

# Electronic Supplementary Information

## Palladium Supported on N-doped Carbon : A simple Heterogeneous Catalyst for Base-Free Alkoxyacylation of Aryl Iodides

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## Experimental Procedures

**General information:** The structure and morphology of the catalyst were characterized by transmission and scanning electron microscopy (TEM and SEM). TEM images were obtained using an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS) operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a VG ESCALAB220iXL (ThermoScientific) with monochromatic Al K $\alpha$  (1486.6 eV) radiation. X-ray powder diffraction (XRD) pattern of the materials were recorded on a Stoe STADI P diffractometer, equipped with a linear Position Sensitive Detector (PSD) using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The C/H/N/S-elemental analysis (EA) was performed by combustion of a 10 mg sample at 1000°C under O<sub>2</sub>/He-flow using a Leco Microanalyser TruSpec. Reaction temperatures refer to external bath temperatures. All reactions were analyzed by Gas Chromatography on a HP 6890N chromatograph with a HP5 column and by TLC on silica gel 60 F<sub>254</sub> (components were located by observation under UV light). Column chromatography was performed on silica gel 60 (70-230 mesh) using ethyl acetate/heptane as eluent. Evaporation refers to the removal of solvent under reduced pressure. Mass spectra were obtained using a GC-MS apparatus at 70 eV ionization voltage. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were performed in a Bruker Avance 400 spectrometer and recorded at 25 °C in CDCl<sub>3</sub> solution at 300 MHz and 75 MHz, respectively using the residual solvent signal as internal standard [chloroform: 7.26 ppm (<sup>1</sup>H), 77.16 ppm (<sup>13</sup>C)]. Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are given in *ppm* and in *Hz*, respectively. In addition, the metal content was determined by ICP-MS (Instrument Sensitivity= 0.5 ppm). Unless otherwise statement, commercial reagents were used as received without purification.

### Preparation of palladium supported on N-doped carbon

Palladium(II) acetate (Sigma-Aldrich >98%, 112.3 mg, 0.5 mmol) and 1,10-phenanthroline (Sigma-Aldrich,  $\geq$ 99%, 180.2 mg, 1.0 mmol) (Pd:phenanthroline = 1:2 molar ratio) were stirred in ethanol (50 mL) for 1 h at 60 °C. Then, carbon powder (689.7 mg, VULCAN® XC72R) was added and the whole reaction mixture was leave to react at room temperature overnight. Ethanol was carefully removed under vacuo ( 40°C at 130 mBar ). The solid sample obtained was dried at 25 °C for 4 hours, after which it was grinded to a fine powder. Then, the grinded powder was transferred into a ceramic crucible and placed in the oven. The oven was evacuated to ca. 5 mbar and then flushed with argon. The oven was heated to 800 °C at the rate of 25 °C per minute, and held at 800 °C for 2 hours under argon atmosphere. During the whole process argon was

constantly passed through the oven. Finally the pyrolyzed material is grinded again so as to obtain a fine powder. Elemental analysis of Pd-Phenanthroline/C (wt%): C = 85.93, H = 0.52, N = 2.2, Pd = 5.63.

### **General procedure for alkoxy carbonylation of aryl iodides**

Into a reaction glass vial fitted with a magnetic stirring bar and a septum cap was added the palladium-catalyst (0.5 mol%, 5.63 wt% Pd-Phen/C, 9.5 mg) followed by the aryl iodide (1 mmol: **1a**, 204.0 mg; **1b**, 282.9 mg; **1c**, 282.9 mg; **1d**, 238.5 mg; **1e**, 238.5 mg; **1f**, 222.0 mg; **1g**, 262.0 mg; **1h**, 219.0 mg; **1i**, 234.0 mg; **1j**, 218.0 mg; **1k**, 230.1 mg; **1l**, 254.1 mg;), the internal standard (hexadecane, 0.2 equiv, 45.3 mg) and the solvent (MeOH dry, 2 mL). The reaction vial was then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with carbon monoxide (5 bar for 5 times) and then it was pressurized to 20 bar carbon monoxide pressure and placed into an aluminium block preheated at 120 °C. After 24 h the reaction was completed and the autoclave was placed into an ice bath and cooled to room temperature. Finally, carbon monoxide gas was discharged and the samples were removed from the autoclave, diluted with ethyl acetate, filtered through a silica plug and analyzed by GC and GC-MS. All GC-yields are averages from at least 3 runs, the starting materials as well as products were calibrated from the commercially available materials. Isolated yields was determined by column chromatography on silica gel using as eluent only heptane to 9:1 heptane/AcOEt for **2b**, **2c** and **2j**; 95:5 heptane/AcOEt for **2a**, **2d**, **2e**, **2f**, **2g**, **2k** and **2l**; 9:1 heptane/AcOEt for **2i**; 9:1 heptane/AcOEt to 8:2 heptane/AcOEt for **2h**.

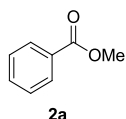
### **Hot Filtration experiment**

Iodobenzene **1a** (10 mmol, 2.04 g) diluted in MeOH (20mL) was stirred into a soxhlet in the presence of catalytic amount of Pd/PdO@NGr-C (0.5 mol%, 5.63 wt% Pd-Phen/C, 95 mg) at 100°C for 1 h. The reaction mixture is filtered while hot, and the filtrate was allowed to react as described above in the “General procedure for alkoxy carbonylation of aryl iodides” under a pressure of 20 bar of carbon monoxide at 120°C for 24 h. GC shown that iodo-benzene did not react.

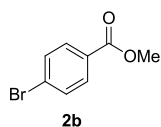
### **Catalyst recycling experiments**

For the catalyst recycling experiments, the reactions were carried on a 5 mmol of iodobenzene **1a** in the presence of 0.1 mol % of the catalyst (10 mg ). All reactions were conducted in glass vials and set up according to procedures described above in the “General procedure for alkoxyacylation of aryl iodides”. The catalyst was separated from the reaction mixture by centrifugation at 8000 RPM for 10 min. The supernatant solution was withdrawn with a Pasteur pipette, the catalyst washed with MeOH for two times and then dried under a high vacuum for 1 h before being resubmitted to the reaction conditions. All yields are averages from at least 2 runs.

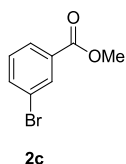
## Characterization Data



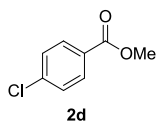
*Methyl benzoate (2a)*<sup>1</sup>. Yield: 93.9 mg, starting from 204.0 mg of iodobenzene (69%). Colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.08-8.04 (m, 2H, CH arom), 7.61-7.53 (m, 1H, CH arom), 7.49-7.41 (m, 2H, CH arom), 3.93 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 167.1 (CO), 132.9 (*p*-CH), 130.2 (C), 129.6 and 128.4 (CH), 52.1 (CH<sub>3</sub>). GC-MS: *m/z* = 136 (39) [M<sup>+</sup>], 105 (100), 77 (54), 59 (1), 51 (20).



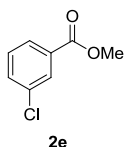
*Methyl 4-bromobenzoate (2b)*<sup>2</sup>. Yield: 180.6 mg, starting from 282.9 mg of 1-bromo-4-iodobenzene (84%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.92- 7.86 (m, 2H, CH arom), 7.60-7.54 (m, 2H, CH arom), 3.91 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 166.4 (CO), 131.7 and 131.1 (CH), 129.1 and 128.1 (C), 52.3 (CH<sub>3</sub>). GC-MS: *m/z* = 216 (36) [M<sup>+</sup>], 215 (6), 214 (35), 185 (99), 184 (9), 183 (100), 157 (34), 155 (35), 76 (20), 50 (17).



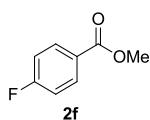
*Methyl 3-bromobenzoate (2c)*<sup>3</sup>. Yield: 159.1 mg, starting from 282.9 mg of 1-bromo-3-iodobenzene (74%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.18 (t, *J*= 1.8, 1H, CH arom), 7.97 (dt, *J*= 7.8, 1.3, 1H, CH arom), 7.68 (ddd, *J*= 8.0, 2.1, 1.1, 1H, CH arom), 7.32 (t, *J*= 7.9, 1H, CH arom), 3.92 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 165.8 (CO), 135.9 and 132.7 (CH), 132.1 (C) , 130.0 and 128.2 (CH), 122.5 (C), 52.5 (CH<sub>3</sub>). GC-MS: *m/z* = 216 (36) [M<sup>+</sup>], 214 (35), 185 (99), 184 (9), 183 (100), 157 (34), 155 (35), 76 (20), 50 (17).



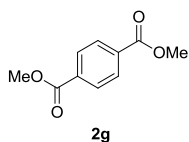
*Methyl 4-chlorobenzoate (2d)*<sup>3,4</sup>. Yield: 139.9 mg, starting from 238.5 mg of 1-chloro-4-iodobenzene (82%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.00- 7.95 (m, 2H, CH arom), 7.44-7.38 (m, 2H, CH arom), 3.91 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 166.4 (CO), 139.5 and 131.1 (CH), 128.9 and 128.7 (C), 52.4 (CH<sub>3</sub>). GC-MS:  $m/z$  = 170 (32) [M<sup>+</sup>], 141 (33), 139 (100), 113 (12), 111 (38), 75 (23).



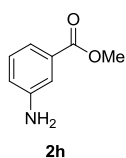
*Methyl 3-chlorobenzoate (2e)*<sup>3</sup>. Yield: 126.2 mg, starting from 238.5 mg of 1-chloro-3-iodobenzene (74%). Colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.04- 7.99 (m, 1H, CH arom), 7.92 (dt,  $J$ = 7.7, 1.4, 1H, CH arom), 7.52 (ddd,  $J$ = 8.0, 2.2, 1.1, 1H, CH arom), 7.42- 7.33 (m, 1H, CH arom), 3.92 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 166.0, 134.7 and 133.1, 132.0, 128.8 and 128.8, 52.5. GC-MS:  $m/z$  = 170 (37) [M<sup>+</sup>], 141 (33), 139 (100), 113 (14), 111 (44), 75 (25).



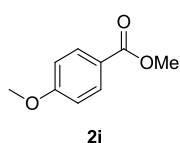
*Methyl 4-fluorobenzoate (2f)*<sup>5</sup>. Yield: 80.2 mg, starting from 222.0 mg of 1-fluoro-4-iodobenzene (52%). Colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.11- 7.99 (m, 2H, CH arom), 7.16-7.02 (m, 2H, CH arom), 3.91 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.6 (CF), 166.2 (CO), 164.2 (CF), 132.30 and 132.18 (CH), 126.56 and 126.52 (C), 115.78 and 115.49 (CH), 52.3 (CH<sub>3</sub>). GC-MS:  $m/z$  = 154 (33) [M<sup>+</sup>], 123 (100), 95 (44), 75 (17).



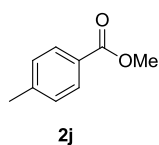
*Dimethyl terephthalate (2g)*<sup>6</sup>. Yield: 106.8 mg, starting from 262.0 mg of methyl 4-iodobenzoate (55%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.09 (s, 4H, CH arom), 3.94 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.4 (CO), 134.0 (C), 129.7 (CH), 52.57 (CH<sub>3</sub>). GC-MS:  $m/z$  = 194 (23) [M<sup>+</sup>], 163 (100), 135 (19), 103 (11), 76 (9).



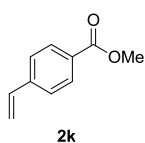
*Methyl 3-aminobenzoate (2h)*<sup>7</sup>. Yield: 105.8 mg, starting from 219.2 mg of 3-iodoaniline (70%). Yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.42 (dt,  $J$ =7.7, 1.3, 1H, CH arom), 7.36 – 7.33 (m, 1H, CH arom), 7.20 (t,  $J$ =7.8, 1H, CH arom), 6.85 (ddd,  $J$ =8.0, 2.5, 1.0, 1H, CH arom), 3.88 (s, 3H, CH<sub>3</sub>), 3.65 (d,  $J$ =7.6, 2H, NH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.40 (CO), 146.55 (CNH<sub>2</sub>), 131.24 (C), 129.38 (CH), 119.84 (CH), 119.53 (CH), 115.90 (CH), 52.16 (CO<sub>2</sub>CH<sub>3</sub>). GC-MS:  $m/z$  = 151 (100) [M<sup>+</sup>], 121 (8), 120 (9), 93 (19), 92 (70), 65 (32).



*Methyl 4-methoxybenzoate (2i)*<sup>3</sup>. Yield: 139.6 mg, starting from 234.0 mg of 1-iodo-4-methoxybenzene (84%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.99 (d,  $J$ =9.0, 2H, CH arom), 6.91 (d,  $J$ =8.9, 2H, CH arom), 3.88 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.85 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.00 (CO), 163.45 (COCH<sub>3</sub>), 131.71 (CH), 122.74 (C), 113.73 (CH), 55.54 (CO<sub>2</sub>CH<sub>3</sub>), 51.99 (OCH<sub>3</sub>). GC-MS:  $m/z$  = 166 (37) [M<sup>+</sup>], 135 (100), 107 (9), 92 (13), 77 (15).

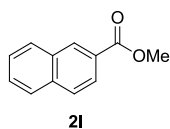


*Methyl 4-methylbenzoate (2j)*<sup>8</sup>. Yield: 85.6 mg, starting from 218.0 mg of 1-iodo-4-methylbenzene (57%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.93 (d,  $J$ =8.2, 2H, CH arom), 7.23 (d,  $J$ =8.0, 2H, CH arom), 3.90 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 166.3 (CO), 143.7 (CCH<sub>3</sub>), 129.7 and 129.2 (CH), 127.6 (C), 52.1 (CO<sub>2</sub>CH<sub>3</sub>), 21.8 (CH<sub>3</sub>). GC-MS:  $m/z$  = 150 (35) [M<sup>+</sup>], 120 (10), 119 (100), 91 (43), 65 (15).



*Methyl 4-vinylbenzoate (2k)*<sup>9</sup>. Yield: 86.0 mg, starting from 230.1 mg of 1-iodo-4-vinylbenzene (53%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.05 – 7.94 (m, 2H arom), 7.51 – 7.40 (m, 2H arom), 6.75

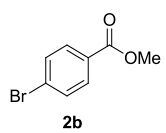
(dd,  $J=17.6, 10.9$ , 1H vinyl), 5.86 (dd,  $J=17.6, 0.8$ , 1H vinyl), 5.38 (dd,  $J=10.9, 0.7$ , 1H vinyl), 3.91 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 166.99 (CO), 142.05 (CCHCH<sub>2</sub>), 136.15 (CHCH<sub>2</sub>), 130.01 (CH), 129.41 (CH), 126.24 (CH), 116.60 (CHCH<sub>2</sub>), 52.20 (CO<sub>2</sub>CH<sub>3</sub>). GC-MS:  $m/z$  = 162 (44) [M<sup>+</sup>], 132 (10), 131 (100), 103 (34), 77 (26), 51 (9).



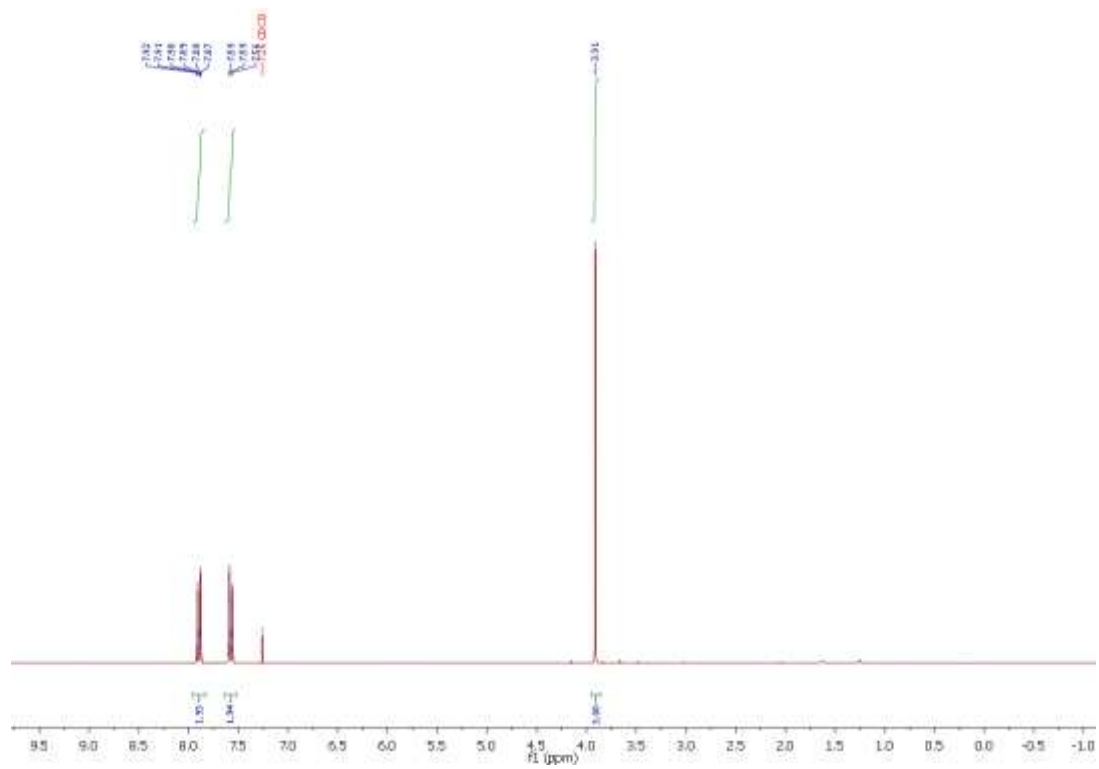
*Methyl 2-naphthoate (21)*<sup>2</sup>. Yield: 167.6 mg, starting from 254.1 mg of 2-iodonaphthalene (90%). White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.62 (s, 1H, CH arom), 8.07 (dd,  $J=8.6, 1.7$ , 1H, CH arom), 7.96 (d,  $J=8.1$ , 1H, CH arom), 7.88 (d,  $J=8.4$ , 2H, CH arom), 7.63 – 7.49 (m, 2H, CH arom), 3.99 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 167.4, 135.6, 132.6, 131.2, 129.5, 128.4, 128.3, 127.9, 127.5, 126.8, 125.4, 52.4. GC-MS:  $m/z$  = 186 (71) [M<sup>+</sup>], 156 (12), 155 (100), 127 (86), 126 (19), 77 (10)



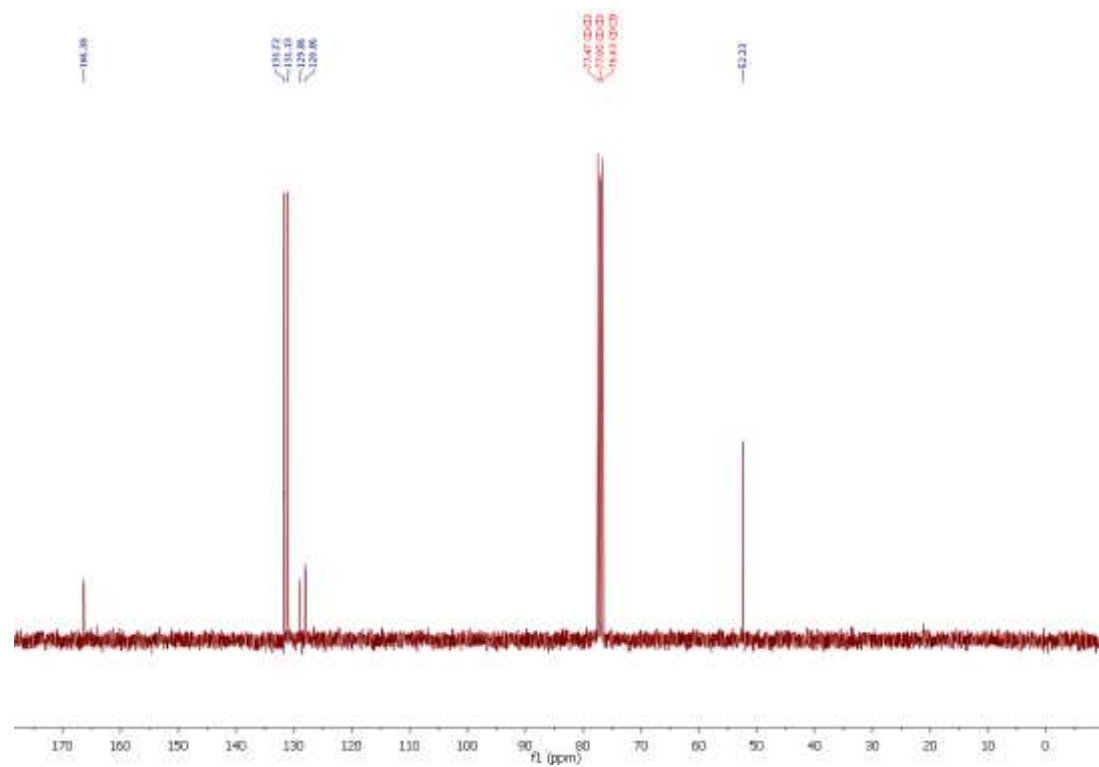


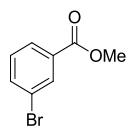


<sup>1</sup>H-NMR



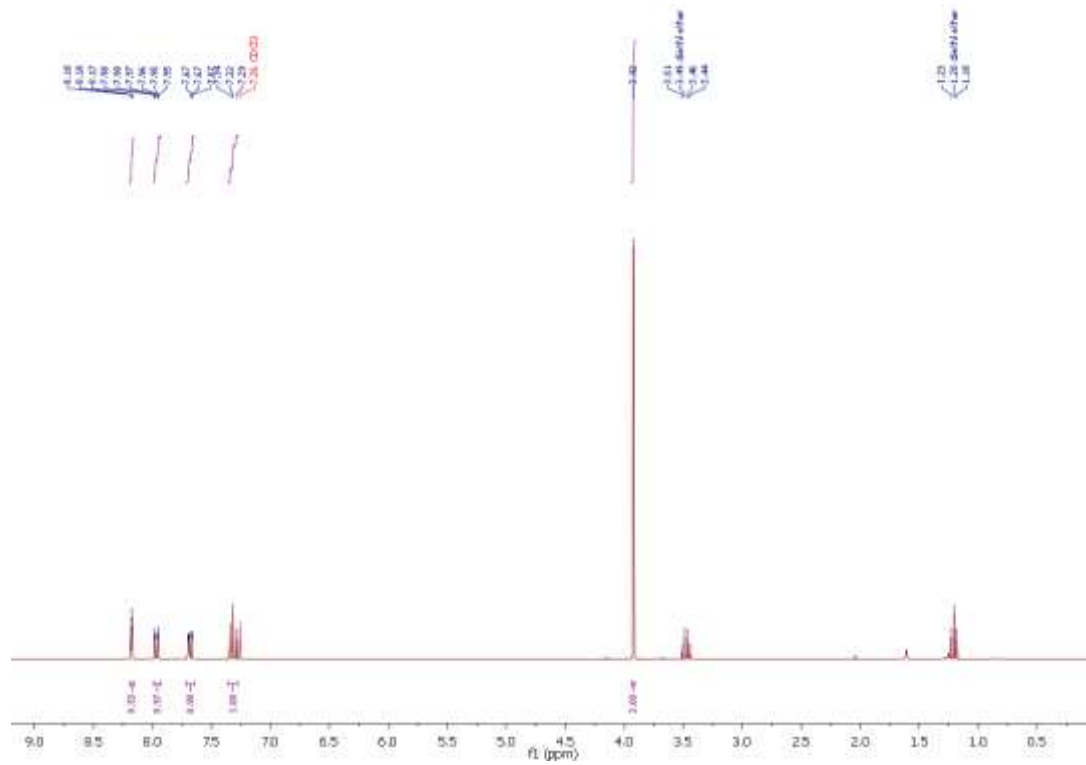
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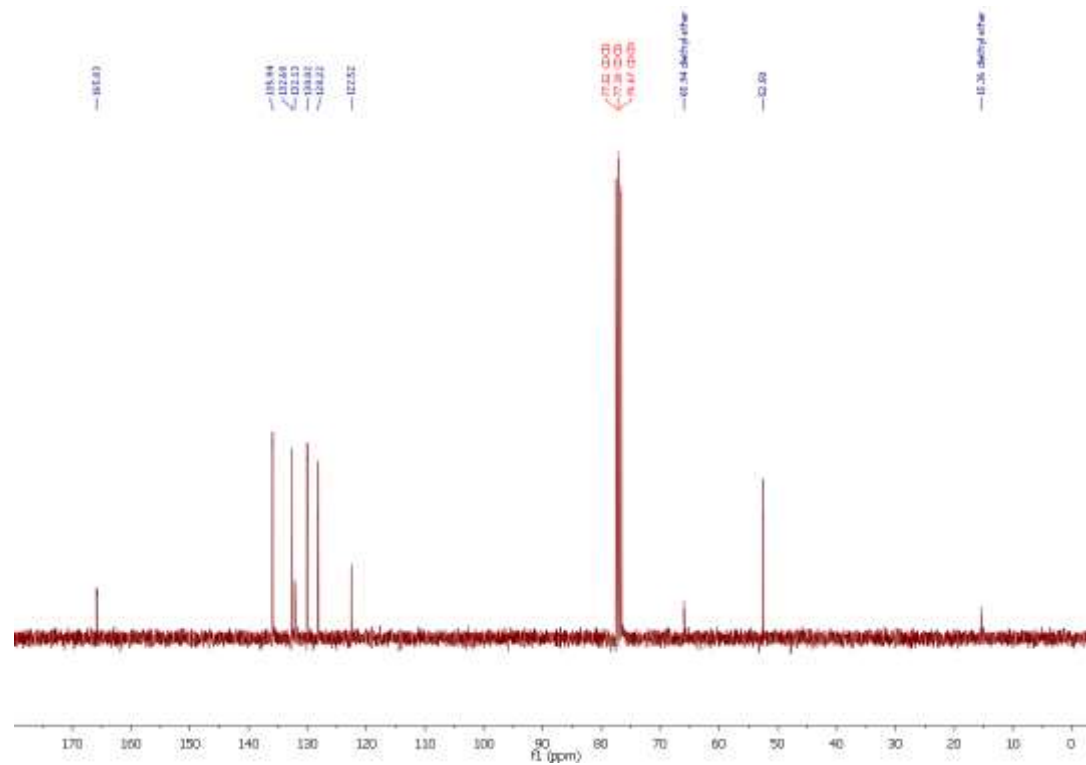


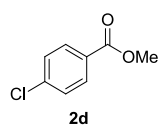
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<sup>1</sup>H-NMR

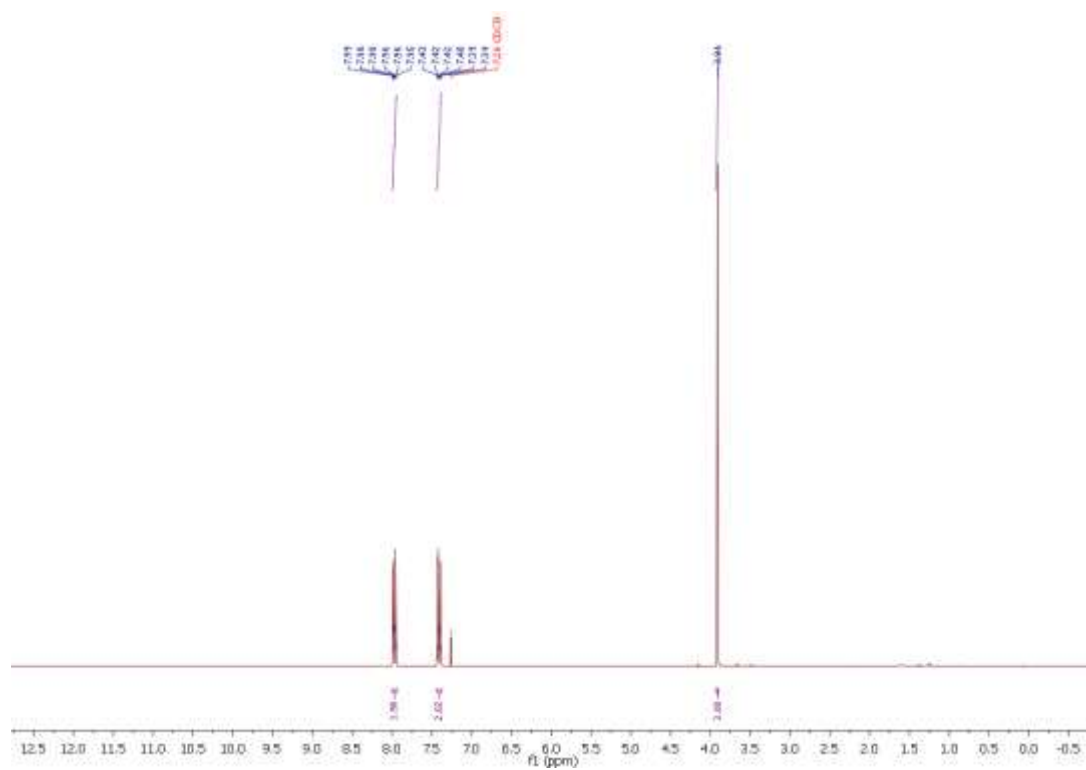


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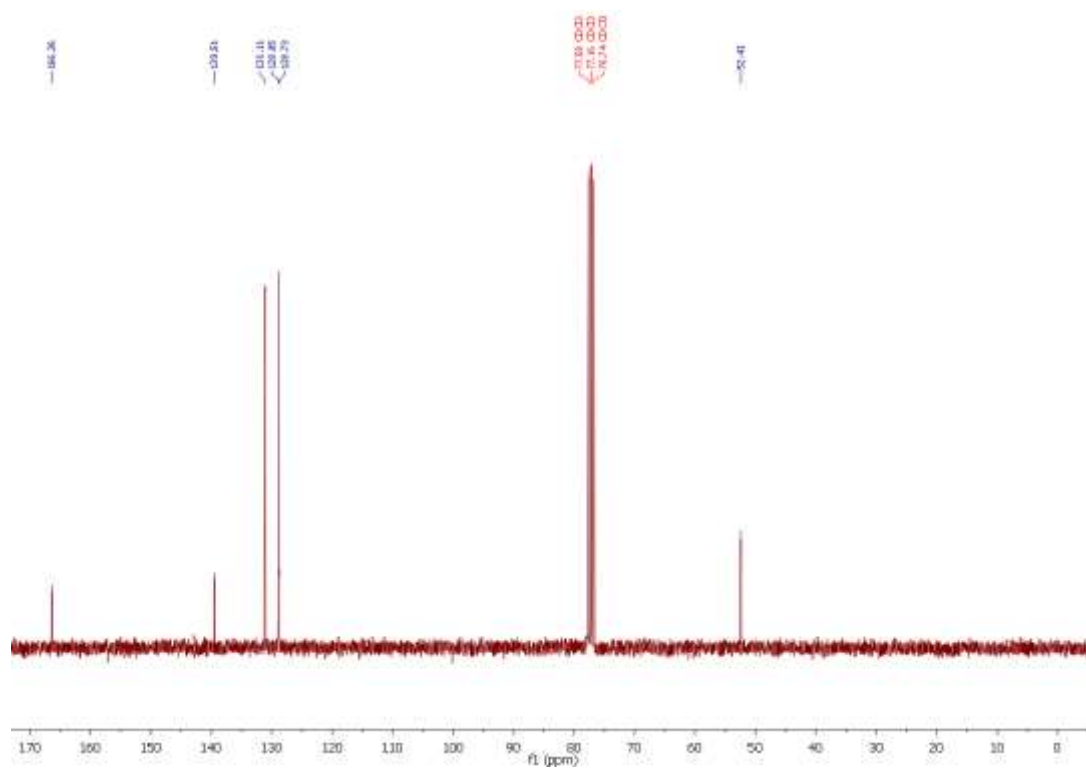




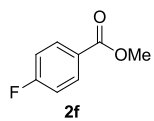
$^1\text{H-NMR}$



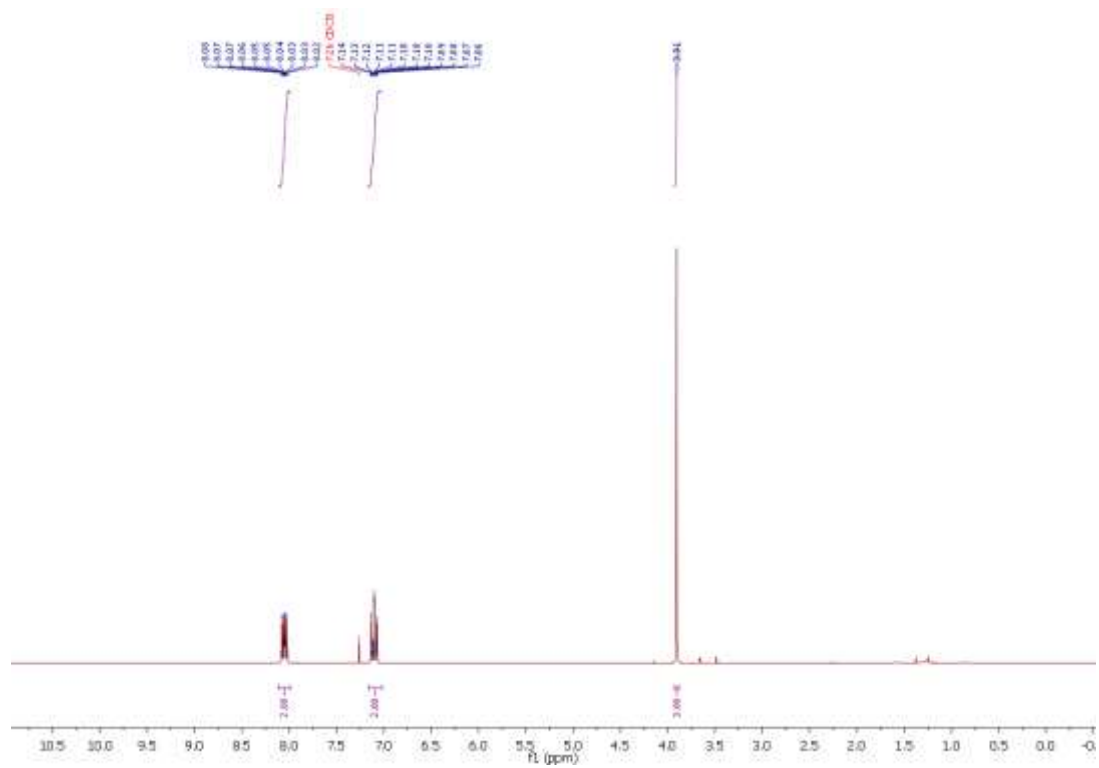
$^{13}\text{C-NMR}$



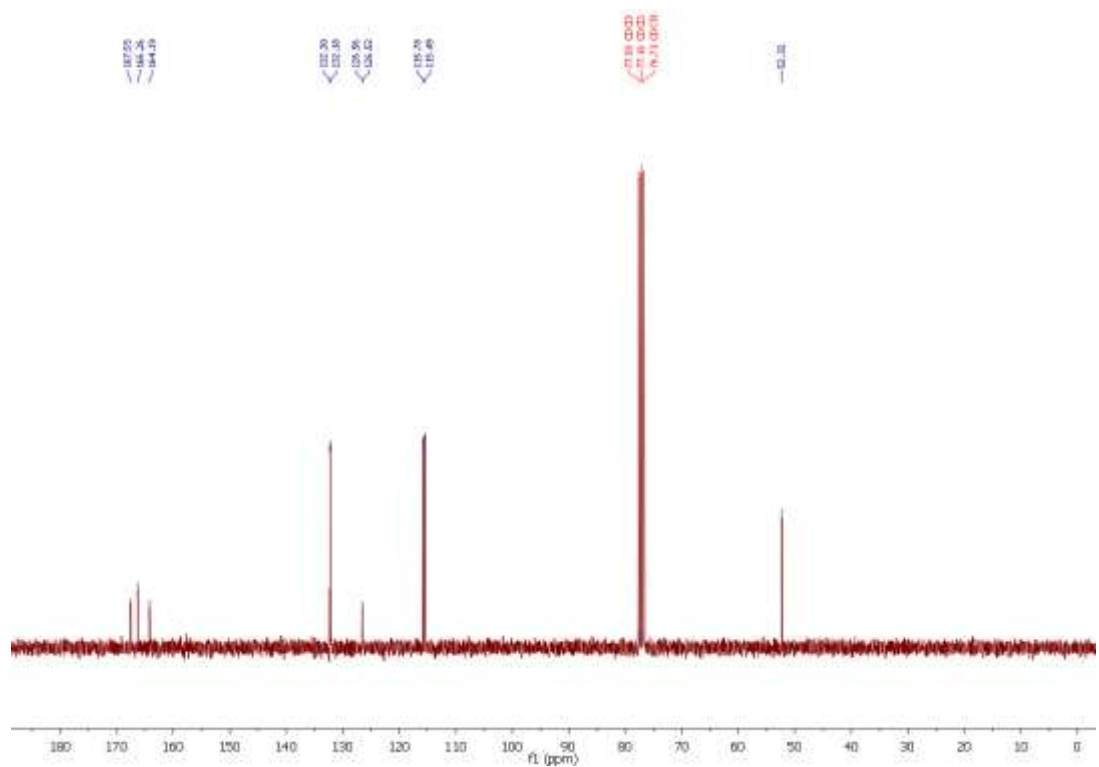


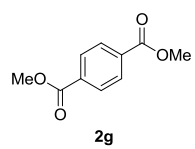


<sup>1</sup>H-NMR

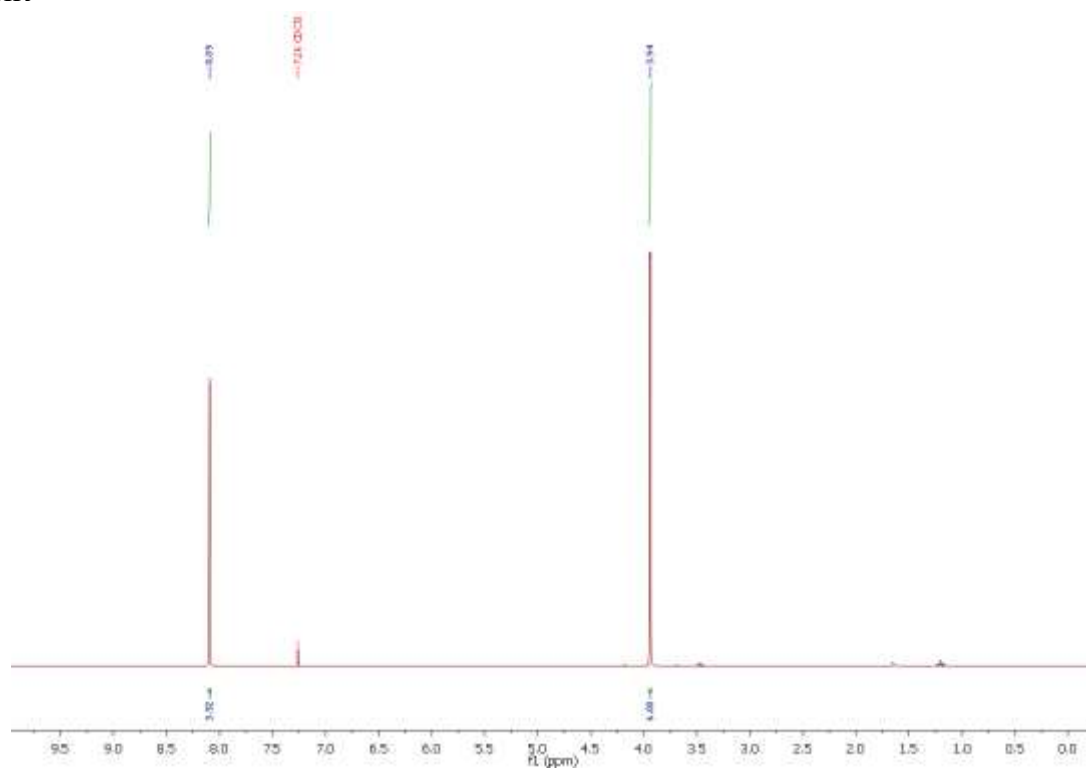


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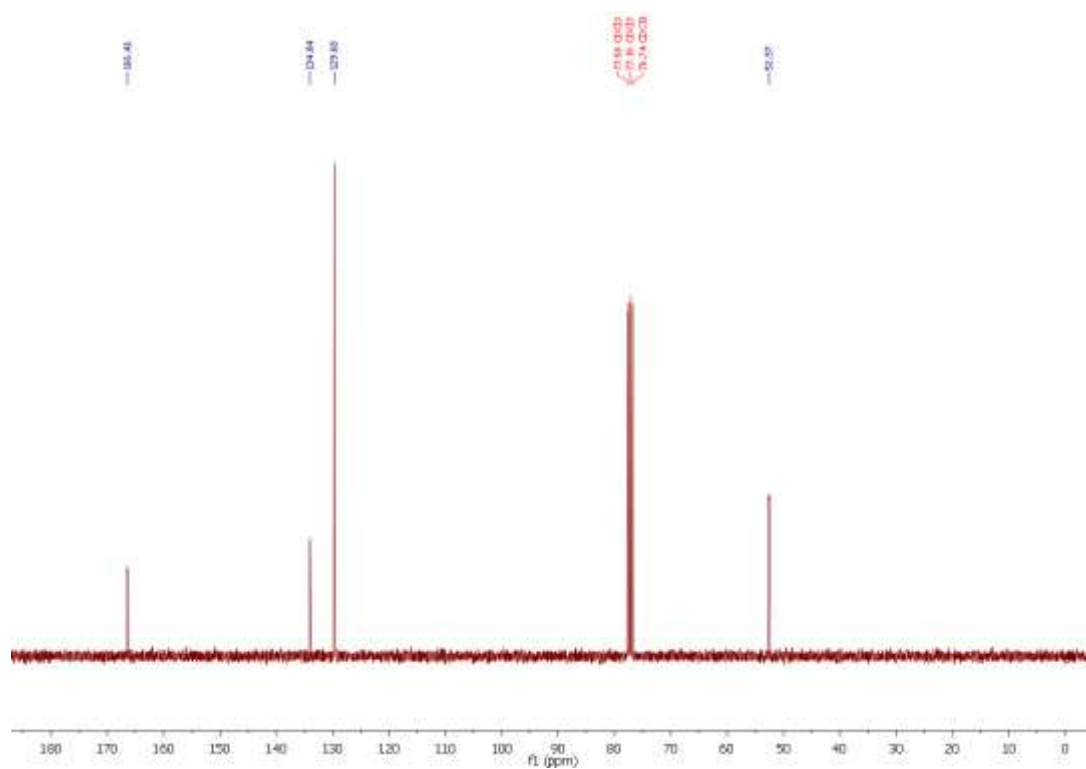




<sup>1</sup>H-NMR

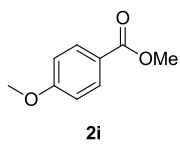


<sup>13</sup>C-NMR

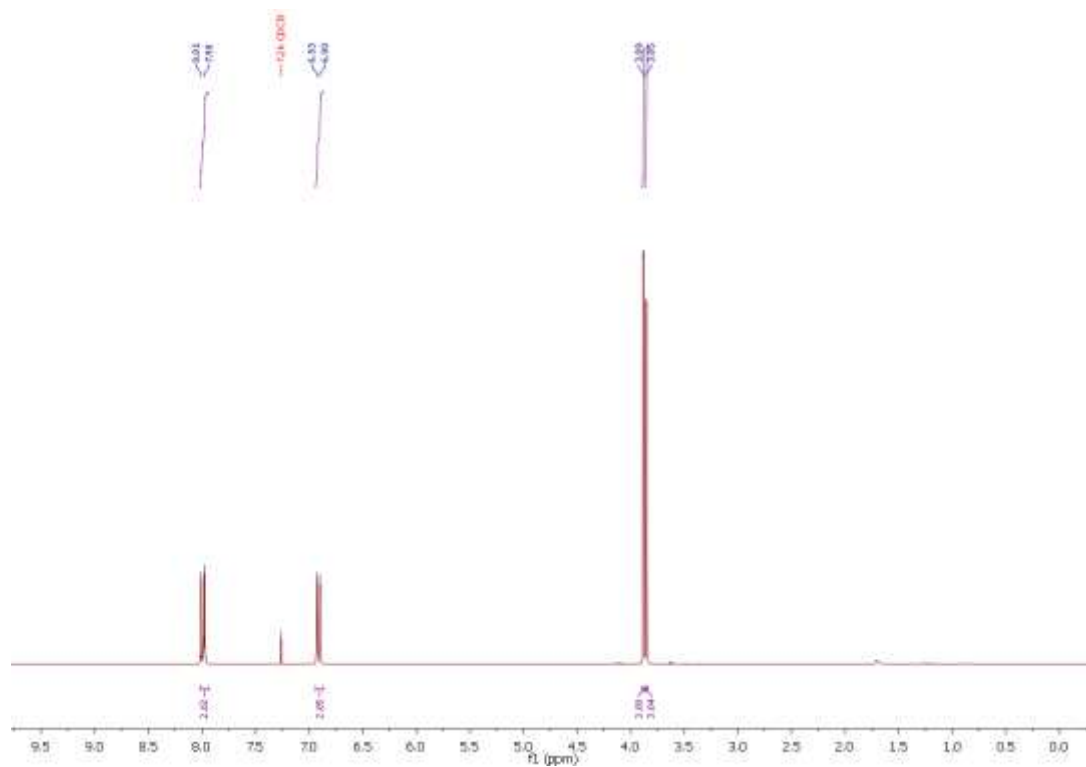




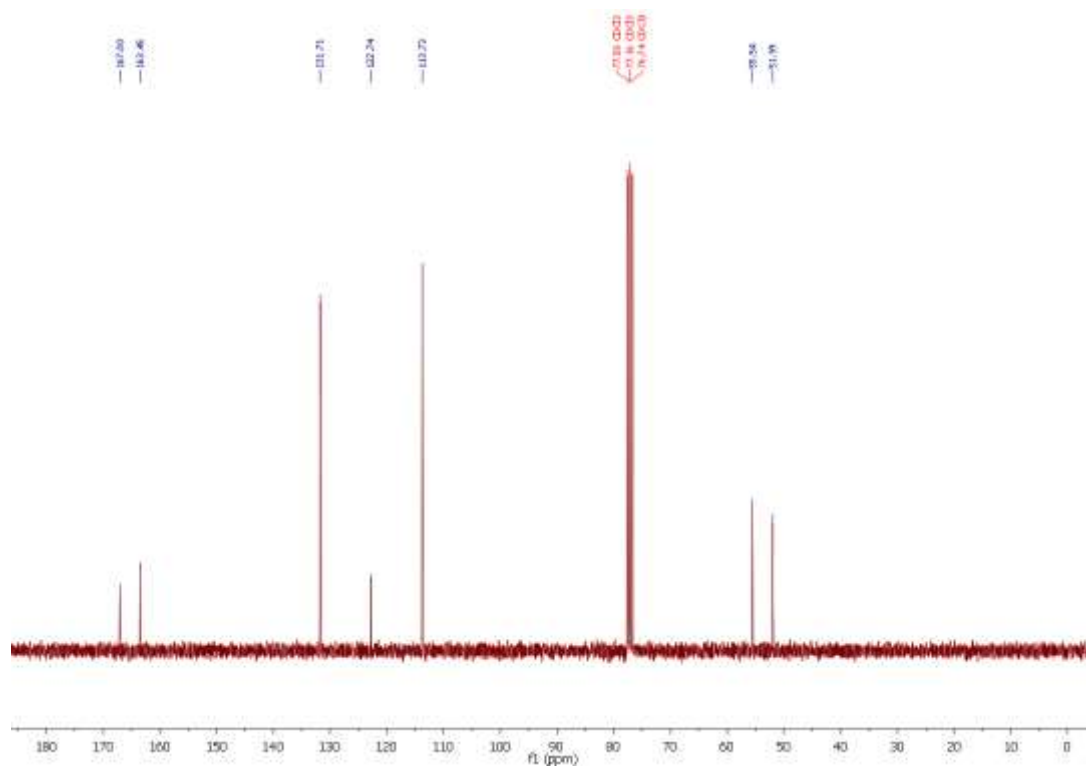


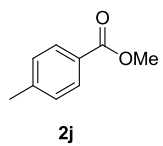


<sup>1</sup>H-NMR

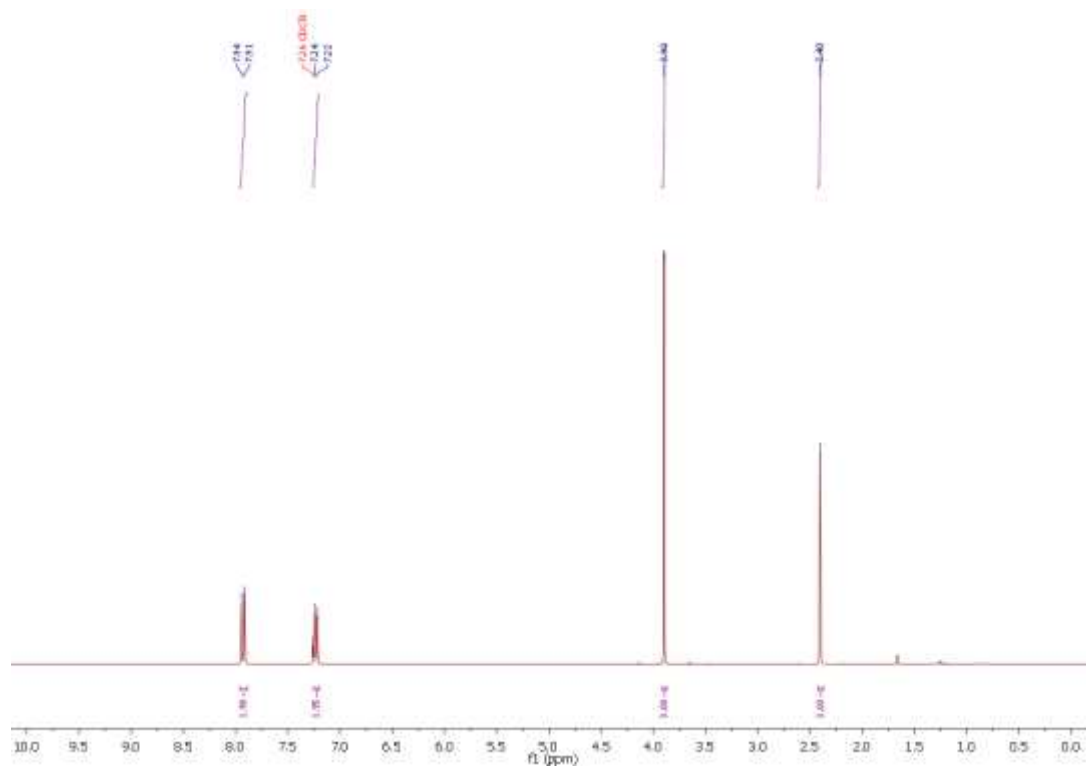


<sup>13</sup>C-NMR

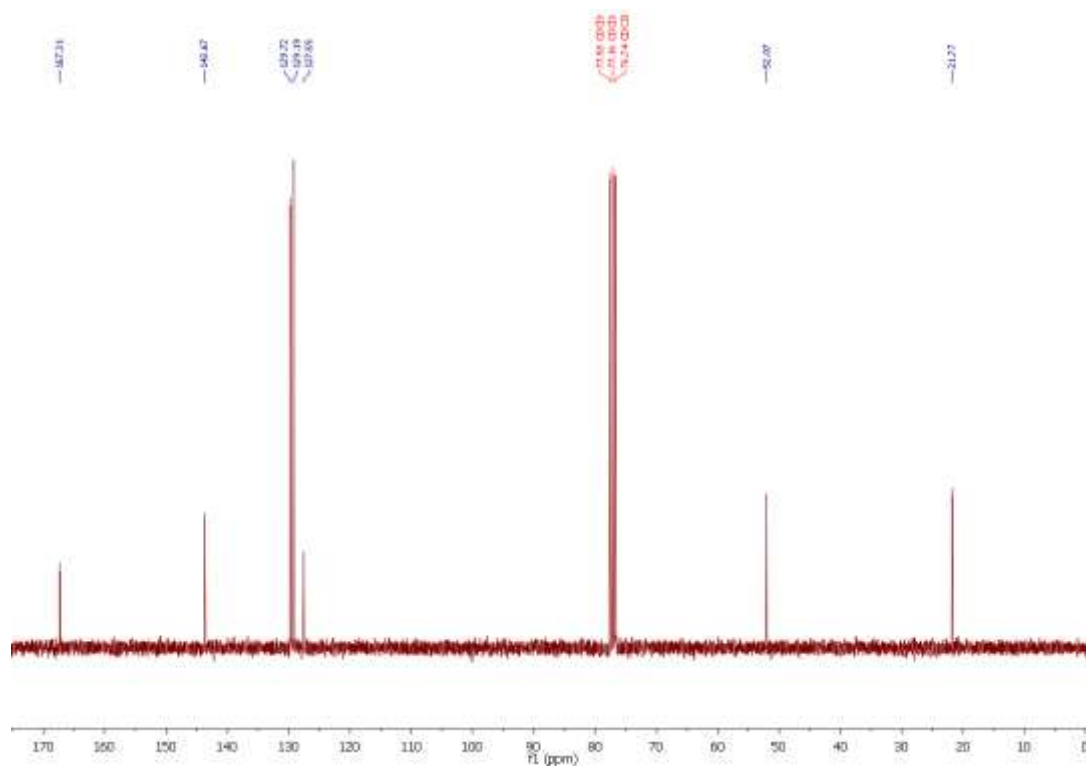


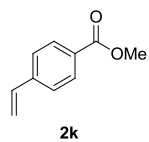


<sup>1</sup>H-NMR

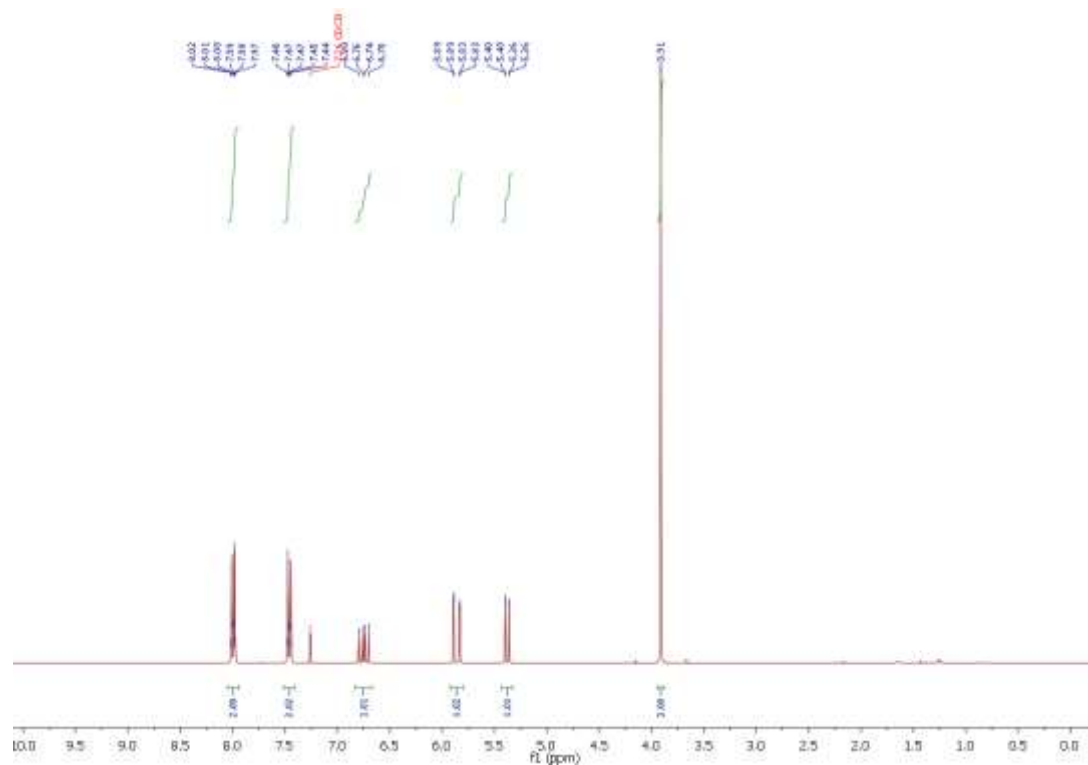


<sup>13</sup>C-NMR

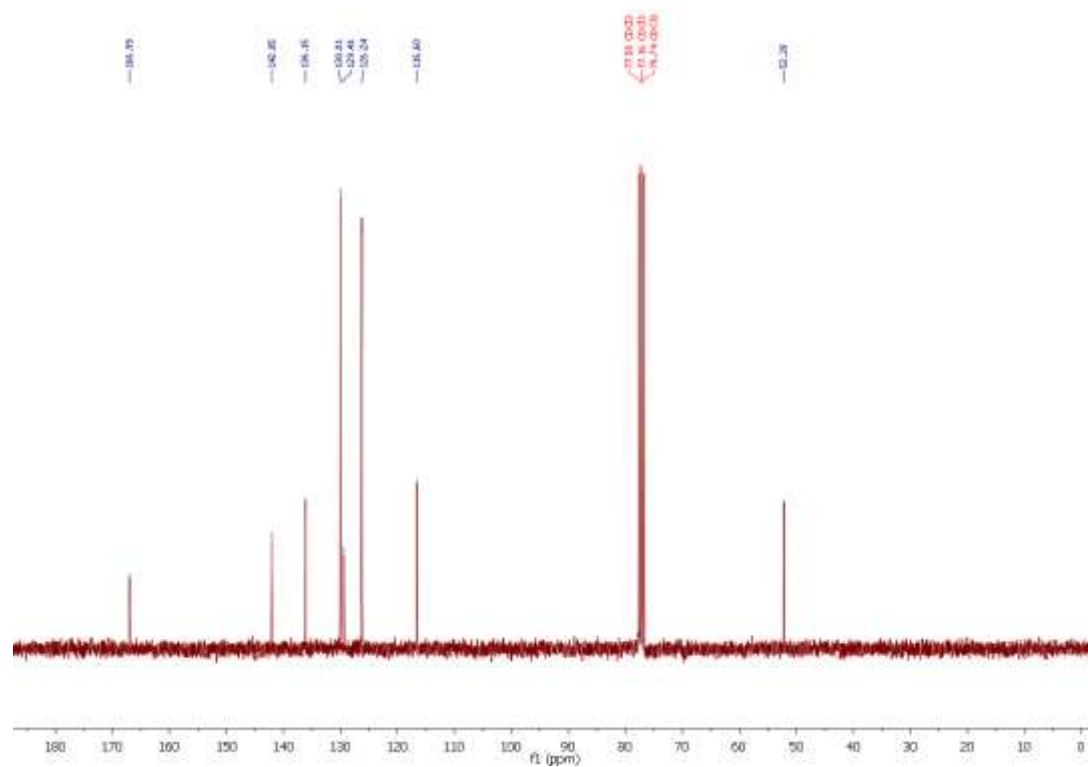


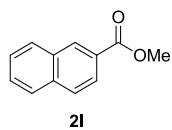


<sup>1</sup>H-NMR

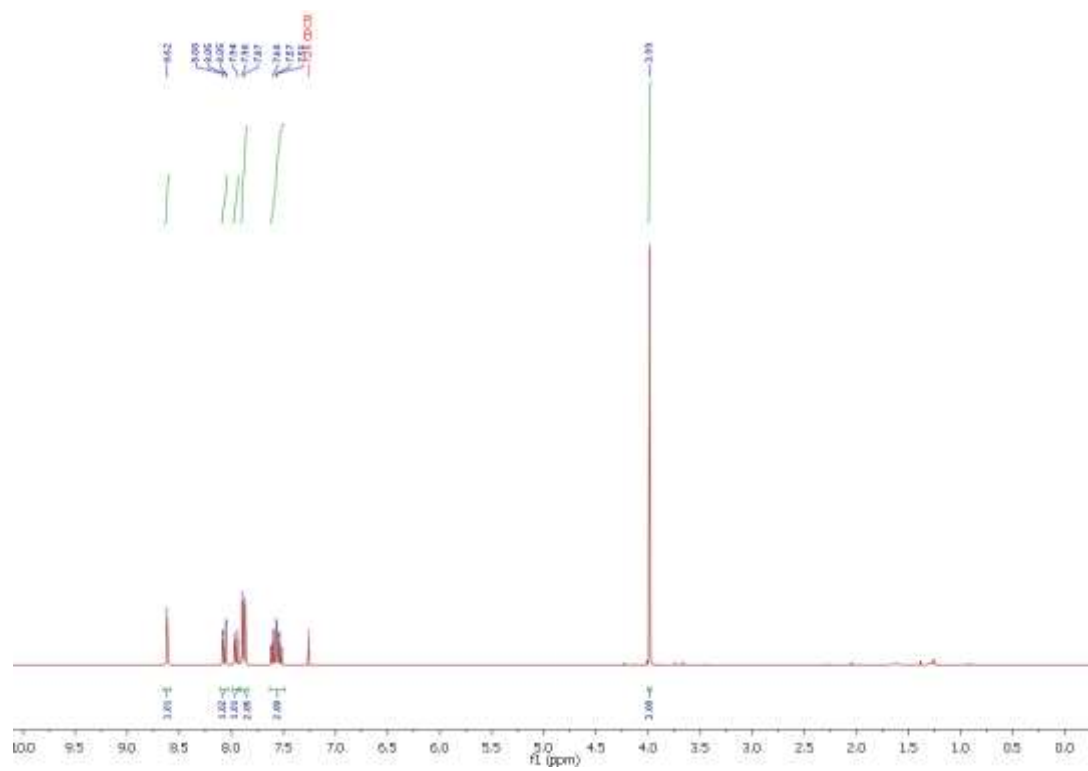


<sup>13</sup>C-NMR

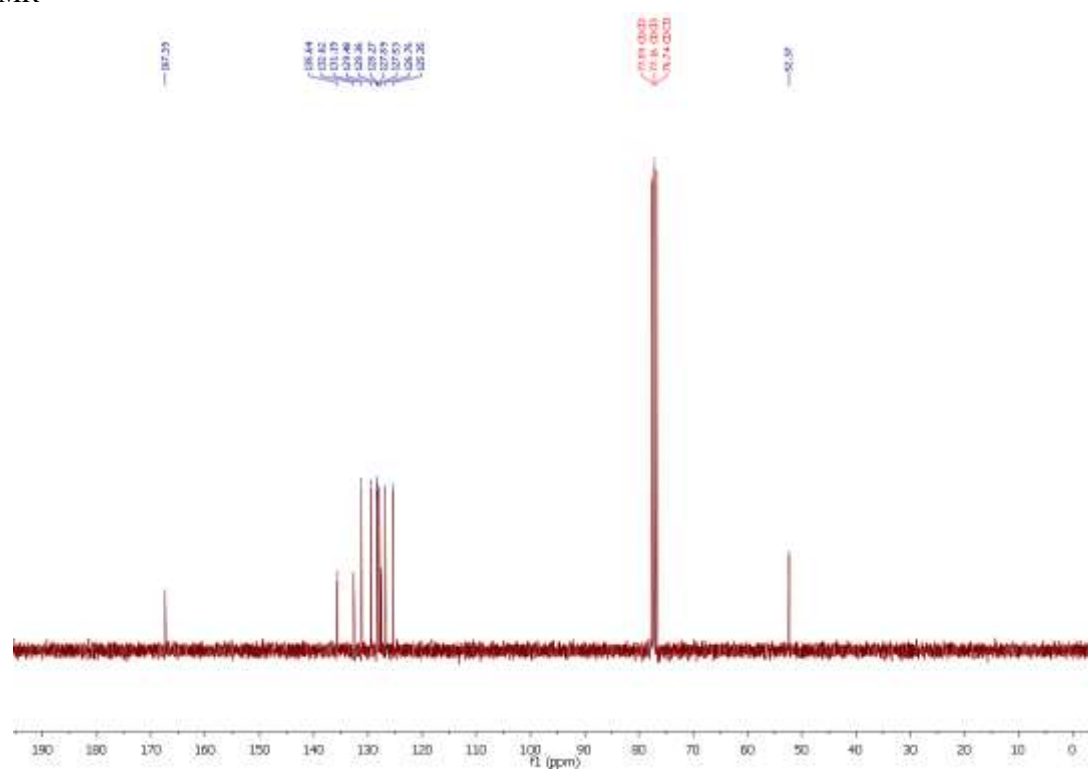




$^1\text{H-NMR}$



$^{13}\text{C-NMR}$



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