Electronic Supplementary Information

An imidazolium ionic compound-supported palladium complex as an efficient catalyst for Suzuki–Miyaura reactions in aqueous media

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1. Materials and methods

General information

All reagents were commercially available and used as supplied. Unless otherwise stated, analytical grade solvents and commercially available reagents were used as received. Thin layer chromatography (TLC) employed glass 0.20 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. All new compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and HR-MS. The IR spectra were run on a Nicolete spectrometer (KBr). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCEⅢ 400 MHz spectrometer. The chemical shifts (δ) were given in parts per million relative to an internal standard tetramethylsilane, High resolution mass spectra (HR-MS) were measured with Bruker MICROTOF-Q Ⅲ instrument and accurate masses were reported for the molecular ion. Inductively coupled plasma atomic emission spectrometer (ICP-OES) were run on PerkinElmer Optima 7300 DV. Melting points were determined on a Perkin-Elmer differential scanning calorimeter and the thermometer was uncorrected.

2.Optimization of the catalyticconditions

Table 1 Optimization of the reaction conditions for the Suzuki reaction catalyzed by **3**[a]

Br——⟨benzene⟩——O + ⟨benzene⟩——B(OH)$_2$ →(Catalyst **3** / Base, Solvent, R. T.)→ ⟨benzene⟩——⟨benzene⟩——O
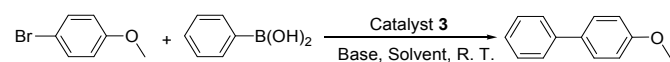
Entry	Solvent	Catalyst (Pd mol%)	Base	Time(h)	Yield(%)[b]
1	H$_2$O	0.05	K$_2$CO$_3$	2	75
2	H$_2$O	0.05	KOAc	2	70
3	H$_2$O	0.05	Na$_2$CO$_3$	2	54
4	H$_2$O	0.05	NaOAc	2	40
5	H$_2$O	0.05	TEA	2	34
6	H$_2$O	0.05	Pyridine	2	20
7	H$_2$O	0	K$_2$CO$_3$	2	0
8	H$_2$O	0.01	K$_2$CO$_3$	2	61
9	H$_2$O	0.08	K$_2$CO$_3$	2	85
10	H$_2$O	0.10	K$_2$CO$_3$	2	92
11	H$_2$O	0.10	K$_2$CO$_3$	4	98
12	H$_2$O	0.10	K$_2$CO$_3$	5	98
13	EtOH	0.10	K$_2$CO$_3$	8	92
14	DMF	0.10	K$_2$CO$_3$	12	78
15	DMF/H$_2$O (V/V, 1:1)	0.10	K$_2$CO$_3$	8	94

[a]Reaction conditions: the catalyst **3**, 1 mmol of p-bromoanisole, 1 mmol of phenylboronic acid, 2 mmol of base, 5 ml of solvent, 2 mmol of base, 5 ml of solvent, R.T. in air.
[b]Isolated yield.

3. Preparation and analyticaldata of catalyst C

The synthesis of 5-chloromethylsalicylaldehyde

To a 100 mL round-bottom flask equipped with a magnetic stirring bar was concentrated hydrochloric acid (80 mL), poly formaldehyde (4.7 g) and salicylic aldehyde (12 g). The mixture was stirred for approximately 0.5 h at room temperature. POCl3 was slowly added within 1 h, and the mixture was stirred for 20 h to obtain the solid(16 g, 98%). The analytical sample was afforded by the recrystallization from petroleum ether. mp: 264-268°C; ^{1}H NMR (400 MHz, DMSO) δ 10.92 (s, 1H), 10.27 (s, 1H), 7.72 (d, J = 2.3 Hz, 1H), 7.58 (dd, J = 8.5, 2.4 Hz, 1H), 7.02 (d, J = 8.5 Hz, 1H), 4.75 (s, 2H).

The synthesis of the ionic compound-supported salicylic aldehyde

A mixture of 1-methylimidazole (5 mmol) and 2 (5 mol) was refluxed in ethanol for 24 h, followed by the vacuum distillation to give a pale yellow solid, which was washed with ethyl acetate to give the ionic compound-supported salicylic aldehyde 2 in almost quantitative yield. mp: 264-268°C; ^{1}H NMR (400 MHz, D2O) δ 9.86 (d, J = 2.4 Hz, 1H), 8.68 (s, 1H), 7.69 (s, 1H), 7.58 – 7.48 (m, 1H), 7.44 – 7.30 (m, 2H), 6.97 (dd, J = 8.6, 2.5 Hz, 1H), 5.30 (d, J = 2.1 Hz, 2H), 3.81 (d, J = 2.6 Hz, 3H).^{13}C NMR (101 MHz, D2O) δ 196.54, 160.27, 137.45, 136.06, 133.45, 125.63, 124.03, 122.16, 121.16, 118.19, 51.79, 35.90. HR-MS: m/z calcd for $C_{12}H_{13}N_2O_2$ [M-Cl]$^+$: 217.0977 found: 217.0985

The synthesis of the ionic compound-supported Schiff base

A round-bottom flask equipped with a stirring bar was charged with the ionic compound-supported salicylic aldehyde(2.0 mmol) and 4-methylaniline (2.2 mmol) in 10 mL of ethanol. The mixture was refluxed for 6 h, and cooled to room temperature to form the solid product. The crude product was purified by recrystallization from ethanol to obtain the analytical sample (yield, 97%) . mp: >250°C; ^{1}H NMR (400 MHz, DMSO) δ 13.20 (s, 1H), 9.26 (d, J = 18.5 Hz, 1H), 8.93 (s, 1H), 7.89 – 7.67 (m, 3H), 7.50 (d, J = 6.4 Hz, 1H), 7.31 (dd, J = 19.7, 8.2 Hz, 4H), 7.04 (d, J = 8.5 Hz, 1H), 5.40 (s, 2H), 3.86 (s, 3H), 2.35 (s, 3H); 13C NMR (101 MHz, DMSO) δ 161.45, 160.85, 146.09, 137.01, 133.87, 132.60, 130.41, 125.88, 124.36, 122.63, 121.63, 120.14, 117.70, 51.66, 36.31, 21.07. HR-MS: m/z calcd for $C_{19}H_{20}N_3O$ [M-Cl]$^+$: 306.1601, found: 306.1640.

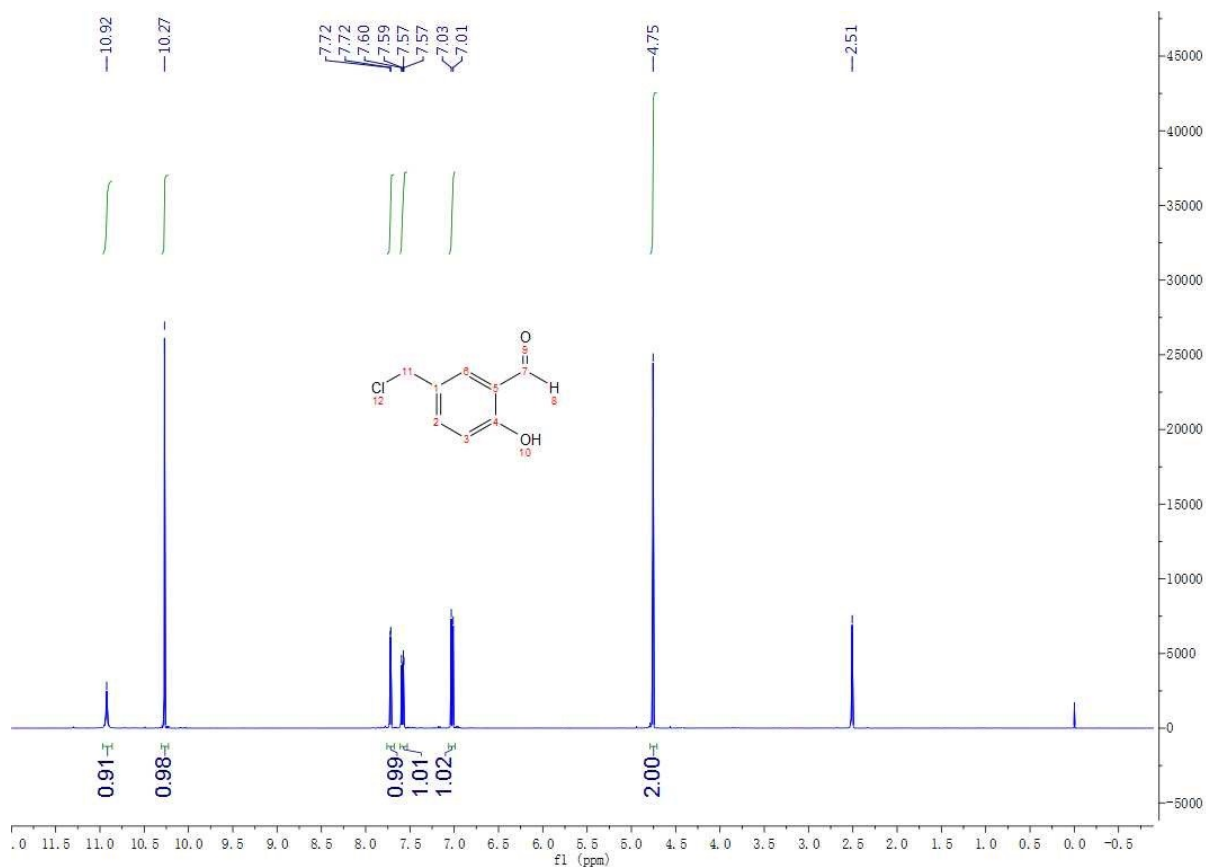**The synthesis of the ionic compound-supported palladium complex**

A mixture of the ionic compound-supported Schiff base (2.0 mmol) and palladium acetate (224 mg, 1.0 mmol) was added in methanol (5.0 mL) and refluxed for 6 h until the product had completely precipitated. After cooling, the palladium complex was separated by filtration and recrystallized from ethanol (5 mL) (yield, 97%). mp: 264-268°C; ^{1}H NMR (400 MHz, DMSO) δ 9.10 (s, 1H), 8.45 (s, 1H), 7.72 (dt, J = 22.7, 1.8 Hz, 2H), 7.49 (dd, J = 14.0, 5.2 Hz, 3H), 7.35 – 7.22 (m, 3H), 6.65 (d, J = 8.8 Hz, 1H), 5.23 (s, 2H), 3.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 171.46, 167.42, 147.09, 138.25, 136.57, 135.65, 130.15, 124.30, 123.87, 122.52, 122.16, 119.09, 52.27, 36.30, 20.99. HR-MS: m/z calcd for $C_{38}H_{38}Cl_2N_6O_2Pd$ [M+2-Cl]$^+$: 753.1936, found: 753.1833. Elemental analysis cald (%) for $C_{38}H_{38}Cl_2N_6O_2Pd$: C, 57.92; H, 4.86; found: C 57.85, H 4.92.

**General Experimental Procedures for Suzuki-Miyaura Couplings**

In a typical experiment, the ionic compound-supported palladium complex (0.001 mmol of Pd) was added to a mixture of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol) and K_2CO_3 (2.0 mmol) in water (5.0 mL), and the reaction mixture was stirred at R.T.. The progress of the reaction was monitored by means of TLC. After the completion of the reaction, the reaction mixture was extracted with a mixture of ethyl acetate (3 × 5 mL). The organic layer was dried with anhydrous Na_2SO_4, and then the solvent was evaporated under reduced pressure. The resulting residue was purified by column chromatography over silica gel (mesh 200–300), using *n*-hexane–ethyl acetate as an eluent, to give the desired product. All of the products are known compounds, and their ^{1}H NMR data were identical to those reported in literature.

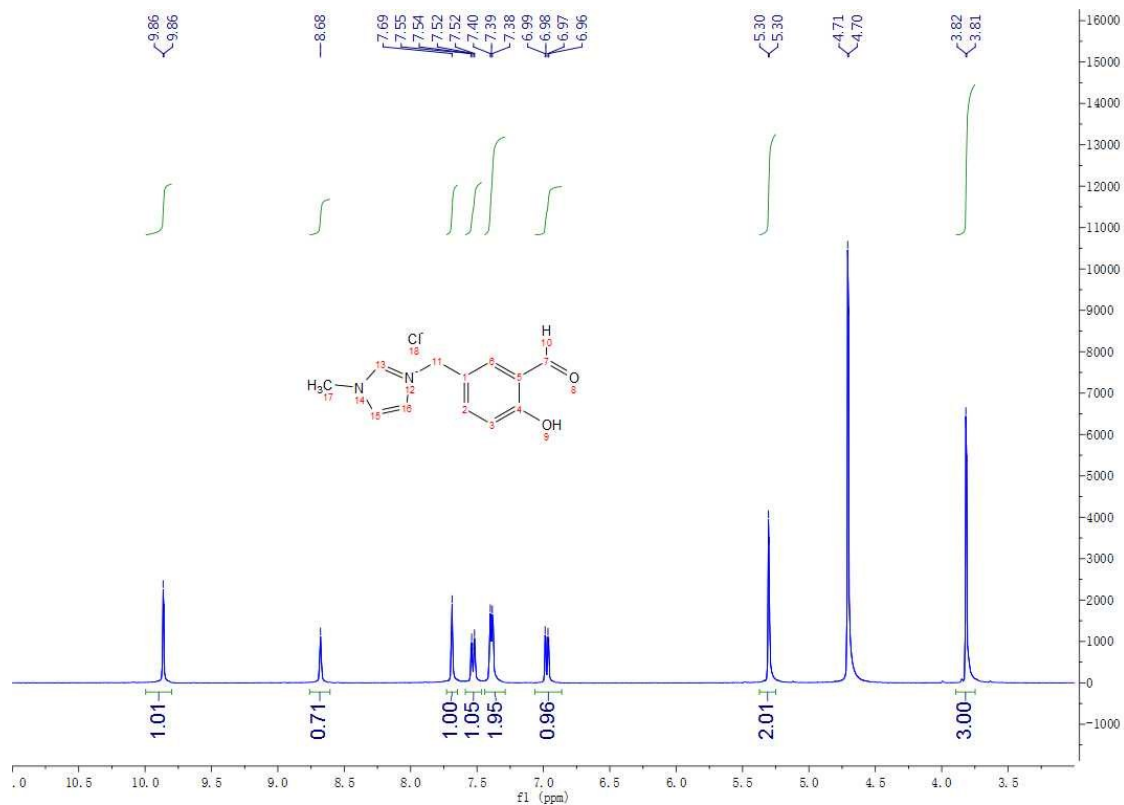## 5. The characterization of the catalyst
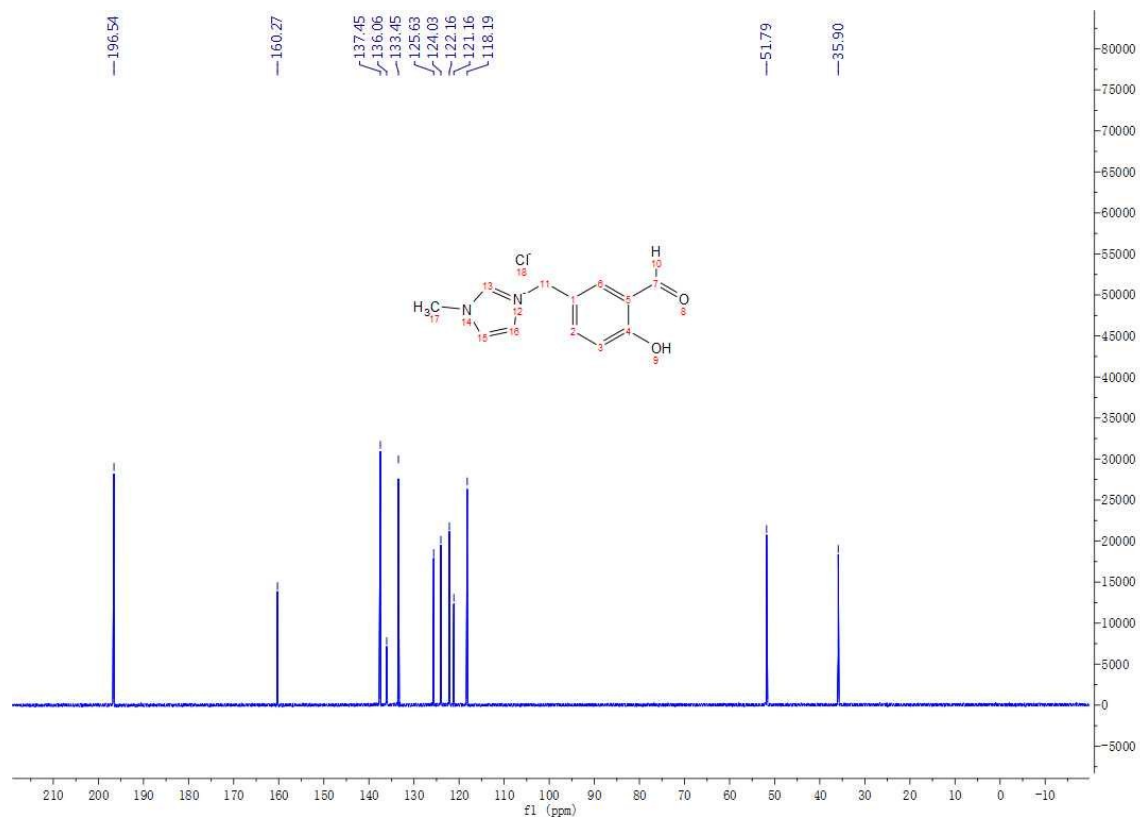
5.1 ^{1}H NMR of 5-chloromethylsalicylaldehyde

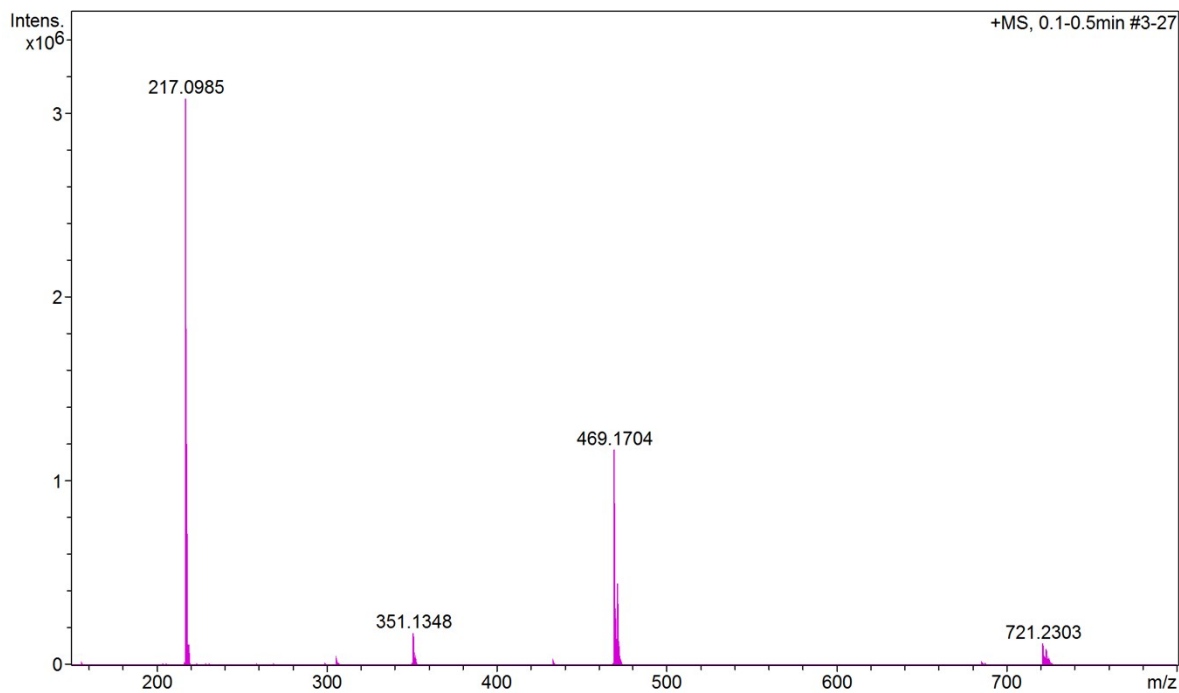## 5.2 IR of the ionic compound-supported salicylic aldehyde
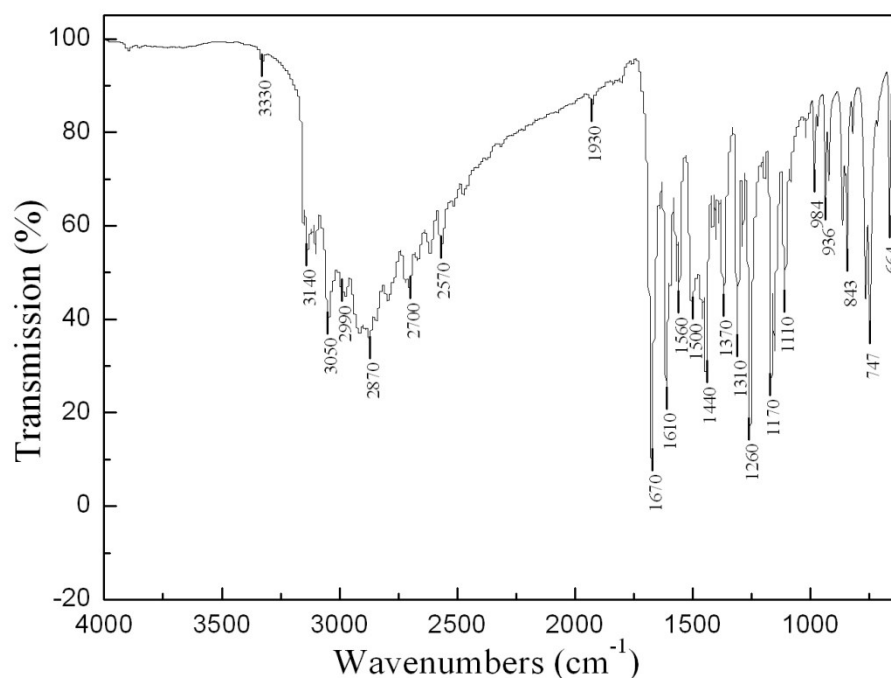
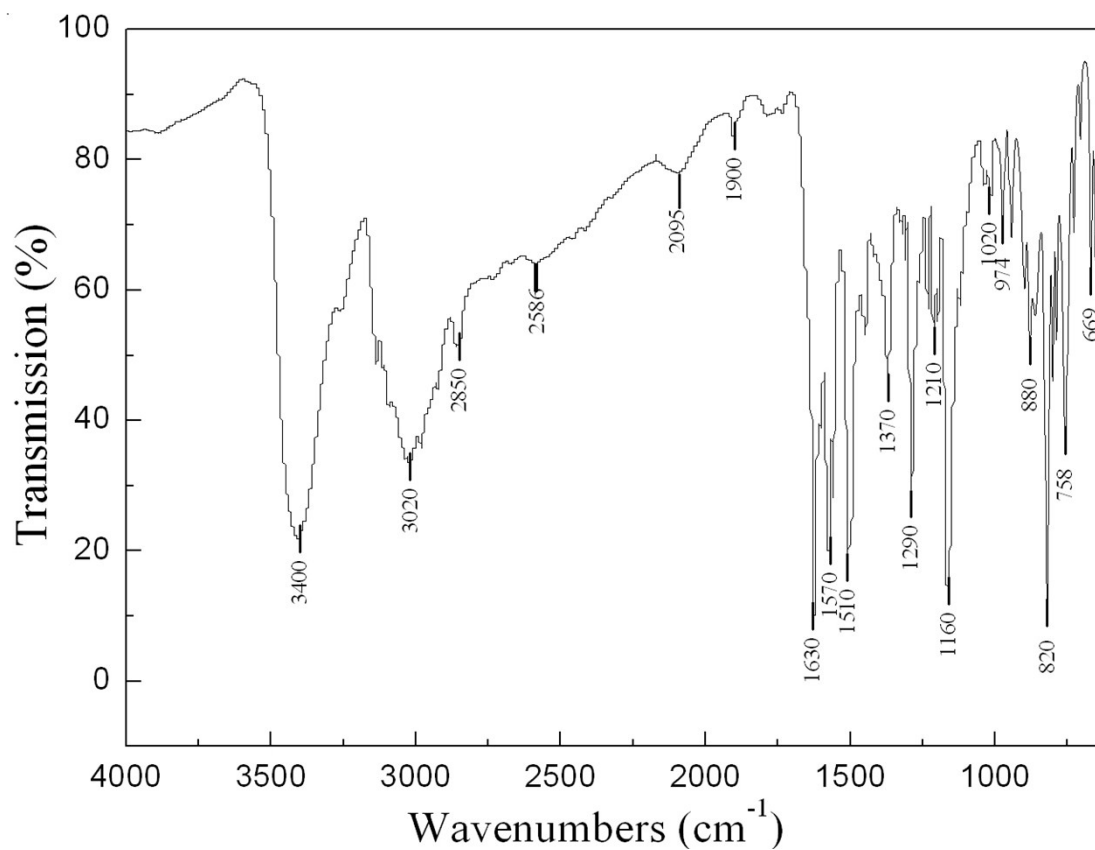## 5.3 ^{1}H NMR of the ionic compound-supported salicylic aldehyde

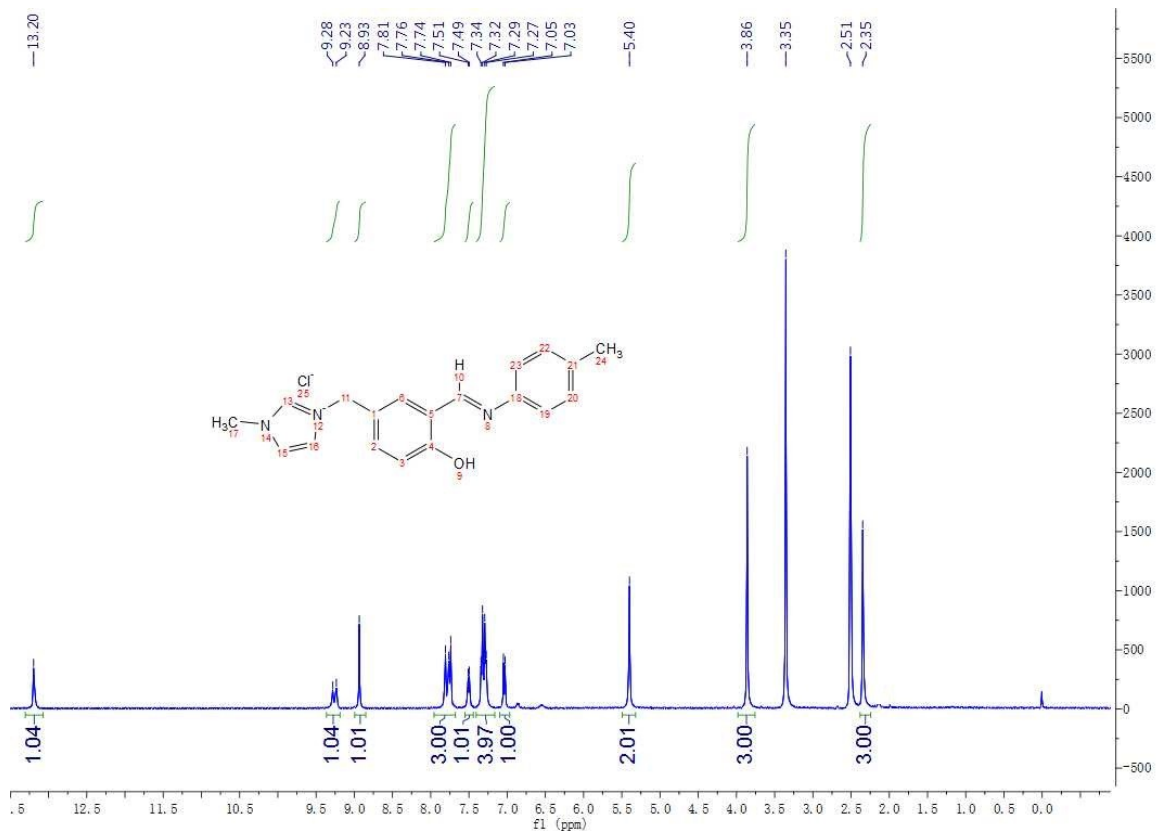5.4 ^{13}C NMR of the ionic compound-supported salicylic aldehyde

5.5 HR-MS of the ionic compound-supported salicylic aldehyde

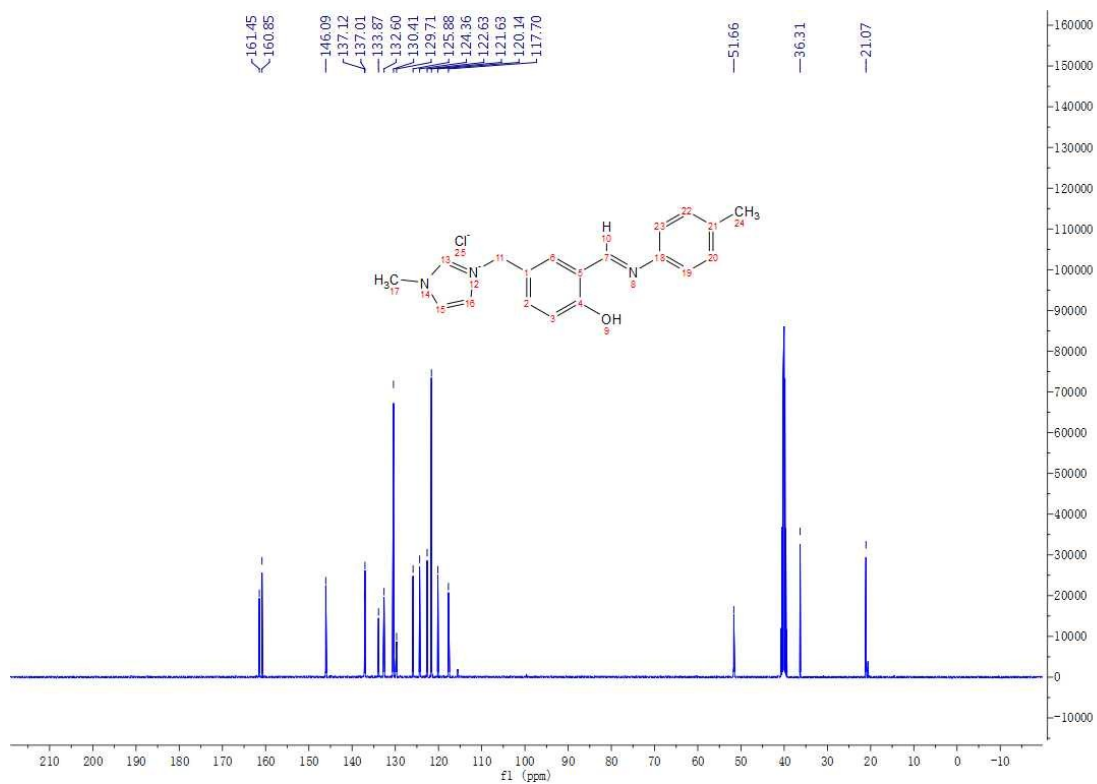5.6 IR of the ionic compound-supported Schiff base

5.6 ^{1}H NMR of the ionic compound-supported Schiff base

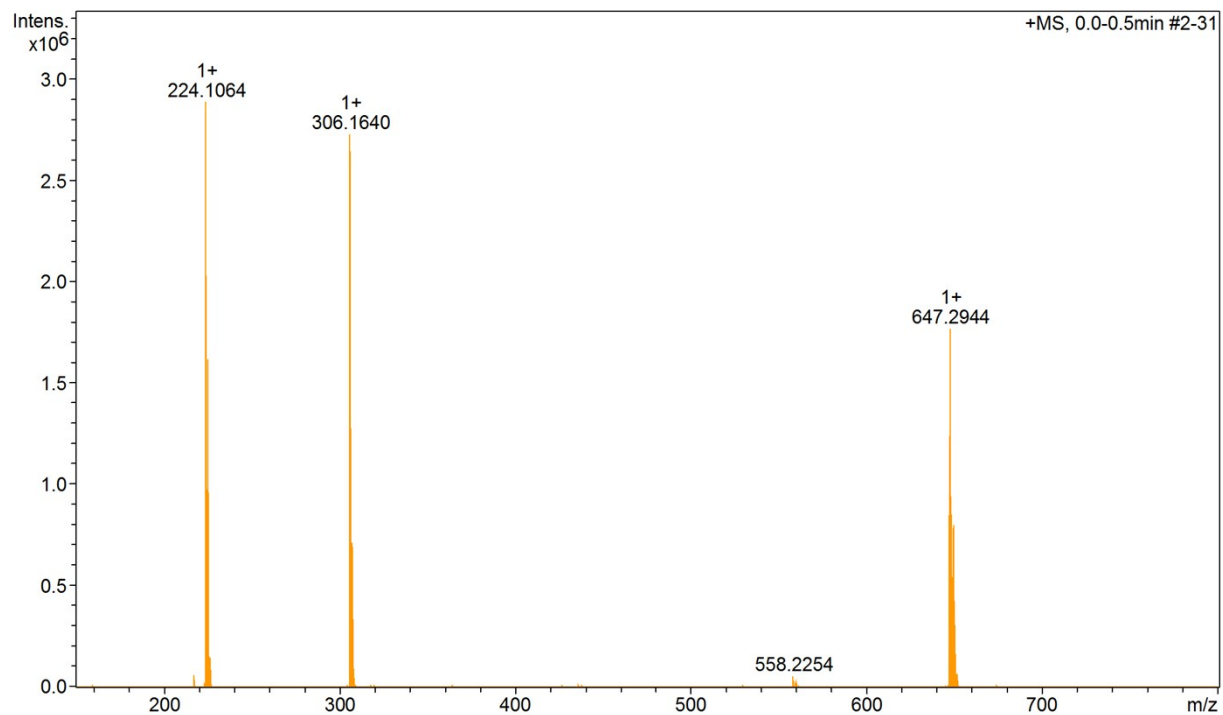**5.7** ^{13}C NMR of the ionic compound-supported Schiff base

5.8 HR-MS of the ionic compound-supported Schiff base

5.9 ¹H NMR of the ionic compound-supported palladium complex
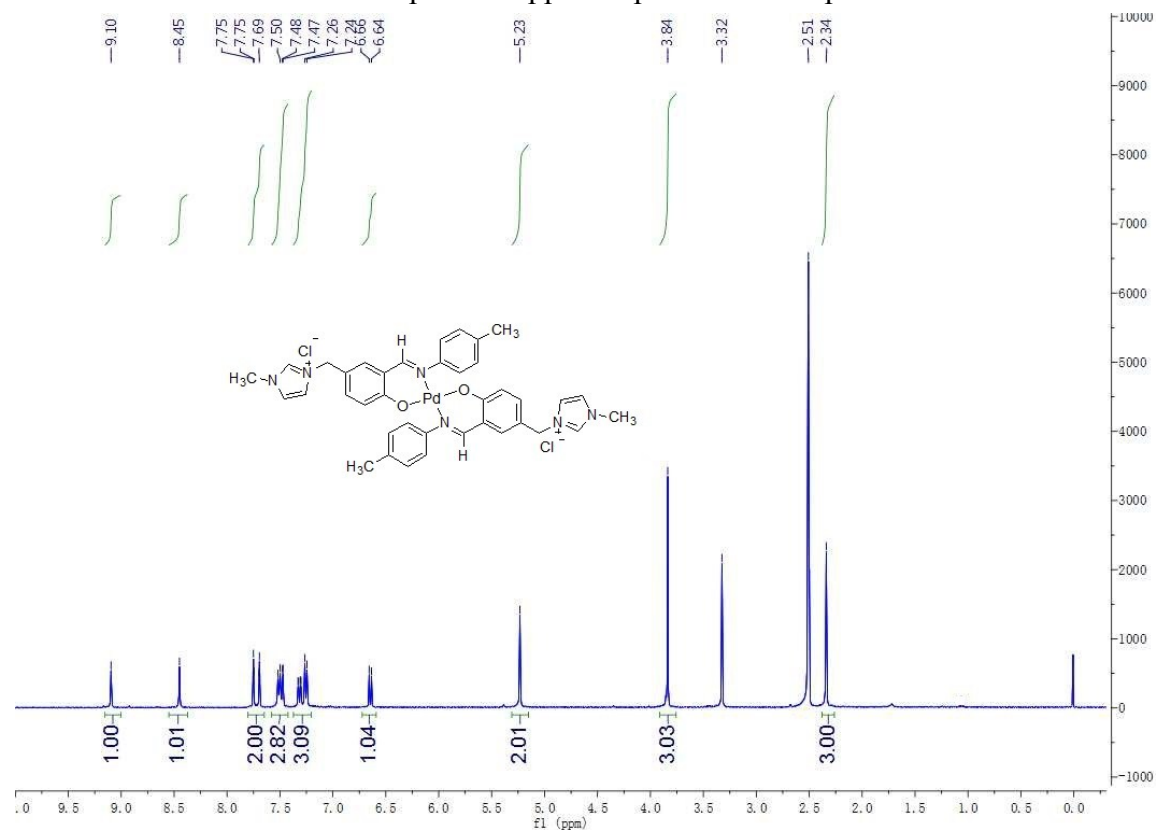
5.10 IR of the ionic compound-supported palladium complex
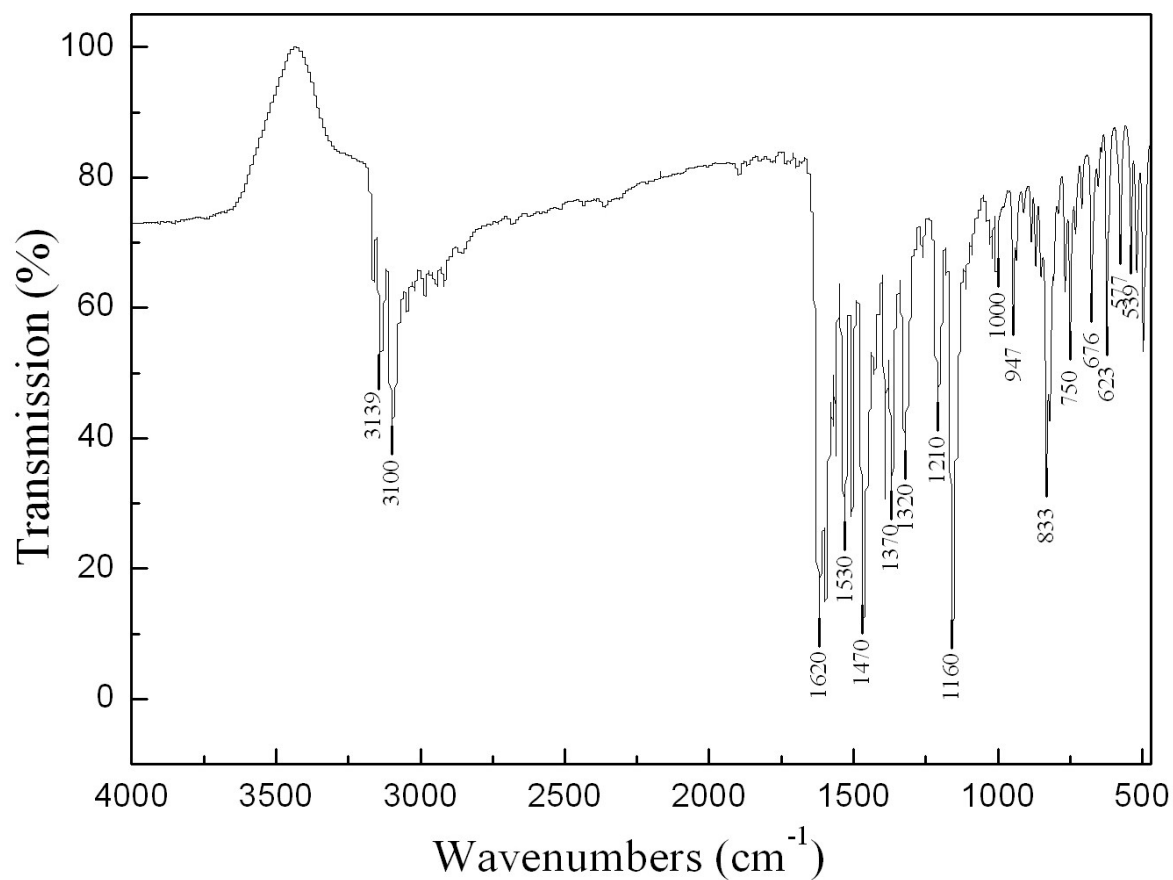
5.11 HR-MS of the ionic compound-supported palladium complex
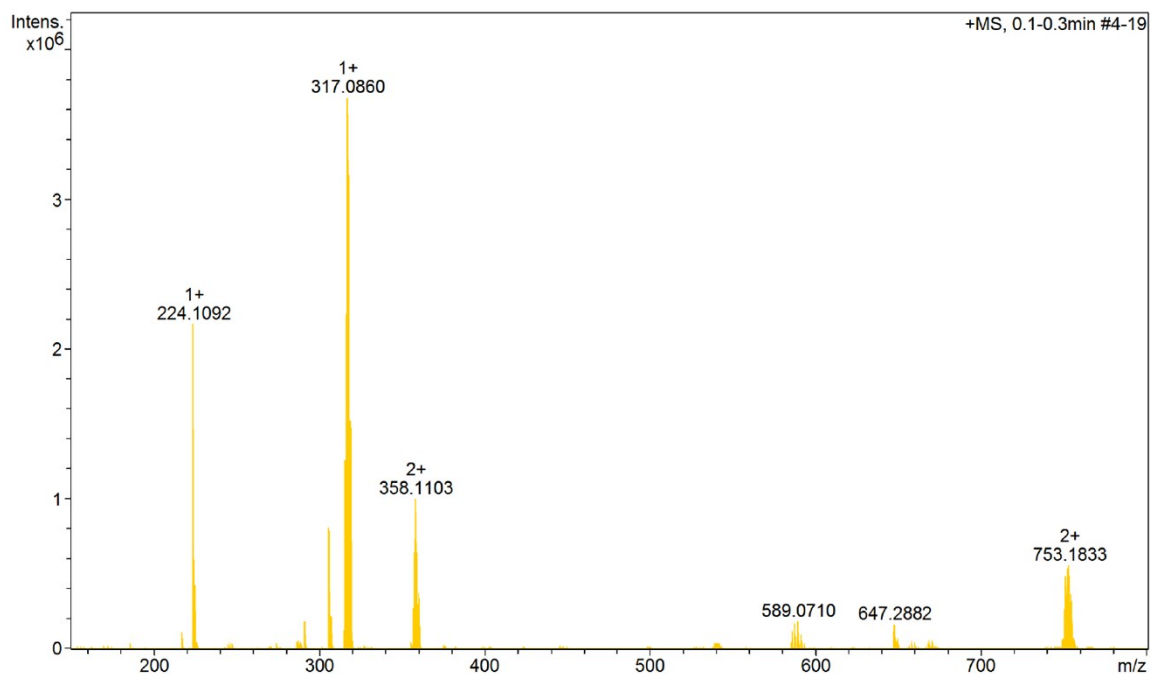
5.12 ^{13}C NMR of the ionic compound-supported palladium complex
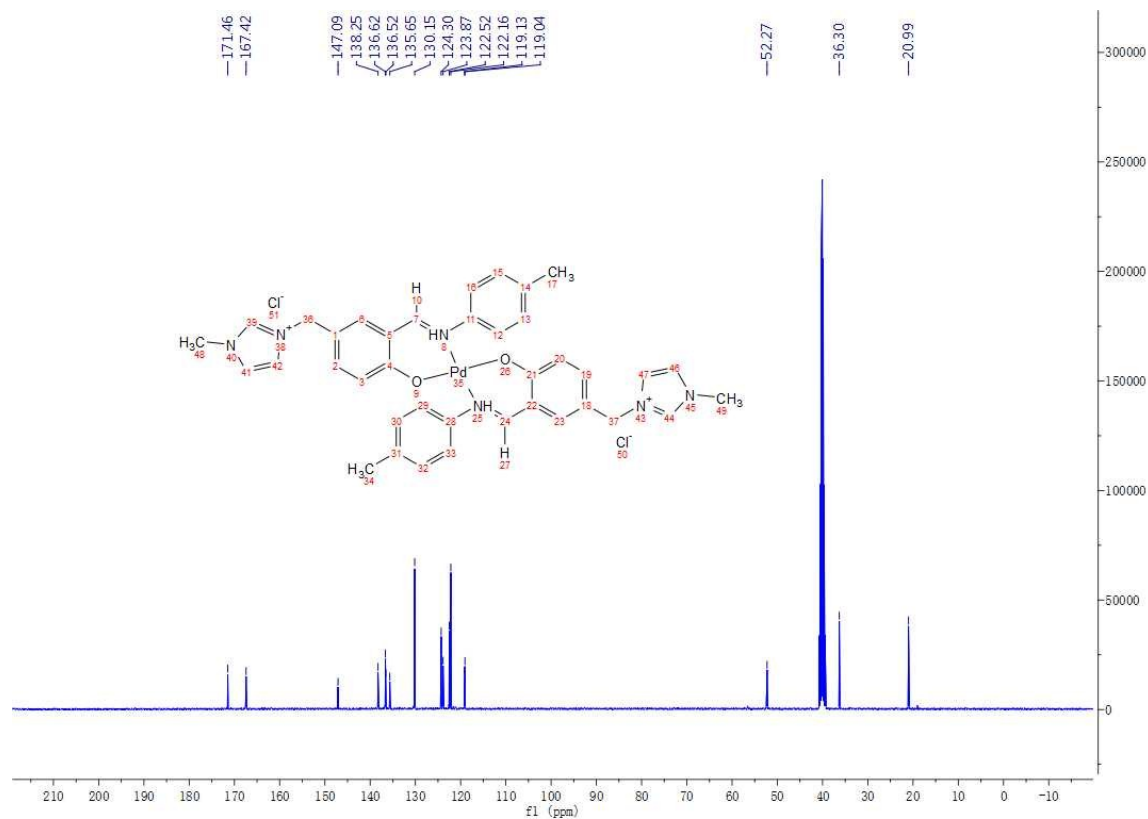
5.13 ^{1}H NMR of the spent palladium complex
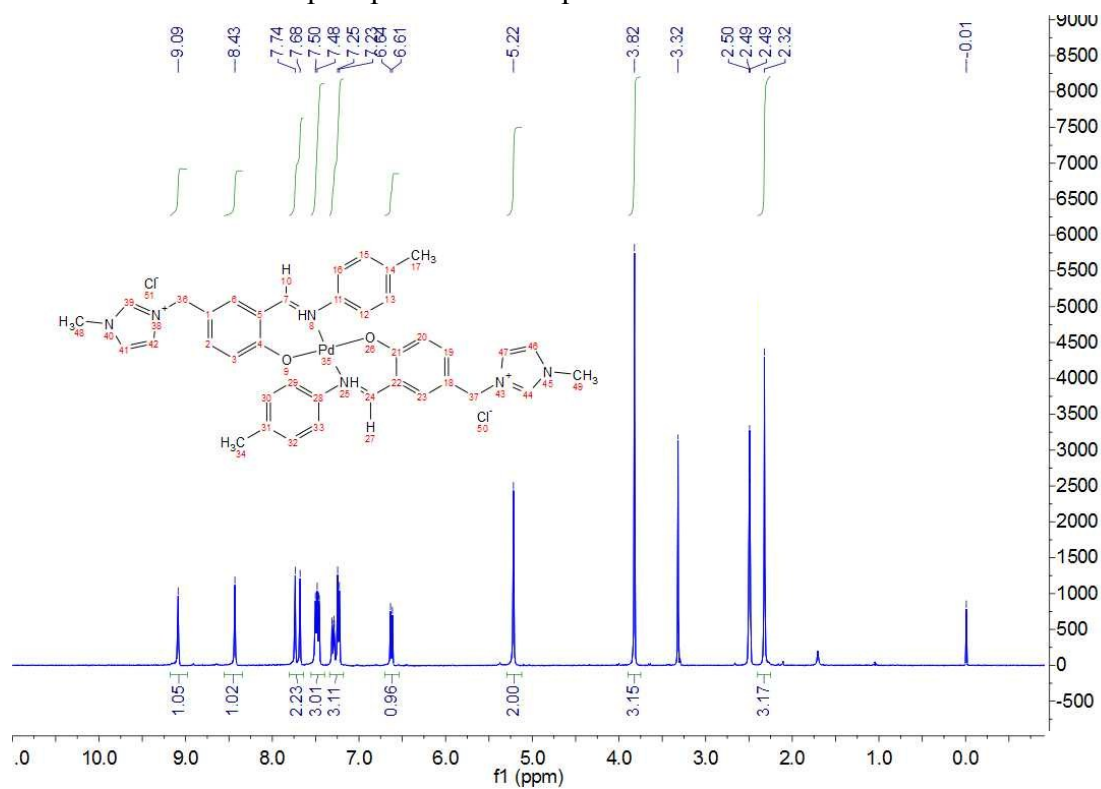
5.13 Copies of ¹H NMR of Suzuki coupled products

8.12
8.10
7.64
7.62
7.57
7.55
7.45
7.43
7.26
3.95

1.98 2.01 1.99 1.99 3.00

f1 (ppm)

8.14
8.12
7.56
7.54
7.53
7.52
7.51
7.50
7.37
7.36
7.35
7.34
3.97

2.04 3.37 4.33 3.00

f1 (ppm)

Top spectrum peak labels: 7.61, 7.61, 7.59, 7.59, 7.59, 7.47, 7.46, 7.45, 7.44, 7.43, 7.43, 7.37, 7.35, 7.25

0.00

Y-axis: 38000, 36000, 34000, 32000, 30000, 28000, 26000, 24000, 22000, 20000, 18000, 16000, 14000, 12000, 10000, 8000, 6000, 4000, 2000, 0, -2000

Integrations: 4.09, 4.09, 2.00

X-axis: .5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0, -0.5
f1 (ppm)

Bottom spectrum peak labels: 8.038, 8.026, 8.021, 8.017, 7.662, 7.658, 7.653, 7.641, 7.636, 7.631, 7.567, 7.562, 7.550, 7.545, 7.539, 7.456, 7.450, 7.445, 7.434, 7.428, 7.262

2.642

0.000

Integrations: 2.04, 2.07, 2.00, 2.05, 3.00

X-axis: 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, ppm

7.50 7.49 7.49 7.48 7.47 7.46 7.39 7.37 7.26 6.99 6.97 6.95

3.85 3.85

2.99 0.97 1.95

7.63 7.63 7.62 7.61 7.61 7.55 7.54 7.53 7.53 7.48 7.47 7.46 7.45 7.45 7.38 7.36 7.30 7.28

2.44

2.01 1.98 2.01 0.99 2.11

3.01