

## Supporting Information

# Copper-catalyzed reductive cross-coupling of aryl chlorides and aryl bromides

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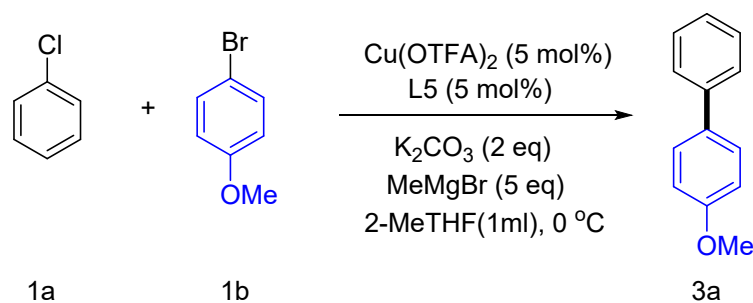
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## A. General information

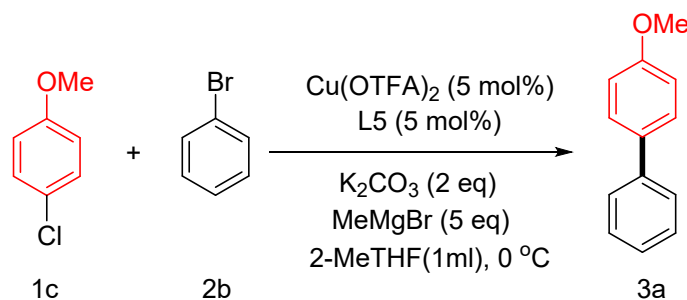
Reagents and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (TLC Silica Gel 60 F<sub>254</sub>); Visualization of the developed chromatogram was performed by fluorescence. Flash chromatography was performed with silica gel (300-400 mesh). All yields refer to isolated yields. <sup>1</sup>H NMR spectra were recorded on Bruker Ascend 400 (400 MHz) spectrometer. <sup>1</sup>H NMR spectra were calibrated using residual undeuterated solvent as an internal reference (CDCl<sub>3</sub> δ=7.26). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, triplet of doublets; td, doublet of triplets; q, quartet; m, multiplet; Coupling constants J are quoted in Hz. Chemical shifts (δ) are reported in ppm. .

## B. General procedures of the synthesis of biaryl compounds



**General procedure for the synthesis of 3a from aryl bromides and chlorobenzene.** In a glovebox,  $\text{Cu}(\text{OTFA})_2$  (0.05 equiv, 3.6 mg), the bisoxazoline (4*R*,4'*R*)-2,2'-methylenebis[4,5-dihydro-4-(phenylmethyl)oxazole] (0.05 equiv, 3.06 mg), and  $\text{K}_2\text{CO}_3$  (2.0 equiv, 55.29 mg) were added sequentially to a 5 mL vial equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with nitrogen three times. Anhydrous 2-MeTHF (1.0 mL) was then added, and the resulting mixture was stirred at room temperature for 10 min to facilitate formation of the catalytic system. Under a nitrogen atmosphere, chlorobenzene (**1a**) (0.20 mmol, 1.0 equiv, 22.52 mg) and *p*-bromoanisole (**1b**) (0.40 mmol, 2.0 equiv, 50.0  $\mu\text{L}$ ) were added sequentially. The reaction mixture was cooled to 0 °C, followed by slow dropwise addition of  $\text{MeMgBr}$  (5.0 equiv, 0.12 mL). The reaction was stirred at 0 °C for 12 h. After completion of the reaction, water was added to quench the reaction, and the mixture was extracted with ethyl acetate (3  $\times$  20 mL). The combined organic layers were washed with saturated brine, dried over anhydrous

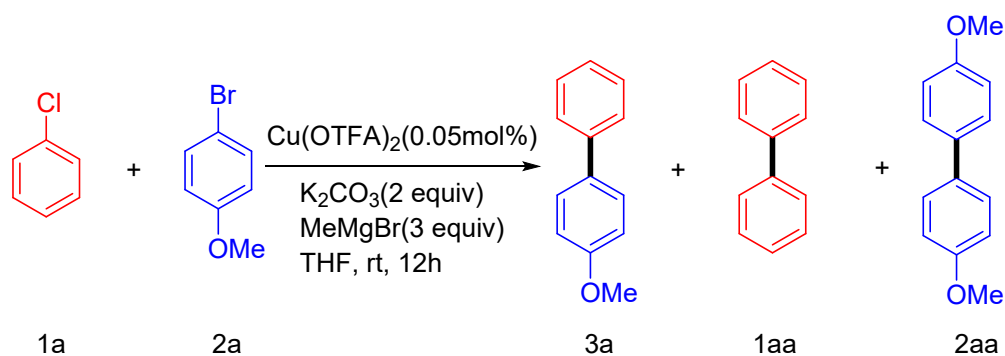
Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel (PE/EA = 80:1) to afford the desired product **3a**.



**General procedure for synthesising 3a from aryl chlorides and bromobenzene.** In a glovebox, Cu(OTFA)<sub>2</sub> (0.05 equiv, 3.6 mg), the bisoxazoline(4R,4'R)-2,2'-methylenebis[4,5-dihydro-4-(phenylmethyl)oxazole] (0.05 equiv, 3.06 mg), and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv, 55.29 mg) were added sequentially to a 5 mL vial equipped with a magnetic stir bar. The reaction vessel was evacuated and backfilled with nitrogen three times, after which anhydrous 2-MeTHF (1.0 mL) was added. The resulting mixture was stirred at room temperature for 10 min to facilitate formation of the catalytic system. Under a nitrogen atmosphere, bromobenzene (**2b**) (0.20 mmol, 1.0 equiv, 31.41 mg) and p-chloroanisole (**1c**) (0.40 mmol, 2.0 equiv, 49.0 μL) were added sequentially. The reaction mixture was cooled to 0 °C, followed by slow dropwise addition of MeMgBr (5.0 equiv, 0.12 mL). The reaction was stirred at 0 °C for 12 h. After completion of the reaction, water was added

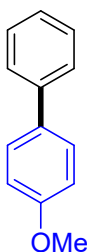
to quench the reaction, and the mixture was extracted with ethyl acetate (3 times). The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (PE/EA = 80:1) to afford the desired product **3a**.

## C. Reaction optimization



Entry	2a/1a	[Cu] (eq)	Ligand (eq)	Base (eq)	Reductant (eq)	Solvent (mL)	Yield of 3a (%) <sup>[a]</sup>	Ratio of 3a/1aa/2aa
1	1.5	Cu(OAc) <sub>2</sub> (0.05)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	15	4/2/1
2	1.5	CuBr <sub>2</sub> (0.05)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	21	3/2/5
3	1.5	CuCl <sub>2</sub> (0.05)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	20	1/1/2
4	1.5	Cu(OTFA) <sub>2</sub> (0.05)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	33	2/1/1
5	1.5	CuSO <sub>4</sub> (0.05)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	10	1/2/2
6	1.5	Cu(OTFA) <sub>2</sub> (0.1)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	37	2.5/1.1/1
7	1.5	Cu(OTFA) <sub>2</sub> (0.15)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	38	2.5/1/1
8	1.5	Cu(OTFA) <sub>2</sub> (0.20)	–	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	37	2/1/1
9	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L1 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	21	3/1/1
10	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L2 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	35	6/2/1
11	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L3 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	37	3/2/2
12	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L4 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	38	4/1/2
13	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	54	7/0.5/1
14	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L6 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	56	6/0.7/1
15	1.5	Cu(OTFA) <sub>2</sub> (0.05)	L7 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	40	6/1.4/1
16	1.75	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	58	6/1/2
17	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	59	6/1/2
18	2.5	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	THF (1)	56	6/1/2.1
19	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (1)	MeMgBr (3)	THF (1)	40	7/1/2
20	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (1.5)	MeMgBr (3)	THF (1)	43	7/1/2
21	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2.5)	MeMgBr (3)	THF (1)	61	6/1/2
22	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (3)	MeMgBr (3)	THF (1)	64	6/1/2
23	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (3.5)	MeMgBr (3)	THF (1)	65	6/1/2
24	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (4)	MeMgBr (3)	THF (1)	63	6/1/2
25	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	Toluene (1)	0	–
26	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	Benzene (1)	0	–
27	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	Et <sub>2</sub> O (1)	0	–
28	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	MeOrBu (1)	0	–
29	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (3)	2-MeTHF (1)	69	7/1/1.5
30	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	Zn (2)	2-MeTHF (1)	0	–
31	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	Fe (2)	2-MeTHF (1)	0	–
32	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (1)	2-MeTHF (1)	55	7/1/1.5
33	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (5)	2-MeTHF (1)	76	7/1/1.5
34	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (7)	2-MeTHF (1)	76	7/1/1.5
35	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (5)	2-MeTHF (1) -20°C	66	10/0.5/1
36	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (5)	2-MeTHF (1) 0°C	82	10/1/1.2
37	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (5)	2-MeTHF (1) 50°C	84	2/1/1.3
38	2	Cu(OTFA) <sub>2</sub> (0.05)	L5 (0.05)	K <sub>2</sub> CO <sub>3</sub> (2)	MeMgBr (5)	2-MeTHF (1) 75°C	60	2/1/1.3

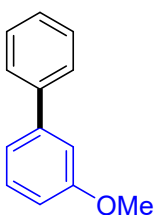
#### D. Analytical data of products



4-methoxy-1,1'-biphenyl(**3a**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (100:1 to 80:1), to give a white powdery solid (15.10 mg, 82%).  $^1\text{H NMR}$  (400 MHz, Chloroform-d)  $\delta$  = 3.85 (s, 3H), 6.94 – 7.03 (m, 2H), 7.27 – 7.35 (m, 1H), 7.42 (dd,  $J=6.93, 8.57$ , 2H), 7.55 (ddd,  $J=1.68, 7.63, 9.24$ , 4H).  $\text{HRMS}$  (ESI) calcd for  $\text{C}_{13}\text{H}_{12}\text{O}$   $[\text{M}+\text{H}]^+$ : 185.0961, found: 185.0956.

The  $^{13}\text{C NMR}$  data are consistent with those reported in the literature<sup>[1]</sup>.

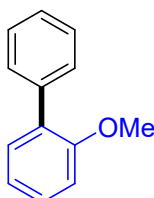


3-methoxy-1,1'-biphenyl(**3b**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (100:1 to 75:1), to give a colourless liquid (16.40 mg, 89%).  $^1\text{H NMR}$  (400 MHz, Chloroform-d)  $\delta$  = 3.97 (s, 3H), 7.05 (ddd,  $J=0.95, 2.64, 8.18$ ,

1H), 7.34 (dt, J=1.30, 7.67, 1H), 7.49 (td, J=2.50, 7.61, 2H), 7.55 – 7.60 (m, 2H), 7.72 – 7.77 (m, 2H). **HRMS** (ESI) calcd for  $C_{13}H_{12}O[M+Na]^+$ :207.0781, found: 207.0787.

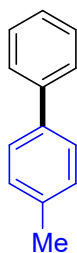
The  $^{13}C$  **NMR** data are consistent with those reported in the literature<sup>[2]</sup>.



2-methoxy-1,1'-biphenyl(**3c**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (100 to 70:1) to afford a white solid (16.03 mg, 87%).  $^1H$  **NMR** (400 MHz, Chloroform-d)  $\delta$  = 3.99 (s, 3H), 7.19 (d, J=8.24, 1H), 7.50 – 7.59 (m, 3H), 7.64 (t, J=7.61, 2H), 7.77 – 7.82 (m, 2H). **HRMS** (ESI) calcd for  $C_{13}H_{12}O [M+H]^+$ :185.0961, found: 185.0967.

The  $^{13}C$  **NMR** data are consistent with those reported in the literature<sup>[1]</sup>.

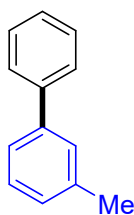


4-methyl-1,1'-biphenyl(**3d**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (100:1 to 75:1) to afford a white solid (15.65 mg, 93%).  $^1H$  **NMR** (400

MHz, Chloroform-*d*)  $\delta = 2.33$  (s, 3H), 7.19 (d,  $J=7.84$ , 2H), 7.36 (dd,  $J=6.89, 8.43$ , 2H), 7.42 – 7.46 (m, 2H), 7.50 – 7.55 (m, 2H). **HRMS** (ESI) calcd for C<sub>13</sub>H<sub>12</sub> [M+Na]<sup>+</sup>:191.0832, found: 191.0827.

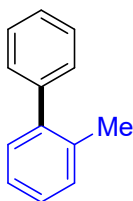
The <sup>13</sup>C **NMR** data are consistent with those reported in the literature<sup>[1]</sup>.



3-methyl-1,1'-biphenyl(**3e**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (95:1 to 80:1), to give a colourless liquid (15.14 mg, 90%). <sup>1</sup>H **NMR** (400 MHz, Chloroform-*d*)  $\delta = 2.58$  (d,  $J=2.37$ , 3H), 7.32 (d,  $J=7.50$ , 1H), 7.43 – 7.52 (m, 2H), 7.53 – 7.63 (m, 4H), 7.75 (ddd,  $J=1.27, 2.59, 8.31$ , 2H). **HRMS** (ESI) calcd for C<sub>13</sub>H<sub>12</sub> [M+Na]<sup>+</sup>:191.0832, found: 191.0838.

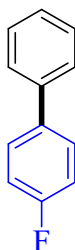
The <sup>13</sup>C **NMR** data are consistent with those reported in the literature<sup>[1]</sup>.



2-methyl-1,1'-biphenyl(**3f**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (100:1 to 70:1), to give a colourless liquid (14.81 mg, 88%). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 2.51 (s, 3H), 7.42 – 7.51 (m, 4H), 7.51 – 7.58 (m, 3H), 7.59 – 7.62 (m, 1H). **HRMS** (ESI) calcd for C<sub>13</sub>H<sub>12</sub> [M+Na]<sup>+</sup>: 191.0832, found: 191.0828.

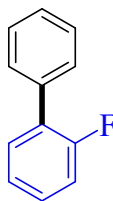
The **<sup>13</sup>C NMR** data are consistent with those reported in the literature<sup>[1]</sup>.



4-fluoro-1,1'-biphenyl(**3g**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (100:1 to 70:1), to give a white solid (14.81 mg, 88%). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 7.10 – 7.17 (m, 4H), 7.32 – 7.38 (m, 2H), 7.41 – 7.47 (m, 1H), 7.53 – 7.57 (m, 2H). **HRMS** (ESI) calcd for C<sub>12</sub>H<sub>9</sub>F [M+H]<sup>+</sup>: 173.0762, found: 173.0768.

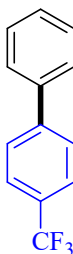
The **<sup>13</sup>C NMR** data are consistent with those reported in the literature<sup>[3]</sup>.



2-fluoro-1,1'-biphenyl(**3h**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (75:1 to 60:1) to afford a white solid (13.43mg, 78%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.19 – 7.26 (m, 2H), 7.26 – 7.31 (m, 3H), 7.39 (dddd,  $J=1.85, 5.00, 6.98, 8.06$ , 1H), 7.42 – 7.48 (m, 1H), 7.49 – 7.57 (m, 1H), 7.65 (dt,  $J=1.50, 8.14$ , 1H). HRMS (ESI) calcd for C<sub>12</sub>H<sub>9</sub>F [M+Na]<sup>+</sup>: 195.0581, found: 195.0586.

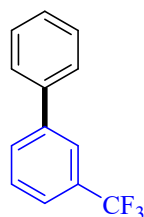
The <sup>13</sup>C NMR data are consistent with those reported in the literature<sup>[4]</sup>.



4-(trifluoromethyl)-1,1'-biphenyl(**3i**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (50:1 to 20:1) to afford a white solid (18.01mg, 81%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.40 – 7.46 (m, 4H), 7.47 – 7.53 (m, 2H), 7.60 – 7.64 (m, 2H), 7.71 (s, 1H). HRMS (ESI) calcd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub> [M+H]<sup>+</sup>: 183.1169, found: 183.1175.

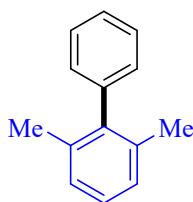
The  $^{13}\text{C}$  NMR data are consistent with those reported in the literature<sup>[1]</sup>.



3-(trifluoromethyl)-1,1'-biphenyl(**3j**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (60:1 to 20:1) to afford a white solid (17.38mg, 78%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 7.42 – 7.47 (m, 1H), 7.52 (dd,  $J=6.63, 8.33$ , 2H), 7.58 – 7.67 (m, 4H), 7.81 (d,  $J=7.63$ , 1H), 7.89 (s, 1H). **HRMS** (ESI) calcd for  $\text{C}_{13}\text{H}_9\text{F}_3$   $[\text{M}+\text{Na}]^+$ : 205.0988, found: 205.0993.

The  $^{13}\text{C}$  NMR data are consistent with those reported in the literature<sup>[5]</sup>.

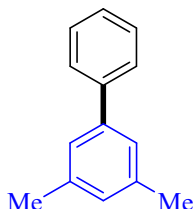


2,6-dimethyl-1,1'-biphenyl(**3k**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (65:1 to 40:1) to afford a white solid (13.67mg, 75%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  = 1.89 (s, 6H), 6.90 – 7.01 (m, 4H), 7.01 – 7.08

(m, 1H), 7.14 – 7.22 (m, 1H), 7.23 – 7.30 (m, 2H). **HRMS** (ESI) calcd for  $C_{14}H_{14}[M+H]^+$ : 183.1169, found: 183.1175.

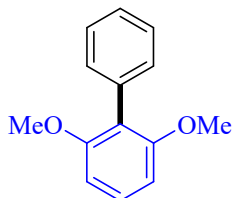
The  $^{13}C$  **NMR** data are consistent with those reported in the literature<sup>[6]</sup>.



3,5-dimethyl-1,1'-biphenyl(**3l**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (75:1 to 60:1), yielding a pale yellow liquid (14.95 mg, 82%).  $^1H$  **NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 2.41 (s, 6H), 7.02 (s, 1H), 7.24 (d,  $J=1.52$ , 2H), 7.33 – 7.38 (m, 1H), 7.40 – 7.49 (m, 2H), 7.56 – 7.63 (m, 2H). **HRMS** (ESI) calcd for  $C_{14}H_{14}[M+Na]^+$ : 205.0988, found: 205.0983.

The  $^{13}C$  **NMR** data are consistent with those reported in the literature<sup>[7]</sup>.

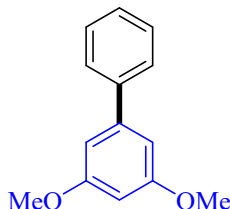


2,6-dimethoxy-1,1'-biphenyl(**3m**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate

(50:1 to 40:1), yielding a pale yellow solid (12.76 mg, 70%). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 3.73 (s, 6H), 6.66 (d,  $J$ =8.37, 2H), 7.28 (s, 1H), 7.29 – 7.33 (m, 1H), 7.33 – 7.36 (m, 2H), 7.41 (t,  $J$ =7.48, 2H). **HRMS** (ESI) calcd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 215.1067, found: 215.1072.

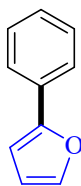
The **<sup>13</sup>C NMR** data are consistent with those reported in the literature<sup>[8]</sup>.



3,5-dimethoxy-1,1'-biphenyl(**3n**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (75:1 to 60:1), yielding a pale yellow liquid (16.04 mg, 88%). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 3.88 (s, 6H), 6.52 (dt,  $J$ =1.54, 3.09, 1H), 6.79 (dd,  $J$ =0.79, 2.30, 2H), 7.36 – 7.42 (m, 1H), 7.44 – 7.50 (m, 2H), 7.60 – 7.65 (m, 2H). **HRMS** (ESI) calcd for C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> [M+Na]<sup>+</sup>: 237.0886, found: 237.0892.

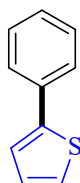
The **<sup>13</sup>C NMR** data are consistent with those reported in the literature<sup>[3]</sup>.



2-phenylfuran(**3o**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (90:1 to 70:1), yielding a pale yellow liquid (12.25 mg, 85%). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 6.52 (dd,  $J=1.81, 3.44$ , 1H), 6.70 (d,  $J=3.41$ , 1H), 7.29 – 7.35 (m, 1H), 7.43 (dd,  $J=7.09, 8.36$ , 2H), 7.52 (dd,  $J=0.81, 1.80$ , 1H), 7.72 – 7.76 (m, 2H). **HRMS** (ESI) calcd for C<sub>10</sub>H<sub>8</sub>O [M+H]<sup>+</sup>: 145.0648, found: 145.0642.

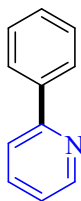
The **<sup>13</sup>C NMR** data are consistent with those reported in the literature<sup>[9]</sup>.



2-phenylthiophene(**3p**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (75:1 to 60:1) to afford a white solid (12.02mg, 75%). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  = 7.15 (dd,  $J=3.60, 5.08$ , 1H), 7.31 – 7.40 (m, 3H), 7.42 – 7.47 (m, 2H), 7.67 – 7.72 (m, 2H). **HRMS** (ESI) calcd for C<sub>10</sub>H<sub>8</sub>S [M+H]<sup>+</sup>: 161.0420, found: 161.0420.

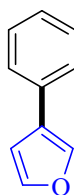
The  $^{13}\text{C}$  NMR data are consistent with those reported in the literature<sup>[6]</sup>.



2-phenylpyridine(3q)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (35:1 to 20:1), to give a colourless liquid (9.47 mg, 61%).  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  = 7.11 (ddtt,  $J=1.62, 3.19, 4.78, 6.32$ , 1H), 7.33 – 7.50 (m, 3H), 7.61 (dddt,  $J=1.77, 3.97, 7.16, 11.00$ , 2H), 8.00 (dt,  $J=1.48, 8.23$ , 2H), 8.65 – 8.69 (m, 1H). HRMS (ESI) calcd for  $\text{C}_{11}\text{H}_9\text{N}$   $[\text{M}+\text{Na}]^+$ : 178.0625, found: 178.0632.

The  $^{13}\text{C}$  NMR data are consistent with those reported in the literature<sup>[3]</sup>.



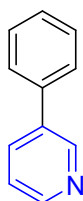
3-phenylfuran(3r)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (80:1 to 60:1) to afford a white solid (11.82mg, 81%).  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  = 6.75 (t,  $J=1.32$ , 1H), 7.27 – 7.34 (m, 1H), 7.41

(dd,  $J=6.90, 8.52, 2H$ ), 7.49 – 7.57 (m, 3H), 7.77 (t,  $J=1.21, 1H$ ). **HRMS**

(ESI) calcd for  $C_{10}H_8O [M+Na]^+$ : 167.0468, found: 167.0459.

The  $^{13}C$  **NMR** data are consistent with those reported in the literature<sup>[10]</sup>.



3-phenylpyridine(**3s**)

Prepared according to the general procedure and purified by silica gel column chromatography, eluted with petroleum ether/ethyl acetate (80:1 to 60:1) to afford a colourless liquid (12.41mg, 81%).  $^1H$  **NMR** (400 MHz, Chloroform-d)  $\delta = 7.17 - 7.23$  (m, 1H), 7.27 – 7.31 (m, 1H), 7.35 (dd,  $J=6.73, 8.35, 2H$ ), 7.43 – 7.47 (m, 2H), 7.71 (ddd,  $J=1.59, 2.42, 7.91, 1H$ ), 8.49 (dd,  $J=1.61, 4.85, 1H$ ), 8.76 (dd,  $J=0.85, 2.46, 1H$ ). **HRMS** (ESI) calcd for  $C_{11}H_9N [M+H]^+$ : 156.0808, found: 156.0810.

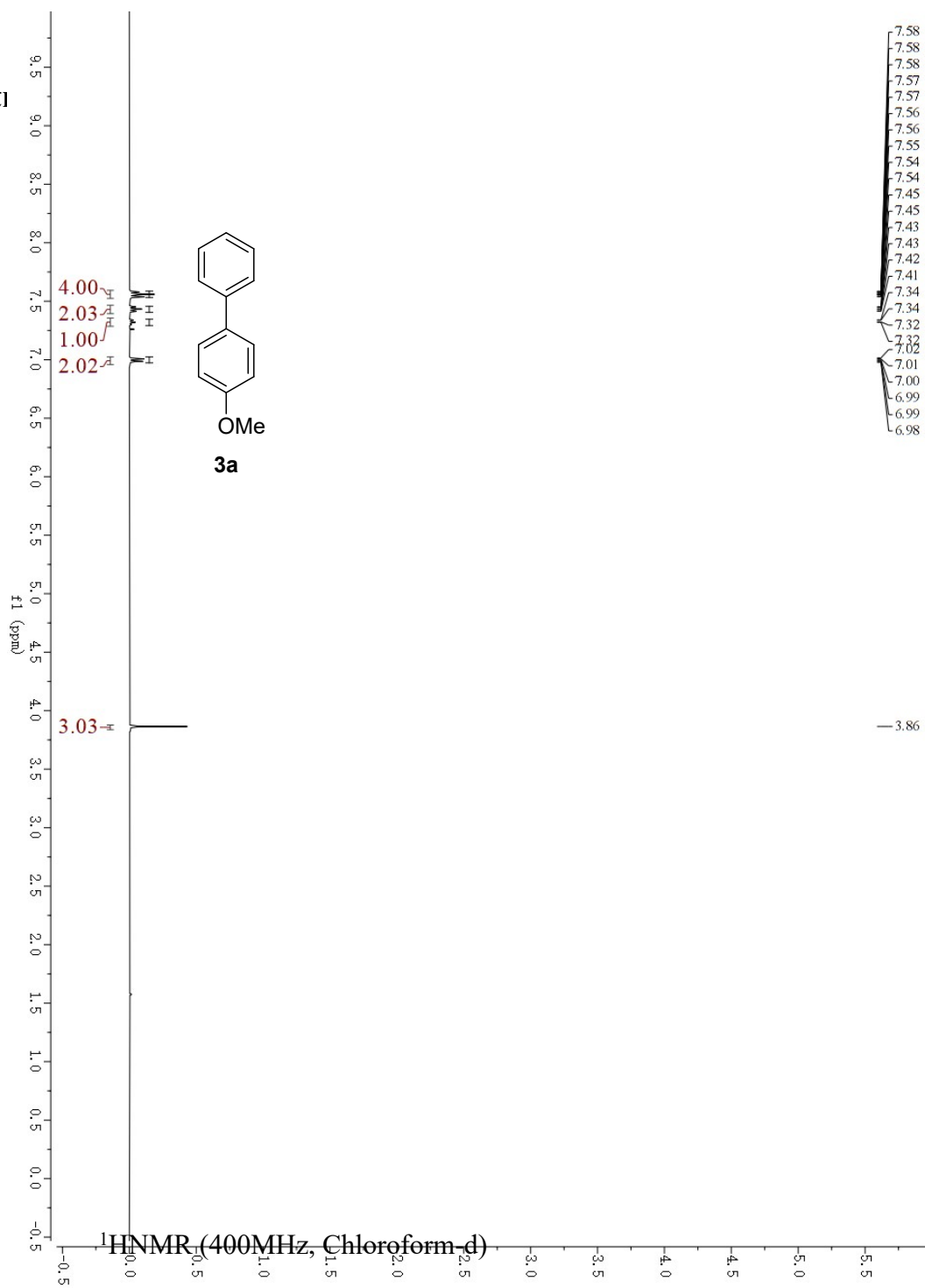
The  $^{13}C$  **NMR** data are consistent with those reported in the literature<sup>[10]</sup>

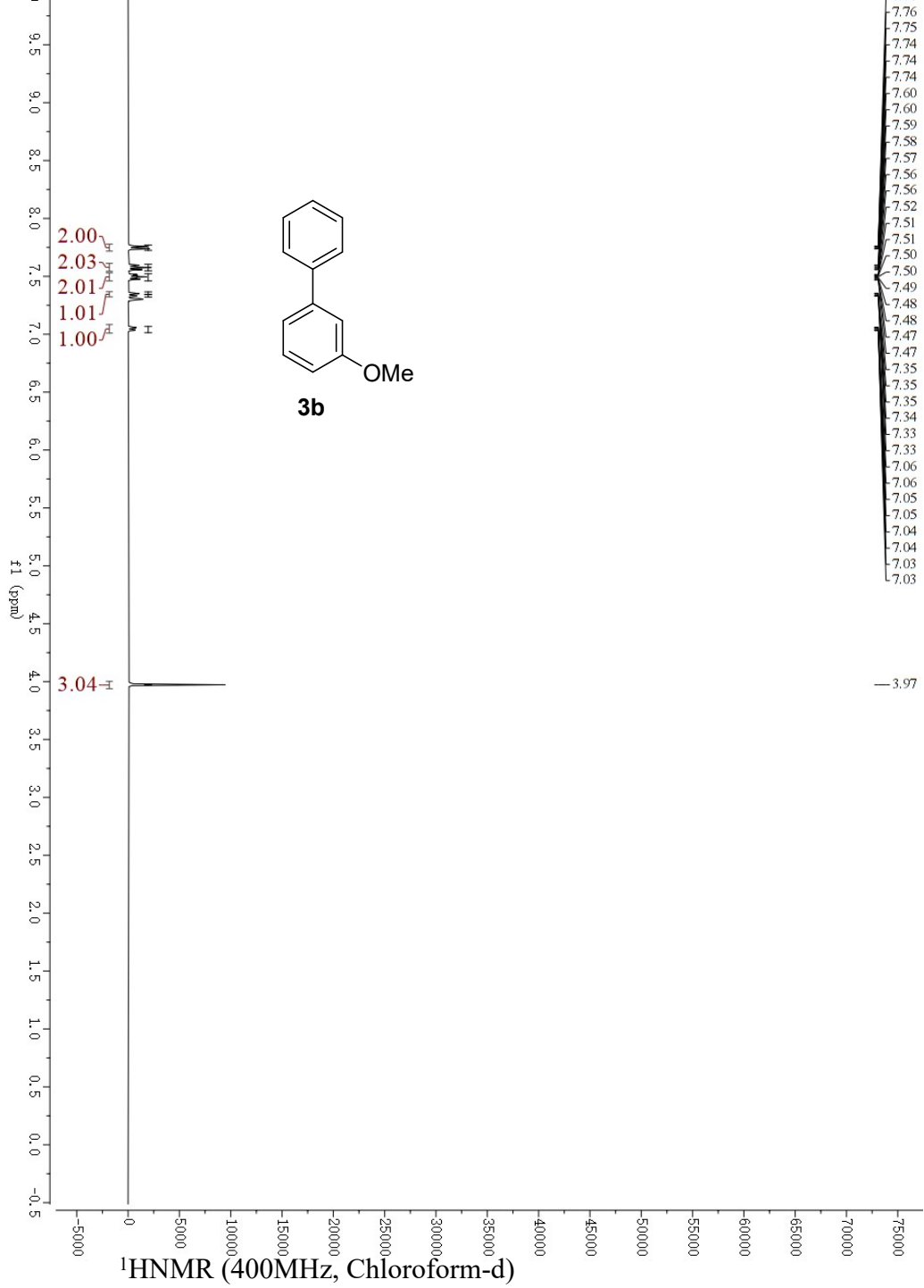
## E. References

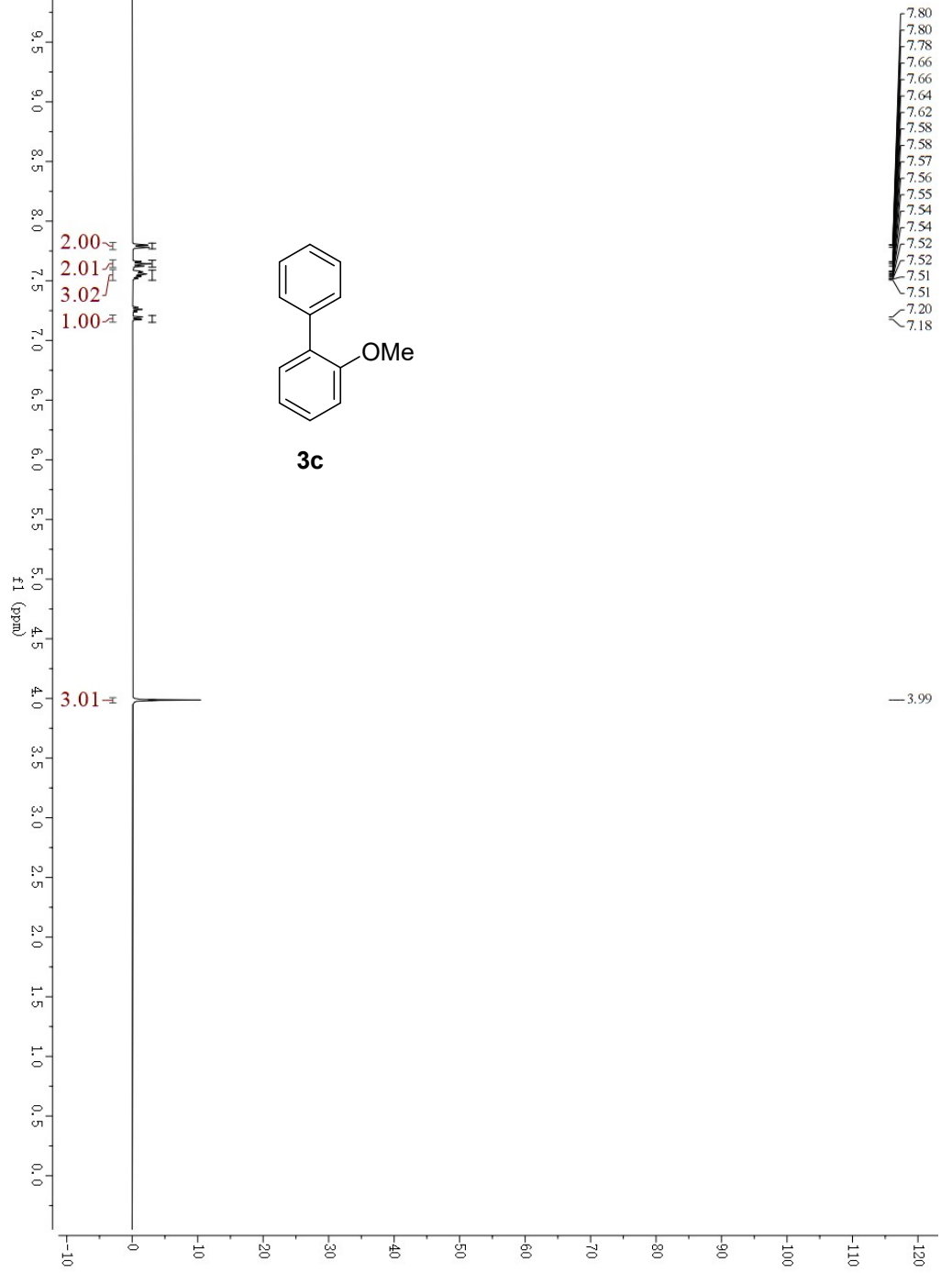
- [1] PUTHIARAJ P, AHN W-S. Highly active palladium nanoparticles immobilized on NH<sub>2</sub>-MIL-125 as efficient and recyclable catalysts for Suzuki–Miyaura cross coupling reaction [J]. *Catalysis Communications*, 2015, 65: 91–5
- [2] WASIAK T, ŁUKOWIEC D, WACŁAWEK S, et al. Ni nanowires decorated with Pd nanoparticles as an efficient nanocatalytic system for Suzuki coupling of anisole derivatives [J]. *Nano-Structures & Nano-Objects*, 2023, 36.
- [3] XU X H, AZUMA A, KUSUDA A, et al. Suzuki–Miyaura Cross-Coupling Reactions in a Solkane365/227/Ethanol Blend at Ambient Temperature [J]. *European Journal of Organic Chemistry*, 2012, 2012(8): 1504–8.
- [4] M X, GAO L, WENG Z, et al. Highly active PdCu/graphene catalyst for an efficient Suzuki cross-coupling reaction [J]. *New Journal of Chemistry*, 2020, 44(47): 20525–9.
- [5] A. Bezaatpour, M. Amiri, H. Vocke, A. Akhundi and M. Wark, *Journal of Organometallic Chemistry*, 2025, 1030, 123573.
- [6] CHEN M T, KAO Z L. Effect on orthometallation of NHC palladium complexes toward the catalytic activity studies in Suzuki coupling reaction [J]. *Dalton Trans*, 2017, 46(47): 16394–8.

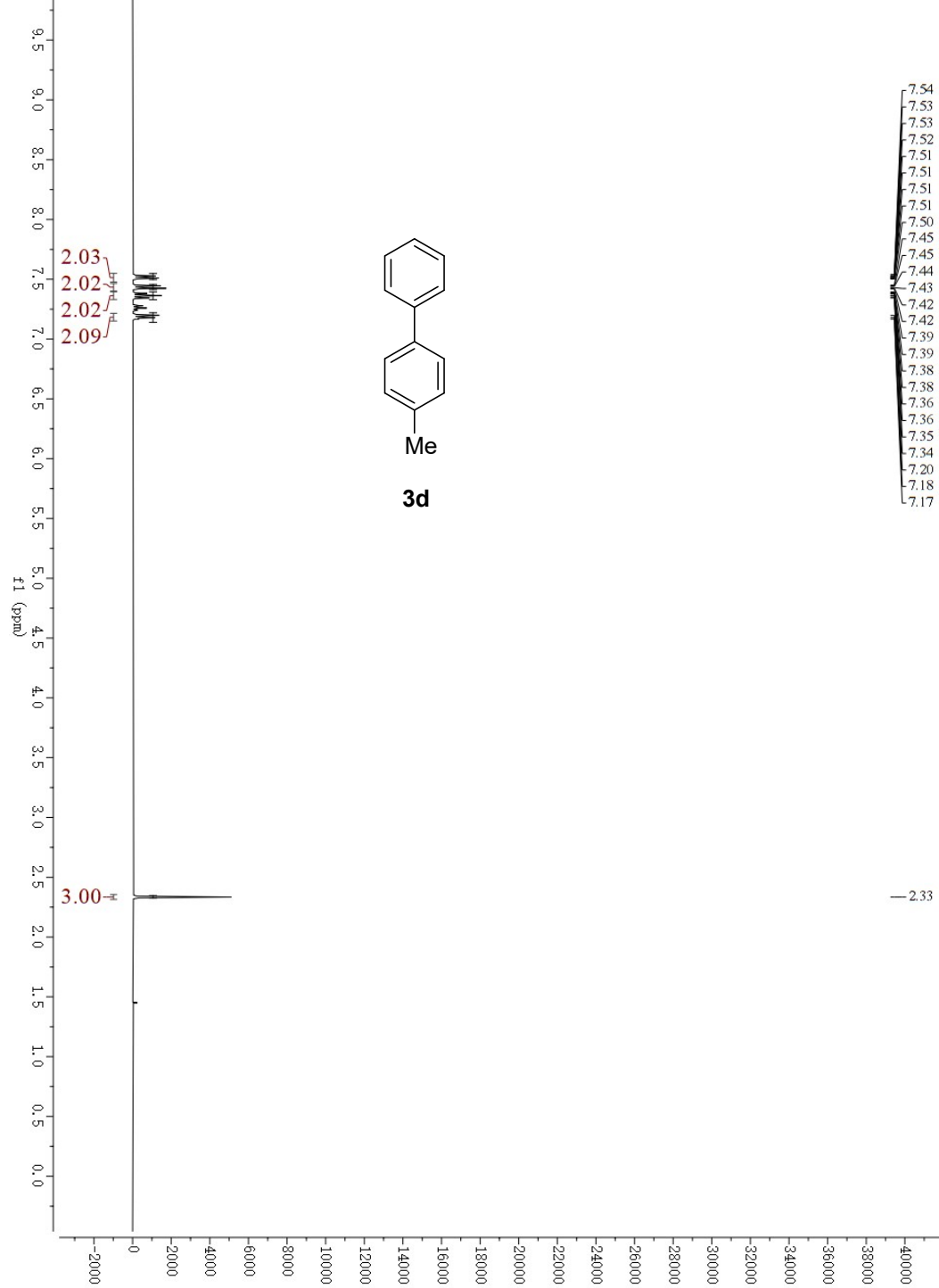
- [7] RIZZO G, ALBANO G, LO PRESTI M, et al. Palladium Supported on Silk Fibroin for Suzuki–Miyaura Cross-Coupling Reactions [J]. *European Journal of Organic Chemistry*, 2020, 2020(45): 6992–6.
- [8] TRUONG T, DAUGULIS O. Base-mediated intermolecular sp<sup>2</sup> C-H bond arylation via benzyne intermediates [J]. *J Am Chem Soc*, 2011, 133(12): 4243–5.
- [9] LUO W, JIANG K, LI Y, et al. Direct Alkoxy carbonylation of Heteroarenes via Cu-Mediated Trichloromethylation and In Situ Alcoholysis [J]. *Organic Letters*, 2020, 22(5): 2093–8.
- [10] KONDOLFF I, DOUCET H, SANTELLI M. Palladium / tetraphosphine catalyzed Suzuki cross-coupling of heteroarylboronic acids with aryl halides [J]. *Journal of Heterocyclic Chemistry*, 2008, 45: 109–118.

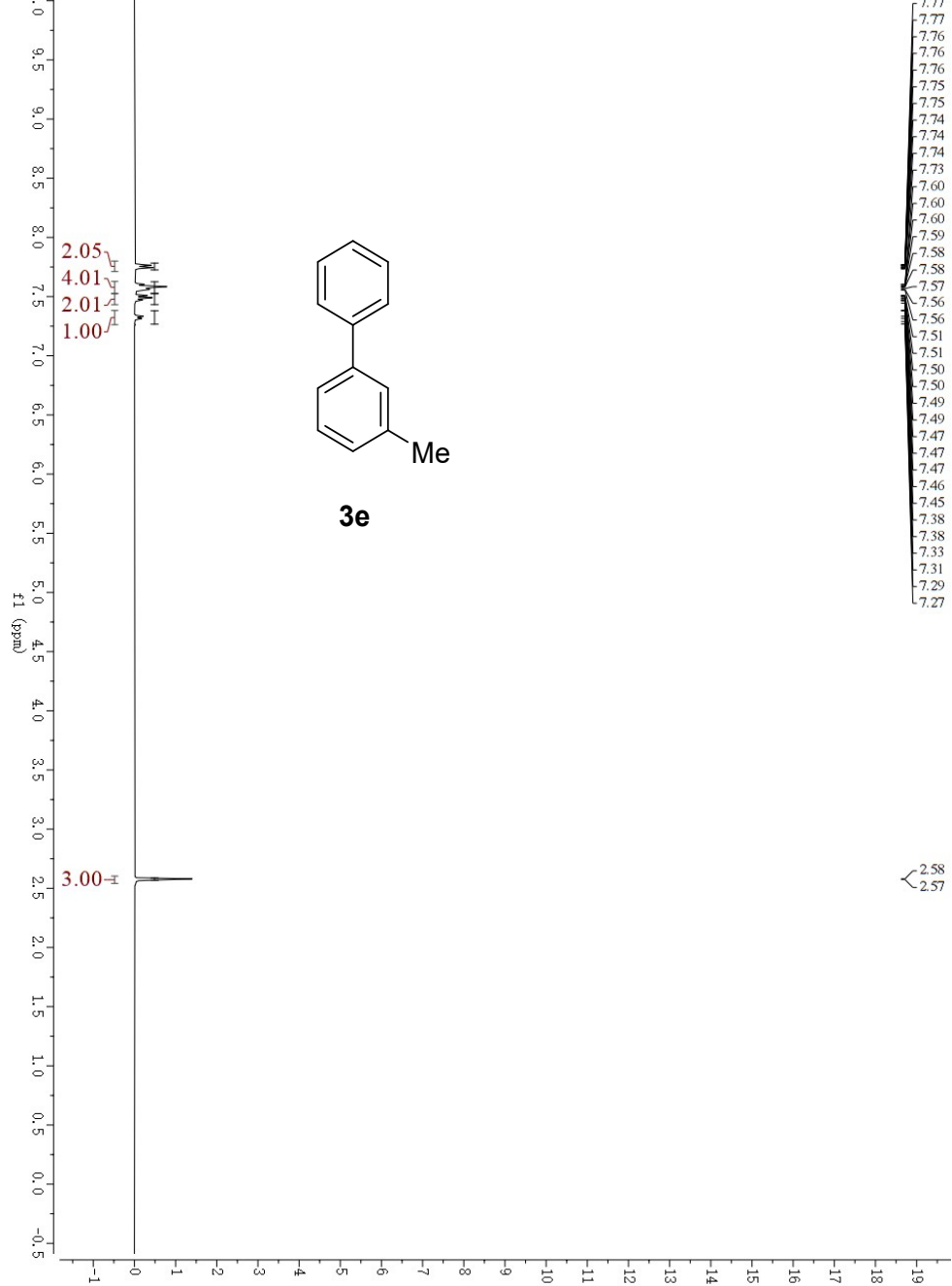
## F. NMR spectra



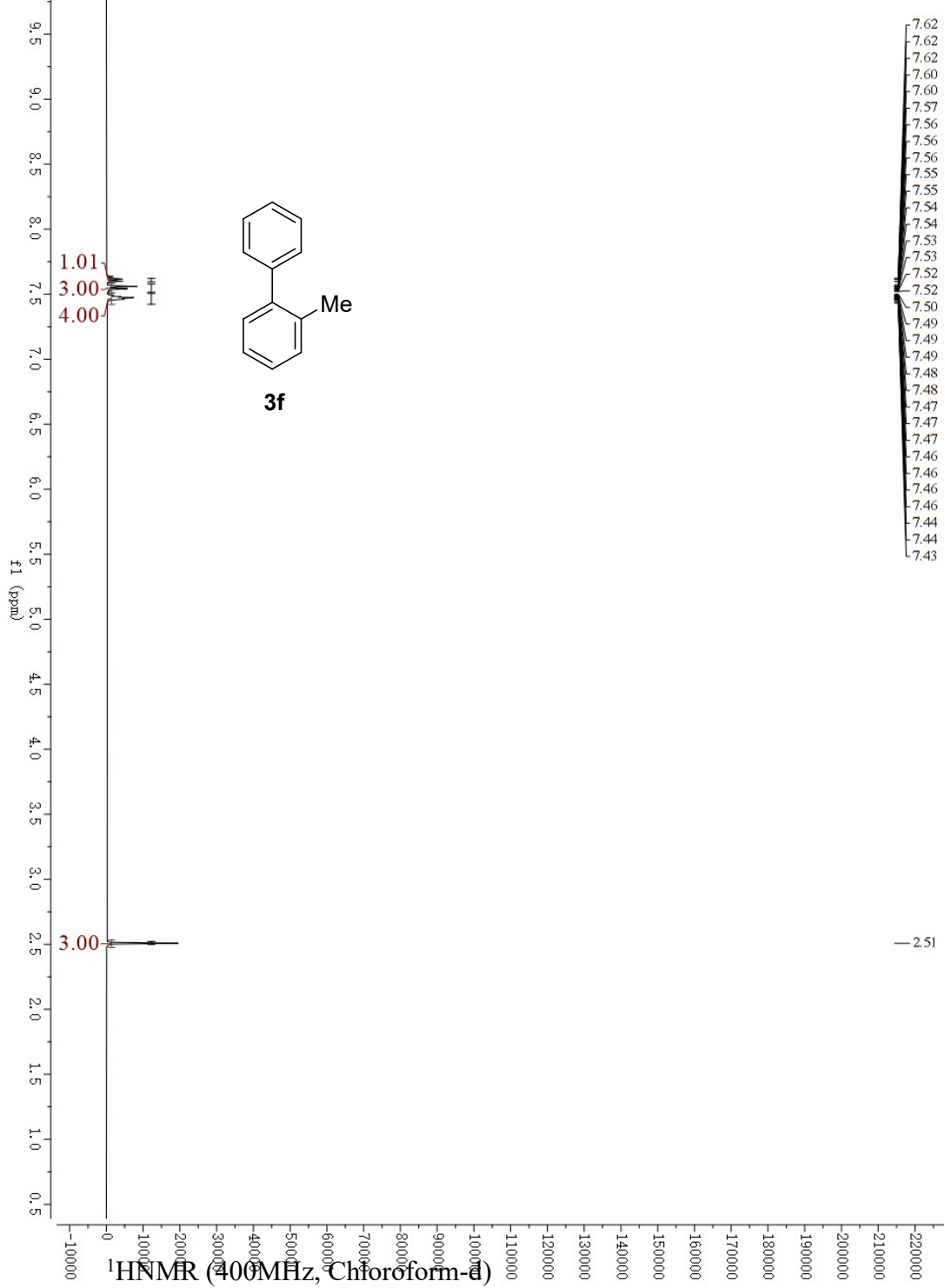


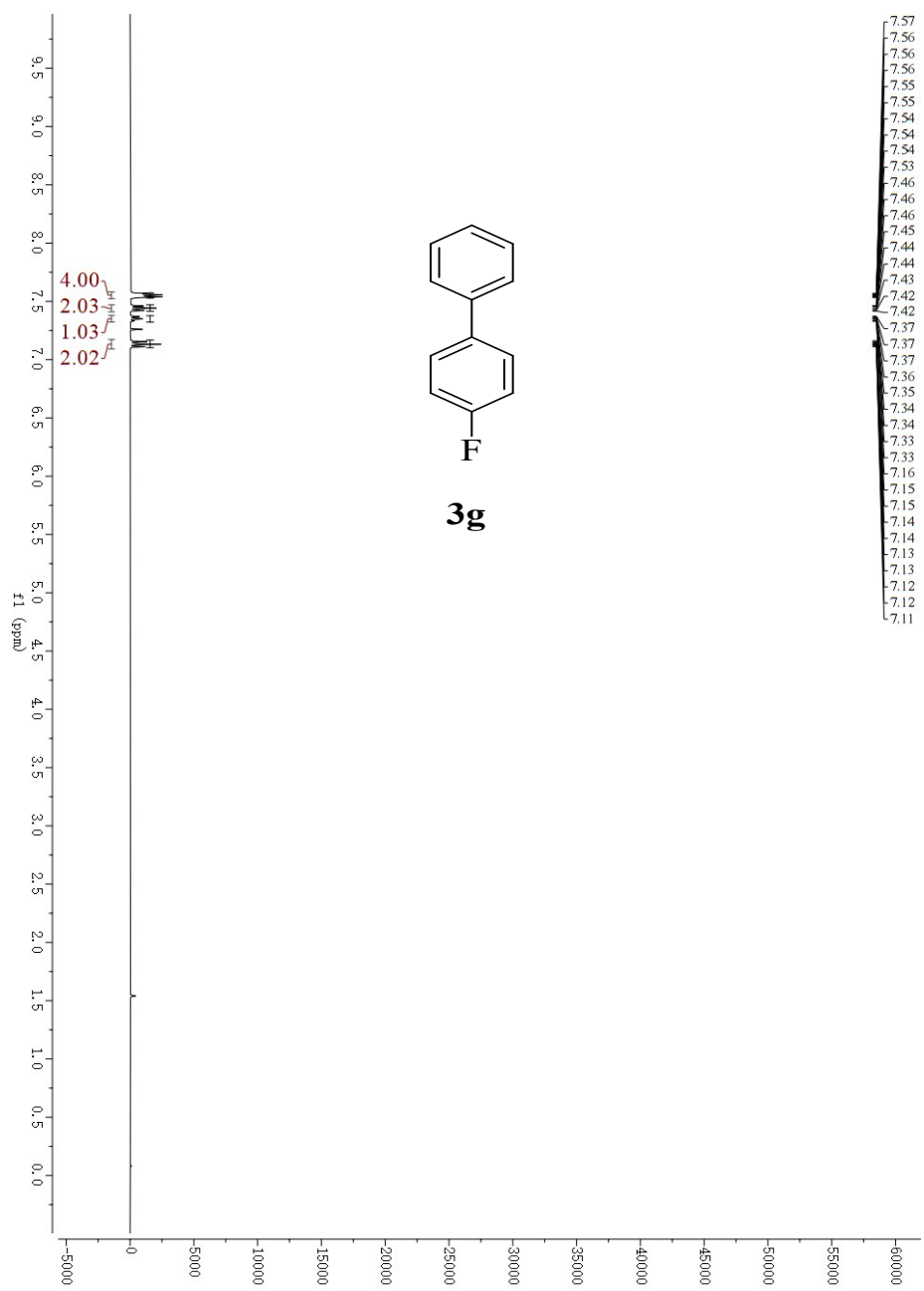




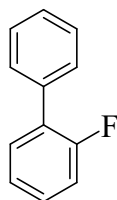


$^1\text{H NMR}$  (400MHz, Chloroform-d)

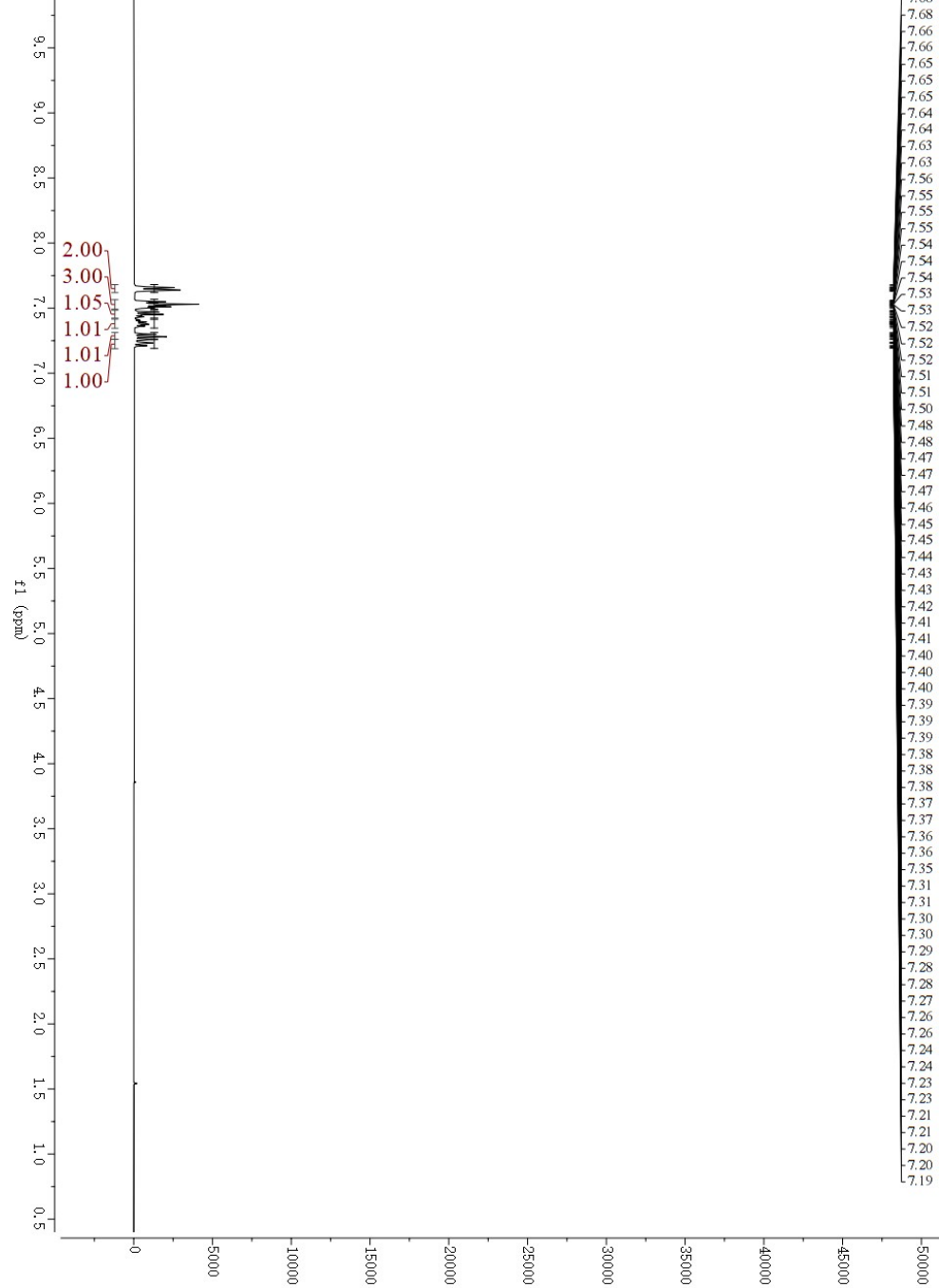




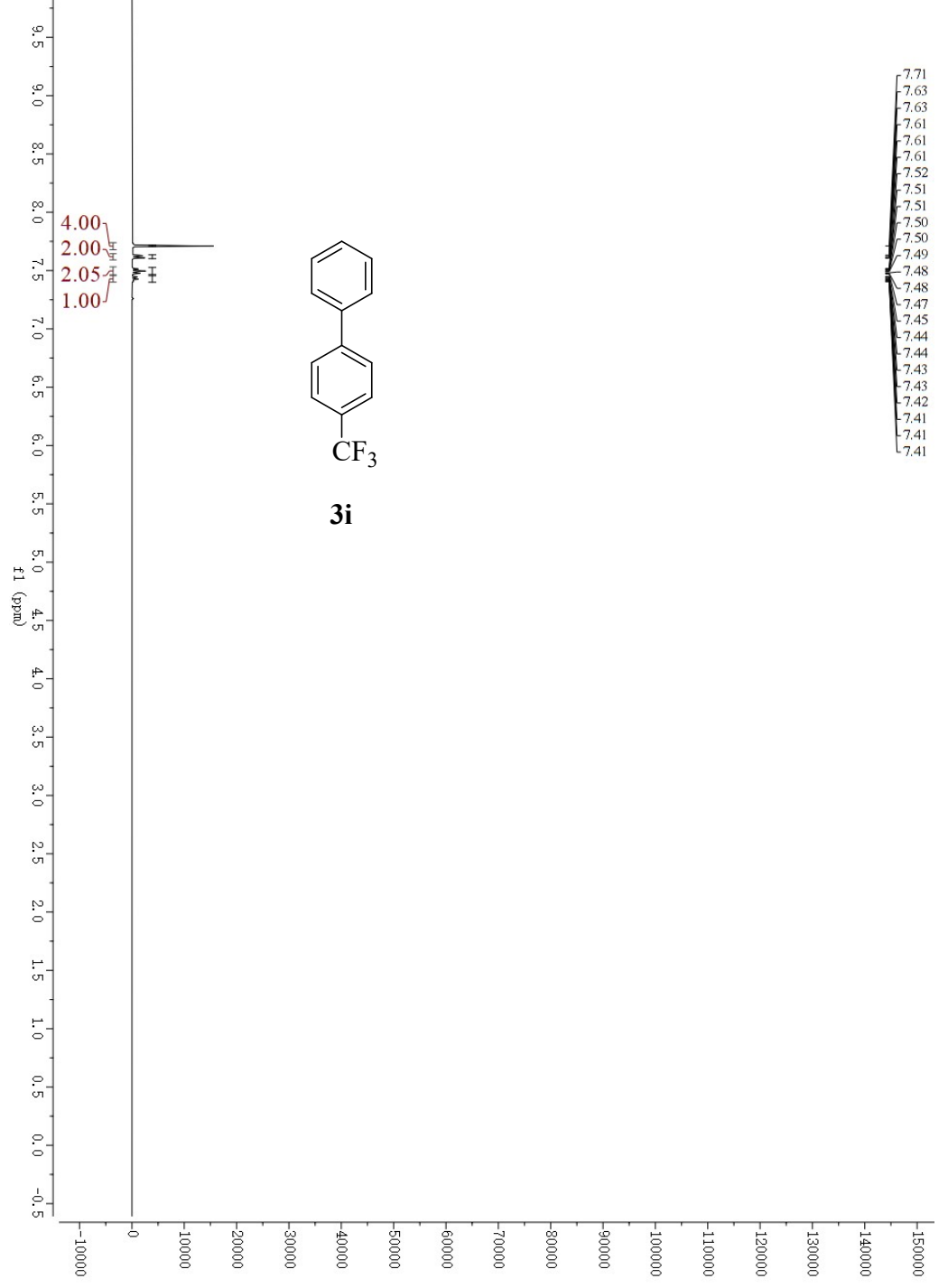
<sup>1</sup>H NMR (400MHz, Chloroform-d)



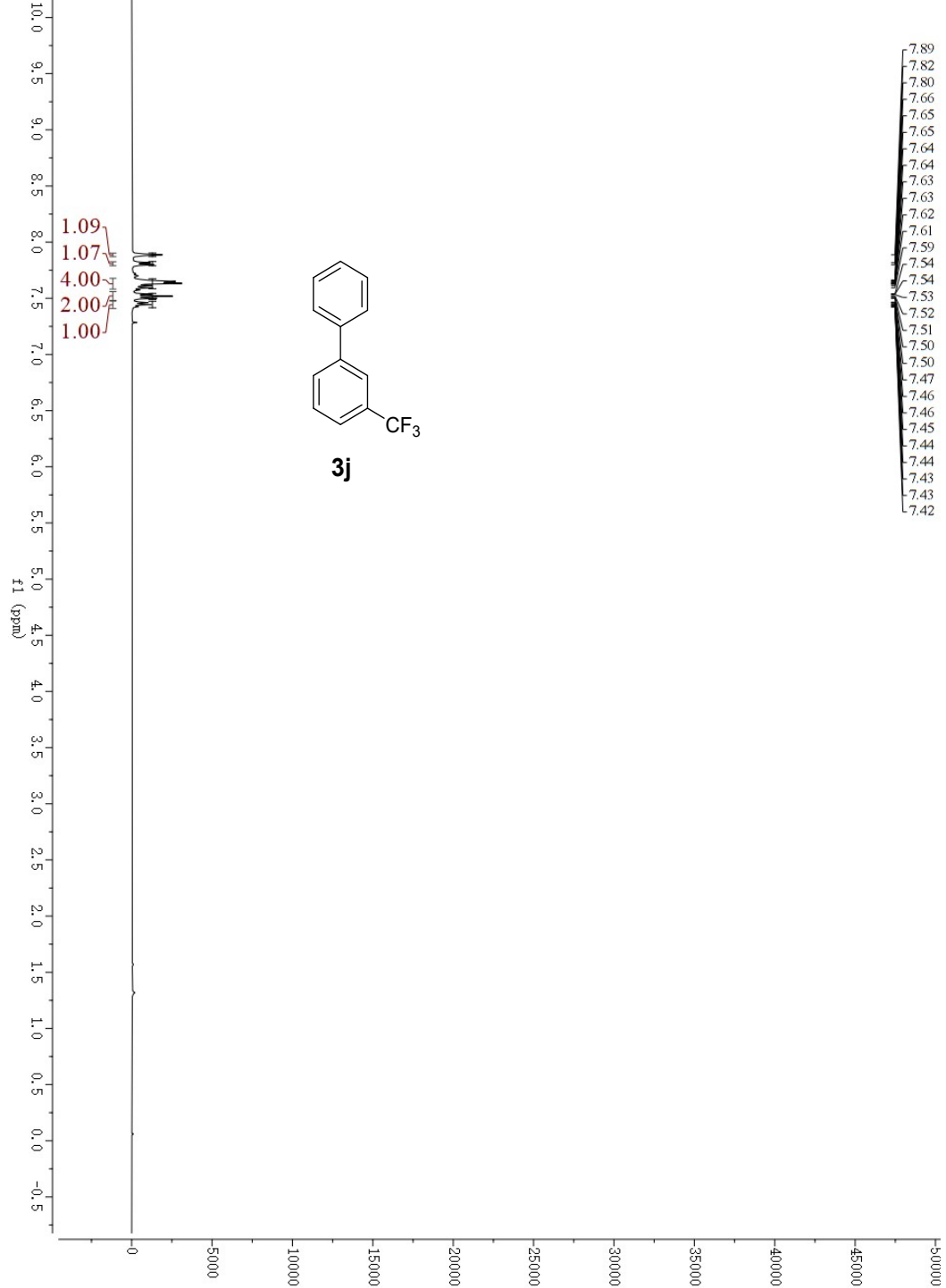
**3h**

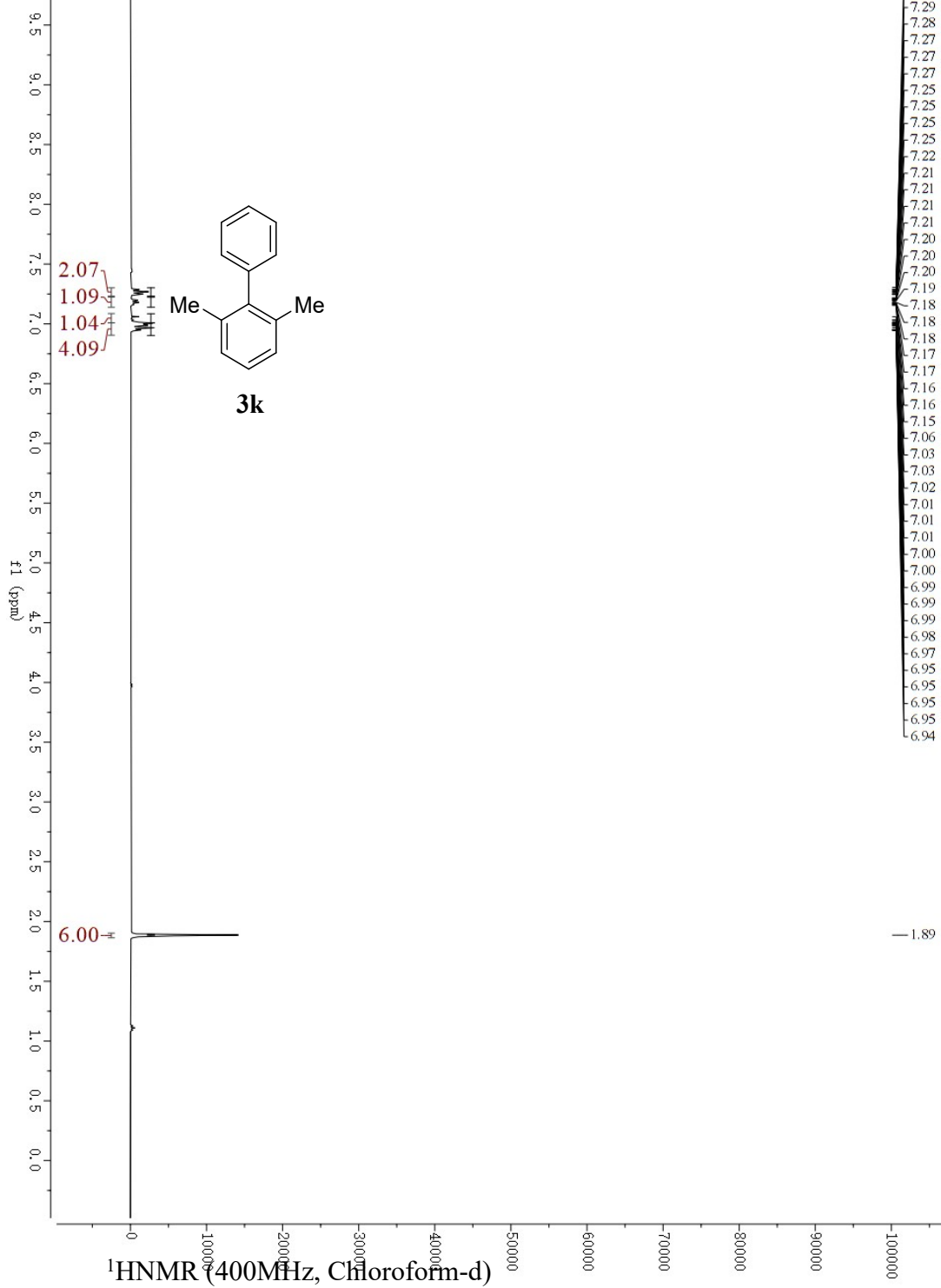


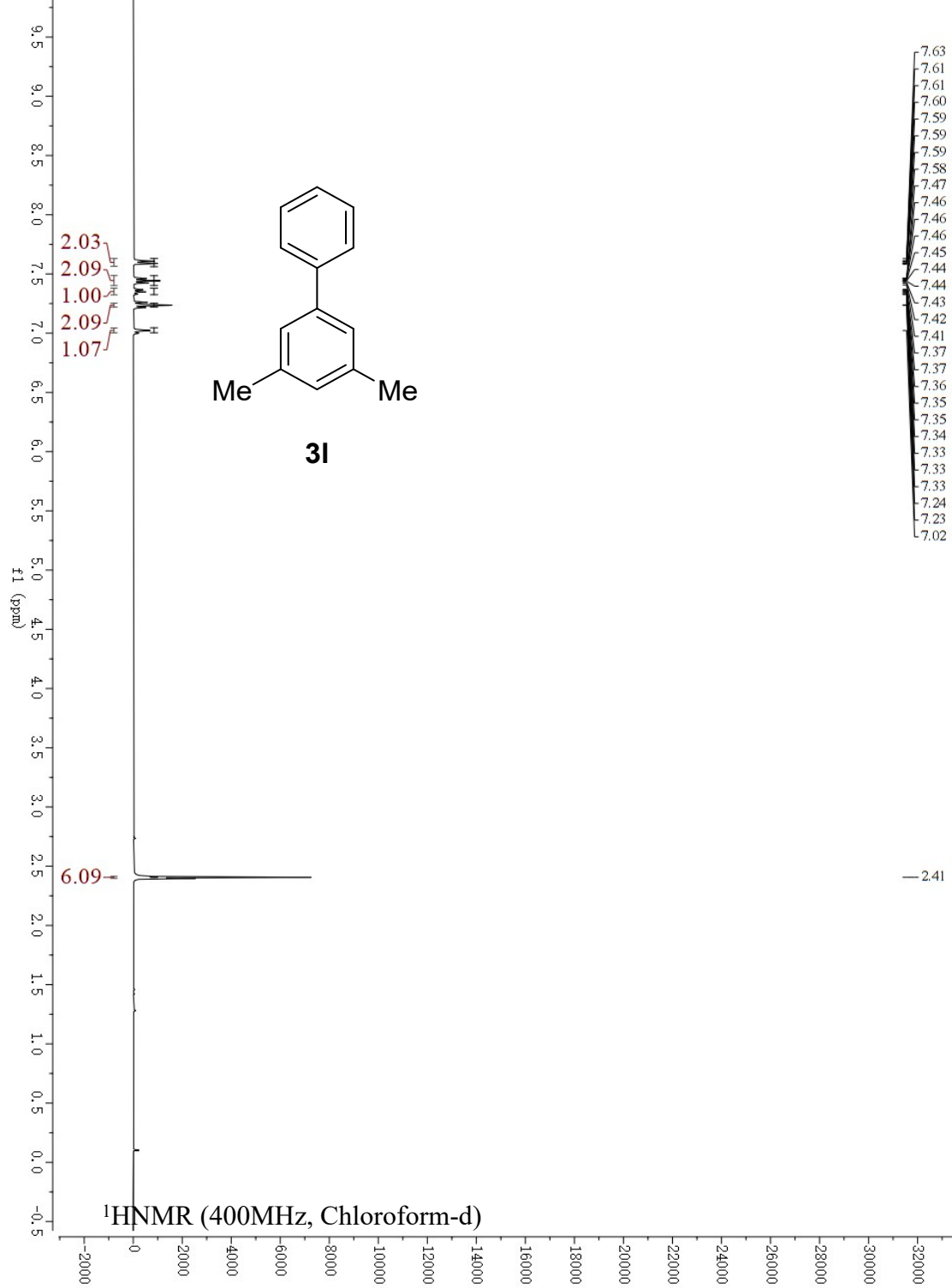
$^1\text{H}$ NMR (400MHz, Chloroform-d)

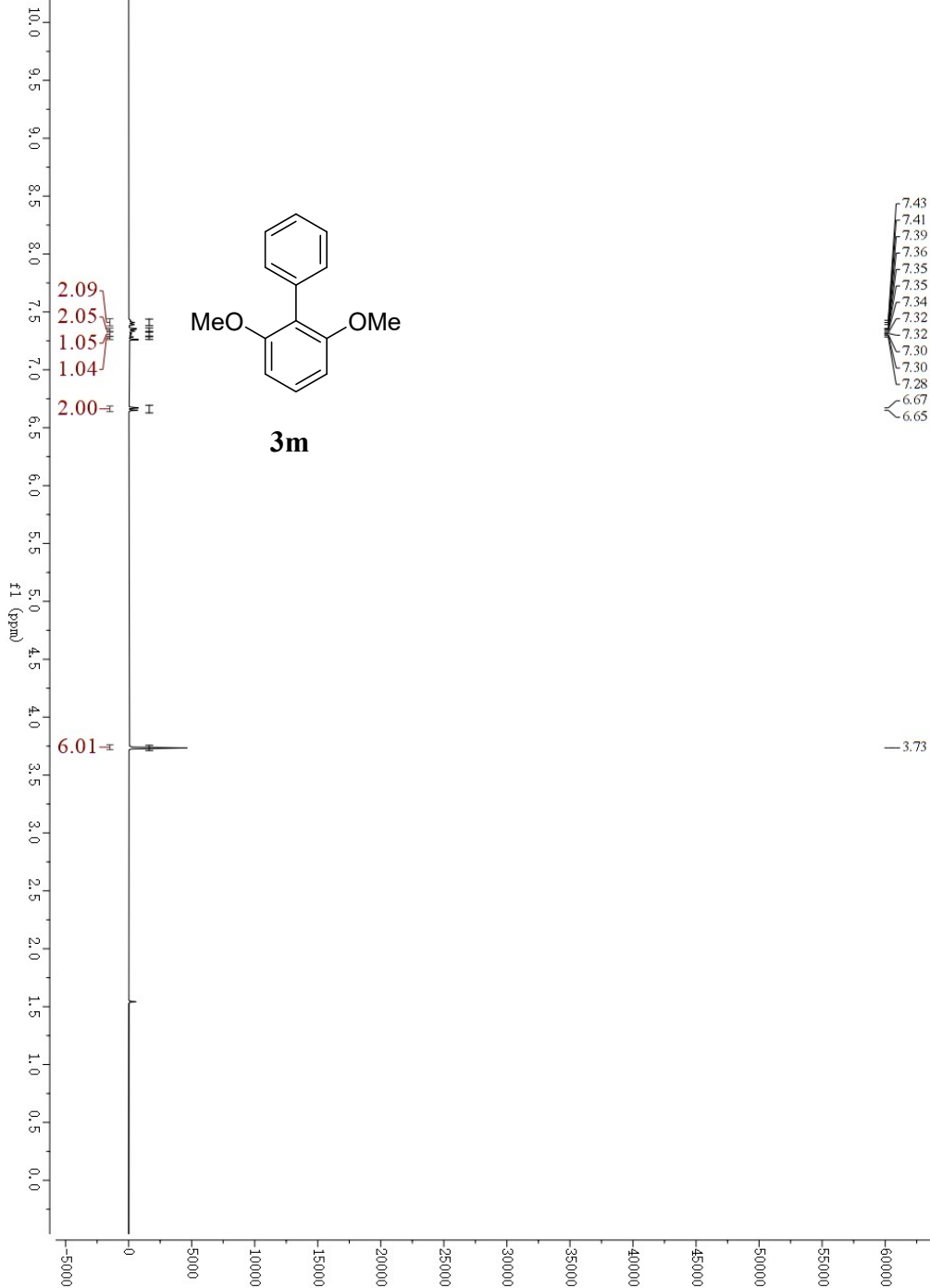


<sup>1</sup>H NMR (400MHz, Chloroform-d)

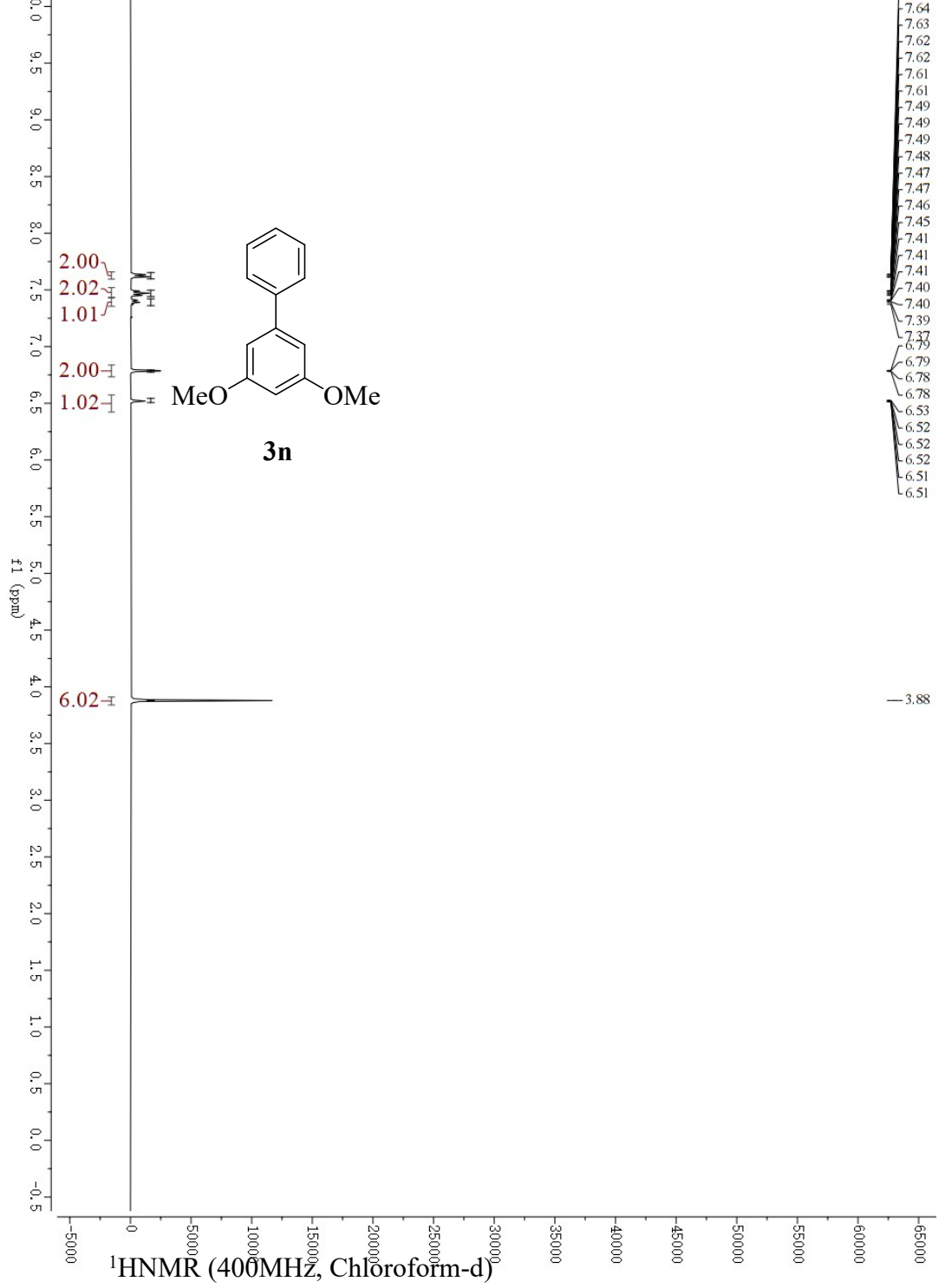


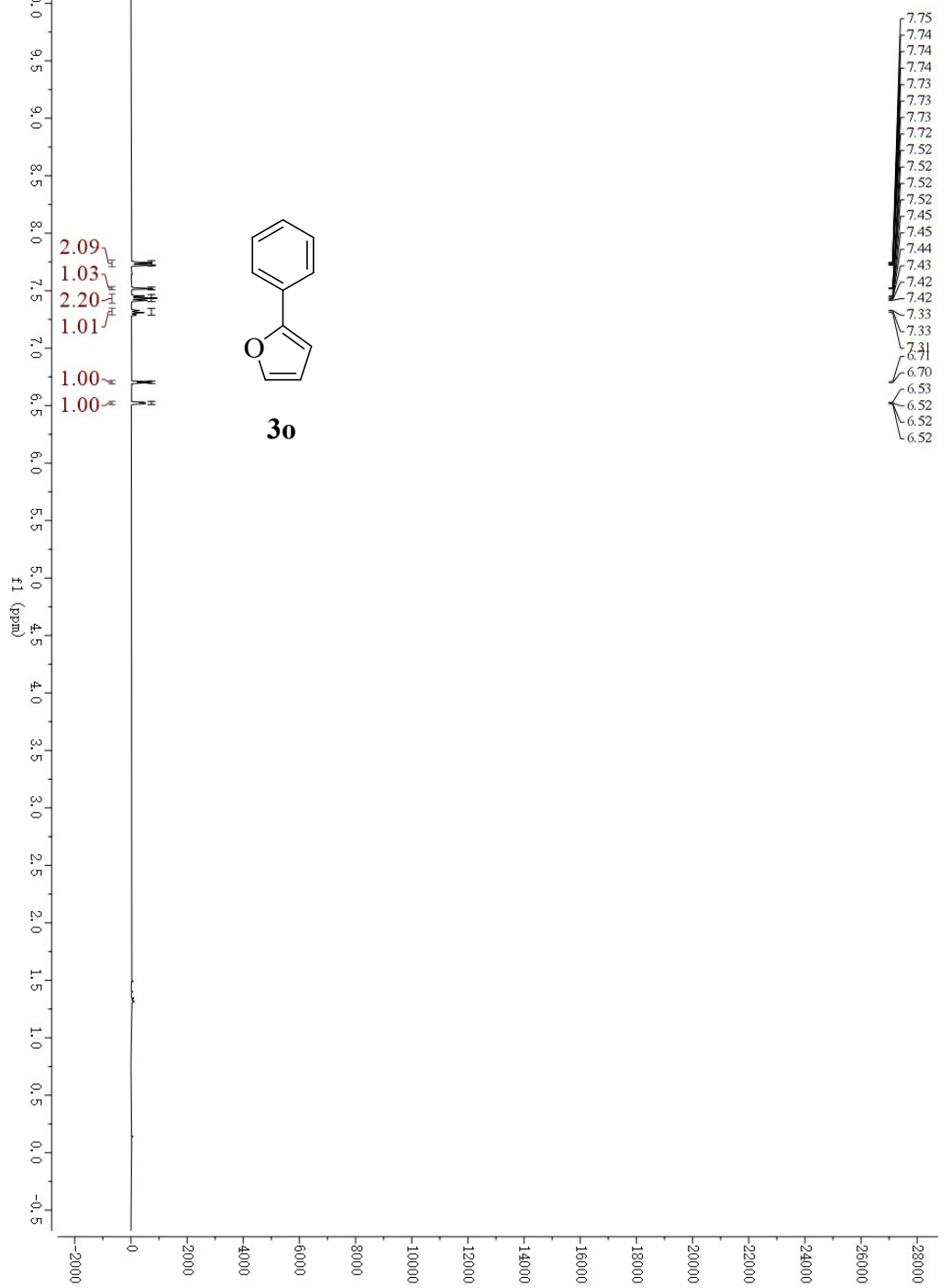




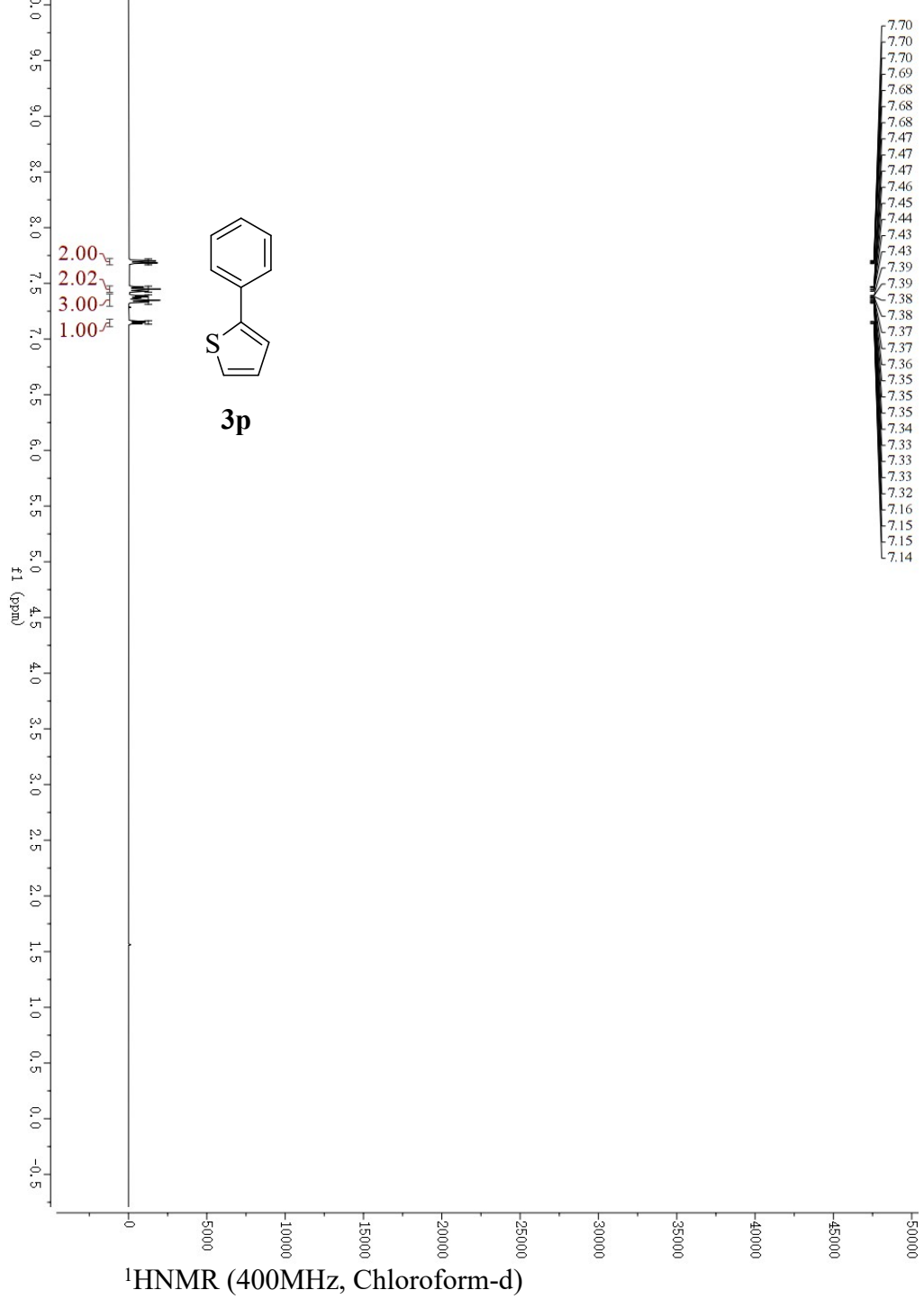


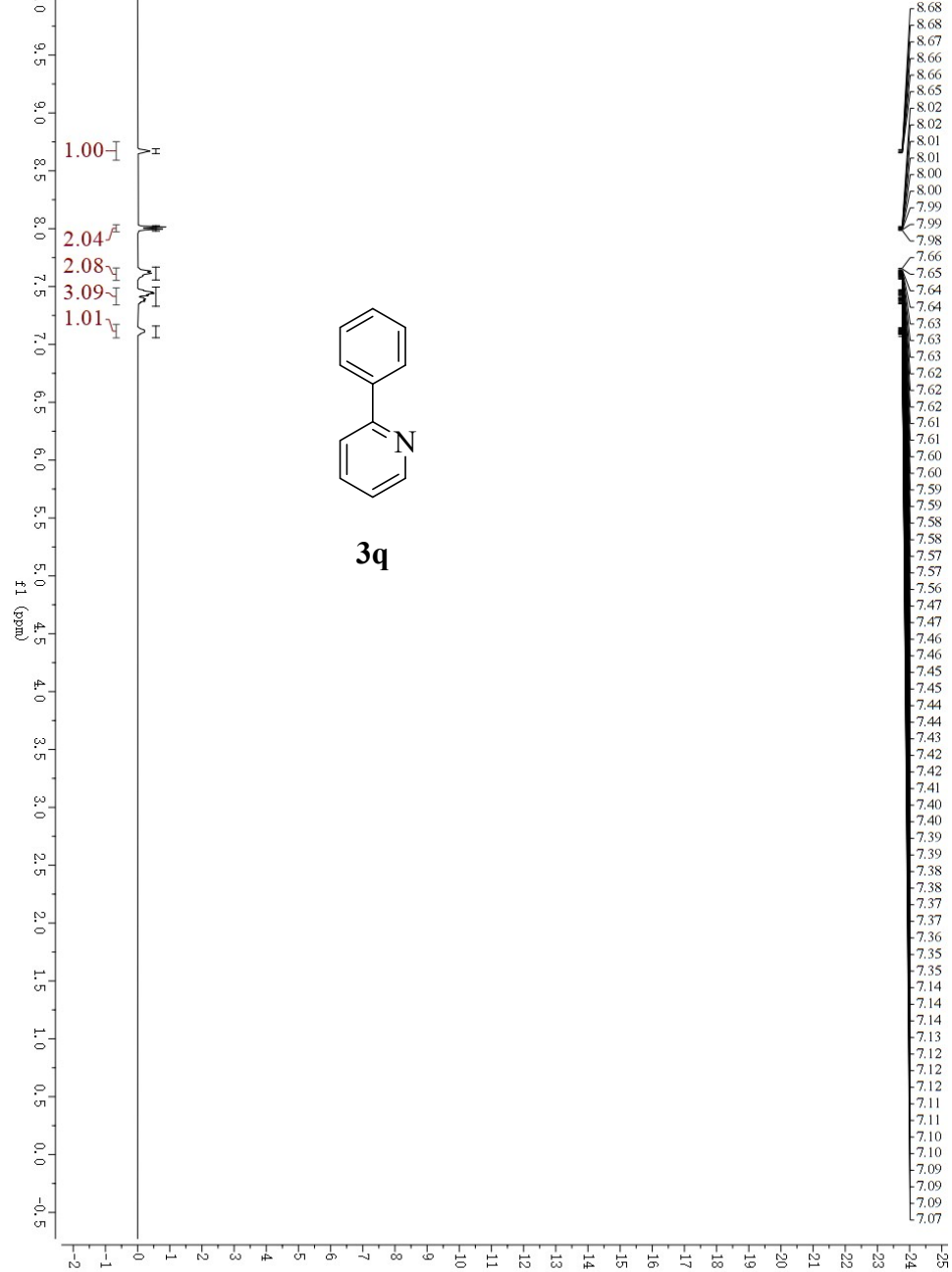
$^1\text{H}$ NMR (400MHz, Chloroform-d)



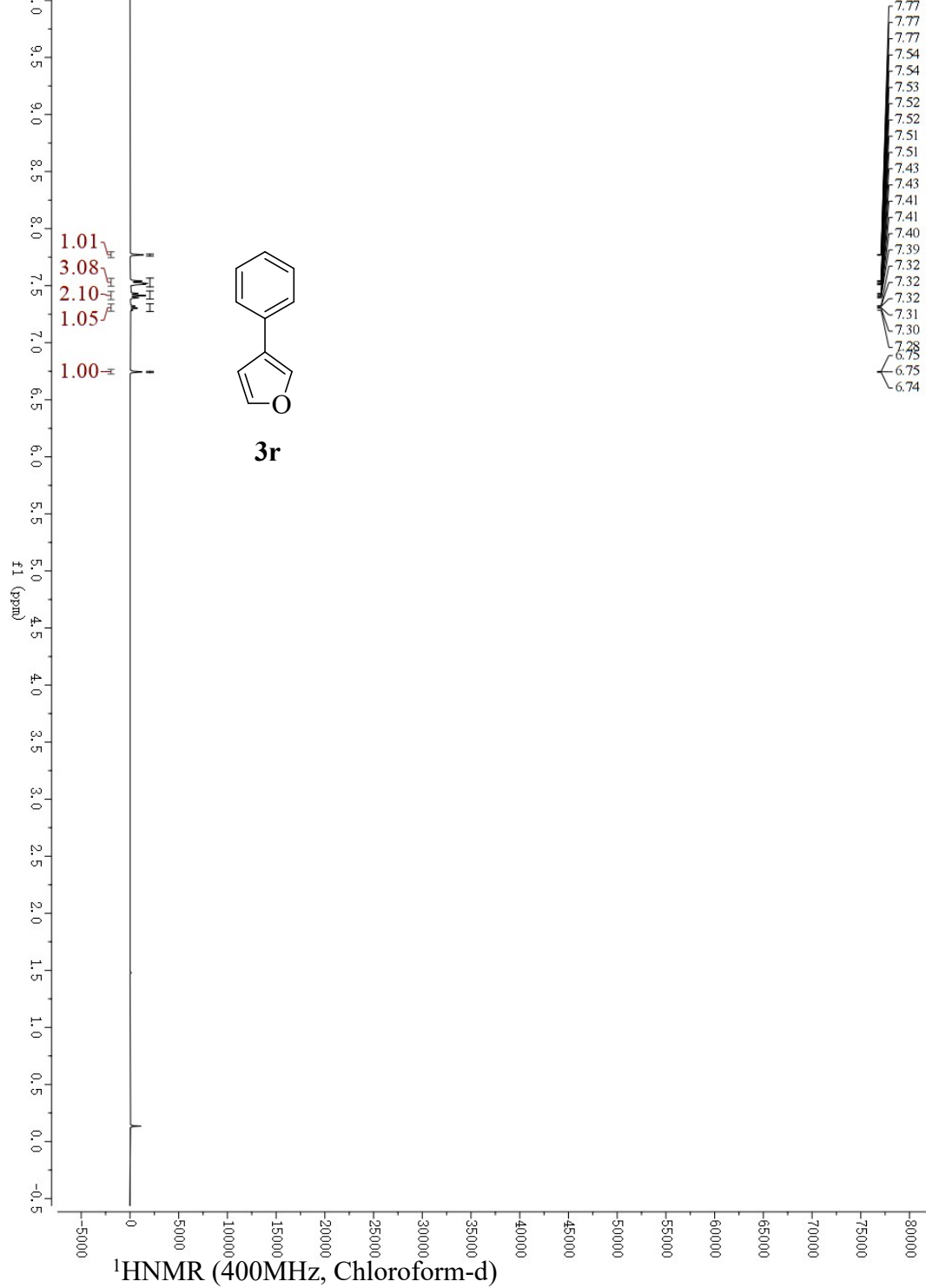


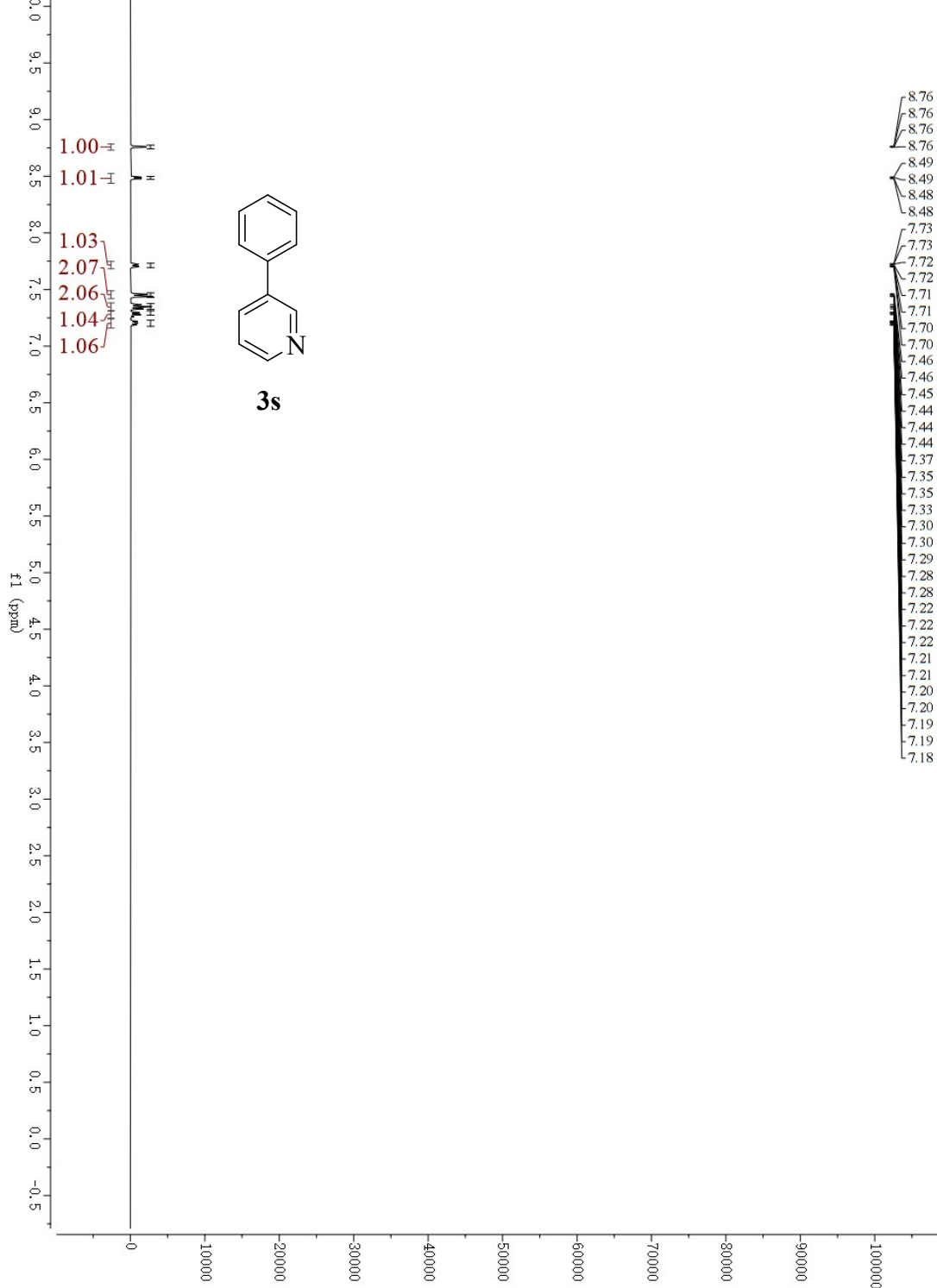
$^1\text{H}$ NMR (400MHz, Chloroform-d)





$^1\text{H NMR}$  (400MHz, Chloroform-d)





The data that support the findings of this study are openly available in the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6ob00403b>.