Electronic Supplementary Information

Palladium supported on triazolyl-functionalized hypercrosslinked polymers as recyclable catalyst for Suzuki-Miyaura coupling reactions

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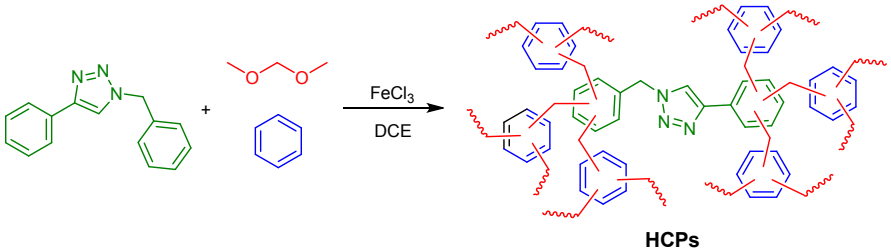
I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. Nitrogen adsorption-desorption was assessed using a Surface and Pore Size Analysis Instrument (3H-2000PM1, Beishide Instrument-S&T Co., Ltd., China) at 77.3K. All samples were out gassed under vacuum at 80°C for 5 h prior to the measurement. The special surface area was calculated by the BET method. The micropore volume derived using a t-plot method based on the Halsey thickness equation. The pore size distribution was obtained by applying the BJH formalism to both the adsorption and desorption branch of the isotherm. The micropore size was analyzed by and Dubinin-Astaknov equation (D-A). XPS was performed on a thermo ESCALAB 250XI by using Al Ka radiation as excitation source. TGA was performed on a thermogravimetric analyser (DSC Q2000) under N_2 environment with a temperature rate of 10°C/min from room temperature to 800°C. The structure and morphology of the MOPs and MOPs-Pd were observed using transmission electron microscopy (TEM, FEI Tecnai G20) and scanning electron microscopy (SEM, zeiss, sigma HD). The content of Pd was measured by inductively coupled plasma emission spectrometry (ICP-AES, Agilent, Icpoes 730). The products were purified by recrystallization and column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C at 500 MHz and 125 MHz, respectively, with TMS as internal standard.

II. Synthesis of MOPs

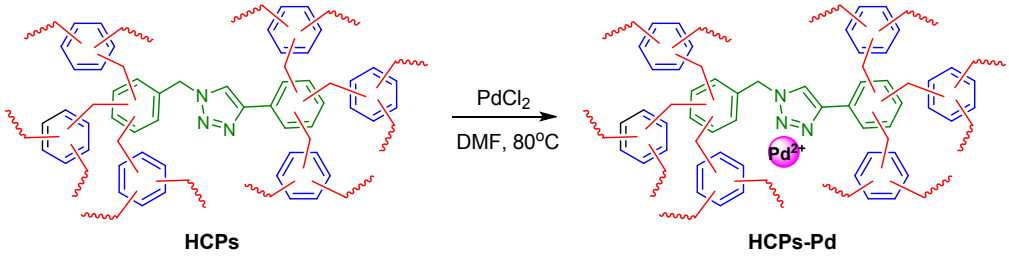
1) Synthesis of HCPs

Typical procedure for the preparation of HCPs: $FeCl_3$ (anhydrous, 0.27mol, 4.38g) was added to a solution of benzene (9mmol, 0.705g), 1,2,3-triazoles (3mmol, 0.714g), and formaldehyde dimethyl acetal (FDA, 0.27mol, 2.055g) in 6mL 1,2-dichloroethane (DCE). The resulting mixture was stirred at room temperature for good mixing, stirred at 45°C for 5h to form original network, and then heated at 80°C for 48h to react completely. The resulting precipitate was washed three times with methanol, then washed with methanol in a Soxhlet for 48 h, and finally dried under reduced pressure at 60°C for 24h to give HCP.



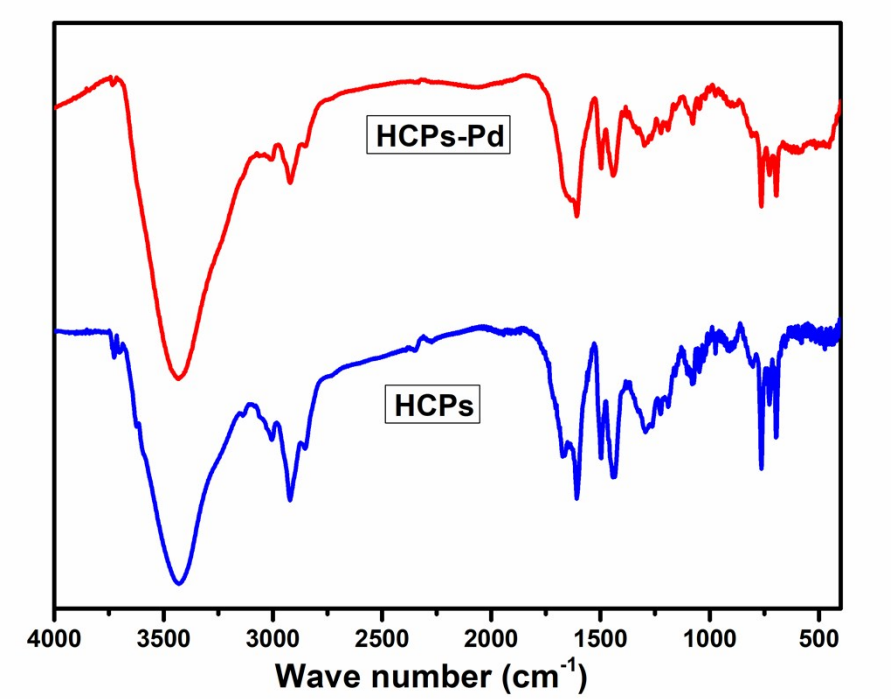
2) 2.3 Synthesis of HCPs-Pd

Typical procedure for the preparation of HCPs-Pd: HCPs (4.0g), $PdCl_2$ (0.20g) and 40mL of DMF were placed in a three-necked flask. Then, the reaction mixture was stirred under refluxing for 24h. Finally, the solid was filtered and washed with acetone several times, then washed with acetone in a Soxhlet for 48h, and dried under reduced pressure at 60°C for 24h to give HCPs-Pd.

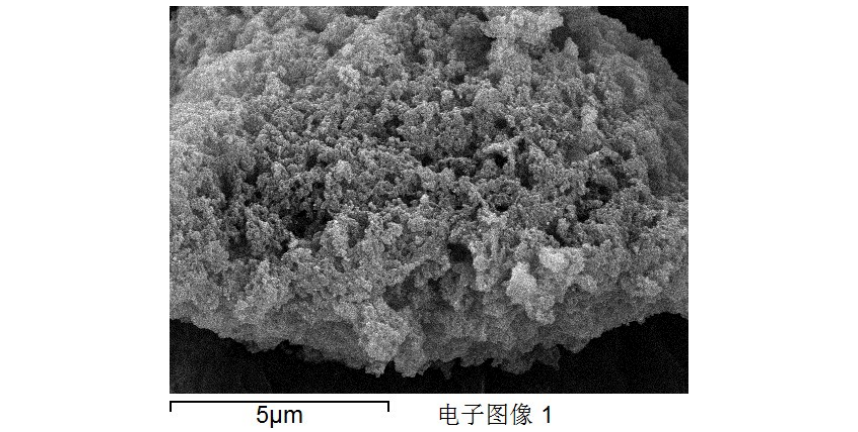


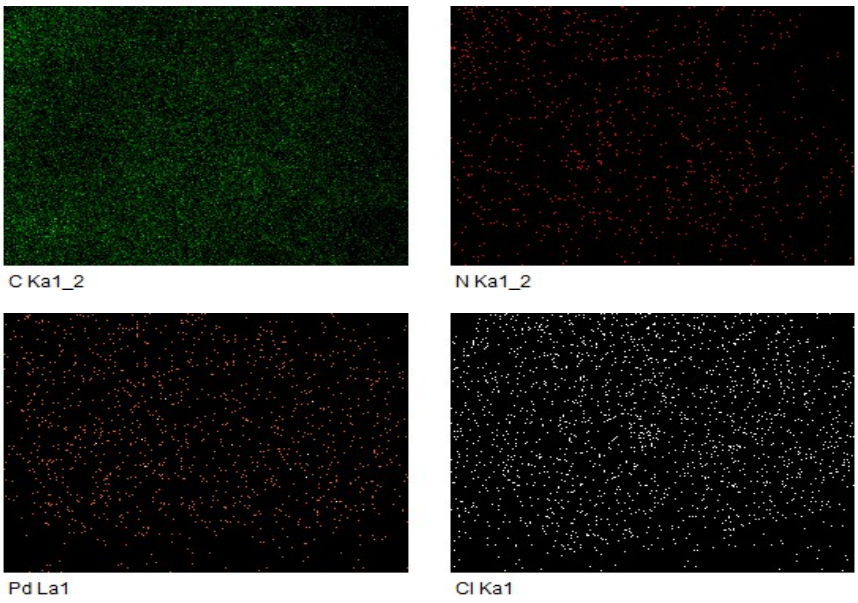
III. Analytical data of HCPs and HCPs-Pd

1) FT-IR spectra of HCPs-Pd

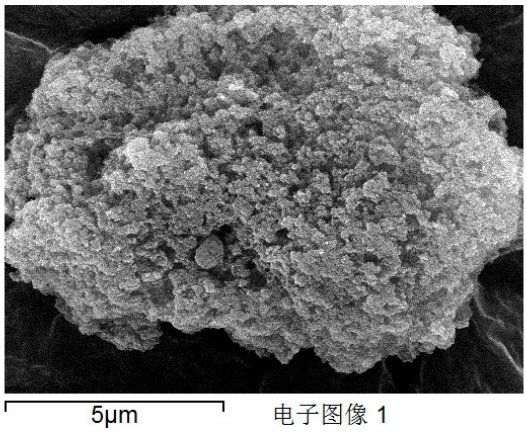


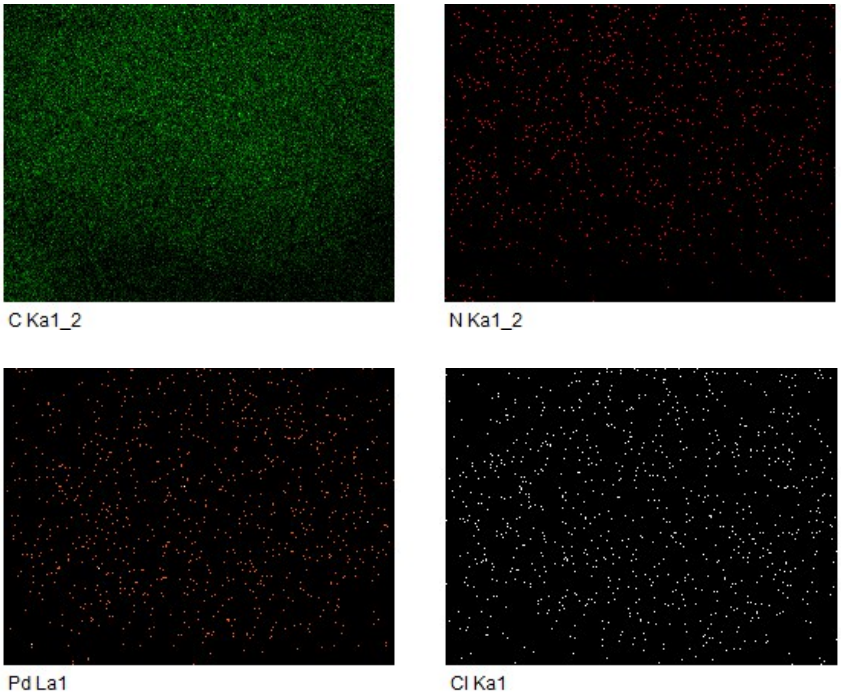
2) EDX image of HCPs-Pd





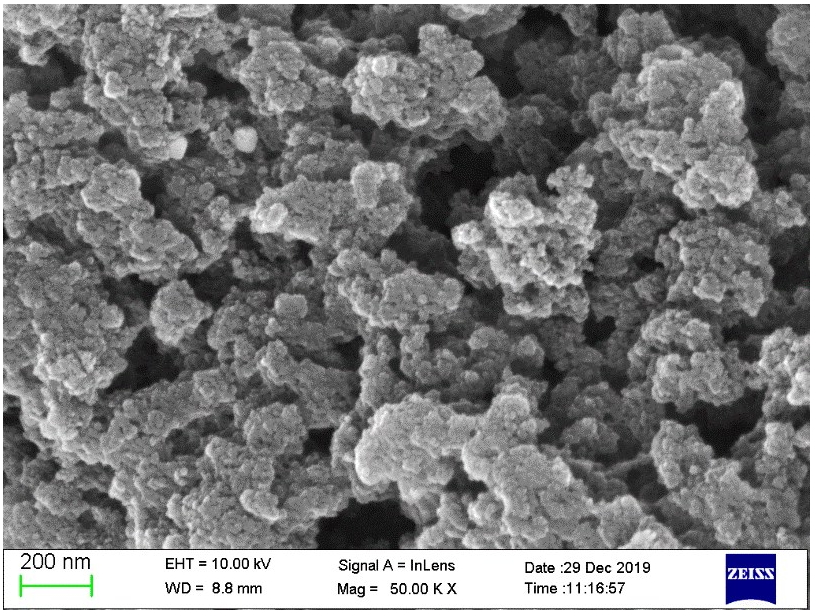
2) EDX image of recycled HCPs-Pd

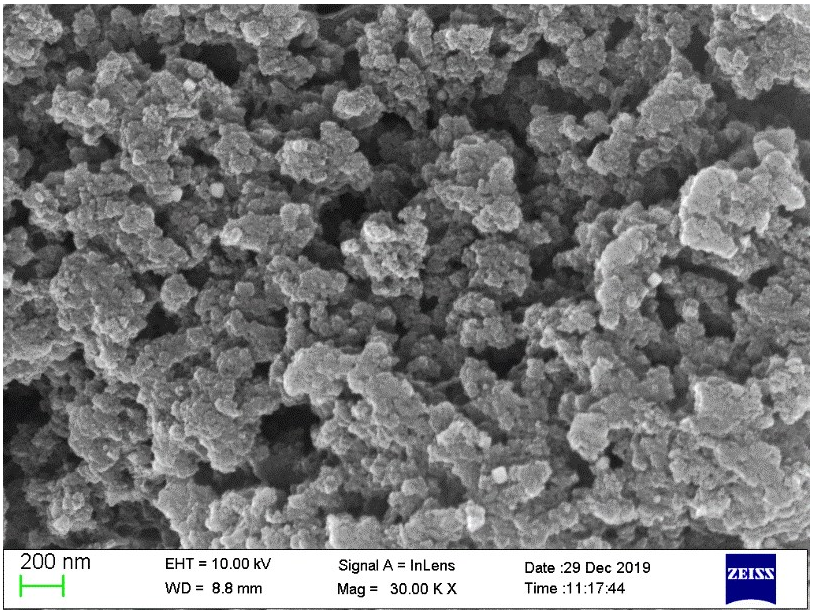




MOPs-Pd-II

3) TEM image of recycled HCPs-Pd



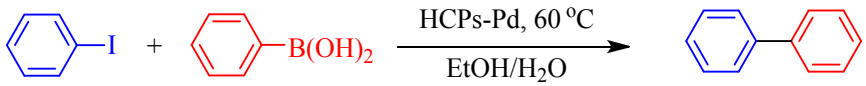


TEM image of recycled HCPs-Pd

IV. Synthesis and analytical data of 3

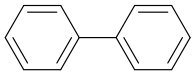
1) Procedure for Suzuki–Miyaura Coupling Reaction

Typical procedure for the preparation of 3 (3a as example): HCPs-Pd (1.0mg) was added to a solution of iodobenzene (2.5mmol), phenylboronic acid (3.5mmol), and NaOH (4.0mmol) in EtOH/H_2O=4/1(10mL). The mixture was stirred under a N_2 atmosphere at 60℃ for 1.0 hour. After the substrate iodobenzene 1a was consumed as indicated by TLC, and then poured into ice-water (100mL) under stirring. The mixture was extracted with dichloromethane (3 × 20mL), the combined organic phase was washed with water (3× 20mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (silica gel, petroleum ether: diethyl ether = 20: 1) to give 3a as a white solid (381 mg, 99%).

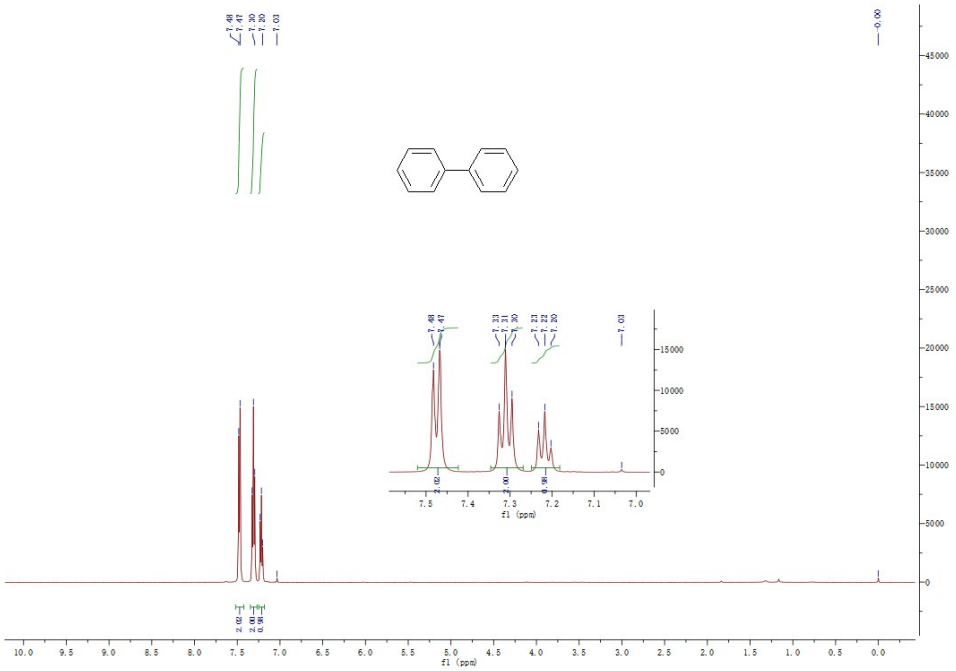


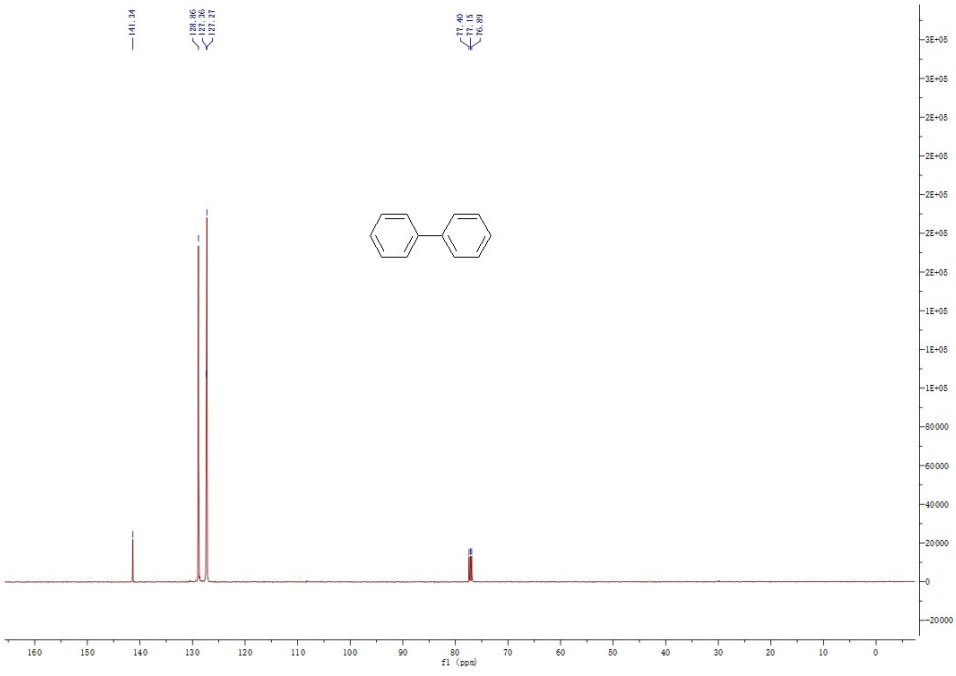
1a **2a** **3a**

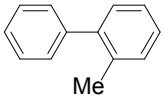
The analytical data of **3a-h** was reported by reference (X. Liu, W. Xu, D. Xiang, Z. Zhang, D. Chen, Y. Hu, Y. Li, Y. Ouyang and H. Lin, *New J. Chem.*, 2019, **43**, 12206-12210.

3a: 

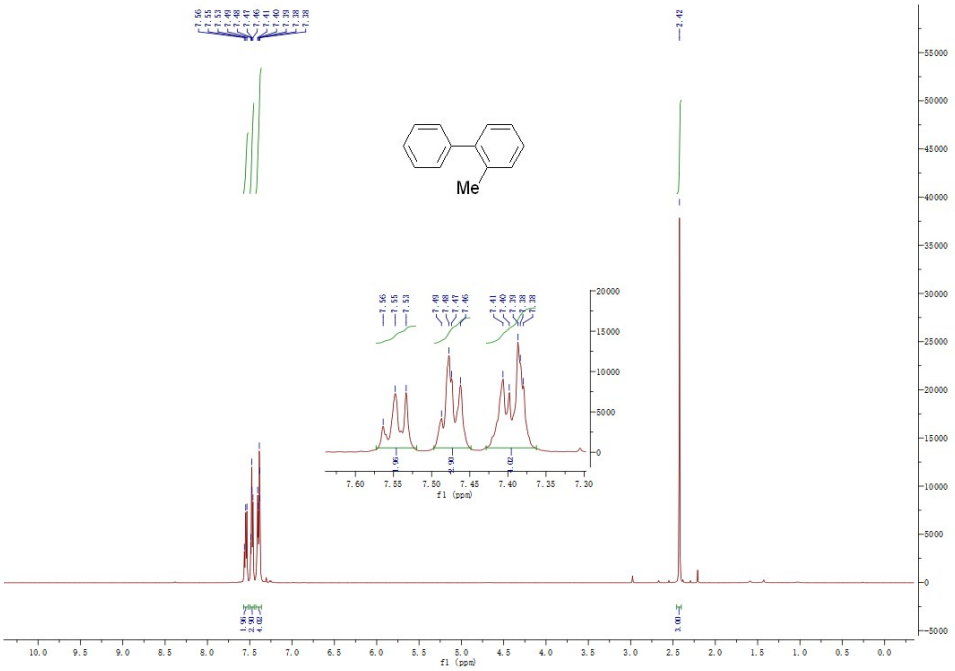
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 127.3, 127.4, 128.9, 141.3; IR (KBr) 3034, 1479, 1429, 1170, 1007, 727, 696, 611.

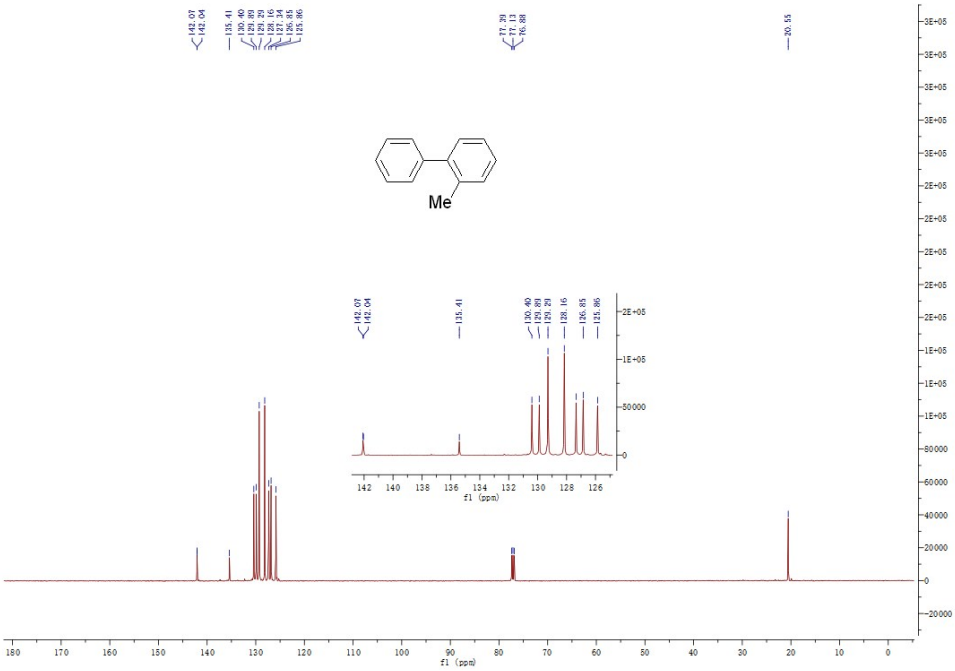


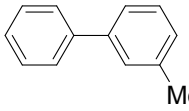


3b: 

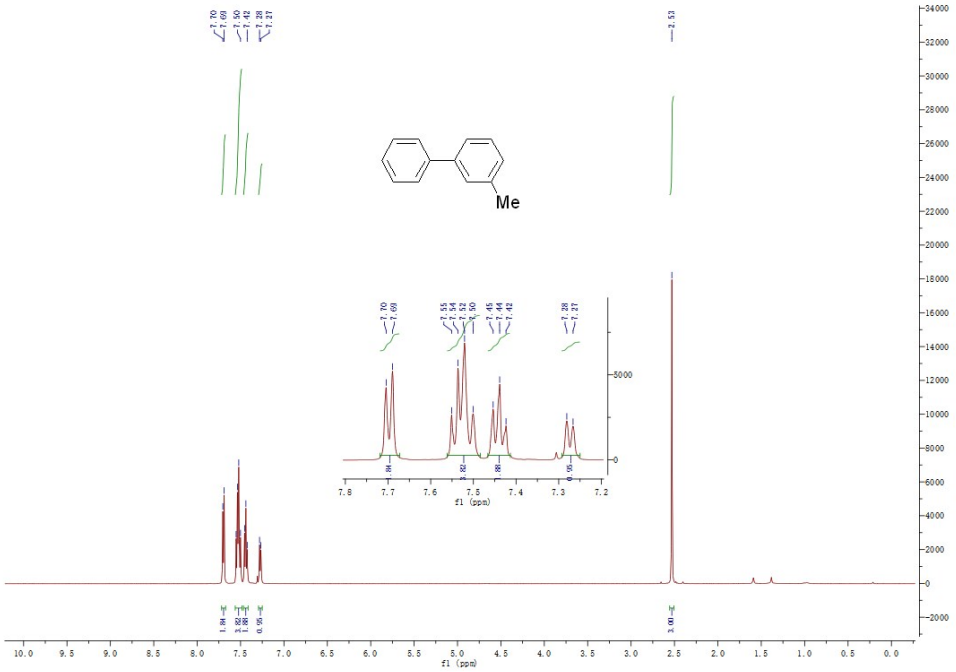
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.52 (m, 2H), 7.48 (dd, *J* = 7.1, 5.4 Hz, 3H), 7.43-7.36 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 20.6, 125.9, 126.9, 128.2, 129.3, 129.9, 130.4, 135.4, 142.0, 142.1; IR (KBr) 3020, 1599, 1479, 1341, 1009, 726, 701, 617.

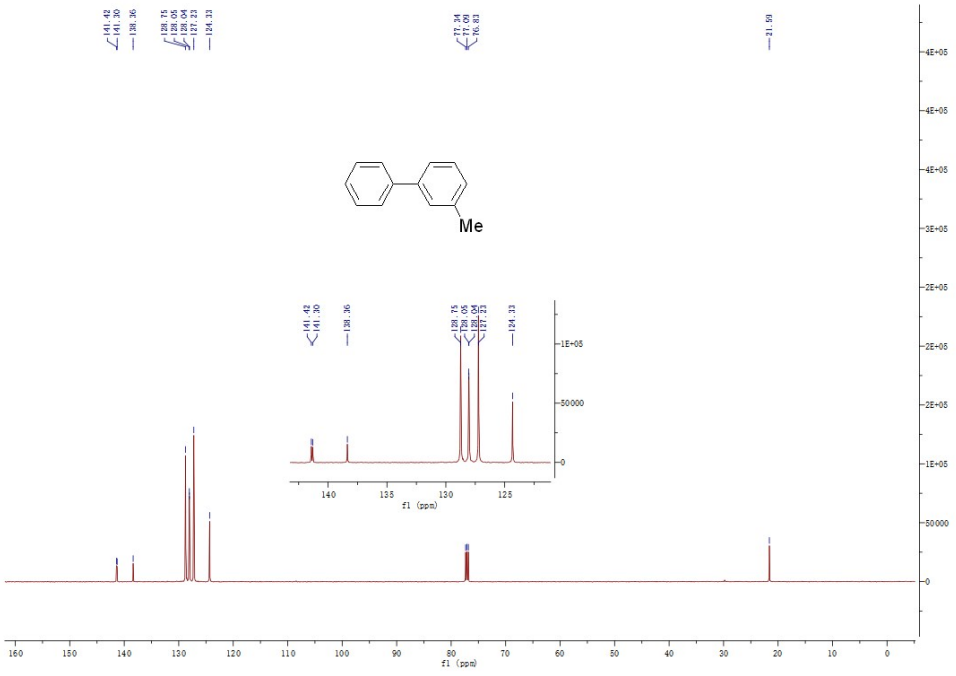


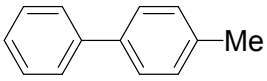


3c: 

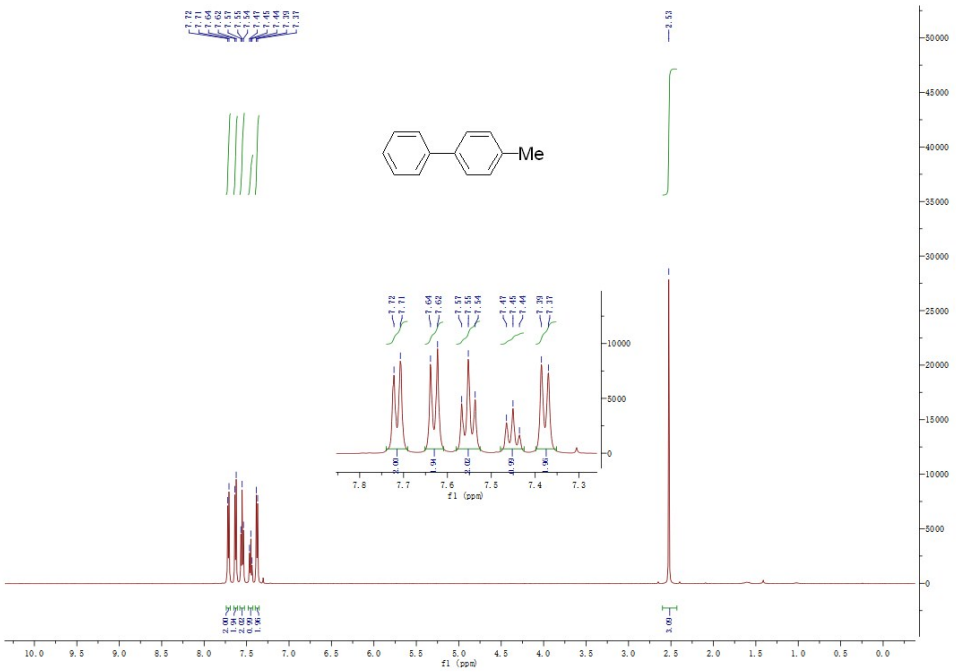
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.5 Hz, 2H), 7.53 (dd, *J* = 16.4, 8.7 Hz, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.6, 124.3, 127.2, 128.0, 128.1, 128.8, 138.4, 141.3, 141.4; IR (KBr) 3029, 1600, 1481, 791, 752, 697, 616.

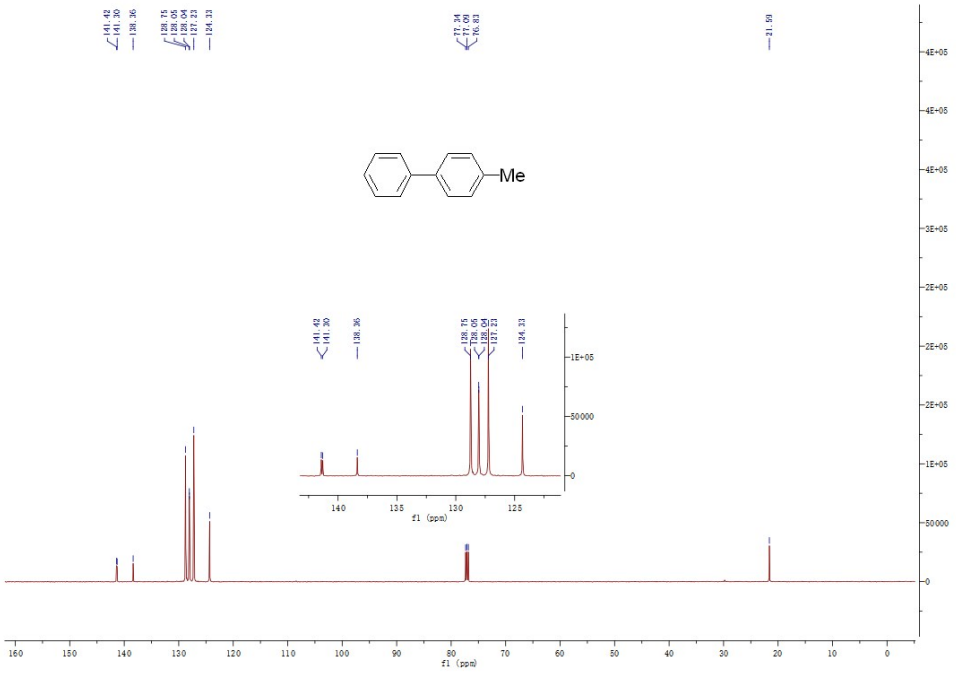


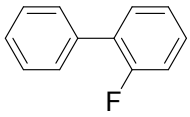


3d: 

White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 7.3 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 21.6, 124.3, 127.2, 128.0, 128.1, 128.8, 138.4, 141.3, 141.4; IR (KBr) 2917, 1487, 1377, 1006, 822, 754, 689.

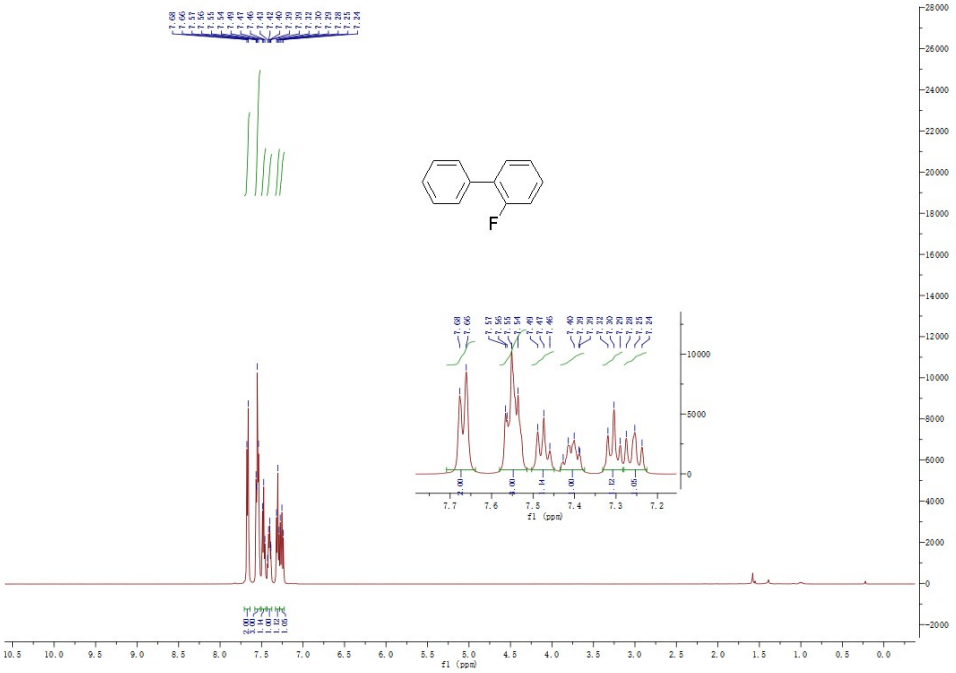


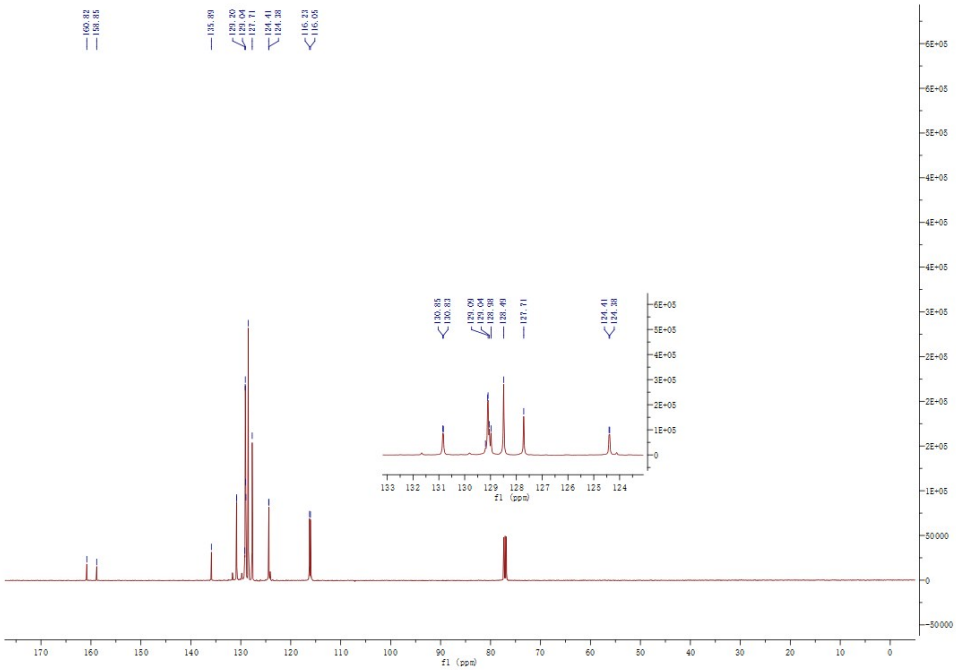


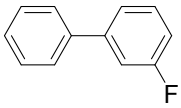


3e:

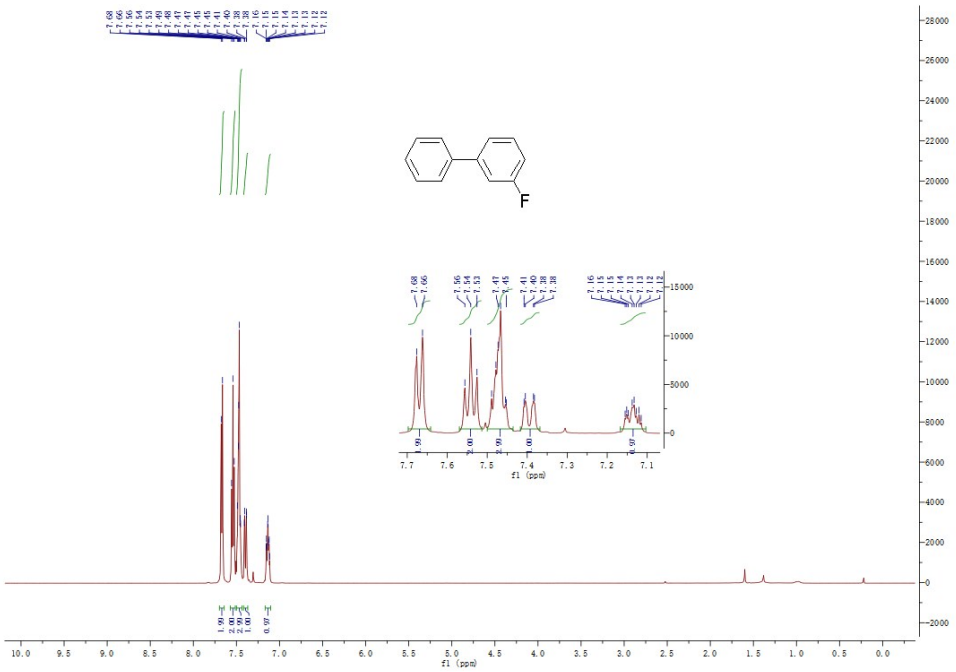
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 7.8 Hz, 2H), 7.55 (dd, *J* = 10.4, 4.7 Hz, 3H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.43-7.38 (m, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.28-7.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 124.4, 127.7, 128.5, 128.9, 129.0, 129.1, 130.8, 135.9, 158.6, 160.8; IR (KBr) 2924, 1476, 1435, 1202, 1106, 727, 698, 611.

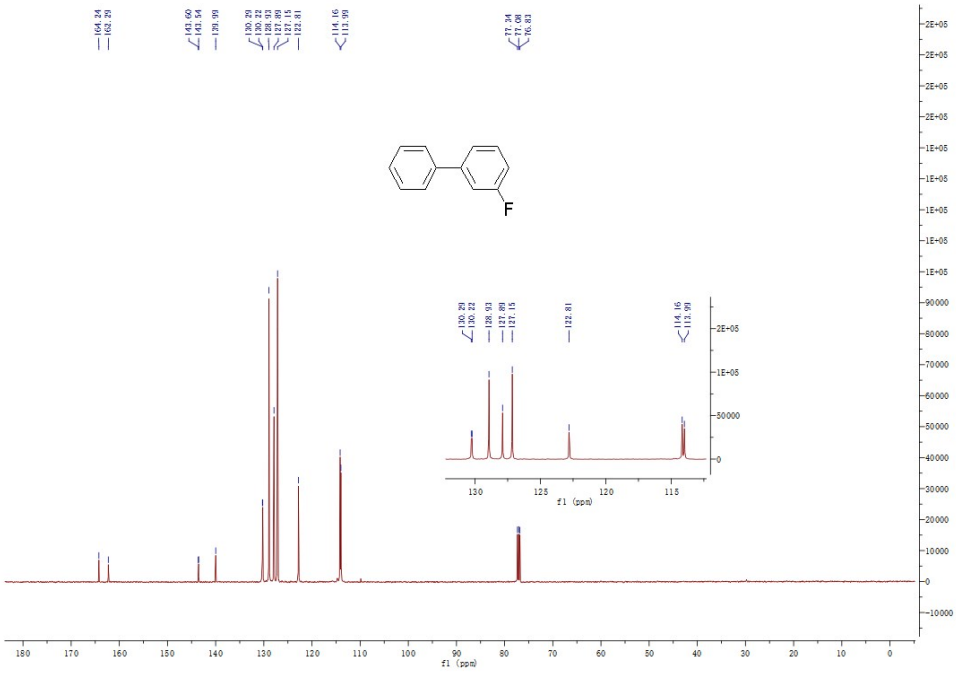


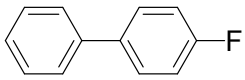


3f: 

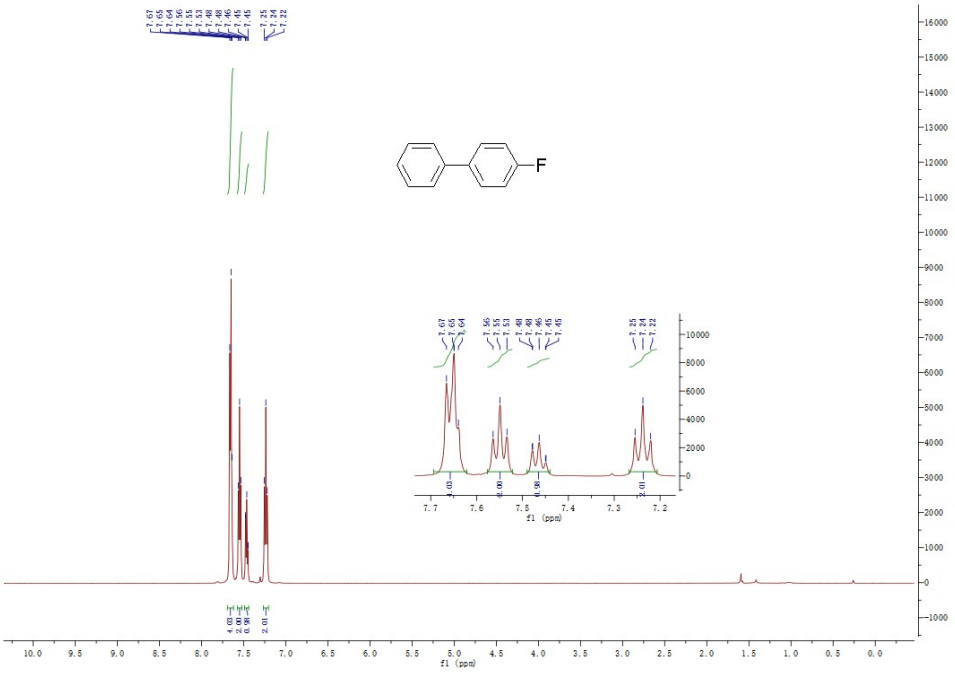
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.50-7.44 (m, 3H), 7.39 (dd, *J* = 11.6, 1.4 Hz, 1H), 7.14 (ddd, *J* = 8.8, 5.1, 2.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 140.1, 122.8, 127.2, 127.9, 128.9, 130.2, 140.0, 143.5, 162.3, 164.2; IR (KBr) 1589, 1479, 1422, 1290, 1185, 1077, 877, 756, 695, 613.

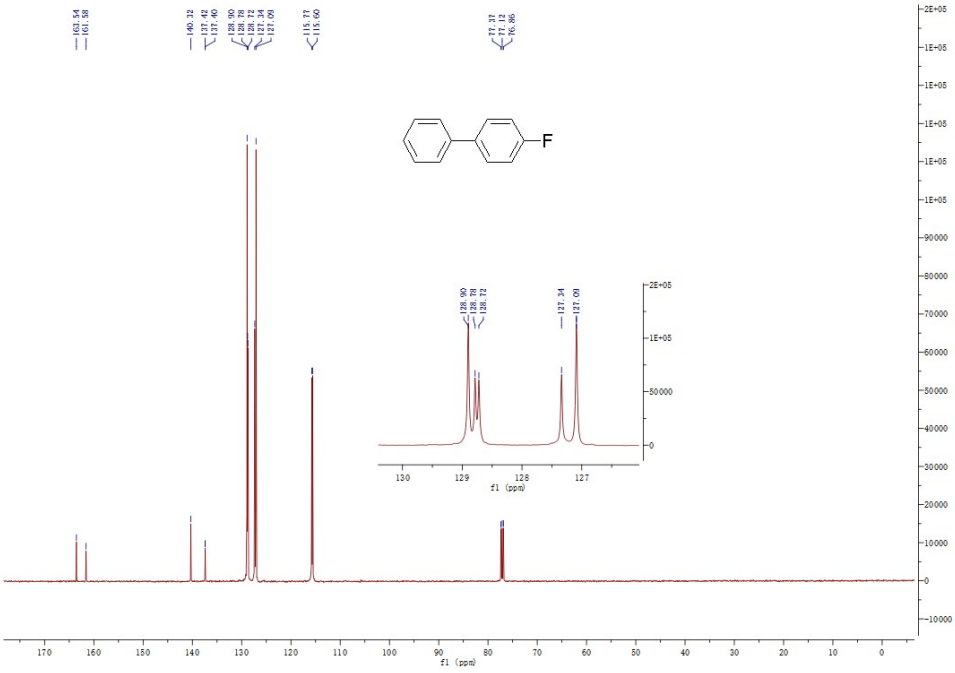


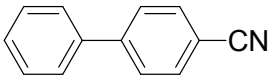


3g: 

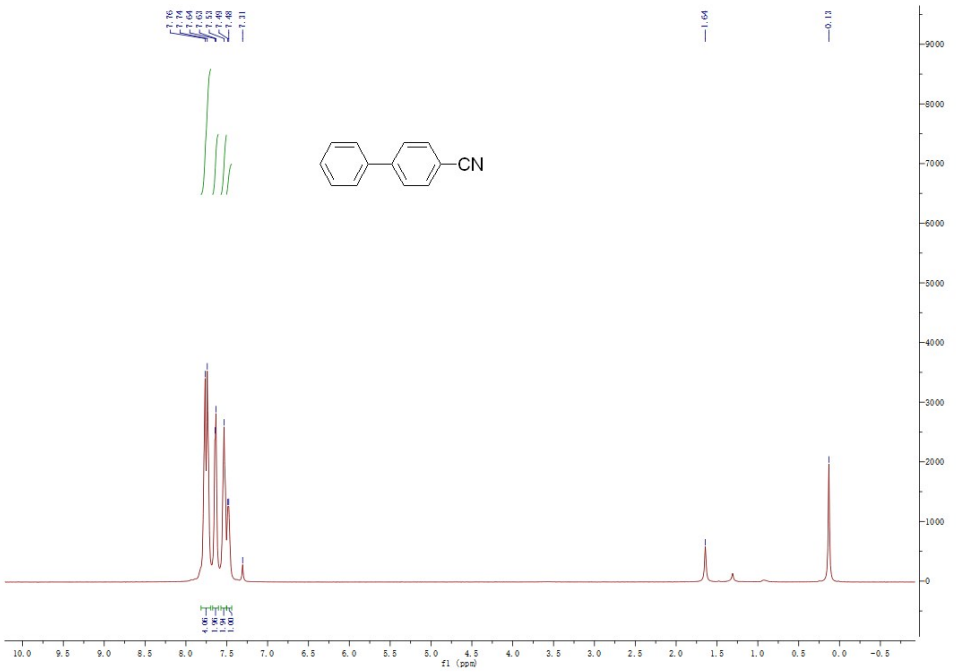
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (t, *J* = 6.5 Hz, 4H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.49-7.44 (m, 1H), 7.24 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 115.7, 127.1, 127.3, 128.8, 137.4, 140.3, 161.6, 163.5; IR (KBr) 1598, 1519, 1484, 1236, 1195, 1006, 837, 758, 687.

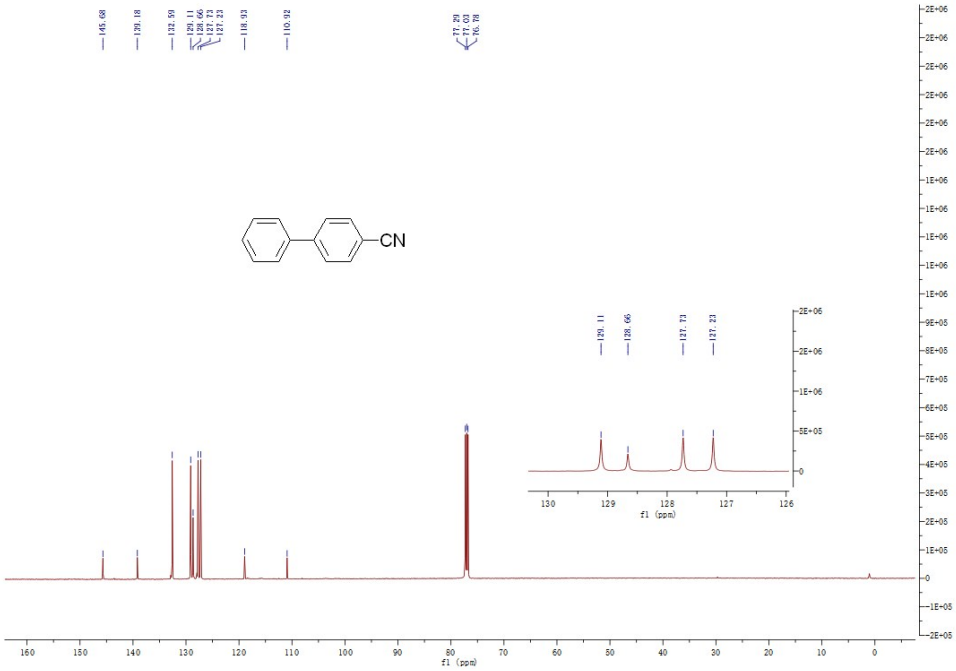


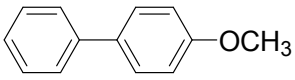


3h: 

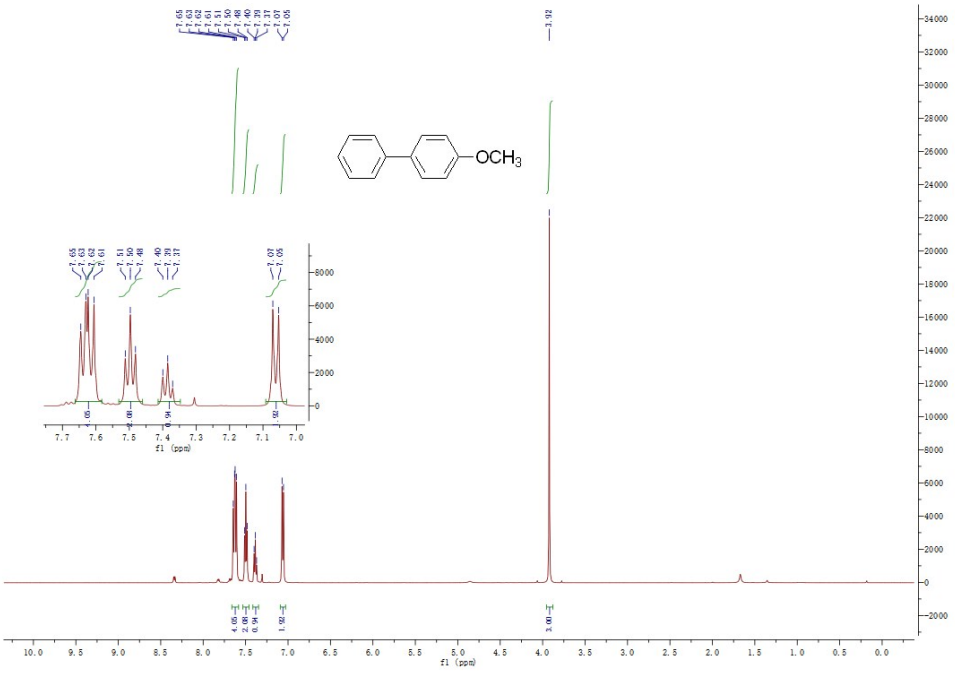
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.57-7.52 (m, 2H), 7.48 (dd, *J* = 7.1, 5.4 Hz, 3H), 7.43-7.36 (m, 4H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 110.9, 118.9, 127.2, 127.7, 128.7, 129.1, 132.6, 139.2, 145.7; IR (KBr) 2965, 2226, 1605, 1484, 1261, 1077, 848, 769, 697.

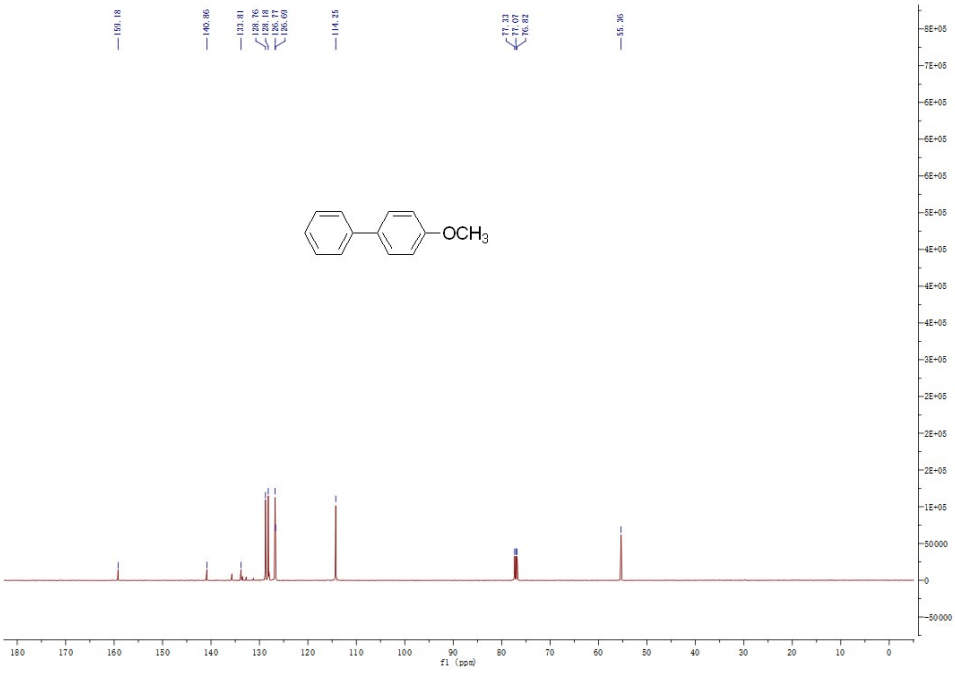


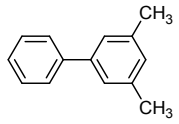


3i: 

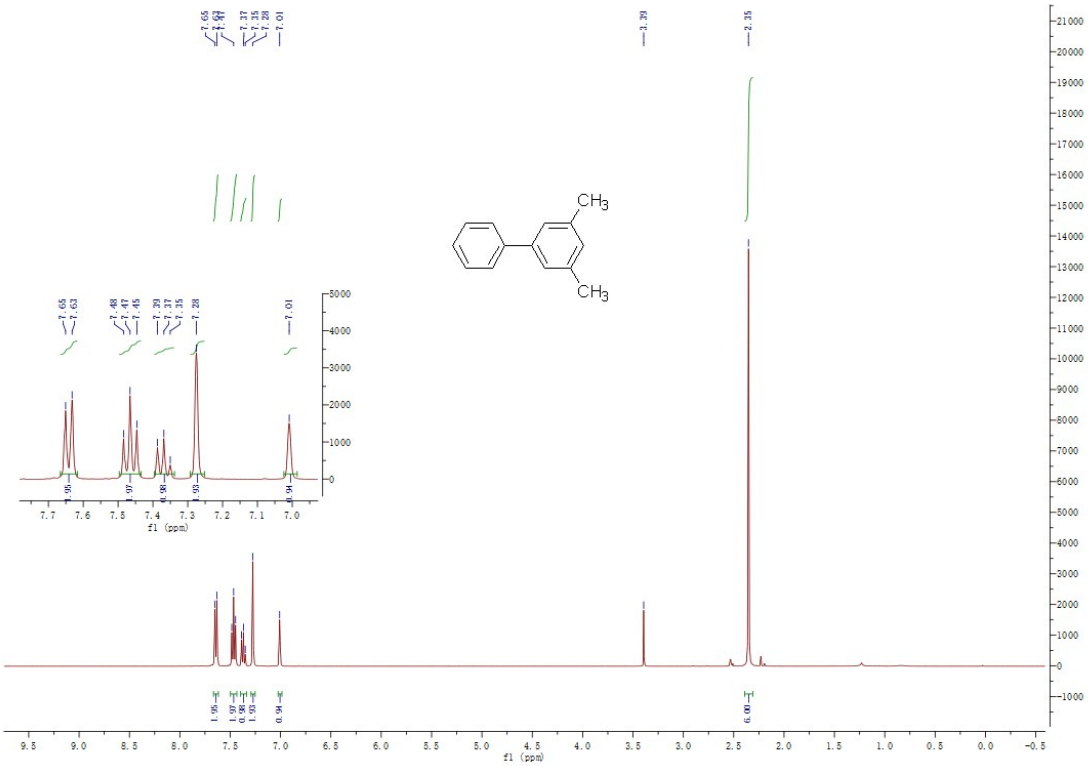
White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 11.5, 8.2 Hz, 4H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 55.4, 114.3, 126.7, 126.8, 128.2, 128.7, 133.8, 140.9, 159.2; IR (KBr) 1605, 1485, 1248, 1199, 1036, 834, 760, 688.

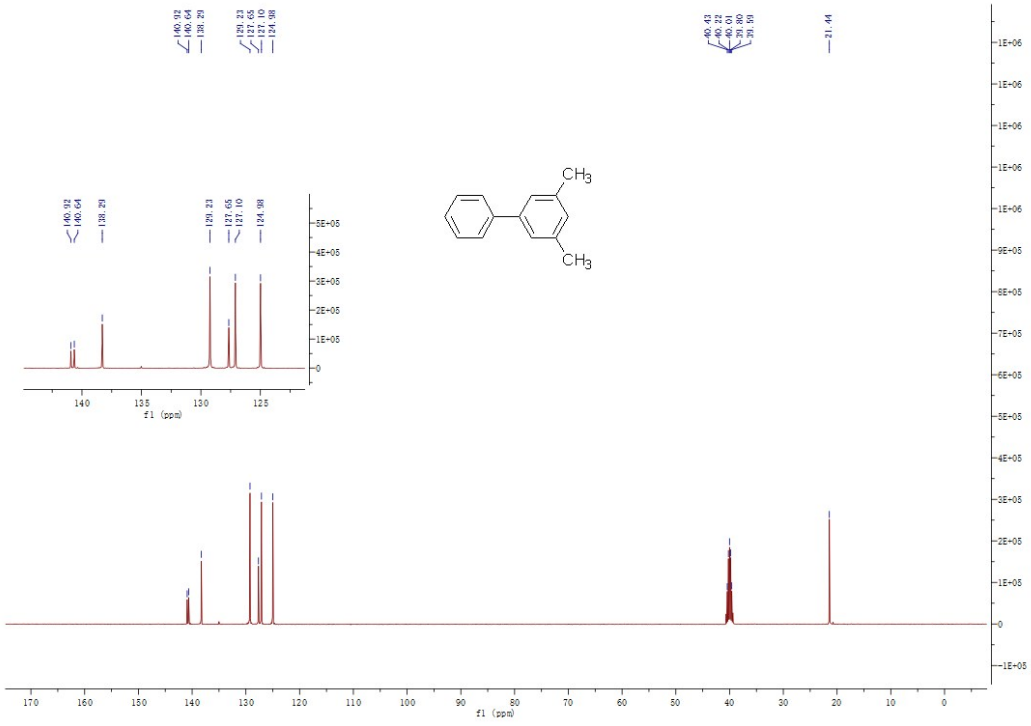


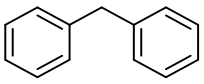


3i: 

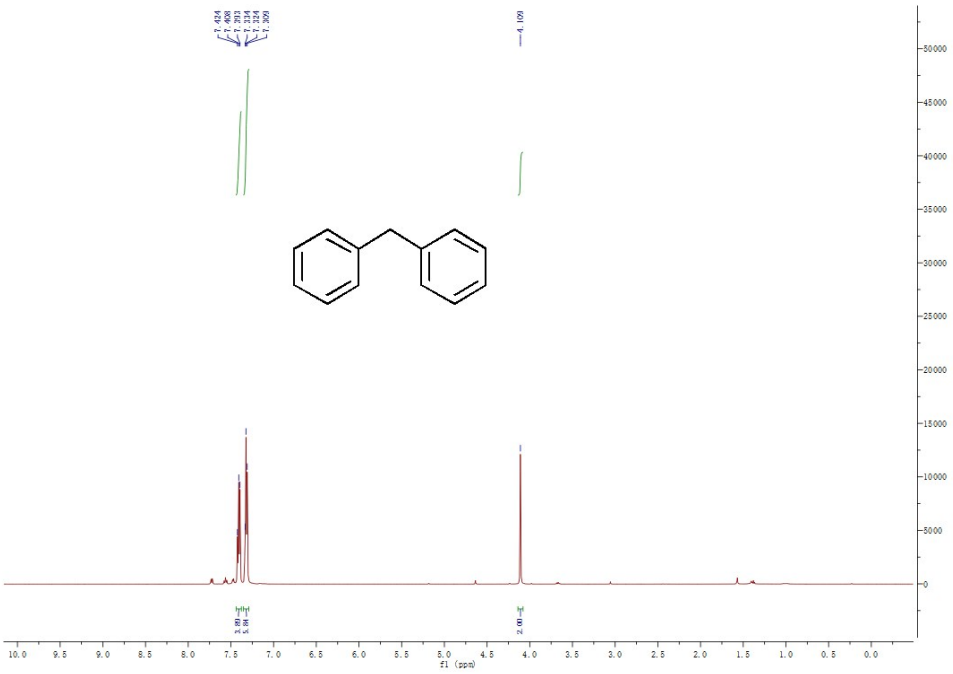
White solid: ^{1}H NMR (400 MHz, DMSO) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.28 (s, 2H), 7.01 (s, 1H), 2.35 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 140.92, 140.64, 138.29, 129.23, 127.65, 127.10, 124.98, 21.44.

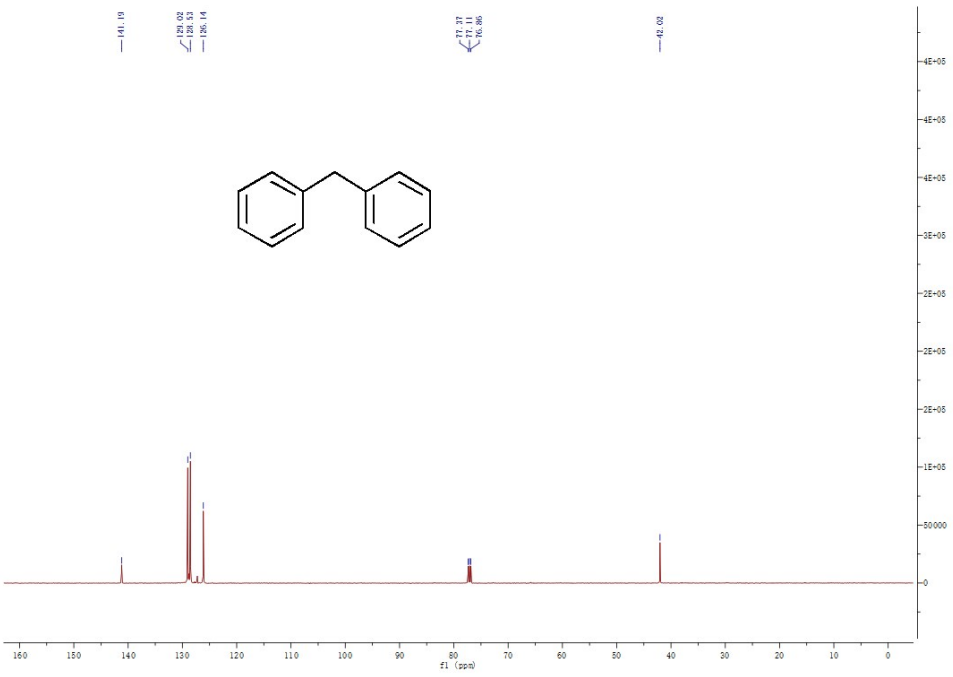


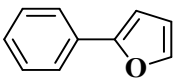


3k: 

White solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 - 7.38 (m, 4H), 7.32 (t, J = 6.3 Hz, 6H), 4.11 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 129.0, 128.5, 126.1, 42.0; IR (KBr) 3026, 1599, 1494, 1451, 1077, 1030, 735, 696, 608.





3l: 

Light red liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 - 7.71 (m, 2H), 7.57 - 7.52 (m, 1H), 7.46 (dd, *J* = 10.6, 4.9 Hz, 2H), 7.32 (dd, *J* = 11.8, 4.1 Hz, 1H), 6.73 (d, *J* = 3.3 Hz, 1H), 6.54 (dd, *J* = 3.3, 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.01, 142.06, 130.91, 128.69, 127.34, 123.80, 111.65, 104.97; IR (KBr) 3061, 1770, 1685, 1449, 1261, 1107, 1022, 761, 692.