

# Supporting Information

## Synthesis of 3-Chloropiperidines by Iodide-Mediated Electrolysis

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### 1. General Considerations

All solvents were purified by distillation prior to use. For anhydrous solvents, AcroSeal™ bottles from ACROS Organics™ were used. Commercially available chemicals were used as

obtained from the supplier unless otherwise stated. Syntheses prepared under anhydrous conditions were generally performed under standard Schlenk technique. For purification by column chromatography, silica gel 60 (Merck) was used.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at the Bruker Avance II 400, the Bruker Avance III 400 and the Bruker Avance II 200 "Microbay" spectrometers in deuterated solvents.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were determined by reference to the residual solvent signals. High-resolution ESI mass spectra were recorded in methanol with an ESI microTOF spectrometer from Bruker Daltonics in positive ion mode unless otherwise stated. As a power supply, the Sky Toppower PS1110 was used. Electrodes were sonicated in acetone and abraded with sand paper (120 grid, then 180 grid) prior to usage.

## 2. General Procedure for the Electrosynthesis of Compounds 2a-k

### 2.1 General procedure for method A:

A 20 mL cylindrical beaker-type cell (Figure 1) was charged with 0.05 mol TBAI. The cell was then equipped with a graphite rod anode (110 mm, 8 mm) and a nickel rod cathode (110 mm, 8 mm) at a distance of 8 mm. 20 mL of a mixture of acetonitrile/DCM 19:1 and 2 mmol unsaturated amine were added. The electrolysis was then carried out under potentiostatic conditions at 3.9 V for 2 hours. The reaction mixture was then concentrated under reduced pressure. The remaining residue was taken up in *n*-pentane, filtered and the filtrate was again concentrated under reduced pressure. The crude product was then purified via column chromatography (*n*-pentane/TBME).

### 2.2 General procedure for method B:

A 20 mL cylindrical beaker-type cell (Figure 1) was charged with 0.25 mmol TBAI. The cell was then equipped with a graphite rod anode (110 mm, 8 mm) and a nickel rod (or graphite rod) cathode (110 mm, 8 mm) at a distance of 8 mm. 20 mL acetonitrile and 2 mmol amine hydrochloride were added. The electrolysis was then carried out under potentiostatic conditions at 3.0 V for 18 hours (~3.6F/mol electricity were passed). The reaction mixture was then concentrated under reduced pressure. The remaining residue was taken up in *n*-pentane, filtered and the filtrate was again concentrated under reduced pressure. The crude product was then purified via column chromatography (*n*-pentane/TBME).



**Figure 1.** Electrolytic cell and power supply (SKY TOPPOWER PS1110). Electrolytic cell consists of a cylindric glass container (length: 100 mm, diameter: 30 mm), a nickel rod electrode (length: 110 mm, diameter: 8 mm) and a graphite rod electrode (length: 110 mm, diameter: 8 mm) at a distance of 8 mm. The electrodes were suspended 40mm into the solution (equals 11cm<sup>2</sup> of active surface per electrode).

**1-Butyl-3-chloro-5,5-dimethylpiperidine (2a)** was prepared according to the general procedure of method A from 0.362 g (2.14 mmol) **1a**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_F = 0.71$ ) as a slightly yellow oil (0.322 g, 1.58 mmol, 74%). Synthesis *via* method B from 0.412 g (2.00 mmol) **3a** gave 0.336 g (1.65 mmol, 82%) after purification as a slightly yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 4.18 - 3.98$  (m, 1H), 3.15 (dd,  $J = 10.9, 4.4$  Hz, 1H), 2.46 – 2.37 (m, 1H), 2.30 (tq,  $J = 12.3, 6.1$  Hz, 2H), 1.98 – 1.86 (m, 2H), 1.69 (s, 1H), 1.42 (ddd,  $J = 14.2, 7.9, 4.7$  Hz, 2H), 1.37 – 1.25 (m, 3H), 1.02 (s, 3H), 0.93 – 0.87 (m, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 64.8, 62.4, 57.7, 54.4, 48.5, 33.3, 29.5, 29.1, 25.2, 20.5, 14.0$  ppm; HRMS(ESI):  $m/z$  calculated for C<sub>11</sub>H<sub>23</sub>NCl {M+H<sup>+</sup>}: 204.1514. Found: 204.1518. These data are consistent with the literature.<sup>1</sup>

**1-Benzyl-3-chloro-5,5-dimethylpiperidine (2b)** was prepared according to the general procedure of method A from 0.359 g (1.77 mmol) **1b**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_F = 0.79$ ) as a slightly yellow oil (0.203 g, 0.854 mmol, 48%). Synthesis *via* method B from 0.480 g (2.00 mmol) **3b** gave 0.339 g (1.43 mmol, 71%) **2b** after purification as a slightly yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.35 - 7.15$  (m, 5H), 4.07 (ddt,  $J = 12.0, 10.7, 4.5$  Hz, 1H), 3.57 – 3.36 (m, 2H), 3.12 (ddt,  $J = 10.6, 3.9, 1.7$  Hz, 1H), 2.35 (dt,  $J = 11.1, 1.9$  Hz, 1H), 1.96 (t,  $J = 10.6$  Hz, 1H), 1.92 – 1.86 (m, 1H), 1.73 (d,  $J = 10.7$  Hz, 1H), 1.31 (t,  $J = 12.3$  Hz, 1H), 1.02 (s, 3H), 0.84 (s, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 138.6, 128.7, 128.2, 127.0, 64.5, 62.3,$

61.9, 54.3, 48.4, 33.4, 29.3, 25.1, 1.0 ppm; HRMS(ESI):  $m/z$  calculated for  $C_{14}H_{20}NCl$   $\{M+H^+\}$ : 238.1357. Found: 238.1359. These data are consistent with the literature.<sup>2</sup>

**1-Propenyl-3-chloro-5,5-dimethylpiperidine (2c)** was prepared according to the general procedure of method A from 0.137 g (0.89 mmol) **1c**. The title compound was obtained after column chromatography (n-pentane/TBME 9:1,  $R_f$  = 0.58) as a slightly yellow oil (0.124 g, 0.66 mmol, 74%). Synthesis *via* method B from 0.379 g (2.00 mmol) **3c** gave 0.270 g (1.44 mmol, 72%) **2c** after purification as a slightly yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 5.80 (ddt,  $J$  = 16.7, 10.2, 6.3 Hz, 1H), 5.30 – 5.01 (m, 2H), 4.19 – 3.97 (m, 1H), 3.17 (dd,  $J$  = 11.1, 4.5 Hz, 1H), 2.98 (qd,  $J$  = 13.7, 6.3 Hz, 2H), 2.43 (dt,  $J$  = 11.1, 1.9 Hz, 1H), 2.01 – 1.86 (m, 2H), 1.70 (d,  $J$  = 11.1 Hz, 1H), 1.40 – 1.25 (m, 1H), 1.03 (s, 3H), 0.91 (s, 3H) ppm;  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 135.2, 117.5, 64.6, 61.9, 61.1, 54.3, 48.4, 33.3, 29.4, 25.2 ppm; HRMS(ESI):  $m/z$  calculated for  $C_{10}H_{18}NCl$   $\{M+H^+\}$ : 188.1201. Found: 188.1199. These data are consistent with the literature.<sup>2</sup>

**1-tert.-Butyl-3-chloro-5,5-dimethylpiperidine (2d)** was prepared according to the general procedure of method A from 0.106 g (0.626 mmol) **1d**. The title compound was obtained after column chromatography (n-pentane/TBME 9:1,  $R_f$  = 0.76) as a slightly yellow oil (0.080 g, 0.39 mmol, 63%). Synthesis *via* method B from 0.412 g (2.00 mmol) **3d** gave 0.282 g (1.38 mmol, 69%) **2d** after purification as a slightly yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 4.02 (ddt,  $J$  = 11.9, 10.5, 4.5 Hz, 1H), 3.34 (ddt,  $J$  = 10.6, 4.2, 2.0 Hz, 1H), 2.53 (dt,  $J$  = 11.1, 2.1 Hz, 1H), 2.00 (t,  $J$  = 10.6 Hz, 1H), 1.91 (ddt,  $J$  = 12.5, 4.2, 1.8 Hz, 1H), 1.79 (d,  $J$  = 11.2 Hz, 1H), 1.29 (t,  $J$  = 12.2 Hz, 1H), 1.02 (s, 9H), 0.99 (s, 3H), 0.90 (s, 3H) ppm;  $^{13}C$  NMR (101 MHz,  $CDCl_3$ ):  $\delta$  = 77.2, 57.8, 56.3, 55.6, 53.5, 48.9, 33.3, 29.5, 26.5, 25.0, 1.0 ppm; HRMS(ESI):  $m/z$  calculated for  $C_{11}H_{22}NCl$   $\{M+H^+\}$ : 204.1514. Found: 204.1514. These data are consistent with the literature.<sup>3</sup>

**1-[3-[[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-3-chloro-5,5-dimethylpiperidine (2e)** was prepared according to the general procedure of method A from 0.297 g (1.04 mmol) **1e**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_f$  = 0.73) as a slightly yellow oil (0.235 g, 0.734 mmol, 71%). Synthesis *via* method B from 0.642 g (1.99 mmol) **3e** gave 0.540 g (1.69 mmol, 84%) after purification as a slightly yellow oil.  $^1H$  NMR (600 MHz,  $CDCl_3$ ):  $\delta$  = 4.06 (m, 1H), 3.64 (t,  $J$  = 6.4 Hz, 2H), 3.13 (m, 1H), 2.49 – 2.29 (m, 3H), 1.93 (m, 2H), 1.76 – 1.60 (m, 3H), 1.32 (m, 1H), 1.02 (s, 3H), 0.91 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H);  $^{13}C$  NMR (151 MHz,  $CDCl_3$ ):  $\delta$  = 64.7, 62.5, 61.1, 54.3, 48.4, 33.3, 30.1, 29.4, 26.0, 25.2, 18.4, 1.0, -5.3; HRMS(ESI):  $m/z$  calculated for  $C_{16}H_{35}NClOSi$   $\{M+H^+\}$ : 320.2171. Found: 320.2173.

**1-Butyl-3-chloro-4,4-dimethylpiperidine (2f)** was prepared according to the general procedure of method B from 0.412 g (2.00 mmol) **3f**. The title compound was obtained after column chromatography (n-pentane/TBME 9:1,  $R_f$  = 0.10) as a slightly yellow oil (0.203 g, 1.08 mmol, 54%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.97 – 3.81 (m, 1H), 3.01 – 2.85 (m, 1H), 2.73 – 2.60 (m, 1H), 2.46 – 2.34 (m, 2H), 2.30 (t,  $J$  = 10.9 Hz, 1H), 2.26 – 2.13 (m, 1H), 1.69 – 1.53 (m, 2H), 1.52 – 1.39 (m, 2H), 1.31 (h,  $J$  = 7.3 Hz, 2H), 1.06 (s, 3H), 0.98 (s, 3H), 0.91 (t,  $J$  = 6.8 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 65.9, 56.9, 55.9, 48.2, 38.0, 33.8, 28.3, 28.1, 19.7, 18.0, 13.0 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{11}\text{H}_{22}\text{NCl}$   $\{\text{M}+\text{H}^+\}$ : 204.1514. Found: 204.1513.

**1-Butyl-3-chloropiperidine (2g)** was prepared according to the general procedure of method B from 0.355 g (2.00 mmol) **3g**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_f$  = 0.23) as a slightly yellow oil (0.271 g, 1.54 mmol, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.09 – 3.92 (m, 1H), 3.07 (d,  $J$  = 11.0 Hz, 1H), 2.83 – 2.63 (m, 1H), 2.47 – 2.28 (m, 2H), 2.28 – 2.09 (m, 2H), 2.09 – 1.97 (m, 1H), 1.85 – 1.68 (m, 1H), 1.69 – 1.58 (m, 1H), 1.58 – 1.50 (m, 1H), 1.50 – 1.41 (m, 2H), 1.31 (h,  $J$  = 7.3 Hz, 2H), 0.91 (t,  $J$  = 7.3 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 61.5, 58.2, 56.1, 53.1, 35.0, 28.9, 24.8, 20.7, 14.0 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_9\text{H}_{18}\text{NCl}$   $\{\text{M}+\text{H}^+\}$ : 176.1201. Found: 176.1202. These data are consistent with the literature.<sup>1</sup>

**1-Butyl-3-chloro-5-methylpiperidine (2h)** was prepared according to the general procedure of method B from 0.384 g (2.00 mmol) **3h**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_f$  = 0.39/0.31) as a slightly yellow oil (0.298 g, 1.57 mmol, 79%, d.r. 80:20).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.31 (m, 1H), 3.96 (m, 1H), 3.20 (d,  $J$  = 10.5 Hz, 1H), 2.81 (d,  $J$  = 11.6 Hz, 1H), 2.70 (d,  $J$  = 11.3 Hz, 1H), 2.46 – 2.31 (m, 2H), 2.25 – 2.13 (m, 1H), 1.96 (t,  $J$  = 10.9 Hz, 1H), 1.87 – 1.69 (m, 1H), 1.56 (t,  $J$  = 10.9 Hz, 1H), 1.53 – 1.38 (m, 3H), 1.31 (h,  $J$  = 7.3 Hz, 3H), 1.16 (q,  $J$  = 12.1 Hz, 1H), 0.91 (d, 3H), 0.91 (t,  $J$  = 7.1 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 60.3, 59.6, 57.2, 56.9, 54.4, 42.9, 39.7, 30.3, 27.9, 27.8, 19.7, 19.7, 18.0, 17.8, 13.0, 13.0 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{10}\text{H}_{20}\text{NCl}$   $\{\text{M}+\text{H}^+\}$ : 190.1357. Found: 190.1360. These data are consistent with the literature.<sup>3</sup>

**1-Butyl-3-chloro-4-methylpiperidine (2i)** was prepared according to the general procedure of method B from 0.385 g (2.01 mmol) **3i**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_f$  = 0.33/0.22) as a slightly yellow oil (0.146 g, 0.770 mmol, 38%, d.r. 65:35).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.15 (m, 1H), 3.60 (td,  $J$  = 10.1, 4.0 Hz, 1H), 3.21 (ddd,  $J$  = 11.0, 4.5, 1.9 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.48 – 2.23 (m, 2H), 2.08 (t,  $J$  = 10.8 Hz, 1H), 1.97 (td,  $J$  = 11.9, 2.6 Hz, 1H), 1.87 – 1.65 (m, 1H), 1.60 – 1.37 (m, 3H), 1.37 – 1.22 (m, 2H), 1.10 (d,  $J$  = 6.3 Hz, 3H), 1.03 (d,  $J$  = 6.5 Hz, 3H), 0.91 (td,  $J$  = 7.3, 1.1 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 63.4, 61.7, 58.2, 57.9, 53.4, 39.9, 35.2, 33.8, 29.1, 28.9, 20.8, 20.7, 19.2, 14.1, 14.0 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{10}\text{H}_{20}\text{NCl}$   $\{\text{M}+\text{H}^+\}$ : 190.1357. Found: 190.1358. These data are consistent with the literature.<sup>3</sup>

**1-Butyl-3-chloro-5,5-diphenylpiperidine (2j)** was prepared according to the general procedure of method B from 0.661 g (2.00 mmol) **3j**. The title compound was obtained after column

chromatography (n-pentane/TBME 4:1,  $R_f$  = ) as a slightly yellow oil (0.551 g, 1.68 mmol, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.43 – 7.39 (m, 2H), 7.31 – 7.24 (m, 4H), 7.20 – 7.14 (m, 4H), 3.90 – 3.78 (m, 1H), 3.63 (d,  $J$  = 12.1 Hz, 1H), 3.25 (dd,  $J$  = 10.2, 3.9 Hz, 1H), 2.96 (d,  $J$  = 12.3 Hz, 1H), 2.46 (t,  $J$  = 7.4 Hz, 2H), 2.34 (t,  $J$  = 12.2 Hz, 1H), 2.23 – 2.14 (m, 2H), 1.56 (ddt,  $J$  = 20.6, 13.1, 6.4 Hz, 2H), 1.37 (h,  $J$  = 7.4 Hz, 2H), 0.96 (t,  $J$  = 7.3 Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 147.7, 145.4, 128.7, 128.5, 128.2, 126.6, 126.5, 126.1, 62.6, 61.8, 58.0, 54.0, 48.3, 46.2, 28.9, 20.8, 14.2 ppm; HRMS (ESI):  $m/z$  calculated for  $\text{C}_{21}\text{H}_{27}\text{ClN}$   $\{M+H^+\}$ : 328.1827, found: 328.1826. These data are consistent with the literature.<sup>4</sup>

**1-Butyl-3-chloro-6-methylpiperidine (2k)** was prepared according to the general procedure of method B from 0.385 g (2.01 mmol) **3k**. The title compound was obtained after column chromatography (n-pentane/TBME 4:1,  $R_f$  = 0.23/0.17) as a slightly yellow oil (0.249 g, 1.31 mmol, 66%, d.r. 83:17).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.06 – 3.82 (m, 1H), 3.39 – 3.11 (m, 1H), 2.84 – 2.56 (m, 2H), 2.56 – 2.35 (m, 1H), 2.35 – 2.09 (m, 3H), 1.80 – 1.66 (m, 1H), 1.64 – 1.47 (m, 2H), 1.47 – 1.36 (m, 3H), 1.36 – 1.22 (m, 3H), 1.07 (d,  $J$  = 6.6 Hz, 4H), 0.92 (t,  $J$  = 7.3 Hz, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 60.4, 55.0, 53.7, 53.0, 35.6, 34.5, 26.9, 20.7, 19.6, 14.0 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{10}\text{H}_{20}\text{NCl}$   $\{M+H^+\}$ : 190.1357. Found: 190.1358. These data are consistent with the literature.<sup>1</sup>

**1-Butyl-3-chloro-2-methylpiperidine (2l)** was prepared according to the general procedure of method B from 0.262 g (1.36 mmol) **3l**. The title compound was obtained after column chromatography (n-pentane/TBME 1:1) as a slightly yellow oil (0.165 g, 0.870 mmol, 64%, d.r. 78:22).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.25 – 4.01 (m, 1H), 2.95 (s, 1H), 2.73 – 2.27 (m, 4H), 1.94 – 1.77 (m, 2H), 1.76 – 1.54 (m, 2H), 1.49 – 1.36 (m, 2H), 1.33 – 1.20 (m, 2H), 1.11 (d,  $J$  = 6.5 Hz, 3H), 0.98 – 0.82 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 69.2, 62.4, 59.3, 58.0, 55.6, 54.9, 53.9, 53.3, 51.5, 47.9, 35.1, 31.1, 29.7, 27.7, 26.9, 26.4, 25.7, 24.7, 24.1, 23.3, 20.7, 20.5, 18.4, 16.3, 14.0, 1.0. HRMS(ESI):  $m/z$  calculated for  $\text{C}_{10}\text{H}_{20}\text{NCl}$   $\{M+H^+\}$ : 190.1357. Found: 190.1360. These data are consistent with the literature.<sup>3</sup>

**Methyl 3-chloro-5,5-dimethyl-1-piperidinepropanoate (2m)** was prepared according to the general procedure of method B from 0.472 g (2.00 mmol) **3m**. The title compound was obtained after column chromatography (n-pentane/TBME 6:1,  $R_f$  = 0.37) as a colourless oil (0.301 g, 1.29 mmol, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 4.19 – 3.94 (m, 1H), 3.67 (s, 3H), 3.21 – 3.08 (m, 1H), 2.82 – 2.59 (m, 2H), 2.59 – 2.32 (m, 3H), 2.08 – 1.85 (m, 2H), 1.85 – 1.73 (m, 1H), 1.39 – 1.22 (m, 1H), 0.99 (s, 3H), 0.91 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 64.3, 61.8, 54.0, 53.1, 51.6, 48.2, 33.2, 32.5, 29.3, 25.0, 14.2 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{11}\text{H}_{21}\text{NClO}_2$   $\{M+H^+\}$ : 234.1256. Found: 234.1256.

**1-Cyclopropyl-3-chloro-5,5-dimethylpiperidine (2n)** was prepared according to the general procedure of method B from 0.379 g (2.00 mmol) **3n**. The title compound was obtained after column chromatography (n-pentane/TBME 5:1,  $R_f$  = 0.78) as a colourless oil (0.258 g, 1.37 mmol, 69%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.95 (m, 1H), 3.34 – 3.20 (m, 1H), 2.51 (m, 1H), 2.14 (m, 1H), 2.03 – 1.82 (m, 2H),

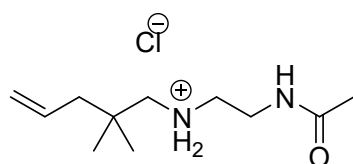
1.68 – 1.52 (m, 1H), 1.33 (m, 1H), 0.99 – 0.86 (m, 6H), 0.51 – 0.19 (m, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 65.0, 62.0, 54.2, 48.5, 37.8, 33.1, 29.3, 25.0, 6.6, 6.3 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{11}\text{H}_{22}\text{NO}$   $\{\text{M}+\text{H}^+\}$ : 184.1701. Found: 184.1698 (Degradation of 1-Cyclopropyl-3-chloro-5,5-dimethylpiperidine to 1-Cyclopropyl-3-methoxy-5,5-dimethylpiperidine observed on HRMS).

**3-Chloro-1-[(4-methoxyphenyl)methyl]-5,5-dimethylpiperidine (2o)** was prepared according to the general procedure of method B from 0.540 g (2.00 mmol) **3o**. The title compound was obtained after column chromatography (n-pentane/TBME 7:1,  $R_f$  = 0.63) as a colourless oil (0.508 g, 1.90 mmol, 95%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.21 (d,  $J$  = 8.1 Hz, 2H), 6.85 (d,  $J$  = 8.1 Hz, 2H), 4.17 – 4.01 (m, 1H), 3.81 (s, 3H), 3.54 – 3.33 (m, 2H), 3.20 – 3.00 (m, 1H), 2.45 – 2.28 (m, 1H), 2.03 – 1.86 (m, 2H), 1.77 – 1.63 (m, 1H), 1.43 – 1.29 (m, 2H), 1.04 (s, 3H), 0.88 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.7, 130.5, 129.8, 113.6, 64.4, 61.8, 61.7, 55.3, 54.3, 48.5, 33.4, 29.7, 29.3, 27.0, 25.1 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{15}\text{H}_{23}\text{NClO}$   $\{\text{M}+\text{H}^+\}$ : 268.1463. Found: 268.1463.

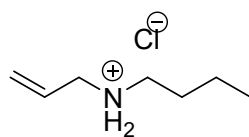
**3-Chloro-1-[(4-cyanophenyl)methyl]-5,5-dimethylpiperidine (2p)** was prepared according to the general procedure of method B from 0.530 g (2.00 mmol) **3p**. The title compound was obtained after column chromatography (n-pentane/TBME 8:1,  $R_f$  = 0.43) as a colourless oil (0.404 g, 1.54 mmol, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.54 (d,  $J$  = 7.9 Hz, 2H), 7.36 (d,  $J$  = 7.9 Hz, 2H), 4.03 (tt,  $J$  = 11.0, 4.5 Hz, 1H), 3.62 – 3.33 (m, 2H), 3.04 (dd,  $J$  = 11.0, 4.3 Hz, 1H), 2.25 (d,  $J$  = 11.0 Hz, 1H), 1.98 (t,  $J$  = 10.6 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.74 (s, 1H), 1.29 (t,  $J$  = 12.3 Hz, 1H), 0.99 (s, 3H), 0.83 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 144.4, 132.2, 129.1, 119.0, 111.0, 64.6, 62.0, 61.8, 53.8, 48.1, 33.4, 29.2, 25.1 ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{15}\text{H}_{20}\text{ClN}_2$   $\{\text{M}+\text{H}^+\}$ : 263.1310. Found: 263.1309.

## 2.3 Unsuccessful Cyclizations

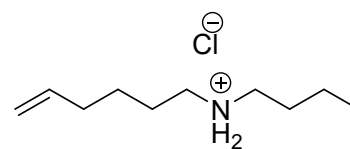
Using method B to attempt the intramolecular aminochlorination resulted in uncharacterized side products for the following precursors.



**3q**



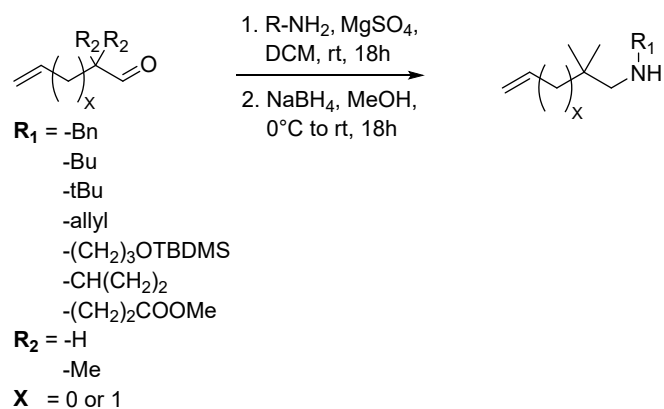
**3r**



**3s**

### 3. Experimental Procedures

#### 3.1 General Procedure for the Synthesis of Secondary Amines 1a-e, 1m, 1n and 1r



To a solution of 1 mmol/mL aldehyde were added 1.5 equivalents amine and 0.1 g/mL magnesium sulfate. The suspension was then stirred for 18 hours at room temperature and subsequently filtered. The filtrate was concentrated under reduced pressure to obtain the crude imine. The crude imine was then solved in methanol (1mmol/mL) and 1.1 equivalents of sodium borohydride was added at 0°C. The suspension was then allowed to room temperature. The suspension was then stirred for 18 hours. Then, 20% w/w aqueous NaOH solution was added. The layers were separated and the aqueous layer



was extracted three times with DCM. The combined organic layers were washed with brine and dried over sodium sulfate. After filtration, the filtrate was then concentrated under reduced pressure. The crude product can be purified by vacuum distillation.

**N-Butyl-2,2-dimethyl-4-penten-1-amine (1a)** was prepared according to the general procedure from butyl amine (51 mmol) and 2,2-dimethylpent-4-enal (58.37 mmol). The title compound was obtained after purification as a colourless liquid (7.308 g, 43.16 mmol, 85% over two steps). b.p. 100 °C (oil bath), 5 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.90 – 5.74 (m, 1H), 5.09 – 4.95 (m, 2H), 2.59 (t, *J* = 7.9, 6.6 Hz, 2H), 2.36 (s, 2H), 2.01 (d, *J* = 7.5, 1.2 Hz, 2H), 1.46 (p, *J* = 7.6 Hz, 4H), 1.33 (h, 3H), 0.97 – 0.84 (m, 9H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 135.6, 116.8, 60.4, 50.7, 44.8, 32.1, 25.6, 20.5, 14.0, 1.0 ppm; HRMS(ESI): *m/z* calculated for C<sub>11</sub>H<sub>24</sub>N {M+H<sup>+</sup>}: 170.1903. Found: 170.1903. These data are consistent with the literature.<sup>3</sup>

**N-Benzyl-2,2-dimethyl-4-penten-1-amine (1b)** was prepared according to the general procedure from benzyl amine (49 mmol) and 2,2-dimethylpent-4-enal (44.57 mmol). The title compound was obtained after purification as a colourless liquid (4.240 g, 20.85 mmol, 47% over two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.44 – 7.20 (m, 5H), 5.87 – 5.70 (m, 1H), 5.06 – 4.93 (m, 2H), 3.82 (s, 2H), 2.38 (s, 2H), 2.03 (dt, *J* = 7.6, 1.2 Hz, 2H), 0.91 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 135.4, 128.4, 126.9, 116.9, 59.4, 54.5, 44.6, 34.3, 25.5 ppm; HRMS(ESI): *m/z* calculated for C<sub>14</sub>H<sub>21</sub>N {M+H<sup>+</sup>}: 204.1747. Found: 204.1749. These data are consistent with the literature.<sup>2</sup>

**N-Propenyl-2,2-dimethyl-4-penten-1-amine (1c)** was prepared according to the general procedure from allyl amine (69 mmol) and 2,2-dimethylpent-4-enal (47.74 mmol). The title compound was obtained after purification as a colourless liquid (3.523 g, 22.99 mmol, 48% over two steps). b.p. 60 °C, 15 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.02 – 5.70 (m, 2H), 5.26 – 4.88 (m, 4H), 3.24 (dt, *J* = 6.0, 1.5 Hz, 2H), 2.36 (s, 2H), 2.01 (dt, *J* = 7.5, 1.2 Hz, 2H), 0.89 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 136.4, 134.5, 115.8, 114.6, 58.8, 52.3, 43.7, 33.2, 24.5 ppm; HRMS(ESI): *m/z* calculated for C<sub>10</sub>H<sub>20</sub>N {M+H<sup>+</sup>}: 154.1590. Found: 154.1590. These data are consistent with the literature.<sup>2</sup>

**N-tert.-butyl-2,2-dimethyl-4-penten-1-amine (1d)** was prepared according to the general procedure from tert.-butyl amine (77 mmol) and 2,2-dimethylpent-4-enal (47.43 mmol). The title compound was obtained after purification as a colourless liquid (3.670 g, 21.68 mmol, 46% over two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.91 – 5.74 (m, 1H), 5.10 – 4.93 (m, 2H), 2.29 (s, 2H), 1.99 (d, *J* = 7.6 Hz, 2H), 1.06 (s, 9H), 0.86 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 135.9, 116.5, 52.6, 50.0, 44.5, 33.8, 29.2, 25.4 ppm; HRMS(ESI): *m/z* calculated for C<sub>11</sub>H<sub>24</sub>N {M+H<sup>+</sup>}: 170.1903. Found: 170.1905. These data are consistent with the literature.<sup>3</sup>

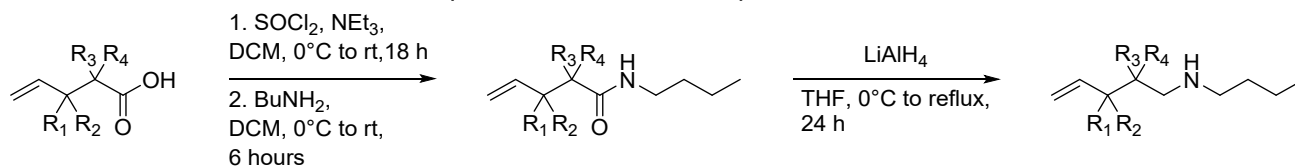
**N-[3-[[[(1,1-Dimethylethyl)dimethylsilyl]oxy]propyl]-2,2-dimethyl-4-penten-1-amine (1e)** was prepared according to the general procedure from 3-[[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-1-propanamine (56.17 mmol) and 2,2-dimethylpent-4-enal (56.15 mmol). The title compound was obtained after purification as a colourless liquid (6.930 g, 24.27 mmol, 43% over two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.89 – 5.75 (m, 1H), 5.07 – 4.95 (m, 2H), 3.69 (t, *J* = 6.2 Hz, 2H), 2.67 (t, *J* = 6.9 Hz, 2H), 2.35 (s, 2H), 2.00 (d, *J* = 7.5 Hz, 2H), 1.69 (p, 2H), 0.89 (s, 9H), 0.88 (s, 6H), 0.05 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 134.6, 115.7, 60.8, 59.5, 47.0, 43.8, 33.2, 31.9, 25.0, 24.5, 17.4, -6.3 ppm; HRMS(ESI): *m/z* calculated for C<sub>16</sub>H<sub>35</sub>NOSi {M+H<sup>+</sup>}: 286.2561. Found: 286.2562.

**N-(2,2-Dimethyl-4-penten-1-yl)-β-alanine methyl ester (1m)** was prepared according to the general procedure from β-alanine methyl ester hydrochloride (14.33 mmol) and 2,2-dimethylpent-4-enal (15.76 mmol). The title compound was obtained after purification as a colourless liquid (2.312 g, 11.60 mmol, 81%). b.p. 150°C (oil bath), 1 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.87 – 5.73 (m, 1H), 5.10 – 4.95 (m, 2H), 3.68 (s, 3H), 2.94 – 2.85 (m, 2H), 2.58 – 2.49 (m, 2H), 2.37 (s, 2H), 2.00 (d, *J* = 7.3 Hz, 2H), 0.88 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 173.4, 135.4, 117.0, 59.9, 51.6, 46.1, 44.6, 34.4, 34.3, 25.5, 14.2 ppm.

**N-(2,2-Dimethyl-4-penten-1-yl)cyclopropanamine (1n)** was prepared according to the general procedure from cyclopropyl amine (19.53 mmol) and 2,2-dimethylpent-4-enal (17.83 mmol). The title compound was obtained after purification as a colourless liquid (1.405 g, 9.170 mmol, 51% over two steps). b.p. 57°C, 15 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.92 – 5.65 (m, 1H), 5.16 – 4.91 (m, 2H), 2.48 (s, 2H), 2.21 – 2.06 (m, 1H), 1.98 (d, *J* = 7.5 Hz, 2H), 0.87 (s, 6H), 0.53 – 0.21 (m, 4H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 135.5, 116.9, 60.0, 44.6, 34.0, 31.4, 25.6, 25.5, 6.3 ppm; HRMS(ESI): *m/z* calculated for C<sub>10</sub>H<sub>19</sub>N {M+H<sup>+</sup>}: 154.150. Found: 154.1592.

**N-2-Propen-1-yl-1-butanamine (1r)** was prepared according to the general procedure from allyl amine (87.60 mmol) and *n*-butyraldehyde (79.66 mmol). The title compound was obtained after purification as a colourless liquid (5.601 g, 49.48 mmol, 62%). b.p. 47 °C, 40 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.10 – 5.76 (m, 1H), 5.37 – 4.97 (m, 2H), 3.25 (dd, *J* = 6.1, 1.3 Hz, 2H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.82 – 1.60 (bs, 1H), 1.48 (p, *J* = 7.3 Hz, 2H), 1.35 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 136.8, 115.9, 52.5, 49.1, 32.1, 20.5, 14.0 ppm; HRMS(ESI): *m/z* calculated for C<sub>7</sub>H<sub>16</sub>N {M+H<sup>+</sup>}: 114.1277. Found: 114.1279.

### 3.2 General Procedure for the Synthesis of Secondary Amines 1f-I and 1s



To a 0.3 mmol/mL solution of carboxylic acid in DCM were added 0.85 equivalents of triethyl amine and 1.1 equivalents of thionyl chloride at  $0^\circ\text{C}$ . The solution was then allowed to warm to room temperature. After 18 hours, 4 equivalents of *n*-butyl amine were added at  $0^\circ\text{C}$ . The solution was then stirred for six hours at room temperature. Then, 2M aqueous hydrochloric acid solution was added. The layers were separated and aqueous layer was extracted three times with DCM. The combined organic layers were washed with saturated sodium bicarbonate solution and dried over sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to obtain crude amide. The crude amide was dissolved in THF (0.3mmol/mL). Then, 2.2 equivalents  $\text{LiAlH}_4$  were added at  $0^\circ\text{C}$ . The suspension was then refluxed for 24 hours. The reaction was then worked up *via* Fieser workup. After filtration, the filtrate was concentrated under reduced pressure. The crude amine was then purified *via* vacuum distillation.

***N*-Butyl-3,3-dimethyl-4-penten-1-amine (1f)** was prepared according to the general procedure from 3,3-dimethylpent-4-enoic acid (21.98 mmol). The title compound was obtained after purification as a colourless liquid (2.900 g, 15.28 mmol, 72% over three steps). b.p.  $60^\circ\text{C}$ , 1 mbar<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.79$  (dd,  $J = 17.8, 10.4$  Hz, 1H), 4.98 – 4.84 (m, 2H), 2.66 – 2.46 (m, 4H), 1.55 – 1.41 (m, 4H), 1.33 (h,  $J = 7.3$  Hz, 2H), 1.00 (s, 6H), 0.91 (t,  $J = 7.3$  Hz, 3H); <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1, 109.4, 76.2, 48.8, 45.1, 41.6, 41.6, 34.9, 31.2, 31.2, 25.9, 19.5, 13.0; HRMS(ESI):  $m/z$  calculated for  $\text{C}_{11}\text{H}_{24}\text{N}$  { $\text{M}+\text{H}^+$ }: 170.1903. Found: 170.1903.

***N*-Butyl-4-penten-1-amine (1g)** was prepared according to the general procedure from pent-4-enoic acid (97.9 mmol). The title compound was obtained after purification as a colourless liquid (5.434 g, 38.47 mmol, 40% over three steps). <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 5.81$  (ddt,  $J = 16.9, 10.2, 6.6$  Hz, 1H), 5.07 – 4.88 (m, 2H), 2.69 – 2.52 (m, 4H), 2.18 – 2.01 (m, 2H), 1.58 (p,  $J = 7.4$  Hz, 2H), 1.46 (p,  $J = 7.4$  Hz, 2H), 1.32 (h,  $J = 7.3$  Hz, 2H), 1.17 (s, 1H), 0.91 (t,  $J = 7.3$  Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 138.6, 114.6, 49.8, 49.6, 32.3, 31.6, 29.3, 20.5, 14.0$  ppm; HRMS(ESI):  $m/z$  calculated for  $\text{C}_9\text{H}_{20}\text{N}$  { $\text{M}+\text{H}^+$ }: 142.1590. Found: 142.1588. These data are consistent with the literature.<sup>2</sup>

***N*-Butyl-2-methyl-4-penten-1-amine (1h)** was prepared according to the general procedure from 2-methyl-pent-4-enoic acid (94.44 mmol). The title compound was obtained after purification as a colourless liquid (8.724 g, 56.18 mmol, 59% over three steps). b.p.  $66^\circ\text{C}$ , 10mbar; <sup>1</sup>H NMR (400 MHz,

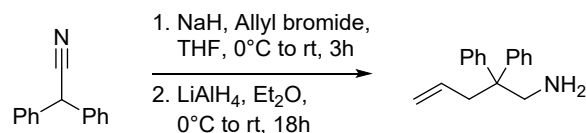
CDCl<sub>3</sub>):  $\delta$  = 5.79 (ddt,  $J$  = 17.2, 10.2, 7.1 Hz, 1H), 5.09 – 4.91 (m, 2H), 2.64 – 2.48 (m, 3H), 2.40 (dd,  $J$  = 11.7, 7.2 Hz, 1H), 2.13 (dddd,  $J$  = 13.9, 5.6, 4.3, 2.9 Hz, 1H), 1.98 – 1.83 (m, 1H), 1.70 (dt,  $J$  = 13.3, 6.7 Hz, 1H), 1.54 – 1.39 (m, 3H), 1.39 – 1.28 (m, 3H), 0.99 – 0.84 (m, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 136.2, 114.8, 55.08, 48.9, 38.5, 32.1, 31.3, 19.5, 17.0, 13.0 ppm; HRMS(ESI):  $m/z$  calculated for C<sub>10</sub>H<sub>22</sub>N {M+H<sup>+</sup>}: 156.1747. Found: 156.1750. These data are consistent with the literature.<sup>3</sup>

**N-Butyl-3-methyl-4-penten-1-amine (1i)** was prepared according to the general procedure from 3-methyl-pent-4-enoic acid (90.675 mmol). The title compound was obtained after purification as a colourless liquid (7.491 g, 48.24 mmol, 53% over three steps). b.p. 53°C, 10 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.79 (ddt,  $J$  = 17.2, 10.2, 7.1 Hz, 1H), 5.09 – 4.91 (m, 2H), 2.64 – 2.48 (m, 3H), 2.40 (dd,  $J$  = 11.7, 7.2 Hz, 1H), 2.13 (dddd,  $J$  = 13.9, 5.6, 4.3, 2.9 Hz, 1H), 1.98 – 1.83 (m, 1H), 1.70 (dt,  $J$  = 13.3, 6.7 Hz, 1H), 1.54 – 1.39 (m, 3H), 1.39 – 1.28 (m, 3H), 0.99 – 0.84 (m, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 136.2, 114.8, 55.1, 48.9, 38.5, 32.1, 31.3, 19.5, 17.0, 13.0 ppm; HRMS(ESI):  $m/z$  calculated for C<sub>10</sub>H<sub>22</sub>N {M+H<sup>+</sup>}: 156.1747. Found: 156.1750. These data are consistent with the literature.<sup>3</sup>

**N-Butyl-5-hexen-1-amine (1s)** was prepared according to the general procedure from hex-5-enoic acid (13.64 mmol). The title compound was obtained after purification as a colourless liquid (0.488 g, 3.14 mmol, 23 % over three steps). b.p. 56 °C, 10 mbar. Remaining impurities could be removed during precipitation of the hydrochloric acid salt; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 5.97 – 5.67 (m, 1H), 5.24 – 4.82 (m, 2H), 3.81 – 3.47 (m, 1H), 2.63 (dd,  $J$  = 8.0, 6.0 Hz, 2H), 2.26 – 1.96 (m, 2H), 1.74 – 1.12 (m, 6H), 0.91 (t,  $J$  = 7.1 Hz, 1H) ppm; HRMS(ESI):  $m/z$  calculated for C<sub>10</sub>H<sub>22</sub>N {M+H<sup>+</sup>}: 156.1747. Found: 156.1748.

### 3.3 Procedures for the Synthesis of Secondary Amines 1j and 1k

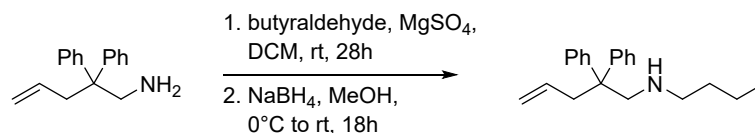
#### 2,2-Diphenyl-4-penten-1-amine (J)



To a suspension of 1.576 g NaH (60% in mineral oil, 39.42 mmol) in 35 mL THF was added dropwise a solution of 6.923 g (35.82 mmol) diphenylacetonitrile in 35 mL THF at 0°C. After one hour, 3.39 mL (39.23 mmol) allyl bromide were added. The mixture was then allowed to warm to room temperature. After another two hours, 20 mL saturated ammonium chloride solution were added at 0°C. The layers were separated and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed with brine and dried over magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The residue was solved in diethyl ether and then added dropwise to a suspension of 2.806 g (73.94 mmol) LAH in 35 mL diethyl ether at 0°C. The mixture was

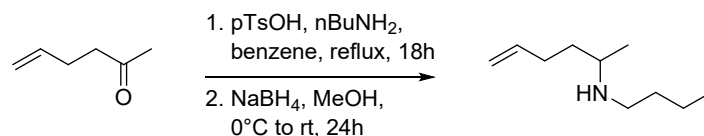
then allowed to warm to room temperature. After 18 hours, 3 mL water were added, followed by 3 mL 20% w/w aqueous NaOH solution and another 9 mL water at 0°C. After the addition of magnesium sulfate, the suspension was filtered. The filtrate was concentrated under reduced pressure to yield 6.997 g (29.48 mmol, 82% over two steps) **J**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.32 – 7.26 (m, 4H), 7.23 – 7.16 (m, 6H), 5.46 – 5.35 (m, 1H), 5.09 – 4.95 (m, 2H), 3.33 (s, 2H), 2.93 (d, J = 7.1 Hz, 2H), 0.84 (bs, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 146.4, 134.8, 128.3, 128.2, 126.2, 117.8, 51.5, 48.7, 41.3 ppm; HRMS(ESI): m/z calculated for C<sub>17</sub>H<sub>20</sub>N {M+H<sup>+</sup>}: 238.1590, found: 238.1591.

### **N-Butyl-2,2-diphenyl-4-penten-1-amine (1j)**



To a solution of 6.997 g (29.48 mmol) **J** in 30 mL DCM were added 3.80 mL butyraldehyde (42.16 mmol) and 5.0 g magnesium sulfate. After 28 hours, the suspension was filtered. The filtrate was then concentrated under reduced pressure. The residue was taken up in 30 mL methanol and 1.664 g (43.99 mmol) sodium borohydride were added at 0°C. The suspension was then allowed to warm to room temperature. After 18 hours, 20 mL 20% w/w aqueous sodium hydroxide solution were added. The layers were separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with brine and dried over sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure to yield 7.005 g (23.87 mmol, 81%) **1j**. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.29–7.25 (m, 4H), 7.20–7.17 (m, 6H), 5.43–5.34 (m, 1H), 5.04–4.93 (m, 2H), 3.19 (s, 2H), 3.01 (d, J = 7.1 Hz, 2H), 2.52 (m, 2H), 1.37–1.31 (m, 2H), 1.27–1.19 (m, 3H), 0.84 (t, J = 7.3 Hz) ppm; HRMS (ESI): m/z calculated for C<sub>21</sub>H<sub>28</sub>N<sup>+</sup> {M+H<sup>+</sup>}: 294.2216, found: 294.2216. These data are consistent with the literature.<sup>5</sup>

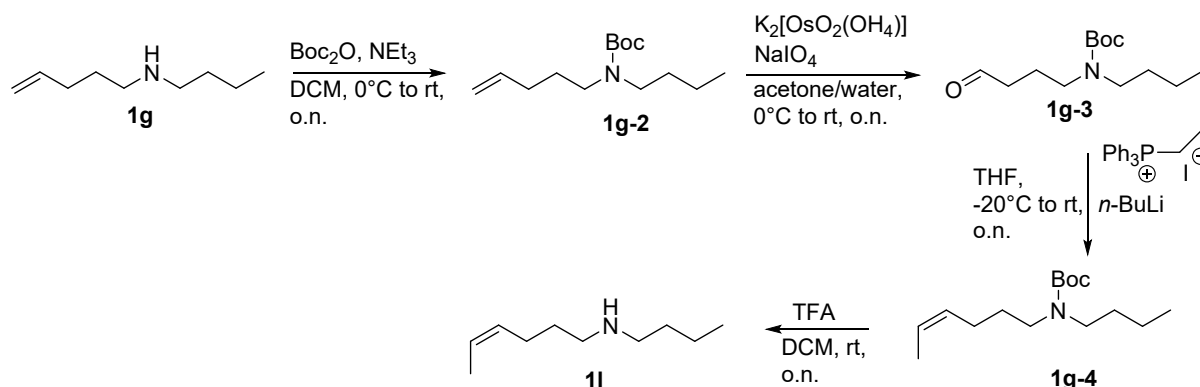
### **N-Butyl-5-hexen-2-amine (1k)**



To a solution of 2.899 g (29.54 mmol) hex-5-en-2-one in 50 mL benzene were added 0.136 g (0.790 mmol) p-toluenesulfonic acid and 6.35 mL (64.25 mmol) n-butylamine. The suspension was then refluxed over a short column with 3 angstrom molecular sieves. After 18 hours, the suspension was concentrated under reduced pressure. The residue was taken up with n-pentane, filtered, and the

filtrate was again concentrated under reduced pressure. The residue was taken up in 30 mL methanol. Then, 1.433 g (37.88 mmol) sodium borohydride were added at 0°C. After 24 hours, 20 mL 20% w/w aqueous NaOH were added. The solution was then extracted three times with DCM. The combined organic layers were washed with brine and dried over sodium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The title compound was obtained after vacuum distillation as a colourless oil (2.332 g, 15.02 mmol, 51% over two steps). b.p. 51°C, 6 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.11 – 4.86 (m, 2H), 2.69 – 2.58 (m, 2H), 2.54 (dt, *J* = 11.2, 7.2 Hz, 1H), 2.17 – 1.99 (m, 2H), 1.64 – 1.49 (m, 1H), 1.49 – 1.40 (m, 3H), 1.35 (dddd, *J* = 13.8, 8.2, 6.7, 1.9 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 137.8, 113.4, 51.7, 46.0, 35.2, 31.6, 29.4, 19.6, 19.3, 13.0 ppm; HRMS (ESI): *m/z* calculated for C<sub>10</sub>H<sub>22</sub>N {M+H<sup>+</sup>}: 156.1747. Found: 156.1746. These data are consistent with the literature.<sup>6</sup>

### 3.4 Procedure for the Synthesis of Secondary Amine 1l from 1g



To a solution of 5.624 g (39.81 mmol) **1g** in 50 mL DCM were added 8.273 mL (59.68 mmol) triethyl amine and 9.513 g (43.59 mmol) tert. butyl dicarbonate at 0°C. The mixture was then allowed to warm to room temperature. After 18 hours, 10 mL saturated ammonium chloride solution were added. The layers were separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with brine and dried over magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The crude residue was purified *via* column chromatography (cyclohexanes/EtOAc, 9:1) to obtain 9.059 g (37.53 mmol, 94%) **1g-2**.

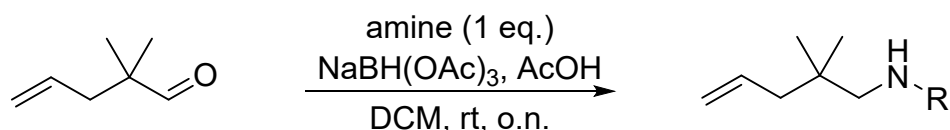
To a solution of 7.059 g (29.24 mmol) in 150 mL acetone was added a solution of 0.520 g (1.41 mmol) potassium osmate dihydrate at 0°C. Then, 24.587 g (114.95 mmol) sodium metaperiodate were added. The suspension was then allowed to warm to room temperature. After 18 hours, the suspension was

filtered and the filtrate was concentrated under reduced pressure. To the remaining emulsion, 100 mL ethyl acetate was added. The organic layer was then washed two times with sodium thiosulfate solution. The organic layer was then concentrated under reduced pressure. The crude product was then purified via column chromatography (cyclohexanes/EtOAc, 2:1) to obtain 6,099 g (25.06 mmol, 86%) **1g-3**.

To a solution of 10.310 g (24.65 mmol) ethyl triphenylphosphonium iodide in 200 mL THF was added 11.84 mL (29.60 mmol) 2.5M solution *n*-BuLi in hexanes. The suspension was then stirred for 30 minutes. Then, the mixture was cooled to -20°C and a solution of 3.00 g (12.33 mmol) **1g-3** in 100 mL THF was added. After 20 hours, the mixture was concentrated under reduced pressure. The crude residue was then purified via column chromatography to obtain 3.259 g crude **1g-4** that was used in the next step without further purification.

To a solution of 1.200 g (<4.698 mmol) crude **1g-4** in 60 mL DCM were added 4.7 mL (61.38 mmol) trifluoroacetic acid at 0°C. The solution was then allowed to warm to room temperature. After 18 hours, 10 mL 20% w/w aqueous NaOH were added. The layers were separated and the aqueous layer was extracted three times with DCM. The combined organic layers were washed with brine and dried over magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The crude residue was purified via distillation (120°C oil bath, 10 mbar) to obtain 0.260 g (1.67 mmol, 37% over two steps, d.r. 3:1) **1l** as a colourless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.54 – 5.33 (m, 2H), 2.76 – 2.51 (m, 4H), 2.21 – 1.93 (m, 2H), 1.67 – 1.52 (m, 6H), 1.47 (p, *J* = 7.3 Hz, 3H), 1.35 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 131.0, 130.2, 125.1, 124.2, 49.8, 49.7, 49.6, 32.2, 30.4, 29.9, 24.7, 20.5, 17.9, 14.0, 12.8 ppm. HRMS (ESI): *m/z* calculated for C<sub>10</sub>H<sub>22</sub>N {M+H<sup>+</sup>}: 156.1747. Found: 156.1745. These data are consistent with the literature.<sup>3</sup>

### 3.5 Procedure for the Synthesis of Secondary Amines 1o-1q



To a 3mmol/mL solution of 2,2-dimethylpent-4-enal in dichloromethane was added one equivalent of the respective amine. Then, two equivalents of glacial acetic acid were added and the reaction was cooled to 0°C, followed by the addition of 1.5 equivalents of sodium triacetoxyborohydride. The ice bath was then removed. After 18 hours, 20% aqueous sodium hydroxide solution was added. The

layers were separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were washed with brine and then dried over magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The crude residue was then subjected to vacuum distillation to afford the product.

***N*-(2,2-Dimethyl-4-penten-1-yl)-4-methoxybenzenemethanamine (1o)** was prepared according to the general procedure from 2,2-dimethylpent-4-enal (26.74 mmol) and 4-methoxybenzylamine (26.74 mmol). The product was obtained after purification as a colourless liquid (3.354 g, 14.37 mmol, 54%). b.p. 77 °C, 1mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.26 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.86 – 5.70 (m, 1H), 5.10 – 4.92 (m, 2H), 3.80 (s, 3H), 3.76 (s, 2H), 2.36 (s, 2H), 2.08 – 1.96 (m, 2H), 0.90 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 158.7, 135.4, 129.4, 116.9, 113.7, 59.2, 55.3, 53.8, 44.6, 34.3, 25.5 ppm; HRMS(ESI): *m/z* calculated for C<sub>15</sub>H<sub>24</sub>NO {M+H<sup>+</sup>}: 234.1853. Found: 234.1855.

***N*-(2,2-Dimethyl-4-penten-1-yl)-4-cyanobenzenemethanamine (1p)** was prepared according to the general procedure from 2,2-dimethylpent-4-enal (9.10 mmol) and 4-cyanobenzylamine (9.10 mmol). The product was obtained after purification as a colourless liquid (1.214 g, 5.320 mmol, 58%). b.p. 108 °C, 1 mbar; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.61 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.9 Hz, 2H), 5.85 – 5.67 (m, 1H), 5.08 – 4.94 (m, 2H), 3.85 (s, 2H), 2.33 (s, 2H), 2.02 (d, *J* = 7.4 Hz, 2H), 0.90 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 135.3, 132.1, 128.6, 119.1, 117.0, 110.6, 59.6, 54.0, 44.6, 34.4, 25.5 ppm.

***N*-[2-[(2,2-Dimethyl-4-penten-1-yl)amino]ethyl]acetamide (1q)** was prepared according to the general procedure from 2,2-dimethylpent-4-enal (44.57 mmol) and *N*-acetyethylenediamine (44.57 mmol). The product could be used without further purification (6.197 g, 31.25 mmol, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.30 (bs, 1H), 5.88 – 5.71 (m, 1H), 5.11 – 4.95 (m, 2H), 3.35 (m, 2H), 2.78 (m, 2H), 2.43 – 2.33 (m, 2H), 2.03 (d, *J* = 8.1 Hz, 2H), 1.99 (s, 3H), 0.91 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 170.3, 135.2, 117.2, 59.3, 49.1, 44.6, 38.6, 34.2, 25.5, 23.3, 6.2 ppm; HRMS(ESI): *m/z* calculated for C<sub>11</sub>H<sub>22</sub>N<sub>2</sub>ONa {M+Na<sup>+</sup>}: 221.1624. Found: 221.1627.

### 3.6 General Procedure for the Preparation of Hydrochloric Acid salts 3a-s



To a 0.05M solution of amine **1a-s** in *n*-pentane was added 1 equivalent of a 2M solution of HCl in diethyl ether. The solution was filtered and the remaining solid was then dried in vacuo. Hydrochloric acid salts **3a-s** were obtained quantitatively.

**N-Butyl-2,2-dimethyl-4-penten-1-amine hydrochloride(3a)** was prepared according to the general procedure from **1a**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.88 (ddt, *J* = 16.8, 10.4, 7.5 Hz, 1H), 5.22 – 5.08 (m, 2H), 3.12 – 2.99 (m, 2H), 2.91 (s, 2H), 2.11 (d, *J* = 7.5 Hz, 2H), 1.75 – 1.60 (m, 2H), 1.37 (h, *J* = 7.4 Hz, 2H), 1.02 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 138.4, 123.1, 61.8, 53.3, 48.3, 37.1, 31.6, 28.4, 23.8, 17.3 ppm.

**N-Benzyl-2,2-dimethyl-4-penten-1-amine hydrochloride(3b)** was prepared according to the general procedure from **1b**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 7.55 – 7.44 (m, 5H), 5.75 (ddt, *J* = 16.9, 10.3, 7.5 Hz, 1H), 5.10 - 4.97 (m, 2H), 4.26 (s, 2H), 2.85 (s, 2H), 2.04 (d, *J* = 7.5 Hz, 2H), 0.96 (s, 6H) ppm.

**N-Propenyl-2,2-dimethyl-4-penten-1-amine hydrochloride(3c)** was prepared according to the general procedure from **1c**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.98 – 5.79 (m, 2H), 5.62 – 5.47 (m, 2H), 5.24 – 5.07 (m, 2H), 3.68 (d, *J* = 6.9 Hz, 2H), 2.91 (s, 2H), 2.10 (d, *J* = 7.3 Hz, 2H), 1.02 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 138.3, 131.6, 128.9, 123.2, 61.2, 55.3, 48.3, 37.0, 28.4 ppm.

**N-tert.-butyl-2,2-dimethyl-4-penten-1-amine hydrochloride(3d)** was prepared according to the general procedure from **1d**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.89 (ddt, *J* = 16.7, 10.4, 7.4 Hz, 1H), 5.24 – 5.10 (m, 2H), 2.89 (s, 2H), 2.13 (d, *J* = 7.5 Hz, 2H), 1.38 (s, 9H), 1.02 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 138.3, 123.2, 62.7, 55.9, 48.2, 36.8, 29.2, 28.2 ppm.

**N-[3-[[[1,1-Dimethylethyl]dimethylsilyl]oxy]propyl]-2,2-dimethyl-4-penten-1-amine hydrochloride (3e)** was prepared according to the general procedure from **1e**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.89 (ddt, *J* = 16.7, 10.3, 7.4 Hz, 1H), 5.26 – 5.09 (m, 2H), 3.84 (t, *J* = 5.9 Hz, 2H), 3.23 – 3.09 (m, 2H), 2.94 (s, 2H), 2.11 (d, *J* = 7.5 Hz, 2H), 2.04 – 1.89 (m, 2H), 1.02 (s, 7H), 0.92 (s, 9H), 0.15 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 138.3, 123.2, 65.8, 62.2, 51.6, 48.3, 37.1, 32.3, 29.8, 28.4, 28.4, -1.6 ppm.

**N-Butyl-3,3-dimethyl-4-penten-1-amine hydrochloride(3f)** was prepared according to the general procedure from **1f**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.85 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.10 – 5.00 (m, 2H), 3.05 – 2.94 (m, 4H), 1.73 – 1.57 (m, 4H), 1.38 (h, *J* = 7.4 Hz, 2H), 1.05 (s, 6H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 151.4, 116.5, 51.8, 49.0, 41.8, 39.7, 32.1, 30.3, 23.7, 17.3 ppm.

**N-Butyl-4-penten-1-amine hydrochloride(3g)** was prepared according to the general procedure from **1g**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (200 MHz, D<sub>2</sub>O): δ = 5.76 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.12 – 4.87 (m, 2H), 3.13 – 2.76 (m, 4H), 2.20 – 1.92 (m, 2H), 1.81 – 1.61 (m, 2H), 1.53 (dddd, *J* = 9.8, 7.8, 4.8, 1.1 Hz, 2H), 1.44 – 1.16 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H).

**N-Butyl-2-methyl-4-penten-1-amine hydrochloride(3h)** was prepared according to the general procedure from **1h**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.86 (ddt, *J* = 17.5, 10.4, 7.1 Hz, 1H), 5.22 – 5.08 (m, 2H), 3.13 – 2.98 (m, 3H), 2.87 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.22 – 2.06 (m, 2H), 2.06 – 1.93 (m, 1H), 1.75 – 1.61 (m, 2H), 1.40 (h, *J* = 7.4 Hz, 2H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 140.3, 121.8, 57.4, 52.5, 42.5, 34.6, 31.9, 23.8, 21.0, 17.3 ppm.

**N-Butyl-3-methyl-4-penten-1-amine hydrochloride(3i)** was prepared according to the general procedure from **1i**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.76 (ddd, *J* = 17.3, 10.3, 7.7 Hz, 1H), 5.22 – 4.96 (m, 2H), 3.15 – 2.89 (m, 4H), 2.26 (hept, 1H), 1.85 – 1.57 (m, 4H), 1.47 – 1.30 (m, 2H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 147.7, 118.6, 51.9, 50.4, 39.6, 36.3, 32.1, 23.9, 23.7, 17.3 ppm.

**N-Butyl-2,2-diphenyl-4-penten-1-amine hydrochloride(3j)** was prepared according to the general procedure from **1j**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 8.70 (s, 1H), 7.39 – 7.02 (m, 10H), 5.44 – 5.19 (m, 2H), 5.14 – 4.86 (m, 1H), 3.74 – 3.46 (m, 2H), 3.29 – 3.17 (m, 2H), 2.72 – 2.19 (m, 2H), 1.67 – 1.33 (m, 2H), 1.03 (h, *J* = 7.2 Hz, 2H), 0.75 (t, *J* = 7.2 Hz, 3H).

**N-Butyl-5-hexen-2-amine hydrochloride(3k)** was prepared according to the general procedure from **1k**. The title compound was obtained after purification as a colourless solid. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 5.87 (dddd, *J* = 17.3, 10.3, 7.0, 6.2 Hz, 1H), 5.20 – 5.00 (m, 2H), 3.29 (dq, *J* = 9.2, 6.6, 4.2 Hz, 1H), 3.14 – 2.97 (m, 2H), 2.31 – 2.16 (m, 1H), 2.17 – 2.05 (m, 1H), 1.87 (dddd, *J* = 13.5, 9.3, 7.0, 4.2 Hz, 1H), 1.75 – 1.55 (m, 3H), 1.39 (h, *J* = 7.4 Hz, 2H), 1.31 (d, *J* = 6.6 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O): δ = 141.9, 120.2, 58.4, 49.0, 36.0, 33.3, 32.3, 23.8, 19.8, 17.3 ppm.

**N-Butyl-4-hexen-1-amine hydrochloride (3l)** was prepared according to the general procedure from **1l**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 5.67 - 5.38$  (m, 3H),  $3.18 - 2.91$  (m, 4H),  $2.28 - 1.97$  (m, 2H),  $1.83 - 1.51$  (m, 7H),  $1.38$  (h,  $J = 7.5$  Hz, 2H),  $0.92$  (t,  $J = 7.4$  Hz, 3H).

**N-(2,2-Dimethyl-4-penten-1-yl)- $\beta$ -alanine methyl ester hydrochloride (3m)** was prepared according to the general procedure from **1m**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 6.03 - 5.72$  (m, 1H),  $5.29 - 5.05$  (m, 2H),  $3.75$  (s, 3H),  $3.37$  (t,  $J = 6.8$  Hz, 2H),  $2.94$  (s, 2H),  $2.88$  (t,  $J = 6.8$  Hz, 2H),  $2.12$  (d,  $J = 7.4$  Hz, 2H),  $1.03$  (s, 6H) ppm.

**N-(2,2-Dimethyl-4-penten-1-yl)cyclopropanamine hydrochloride (3n)** was prepared according to the general procedure from **1n**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 5.88$  (ddt,  $J = 16.0, 11.1, 7.5$  Hz, 1H),  $5.29 - 5.04$  (m, 2H),  $3.05$  (s, 2H),  $2.85 - 2.62$  (m, 1H),  $2.09$  (dt,  $J = 7.5, 1.1$  Hz, 2H),  $1.00$  (s, 6H),  $0.94 - 0.81$  (m, 4H) ppm.

**N-(2,2-Dimethyl-4-penten-1-yl)-4-methoxybenzenemethanamine hydrochloride (3o)** was prepared according to the general procedure from **1o**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 7.43$  (d,  $J = 8.8$  Hz, 2H),  $7.05$  (d,  $J = 8.8$  Hz, 2H),  $5.73$  (ddt,  $J = 16.7, 10.5, 7.5$  Hz, 1H),  $5.17 - 4.93$  (m, 2H),  $4.20$  (s, 2H),  $3.85$  (s, 3H),  $2.82$  (s, 2H),  $2.02$  (dt,  $J = 7.4, 1.1$  Hz, 2H),  $0.95$  (s, 6H) ppm.

**N-(2,2-Dimethyl-4-penten-1-yl)-4-cyanobenzenemethanamine hydrochloride (3p)** was prepared according to the general procedure from **1p**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 7.85$  (d,  $J = 8.6$  Hz, 2H),  $7.66$  (d,  $J = 8.6$  Hz, 2H),  $5.76$  (ddt,  $J = 16.6, 10.6, 7.4$  Hz, 1H),  $5.12 - 4.91$  (m, 2H),  $4.34$  (s, 2H),  $2.88$  (s, 2H),  $2.05$  (dt,  $J = 7.5, 1.1$  Hz, 2H),  $0.97$  (s, 6H) ppm.

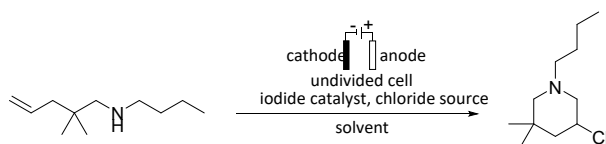
**N-[2-[(2,2-Dimethyl-4-penten-1-yl)amino]ethyl]acetamide hydrochloride (3q)** was prepared according to the general procedure from **1q**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 5.98 - 5.69$  (m, 1H),  $5.23 - 4.97$  (m, 2H),  $3.49$  (t,  $J = 5.7$  Hz, 2H),  $3.18$  (t,  $J = 5.8$  Hz, 2H),  $2.91$  (s, 2H),  $2.18 - 2.01$  (m, 2H),  $1.98$  (s, 3H),  $0.97$  (s, 6H) ppm.

**N-2-Propen-1-yl-1-butanamine hydrochloride (3r)** was prepared according to the general procedure from **1r**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):  $\delta = 5.91$  (ddt,  $J = 16.8, 10.1, 6.7$  Hz, 1H),  $5.63 - 5.37$  (m, 2H),  $3.65$  (dt,  $J = 6.7, 1.1$  Hz, 2H),  $3.16 - 2.90$  (m, 2H),  $1.80 - 1.52$  (m, 2H),  $1.52 - 1.20$  (m, 2H),  $0.91$  (t,  $J = 7.2$  Hz, 3H) ppm.

**N-Butyl-5-hexen-1-amine hydrochloride (3s)** was prepared according to the general procedure from **1s**. The title compound was obtained after purification as a colourless solid.  $^1\text{H}$  NMR (200 MHz,  $\text{D}_2\text{O}$ ):

$\delta = 5.86$  (dtd,  $J = 17.0, 6.7, 3.3$  Hz, 1H), 5.25 – 4.94 (m, 2H), 3.21 – 2.89 (m, 4H), 2.12 (m, 2H), 1.85 – 1.56 (m, 4H), 1.56 – 1.23 (m, 4H), 0.91 (t,  $J = 7.3$  Hz, 3H) ppm.

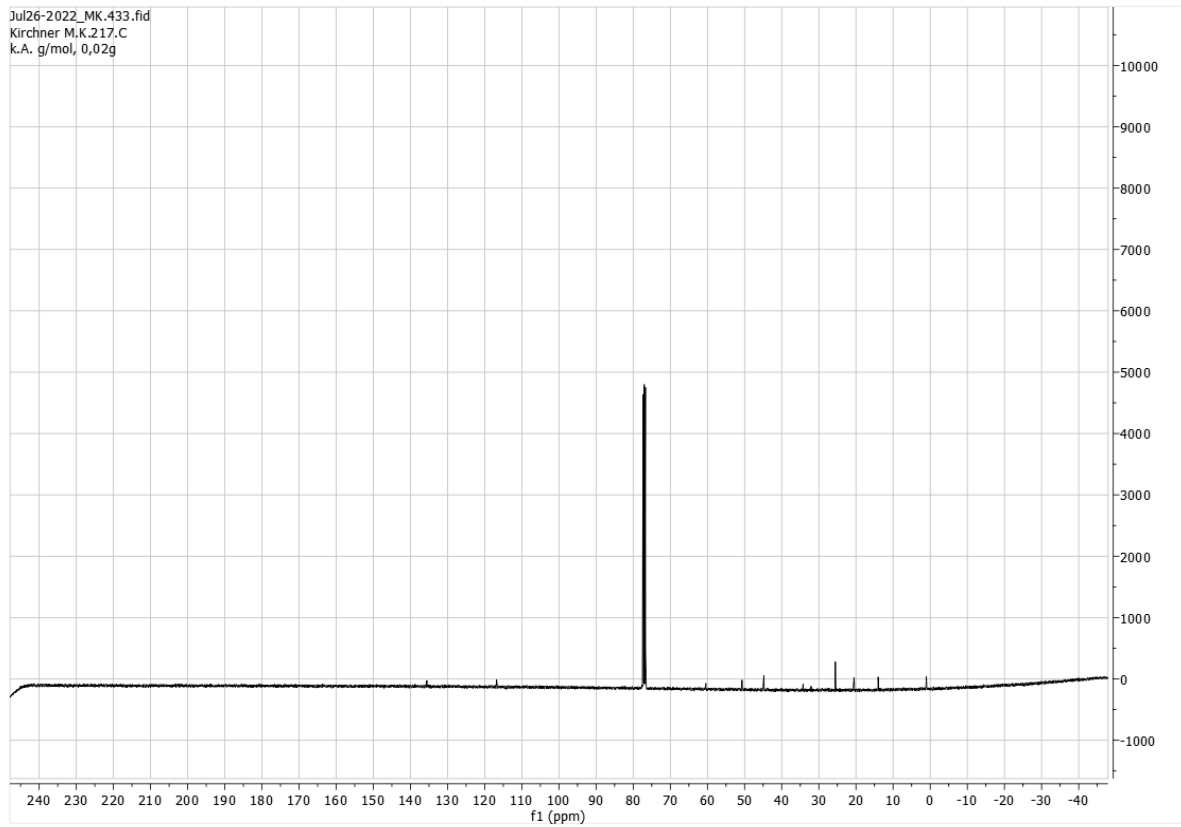
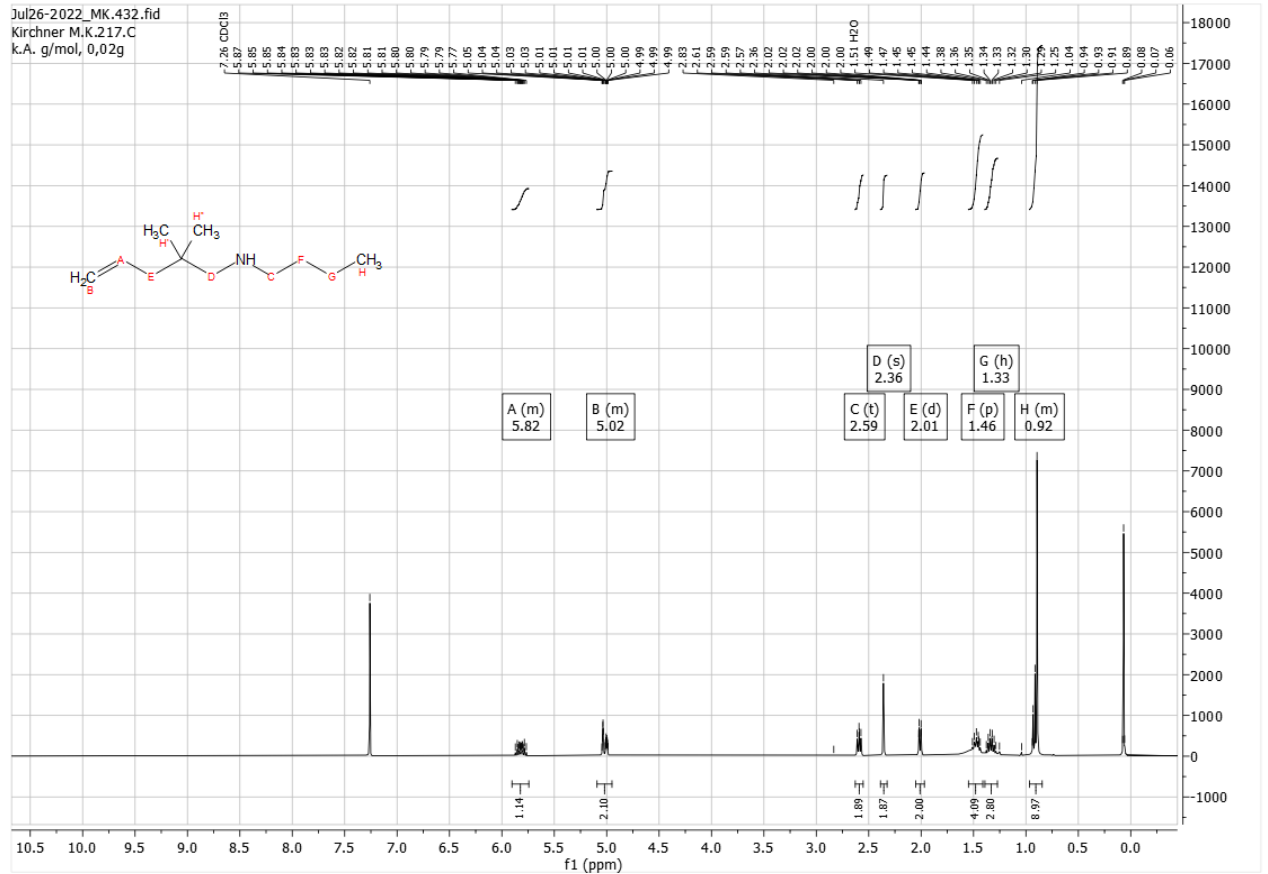
#### 4. Optimization Table



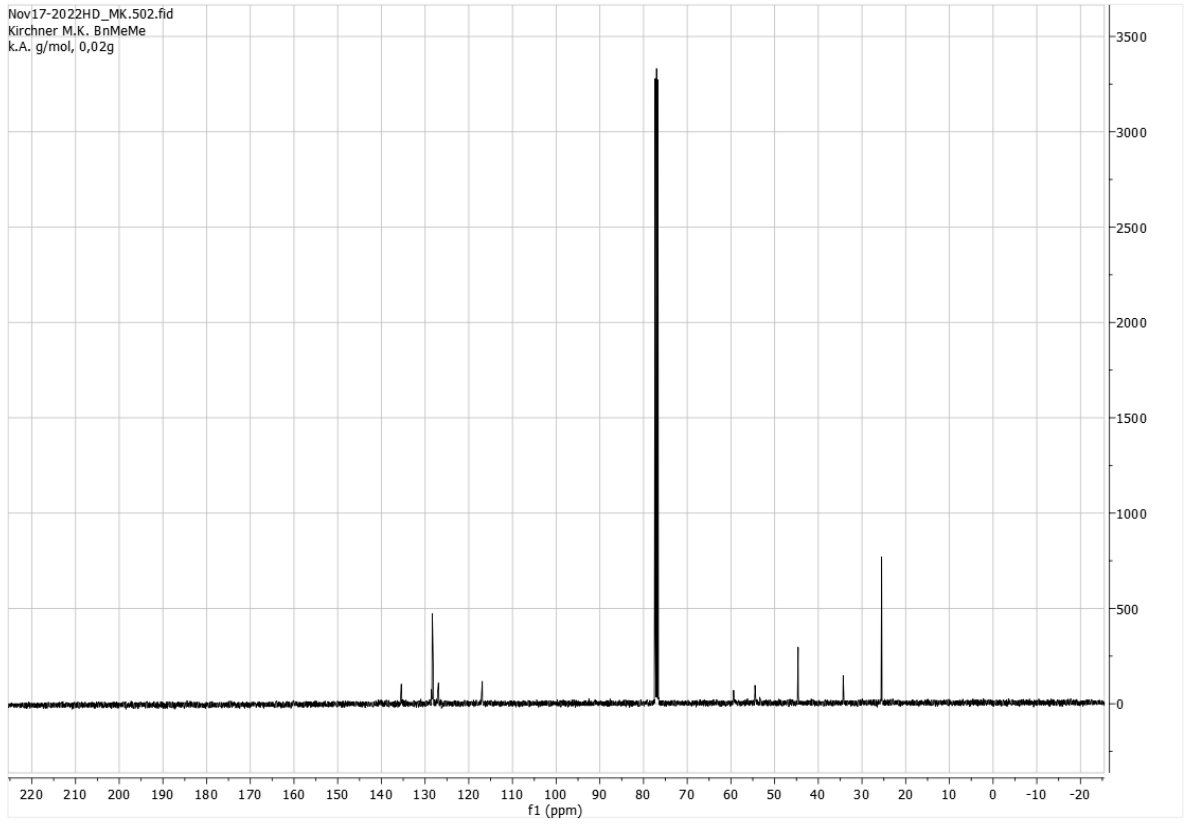
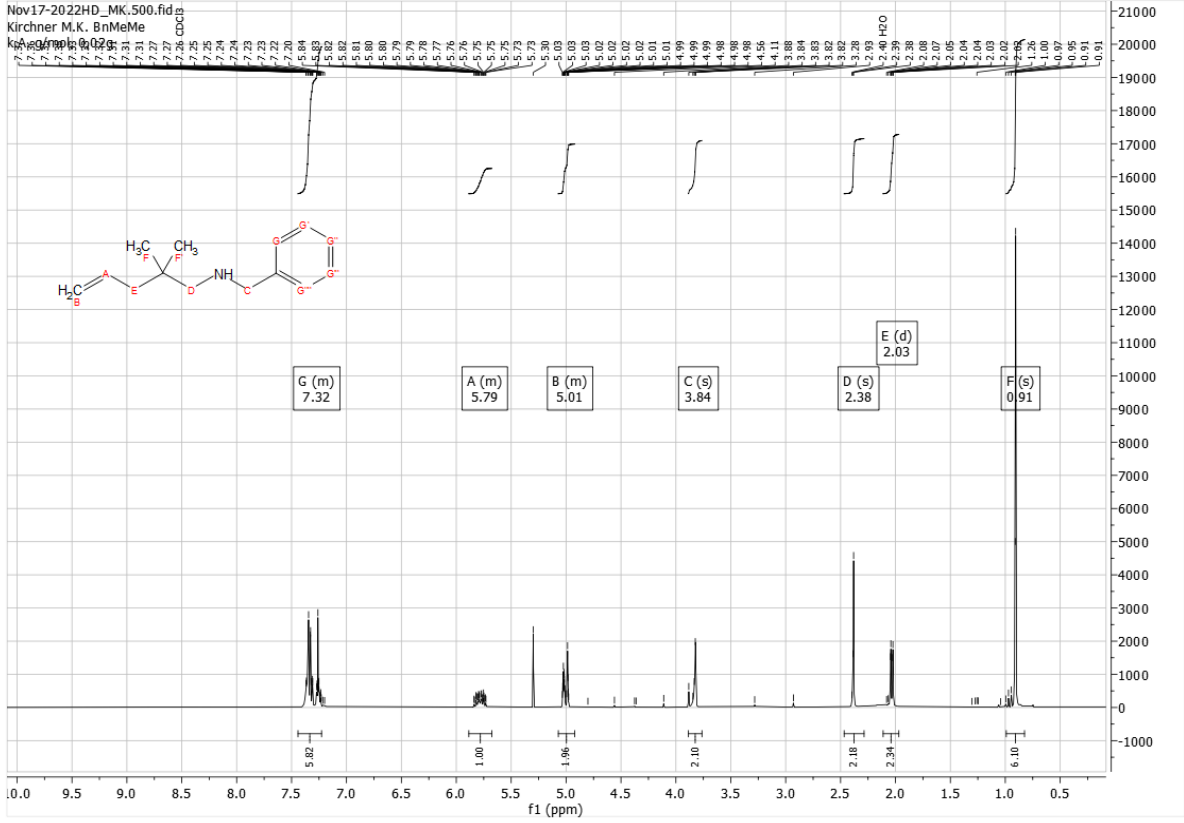
Entry	Solvent	Chloride source	Catalyst	Catalyst concentration	Cathode material	Anode material	$T / ^\circ\text{C}$	Solvent volume	Cell Potential / V	Yield / %
1	MeCN	HCl Salt	Nal	0.0125M	Nickel	Graphite	22	20 mL	3.0	75
2	MeCN	HCl Salt	LiI	0.0125M	Nickel	Graphite	22	20 mL	3.0	79
3	MeCN	HCl Salt	TBAI	0.01M	Nickel	Graphite	22	20mL	3.0	77
4	MeCN	HCl Salt	TBAI	0.025M	Nickel	Graphite	22	20mL	3.0	71
5	MeCN	HCl Salt	TBAI	0.05M	Nickel	Graphite	22	20mL	3.0	64

#### 5. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

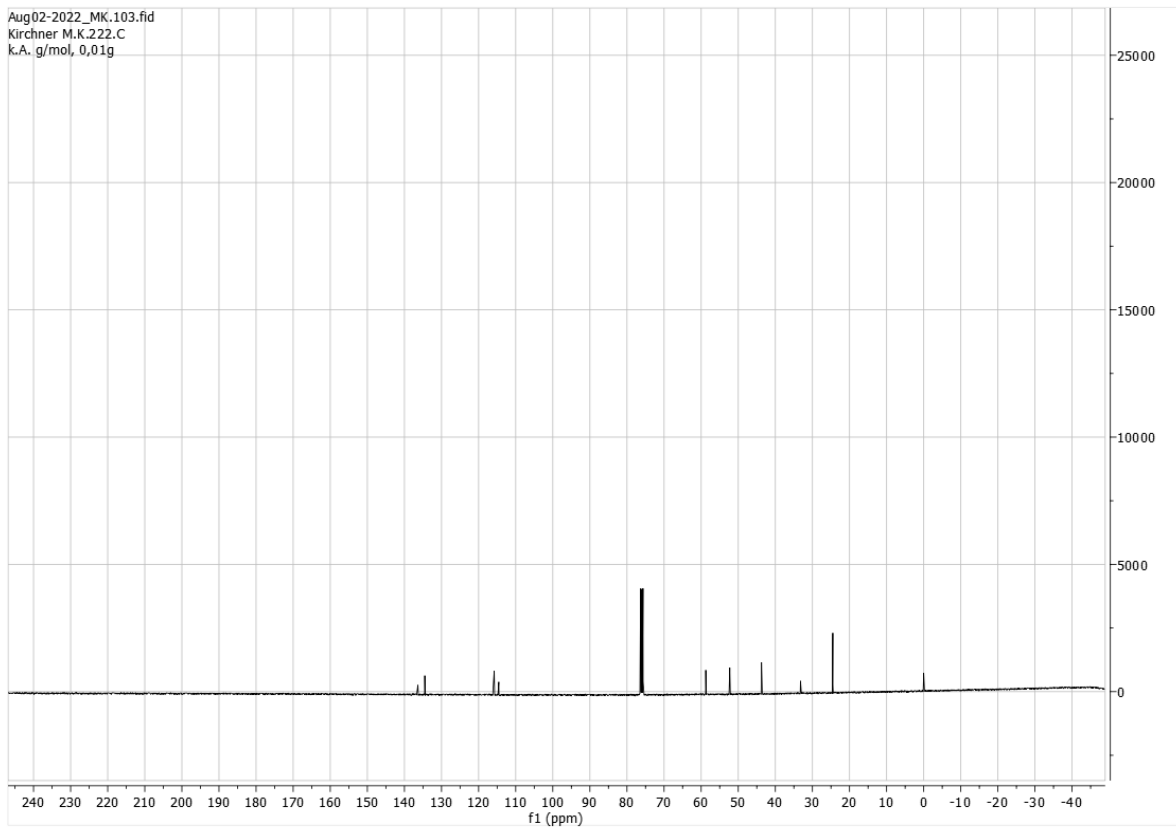
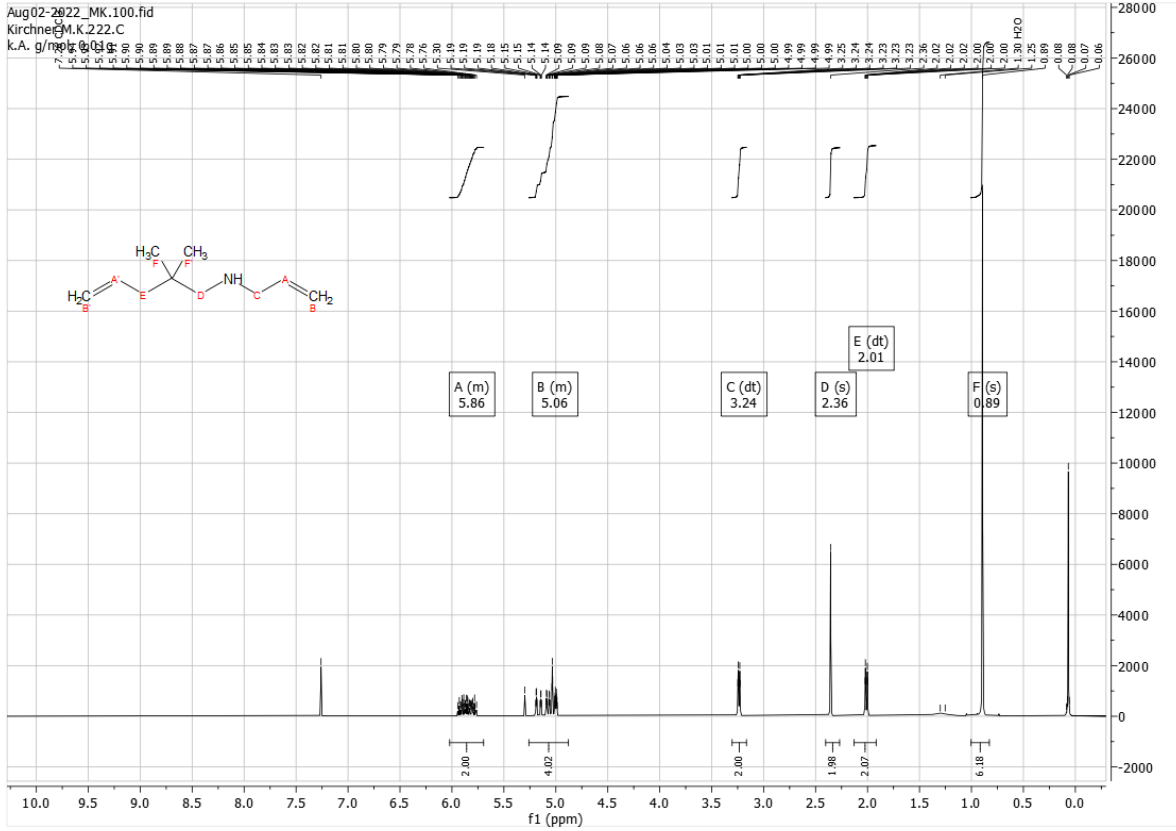
**Compound 1a**



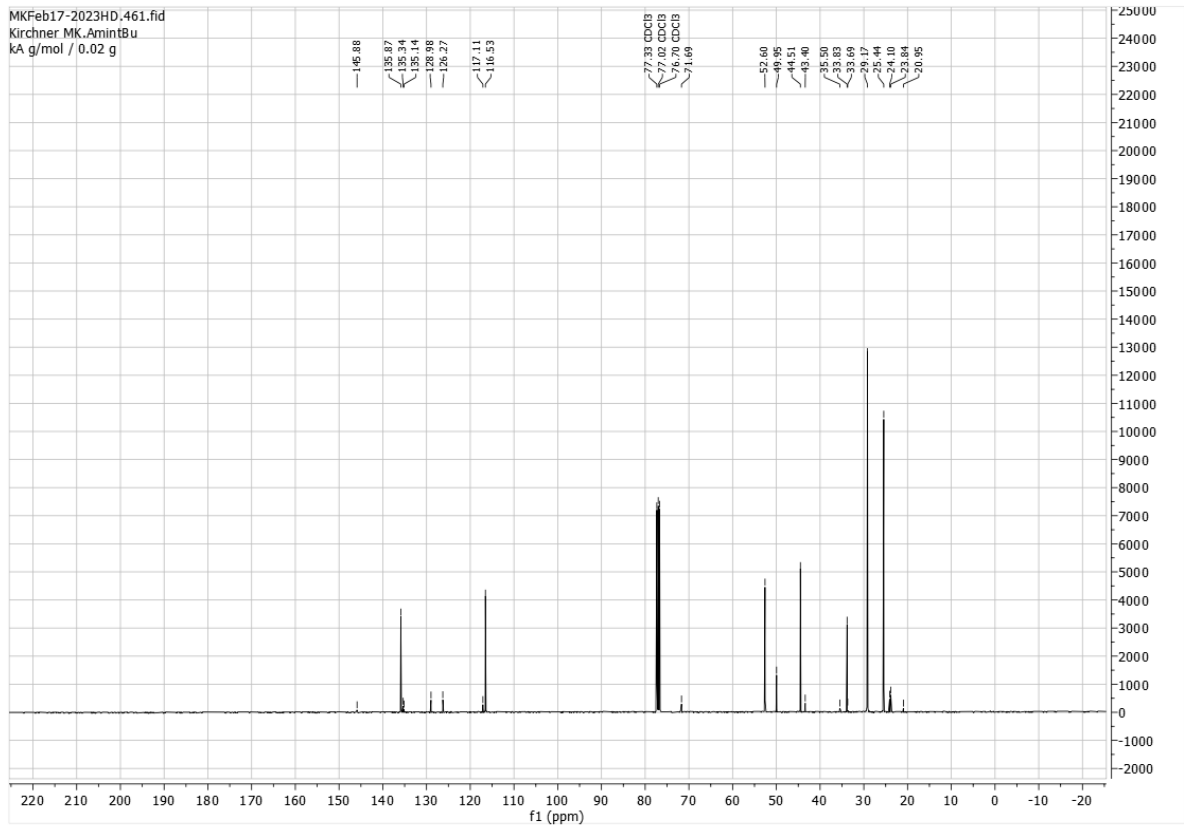
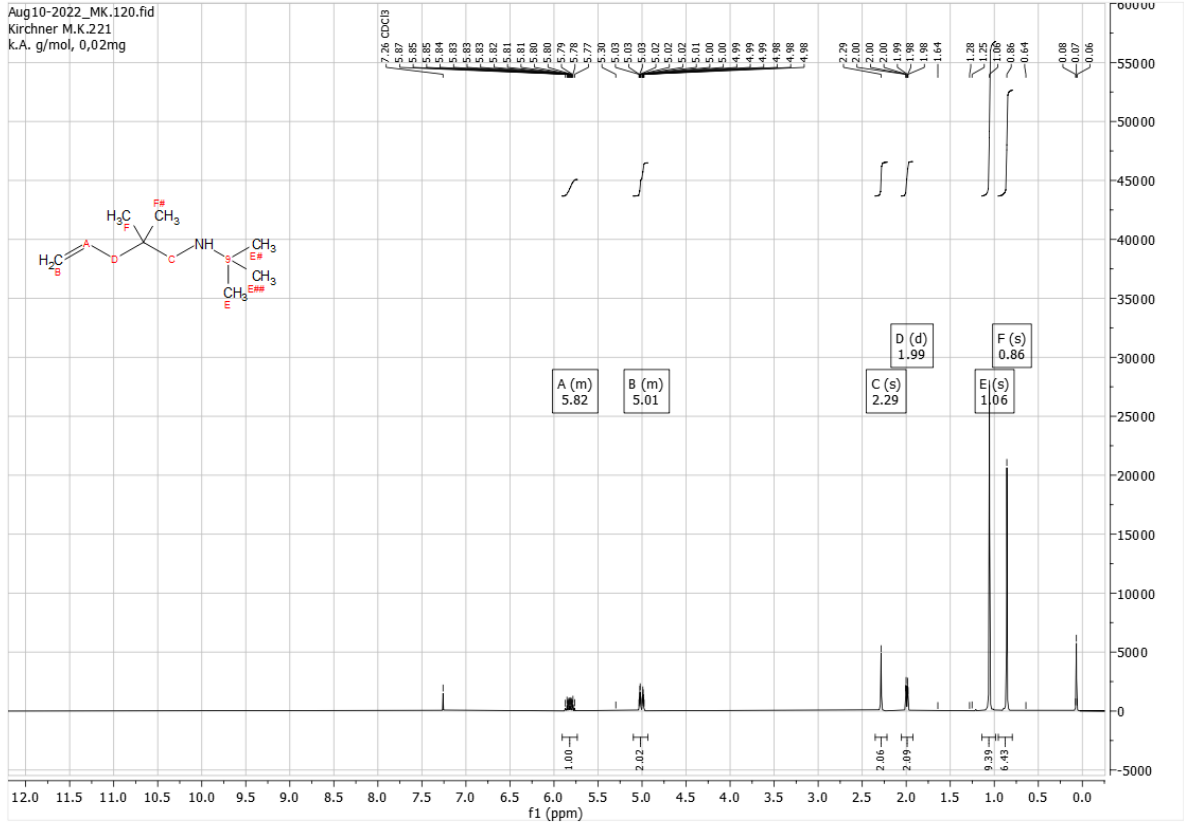
Compound 1b



Compound 1c



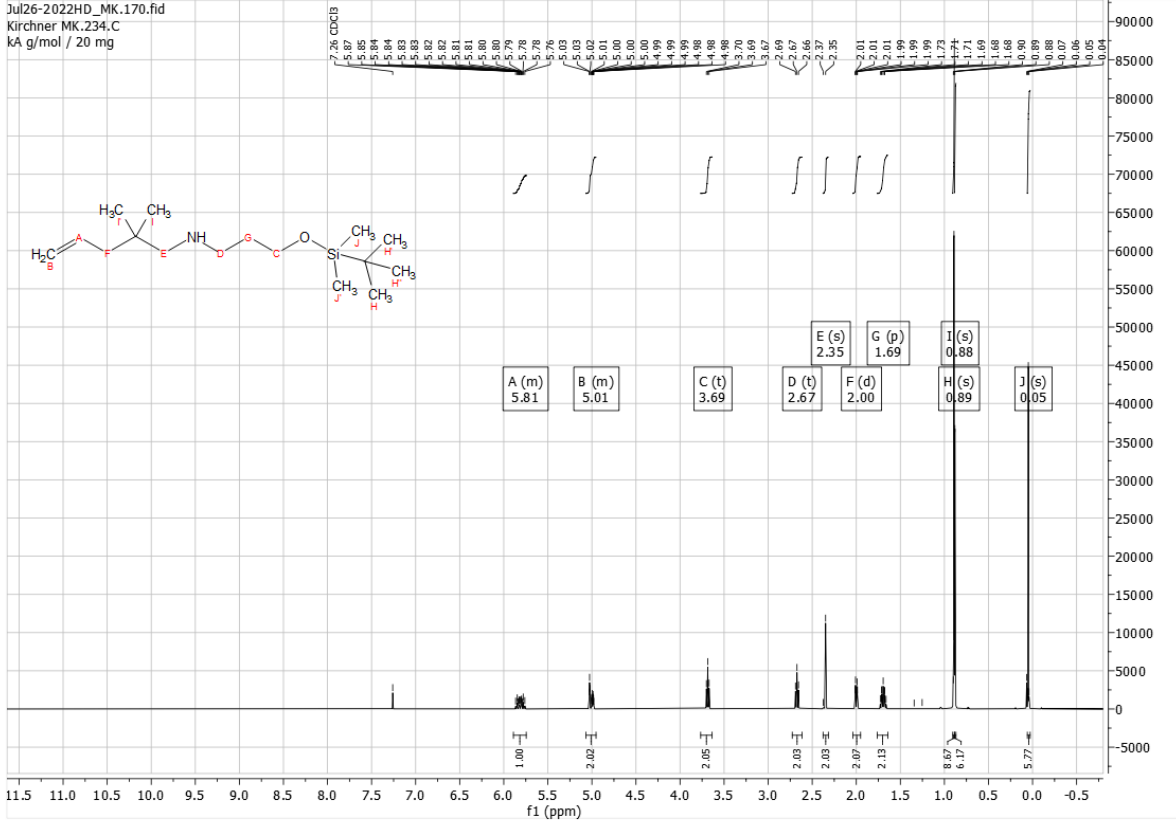
Compound 1d



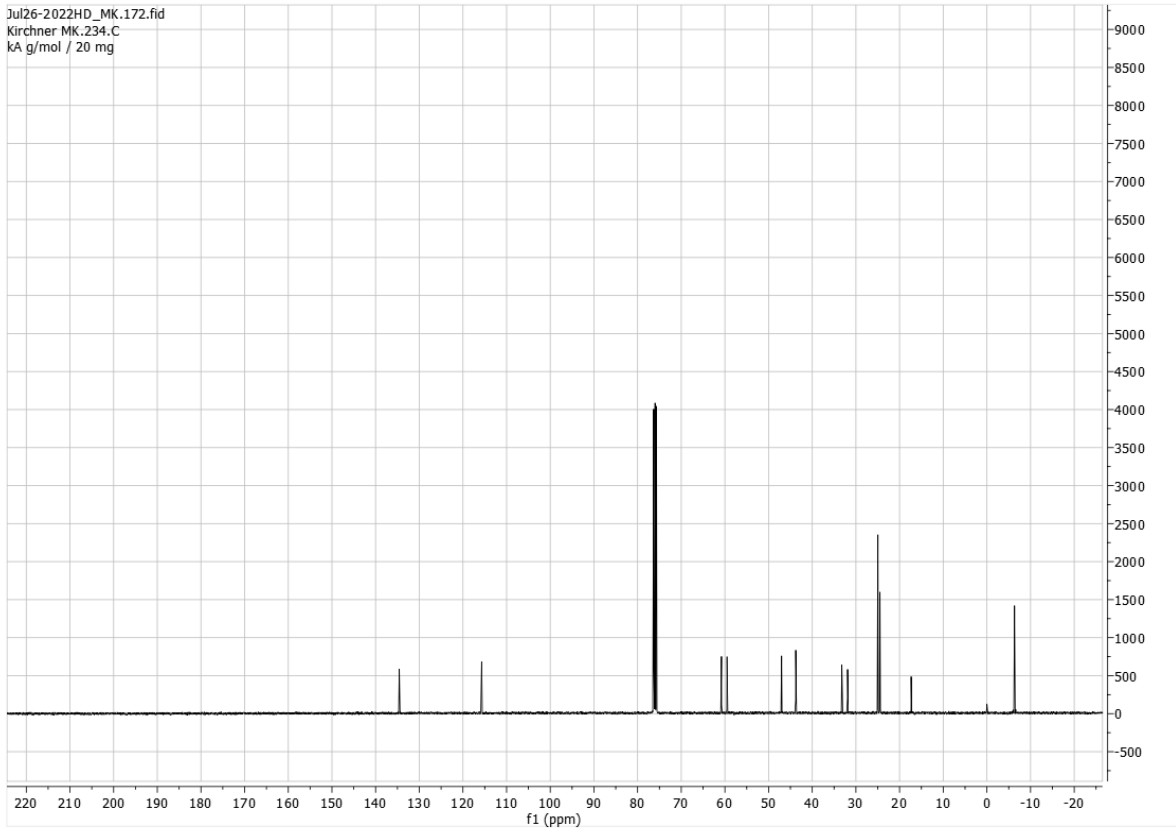
Compound 1e



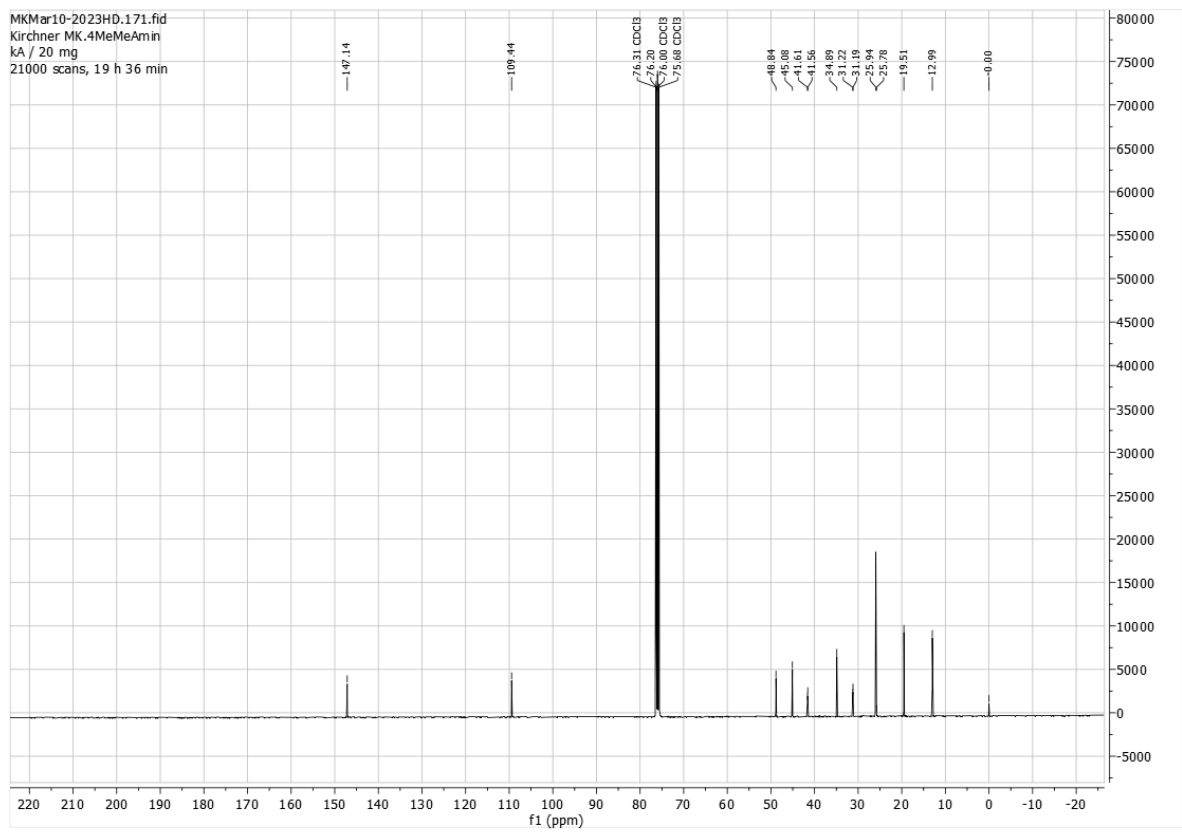
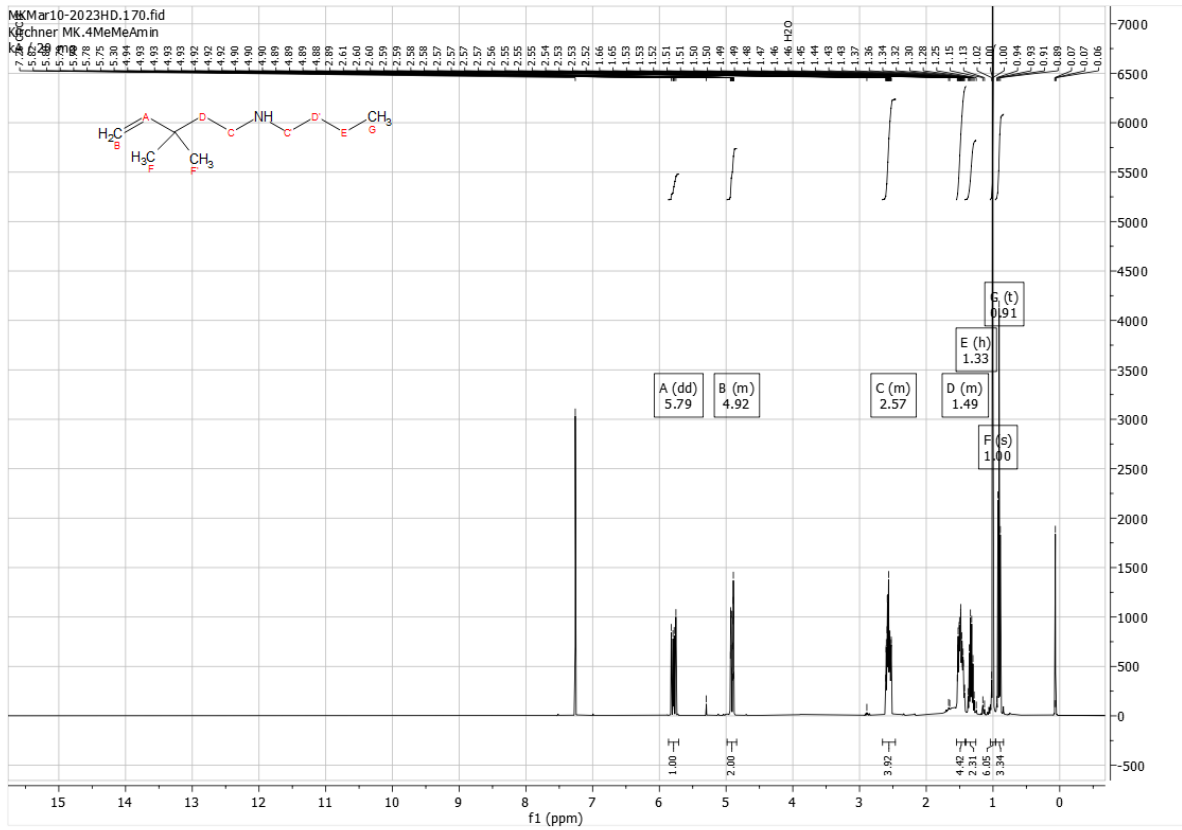
Jul26-2022HD\_MK.170.fid  
Kirchner MK.234.C  
kA g/mol / 20 mg



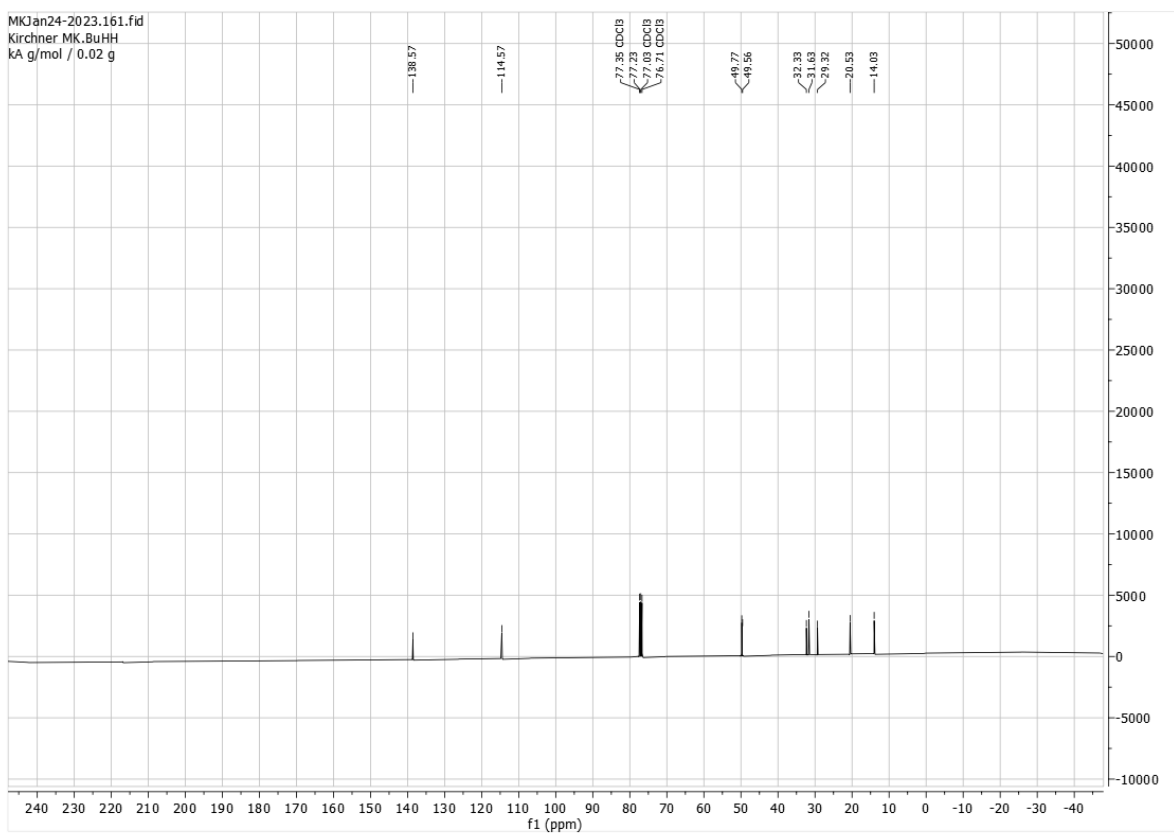
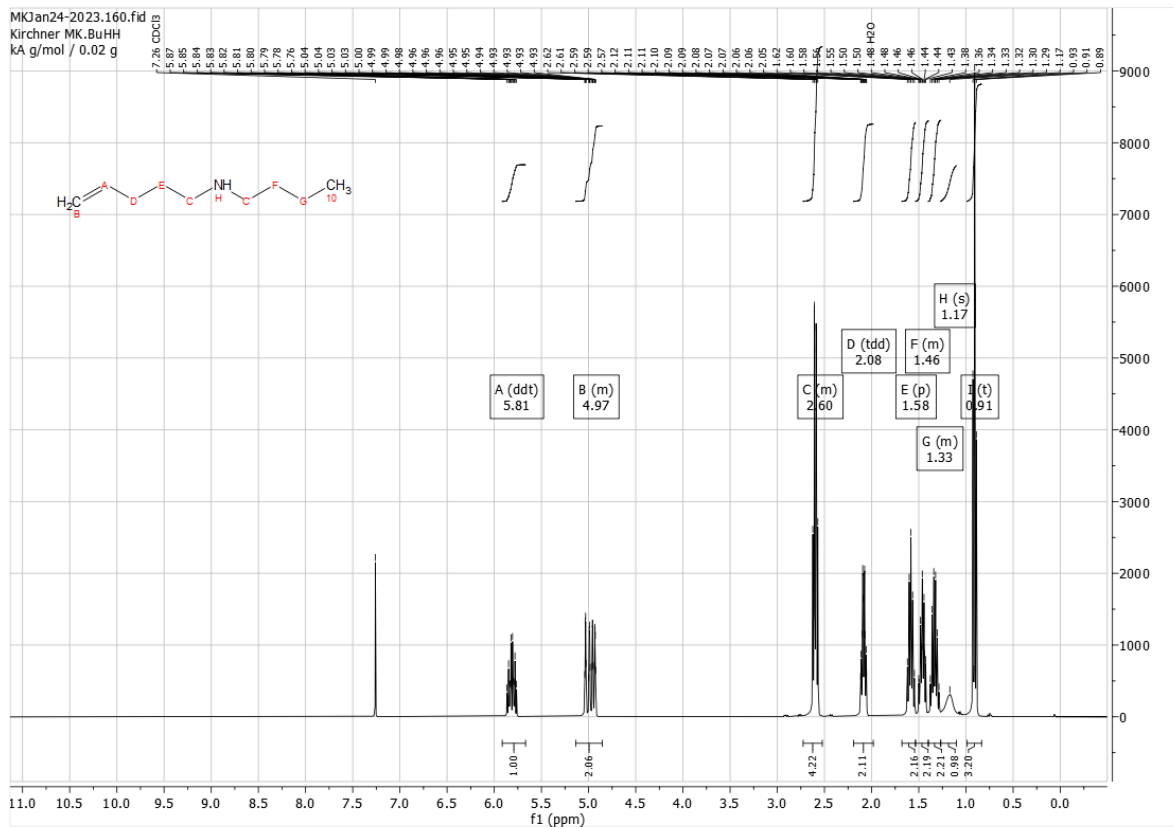
Jul26-2022HD\_MK.172.fid  
Kirchner MK.234.C  
kA g/mol / 20 mg



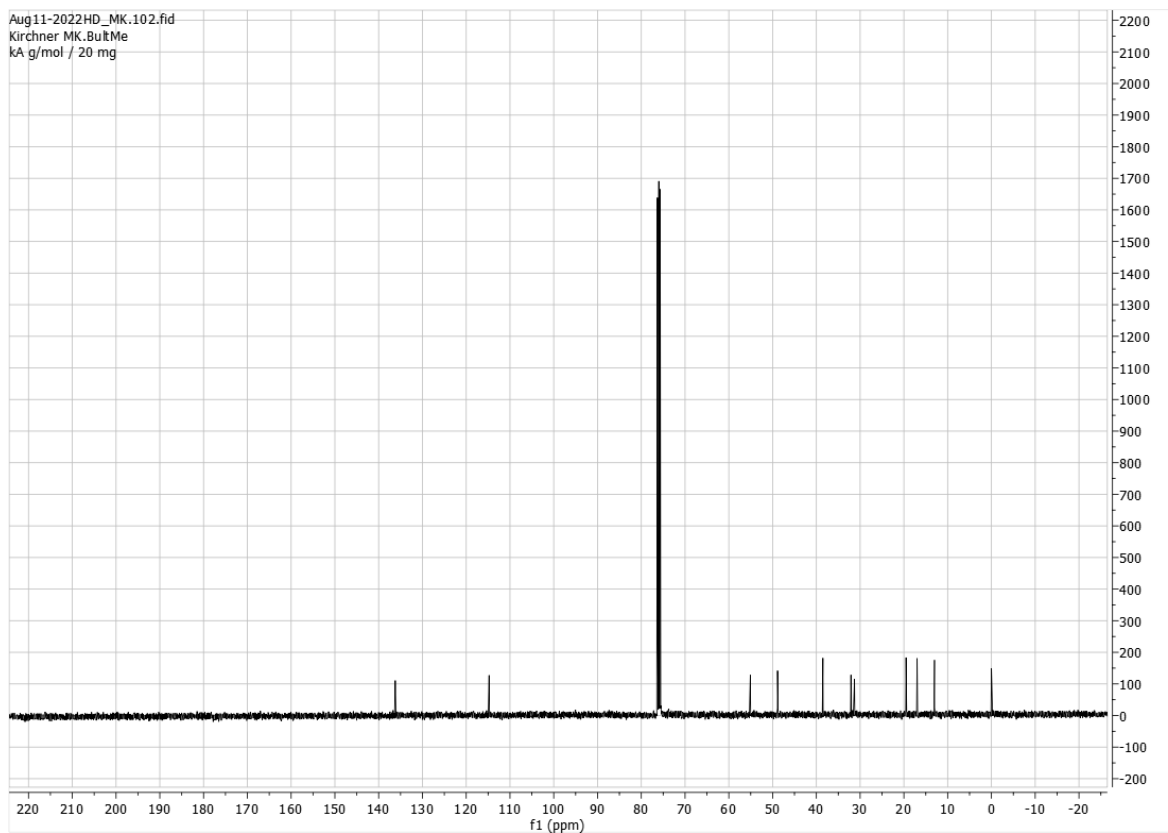
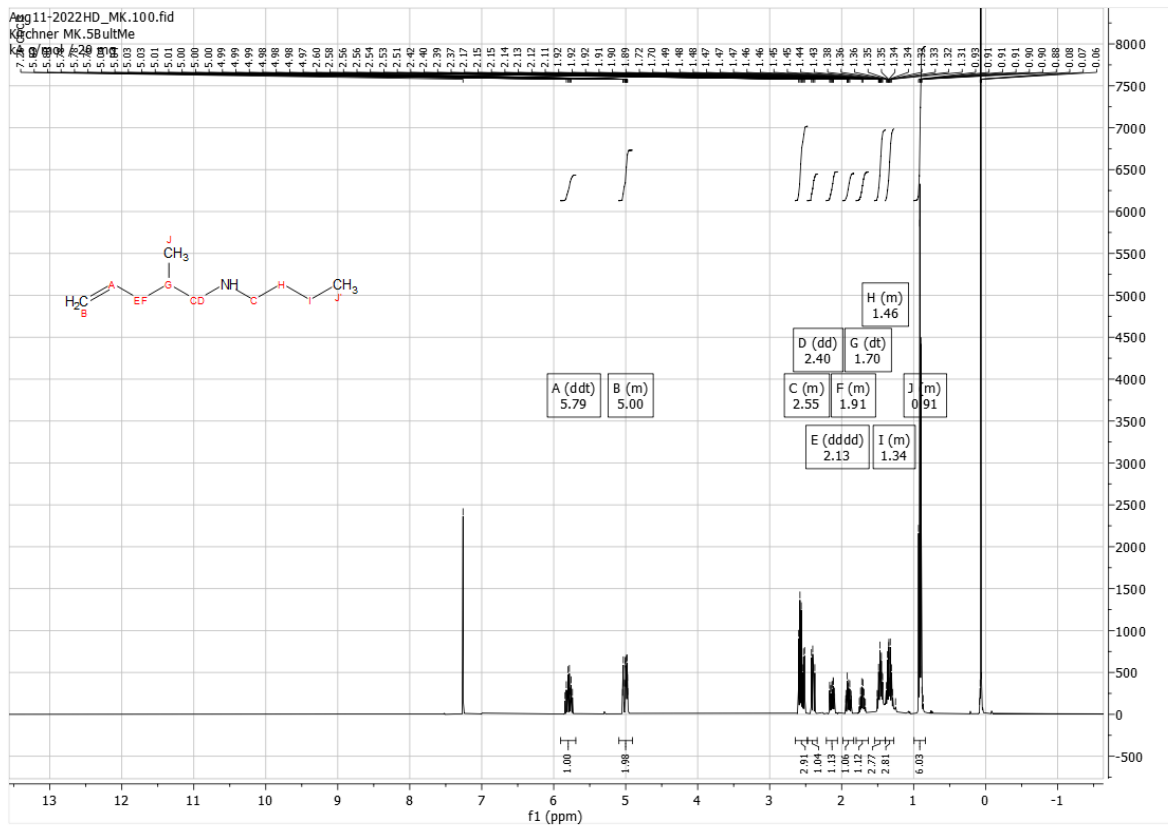
Compound 1f



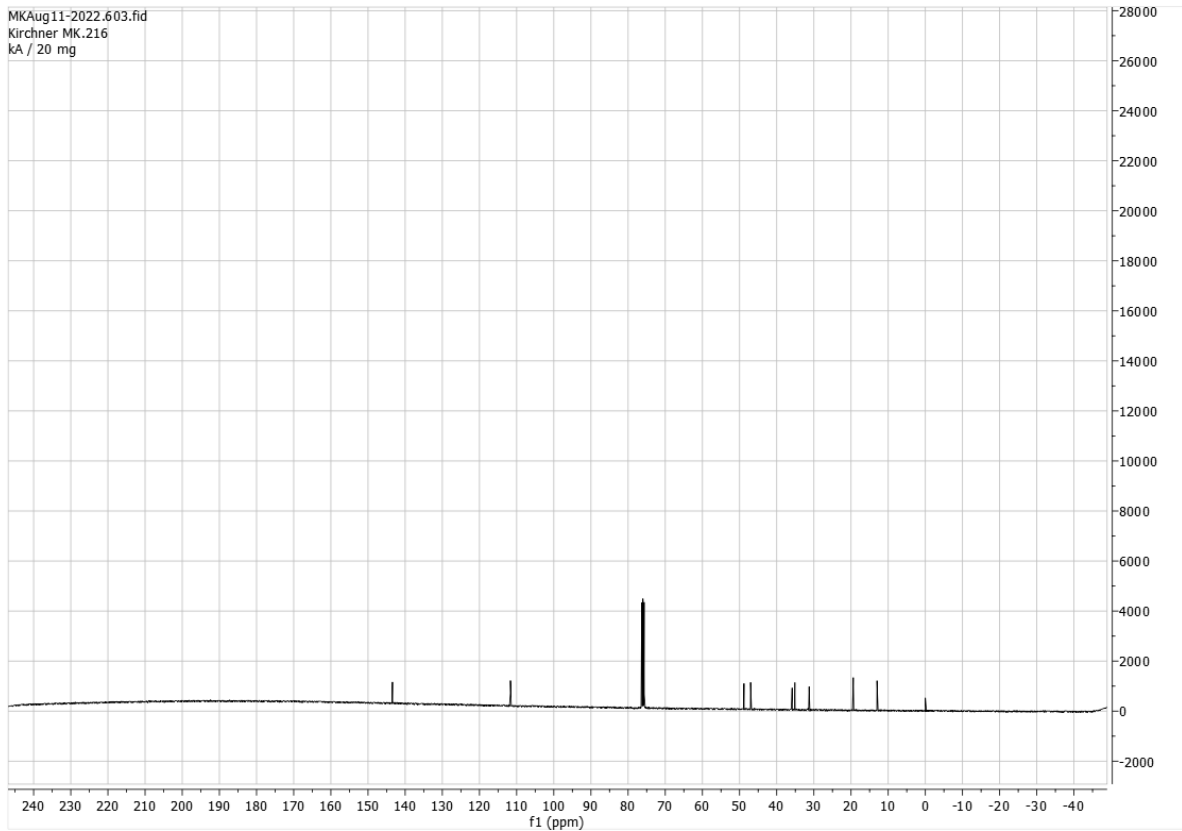
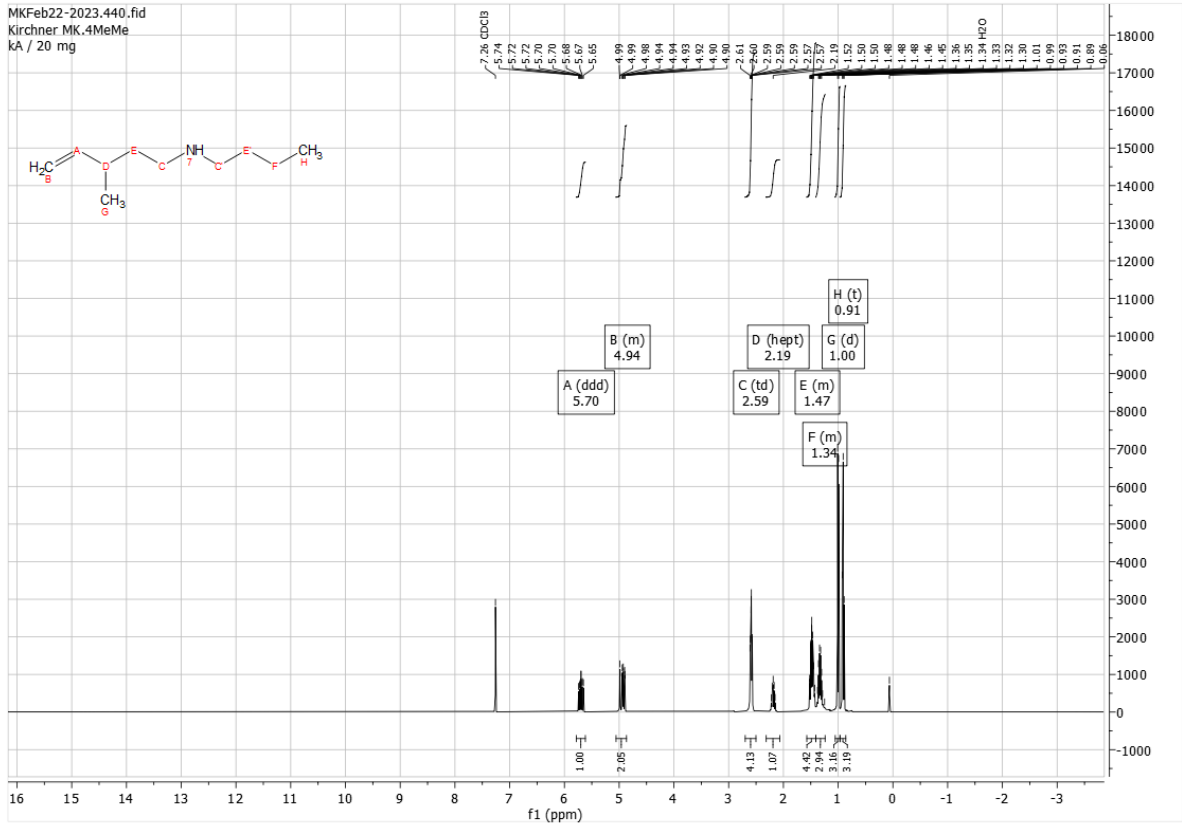
Compound 1g



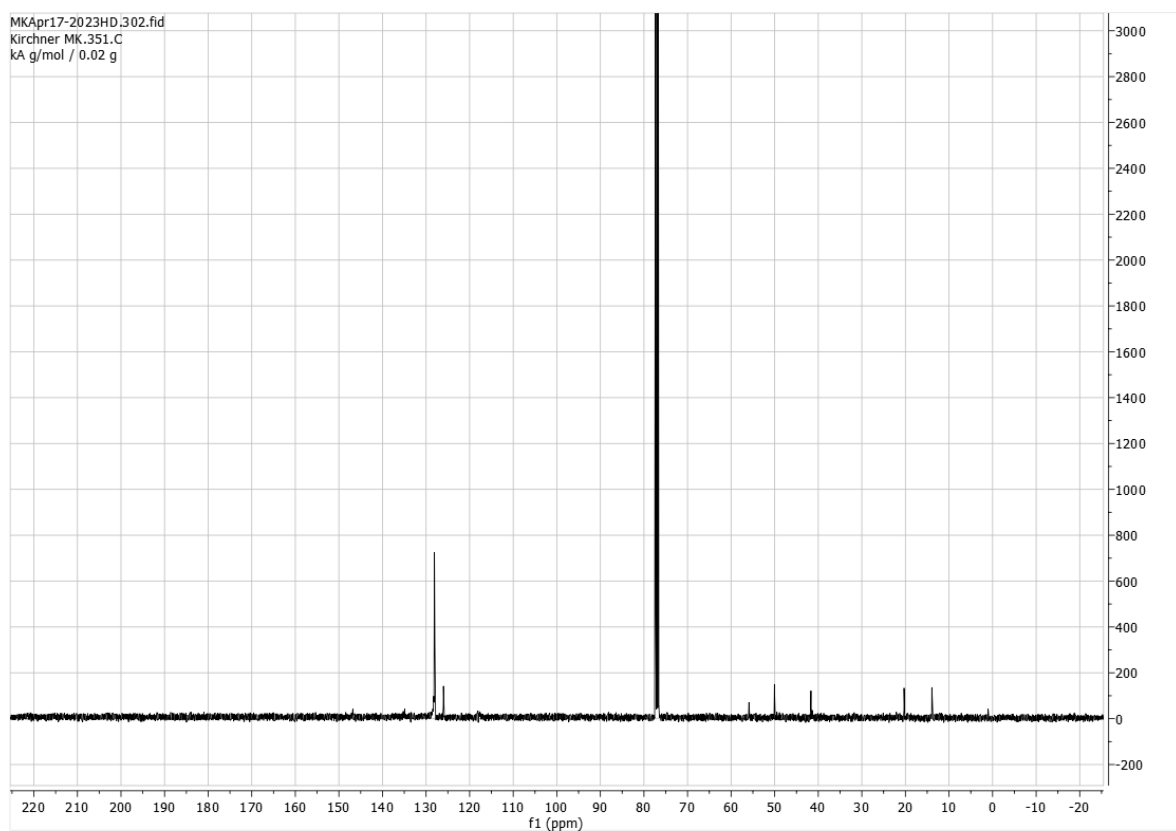
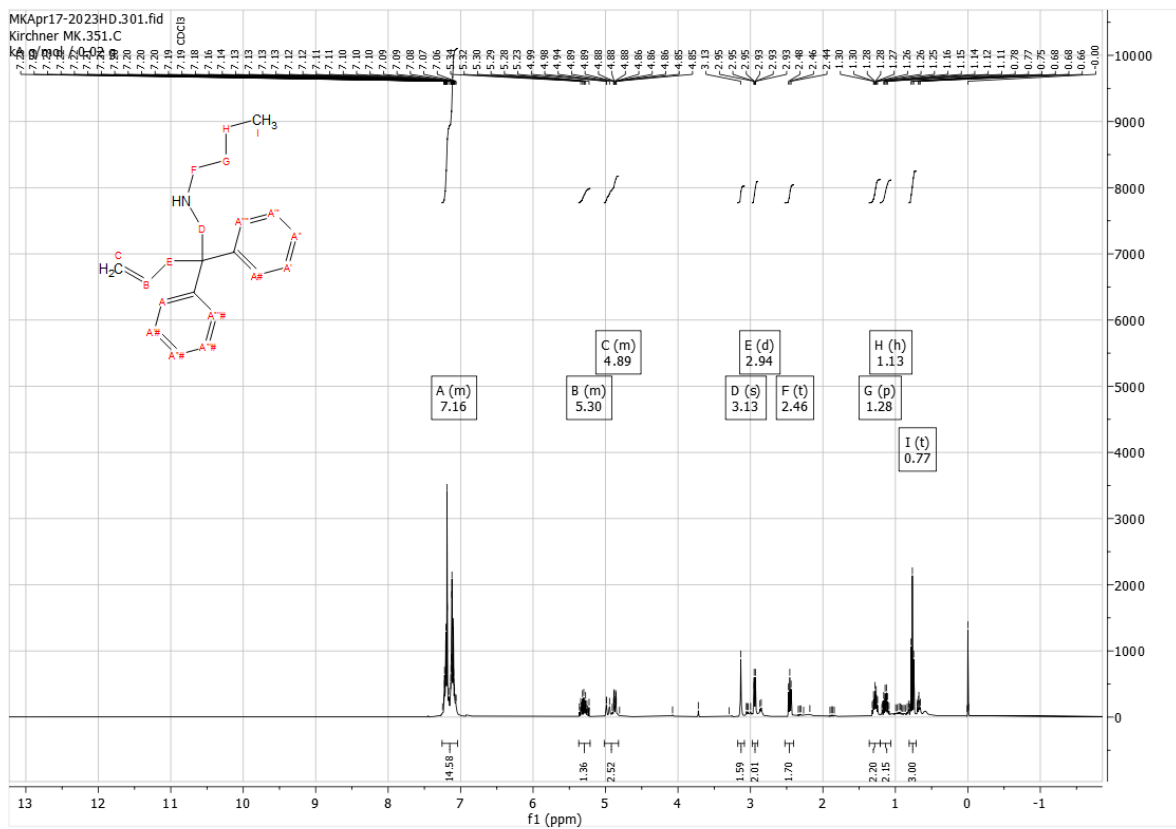
Compound 1h



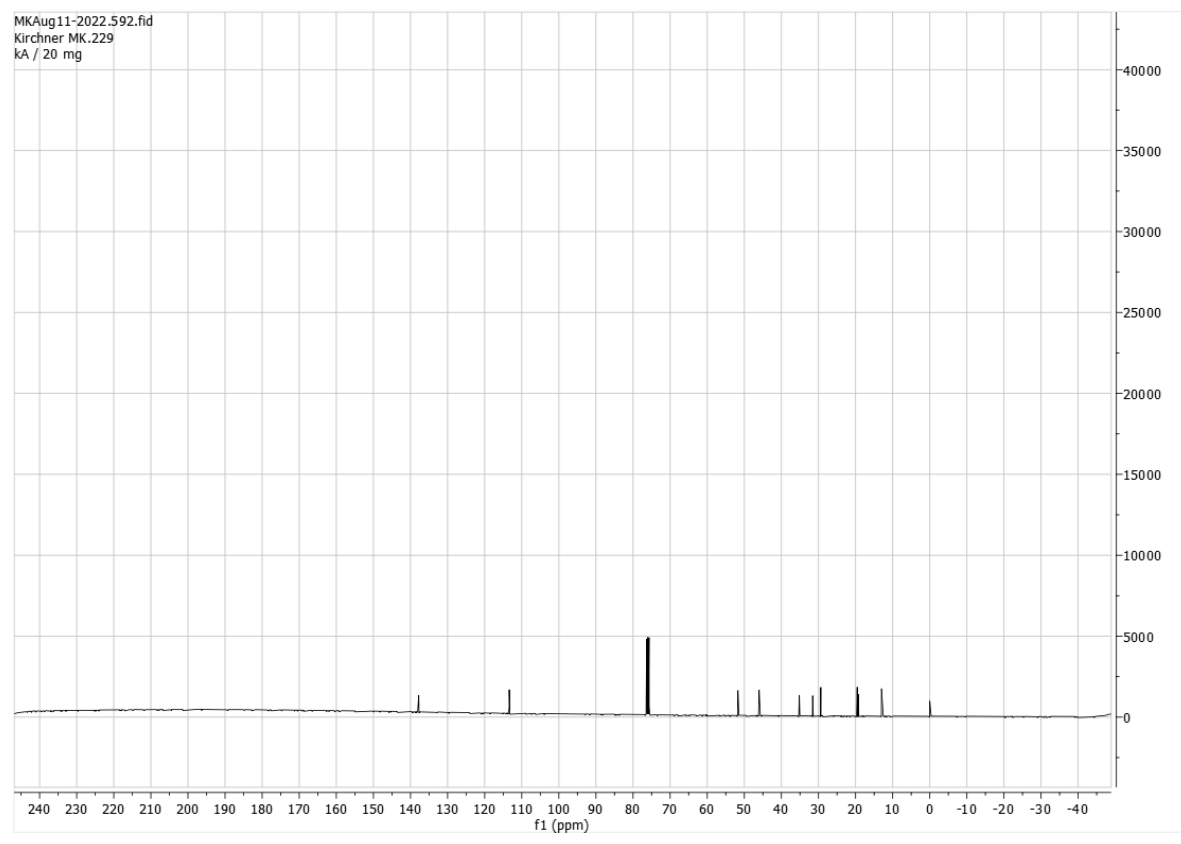
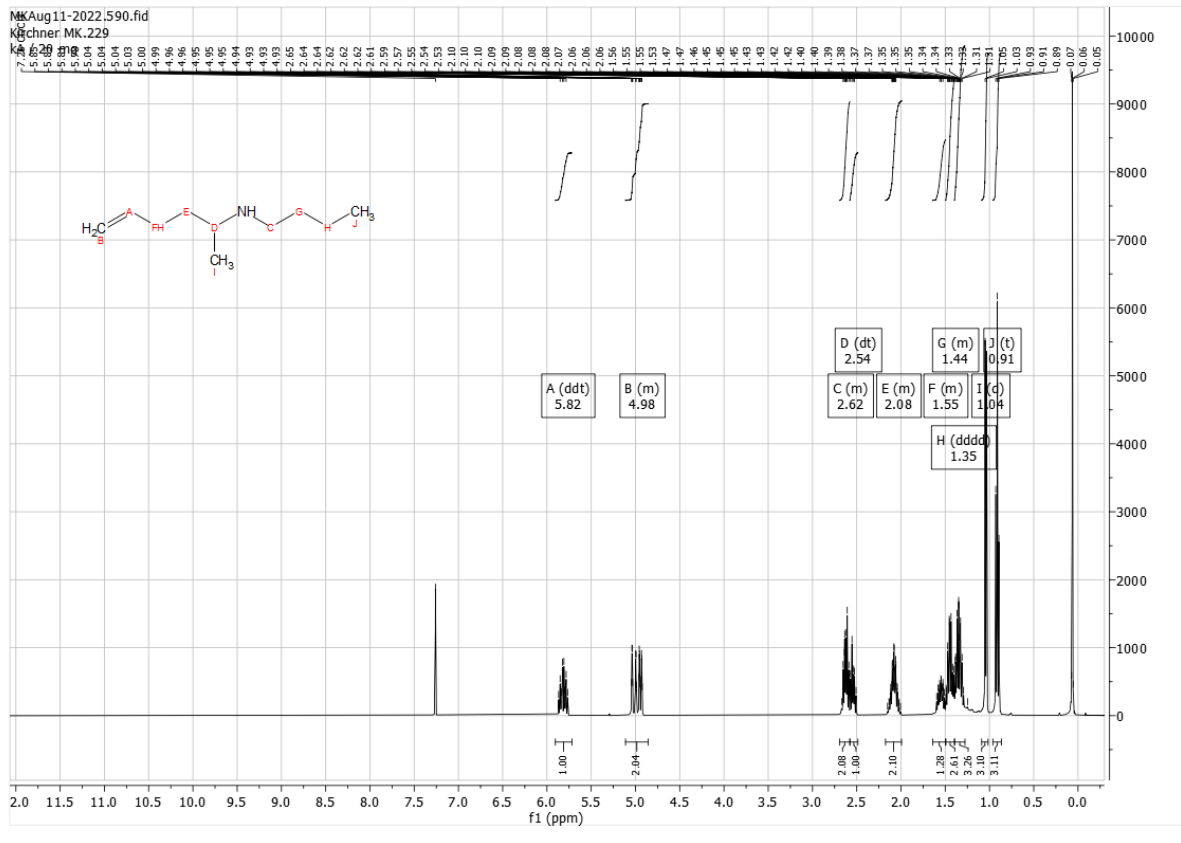
Compound 1i



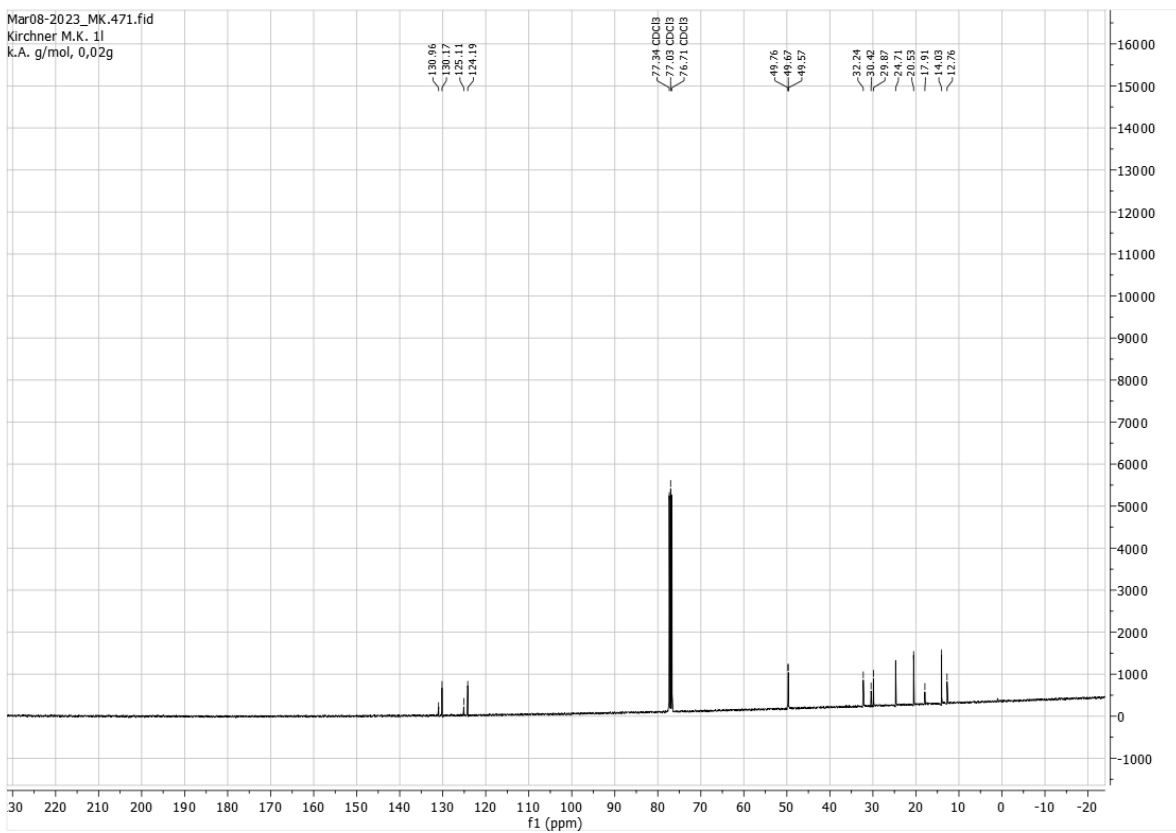
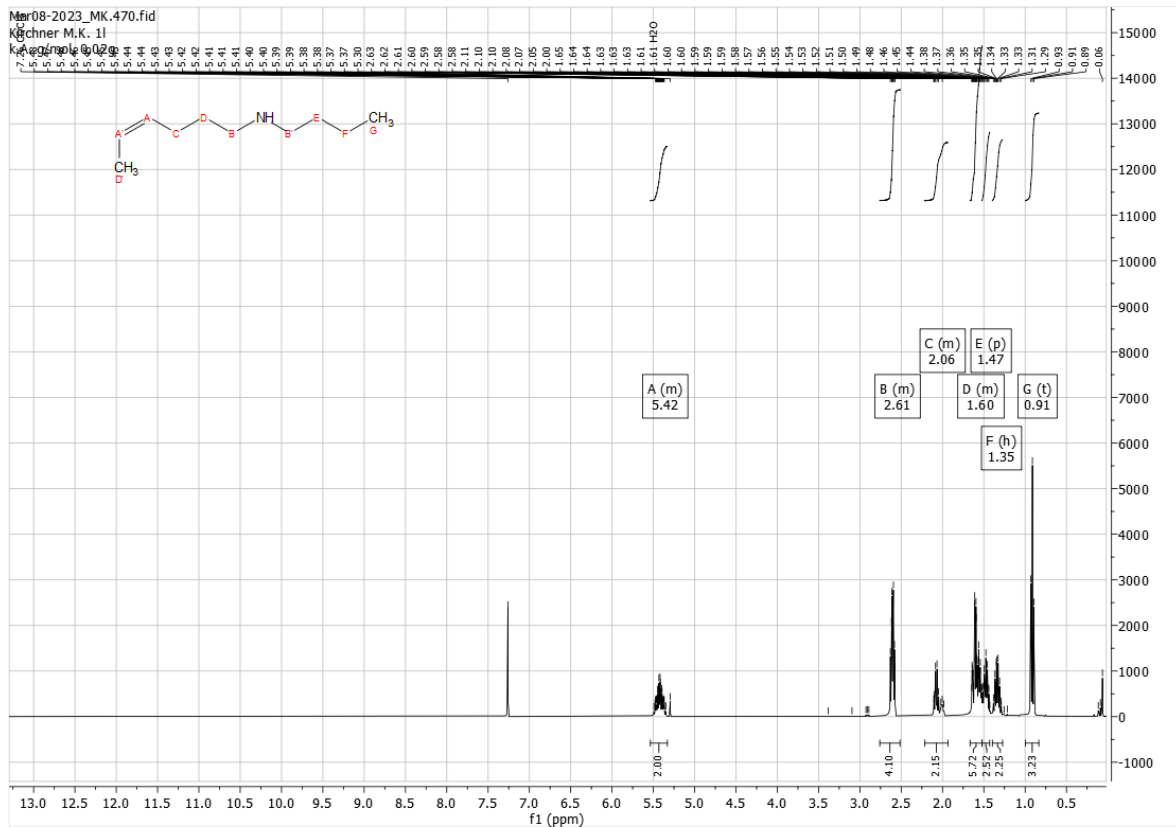
Compound 1j



Compound 1k

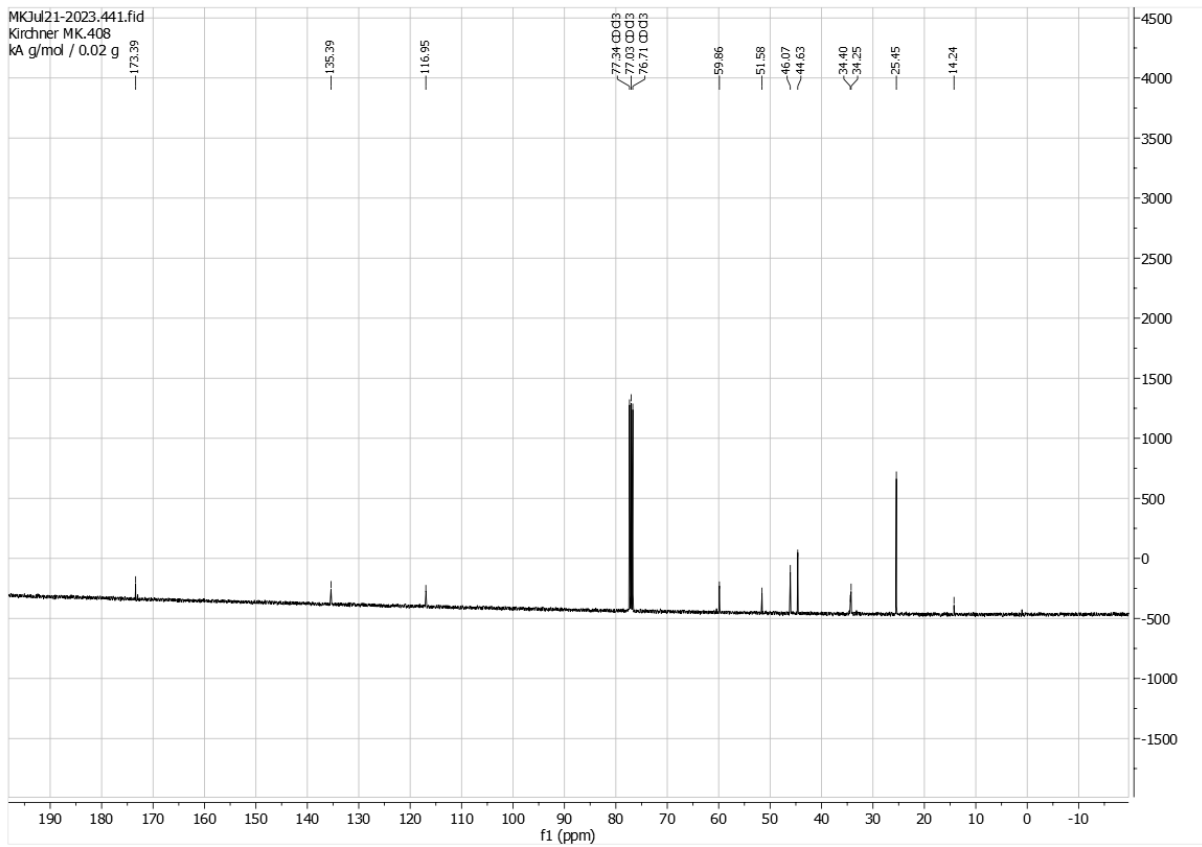
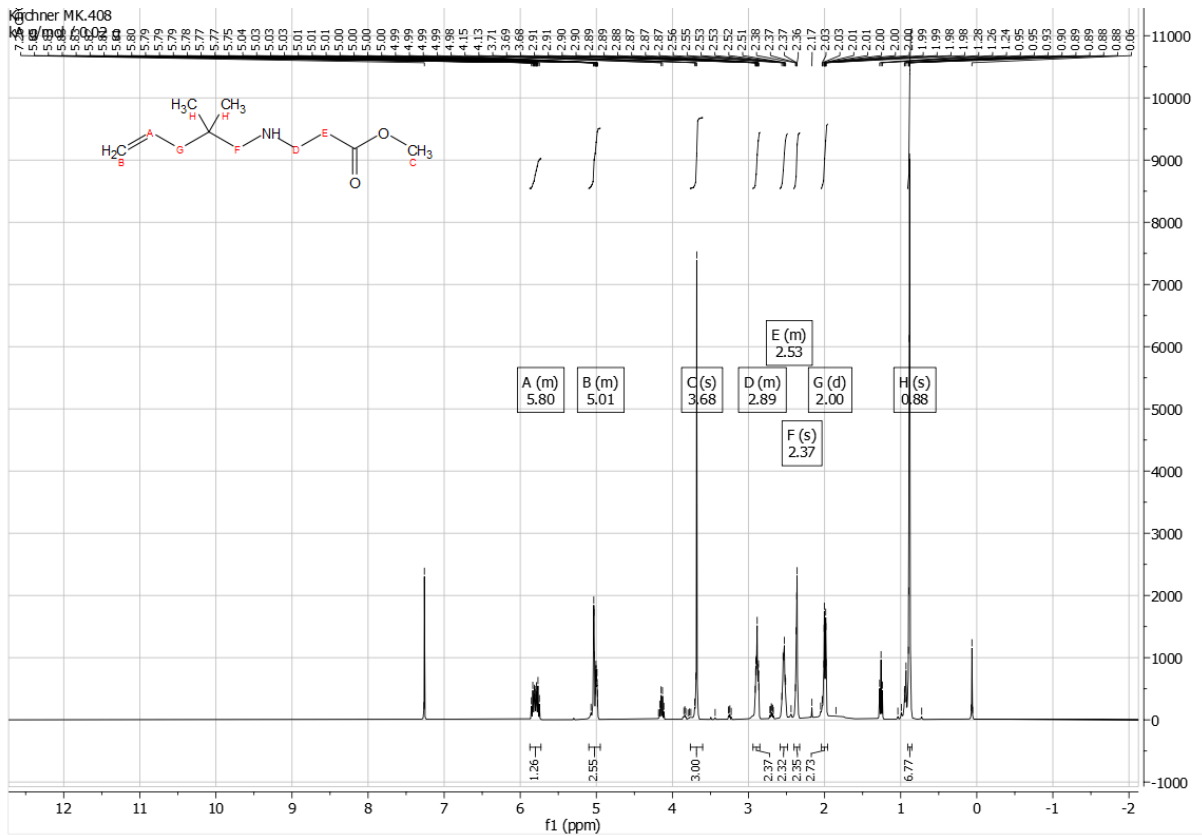


Compound 11

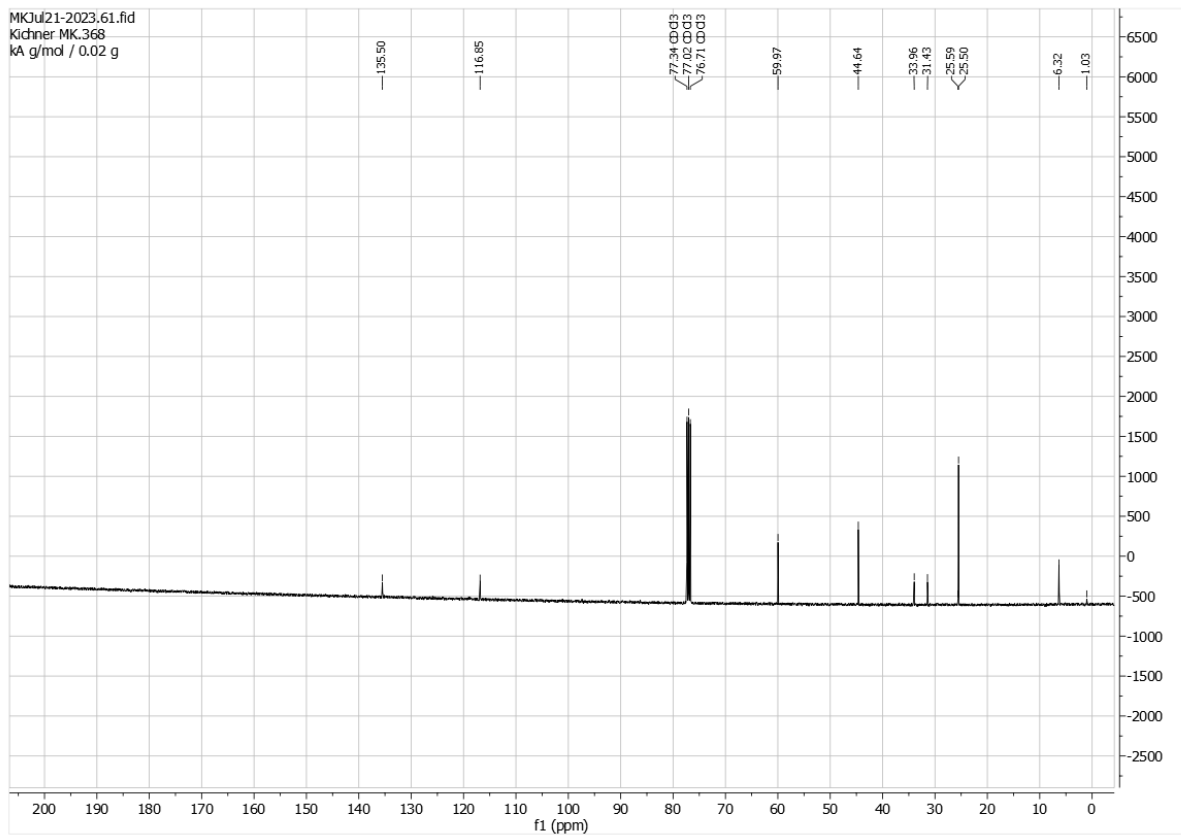
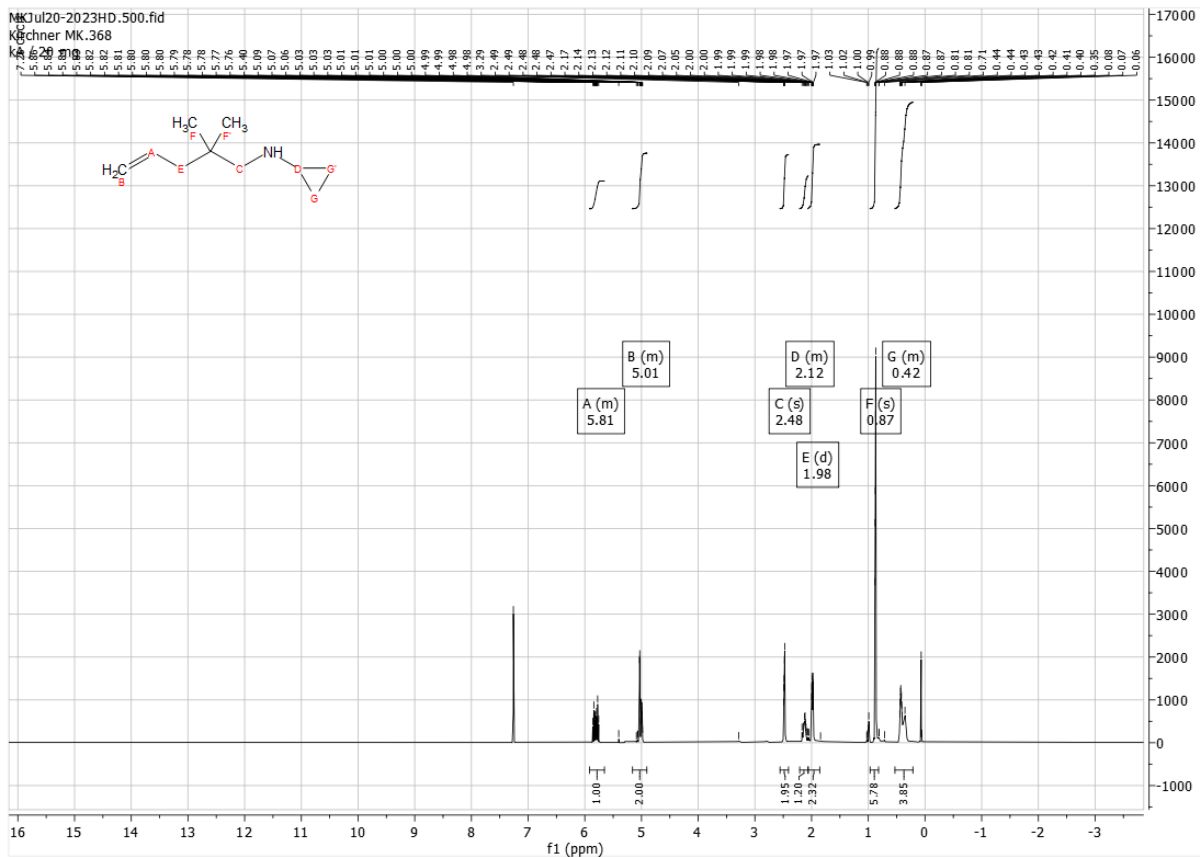


Compound 1m

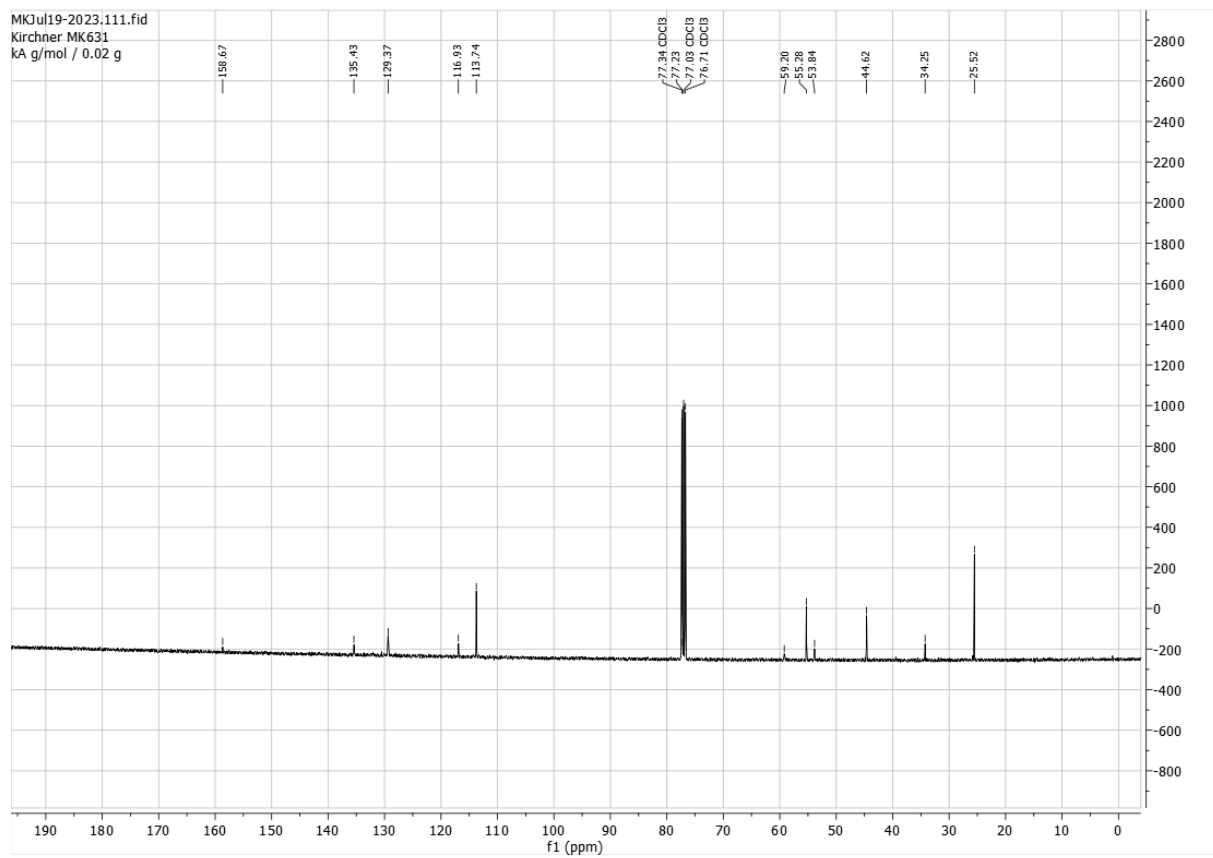
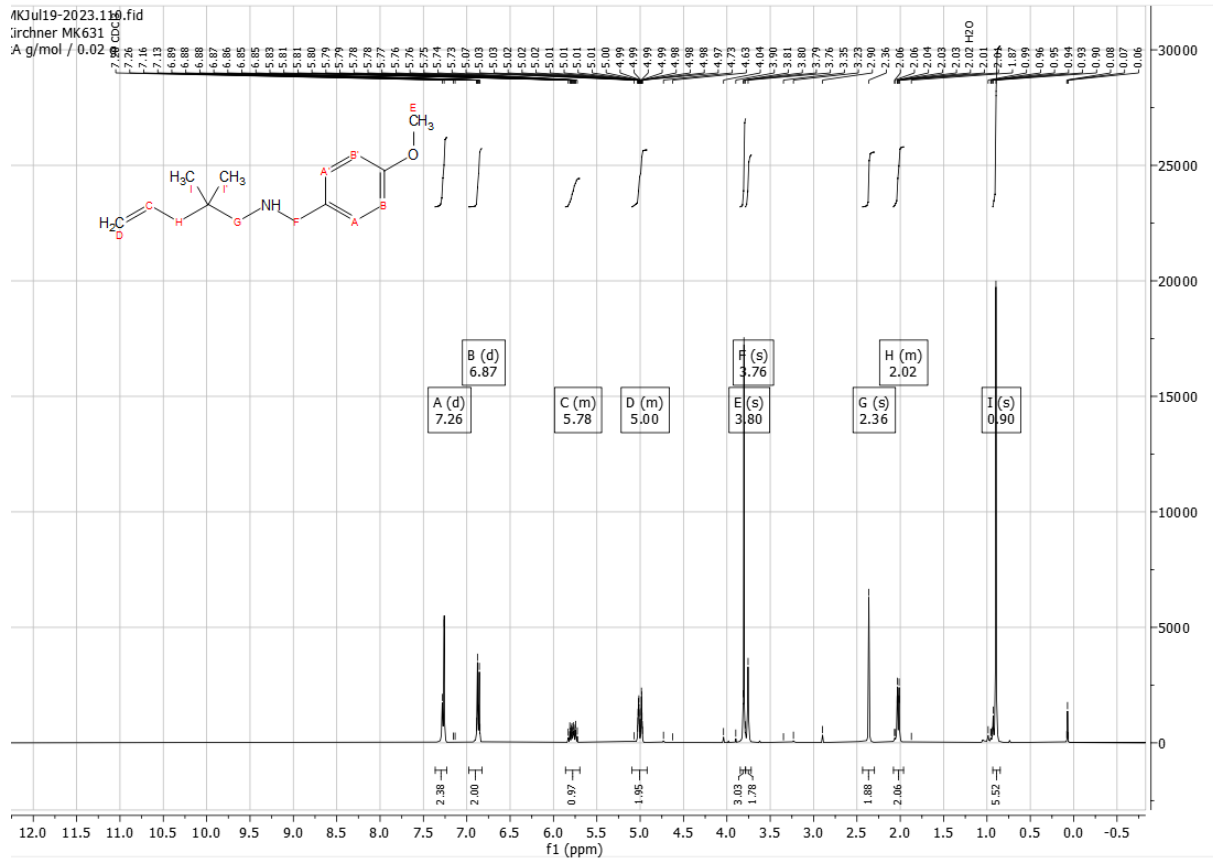




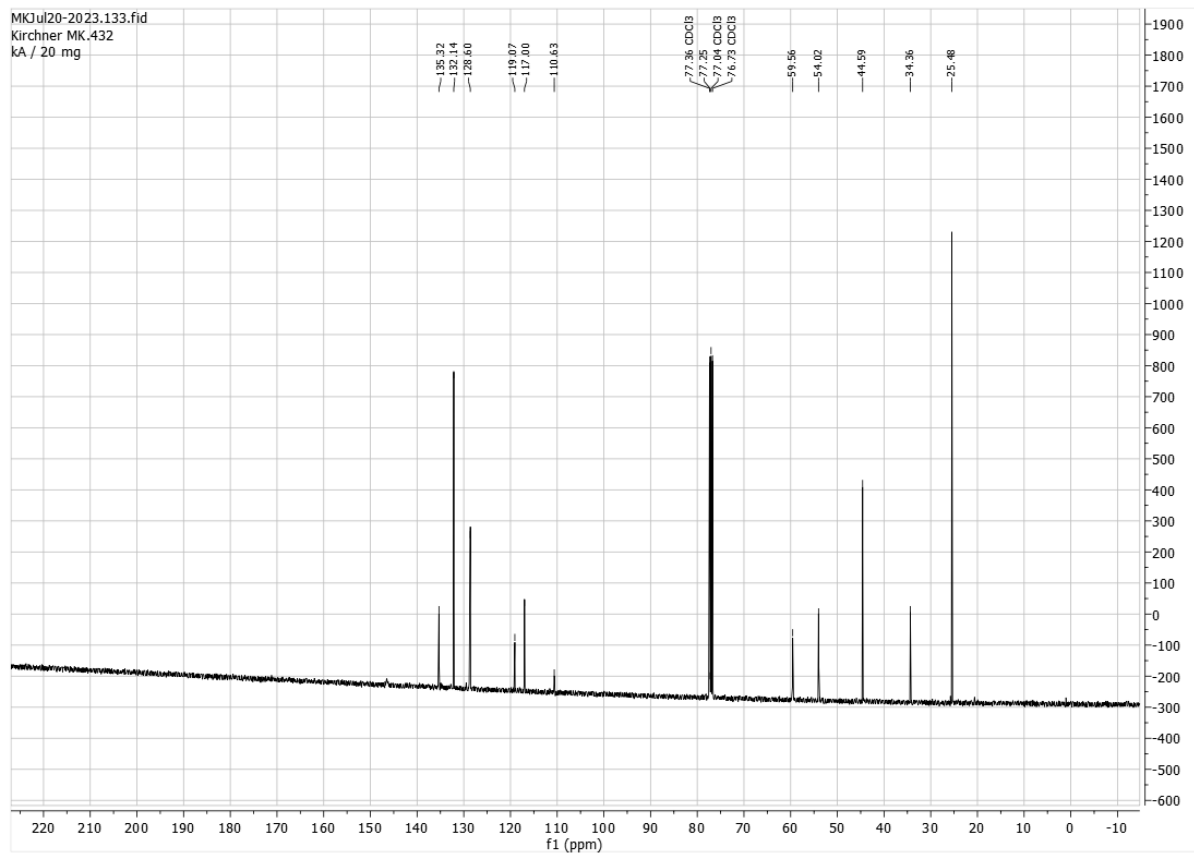
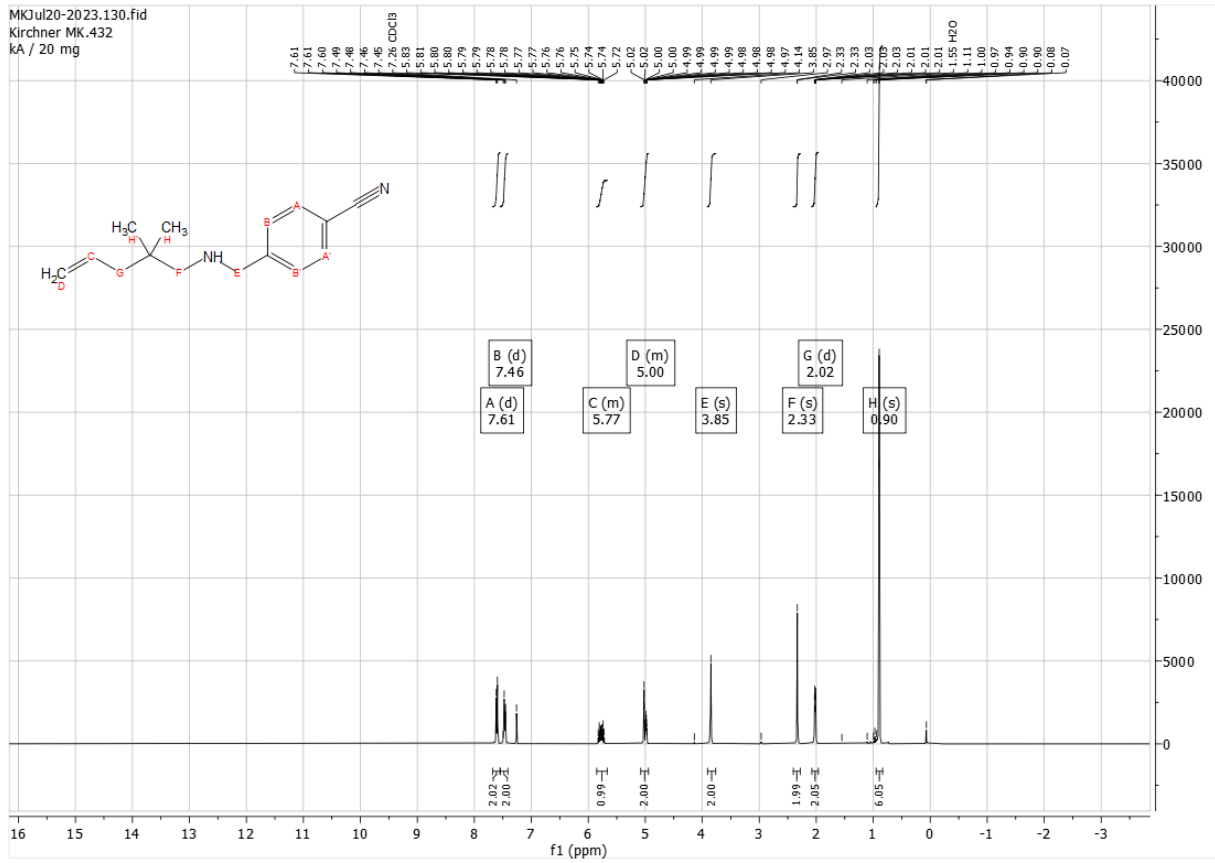
Compound 1n



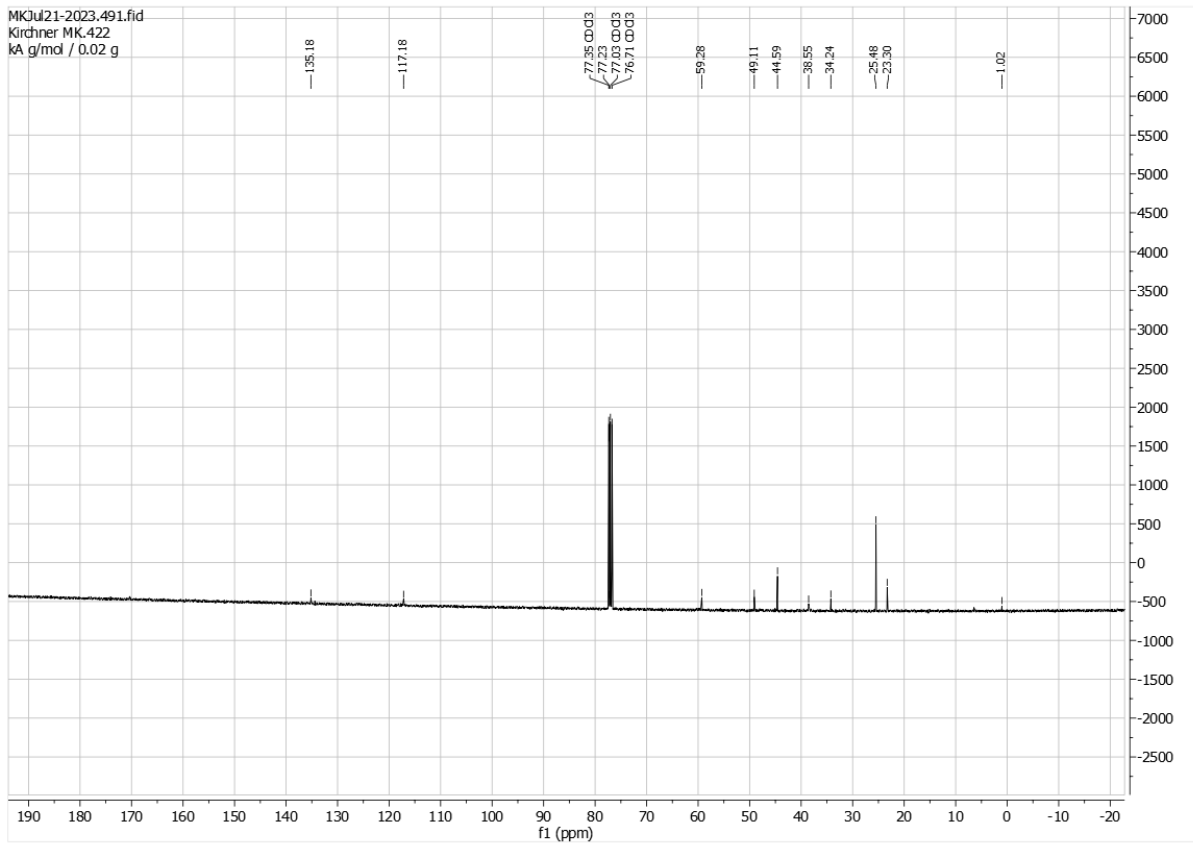
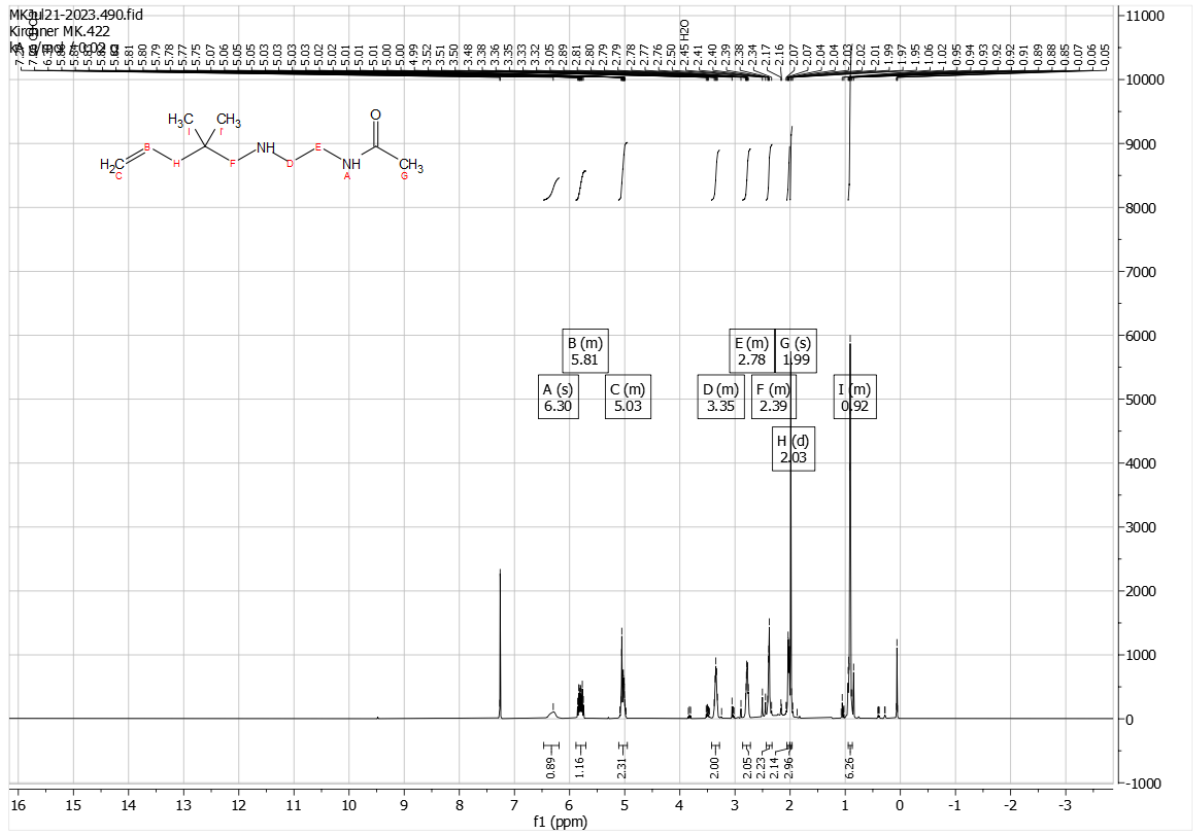
Compound 10



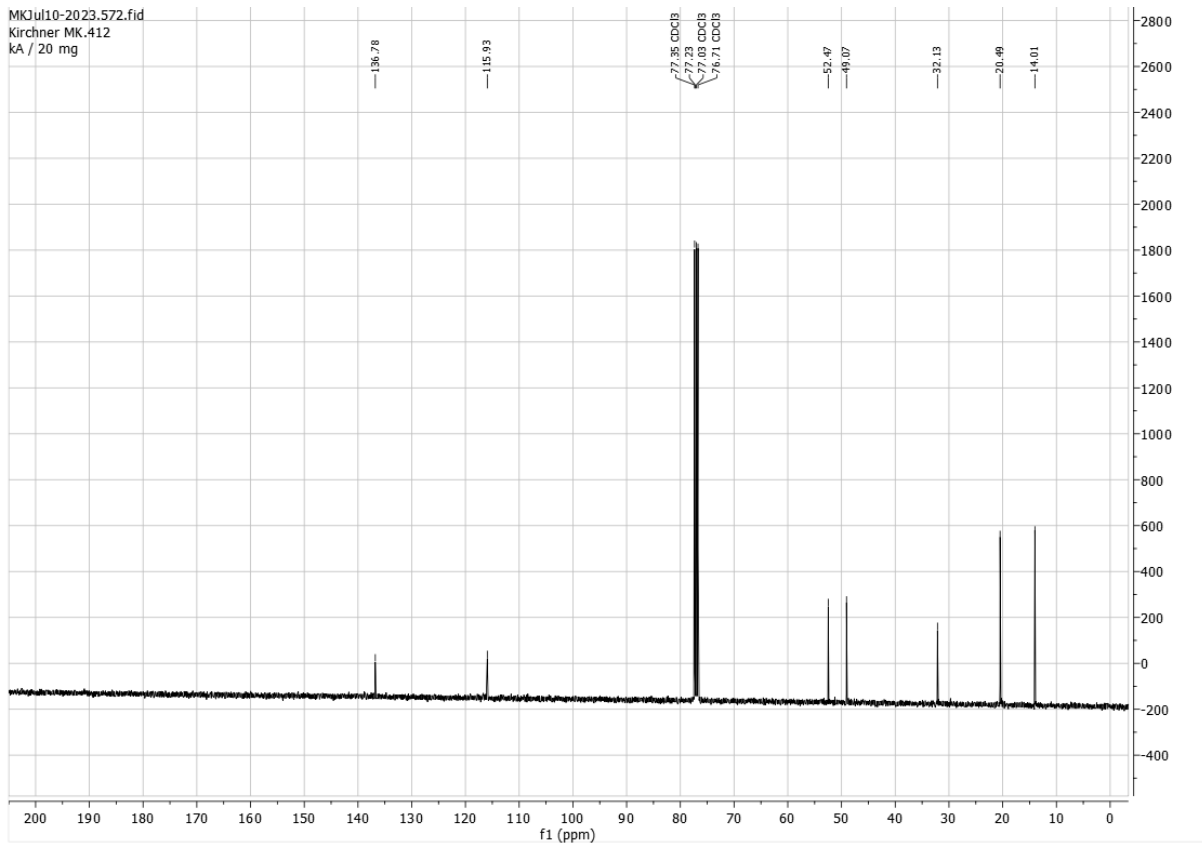
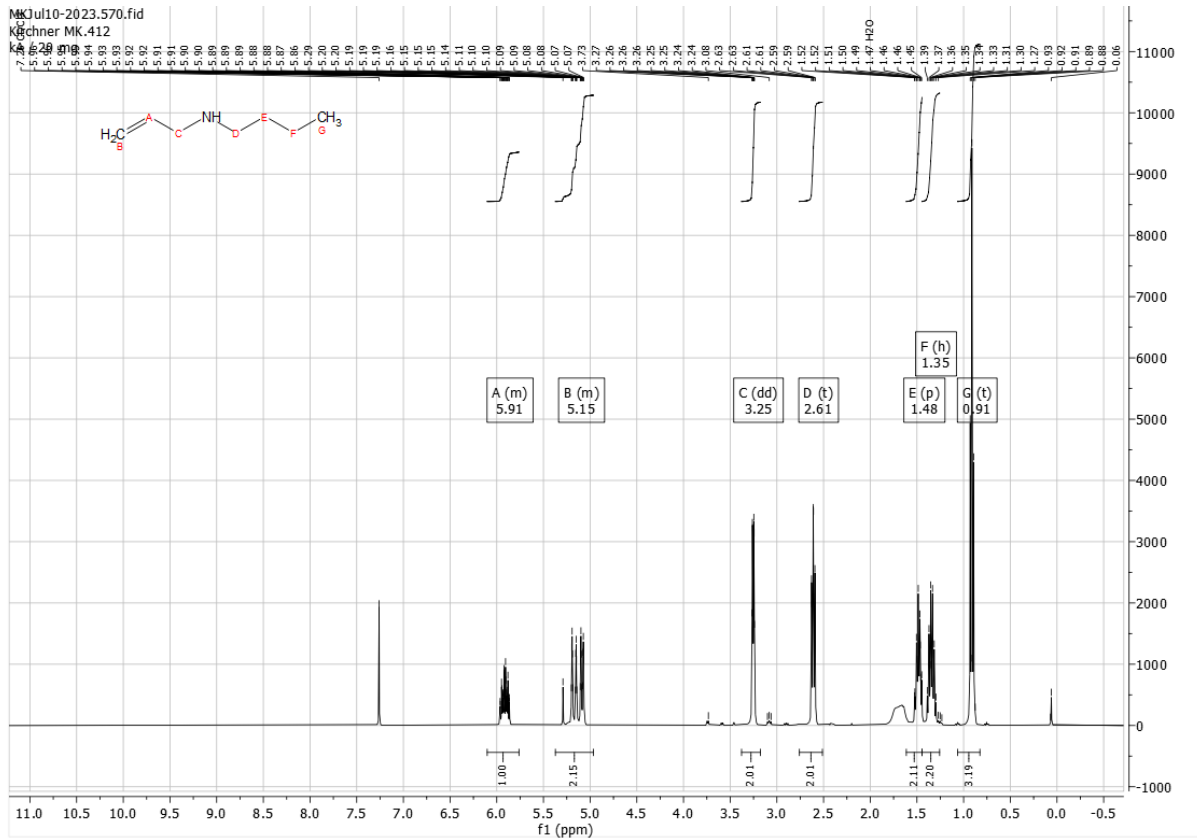
Compound 1p



Compound 1q

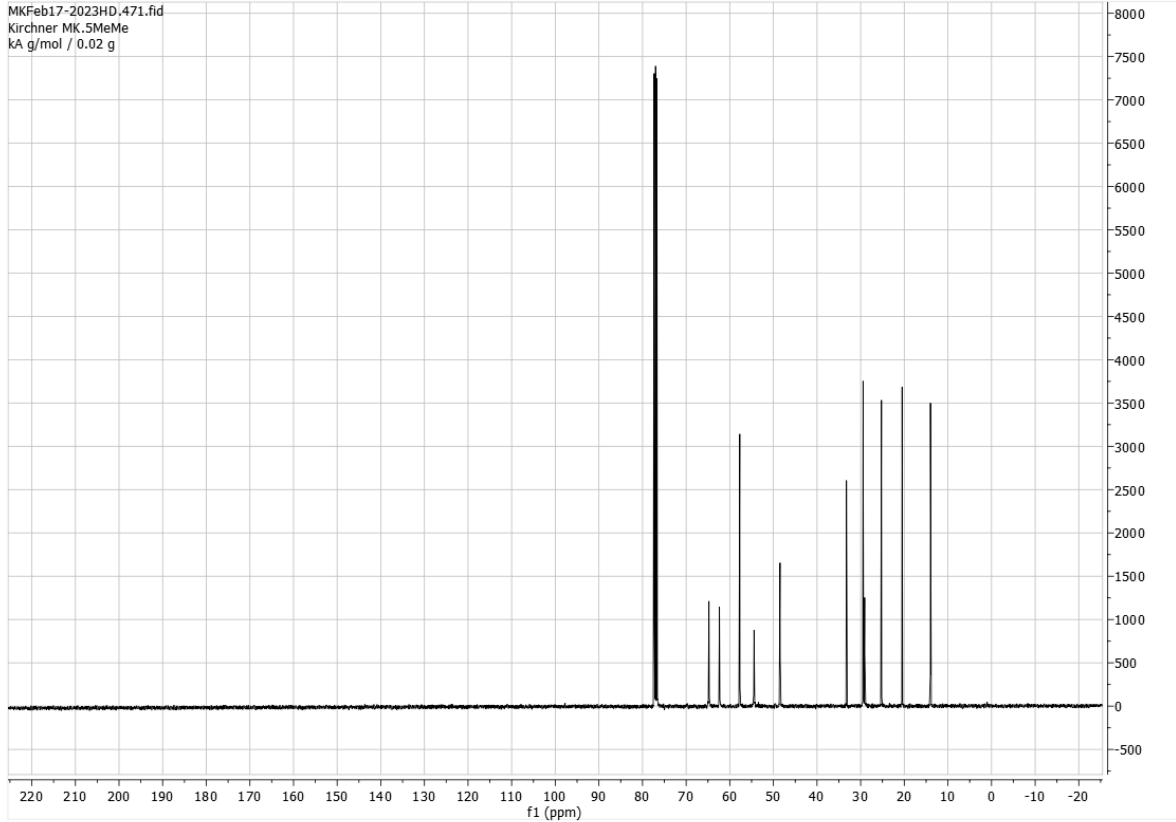


Compound 1r

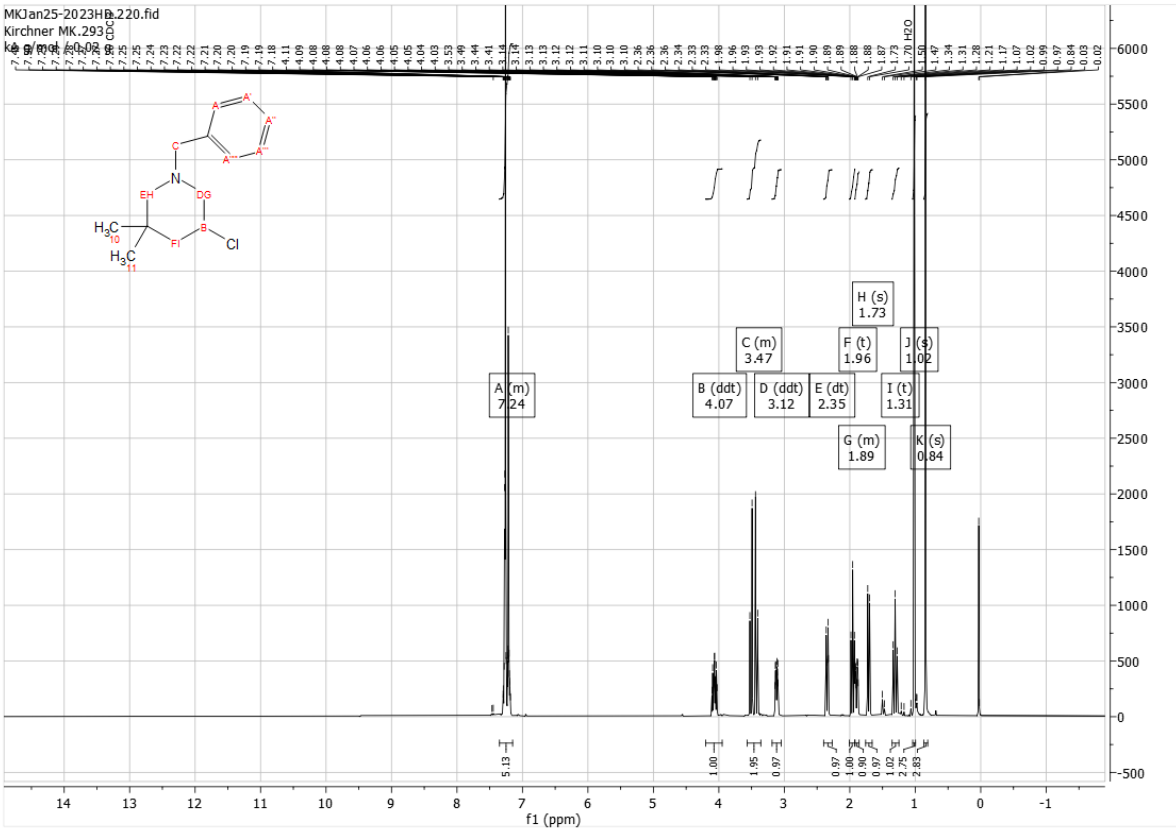


Compound 1s

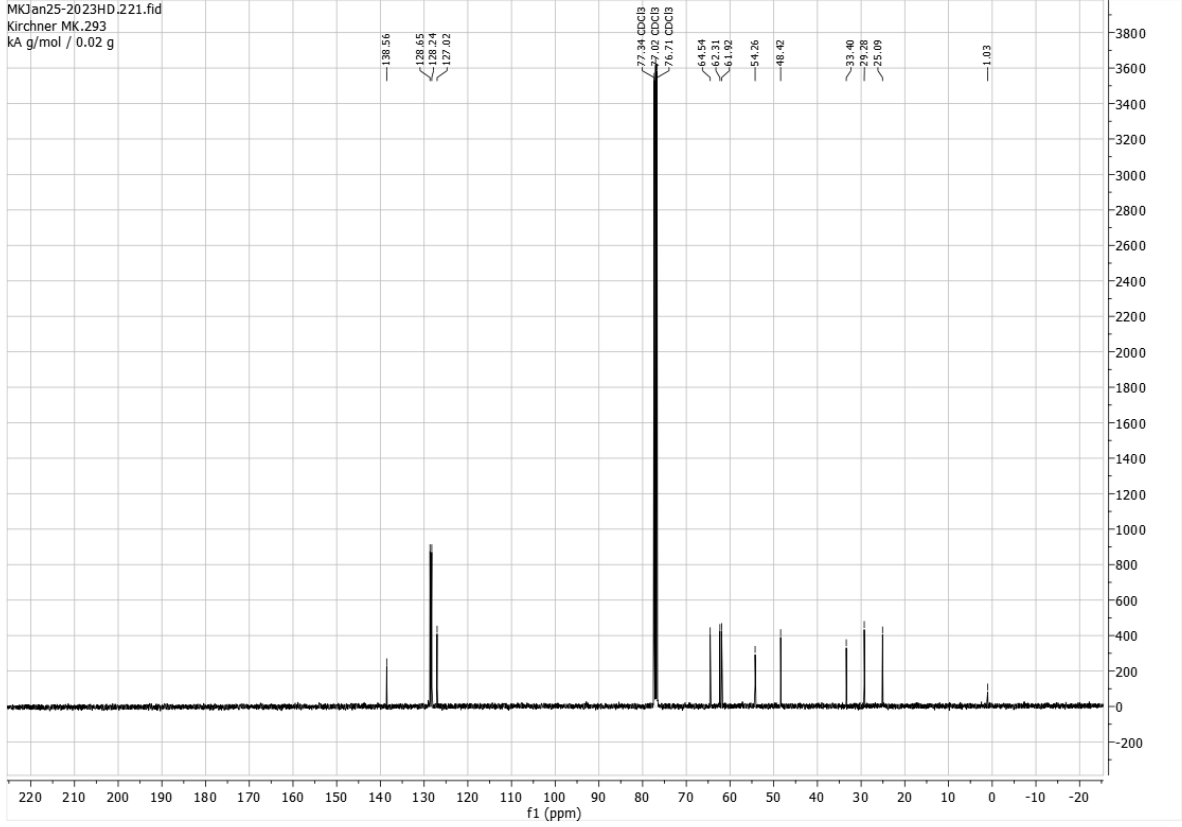




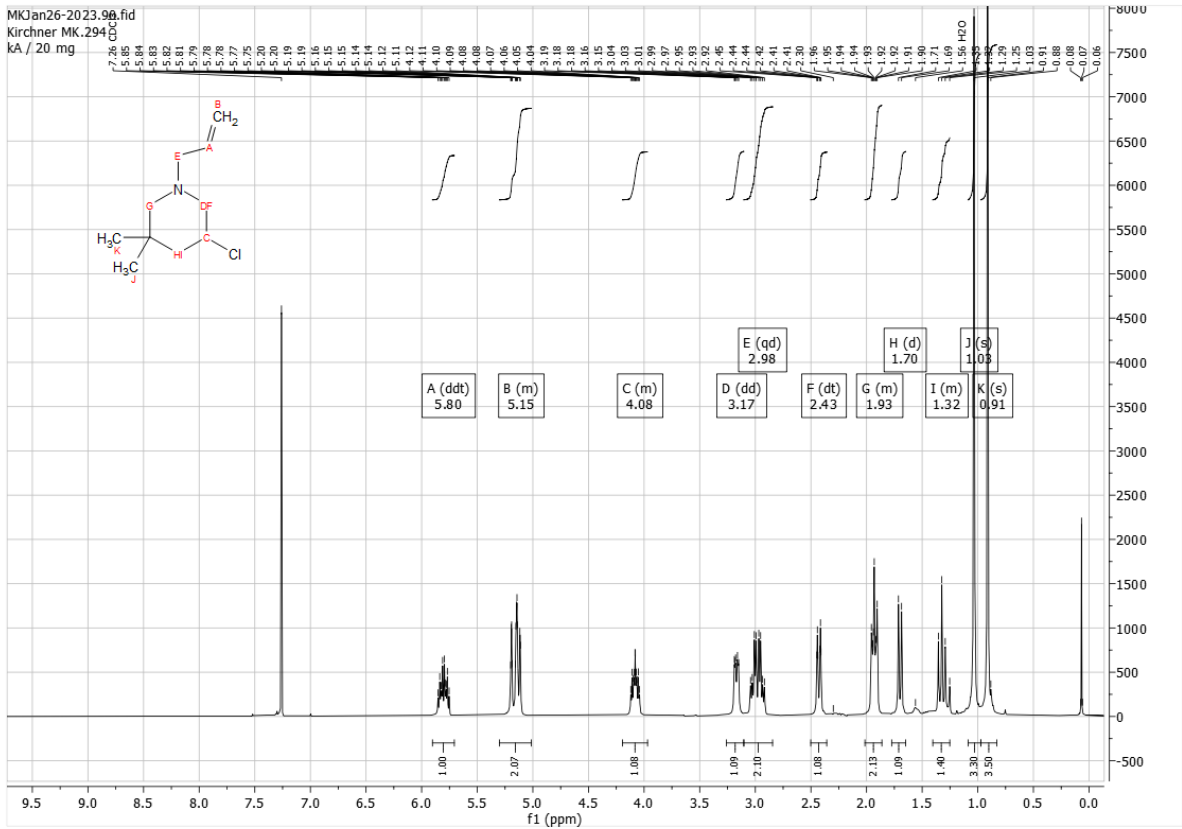
### Compound 2b

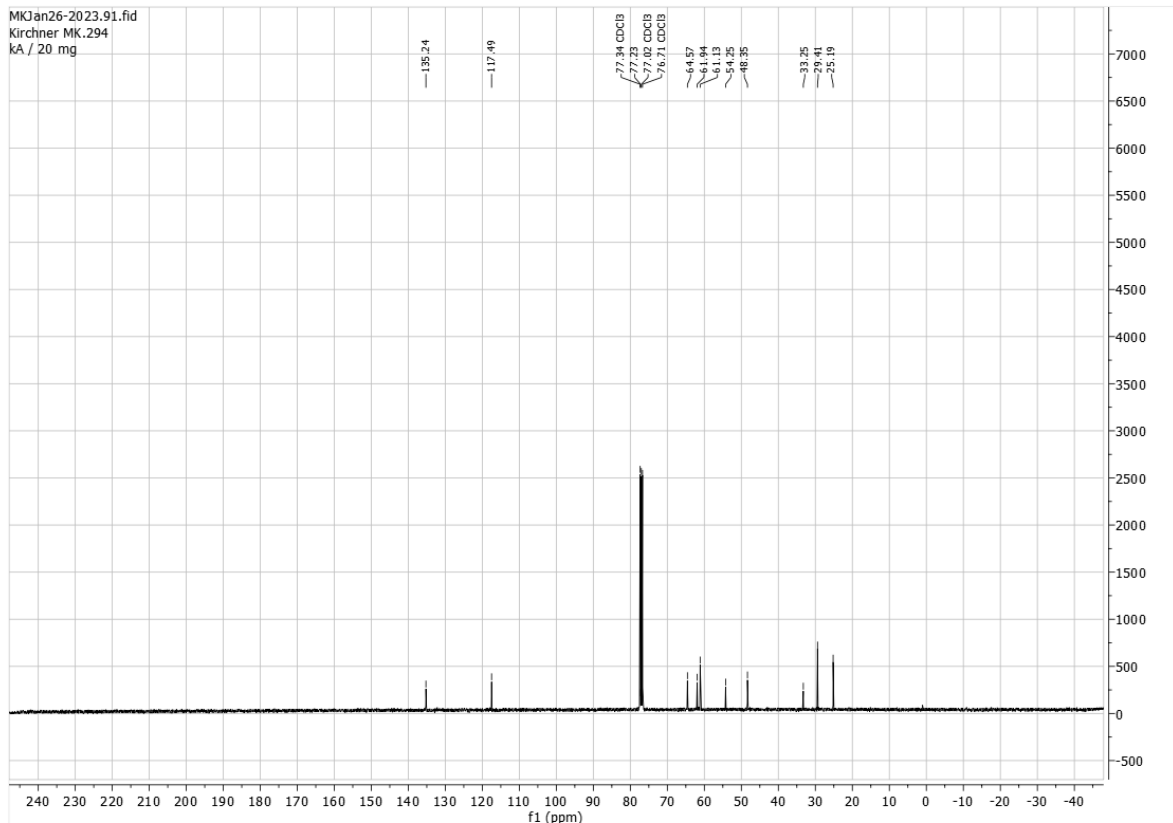




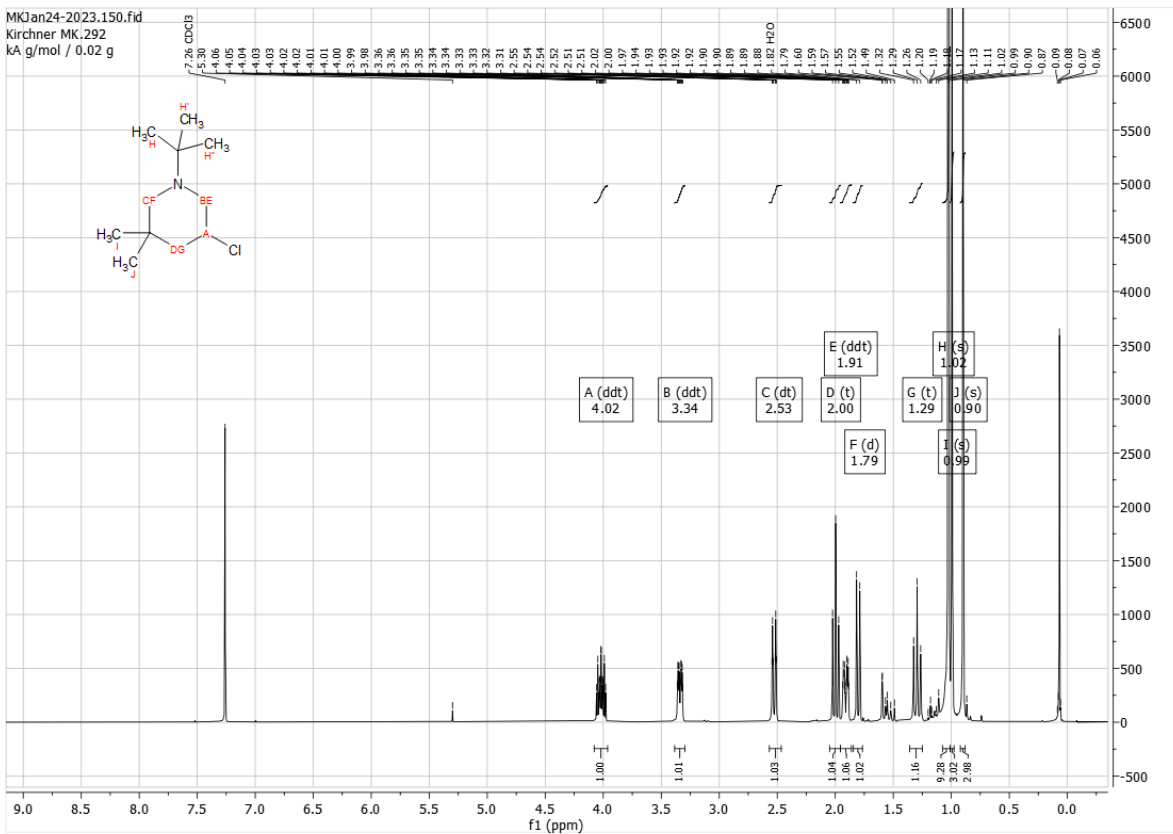


## Compound 2c



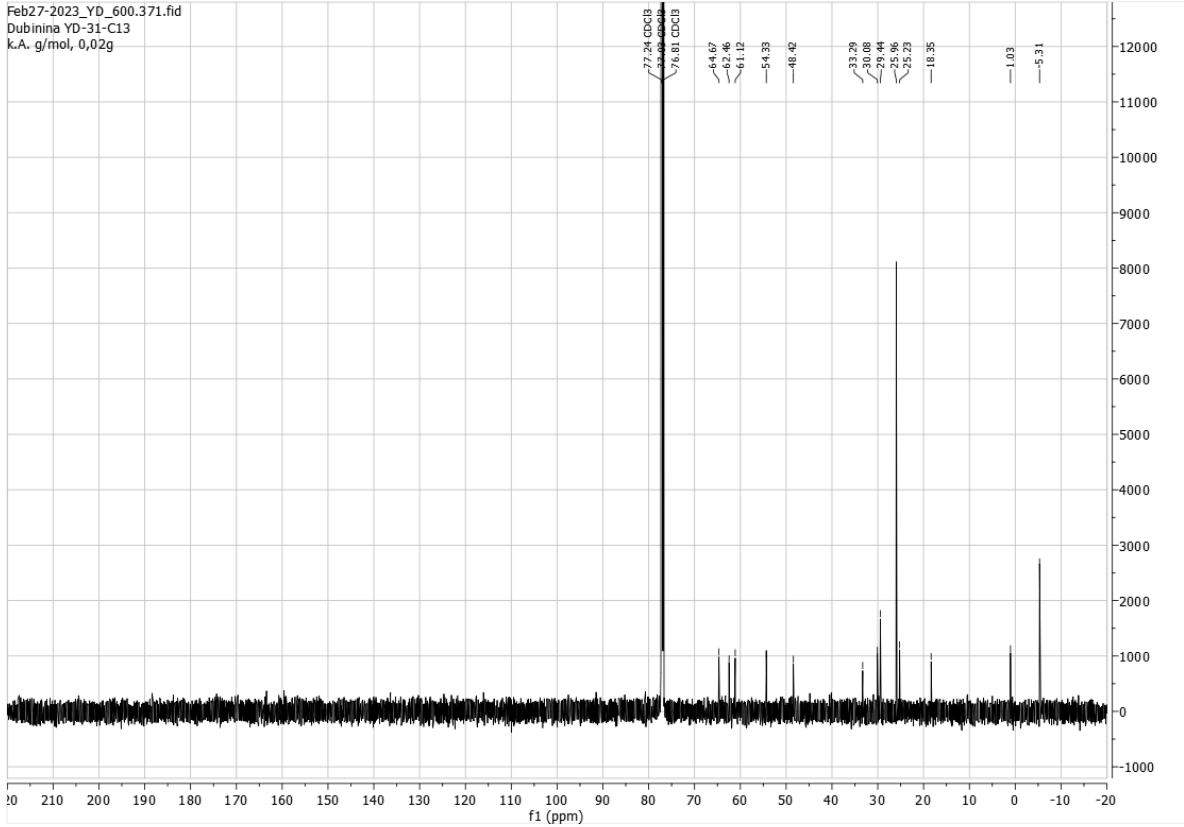


## Compound 2d



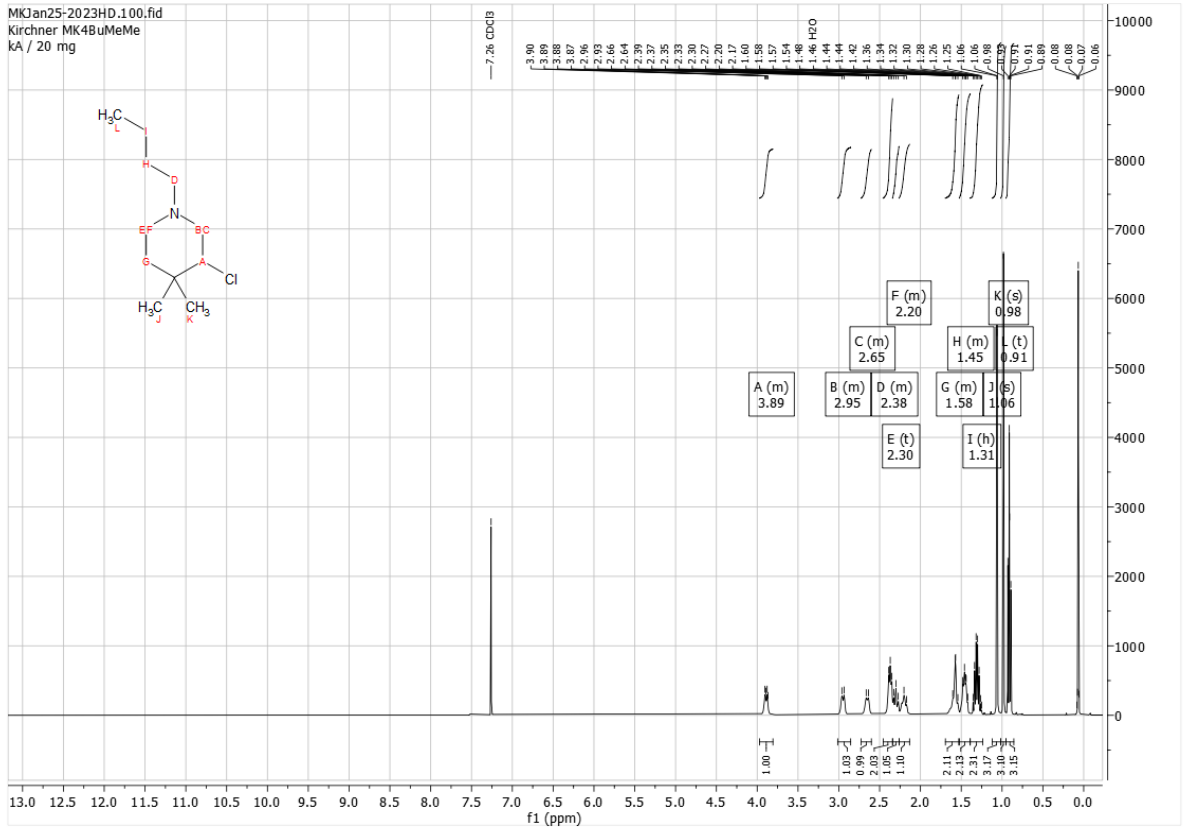


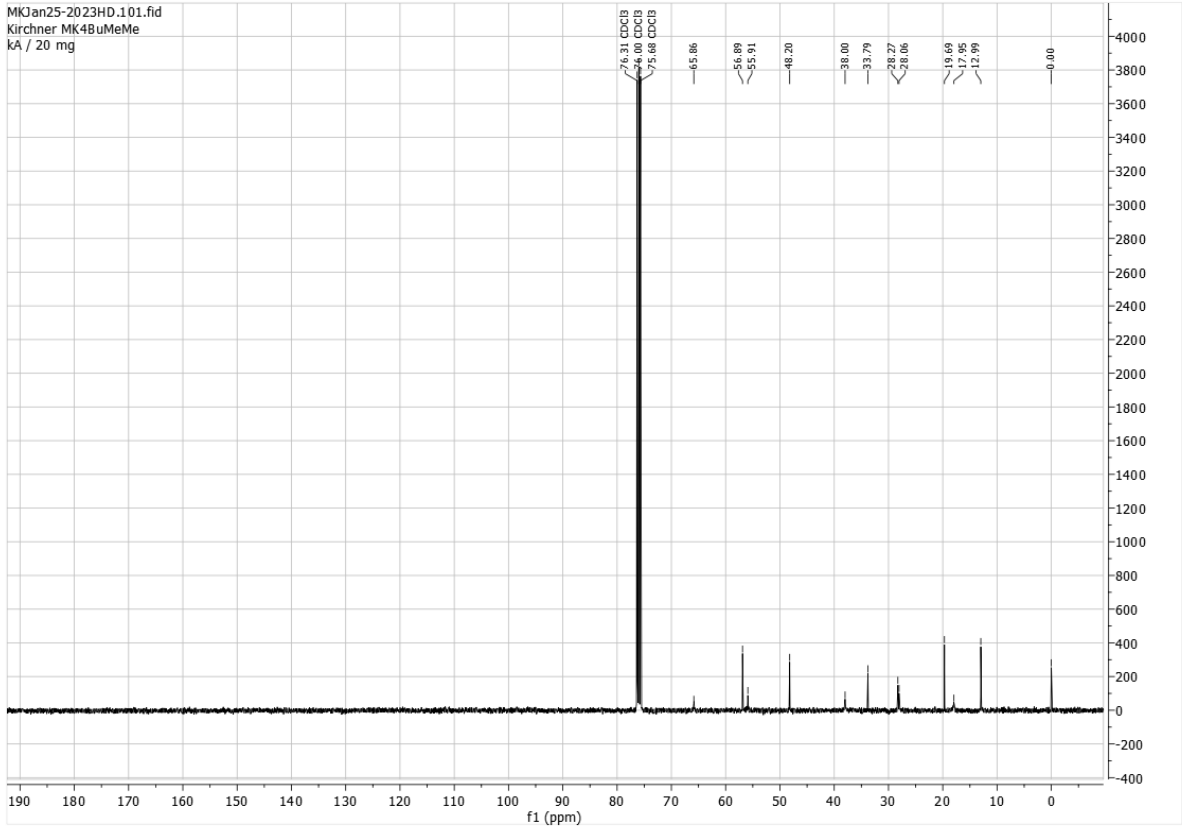
Feb27-2023\_YD\_600.371.fid  
 Dubinina YD-31-C13  
 k.A. g/mol, 0,02g



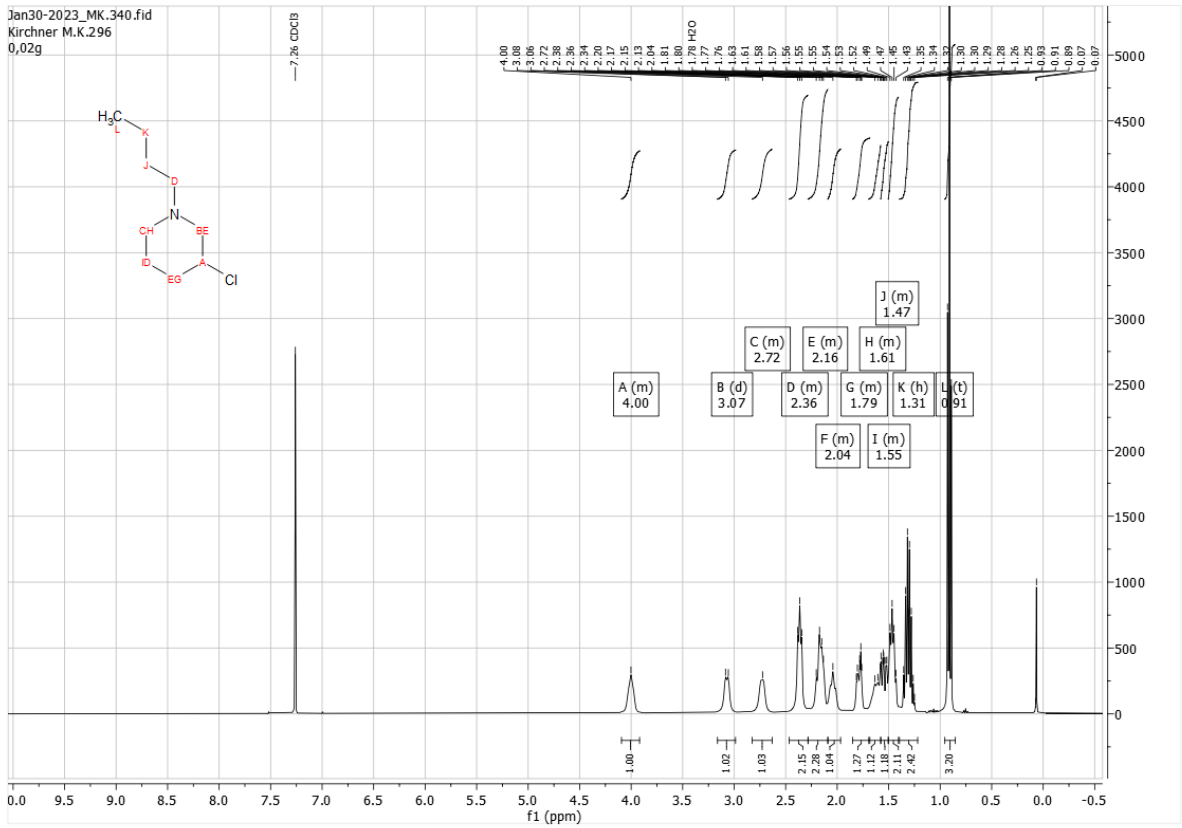
**Compound 2f**

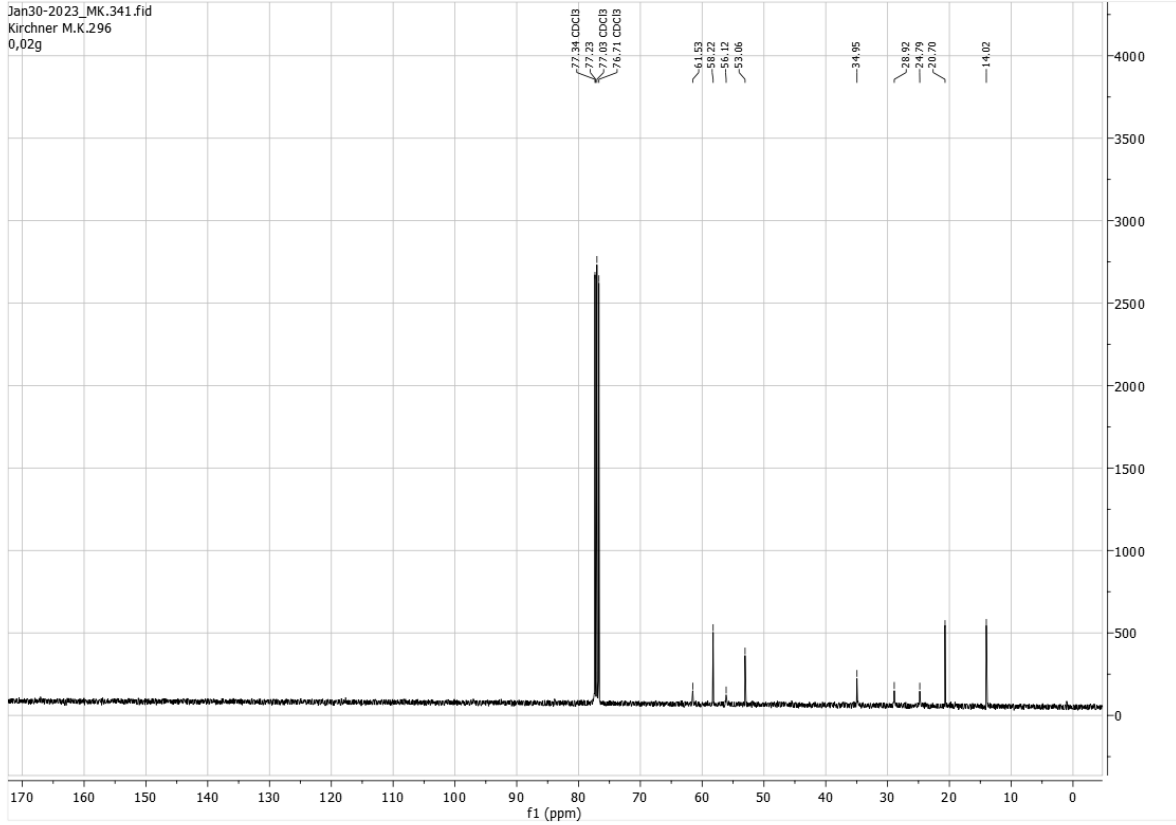
MKJan25-2023HD.100.fid  
 Kirchner MK4BuMeMe  
 kA / 20 mg



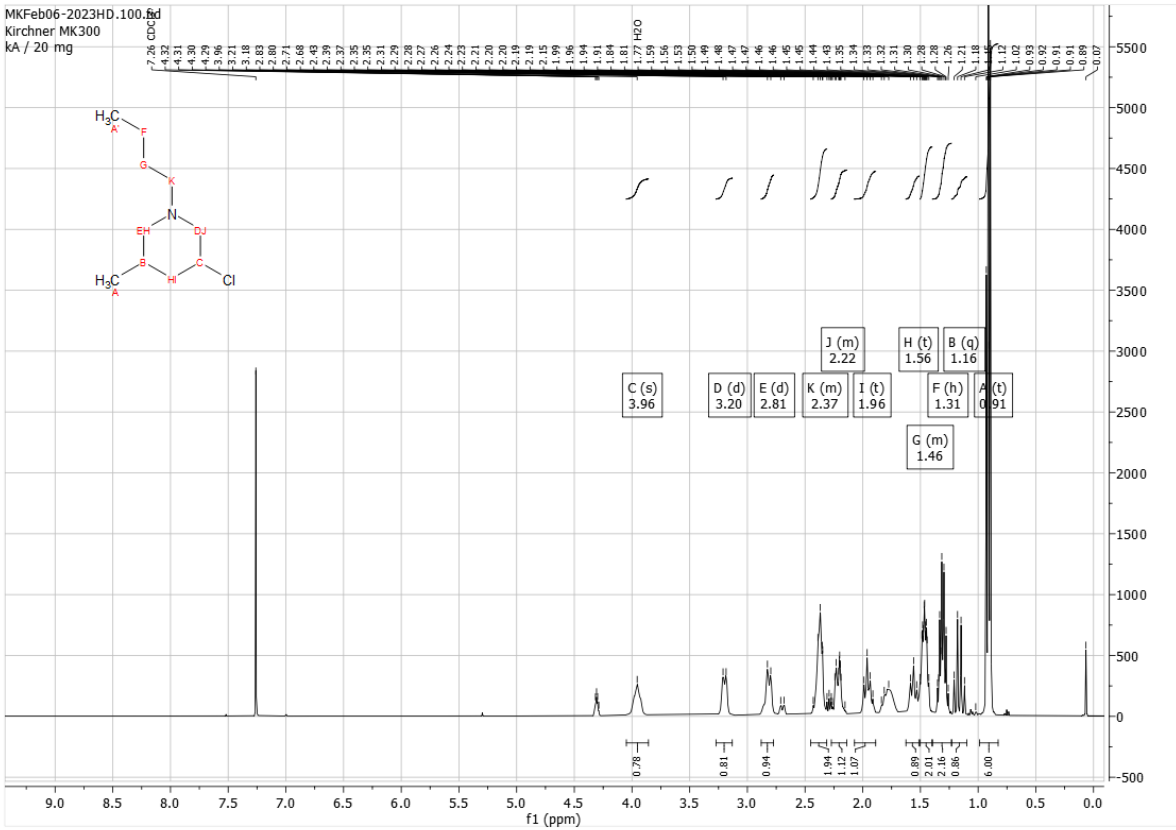


### Compound 2g

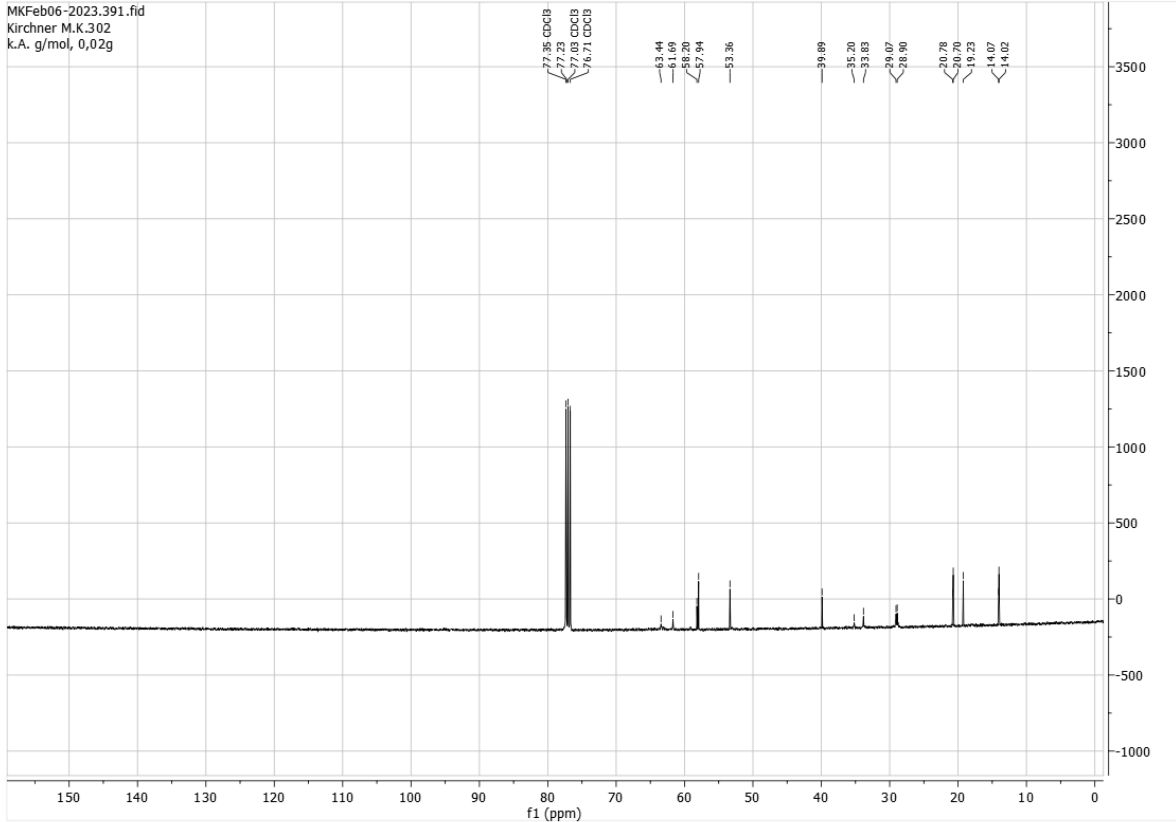




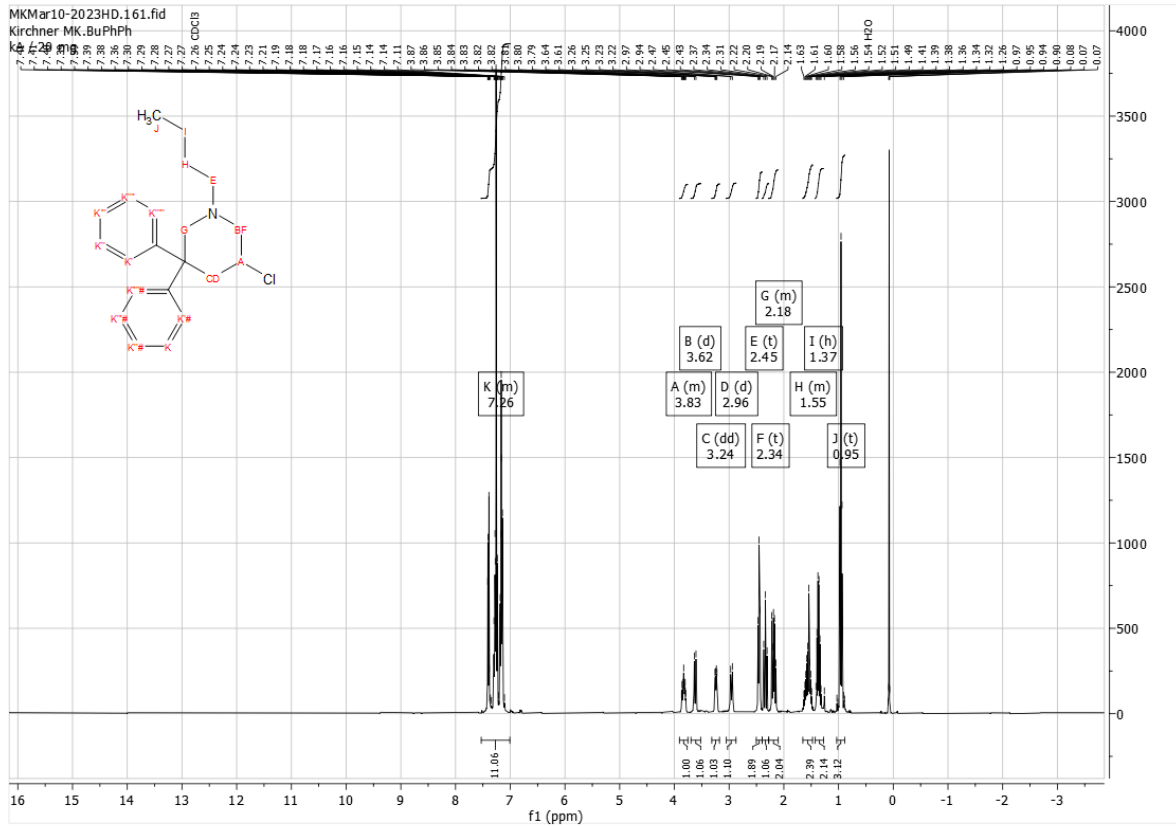
### Compound 2h



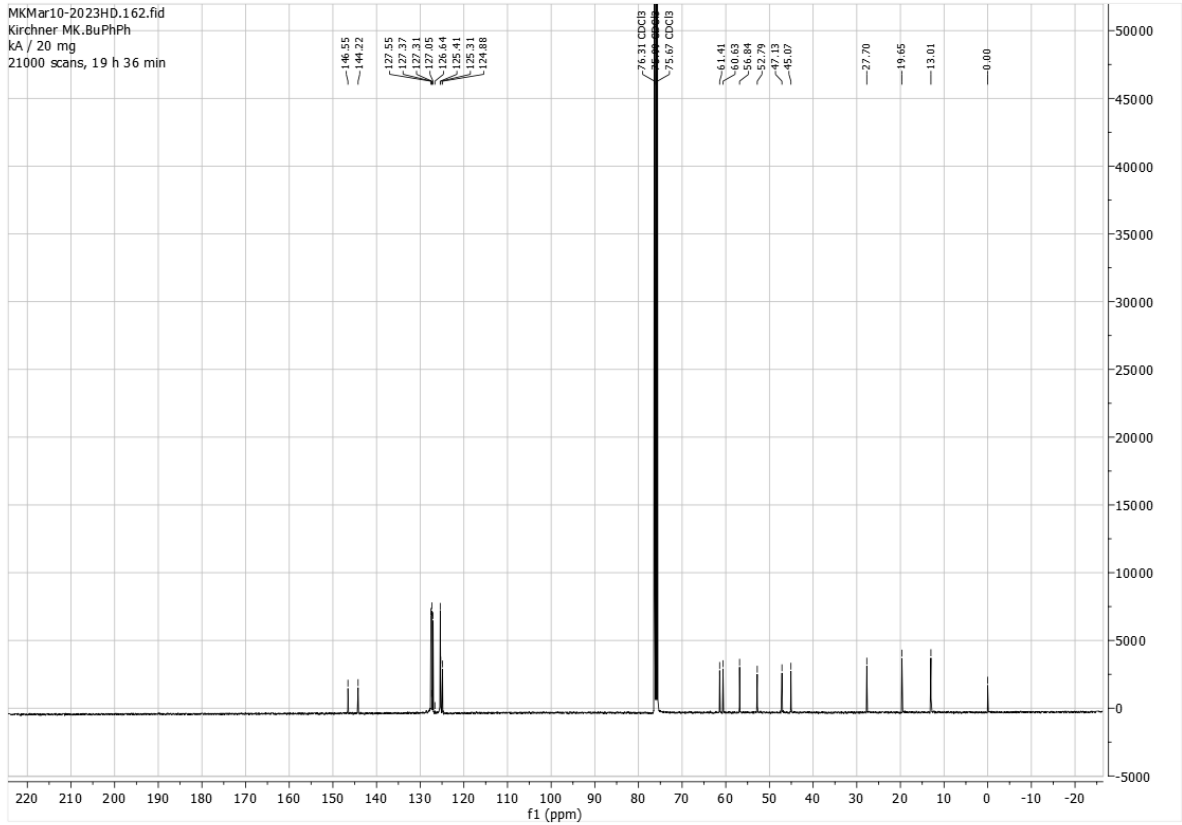




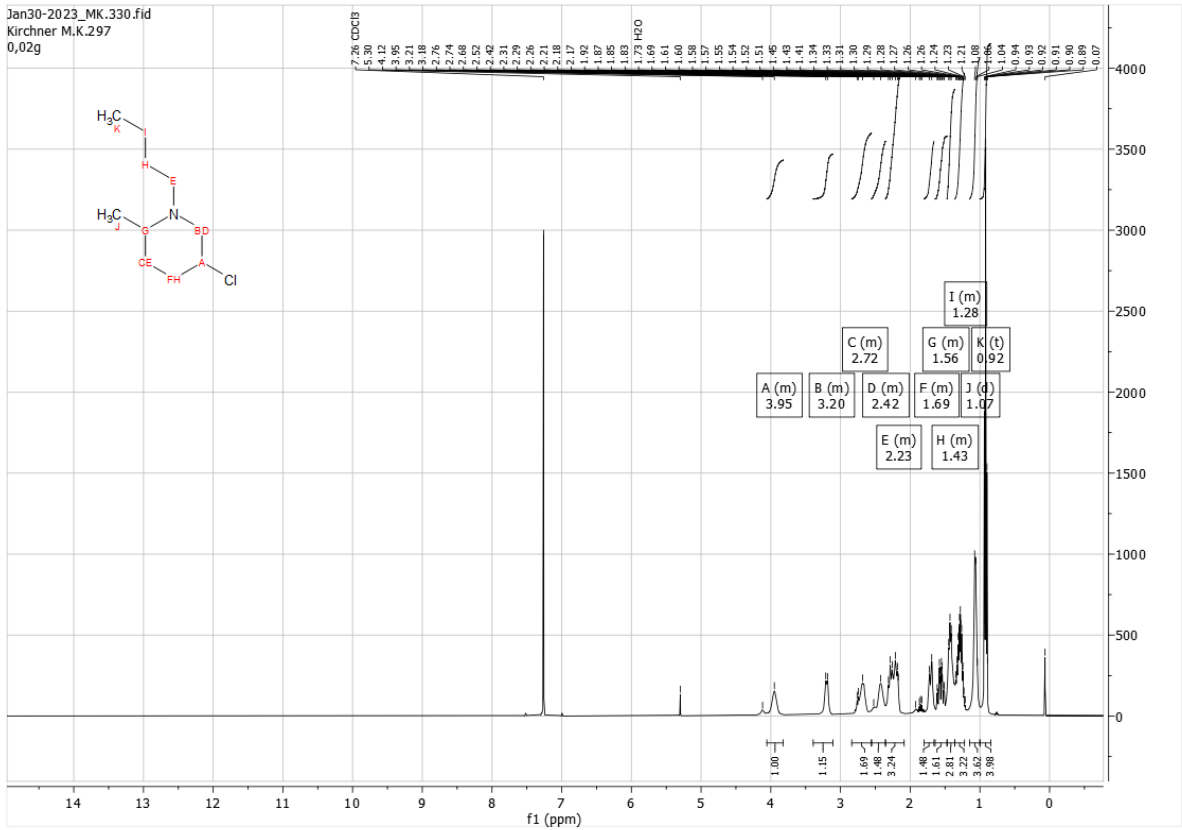
**Compound 2j**

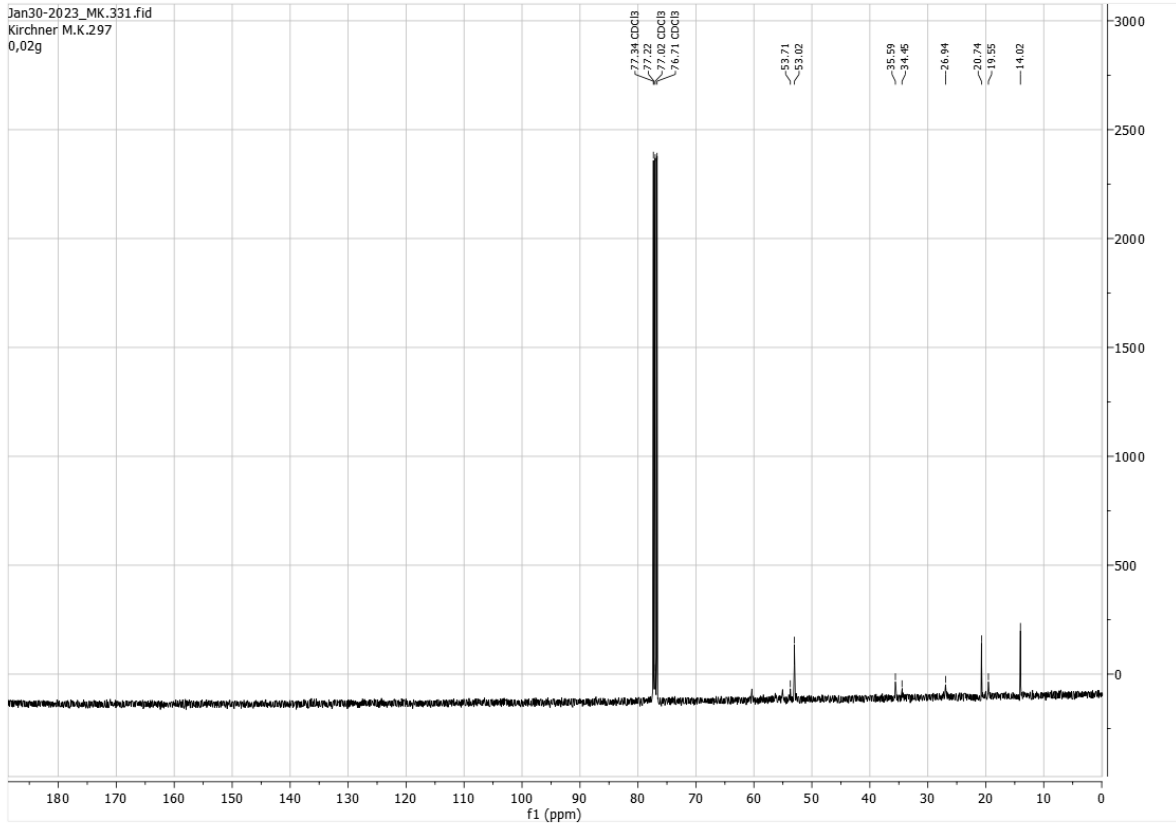




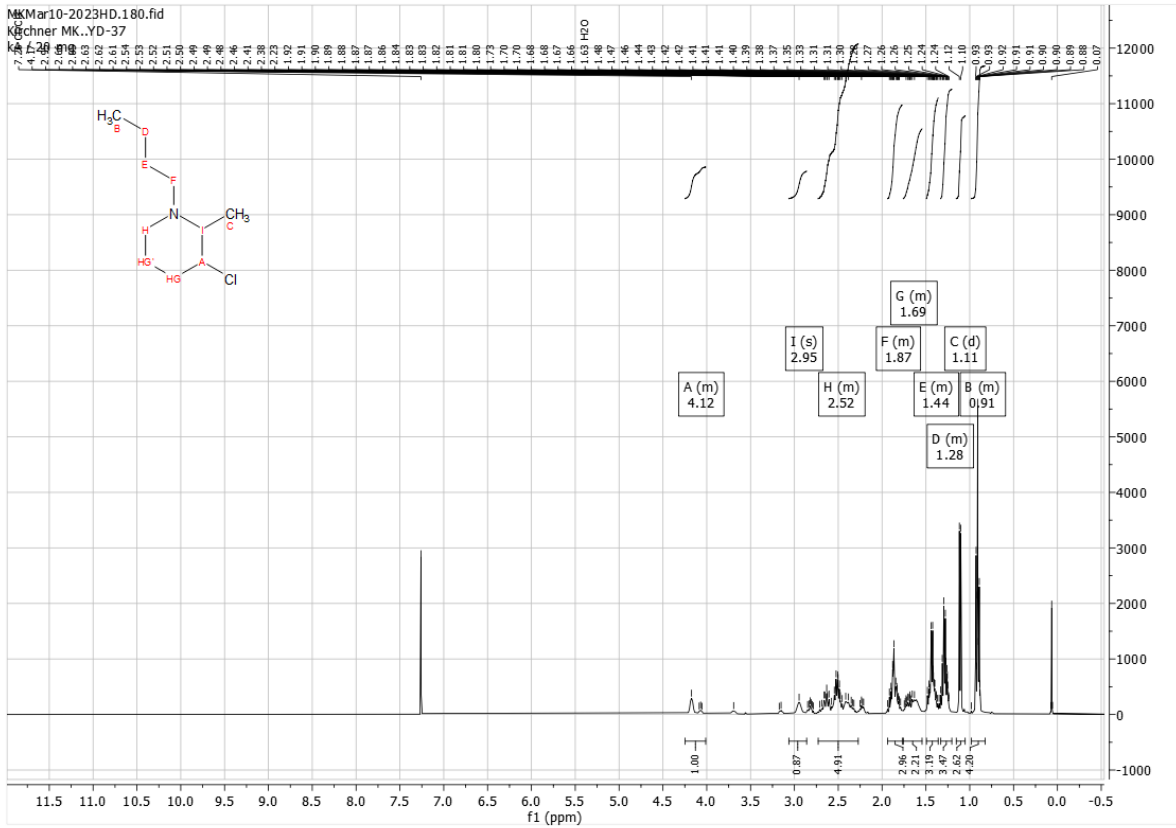


## Compound 2k

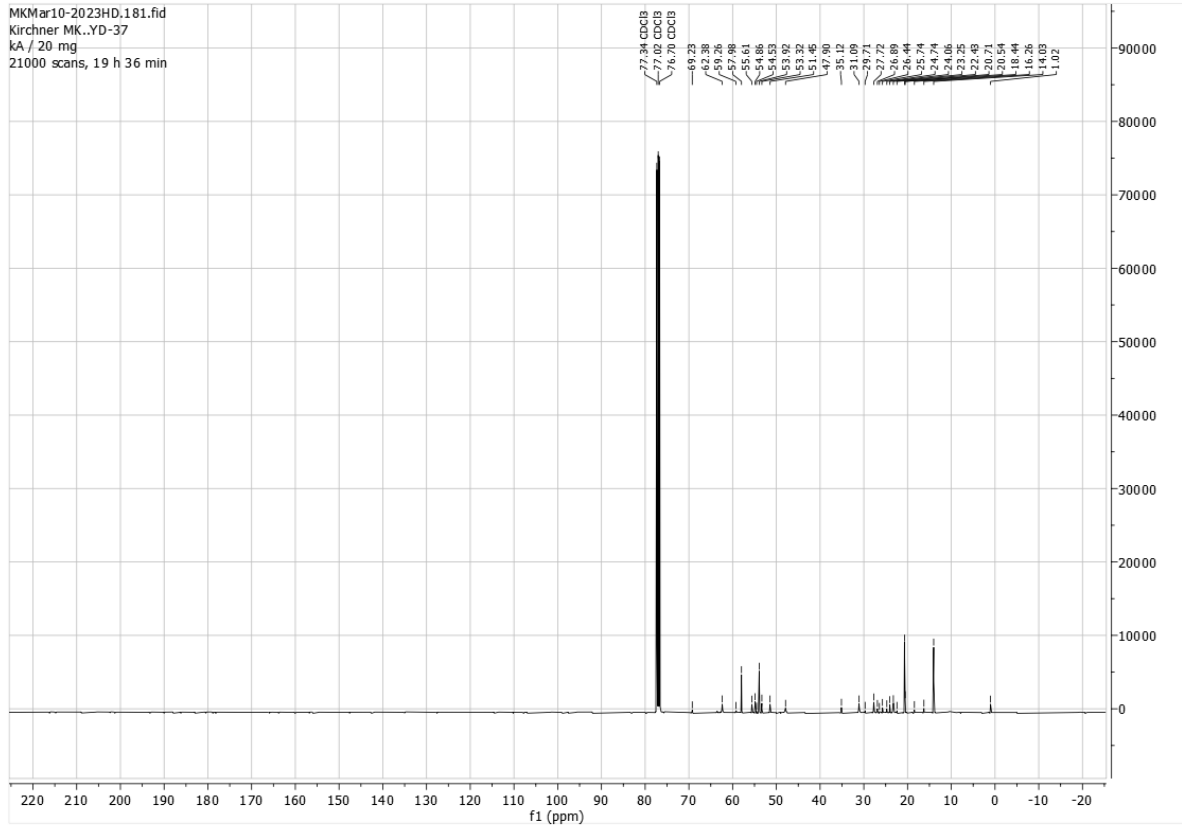




### Compound 21

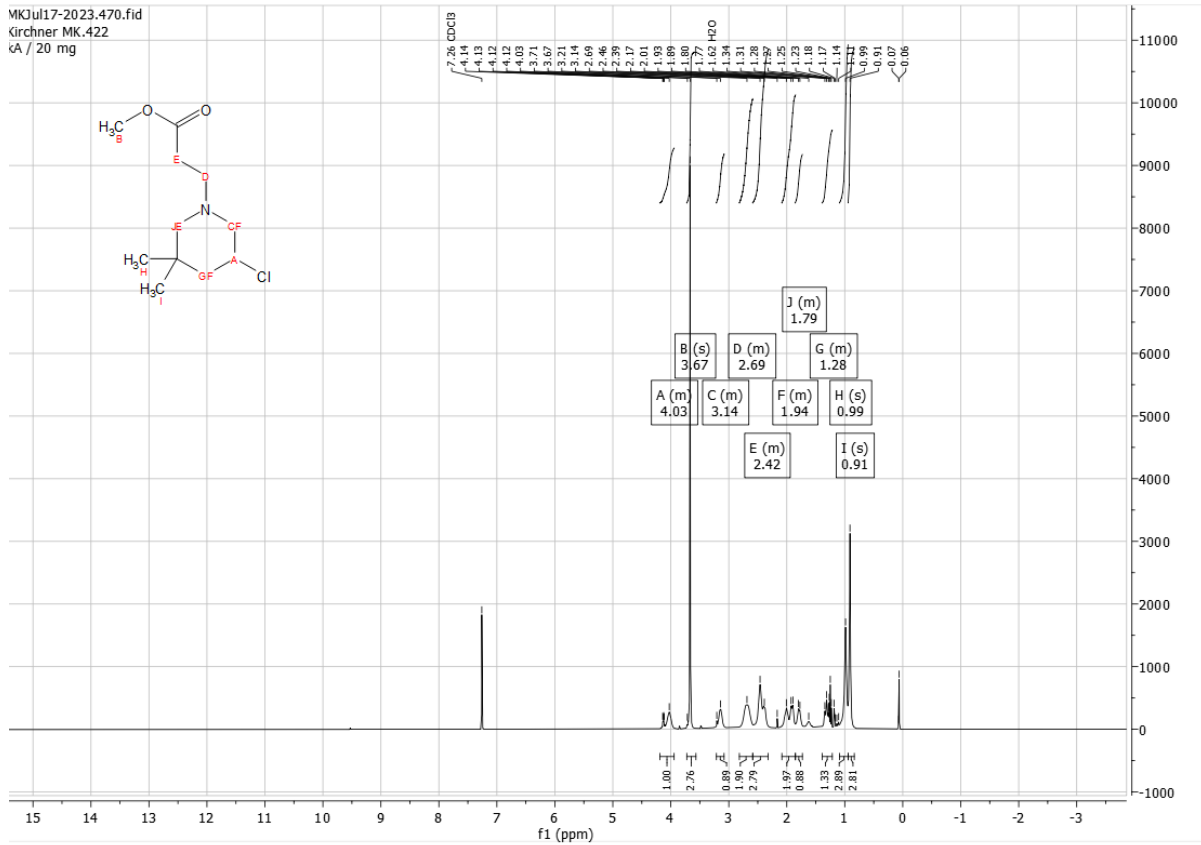


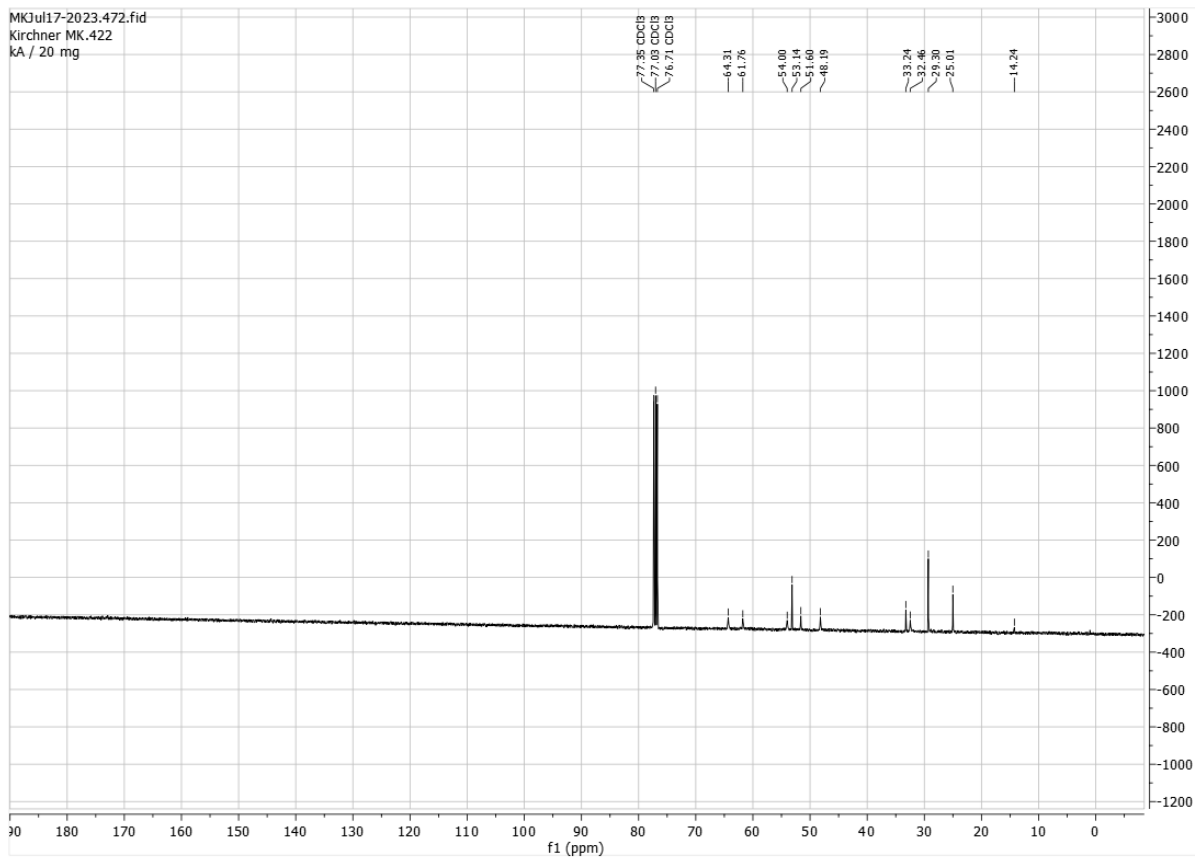
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 Kirchner MK..YD-37  
 kA / 20 mg  
 21000 scans, 19 h 36 min



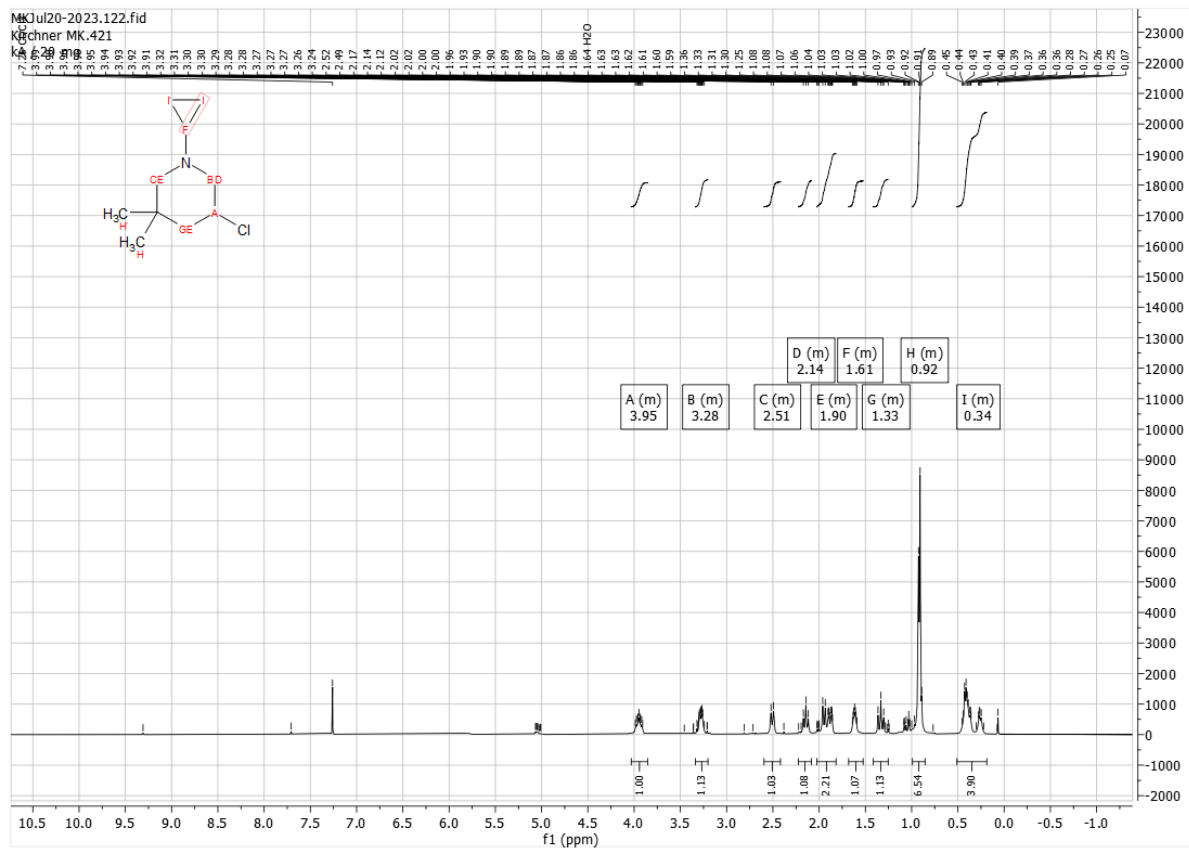
## Compound 2m

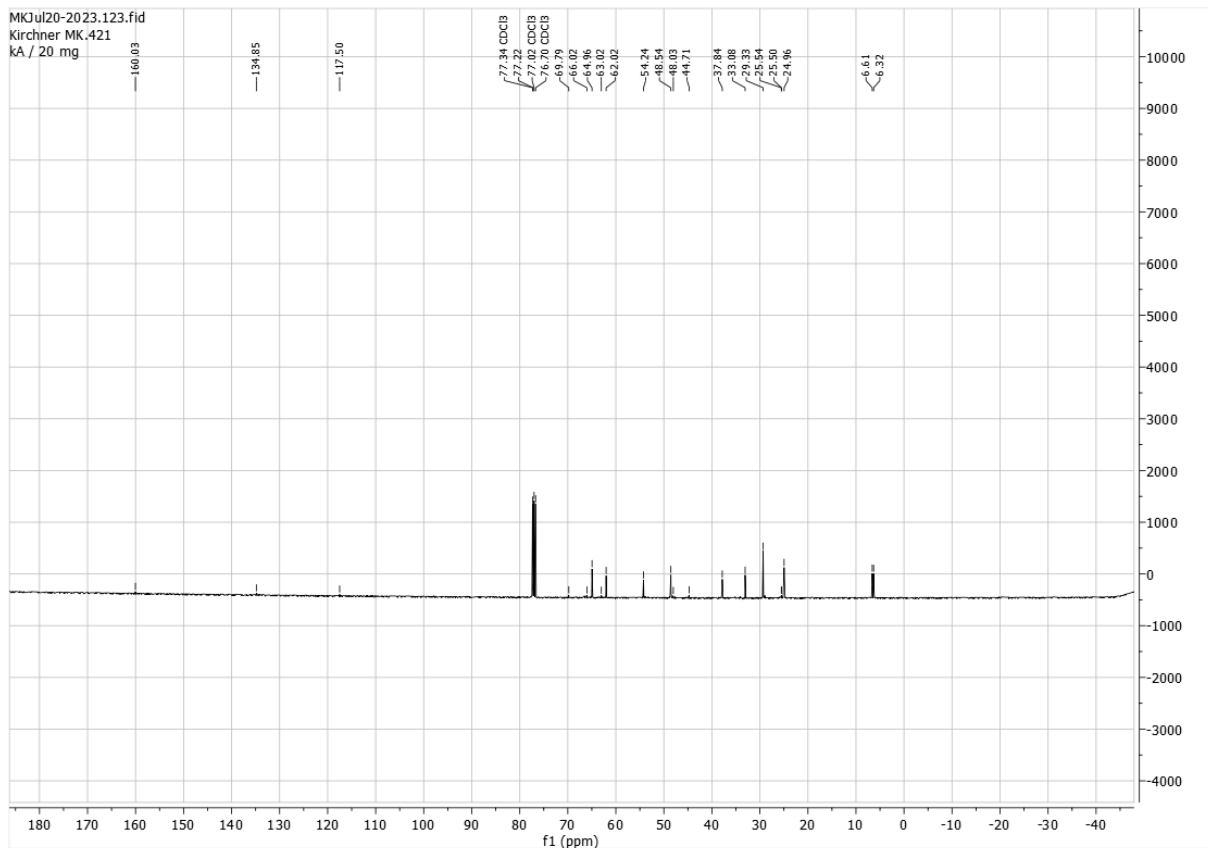
MKJul17-2023.470.fid  
 Kirchner MK.422  
 kA / 20 mg



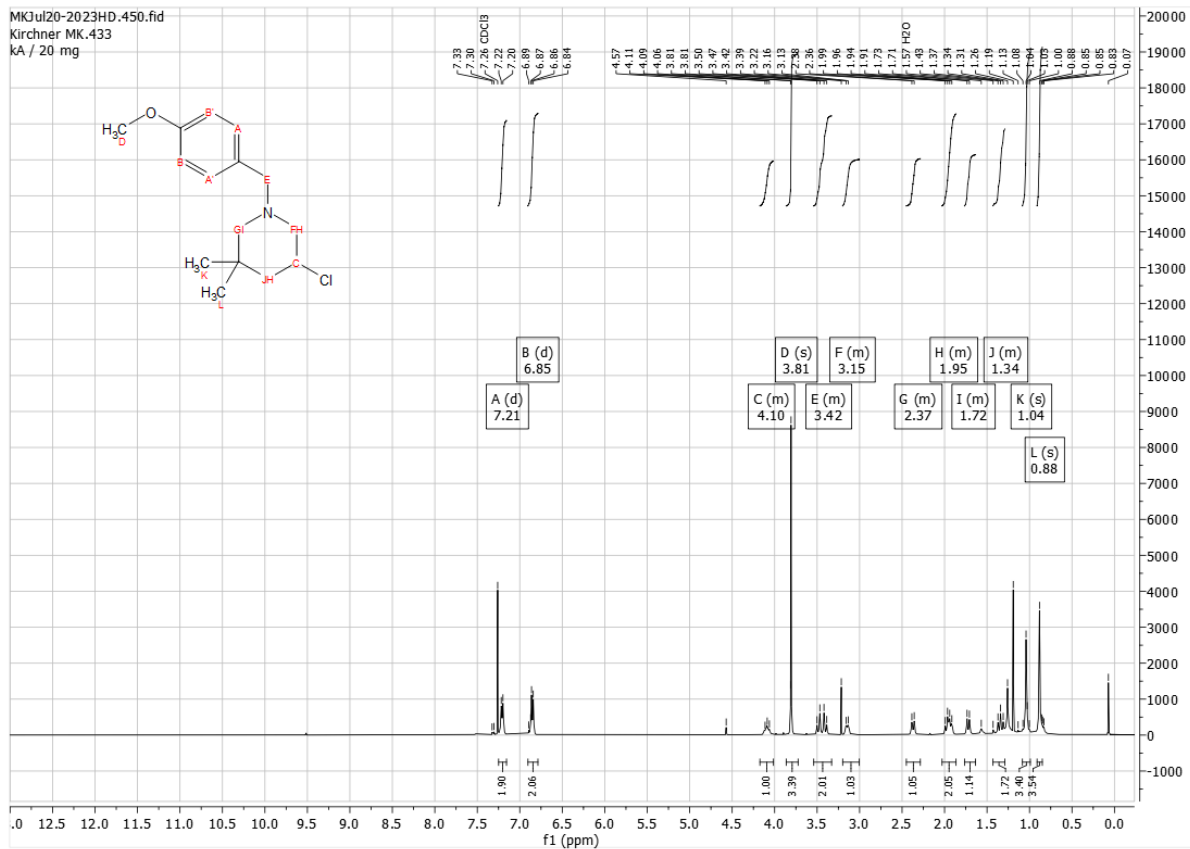


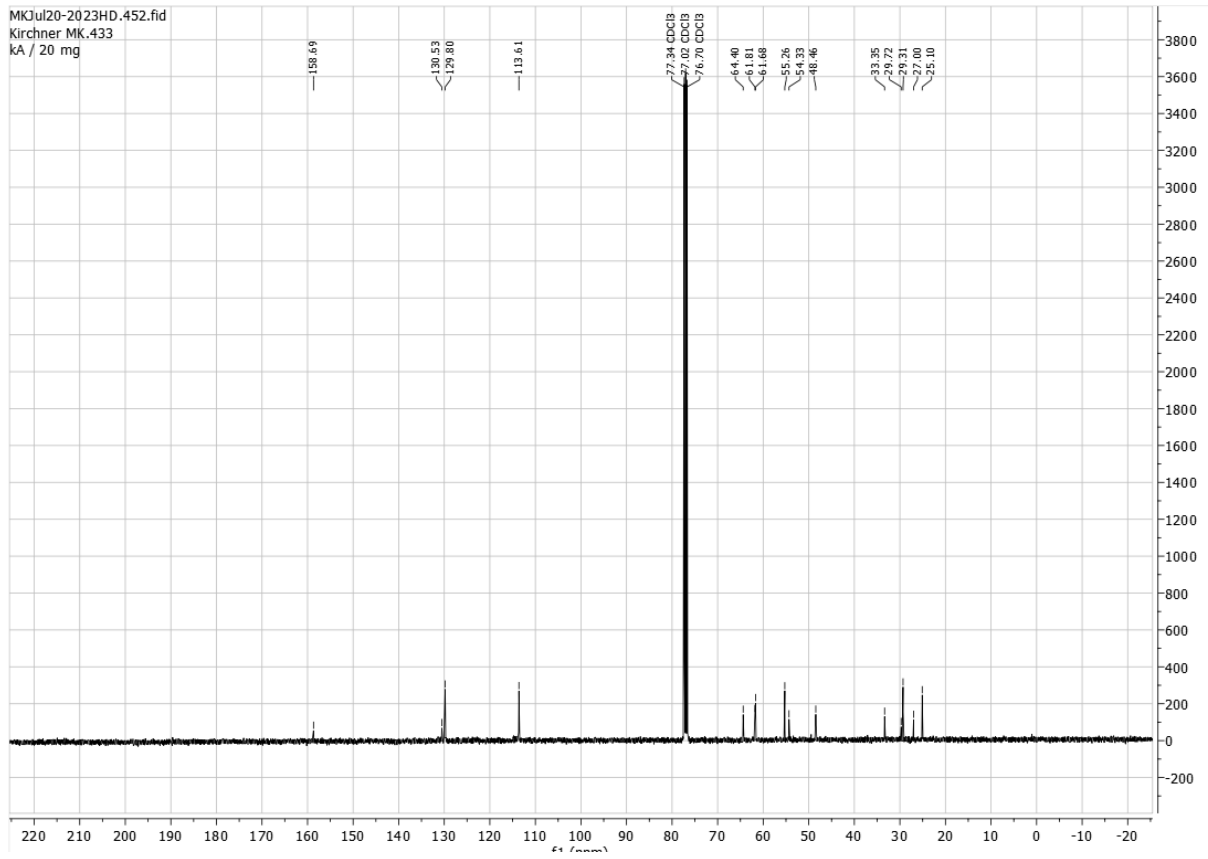
### Compound 2n



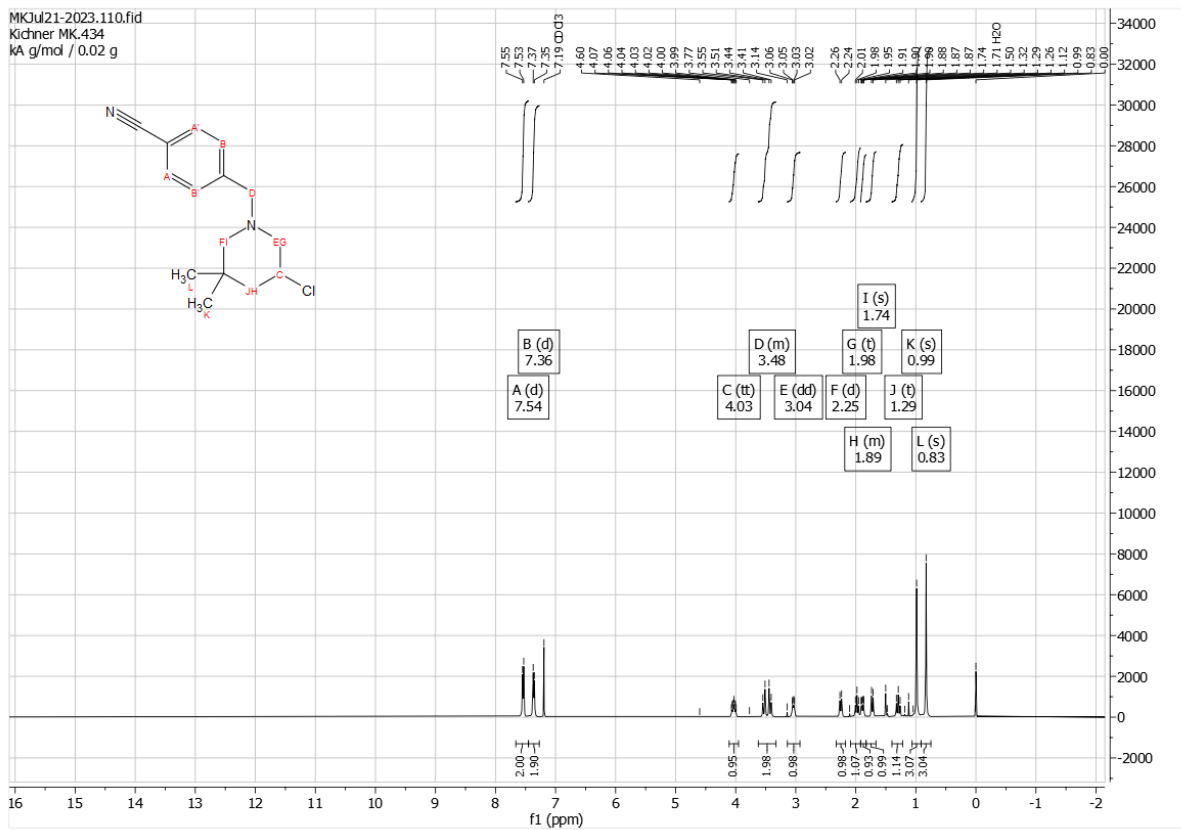


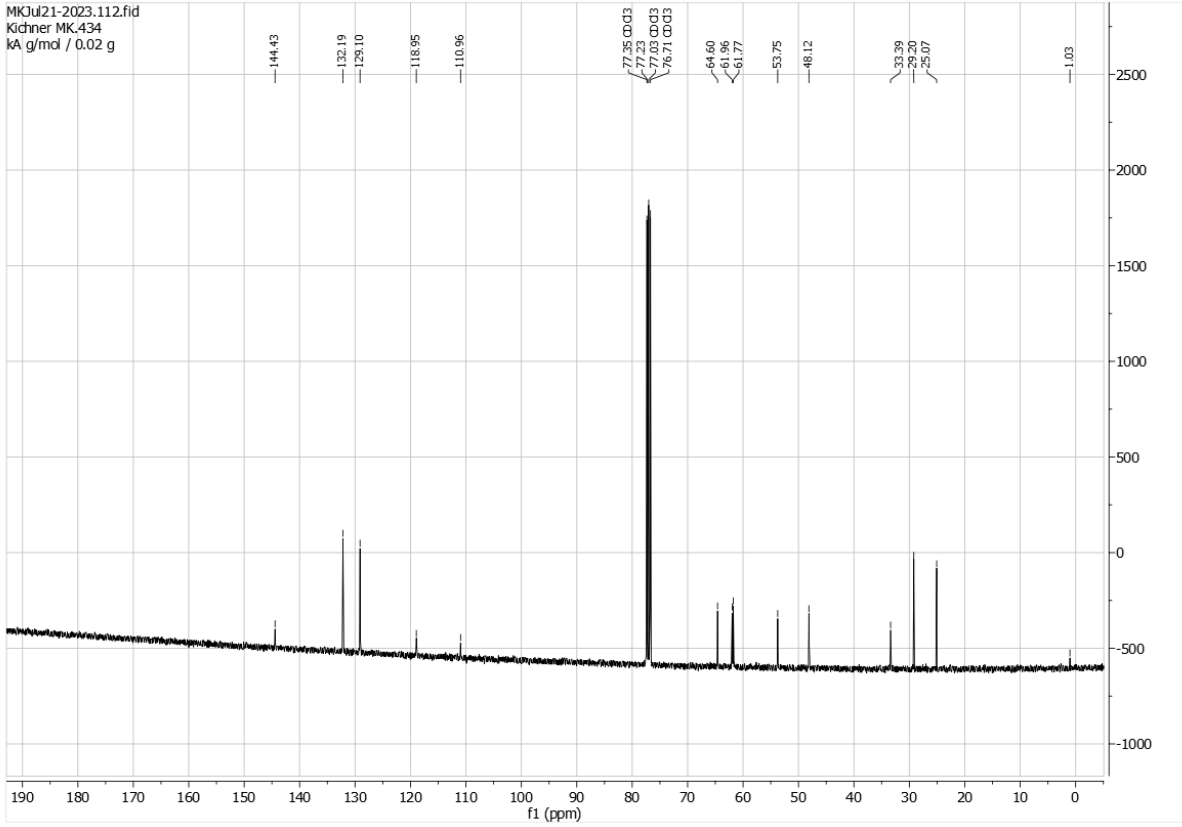
## Compound 2o



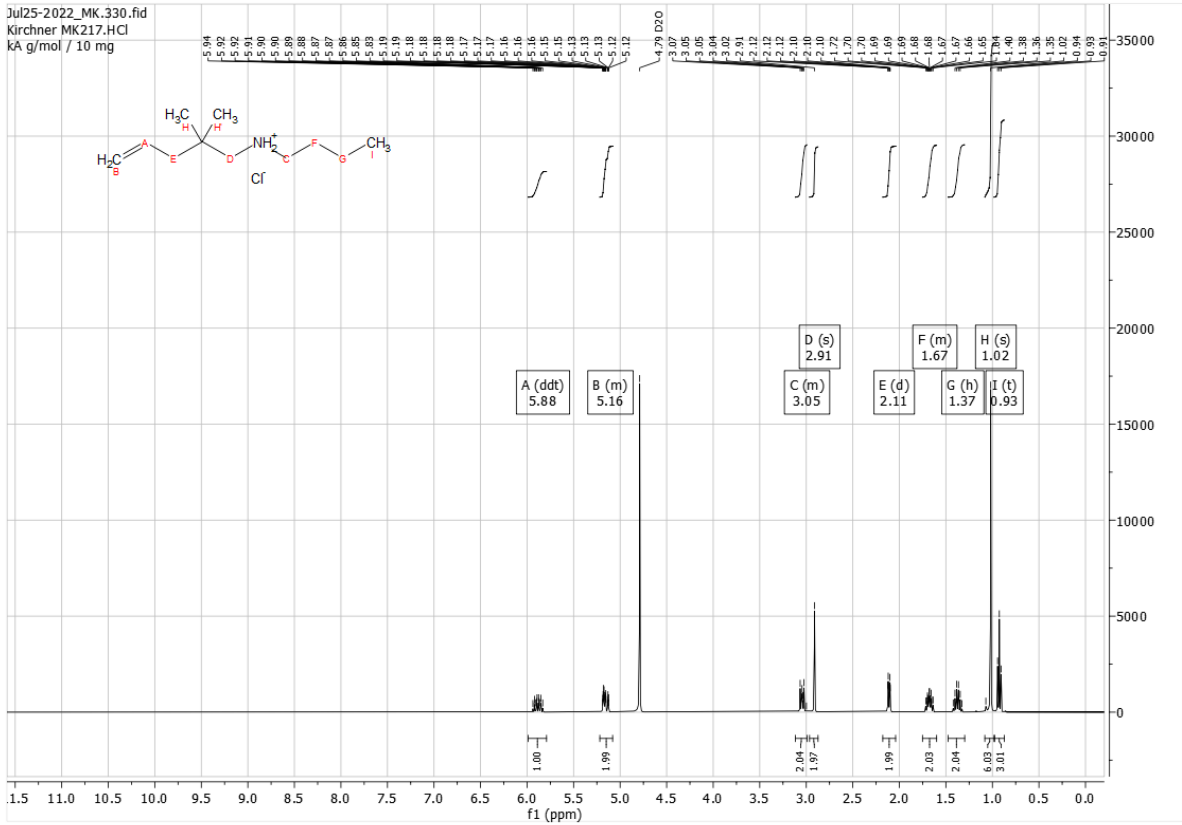


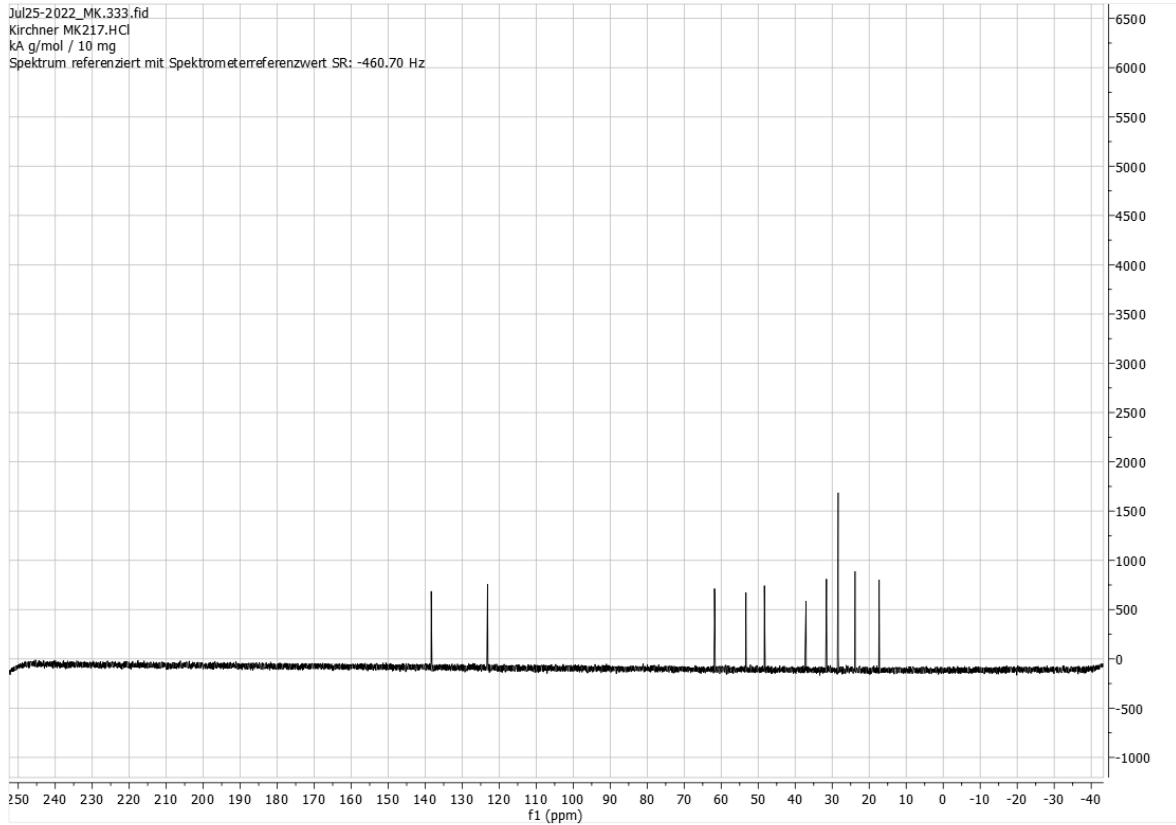
### Compound 2p



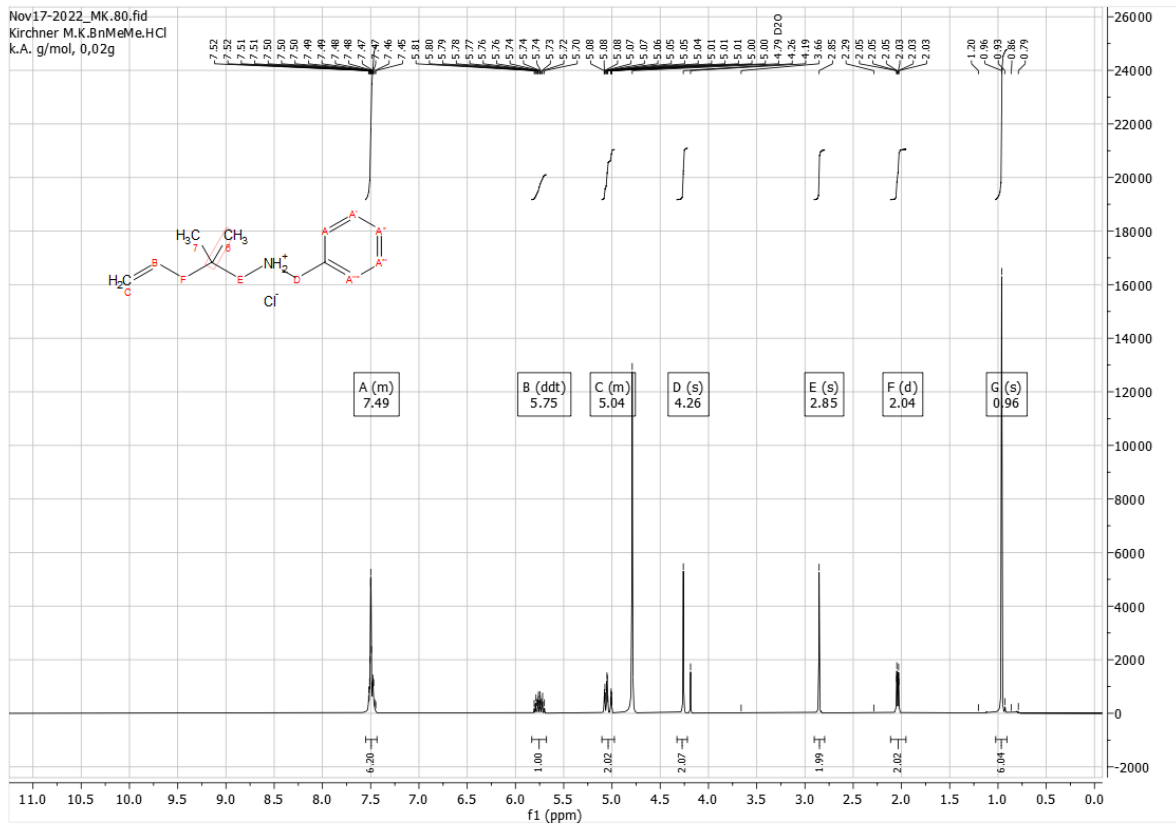


### Compound 3a



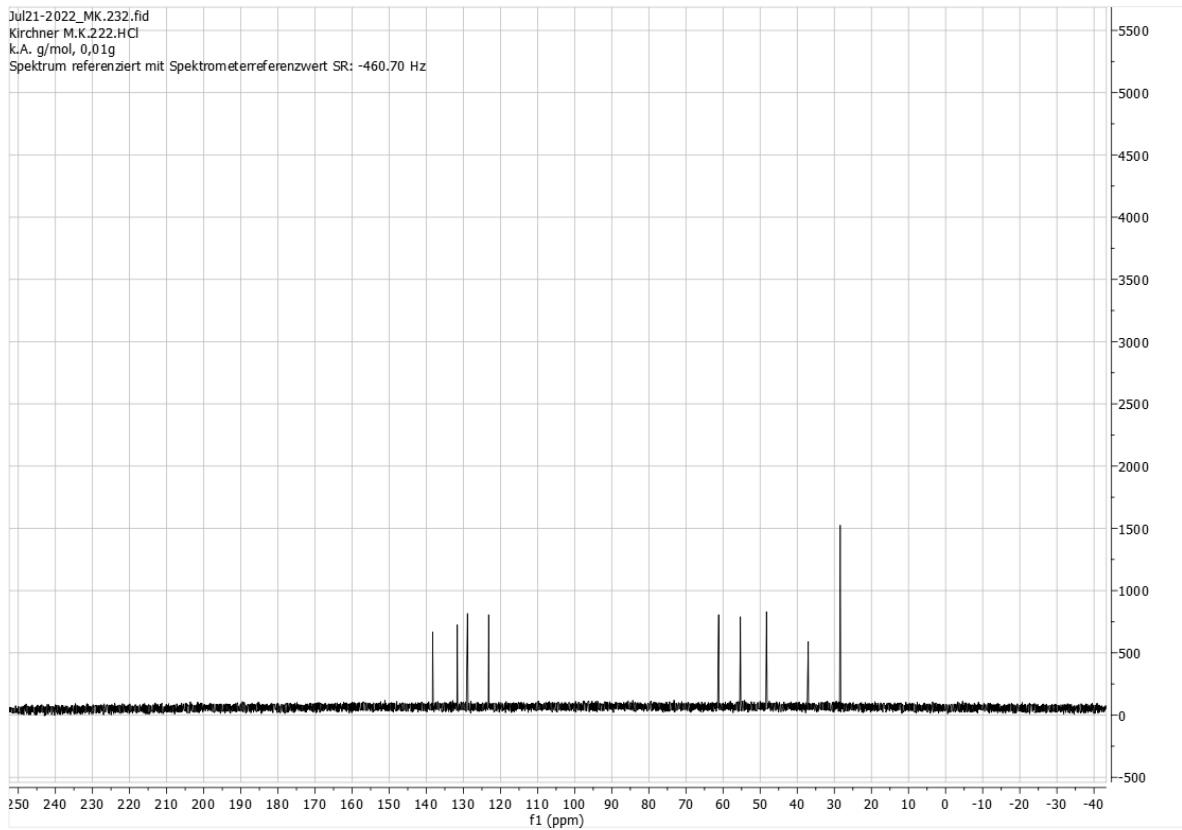
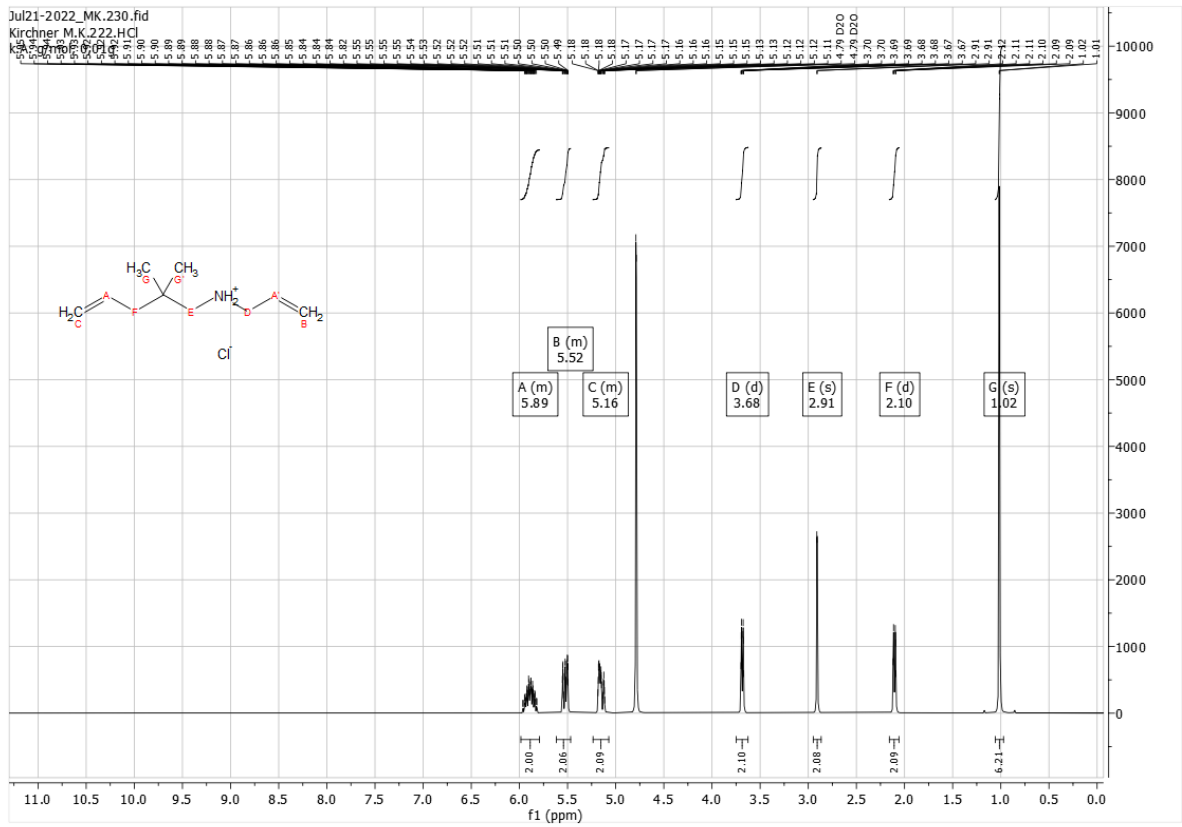


### Compound 3b

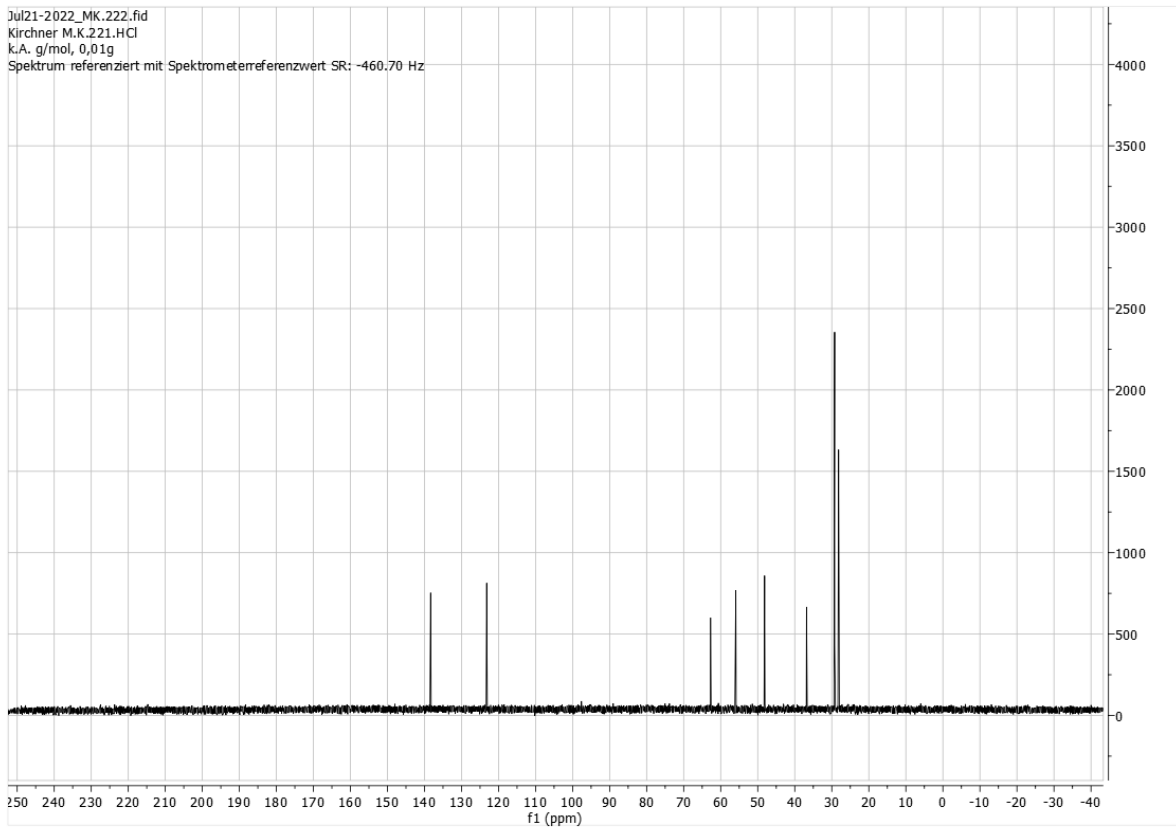
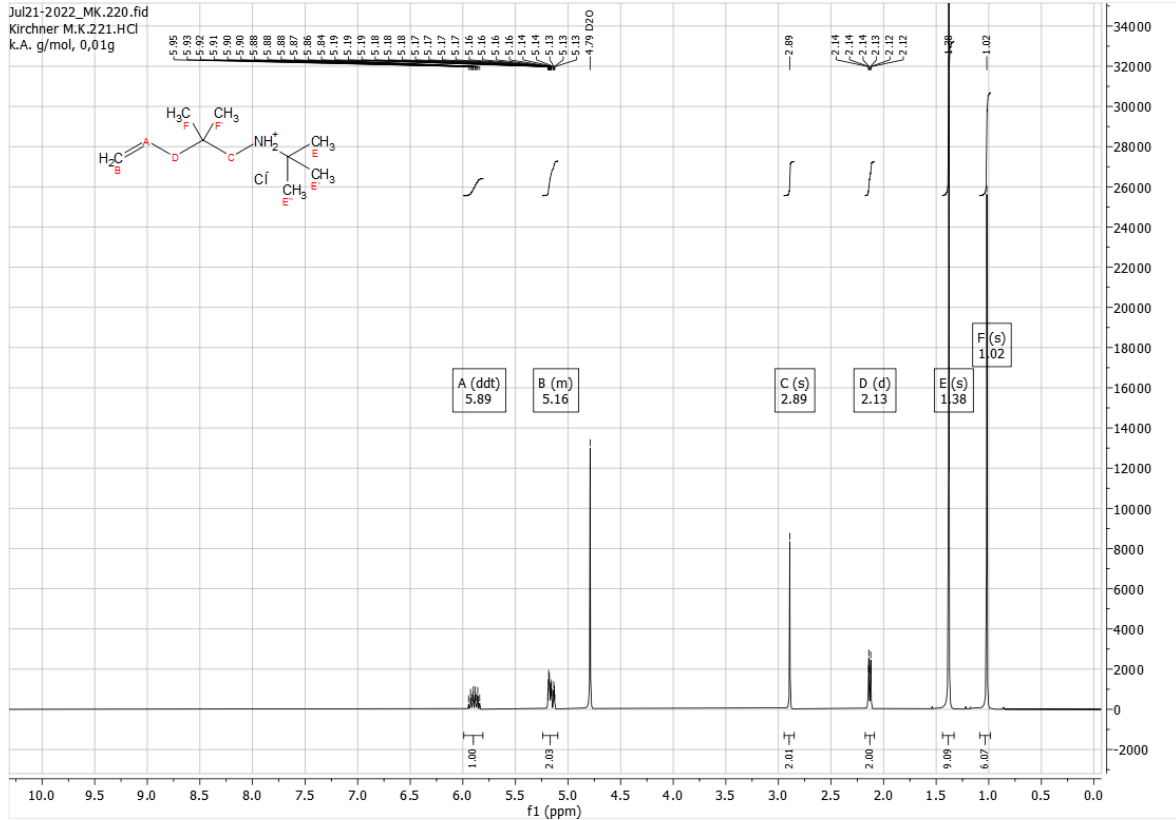


### Compound 3c

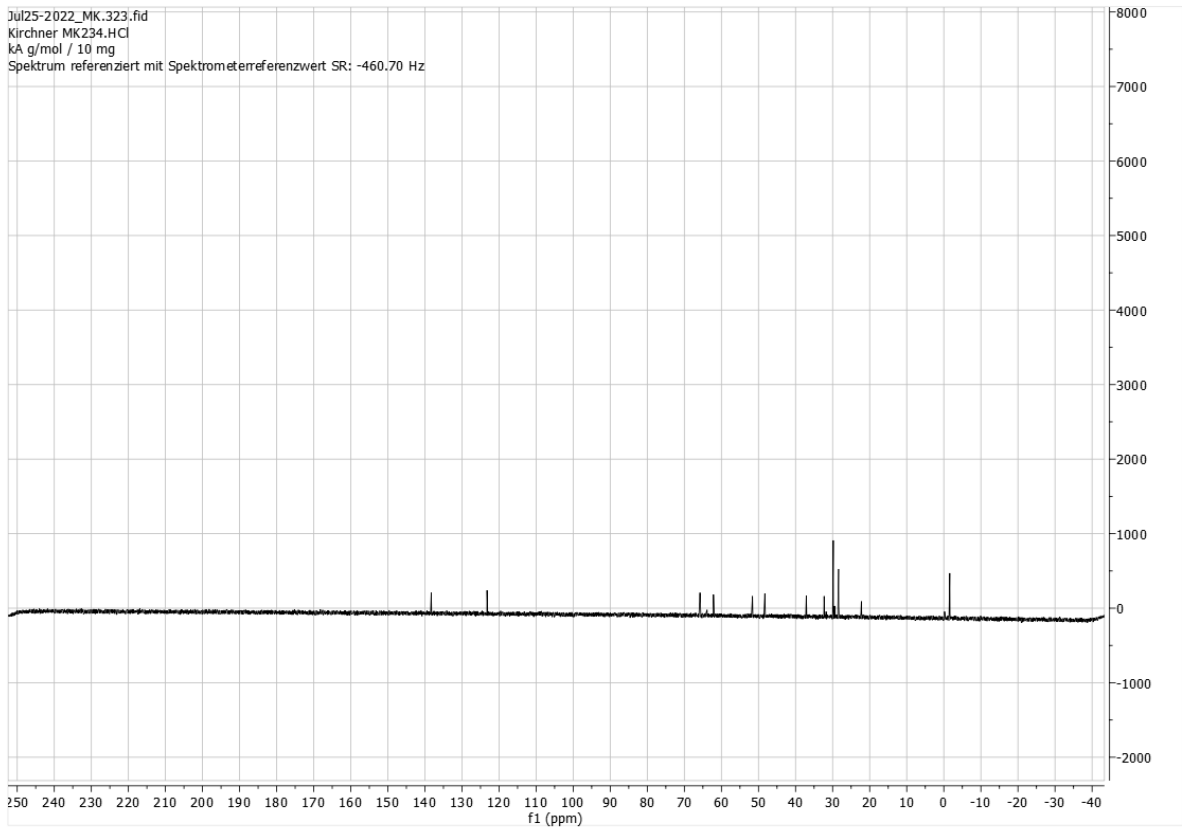
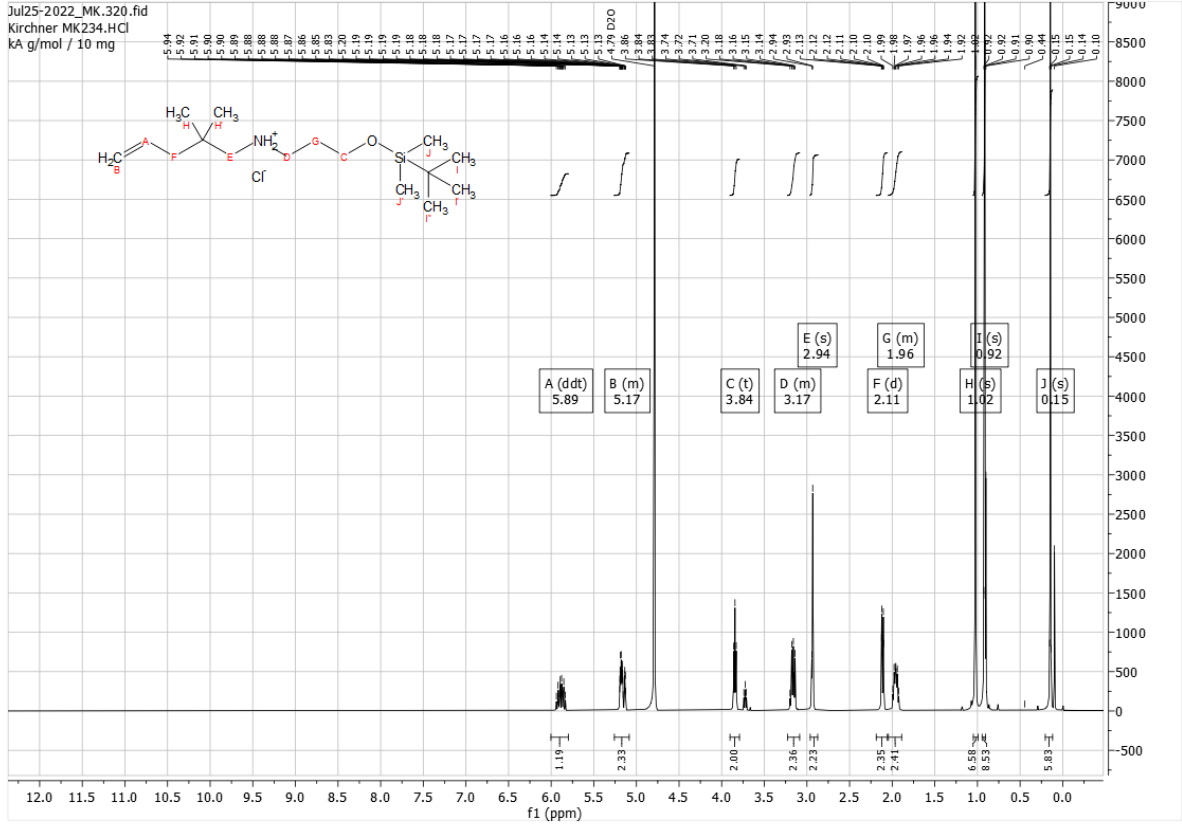




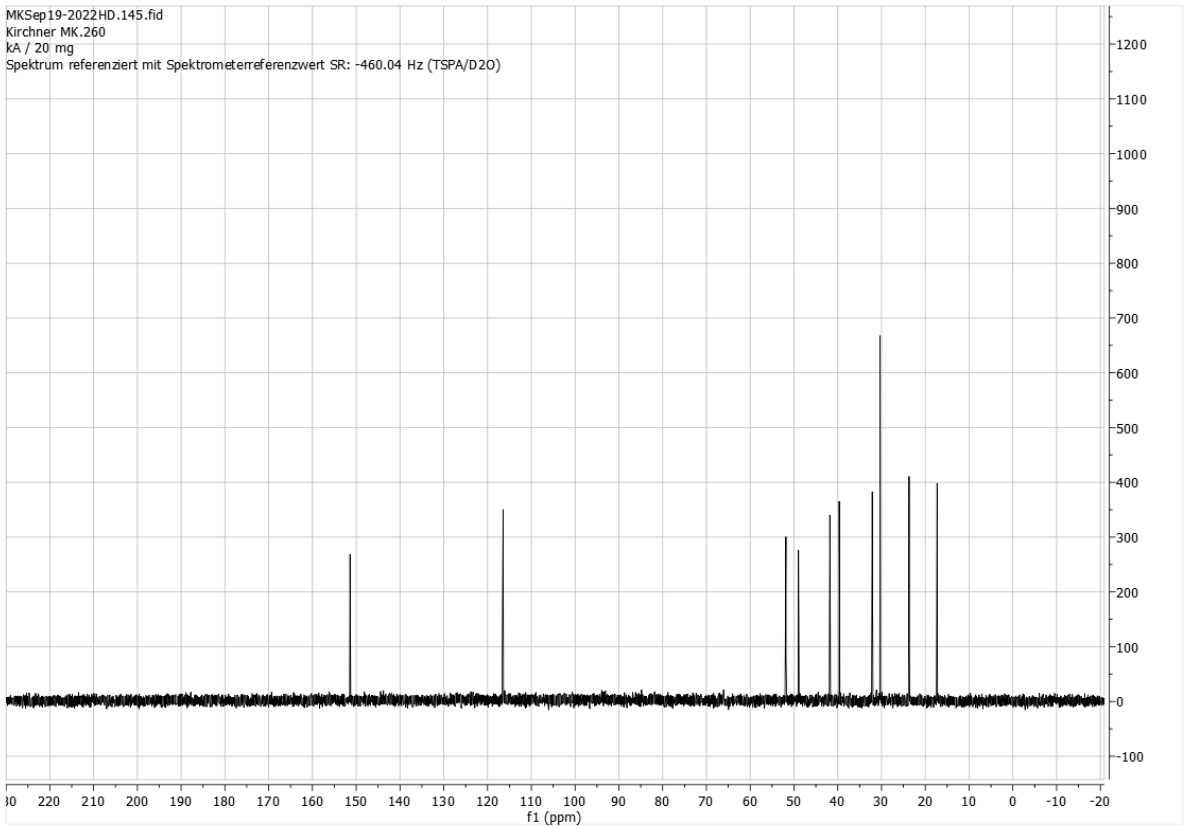
Compound 3d



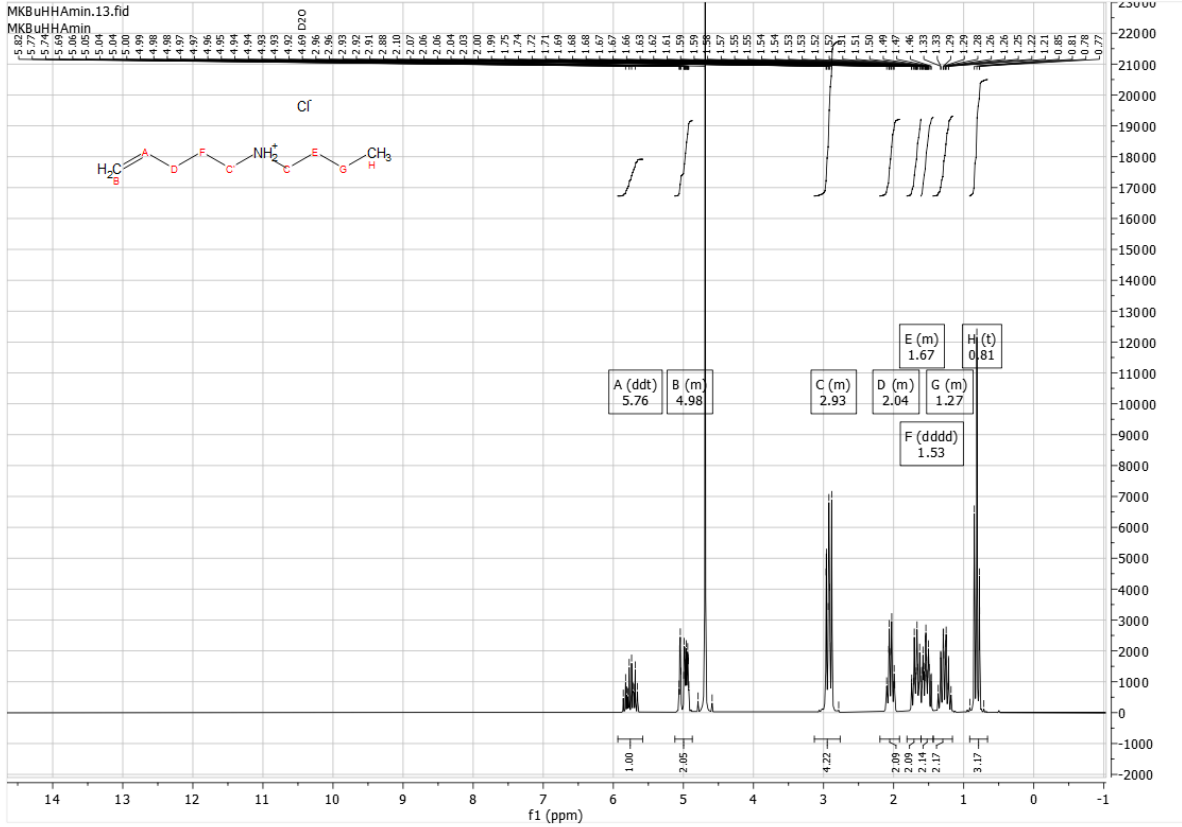
Compound 3e



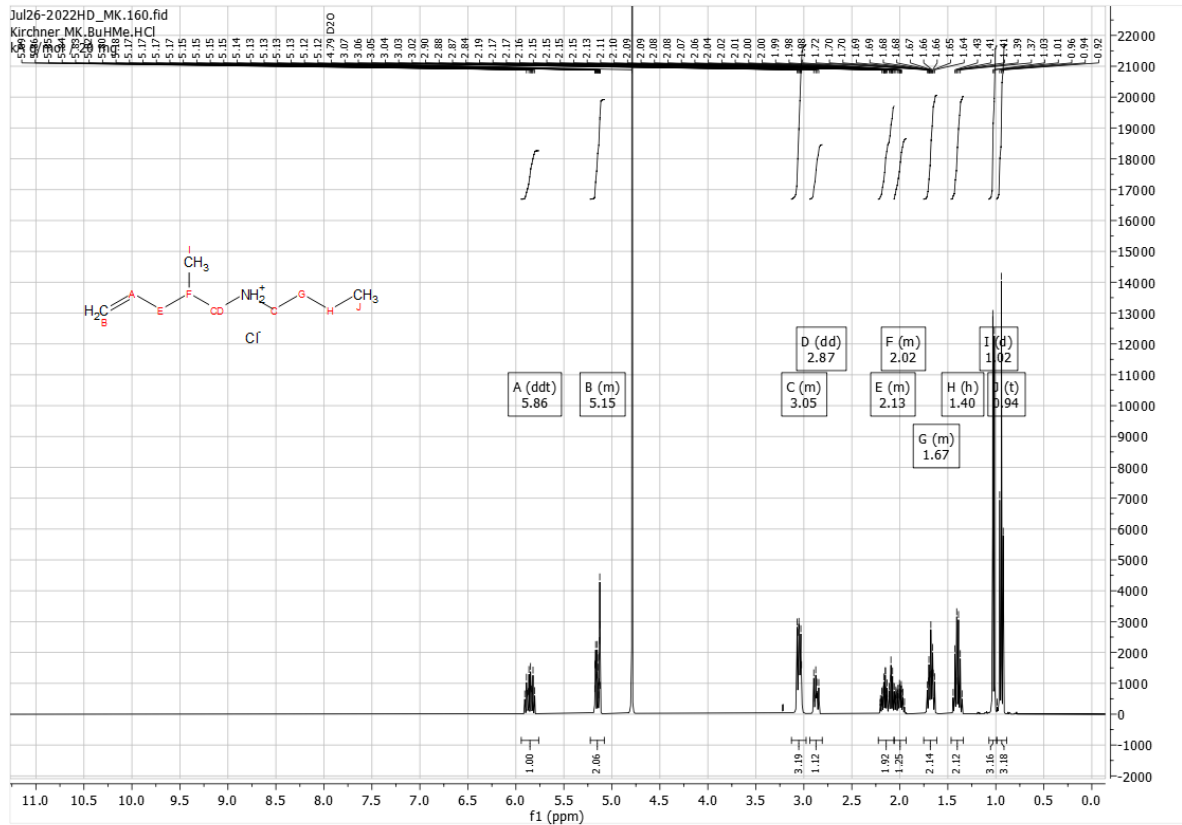
**Compound 3f**

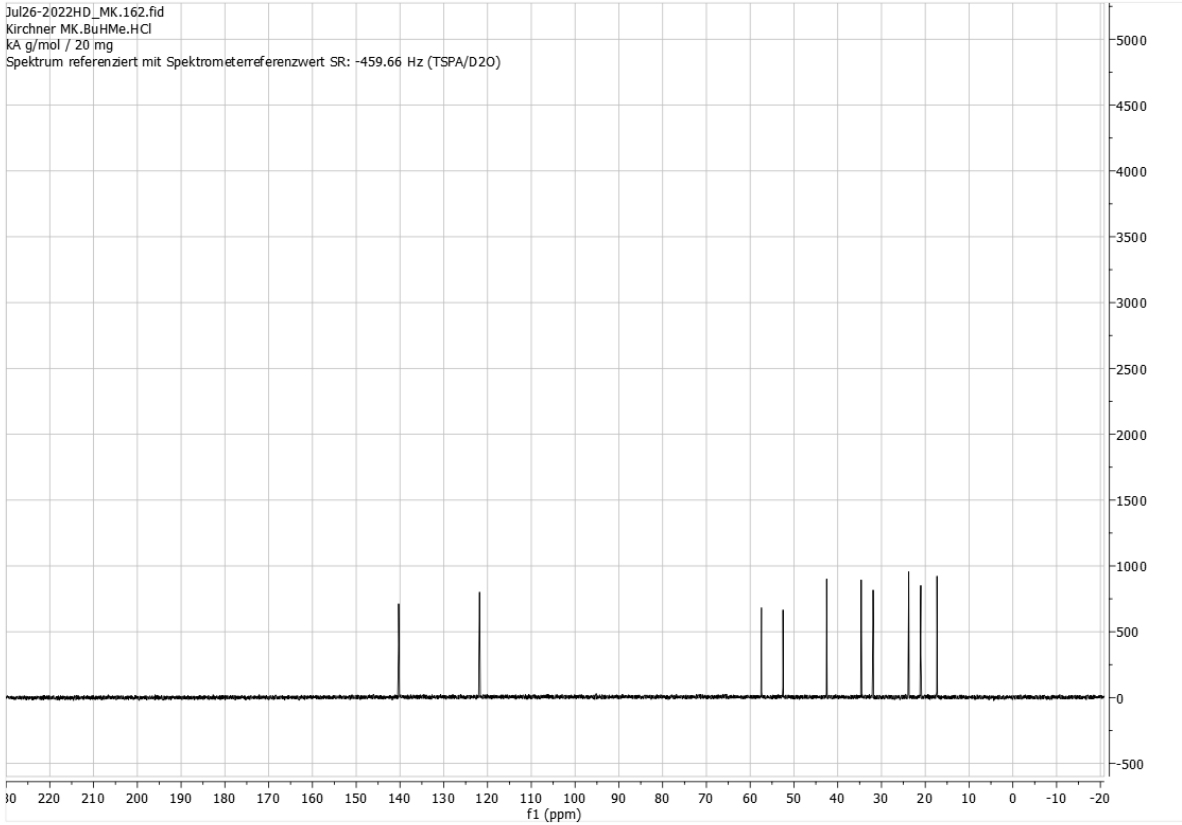


Compound 3g

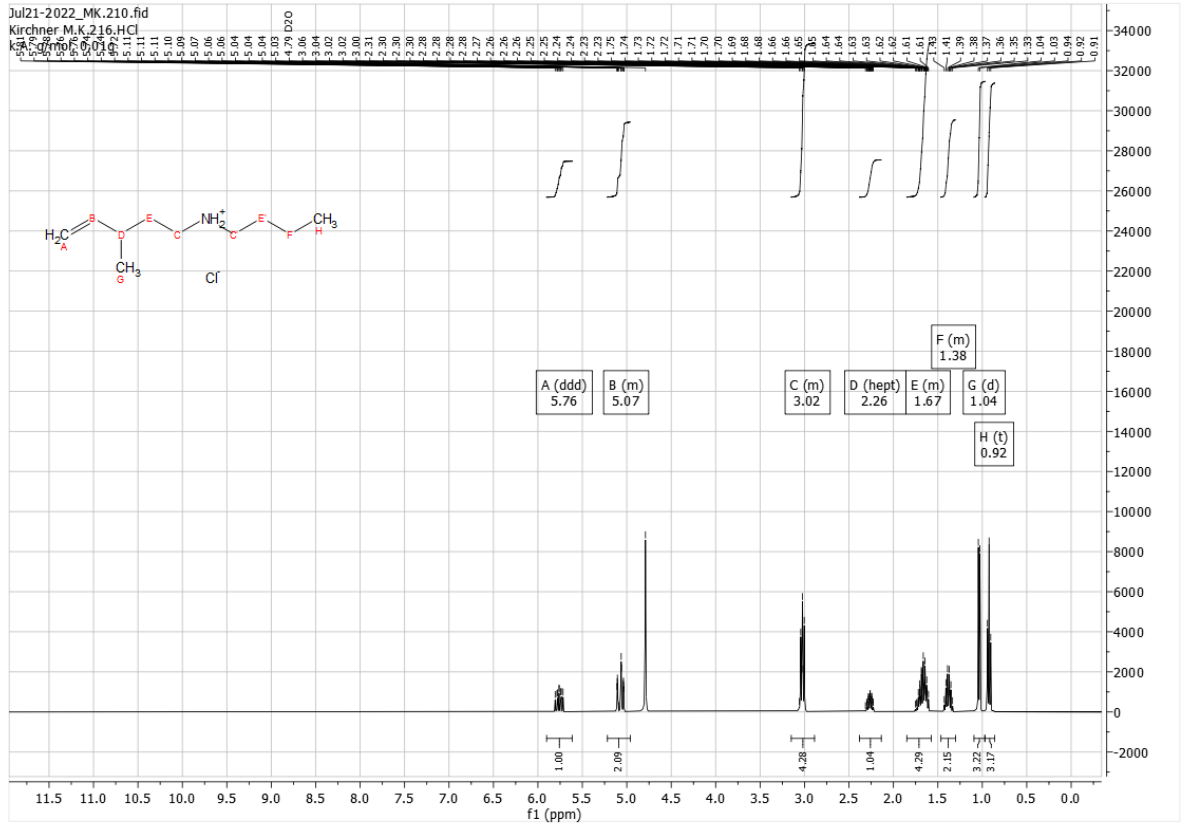


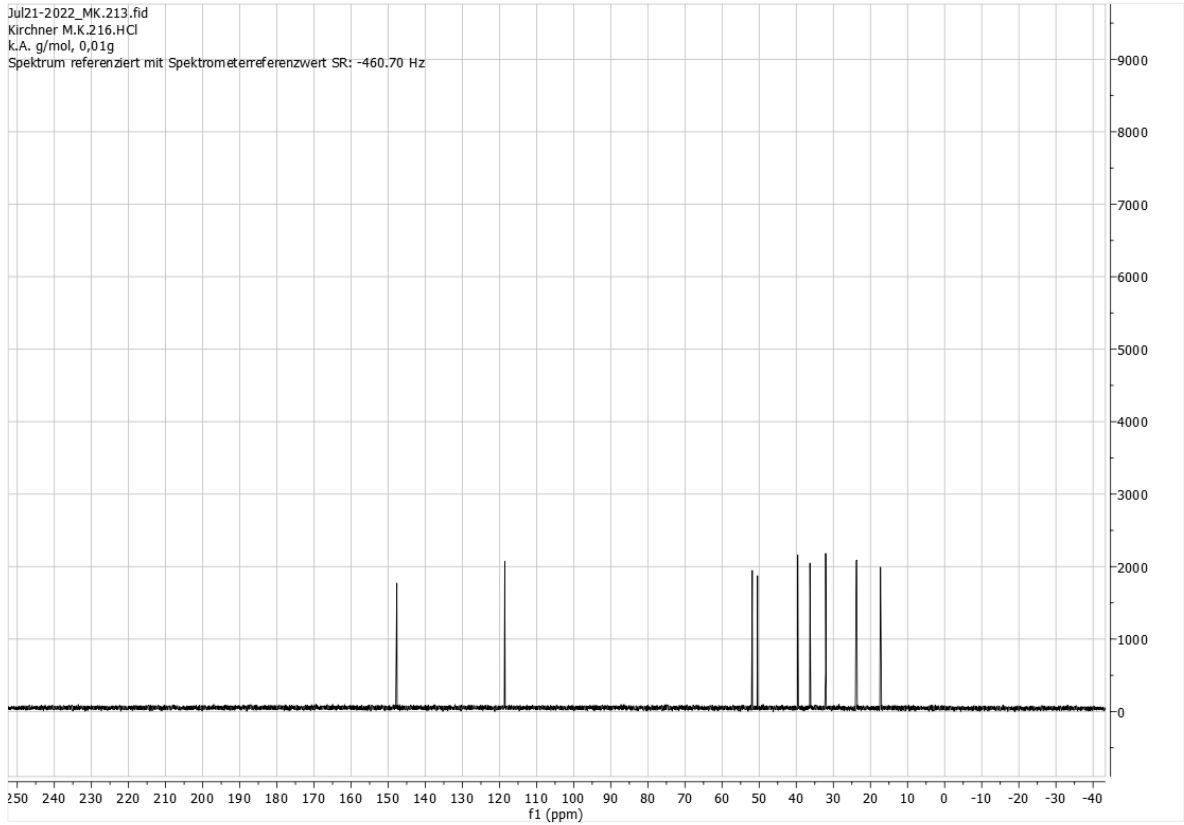
### Compound 3h



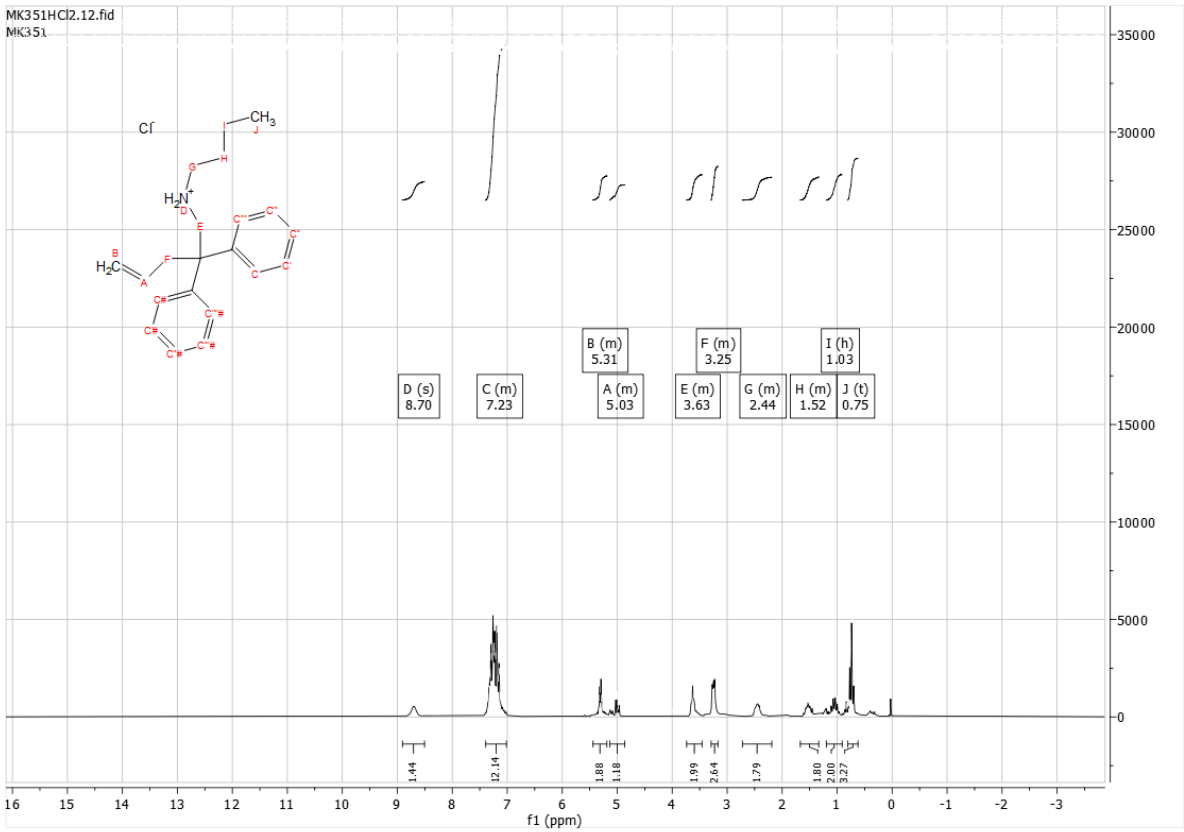


### Compound 3i

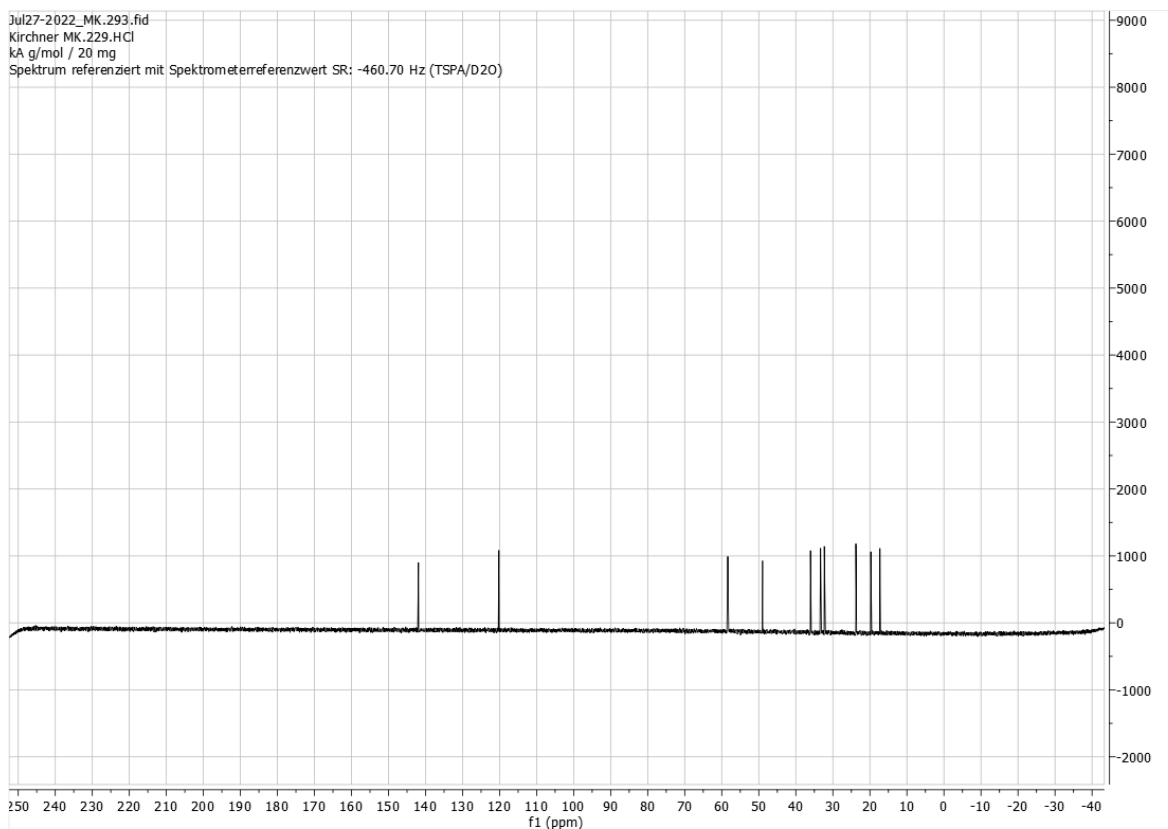
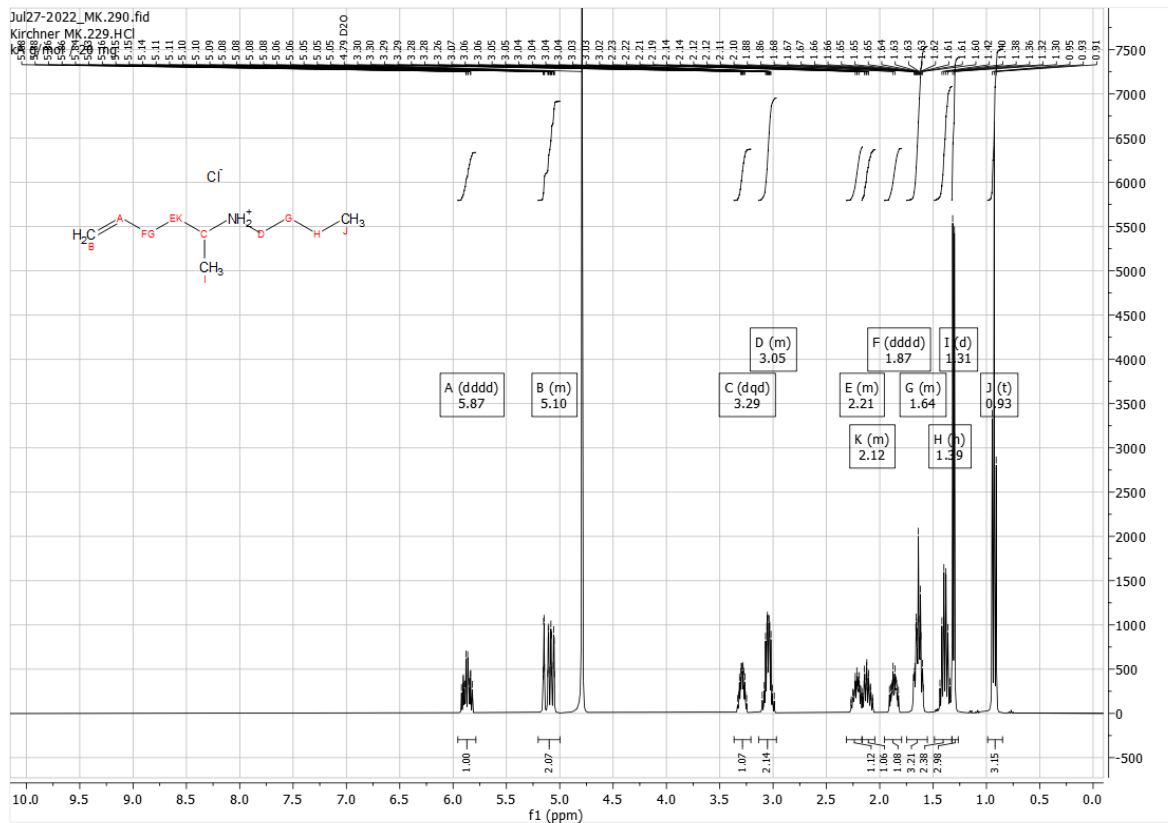




### Compound 3j

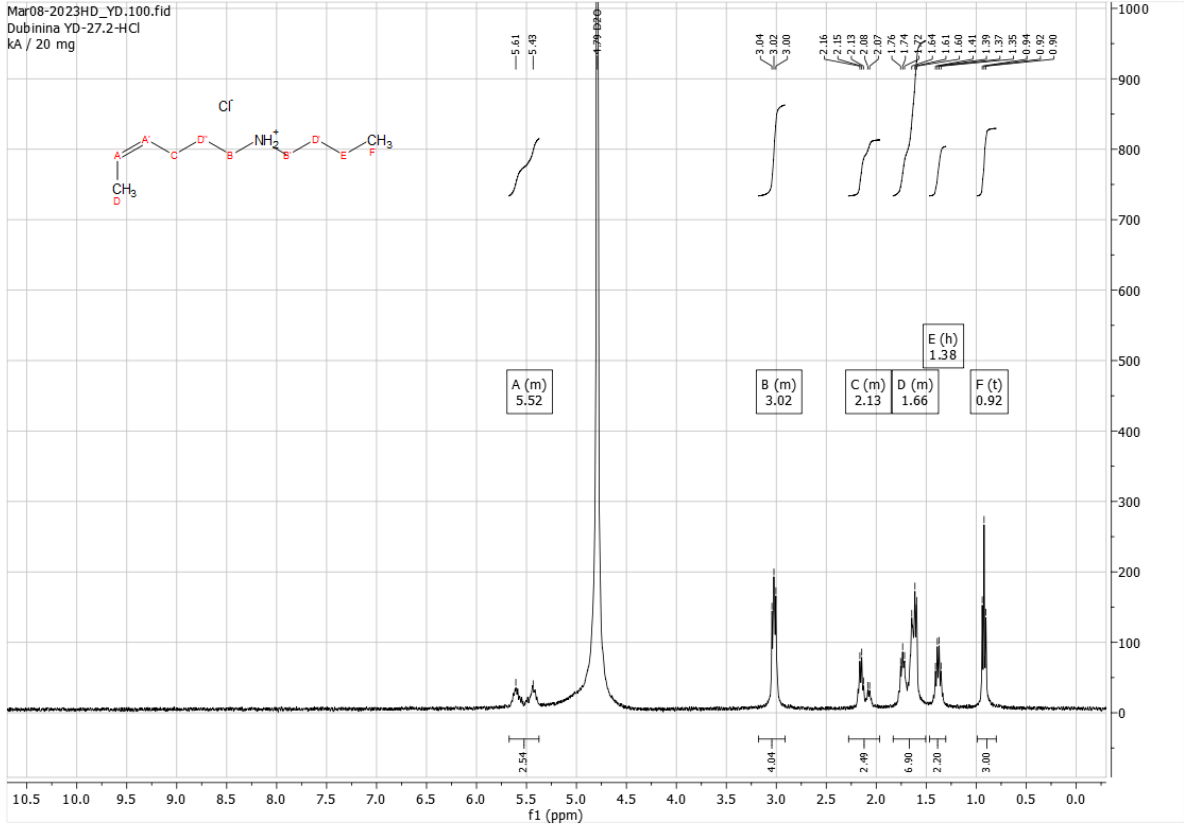


### Compound 3k

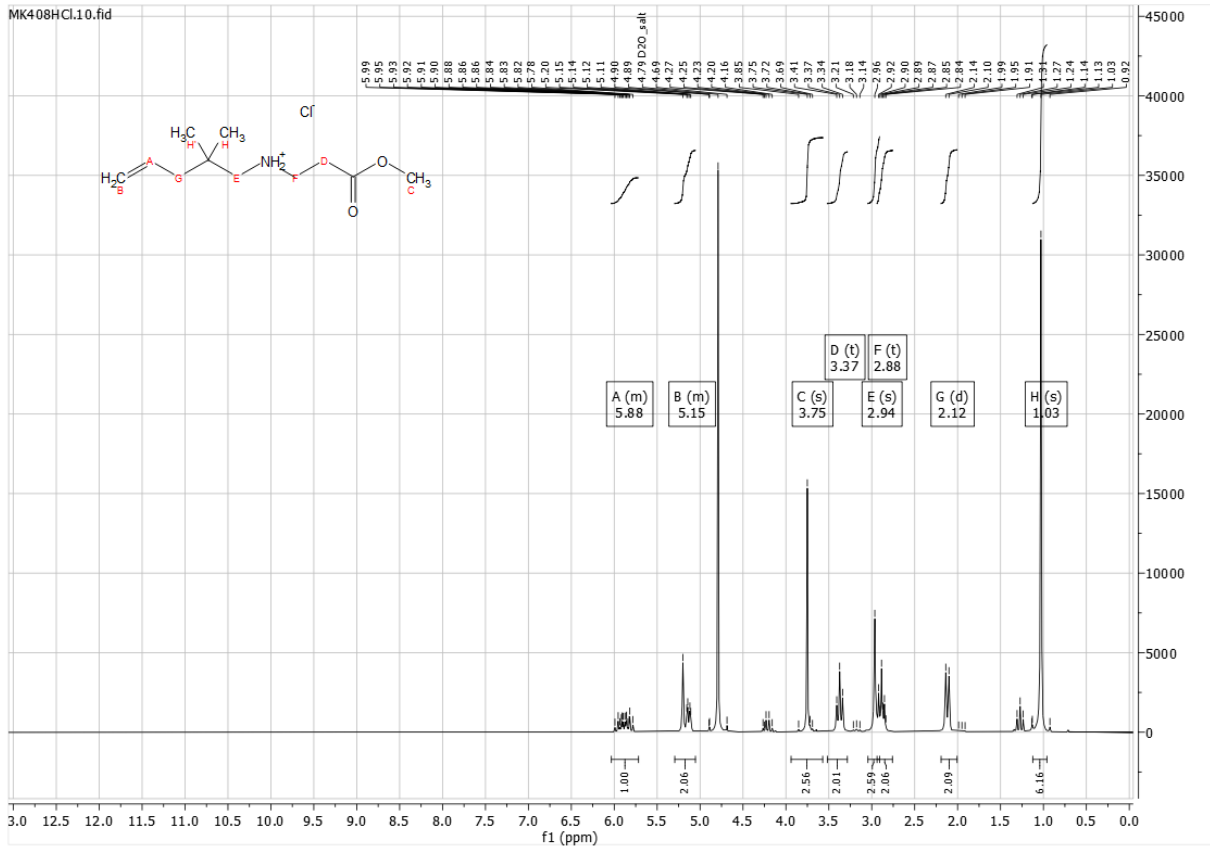


Compound 31

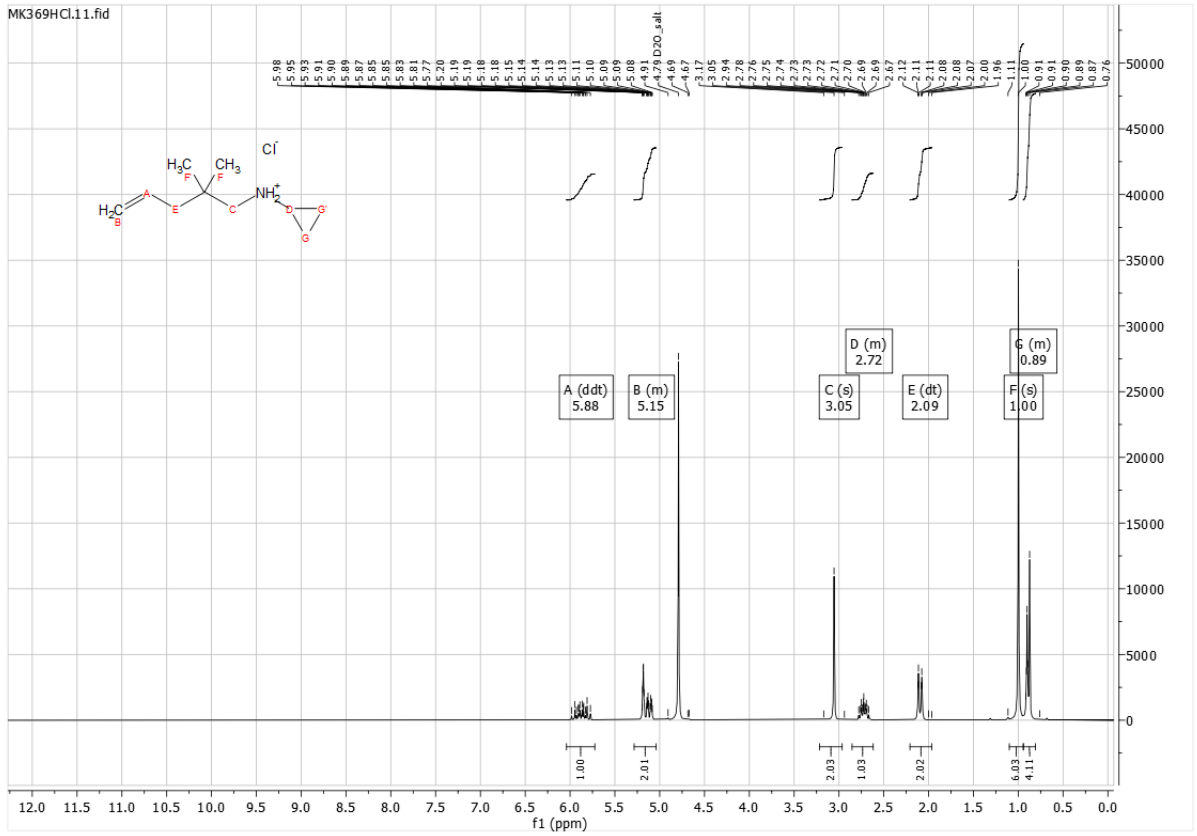




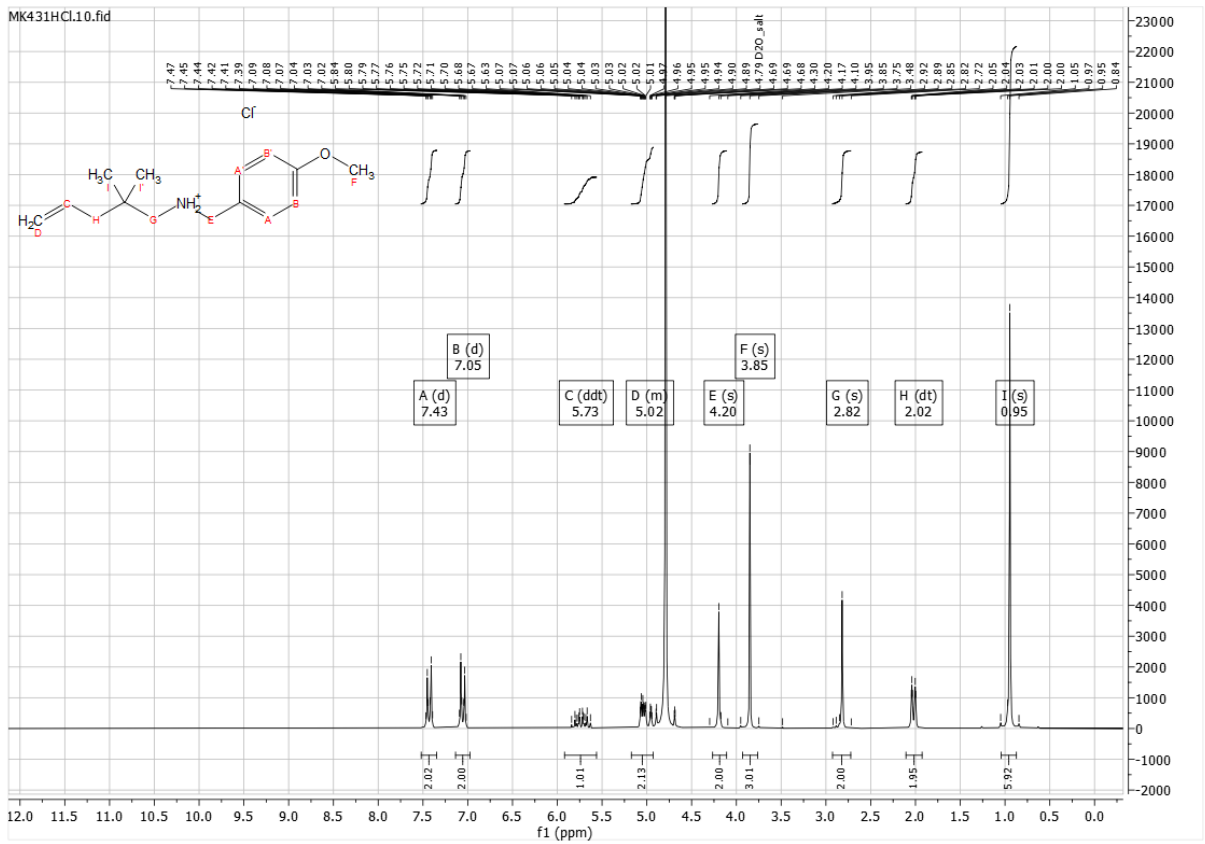
### Compound 3m



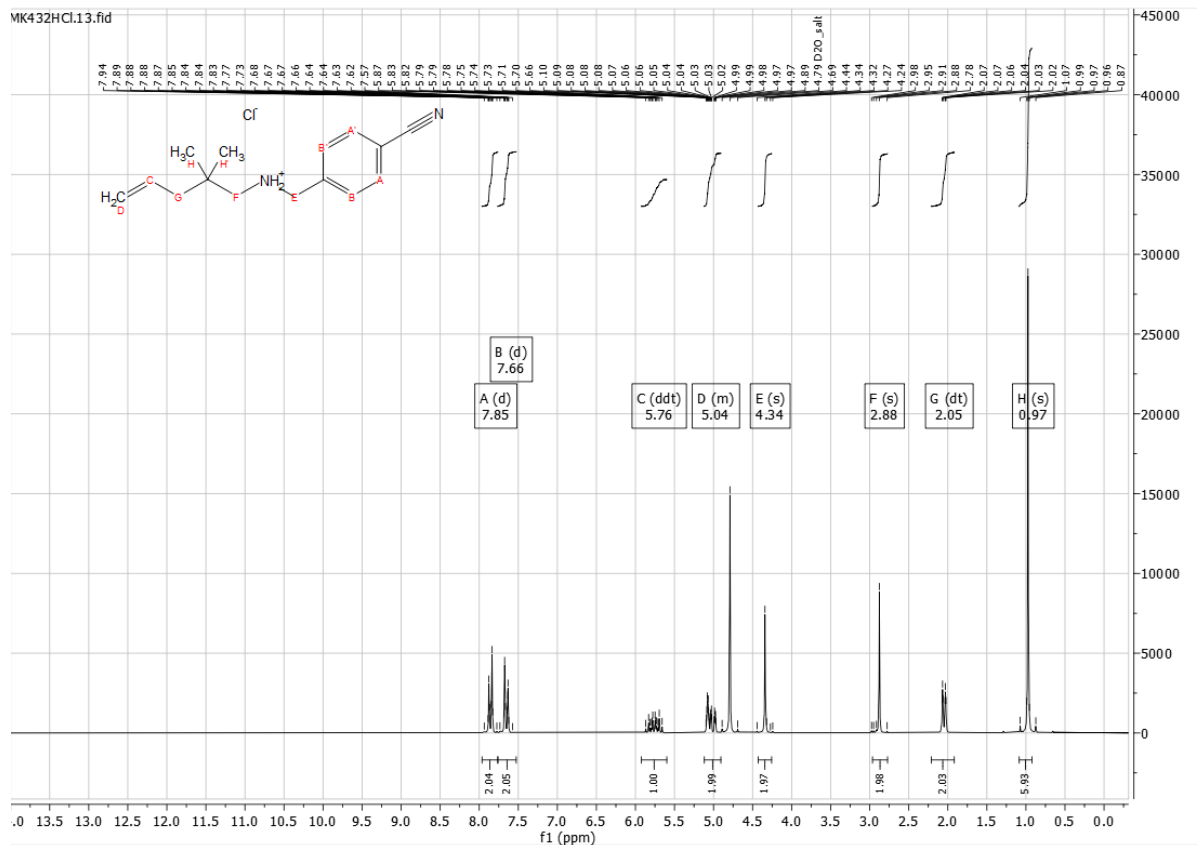
### Compound 3n



### Compound 30



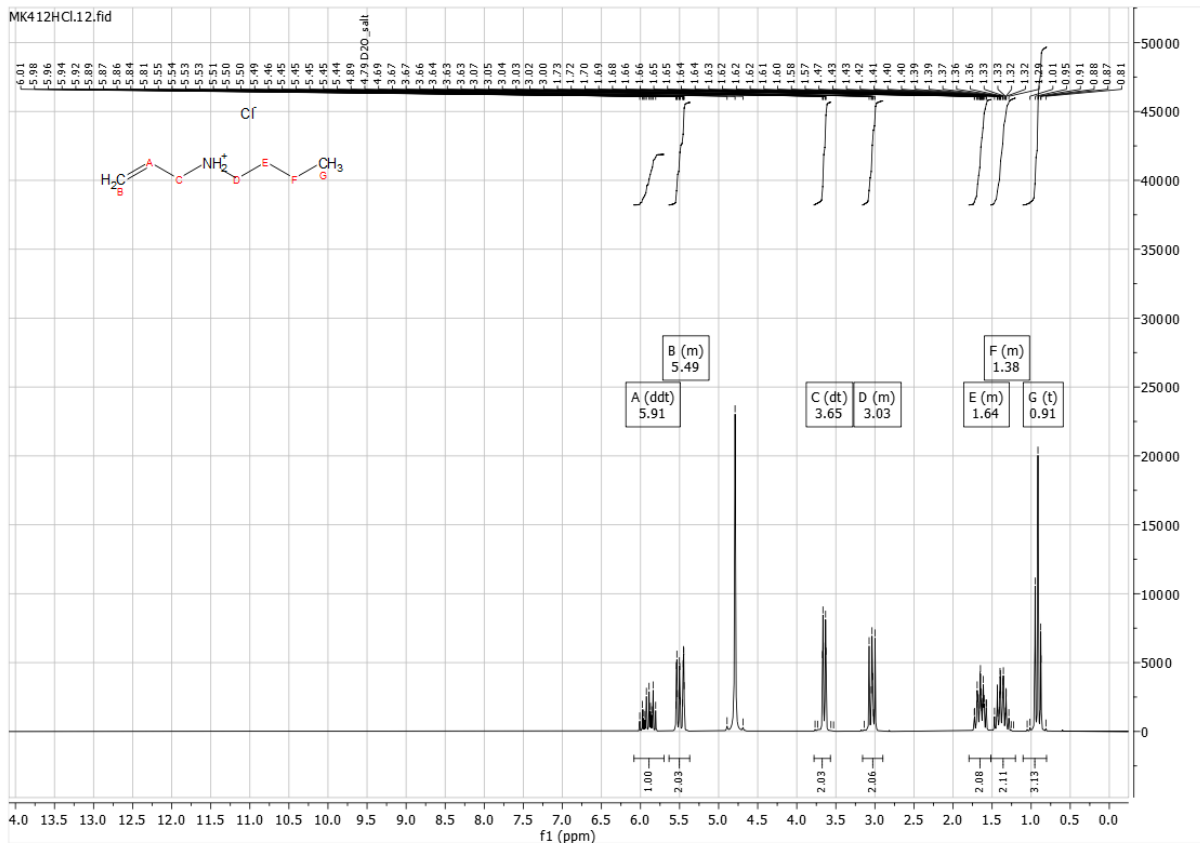
### Compound 3p



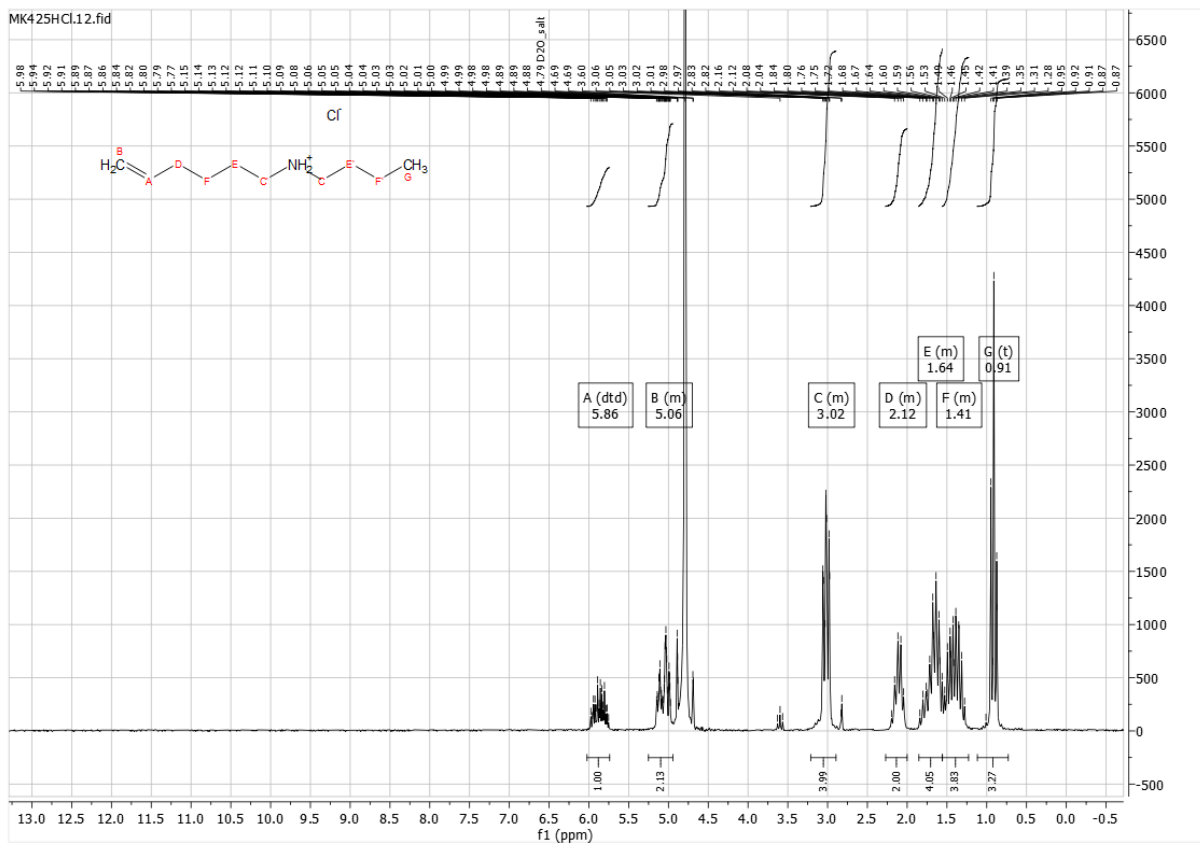
Compound 3q



Compound 3r



### Compound 3s



## 6. Author Contribution

Michael Kirchner: Writing - original draft (lead), Investigation (lead).

Yana Dubinina: Investigation (supporting)

Richard Göttlich: Writing original draft (supporting), project administration (lead).

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