

## Supporting Information

### **A Scalable Continuous Photo-Flow Protocol for Anaerobic Oxidative Cleavage of Styrenes**

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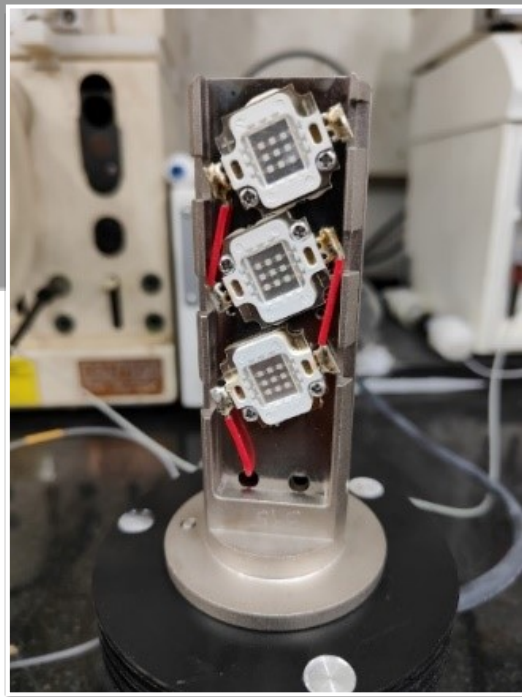
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## 1. General Consideration:

**a. Reagents Information.** All the solvents were bought from Aldrich/Alfa Aesar (India)/TCI (India)/Merck in a sure-seal bottle and were used as received. 4-Nitrobenzotrile was bought from Sigma Aldrich. TCI (India). All the styrene derivatives were bought from Aldrich/Alfa Aesar and (India)/TCI (India)/Spectrochem. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254).

**b. Analytical information.** All isolated compounds are characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy. NMR spectra were recorded either on a Bruker 500 or 400 MHz instrument. All  $^1\text{H}$  NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All  $^{13}\text{C}$  NMR spectra were reported in ppm relative to  $\text{CDCl}_3$  (77.20 ppm), All coupling constants were reported in Hertz (Hz) and all were obtained with  $^1\text{H}$  decoupling. High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer.

**c. Reactor Design-** Vapourtec flow chemistry system was used for optimization experiments, evaluation of the substrate scope and scale-up. Vapourtec UV-150 photochemical reactor with 60 W 365 nm LED was used. All the polymeric tubing and fittings were procured from IDEX Life Sciences.



**Figure S1:** Overview and details of the Vapourtec system and LEDs.

#### d. Calculations-

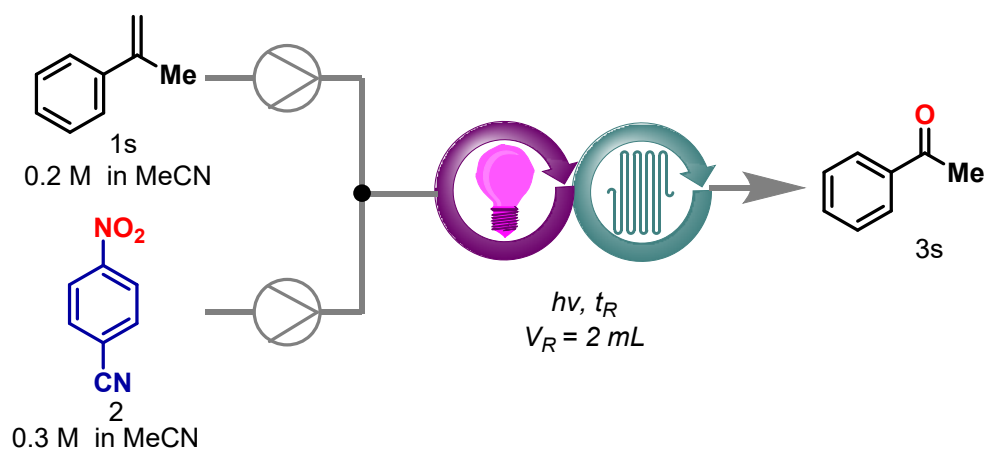
$$\text{Residence time (min)} = \frac{\text{reactor volume (ml)}}{\text{Total flow rate } \left(\frac{\text{mL}}{\text{min}}\right)}$$

Space time yield (STY) was calculated by dividing the production rate with reactor volume for optimized conditions.

$$\text{Space Time Yield, STY (gh}^{-1}\text{L}^{-1}\text{)} = \frac{\text{amount of material produced (in gram)}}{\text{Time (in hour)} \times \text{Reactor volume (in litre)}}$$

## 2. General procedures

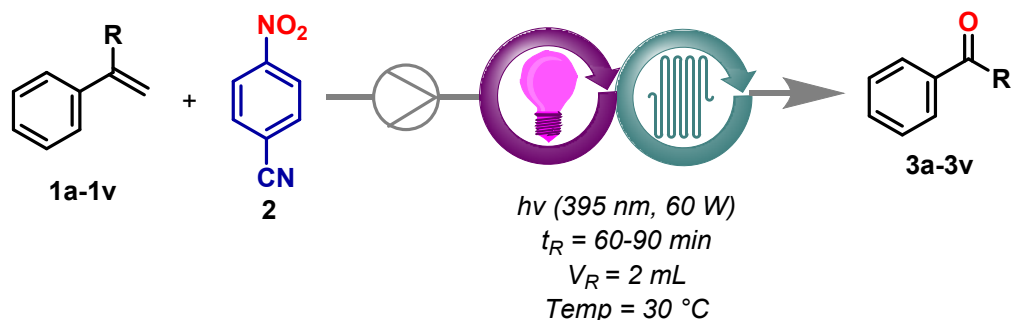
### a. Procedure for optimization



A 0.2 M solution of  $\alpha$ -methyl styrene (1s) and another 0.3 M solution of 4-nitrobenzonitrile (2) in dry MeCN were prepared in dry MeCN. Both the solutions were fed using plastic syringes (from HSW) and pumped using Chemyx syringe pump. The two solutions were connected to a T-mixer and flown through a 2 mL PFA reactor (1/16" OD, 1 mm ID). Flow rates of two reagents were adjusted to achieve the desired mole ratio and residence time. The reactor was irradiated with a 60 W, 395 nm blue LED supplied by Vapourtec. Mole ratio, light

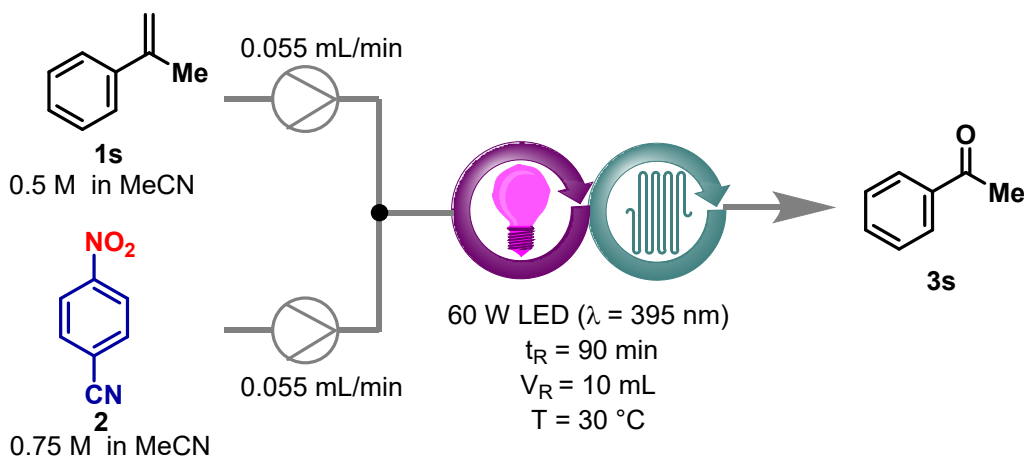
source, and residence time were varied to find the optimum conditions for the reaction. The reaction was monitored through GC yield against *n*-decane as an internal standard.

### b. Procedure for substrate scope



A solution was prepared with 0.2 M styrene substrate (1a-1v) and 0.3 M 4-nitrobenzonitrile (2) in dry MeCN. 2 mmole styrene compounds 1a-1v was dissolved into a 10 mL dry acetonitrile to get a 0.2 M solution of styrenes. The solution was pumped filled in a 10 mL syringe and pumped using a syringe pump in a 2 mL PFA reactor. The flow rate was adjusted to achieve the residence time of 60 min ( $t_R = 60 \text{ min}$ ,  $f_R = 0.167 \text{ mL/min}$ ), unless mentioned otherwise. The reactor was irradiated with a 60 W, 395 nm blue LED supplied by Vapourtec. When the syringe was fully empty, again dry acetonitrile was loaded into a syringe and injected to collect all product at the end of the reactor. The solvent of the resulting reaction mixture was removed under reduced pressure and purification by flash column chromatography on silica gel gave the corresponding products in the stated yield.

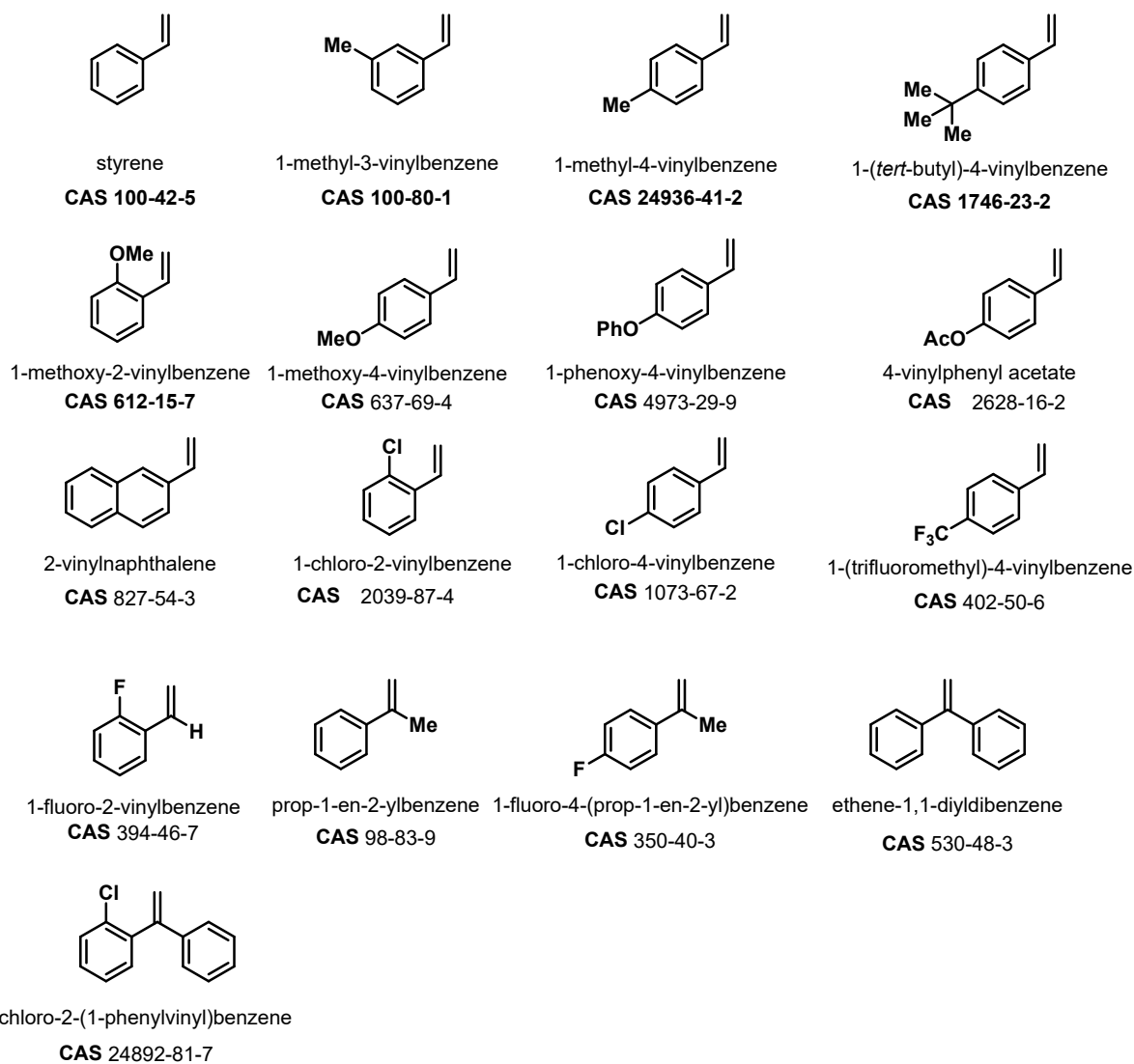
### c. Procedure for scale-up



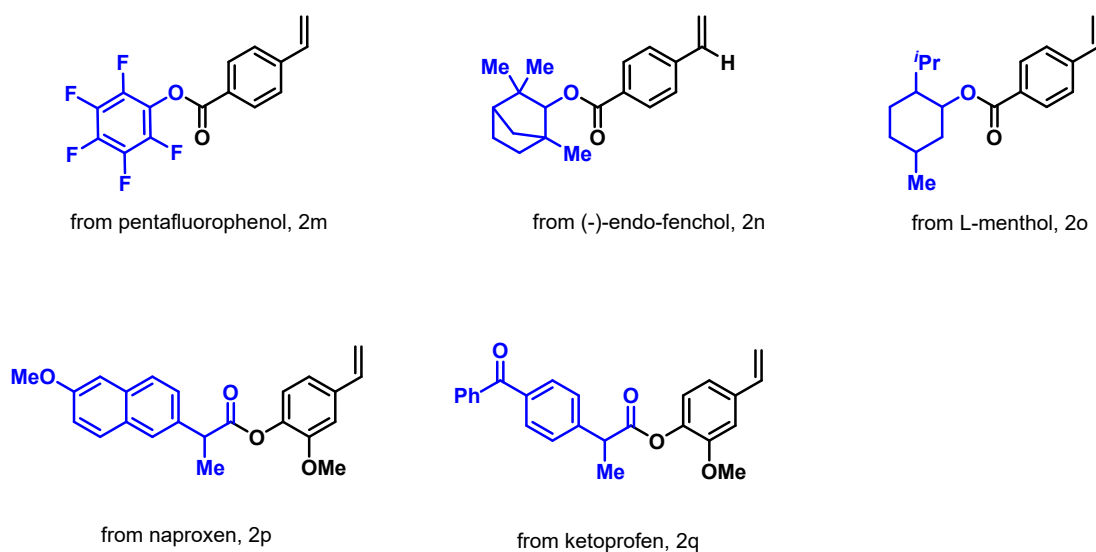
The two Reagents, 0.5 M solution of **1s** and 0.75 M solution of **2**, were pumped using Vapourtec HPLC pumps. UV-150 photochemical reactor assembly with 10 mL PFA tube reactor (1/16" OD, 1 mm ID) was employed. The reaction was run for 18 hrs. Solvent was evaporated using rota vapor and compound **3s** was isolated using column chromatography. Theoretical expected compound =  $0.055 \text{ mL/min} * 1/1000 \text{ L/mL} * 60 \text{ min/h} * 18 \text{ h} * 0.5 \text{ M} * 120 \text{ g/mole} = 3.56 \text{ g}$ . Isolated compounds was 2.8 g, corresponding to 78% yield.

#### d. General procedures for the preparation of substrates:

I. Commercially available starting materials are mostly purchased from Sigma Aldrich, TCI, Bld Pharma and Zeta Scientific.



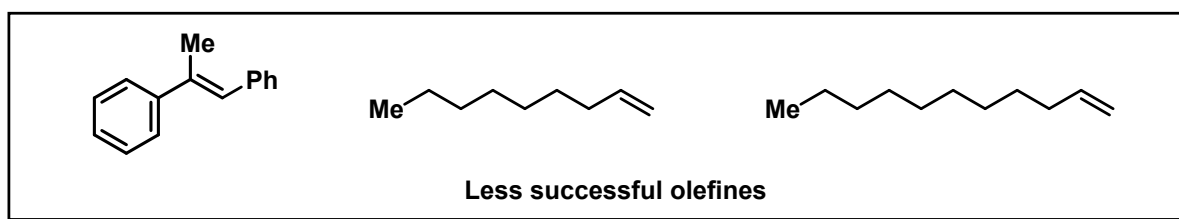
**II. Prepared starting materials:** following starting materials were synthesized according to published procedures. According to the following references.<sup>1-2</sup>





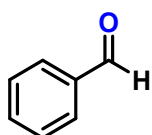
**For 2m to 2o:** To a stirred solution of 4-vinyl benzoic acid (1 equiv, 5 mmol) and DMAP (1 mmol) in 30 mL anhydrous  $\text{CH}_2\text{Cl}_2$ , respective alcohol (1.5 equiv) was added. After 15 minute of stirring, *N, N'*-dicyclohexylcarbodiimide, DCC (1.2 equiv) was added to the reaction mixture at  $0^\circ\text{C}$  and then allowed to stir for 48 hours at room temperature under nitrogen atmosphere. Upon completion of reaction, precipitate was then filtered off. Filtrate is evaporated and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with saturated  $\text{NaHCO}_3$  solution, and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent is removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to give the desired ester.

**For 2p and 2q:** To a stirred suspension of respective acid (1 equiv, 5 mmol) and DMAP (1 mmol) in 30 mL anhydrous  $\text{CH}_2\text{Cl}_2$ , 2-methoxy-4-vinylphenol (1.5 equiv) was added. After 15 minute of stirring, *N, N'*-dicyclohexylcarbodiimide, DCC (1.2 equiv) was added to the reaction mixture at  $0^\circ\text{C}$  and then allowed to stir for 48 hours at room temperature under nitrogen atmosphere. Upon completion of reaction, precipitate was then filtered off. Filtrate is evaporated and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and washed with saturated  $\text{NaHCO}_3$  solution, and then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent is removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to give the desired ester.



### 3. Characterization data

#### 1. benzaldehyde (3a)



Following the general procedure 2b, Compound 3a was obtained from styrene, isolated by column chromatography. All analytical data for 3a was in accordance with literature data.<sup>3</sup>

**Column material:** 100-200 mesh silica

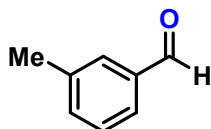
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 75%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.88 (s, 1H), 7.75 (dt, *J* = 8.4, 1.7 Hz, 2H), 7.48 (ddd, *J* = 8.9, 5.0, 1.4 Hz, 1H), 7.41 – 7.36 (m, 2H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 192.10, 136.20, 134.22, 129.46, 128.78.

## 2. 3-methylbenzaldehyde (3b)



Following the general procedure 2b, Compound 3b was obtained from 3-methyl styrene, isolated by column chromatography. All analytical data for 3b was in accordance with literature data.<sup>4</sup>

**Column material:** 100-200 mesh silica

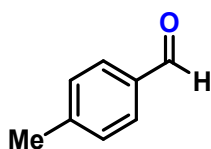
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 72%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.98 (s, 1H), 7.70 – 7.62 (m, 2H), 7.54 – 7.34 (m, 2H), 2.42 (s, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 192.76, 139.05, 136.60, 135.43, 130.16, 129.02, 127.36, 21.32.

## 3. 4-methylbenzaldehyde (3c)



Following the general procedure 2b, Compound 3c was obtained from 4-methyl styrene, isolated by column chromatography. All analytical data for 3c was in accordance with literature data.<sup>3</sup>

**Column material:** 100-200 mesh silica

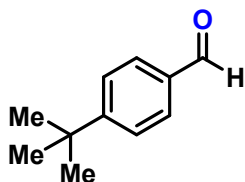
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 78%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.93 (s, 1H), 7.75 (dd, *J* = 8.1, 1.9 Hz, 2H), 7.30 (dd, *J* = 8.2, 2.0 Hz, 2H), 2.41 (s, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 192.07, 145.62, 134.25, 129.91, 129.78, 21.93.

## 4. 4-(*tert*-butyl)benzaldehyde (3d)



Following the general procedure 2b, Compound 3d was obtained from 4-*tert*butyl styrene, isolated by column chromatography. All analytical data for 3d was in accordance with literature data.<sup>5</sup>

**Column material:** 100-200 mesh silica

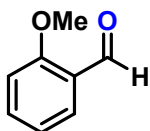
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 77%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.95 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 1.33 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 192.07, 158.48, 134.16, 129.76, 126.06, 35.41, 31.13.

### 5. 2-methoxybenzaldehyde (3e)



Following the general procedure 2b, Compound 3e was obtained from 2-methoxy styrene, isolated by column chromatography. All analytical data for 3e was in accordance with literature data.<sup>6</sup>

**Column material:** 100-200 mesh silica

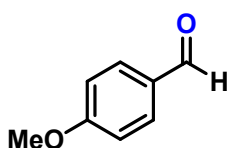
**Eluent:** pet ether: ethyl acetate (98:02)

**Yield:** 61%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.47 (s, 1H), 7.82 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.68 – 7.45 (m, 1H), 7.20 – 6.82 (m, 2H), 3.93 (s, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 190.02, 162.00, 136.12, 128.72, 124.99, 120.82, 111.78, 55.79.

### 6. 4-methoxybenzaldehyde (3f)



Following the general procedure 2b, Compound 3f was obtained from 4-methoxy styrene, isolated by column chromatography. All analytical data for 3f was in accordance with literature data.<sup>3</sup>

**Column material:** 100-200 mesh silica

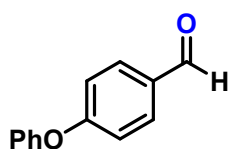
**Eluent:** pet ether: ethyl acetate (98:02)

**Yield:** 63%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.84 (s, 1H), 7.80 (d, *J* = 5.1 Hz, 2H), 6.97 (d, *J* = 5.1 Hz, 2H), 3.85 (s, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 190.90, 164.68, 132.05, 130.00, 114.38, 55.65.

### 7. 4-phenoxybenzaldehyde (3g)



Following the general procedure 2b, Compound 3g was obtained from 4-phenoxy styrene, isolated by column chromatography. All analytical data for 3g was in accordance with literature data.<sup>7</sup>

**Column material:** 100-200 mesh silica

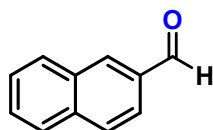
**Eluent:** pet ether: ethyl acetate (98:02)

**Yield:** 61%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.91 (s, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.41 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.31 – 7.14 (m, 1H), 7.17 – 6.88 (m, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 190.87, 163.33, 155.20, 132.05, 131.36, 130.26, 125.06, 120.53, 117.67.

### 8. 2-naphthaldehyde (3h)



Following the general procedure 2b, Compound 3h was obtained from 2-vinylnaphthalene, isolated by column chromatography. All analytical data for 3h was in accordance with literature data.<sup>3</sup>

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (98:02)

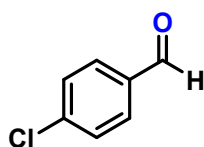
**Yield:** 70%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.17 (s, 1H), 8.35 (s, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.98 – 7.88 (m, 3H), 7.65 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.60 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 192.46, 136.64, 134.75, 134.29, 132.82, 129.71, 129.31, 129.29, 128.26, 127.28, 122.95.

### 9. 4-chlorobenzaldehyde (3i)

Following the general procedure 2b, Compound 3i was obtained from 1-chloro-4-vinylbenzene, isolated by column chromatography. All analytical data for 3j was in accordance with literature data.<sup>3</sup>



**Column material:** 100-200 mesh silica

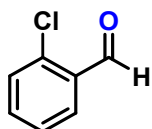
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 63%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.98 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 191.05, 141.14, 134.88, 131.08, 129.64.

### 10. 2-chlorobenzaldehyde (3i)



Following the general procedure 2b, Compound 3i was obtained from 2-chlorostyrene, isolated by column chromatography. All analytical data for 3i was in accordance with literature data.<sup>8</sup>

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (99:01)

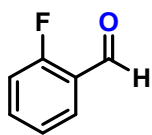
**Yield:** 65%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.96 (s, 1H), 7.83 (t, *J* = 1.8 Hz, 1H), 7.75 (dt, *J* = 7.6, 1.3 Hz, 1H), 7.58 (ddd, *J* = 8.1, 2.2, 1.2 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.07, 137.96, 135.61, 134.58, 130.57, 129.46, 128.18.

### 11. 2-fluorobenzaldehyde (3k)

Following the general procedure 2b, Compound 3k was obtained from 2-fluorostyrene, isolated by column chromatography. All analytical data for 3k was in accordance with literature data.<sup>5</sup>



**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (98:02)

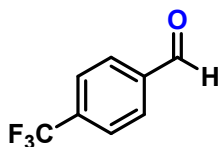
**Yield:** 73%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.35 (s, 1H), 7.90 – 7.82 (m, 1H), 7.72 – 7.55 (m, 1H), 7.39 – 7.23 (m, 1H), 7.22 – 7.11 (m, 1H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 187.29 (d, *J* = 6 Hz, 1 C), 164.76 (d, *J* = 259 Hz, 1 C), 136.47 (d, *J* = 9 Hz, 1C), 128.78 (d, *J* = 2 Hz, 1C), 124.74 (d, *J* = 4 Hz, 1C), 124.23 (d, *J* = 8 Hz, 1C), 116.59 (d, *J* = 21 Hz, 1C).

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -121.98.

## 12. 4-trifluoromethylbenzaldehyde (3l)



Following the general procedure 2b, Compound 3l was obtained from 1-(trifluoromethyl)-4-vinylbenzene, isolated by column chromatography. All analytical data for 3l was in accordance with literature data.<sup>3</sup>

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (98:02)

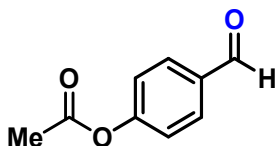
**Yield:** 68%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.10 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 191.25, 138.81, 135.67 (q, *J* = 32.7 Hz, 1C), 130.03, 126.21 (q, *J* = 3.78 Hz, 2C), 123.59 (q, *J* = 273 Hz, 1C).

**<sup>19</sup>F NMR** (471 MHz, CDCl<sub>3</sub>) δ -63.21.

## 13. 4-acetoxybenzaldehyde (3m)



Following the general procedure 2b, Compound 3m was obtained from 4-acetoxystyrene, isolated by column chromatography. All analytical data for 3m was in accordance with literature data.<sup>9</sup>

**Column material:** 100-200 mesh silica

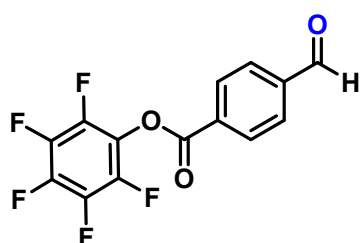
**Eluent:** pet ether: ethyl acetate (95:05)

**Yield:** 75 %

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.96 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 2.31 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.07, 168.82, 155.45, 134.09, 131.31, 122.48, 21.23.

#### 14. perfluorophenyl 4-formylbenzoate (3n)



Following the general procedure 2b, Compound 3n was obtained from perfluorophenyl 4-vinylbenzoate, isolated by column chromatography.

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (95:05)

**Yield:** 65 %

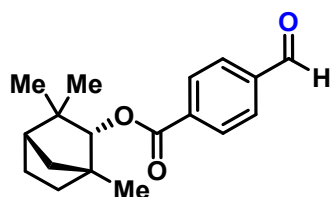
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.16 (s, 1H), 8.37 (d, *J* = 8.3 Hz, 2H), 8.06 (d, *J* = 8.3 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.39, 161.88, 142.73, 141.22, 140.46, 140.22, 139.43, 138.70, 136.96, 131.90, 131.51, 131.16, 130.70, 129.99, 128.42.

**<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>) δ -152.30 (d, *J* = 17.3 Hz), -157.13 (t, *J* = 21.8 Hz), -161.82 (dd, *J* = 21.7, 17.3 Hz).

**HR-MS (ESI-QTOF):** [M+Na]<sup>+</sup> calculated for C<sub>14</sub>H<sub>5</sub>F<sub>5</sub>NaO<sub>3</sub> m/z 339.0051 and found m/z 339.0052.

#### 15. (1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-formylbenzoate (3o)



Following the general procedure 2b, Compound 3o was obtained from (1R,2R,4S)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl 4-vinylbenzoate, isolated by column chromatography. All analytical data for 3o was in accordance with literature data.<sup>10</sup>

**Column material:** 100-200 mesh silica

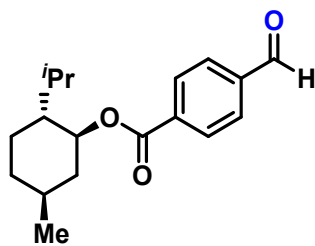
**Eluent:** pet ether: ethyl acetate (95:05)

**Yield:** 72%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.11 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 4.65 (d, *J* = 1.9 Hz, 1H), 2.02 – 1.86 (m, 1H), 1.79 (dtd, *J* = 9.0, 6.4, 5.8, 3.2 Hz, 2H), 1.68 (dq, *J* = 10.4, 2.2 Hz, 1H), 1.26 (d, *J* = 1.5 Hz, 1H), 1.19 (s, 3H), 1.12 (s, 3H), 0.85 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.85, 166.06, 139.27, 135.87, 130.30, 129.76, 87.68, 48.85, 48.58, 41.64, 40.08, 29.94, 27.07, 26.08, 20.49, 19.68.

### 16. (1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-formylbenzoate (3p)



Following the general procedure 2b, Compound 3p was obtained from (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-vinylbenzoate, isolated by column chromatography. (*t<sub>R</sub>* = 60 min, *f<sub>R</sub>* = 0.167 mL/min). All analytical data for 3p was in accordance with literature data.<sup>11</sup>

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (95:05)

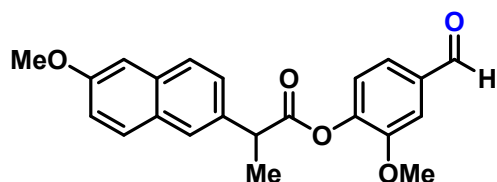
**Yield:** 74%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 10.09 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 4.95 (td, *J* = 10.9, 4.4 Hz, 1H), 2.12 (dt, *J* = 7.7, 2.6 Hz, 1H), 1.93 (pd, *J* = 7.0, 2.8 Hz, 1H), 1.72 (dt, *J* = 14.8, 4.0 Hz, 2H), 1.56 (tt, *J* = 12.2, 3.2 Hz, 2H), 1.39 – 1.20 (m, 1H), 1.17 – 1.02 (m, 2H), 0.91 (dd, *J* = 6.8, 5.1 Hz, 7H), 0.78 (d, *J* = 6.9 Hz, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 191.81, 165.19, 139.16, 135.97, 130.28, 129.62, 75.79, 47.35, 41.02, 34.38, 31.59, 26.69, 23.74, 22.16, 20.89, 16.64.

### 17. 4-formyl-2-methoxyphenyl 2-(6-methoxynaphthalen-2-yl)propanoate (3q)





Following the general procedure 2b, Compound 3q was obtained from 2-methoxy-4-vinylphenyl 2-(6-methoxynaphthalen-2-yl)propanoate, isolated by column chromatography. All analytical data for 3q was in accordance with literature data.<sup>12</sup>

**Column material:** 100-200 mesh silica

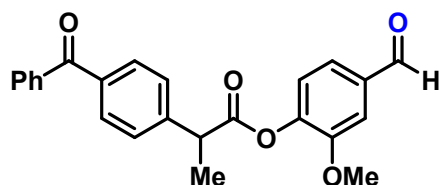
**Eluent:** pet ether: ethyl acetate (94:06)

**Yield:** 67%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.90 (s, 1H), 7.87 – 7.68 (m, 3H), 7.52 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.22 – 7.14 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 1H), 3.92 (s, 3H), 3.73 (s, 3H), 1.72 (d, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 191.24, 172.32, 157.90, 152.18, 145.32, 135.29, 135.04, 133.99, 129.45, 129.09, 127.33, 126.46, 124.83, 123.40, 119.25, 110.89, 105.75, 56.05, 55.46, 45.49, 18.78.

#### 18. 4-formyl-2-methoxyphenyl 2-(4-benzoylphenyl)propanoate (3r)



Following the general procedure 2b, Compound 3r was obtained from 2-methoxy-4-vinylphenyl 2-(4-benzoylphenyl)propanoate, isolated by column chromatography. (*t<sub>R</sub>* = 60 min, *f<sub>R</sub>* = 0.167 mL/min).

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (94:06)

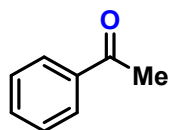
**Yield:** 70%

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.91 (s, 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.72 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 – 7.47 (m, 2H), 7.46 – 7.41 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 196.63, 191.20, 171.69, 152.08, 145.10, 140.32, 138.14, 137.56, 135.39, 132.75, 131.91, 130.22, 129.51, 129.43, 128.72, 128.50, 124.79, 123.32, 110.95, 56.07, 45.42, 18.74.

**HR-MS (ESI-QTOF):**  $[M+Na]^+$  calculated for  $C_{24}H_{20}NaO_5$   $m/z$  411.1203 and found  $m/z$  411.1205.

### 19. Acetophenone (3s)



Following the general procedure 2b, Compound 3s was obtained from prop-1-en-2-ylbenzene, isolated by column chromatography. All analytical data for 3s was in accordance with literature data.<sup>13</sup> ( $t_R = 90$  min)

**Column material:** 100-200 mesh silica

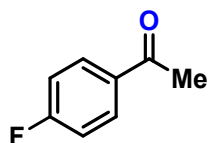
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 78%

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.98 – 7.91 (m, 2H), 7.55 (ddt,  $J = 7.7, 5.7, 1.1$  Hz, 1H), 7.45 (tt,  $J = 6.9, 1.1$  Hz, 2H), 2.59 (s, 3H).

**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  198.34, 137.21, 133.24, 128.69, 128.42, 26.73.

### 20. 1-(4-fluorophenyl)ethan-1-one (3t)



Following the general procedure 2b, Compound 3t was obtained from 1-fluoro-4-(prop-1-en-2-yl)benzene, isolated by column chromatography. All analytical data for 3t was in accordance with literature data.<sup>14</sup> ( $t_R = 90$  min)

**Column material:** 100-200 mesh silica

**Eluent:** pet ether: ethyl acetate (99:01)

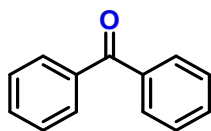
**Yield:** 72%

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.07 – 7.88 (m, 2H), 7.11 (ddd,  $J = 9.1, 8.4, 0.9$  Hz, 2H), 2.58 (s, 3H).

**$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  196.74, 165.96 (d,  $J = 255$  Hz), 133.77 (d,  $J = 3$  Hz), 131.15 (d,  $J = 10$  Hz), 115.85 (d,  $J = 22.2$  Hz), 26.73.

**$^{19}F$  NMR** (377 MHz,  $CDCl_3$ )  $\delta$  -105.35.

### 21. benzophenone (3u)



Following the general procedure 2b, Compound 3u was obtained from 1-fluoro-4-(prop-1-en-2-yl)benzene, isolated by column chromatography. All analytical data for 3u was in accordance with literature data.<sup>13</sup>( $t_R = 90$  min)

**Column material:** 100-200 mesh silica

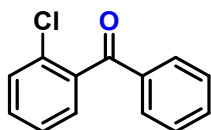
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 78%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (dd,  $J = 8.3, 1.5$  Hz, 4H), 7.64 – 7.56 (m, 2H), 7.54 – 7.45 (m, 4H9).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  196.93, 137.73, 132.58, 130.21, 128.43.

## 22. (2-chlorophenyl)(phenyl)methanone (3v)



Following the general procedure 2b, Compound 3v was obtained from 1-chloro-2-(1-phenylvinyl)benzene, isolated by column chromatography. All analytical data for 3v was in accordance with literature data.<sup>15</sup>( $t_R = 90$  min)

**Column material:** 100-200 mesh silica

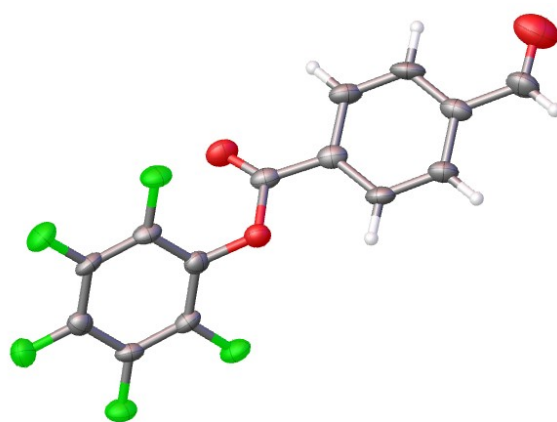
**Eluent:** pet ether: ethyl acetate (99:01)

**Yield:** 68%

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82 (dd,  $J = 8.3, 1.4$  Hz, 2H), 7.69 – 7.55 (m, 1H), 7.52 – 7.41 (m, 4H), 7.40 – 7.33 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  195.47, 138.76, 136.62, 133.88, 131.46, 131.30, 130.24 (2C), 129.28, 128.78, 126.85.

**<sup>13</sup>C NMR (101 MHz, DMSO)**  $\delta$  194.55, 138.13, 135.80, 134.18, 131.69, 129.84, 129.71, 129.59, 129.04, 128.98, 127.38.



**Crystal Data of 3n CCDC 2334058:**

Crystal data and structure refinement for C <sub>14</sub> H <sub>5</sub> F <sub>5</sub> O <sub>3</sub>	
Identification code	<b>3n</b>
Empirical formula	C <sub>14</sub> H <sub>5</sub> F <sub>5</sub> O <sub>3</sub>
Formula weight	316.18
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/Å	5.8662(2)
b/Å	4.6407(2)
c/Å	22.0751(9)
α/°	90
β/°	93.735(4)
γ/°	90
Volume/Å <sup>3</sup>	599.68(4)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.751
μ/mm <sup>-1</sup>	0.173
F(000)	316.0
Crystal size/mm <sup>3</sup>	0.116 × 0.099 × 0.096

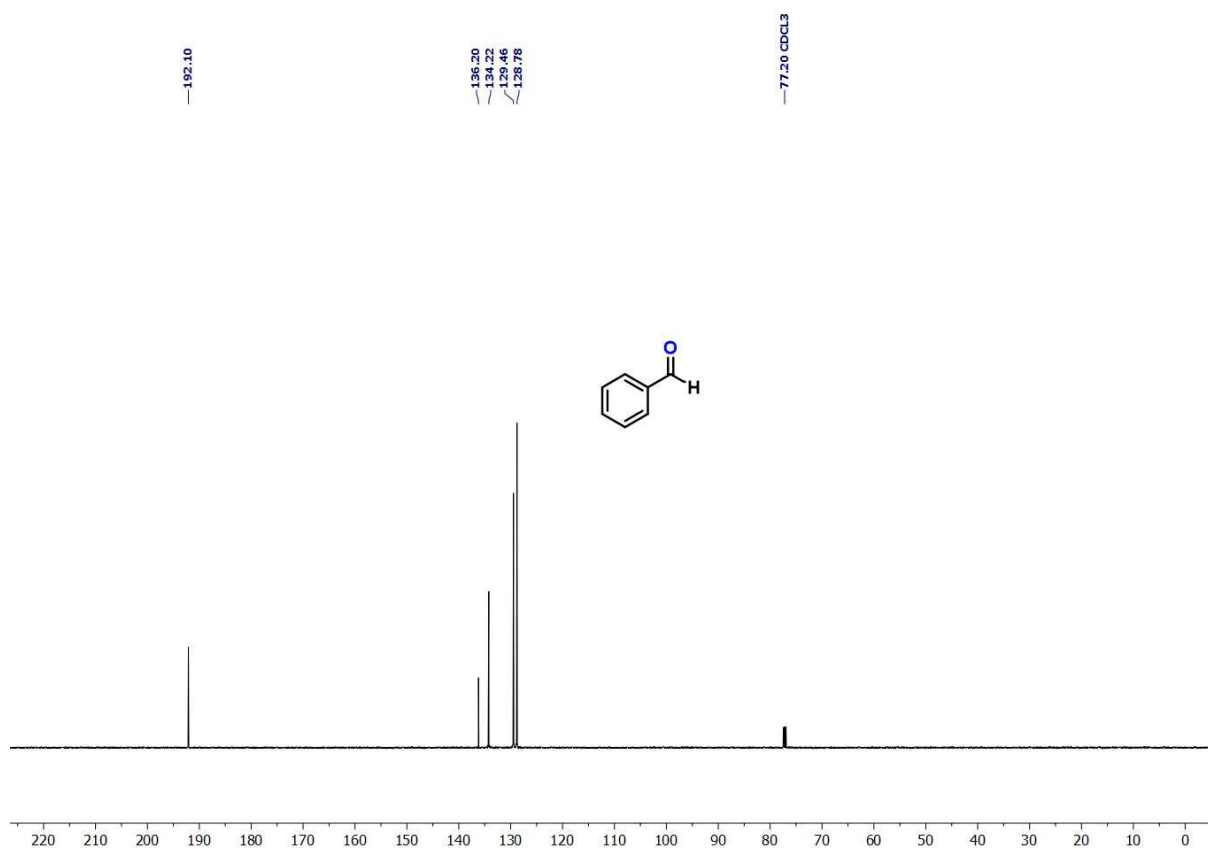
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^{\circ}$	3.698 to 49.978
Index ranges	$-6 \leq h \leq 6, -5 \leq k \leq 5, -26 \leq l \leq 26$
Goodness-of-fit on F <sup>2</sup>	1.096
Final R indexes [all data]	R <sub>1</sub> = 0.0723, wR <sub>2</sub> = 0.1953
Largest diff. peak/hole / e $\text{\AA}^{-3}$	1.72/-0.64

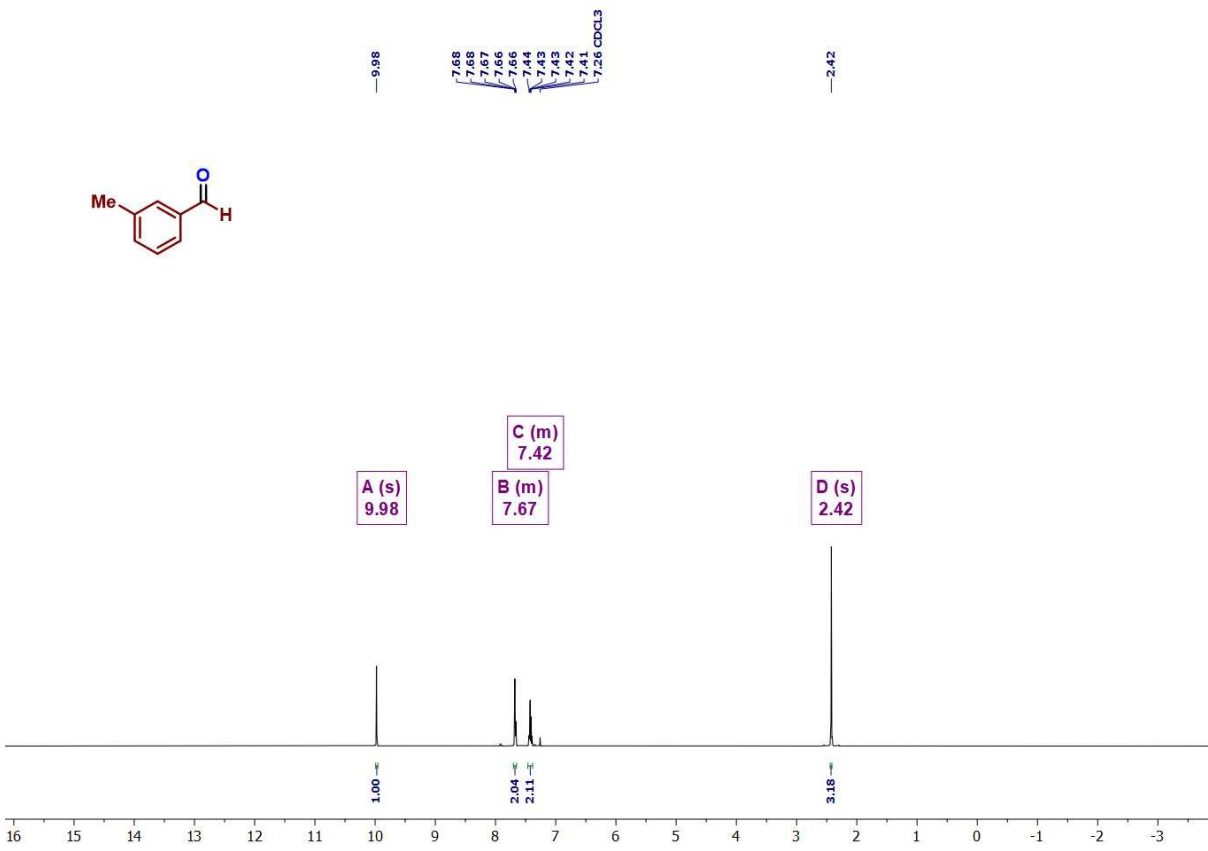
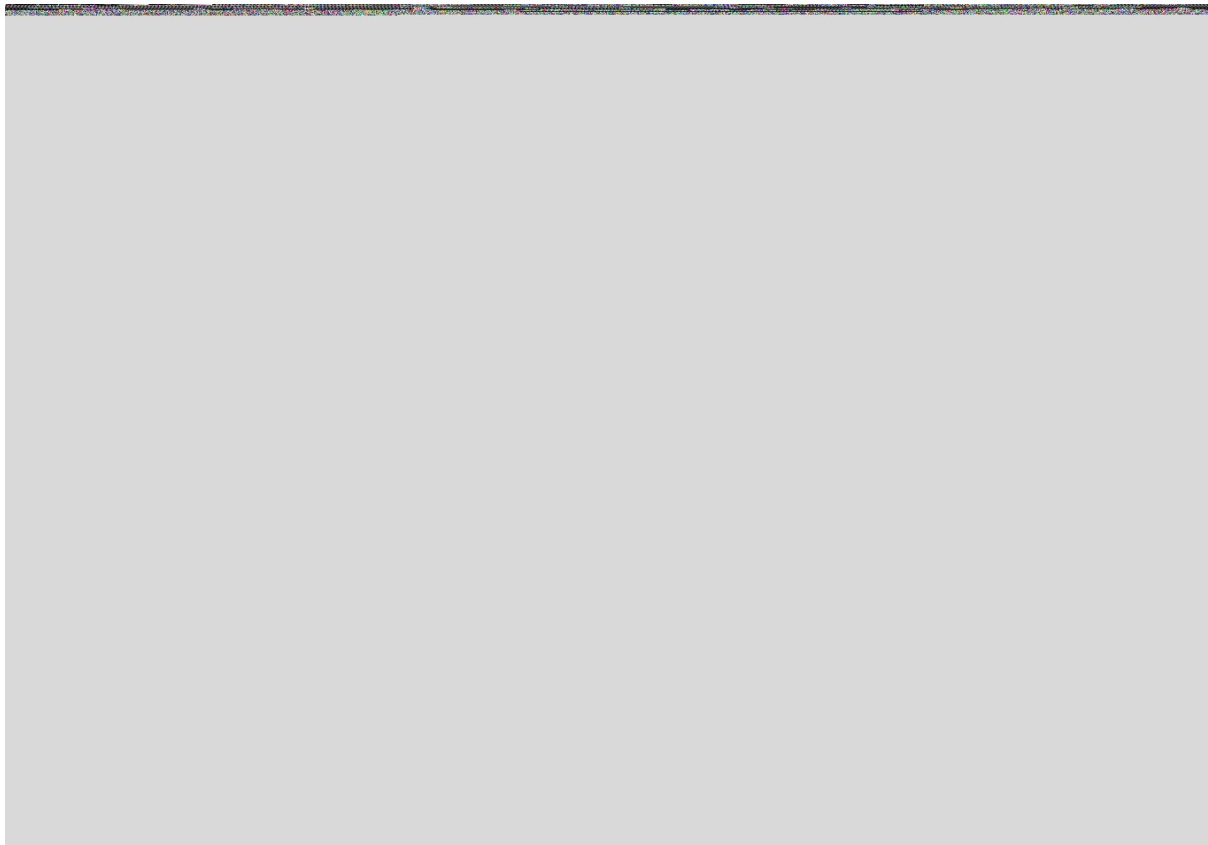
## 5. References

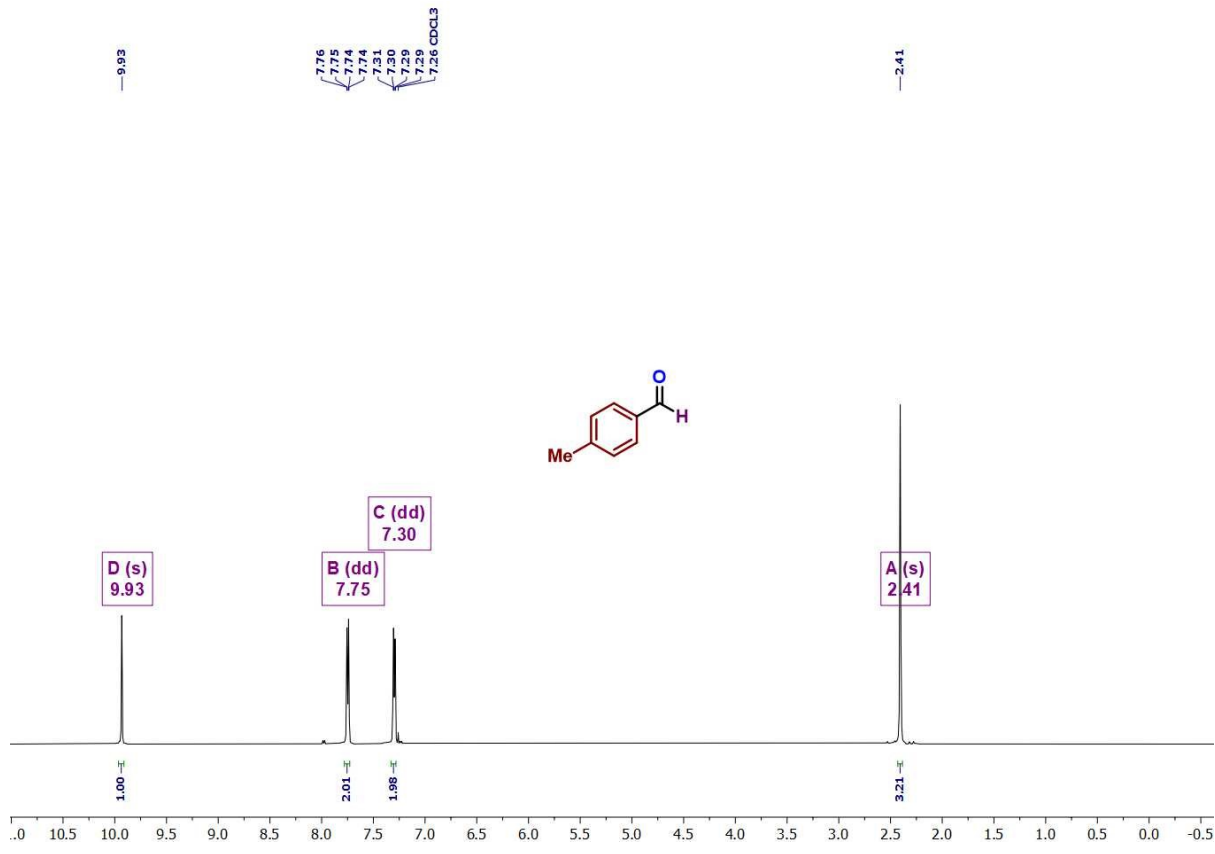
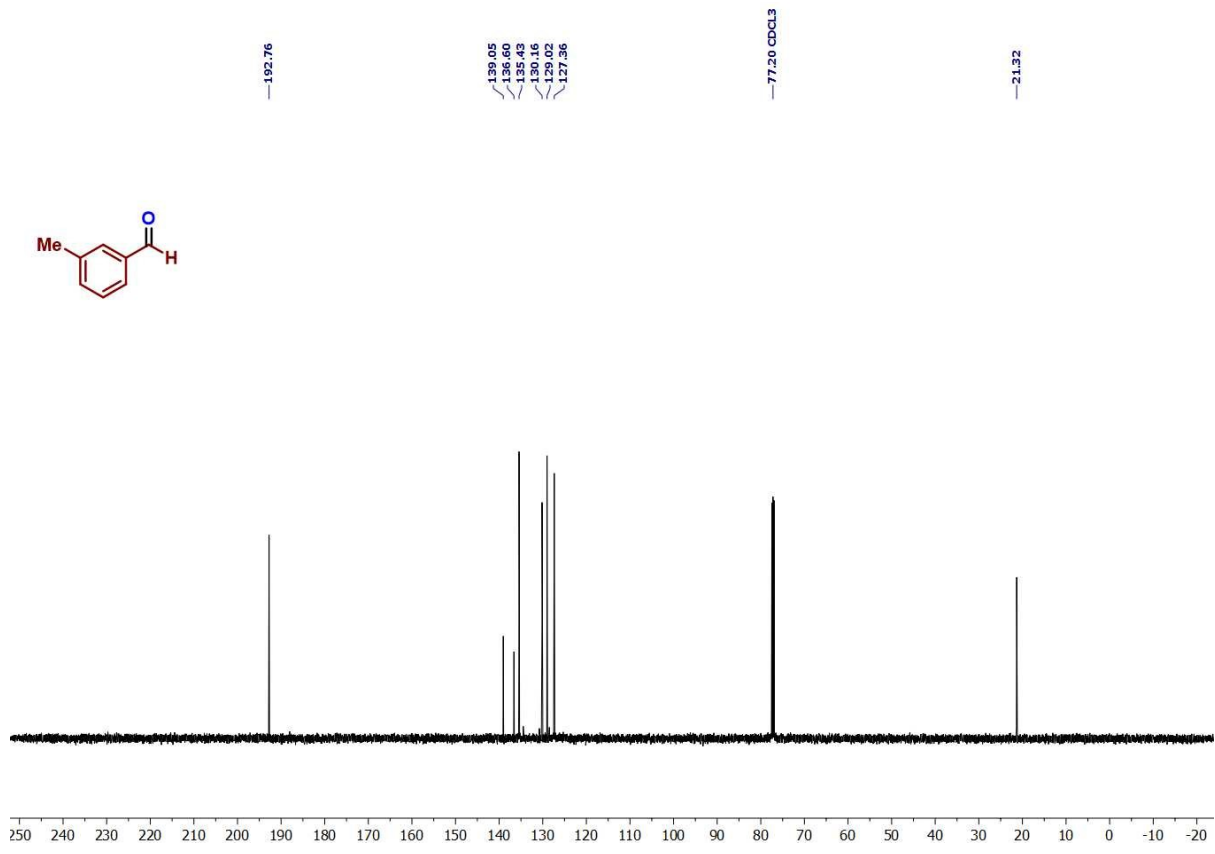
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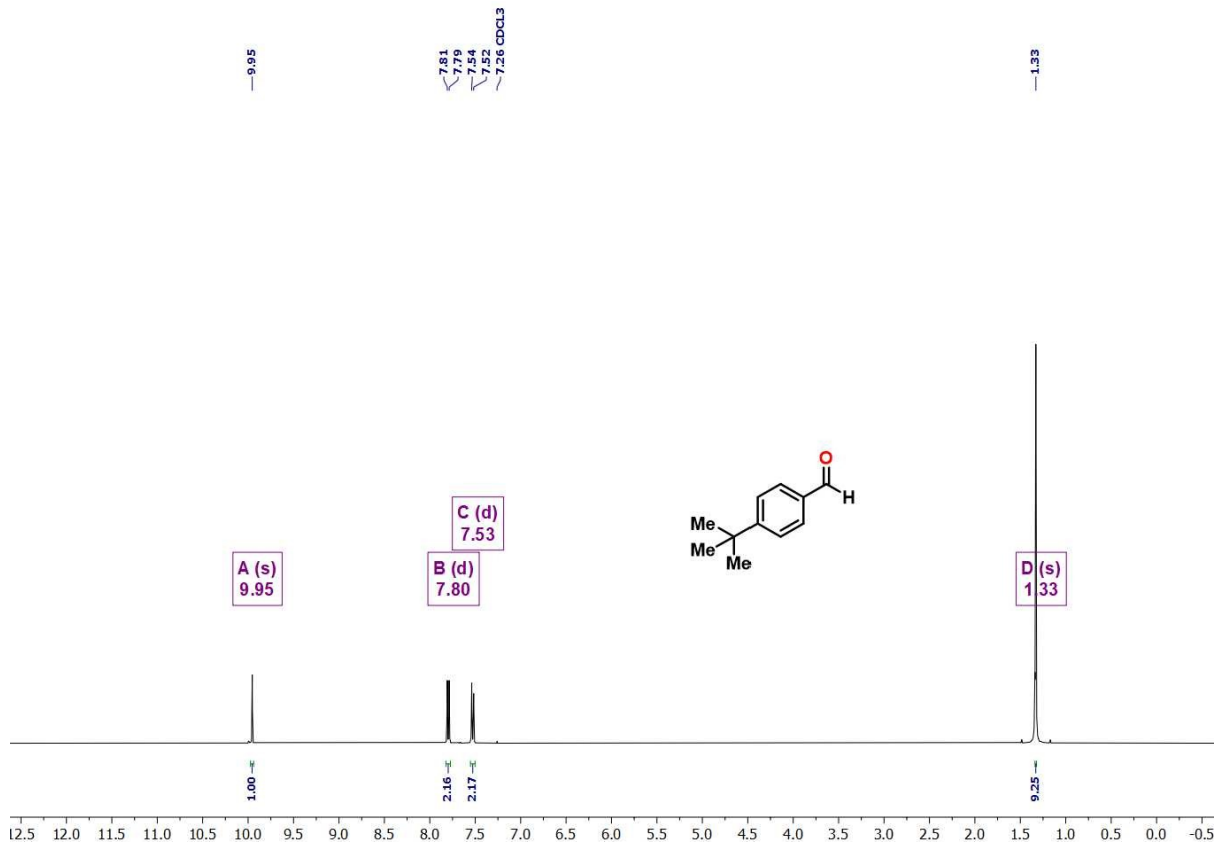
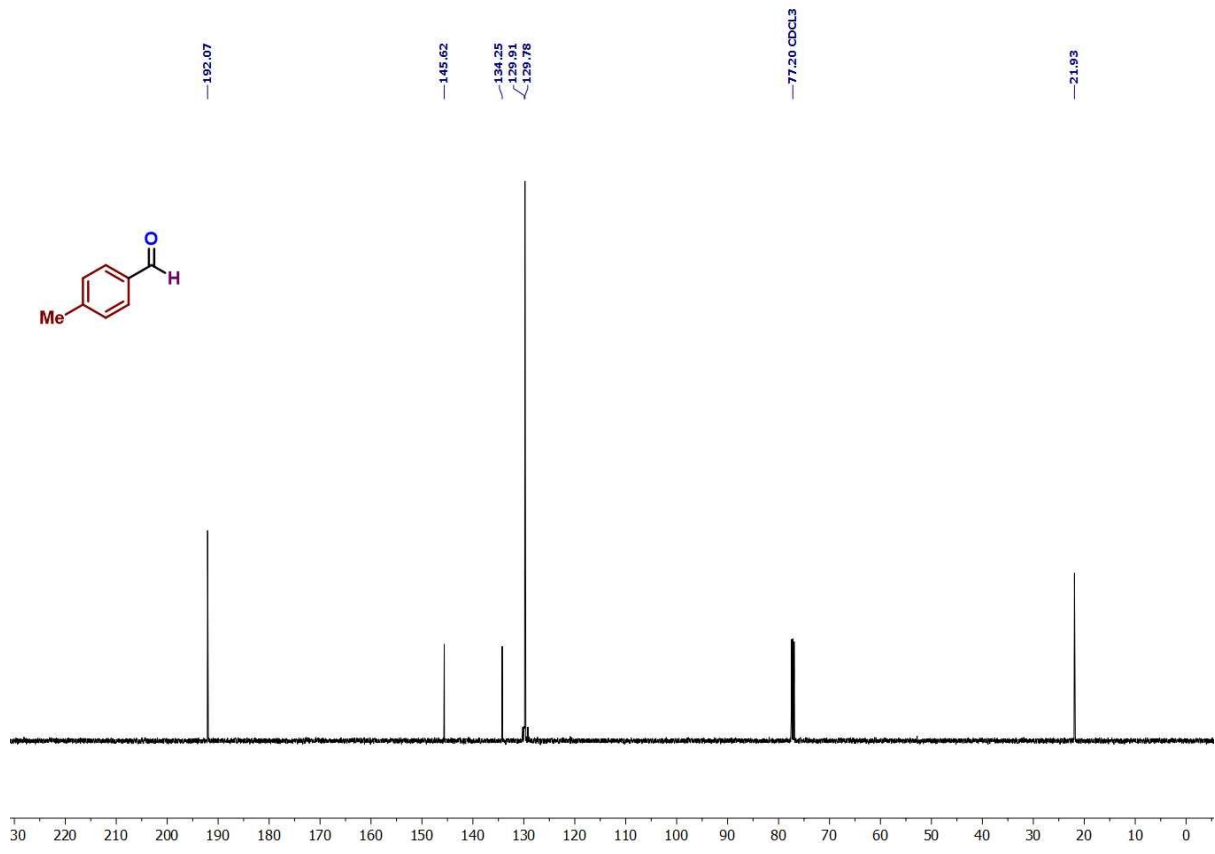
## 6. NMR Spectra

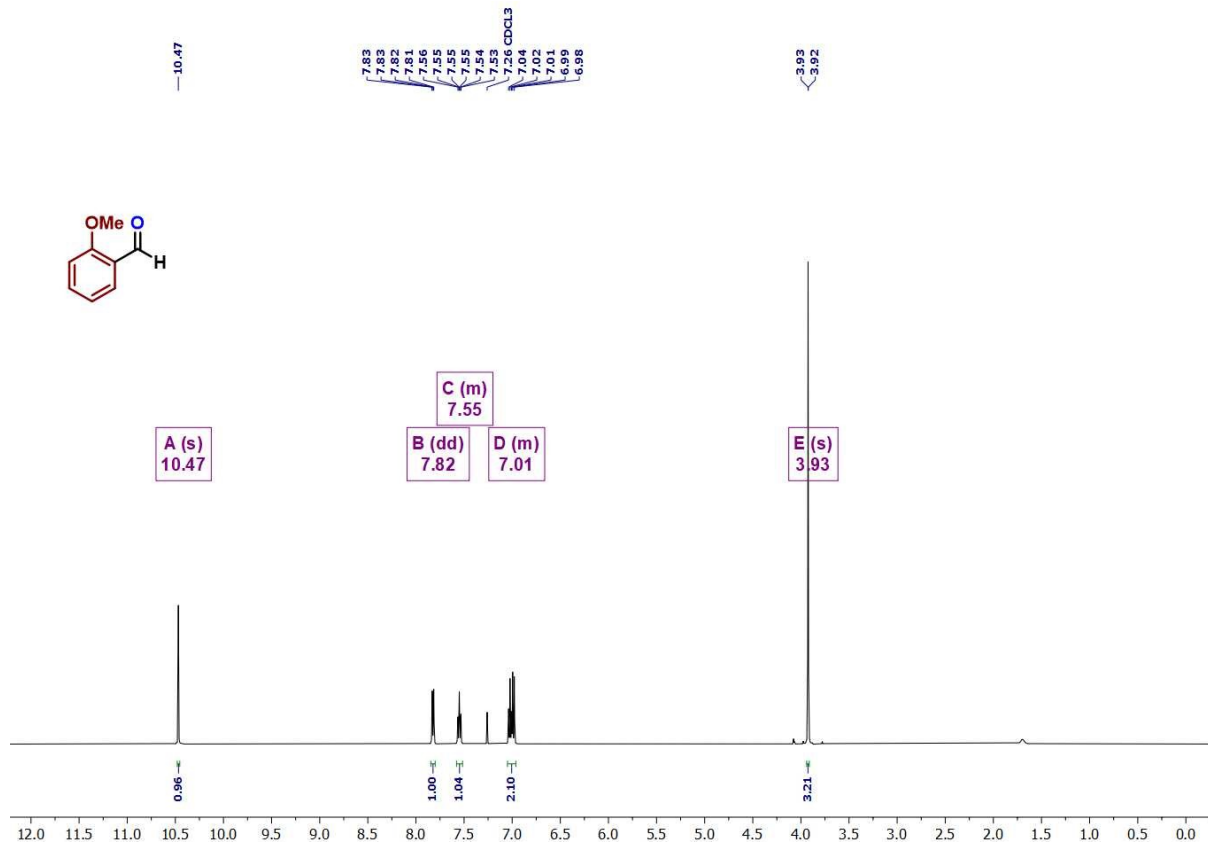
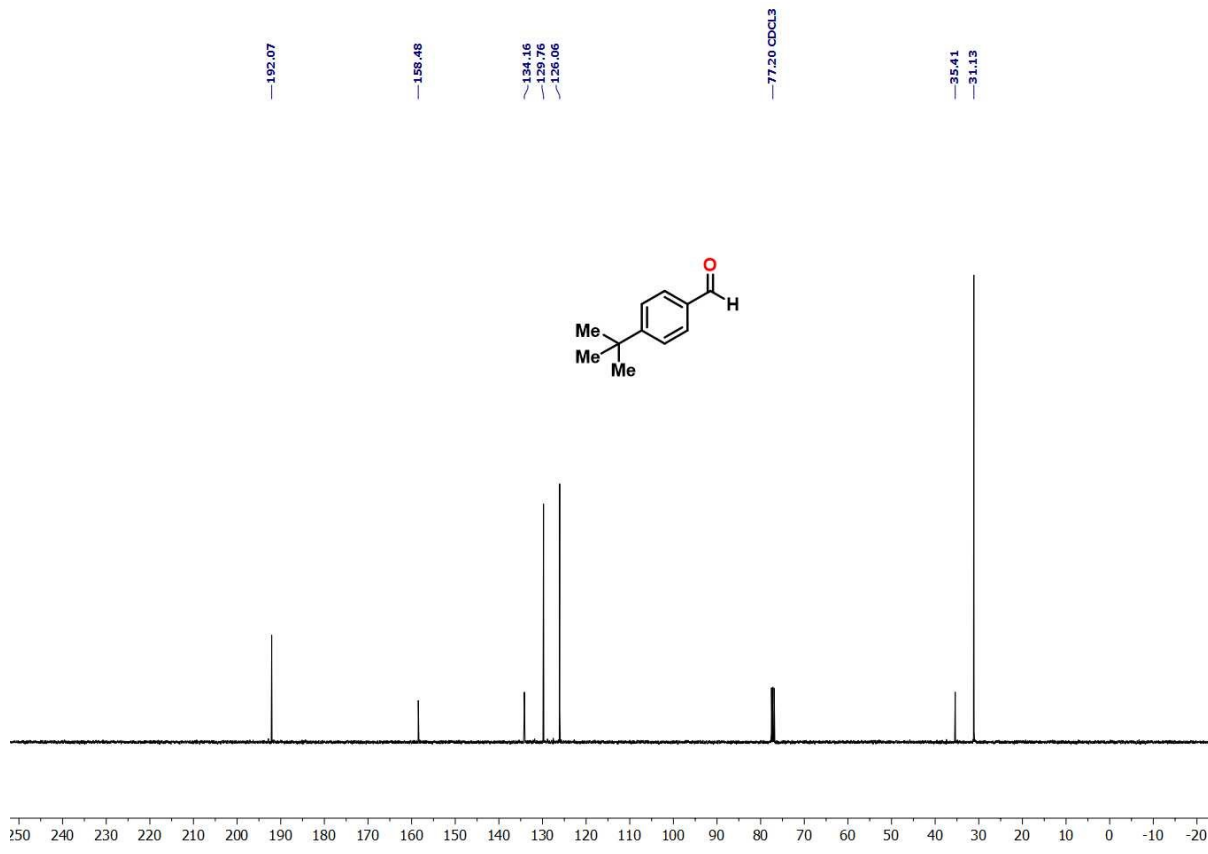


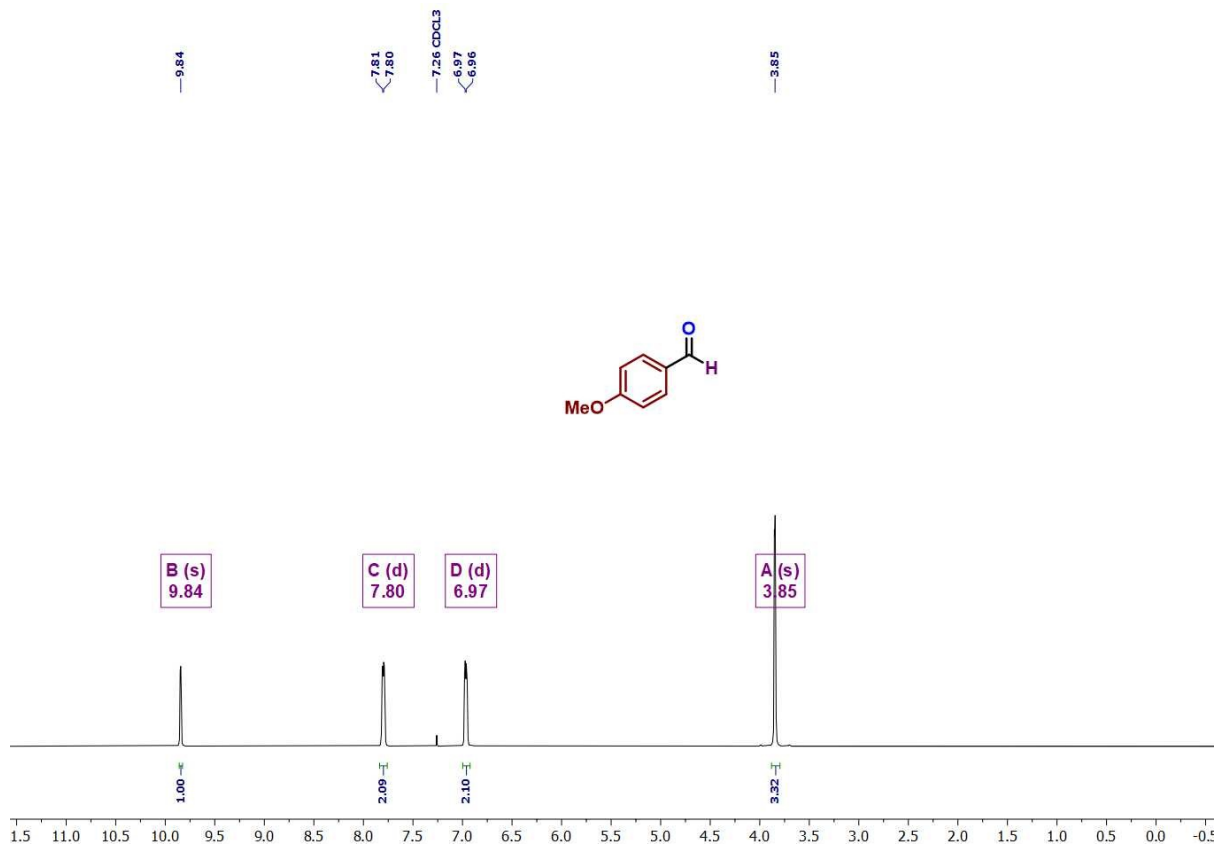
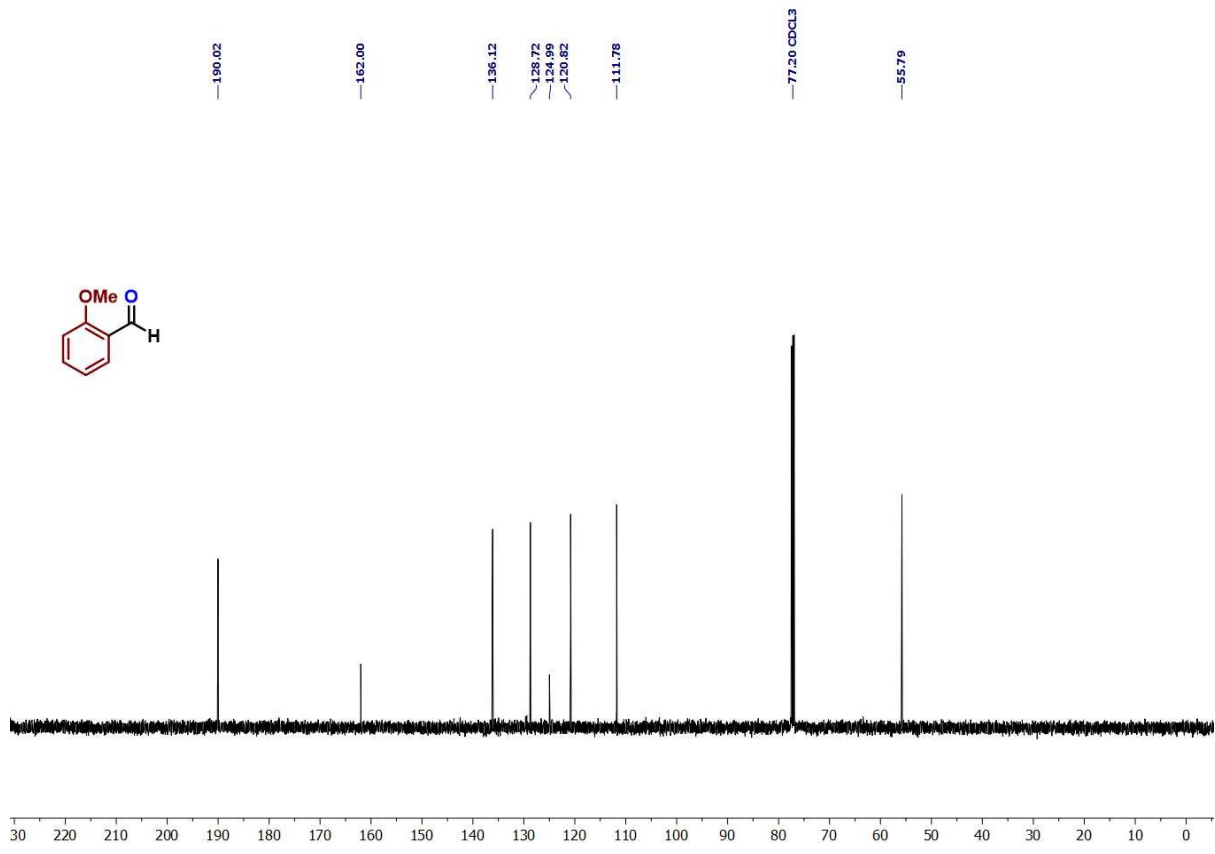


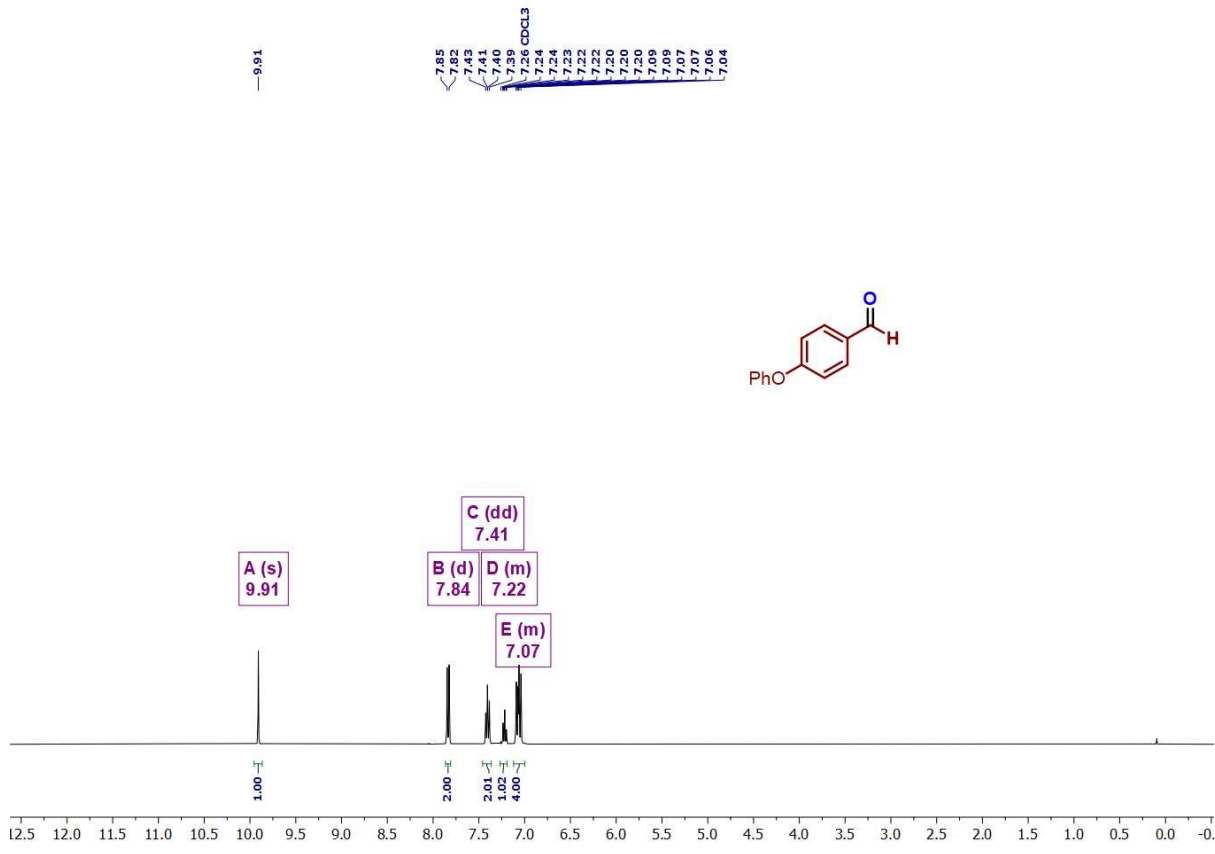
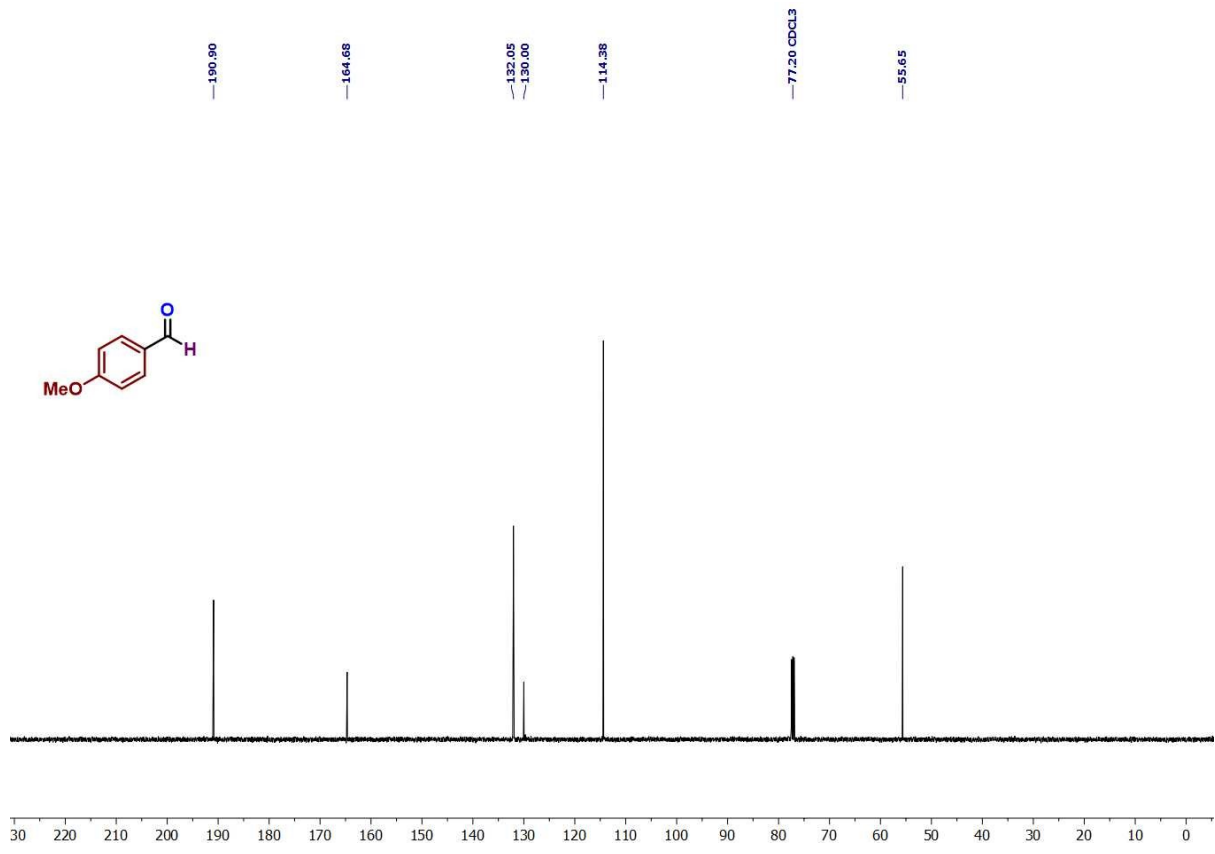


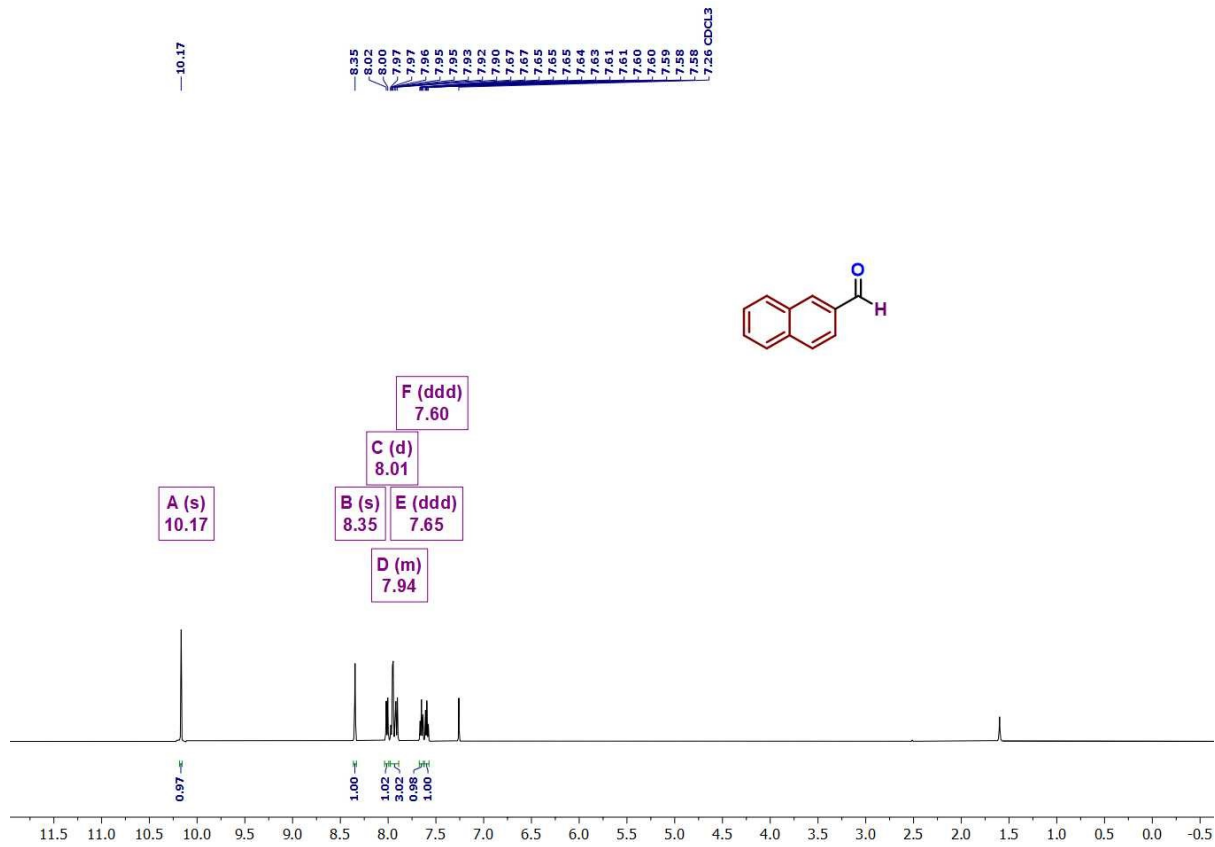
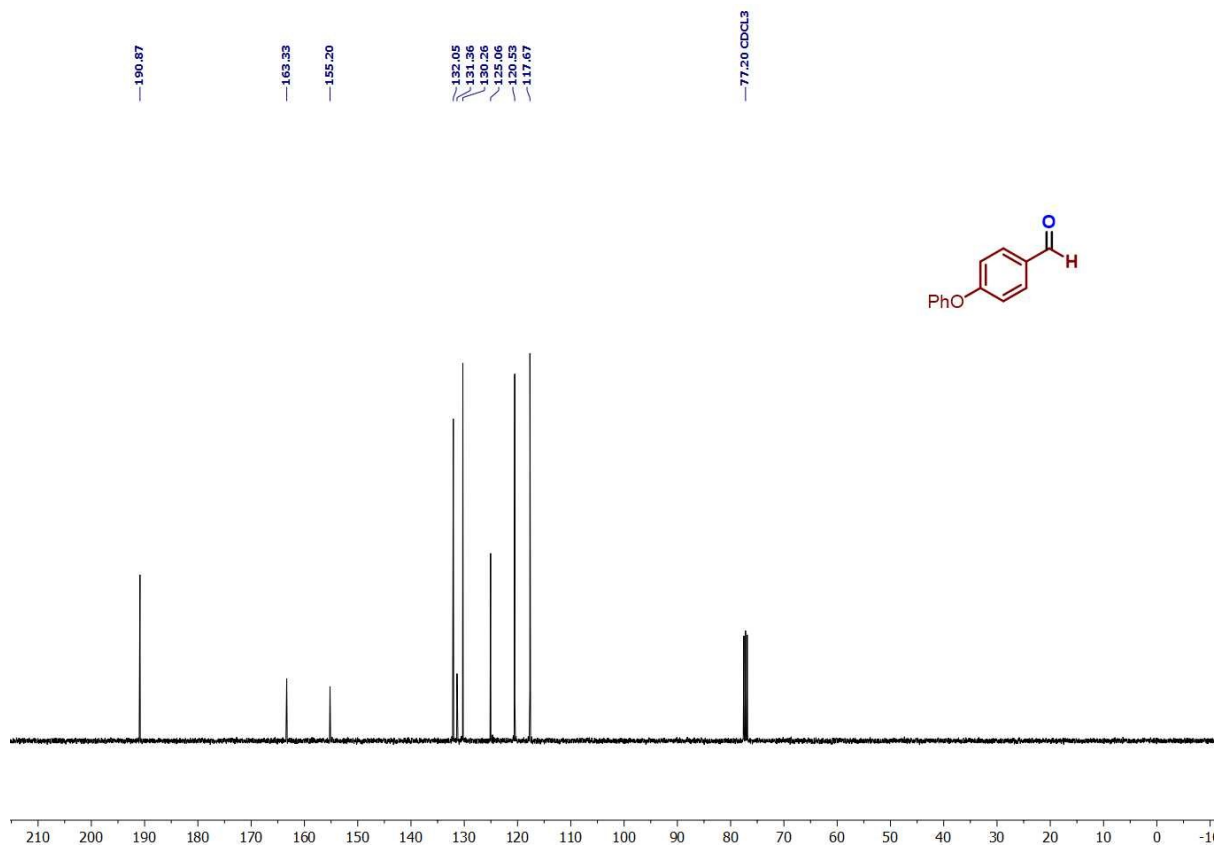


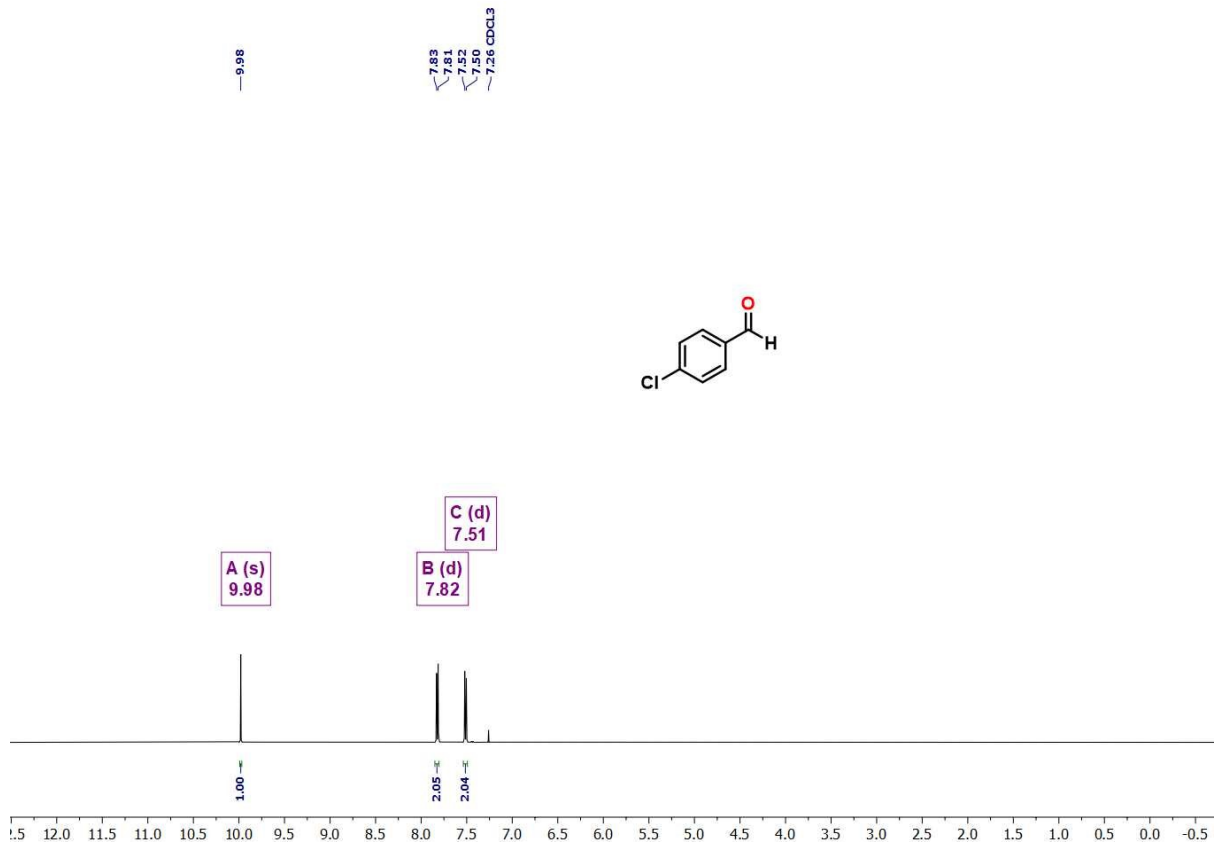
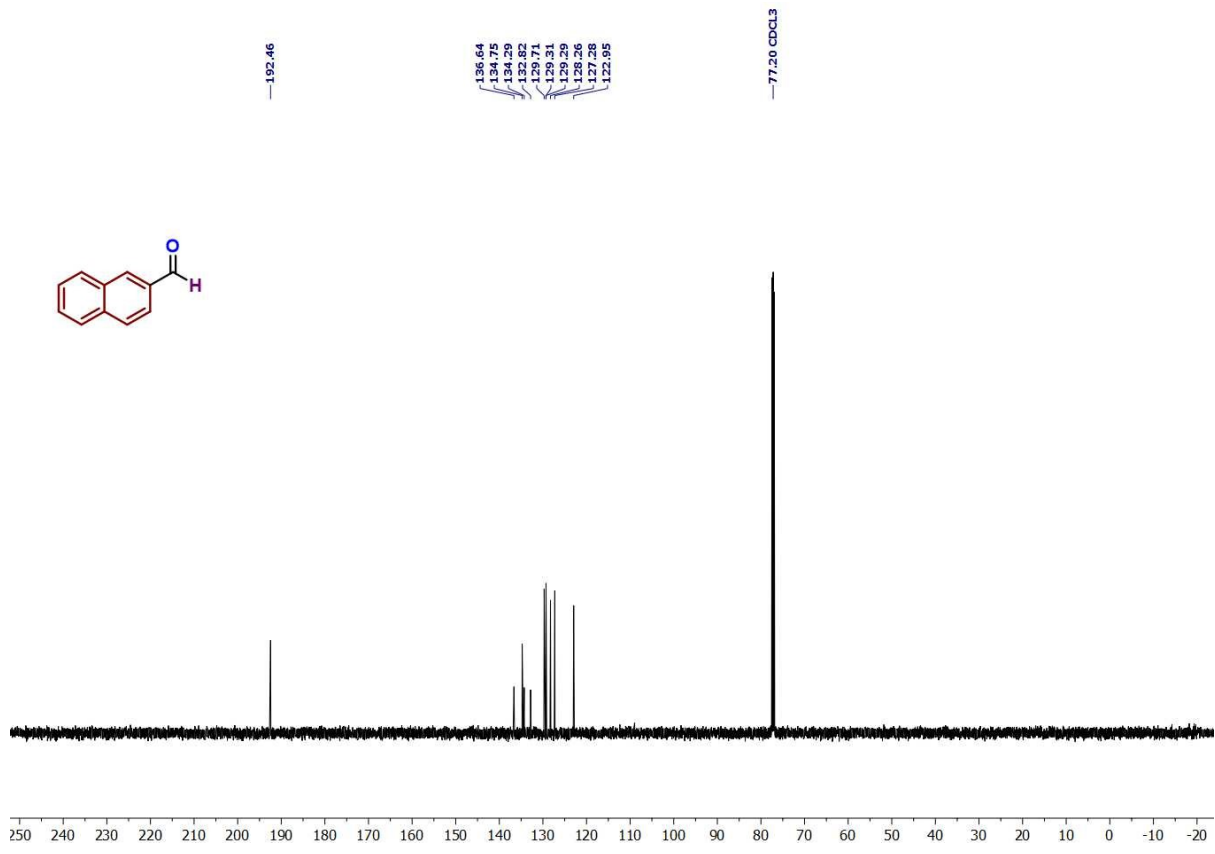


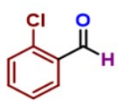
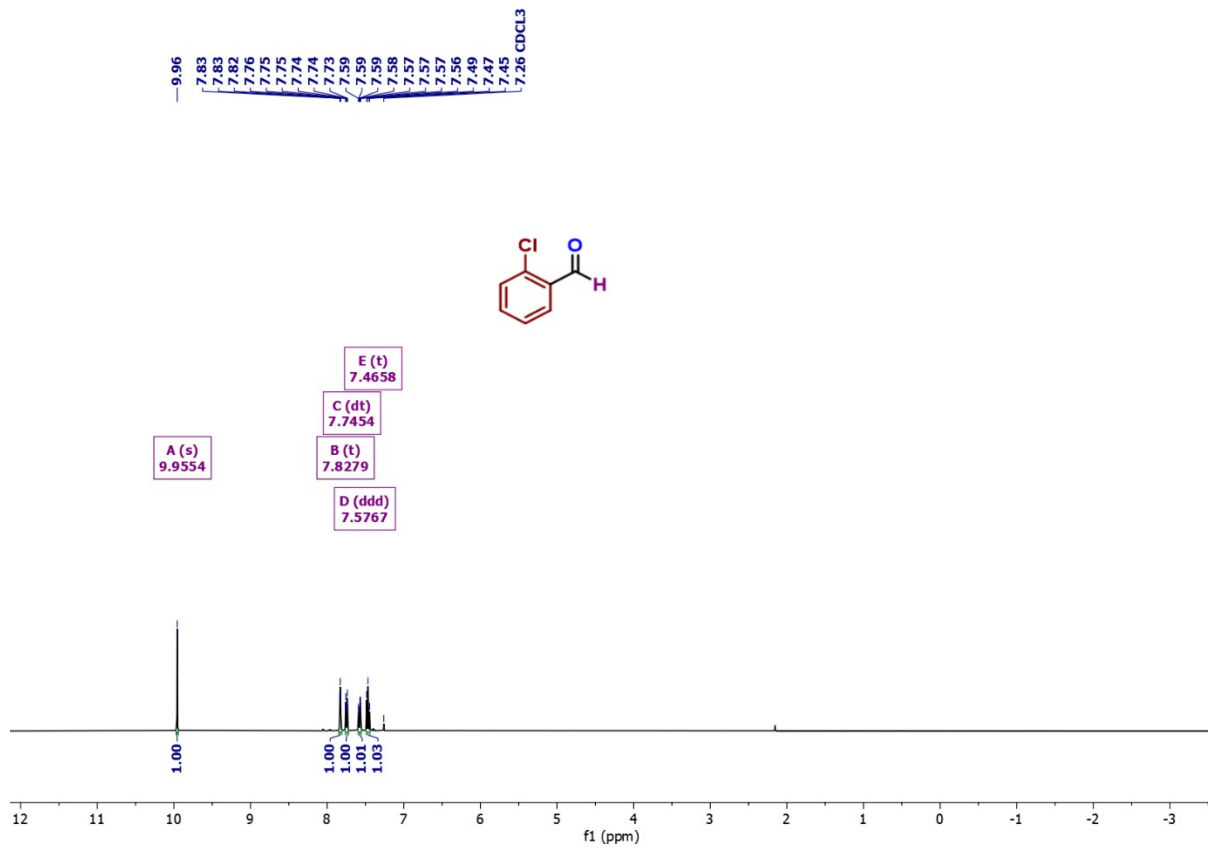
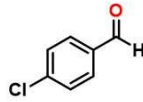
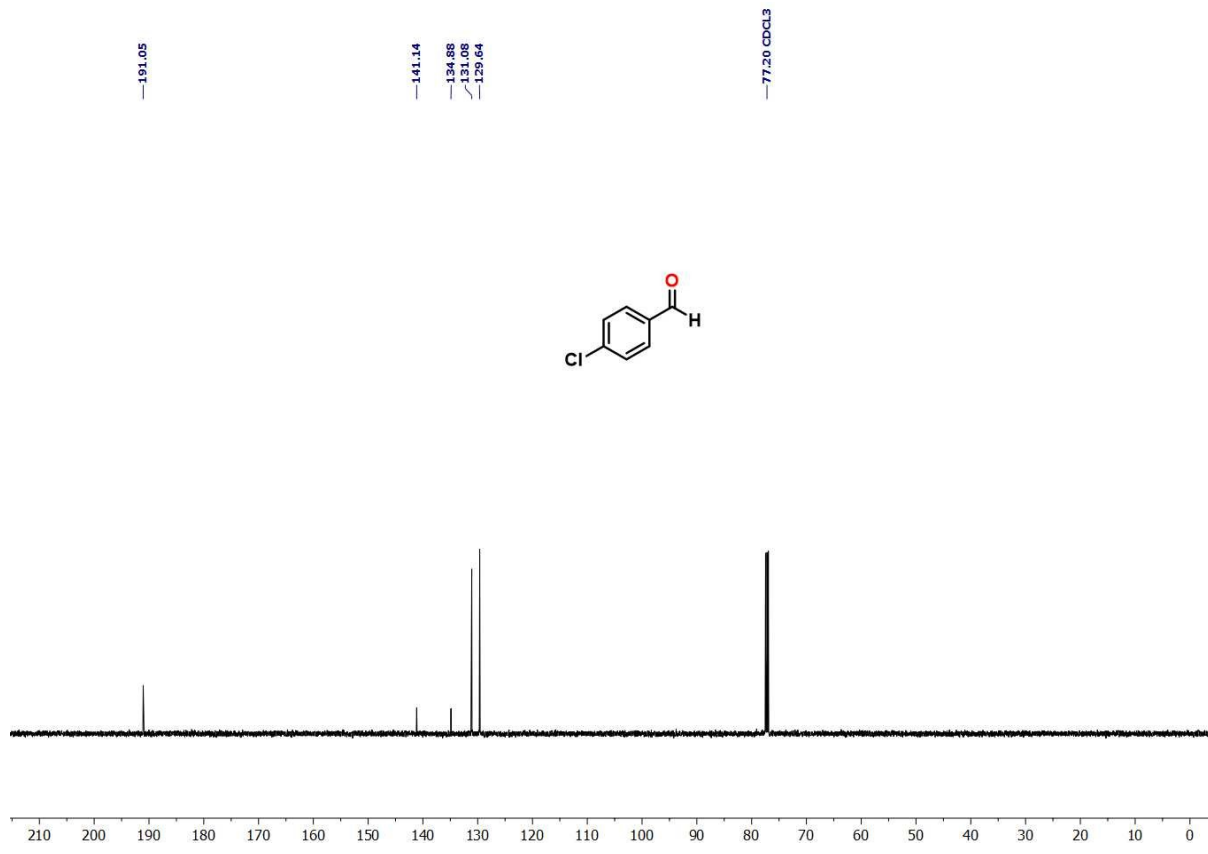






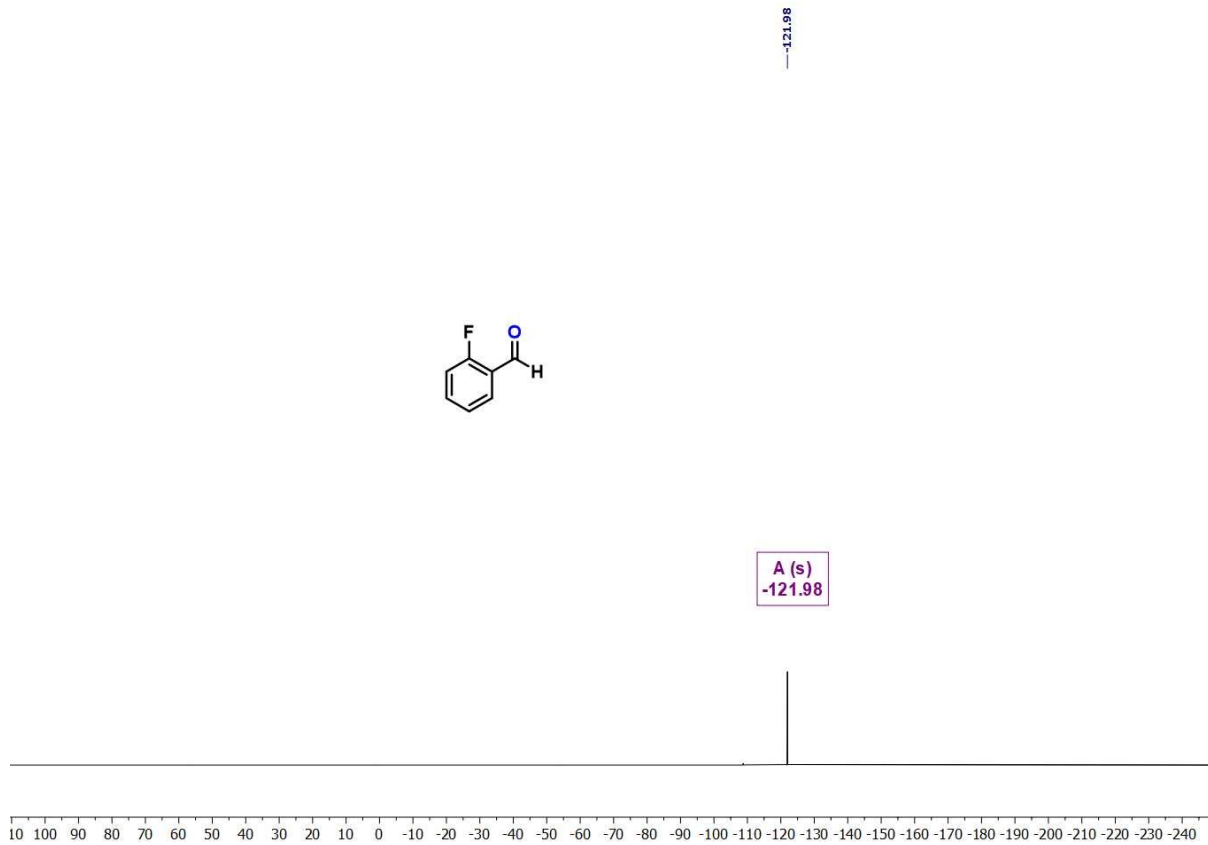
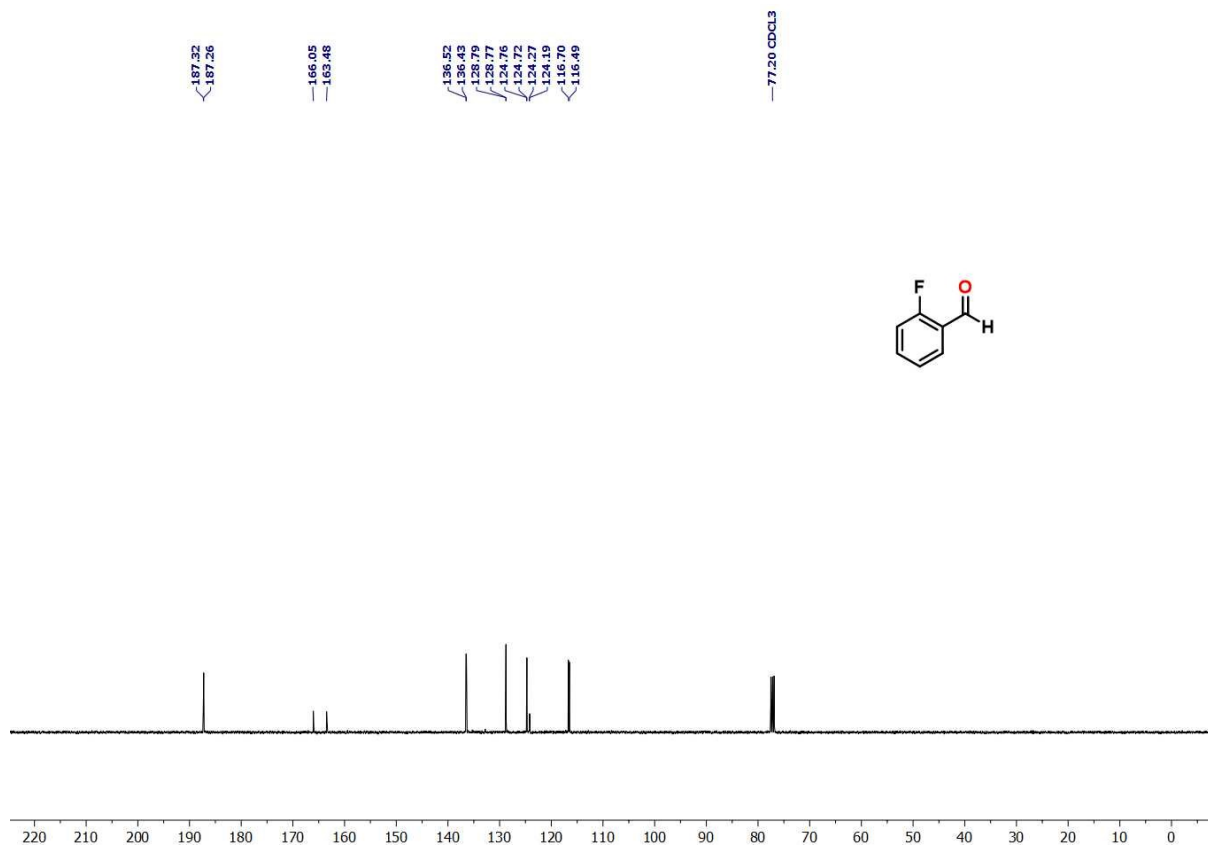


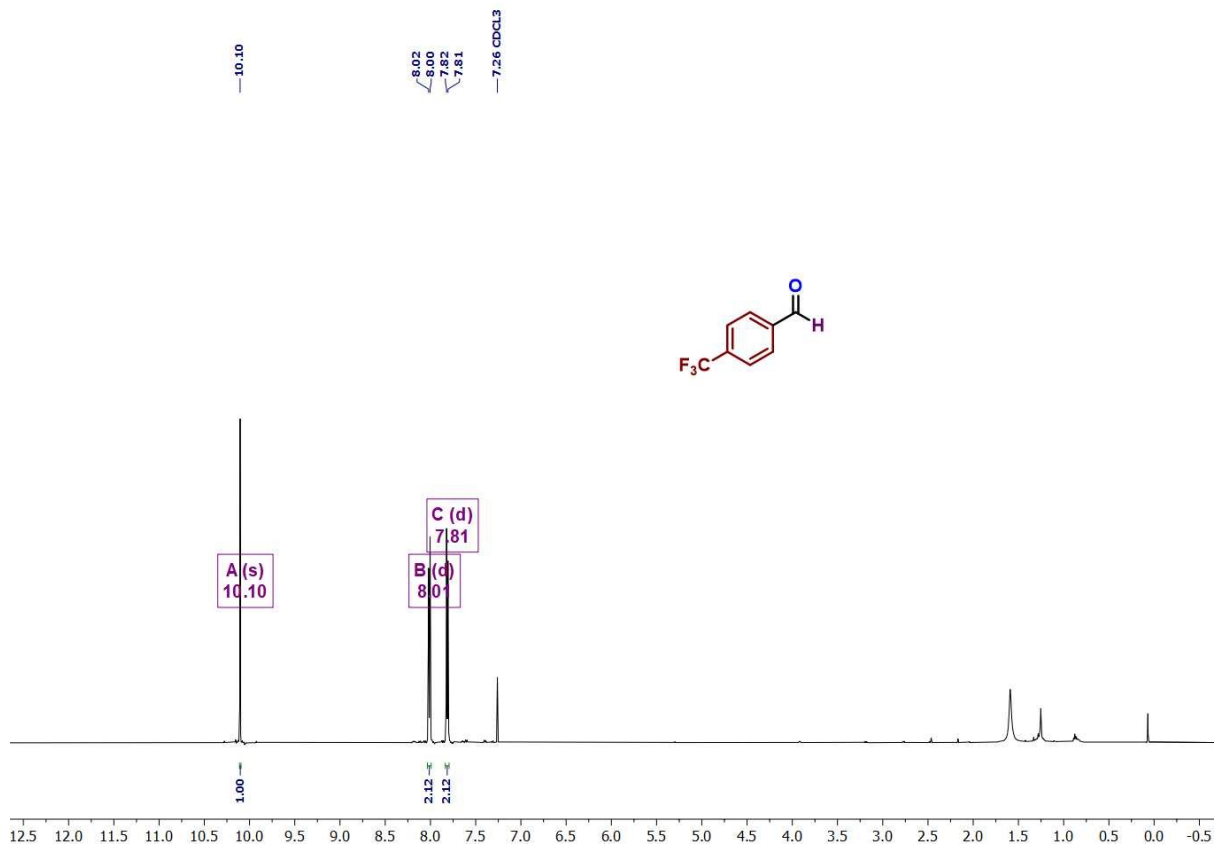


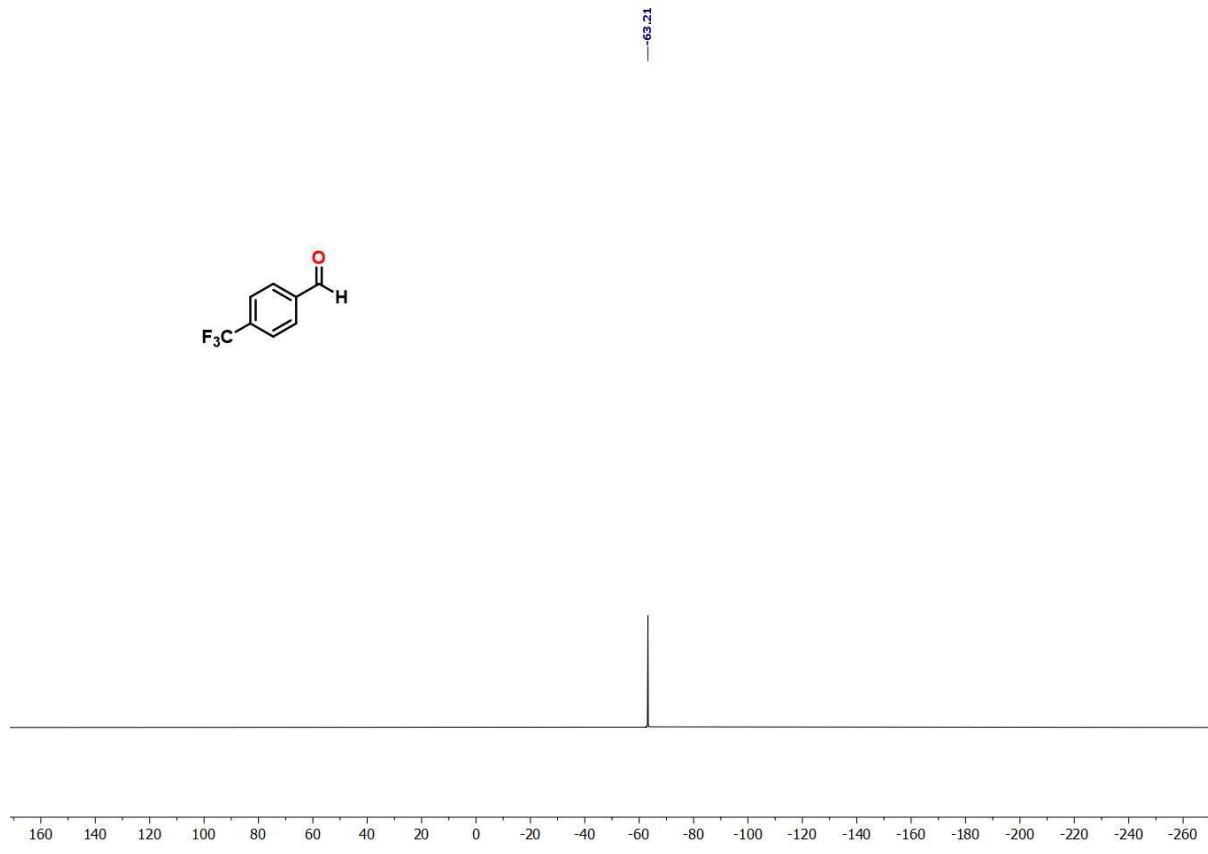
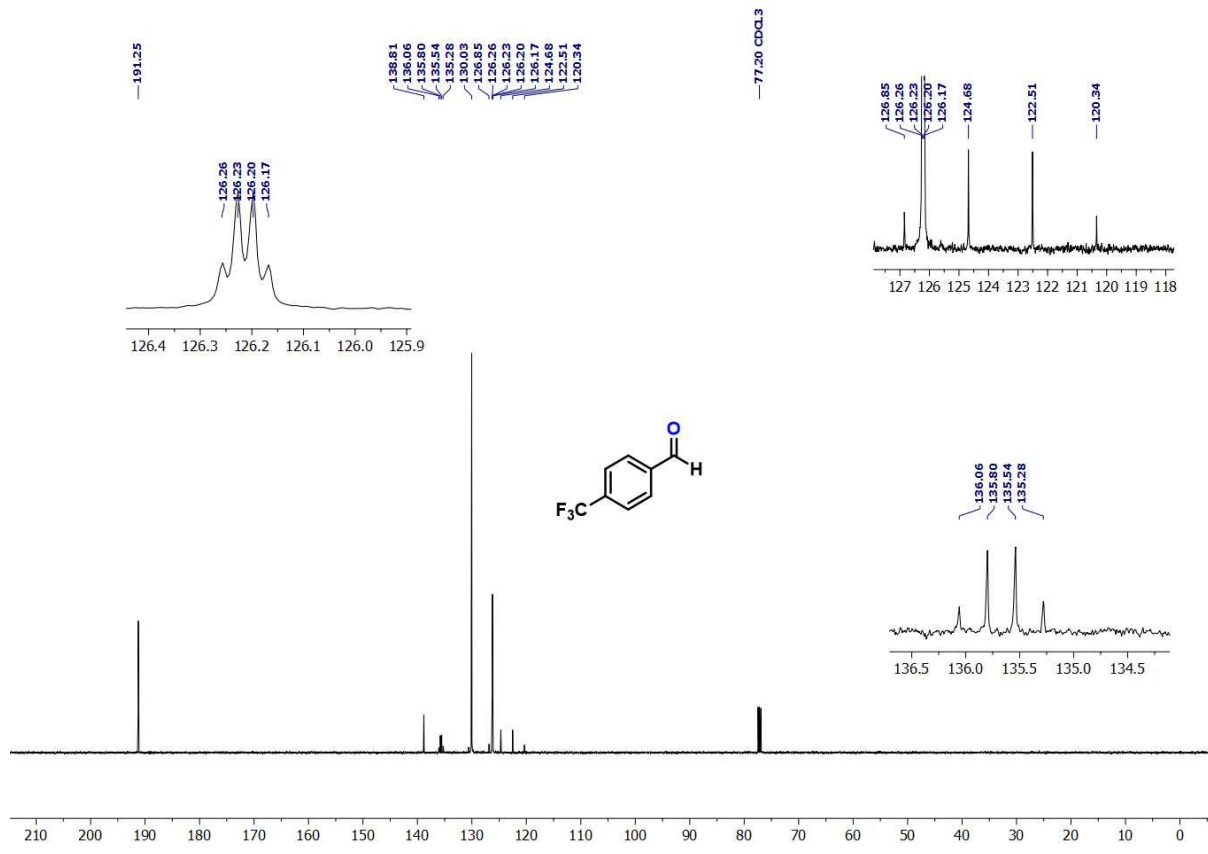


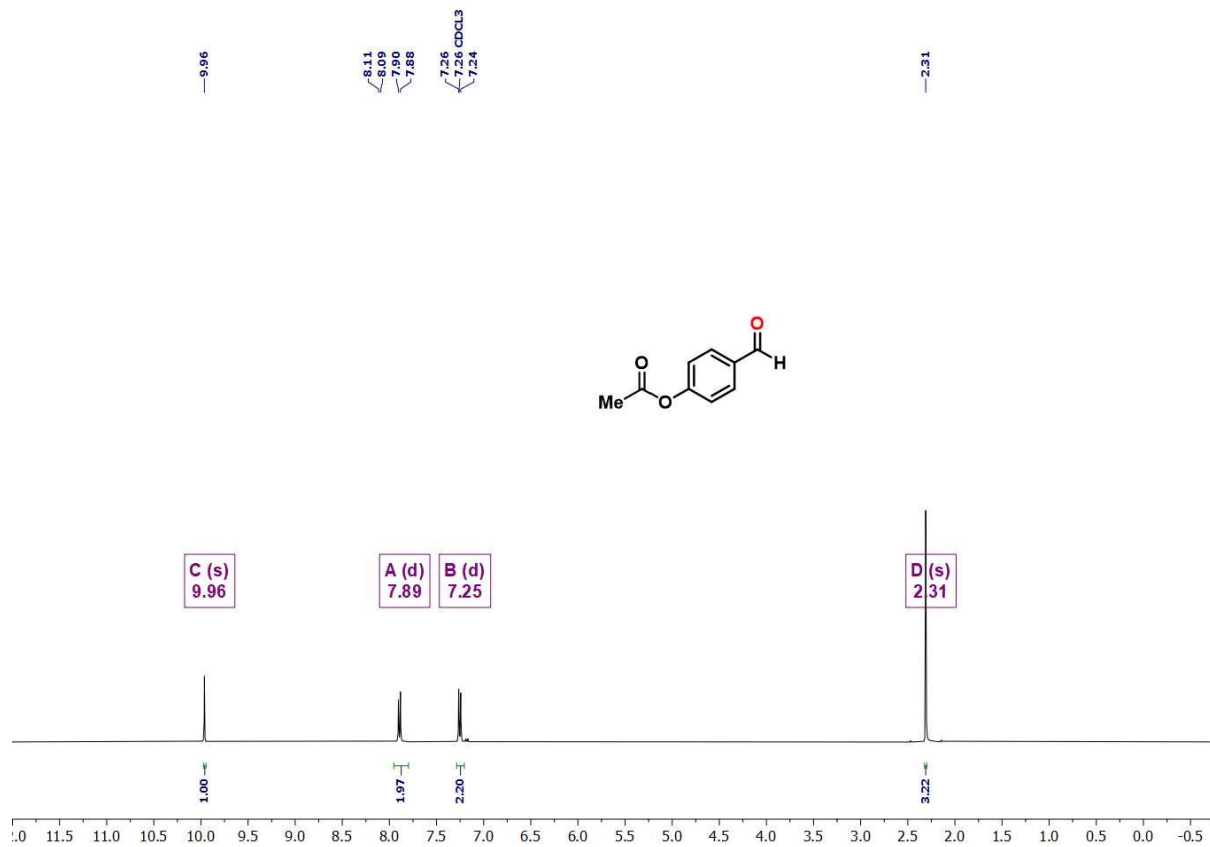


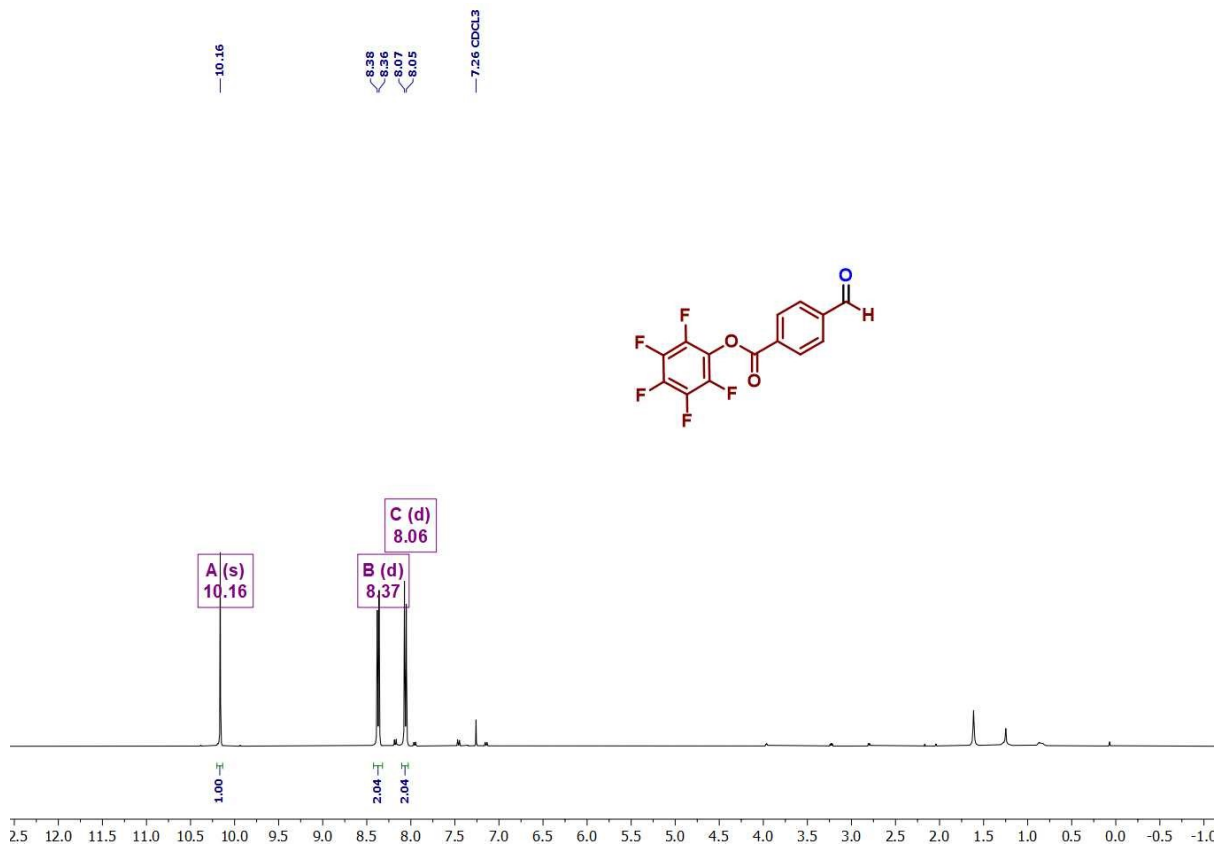
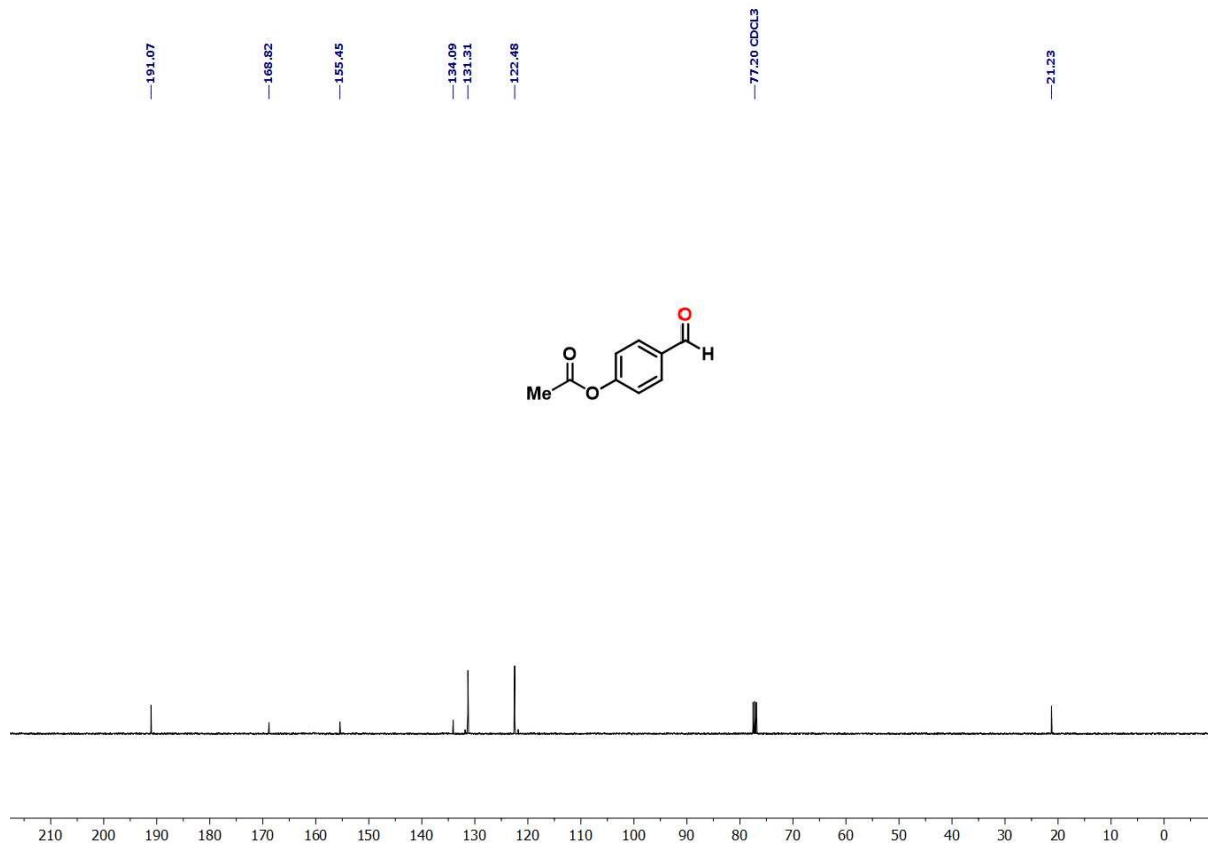


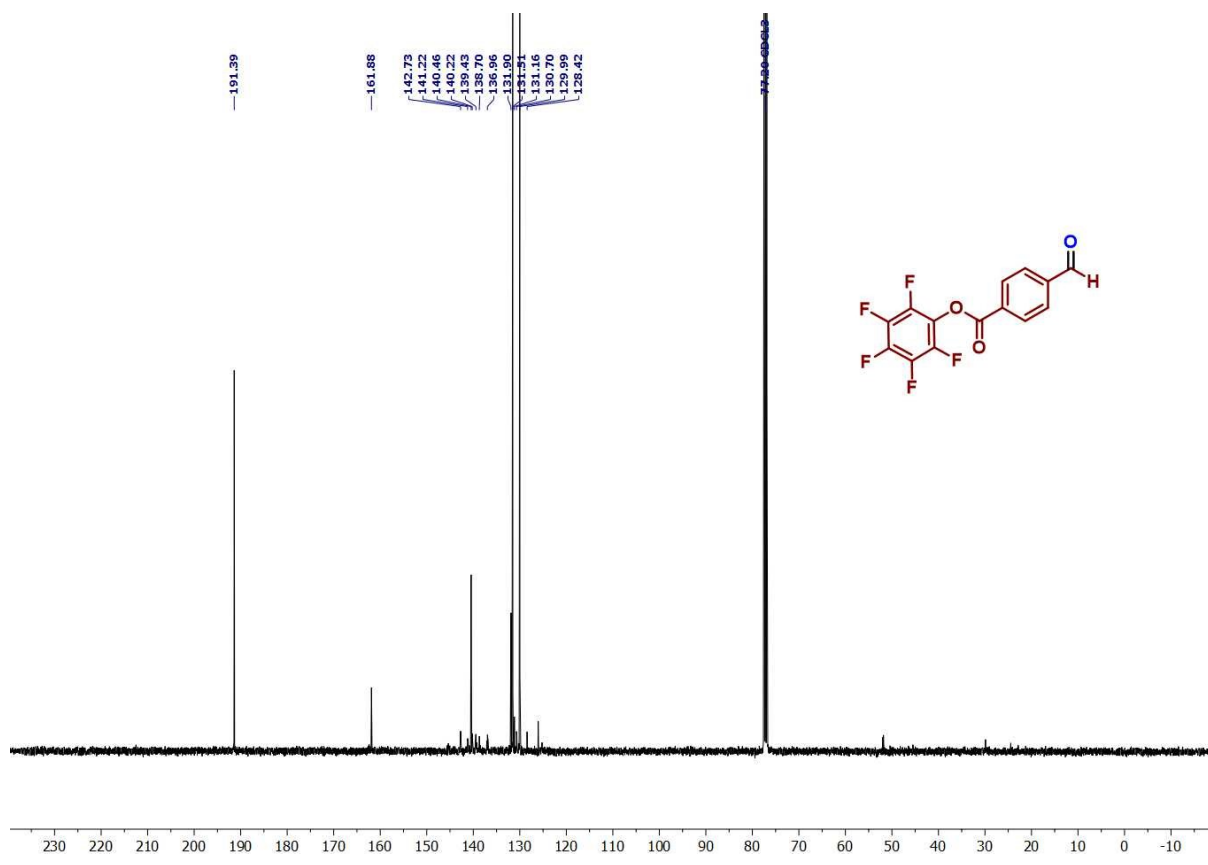












152.27  
152.32  
157.13  
157.19  
161.77  
161.82  
161.83  
161.87

