Electronic Supplementary Material (ESI) for Polymer Chemistry.

Bulky Pd-PEPPSI-Embedded Conjugated Microporous Polymers-Catalyzed Suzuki-Miyaura Cross-Coupling of Aryl Chlorides and Arylboronic Acids

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1. General Information

(1) Materials: All reagents were purchased from commercial sources and used as received without further purification. All the substrates were purchased from Energy Chemical (Shanghai, China) and used as received. DMF was dried by calcium hydride and used after distillation. [$Pd(PPh_3)_2Cl_2$] and 1,3,5-tri(4-ethynylphenyl)benzene were prepared and purified according to the literature procedures. All anhydrous reactions were carried out under dry nitrogen by using Schlenk tube techniques. All catalytic reactions were performed in a 10 mL glass tube.

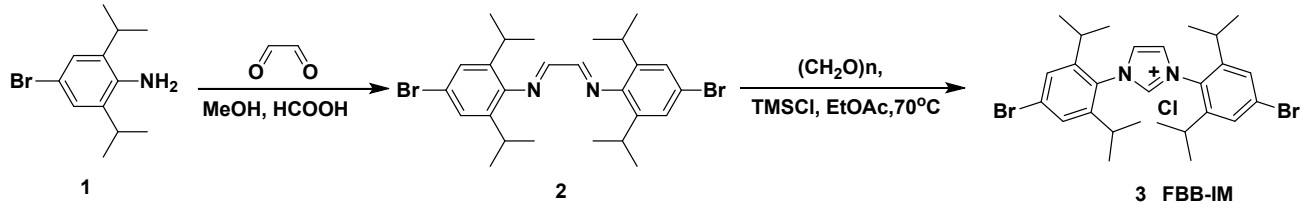
(2) Methods: Chemicals and solvents were purchased from commercial suppliers. All equipment was thoroughly oven-dried. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ^{1}H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer. N_2 adsorption and desorption isotherms were measured at 77 K using a Quantachrome autosorb IQ-2. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDPT) method. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz NMR spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s on a 2.5 mm double resonance probe. FT-IR spectra were collected on a Nicolet 6700 instrument. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in the temperature range of 25 to 1000 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Surface morphologies and microstructures of the synthesized materials were examined with a ZEISS Gemini-500 scanning electron microscope (SEM) and with a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV. The Pd contents in polymer frameworks were determined by Perkin-Elmer ICP-OES Optima 8300 spectroscopy. Powder X-ray diffraction (PXRD) data were collected with a Rigaku D/MAX-2400 X-ray diffractometer operated at 40 kV and 100 mA with Cu Kα radiation at a scan rate of 15°/min. X-ray photoelectron spectroscopy (XPS) date were obtained with an Thermo ESCALAB 250XI Scientific electron spectrometer using 150W Al Kα radiation.

(3) General procedure for the Suzuki-Miyaura reaction: Unless otherwise noted, the Suzuki-Miyaura reaction was carried out under aerobic conditions. All solvents were used as received, and

no further purification was needed. A parallel reactor containing a stir bar was charged with catalyst (0.5 mol%), aryl halides (0.2 mmol), boronic acid (0.3 mmol), base (0.4 mmol), and 0.5 mL of solvent. The reaction mixture was carried out at 80 ^{o}C for 12 h. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid was washed with MeOH (2 x 5 mL) and MeOH/H_2O (3 x 5 mL). The combined organic phase was diluted with dichloromethane, followed by extraction three times with dichloromethane. The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The crude products were purified by silica-gel column chromatography using petroleum ether- dichloromethane (20/1) as eluent, the isolated yield was then calculated based on the feeding of aryl halides. The isolated cross-coupling products were characterized by ^{1}H NMR and ^{13}C NMR spectra.

2. Synthetic Procedures

(1) Synthesis of 1,3-bis(2,6-diisopropyl-4-bromophenyl)imidazolium chloride[1]



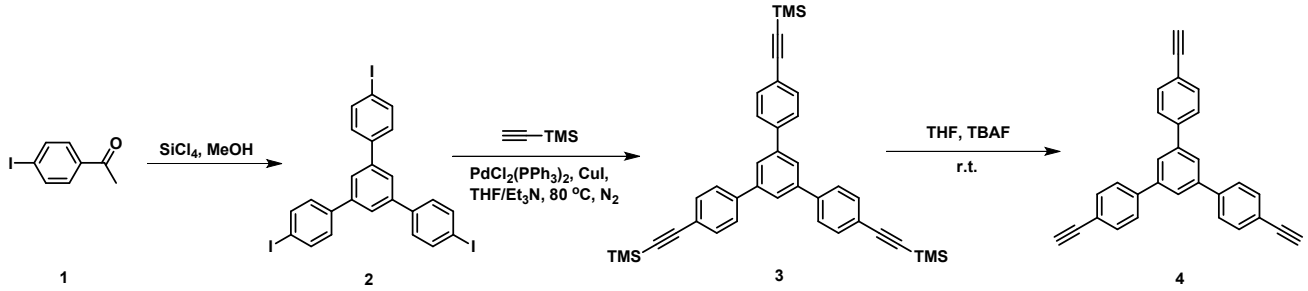
Scheme S1. Synthesis of FBB-IM

A 100 mL round-bottom flask was charged with 1.02 g (4.0 mmol, 2.0 eq) of 4-bromo-2,6-diisopropylaniline, 290 mg (2.0 mmol, 40% in water) of glyoxal and 10 ml of methanol. A few drops of formic acid were added as catalyst. The color of the reaction mixture turned from colorless to yellow immediately, and a yellow precipitate appeared after a few hours. The reaction mixture was stirred for 24 h and the yellow solid was collected by filtration and washed with cold methanol to afford the analytically pure **2**. Yield: 748 mg (70 %).

The corresponding diimine **2** (608 mg, 1.1 mmol) and paraformaldehyde (60 mg, 2.0 mmol) was dissolved in 5.0 mL ethyl acetate. TMSCl (216 mg, 2.0 mmol) was added to the diimine solution at rt via syringe. The reaction mixture was stirred at 70°C for 12 h, the white precipitate was filtered off, washed with EtOAc and dried in vacuo to give the product **FBB-IM**. Yield: 416 mg (65 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 11.00 (s, 1H), 7.87 (s, 2H), 7.41 (s, 4H), 2.32 (dt, *J* = 13.6, 6.8 Hz, 4H), 1.20 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.15, 140.47, 129.10, 128.06, 126.63, 126.06, 29.23, 24.26, 23.51.

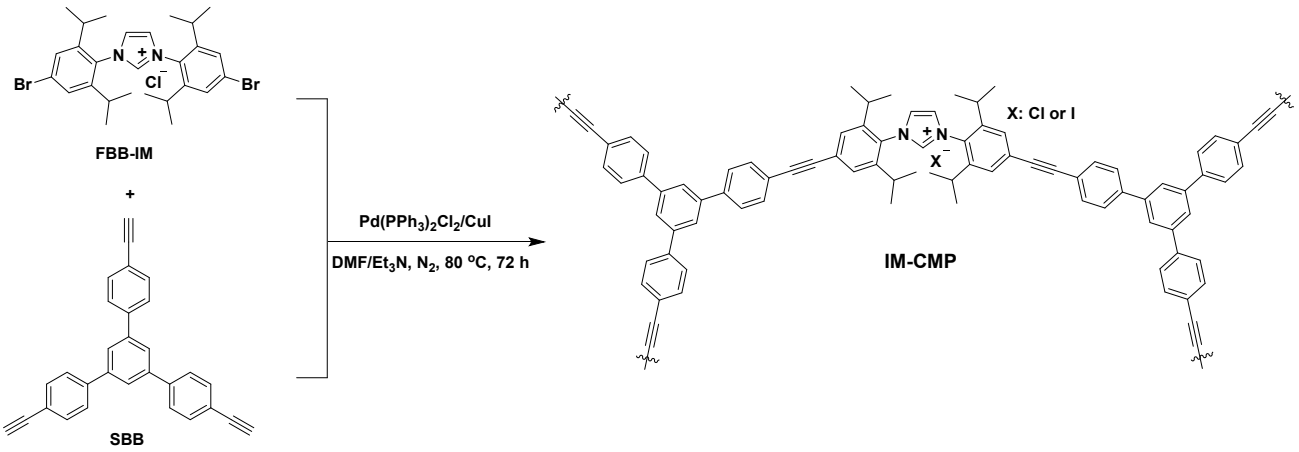
(2) Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene (SBB)[2]



Scheme S2. Synthesis of 1,3,5-tri(4-ethynylphenyl)benzene (SBB)

4-iodooacetophenone (500 mg, 2.03 mmol) was dissolved in ethanol (5 mL) andsilicon tetrachloride (575 mg, 3.39 mmol) was quickly added at 0 °C (a tube is needed to release hydrogen chloride into the fume hood) and the resulting orange solution was stirred at room temperature for 3 d. The mixture was quenched with water (5 mL) and the solution was concentrated to 6 mL. CH_2Cl_2 (5 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on aluminum oxide (hexane/ethyl acetate = 10:1) to give 1,3,5-tris(4-iodophenyl)benzene (396 mg, 85%) as a yellow solid. A mixture of 1,3,5-tris(4-iodophenyl)benzene (350 mg, 512 μmol), ethynyltrimethylsilane (201 mg, 2.05 mmol), $PdCl_2(PPh_3)_2$ (60 mg), and CuI (10 mg) in THF (2.5 mL) and triethylamine (2.5 mL) was heated to 80 °C for 16 h under N_2 atmosphere. The volatile components were removed under reduced pressure and the residue was diluted with CH_2Cl_2 (10 mL). Satd. aq. NH_4Cl solution (10 mL) was added, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to give **3** (211 mg, 70%) as a pale brownish solid. A solution of **3** (200 mg, 336 μmol) and TBAF (1.2 ml, 1.18 mmol, 1 M in THF) in THF (2 mL) was stirred at room temperature for 30 min. The mixture was quenched with satd. aq. NH_4Cl solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated to dryness. The residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 10:1) to give 1,3,5-tri(4-ethynylphenyl)benzene (102 mg, 80%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (s, 3H); 7.67-7.61 (m, 12H); 3.17 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 141.6, 141.2, 132.7, 127.2, 125.3, 121.5, 83.4, 78.2.

(3) Synthesis of IM-CMP[3]

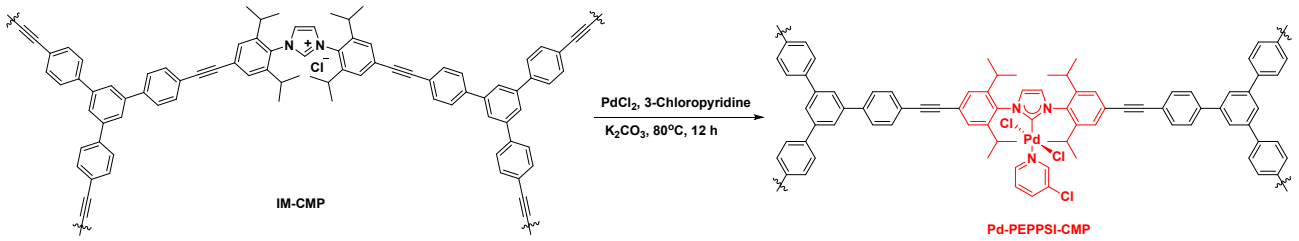


Scheme S3. Synthesis of IM-CMP

FBB-IM (273 mg, 0.50 mmol), 1,3,5-tri(4-ethynylphenyl)benzene (125 mg, 0.33 mmol), bis-(triphenylphosphine)palladium(II) dichloride (42 mg) , and copper (I) iodide (24 mg) were added into a dried round-bottom flask under nitrogen atmosphere. Anhydrous DMF (6.0 mL) and Et_3N (6.0 mL) were added to the mixture via a syringe. The resulting mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. After cooling to room temperature, the precipitate network polymer was filtered and washed four times (once each) with chloroform, water, methanol and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymer was carried out by soxhlet extraction with methanol for 48 h. The product was dried at 70 °C under vacuum for 6 h to give a brown powder. Yield: 302 mg (95%). Elemental combustion analysis (%) Calcd for $C_{47}H_{45}N_2Cl$: C 83.87, N 4.16, H 6.69; Found: C 72.08, N 2.97, H 6.60.

Note: Since the loading of the CuI was 25 mol% relative to the FBB-IM, the iodide ions would be incorporated into the IM-CMP frameworks. The speculation was verified by the EDX analysis, which both chloride and iodine ions were found. Moreover, the elemental analysis revealed the value of 72.08, 2.97 and 6.60 % for C, N, H, respectively. These data showed deviations from theoretical values for $C_{47}H_{45}N_2Cl$, as the calculated value turned out to be 83.87, 4.16 and 6.69 % for C, N, H, respectively. Therefore, it is reasonable that both the chloride and iodine ions were served as counterions in the IM-CMP.

(4) Synthesis of Pd-PEPPSI-CMP[4]



Scheme S4. Synthesis of Pd-PEPPSI-CMP

IM-CMP (100 mg, 1.06 mmol/g), $PdCl_2$ (35.0 mg, 2.0 eq) and K_2CO_3 (69 mg, 5.0 eq) were mixed and stirred in 1.0 mL 3-chloropyridine at 80 °C for 12 h. After the reaction was complete, the obtained polymer was filtered and washed thoroughly with dichloromethane (10 mL × 3), distilled water (10 mL × 3) and acetone (10 mL × 3), then dried at 80 °C under vacuum for 12 h to yield Pd-PEPPSI-CMP as a dark powder (109 mg). The Pd content in Pd-PEPPSI-CMP frameworks was 2.38% as determined by ICP-OES.

3. Characterization of IM-CMP and Pd-PEPPSI-CMP

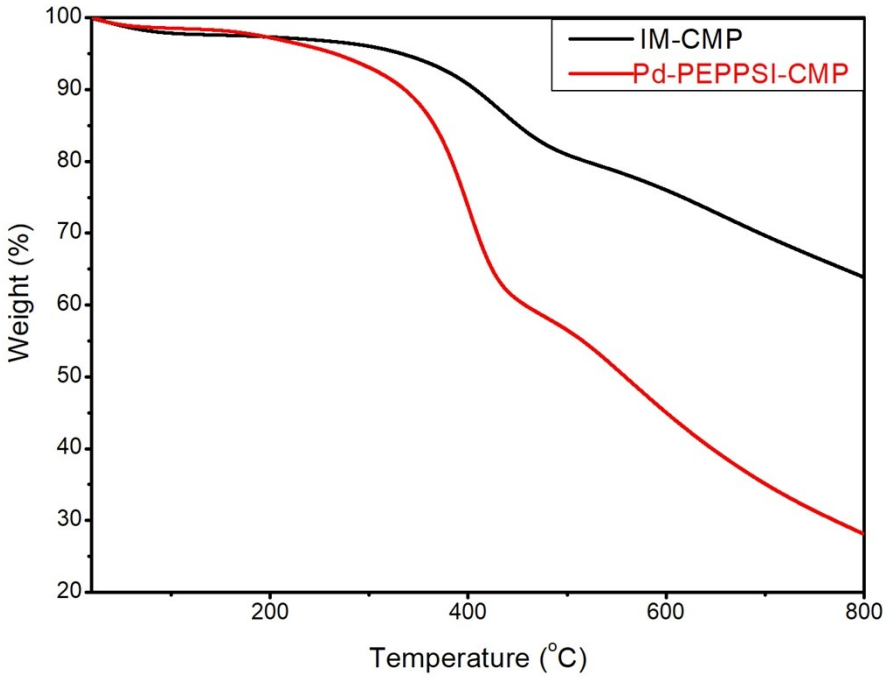


Figure S1. TGA curves of IM-CMP and Pd-PEPPSI-CMP

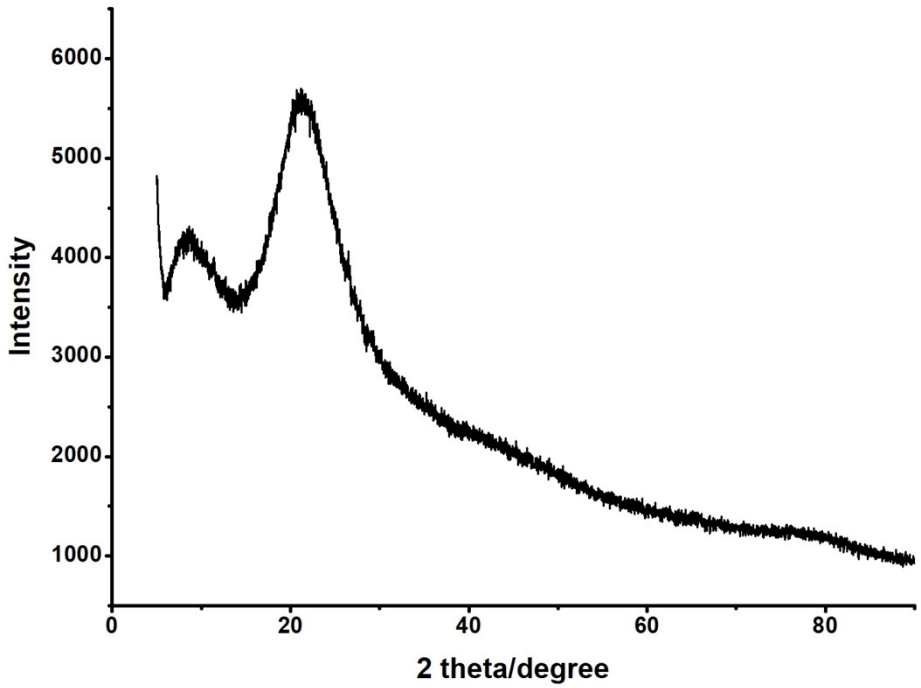


Figure S2. Powder X-ray diffraction pattern of IM-CMP. No intensive diffraction peaks were observable.

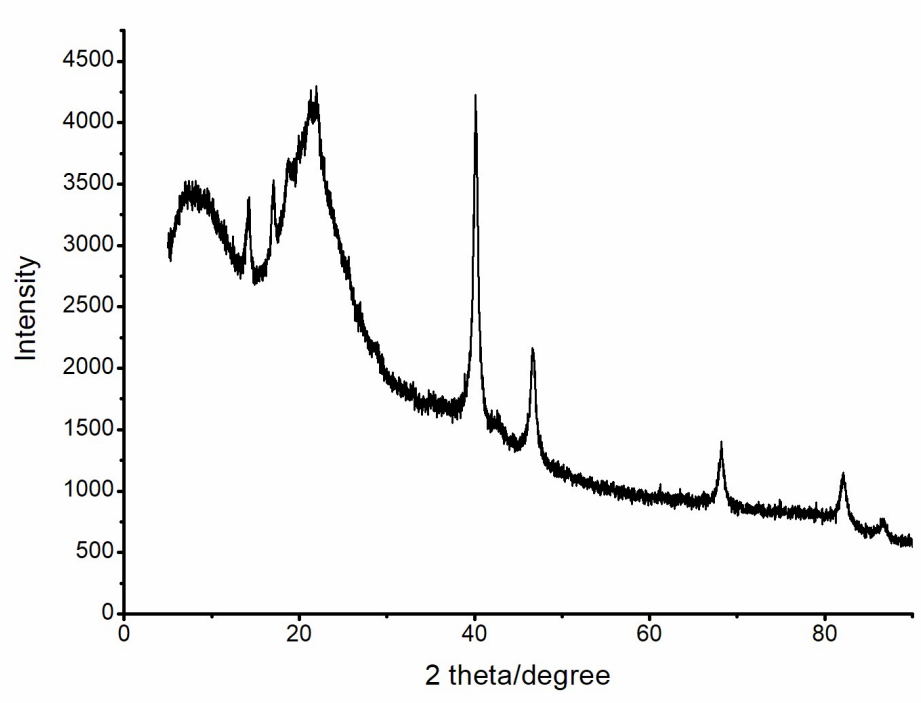


Figure S3. Powder X-ray diffraction pattern of Pd-PEPPSI-CMP.

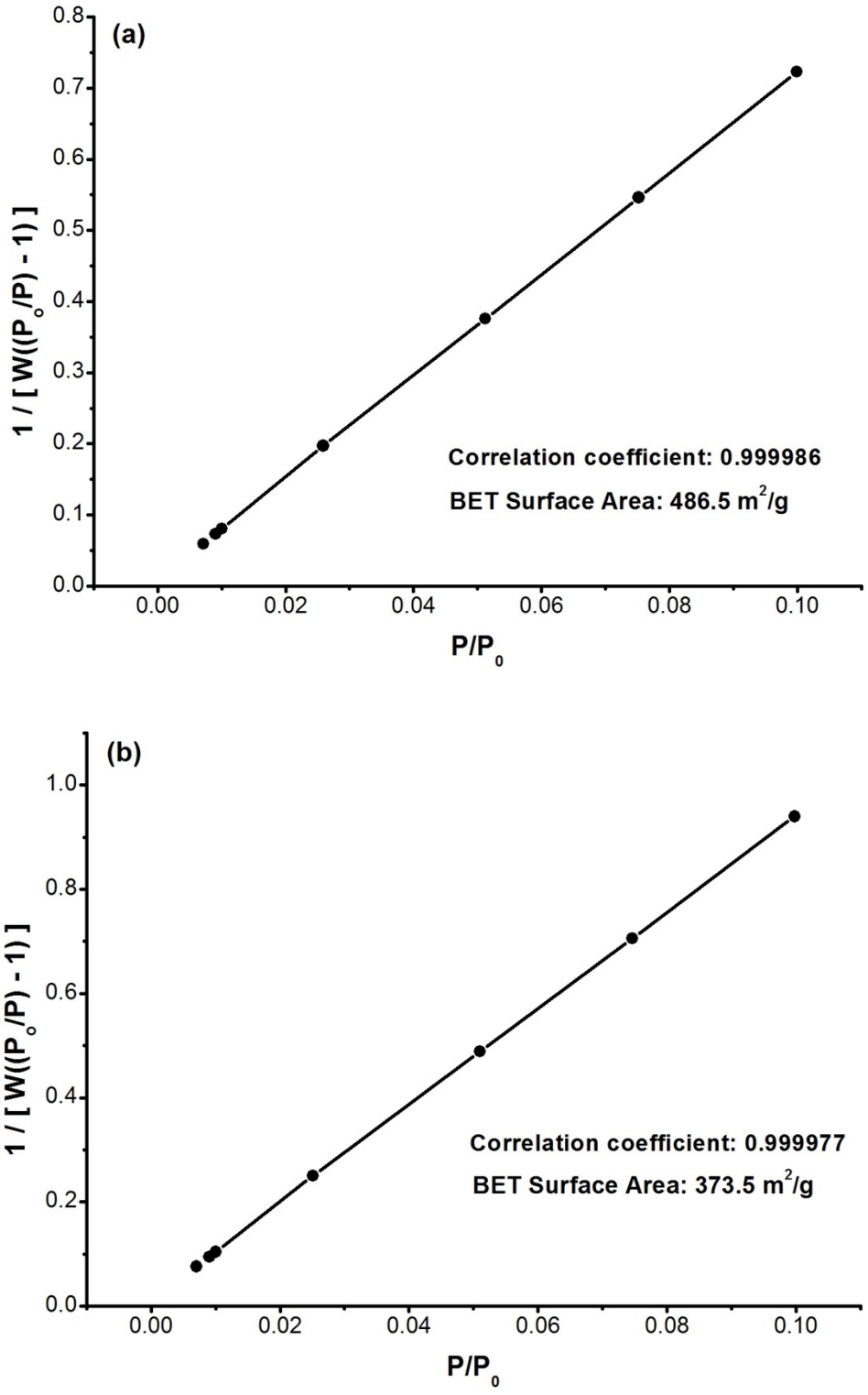
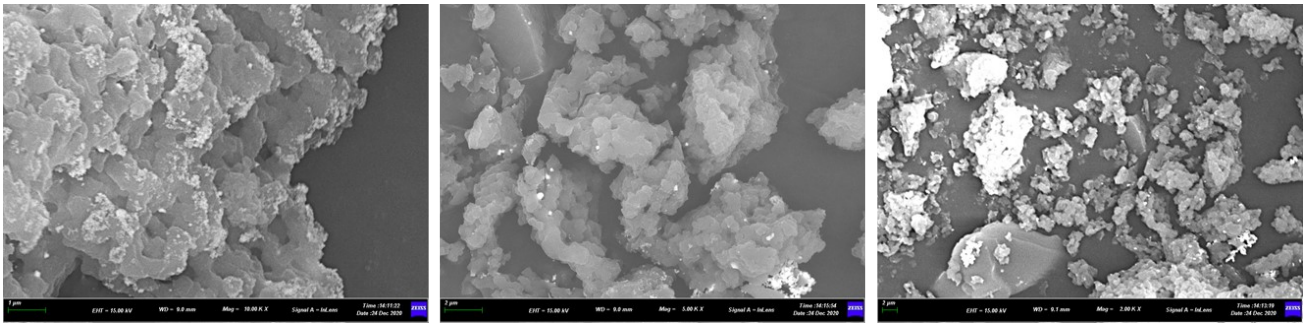
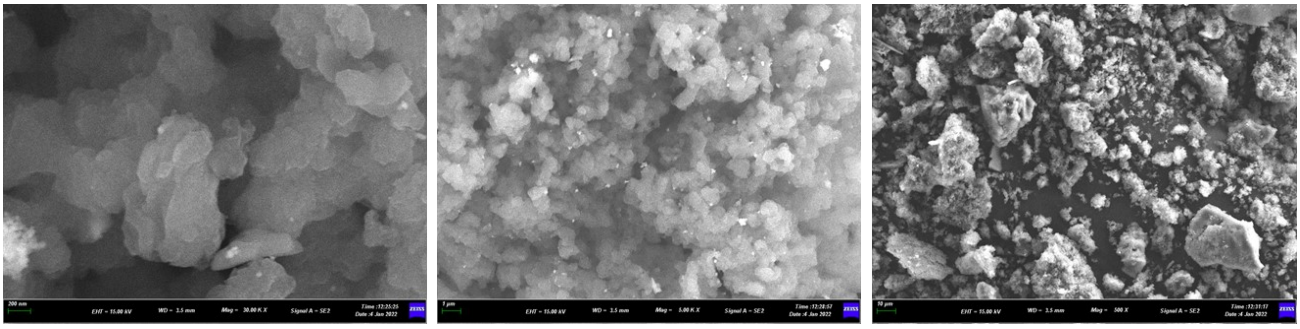


Figure S4. BET surface area plots of IM-CMP (a) and Pd-PEPPSI-CMP (b)



(a) IM-CMP



(b) Pd-PEPPSI-CMP

Figure S5. SEM images of IM-CMP and Pd-PEPPSI-CMP

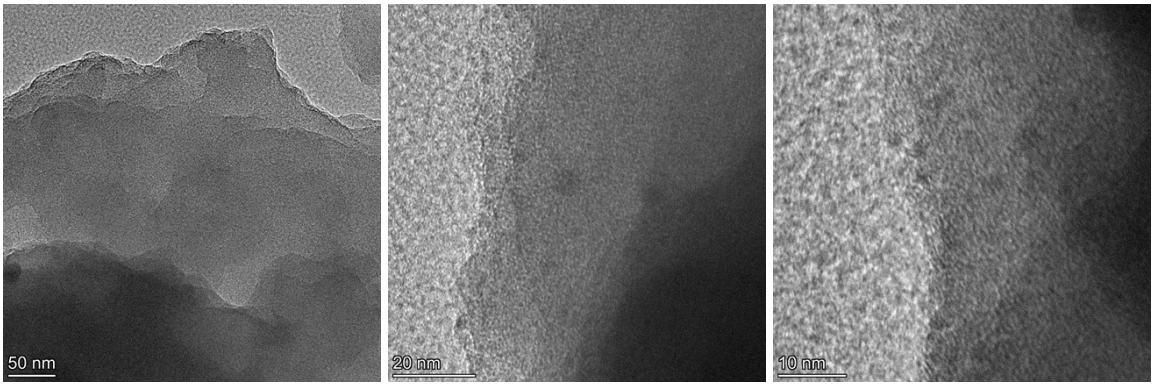


Figure S6. HR-TEM images of Pd-PEPPSI-CMP

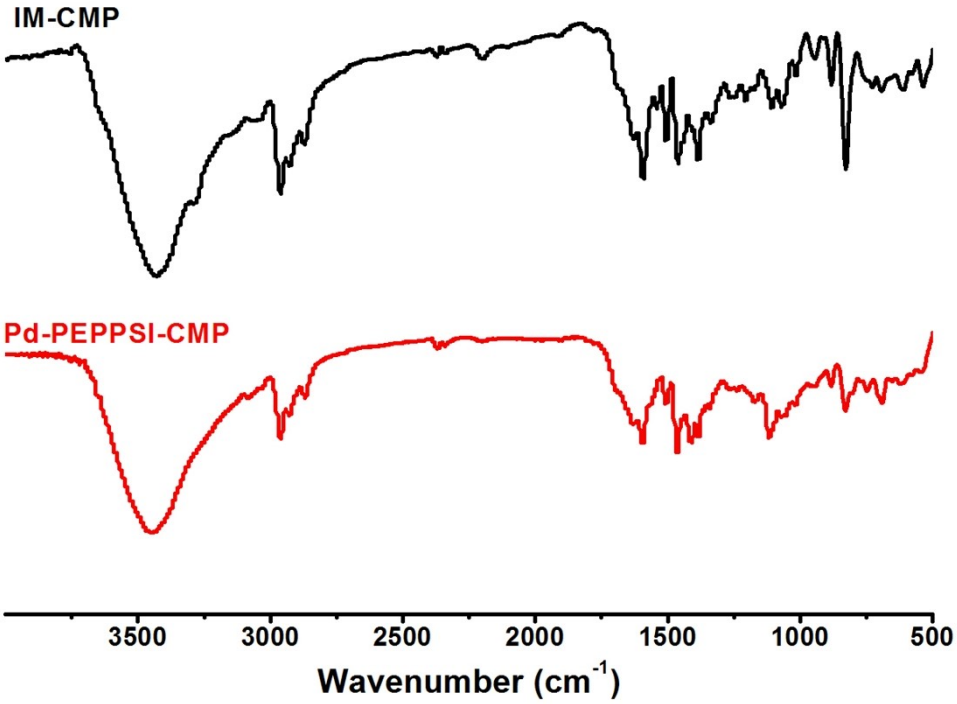


Figure S7. FT-IR spectra of IM-CMP and Pd-PEPPSI-CMP

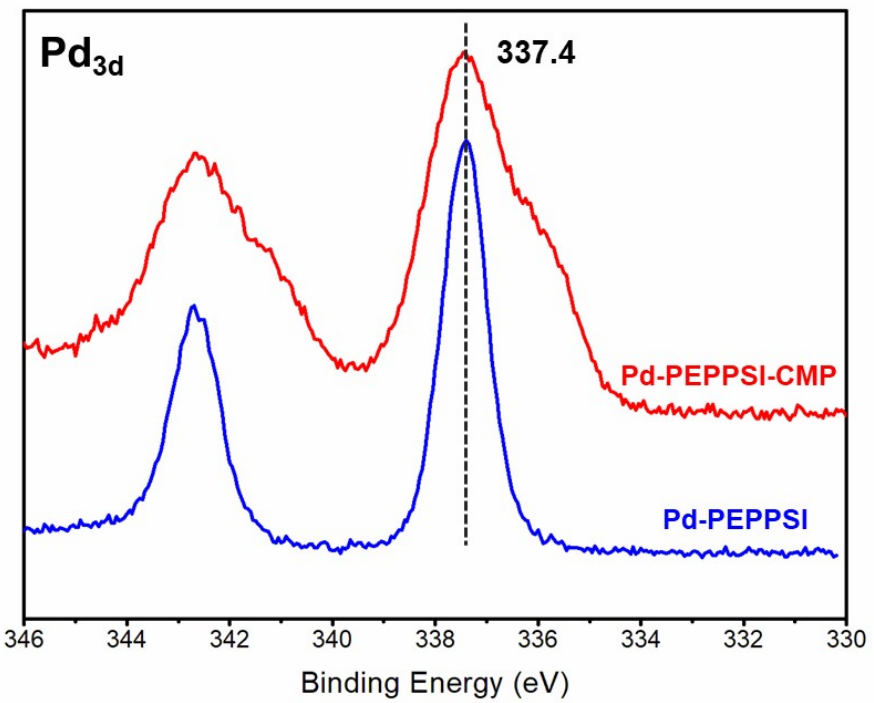
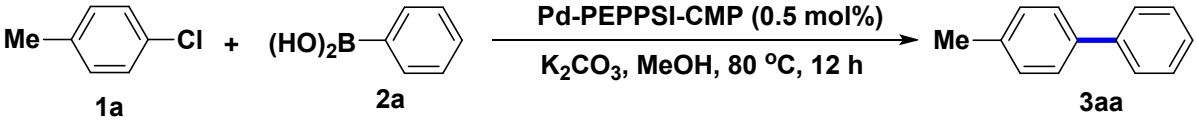


Figure S8. XPS spectra of Pd-PEPPSI-CMP (red) and Pd-PEPPSI complex (bule).

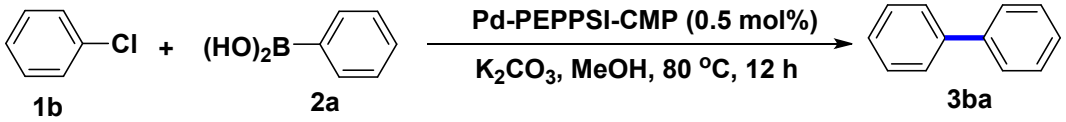
4. Suzuki-Miyaura Coupling of Aryl Chlorides and Arylboronic acides: Variation of Aryl Chlorides[5]

1-chloro-4-methylbenzene



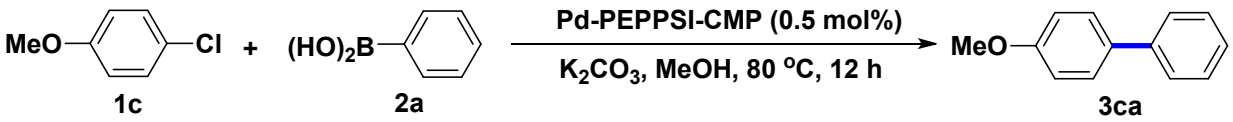
According to the general procedure, the reaction of 1-chloro-4-methylbenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (32.3 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.23 (t, *J* = 9.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.23, 138.43, 137.04, 129.52, 128.74, 127.04, 127.01, 127.00, 21.12.

Chlorobenzene



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (29.6 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 4H), 7.44 (t, *J* = 7.3 Hz, 4H), 7.38 – 7.26 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.28, 128.75, 127.25, 127.17.

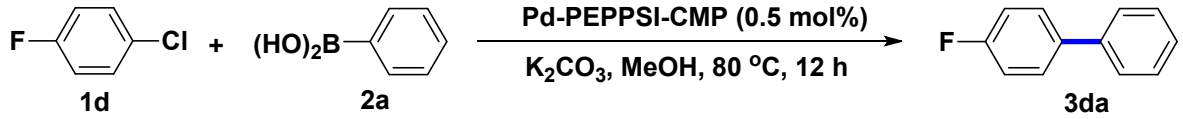
1-chloro-4-methoxybenzene



According to the general procedure, the reaction of 1-chloro-4-methoxybenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 97% yield (35.7 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 8.8, 7.6, 1.7 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.94 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz,

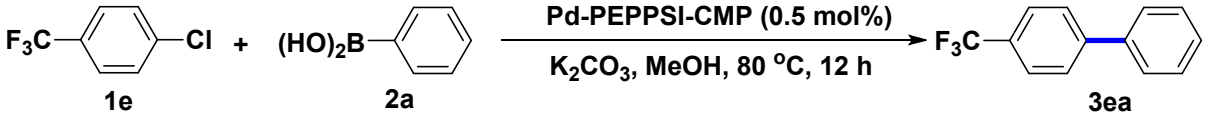
$CDCl_3$) δ 159.15, 140.84, 133.79, 128.72, 128.16, 126.74, 126.65, 114.21, 55.35.

1-chloro-4-fluorobenzene



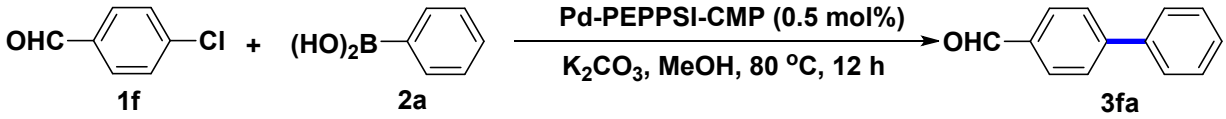
According to the general procedure, the reaction of 1-chloro-4-fluorobenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 92% yield (31.6 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.1, 4.6 Hz, 4H), 7.45 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.47, 161.52, 140.29, 137.39, 137.36, 128.81, 128.72, 128.65, 127.26, 127.03, 115.69, 115.52. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.88.

1-chloro-4-(trifluoromethyl)benzene



According to the general procedure, the reaction of 1-chloro-4-(trifluoromethyl)benzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 89% yield (39.6 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.62 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.76, 139.80, 129.50 (q, J^F = 32.8 Hz), 129.13, 128.33, 127.56, 127.42, 125.85 (q, J^F = 3.7 Hz), 124.47 (q, J^F = 272.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.42.

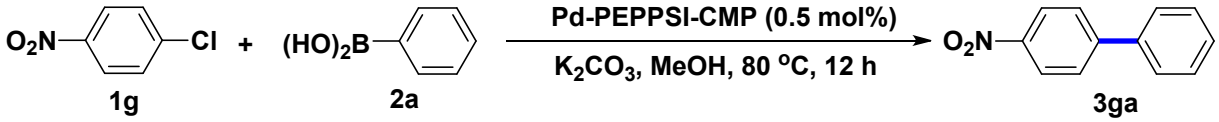
4-chlorobenzaldehyde



According to the general procedure, the reaction of 4-chlorobenzaldehyde (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 88% yield (32.4 mg). yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.07 (s, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.77 (d, J =

8.2 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.85, 147.23, 139.76, 135.27, 130.26, 129.02, 128.47, 127.70, 127.37.

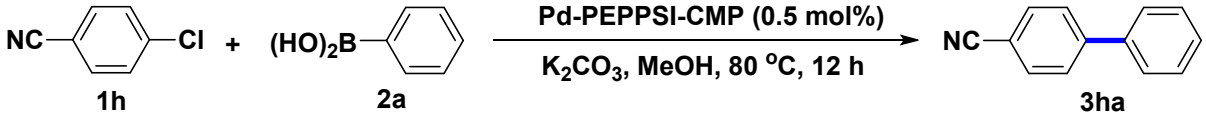
1-chloro-4-nitrobenzene



1g 2a 3ga

According to the general procedure, the reaction of 1-chloro-4-nitrobenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 94% yield (37.4 mg). yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.26 (m, 2H), 7.79 – 7.71 (m, 2H), 7.64 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.46 (ddd, *J* = 7.3, 3.6, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.65, 147.18, 138.81, 129.15, 128.91, 127.81, 127.39, 124.10.

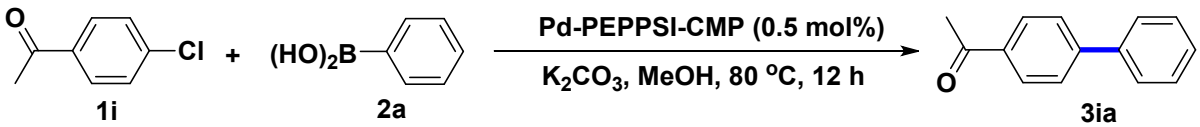
4-chlorobenzonitrile



1h 2a 3ha

According to the general procedure, the reaction of 4-chlorobenzonitrile (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 92% yield (32.9 mg). yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.72 – 7.66 (m, 2H), 7.64 – 7.57 (m, 2H), 7.50 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.47 – 7.40 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.71, 139.21, 132.59, 129.11, 128.66, 127.74, 127.23, 118.91, 110.97.

1-(4-chlorophenyl)ethanone

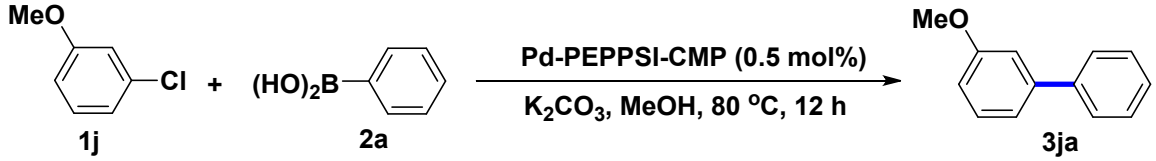


1i 2a 3ia

According to the general procedure, the reaction of 1-(4-chlorophenyl)ethanone (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 92% yield (36.1 mg). yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 1H), 2.65 (s, 3H). ^{13}C

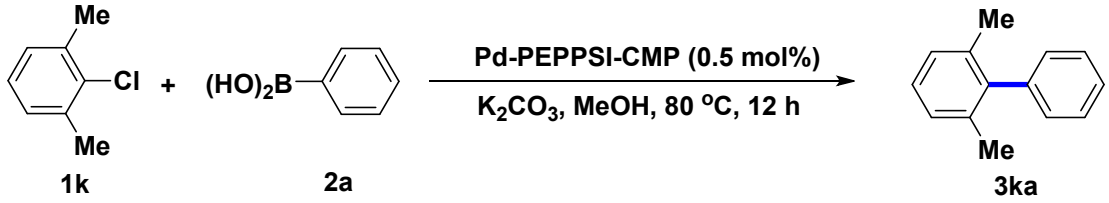
NMR (126 MHz, $CDCl_3$) δ 197.70, 145.81, 139.92, 135.92, 128.95, 128.91, 128.22, 127.28, 127.23, 26.62.

1-chloro-3-methoxybenzene



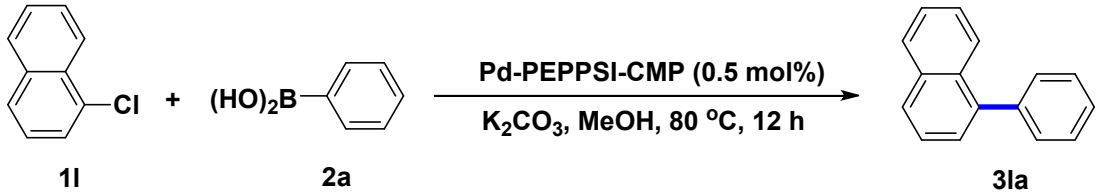
According to the general procedure, the reaction of 1-chloro-3-methoxybenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (35.4 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.6 Hz, 2H), 7.37 (dt, J = 7.3, 4.0 Hz, 2H), 7.21 (d, J = 7.6 Hz, 1H), 7.17 – 7.13 (m, 1H), 6.92 (dd, J = 8.2, 2.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.99, 142.81, 141.15, 129.74, 128.73, 127.41, 127.20, 119.71, 112.95, 112.72, 55.31.

2-chloro-1,3-dimethylbenzene



According to the general procedure, the reaction of 2-chloro-1,3-dimethylbenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 92% yield (33.5 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.17 (ddd, J = 24.1, 13.9, 7.0 Hz, 5H), 2.05 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.88, 141.12, 136.05, 129.04, 128.40, 127.27, 127.00, 126.60, 20.80.

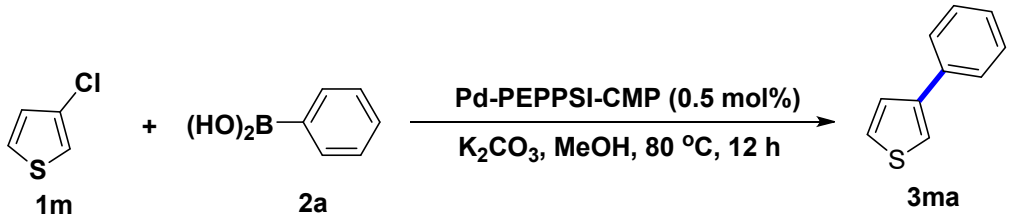
1-chloronaphthalene



According to the general procedure, the reaction of 1-chloronaphthalene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL

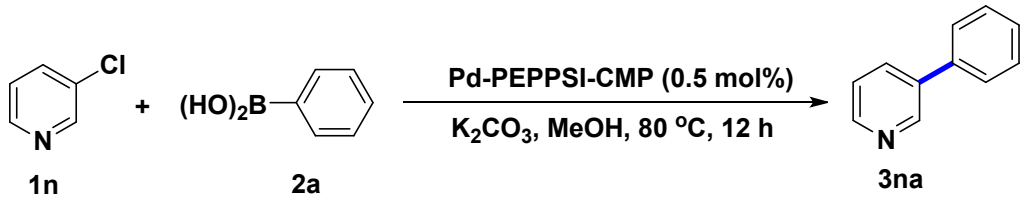
MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 98% yield (40.0 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.2 Hz, 1H), 7.57 – 7.49 (m, 6H), 7.48 – 7.42 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.80, 140.29, 133.83, 131.66, 130.08, 128.25, 127.63, 127.23, 126.92, 126.04, 126.01, 125.76, 125.37.

3-chlorothiophene



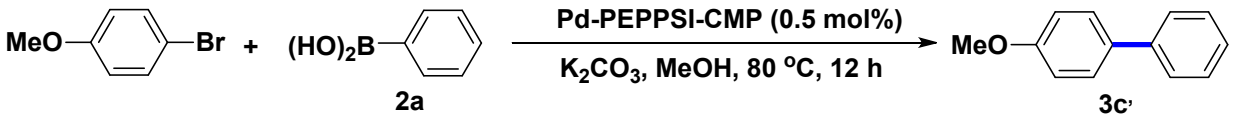
According to the general procedure, the reaction of 3-chlorothiophene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 85% yield (27.2 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.46 (dd, J = 4.5, 2.1 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.31 (t, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.41, 135.90, 128.79, 127.12, 126.46, 126.35, 126.16, 120.25.

3-chloropyridine



According to the general procedure, the reaction of 3-chloropyridine (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 90% yield (27.9 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.60 (d, J = 3.8 Hz, 1H), 7.94 – 7.84 (m, 1H), 7.65 – 7.55 (m, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.46 – 7.35 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.48, 148.36, 137.88, 136.68, 134.33, 129.07, 128.09, 127.16, 123.52.

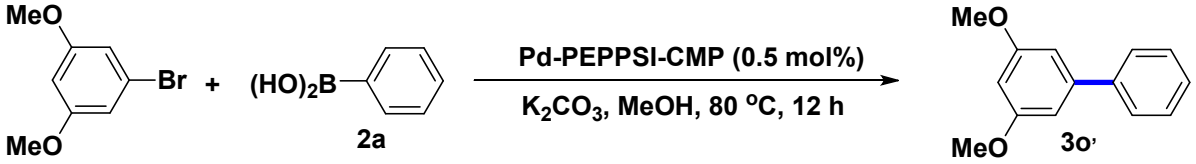
1-bromo-4-methoxybenzene



According to the general procedure, the reaction of 1-bromo-4-methoxybenzene (0.20 mmol, 1.0

equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 1 h at 80 °C, afforded after filtration and chromatography the product in 98% yield (36.1 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (ddd, *J* = 8.8, 7.6, 1.7 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.94 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.15, 140.84, 133.79, 128.72, 128.16, 126.74, 126.65, 114.21, 55.35.

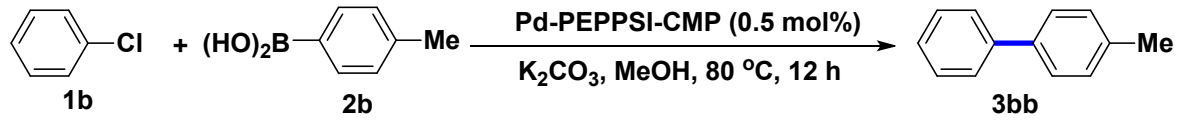
1-bromo-3,5-dimethoxybenzene



According to the general procedure, the reaction of 1-bromo-3,5-dimethoxybenzene (0.20 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 1 h at 80 °C, afforded after filtration and chromatography the product in 98% yield (42.0 mg). yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.76 (d, *J* = 2.2 Hz, 2H), 6.50 (t, *J* = 2.2 Hz, 1H), 3.87 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.07, 143.51, 141.23, 128.69, 127.54, 127.20, 109.87, 105.50, 99.32, 55.41.

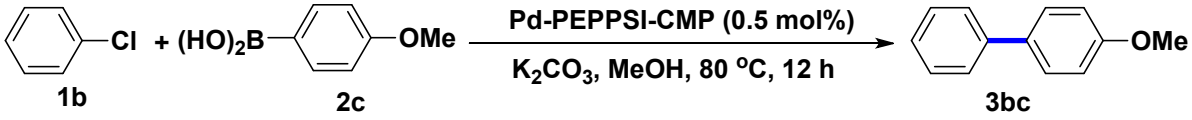
5. Suzuki-Miyaura Coupling of Aryl Chlorides and Arylboronic acides: Variation of Boronic Acids[5]

***p*-tolylboronic acid**



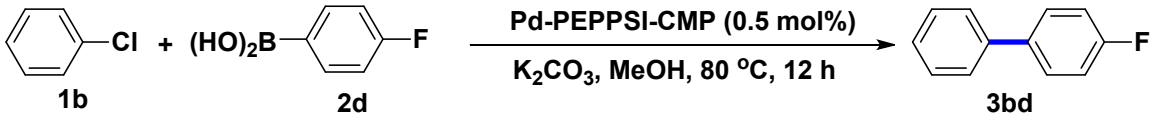
According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), *p*-tolylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 95% yield (32.0 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 7.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 9.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.23, 138.43, 137.04, 129.52, 128.74, 127.04, 127.01, 127.00, 21.12.

(4-methoxyphenyl)boronic acid



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (35.3 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (ddd, J = 8.8, 7.6, 1.7 Hz, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.06 – 6.94 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.15, 140.84, 133.79, 128.72, 128.16, 126.74, 126.65, 114.21, 55.35.

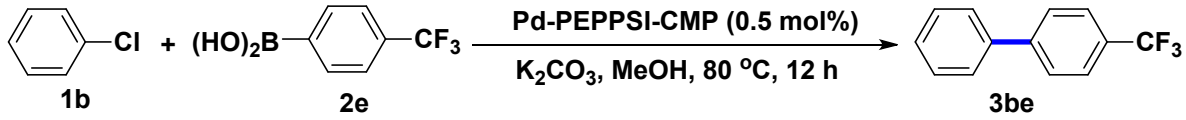
(4-fluorophenyl)boronic acid



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), (4-fluorophenyl)boronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 93% yield (32.0 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.1, 4.6 Hz, 4H), 7.45 (t, J =

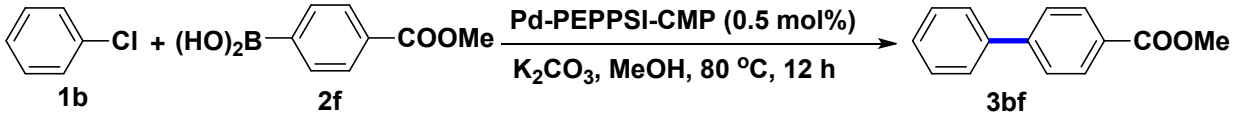
7.7 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.47, 161.52, 140.29, 137.39, 137.36, 128.81, 128.72, 128.65, 127.26, 127.03, 115.69, 115.52. ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.88.

(4-(trifluoromethyl)phenyl)boronic acid



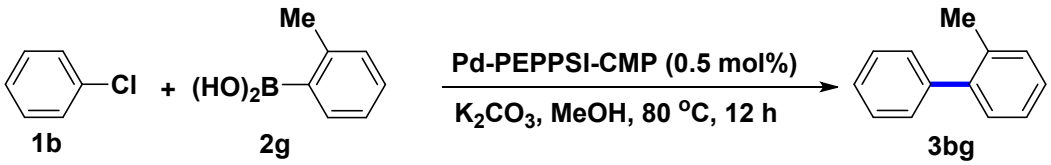
According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), (4-(trifluoromethyl)phenyl)boronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (42.7 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.62 (d, J = 7.4 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.76, 139.80, 129.50 (q, J^F = 32.8 Hz), 129.13, 128.33, 127.56, 127.42, 125.85 (q, J^F = 3.7 Hz), 124.47 (q, J^F = 272.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.42.

(4-(methoxycarbonyl)phenyl)boronic acid



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), (4-(methoxycarbonyl)phenyl)boronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 94% yield (39.9 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.66–7.61 (m, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.02, 145.66, 140.04, 130.11, 128.93, 128.15, 127.29, 127.06, 52.13.

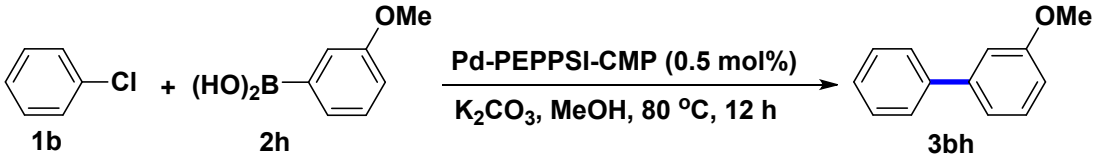
***o*-tolylboronic acid**



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), *o*-tolylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH

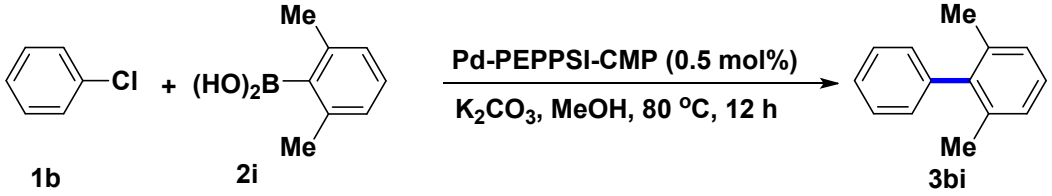
for 12 h at 80 °C, afforded after filtration and chromatography the product in 90% yield (30.2 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.3 Hz, 2H), 7.33 (td, *J* = 7.9, 4.0 Hz, 3H), 7.29 – 7.21 (m, 5H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.00, 141.97, 135.33, 130.28, 129.77, 129.18, 128.04, 127.22, 126.74, 125.73, 20.41.

(3-methoxyphenyl)boronic acid



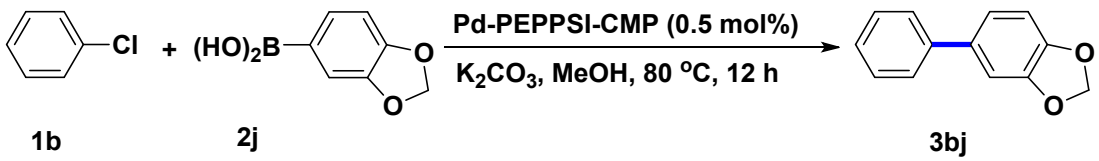
According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), (3-methoxyphenyl)boronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 92% yield (33.8 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (dt, *J* = 7.3, 4.0 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.17 – 7.13 (m, 1H), 6.92 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.99, 142.81, 141.15, 129.74, 128.73, 127.41, 127.20, 119.71, 112.95, 112.72, 55.31.

(2,6-dimethylphenyl)boronic acid



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), (2,6-dimethylphenyl)boronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 80% yield (29.1 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.17 (ddd, *J* = 24.1, 13.9, 7.0 Hz, 5H), 2.05 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.88, 141.12, 136.05, 129.04, 128.40, 127.27, 127.00, 126.60, 20.80.

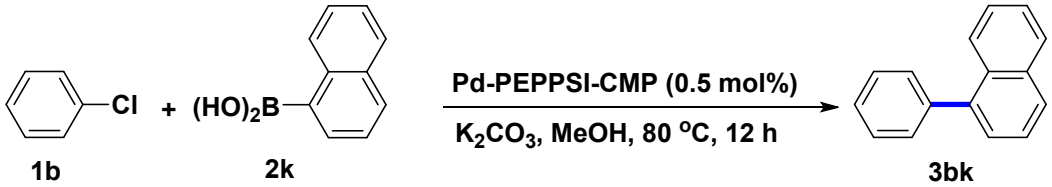
benzo[d][1,3]dioxol-5-ylboronic acid



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv),

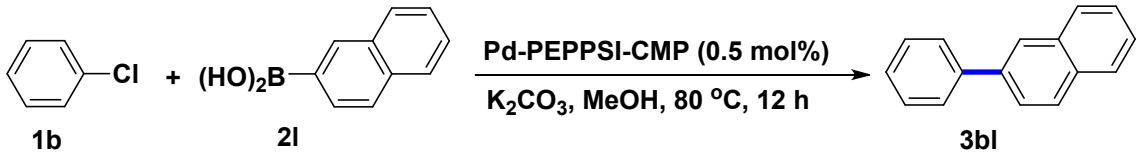
benzo[d][1,3]dioxol-5-ylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 92% yield (36.4 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.91 (d, *J* = 7.9 Hz, 1H), 6.02 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.15, 147.09, 140.98, 135.67, 128.74, 126.93, 126.91, 120.64, 108.57, 107.71, 101.13.

naphthalen-1-ylboronic acid



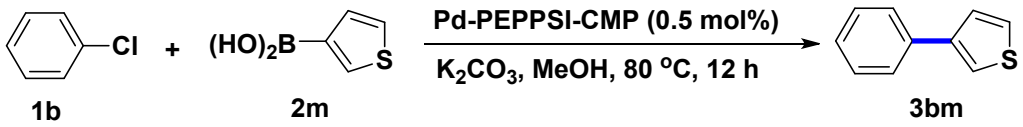
According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), naphthalen-1-ylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (39.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.49 (m, 6H), 7.48 – 7.42 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.80, 140.29, 133.83, 131.66, 130.08, 128.25, 127.63, 127.23, 126.92, 126.04, 126.01, 125.76, 125.37.

naphthalen-2-ylboronic acid



According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), naphthalen-2-ylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 96% yield (39.2 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.85 (ddd, *J* = 11.3, 9.5, 5.9 Hz, 3H), 7.76 – 7.68 (m, 3H), 7.51 – 7.44 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.20, 138.63, 133.75, 132.69, 128.89, 128.45, 128.24, 127.92, 127.68, 127.47, 127.38, 126.32, 125.96, 125.85, 125.63.

thiophen-3-ylboronic acid

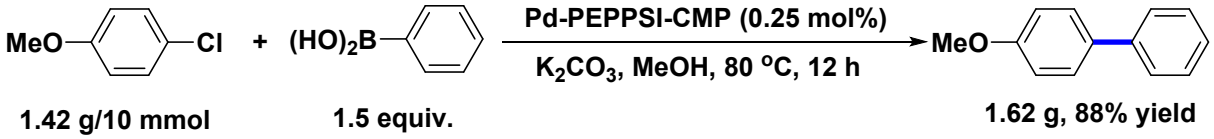


1b 2m 3bm

According to the general procedure, the reaction of chlorobenzene (0.20 mmol, 1.0 equiv), thiophen-3-ylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 0.5 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 90% yield (28.8 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 2H), 7.46 (dd, J = 4.5, 2.1 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.31 (t, J = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.41, 135.90, 128.79, 127.12, 126.46, 126.35, 126.16, 120.25.

6. The practical application of Pd-PEPPSI-CMP catalyst

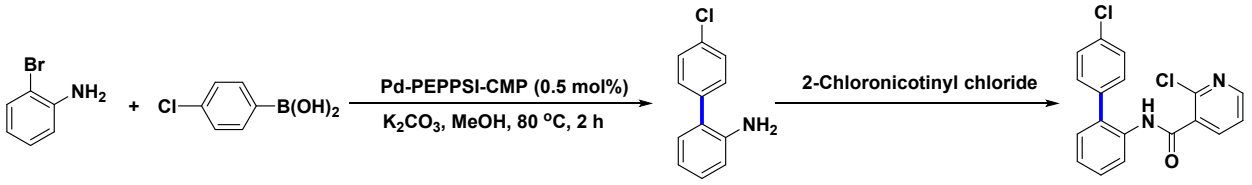
a. Gram scale-up at low catalyst loading



1.42 g/10 mmol 1.5 equiv. 1.62 g, 88% yield

A 100 mL round-bottom flask containing a stir bar was charged with Pd-PEPPSI-CMP (0.25 mol%), 1-chloro-4-methoxybenzene (10.0 mmol), phenylboronic acid (15.0 mmol), K_2CO_3 (20.0 mmol), and 25 mL of methanol. The reaction mixture was carried out at 80 °C for 12 h. After the reaction was completed (monitored by TLC), the mixture was filtered and the solid was washed with dichloromethane (3 x 30 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The product was collected as a white solid (1.62 g) after silica-gel column chromatography with petroleum ether/dichloromethane (20/1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (ddd, J = 8.8, 7.6, 1.7 Hz, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.06 – 6.94 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.15, 140.84, 133.79, 128.72, 128.16, 126.74, 126.65, 114.21, 55.35.

b. Synthesis of boscalid



206.4 mg, 1.2 equiv. 156.4 mg/1.0 mmol 167.0 mg, 82% yield 239.2 mg, 85% yield

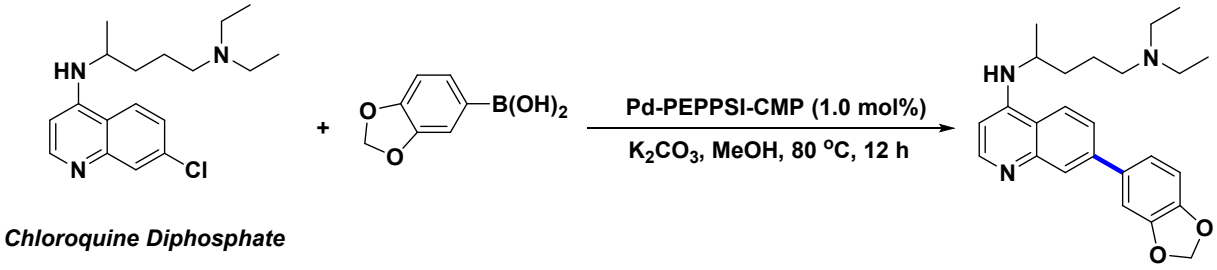
Boscalid

A 25 mL round-bottom flask containing a stir bar was charged with Pd-PEPPSI-CMP (0.5 mol%), 2-bromoaniline (1.2 mmol), (4-chlorophenyl)boronic acid (1.0 mmol), K_2CO_3 (1.5 mmol), and 5 mL of methanol. The reaction mixture was carried out at 80 °C for 2 h. After the reaction was completed (monitored by TLC), the mixture was filtered and the solid was washed with dichloromethane (3 x 10 mL). The organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure. The product 4'-chloro-[1,1'-biphenyl]-2-amine was collected as a colorless oil (167.0 mg) after silica-gel column chromatography with petroleum ether/EtOAc (20/1) as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 4H), 7.18 (td, J = 7.9, 1.4 Hz, 1H), 7.11 (dd, J = 7.6, 1.3 Hz, 1H), 6.89 – 6.82 (m, 1H), 6.78 (d, J = 8.0 Hz, 1H), 3.72 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$)

δ 143.44, 137.98, 133.13, 130.48, 130.34, 129.00, 128.84, 126.34, 118.78, 115.74.

The treatment of 4'-chloro-[1,1'-biphenyl]-2-amine with 2-chloronicotinoyl chloride produced the drug boscalid in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 4.8, 1.8 Hz, 2H), 7.65 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.29 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 2H), 7.15 (dd, *J* = 7.6, 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.14, 150.92, 147.22, 139.81, 137.24, 136.18, 134.87, 134.53, 131.46, 131.36, 130.57, 130.12, 129.73, 129.17, 129.09, 121.73.

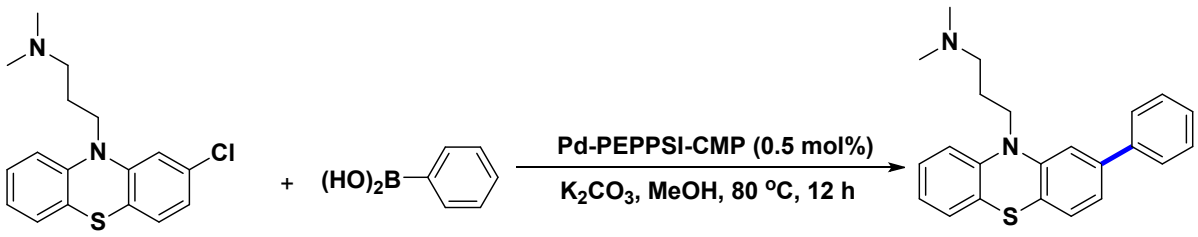
c. Late-stage modification of pharmaceuticals[6]



Chloroquine Diphosphate

160.0 mg/0.5 mmol **1.5 equiv.** **154.1 mg, 76% yield**

According to the general procedure, the reaction of chloroquine diphosphate (0.50 mmol, 1.0 equiv), benzo[d][1,3]dioxol-5-ylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 1.0 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 76% yield (154.1 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.4 Hz, 1H), 8.11 (d, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.60 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.24 – 7.18 (m, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.42 (d, *J* = 5.5 Hz, 1H), 6.02 (s, 2H), 2.57 (q, *J* = 7.1 Hz, 5H), 2.50 (t, *J* = 6.8 Hz, 2H), 1.78 (dd, *J* = 13.8, 6.9 Hz, 1H), 1.72 – 1.59 (m, 3H), 1.34 (d, *J* = 6.3 Hz, 4H), 1.04 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.24, 149.06, 148.79, 148.30, 147.51, 141.38, 134.64, 126.90, 123.68, 121.01, 120.15, 117.69, 108.71, 107.78, 101.23, 98.88, 52.62, 48.29, 46.84, 34.57, 23.70, 20.31, 11.27.

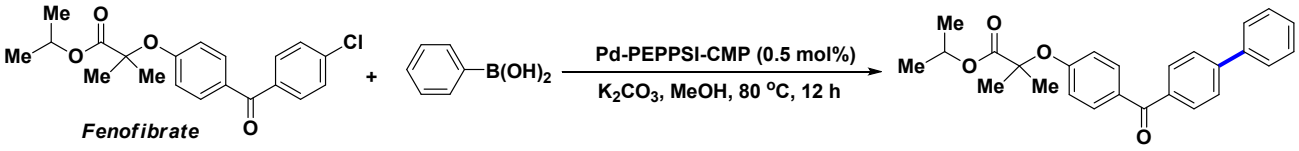


Chlorpromazine
159.5 mg/0.5 mmol

1.5 equiv.

147.8 mg, 82% yield

According to the general procedure, the reaction of chlorpromazine (0.50 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 1.0 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 82% yield (147.8 mg). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.3 Hz, 1H), 7.19 – 7.09 (m, 4H), 7.08 (d, J = 1.3 Hz, 1H), 6.95 – 6.85 (m, 2H), 3.96 (t, J = 7.0 Hz, 2H), 2.41 (d, J = 7.0 Hz, 2H), 2.18 (s, 6H), 2.06 – 1.91 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.73, 145.22, 141.04, 140.73, 128.78, 127.63, 127.50, 127.38, 127.29, 127.03, 125.13, 124.41, 122.53, 121.39, 115.71, 114.53, 57.26, 45.64, 45.57, 25.39.

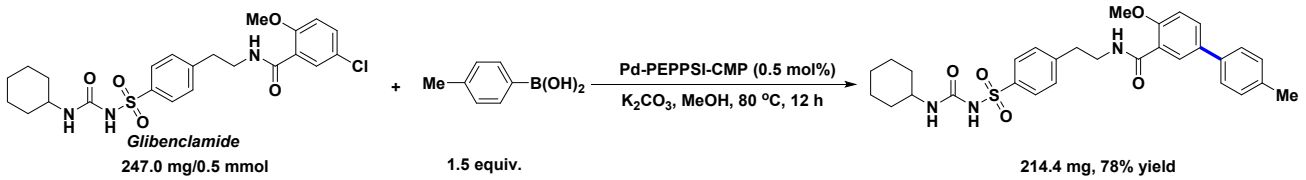


Fenofibrate
180.0 mg/1.0 mmol

1.5 equiv.

170.1 mg, 85% yield

According to the general procedure, the reaction of fenofibrate (0.50 mmol, 1.0 equiv), phenylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 1.0 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 85% yield (170.1 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (dd, J = 10.6, 4.0 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 5.10 (dt, J = 12.5, 6.3 Hz, 1H), 1.67 (s, 6H), 1.21 (d, J = 6.3 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.10, 173.16, 159.56, 144.81, 140.10, 136.84, 131.98, 130.83, 130.40, 128.94, 128.09, 127.28, 126.90, 117.30, 79.43, 69.31, 25.41, 21.53.

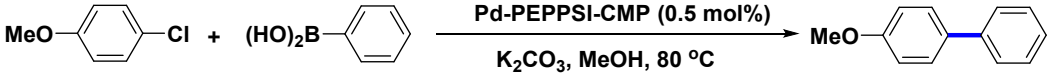


According to the general procedure, the reaction of glibenclamide (0.50 mmol, 1.0 equiv), *p*-tolylboronic acid (1.5 equiv), K_2CO_3 (2.0 equiv), and Pd-PEPPSI-CMP (0.5 mol%) in 1.0 mL MeOH for 12 h at 80 °C, afforded after filtration and chromatography the product in 78% yield (214.4 mg). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.4 Hz, 1H), 7.99 (t, *J* = 5.7 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.66 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 3.82 (s, 3H), 3.80 – 3.75 (m, 2H), 3.57 (dd, *J* = 11.0, 7.1 Hz, 1H), 3.04 (t, *J* = 6.8 Hz, 2H), 2.38 (s, 3H), 1.87 – 1.76 (m, 2H), 1.63 (dd, *J* = 9.6, 3.9 Hz, 2H), 1.55 (dd, *J* = 9.0, 4.0 Hz, 1H), 1.29 (dd, *J* = 22.6, 9.4 Hz, 3H), 1.23 – 1.08 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.58, 156.68, 150.73, 145.92, 138.01, 136.96, 136.81, 134.40, 131.06, 130.42, 129.74, 129.52, 127.35, 126.61, 121.27, 111.92, 56.06, 49.10, 40.59, 35.62, 32.91, 25.33, 24.53, 21.04.

7. Recyclability Tests of Pd-PEPPSI-CMP

The recycling experiments were performed by recovering the **Pd-PEPPSI-CMP** catalyst using the centrifugation method. The recovered **Pd-PEPPSI-CMP** catalyst was washed with MeOH and MeOH/H_2O to remove the residual product and simply dried before reuse. We chose the Suzuki-Miyaura coupling reaction of 1-chloro-4-methoxybenzene, 1-bromo-4-methoxybenzene with phenylboronic acid to investigate the recyclability of **Pd-PEPPSI-CMP** catalyst, and the results are summarized in **Table S1 and Table S2.**

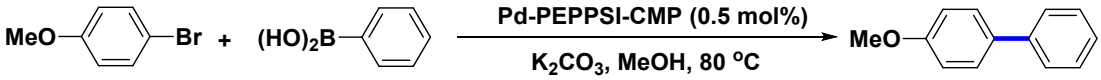
Table S1. Recycling of Pd-PEPPSI-CMP for the Suzuki-Miyaura coupling reaction of 1-chloro-4-methoxybenzene.[a]



Cycle	Time (h)	Yield (%)[b]
1	12	96
2	12	92
3	12	91
4	24	56

[a] Reaction conditions: 1-chloro-4-methoxybenzene (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.4 mmol), MeOH: 0.5 mL in aerobic environment, Pd-PEPPSI-CMP (0.5 mol%). [b]Isolated yield.

Table S2. Recycling of Pd-PEPPSI-CMP for the Suzuki-Miyaura coupling reaction of 1-bromo-4-methoxybenzene.[a]



Cycle	Time (h)	Yield (%)[b]	Cycle	Time (h)	Yield (%)[b]
1	2	98	9	3	96
2	2	98	10	3	95
3	2	98	11	3	94
4	2	97	12	3	94
5	2	97	13	4	93
6	2	97	14	4	92
7	2	98	15	4	92
8	3	96			

[a] Reaction conditions: 1-bromo-4-methoxybenzene (0.2 mmol), phenylboronic acid (0.3 mmol), K_2CO_3 (0.4 mmol), MeOH: 0.5 mL in aerobic environment, Pd-PEPPSI-CMP (0.5 mol%). [b]Isolated yield.

8. XPS characterization of Pd-PEPPSI-CMP after catalytic runs

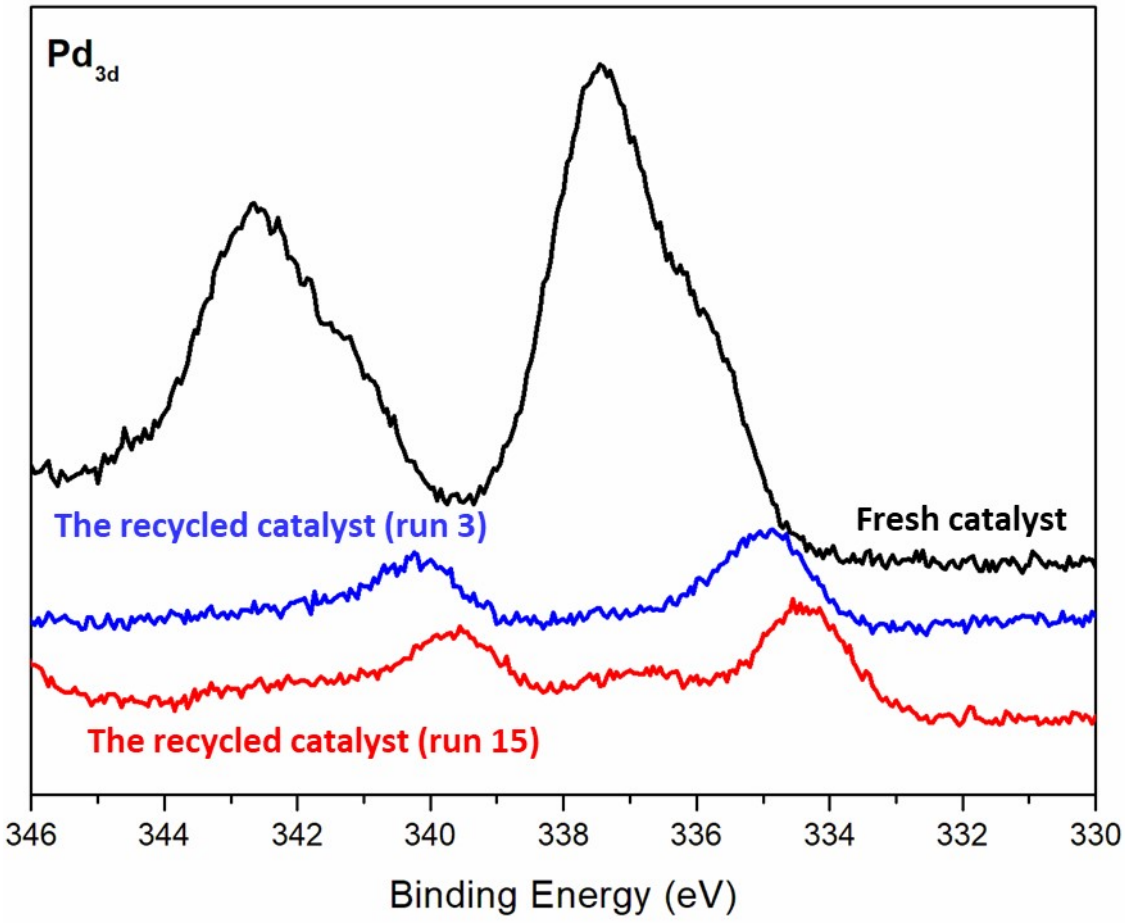


Figure S9. XPS characterization of **Pd-PEPPSI-CMP** (in black) and **the recycled Pd-PEPPSI-CMP catalyst** (run 3 in bule and run 15 in red).

9. References

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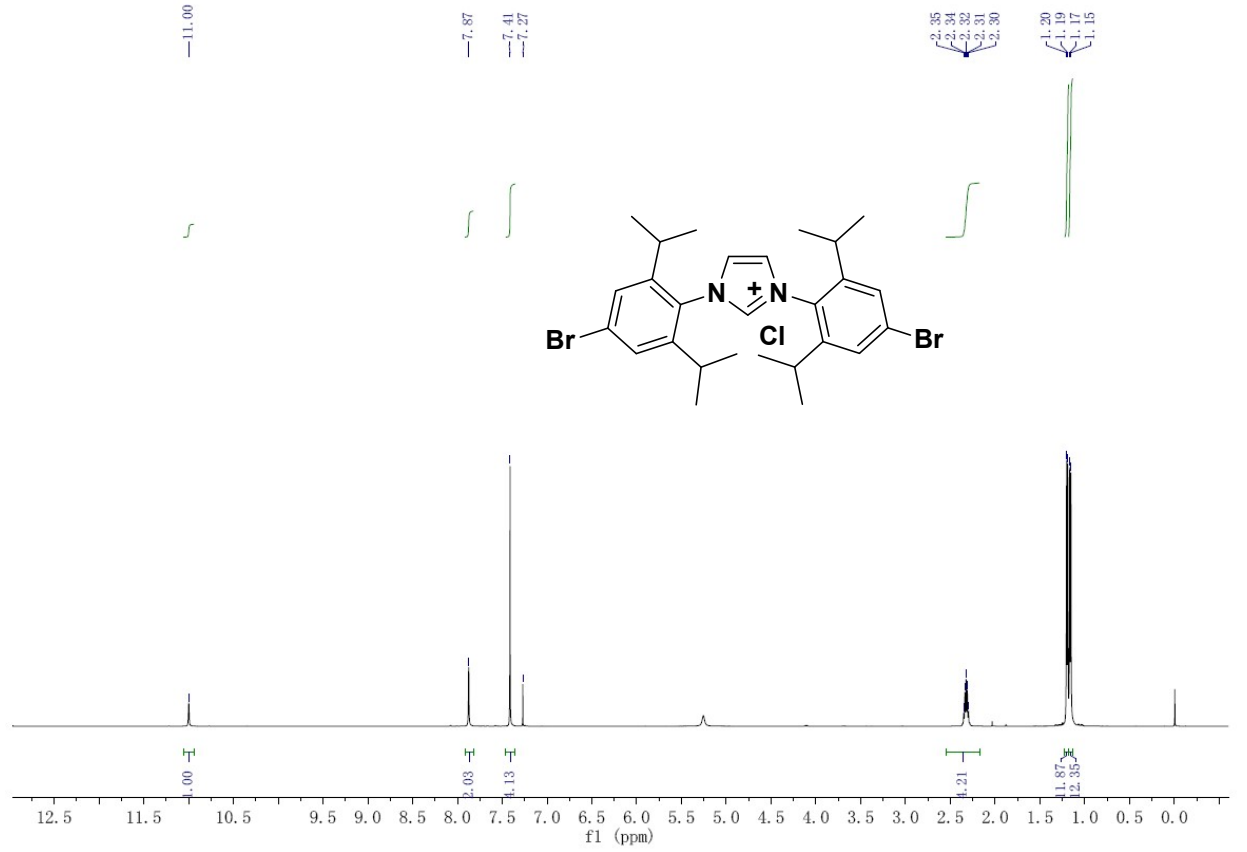
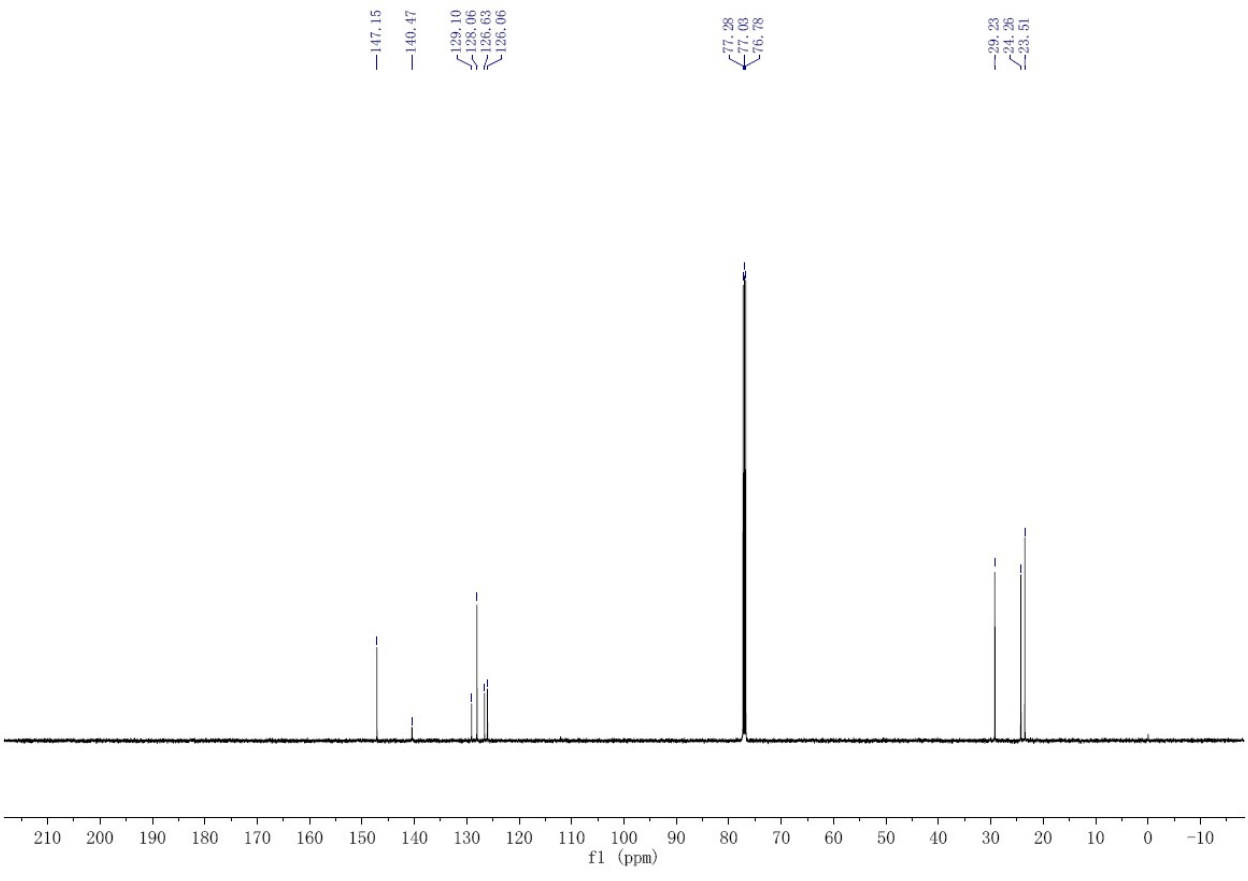
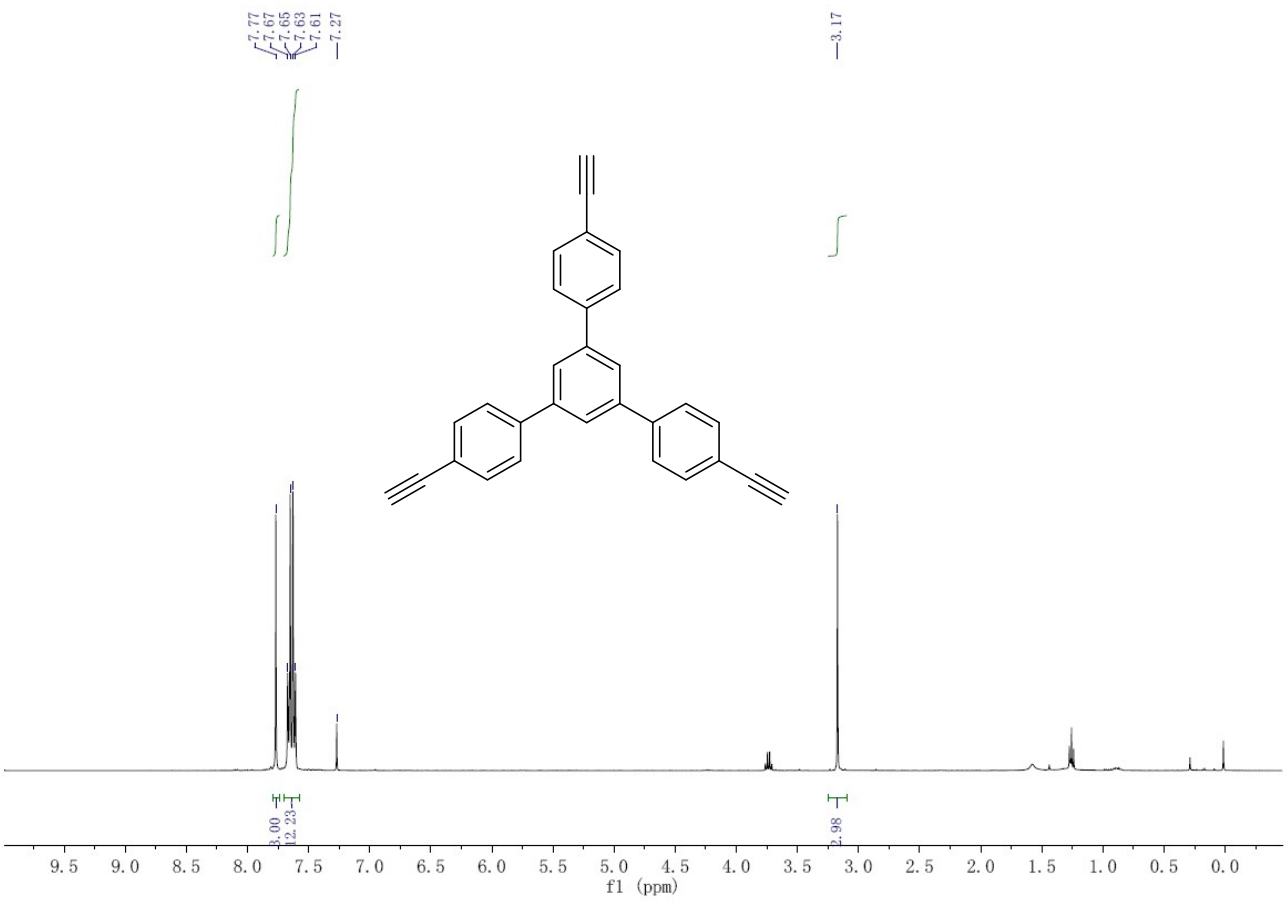
10. ^{1}H NMR and ^{13}C NMR spectra for the products



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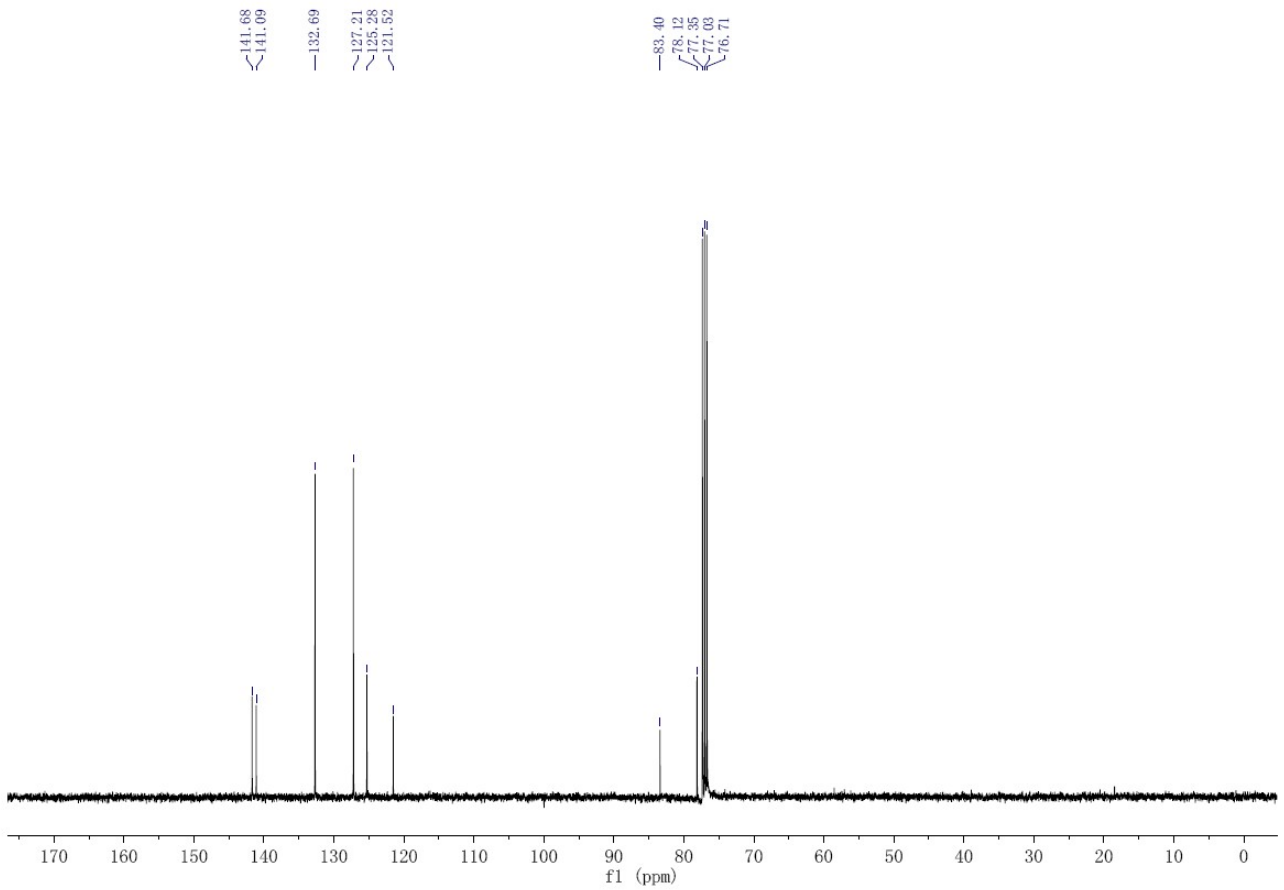
7.63
7.61
7.27
3.17
3.00
12.23
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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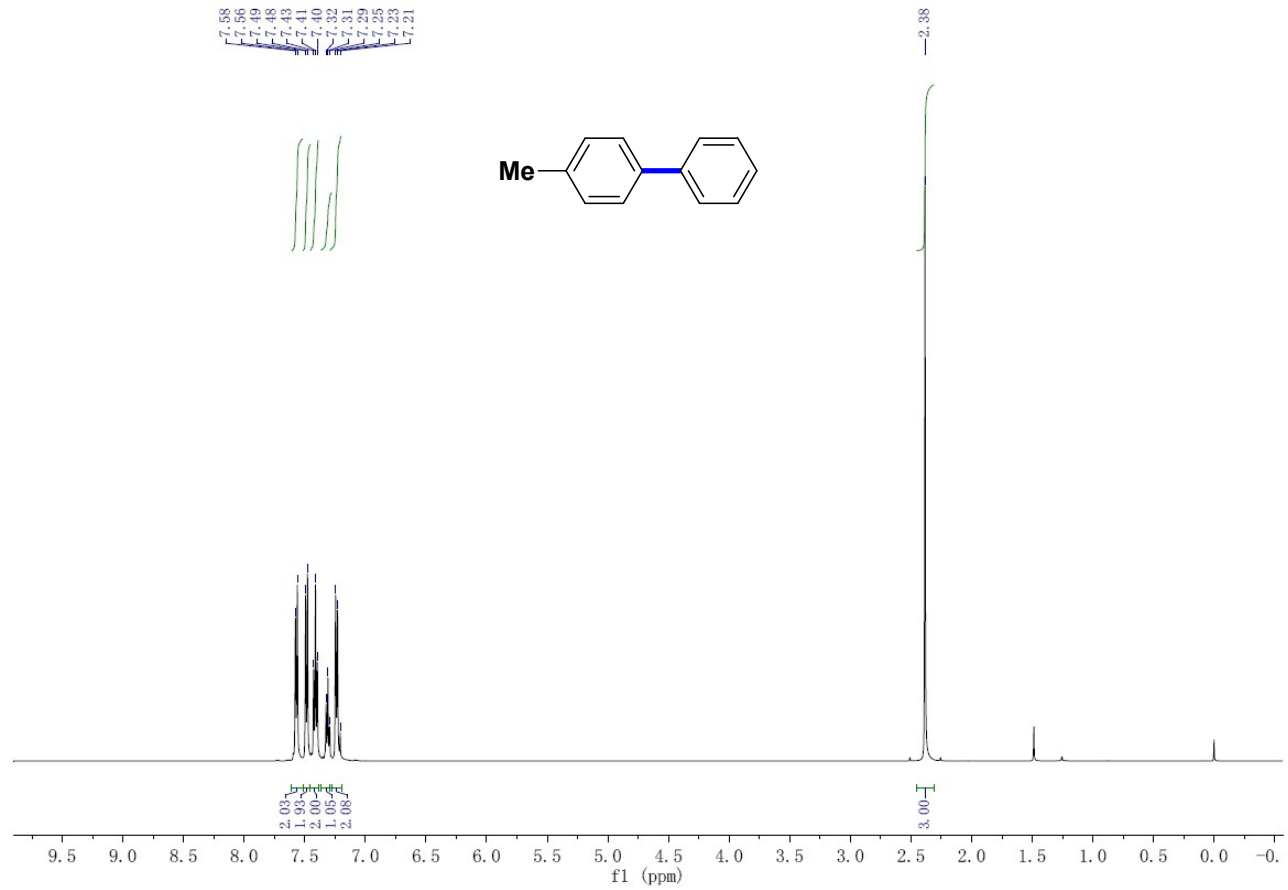
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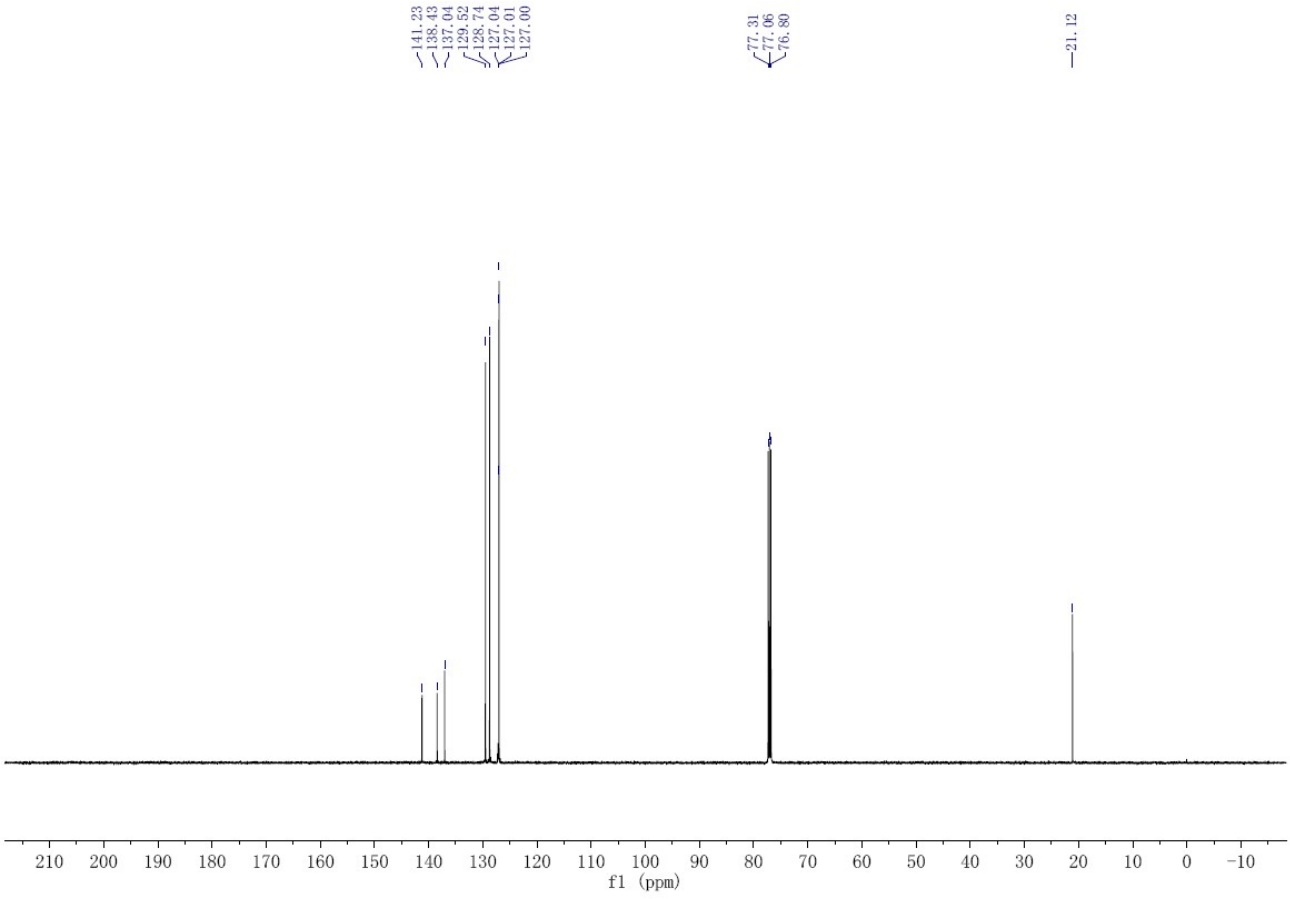
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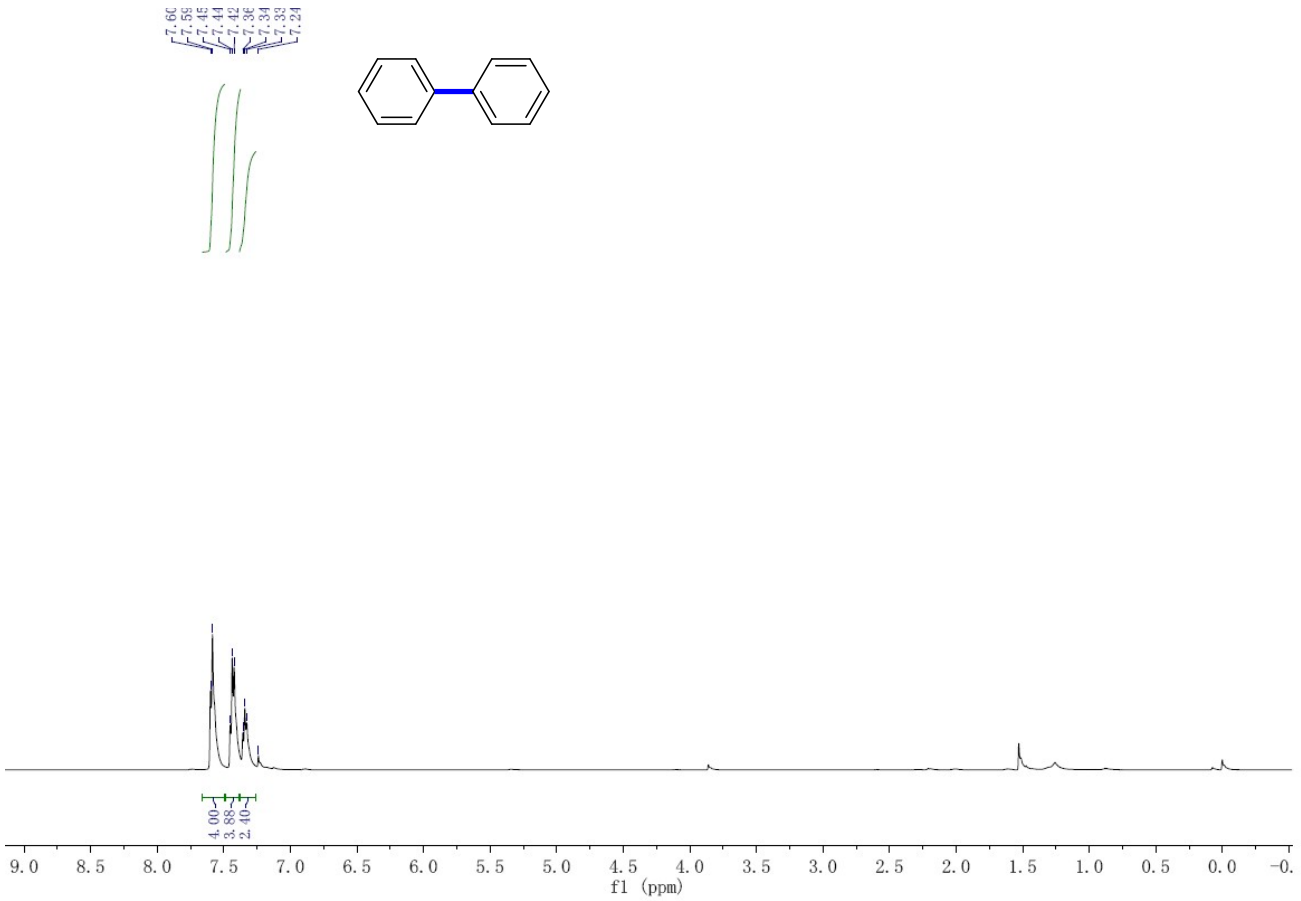
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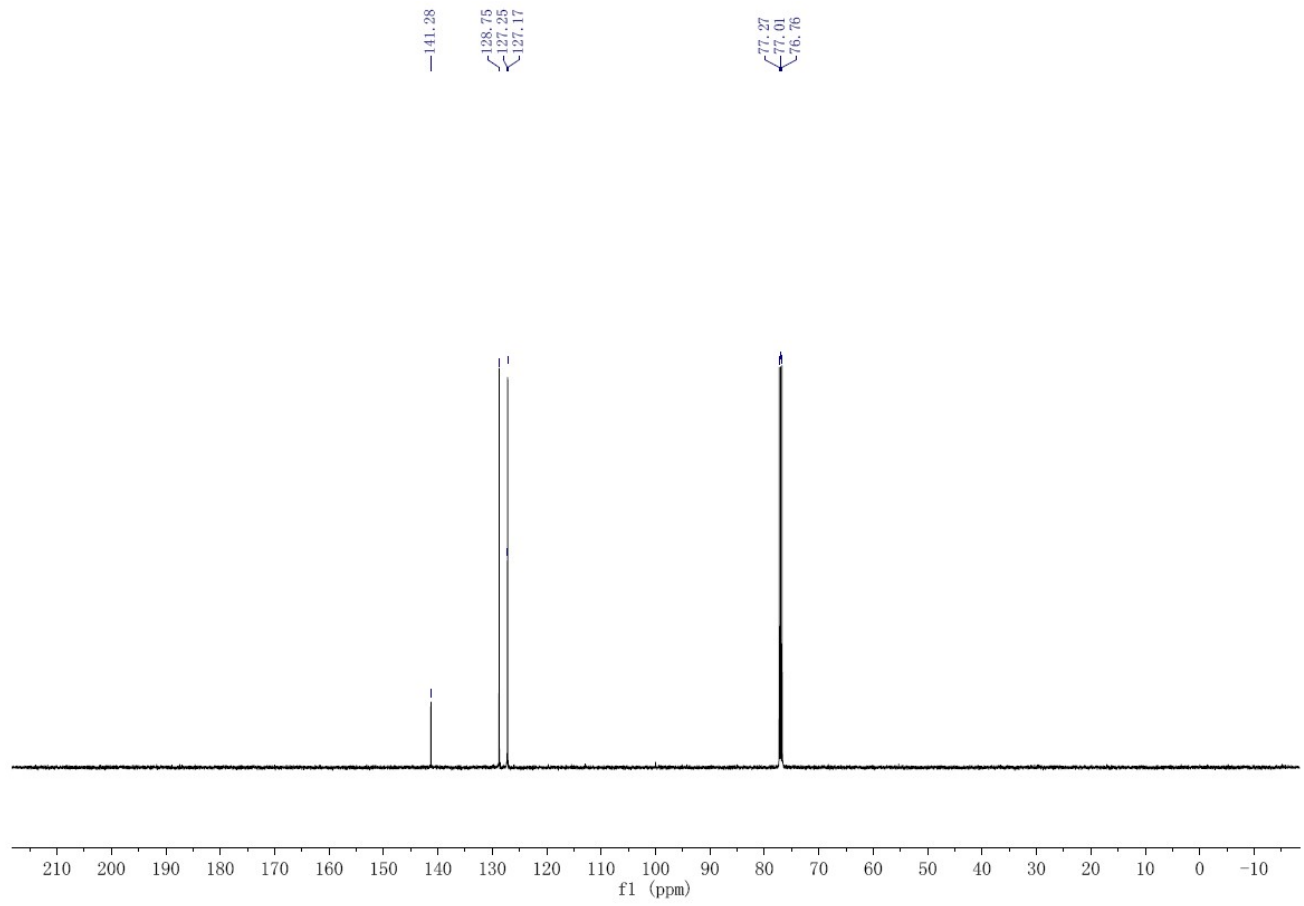
f1 (ppm)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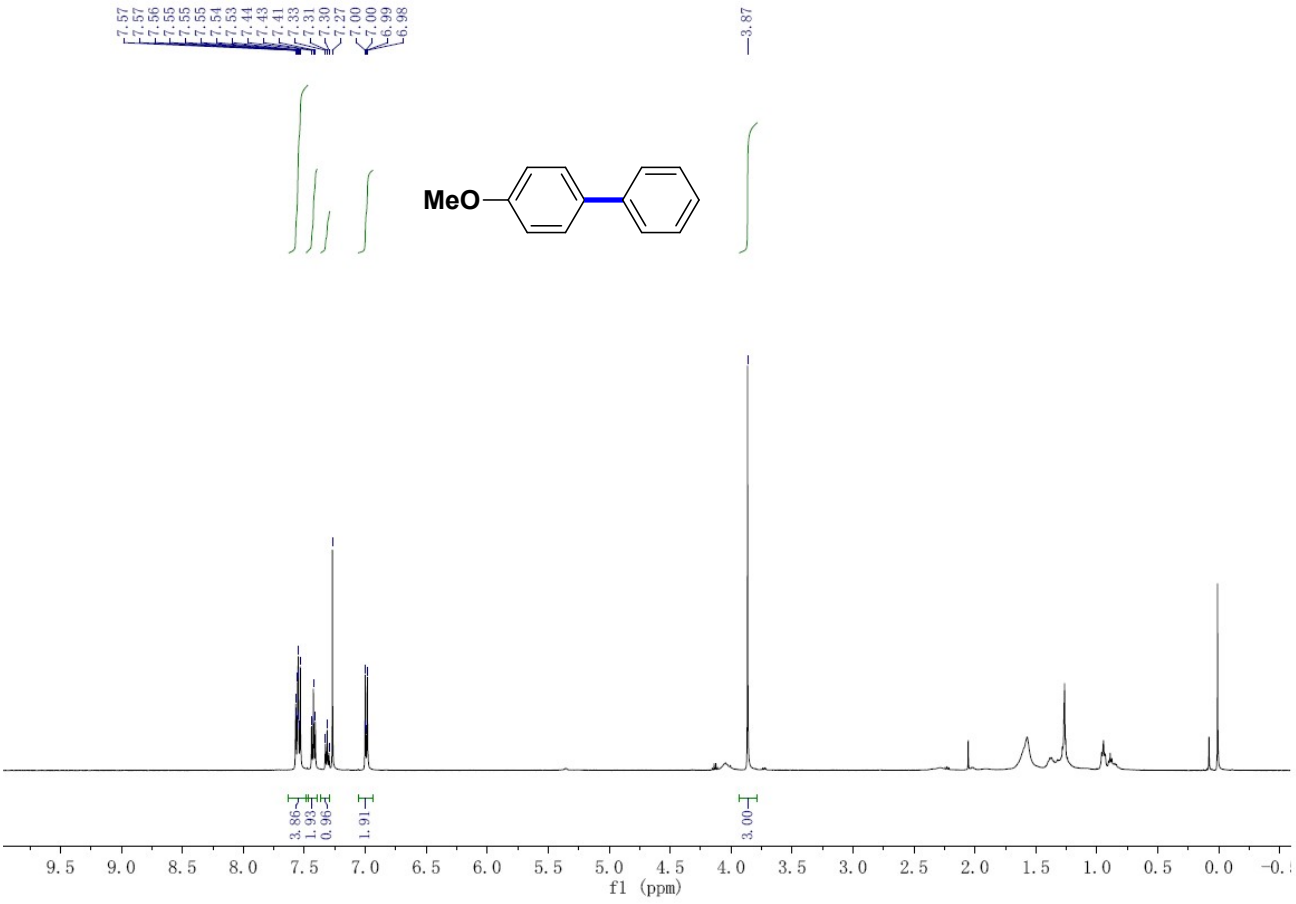
f1 (ppm)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3.86
1.93
0.96
1.91
3.00
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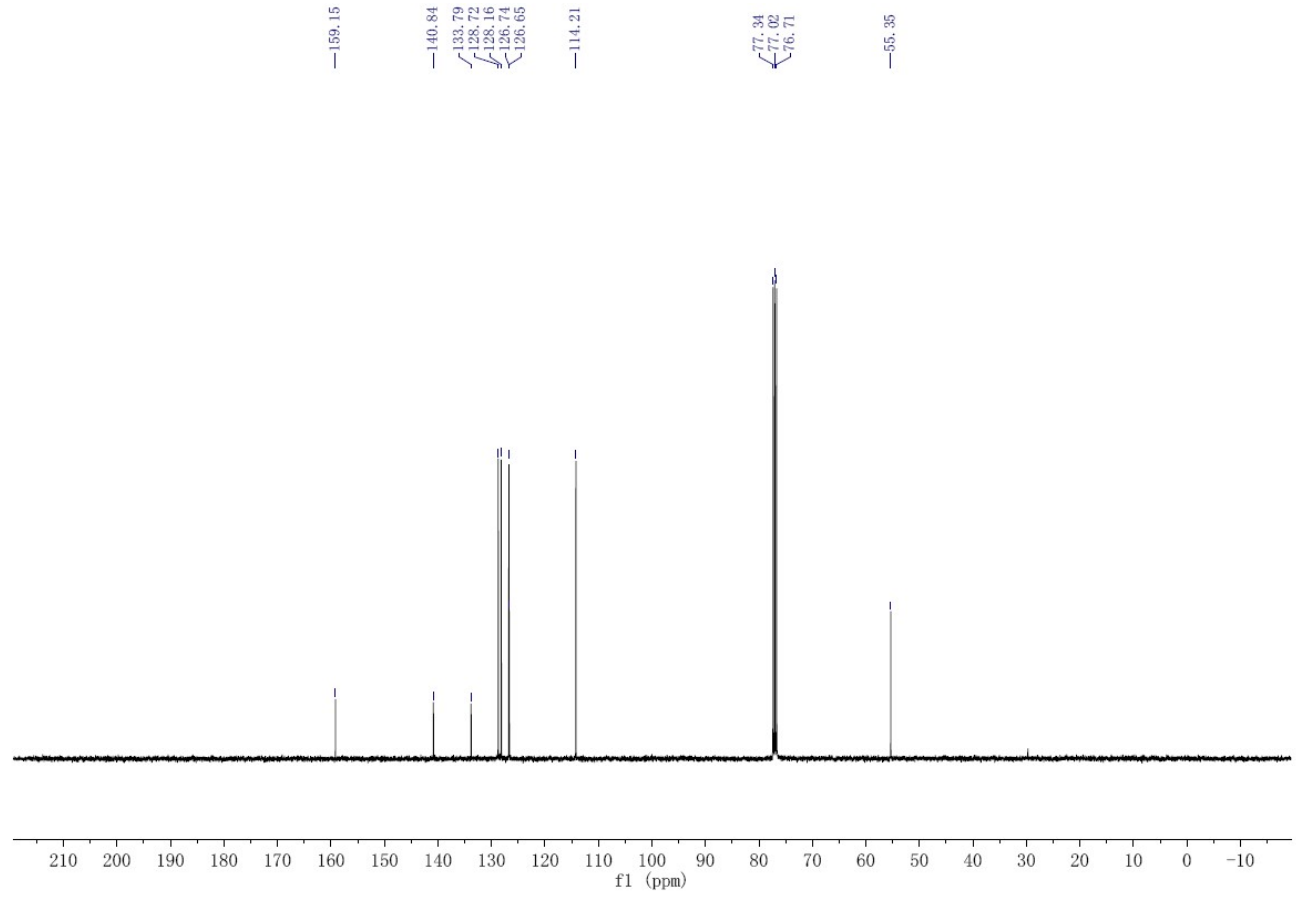
f1 (ppm)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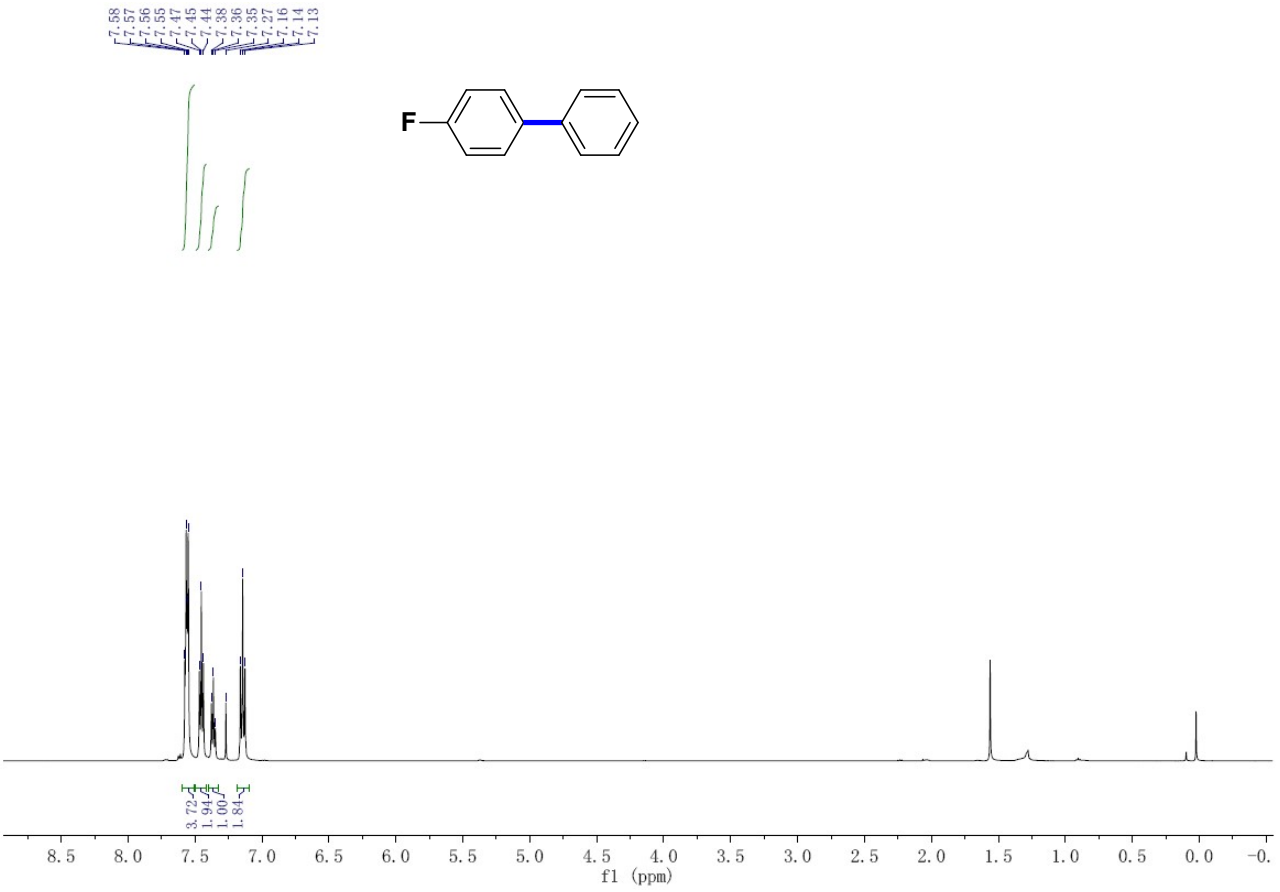
76.71
55.35
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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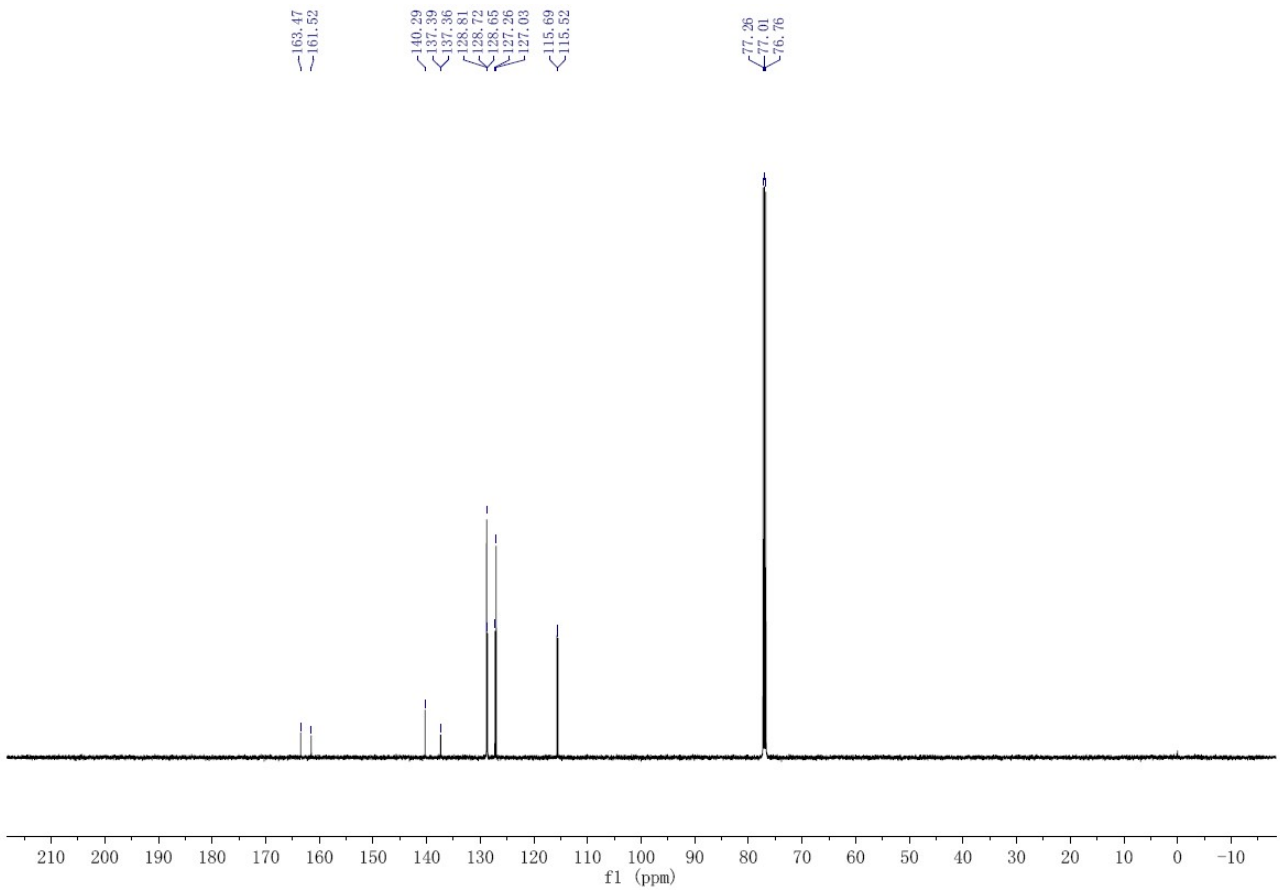
7.57
7.56
7.55
7.47
7.45
7.44
7.38
7.36
7.35
7.27
7.16
7.14
7.13
F
3.72
1.94
1.00
1.84
f1 (ppm)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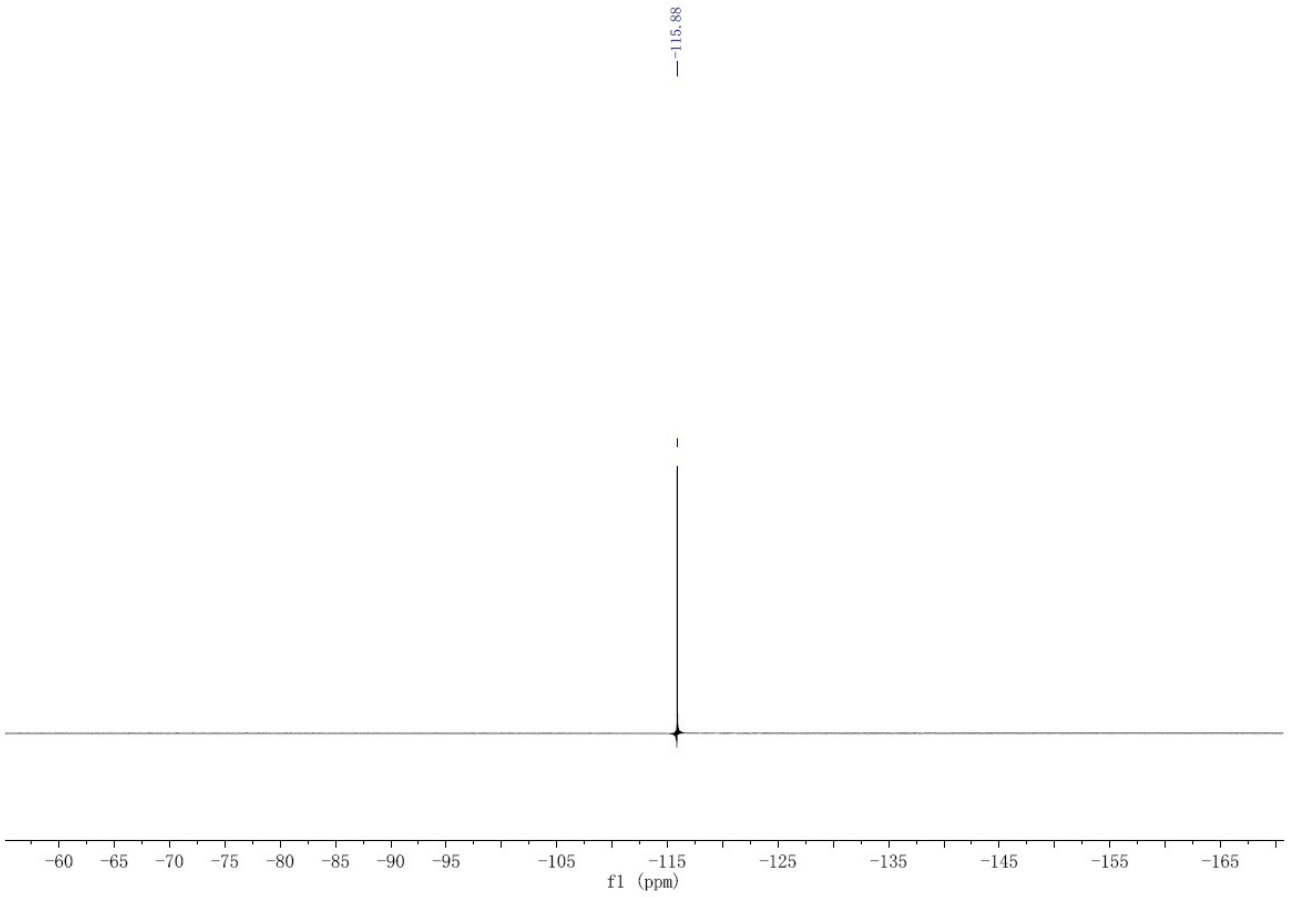
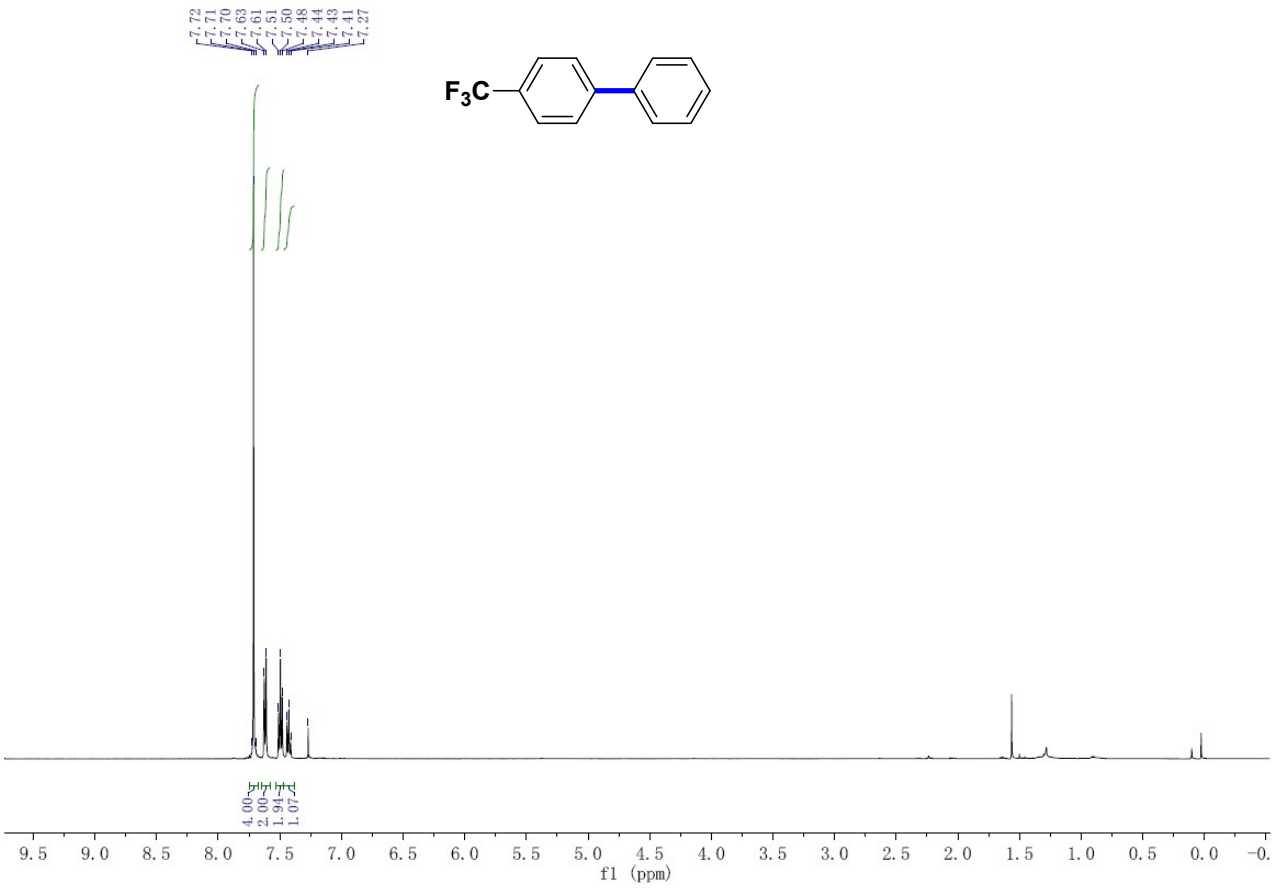
128.65
127.26
127.03
115.69
115.52
77.26
77.01
76.76
f1 (ppm)


−115.88
−60
−65
−70
−75
−80
−85
−90
−95
−105
−115
−125
−135
−145
−155
−165
f1 (ppm)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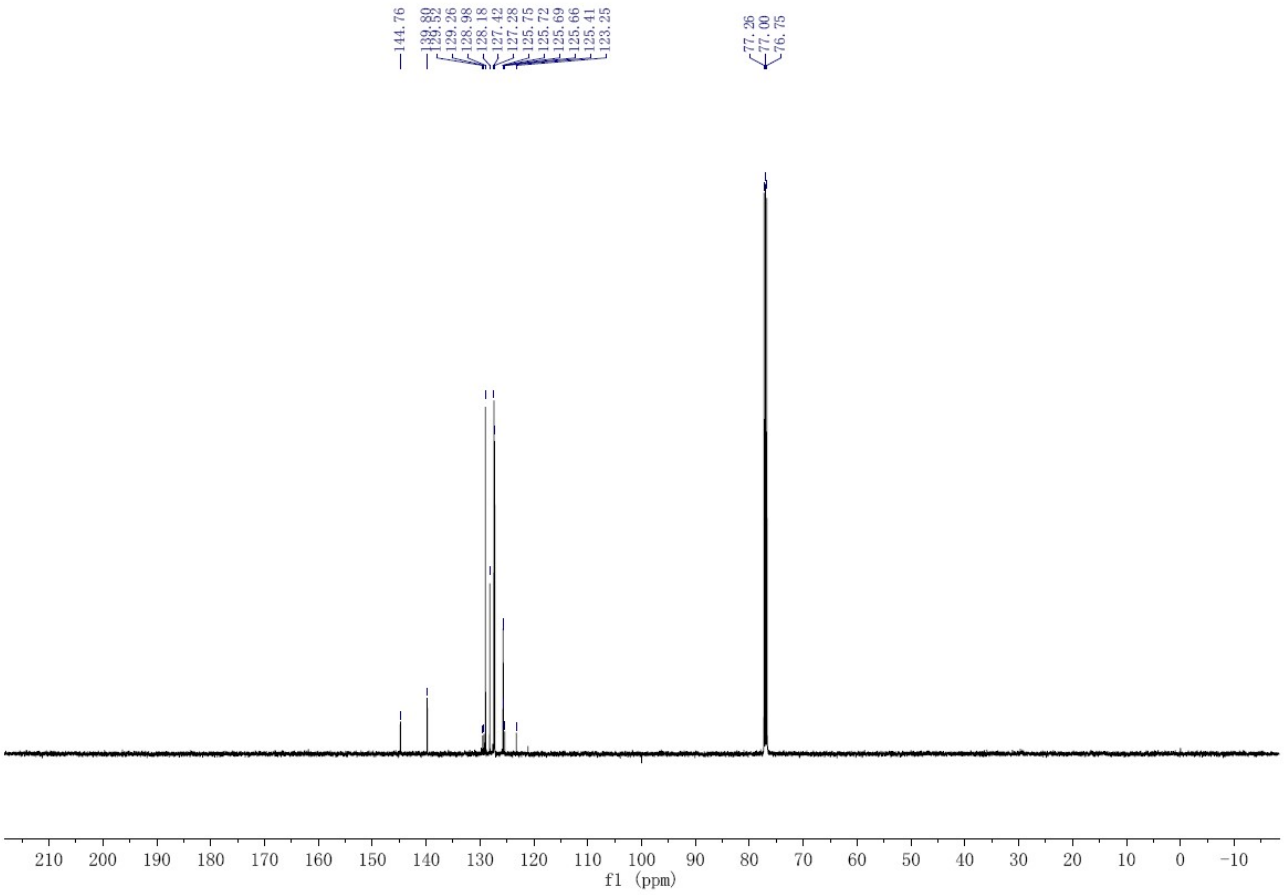
7.71
7.70
7.63
7.61
7.51
7.50
7.48
7.44
7.43
7.41
7.27
F3C
4.00
2.00
1.94
1.07
f1 (ppm)


144.76
139.80
139.52
129.26
128.98
128.18
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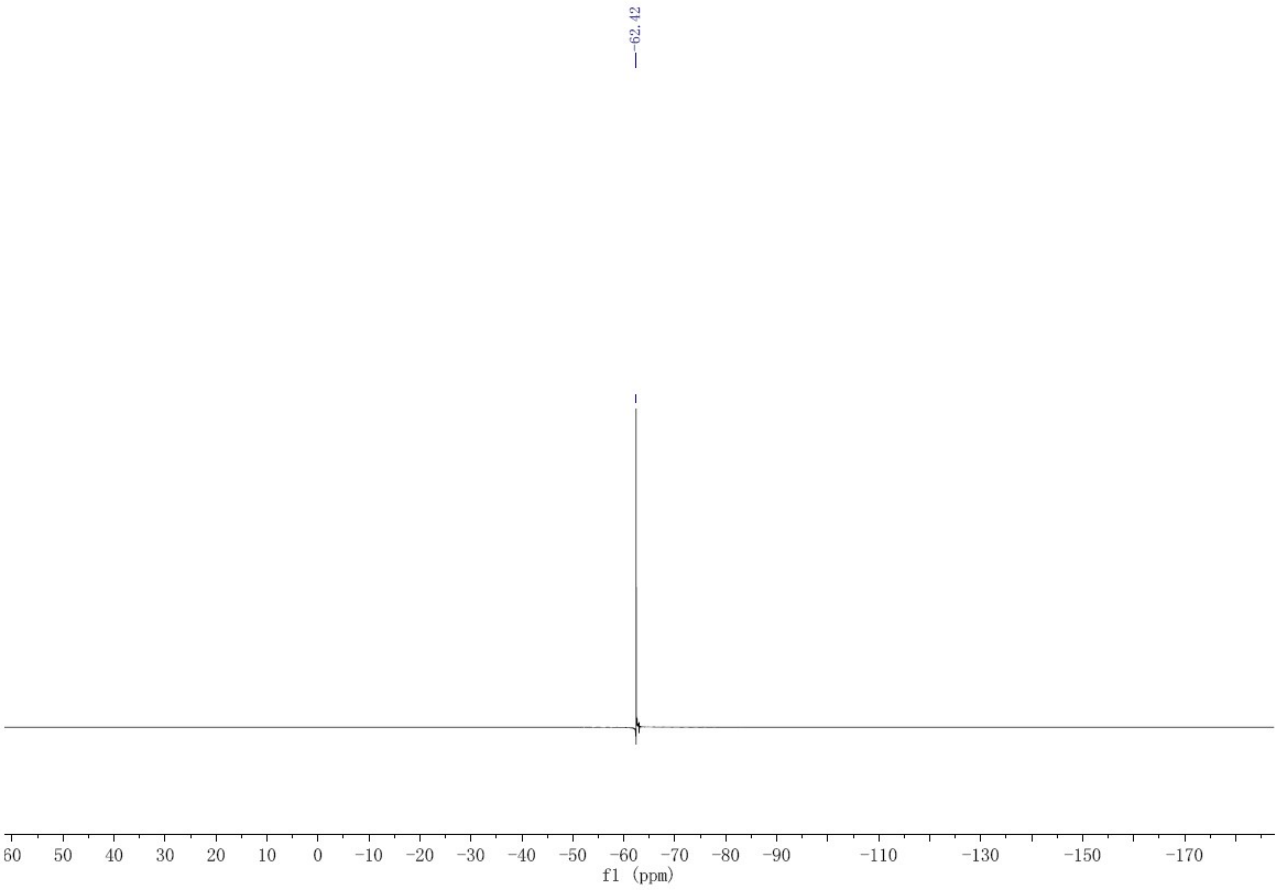
127.28
125.75
125.72
125.69
125.66
125.41
123.25
77.26
77.00
76.75
f1 (ppm)


-62.42
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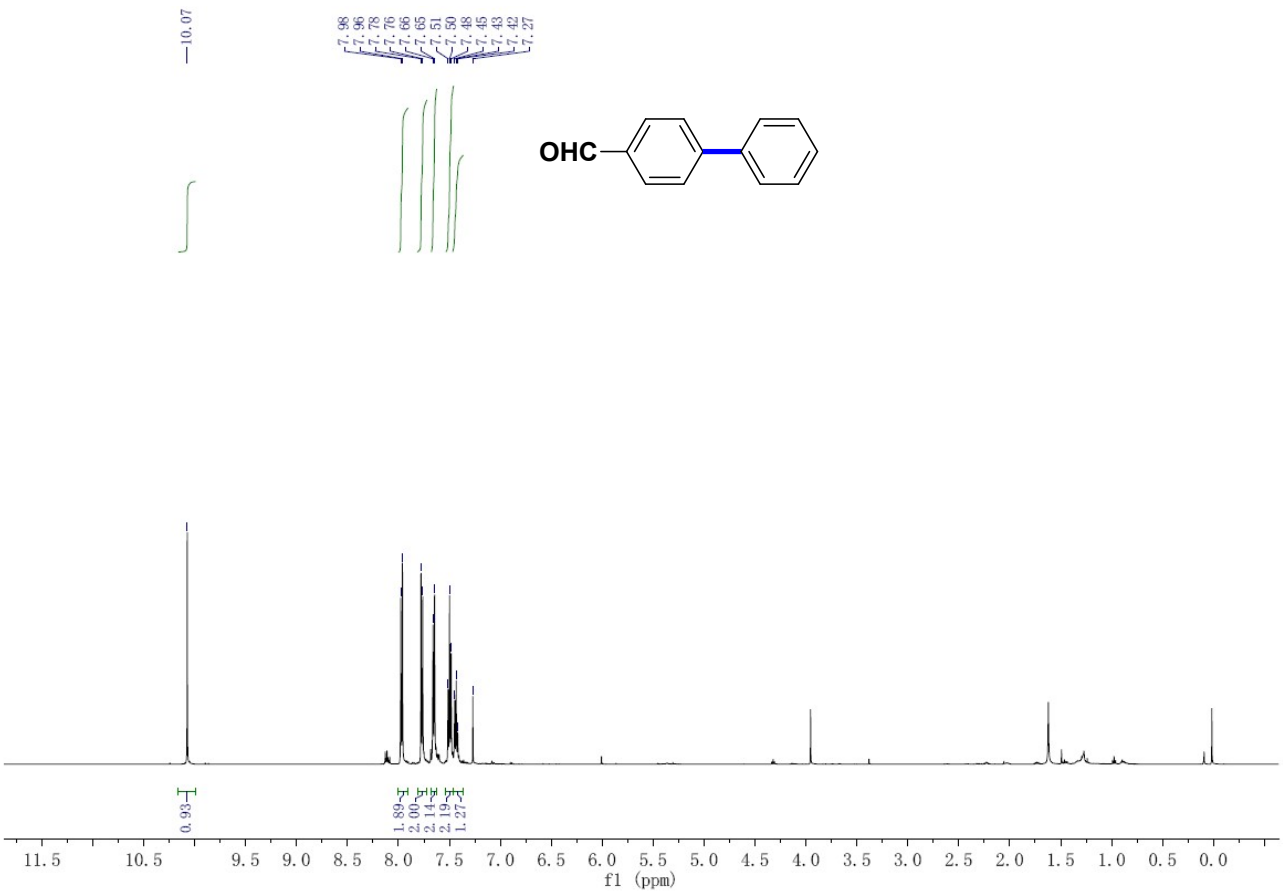
f1 (ppm)


10.07
7.98
7.96
7.78
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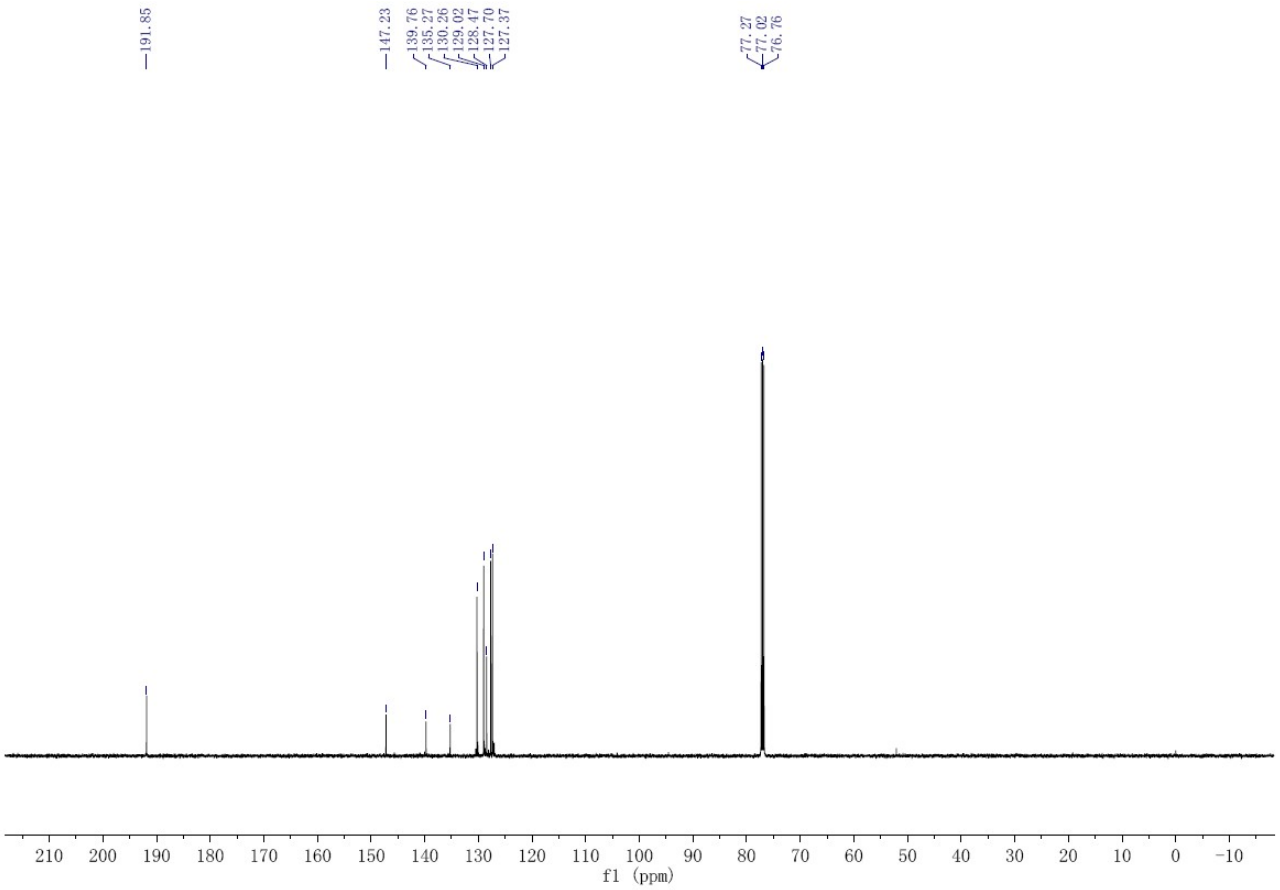
7.66
7.65
7.51
7.50
7.48
7.45
7.43
7.42
7.27
OHC
0.93
1.89
2.00
2.14
2.19
1.27
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


191.85
147.23
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129.02
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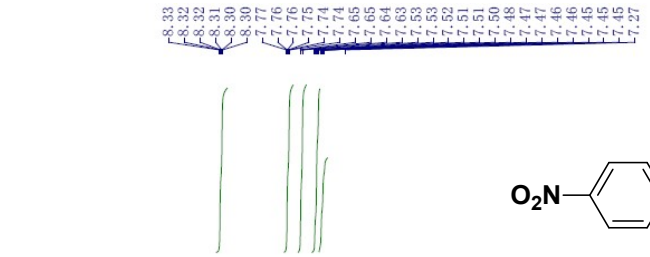
127.70
127.37
77.27
77.02
76.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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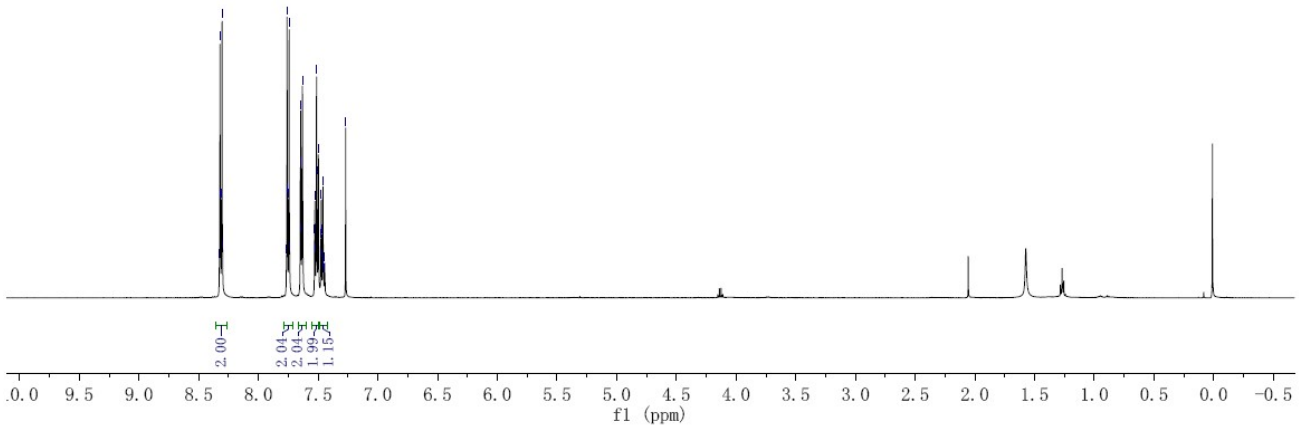
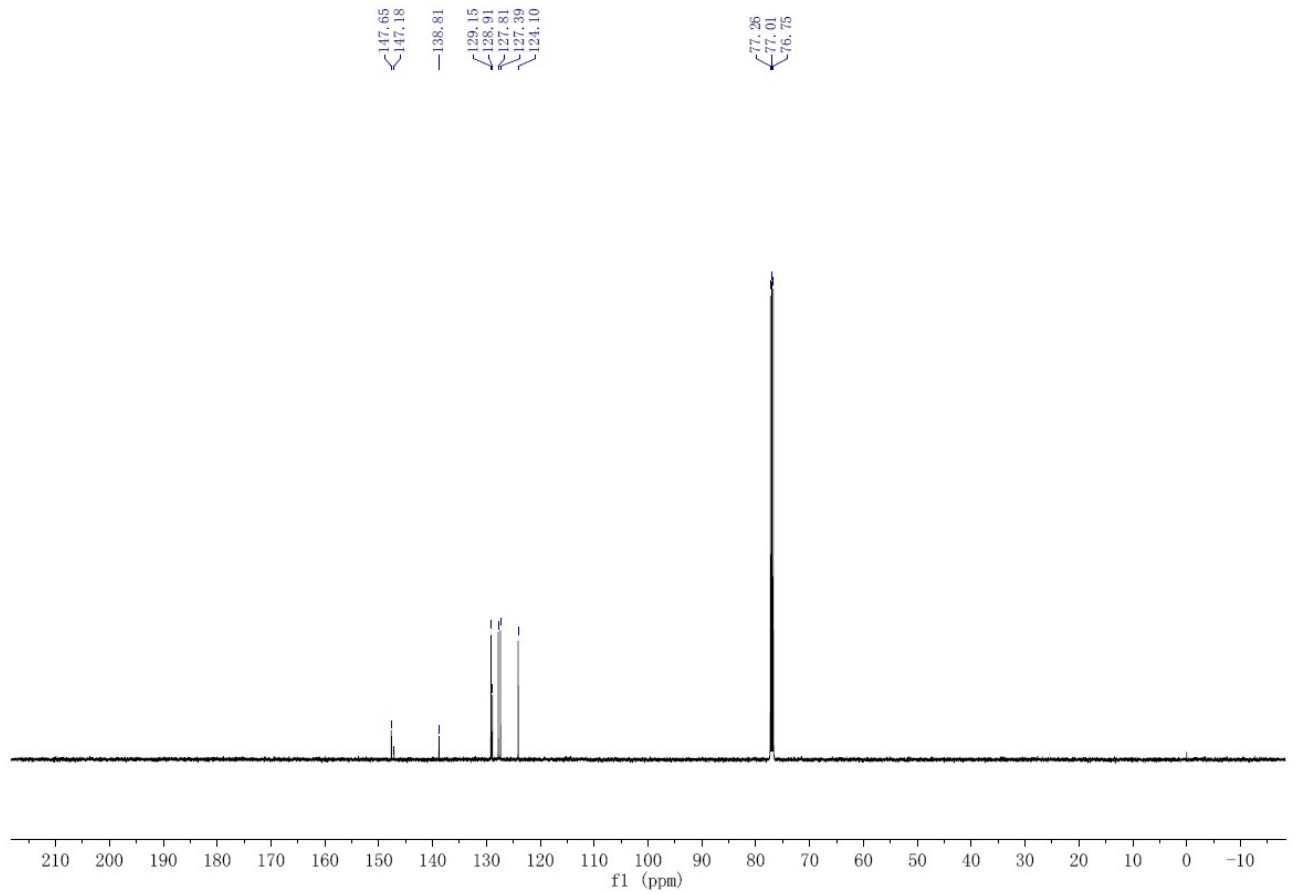
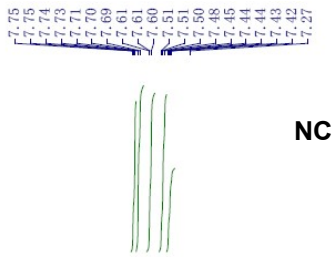
8.30
7.77
7.76
7.76
7.75
7.74
7.74
7.65
7.64
7.63
7.53
7.53
7.52
7.51
7.51
7.50
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.27

O2N


2.00
2.04
2.04
1.99
1.15
f1 (ppm)


147.65
147.18
138.81
129.15
128.91
127.81
127.39
124.10
77.26
77.01
76.75
f1 (ppm)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7.75
7.74
7.73
7.71
7.70
7.69
7.61
7.61
7.60
7.51
7.51
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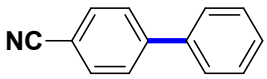
7.45
7.44
7.44
7.43
7.42
7.27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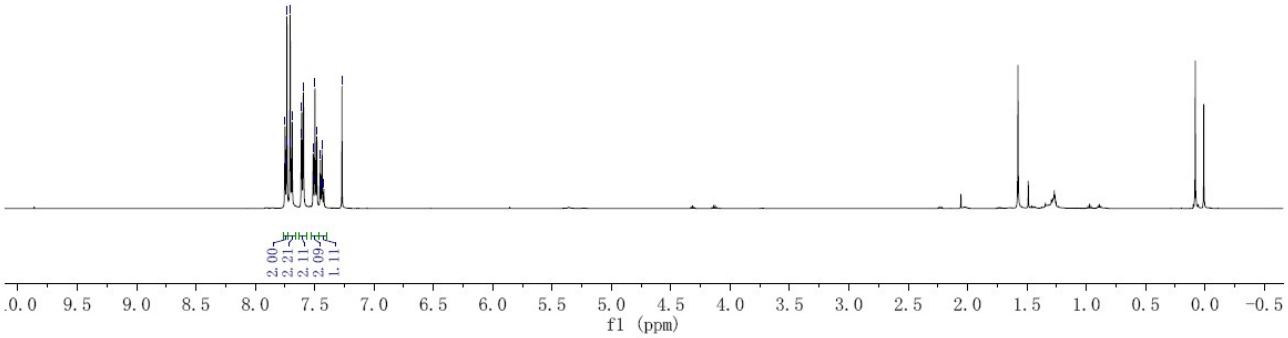
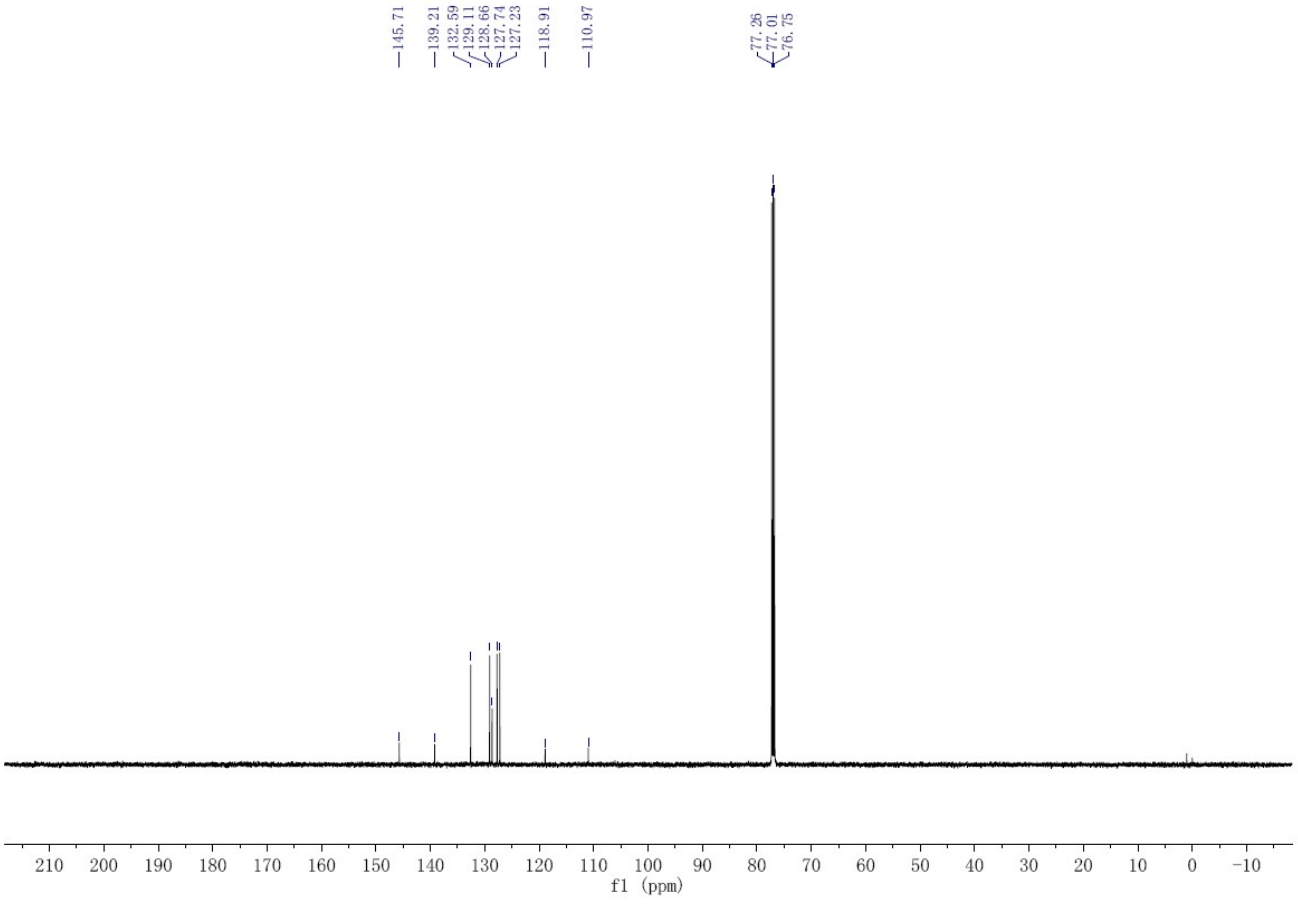
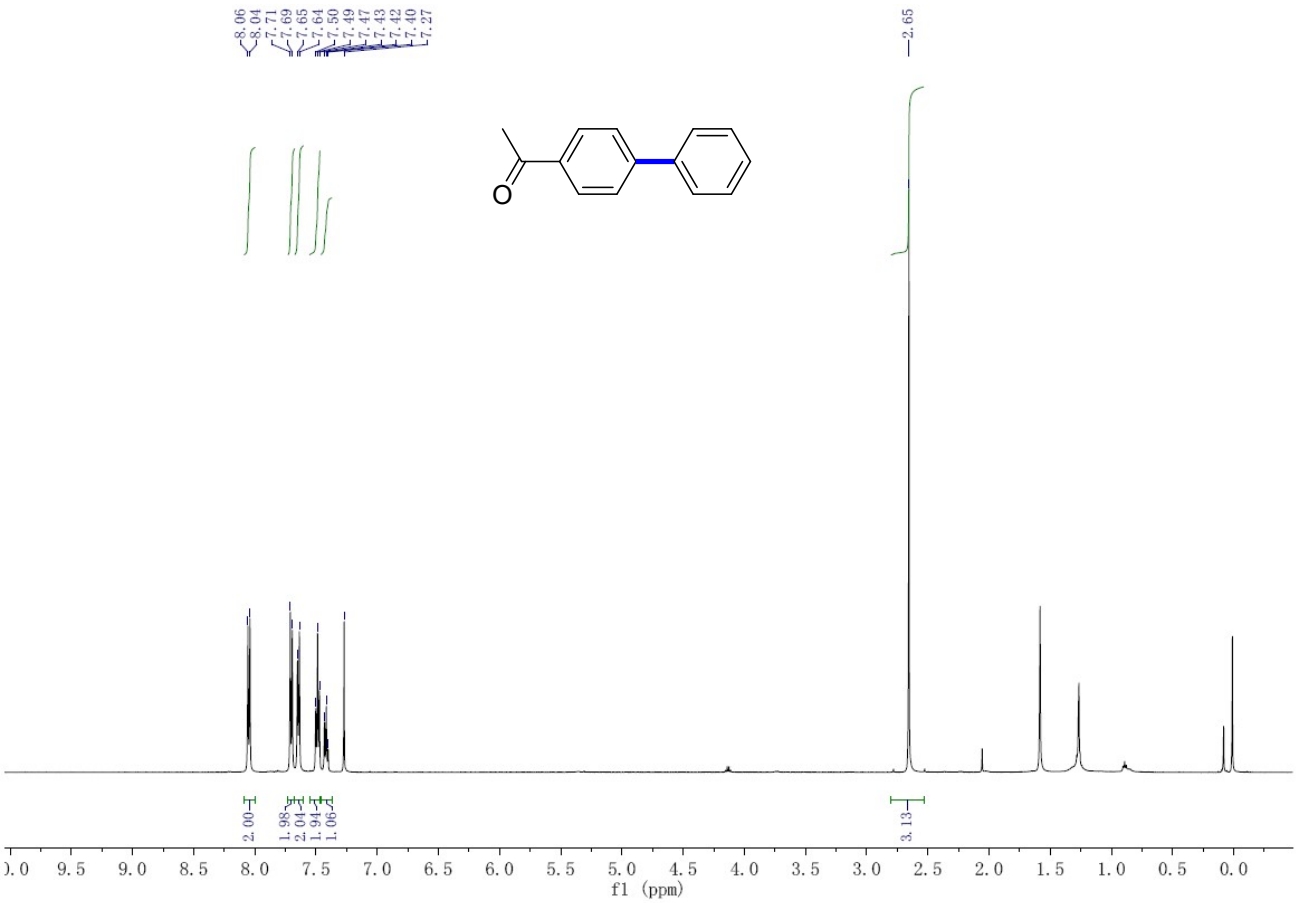

2.00
2.21
2.11
2.09
1.11
f1 (ppm)


145.71
139.21
132.59
129.11
128.66
127.74
127.23
118.91
110.97
77.26
77.01
76.75
f1 (ppm)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8.04
7.71
7.69
7.65
7.64
7.50
7.49
7.47
7.43
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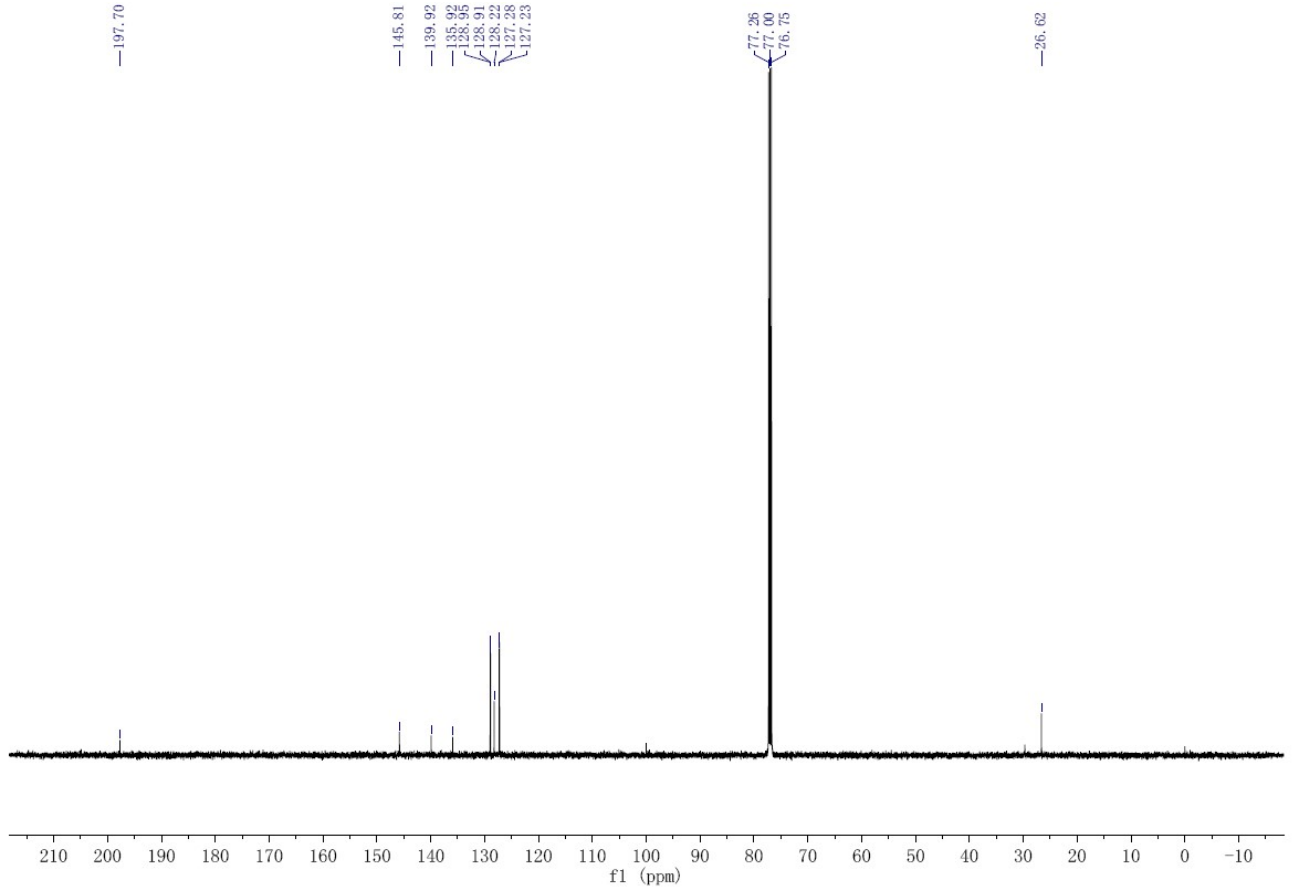
7.40
7.27
2.65
O
2.00
1.98
2.04
1.94
1.06
3.13
f1 (ppm)


197.70
145.81
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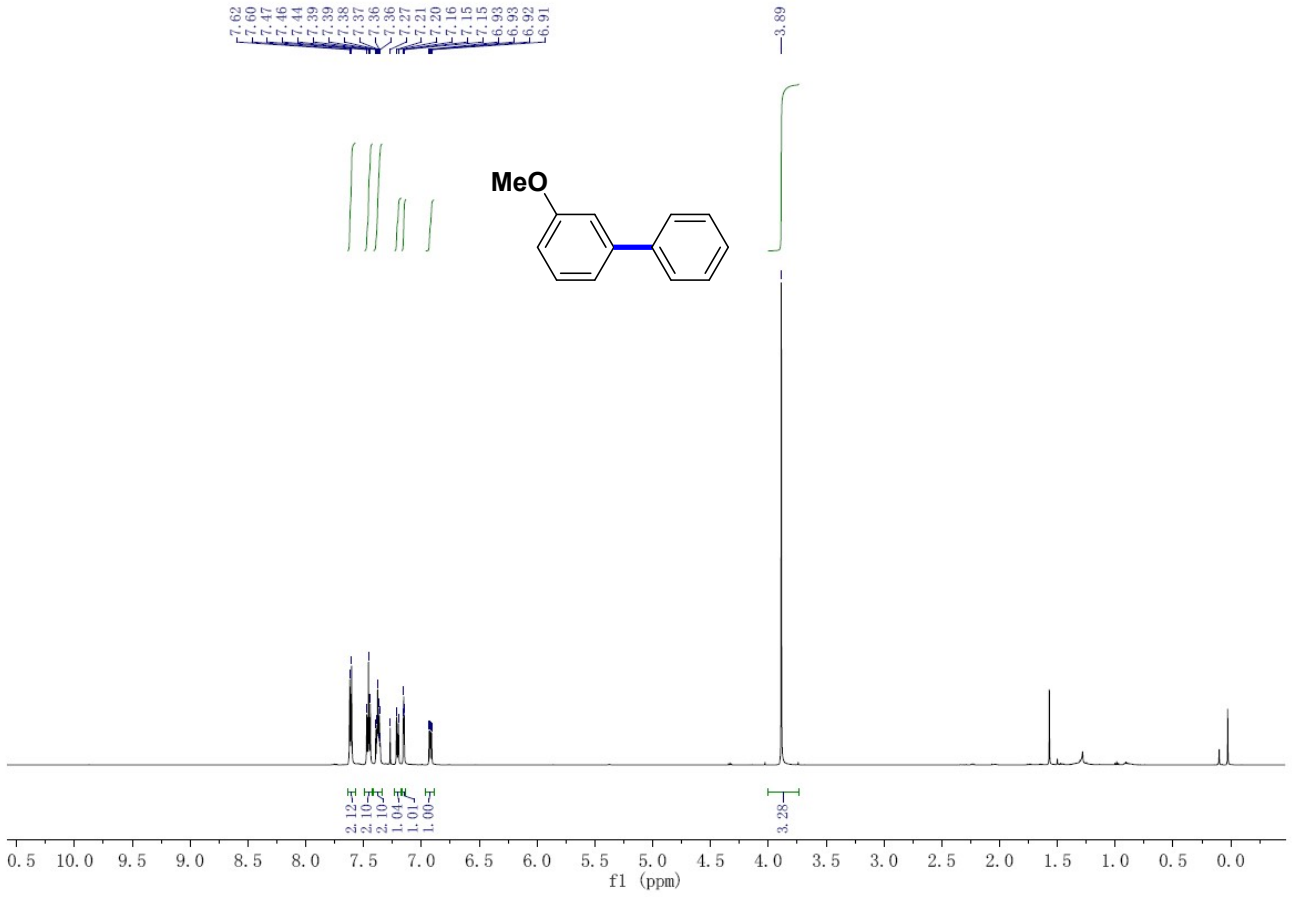
128.91
128.22
127.28
127.23
77.26
77.00
76.75
26.62
f1 (ppm)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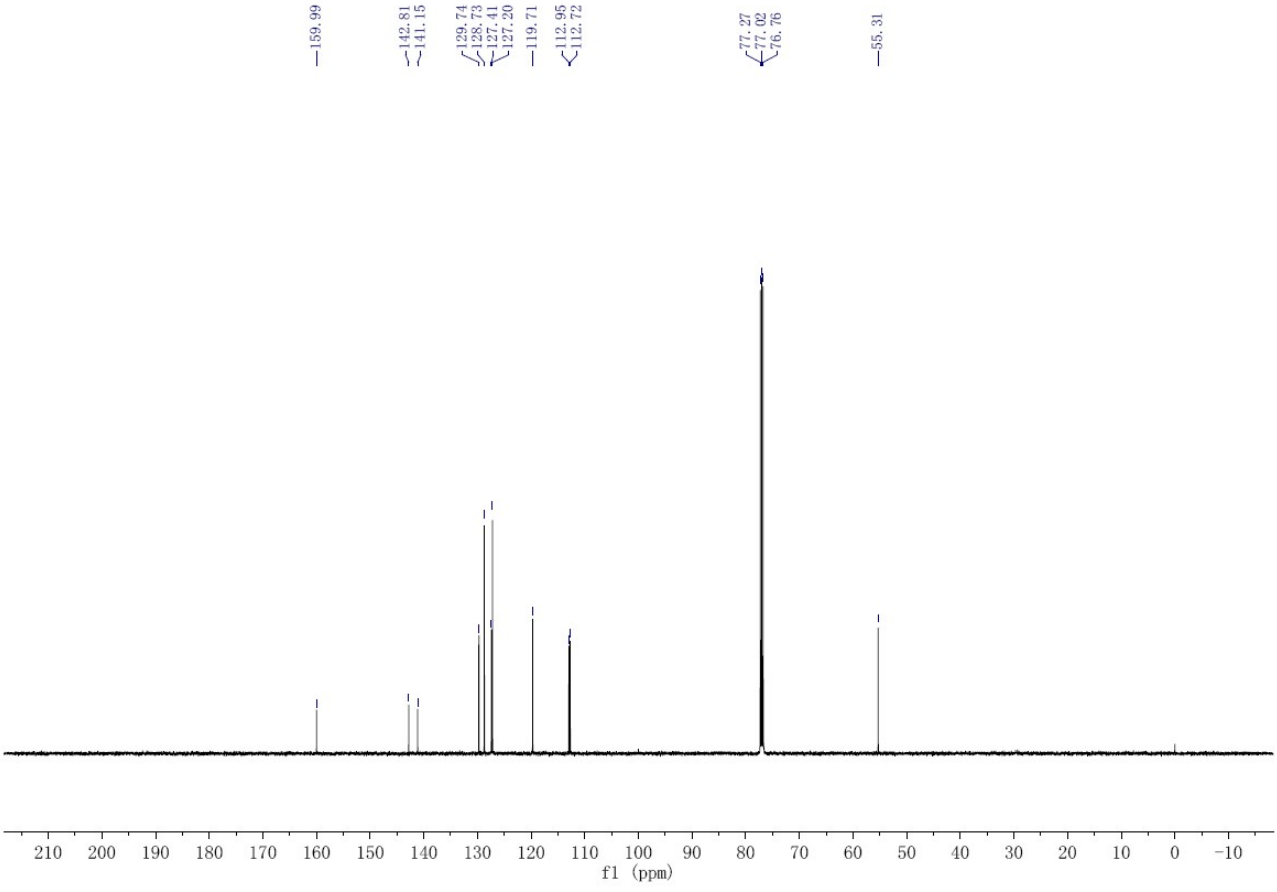
7.60
7.47
7.46
7.44
7.39
7.39
7.38
7.37
7.36
7.36
7.27
7.21
7.20
7.16
7.15
7.15
6.93
6.92
6.91
3.89
MeO
2.12
2.10
2.10
1.04
1.01
1.00
3.28
f1 (ppm)


159.99
142.81
141.15
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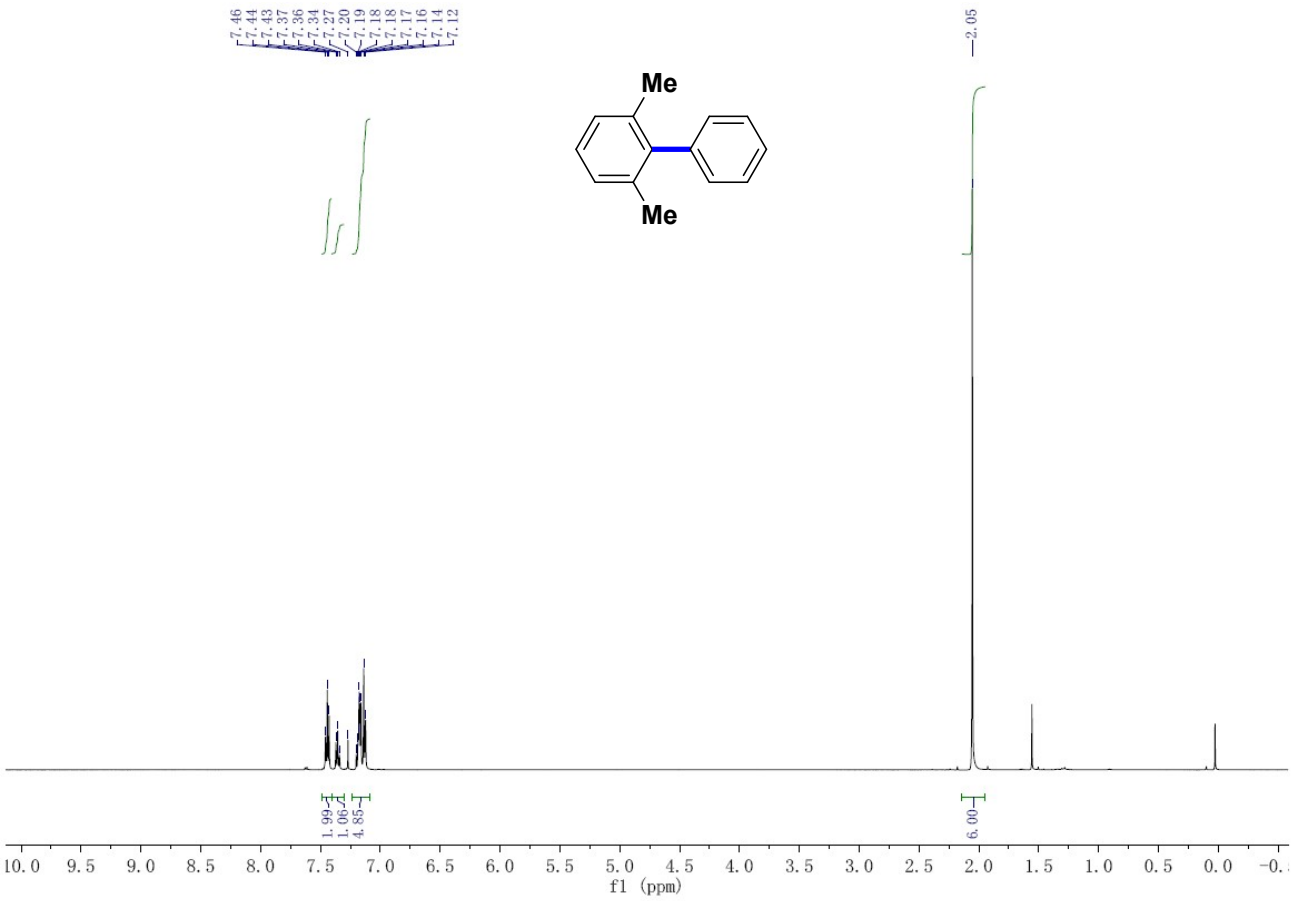
127.20
119.71
112.95
112.72
77.27
77.02
76.76
55.31
f1 (ppm)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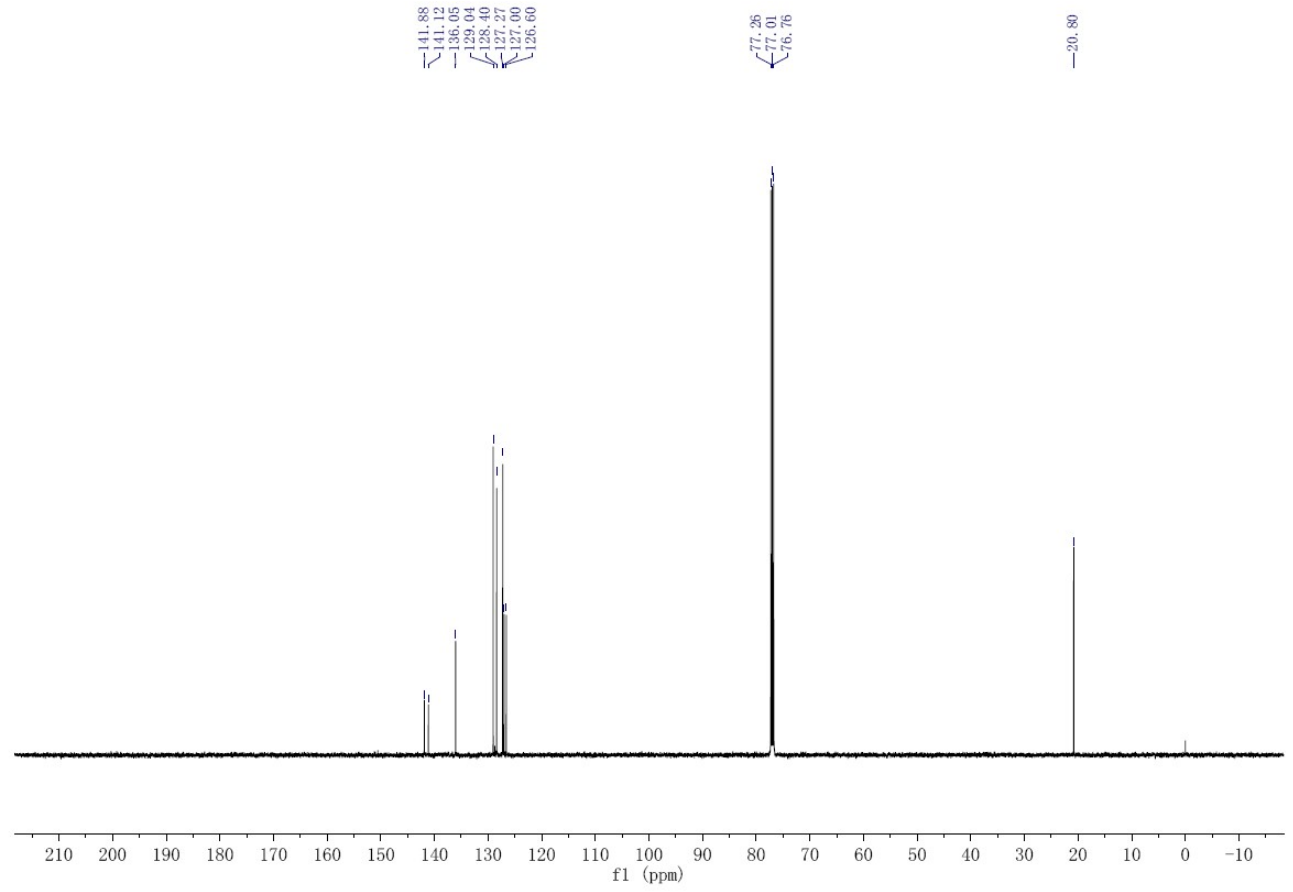
7.44
7.43
7.37
7.36
7.34
7.27
7.20
7.19
7.18
7.18
7.17
7.16
7.14
7.12
2.05
Me
Me
1.99
1.06
4.85
6.00
f1 (ppm)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136.05
129.04
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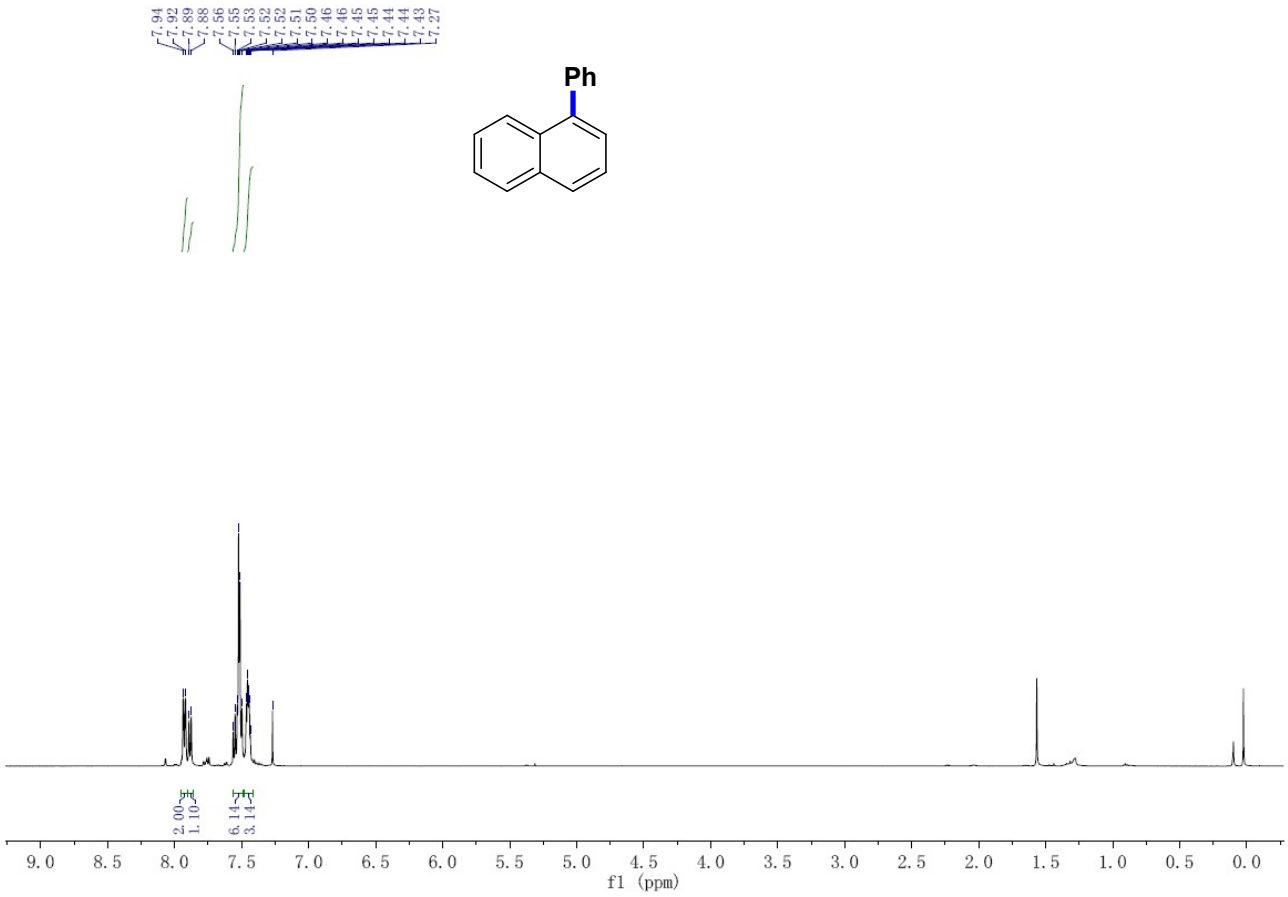
127.27
127.00
126.60
77.26
77.01
76.76
20.80
f1 (ppm)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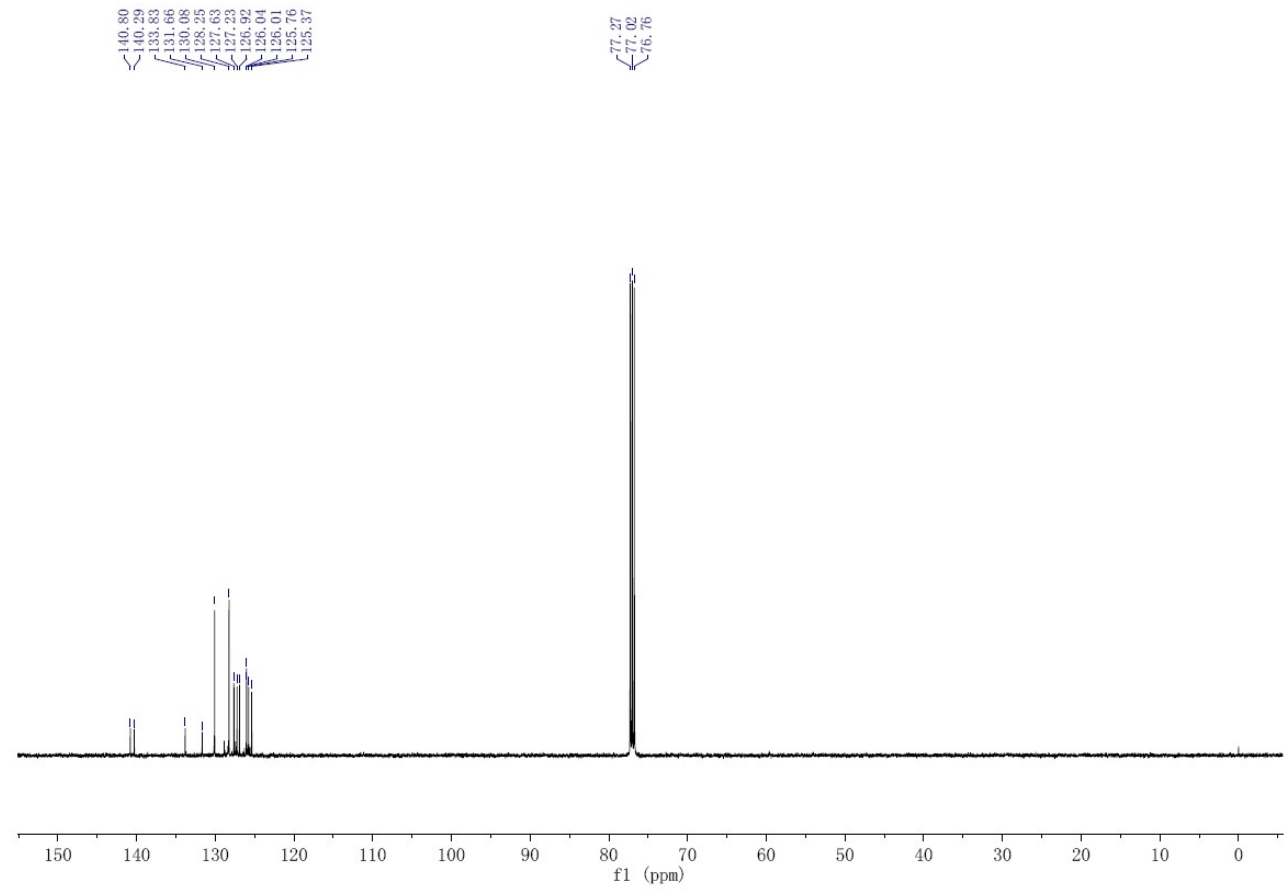
7.92
7.89
7.88
7.56
7.55
7.53
7.52
7.52
7.51
7.50
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.27
Ph
2.00
1.10
6.14
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


140.80
140.29
133.83
131.66
130.08
128.25
127.63
127.23
126.92
126.04
126.01
125.76
125.37
77.27
77.02
76.76
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.62
7.62
7.61
7.47
7.47
7.47
7.46
7.46
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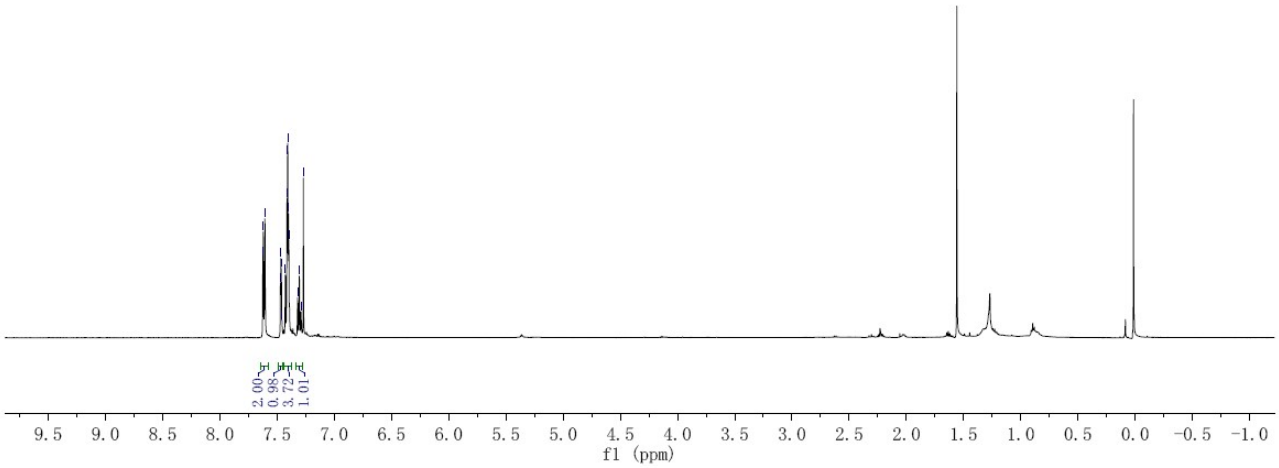
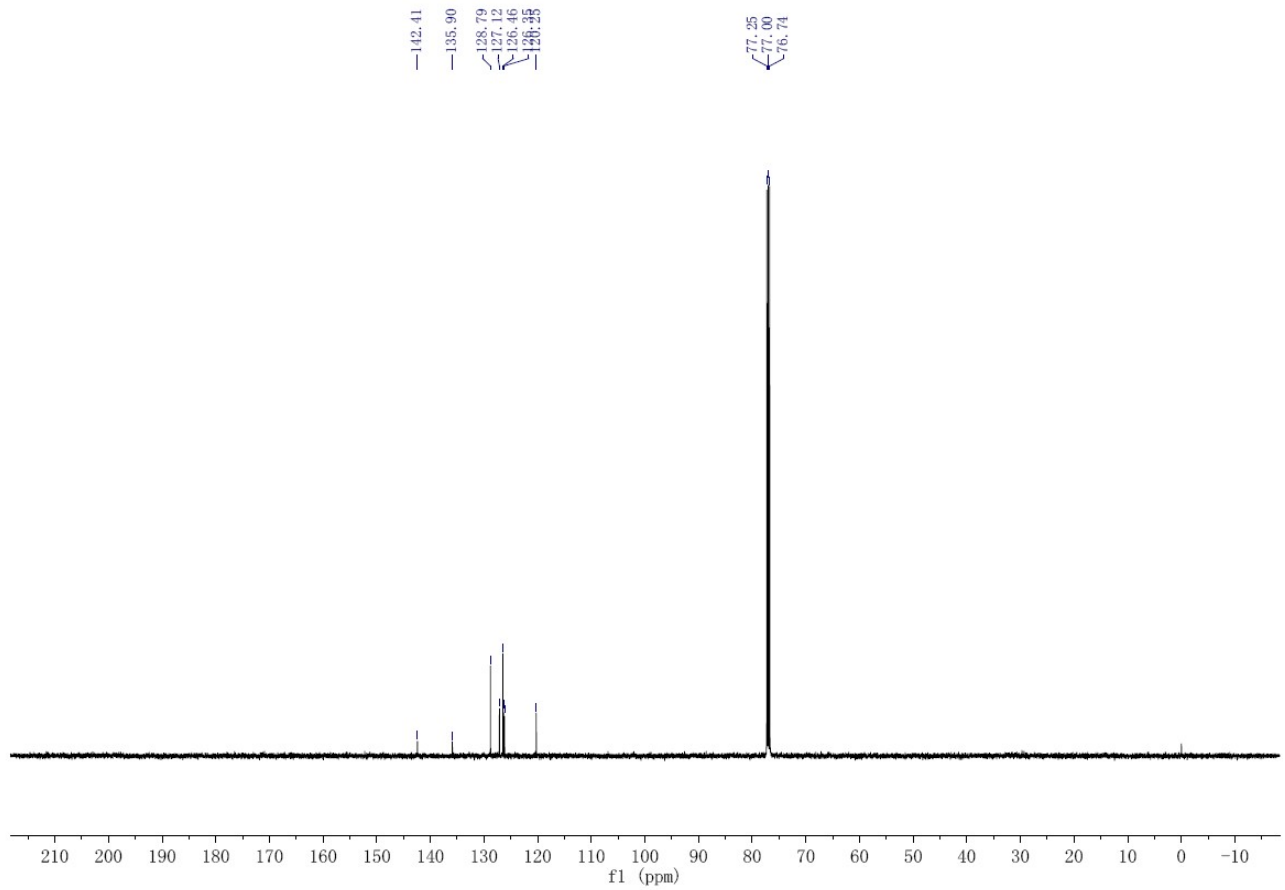
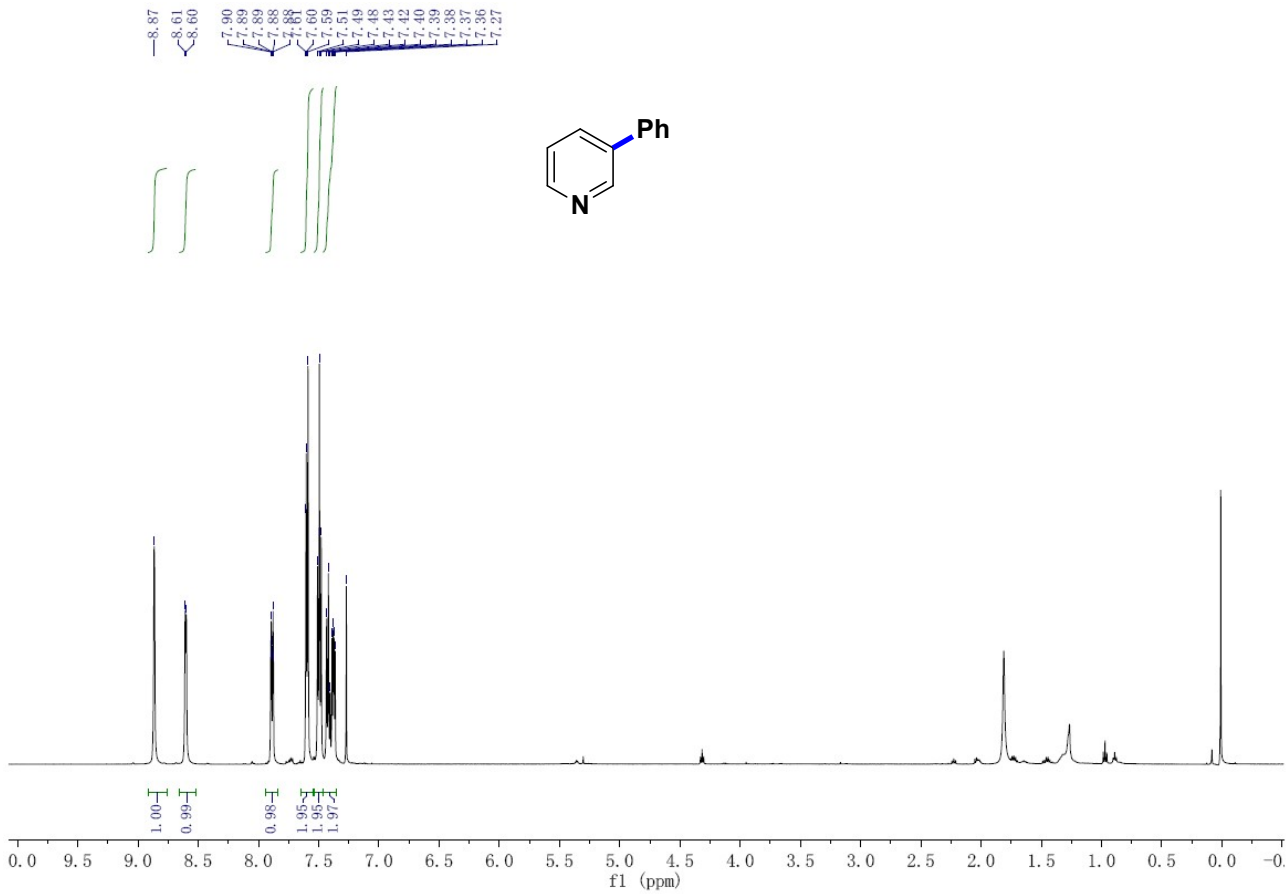
7.41
7.41
7.40
7.40
7.32
7.31
7.29
7.27


Ph
S


2.00
0.98
3.72
1.01
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 -1.0
f1 (ppm)


142.41
135.90
128.79
127.12
126.46
77.25
77.00
76.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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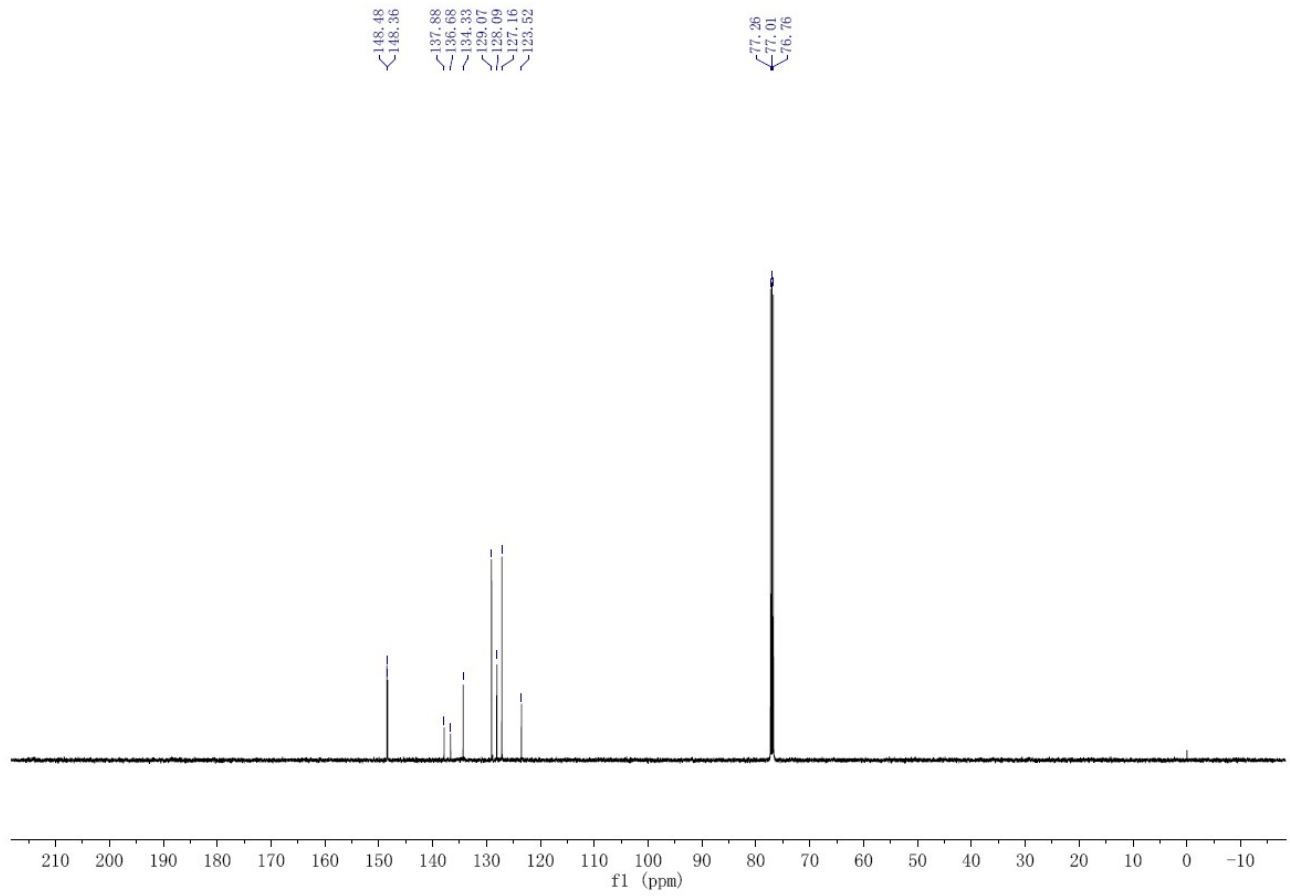
7.89
7.89
7.88
7.88
7.61
7.60
7.59
7.51
7.49
7.48
7.43
7.42
7.40
7.39
7.38
7.37
7.36
7.27
Ph
N
1.00
0.99
0.98
1.95
1.95
1.97
f1 (ppm)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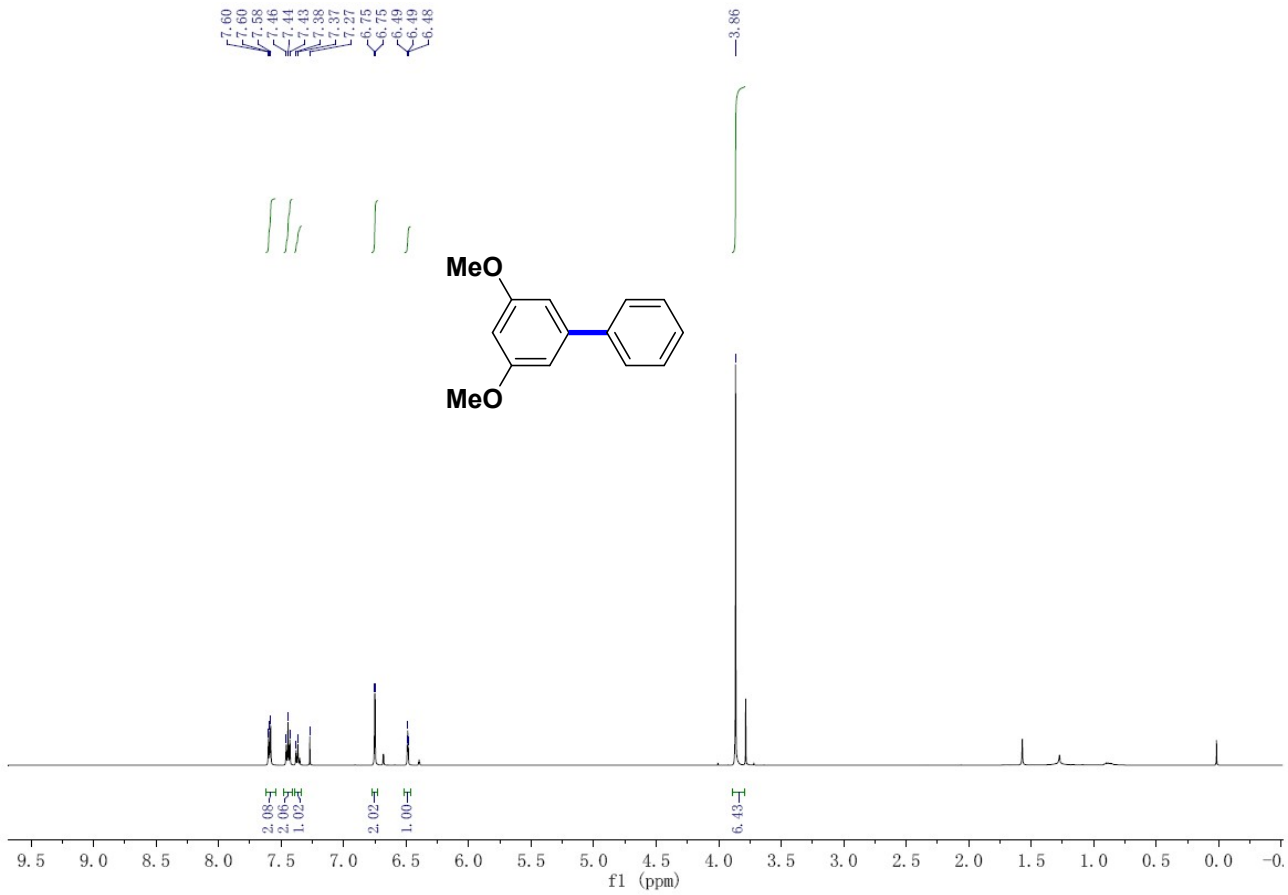
127.16
123.52
77.26
77.01
76.76
f1 (ppm)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7.43
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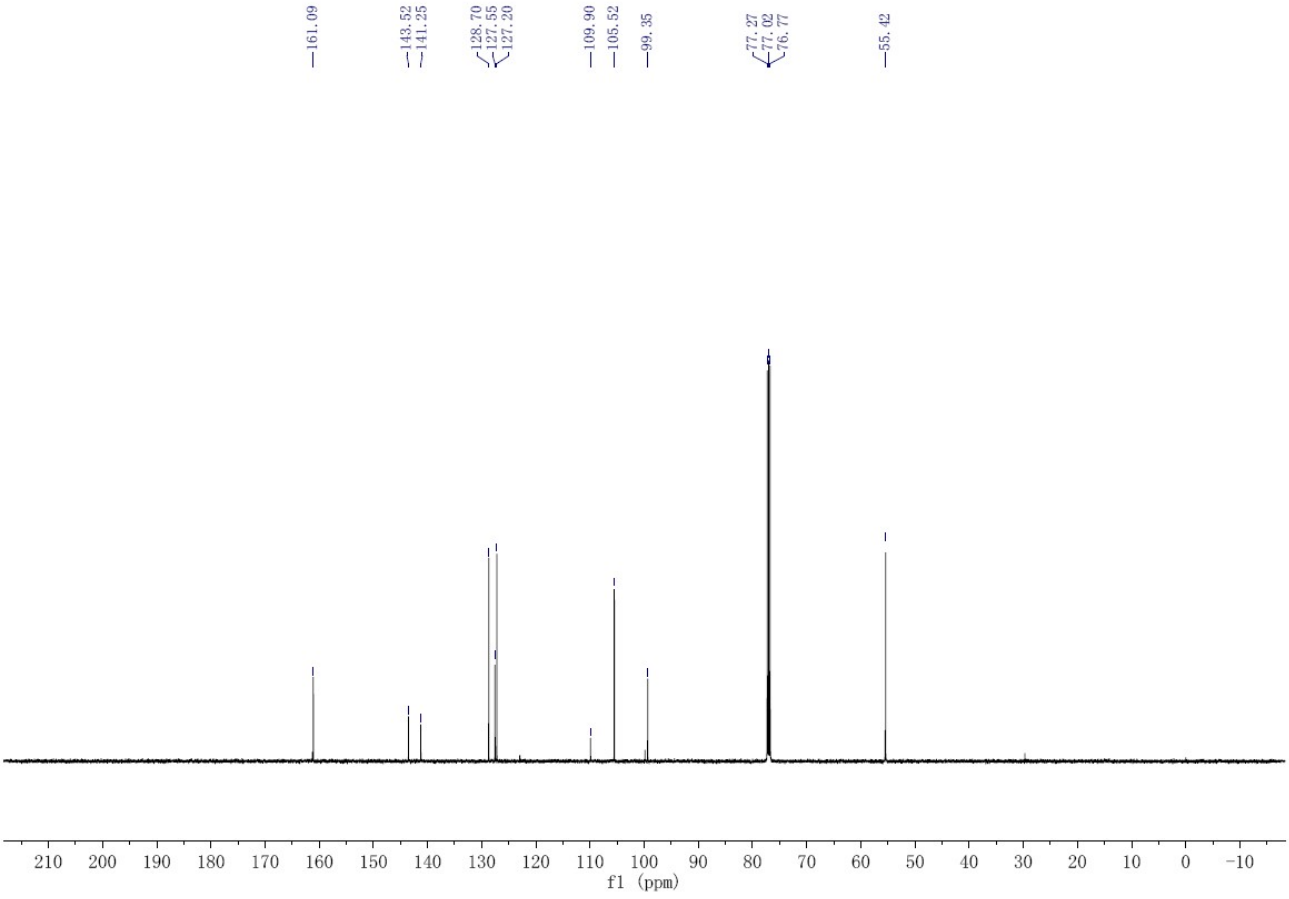
7.37
7.27
6.75
6.75
6.49
6.49
6.48
3.86
MeO
MeO
2.08
2.06
1.02
2.02
1.00
6.43
f1 (ppm)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143.52
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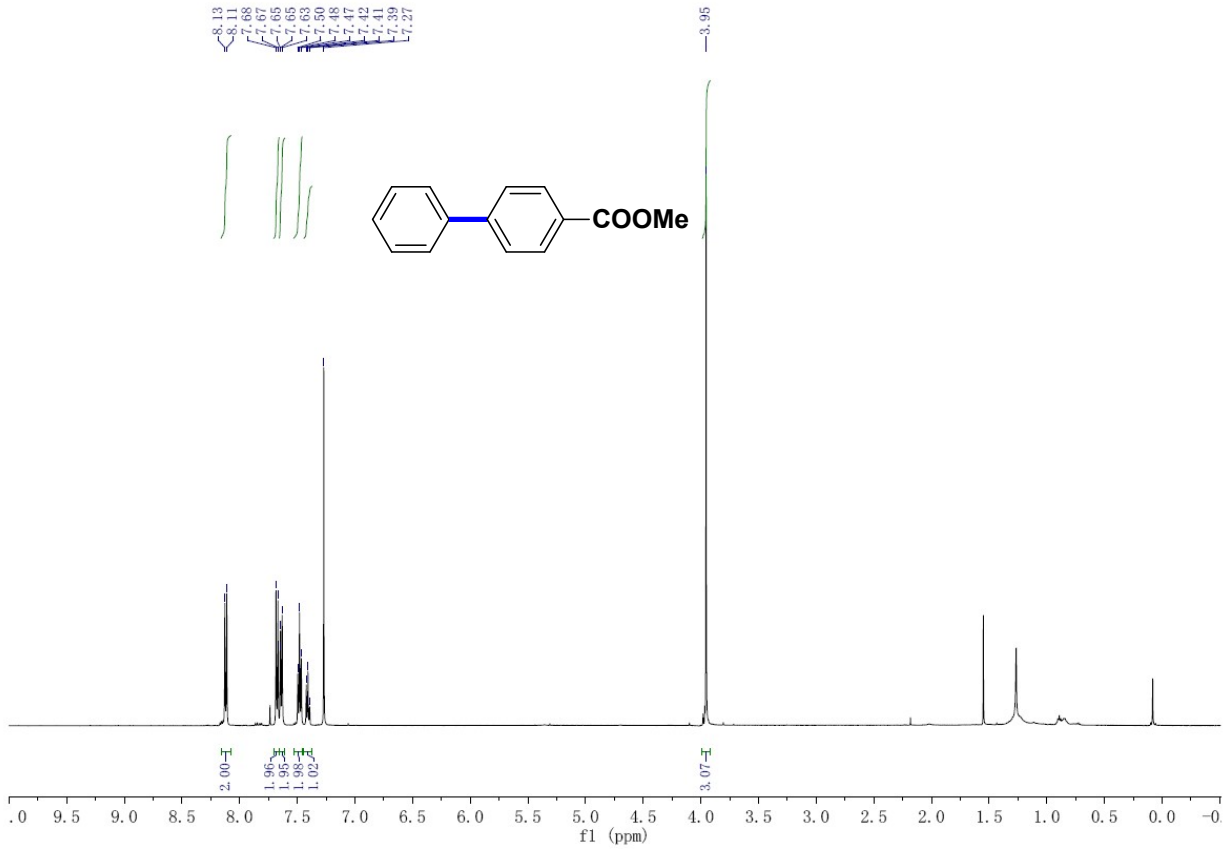
127.20
109.90
105.52
99.35
77.27
77.02
76.77
55.42
f1 (ppm)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7.63
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7.47
7.42
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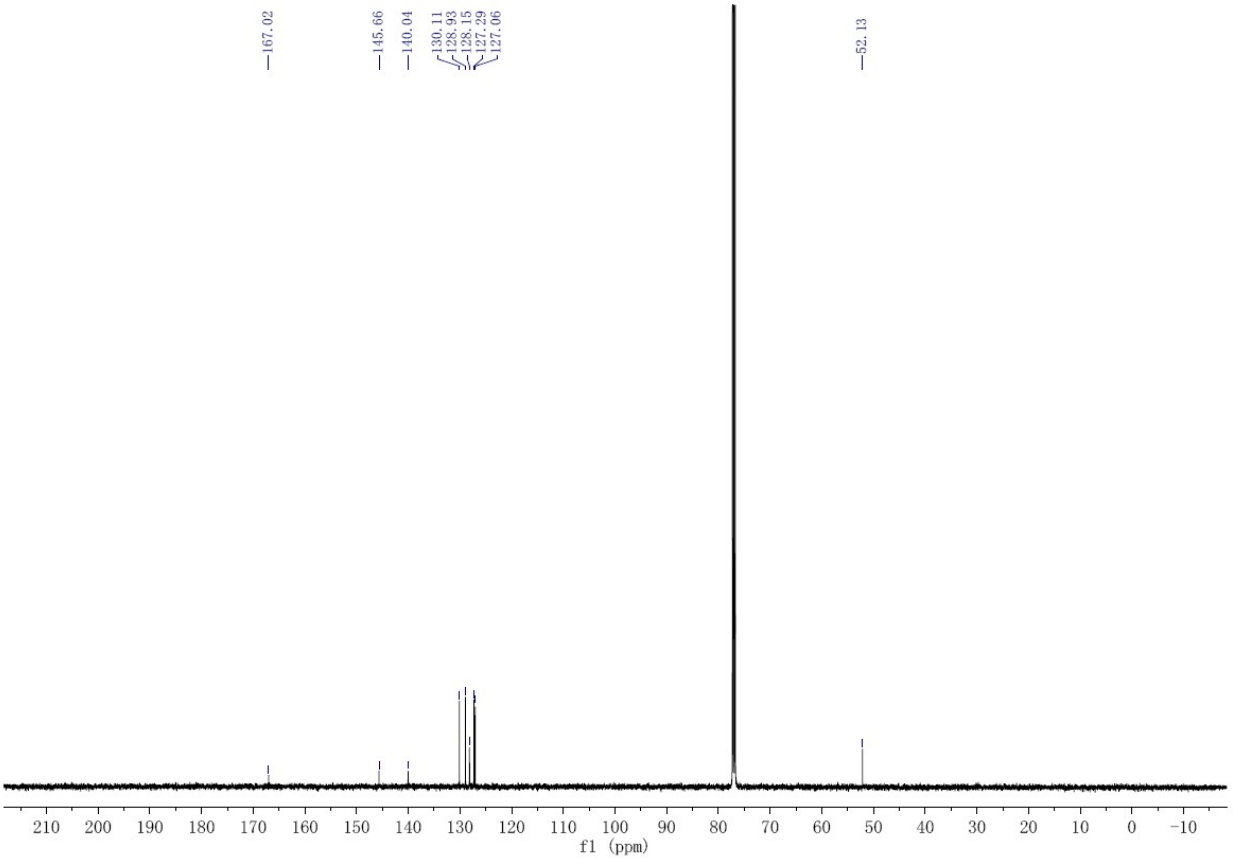
3.95
COOMe
2.00
1.96
1.95
1.98
1.02
3.07
f1 (ppm)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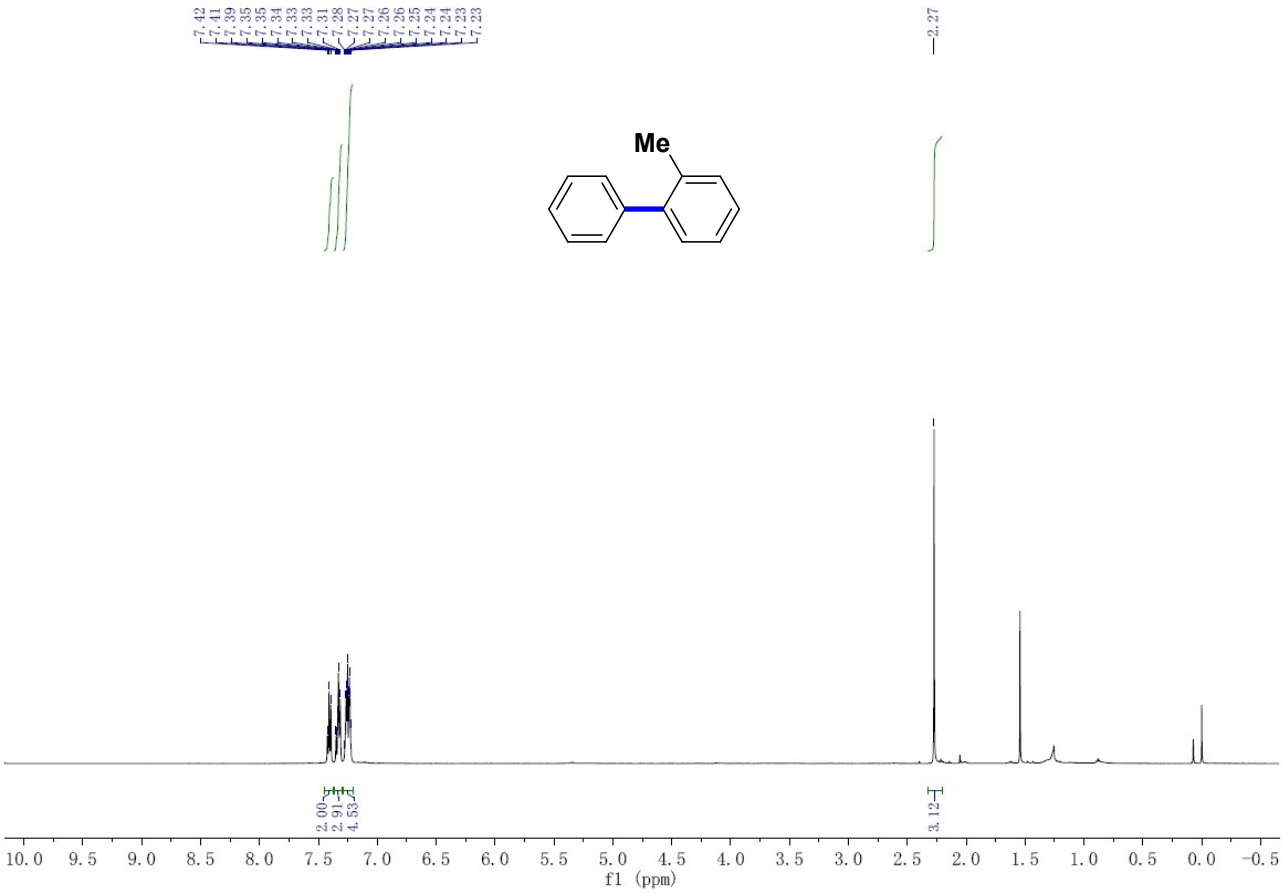
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7.27
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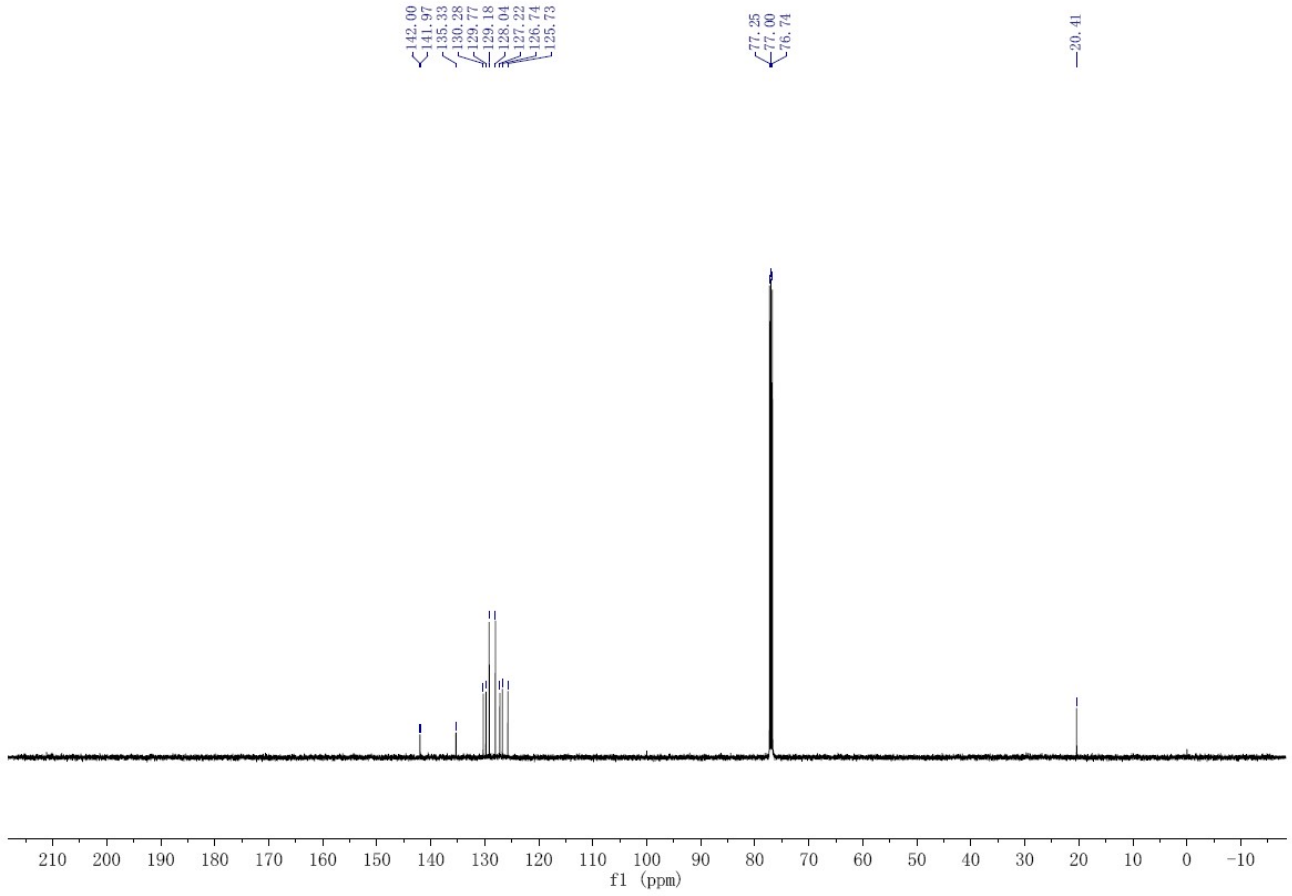
7.26
7.26
7.25
7.24
7.24
7.23
7.23
2.27
Me
2.00
2.91
4.53
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.04
127.22
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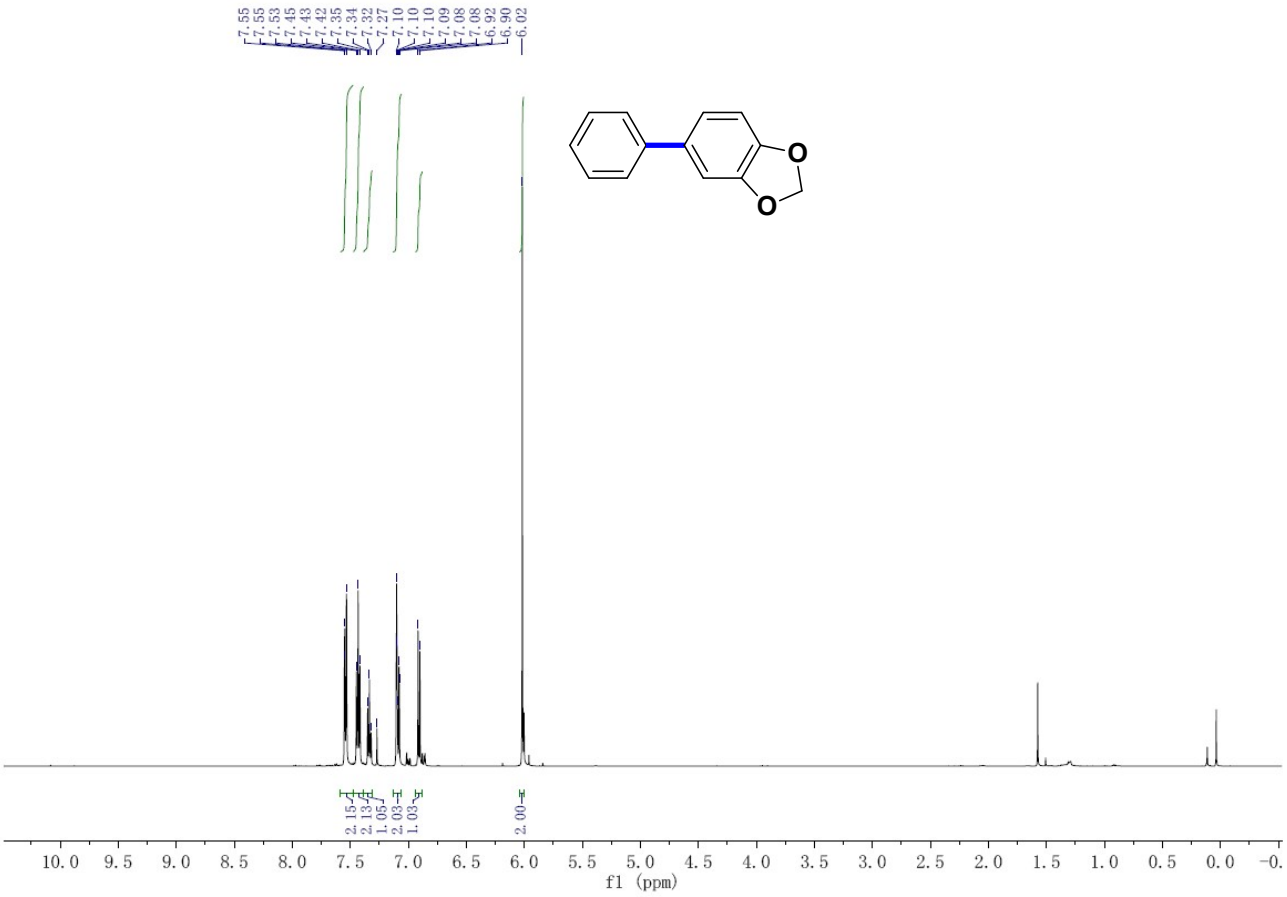
77.00
76.74
20.41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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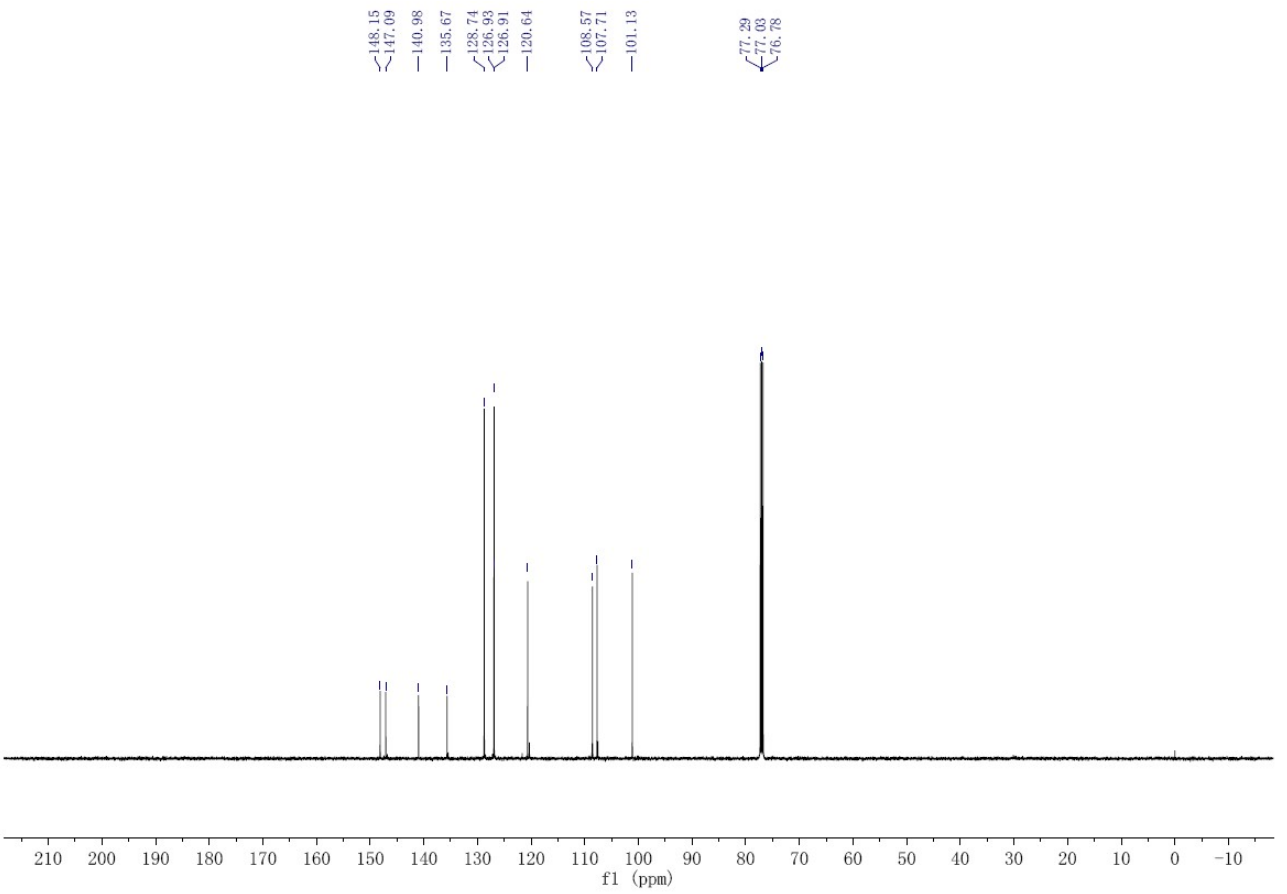
7.34
7.32
7.27
7.10
7.10
7.10
7.09
7.08
7.08
6.92
6.90
6.02
O
O
2.15
2.13
1.05
2.03
1.03
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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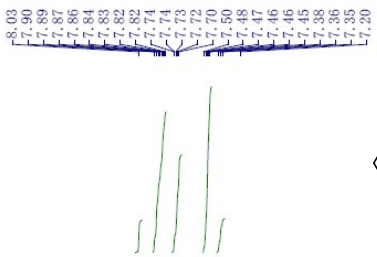
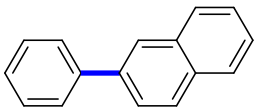
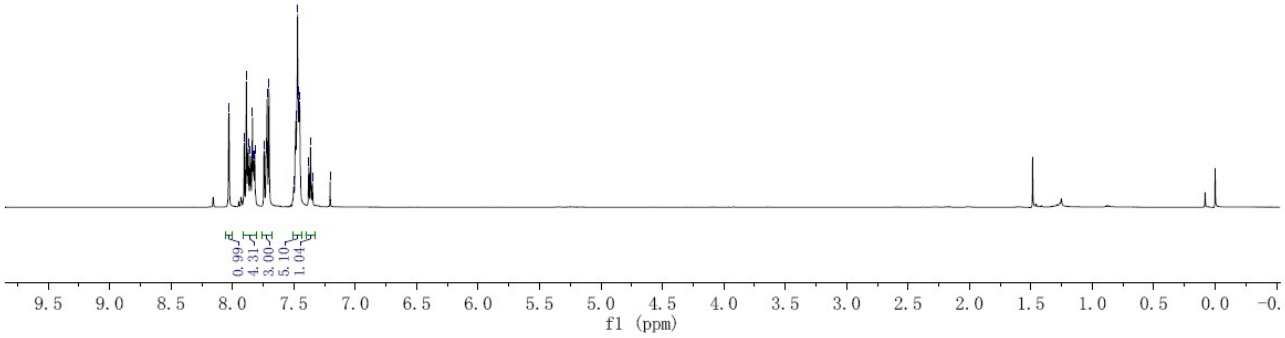
120.64
108.57
107.71
101.13
77.29
77.03
76.78
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

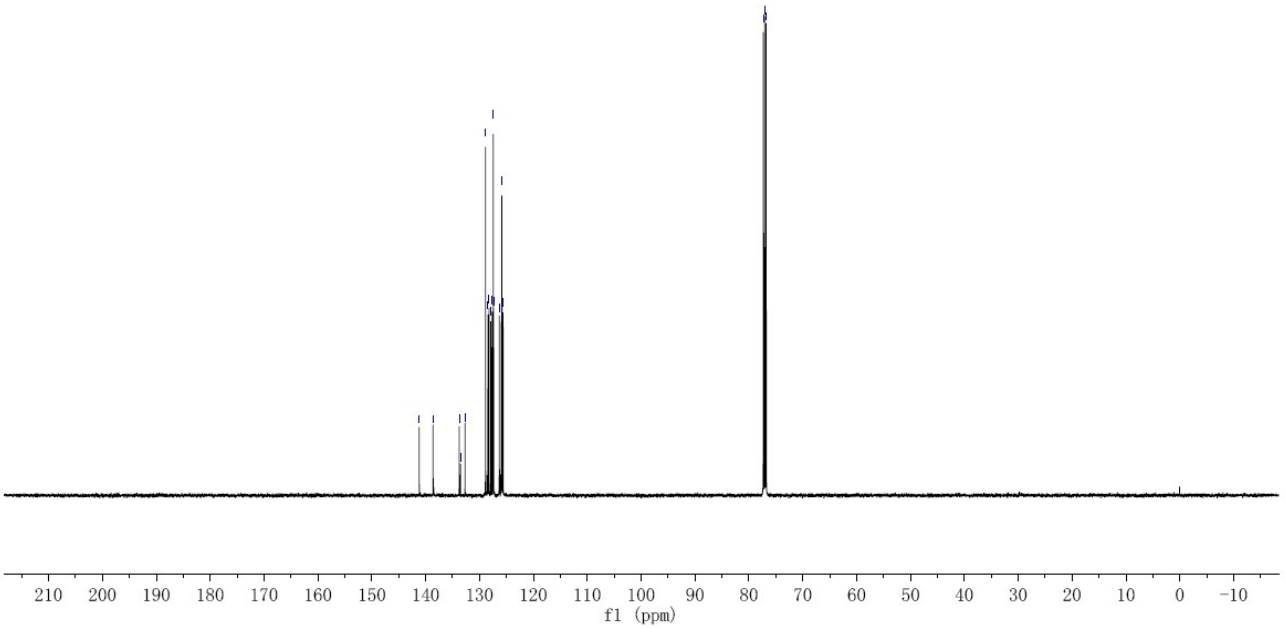

8.03
7.90
7.89
7.87
7.86
7.84
7.83
7.82
7.82
7.74
7.74
7.73
7.72
7.70
7.50
7.48
7.47
7.46
7.46
7.45
7.38
7.36
7.35
7.20




0.99
4.31
3.00
5.10
1.04
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.
f1 (ppm)


141.20
138.63
133.75
133.52
132.69
128.89
128.45
128.24
127.92
127.68
127.47
127.38
126.32
125.96
125.85
125.63

77.31
77.06
76.80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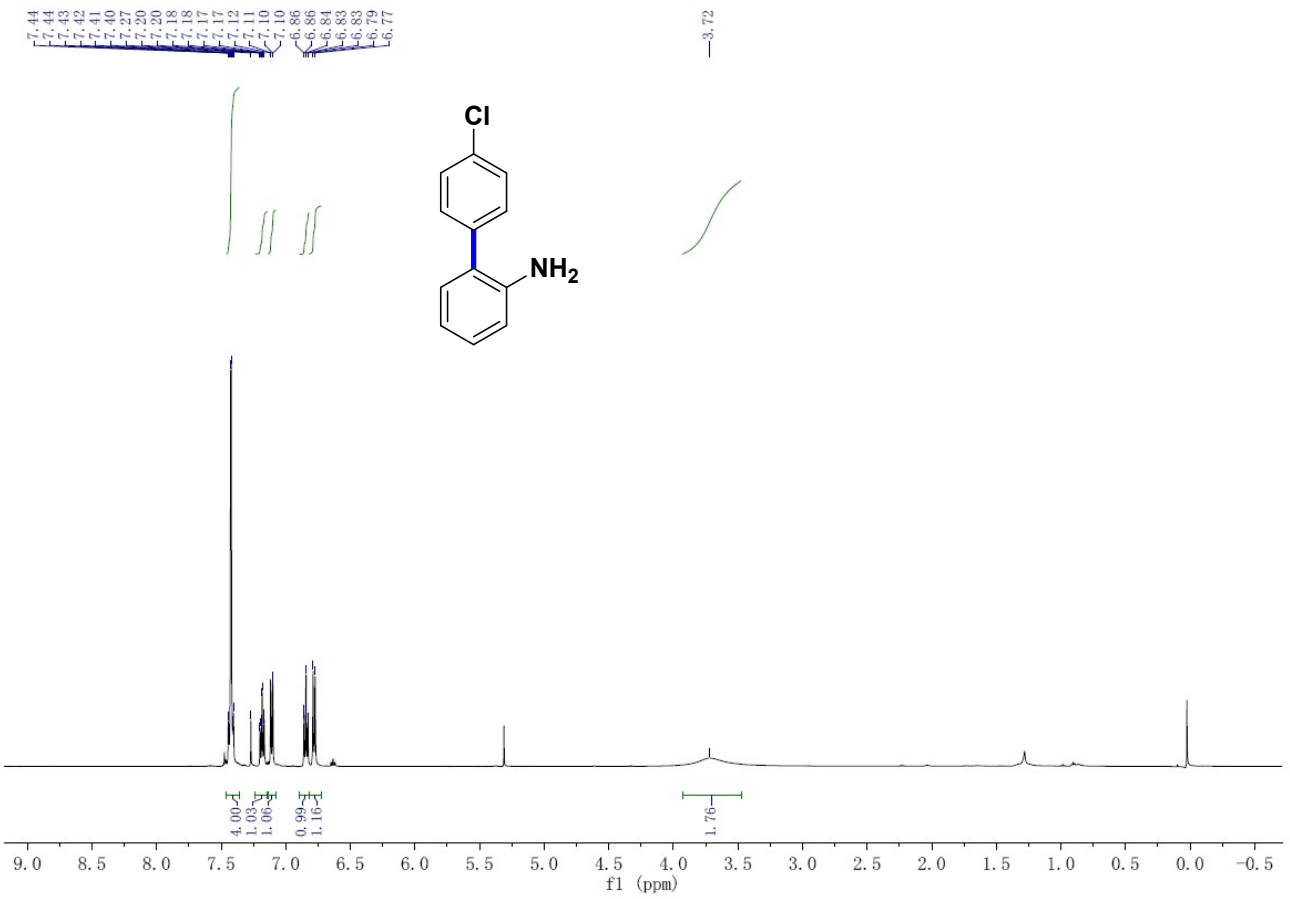
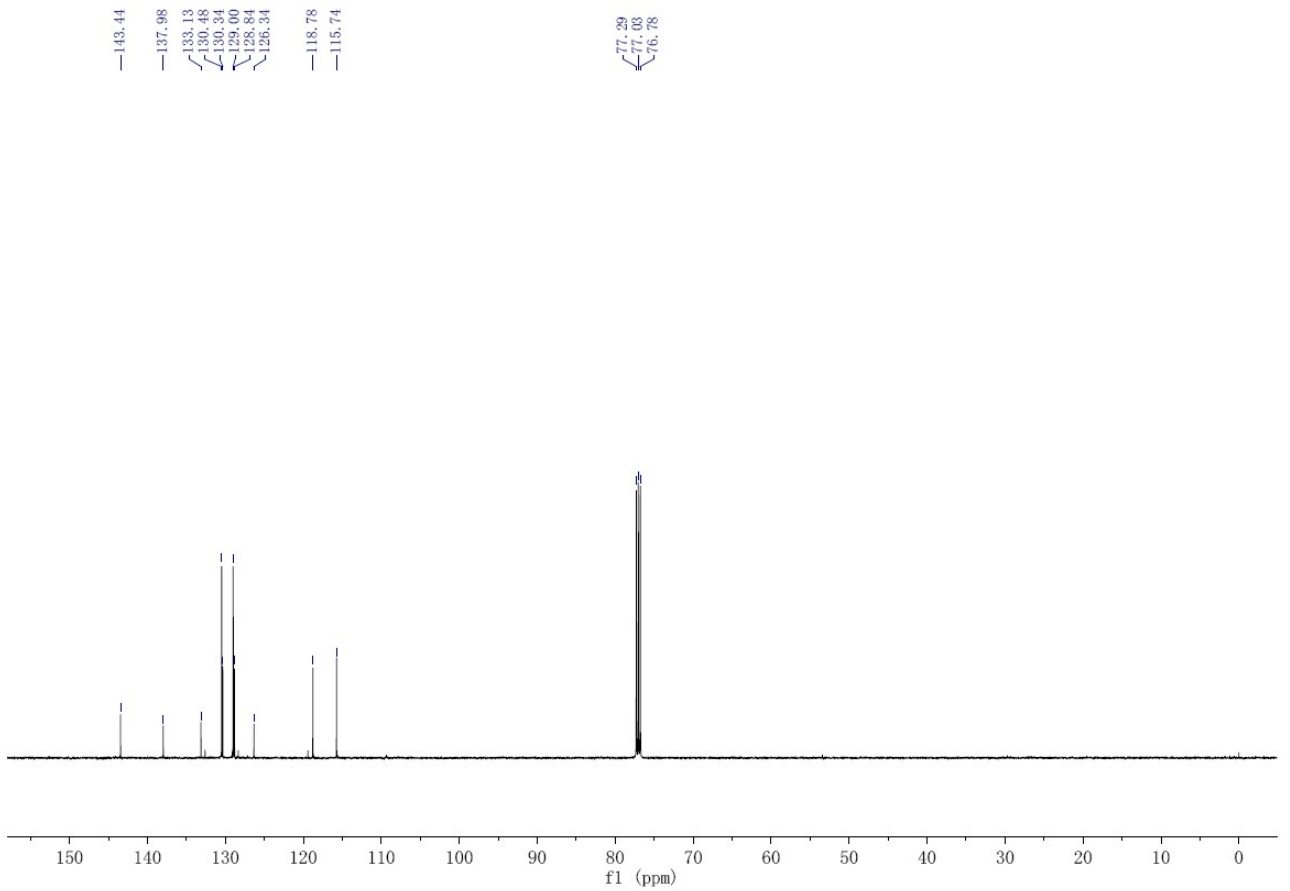
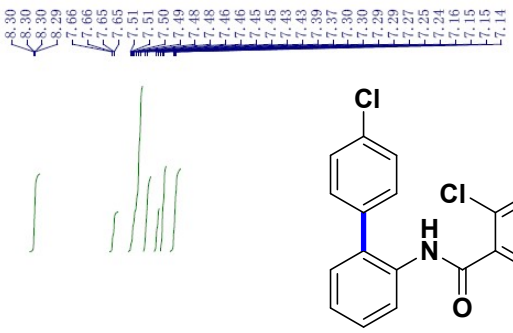
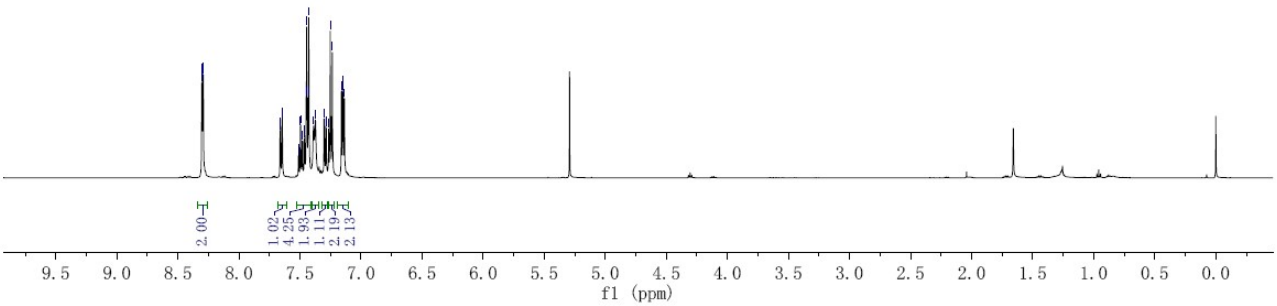
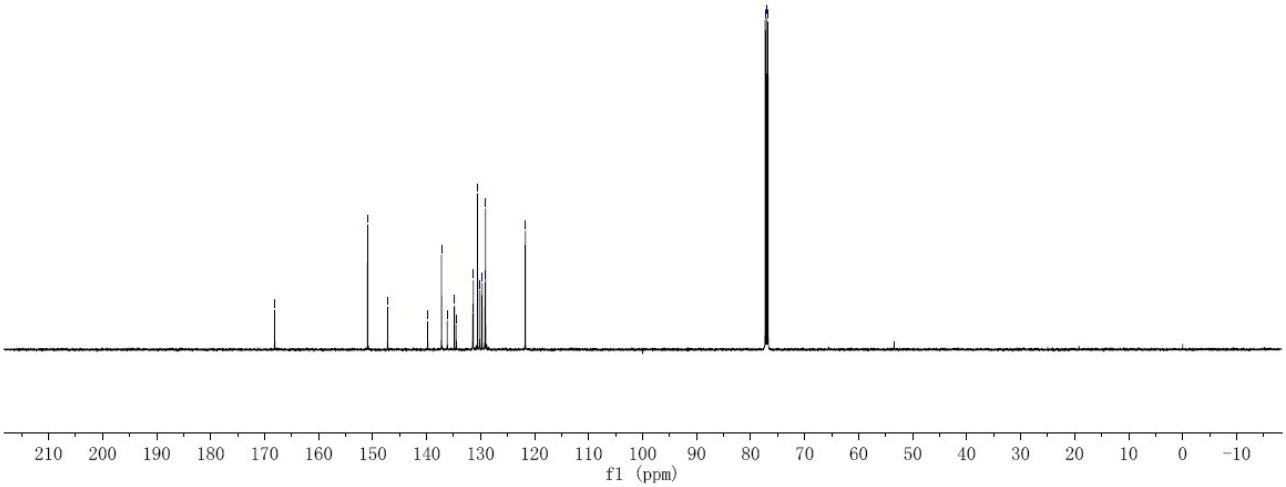
f1 (ppm)

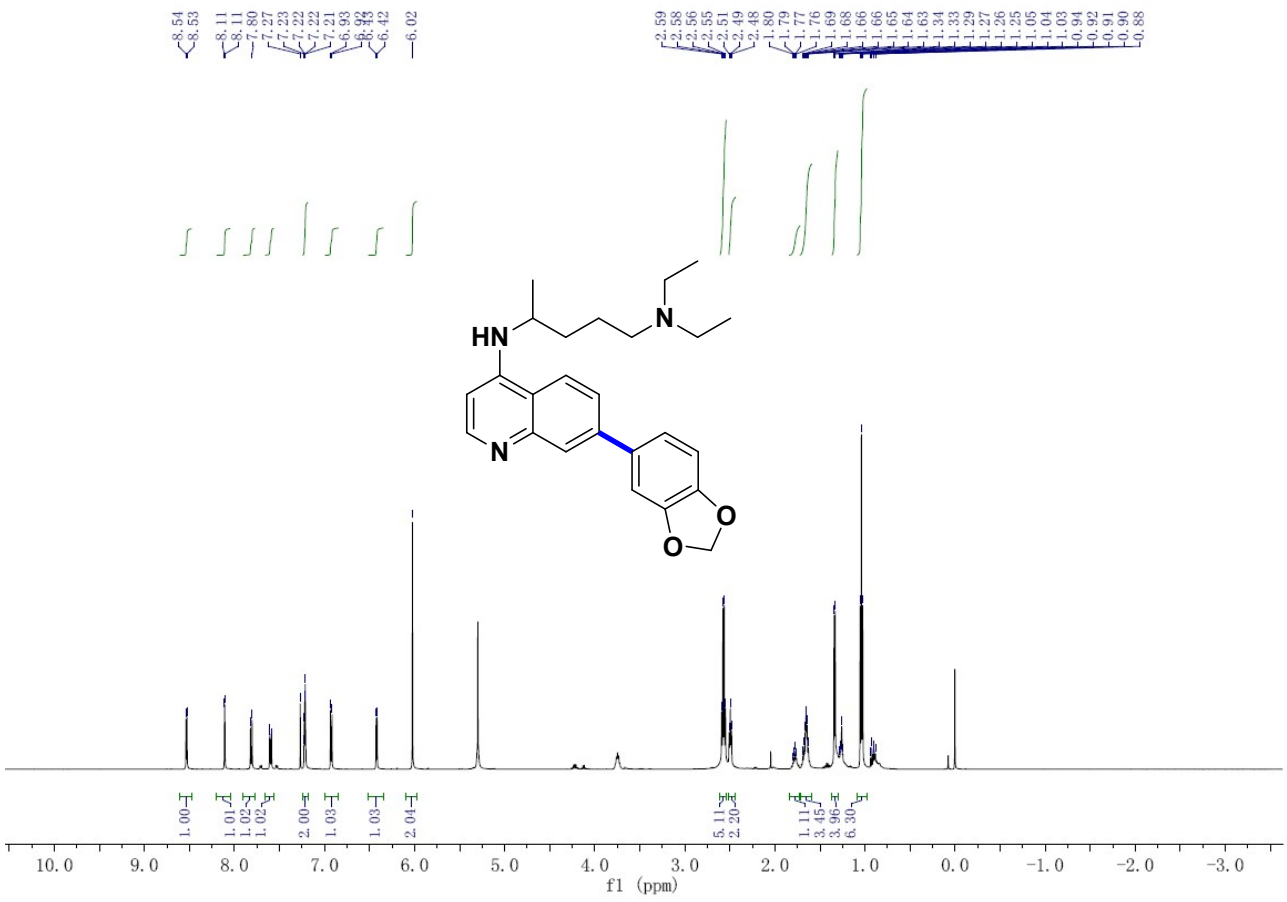

7.44
7.44
7.43
7.42
7.41
7.40
7.27
7.20
7.20
7.18
7.17
7.17
7.17
7.12
7.11
7.10
7.10
6.86
6.86
6.84
6.83
6.83
6.79
6.77
3.72
Cl
NH2
4.00
1.03
1.06
0.99
1.16
1.76
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

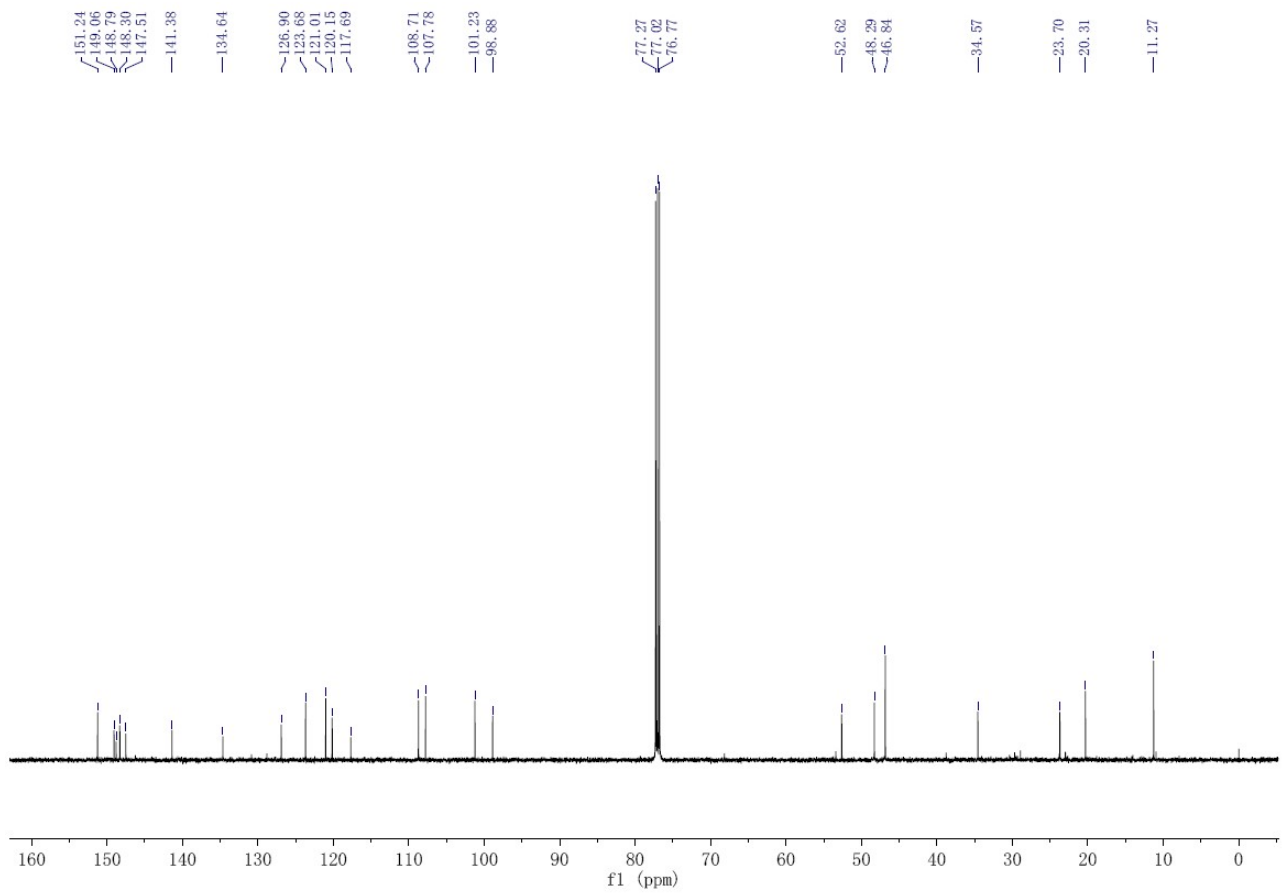

143.44
137.98
133.13
130.48
130.34
129.00
128.84
126.34
118.78
115.74
77.29
77.03
76.78
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
Cl
N
H
N
O


f1 (ppm)


f1 (ppm)


8.54
8.53
8.11
8.11
7.80
7.27
7.23
7.22
7.22
7.21
6.93
6.92
6.43
6.42
6.02
2.59
2.58
2.56
2.55
2.51
2.49
2.48
1.80
1.79
1.77
1.76
1.69
1.68
1.66
1.66
1.65
1.64
1.63
1.34
1.33
1.29
1.27
1.26
1.25
1.05
1.04
1.03
0.94
0.92
0.91
0.90
0.88
HN
N
N
O
O
1.00
1.01
1.02
1.02
2.00
1.03
1.03
2.04
5.11
2.20
1.11
3.45
3.96
6.30
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
f1 (ppm)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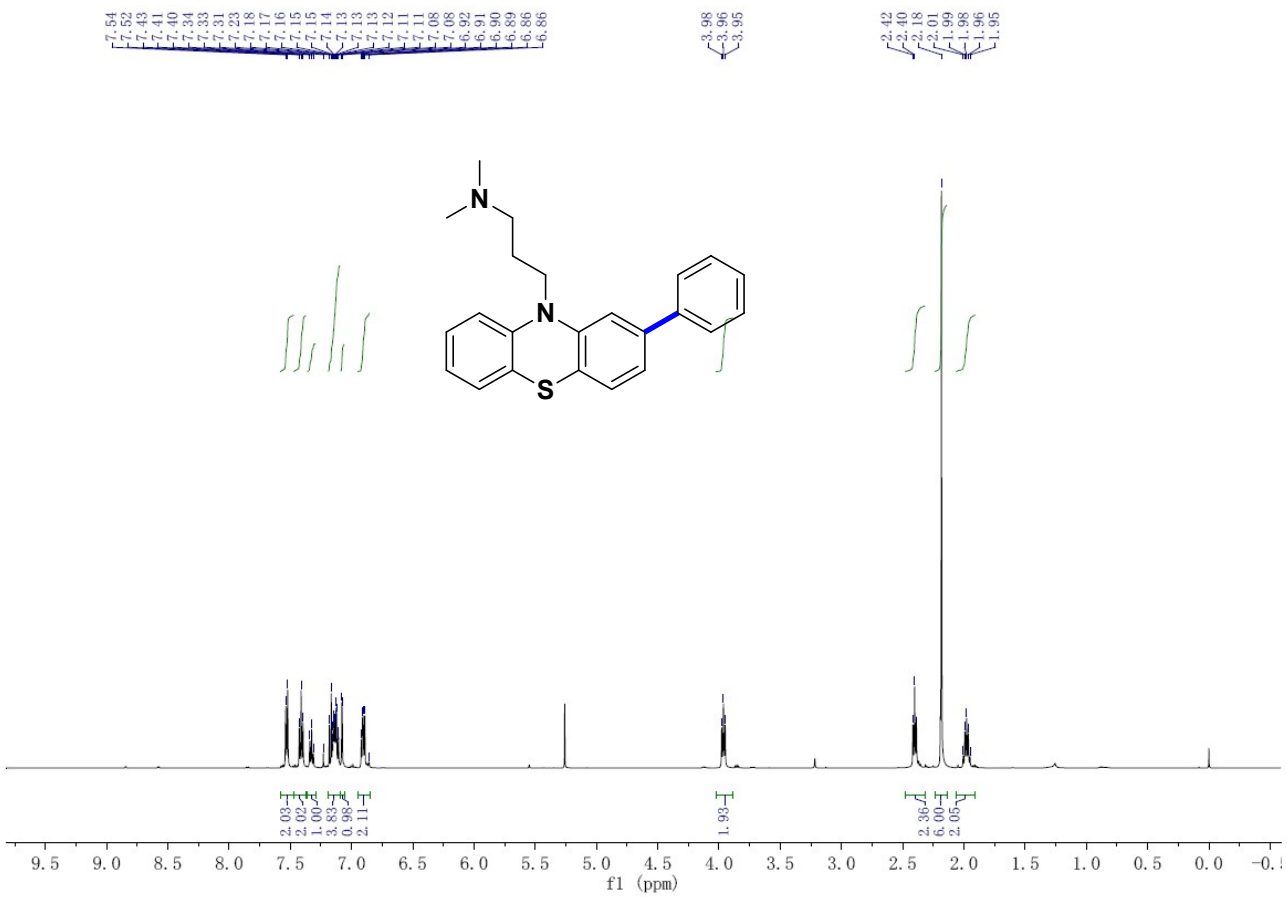
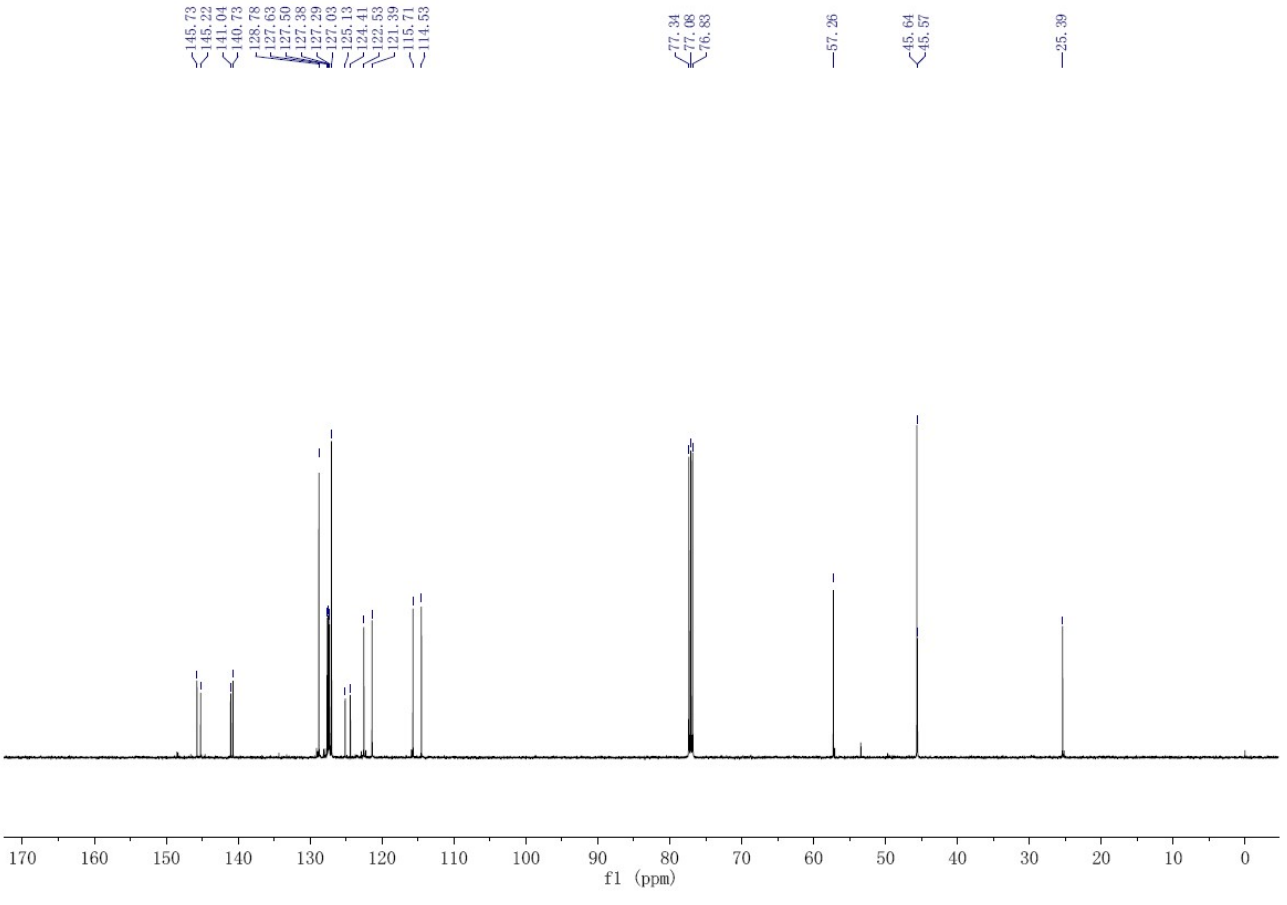
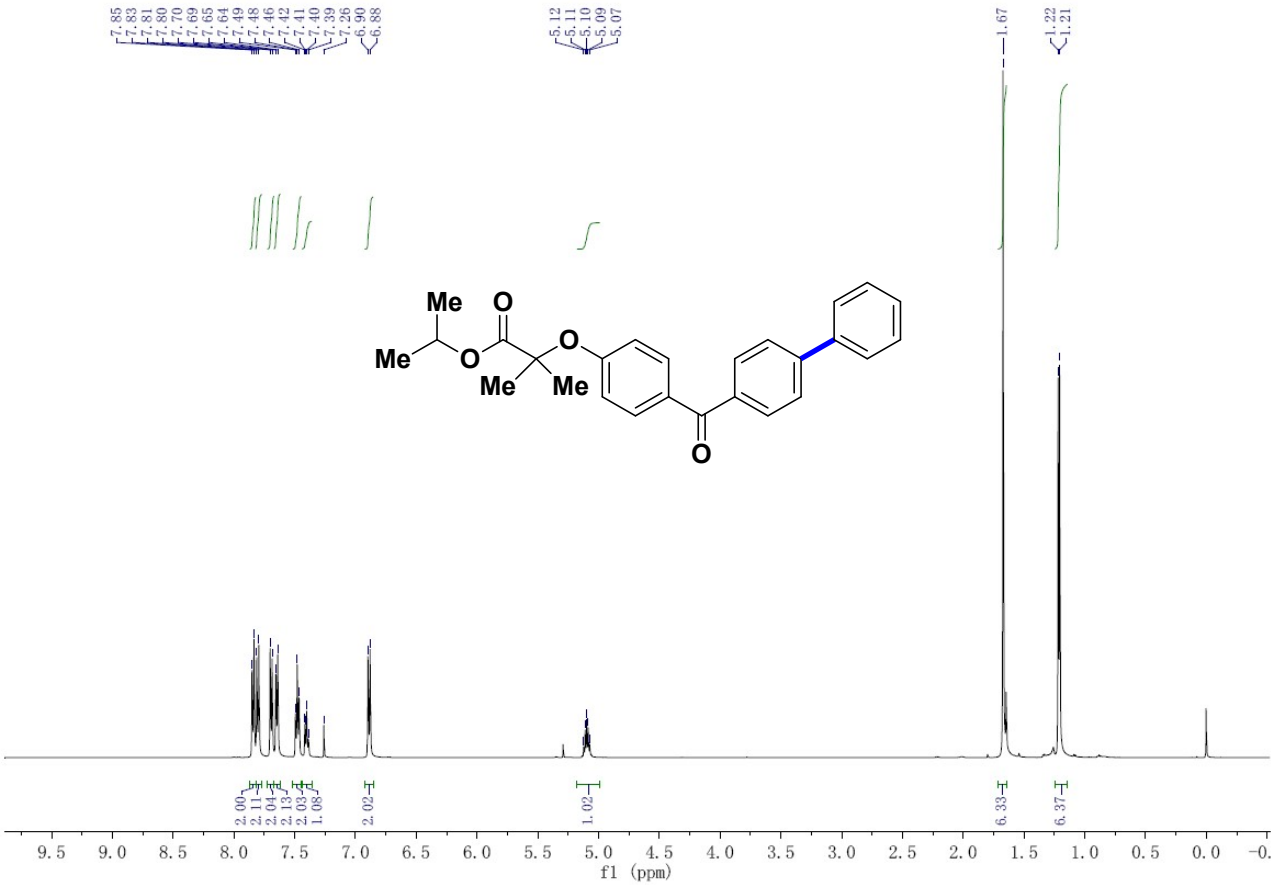
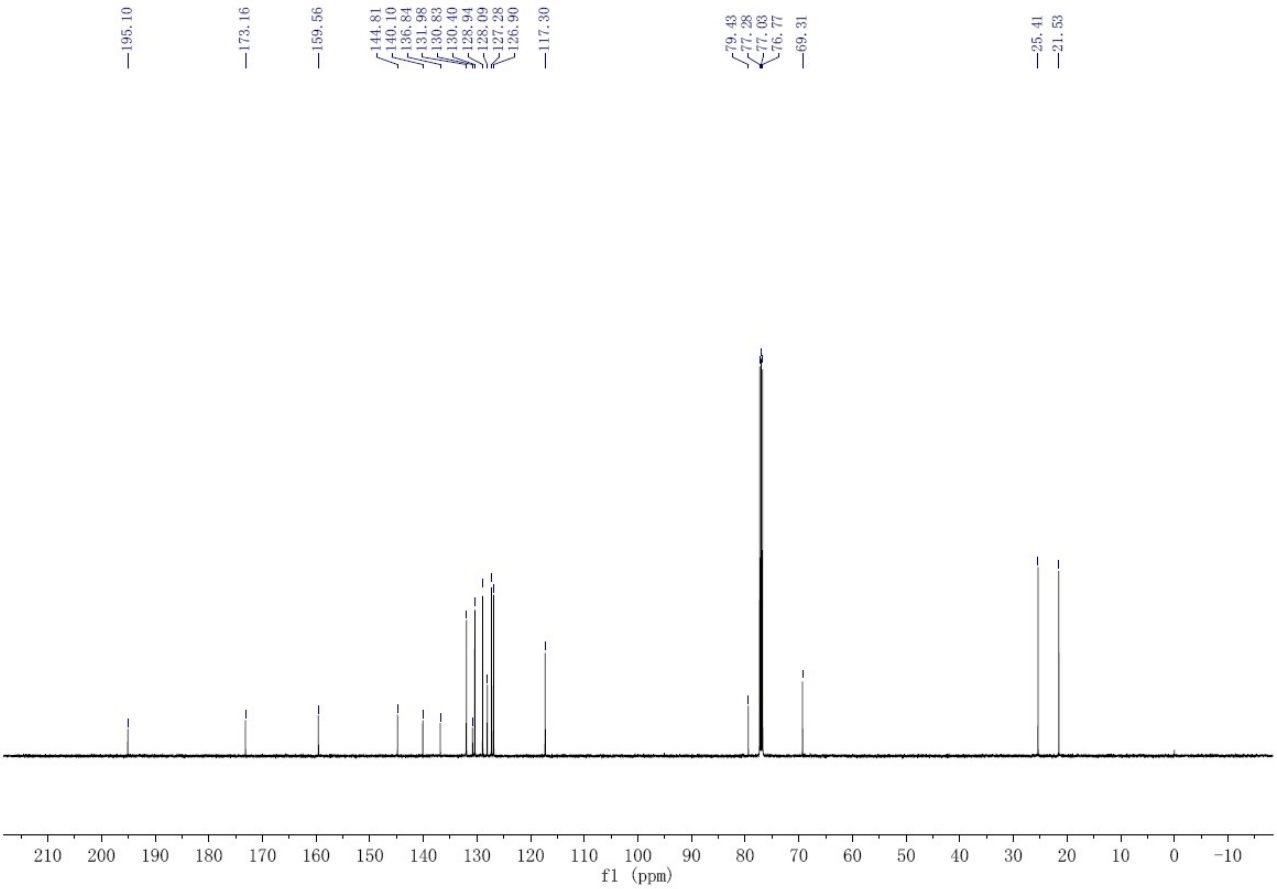
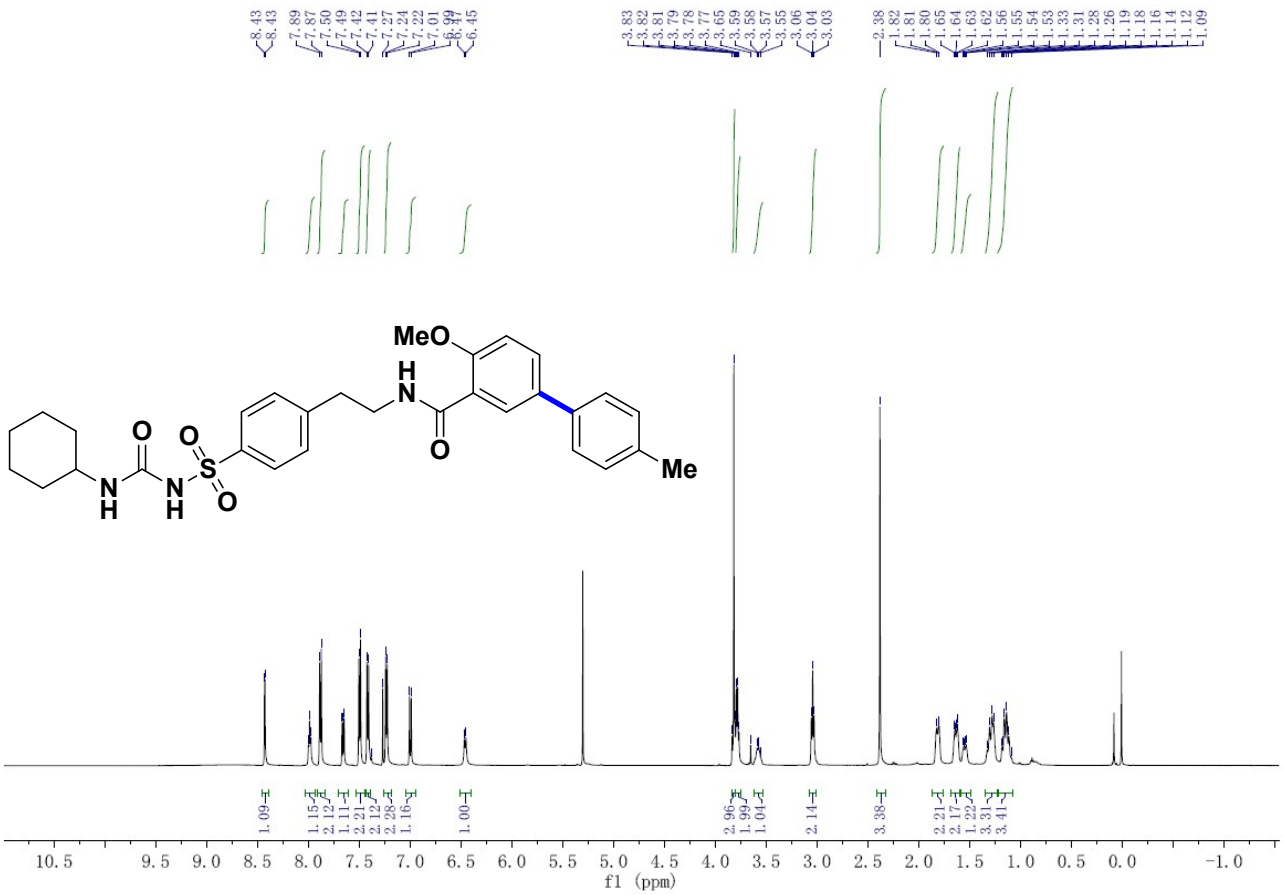
149.06
148.79
148.30
147.51
141.38
134.64
126.90
123.68
121.01
120.15
117.69
108.71
107.78
101.23
98.88
77.27
77.02
76.77
52.62
48.29
46.84
34.57
23.70
20.31
11.27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

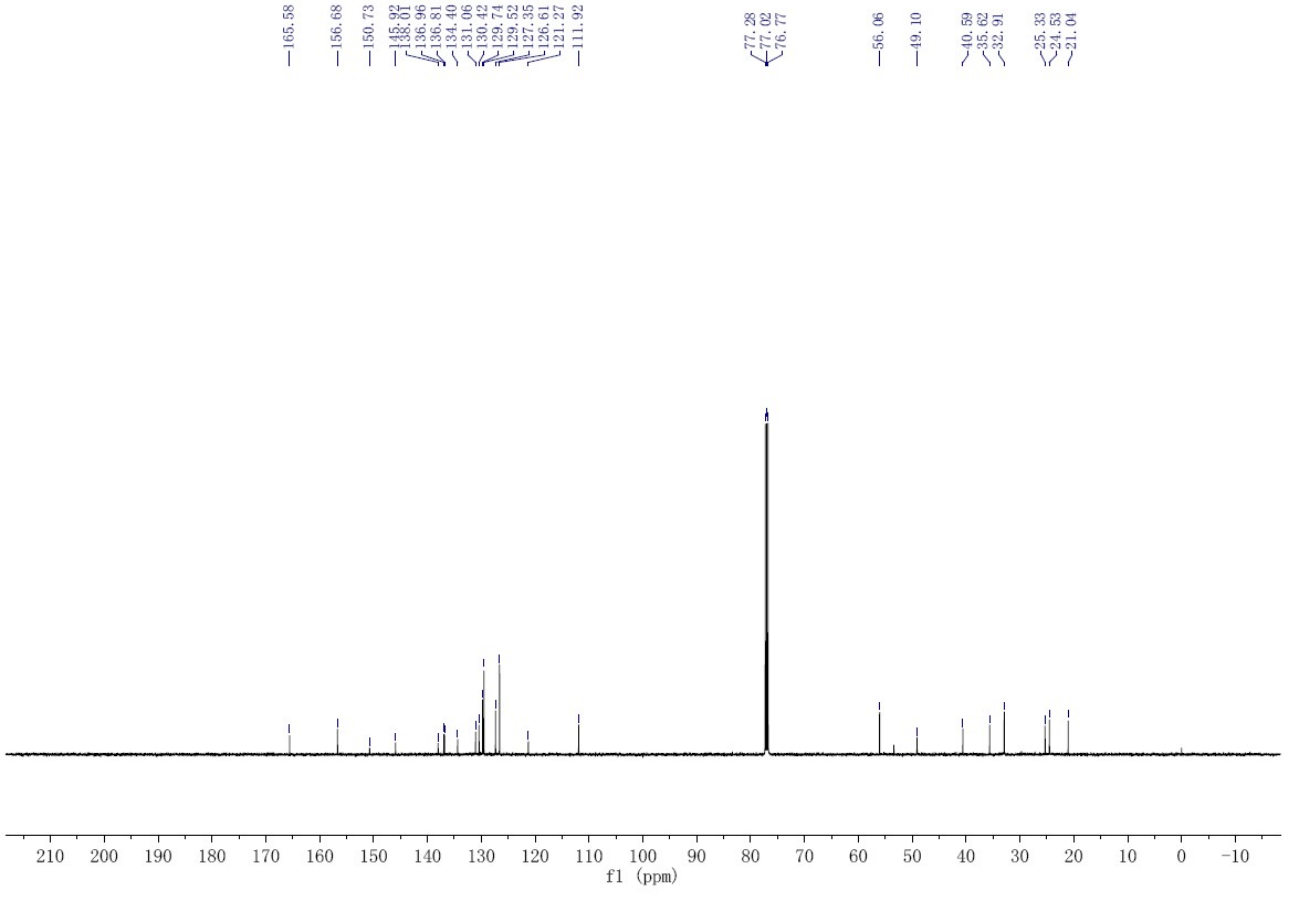

7.54
7.52
7.43
7.41
7.40
7.34
7.33
7.31
7.23
7.18
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.13
7.12
7.11
7.11
7.08
7.08
6.92
6.91
6.90
6.89
6.86
6.86
3.98
3.96
3.95
2.42
2.40
2.18
2.01
1.99
1.98
1.96
1.95
N
N
S
2.03
2.02
1.00
3.83
0.98
2.11
1.93
2.36
6.00
2.05
f1 (ppm)


145.73
145.22
141.04
140.73
128.78
127.63
127.50
127.38
127.29
127.03
125.13
124.41
122.53
121.39
115.71
114.53
77.34
77.08
76.83
57.26
45.64
45.57
25.39
f1 (ppm)


7.85
7.83
7.81
7.80
7.70
7.69
7.65
7.64
7.49
7.48
7.46
7.42
7.41
7.40
7.39
7.26
6.90
6.88
5.12
5.11
5.10
5.09
5.07
1.67
1.22
1.21
Me
O
Me
O
O
Me
Me
O
2.00
2.11
2.04
2.13
2.03
1.08
2.02
1.02
6.33
6.37
f1 (ppm)


195.10
173.16
159.56
144.81
140.10
136.84
131.98
130.83
130.40
128.94
128.09
127.28
126.90
117.30
79.43
77.28
77.03
76.77
69.31
25.41
21.53
f1 (ppm)


MeO
H
N
O
O
O
S
O
N
H
N
H
O
Me
f1 (ppm)


f1 (ppm)