Supporting Information

A Foldamer-Based Organocatalyst for Direct Arylations of Unactivated Arenes

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1. General remarks

^{1}H NMR data were obtained on a Bruker AMX500 (500 MHz) or Avance III (400MHz) nuclear resonance spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectra as 0.00 ppm (chloroform, 7.26 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (*J* values) in Hz and integration. Mass spectra were obtained using instrumentation which includes Finnigan MAT95XL-T and Micromass VG7035. Flash column chromatography was performed using 300 - 400 mesh silica with the indicated solvent system according to standard techniques. Analytical thin layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). All reagents were purchased from Acros, Aldrich, and Alfa Aesar without further purification in advance before use.

2. Synthesis of catalysts F1-F5 had been reported in the following journal article

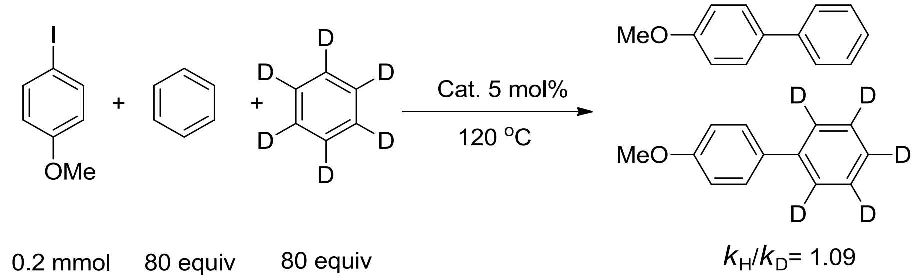
Changliang Ren, Victor Maurizot, Huaiqing Zhao, Jie Shen, Feng Zhou, Wei Qiang Ong, Zhiyun Du, Kun Zhang, Haibin Su and Huaqiang Zeng *J. Am. Chem. Soc.* **2011**, *133*, 13930-13933.

3. General experimental procedures for the arylation

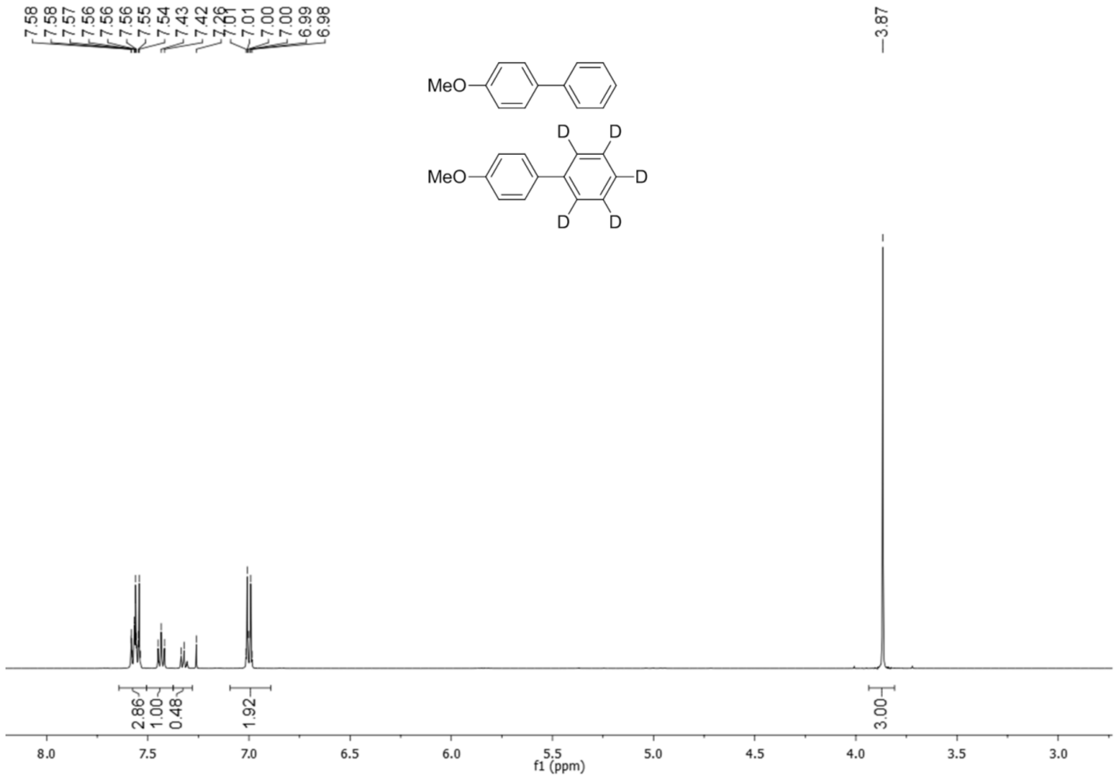
At the 0.2 mmol scale: Aryl iodides (0.2 mmol) and **F2** (0.01 mmol, 5 mol %) were mixed in dried Schlenk tubes, followed by addition of *t*-BuOK (0.6 mmol, 3.0 equiv). Benzene (3 mL) and aryl iodides (0.2 mmol) were then added via syringe. The Schlenk tube was sealed using septum-sealed and the air inside was removed by flushing with Argon three times. The mixture was stirred under an argon atmosphere in the sealed tube at 120 °C for 24 h. After cooling down to room temperature, the reaction mixture was filtered through a short plug of silica gel, and washed with a copious amount of ethyl acetate. The combined organic phase was concentrated under vacuum. The product was purified through flash column chromatography on 300 - 400 mesh silica gel with pure hexane or hexane/ethyl acetate at various ratios as eluent.

At the 1.0 mmol scale: Except for a five-fold increase in the amount of reagents used, experimental procedure at the 1.0 mmol scale was identical to that at the 0.2 mmol scale. The 4-Iodoanisole (1 mmol, 0.234 g) was tested to ensure that the catalytic reaction can be scaled up with satisfying yields. Purification of the product through flash column chromatography using hexane-ethyl acetate (100:0.5, v:v) as eluent gave a white solid (0.171 g, 93%). This isolated yield of 93% is near-identical to 96% yield obtained at the 0.2 mmol scale (entry 1 of Table 2).

4. Kinetic isotope effect experiments



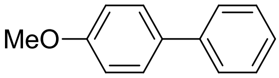
4-iodoanisole (0.2 mmol), *t*-BuOK (0.6 mmol) and **F2** (5 mol%) were mixed in a Schlenk tube, and then benzene-H_6 (1.4 mL) and benzene-D_6 (1.4 mL) were added into the tube using syringe. The septum-sealed tube was flushed with Ar three times. The mixture was stirred under an argon atmosphere at 120 ^{o}C for 24 h. After cooling to room temperature, the reaction mixture was quenched and extracted with ether (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph using hexane-ethyl acetate (100:0.5, v:v) to yield the desired product. The product distribution (k_H/k_D = 1.09) was analyzed by ^{1}H NMR.



5. Characterization of products

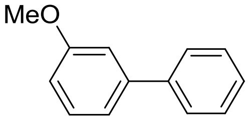
All the known compounds were in accordance with the data reported in the literatures.

4-Methoxybiphenyl (3a)[1]



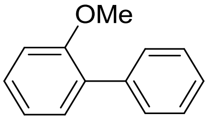
Compound **3a** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 0.5, v:v) as eluent to give **3a** as white solid (35 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 -7.54 (m, 4H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H).

3-Methoxylbiphenyl (3b)[1]



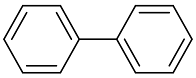
Compound **3b** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 0.5, v:v) as eluent as to give **3b** white solid (32mg, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.23 – 7.16 (m, 2H), 6.95 – 6.92 (m, 1H), 3.89 (s, 3H).

2-Methoxylbiphenyl (3c)[1]



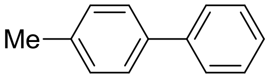
Compound **3c** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 0.5, v:v) as eluent to give **3c** as white solid (33 mg, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.54 (m, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.37 -7.33 (m, 3H), 7.08 – 7.00 (m, 2H), 3.83 (s, 3H).

Biphenyl (3d)[1]



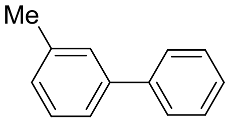
Compound **3d** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3d** as white solid (30 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 4H), 7.49 – 7.45 (m, 4H), 7.39 – 7.35 (m, 2H).

4-Methylbiphenyl (3e)[1]



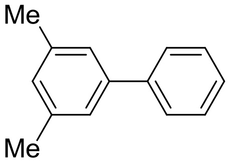
Compound **3e** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3e** as white solid (29 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.53 – 7.51 (m, 2H), 7.47 – 7.43 (m, 2H), 7.37 – 7.33 (m, 1H), 7.29 – 7.26 (m, 2H), 2.42 (s, 3H).

3-Methylbiphenyl (3f)[1]



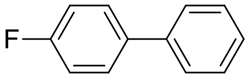
Compound **3f** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3f** as colorless oil (30 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.48 – 7.42 (m, 4H), 7.38 – 7.34 (m, 2H), 7.19 (d, J = 7.5 Hz, 1H), 2.45 (s, 2H).

3,5-Dimethylbiphenyl (3g)[1]



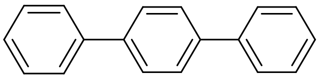
Compound **3g** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3g** as colorless oil (26 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.47 – 7.43 (m, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.24 (s, 2H), 7.03 (s, 1H), 2.41 (s, 6H).

4 - Fluorobiphenyl (3h)[1]



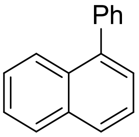
Compound **3h** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3h** as white solid (29 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.46 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 7.16 – 7.13 (m, 2H).

p - Terphenyl (3i)[1]



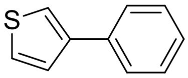
Compound **3i** was prepared according to the general experiment procedure described above (5 equiv of *t*-BuOK was used) and purified by flash column chromatography with hexane as eluent to give **3i** as white solid (39 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 8H), 7.50 -7.46 (m, 4H), 7.40 – 7.36 (m, 2H).

1 - Phenylnaphthalene (3j)[1]



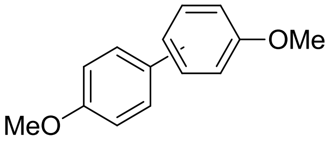
Compound **3j** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3j** as white solid (27 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 3H), 7.58– 7.51 (m, 6H), 7.49 – 7.45(m, 3H).

3-Phenylthiophene (3k)[2]



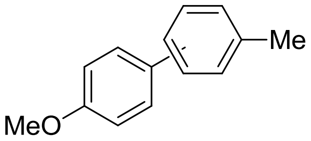
Compound **3k** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane as eluent to give **3k** as white solid (20 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.47 – 7.46 (m, 1H), 7.44 – 7.39 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 1H).

(p-Methoxyphenyl)anisole (3l)[1] (the mixture of o/m/p)



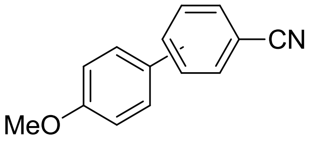
Compound **3l** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 2, v:v) as eluent to give **3l** as white solid (21 mg, 50%). MS(EI) Calcd for $C_{14}H_{14}O_2$: 214.0994; Found:214.0993.

(p-Methoxyphenyl)toluene (3m)[1] (the mixture of o/m/p)



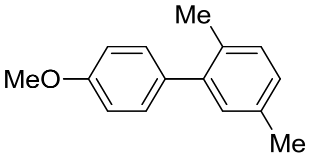
Compound **3m** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 1, v:v) as eluent to give **3m** as white solid (19 mg, 47%). MS(EI) Calcd for $C_{14}H_{14}O$: 198.1045; Found:198.1045.

(p-Methoxyphenyl)benzonitrile (3n)[2] (the mixture of o/m/p)



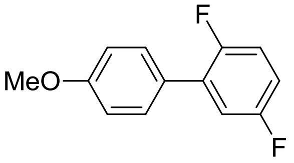
Compound **3n** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 2, v:v) as eluent to give **3n** as white solid (31 mg, 73%). MS(EI) Calcd for $C_{14}H_{14}ON$: 209.0841; Found:209.0841.

2,5 - dimethyl - 4' - methoxybiphenyl (3o)[1]



Compound **3o** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 1, v:v) as eluent to give **3o** as light yellow oil (17 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 3H), 7.16 – 7.04 (m, 2H), 6.96 – 6.93 (m, 2H), 3.85 (s,3H), 2.34 (s,3H), 2.23 (s,3H).

2,5−difluoro−4'−methoxybiphenyl (3p)[1]

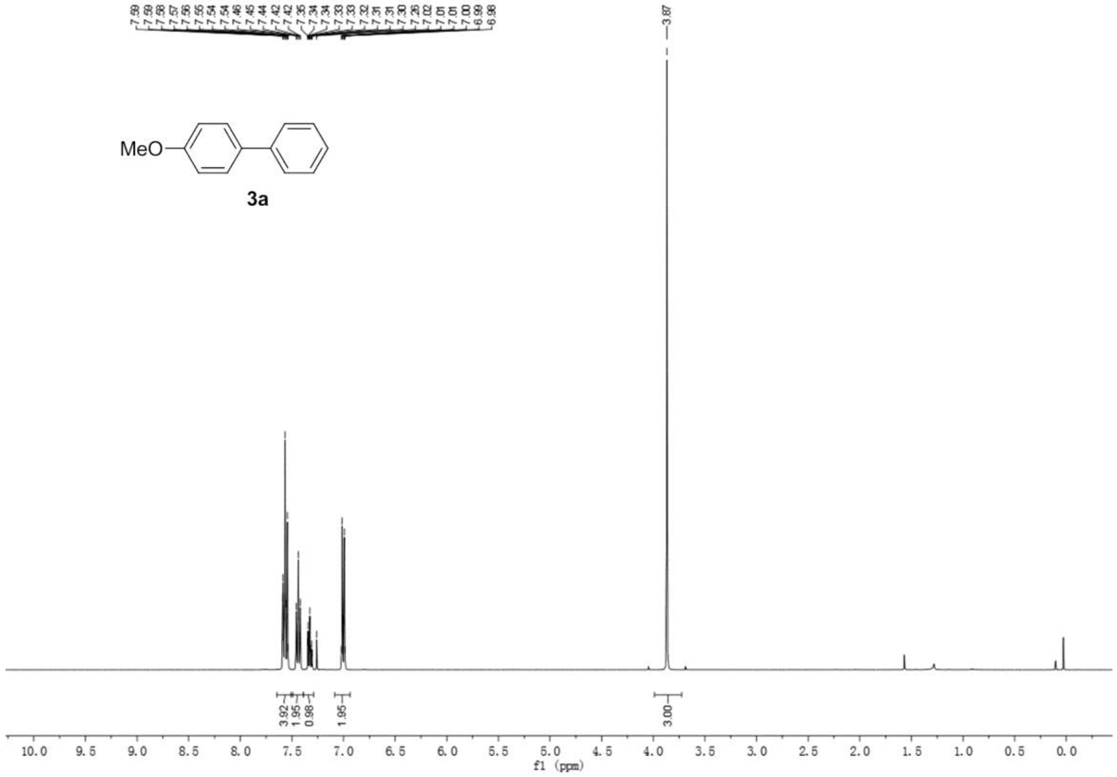


Compound **3p** was prepared according to the general experiment procedure described above and purified by flash column chromatography with hexane–ethyl acetate (100 : 1, v:v) as eluent to give **3p** as light yellow solid (23 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.14 – 7.06 (m, 2H), 7.01 – 6.93 (m, 3H), 3.86 (s, 3H).

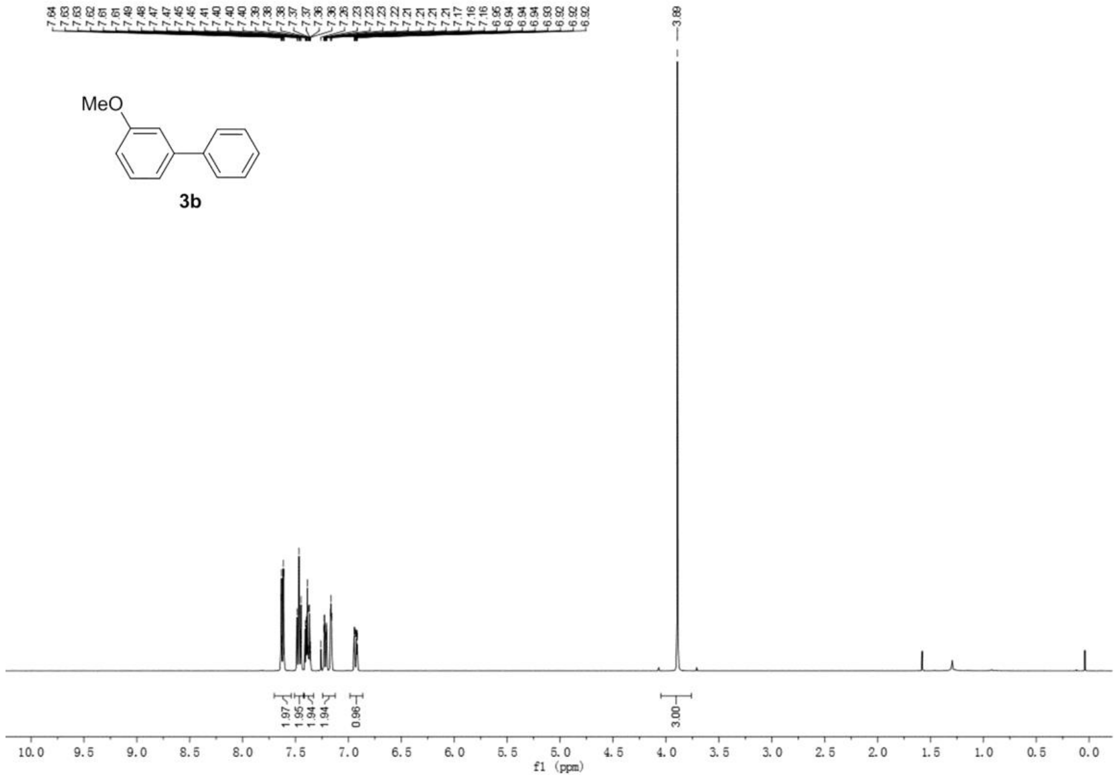
References:

1. Sun, C.-L.; Hu, L.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. *Nat. Chem.* **2010**, *2*, 1042.
2. Tanimoro, K.; Ueno, M.; Takeda, K.; Kirihata, M.; Tanimori, S. *J. Org. Chem.* **2012**, *77*, 7844.

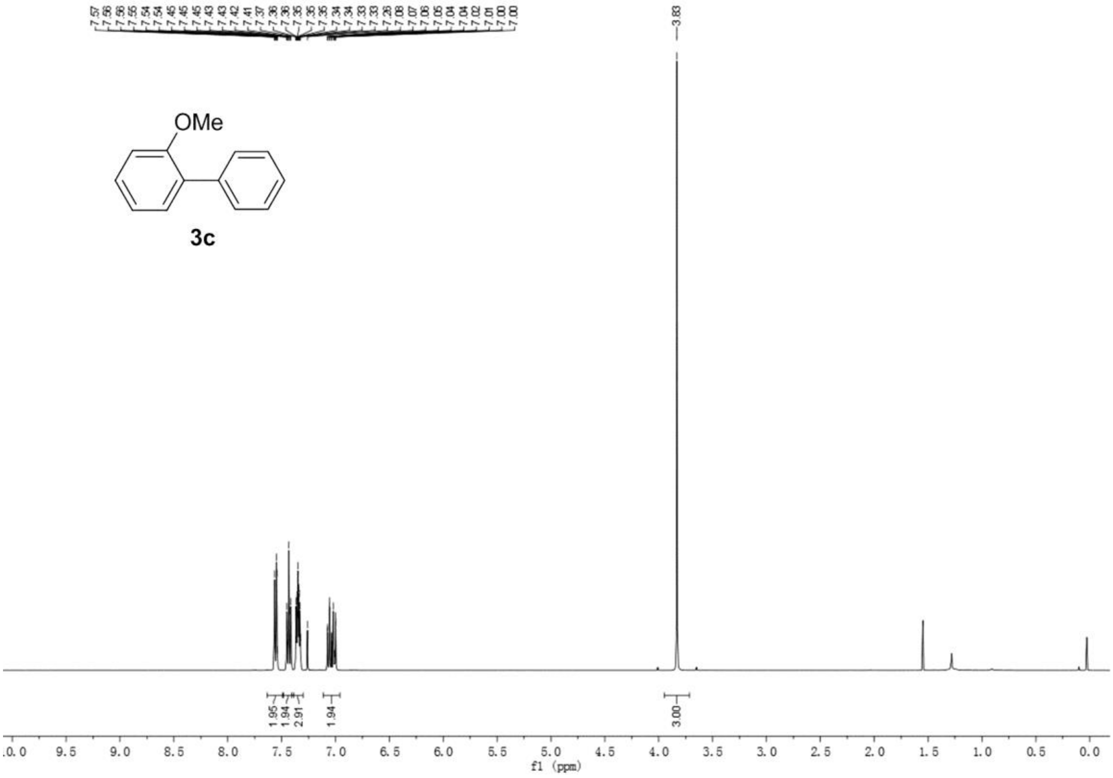
^{1}H Spectra:



3a



3b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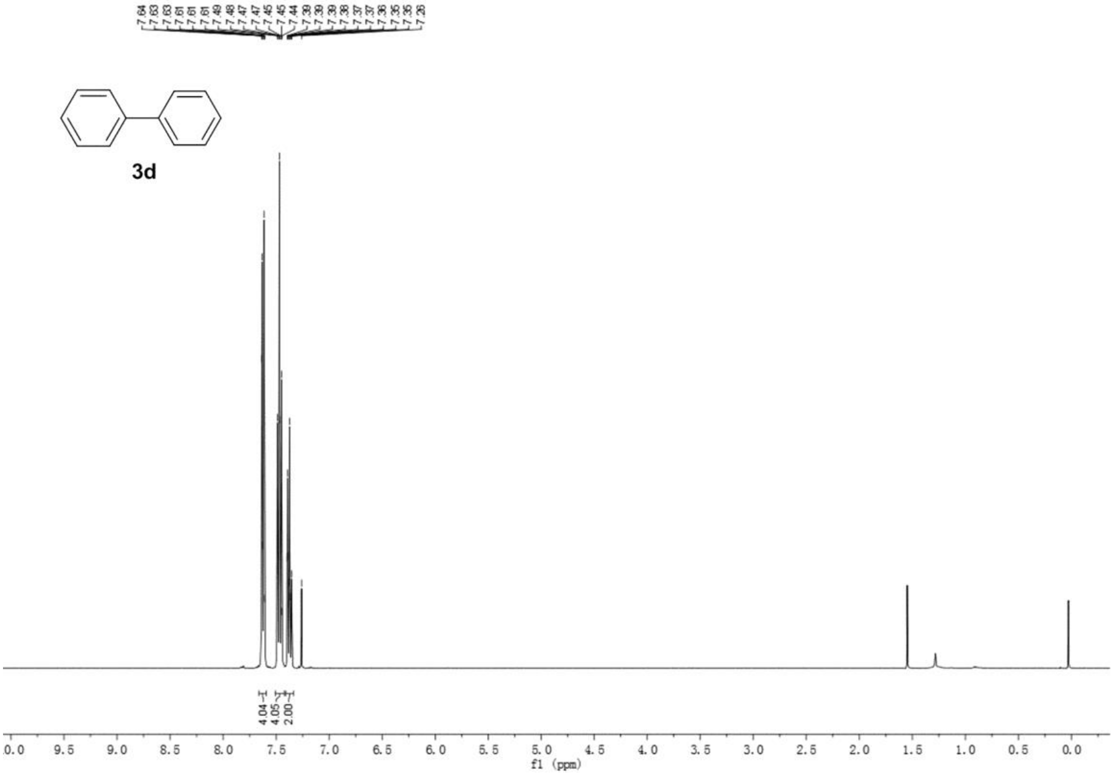
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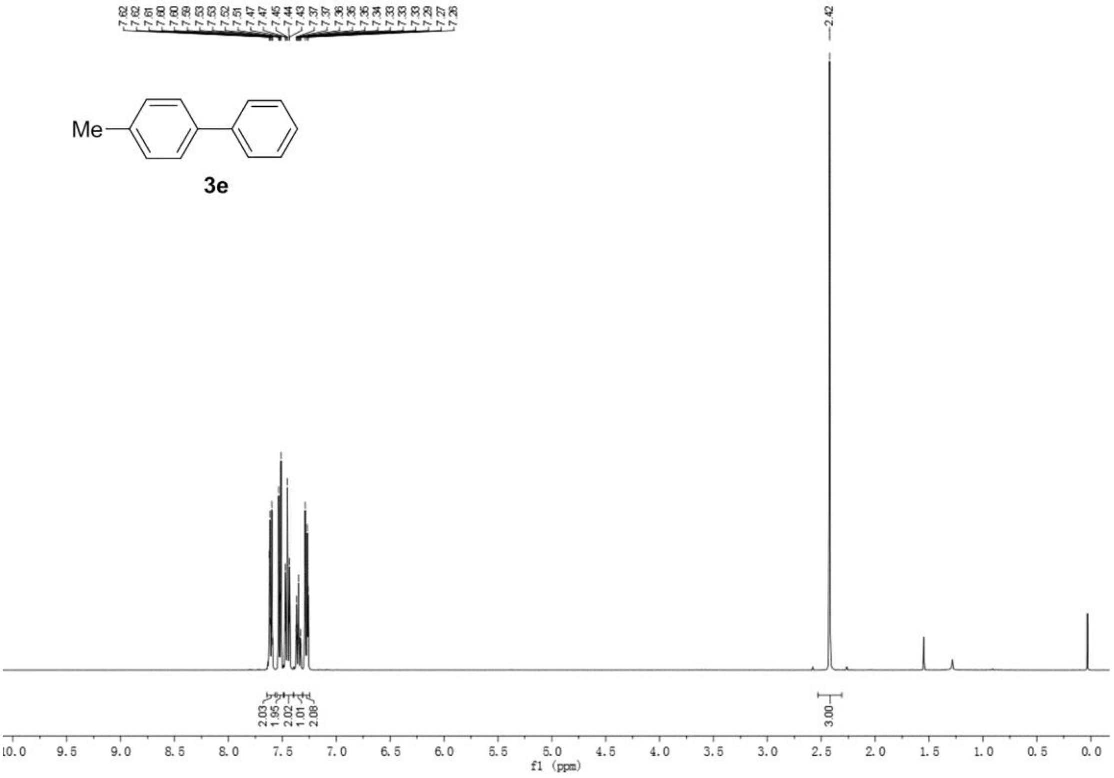
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f1 (ppm)

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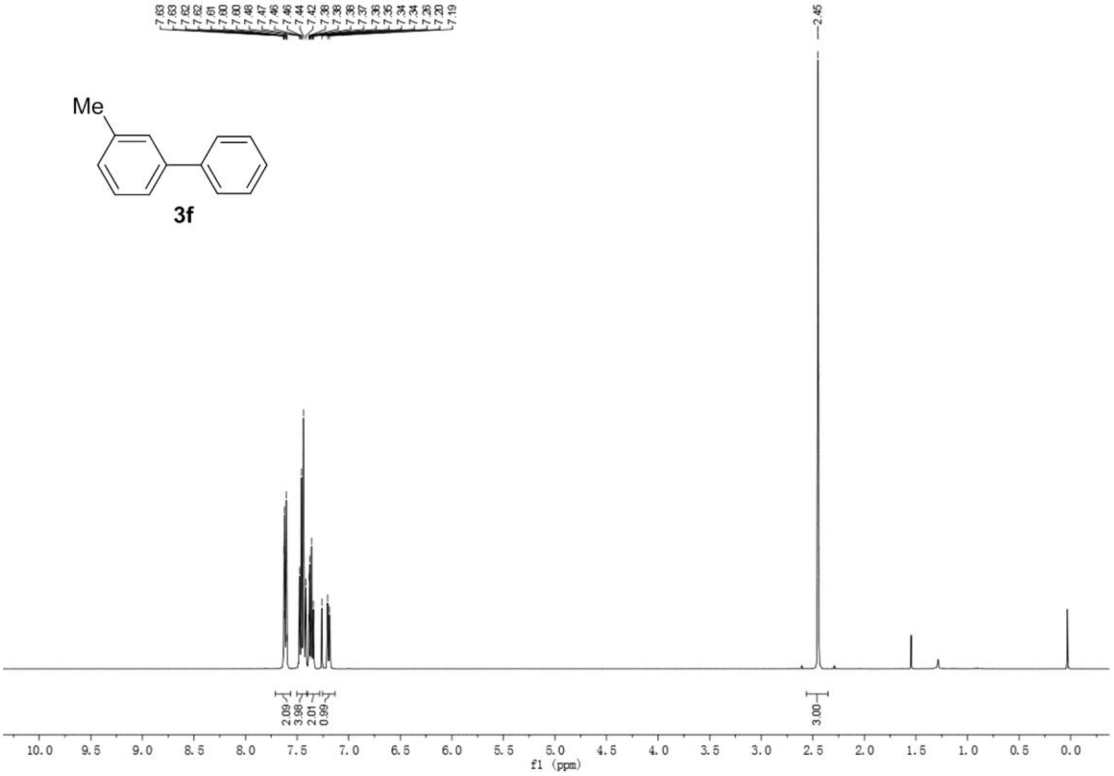
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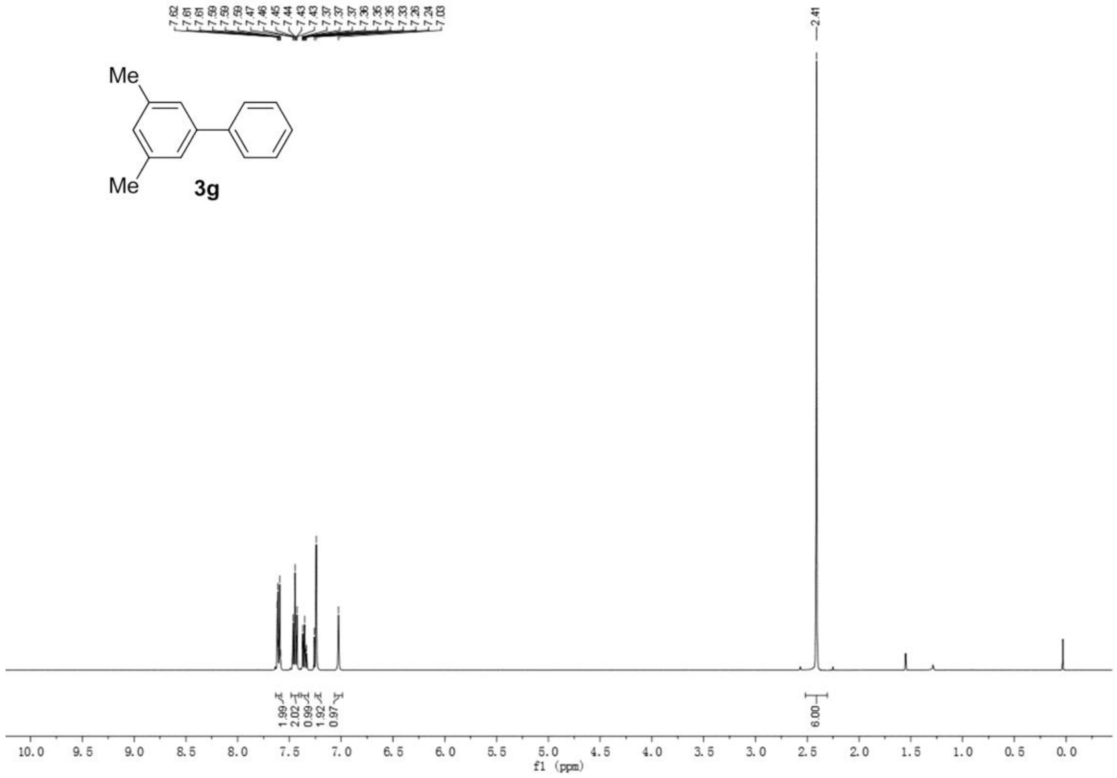
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f1 (ppm)

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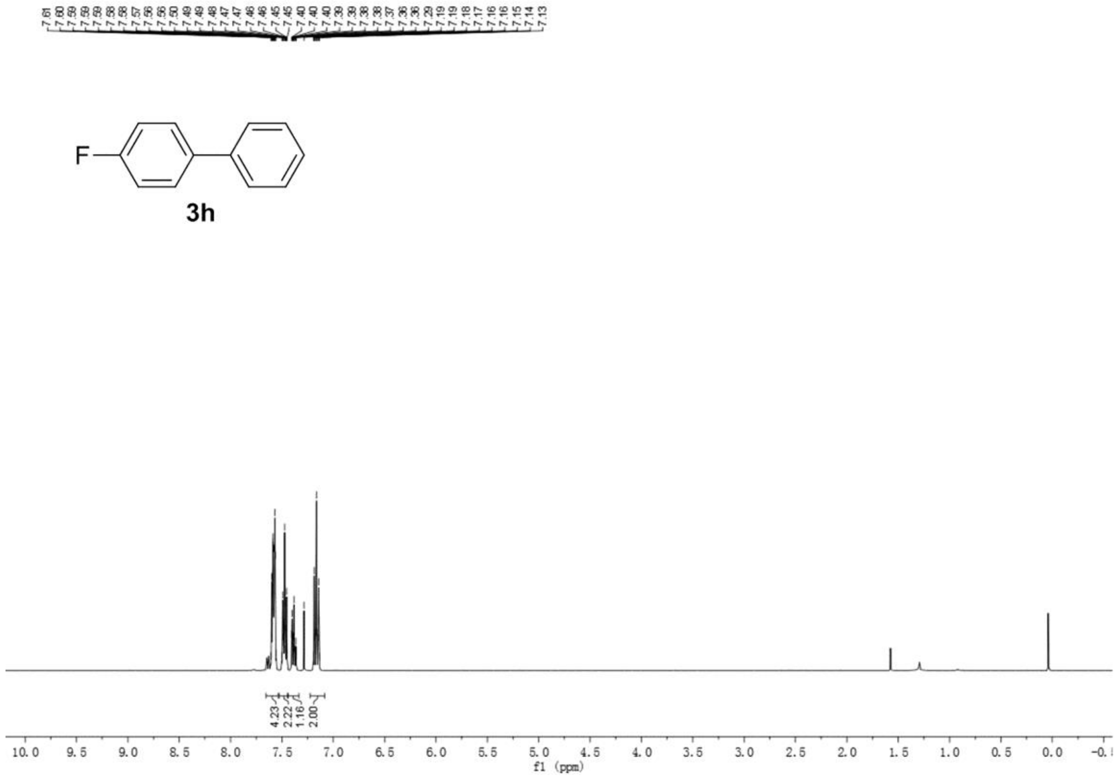
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f1 (ppm)

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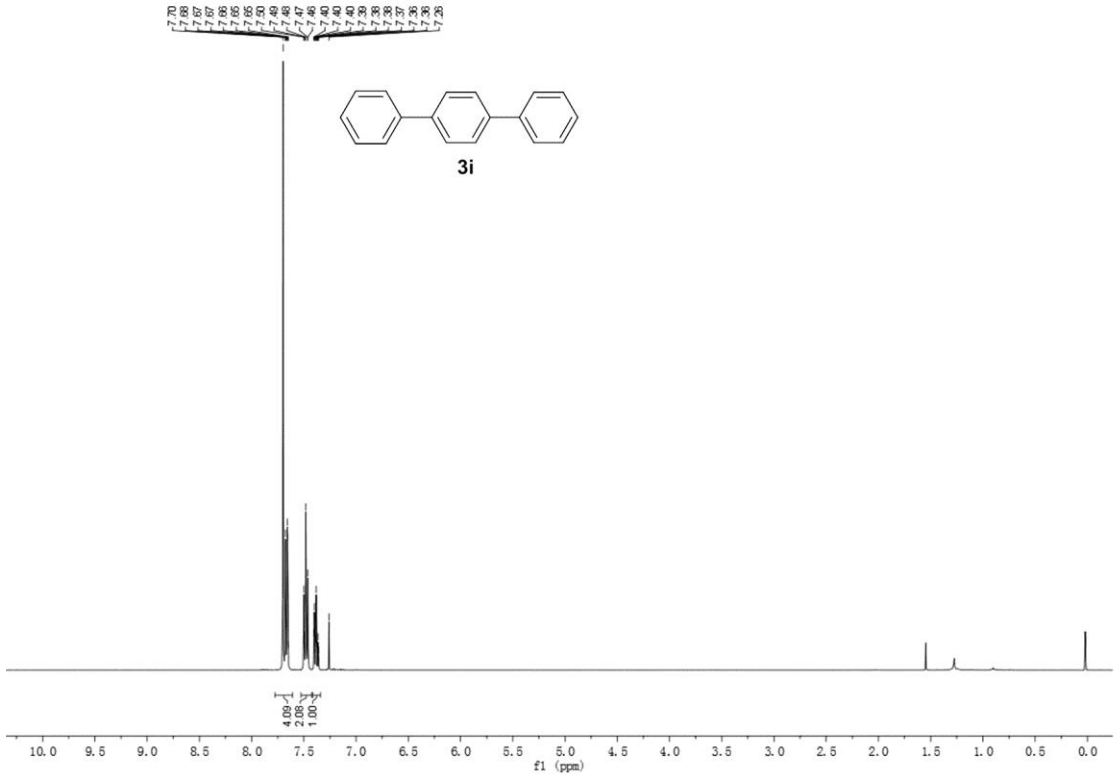
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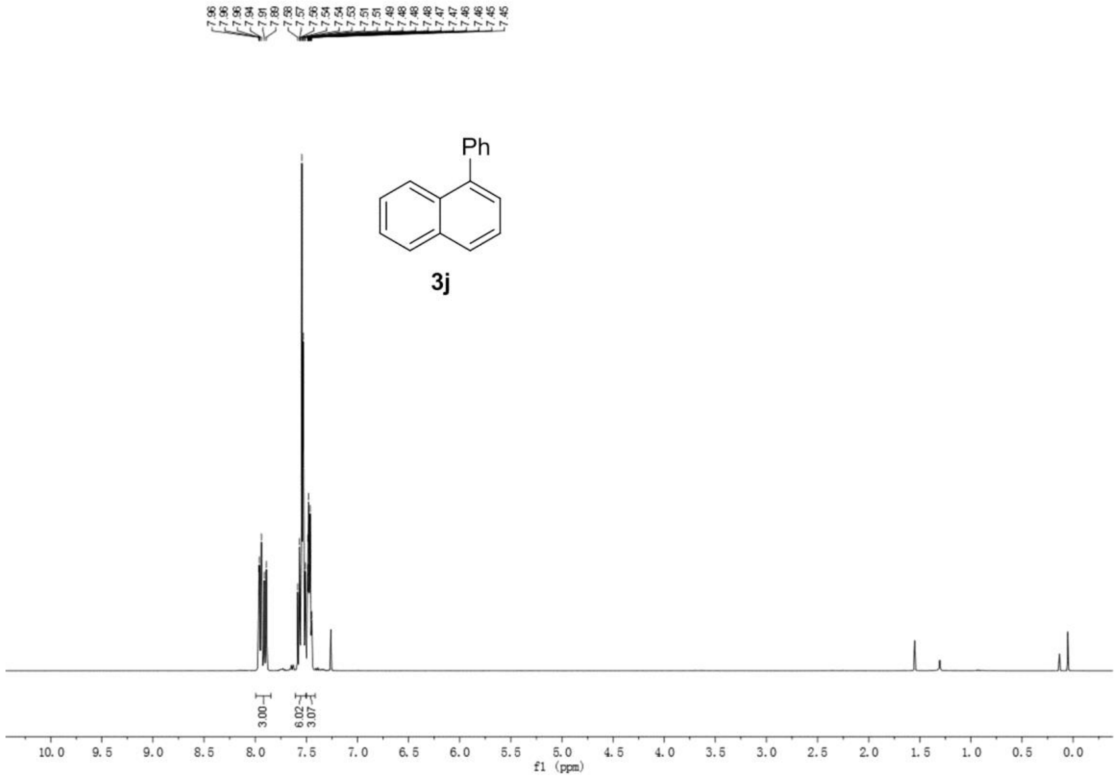
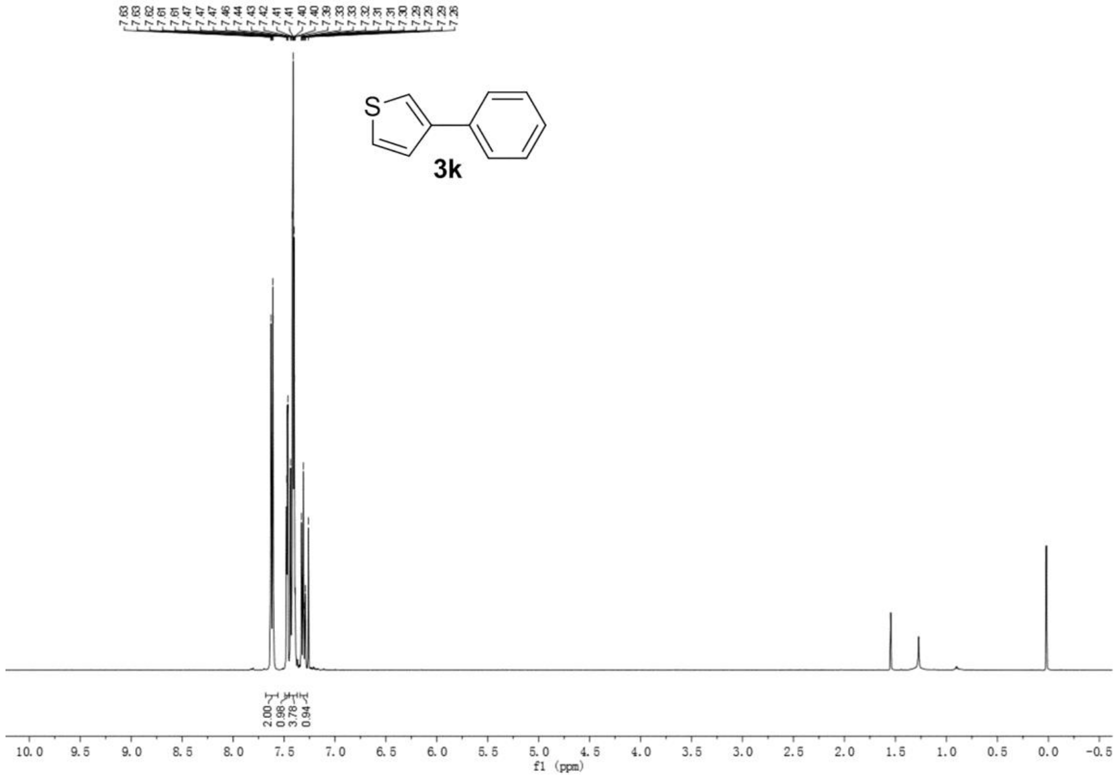
f1 (ppm)

3i


7.96
7.96
7.96
7.94
7.91
7.89
7.58
7.57
7.56
7.54
7.54
7.53
7.51
7.51
7.49
7.48
7.48
7.48
7.47
7.47
7.46
7.46
7.45
7.45
Ph
3.00
6.02
3.07
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)

3j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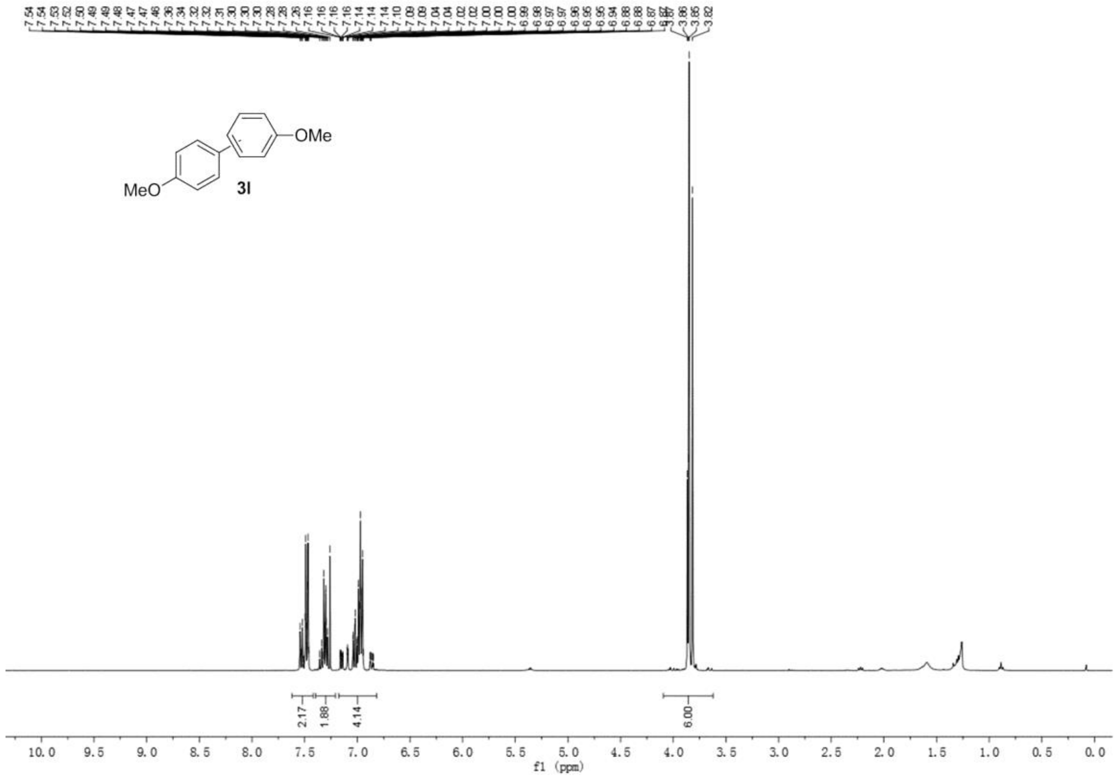
7.62
7.61
7.61
7.47
7.47
7.47
7.46
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.29
7.29
7.26
S
2.00
0.98
3.78
0.94
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3k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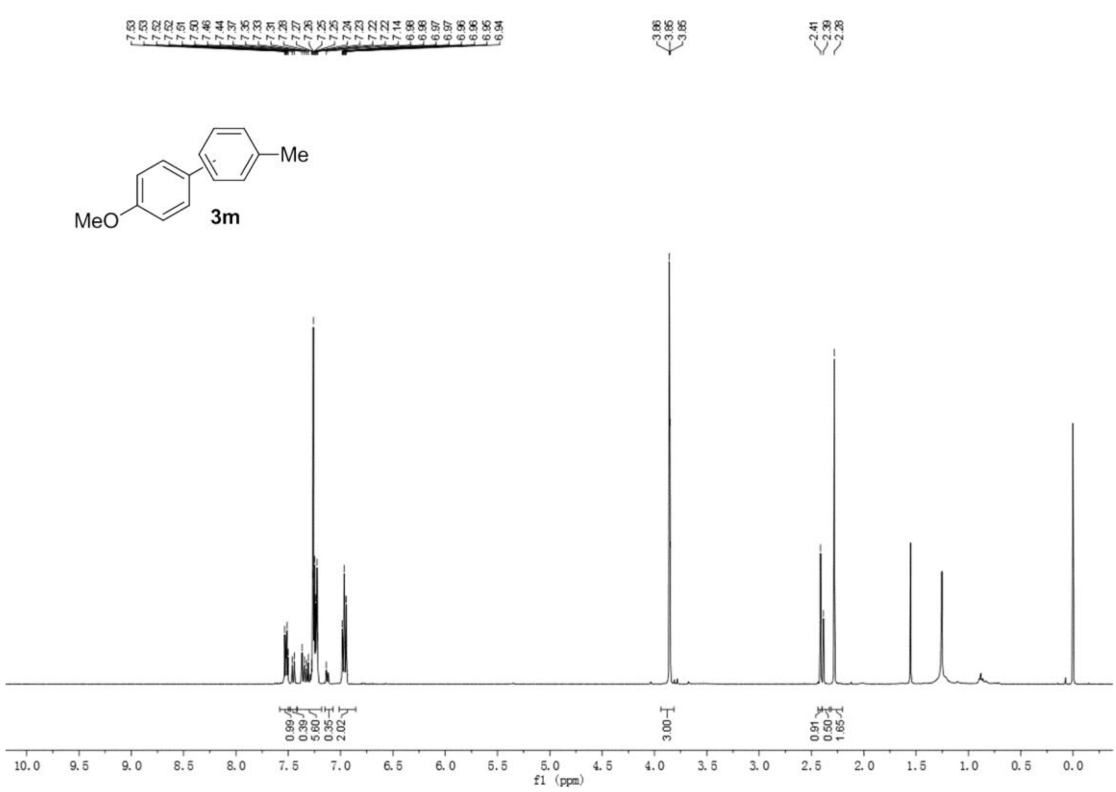
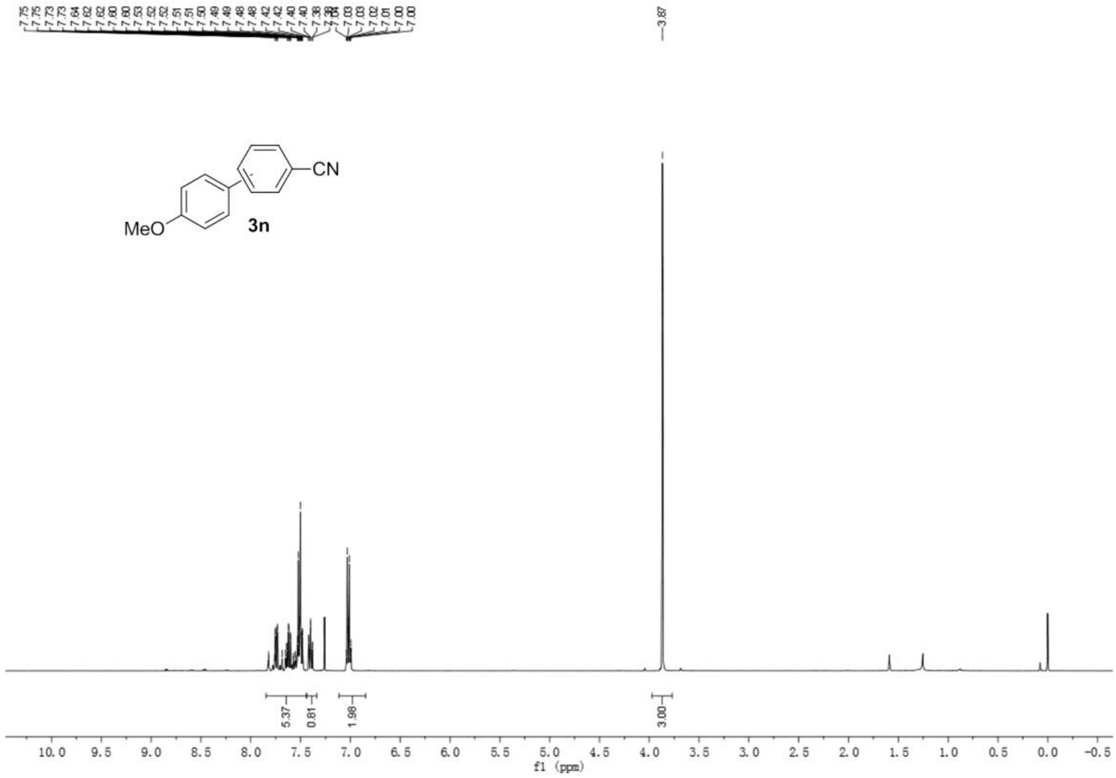
7.53
7.52
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.36
7.34
7.32
7.32
7.31
7.30
7.30
7.30
7.28
7.28
7.26
7.16
7.16
7.16
7.16
7.14
7.14
7.14
7.10
7.09
7.09
7.04
7.04
7.02
7.02
7.00
7.00
7.00
6.99
6.98
6.97
6.97
6.96
6.95
6.95
6.94
6.88
6.88
6.87
6.87
3.87
3.86
3.85
3.82
OMe
MeO
2.17
1.88
4.14
6.00
10.0
9.5
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)

3l



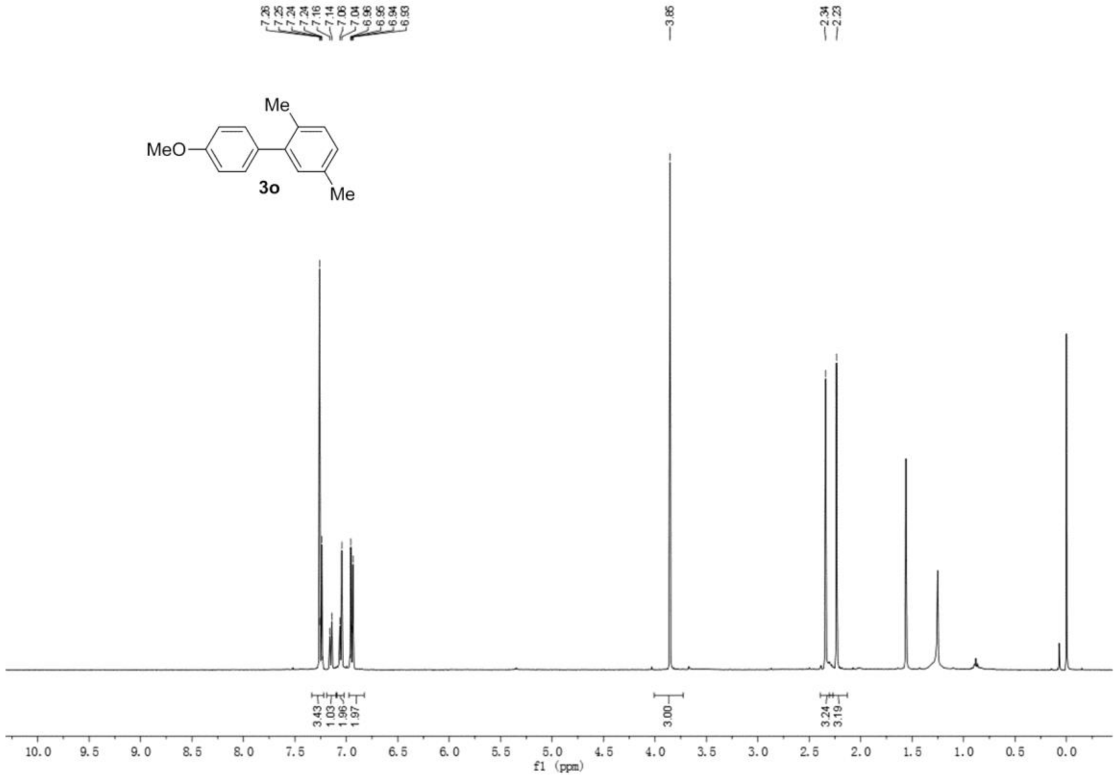
3m

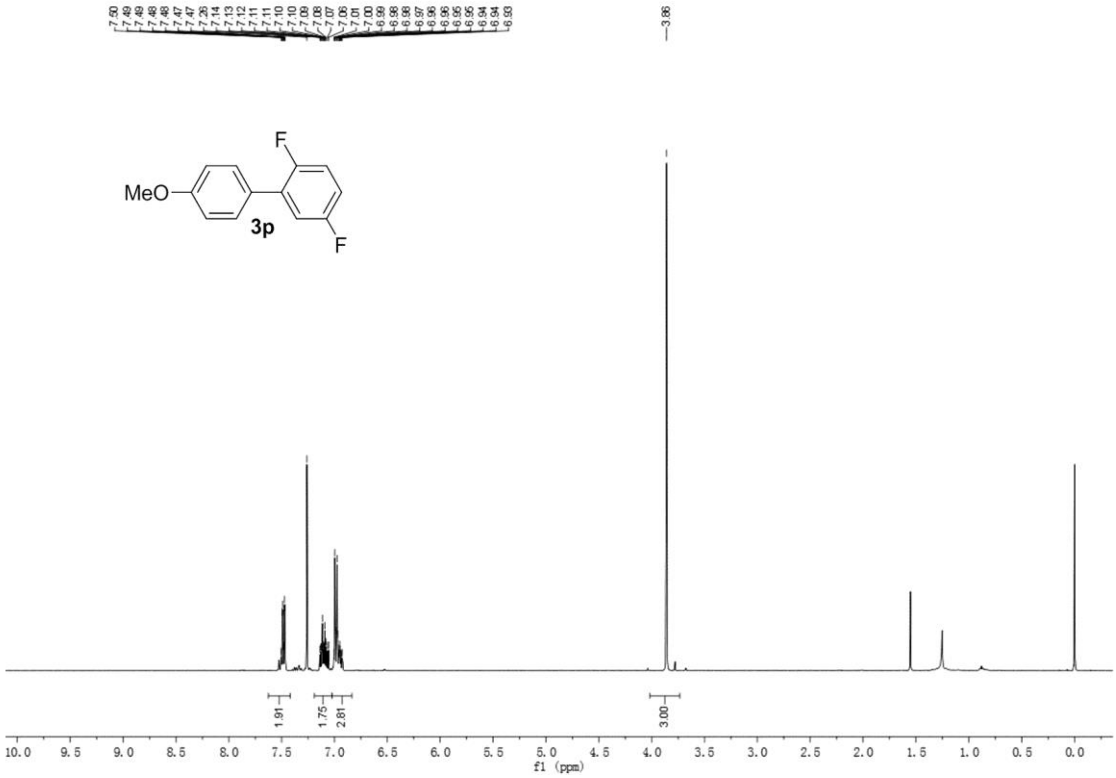
7.53
7.53
7.52
7.52
7.51
7.50
7.46
7.44
7.37
7.35
7.33
7.31
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.14
6.98
6.98
6.97
6.97
6.96
6.96
6.95
6.94
3.86
3.85
3.85
2.41
2.39
2.28
Me
MeO
0.99
0.39
5.60
0.35
2.02
3.00
0.91
0.50
1.65
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3n

7.75
7.75
7.73
7.73
7.64
7.62
7.62
7.60
7.60
7.53
7.52
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.42
7.42
7.40
7.40
7.38
7.38
7.04
7.03
7.03
7.02
7.01
7.00
7.00
3.87
CN
MeO
5.37
0.81
1.98
3.00
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
-0.5
f1 (ppm)


7.26
7.25
7.24
7.24
7.16
7.14
7.06
7.04
6.96
6.95
6.94
6.93
3.85
2.34
2.23
Me
MeO
Me
3o
3.43
1.03
1.96
1.97
3.00
3.24
3.19
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)


7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.26
7.14
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.08
7.07
7.06
7.01
7.00
6.99
6.98
6.98
6.97
6.96
6.96
6.95
6.95
6.94
6.94
6.93
3.86
F
MeO
F
3p
1.91
1.75
2.81
3.00
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)