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β-Cyclodextrin-stabilized Cu nanoparticles catalyzed C–O coupling to access 2-aryloxypyridines

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Contents

General Experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. ^{1}H NMR were recorded in $CDCl_3$ at ambient temperature on a 300 MHz NMR spectrometer. Powder X-ray diffraction (PXRD) patterns of the as-synthesized and recycled samples were obtained using a Rigaku D/max 2500 PC X-ray diffractometer with Cu Kα (1.5406 Å) radiation at 10 min^{-1}. Field-emission Scanning Electron Microscopy (SEM) images of the samples were taken at 30 kV with a ZEISS Supra 55 microscope. Transmission electron microscope (TEM) images TEM images were collected on a JEOL-2100 transmission electron microscopy at 200 kV and the images were recorded digitally with a Gatan 794 charge-coupled device (CCD) camera.

Experimental Procedure

General procedure for the preparation of β-CD-CuNPs

The *β*-CD-CuNPs were prepared according to our previous reports.[S1,S2] Generally, to a 20 mL of 0.5 molar $CuSO_4$•$5H_2O$ solution were added *β*-CD (0.02 equiv.) and rongalite (5 equiv.). The mixture was stirred with magnetic vigorous agitation (700 rpm) at 80 ºC for 60 minutes. A blackish brown color was observed from initial blue color, and the precipitate was isolated by centrifugation. The precipitate was washed with distilled water and ethanol, and then was dried under vacuum for catalytic activity test.

*General procedure for the synthesis of **3a-m***

In an oven dried round bottom flask, phenol **1** (1.2 mmol), 2-bromopyridine **2** (1.0 mmol), Cs_2CO_3 (2 mmol) and *β*-CD-CuNPs (12.5 mg, 10 mol%) in DMF (2 mL) were placed. The mixture was stirred at 100 °C for 12 h. After reaction, the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1, *v*/*v*) as eluent.

*General procedure for the synthesis of **4***[S3]

In an oven dried round bottom flask, **3a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), $PhI(OAc)_2$ (1.5 equiv.) and MeCN (2 mL) were added. The reaction mixture was heated at 80 °C for 24 h. After being cooled to room temperature, the mixture was diluted with ethyl acetate, filtered through a plug of celite, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether to afford the desired product **4** in 72% yield (82 mg).

*General procedure for the synthesis of **5***[S4]

In an oven dried round bottom flask, compound **4** (0.3 mmol), MeOTf (0.6 mmol) and toluene (5 mL) were added. The reaction mixture was heated at 100 °C for 2 h. After being cooled to room temperature, the solution was evaporated under vacuum. Without purification, the crude product was added into a pre-prepared solution Na (7.2 mmol) in dry MeOH (5 mL), and stirred for 15 min under reflux conditions. After being cooled to room temperature, I_2 (0.15 mmol) was added, the reaction mixture was stirred at room temperature for another 3 h. After completion of the reaction, MeOH was removed under reduced pressure and the residue was extracted with EtOAc. The concentrated extract was subjected to column chromatography over silica gel to afford pyrocatechol in 85% yield (28 mg).

Characterization of the CuNPs

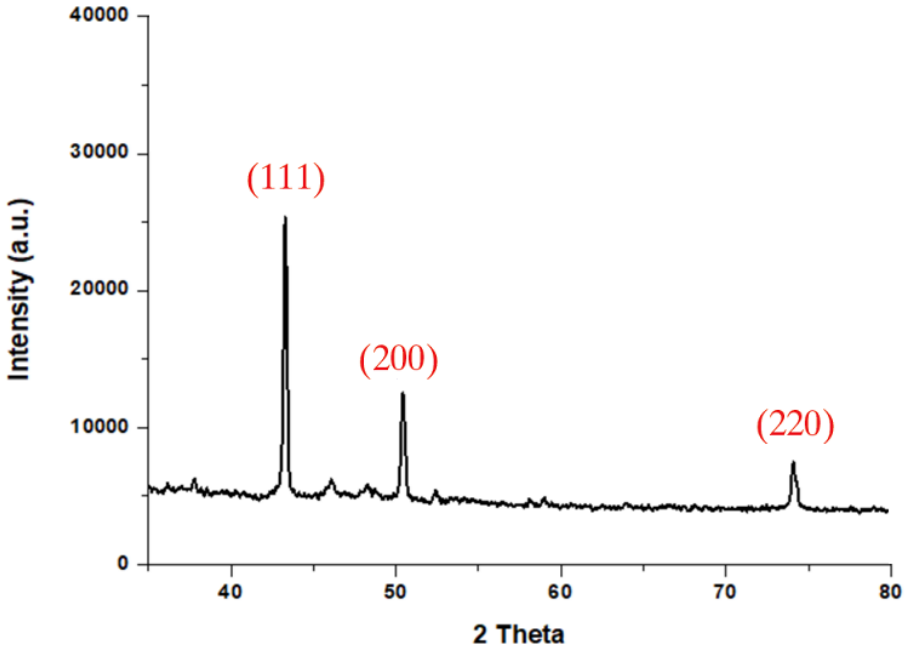


Figure S1. XRD pattern of synthesized CuNPs

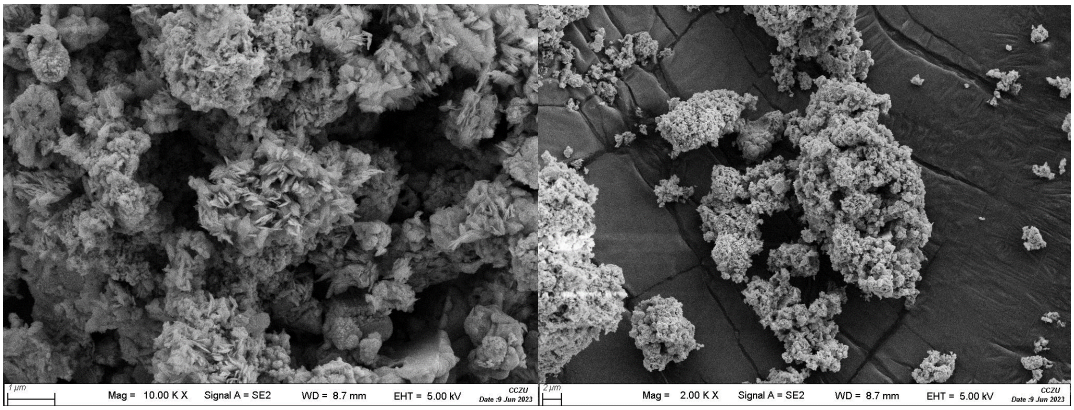


Figure S2. SEM image (left: fresh catalyst; right: recovered catalyst after five runs)

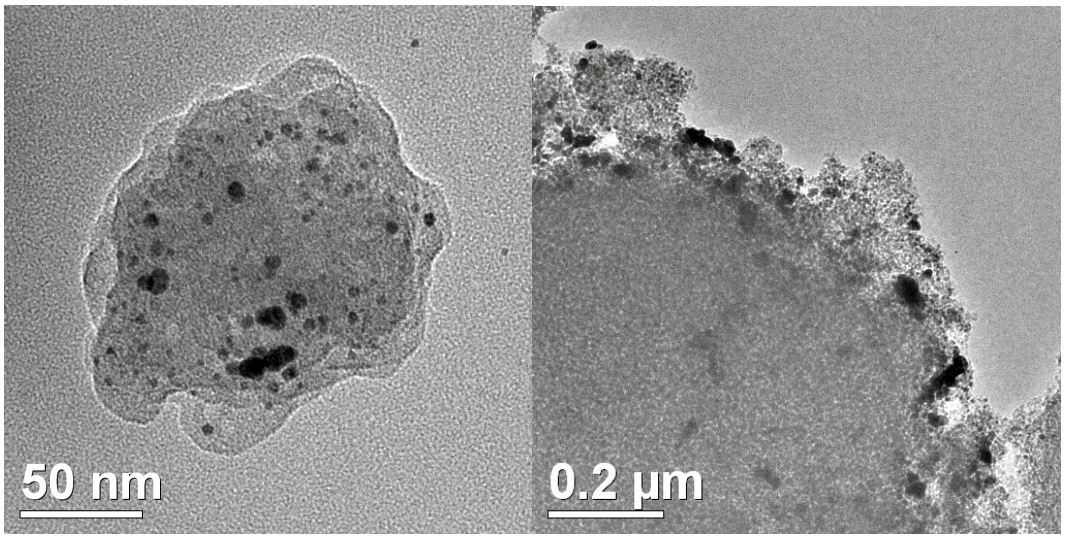
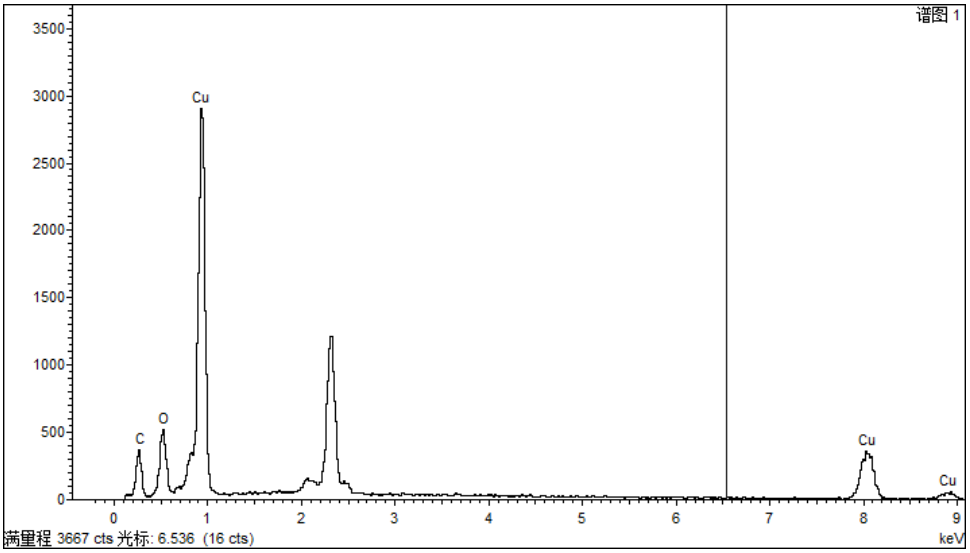
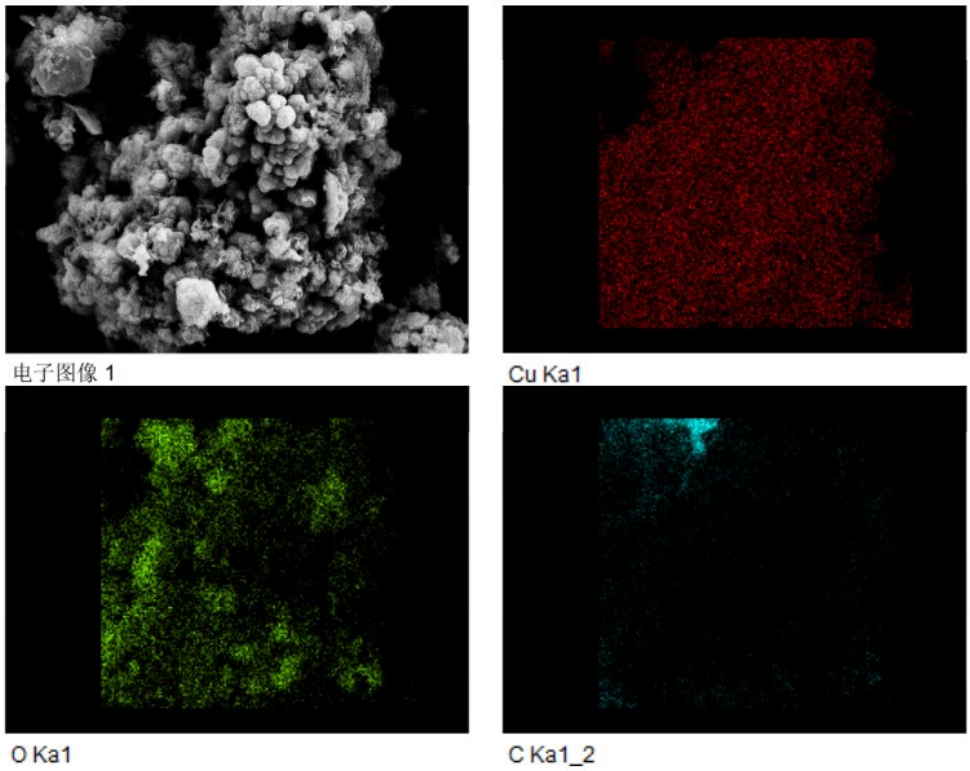


Figure S3. TEM image (left: fresh catalyst; right: recovered catalyst after five runs)

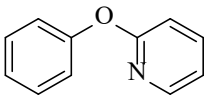




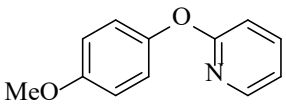
Element	C	O	Cu
Weight Percentage (%)	31.75	17.04	51.21
Atomic Percentage (%)	58.56	23.59	17.85

Figure S4. The EDS element analysis

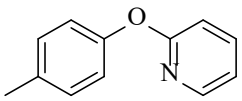
Characterization data



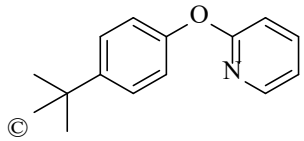
2-Phenoxypyridine **3a**.[S5] Colorless oil (154 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18-8.21 (m, 1H), 7.66 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.36-7.42 (m, 2H), 7.11-7.25 (m, 3H), 6.98 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.89 (dt, *J* = 8.3, 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 154.1, 147.7, 139.3, 129.6, 124.6, 121.1, 118.4, 111.4.



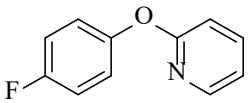
2-(4-Methoxyphenoxy)pyridine **3b**.[S6] Colorless oil (185 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 5.0, 2.0, 0.8 Hz, 1H), 7.61-7.70 (m, 1H), 7.04-7.11 (m, 2H), 6.90- 6.98 (m, 3H), 6.86 (dt, *J* = 8.3, 0.8 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 156.5, 147.8, 147.5, 139.5, 122.6, 118.2, 114.9, 111.1, 55.8.



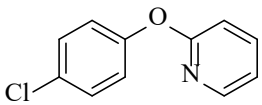
2-(*p*-Tolyloxy)pyridine **3c**.[S7] Colorless oil (166 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (ddd, *J* = 5.0, 2.0, 0.7 Hz, 1H), 7.66 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.01-7.08 (m, 2H), 6.97 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.89 (dt, *J* = 8.3, 0.8 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 151.6, 147.6, 139.2, 134.2, 130.1, 121.0, 118.1, 111.2, 20.8.



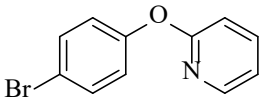
2-(4-(*tert*-Butyl)phenoxy)pyridine **3d**.[S8] White solid (195 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18-8.24 (m, 1H), 7.67 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.37- 7.45 (m, 2H), 7.03- 7.11 (m, 2H), 6.97 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.89 (dd, *J* = 8.3, 0.7 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 151.6, 147.7, 147.2, 139.3, 126.5, 120.4, 118.2, 111.4, 34.4, 31.4.



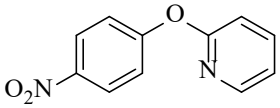
2-(4-Fluorophenoxy)pyridine **3e**.[S9] Yellow oil (138 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 5.0, 2.0, 0.7 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.2, 2.0 Hz, 1H), 7.06-7.14 (m, 4H), 6.99 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.91 (dt, *J* = 8.3, 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.7, 159.5 (d, *J* = 242.8 Hz), 149.7, 147.6, 139.5, 122.7 (d, *J* = 8.4 Hz), 118.5, 116.2 (d, *J* = 23.4 Hz), 111.4.



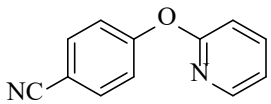
2-(4-Chlorophenoxy)pyridine **3f**.[S8] Yellow oil (168 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 5.0, 2.0, 0.7 Hz, 1H), 7.70 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.32-7.40 (m, 2H), 7.05-7.14 (m, 2H), 7.01 (ddd, *J* = 7.2, 5.0, 0.9 Hz, 1H), 6.93 (dt, *J* = 8.3, 0.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 152.5, 147.6, 139.5, 129.8, 129.6, 122.6, 118.7, 111.6.



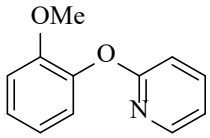
2-(4-Bromophenoxy)pyridine **3g**.[S6] Yellow oil (157 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 5.0, 1.9, 0.6 Hz, 1H), 7.70 (ddd, *J* = 8.3, 7.2, 2.0 Hz, 1H), 7.44-7.56 (m, 2H), 6.97-7.08 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 153.1, 147.6, 139.6, 132.6, 123.0, 118.7, 117.4, 111.7.



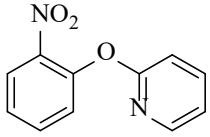
2-(4-Nitrophenoxy)pyridine **3h**.[S6] White solid (179 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 9.7, 2.5 Hz, 2H), 8.21-8.25 (m, 1H), 7.80 (ddd, *J* = 8.3, 7.4, 2.0 Hz, 1H), 7.23-7.30 (m, 2H), 7.13 (ddd, *J* = 7.2, 5.0, 0.7 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 159.5, 147.7, 143.8, 140.1, 125.5, 120.7, 120.0, 112.7.



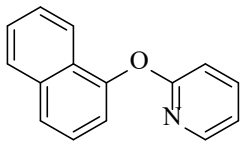
4-(Pyridin-2-yloxy)benzonitrile **3i**.[S6] White solid (157 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 9.7, 2.5 Hz, 2H), 8.21-8.25 (m, 1H), 7.80 (ddd, *J* = 8.3, 7.4, 2.0 Hz, 1H), 7.23-7.30 (m, 2H), 7.13 (ddd, *J* = 7.2, 5.0, 0.7 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 157.9, 147.7, 140.0, 133.9, 121.4, 119.8, 118.7, 112.6, 107.7.



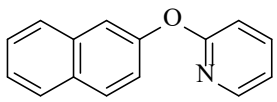
2-(2-Methoxyphenoxy)pyridine **3j**.[S10] White solid (145 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19-8.23 (m, 1H), 7.63-7.71 (m, 1H), 7.29 (t, *J* = 8.1 Hz, 1H), 6.99 (ddd, *J* = 7.1, 5.0, 0.8 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.67-6.79 (m, 3H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 160.7, 155.2, 147.7, 139.4, 130.0, 118.5, 113.2, 111.5, 110.3, 107.0, 55.2.



2-(2-Nitrophenoxy)pyridine **3k**.[S11] White solid (151 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 5.4, 4.2 Hz, 2H), 7.61-7.80 (m, 2H), 7.30-7.42 (m, 2H), 6.97-7.11 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 147.1, 146.8, 142.6, 139.8, 134.5, 125.7, 125.4, 125.3, 119.1, 111.6.



2-(Naphthalen-1-yloxy)pyridine **3l**.[S6] White solid (186 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14-8.20 (m, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.65 (ddd, *J* = 8.3, 7.3, 2.0 Hz, 1H), 7.39-7.52 (m, 3H), 7.20-7.26 (m, 1H), 6.89-7.01 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 149.9, 147.9, 139.5, 134.9, 127.9, 127.4, 126.4, 126.1, 125.7, 125.0, 122.0, 118.4, 117.1, 110.9.



2-(Naphthalen-2-yloxy)pyridine **3m**.[S6] Yellow solid (192 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 4.9, 1.5 Hz, 1H), 7.88 (dd, *J* = 12.7, 8.4 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.70 (td, *J* = 8.4, 2.0 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.43-7.52 (m, 2H), 7.33 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.94-7.05 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 151.8, 147.8, 139.4, 134.2, 130.9, 129.6, 127.7, 127.4, 126.4, 125.1, 121.3, 118.5, 117.4, 111.6.

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Copies of ^{1}H and ^{13}C NMR spectrum

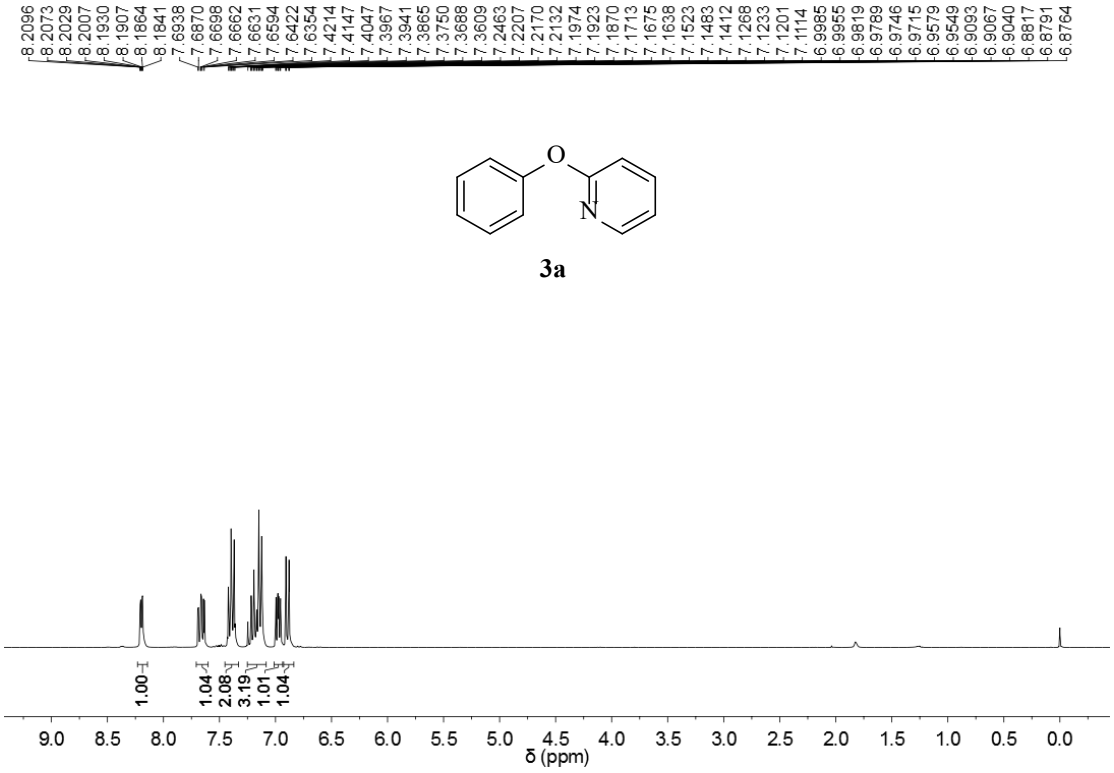


Figure S5.The ^{1}H NMR for compound **3a**

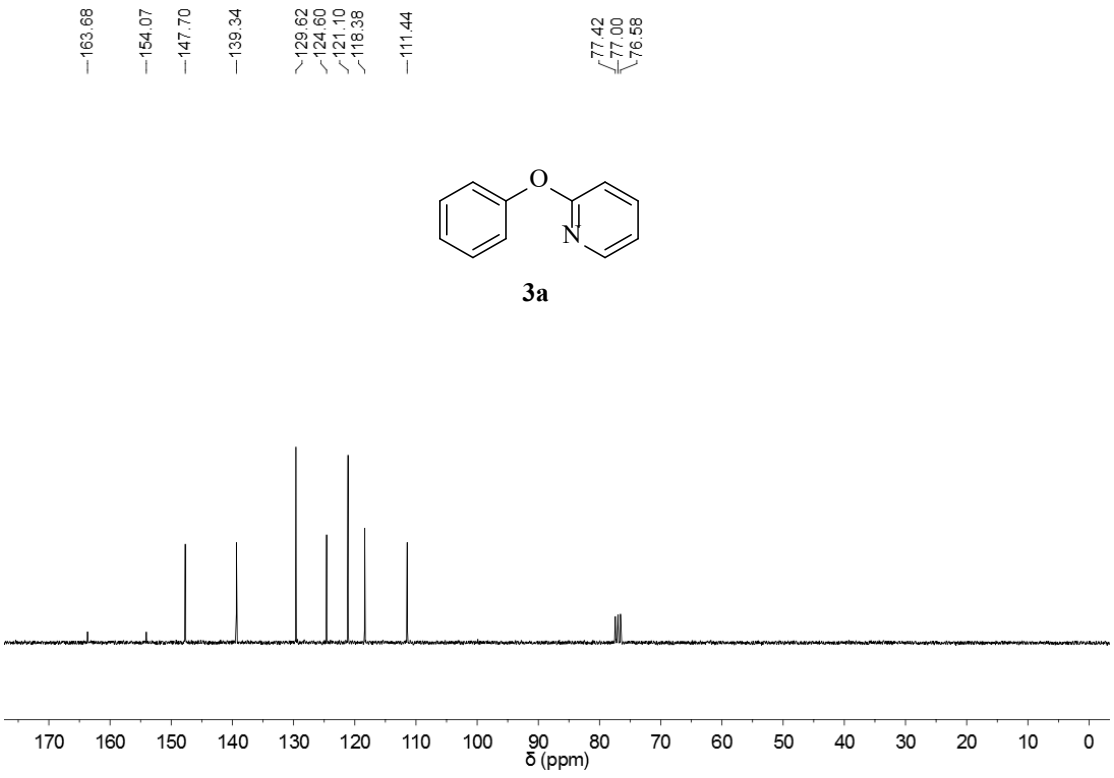
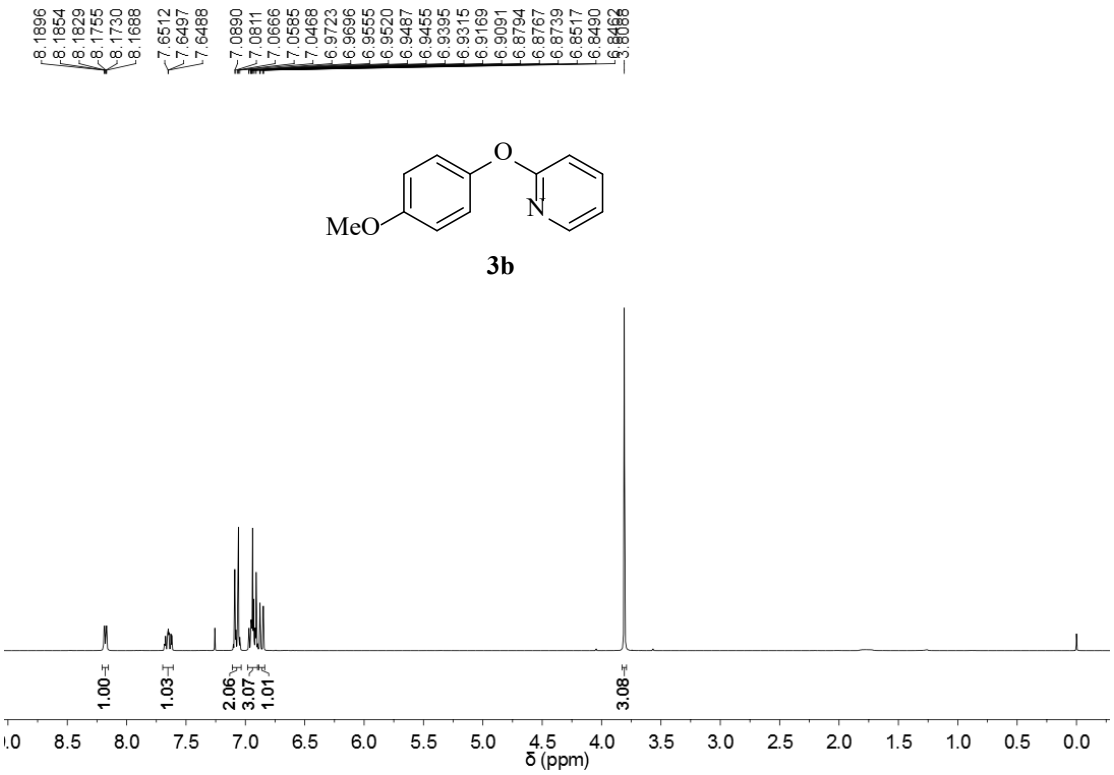
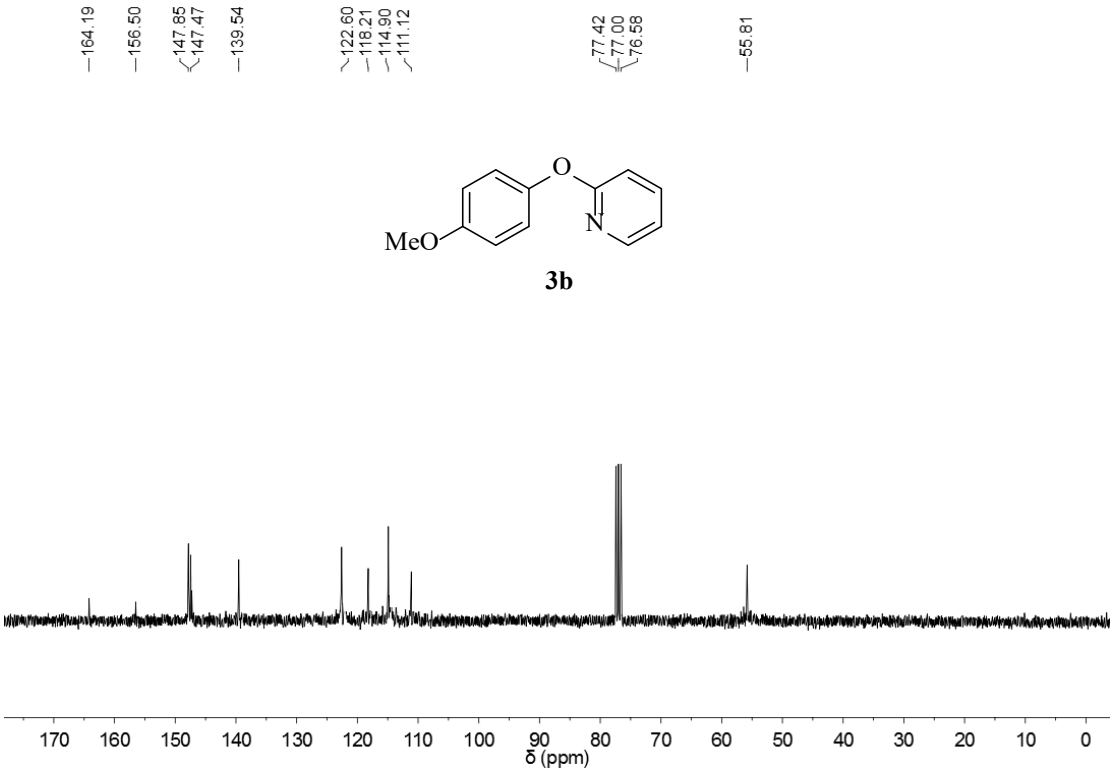


Figure S6. The ^{13}C NMR for compound **3a**



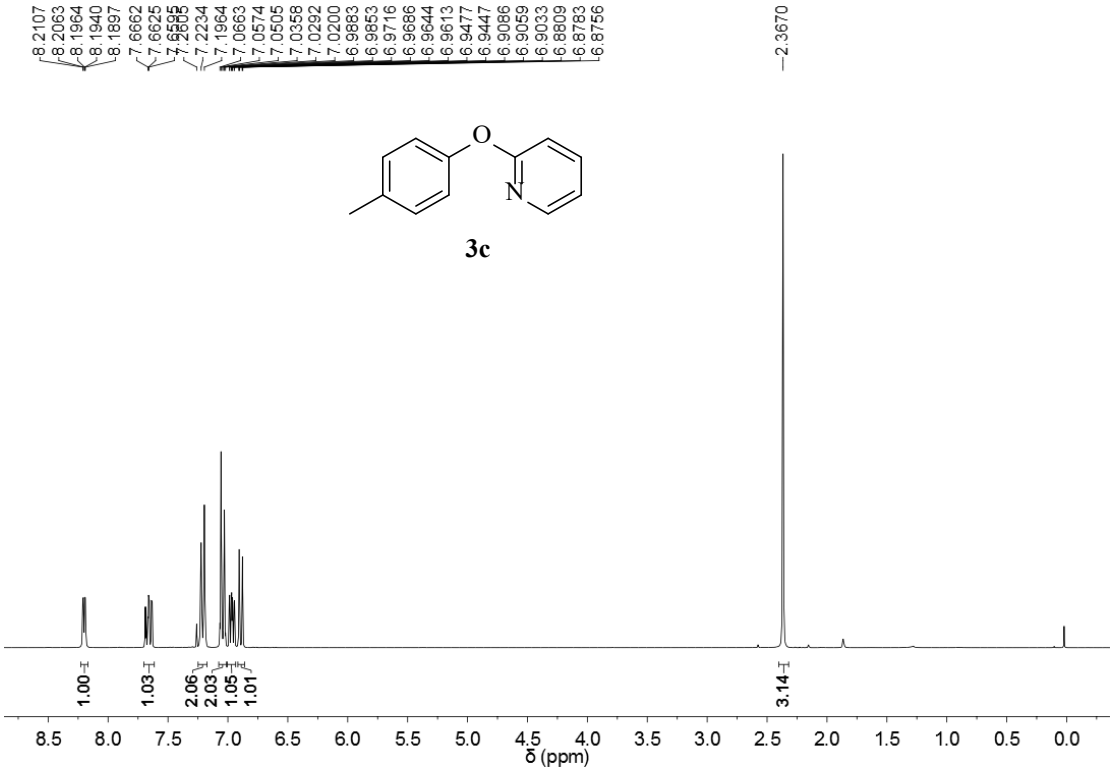
3b

Figure S7.The ^{1}H NMR for compound **3b**



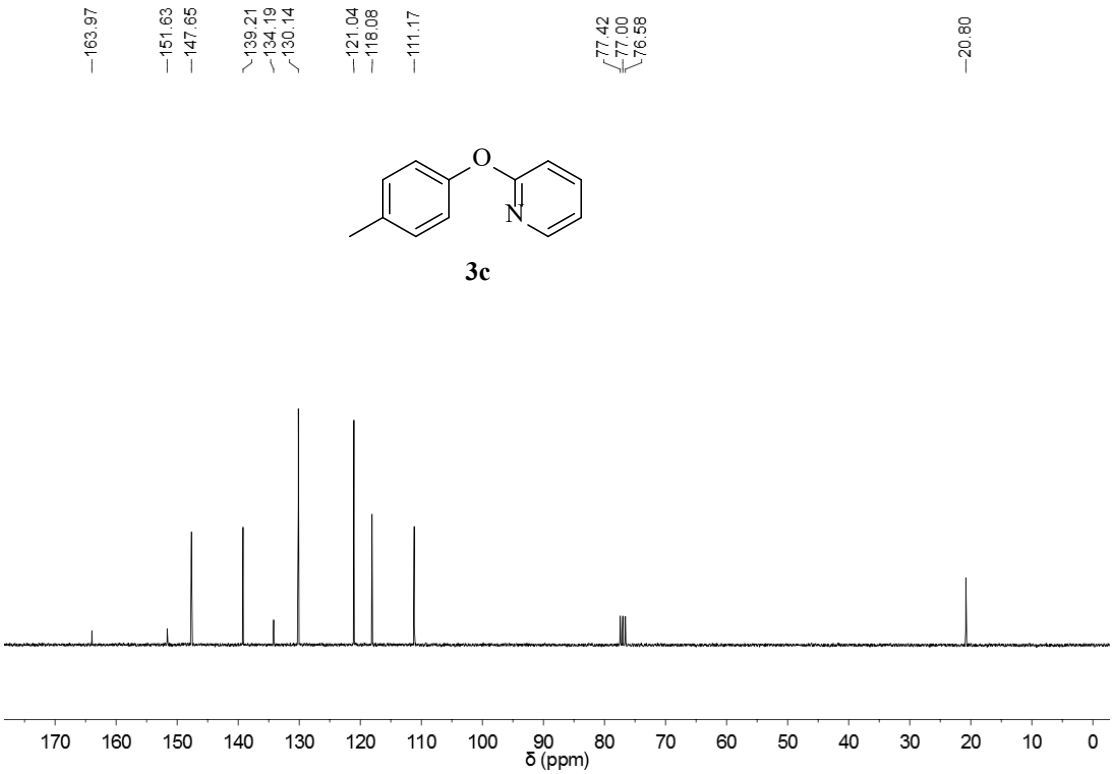
3b

Figure S8. The ^{13}C NMR for compound **3b**



3c

Figure S9.The ^{1}H NMR for compound **3c**



3c

Figure S10. The ^{13}C NMR for compound **3c**

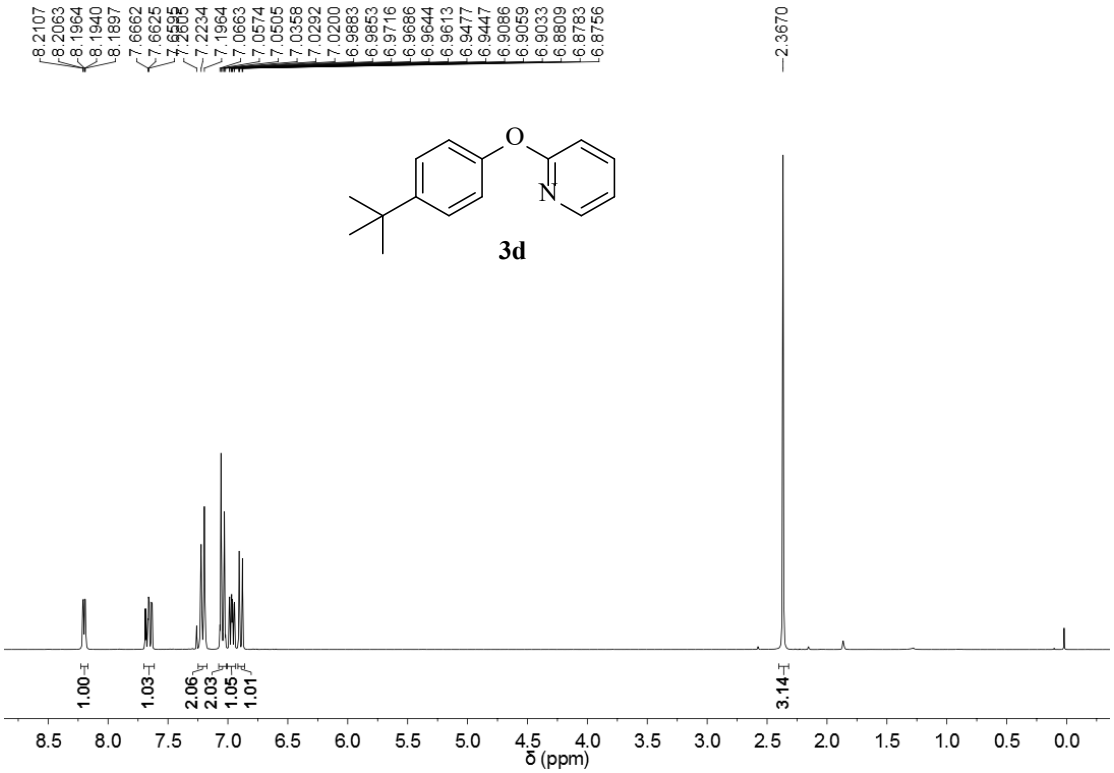


Figure S11.The ^{1}H NMR for compound **3d**

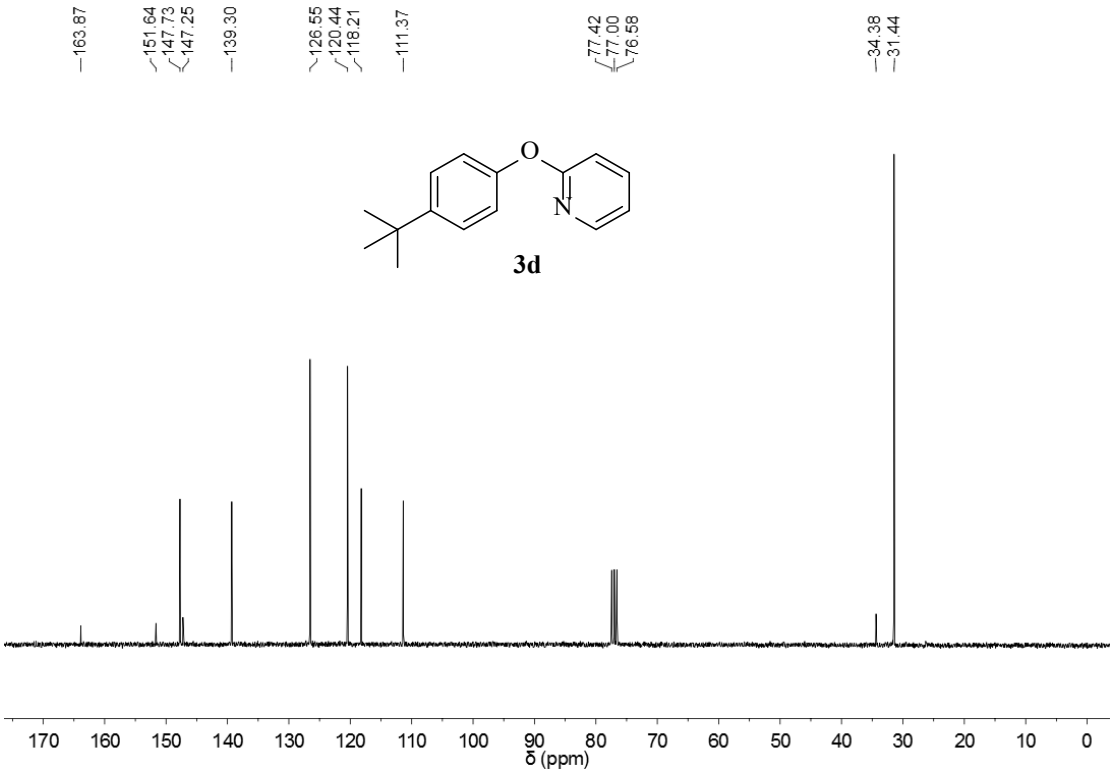


Figure S12. The ^{13}C NMR for compound **3d**

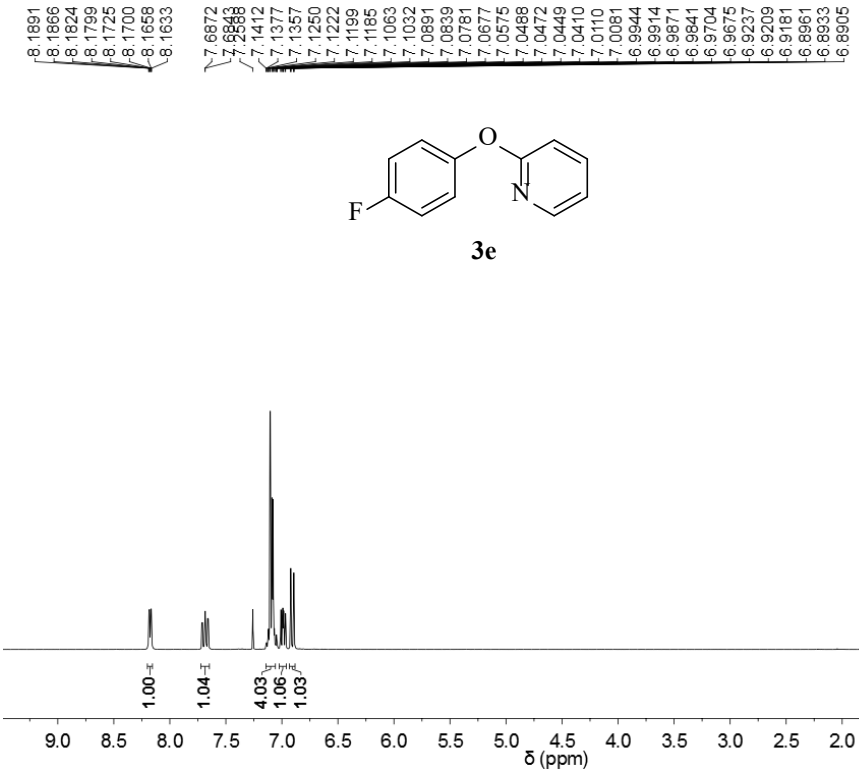


Figure S13.The ^{1}H NMR for compound **3e**

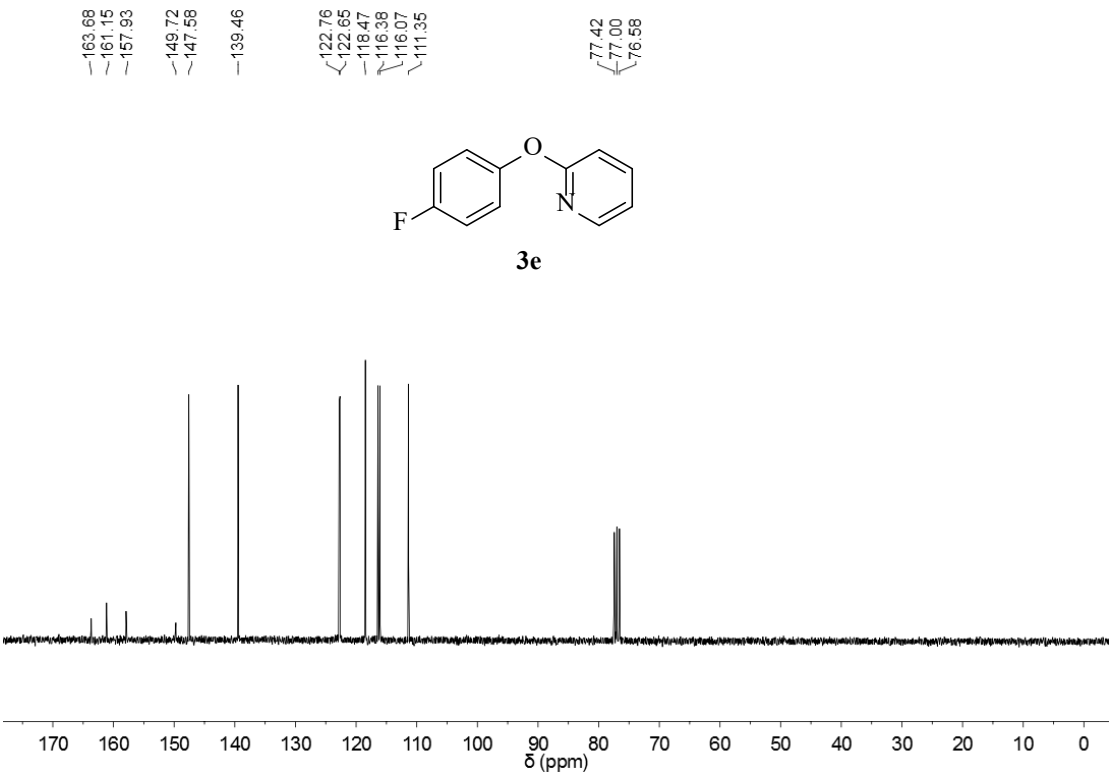
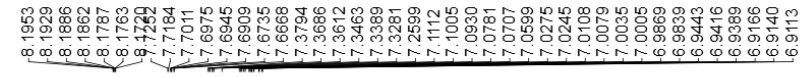
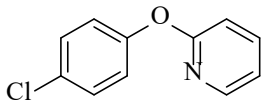


Figure S14. The ^{13}C NMR for compound **3e**





3f

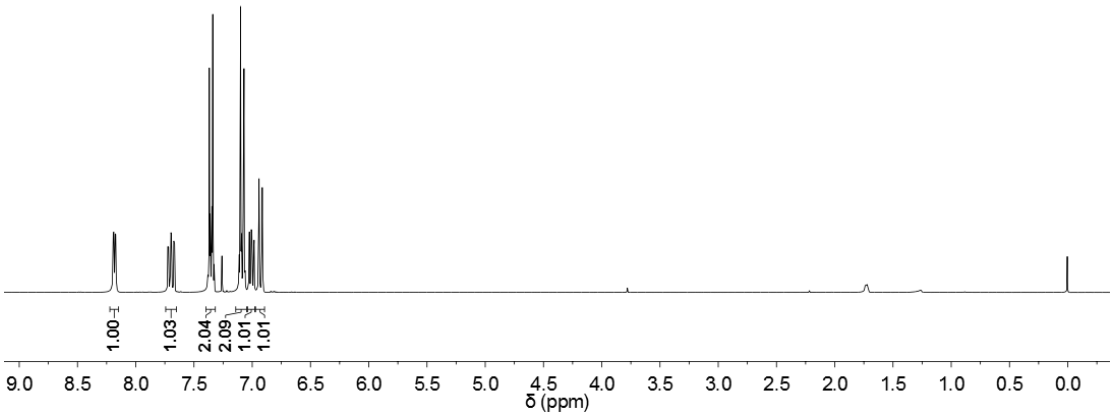
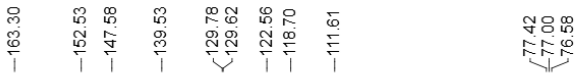
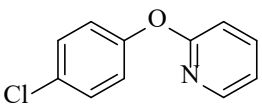


Figure S15.The ^{1}H NMR for compound **3f**





3f

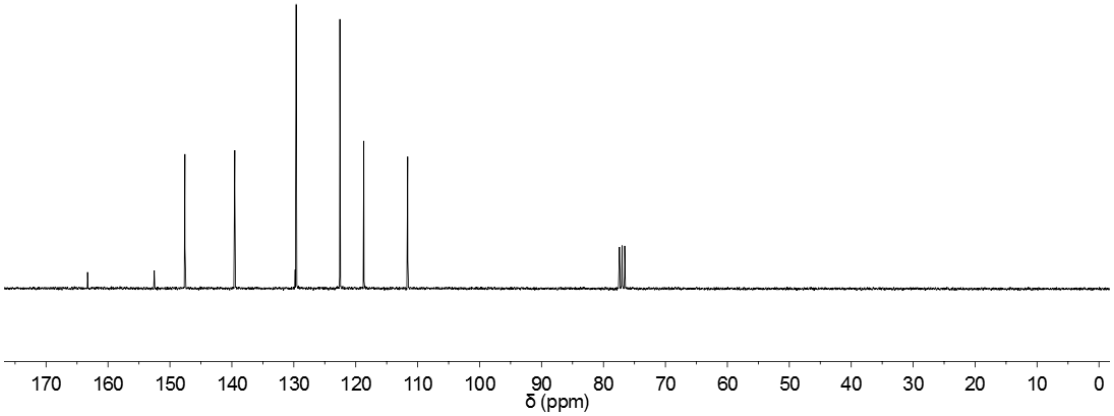
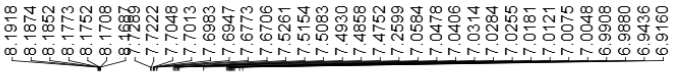
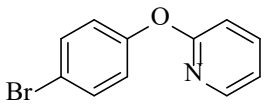


Figure S16. The ^{13}C NMR for compound **3f**





3g

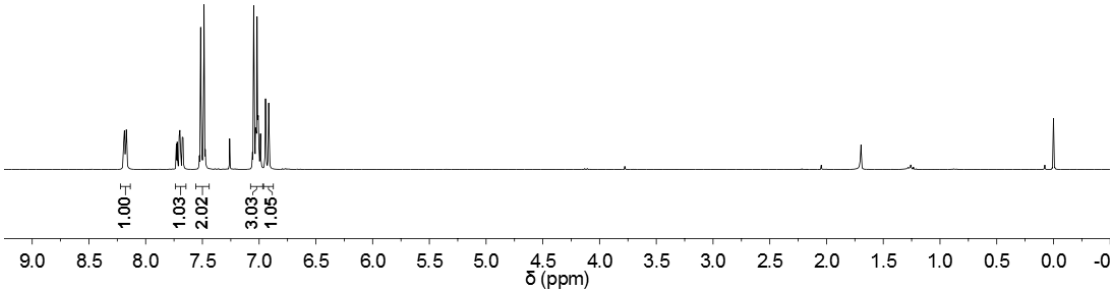
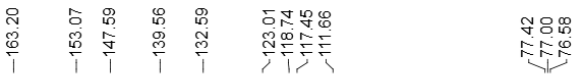
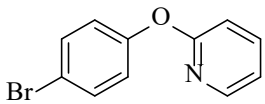


Figure S17.The ^{1}H NMR for compound **3g**





3g

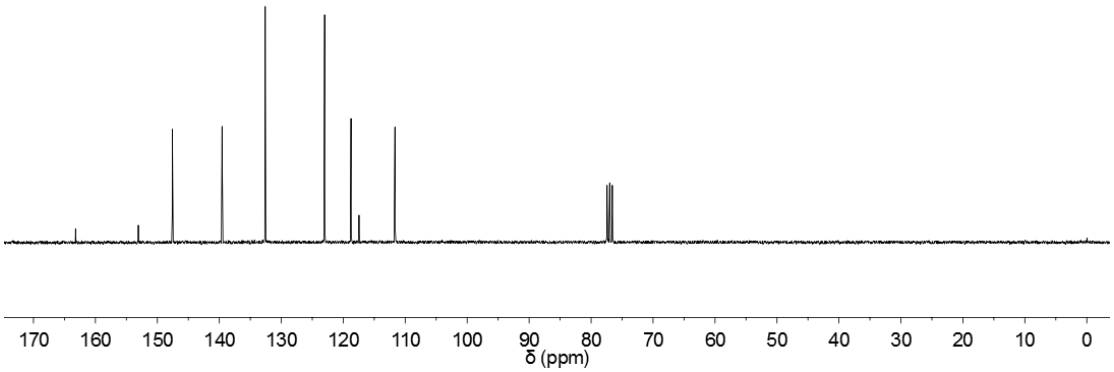
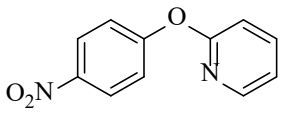


Figure S18. The ^{13}C NMR for compound **3g**



3h

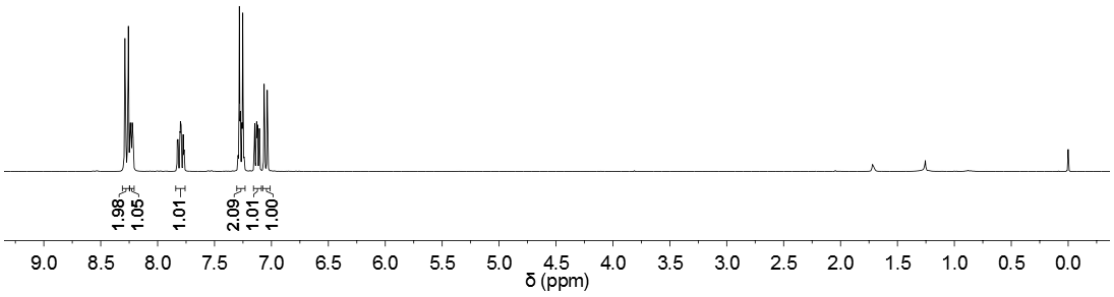
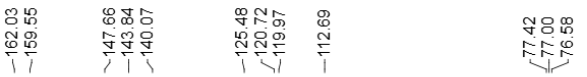
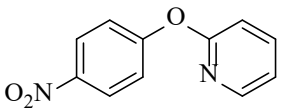


Figure S19.The ^{1}H NMR for compound **3h**





3h

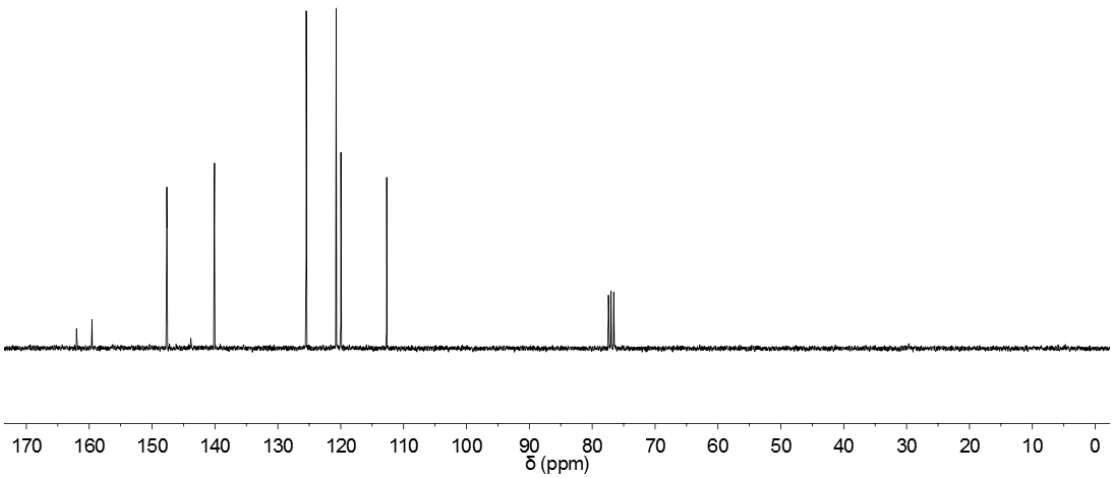
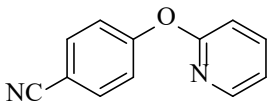


Figure S20. The ^{13}C NMR for compound **3h**



3i

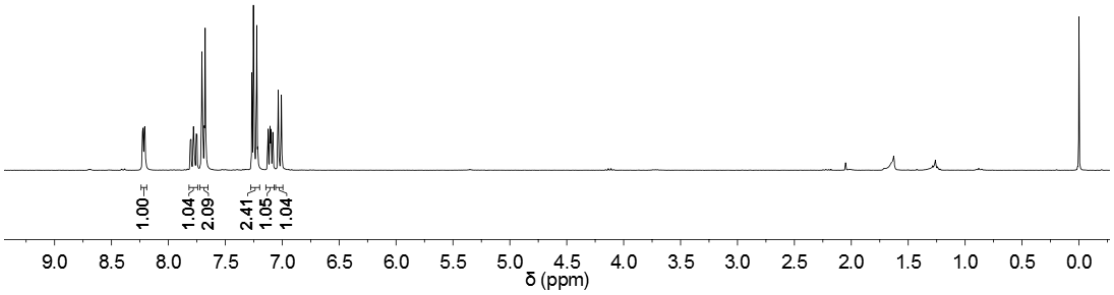
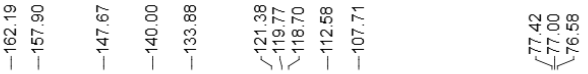
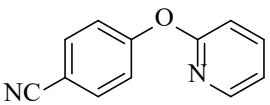


Figure S21.The ^{1}H NMR for compound **3i**





3i

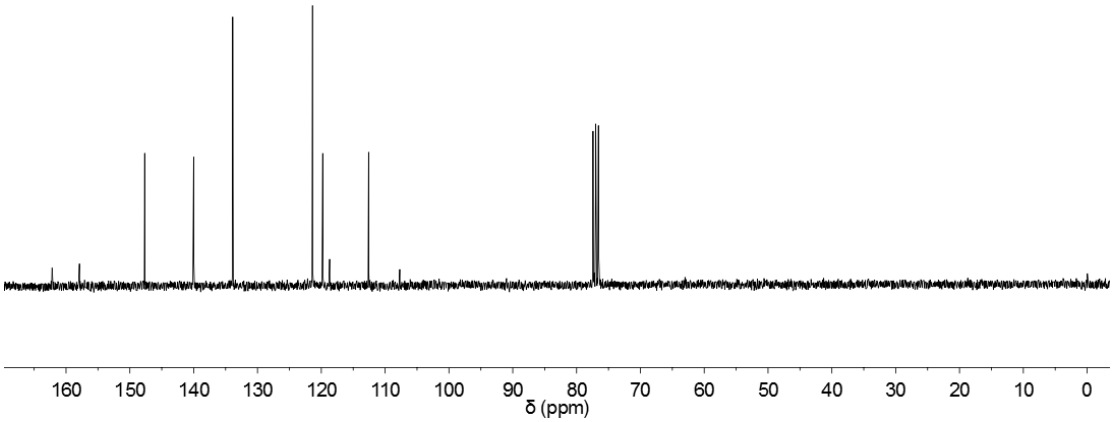


Figure S22. The ^{13}C NMR for compound **3i**

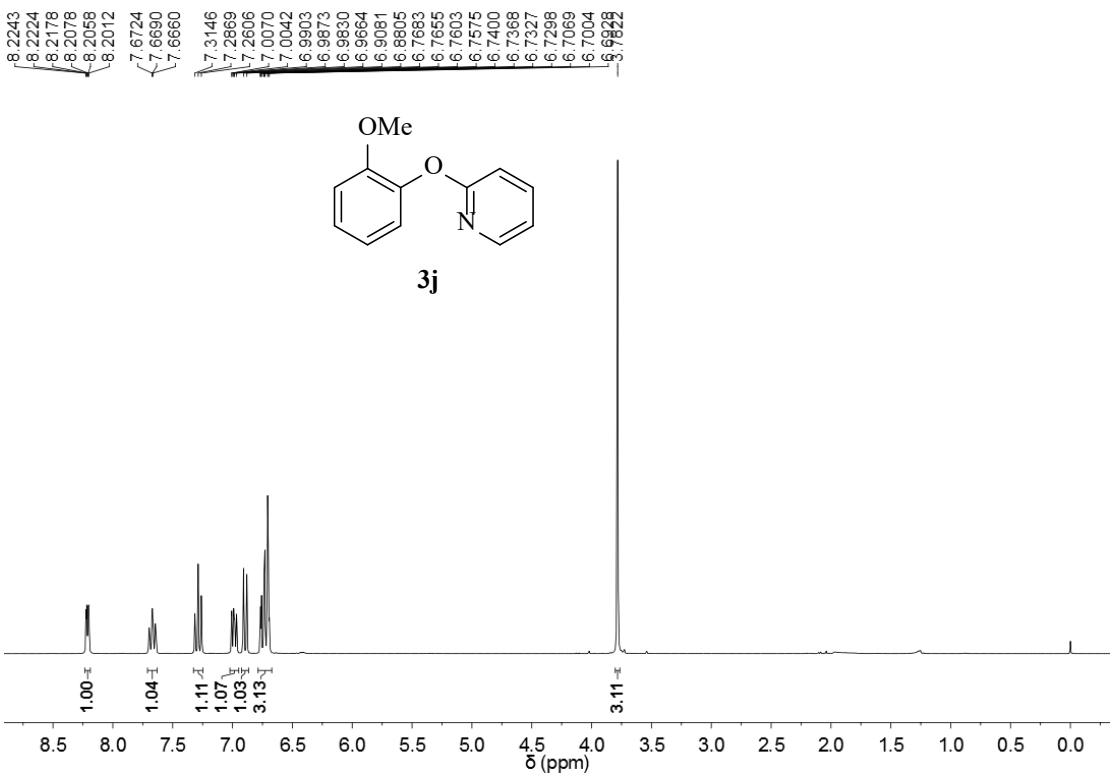


Figure S23.The ^{1}H NMR for compound **3j**

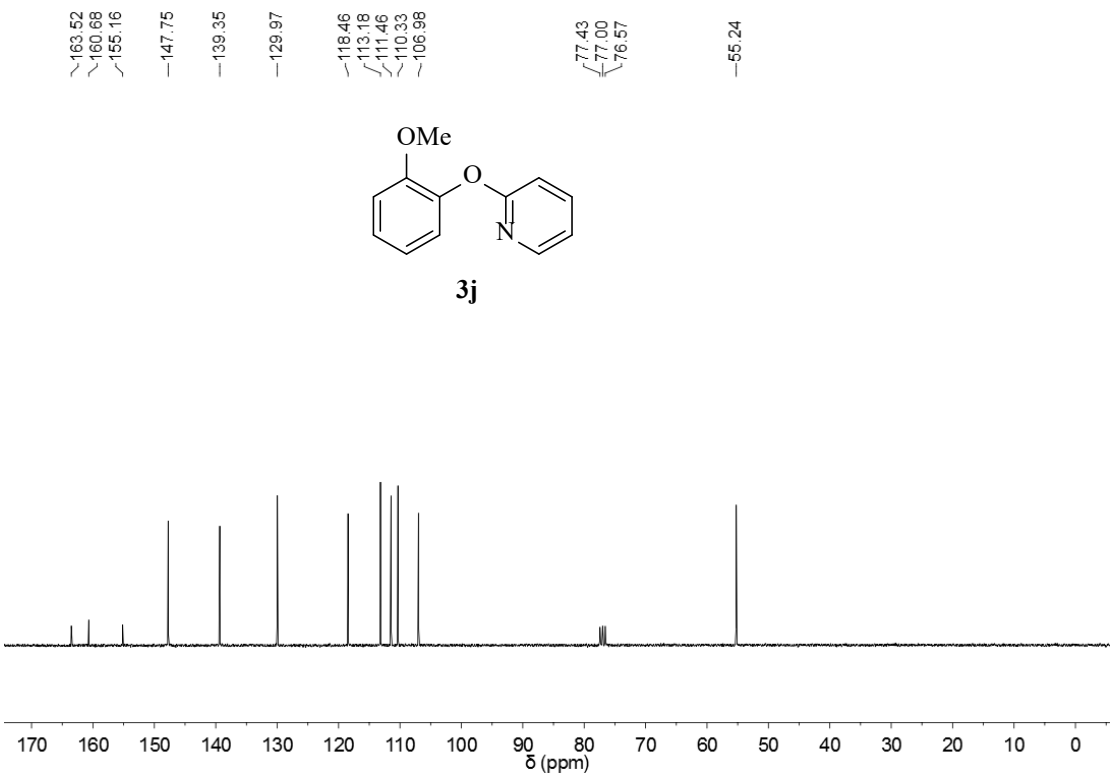
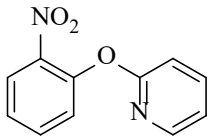


Figure S24. The ^{13}C NMR for compound **3j**



3k

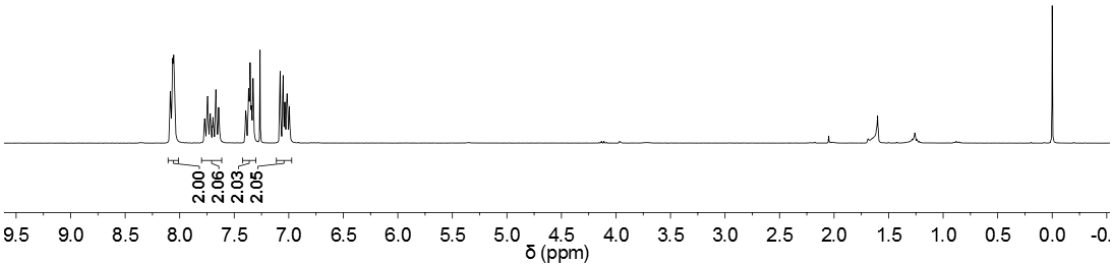
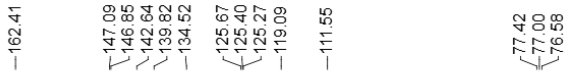
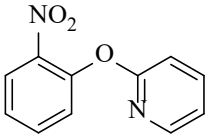


Figure S25.The ^{1}H NMR for compound **3k**





3k

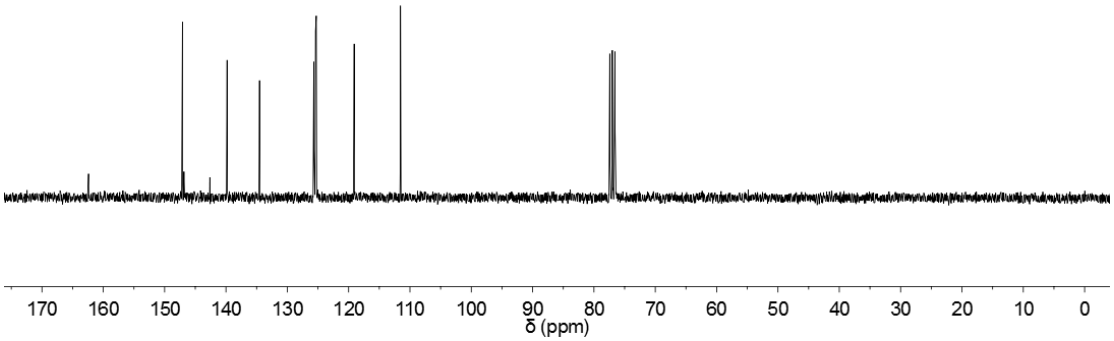


Figure S26. The ^{13}C NMR for compound **3k**

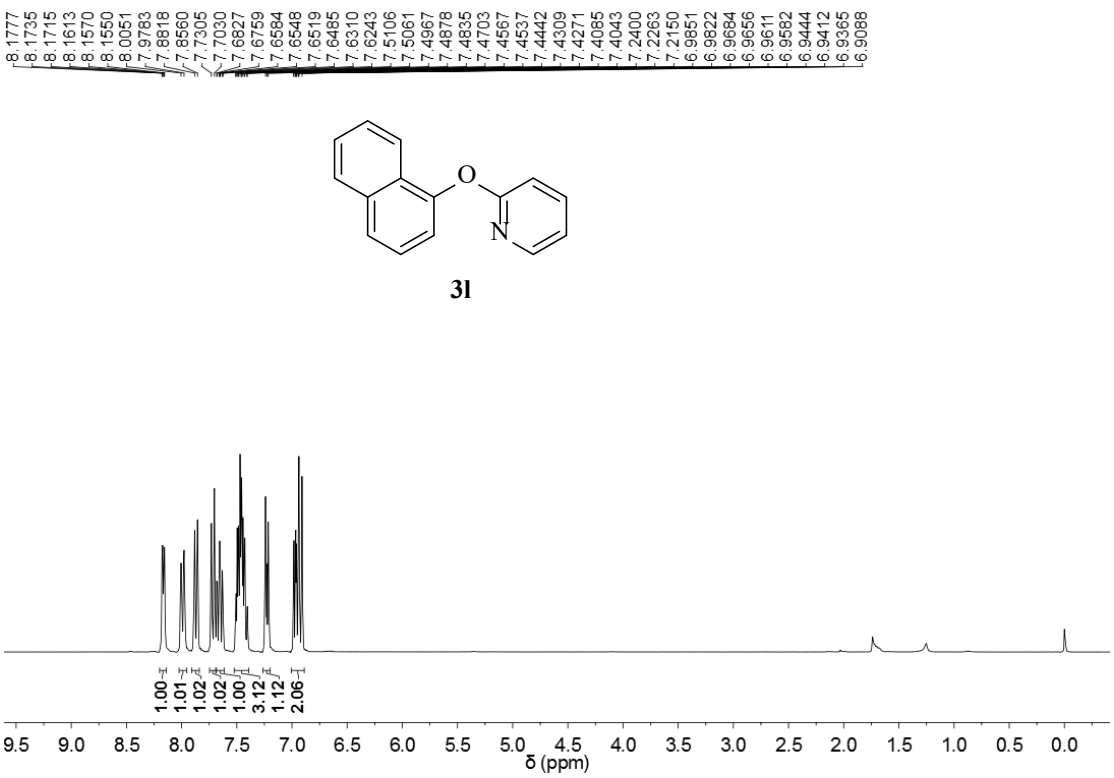


Figure S27.The ^{1}H NMR for compound **3l**

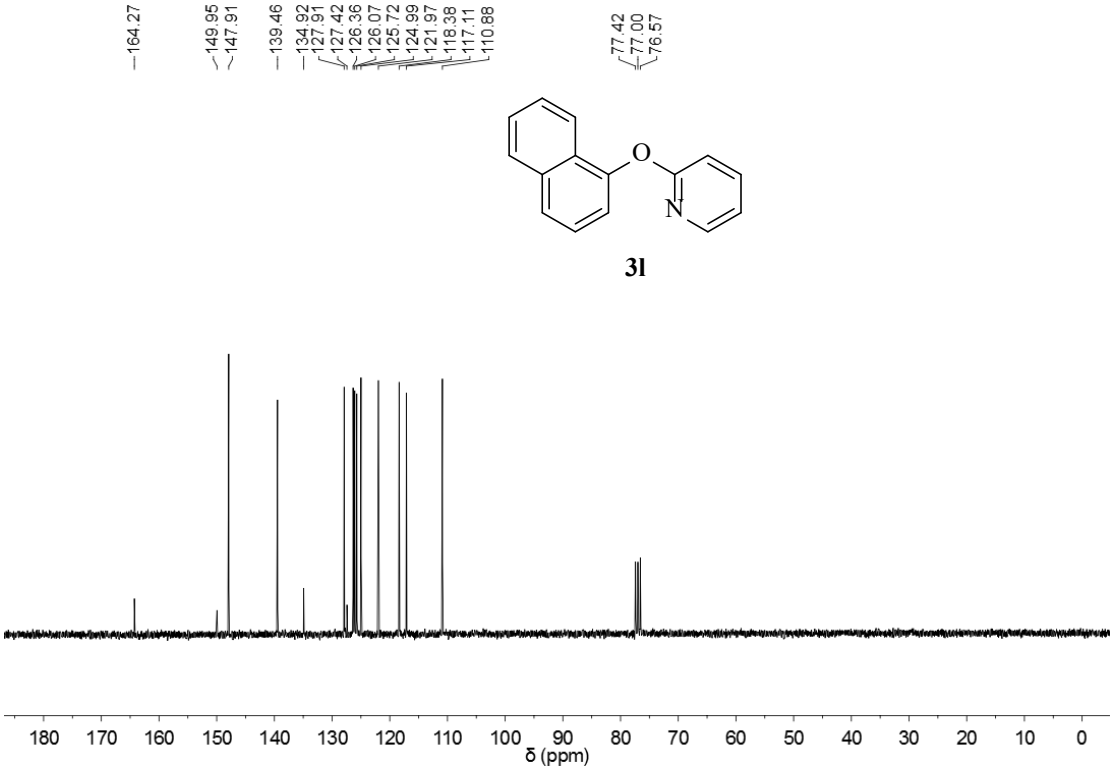


Figure S28. The ^{13}C NMR for compound **3l**

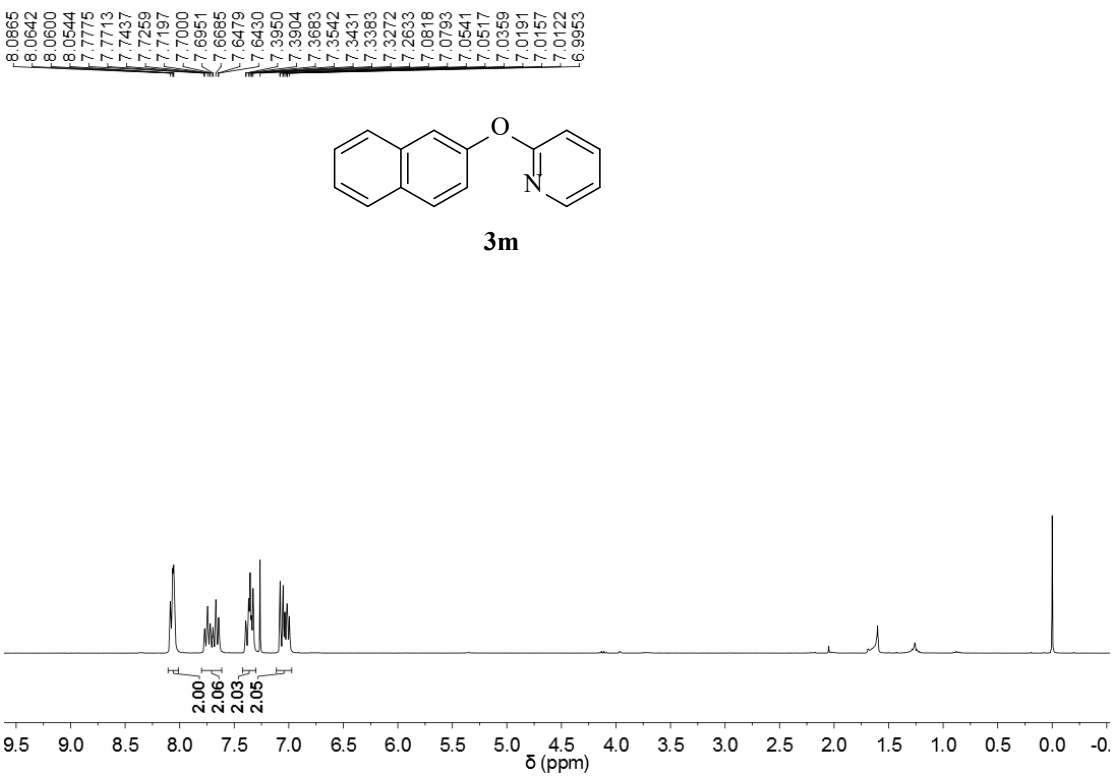


Figure S29.The ^{1}H NMR for compound **3m**

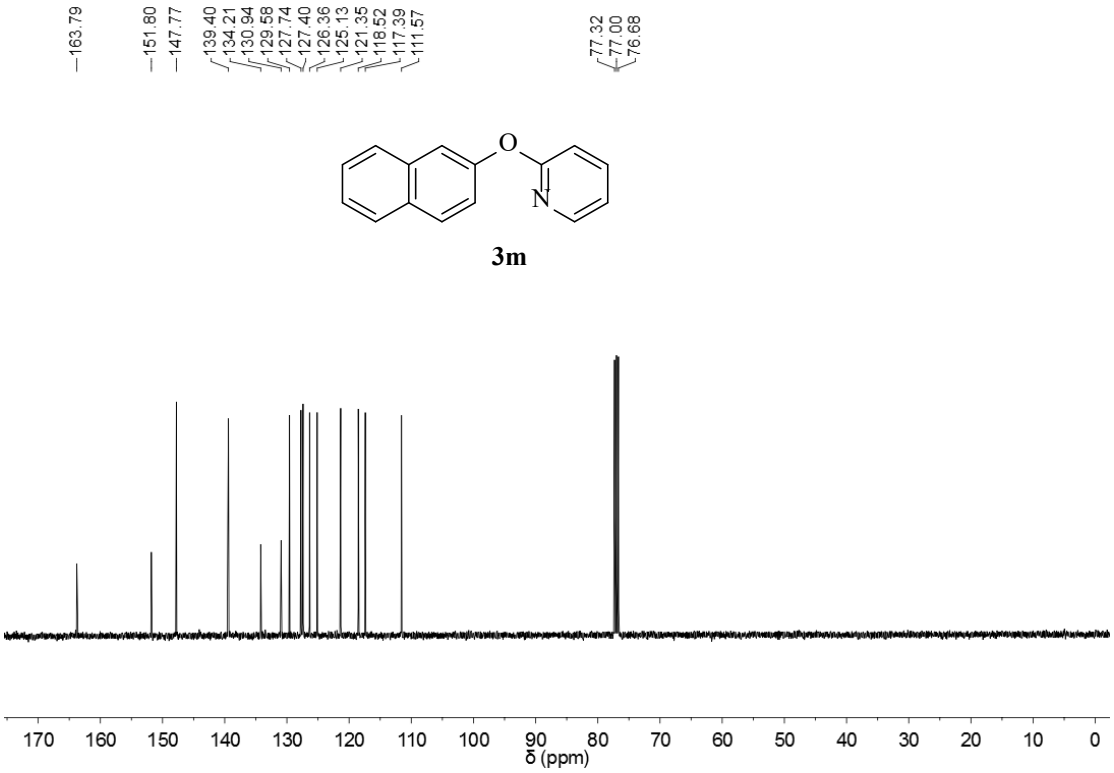


Figure S30. The ^{13}C NMR for compound **3m**