

## Supporting Information

### Robust Phosphine-based Covalent-Organic Framework Palladium Catalysts for the Highly Efficient Carbonylation Coupling Reaction

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## 1. Experimental Procedures

### General Materials and Measurements

All of the reagents were commercially available and were used without further purification. Powder X-ray diffraction (PXRD) patterns were collected on an Advance D8 equipped with Ni-filtered Cu K radiation (40 kV, 100 mA) at room temperature with a scan speed of  $10^\circ \cdot \text{min}^{-1}$ . Thermogravimetric analysis (TGA) was performed on a thermal analysis instrument (METTLER TOLEDO Thermal Analysis) under a flow of air at a heating rate of  $10^\circ \text{C} \cdot \text{min}^{-1}$  from 30-800  $^\circ \text{C}$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were done on a Bruker Model AM-400 (400 MHz) spectrometer. Infrared (IR) spectra were measured from a KBr pellets on Nicolet iN10 MX microscopic infrared spectrometer (Thermo Scientific Co., USA) in the range of 4000 to 400  $\text{cm}^{-1}$  under ambient condition. The content of metal ions was determined by the inductively coupled plasma mass spectrometry (ICP-MS). The pore structure of the materials was measured by  $\text{N}_2$  adsorption-desorption isotherms at 77 K with Micromeritics ASAP 2460 surface area. The SBET of the polymers was calculated using the BET model in the ranging of  $P/P_0 = 0.05 - 0.30$ , the total pore volume ( $V_{\text{total}}$ ) of the materials was calculated from the isotherms at  $P/P_0 = 0.99$ , the pore size distribution (PSD), micropore area ( $S_{\text{micro}}$ ), and  $V_{\text{micro}}$  were all calculated by the non-local density functional theory (NLDFT) method. The X-ray photoelectron spectroscopy (XPS) experiments were conducted using Thermo ESCALAB spectrometer with an Al K- $\alpha$  source. Scanning electron microscopy (SEM) measurements were performed on a JSM-7610FPlus microscope at an acceleration voltage of 10 kV. The catalytic reaction products were measured by gas chromatography (GC, FID detector, Agilent 7890A,

crosslinked capillary HP-5 column).

**Synthesis of TMBen-PPh<sub>3</sub>.** Typically, a mixture of 2,4,6-trimethyl-1,3,5-triazine (61.58 mg, 0.5 mmol), terephthalaldehyde (100.6 mg, 0.75 mmol), 2-diphenylphosphine benzaldehyde (43.55 mg, 0.15 mmol), KOH (84.15 mg, 1.5 mmol), o-dichlorobenzene 3 mL and n-butanol 7 mL were added to a 25 mL Schlenk tube and sonicated for 15 min. The Schlenk tube containing the mixture was frozen in liquid nitrogen, and after three cycles of freezing-extraction-thawing, the reaction was heated at 120 °C for 72 h. The solid was collected by centrifugation, washed three times with methanol, THF and dichloromethane, extracted by Soxhlet extraction in methanol for one day, and dried overnight under vacuum. Yellow powder was obtained in a yield of 79%.

**Synthesis of Pd@TMBen-PPh<sub>3</sub>.** The activated TMBen-PPh<sub>3</sub> (30 mg) was dispersed into acetonitrile (4 mL) and sonicated for 30 min. Then Pd(OAc)<sub>2</sub> (10 mg) was added. The mixture was heated at 50 °C for 12 h. The resulting precipitate was collected by centrifugation and washed with acetonitrile four times. The dried solid was dispersed into acetone (2 mL) and NaBH<sub>4</sub> solution (2 mL, 4 mg/mL) was added quickly under an ice-water bath, and the reaction was carried out for 12 h. At the end of the reaction, grey-green powder was obtained, and the solid was washed thoroughly with acetone and water and dried in a vacuum drying oven at 80 °C overnight.

#### **Synthesis of TMBen-4F-PPh<sub>3</sub>**

A mixture of 2,4,6-trimethyl-1,3,5-triazine (TMTA) (12.316 mg, 0.1 mmol) and tetrafluoroterephthalaldehyde (TFTA) (30.92 mg 0.15 mmol), 2-diphenylphosphine

benzaldehyde (8.71 mg, 0.03 mmol), mesitylene (0.9 mL), dioxane (0.9 mL) and acetonitrile (50  $\mu$ L) were added to a 25 mL Schlenk tube. After sonicated for 15 min, 0.4 mL of trifluoroacetic acid was quickly added as a catalyst. The Schlenk tube containing the mixture was frozen in liquid nitrogen, and after three cycles of freezing-extraction-thawing, it was placed in an oven of 150 °C for 72 h. After the reaction, the solid was collected by centrifugation, washed three times with methanol and acetone, and extracted by Soxhlet extraction in methanol for one day. Finally, the product was dried in a vacuum drying oven at 80 °C for 12 h to obtain an orange-red powder with 75% yield.<sup>1</sup>

#### **Synthesis of Pd@TMBen-4F-PPh<sub>3</sub>**

Pd@TMBen-4F-PPh<sub>3</sub> was prepared by a similar method described above. The activated TMBen-4F-PPh<sub>3</sub> (30 mg) was dispersed into acetonitrile (4 mL) and sonicated for 30 min. Then Pd(OAc)<sub>2</sub> (10 mg) was added. The mixture was heated at 50 °C for 12 h. The resulting precipitate was collected by centrifugation and washed with acetonitrile four times. The dried solid was dispersed into acetone (2 mL) and NaBH<sub>4</sub> solution (2 mL, 4 mg/mL) was added quickly under an ice-water bath, and the reaction was carried out for 12 h. At the end of the reaction, taupe powder was obtained, and the solid was washed thoroughly with acetone and water and dried in a vacuum drying oven at 60 °C overnight.<sup>2</sup>

#### **General procedure for the catalytic reactions**

Pd@TMBen-PPh<sub>3</sub> (30 mg, 5 mol%), arylboronic acid (0.3 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.75 mmol) were transferred into an oven-dried reaction tube. 1,4-Dioxane (1.5 ml), formic

acid (0.75 mmol) and aryl iodide (0.25 mmol) were added to the reaction tube. After DCC (0.75 mmol) was added, the tube was sealed, and the mixture was stirred at 80 °C for 18 h. After the reaction was completed, the catalyst was separated and the reaction mixture was filtered and concentrated under vacuum and then purified by flash chromatography to afford the corresponding product **3**. The recovered catalyst was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 2 ml), distilled water (2 × 2 ml) and ethanol (2 × 2 ml), vacuum-dried and used directly for the next run. The characterization data and copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compounds **3a-3i** have been provided in the Supporting Information.

#### **The Recycling experiment of Pd@TMBen-PPh<sub>3</sub>**

After reaction, the catalyst was firstly collected by centrifugation. Then, it was washed stepwise with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 ml), distilled water (3 × 5 ml) and ethanol (3 × 5 ml). At last, the catalyst was dried under vacuum at 60 °C overnight and be directly used for the next catalytic run.

## 2. Results and Discussion

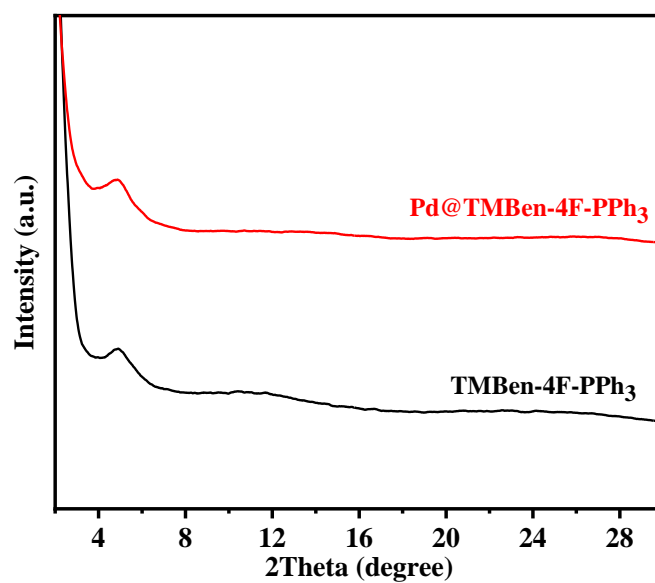


Figure S1. PXRD patterns of TMBen-4F-PPh<sub>3</sub> and Pd@TMBen-4F-PPh<sub>3</sub>

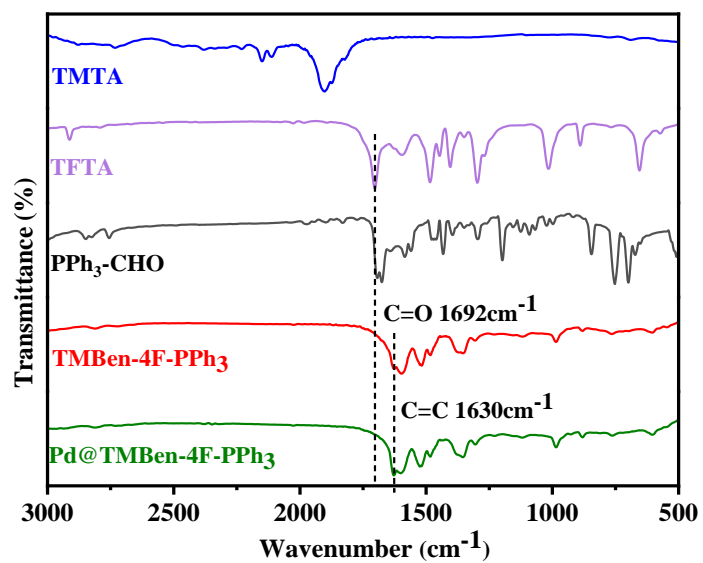


Figure S2. FT-IR spectra of TMTA, TFTA, PPh<sub>3</sub>-CHO, TMBen-4F-PPh<sub>3</sub> and Pd@TMBen-4F-PPh<sub>3</sub>

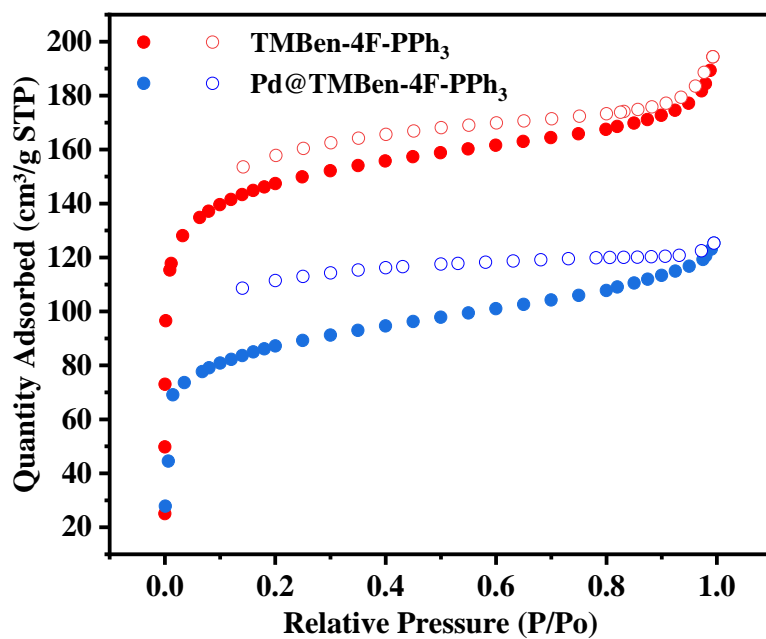


Figure S3. N<sub>2</sub> adsorption and desorption isotherms TMBen-4F-PPh<sub>3</sub> and Pd@TMBen-4F-PPh<sub>3</sub> at 77 K

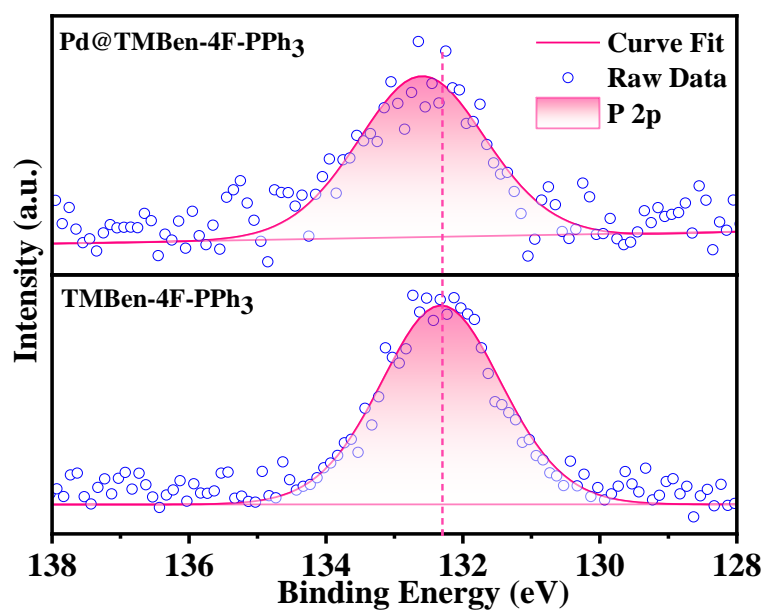
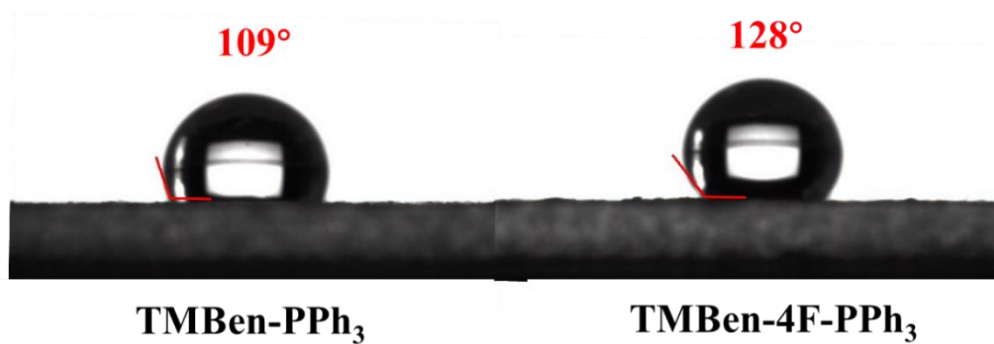
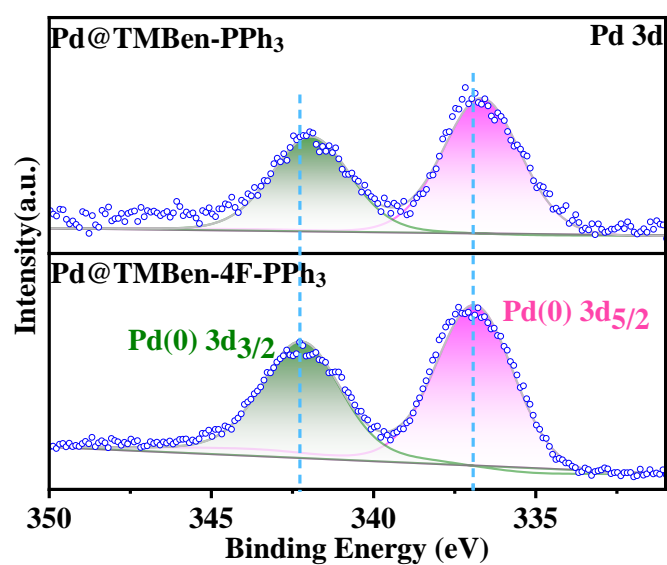


Figure S4. XPS spectra in P 2p region of TMBen-4F-PPh<sub>3</sub> and Pd@TMBen-4F-PPh<sub>3</sub>

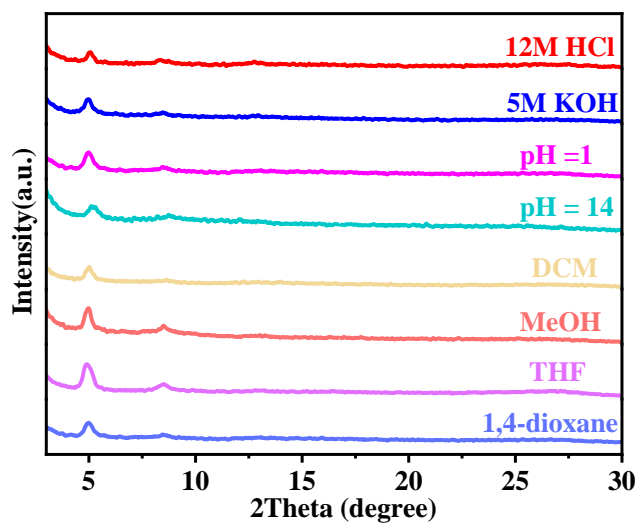


**Figure S5.** Water contact angle tests of TMBen-PPh<sub>3</sub> and TMBen-4F-PPh<sub>3</sub>

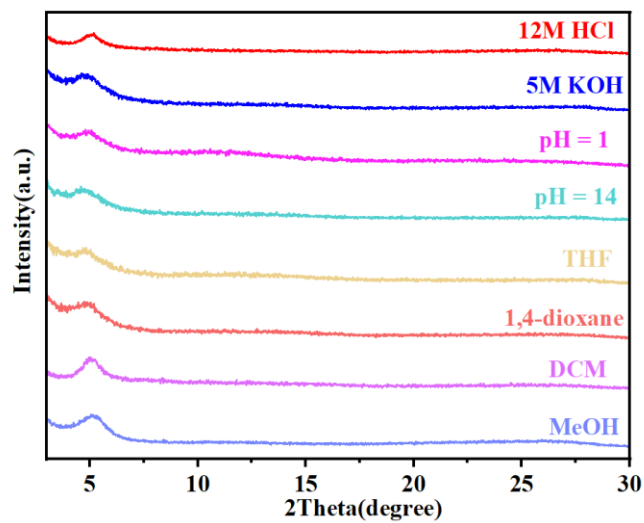


**Figure S6.** XPS spectra in Pd 3d region of Pd@TMBen-4F-PPh<sub>3</sub> and Pd@TMBen-PPh<sub>3</sub>

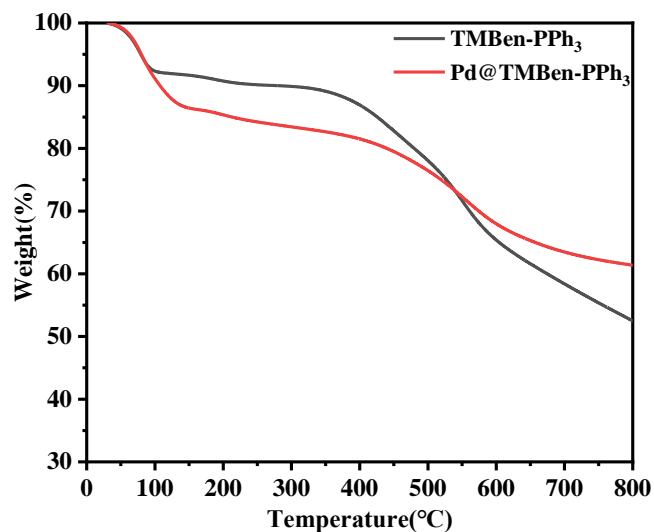




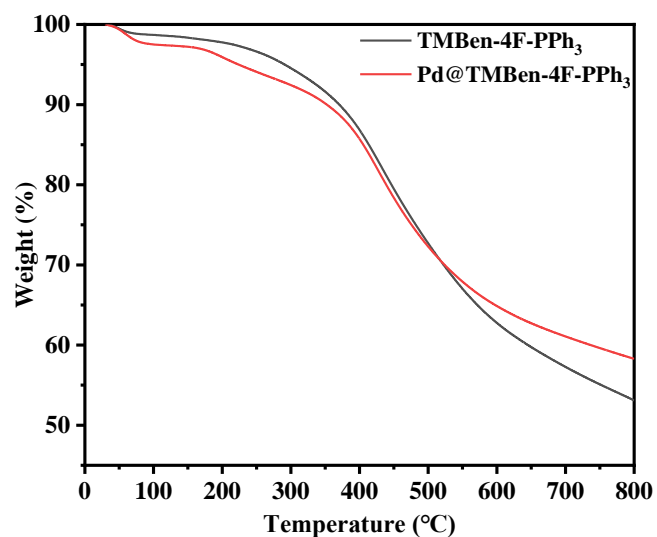
**Figure S7.** PXRD patterns of Pd@TMBen-PPh<sub>3</sub> after immersing in different solvents for 24 h



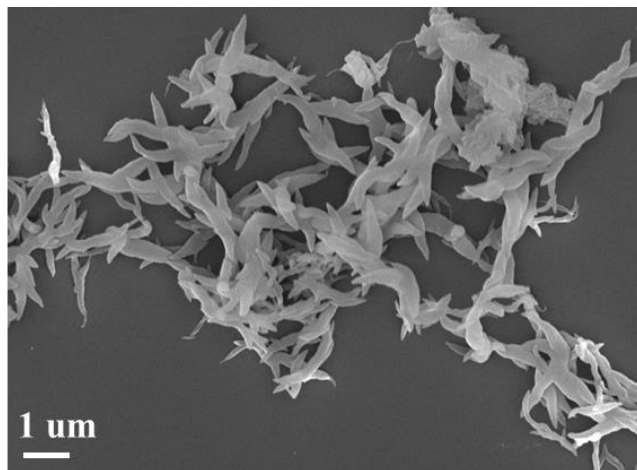
**Figure S8.** PXRD patterns of Pd@TMBen-4F-PPh<sub>3</sub> after immersing in different solvents for 24 h.



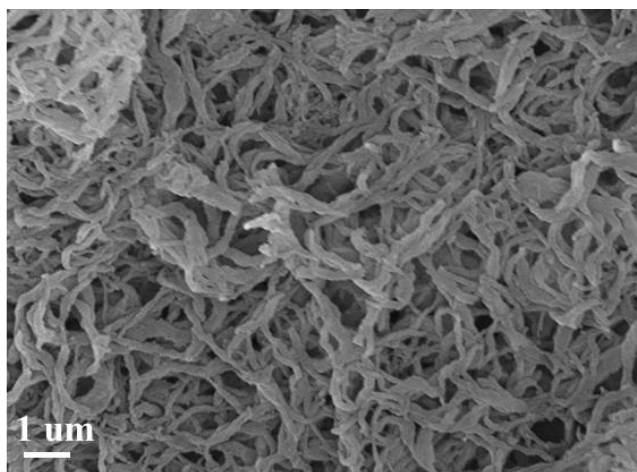
**Figure S9.** TGA curves of TMBen-PPh<sub>3</sub> and Pd@TMBen-PPh<sub>3</sub> under N<sub>2</sub> atmosphere



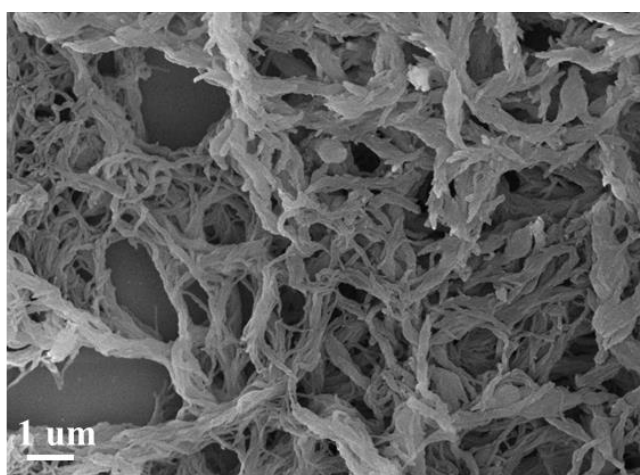
**Figure S10.** TGA curves of TMBen-4F-PPh<sub>3</sub> and Pd@TMBen-4F-PPh<sub>3</sub> under N<sub>2</sub> atmosphere



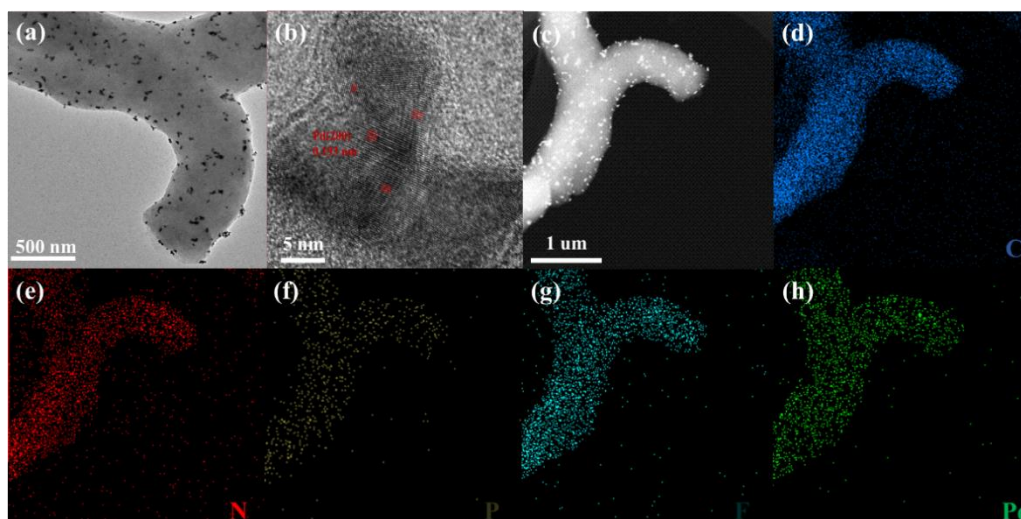
**Figure S11.** SEM image of Pd@TMBen-PPh<sub>3</sub>



**Figure S12.** SEM image of TMBen-4F-PPh<sub>3</sub>



**Figure S13.** SEM image of Pd@TMBen-4F-PPh<sub>3</sub>

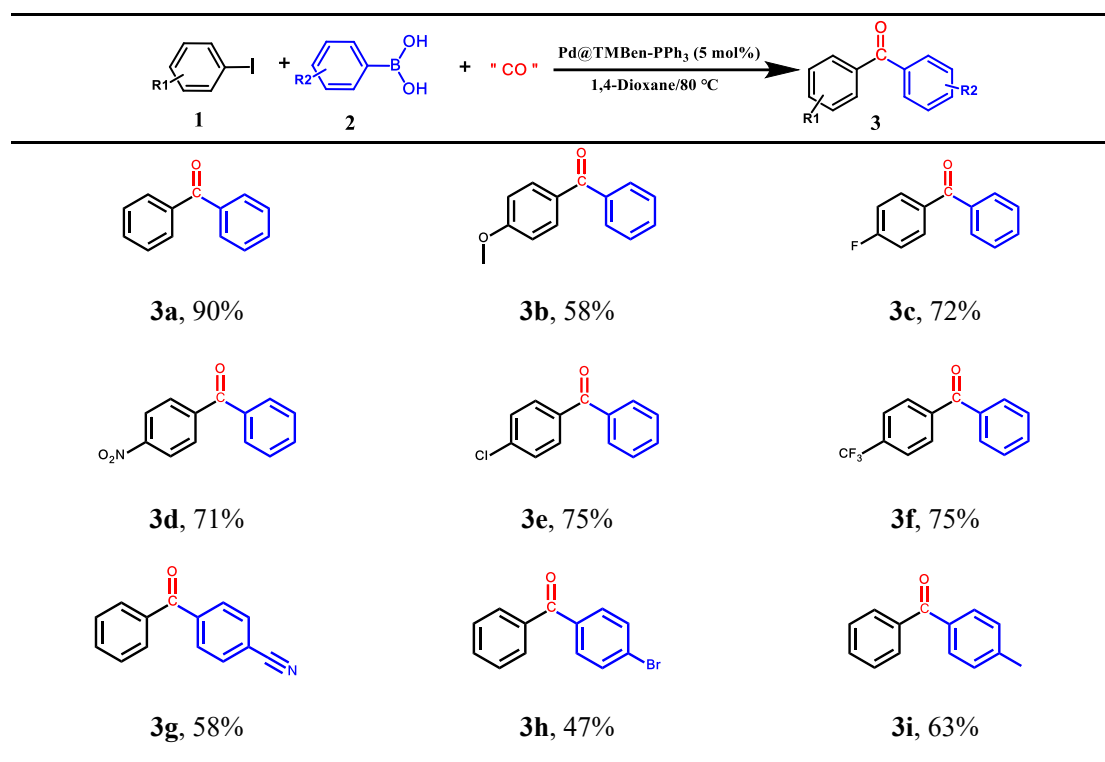


**Figure S14.** (a) TEM image of TMBen-4F-PPh<sub>3</sub>. (b) High-resolution TEM image of Pd nanoparticle. and (c-h) corresponding EDX-mapping images of C, N, P, F, Pd

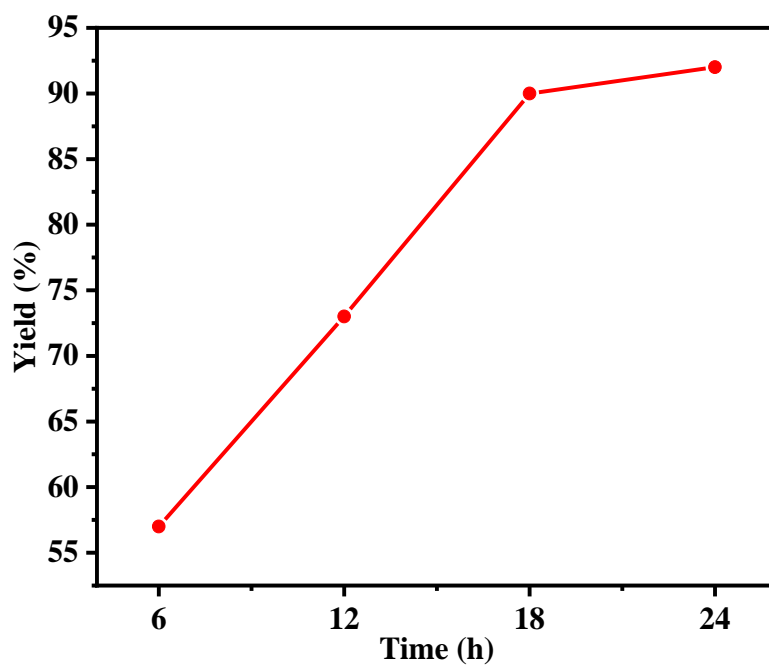
**Table. S1** ICP results of Pd contents in different catalysts and reaction filtrate

catalysts	Pd (%)
Pd@TMBen-PPh <sub>3</sub>	10.65%
Pd@TMBen-4F-PPh <sub>3</sub>	10.54%
Reaction filtrate	0.0046%

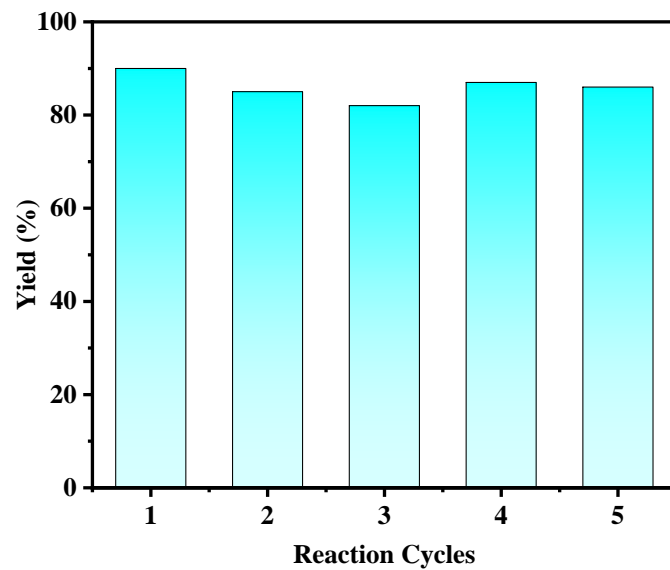
**Table. S2** Substrate scope<sup>a</sup>



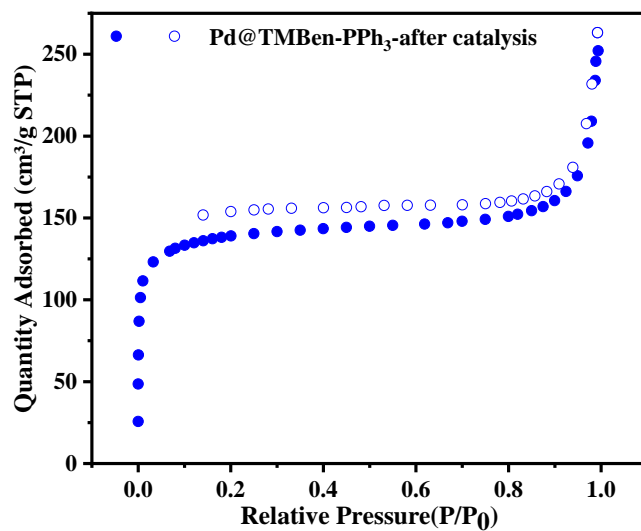
<sup>a</sup> Isolated yields.



**Figure S15.** Yields-versus-time curve of Pd@TMBen-PPh<sub>3</sub>



**Figure S16.** Recycling tests of Pd@TMBen-PPh<sub>3</sub>



**Figure S17.** N<sub>2</sub> adsorption and desorption isotherms of Pd@TMBen-PPh<sub>3</sub> at 77 K  
after catalysis

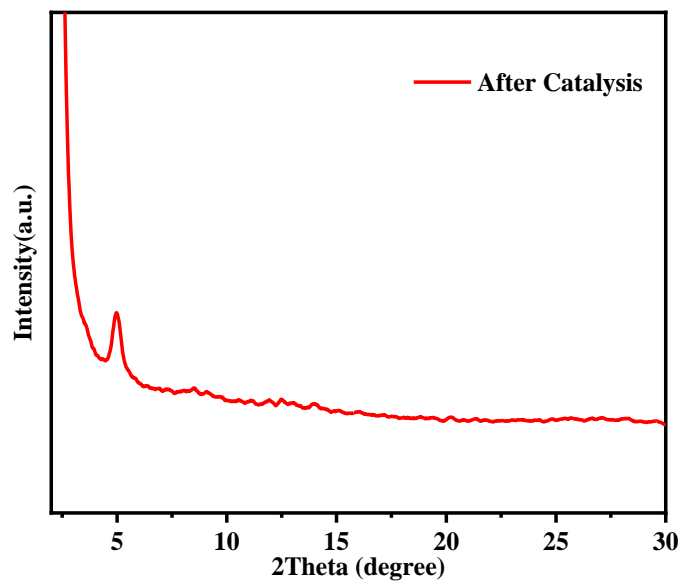


Figure S18. PXRD patterns of Pd@TMBen-PPh<sub>3</sub> after catalysis.

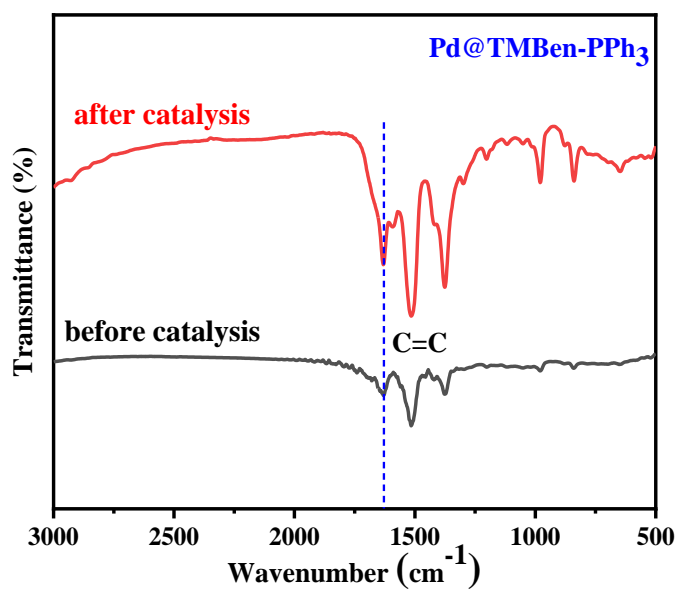
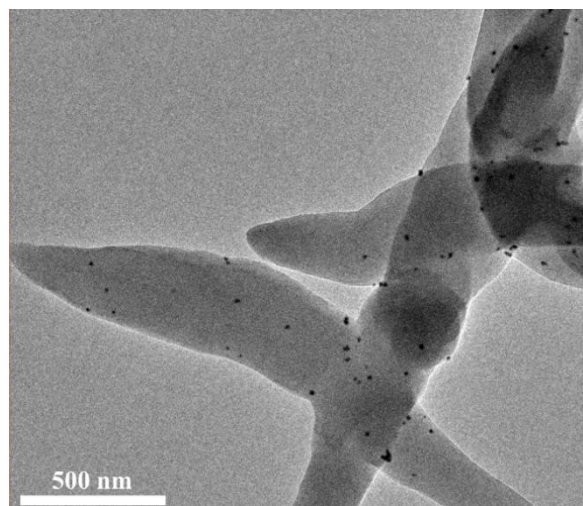
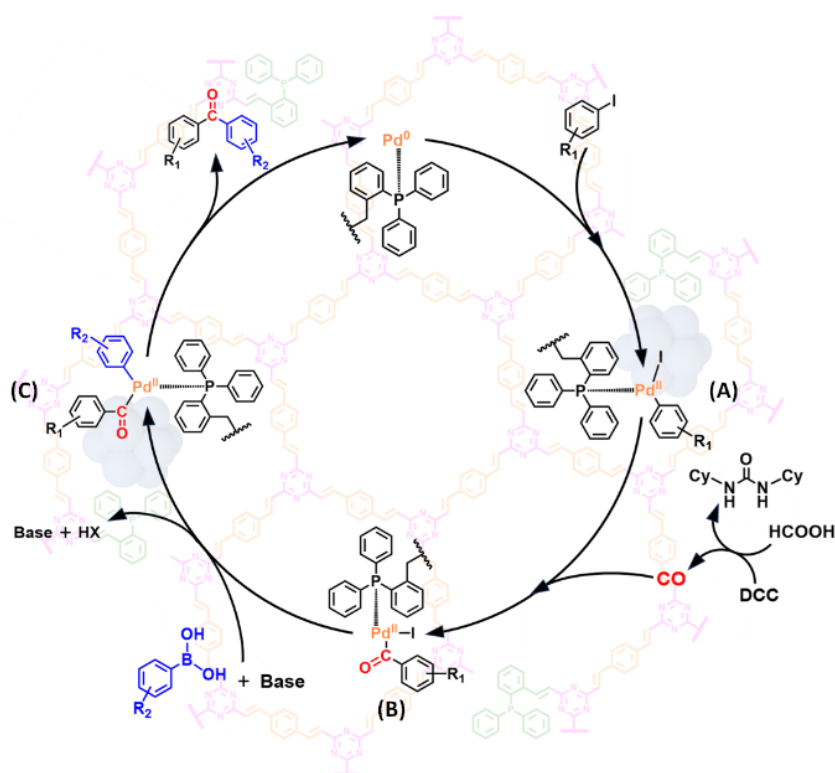


Figure S19. FT-IR spectra of Pd@TMBen-PPh<sub>3</sub> after catalysis.



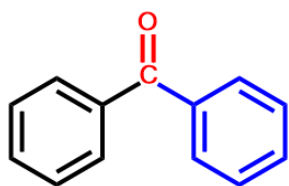
**Figure S20.** TEM image of Pd@TMBen-PPh<sub>3</sub> after catalysis.



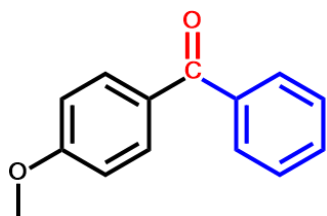
**Figure S21.** Proposed Mechanism of Pd@TMBen-PPh<sub>3</sub>-catalyzed carbonylation reaction.



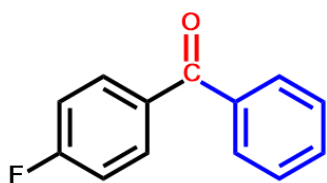
### 3. NMR Analysis of Oxazolidinone Products



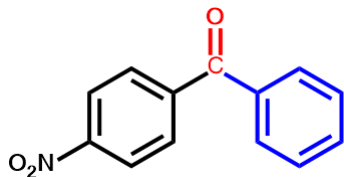
Benzophenone (3a): White solid, yield: 90%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.73 (t,  $J$  = 4.2 Hz, 4H), 7.52 (t,  $J$  = 7.4 Hz, 2H), 7.42 (t,  $J$  = 7.6 Hz, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 195.72, 136.54, 131.38, 129.02, 127.24; HR-MS (ESI-TOF):  $m/z$  205.0624  $[\text{M}+\text{Na}^+]$ .



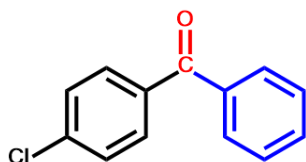
(4-Methoxyphenyl)(phenyl)methanone (3b): White solid, yield: 58%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.75 (d,  $J$  = 8.8 Hz, 2H), 7.69 (d,  $J$  = 7.3 Hz, 2H), 7.49 (t,  $J$  = 7.4 Hz, 1H), 7.38 (t,  $J$  = 7.6 Hz, 2H), 6.88 (d,  $J$  = 8.8 Hz, 2H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 195.60, 163.24, 138.30, 132.59, 131.17, 130.17, 129.76, 128.21, 113.57, 55.52; HR-MS (ESI-TOF):  $m/z$  235.0730  $[\text{M}+\text{Na}^+]$ .



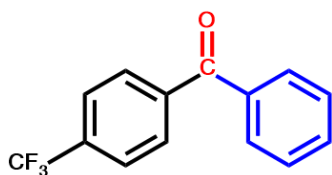
(4-Fluorophenyl)(phenyl)methanone (3c): White solid, yield: 72%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.85 (q,  $J$  = 8.0 Hz, 2H), 7.77 (d,  $J$  = 7.2 Hz, 2H), 7.60 (t,  $J$  = 7.4 Hz, 1H), 7.49 (t,  $J$  = 7.6 Hz, 2H), 7.17 (t,  $J$  = 8.6 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 195.22, 166.66 (d,  $J$  = 253.6 Hz), 164.13, 137.53, 133.85, 133.82, 132.70, 132.61, 129.87, 128.36, 115.54 (d,  $J$  = 21.8 Hz); HR-MS (ESI-TOF):  $m/z$  223.0530  $[\text{M}+\text{Na}^+]$ .



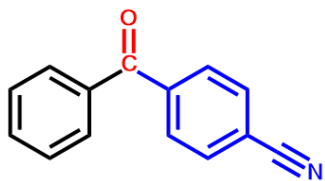
(4-Nitrophenyl)(phenyl)methanone (3d): Light yellow solid, yield: 71%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.34 (t,  $J = 8.9$  Hz, 2H), 7.92 (d,  $J = 8.3$  Hz, 2H), 7.79 (d,  $J = 7.7$  Hz, 2H), 7.64 (t,  $J = 7.4$  Hz, 1H), 7.50 (d,  $J = 16.5, 8.9$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 194.75, 149.83, 142.90, 136.30, 133.46, 130.68, 130.09, 128.69, 123.53$ ; HR-MS (ESI-TOF):  $m/z$  250.0475 [ $\text{M}+\text{Na}^+$ ].



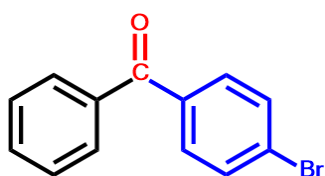
(4-Chlorophenyl)(phenyl)methanone (3e): White solid, yield: 75%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.76$  (t,  $J = 7.2$  Hz, 4H), 7.61 (t,  $J = 7.4$  Hz, 1H), 7.50-7.44 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 195.46, 138.90, 137.28, 135.91, 132.63, 131.46, 129.92, 128.64, 128.41$ ; HR-MS (ESI-TOF):  $m/z$  239.0234 [ $\text{M}+\text{Na}^+$ ].



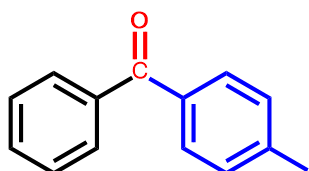
4-(Trifluoromethyl)benzophenone (3f): White solid, yield: 75%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.88$  (d,  $J = 8.0$  Hz, 2H), 7.78 (t,  $J = 8.4$  Hz, 2H), 7.74 (d,  $J = 8.0$  Hz, 2H), 7.62 (t,  $J = 7.4$  Hz, 1H), 7.50 (t,  $J = 7.5$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta = 195.52, 140.77, 136.77, 133.91$  (q,  $J = 33.5$  Hz), 133.58, 130.10, 128.53, 125.33 (q,  $J = 3.5$  Hz), 122.33 (q,  $J = 275.3$  Hz); HR-MS (ESI-TOF):  $m/z$  273.0498 [ $\text{M}+\text{Na}^+$ ].



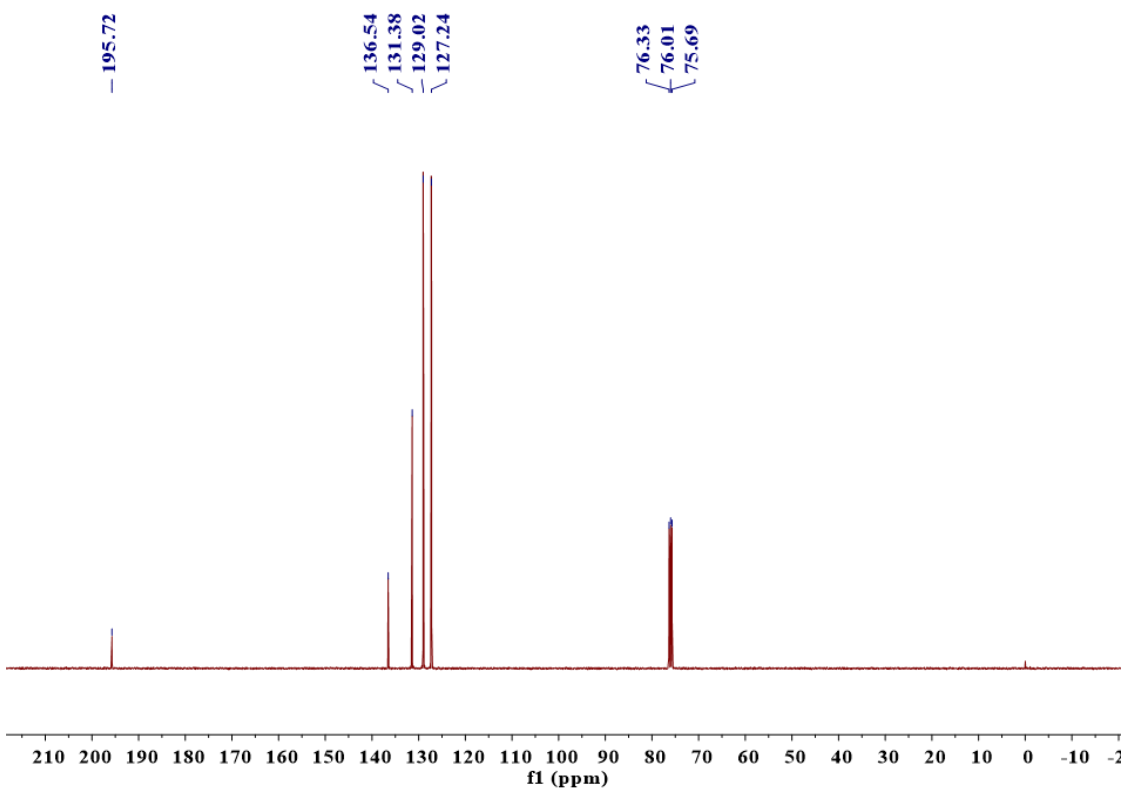
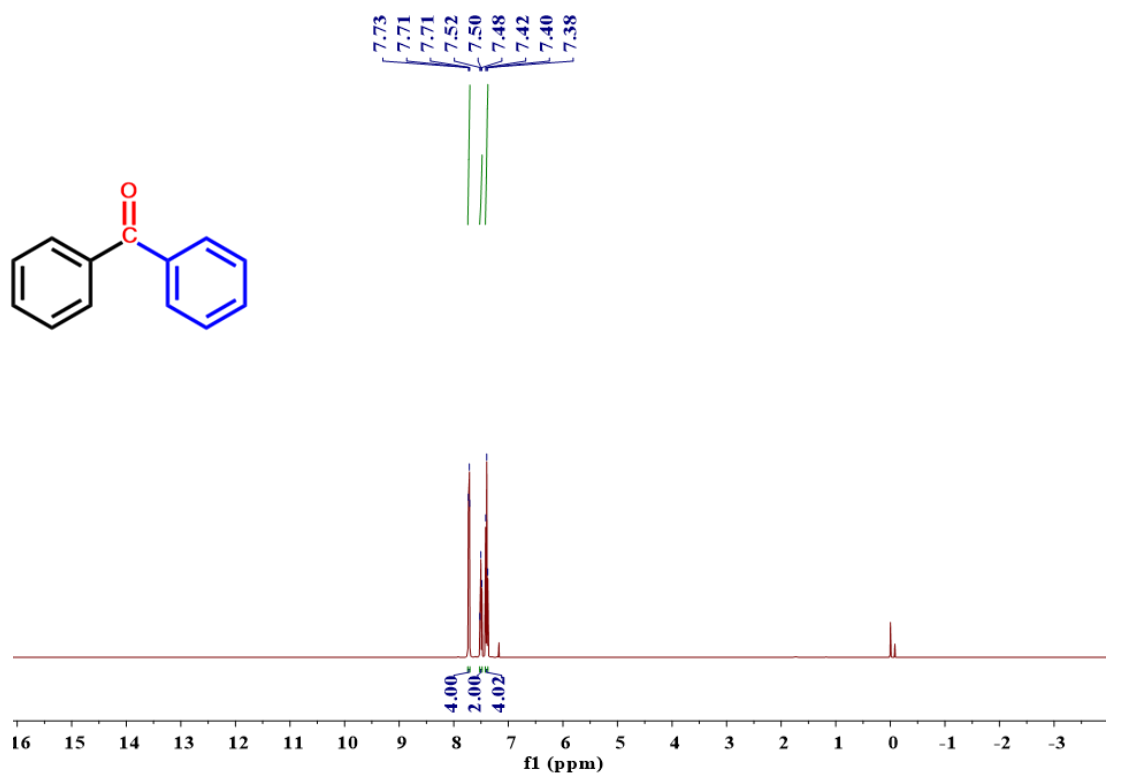
4-Benzoylbenzonitrile (3g): Light-yellow solid, yield: 58%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.88 (d,  $J$  = 8.2 Hz, 2H), 7.79 (m, 4H), 7.65 (t,  $J$  = 7.4 Hz, 1H), 7.52 (t,  $J$  = 7.7 Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 195.01, 141.25, 136.35, 133.31, 132.17, 130.22, 130.05, 128.63, 117.99, 115.68; HR-MS (ESI-TOF):  $m/z$  230.0576 [ $\text{M}+\text{Na}^+$ ].

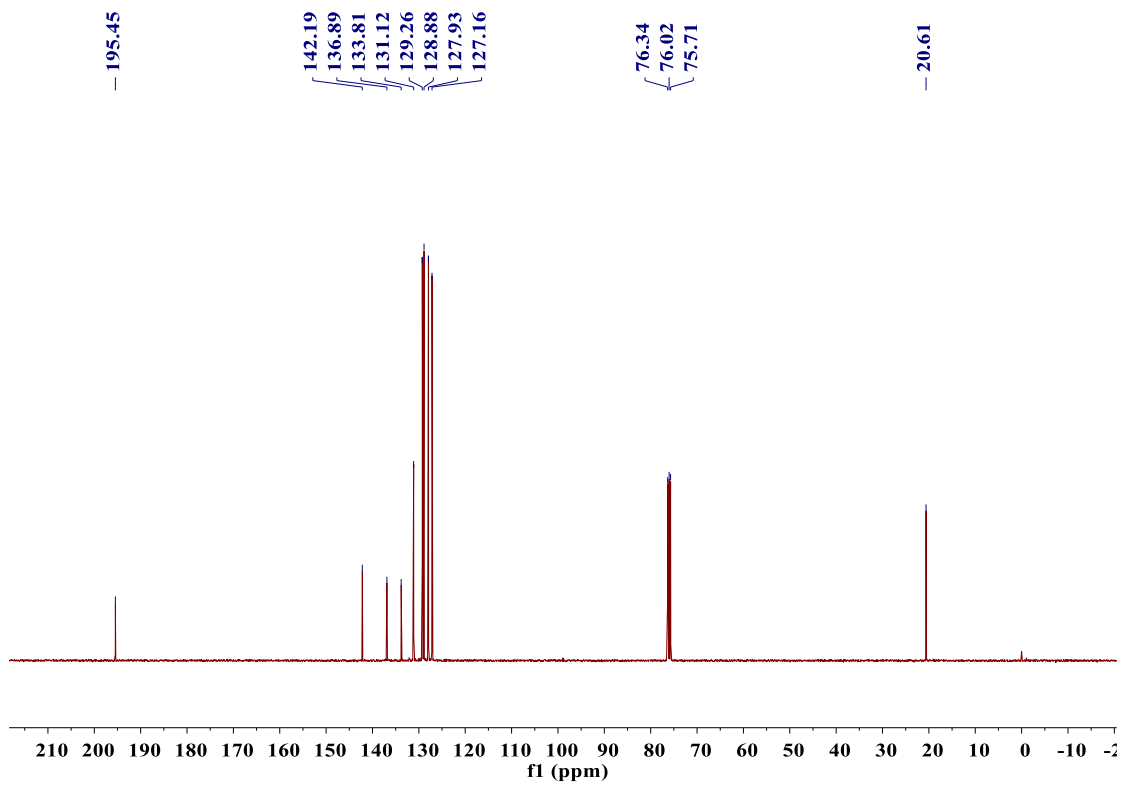
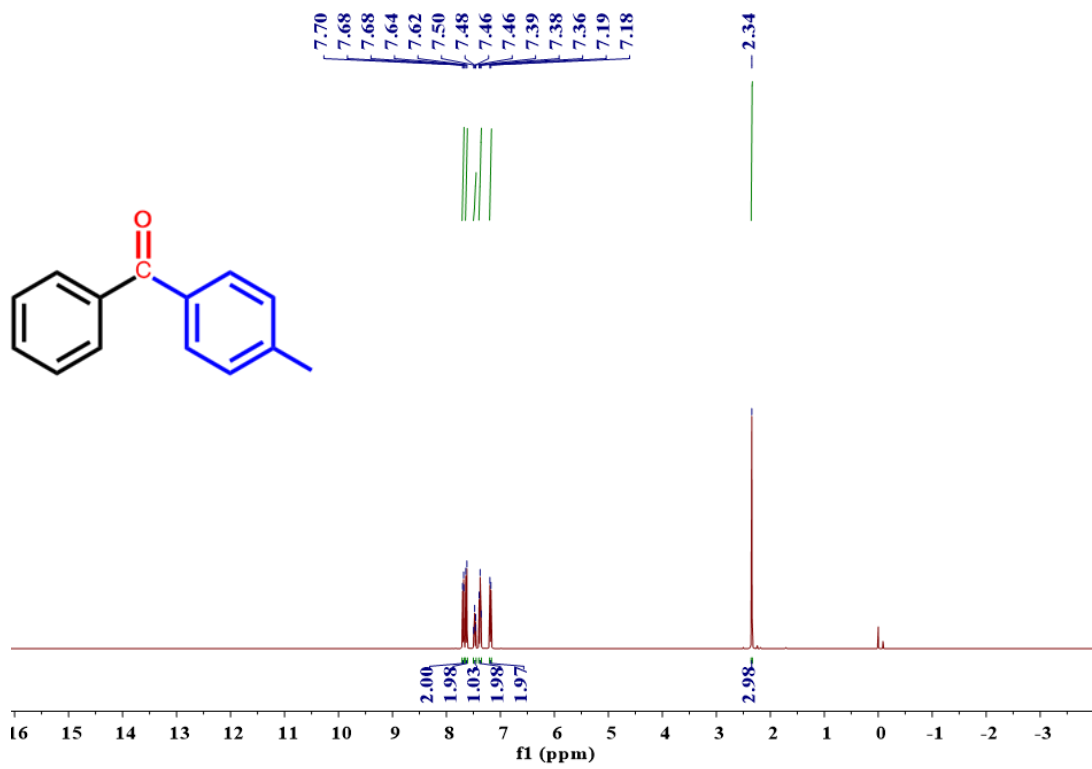


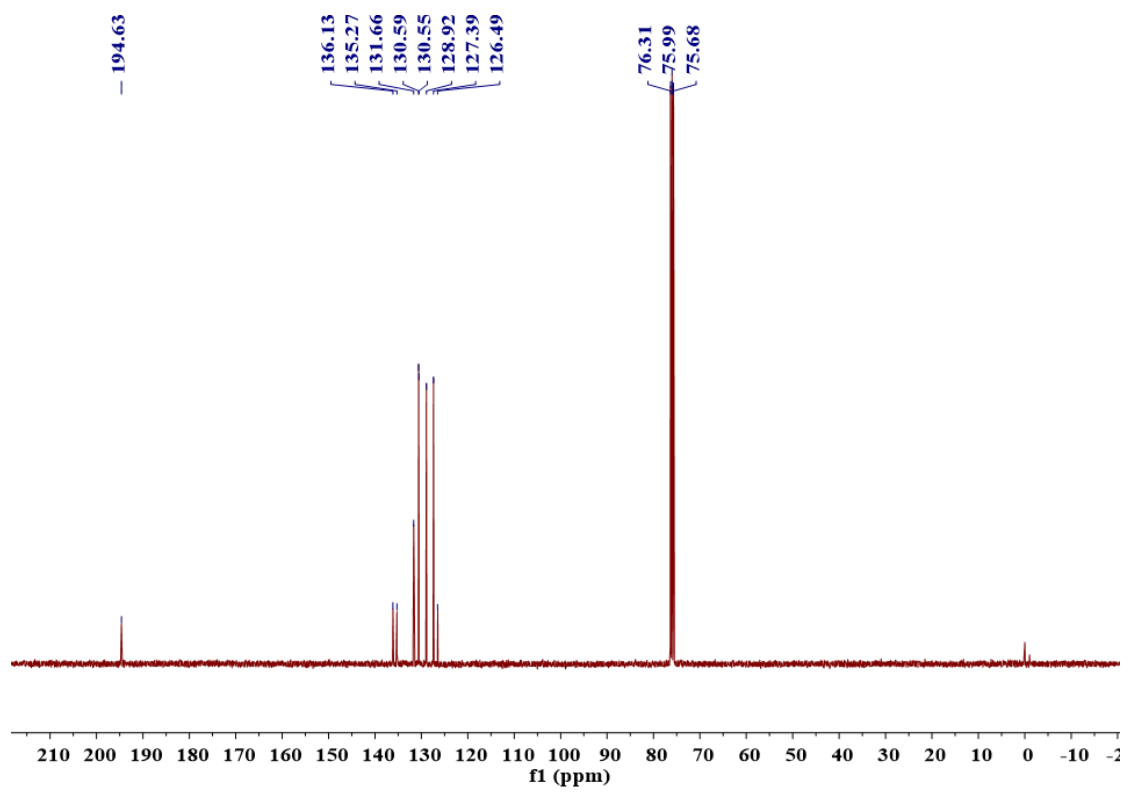
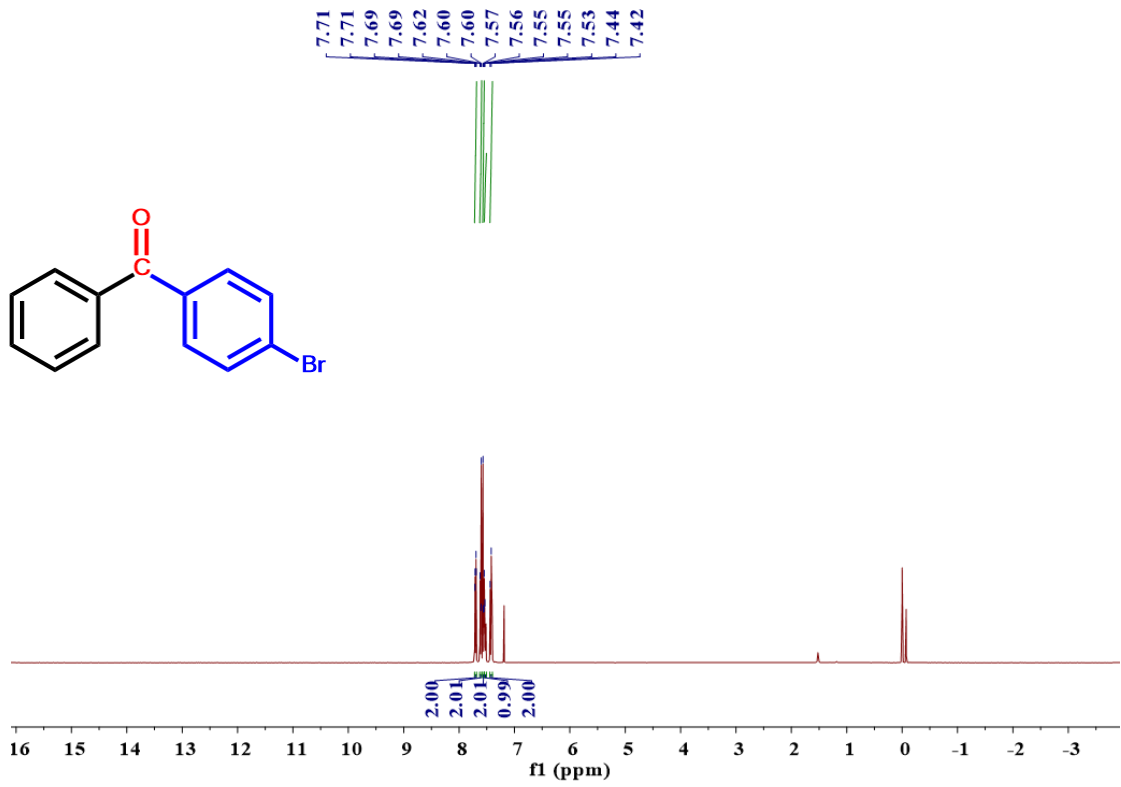
4-Bromobenzophenone (3h): White solid; yield: 47%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.71 (m, 2H), 7.69 (m, 2H), 7.56 (m, 3H), 7.42 (t,  $J$  = 7.6 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 194.63, 136.13, 135.27, 131.66, 130.59, 130.55, 128.92, 127.39, 126.49; HR-MS (ESI-TOF):  $m/z$  282.9729 [ $\text{M}+\text{Na}^+$ ].

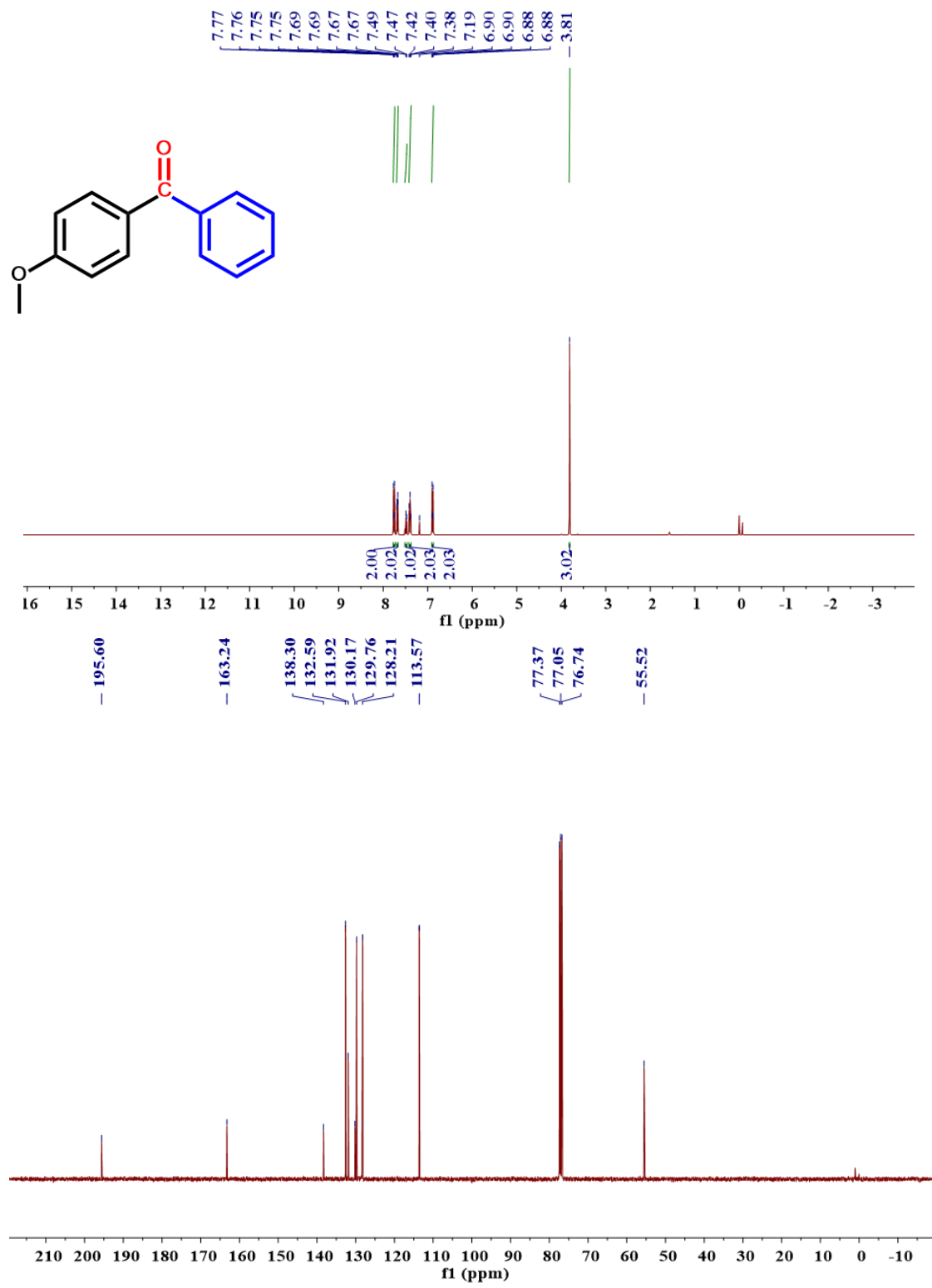


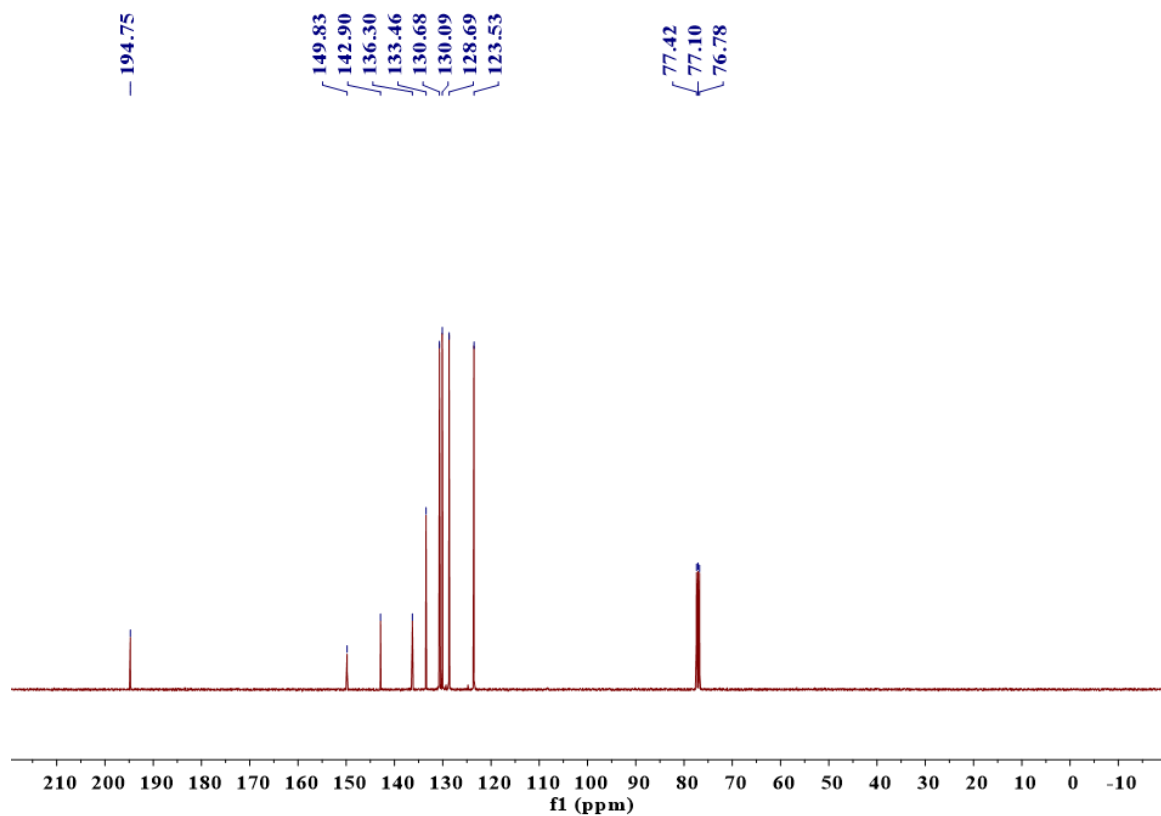
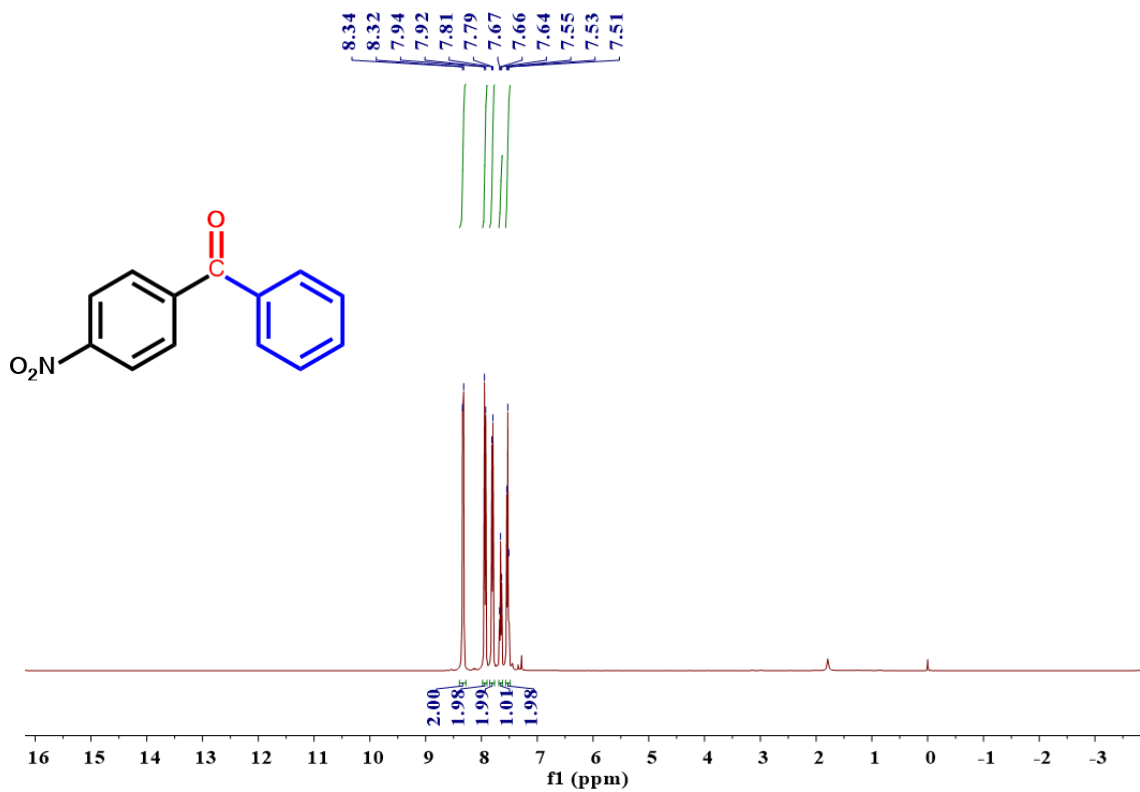
Phenyl(*p*-tolyl)methanone (3i): White solid, yield: 63%,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.68 (d,  $J$  = 7.1 Hz, 2H), 7.64 (d,  $J$  = 8.1 Hz, 2H), 7.50 (t,  $J$  = 7.4 Hz, 1H), 7.46 (t,  $J$  = 7.5 Hz, 2H), 7.38 (t,  $J$  = 7.9 Hz, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 195.45, 142.19, 136.89, 133.81, 131.12, 129.26, 128.88, 127.93, 127.16, 20.61; HR-MS (ESI-TOF):  $m/z$  219.0780 [ $\text{M}+\text{Na}^+$ ].



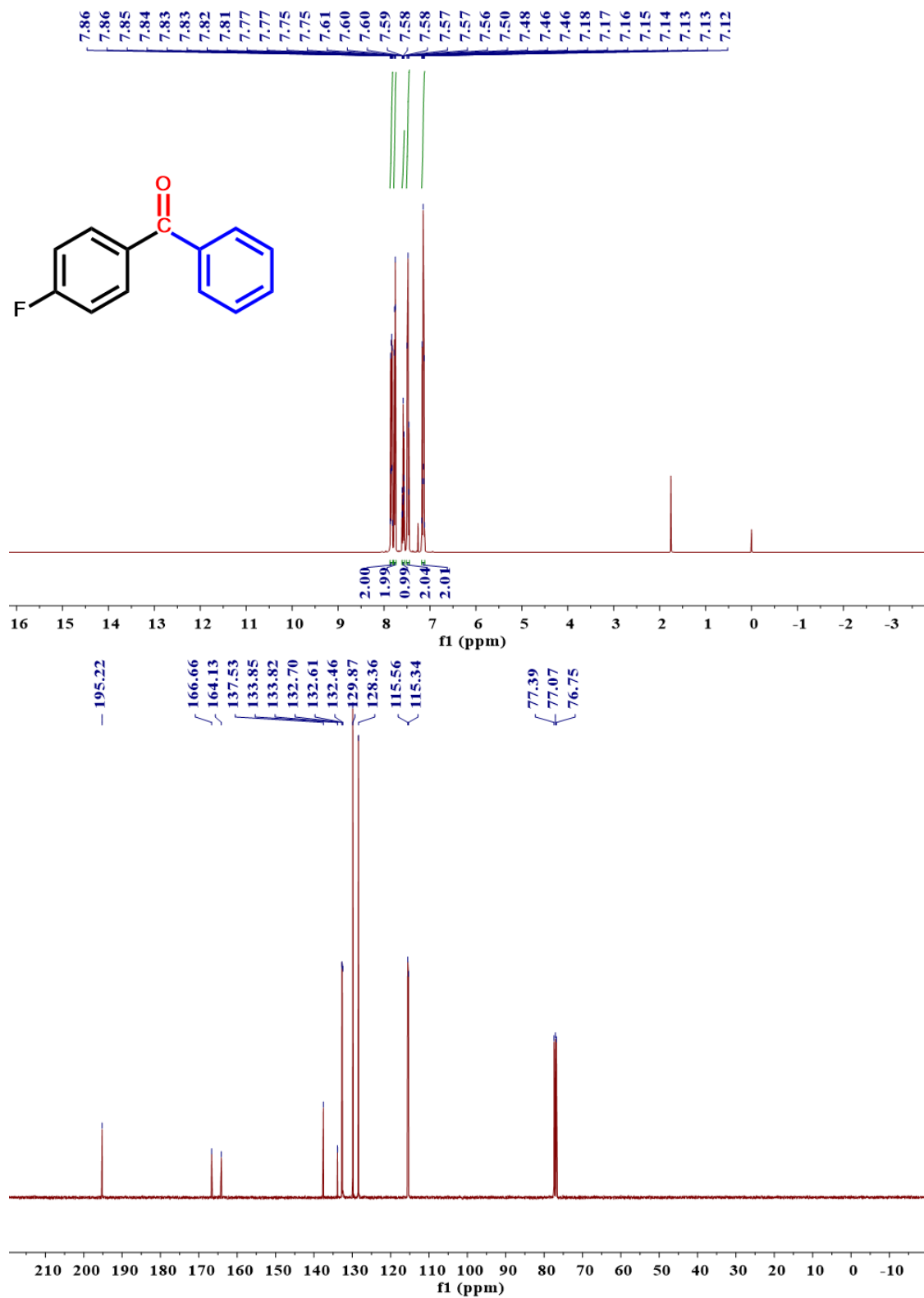


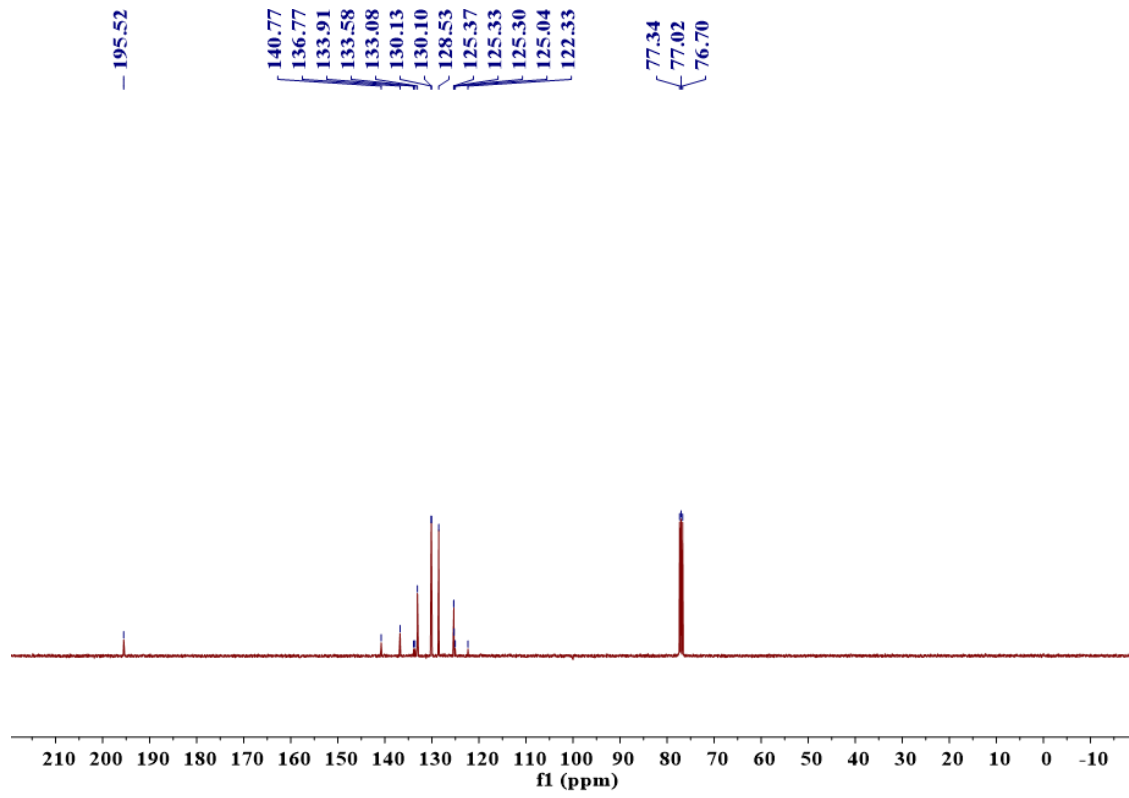
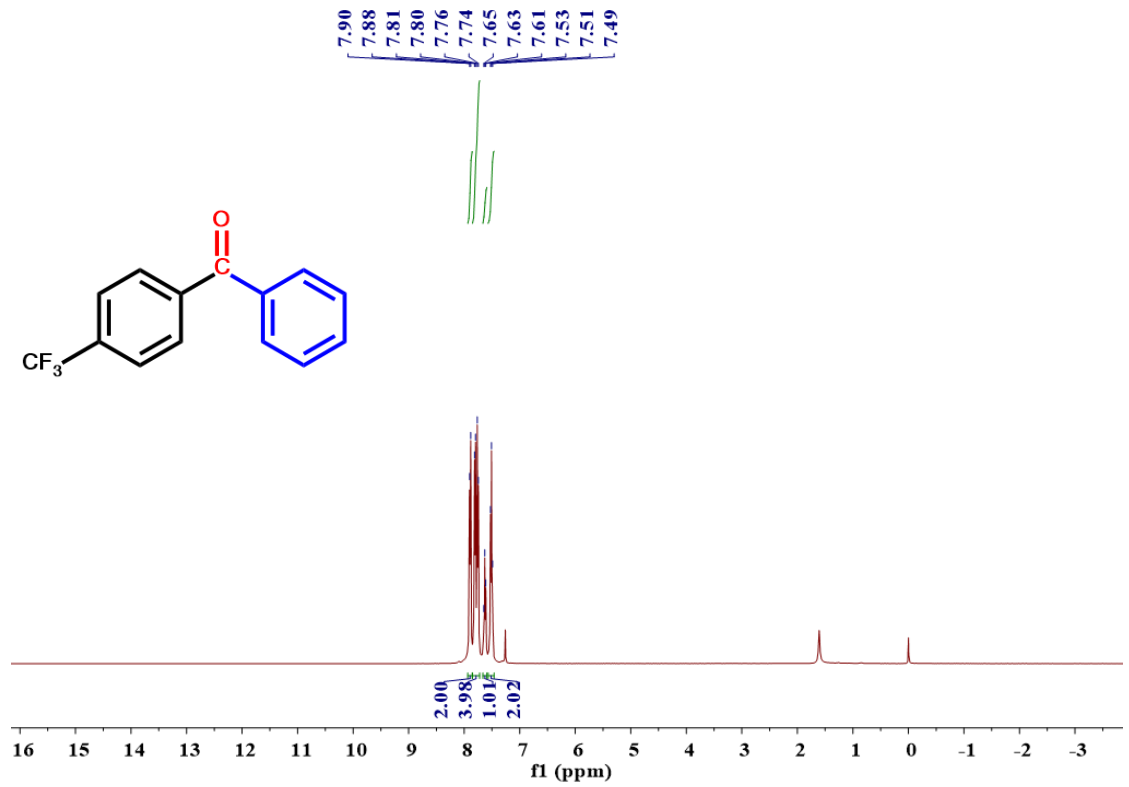


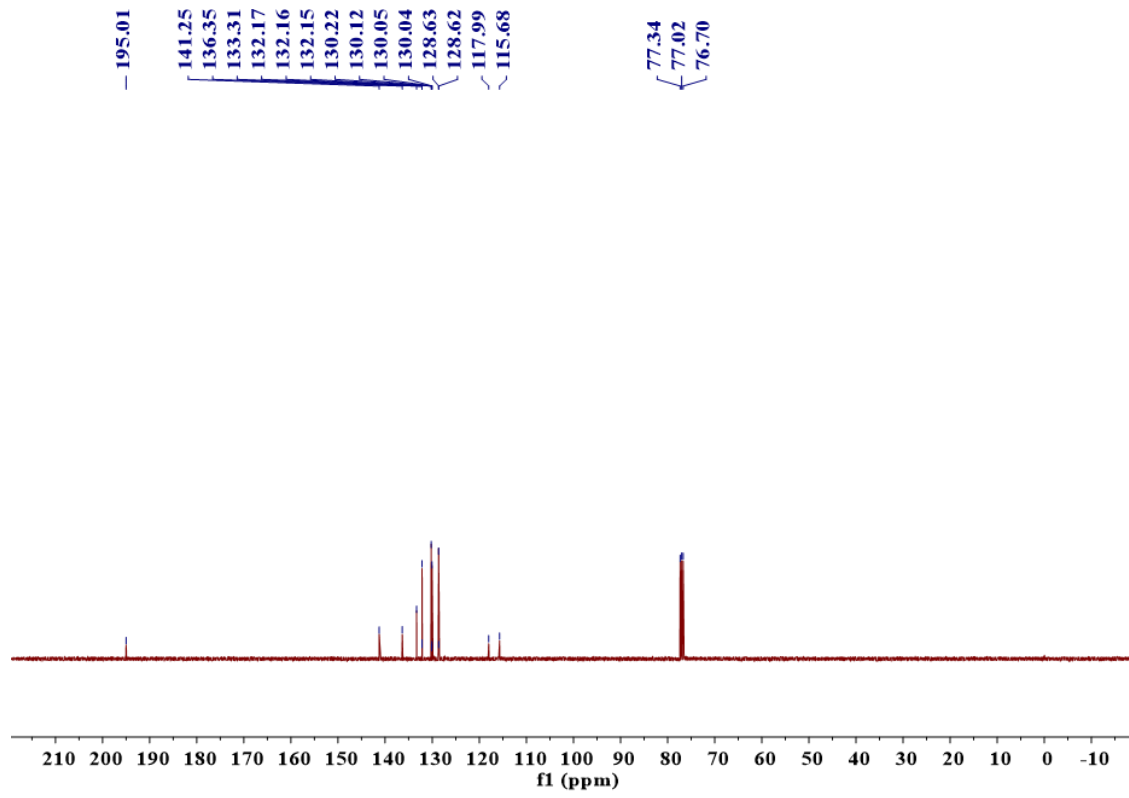
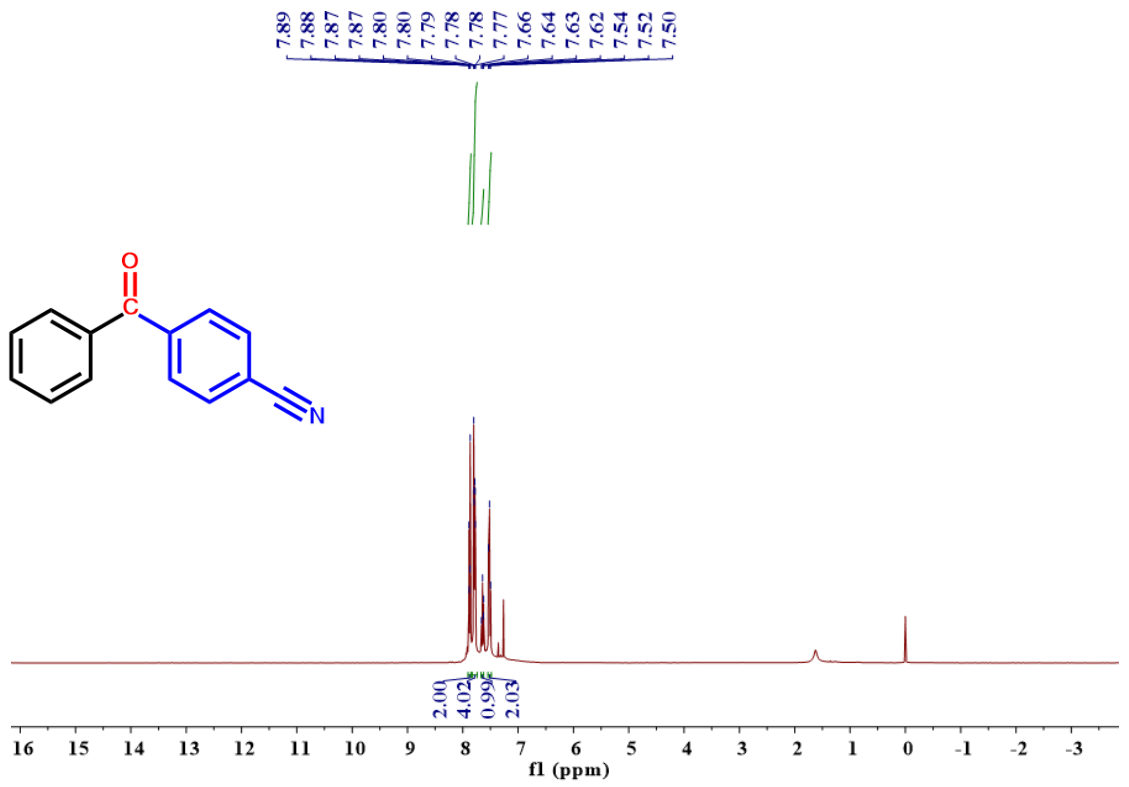


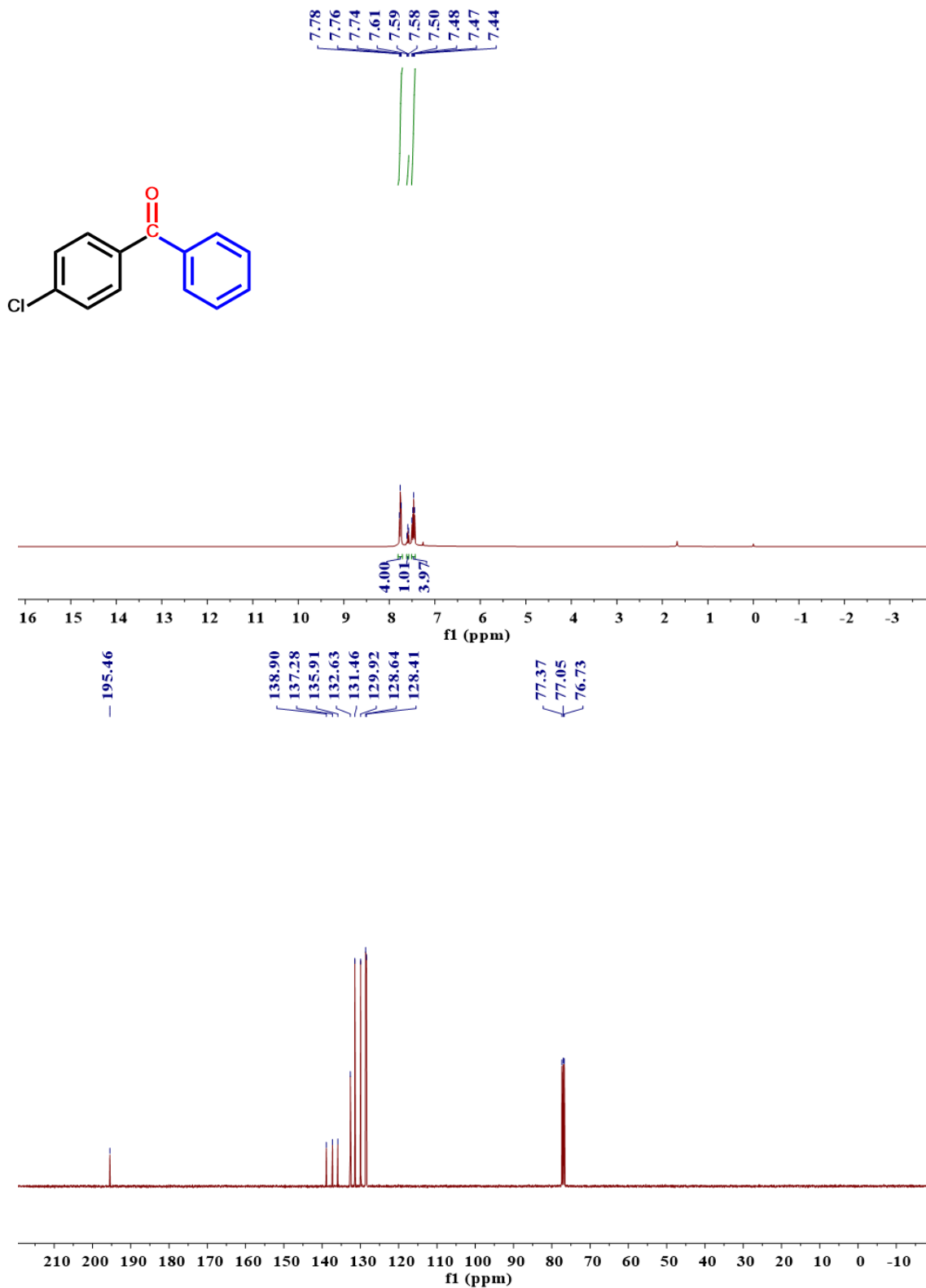












#### 4. References

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