

## Electronic Supplementary Information for

# ***In Situ* Formation of *N,O*-Bidentate Ligand via the Hydrogen Bond for Highly Efficient Suzuki Reaction of Aryl Chlorides**

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### Contents

Materials and Methods and Experimental Procedure	S1
Characterization Data	S2-S3
<sup>1</sup> H NMR Spectra for all Cross-Coupling Products	S5-S14
UV spectra of Pd at Different Stages	S15

### Materials and Methods

All aryl chlorides and arylboronic acids were used as received (Alfa Aesar, Avocado). All other chemicals were purchased from commercial sources and used without further purification. <sup>1</sup>H NMR spectra were recorded on Varian Inova 400 spectrometer or Bruker AvanceII 400 spectrometer. Chemical shifts were reported in ppm relative to TMS. All products were isolated by short chromatography on a silica gel (200-300 mesh) column using petroleum ether (60-90 °C), unless otherwise noted. Compounds described in the literature were characterized by <sup>1</sup>H NMR spectra to reported data.

### Typical Procedure for Suzuki Reaction of Aryl Chlorides with Arylboronic Acids

A mixture of aryl chlorides (0.5 mmol), arylboronic acid (0.75 mmol), Pd(OAc)<sub>2</sub> (0.5 mol%, 0.56 mg), K<sub>2</sub>CO<sub>3</sub> (1 mmol, 138.2 mg) and EtOH/DMA (2:2mL) was stirred at 80 °C for indicated time. The mixture was added to brine (15 mL) and extracted four times with ethyl acetate (3 × 10 mL). The solvent was concentrated *in vacuo* and the product was isolated by short chromatography on a silica gel (200-300 mesh) column.

## Characterization Data

### 4-Nitrobiphenyl<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.31 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 7.52-7.43 (m, 3H), ppm.

### 4-Methyl-4'-nitrobiphenyl<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H) ppm.

### 3-Methyl-4'-nitrobiphenyl<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.43 (m, 3H), 7.27 (s, 1H), 2.44 (s, 3H) ppm.

### 2-Methyl-4'-nitrobiphenyl<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.29 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.35 (m, 3H), 7.22 (d, *J* = 7.2 Hz, 1H), 2.27 (s, 3H) ppm.

### 4-Methoxy-4'-nitrobiphenyl<sup>1</sup>

(lit.<sup>[97]</sup> m.p.: 107-108 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H) ppm.

### 2-Methoxy-4'-nitrobiphenyl<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.84 (s, 3H), 7.01-7.09 (m, 2H), 7.26-7.35 (m, 2H), 7.38-7.43 (m, 2H), 7.69 (t, *J* = 6.8 Hz, 2H) ppm.

### 4-Fluoro-4'-nitrobiphenyl<sup>2</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.19 (t, *J* = 8.4 Hz, 2H), 7.60 (t, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 2H) ppm.

### 2,4-Dinitrobiphenyl<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.69 (d, *J* = 2.4 Hz, 1H), 8.47-8.45 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 2.8 Hz, 3H), 7.35-7.33 (m, 2H) ppm.

### 2,4-Dinitro-4'-fluorobiphenyl<sup>3</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.72 (d, *J* = 2.4 Hz, 1H), 8.49-8.46 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.35-7.32 (m, 2H), 7.20 (t, *J* = 8.0 Hz, 2H) ppm.

### 2-Nitro-biphenyl<sup>1</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.85 (d, *J* = 8 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H),

7.50-7.49 (m, 5H), 7.33-7.31 (m, 2H) ppm.

**4-Cyanobiphenyl<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.72 (m, 4H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H) ppm.

**4-Methyl-4'-cyanobiphenyl<sup>4</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.04 (s, 3H), 7.28 (t, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.68 (m, 4H) ppm.

**4-Trifluoromethyl-biphenyl<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.69 (s, 4H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H) ppm.

**4-Methyl-4'-trifluoromethylbiphenyl<sup>5</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.40 (s, 3H), 7.26 (t, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.67 (s, 4H) ppm.

**3-Methoxy-biphenyl<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.36 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.13 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H) ppm.

**3-Methoxy-4-methylbiphenyl<sup>6</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.11 (s, 1H), 6.88 (t, *J* = 4.0 Hz, 1H), 3.84 (s, 3H), 2.34 (s, 3H) ppm.

**4-Acetylbiphenyl<sup>1</sup>**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H) ppm.

**4-Methyl-4'-acetylbiphenyl<sup>7</sup>**

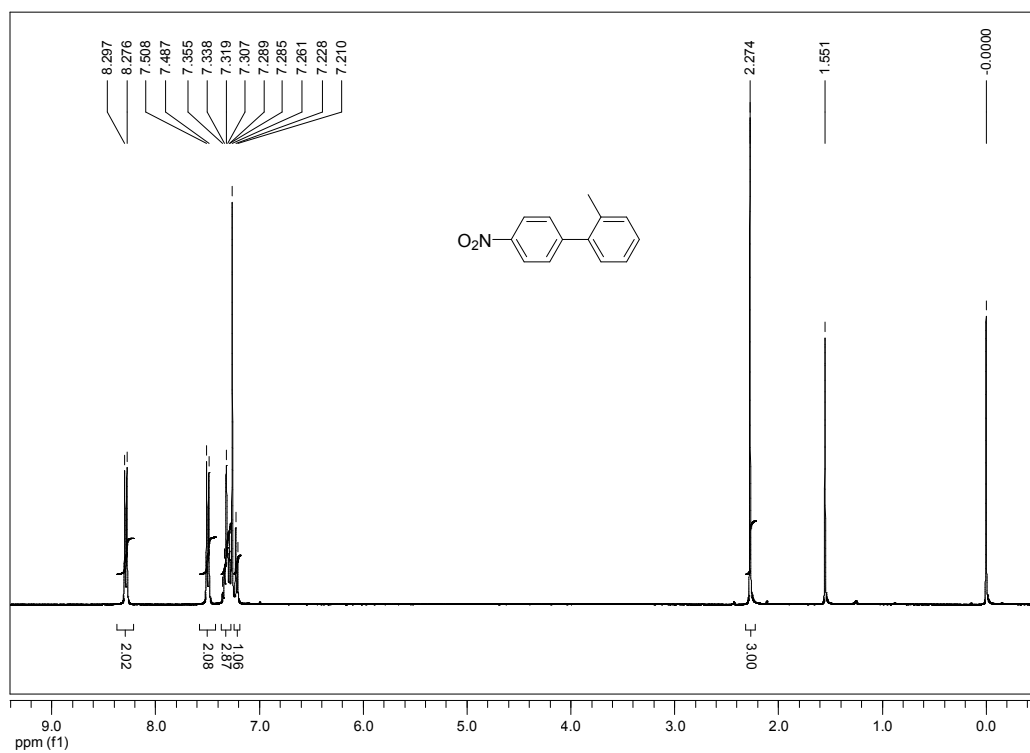
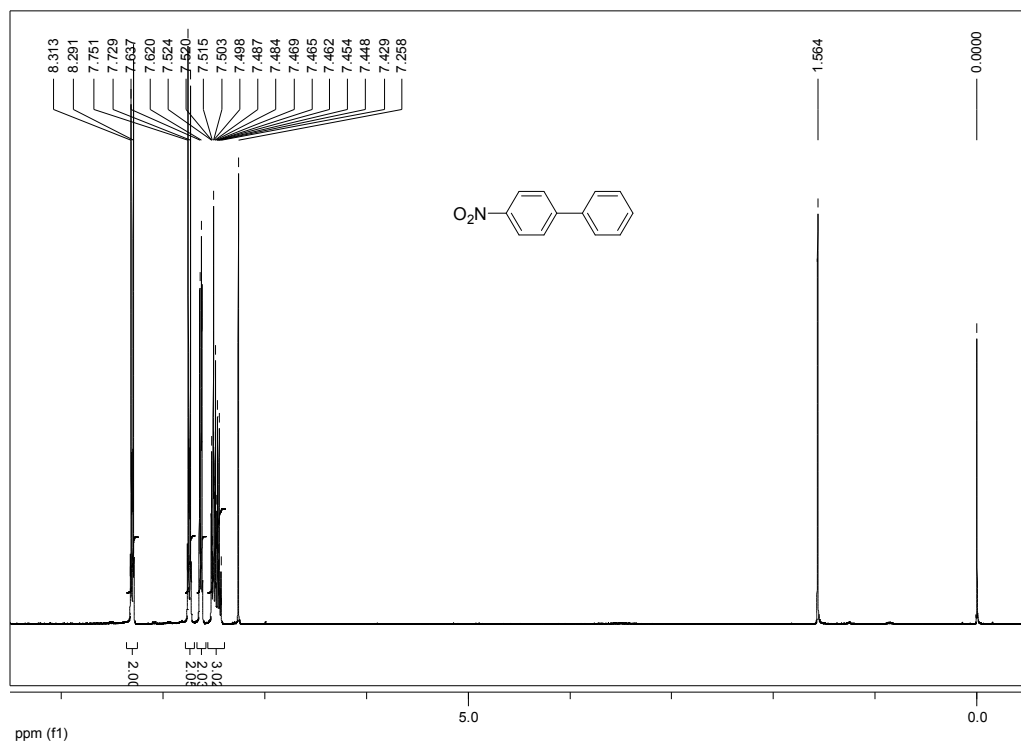
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.63 (s, 3H), 2.41 (s, 3H) ppm.

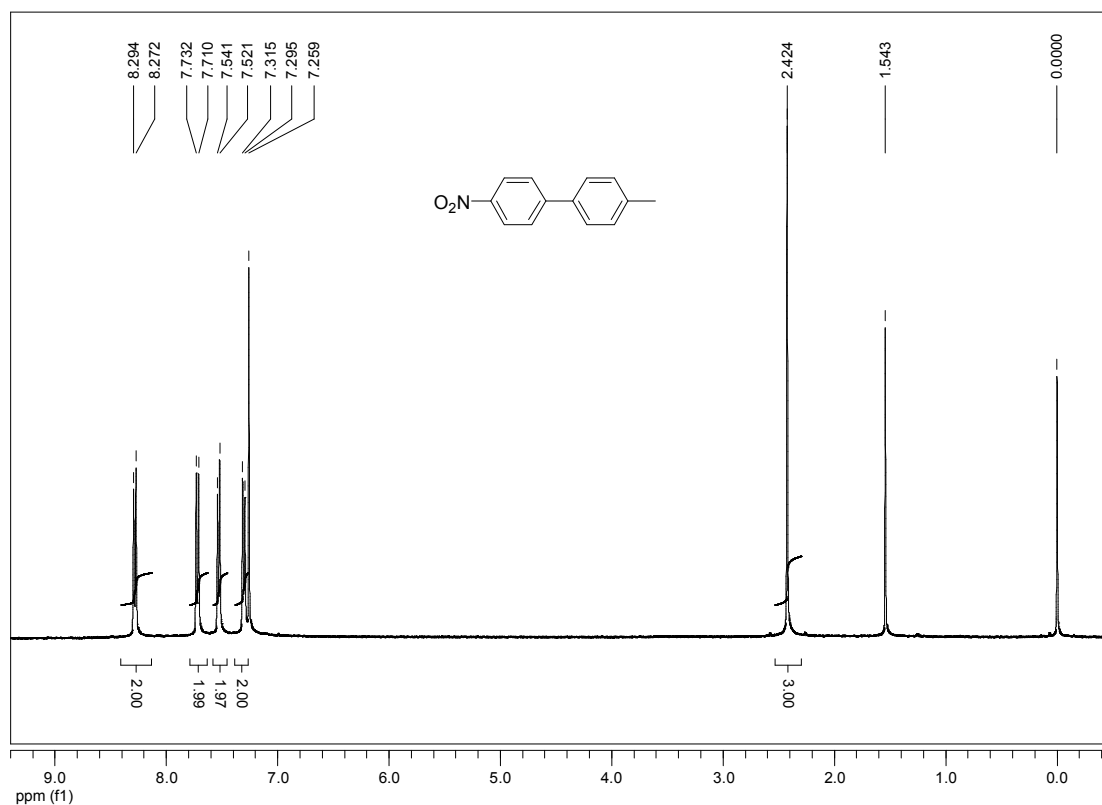
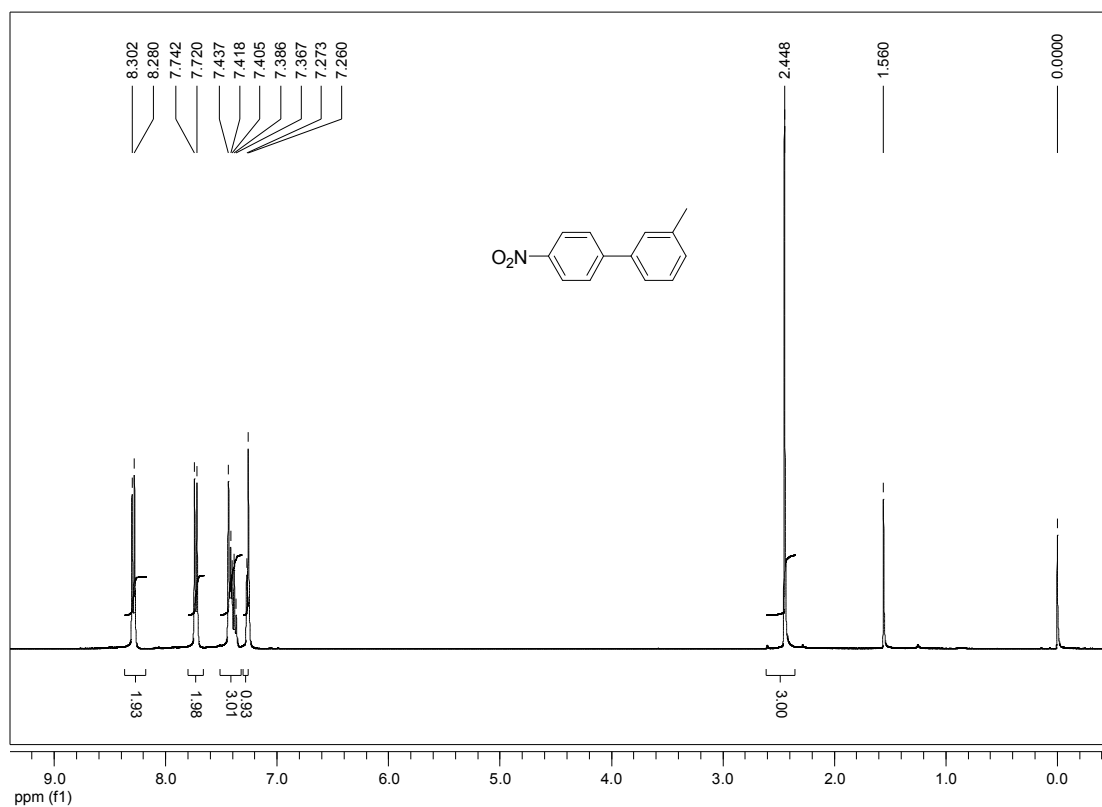
**Biphenyl<sup>1</sup>**

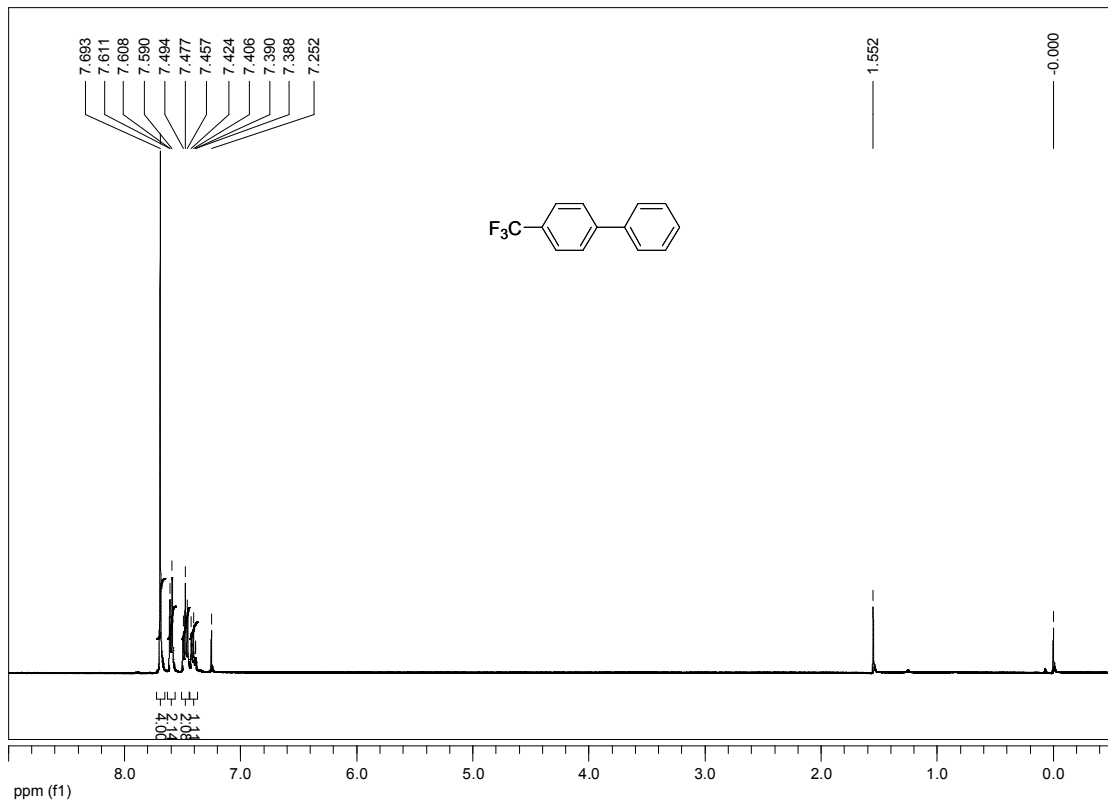
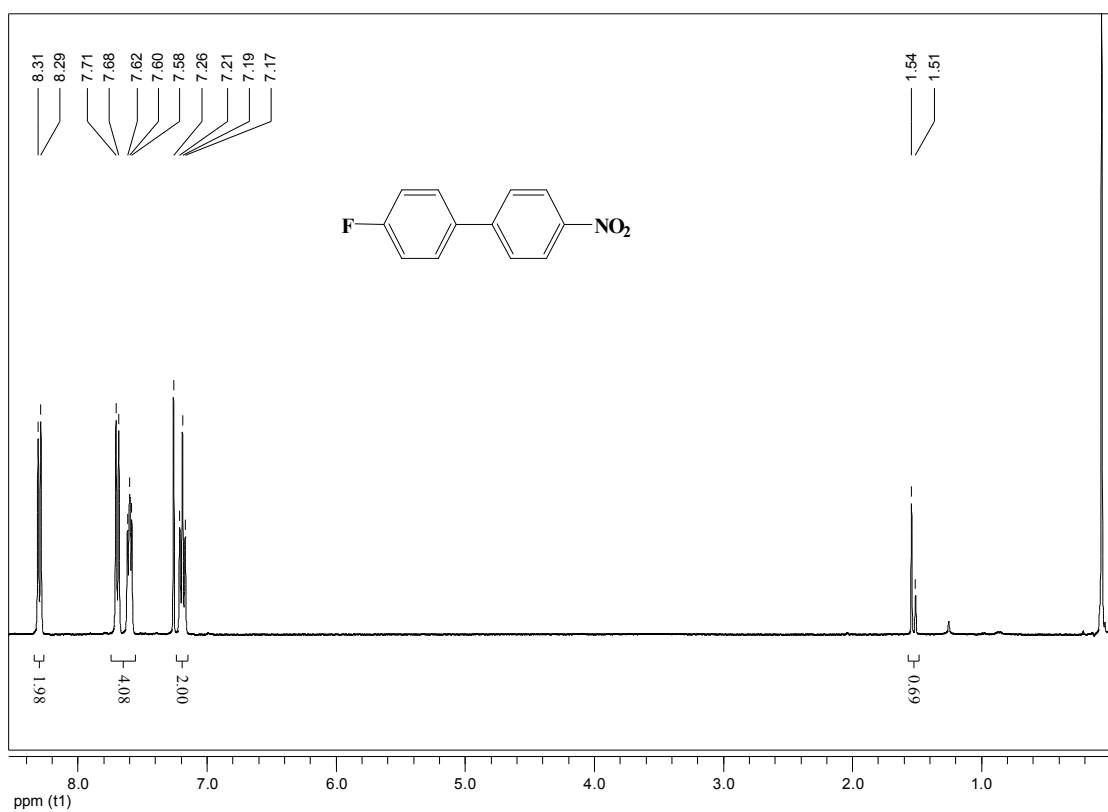
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.59 (d, *J* = 8.4 Hz, 4H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H) ppm.

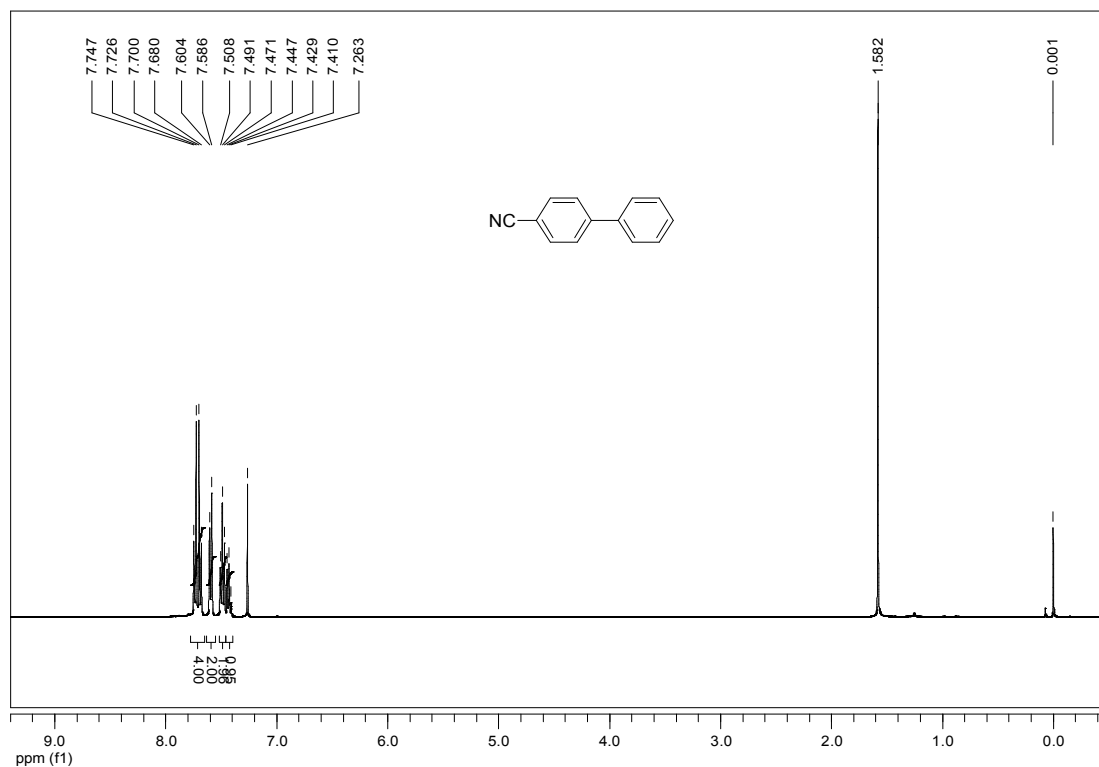
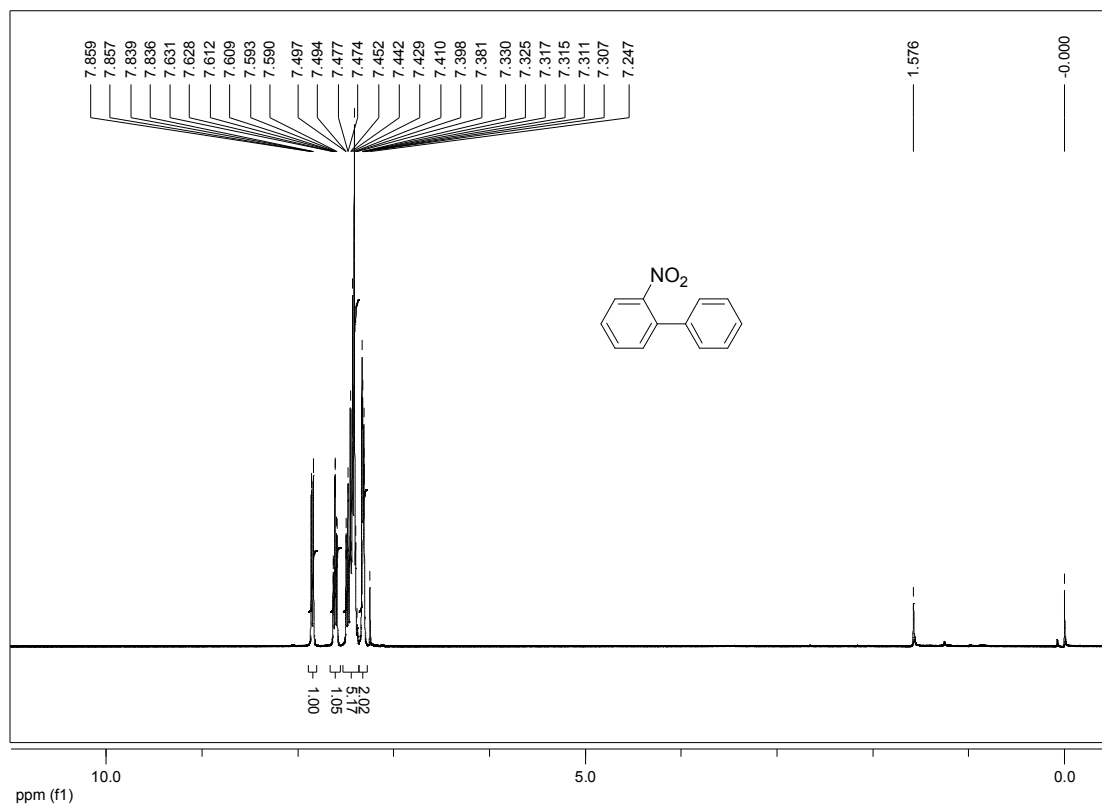
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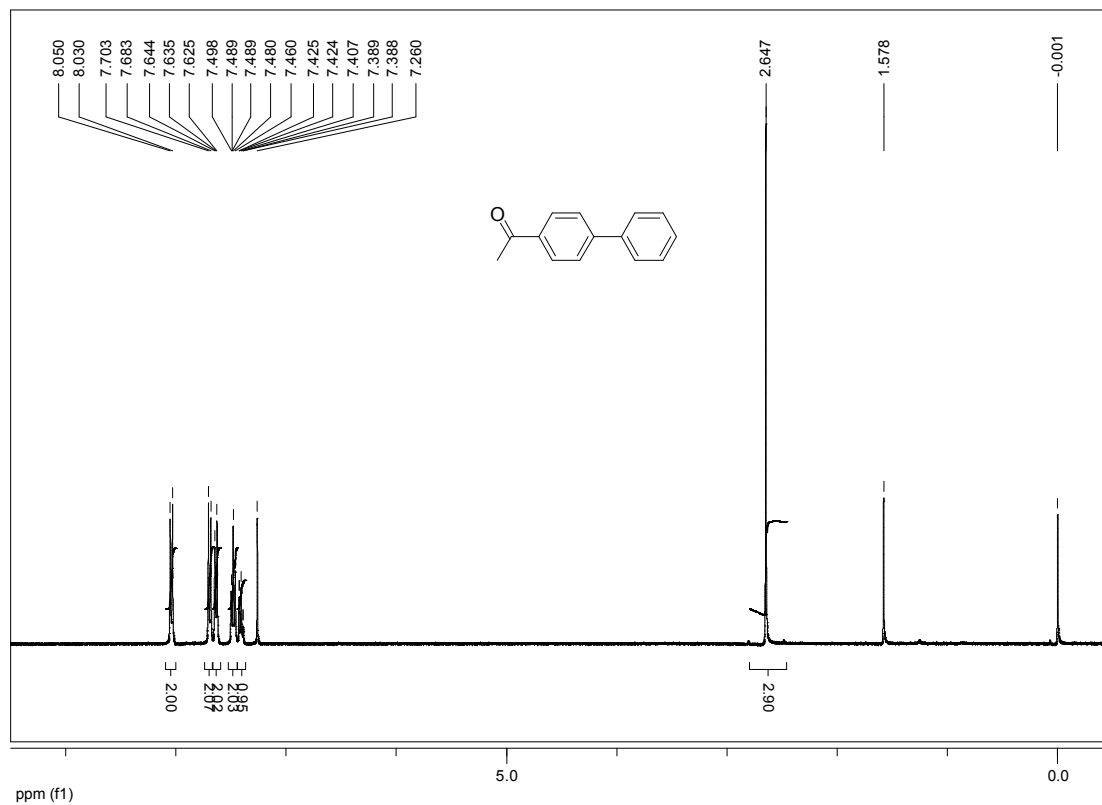
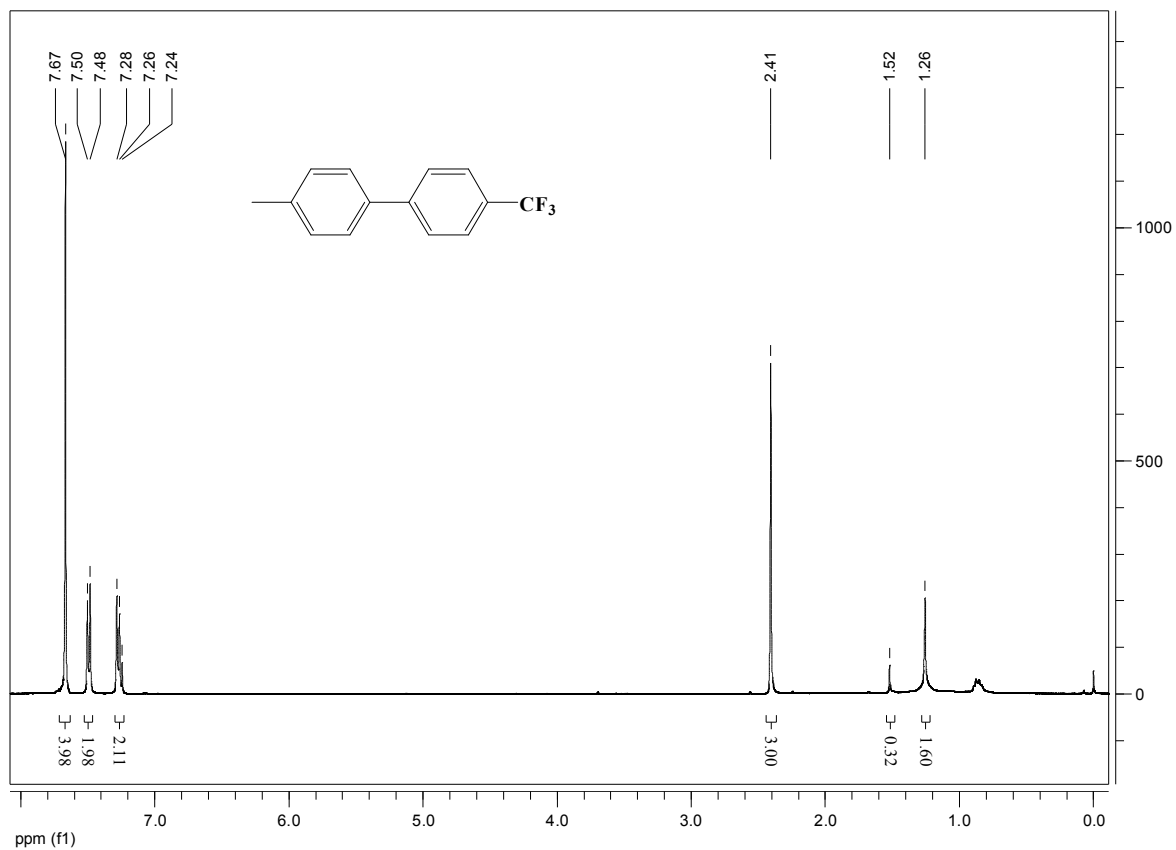




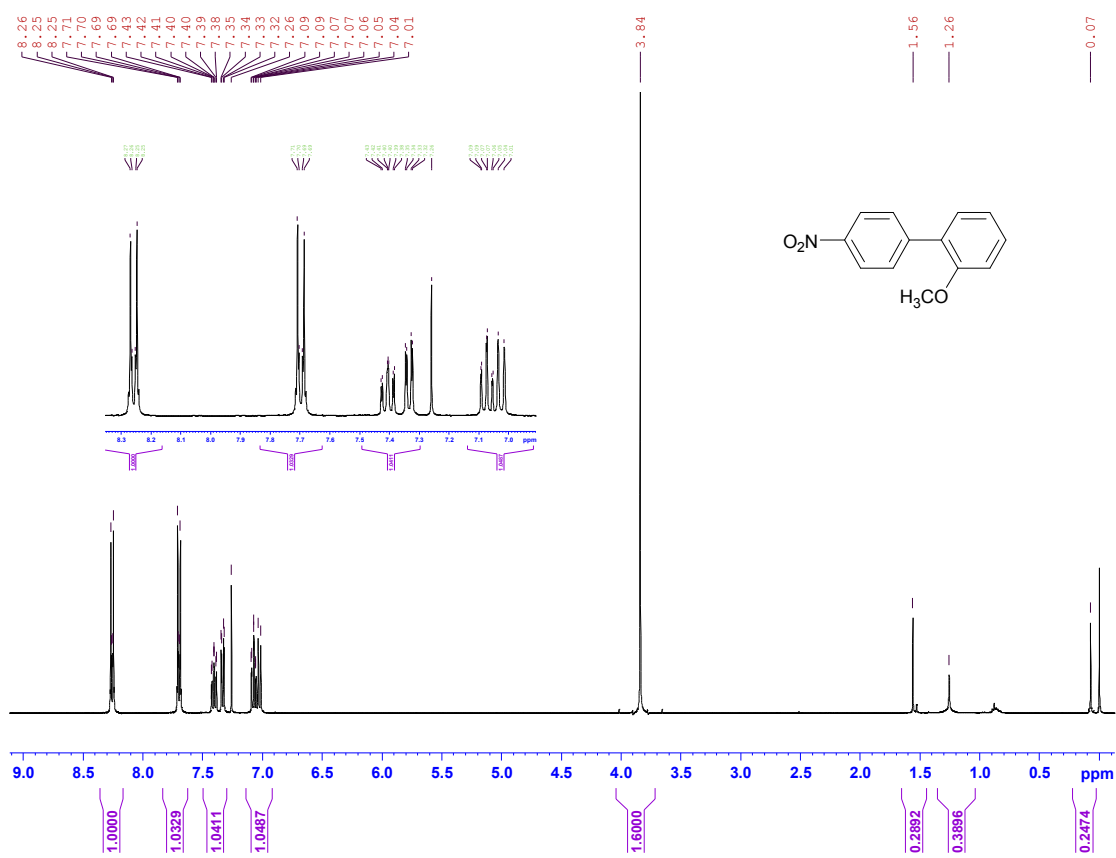
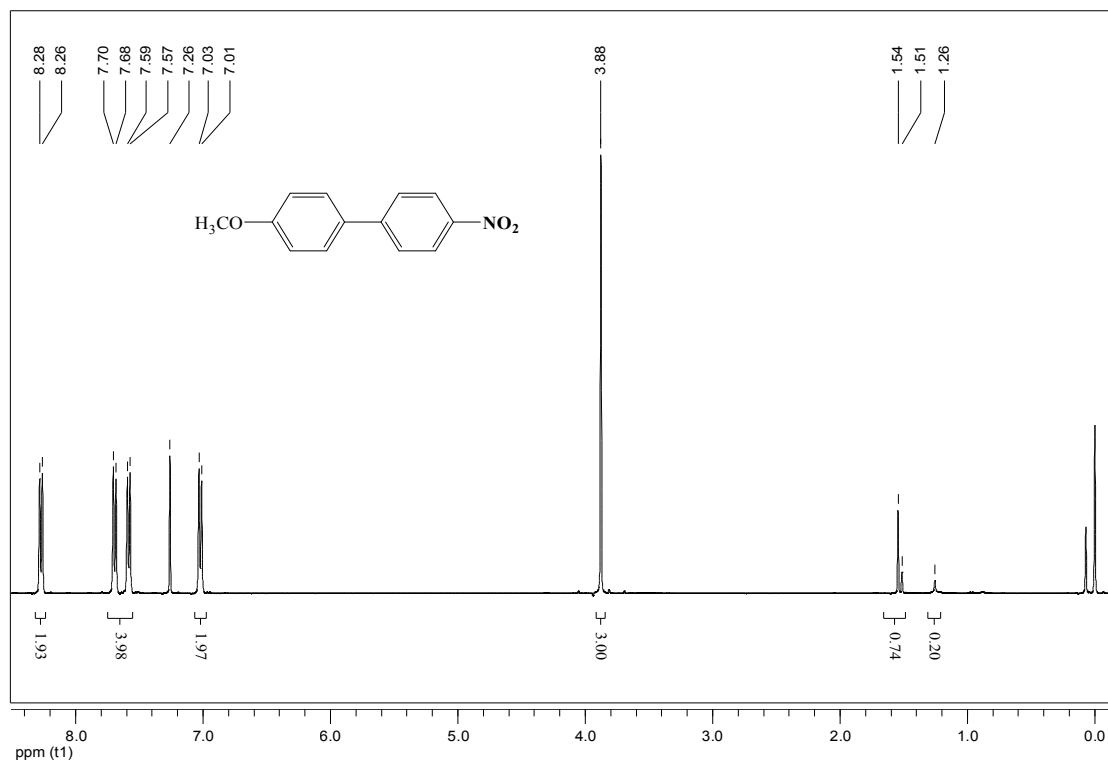


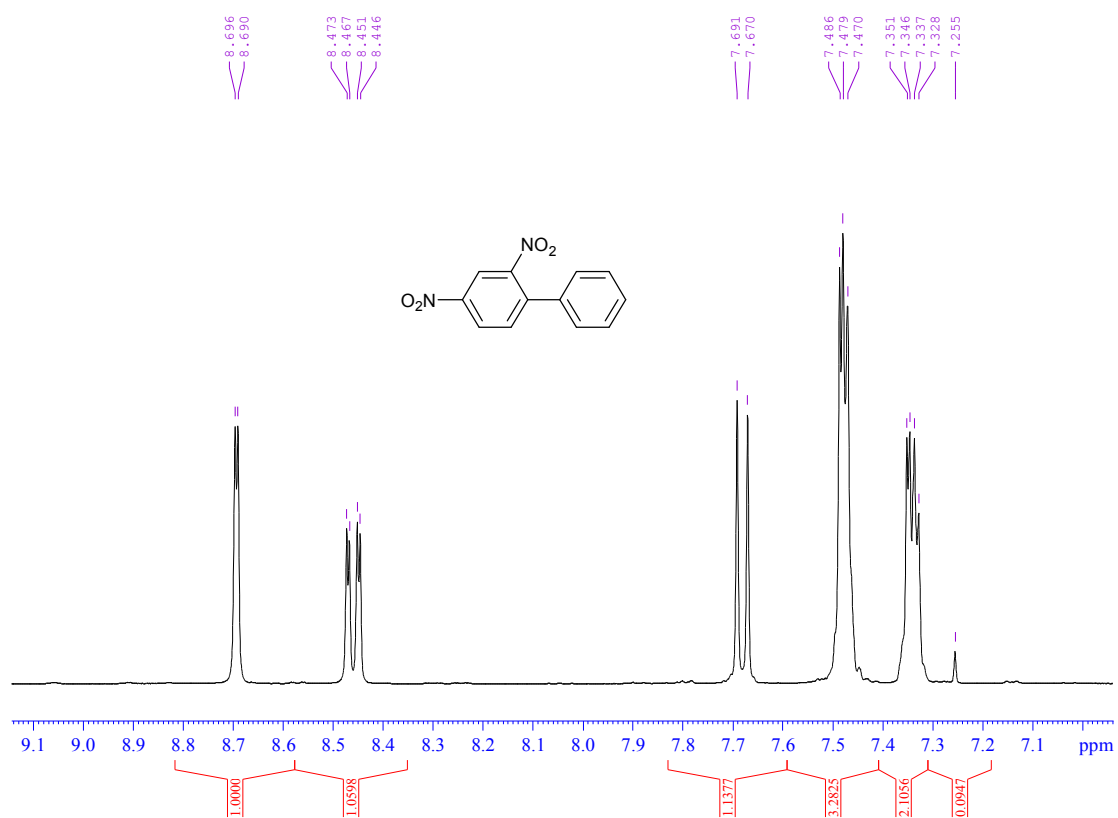
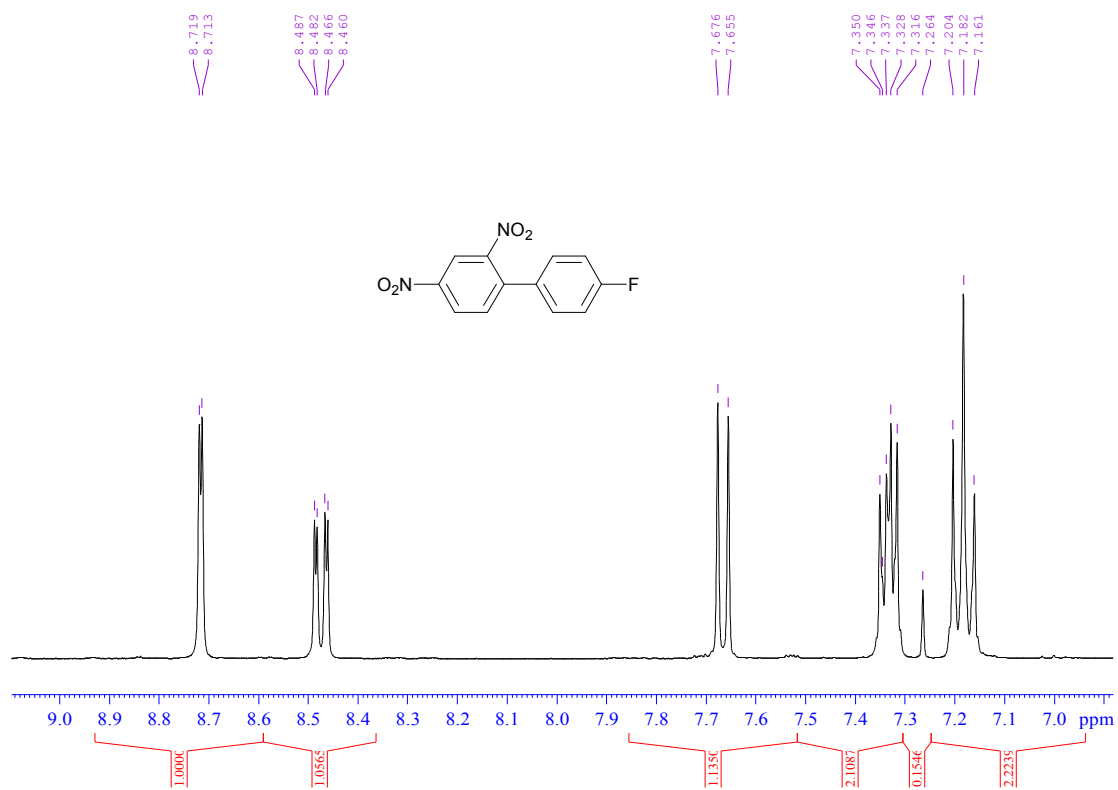


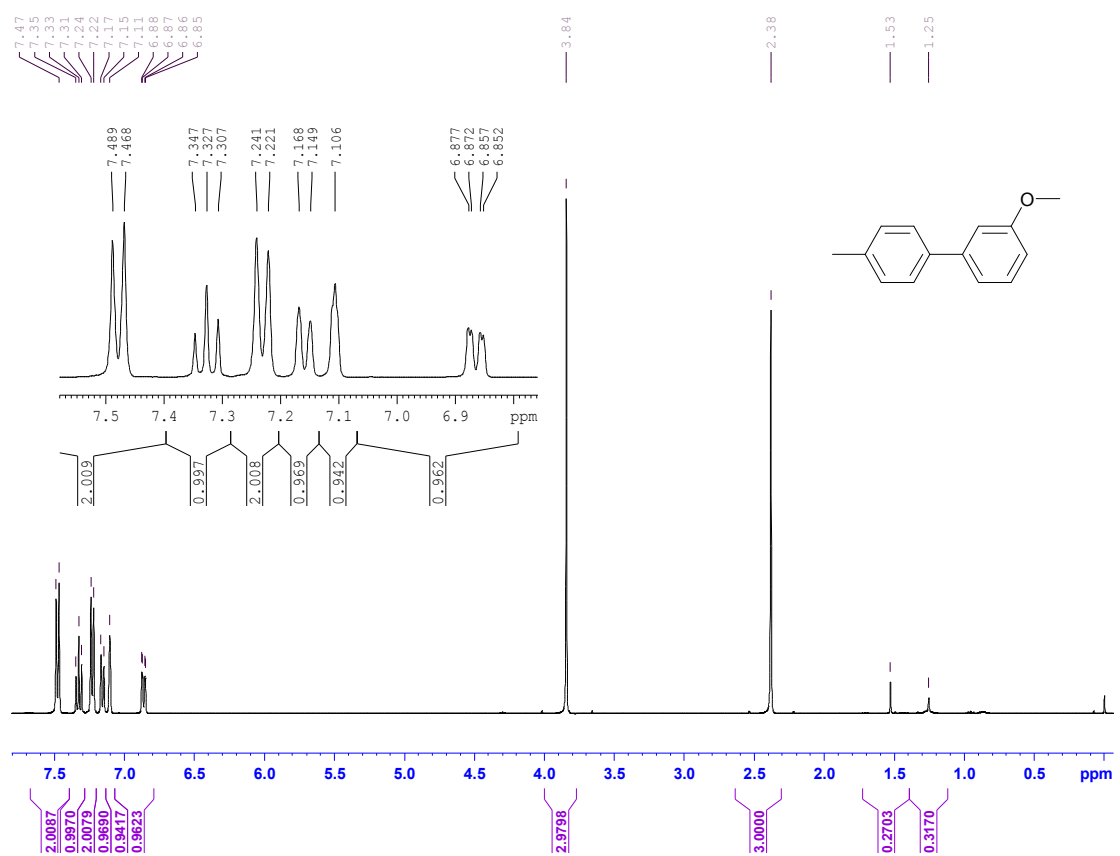
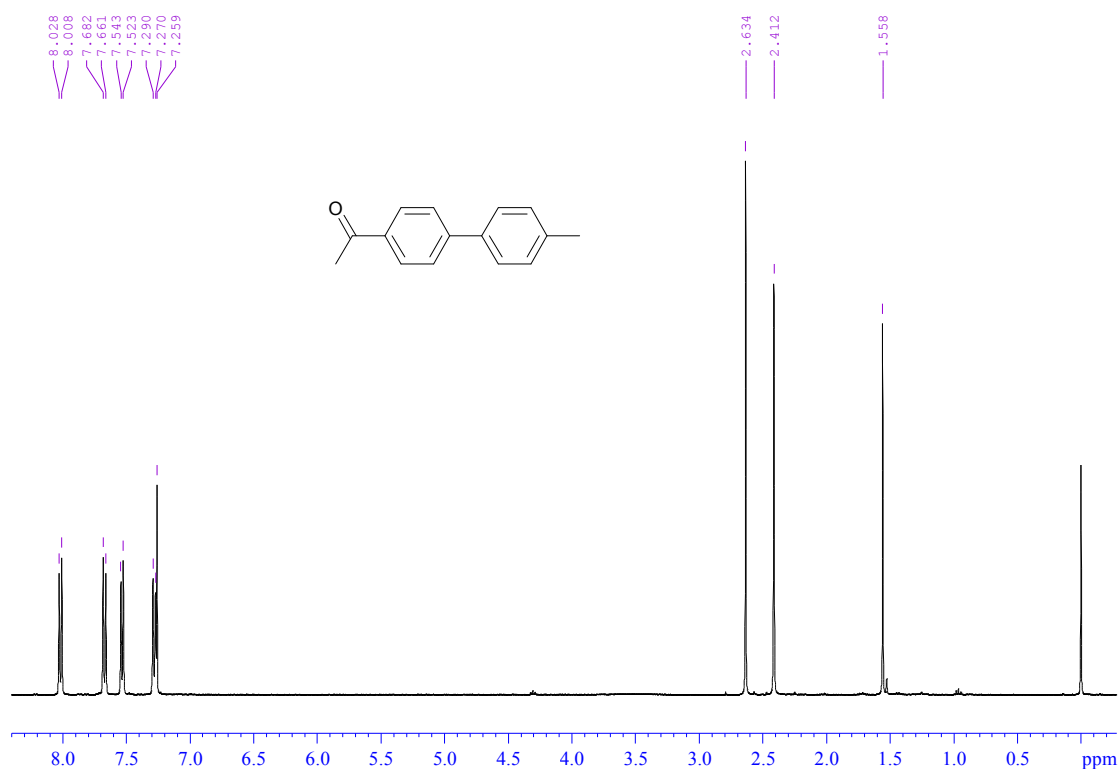


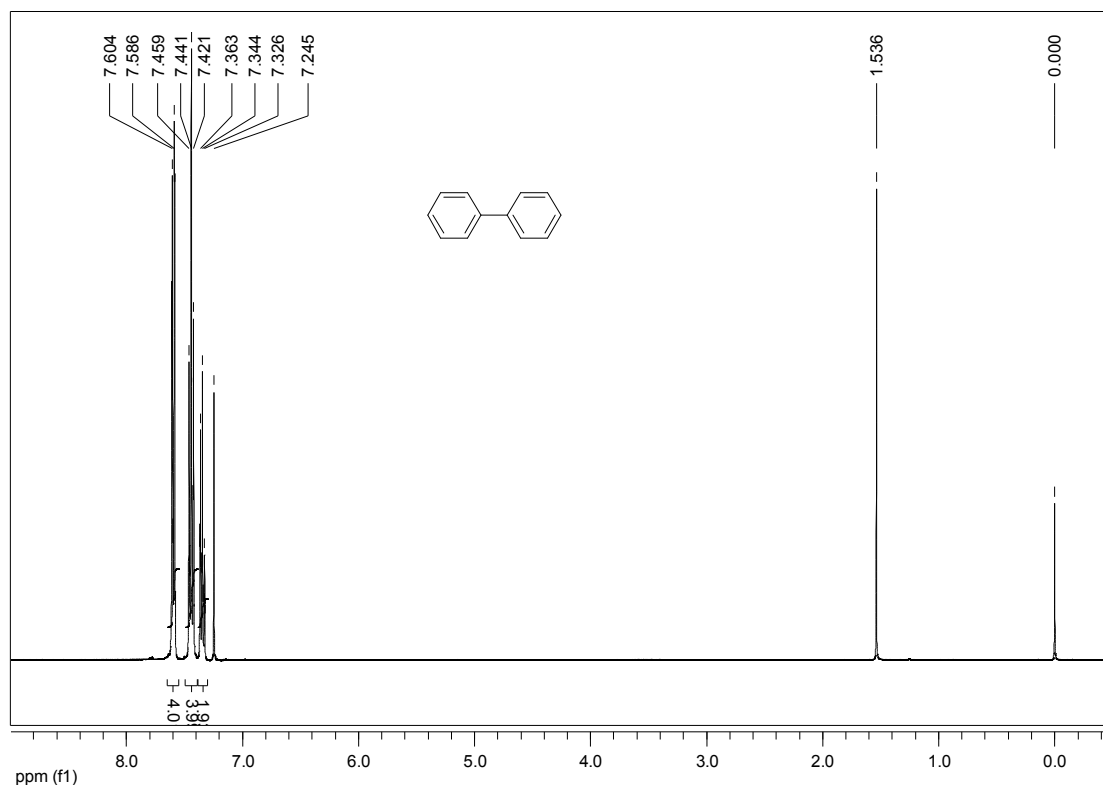






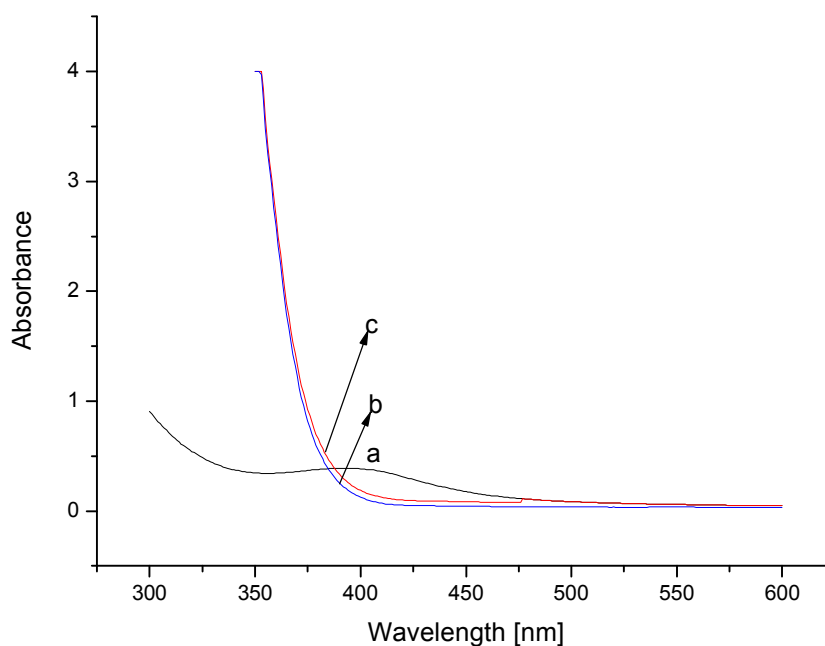






## UV spectra of Pd at Different Stages

Figure 1



**Figure 1** UV-vis absorption spectra of Pd(OAc)<sub>2</sub> (0.005 mmol) in DMF (a), and a mixture of 4-chloronitrobenzene (0.5 mmol), phenylboronic acid (0.75 mmol), Pd(OAc)<sub>2</sub> (0.5 mol%), K<sub>2</sub>CO<sub>3</sub> (1 mmol) in EtOH/DMA (2:2mL) was stirred in air at 80 °C for 30 sec (b), and 1 min (c).

From the spectra, we can see that there was a peak at 400 nm assigned to Pd(II) (Figure 1, a). After stirring for 30 sec under the cross-coupling conditions, this peak completely disappeared, revealing the fast conversion of Pd(II) to Pd(0) (Figure 1, b).