Supporting Information

Magnetic Pd-Fe Nanoparticles for Sustainable Suzuki-Miyaura

Cross-coupling Reactions

List of Contents

1. Controlled Catalytic Reactions and Calculation of Pd% loading

It was found that successful couplings require the presence of Pd-Fe@Fe$_3$O$_4$, as determined by the control reactions in preliminary experiment in Scheme S1, where only reaction catalyzed by prepared Pd-Fe@Fe$_3$O$_4$ containing 320ppm gave 85% yield while reactions that we attempted using equal amounts of Pd(OAc)$_2$, Fe$_3$O$_4$, or Pd(OAc)$_2$ and Fe$_3$O$_4$ did not lead to product formation.
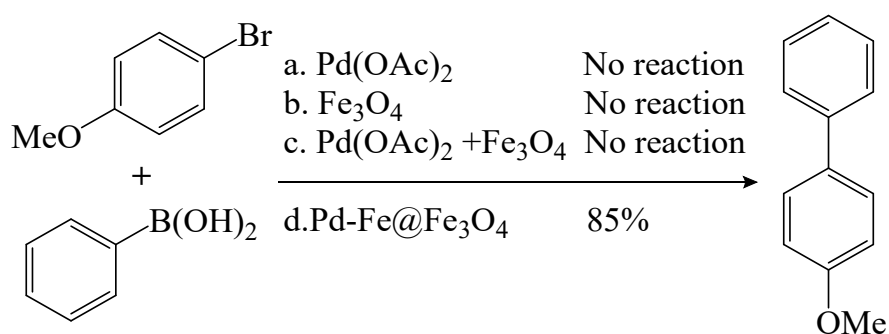

Scheme S1 Control reactions proved the importance of Pd-Fe@Fe$_3$O$_4$

The Pd loading was determined based on the actual amount of Pd utilized in the preparation of the catalyst, rather than the nominal loading with the following formula:

$$Pd\ mol\% = \frac{n(Pd(OAc)_2) * \dfrac{m(catalyst\ in\ a\ reaction)}{m_0(all\ prepared\ catalyst)}}{n(reaction)} * 100\%$$

$$= \frac{0.027mmol * \dfrac{0.825mg}{110mg}}{0.5mmol} * 100\%$$

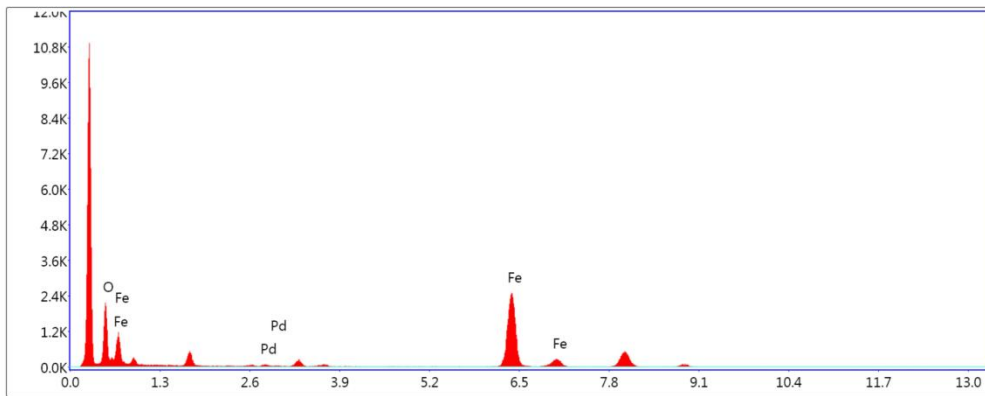## 2. XPS details of Fe-Pd@Fe$_3$O$_4$
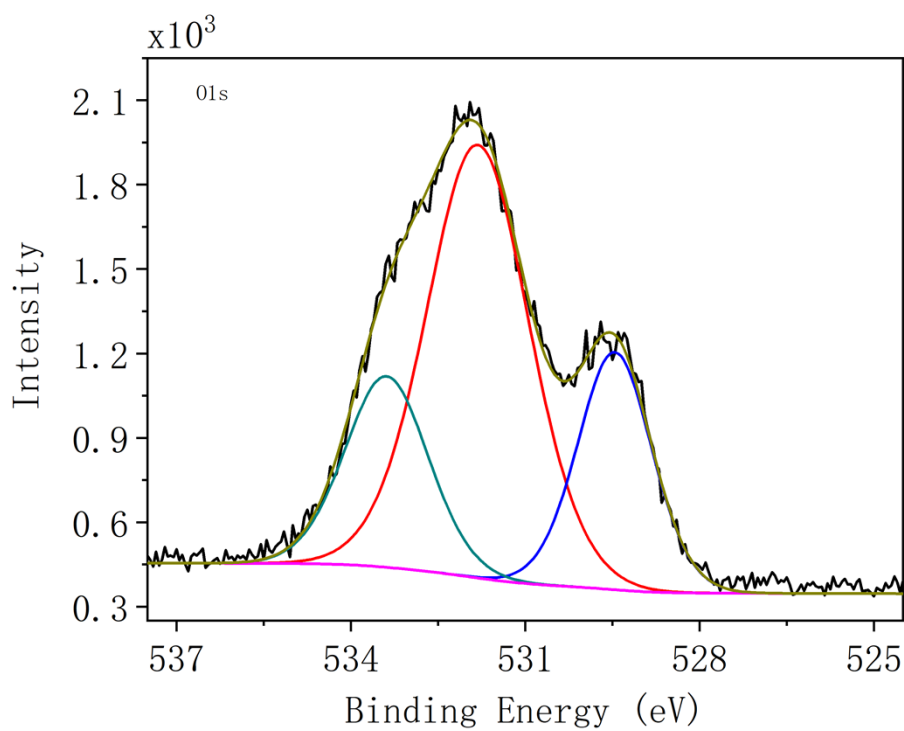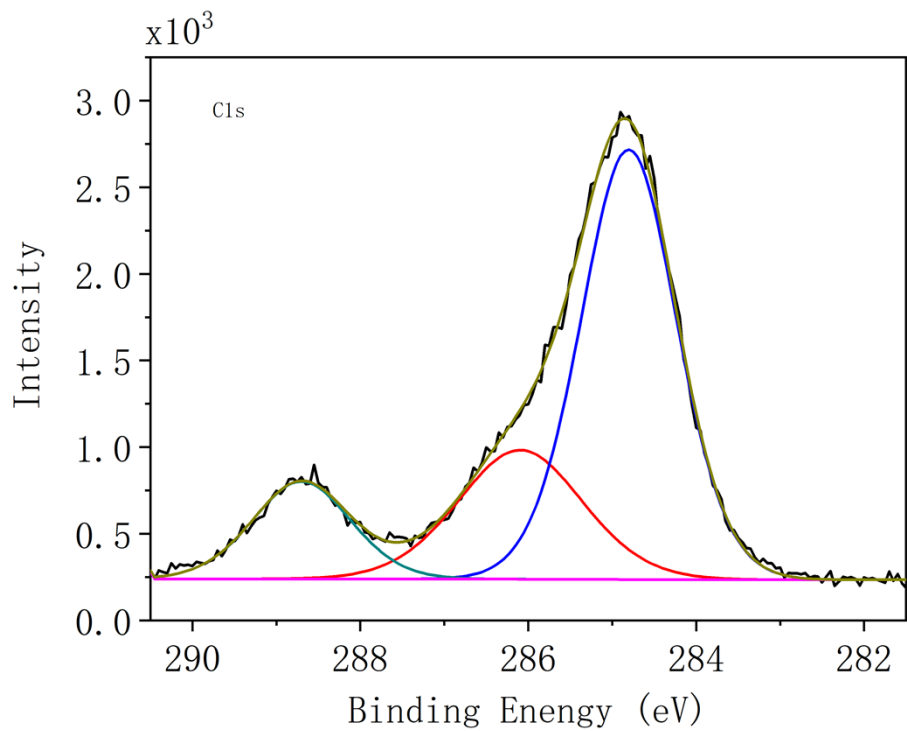
3. EDAX mapping details of Fe-Pd@Fe₃O₄
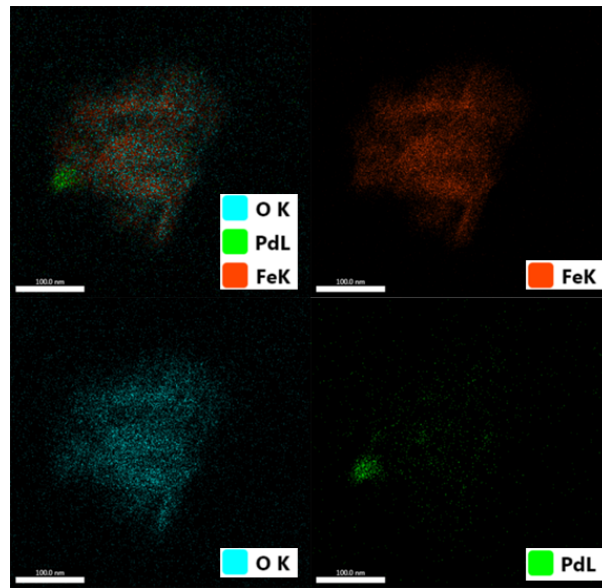
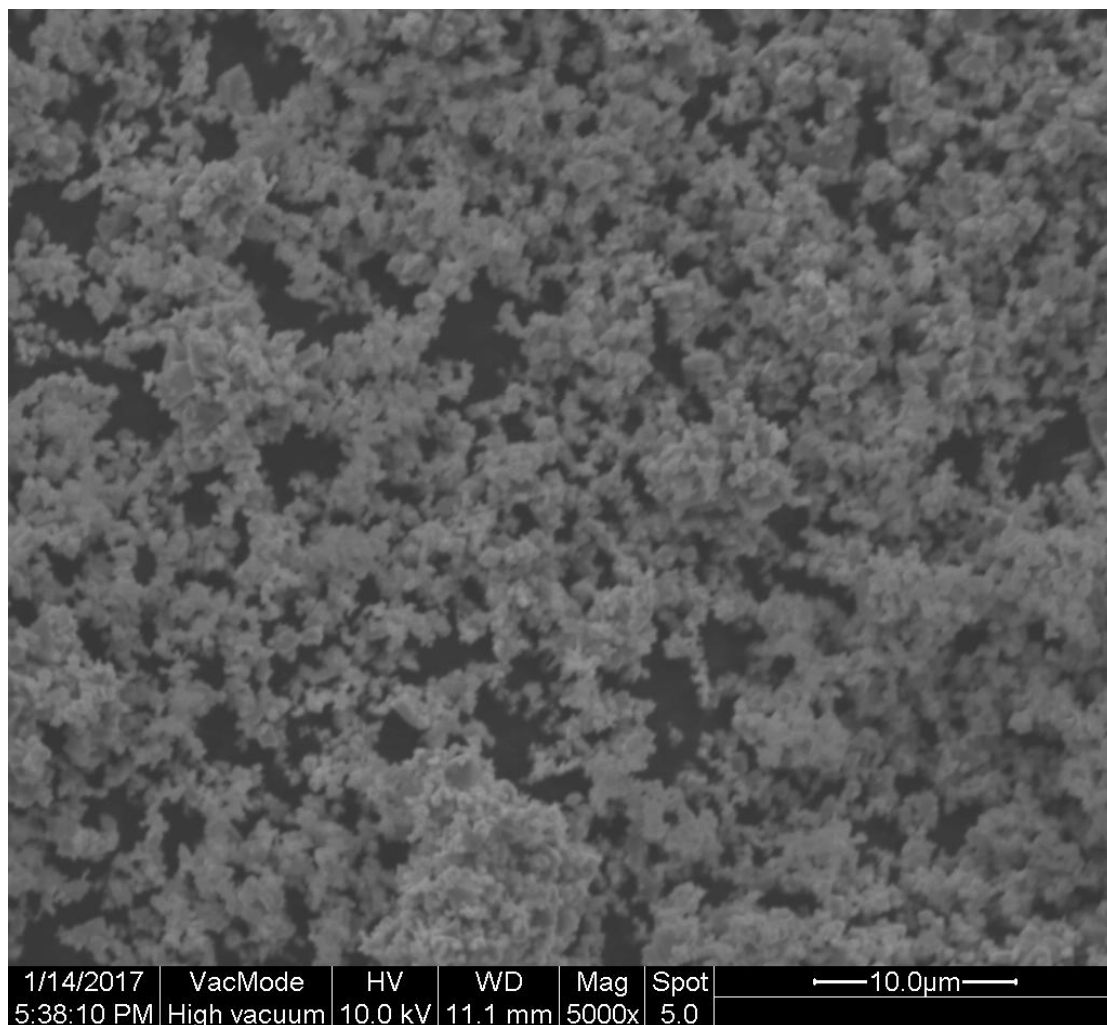| kV: 200 | Mag:160000 | Takeoff:14.8 | Live Time(s):38.9 | Amp Time(µs):7.68 | Resolution(eV):127.6 |

Phase: O K/FeK

Lsec: 38.9 0 Cnts 0.000 keV Det: Apollo XLT2 SUTW Det

MThin Smart Quant Results (Theoretical)

Element	Weight %	Atomic %	Net Int.	Net	KABFacto
O K	22.78	51.30	346.7	0.96	0.8
PdL	3.62	1.23	16.7	5.74	2.65
FeK	73.60	47.47	898.5	0.62	1

4. SEM images of Fe-Pd@Fe$_3$O$_4$

| 1/14/2017	VacMode	HV	WD	Mag	Spot	—10.0µm—
5:38:10 PM	High vacuum	10.0 kV	11.1 mm	5000x	5.0	

5. FT-IR analysis of Fe-Pd@Fe₃O₄
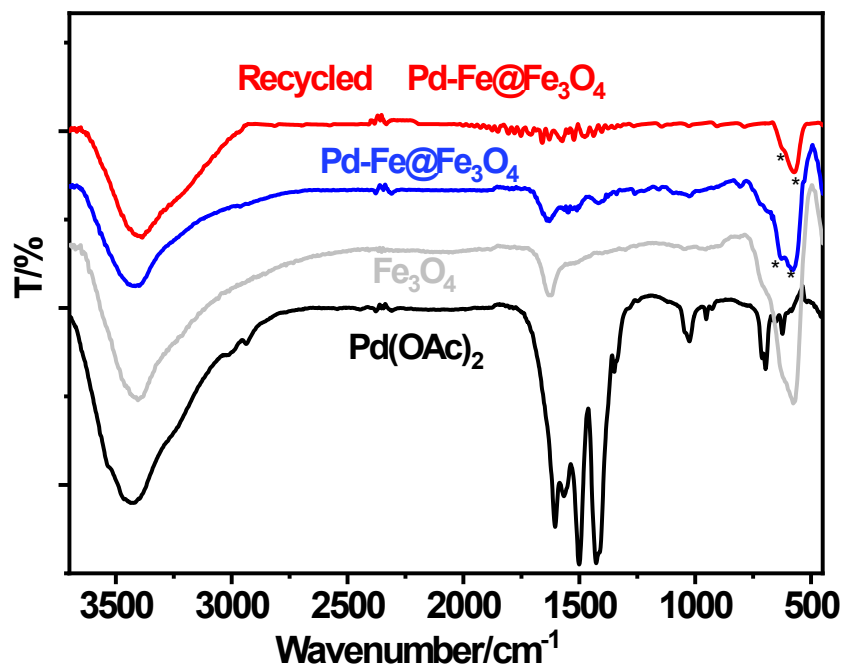
FT-IR of recycled Pd-Fe@Fe₃O₄, Pd-Fe@Fe₃O₄, Fe₃O₄ and Pd(OAc)₂

Fourier transform infrared (FT-IR) spectroscopy analysis of the recycled Pd-Fe@Fe₃O₄, Pd-Fe@Fe₃O₄, Fe₃O₄ and Pd(OAc)₂ was displayed. As we all know, the peaks around 3400 and 1600 wavenumbers are hydroxyl absorption peaks and the peaks around 2350 wavenumbers are O=C=O absorption peaks in the environment, while the infrared characteristic peaks of Fe-O bonds are generally below 700 wavenumbers. Comparing the infrared absorption curves of Pd-Fe@Fe₃O₄ and Fe₃O₄, we find that the absorption peak is divided from 577 wavenumber splitting into 628 and 578 wavenumbers, respectively, which is likely caused by the introduction of additional iron. At the same time, comparing the infrared absorption curve of Pd(OAc)₂, we found that the characteristic peak of acetate disappeared, indicating that palladium was completely reduced. The infrared absorption curve of recycled Pd-Fe@Fe₃O₄ showed that the nano-catalyst remain a stable structure after a gram-scale reaction.
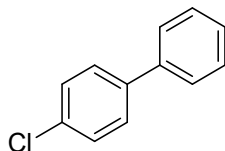
6. Characterization of the Products.
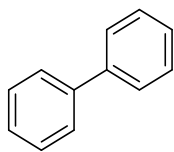
1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.51 (d, *J* = 7.6 Hz, 4H), 7.35 (t, *J* = 7.5 Hz, 4H), 7.25 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 141.37, 128.88, 127.38, 127.30.
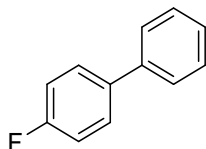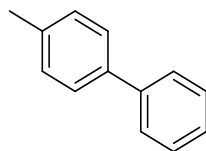

4-fluoro-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.42 (d, *J* = 7.9 Hz, 4H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 162.4 (d, J = 246.3), 140.2, 137.3 (d, J = 3.3), 128.8, 128.6 (d, J = 8.0).
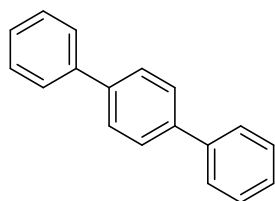

4-chloro-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.40 (dd, J = 16.5, 8.0 Hz, 4H), 7.28 (dt, J = 20.7, 9.9 Hz, 5H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): δ 138.57, 127.83, 127.80, 127.30, 126.51, 125.89.
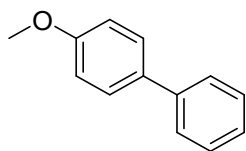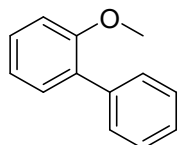

4-methoxy-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.42 (t, J = 9.1 Hz, 4H), 7.29 (t, J = 7.5 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 6.85 (d, J = 8.3 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 159.25, 140.90, 133.85, 128.81, 128.22, 126.81, 126.74, 114.31, 55.38.
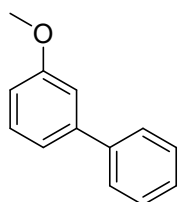

4-methyl-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.44 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7.6 Hz, 2H), 7.28 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.7 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 141.25, 138.45, 137.07, 129.57, 128.84, 128.80, 127.08, 127.05, 21.17.

1,1',4',1''-terphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.63 – 7.54 (m), 7.38 (t, J = 7.5 Hz), 7.28 (t, J = 7.3 Hz). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 139.67, 139.09, 127.78, 126.46, 126.30, 126.01.


2-methoxy-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.42 (d, J = 7.9 Hz, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 8.4 Hz, 3H), 6.91 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 156.57, 138.66, 130.97, 130.84, 129.64, 128.70, 128.06, 126.99, 120.93, 111.36, 55.60.


3-methoxy-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.48 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.28 – 7.17 (m, 2H), 7.08 (d, J = 7.6 Hz, 1H), 7.03 (s, 1H), 6.79 (d, J = 8.1 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 158.89, 141.71, 140.04, 128.69, 127.67, 126.35, 126.13, 118.62, 111.85, 111.62, 54.21.
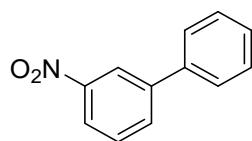
3-nitro-1,1'-biphenyl. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.30 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.33 (dt, J = 24.6, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 148.73, 142.84, 138.63, 133.03, 129.73, 129.18, 128.56, 127.15, 122.02, 121.90.
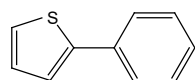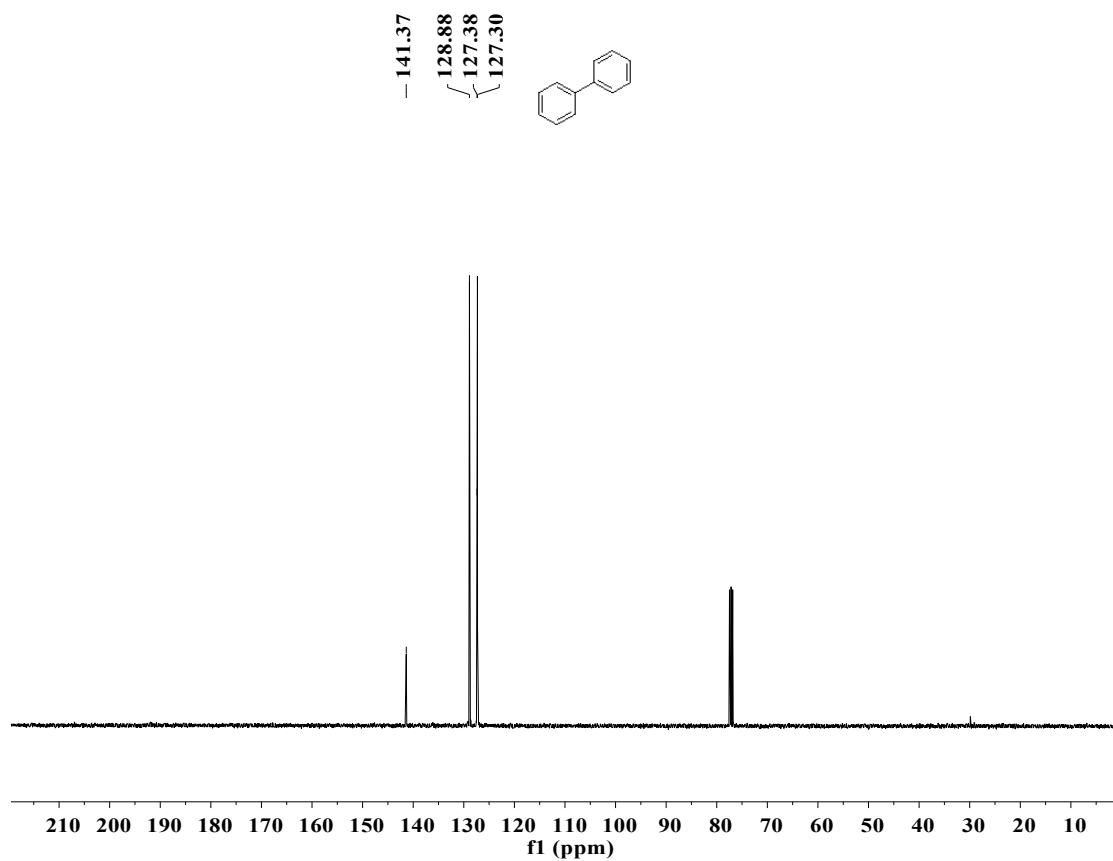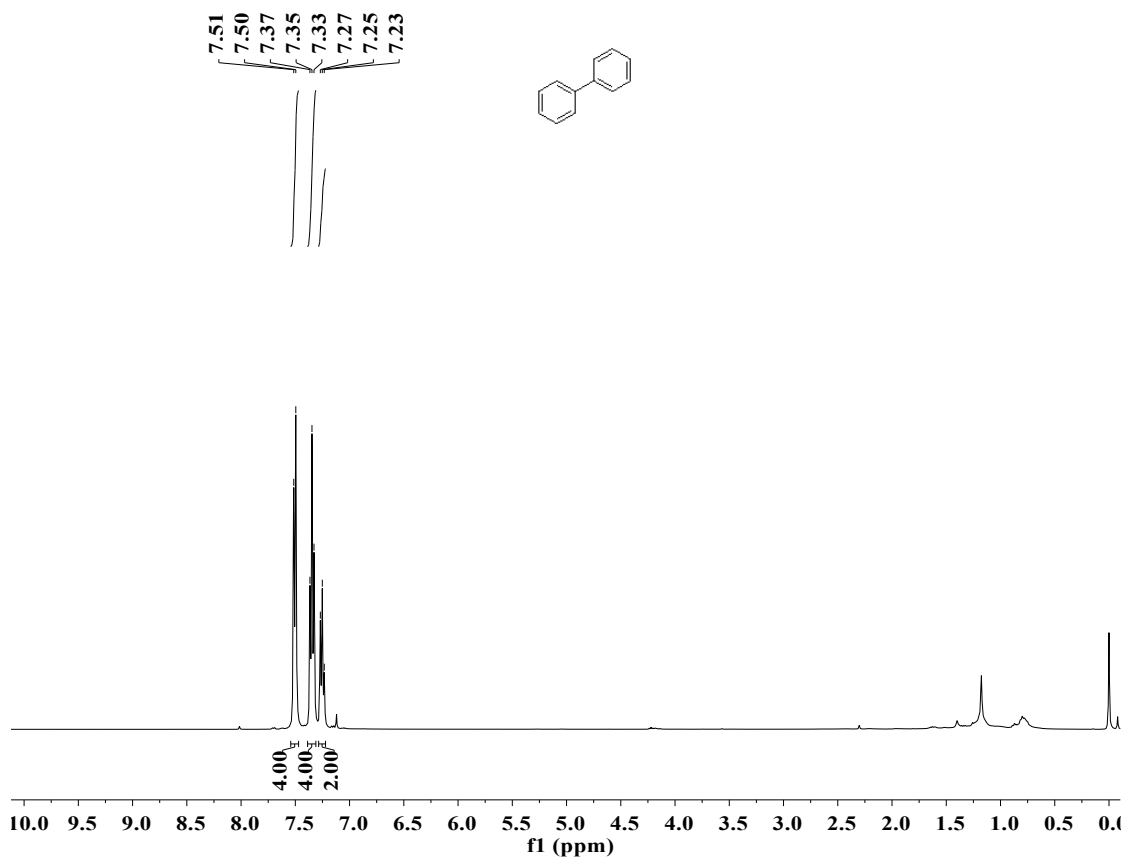
2-Phenylthiophene. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.66 – 7.60 (m, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.35 – 7.31 (m, 1H), 7.29 (dd, J = 5.7, 3.8 Hz, 2H), 7.09 (dd, J = 5.0, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 144.51, 134.47, 128.97, 128.10, 127.55, 126.04, 124.90, 123.16.
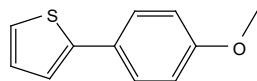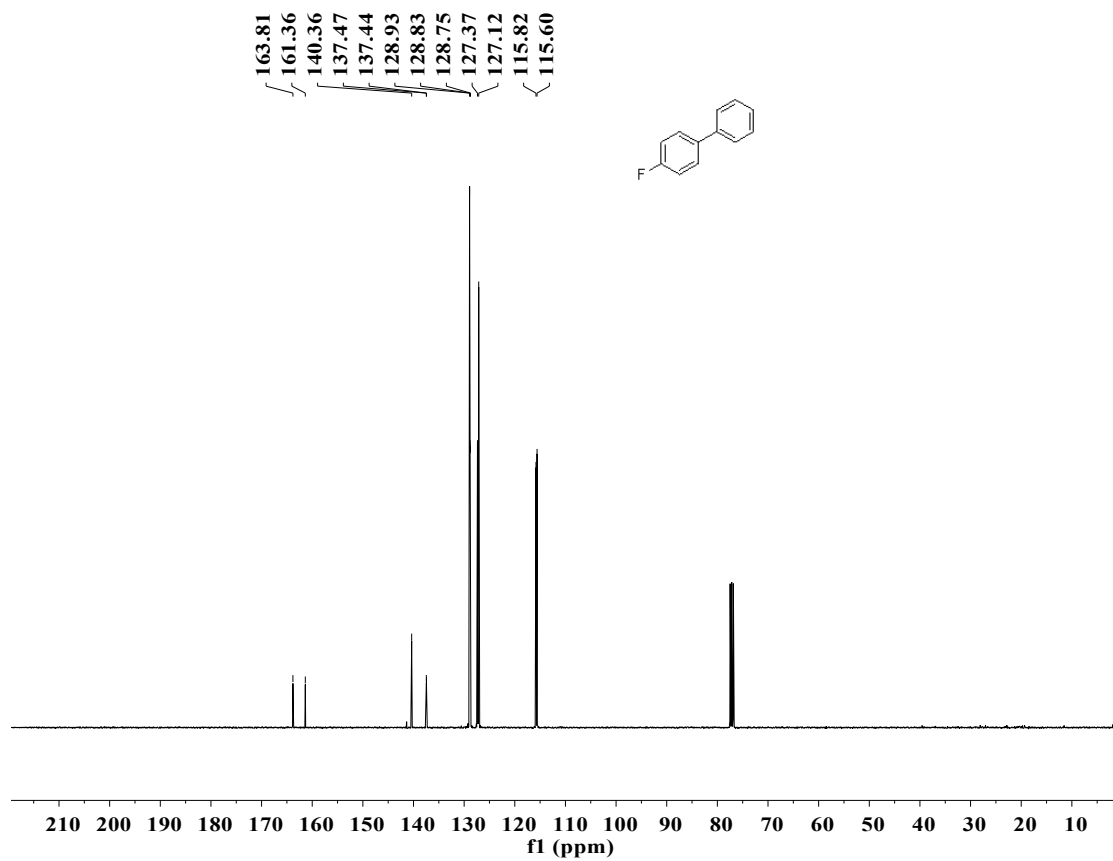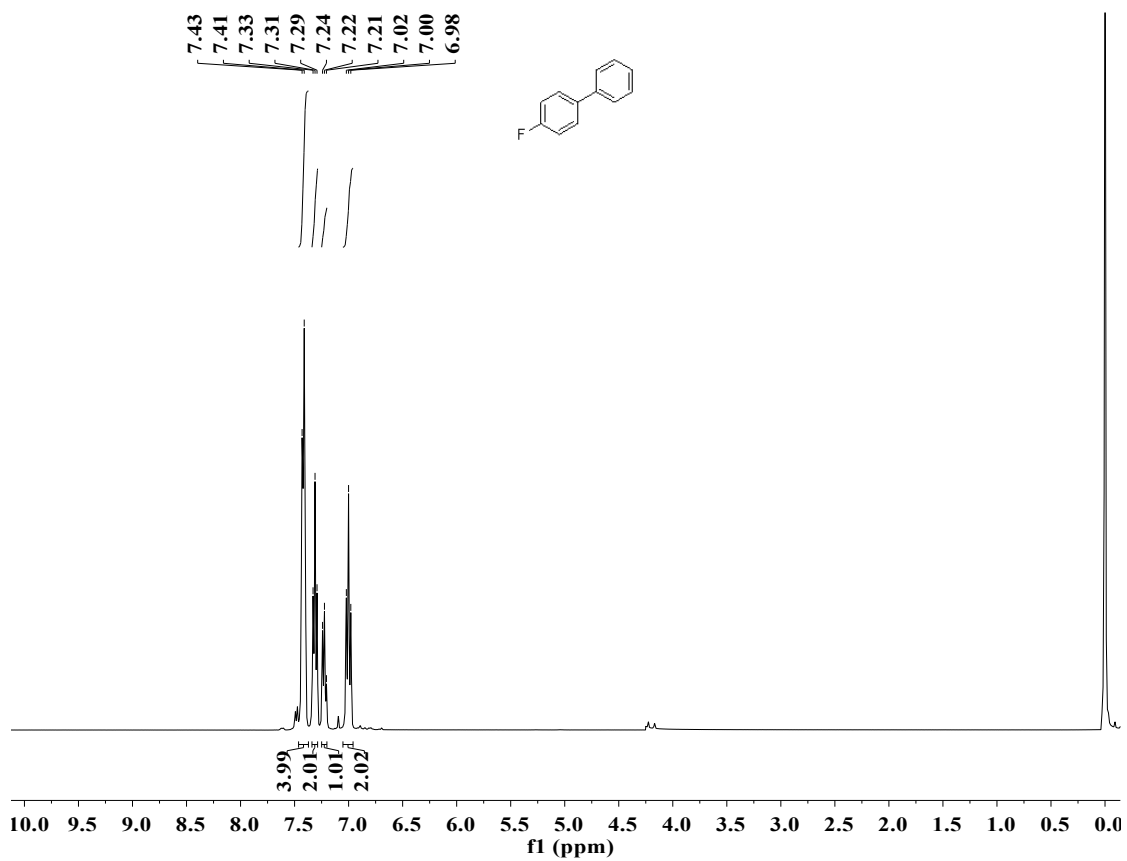

1-(4-Thiophen-2-yl-phenyl)-ethanon. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.54 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 5.8 Hz, 1H), 7.20 (d, 1H), 7.05 (dd, J = 4.9, 3.7 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm): 159.23, 144.40, 128.01, 127.36, 127.30, 123.92, 122.16, 114.33, 55.45.
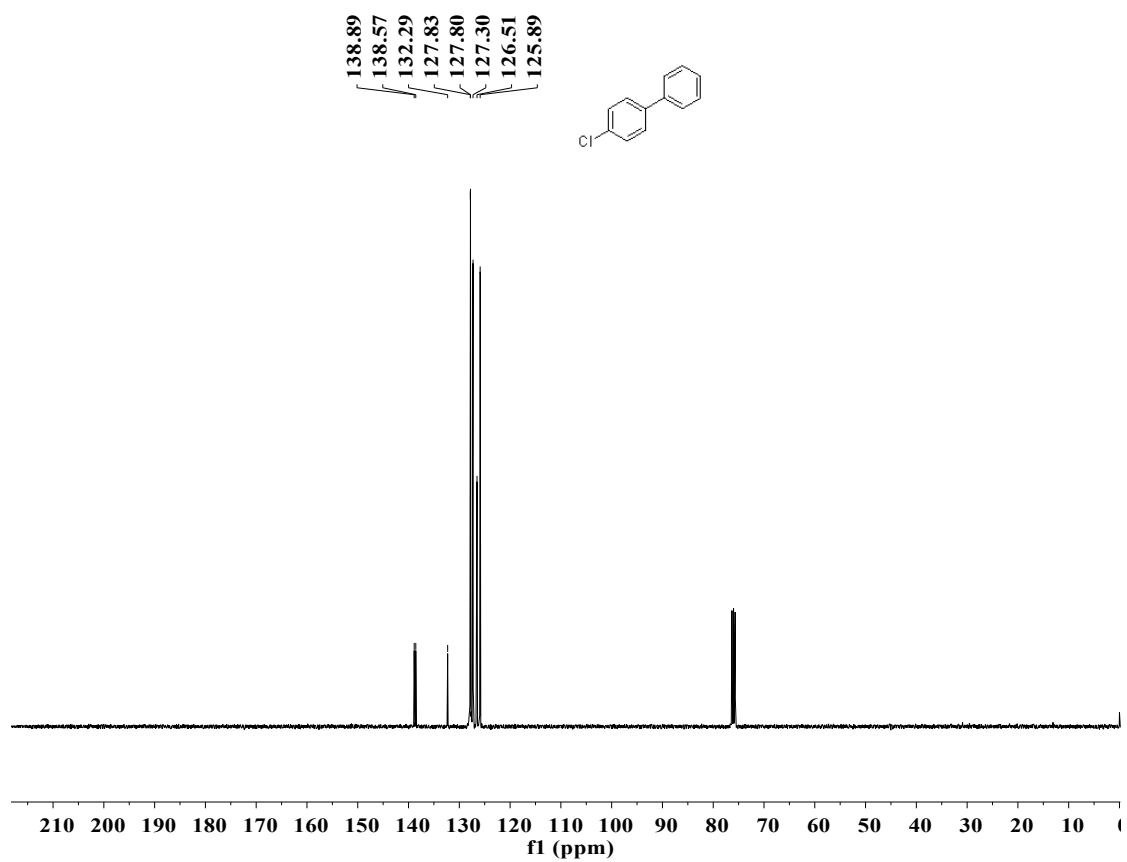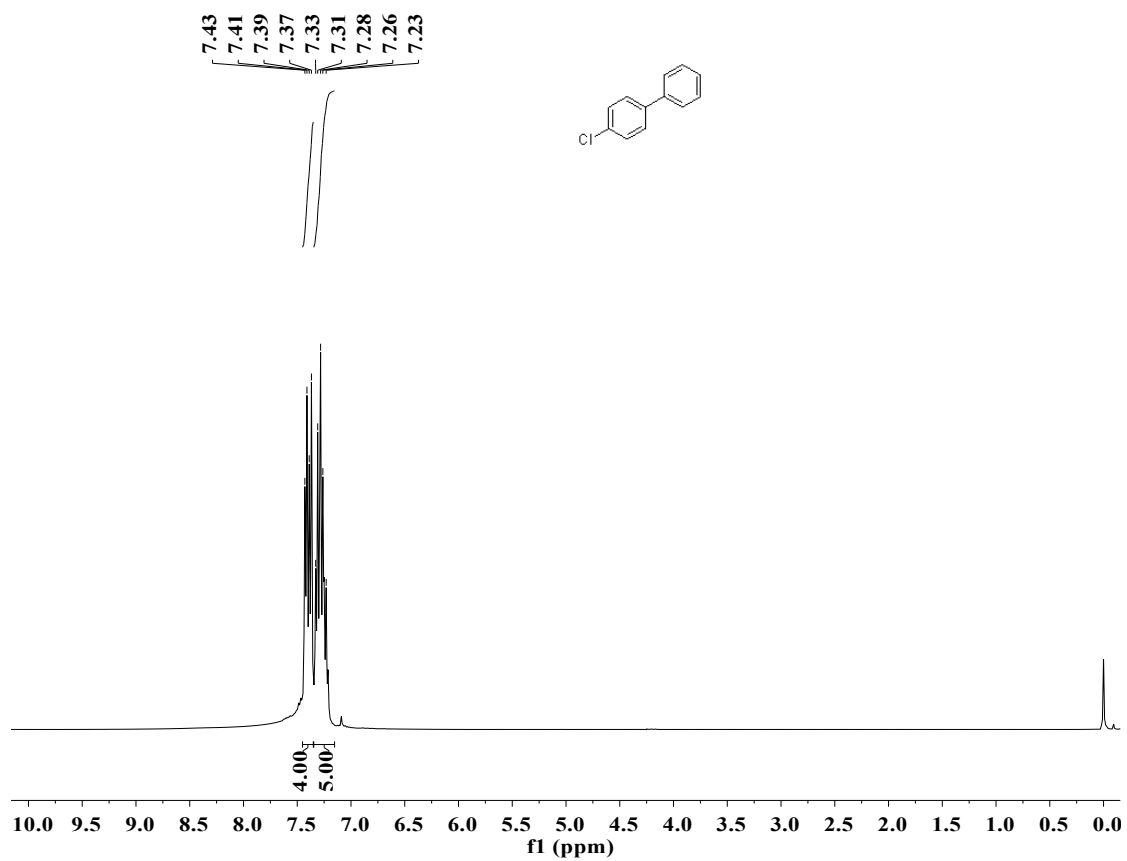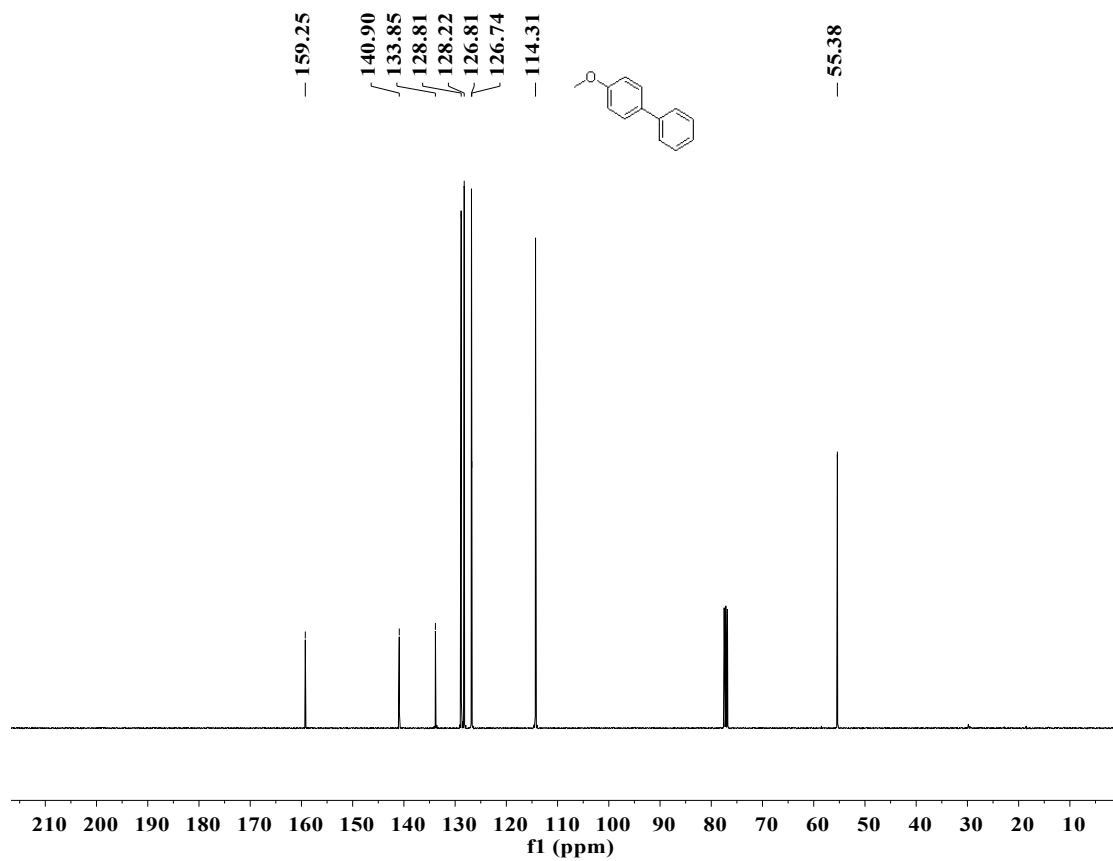
7. Copies of 1H-NMR and 13C-NMR Spectra.

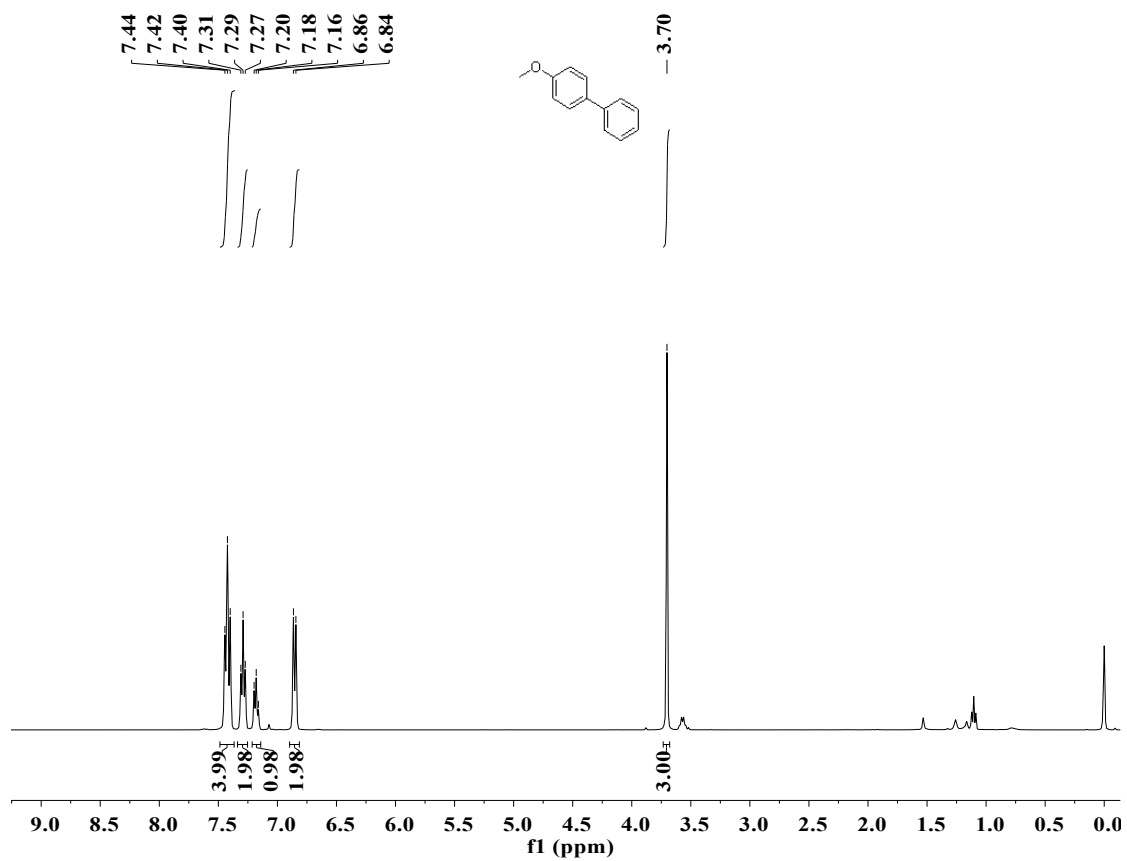

^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 1,1'-biphenyl (CDCl$_3$).

7.43
7.41
7.33
7.31
7.29
7.24
7.22
7.21
7.02
7.00
6.98

3.99
2.01
1.01
2.02

10.0 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 0.0
f1 (ppm)

163.81
161.36
140.36
137.47
137.44
128.93
128.83
128.75
127.37
127.12
115.82
115.60

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
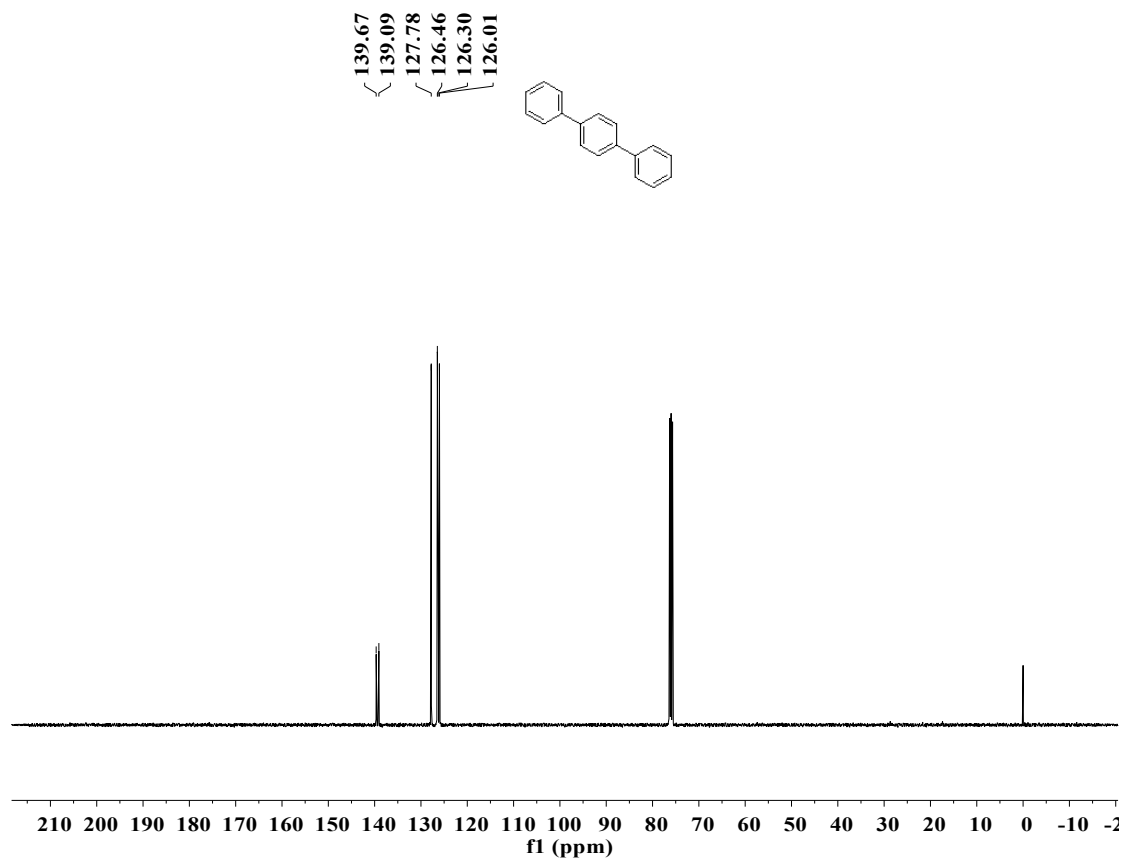f1 (ppm)

¹H NMR (400 MHz) and ¹³C{¹H} NMR (101 MHz) spectra of 4-fluoro-1,1'-biphenyl (CDCl₃).

7.43
7.41
7.39
7.37
7.33
7.31
7.28
7.26
7.23

4.00
5.00

10.0 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 0.0
f1 (ppm)

138.89
138.57
132.29
127.83
127.80
127.30
126.51
125.89

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 4-chloro-1,1'-biphenyl (CDCl$_3$).

¹H NMR (400 MHz) and ¹³C{¹H} NMR (101 MHz) spectra of 4-methoxy-1,1'-biphenyl (CDCl₃).
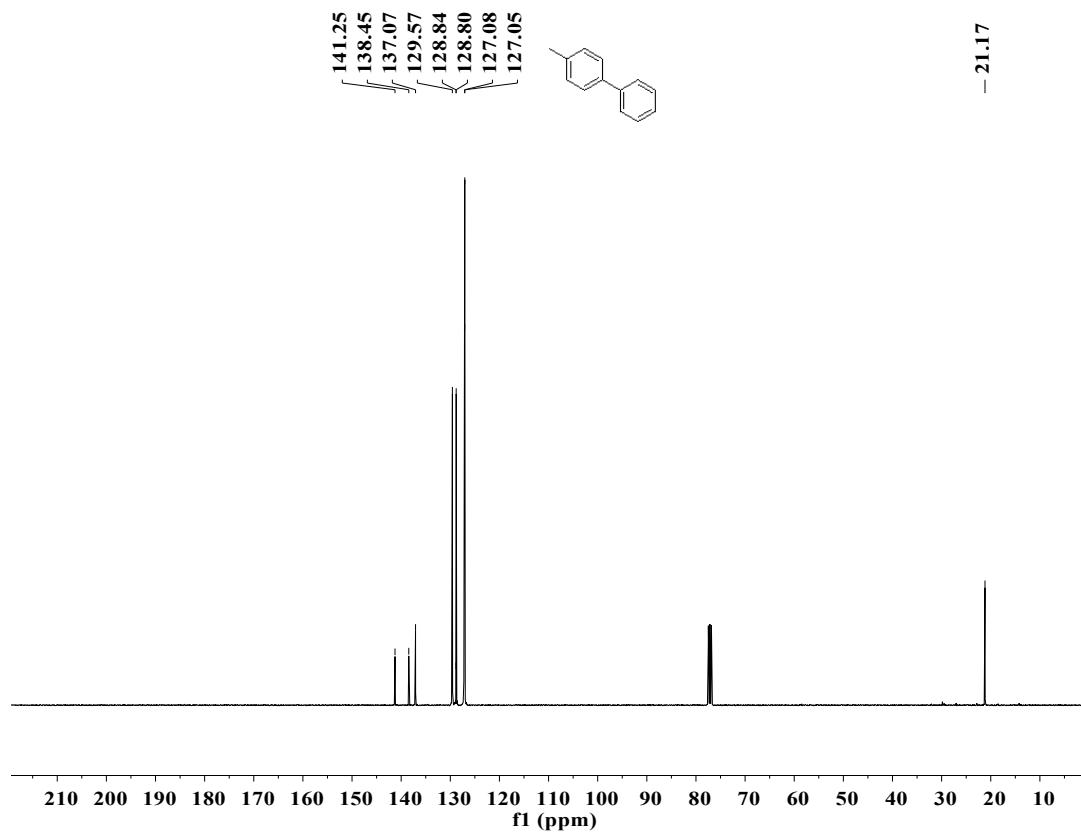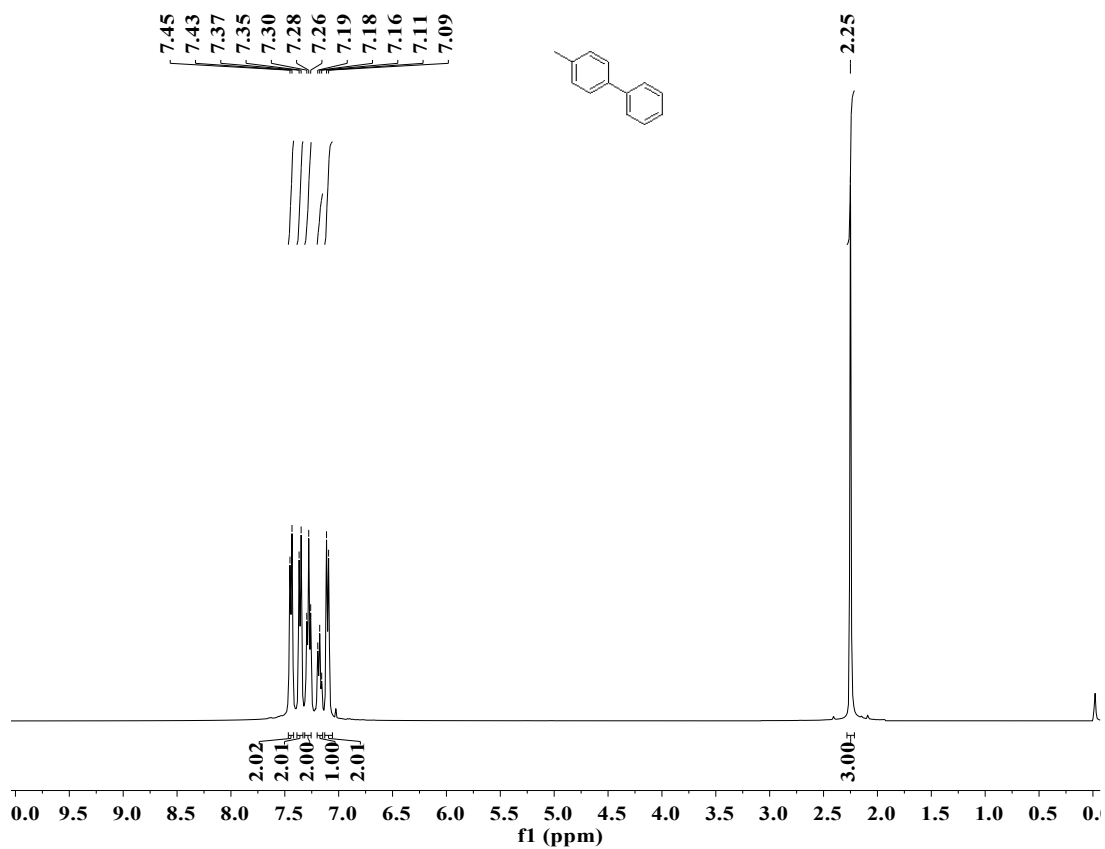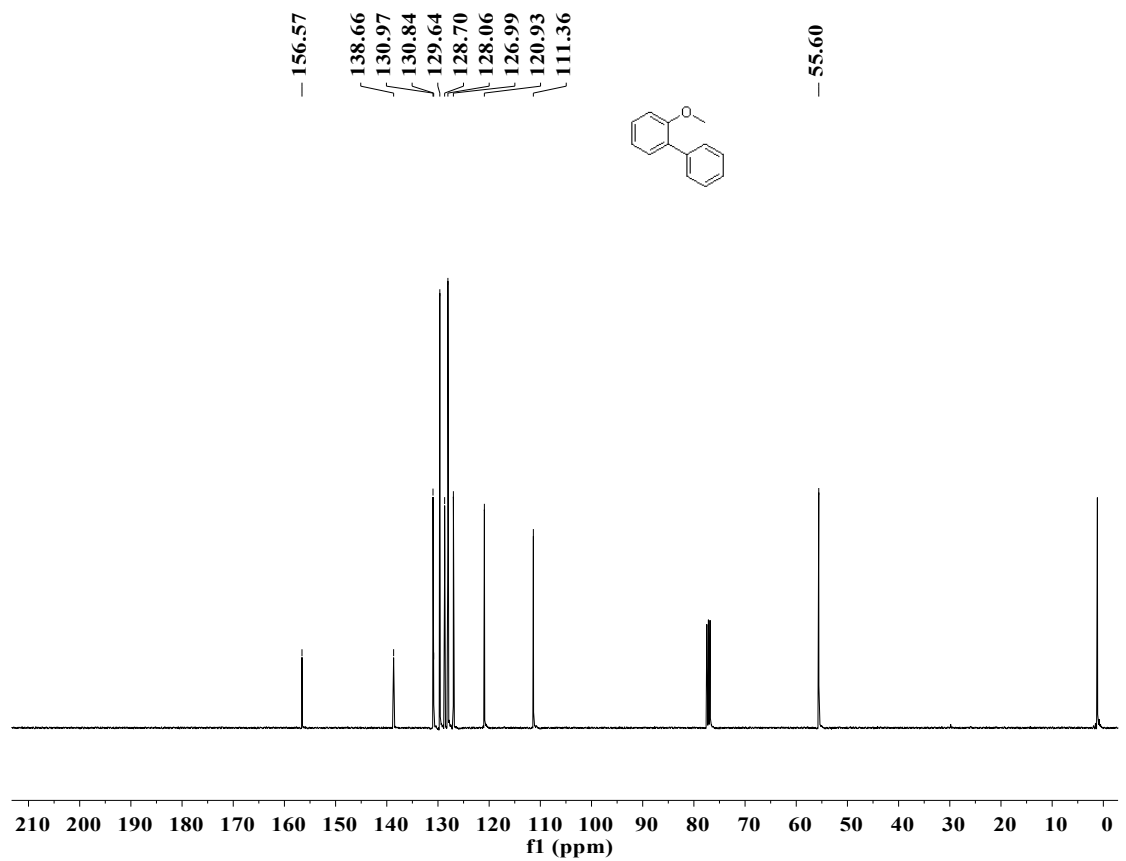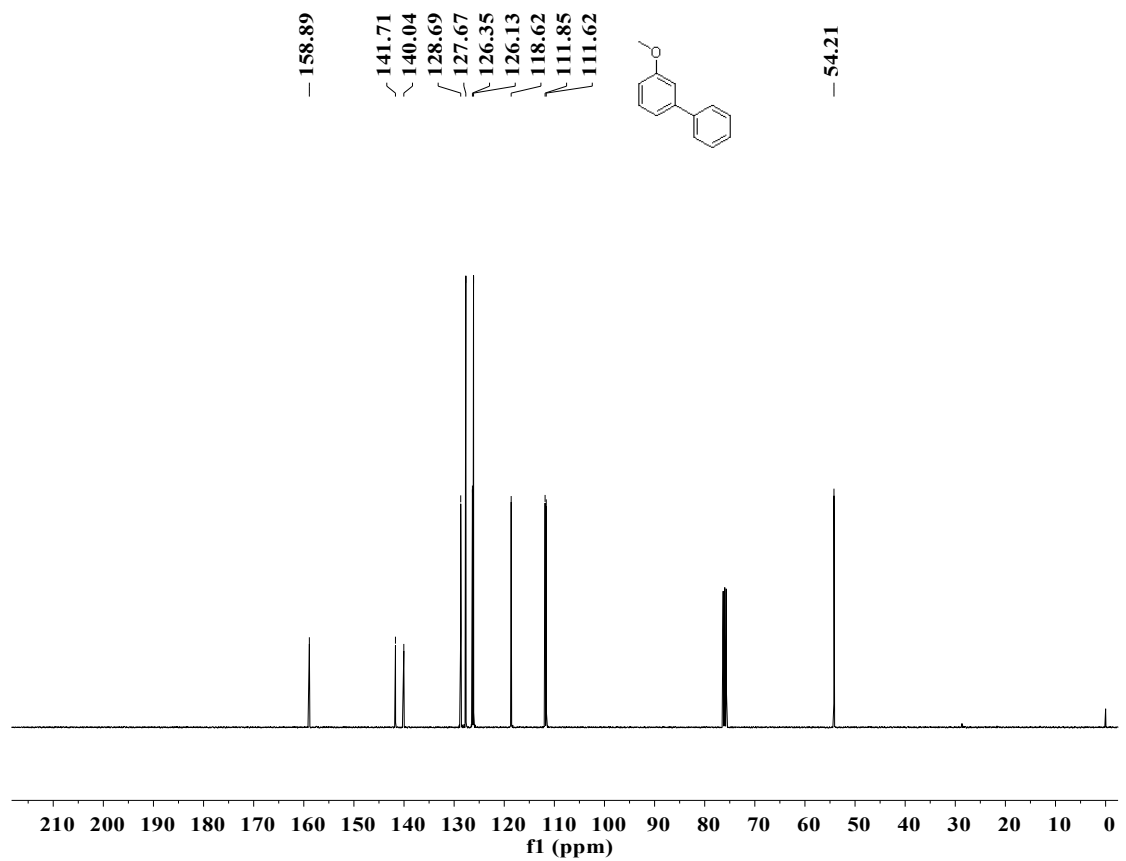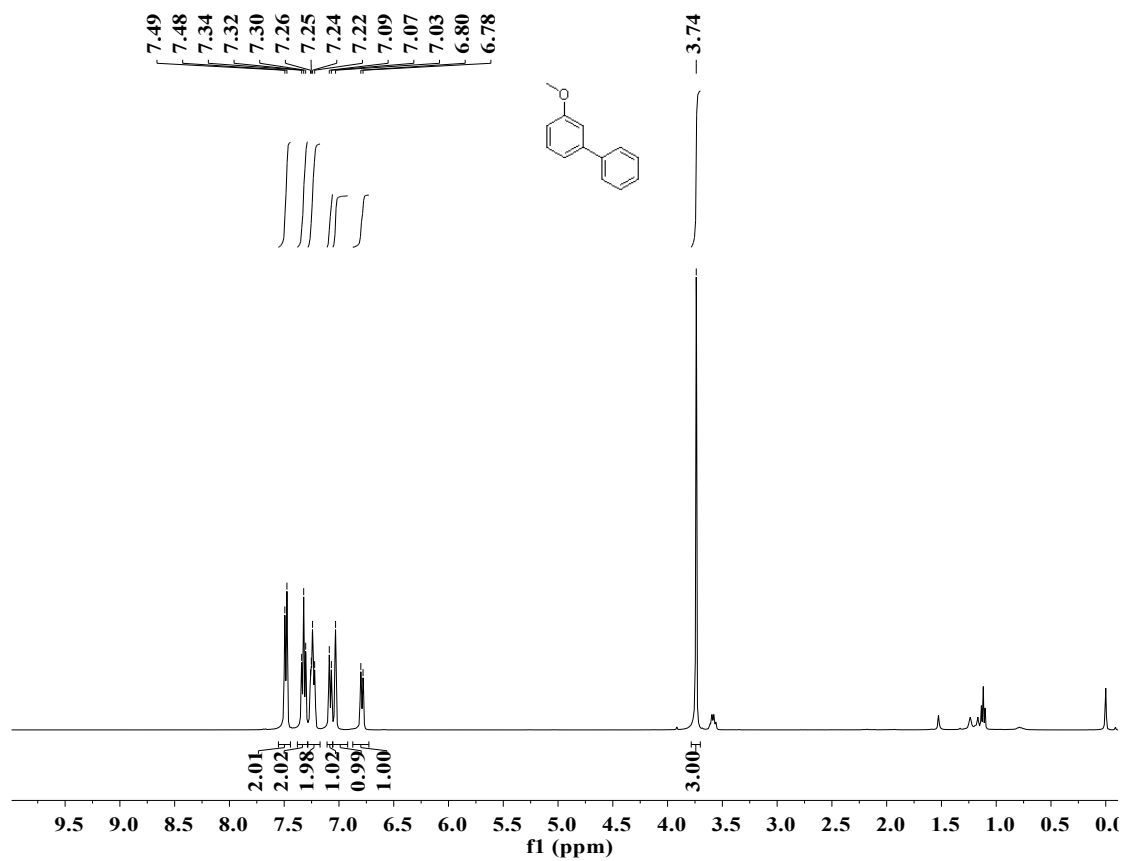
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 4-methyl-1,1'-biphenyl (CDCl$_3$).
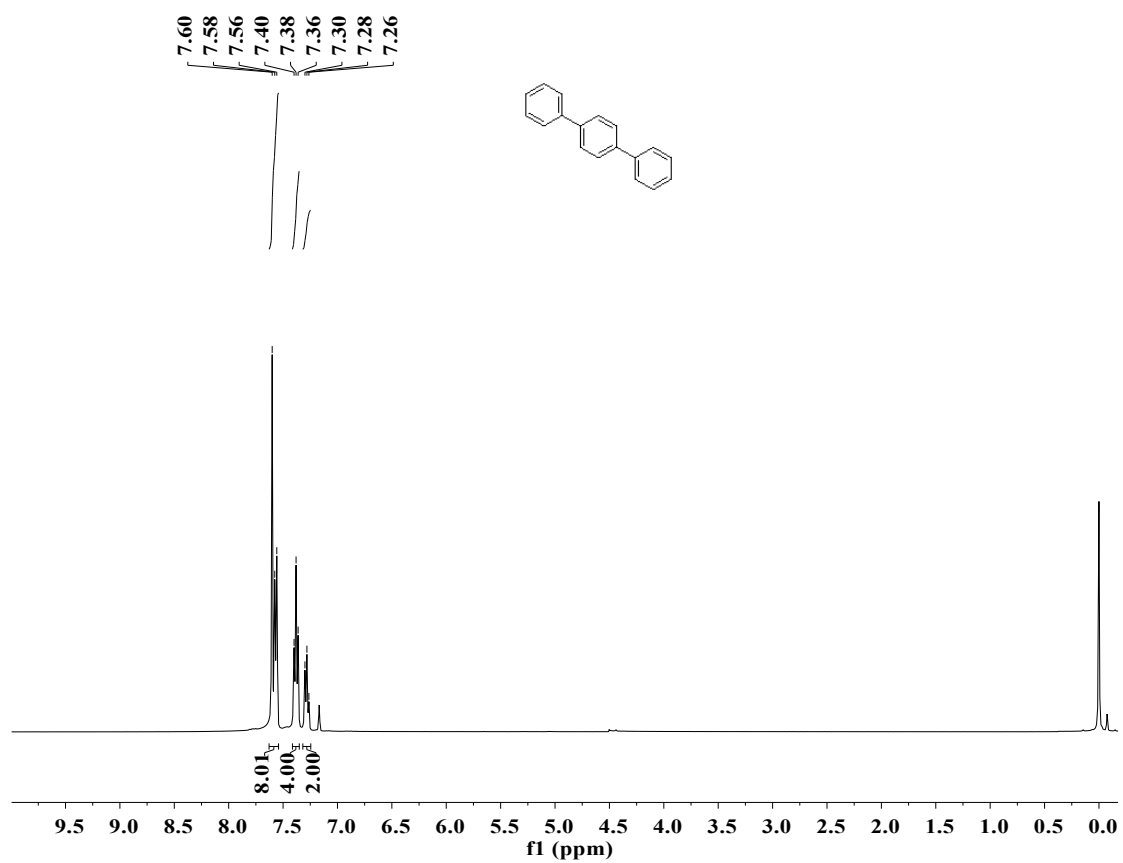
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 1,1',4',1''-terphenyl (CDCl$_3$).

7.43
7.41
7.30
7.29
7.27
7.22
7.20
7.17
6.93
6.91
6.89
6.86
6.84

3.66

1.99
2.00
3.02
1.00
1.01

3.02

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 0.0
f1 (ppm)

156.57

138.66
130.97
130.84
129.64
128.70
128.06
126.99
120.93
111.36

55.60

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
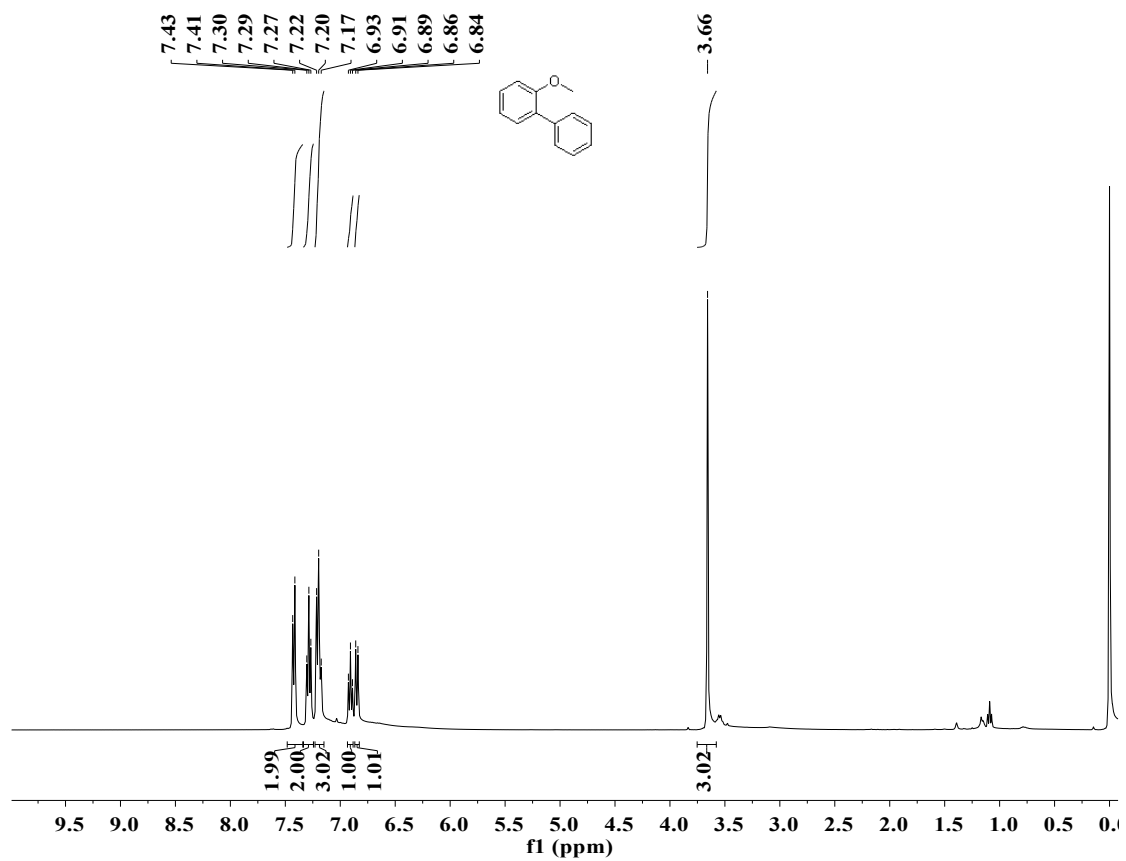
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 2-methoxy-1,1'-biphenyl (CDCl$_3$).

^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 3-methoxy-1,1'-biphenyl (CDCl$_3$).
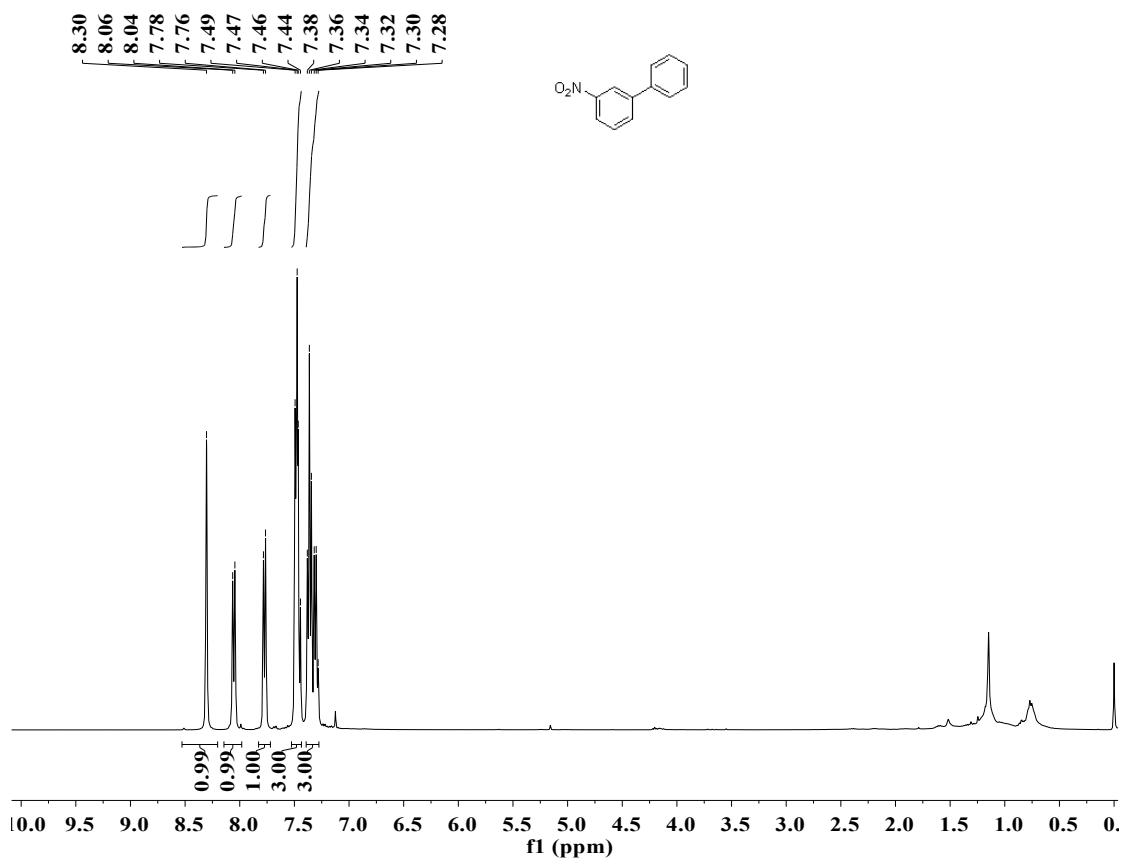
¹H NMR (400 MHz) and ¹³C{¹H} NMR (101 MHz) spectra of 3-nitro-1,1'-biphenyl (CDCl₃).
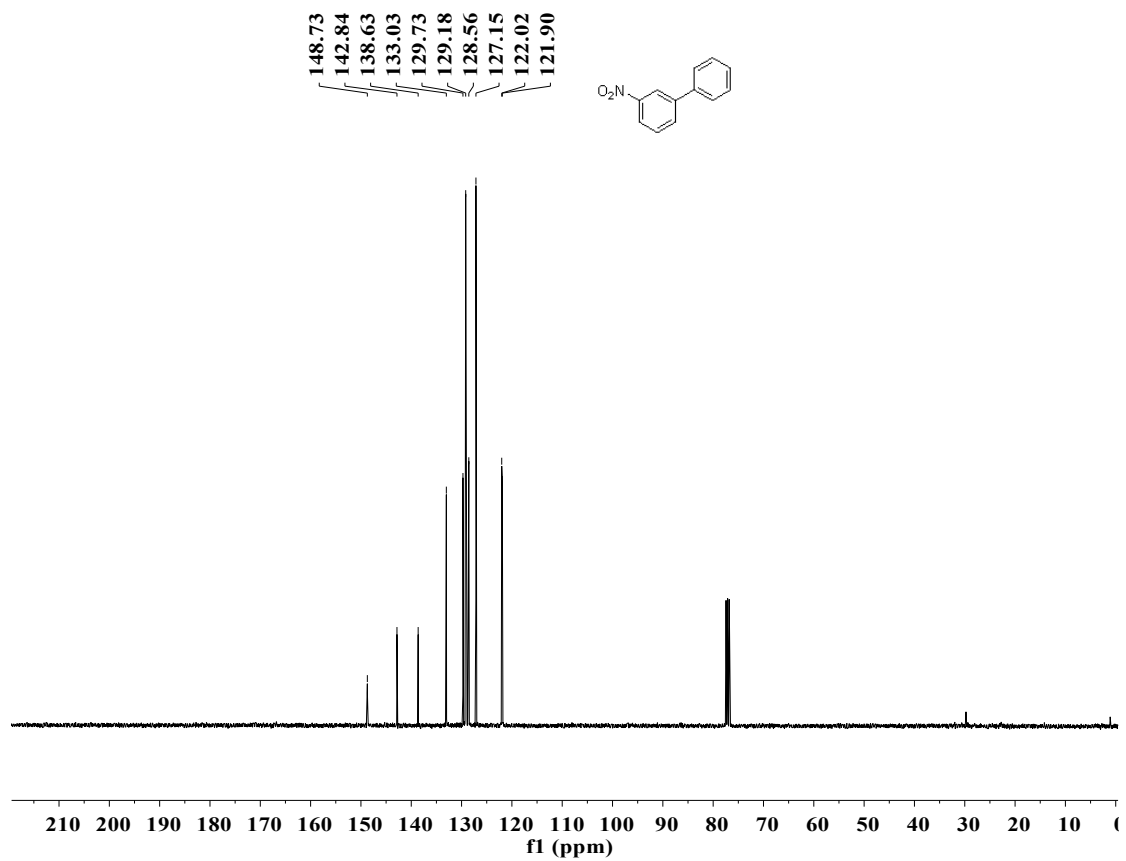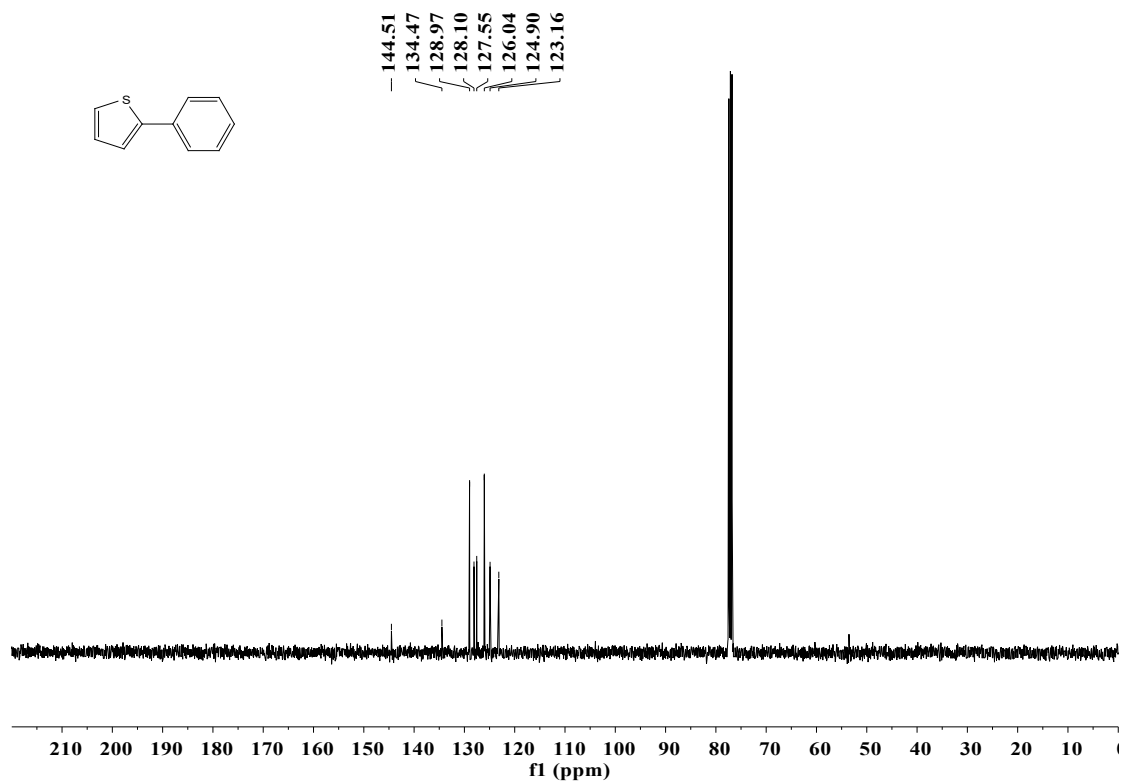
7.64, 7.63, 7.61, 7.41, 7.39, 7.37, 7.33, 7.33, 7.32, 7.32, 7.31, 7.29, 7.28, 7.27, 7.10, 7.09, 7.09, 7.08

2.00, 2.00, 1.00, 2.00, 1.01

144.51, 134.47, 128.97, 128.10, 127.55, 126.04, 124.90, 123.16
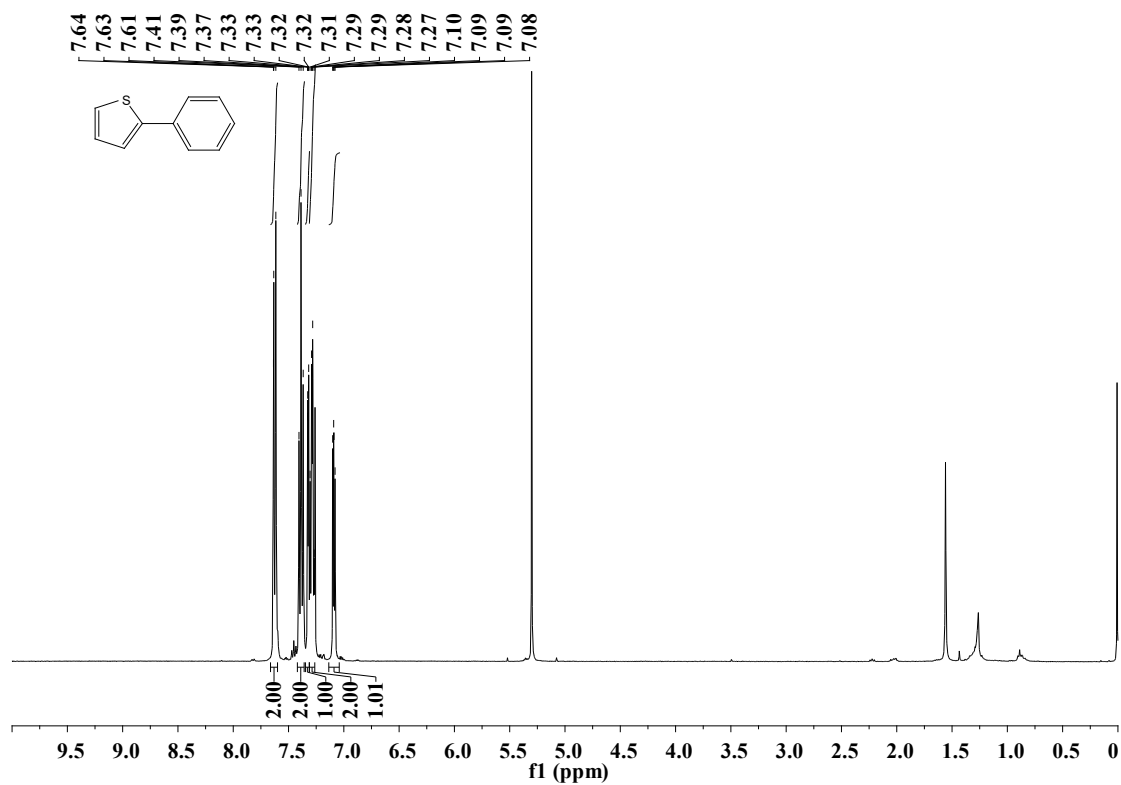
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 2-Phenylthiophene (CDCl$_3$).
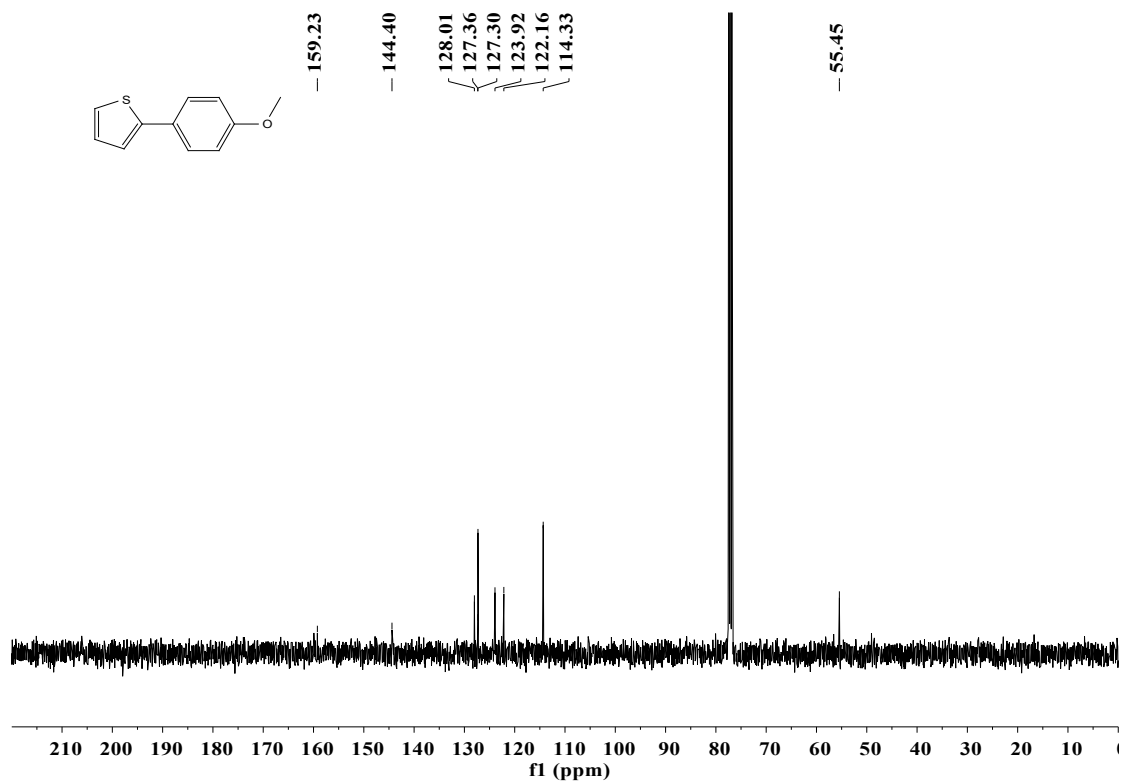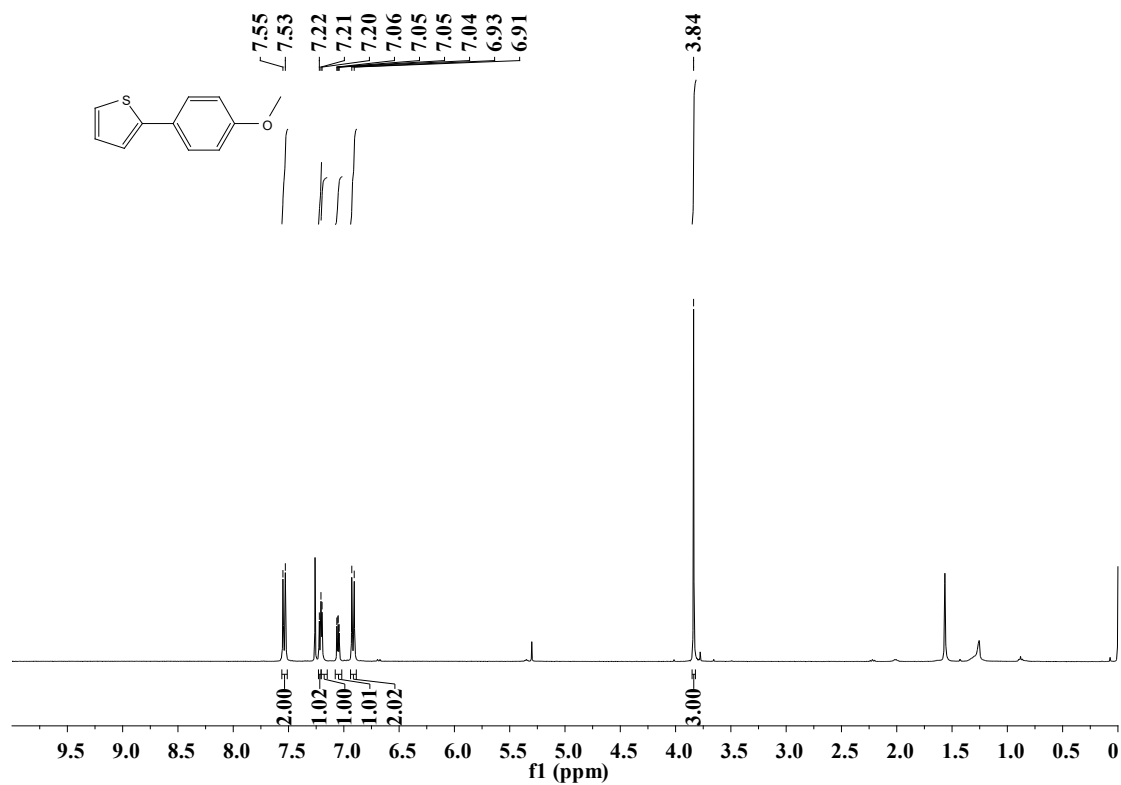
^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (101 MHz) spectra of 1-(4-Thiophen-2-yl-phenyl)-ethanon (CDCl$_3$).