

## Supporting Information

### **Cobalt-catalyzed Synthesis of Unsymmetrically *N,N*-Disubstituted Formamides via Reductive Coupling of Primary Amines and Aldehydes with CO<sub>2</sub> and H<sub>2</sub>**

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# Experimental Procedures

## 1. Materials

The cobalt salts including  $\text{CoF}_2$ ,  $\text{Co}(\text{OAc})_2$ ,  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoBr}_2$ ,  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{acac})_2$  and  $\text{Co}_2(\text{CO})_8$ , other metal salts including  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Fe}(\text{OAc})_2$ , bases including  $\text{K}_2\text{CO}_3$ ,  $\text{KOH}$ ,  $\text{K}_3\text{PO}_4$ ,  $t\text{BuOK}$  and  $\text{Cs}_2\text{CO}_3$ , ligands including  $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ , triphos, dppp, BINAP, 2-Bis(diphenylphosphino)ethane, tris(pentafluorophenyl)phosphine,  $\text{PPh}_3$ , biPy, *o*-Phenanthroline and 1,3,5-triaza-7-phosphaadamantane, anhydrous solvents including ethyl alcohol ( $\text{EtOH}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), toluene, *n*-heptane, tetrahydrofuran (THF), 1,4-dioxane, acetonitrile ( $\text{CH}_3\text{CN}$ ), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) were purchased from commercial sources (J&K Scientific Ltd. and Innochem Science & Technology Co., Ltd.) and were used without further purification.  $\text{CO}_2$  (purity of > 99.99%),  $\text{H}_2$  (purity of > 99.99%) was supplied by Beijing Analytical Instrument Factory.

## 2. Instrumentation

$^1\text{H}$  NMR spectra were acquired at 400 MHz from solutions in  $\text{CDCl}_3$  on a Bruker Avance NMR spectrometer (400 MHz) at ambient temperature; chemical shifts are given in ppm relative to tetramethylsilane (TMS). GC analysis was performed on Agilent 7890B with a FID detector and a nonpolar capillary column (DB-5) (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ). The column oven was temperature-programmed with a 2 min initial hold at 323 K, followed by the temperature increase to 538 K at a rate of 10 K/min and kept at 538 K for 10 min. High purity nitrogen was used as a carrier gas. The gaseous mixture was collected and analyzed by gas chromatography equipped with thermal conductivity detector (4890, Agilent Technology) with Argon as the carrier gas. The GC-MS analysis was performed using gas chromatography-mass spectrometry (GC-MS, 7890A and 5975C, Agilent).

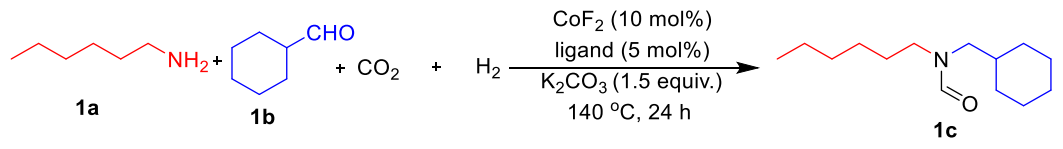
## 3. General procedure for the synthesis of **1c**

All the reductive coupling reactions were performed in a 16 mL high-pressure reactor with a Teflon inner container in batch operation mode. Typically, in a glovebox, hexylamine (101 mg), cyclohexanecarboxaldehyde (112 mg),  $\text{CoF}_2$  (10 mg),  $\text{PP}_3$  (34 mg),  $\text{Na}_2\text{CO}_3$  (160 mg) and  $\text{EtOH}$  (3 mL) were loaded into the reactor. The autoclave was screwed up, charged with  $\text{CO}_2$  to 3 MPa, then  $\text{H}_2$  to total pressure of 6 MPa and transferred to an oil bath at 140  $^\circ\text{C}$ , which was controlled by a Haake-D3 temperature controller. After the reaction, the reactor was cooled in iced water and the gas inside was carefully vented. The yield was determined by  $^1\text{H}$  NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard. For yield determination of the products shown in Scheme 2, the reaction mixture was firstly analyzed by GC-MS and  $^1\text{H}$  NMR to determine the structures and yield of the unsymmetrical NNFA products. Then, the crude reaction mixture was concentrated by a rotary evaporator and purified by column chromatography to give the isolated compound. **1c** was obtained and purified by column chromatography, with 93 % isolated yields of **1c** (109 mg), using petroleum ether/ethyl acetate (100 : 1 – 5 : 1) to get the pure product.

# Results and Discussion

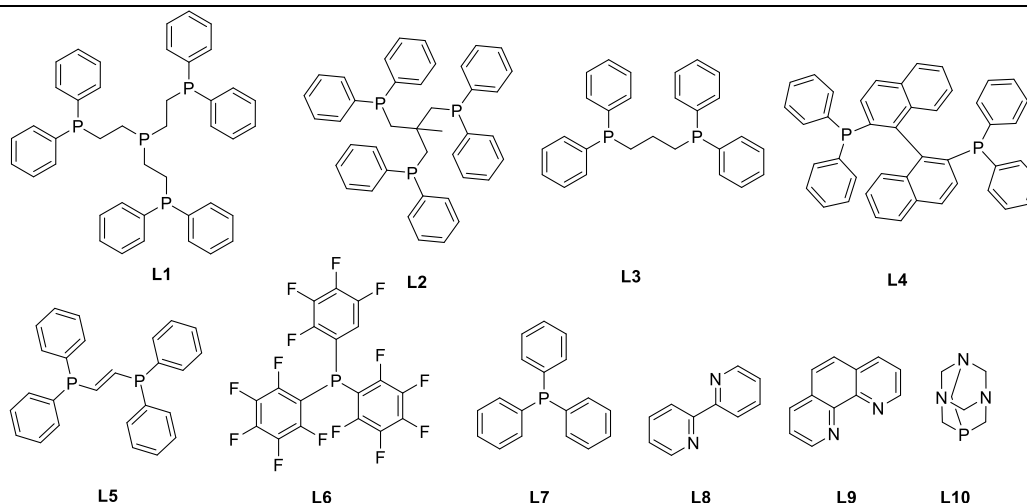
## 1.Effects of ligands

**Table S1** Effects of ligands on the reductive coupling reaction<sup>[a]</sup>.

		
Entry	Ligand	Yield/% <sup>[b]</sup>
1	L1	4
2	L2	5
3	L3	0
4	L4	5
5	L5	0
6	L6	8
7	L7	3
8	L8	1
9	L9	3
10	L10	4

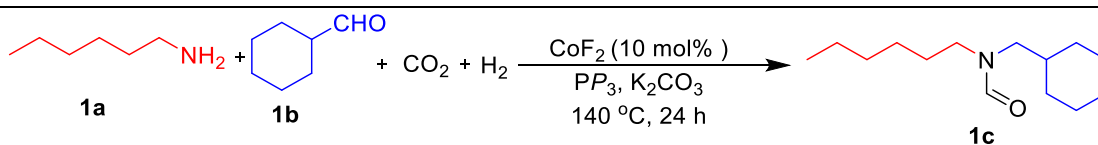
[a] Reaction conditions : **1a** (1.0 mmol), **1b** (1 mmol), CoF<sub>2</sub> (10 mol%), ligand (5 mol%), K<sub>2</sub>CO<sub>3</sub> (1.5 mmol), EtOH (3 mL), CO<sub>2</sub> (3 MPa), H<sub>2</sub> (3 MPa), 140 °C, 24 h. [b] The yield was determined by <sup>1</sup>H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.





## 2. Effects of base and ligand amounts

**Table S2** Effects of base and ligand amounts on the reductive coupling reaction<sup>[a]</sup>.



Entry	CoF <sub>2</sub> /mol%	PP <sub>3</sub> /mol%	K <sub>2</sub> CO <sub>3</sub> /equiv.	Yield/% <sup>[b]</sup>
1	10	5	2	93
2	10	5	1	71
3	10	5	0.2	63
4	10	1	2	83
5	10	1	0.5	57
6	10	1	0.2	48
7	5	5	2	74
8	1	1	2	63

[a] Reaction conditions : **1a** (1.0 mmol), **1b** (1 mmol), CoF<sub>2</sub> (0.1 mmol), PP<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, EtOH (3 mL), CO<sub>2</sub> (3 MPa), H<sub>2</sub> (3 MPa), 140 °C, 24 h. [b] The yield was determined by <sup>1</sup>H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.

# Control experiments

## 1. Typical procedures for control experiments

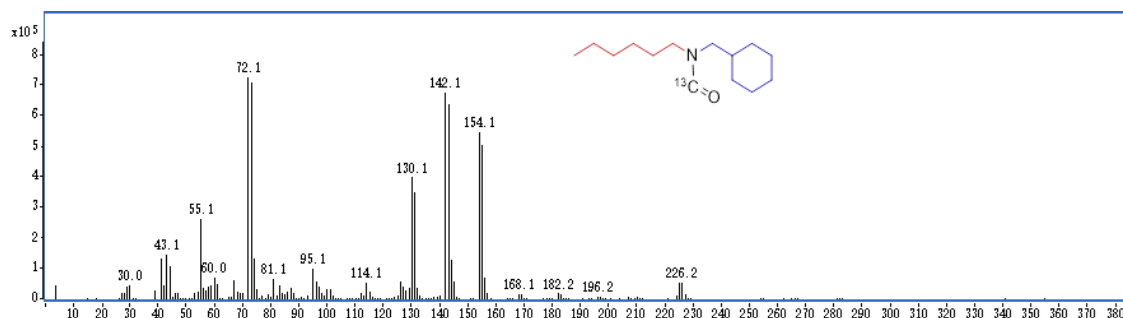
**For Scheme 2a:** CoF<sub>2</sub> (10 mg), PP<sub>3</sub> (34 mg), K<sub>2</sub>CO<sub>3</sub> (160 mg), **1a** (101 mg), **1b** (112 mg) and EtOH (3 mL) were loaded into a stainless steel autoclave with a Teflon tube (25 mL inner volume) under N<sub>2</sub> atmosphere. The autoclave was sealed, and the reactor was charged with <sup>13</sup>CO<sub>2</sub> up to 1 MPa and then with H<sub>2</sub> until the total pressure reached 4 MPa at room temperature. The autoclave was moved to an oil bath of 140 °C, and magnetically stirred for 24 h. After reaction, the autoclave was cooled down to room temperature, and the gas inside the reactor was vented slowly. The reaction product was analysed by GC and GC-MS.

**For Scheme 2b:** CoF<sub>2</sub> (10 mg), PP<sub>3</sub> (34 mg), K<sub>2</sub>CO<sub>3</sub> (160 mg) and EtOH (3 mL) were loaded into a stainless steel autoclave with a Teflon tube (25 mL inner volume) under N<sub>2</sub> atmosphere. After the autoclave was sealed, it was charged with CO<sub>2</sub> up to 3 MPa and then with H<sub>2</sub> until the total pressure reached 6 MPa at room temperature. The autoclave was moved to an oil bath of 140 °C, and magnetically stirred for 24 h. After reaction, the autoclave was cooled down to room temperature, and the gas inside the reactor was vented slowly. The reaction product was analysed by <sup>1</sup>H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.

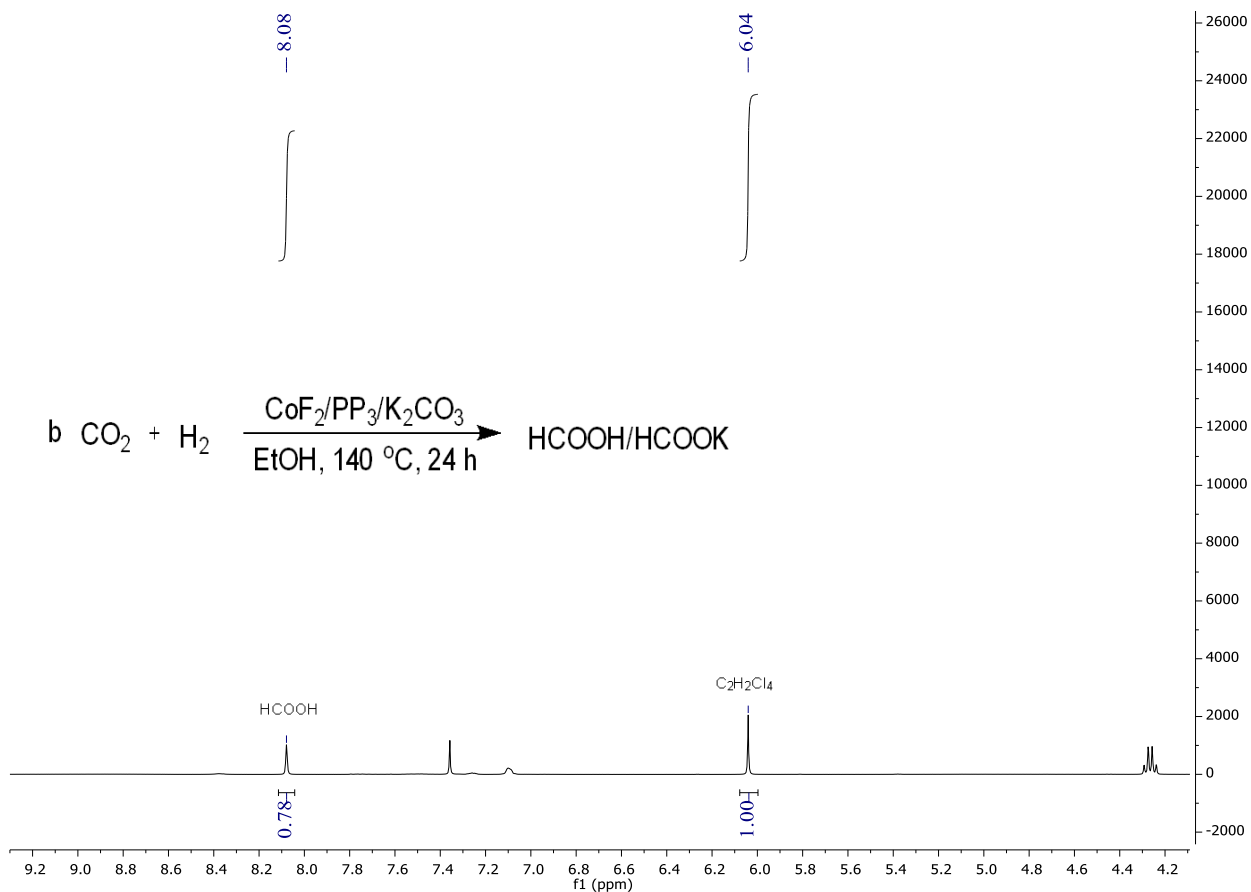
**For Scheme 2c:** CoF<sub>2</sub> (10 mg), PP<sub>3</sub> (34 mg), K<sub>2</sub>CO<sub>3</sub> (160 mg), **1a** (101 mg), **1b** (112 mg) and EtOH (3 mL) were loaded into a stainless steel autoclave with a Teflon tube (25 mL inner volume) under N<sub>2</sub> atmosphere. After the autoclave was sealed, and it was charged with H<sub>2</sub> up to 3 MPa, and then moved to an oil-bath of 140 °C. After magnetically being stirred for 24 h, the autoclave was cooled down to room temperature, and the gas inside the reactor was vented slowly. The reaction product was analysed by GC-MS.

**For Scheme 2d:** CoF<sub>2</sub> (10 mg), PP<sub>3</sub> (34 mg), K<sub>2</sub>CO<sub>3</sub> (160 mg), HCOOH (92 mg), *N*-hexyl-hexanamine (185 mg) and EtOH (3 mL) were loaded into a stainless steel autoclave with a Teflon tube (25 mL inner volume) under N<sub>2</sub> atmosphere. The autoclave was moved to an oil bath of 140 °C, and magnetically stirred for 24 h. After reaction, the autoclave was cooled down to room temperature. The reaction product was analysed by GC-MS.

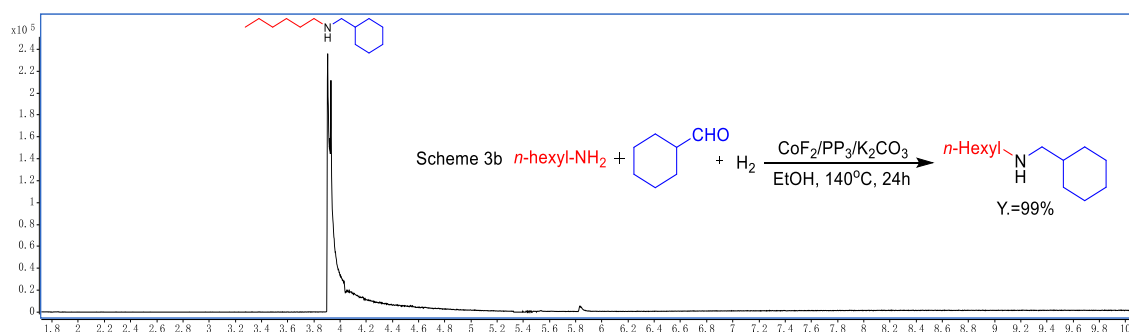
## 2. Analysis of the reaction solutions of the control experiments



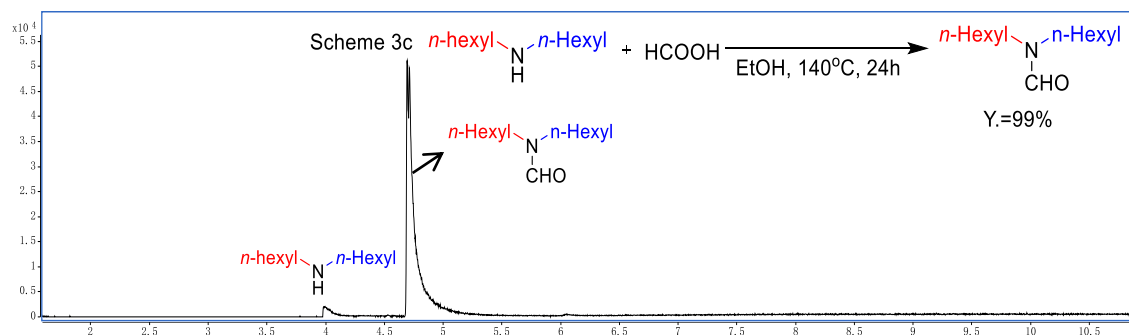
**Figure S1** MS spectrum of the reductive coupling product in the <sup>13</sup>CO<sub>2</sub> isotope labelling experiment, Scheme 2a.



**Figure S2** <sup>1</sup>H NMR spectrum of the product of Scheme 2b. The yield was determined by <sup>1</sup>H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.

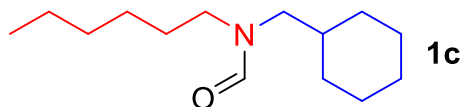


**Figure S3** GC-MS spectrum of the product of Scheme 2c.

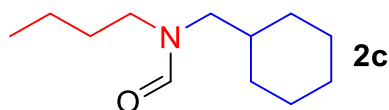


**Figure S4** GC-MS spectrum of the product of Scheme 2d.

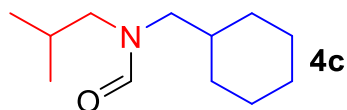
## <sup>1</sup>H and <sup>13</sup>C NMR data of the products



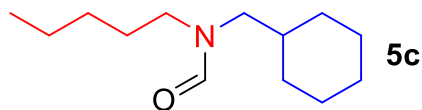
*N*-(cyclohexylmethyl)-*N*-hexylformamide; isolated yield = 93 % (209 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07, 7.97 (d, 1H), 3.29 – 3.21 (m, 1H), 3.20 – 3.09 (m, 2H), 2.98 (d, 1H), 1.80 – 1.57 (m, 6H), 1.56 – 1.43 (m, 2H), 1.33 – 1.09 (m, 9H), 0.86 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.19, 163.09, 54.09, 48.11, 48.07, 42.85, 36.10, 35.81, 31.67, 31.51, 30.96, 30.78, 28.67, 27.29, 26.77, 26.51, 26.47, 26.31, 25.94, 25.83, 22.69, 22.66, 14.12, 14.08. M (C<sub>14</sub>H<sub>27</sub>NO) = 225.2, EI-MS found 225.2 [M], 196.1 [M-CHO]. HR-MS (ESI) calculated for C<sub>14</sub>H<sub>28</sub>NO [M+H]<sup>+</sup>: 226.2166, found: 226.2164.



*N*-butyl-*N*-(cyclohexylmethyl)formamide; isolated yield = 94 % (185 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06, 7.95 (d, 1H), 3.31 – 3.20 (t, 1H), 3.17 (t, 1H), 3.11 (d, 1H), 2.98 (d, 1H), 1.65 (m, 6H), 1.48 (m, 3H), 1.27 (m, 2H), 1.23 – 1.06 (m, 3H), 1.02 – 0.85 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.14, 163.06, 77.48, 77.16, 76.84, 54.02, 48.03, 47.71, 42.50, 36.00, 35.72, 30.89, 30.70, 29.33, 26.45, 26.41, 25.88, 25.77, 20.24, 19.74, 13.87, 13.71. M (C<sub>12</sub>H<sub>23</sub>NO) = 197.2, EI-MS found 197.2 [M], 168.1 [M-CHO]. HR-MS (ESI) calculated for C<sub>12</sub>H<sub>23</sub>NO [M+H]<sup>+</sup>: 198.1853, found: 198.1852.



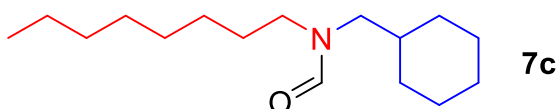
*N*-(cyclohexylmethyl)-*N*-isobutylformamide; isolated yield = 85 % (167mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04, 8.03 (d, 1H), 3.11 (t, 2H), 2.99 (m, 2H), 2.02 – 1.81 (m, 1H), 1.70 (m, 2H), 1.63 (d, 3H), 1.53 (m, 1H), 1.18 (m, 3H), 0.87 (m, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.46, 163.43, 77.48, 77.16, 76.84, 55.76, 54.31, 49.72, 48.51, 35.90, 35.65, 30.95, 30.77, 26.63, 26.49, 26.44, 26.30, 25.91, 25.81, 20.19, 19.92. M (C<sub>12</sub>H<sub>23</sub>NO) = 197.2, EI-MS found 197.2 [M], 168.1 [M-CHO]. HR-MS (ESI) calculated for C<sub>12</sub>H<sub>23</sub>NO [M+H]<sup>+</sup>: 198.1853, found: 198.1852.



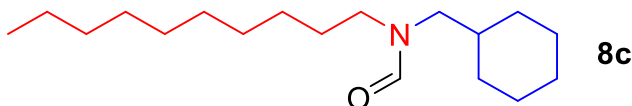
*N*-(cyclohexylmethyl)-*N*-pentylformamide; isolated yield = 99 % (209 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04, 8.00 (d, 1H), 3.25 (t, 1H), 3.20 – 3.09 (m, 2H), 2.98 (d, 1H), 1.68 (m, 6H), 1.50 (m, 3H), 1.38 – 1.07 (m, 7H), 1.01 – 0.74 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.17, 163.08, 54.07, 48.10, 48.03, 42.79, 36.08, 35.79, 30.94, 30.76, 29.21, 28.75, 28.35, 26.96, 26.49, 26.45, 25.92, 25.81, 22.51, 22.38, 14.08, 14.03. M (C<sub>13</sub>H<sub>25</sub>NO) = 211.2, EI-MS found 211.2 [M], 182.1 [M-CHO]. HR-MS (ESI) calculated for C<sub>13</sub>H<sub>26</sub>NO [M+H]<sup>+</sup>: 212.2009, found: 212.2008.



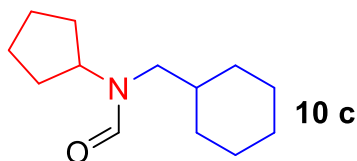
*N*-(cyclohexylmethyl)-*N*-heptylformamide; isolated yield = 87 % (208 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07, 1.79 (d, 1H), 3.32 – 3.21 (m, 1H), 3.21 – 3.09 (m, 2H), 2.99 (d, 1H), 1.79 – 1.68 (m, 2H), 1.68 – 1.58 (m, 3H), 1.51 (m, 3H), 1.35 – 1.19 (m, 10H), 1.19 – 1.08 (m, 2H), 1.01 – 0.90 (m, 1H), 0.90 – 0.77 (m, 5H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.21, 163.11, 54.11, 48.12, 48.08, 42.86, 36.07, 35.79, 31.89, 31.83, 31.71, 30.95, 30.77, 29.15, 29.00, 28.69, 27.32, 27.07, 26.60, 26.51, 26.47, 25.94, 25.83, 22.70, 22.67, 14.24, 14.18, 14.16, 0.11.  $M$  ( $\text{C}_{15}\text{H}_{29}\text{NO}$ ) = 239.2, EI-MS found 239.2 [M], 210.1 [M-CHO]. HR-MS (ESI) calculated for  $\text{C}_{15}\text{H}_{30}\text{NO}$  [M+H] $^+$ : 240.2322, found: 240.2321.



*N*-(cyclohexylmethyl)-*N*-octylformamide; isolated yield = 79 % (200 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07, 7.96 (d, 1H), 3.70 (m, 1H), 3.29 – 3.20 (m, 2H), 3.16 (t, 1H), 1.72 (m, 1H), 1.67 – 1.59 (m, 5H), 1.50 (m, 3H), 1.34 – 1.21 (m, 15H), 1.00 – 0.75 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.20, 163.09, 58.46, 54.09, 48.09, 48.06, 42.84, 36.05, 35.77, 31.89, 31.85, 31.69, 30.93, 30.75, 29.42, 29.32, 29.27, 29.16, 28.67, 27.30, 27.09, 26.62, 26.49, 26.45, 25.92, 25.81, 22.76, 22.73, 22.72, 18.52, 14.30, 14.21, 14.18, 14.16, 0.09.  $M$  ( $\text{C}_{16}\text{H}_{31}\text{NO}$ ) = 253.2, EI-MS found 253.2 [M], 224.2 [M-CHO]. HR-MS (ESI) calculated for  $\text{C}_{16}\text{H}_{32}\text{NO}$  [M+H] $^+$ : 254.2479, found: 254.2477.

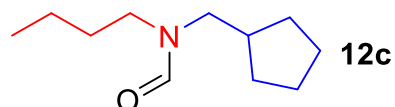


*N*-(cyclohexylmethyl)-*N*-decylformamide; isolated yield = 80 % (225 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09, 7.97 (d, 1H), 3.25 (m, 1H), 3.22 – 3.11 (m, 2H), 2.99 (d, 1H), 1.78 – 1.68 (m, 2H), 1.68 – 1.59 (m, 3H), 1.51 (m, 3H), 1.26 (m, 16H), 1.19 – 1.10 (m, 2H), 1.00 – 0.90 (m, 1H), 0.87 (t, 3H), 0.81 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.25, 163.14, 76.84, 54.17, 48.18, 48.15, 42.92, 36.07, 35.79, 32.01, 31.99, 30.95, 30.77, 29.68, 29.66, 29.63, 29.48, 29.42, 29.40, 29.33, 28.68, 27.32, 27.11, 26.64, 26.50, 26.47, 25.94, 25.83, 22.80, 14.23, 0.12. HR-MS (ESI) calculated for  $\text{C}_{18}\text{H}_{36}\text{NO}$  [M+H] $^+$ : 282.2792, found: 282.2790.

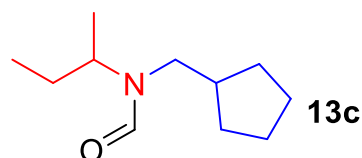


*N*-(cyclohexylmethyl)-*N*-cyclopentylformamide; isolated yield = 84 % (176 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04, 8.0 (d, 1H), 3.31 – 3.21 (m, 2H), 3.18 (t,  $J$  = 7.2 Hz, 1H), 3.06 (d,  $J$  = 7.6 Hz, 1H), 2.13 (m, 1H), 1.75 – 1.56 (m, 4H), 1.50 (m, 4H), 1.38 – 1.26 (m, 2H), 1.26 – 1.14 (m, 3H), 1.10 (m, 1H), 0.86 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.06, 162.72, 52.60, 47.52, 46.35, 42.51, 38.48, 37.90, 30.50, 30.28, 29.17, 28.70, 28.29, 27.00, 25.08, 25.00, 22.47, 22.34,

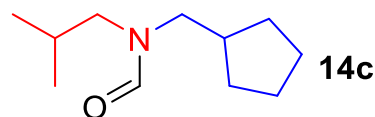
14.04, 13.99. M ( $C_{13}H_{23}NO$ ) = 209.1, EI-MS found 209.1 [M], 180.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{13}H_{24}NO$  [M+H]<sup>+</sup>: 210.1853, found: 210.1853.



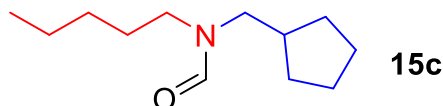
*N*-butyl-*N*-(cyclopentylmethyl)formamide; isolated yield = 73 % (134 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07, 8.04 (d, 1H), 3.34 – 3.28 (t, 1H), 3.27 (d, 1H), 3.22 (t, 1H), 3.10 (d, 1H), 2.17 (m, 1H), 1.78 – 1.57 (m, 5H), 1.57 – 1.47 (m, 3H), 1.31 (dt, 3H), 1.18 (m, 2H), 0.93 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.11, 162.77, 77.48, 77.16, 76.84, 52.64, 47.27, 46.36, 42.31, 38.46, 37.90, 30.69, 30.52, 30.30, 29.44, 25.11, 25.03, 20.27, 19.75, 13.90, 13.74. M ( $C_{11}H_{21}NO$ ) = 183.2, EI-MS found 183.1 [M], 154.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{11}H_{21}NO$  [M+H]<sup>+</sup>: 184.1697, found: 184.1696.



*N*-sec-butyl-*N*-(cyclopentylmethyl)formamide; isolated yield = 80 % (147 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17, 8.08 (d, 1H), 4.17 – 3.85 (m, 1H), 3.24 – 3.11 (m, 1H), 3.10 – 2.96 (m, 1H), 2.15 (m, 1H), 1.87 – 1.36 (m, 10H), 1.37 – 1.16 (m, 6H), 0.94 – 0.71 (m, 5H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.43, 162.97, 77.48, 77.16, 76.84, 56.48, 51.53, 50.96, 46.75, 40.40, 39.57, 31.71, 30.94, 30.90, 30.63, 29.19, 29.08, 27.18, 25.13, 25.06, 25.03, 22.78, 20.91, 18.39, 14.24, 11.47, 11.25. M ( $C_{11}H_{21}NO$ ) = 183.2, EI-MS found 183.1 [M], 154.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{11}H_{21}NO$  [M+H]<sup>+</sup>: 184.1697, found: 184.1696.



*N*-(cyclopentylmethyl)-*N*-isobutylformamide; isolated yield = 85 % (165mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09, 8.02 (d, 1H), 3.24 (d, 1H), 3.13 (d, 1H), 3.09 (d, 1H), 2.98 (d, 1H), 2.15 (m, 1H), 1.92 (m, 1H), 1.78 – 1.43 (m, 6H), 1.26 – 1.04 (m, 2H), 0.87 (t, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.40, 163.18, 77.48, 77.16, 76.84, 55.32, 52.87, 49.46, 46.80, 38.39, 37.83, 30.55, 30.34, 26.56, 26.31, 25.12, 25.02, 20.16, 19.89. M ( $C_{11}H_{21}NO$ ) = 183.2, EI-MS found 183.2 [M], 154.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{11}H_{21}NO$  [M+H]<sup>+</sup>: 184.1697, found: 184.1696.

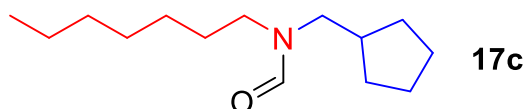


*N*-(cyclopentylmethyl)-*N*-pentylformamide<sup>[1]</sup>; isolated yield = 84 % (165 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24, 7.99 (d, 1H), 3.67 (m, 1H), 3.09 (d, 1H), 2.96 (d, 1H), 1.97 – 1.79 (m, 2H), 1.79 – 1.51 (m, 12H), 1.46 (m, 1H), 1.37 – 1.03 (m, 3H), 1.01 – 0.72 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.71, 162.74, 60.43, 55.87, 53.27, 48.87,

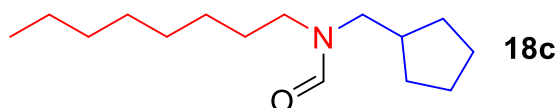
38.04, 36.86, 31.62, 31.15, 30.86, 29.01, 26.54, 26.48, 26.07, 25.91, 23.80, 23.44, 13.82. M ( $C_{12}H_{23}NO$ ) = 197.2, EI-MS found 197.1 [M], 168.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{12}H_{24}NO$  [M+H]<sup>+</sup>: 198.1853, found: 198.1852.



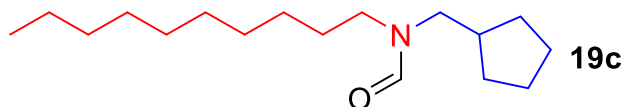
*N*-(cyclopentylmethyl)-*N*-hexylformamide<sup>[1]</sup>; isolated yield = 91 % (192 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06, 8.02 (s, 1H), 3.34 – 3.22 (m, 2H), 3.19 (t, 1H), 3.07 (d, 1H), 2.15 (m, 1H), 1.77 – 1.41 (m, 8H), 1.35 – 1.16 (m, 7H), 1.11 (m, 1H), 0.86 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.14, 162.79, 52.66, 47.60, 46.41, 42.61, 38.52, 37.94, 31.64, 31.49, 30.54, 30.32, 28.62, 27.34, 26.74, 26.27, 25.12, 25.04, 22.66, 22.63, 14.09, 14.06. M ( $C_{13}H_{25}NO$ ) = 211.2, EI-MS found 211.1 [M], 182.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{13}H_{26}NO$  [M+H]<sup>+</sup>: 212.2009, found: 212.2007.



*N*-(cyclopentylmethyl)-*N*-heptylformamide; isolated yield = 81 % (182 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05, 8.02 (s, 1H), 3.31 – 3.22 (m, 2H), 3.19 (t, *J* = 7.2 Hz, 1H), 3.08 (d, 1H), 2.14 (m, 1H), 1.77 – 1.44 (m, 8H), 1.36 – 1.17 (m, 11H), 1.11 (m, 1H), 0.86 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.12, 162.77, 52.67, 47.60, 46.41, 42.61, 38.52, 37.94, 31.89, 31.85, 30.55, 30.33, 29.43, 29.33, 29.28, 28.66, 27.39, 27.10, 26.62, 25.13, 25.05, 22.73, 22.72, 14.18, 14.16. M ( $C_{14}H_{27}NO$ ) = 225.2, EI-MS found 225.1 [M], 196.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{14}H_{28}NO$  [M+H]<sup>+</sup>: 226.2166, found: 226.2166.



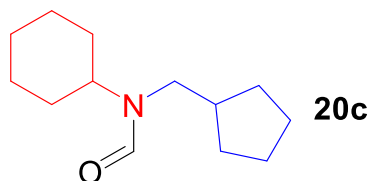
*N*-(cyclopentylmethyl)-*N*-octylformamide; isolated yield = 84 % (201 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06, 8.02 (s, 1H), 3.43 – 3.23 (m, 2H), 3.19 (t, 1H), 3.08 (d, 1H), 2.14 (m, 1H), 1.78 – 1.41 (m, 8H), 1.39 – 1.17 (m, 9H), 1.11 (m, 1H), 0.86 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.13, 162.78, 52.67, 47.60, 46.41, 42.62, 38.52, 37.95, 31.88, 31.82, 30.56, 30.34, 29.14, 28.99, 28.67, 27.40, 27.21, 27.06, 26.58, 25.14, 25.06, 22.69, 22.66, 14.16, 14.14. M ( $C_{15}H_{29}NO$ ) = 239.2, EI-MS found 239.1 [M], 210.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{15}H_{30}NO$  [M+H]<sup>+</sup>: 240.2322, found: 240.2320.



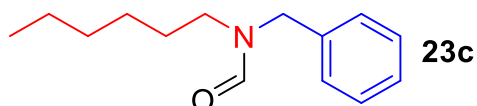
*N*-(cyclopentylmethyl)-*N*-decylformamide; isolated yield = 77 % (206 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06, 8.02 (d, 1H), 3.34 – 3.22 (m, 2H), 3.19 (t, 1H), 3.08 (d, 1H), 2.14 (m, 1H), 1.79 – 1.55 (m, 5H), 1.51 (m, 3H), 1.25 (m, 16H), 1.11 (m, 1H), 0.86 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.12, 162.77, 52.67, 47.60, 46.41, 42.62, 38.52, 37.95, 31.99, 31.97, 30.55, 30.33, 29.67, 29.64, 29.62, 29.60, 29.47, 29.40, 29.38, 29.32, 28.66, 27.39, 27.10, 26.62,



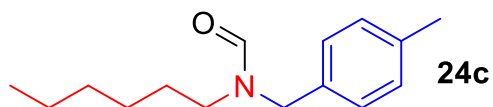
25.13, 25.05, 22.78, 14.20, 11.06. M ( $C_{17}H_{33}NO$ ) = 267.3, EI-MS found 267.3 [M], 238.2 [M-CHO]. HR-MS (ESI) calculated for  $C_{17}H_{34}NO$  [M+H]<sup>+</sup>: 268.2635, found: 268.2633.



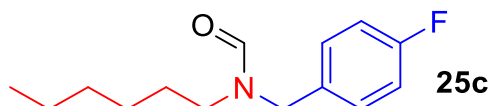
*N*-cyclohexyl-*N*-(cyclopentylmethyl)formamide; isolated yield = 71 % (149.1 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 1:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21, 8.03 (d, 1H), 3.22 (d, 1H), 3.06 (d, 1H), 2.23 – 2.06 (m, 1H), 1.85 (d, 3H), 1.79 – 1.41 (m, 11H), 1.38 – 1.18 (m, 4H), 1.12 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.18, 162.66, 77.48, 77.16, 76.84, 58.87, 53.50, 50.82, 47.19, 40.77, 39.64, 33.51, 30.74, 30.67, 30.50, 26.26, 26.07, 25.66, 25.46, 25.12, 25.00. M ( $C_{13}H_{23}NO$ ) = 209.2, EI-MS found 209.2 [M], 180.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{13}H_{23}NO$  [M+H]<sup>+</sup>: 210.1854, found: 210.1852.



*N*-benzyl-*N*-hexylformamide<sup>[1]</sup>; isolated yield = 77 % (169 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28, 8.18 (t, 1H), 7.22 (m, 2H), 7.09 – 6.99 (m, 2H), 4.44 (d, 2H), 3.17 (m, 2H), 1.50 (m, 2H), 1.26 (m, 6H), 0.96 – 0.81 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.89, 163.62, 163.04, 162.86, 161.43, 161.17, 132.64, 132.60, 132.17, 132.13, 130.04, 129.96, 129.33, 129.25, 128.93, 116.05, 115.83, 115.74, 115.52, 50.74, 47.01, 44.78, 42.09, 31.56, 31.42, 26.97, 26.63, 26.21, 22.61, 22.59, 14.14, 14.07, 14.04, 1.13, 0.10. M ( $C_{14}H_{21}NO$ ) = 219.2, EI-MS found 219.2 [M], 190.1 [M-CHO].

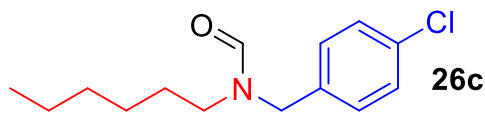


*N*-hexyl-*N*-(4-methylbenzyl)formamide; isolated yield = 80 % (186 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25, 8.16 (d, 1H), 7.19 (m, 2H), 7.09 – 6.92 (m, 2H), 4.48 (s, 1H), 4.34 (s, 1H), 3.23 – 3.02 (m, 2H), 1.55 – 1.37 (m, 2H), 1.34 – 1.11 (m, 6H), 0.86 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.83, 163.56, 162.97, 162.79, 161.38, 161.12, 132.58, 132.55, 132.10, 132.07, 130.00, 129.92, 129.30, 129.21, 128.83, 128.75, 116.01, 115.80, 115.71, 115.50, 115.27, 64.57, 50.67, 46.95, 44.68, 42.01, 31.53, 31.39, 28.22, 26.91, 26.59, 26.17, 22.60, 22.58, 14.07, 14.04. M ( $C_{15}H_{23}NO$ ) = 233.2, EI-MS found 233.2 [M], 202.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{15}H_{24}NO$  [M+H]<sup>+</sup>: 234.1853, found: 234.1851.

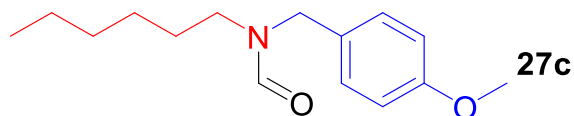


*N*-(4-fluorobenzyl)-*N*-hexylformamide<sup>[1]</sup>; isolated yield = 73 % (173 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27, 8.17 (d, 1H), 7.21 – 7.03 (m, 4H), 4.48 (s, 1H), 4.33 (s, 1H), 3.24 – 3.14 (m, 1H), 3.10 (t, 1H), 2.33 (d, 3H), 1.49 (d, 2H), 1.24 (s, 6H), 0.86 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.91, 162.86, 137.90, 137.32, 133.62, 133.27,

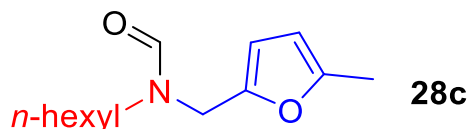
129.60, 129.40, 128.31, 127.55, 51.08, 46.75, 44.92, 41.94, 31.56, 31.42, 28.14, 26.91, 26.62, 26.19, 22.62, 22.60, 21.19, 14.09, 14.06. M ( $C_{14}H_{20}FNO$ ) = 237.2, EI-MS found 237.2 [M], 206.1 [M-CHO].



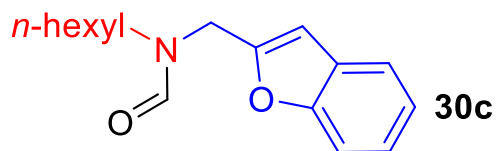
*N*-(4-chlorobenzyl)-*N*-hexylformamide<sup>[1]</sup>; isolated yield = 72 % (182 mg). This compound was obtained and purified by column chromatography using petroleum (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give brown oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.18 (d, 1H), 7.33 – 7.25 (m, 2H), 7.17 (m, 2H), 4.42 (d, 2H), 3.16 (m, 2H), 1.54 – 1.40 (m, 2H), 1.25 (d, 6H), 0.91 – 0.83 (m, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  163.04, 162.88, 135.36, 134.96, 134.14, 133.58, 129.68, 129.21, 128.95, 128.93, 50.76, 47.09, 44.89, 42.18, 31.56, 31.42, 28.30, 26.97, 26.63, 26.21, 22.63, 22.61, 14.08, 14.05, 0.12. M ( $C_{14}H_{20}ClNO$ ) = 253.1, EI-MS found 253.1 [M], 224.1 [M-CHO].



*N*-hexyl-*N*-(4-methoxybenzyl)formamide; isolated yield = 60 % (149 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.24, 8.18 (d, 1H), 7.17 (d, 1H), 7.11 (d, 1H), 6.85 (m, 2H), 4.45 (s, 1H), 4.30 (s, 1H), 3.78 (d, 3H), 3.23 – 3.13 (t, 1H), 3.08 (t, 1H), 1.54 – 1.36 (m, 2H), 1.23 (s, 6H), 0.85 (t, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.87, 162.74, 159.54, 159.17, 129.64, 128.88, 128.78, 128.66, 128.22, 114.31, 114.10, 113.99, 77.48, 77.16, 76.84, 55.39, 55.34, 50.83, 46.71, 44.64, 41.86, 31.53, 31.39, 28.15, 26.89, 26.60, 26.17, 22.59, 22.57, 14.06, 14.03. M ( $C_{15}H_{23}NO_2$ ) = 249.2, EI-MS found 249.2 [M], 218.1 [M-CHO]. HR-MS (ESI) calculated for  $C_{15}H_{23}NO_2$  [M+H]<sup>+</sup>: 250.1803, found: 250.1806.

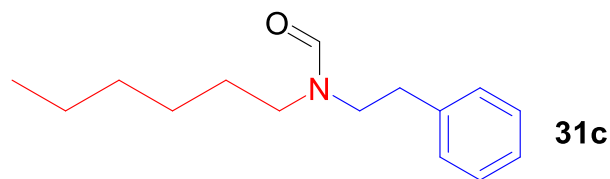


*N*-hexyl-*N*-((5-methylfuran-2-yl)methyl)formamide; isolated yield = 75 % (164 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.20, 8.09 (d, 1H), 6.13 (t, 1H), 5.97 – 5.84 (m, 1H), 4.45 (s, 1H), 4.27 (s, 1H), 3.26 (d, 1H), 3.19 (t, 1H), 2.26 (s, 3H), 1.61 – 1.39 (m, 2H), 1.26 (d, 6H), 0.88 (t, 3H).  $^{13}C$  NMR (101 MHz, DMSO)  $\delta$  162.81, 162.67, 152.85, 152.15, 148.24, 147.79, 109.73, 109.65, 106.37, 77.48, 77.16, 76.84, 47.16, 44.61, 42.31, 38.33, 31.59, 31.45, 28.24, 27.02, 26.58, 26.18, 22.64, 14.12, 14.09, 13.68, 13.63. HR-MS (ESI) calculated for  $C_{13}H_{23}NO_2$  [M+H]<sup>+</sup>: 224.1647, found: 224.1645.

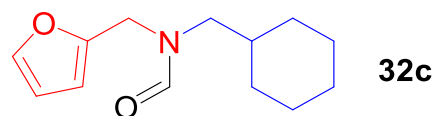


*N*-(benzofuran-2-ylmethyl)-*N*-hexylformamide; isolated yield = 90 % (233 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.30, 8.16 (d, 1H), 7.51 (s, 1H), 7.44 (d, 1H), 7.32 – 7.16 (m, 2H), 6.64 (d, 1H), 4.66 (s, 1H), 4.48 (s, 1H), 3.37 – 3.30 (m, 2H), 3.27 (t, 1H), 1.66 – 1.45 (m, 1H), 1.26 (s, 7H), 0.86 (t, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.96, 162.85, 155.29, 155.07, 152.94, 152.59, 128.29, 128.01, 124.78, 124.38, 123.87, 122.97, 122.72, 121.14, 121.05, 120.81, 111.41,

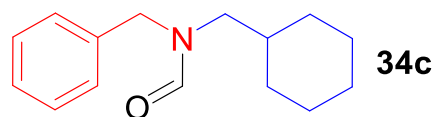
111.33, 111.19, 105.57, 105.48, 103.92, 77.48, 77.16, 76.84, 49.32, 47.49, 46.74, 45.00, 42.63, 38.93, 31.86, 31.56, 31.43, 29.99, 28.32, 27.11, 22.62, 14.07. HR-MS (ESI) calculated for  $C_{16}H_{21}NO_2$   $[M+H]^+$ : 260.1647, found: 260.1645.



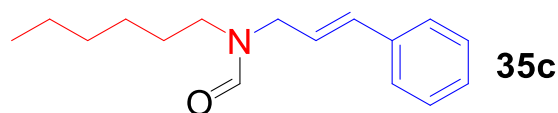
*N*-hexyl-*N*-phenethylformamide; isolated yield = 53 % (123.6 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04, 7.83 (d, 1H), 7.40 – 7.02 (m, 5H), 3.57 – 3.47 (t, 1H), 3.44 (t, 1H), 3.36 – 3.28 (t, 1H), 3.09 (t, 1H), 2.84 (m, 2H), 1.52 – 1.43 (t, 1H), 1.28 (m, 7H), 0.93 – 0.81 (m, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  92.83, 92.78, 68.97, 67.99, 58.88, 58.87, 58.83, 58.64, 58.41, 57.07, 56.92, 56.56, 7.48, 7.16, 6.84, -20.88, -21.90, -25.68, -27.55, -34.35, -36.13, -38.35, -38.54, -41.23, -42.53, -43.27, -43.78, -47.32, -47.38, -55.88, -55.93.  $M$  ( $C_{15}H_{23}NO$ ) = 233.2, EI-MS found 233.2  $[M]$ , 204.1  $[M-CHO]$ . HR-MS (ESI) calculated for  $C_{15}H_{23}NO$   $[M+H]^+$ : 234.1854, found: 234.1852.



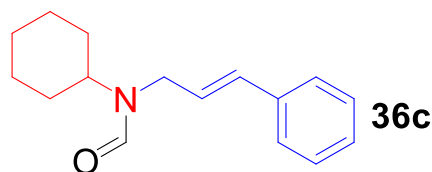
*N*-(cyclohexylmethyl)-*N*-(furan-2-ylmethyl)formamide; isolated yield = 80 % (176.8 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1H$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.24, 8.02 (d, 1H), 7.34 (d, 1H), 6.29 (m, 1H), 6.24 (m, 1H), 4.48 (s, 1H), 4.31 (s, 1H), 3.73 (s, 1H), 3.10 (d, 1H), 2.98 (d, 1H), 2.42 (d, 1H), 1.69 (m, 4H), 1.60 (m, 3H), 1.16 (m, 4H), 1.00 – 0.67 (m, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  163.18, 162.93, 154.26, 150.26, 149.85, 142.94, 142.30, 141.72, 110.53, 110.12, 108.82, 108.73, 106.75, 77.48, 77.16, 76.84, 56.01, 53.75, 48.39, 46.54, 45.05, 38.83, 38.00, 35.70, 35.65, 31.48, 30.78, 30.63, 26.73, 26.41, 26.39, 26.11, 25.86, 25.75.  $M$  ( $C_{13}H_{19}NO_2$ ) = 221.2, EI-MS found 221.2  $[M]$ , 192.2  $[M-CHO]$ . HR-MS (ESI) calculated for  $C_{13}H_{20}NO_2$   $[M+H]^+$ : 222.1489, found: 222.1489.



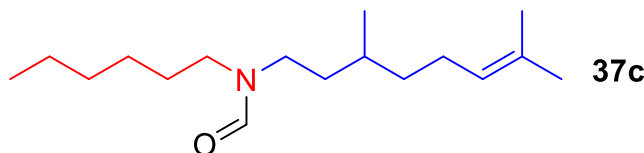
*N*-benzyl-*N*-(cyclohexylmethyl)formamide; isolated yield = 50 % (116.1 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.23 (d,  $J$  = 76.9 Hz, 1H), 7.43 – 7.11 (m, 3H), 4.52 (s, 1H), 4.39 (s, 0H), 3.07 (d,  $J$  = 7.1 Hz, 0H), 2.93 (d,  $J$  = 7.2 Hz, 1H), 1.80 – 1.66 (m, 2H), 1.66 – 1.57 (m, 2H), 1.30 – 1.07 (m, 1H), 0.88 (dq,  $J$  = 46.5, 12.0 Hz, 1H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  163.31, 163.22, 136.68, 136.37, 128.95, 128.72, 128.43, 128.32, 128.18, 128.11, 127.63, 127.54, 126.91, 77.48, 77.16, 76.84, 56.28, 54.23, 53.29, 51.97, 48.02, 45.81, 38.09, 35.60, 31.57, 30.90, 30.71, 26.80, 26.44, 26.41, 26.18, 25.89, 25.78.  $M$  ( $C_{15}H_{21}NO$ ) = 231.2, EI-MS found 231.2  $[M]$ , 202.1  $[M-CHO]$ . HR-MS (ESI) calculated for  $C_{15}H_{21}NO$   $[M+H]^+$ : 232.1697, found: 232.1696.



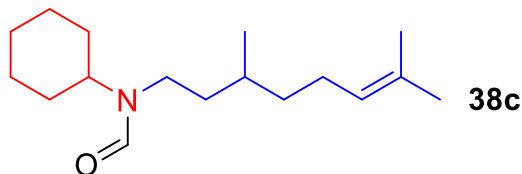
*N*-cinnamyl-*N*-hexylformamide; isolated yield = 70 % (172.4 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.15, 8.12 (d, 1H), 7.39 – 7.14 (m, 5H), 6.53 (m, 1H), 6.10 (m, 1H), 4.10 (d, 1H), 3.98 (d, 1H), 3.38 – 3.27 (m, 1H), 3.23 (m, 1H), 1.86 (m, 1H), 1.55 (m, 3H), 1.28 (s, 8H), 0.87 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.78, 162.66, 136.52, 136.11, 133.46, 133.31, 128.80, 128.70, 128.20, 127.90, 126.50, 124.75, 124.11, 77.48, 77.16, 76.84, 49.72, 47.15, 44.14, 42.32, 31.60, 31.44, 28.52, 27.24, 26.66, 26.20, 22.63, 14.06. M (C<sub>16</sub>H<sub>23</sub>NO) = 245.2, EI-MS found 245.2 [M], 216.2 [M-CHO]. HR-MS (ESI) calculated for C<sub>16</sub>H<sub>23</sub>NO [M+H]<sup>+</sup>: 246.1854, found: 246.1852.



*N*-cinnamyl-*N*-cyclohexylformamide; isolated yield = 75 % (182.4 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17, 8.07 (d, 1H), 7.33 – 7.07 (m, 5H), 6.45 (m, 1H), 6.07 (m, 1H), 4.00 (d, 1H), 3.90 (d, 1H), 3.25 – 3.13 (m, 1H), 1.83 – 1.71 (m, 4H), 1.60 (d, 1H), 1.51 – 1.39 (m, 1H), 1.34 – 1.15 (m, 3H), 1.12 – 0.94 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.25, 162.33, 136.78, 132.29, 132.19, 128.79, 128.64, 127.71, 126.48, 77.48, 77.16, 76.84, 58.50, 52.54, 46.87, 43.51, 33.09, 30.82, 25.99, 25.90, 25.34. M (C<sub>16</sub>H<sub>21</sub>NO) = 243.2, EI-MS found 243.2 [M], 214.1 [M-CHO]. HR-MS (ESI) calculated for C<sub>16</sub>H<sub>22</sub>NO [M+H]<sup>+</sup>: 244.1696, found: 244.1695.

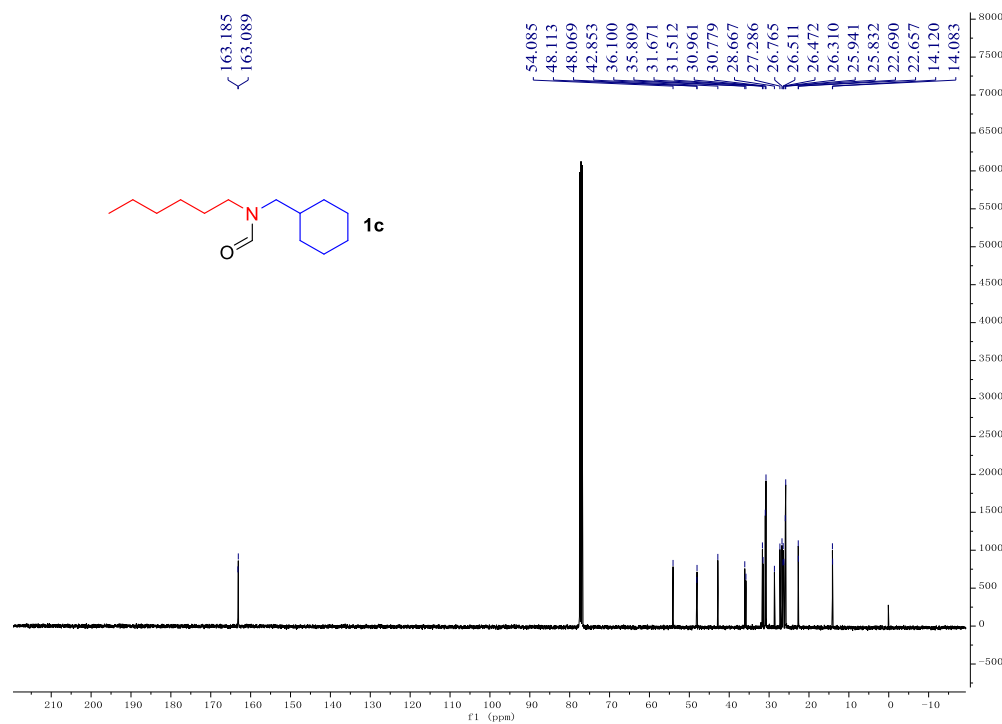
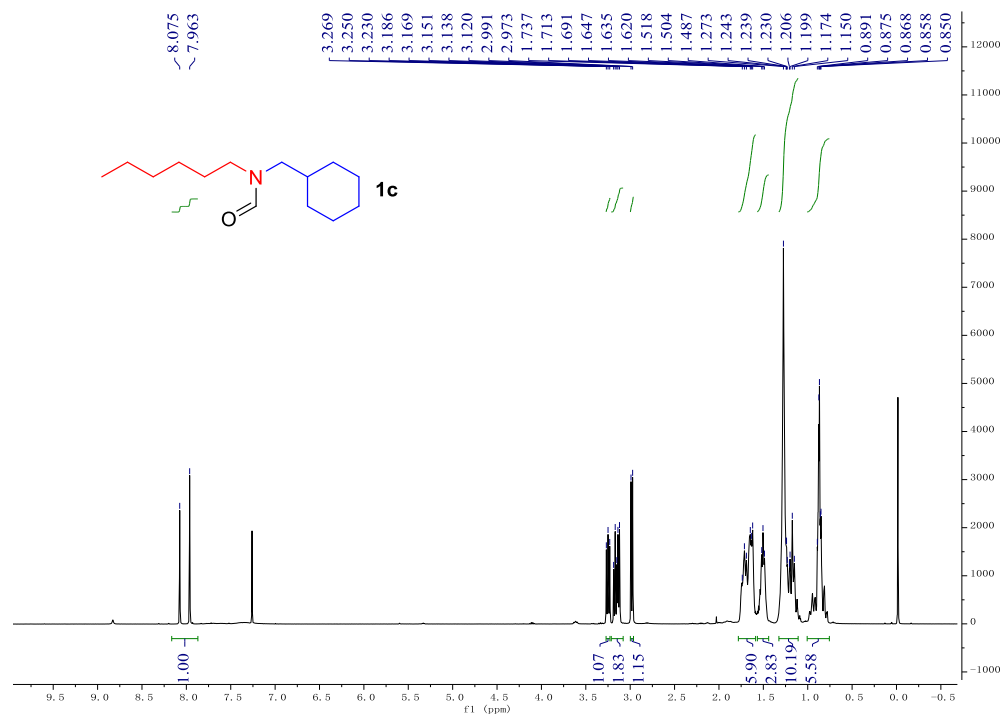


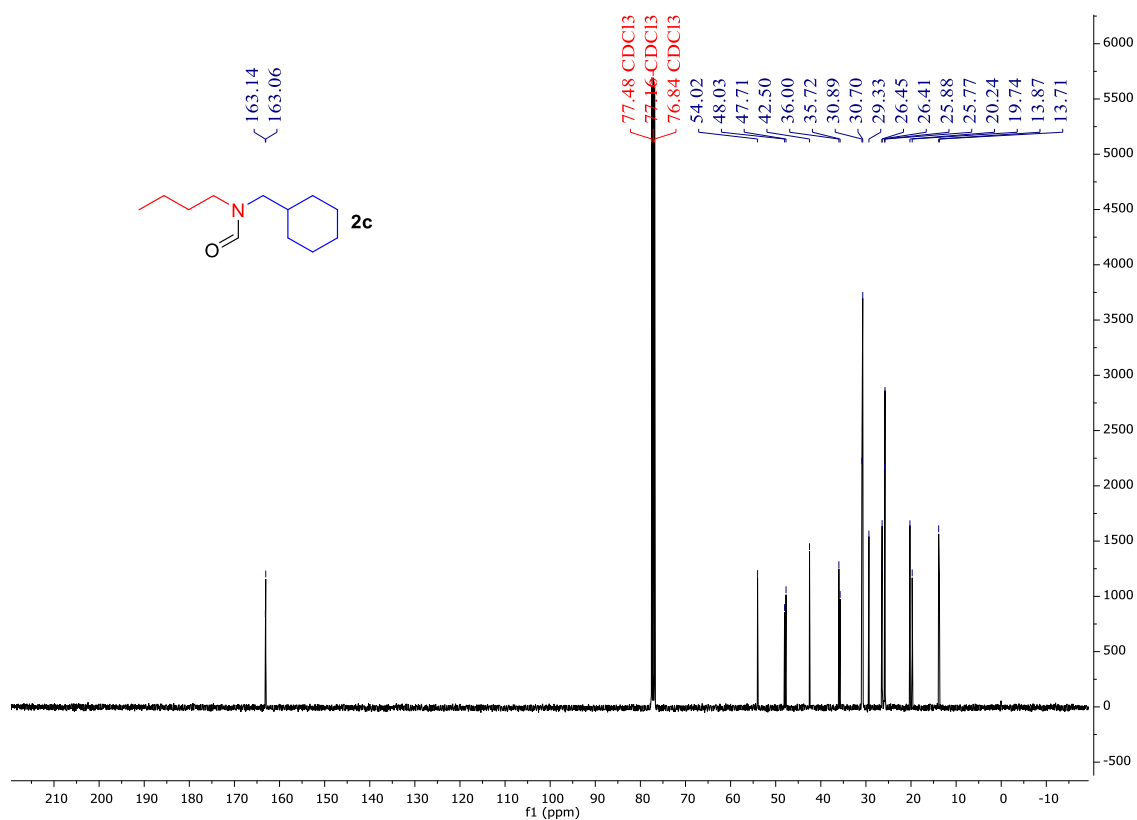
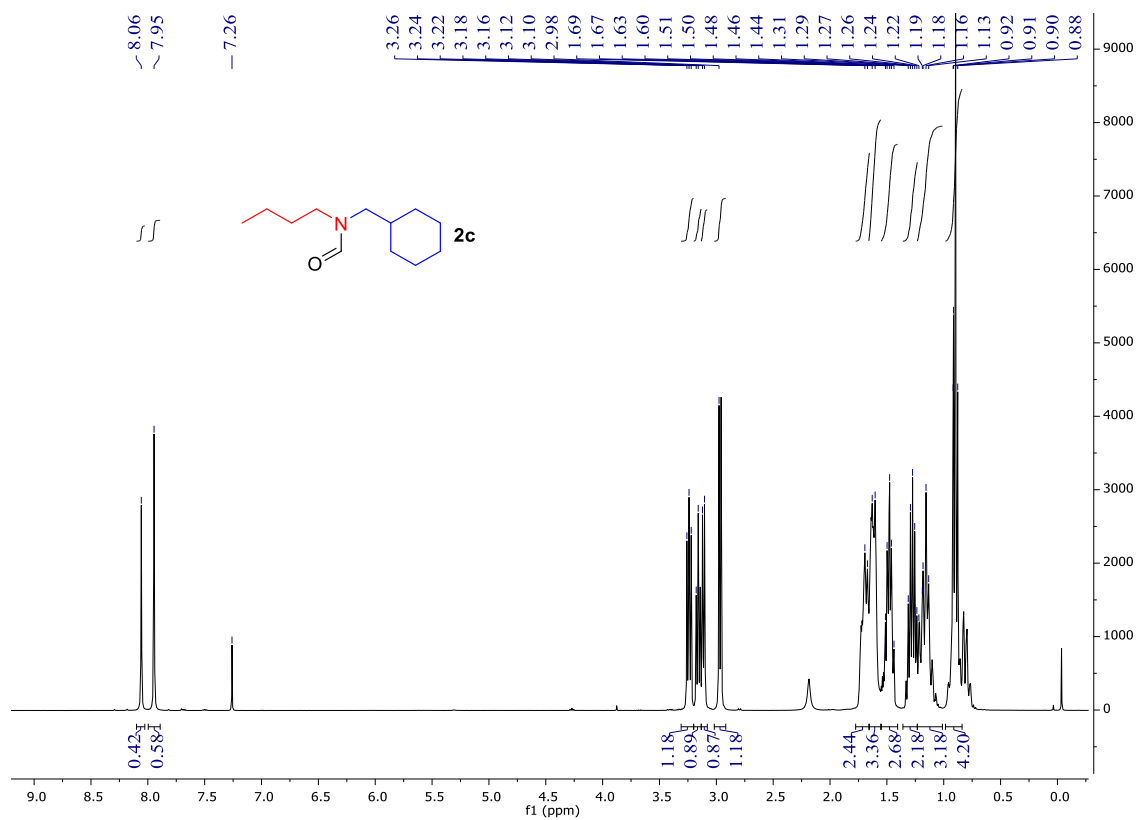
*N*-(3,7-dimethyloct-6-en-1-yl)-*N*-hexylformamide; isolated yield = 81 % (216 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03, 8.01 (s, 1H), 5.06 (m, 1H), 3.35 – 3.12 (m, 4H), 1.96 (m, 2H), 1.71 – 1.62 (m, 3H), 1.58 (s, 3H), 1.56 – 1.46 (m, 3H), 1.42 (m, 1H), 1.37 – 1.21 (m, 9H), 1.21 – 1.11 (m, 1H), 0.89 (t, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.72, 131.69, 131.39, 124.73, 124.42, 47.51, 45.58, 42.24, 40.41, 37.07, 36.96, 36.02, 34.31, 31.64, 31.49, 30.63, 29.89, 28.74, 27.41, 26.73, 26.26, 25.80, 25.52, 25.45, 22.67, 22.64, 19.50, 19.45, 17.75, 17.74, 14.10, 14.07. M (C<sub>17</sub>H<sub>33</sub>NO) = 267.3, EI-MS found 267.3 [M], 238.2 [M-CHO]. HR-MS (ESI) calculated for C<sub>17</sub>H<sub>34</sub>NO [M+H]<sup>+</sup>: 268.2635, found: 268.2634.

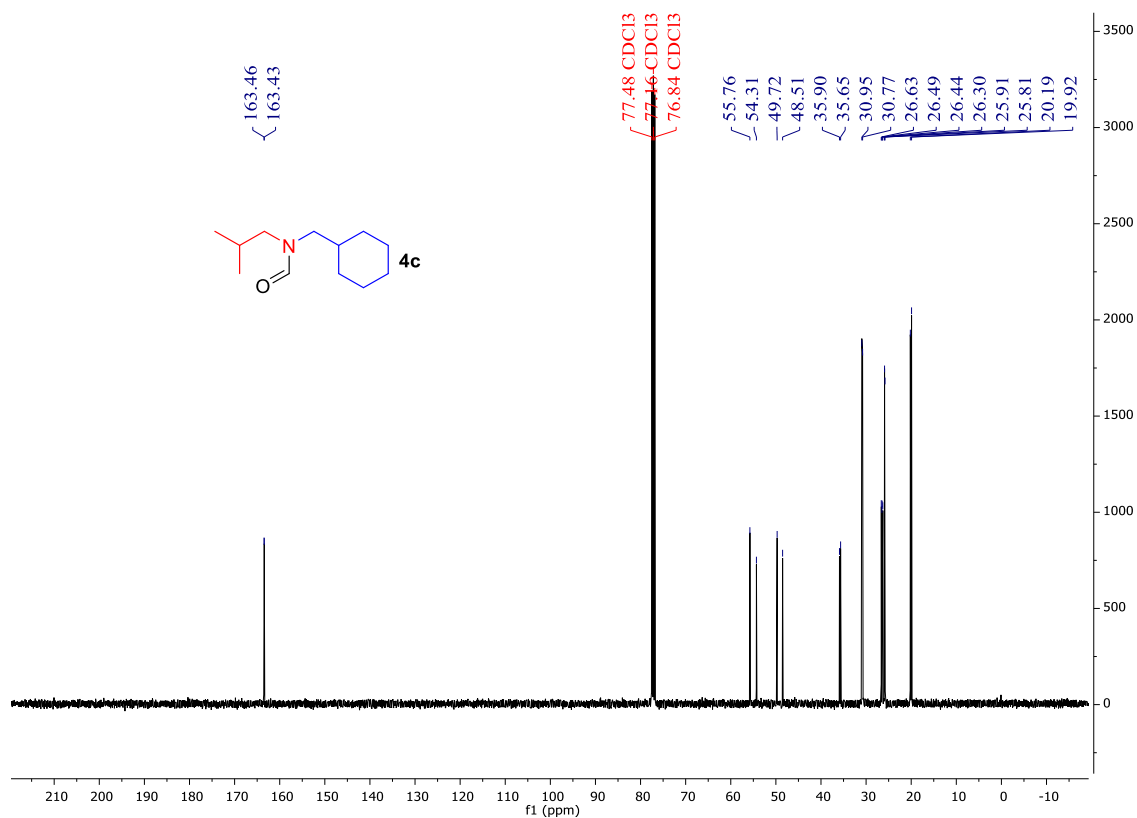
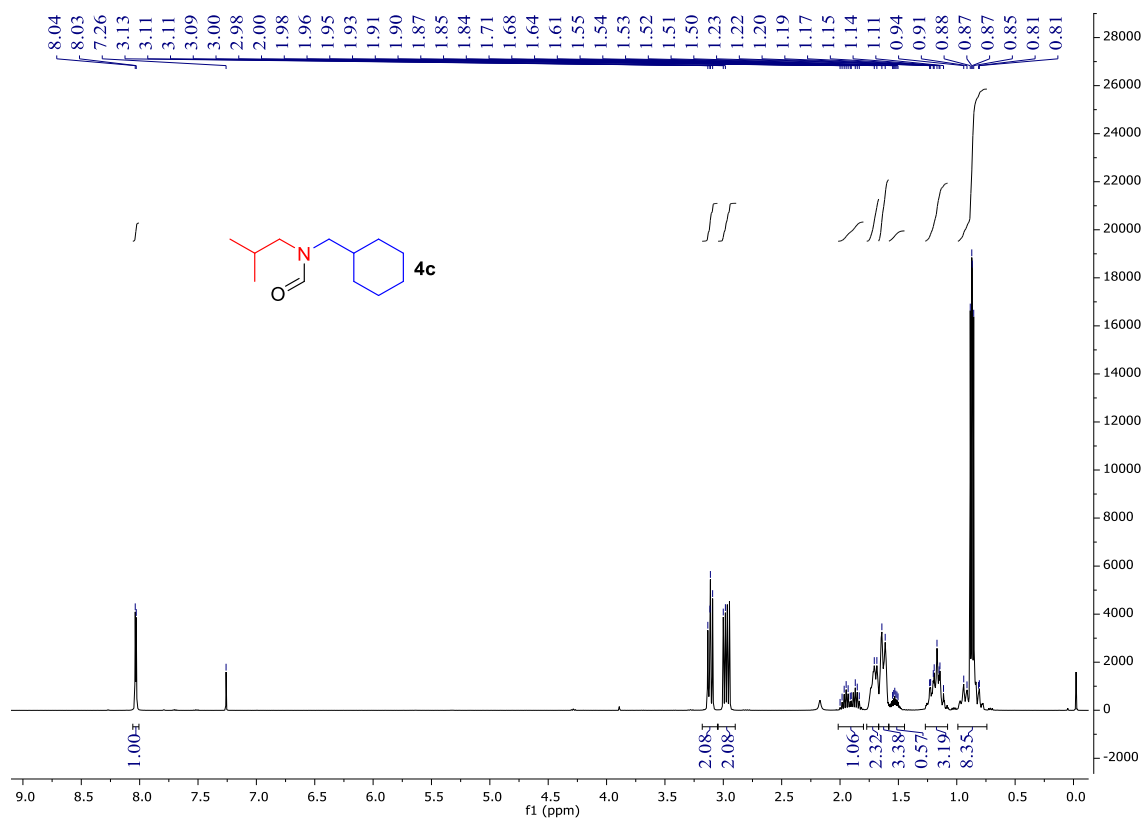


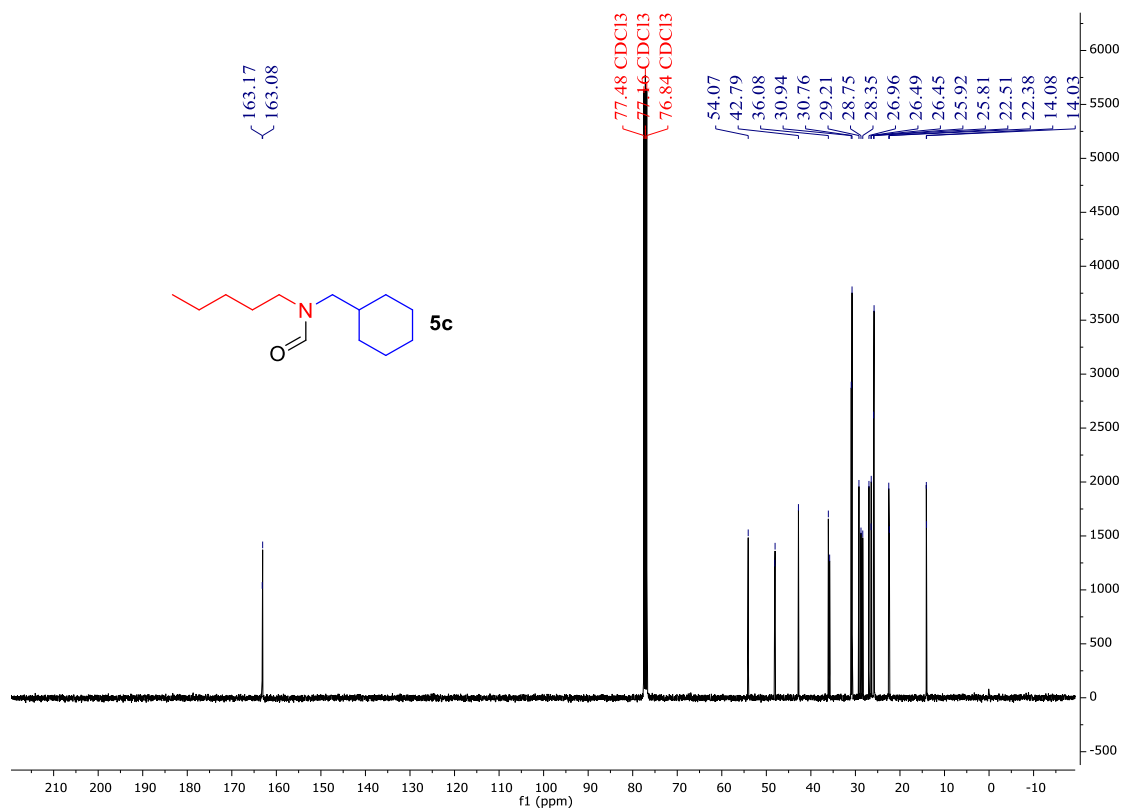
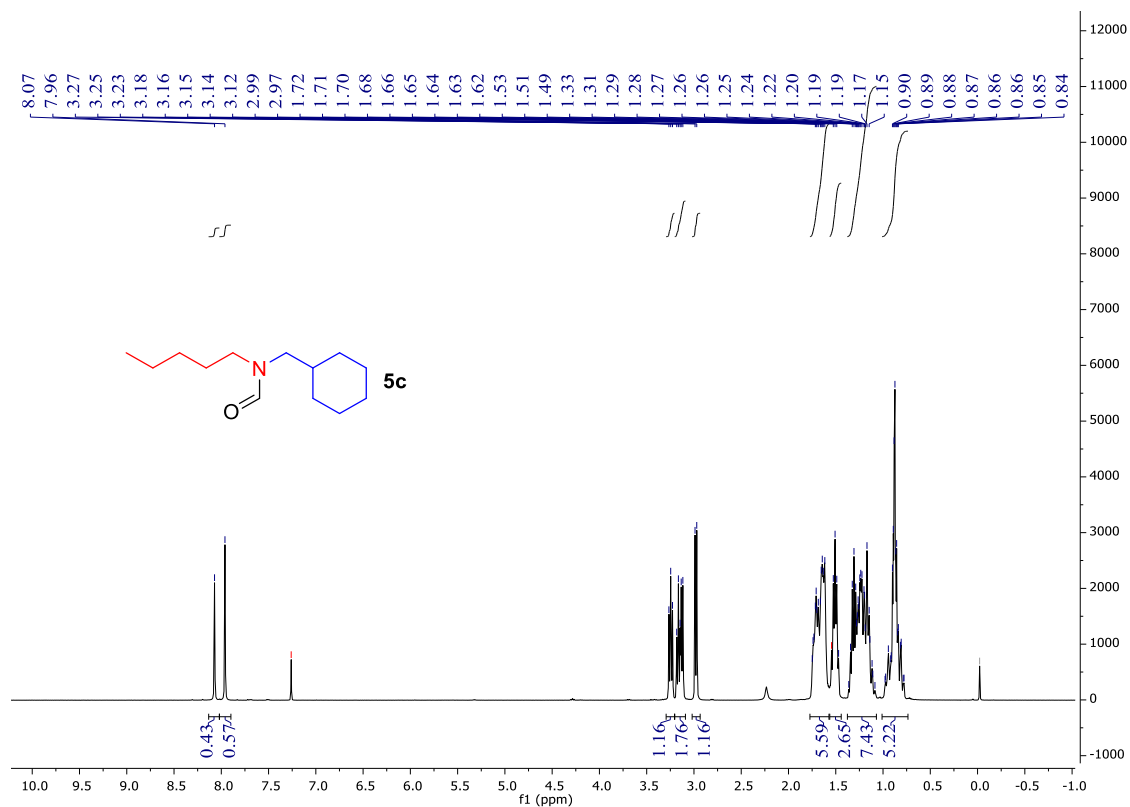
*N*-cyclohexyl-*N*-(3,7-dimethyloct-6-en-1-yl)formamide; isolated yield = 75 % (199 mg). This compound was obtained and purified by column chromatography using petroleum ether (b.p. 30 – 60 °C)/ethyl acetate = (100:1 – 5:1) to give colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12, 8.04 (d, 1H), 5.07 (m, 1H), 3.28 – 3.06 (m, 3H), 1.98 (m, 2H), 1.89 – 1.73 (m, 4H), 1.72 – 1.62 (m, 5H), 1.59 (s, 3H), 1.49 (m, 4H), 1.40 – 1.22 (m, 5H), 1.22 – 1.04 (m, 4H), 0.91 (t, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.09, 162.30, 131.70, 131.36, 124.83, 124.48, 58.67, 52.85, 43.35, 40.34, 39.35, 37.05, 36.96, 36.15, 33.12, 33.09, 31.09, 30.99, 30.90, 30.43, 29.82, 26.05, 26.00, 25.83, 25.65, 25.56, 25.49, 25.39, 19.53, 17.79, 17.77. HR-MS (ESI) calculated for C<sub>17</sub>H<sub>31</sub>NO [M+H]<sup>+</sup>: 265.2406, found: 265.2402.

# $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of the products

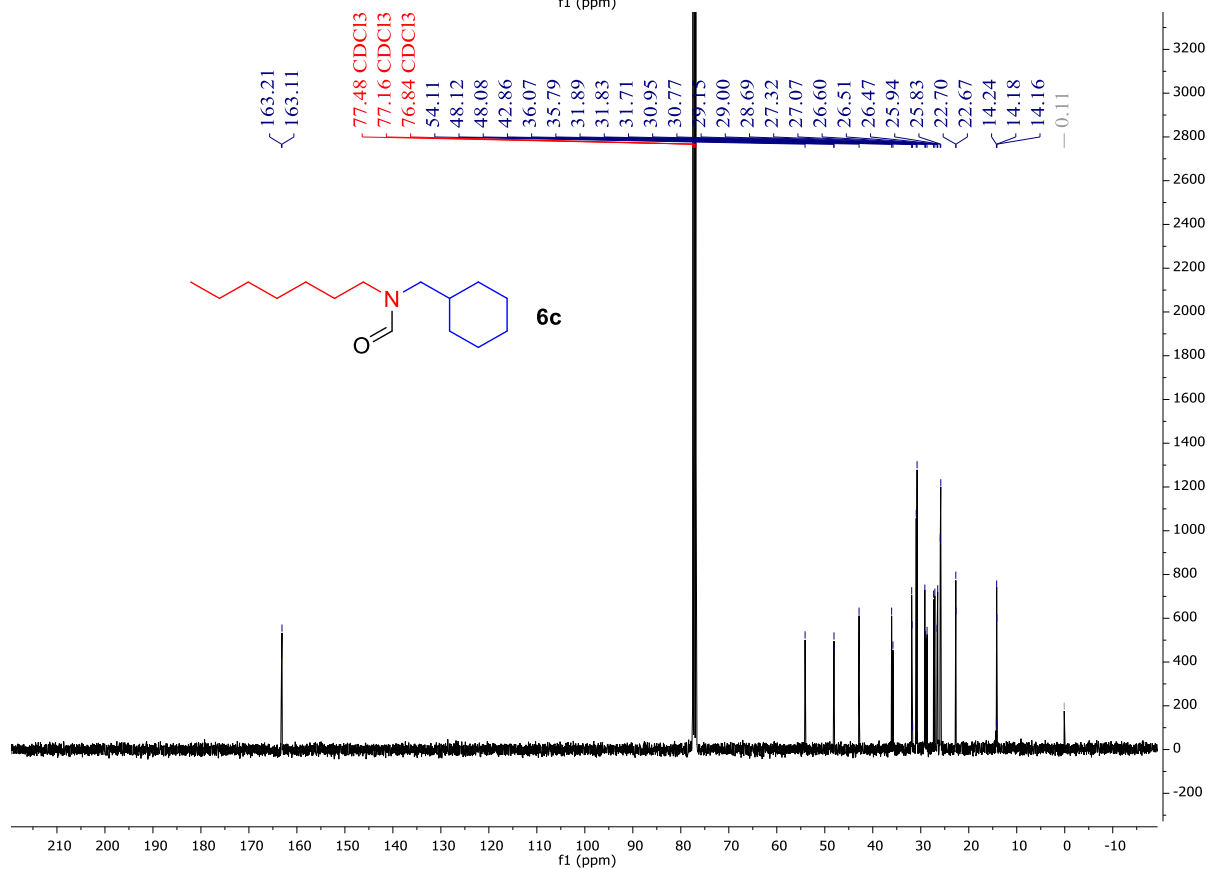
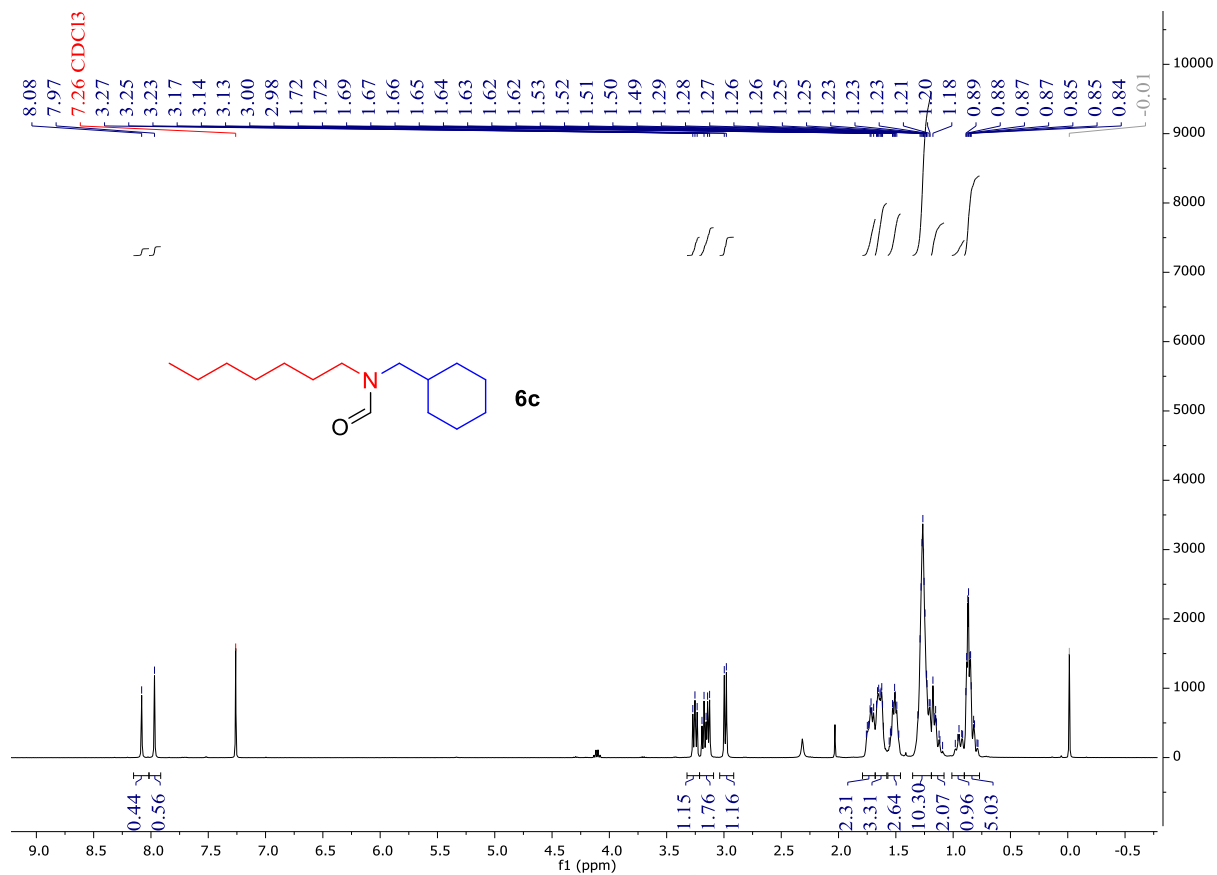


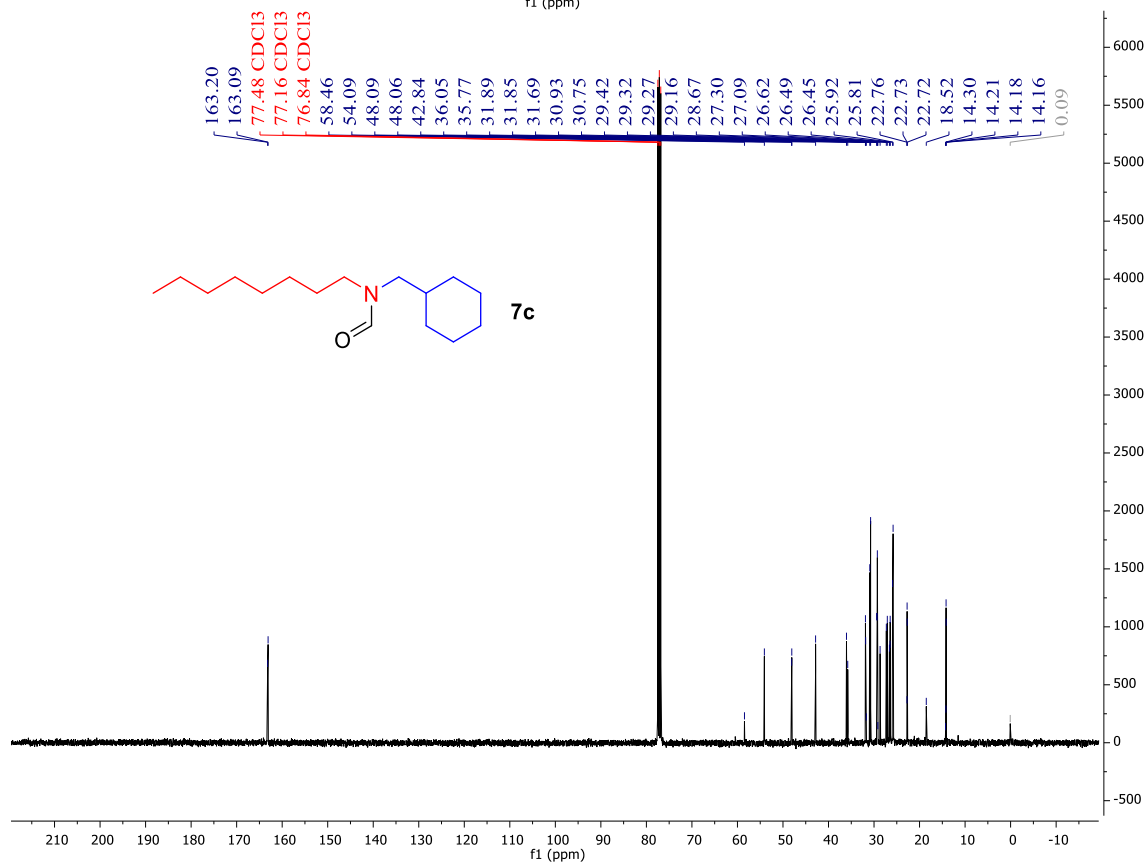
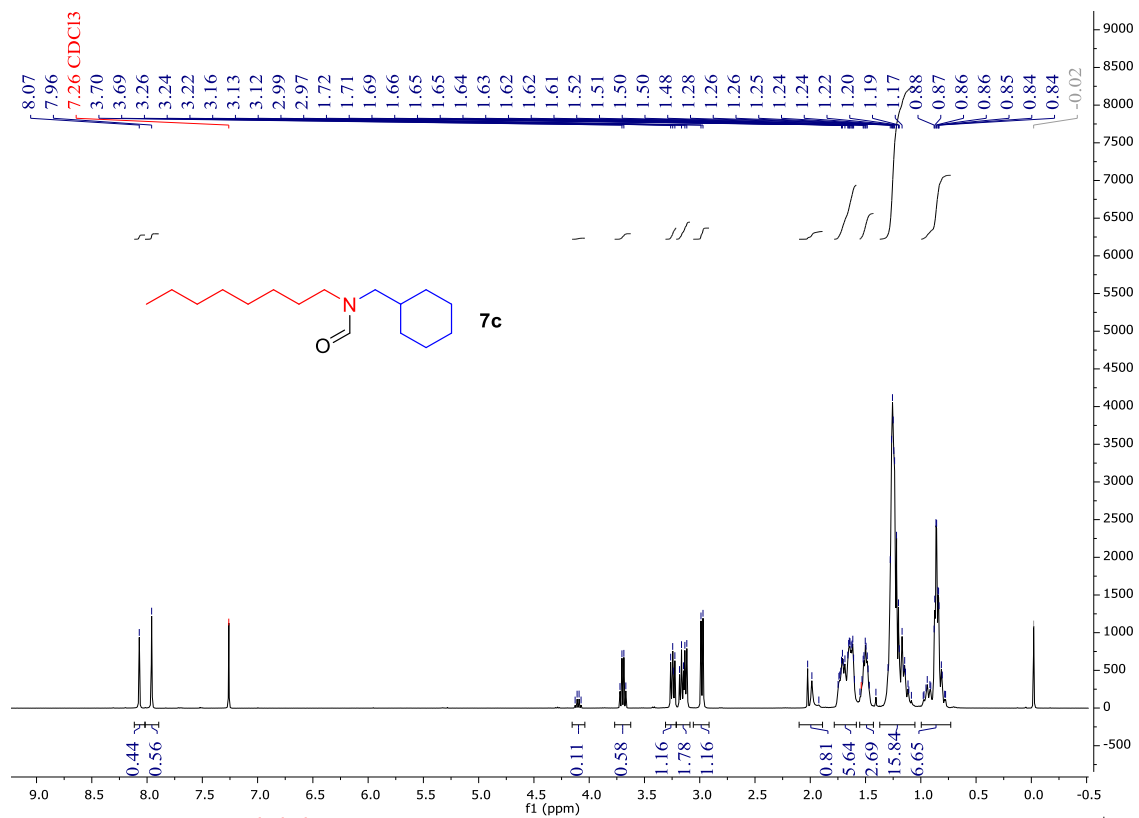


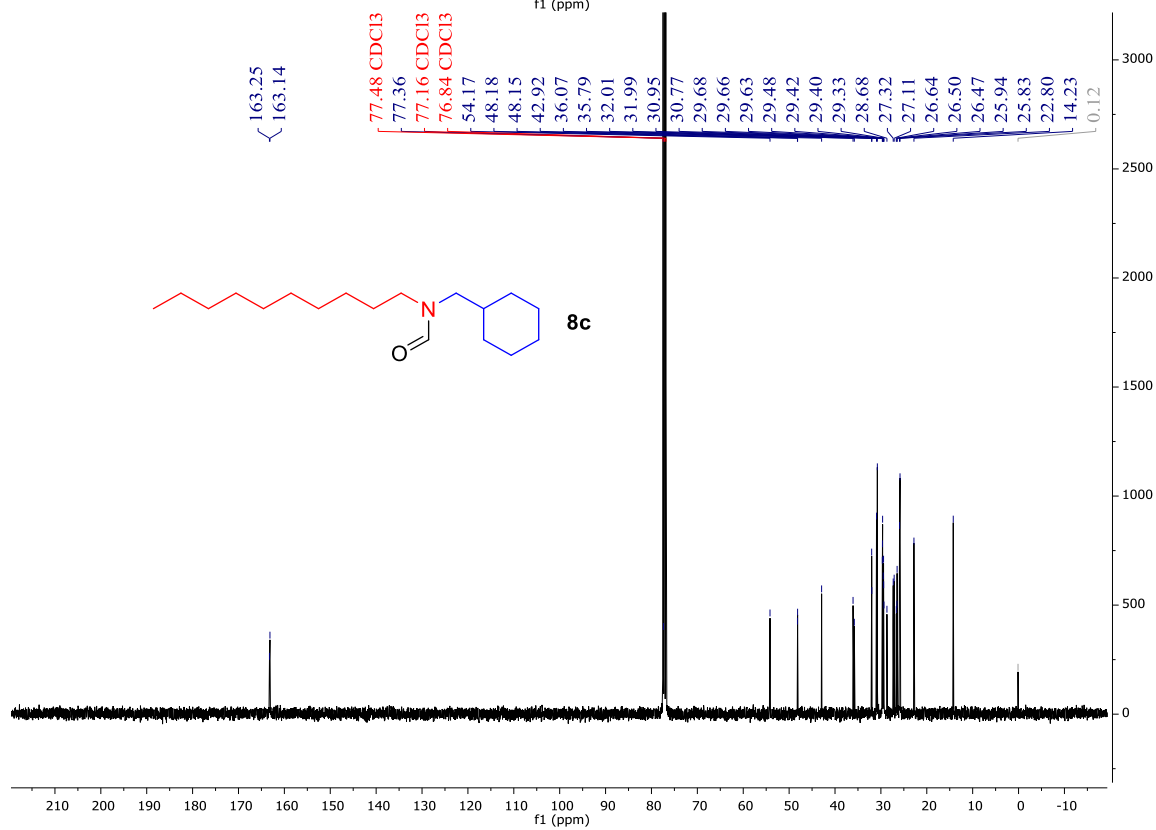
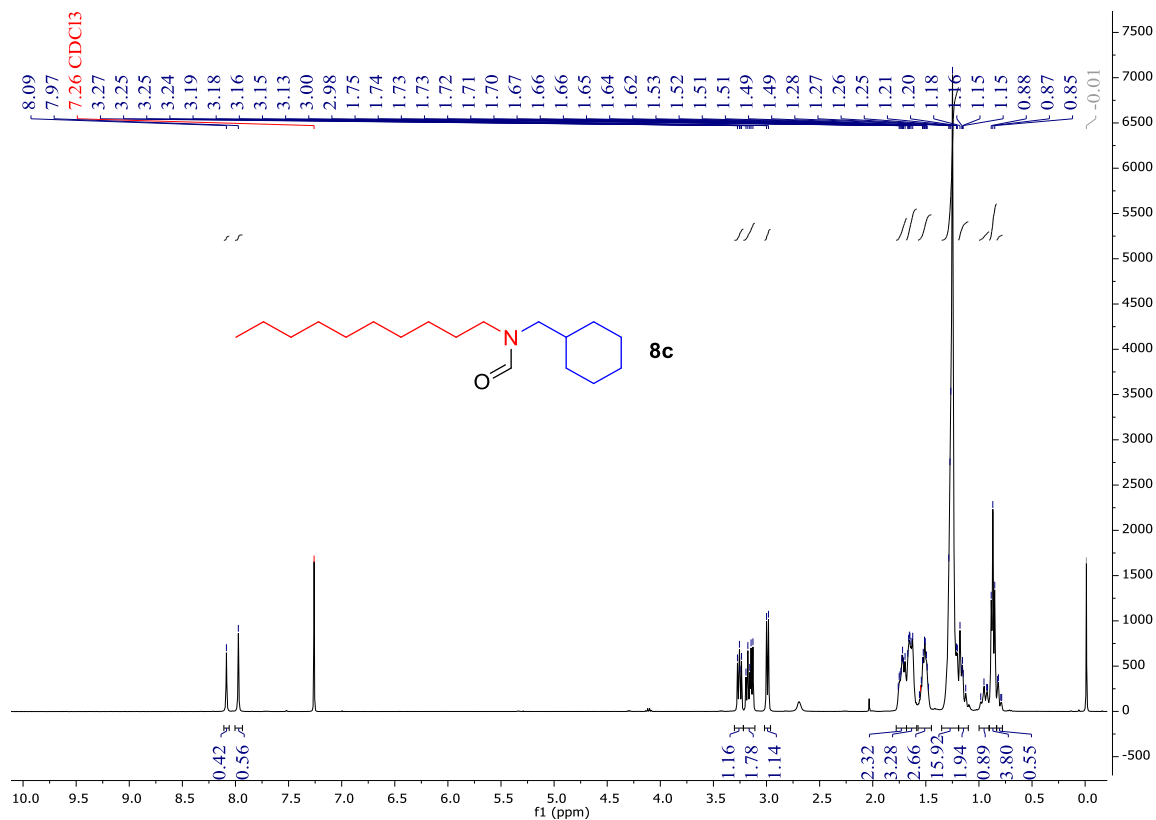


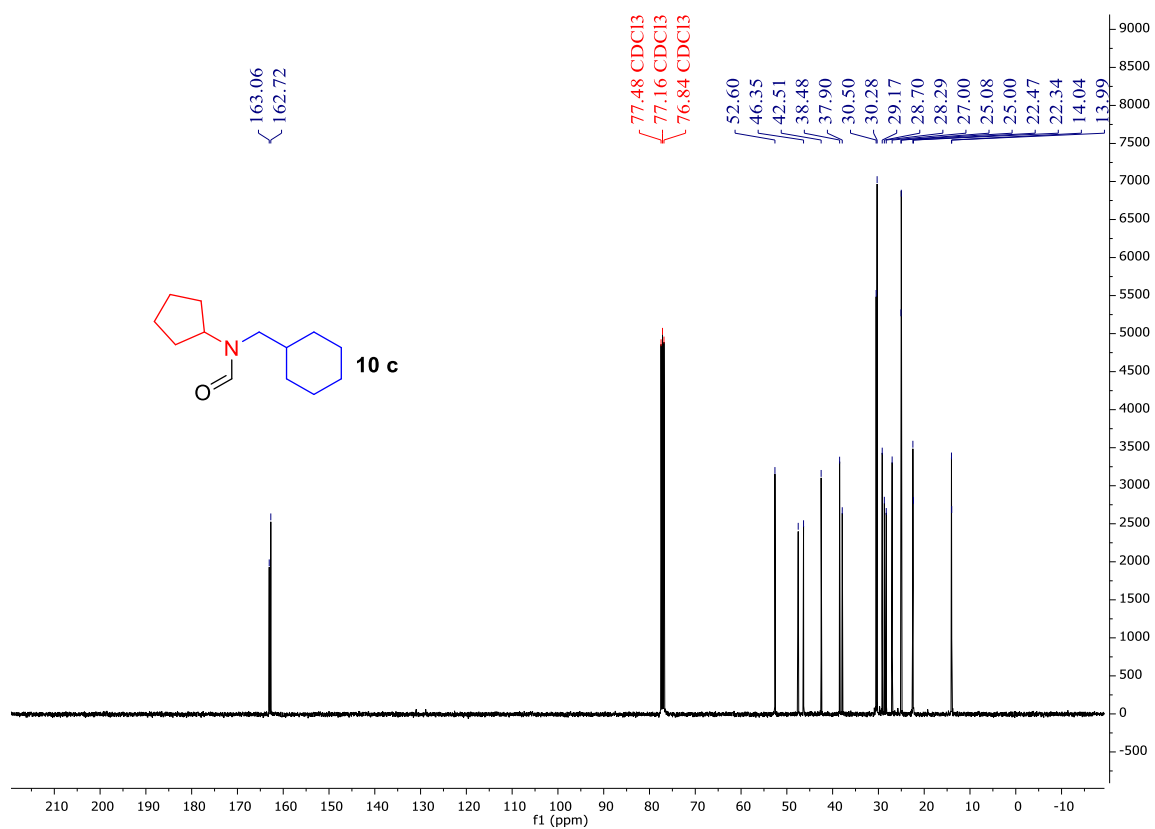
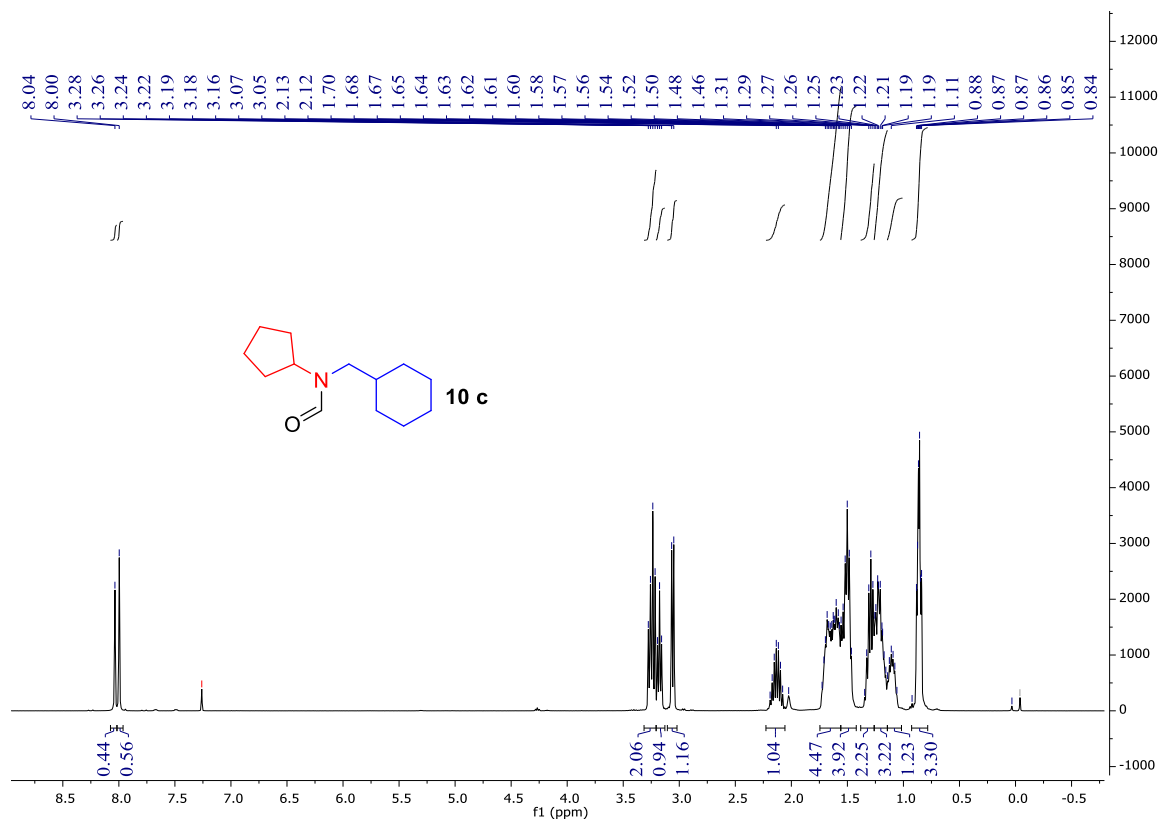


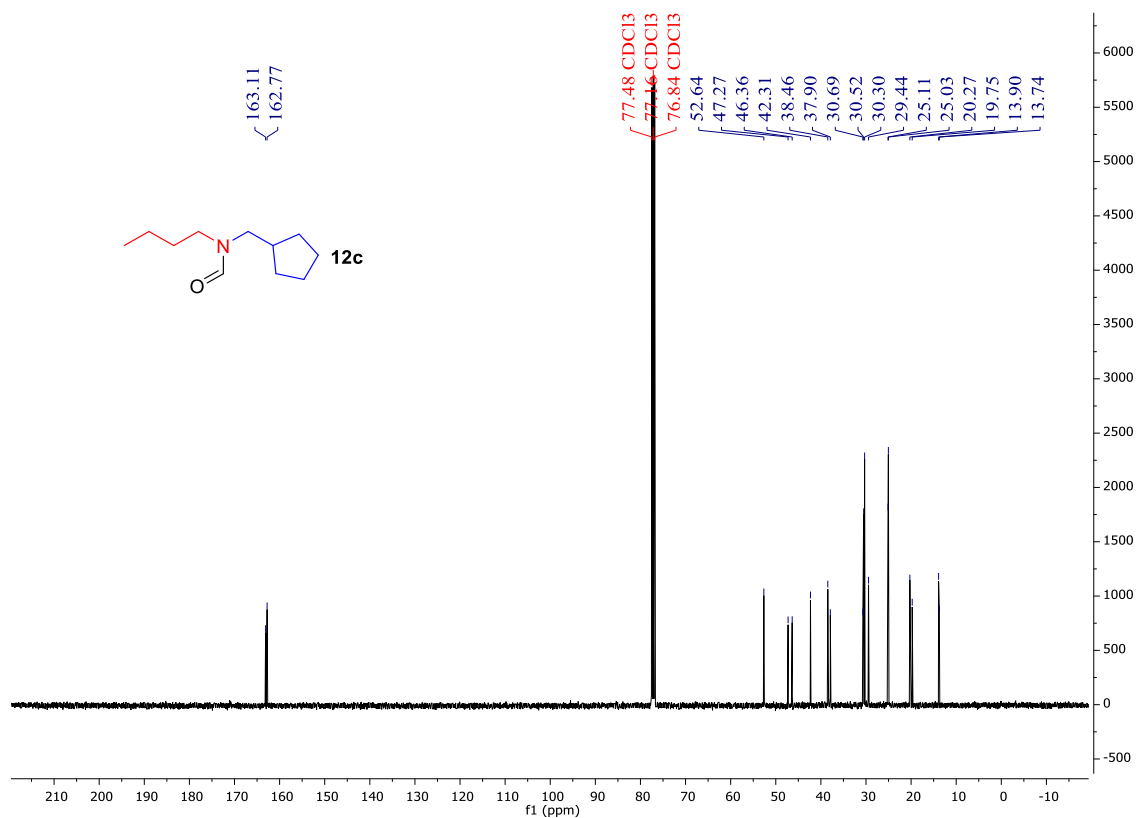
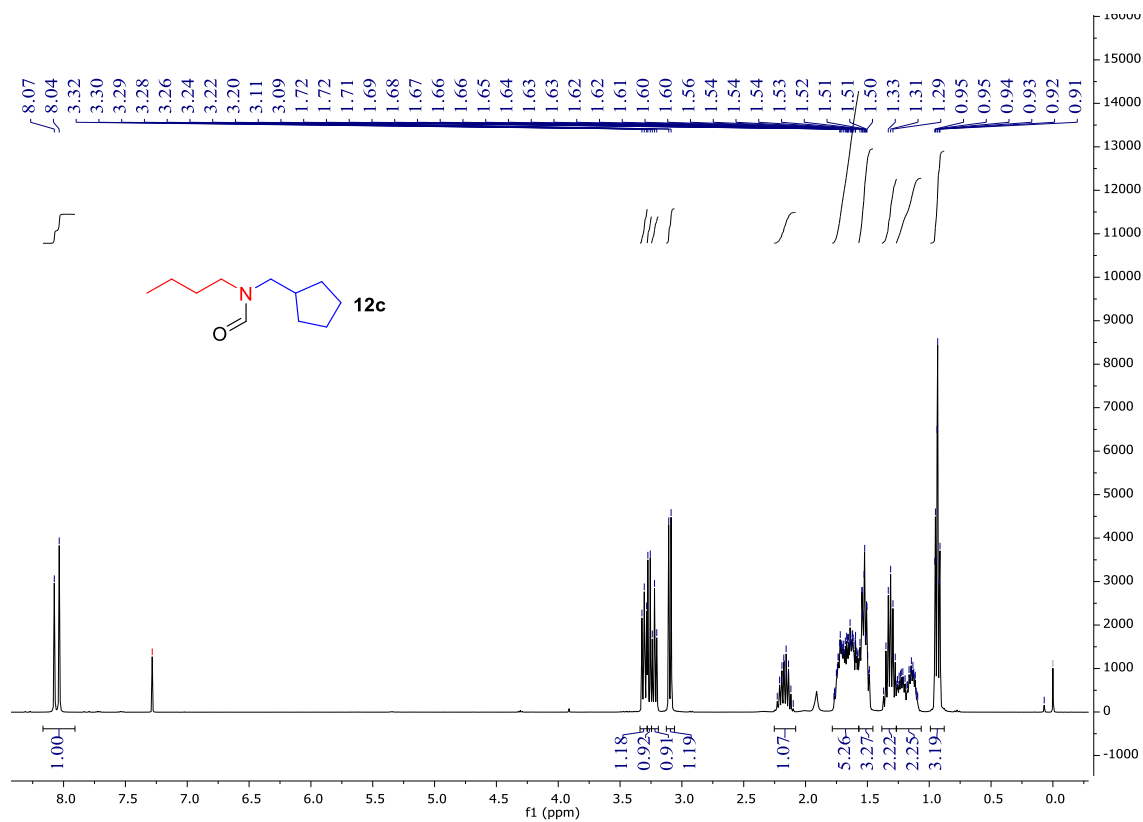


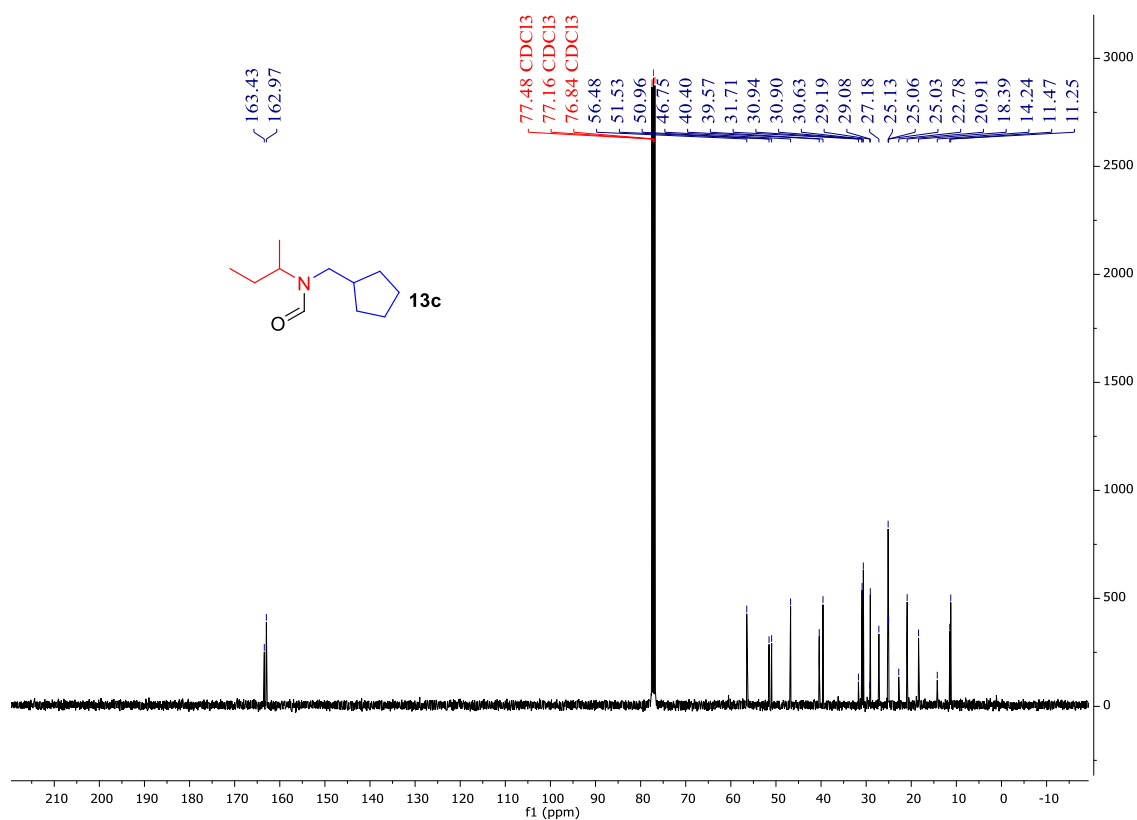
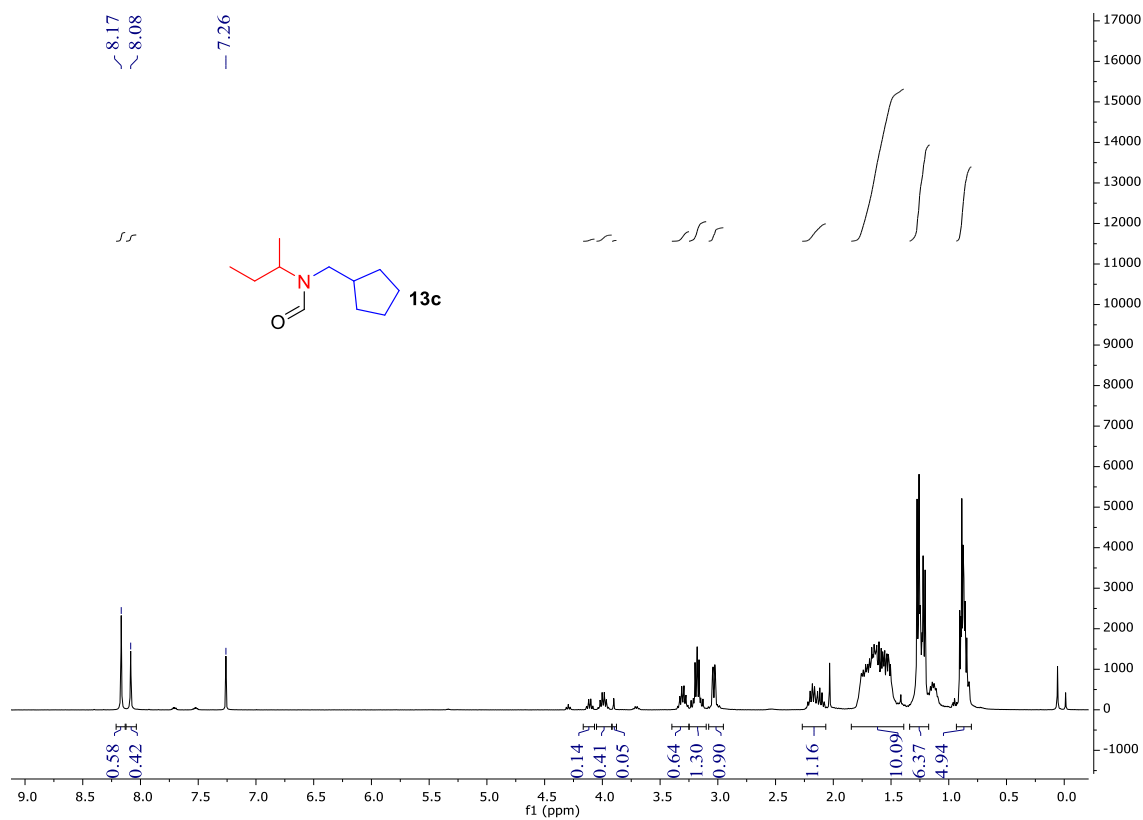


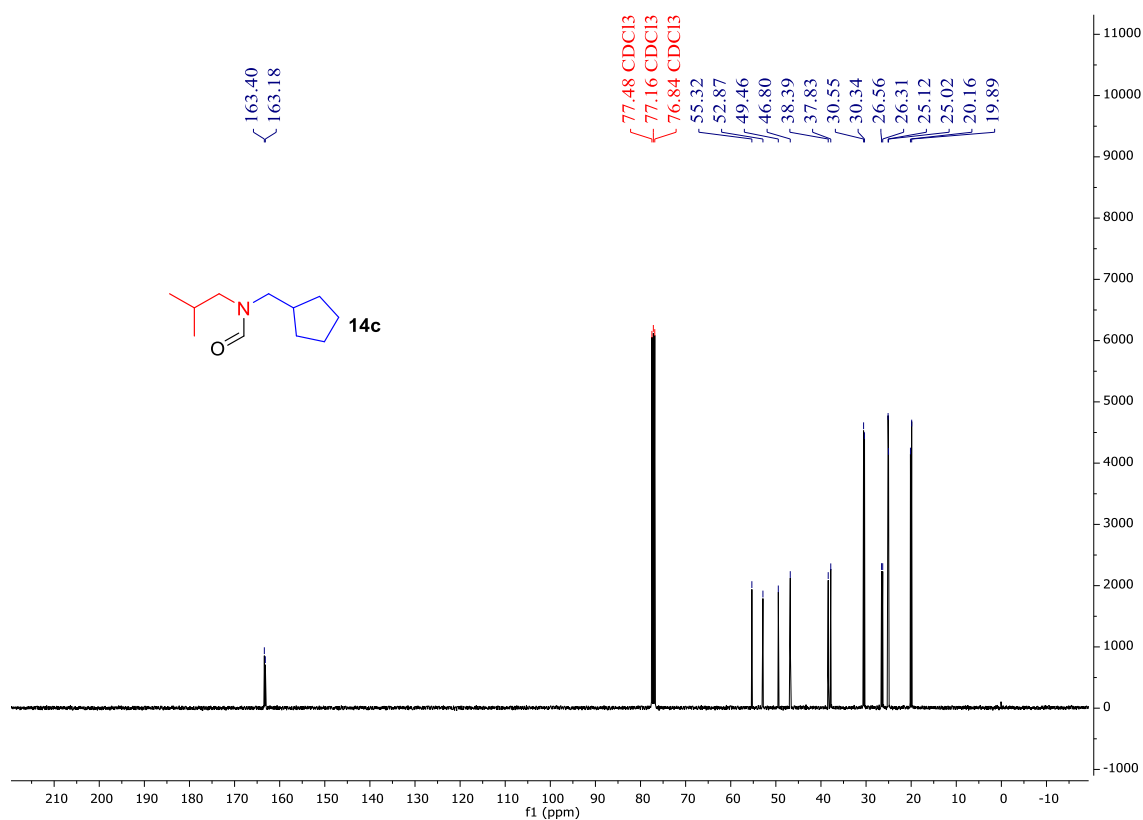
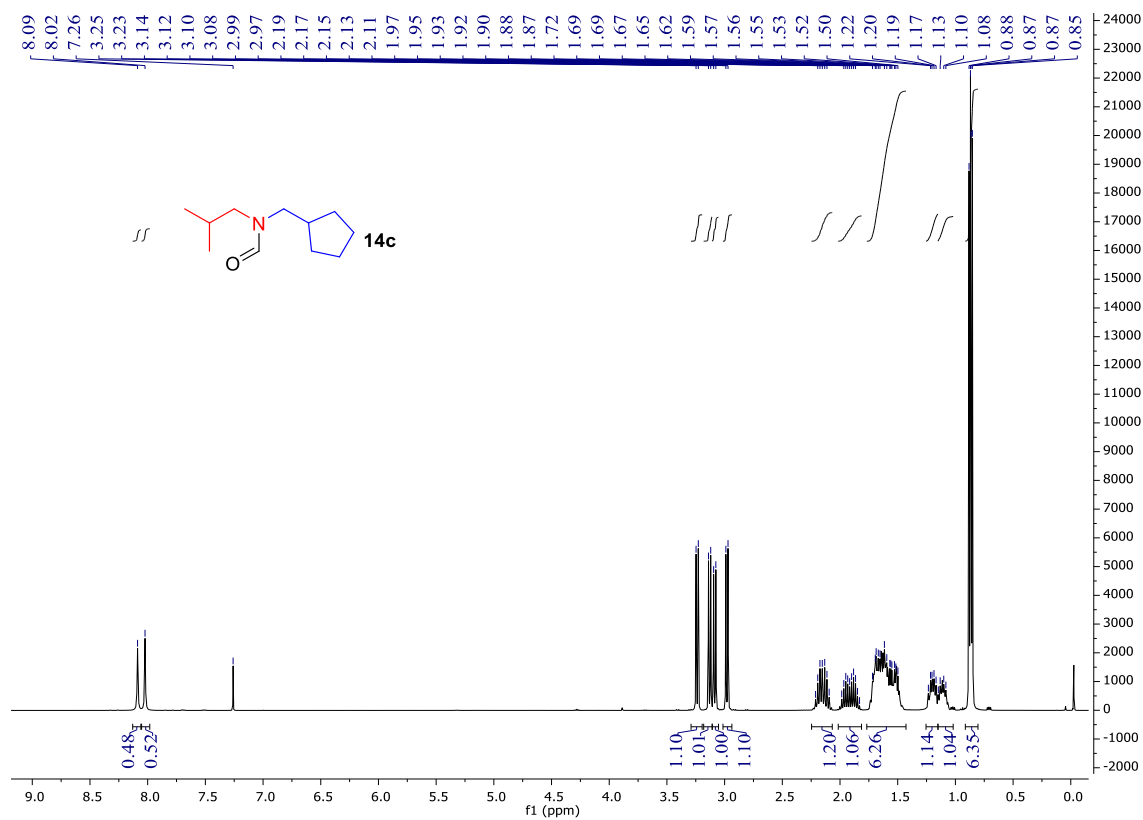


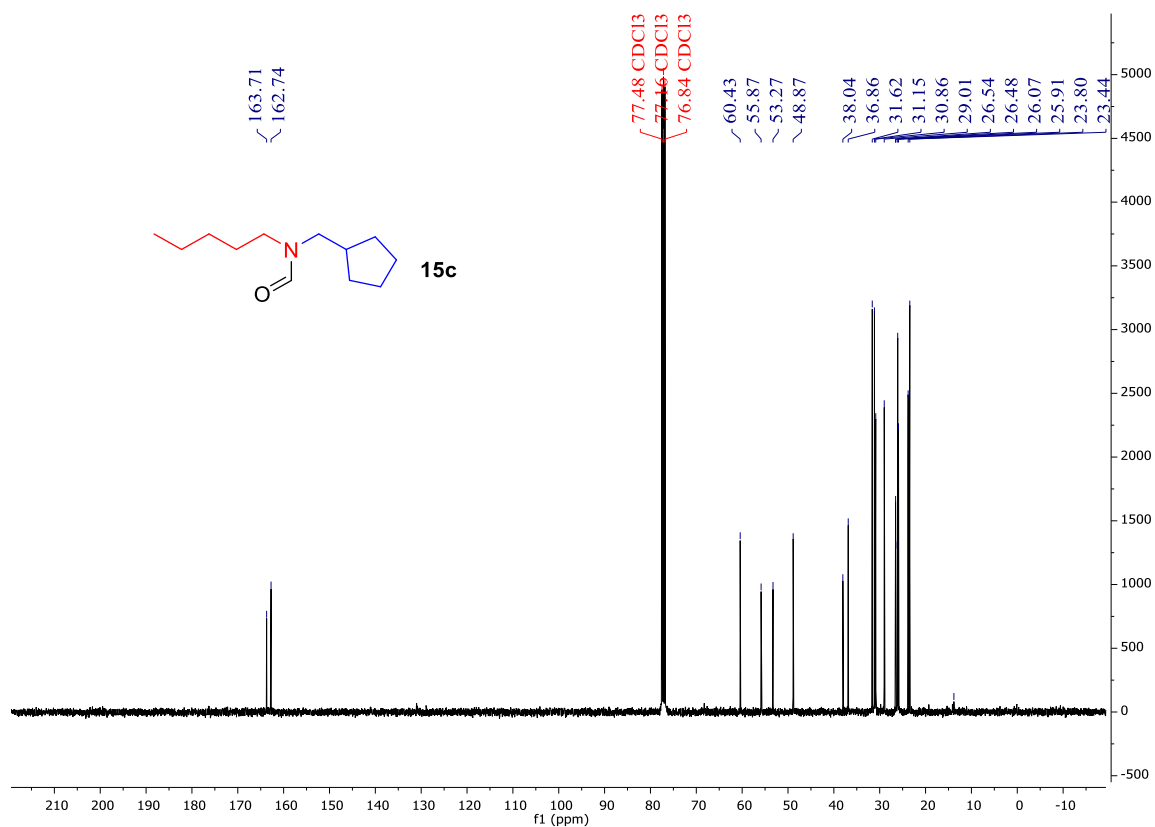
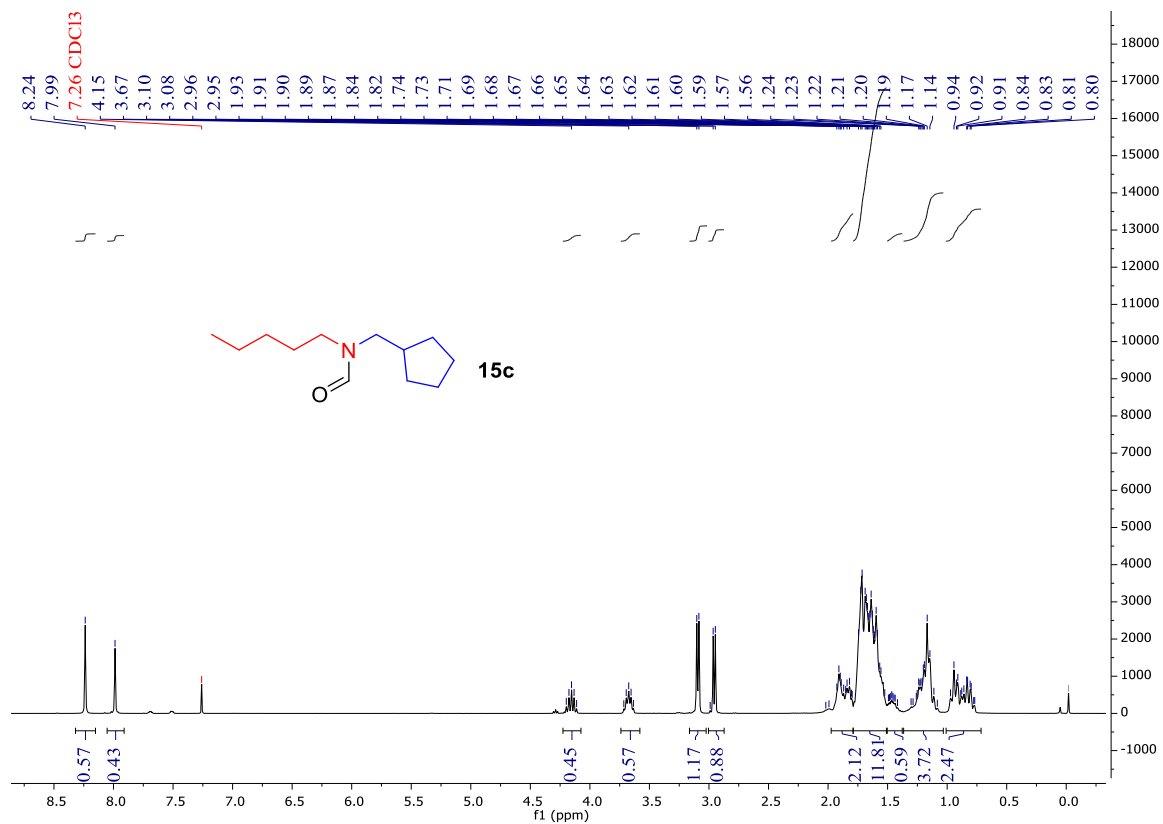




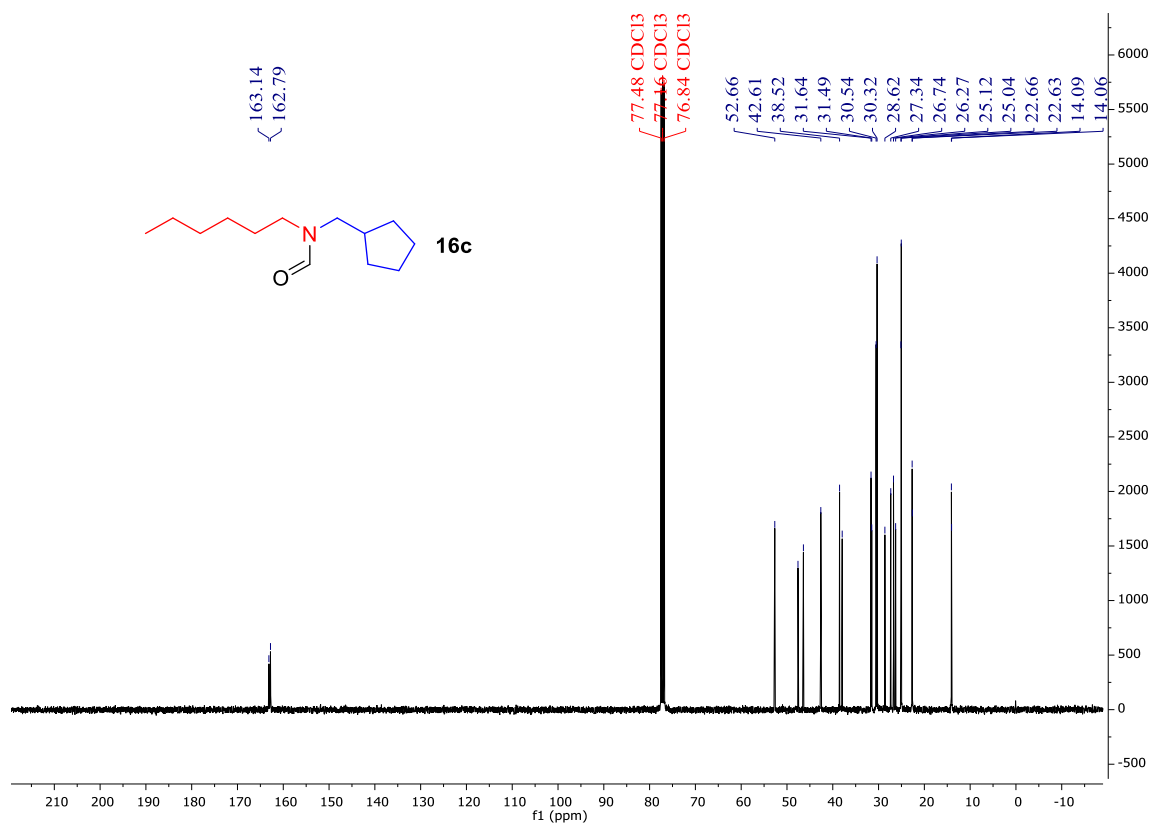
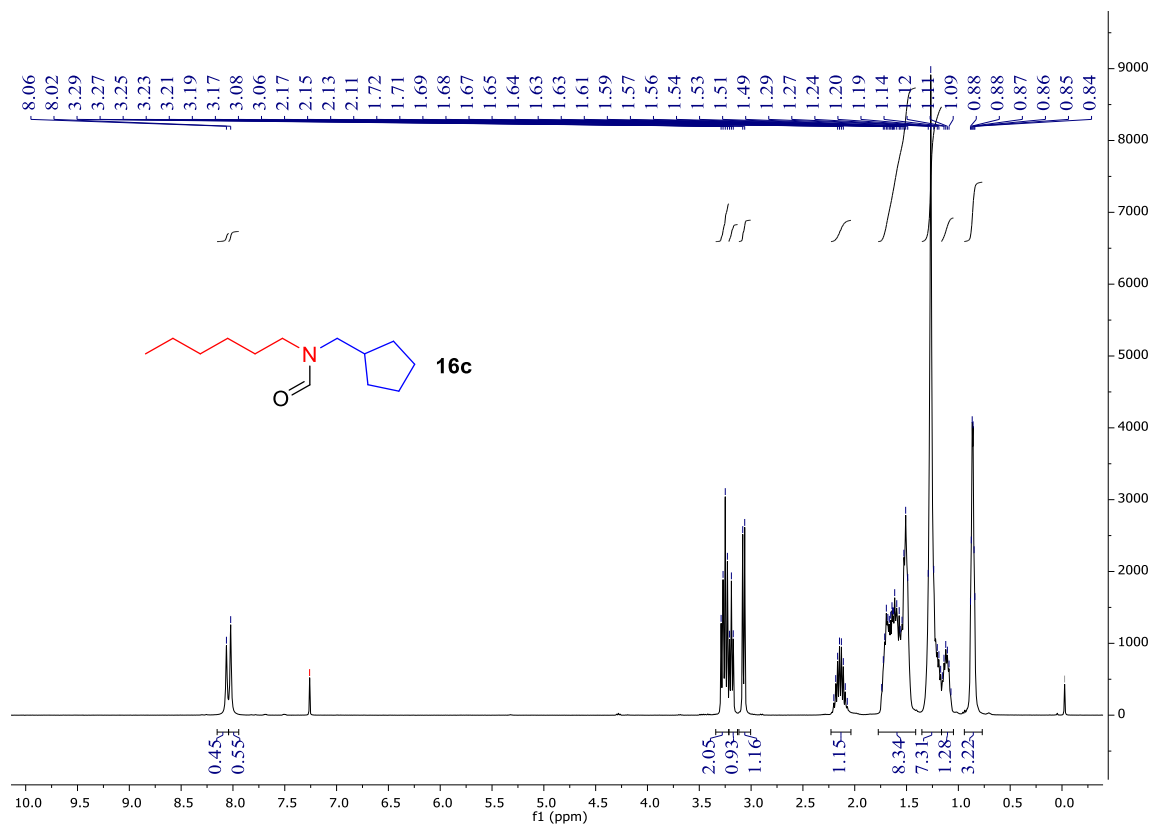


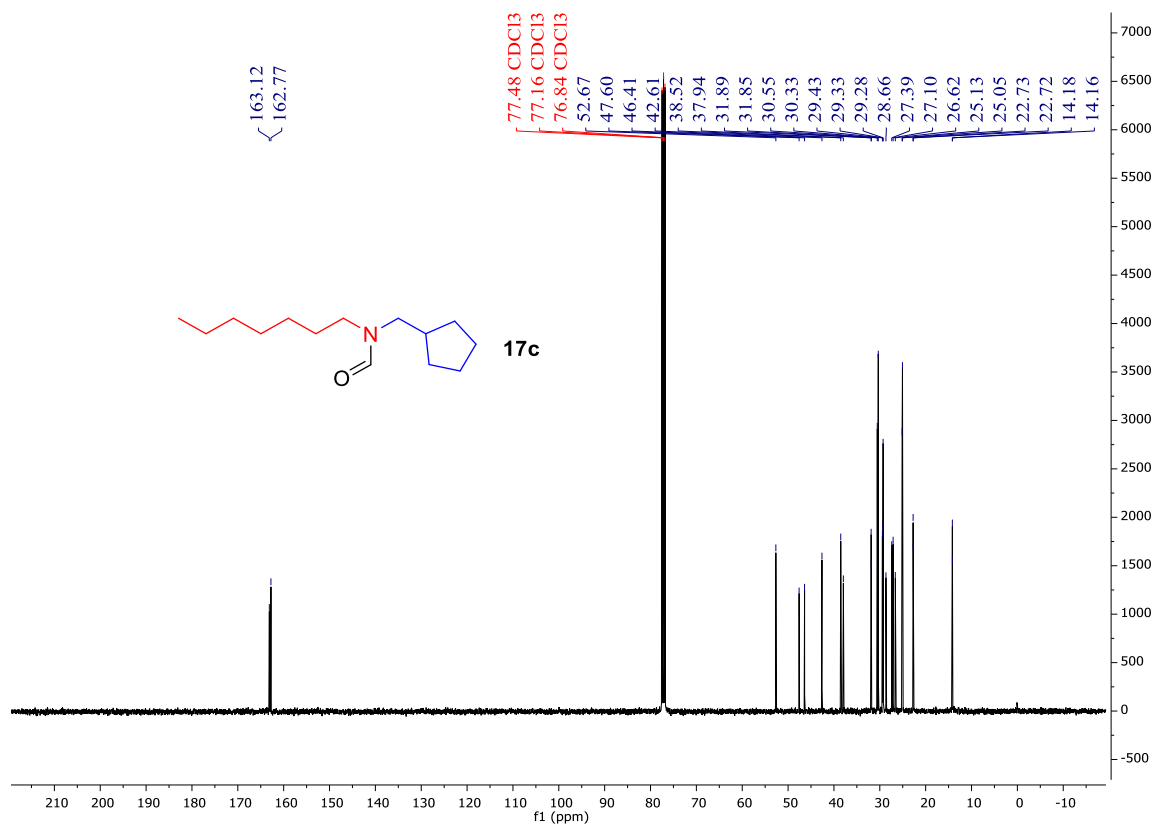
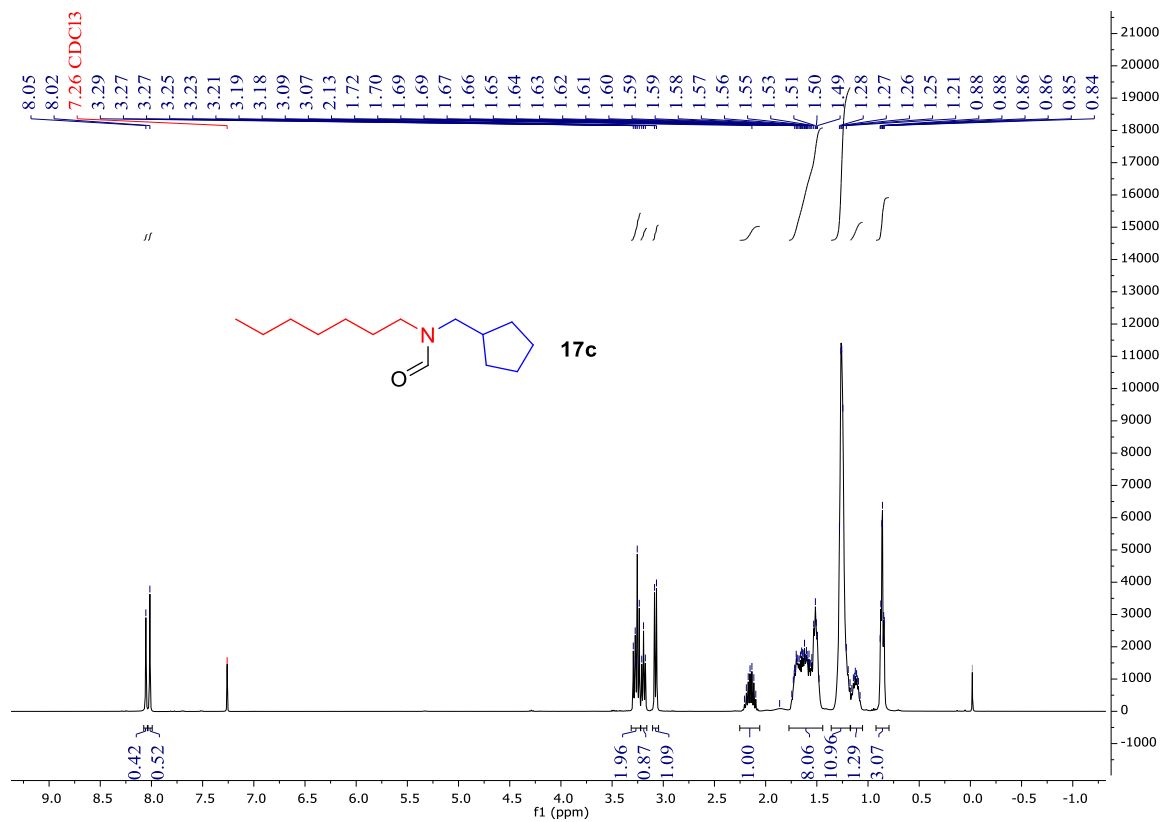


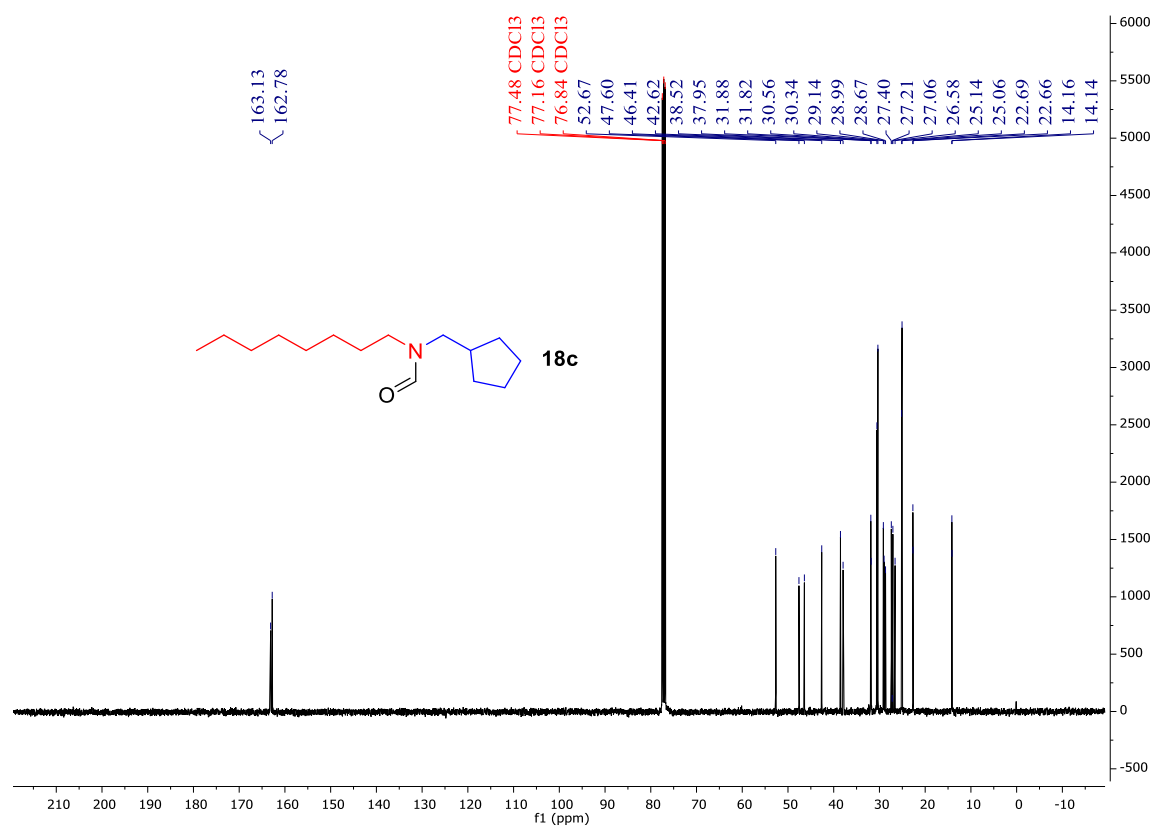
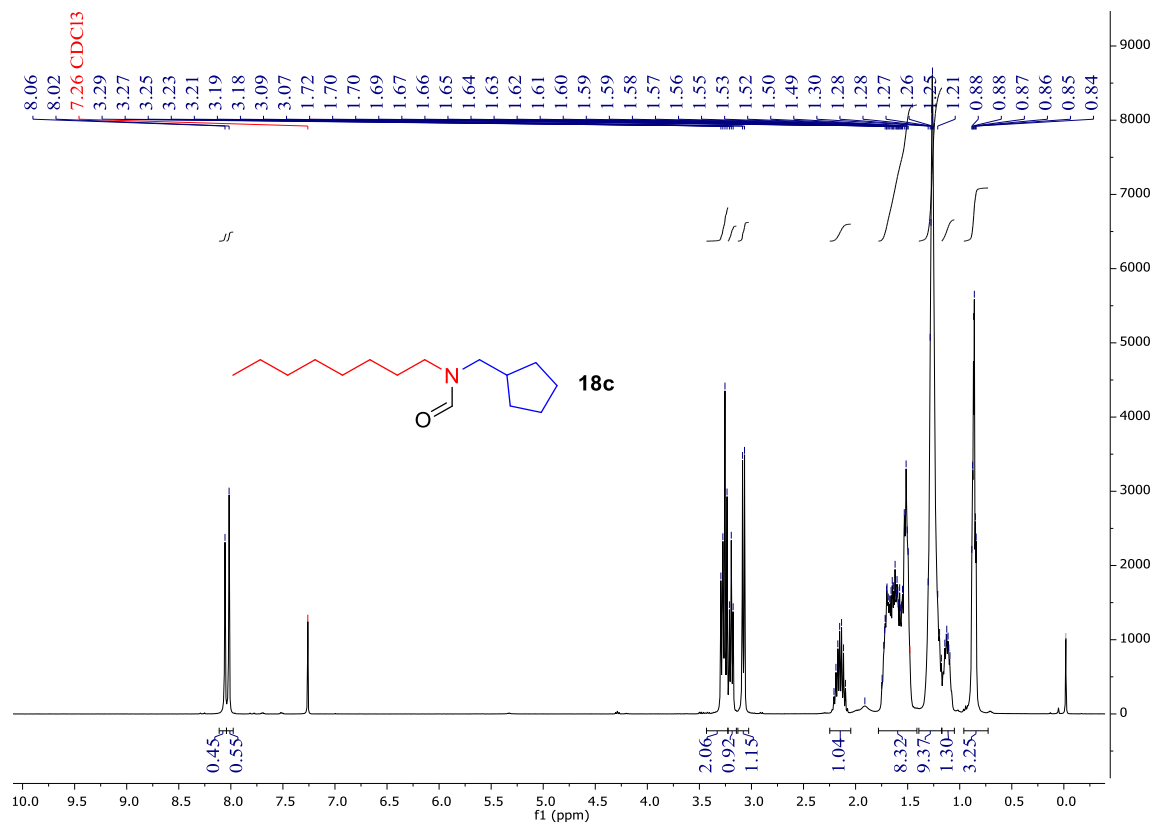


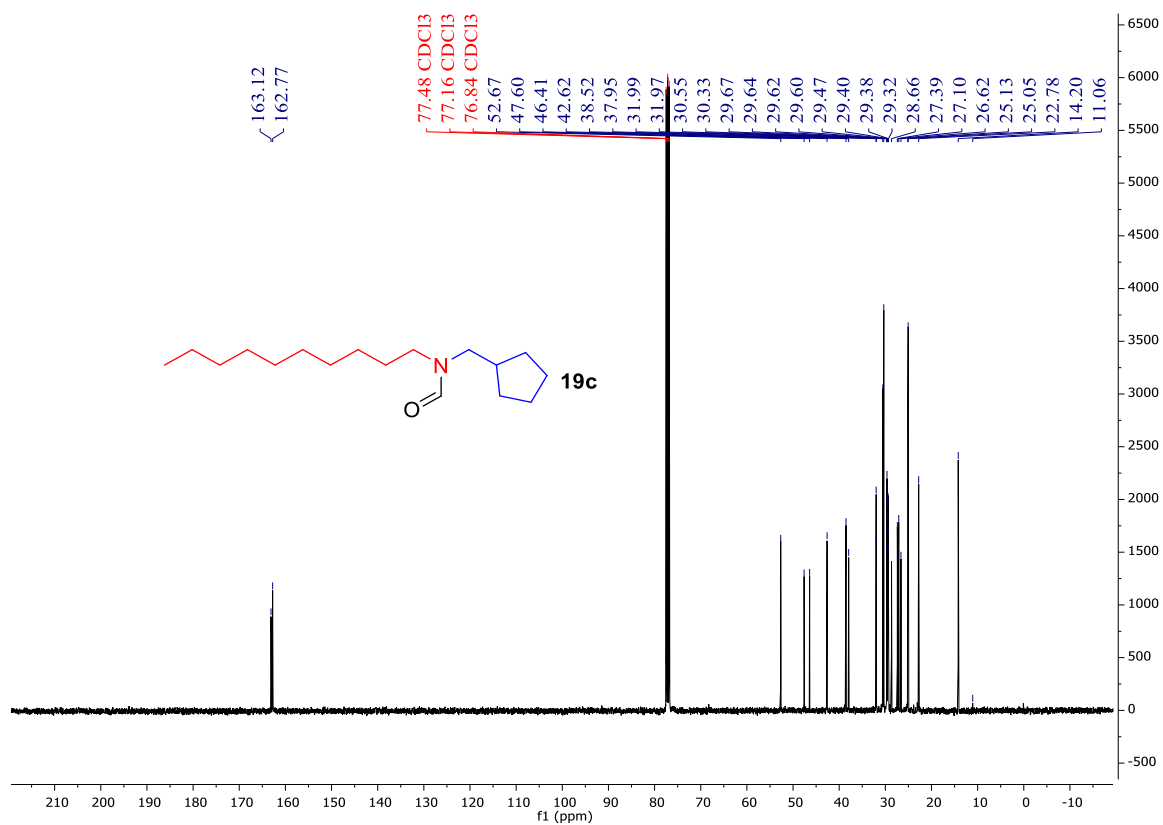
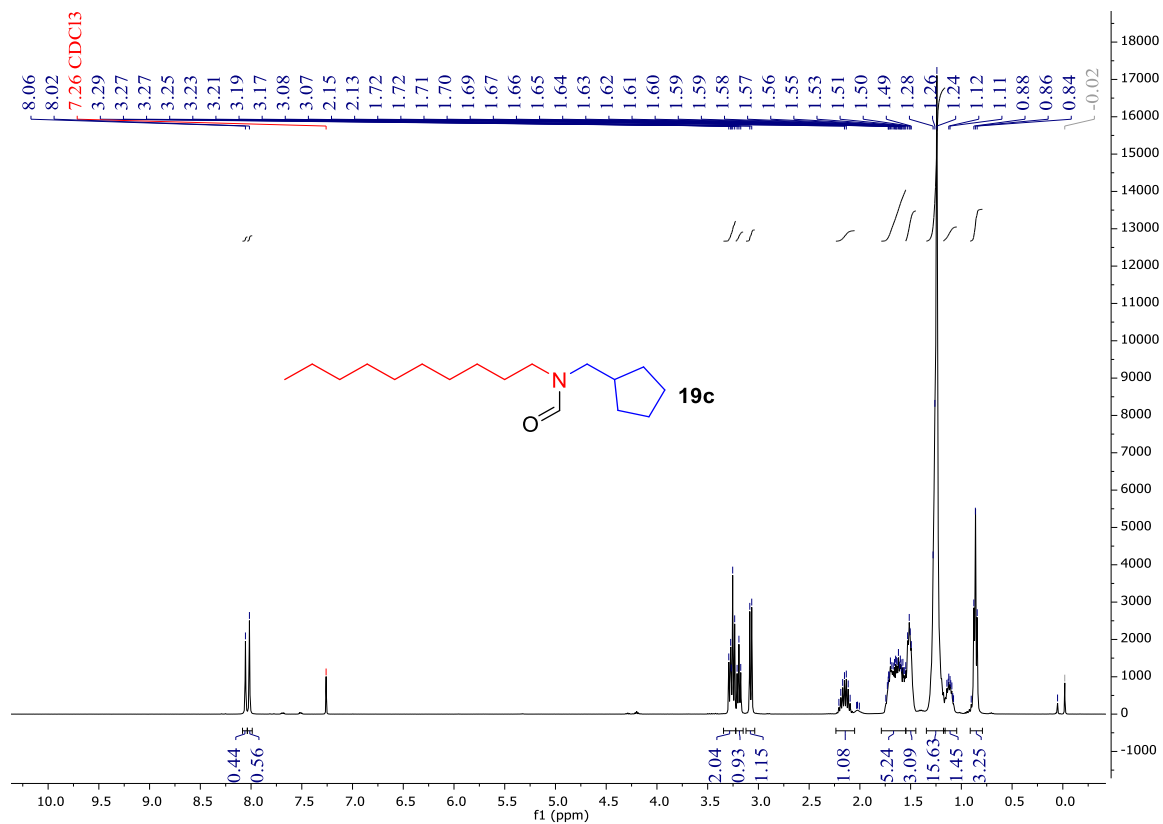


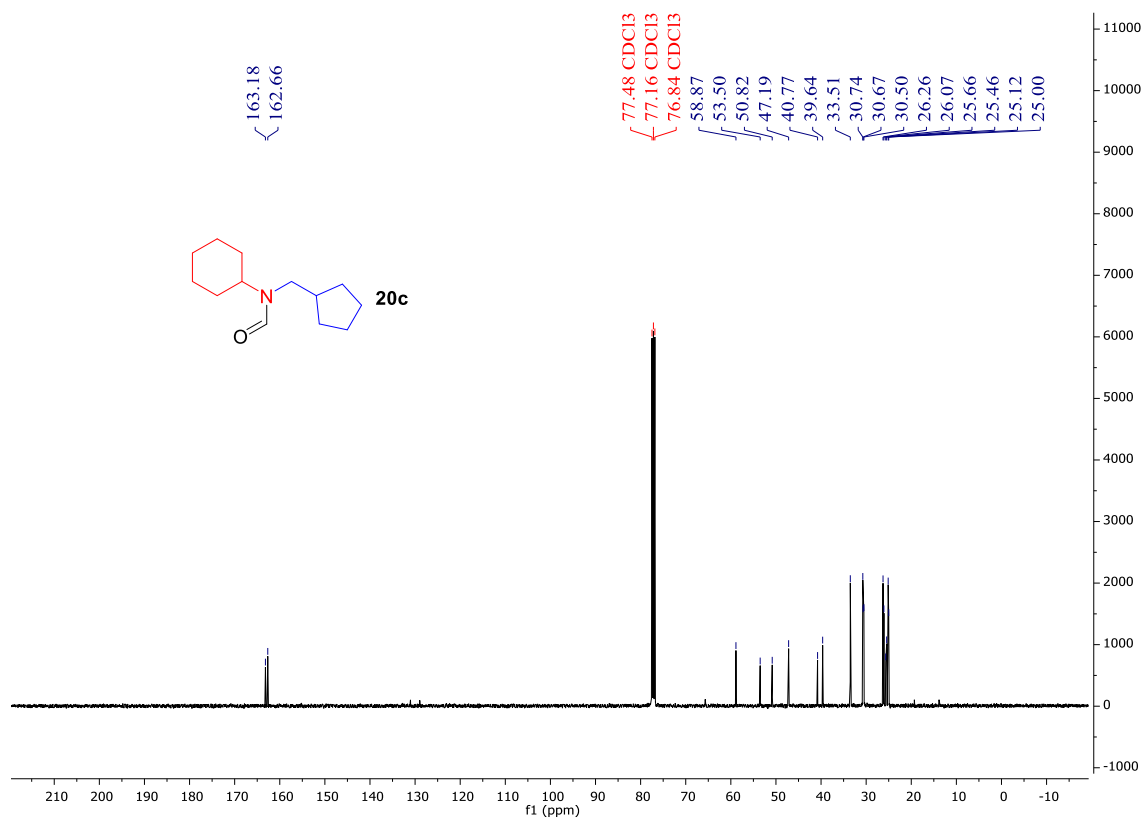
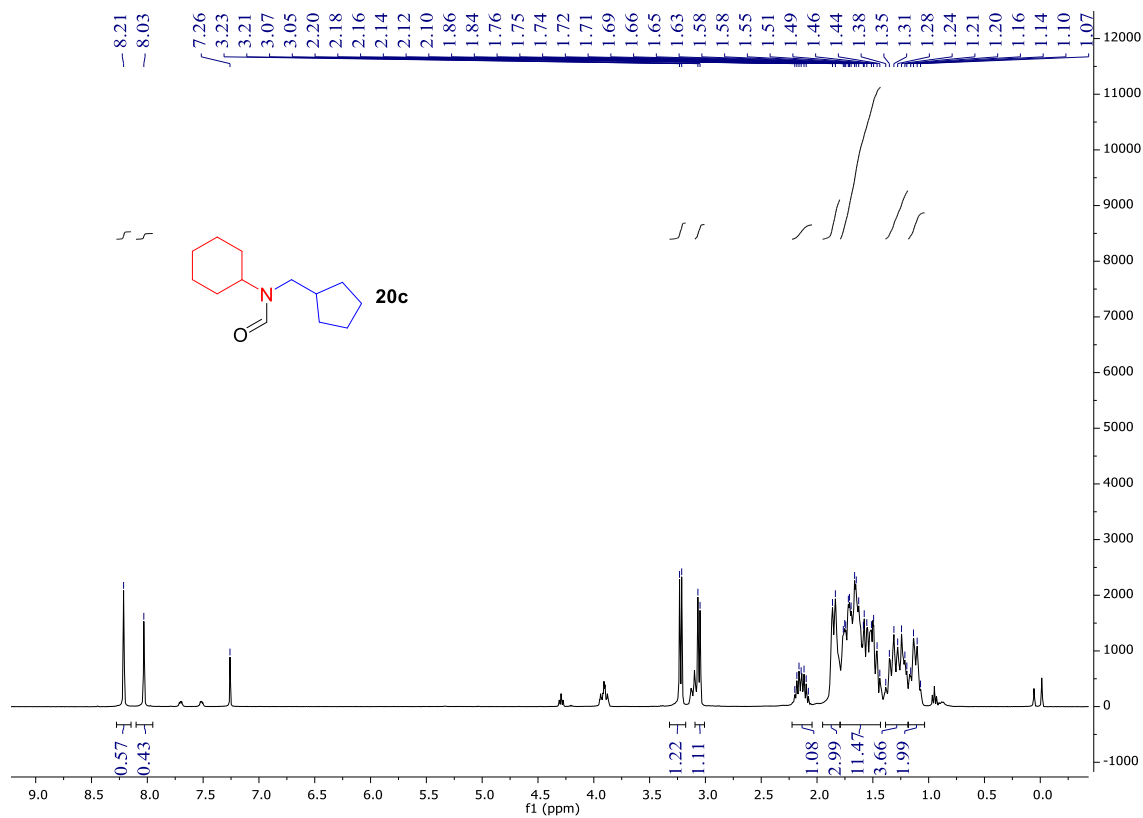


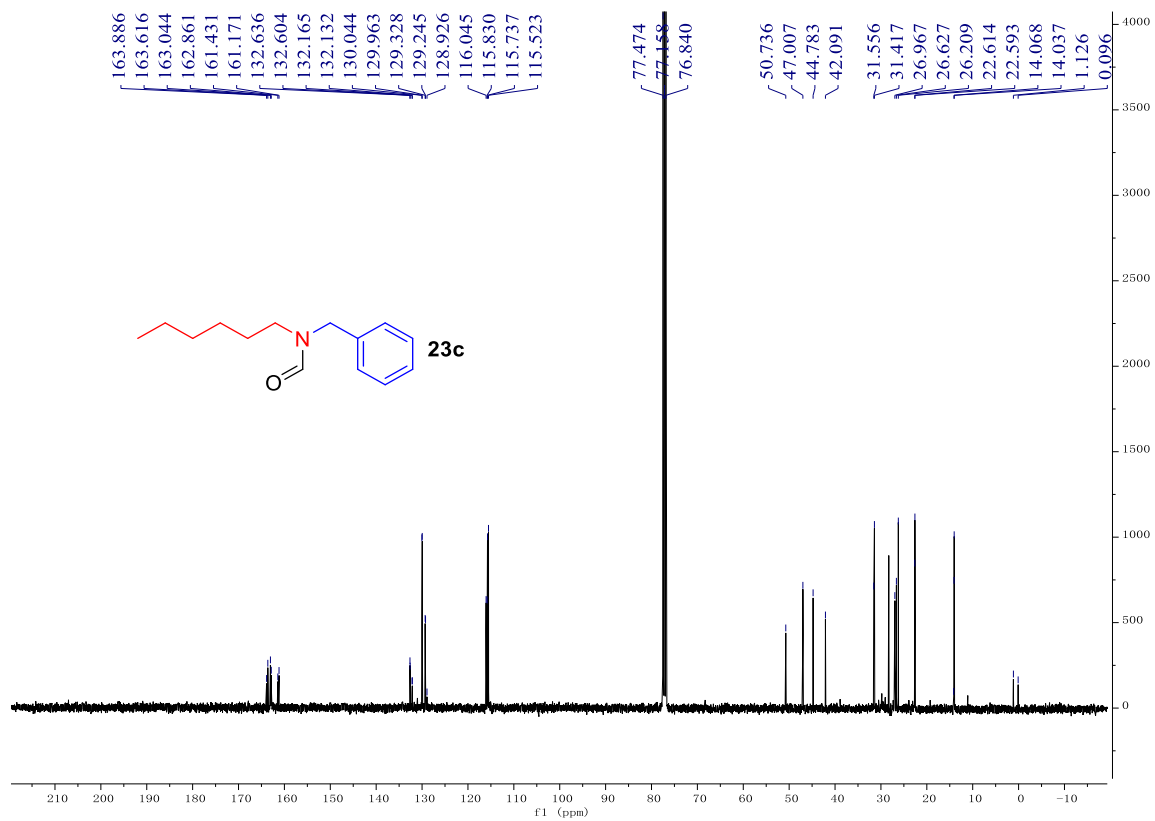
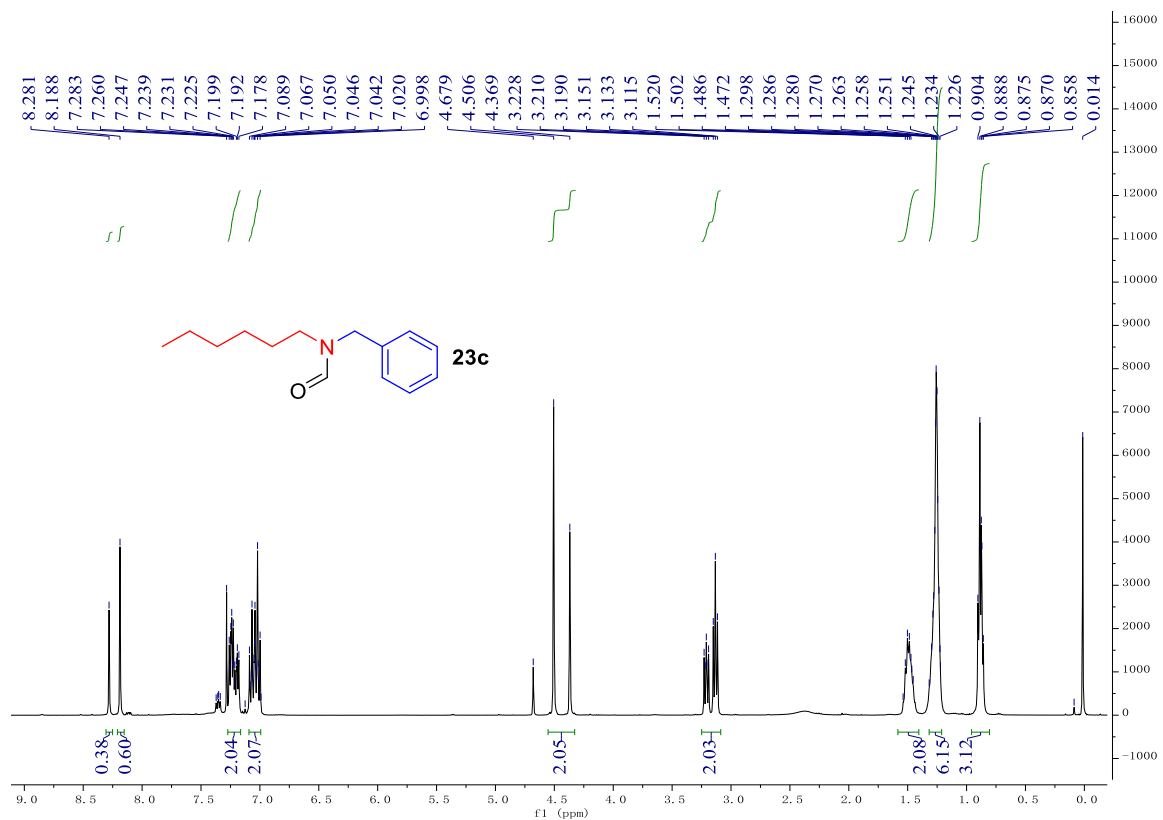


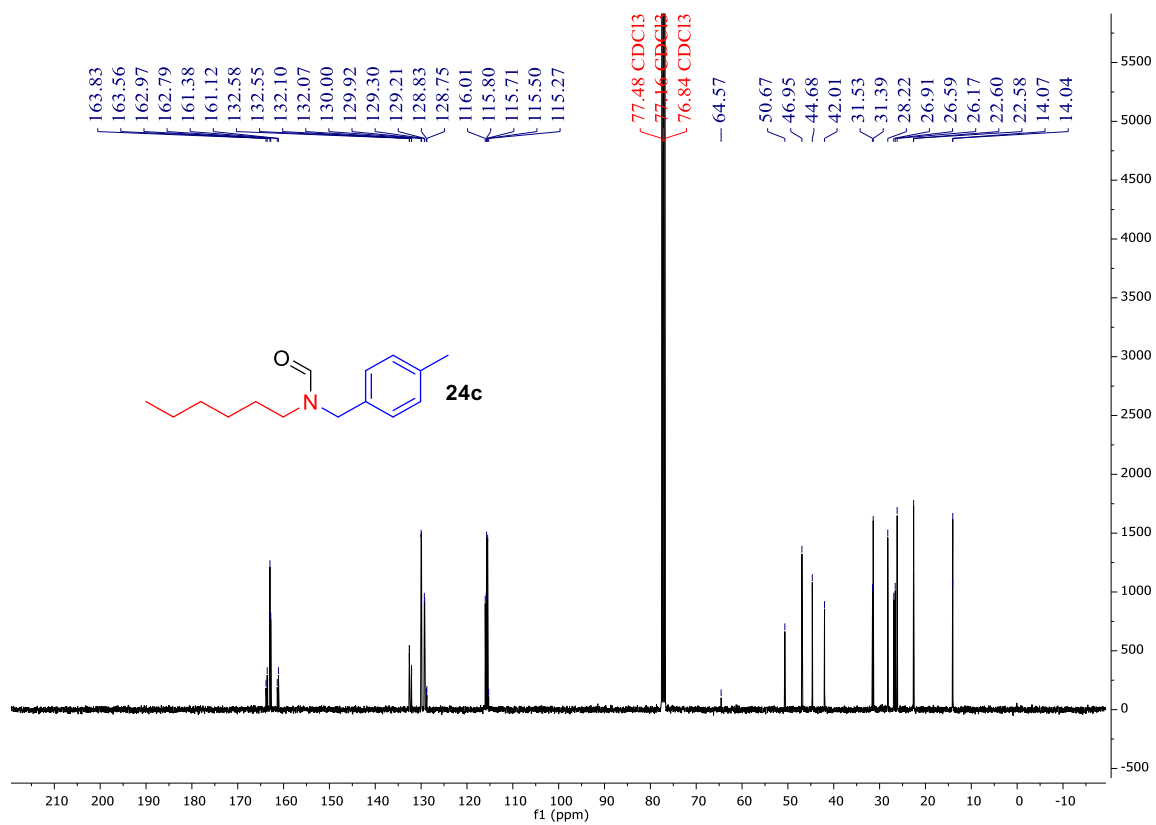
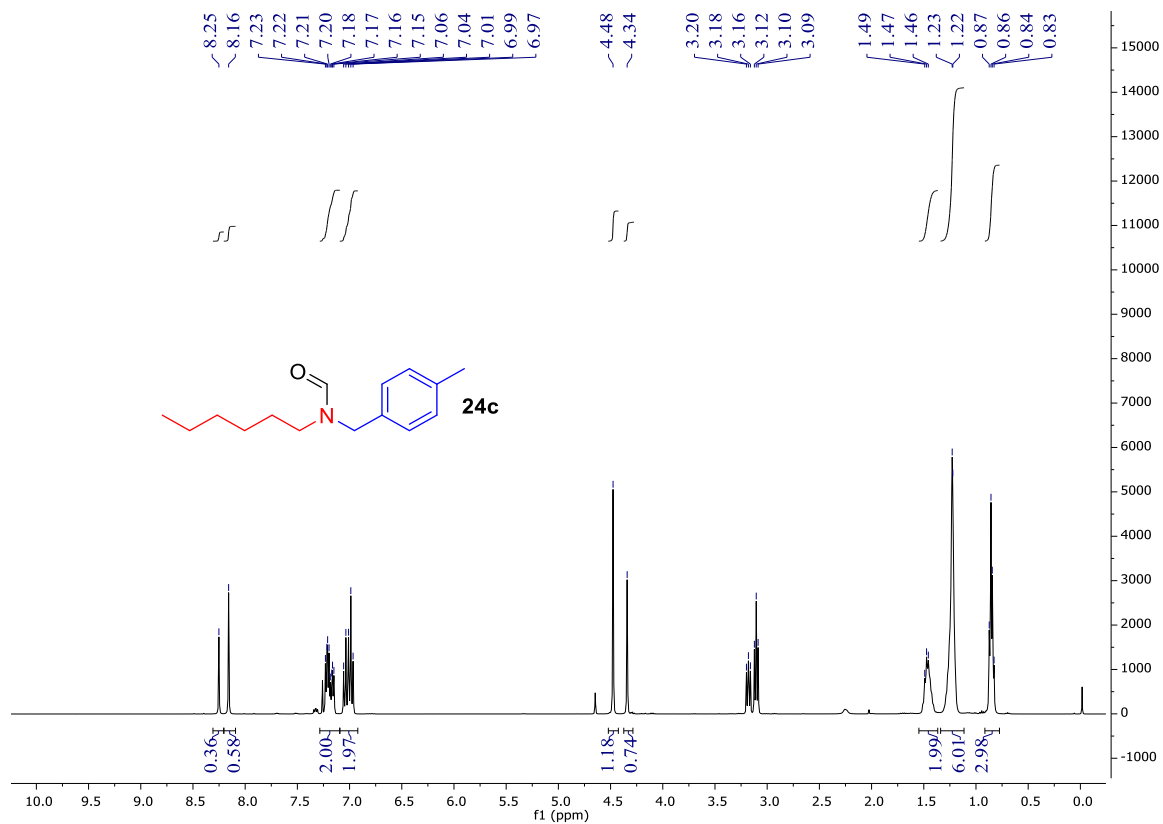


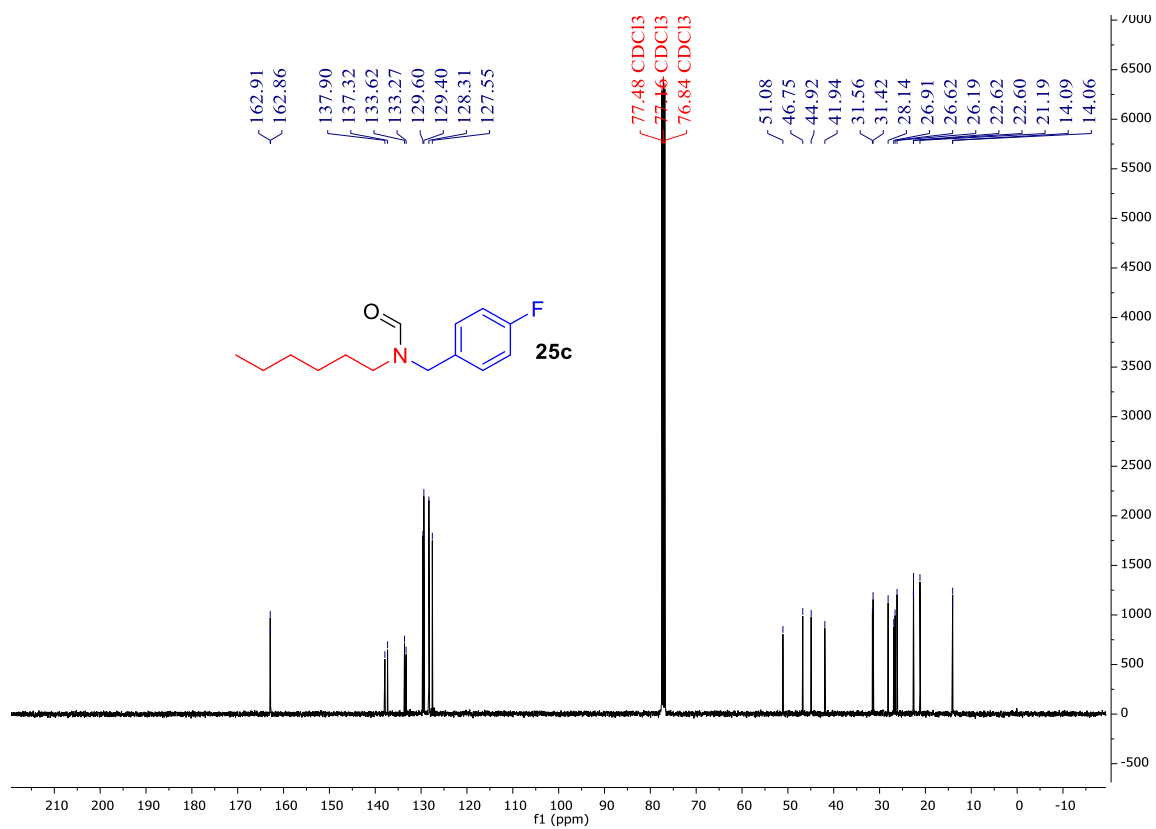
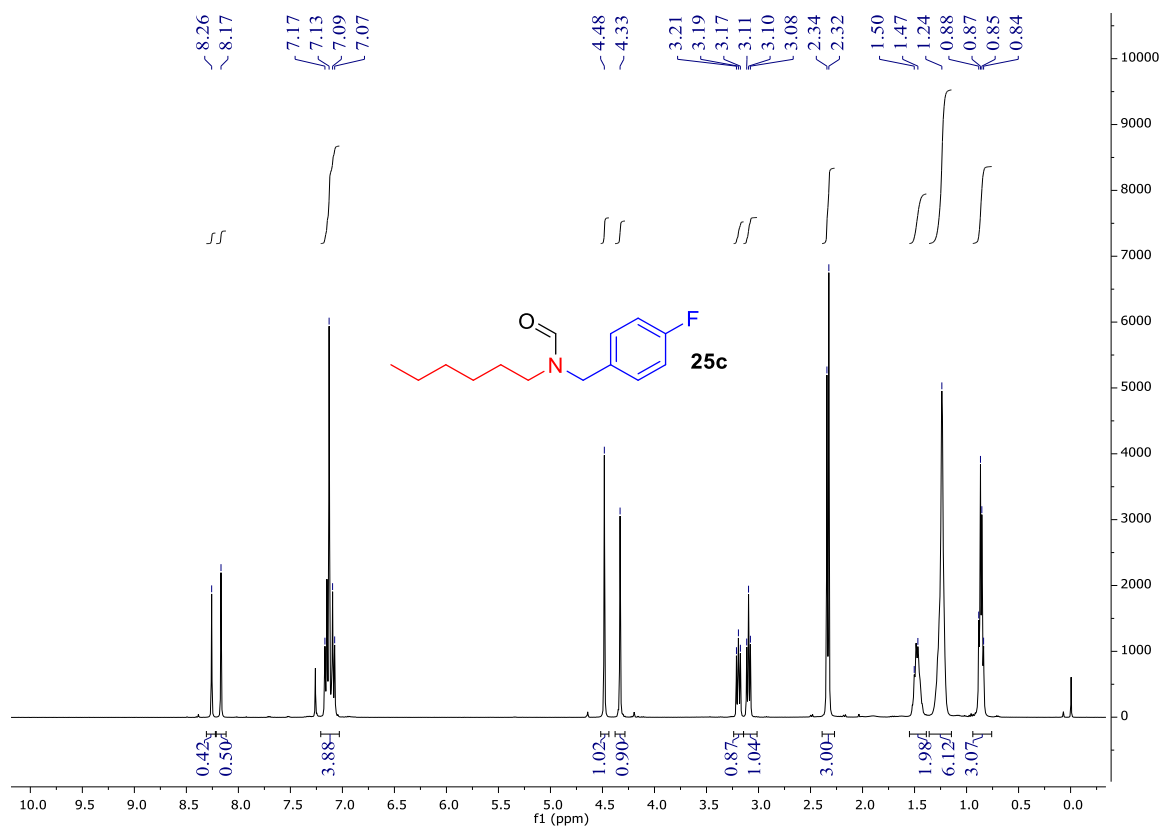




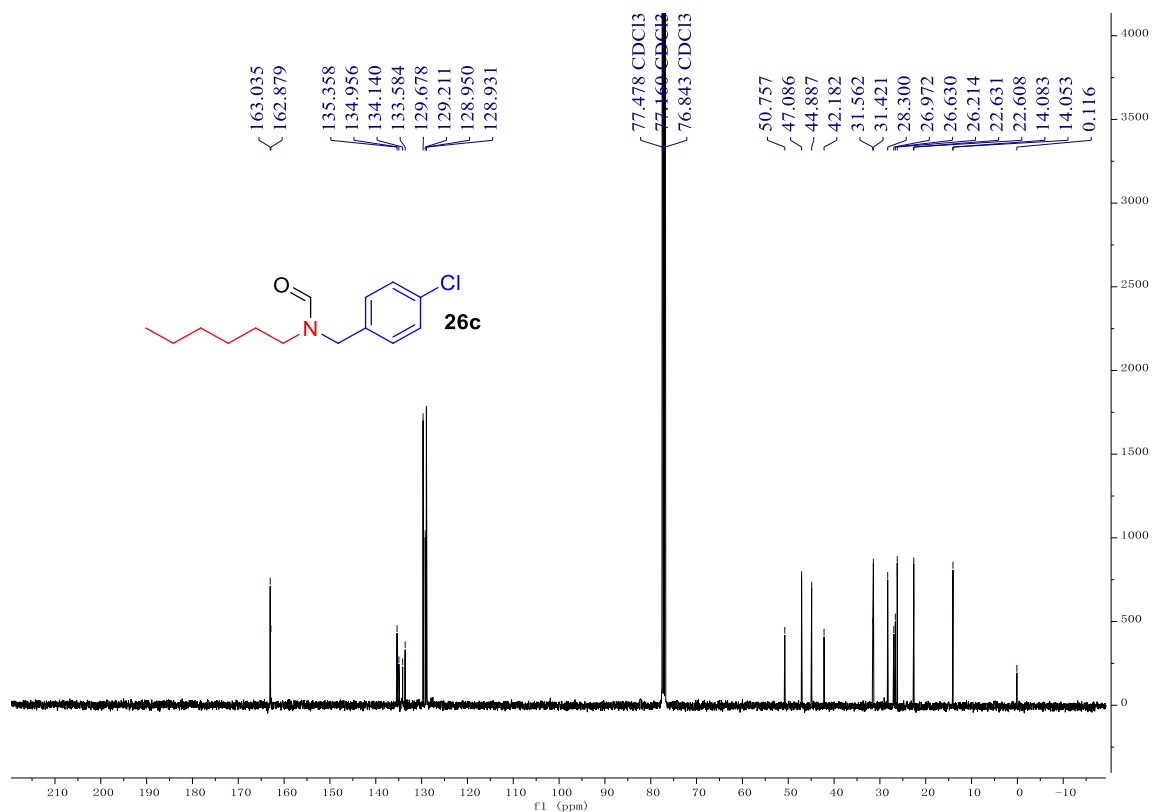
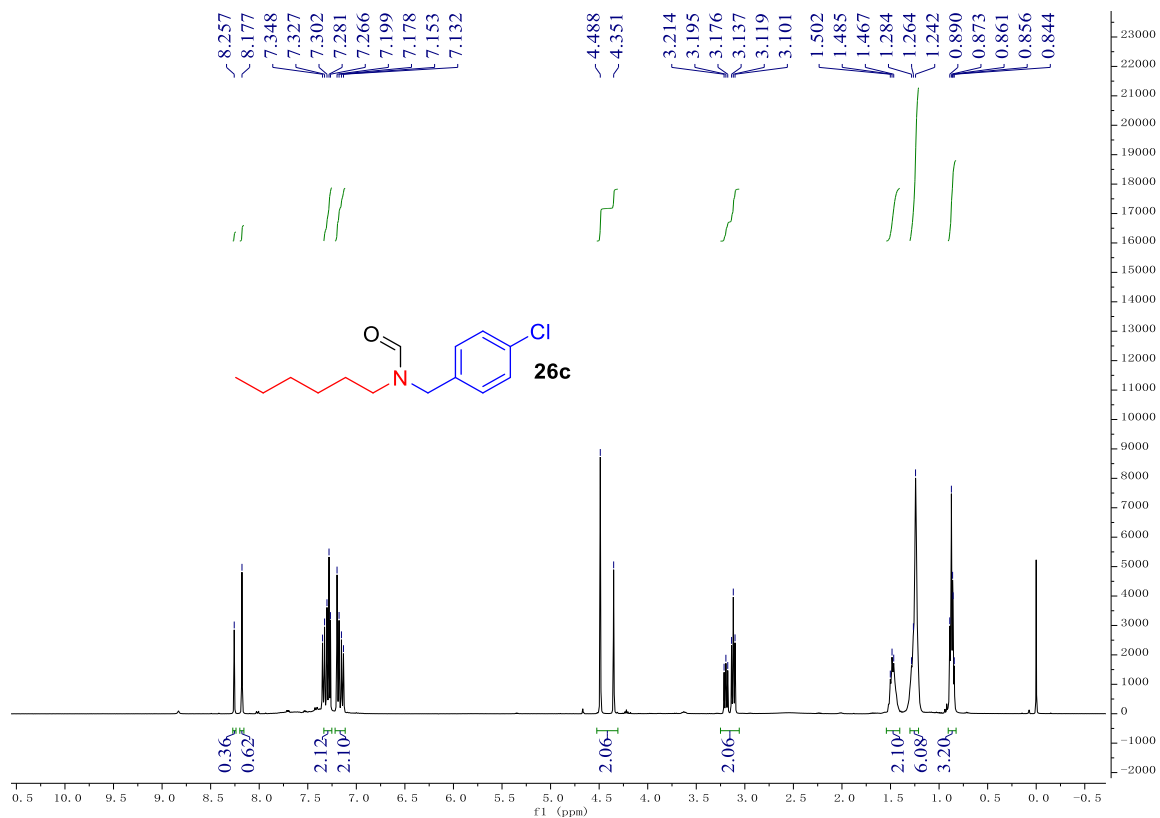


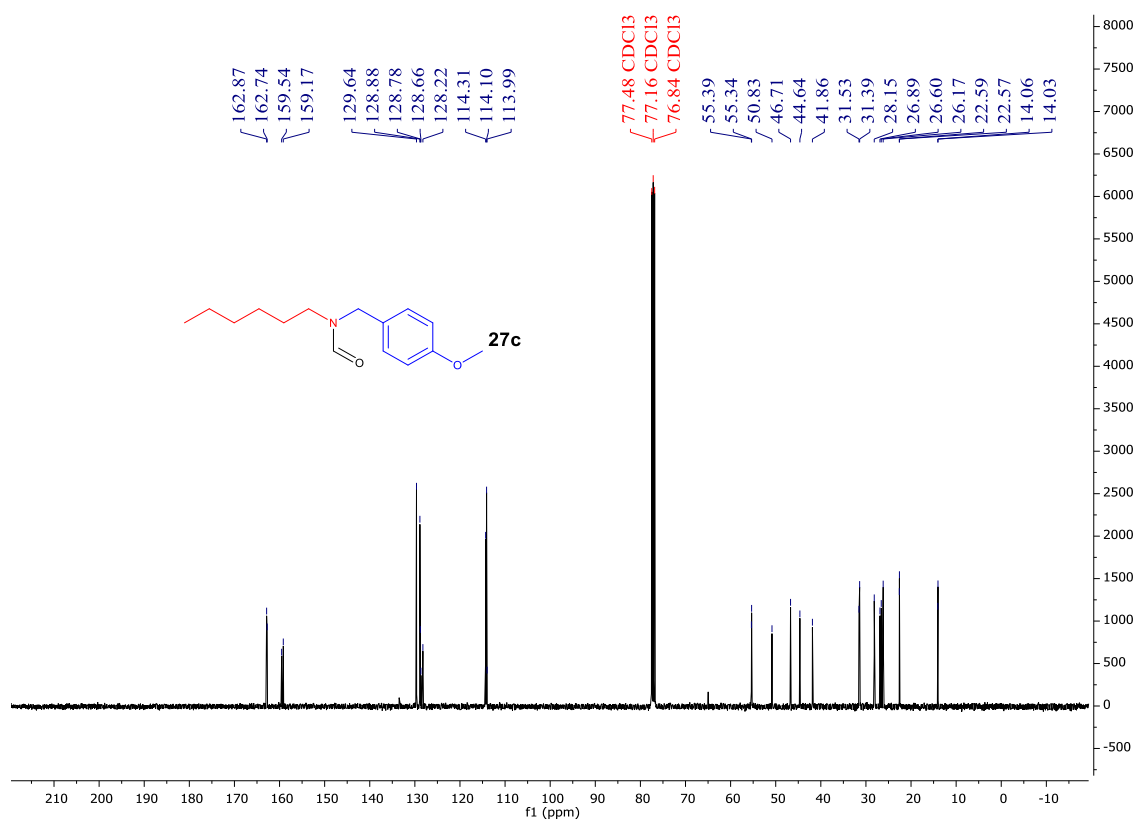
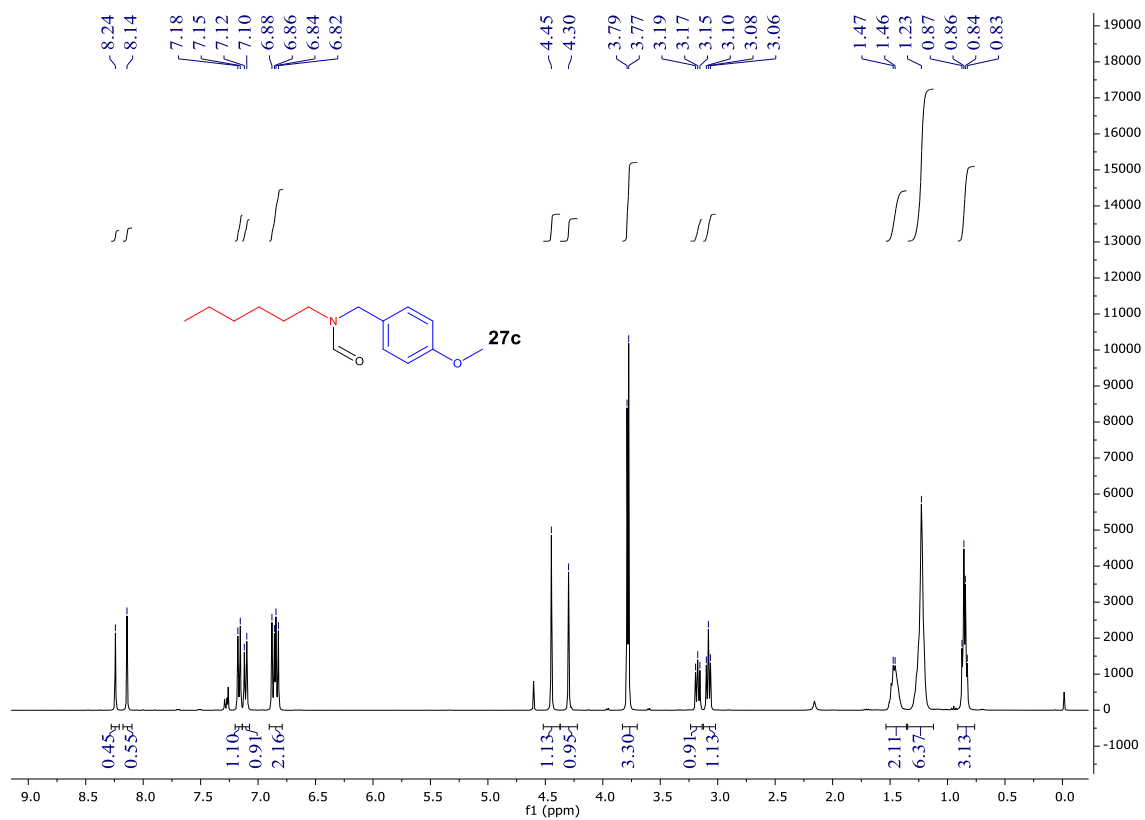


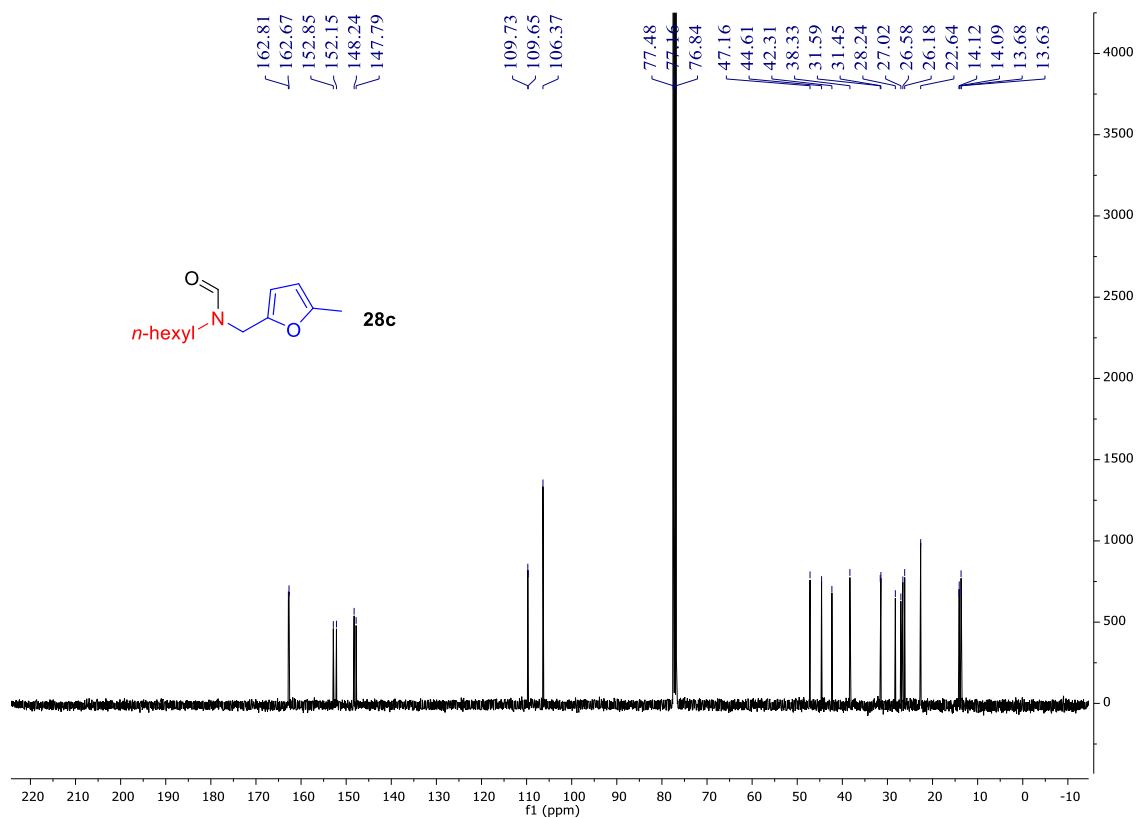
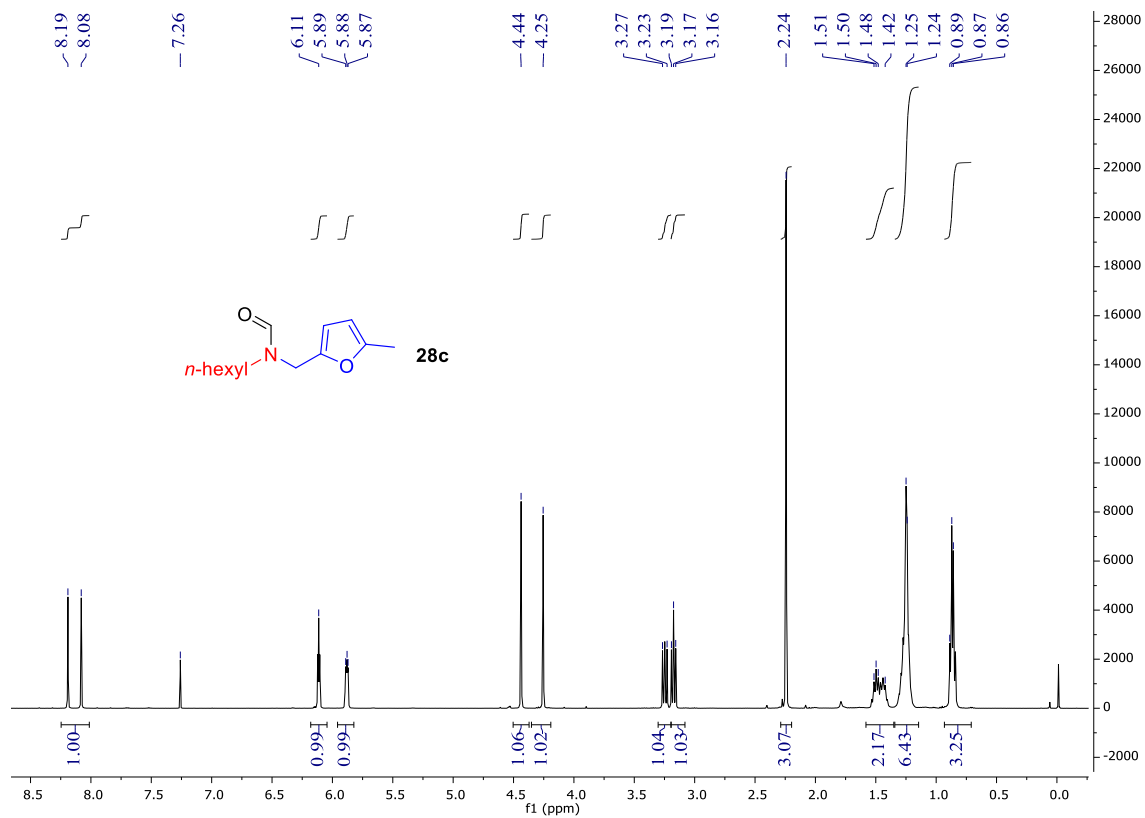


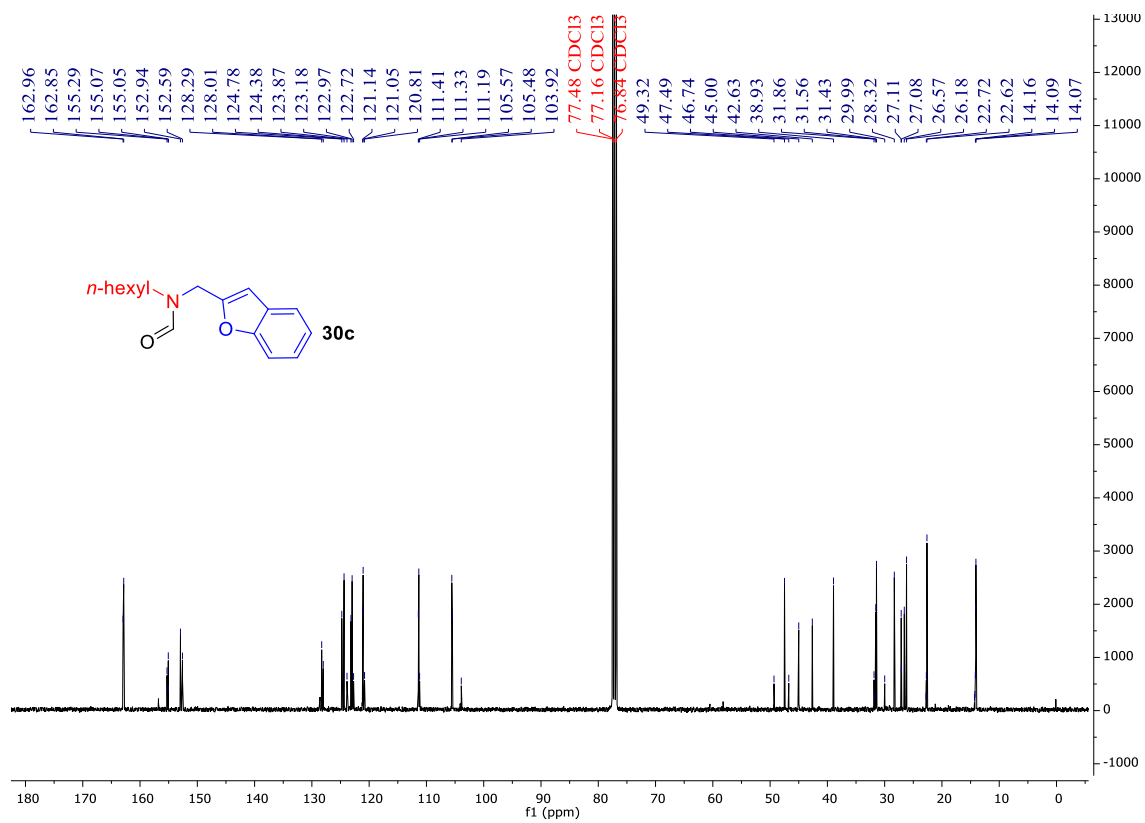
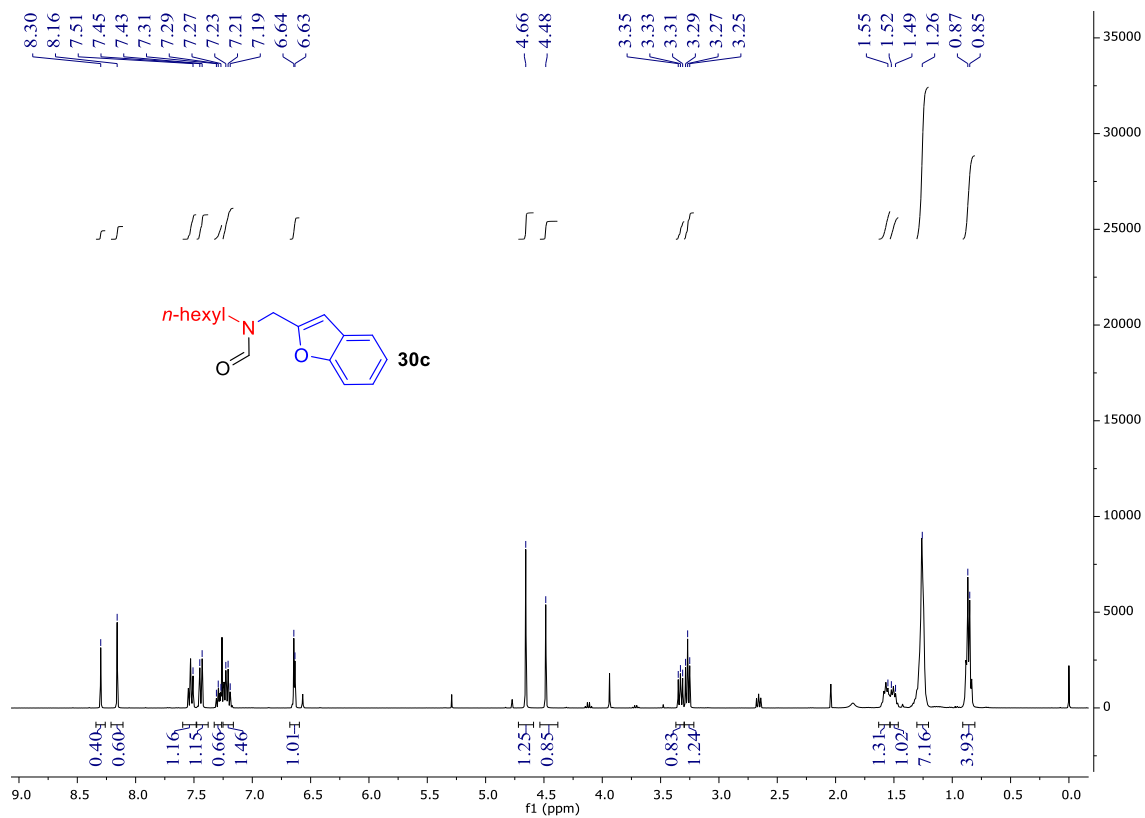


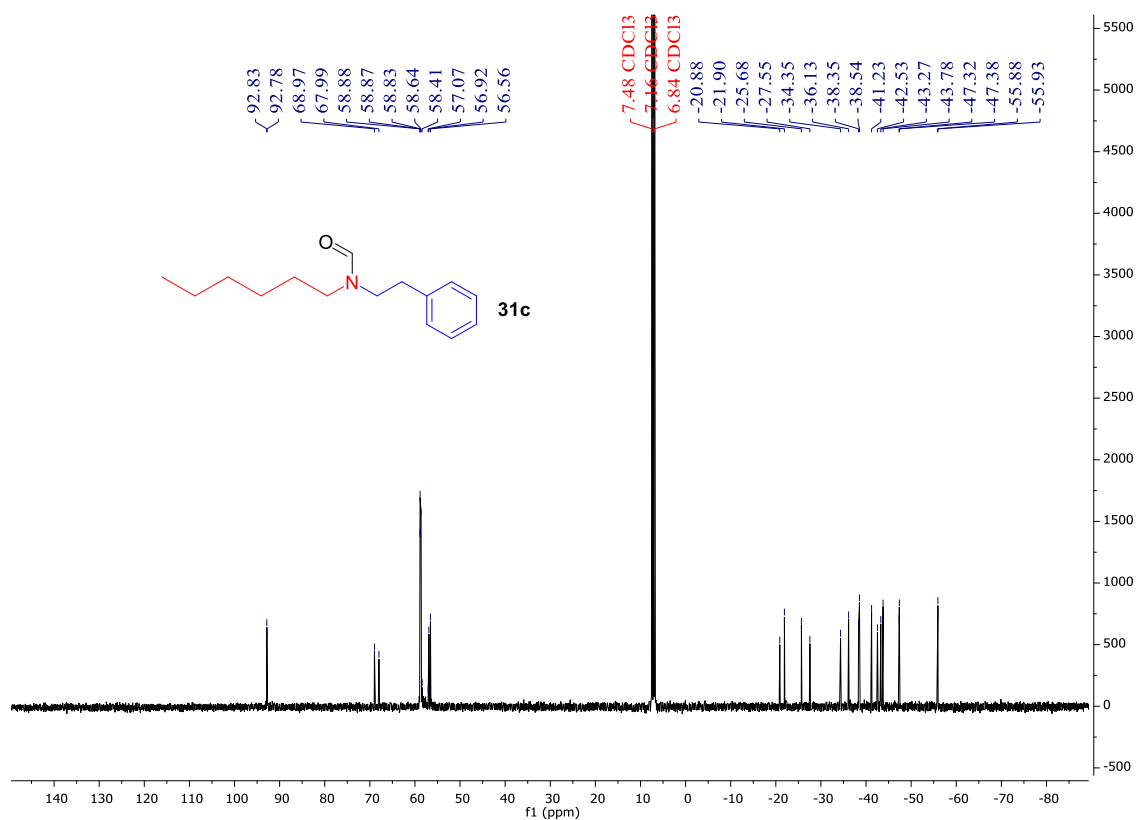
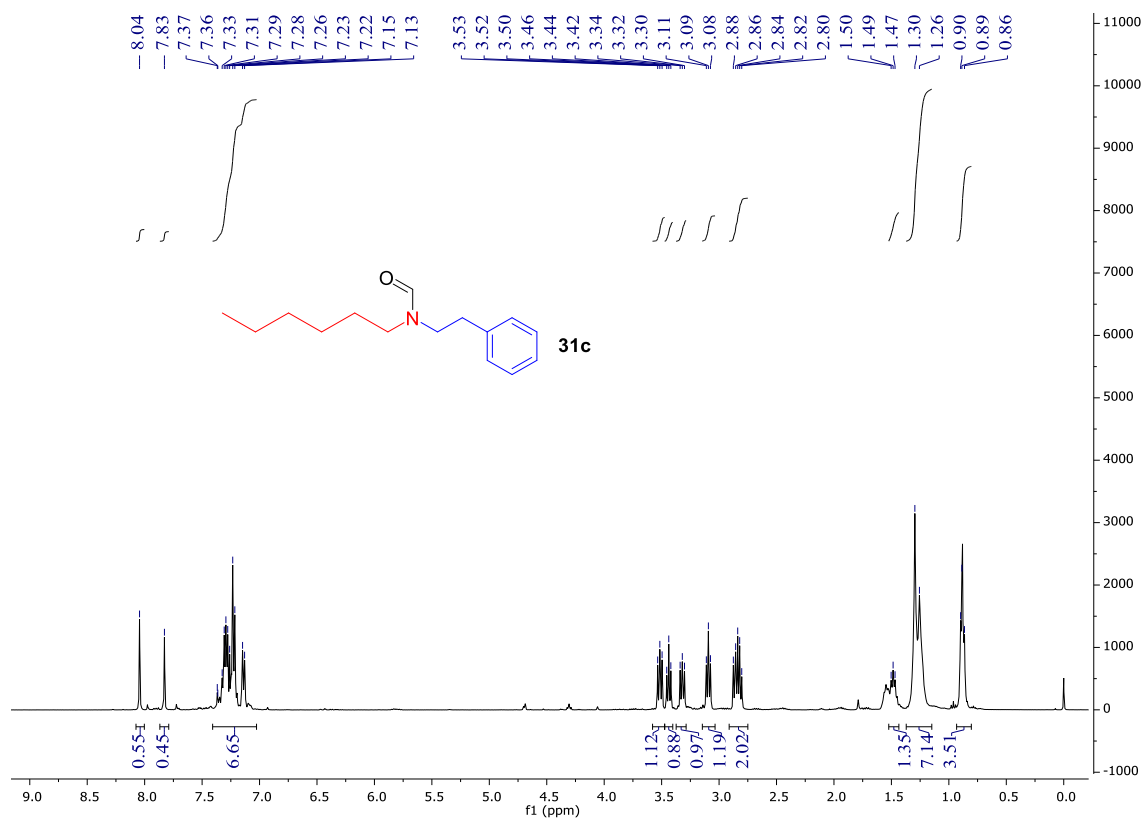


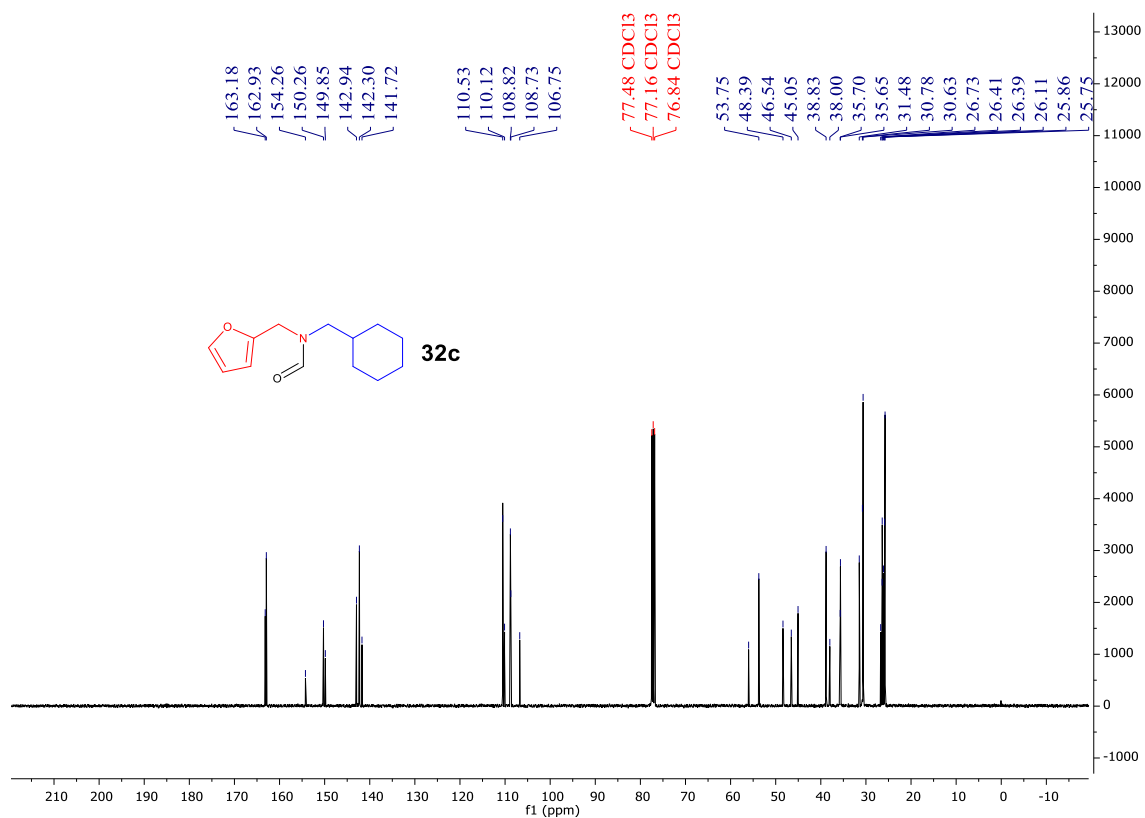
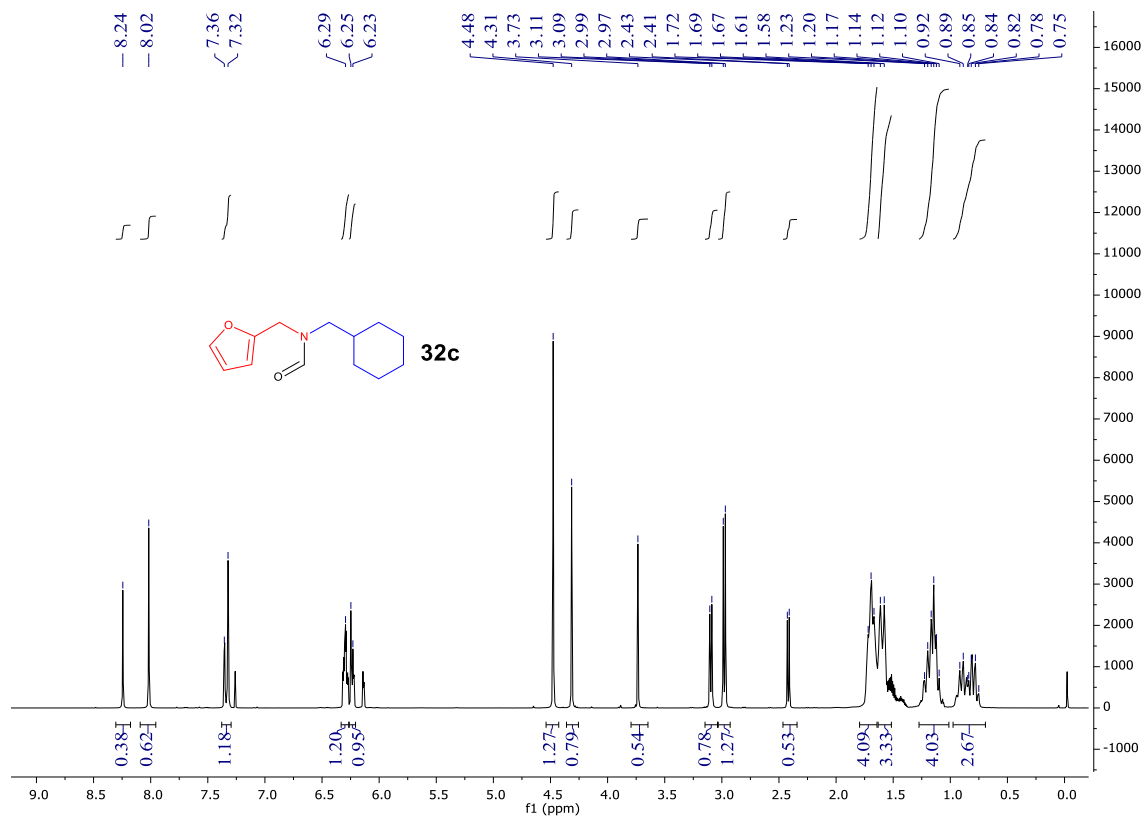


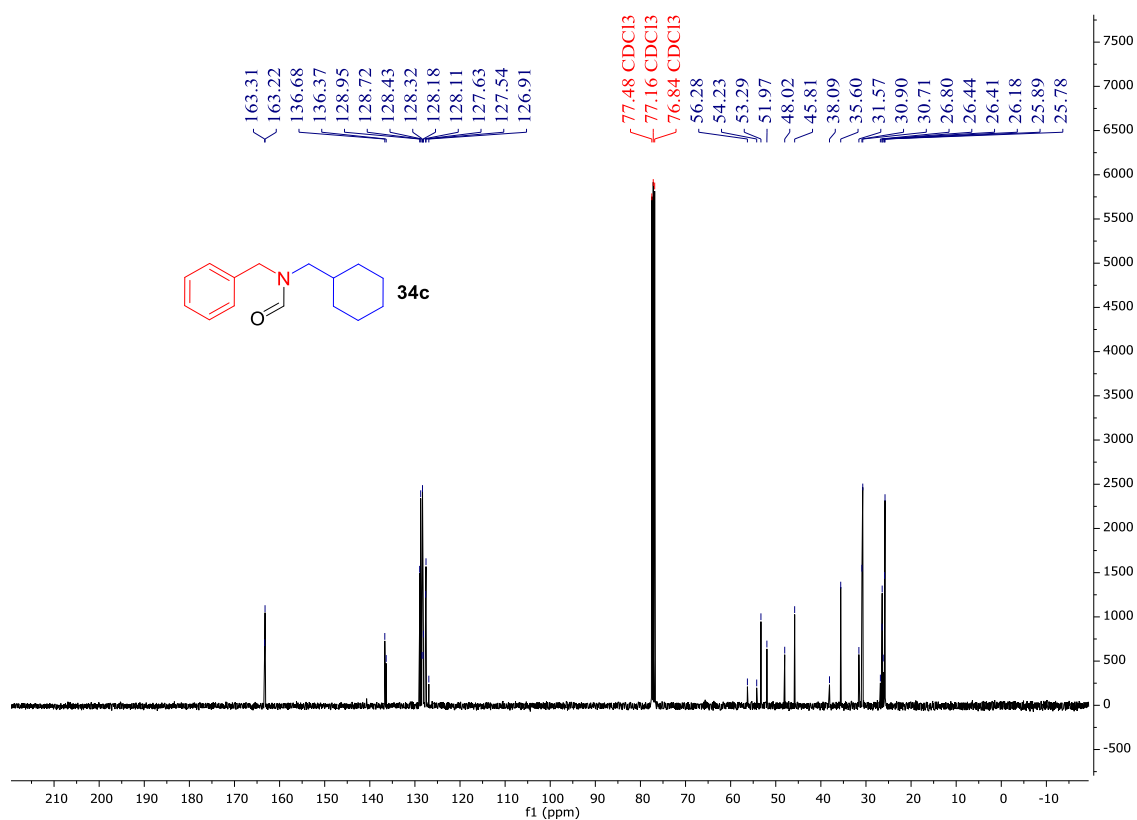
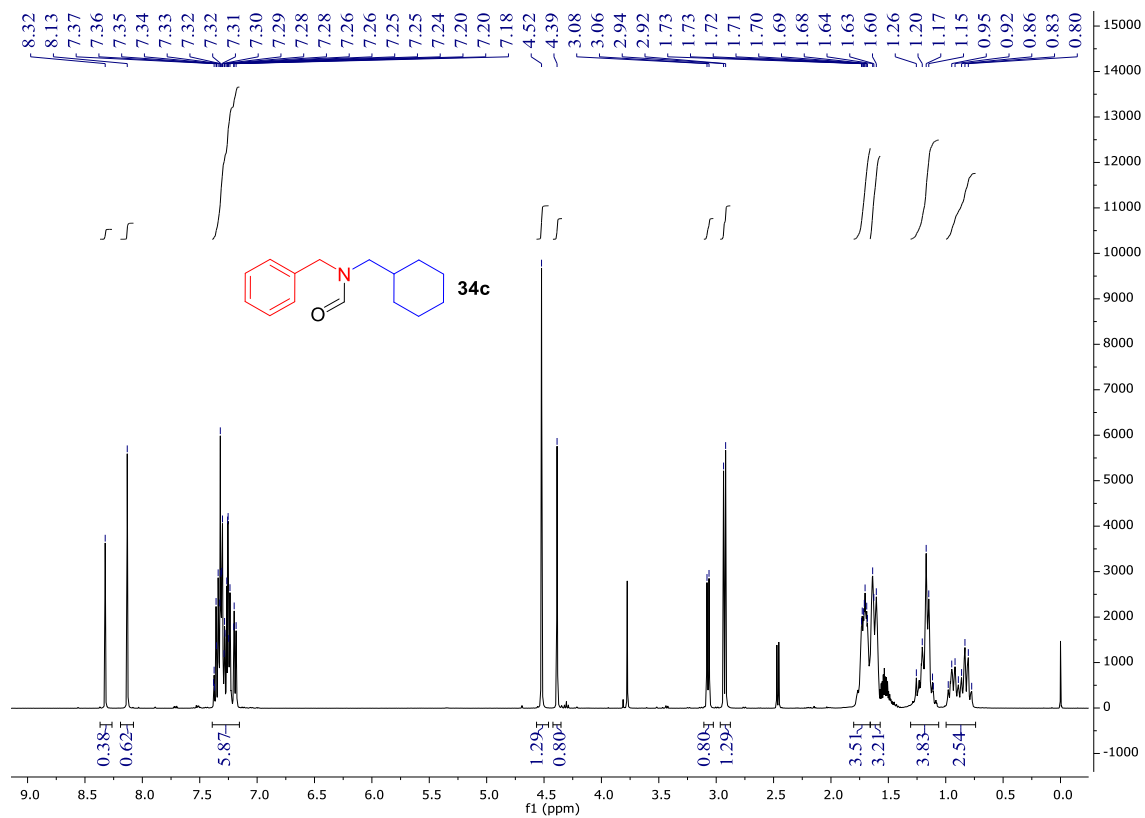


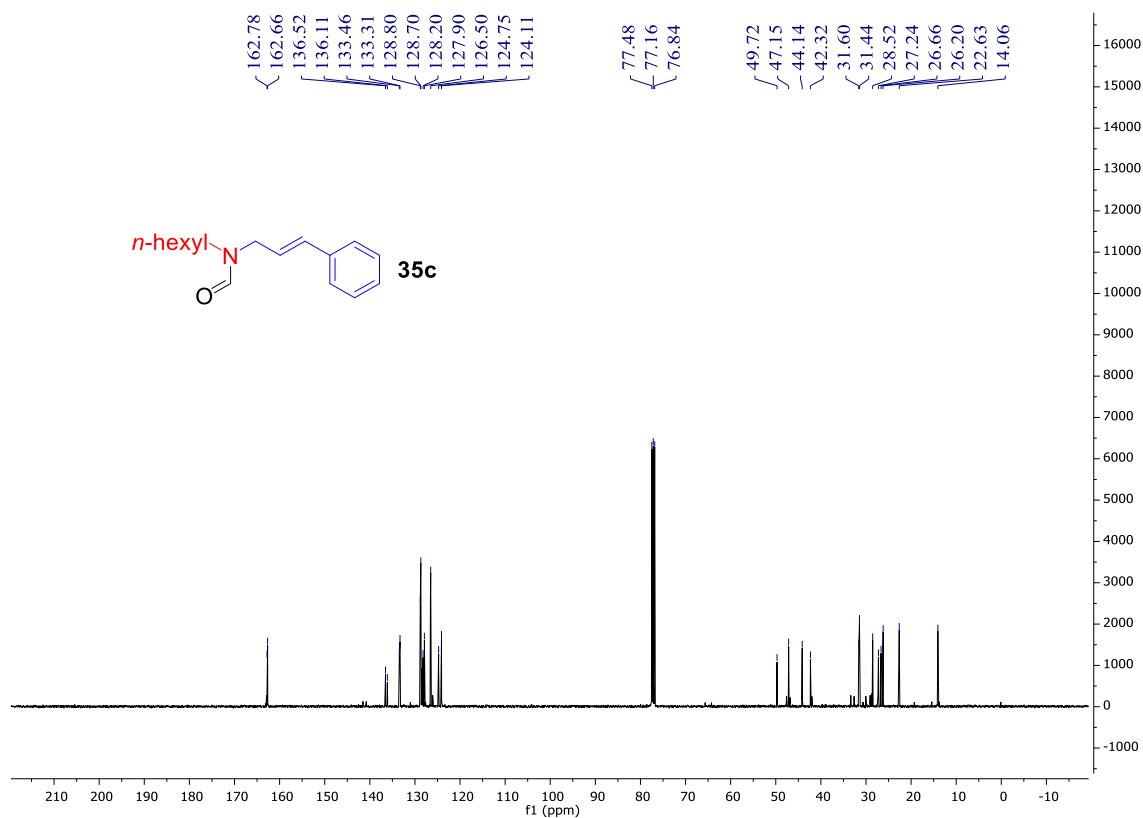
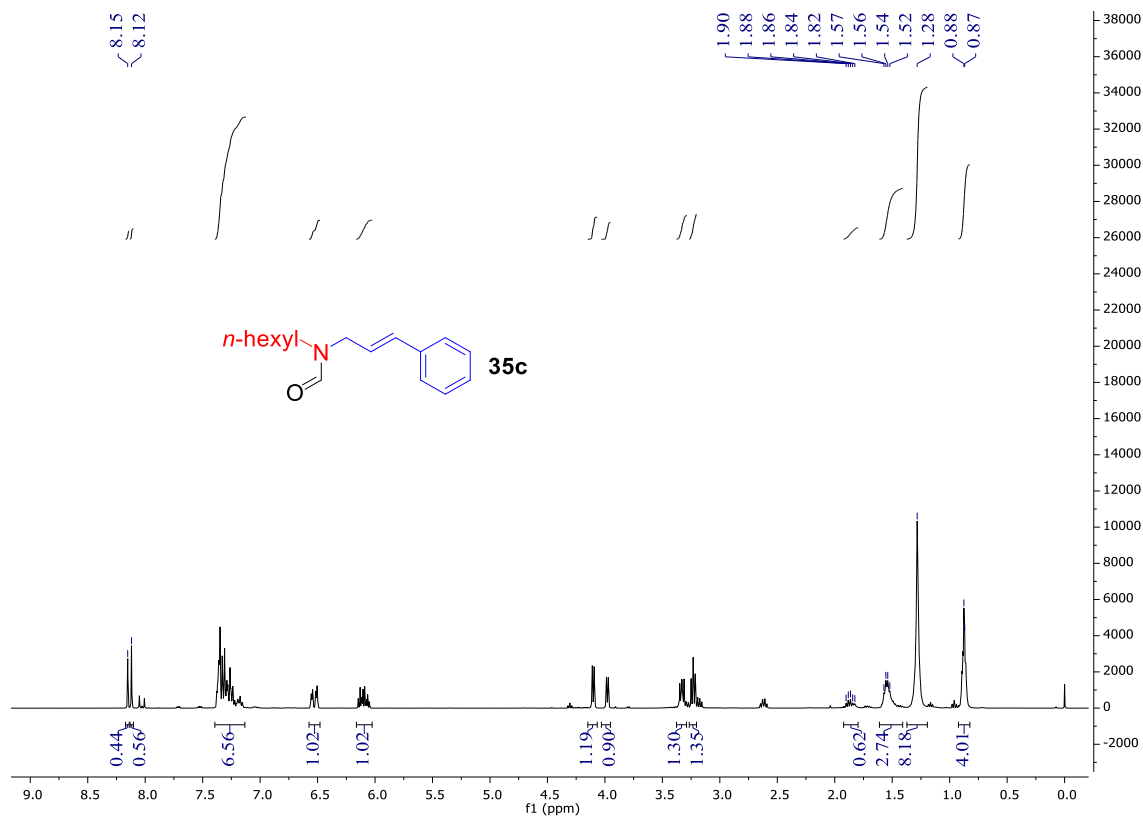




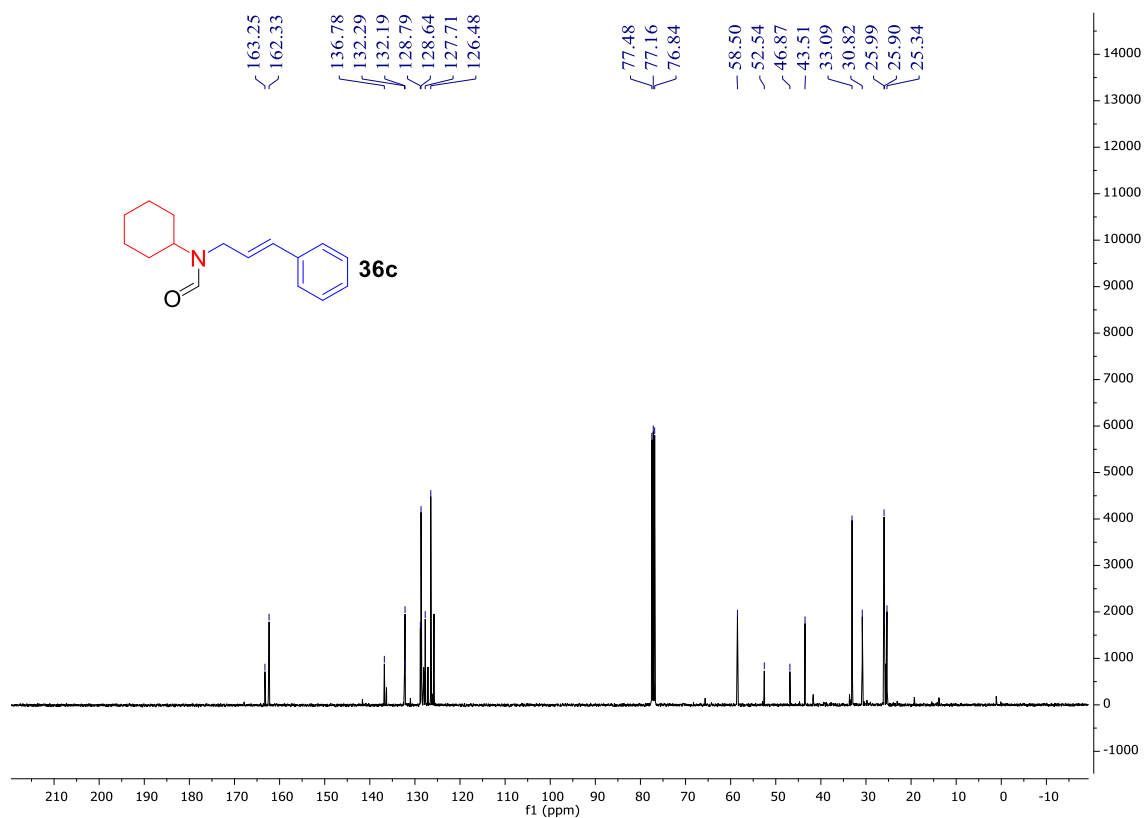
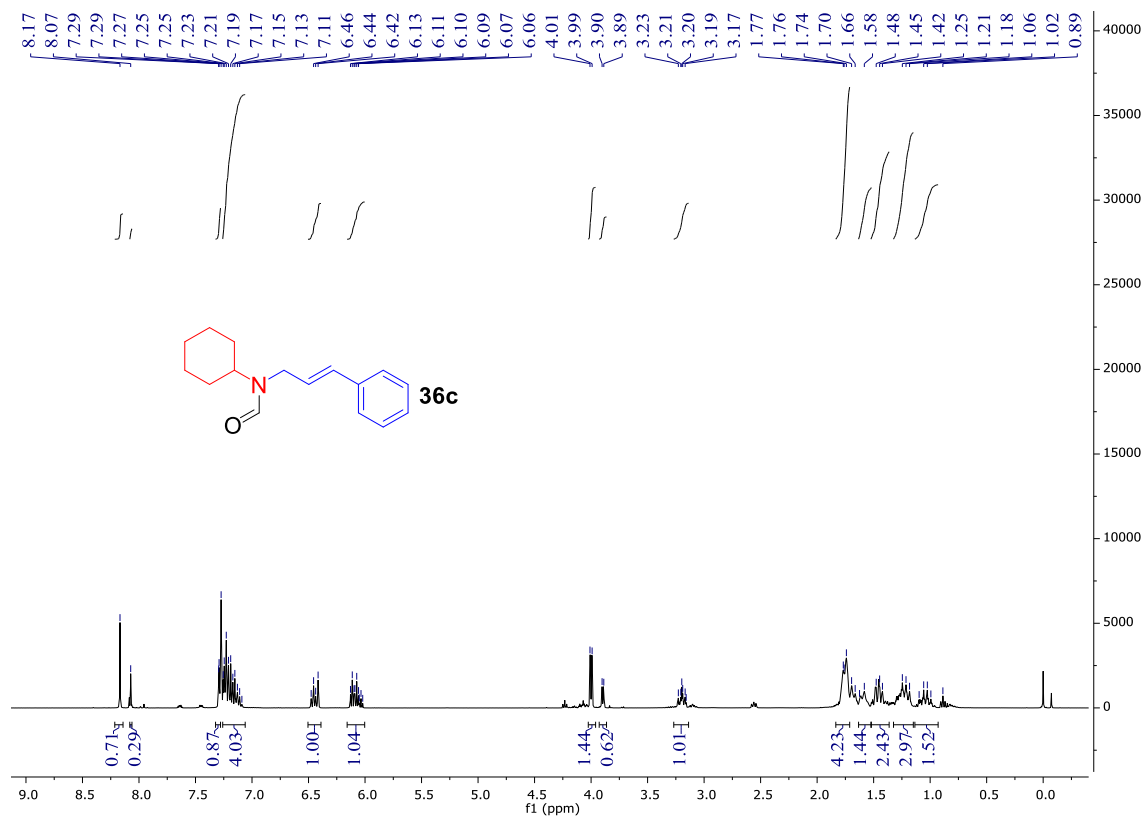


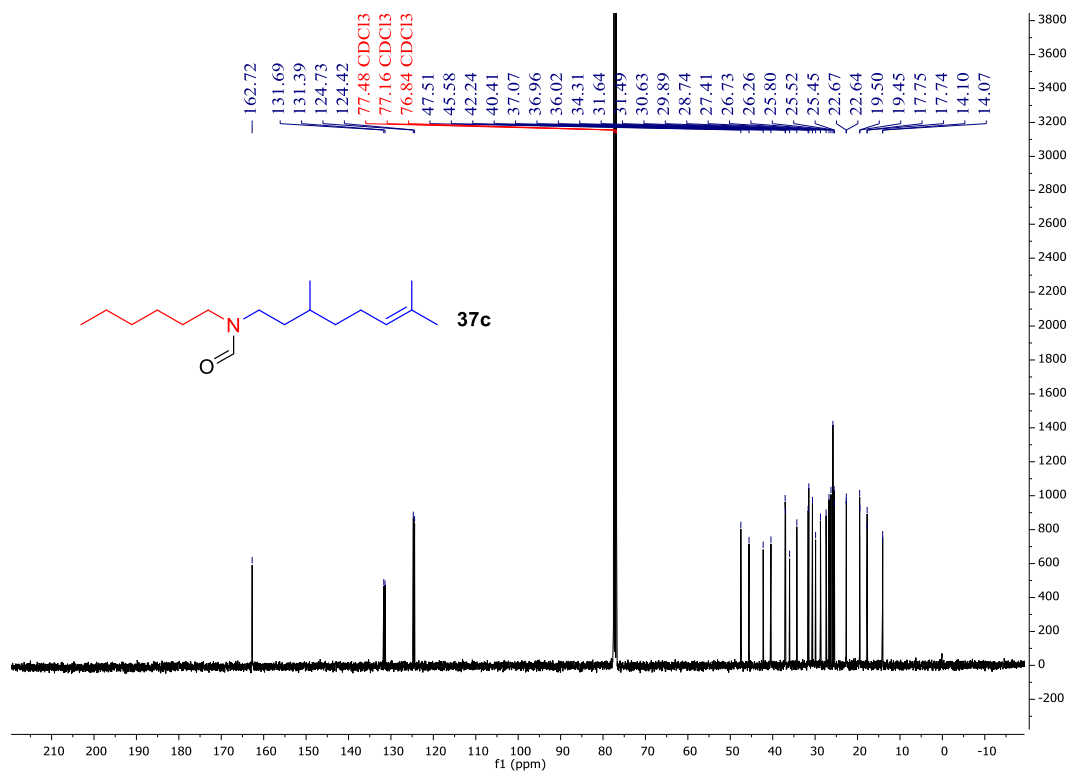
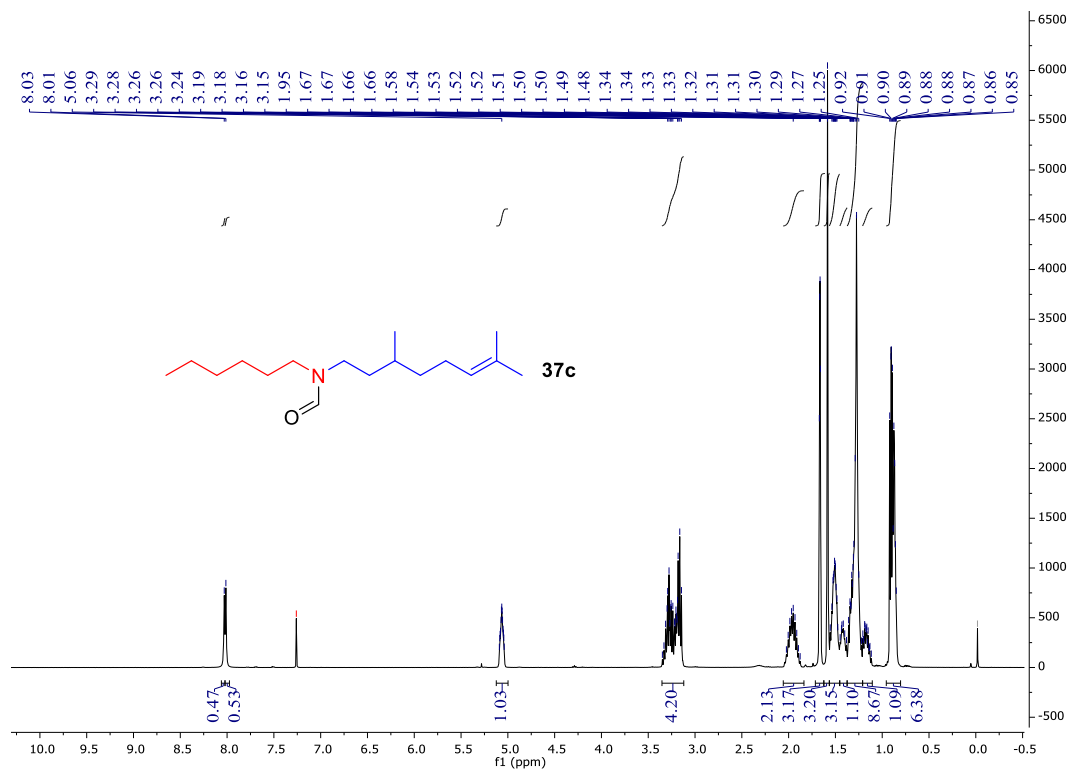


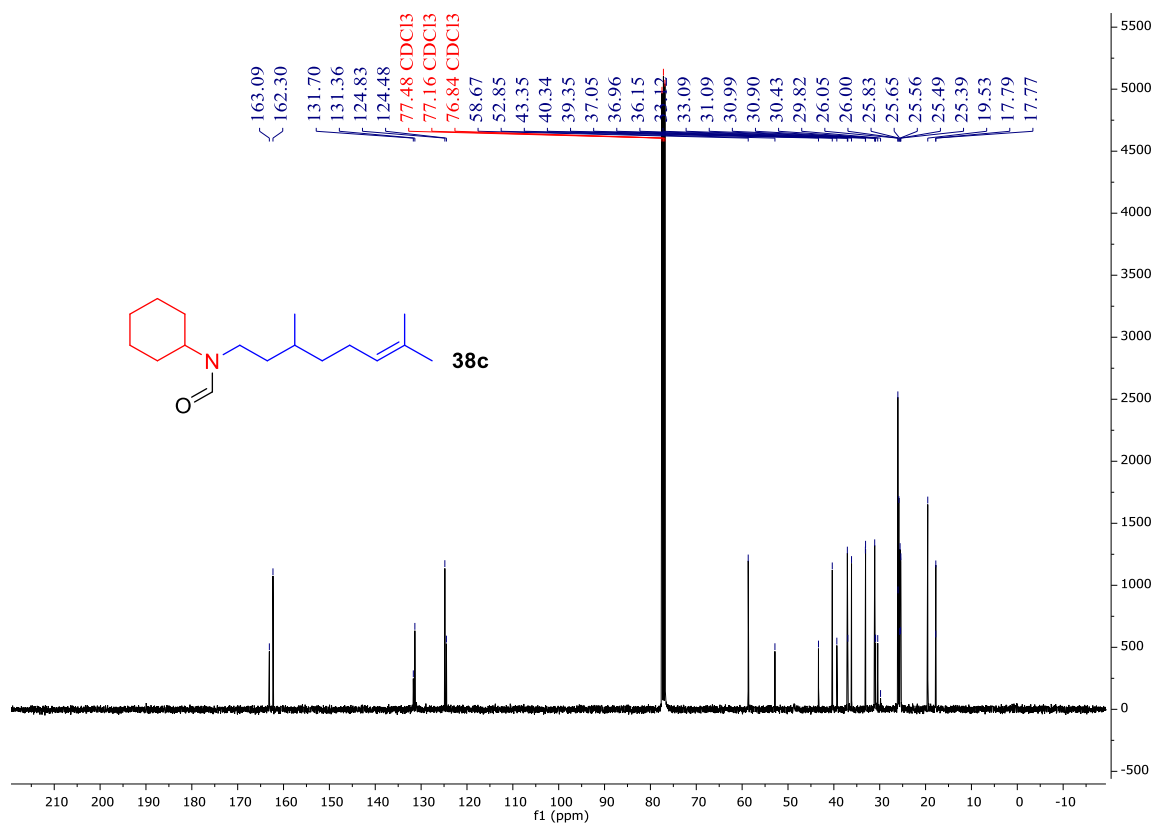
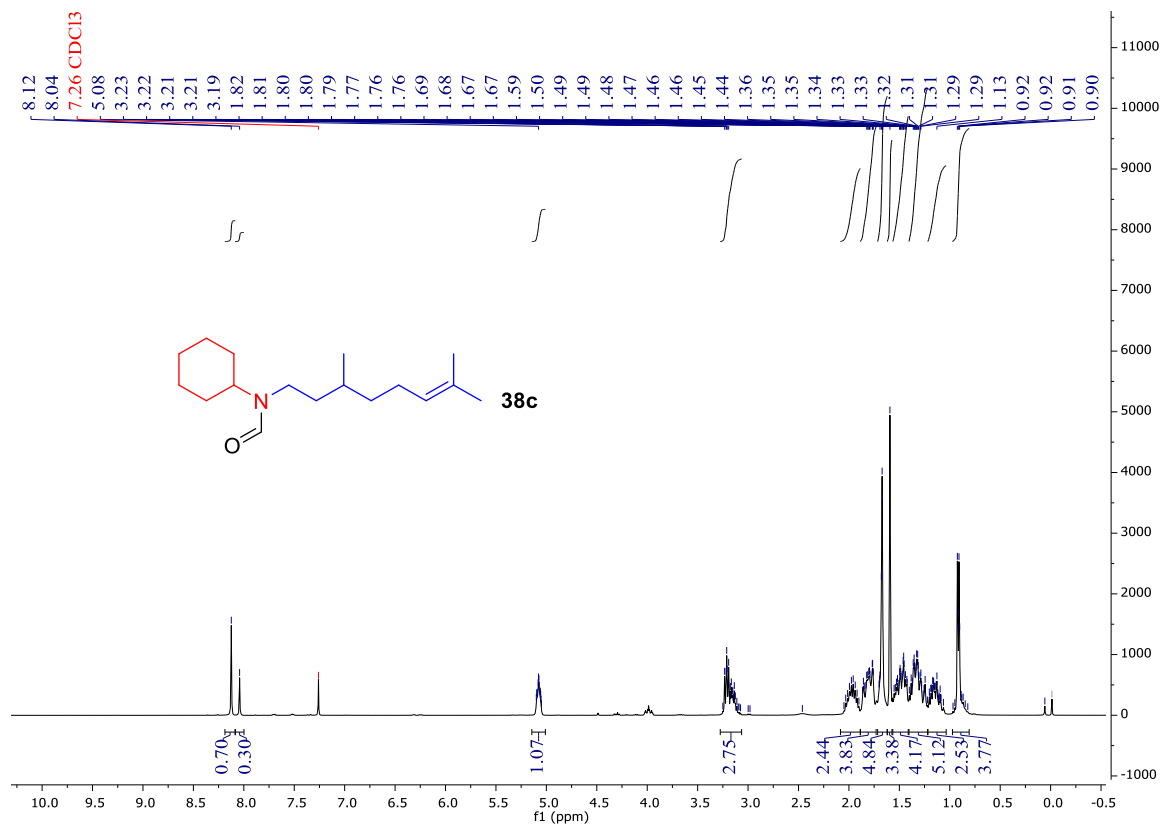




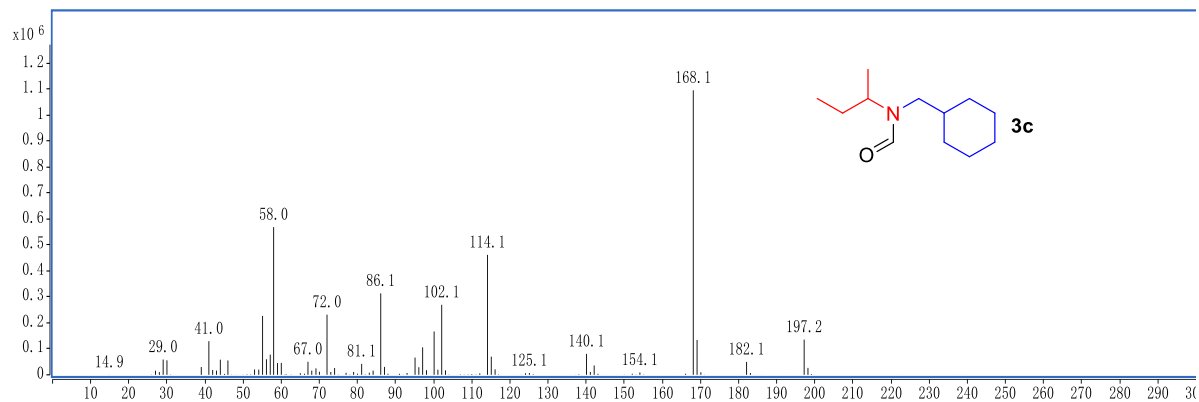
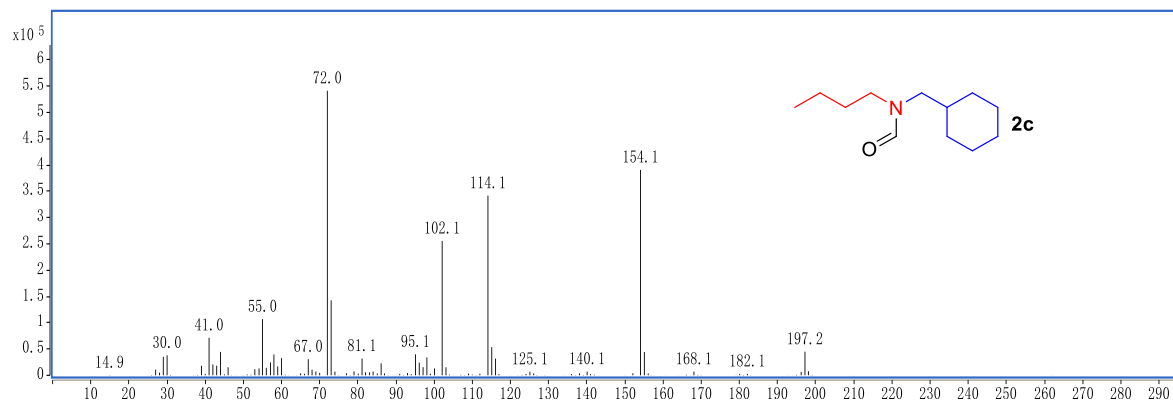
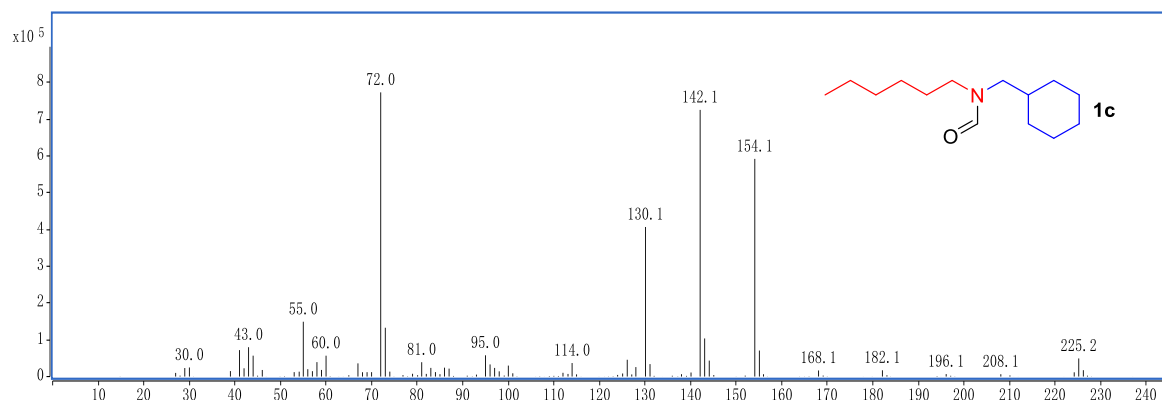


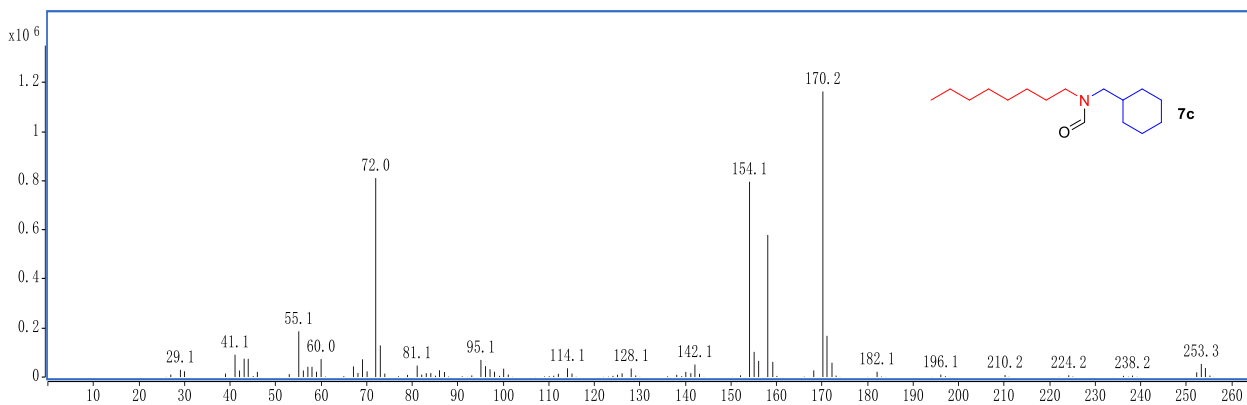
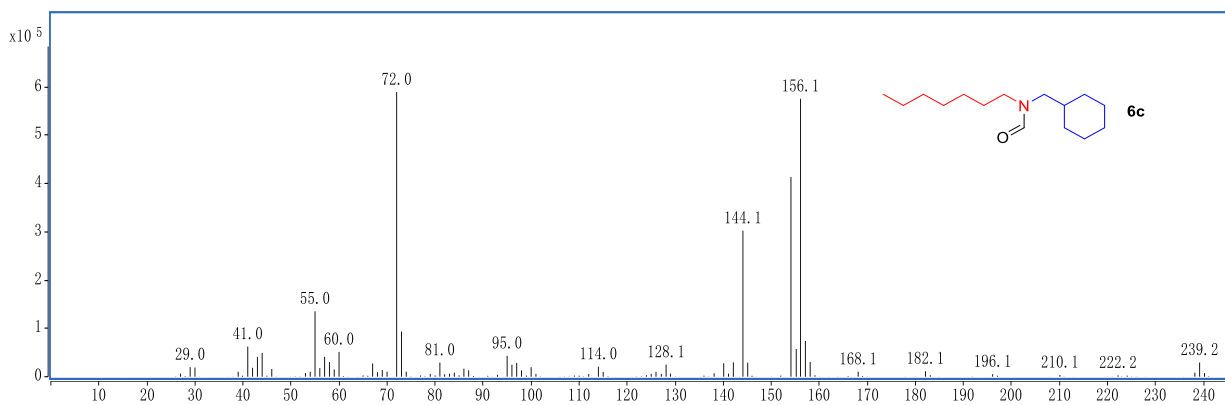
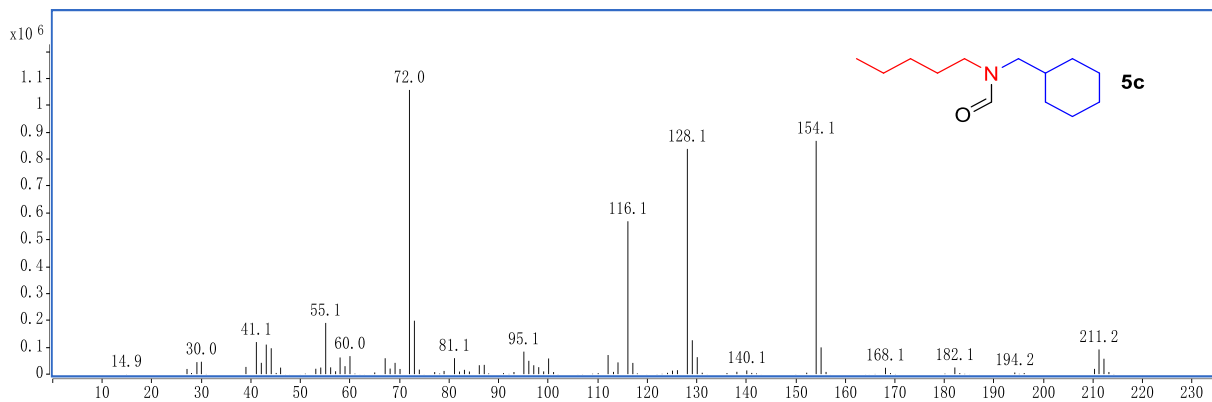
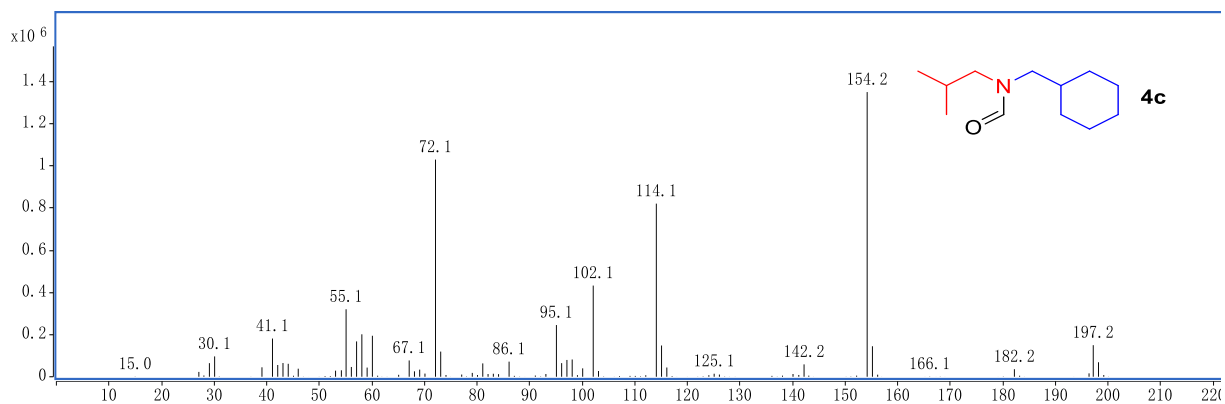


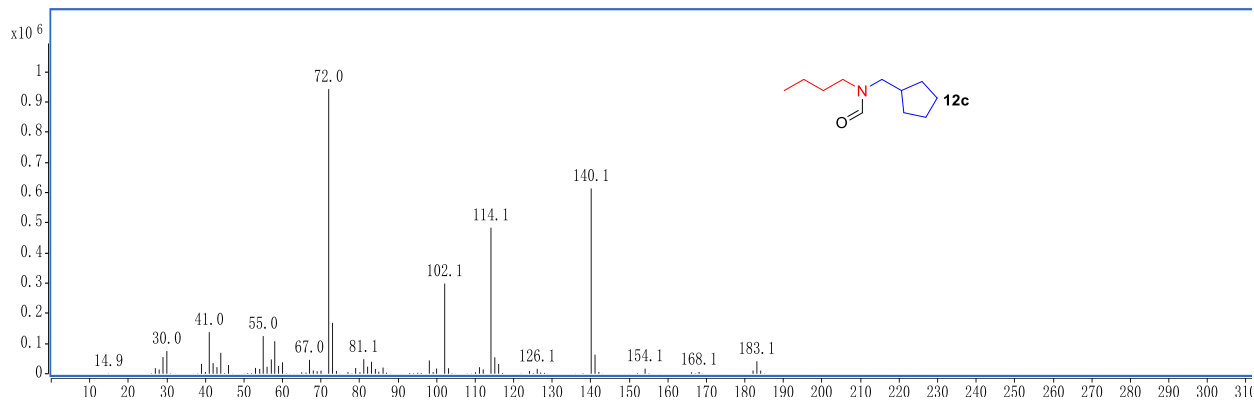
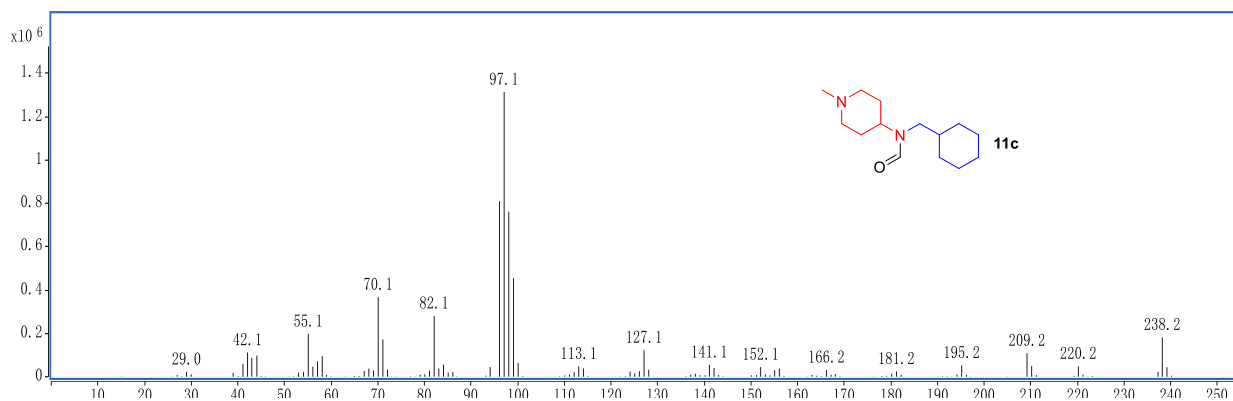
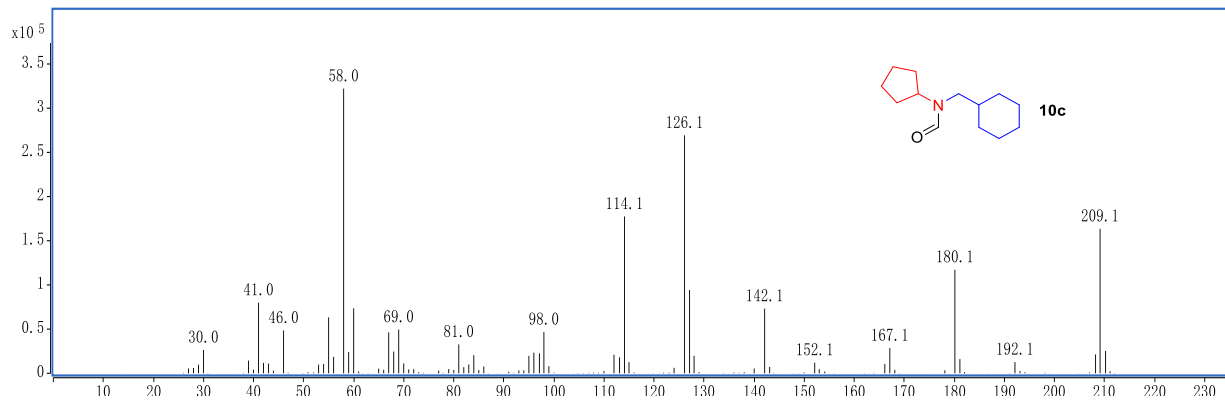
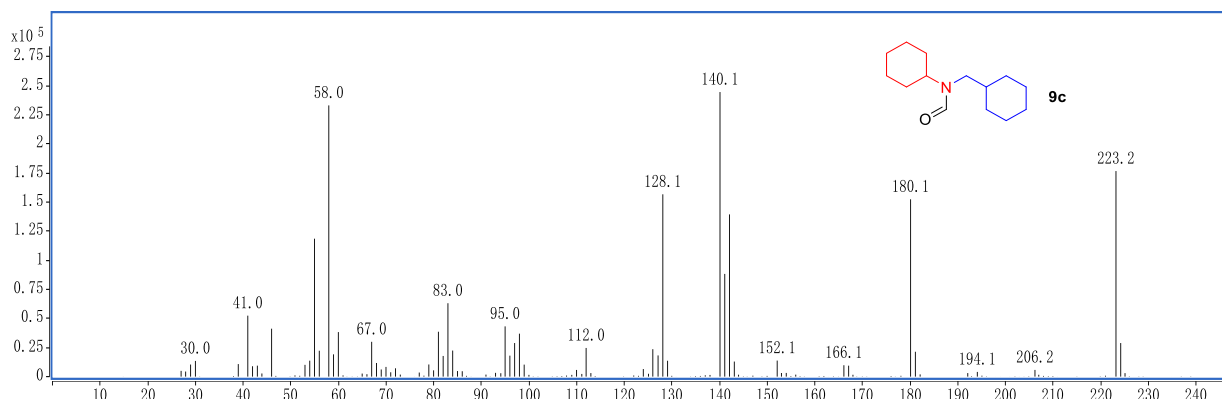


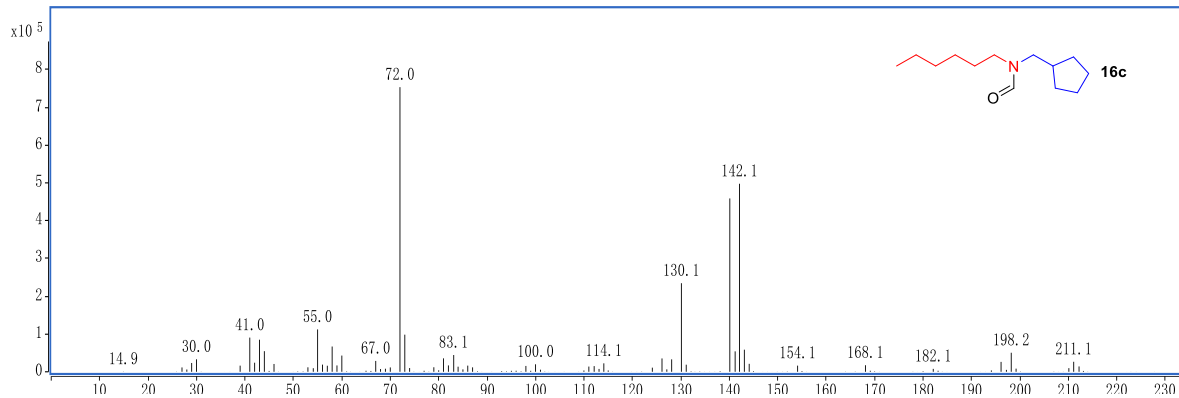
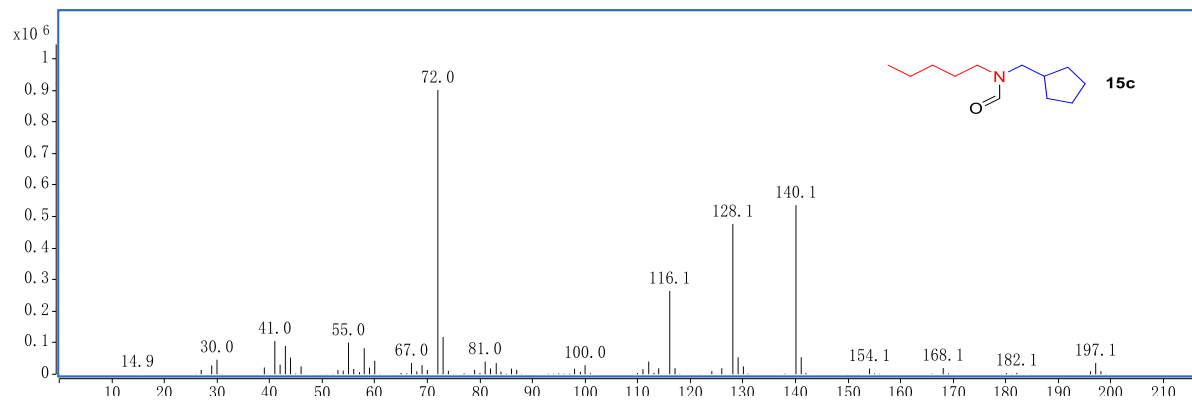
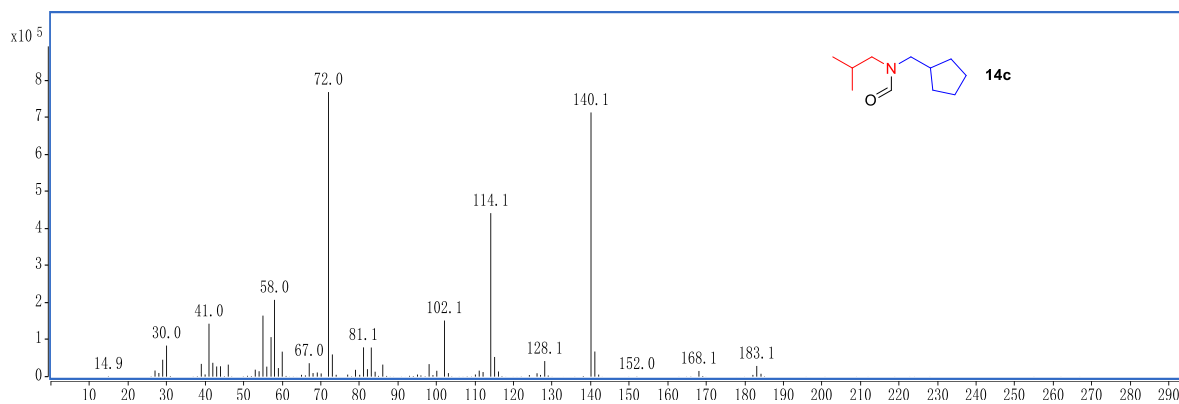
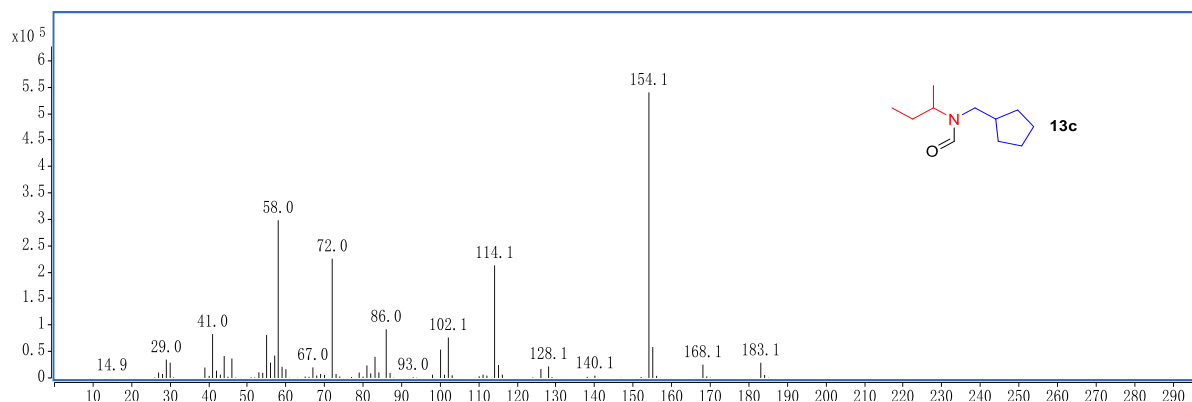


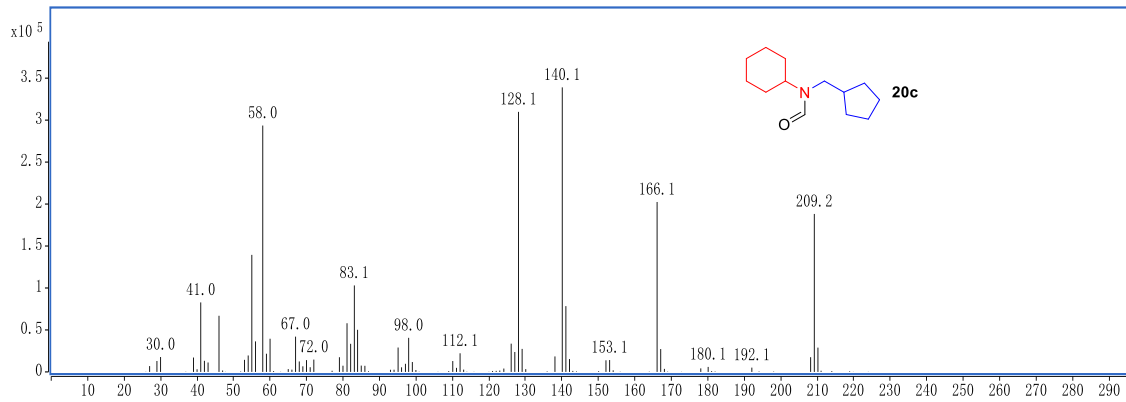
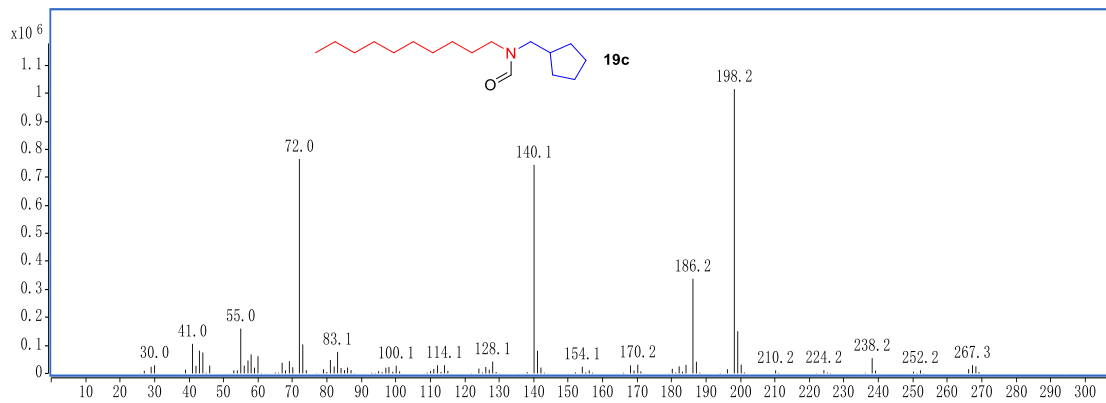
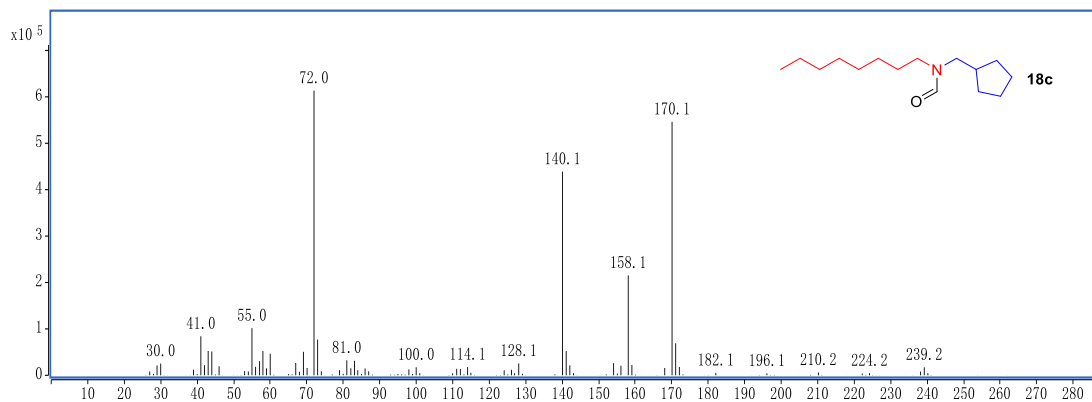
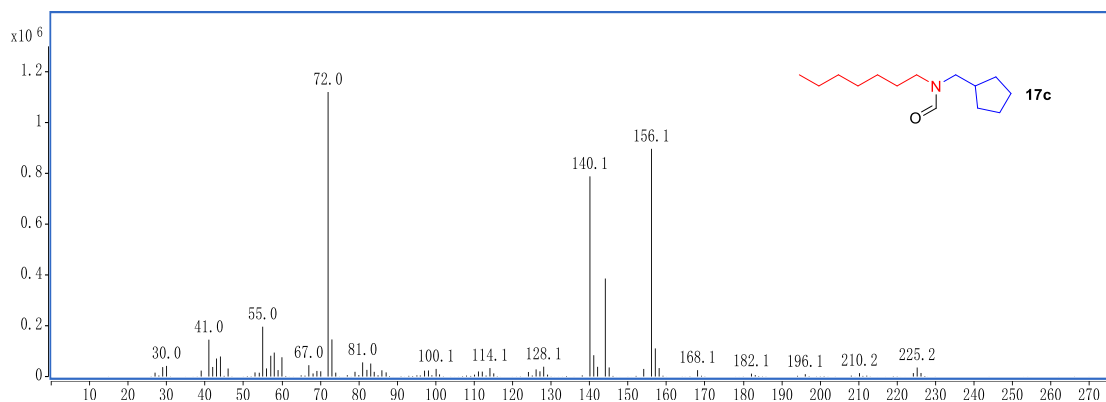
## MS spectra of the products



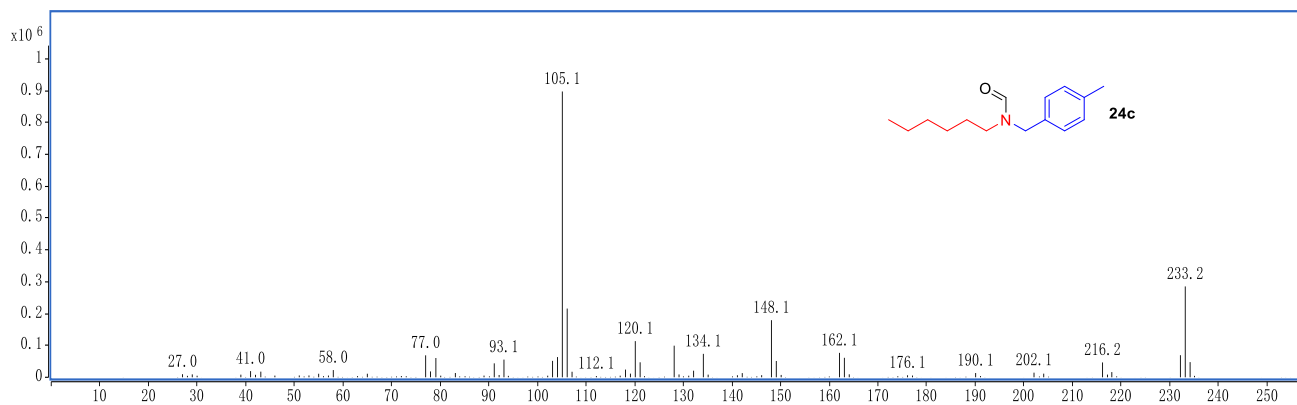
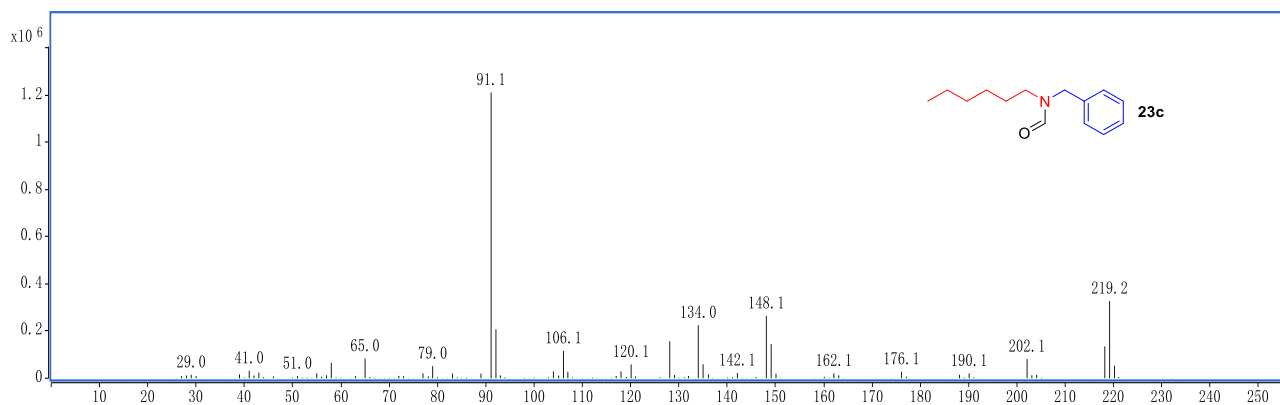
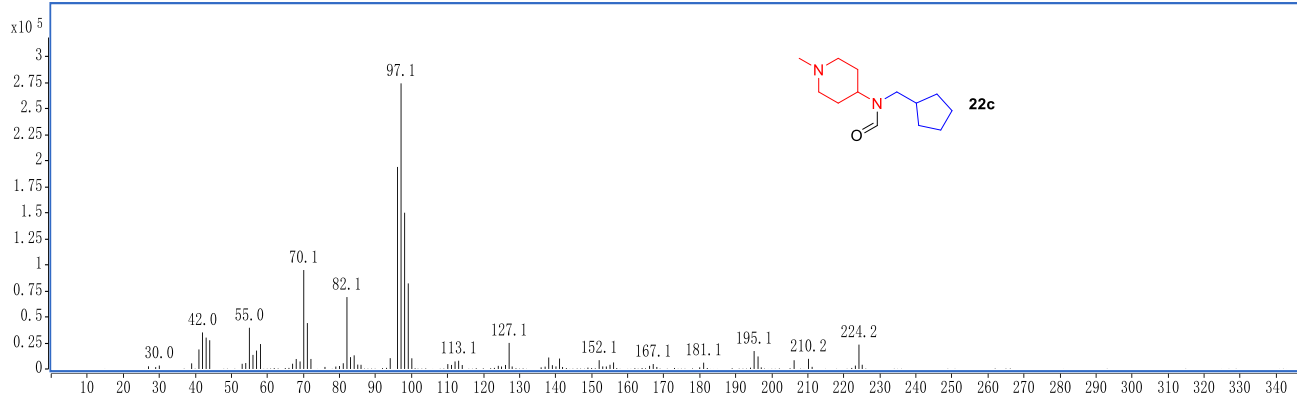
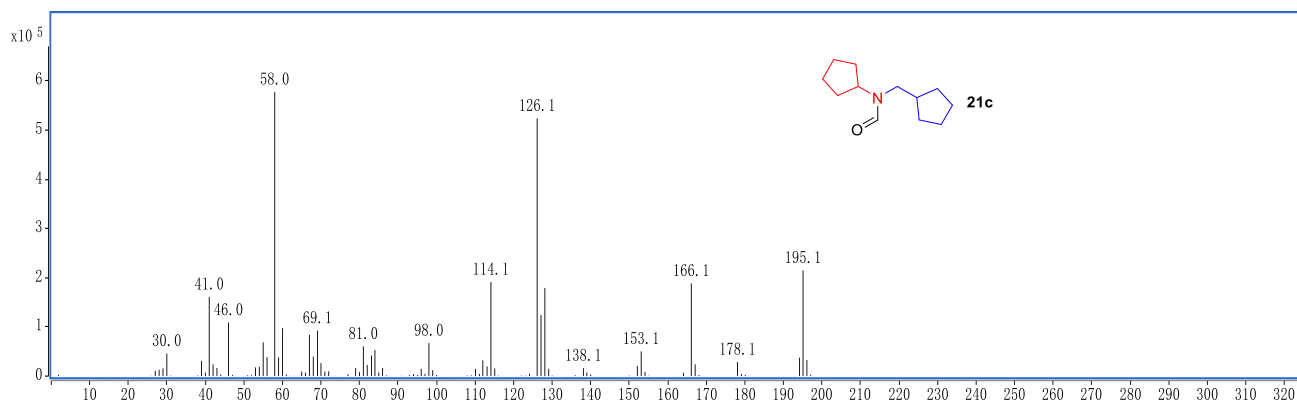


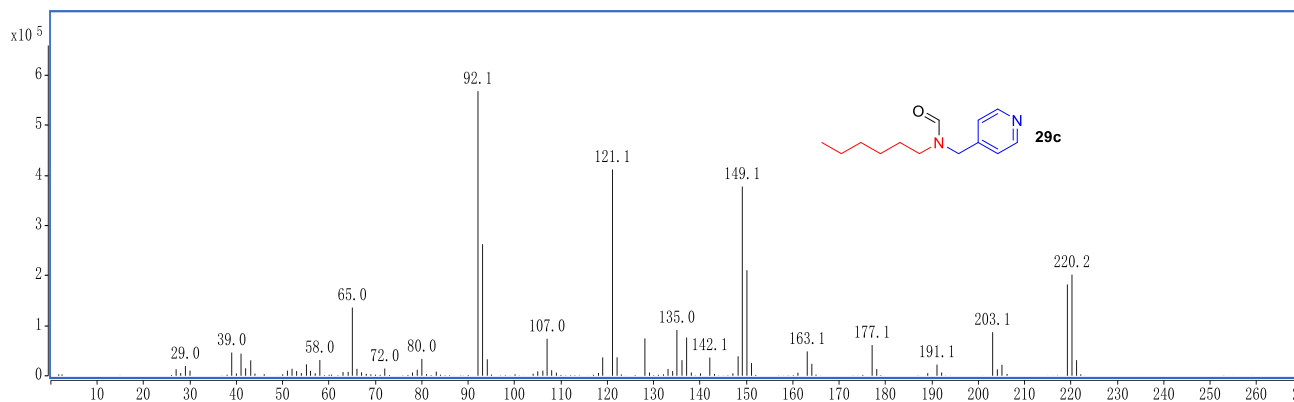
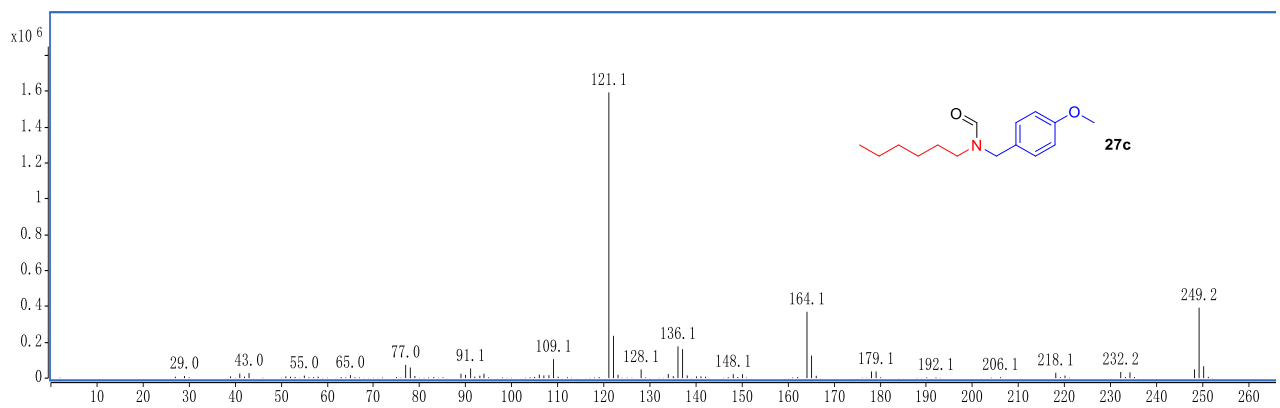
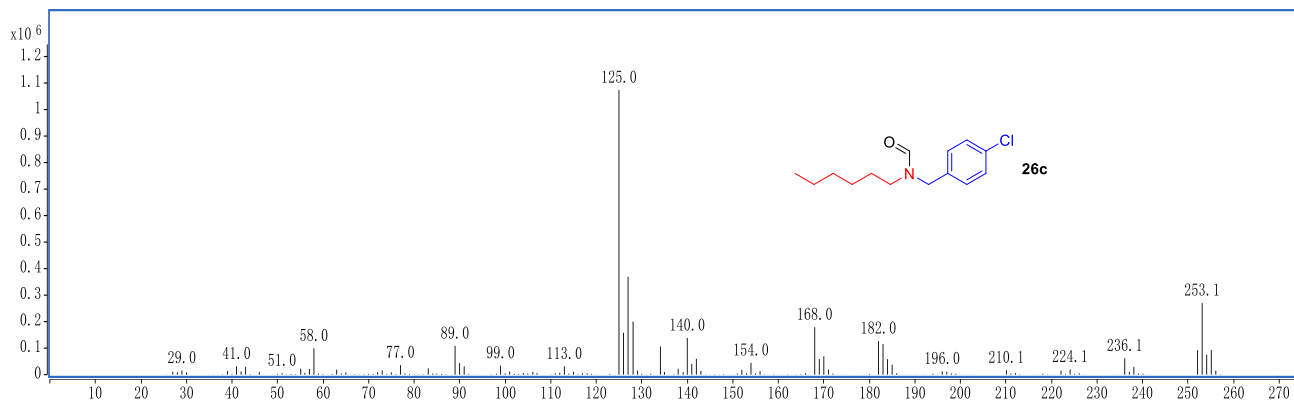
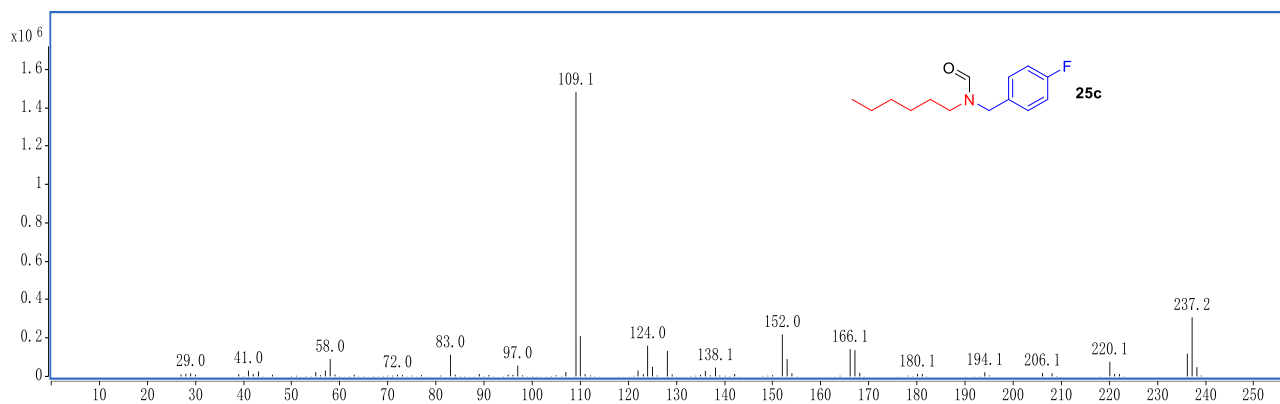


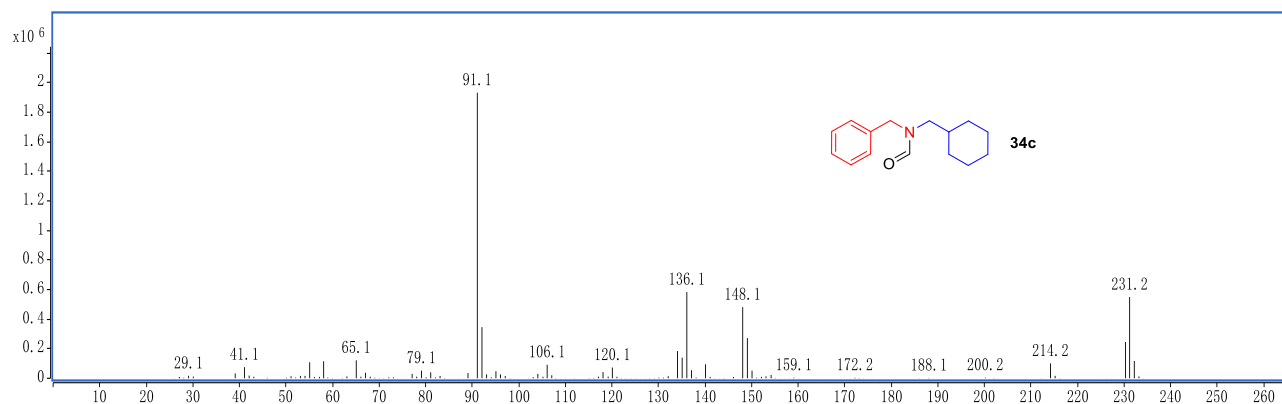
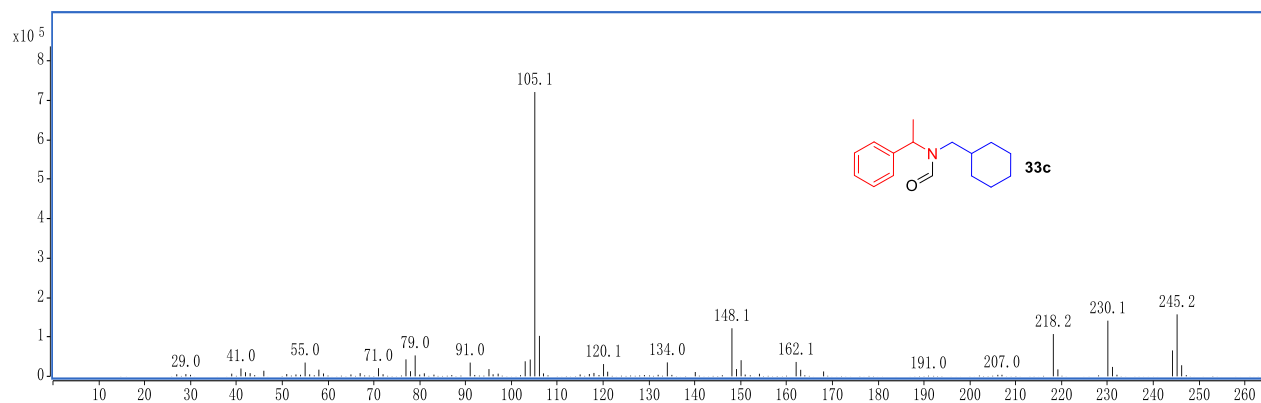
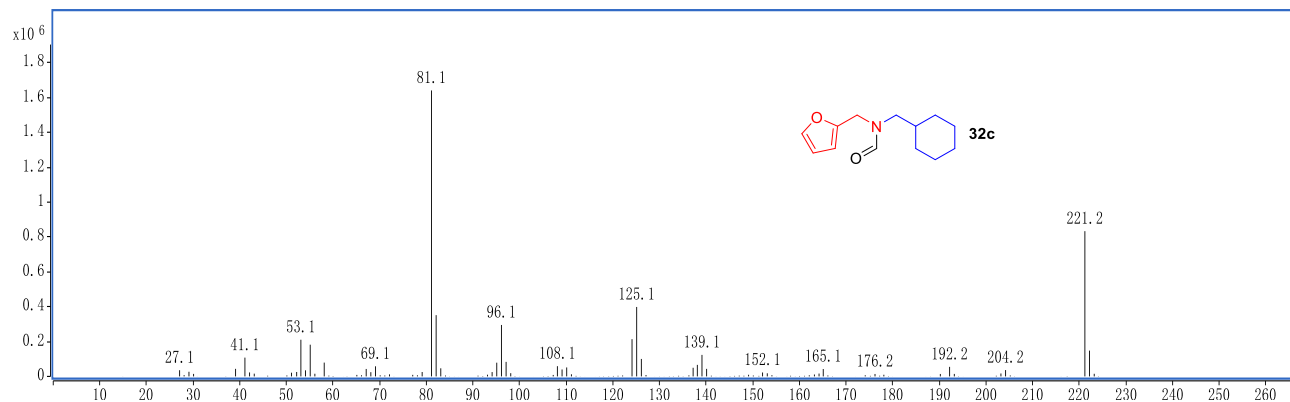
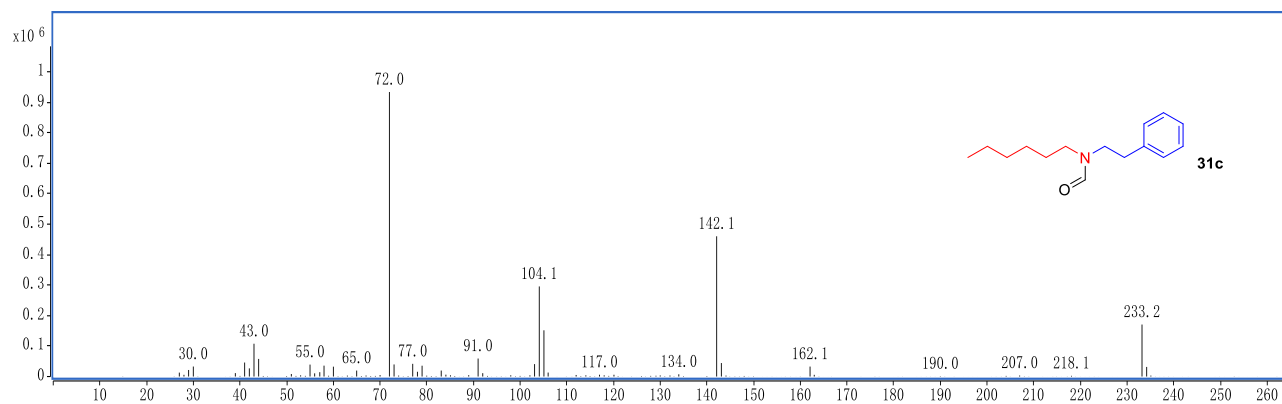


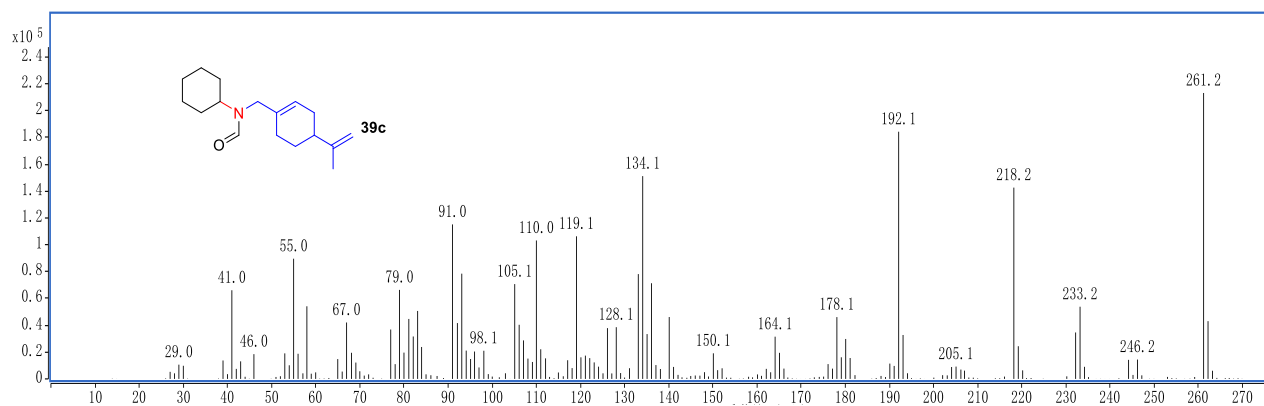
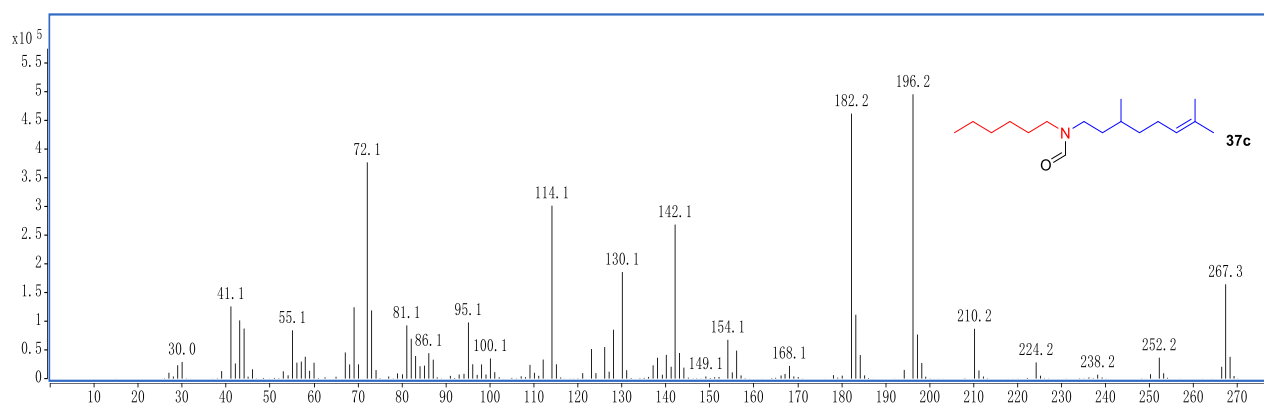
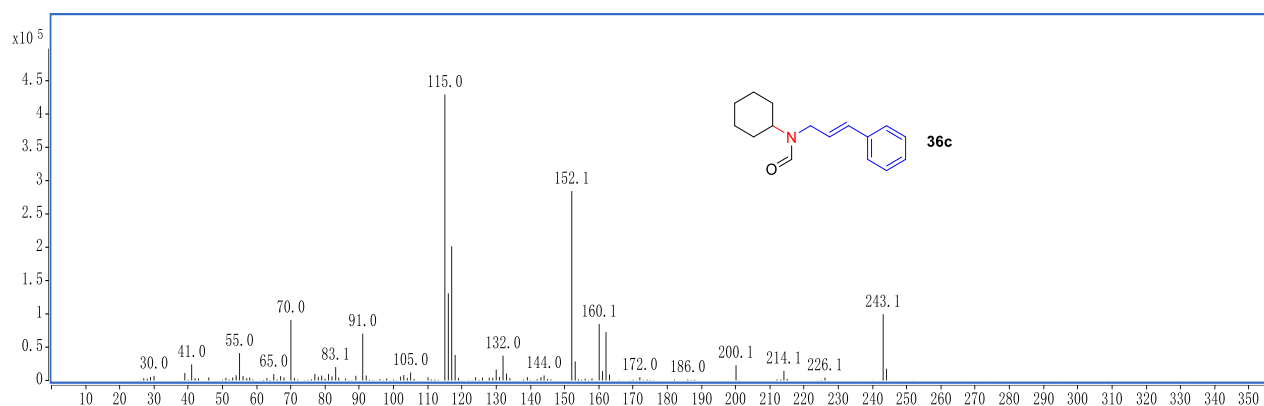
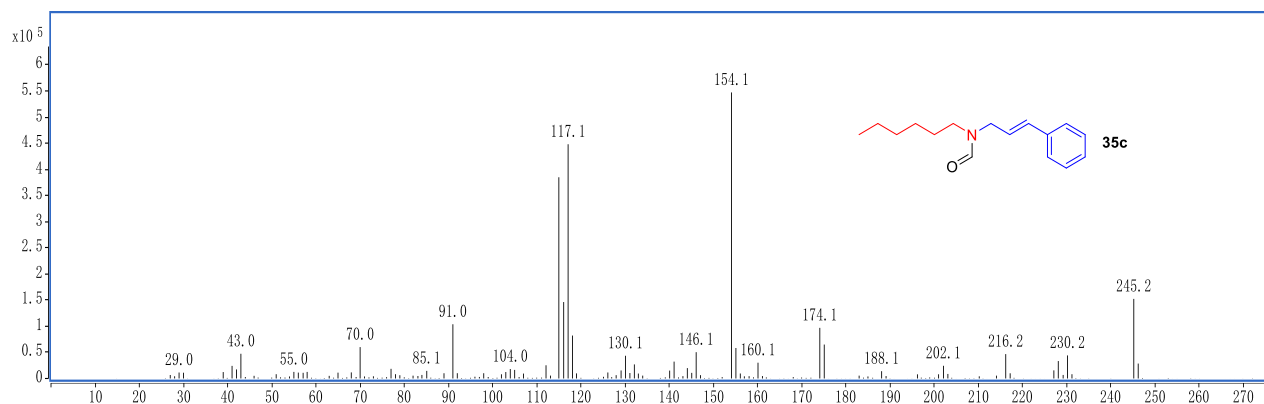












## References

- [1] Z. Ke, L. Hao, X. Gao, H. Zhang, Y. Zhao, B. Yu, Z. Yang, Y. Chen, Z. Liu, *Chem. Eur. J.* **2017**, 23, 9721 – 9725.