

# N-Formylation of Amines by Methanol Activation

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## 1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: *n*-hexane (CaH<sub>2</sub>), THF (Na-benzophenone), toluene (CaH<sub>2</sub>).

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated. Dicyclohexylimidazolium chloride (ICy·HCl) was prepared as previously reported.<sup>1</sup>

Analytical thin layer chromatography was performed on Polygram SIL G/UV<sub>254</sub> plates. Visualization was accomplished with short wave UV light, vanillin, ninhydrine and/or KMnO<sub>4</sub> staining solutions followed by heating. Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique eluting with solvents as indicated. GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 μm). The major signals are quoted in *m/z* with the relative intensity in parentheses. The methods used start with the injection temperature *T*<sub>0</sub>; after holding this temperature for 3 min, the column is heated to temperature *T*<sub>1</sub> (ramp) and this temperature is held for an additional time *t*:

Method **50\_40**: *T*<sub>0</sub> = 50 °C, *T*<sub>1</sub> = 290 °C, ramp = 40 °C/min, *t* = 4 min;

<sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicate. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl<sub>3</sub>: δ<sub>H</sub> = 7.26 ppm, δ<sub>C</sub> = 77.16 ppm). ESI mass spectra were recorded on a Bruker Daltonics MicroTof. Infrared spectra were recorded on a Varian Associates FT-IR 3100 Excalibur and Shimadzu FTIR 8400S. The wave numbers (*ν*) of recorded IR-signals are quoted in cm<sup>-1</sup>.

## 2. General Procedures

### 2.1. Synthesis of ester:

A Schlenk tube was charged with [Ru(cod)(2-methylallyl)<sub>2</sub>] (4.8 mg, 0.015 mmol, 0.1%), ICy HCl (8.1 mg, 0.03 mmol, 0.2%) and dry KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 0.25%) in a glove box. The mixture was suspended in toluene (15 mL) and stirred at 70 °C for 12 h under argon. After cooling to RT 1-nonanol (2.62 mL, 15.0 mmol, 1 eq.) was added and the schlenk tube was equipped with a reflux condenser. The mixture was refluxed at 125 °C under an argon flow for 24 h. Flash coloumn chromatography (Pentane/EtOAc 98:2) afforded the pure ester (2.070 g, 97%).

Note: Preforming the complex **3** in situ or starting with the isolated complex lead to identical results.

### 2.2. Synthesis of amide:

A Schlenk tube was charged with [Ru(cod)(2-methylallyl)<sub>2</sub>] (9.6 mg, 0.03 mmol, 2.0%), ICy HCl (16.2 mg, 0.06 mmol, 0.4%) and dry KO<sup>t</sup>Bu (8.4 mg, 0.075 mmol, 0.5%) in a glove box. The mixture was suspended in toluene (1.5 mL) and stirred at 70 °C for 12 h under argon. After cooling to RT 1-nonanol (392 μL, 2.25 mmol, 1.5 eq.) and cyclohexylamine (172 μL, 1.50 mmol, 1.0 eq.) were added and the schlenk tube was equipped with a reflux condenser. The mixture was refluxed at 125 °C under an argon flow for 24 h. Flash coloumn chromatography (Pentane/EtOAc 8:2) afforded the pure amide (356 mg, 99%).

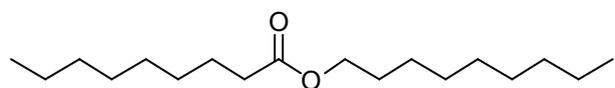
### 2.3. Synthesis of *N*-formamides:

To a flame-dried screw-capped tube equipped with a magnetic stir bar was added [Ru(cod)(2-methylallyl)<sub>2</sub>] (9.6 mg, 0.03 mmol), imidazolium salt ICy HCl (16.2 mg, 0.06 mmol) and dry KO<sup>t</sup>Bu (8.4 mg, 0.075 mmol) in a glove box. The mixture was suspended in toluene (1.5 mL) and stirred at 70 °C for 12 h under argon. Then styrene (0.52 mL, 4.50 mmol), methanol (0.20 mL, 5.00 mmol) and the corresponding amine (1.50 mmol) were added and the mixture was heated at 125 °C for 24 h.

The reaction mixture was directly transferred on a plug of silica and pure compounds were obtained by eluting with mixtures of pentane/EtOAc (8/2 → 1/1 → 0/1).

### 3. Characterization of Products

#### Nonyl nonanoate

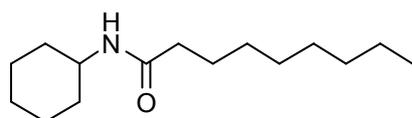


The product was obtained as colorless oil in 97% yield (2.070 g, 7.27 mmol).

**R<sub>F</sub>** (pentane/EtOAc 100:5): 0.42. **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** 4.06 (t, J=6.7 Hz, 2H, CH<sub>2</sub>O), 2.29 (t, J=7.5 Hz, 2H, COCH<sub>2</sub>), 1.71 – 1.53 (m, 4H, CH<sub>2</sub>), 1.40 – 1.18 (m, 22H, CH<sub>2</sub>), 0.94 – 0.80 (m, 6H, CH<sub>3</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** 174.14, 64.53, 34.56, 32.00, 31.96, 29.63, 29.40, 29.38, 29.31, 29.28, 28.80, 26.08, 25.18, 22.81, 22.79, 14.24.

**ATR-FTIR (cm<sup>-1</sup>):** 2924, 2855, 1738, 1467, 1167, 1109, 631, 529. **ESI-MS:** found: 285.2800 (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>H), calculated: 285.2788, found: 307.2612 (C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>Na), calculated: 307.2608, found: 591.5318 ((C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>)<sub>2</sub>Na), calculated: 591.5323.

#### N-cyclohexylnonanamide

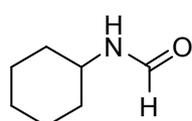


The product was obtained as white solid in 99% yield (356 mg, 1.49 mmol).

**R<sub>F</sub>** (pentane/EtOAc 1:1): 0.69. **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** 5.74 (d, J=8.3 Hz, 1H, NH), 3.70 (dddd, J=14.8 Hz, 10.8 Hz, 8.0 Hz, 3.9 Hz, 1H, CHN), 2.14 – 2.03 (m, 2H, CH<sub>2</sub>CO), 1.90 – 1.78 (m, 2H), 1.69 – 1.50 (m, 5H, CH<sub>2</sub>), 1.37 – 0.99 (m, 15H, CH<sub>2</sub>), 0.87 – 0.75 (m, 3H, CH<sub>3</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** 172.31, 48.04, 37.04, 33.23, 31.84, 29.38, 29.33, 29.20, 26.00, 25.58, 24.97, 22.66, 14.11.

**ATR-FTIR (cm<sup>-1</sup>):** 2924, 2855, 1738, 1467, 1167, 1109, 631, 529. **ESI-MS:** found: 262.2144 (C<sub>15</sub>H<sub>29</sub>NONa), calculated: 262.2141, found: 501.4397 ((C<sub>15</sub>H<sub>29</sub>NO)<sub>2</sub>Na), calculated 501.4391, found: 740.6646 ((C<sub>15</sub>H<sub>29</sub>NO)<sub>3</sub>Na), calculated 740.6640.

#### N-Cyclohexylformamide (5a)

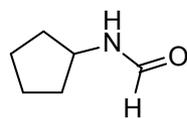


The product was obtained as colorless oil in 96% yield (183 mg, 1.44 mmol).

**R<sub>F</sub>** (EtOAc): 0.47; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** Mixture of rotameres is observed. Ratio: 8/2. Major rotamer: 8.10 (s, 1H, CHO), 5.44 (s, 1H, NH), 3.97 – 3.77 (m, 1H, CHN), 1.99 – 1.85 (m, 2H, CH<sub>2</sub>), 1.80 – 1.66 (m, 2H, CH<sub>2</sub>), 1.62 (m, 1H, CH<sub>2</sub>), 1.43 – 1.08 (m, 5H, CH<sub>2</sub>). Minor rotamer: 8.14 (s, 1H, CHO), 5.62 (s, 1H, NH), 3.41 – 3.22 (m, 1H, CHN), 1.99 – 1.85 (m, 2H, CH<sub>2</sub>), 1.80 – 1.66 (m, 2H, CH<sub>2</sub>), 1.62 (m, 1H, CH<sub>2</sub>), 1.43 – 1.08 (m, 5H, CH<sub>2</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Major rotamer: 160.55, 46.96, 32.78,

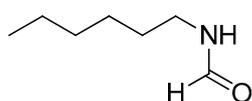
25.30, 24.68. Minor rotamer: 163.73, 51.08, 34.47, 24.89, 24.64. **ATR-FTIR (cm<sup>-1</sup>):** 3391, 2925, 2855, 1734, 1682, 1603, 1505, 1464, 1320, 1256, 1177, 1105, 1053, 991, 867, 747, 692, 623. **ESI-MS:** found: 150.0893 (C<sub>7</sub>H<sub>13</sub>NONa), calculated: 150.0889.

### ***N*-Cyclopentylformamide (5b)**



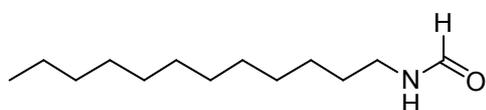
The product was obtained as colorless oil in 95% yield (161 mg, 1.42 mmol). **R<sub>F</sub>** (pentane/EtOAc 40:60): 0.18; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** Mixture of rotamers is observed. Ratio: 8.5/1.5. Major rotamer: 7.94 (s, 1H, CHO), 6.93 – 6.52 (m, 1H, NH), 4.10 (h, *J* = 6.9 Hz, 1H, CHN), 1.94 – 1.74 (m, 2H, C<sub>5</sub>H<sub>9</sub>), 1.67 – 1.41 (m, 4H, C<sub>5</sub>H<sub>9</sub>), 1.39 – 1.20 (m, 2H, C<sub>5</sub>H<sub>9</sub>). Minor rotamer: 7.98 (s, 1H, CHO), 3.81 – 3.63 (m, 1H, CHN), 2.92 (s, 1H, NH), 1.94 – 1.74 (m, 2H, C<sub>5</sub>H<sub>9</sub>), 1.67 – 1.41 (m, 4H, C<sub>5</sub>H<sub>9</sub>), 1.39 – 1.20 (m, 2H, C<sub>5</sub>H<sub>9</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Major rotamer: 161.08, 49.72, 32.73, 23.54. Minor rotamer: 164.10, 53.63, 33.81, 23.29. **ATR-FTIR (cm<sup>-1</sup>):** 3268, 3048, 2958, 2869, 1653, 1536, 1452, 1383, 1243, 630. **ESI-MS:** found: 136.0727 (C<sub>6</sub>H<sub>11</sub>NONa), calculated: 136.0733.

### ***N*-Hexylformamide (5c)**



The product was obtained as colorless oil in 84% yield (163 mg, 1.26 mmol). **R<sub>F</sub>** (EtOAc 40:60): 0.49; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** Mixture of rotamers is observed. Ratio: 8/2. Major rotamer: 8.11 (s, 1H, CHO), 6.04 (s, 1H, NH), 3.34 – 3.20 (m, 2H, CH<sub>2</sub>N), 1.59 – 1.41 (m, 2H, CH<sub>2</sub>), 1.36 – 1.18 (m, 6H, CH<sub>2</sub>), 0.97 – 0.60 (m, 3H, CH<sub>3</sub>). Minor rotamer: 7.99 (d, *J* = 12.0 Hz, 1H, CHO), 3.21 – 3.10 (m, 2H, CH<sub>2</sub>N), 2.22 (s, 1H, NH), 1.59 – 1.41 (m, 2H, CH<sub>2</sub>), 1.36 – 1.18 (m, 6H, CH<sub>2</sub>), 0.97 – 0.60 (m, 3H, CH<sub>3</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Major rotamer: 161.42, 38.27, 31.48, 29.51, 26.58, 22.60, 14.06. Minor rotamer: 164.84, 41.92, 31.37, 31.23, 26.11, 22.57, 14.04. **ATR-FTIR (cm<sup>-1</sup>):** 3281, 3056, 2957, 2929, 2858, 1658, 1466, 1382, 1466, 1382, 1241, 771 725, 650, 622. **ESI-MS:** found: 130.1223 (C<sub>7</sub>H<sub>15</sub>NOH), calculated: 130.1226, found: 152.1046 (C<sub>7</sub>H<sub>15</sub>NONa), calculated: 152.1046.

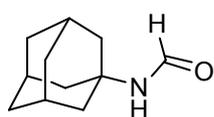
### ***N*-dodecylformamide (5d)**



The product was obtained as white solid in 83% yield (263 mg, 1.25 mmol).

**R<sub>F</sub>** (pentane/EtOAc 40:60): 0.34; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers is observed. Ratio: 8/2. Major rotamer: 8.13 (s, 1H, CHO), 5.88 (s, 1H, NH), 3.26 (q, *J* = 6.7 Hz, 2H, CH<sub>2</sub>N), 1.50 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>NH), 1.25 (d, *J*=9.6, 18H, CH<sub>2</sub>), 0.92 – 0.77 (m, 3H, CH<sub>3</sub>). Minor rotamer: 8.01 (d, *J* = 12.0 Hz, 1H, CHO), 3.18 (q, *J*=6.8 Hz, 1H, CH<sub>2</sub>N), 1.50 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>NH), 1.25 (d, *J*=9.6, 18H, CH<sub>2</sub>), 0.92 – 0.77 (m, 3H, CH<sub>3</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**: Major rotamer: 161.34, 38.30, 32.01, 29.74, 29.72, 29.67, 29.63, 29.60, 29.44, 29.35, 26.96, 22.78, 14.22. Minor rotamer: 164.77, 41.91, 31.33, 29.72, 29.67, 29.63, 29.60, 29.44, 29.24, 26.48, 14.22. **ATR-FTIR (cm<sup>-1</sup>)**: 3292, 2954, 2919, 2849, 1741, 1644, 1535, 1467, 1377, 1235, 1215, 1047, 779, 722, 668. **ESI-MS**: found: 236.1985 (C<sub>13</sub>H<sub>27</sub>NONa), calculated: 236.1985.

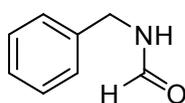
### ***N*-Adamantan-1-ylformamide (5e)**



The product was obtained as white solid in 27% yield (73 mg, 0.40 mmol).

**R<sub>F</sub>** (pentane/EtOAc 40:60): 0.31; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers is observed. Ratio: 7/3. Major rotamer: 8.25 (d, *J* = 12.3 Hz, 1H, CHO), 6.36 (s, 1H, NH), 2.15 – 2.03 (m, 3H), 2.03 – 1.95 (m, 1H), 1.85 – 1.79 (m, 4H), 1.73 – 1.57 (m, 6H). Minor rotamer: 8.00 (d, *J* = 2.1, 1H, CHO), 5.30 (s, 1H, NH), 2.15 – 2.03 (m, 3H), 2.03 – 1.95 (m, 1H), 1.85 – 1.79 (m, 4H), 1.73 – 1.57 (m, 6H). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**: Major rotamer: 160.38, 50.75, 44.18, 35.95, 29.34. Minor rotamer: 162.38, 52.18, 41.88, 36.31, 29.44. **ATR-FTIR (cm<sup>-1</sup>)**: 3184, 3087, 2898, 2851, 1689, 1450, 1395, 1362, 1304, 1259, 1134, 1098, 1040, 786, 750, 671. **ESI-MS**: found: 202.1206 (C<sub>11</sub>H<sub>17</sub>NONa), calculated: 202.1202.

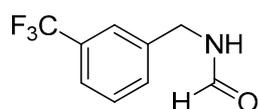
### ***N*-benzylformamide (5f)**



The product was obtained as colorless oil in 83% yield (168 mg, 1.25 mmol).

**R<sub>F</sub>** (pentane/EtOAc 40:60): 0.25; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers is observed. Ratio: 8/2. Major rotamer: 8.01 (s, 1H, CHO), 7.28 – 7.04 (m, 5H, H<sub>Ar</sub>), 6.77 (s, 1H, NH), 4.27 (d, *J* = 6.0 Hz, 2H, CH<sub>2</sub>N). Minor rotamer: 7.92 (d, *J* = 12.0 Hz, 1H, CHO), 7.28 – 7.04 (m, 5H, H<sub>Ar</sub>), 6.36 (s, 1H, NH), 4.21 (d, *J*=6.4 Hz, 2H, CH<sub>2</sub>N). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**: Major rotamer: 161.41, 137.68, 128.63, 127.60, 127.46, 41.95. Minor rotamer: 164.89, 137.55, 128.82, 127.84, 126.93, 45.62. **ATR-FTIR (cm<sup>-1</sup>)**: 3271, 2885, 1638, 1532, 1454, 1387, 1226, 1079, 1029, 738, 696. **ESI-MS**: found: 158.0576 (C<sub>8</sub>H<sub>9</sub>NONa), calculated: 158.0576

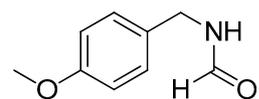
### ***N*-(3-Trifluoromethylbenzyl)formamide (5g)**



The product was obtained as white solid in 33% yield (101 mg, 0.49 mmol).

**R<sub>F</sub>** (EtOAc): 0.40; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers is observed. Ratio: 9/1. Major rotamer: 8.22 (s, 1H, CHO), 7.58 – 7.37 (m, 4H, H<sub>Ar</sub>), 6.62 (s, 1H, NH), 4.47 (d, *J* = 6.2 Hz, 2H, CH<sub>2</sub>N) Minor rotamer: 8.13 (d, *J* = 11.8, 1H, CHO), 7.58 – 7.37 (m, 4H, H<sub>Ar</sub>), 6.46 (s, 1H, NH), 4.46 – 4.42 (m, 2H, CH<sub>2</sub>N). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers: 164.86, 161.46, 138.83, 131.28, 131.11 (d, *J* = 1.5 Hz), 130.85, 129.56, 129.30, 125.86, 124.39 (dq, *J* = 12.6 Hz, 3.9 Hz), 122.25, 118.64, 45.28, 41.62. **ATR-FTIR (cm<sup>-1</sup>)**: 3301, 3261, 3055, 2927, 2865, 1659, 1535, 1451, 1384, 1326, 1237, 1158, 1115, 1073, 977, 922, 905, 888, 801, 699, 660. **ESI-MS**: found: 226.0455 (C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>NONa), calculated: 226.0450.

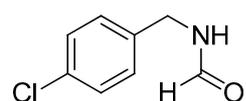
### ***N*-(4-Methoxybenzyl)formamide (5h)**



The product was obtained as white solid in 44% yield (110 mg, 0.66 mmol).

**R<sub>F</sub>** (EtOAc): 0.44; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers is observed. Ratio: 8.5/1.5. Major rotamer: 8.10 (s, 1H, CHO), 7.21 – 7.04 (m, 2H, H<sub>Ar</sub>), 6.95 – 6.73 (m, 2H, H<sub>Ar</sub>), 6.67 (s, 1H, NH), 4.30 (d, *J* = 5.8 Hz, 2H, CH<sub>2</sub>N), 3.82 – 3.56 (m, 3H, OCH<sub>3</sub>). Minor rotamer: 8.02 (d, *J* = 11.9 Hz, 1H, CHO), 7.21 – 7.04 (m, 2H, H<sub>Ar</sub>), 6.95 – 6.73 (m, 2H, H<sub>Ar</sub>), 6.30 (s, 1H, NH), 4.24 (d, *J* = 6.4 Hz, 2H, CH<sub>2</sub>N), 3.82 – 3.56 (m, 3H, OCH<sub>3</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)**: Major rotamer: 161.41, 137.68, 128.63, 127.60, 127.46, 41.95. Minor rotamer: 164.89, 137.55, 128.82, 127.84, 126.93, 45.62. **ATR-FTIR (cm<sup>-1</sup>)**: 3284, 2933, 2895, 2835, 1641, 1512, 1460, 1377, 1352, 1304, 1241, 1213, 1179, 1116, 1033, 828, 795, 696. **ESI-MS**: found: 188.0685 (C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>Na), calculated: 188.0682.

### ***N*-(4-Chlorobenzyl)formamide (5i)**

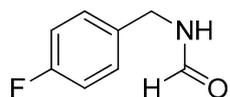


The product was obtained as white solid in 47% yield (120 mg, 0.71 mmol).

**R<sub>F</sub>** (EtOAc): 0.40; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)**: Mixture of rotamers is observed. Ratio: 9/1. Major rotamer: 8.13 (s, 1H, CHO), 7.28 – 7.16 (m, 2H, H<sub>Ar</sub>), 7.16 – 7.06 (m, 2H, H<sub>Ar</sub>), 6.34 (s, 1H, NH), 4.32 (d, *J* = 6.0 Hz, 2H, CH<sub>2</sub>N). Minor rotamer: 8.03 (d, *J* = 11.9 Hz, 1H, CHO), 7.28 – 7.16 (m, 2H, H<sub>Ar</sub>), 7.16 – 7.06 (m, 2H, H<sub>Ar</sub>), 4.28 (d, *J* = 6.5 Hz,

2H, CH<sub>2</sub>N). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Major rotamer: 161.29, 136.26, 133.46, 129.13, 128.91, 41.47. Minor rotamer: 164.79, 136.09, 133.87, 128.39, 45.10. **ATR-FTIR (cm<sup>-1</sup>):** 3277, 3028, 2897, 1648, 1532, 1491, 1382, 1225, 1089, 10014, 871, 820, 759, 682. **ESI-MS:** found: 192.0190 (C<sub>8</sub>H<sub>8</sub>ClNONa), calculated: 192.0187.

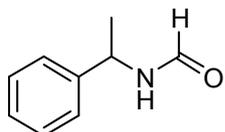
#### ***N*-(4-Fluorobenzyl)formamide (5j)**



The product was obtained as white solid in 57% yield (131 mg, 0.86 mmol).

**R<sub>F</sub>** (EtOAc): 0.43; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** Mixture of rotamers is observed. <sup>1</sup>H NMR-signals are completely overlapping. Mixture of rotamers: 8.11 (s, 1H, CHO), 7.23 – 7.09 (m, 2H, H<sub>Ar</sub>), 7.05 – 6.79 (m, 3H, H<sub>Ar</sub>, NH), 4.32 (d, *J* = 6.1 Hz, 2H, CH<sub>2</sub>N). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Major rotamer: 162.08 (d, *J* = 245.7 Hz), 161.42, 133.55 (d, *J* = 3.3 Hz), 129.31 (d, *J* = 8.1 Hz), 115.45 (d, *J* = 21.4 Hz), 41.27. Minor rotamer: 164.81, 162.29 (d, *J* = 246.4 Hz), 133.38 (d, *J* = 3.2 Hz), 128.70 (d, *J* = 8.2 Hz), 115.86, 45.01. **ATR-FTIR (cm<sup>-1</sup>):** 3276, 3036, 2936, 2897, 1718, 1650, 1538, 1508, 1462, 1419, 1383, 1350, 1213, 1159, 1096, 1014, 965, 869, 805, 697. **ESI-MS:** found: 176.0484 (C<sub>8</sub>H<sub>8</sub>FNONa), calculated: 176.04682.

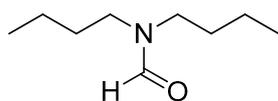
#### ***N*-(1-phenylethyl)formamide (5k)**



The product was obtained as white solid in 77% yield (172 mg, 1.16 mmol).

**R<sub>F</sub>** (EtOAc): 0.53; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** Mixture of rotamers is observed. Ratio: 8.5/1.5. Major rotamer: 7.91 (s, 1H, CHO), 7.25 – 7.10 (m, 5H, H<sub>Ar</sub>), 7.04 (s, 1H, NH), 5.01 (p, *J* = 8.0 Hz, 1H, CHN), 1.34 (d, *J* = 7.0 Hz, 3H, CH<sub>3</sub>). Minor rotamer: 7.94 (d, *J* = 12.0 Hz, 1H, CHO), 7.25 – 7.10 (m, 5H, H<sub>Ar</sub>), 4.79 – 4.13 (m, 1H, CHN), 2.68 (s, 1H, NH), 1.40 (d, *J* = 6.9 Hz, 3H, CH<sub>3</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Major rotamer: 160.71, 142.79, 128.51, 127.22, 125.98, 47.49, 21.83. Minor rotamer: 164.42, 142.87, 128.76, 127.56, 125.69, 51.79, 23.35. **ATR-FTIR (cm<sup>-1</sup>):** 3268, 3032, 2976, 2868, 1653, 1530, 1495, 1450, 1379, 1236, 1088, 1021, 912, 807, 760, 697. **ESI-MS:** found: 172.0735 (C<sub>9</sub>H<sub>11</sub>NONa), calculated: 172.0733.

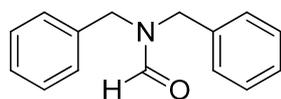
### ***N,N*-dibutylformamide (5l)**



The product was obtained as colourless oil in 64% yield (151 mg, 0.96 mmol).

$R_F$  (pentane/EtOAc 80:20): 0.28;  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 7.93 (s, 1H, CHO), 3.18 (t,  $J = 7.5$  Hz, 2H,  $CH_2N$ ), 3.09 (t,  $J = 7.1$  Hz, 2H,  $CH_2N$ ), 1.49 – 1.34 (m, 4H,  $CH_2$ ), 1.30 – 1.10 (m, 4H,  $CH_2$ ), 0.82 (td,  $J = 7.3$  Hz, 2.2 Hz, 6H,  $CH_3$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ): 162.53, 47.02, 41.69, 30.60, 29.27, 20.04, 19.51, 13.69, 13.53. ATR-FTIR ( $cm^{-1}$ ): 3346, 2958, 2932, 2871, 1667, 1460, 1427, 1399, 1378, 1291, 1253, 1117, 1056, 950, 733, 687, 626. ESI-MS: found: 180.1363 ( $C_9H_{19}NONa$ ), calculated: 180.1359.

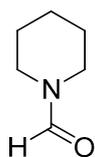
### ***N,N*-dibenzylformamide (5m)**



The product was obtained as colourless oil in 71% yield (240 mg, 1.06 mmol).

$R_F$  (pentane/EtOAc 80:20): 0.38;  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 8.27 (s, 1H, CHO), 7.29 – 7.10 (m, 6H,  $H_{Ar}$ ), 7.10 – 6.99 (m, 4H,  $H_{Ar}$ ), 4.27 (s, 2H,  $CH_2N$ ), 4.10 (s, 2H,  $CH_2N$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ): 162.70, 135.90, 135.53, 128.78, 128.56, 128.36, 127.99, 127.58, 127.52, 50.06, 44.45. ATR-FTIR ( $cm^{-1}$ ): 3030, 2922, 2864, 1666, 1495, 1425, 1397, 1263, 1198, 1158, 1077, 1029, 979, 823, 738, 699, 610. ESI-MS: found: 248.1046 ( $C_{15}H_{15}NONa$ ), calculated: 248.1046.

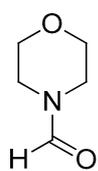
### **Piperidine-1-carbaldehyde (5n)**



The product was obtained as colourless oil in 90% yield (152 mg, 1.35 mmol).

$R_F$  (EtOAc): 0.28;  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 7.92 (s, 1H, CHO), 3.44 – 3.36 (m, 2H,  $CH_2N$ ), 3.27 – 3.20 (m, 2H,  $CH_2N$ ), 1.66 – 1.56 (m, 2H,  $CH_2$ ), 1.55 – 1.40 (m, 4H,  $CH_2$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ): 160.81, 46.82, 40.58, 26.53, 25.03, 24.65. ATR-FTIR ( $cm^{-1}$ ): 2937, 2857, 1658, 1440, 1398, 1258, 1210, 1118, 1028, 996, 854, 655, 628. ESI-MS: found: 136.0730 ( $C_6H_{11}NONa$ ), calculated: 136.0733.

### **Morpholine-4-carbaldehyde (5o)**



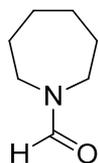
The product was obtained as colourless oil in 74% yield (128 mg, 1.11 mmol).

$R_F$  (EtOAc): 0.15;  $^1H$  NMR (300 MHz,  $CDCl_3$ ): 8.02 (s, 1H, CHO), 3.76 – 3.59 (m, 4H,  $CH_2$ ), 3.57 – 3.50 (m, 2H,  $CH_2$ ), 3.41 – 3.31 (m, 2H,  $CH_2$ ).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ): 160.91, 67.28, 66.48, 45.85, 40.65. ATR-FTIR ( $cm^{-1}$ ): 2969, 2914,

2858, 1656, 1434, 1398, 1363, 1300, 1270, 1230, 1186, 1109, 1069, 1004, 855, 812, 660.

**ESI-MS:** found: 138.0528 (C<sub>5</sub>H<sub>9</sub>NO<sub>2</sub>Na), calculated: 138.0525.

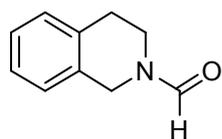
### Azepane-1-carbaldehyde (5p)



The product was obtained as colourless oil in 99% yield (189 mg, 1.48 mmol).

**R<sub>F</sub>** (EtOAc): 0.34; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** 7.88 (s, 1H, CHO), 3.28 – 3.16 (m, 4H, CH<sub>2</sub>N), 1.60 – 1.48 (m, 4H, CH<sub>2</sub>), 1.45 – 1.32 (m, 4H, CH<sub>2</sub>) **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** 162.49, 47.31, 43.00, 29.90, 27.62, 26.56, 26.51. **ATR-FTIR (cm<sup>-1</sup>):** 2925, 2855, 1658, 1426, 1401, 1298, 1259, 1199, 1155, 1105, 1001, 972, 873, 743, 652. **ESI-MS:** found: 150.0884 (C<sub>7</sub>H<sub>13</sub>NONa), calculated: 150.0889, found: 277.1886 ((C<sub>7</sub>H<sub>13</sub>NO)<sub>2</sub>Na), calculated: 277.1886.

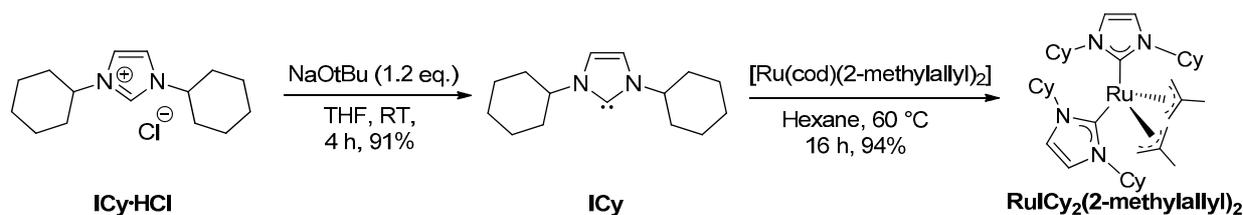
### 3,4-Dihydroisoquinoline-2(1H)-carbaldehyde (5q)



The product was obtained as colourless oil in 90% yield (218 mg, 1.35 mmol).

**R<sub>F</sub>** (EtOAc): 0.44; **<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):** Mixture of rotamers is observed. Ratio: 6/4. Major rotamer: 8.18 (s, 1H, CHO), 7.24 – 7.07 (m, 4H, H<sub>Ar</sub>), 4.68 (s, 2H, C<sub>Ar</sub>CH<sub>2</sub>N), 3.64 (t, J=5.9 Hz, 2H, CH<sub>2</sub>), 2.93 – 2.83 (m, 2H, CH<sub>2</sub>). Minor rotamer: 8.23 (s, 1H, CHO), 7.24 – 7.07 (m, 4H, H<sub>Ar</sub>), 4.53 (s, 2H, C<sub>Ar</sub>CH<sub>2</sub>N), 3.78 (t, J=6.2 Hz, 2H, CH<sub>2</sub>), 2.93 – 2.83 (m, 2H, CH<sub>2</sub>). **<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):** Mixture of rotamers: 161.74, 161.23, 134.47, 134.15, 133.59, 132.28, 131.80, 129.25, 128.98, 127.16, 126.79, 126.69, 126.55, 125.95, 47.38, 43.30, 42.37, 38.05, 29.78, 27.99. **ATR-FTIR (cm<sup>-1</sup>):** 2930, 2859, 1660, 1496, 1437, 1398, 1367, 1280, 1253, 1196, 1164, 1108, 1050, 983, 930, 814, 749, 706, 674, 629. **ESI-MS:** found: 184.0738 (C<sub>10</sub>H<sub>11</sub>NONa), calculated: 184.0733.

#### 4. Synthesis of the isolated complex $\text{RuICy}_2(2\text{-methylallyl})_2$ (3)



##### Free carbene ( $\text{ICy}$ ):

According to a modified procedure,<sup>2</sup> a schlenk flask was charged with  $\text{ICy}\cdot\text{HCl}$  (7.000 g, 26 mmol, 1.00 eq.) and  $\text{NaOtBu}$  (3.003 g, 31 mmol, 1.2 eq.). The solids were suspended in THF (40 mL) and stirred at RT for 4 h. The solvent was removed in vacuum and the residue was suspended in warm toluene (20 mL,  $\approx 60\text{ }^\circ\text{C}$ ). The suspension was filtered through a short plug of dry celite (3x6 cm) under argon atmosphere and eluted with an additional portion of toluene (20 mL). The solvent of the eluate was removed in vacuum to obtain a sticky red residue. Upon heating to  $60\text{ }^\circ\text{C}$  ( $\approx 30$  min) under vacuum and cooling to RT the residue solidifies and  $\text{ICy}$  was obtained as a red solid (5.524 g, 24 mmol, 91%).

**$^1\text{H}$  NMR (300 MHz, Benzene- $\text{d}_6$ ):** 6.62 (s, 4H,  $\text{H}_{\text{Ar}}$ ), 4.13 (tt,  $J = 11.7$  Hz, 3.7 Hz, 2H, CHN), 2.17 – 2.02 (m, 4H,  $\text{CH}_2$ ), 1.76 – 1.54 (m, 8H,  $\text{CH}_2$ ), 1.49 – 1.38 (m, 2H,  $\text{CH}_2$ ), 1.23 – 0.95 (m, 6H,  $\text{CH}_2$ ).  **$^{13}\text{C}$  NMR (75 MHz, Benzene- $\text{d}_6$ ):** 212.04, 115.89, 60.01, 35.29, 26.00, 25.88.

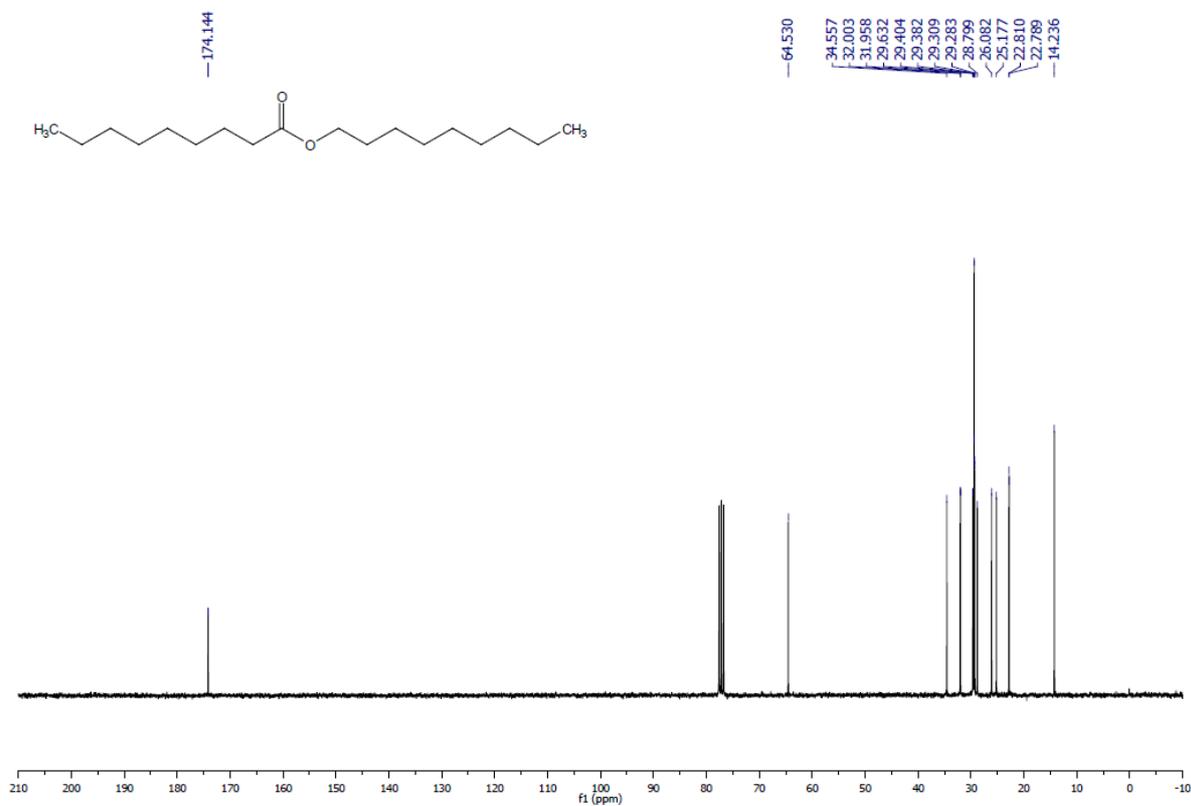
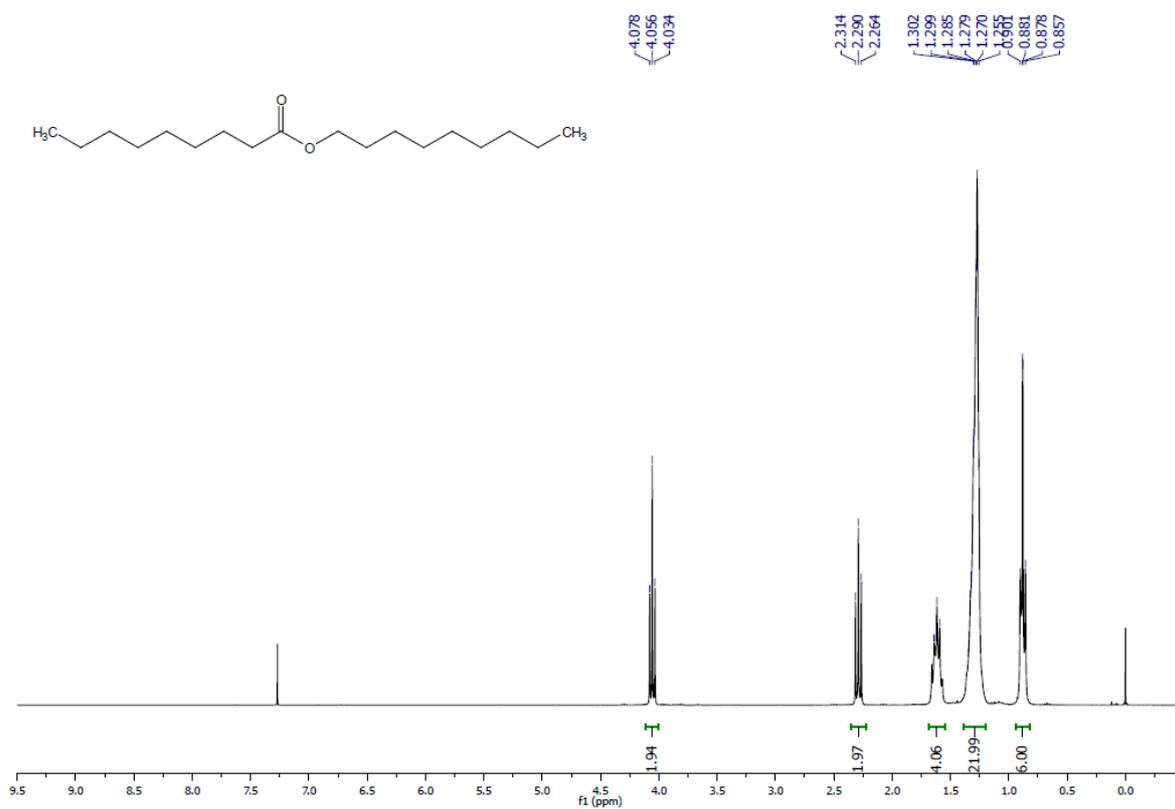
##### $\text{RuICy}_2(2\text{-methallyl})_2$ (3):

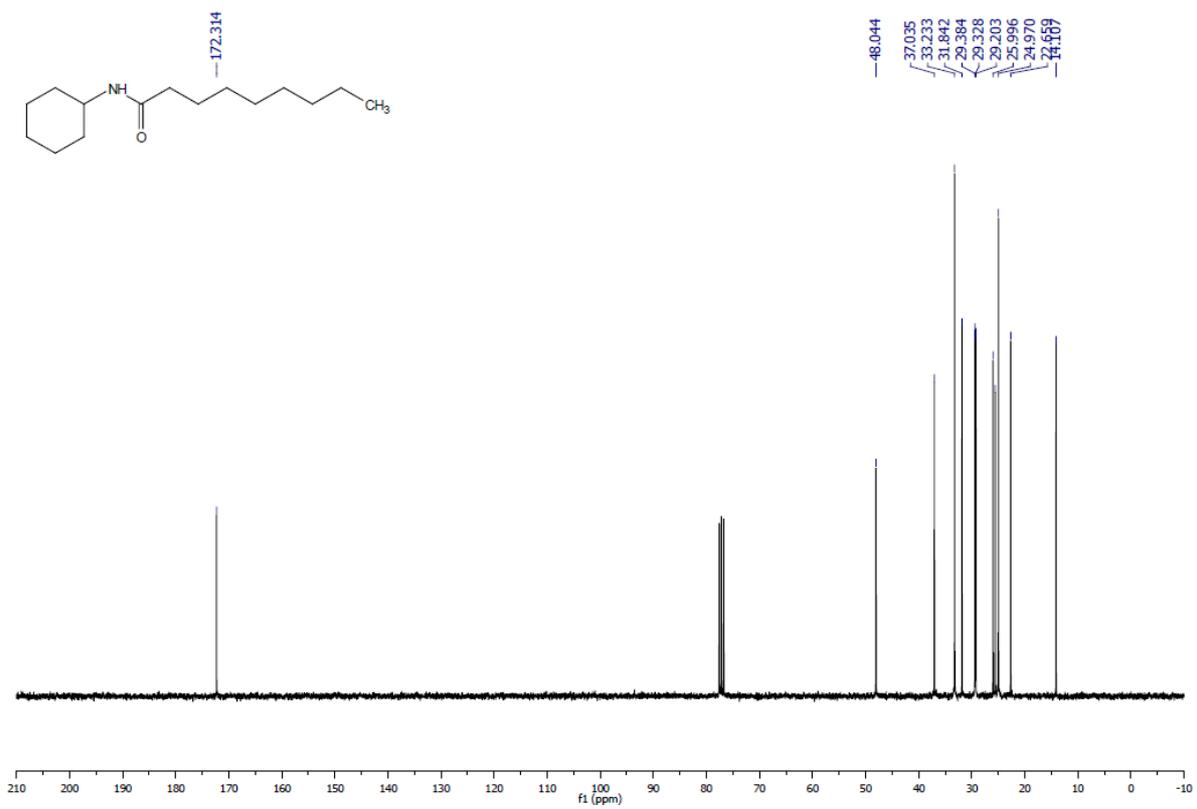
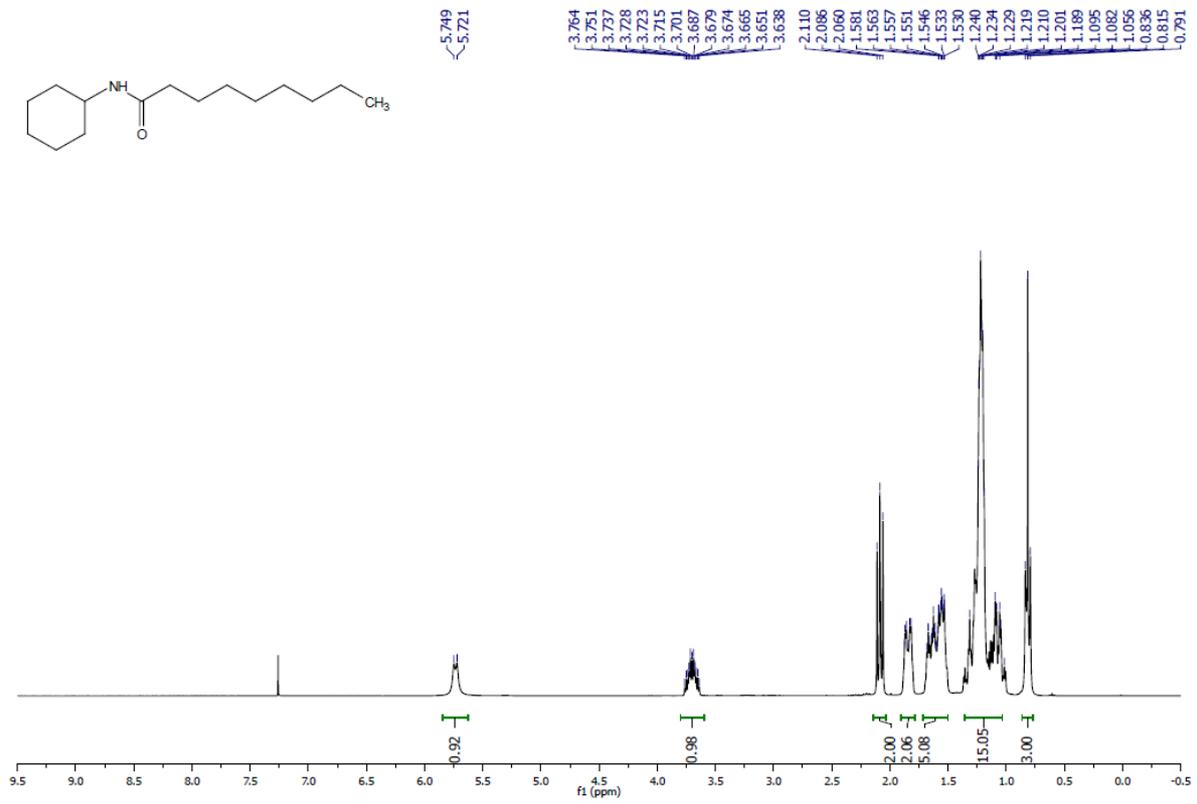
A Schlenk flask was charged with  $\text{Ru}(\text{COD})(\text{methallyl})_2$  (100 mg, 0.31 mmol, 1.00 eq.) and  $\text{ICy}$  (149 mg, 0.64 mmol, 2.05 eq.) and the solids were suspended in hexane (1 mL). After short stirring at room temperature the red solution was heated to  $60\text{ }^\circ\text{C}$ . After 16 h a fine suspension was obtained and stirring was stopped. The supernatant solution was removed by syringe and the residue was washed again with hexane (2 mL). The residue was dried in vacuum and once again suspended in hexane (2 mL). After removing the supernatant solution and drying in vacuum the complex was obtained as a free flowing off-white powder (197 mg, 0.29 mmol, 94%).

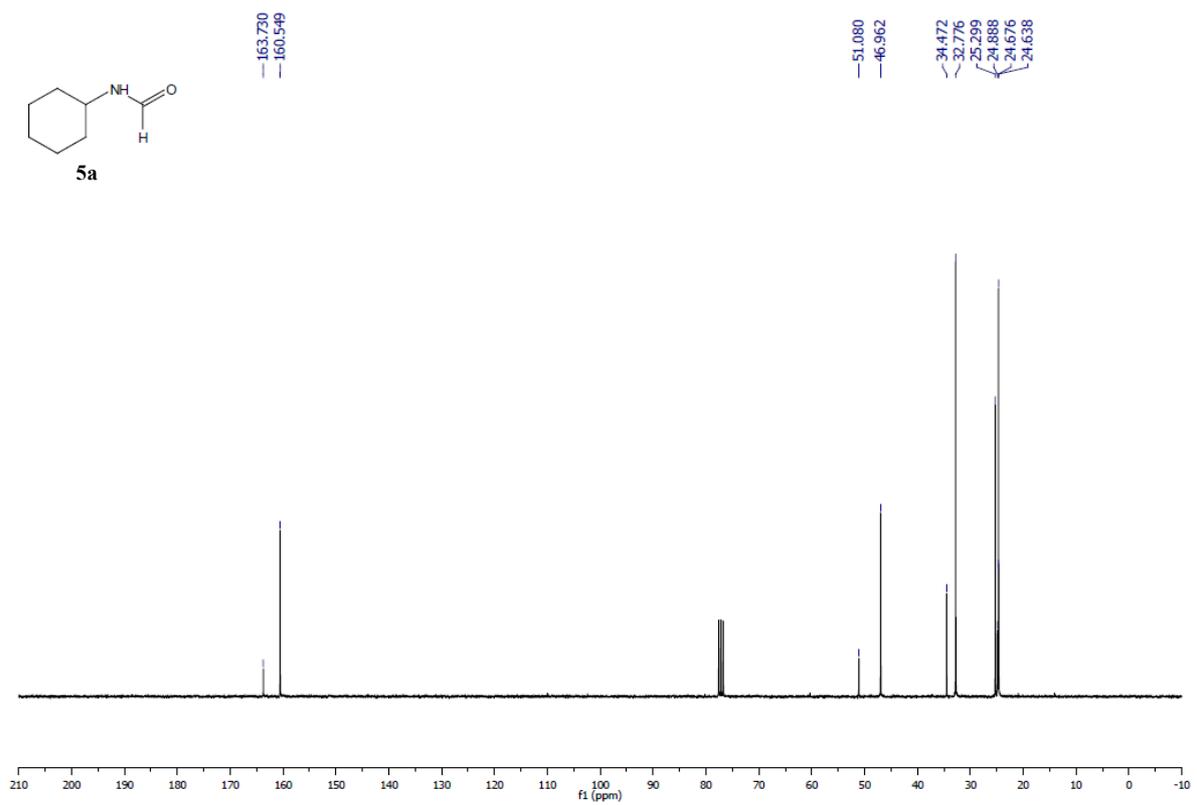
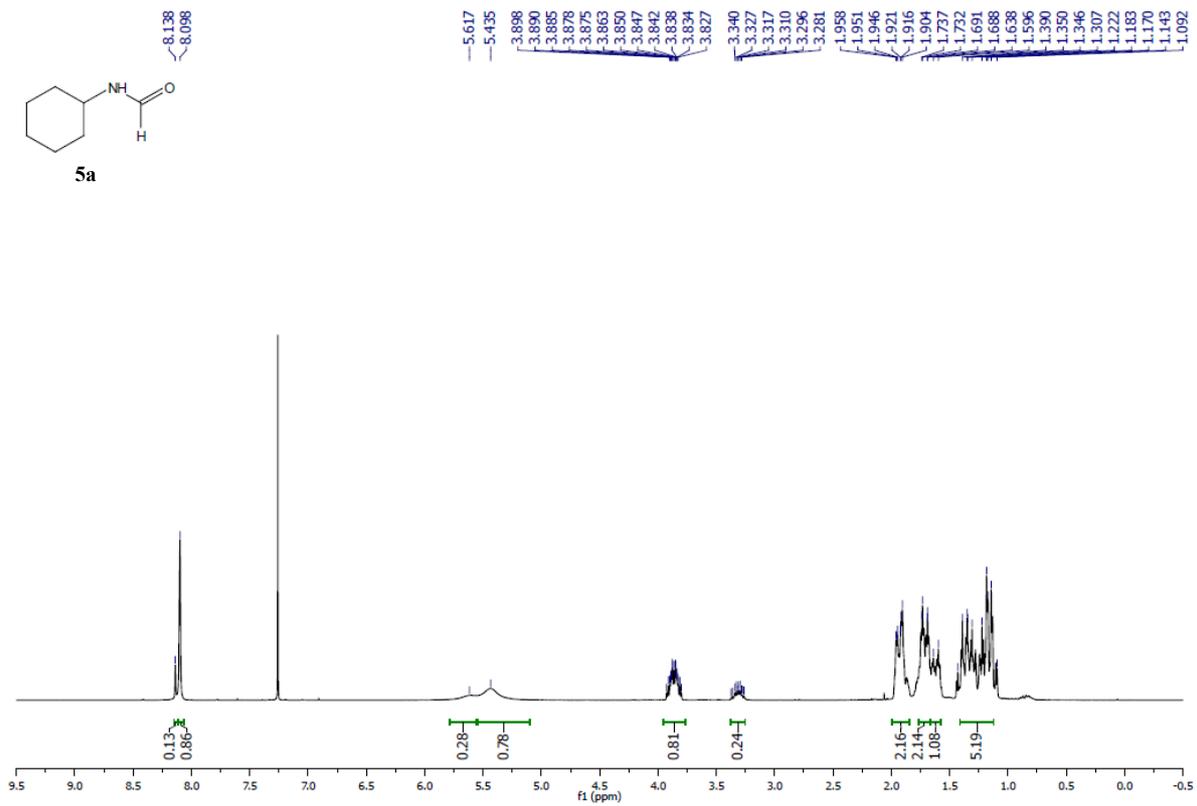
**$^1\text{H}$  NMR (300 MHz, Benzene- $\text{d}_6$ ):** 6.58 (d,  $J = 2.1$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.43 (d,  $J = 2.1$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.20 (tt,  $J = 11.8$  Hz, 3.4 Hz, 1H, CHN), 5.02 (tt,  $J = 11.3$  Hz, 3.2 Hz, 1H, CHN), 2.60

(d,  $J = 11.9$  Hz, 1H, CH<sub>2</sub>), 2.52 (d,  $J = 2.6$  Hz, 1H, H<sub>allyl</sub>), 2.45 (s, 3H, CH<sub>3allyl</sub>), 1.95 – 1.77 (m, 4H, CH<sub>2</sub>), 1.72 – 1.31 (m, 9H, CH<sub>2</sub>) overlapping with: 1.45 (d, 1H, H<sub>allyl</sub>), 1.27 – 1.05 (m, 4H, CH<sub>2</sub>), 1.03 – 0.87 (m, 2H, CH<sub>2</sub>), 0.68 (s, 1H, H<sub>allyl</sub>), 0.46 (s, 1H<sub>allyl</sub>). **<sup>13</sup>C NMR (75 MHz, Benzene-d<sub>6</sub>):** 202.96, 117.35, 116.46, 93.58, 60.55, 58.24, 40.01, 37.91, 35.85, 35.83, 35.03, 32.90, 26.82, 26.77, 26.19, 26.11, 26.09, 26.05. . **KBr-FTIR (cm<sup>-1</sup>):** 3173, 3138, 3031, 2978, 2935, 2853, 2667, 2602, 2196, 1613, 1584, 1521, 1452, 1412, 1387, 1366, 1304, 1269, 1222, 1207, 1185, 1090, 1056, 1021, 991, 972, 894, 849, 817, 761, 714, 681, 546, 508, 418. **ESI-MS:** found: 676.39991 (C<sub>38</sub>H<sub>62</sub>N<sub>4</sub>Ru), calculated: 676.40228 (During the measurement Ru was oxidized from +2 to +3, leading to the observed charge of +1 of the complex).

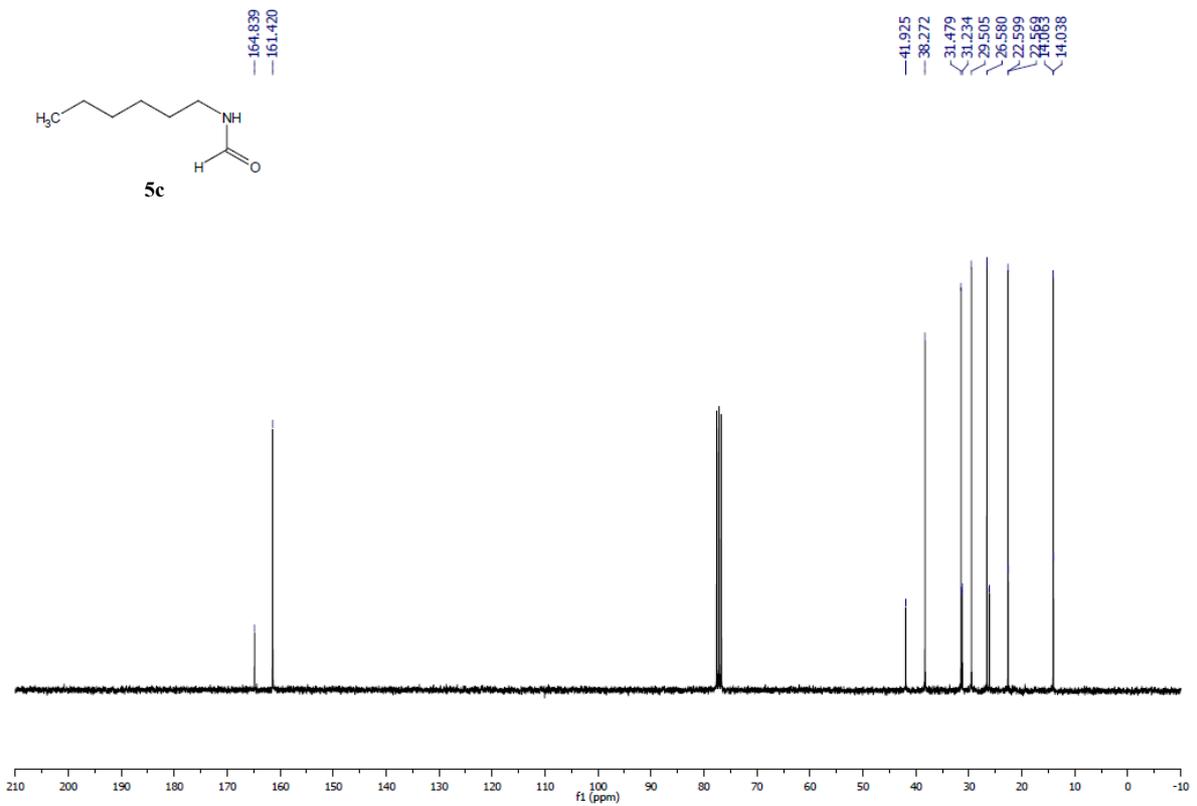
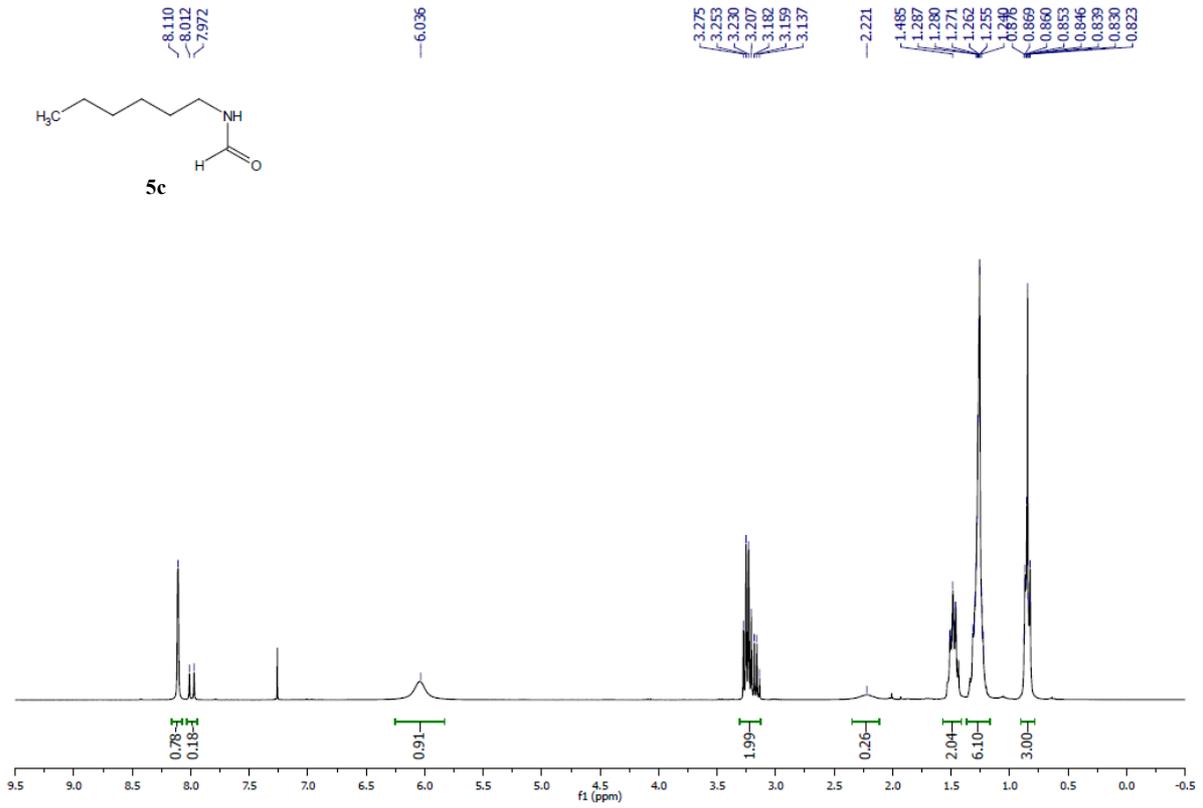
## 5. NMR spectra

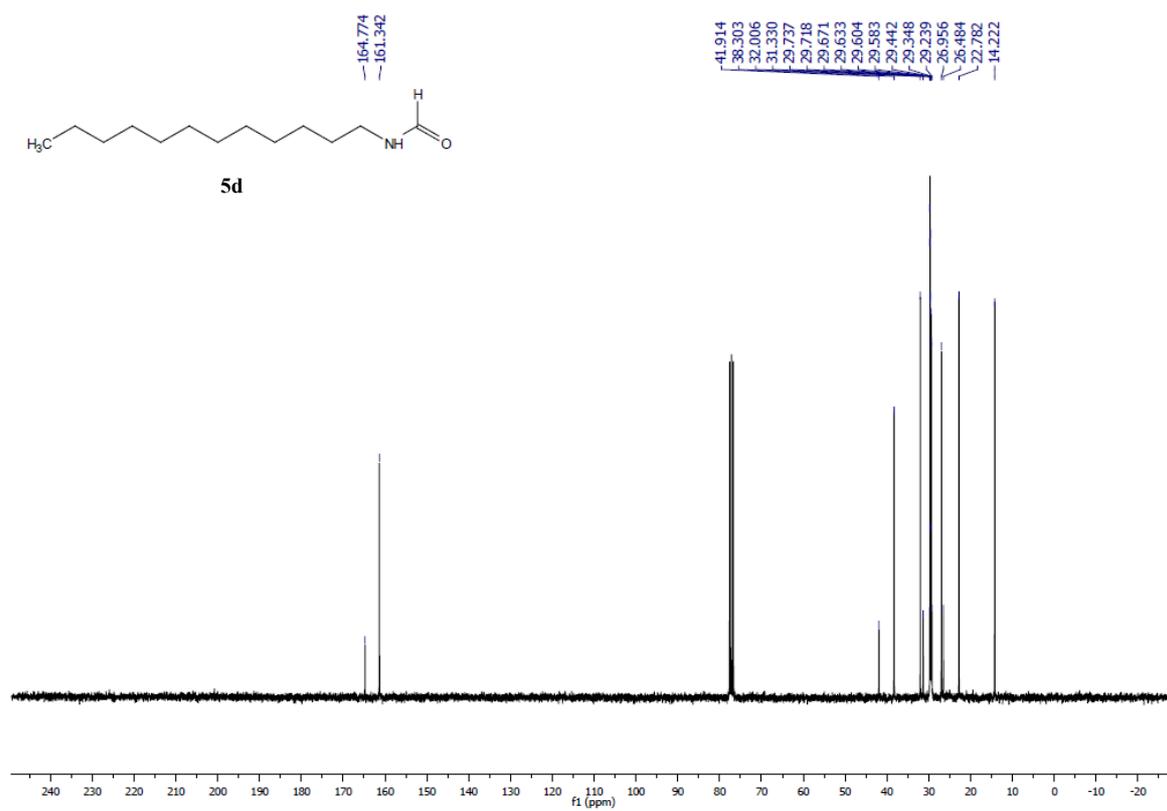
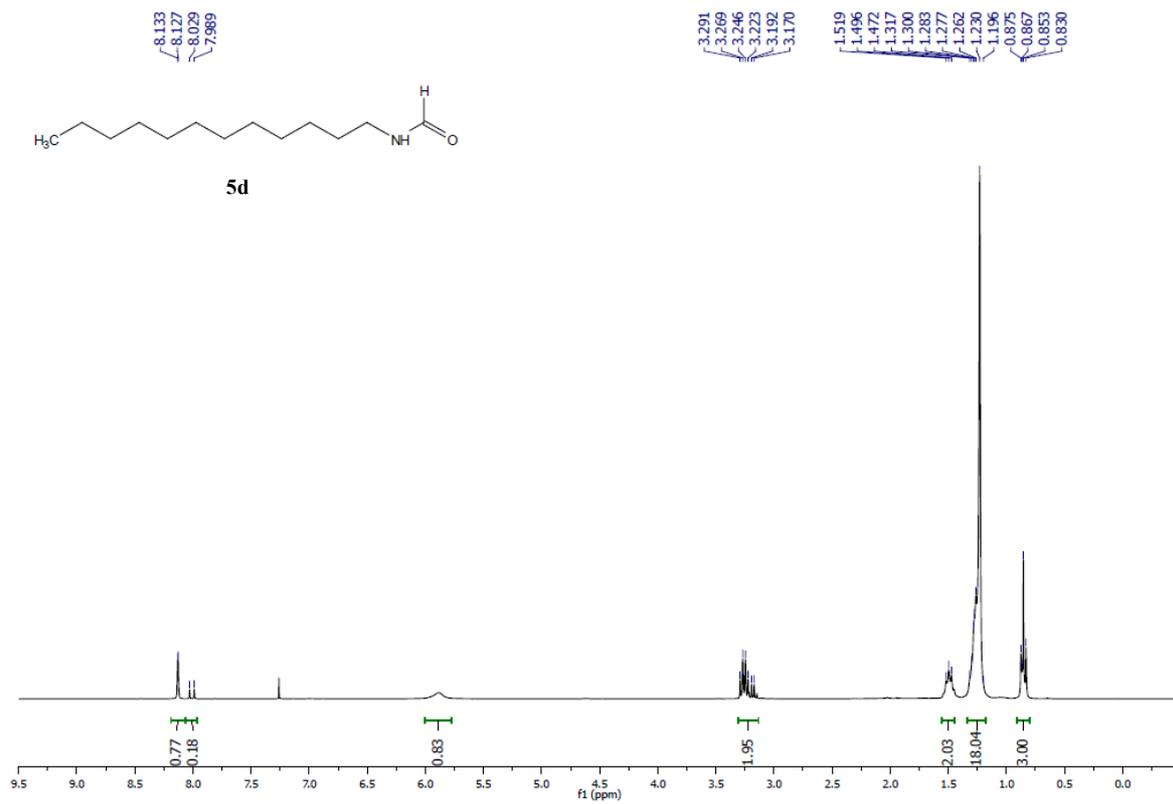


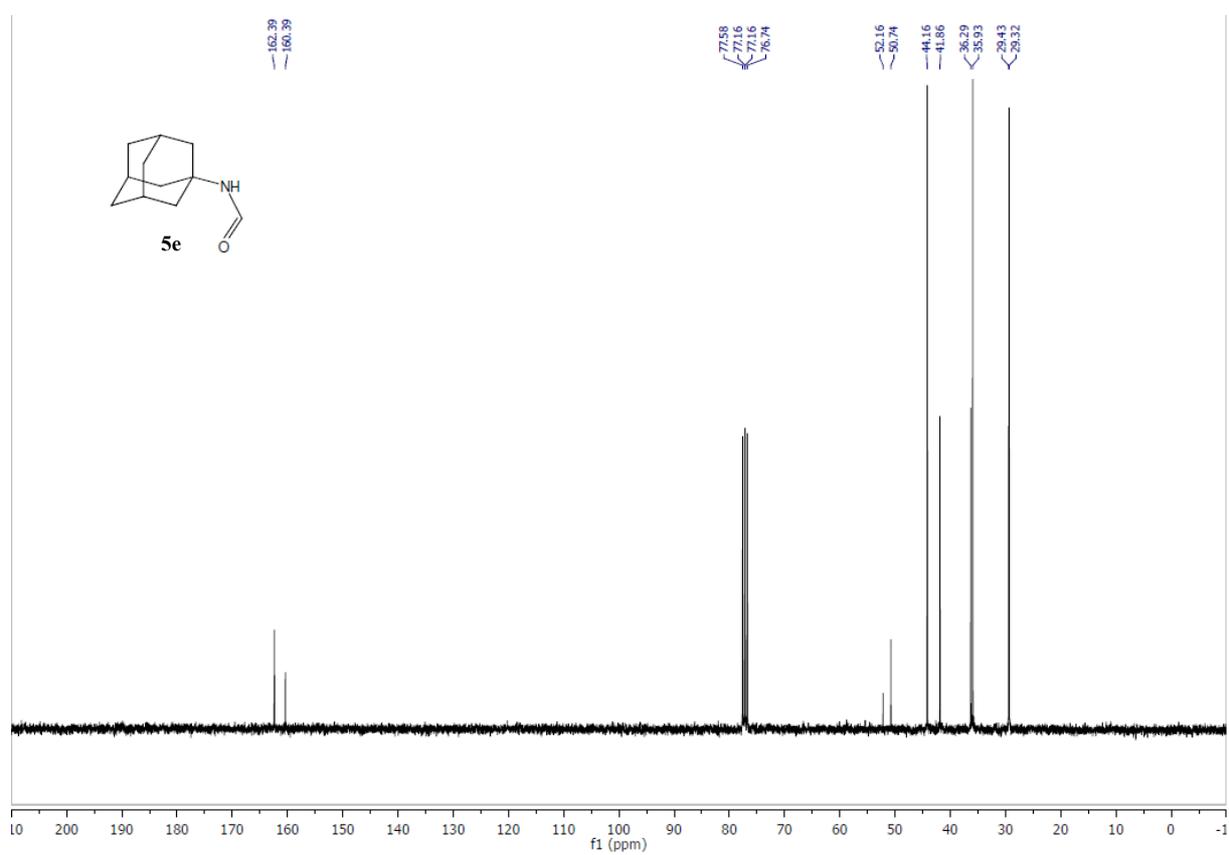
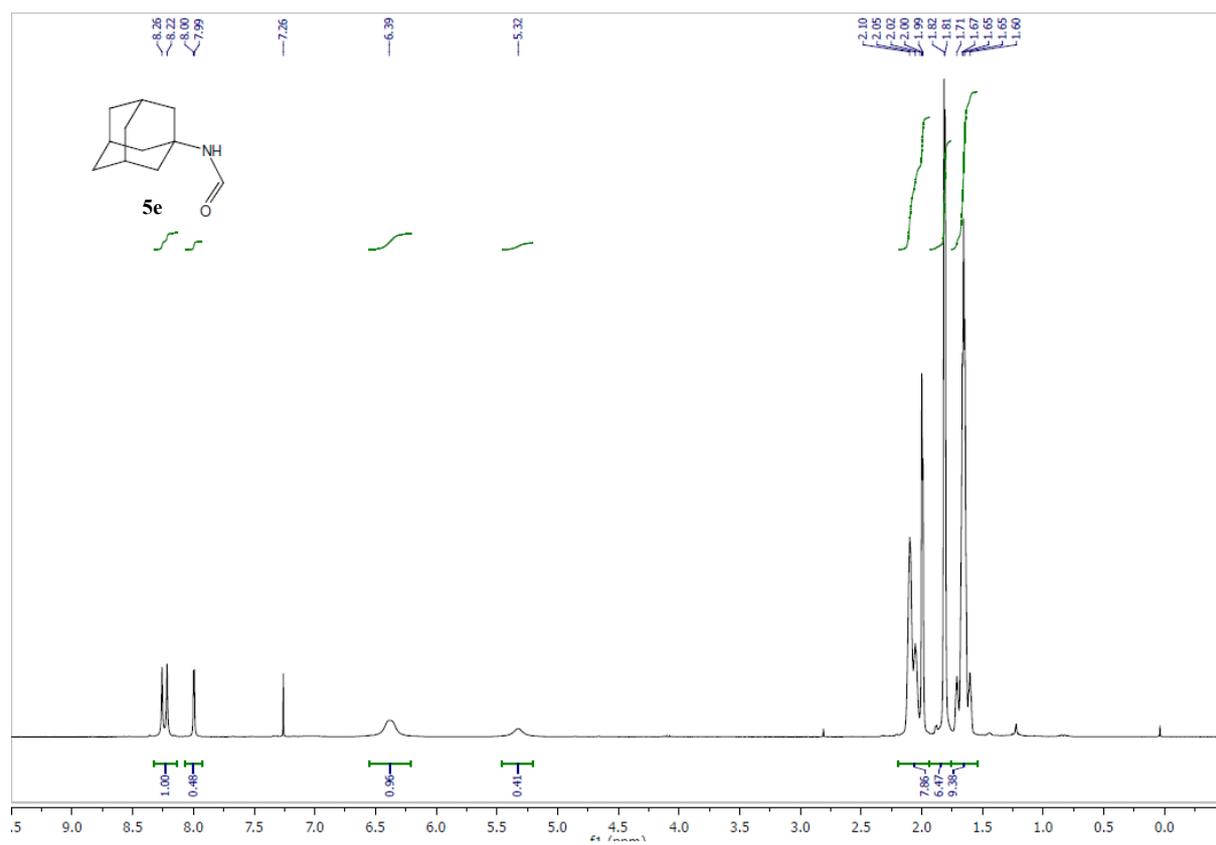


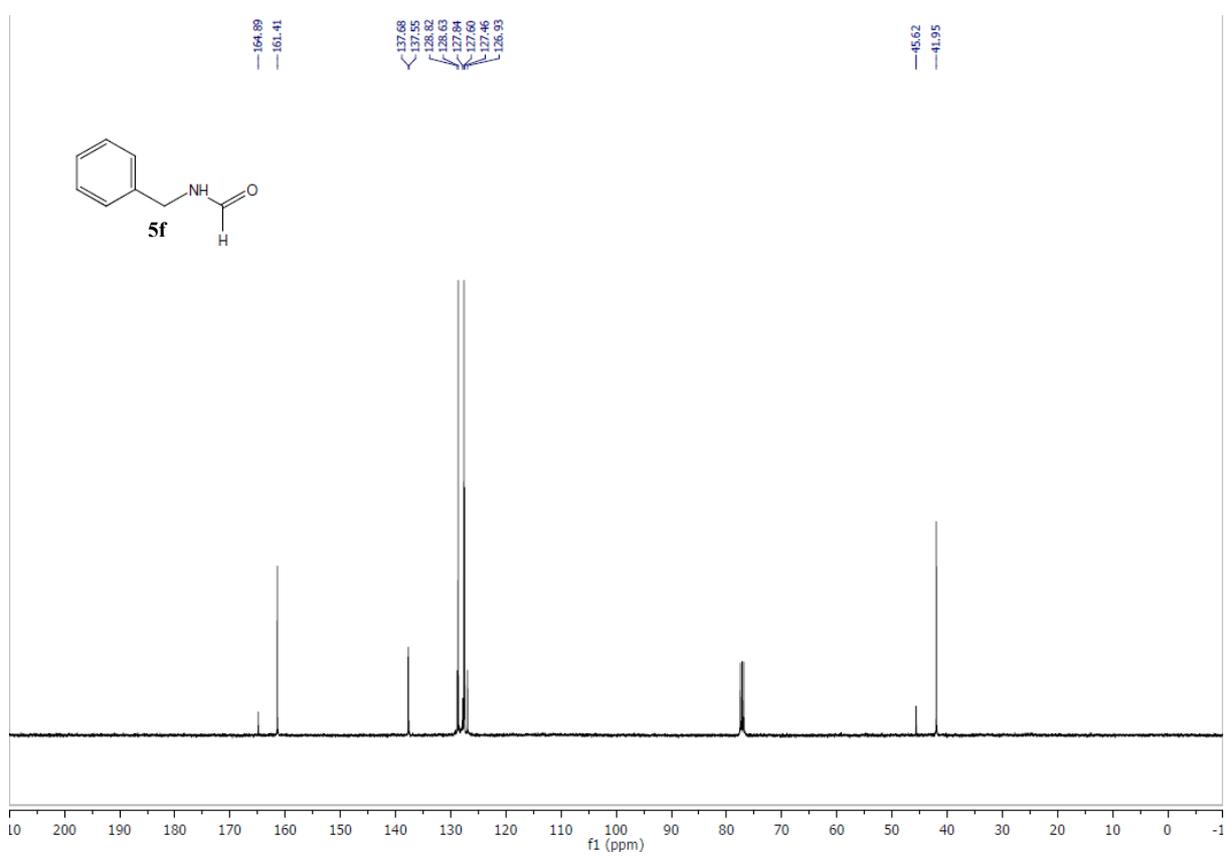
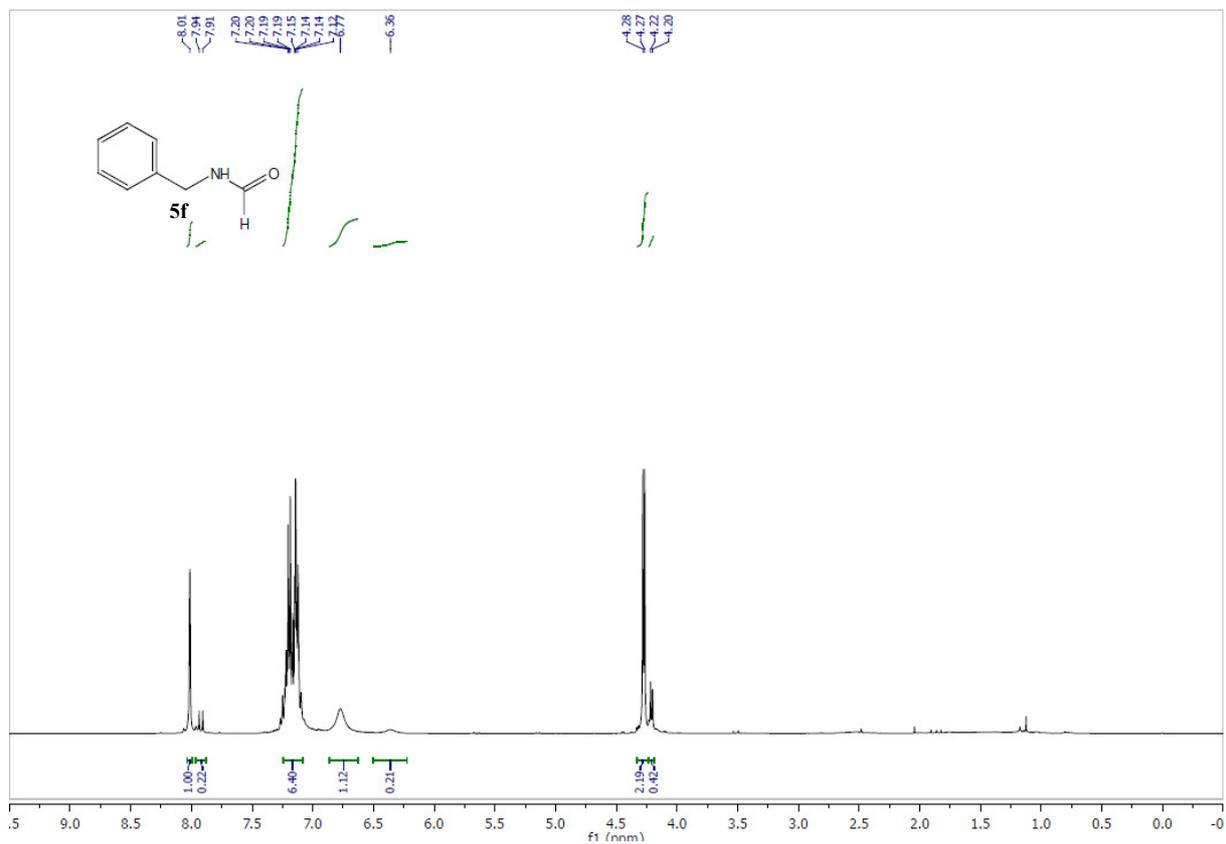


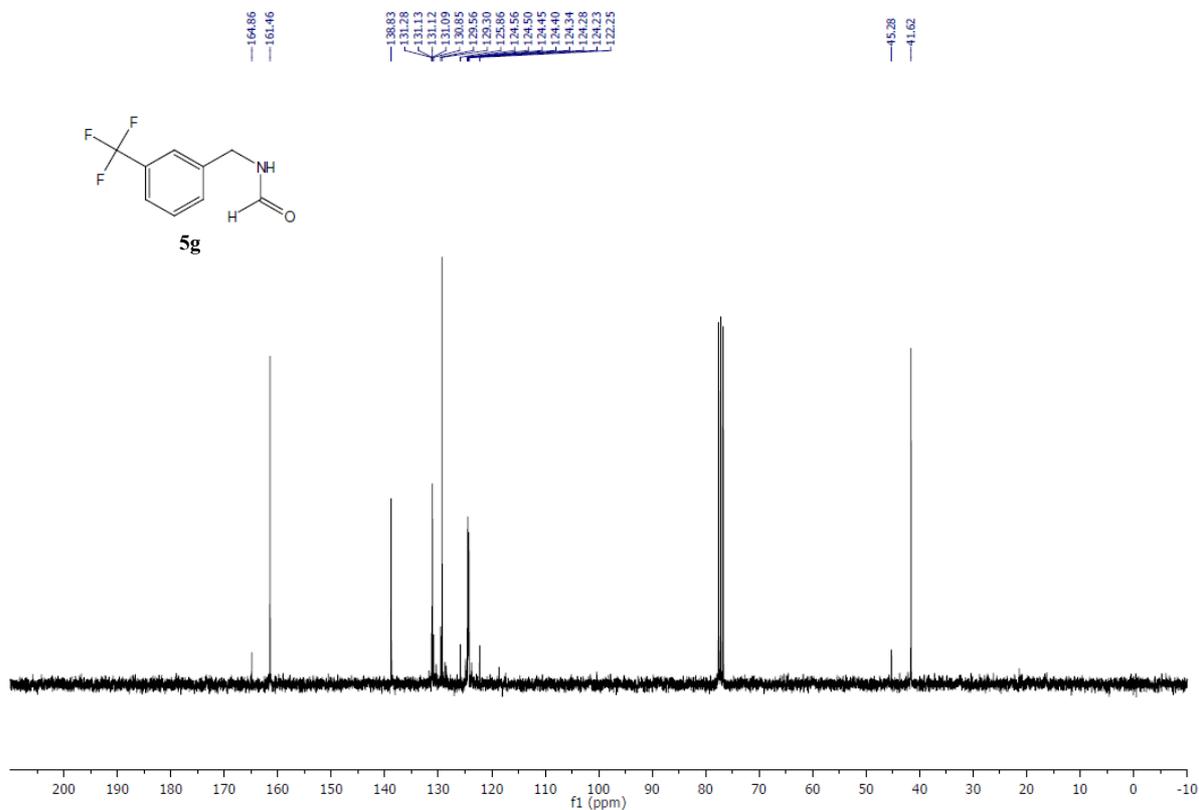
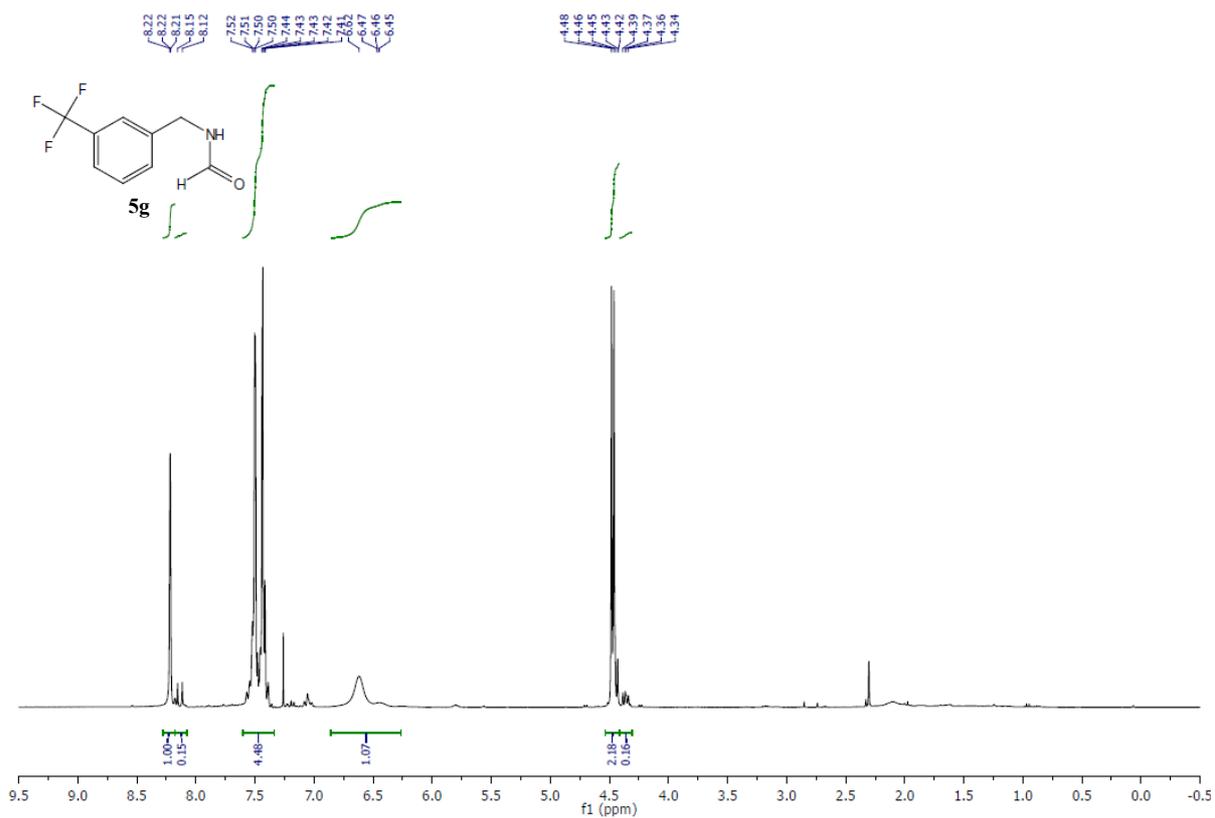


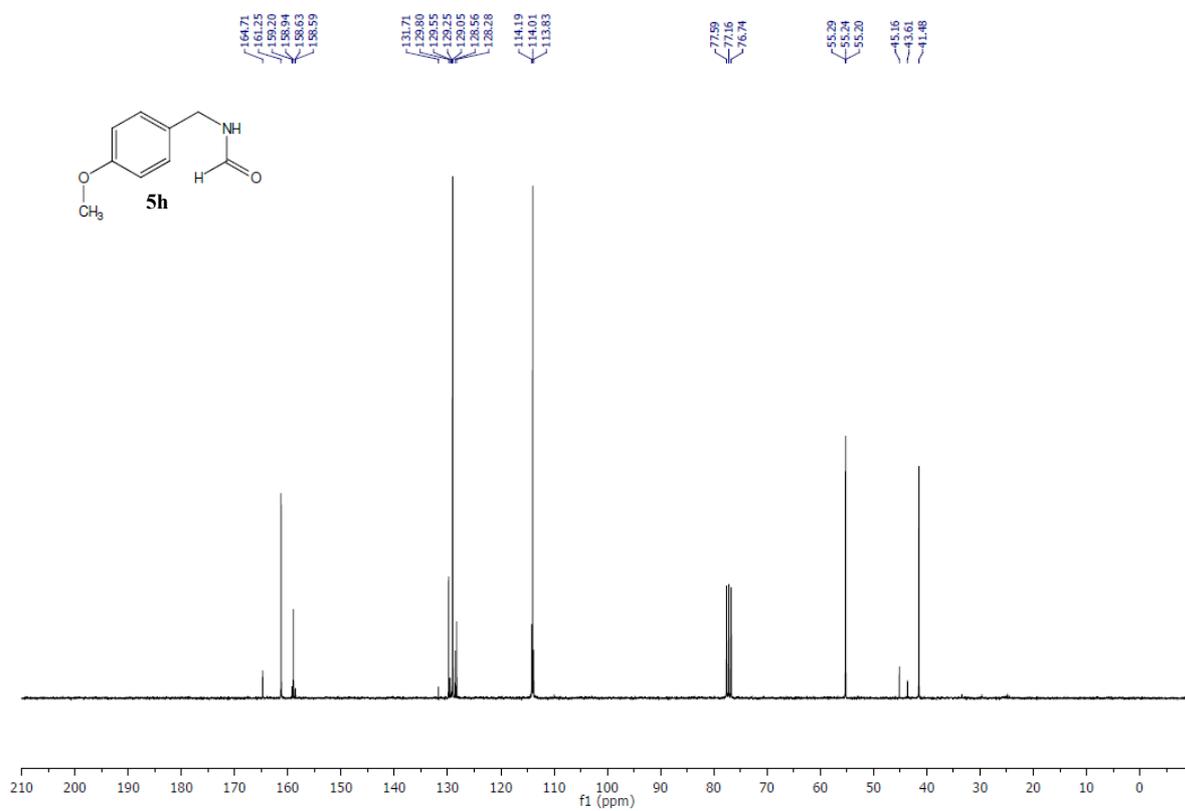
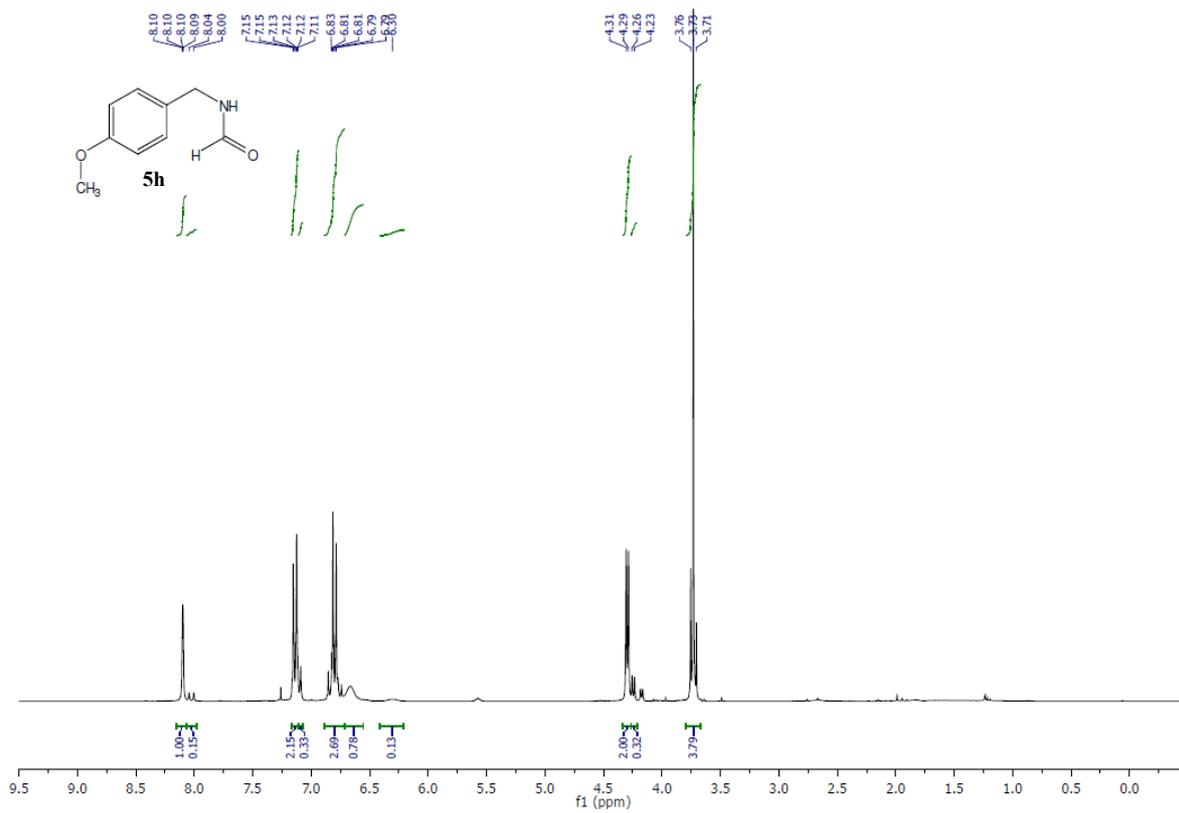


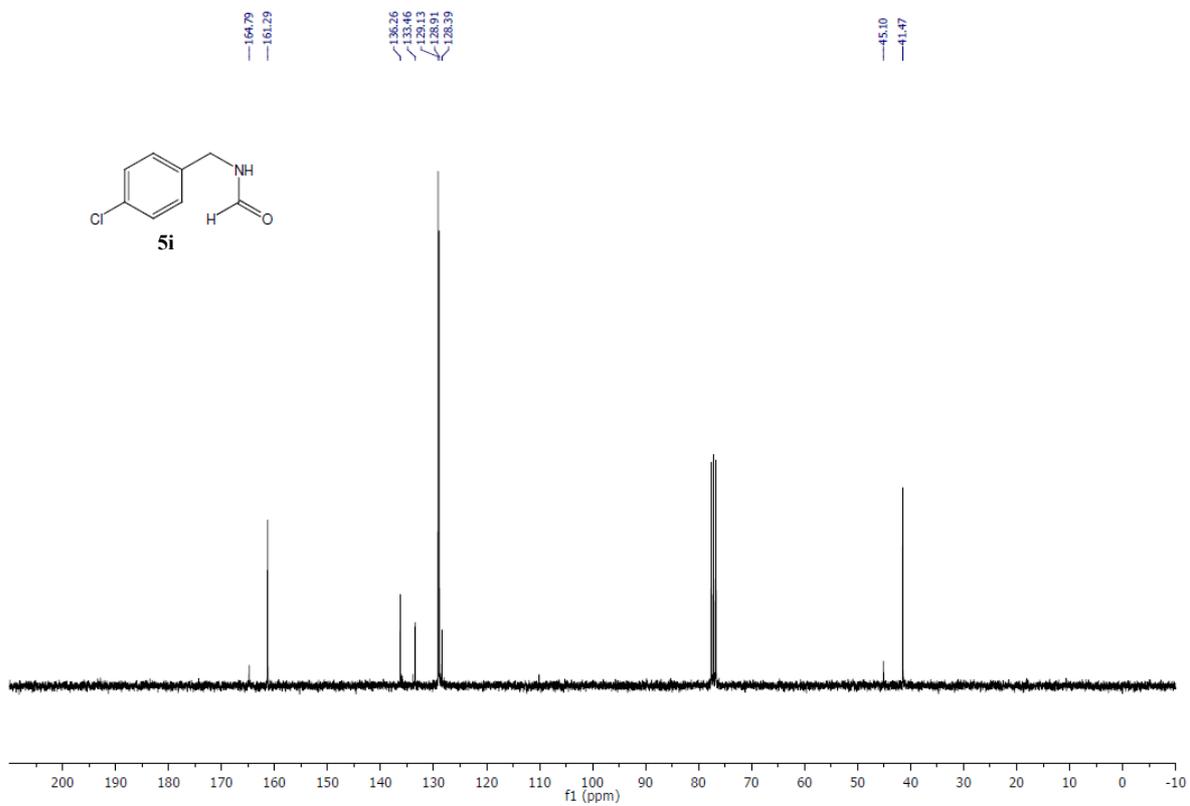
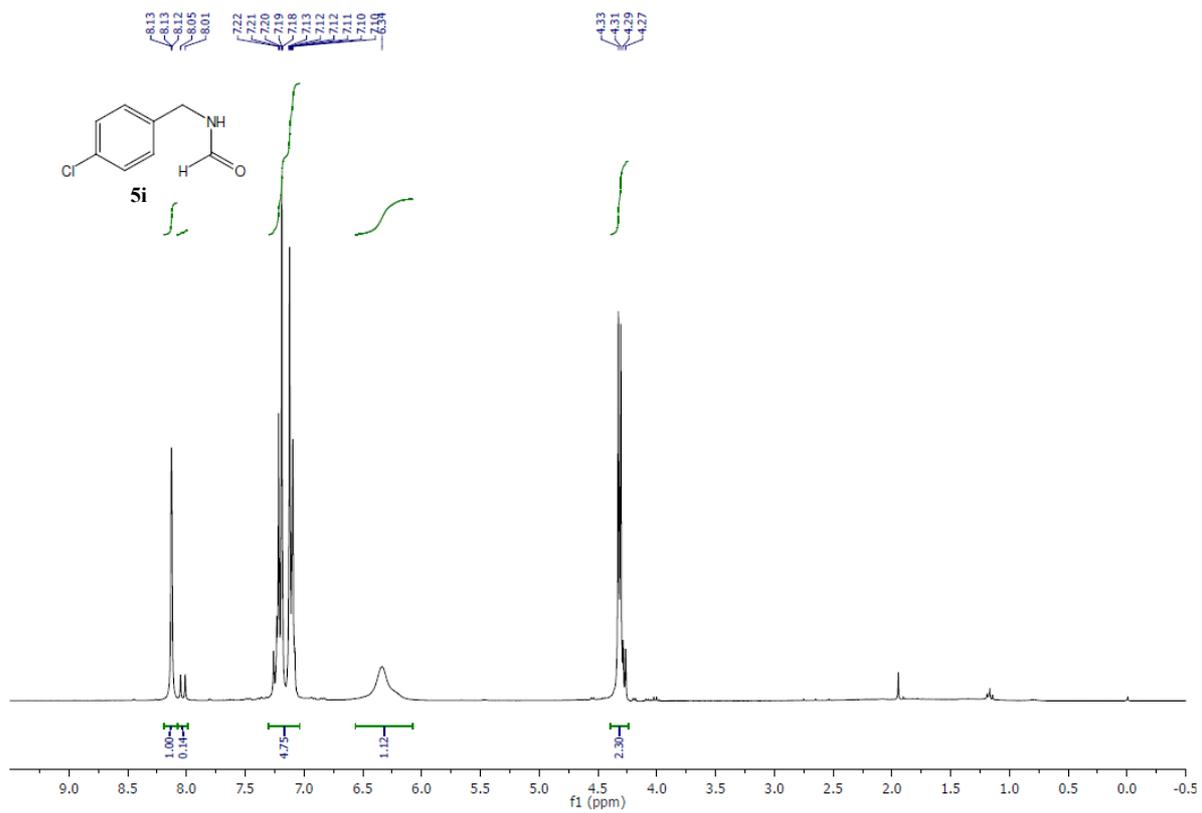


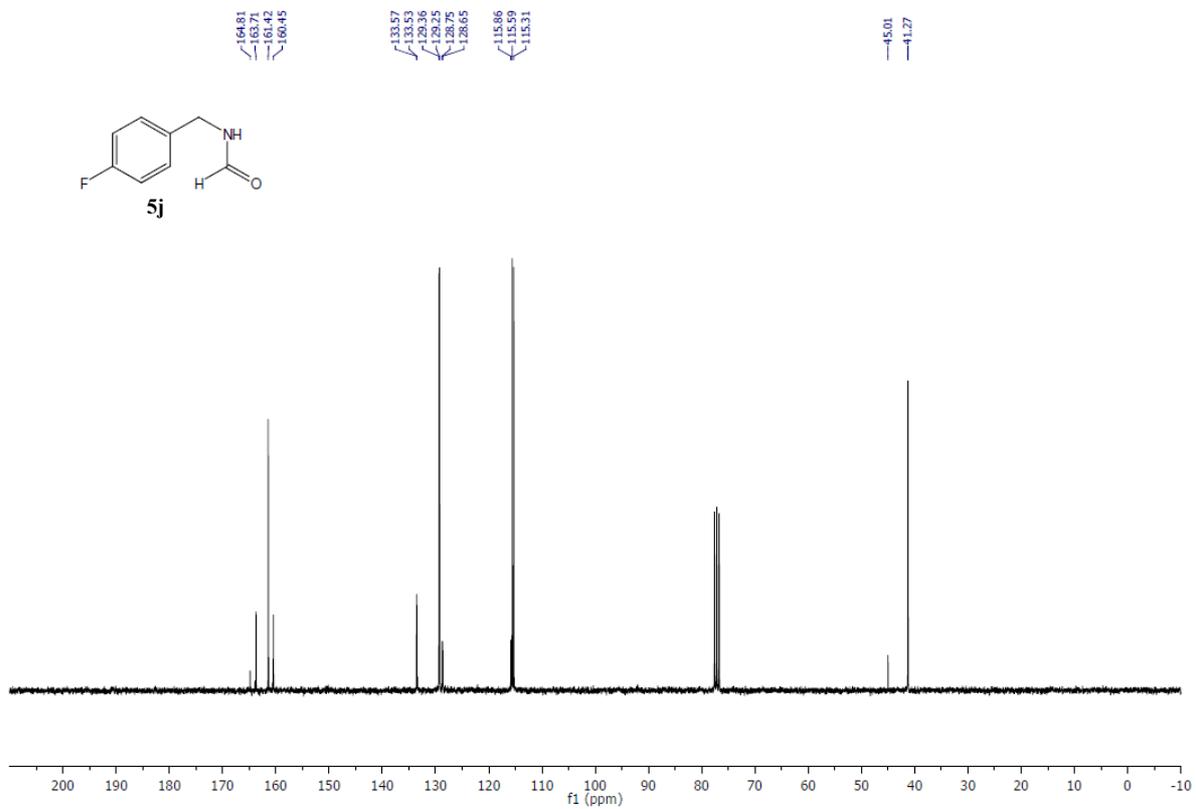
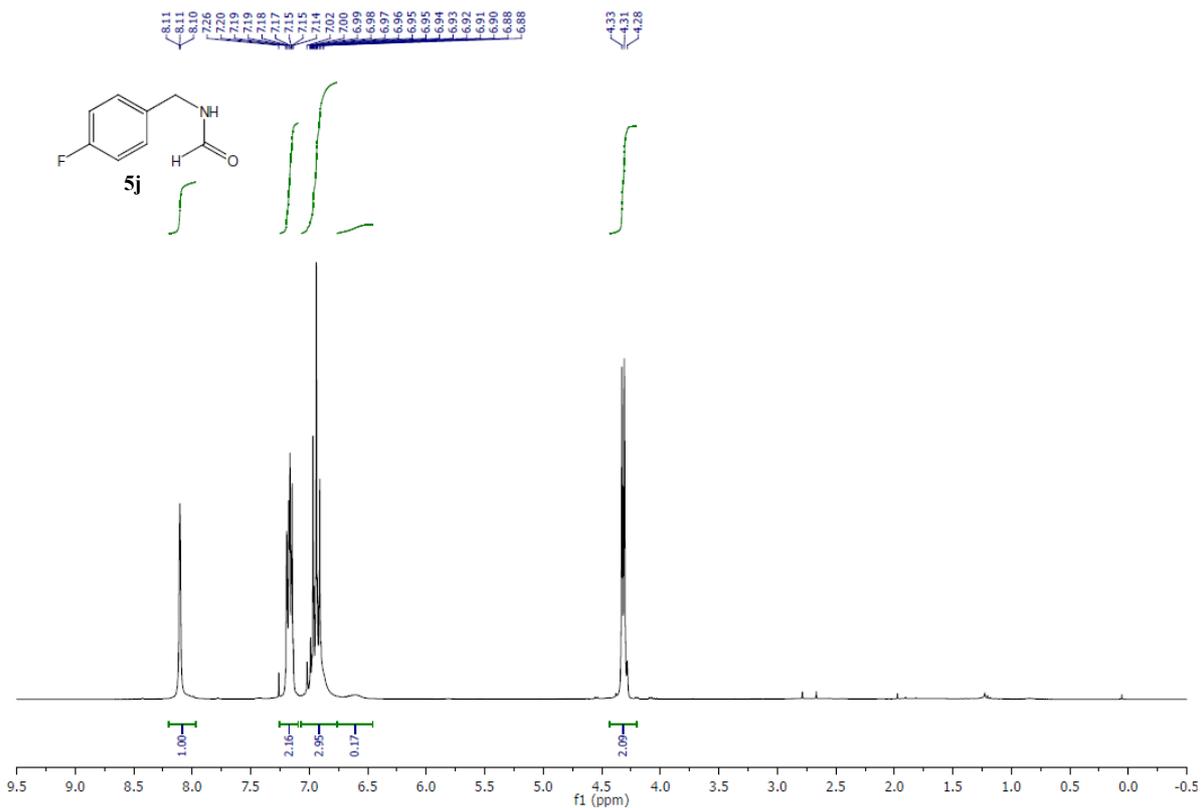


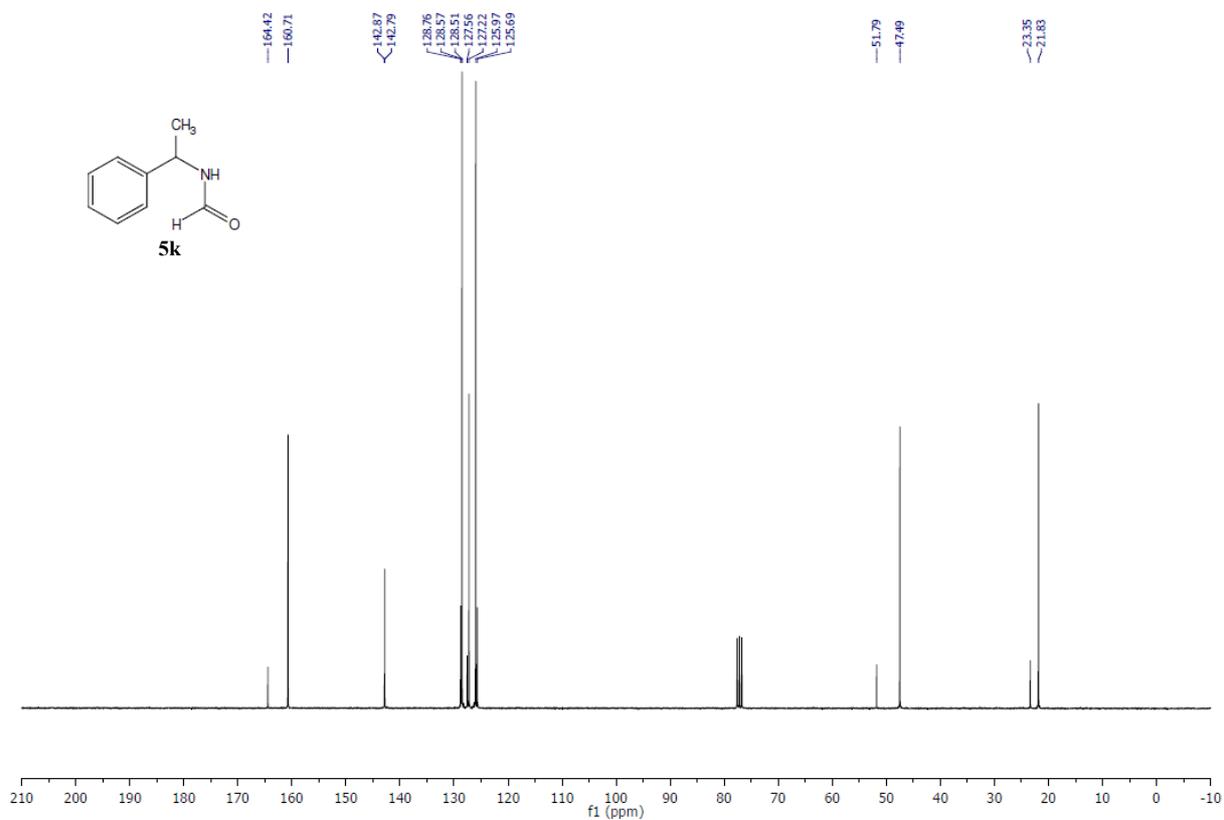
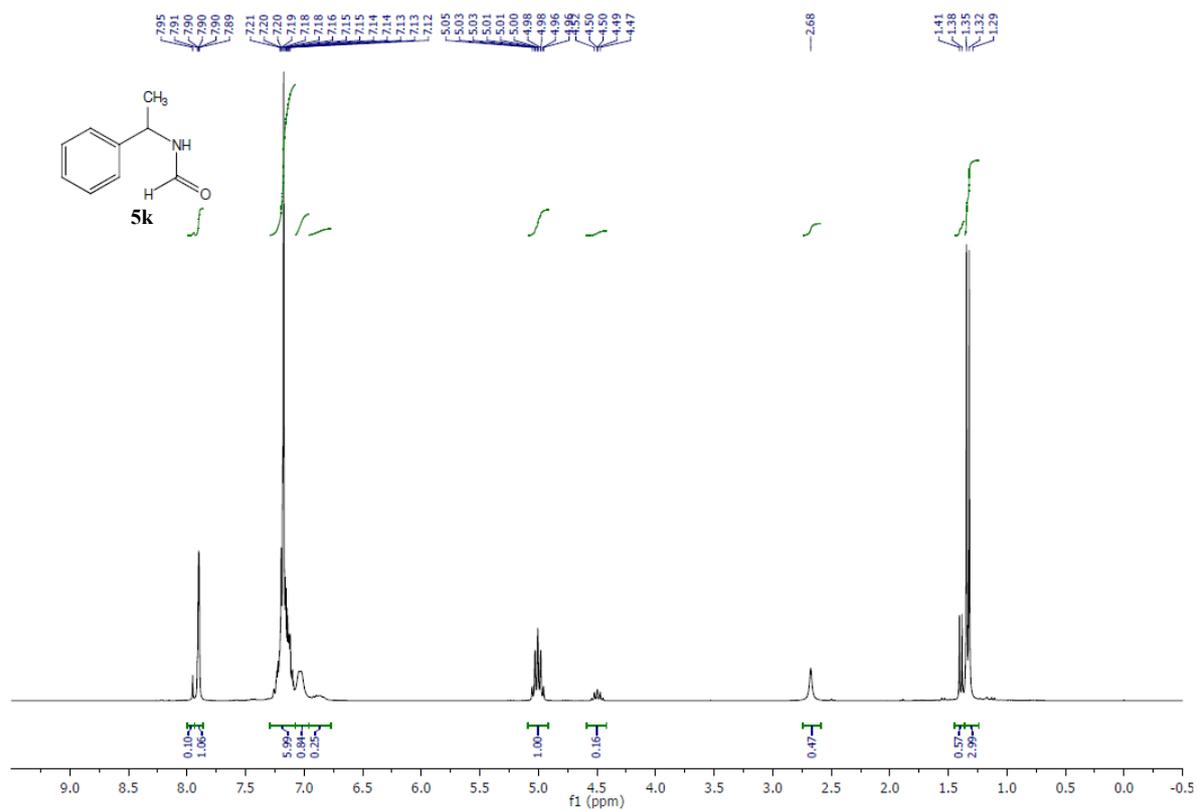


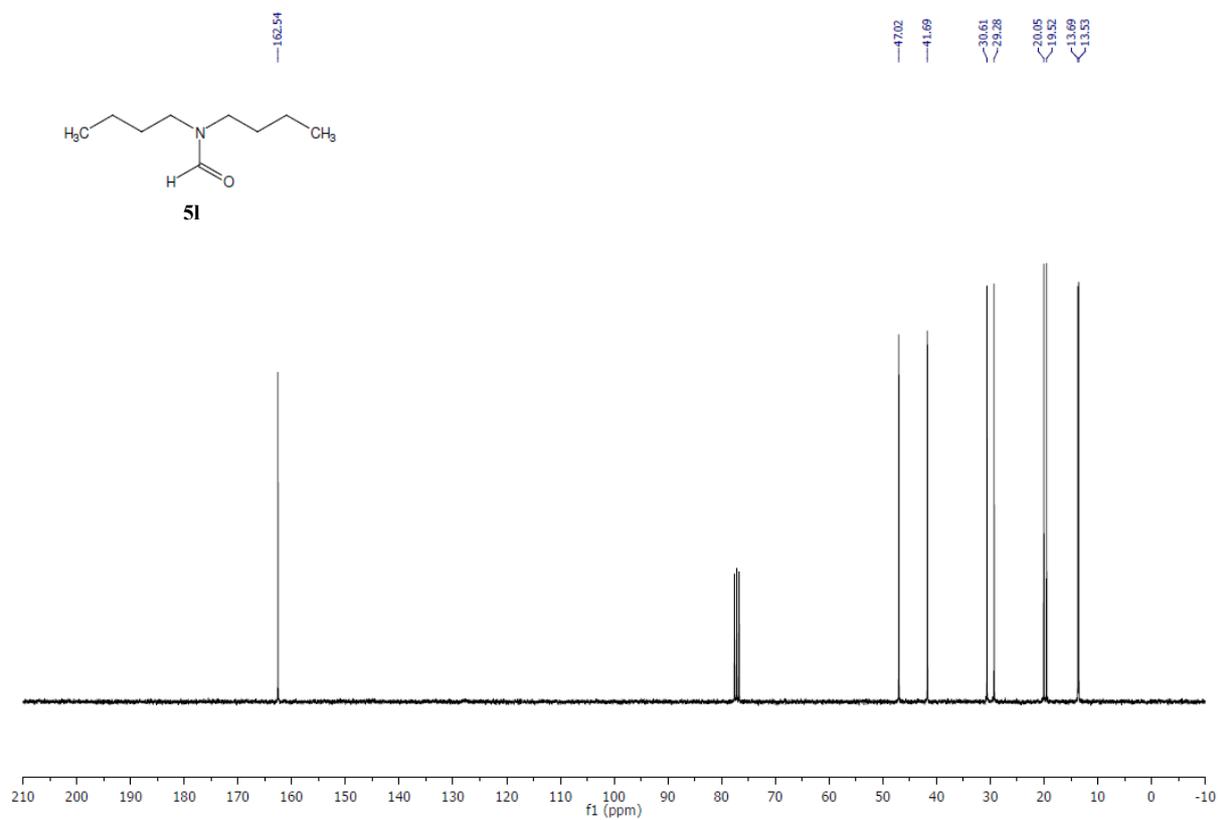
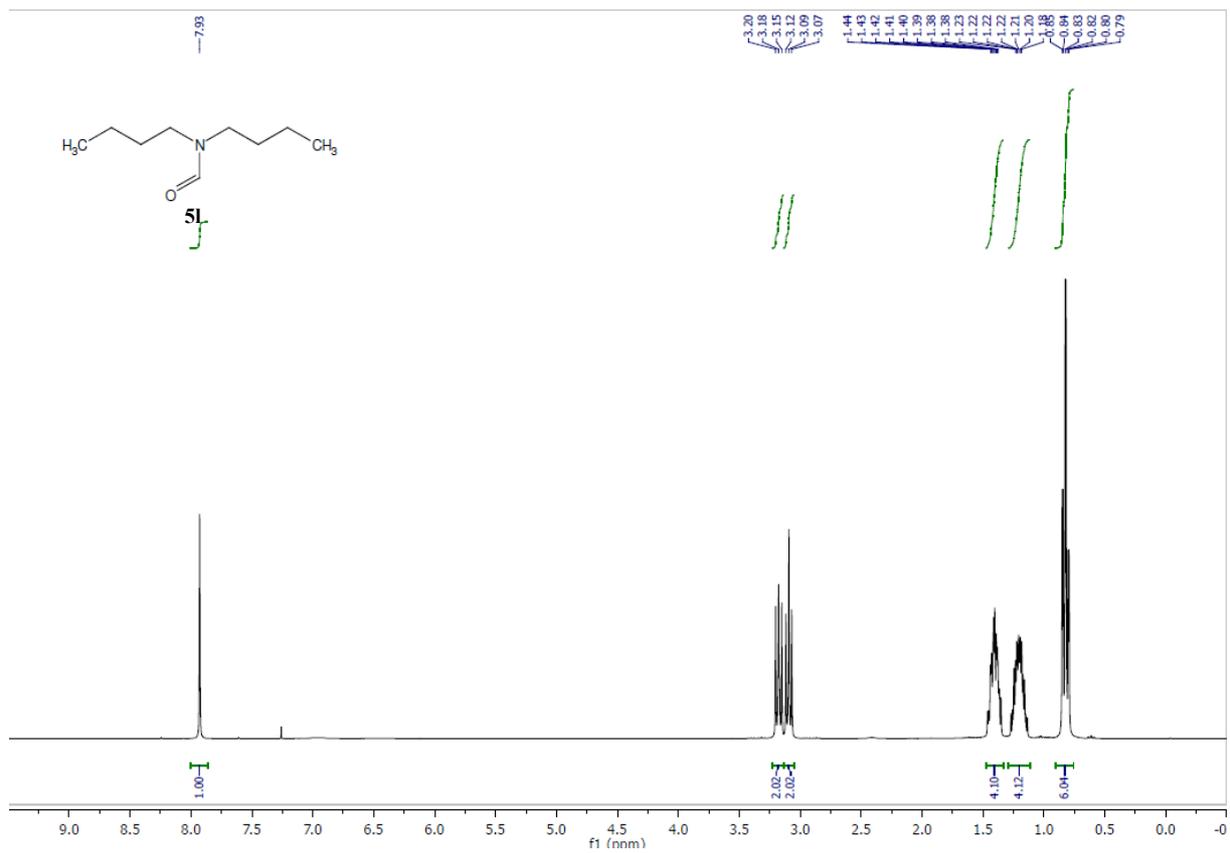


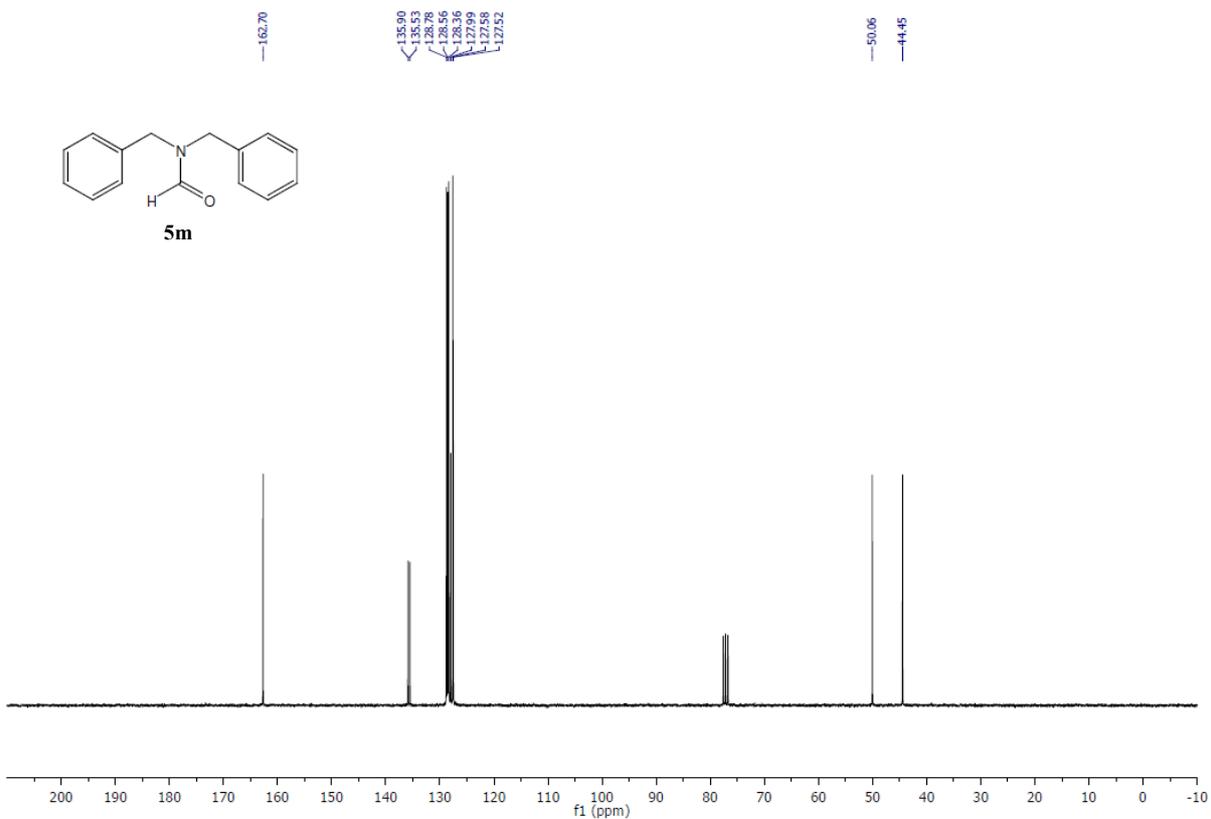
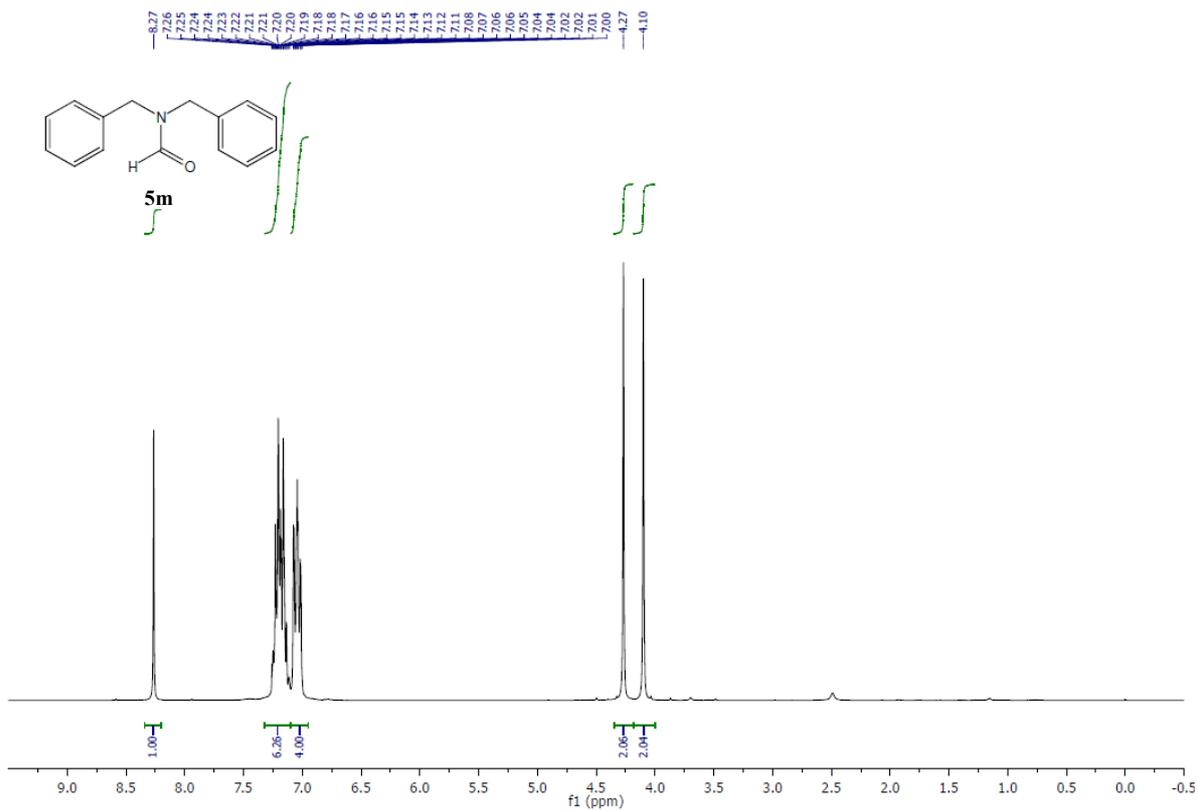


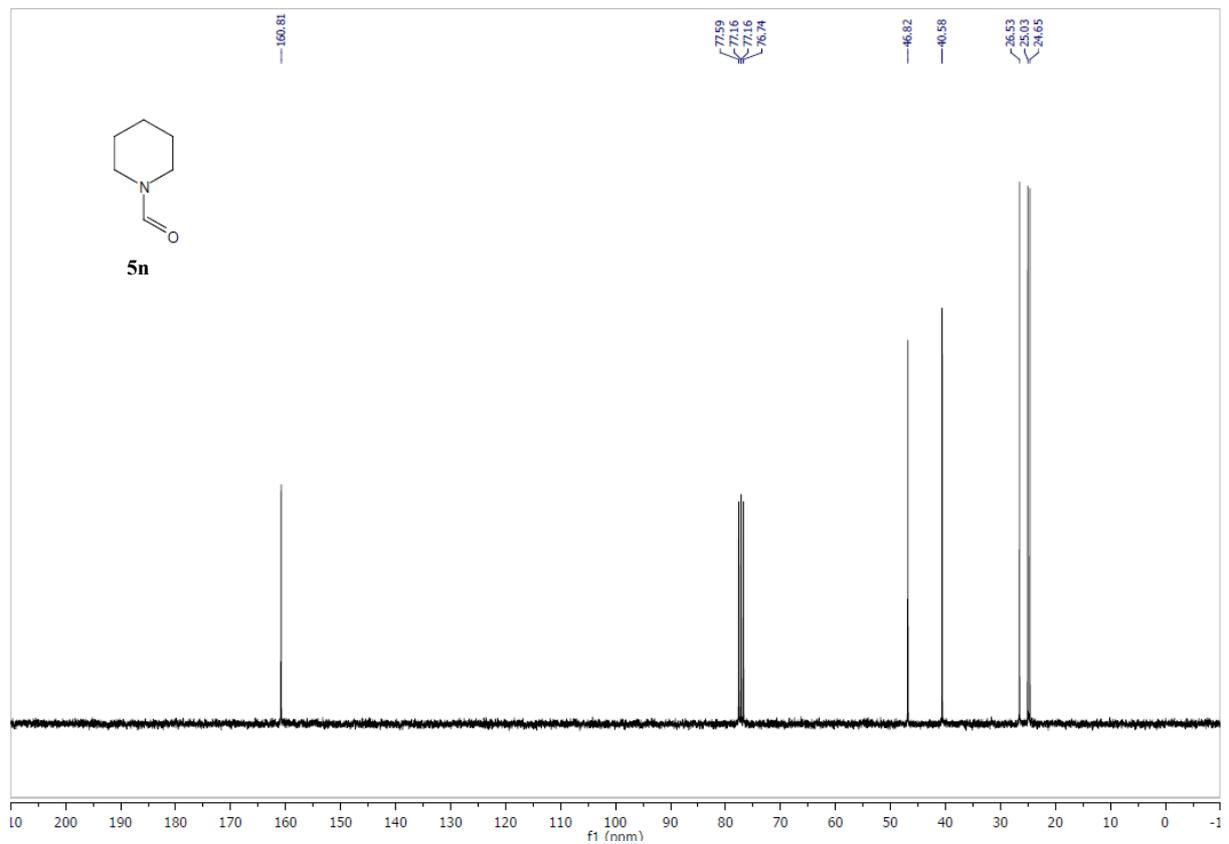
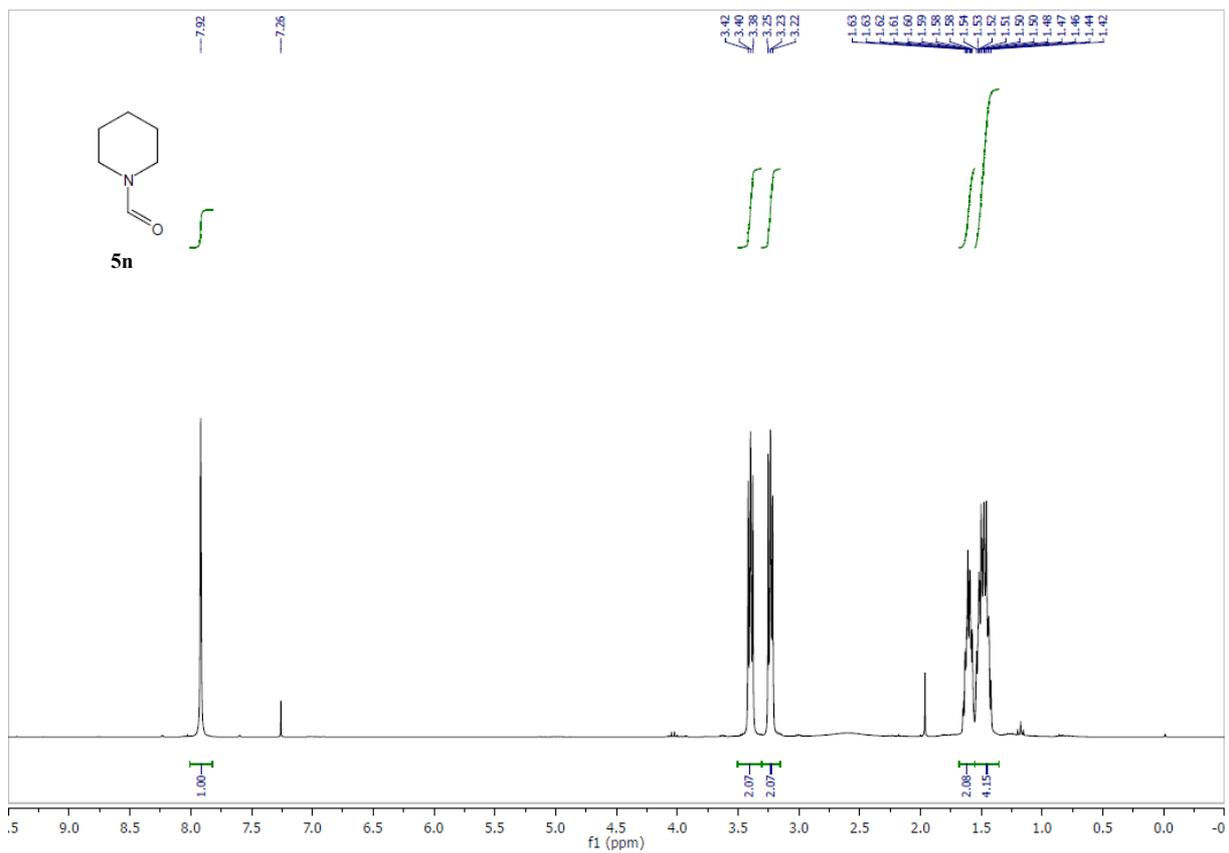


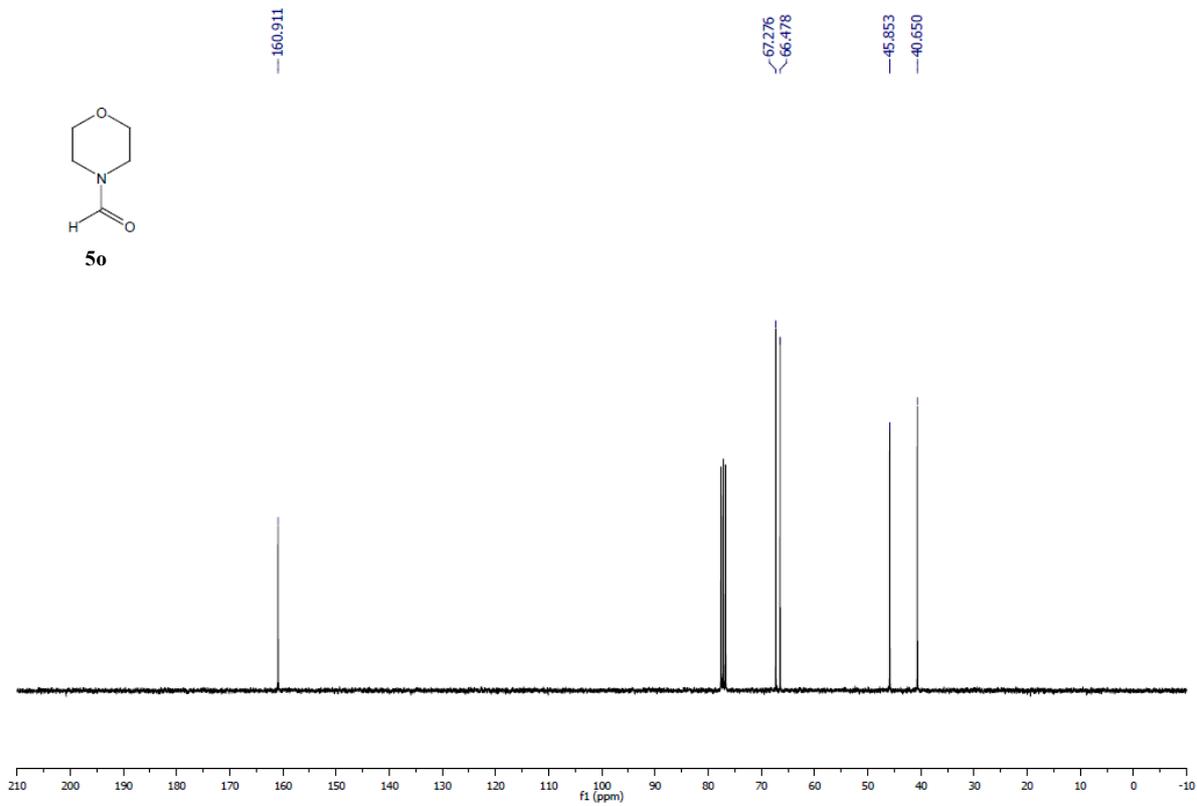
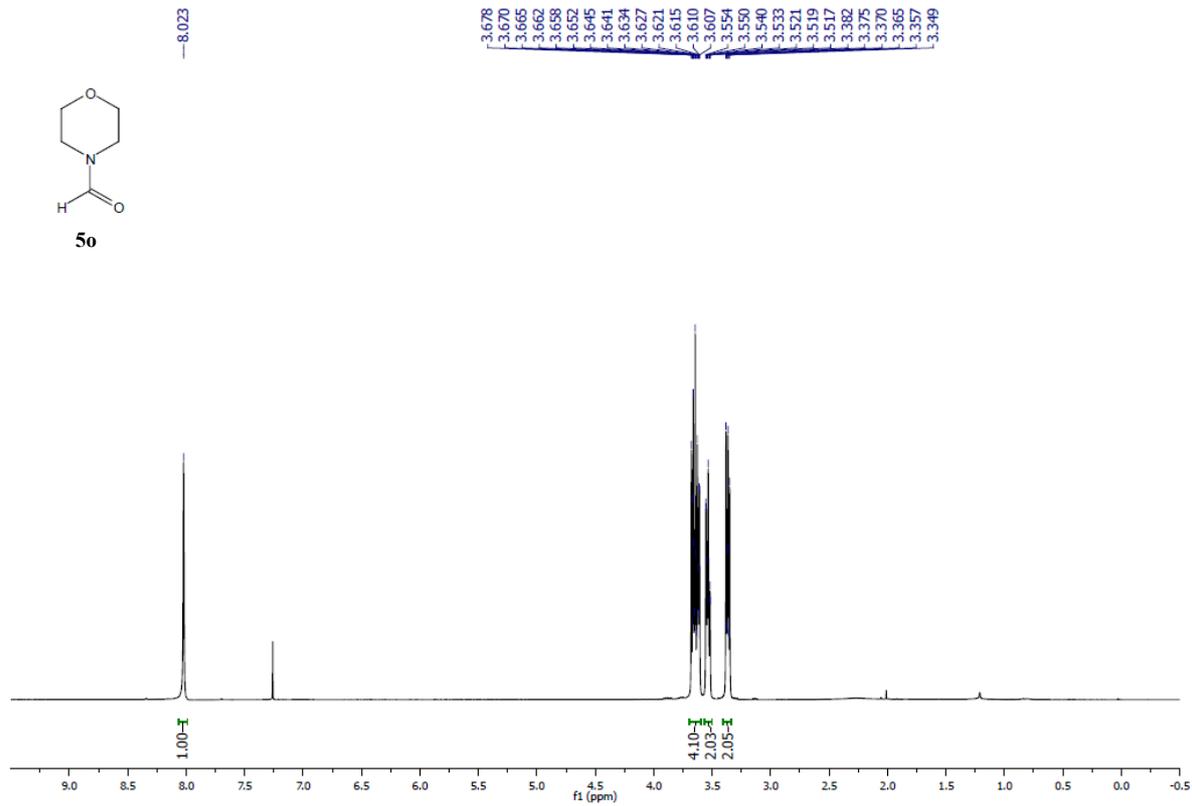


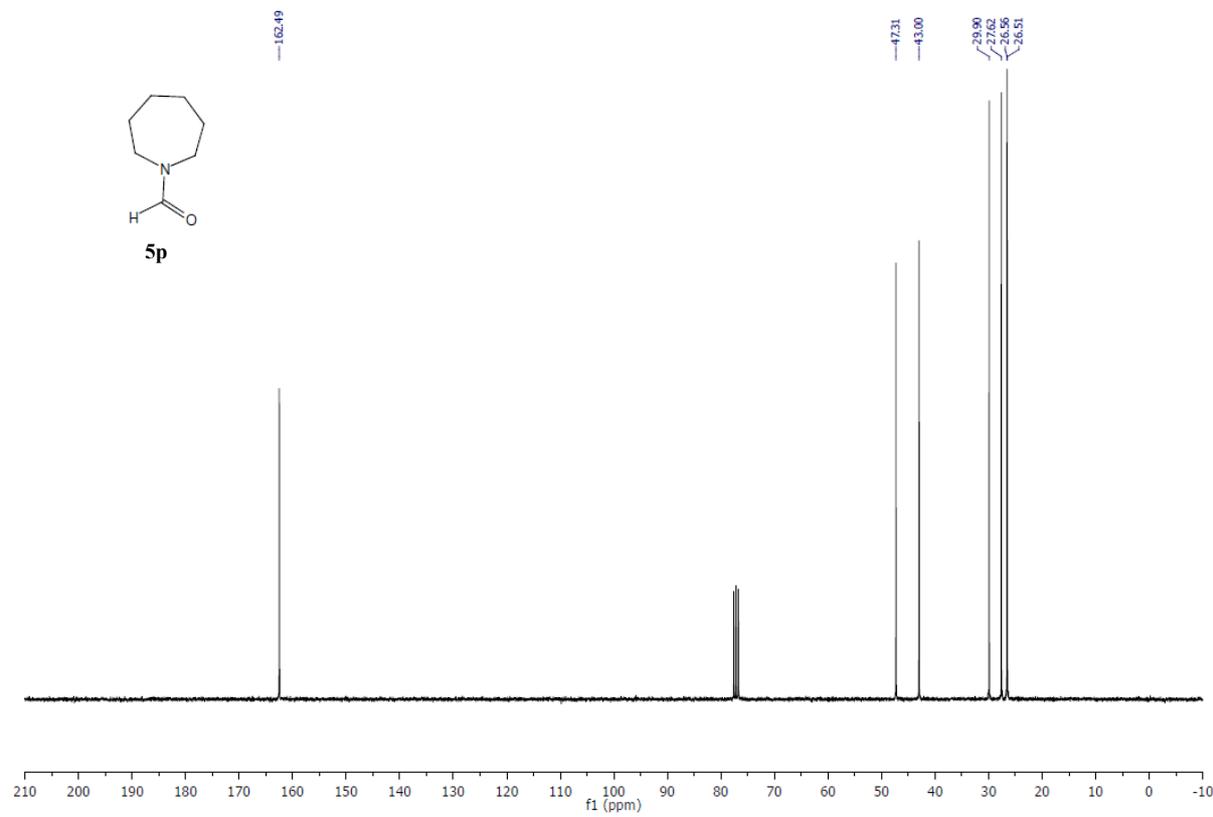
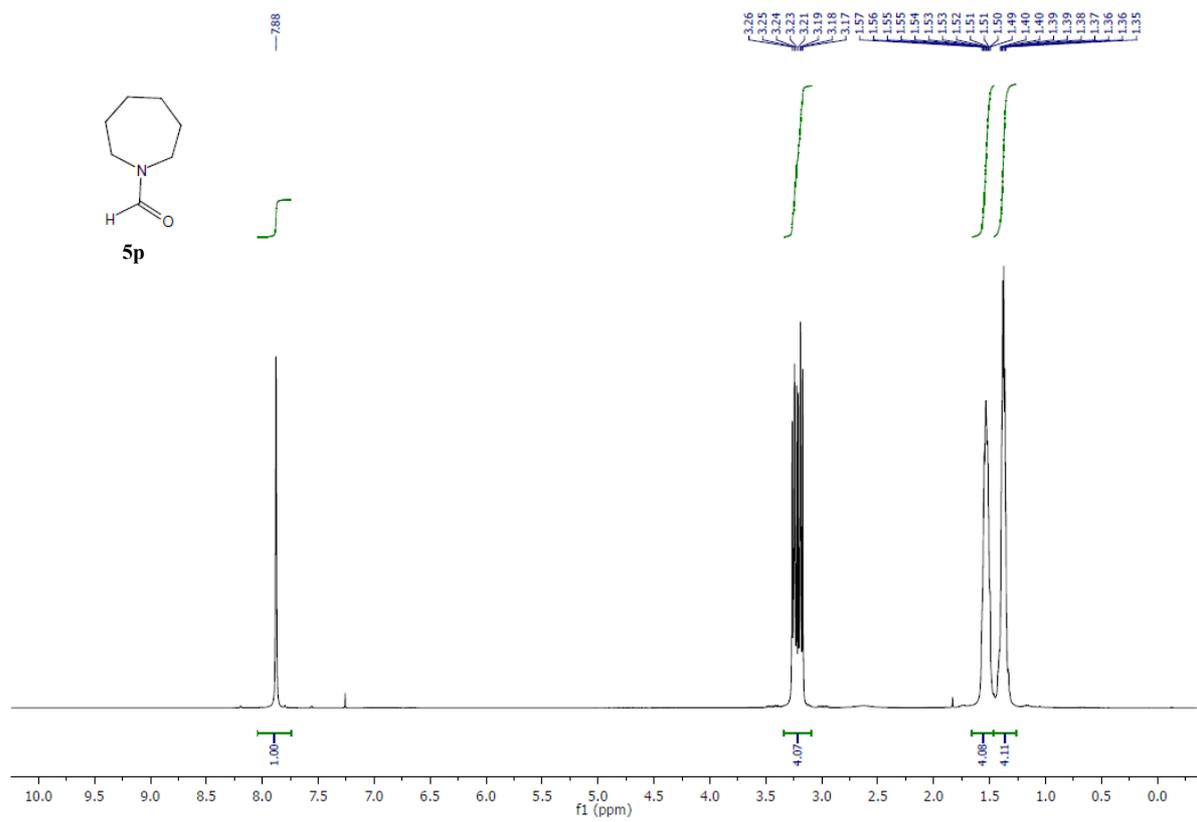


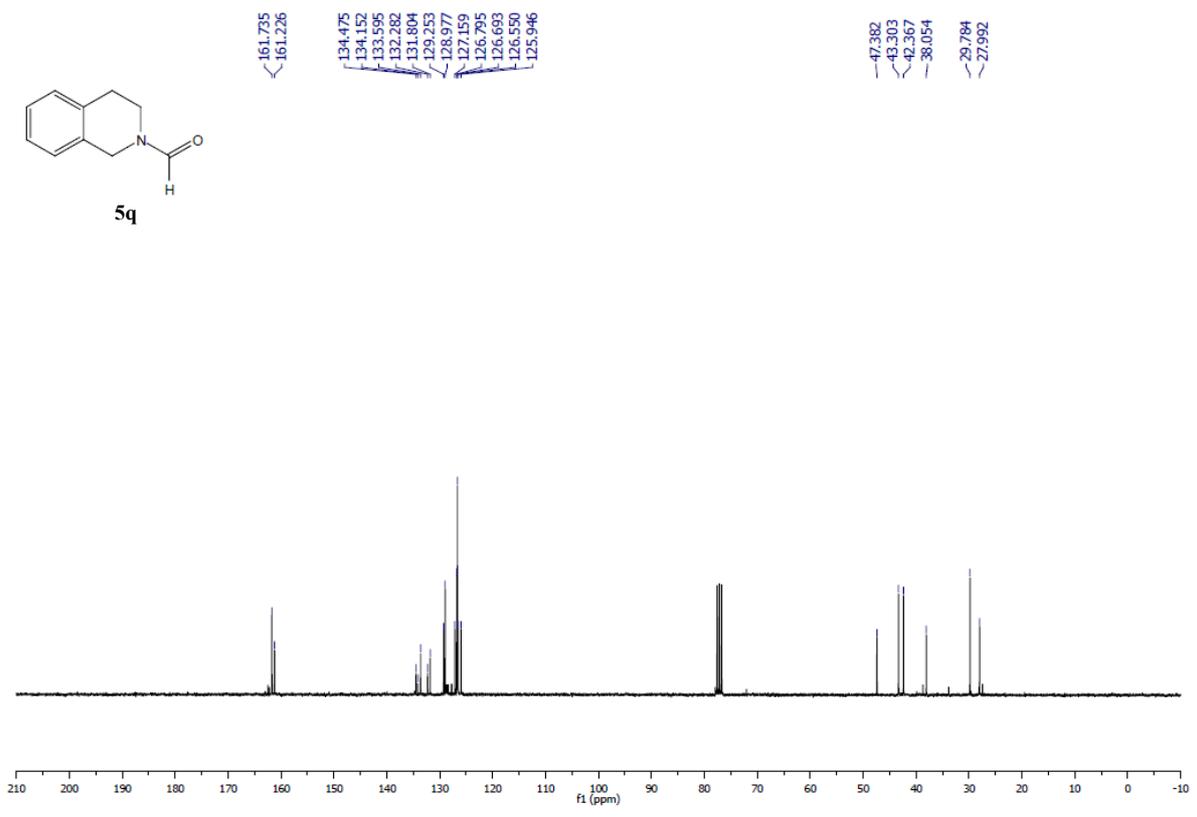
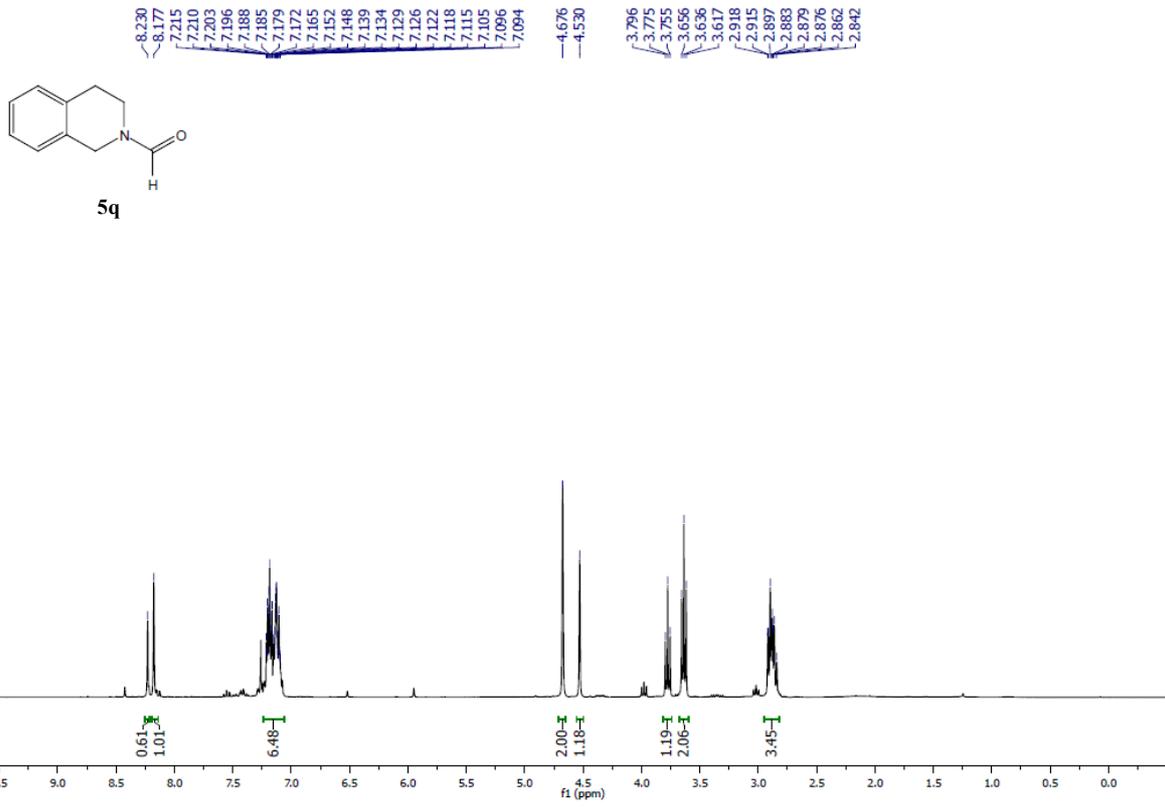


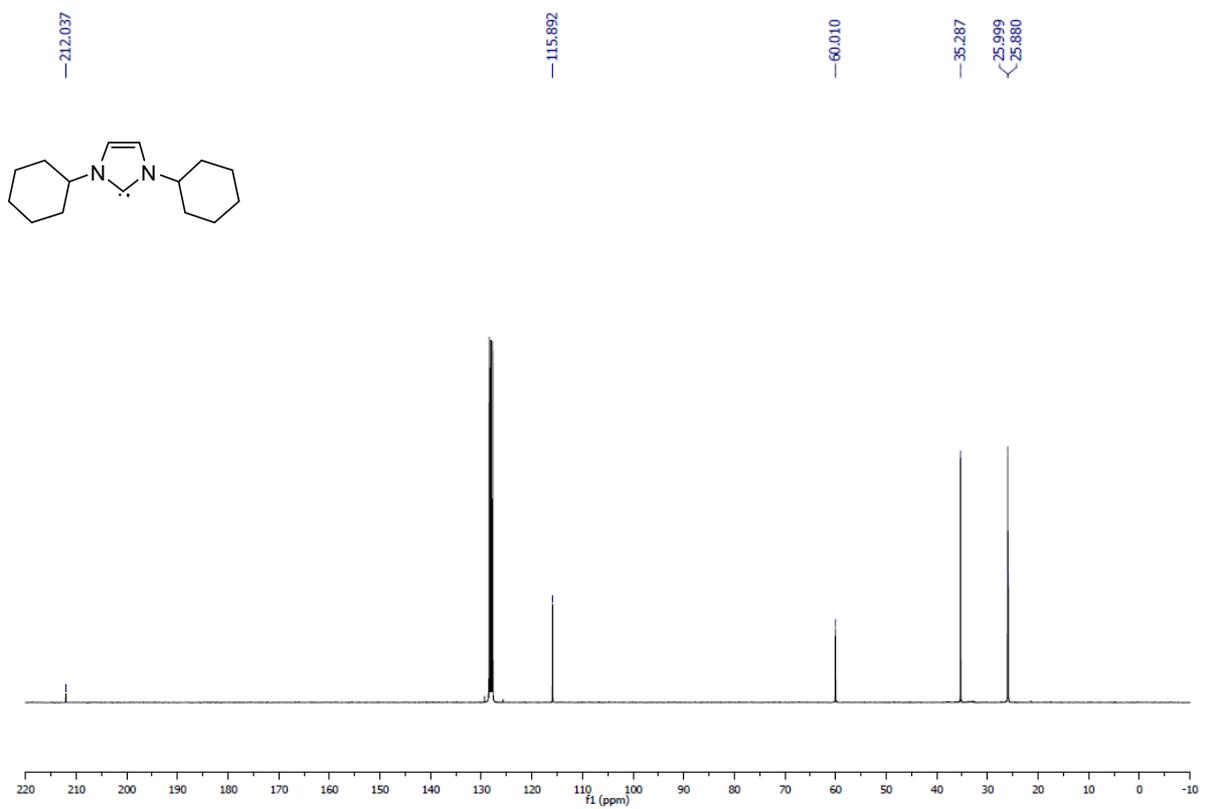
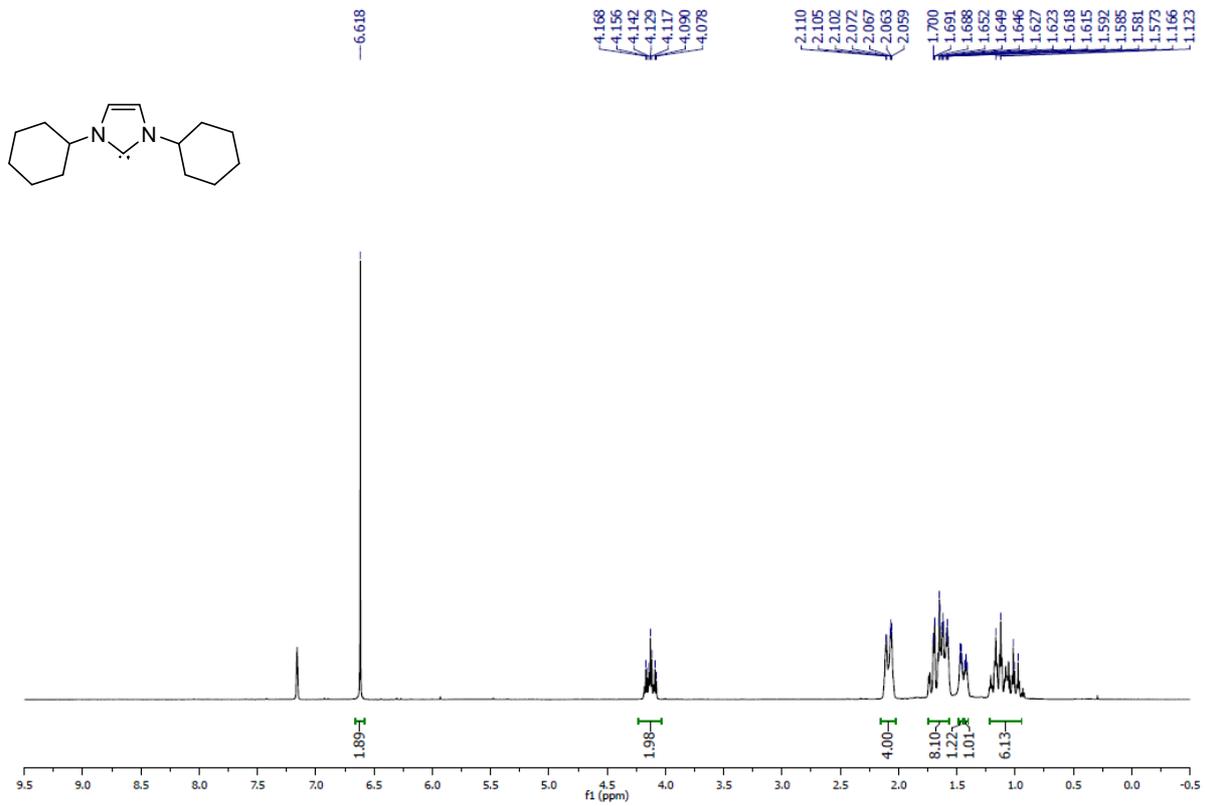


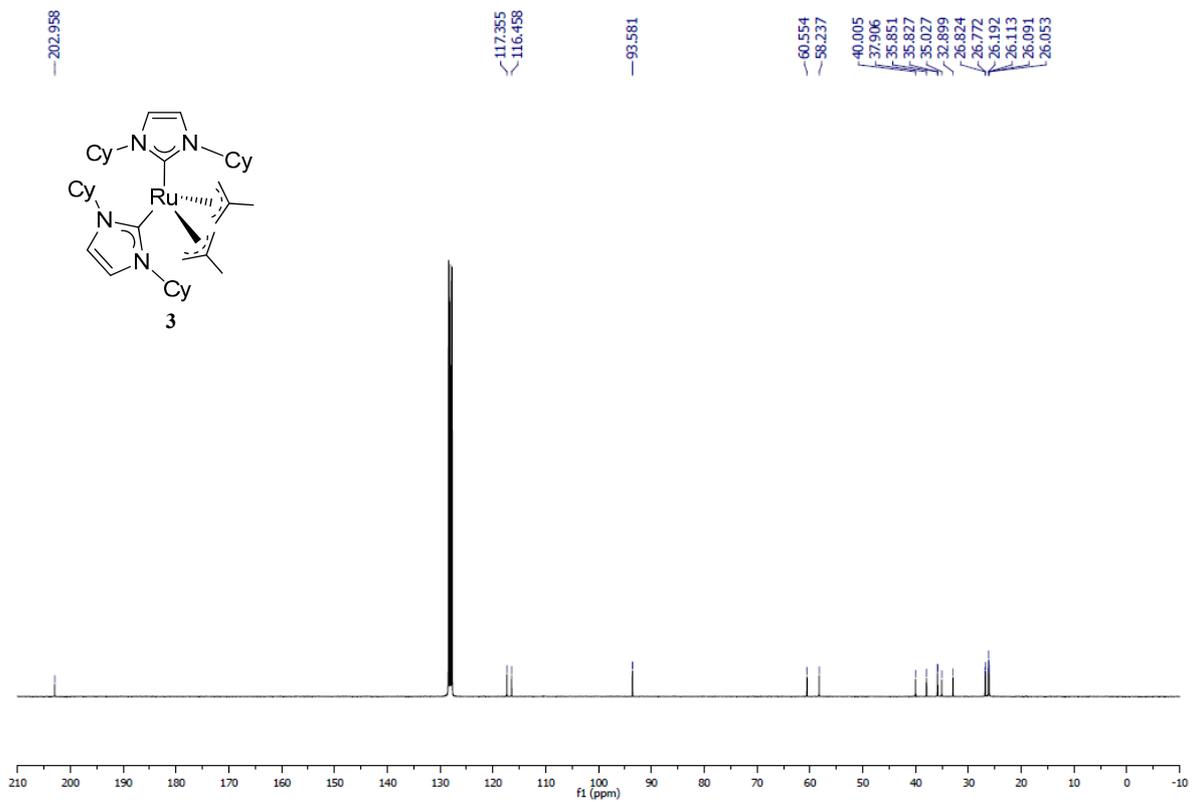
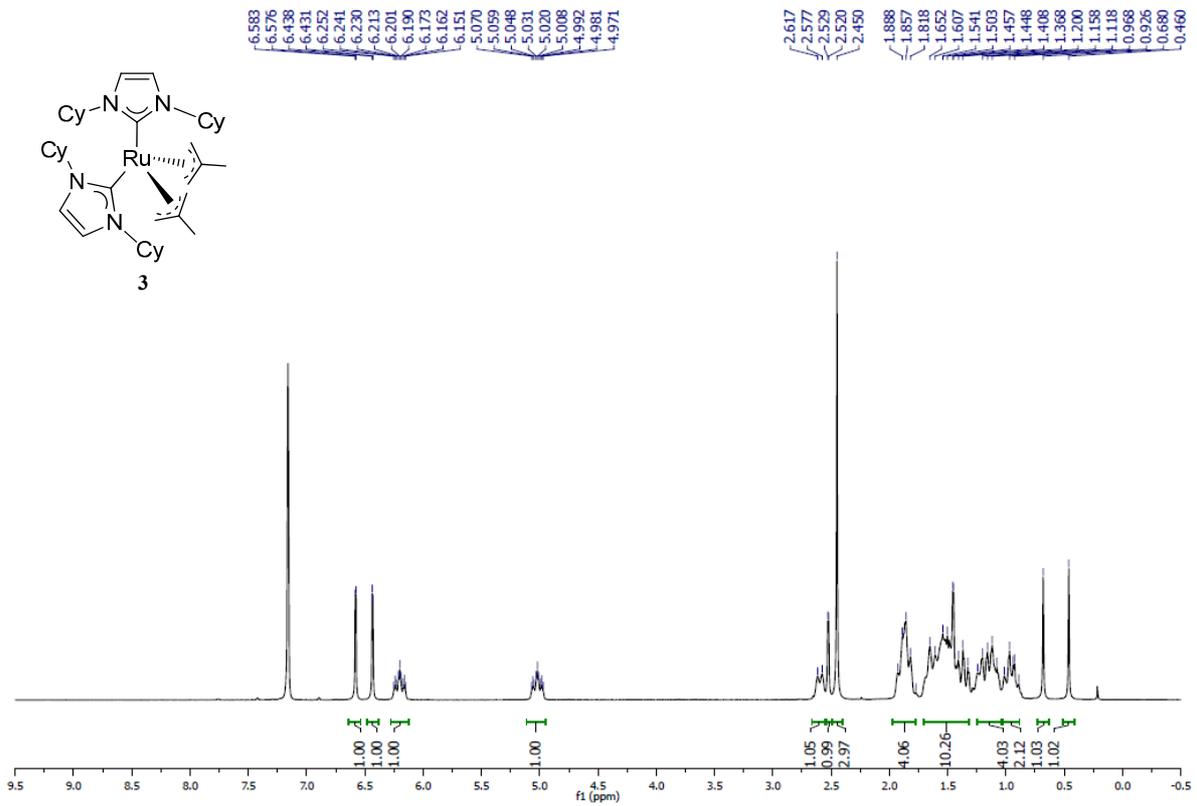






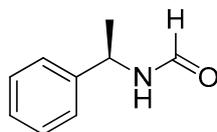




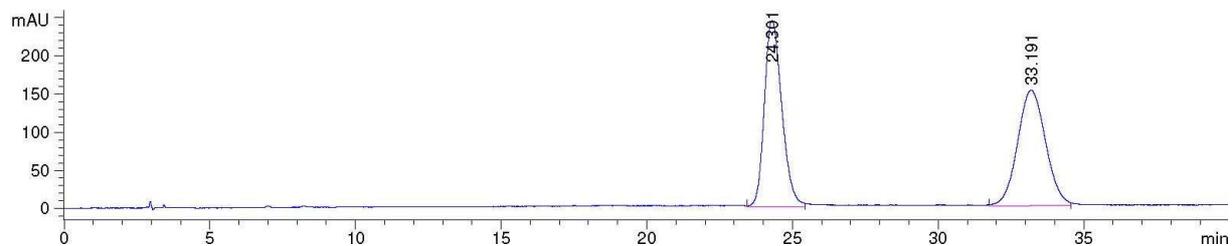
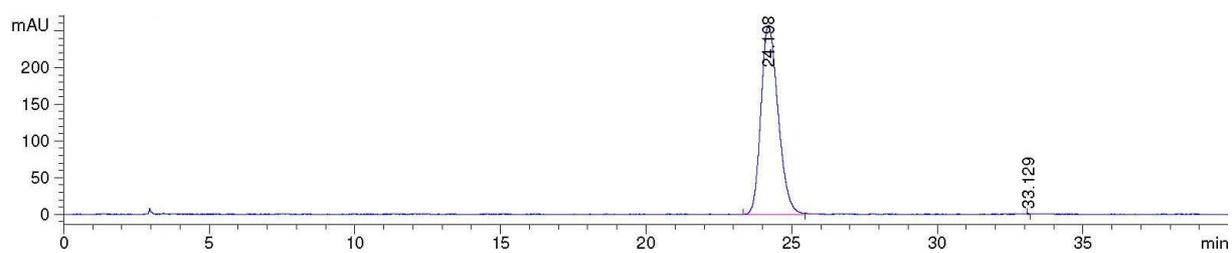


## 6. HPLC traces

### (R)-N-(1-phenylethyl)formamide



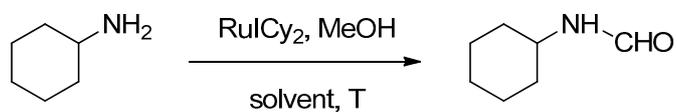
HPLC (OD-H, elute: hexane/*i*-PrOH = 95/5, detector: 210 nm, flowrate: 1 mL/min),  $t_{1(\text{major})} = 24.2$ ; min,  $t_{2(\text{minor})} = 33.2$  min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.198	VV	0.4908	1.05720e4	258.15112	99.9152
2	33.129	VV	0.0677	8.97657	1.75310	0.0848
Totals :				1.05810e4	259.90423	

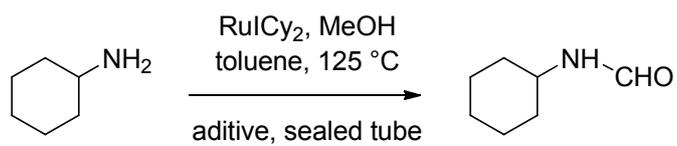
## 7. Optimization tables

Optimization conditions under reflux:



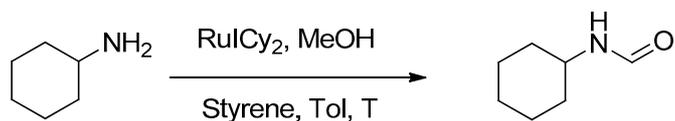
Entry	RuI(Cy) <sub>2</sub>	MeOH (eq)	Solvent	C (M)	T (°C)	Yield (%)
1	no NHC	3.3	Toluene	1M	125	-
2	2%	3.3	Toluene	1M	125	63
3	2%	2	Toluene	1M	125	traces
4	2%	0.5	Toluene	1M	125	-
5	2%	10	Toluene	1M	125	23
6	2%	10	Toluene	0.5M	125	16
7	2%	10	Toluene	0.1M	125	12
8	not pre-formed	10	Toluene	0.1M	125	11
9	2%	10	Xylene	1M	25	21
10	2% sealed tube	3.3	Toluene	1M	125	26
11	2%	3.3	Hexane	1M	125	traces
12	2% (+30%base)	3.3	Toluene	1M	125	22
13	2%	3.3	Toluene	1M	100	35
14	2%	3.3	Toluene	1M	80	9
15	2%	3.3	Toluene	1M	60	5

## Additives



Entry	Additive	Yield (%)
1	4-octyne (1eq)	60
2	norbornene (2eq)	60
3	TMS-acetylene (1eq)	3
4	styrene (2eq)	78
5	isoprene (2eq)	21

## Styrene optimization



Entry	MeOH (eq)	Styrene (eq)	T (°C)	Yield (%)
1	1	2	125	traces
2	2	2	125	12
3	3.3	2	125	78
4	10	2	125	47
5	20	2	125	traces
6	neat MeOH	2	125	2
7	3.3	2	100	22
8	3.3	2	80	8
9	3.3	3	60	4
10	3.3	3	125	96
11	10	3	125	45
12	3.3	1	125	60



## 9. References

- [1] S. Urban, N. Ortega, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 3803.
- [2] A. J. Arduengo, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523.