A Bipyridine-Based MOF-Supported Single-Site Palladium Catalyst for Efficient and Recyclable Carbonylation of Aryl Iodides to Esters

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1. General Information.

Unless otherwise specified, all materials were purchased from commercial suppliers and were not further purified. The transformation process was monitored by thin-layer chromatography (TLC). Flash-column chromatography separation was performed using silica gel (200-300 mesh). Fourier transform infrared (FT-IR) spectra were measured using a Thermo Fisher Scientific Fourier infrared spectrometer with potassium bromide pellets. Powder X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance polycrystalline X-ray diffractometer (Germany). Scanning electron microscopy (SEM) samples were prepared on carbon tape SEM holders, and images were acquired using a Zeiss-Supra55 instrument. Transmission electron microscopy (TEM) morphology characterization was performed using a JEM-2100 instrument, while elemental mapping was acquired with a Tecnai G2 F30 S-TWIN instrument. Nitrogen adsorption isotherm data were obtained using an Autosorb IQ3 specific surface area and pore size analyzer. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi XPS instrument. The palladium content was determined using an inductively coupled plasma optical emission spectrometer (Optima 7300 DV). Gas chromatography analysis employed a Shimadzu GC-2014 instrument equipped with an SH-1 glass capillary column and a flame ionization detector (FID). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on an Agilent DD2 400 MHz NMR instrument. Chemical shifts in ^{1}H spectra were referenced to $CDCl_3$ (δ 7.26), while those in ^{13}C spectra were referenced to $CDCl_3$ (δ 77.0).

2. Catalyst Preparation.

Synthesis of m-bpy-MOF.

$ZrCl_4$ (1.4 g, 6 mmol), glacial acetic acid (1.1 g, 18 mmol), biphenyl-4,4′-dicarboxylic acid (726.7 mg, 3 mmol) and 2,2′-bipyridine-5,5′-dicarboxylic acid (732.6 mg, 3 mmol) were placed in a reaction flask containing 40 mL of DMF (anhydrous). The reagents were dispersed by ultrasonic treatment for 10 minutes and then transferred to a polytetrafluoroethylene autoclave. The reaction was carried out at 120 °C in an oven for 24 hours. The mixture was naturally cooled to room temperature, and the solid was washed with DMF three times and then soaked in methanol for 1 day. The MOF was collected by centrifugation and activated at 150 °C under vacuum for 12 hours.

Synthesis of m-bpy-MOF-$PdCl_2$.

Disperse 500 mg of MOF in 20 mL of acetonitrile, and sonicate for 10 minutes. Then add the acetonitrile solution of $PdCl_2(CH_3CN)_2$ (45 mg $PdCl_2(CH_3CN)_2$ in 15 mL CH_3CN) and react the mixture at 65 °C for 24 hours. Subsequently, separate the solid by centrifugation and wash it with acetonitrile three times. Suspend the solid in methanol for 1 day, then collect the solid by centrifugation and vacuum dry it at 80 °C to obtain the final MOF catalyst.

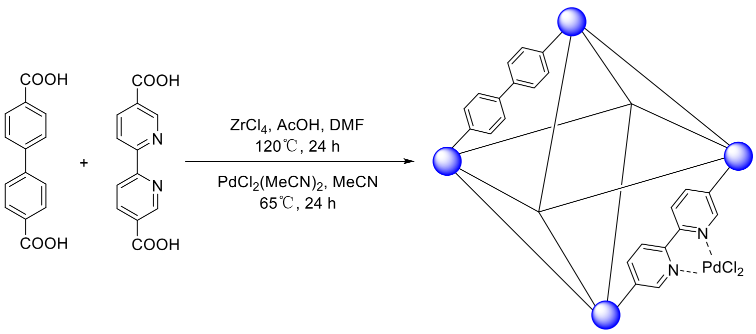


Fig. S1 Schematic structures of m-bpy-MOF-$PdCl_2$ precatalysts.

3. General Steps of the Iodobenzene Carbonylation Reaction.

Add iodobenzene (0.2 mmol, 40.8 mg), catalyst (10.0 mg), and isopropanol (1.0 mL) to a 5 mL vial. Seal tightly with a rubber diaphragm stopper, cap with an aluminum cap, and connect with a needle. The vial was secured in an alloy holder and placed in an SLM250 autoclave. After purging three times with nitrogen, the reactor was filled with carbon monoxide at 30 bar. The reaction proceeded at 120 °C for 3 hours. Upon completion, the reactor was cooled to room temperature, and carbon monoxide was carefully vented outdoors. After reaction completion, verify reaction thoroughness via thin-layer chromatography (TLC). Remove the reaction flask, cool it, and separate the solid catalyst using centrifugal separation. Remove the solvent by vacuum rotary evaporation. Isolate the product via silica gel column chromatography using a petroleum ether:ethyl acetate eluent ratio of 10:1. Remove residual petroleum ether and ethyl acetate from the purified target product via vacuum rotary evaporation. After drying, weigh and record the product mass to calculate yield. Verify the structural integrity of the product using nuclear magnetic resonance (NMR) spectroscopy.

4. Catalyst Recycling.

The used catalyst was collected in a centrifuge tube and washed with a mixture of acetonitrile (20 mL) and saturated aqueous sodium bicarbonate solution (0.5 mL). The washing procedure was then repeated twice using acetonitrile (20 mL each time), followed by three additional washes with methanol (20 mL each). Finally, the catalyst was dried overnight in a vacuum oven at 80 °C.

5. Catalyst Characterization.

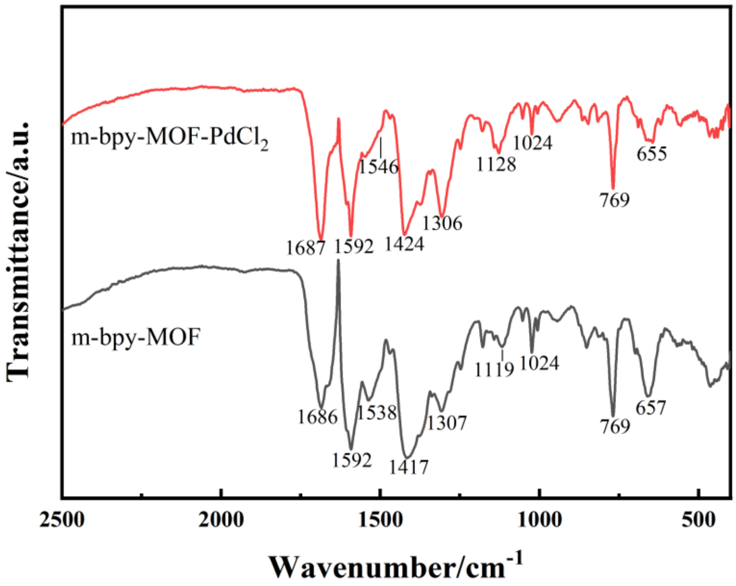


Fig. S2 FT-IR spectrum of m-bpy-MOF and m-bpy-MOF-$PdCl_2$.

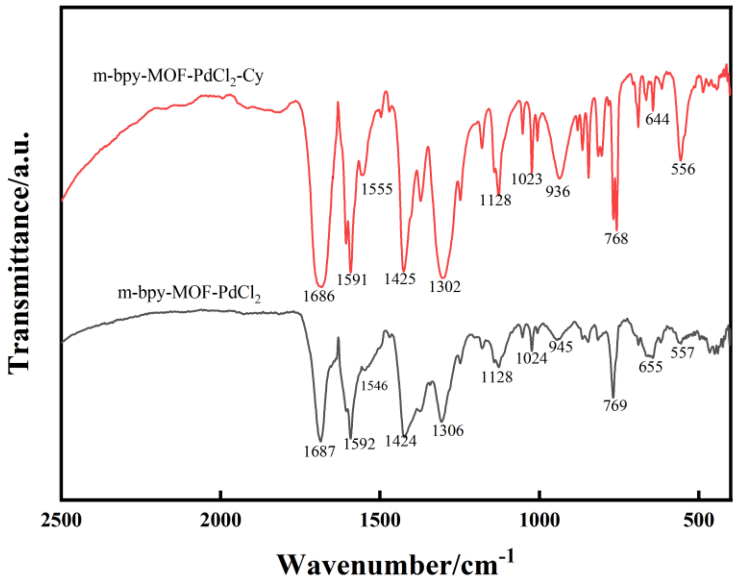


Fig. S3 FT-IR spectrum of m-bpy-MOF-$PdCl_2$ and m-bpy-MOF-$PdCl_2$ after cycling.

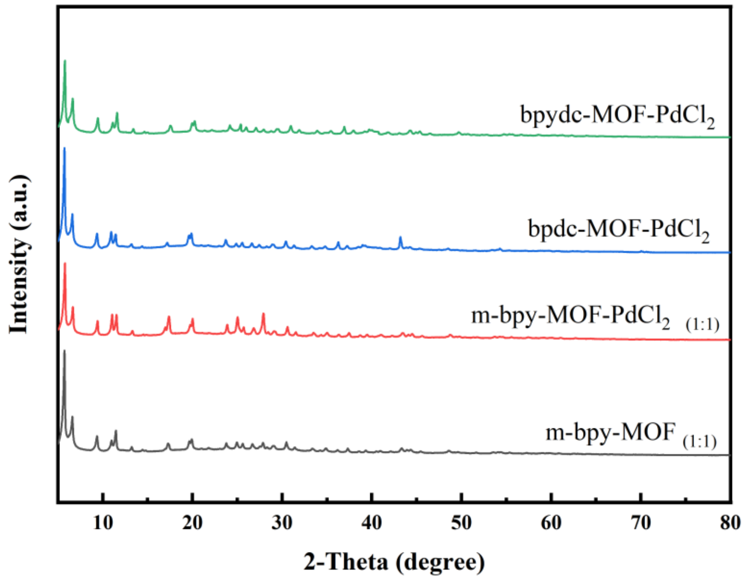


Fig. S4 XRD spectrum of m-bpy-MOF, m-bpy-MOF-$PdCl_2$(1:1), bpdc-MOF-$PdCl_2$ and bpydc-MOF-$PdCl_2$. m = mixed linkers, (1:1) denotes the ratio of biphenylenedicarboxylic acid to bipyridinedicarboxylic acid.

Digestion Procedure

Weigh out 20 mg of catalyst, add 5 mL of saturated $NaHCO_3$ solution, and heat to 60 °C until completely clear. Centrifuge to remove the insoluble metal precipitate, collect the supernatant, adjust the pH to acidic, and extract the organic phase with ethyl acetate. Spin-dry the organic phase to obtain a mixture of two ligands. Then, add DMSO-*d6* for ^{1}H NMR analysis.

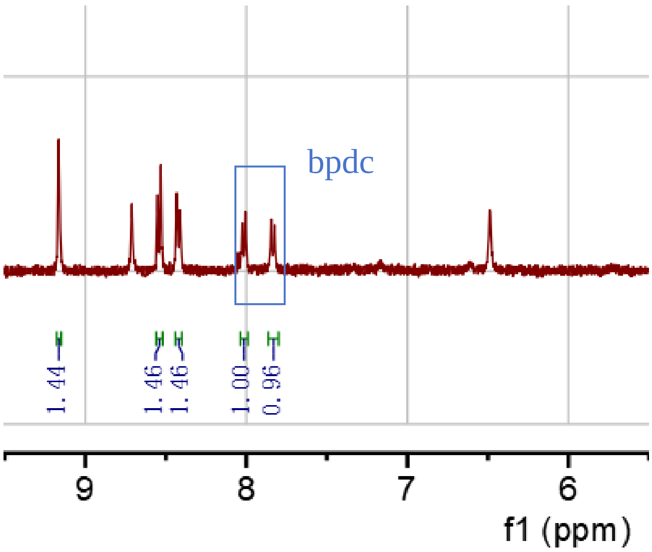


Fig. S5 Normalized ^{1}H NMR of $NaHCO_3$/DMSO-*d6* digested m-bpy-MOF-$PdCl_2$.

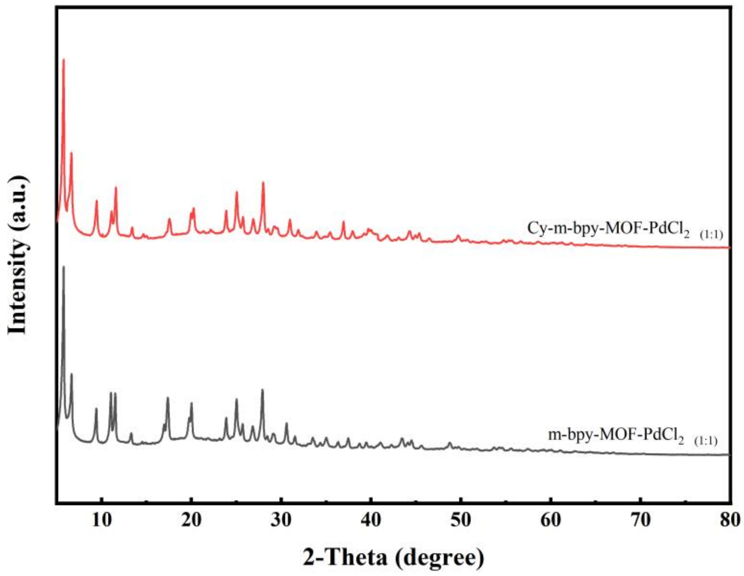


Fig. S6 XRD spectrum of m-bpy-MOF-$PdCl_2$ and m-bpy-MOF-$PdCl_2$ after cycling.

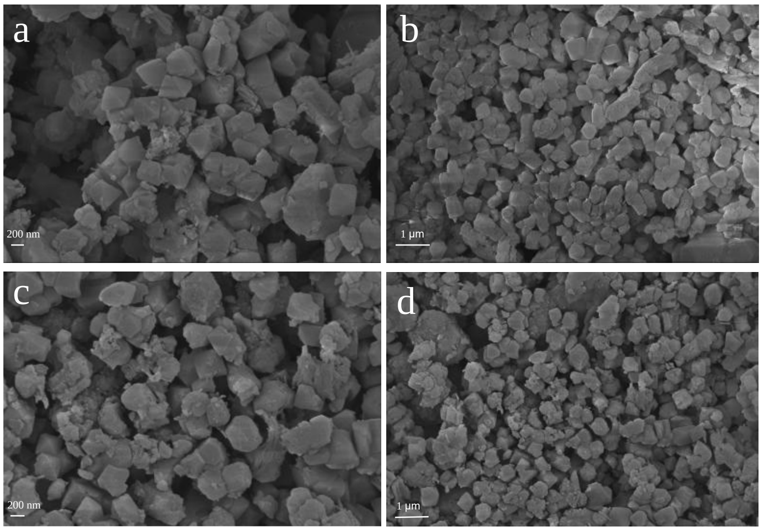


Fig. S7 (a-b) SEM spectra of m-bpy-MOF-$PdCl_2$;(c-d) SEM spectra of m-bpy-MOF-$PdCl_2$ after cycling.

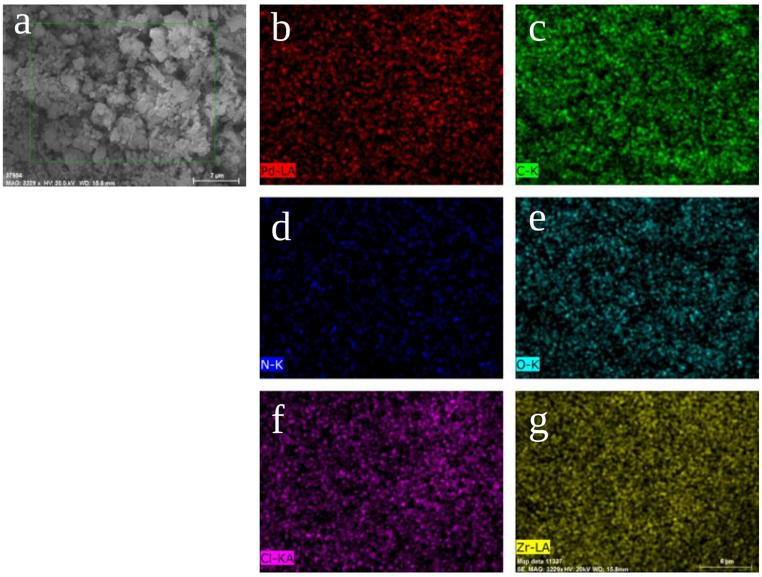


Fig. S8 EDS scanning spectrum of m-bpy-MOF-$PdCl_2$ after cycling.

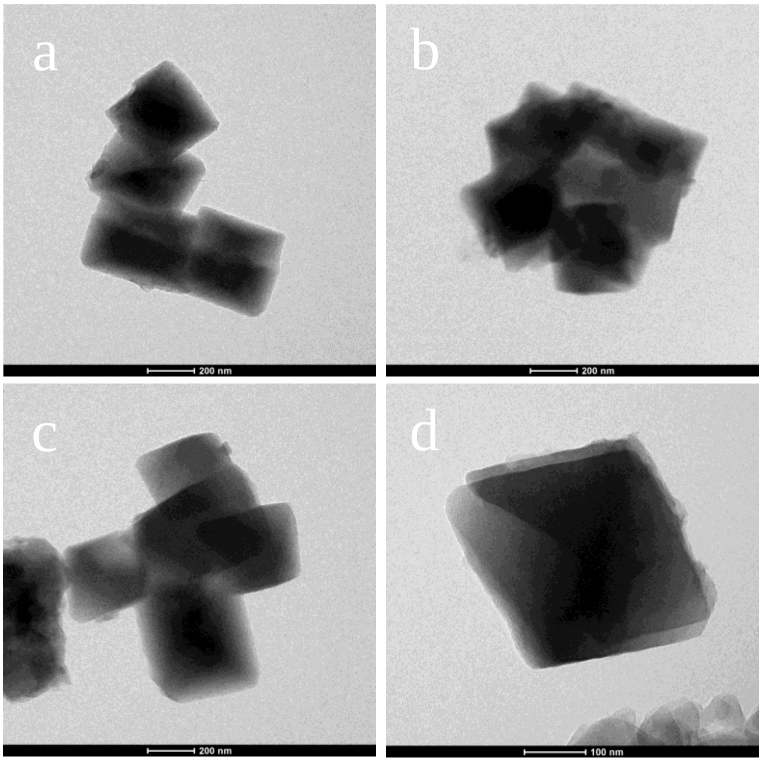


Fig. S9 (a-b) TEM spectra of m-bpy-MOF-$PdCl_2$; (c-d) TEM spectra of m-bpy-MOF-$PdCl_2$ after cycling.

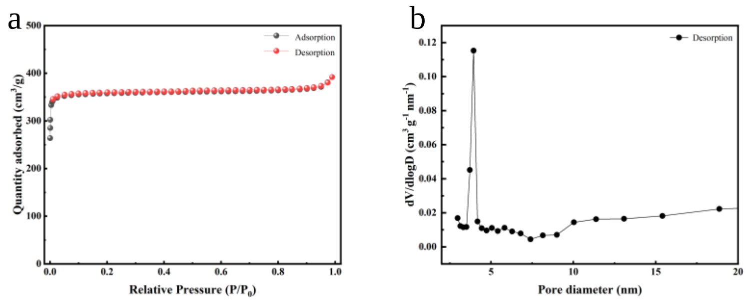


Fig. S10 N_2 adsorption-desorption isotherm and pore size distribution of m-bpy-MOF-$PdCl_2$.

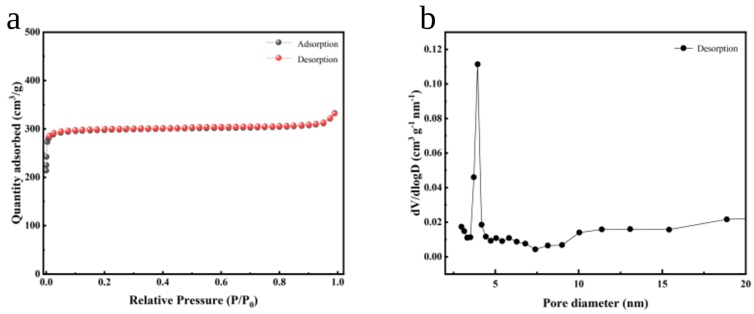


Fig. S11 N_2 adsorption-desorption isotherm and pore size distribution of used m-bpy-MOF-$PdCl_2$.

Table S1. BET analysis of m-bpy-MOF-$PdCl_2$

Relative Pressure (P/Po)	**Volume @ STP (cc/g)**	**1 / [W((Po/P) -1)]**
3.84469e-04	263.7727	4.8255e-03
6.65117e-04	285.0611	6.2605e-03
9.55941e-04	302.3288	7.4817e-03
4.06757e-03	332.9865	2.4572e-02
6.90907e-03	339.0109	4.0043e-02
9.88186e-03	342.1475	5.6178e-02
2.48132e-02	348.3841	1.3720e-01
BET Summary		
slope	5.426	
Intercept	2.551e-03	
Correlation coefficient, r	0.999996	
C constant	2128.026	

Table S2. BET analysis of used m-bpy-MOF-$PdCl_2$

Relative Pressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) -1)]
2.45953e-02	288.3841	1.2354e+01
4.99100e-02	292.0314	2.1830e+01
7.52552e-02	293.8487	3.0952e+01
1.00447e-01	295.0705	4.0026e+01
1.25517e-01	295.8598	4.9165e+01
1.50158e-01	296.5771	5.7761e+01
1.74735e-01	297.0716	6.6940e+01
BET Summary		
slope	362.018	
Intercept	3.627e+00	
Correlation coefficient, r	0.999974	
C constant	100.804	

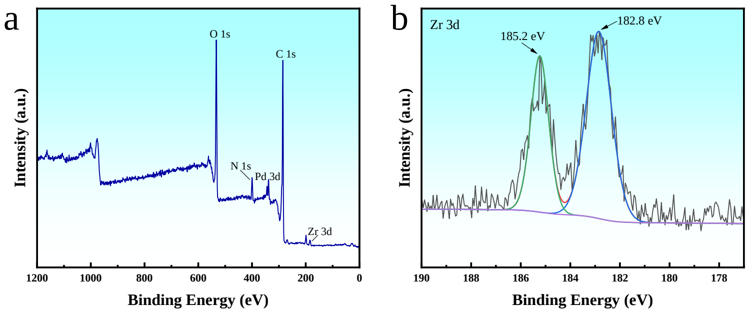


Fig. S12 XPS spectrum of m-bpy-MOF-$PdCl_2$.

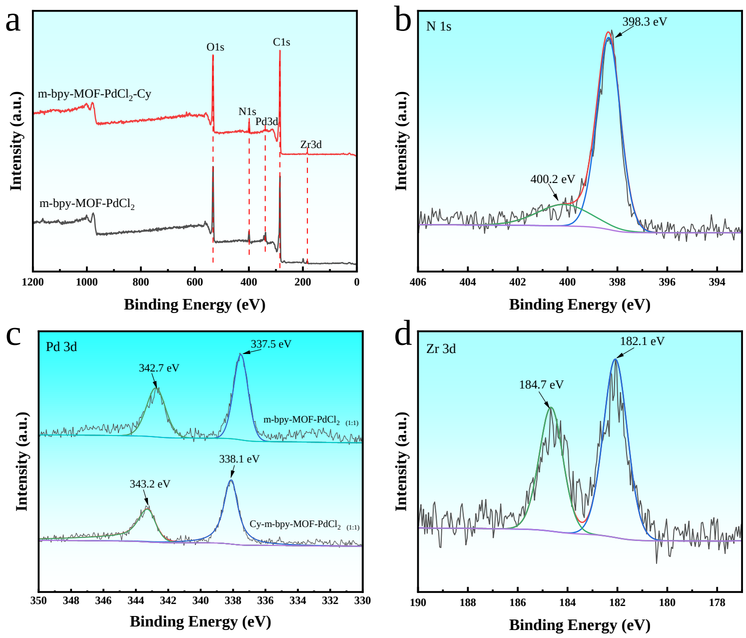


Fig. S13 XPS spectrum of m-bpy-MOF-$PdCl_2$ after cycling.

6. Optimization of Conditions for the Iodobenzaldehyde Reaction.

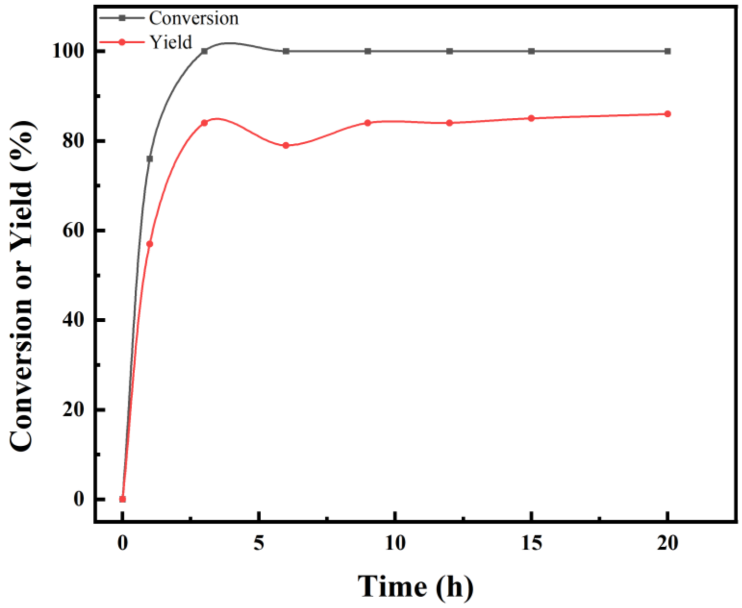


Fig. S14 Effects of m-bpy-MOF-$PdCl_2$ catalyst at different times on the carbonylation reaction of iodobenzene.

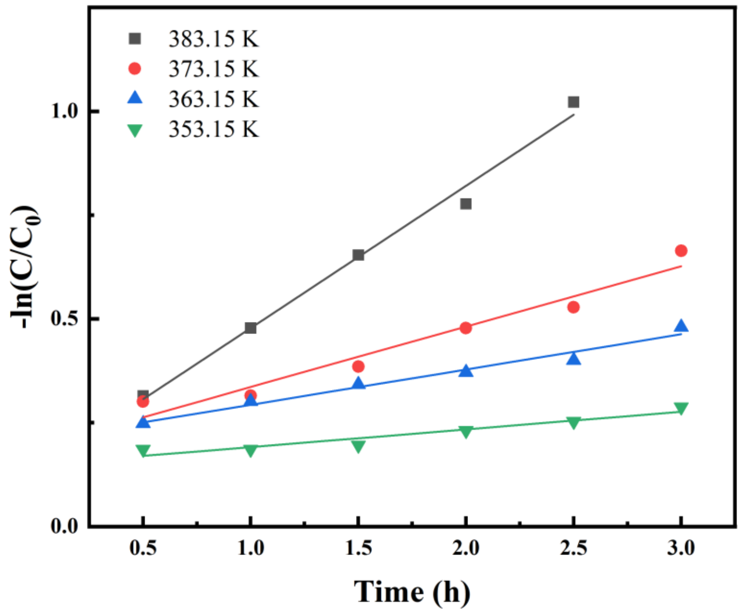
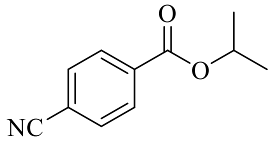


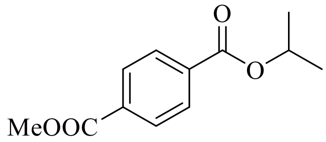
Fig. S15 ln(C/C_0) versus reaction time of the iodobenzene carbonylation reaction catalyzed by the m-bpy-MOF-$PdCl_2$.

7. Characterization data of the compounds.



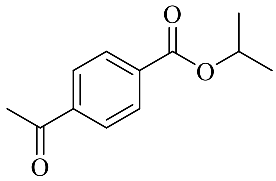
Benzoic acid, 4-cyano-, 1-Methylethyl ester (**2b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H), 7.77 – 7.71 (m, 2H), 5.27 (dq, *J* = 12.3, 5.9 Hz, 1H), 1.38 (d, *J* = 5.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.40, 134.67, 132.11, 130.01, 118.06, 116.10, 69.53, 21.84.



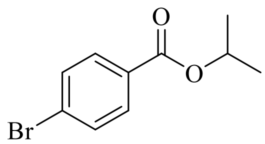
1,4-Benzenedicarboxylic acid, 1-methyl 4-(1-methylethyl) ester (**2c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 4H), 5.26 (p, *J* = 6.2 Hz, 1H), 3.93 (s, 3H), 1.37 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.31, 134.64, 133.63, 129.42, 68.92, 52.36, 21.86.



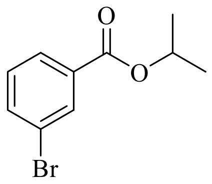
Benzoic acid, 4-acetyl-, 1-methylethyl ester (**2d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.5 Hz, 2H), 5.31 – 5.20 (m, 1H), 2.62 (s, 3H), 1.37 (d, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.60, 165.18, 139.98, 134.63, 129.70, 128.09, 69.01, 26.87, 21.86.



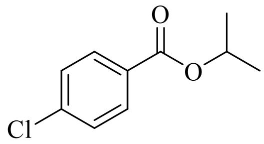
isopropyl 4-bromobenzoate (**2e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 5.23 (hept, *J* = 6.1 Hz, 1H), 1.36 (d, *J* = 6.4 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.32, 131.55, 131.04, 129.74, 127.73, 68.73, 21.89.



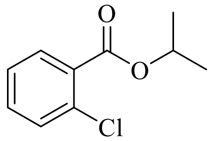
isopropyl 3-bromobenzoate (**2f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 5.24 (dq, *J* = 12.5, 6.3 Hz, 1H), 1.37 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.71, 135.61, 132.79, 132.46, 129.83, 128.09, 122.33, 68.92, 21.88.



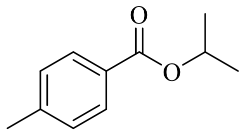
4-Chlorobenzoic acid isopropyl ester (**2g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 5.23 (dq, *J* = 12.5, 6.2 Hz, 1H), 1.36 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.22, 139.07, 130.89, 129.30, 128.56, 68.71, 21.89.



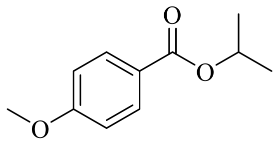
Benzoic acid, 2-chloro-, 1-methylethyl ester (**2h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.33 – 7.27 (m, 1H), 5.27 (dq, *J* = 12.5, 6.2 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.42, 133.36, 132.18, 131.06, 130.99, 130.90, 126.50, 69.30, 21.83.



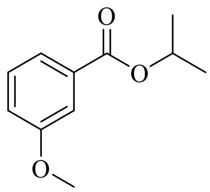
propan-2-yl 4-methylbenzoate (**2i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.6 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 5.24 (hept, J = 6.8 Hz, 1H), 2.40 (s, 3H), 1.36 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.17, 143.25, 129.50, 128.93, 128.13, 68.06, 21.94, 21.61.



Benzoic acid, 4-Methoxy-, 1-Methylethyl ester (**2j**)

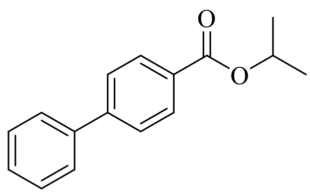
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.1 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 5.21 (h, *J* = 6.2 Hz, 1H), 3.85 (s, 3H), 1.35 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.87, 163.12, 131.47, 123.32, 113.44, 67.93, 55.40, 21.98.



Benzoic acid, 3-methoxy-, 1-methylethyl ester (**2k**)

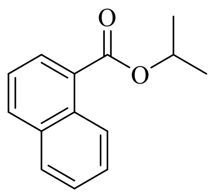
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.56 (dd, *J* = 2.7, 1.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.08 (ddd, *J* = 8.2, 2.7, 1.0 Hz, 1H), 5.24 (p, *J* = 6.3 Hz, 1H), 3.85 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.95, 159.46, 132.19, 129.26, 121.86, 119.08, 114.00, 68.46, 55.40, 21.90.



[1,1'-Biphenyl]-4-carboxylic acid, 1-methylethyl ester (**2l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.64 (dd, *J* = 12.3, 8.1 Hz, 4H), 7.43 (dt, *J* = 29.4, 7.1 Hz, 3H), 5.28 (dq, *J* = 12.4, 6.2 Hz, 1H), 1.40 (d, *J* = 6.2 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.00, 145.41, 140.09, 130.03, 129.64, 128.91, 128.08, 127.28, 126.96, 68.38, 21.99.

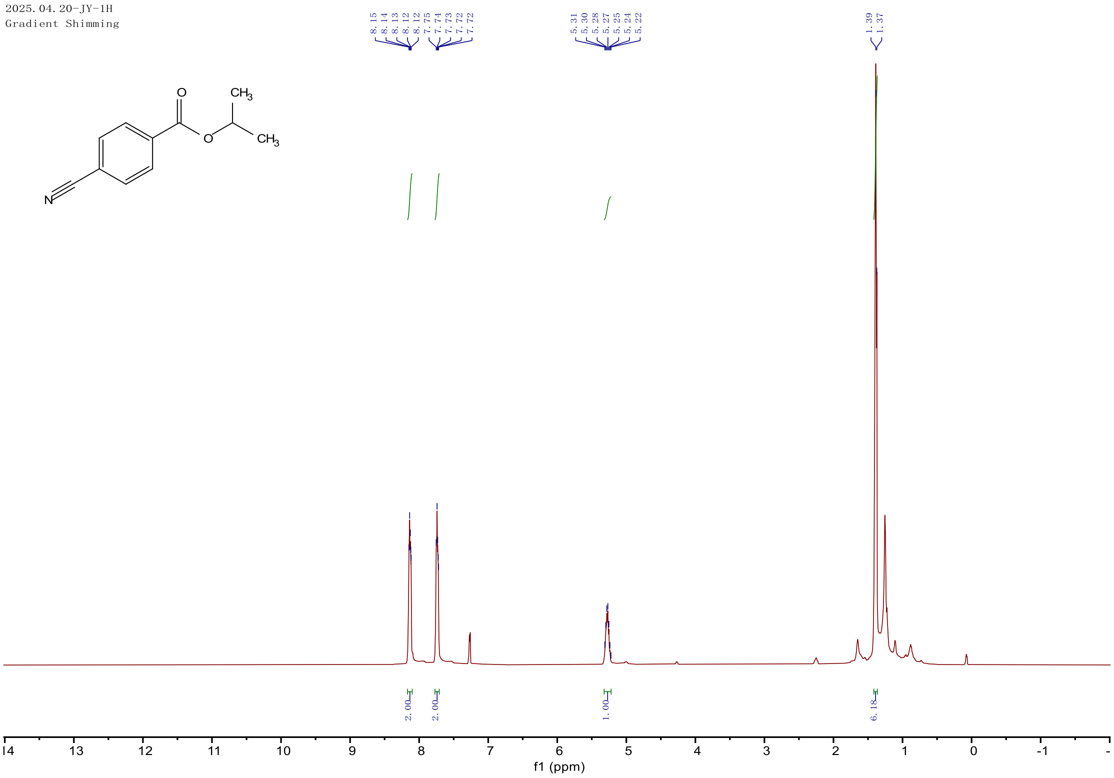


1-Naphthalenecarboxylic acid, 1-Methylethyl ester (**2m**)

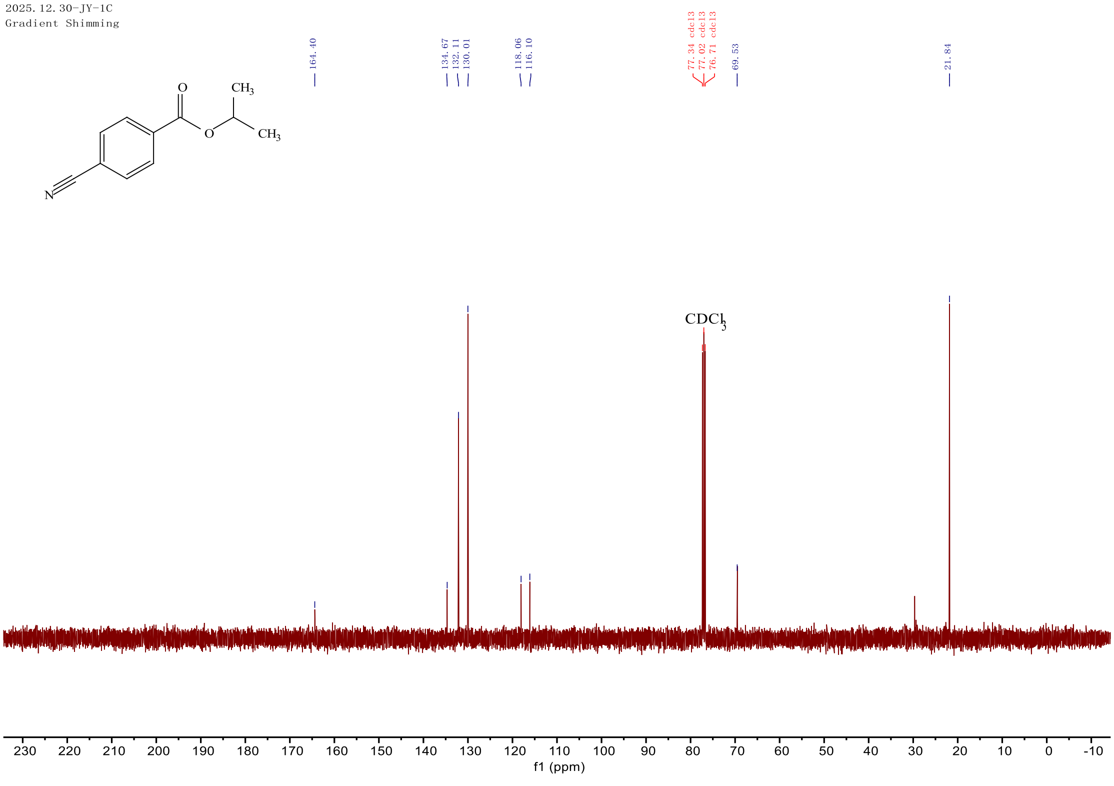
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, *J* = 8.6 Hz, 1H), 8.17 (d, *J* = 7.3 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.52 (dt, *J* = 15.3, 8.0 Hz, 2H), 5.40 (hept, *J* = 6.2 Hz, 1H), 1.46 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.22, 133.82, 133.03, 131.29, 129.88, 128.52, 127.98, 127.61, 126.13, 125.80, 124.50, 68.50, 22.03.

8. Spectra of ^{1}H NMR, ^{13}C NMR.

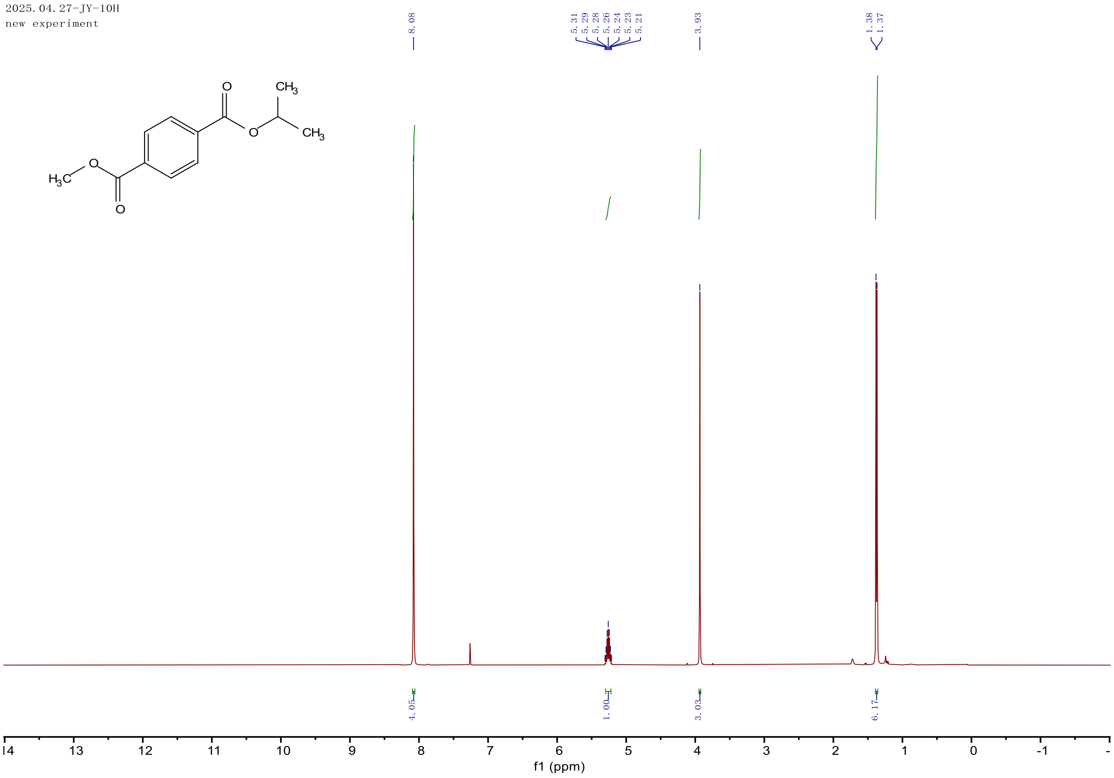
^{1}H NMR Spectra of **2b** (400 MHz, $CDCl_3$)



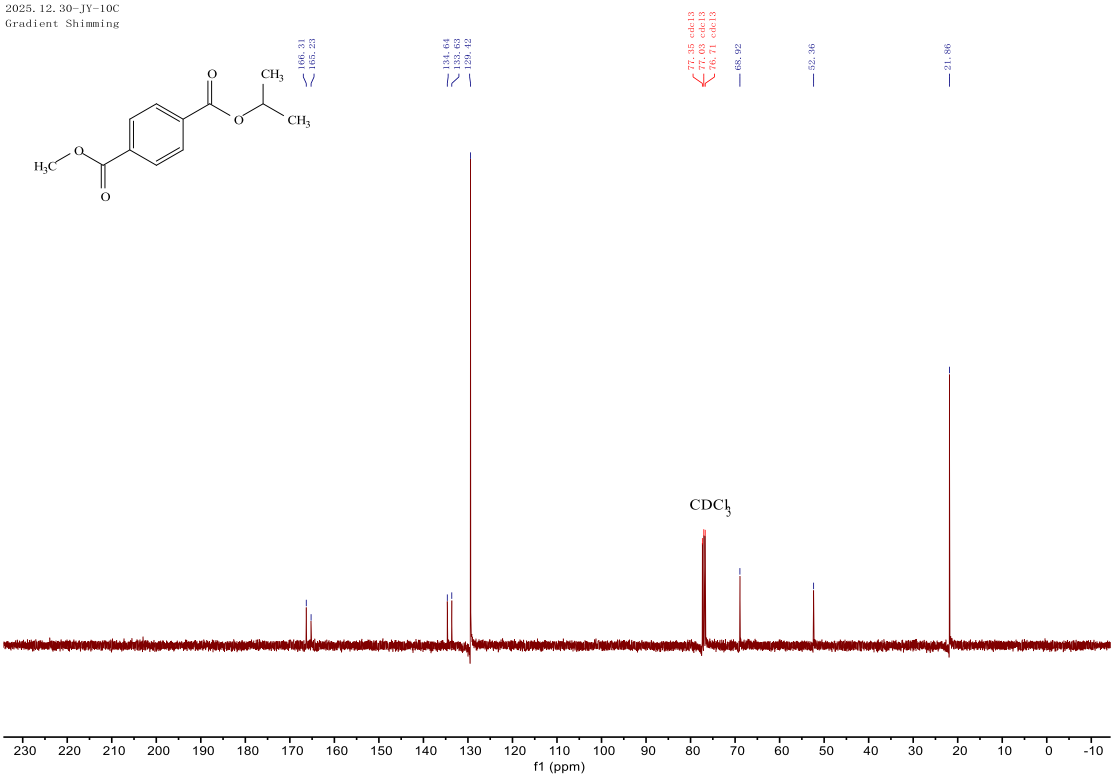
^{13}C NMR Spectra of **2b** (101 MHz, $CDCl_3$)



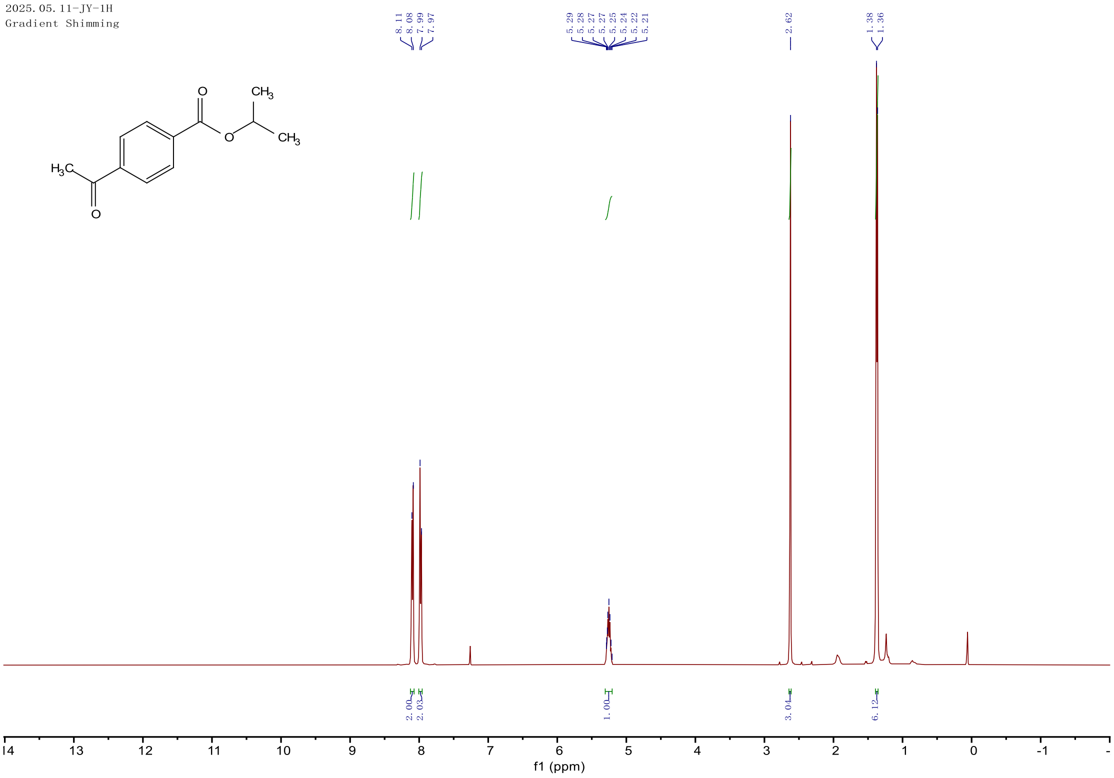
^{1}H NMR Spectra of **2c** (400 MHz, $CDCl_3$)



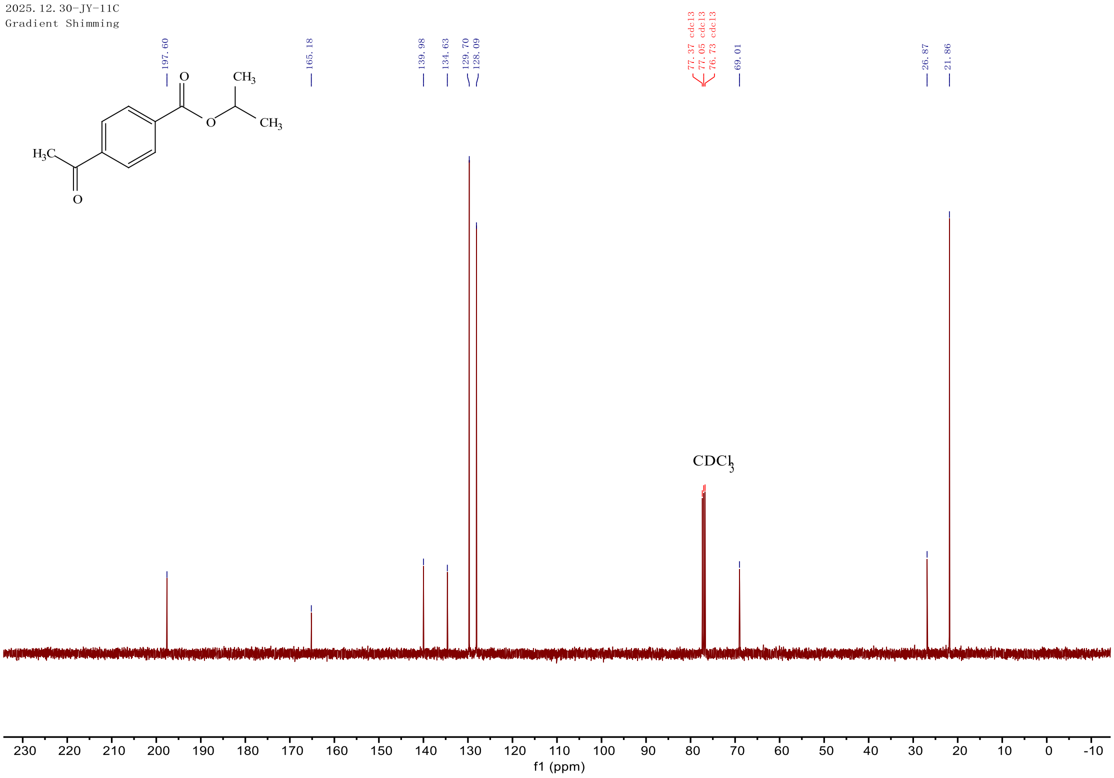
^{13}C NMR Spectra of **2c** (101 MHz, $CDCl_3$)



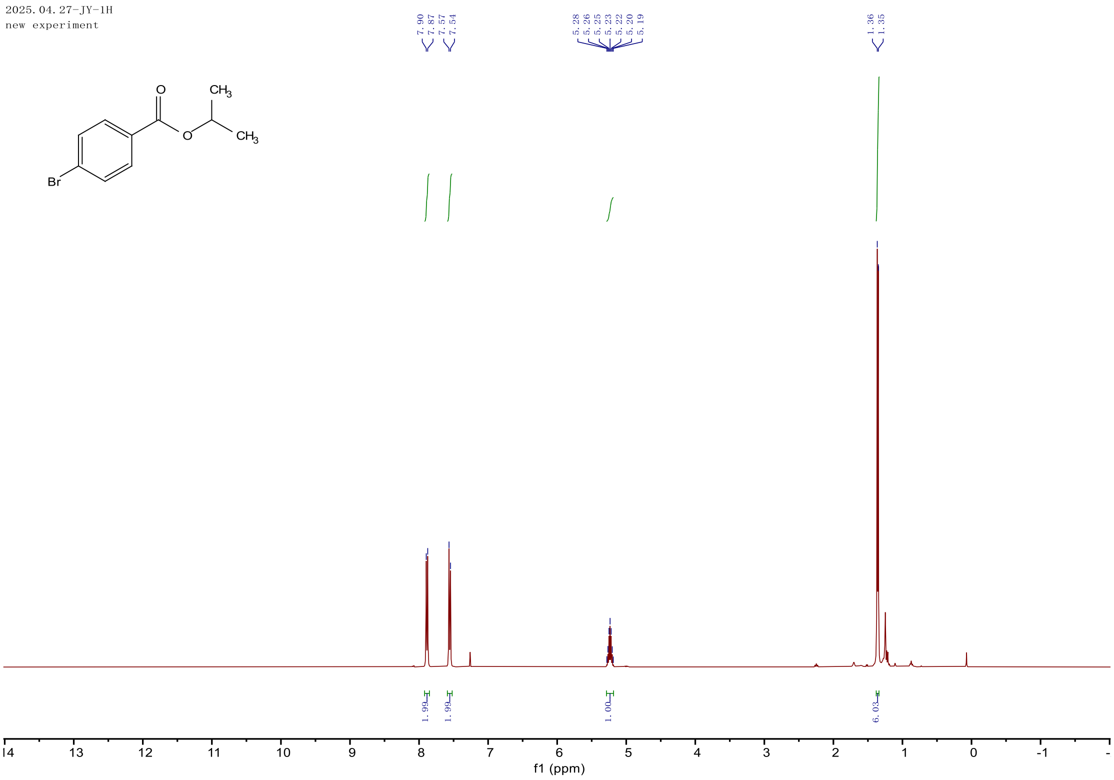
[1]H NMR Spectra of **2d** (400 MHz, $CDCl_3$)



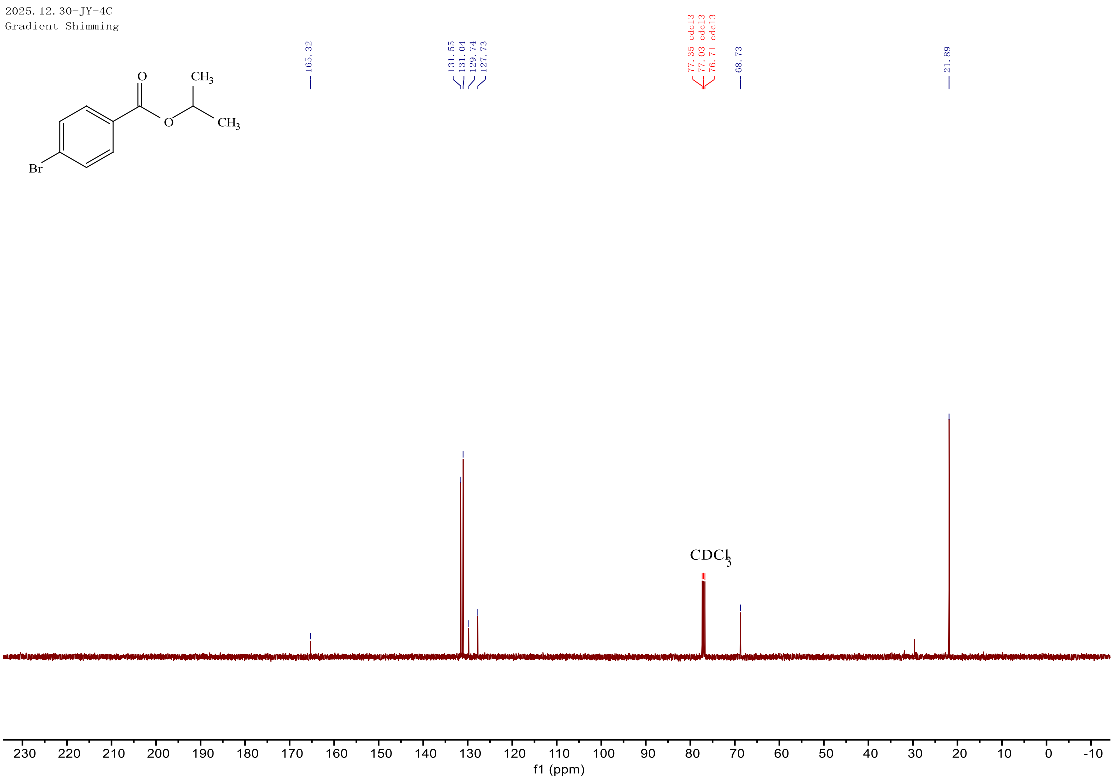
[13]C NMR Spectra of **2d** (101 MHz, $CDCl_3$)



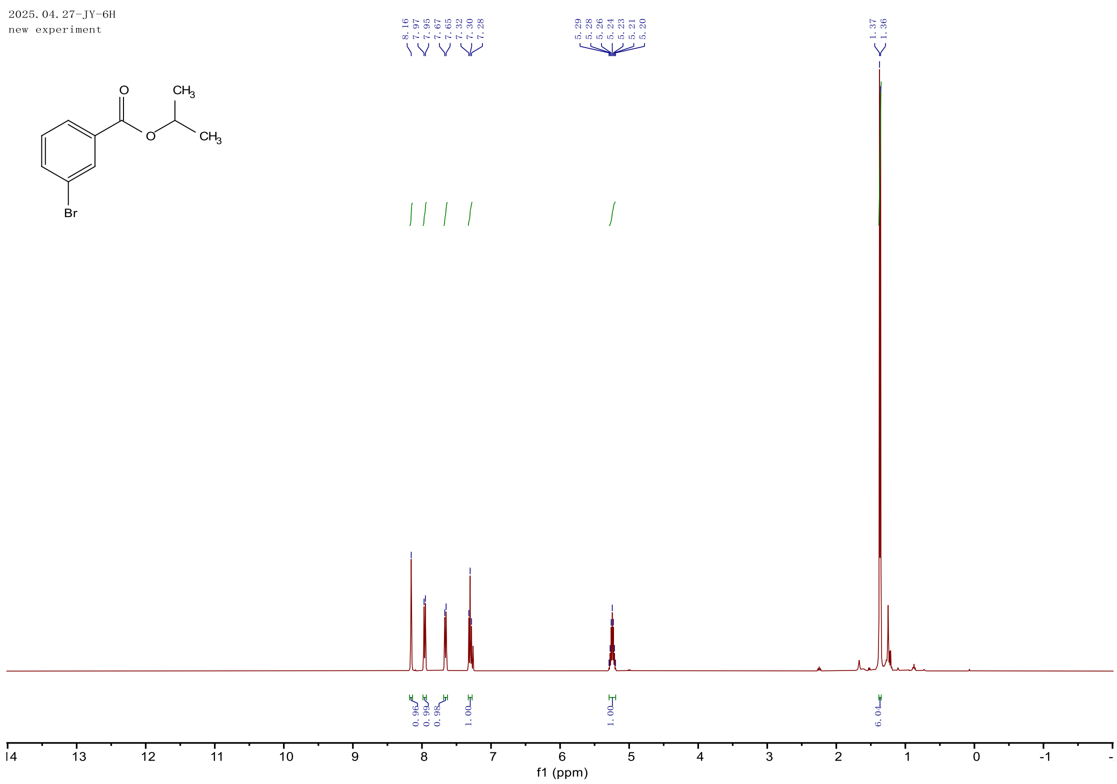
^{1}H NMR Spectra of **2e** (400 MHz, $CDCl_3$)



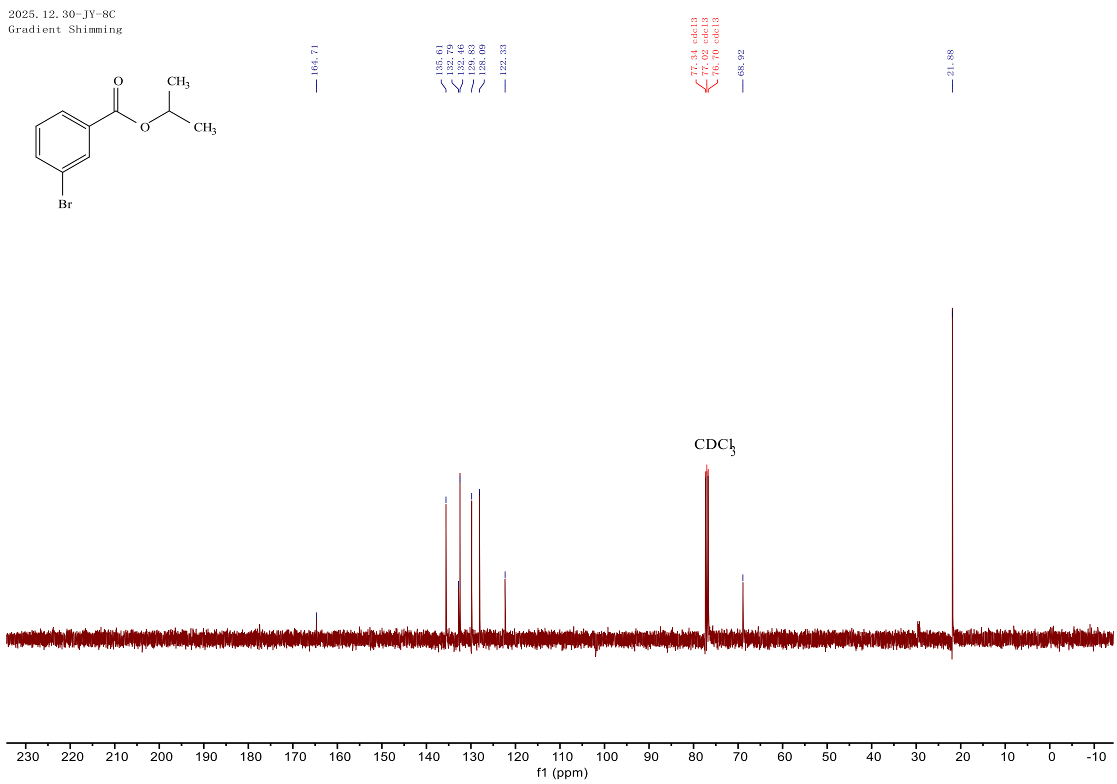
^{13}C NMR Spectra of **2e** (101 MHz, $CDCl_3$)



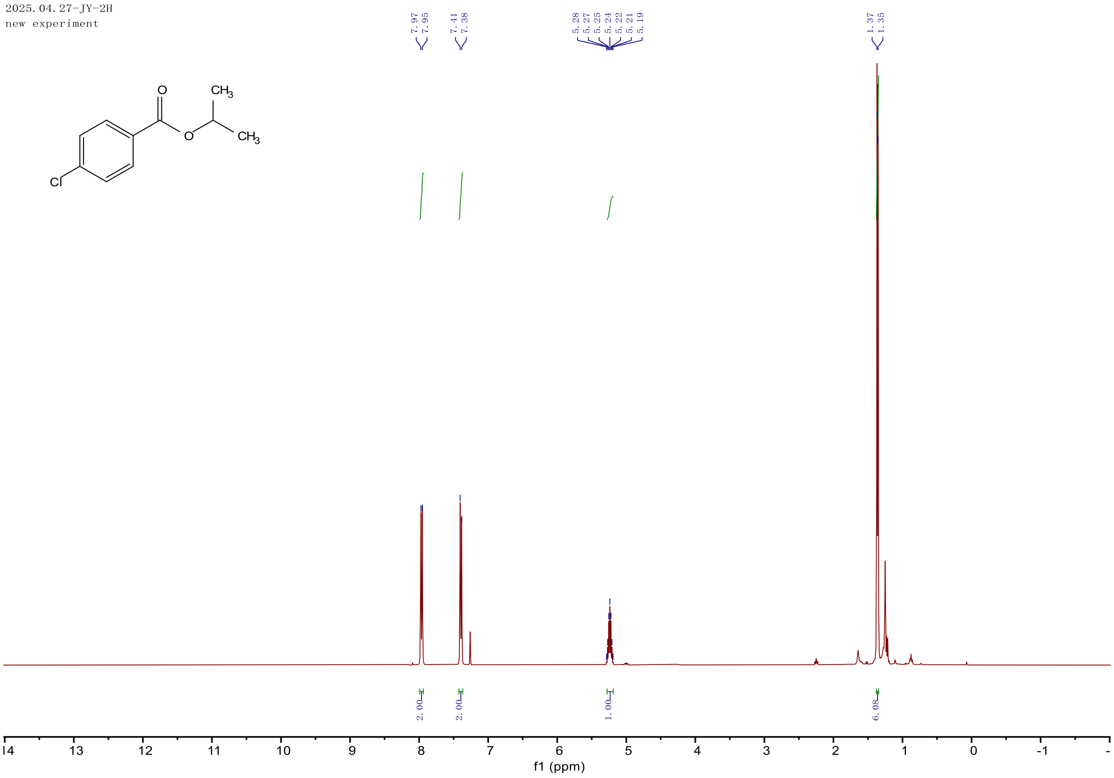
[1]H NMR Spectra of **2f** (400 MHz, $CDCl_3$)



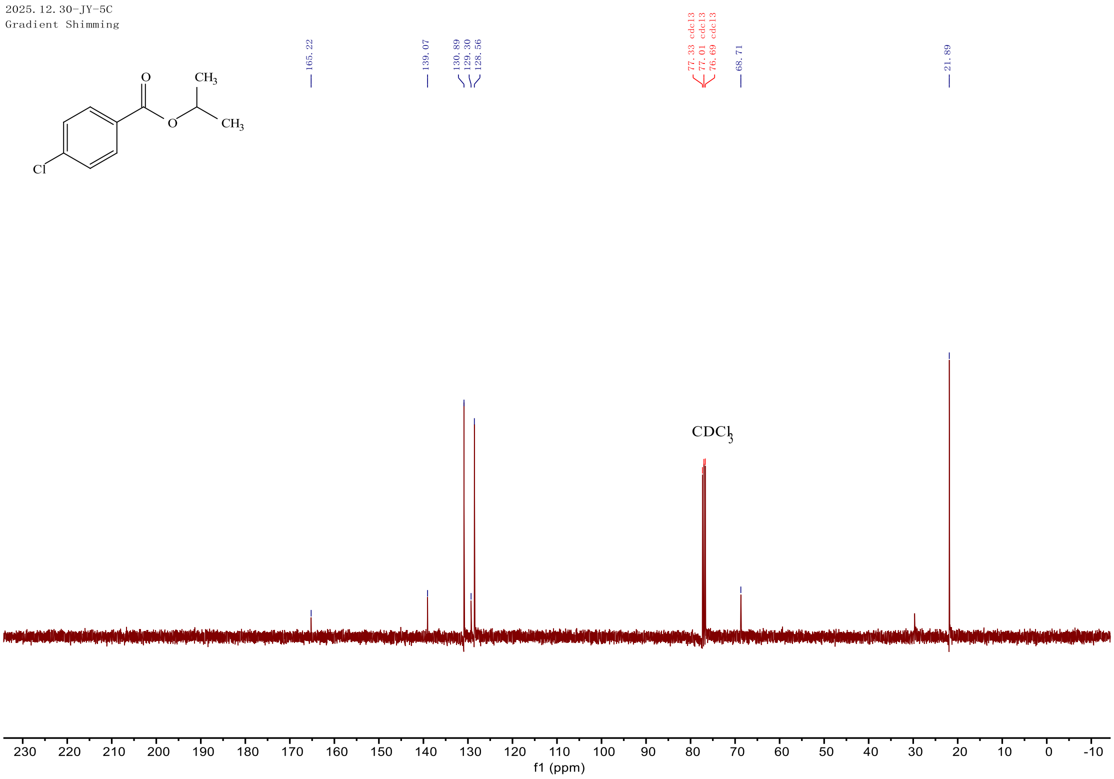
[13]C NMR Spectra of **2f** (101 MHz, $CDCl_3$)



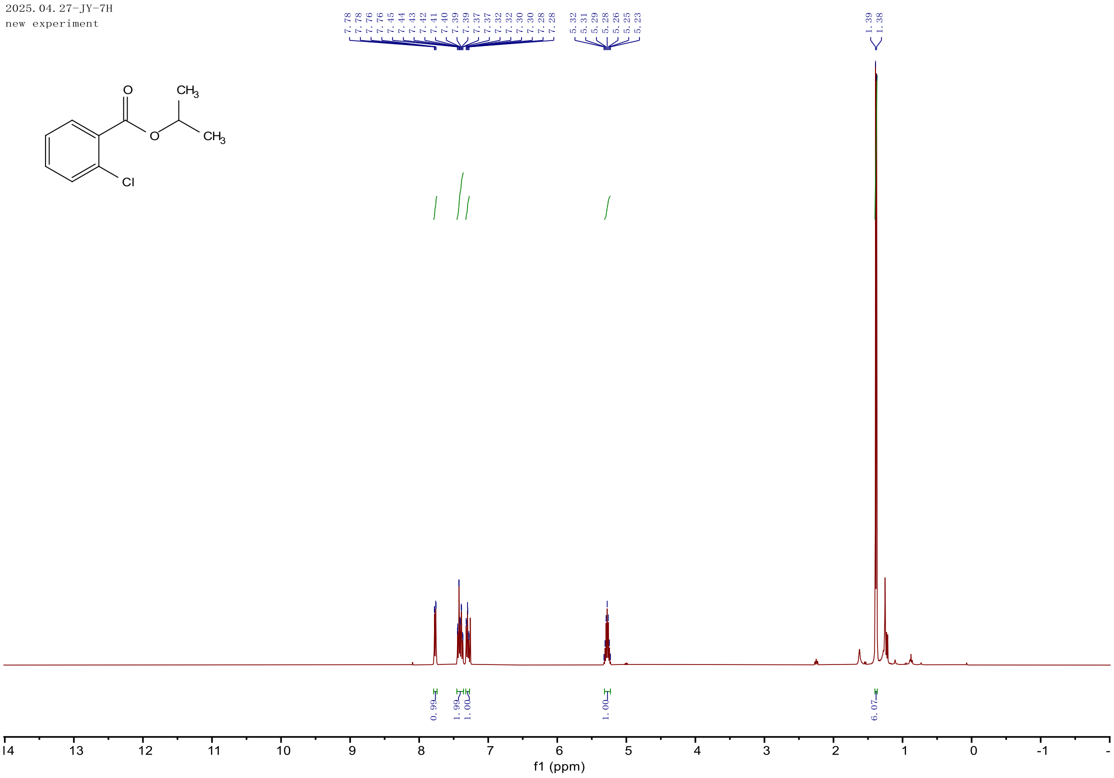
[1]H NMR Spectra of **2g** (400 MHz, $CDCl_3$)



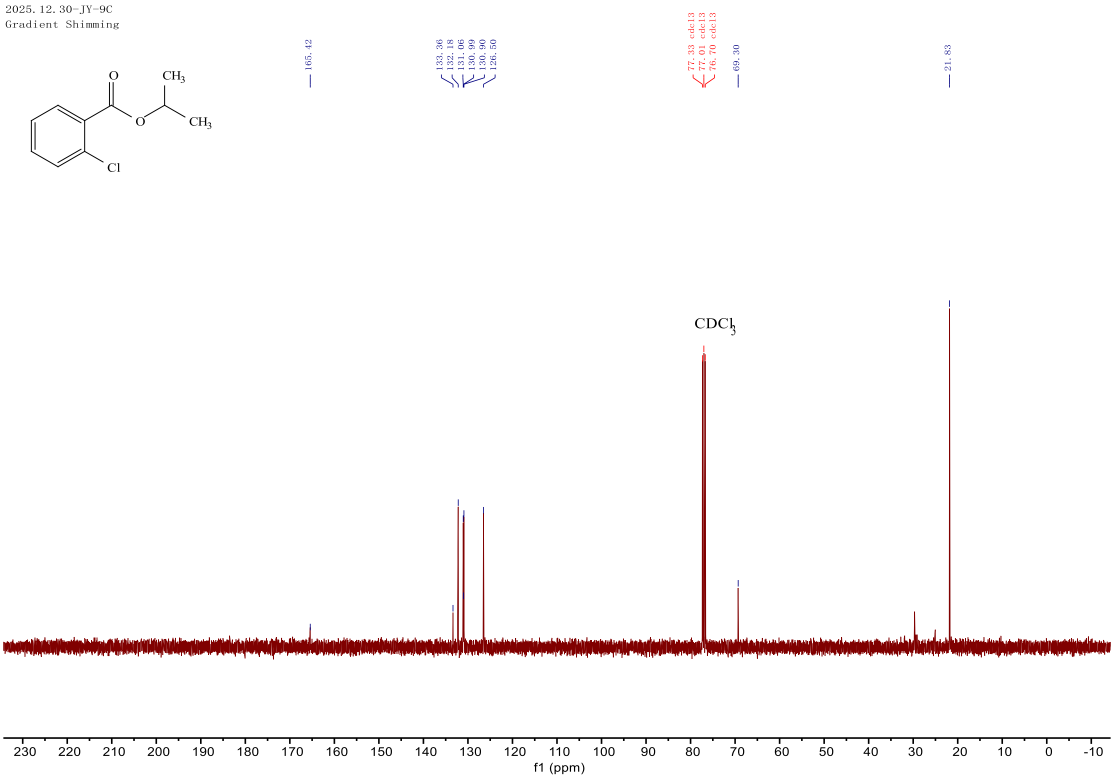
[13]C NMR Spectra of **2g** (101 MHz, $CDCl_3$)



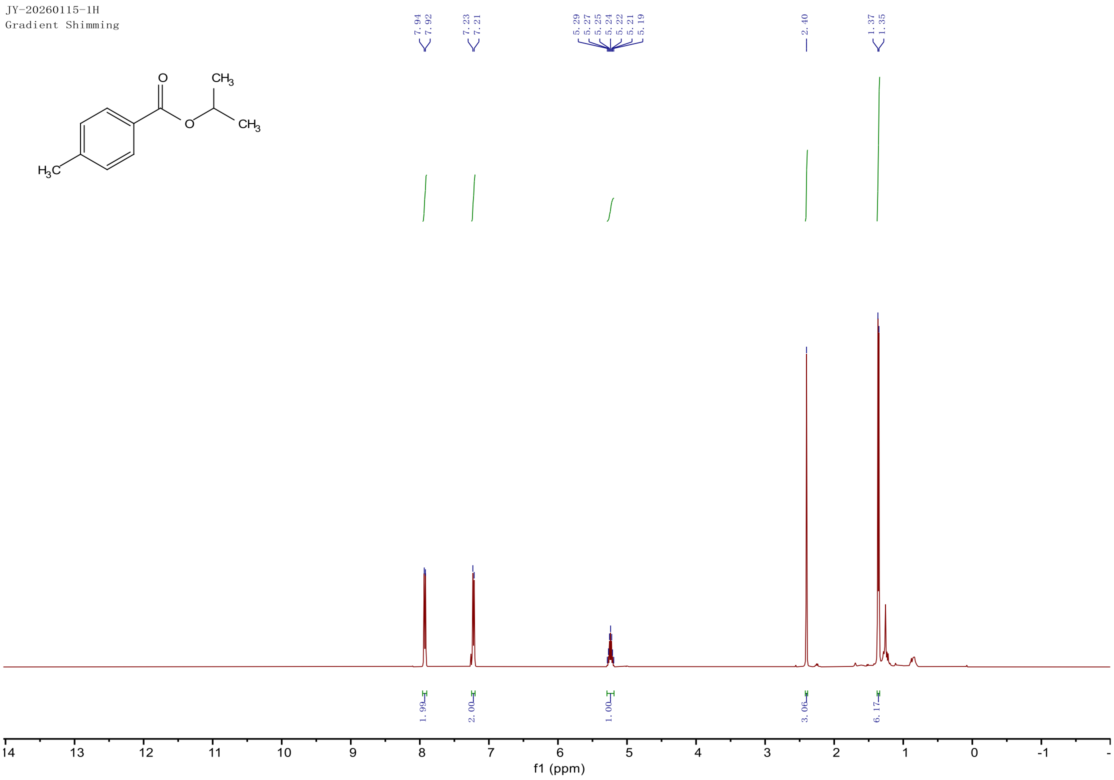
[1]H NMR Spectra of **2h** (400 MHz, $CDCl_3$)



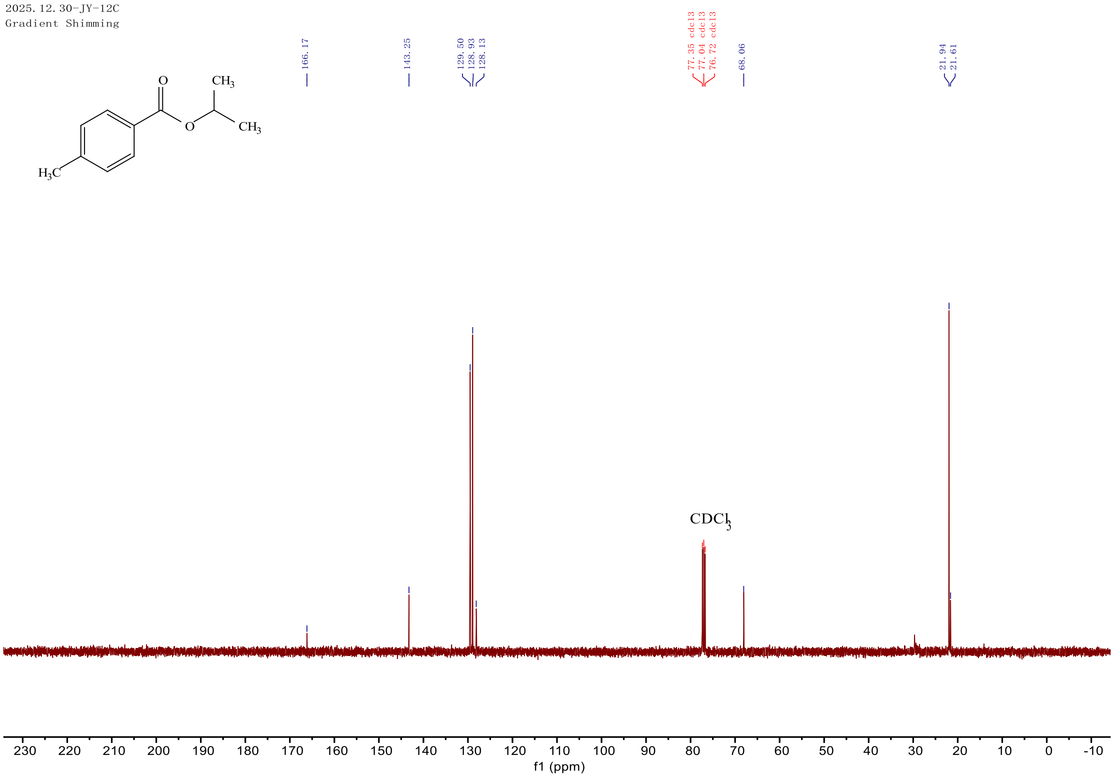
[13]C NMR Spectra of **2h** (101 MHz, $CDCl_3$)



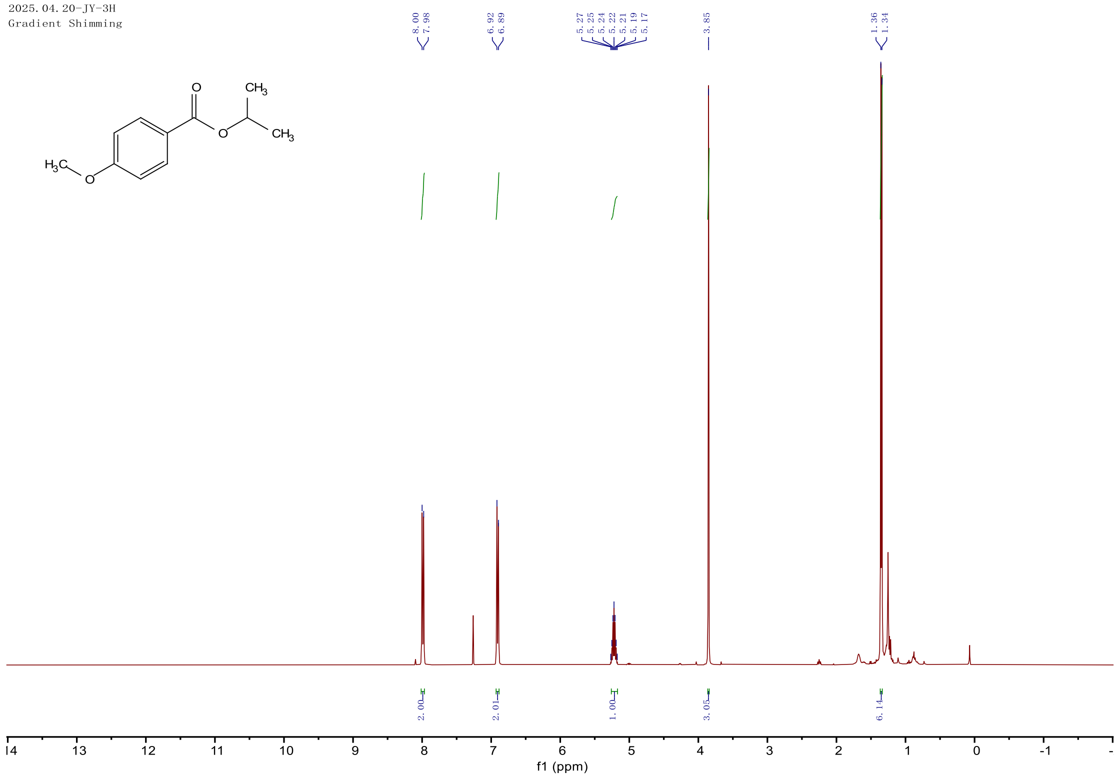
^{1}H NMR Spectra of **2i** (400 MHz, $CDCl_3$)



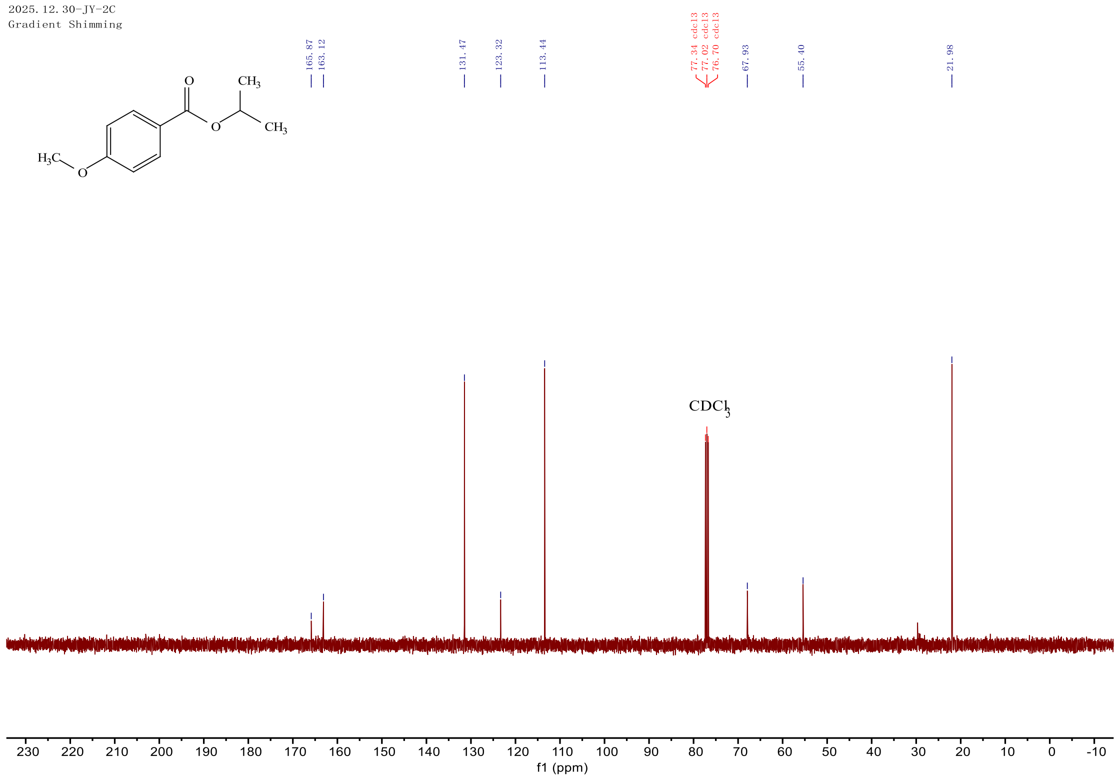
^{13}C NMR Spectra of **2i** (101 MHz, $CDCl_3$)



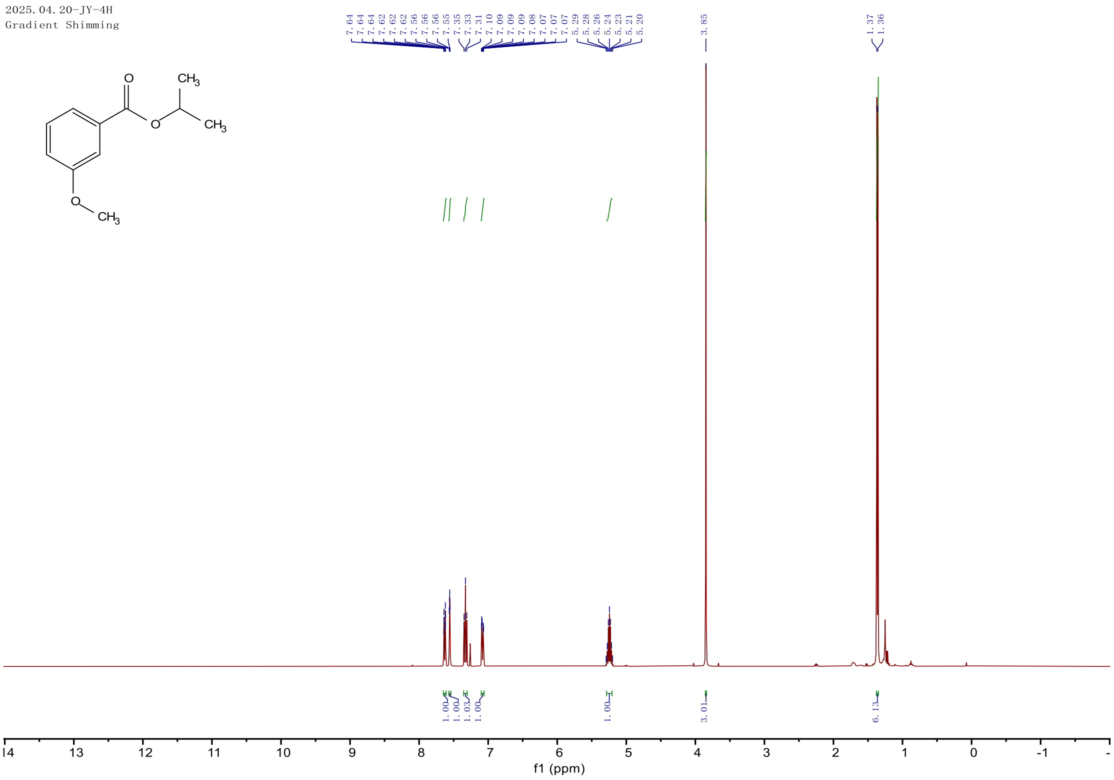
^{1}H NMR Spectra of **2j** (400 MHz, $CDCl_3$)



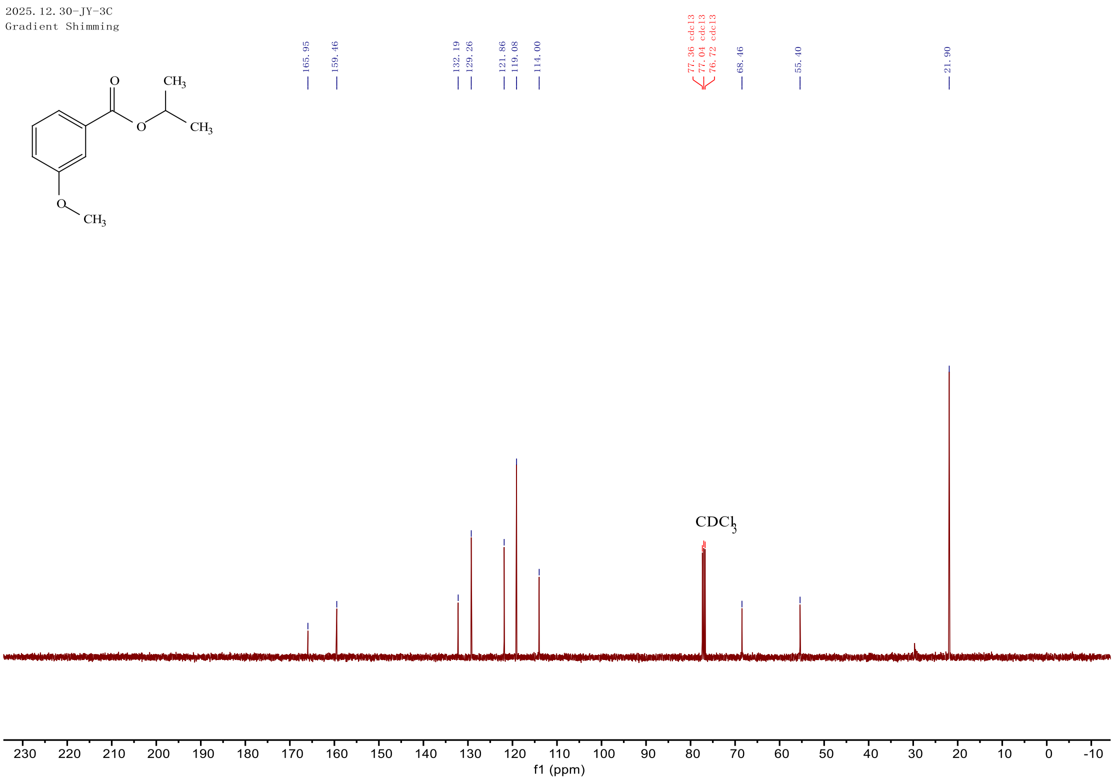
^{13}C NMR Spectra of **2j** (101 MHz, $CDCl_3$)



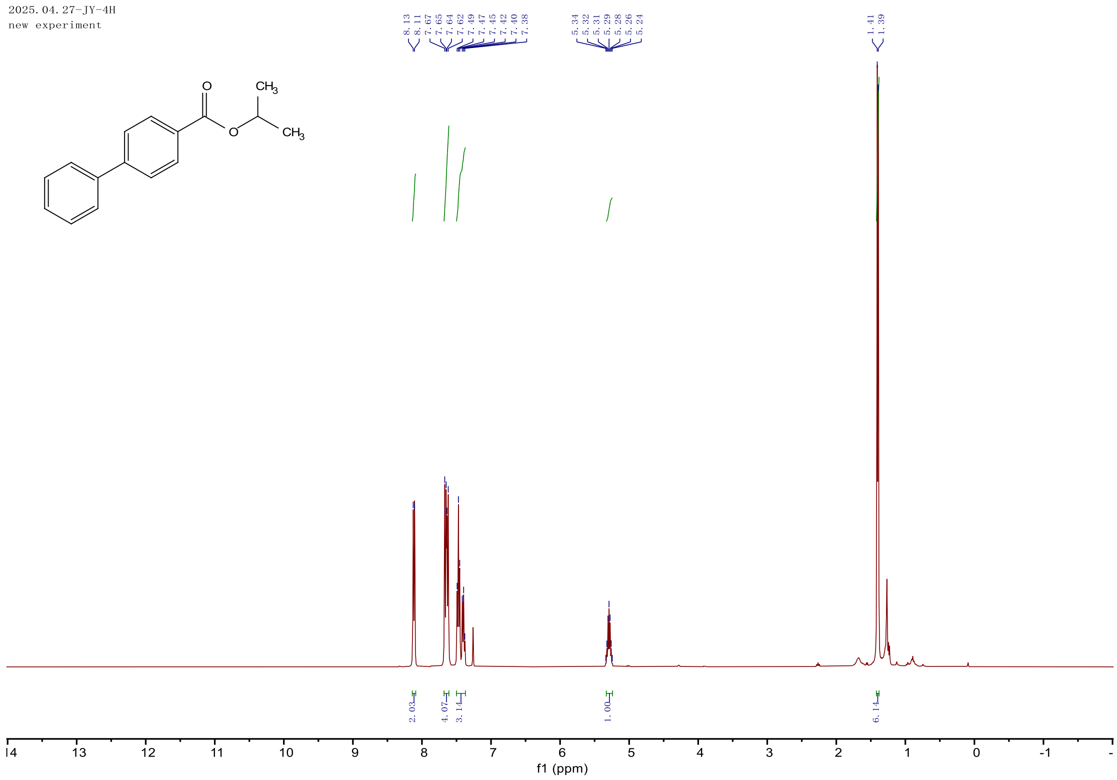
^{1}H NMR Spectra of **2k** (400 MHz, $CDCl_3$)



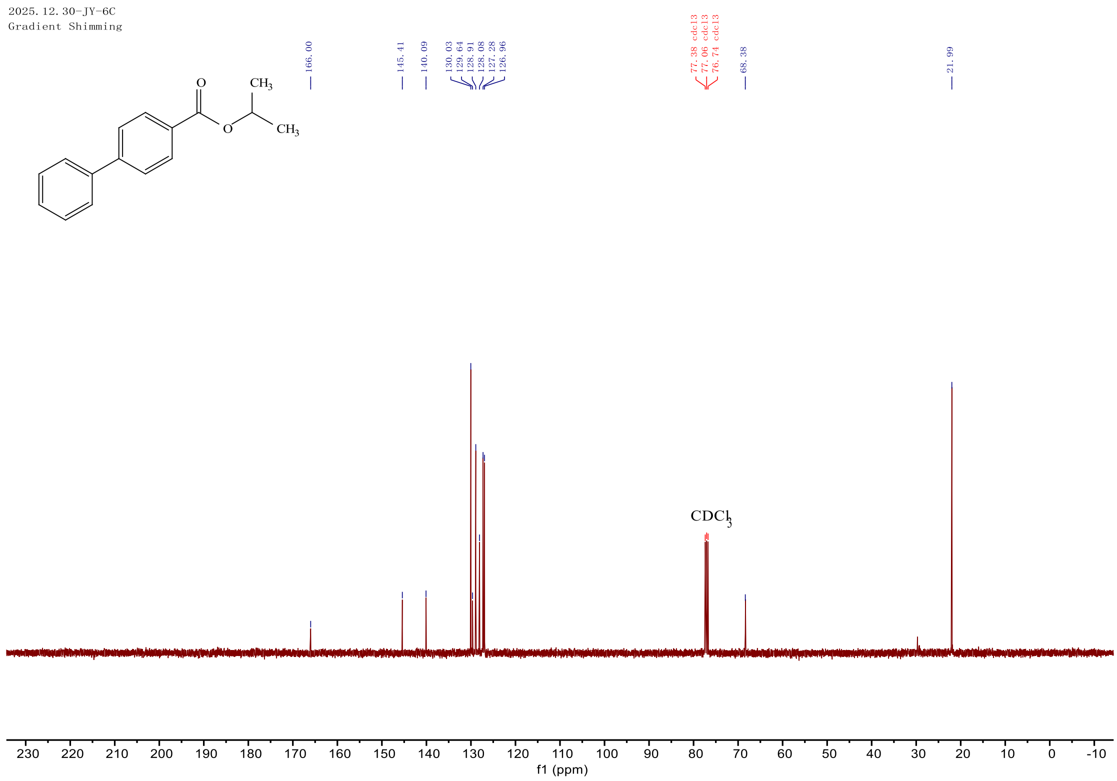
^{13}C NMR Spectra of **2k** (101 MHz, $CDCl_3$)



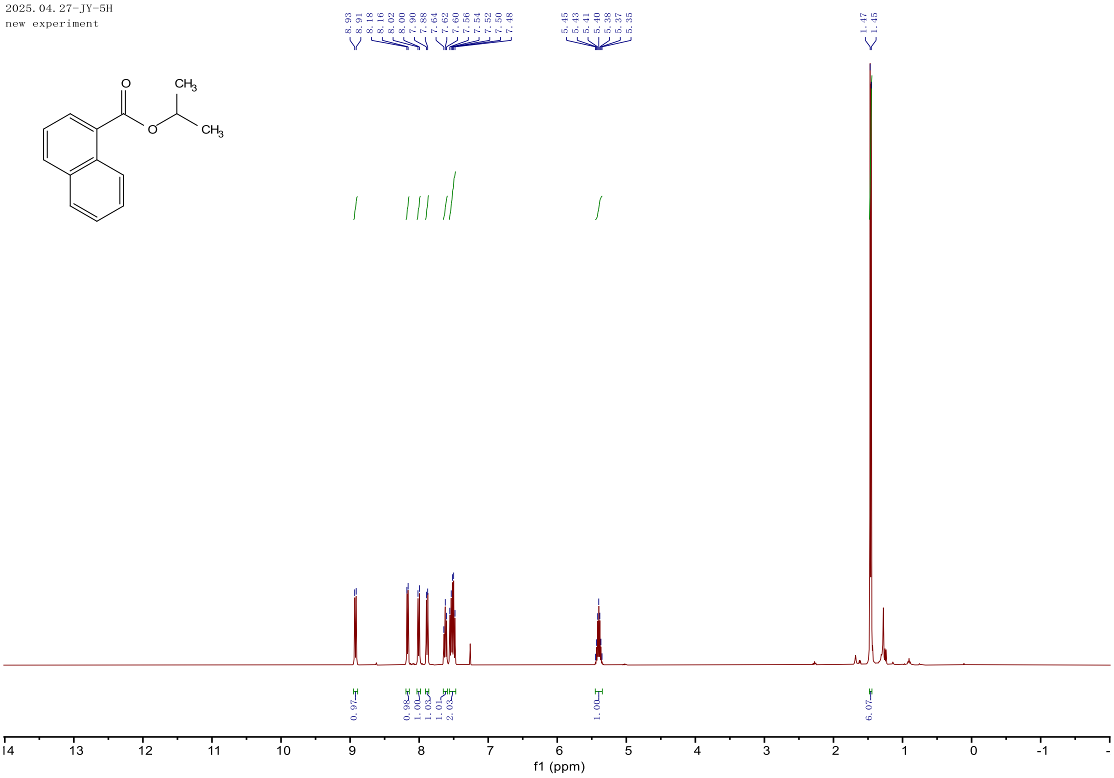
^{1}H NMR Spectra of **2l** (400 MHz, $CDCl_3$)



^{13}C NMR Spectra of **2l** (101 MHz, $CDCl_3$)



[1]H NMR Spectra of **2m** (400 MHz, $CDCl_3$)



[13]C NMR Spectra of **2m** (101 MHz, $CDCl_3$)