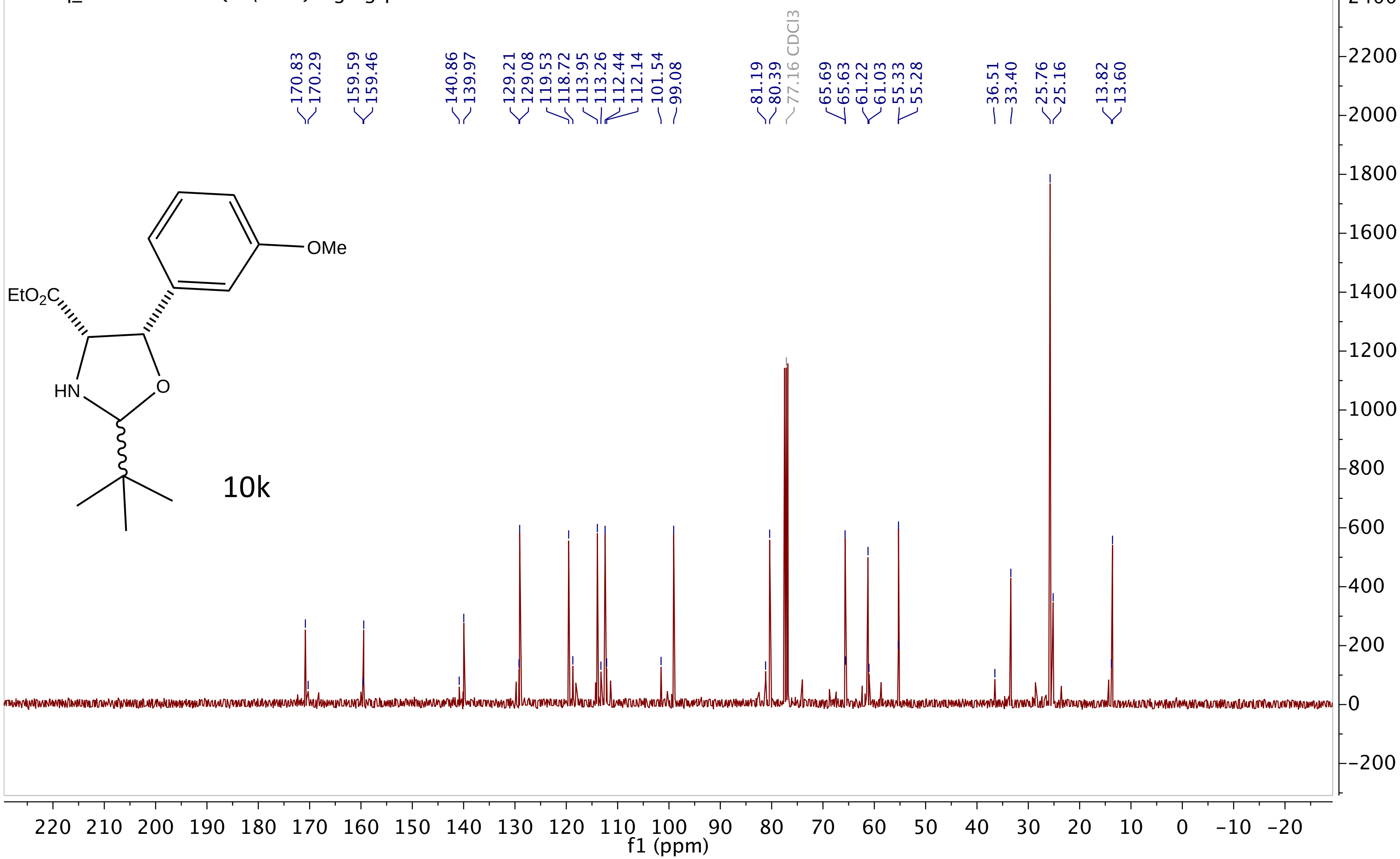
Feb04-2021-16-LS940(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 16

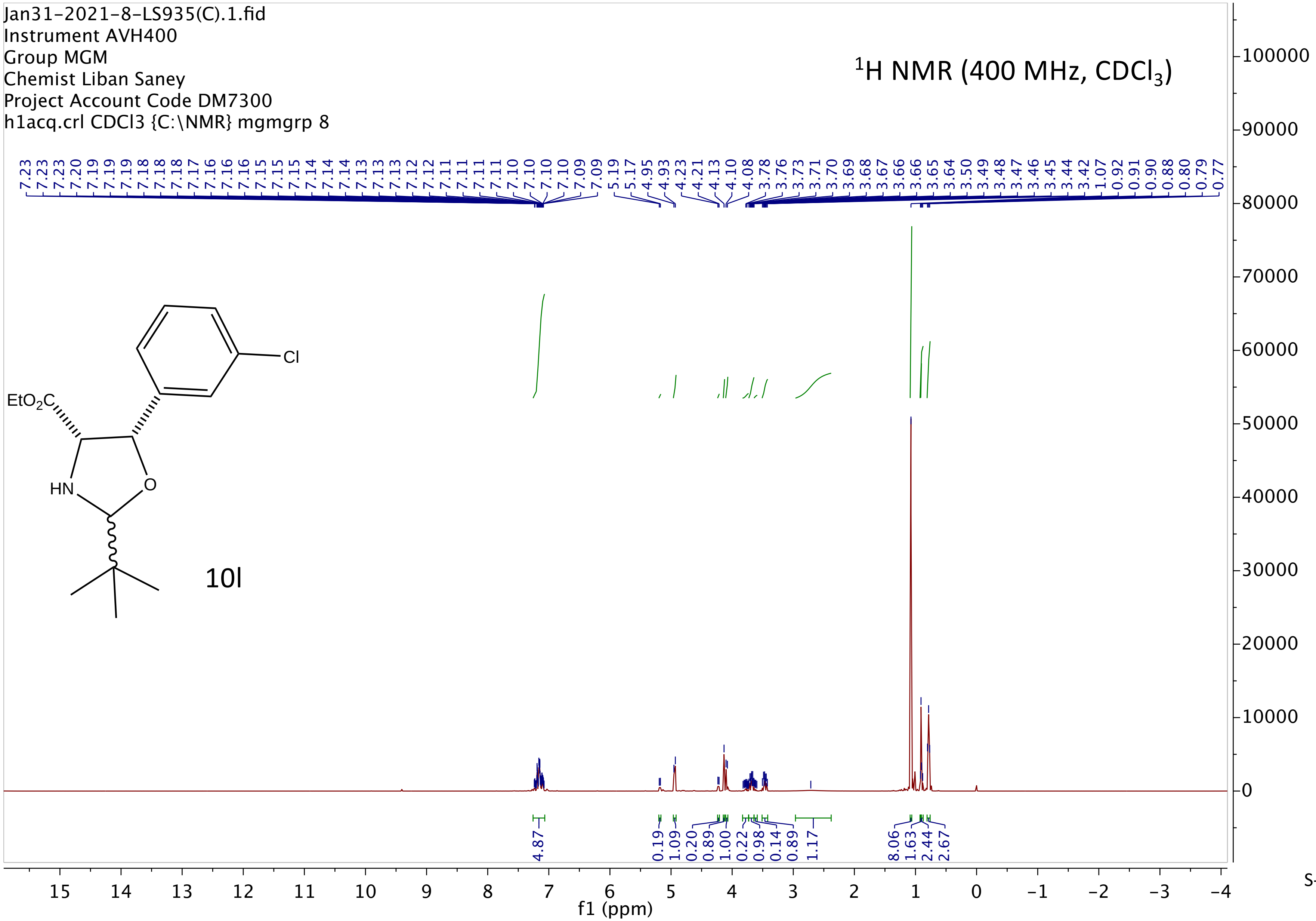
$^1H$ NMR (400 MHz, $CDCl_3$)



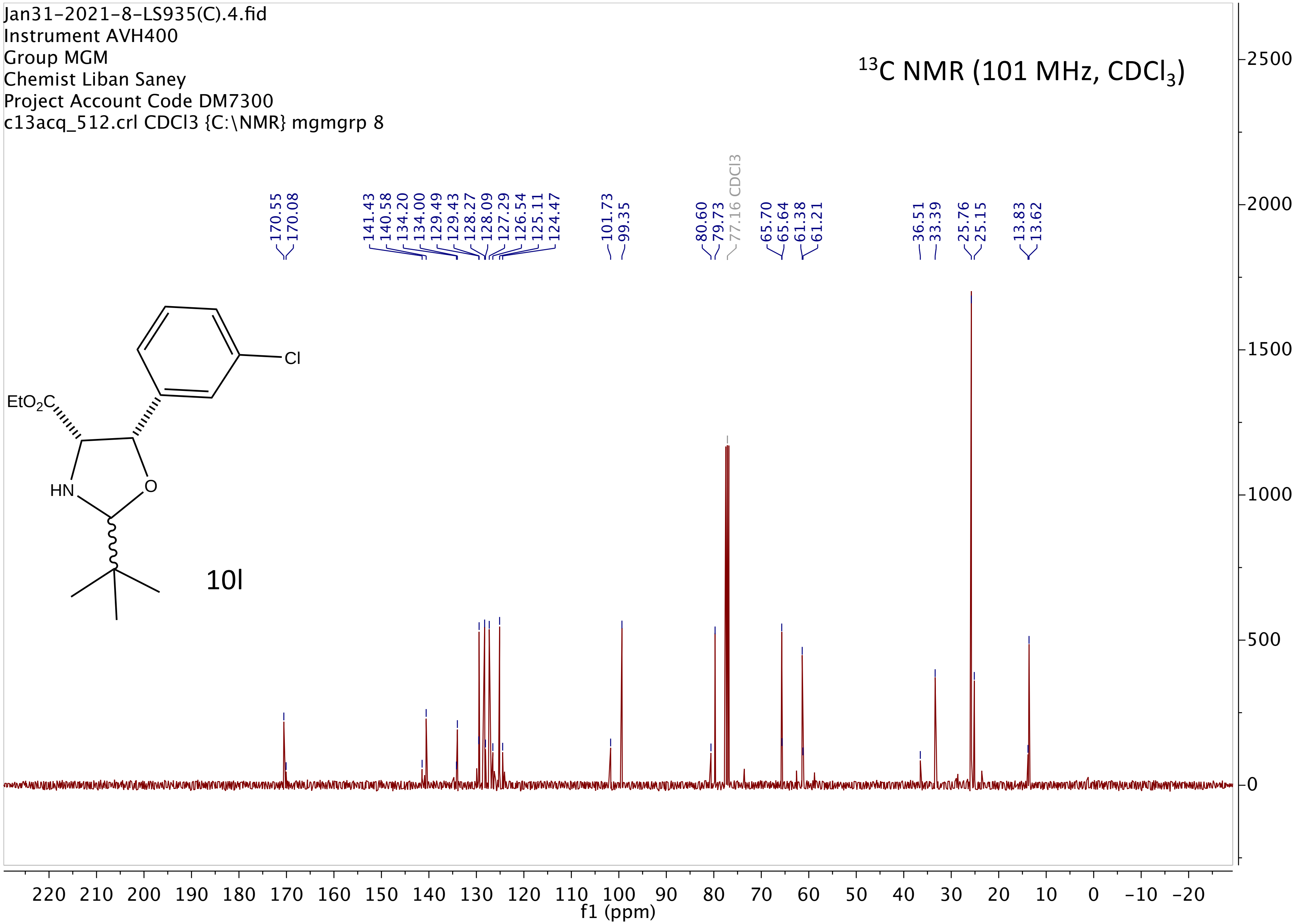
Feb04-2021-16-LS940(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 16

$^{13}C$ NMR (101 MHz, $CDCl_3$)

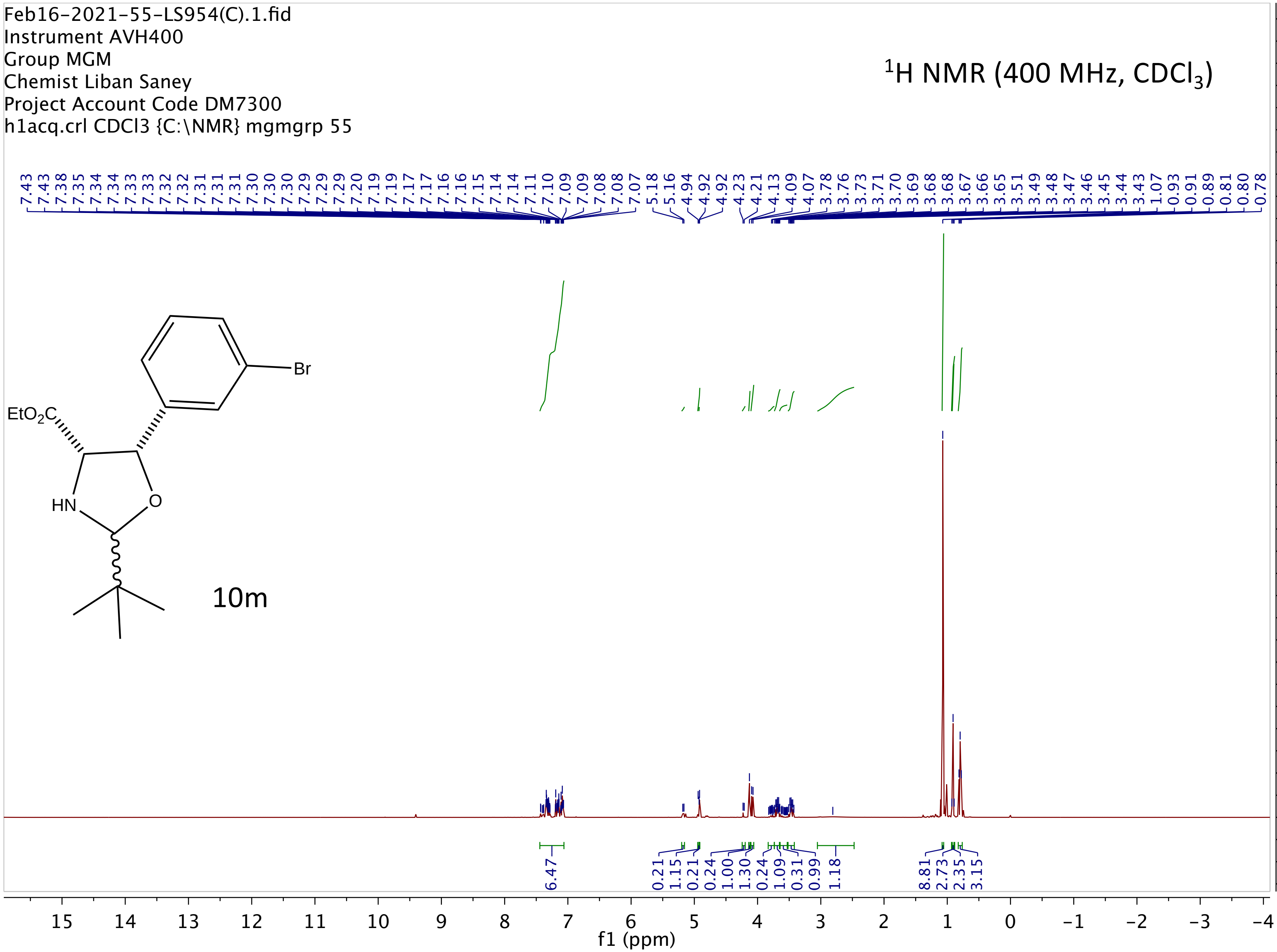




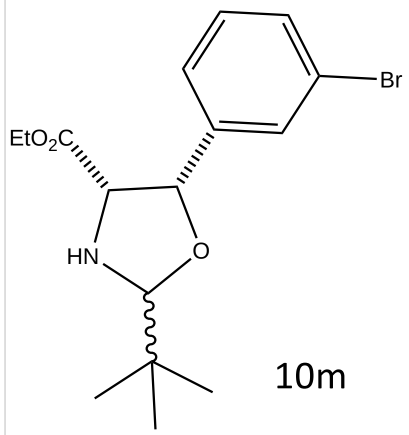
Jan31-2021-8-LS935(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 8
1H NMR (400 MHz, CDCl3)
7.23 7.23 7.23 7.20 7.19 7.19 7.19 7.18 7.18 7.18 7.17 7.16 7.16 7.16 7.15 7.15 7.15 7.14 7.14 7.14 7.13 7.13 7.13 7.12 7.12 7.11 7.11 7.11 7.11 7.10 7.10 7.10 7.10 7.09 5.19 5.17 4.95 4.93 4.23 4.21 4.13 4.10 4.08 3.78 3.76 3.73 3.71 3.70 3.69 3.68 3.67 3.66 3.66 3.65 3.64 3.50 3.49 3.48 3.47 3.46 3.45 3.44 3.42 1.07 0.92 0.91 0.90 0.88 0.80 0.79 0.77
EtO2C
HN
O
Cl
10l
4.87
0.19
1.09
0.20
0.89
1.00
0.22
0.98
0.14
0.89
1.17
8.06
1.63
2.44
2.67
f1 (ppm)


Jan31-2021-8-LS935(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 8
$^{13}$C NMR (101 MHz, $CDCl_3$)
170.55
170.08
141.43
140.58
134.20
134.00
129.49
129.43
128.27
128.09
127.29
126.54
125.11
124.47
101.73
99.35
80.60
79.73
77.16 CDCl3
65.70
65.64
61.38
61.21
36.51
33.39
25.76
25.15
13.83
13.62
EtO2C
Cl
HN
O
10l
f1 (ppm)

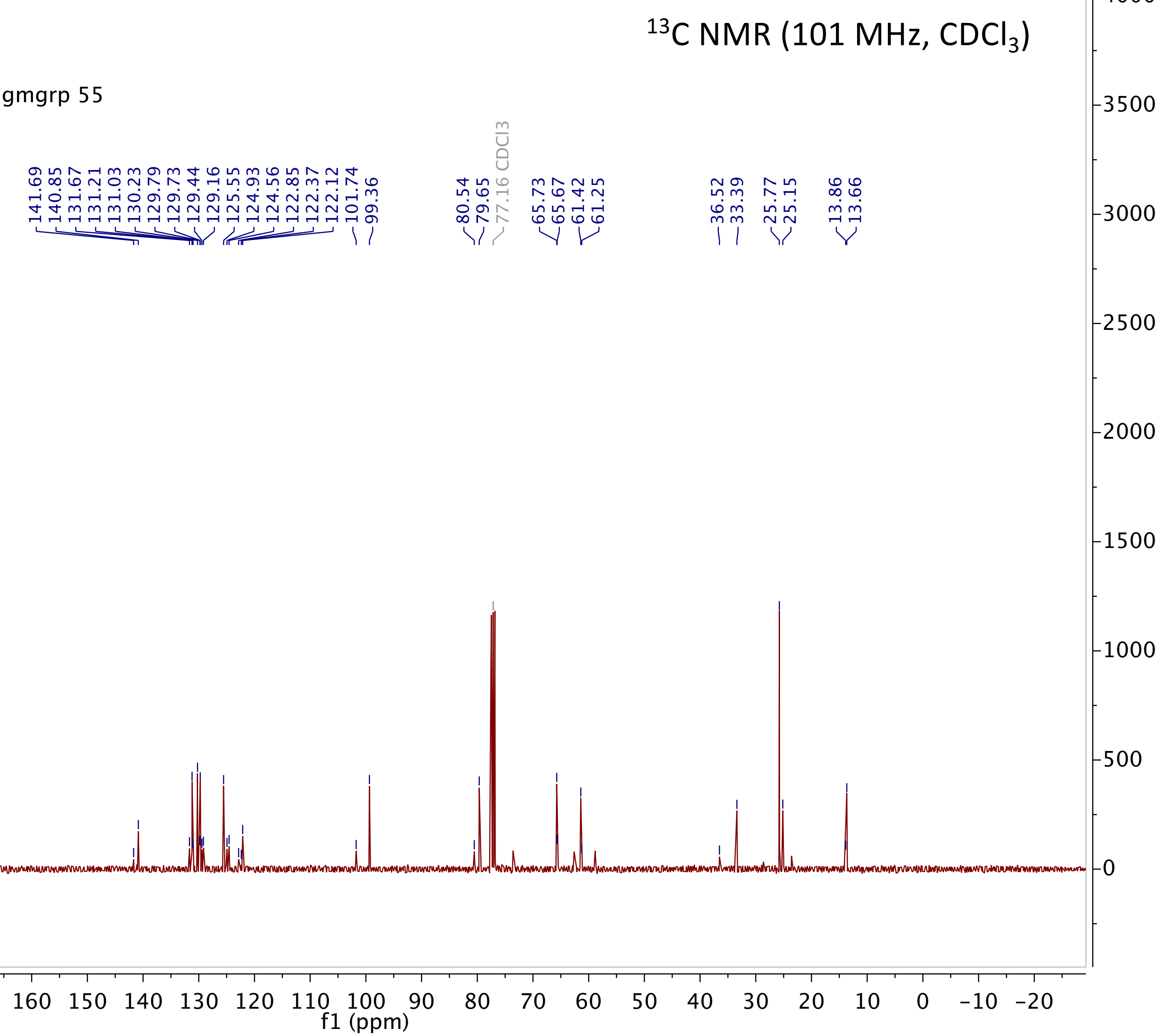
Feb16-2021-55-LS954(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 55



Feb16-2021-55-LS954(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 55

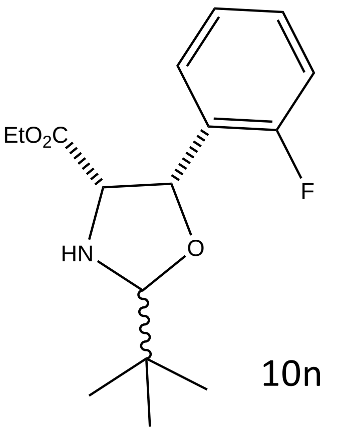


10m

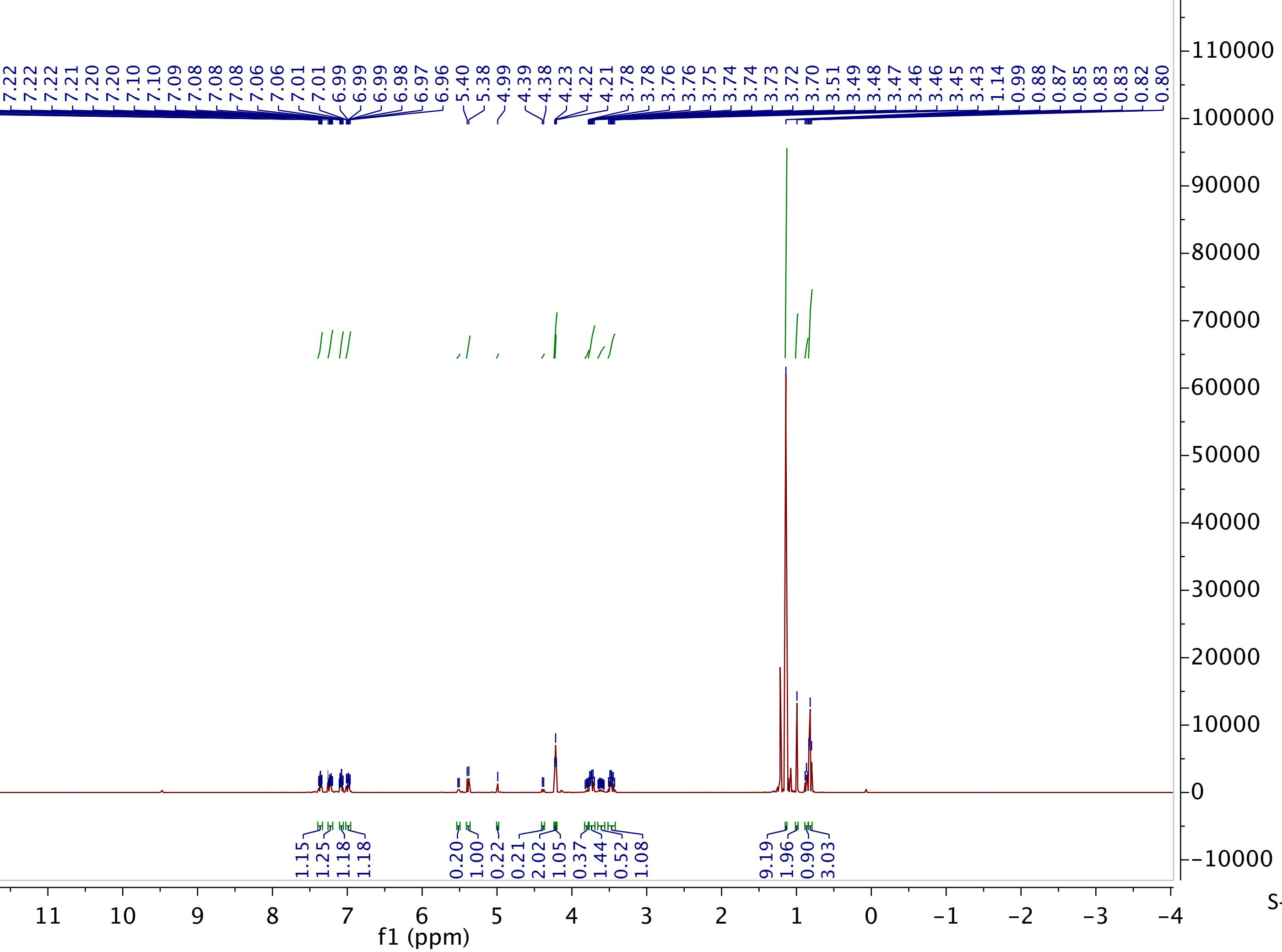


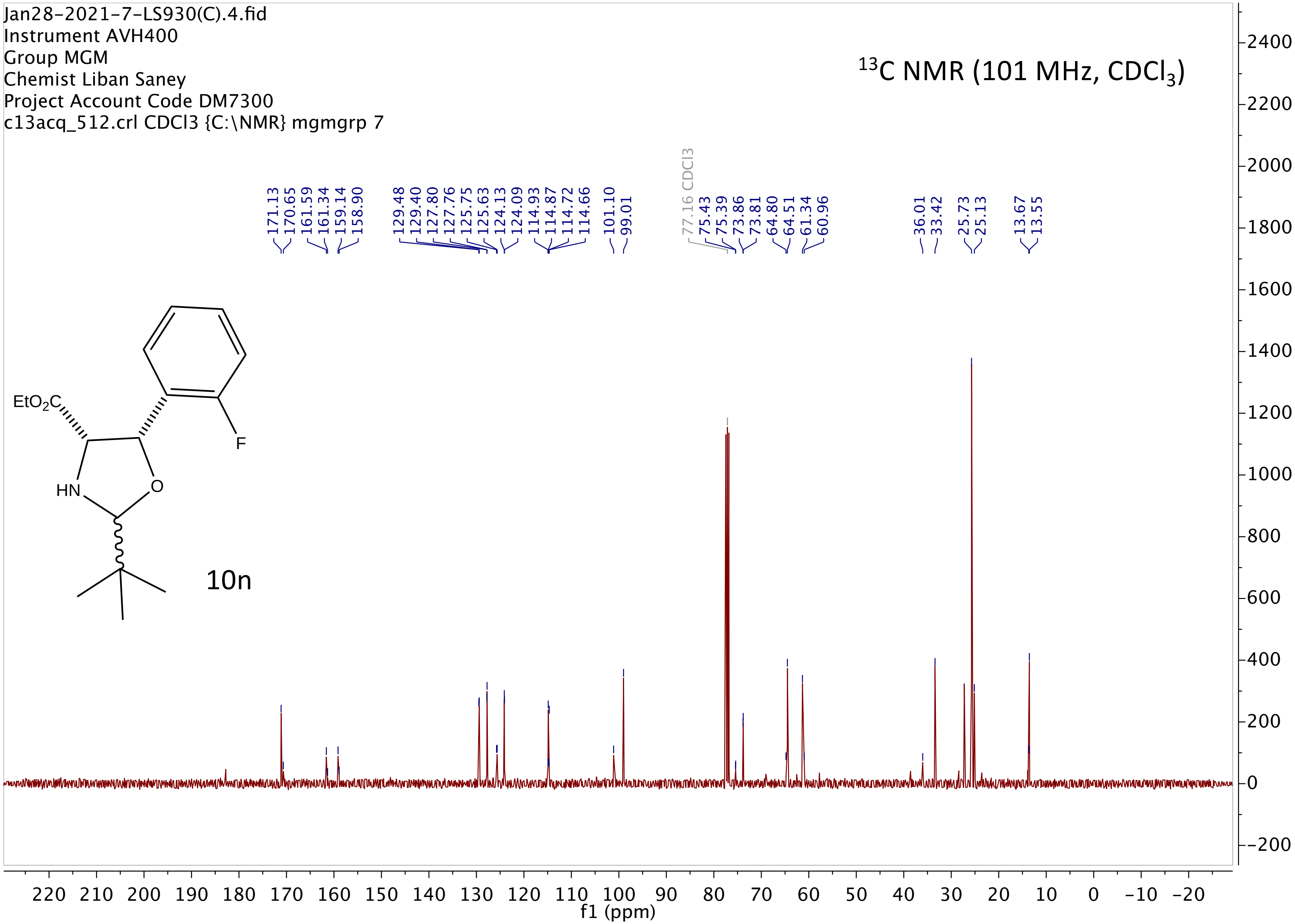
Jan28-2021-7-LS930(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 7

$^1$H NMR (400 MHz, $CDCl_3$)

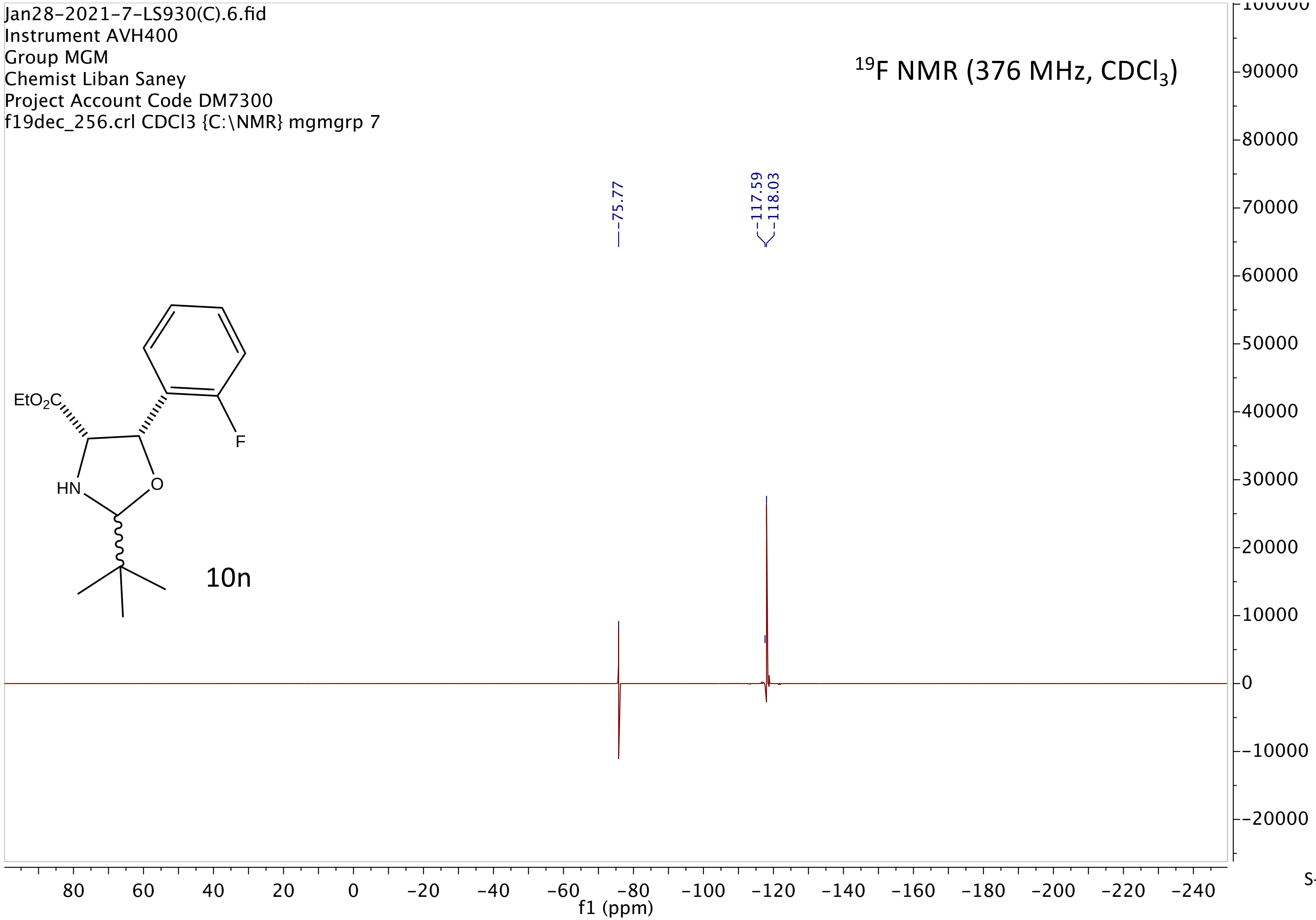


10n



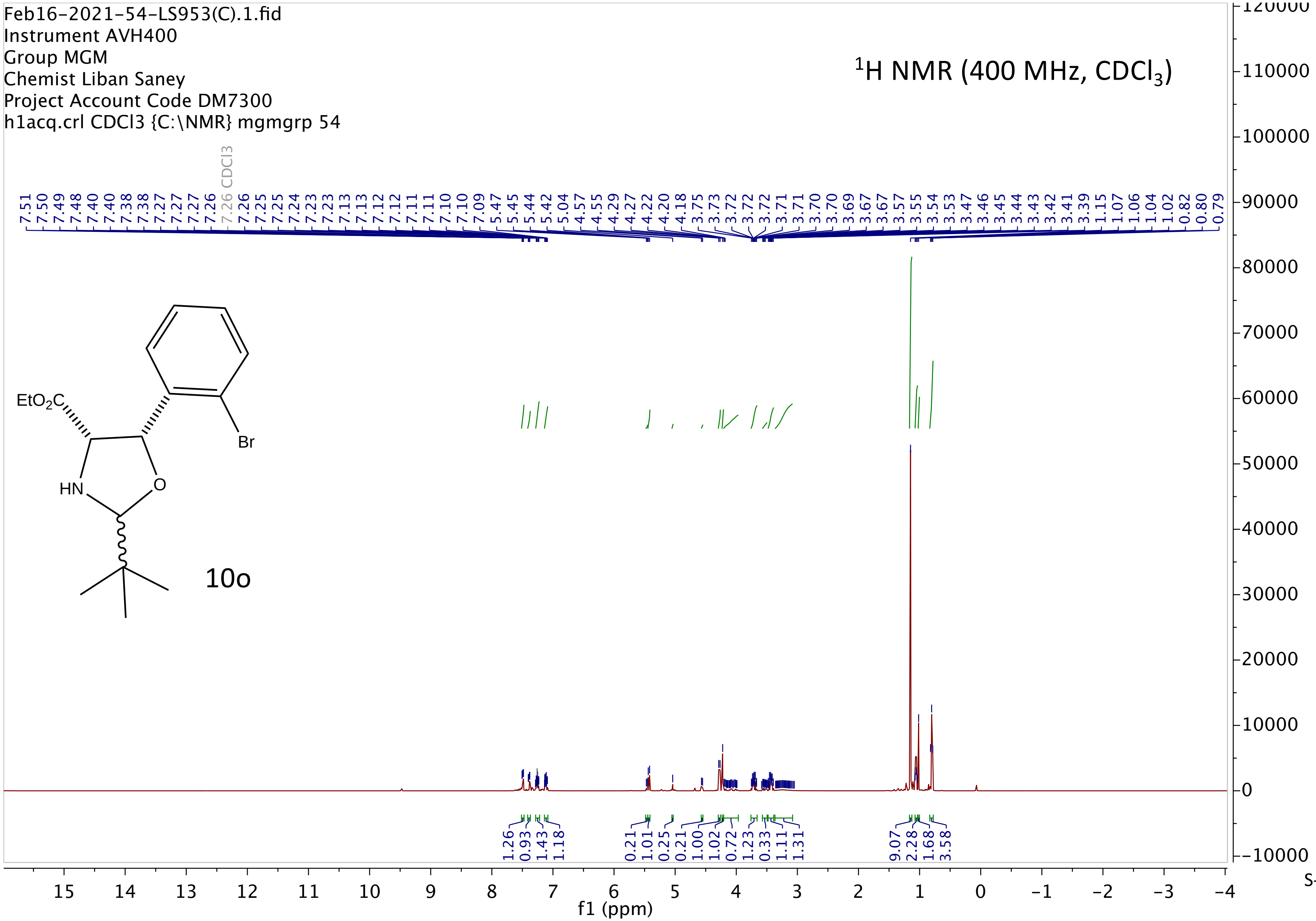


Jan28-2021-7-LS930(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 7
13C NMR (101 MHz, CDCl3)
171.13
170.65
161.59
161.34
159.14
158.90
129.48
129.40
127.80
127.76
125.75
125.63
124.13
124.09
114.93
114.87
114.72
114.66
101.10
99.01
77.16 CDCl3
75.43
75.39
73.86
73.81
64.80
64.51
61.34
60.96
36.01
33.42
25.73
25.13
13.67
13.55
EtO2C
HN
O
F
10n
f1 (ppm)


Jan28-2021-7-LS930(C).6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 7
$^{19}$F NMR (376 MHz, $CDCl_3$)
-75.77
-117.59
-118.03
$EtO_2C$
HN
O
F
10n
f1 (ppm)

Feb16-2021-54-LS953(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 54

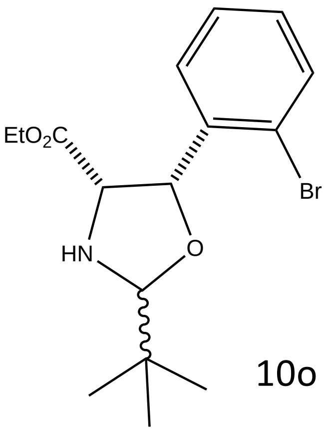
$^1$H NMR (400 MHz, $CDCl_3$)



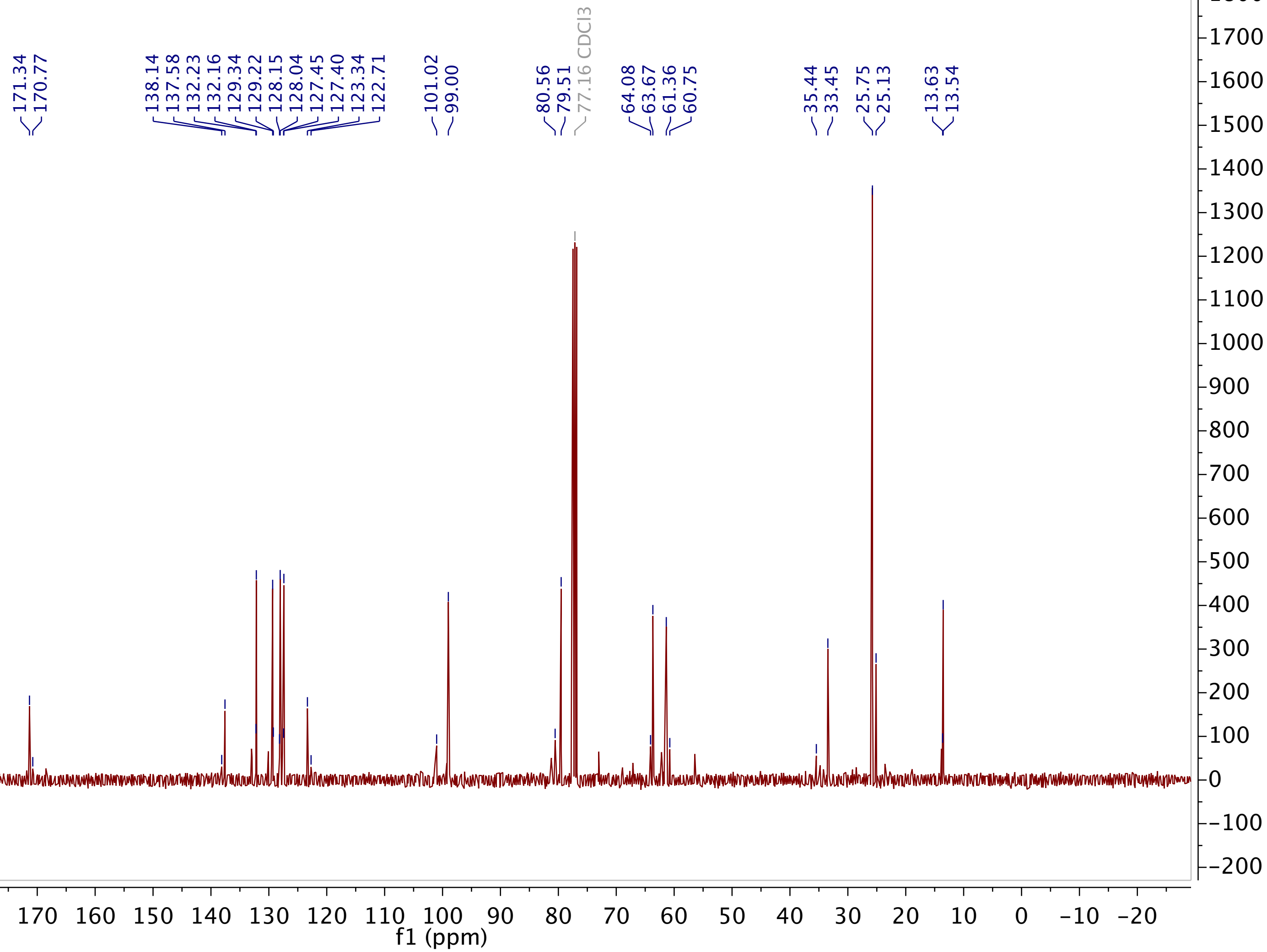
10o

Feb16-2021-54-LS953(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 54

$^{13}C$ NMR (101 MHz, $CDCl_3$)

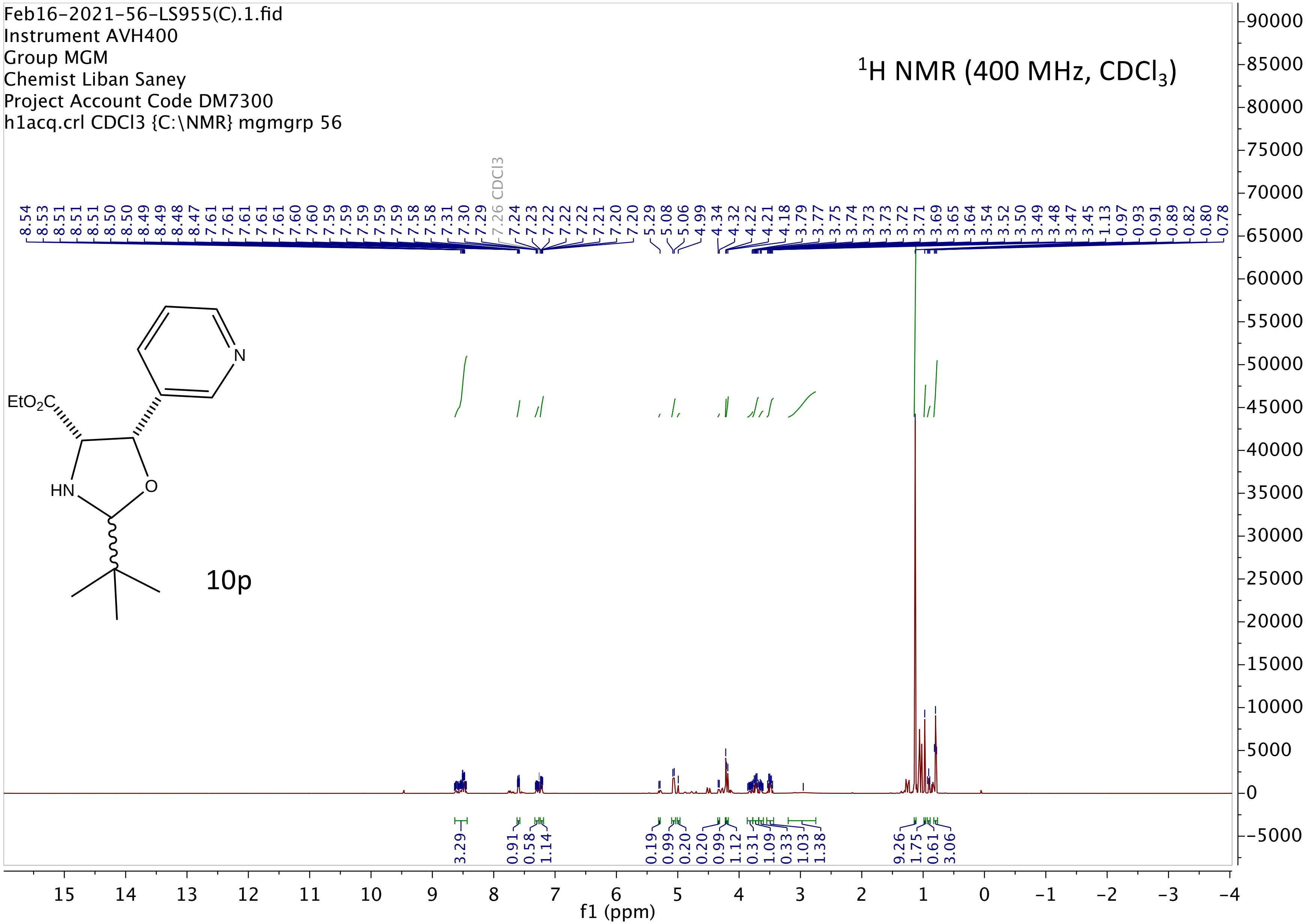


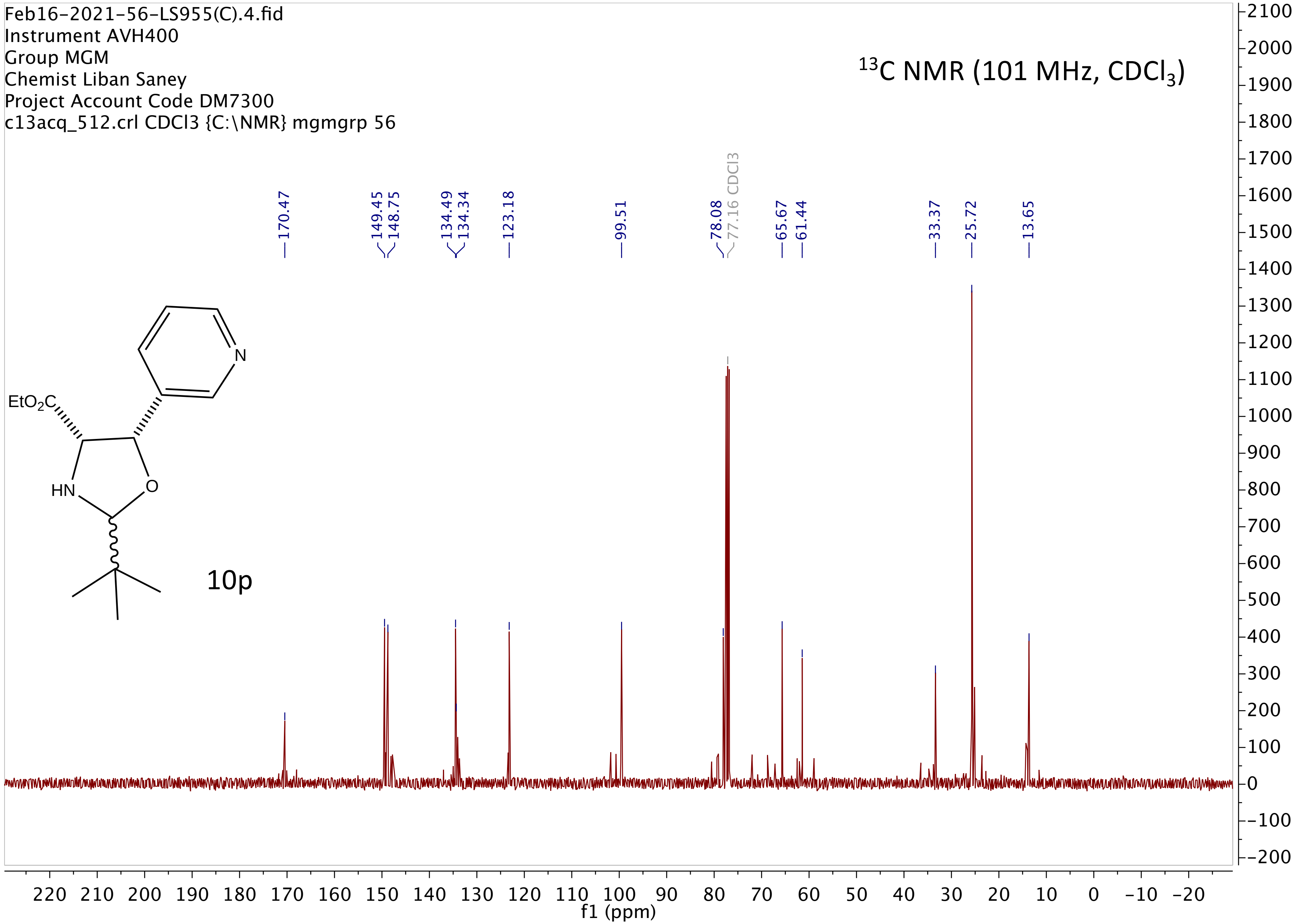

10o



Feb16-2021-56-LS955(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 56

$^1$H NMR (400 MHz, $CDCl_3$)

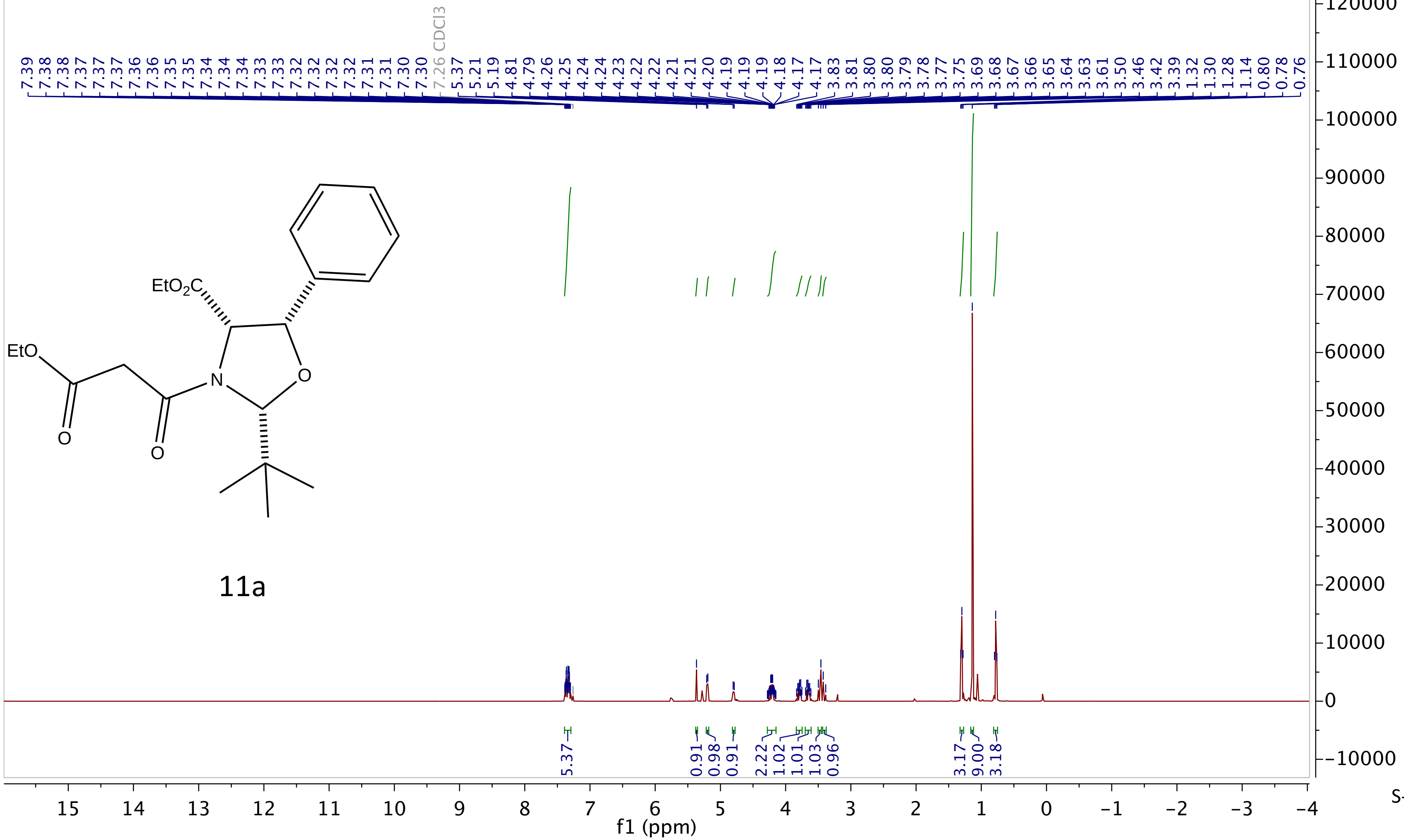




Feb16-2021-56-LS955(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 56
$^{13}$C NMR (101 MHz, $CDCl_3$)
170.47
149.45
148.75
134.49
134.34
123.18
99.51
78.08
77.16 CDCl3
65.67
61.44
33.37
25.72
13.65
$EtO_2C$
HN
O
N
10p
f1 (ppm)

Jun21-2019-60-LS439(P) B6-C8.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

$^1$H NMR (400 MHz, $CDCl_3$)

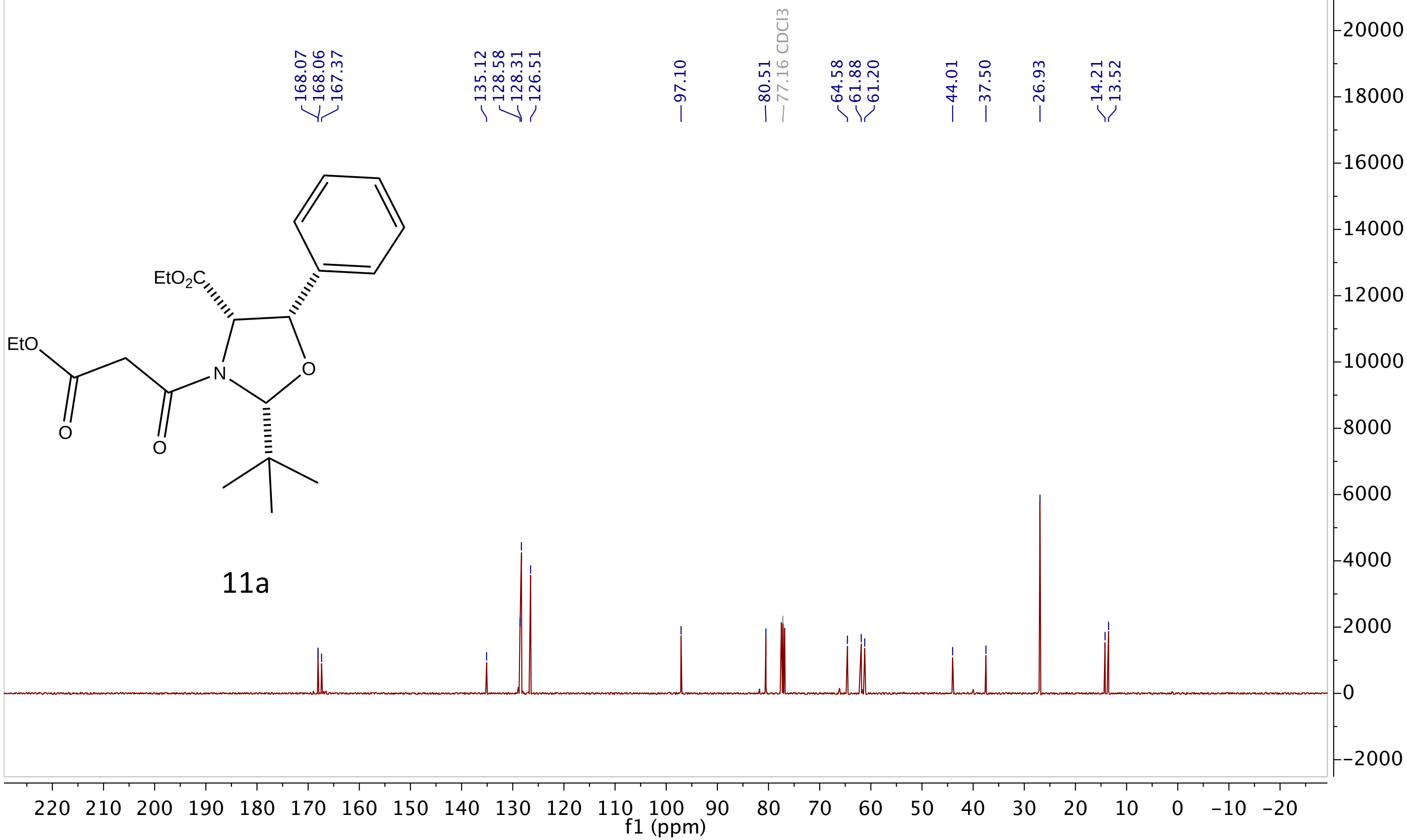


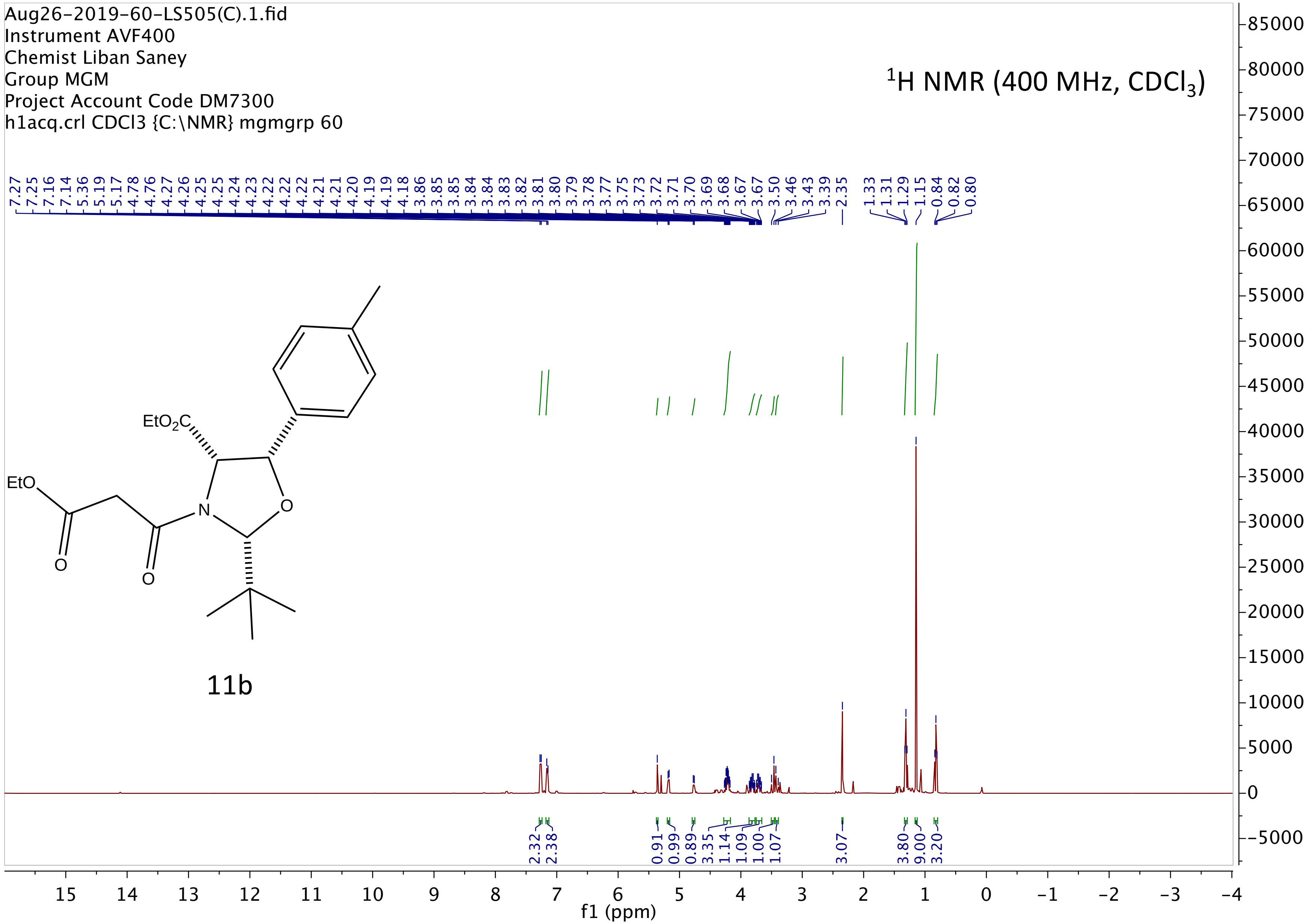

11a

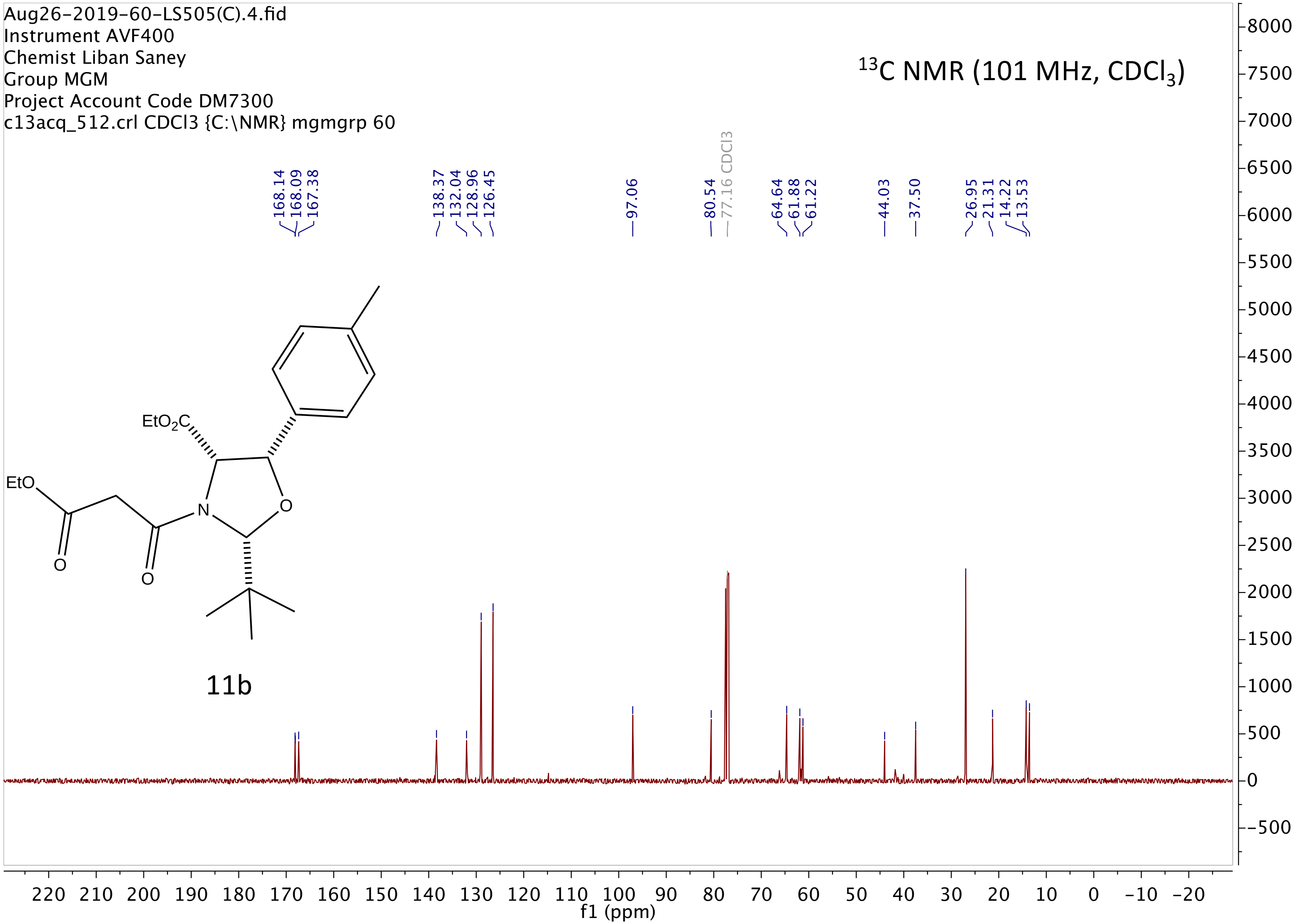
Jun21-2019-60-LS439(P) B6-C8.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

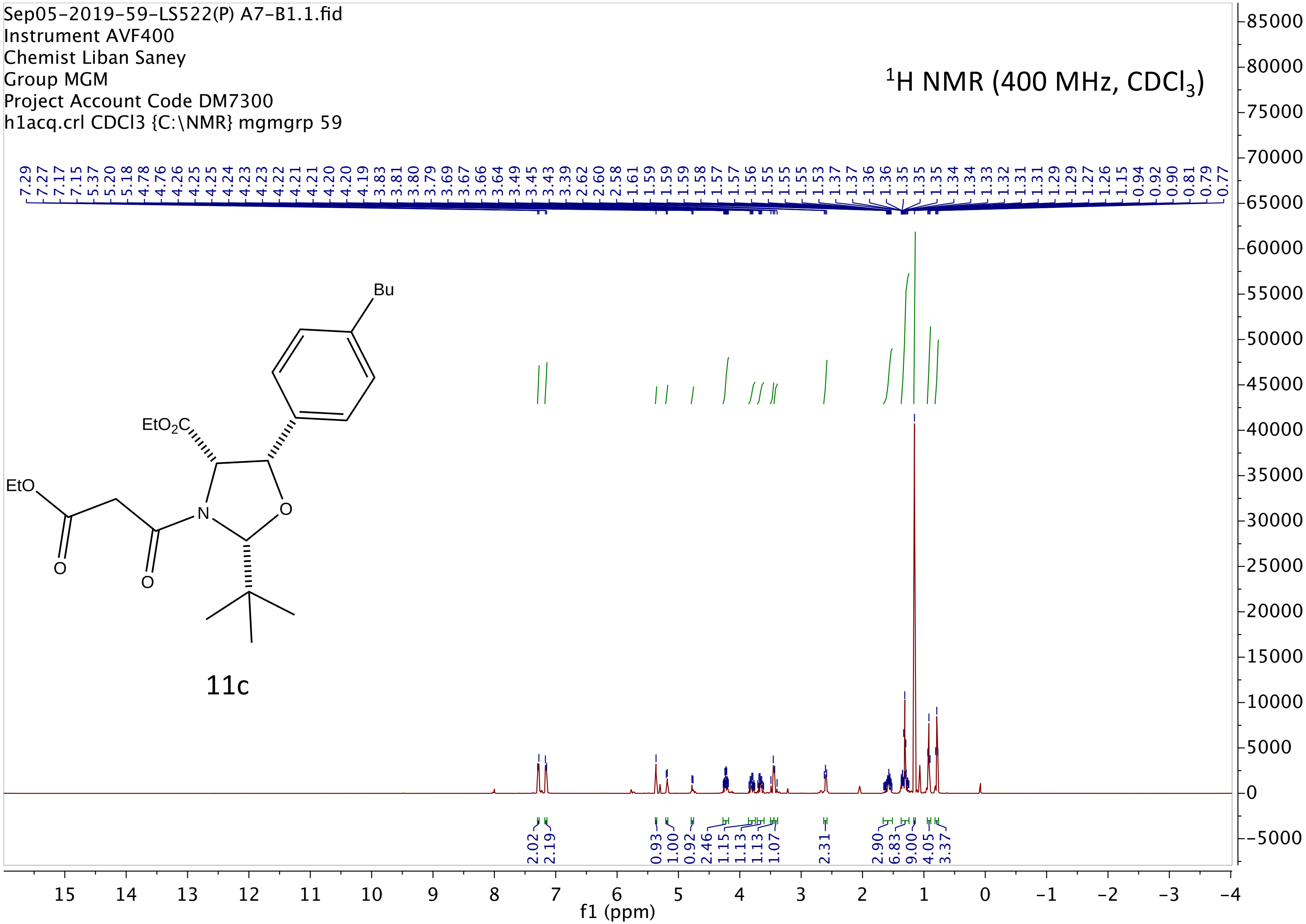
$^{13}$C NMR (101 MHz, $CDCl_3$)

11a



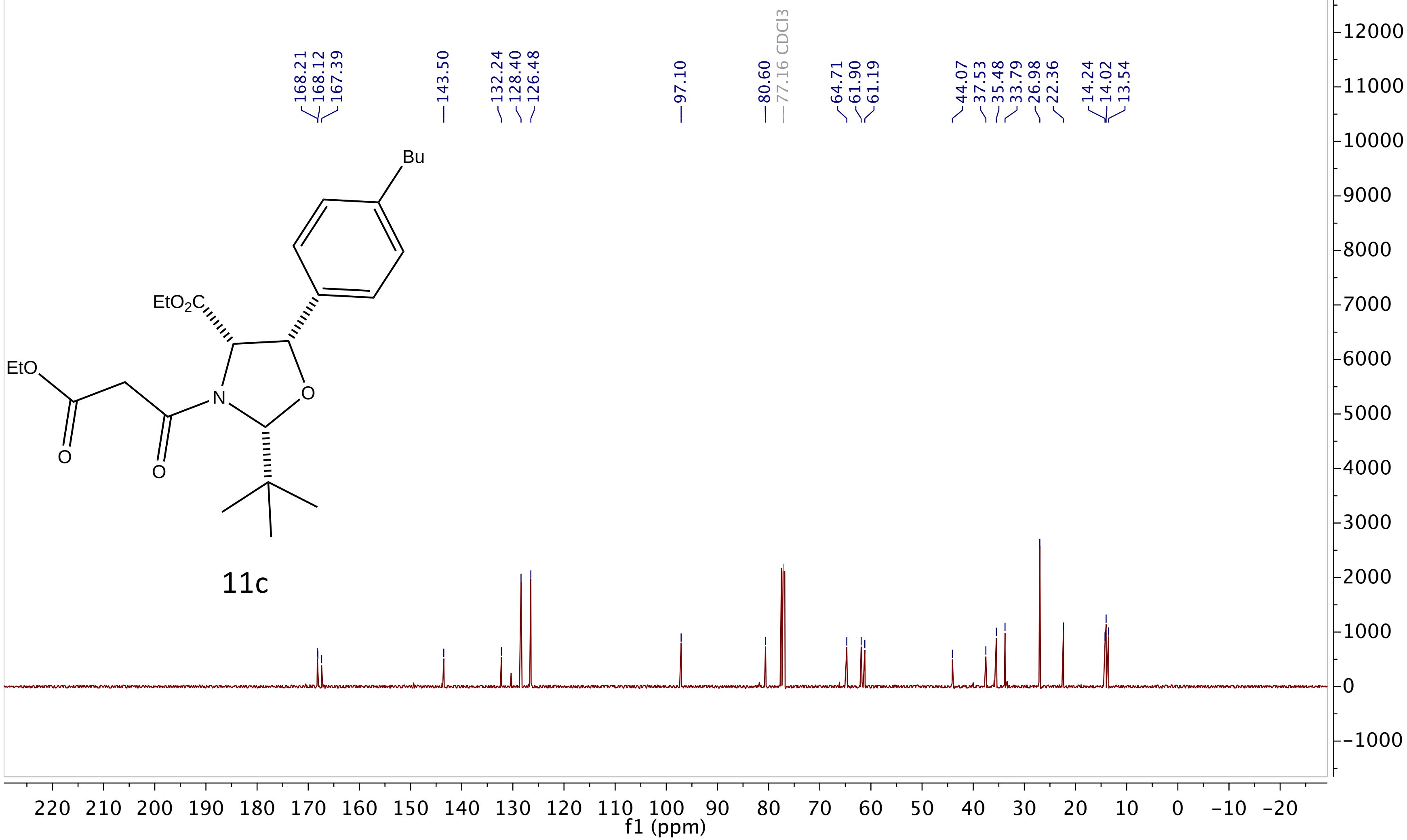

Aug26-2019-60-LS505(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
7.27 7.25 7.16 7.14 5.36 5.19 5.17 4.78 4.76 4.27 4.26 4.25 4.25 4.24 4.23 4.22 4.22 4.22 4.21 4.21 4.20 4.19 4.19 4.18 3.86 3.85 3.84 3.84 3.83 3.82 3.81 3.80 3.79 3.78 3.77 3.75 3.73 3.72 3.71 3.70 3.69 3.68 3.67 3.50 3.46 3.43 3.39 2.35 1.33 1.31 1.29 1.15 0.84 0.82 0.80
EtO2C
EtO
N
O
O
O
11b
2.32 2.38 0.91 0.99 0.89 3.35 1.14 1.09 1.00 1.07 3.07 3.80 9.00 3.20
f1 (ppm)

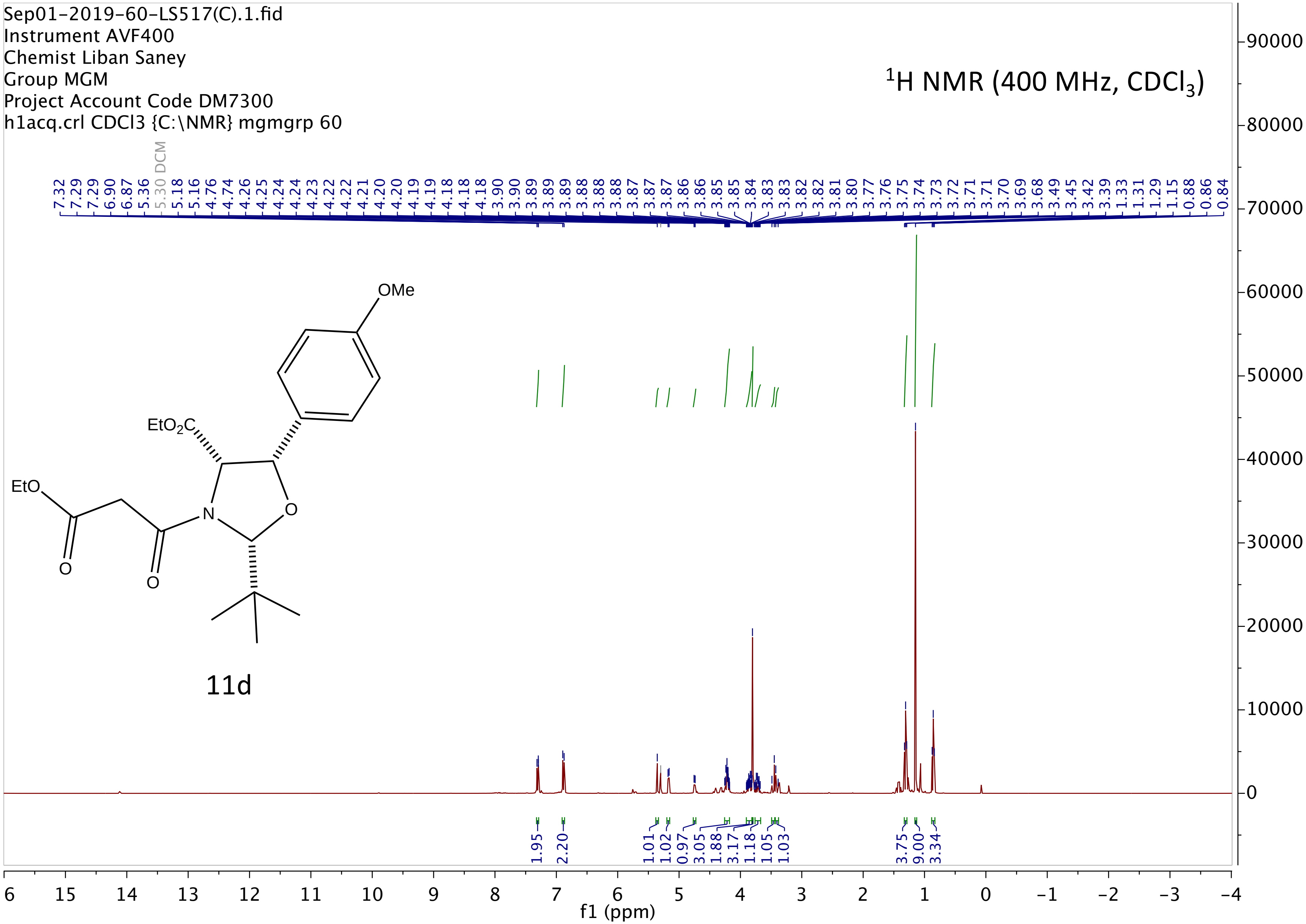

Aug26-2019-60-LS505(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, CDCl$_3$)
168.14
168.09
167.38
138.37
132.04
128.96
126.45
97.06
80.54
77.16 CDCl3
64.64
61.88
61.22
44.03
37.50
26.95
21.31
14.22
13.53
EtO$_2$C
EtO
N
O
O
O
11b
f1 (ppm)


Sep05-2019-59-LS522(P) A7-B1.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59
$^1$H NMR (400 MHz, $CDCl_3$)
7.29 7.27 7.17 7.15 5.37 5.20 5.18 4.78 4.76 4.26 4.25 4.25 4.24 4.23 4.23 4.22 4.21 4.21 4.20 4.20 4.19 3.83 3.81 3.80 3.79 3.69 3.67 3.66 3.64 3.49 3.45 3.43 3.39 2.62 2.60 2.58 1.61 1.59 1.59 1.59 1.58 1.57 1.57 1.56 1.55 1.55 1.55 1.53 1.37 1.37 1.36 1.36 1.35 1.35 1.35 1.34 1.34 1.33 1.32 1.31 1.31 1.29 1.29 1.27 1.26 1.15 0.94 0.92 0.90 0.81 0.79 0.77
2.02 2.19 0.93 1.00 0.92 2.46 1.15 1.13 1.13 1.07 2.31 2.90 6.83 9.00 4.05 3.37
Bu
$EtO_2C$
EtO
N
O
O
O
11c
f1 (ppm)

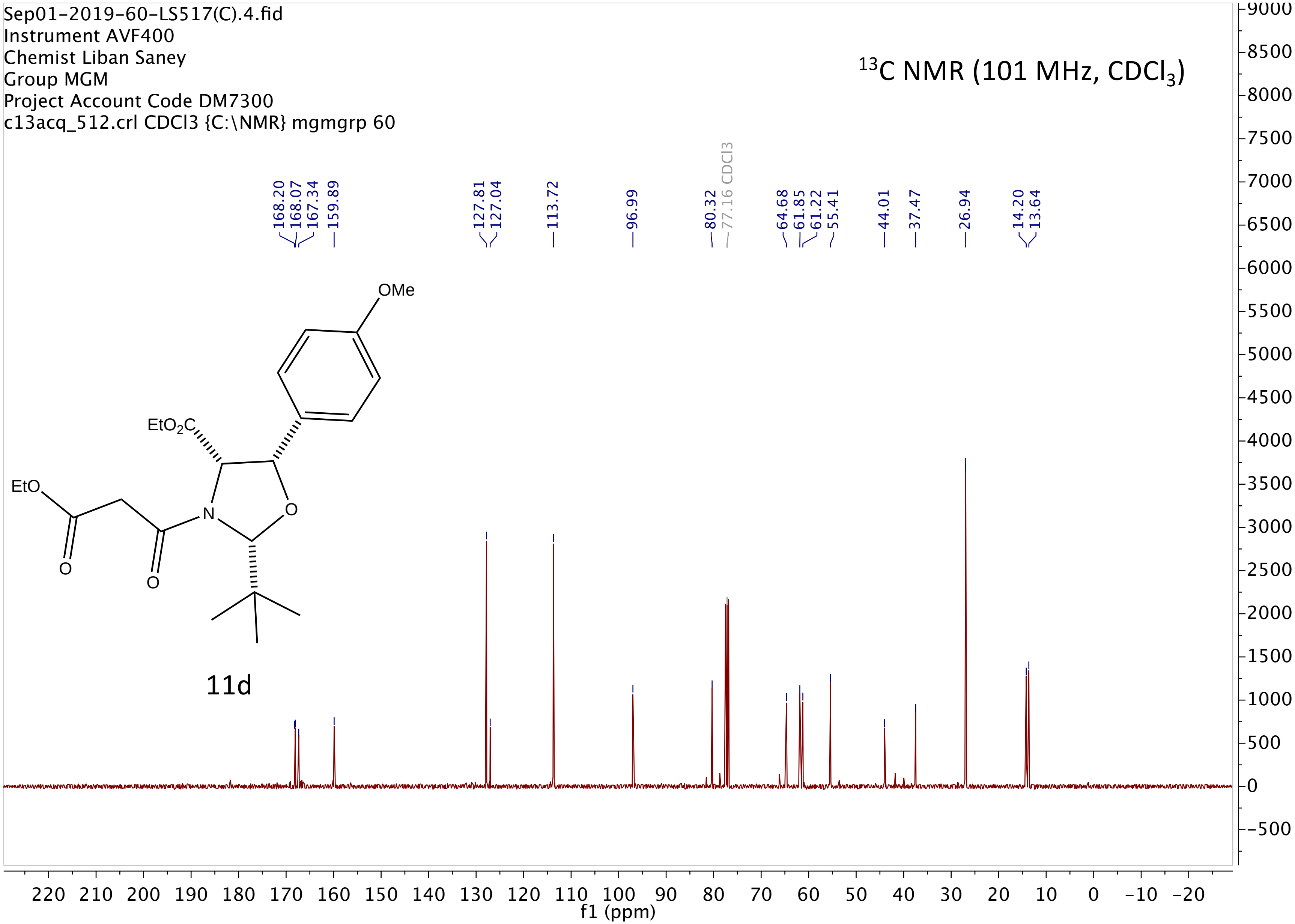
Sep05-2019-59-LS522(P) A7-B1.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59

$^{13}C$ NMR (101 MHz, $CDCl_3$)

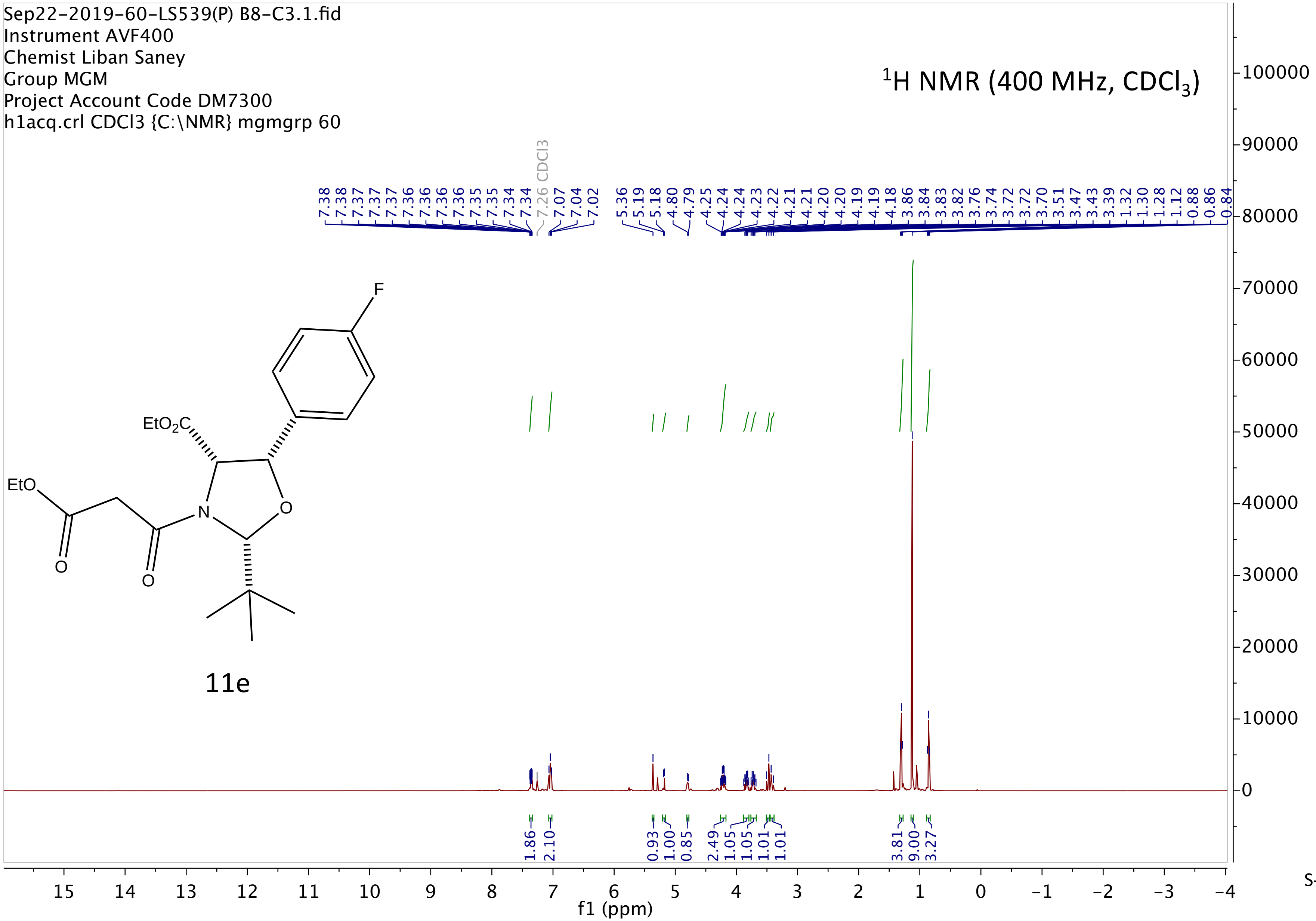


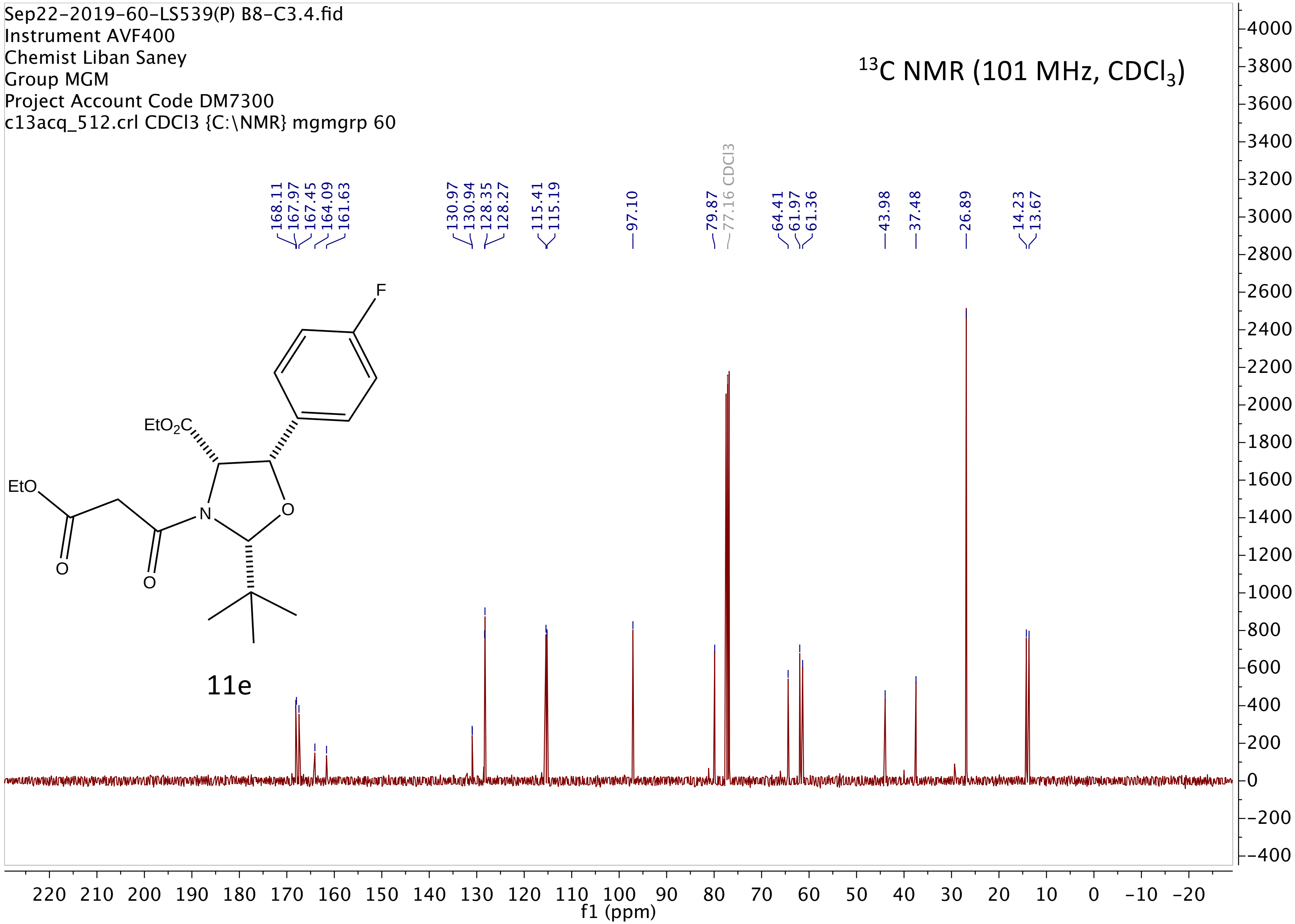

Sep01-2019-60-LS517(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
$^{1}$H NMR (400 MHz, $CDCl_3$)
7.32 7.29 7.29 6.90 6.87 5.36 5.30 DCM 5.18 5.16 4.76 4.74 4.26 4.25 4.24 4.24 4.23 4.22 4.22 4.21 4.20 4.20 4.19 4.18 4.18 4.18 3.90 3.89 3.89 3.89 3.88 3.88 3.87 3.87 3.86 3.85 3.85 3.84 3.83 3.83 3.82 3.81 3.80 3.77 3.76 3.75 3.74 3.73 3.72 3.71 3.71 3.70 3.69 3.68 3.49 3.45 3.42 3.39 1.33 1.31 1.29 1.15 0.88 0.86 0.84
OMe
$EtO_2C$
EtO
N
O
O
O
1.95 2.20 1.01 1.02 0.97 3.05 1.88 3.17 1.18 1.05 1.03 3.75 9.00 3.34
f1 (ppm)

11d


Sep01-2019-60-LS517(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
13C NMR (101 MHz, CDCl3)
168.20
168.07
167.34
159.89
127.81
127.04
113.72
96.99
80.32
77.16 CDCl3
64.68
61.85
61.22
55.41
44.01
37.47
26.94
14.20
13.64
OMe
EtO2C
EtO
N
O
O
O
11d
f1 (ppm)

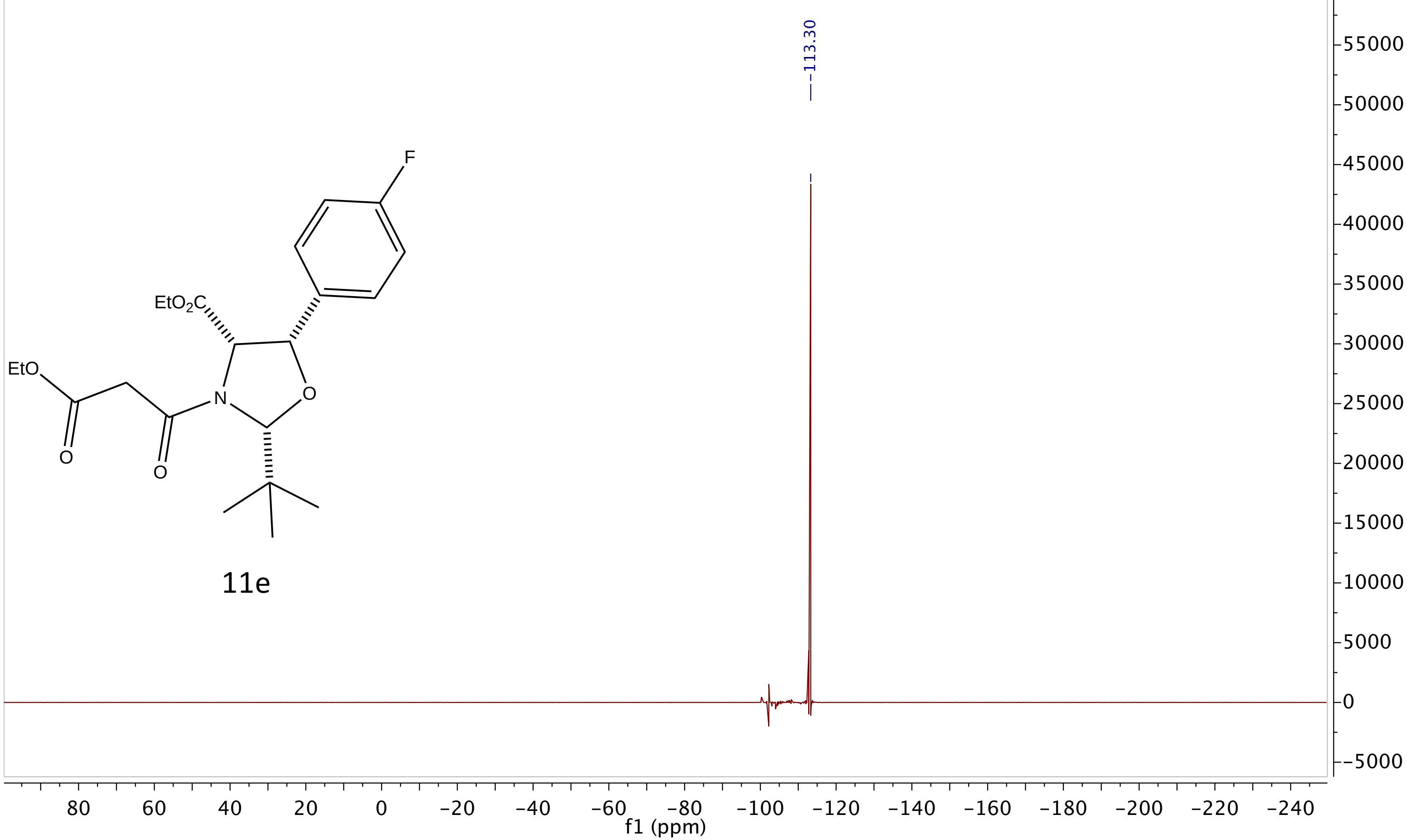
Sep22-2019-60-LS539(P) B8-C3.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60




Sep22-2019-60-LS539(P) B8-C3.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
13C NMR (101 MHz, CDCl3)
168.11
167.97
167.45
164.09
161.63
130.97
130.94
128.35
128.27
115.41
115.19
97.10
79.87
77.16 CDCl3
64.41
61.97
61.36
43.98
37.48
26.89
14.23
13.67
F
EtO2C
EtO
N
O
O
O
11e
f1 (ppm)

Sep22-2019-60-LS539(P) B8-C3.8.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 60

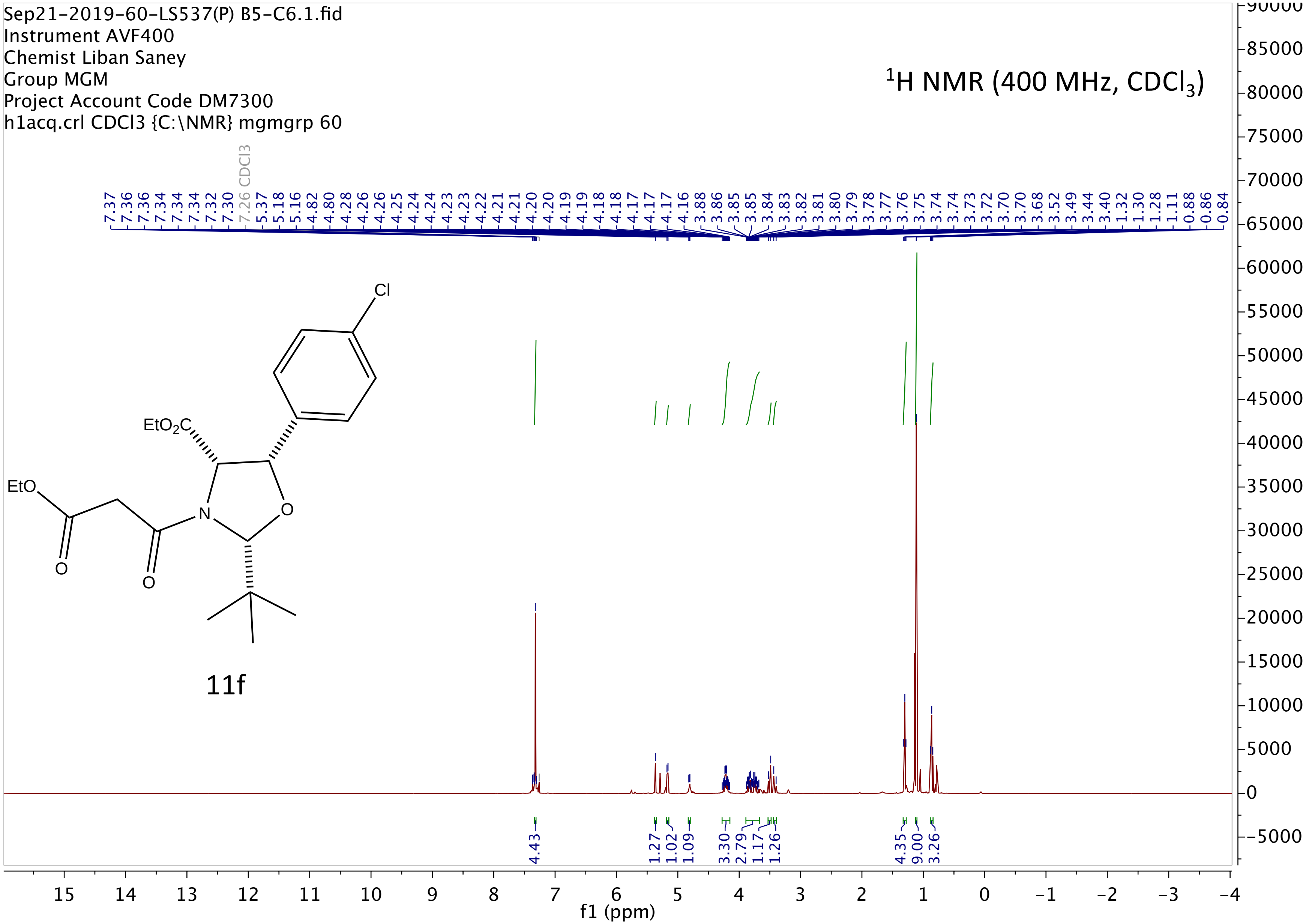
$^{19}$F NMR (377 MHz, $CDCl_3$)




11e

Sep21-2019-60-LS537(P) B5-C6.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

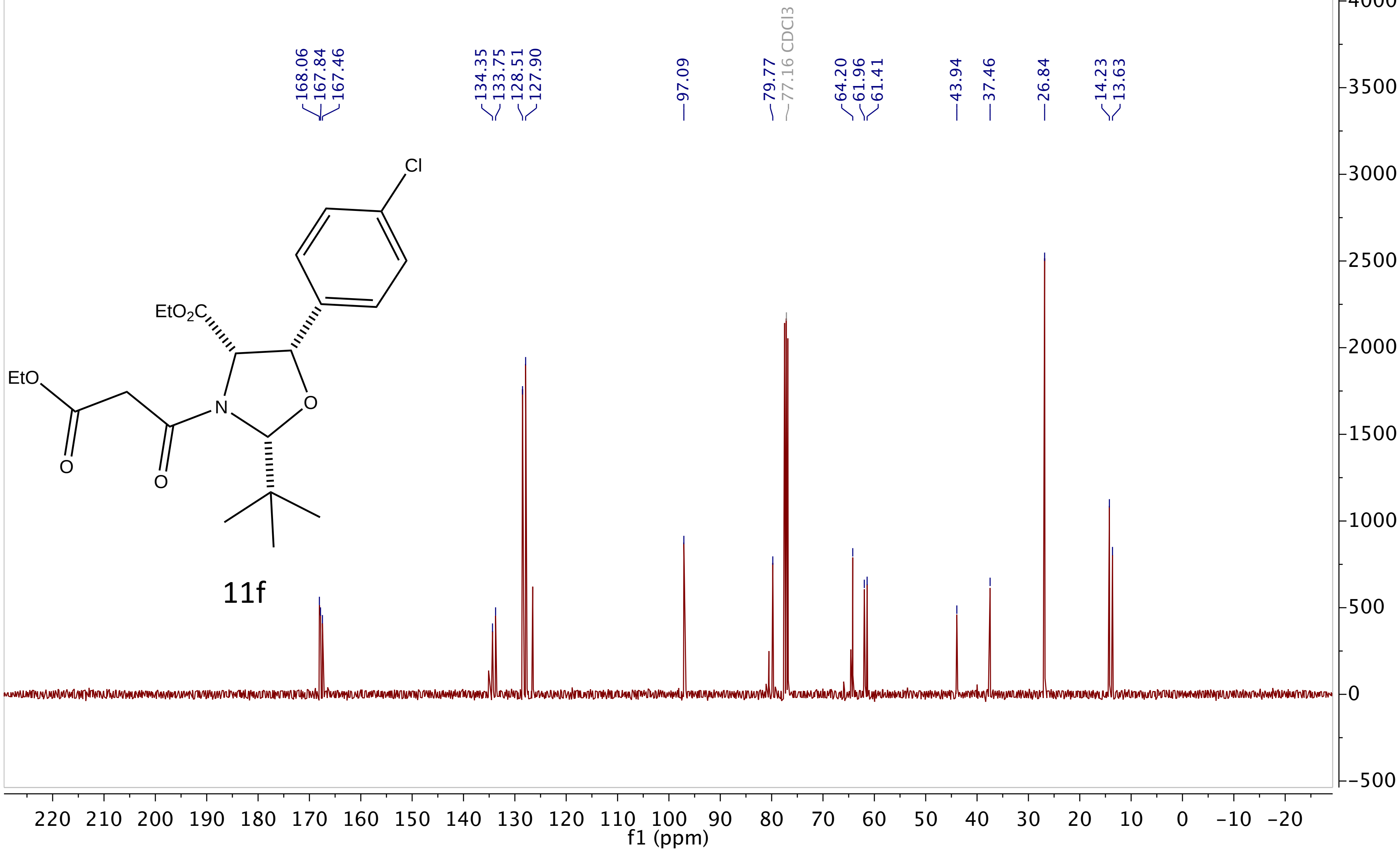
$^1$H NMR (400 MHz, $CDCl_3$)



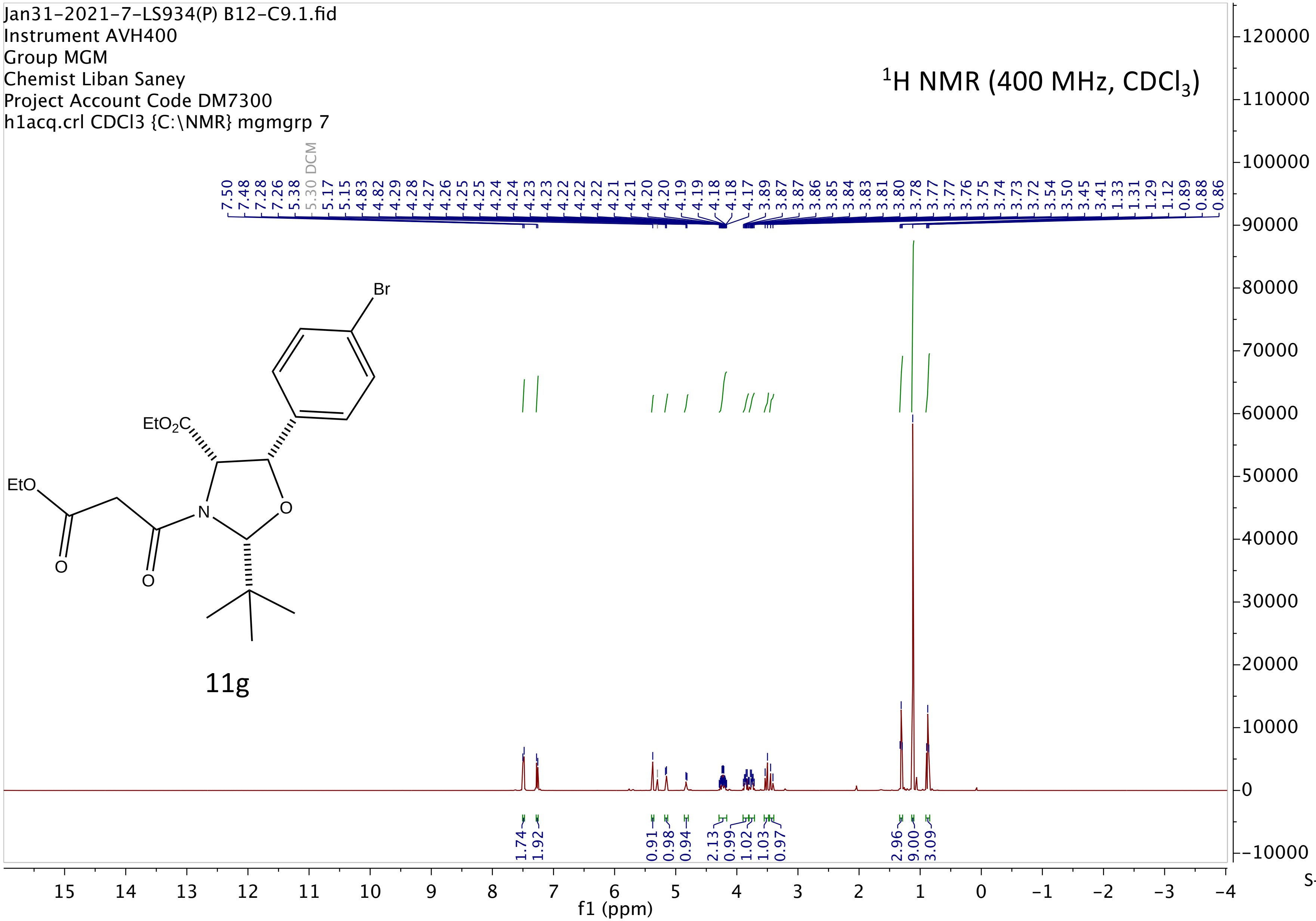

11f

Sep21-2019-60-LS537(P) B5-C6.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}$C NMR (101 MHz, $CDCl_3$)

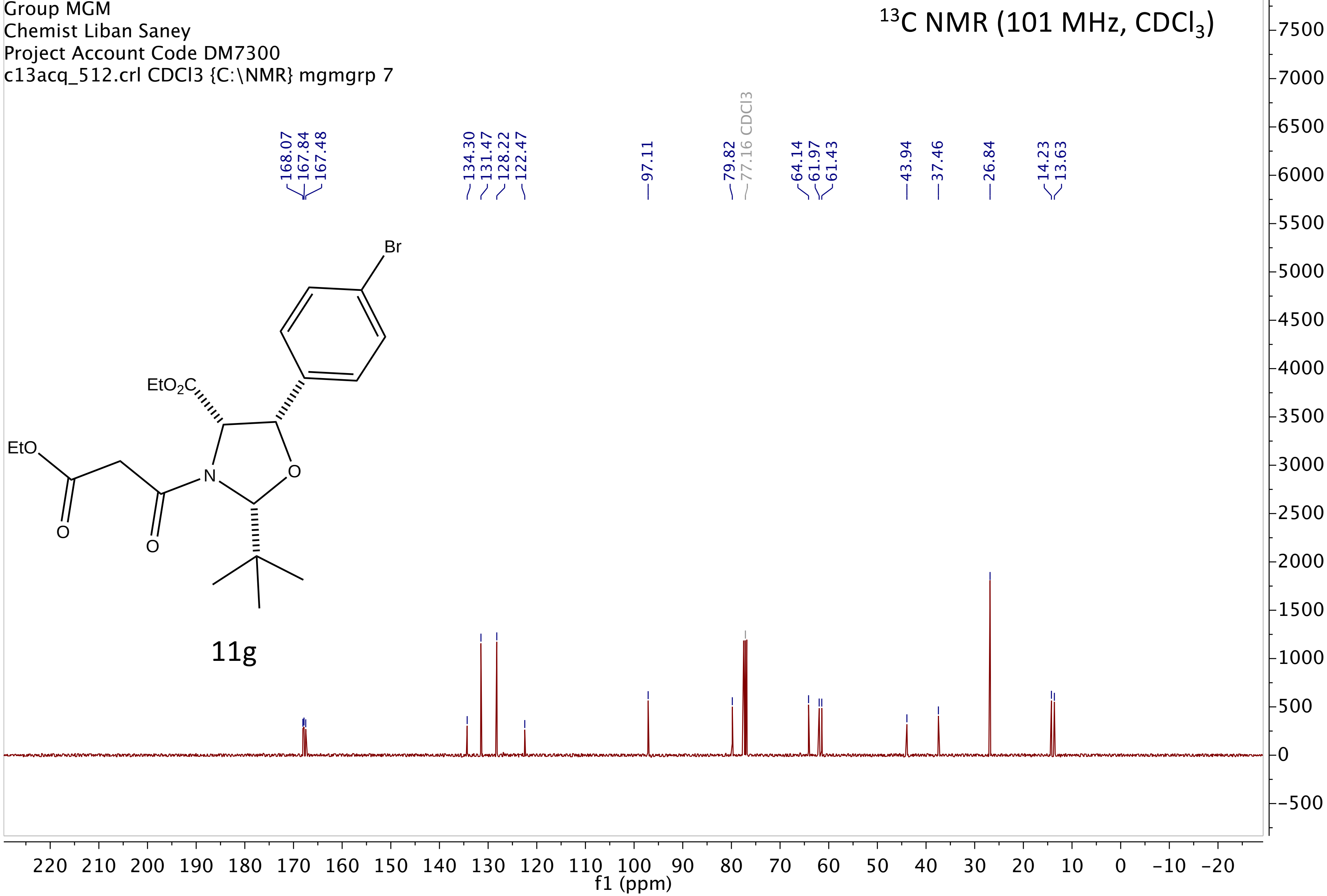


Jan31-2021-7-LS934(P) B12-C9.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 7



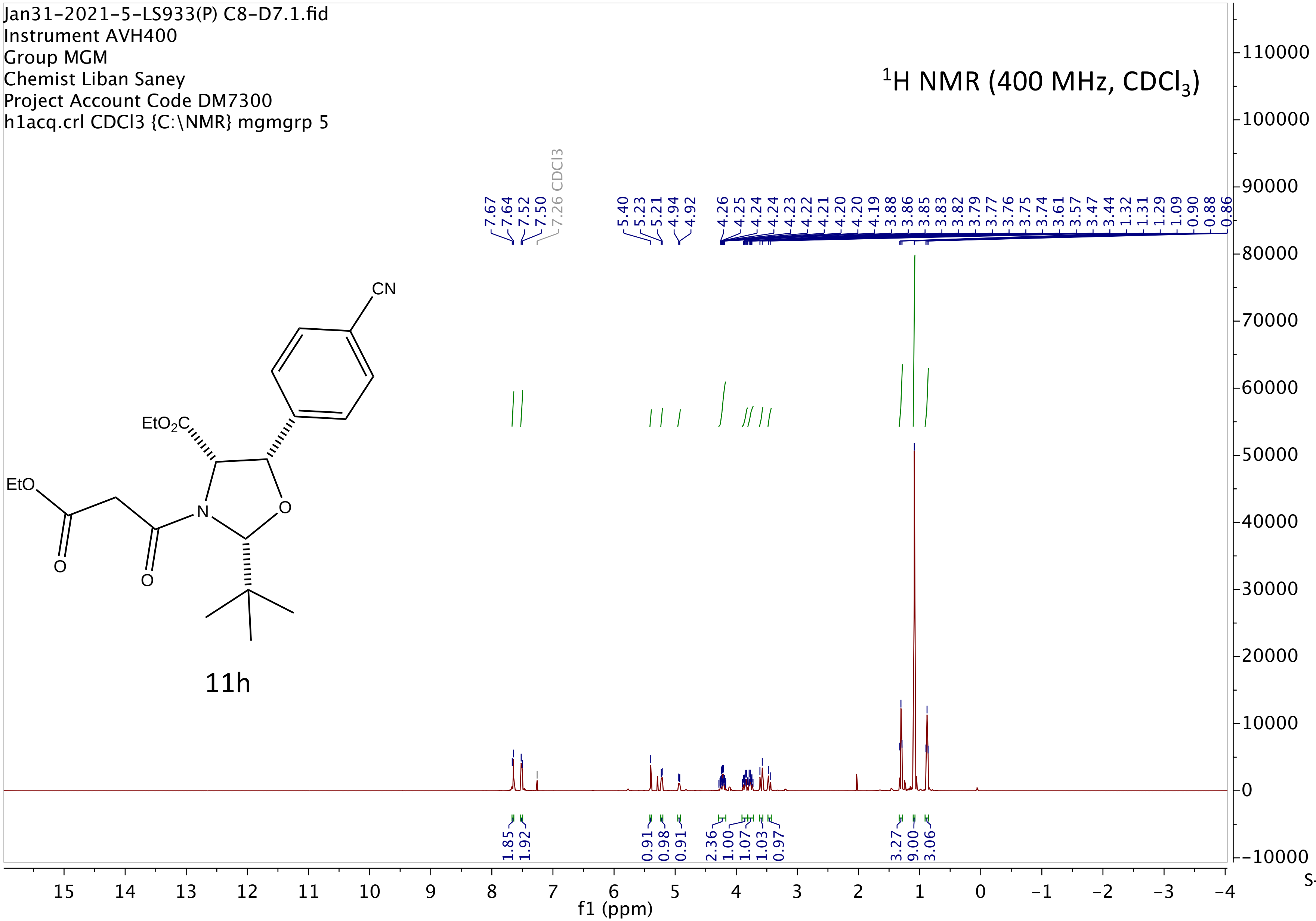

11g

Jan31-2021-7-LS934(P) B12-C9.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 7



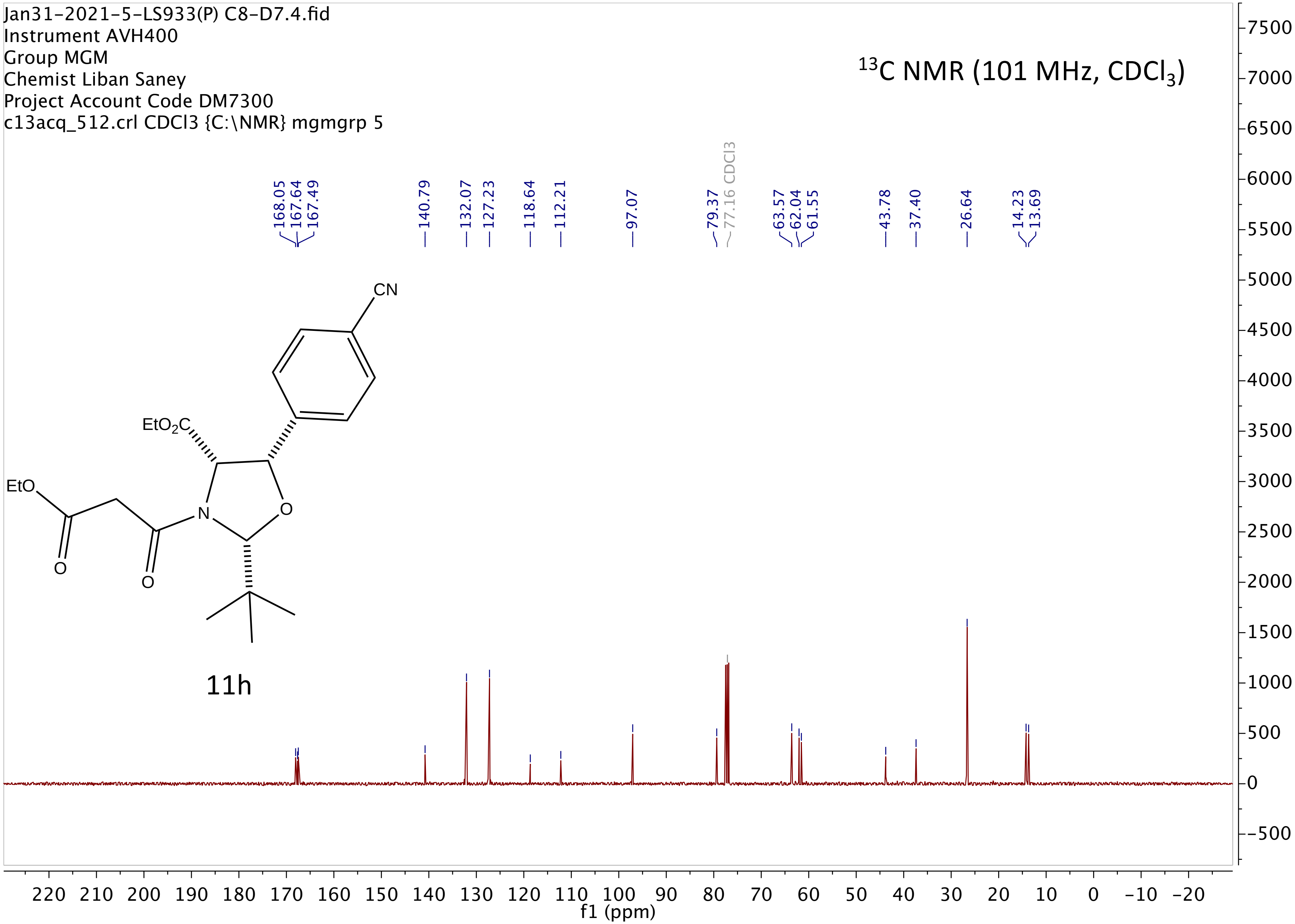

11g

Jan31-2021-5-LS933(P) C8-D7.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 5

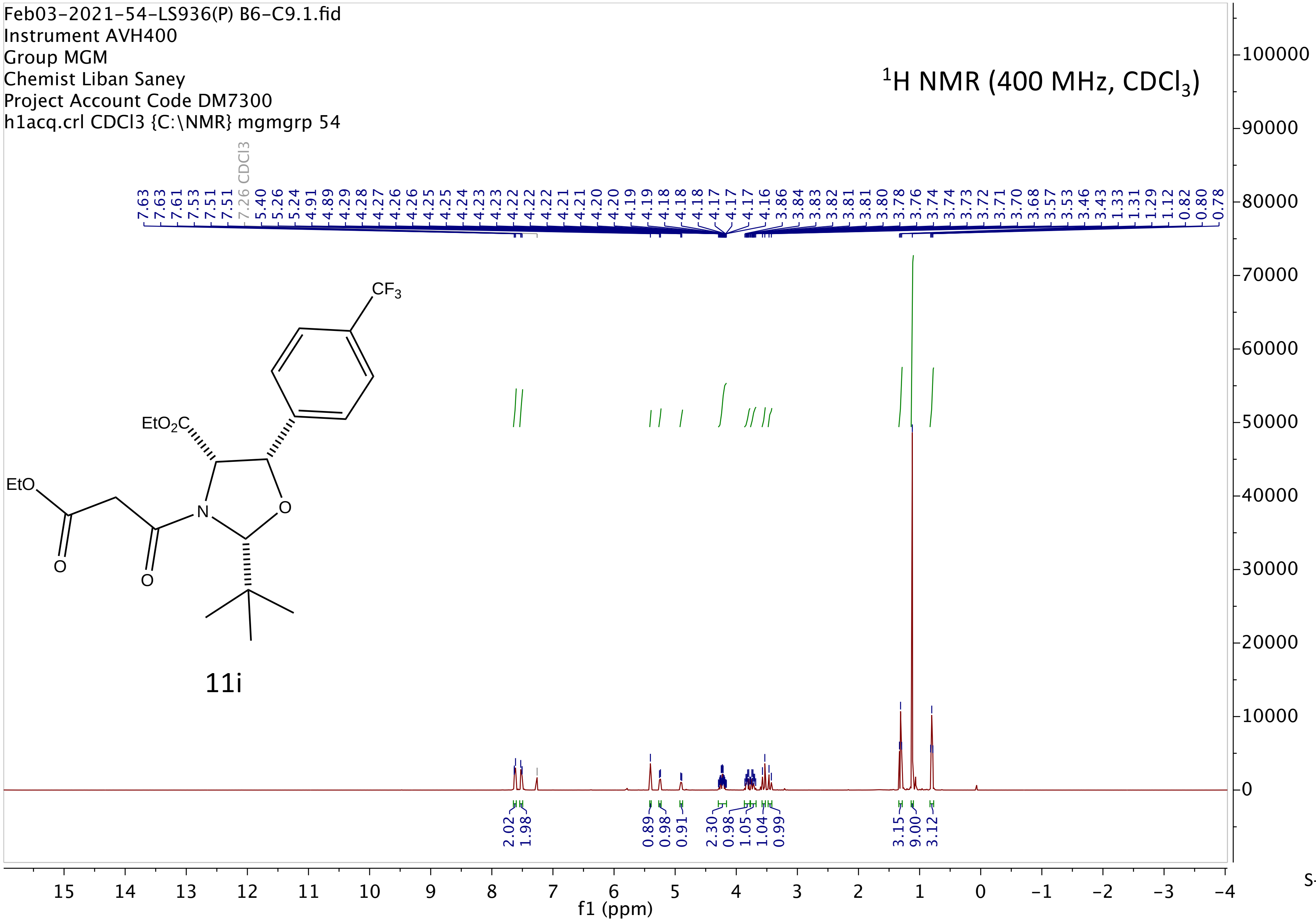



11h

Jan31-2021-5-LS933(P) C8-D7.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 5

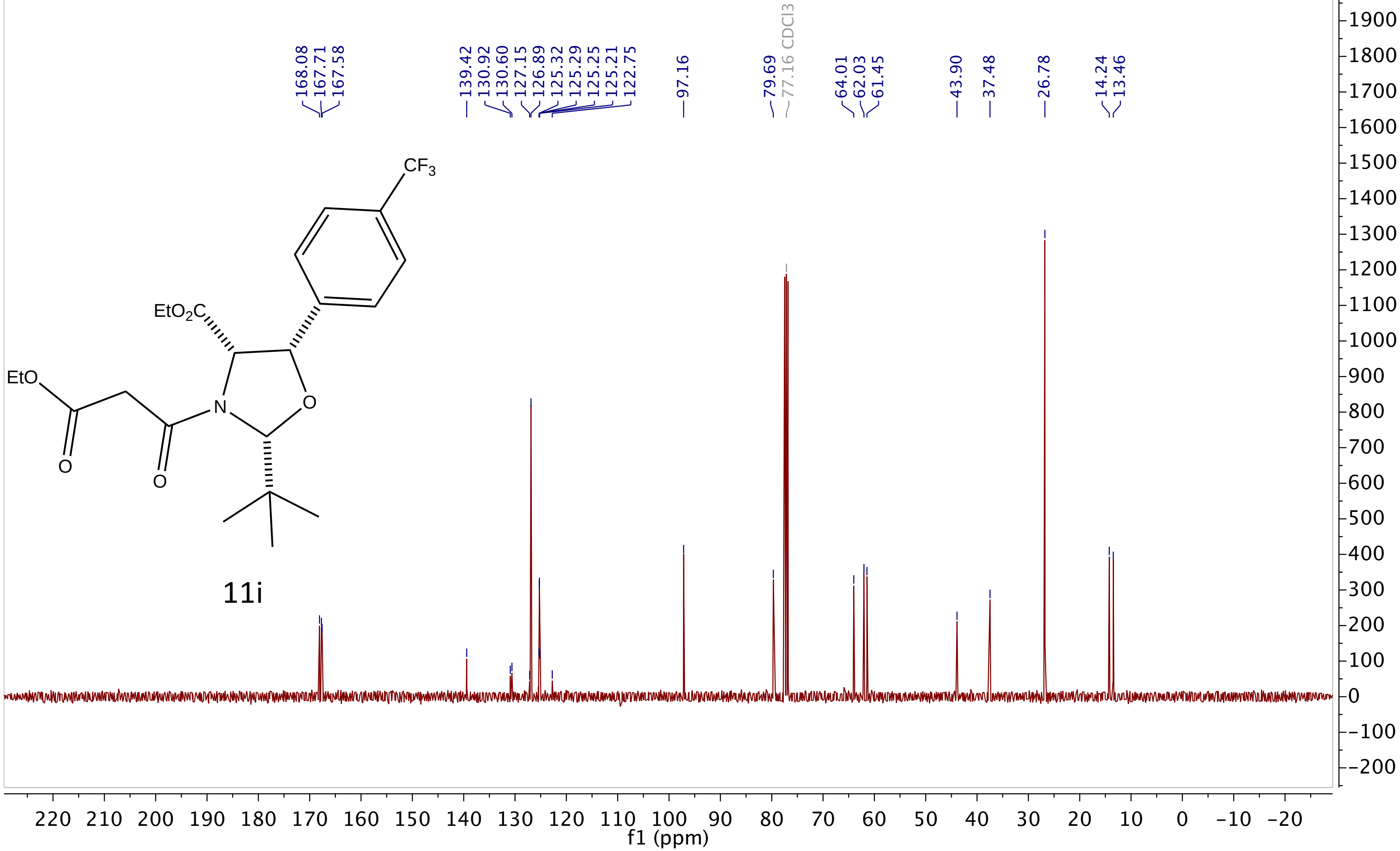


Feb03-2021-54-LS936(P) B6-C9.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 54

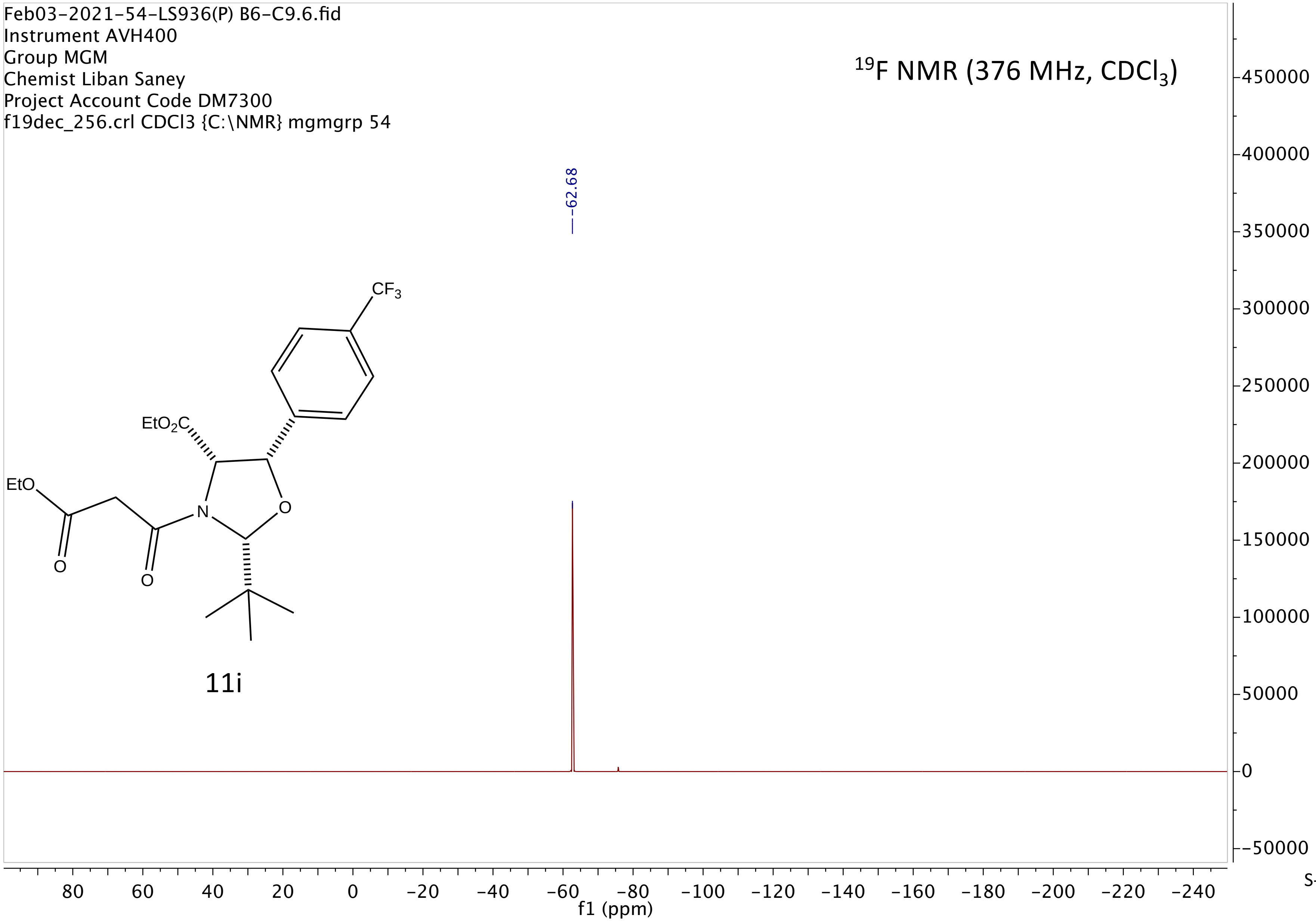


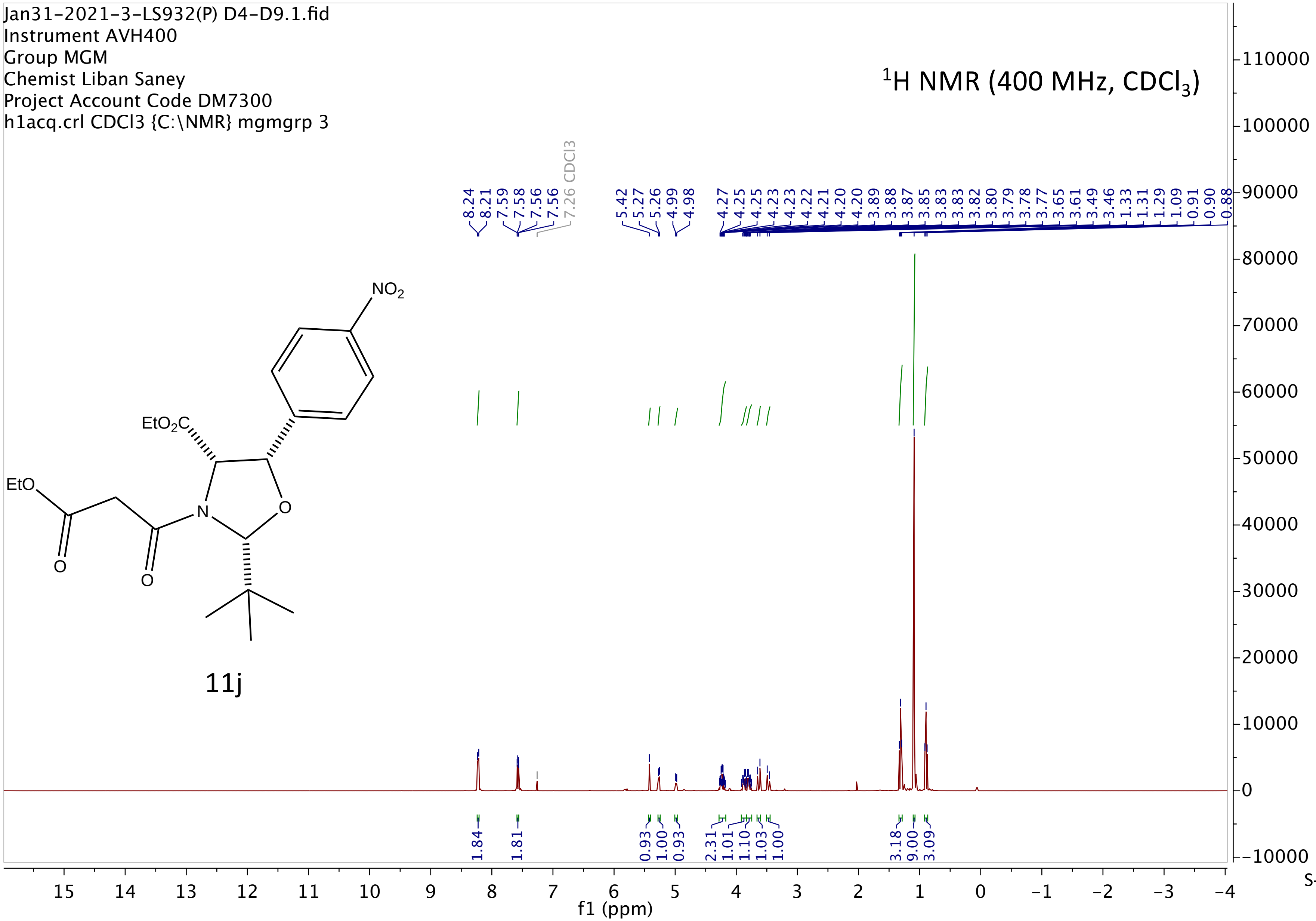
Feb03-2021-54-LS936(P) B6-C9.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 54

$^{13}C$ NMR (101 MHz, $CDCl_3$)




11i

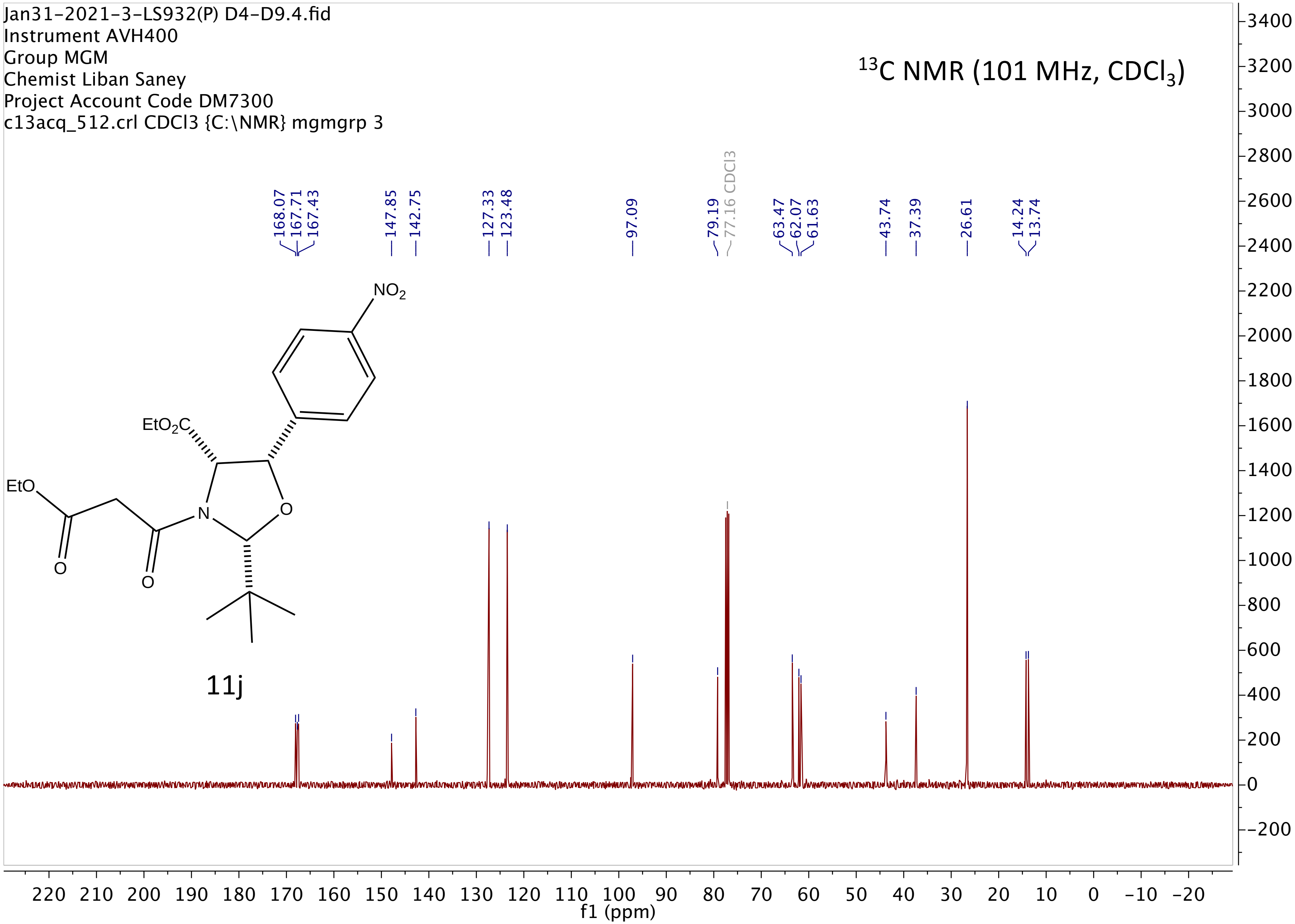

Feb03-2021-54-LS936(P) B6-C9.6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 54
$^{19}$F NMR (376 MHz, $CDCl_3$)
-62.68
$CF_3$
$EtO_2C$
EtO
N
O
O
O
11i
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)



Jan31-2021-3-LS932(P) D4-D9.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 3
1H NMR (400 MHz, CDCl3)
8.24
8.21
7.59
7.58
7.56
7.56
7.26 CDCl3
5.42
5.27
5.26
4.99
4.98
4.27
4.25
4.25
4.23
4.23
4.22
4.21
4.20
4.20
3.89
3.88
3.87
3.85
3.83
3.83
3.82
3.80
3.79
3.78
3.77
3.65
3.61
3.49
3.46
1.33
1.31
1.29
1.09
0.91
0.90
0.88
NO2
EtO2C
EtO
N
O
O
O
1.84
1.81
0.93
1.00
0.93
2.31
1.01
1.10
1.03
1.00
3.18
9.00
3.09
f1 (ppm)

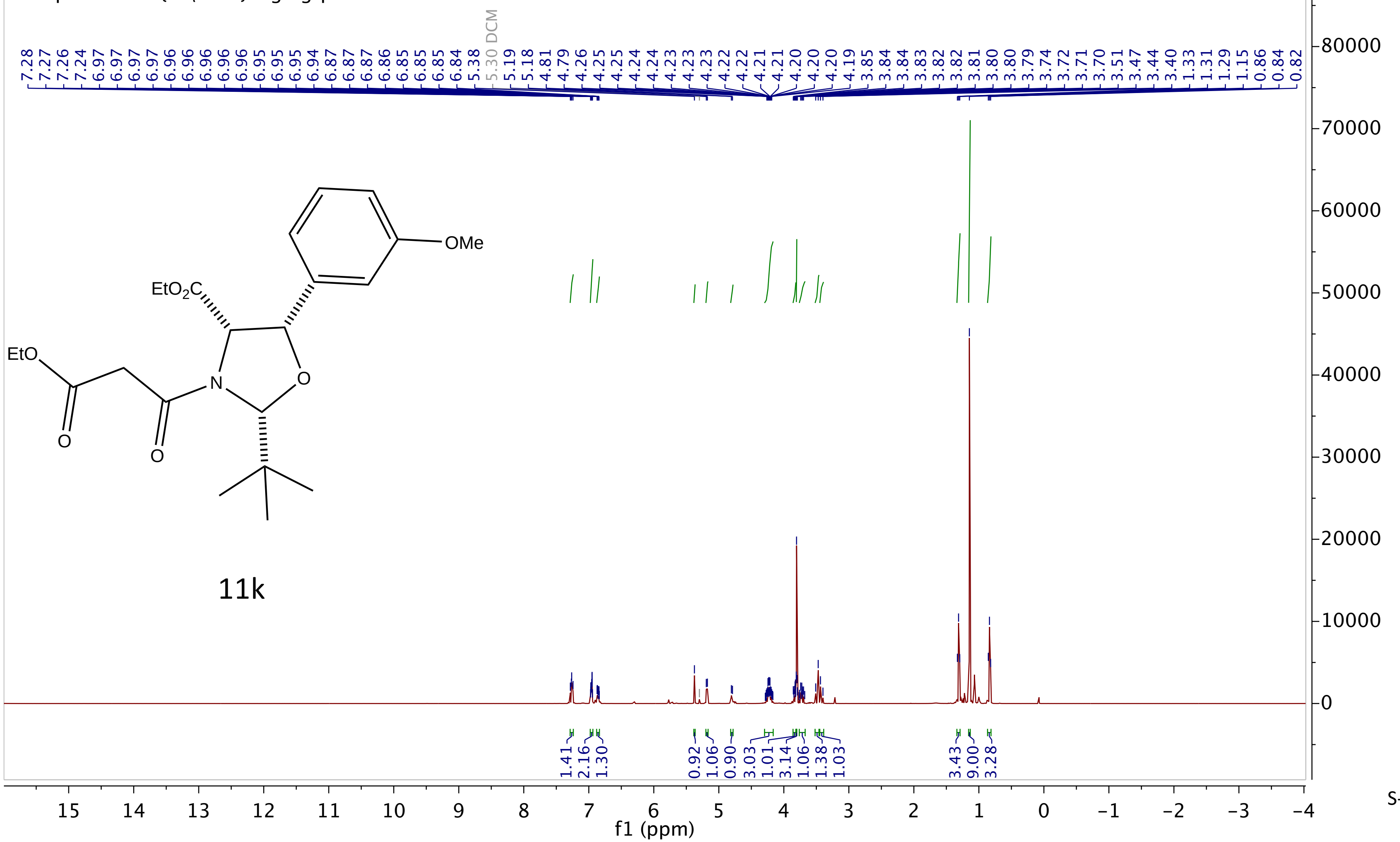

11j

Jan31-2021-3-LS932(P) D4-D9.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 3




11j

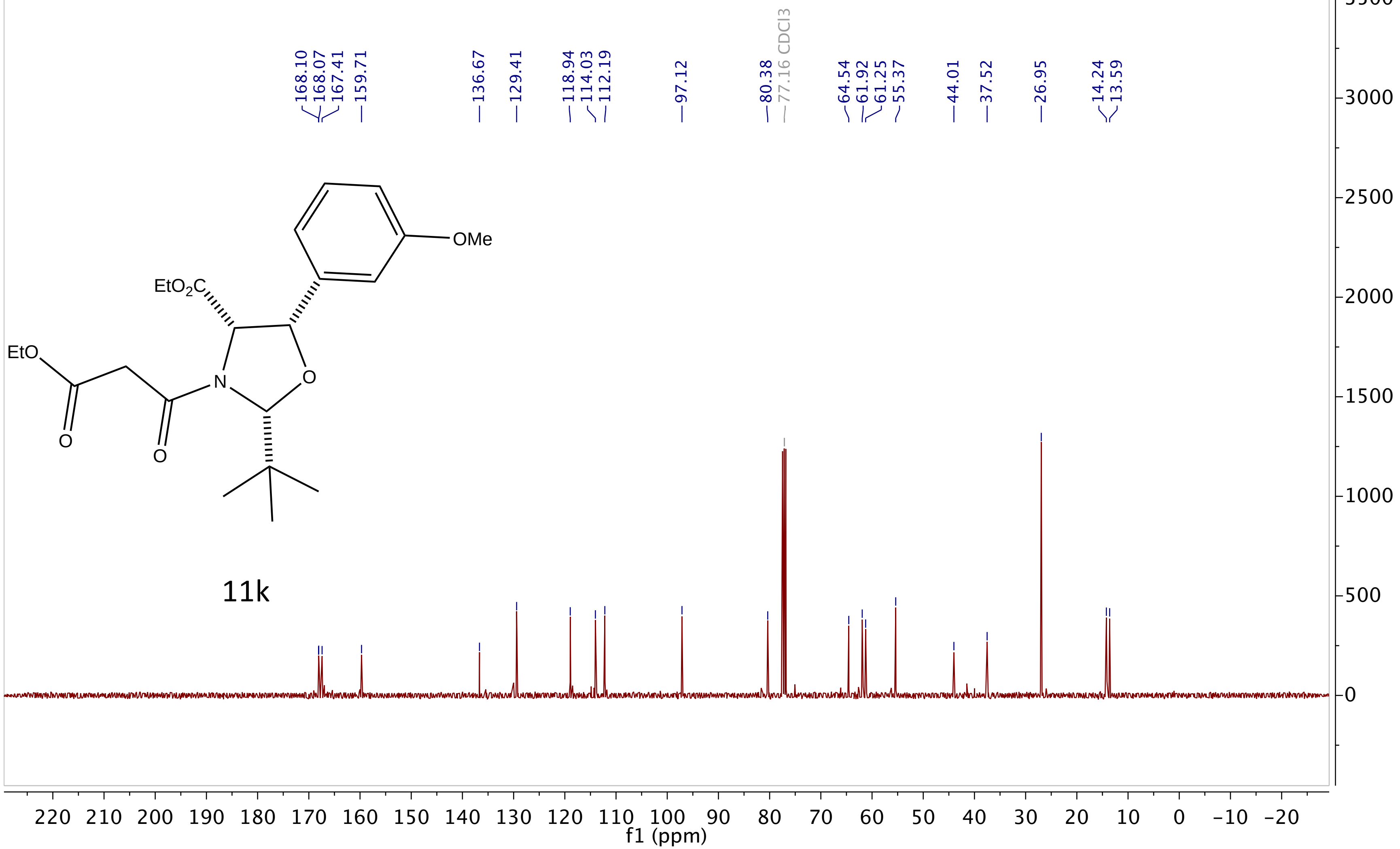
Feb07-2021-3-LS944(P) C10-D7.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 3



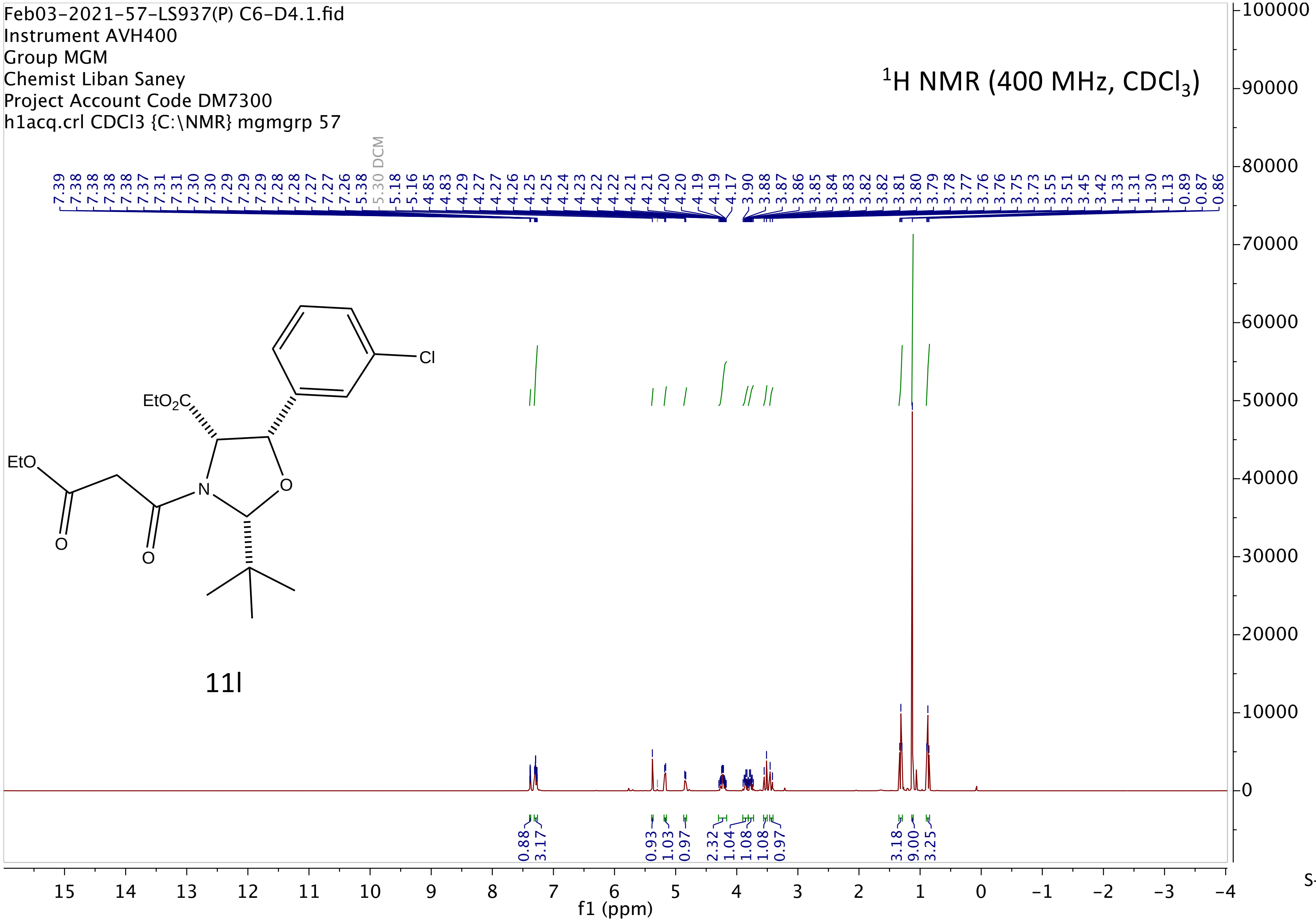

11k

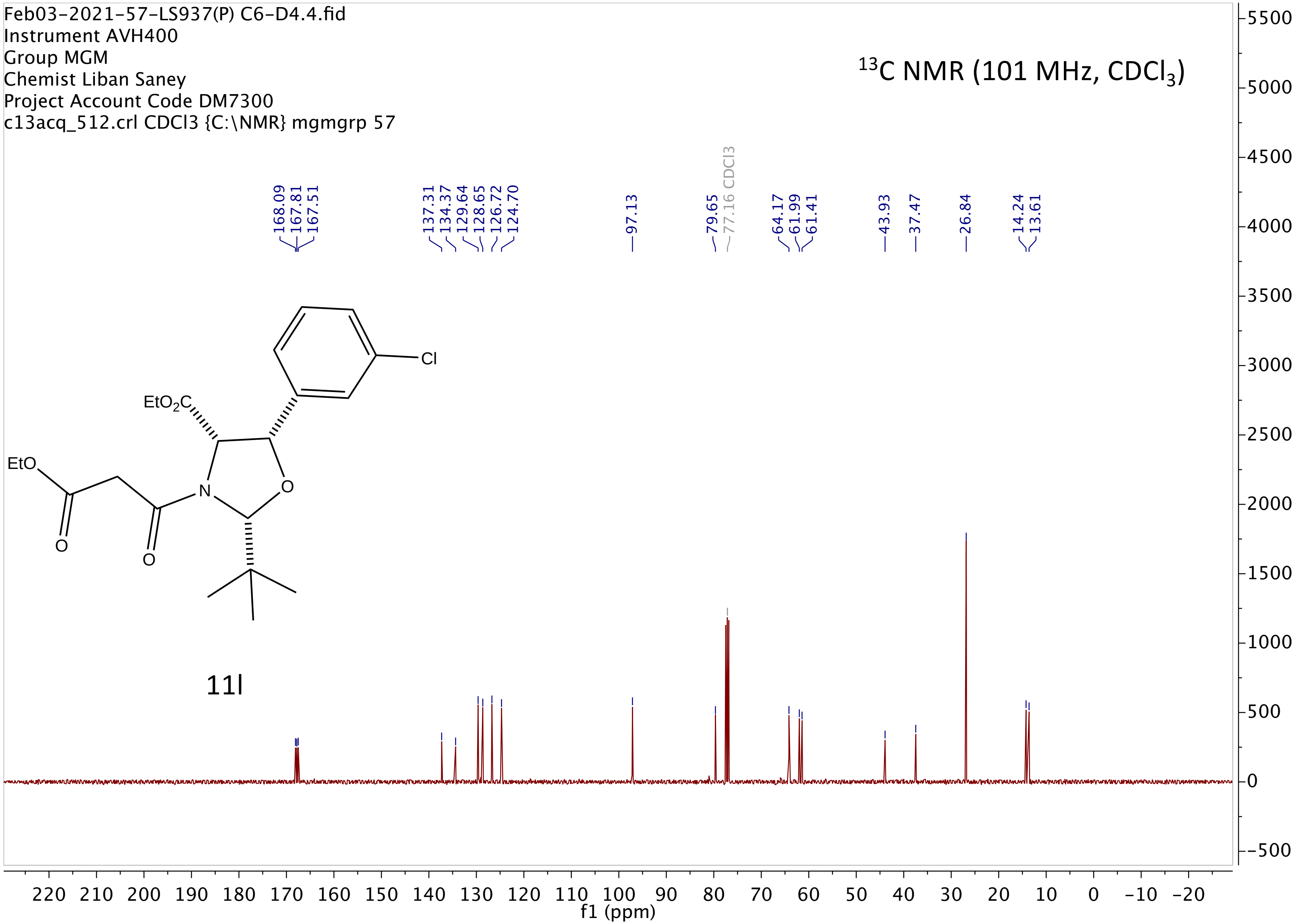
Feb07-2021-3-LS944(P) C10-D7.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 3

$^{13}$C NMR (101 MHz, $CDCl_3$)



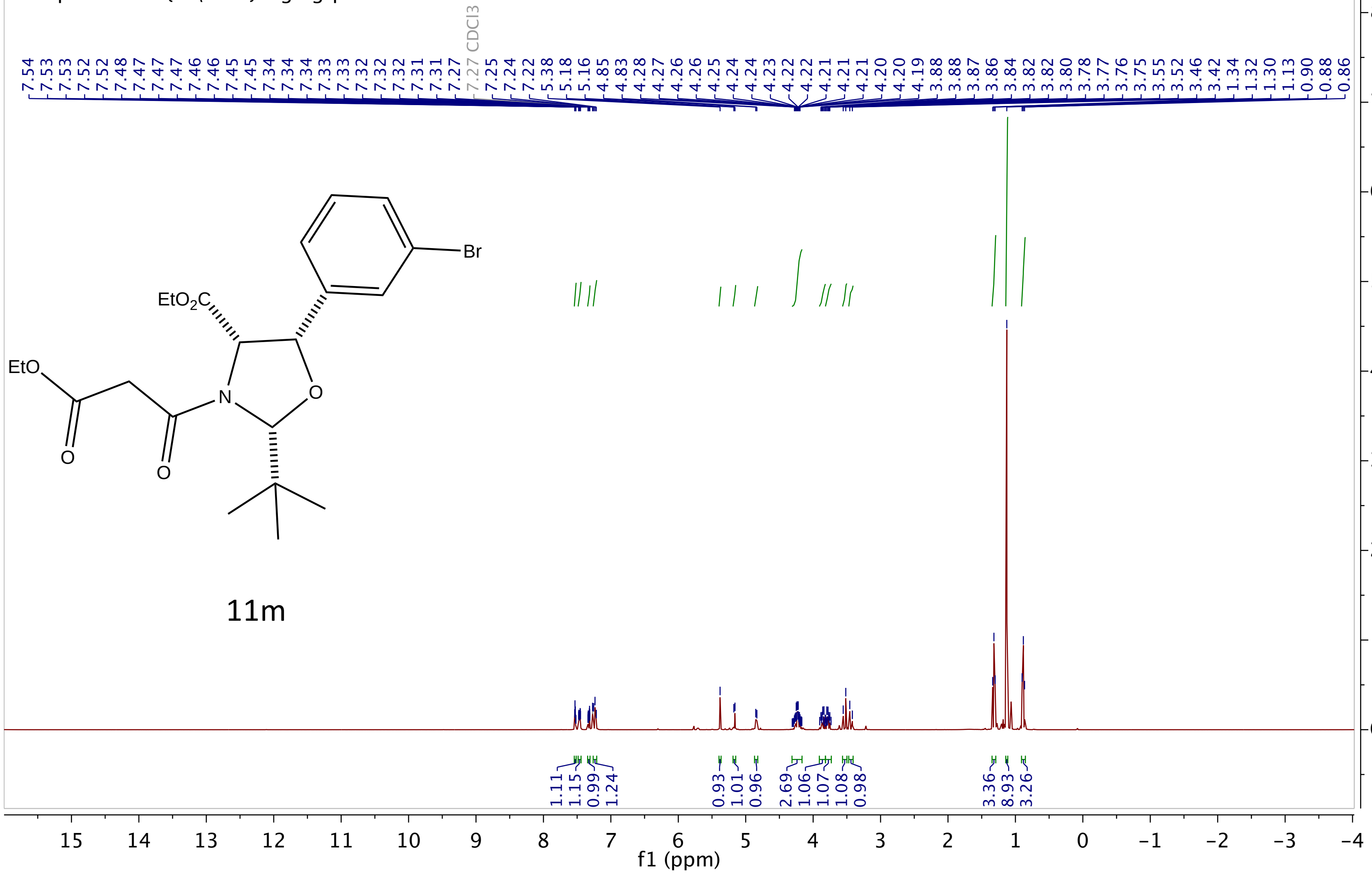

11k


Feb03-2021-57-LS937(P) C6-D4.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 57
¹H NMR (400 MHz, CDCl₃)
5.30 DCM
EtO₂C
EtO
Cl
N
O
11l
f1 (ppm)

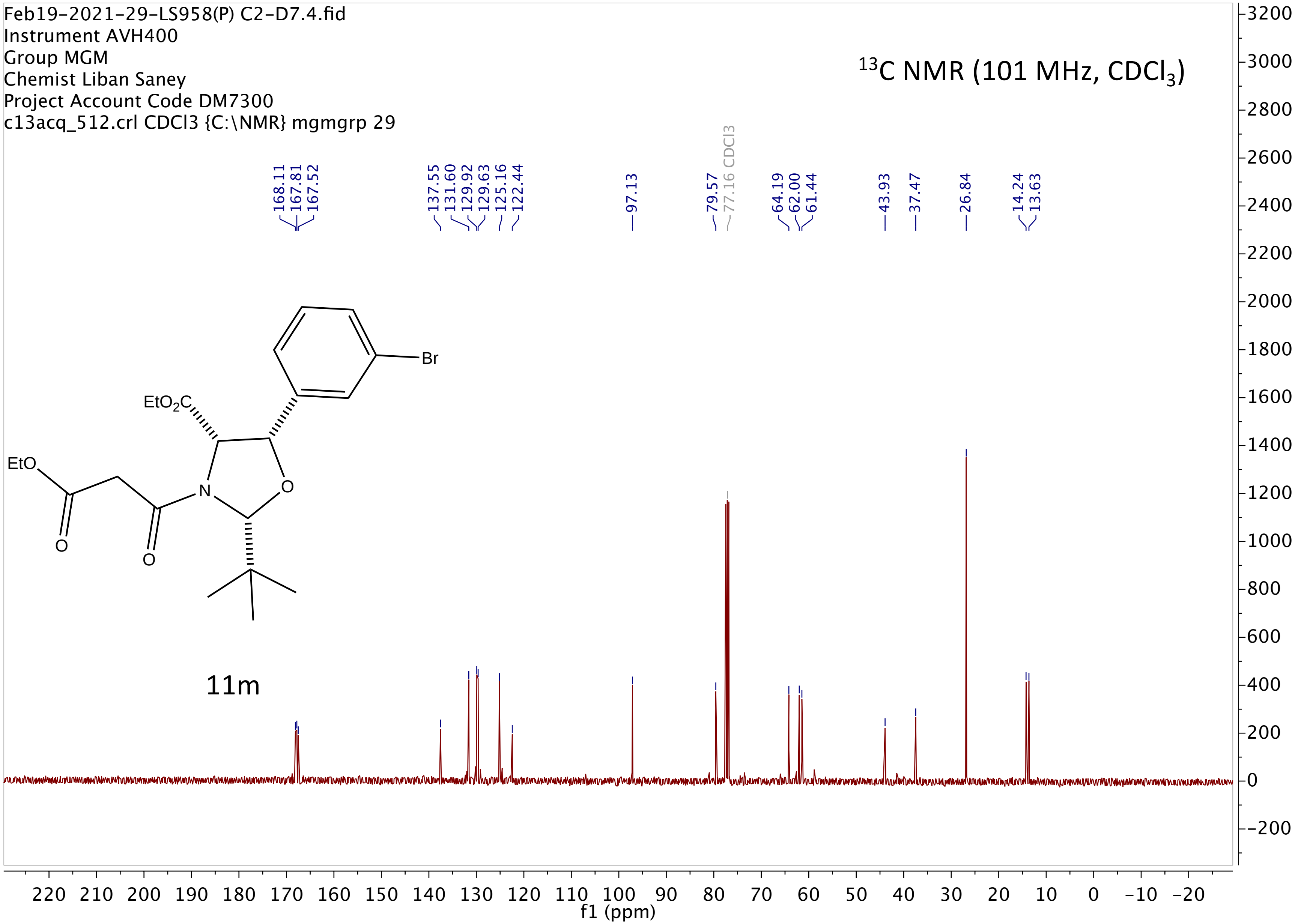

Feb03-2021-57-LS937(P) C6-D4.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 57
13C NMR (101 MHz, CDCl3)
168.09
167.81
167.51
137.31
134.37
129.64
128.65
126.72
124.70
97.13
79.65
77.16 CDCl3
64.17
61.99
61.41
43.93
37.47
26.84
14.24
13.61
EtO2C
Cl
EtO
N
O
O
O
11l
f1 (ppm)

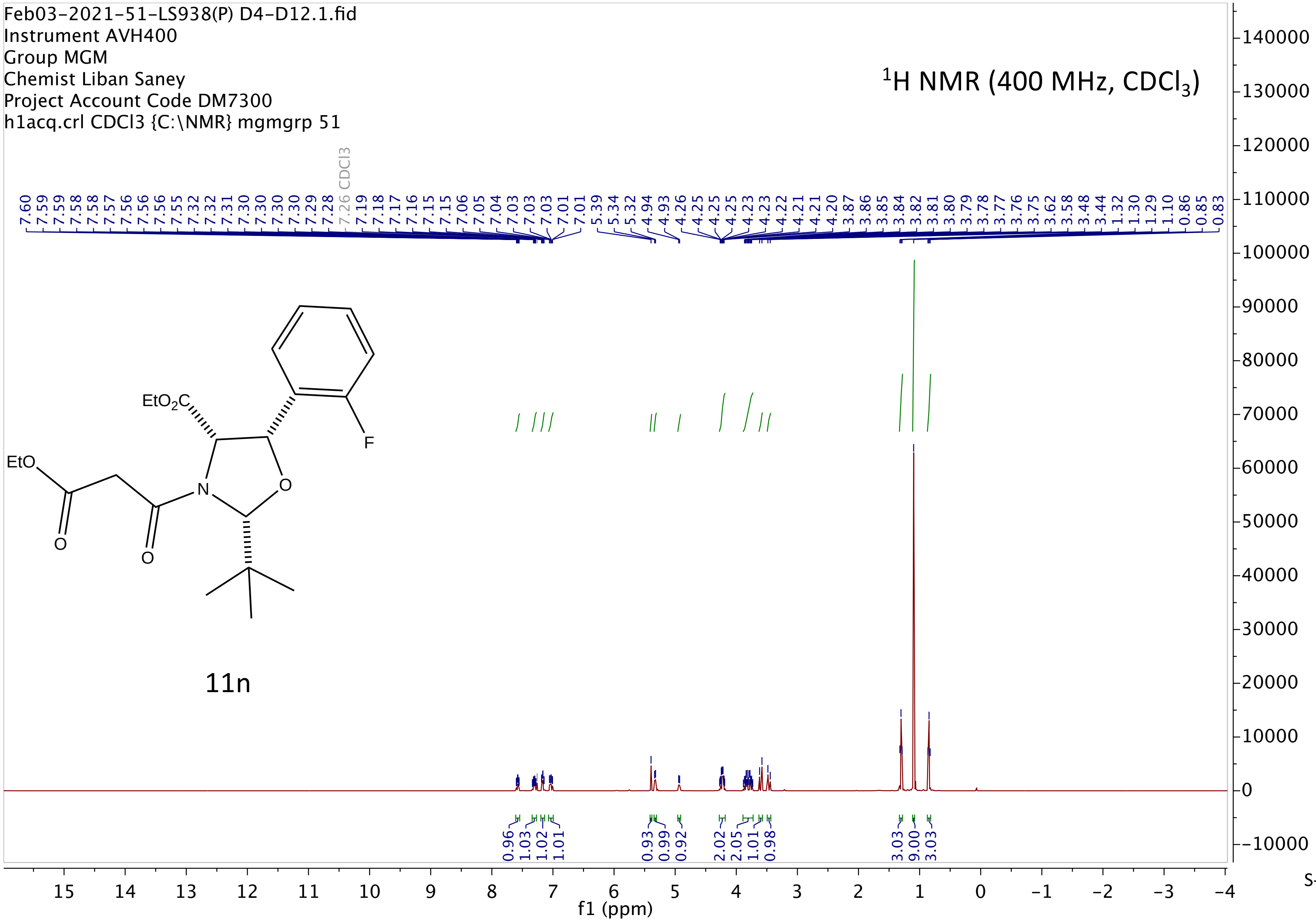
Feb19-2021-29-LS958(P) C2-D7.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 29

$^1H$ NMR (400 MHz, $CDCl_3$)




11m

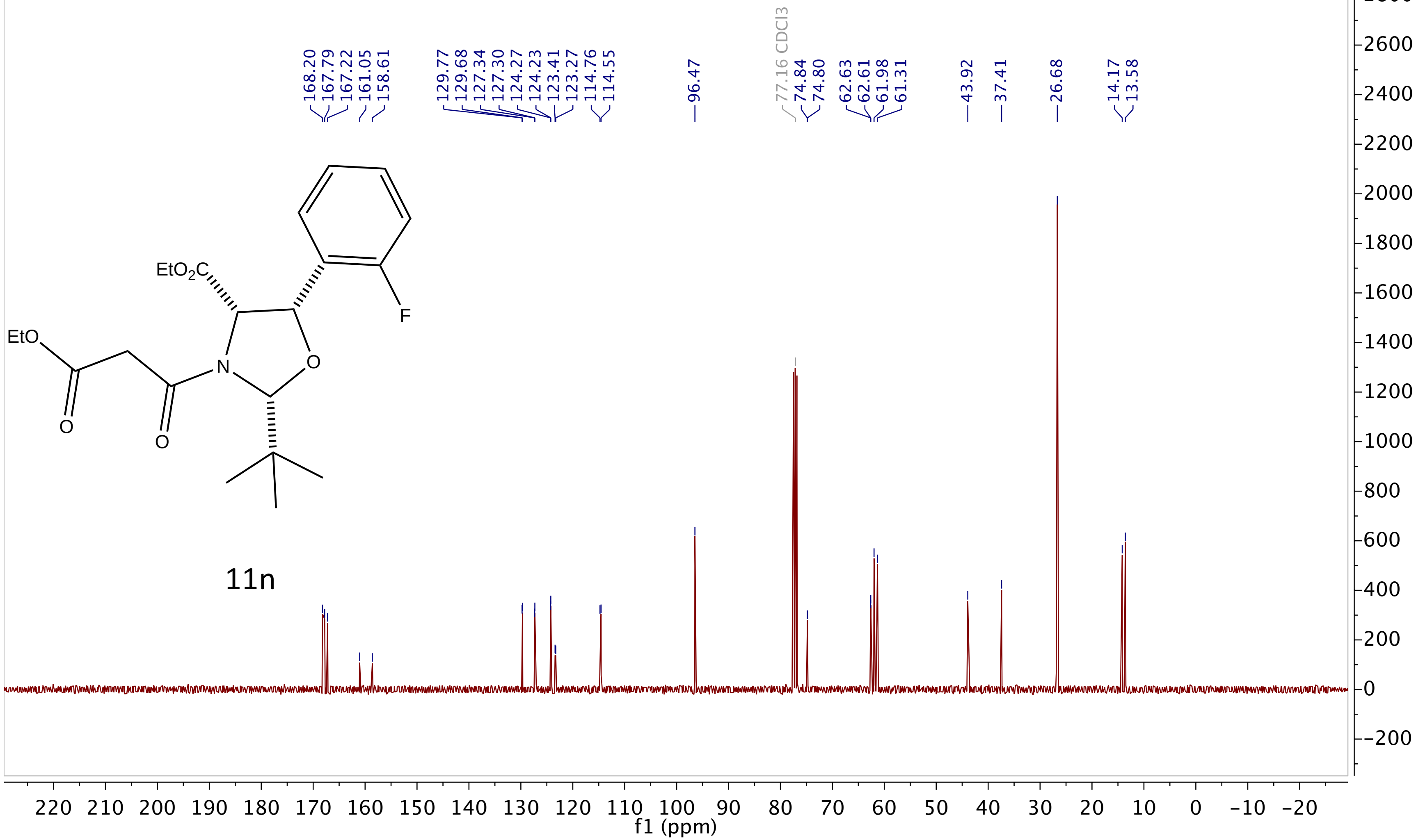

Feb19-2021-29-LS958(P) C2-D7.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 29
13C NMR (101 MHz, CDCl3)
168.11
167.81
167.52
137.55
131.60
129.92
129.63
125.16
122.44
97.13
79.57
77.16 CDCl3
64.19
62.00
61.44
43.93
37.47
26.84
14.24
13.63
Br
EtO2C
EtO
N
O
O
O
11m
f1 (ppm)



Feb03-2021-51-LS938(P) D4-D12.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 51
$^1$H NMR (400 MHz, $CDCl_3$)
11n
f1 (ppm)

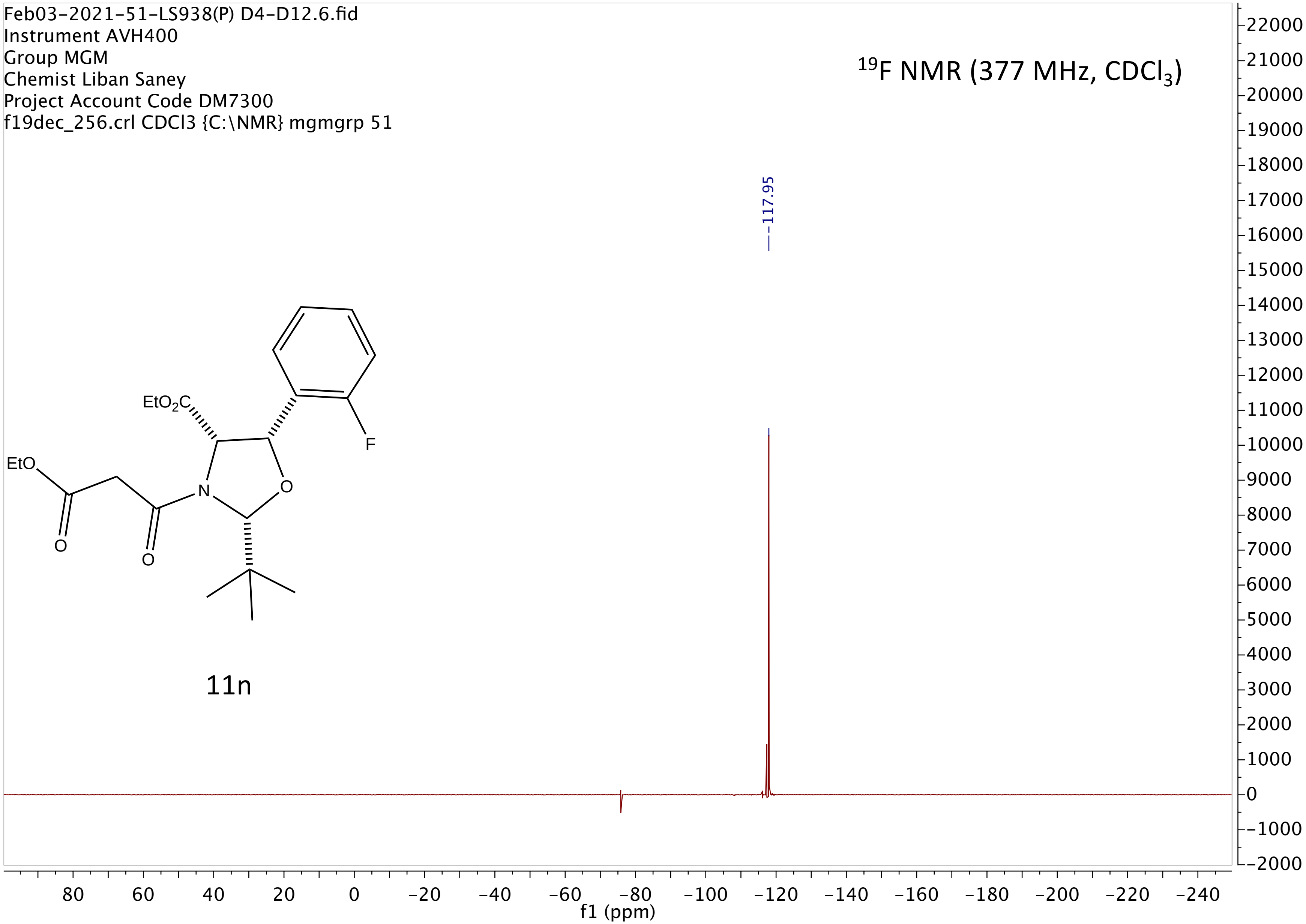
Feb03-2021-51-LS938(P) D4-D12.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 51

$^{13}$C NMR (101 MHz, $CDCl_3$)



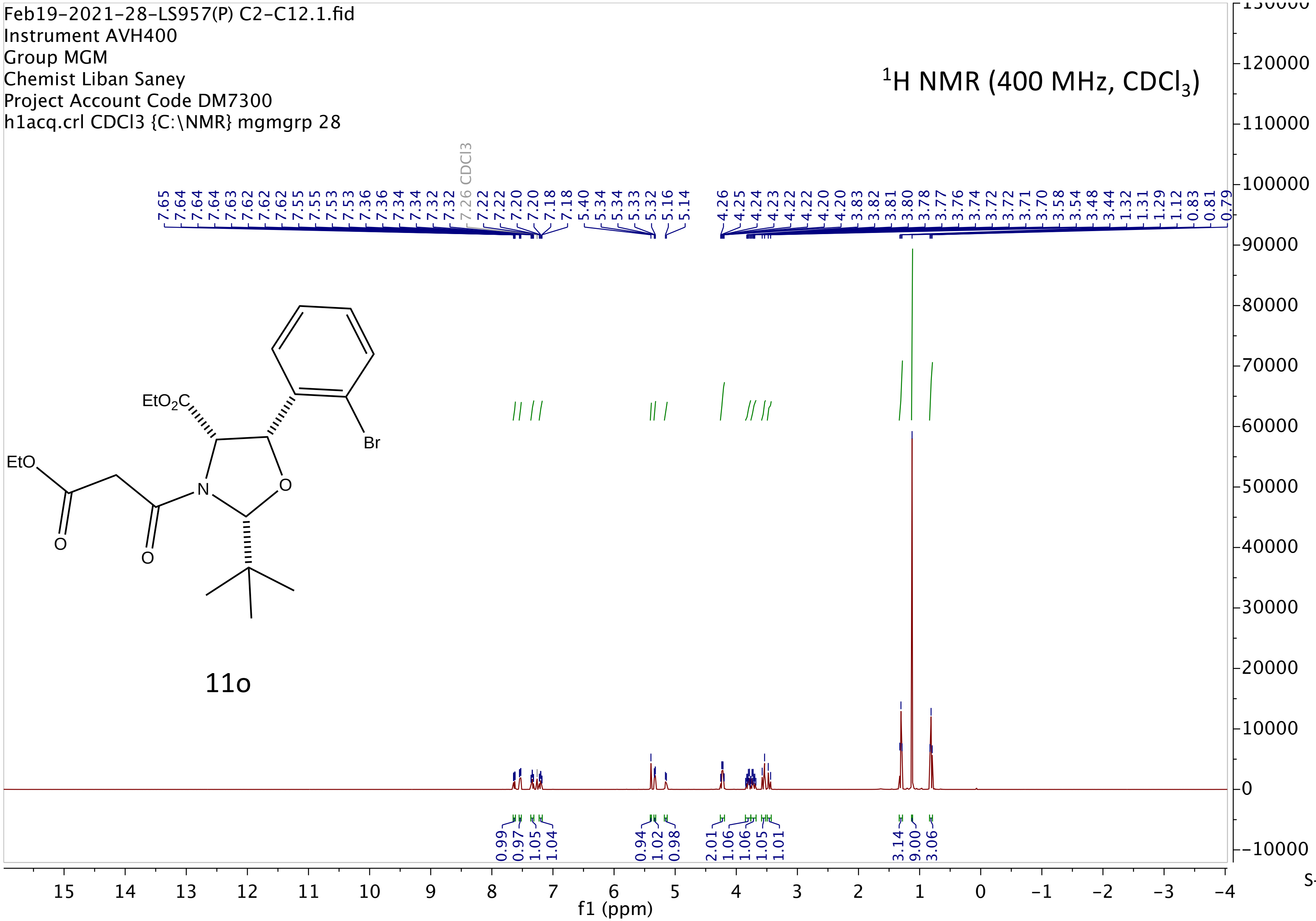
Feb03-2021-51-LS938(P) D4-D12.6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 51

$^{19}$F NMR (377 MHz, $CDCl_3$)

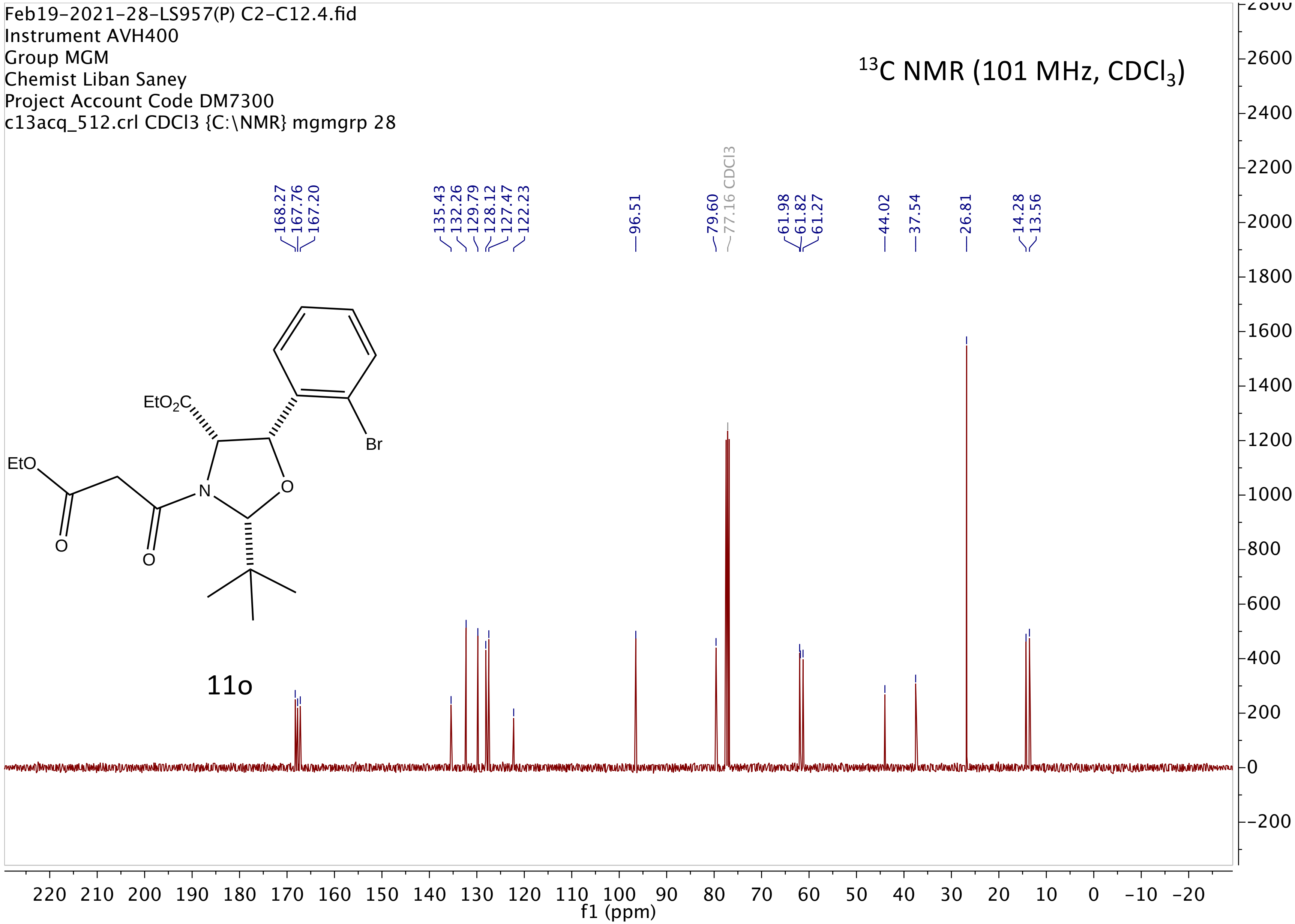


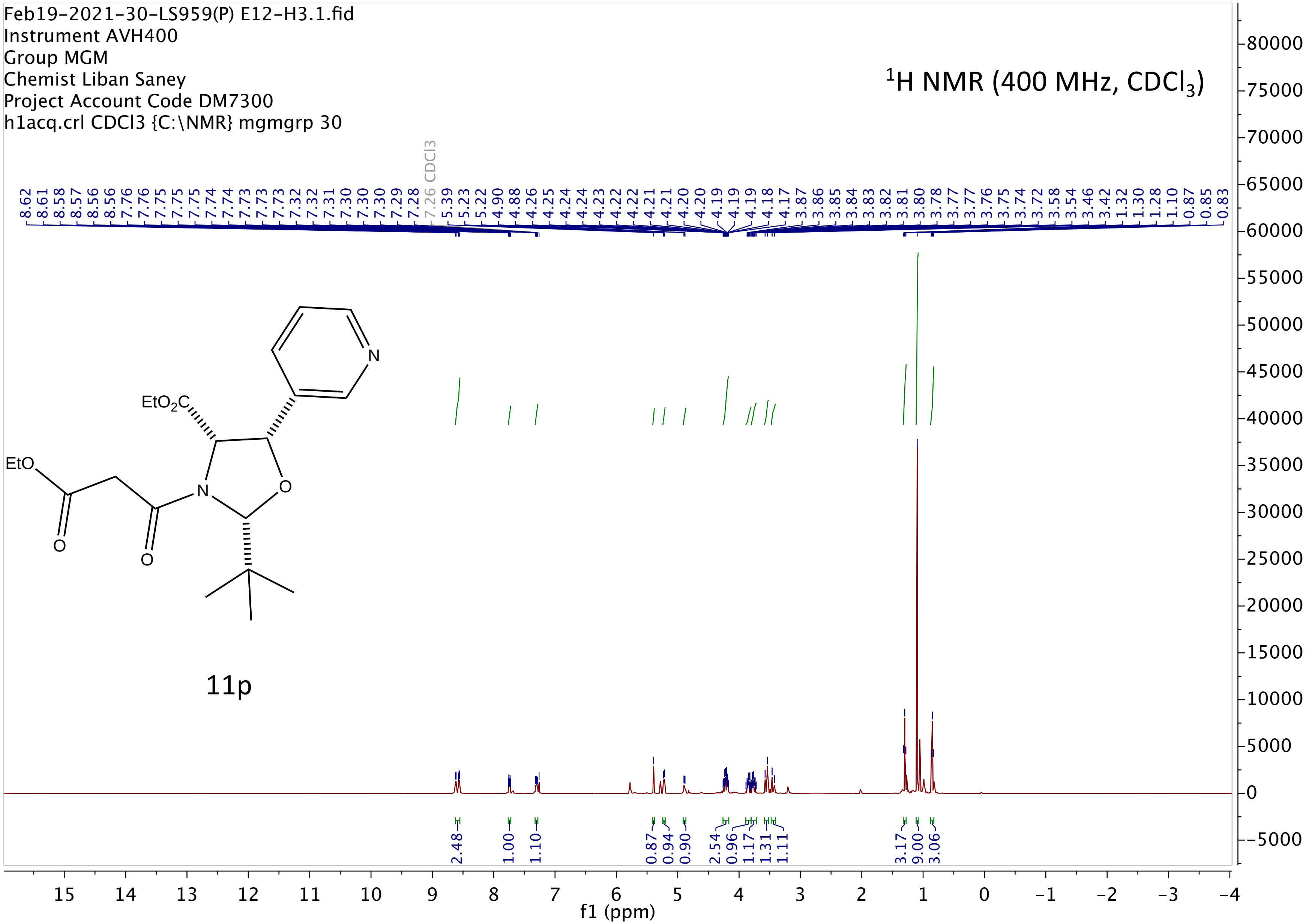
Feb19-2021-28-LS957(P) C2-C12.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 28

$^1$H NMR (400 MHz, $CDCl_3$)



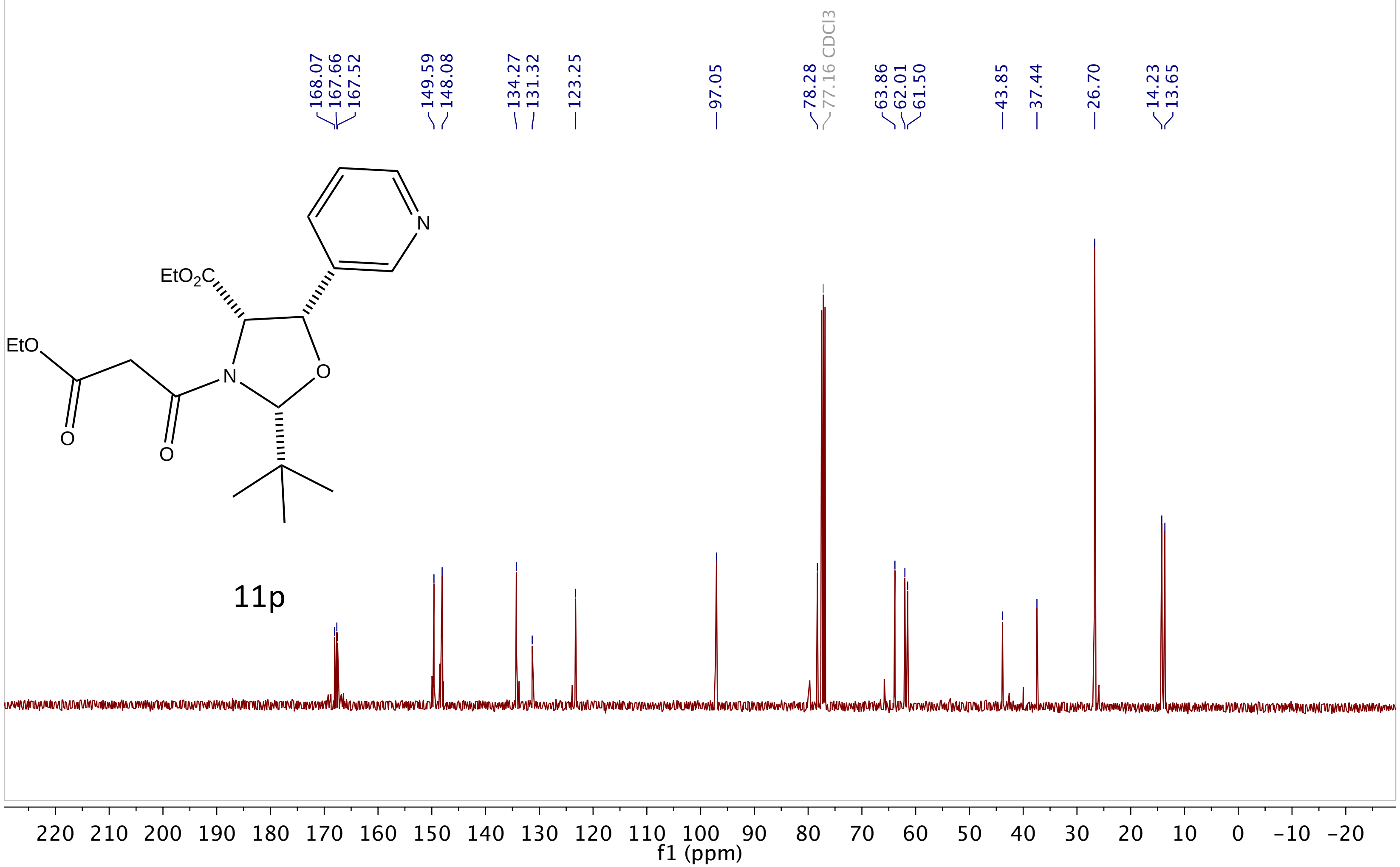

11o

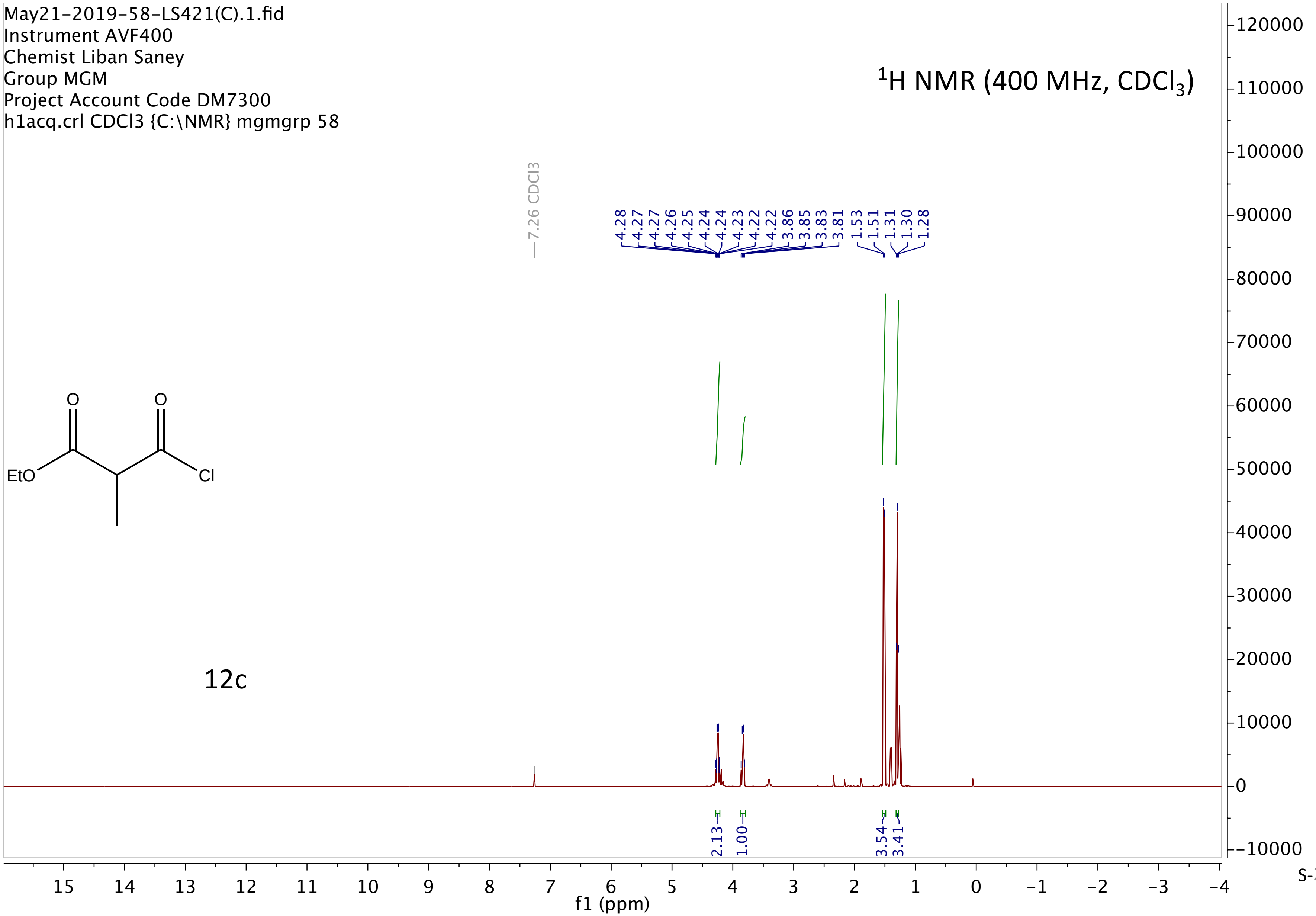

Feb19-2021-28-LS957(P) C2-C12.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 28
13C NMR (101 MHz, CDCl3)
168.27
167.76
167.20
135.43
132.26
129.79
128.12
127.47
122.23
96.51
79.60
77.16 CDCl3
61.98
61.82
61.27
44.02
37.54
26.81
14.28
13.56
EtO2C
EtO
N
O
O
O
Br
11o
f1 (ppm)


Feb19-2021-30-LS959(P) E12-H3.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 30
¹H NMR (400 MHz, CDCl₃)
11p
f1 (ppm)

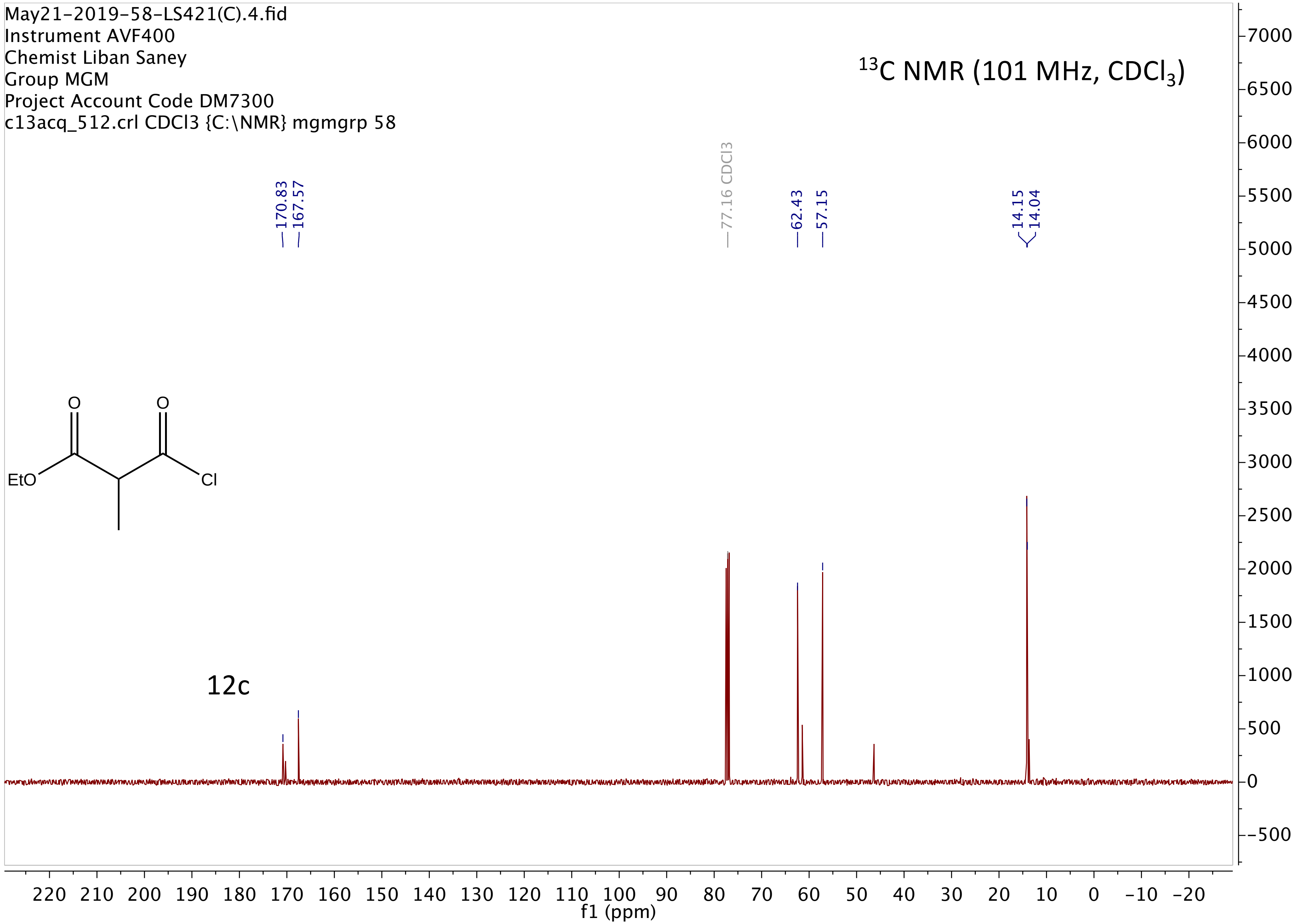
Feb19-2021-30-LS959(P) E12-H3.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 30

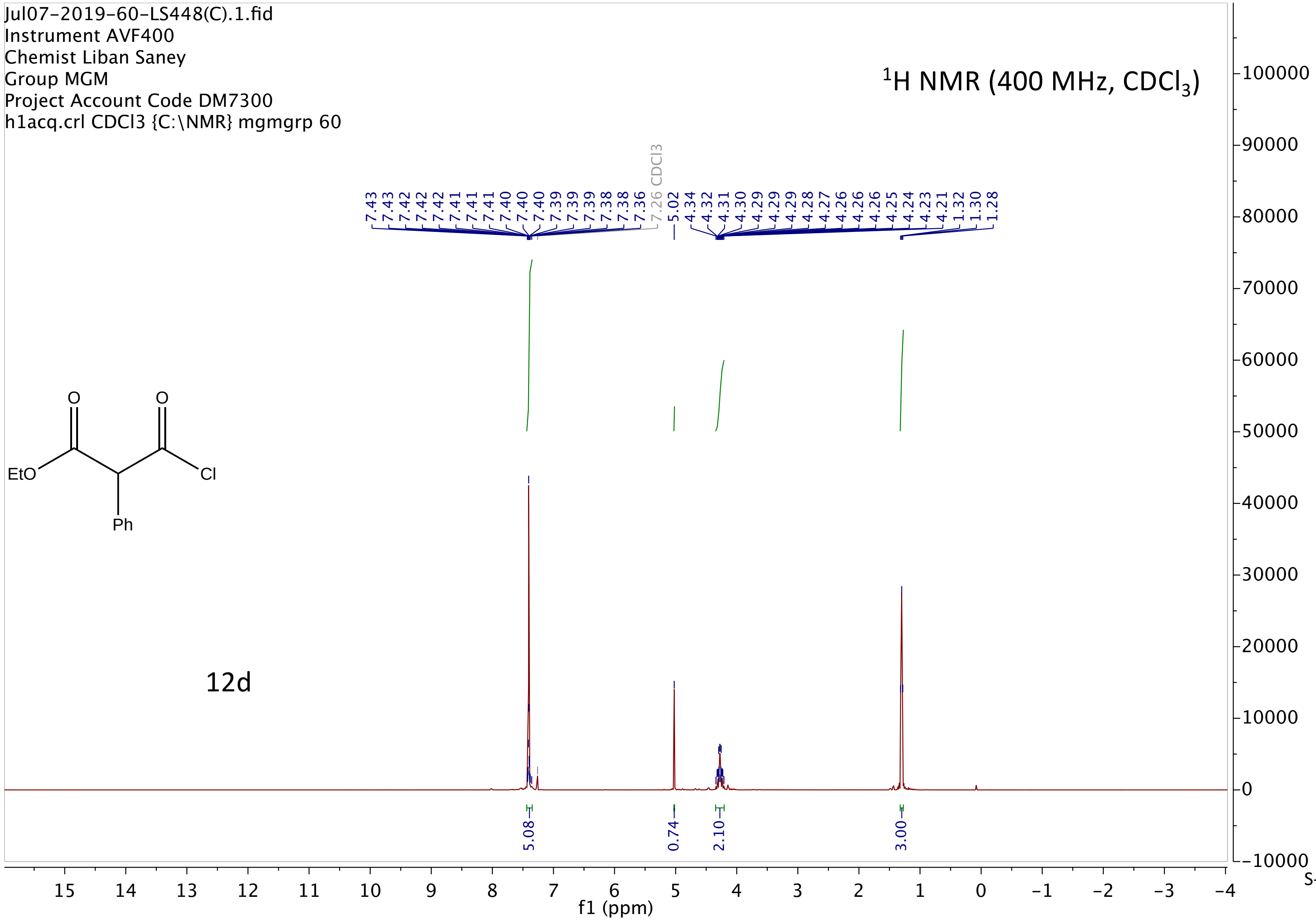
$^{13}$C NMR (101 MHz, $CDCl_3$)

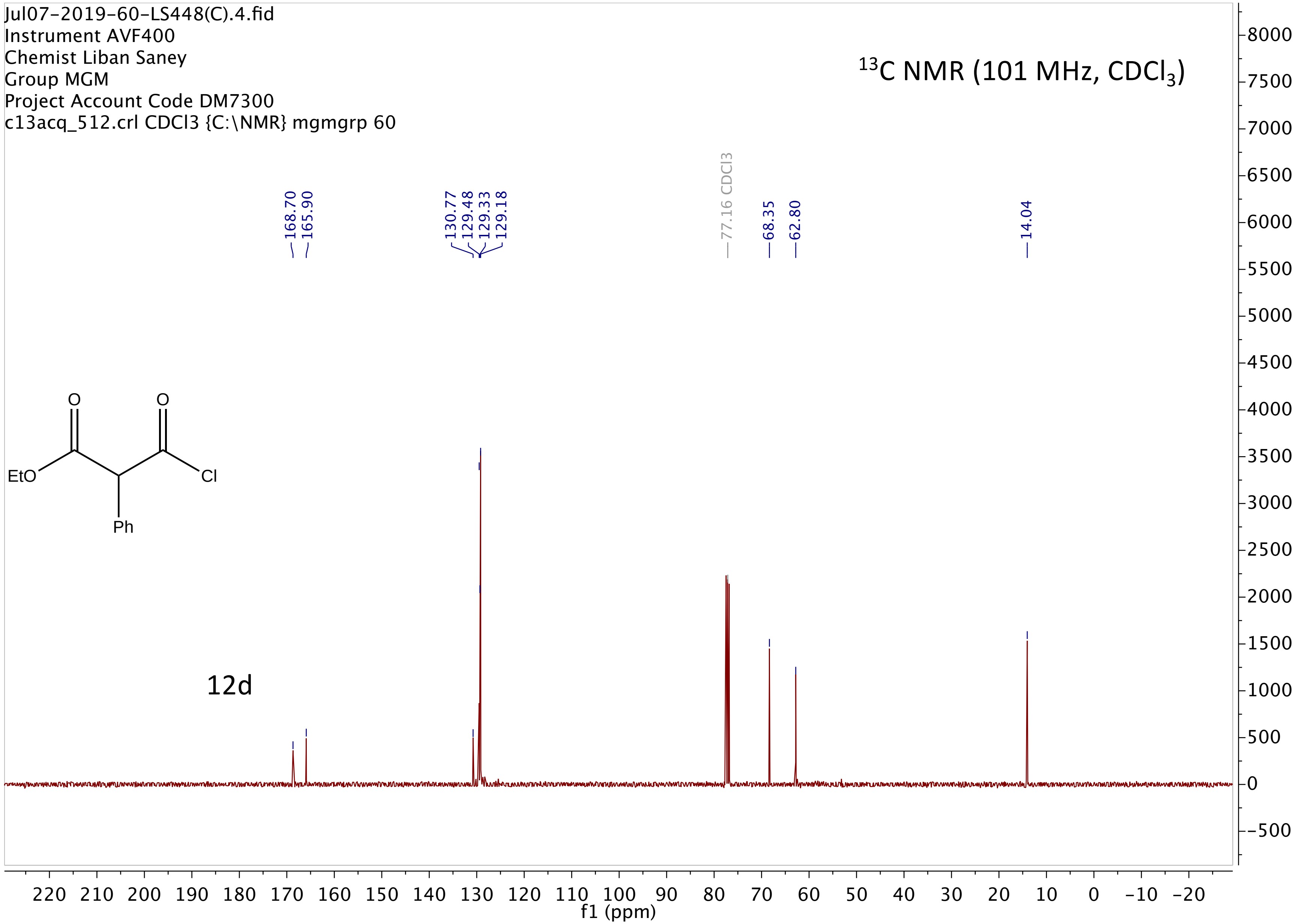



May21-2019-58-LS421(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 58
$^1$H NMR (400 MHz, CDCl$_3$)
7.26 CDCl3
4.28 4.27 4.27 4.26 4.25 4.24 4.24 4.23 4.22 4.22 3.86 3.85 3.83 3.81 1.53 1.51 1.31 1.30 1.28
2.13 1.00 3.54 3.41
f1 (ppm)
EtO
Cl

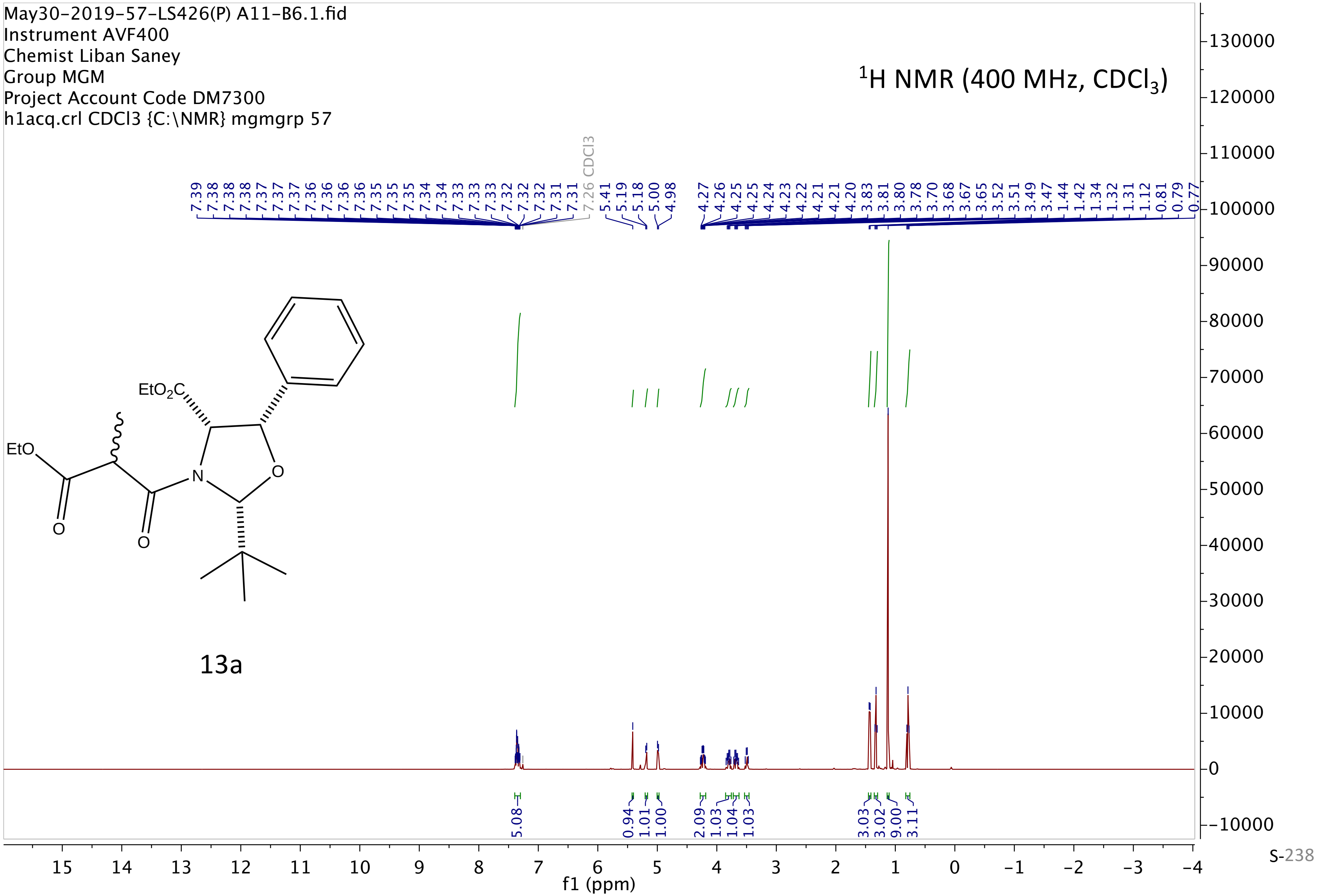
12c

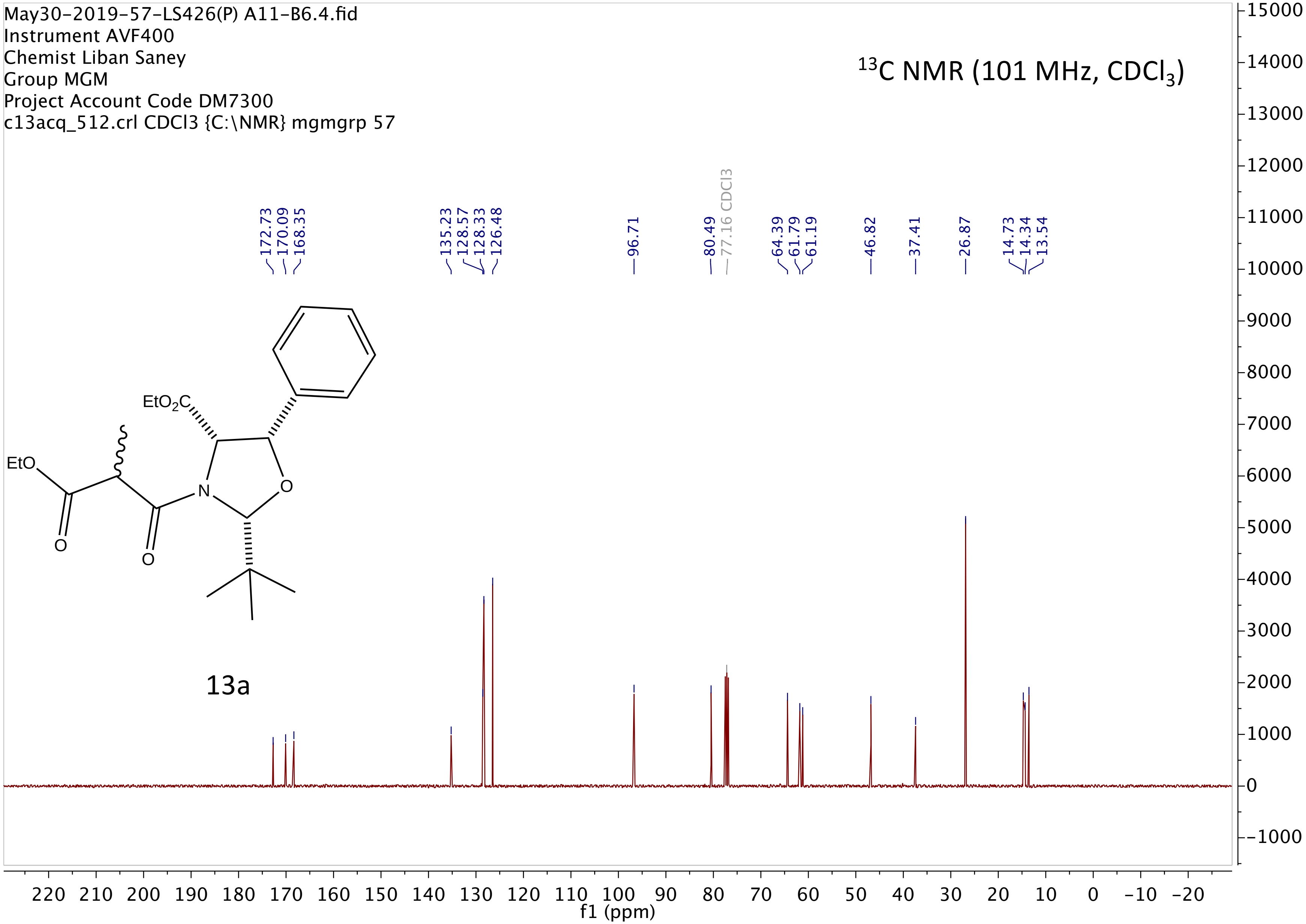

May21-2019-58-LS421(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 58
$^{13}$C NMR (101 MHz, CDCl$_3$)
170.83
167.57
77.16 CDCl3
62.43
57.15
14.15
14.04
O
O
EtO
Cl
12c
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Jul07-2019-60-LS448(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
$^1$H NMR (400 MHz, $CDCl_3$)
7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.36
7.26 CDCl3
5.02
4.34 4.32 4.31 4.30 4.29 4.29 4.28 4.27 4.26 4.26 4.26 4.25 4.24 4.23 4.21
1.32 1.30 1.28
O
O
EtO
Cl
Ph
12d
5.08
0.74
2.10
3.00
f1 (ppm)

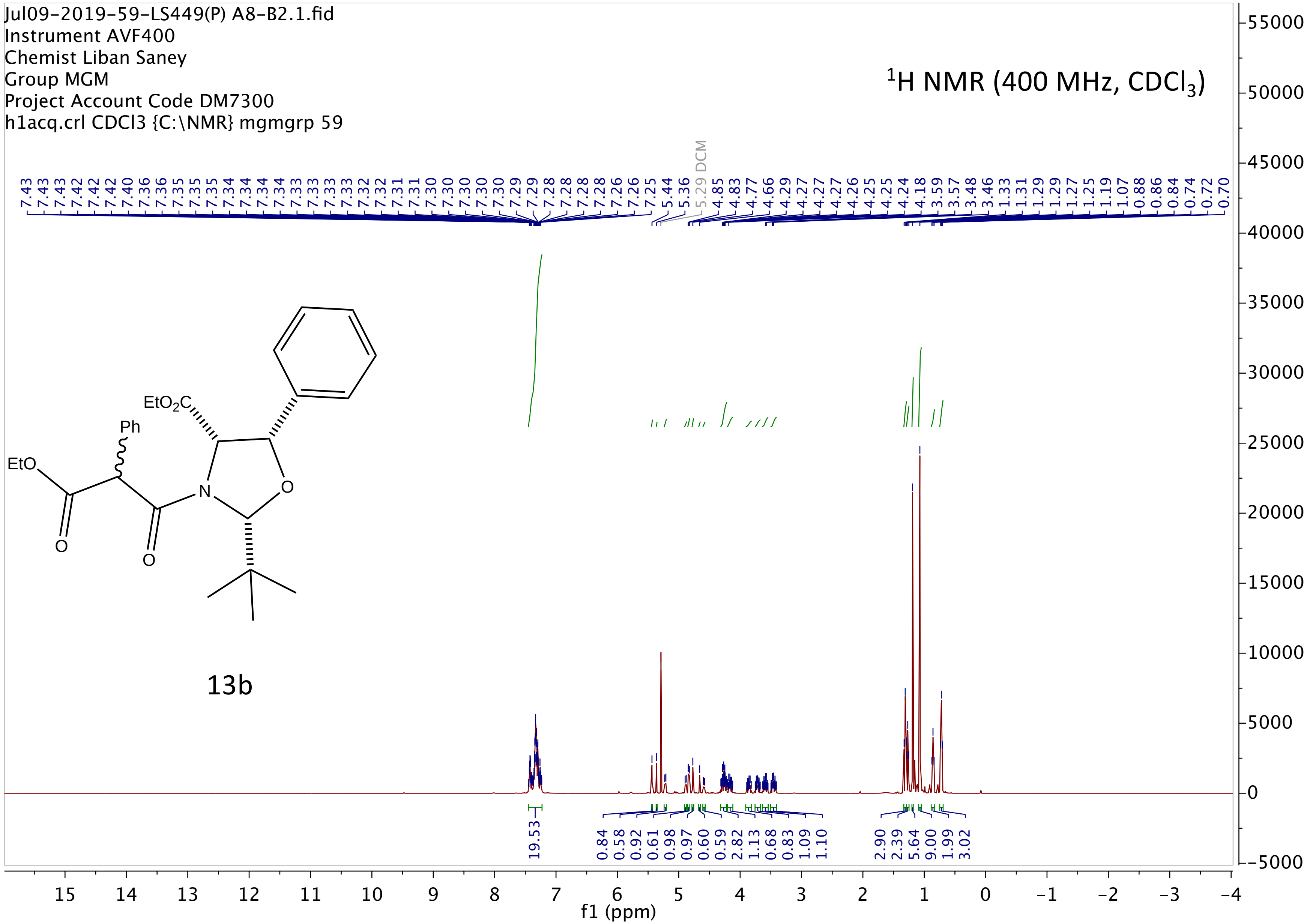

Jul07-2019-60-LS448(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
13C NMR (101 MHz, CDCl3)
168.70
165.90
130.77
129.48
129.33
129.18
77.16 CDCl3
68.35
62.80
14.04
O
O
EtO
Cl
Ph
12d
f1 (ppm)

May30-2019-57-LS426(P) A11-B6.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 57

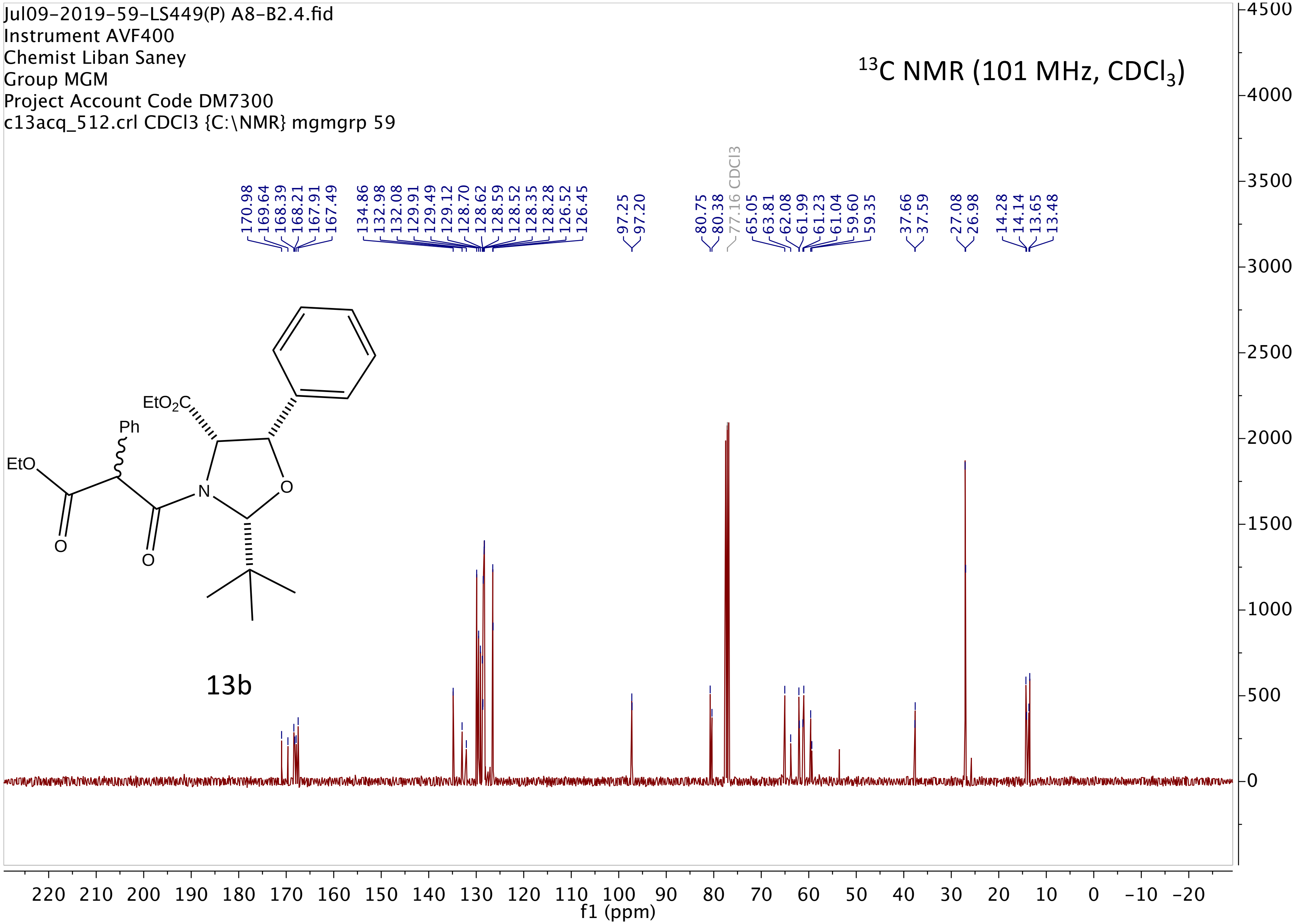


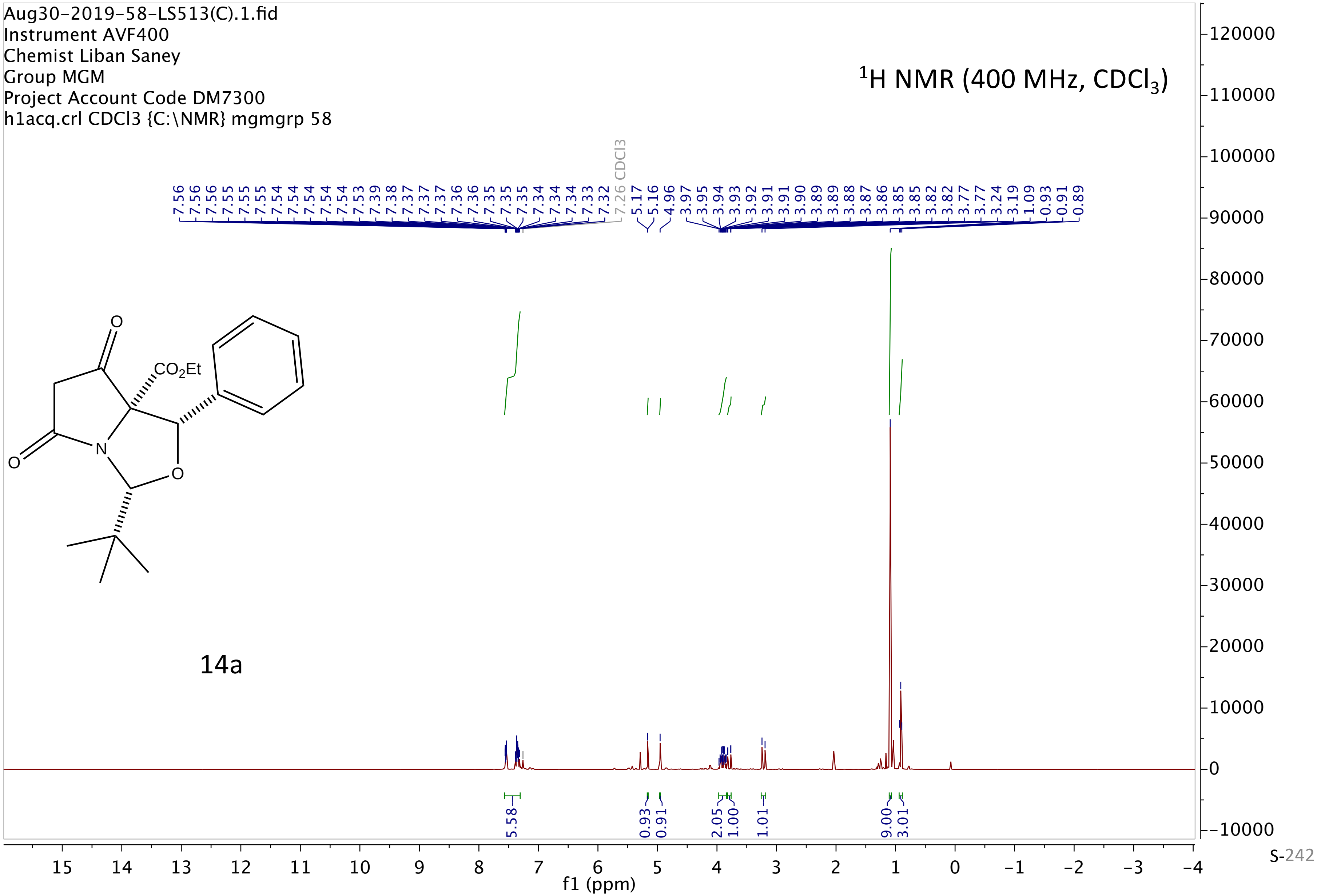


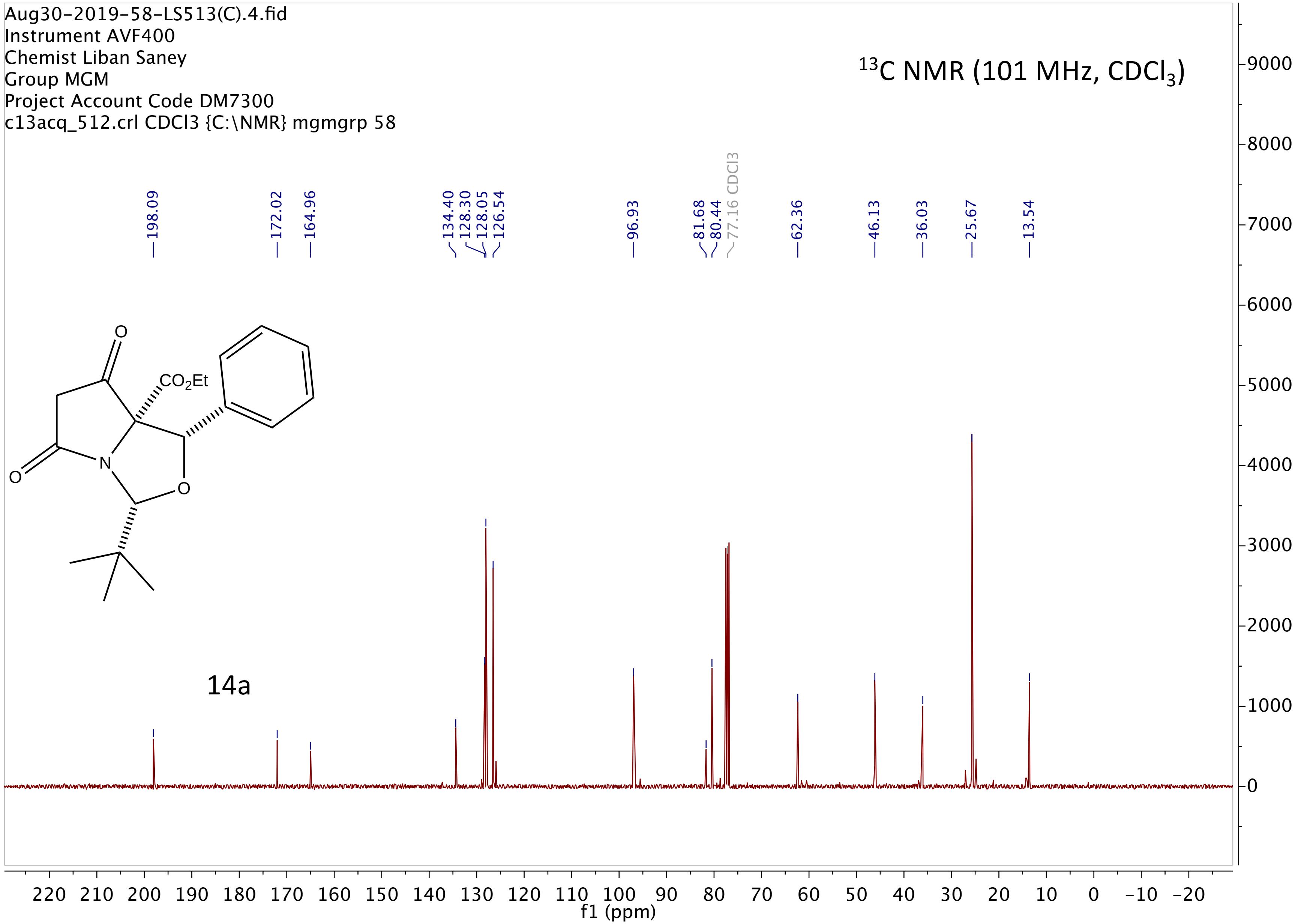
May30-2019-57-LS426(P) A11-B6.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 57
$^{13}$C NMR (101 MHz, $CDCl_3$)
172.73
170.09
168.35
135.23
128.57
128.33
126.48
96.71
80.49
77.16 CDCl3
64.39
61.79
61.19
46.82
37.41
26.87
14.73
14.34
13.54
$EtO_2C$
EtO
N
O
O
O
13a
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



Jul09-2019-59-LS449(P) A8-B2.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59
$^1$H NMR (400 MHz, $CDCl_3$)
7.43 7.43 7.43 7.42 7.42 7.42 7.40 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.28 7.28 7.26 7.26 7.25 5.44 5.36 5.29 DCM 4.85 4.83 4.77 4.66 4.29 4.27 4.27 4.27 4.26 4.25 4.25 4.25 4.24 4.18 3.59 3.57 3.48 3.46 1.33 1.31 1.29 1.29 1.27 1.25 1.19 1.07 0.88 0.86 0.84 0.74 0.72 0.70
EtO
Ph
$EtO_2C$
N
O
O
O
13b
19.53
0.84 0.58 0.92 0.61 0.98 0.97 0.60 0.59 2.82 1.13 0.68 0.83 1.09 1.10
2.90 2.39 5.64 9.00 1.99 3.02
55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 -5000
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

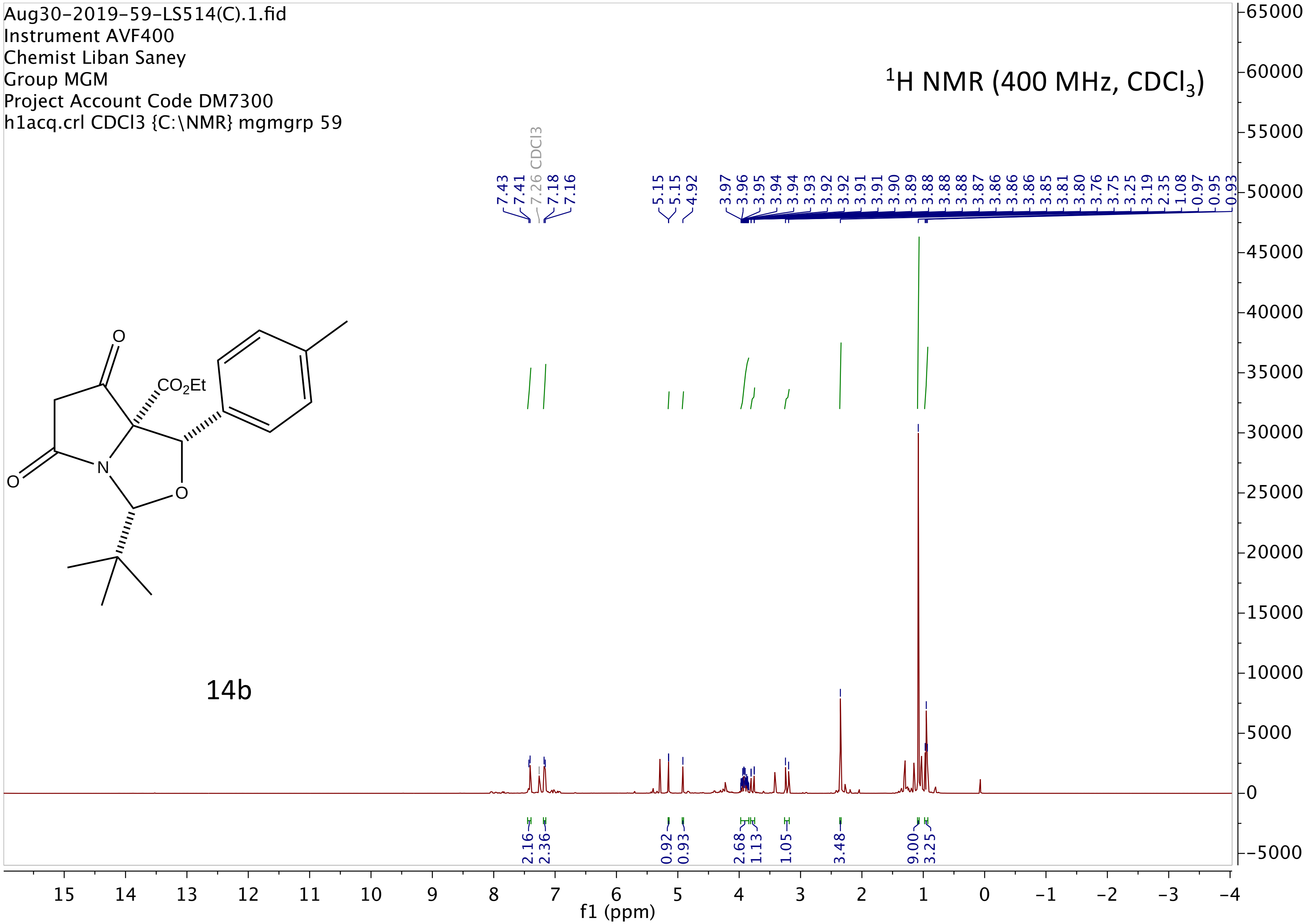

Jul09-2019-59-LS449(P) A8-B2.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59
$^{13}$C NMR (101 MHz, $CDCl_3$)
170.98 169.64 168.39 168.21 167.91 167.49 134.86 132.98 132.08 129.91 129.49 129.12 128.70 128.62 128.59 128.52 128.35 128.28 126.52 126.45 97.25 97.20 80.75 80.38 77.16 CDCl3 65.05 63.81 62.08 61.99 61.23 61.04 59.60 59.35 37.66 37.59 27.08 26.98 14.28 14.14 13.65 13.48
EtO$_2$C
Ph
EtO
N
O
O
O
13b
f1 (ppm)


Aug30-2019-58-LS513(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 58
$^1$H NMR (400 MHz, $CDCl_3$)
7.56 7.56 7.56 7.55 7.55 7.54 7.54 7.54 7.54 7.53 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.32
7.26 CDCl3
5.17 5.16 4.96 3.97 3.95 3.94 3.93 3.92 3.91 3.91 3.90 3.89 3.89 3.88 3.87 3.86 3.85 3.85 3.82 3.82 3.77 3.77 3.24 3.19 1.09 0.93 0.91 0.89
5.58 0.93 0.91 2.05 1.00 1.01 9.00 3.01
O
O
N
O
$CO_2Et$
14a
f1 (ppm)


Aug30-2019-58-LS513(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 58
$^{13}$C NMR (101 MHz, $CDCl_3$)
198.09
172.02
164.96
134.40
128.30
128.05
126.54
96.93
81.68
80.44
77.16 CDCl3
62.36
46.13
36.03
25.67
13.54
$CO_2Et$
14a
f1 (ppm)

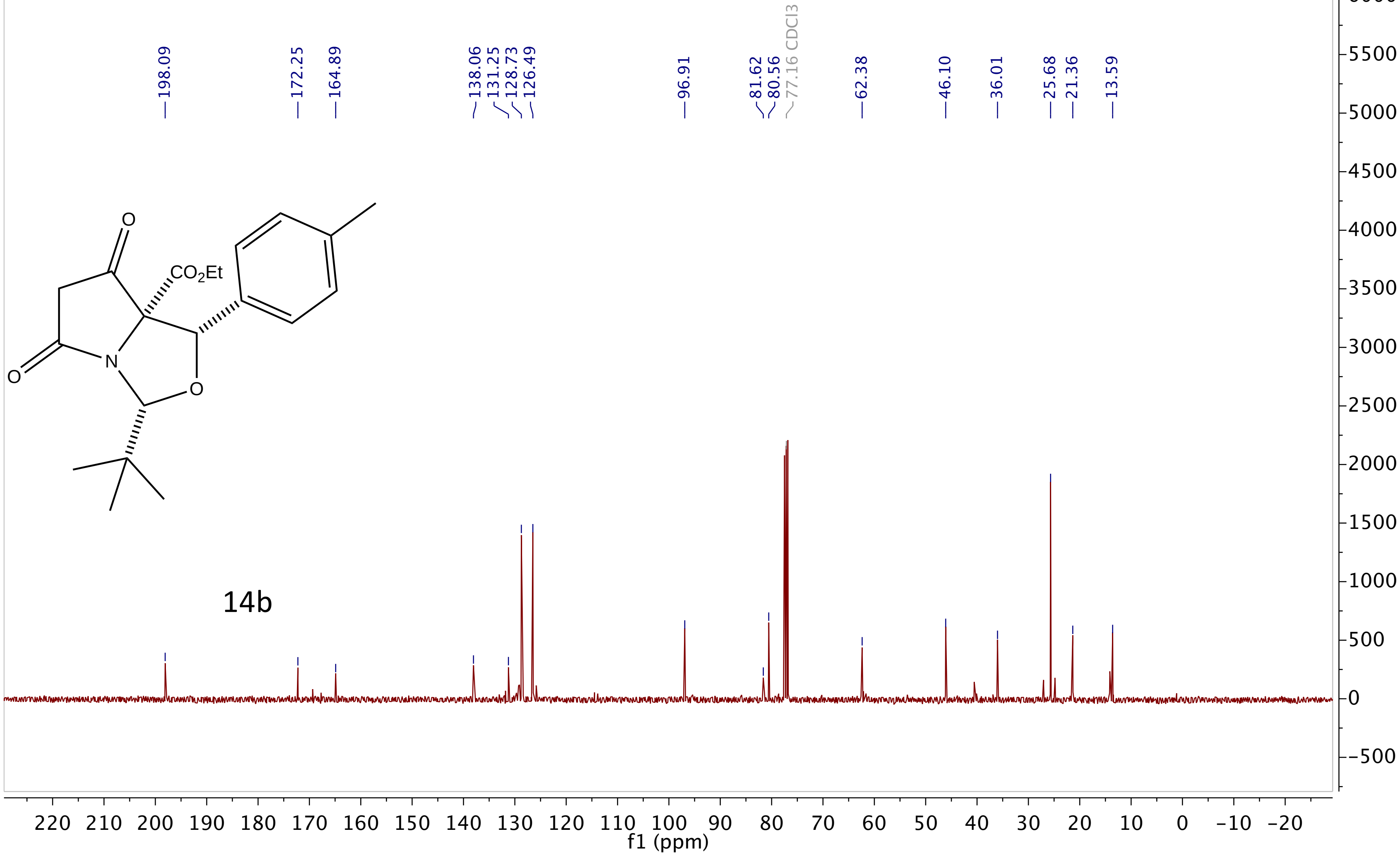
Aug30-2019-59-LS514(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59

$^1H$ NMR (400 MHz, $CDCl_3$)

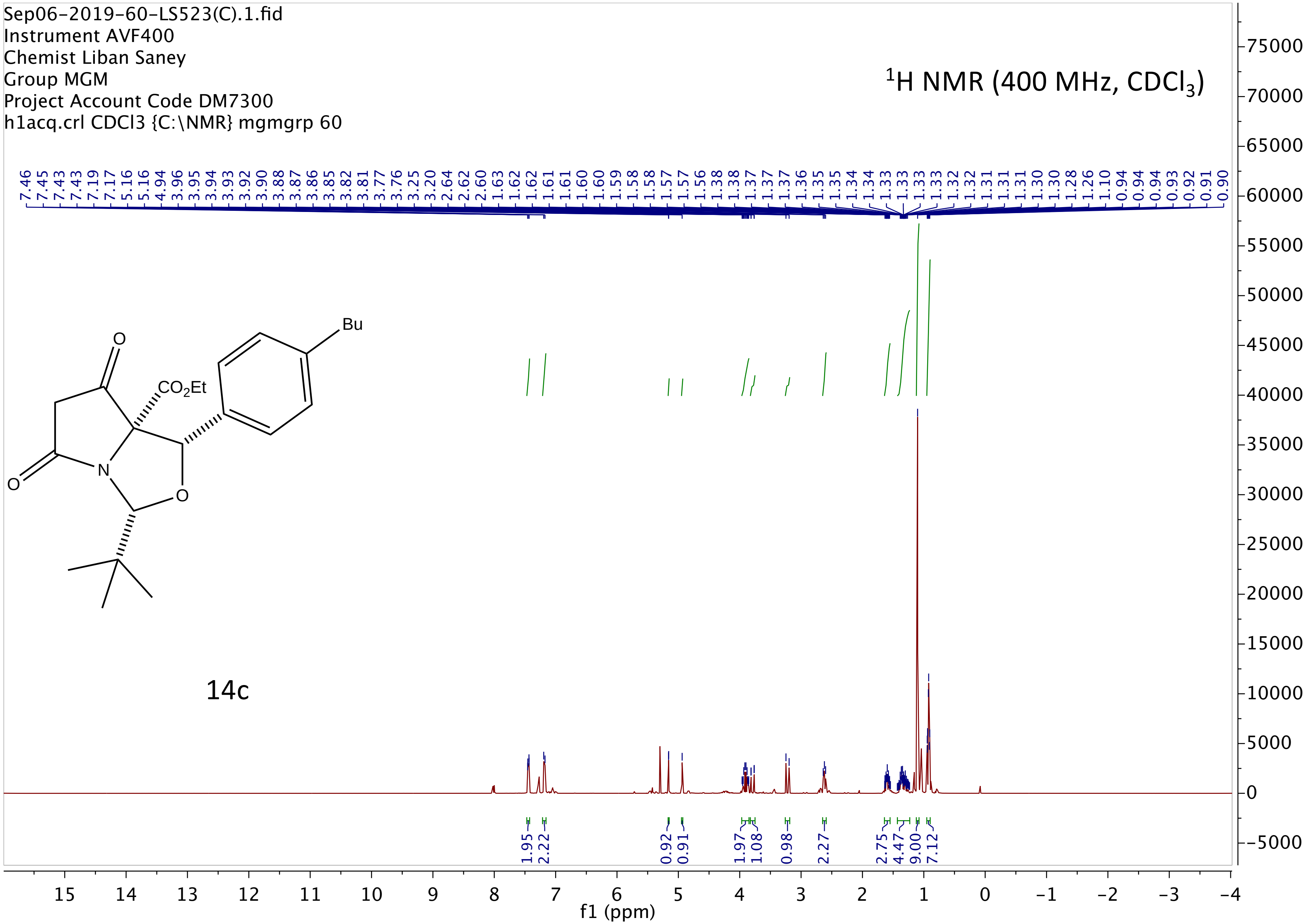



14b

Aug30-2019-59-LS514(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59

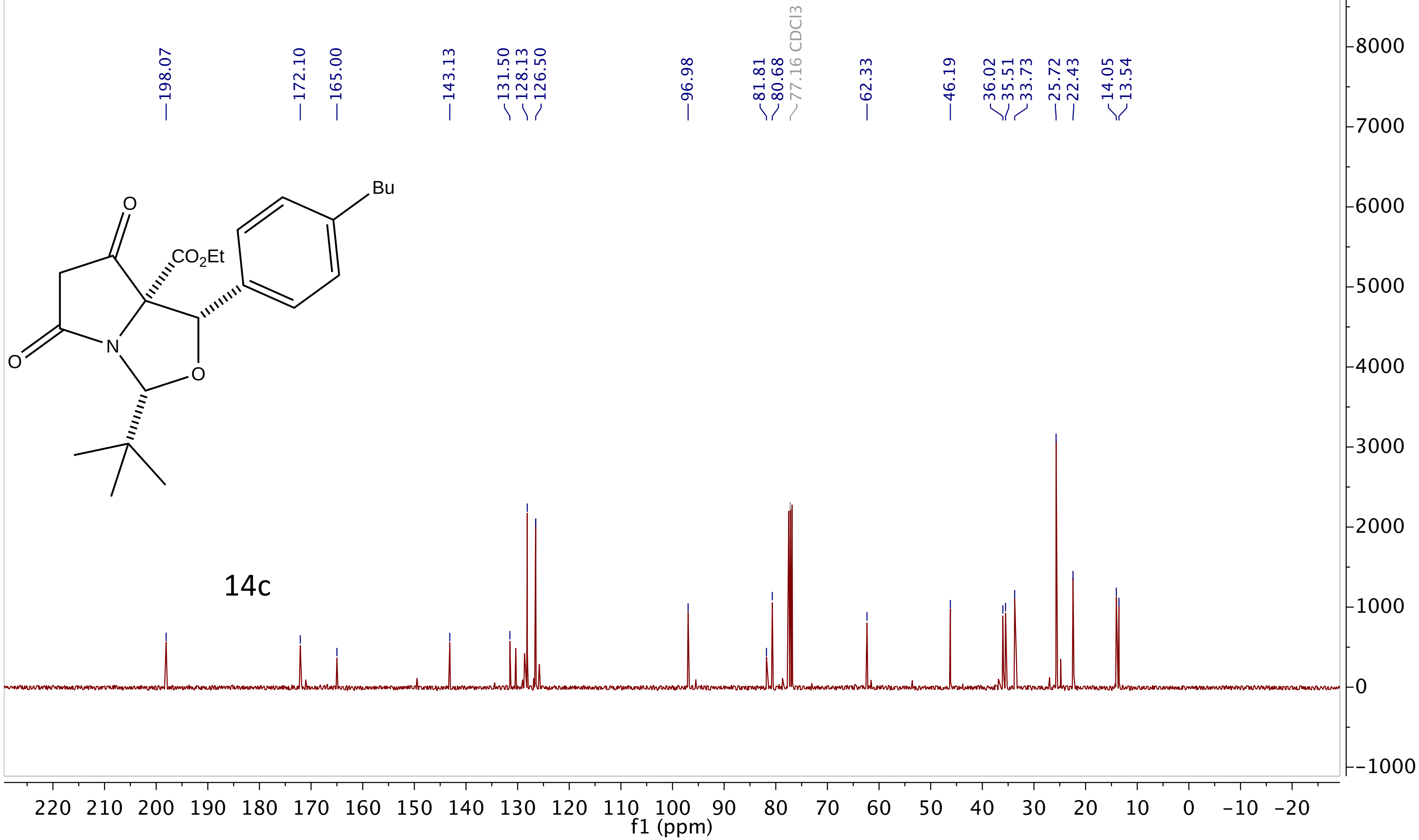


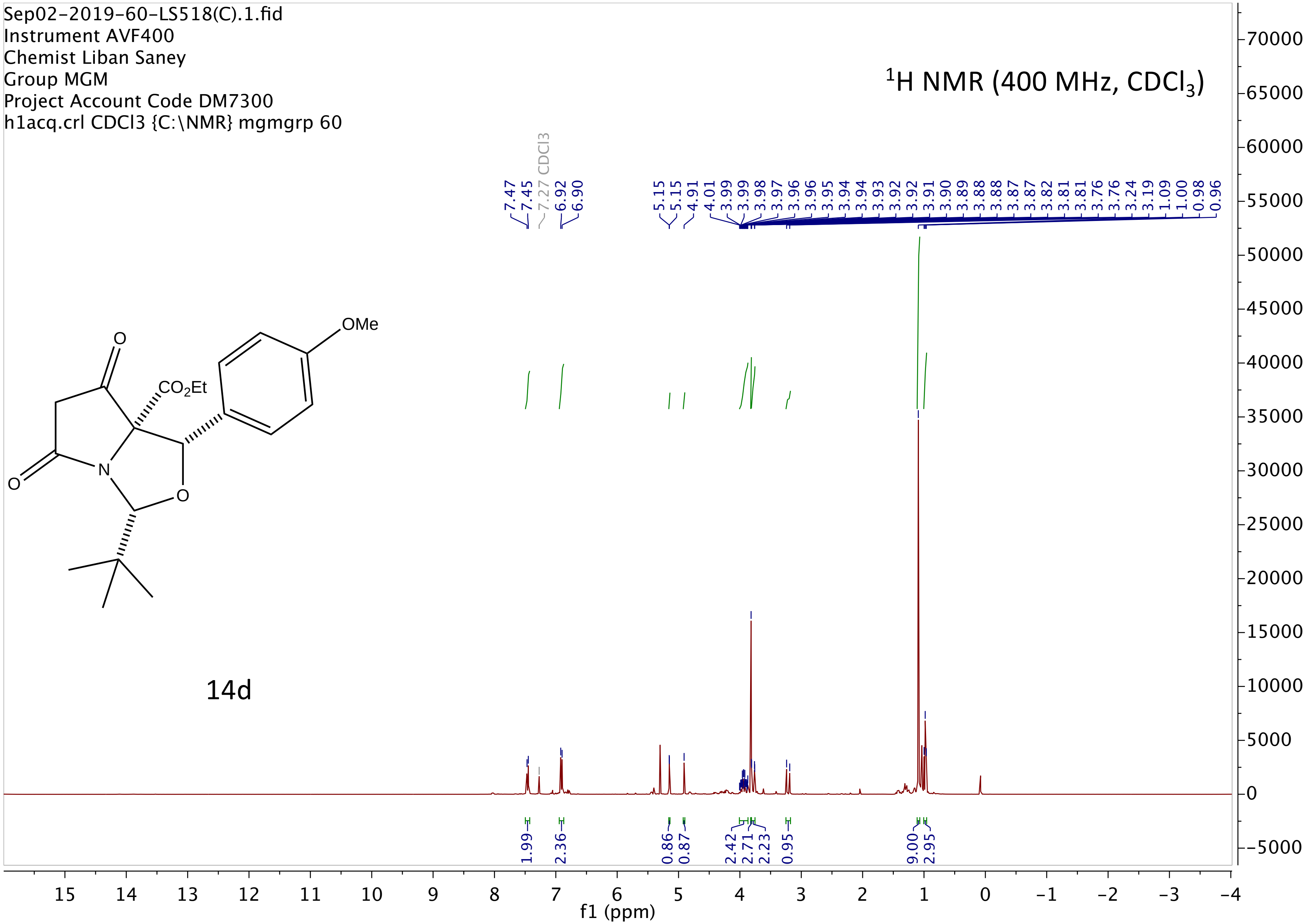

14b


Sep06-2019-60-LS523(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
$^1$H NMR (400 MHz, CDCl$_3$)
Bu
O
CO$_2$Et
N
O
O
14c
f1 (ppm)

Sep06-2019-60-LS523(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

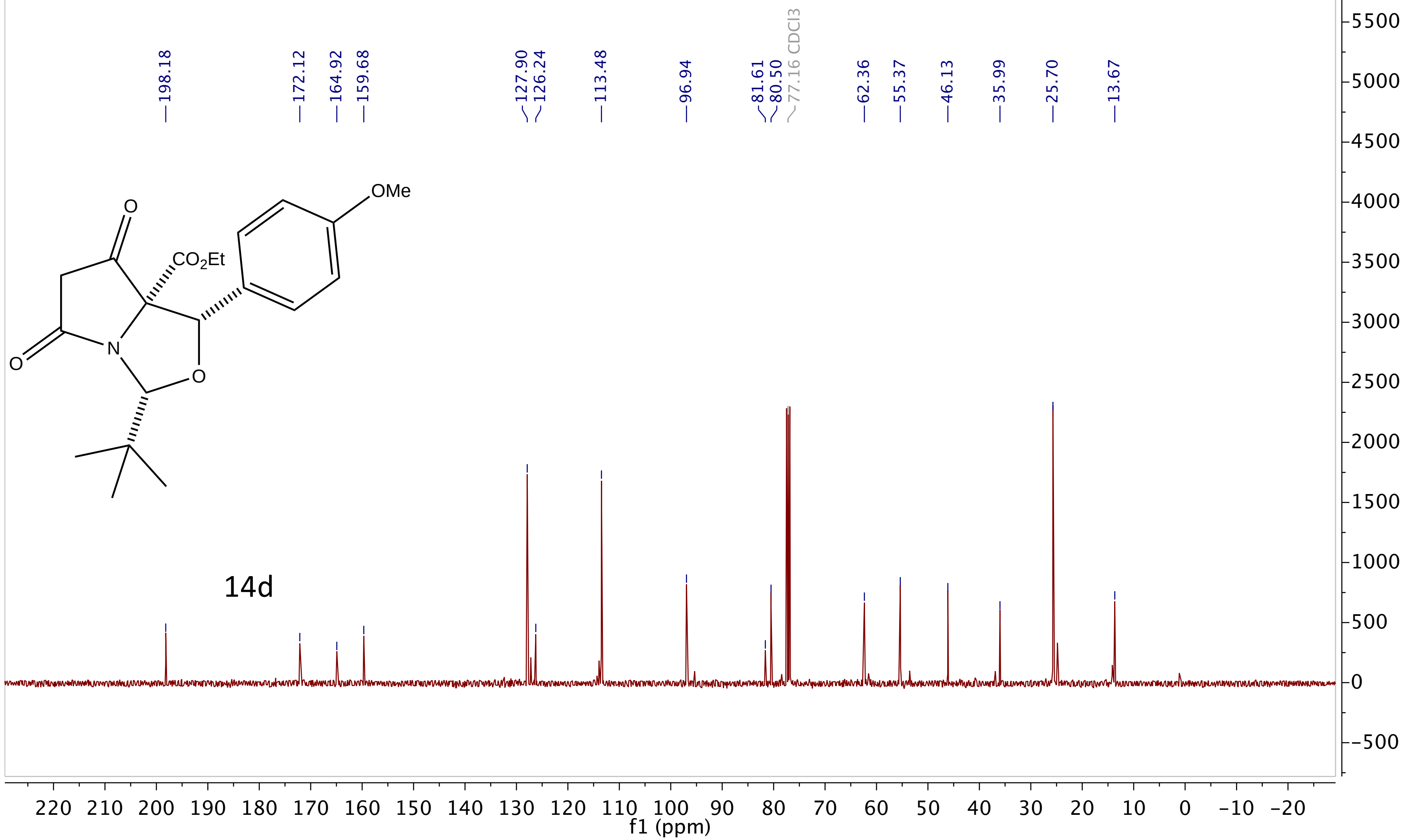
$^{13}C$ NMR (101 MHz, $CDCl_3$)




Sep02-2019-60-LS518(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
$^1$H NMR (400 MHz, $CDCl_3$)
7.47
7.45
7.27 CDCl3
6.92
6.90
5.15
5.15
4.91
4.01
3.99
3.99
3.98
3.97
3.96
3.96
3.95
3.94
3.94
3.93
3.92
3.92
3.91
3.90
3.89
3.88
3.88
3.87
3.87
3.82
3.81
3.81
3.76
3.76
3.24
3.19
1.09
1.00
0.98
0.96
OMe
O
$CO_2Et$
N
O
O
14d
1.99
2.36
0.86
0.87
2.42
2.71
2.23
0.95
9.00
2.95
f1 (ppm)

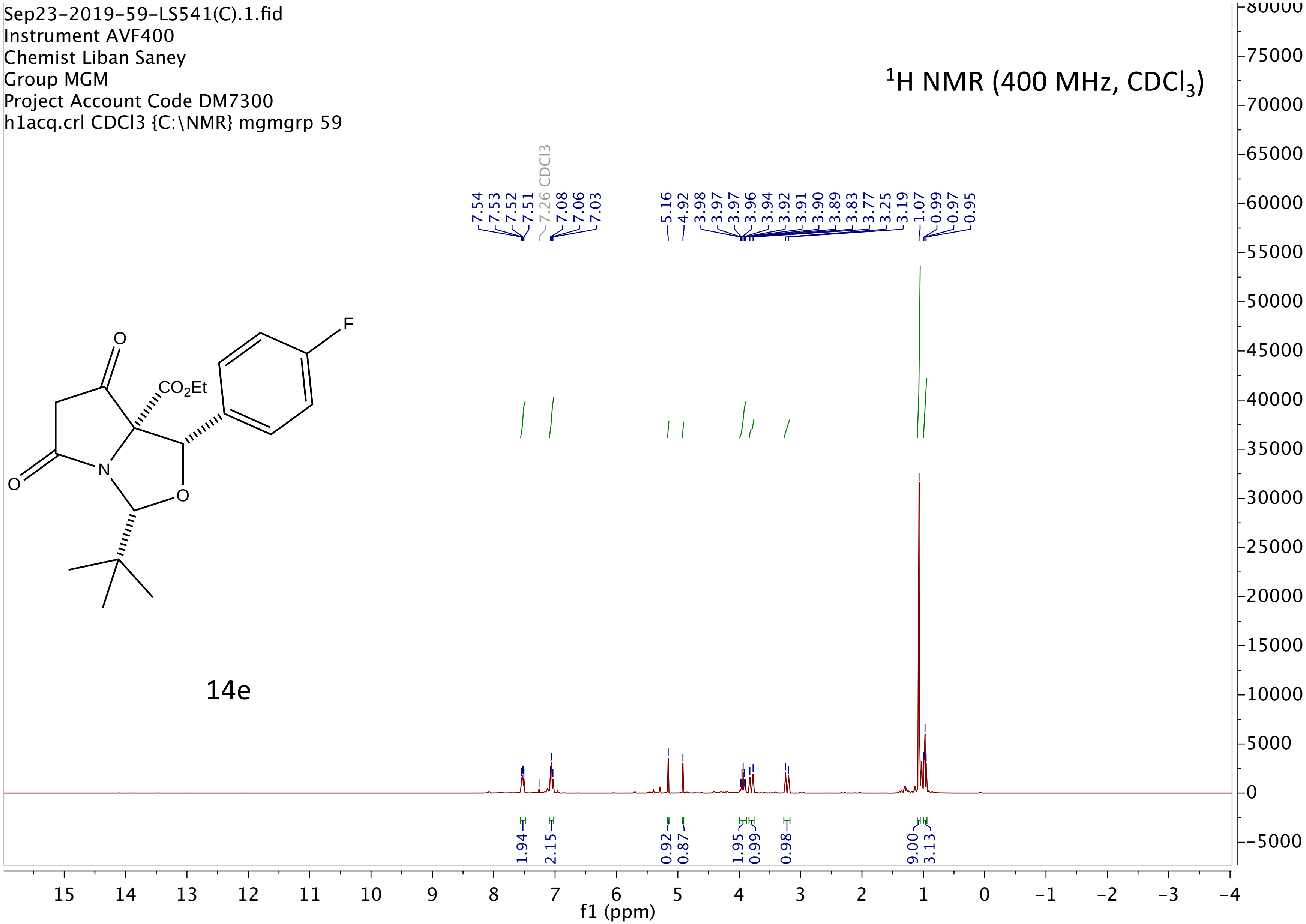
Sep02-2019-60-LS518(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)



Sep23-2019-59-LS541(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59

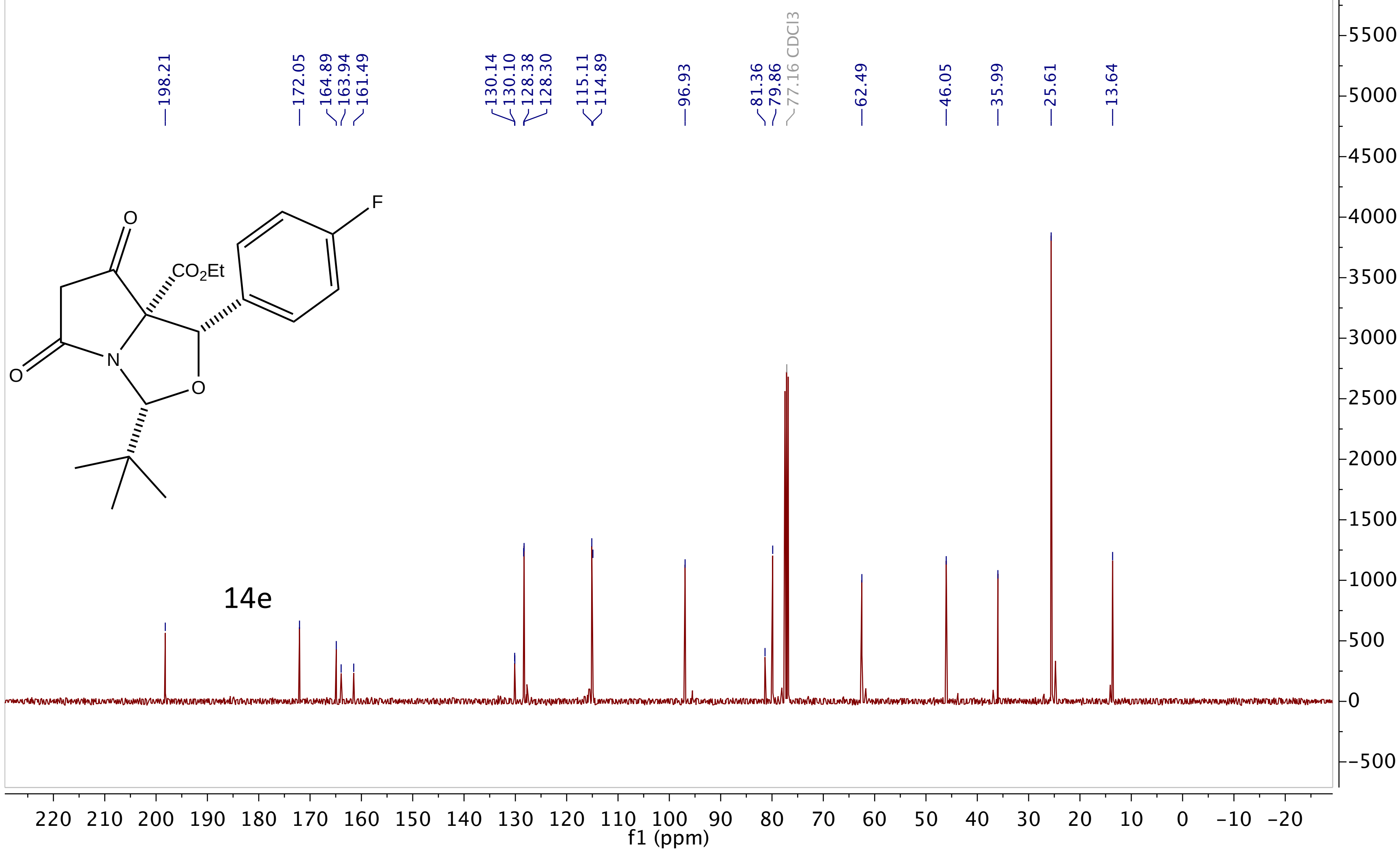
$^1$H NMR (400 MHz, $CDCl_3$)



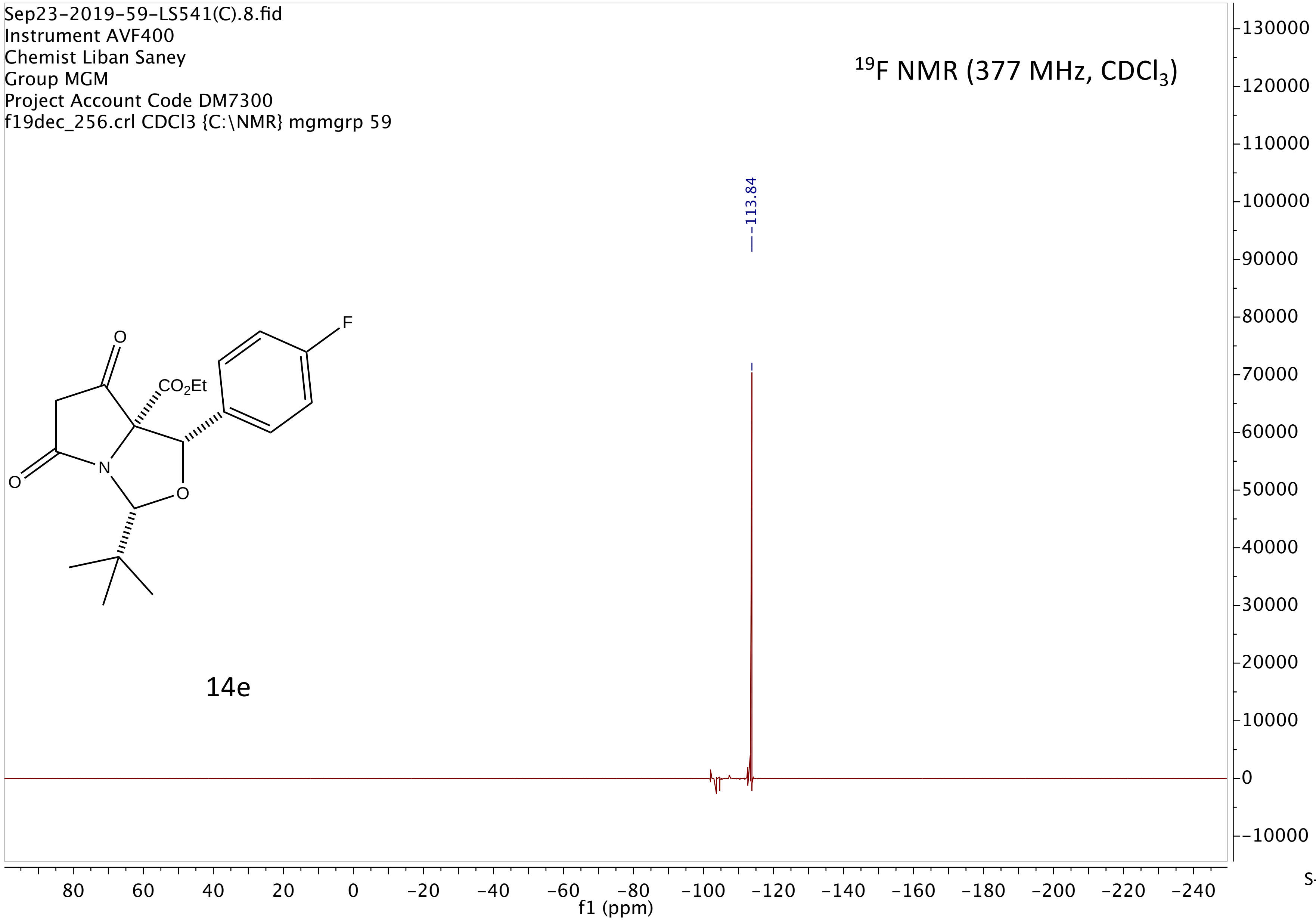

14e

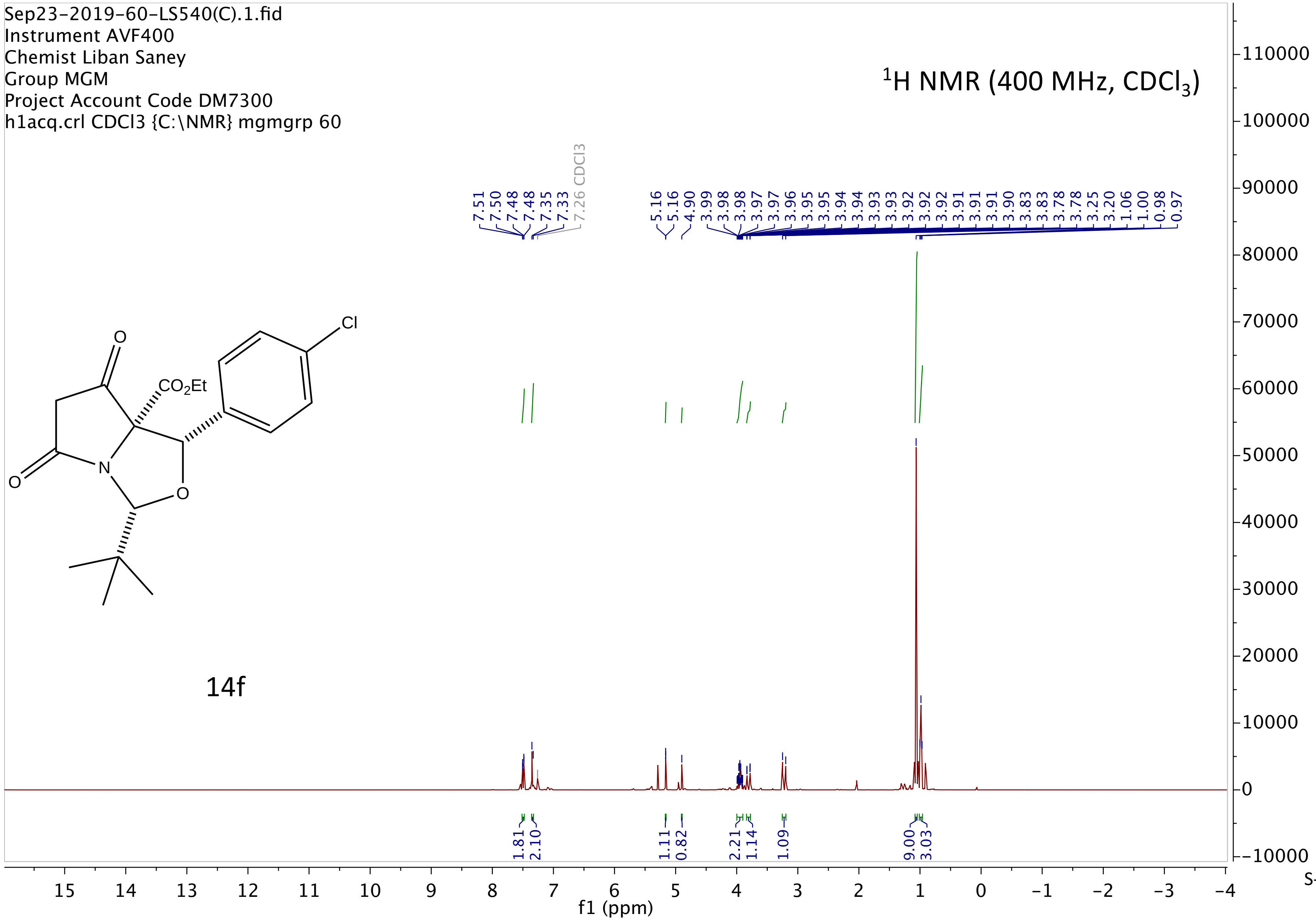
Sep23-2019-59-LS541(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59

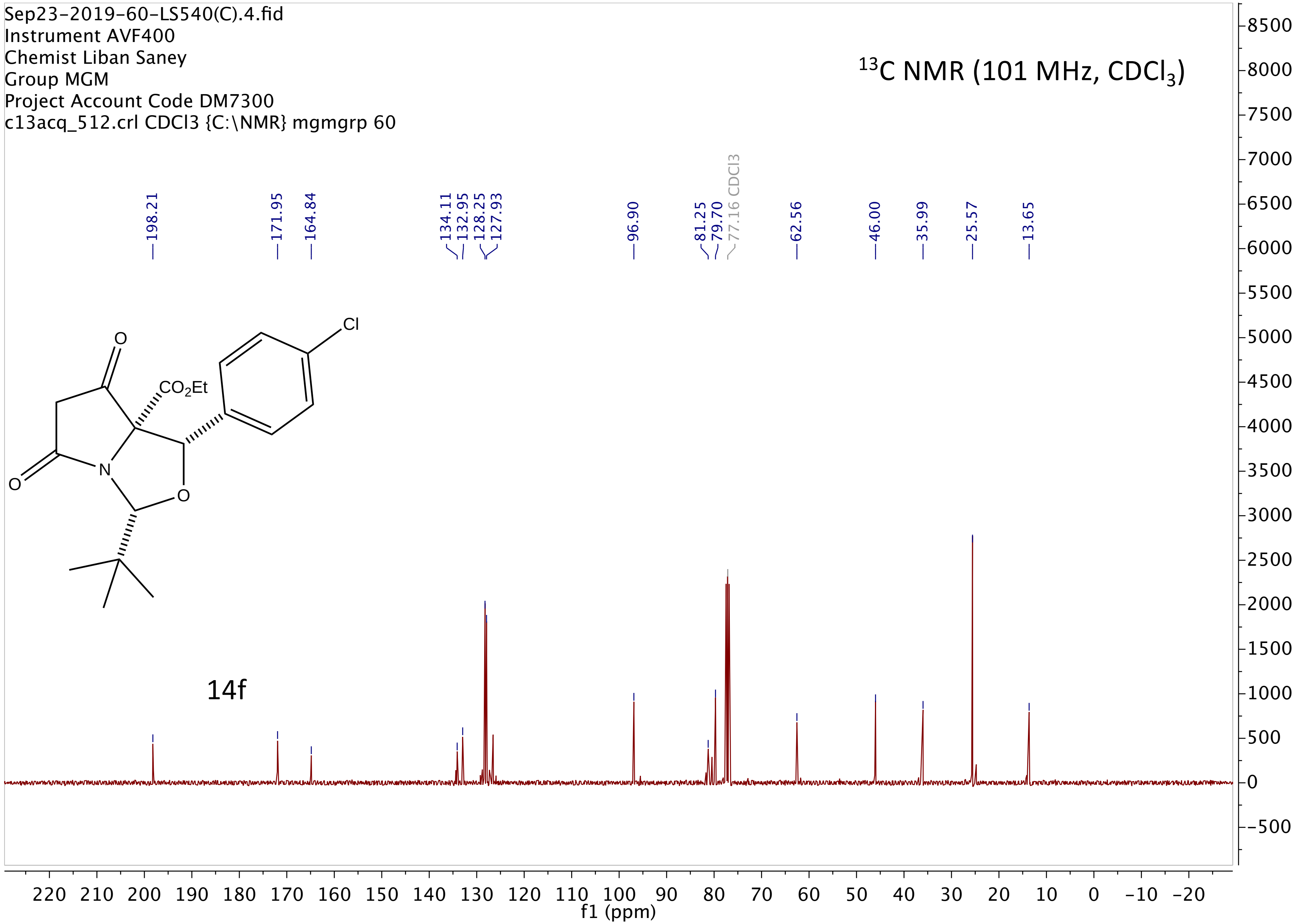
$^{13}C$ NMR (101 MHz, $CDCl_3$)



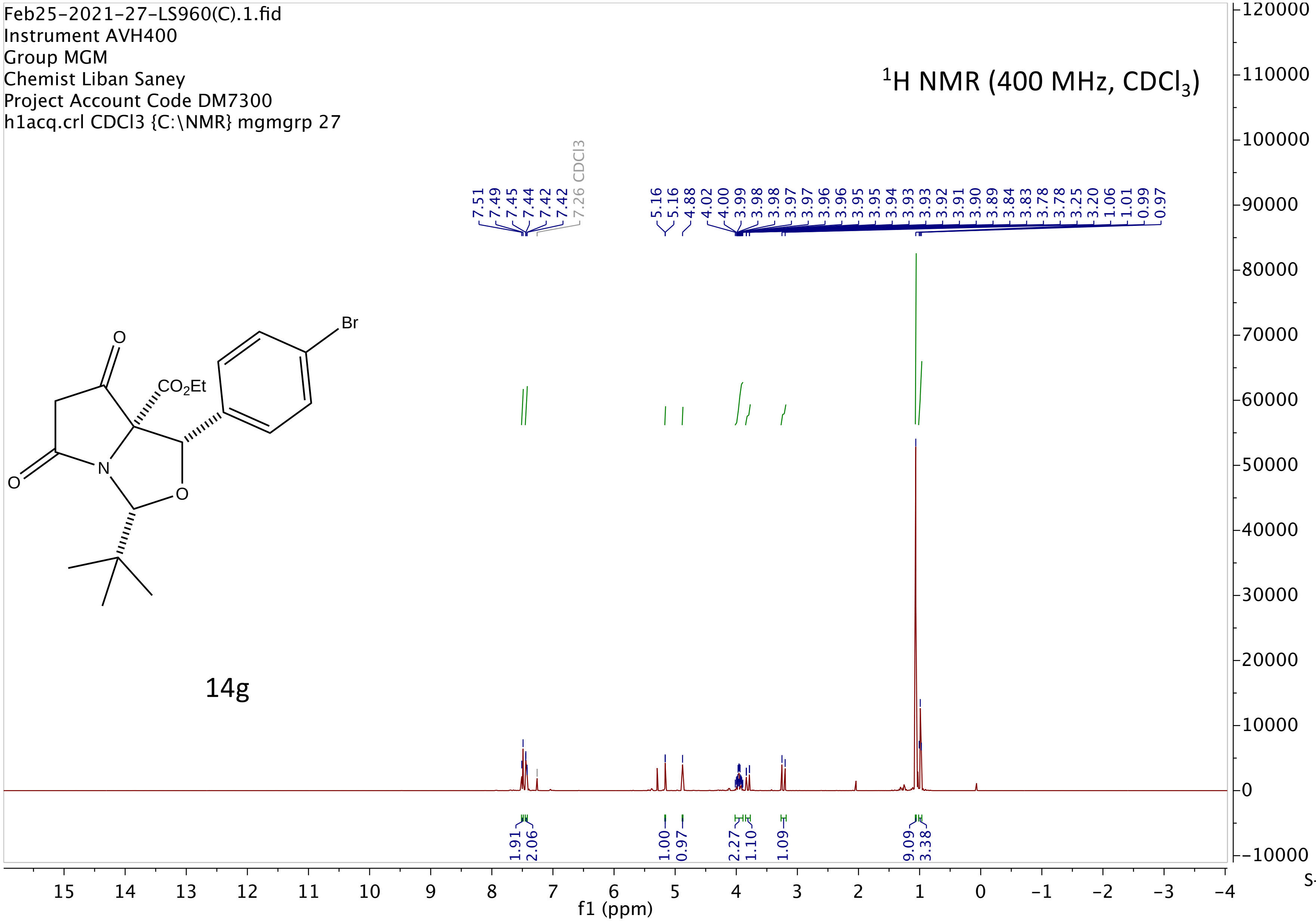

14e


Sep23-2019-59-LS541(C).8.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 59
$^{19}$F NMR (377 MHz, $CDCl_3$)
-113.84
14e
f1 (ppm)


Sep23-2019-60-LS540(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
$^1$H NMR (400 MHz, $CDCl_3$)
7.51 7.50 7.48 7.48 7.35 7.33 7.26 CDCl3
5.16 5.16 4.90 3.99 3.98 3.98 3.97 3.97 3.96 3.95 3.95 3.94 3.94 3.93 3.93 3.92 3.92 3.91 3.91 3.91 3.90 3.83 3.83 3.78 3.78 3.25 3.20 1.06 1.00 0.98 0.97
O
O
O
N
CO$_2$Et
Cl
14f
1.81 2.10 1.11 0.82 2.21 1.14 1.09 9.00 3.03
f1 (ppm)

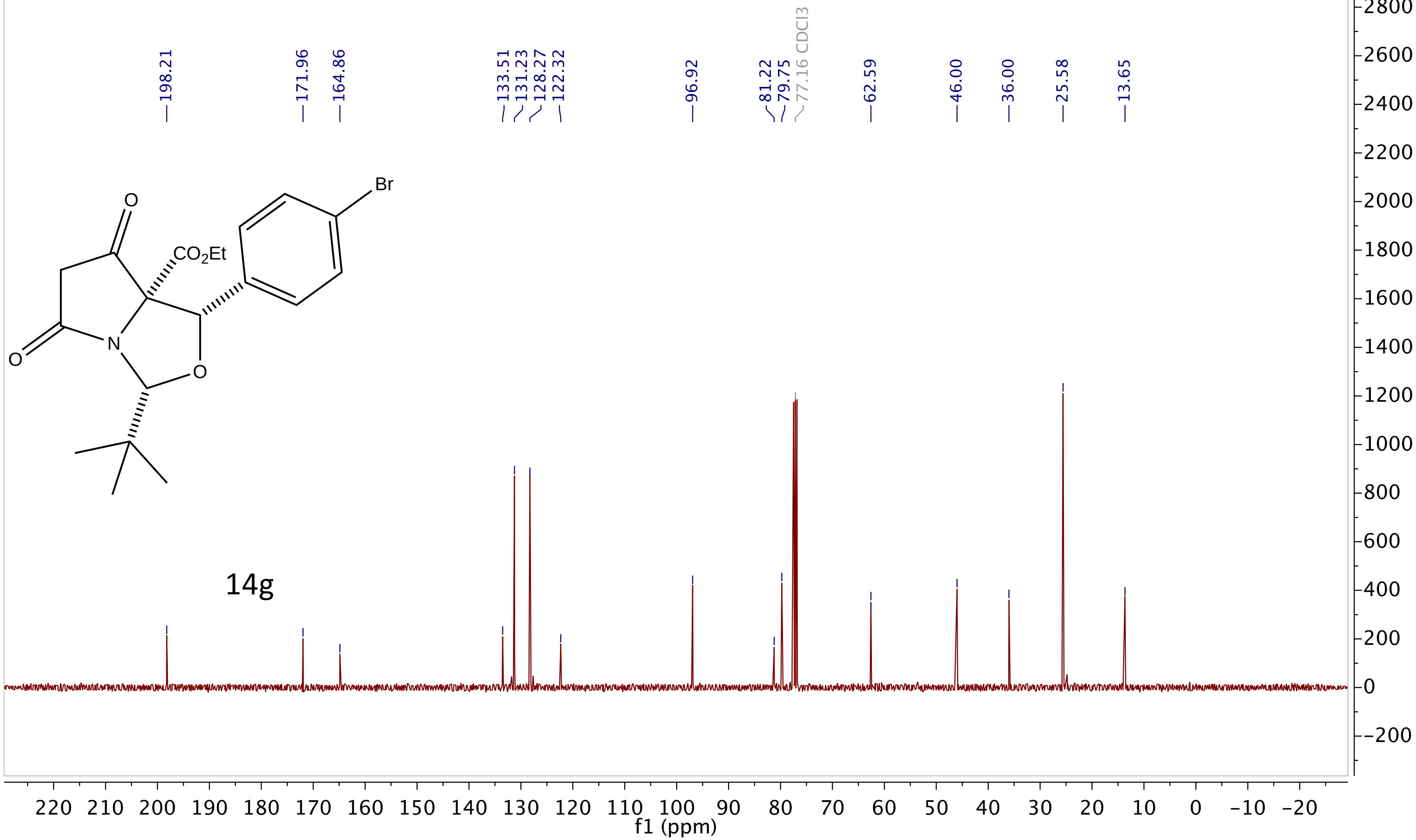

Sep23-2019-60-LS540(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CDCl_3$)
198.21
171.95
164.84
134.11
132.95
128.25
127.93
96.90
81.25
79.70
77.16 CDCl3
62.56
46.00
35.99
25.57
13.65
O
O
N
O
CO$_2$Et
Cl
14f
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

Feb25-2021-27-LS960(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 27



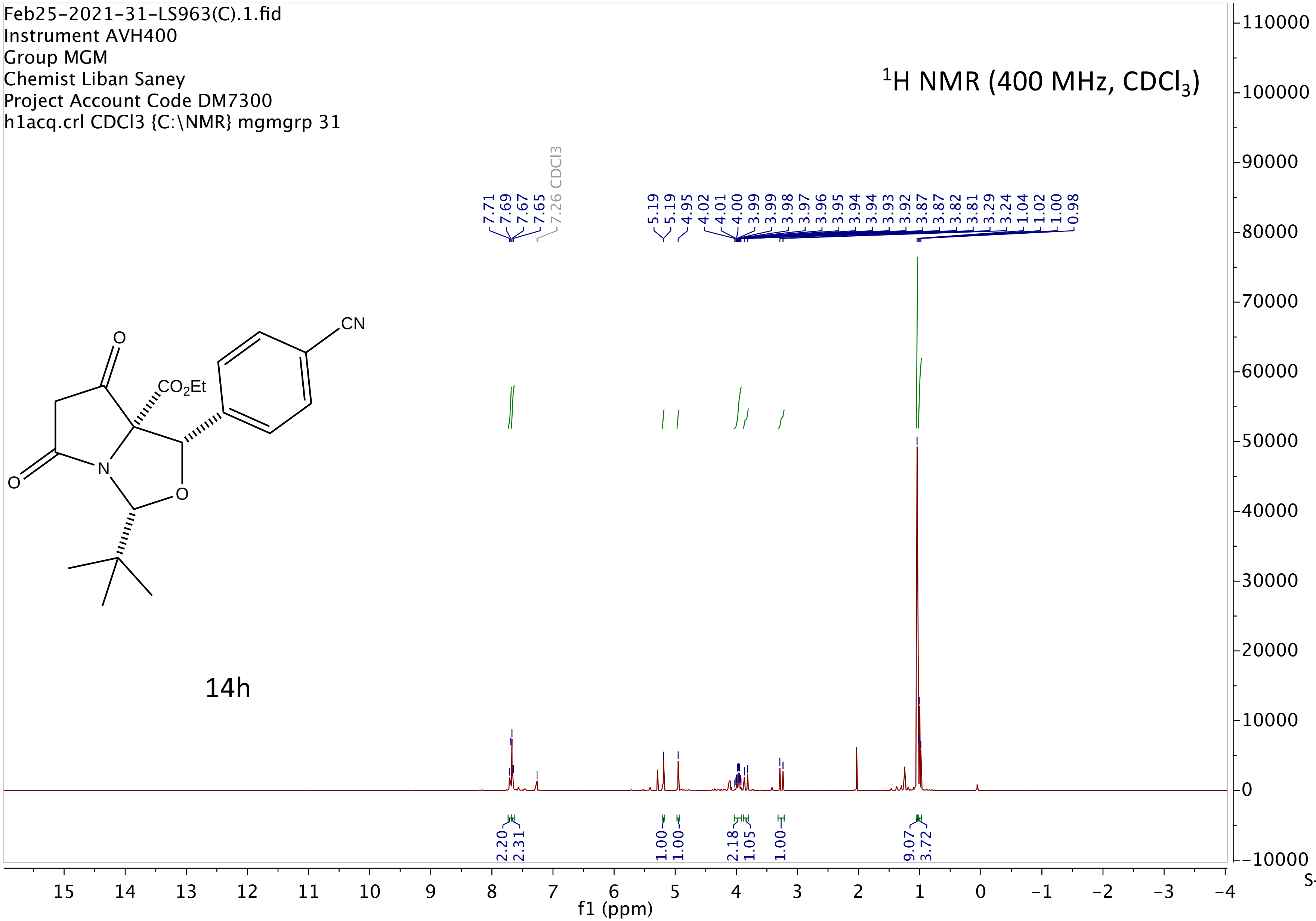
Feb25-2021-27-LS960(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 27

$^{13}C$ NMR (101 MHz, $CDCl_3$)

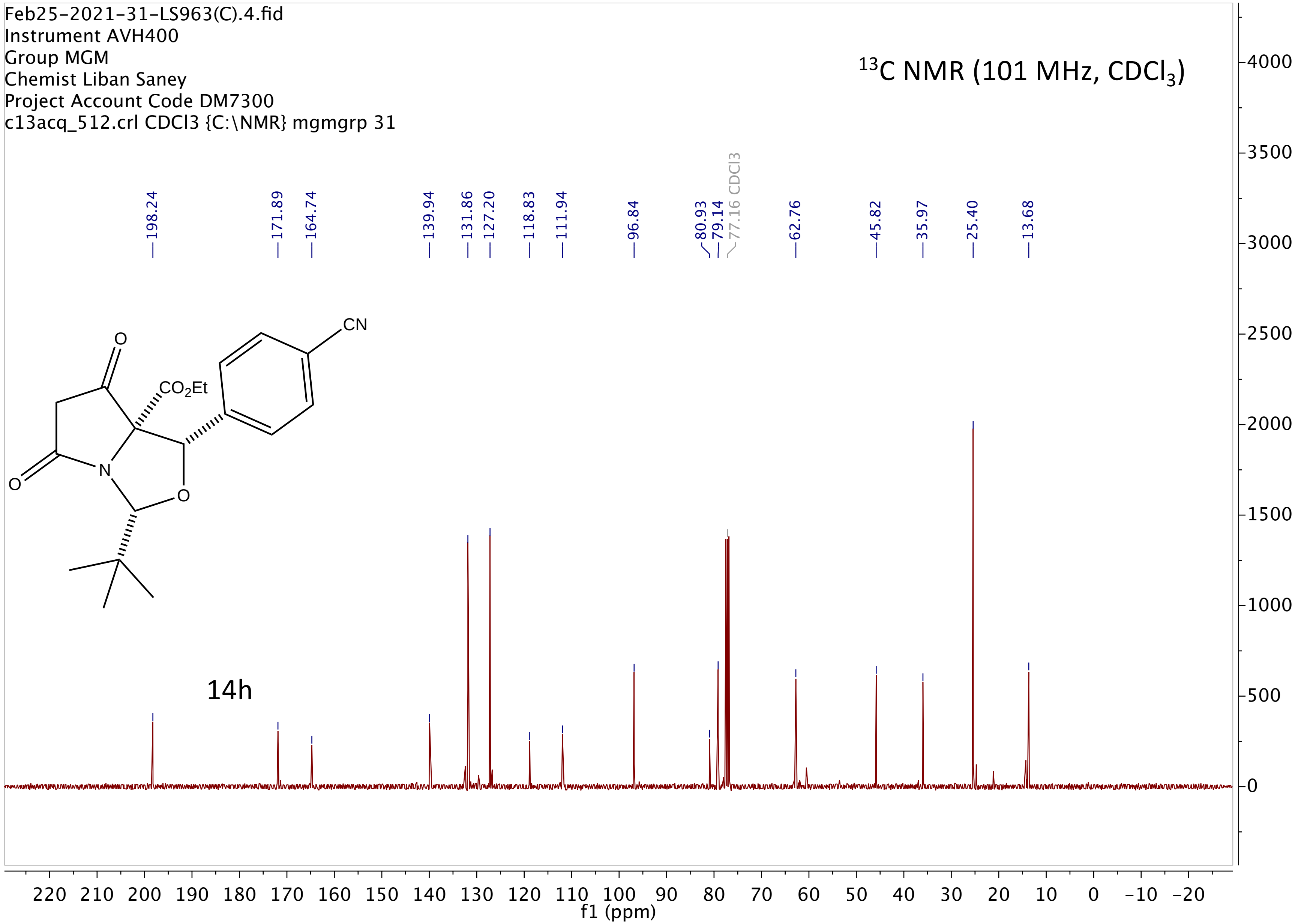


Feb25-2021-31-LS963(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 31

$^1H$ NMR (400 MHz, $CDCl_3$)

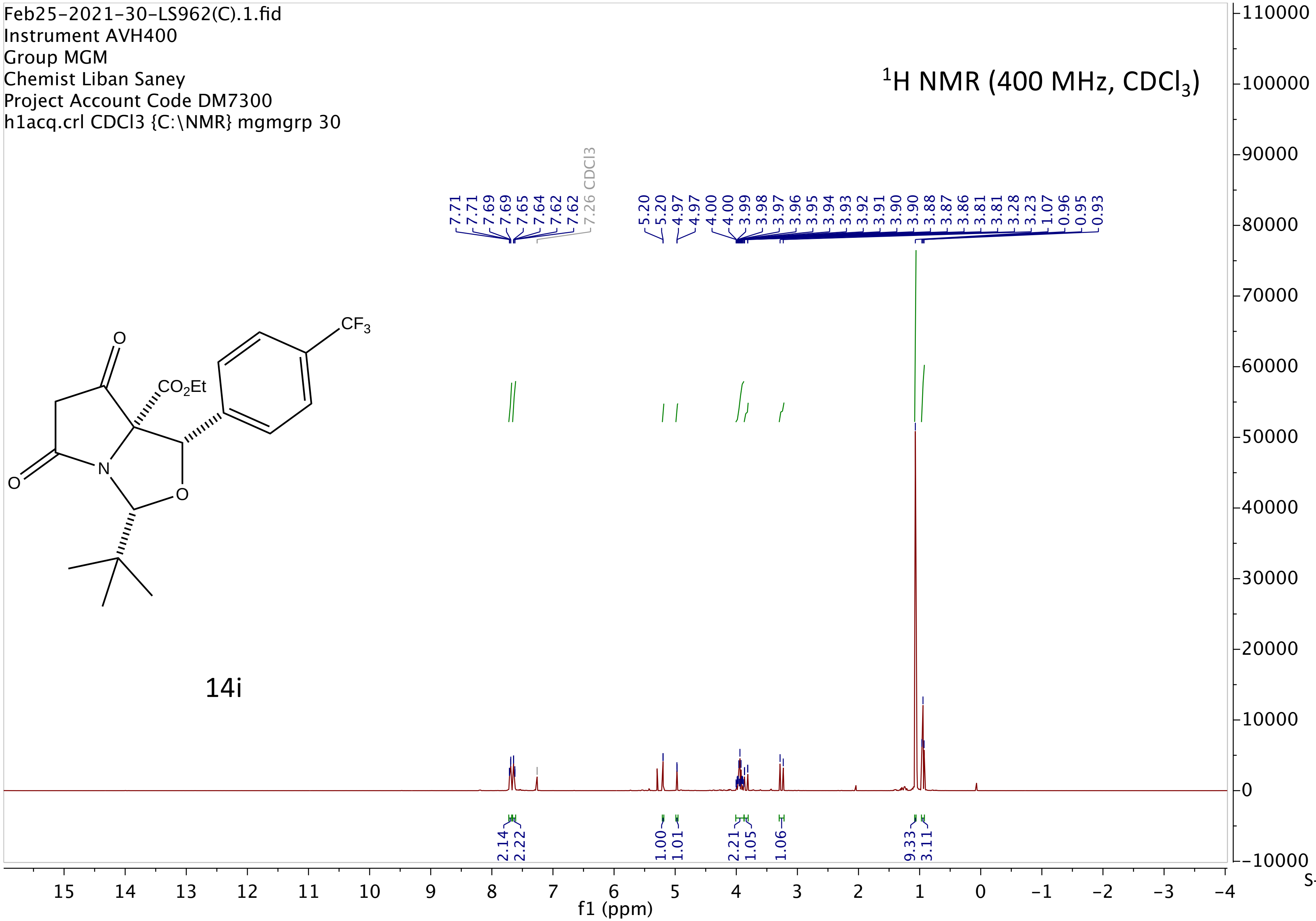



14h


Feb25-2021-31-LS963(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 31
$^{13}C$ NMR (101 MHz, $CDCl_3$)
198.24
171.89
164.74
139.94
131.86
127.20
118.83
111.94
96.84
80.93
79.14
77.16 CDCl3
62.76
45.82
35.97
25.40
13.68
CN
O
$CO_2Et$
N
O
O
14h
f1 (ppm)

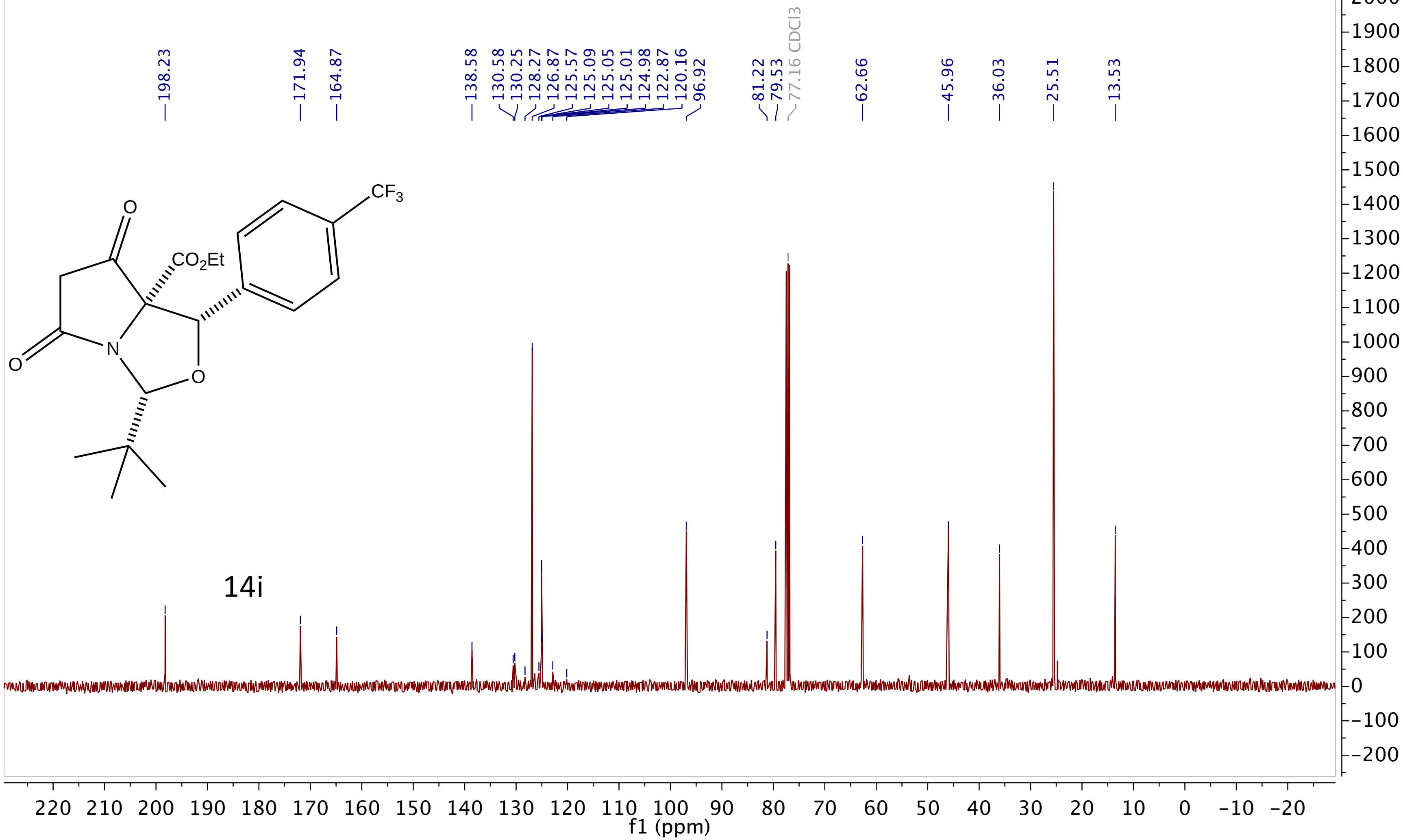
Feb25-2021-30-LS962(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 30

$^1$H NMR (400 MHz, $CDCl_3$)



Feb25-2021-30-LS962(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 30

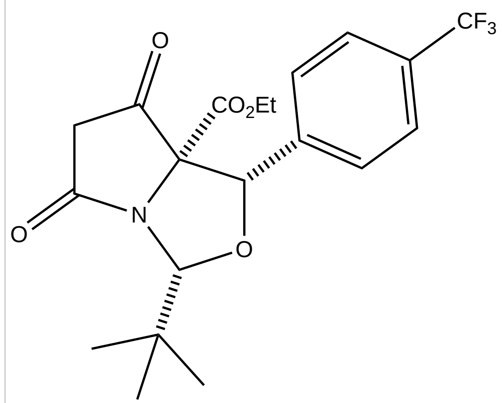
$^{13}C$ NMR (101 MHz, $CDCl_3$)



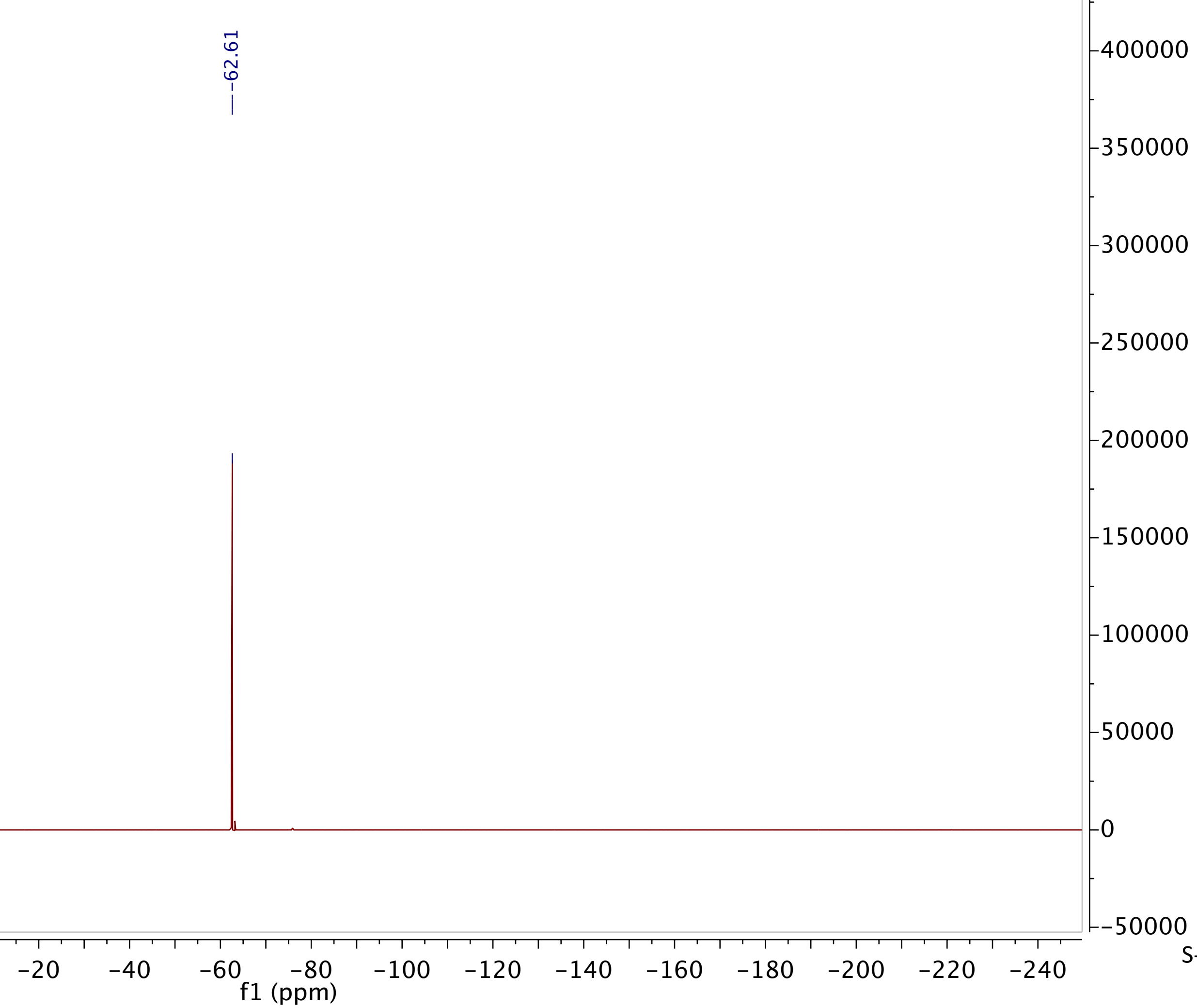

14i

Feb25-2021-30-LS962(C).6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 30

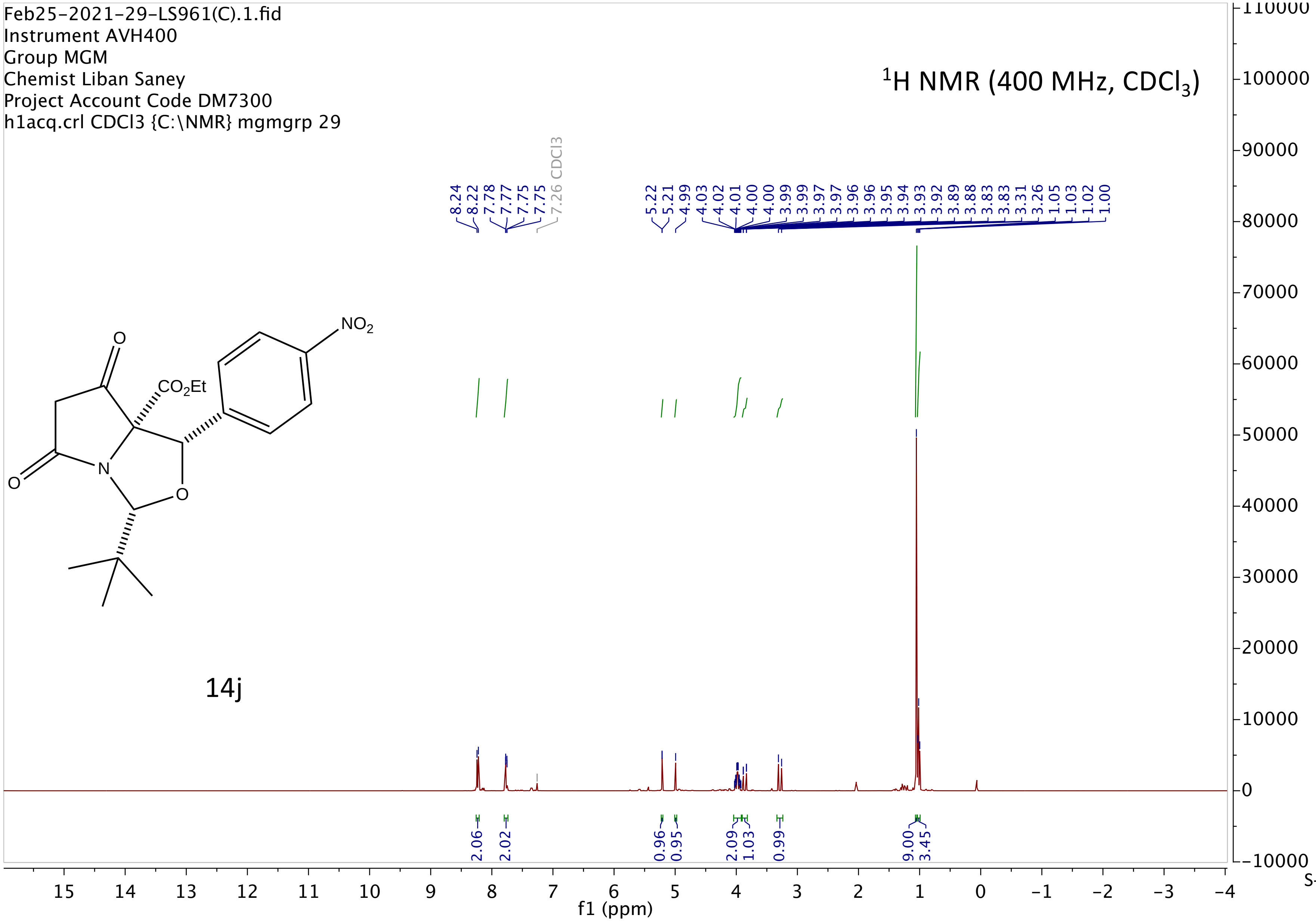
$^{19}F$ NMR (376 MHz, $CDCl_3$)



14i



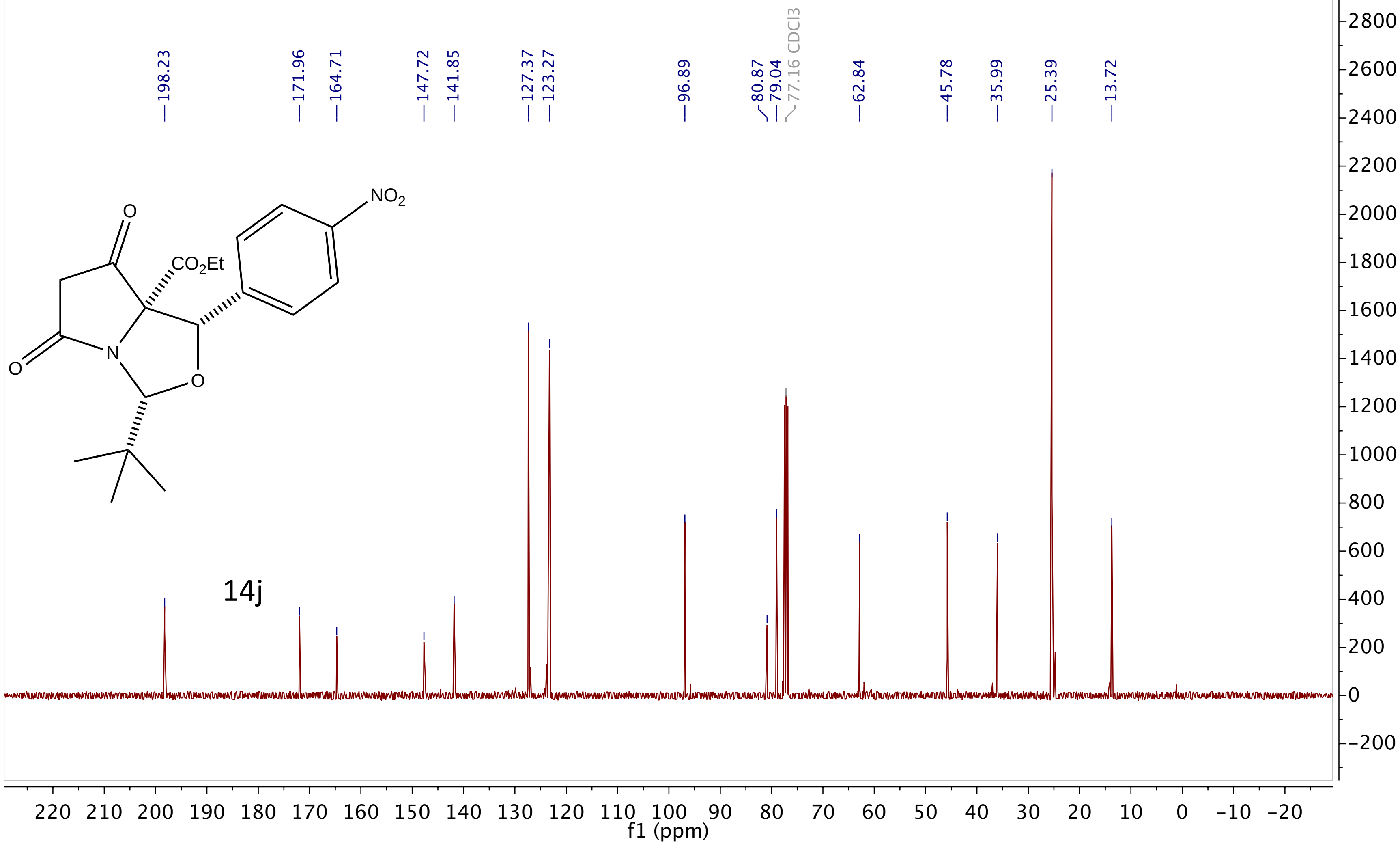
Feb25-2021-29-LS961(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 29

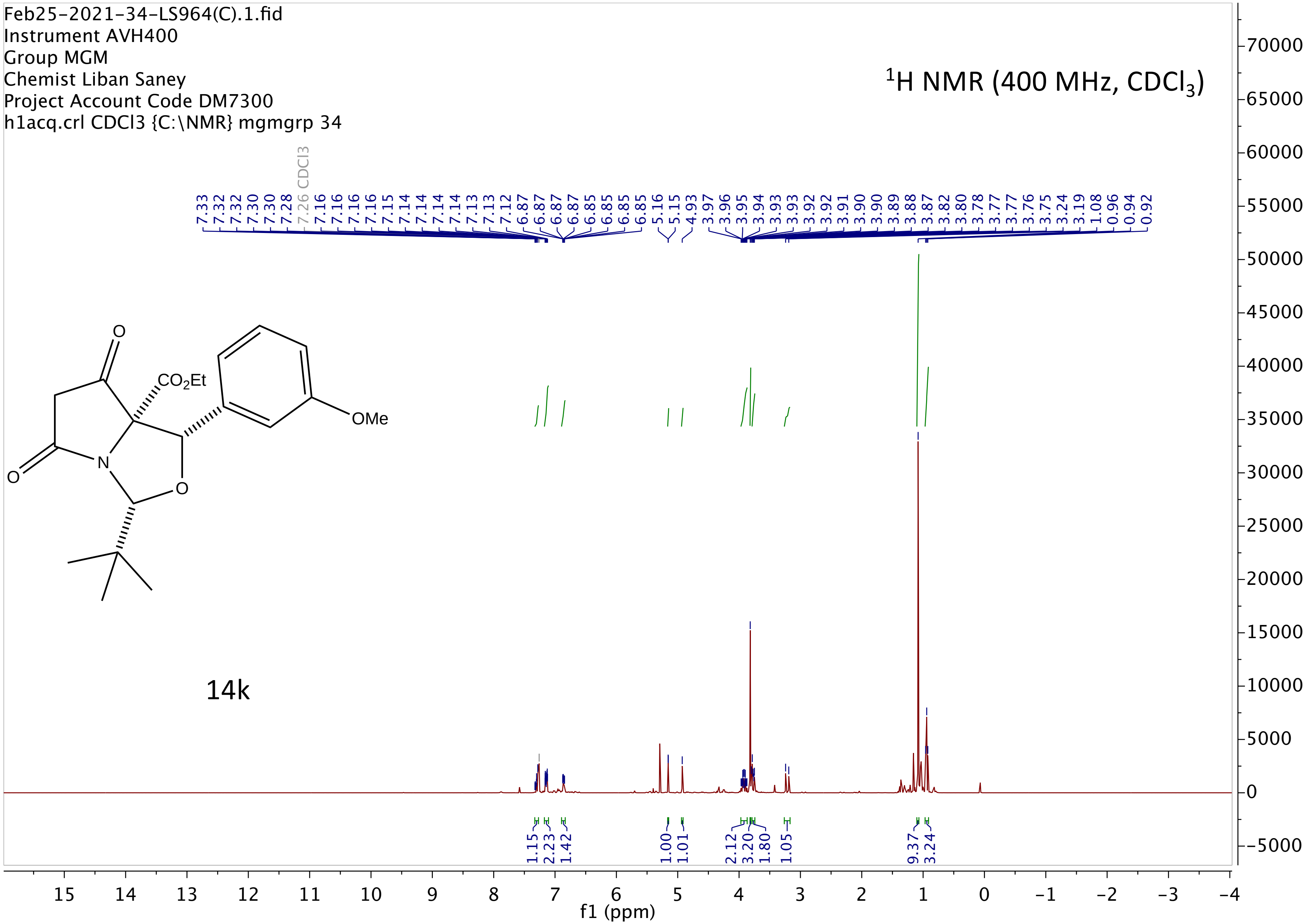



14j

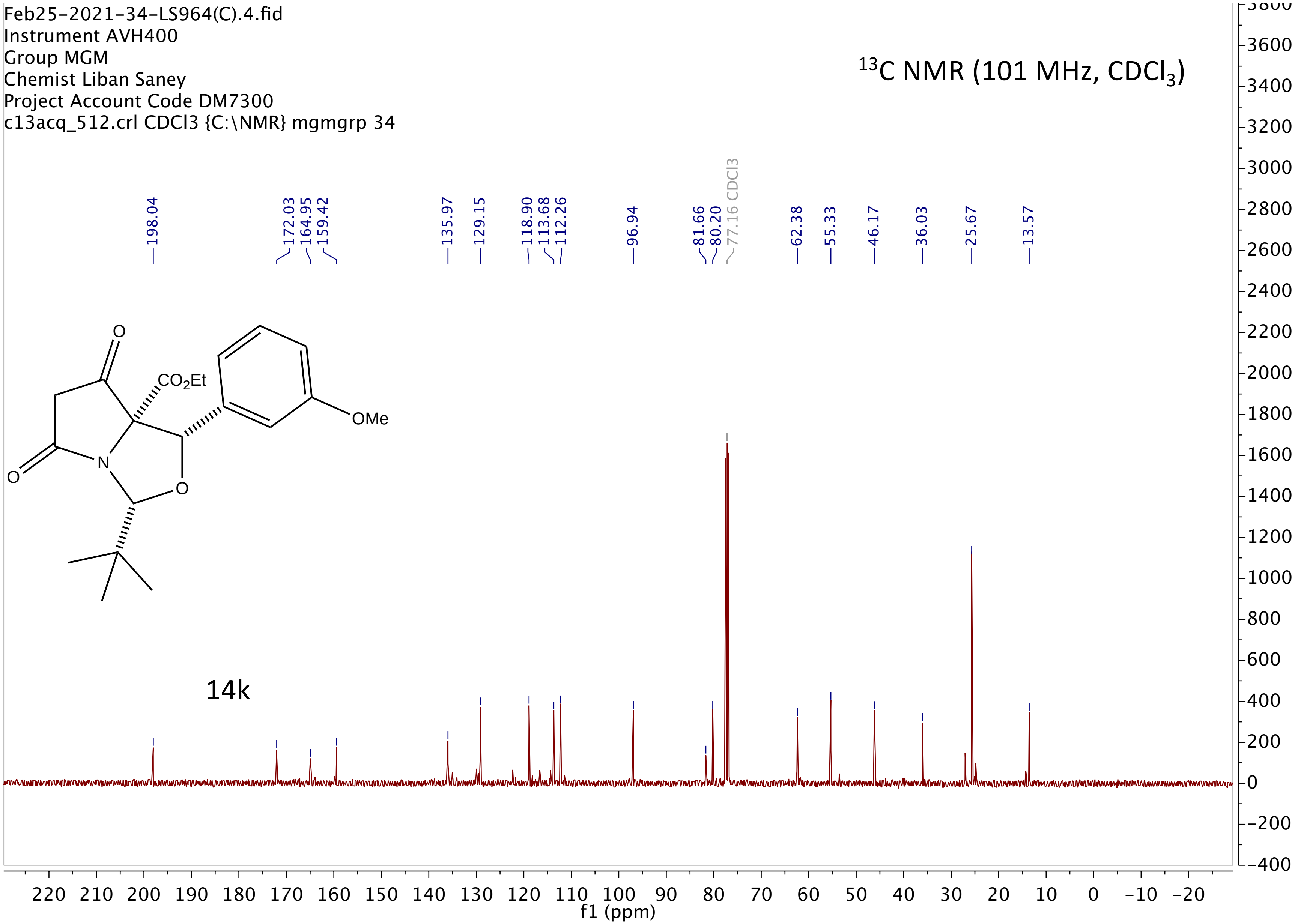
Feb25-2021-29-LS961(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 29

$^{13}$C NMR (101 MHz, $CDCl_3$)



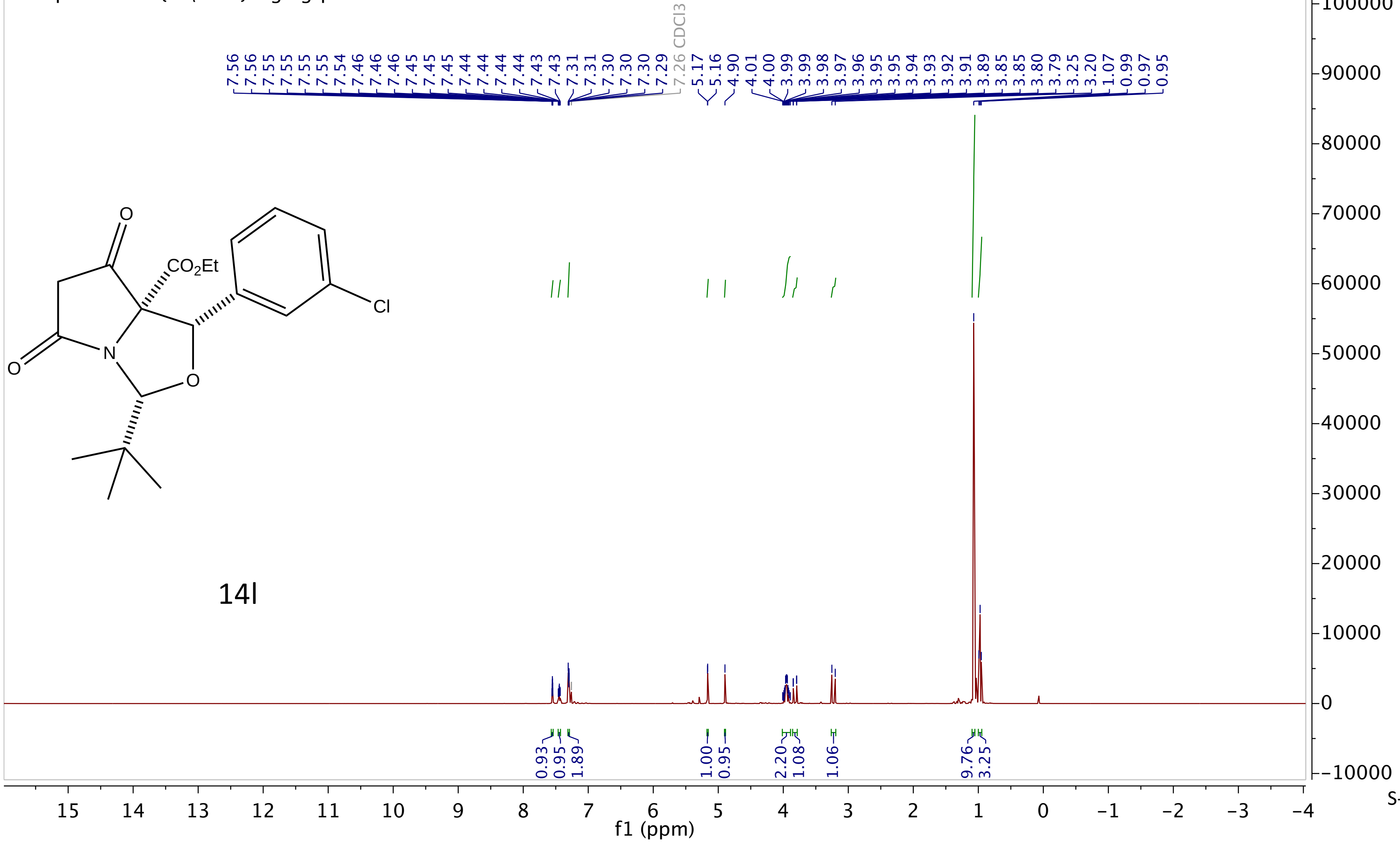

Feb25-2021-34-LS964(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 34
¹H NMR (400 MHz, CDCl₃)
7.33 7.32 7.32 7.30 7.30 7.28 7.26 CDCl3 7.16 7.16 7.16 7.16 7.15 7.14 7.14 7.14 7.14 7.13 7.13 7.12 6.87 6.87 6.87 6.87 6.85 6.85 6.85 6.85 5.16 5.15 4.93 3.97 3.96 3.95 3.94 3.93 3.93 3.92 3.92 3.91 3.90 3.90 3.89 3.88 3.87 3.82 3.80 3.78 3.77 3.77 3.76 3.75 3.24 3.19 1.08 0.96 0.94 0.92
CO2Et
OMe
O
N
1.15 2.23 1.42 1.00 1.01 2.12 3.20 1.80 1.05 9.37 3.24
f1 (ppm)

14k


Feb25-2021-34-LS964(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 34
13C NMR (101 MHz, CDCl3)
198.04
172.03
164.95
159.42
135.97
129.15
118.90
113.68
112.26
96.94
81.66
80.20
77.16 CDCl3
62.38
55.33
46.17
36.03
25.67
13.57
CO2Et
OMe
O
N
14k
f1 (ppm)

Feb27-2021-15-LS966(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 15

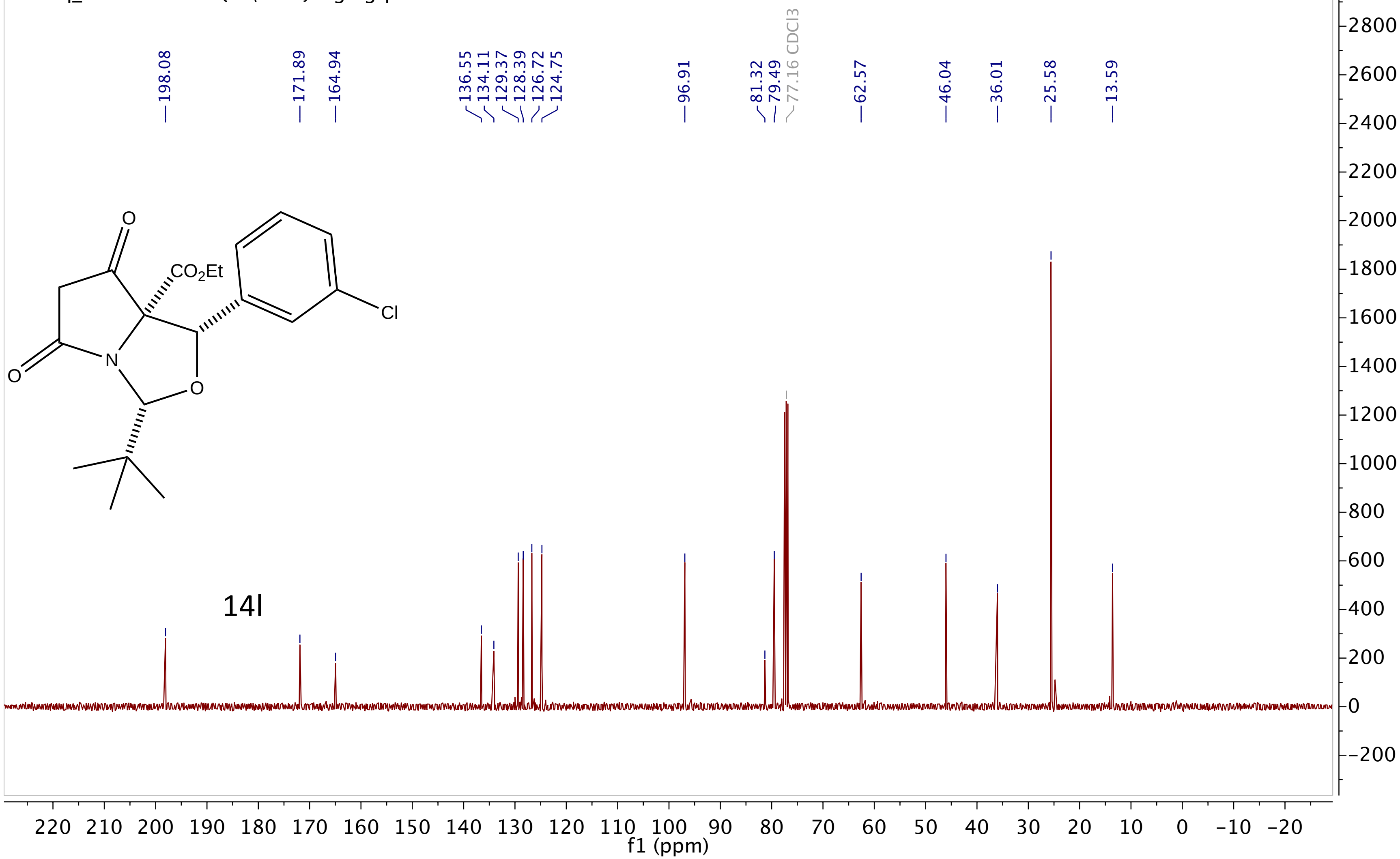
$^1$H NMR (400 MHz, $CDCl_3$)

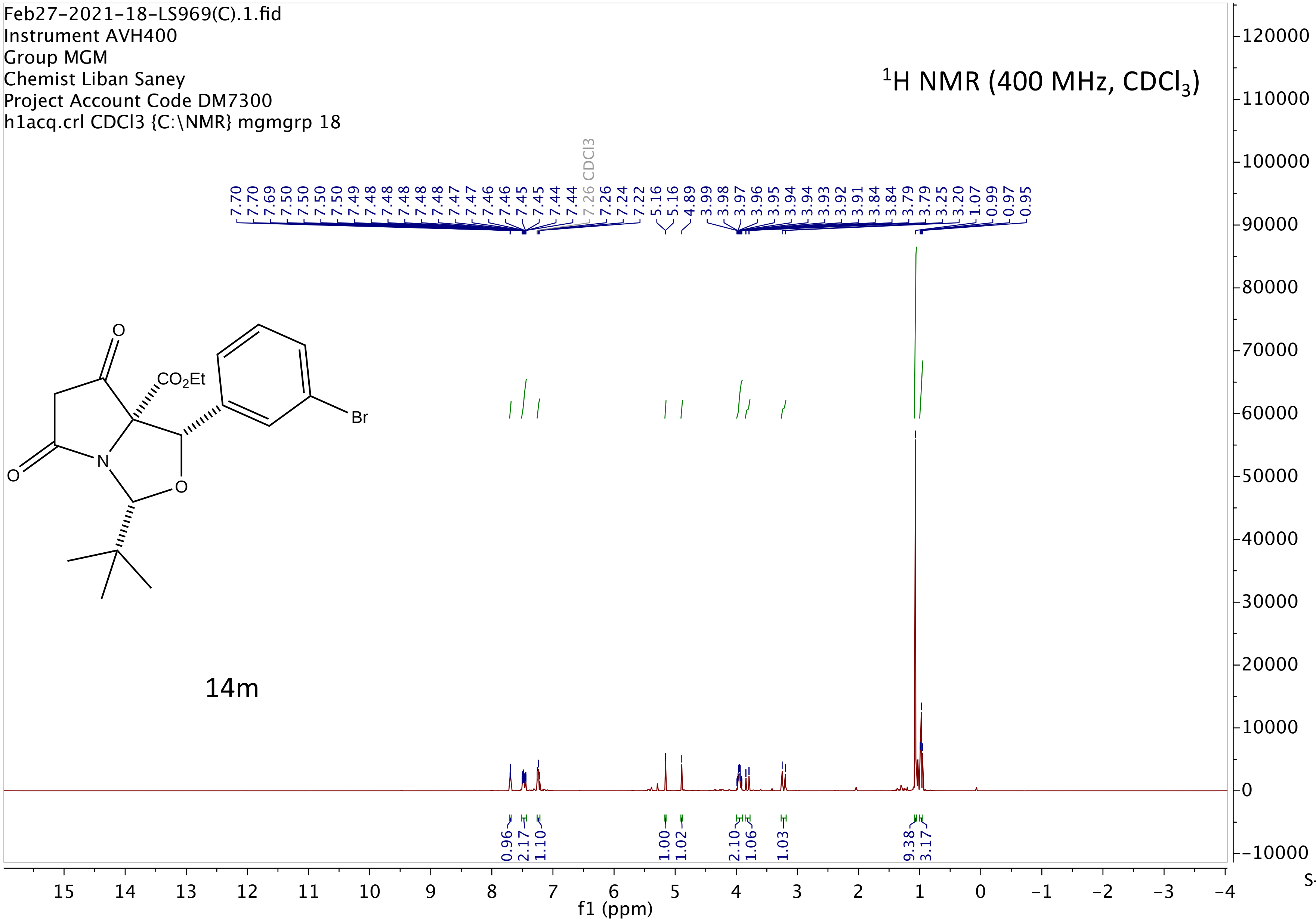



14l

Feb27-2021-15-LS966(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 15

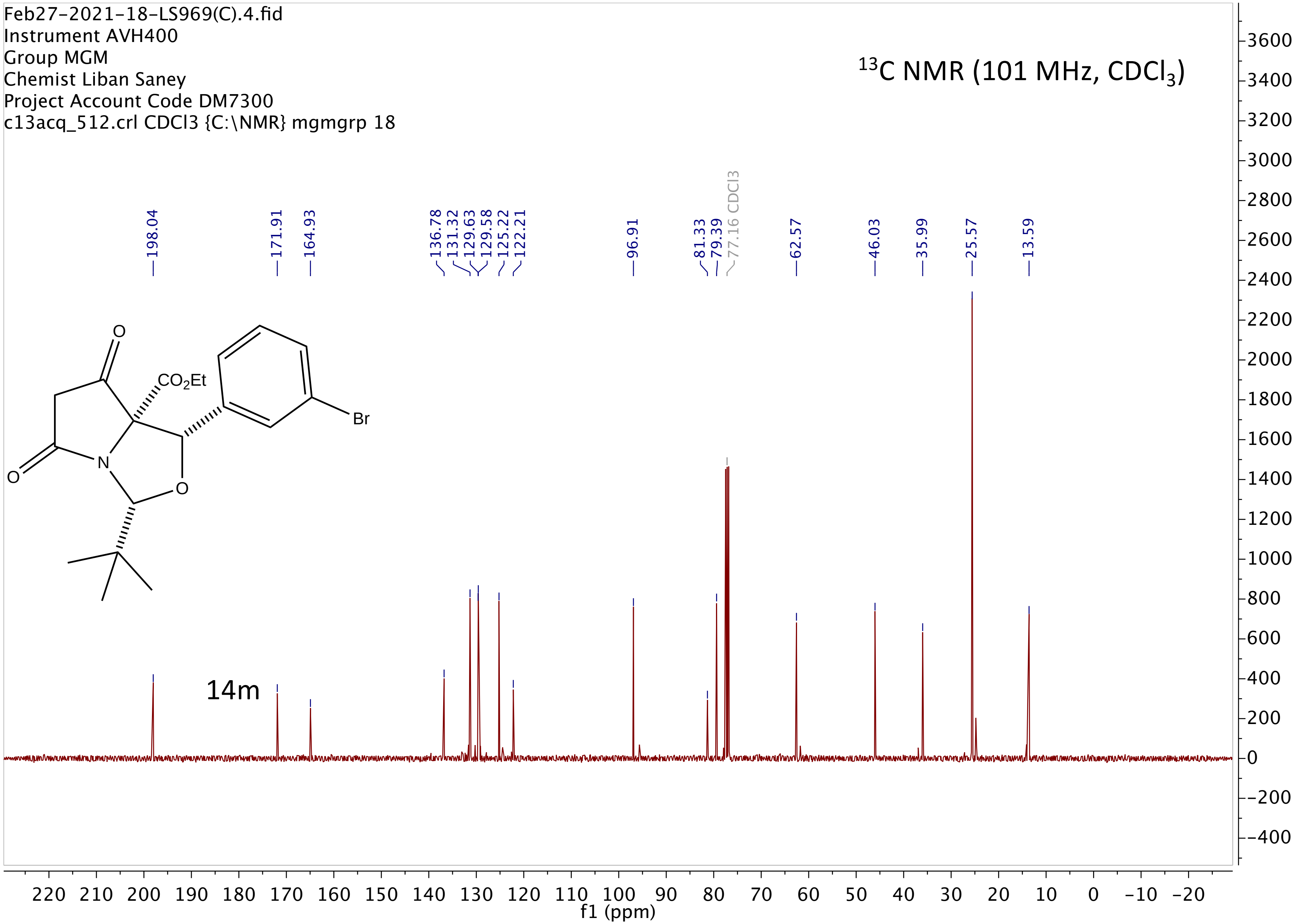
$^{13}C$ NMR (101 MHz, $CDCl_3$)

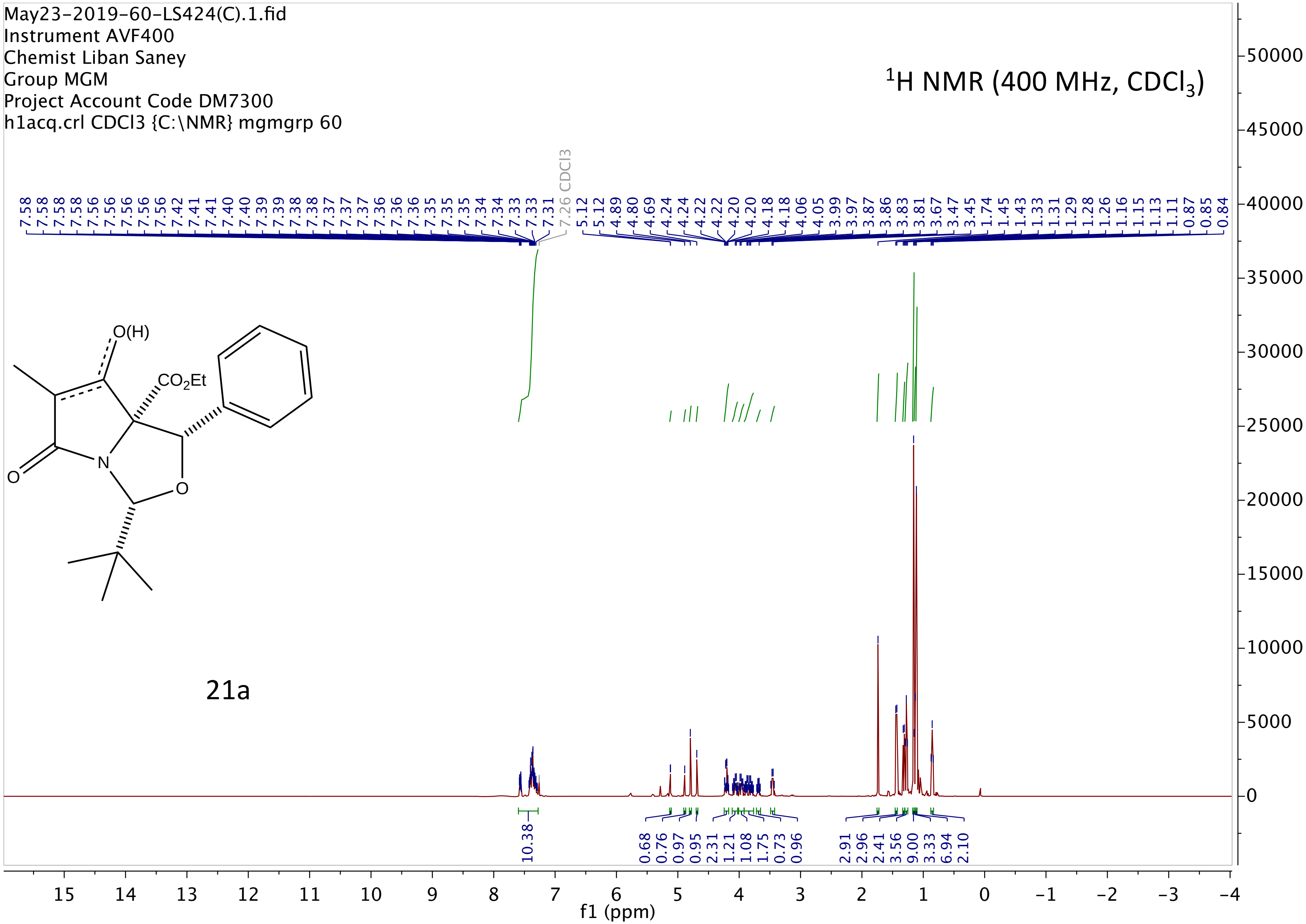


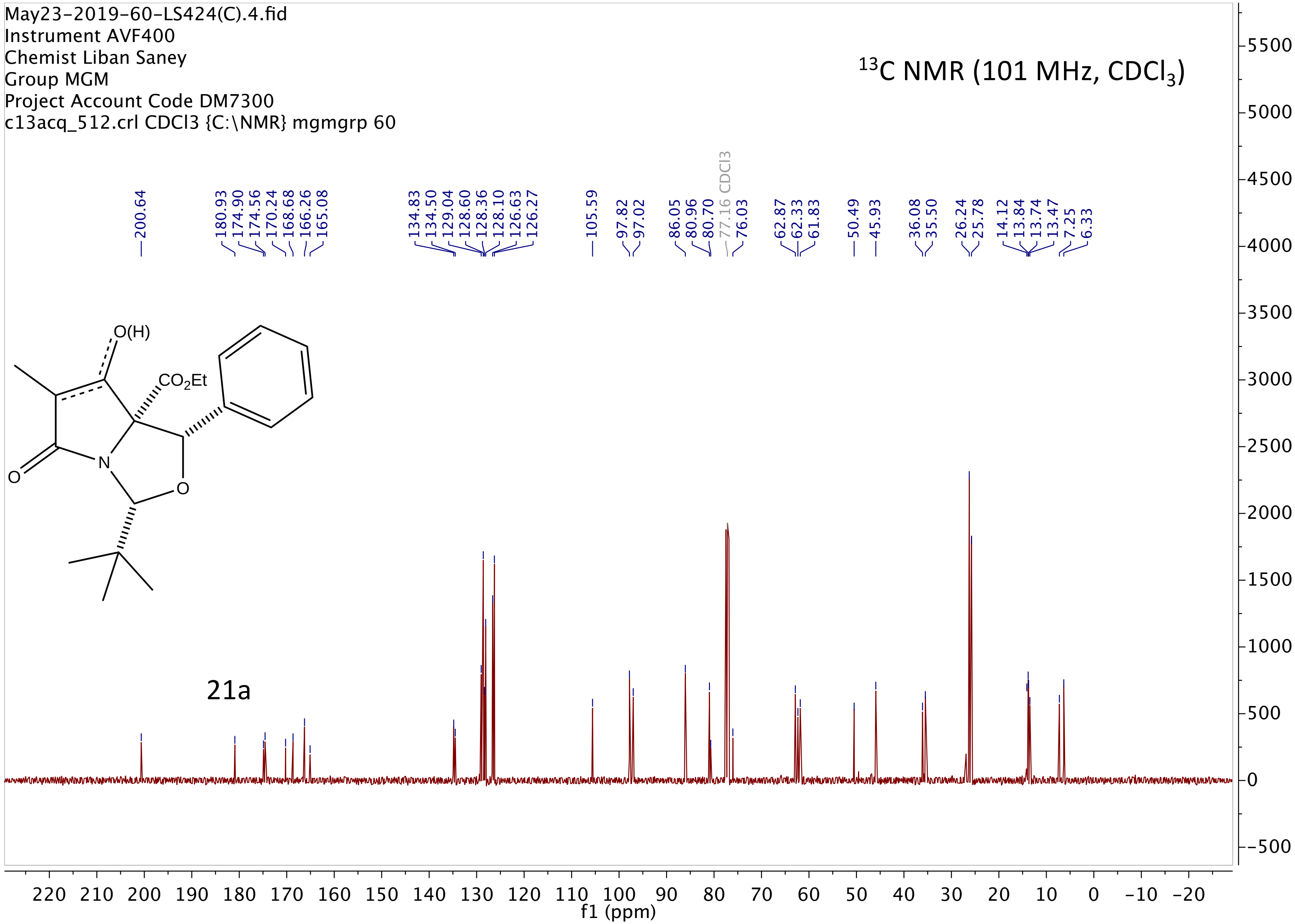

Feb27-2021-18-LS969(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 18
1H NMR (400 MHz, CDCl3)
7.70 7.70 7.69 7.50 7.50 7.50 7.50 7.49 7.48 7.48 7.48 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.26 CDCl3 7.26 7.24 7.22 5.16 5.16 4.89 3.99 3.98 3.97 3.96 3.95 3.94 3.94 3.93 3.92 3.91 3.84 3.84 3.79 3.79 3.25 3.20 1.07 0.99 0.97 0.95
0.96 2.17 1.10 1.00 1.02 2.10 1.06 1.03 9.38 3.17
CO2Et
Br
O
N
14m
f1 (ppm)

Feb27-2021-18-LS969(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 18

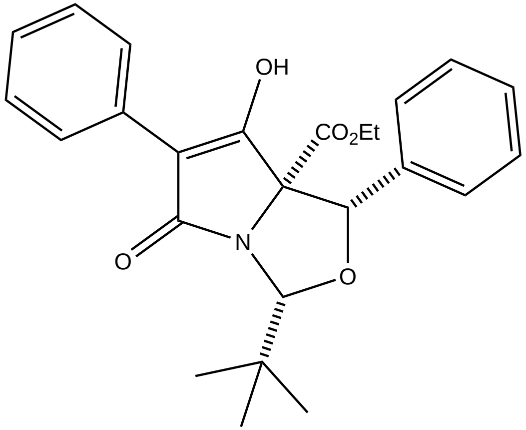
$^{13}$C NMR (101 MHz, $CDCl_3$)



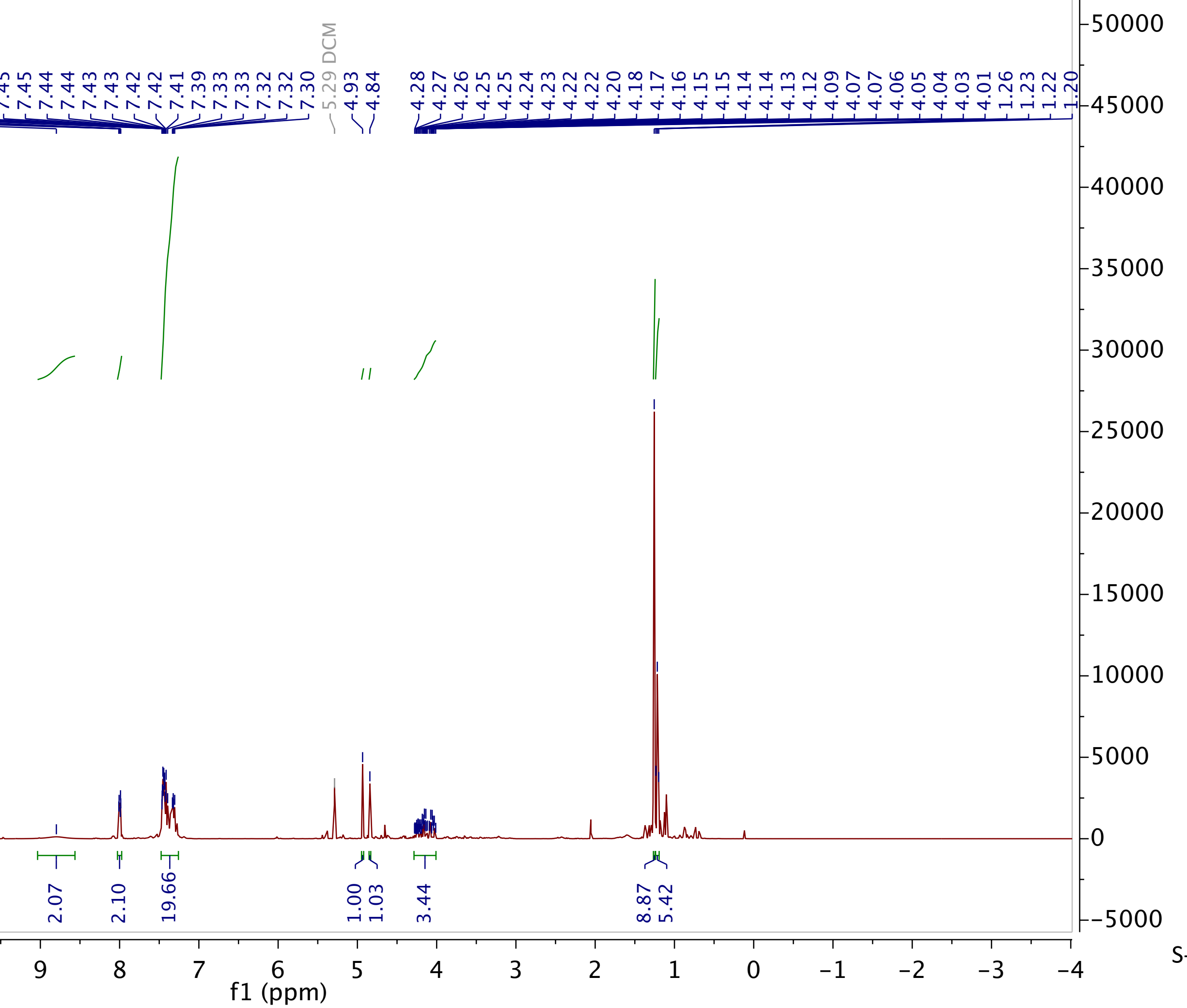

May23-2019-60-LS424(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
7.58 7.58 7.58 7.58 7.56 7.56 7.56 7.56 7.56 7.42 7.41 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 7.31
7.26 CDCl3
5.12 5.12 4.89 4.80 4.69 4.24 4.24 4.22 4.22 4.20 4.20 4.18 4.18 4.06 4.05 3.99 3.97 3.87 3.86 3.83 3.81 3.67 3.47 3.45 1.74 1.45 1.43 1.33 1.31 1.29 1.28 1.26 1.16 1.15 1.13 1.11 0.87 0.85 0.84
O(H)
CO2Et
O
N
O
21a
10.38
0.68 0.76 0.97 0.95 2.31 1.21 1.08 1.75 0.73 0.96
2.91 2.96 2.41 3.56 9.00 3.33 6.94 2.10
50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


May23-2019-60-LS424(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
$^{13}$C NMR (101 MHz, $CDCl_3$)
200.64
180.93
174.90
174.56
170.24
168.68
166.26
165.08
134.83
134.50
129.04
128.60
128.36
128.10
126.63
126.27
105.59
97.82
97.02
86.05
80.96
80.70
77.16 CDCl3
76.03
62.87
62.33
61.83
50.49
45.93
36.08
35.50
26.24
25.78
14.12
13.84
13.74
13.47
7.25
6.33
O(H)
$CO_2Et$
N
O
O
21a
f1 (ppm)

Jul16-2019-60-LS458(C).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

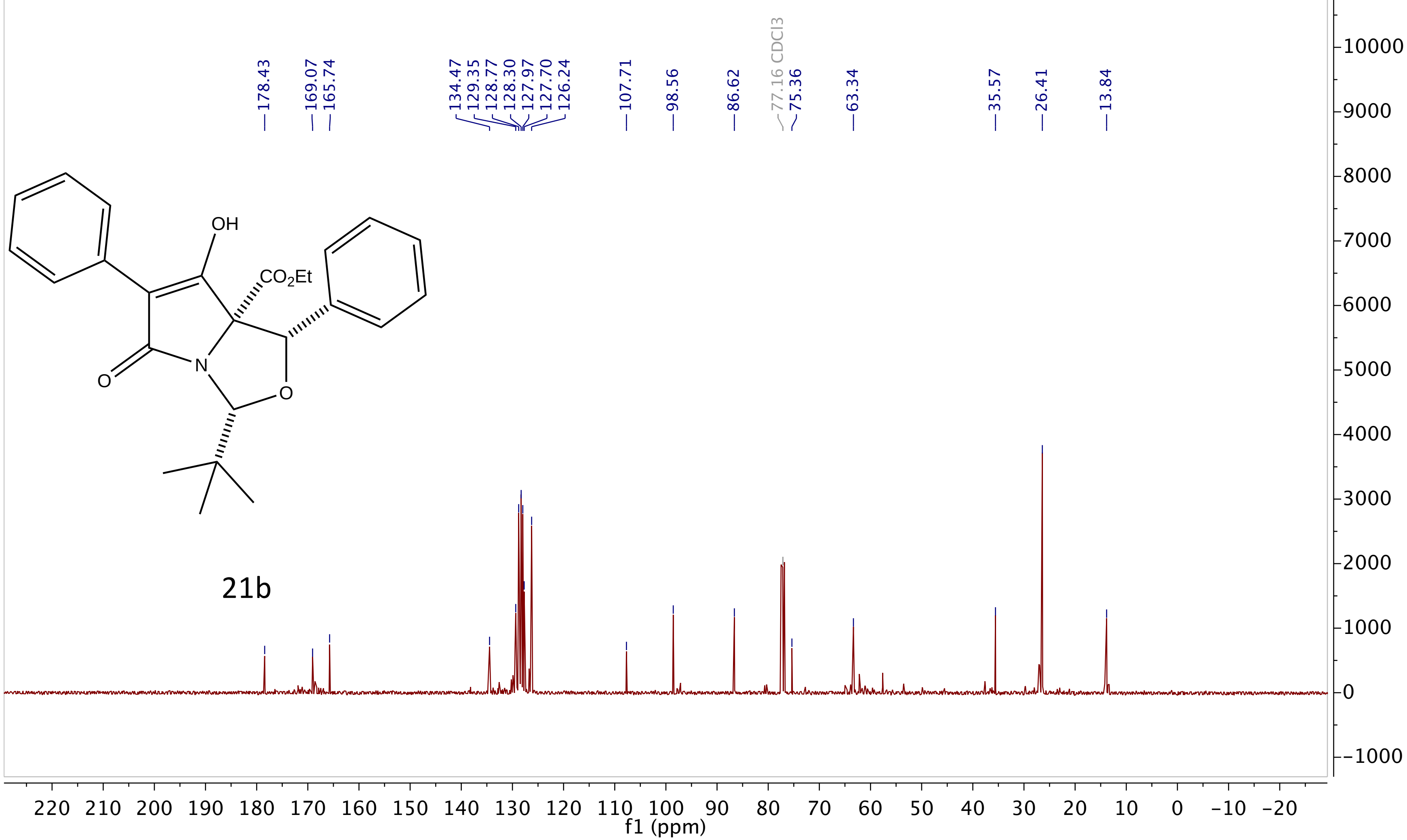



21b



Jul16-2019-60-LS458(C).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

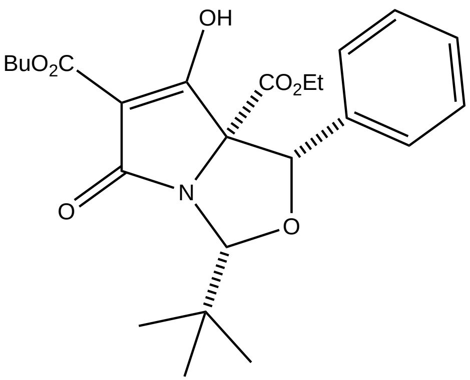
$^{13}$C NMR (101 MHz, $CDCl_3$)



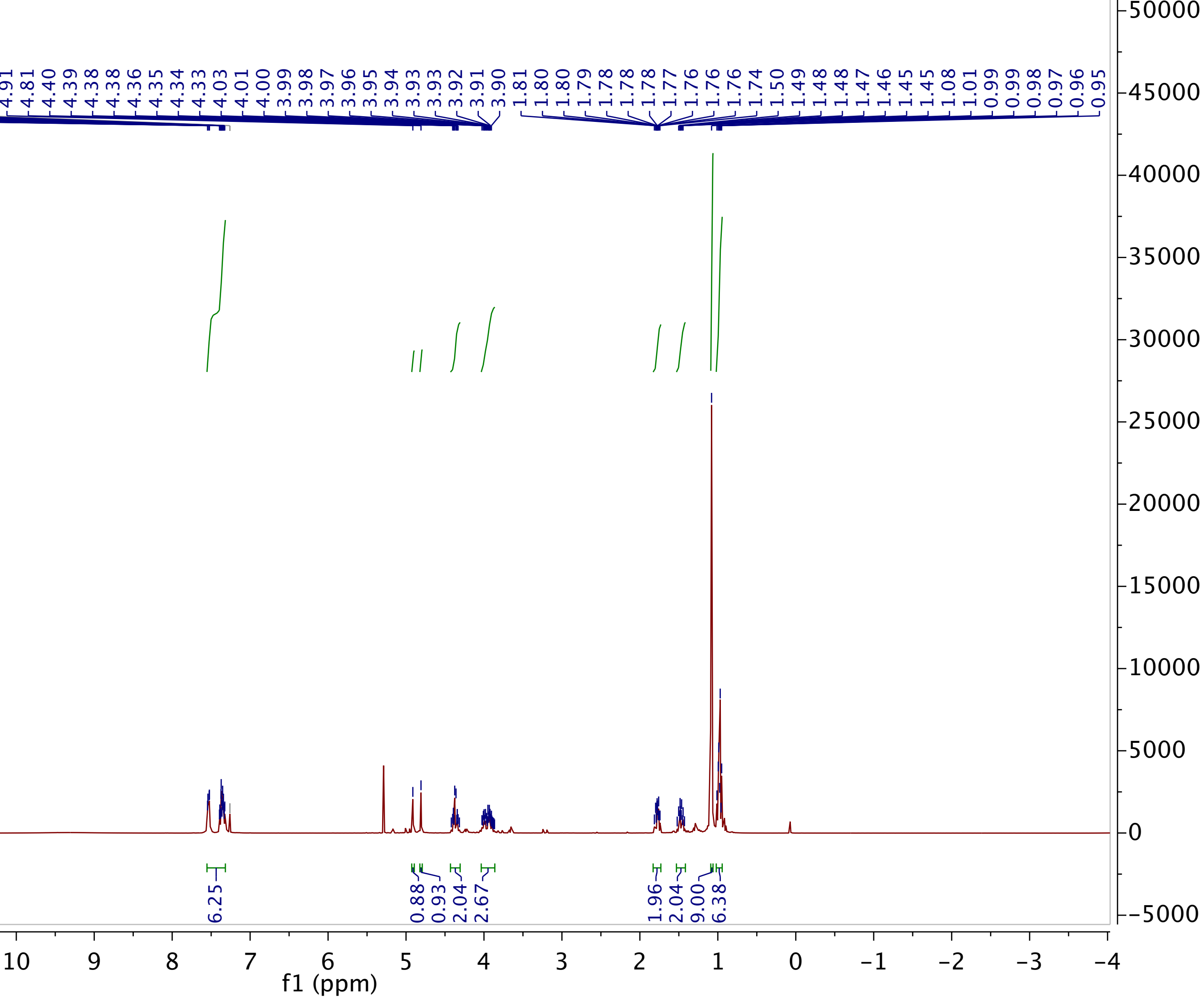

21b

Jul03-2019-60-LS442(P) H2-I9.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

$^1$H NMR (400 MHz, $CDCl_3$)

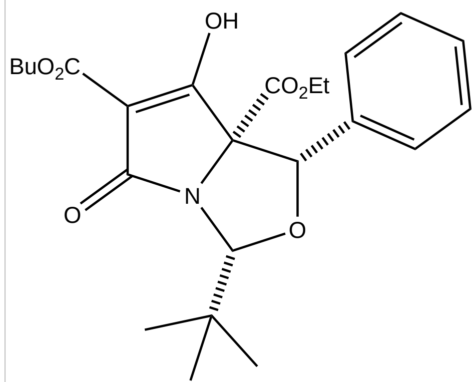



22a

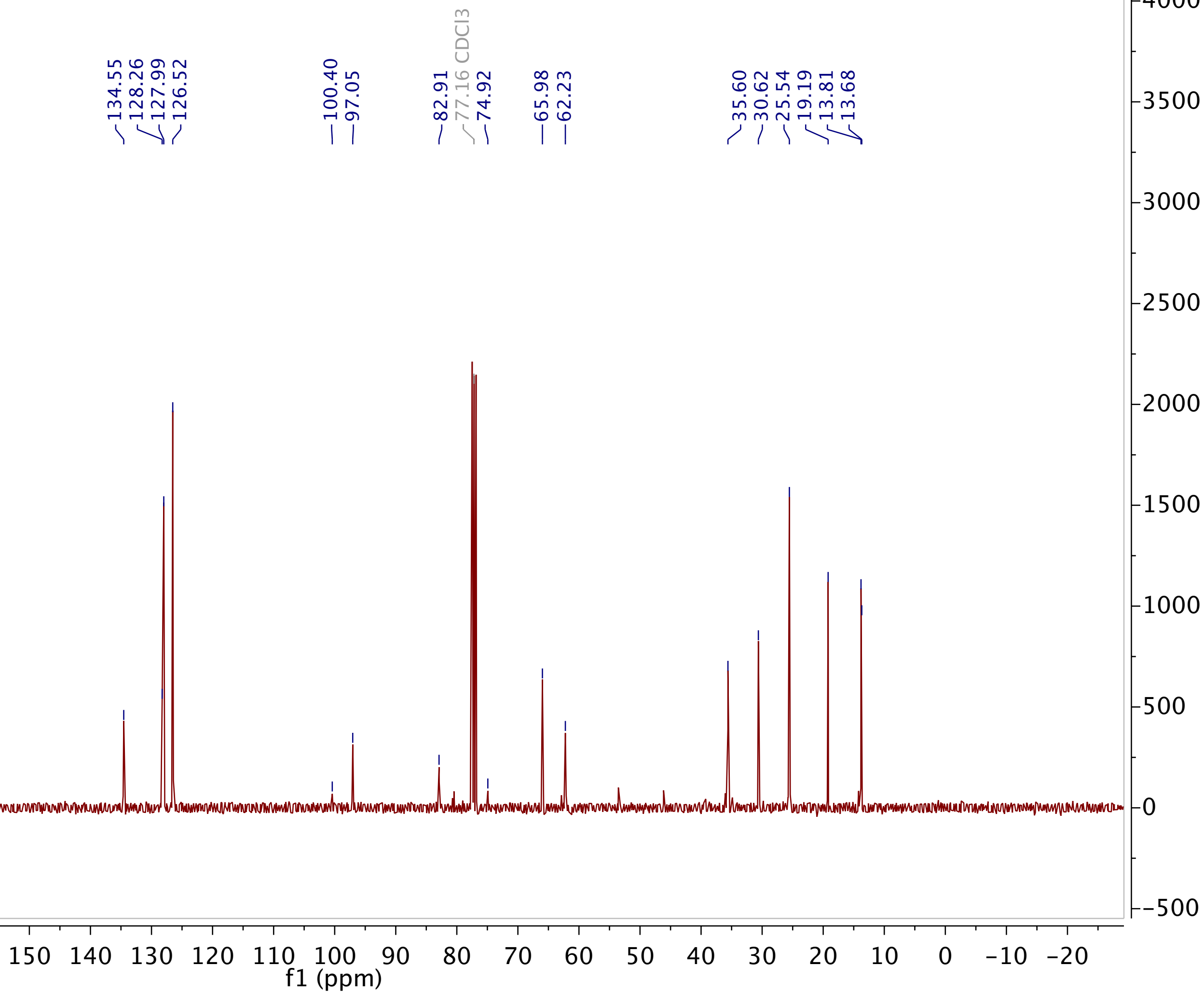


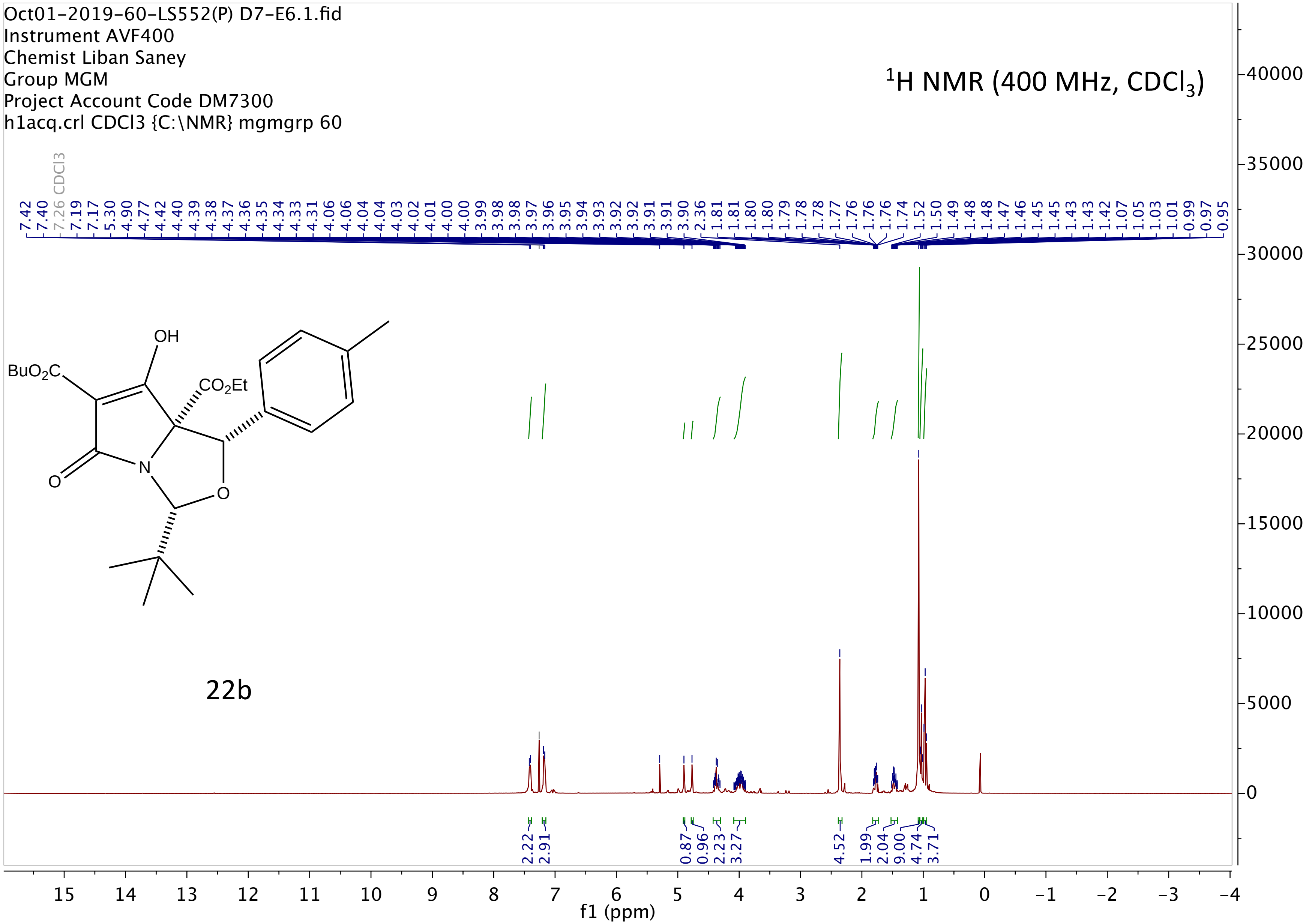
Jul03-2019-60-LS442(P) H2-I9.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)




22a

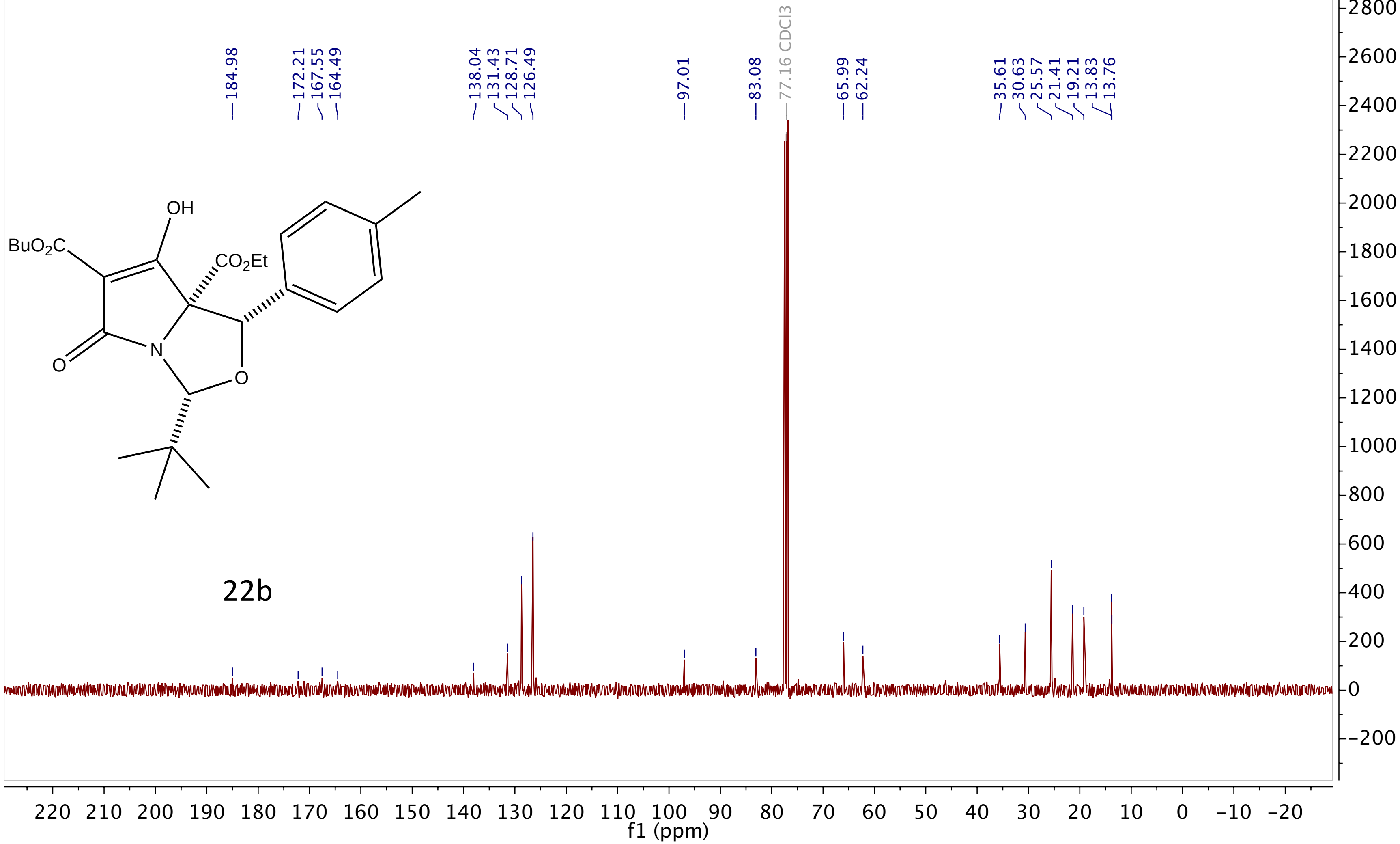




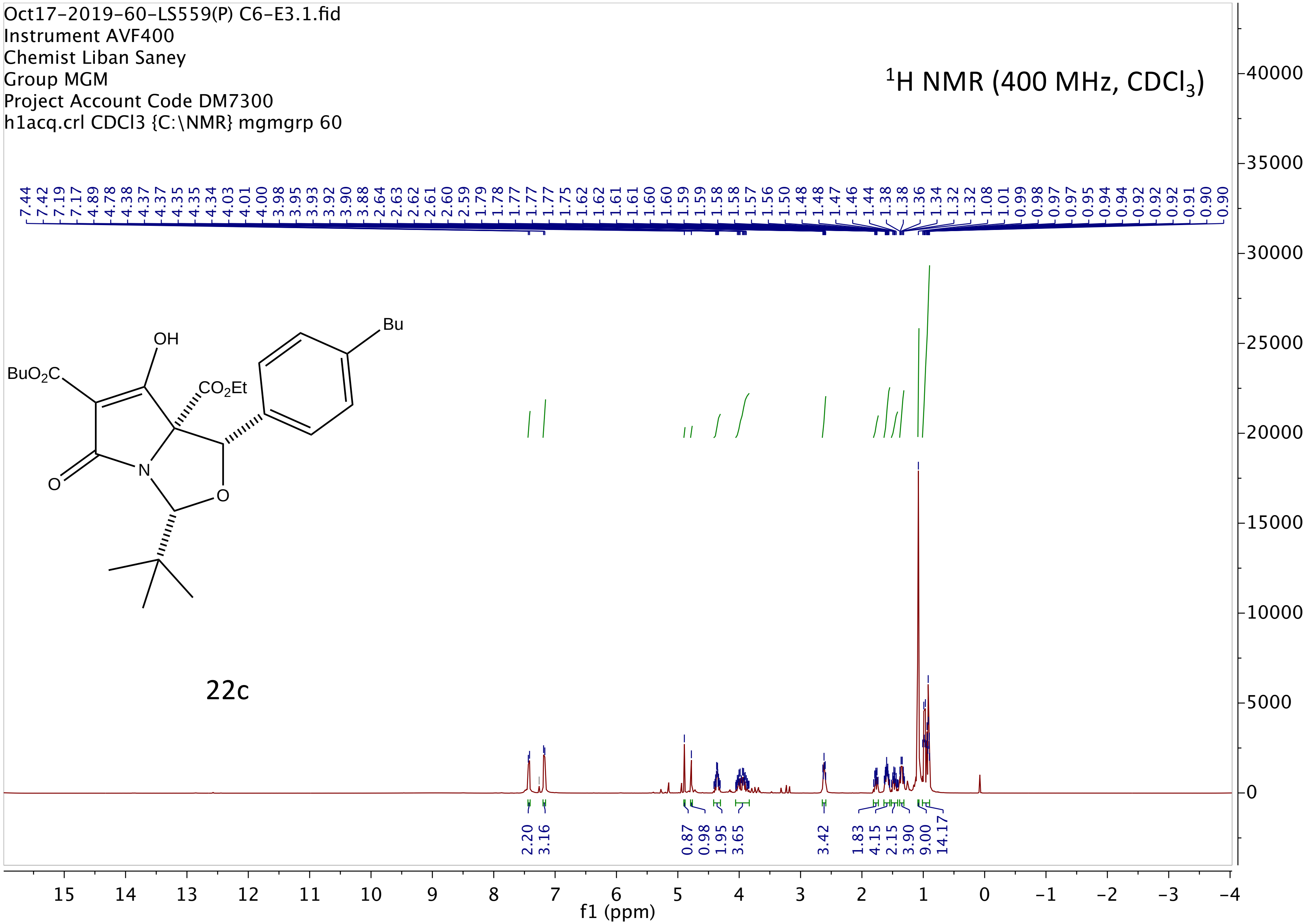
Oct01-2019-60-LS552(P) D7-E6.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
OH
BuO2C
CO2Et
N
O
O
22b
f1 (ppm)

Oct01-2019-60-LS552(P) D7-E6.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)



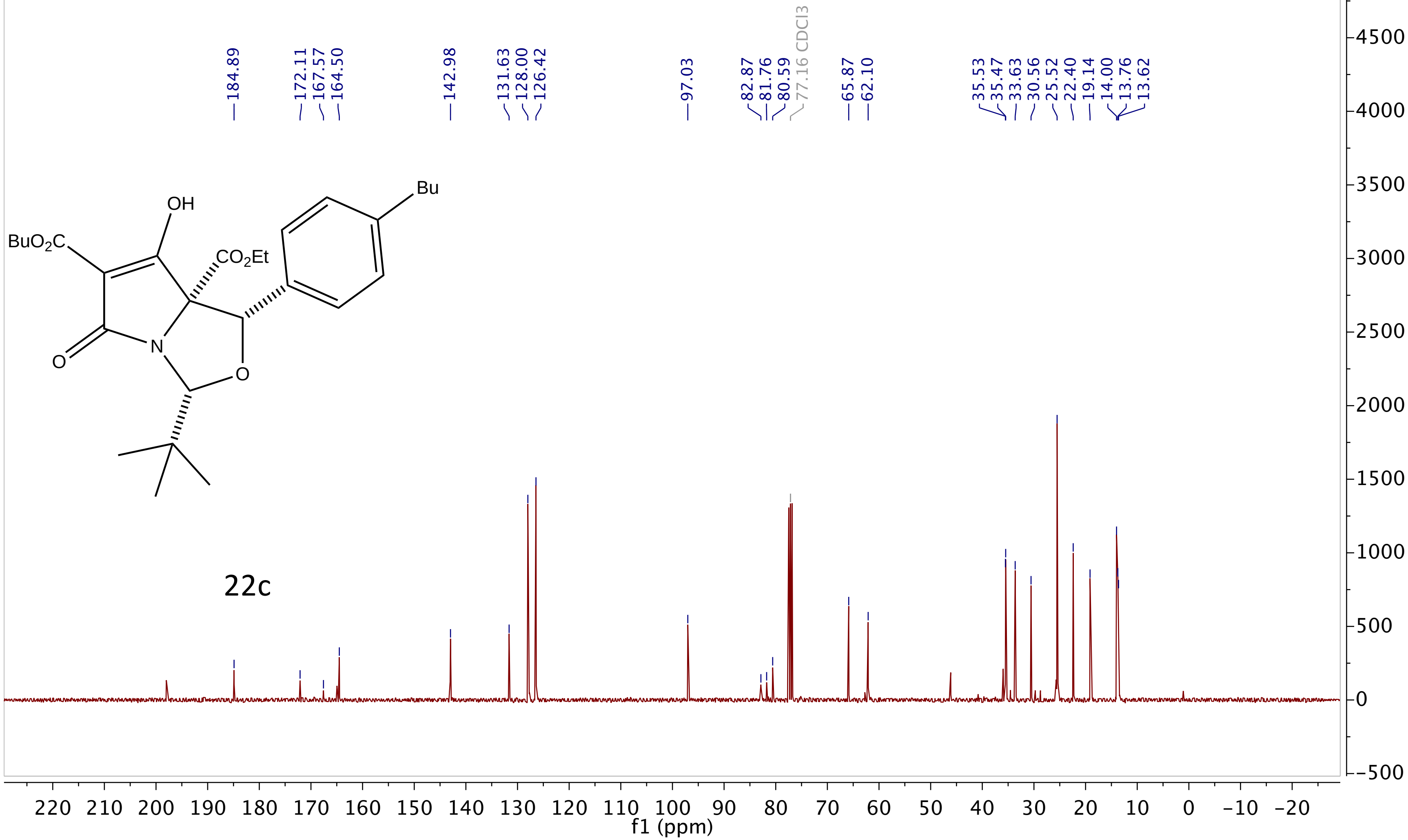
Oct17-2019-60-LS559(P) C6-E3.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60



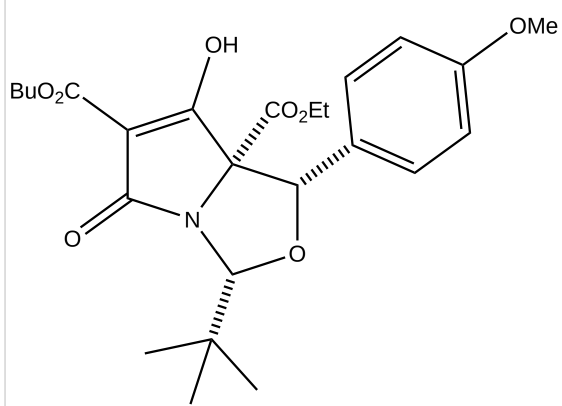
Oct17-2019-60-LS559(P) C6-E3.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)

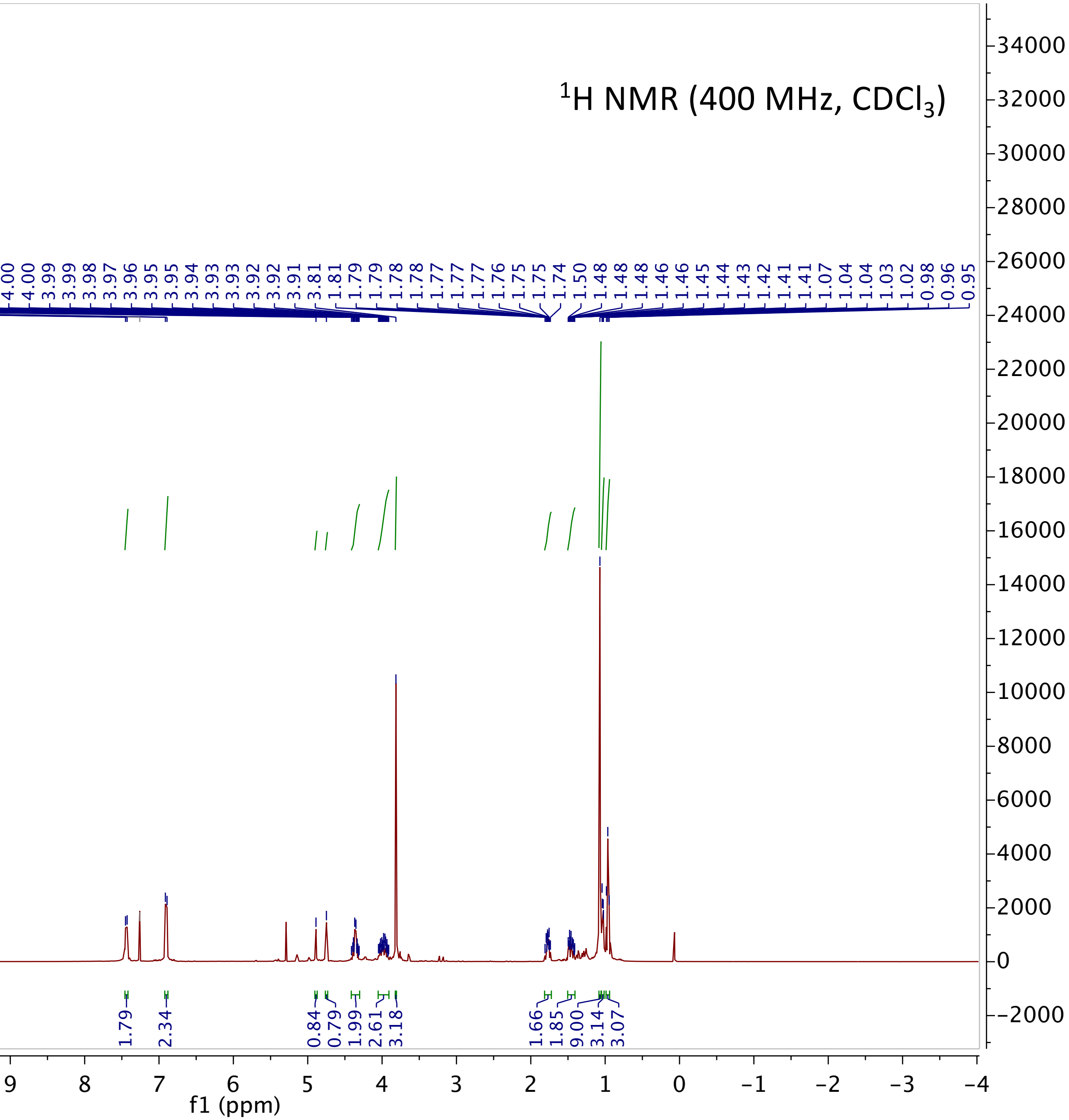
22c



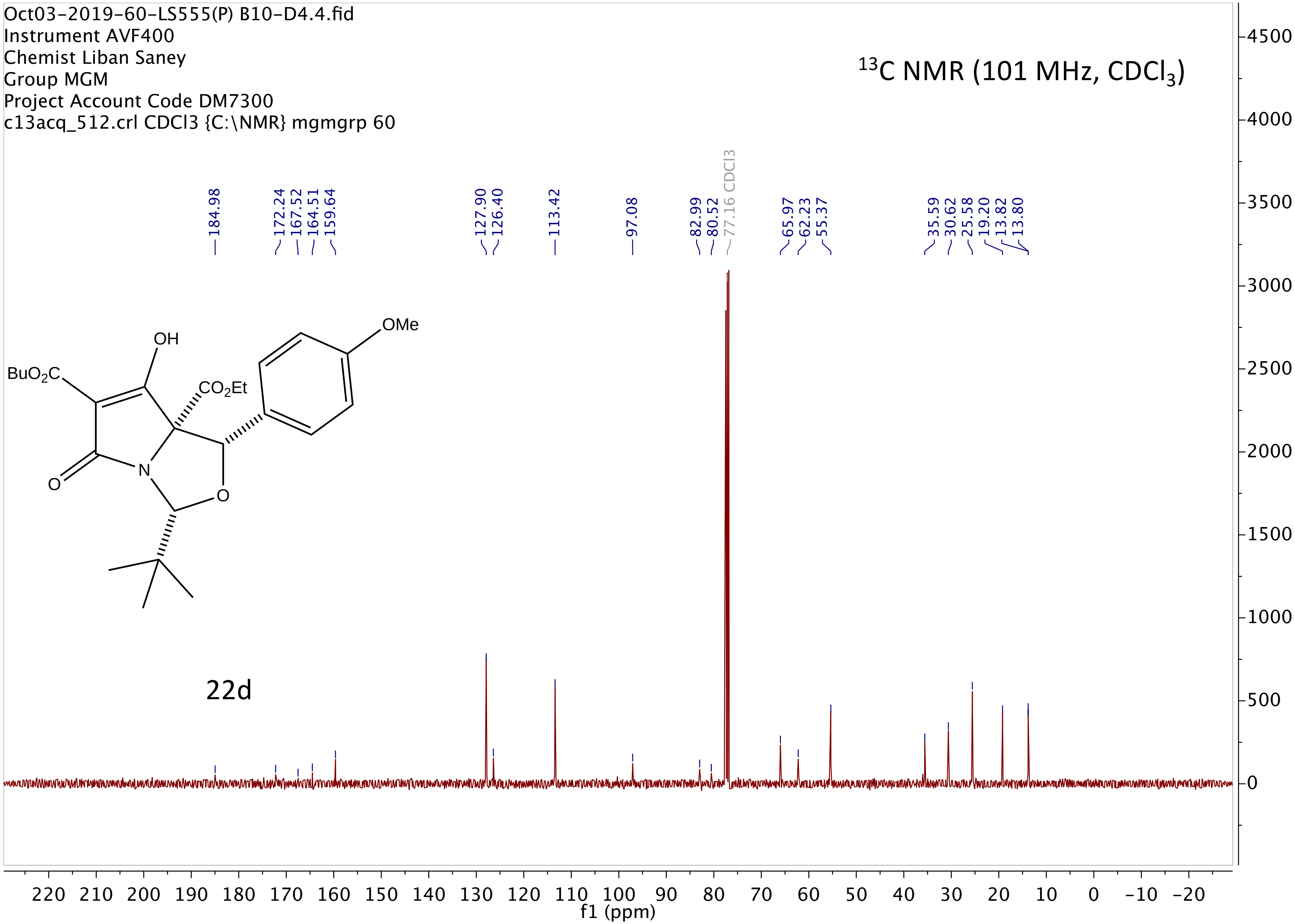
Oct03-2019-60-LS555(P) B10-D4.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60



22d

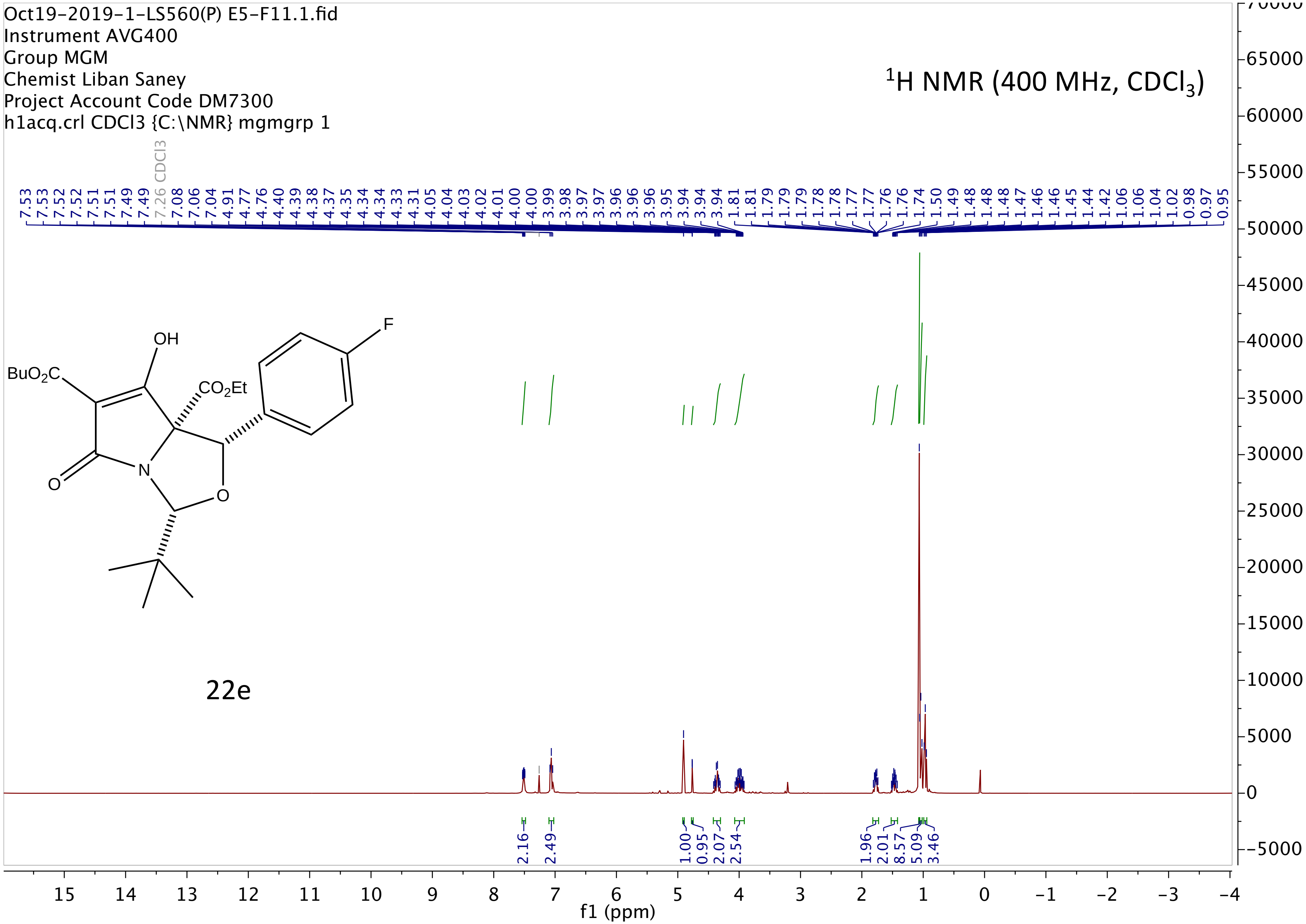


Oct03-2019-60-LS555(P) B10-D4.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60



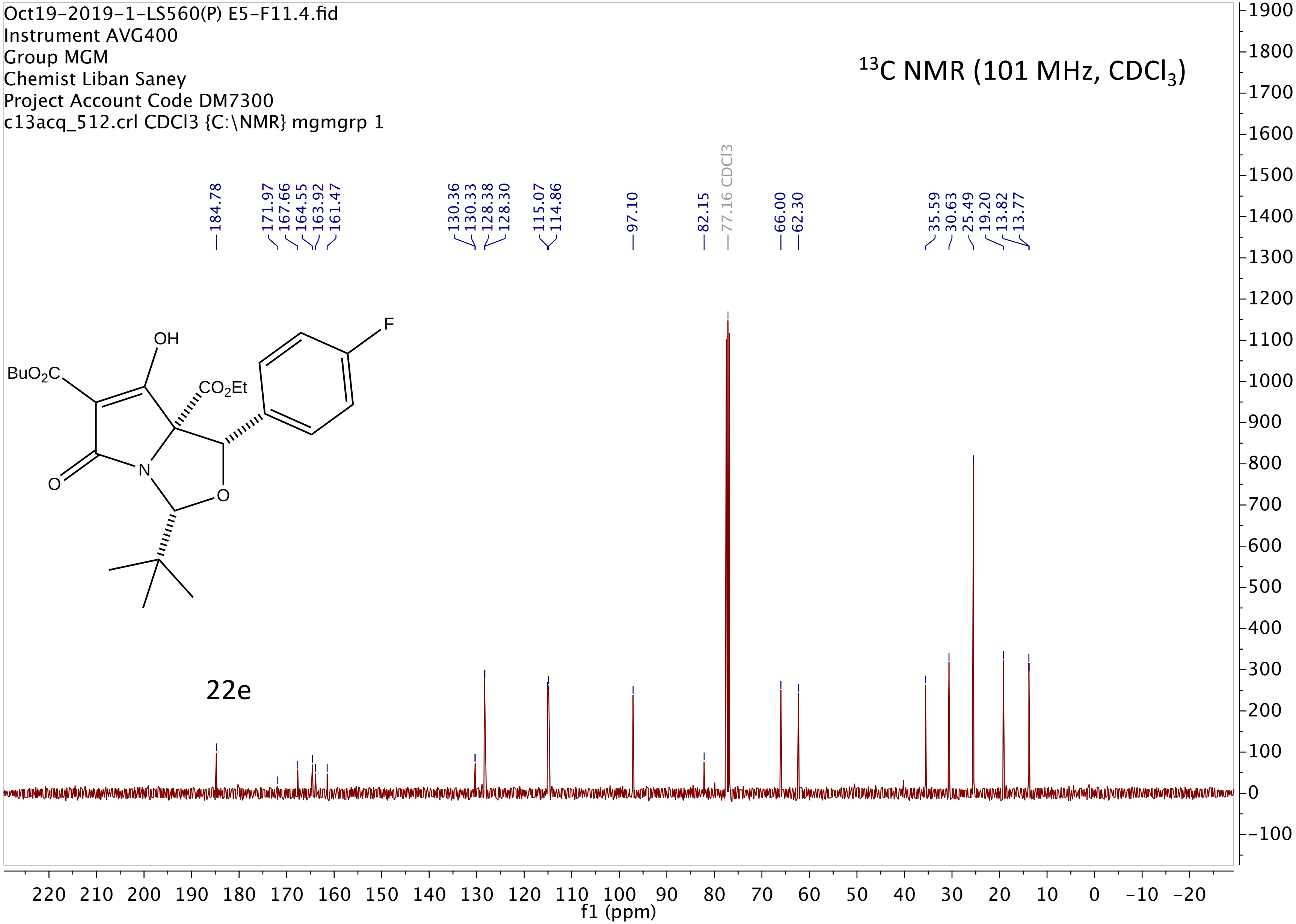
Oct19-2019-1-LS560(P) E5-F11.1.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1

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



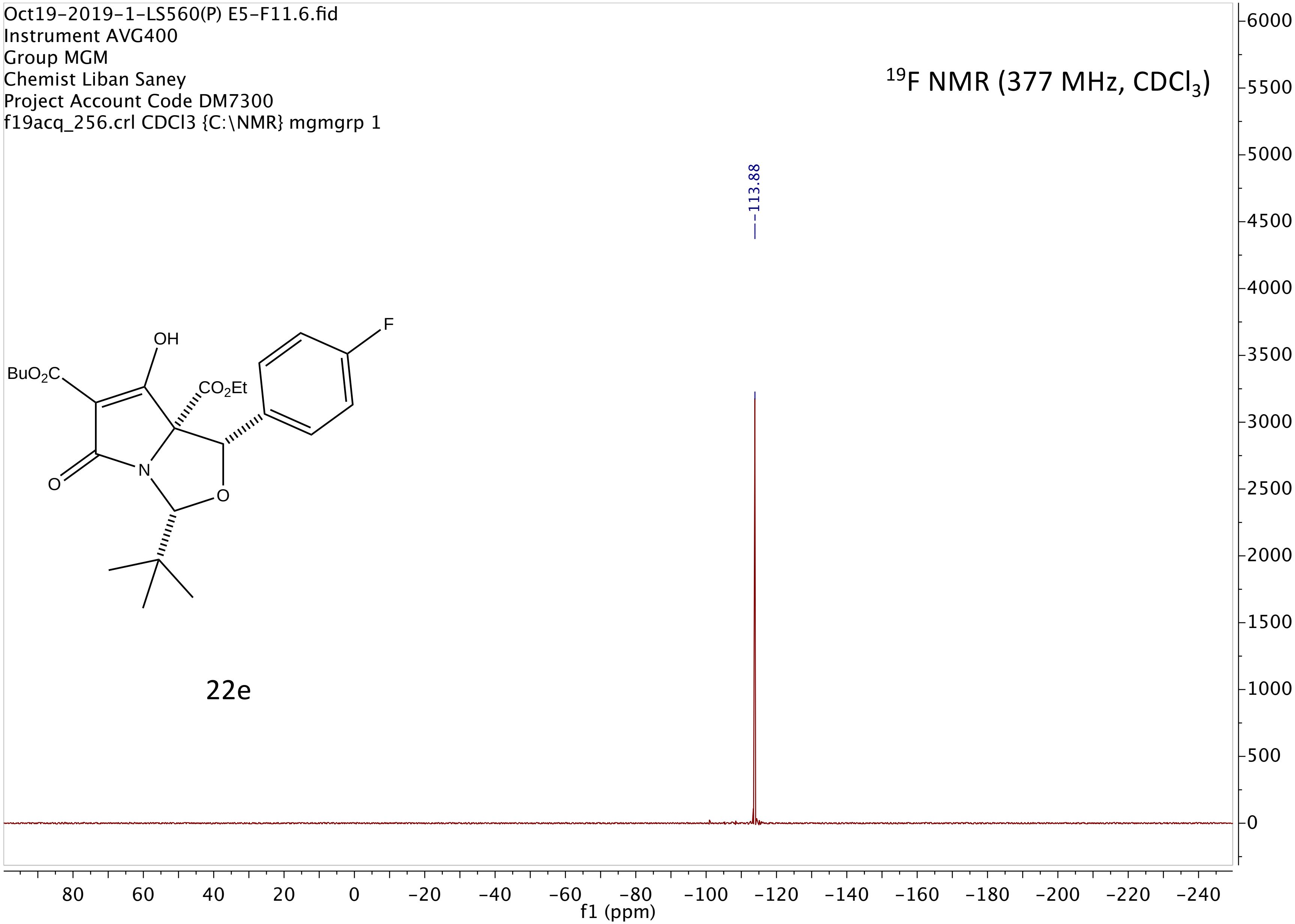

22e

Oct19-2019-1-LS560(P) E5-F11.4.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1

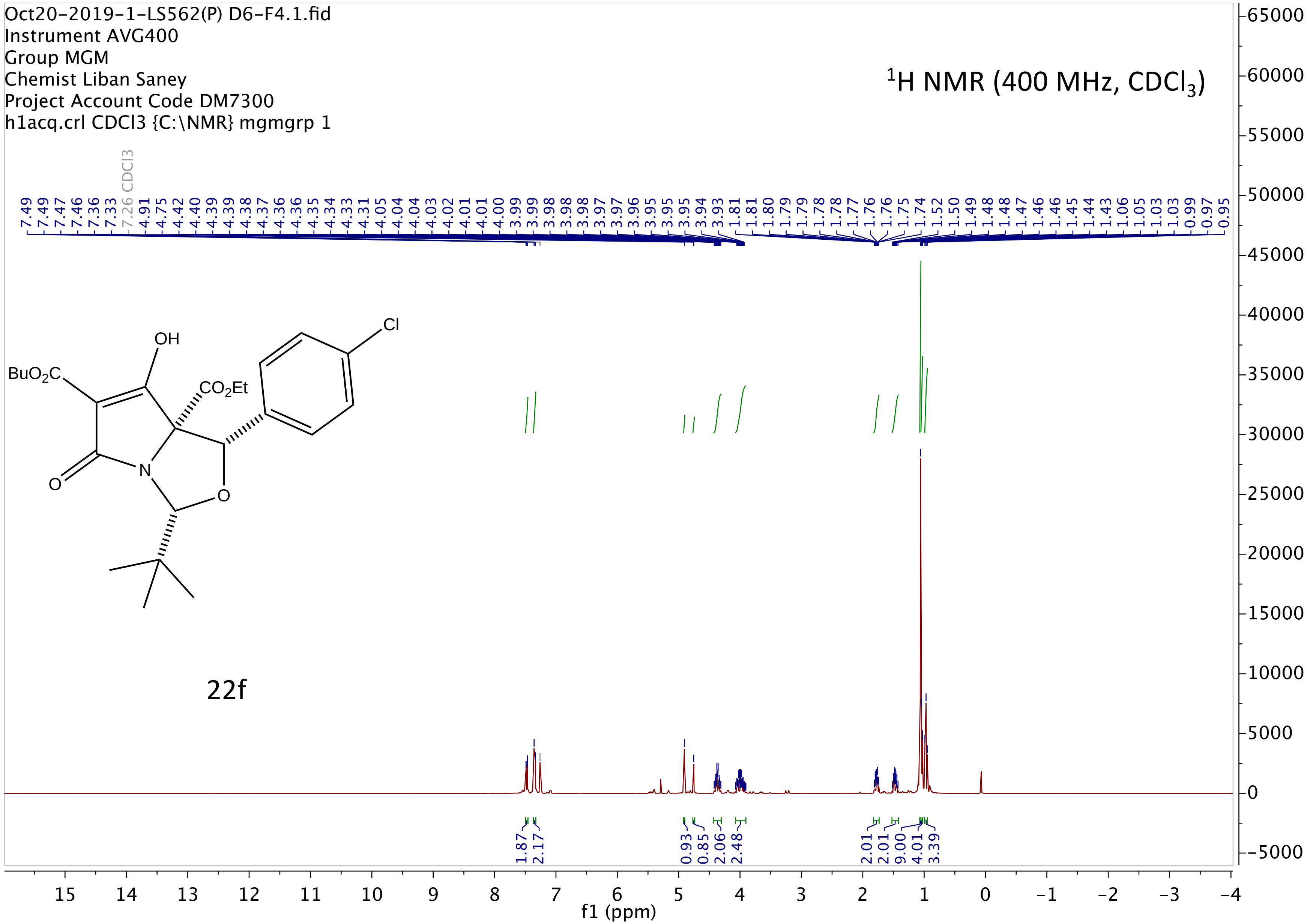


Oct19-2019-1-LS560(P) E5-F11.6.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19acq_256.crl CDCl3 {C:\NMR} mgmgrp 1

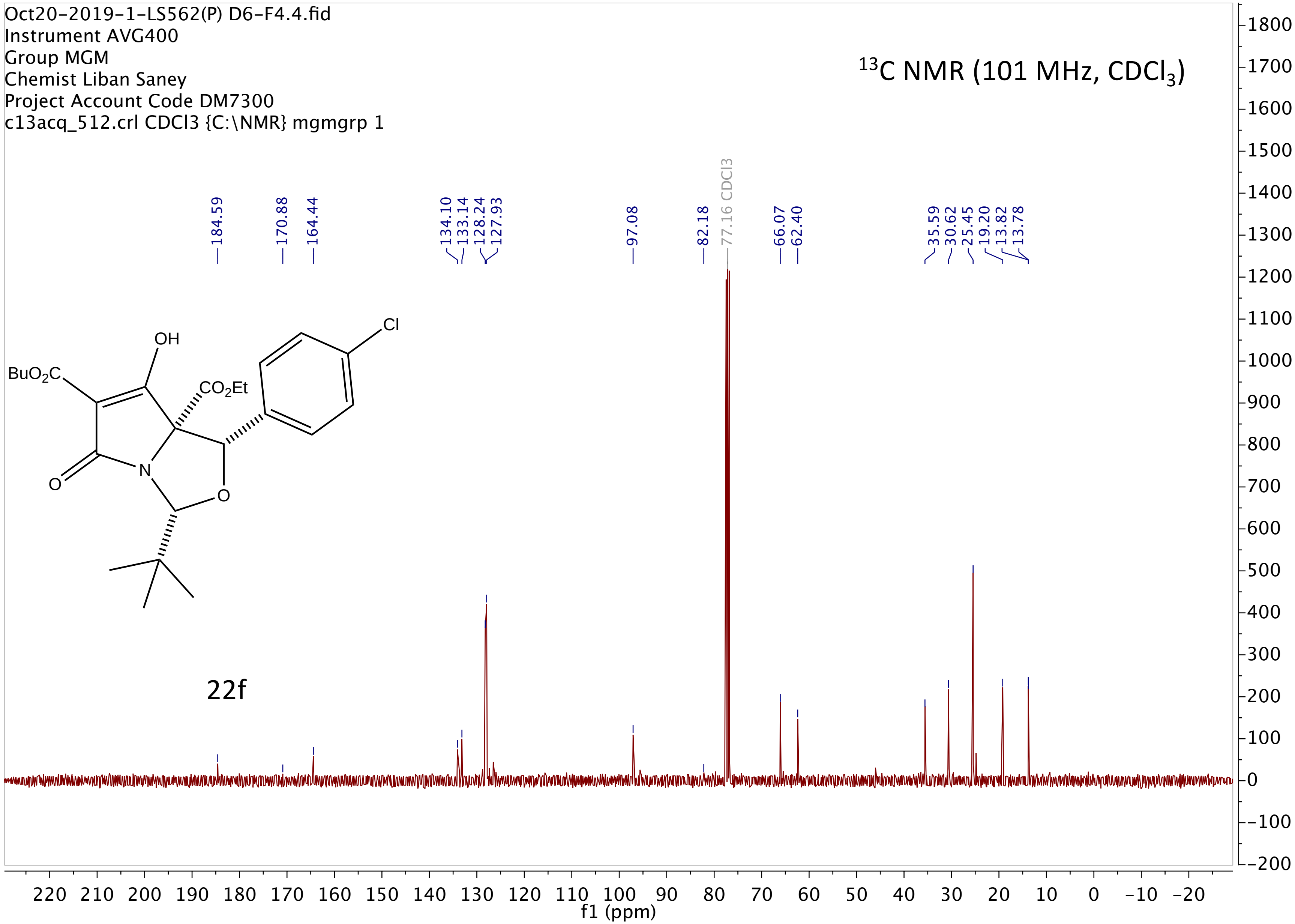
$^{19}$F NMR (377 MHz, $CDCl_3$)



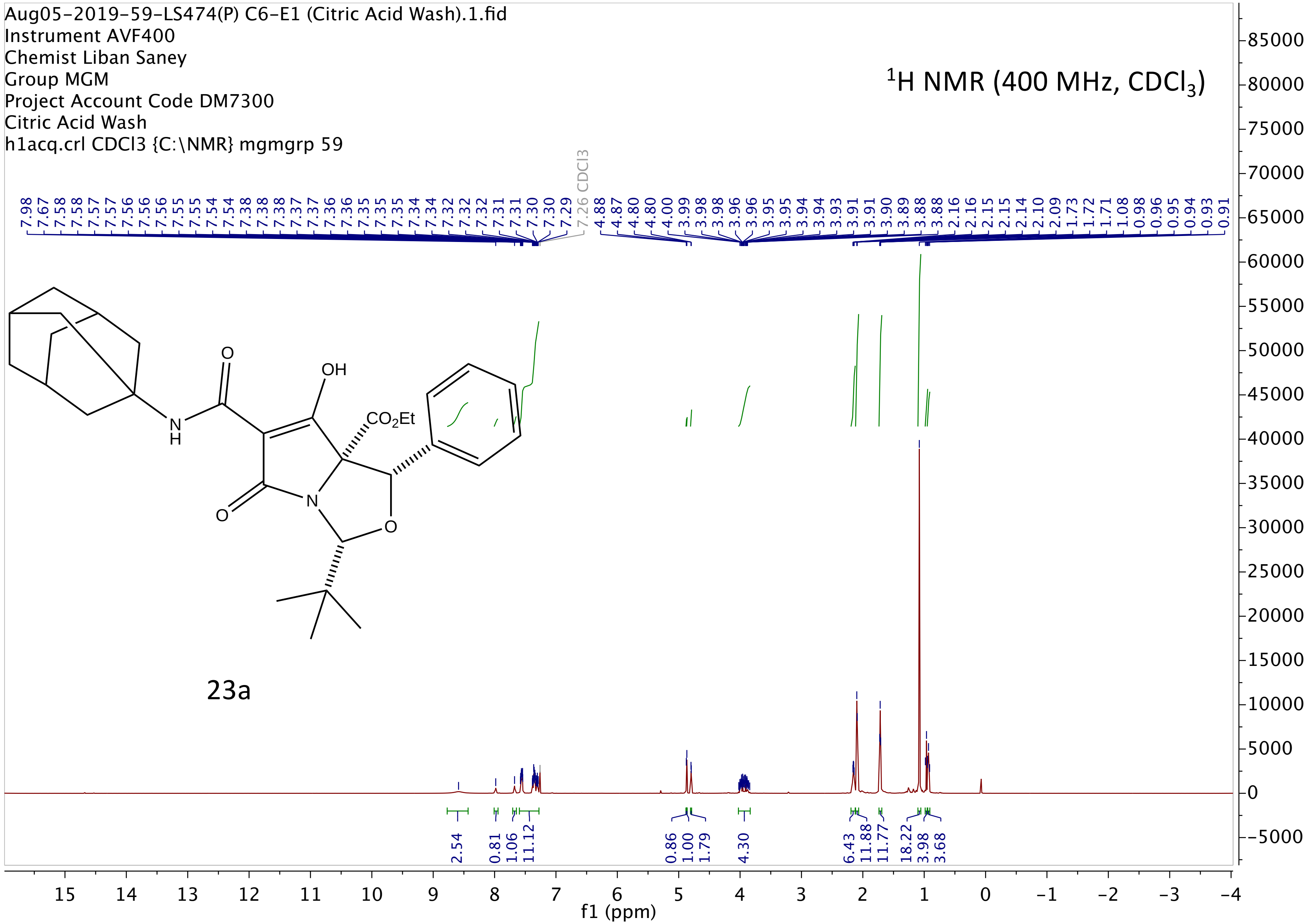

22e



Oct20-2019-1-LS562(P) D6-F4.1.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1
$^{1}$H NMR (400 MHz, $CDCl_3$)
7.49 7.49 7.47 7.46 7.36 7.33 7.26 CDCl3 4.91 4.75 4.42 4.40 4.39 4.39 4.38 4.37 4.36 4.36 4.35 4.34 4.33 4.31 4.05 4.04 4.03 4.02 4.01 4.01 4.00 3.99 3.99 3.98 3.98 3.98 3.97 3.97 3.96 3.95 3.95 3.95 3.94 3.93 1.81 1.81 1.80 1.79 1.79 1.78 1.78 1.77 1.76 1.76 1.75 1.74 1.52 1.50 1.49 1.48 1.48 1.47 1.46 1.46 1.45 1.44 1.43 1.06 1.05 1.03 1.03 0.99 0.97 0.95
OH
$BuO_2C$
$CO_2Et$
Cl
N
O
O
22f
1.87 2.17 0.93 0.85 2.06 2.48 2.01 2.01 9.00 4.01 3.39
f1 (ppm)

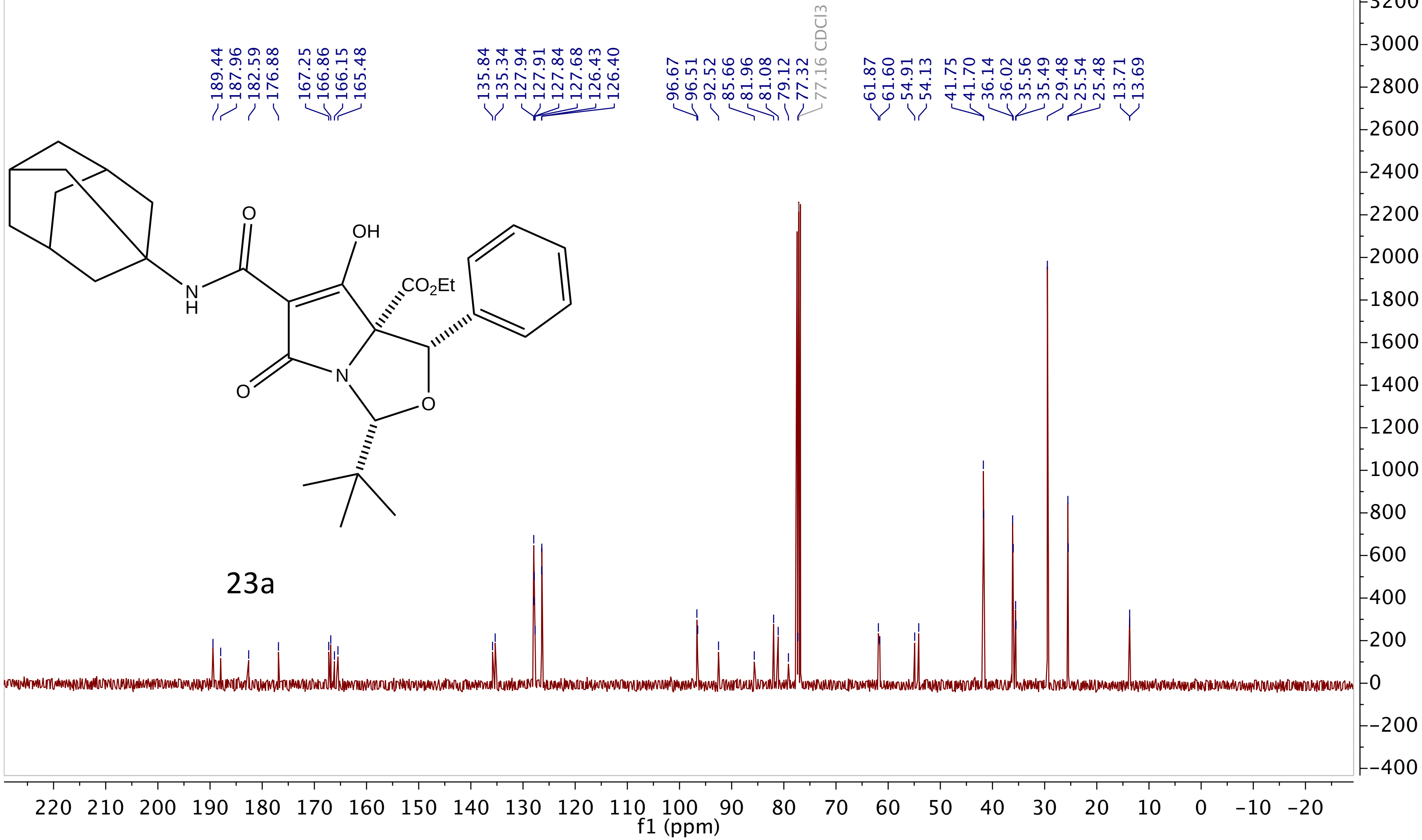


Oct20-2019-1-LS562(P) D6-F4.4.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1
13C NMR (101 MHz, CDCl3)
184.59
170.88
164.44
134.10
133.14
128.24
127.93
97.08
82.18
77.16 CDCl3
66.07
62.40
35.59
30.62
25.45
19.20
13.82
13.78
OH
BuO2C
CO2Et
Cl
N
O
O
22f
f1 (ppm)


Aug05-2019-59-LS474(P) C6-E1 (Citric Acid Wash).1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
Citric Acid Wash
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59
1H NMR (400 MHz, CDCl3)
7.98 7.67 7.58 7.58 7.57 7.57 7.56 7.56 7.55 7.55 7.54 7.54 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29
7.26 CDCl3
4.88 4.87 4.80 4.80 4.00 3.99 3.98 3.98 3.96 3.96 3.95 3.95 3.94 3.94 3.93 3.91 3.91 3.90 3.89 3.88 3.88 2.16 2.16 2.15 2.15 2.14 2.10 2.09 1.73 1.72 1.71 1.08 0.98 0.96 0.95 0.94 0.93 0.91
OH
O
CO2Et
N
H
O
N
O
23a
2.54 0.81 1.06 11.12 0.86 1.00 1.79 4.30 6.43 11.88 11.77 18.22 3.98 3.68
f1 (ppm)

Aug05-2019-59-LS474(P) C6-E1 (Citric Acid Wash).4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
Citric Acid Wash
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59

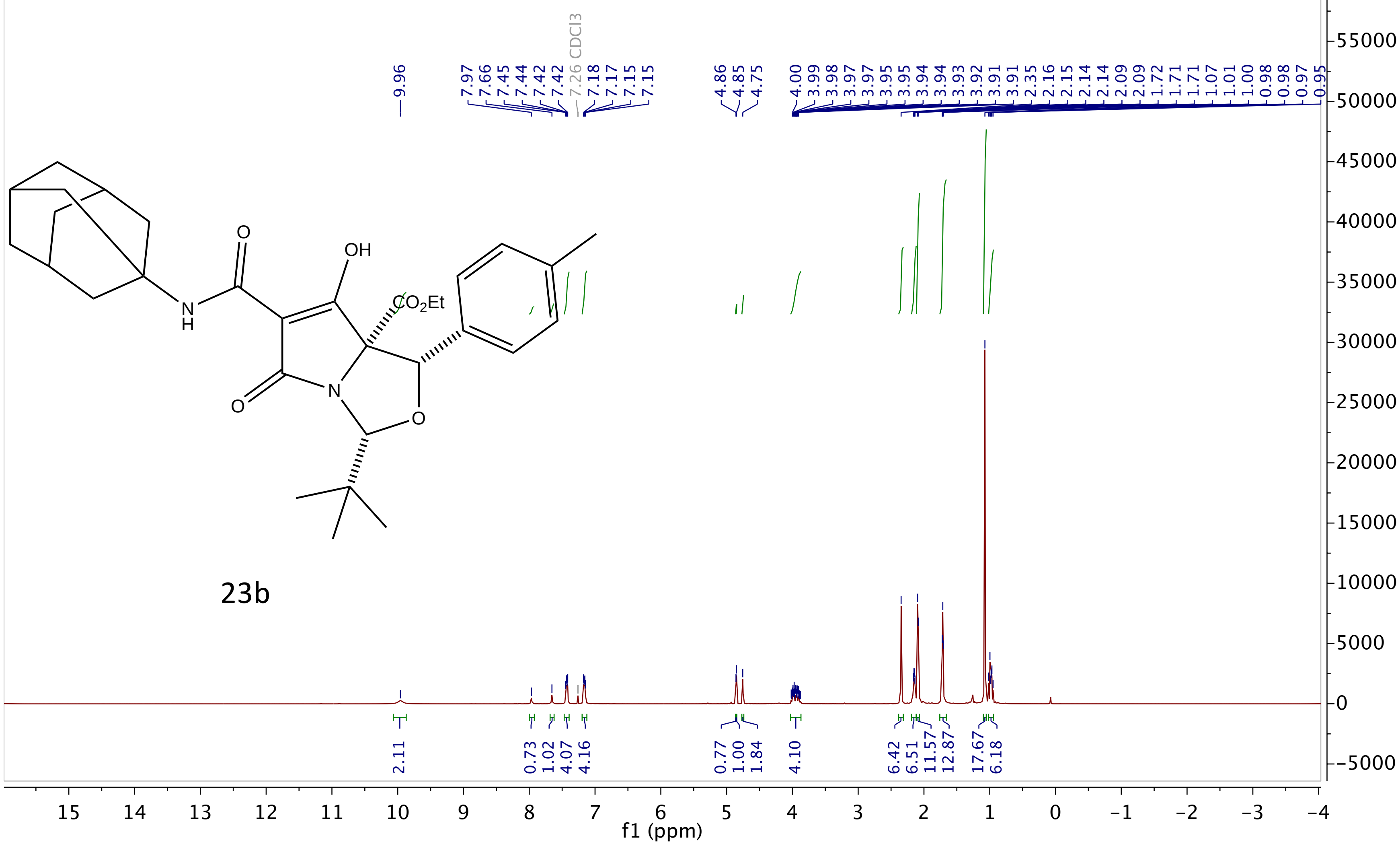
$^{13}C$ NMR (101 MHz, $CDCl_3$)




23a

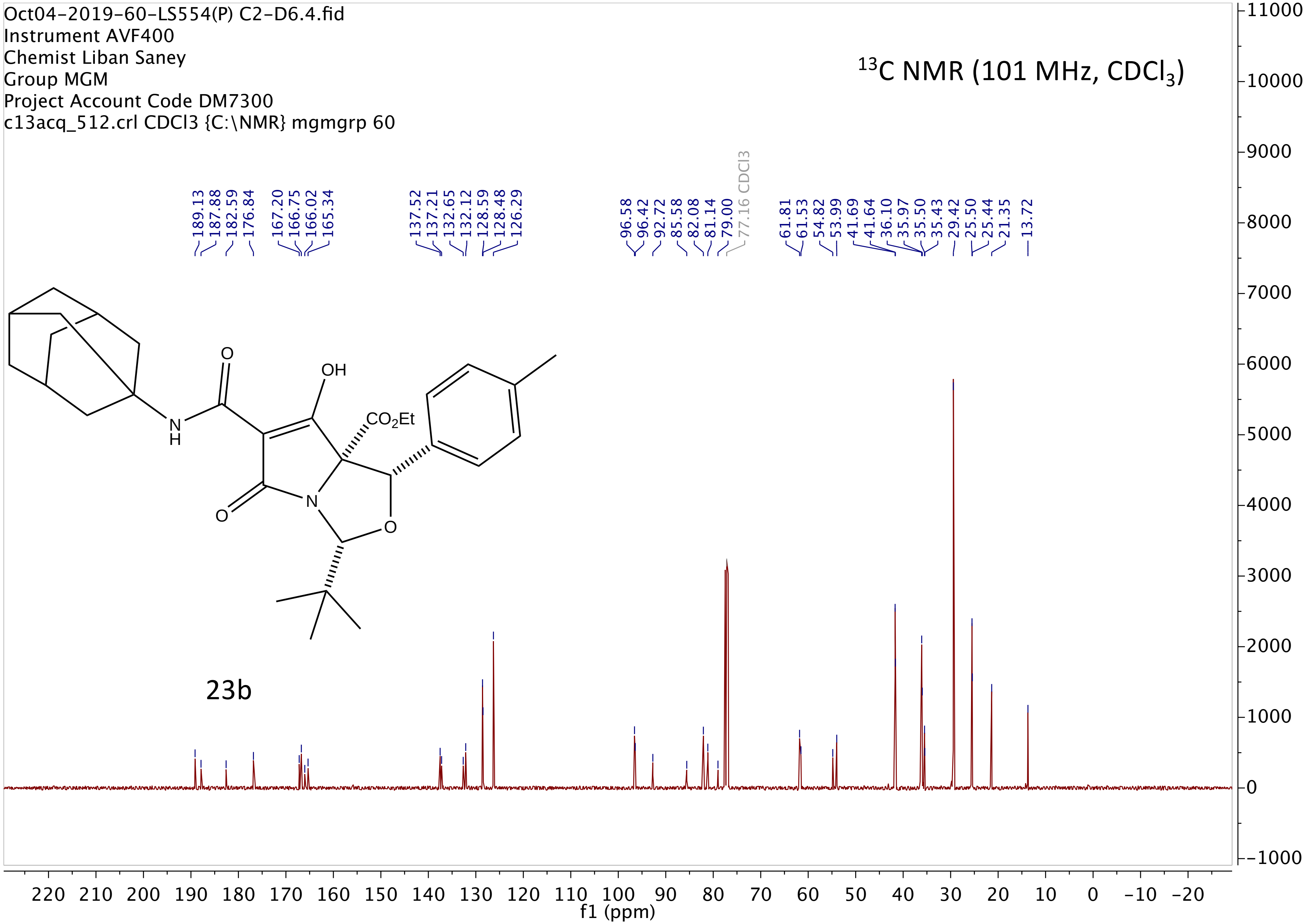
Oct04-2019-60-LS554(P) C2-D6.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

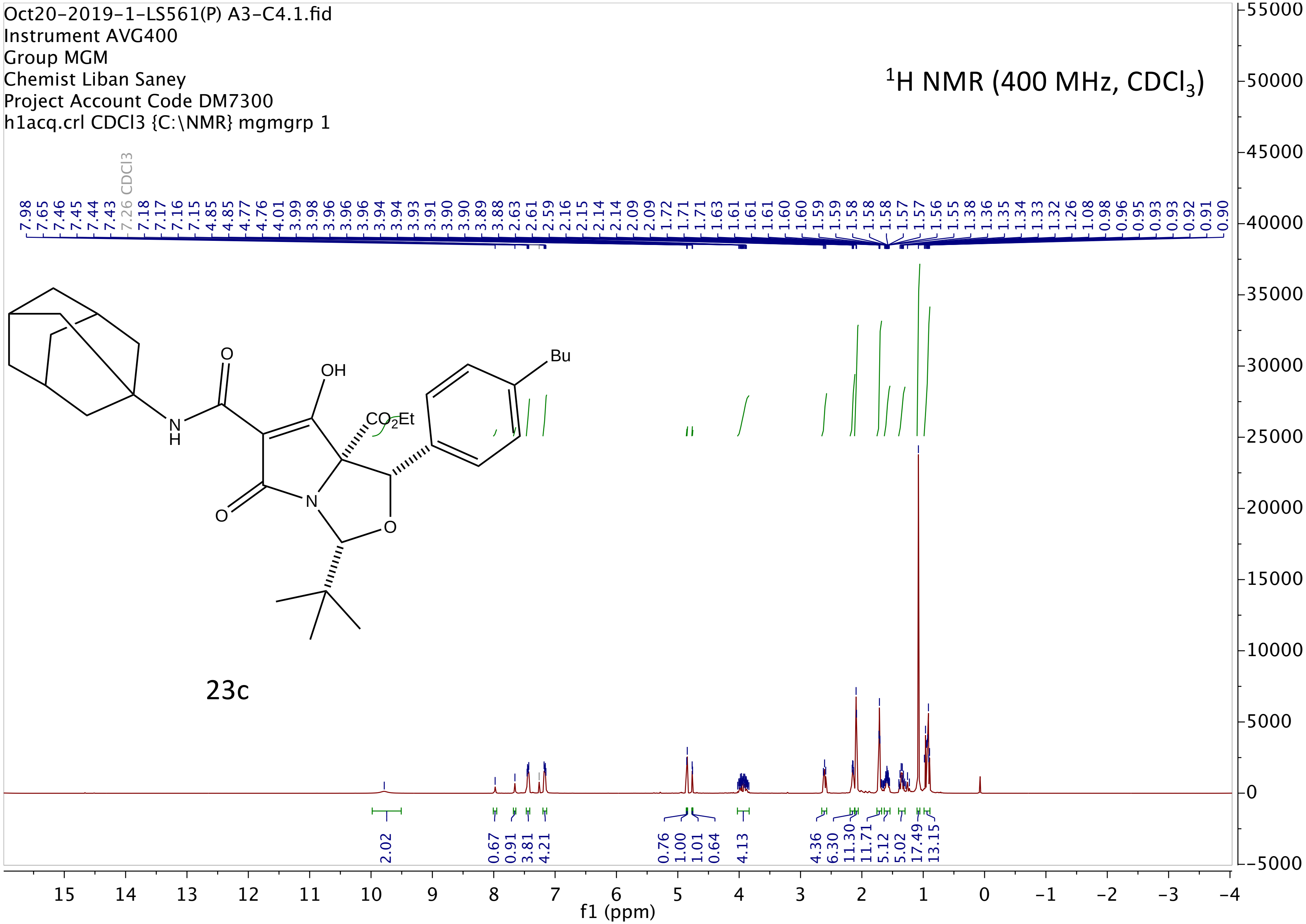
$^1$H NMR (400 MHz, $CDCl_3$)




23b

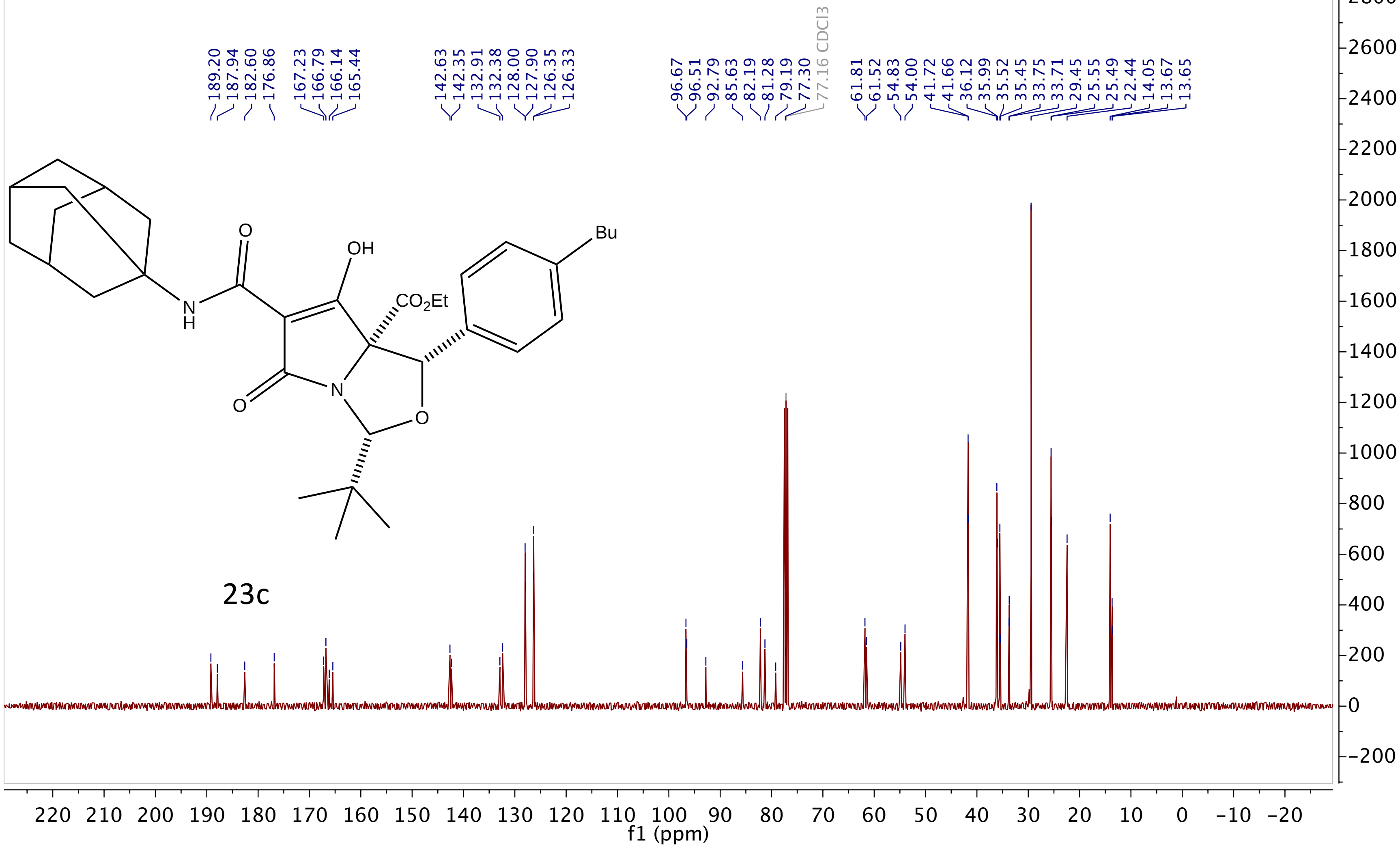
Oct04-2019-60-LS554(P) C2-D6.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60




Oct20-2019-1-LS561(P) A3-C4.1.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1
$^1$H NMR (400 MHz, $CDCl_3$)
7.98 7.65 7.46 7.45 7.44 7.43 7.26 CDCl3 7.18 7.17 7.16 7.15 4.85 4.85 4.77 4.76 4.01 3.99 3.98 3.96 3.96 3.94 3.94 3.93 3.91 3.90 3.90 3.89 3.88 2.63 2.61 2.59 2.16 2.15 2.14 2.14 2.09 2.09 1.72 1.71 1.71 1.63 1.61 1.61 1.61 1.60 1.59 1.59 1.58 1.58 1.58 1.57 1.57 1.56 1.55 1.38 1.36 1.35 1.34 1.33 1.32 1.26 1.08 0.98 0.96 0.95 0.93 0.92 0.91 0.90
O
OH
Bu
N
H
CO2Et
N
O
O
23c
2.02 0.67 0.91 3.81 4.21 0.76 1.00 1.01 0.64 4.13 4.36 6.30 11.30 11.71 5.12 5.02 17.49 13.15
f1 (ppm)

Oct20-2019-1-LS561(P) A3-C4.4.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1

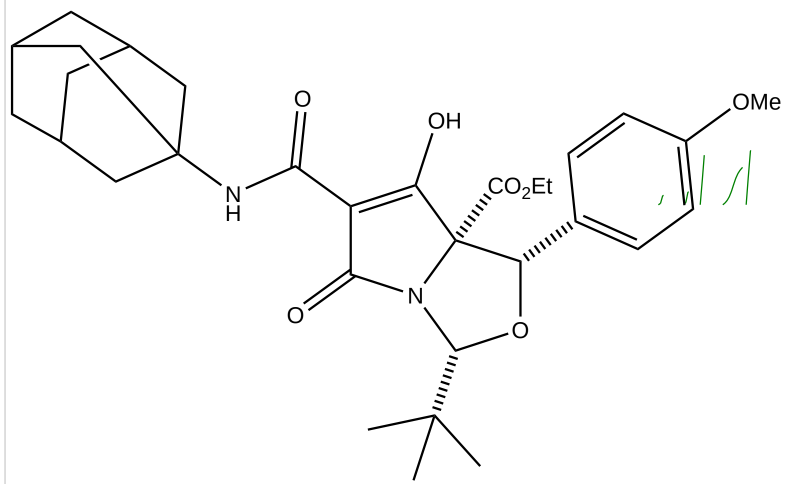
$^{13}C$ NMR (101 MHz, $CDCl_3$)



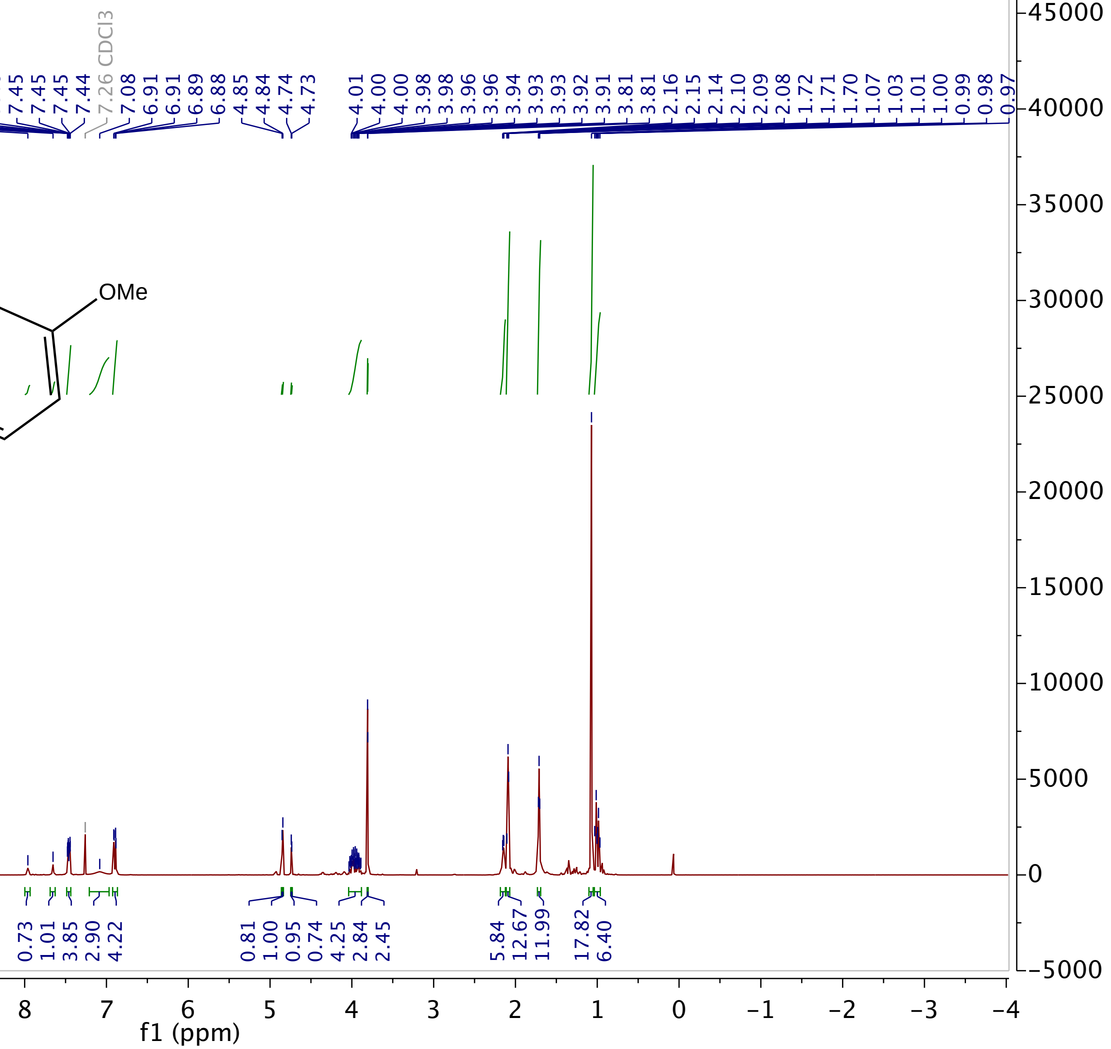
23c

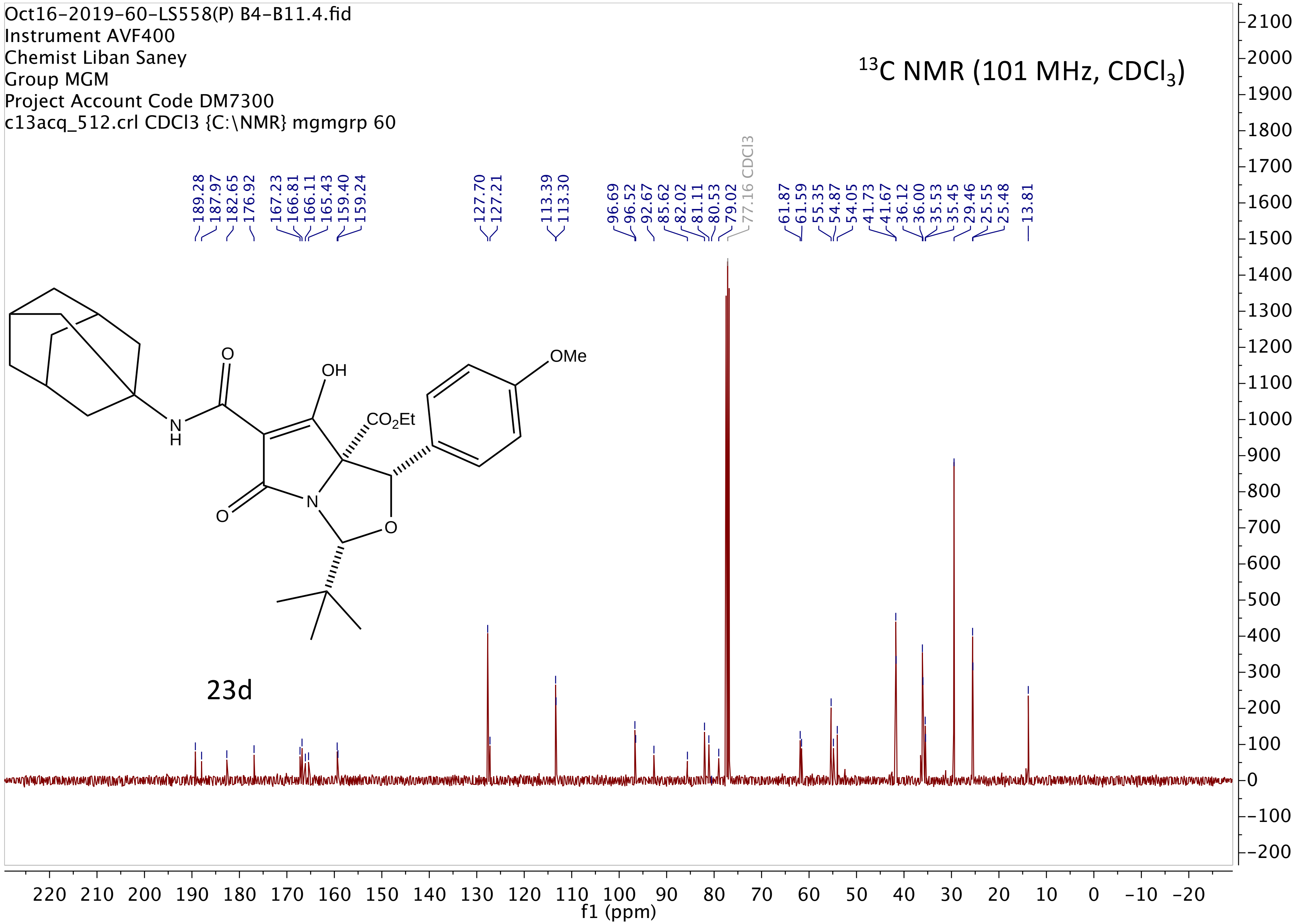
Oct16-2019-60-LS558(P) B4-B11.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60

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



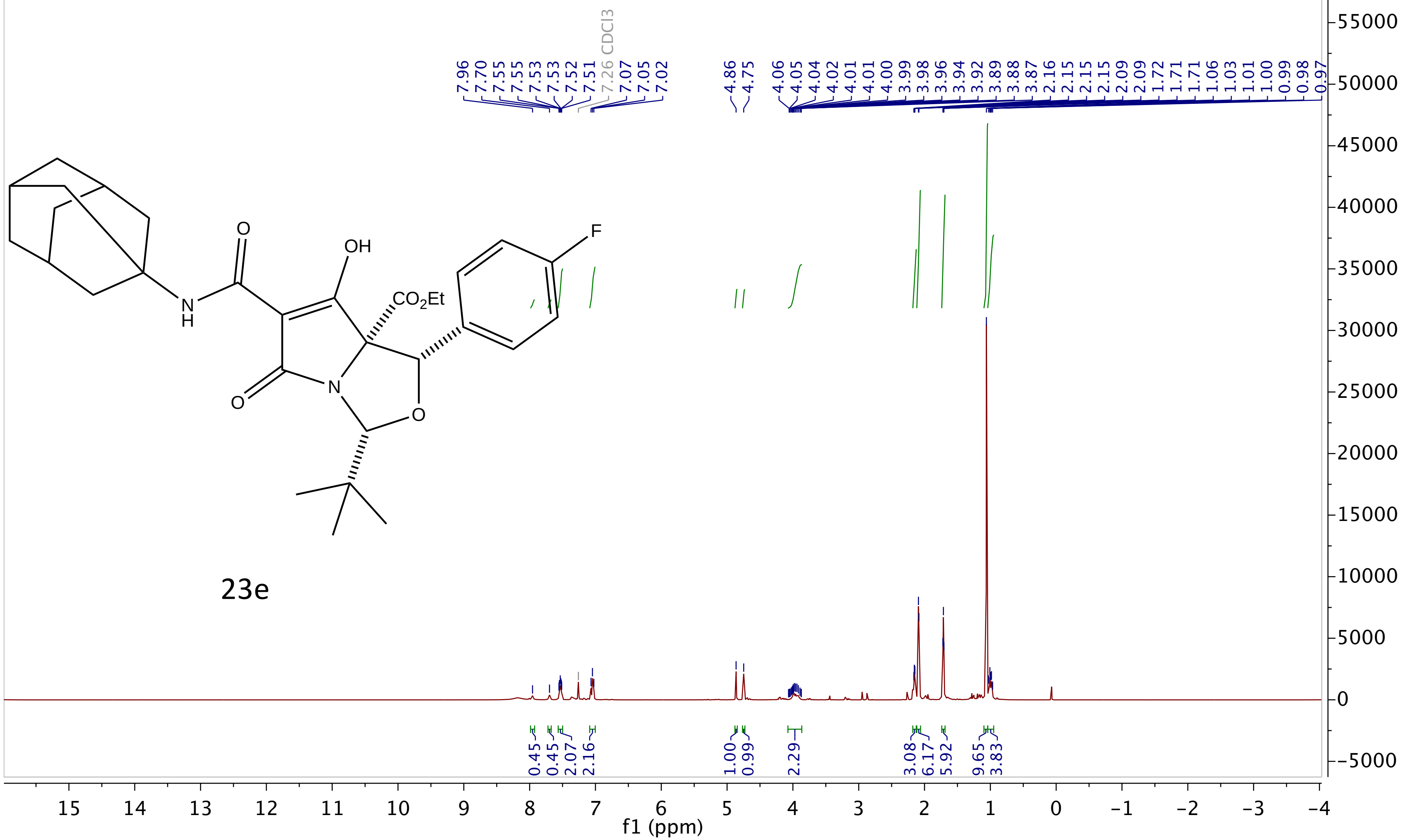

23d



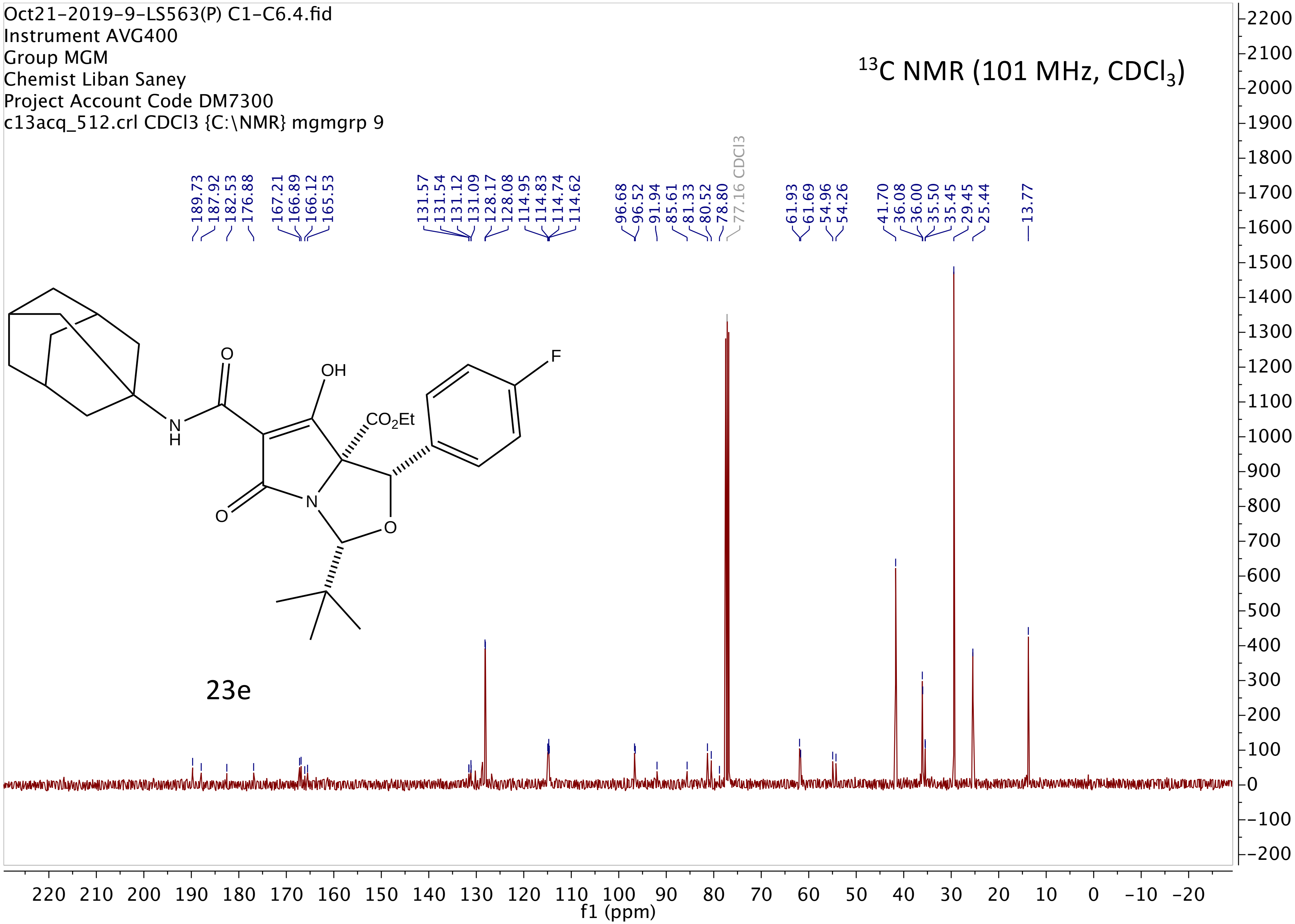

Oct16-2019-60-LS558(P) B4-B11.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60
13C NMR (101 MHz, CDCl3)
189.28
187.97
182.65
176.92
167.23
166.81
166.11
165.43
159.40
159.24
127.70
127.21
113.39
113.30
96.69
96.52
92.67
85.62
82.02
81.11
80.53
79.02
77.16 CDCl3
61.87
61.59
55.35
54.87
54.05
41.73
41.67
36.12
36.00
35.53
35.45
29.46
25.55
25.48
13.81
OMe
O
OH
CO2Et
N
H
N
O
O
23d
f1 (ppm)

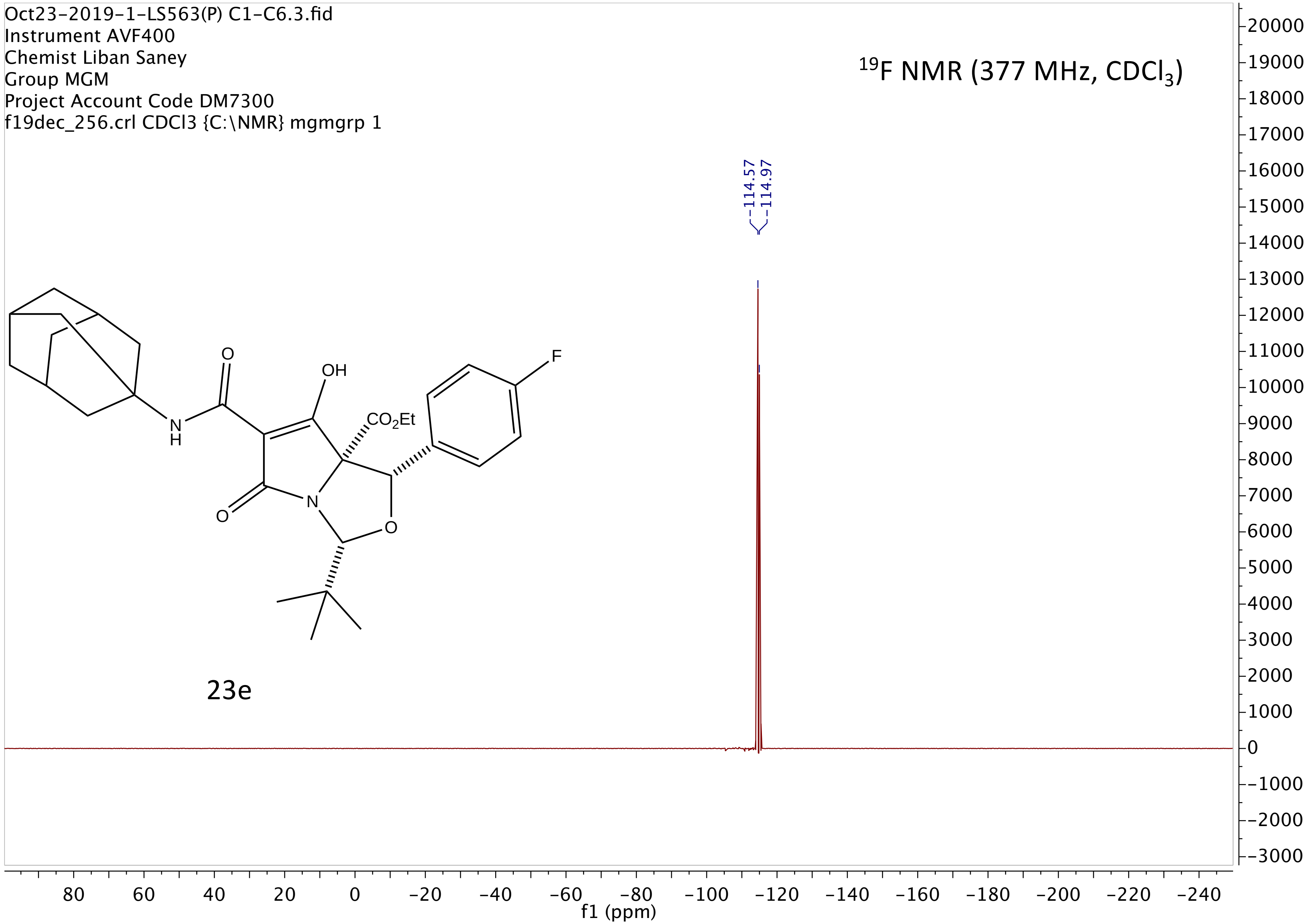
Oct21-2019-9-LS563(P) C1-C6.1.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 9

$^1$H NMR (400 MHz, $CDCl_3$)

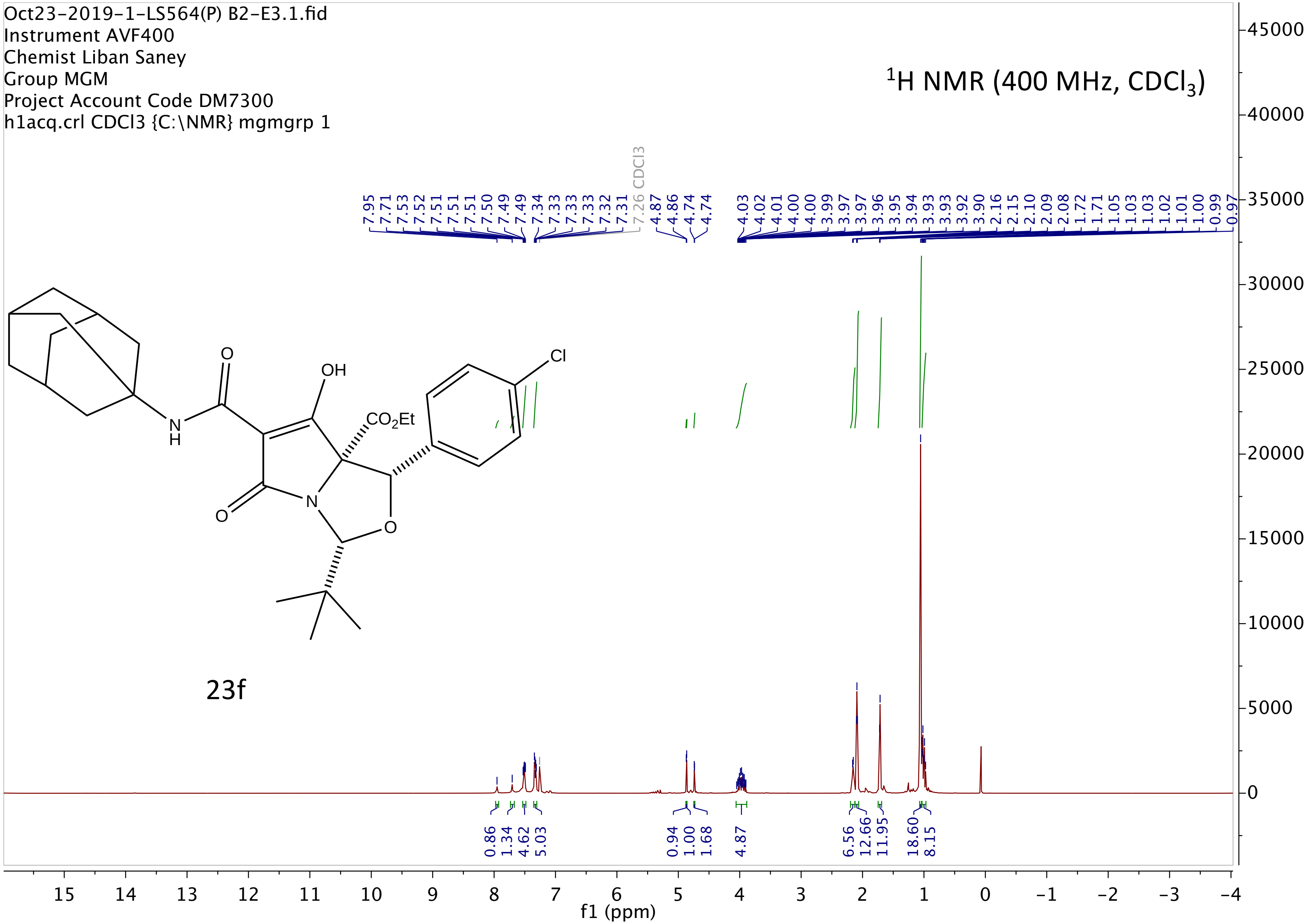



23e


Oct21-2019-9-LS563(P) C1-C6.4.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 9
13C NMR (101 MHz, CDCl3)
189.73
187.92
182.53
176.88
167.21
166.89
166.12
165.53
131.57
131.54
131.12
131.09
128.17
128.08
114.95
114.83
114.74
114.62
96.68
96.52
91.94
85.61
81.33
80.52
78.80
77.16 CDCl3
61.93
61.69
54.96
54.26
41.70
36.08
36.00
35.50
35.45
29.45
25.44
13.77
O
OH
CO2Et
F
N
H
N
O
O
23e
f1 (ppm)

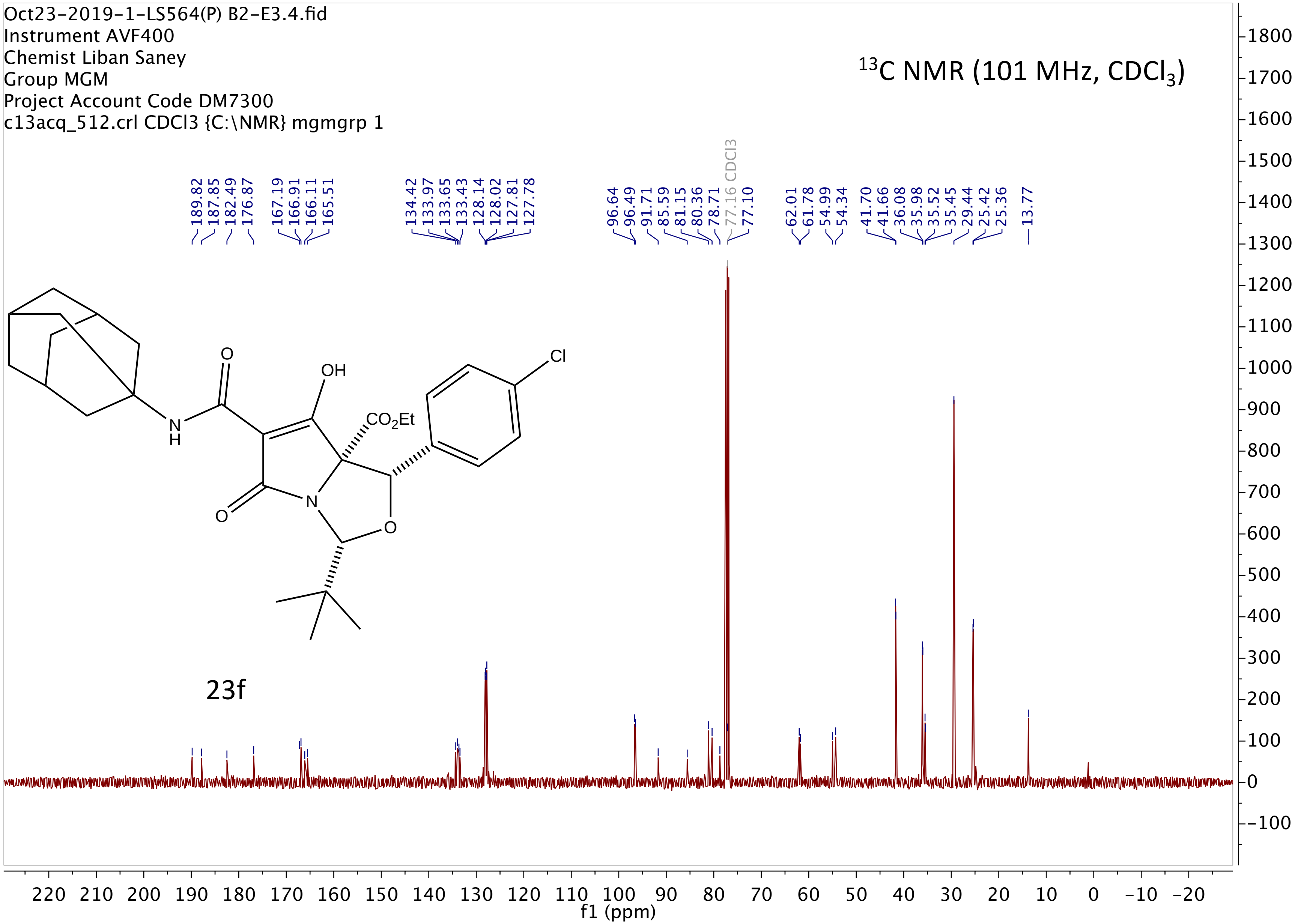

Oct23-2019-1-LS563(P) C1-C6.3.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 1
$^{19}F$ NMR (377 MHz, $CDCl_3$)
-114.57
-114.97
O
OH
F
$CO_2Et$
N
H
N
O
O
23e
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

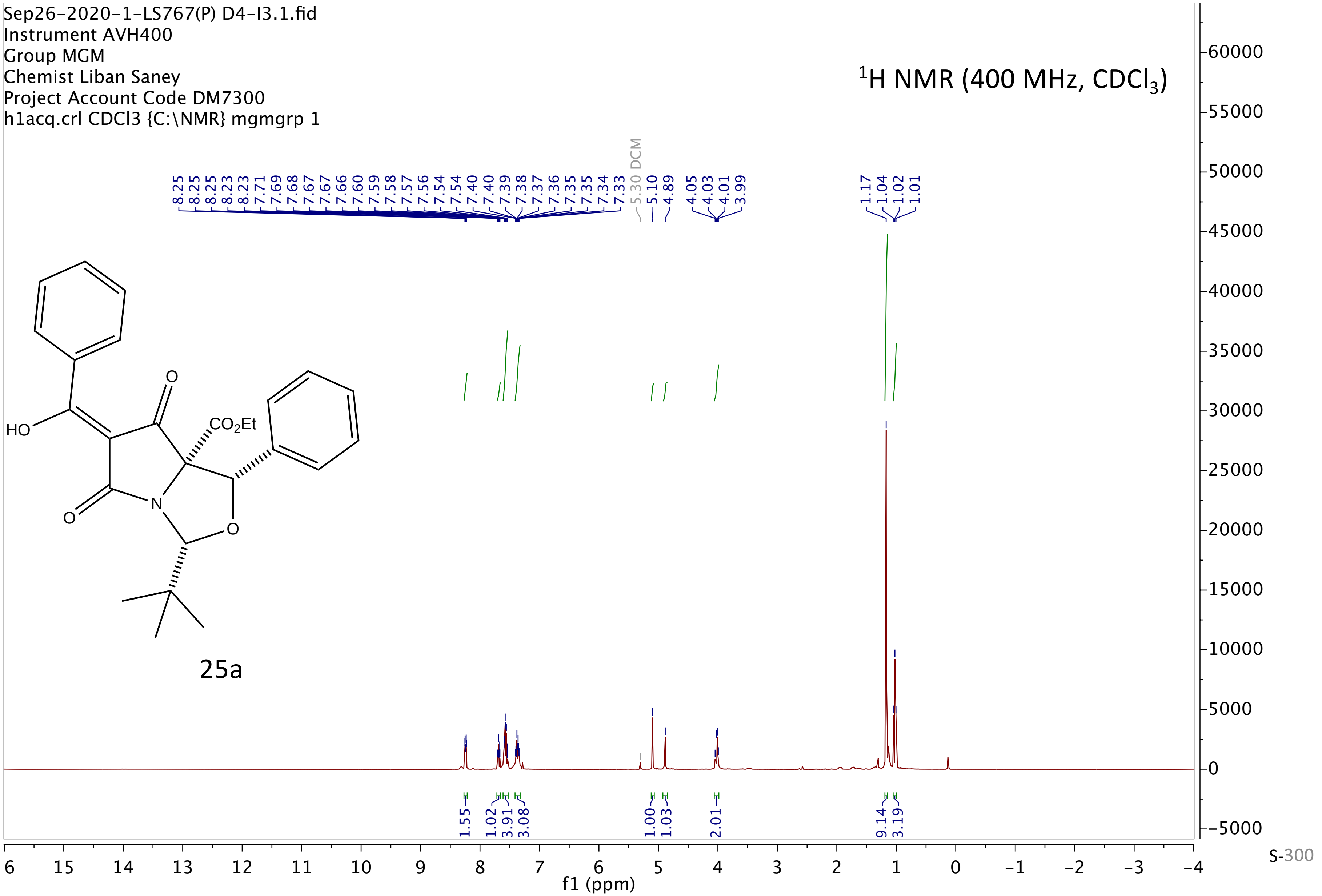
Oct23-2019-1-LS564(P) B2-E3.1.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1



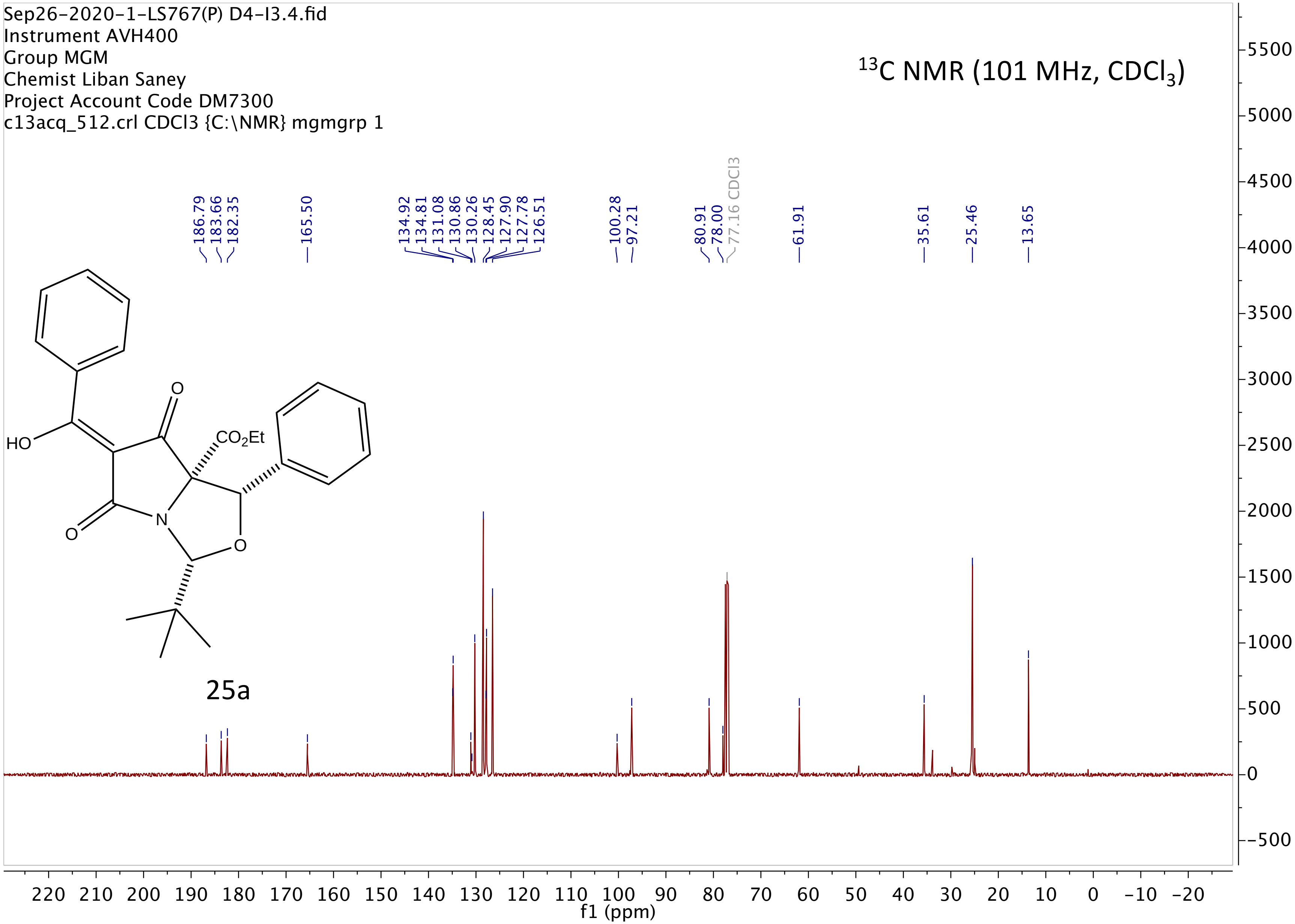
23f

Oct23-2019-1-LS564(P) B2-E3.4.fid
Instrument AVF400
Chemist Liban Saney
Group MGM
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1





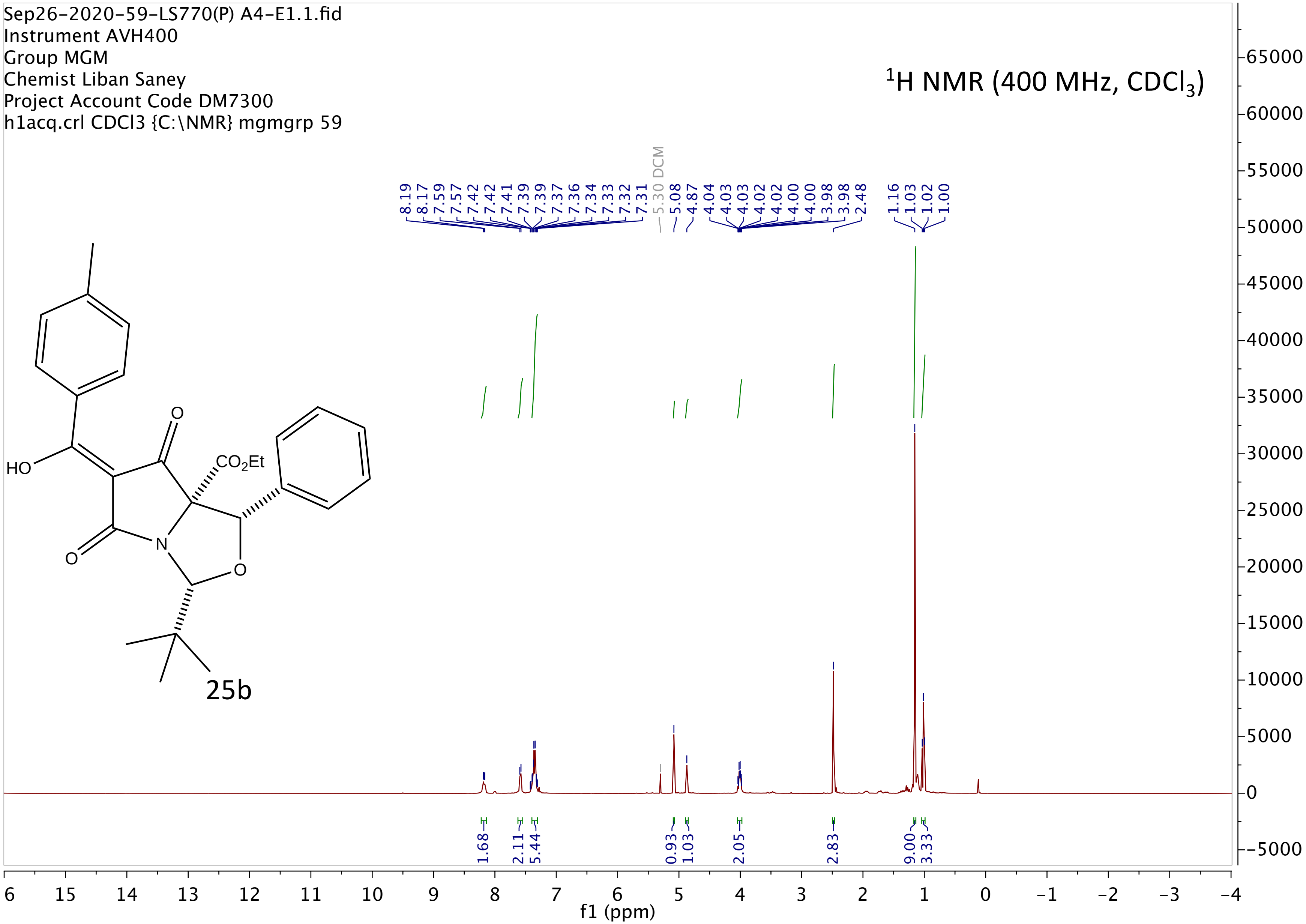
Sep26-2020-1-LS767(P) D4-I3.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1
$^1$H NMR (400 MHz, $CDCl_3$)
8.25 8.25 8.25 8.23 8.23 7.71 7.69 7.68 7.67 7.67 7.66 7.60 7.59 7.58 7.57 7.56 7.54 7.54 7.40 7.40 7.39 7.38 7.37 7.36 7.35 7.35 7.34 7.33
5.30 DCM
5.10 4.89 4.05 4.03 4.01 3.99
1.17 1.04 1.02 1.01
HO
O
O
N
O
$CO_2Et$
25a
1.55 1.02 3.91 3.08 1.00 1.03 2.01 9.14 3.19
f1 (ppm)



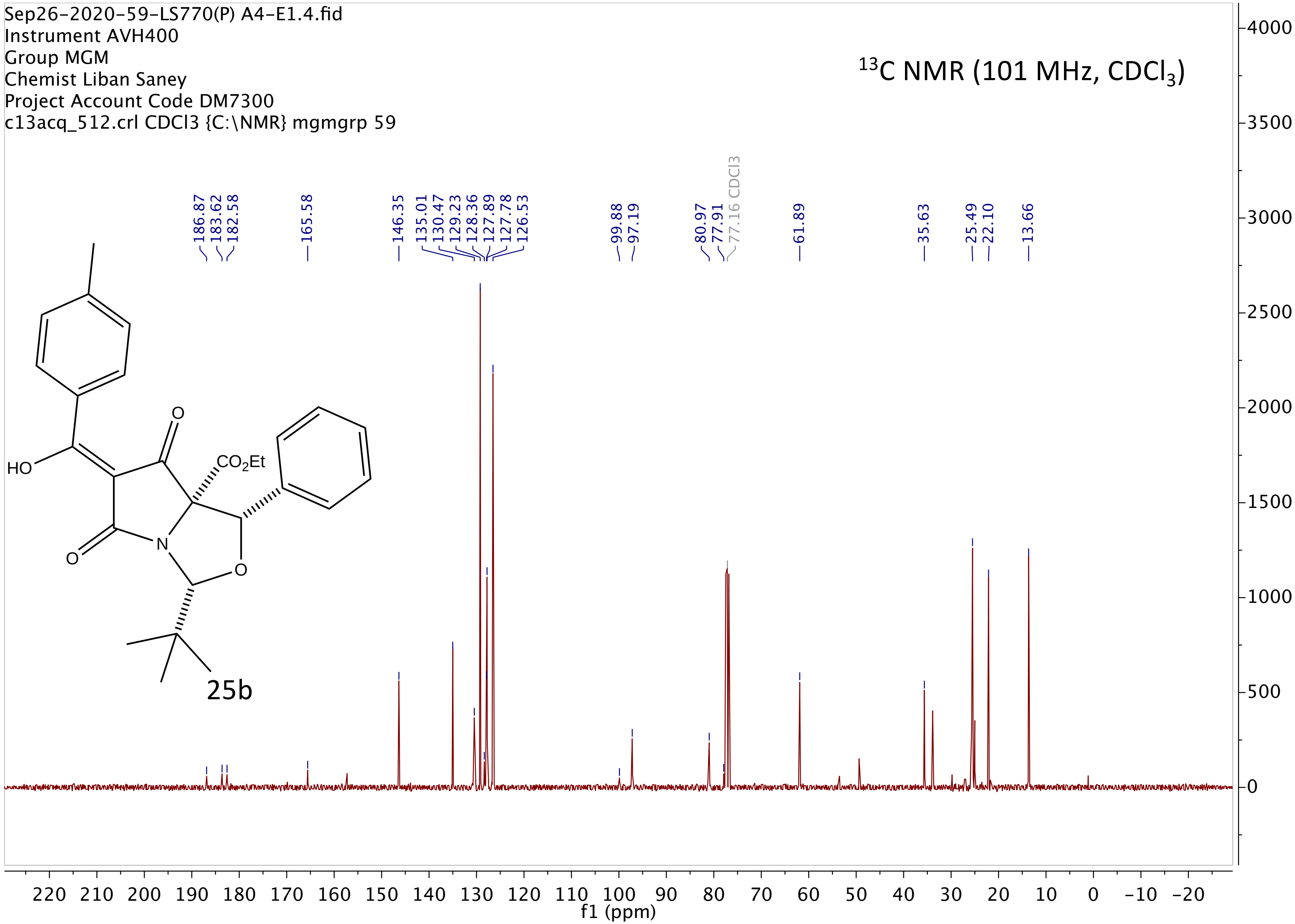
Sep26-2020-1-LS767(P) D4-I3.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1
$^{13}C$ NMR (101 MHz, $CDCl_3$)
186.79
183.66
182.35
165.50
134.92
134.81
131.08
130.86
130.26
128.45
127.90
127.78
126.51
100.28
97.21
80.91
78.00
77.16 CDCl3
61.91
35.61
25.46
13.65
HO
O
O
N
O
$CO_2Et$
25a
f1 (ppm)

Sep26-2020-59-LS770(P) A4-E1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 59

$^1$H NMR (400 MHz, $CDCl_3$)

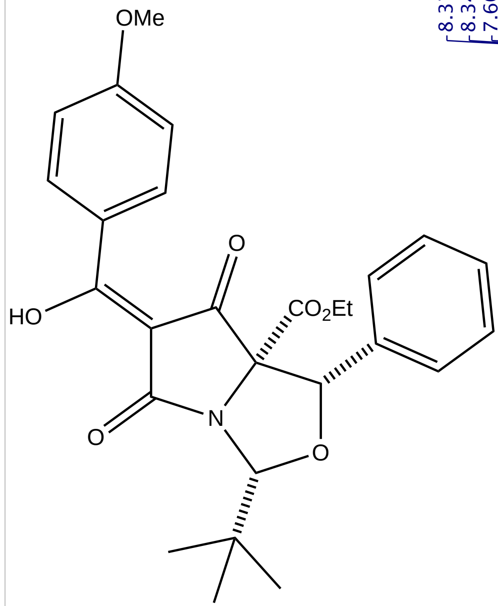



25b

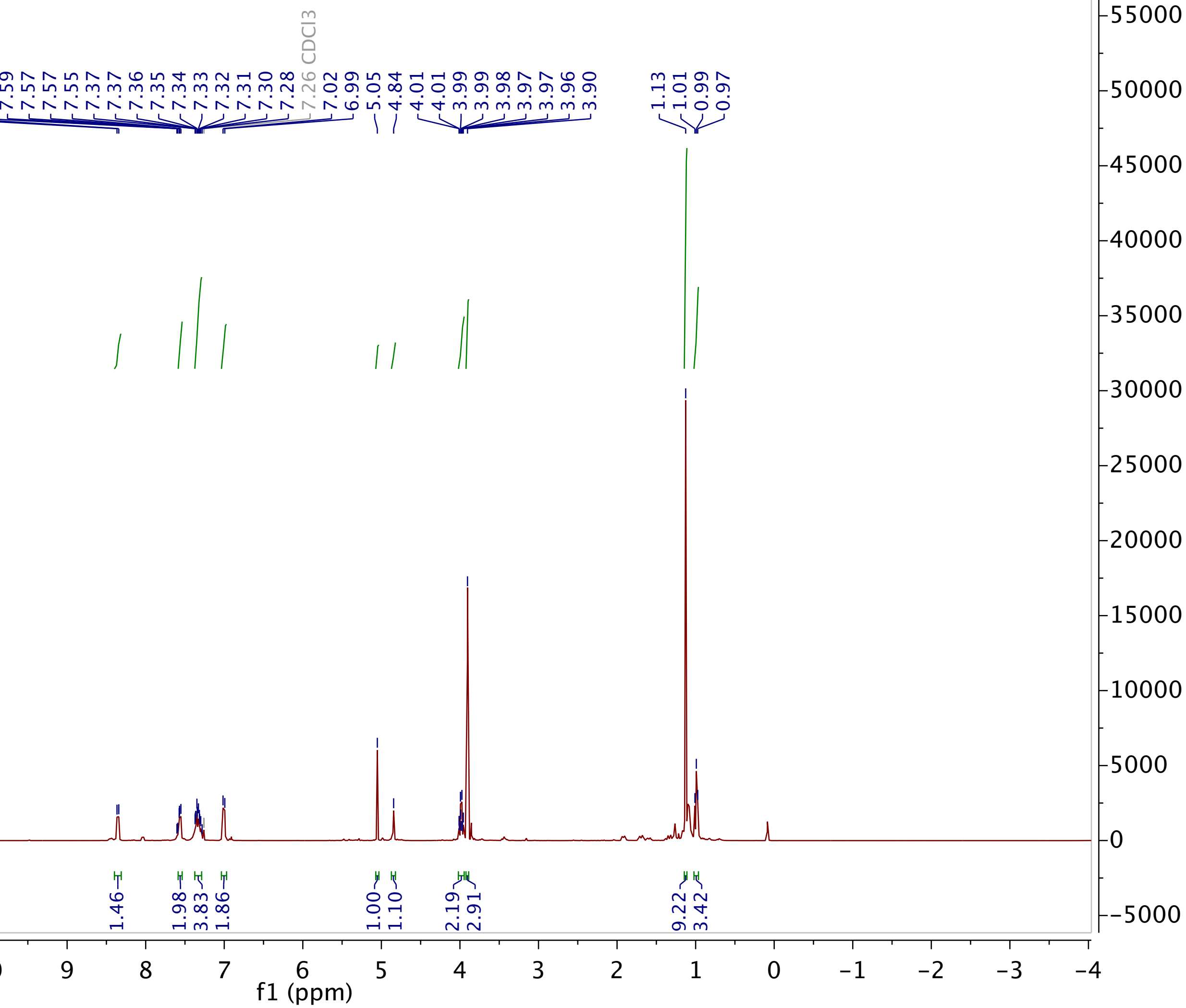

Sep26-2020-59-LS770(P) A4-E1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 59
$^{13}$C NMR (101 MHz, $CDCl_3$)
186.87
183.62
182.58
165.58
146.35
135.01
130.47
129.23
128.36
127.89
127.78
126.53
99.88
97.19
80.97
77.91
77.16 CDCl3
61.89
35.63
25.49
22.10
13.66
HO
O
O
CO$_2$Et
N
O
25b
f1 (ppm)

Sep28-2020-1-LS771(P) B4-F1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1

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

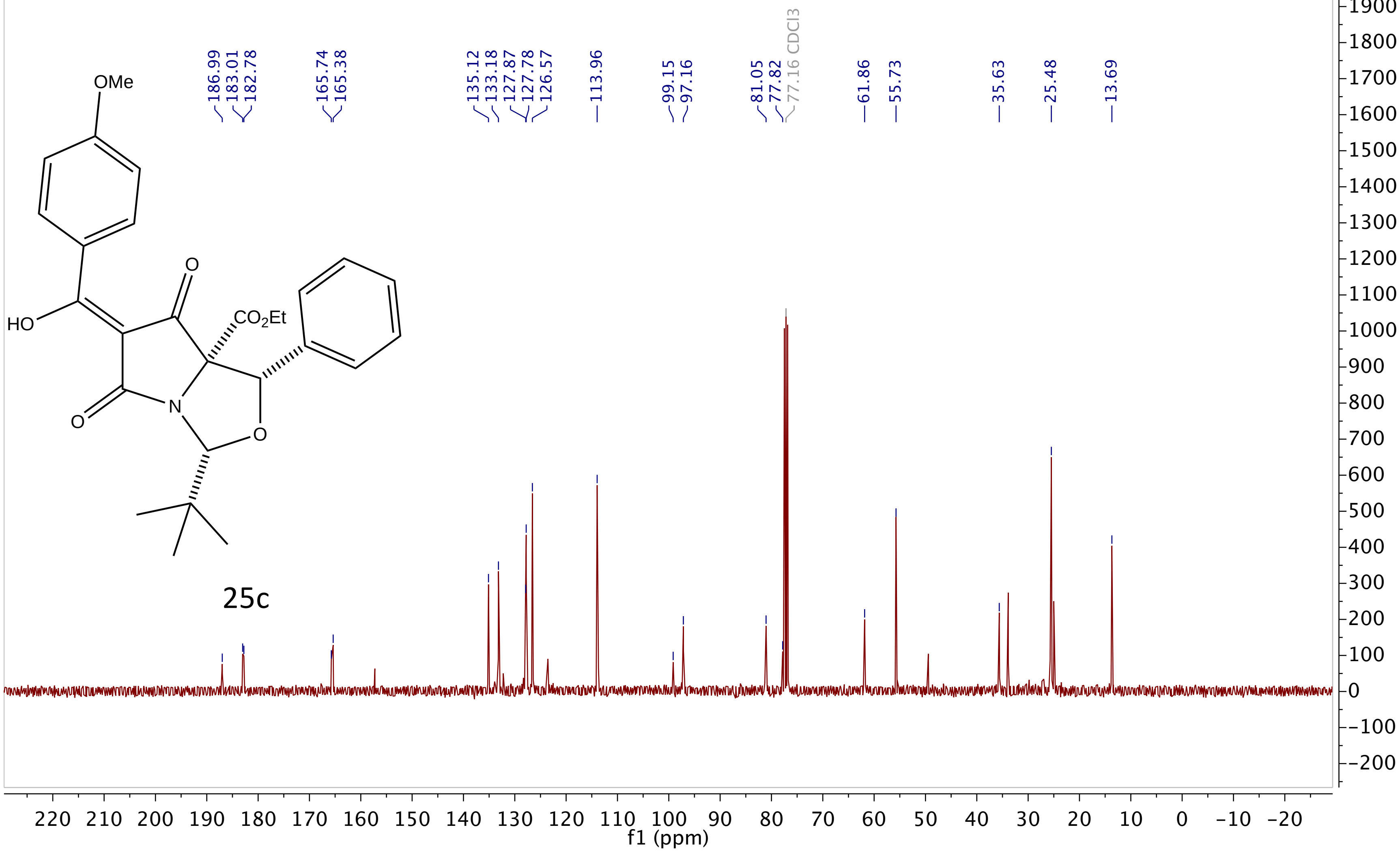


25c



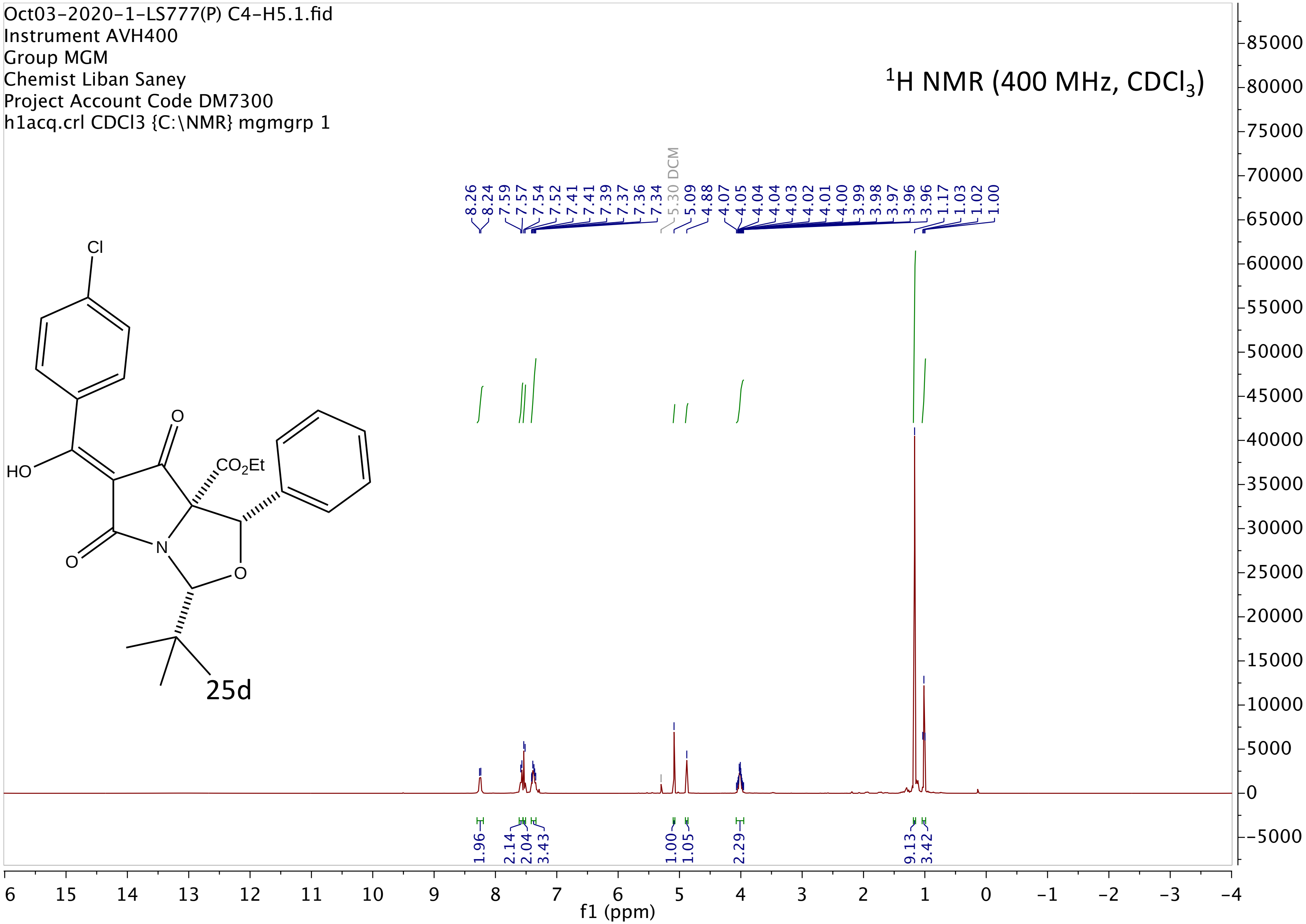
Sep28-2020-1-LS771(P) B4-F1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1

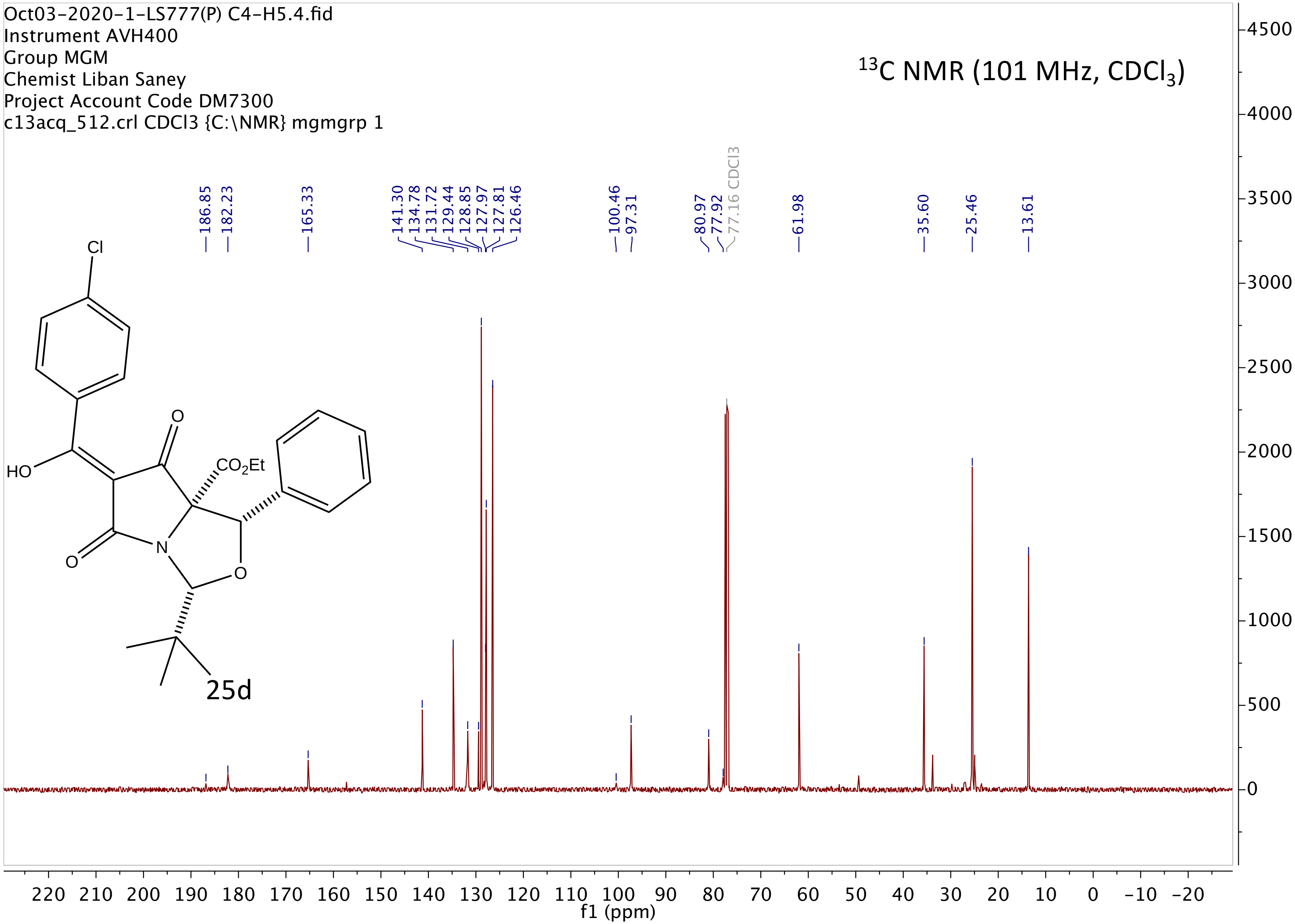
$^{13}C$ NMR (101 MHz, $CDCl_3$)

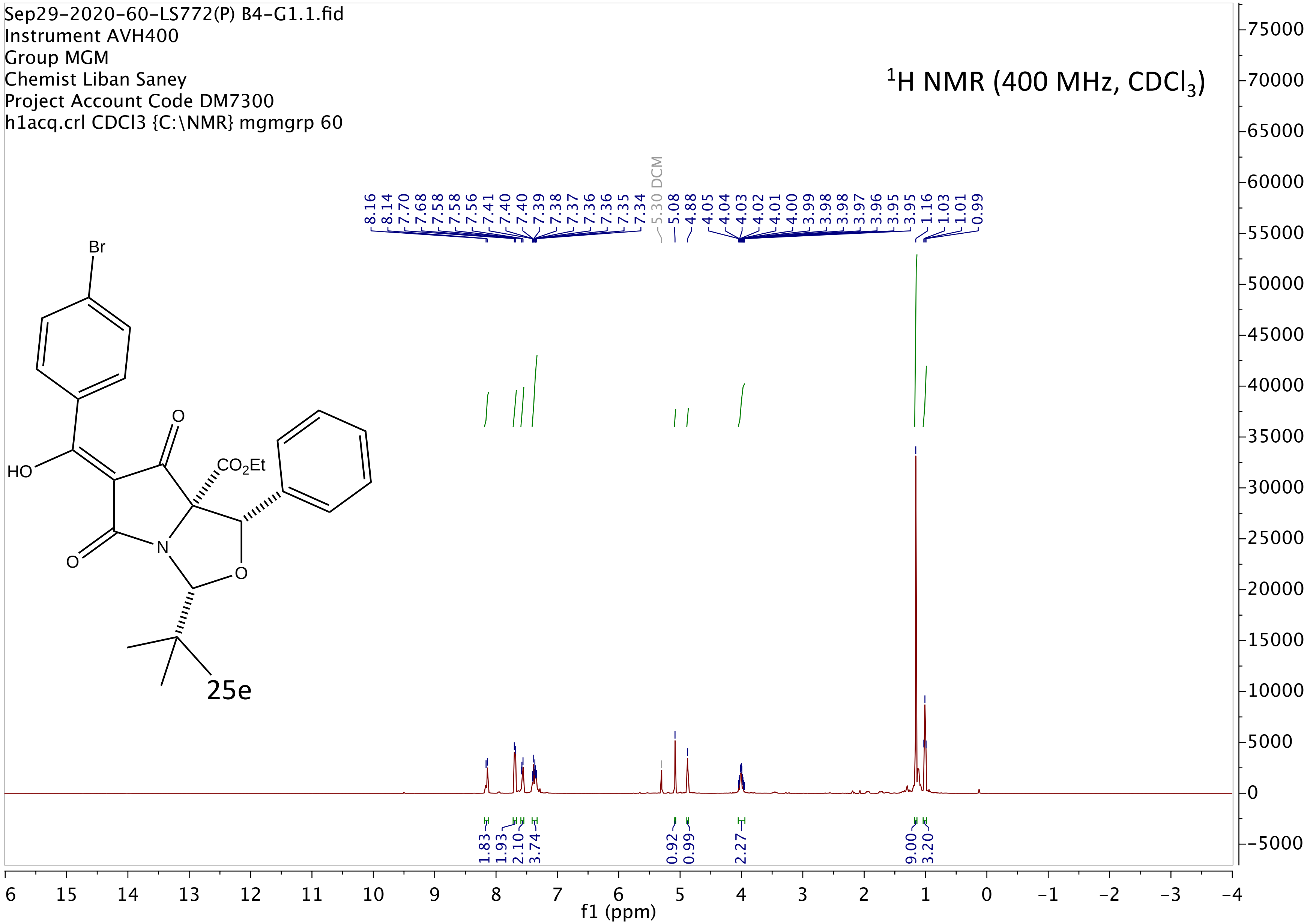



25c

Oct03-2020-1-LS777(P) C4-H5.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1

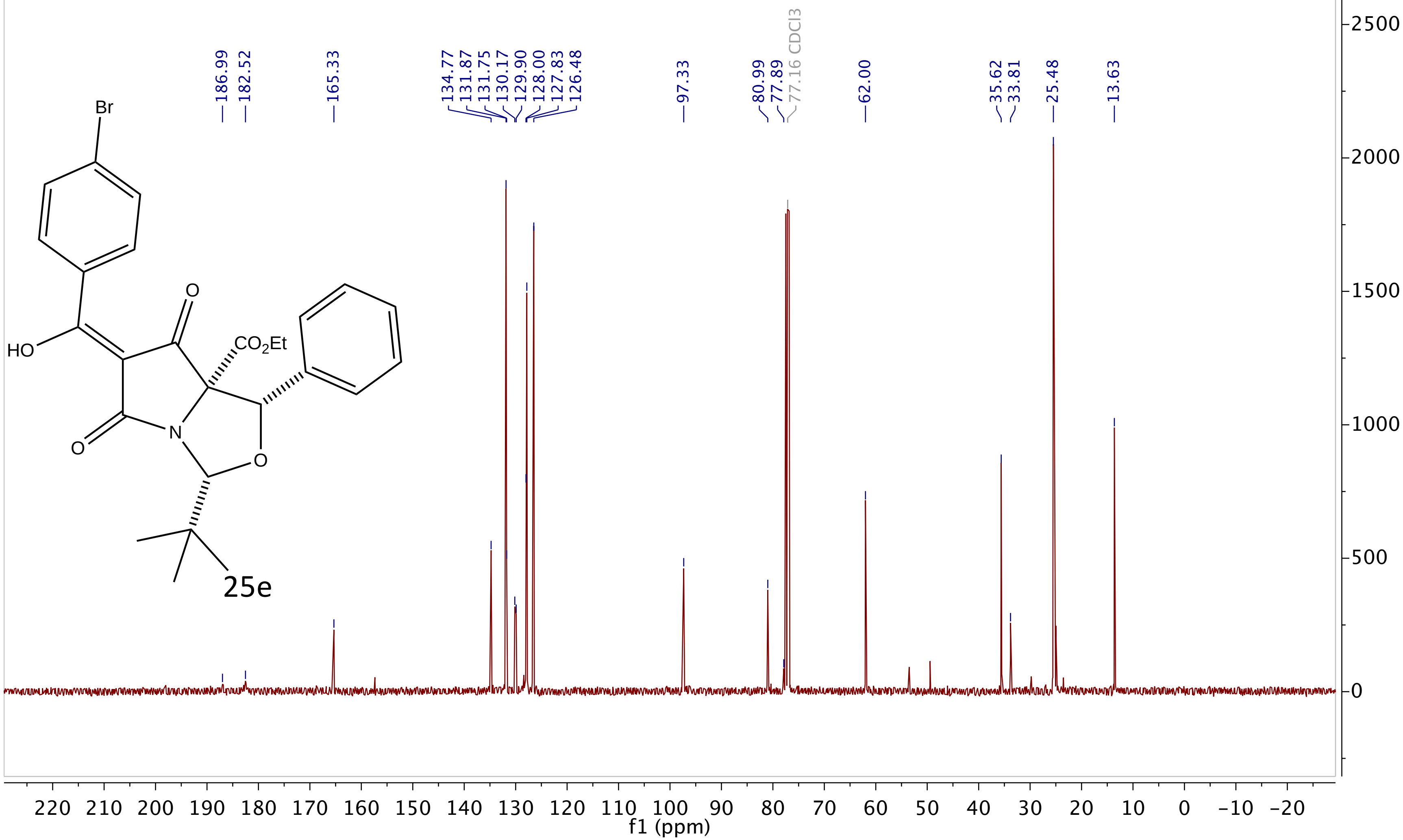


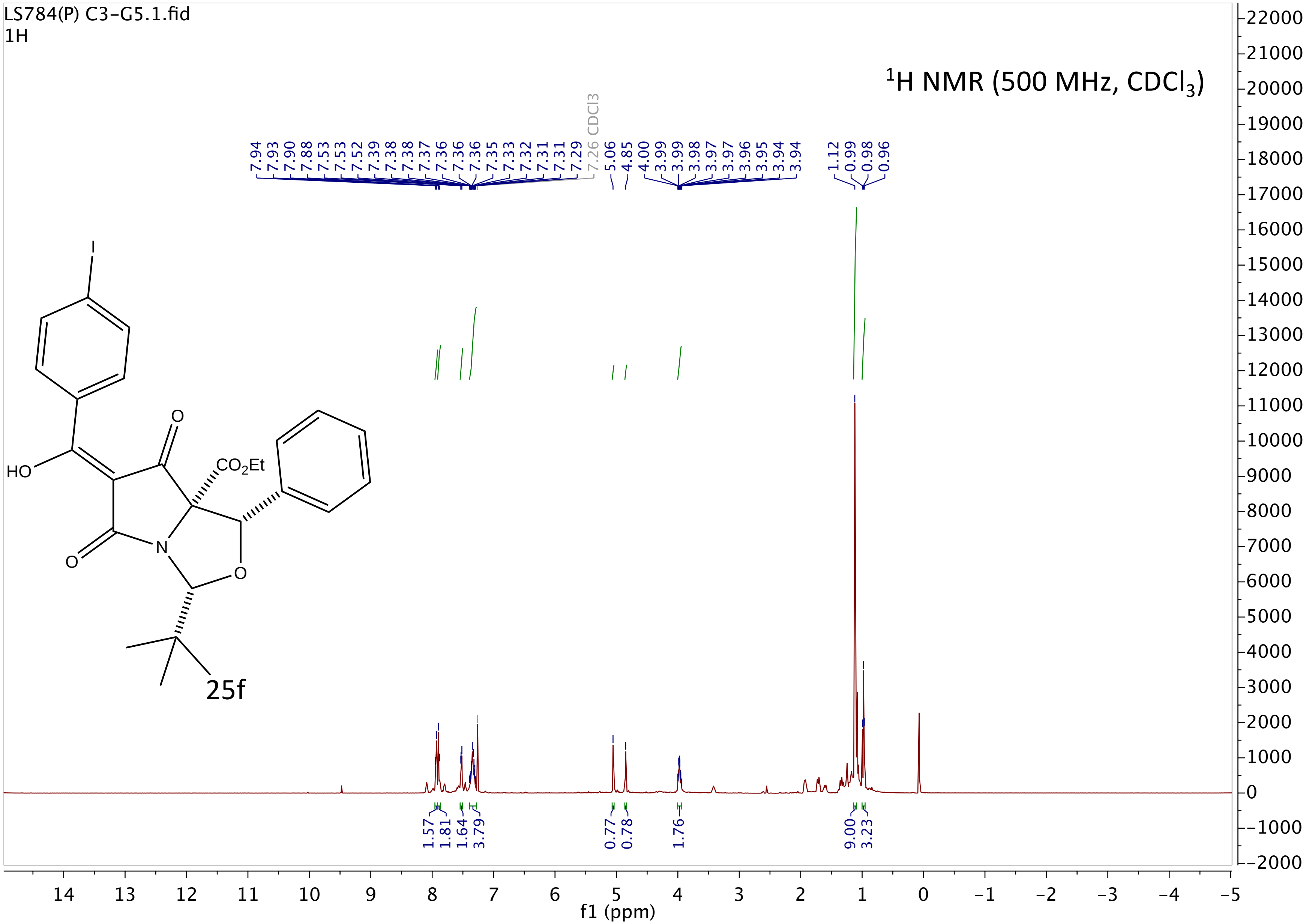

Oct03-2020-1-LS777(P) C4-H5.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1
$^{13}$C NMR (101 MHz, $CDCl_3$)
186.85
182.23
165.33
141.30
134.78
131.72
129.44
128.85
127.97
127.81
126.46
100.46
97.31
80.97
77.92
77.16 CDCl3
61.98
35.60
25.46
13.61
Cl
HO
O
$CO_2Et$
N
O
O
25d
f1 (ppm)

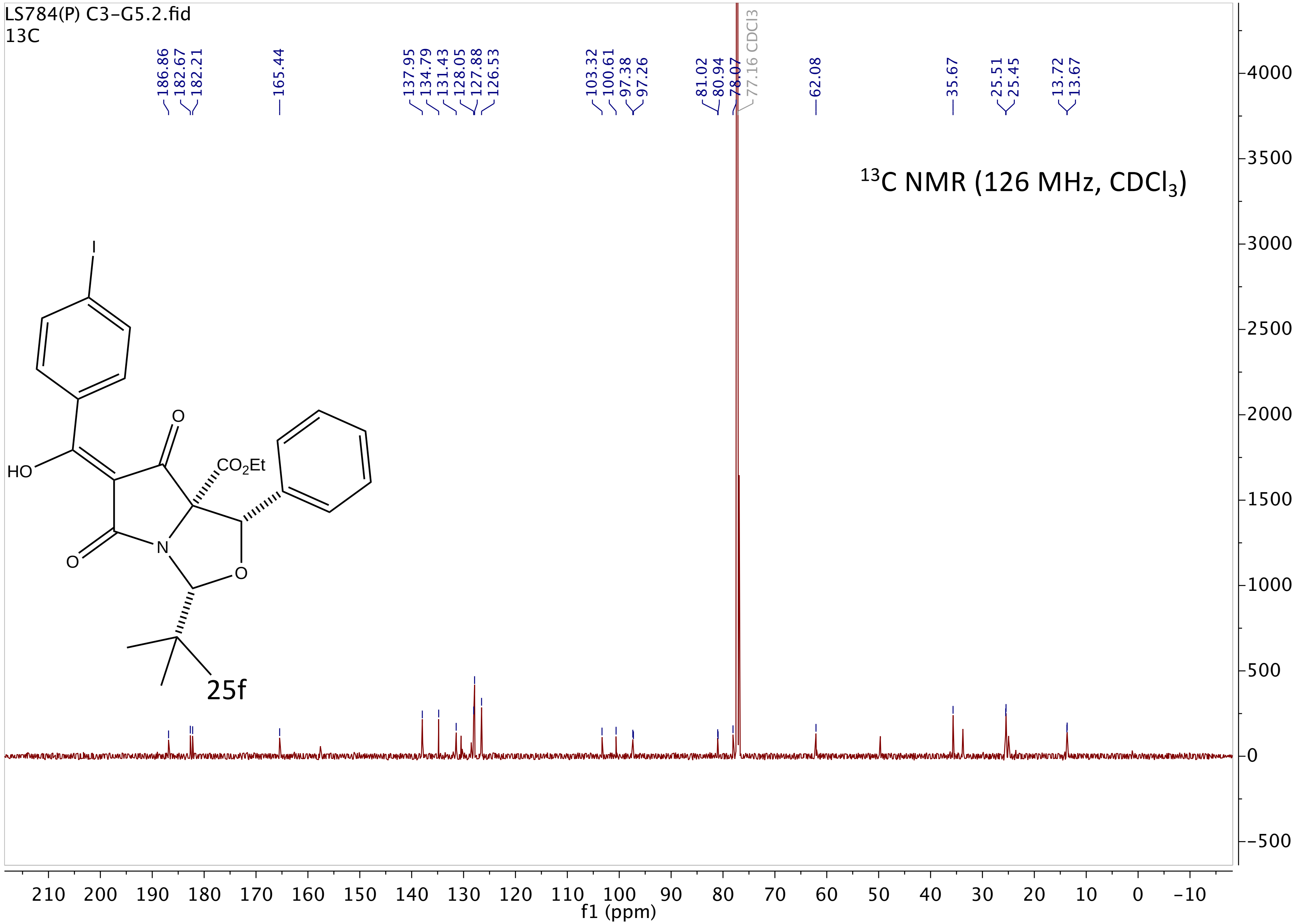

Sep29-2020-60-LS772(P) B4-G1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 60
1H NMR (400 MHz, CDCl3)
8.16 8.14 7.70 7.68 7.58 7.58 7.56 7.41 7.40 7.40 7.39 7.38 7.37 7.36 7.36 7.35 7.34
5.30 DCM
5.08 4.88
4.05 4.04 4.03 4.02 4.01 4.00 3.99 3.98 3.98 3.97 3.96 3.95 3.95
1.16 1.03 1.01 0.99
1.83 1.93 2.10 3.74 0.92 0.99 2.27 9.00 3.20
Br
HO
O
CO2Et
N
O
O
25e
f1 (ppm)

Sep29-2020-60-LS772(P) B4-G1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 60

$^{13}C$ NMR (101 MHz, $CDCl_3$)



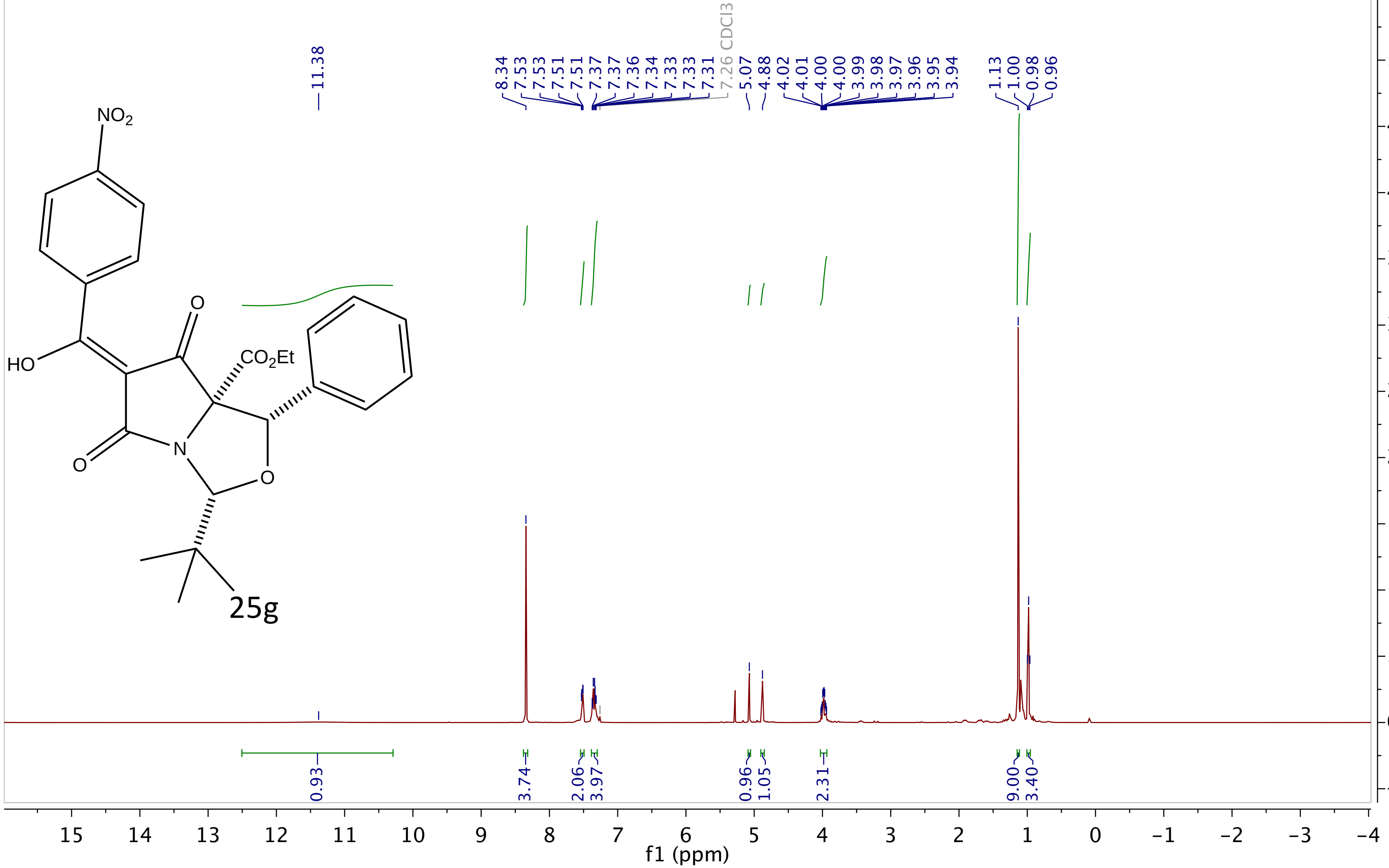

LS784(P) C3-G5.1.fid
1H
$^1$H NMR (500 MHz, $CDCl_3$)
7.94 7.93 7.90 7.88 7.53 7.53 7.52 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.33 7.32 7.31 7.31 7.29 7.26 CDCl3 5.06 4.85 4.00 3.99 3.99 3.98 3.97 3.97 3.96 3.95 3.94 3.94 1.12 0.99 0.98 0.96
25f
1.57 1.81 1.64 3.79 0.77 0.78 1.76 9.00 3.23
f1 (ppm)

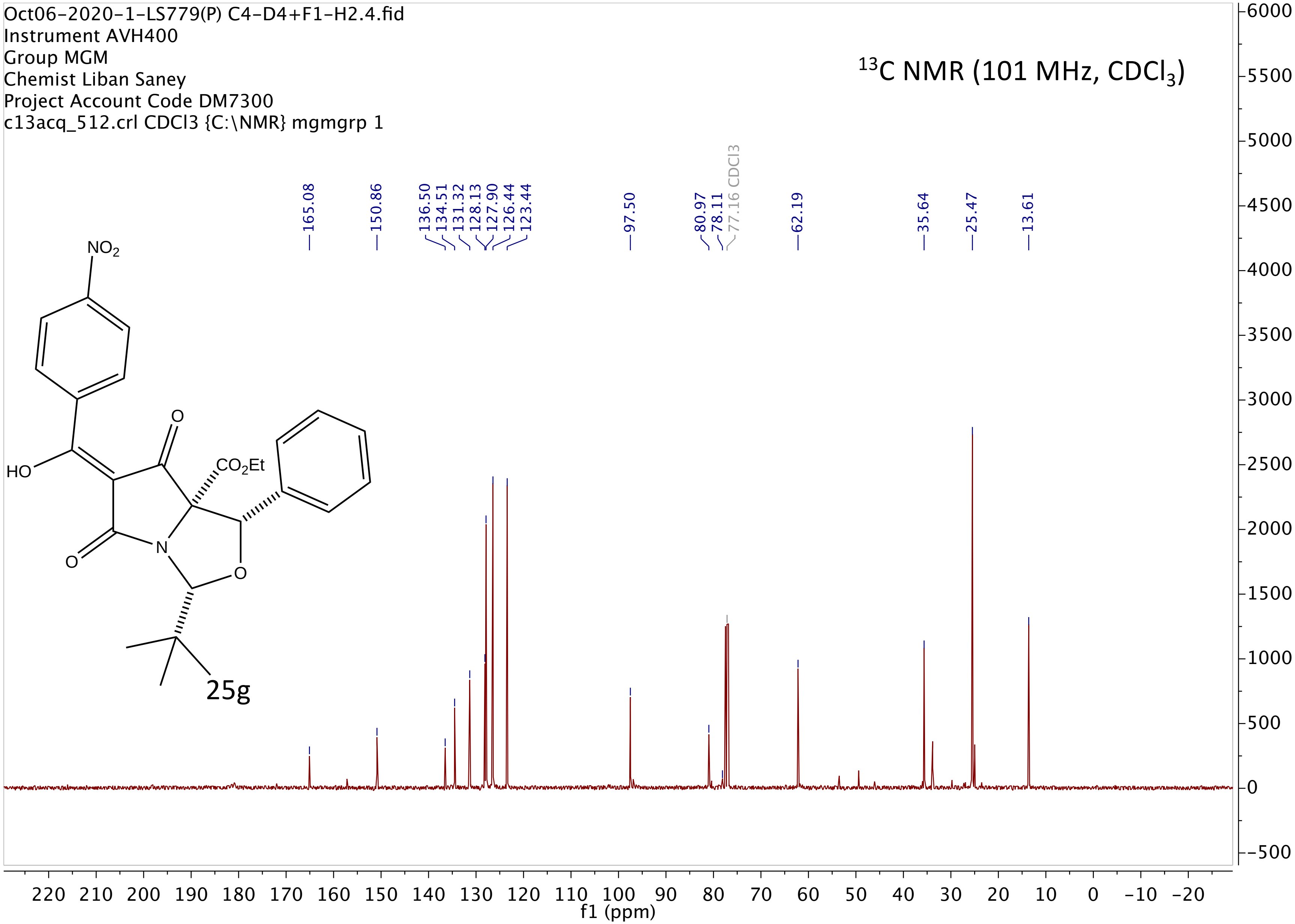


LS784(P) C3-G5.2.fid
13C
186.86
182.67
182.21
165.44
137.95
134.79
131.43
128.05
127.88
126.53
103.32
100.61
97.38
97.26
81.02
80.94
78.07
77.16 CDCl3
62.08
35.67
25.51
25.45
13.72
13.67
$^{13}$C NMR (126 MHz, CDCl$_3$)
I
O
HO
$CO_2Et$
N
O
O
25f
f1 (ppm)

Oct06-2020-1-LS779(P) C4-D4+F1-H2.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 1

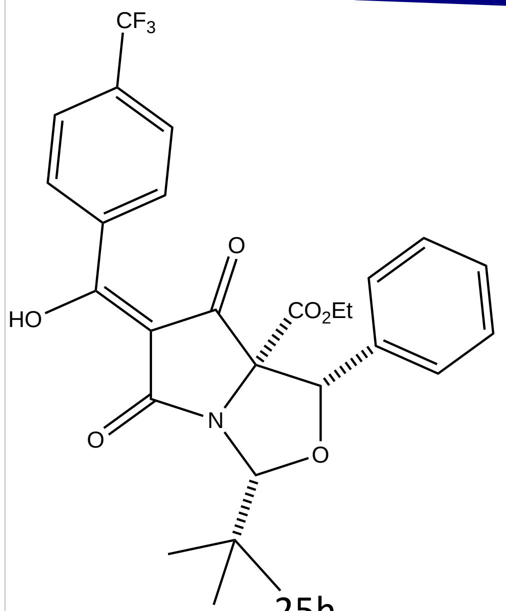
$^1H$ NMR (400 MHz, $CDCl_3$)



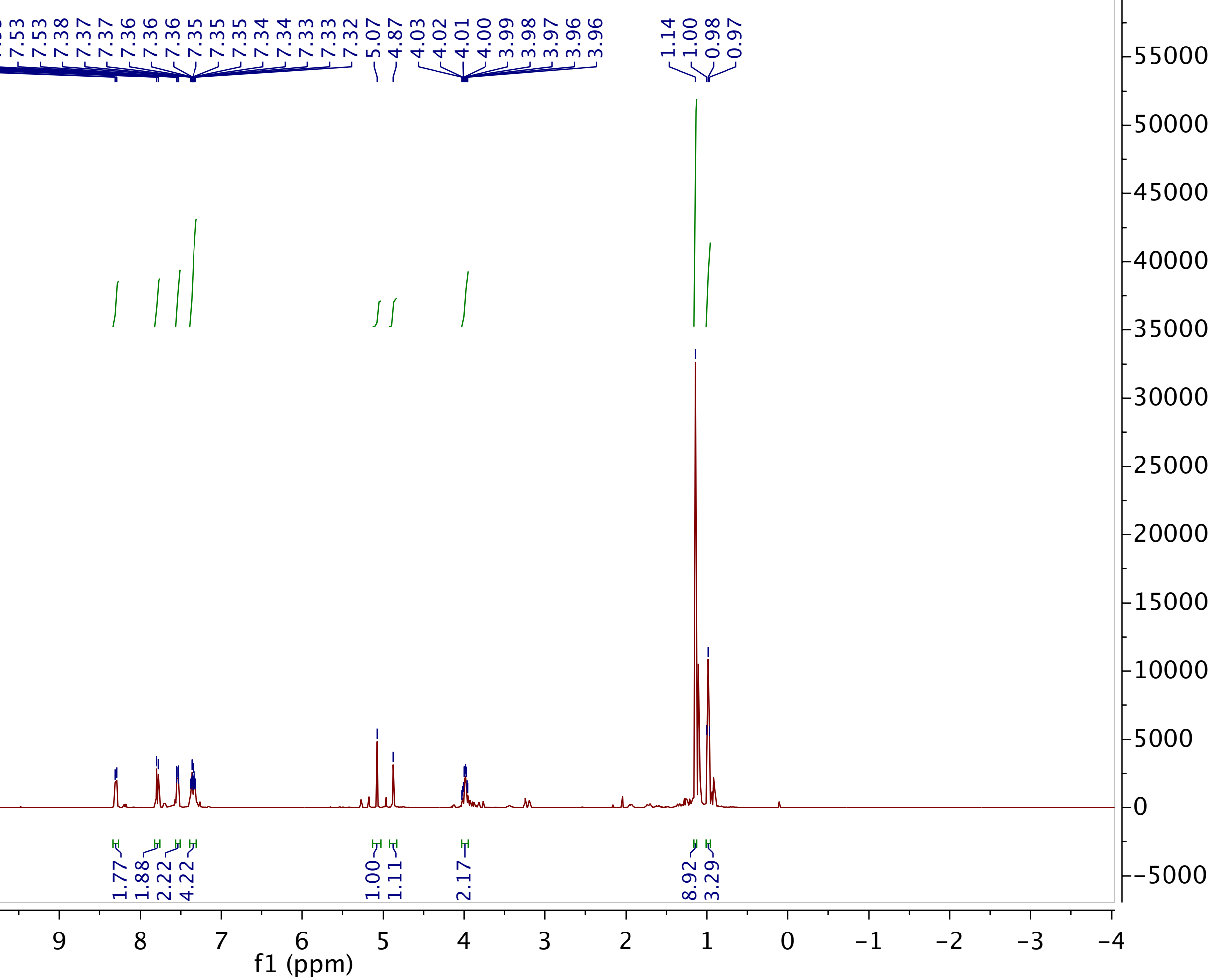

Oct06-2020-1-LS779(P) C4-D4+F1-H2.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 1
$^{13}$C NMR (101 MHz, $CDCl_3$)
165.08
150.86
136.50
134.51
131.32
128.13
127.90
126.44
123.44
97.50
80.97
78.11
77.16 CDCl3
62.19
35.64
25.47
13.61
$NO_2$
HO
O
$CO_2Et$
N
O
O
25g
f1 (ppm)

Oct09-2020-13-LS792(P) C3-H5.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 13

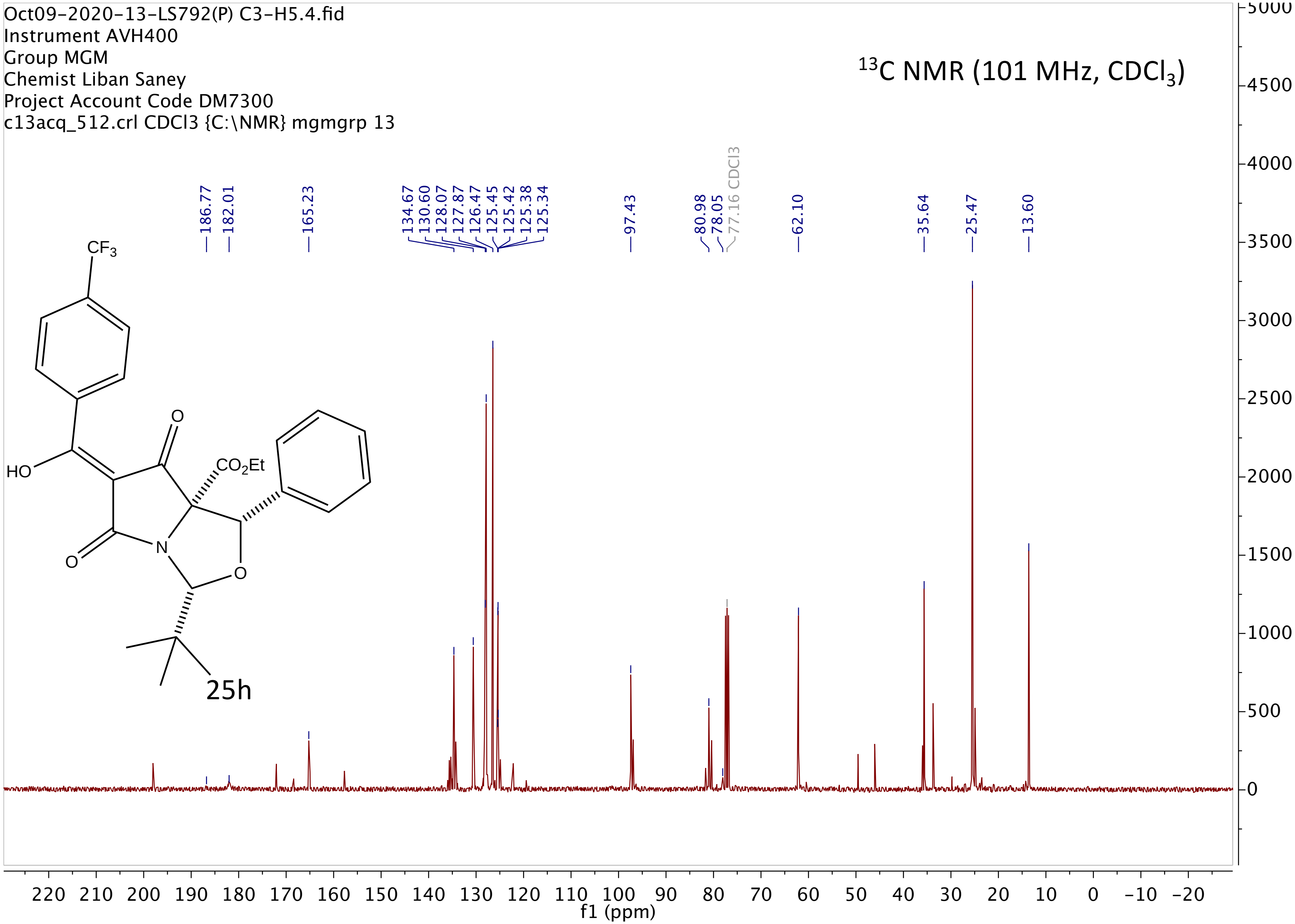
$^1H$ NMR (400 MHz, $CDCl_3$)

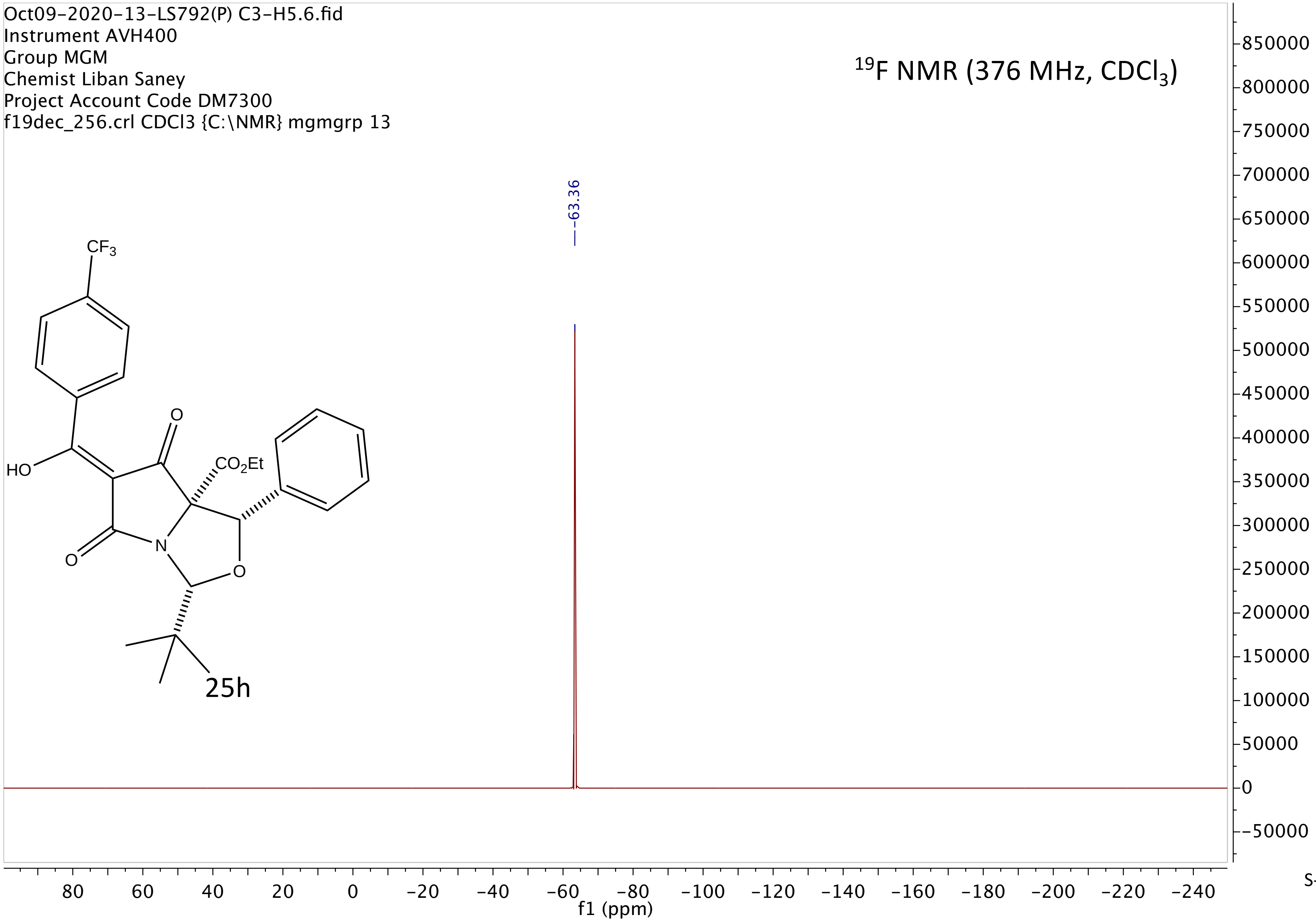


25h



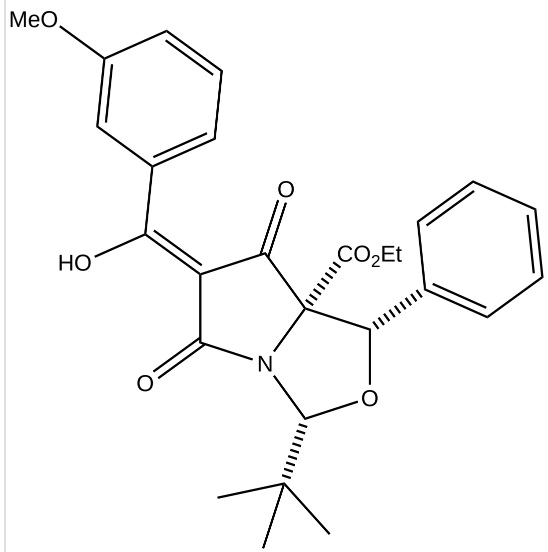
Oct09-2020-13-LS792(P) C3-H5.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 13



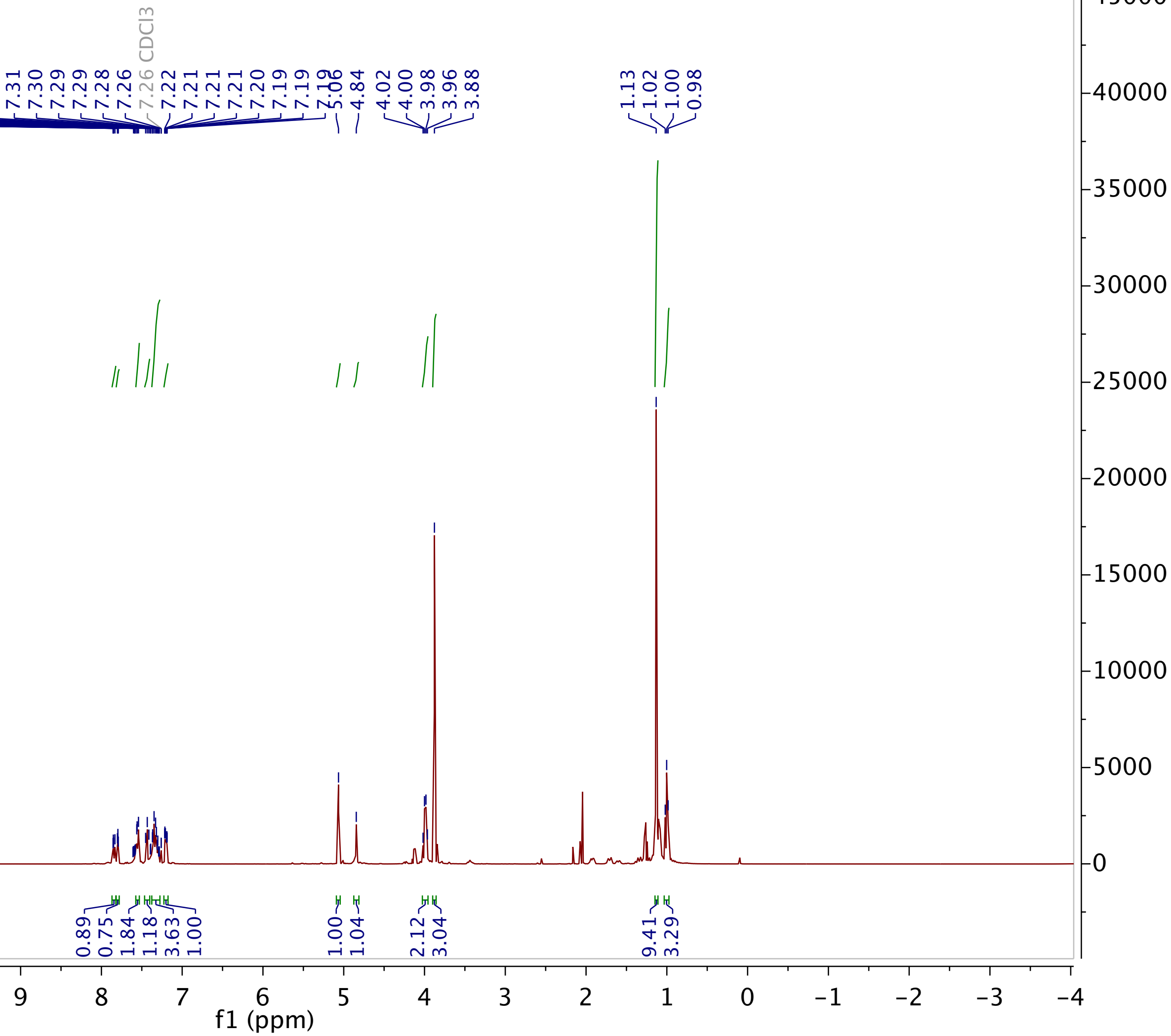

Oct09-2020-13-LS792(P) C3-H5.6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl CDCl3 {C:\NMR} mgmgrp 13
$^{19}$F NMR (376 MHz, $CDCl_3$)
–63.36
$CF_3$
HO
O
$CO_2Et$
N
O
O
25h
f1 (ppm)

Nov24-2020-14-LS838(P) C4-D5+G1-J1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 14

$^1H$ NMR (400 MHz, $CDCl_3$)

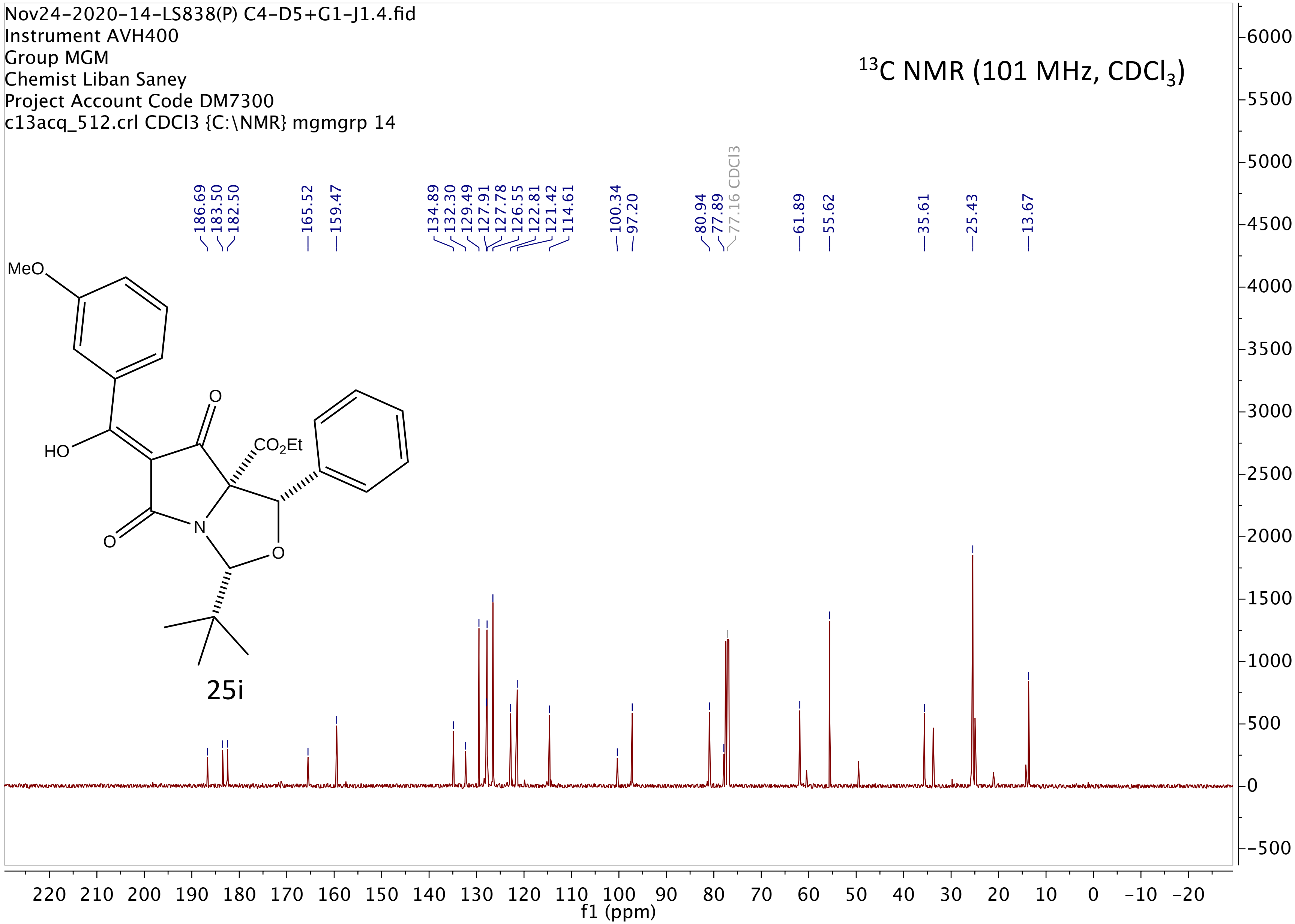



25i

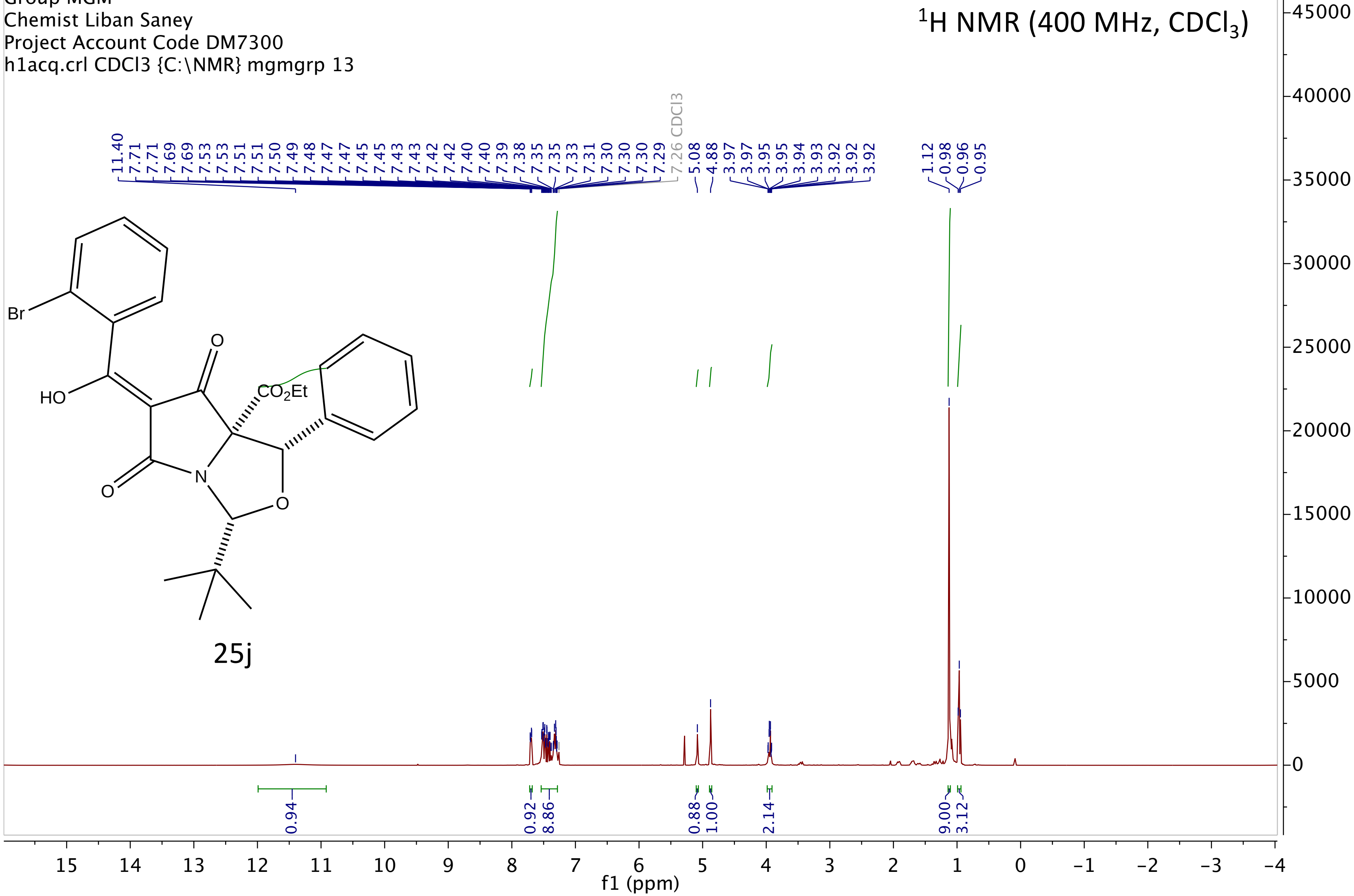


Nov24-2020-14-LS838(P) C4-D5+G1-J1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 14

$^{13}C$ NMR (101 MHz, $CDCl_3$)

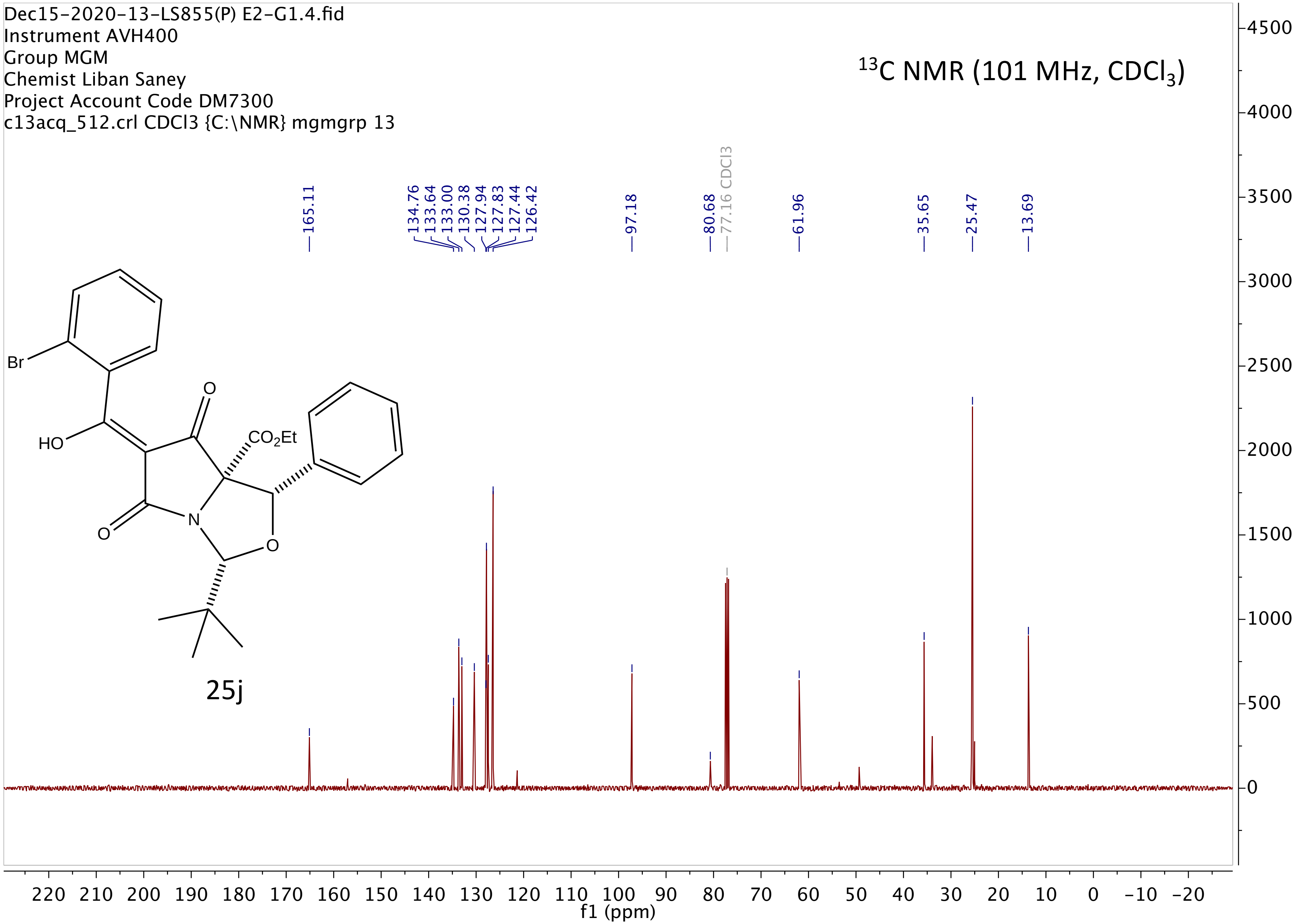


Dec15-2020-13-LS855(P) E2-G1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 13



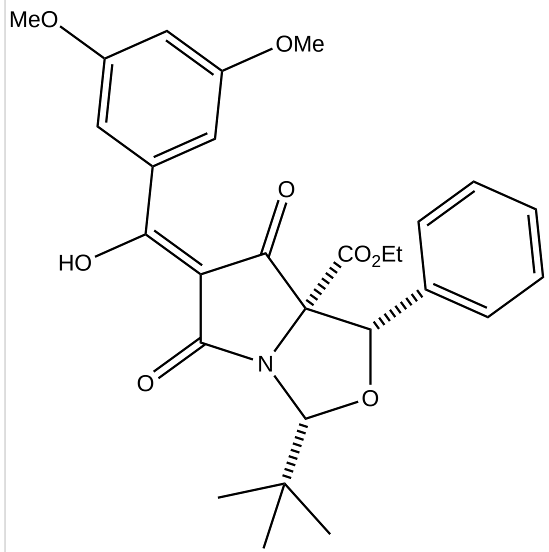

25j

Dec15-2020-13-LS855(P) E2-G1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 13

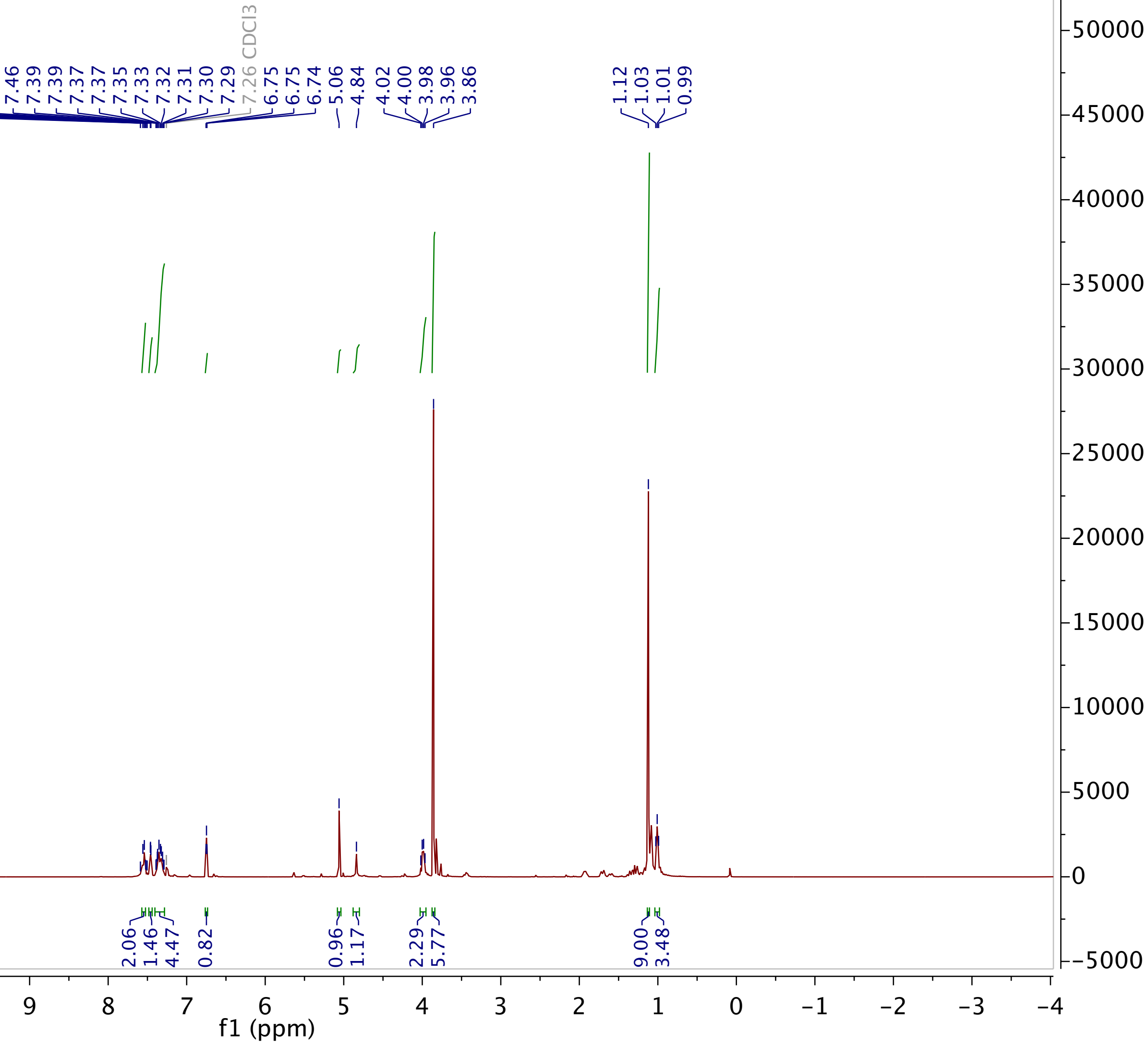


Nov26-2020-13-LS861(P) C3-G3.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 13

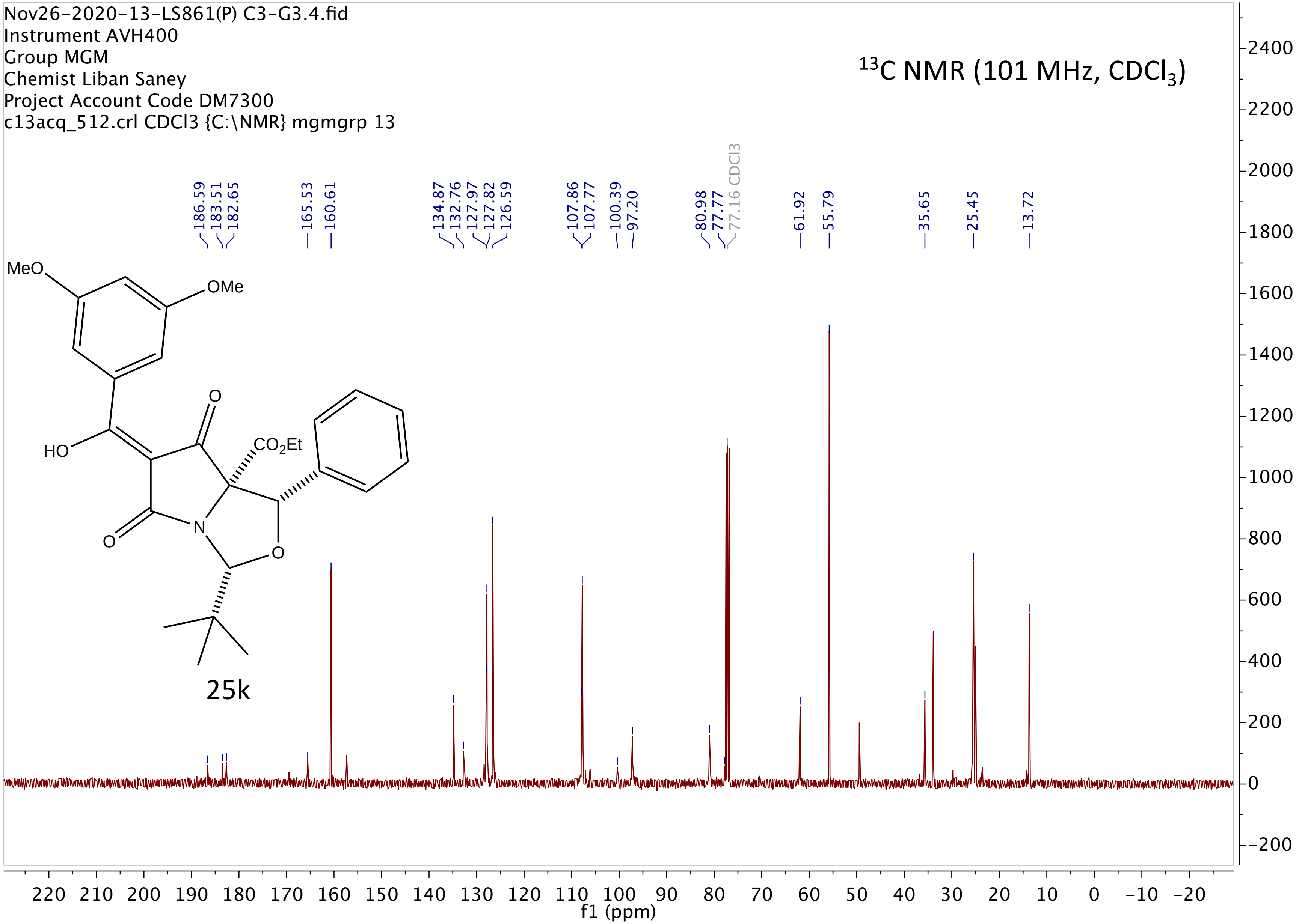
$^1$H NMR (400 MHz, $CDCl_3$)

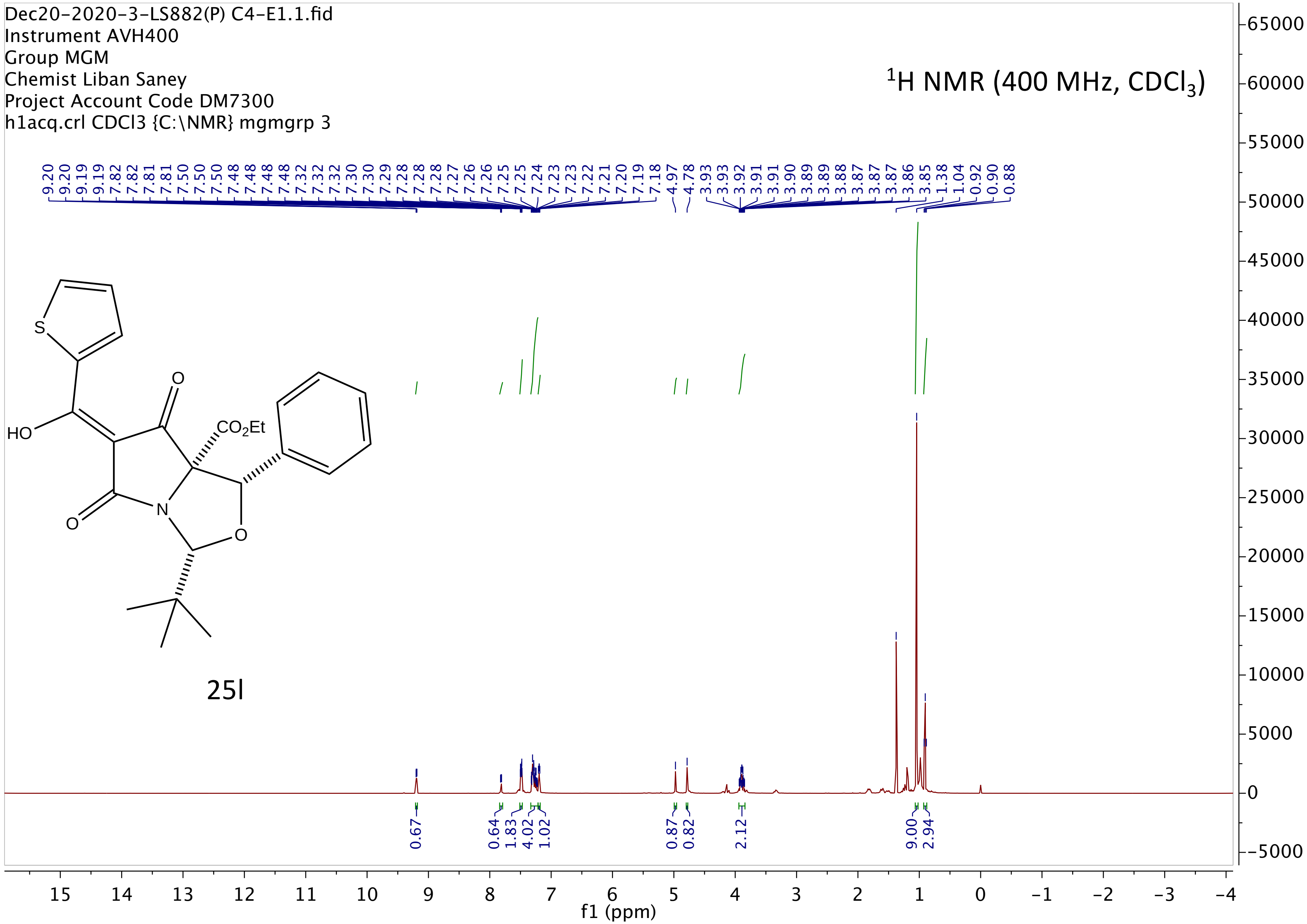


25k



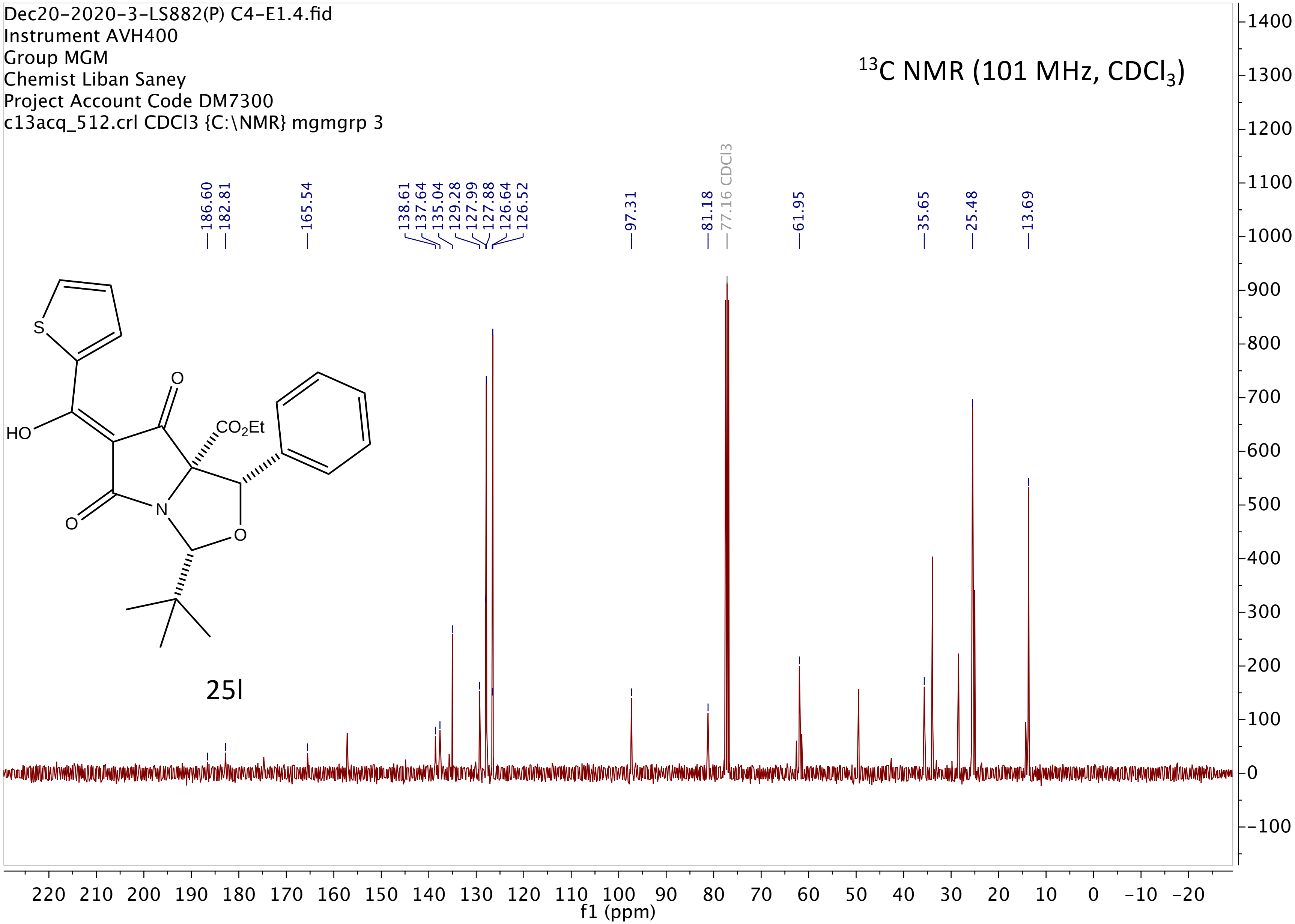
Nov26-2020-13-LS861(P) C3-G3.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 13





Dec20-2020-3-LS882(P) C4-E1.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 3
$^1$H NMR (400 MHz, CDCl$_3$)
9.20 9.20 9.19 9.19 7.82 7.82 7.81 7.50 7.50 7.50 7.48 7.48 7.48 7.32 7.32 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.20 7.19 7.18 4.97 4.78 3.93 3.93 3.92 3.91 3.91 3.90 3.89 3.89 3.88 3.87 3.87 3.87 3.86 3.85 1.38 1.04 0.92 0.90 0.88
S
O
HO
CO$_2$Et
N
O
O
25l
0.67 0.64 1.83 4.02 1.02 0.87 0.82 2.12 9.00 2.94
f1 (ppm)

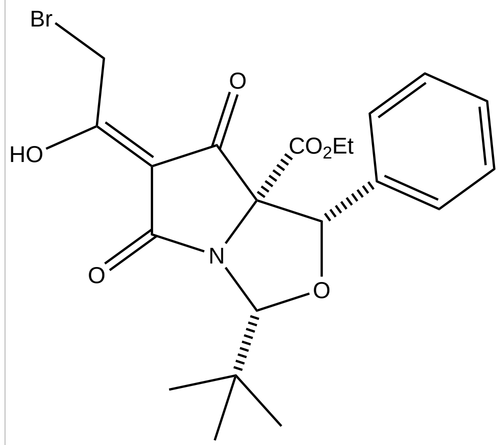
Dec20-2020-3-LS882(P) C4-E1.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 3



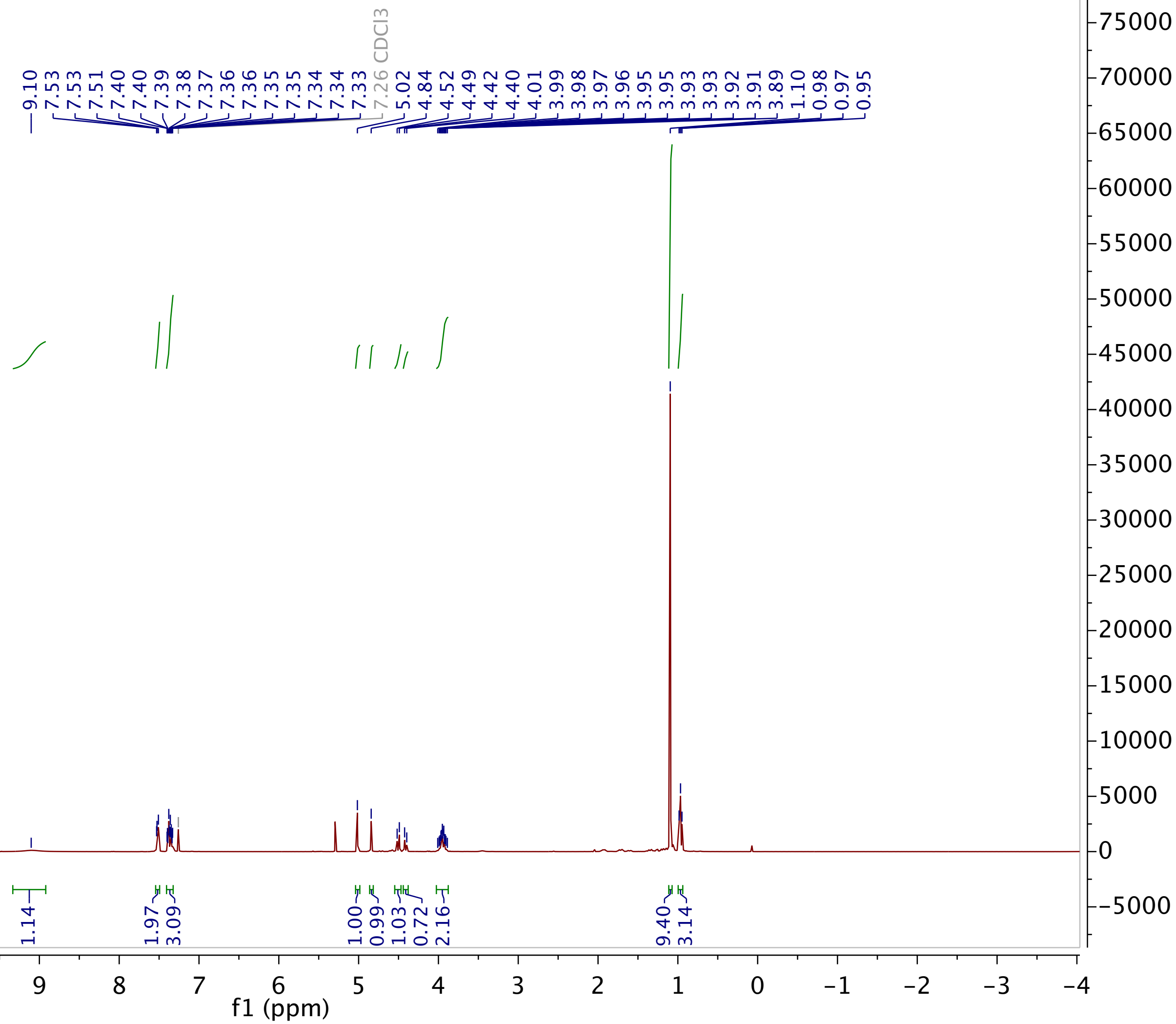

25l

Nov05-2020-51-LS831(P) C1-F8.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 51

$^1H$ NMR (400 MHz, $CDCl_3$)

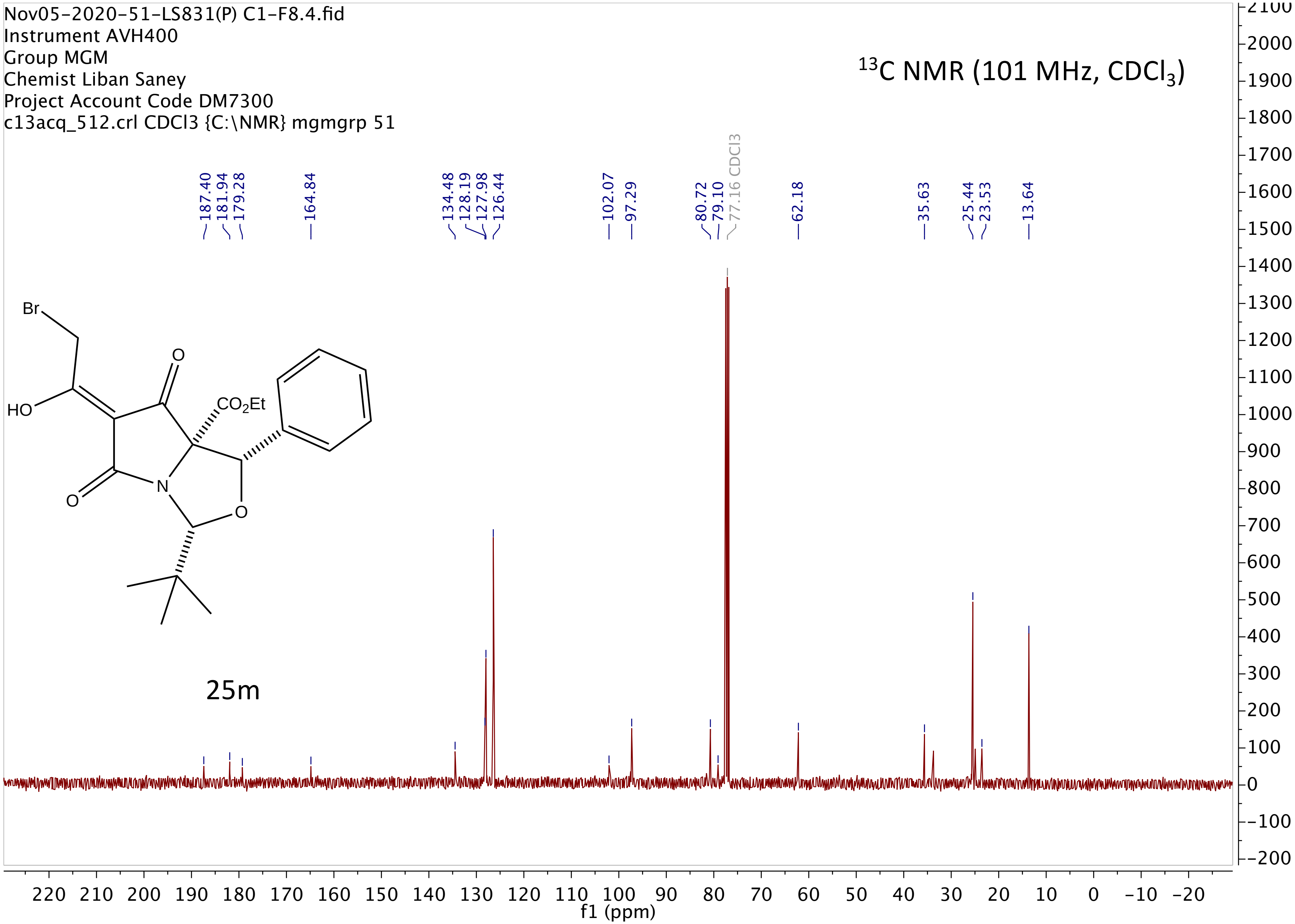



25m



Nov05-2020-51-LS831(P) C1-F8.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 51

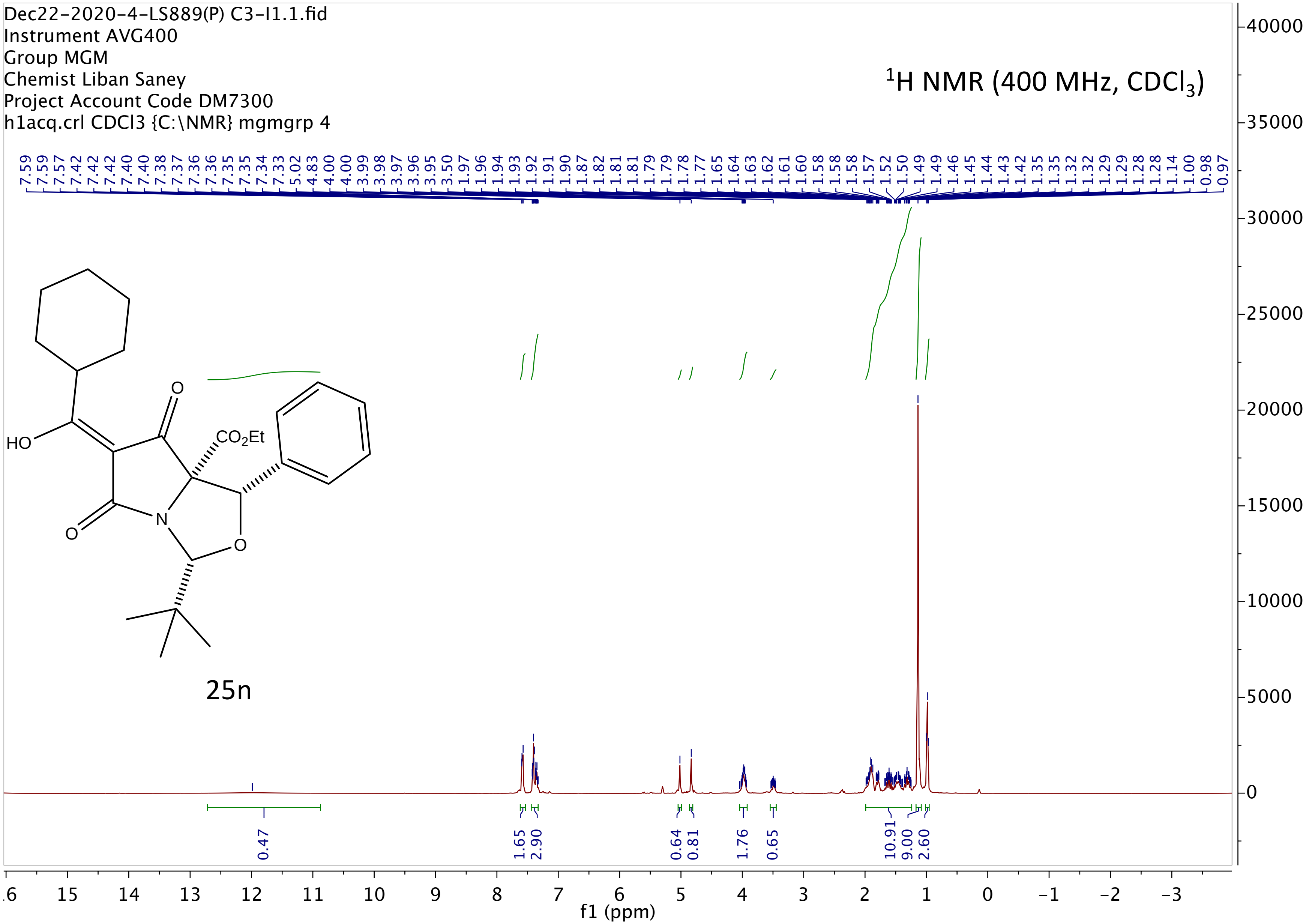
$^{13}$C NMR (101 MHz, $CDCl_3$)




25m

Dec22-2020-4-LS889(P) C3-I1.1.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 4

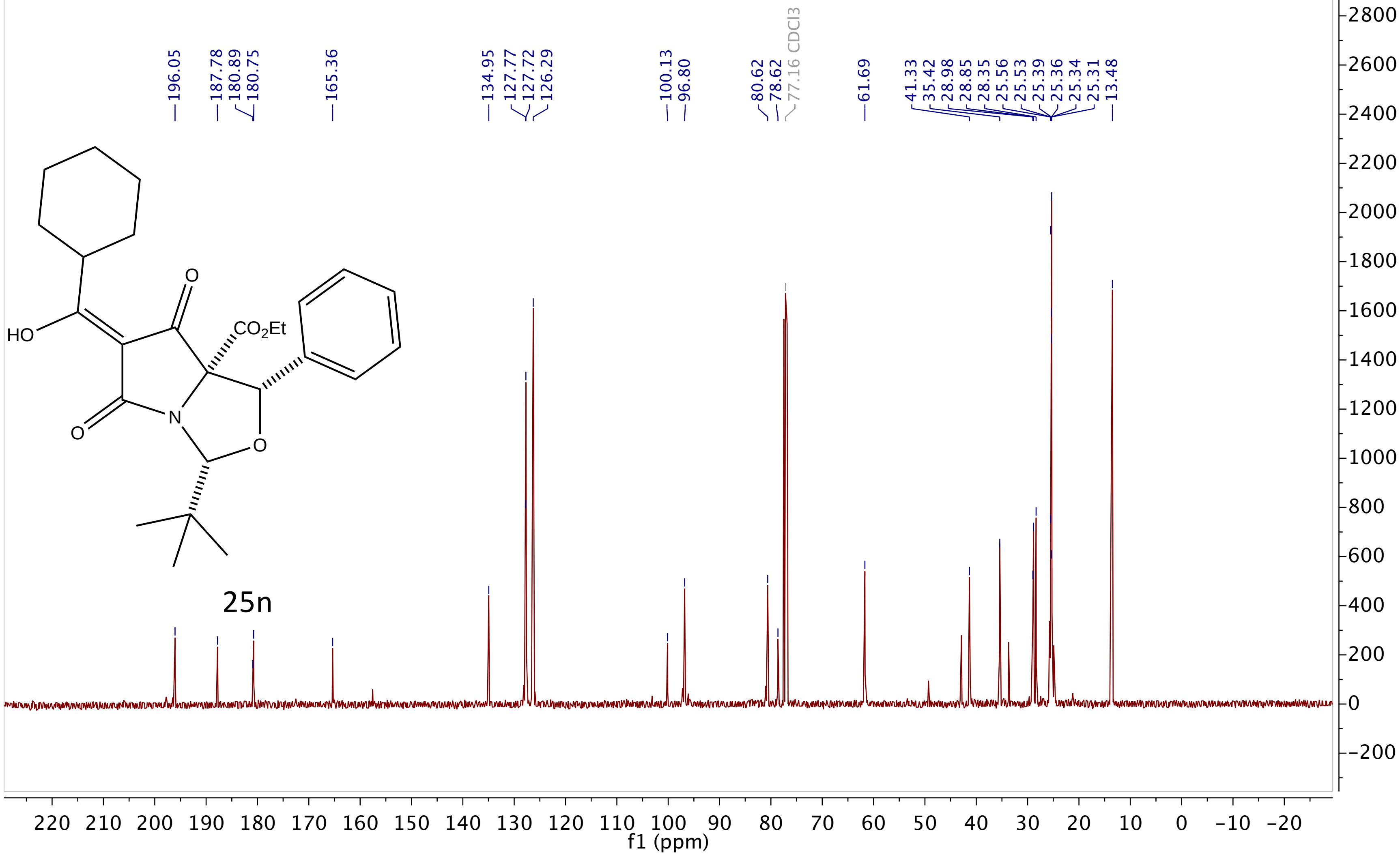
$^1$H NMR (400 MHz, $CDCl_3$)



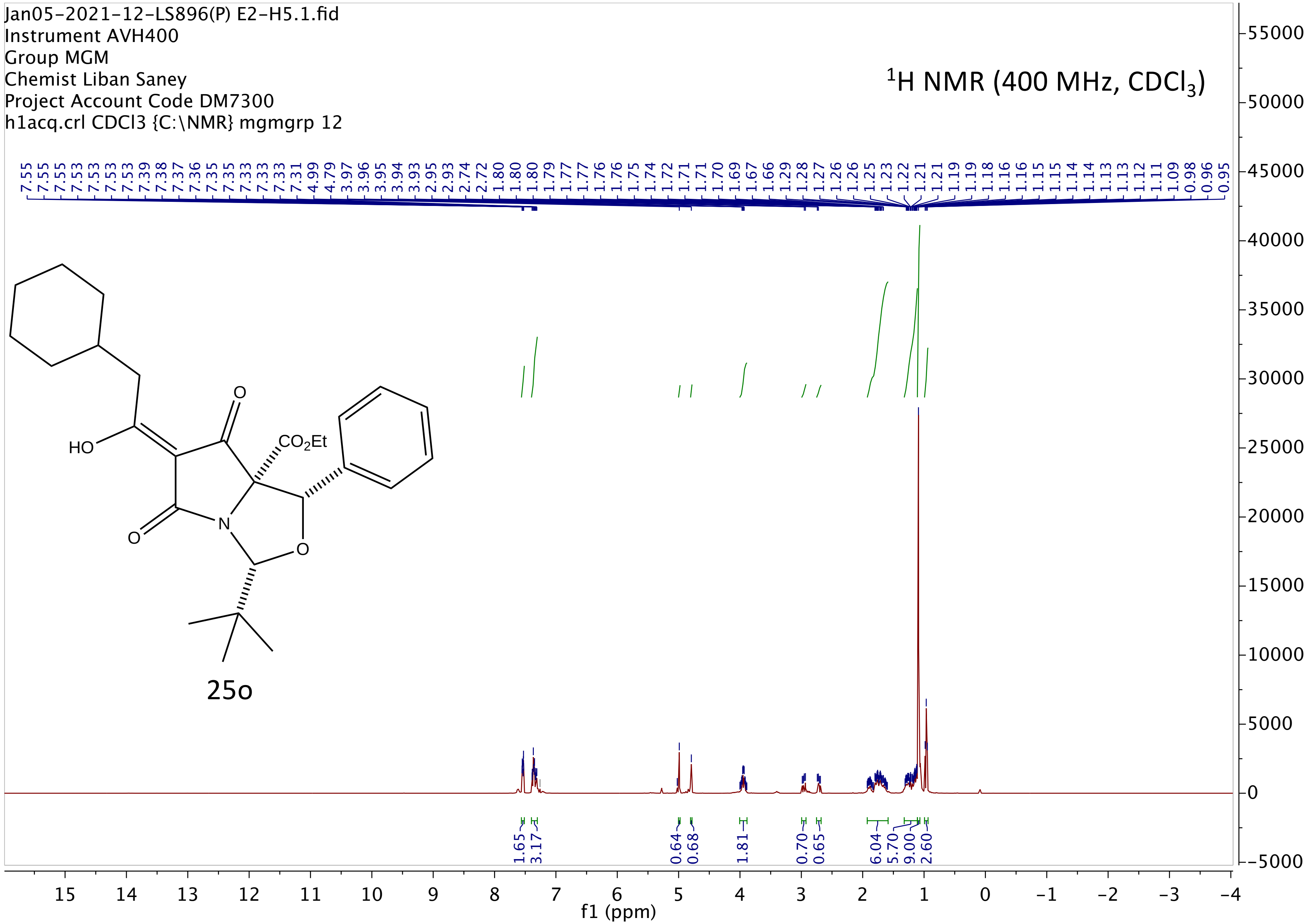
25n

Dec22-2020-4-LS889(P) C3-I1.5.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 4

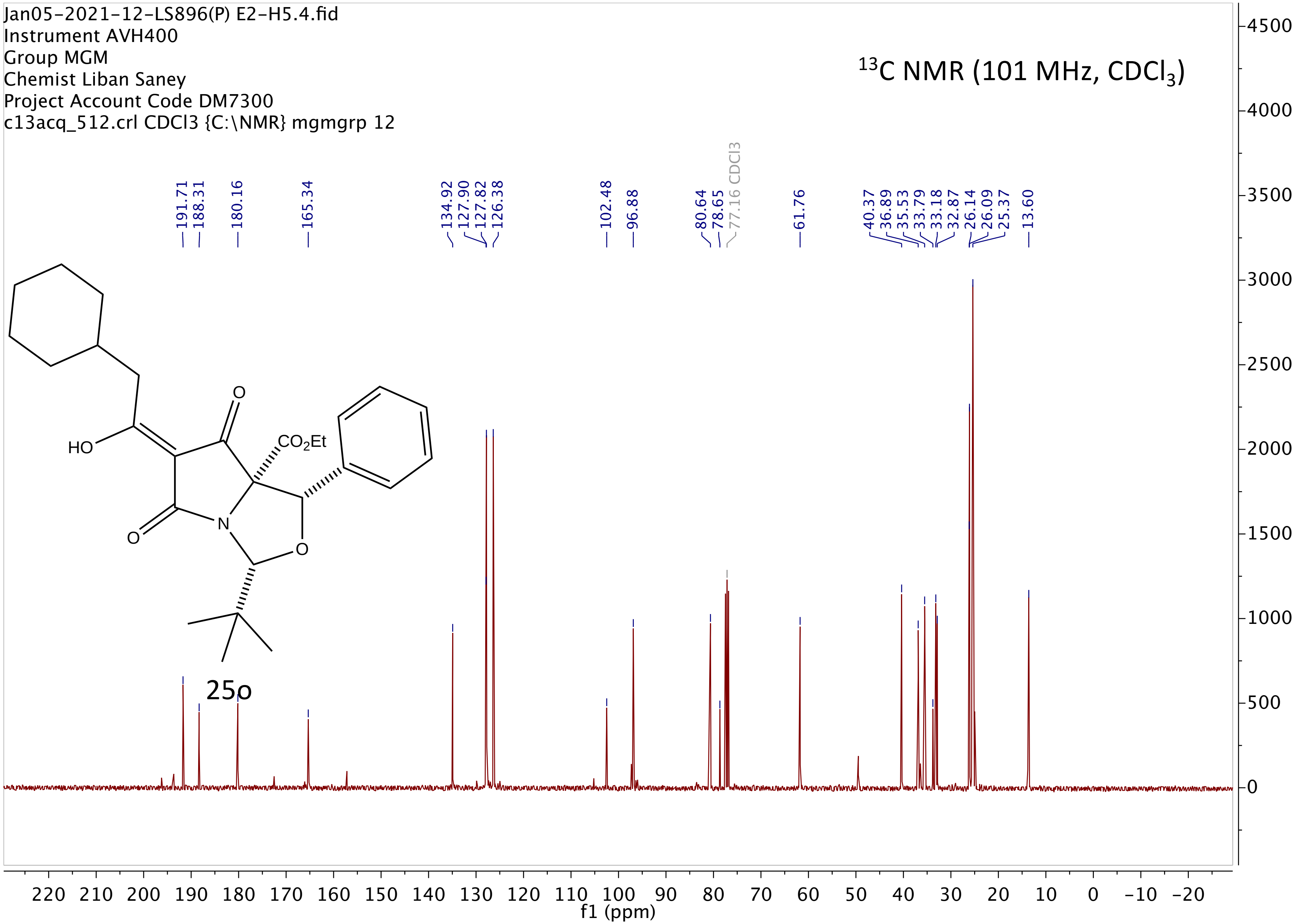
$^{13}$C NMR (101 MHz, $CDCl_3$)



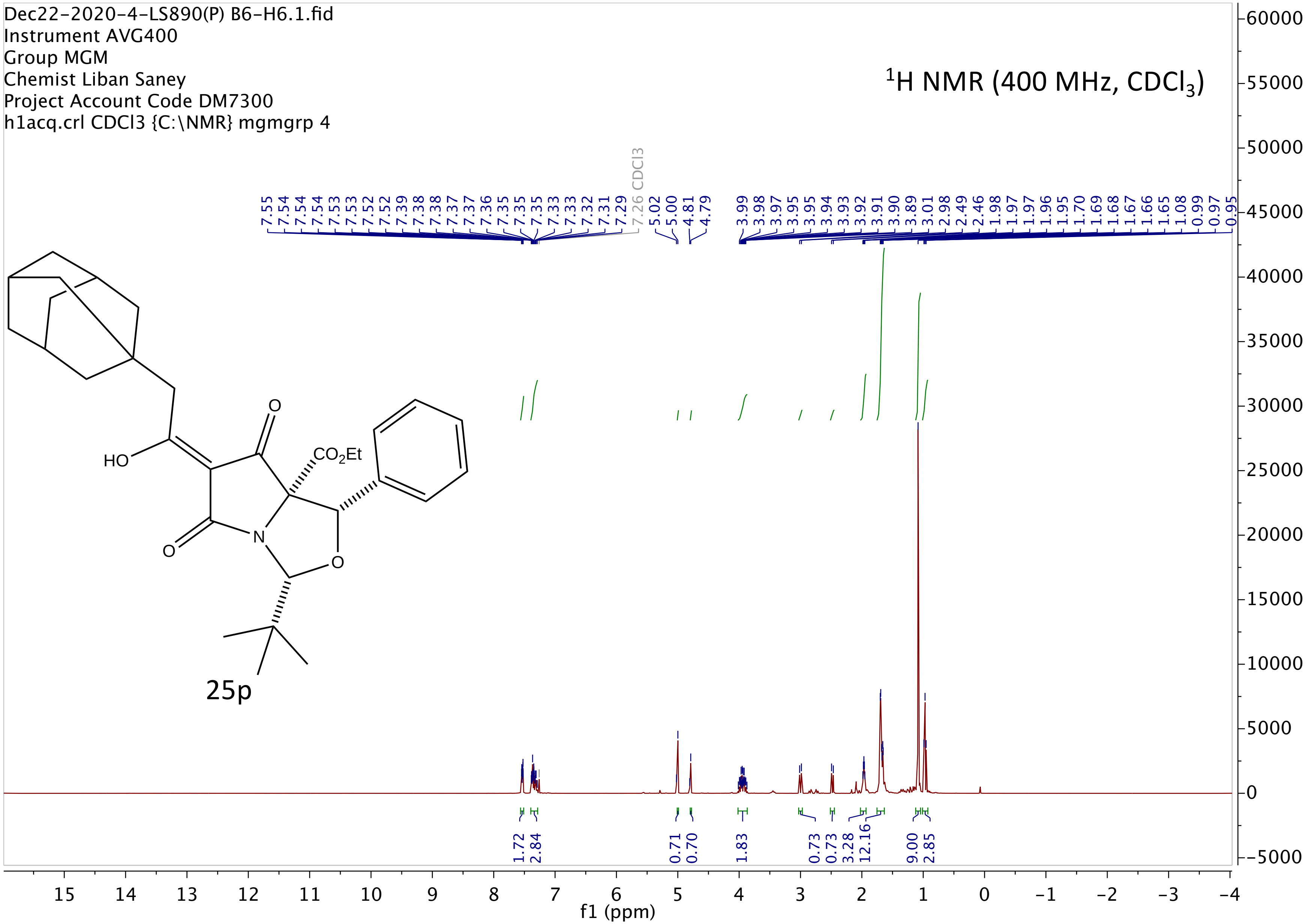

25n


Jan05-2021-12-LS896(P) E2-H5.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 12
1H NMR (400 MHz, CDCl3)
7.55 7.55 7.55 7.53 7.53 7.53 7.53 7.39 7.38 7.37 7.36 7.35 7.35 7.33 7.33 7.31 4.99 4.79 3.97 3.96 3.95 3.94 3.93 2.95 2.93 2.74 2.72 1.80 1.80 1.79 1.77 1.77 1.76 1.76 1.75 1.74 1.72 1.71 1.71 1.70 1.69 1.67 1.66 1.29 1.28 1.27 1.26 1.26 1.25 1.23 1.22 1.21 1.21 1.19 1.19 1.18 1.16 1.16 1.15 1.15 1.14 1.14 1.13 1.13 1.12 1.11 1.09 0.98 0.96 0.95
HO
O
O
CO2Et
N
O
25o
1.65
3.17
0.64
0.68
1.81
0.70
0.65
6.04
5.70
9.00
2.60
f1 (ppm)

Jan05-2021-12-LS896(P) E2-H5.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 12



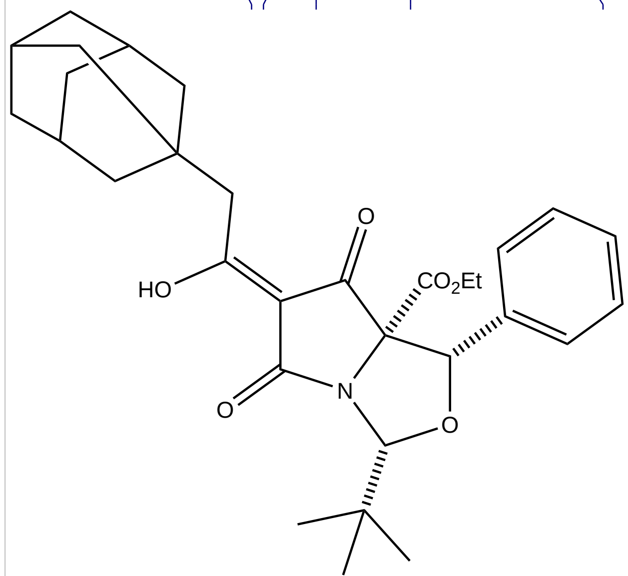

25o



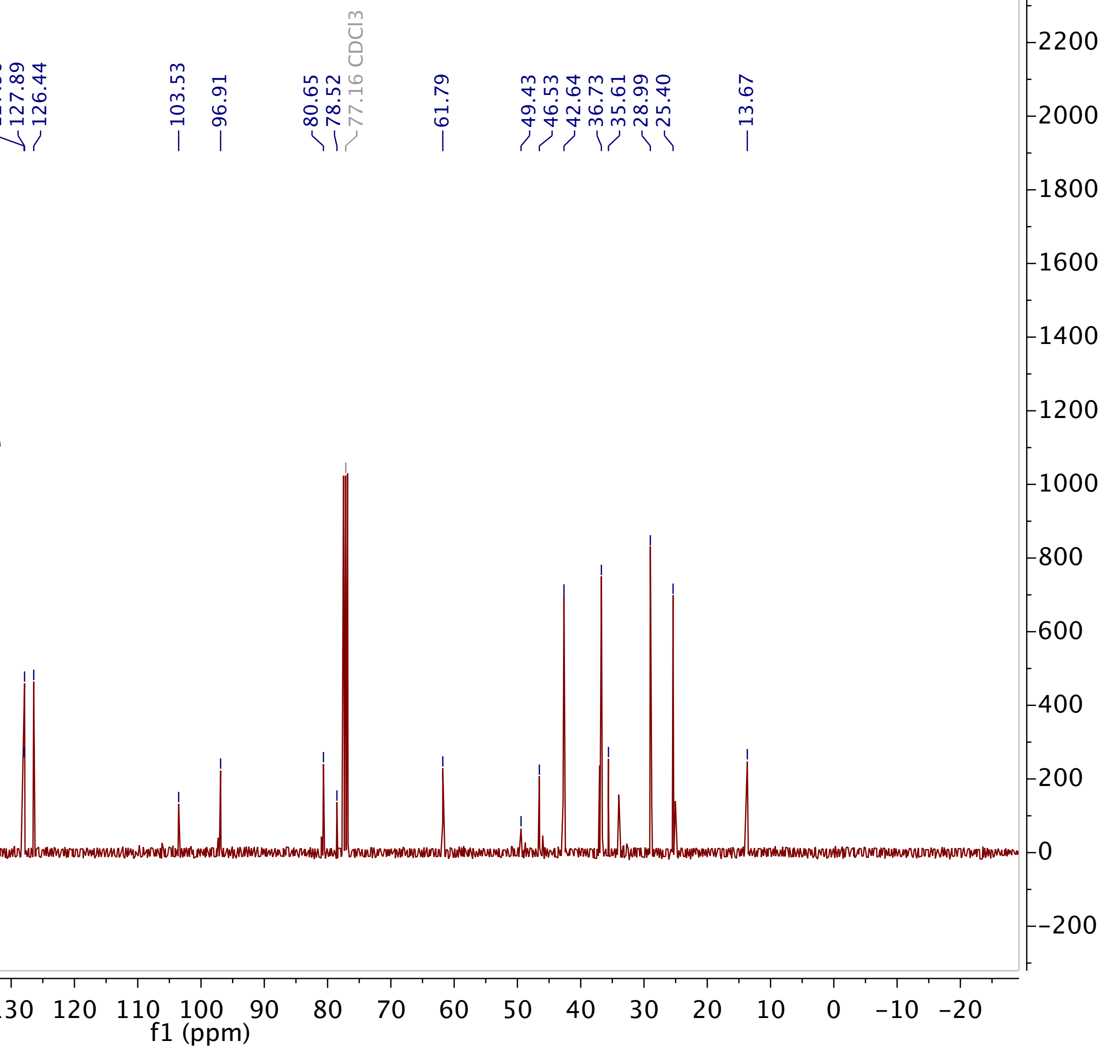
Dec22-2020-4-LS890(P) B6-H6.1.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 4
1H NMR (400 MHz, CDCl3)
7.55 7.54 7.54 7.54 7.53 7.53 7.52 7.52 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.35 7.33 7.33 7.32 7.31 7.29
7.26 CDCl3
5.02 5.00 4.81 4.79
3.99 3.98 3.97 3.95 3.95 3.94 3.93 3.92 3.91 3.90 3.89 3.01 2.98 2.49 2.46 1.98 1.97 1.96 1.95 1.70 1.69 1.68 1.67 1.66 1.65 1.08 0.99 0.97 0.95
HO
O
CO2Et
N
O
O
25p
1.72 2.84 0.71 0.70 1.83 0.73 0.73 3.28 12.16 9.00 2.85
60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 −5000
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)

Dec22-2020-4-LS890(P) B6-H6.4.fid
Instrument AVG400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 4

$^{13}$C NMR (101 MHz, $CDCl_3$)

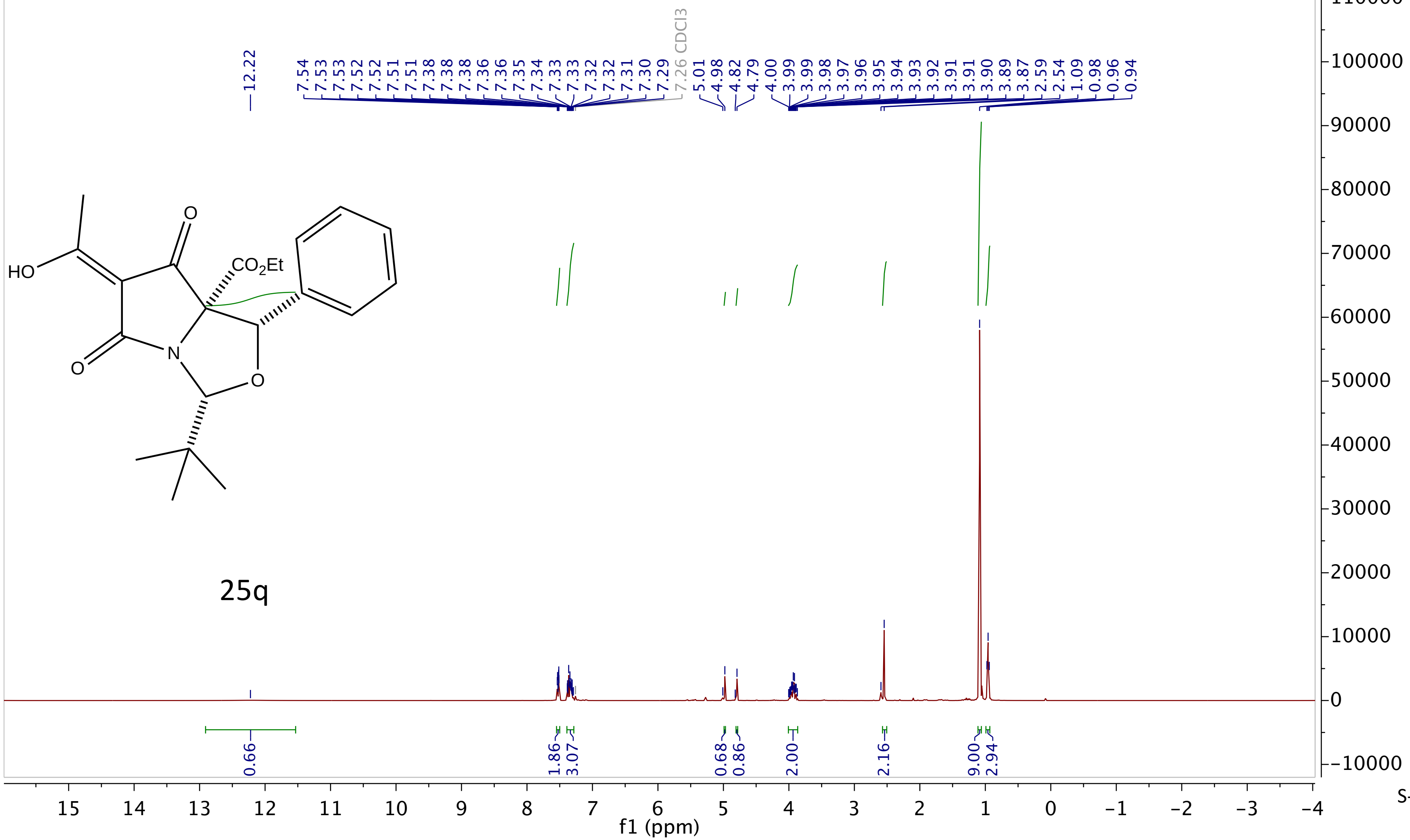



25p

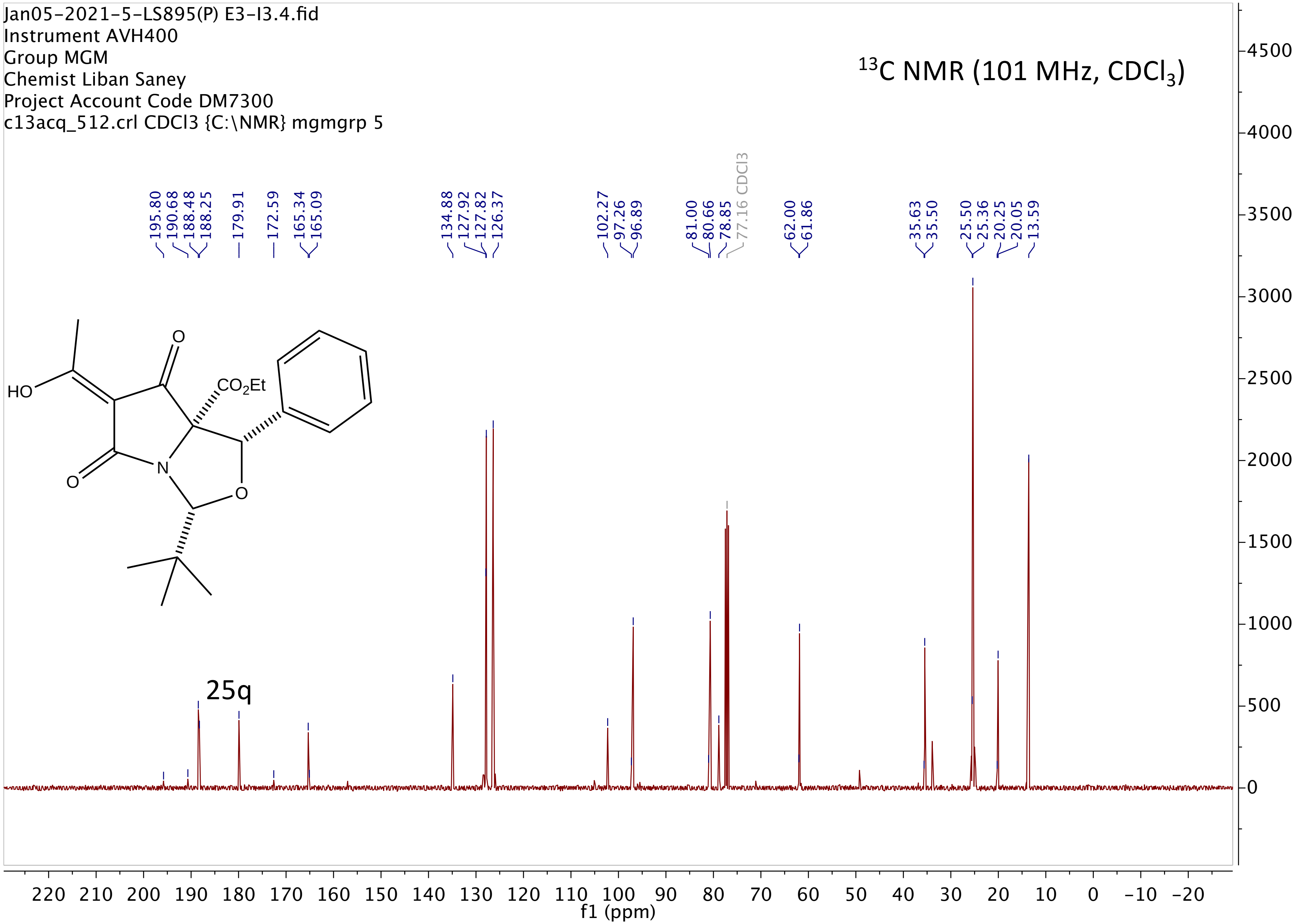


Jan05-2021-5-LS895(P) E3-I3.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 5

$^1$H NMR (400 MHz, $CDCl_3$)

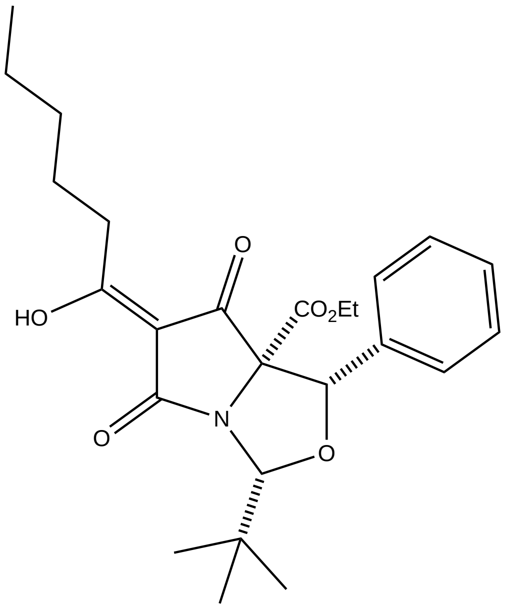


Jan05-2021-5-LS895(P) E3-I3.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 5

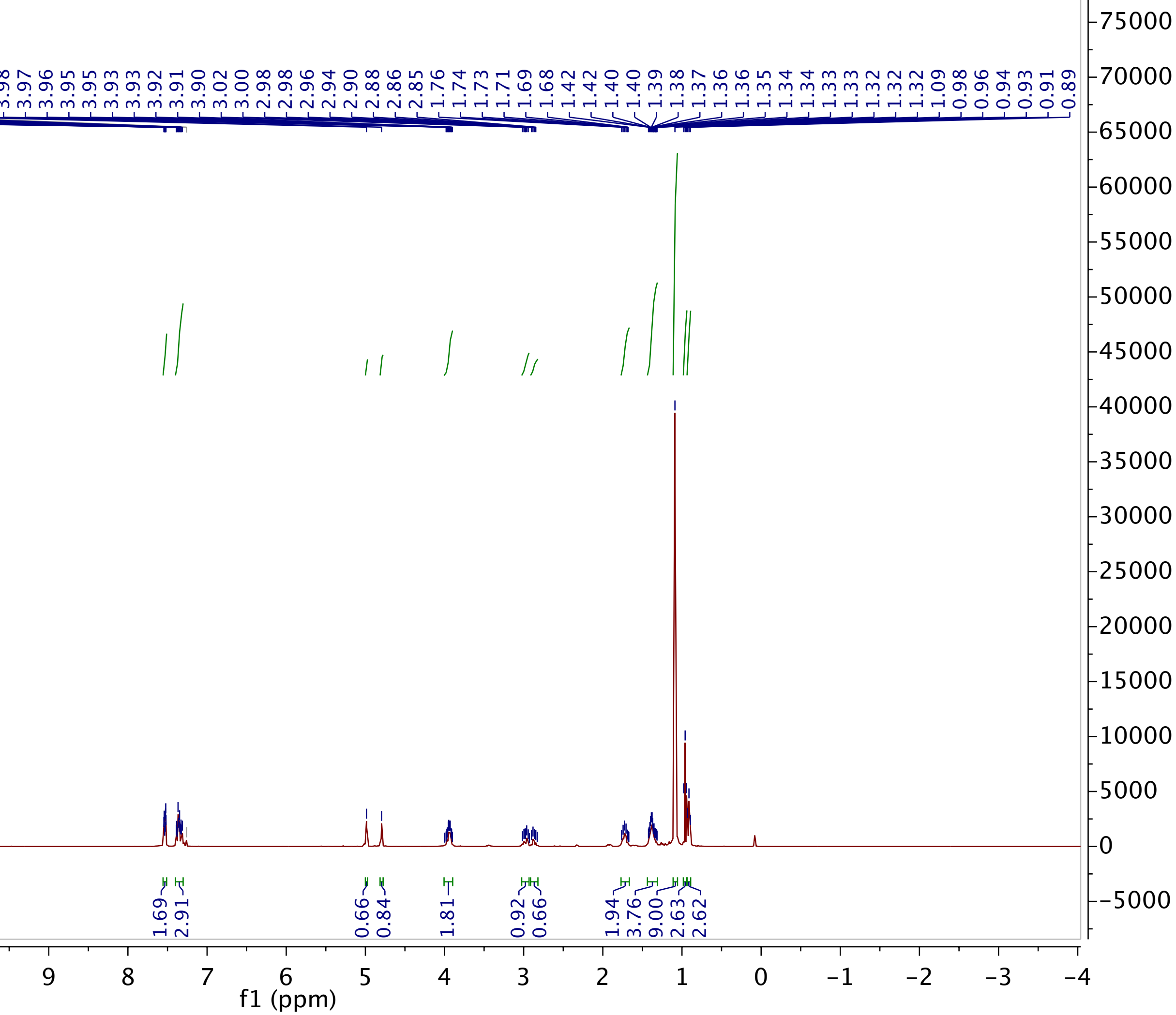


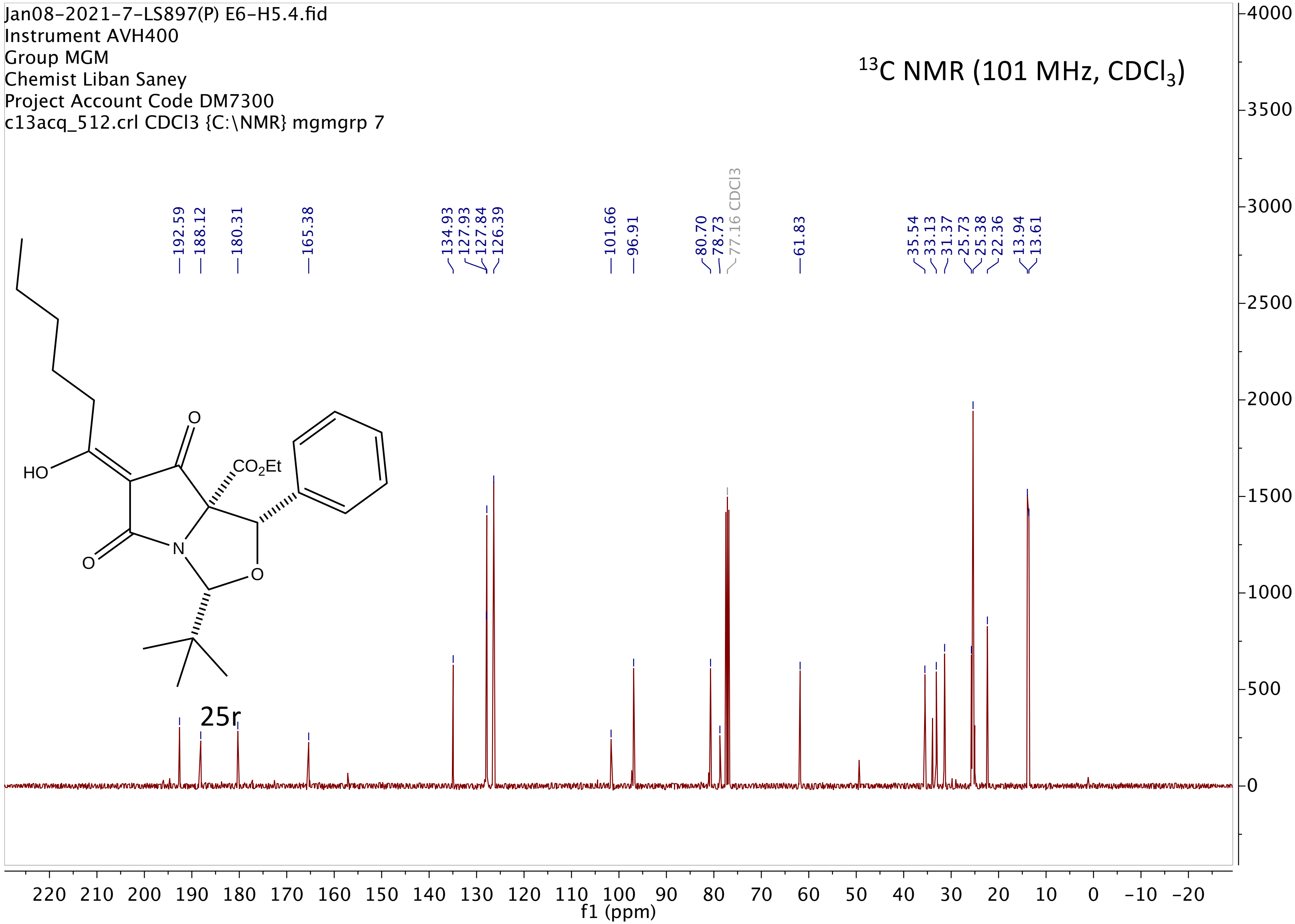
Jan08-2021-7-LS897(P) E6-H5.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 7

$^1$H NMR (400 MHz, $CDCl_3$)



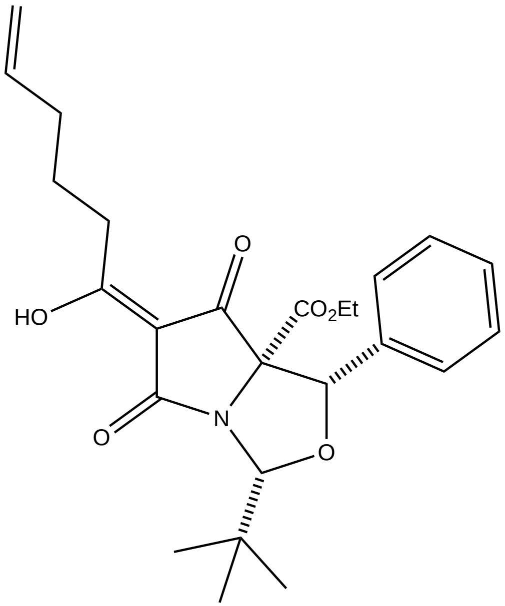
25r



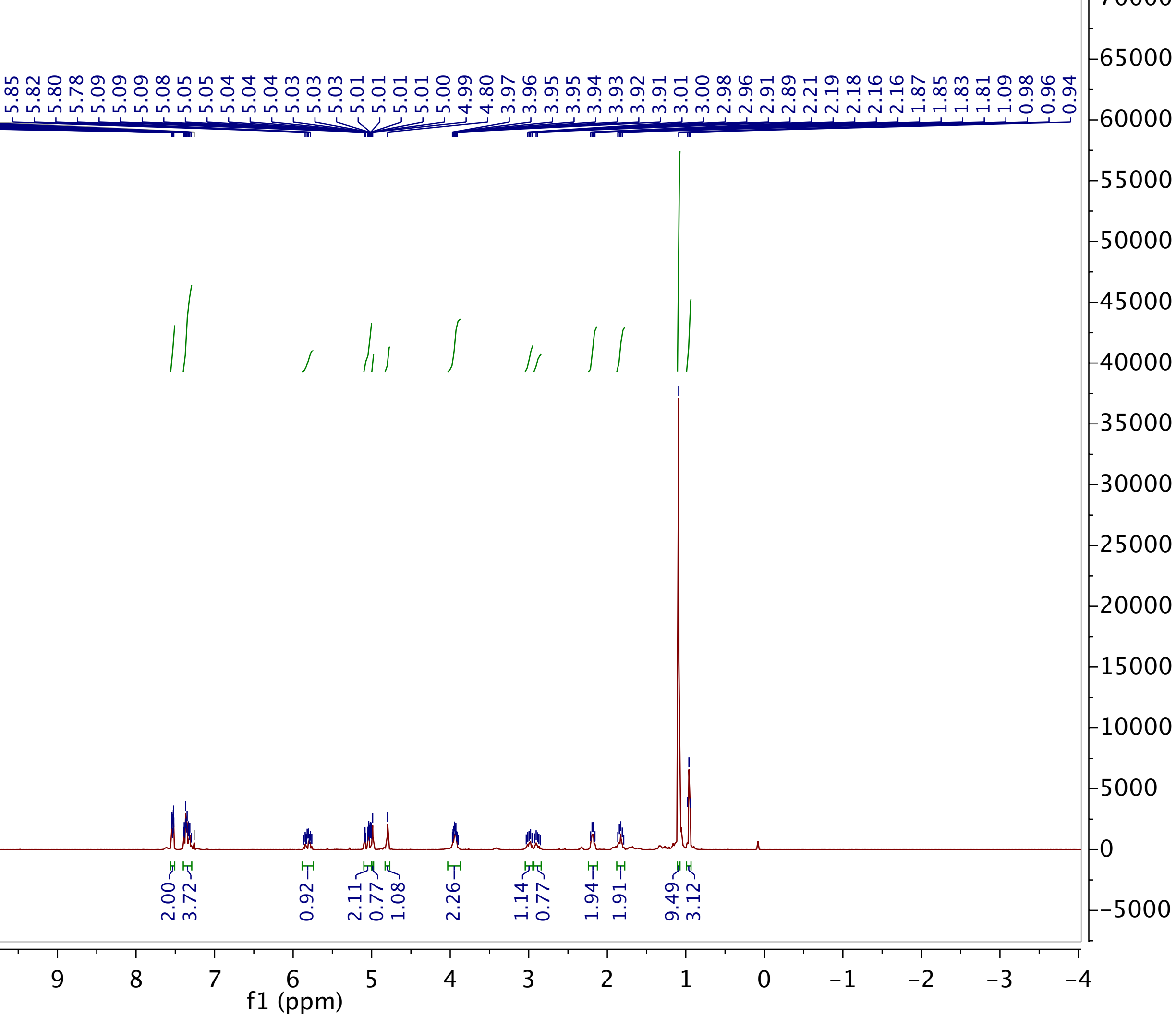

Jan08-2021-7-LS897(P) E6-H5.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 7
13C NMR (101 MHz, CDCl3)
192.59
188.12
180.31
165.38
134.93
127.93
127.84
126.39
101.66
96.91
80.70
78.73
77.16 CDCl3
61.83
35.54
33.13
31.37
25.73
25.38
22.36
13.94
13.61
HO
O
CO2Et
N
O
O
25r
f1 (ppm)

Jan09-2021-5-LS898(P) E1-G5.1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 5

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

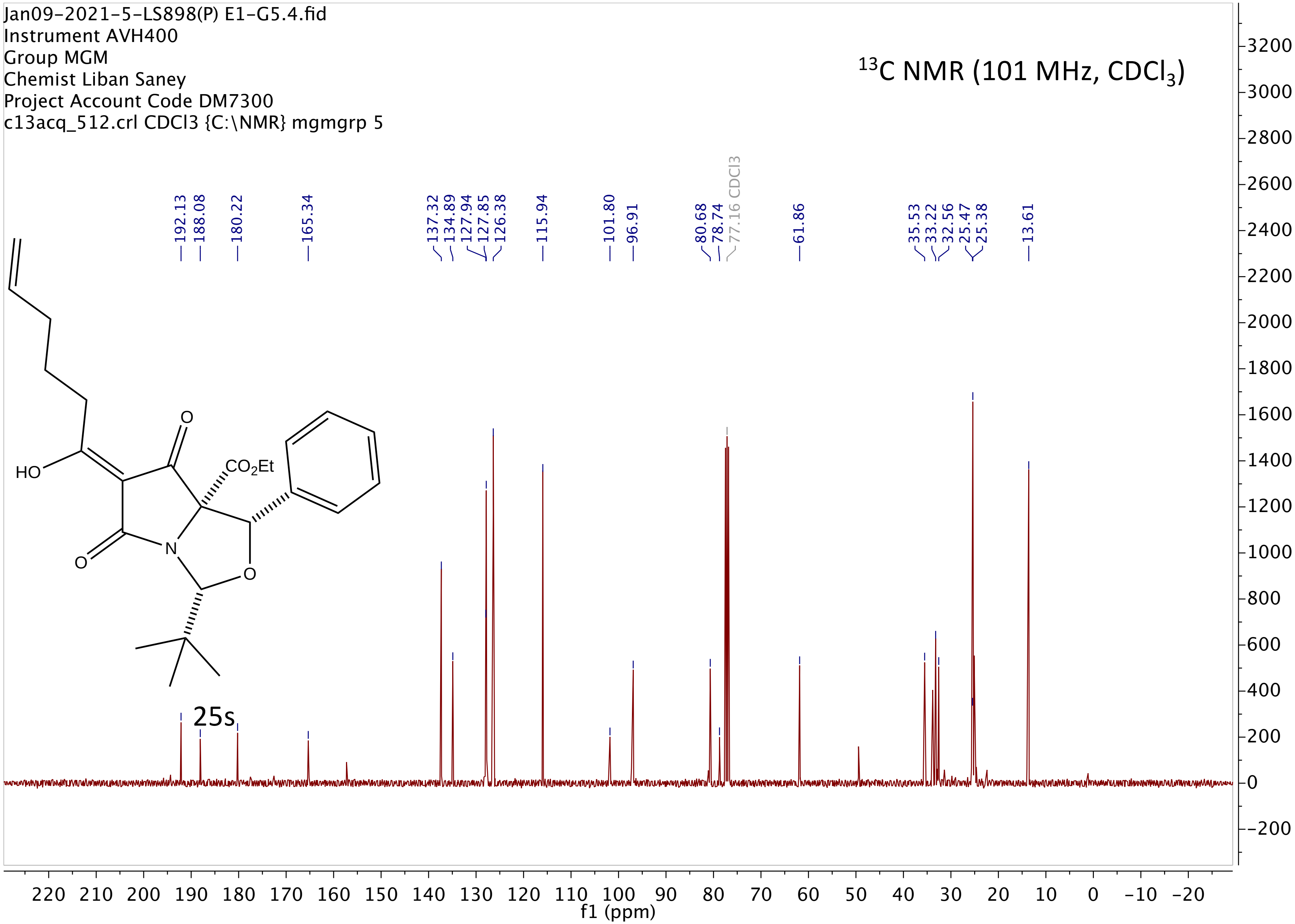


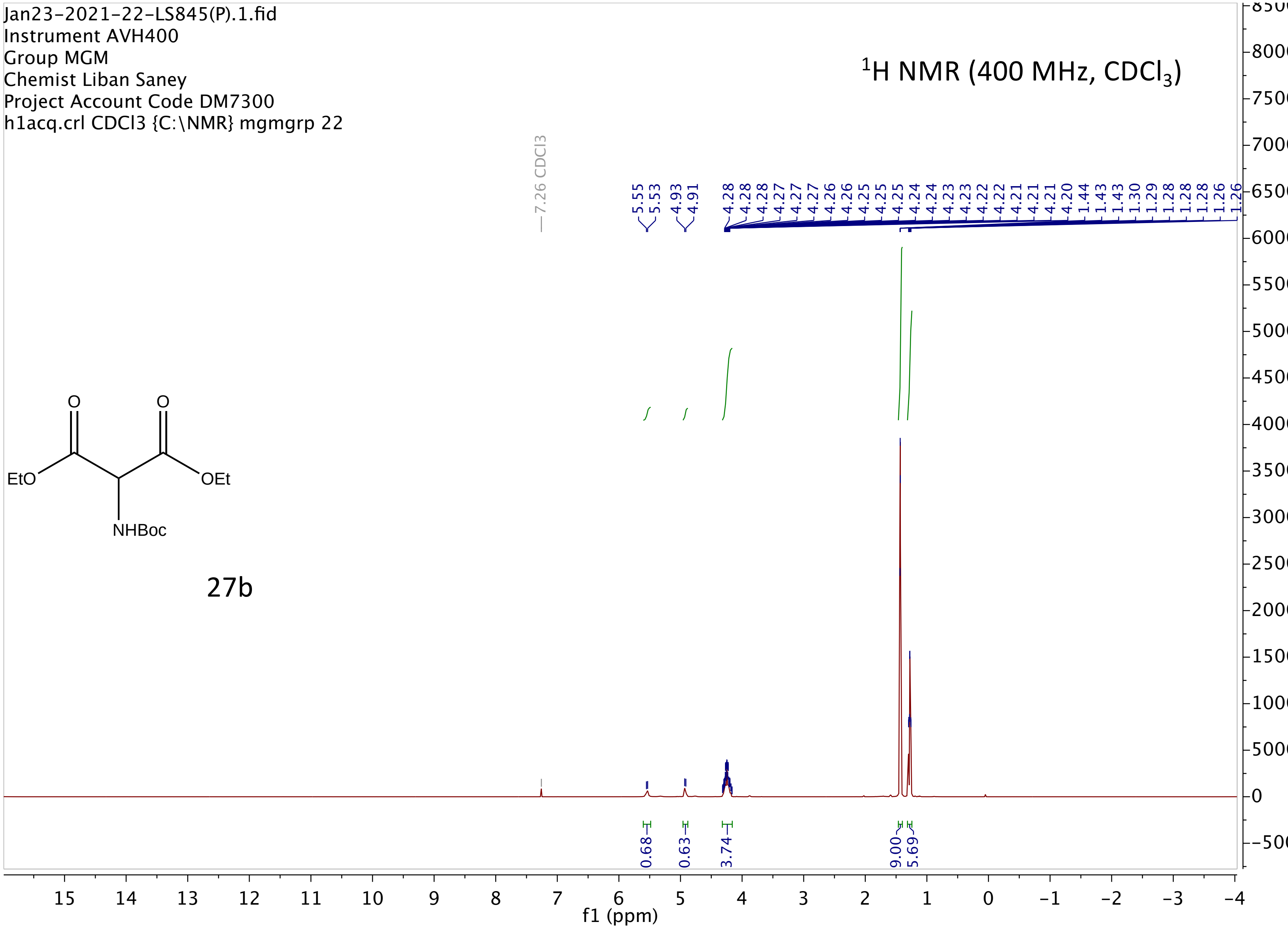

25s



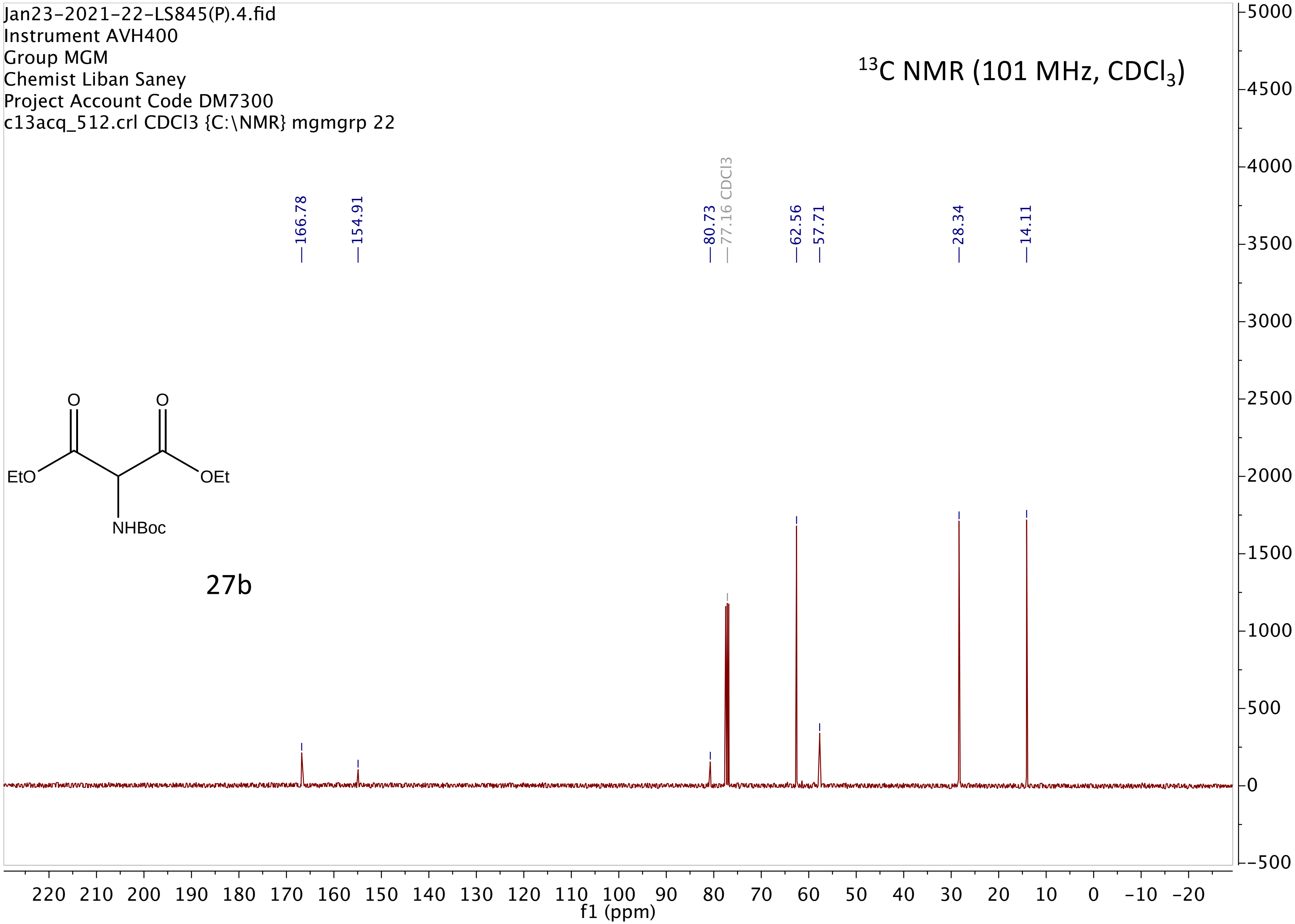
S-337

Jan09-2021-5-LS898(P) E1-G5.4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 5



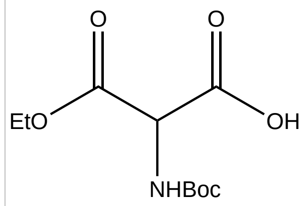

Jan23-2021-22-LS845(P).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 22
$^1$H NMR (400 MHz, $CDCl_3$)
7.26 CDCl3
5.55
5.53
4.93
4.91
4.28
4.28
4.28
4.27
4.27
4.27
4.26
4.26
4.25
4.25
4.25
4.24
4.24
4.23
4.23
4.22
4.22
4.21
4.21
4.21
4.20
1.44
1.43
1.43
1.30
1.29
1.28
1.28
1.28
1.26
1.26
0.68
0.63
3.74
9.00
5.69
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)
O
O
EtO
OEt
NHBoc

27b

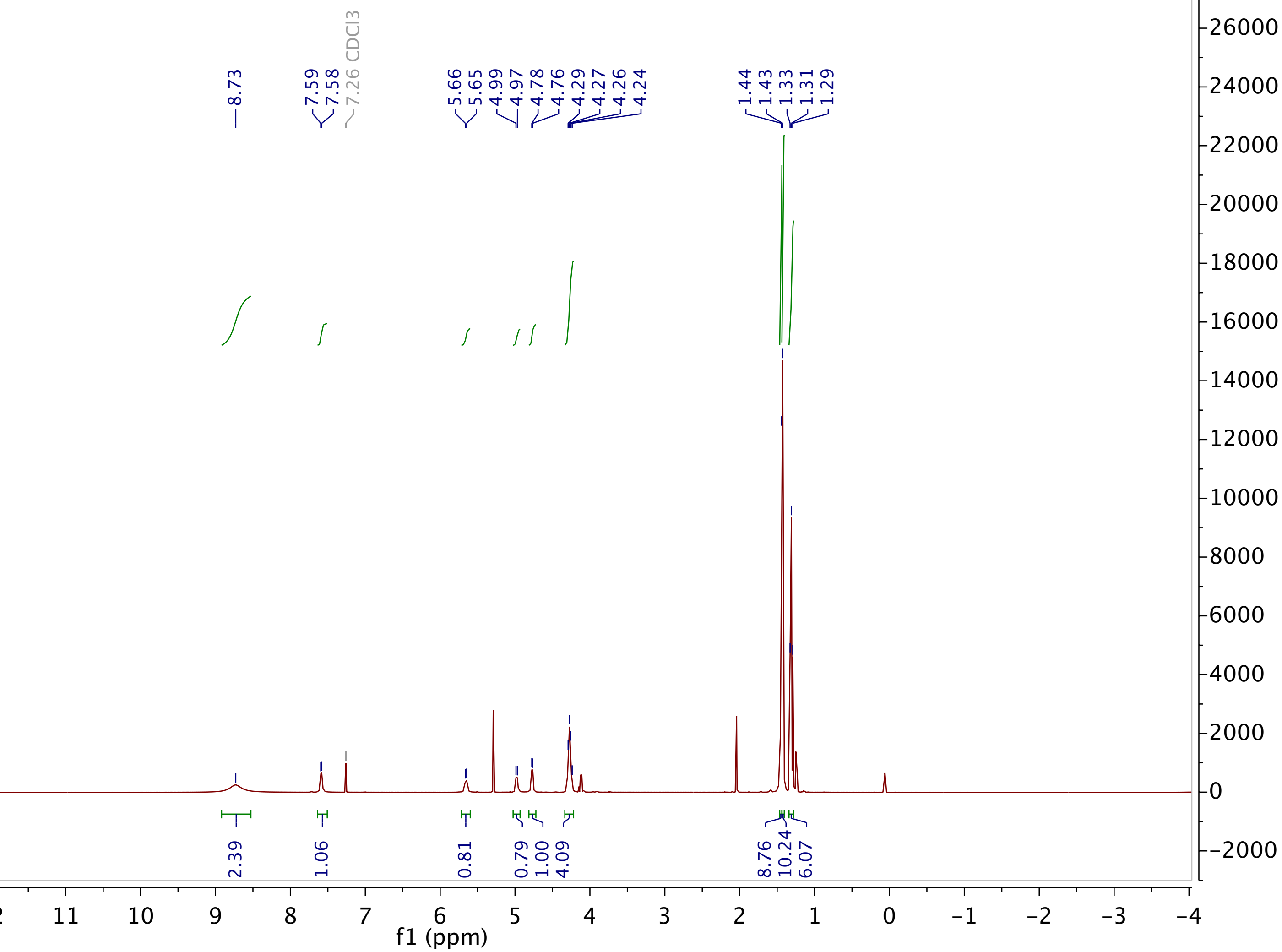

Jan23-2021-22-LS845(P).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 22
13C NMR (101 MHz, CDCl3)
166.78
154.91
80.73
77.16 CDCl3
62.56
57.71
28.34
14.11
EtO
OEt
O
O
NHBoc
27b
f1 (ppm)

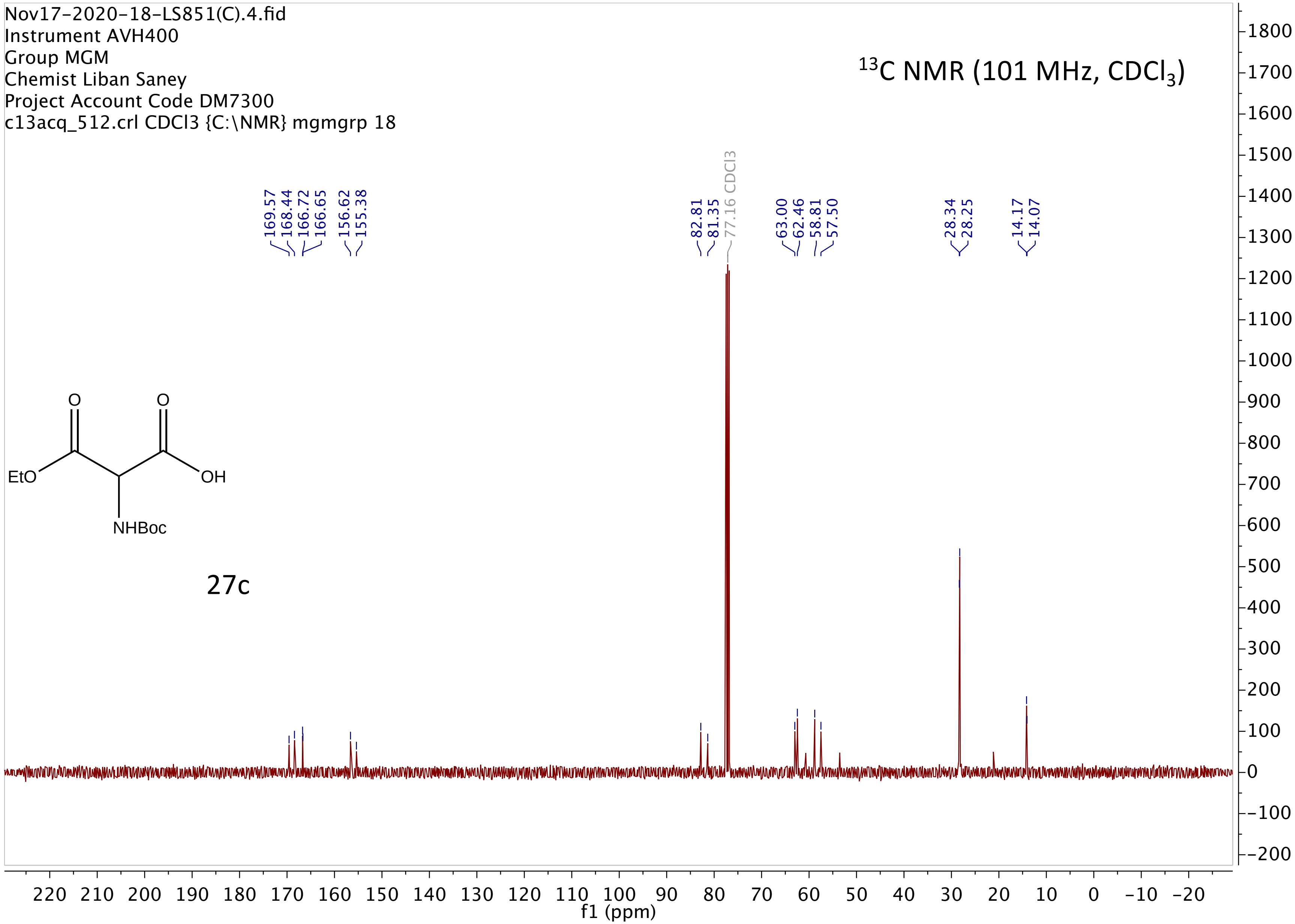
Nov17-2020-18-LS851(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl CDCl3 {C:\NMR} mgmgrp 18

$^1$H NMR (400 MHz, $CDCl_3$)



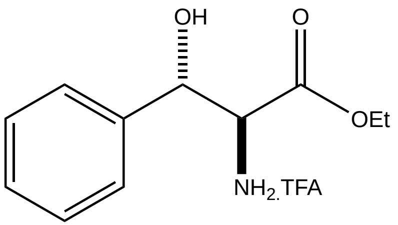
27c



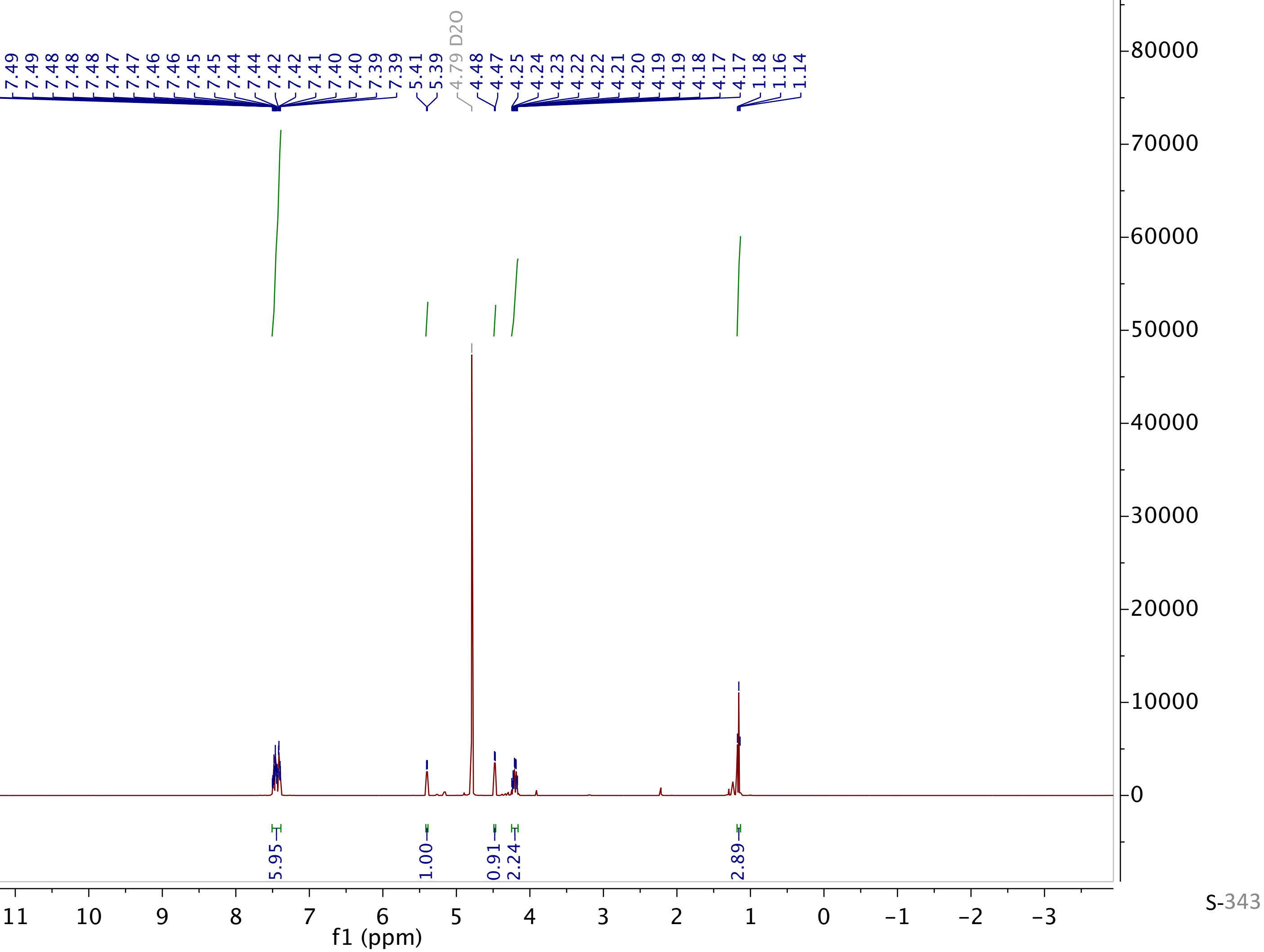

Nov17-2020-18-LS851(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl CDCl3 {C:\NMR} mgmgrp 18
$^{13}$C NMR (101 MHz, CDCl$_3$)
169.57
168.44
166.72
166.65
156.62
155.38
82.81
81.35
77.16 CDCl3
63.00
62.46
58.81
57.50
28.34
28.25
14.17
14.07
EtO
OH
O
O
NHBoc
27c
f1 (ppm)

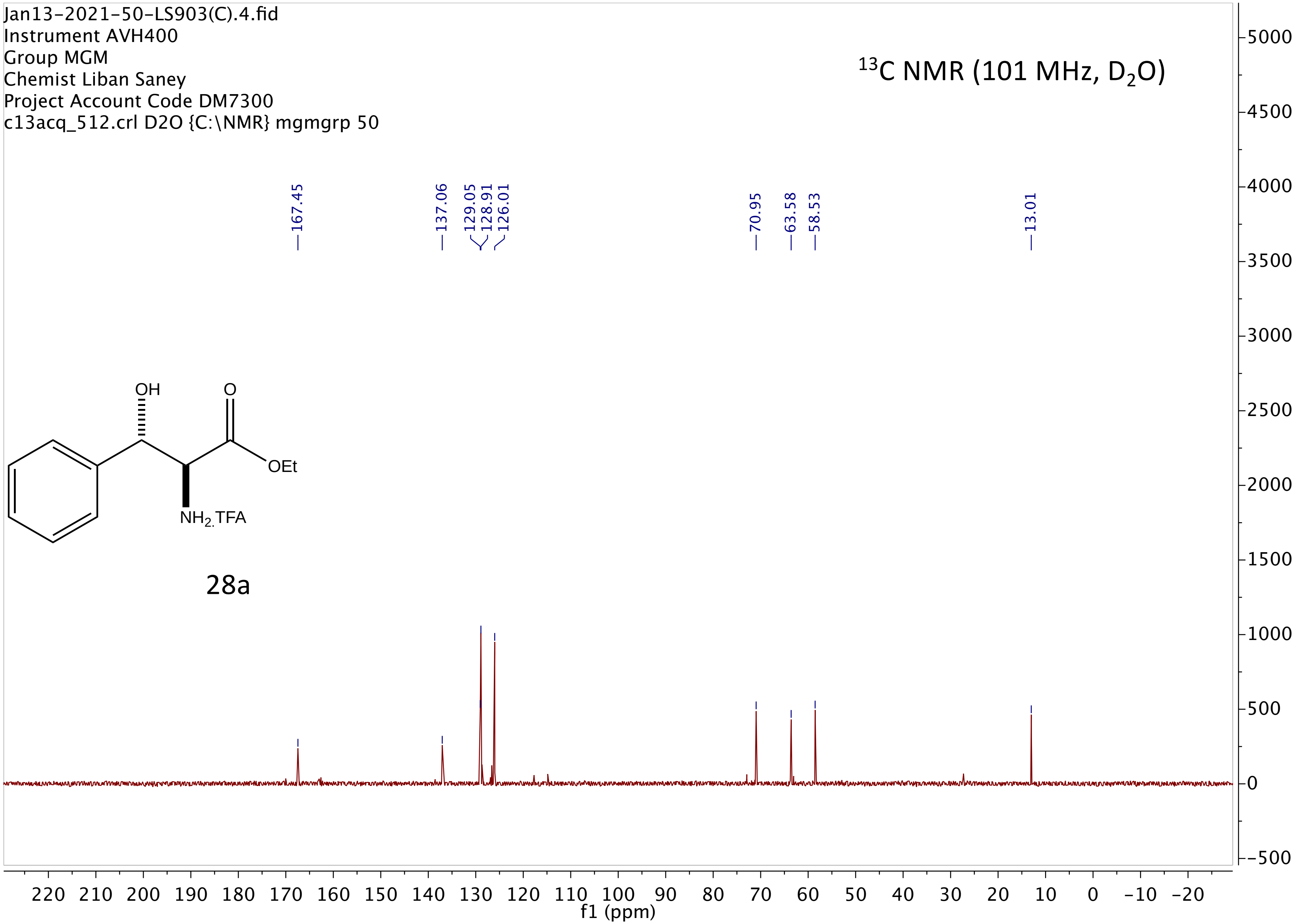
Jan13-2021-50-LS903(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 50

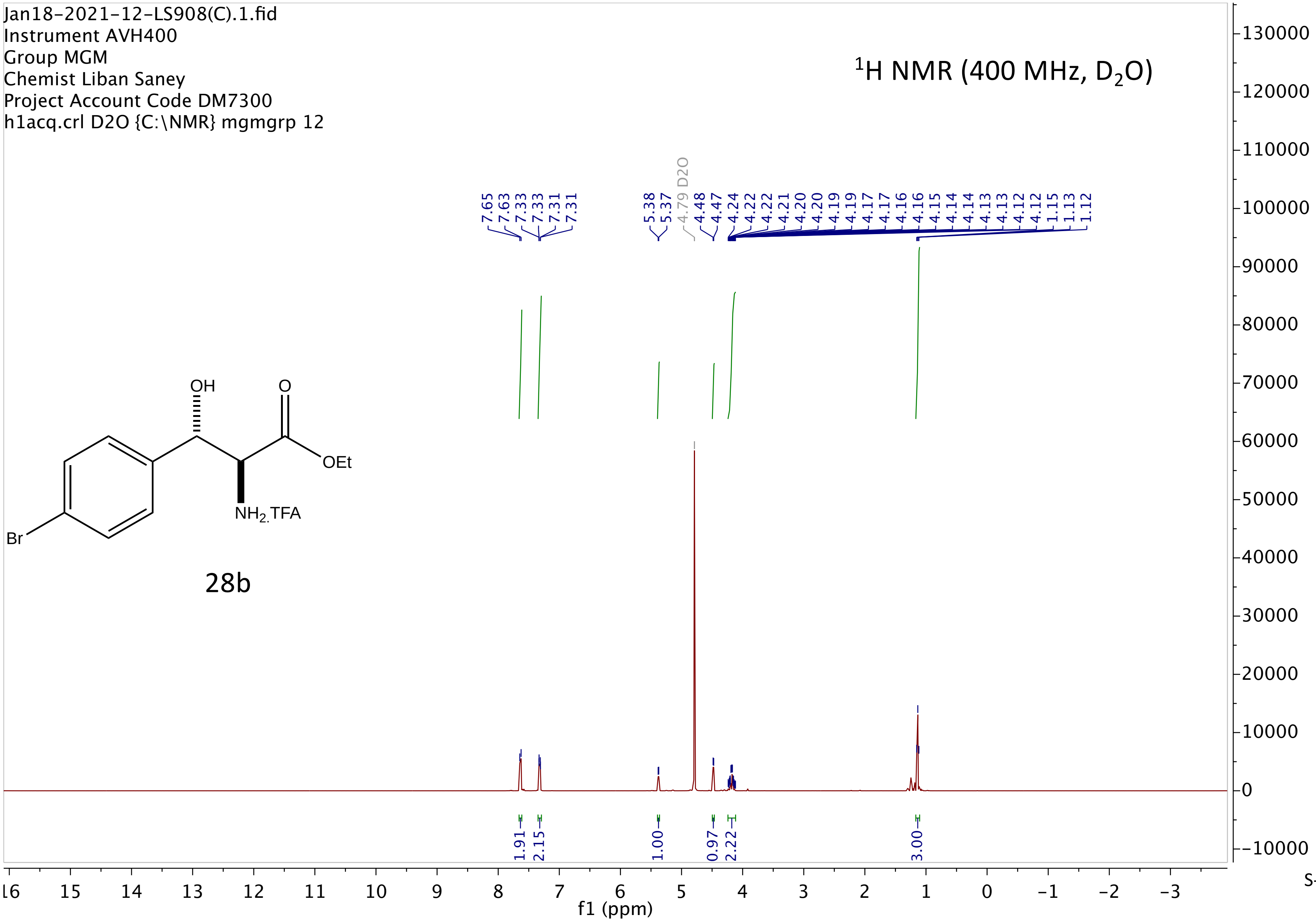
$^1H$ NMR (400 MHz, $D_2O$)

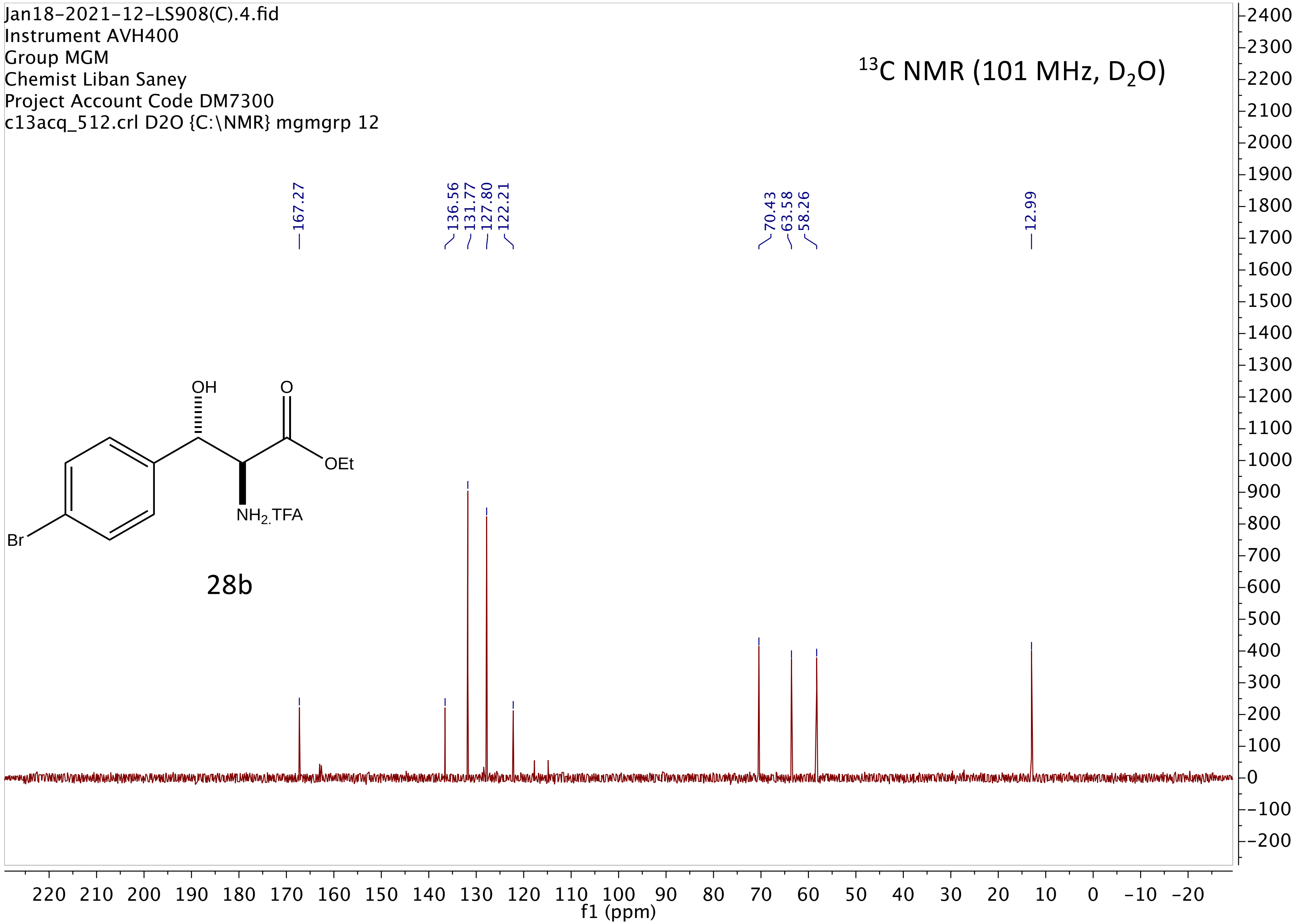


28a



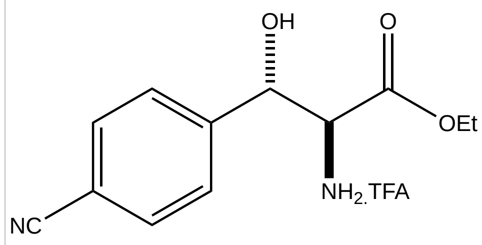

Jan13-2021-50-LS903(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 50
$^{13}C$ NMR (101 MHz, $D_2O$)
167.45
137.06
129.05
128.91
126.01
70.95
63.58
58.53
13.01
OH
O
OEt
NH2.TFA
28a
f1 (ppm)


Jan18-2021-12-LS908(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 12
$^1$H NMR (400 MHz, $D_2O$)
7.65 7.63 7.33 7.33 7.31 7.31
5.38 5.37
4.79 D2O
4.48 4.47
4.24 4.22 4.22 4.21 4.20 4.20 4.19 4.19 4.17 4.17 4.16 4.16 4.15 4.14 4.14 4.13 4.13 4.12 4.12
1.15 1.13 1.12
OH
O
OEt
Br
$NH_2$.TFA
28b
1.91 2.15 1.00 0.97 2.22 3.00
f1 (ppm)

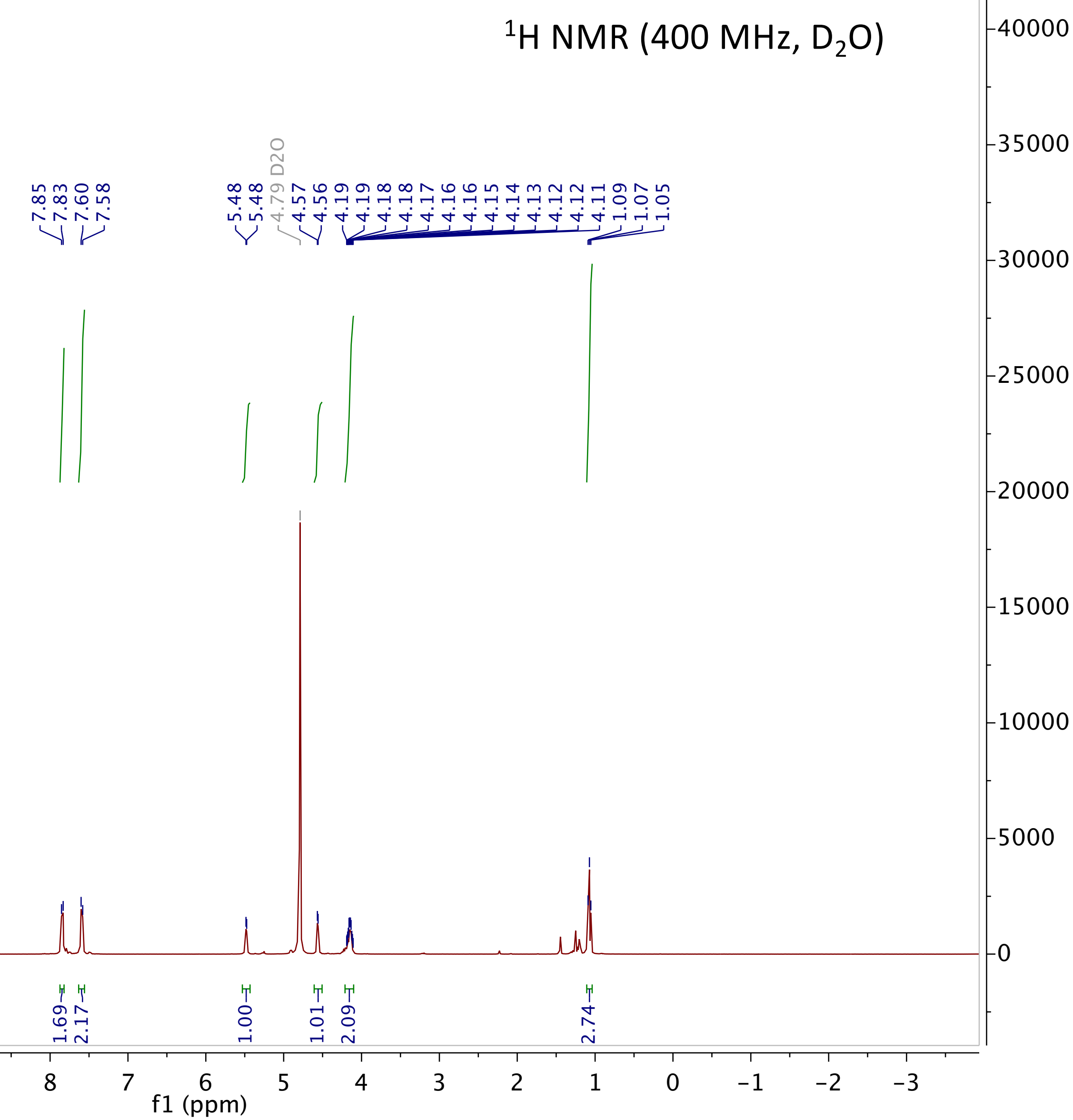


Jan18-2021-12-LS908(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 12
$^{13}$C NMR (101 MHz, $D_2O$)
167.27
136.56
131.77
127.80
122.21
70.43
63.58
58.26
12.99
OH
O
OEt
$NH_2$.TFA
Br
28b
f1 (ppm)

Jan18-2021-11-LS907(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 11

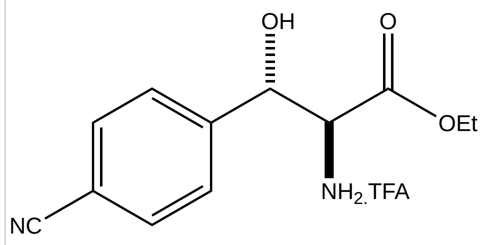


28c

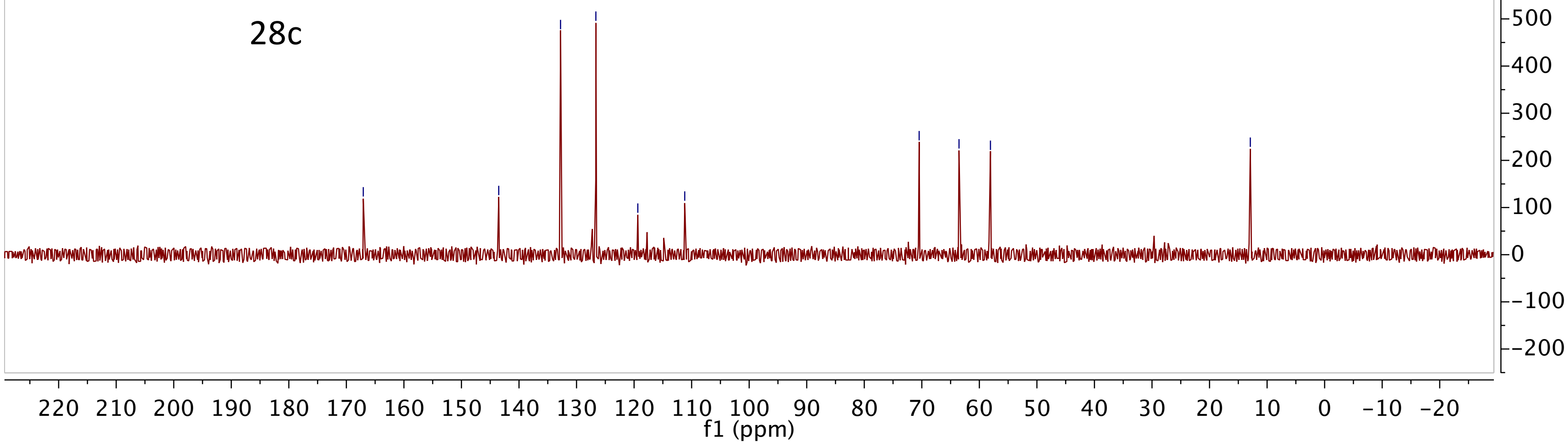


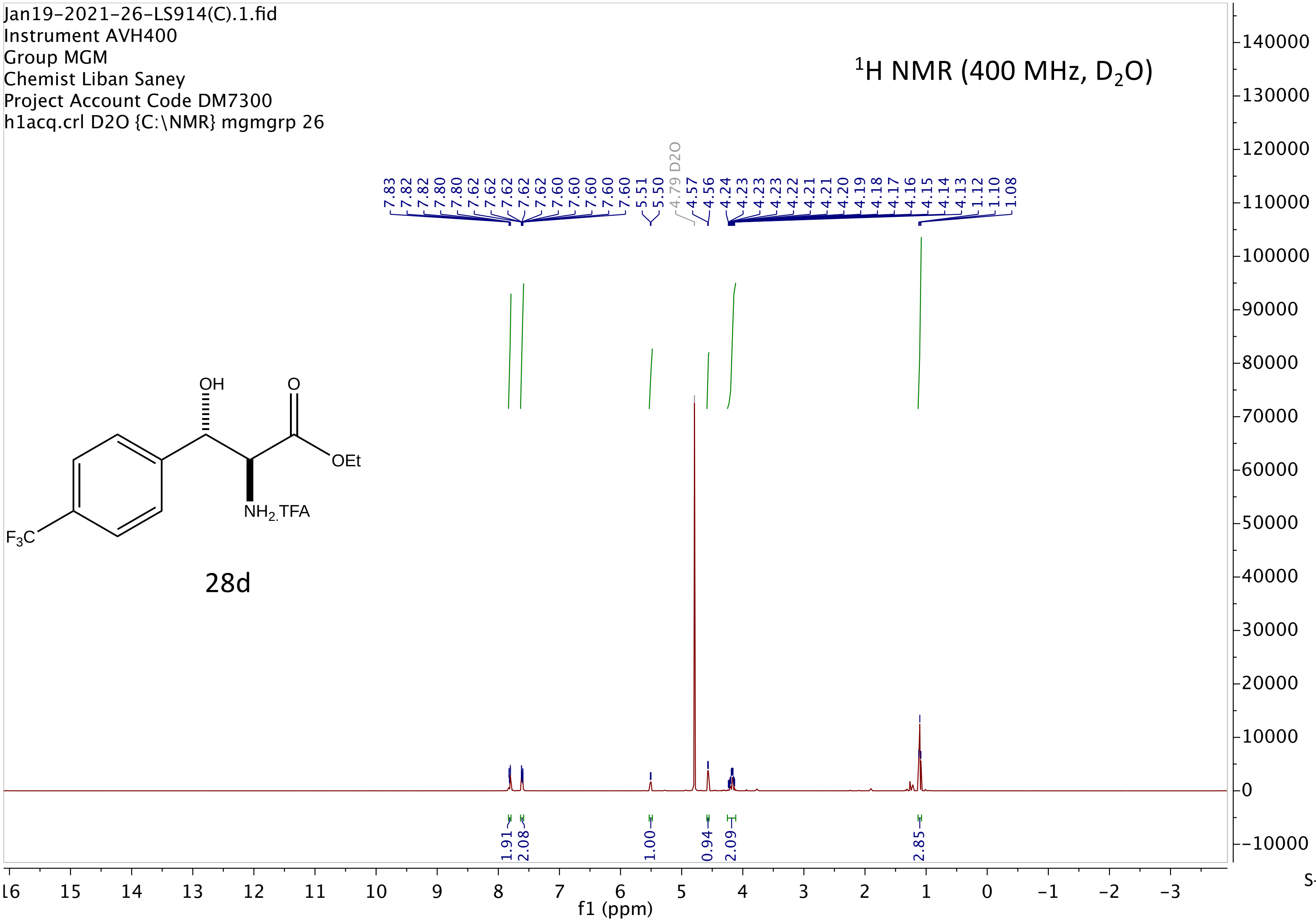
Jan18-2021-11-LS907(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 11

$^{13}C$ NMR (101 MHz, $D_2O$)

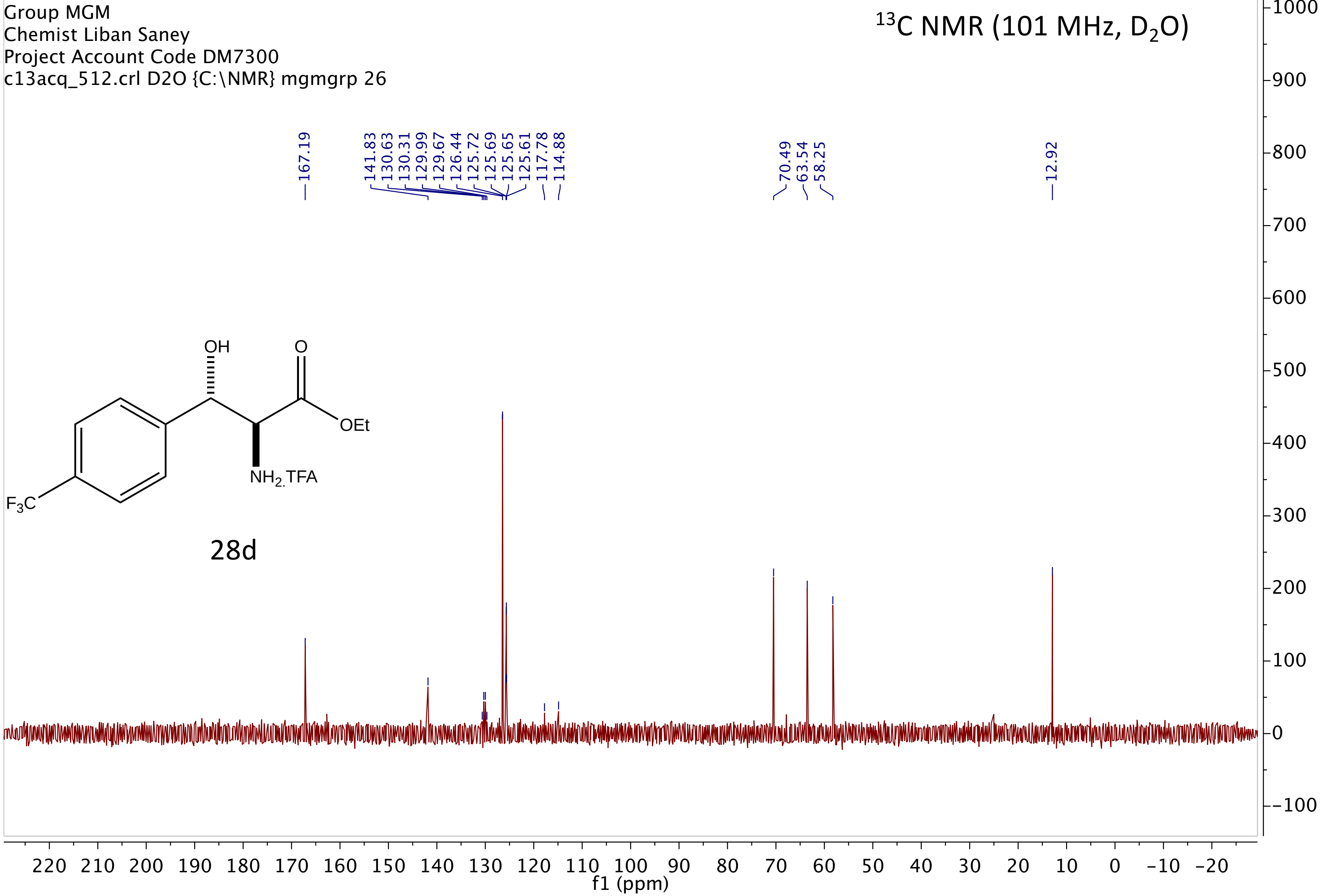


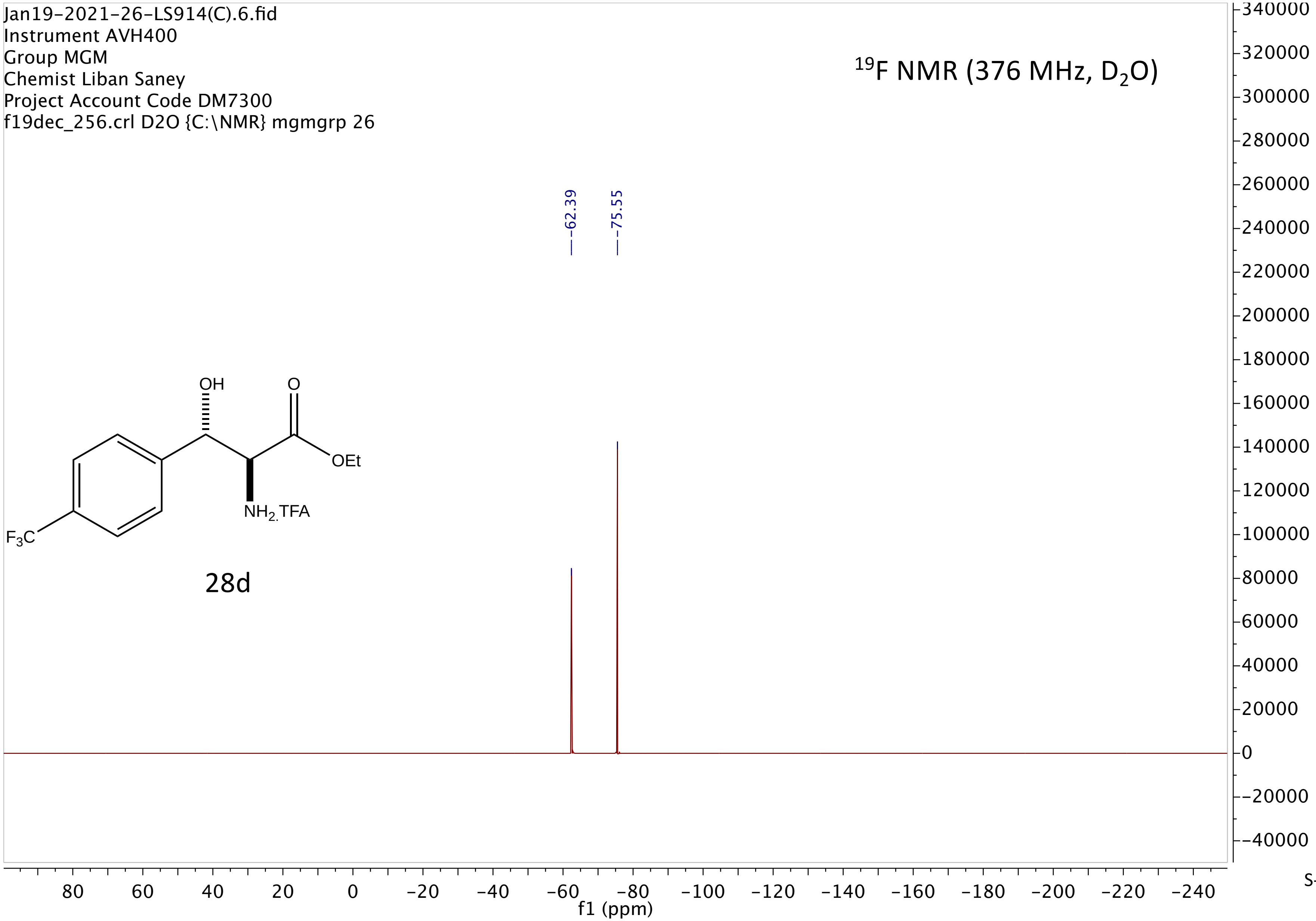
28c



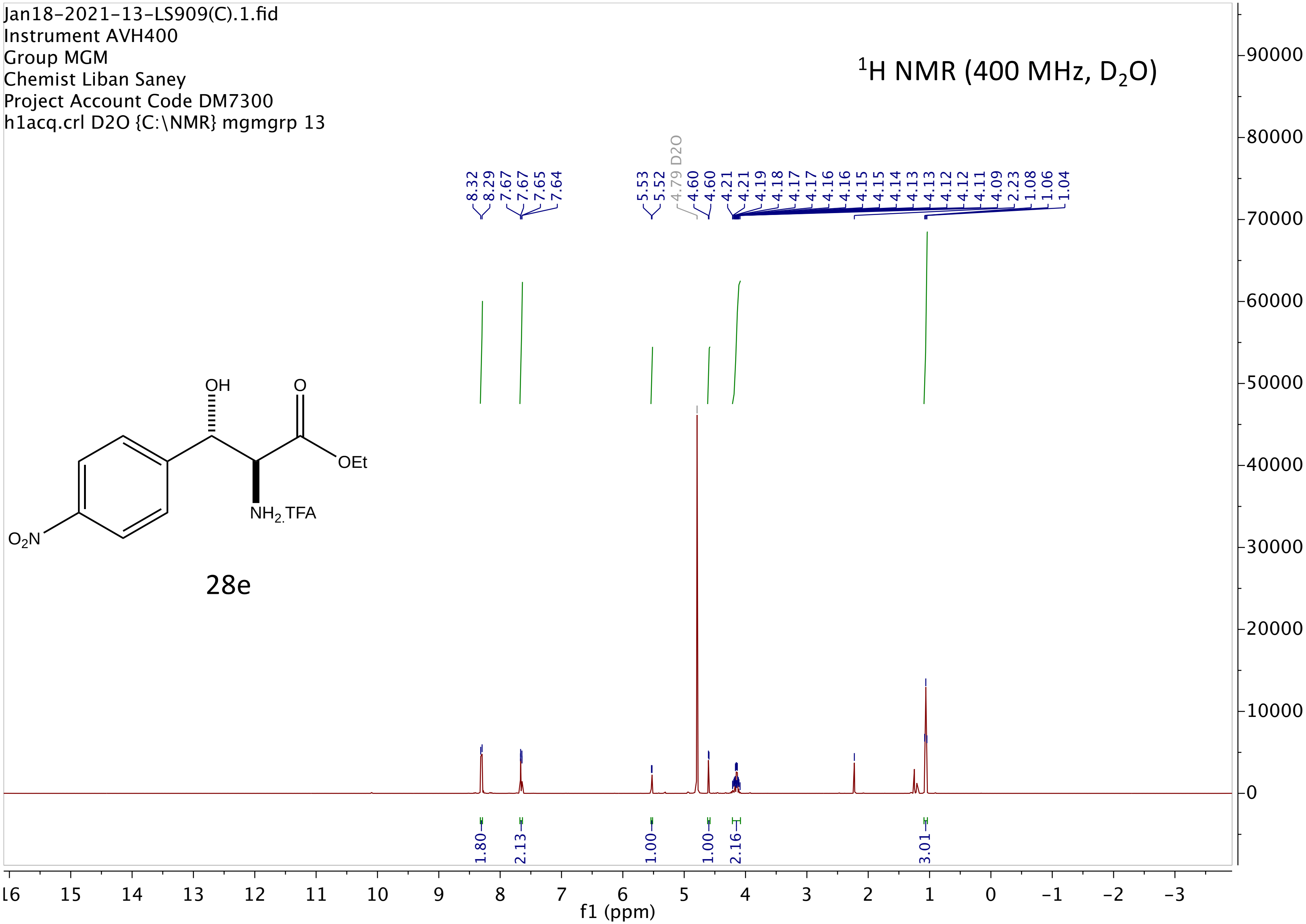

Jan19-2021-26-LS914(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 26
1H NMR (400 MHz, D2O)
7.83 7.82 7.82 7.80 7.80 7.62 7.62 7.62 7.62 7.60 7.60 7.60 7.60 7.60 5.51 5.50 4.79 D2O 4.57 4.56 4.24 4.23 4.23 4.23 4.22 4.21 4.21 4.20 4.19 4.18 4.17 4.16 4.15 4.14 4.13 1.12 1.10 1.08
OH
O
OEt
NH2.TFA
F3C
28d
1.91
2.08
1.00
0.94
2.09
2.85
f1 (ppm)

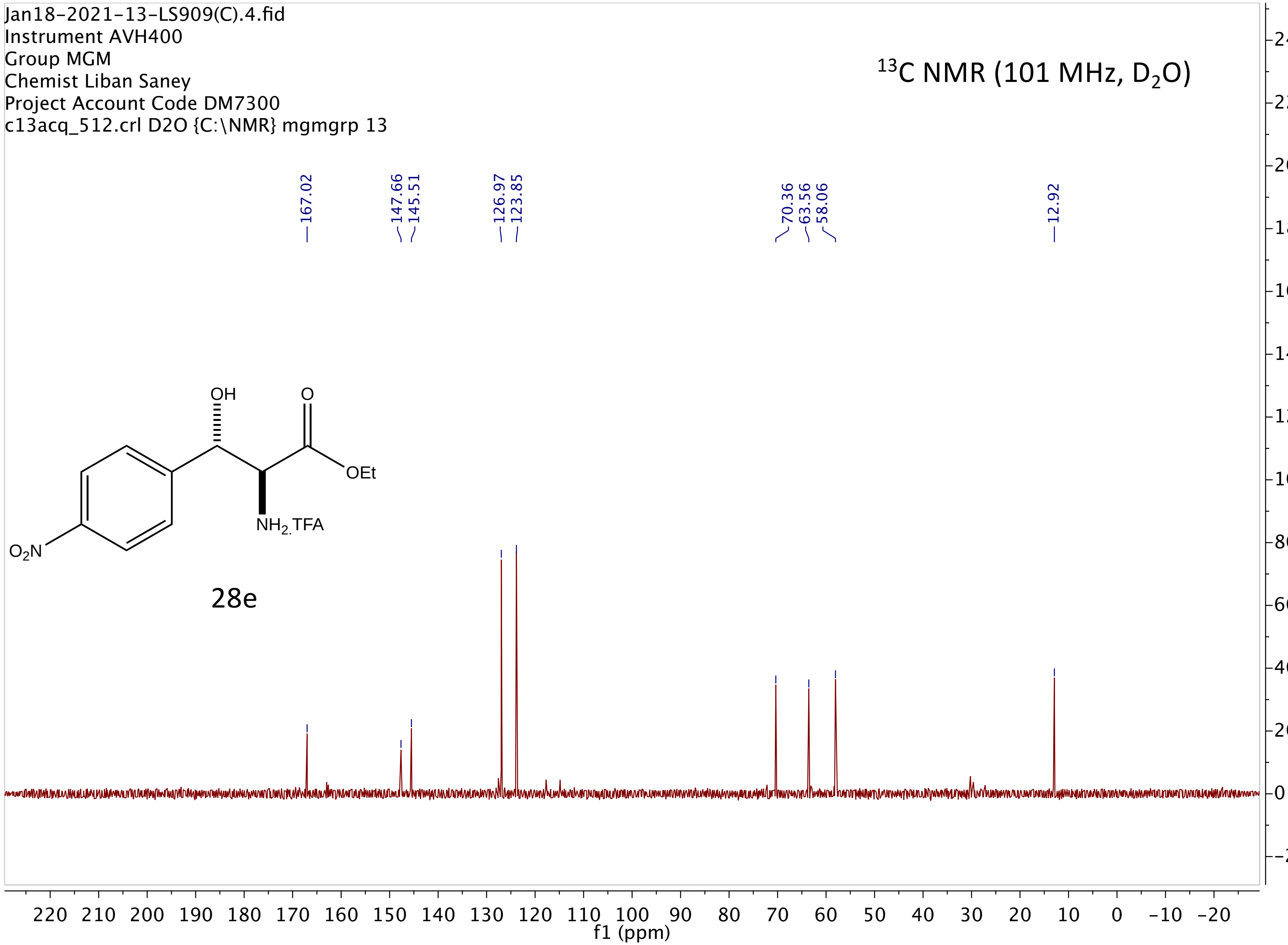
Jan19-2021-26-LS914(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 26




Jan19-2021-26-LS914(C).6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl D2O {C:\NMR} mgmgrp 26
19F NMR (376 MHz, D2O)
-62.39
-75.55
OH
O
OEt
NH2.TFA
F3C
28d
f1 (ppm)

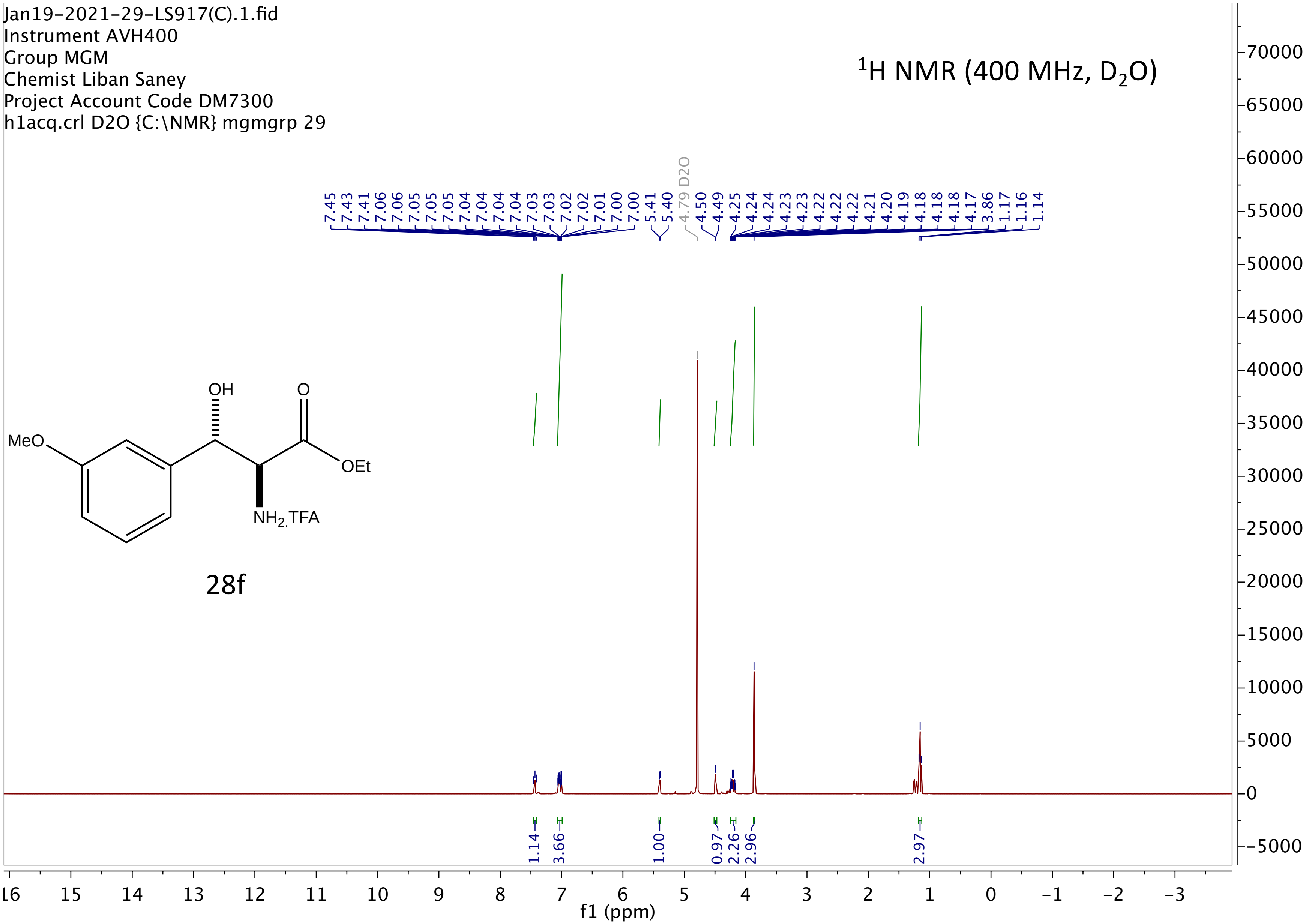
Jan18-2021-13-LS909(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 13





Jan18-2021-13-LS909(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 13
$^{13}C$ NMR (101 MHz, $D_2O$)
167.02
147.66
145.51
126.97
123.85
70.36
63.56
58.06
12.92
OH
O
OEt
$NH_2$.TFA
$O_2N$
28e
f1 (ppm)

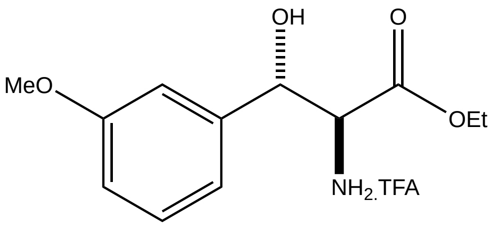
Jan19-2021-29-LS917(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 29



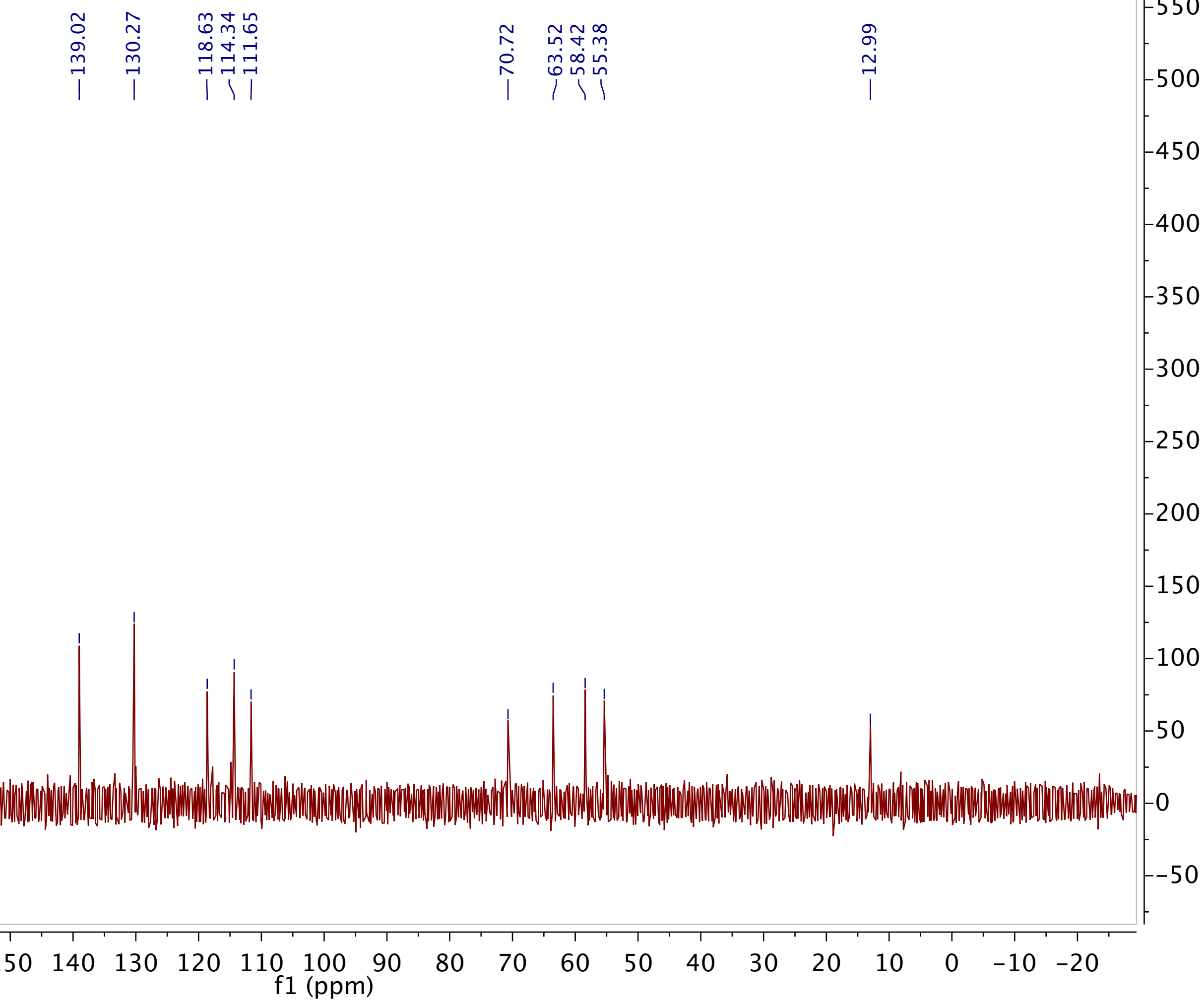

28f

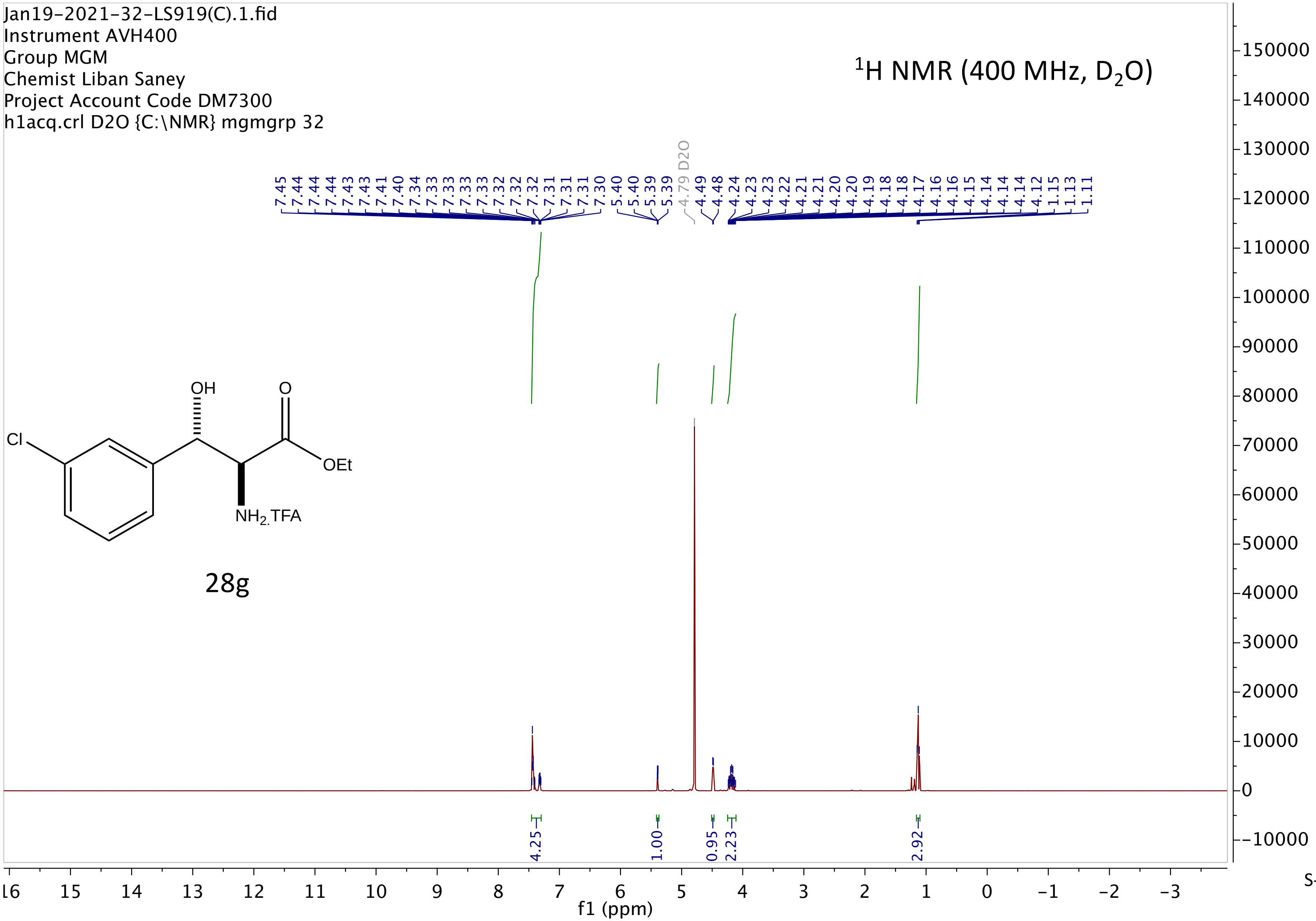
Jan19-2021-29-LS917(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 29

$^{13}C$ NMR (101 MHz, $D_2O$)

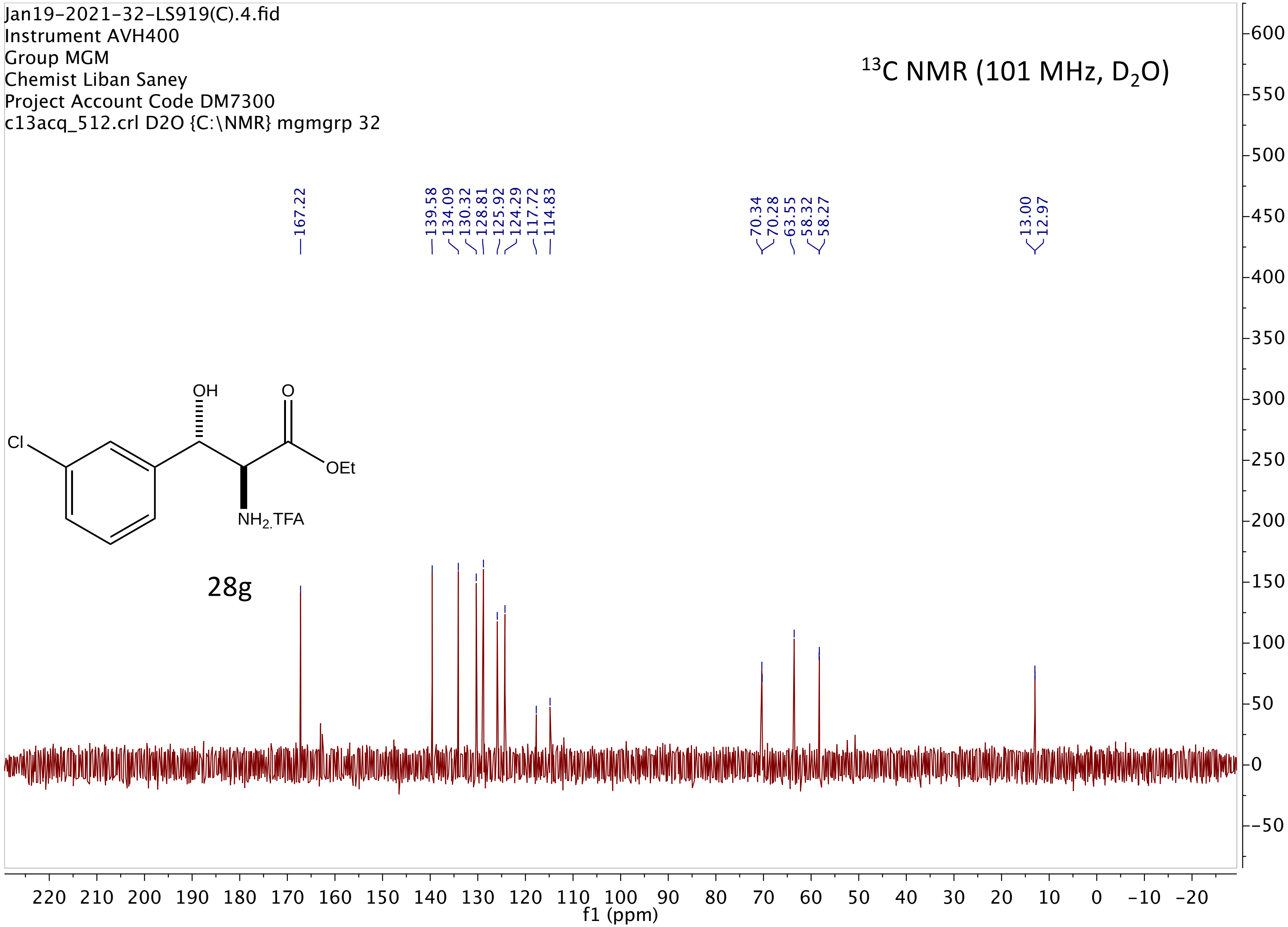



28f

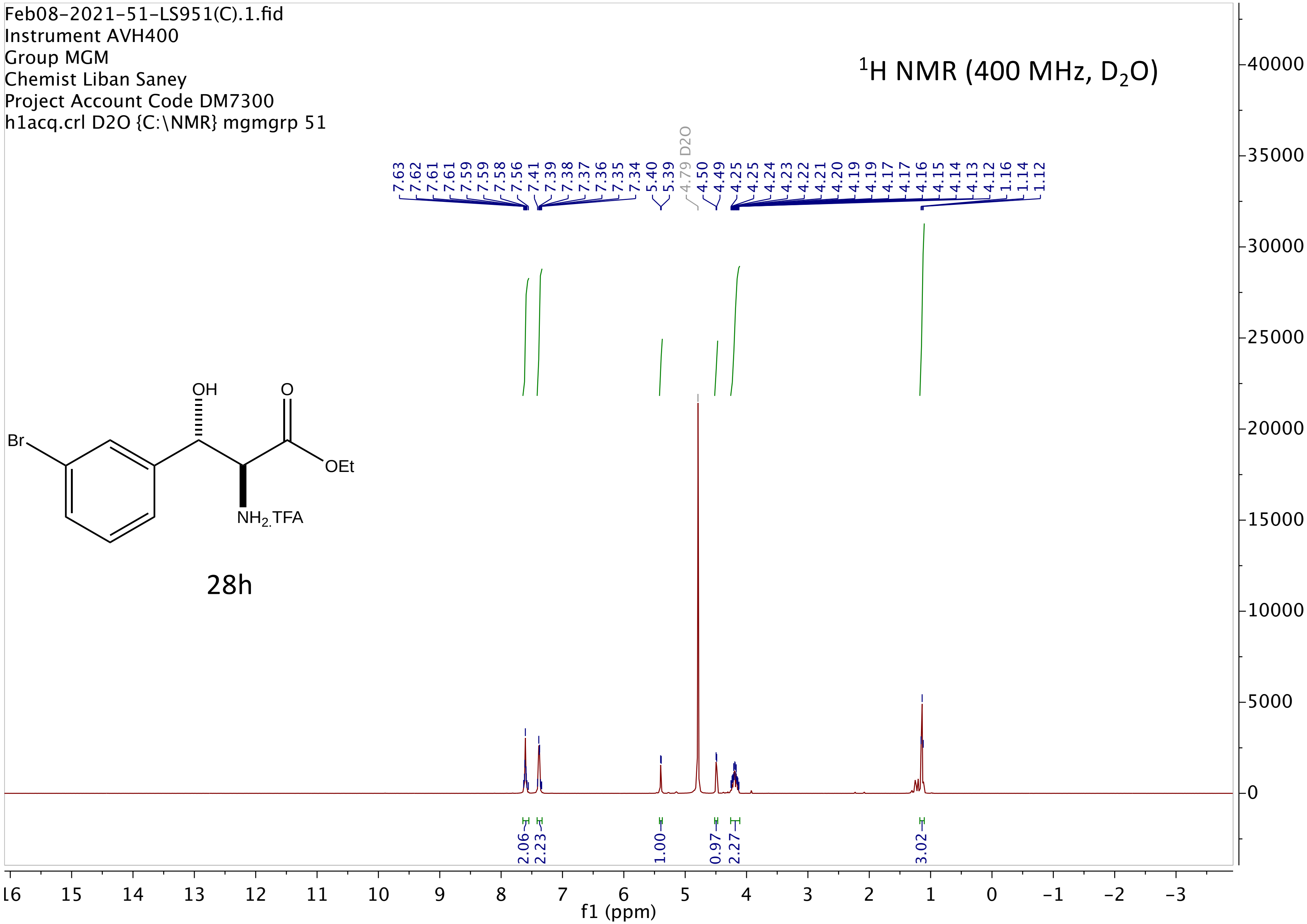



Jan19-2021-32-LS919(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 32
1H NMR (400 MHz, D2O)
7.45 7.44 7.44 7.44 7.43 7.43 7.41 7.40 7.34 7.33 7.33 7.33 7.33 7.32 7.32 7.32 7.31 7.31 7.31 7.30 5.40 5.40 5.39 5.39 4.79 D2O 4.49 4.48 4.24 4.23 4.23 4.22 4.21 4.21 4.20 4.20 4.19 4.18 4.18 4.17 4.16 4.16 4.15 4.14 4.14 4.14 4.12 1.15 1.13 1.11
OH
O
Cl
OEt
NH2.TFA
4.25 1.00 0.95 2.23 2.92
f1 (ppm)

28g

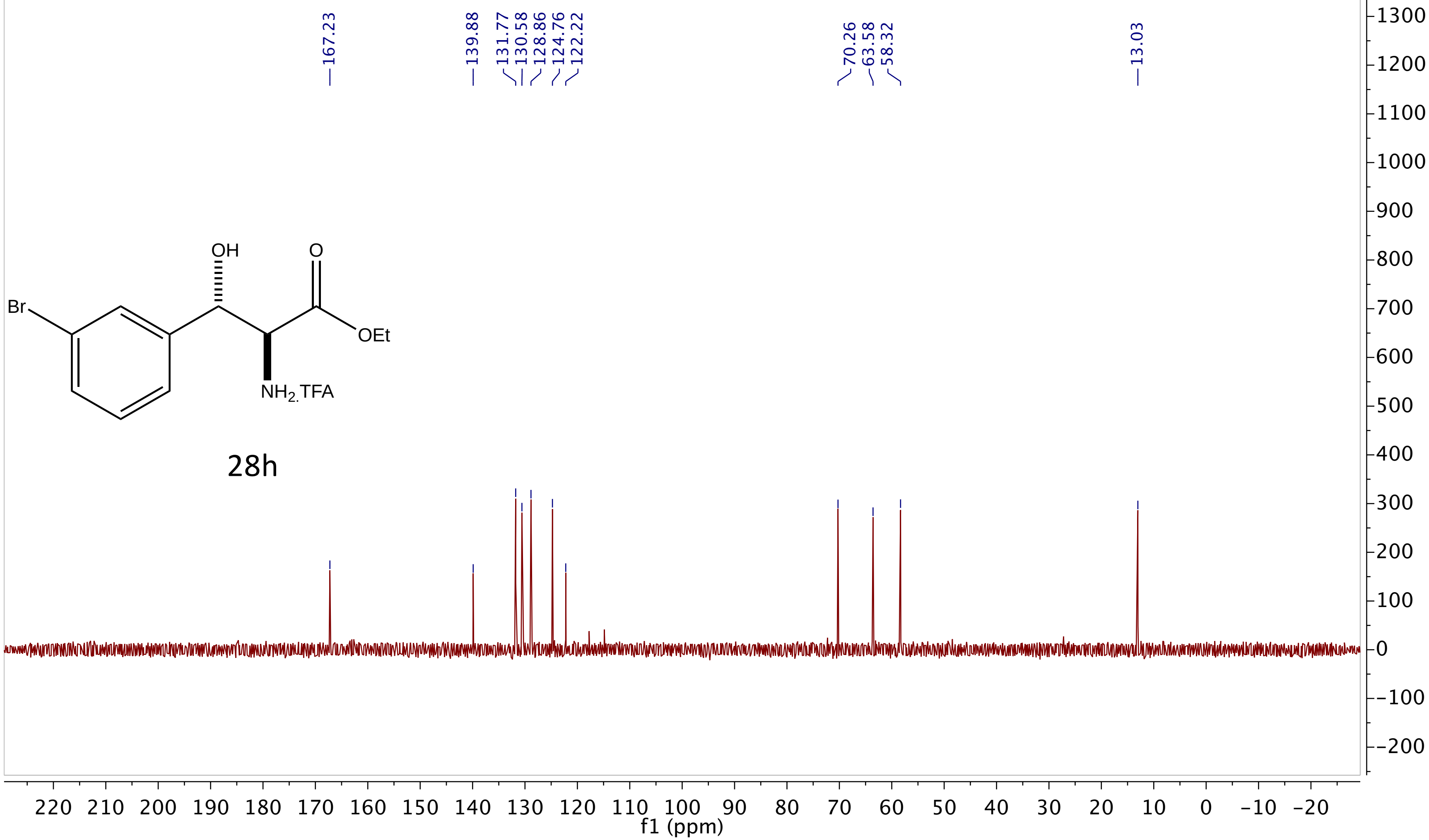


Jan19-2021-32-LS919(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 32
13C NMR (101 MHz, D2O)
167.22
139.58
134.09
130.32
128.81
125.92
124.29
117.72
114.83
70.34
70.28
63.55
58.32
58.27
13.00
12.97
OH
O
Cl
OEt
NH2.TFA
28g
f1 (ppm)

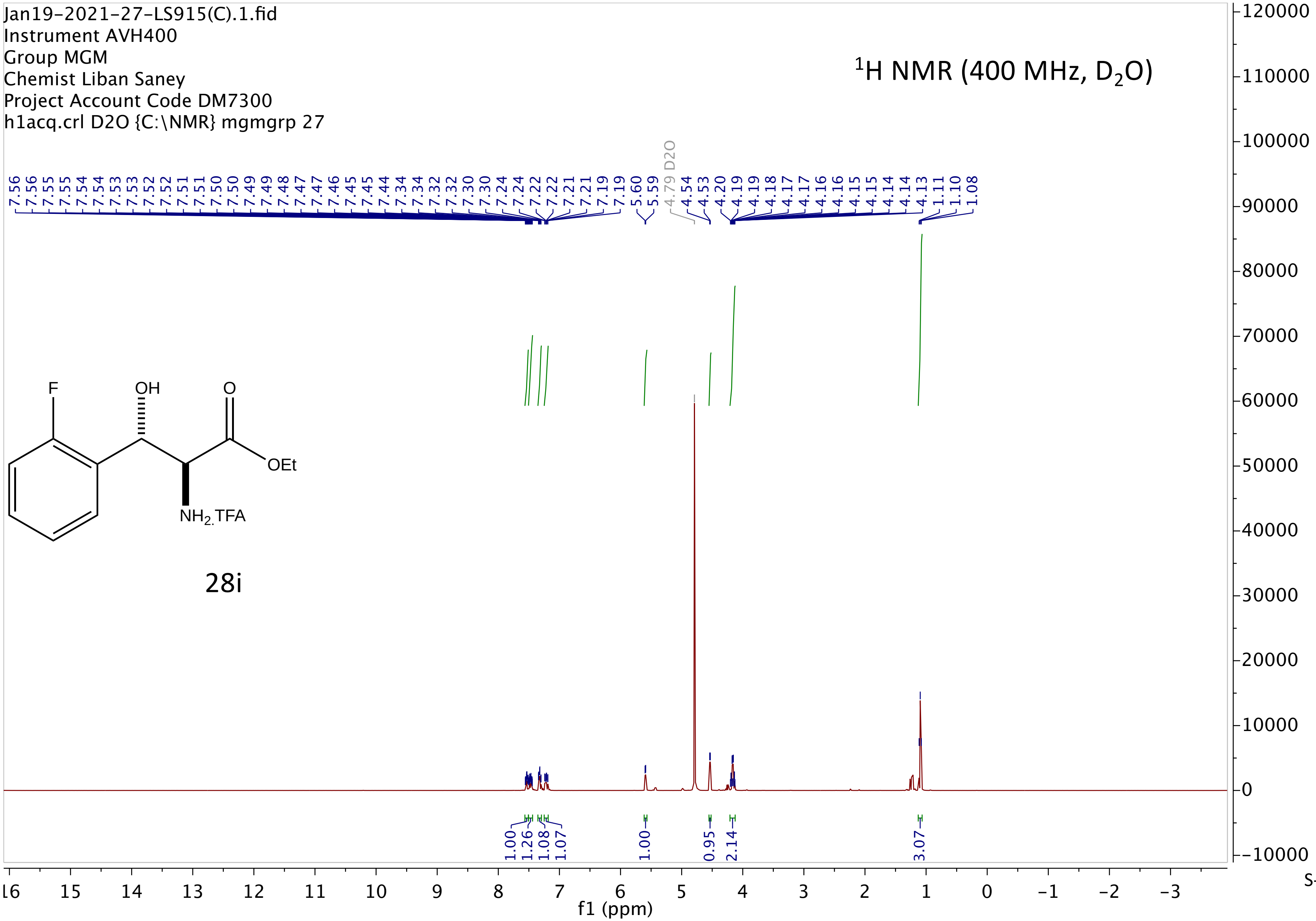

Feb08-2021-51-LS951(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 51
$^{1}$H NMR (400 MHz, $D_2O$)
7.63 7.62 7.61 7.61 7.59 7.59 7.58 7.56 7.41 7.39 7.38 7.37 7.36 7.35 7.34 5.40 5.39 4.79 D2O 4.50 4.49 4.25 4.25 4.24 4.23 4.22 4.21 4.20 4.19 4.19 4.17 4.17 4.16 4.15 4.14 4.13 4.12 1.16 1.14 1.12
2.06 2.23 1.00 0.97 2.27 3.02
OH
O
Br
OEt
NH2.TFA
28h
f1 (ppm)

Feb08-2021-51-LS951(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 51

$^{13}C$ NMR (101 MHz, $D_2O$)



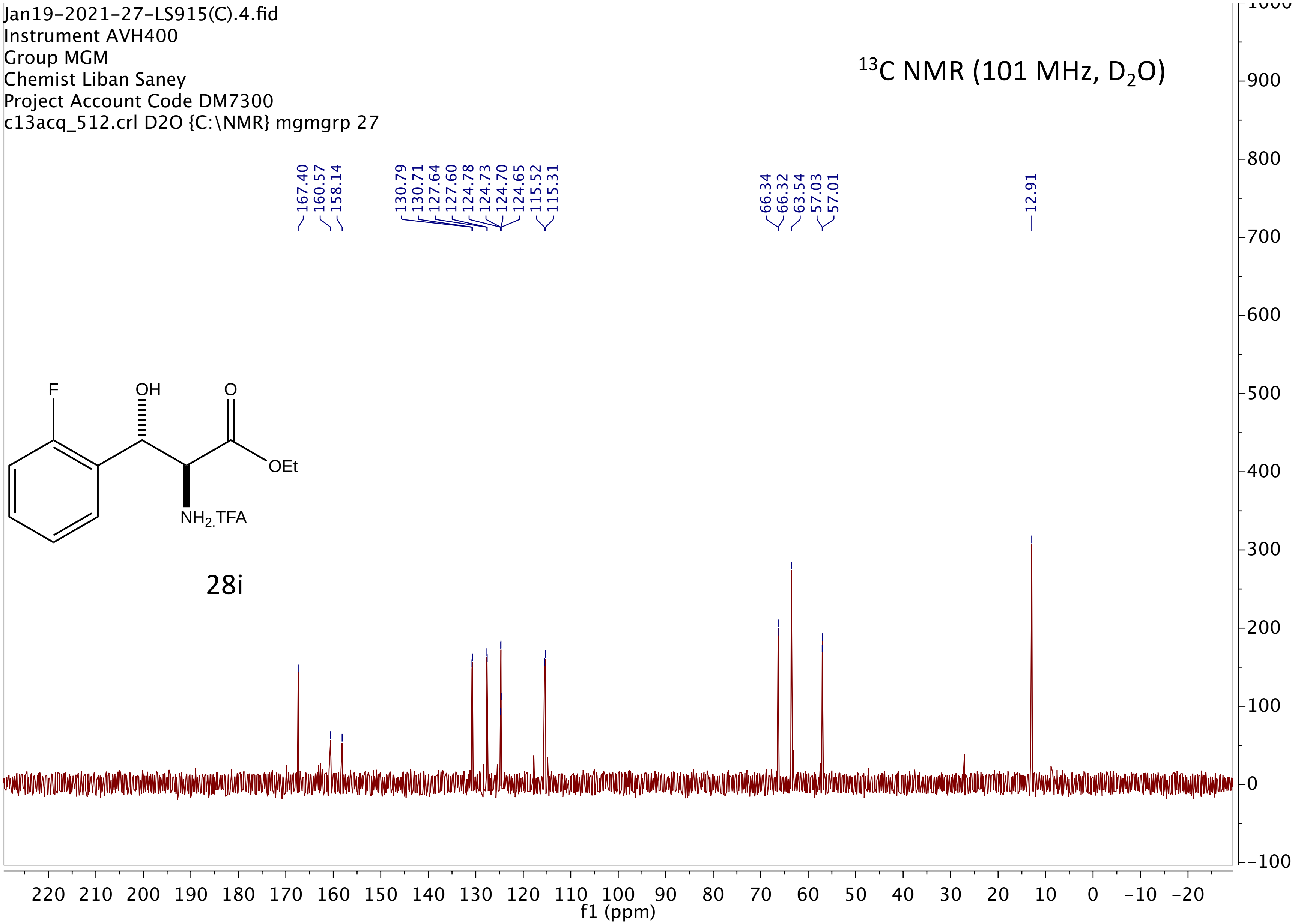

28h

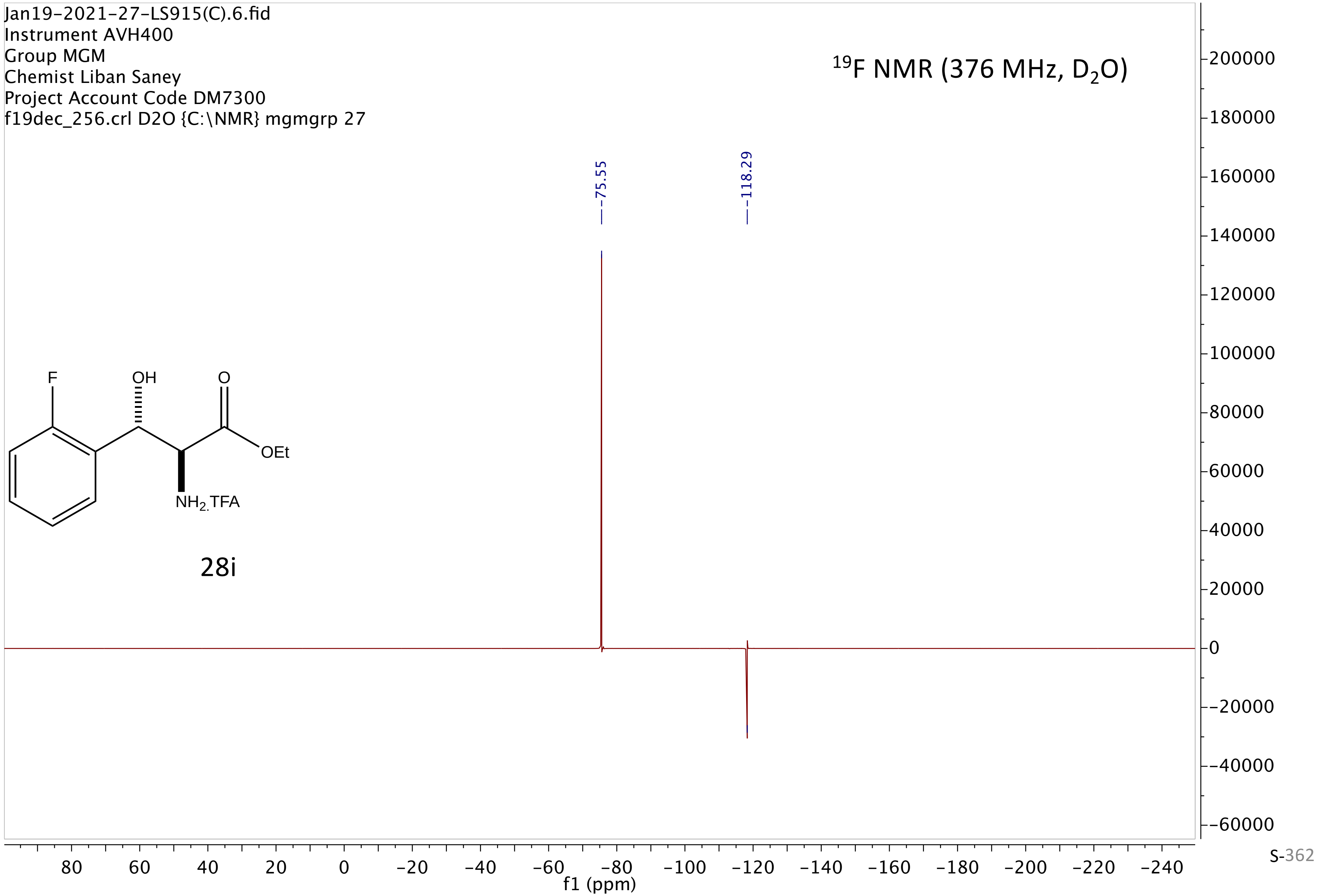


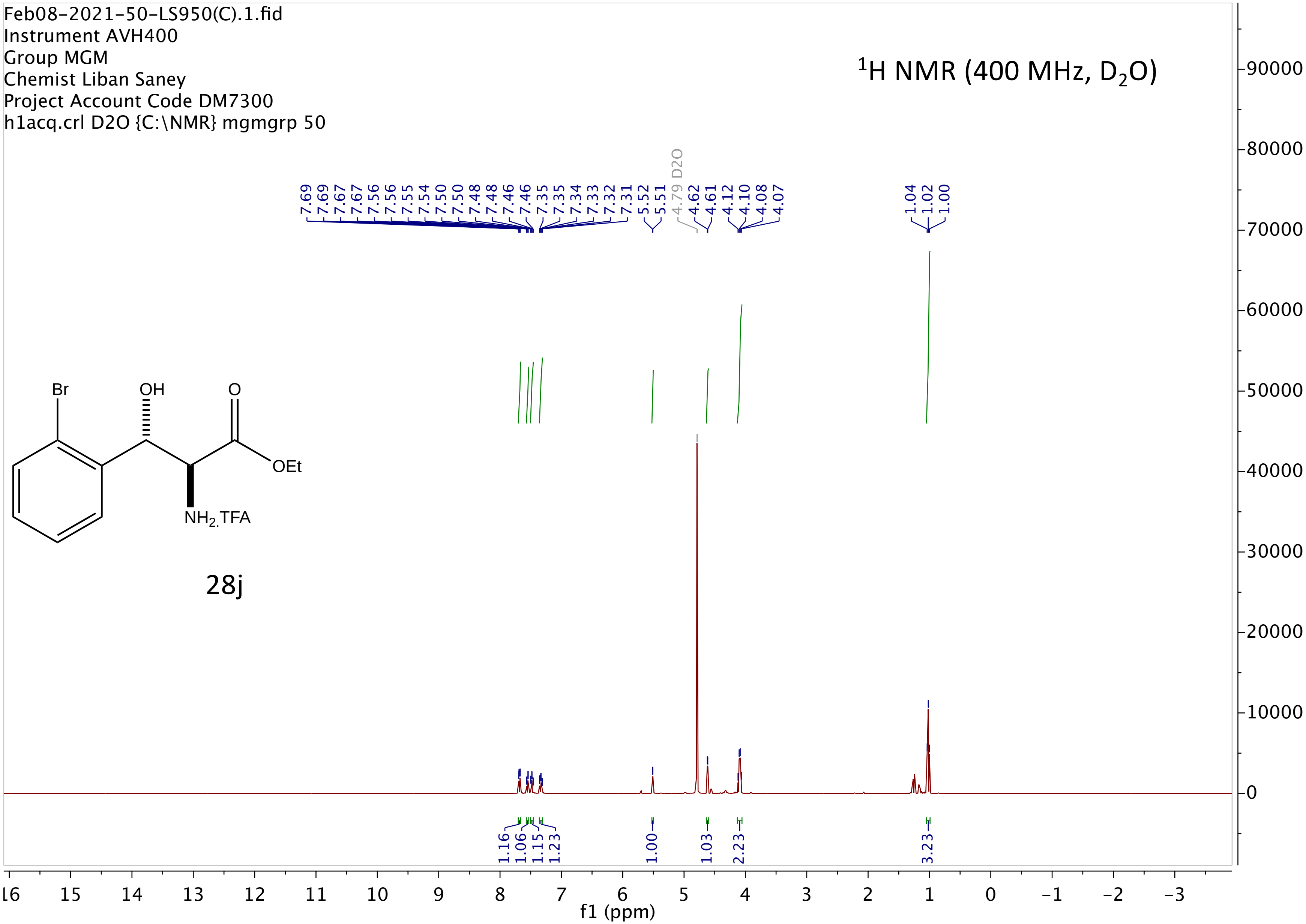
Jan19-2021-27-LS915(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 27
1H NMR (400 MHz, D2O)
7.56 7.56 7.55 7.55 7.54 7.54 7.53 7.53 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.47 7.46 7.45 7.45 7.44 7.34 7.34 7.32 7.32 7.30 7.30 7.24 7.24 7.22 7.22 7.21 7.21 7.19 7.19 5.60 5.59 4.79 D2O 4.54 4.53 4.20 4.19 4.19 4.18 4.17 4.17 4.16 4.16 4.15 4.15 4.14 4.14 4.13 1.11 1.10 1.08
F
OH
O
OEt
NH2.TFA
1.00 1.26 1.08 1.07 1.00 0.95 2.14 3.07
f1 (ppm)


28i

Jan19-2021-27-LS915(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 27



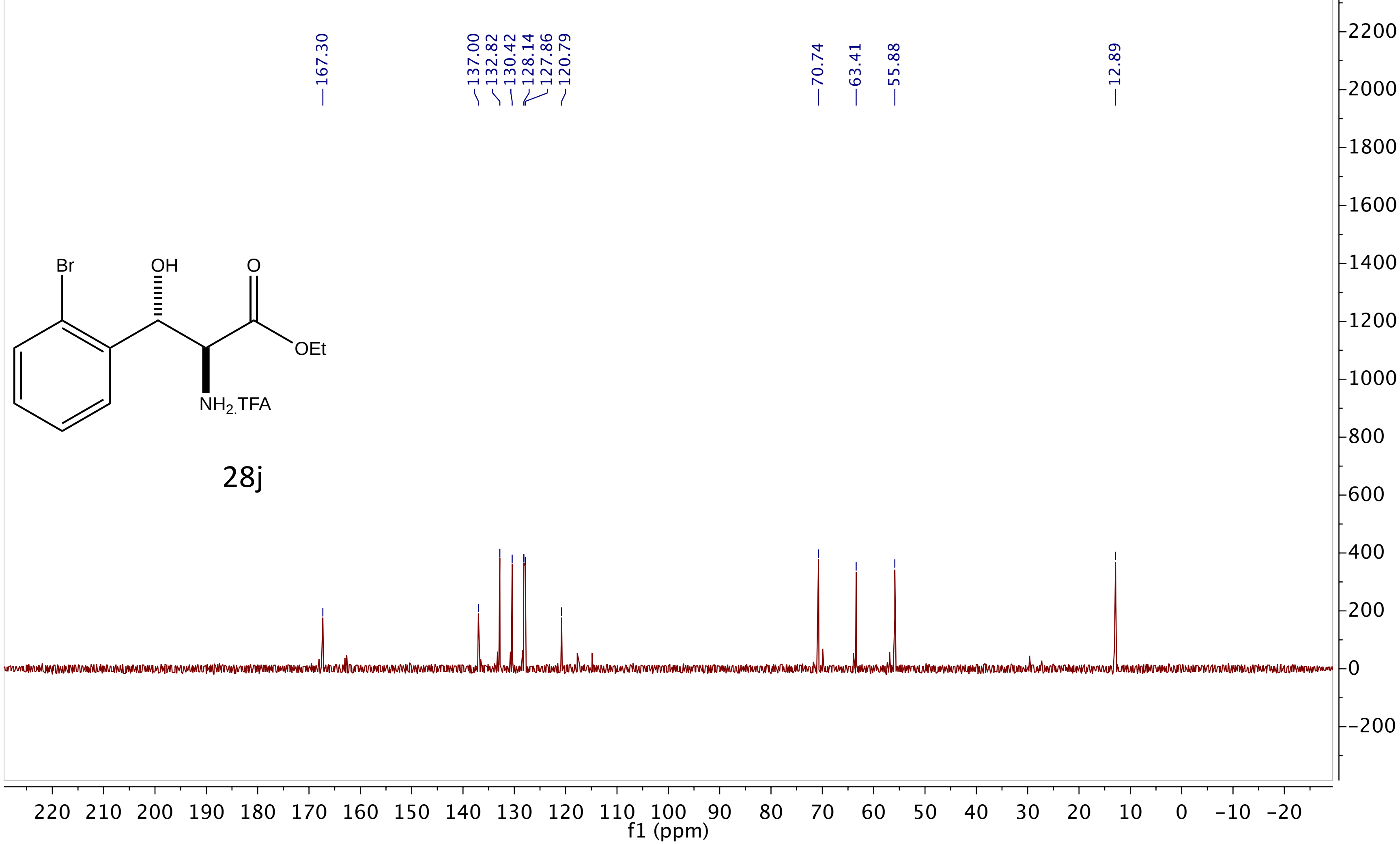

Jan19-2021-27-LS915(C).6.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
f19dec_256.crl D2O {C:\NMR} mgmgrp 27
$^{19}$F NMR (376 MHz, $D_2O$)
-75.55
-118.29
F
OH
O
OEt
$NH_2$.TFA
28i
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
-60000
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)



Feb08-2021-50-LS950(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 50
1H NMR (400 MHz, D2O)
7.69 7.69 7.67 7.67 7.56 7.56 7.55 7.54 7.50 7.50 7.48 7.48 7.46 7.46 7.35 7.35 7.34 7.33 7.32 7.31 5.52 5.51 4.79 D2O 4.62 4.61 4.12 4.10 4.08 4.07
1.04 1.02 1.00
Br
OH
O
OEt
NH2.TFA
28j
1.16 1.06 1.15 1.23 1.00 1.03 2.23 3.23
f1 (ppm)

Feb08-2021-50-LS950(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 50

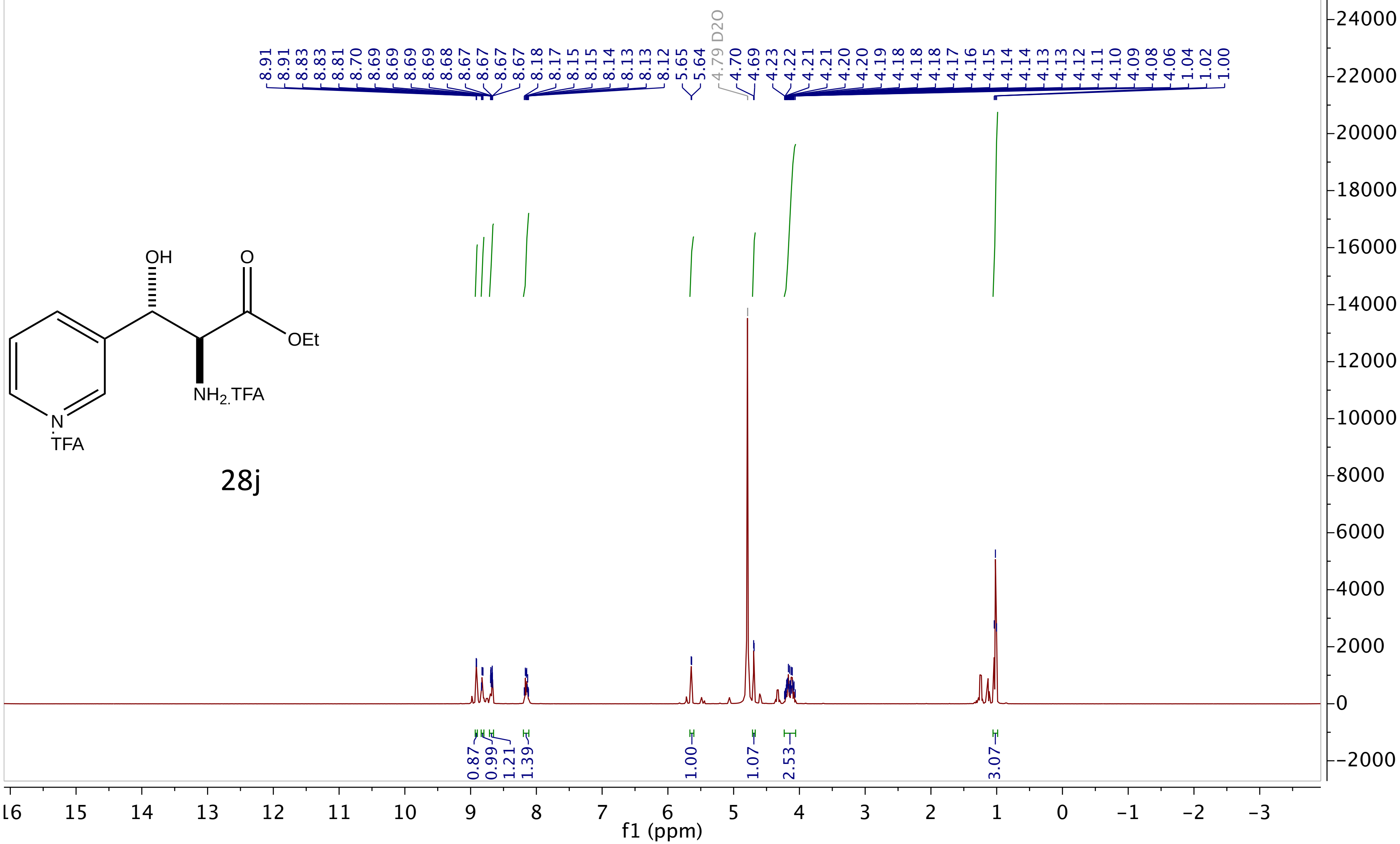
$^{13}C$ NMR (101 MHz, $D_2O$)

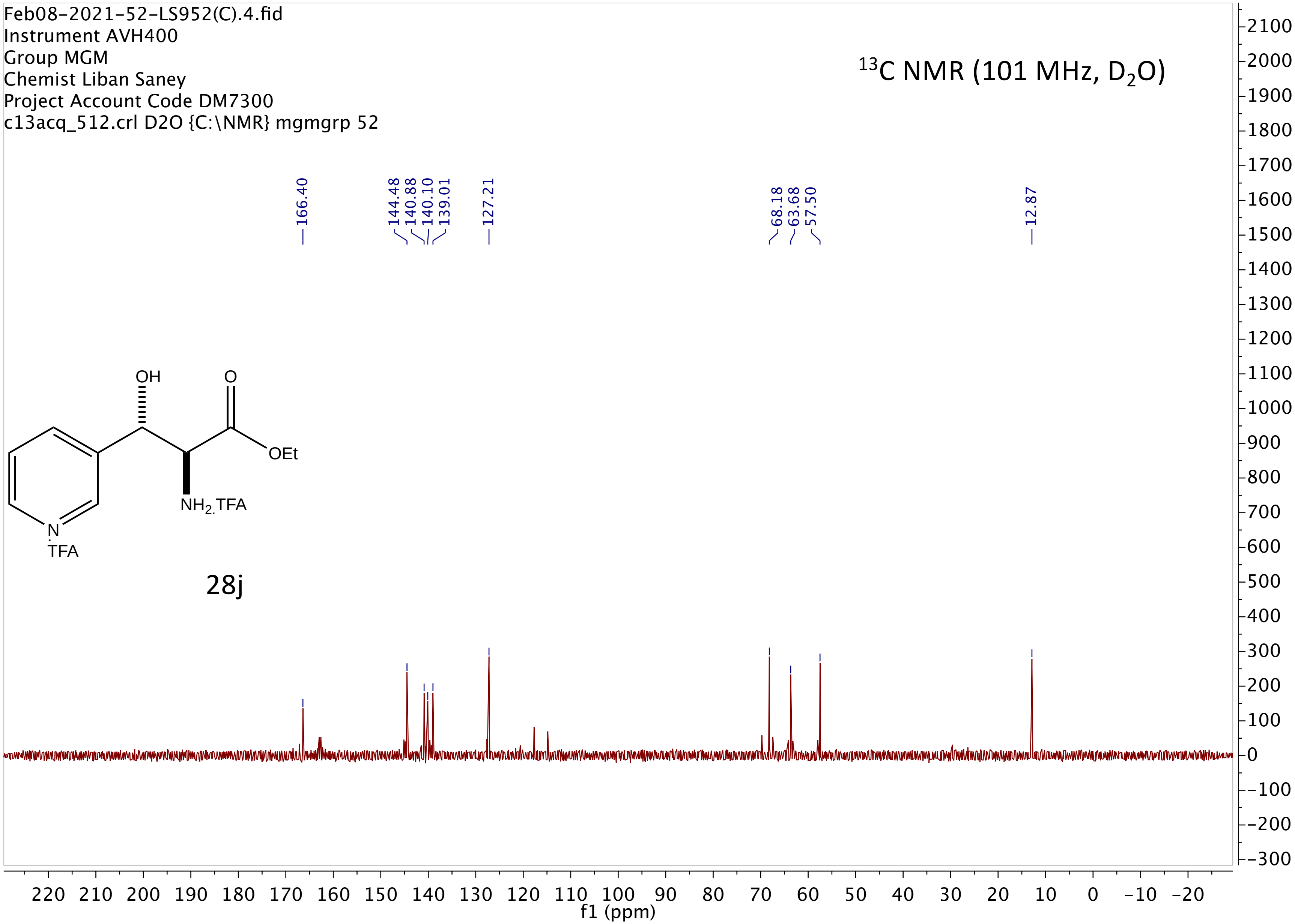


Feb08-2021-52-LS952(C).1.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
h1acq.crl D2O {C:\NMR} mgmgrp 52

$^1H$ NMR (400 MHz, $D_2O$)

28j




Feb08-2021-52-LS952(C).4.fid
Instrument AVH400
Group MGM
Chemist Liban Saney
Project Account Code DM7300
c13acq_512.crl D2O {C:\NMR} mgmgrp 52
$^{13}C$ NMR (101 MHz, $D_2O$)
166.40
144.48
140.88
140.10
139.01
127.21
68.18
63.68
57.50
12.87
OH
O
OEt
$NH_2$.TFA
N
TFA
28j
f1 (ppm)