Supporting Information for

PPh_3 modified-chitosan supported Pd nanocatalyst for heterogeneous Suzuki-Miyaura cross coupling reactions

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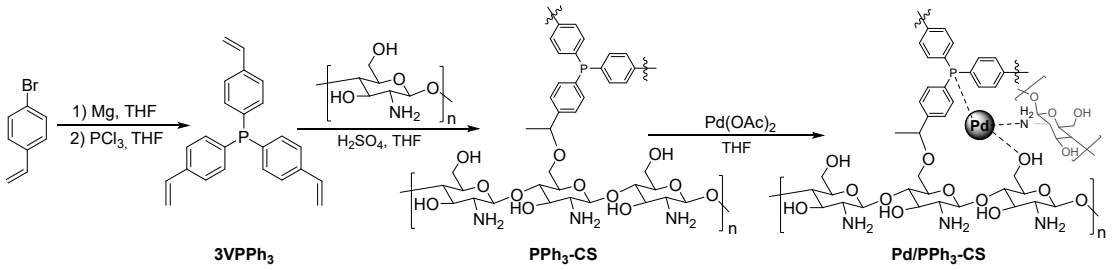
1. General methods.

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^{1}H NMR spectra were recorded on 400 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^{1}H NMR) as the standard. The IR spectra were measured on a Thermo (SCIENTIFC) NICOLET iS10 spectrometer. The SEM and TEM spectra were obtained on a Zeiss sigma 500 and JEOL-2100F spectrometers, respectively. The N_2 sorption isotherm was obtained on a Micromeritics ASAP 2460. Thermo gravimeric analysis was determined on NETZSCH TG 209 F1. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi with the Al Kα radiation as X-ray source (*hv*=1486.6 eV). The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

2. Synthesis of Synthesis of Pd/PPh$_3$-CS catalyst.



Synthesis of 3VPPh$_3$.

Under N_2, Mg powder (460.8 mg, 19.2 mmol), one grain of I_2 and anhydrous THF (5 mL) were added to three neck flasks. *p*-Bromostyrene (2.1 mL, 16 mmol) and anhydrous THF (20 mL) were added to a drip funnel. The mixture was added dropwise to the flasks at 60 ℃. After dripping, the mixture was kept at 60 ℃ for 1 h and cooled to room temperature. PCl_3 (730 mg, 5.3 mmol) was added dropwise to the flasks at 0 ℃ and stirred overnight. The mixture was quenched by saturated ammonium chloride aqueous solution, and extracted by using ethyl acetate The organic phase was dried by anhydrous magnesium sulfate. Tri(4-vinyl) triphenyl

phosphine was obtained by column chromatography purification ($3VPPh_3$, 1.32 g, yield 72%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.35 (d, *J* = 8.0 Hz, 6H), 7.25-7.23 (m, 6H), 6.68 (dd, *J* = 17.5, 11.0 Hz, 3H), 5.75 (d, *J* = 17.5 Hz, 3H), 5.26 (d, *J* = 11.0 Hz, 3H) ppm. ^{31}P NMR (201 MHz, $CDCl_3$) δ -8.1 ppm.

Synthesis of PPh_3-CS.

Under N_2, chitosan (11.9 mg) was added to Schlenk tube and concentrated sulfuric acid (0.1 mL) was added by drops under ice bath. $3VPPh_3$ (75 mg, 0.22 mmol) was dissolved in THF (1 mL) and then dropped into Schlenk tube. The mixture was stirred at room temperature for 24 h. The solid product was separated by centrifugation. The product was washed with water for three times (3×5 mL). The light-yellow polymer (PPh_3&CS, 73 mg) was obtained.

Synthesis of Pd/PPh_3-CS

Under N_2, PPh_3&CS (50 mg), palladium acetate (5 mg) and THF (4 mL) were added to a Schlenk tube. After stirring for 24 h at 60 ℃, the resulting product was separated by using centrifuge. The black solid was washed with petroleum ether and centrifuged for three times. After removing the solvent under vacuum, the product Pd/PPh_3&CS (53 mg) was obtained.

3. General procedure for the Pd/PPh_3-CS-catalyzed Suzuki-Miyaura cross coupling reactions

Under N_2, Pd/PPh_3-CS (1.66 mg), aryl halide (0.5 mmol), arylboronic acid (0.6 mmol), K_2CO_3 (0.5 mmol), EtOH (3 mL) and H_2O (1 mL) was added to a Schlenk tube. The mixture was stirred at 25 ^oC for 4 h. After removing the catalyst by centrifugal, the product was purified by column chromatography.

4 Recycling tests of the Pd/PPh_3-CS in Suzuki-Miyaura cross coupling reactions of bromobenzene and phenylboronic acid

Under N_2, Pd/PPh_3-CS (1.66 mg), bromobenzene (78.5 mg, 0.5 mmol), phenylboronic acid (73.2 mg, 0.6 mmol), K_2CO_3 (69.1 mg, 0.5 mmol), EtOH (3 mL)

and H_2O (1 mL) was added to a Schlenk tube. The mixture was stirred at 25 °C for 4 h. The catalyst was recovered by centrifugal, washed by the EtOH (2 mL) and then used to next run under the same condition and procedure. The mixture subsequently was analyzed by GC.

5. XPS spectra of the used catalyst

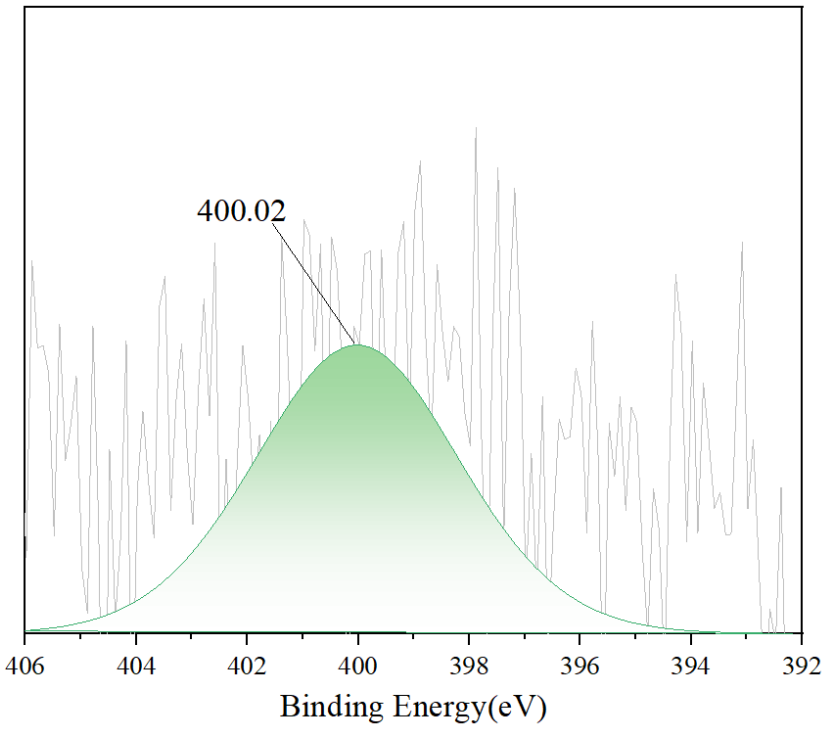


Figure S1. N1s XPS spectra of Pd/PPh_3&CS

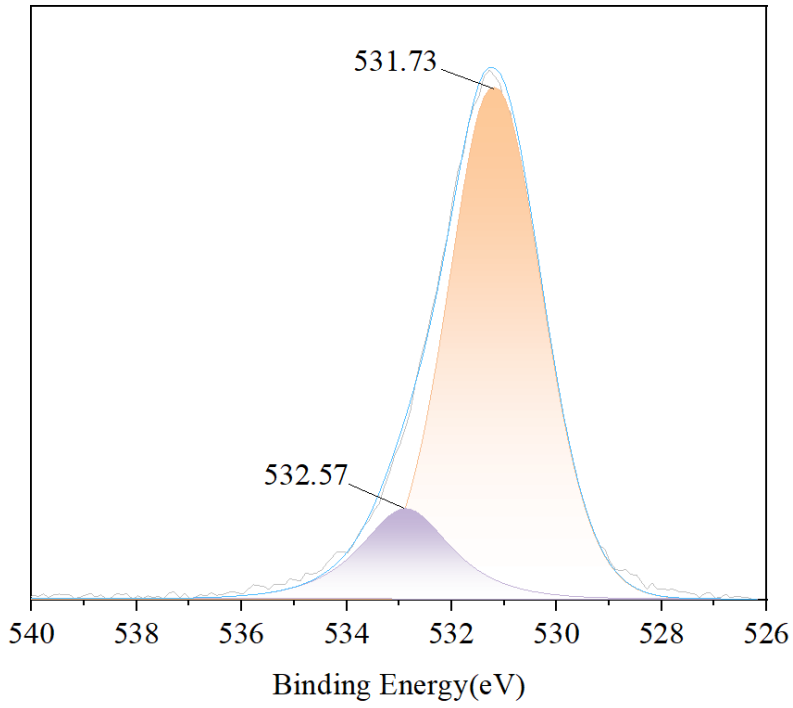


Figure S2. O1s XPS spectra of Pd/PPh_3&CS

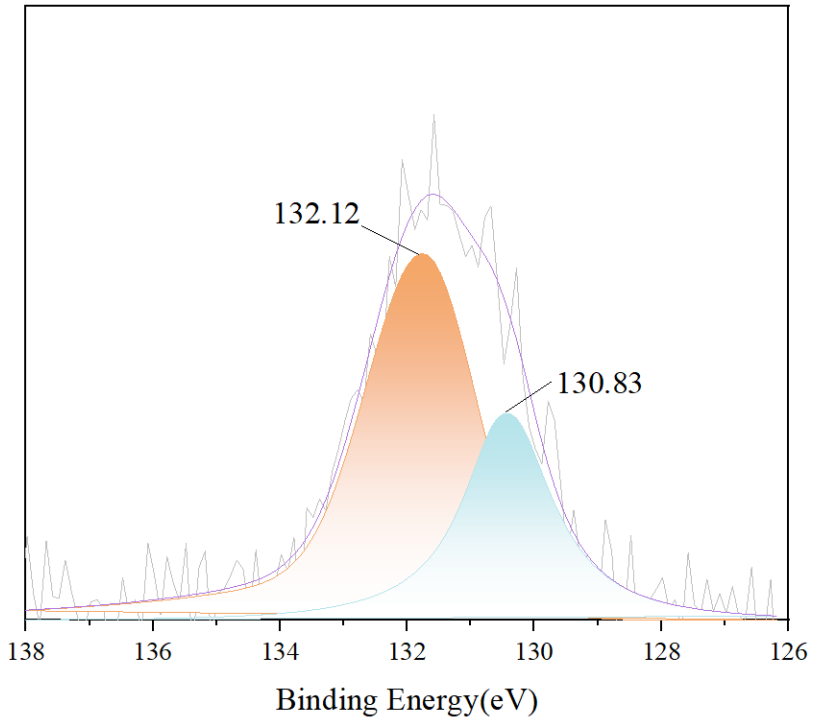


Figure S3. P2p XPS spectra of Pd/PPh_3&CS

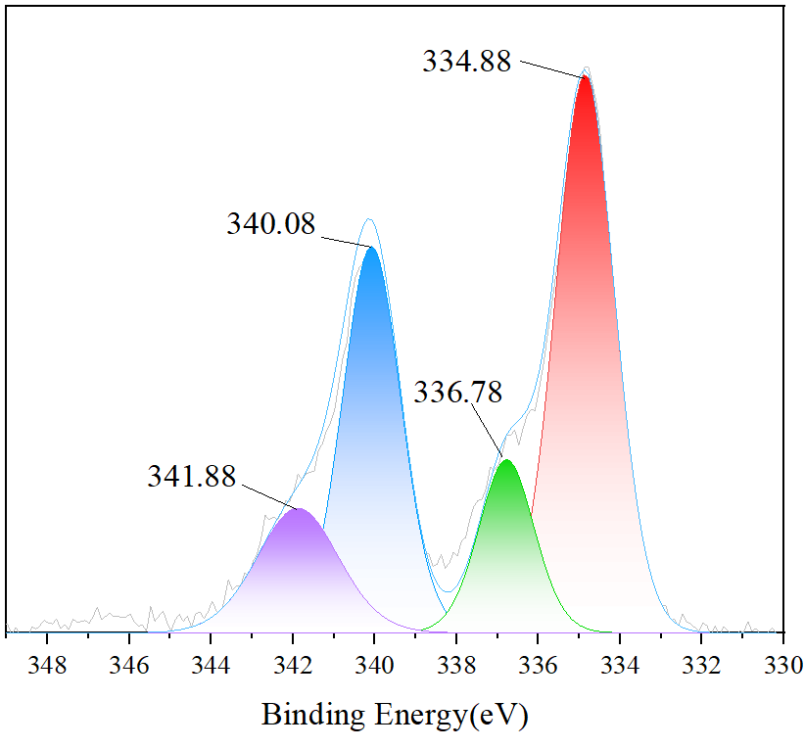
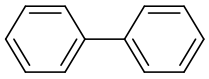
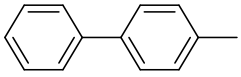


Figure S4. Pd3d XPS spectra of Pd/PPh_3&CS

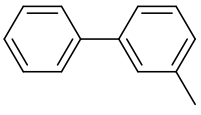
6. NMR data for products (3a-3n).



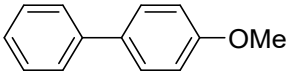
1,1'-biphenyl (3a)[1]: white crystal. 79 mg, 99% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.57 (m, 4H), 7.52-7.46 (m, 4H), 7.45-7.42 (m, 2H) ppm.



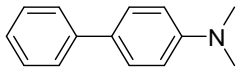
4-Methyl-1,1'-biphenyl (3b)[1]: colorless oil. 80 mg, 96% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.33-7.29 (m, 2H), 7.23-7.19, (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H) ppm.



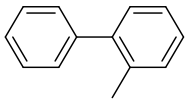
3-Phenyltoluene (3c)[3]**:** colorless oil. 80 mg, 95% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.41-7.36 (m, 4H), 7.31-7.27 (m, 2H), 7.14-7.10 (m, 1H), 2.38 (s, 3H) ppm.



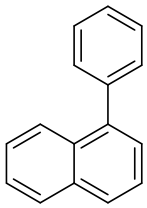
4-Methoxy-1,1'-biphenyl (3d)[1]: white solid. 90 mg, 97% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 4H), 7.42-7.38 (m, 2H), 7.31-7.27 (m, 1H), 6.98-6.96 (m, 2H), 3.83 (s, 3H) ppm.



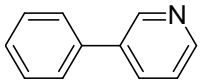
N, N-dimethyl-[1,1'-biphenyl]-4-amine (3e)[2]: white solid. 88 mg, 96% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.41 (m, 4H), 7.32- 7.28 (m, 2H), 7.20-7.11 (m, 1H), 6.71 (d, J = 8.8 Hz, 2H), 2.89 (s, 6H) ppm.



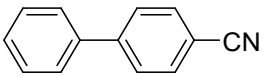
2-Methyl-1,1'-biphenyl (3f)[3]: colorless oil. 80 mg, 96% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.32-7.28 (m, 3H), 7.24-7.21 (m, 4H), 2.25 (s, 3H) ppm.



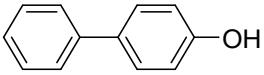
1-Phenylnaphthalene (3g)[4]: white solid, 80 mg, 78% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.83 (m, 3H), 7.53-7.45 (m, 6H), 7.43-7.39 (m, 3H) ppm.



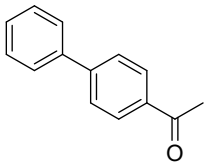
3-Phenylpyridine (3h)[5]**:** colorless oil. 82 mg, 98 % yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, J = 2.4 Hz, 1H), 8.48 (dd, J = 4.8, 1.6 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.46-7.45 (m, 2H), 7.37-7.22 (m, 4H) ppm.



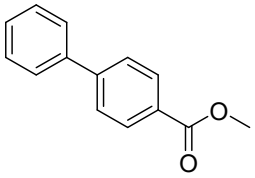
4-Cyanobiphenyl (3i) [7]: white solid. 74 mg, 97% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 4H), 7.48 -7.46 (m, 2H), 7.39-7.29 (m, 3H). ppm.



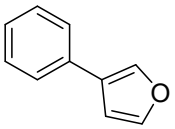
4-Phenylphenol (3j) [3]: colorless oil. 82 mg, 98% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.35-7.32 (m, 2H), 7.25-7.15 (m, 1H), 6.83 (d, J = 8.4 Hz, 2H), 4.93 (s, 1H) ppm.



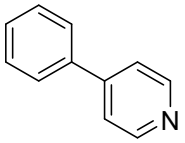
4-Acetylbiphenyl (3k)[8]: yellow solid. 96 mg, 98% yield, ^{1}H NMR (400 MHz, CDCl3): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.50-7.48 (m, 2H), 7.35-7.32 (m, 2H), 7.29-7.25 (m, 1H), 2.49 (s, 3H) ppm.



Methyl 4-phenylbenzoate (3l)[2]：yellow solid. 100 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.38-7.34 (m, 2H), 7.31-7.27(m, 1H), 3.83 (s, 3H) ppm.

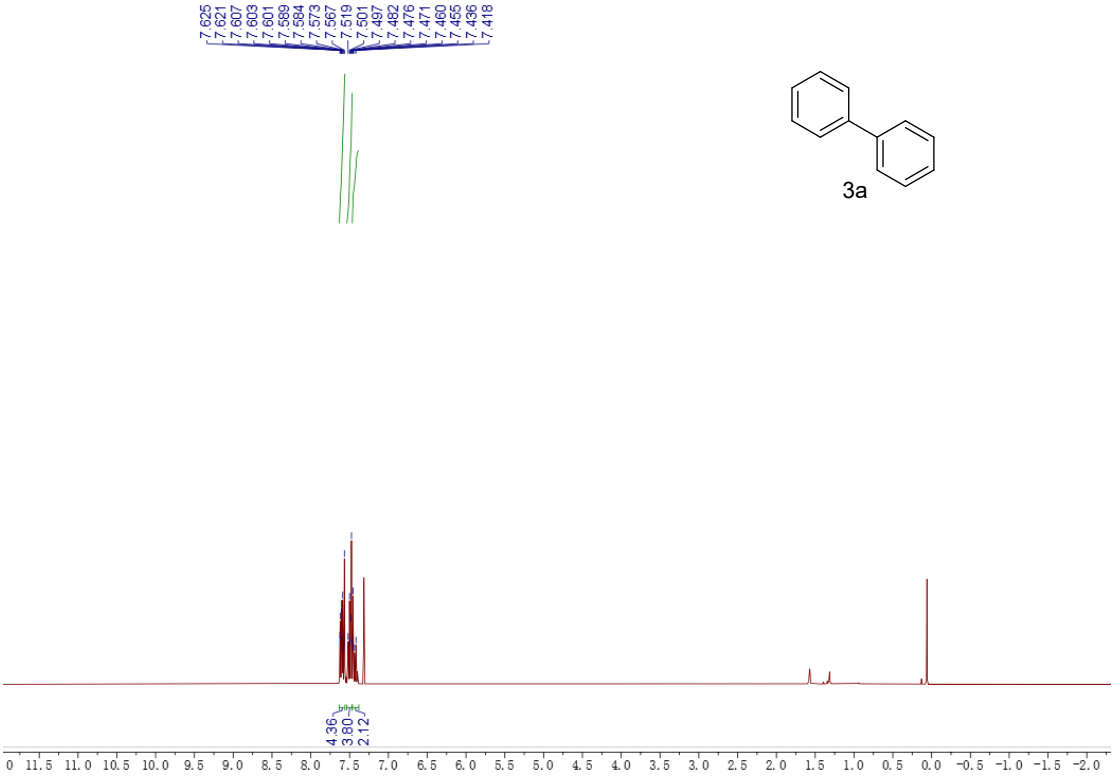


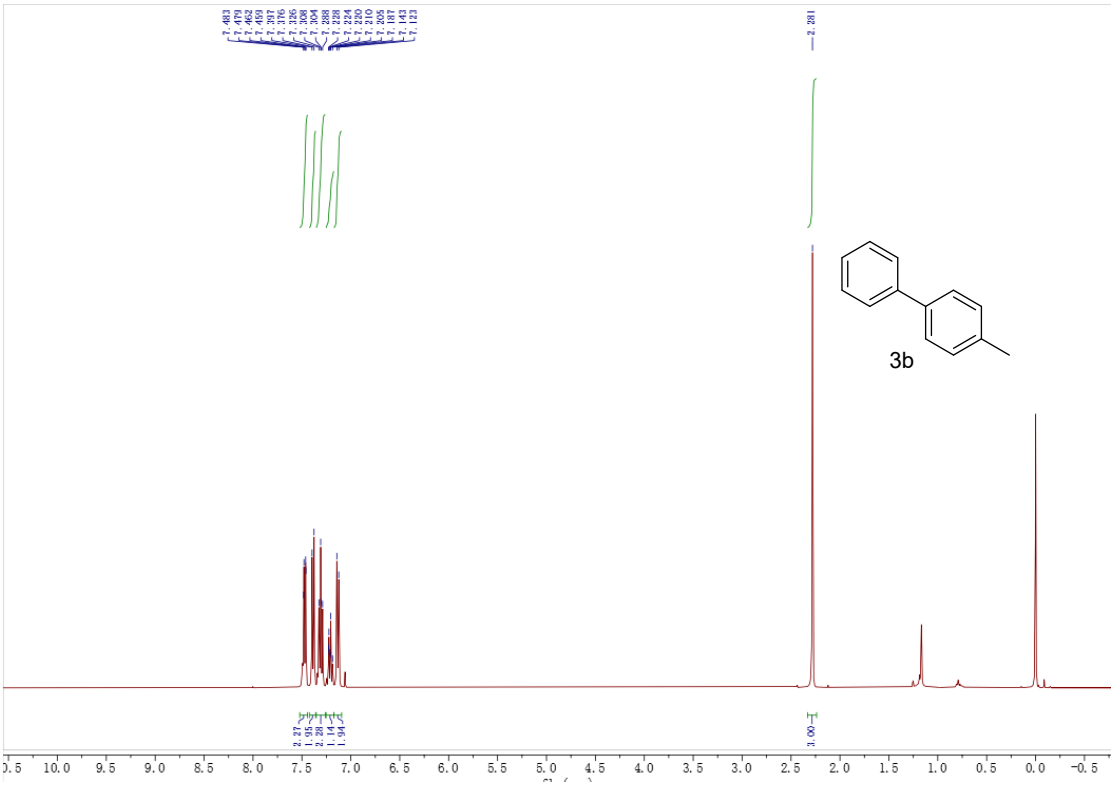
3-Phenylfuran (3m) [9]：white solid. 60 mg, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.42-7.40 (m, 3H), 7.31-7.28 (m, 2H), 7.20-7.17 (m, 1H), 6.62 (s, 1H) ppm.

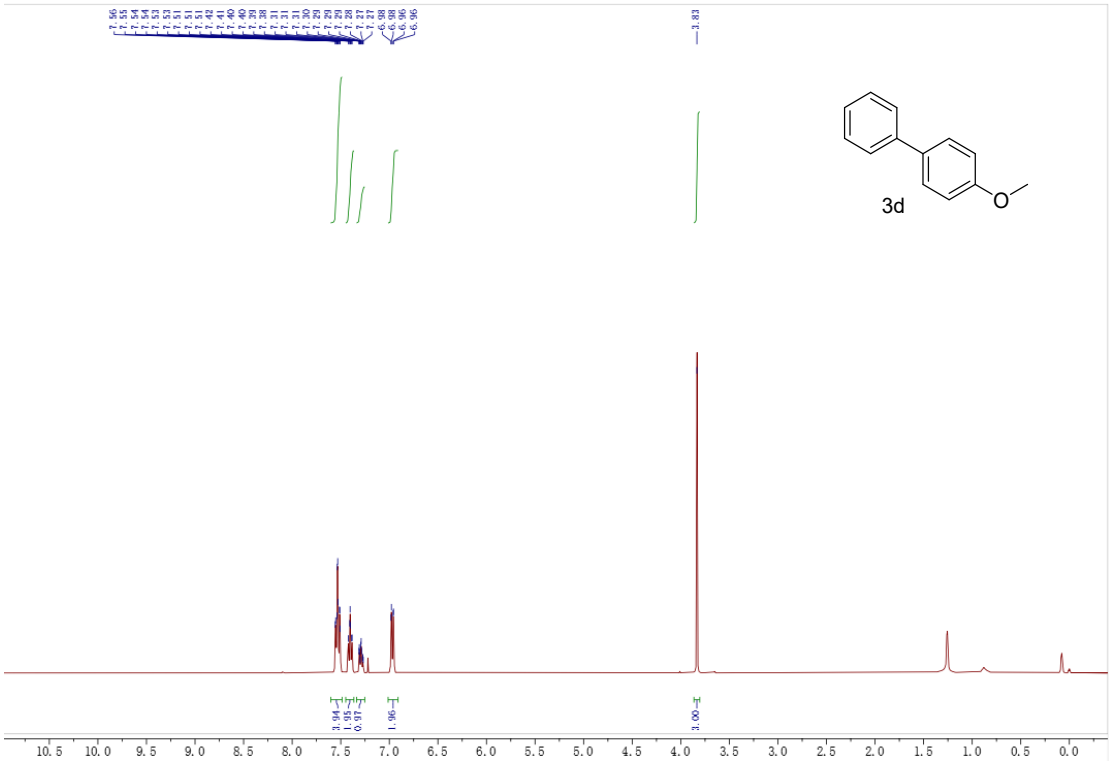


4-Phenylpyridine(3n)[10]：white solid. 66 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 2H), 7.65-7.63 (m, 2H), 7.51-7.46 (m, 5H) ppm.

7. NMR spectra of 3a-3n.



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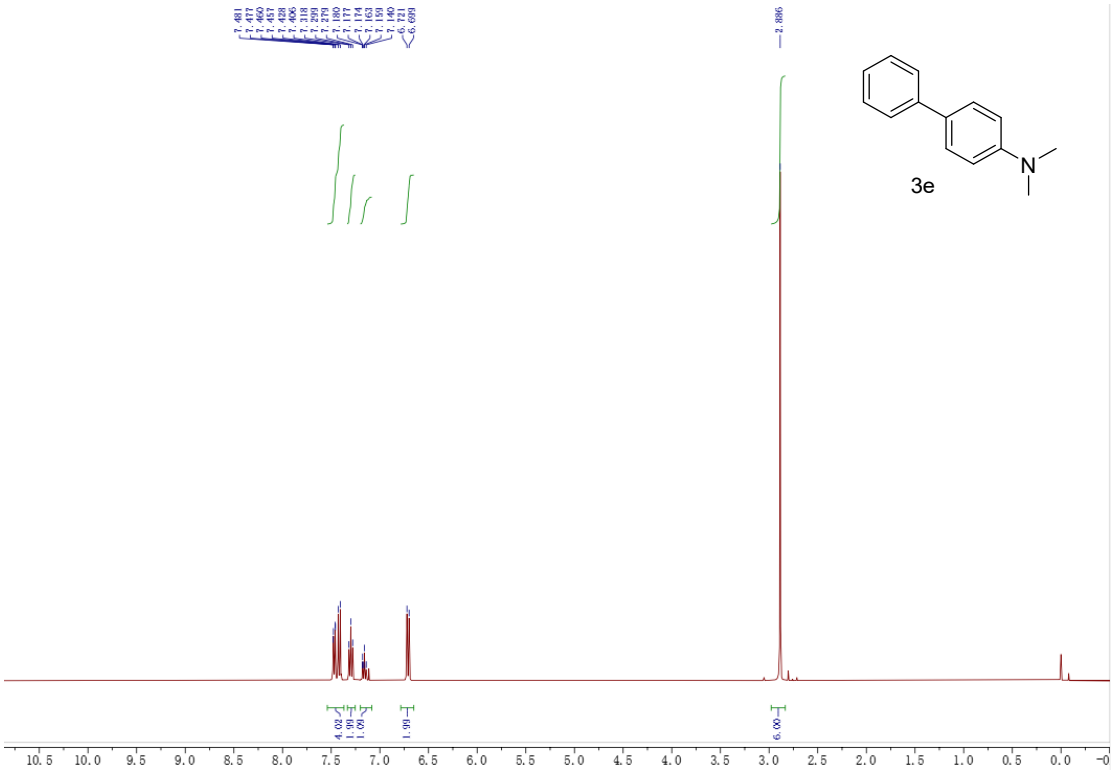
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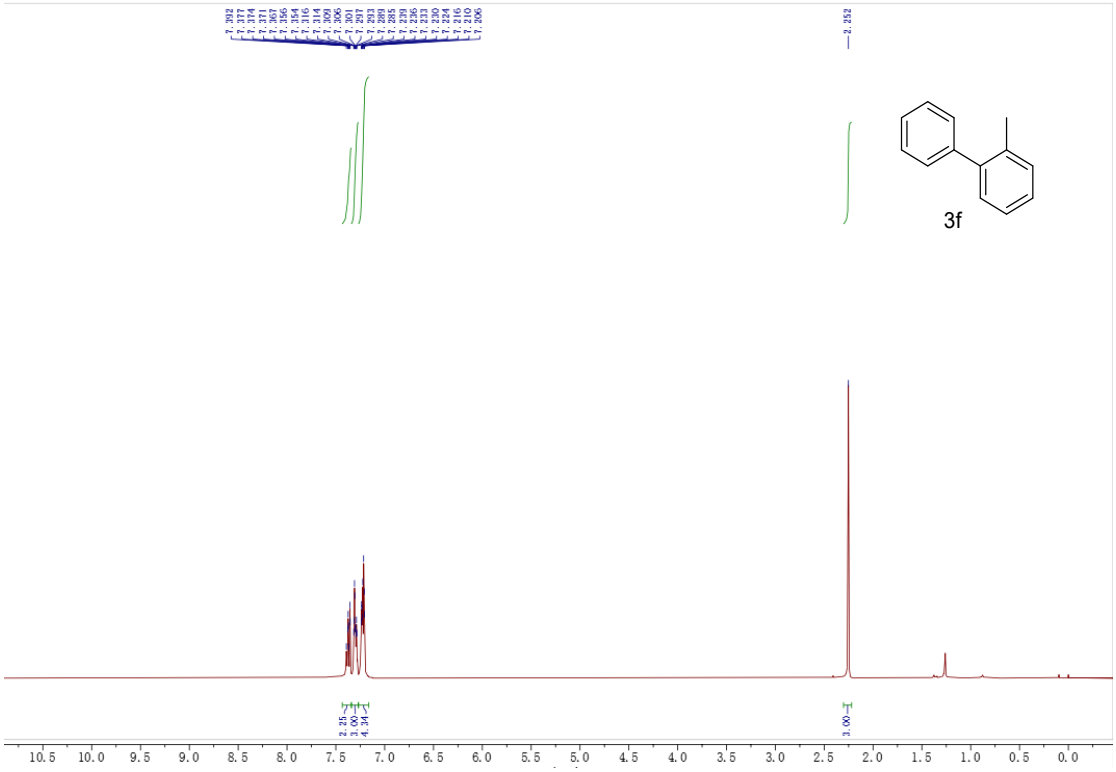

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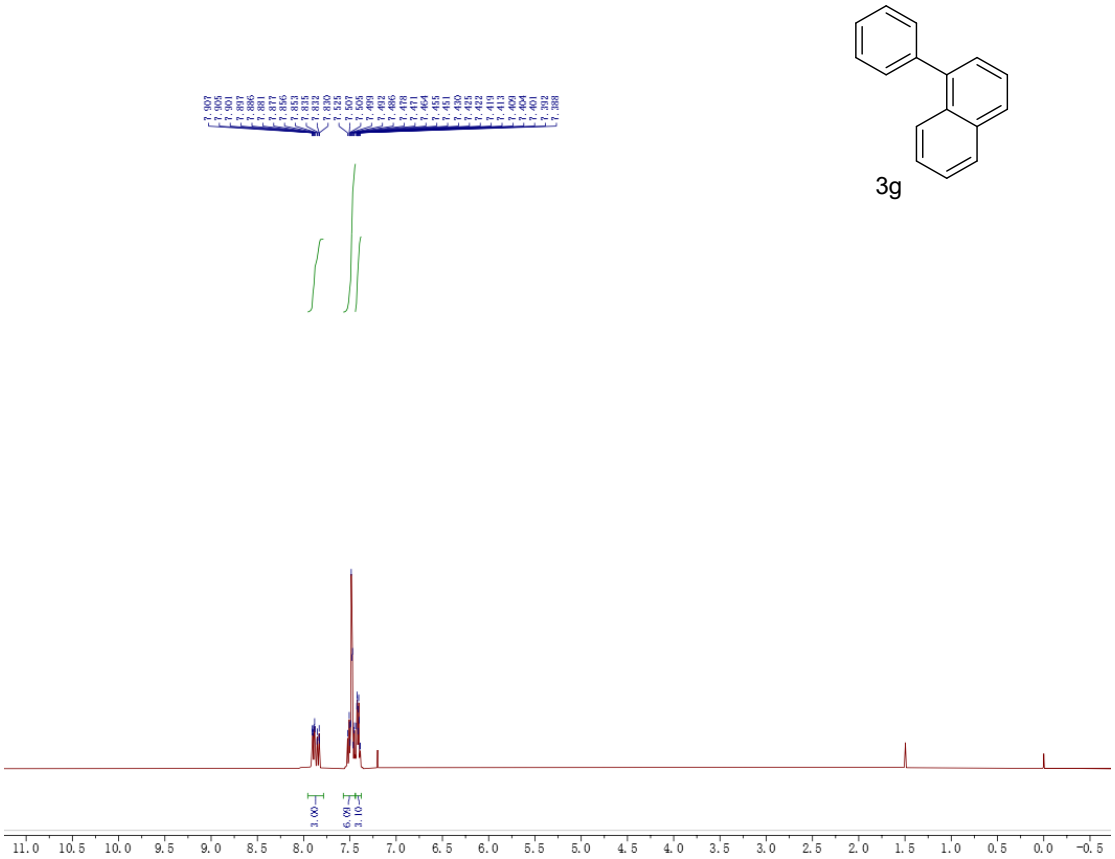

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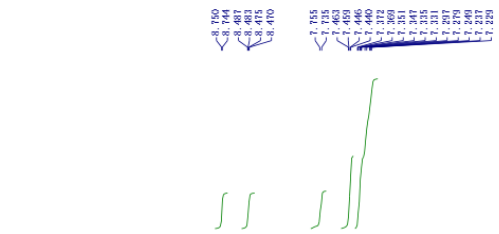

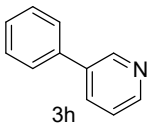

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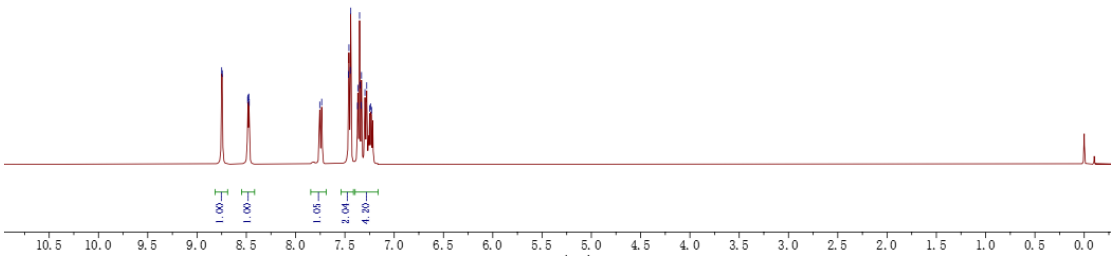

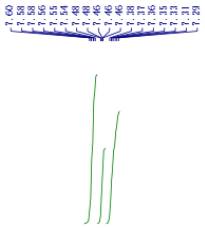

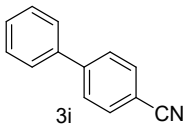

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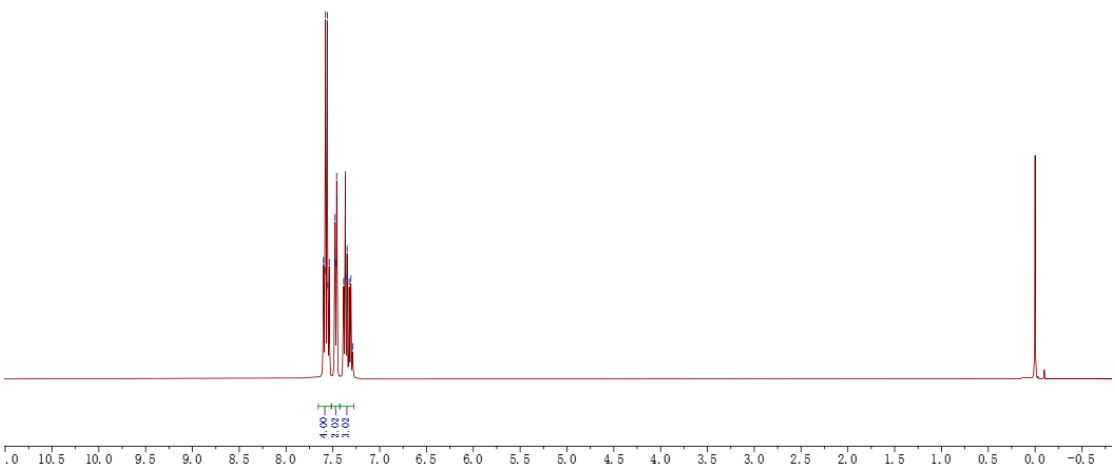

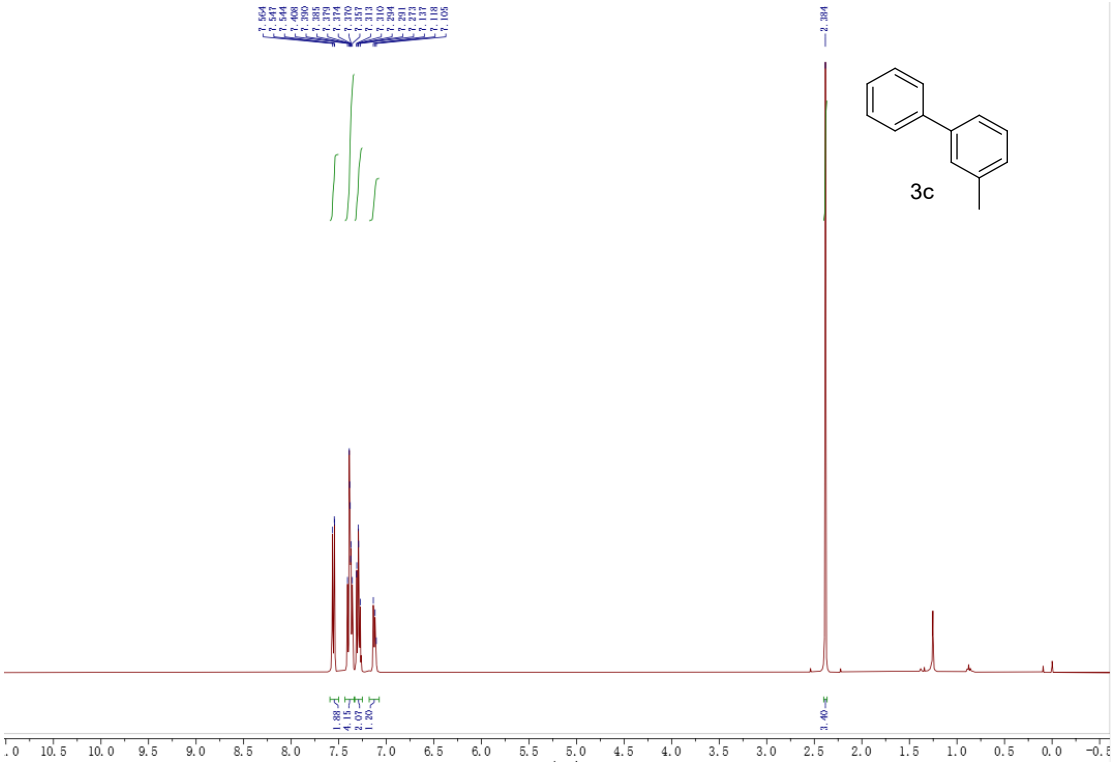
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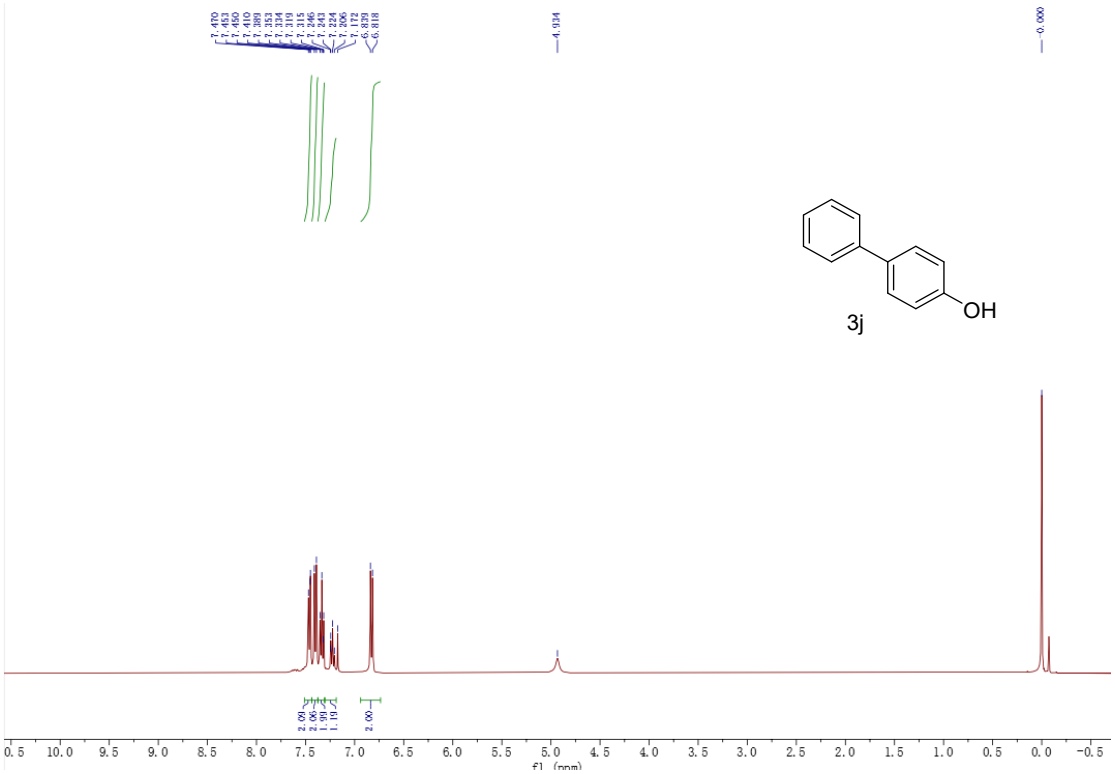
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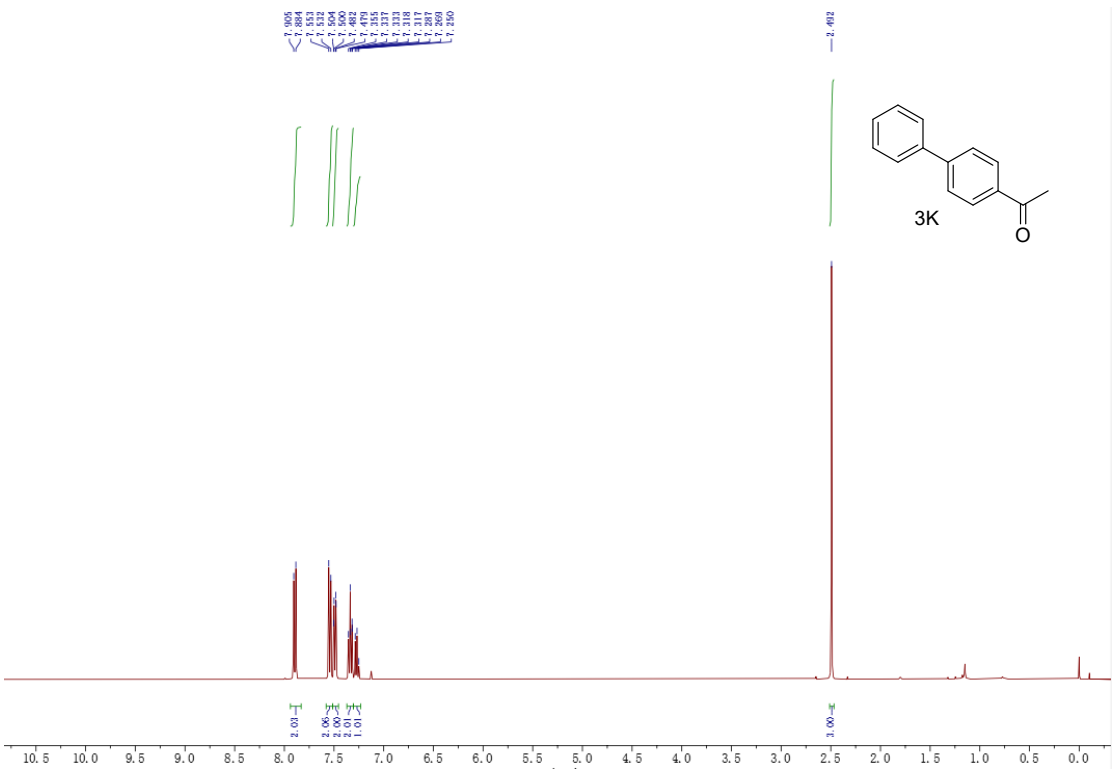
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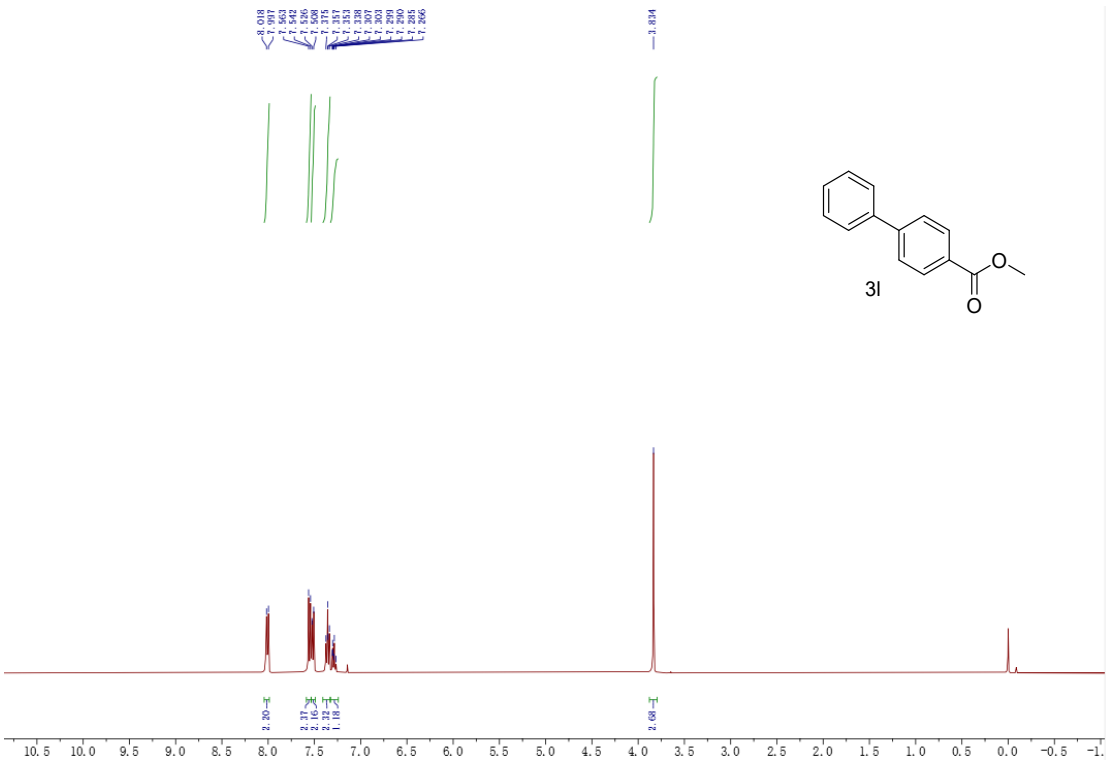
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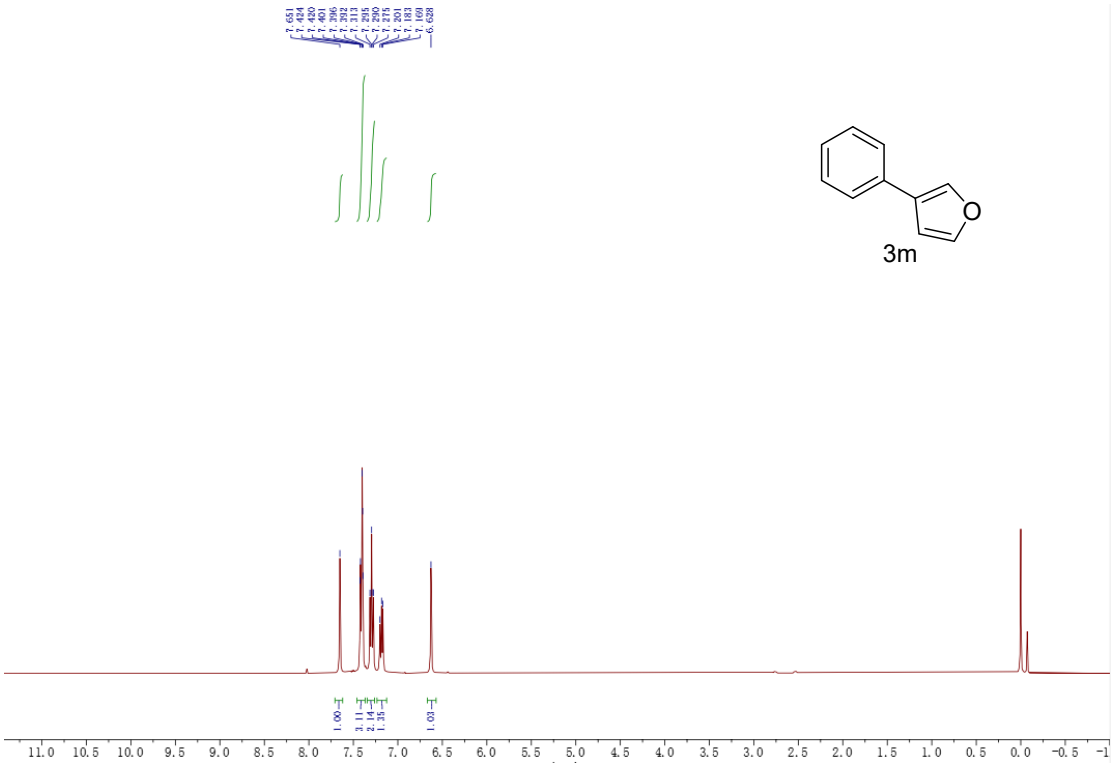
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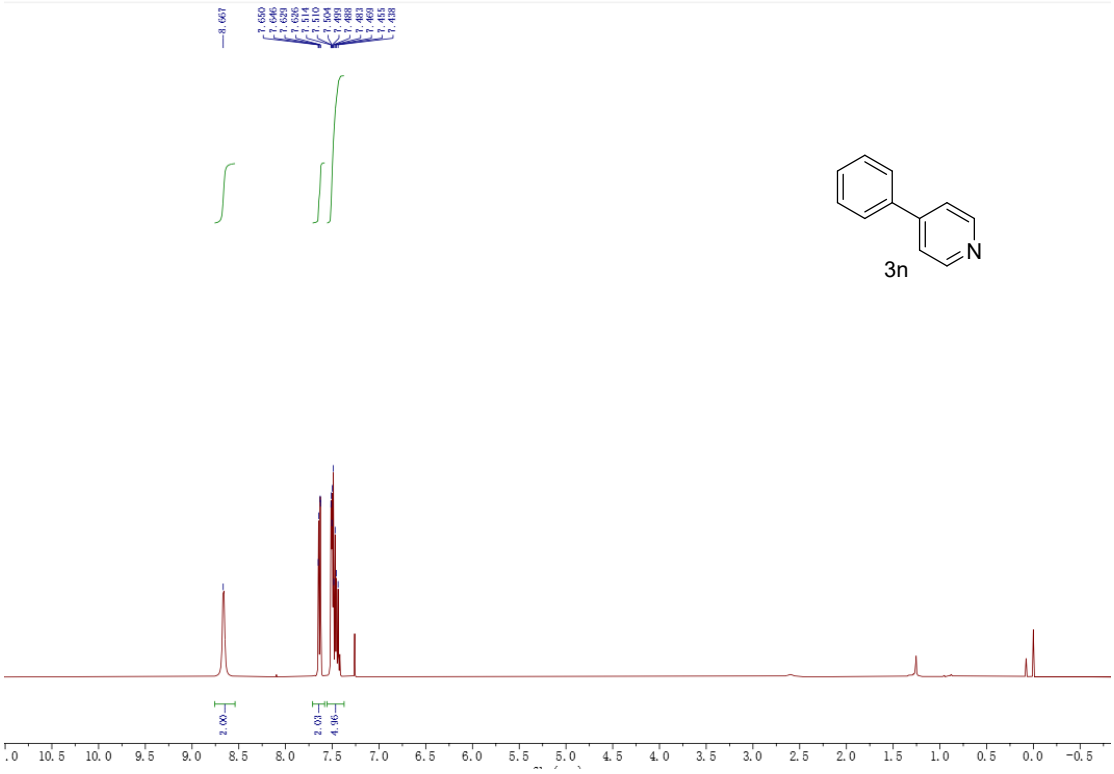
7.392
7.311
7.295
7.290
7.275
7.201
7.193
7.169
6.628
O
3m
1.00
3.11
2.14
1.35
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


8.667
7.650
7.646
7.629
7.625
7.514
7.510
7.504
7.488
7.483
7.469
7.455
7.438
N
3n
2.00
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.0 10.5 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

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