Supporting Information

Photoelectric properties for aromatic triangular tri-palladium complexes and their catalytic applications in Suzuki-Miyaura coupling reaction

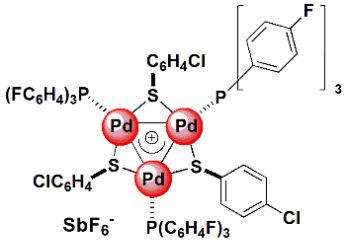
1. General Remarks

All reagents were purchased from commercial sources. Chloroform was dewatered using a dewatering system, but it did not need to be treated with bases. Reactions and filtrations were carried out under N_2 using standard Schlenk technique. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 300K on a Varian spectrometer (500M) using TMS as internal standard (0.00 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR for $CDCl_3$). ^{13}C NMR spectra were recorded at 126 MHz. For ^{31}P NMR, H_3PO_4 was used as external standards (0.00 ppm). ^{19}F NMR spectra were recorded at 471 MHz. Cyclic voltammetry experiments were performed on an electrochemical workstation (CHI 760C) with 0.1 M $^{n}Bu_4NPF_6$ as supporting electrolyte. The reference electrode used in the CV experiment was an Ag/AgCl electrode, the working electrode was a glassy carbon electrode, and the auxiliary electrode was a platinum wire. CV data were referenced relative to the ferrocene/ferrocenium couple. The photoluminescence spectra were measured using a steady state transient fluorescence spectrometer (FLS1000). Exact masses were recorded on a high resolution tandem time LC/MS instrument (G2-XSQTOF Mass Spectrometry). Most of the coupling reactions were qualitative by GC-MS (Agilent Technologies 7000D) and quantified by GC (GC-2014C).

2. Synthesis of catalysts 1-4

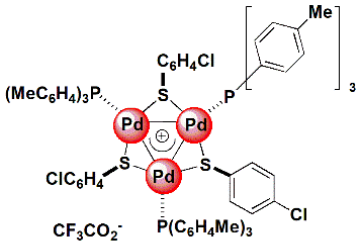
Under nitrogen, $Pd(dba)_2$ (115 mg, 0.2 mmol, 1 equiv.) and freshly degassed $CHCl_3$ (20 mL) were sequentially added to the Schlenk bottle that had been dried at high temperature. After $Pd(dba)_2$ was completely dissolved, the required phosphine (0.2 mmol, 1 equiv.) and disulfide/diselenide (0.1 mmol, 0.5 equiv.) were added under N_2. The resulting mixture was stirred at room temperature for 2 hours until the solution turned deep red. Then silver salt (0.067 mmol, 0.33 equiv.) was introduced under N_2, and the solution was stirred at room temperature in the dark for 1 hour. After the reaction was complete, the mixture was filtered through a pad of celite and the solvent was removed under vacuum. The obtained dark red solid was dissolved in

1 mL of $CHCl_3$ and precipitated with excess n-hexane (1:30 v:v). The yellow solution was removed through a bidirectional needle and the remained solid was dried under vacuum. This operation was repeated 3 times to completely remove the by-products leaving the pure $[Pd_3]^+$ as a red/orange solid. The characterization of the four complexes were consistent with the relevant literatures.[1-3]



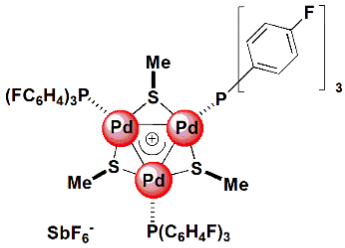
1

Red solid，117 mg, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 – 7.07 (m, 18H), 6.89 (t, *J* = 8.5 Hz, 18H), 6.73 (d, *J* = 8.1 Hz, 6H), 6.32 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.95, 143.34, 134.86, 130.51, 128.99, 128.41, 125.48, 116.29. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 14.10.



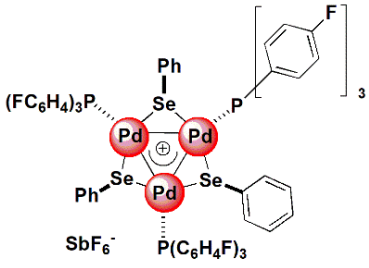
2

Orange solid, 94 mg, 97% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.05 – 6.89 (m, 36H), 6.58 (d, *J* = 8.2 Hz, 6H), 6.16 (d, *J* = 8.3 Hz, 6H), 2.32 (s, 27H). ^{13}C NMR (126 MHz, Chloroform-d) δ 140.97, 135.81, 134.85, 133.47, 133.35, 129.01, 127.95, 21.34. ^{31}P NMR (202 MHz, Chloroform-*d*) δ 15.24.



3

Orange solid, 95 mg, 86% yield, ^{1}H NMR (500 MHz, Chloroform-d) δ 7.49 – 7.46 (m, 18H), 7.15 (t, J = 8.5 Hz, 18H), 1.16 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-d) δ 165.46, 163.43, 136.12, 116.36, 76.76, 17.63. ^{31}P NMR (202 MHz, Chloroform-d) δ 14.14.



4

Product was purified on silica gel (acetone/hexane = 1/2). Dark red solid, 54 mg, 51% yield. ^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.57-7.31 (m, 18H), 7.23 (t, J = 7.6 Hz, 3H), 6.98 (t, J = 8.5 Hz, 18H), 6.91 (t, J = 7.6 Hz, 6H), 6.28 (d, J = 7.6 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-d): δ 165.0, 137.8,137.3, 135.8, 129.4, 129.0, 128.4, 116.4.

3.Photochemical and electrochemical properties of triangular tri-palladium complexes 2-4

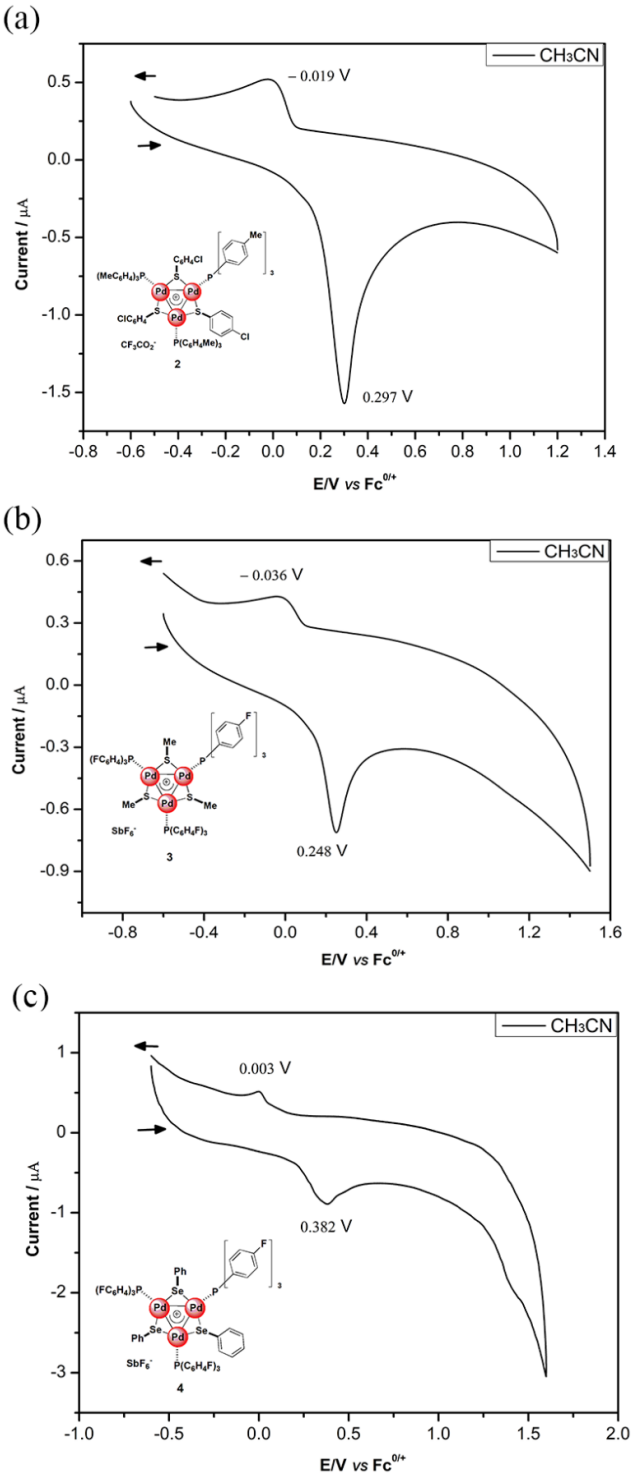


Fig. S1 Cyclic voltammogram of (a) complex **2**, (b) complex **3**, (c) complex **4**. Supporting electrolyte: nBu_4NPF_6 (0.1M); working electrodes: glassy carbon electrodes: counter electrodes: Pt; reference electrode: Ag/AgCl; scan rate: 0.200 Vs^{-1}; solvent: CH_3CN; temperature: 298K; internal reference: $Fe(Cp^*)_2$

The investigations of the cyclic voltametric properties of $[Pd_3]^+$ (**2, 3, 4**) were operated under electrochemical conditions. In general, the redox potential of $[Pd_3]^+$ was referenced vs an Ag/AgCl electrode with the FcH/FcH^+ redox couple as an internal calibrant. When the cyclic voltammogram was carried out in CH_3CN with nBu^4NPF_6 as the supporting electrolyte (Fig. S1), The CV of **2** showed one quasi-reversible wave ($E_{1/2}$=0.139 V). This shows that the electronic effect of the substituent on the phosphine ligand has little effect and the Pd^+/Pd^{2+} redox process in **2** was reversible. The cyclic voltammogram of **3** and **4** also showed quasi-reversible waves (**3**: $E_{1/2}$=0.109 V; **4**: $E_{1/2}$=0.190 V). It can be concluded that $[Pd_3]^+$ had good redox characteristics and could enable stable electron transfer in catalysis.

The emissions of complex **2-4** in different organic solvents (MeOH, CH_3COCH_3, $CHCl_3$, CH_3CN, THF) were examined as well at room temperature (Fig. S2). Like complex **1**, the fluorescence emission intensity of complex **2** in acetone was the largest, while, the intensity in acetonitrile was the lowest. Complex **3** exhibited stable fluorescence characteristics in all five solvents. Complex **4** showed stable fluorescence emissions (350 nm, 540 nm, 625 nm) in five different solvents.

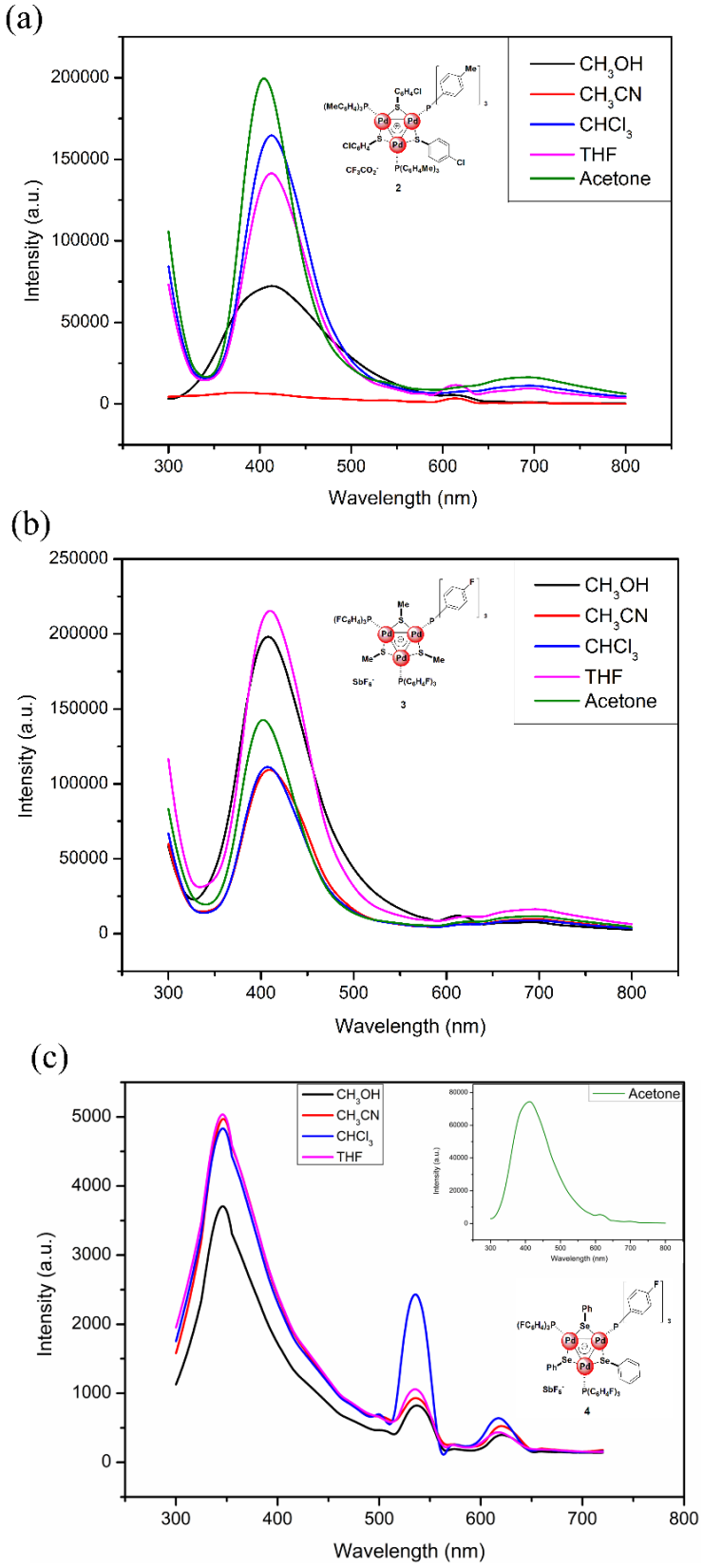


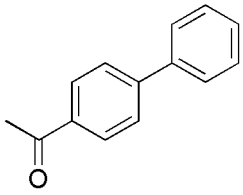
Fig. S2 Fluorescence emission of (a) complex **2** (λ_{ex} = 266 nm) (b) complex **3** (λ_{ex} = 259 nm), (c) complex **4** (λ_{ex} = 280 nm) in different solvents (MeOH, CH_3COCH_3, $CHCl_3$, CH_3CN, THF).

4. Triangular tri-palladium complexes catalyzed Suzuki reactions

General synthesis

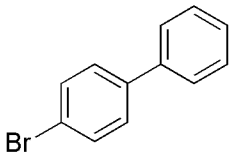
To a 25 ml round-bottom flask aryl halides (0.5 mmol, 1.0 equiv.), arylboronic acid (1.0 mmol, 2.0 equiv.), the $[Pd_3]^+$ (1.25×10^{-3} mmol，0.0025equiv.) and K_2CO_3 were added. The system underwent three vacuum/nitrogen cycles and then CH_3CN/H_2O (3ml/1ml) was injected into the round bottom flask. After stirring at 80°C, the reactions were tracked by TLC and GC-MS analysis, the desired products were purified by silica gel column chromatography. Spectroscopic data corresponds to the literatures.

(Table 1, entry 7) 4-Acetylbiphenyl[4]



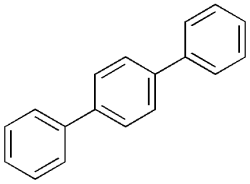
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). Light yellow powder, 96 mg, 98% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.71 – 7.65 (m, 2H), 7.65 – 7.60 (m, 2H), 7.50 – 7.37 (m, 3H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.7, 145.8, 139.9, 135.9, 128.9, 128.9, 128.2, 127.3, 127.2, 26.6.

(Table 2, entry 3) 4-Bromobiphenyl[5]



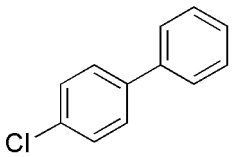
Product was purified on silica gel (petroleum ether). White crystalline powder, 104 mg, 90% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 4H), 7.46 – 7.39 (m, 4H), 7.38 – 7.32 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.2, 140.1, 131.9, 128.9, 128.7, 127.6, 126.9, 121.5.

(Table 2, entry 3) p-Terophenyl[6]



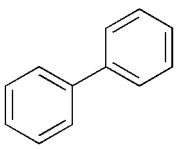
Product was purified on silica gel (petroleum ether). White flake crystal, 12 mg, 10% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s, 4H), 7.64 (d, *J* = 8.7 Hz, 4H), 7.45 (dd, *J* = 8.4, 7.0 Hz, 4H), 7.38 – 7.33 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) δ 140.76, 140.17, 128.85, 127.54, 127.38, 127.09.

(Table 2, entry 6) 4-Chlorobiphenyl[7]



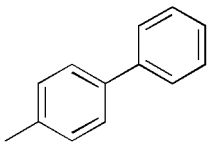
Product was purified on silica gel (petroleum ether). Light yellow crystalline powder, 88 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 4H), 7.49 – 7.36 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.1, 139.7, 133.4, 128.9, 128.9, 128.4, 127.6, 127.1.

(Table 3, entry 1) Biphenyl[8].



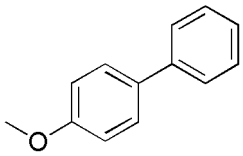
Product was purified on silica gel (petroleum ether). White crystalline powder, 74 mg, 96% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 4H), 7.43 (dd, *J* = 8.5, 6.9 Hz, 4H), 7.37 – 7.31 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.3, 128.8, 127.3, 127.2.

(Table 3, entry 2) 4-Methylbiphenyl[9]



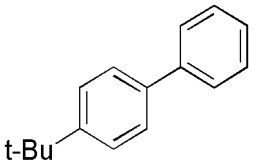
Product was purified on silica gel (petroleum ether). White crystalline powder, 82 mg, 97% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.49 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.2, 138.4, 137.1, 129.5, 128.7, 127.0, 127.0, 21.1.

(Table 3, entry 3) 4-Methoxybiphenyl[10]



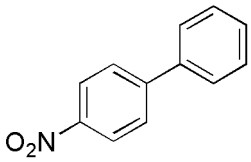
Product was purified on silica gel (petroleum ether). White powder, 87 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 4H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.25 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4.

(Table 3, entry 4) 4-tert-Butylbiphenyl[11]



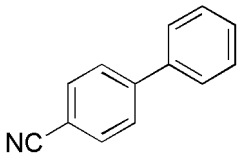
Product was purified on silica gel (petroleum ether). White solid, 96 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-d) δ 150.3, 141.2, 138.4, 128.8, 127.1, 127.1, 126.9, 125.8, 34.6, 31.4.

(Table 3, entry 5) 4-Nitrobiphenyl[12]



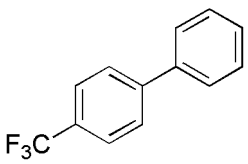
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). White needle crystal, 97 mg, 97% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.65 – 7.60 (m, 2H), 7.53 – 7.42 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.6, 147.1, 138.7, 129.2, 128.9, 127.8, 127.4, 124.1.

(Table 3, entry 6) 4-Cyanobiphenyl[13]



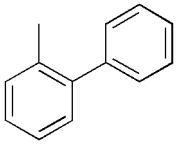
Product was purified on silica gel (petroleum ether). Beige crystalline powder, 85 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 4H), 7.52 – 7.47 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 118.9, 110.9.

(Table 3, entry 7) 4-(Trifluoromethyl)biphenyl[14]



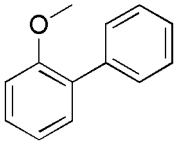
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). White solid, 100 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (s, 4H), 7.60 – 7.57 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.7, 139.8, 129.5, 129.1, 128.2, 127.4, 127.3, 125.7 (q, *J* = 3.8 Hz), 123.2.

(Table 3, entry 8) 2-Phenyltoluene[15]



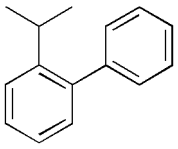
Product was purified on silica gel (petroleum ether). White crystal, 79 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.27 – 7.21 (m, 4H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.1, 127.2, 126.7, 125.7, 20.4.

(Table 3, entry 9) 2-Methoxylbiphenyl[16]



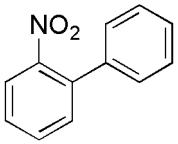
Product was purified on silica gel (petroleum ether/ethyl acetate=10/). White solid, 86 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 3H), 7.10 – 7.00 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.5, 138.6, 130.9, 130.8, 129.6, 128.6, 128.1, 126.9, 120.9, 111.3, 55.6.

(Table 3, entry 10) 2-Isopropylbiphenyl[17]



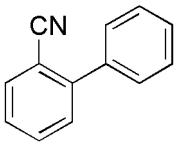
Product was purified on silica gel (petroleum ether). White solid, 94 mg, 96% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 2H), 3.17 – 2.95 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 6H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.4, 142.1, 141.1, 129.9, 129.3, 128.0, 127.7, 126.7, 125.5, 125.3, 29.3, 24.3.

(Table 3, entry 11) 2-Nitrodiphenyl[18]



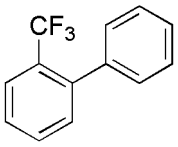
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). Light yellow powder, 92 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64– 7.60 (m, 1H), 7.51 – 7.40 (m, 5H), 7.37 – 7.29 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.3, 137.3, 136.3, 132.2, 131.9, 128.6, 128.1, 128.1, 127.8, 124.0.

(Table 3, entry 12) 2-Cyanobiphenyl[19]



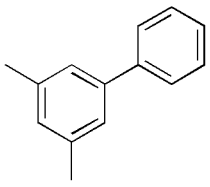
Product was purified on silica gel (petroleum ether). White solid, 85 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 – 7,62 (m, 1H), 7.58 – 7.54 (m, 2H), 7.53 – 7.47 (m, 3H), 7.46 – 7.42 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.5, 139.6, 138.1, 133.7, 132.8, 130.1, 128.7, 127.5, 118.7, 111.3.

(Table 3, entry 13) 2-(Trifluoromethyl)biphenyl[20]



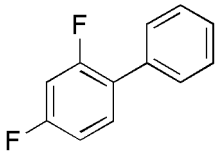
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). White solid, 99 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (dd, J = 7.9, 1.3 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.48 – 7.45 (m, 1H), 7.40 –7.38 (m, 3H), 7.34 –7.31 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.4, 139.8, 132.0, 131.2, 128.9, 128.6, 127.7, 127.6, 127.3, 126.1 (q, *J* = 5.3 Hz), 123.1.

(Table 3, entry 14) 3,5-dimethyl-1,1'-biphenyl[21]



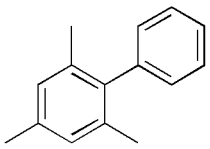
Product was purified on silica gel (petroleum ether). colorless oil, 83 mg, 92% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.20 (s, 2H), 6.98 (s, 1H), 2.37 (s, 6H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.6, 141.4, 138.3, 128.9, 128.7, 127.3, 127.1, 125.2, 21.5.

(Table 3, entry 15) 2,4-Difluorobiphenyl[22]



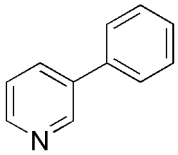
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). White crystal, 86 mg, 91% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50–7,48 (m, 2H), 7.46 – 7.34 (m, 4H), 6.98 – 6.86 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.3 (dd, *J* = 248.9, 11.9 Hz), 159.8 (dd, *J* = 250.2, 11.8 Hz), 135.0, 131.5 (dd, *J* = 9.3, 4.8 Hz), 128.9, 128.6, 127.7, 125.4 (d, *J* = 17.5 Hz), 111.6 (dd, *J* = 21.1, 3.7 Hz), 104.4.

(Table 3, entry 16) 2,4,6-Trimethyl-1,1'-biphenyl[23]



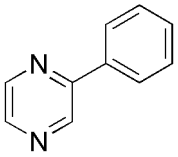
Product was purified on silica gel (petroleum ether). White solid, 88 mg, 90% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.21 – 7.13 (m, 2H), 6.98 (s, 2H), 2.37 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.1, 139.1, 136.5, 136.0, 129.3, 128.3, 128.1, 126.5, 21.1, 20.7.

(Table 4, entry 1) 3-Phenylpyridine[24]



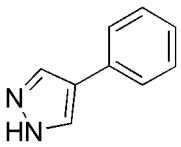
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). Colorless oily liquid, 73 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 8.85 (d, J = 2.3 Hz, 1H), 8.58 (dd, J = 4.8, 1.6 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.57 (dd, J = 7.3, 2.0 Hz, 2H), 7.46 (dd, J = 8.6, 6.8 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7,32 m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.49, 148.37, 137.87, 136.67, 134.35, 129.10, 128.12, 127.17, 123.55.

(Table 4, entry 2) 2-Phenylpyrazine[25]



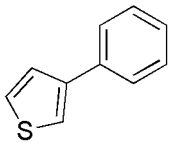
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). Oily liquid, 70 mg, 90% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.04 (d, *J* = 1.6 Hz, 1H), 8.64 (dd, *J* = 2.5, 1.6 Hz, 1H), 8.51 (d, *J* = 2.5 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.54 – 7.48 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.9, 144.2, 142.9, 142.2, 136.4, 129.9, 129.1, 126.9.

(Table 4, entry 3) 3-Phenyl-1H-pyrazole



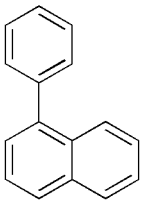
There was the trace amount of desired product.

(Table 4, entry 4) 3-Phenylthiophene[26]



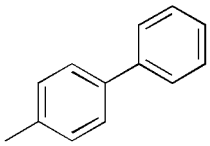
Product was purified on silica gel (petroleum ether). White solid, 76 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.40 (m, 1H), 7.39 – 7.34 (m, 4H), 7.29 – 7.24 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4, 135.9, 128.8, 127.1, 126.5, 126.4, 126.2, 120.3.

(Table 4, entry 5) 1-Phenylnaphthalene[27]



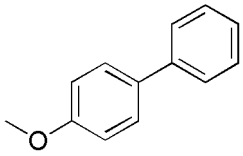
Product was purified on silica gel (petroleum ether). Yellow viscous liquid, 95 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 –7.81 (m, 2H), 7.79 – 7.76 (m, 1H), 7.44 – 7.39 (m, 6H), 7.36 – 7.33 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.7, 140.2, 133.8, 131.6, 130.1, 128.7, 128.2, 127.6, 127.2, 126.9, 126.0, 126.0, 125.7, 125.3.

(Table 5, entry 1) 4-Methylbiphenyl



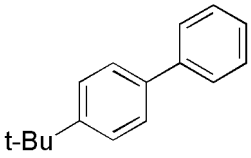
Product was purified on silica gel (petroleum ether). White crystalline powder, 82 mg, 97% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.49 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.2, 138.4, 137.1, 129.5, 128.7, 127.0, 127.0, 21.1. Characterization data is consistent with (Table 3, entry 2)

(Table 5, entry 2) 4-Methoxybiphenyl



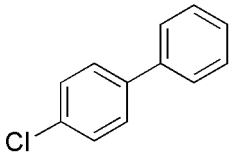
Product was purified on silica gel (petroleum ether). White powder, 87 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 4H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.25 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4. Characterization data is consistent with (Table 3, entry 3)

(Table 5, entry 3) 4-tert-Butylbiphenyl



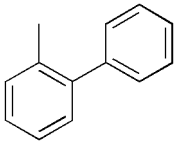
Product was purified on silica gel (petroleum ether). White solid, 96 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-d) δ 150.3, 141.2, 138.4, 128.8, 127.1, 127.1, 126.9, 125.8, 34.6, 31.4. Characterization data is consistent with (Table 3, entry 4).

(Table 5, entry 4) 4-Chlorobiphenyl



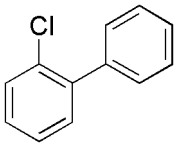
Product was purified on silica gel (petroleum ether). Light yellow crystalline powder, 88 mg, 95% yield, Petroleum ether. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 4H), 7.49 – 7.36 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.1, 139.7, 133.4, 128.9, 128.9, 128.4, 127.6, 127.1. Characterization data is consistent with (Table 2, entry 6).

(Table 5, entry 5) 2-Phenyltoluene



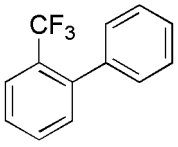
Product was purified on silica gel (petroleum ether). White crystal, 79 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.27 – 7.21 (m, 4H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.1, 127.2, 126.7, 125.7, 20.4. Characterization data is consistent with (Table 3, entry 8)

(Table 5, entry 6) 2-Chlorobiphenyl[28]



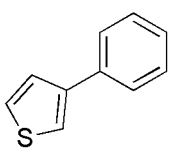
Product was purified on silica gel (petroleum ether). Light yellow powder, 91 mg, 97% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 5H), 7.40 – 7.36 (m, 1H), 7.35 – 7.25 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.5, 139.4, 132.5, 131.4, 129.9, 129.4, 128.5, 128.1, 127.6, 126.8.

(Table 5, entry 7) 2-(Trifluoromethyl)biphenyl



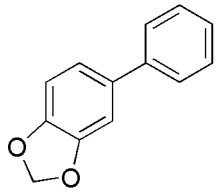
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). White solid, 100 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (dd, J = 7.9, 1.3 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.48 – 7.45 (m, 1H), 7.40 –7.38 (m, 3H), 7.34 –7.31 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.4, 139.8, 132.0, 131.2, 128.9, 128.6, 127.7, 127.6, 127.3, 126.1 (q, *J* = 5.3 Hz), 123.1. Characterization data is consistent with (Table 3, entry 13)

(Table 5, entry 8) 3-Phenylthiophene



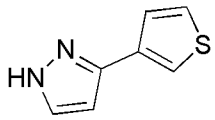
Product was purified on silica gel (petroleum ether). White solid, 77 mg, 96% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.40 (m, 1H), 7.39 – 7.34 (m, 4H), 7.29 – 7.24 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4, 135.9, 128.8, 127.1, 126.5, 126.4, 126.2, 120.3. Characterization data is consistent with (Table 4, entry 4)

(Table 5, entry 9) 5-phenyl-1,3-benzodioxole[29]



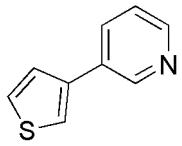
Product was purified on silica gel (petroleum ether). White solid, 93 mg, 94% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.54 (m, 2H), 7.48 – 7.41 (m, 2H), 7.35 (s, 1H), 7.16 – 7.07 (m, 2H), 6.93 – 6.90 (m, 1H), 6.01 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.2, 147.1, 141.0, 135.6, 128.8, 126.9, 126.9, 120.6, 108.6, 107.7, 101.1.

(Table 5, entry 10) 3-(3-thienyl)-1H-pyrazole



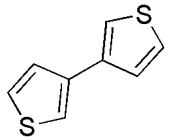
There was the trace amount of desired product.

(Table 5, entry 11) 3-(thiophen-3-yl)pyridine[30]



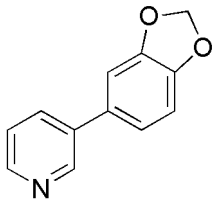
Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). Yellow viscous liquid, 77 mg, 96% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 2.4 Hz, 1H), 8.56 – 8.51 (m, 1H), 7.88 – 7.86 (m, 1H), 7.52 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.45 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.39 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.33 (dd, *J* = 7.9, 4.8 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.1, 147.6, 138.8, 133.6, 131.6, 127.0, 125.9, 123.6, 121.5.

(Table 5, entry 12) 3,3'-Bithiophene[31]



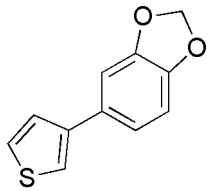
Product was purified on silica gel (petroleum ether). White solid, 79 mg, 96% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 2.8, 1.4 Hz, 2H), 7.37 – 7.33 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.3, 126.4, 126.1, 119.8.

(Table 5, entry 13) 3-(3,4-methylenedioxyphenyl)pyridine[32]



Product was purified on silica gel (petroleum ether/ethyl acetate=10/1). White solid, 93 mg, 93% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 8.55 (d, *J* = 3.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 7.5, 4.7 Hz, 1H), 7.04 (s, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.4, 148.1, 147.8, 136.4, 134.1, 131.9, 123.5, 120.8, 108.9, 107.5, 101.3, 29.7.

(Table 5, entry 14) 5-(thiophen-3-yl)benzo[d][1,3]dioxole[33]



Product was purified on silica gel (petroleum ether). White solid, 97 mg, 95% yield. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 3H), 7.09 – 7.05 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.98 (s, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.1, 146.8, 142.1, 130.3, 126.3, 126.1, 119.9, 119.3, 108.5, 107.1, 101.1, 29.7.

Examination of stabilities of $[Pd_3]^+$ species during catalytic Suzuki reaction

The HRMS tracking study had been realized to investigate whether $[Pd_3]^+$ were present in the reaction process throughout these catalytic Suzuki reaction. Model reaction between 4'-iodoacetophenone and phenylboronic acid catalyzed by **1** was

detected by HRMS from 0 to 6 hours and reaction samples were collected each hour. Experimental results showed that the catalyst (centered at m/z = 1698) remained until complete conversion of the substrate was found.

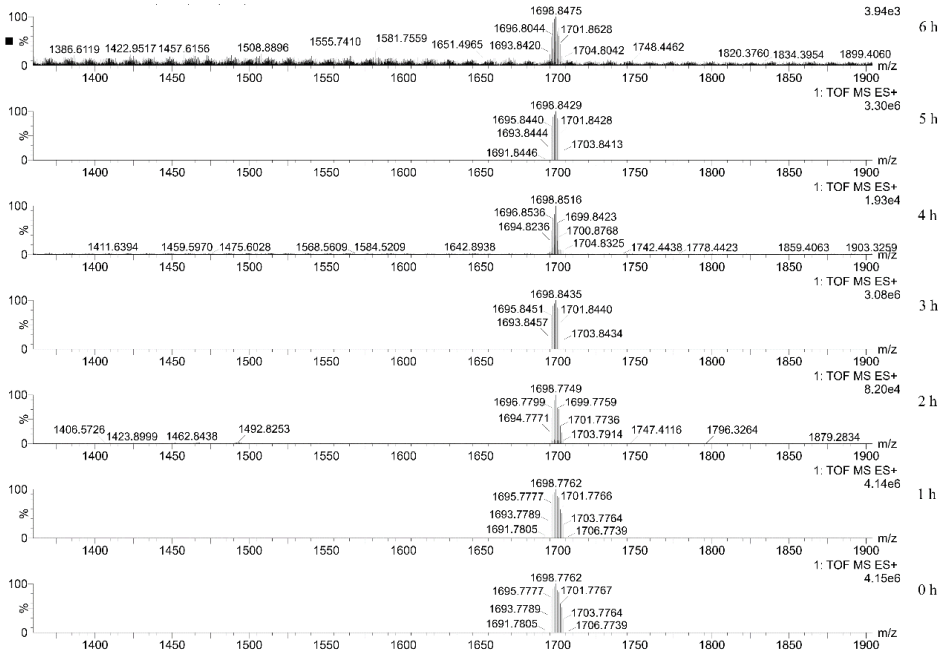


Fig. S3 HRMS tracking of $[Pd_3]^+$ in the Suzuki reaction.

The UV−vis spectrum of the solution showed that the absorption spectrum of $[Pd_3]^+$ remained almost unchanged during the reaction and indicated that there was no obvious cluster size change or decomposition.

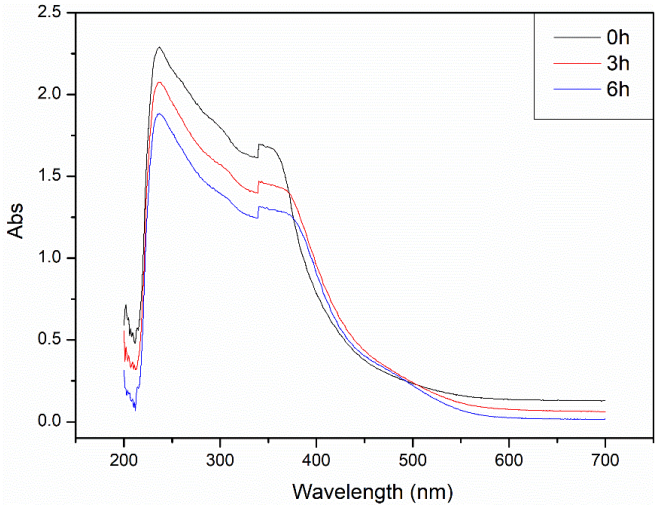
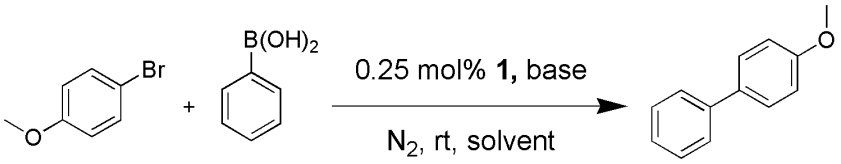


Fig. S4 UV-vis spectrum tracking of $[Pd_3]^+$ in the Suzuki reaction.

5. Reaction condition screening of 1-catalyzed coupling reaction of 4-methoxy-1-bromobenzene

Table S1. Suzuki reaction of 4-methoxy-1-bromobenzene and phenylboronic acid[a]



Entry	Solvent	Base	T[h]	Yield (%)[b]
1	DMF/H_2O=1/1	K_2CO_3	0.5	trace
2	DMF/H_2O=2/1	K_2CO_3	6	trace
3	DMF/H_2O=1/4	K_2CO_3	6	trace
4	CH_2Cl_2	K_2CO_3	5	trace
5	THF	K_2CO_3	5	trace
6	Dioxane	K_2CO_3	5	trace
7	CH_3CN	K_2CO_3	5	trace
8	CH_3OH	K_2CO_3	5	trace
9	CH_3CH_2OH	K_2CO_3	5	trace
10	Dioxane	$N(C_2H_5)_3$	6	trace
11	Dioxane	Na_3PO_4	6	trace
12	CH_3OH	$N(C_2H_5)_3$	6	trace

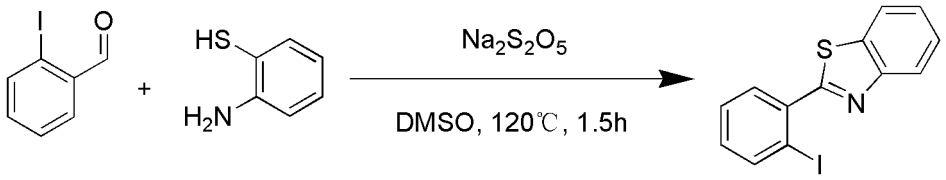
[a]Reaction conditions: 4-methoxy-1-bromobenzene (0.5 mmol, 1.0 equiv.), phenylboronic acid (0.75 mmol, 1.5 equiv.), catalyst **1** (0.00125 mmol, 0.24 g, 0.0025 equiv.), base (1 mmol, 2 equiv.), room temperature, in N_2, the reaction was monitored by TLC and GC. [b]GC yields.

The conditions for the $[Pd_3]^+$ catalyzed reaction between 4-methoxy-1-bromobenzene and phenylboronic acid had been examined (Table S1). However, under general conditions, [34] **1** did not show any catalytic activity for the coupling reaction (Table S1, Entry 1). Therefore, the reaction conditions were adjusted. We first changed the ratio of DMF to H_2O in the original reaction. Two

solvents ratios (DMF/H_2O=2/1, 1/4) were tried, and the reaction time was extended to 6 h, but still only trace products were obtained (Table S1, Entries 2,3). Next, several solvents were examined, including dichloromethane, tetrahydrofuran, dioxane, acetonitrile (Table S1, Entries 4-7) and alcohol (methanol and ethanol) (Table S1, Entries 8, 9). The reaction did not achieve any reactivity in these solvents. Finally, the base was also screened. Regardless of changing from K_2CO_3 to Na_3PO_4 or organic base $N(C_2H_5)_3$, no catalytic reactivity was obtained (Table S1, Entries 10-12).

6. Synthesis of 2-[1,1'-Biphenyl]-2-ylbenzothiazole

Synthesis of precursor 2-(2-Iodophenyl)benzo[*d*]thiazole



Scheme S1. Synthesis of precursor

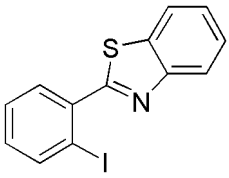
Following a slightly modified procedure from literature, 2-iodobenzaldehyde (0.7 g, 3.0 mmol, 1 equiv.) and sodium disulfite (0.4 g, 3 mmol, 1 equiv.) were added to a 25 ml round bottom flask and then DMSO (4 ml) was added. Then 2-aminothiophenol (0.8 g, 3 mmol, 1 equiv.) was added to the system. The reaction mixture was stirred at 120° C for 1.5 h. After the reaction system was cooled to room temperature, 100 ml of H_2O was added. The mixture was extracted with dichloromethane (3×150 ml) and the combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The solid obtained under vacuum was purified by column chromatography on silica gel (cyclohexane/EtOAc 30:1) to give 2-(2-iodophenyl)benzo[*d*]thiazole (1.5 g, 4.5 mmol, 75%) as a yellow solid.

Synthesis of an analogue of COX-2-selective inhibitor 2-[1,1'-Biphenyl]-2-ylbenzothiazole

To a 25 ml round-bottom flask, phenylboronic acid (0.18 mmol，3 equiv.), 2-(2-iodophenyl)benzo[*d*]thiazole (0.06 mmol, 1 equiv.), **1** (0.00125 mmol, 0.0025 equiv), K_2CO_3 (0.18 mmol, 3 equiv.) and CH_3CN/H_2O (3/1) were added successively. After stirring at 80℃ for 12h, the reaction was tracked by TLC and GC-MS analysis. The solution was filtered and dried under vacuum and then the solid was separated by

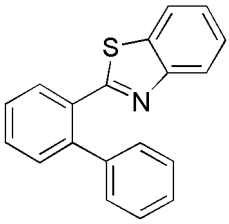
silica gel column (cyclohexane/EtOAc 30:1) to obtain the 2-[1,1'-Biphenyl]-2-ylbenzothiazole (isolated yield = 94%).

2-(2-Iodophenyl)benzo[d]thiazole (Scheme S1)[35]



(Light yellow solid, 1.5 g, 75% yield) ^{1}H NMR (500 MHz, Chloroform-d) δppm 8.17 – 8.15 (m, 1H), 8.04 (dd, J = 8.0, 1.2 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.72 (dd, J = 7.7, 1.7 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 7.19 – 7.15 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-d) δ 167.9, 153.1, 140.7, 138.5, 136.2, 131.5, 131.3, 128.2, 126.4, 125.6, 123.8, 121.6, 96.4.

2-[1,1'-Biphenyl]-2-ylbenzothiazole (Scheme 2) [36]

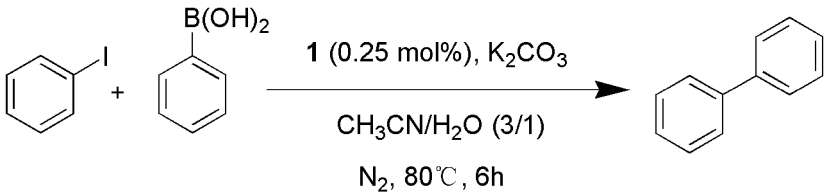


(White solid, 48 mg, 94% yield) ^{1}H NMR (500 MHz, Chloroform-d) δppm 8.09 – 8.06 (m, 1H), 8.05 – 8.03 (m, 1H), 7.72 – 7.70 (m, 1H), 7.54 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 -7.29 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-d) δ 167.9, 152.8, 141.8, 140.3, 136.7, 132.7, 130.9, 130.5, 130.1, 130.0, 128.4, 127.8, 125.9, 124.9, 123.3, 121.4.

7. GC/GC-MS data of reaction GC data of Suzuki-Miyaura coupling reactions

Suzuki reactions of phenyl/ para-substituted phenyl iodides with phenylboronic acid

(Table 3, entry 1)



Scheme S2 1-catalyzed the reaction of iodobenzene and phenylboronic acid.

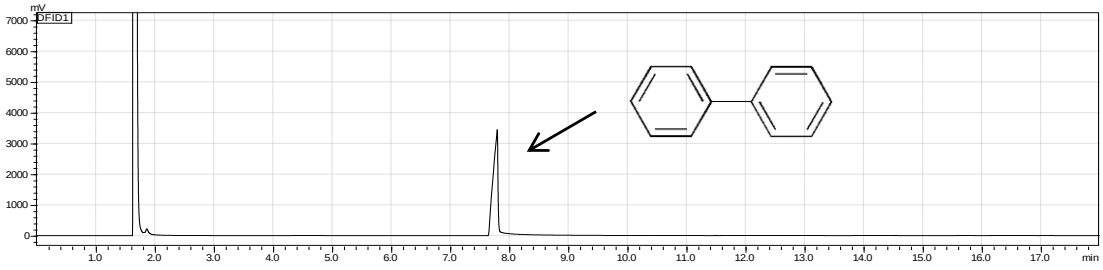
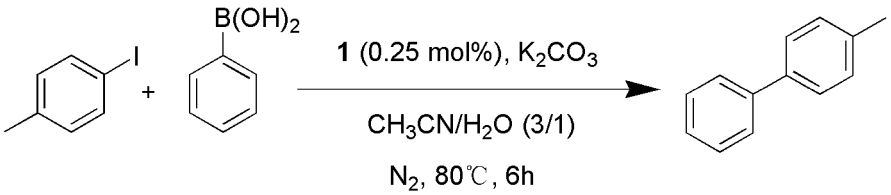


Fig. S5 GC of the reaction of iodobenzene and phenylboronic acid.

(Table 3, entry 2)



Scheme S3 1-catalyzed reaction of 4-iodotoluene and phenylboronic acid.

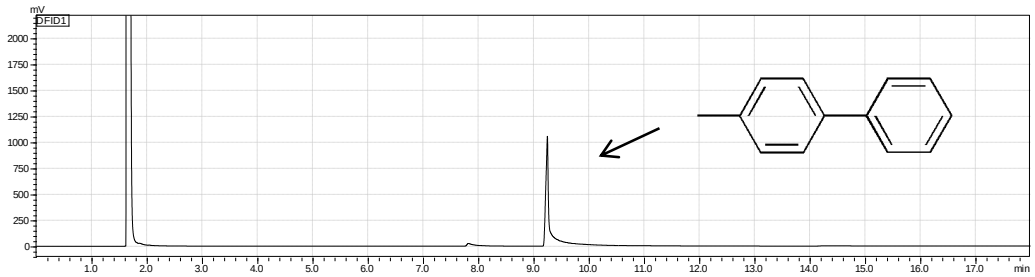
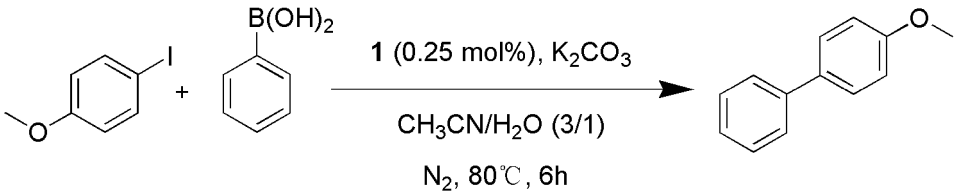


Fig. S6 GC of reaction of 4-iodotoluene and phenylboronic acid.

(Table 3, entry 3)



Scheme S4 1-catalyzed reaction of 4-iodoanisole and phenylboronic acid.

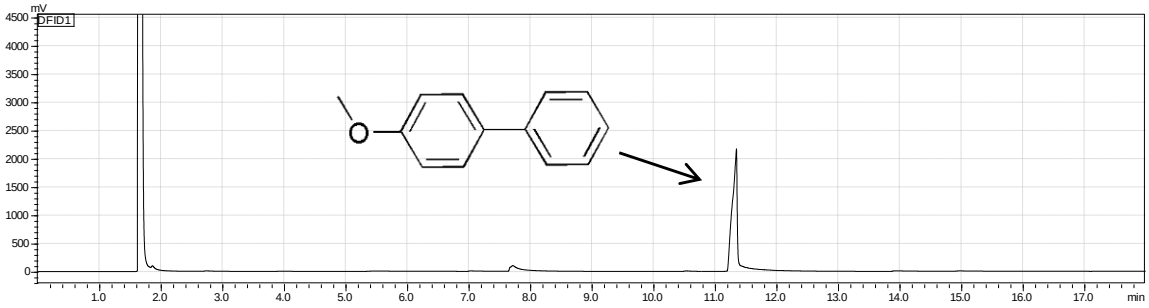
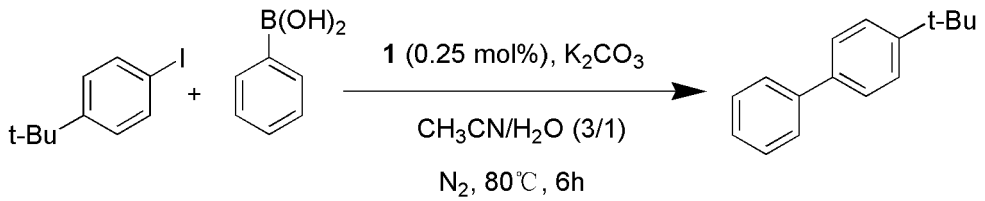


Fig. S7 GC of the reaction of 4-iodoanisole and phenylboronic acid.

(Table 3, entry 4)



Scheme S5 1-catalyzed reaction of 1-tert-butyl-4-iodobenzene and phenylboronic acid.

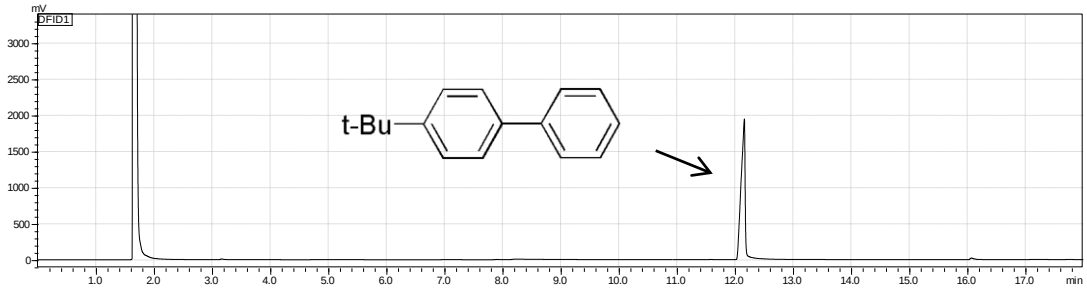
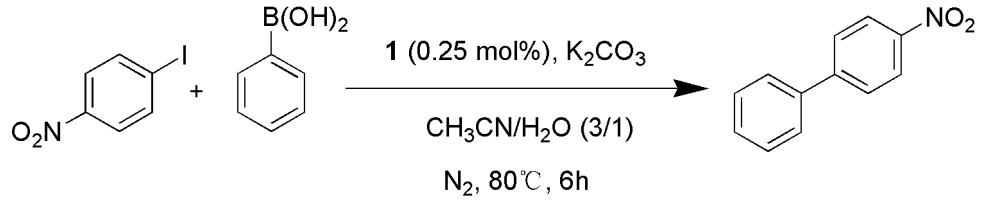


Fig. S8 GC of the reaction of 1-tert-butyl-4-iodobenzene and phenylboronic acid.

(Table 3, entry 5)



Scheme S6 1-catalyzed reaction of 1-iodo-4-nitrobenzene and phenylboronic acid.

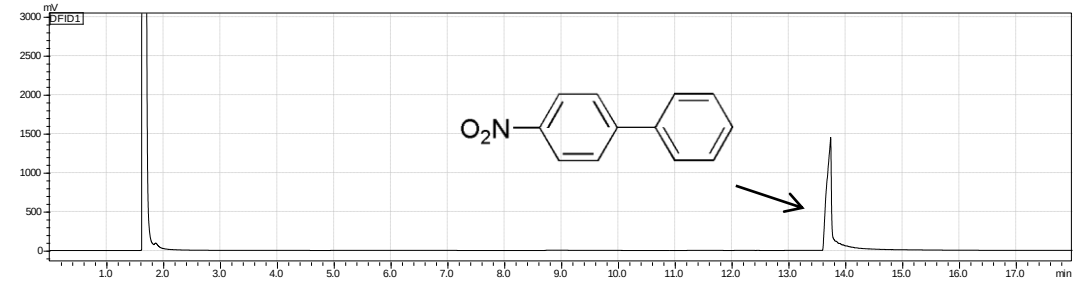
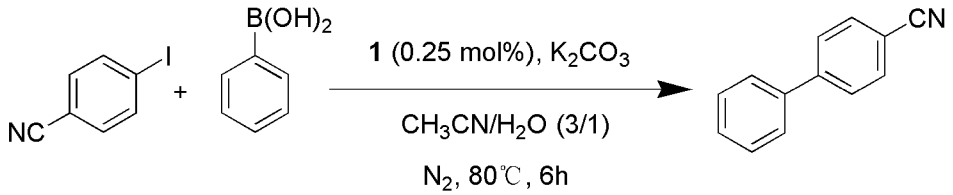


Fig. S9 GC of the reaction of 1-iodo-4-nitrobenzene and phenylboronic acid.

(Table 3, entry 6)



Scheme S7 1-catalyzed reaction of 4-iodobenzonitrile and phenylboronic acid.

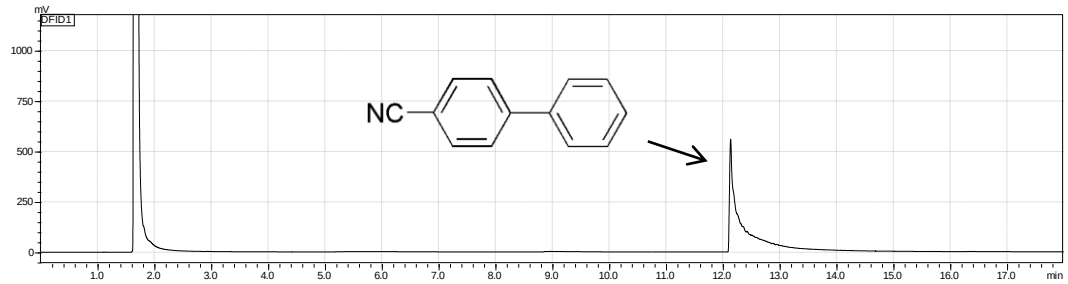
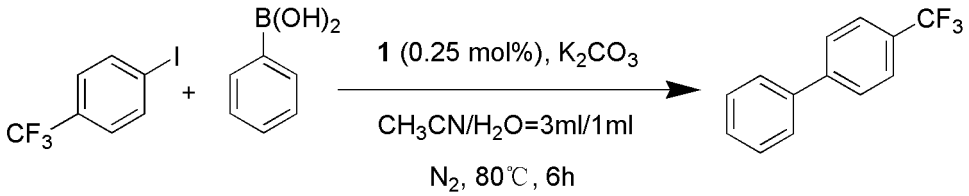


Fig. S10 GC of the reaction of 4-iodobenzonitrile and phenylboronic acid.

(Table 3, entry 7)



Scheme S8 1-catalyzed reaction of 4-iodobenzotrifluoride and phenylboronic acid.

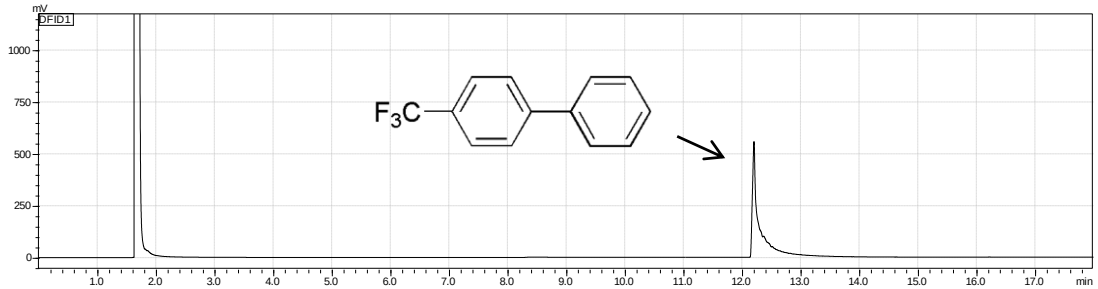
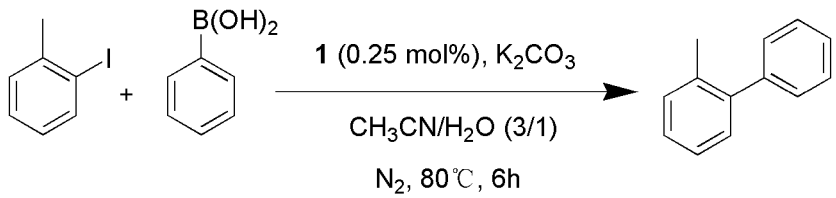


Fig. S11 GC of the reaction of 4-iodobenzotrifluoride and phenylboronic acid.

Suzuki reactions of ortho-substituted and polysubstituted aryl iodides with phenylboronic acid

(Table 3, entry 8)



Scheme S9 1-catalyzed reaction of 2-iodotoluene and phenylboronic acid.

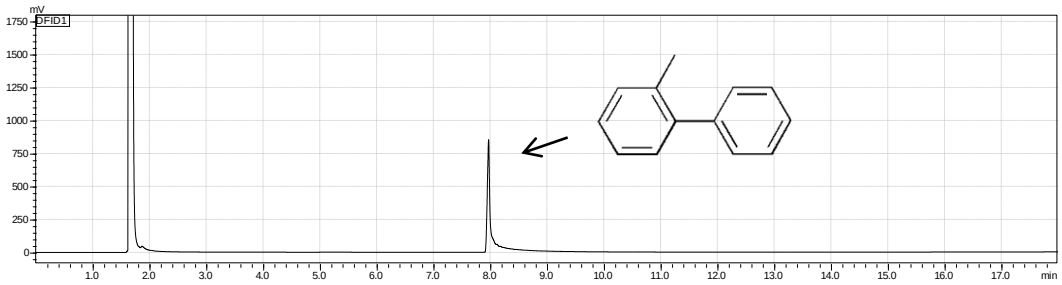
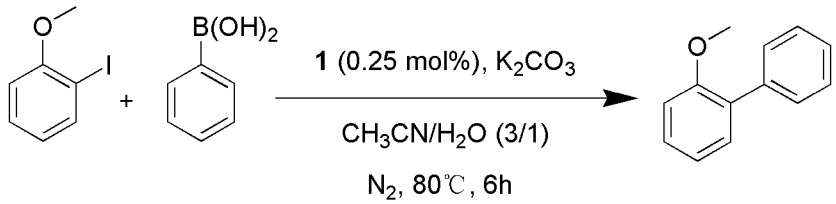


Fig. S12 GC of the reaction of 2-iodotoluene and phenylboronic acid.

(Table 3, entry 9)



Scheme S10 1-catalyzed reaction of 2-iodoanisole and phenylboronic acid.

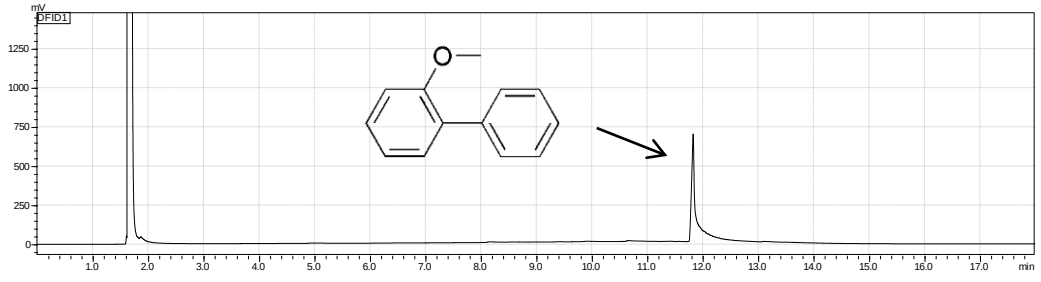
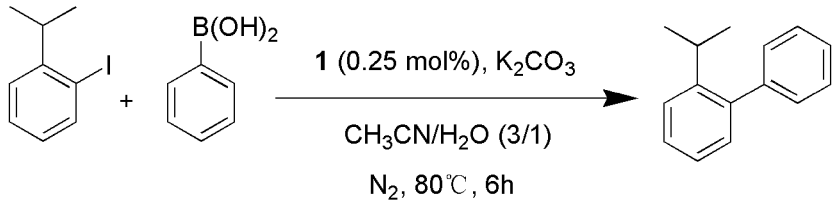


Fig. S13 GC of the reaction of 2-iodoanisole and phenylboronic acid.

(Table 3, entry 10)



Scheme S11 1-catalyzed reaction of 1-iodo-2-isopropylbenzene and phenylboronic acid.

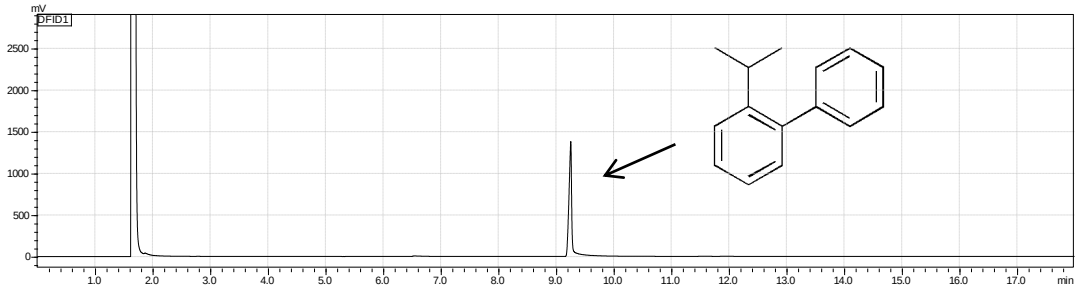
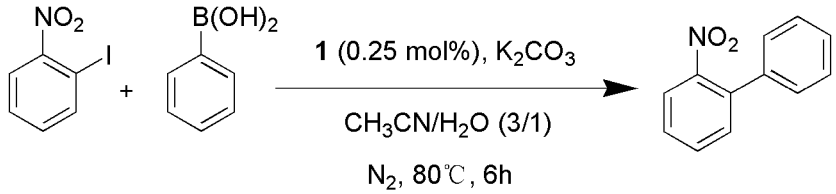


Fig. S14 GC of the reaction of 1-iodo-2-isopropylbenzene and phenylboronic acid.

(Table 3, entry 11)



Scheme S12 1-catalyzed reaction of 2-nitroiodobenzene and phenylboronic acid.

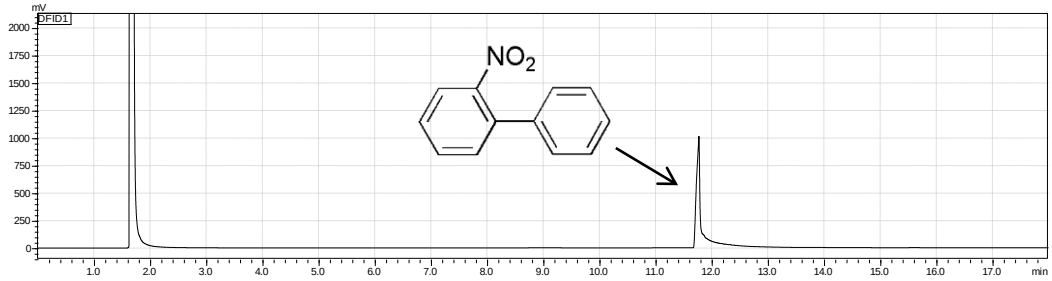
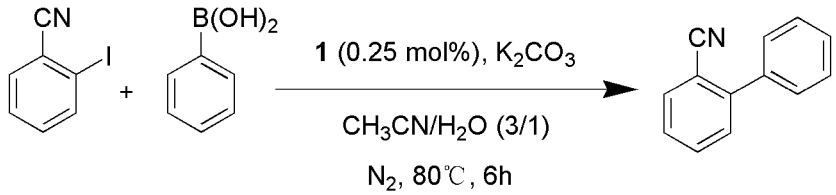


Fig. S15 GC of the reaction of 2-nitroiodobenzene and phenylboronic acid.

(Table 3, entry 12)



Scheme S13 1-catalyzed reaction of 2-iodobenzonitrile and phenylboronic acid.

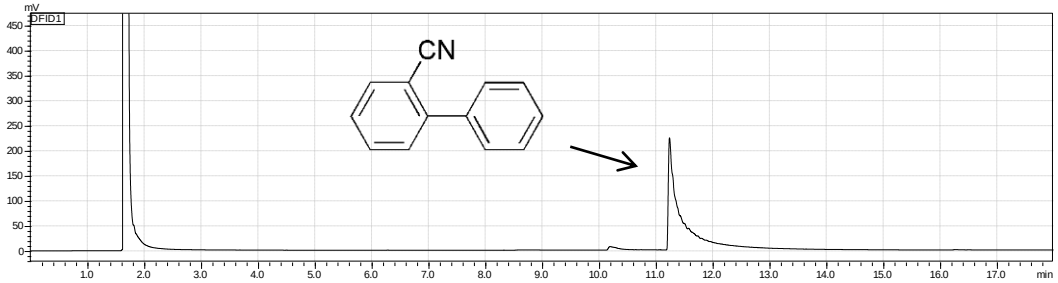
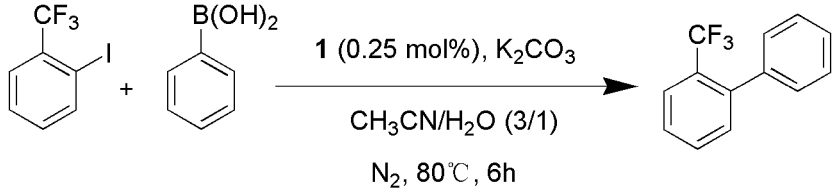


Fig. S16 GC of the reaction of 2-iodobenzonitrile and phenylboronic acid.

(Table 3, entry 13)



Scheme S14 1-catalyzed reaction of 2-iodobenzotrifluoride and phenylboronic acid.

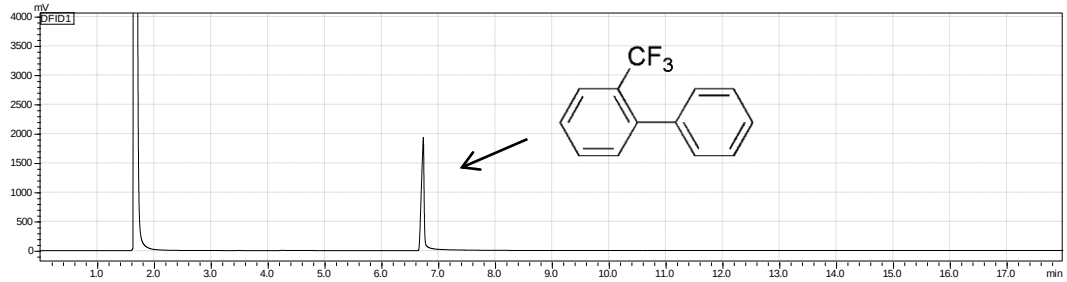
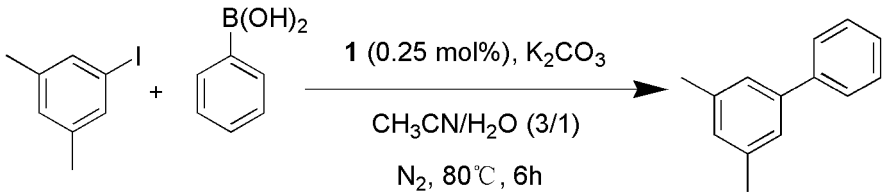


Fig. S17 GC of the reaction of 2-iodobenzotrifluoride and phenylboronic acid.

(Table 3, entry 14)



Scheme S15 1-catalyzed reaction of 1-iodo-3,5-dimethylbenzene and phenylboronic acid.

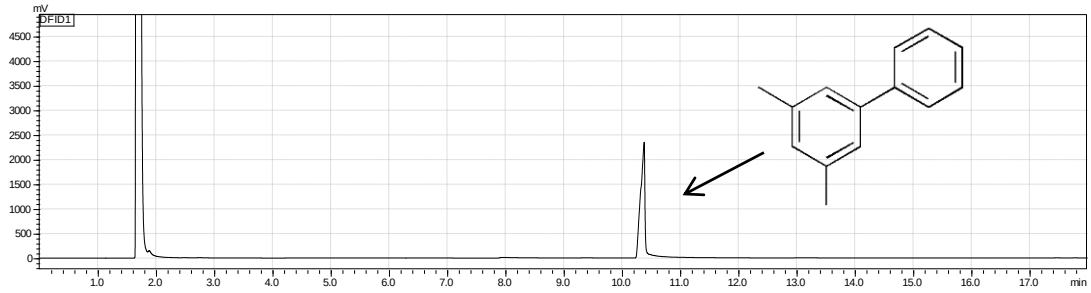
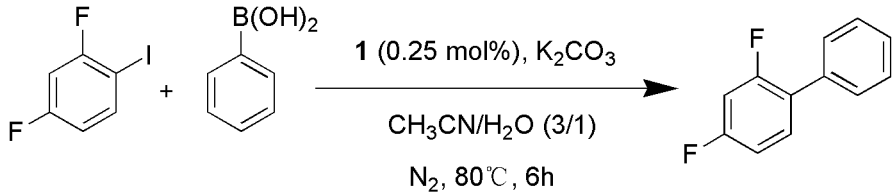


Fig. S18 GC of the reaction of 1-iodo-3,5-dimethylbenzene and phenylboronic acid.

(Table 3, entry 15)



Scheme S16 1-catalyzed reaction of 2,4-difluoroiodobenzene and phenylboronic acid.

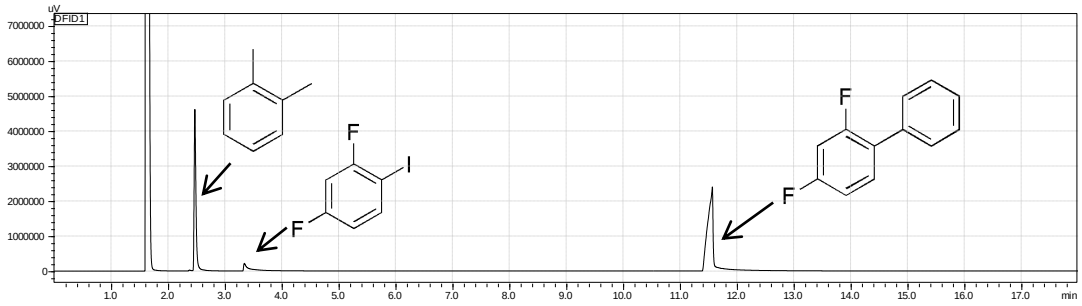


Fig. S19 GC of the reaction of 2,4-difluoroiodobenzene and phenylboronic acid.

The substrate without quantitative conversions was calibrated by internal standard method. The specific operation steps: 100% (0.5mmol), 80%, 60%, 40%, 20% aryl iodide-acetonitrile (1.5ml) solution was prepared. Then 0.3 mmol 1,2-dimethylbenzene was added to each of the five

solutions. According to the GC, the ratio of the peak area of the aryl iodide to the 1,2-dimethylbenzene was calculated as the ordinate and the percentage of the added raw material was used as the abscissa. Through automatic linear fitting, the equation was: y=0.112x+0.032

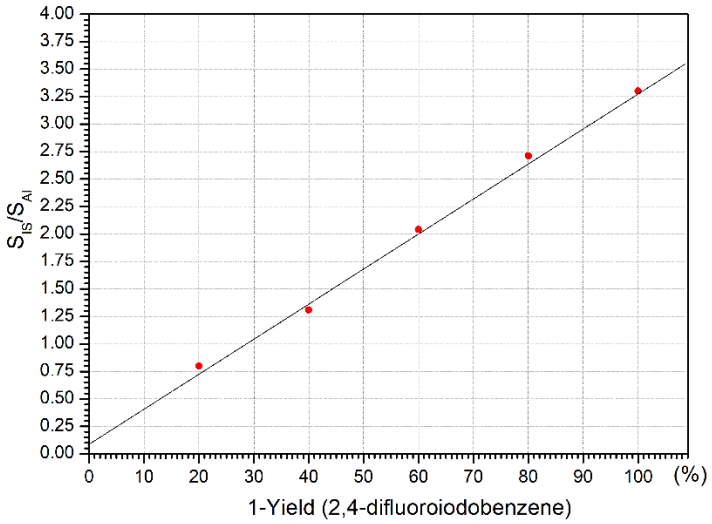
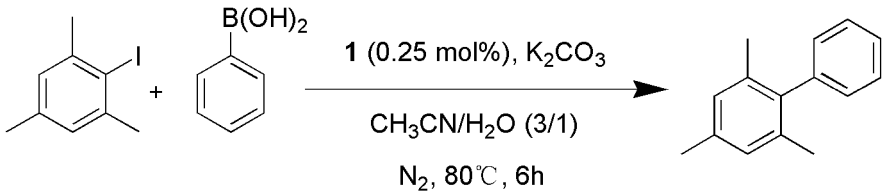


Fig. S20 Calibration chart of the yield of the reaction of 2,4-difluoroiodobenzene and phenylboronic acid.

(Table 3, entry 16)



Scheme S17 1-catalyzed reaction of 2,4,6-trimethyliodobenzene and phenylboronic acid.

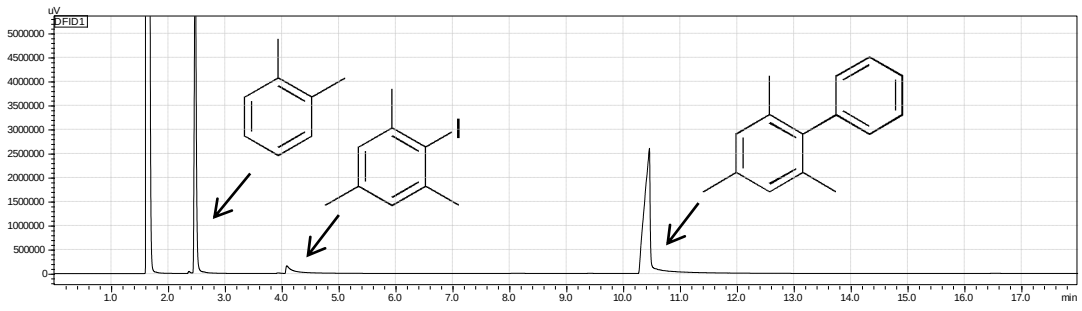
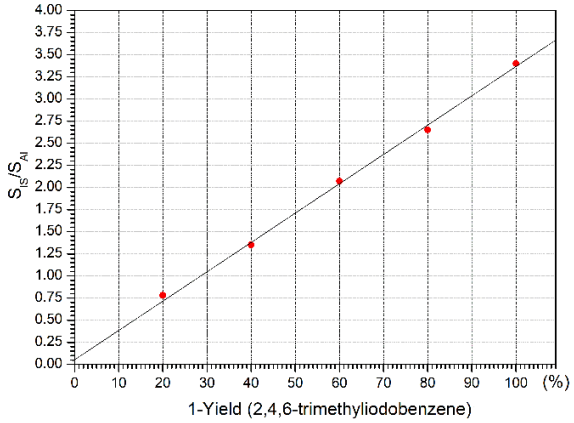


Fig. S21 GC of the reaction of 2,4,6-trimethyliodobenzene and phenylboronic acid.

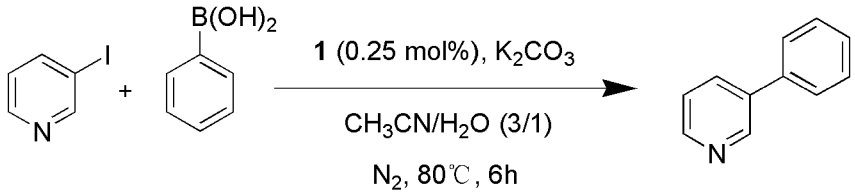


the equation was: y=0.088x+0.033

Fig. S22 Calibration chart of the yield of the reaction of 2,4,6-trimethyliodobenzene and phenylboronic acid.

Suzuki reaction of heterocyclic/polycyclic aryl iodides with phenylboronic acid

(Table 4, entry 1)



Scheme S18 1-catalyzed reaction of 3-iodopyridine and phenylboronic acid.

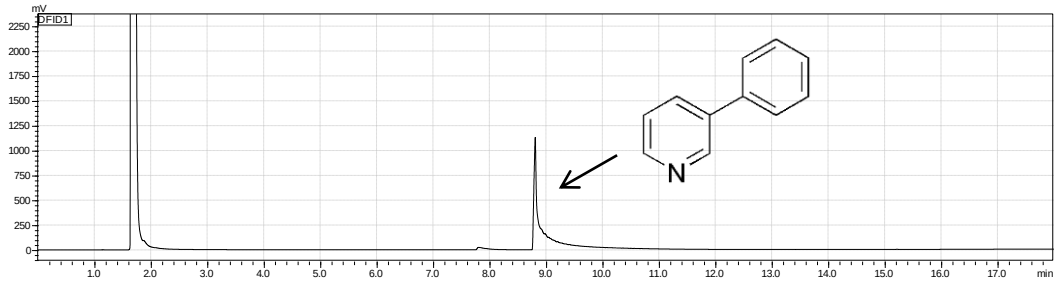
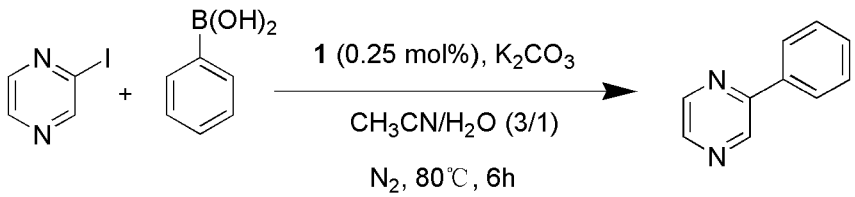


Fig. S23 GC of the reaction of 3-iodopyridine and phenylboronic acid

(Table 4, entry 2)



Scheme S19 1-catalyzed reaction of iodopyrazine and phenylboronic acid.

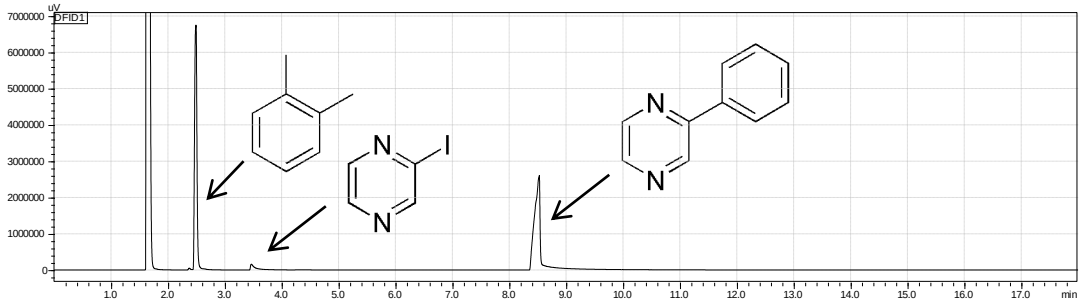
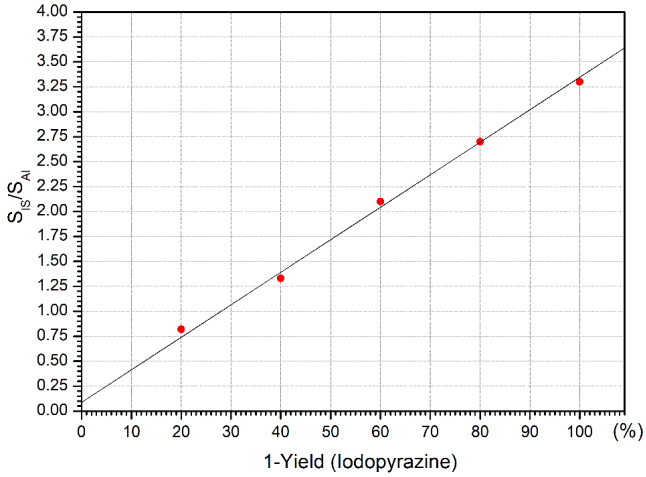


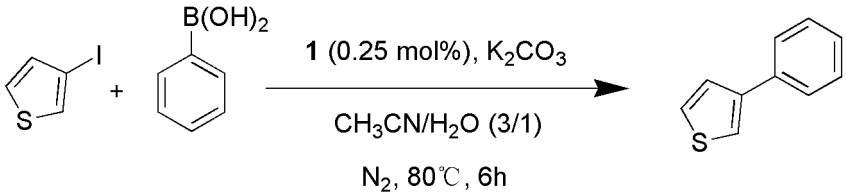
Fig. S24 GC of the reaction of iodopyrazine and phenylboronic acid.



the equation was: y=0.151x+0.031

Fig. S25 Calibration chart of the yield of the reaction of iodopyrazine and phenylboronic acid.

(Table 4, entry 4)



Scheme S20 1-catalyzed reaction of 3-iodothiophene and phenylboronic acid.

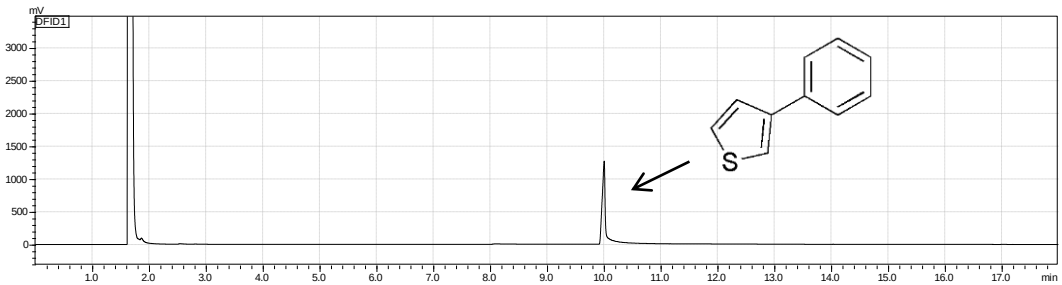
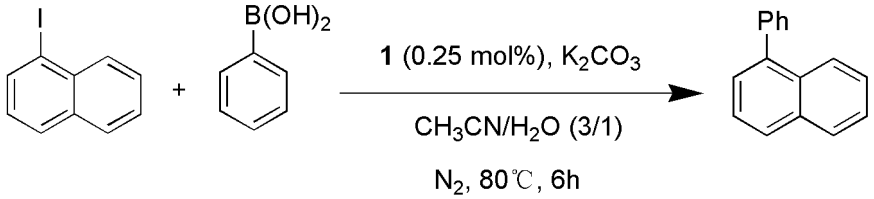


Fig. S26 GC of the reaction of 3-iodothiophene and phenylboronic acid.

(Table 4, entry 5)



Scheme S21 1-catalyzed reaction of 1-iodonaphthalene and phenylboronic acid.

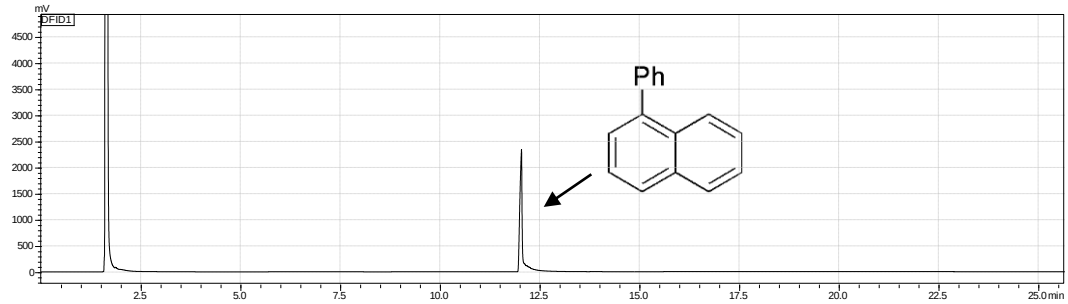
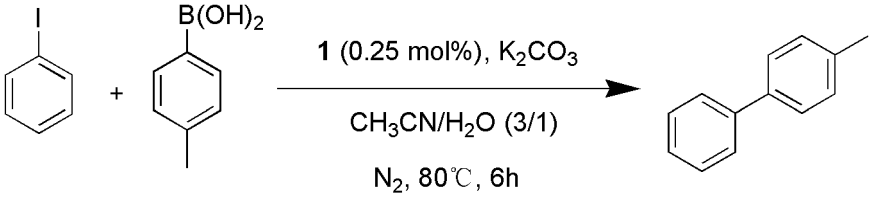


Fig. S27 GC of the reaction of 1-iodonaphthalene and phenylboronic acid.

Suzuki reaction of iodobenzene with substituted arylboronic acids

(Table 5, entry 1)



Scheme S22 1-catalyzed reaction of 4-methylphenylboronic acid and iodobenzene.

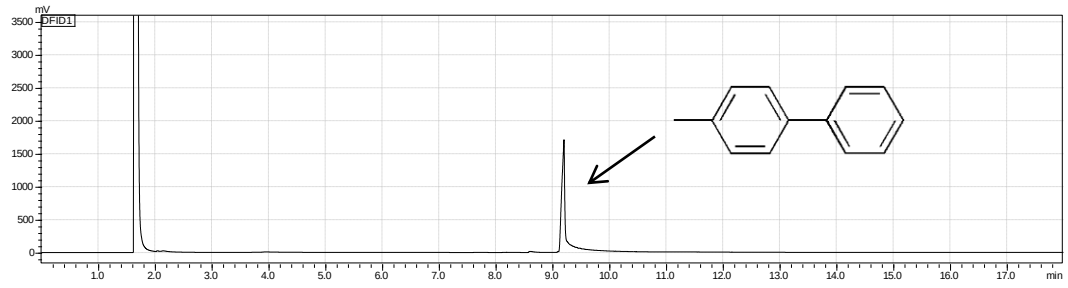
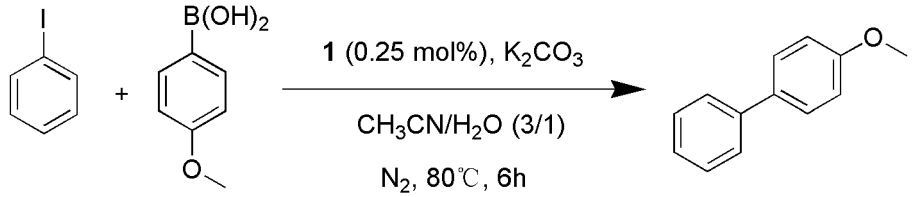


Fig. S28 GC of the reaction of 4-methylphenylboronic acid and iodobenzene.

(Table 5, entry 2)



Scheme S23 1-catalyzed reaction of 4-methoxyphenylboronic acid and iodobenzene.

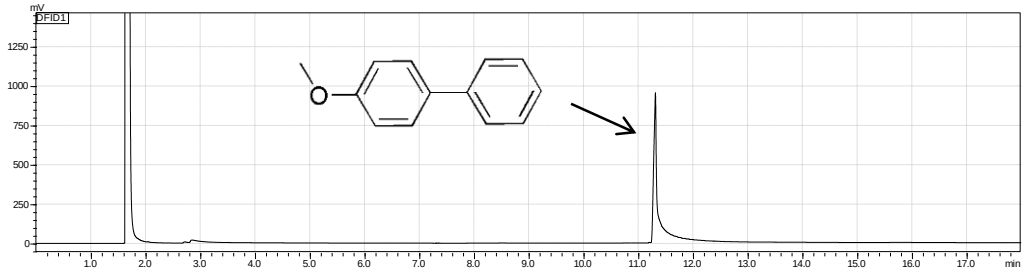
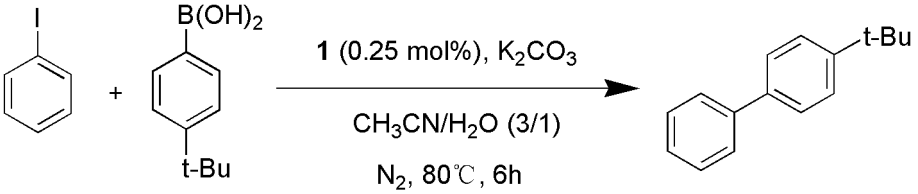


Fig. S29 GC of the reaction of 4-methoxyphenylboronic acid and iodobenzene.

(Table 5, entry 3)



Scheme S24 1-catalyzed reaction of 4-tert-butylphenylboronic acid and iodobenzene.

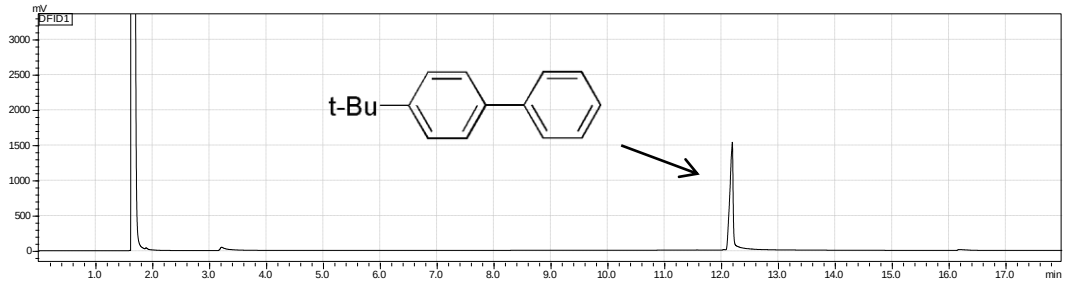
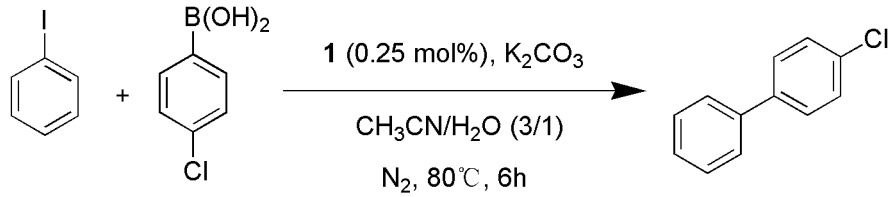


Fig. S30 GC of the of 4-tert-butylphenylboronic acid and iodobenzene.

(Table 5, entry 4)



Scheme S25 1-catalyzed reaction of 4-chlorophenylboronic acid and iodobenzene.

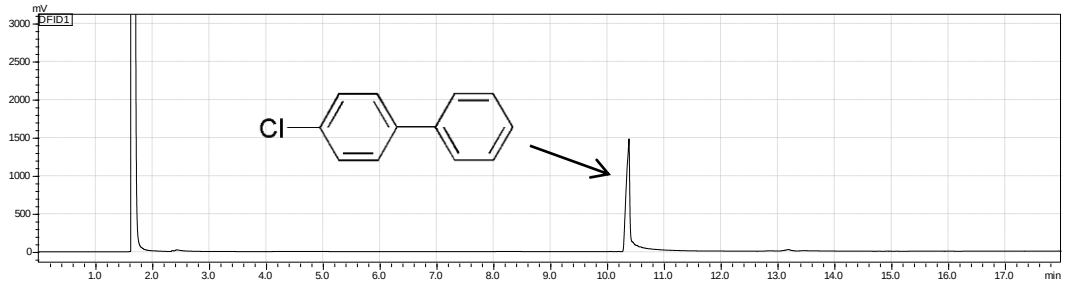
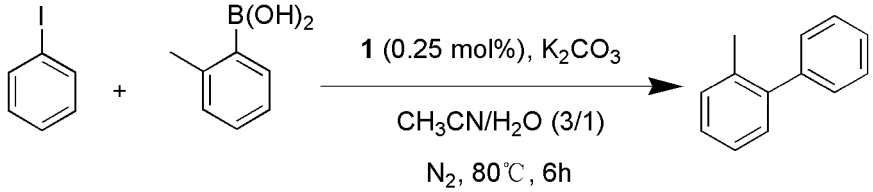


Fig. S31 GC of the reaction of 4-chlorophenylboronic acid and iodobenzene.

(Table 5, entry 5)



Scheme S26 1-catalyzed reaction of 2-methylphenylboronic acid and iodobenzene.

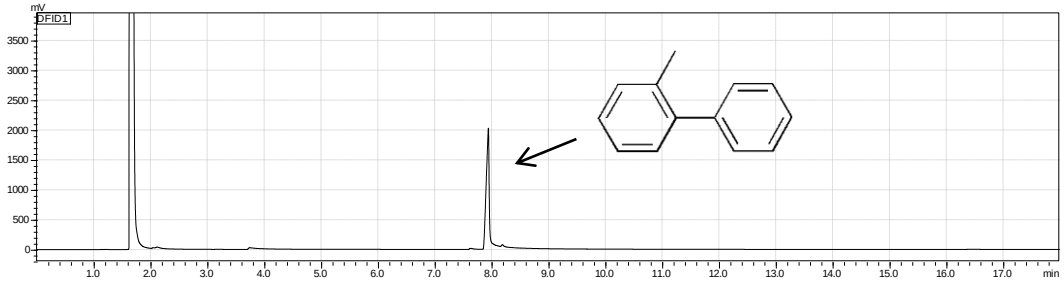
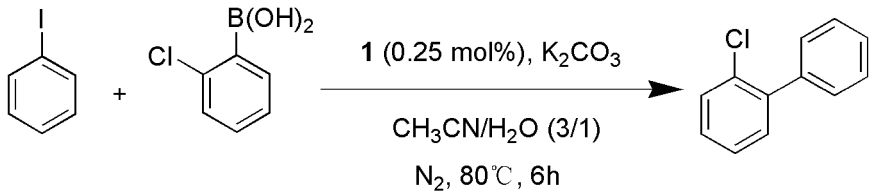


Fig. S32 GC of the reaction of 2-methylphenylboronic acid and iodobenzene.

(Table 5, entry 6)



Scheme S27 1-catalyzed the reaction of 2-chlorophenylboronic acid and iodobenzene.

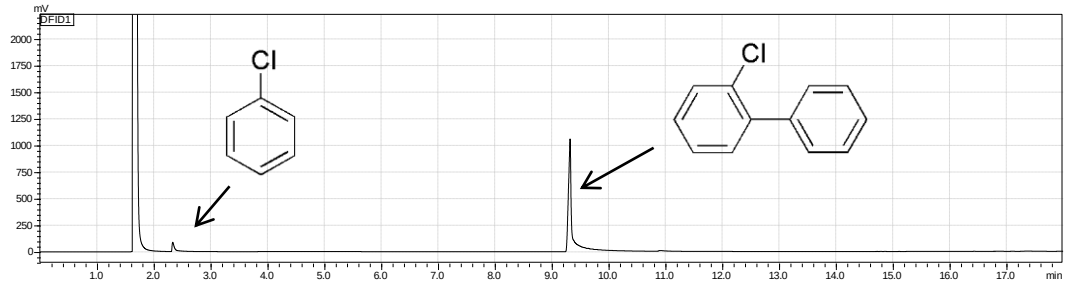
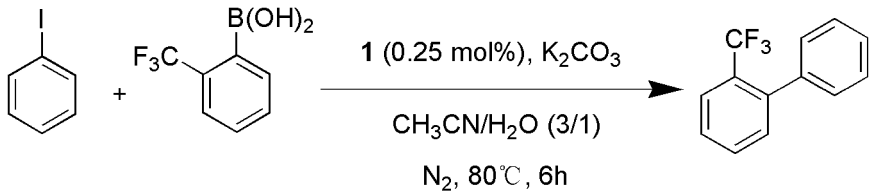


Fig. S33 GC of the reaction of 2-chlorophenylboronic acid and iodobenzene.

(Table 5, entry 7)



Scheme S28 1-catalyzed reaction of 2-(trifluoromethyl)phenylboronic acid and iodobenzene.

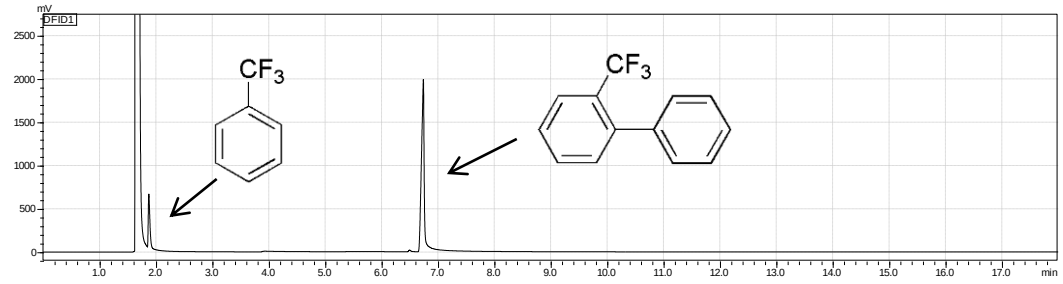
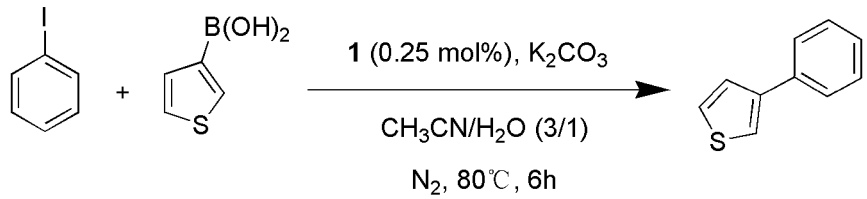


Fig. S34 GC of the reaction of 2-(trifluoromethyl)phenylboronic acid and iodobenzene.

(Table 5, entry 8)



Scheme S29 1-catalyzed reaction of 3-thiopheneboronic acid and iodobenzene

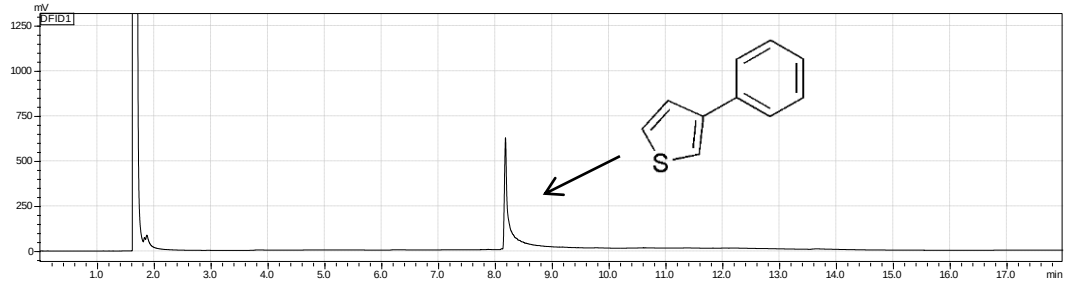
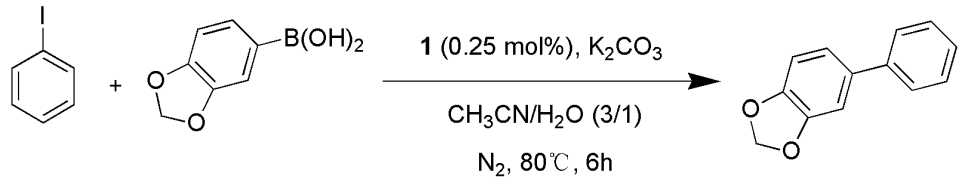


Fig. S35 GC of the reaction of 3-thiopheneboronic acid and iodobenzene.

(Table 3, entry 9)



Scheme S30 1-catalyzed reaction of 3,4-(methylenedioxy)benzeneboronic acid and iodobenzene.

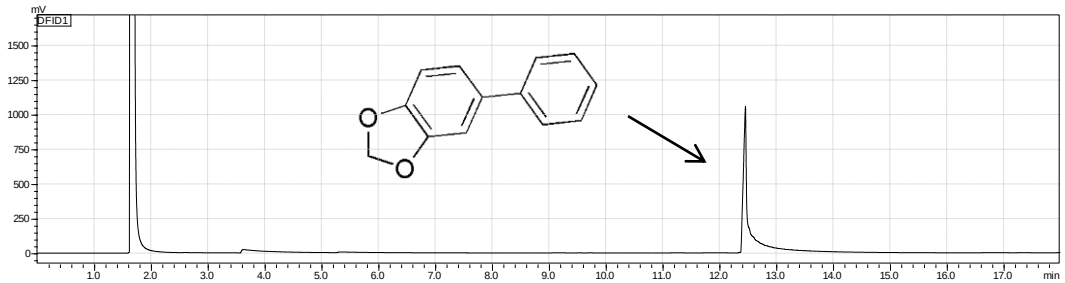
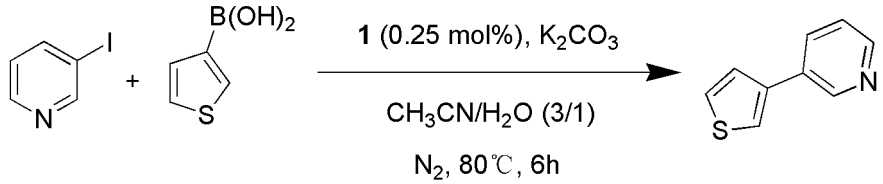


Fig. S36 GC of the reaction of 3,4-(methylenedioxy)benzeneboronic acid and iodobenzene.

Suzuki reaction of heterocyclic aryl iodides with heterocyclic arylboronic acids

(Table 5, entry 11)



Scheme S31 1-catalyzed reaction of 3-iodopyridine and 3-thiopheneboronic acid.

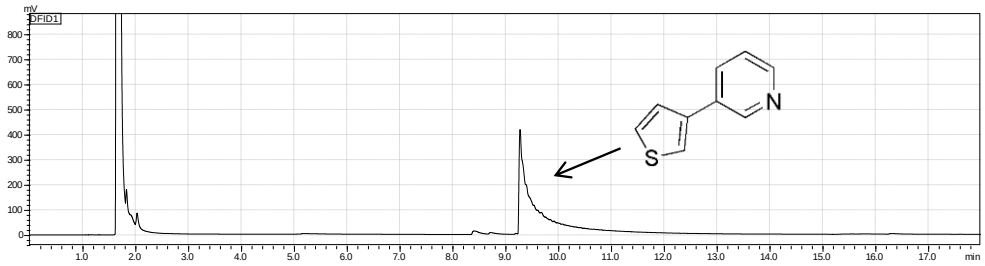
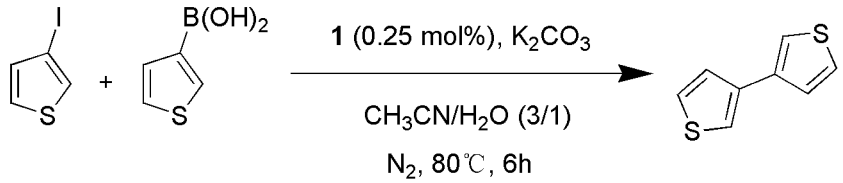


Fig. S37 GC of the reaction of 3-iodopyridine and 3-thiopheneboronic acid.

(Table 3, entry 12)



Scheme S32 1-catalyzed reaction of 3-iodothiophene and 3-thiopheneboronic acid.

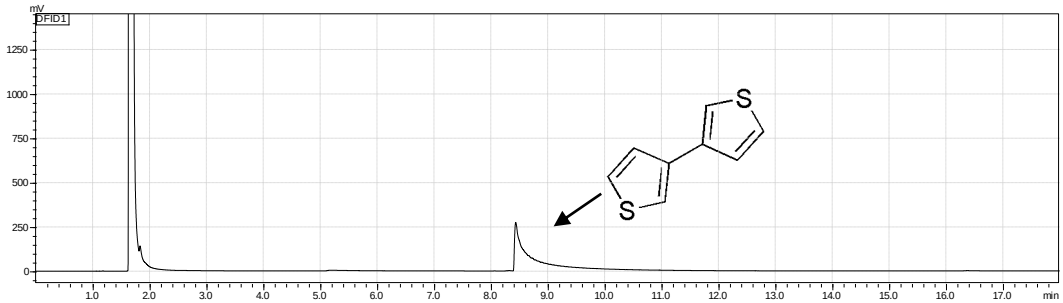
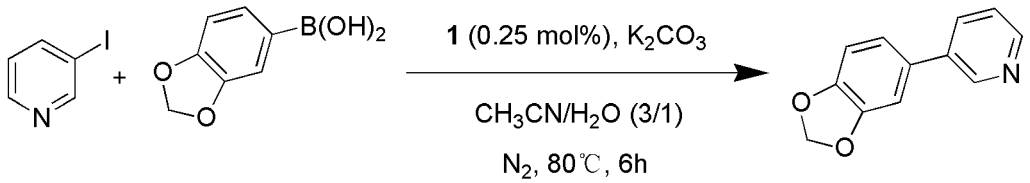


Fig. S38 GC of the reaction of 3-iodothiophene and 3-thiopheneboronic acid.

(Table 5, entry 13)



Scheme S33 1-catalyzed reaction of 3-iodopyridine and 3,4-(methylenedioxy)benzeneboronic acid.

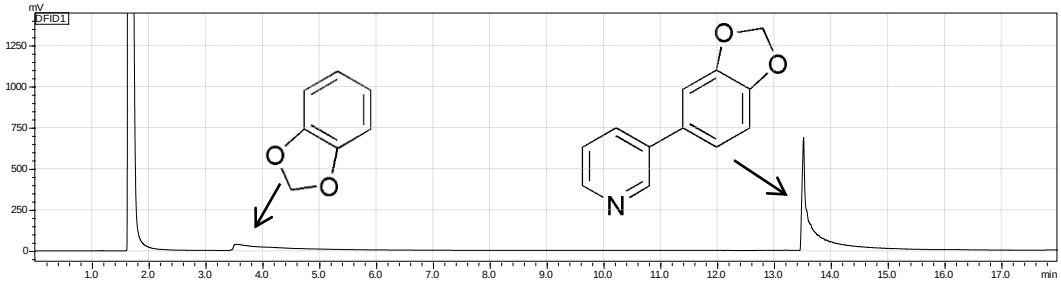
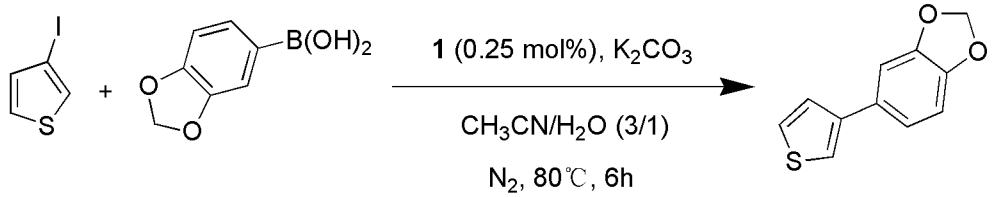


Fig. S39 GC of the reaction of 3-iodopyridine and 3,4-(methylenedioxy)benzeneboronic acid.

(Table 5, entry 14)



Scheme S34 1-catalyzed reaction of 3-iodopyridine and 3,4-(methylenedioxy)benzeneboronic acid.

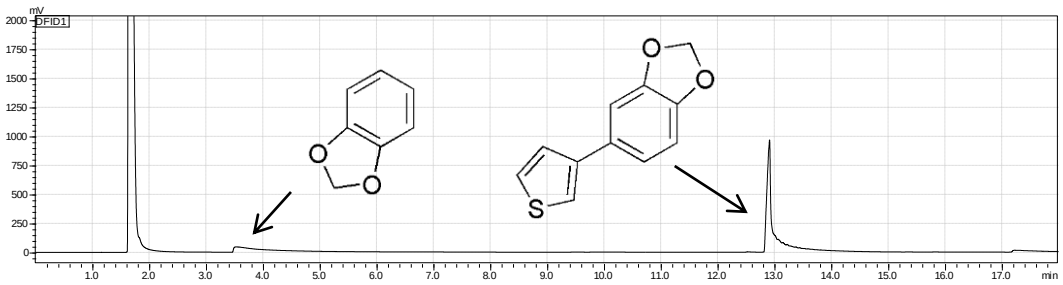


Fig. S40 GC of the reaction of 3-iodothiophene and 3,4-(methylenedioxy)benzeneboronic acid.

GC-MS of the reaction of 1-bromo-4-iodobenzene and phenylboronic acid catalyzed by four common palladium catalysts

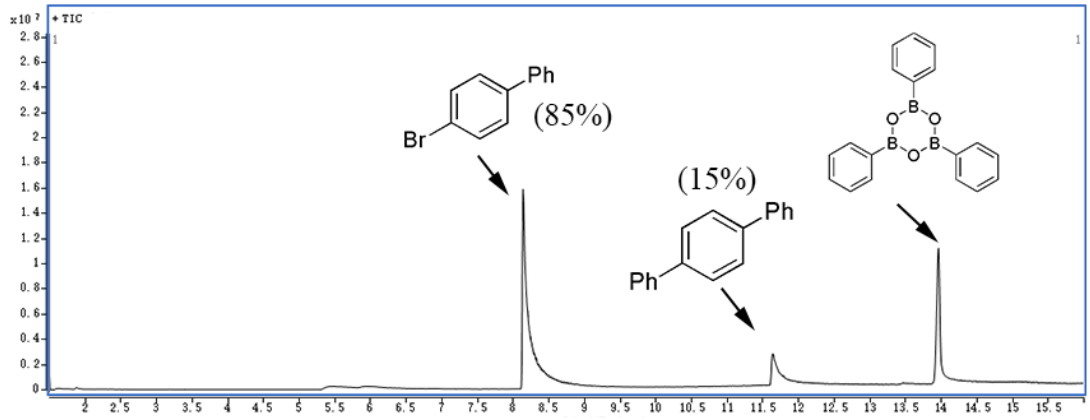


Fig. S41 GC-MS of the reaction catalyzed by $Pd(dba)_2$.

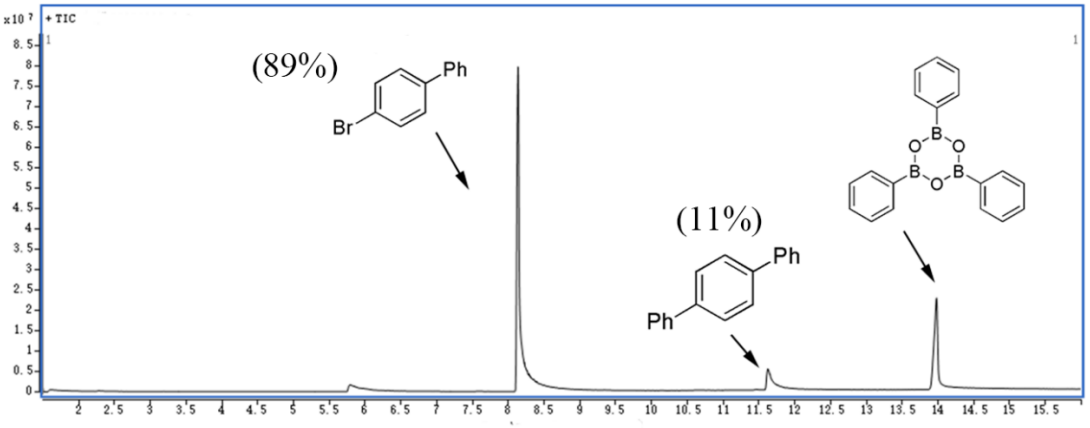


Fig. S42 GC-MS of the reaction catalyzed by $Pd(PPh_3)_4$.

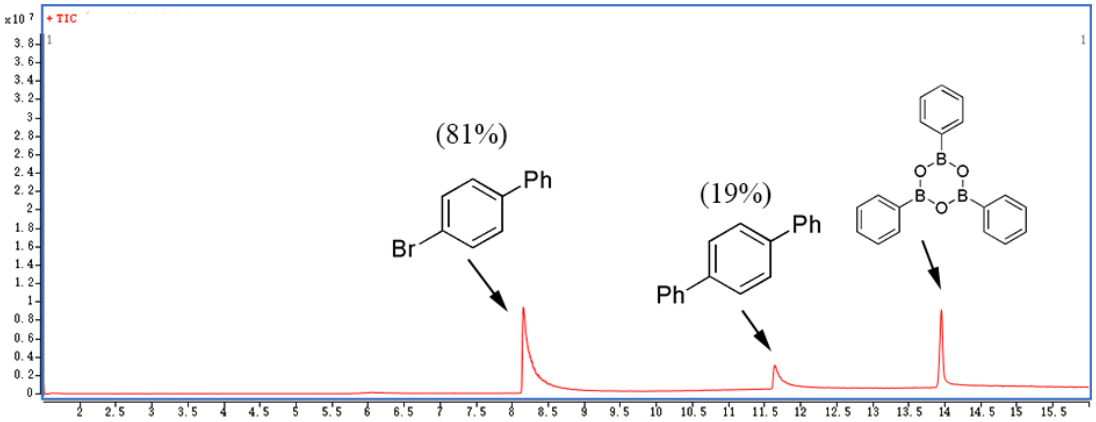


Fig. S43 GC-MS of the reaction catalyzed by $Pd(OAc)_2$.

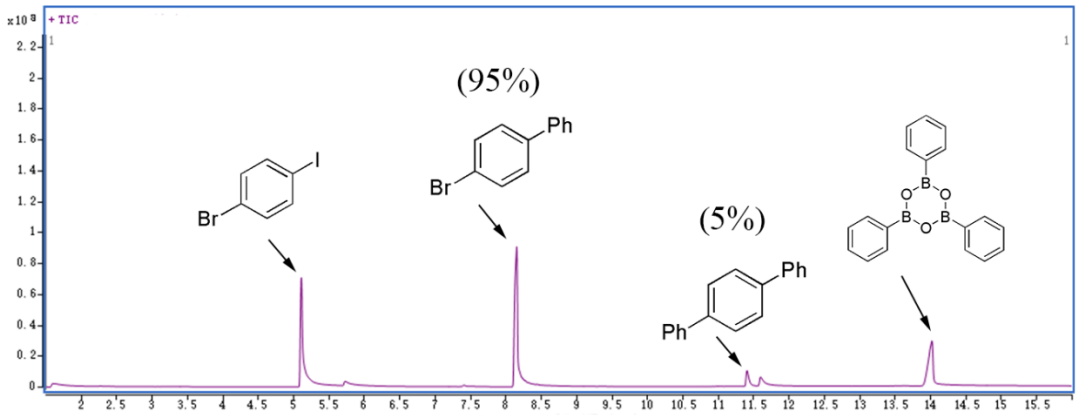
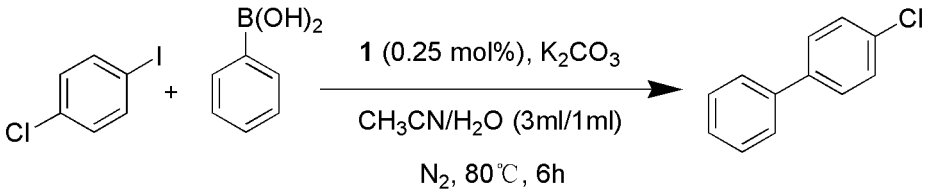


Fig. S44 GC-MS of the reaction catalyzed by $Pd(PPh)_2Cl_2$.

GC of the reaction of 1-chloro-4-iodobenzene and phenylboronic acid catalyzed by 1



Scheme S35 1-catalyzed reaction of 1-chloro-4-iodobenzene and phenylboronic acid.

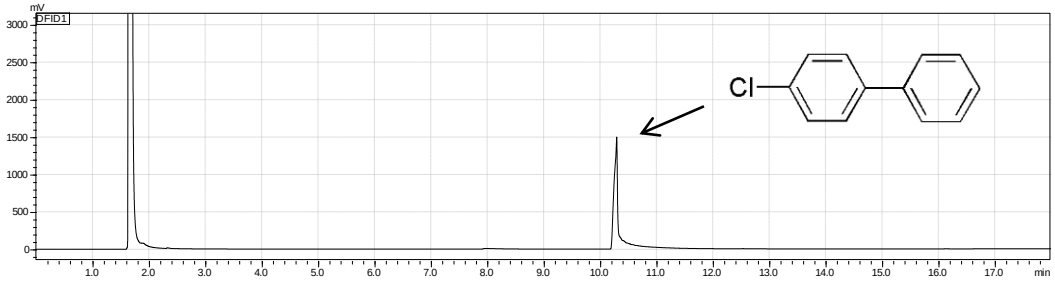


Fig. S45 GC of the reaction of 1-chloro-4-iodobenzene and phenylboronic acid.

8. Mechanism investigation

Experiments were designed to react **1** with iodobenzene and phenylboronic acid, respectively in the presence of K_2CO_3 and monitored the changes by HRMS. After **1** reacted with iodobenzene for 2h, HRMS showed a new peak at 1256.9313 which was consistent with an iodine inserted palladium dimer $Pd_2I(PAr_3)_2(SAr')_2$ (Ar=4-F-C_6H_4, Ar'=4-Cl-C_6H_4). However, no changes were observed in the reaction of **1** with phenylboronic acid.

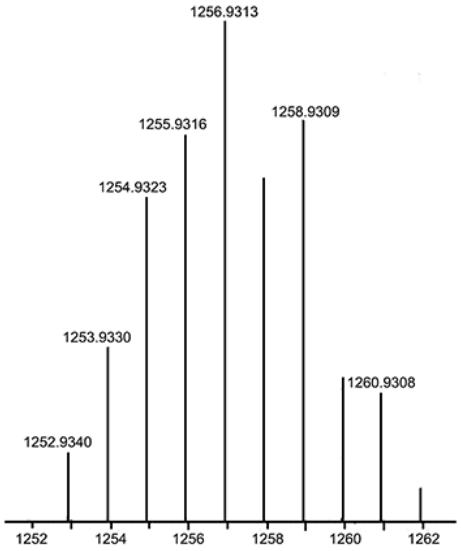
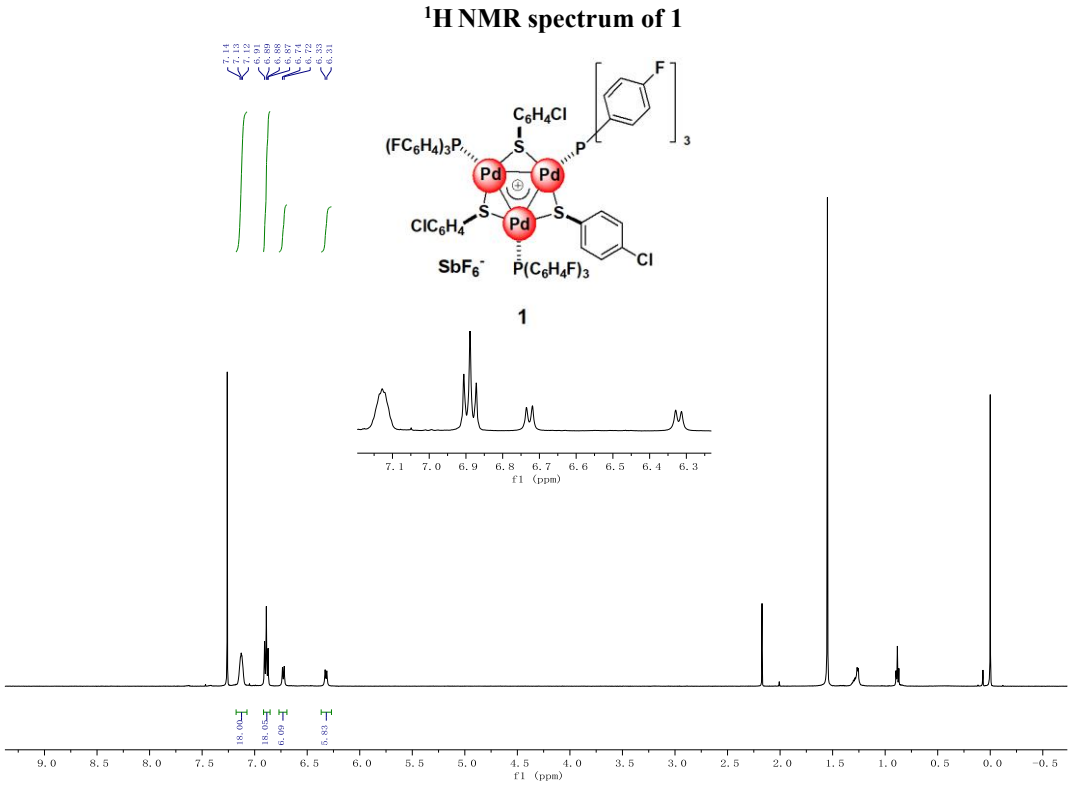


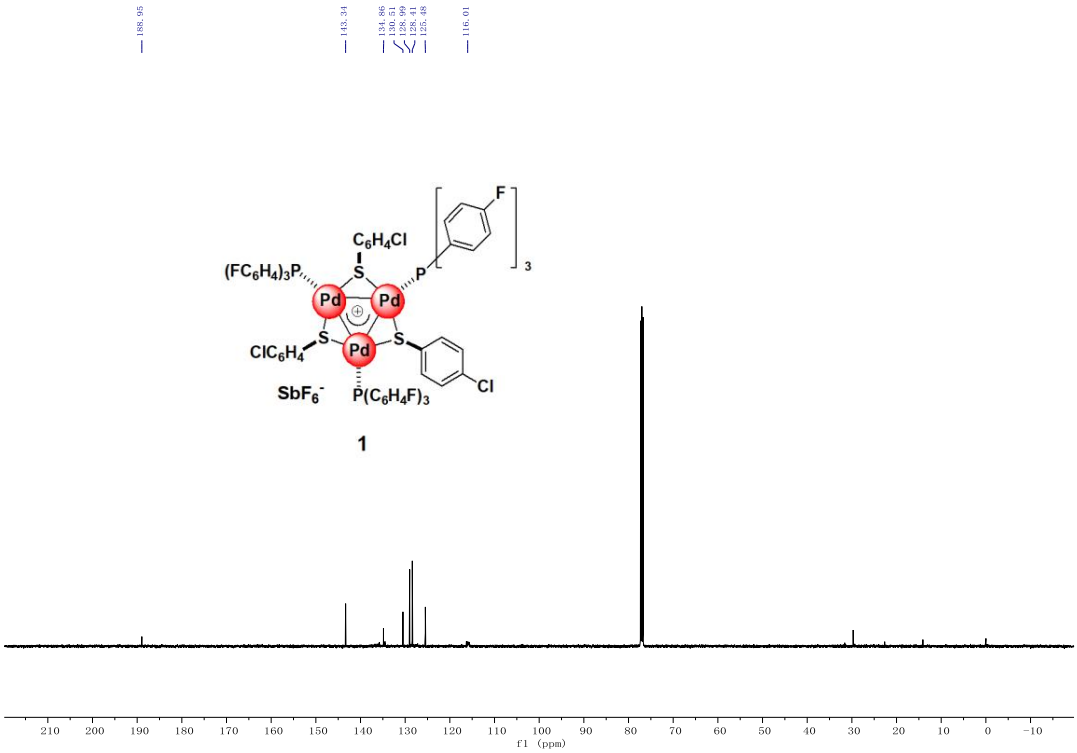
Fig. S46 HRMS of the $[Pd_3]^+$ (**1**) reacts with iodobenzene in the presence of K_2CO_3: 10 μL (0.1 mmol) iodobenzene, 2.4 mg (0.00125 mmol) **1**, K_2CO_3 0.0138 g (0.1 mmol) and 3 mL CH_2Cl_2, rt, 2 h.

9. NMR spectra



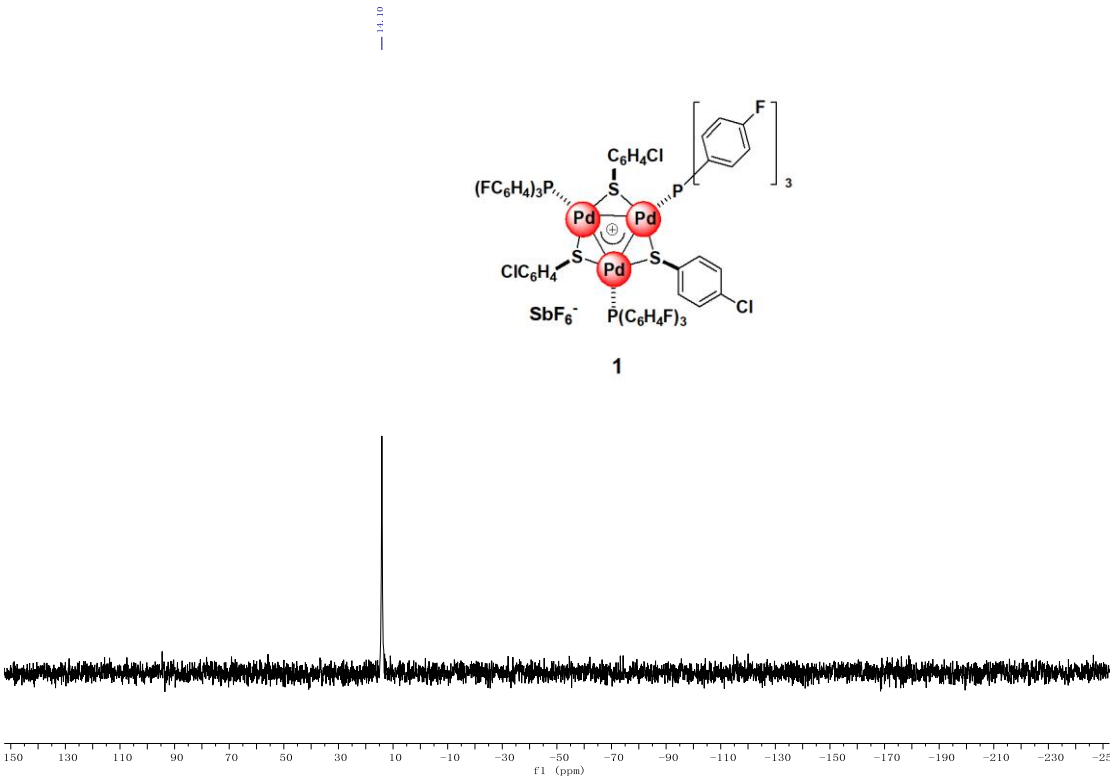
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 – 7.07 (m, 18H), 6.89 (t, *J* = 8.5 Hz, 18H), 6.73 (d, *J* = 8.1 Hz, 6H), 6.32 (d, *J* = 8.0 Hz, 6H).

^{13}C NMR spectrum of 1



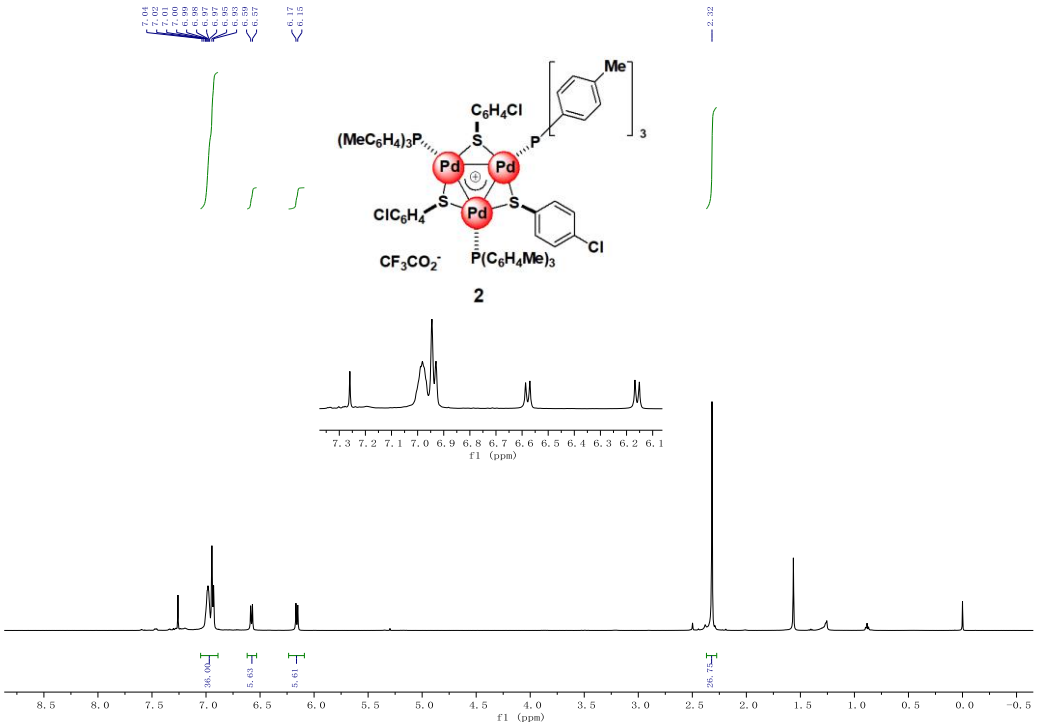
^{13}C NMR (126 MHz, Chloroform-*d*) δ 188.95, 143.34, 134.86, 130.51, 128.99, 128.41, 125.48, 116.29.

^{31}P NMR spectrum of 1



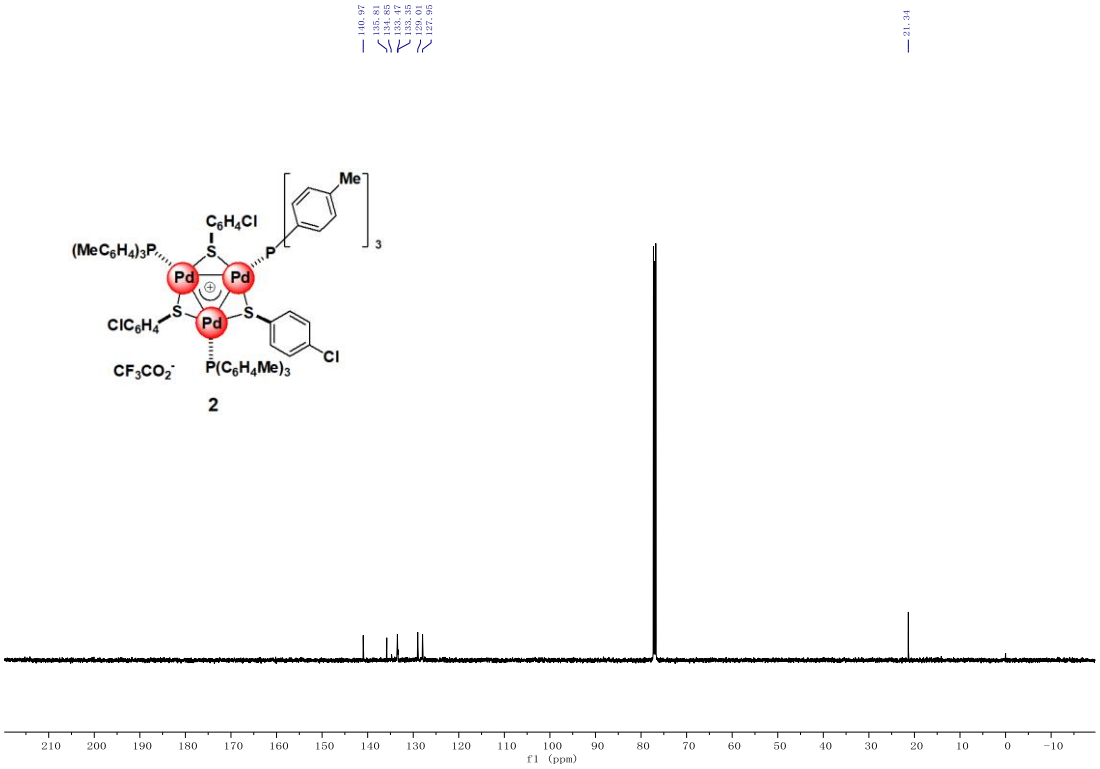
^{31}P NMR (202 MHz, Chloroform-*d*) δ 14.10.

^{1}H NMR spectrum of 2



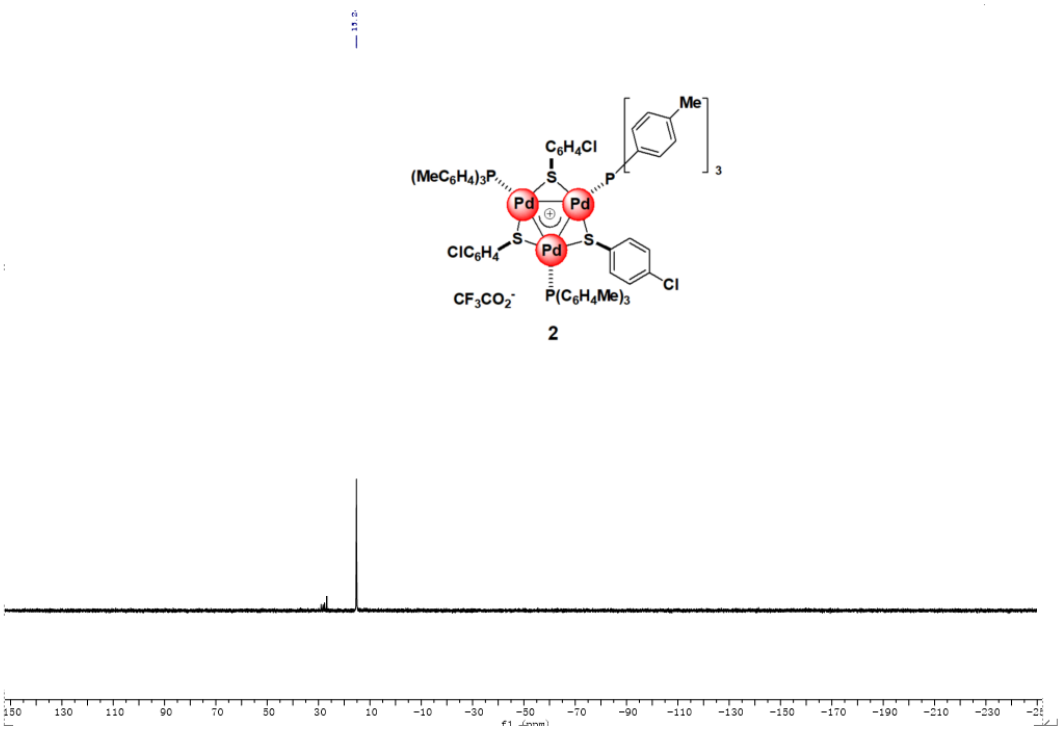
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.05 – 6.89 (m, 36H), 6.58 (d, *J* = 8.2 Hz, 6H), 6.16 (d, *J* = 8.3 Hz, 6H), 2.32 (s, 27H).

^{13}C NMR spectrum of 2



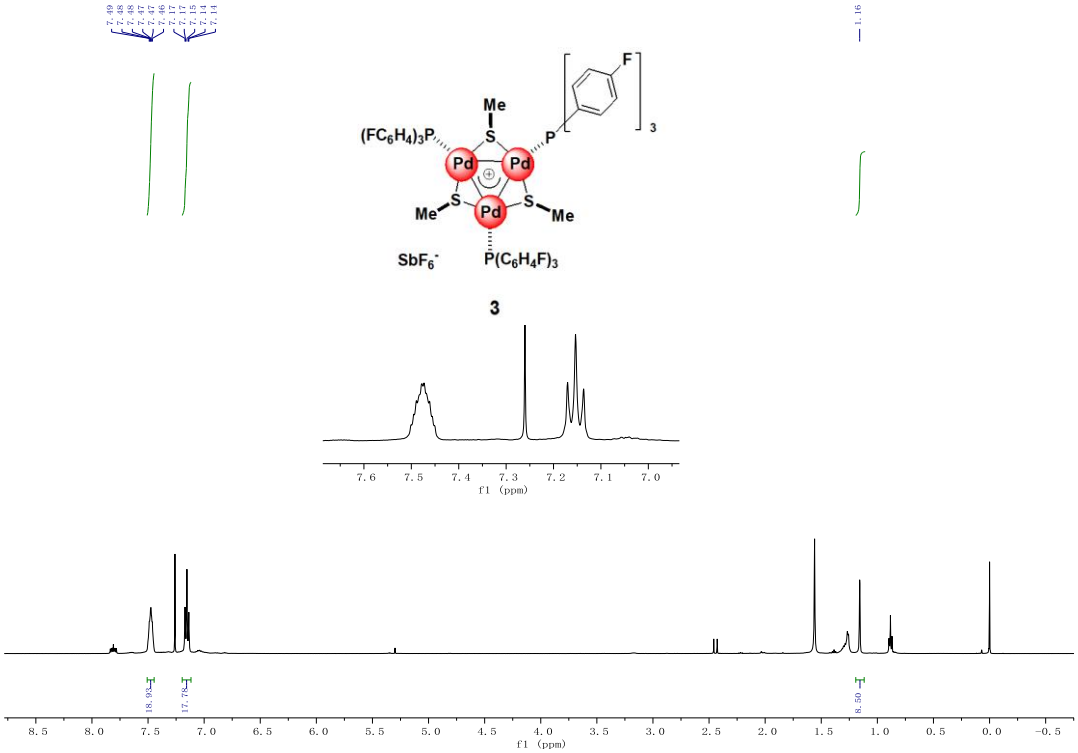
^{13}C NMR (126 MHz, Chloroform-d) δ 140.97, 135.81, 134.85, 133.47, 133.35, 129.01, 127.95, 21.34.

^{31}P NMR spectrum of 2



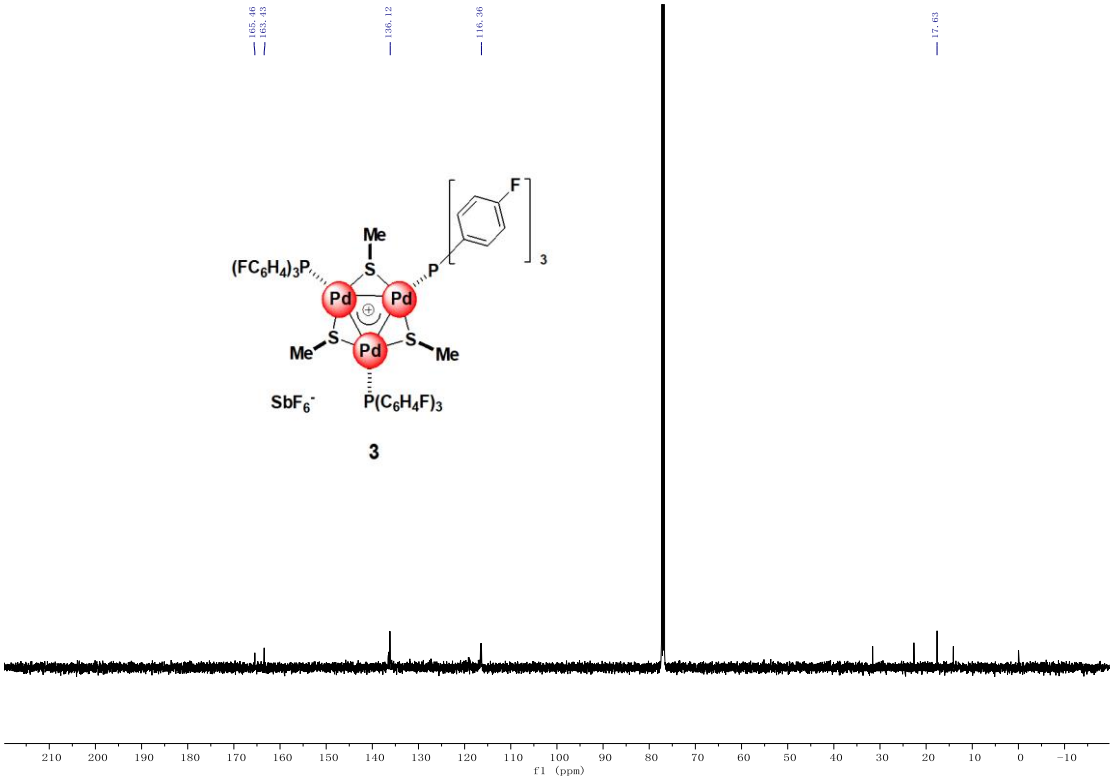
^{31}P NMR (202 MHz, Chloroform-*d*) δ 15.24.

^{1}H NMR spectrum of 3



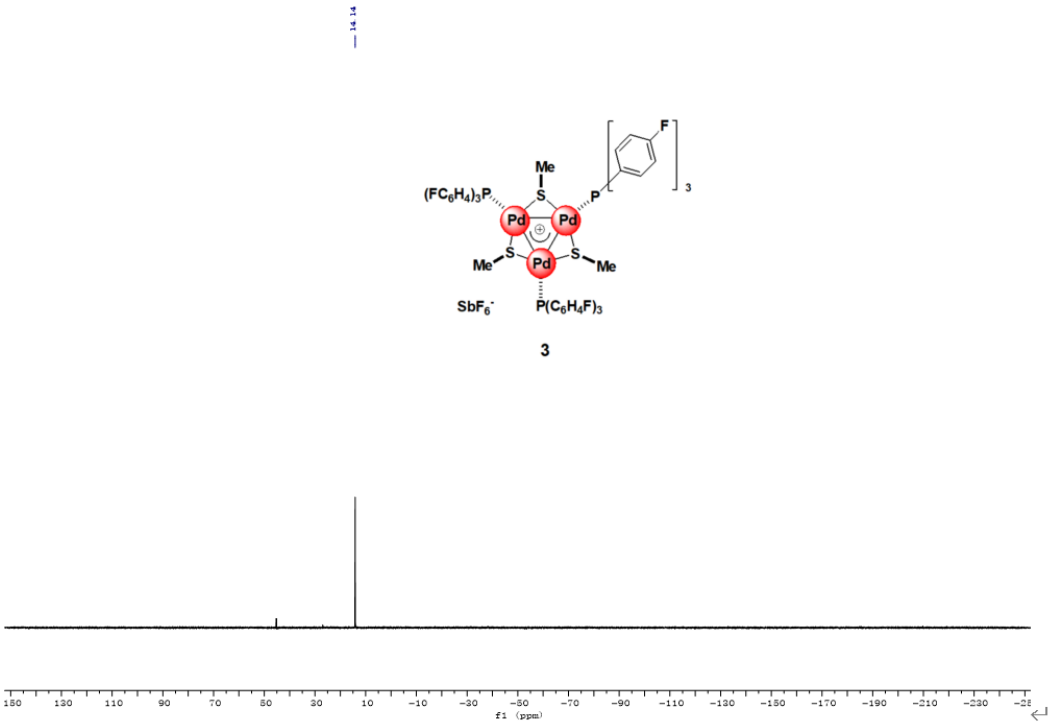
^{1}H NMR (500 MHz, Chloroform-d) δ 7.49–7.46 (m, 18H), 7.15 (t, J = 8.5 Hz, 18H), 1.16 (s, 9H).

^{13}C NMR spectrum of 3



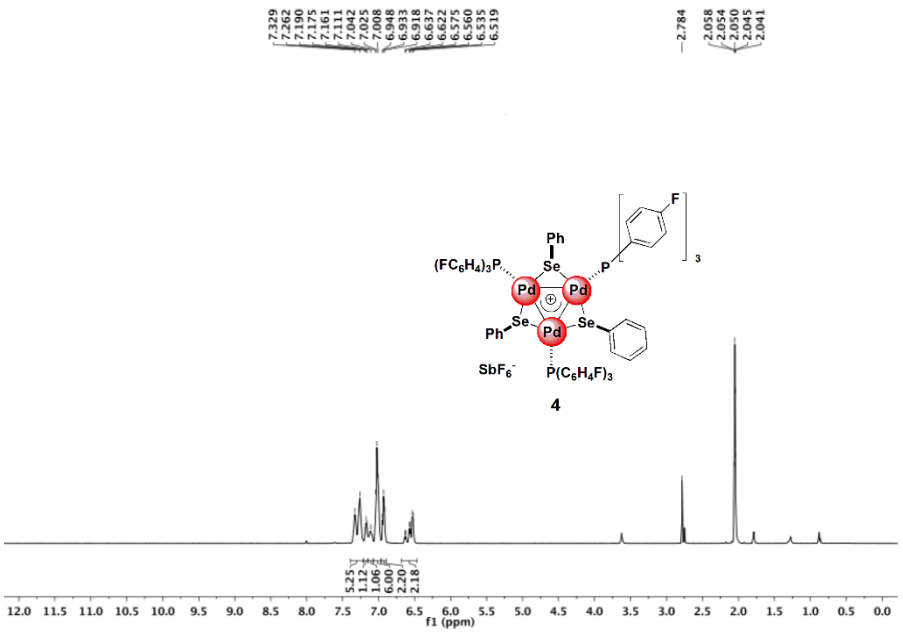
^{13}C NMR (126 MHz, Chloroform-d) δ 165.46, 163.43, 136.12, 116.36, 17.63.

^{31}P NMR spectrum of 3



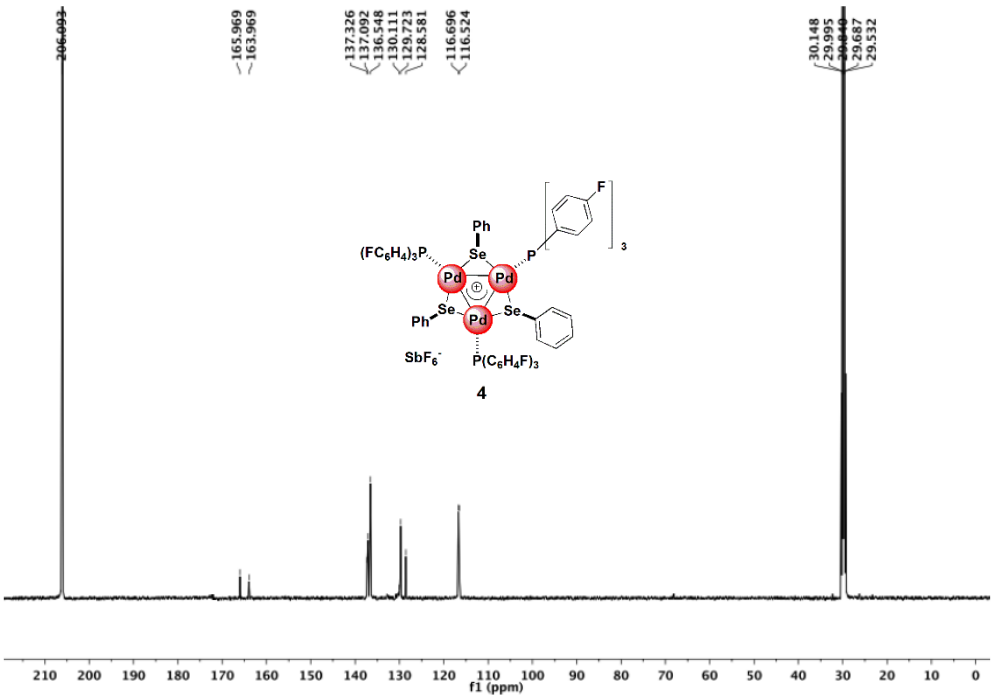
^{31}P NMR (202 MHz, Chloroform-d) δ 14.14.

^{1}H NMR spectrum of 4



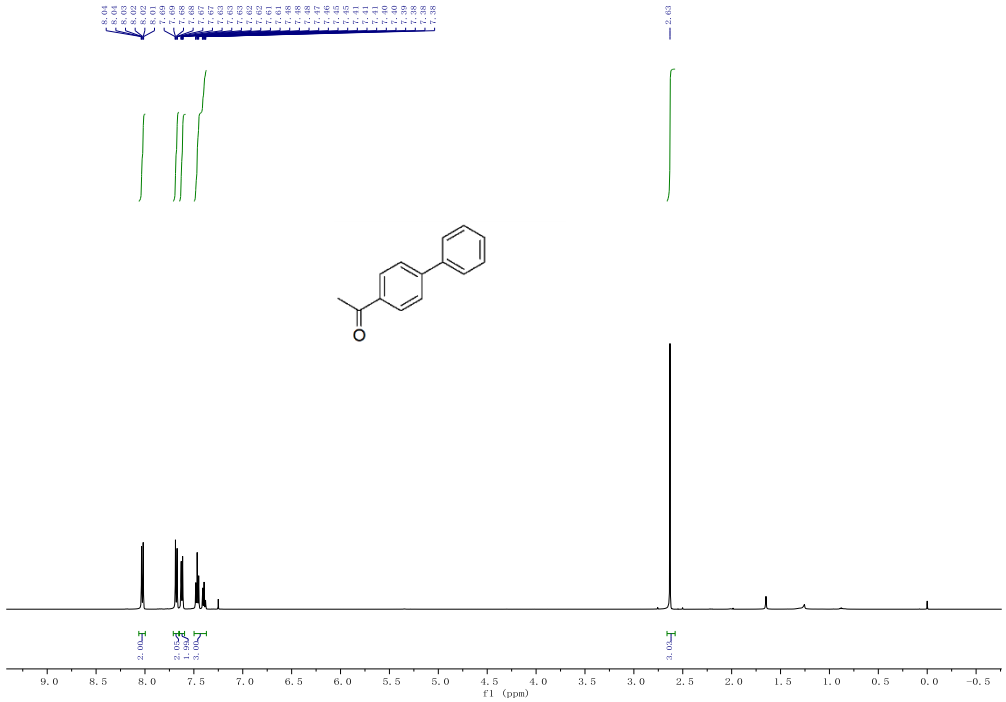
^{1}H NMR (500 MHz, Chloroform-*d*): δ 7.57-7.31 (m, 18H), 7.23 (t, J = 7.6 Hz, 3H), 6.98 (t, J = 8.5 Hz, 18H), 6.91 (t, J = 7.6 Hz, 6H), 6.28 (d, J = 7.6 Hz, 6H).

^{13}C NMR spectrum of 4



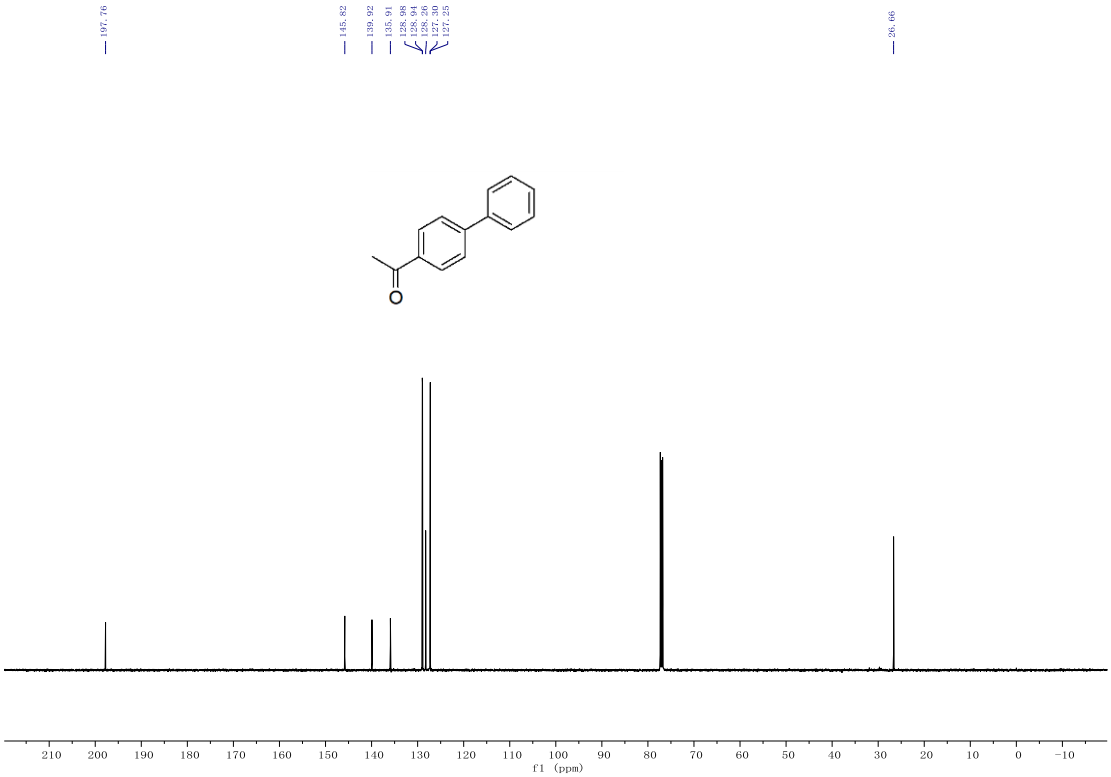
^{13}C NMR (126 MHz, Chloroform-d): δ 165.0, 137.8,137.3, 135.8, 129.4, 129.0, 128.4, 116.4.

(Table 1, entry7) **^{1}H NMR spectrum of 4-Acetylbiphenyl**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 – 8.00 (m, 2H), 7.71 – 7.65 (m, 2H), 7.65 – 7.60 (m, 2H), 7.50 – 7.37 (m, 3H), 2.63 (s, 3H).

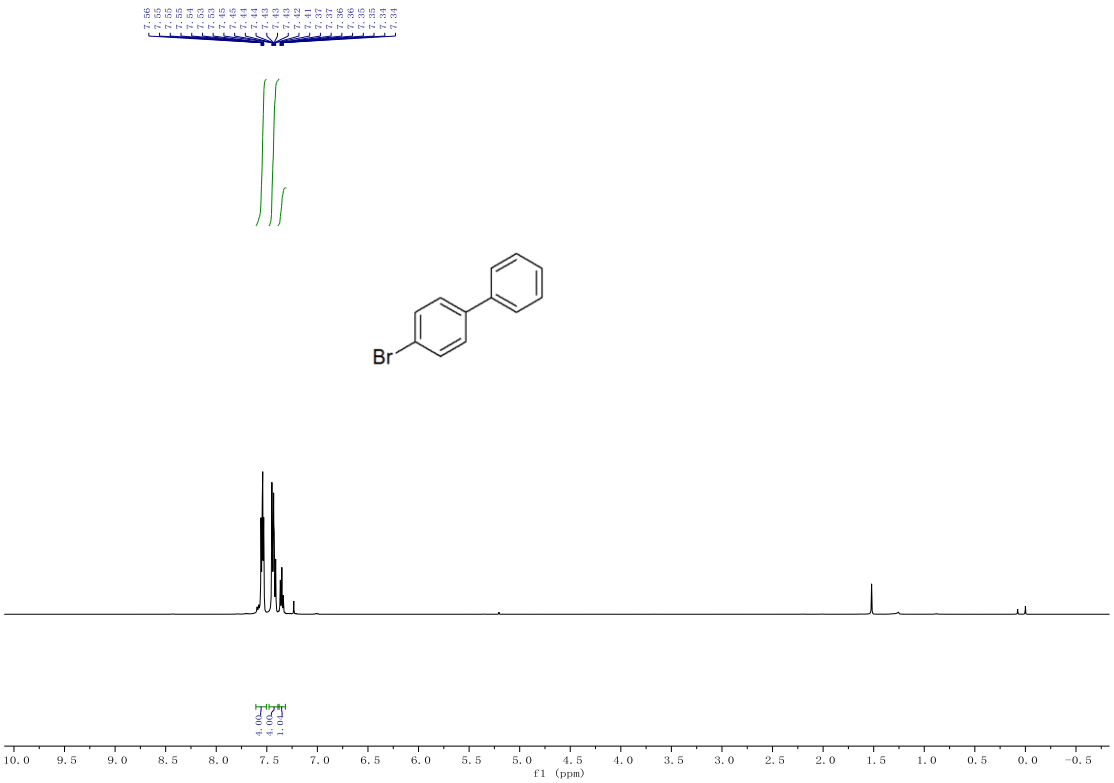
^{13}C NMR spectrum of 4-Acetylbiphenyl



^{13}C NMR (126 MHz, Chloroform-d) δ 197.7, 145.8, 139.9, 135.9, 128.9, 128.9, 128.2, 127.3, 127.2, 26.6.

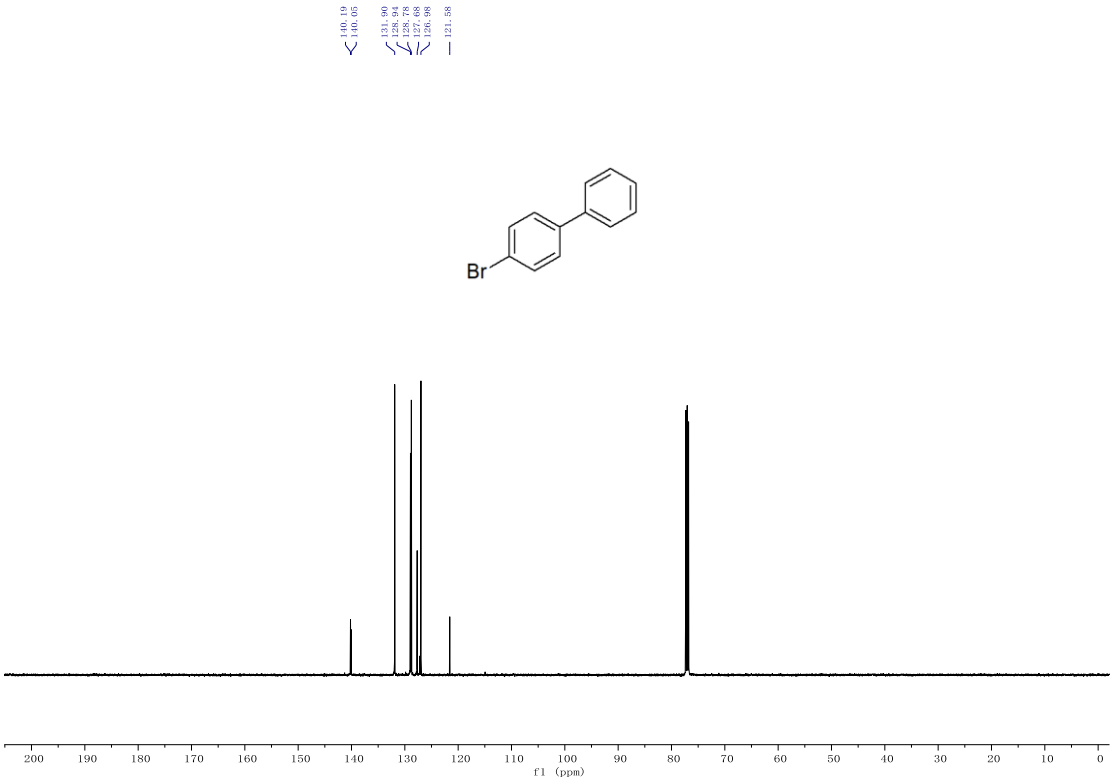
(Table 2, entry 3)

^{1}H NMR spectrum of 4-Bromobiphenyl



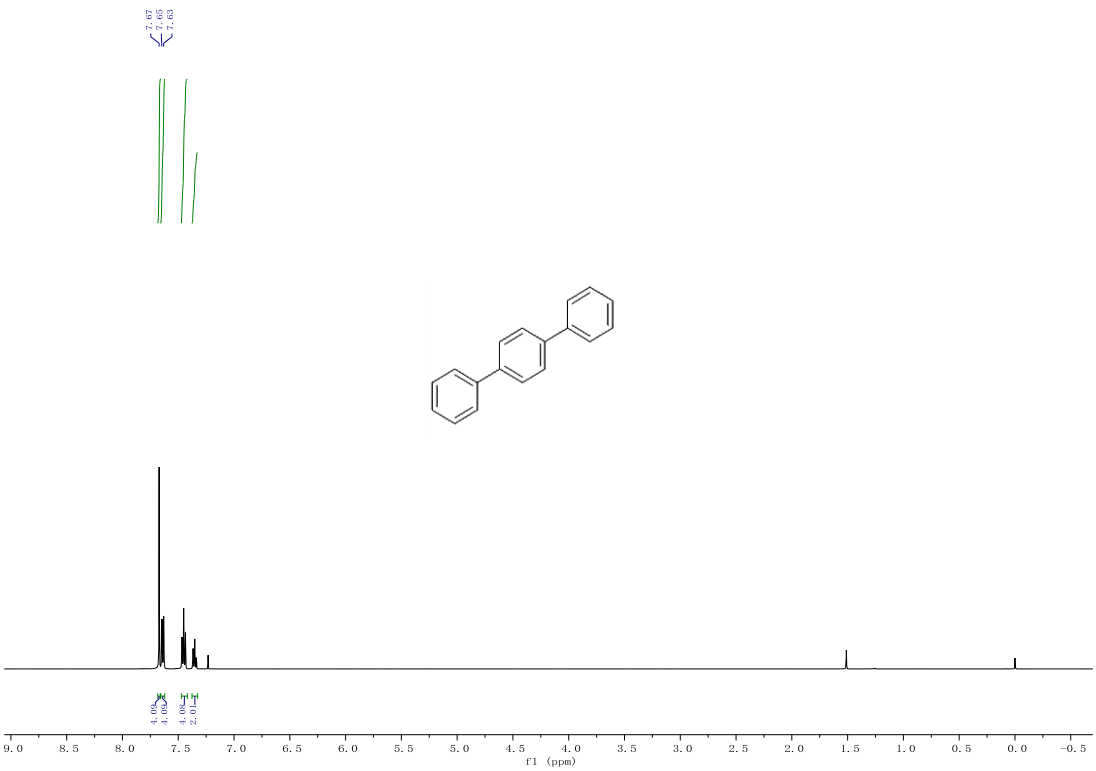
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 4H), 7.46 – 7.39 (m, 4H), 7.38 – 7.32 (m, 1H).

^{13}C NMR spectrum of 4-Bromobiphenyl



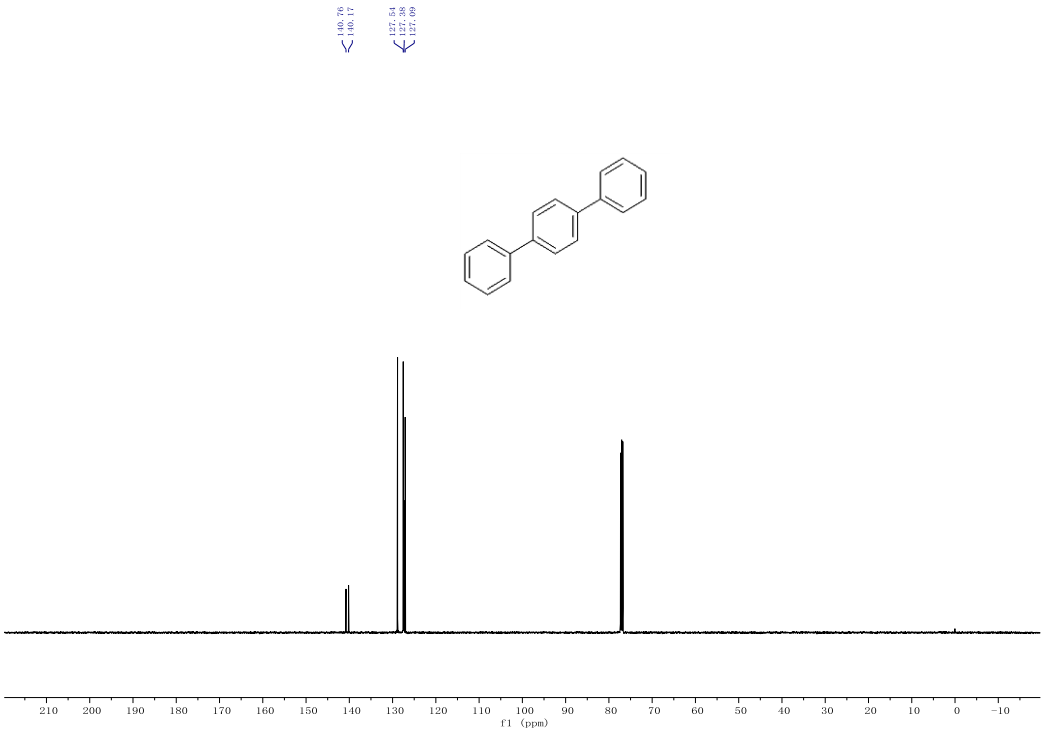
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.2, 140.1, 131.9, 128.9, 128.7, 127.6, 126.9, 121.5.

(Table 2, entry 3) **^{1}H NMR spectrum of *p*-Terophenyl**



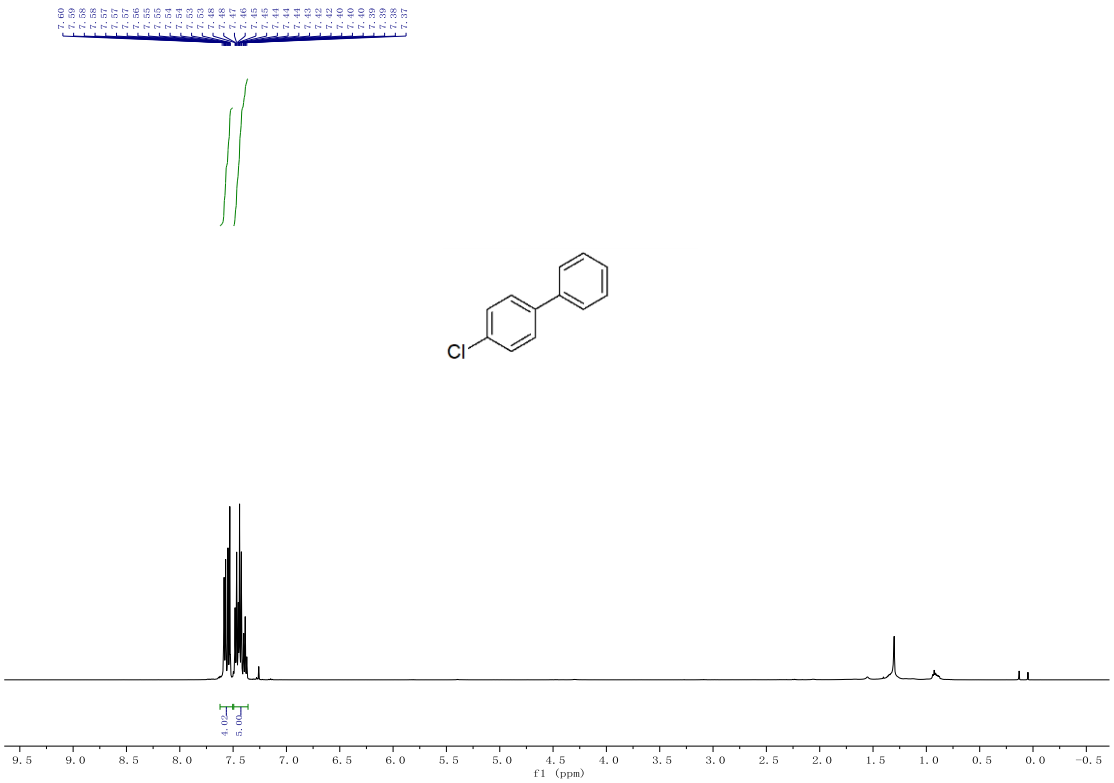
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (s, 4H), 7.64 (d, *J* = 8.7 Hz, 4H), 7.45 (dd, *J* = 8.4, 7.0 Hz, 4H), 7.38 – 7.33 (m, 2H).

^{13}C NMR spectrum of *p*-Terophenyl



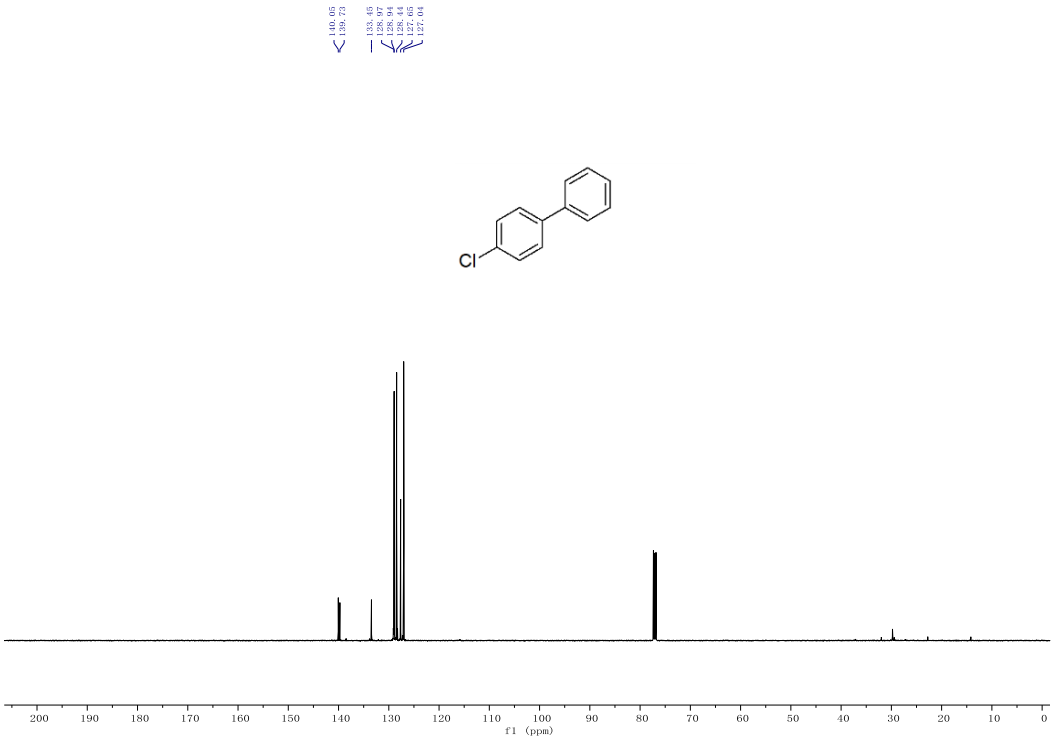
^{13}C NMR (126 MHz, Chloroform-d) δ 140.76, 140.17, 128.85, 127.54, 127.38, 127.09.

(Table 2, entry 6) **^{1}H NMR spectrum of 4-Chlorobiphenyl**



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.50 (m, 4H), 7.49 – 7.36 (m, 5H).

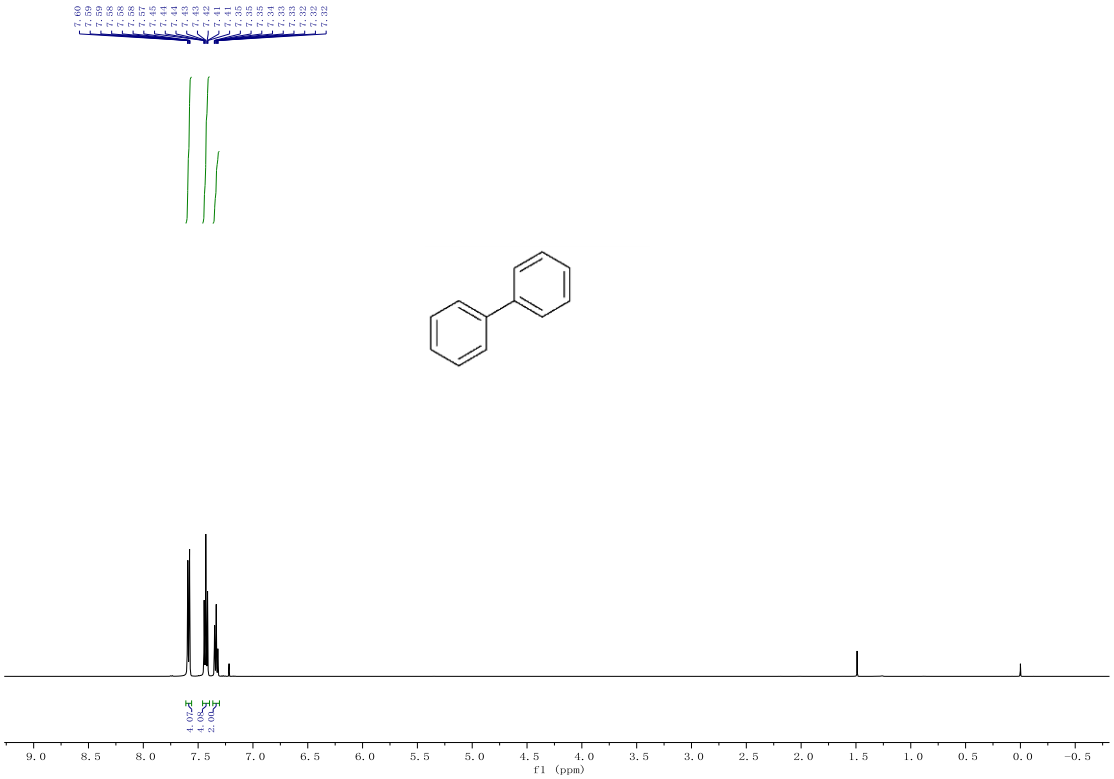
^{13}C NMR spectrum of 4-Chlorobiphenyl



^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.1, 139.7, 133.4, 128.9, 128.9, 128.4, 127.6, 127.1.

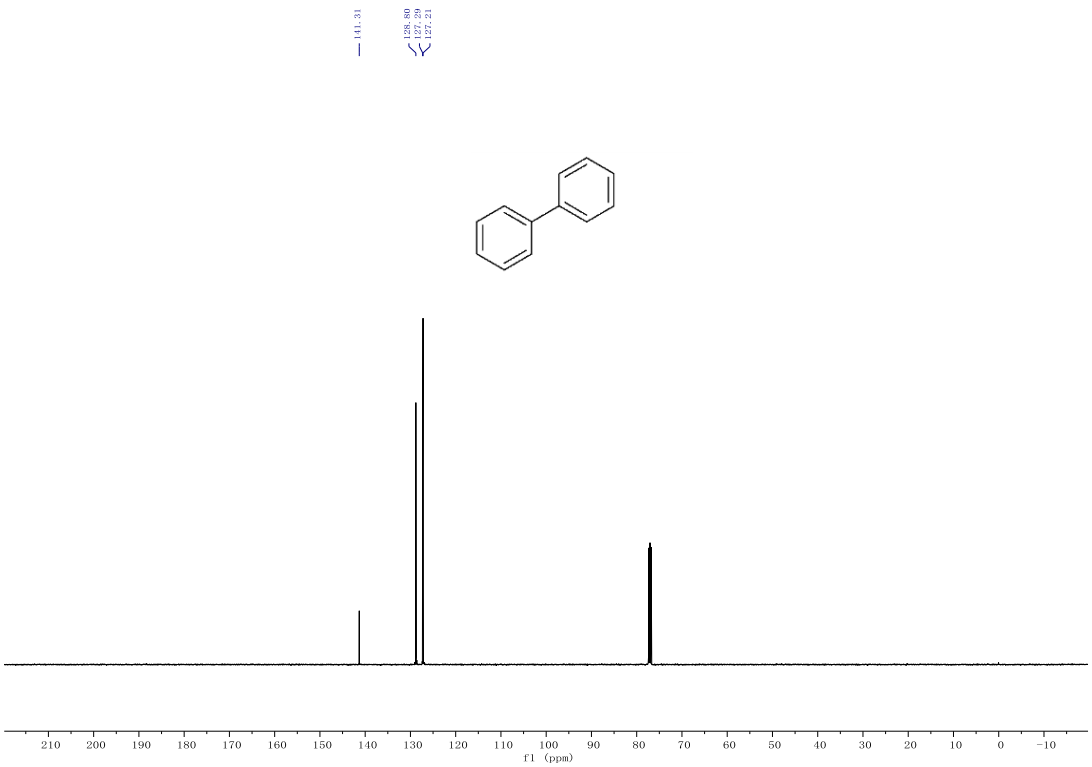
(Table 3, entry 1)

^{1}H NMR spectrum of Biphenyl



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 4H), 7.43 (dd, *J* = 8.5, 6.9 Hz, 4H), 7.37 – 7.31 (m, 2H).

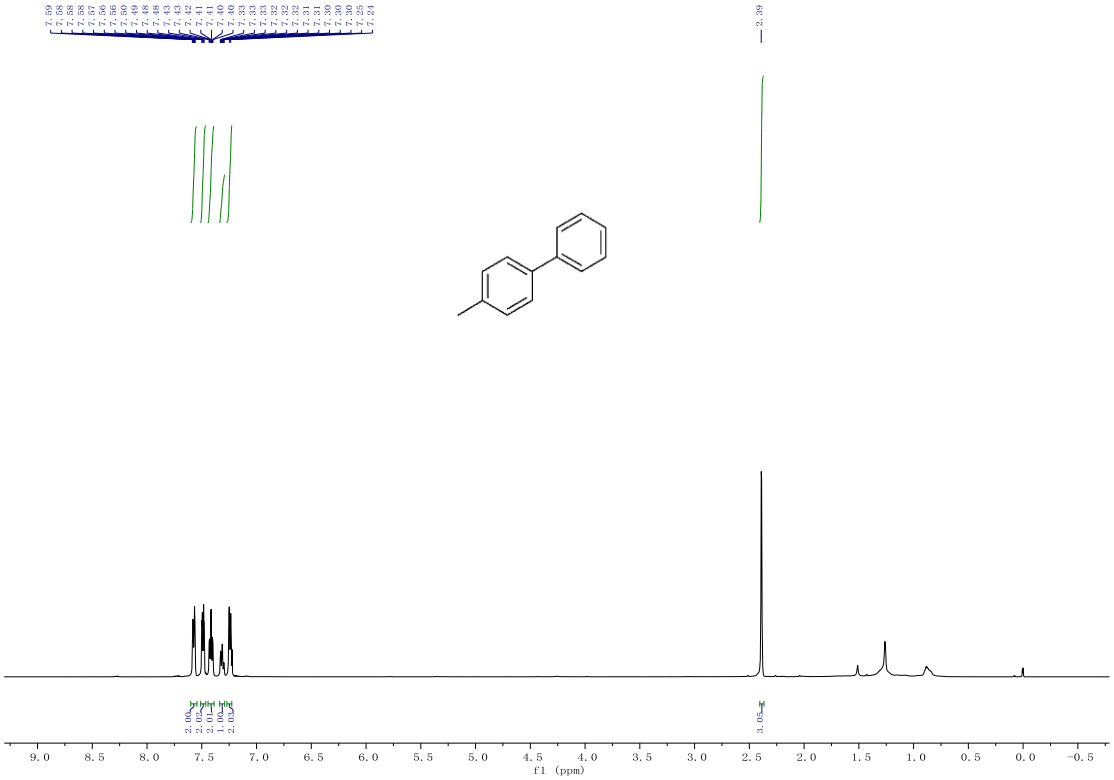
^{13}C NMR spectrum of Biphenyl



^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.3, 128.8, 127.3, 127.2.

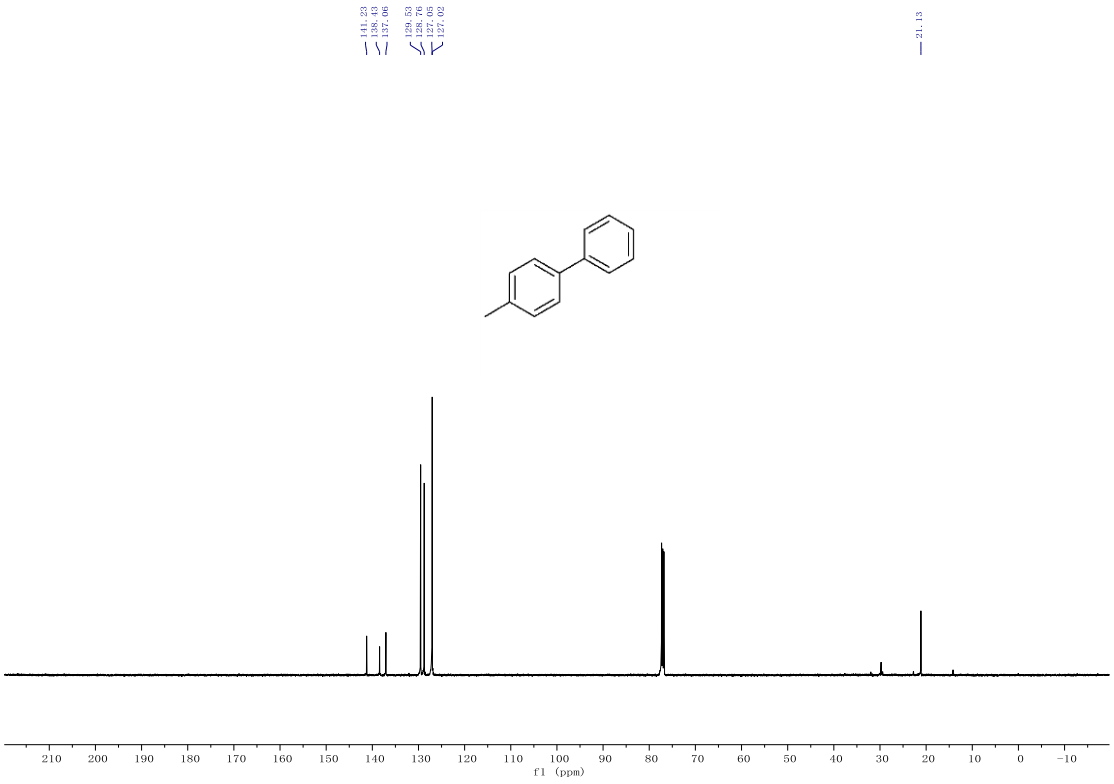
(Table 3, entry 2)

^{1}H NMR spectrum of 4-Methylbiphenyl



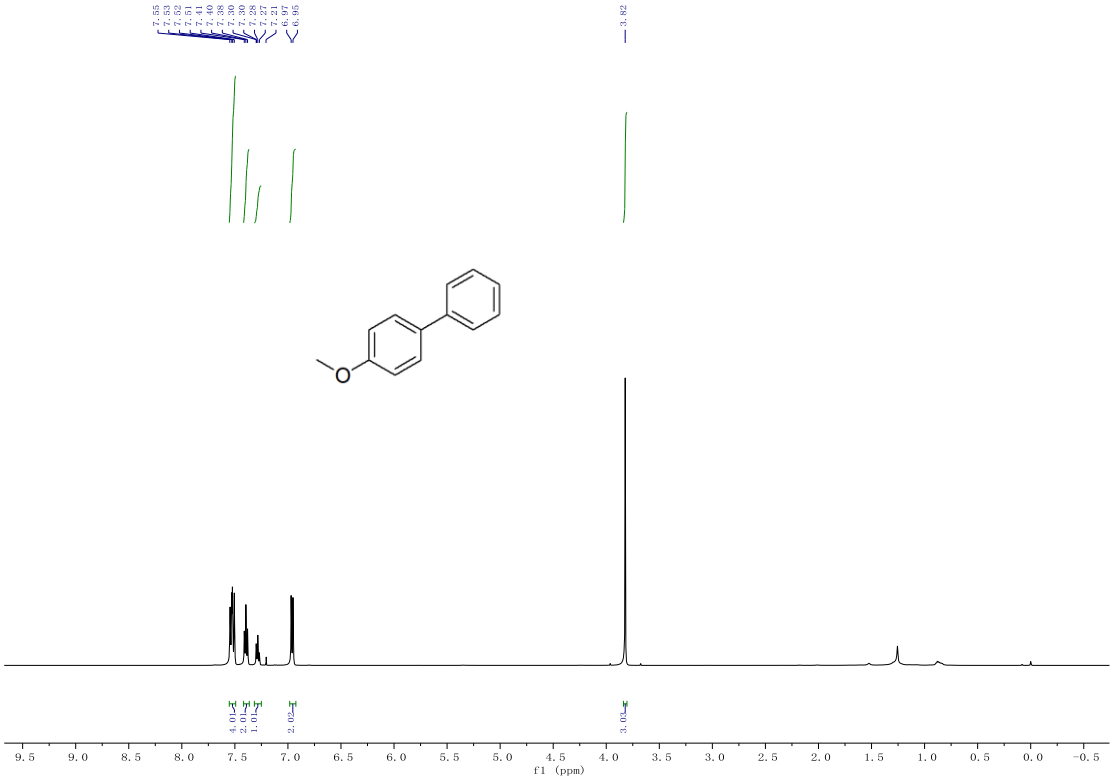
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.49 (dd, *J* = 8.1, 2.3 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.24 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR spectrum of 4-Methylbiphenyl



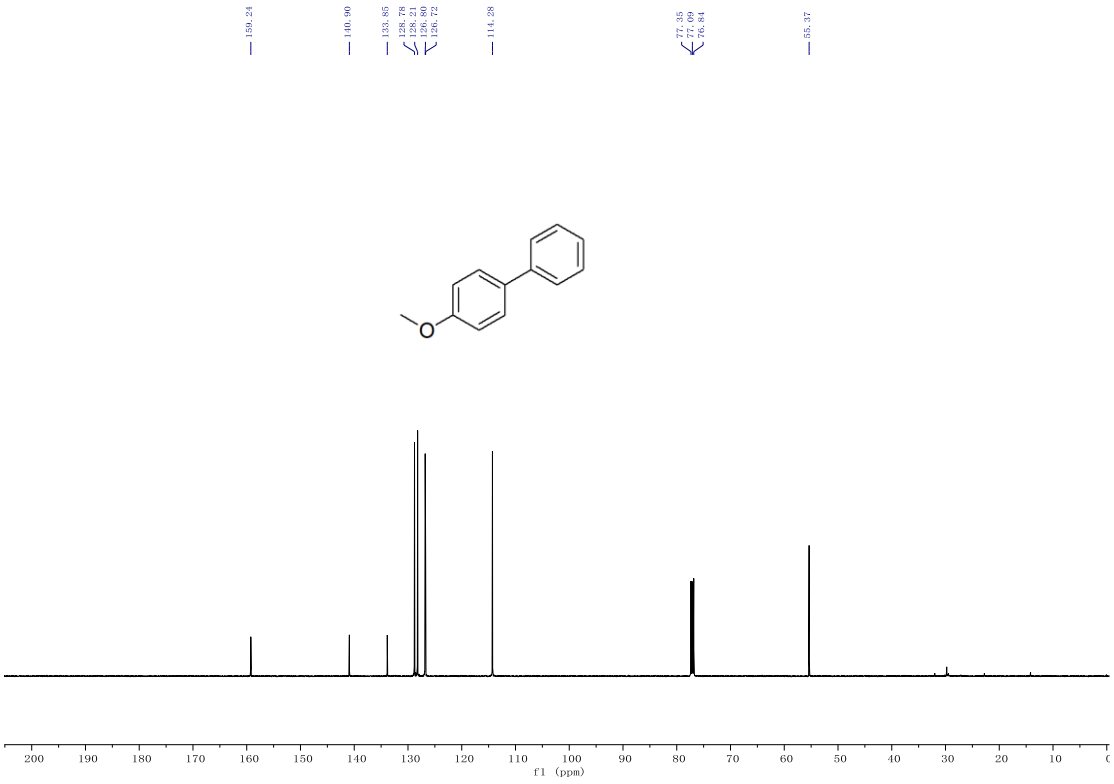
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.2, 138.4, 137.1, 129.5, 128.7, 127.0, 127.0, 21.1.

(Table 3, entry 3) **^{1}H NMR spectrum of 4-Methoxybiphenyl**



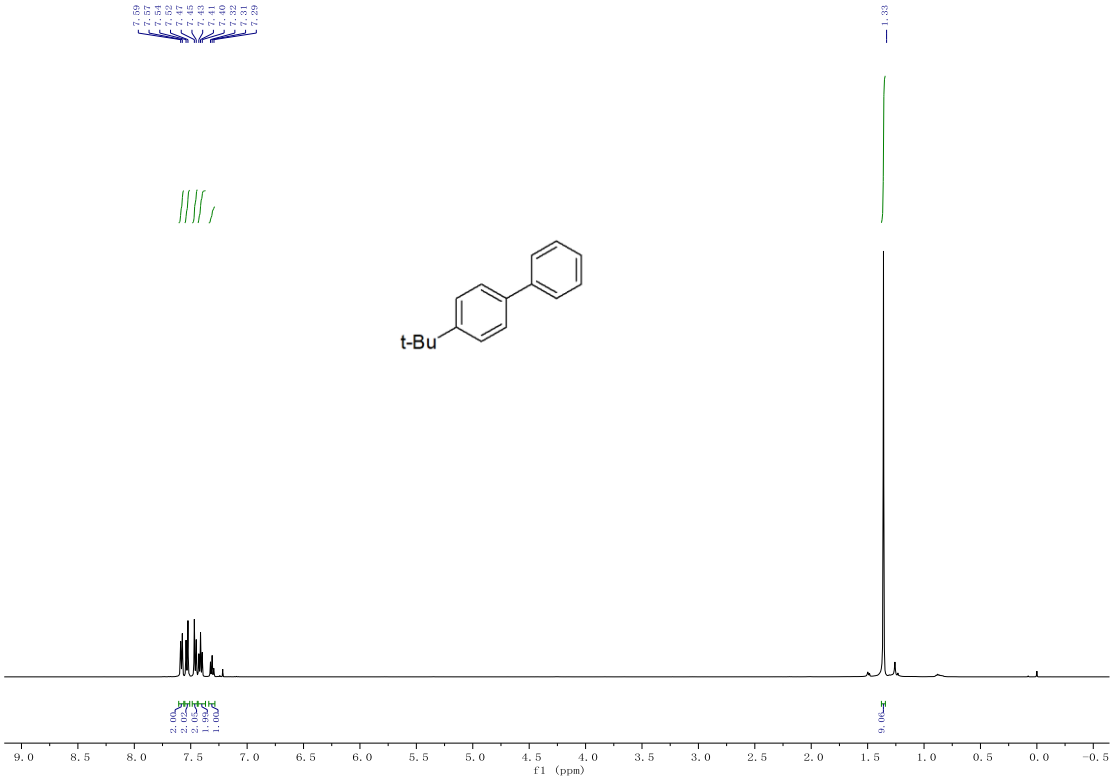
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 4H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.25 (m, 1H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR spectrum of 4-Methoxybiphenyl



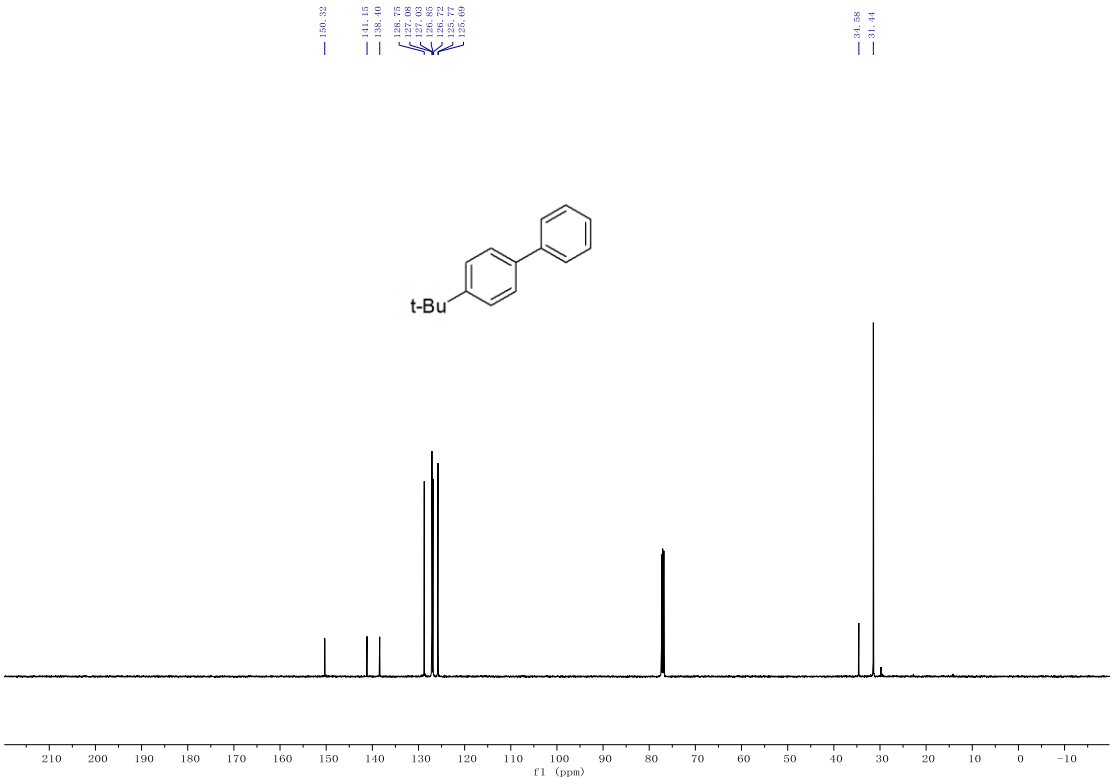
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4.

(Table 3, entry 4) **^{1}H NMR spectrum of 4-tert-Butylbiphenyl**



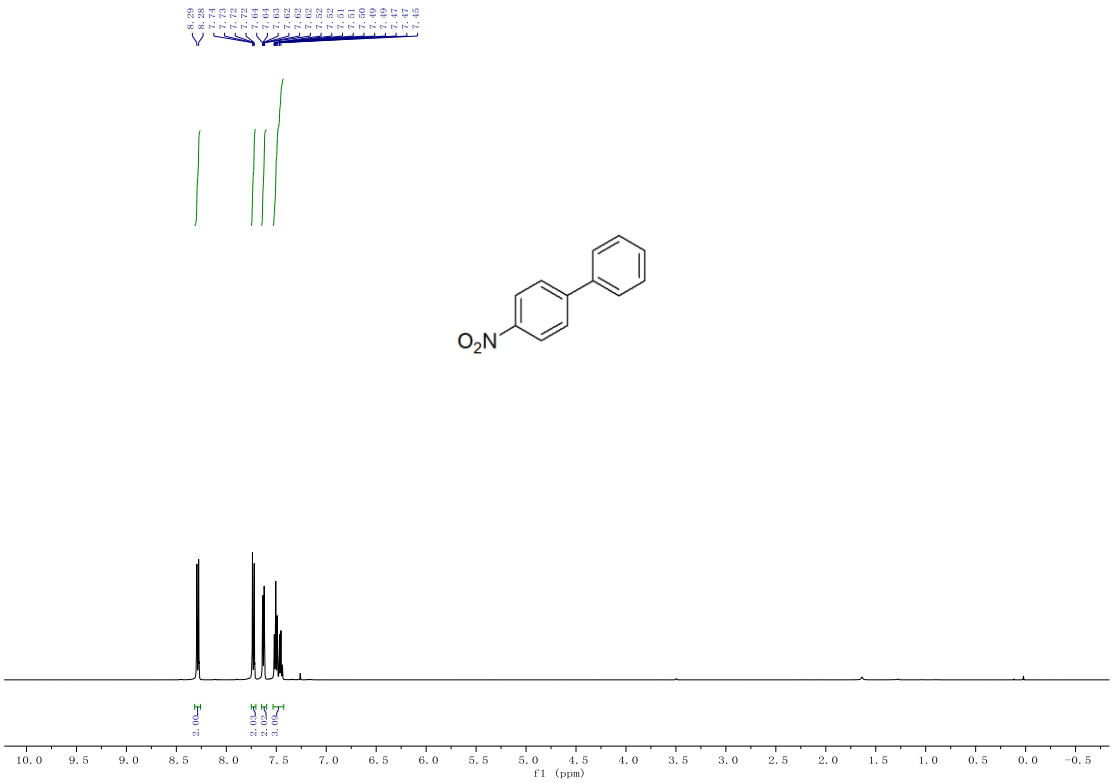
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 1.36 (s, 9H).

^{13}C NMR spectrum of 2 4-tert-Butylbiphenyl



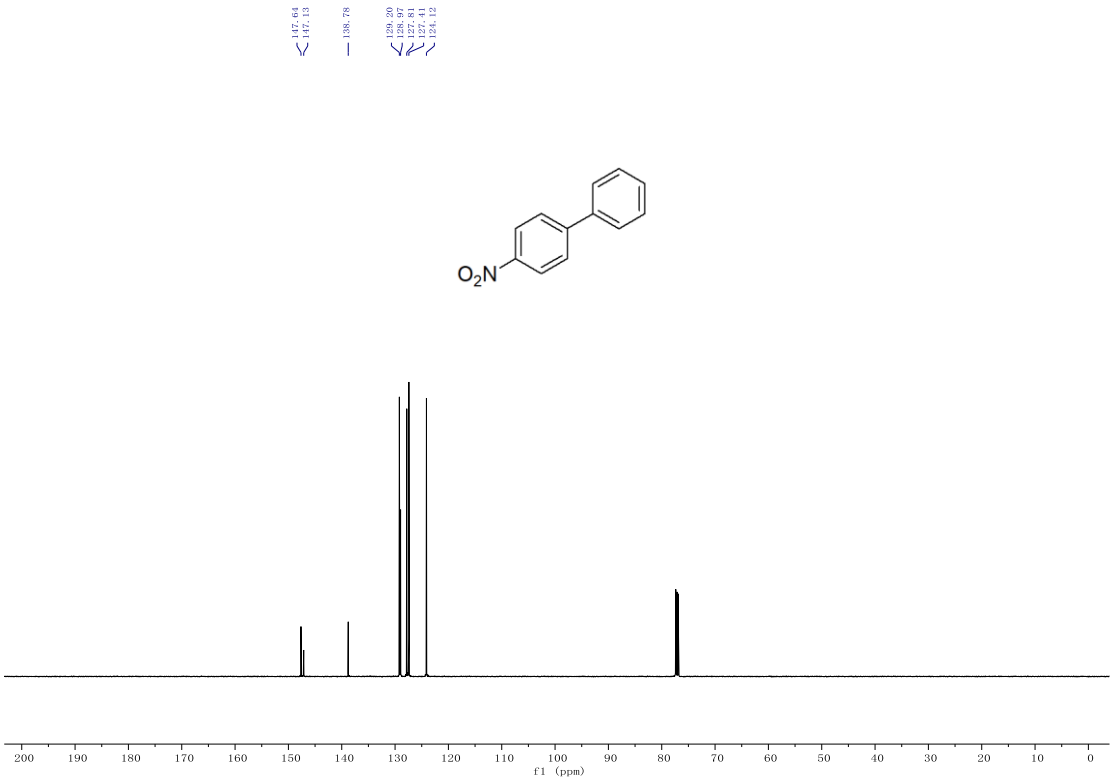
^{13}C NMR (126 MHz, Chloroform-d) δ 150.3, 141.2, 138.4, 128.8, 127.1, 127.1, 126.9, 125.8, 34.6, 31.4.

(Table 3, entry 5) **^{1}H NMR spectrum of 4-Nitrobiphenyl**



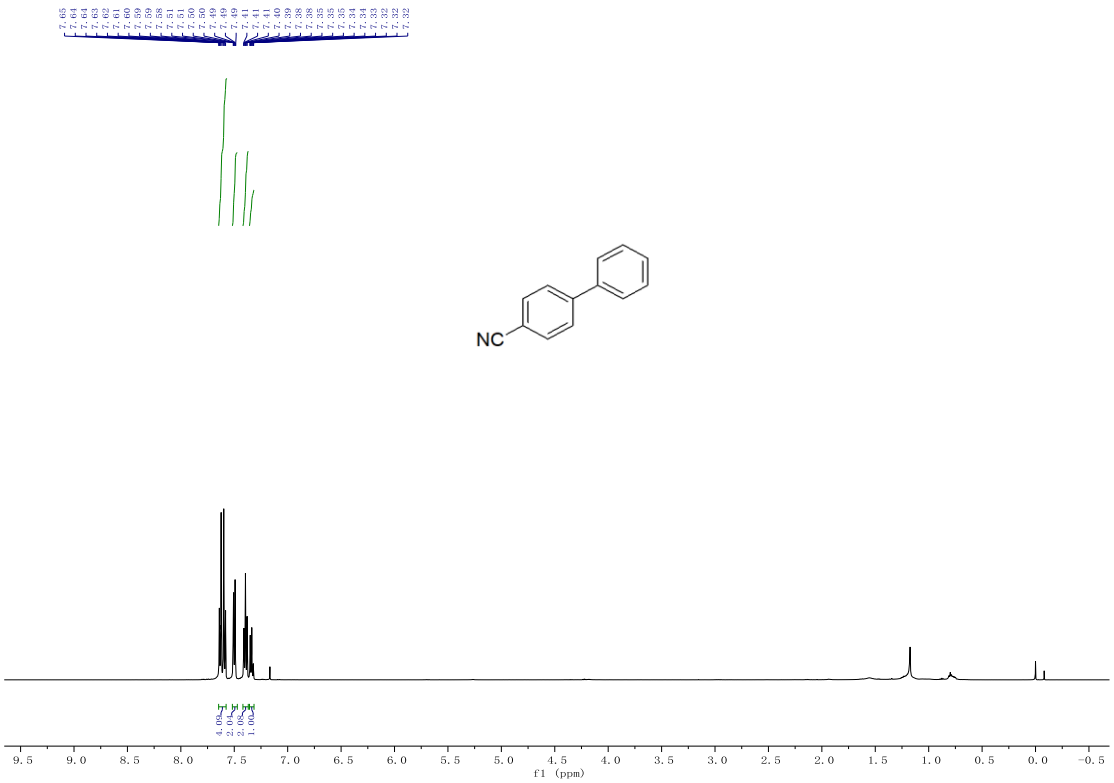
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.75 – 7.70 (m, 2H), 7.65 – 7.60 (m, 2H), 7.53 – 7.42 (m, 3H).

^{13}C NMR spectrum of 4-Nitrobiphenyl



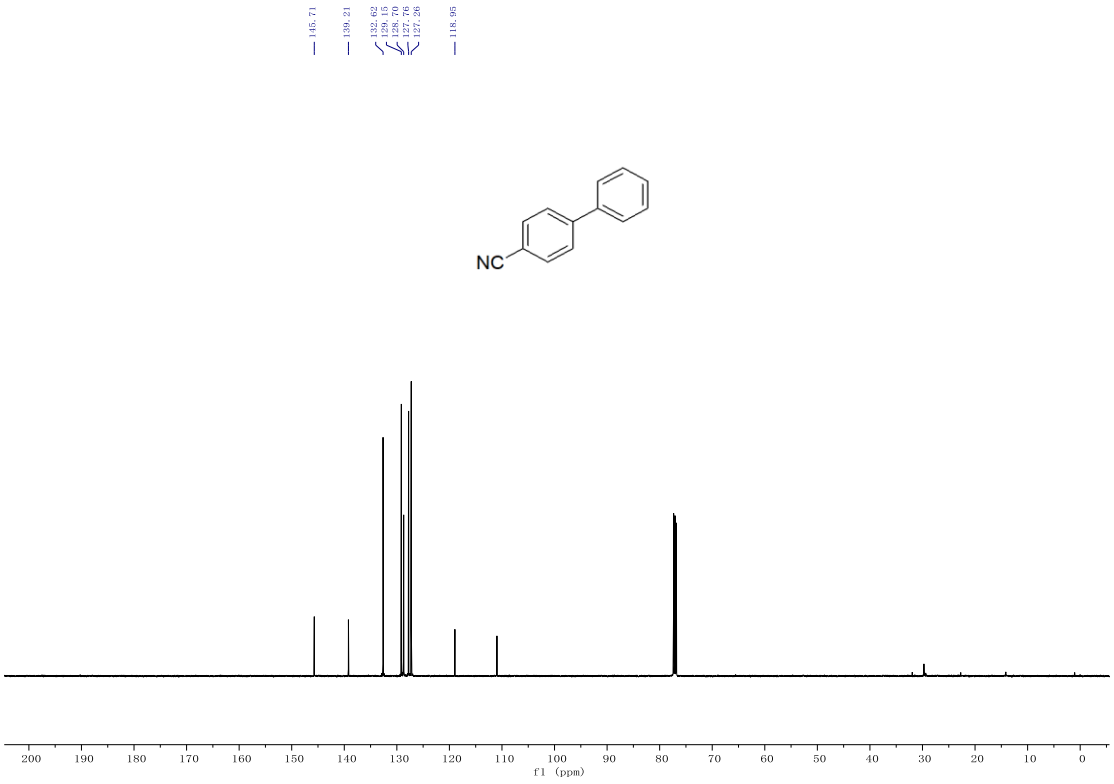
^{13}C NMR (126 MHz, Chloroform-*d*) δ 147.6, 147.1, 138.7, 129.2, 128.9, 127.8, 127.4, 124.1.

(Table 3, entry 6) **^{1}H NMR spectrum of 4-Cyanobiphenyl**



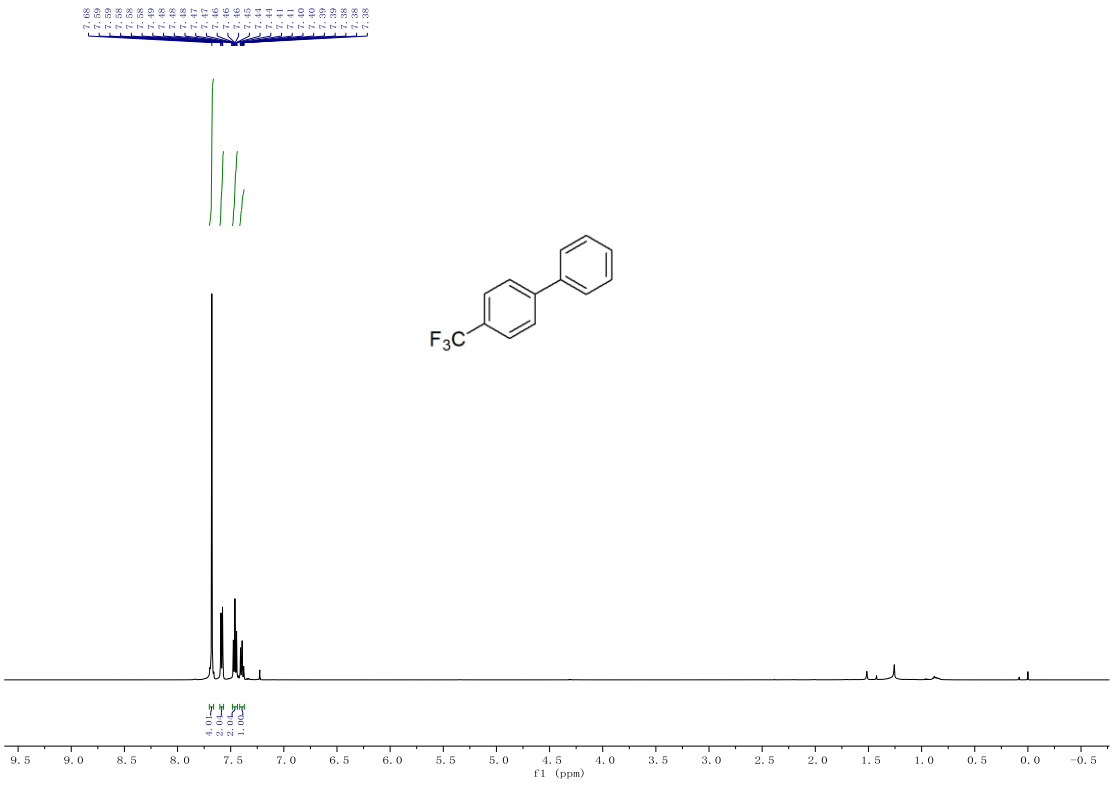
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 4H), 7.52 – 7.47 (m, 2H), 7.42 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H).

^{13}C NMR spectrum of 4-Cyanobiphenyl



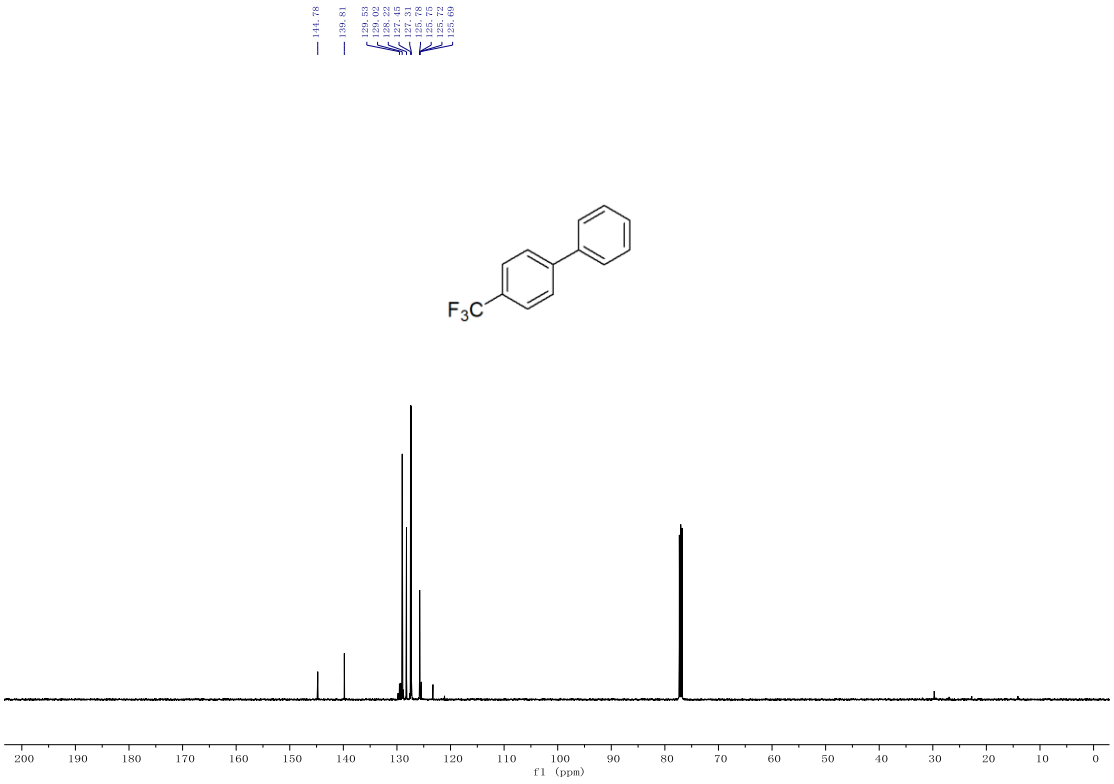
^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 118.9, 110.9.

(Table 3, entry 7) **^{1}H NMR spectrum of 4-(Trifluoromethyl)biphenyl**



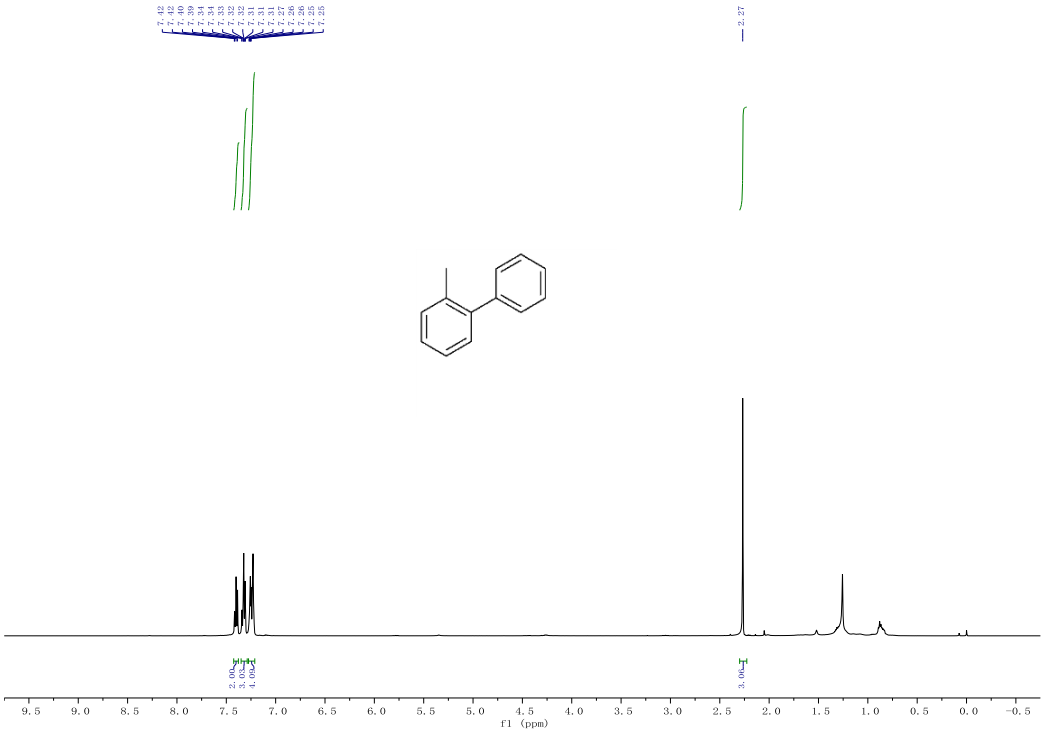
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (s, 4H), 7.60 – 7.57 (m, 2H), 7.48 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H).

^{13}C NMR spectrum of 4-(Trifluoromethyl)biphenyl



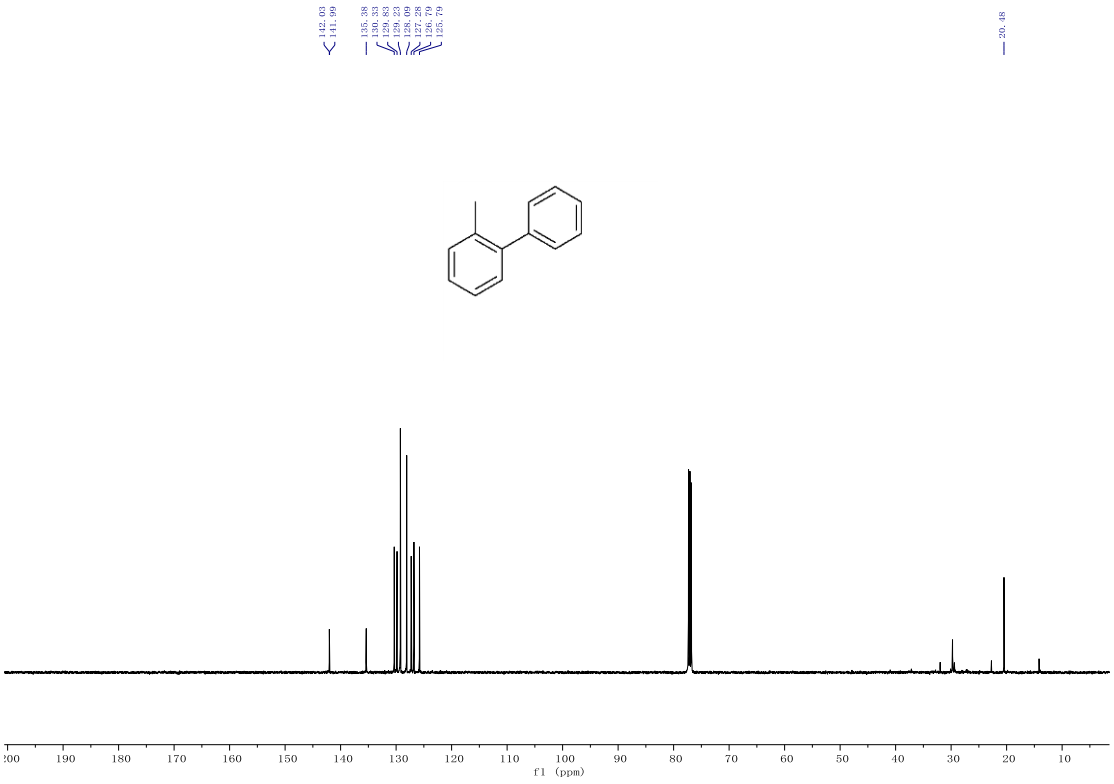
^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.7, 139.8, 129.5, 129.1, 128.2, 127.4, 127.3, 125.7 (q, J = 3.8 Hz), 123.2.

(Table 3, entry 8) **^{1}H NMR spectrum of 2-Phenyltoluene**



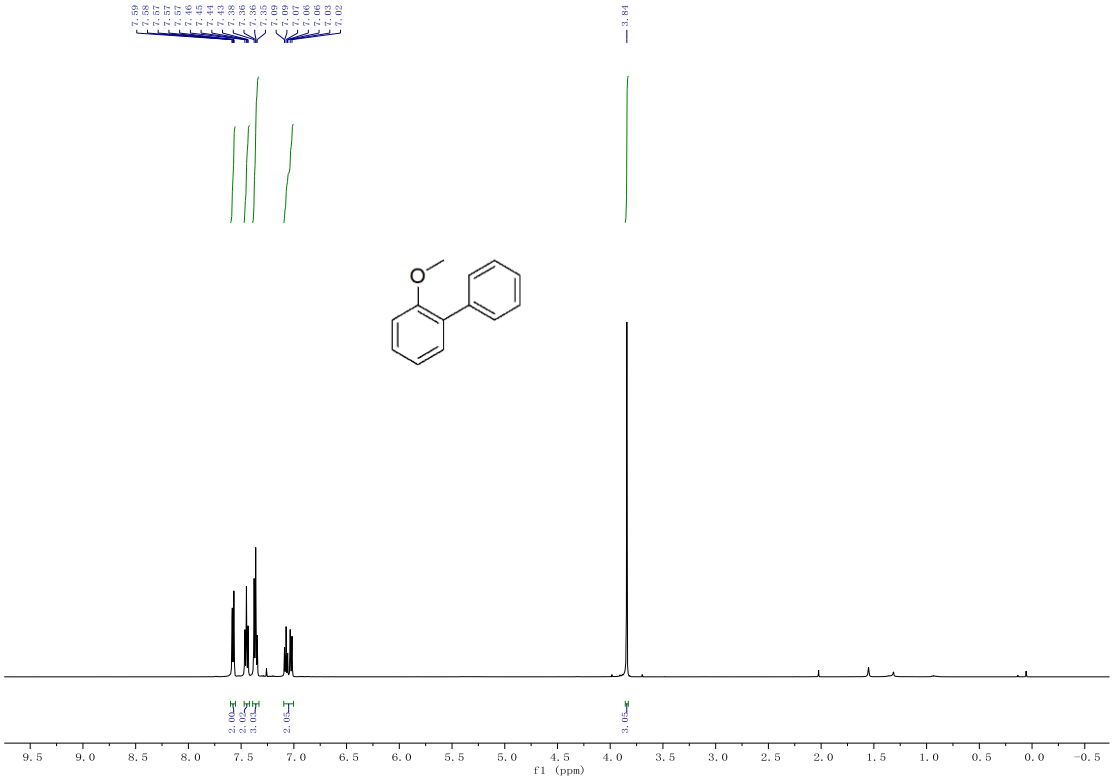
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.27 – 7.21 (m, 4H), 2.27 (s, 3H).

^{13}C NMR spectrum of 2-Phenyltoluene



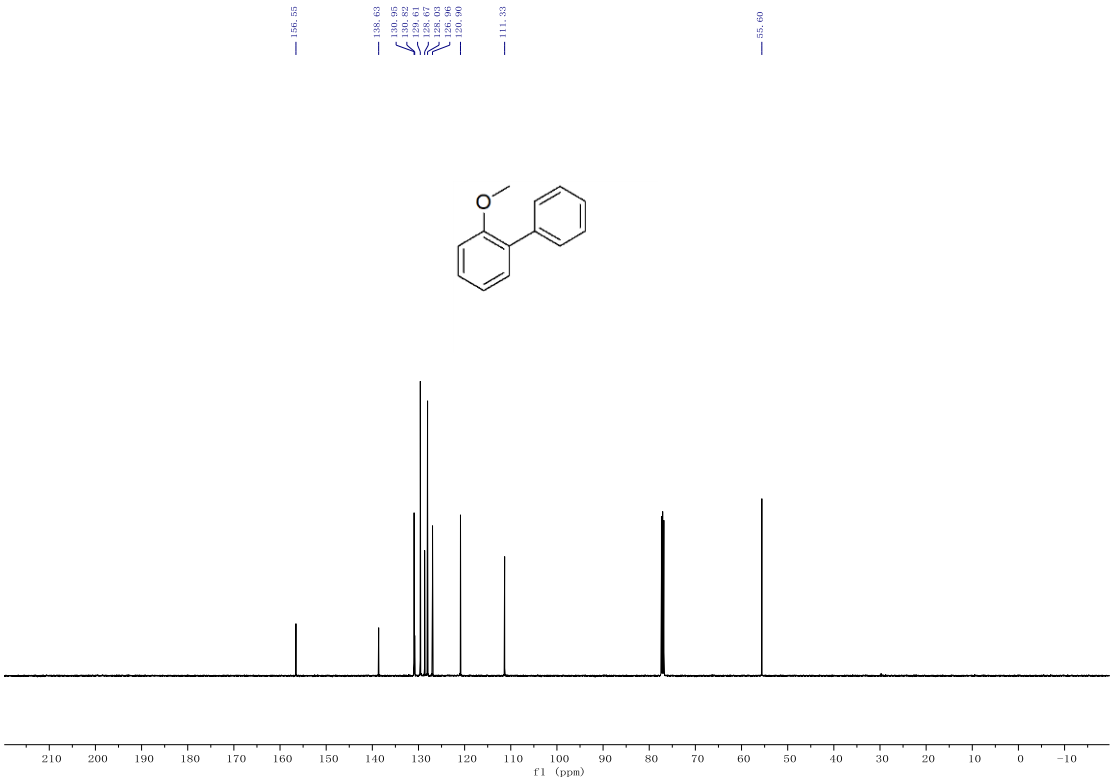
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.0, 141.9, 135.3, 130.3, 129.8, 129.2, 128.1, 127.2, 126.7, 125.7, 20.4.

(Table 3, entry 9) **^{1}H NMR spectrum of 2-Methoxylbiphenyl**



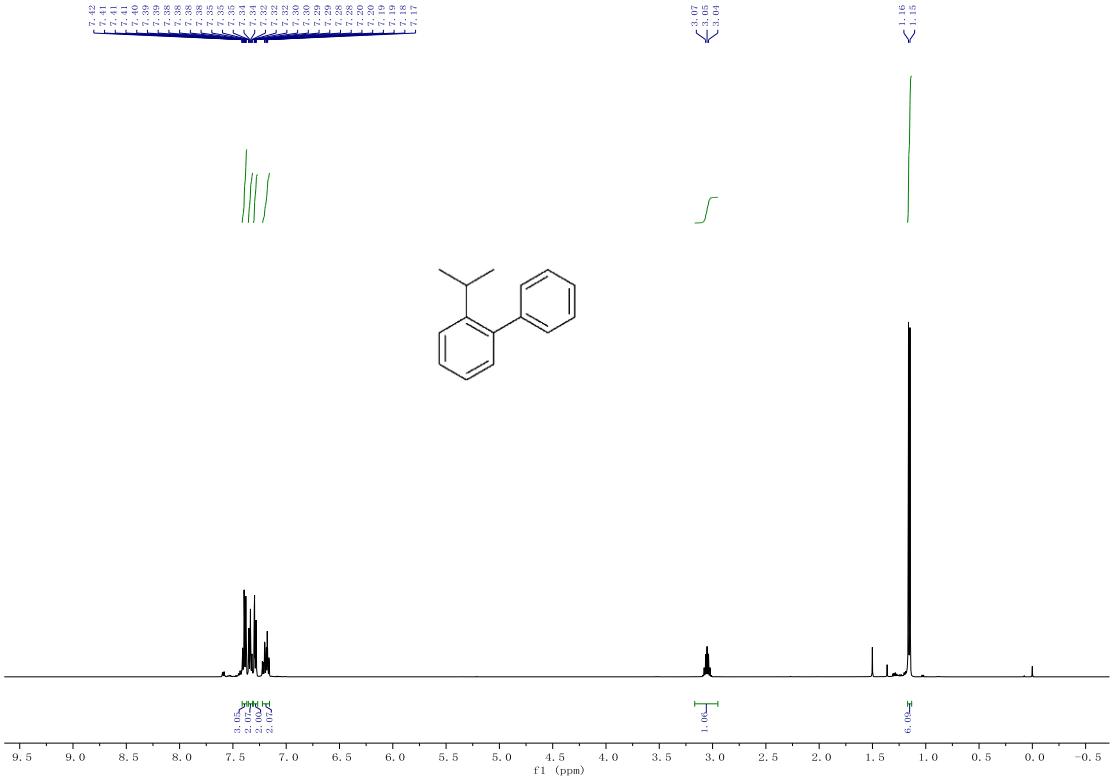
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 3H), 7.10 – 7.00 (m, 2H), 3.84 (s, 3H).

^{13}C NMR spectrum of 2-Methoxylbiphenyl



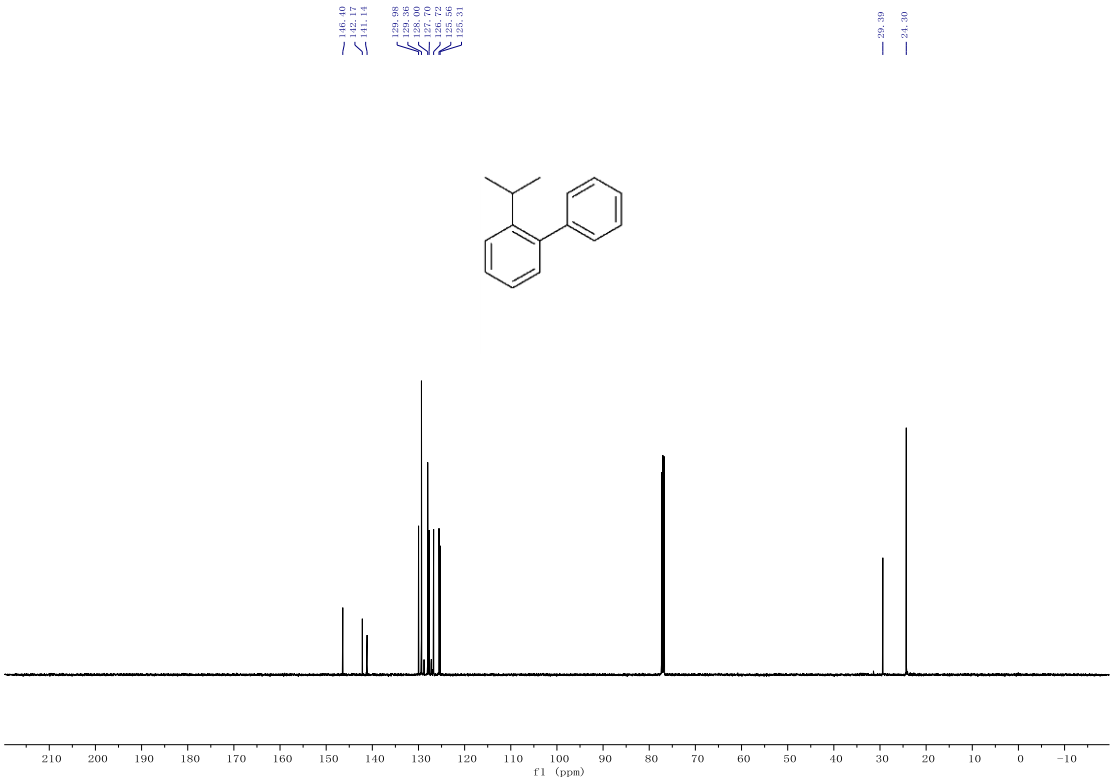
^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.5, 138.6, 130.9, 130.8, 129.6, 128.6, 128.1, 126.9, 120.9, 111.3, 55.6.

(Table 3, entry 10) **^{1}H NMR spectrum of 2-Isopropylbiphenyl**



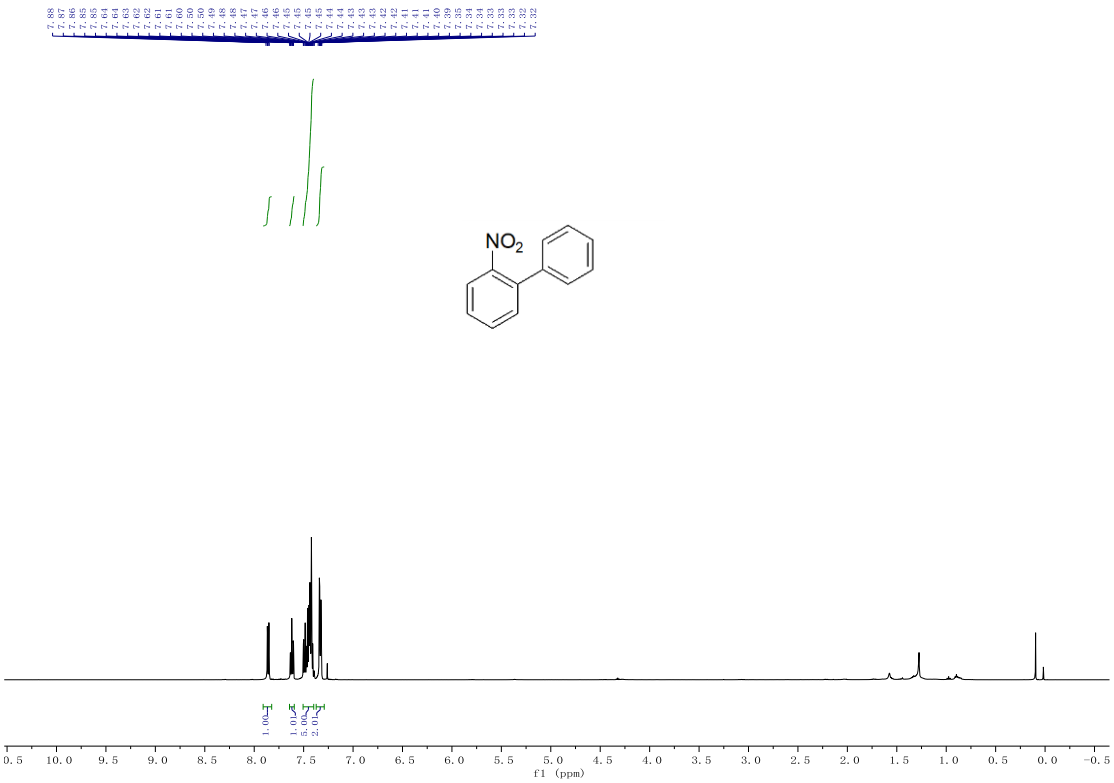
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.37 (m, 3H), 7.36 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 2H), 3.17 – 2.95 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR spectrum of 2-Isopropylbiphenyl



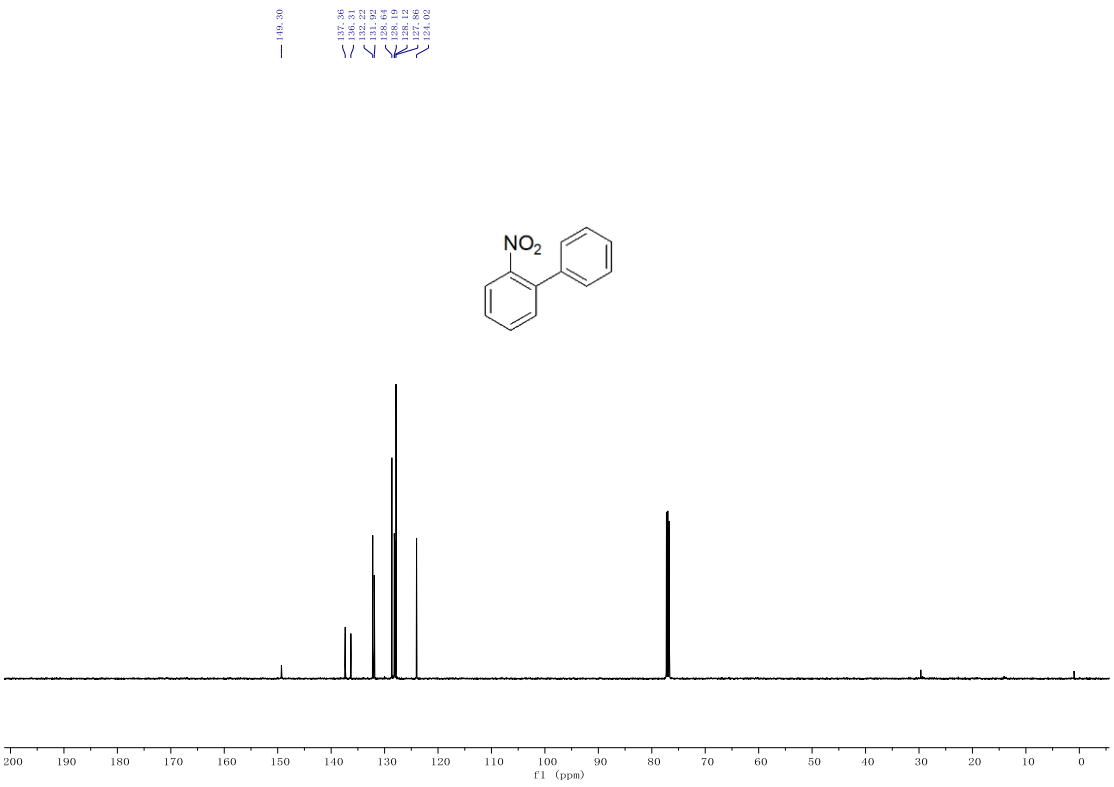
^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.4, 142.1, 141.1, 129.9, 129.3, 128.0, 127.7, 126.7, 125.5, 125.3, 29.3, 24.3.

(Table 3, entry 11) **^{1}H NMR spectrum of 2-Nitrodiphenyl**



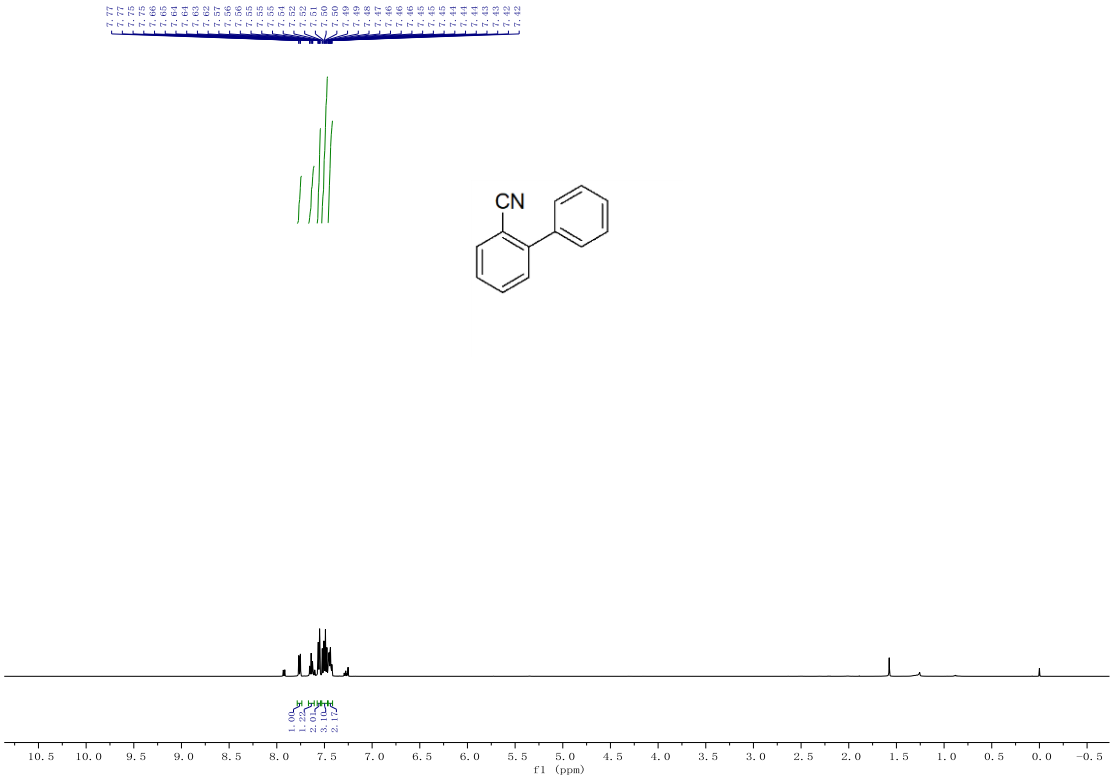
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64– 7.60 (m, 1H), 7.51 – 7.40 (m, 5H), 7.37 – 7.29 (m, 2H).

^{13}C NMR spectrum of 2-Nitrodiphenyl



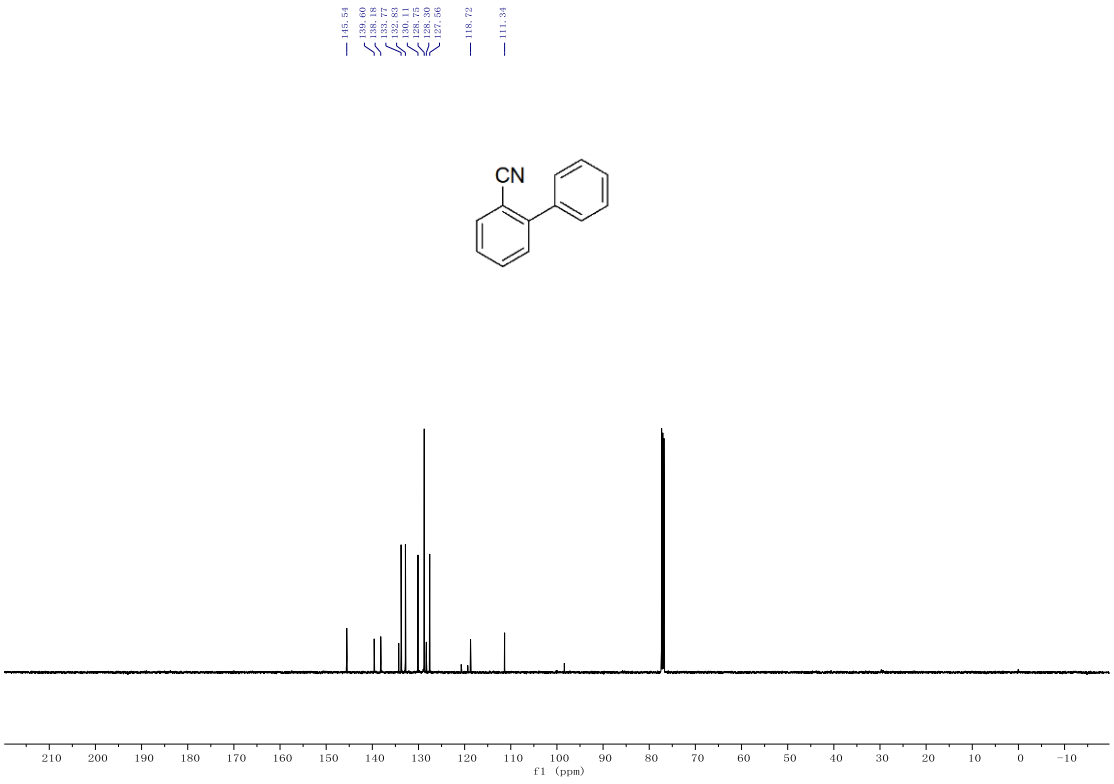
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.3, 137.3, 136.3, 132.2, 131.9, 128.6, 128.1, 128.1, 127.8, 124.0.

(Table 3, entry 12) **^{1}H NMR spectrum of 2-Cyanobiphenyl**



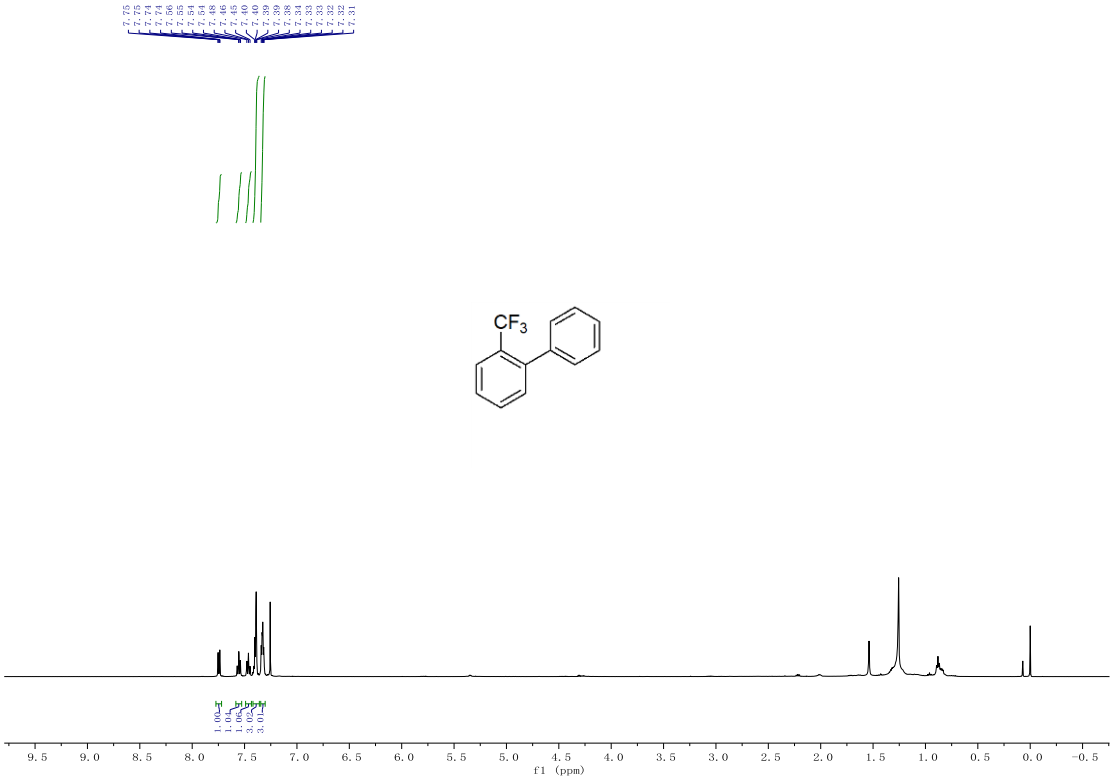
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 – 7,62 (m, 1H), 7.58 – 7.54 (m, 2H), 7.53 – 7.47 (m, 3H), 7.46 – 7.42 (m, 2H).

^{13}C NMR spectrum of 2-Cyanobiphenyl



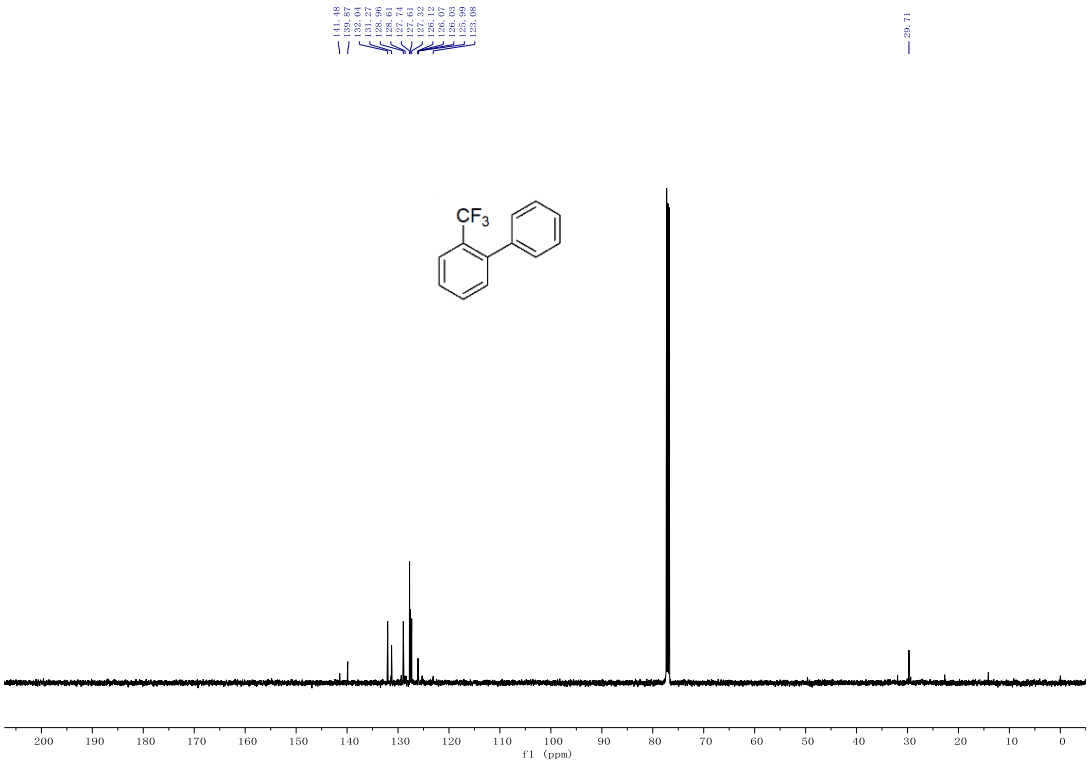
^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.5, 139.6, 138.1, 133.7, 132.8, 130.1, 128.7, 128.3, 127.5, 118.7, 111.3.

(Table 3, entry 13) **^{1}H NMR spectrum of 2-(Trifluoromethyl)biphenyl**



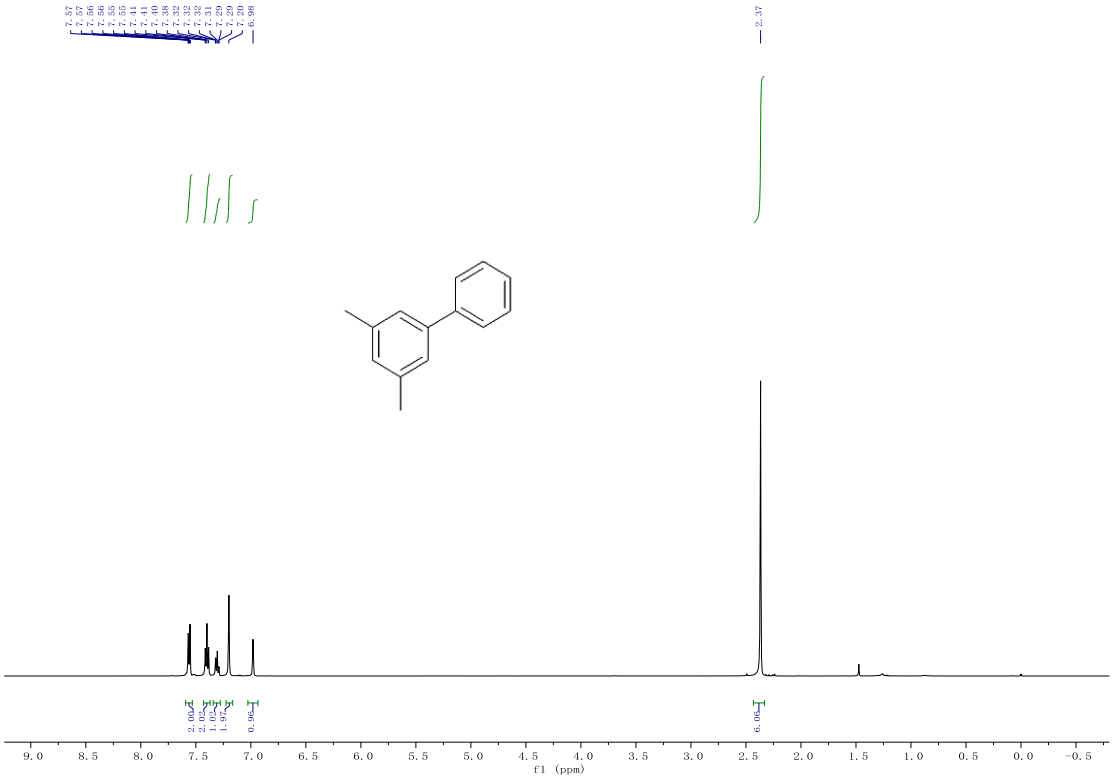
^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (dd, J = 7.9, 1.3 Hz, 1H), 7.56 – 7.54 (m, 1H), 7.48 – 7.45 (m, 1H), 7.40 –7.38 (m, 3H), 7.34 –7.31 (m, 3H).

^{13}C NMR spectrum of 2-(Trifluoromethyl)biphenyl



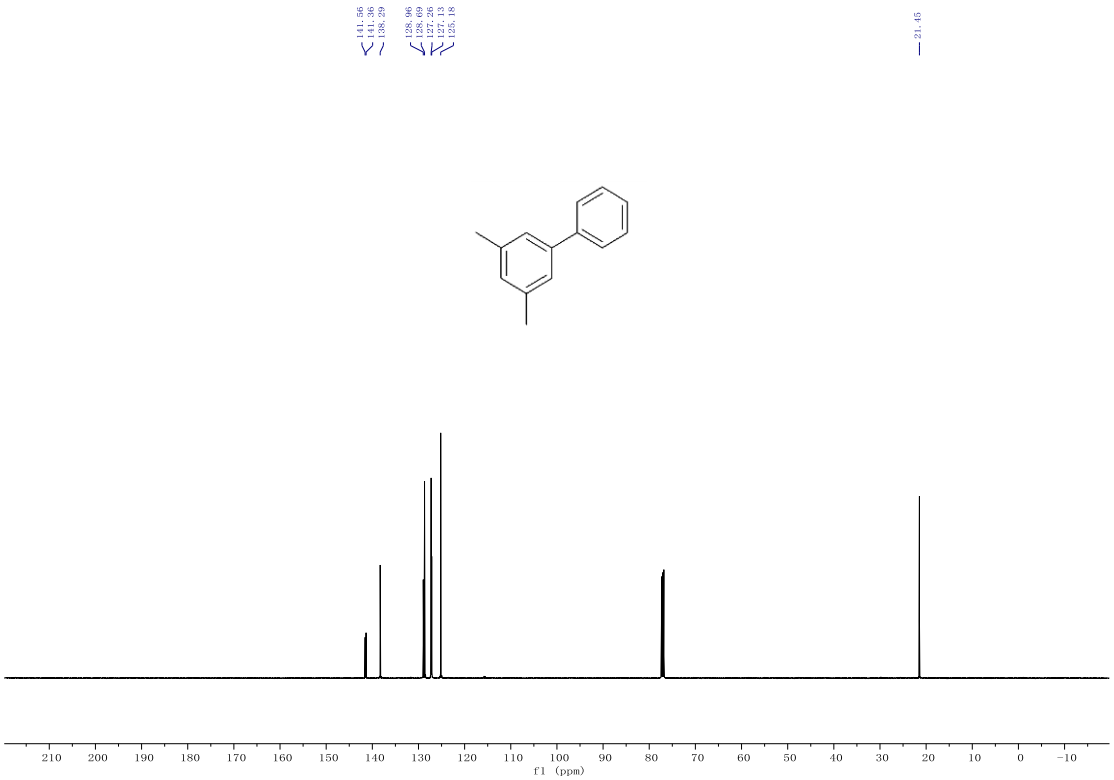
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.4, 139.8, 132.0, 131.2, 128.9, 128.6, 127.7, 127.6, 127.3, 126.1 (q, *J* = 5.3 Hz), 123.1.

(Table 3, entry 14) **^{1}H NMR spectrum of 3,5-dimethyl-1,1'-biphenyl**



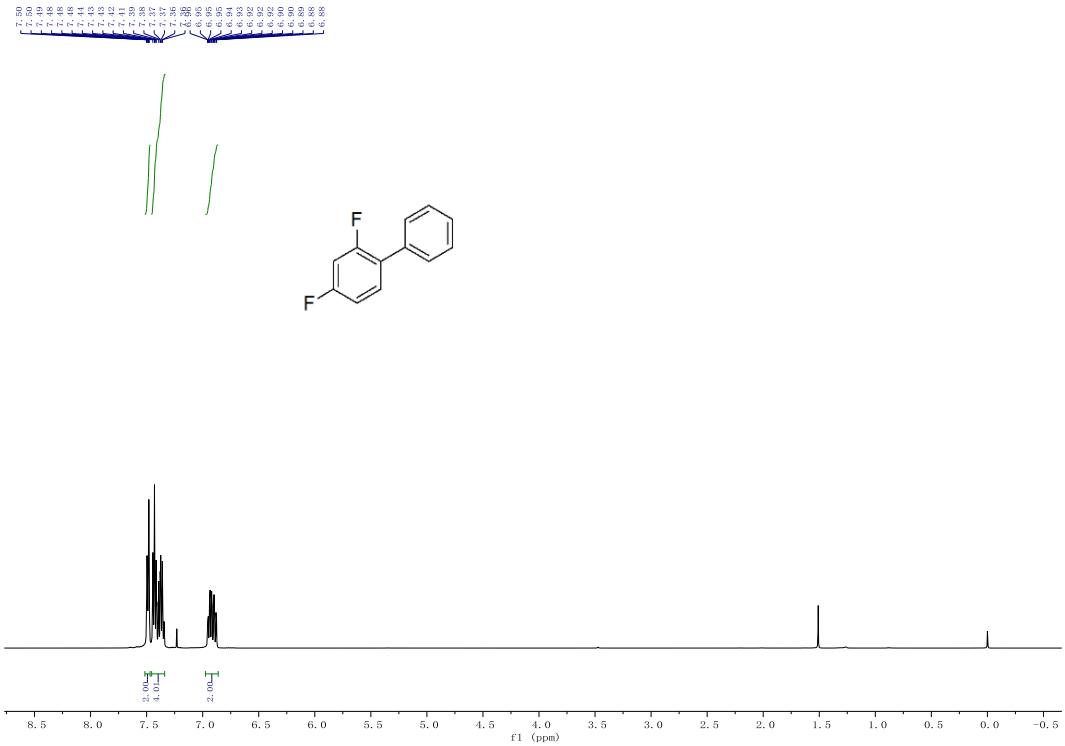
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.20 (s, 2H), 6.98 (s, 1H), 2.37 (s, 6H).

^{13}C NMR spectrum of 3,5-dimethyl-1,1'-biphenyl



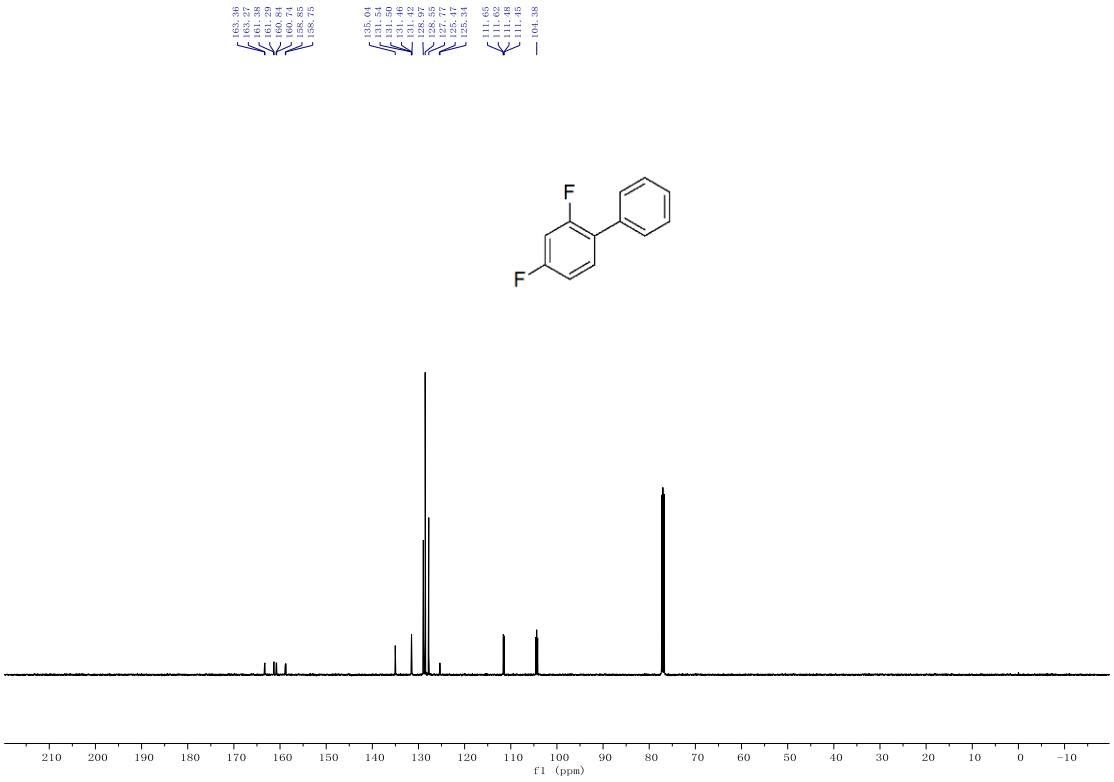
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.6, 141.4, 138.3, 128.9, 128.7, 127.3, 127.1, 125.2, 21.5.

(Table 3, entry 15) **^{1}H NMR spectrum of 2,4-Difluorobiphenyl**



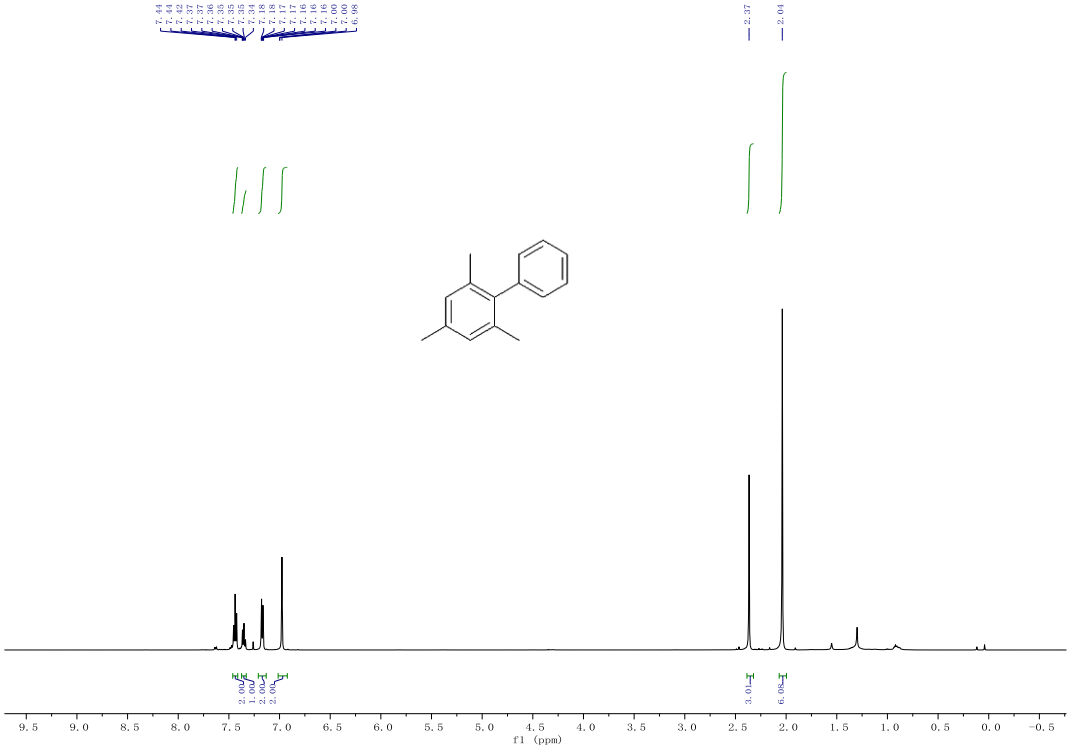
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50–7,48 (m, 2H), 7.46 – 7.34 (m, 4H), 6.98 – 6.86 (m, 2H).

^{13}C NMR spectrum of 2,4-Difluorobiphenyl



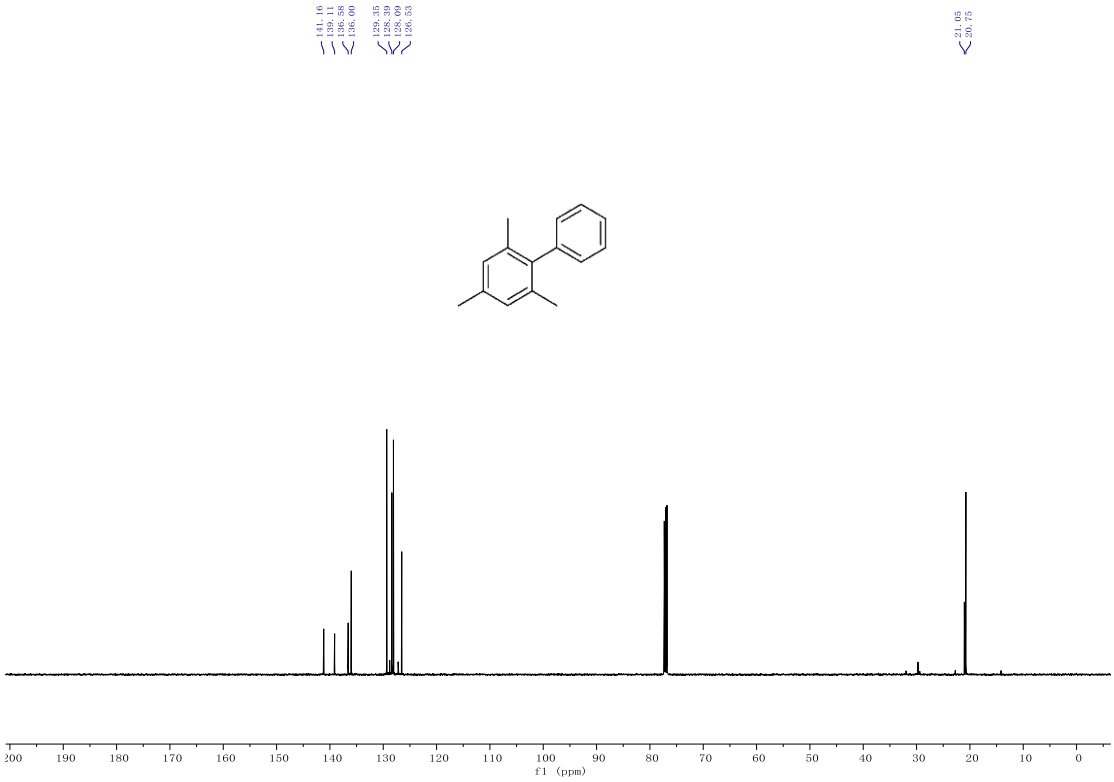
^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.3 (dd, *J* = 248.9, 11.9 Hz), 159.8 (dd, *J* = 250.2, 11.8 Hz), 135.0, 131.5 (dd, *J* = 9.3, 4.8 Hz), 128.9, 128.6, 127.7, 125.4 (d, *J* = 17.5 Hz), 111.6 (dd, *J* = 21.1, 3.7 Hz), 104.4.

(Table 3, entry 16) **^{1}H NMR spectrum of 2,4,6-Trimethyl-1,1'-biphenyl**



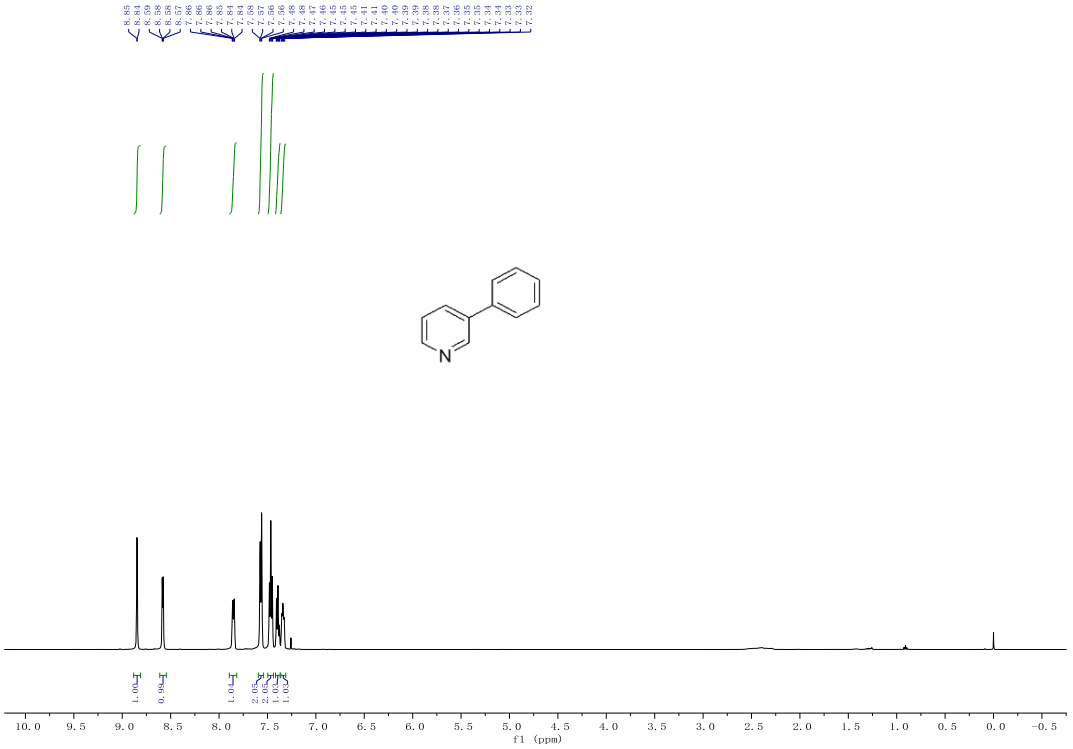
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.21 – 7.13 (m, 2H), 6.98 (s, 2H), 2.37 (s, 3H), 2.04 (s, 6H).

^{13}C NMR spectrum of 2,4,6-Trimethyl-1,1'-biphenyl



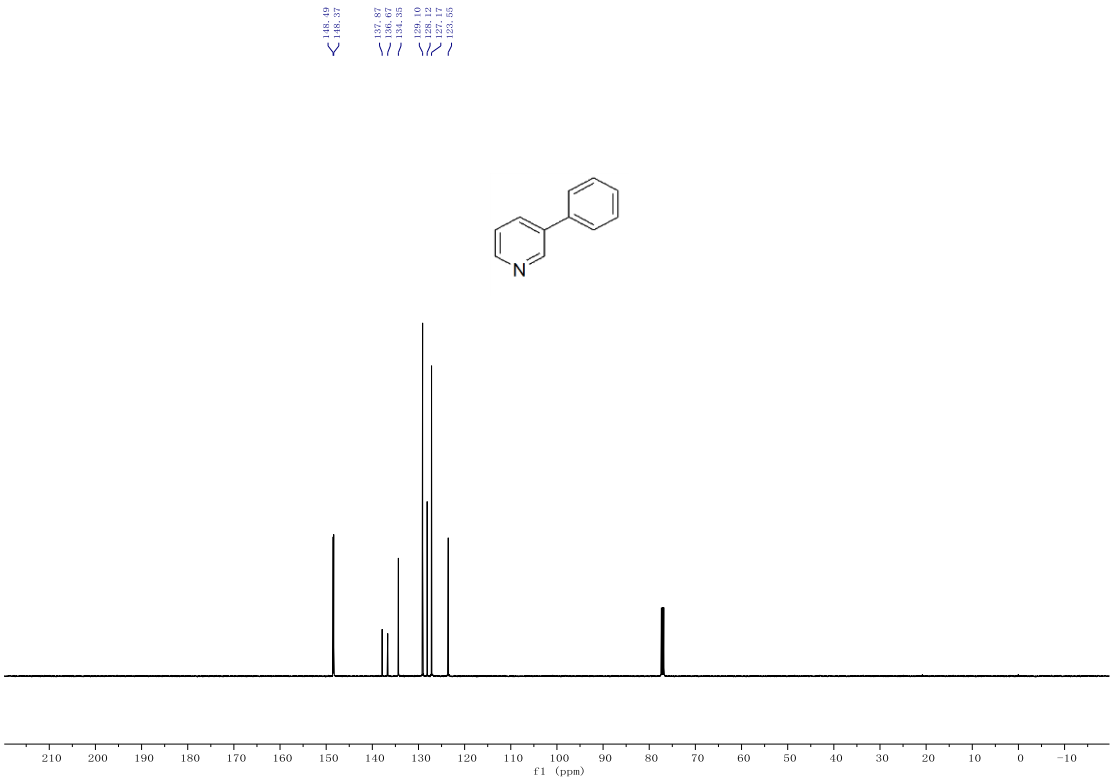
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.56, 141.36, 138.29, 128.96, 128.69, 127.26, 127.13, 125.18, 21.45.

(Table 4, entry 1) **^{1}H NMR spectrum of 3-Phenylpyridine**



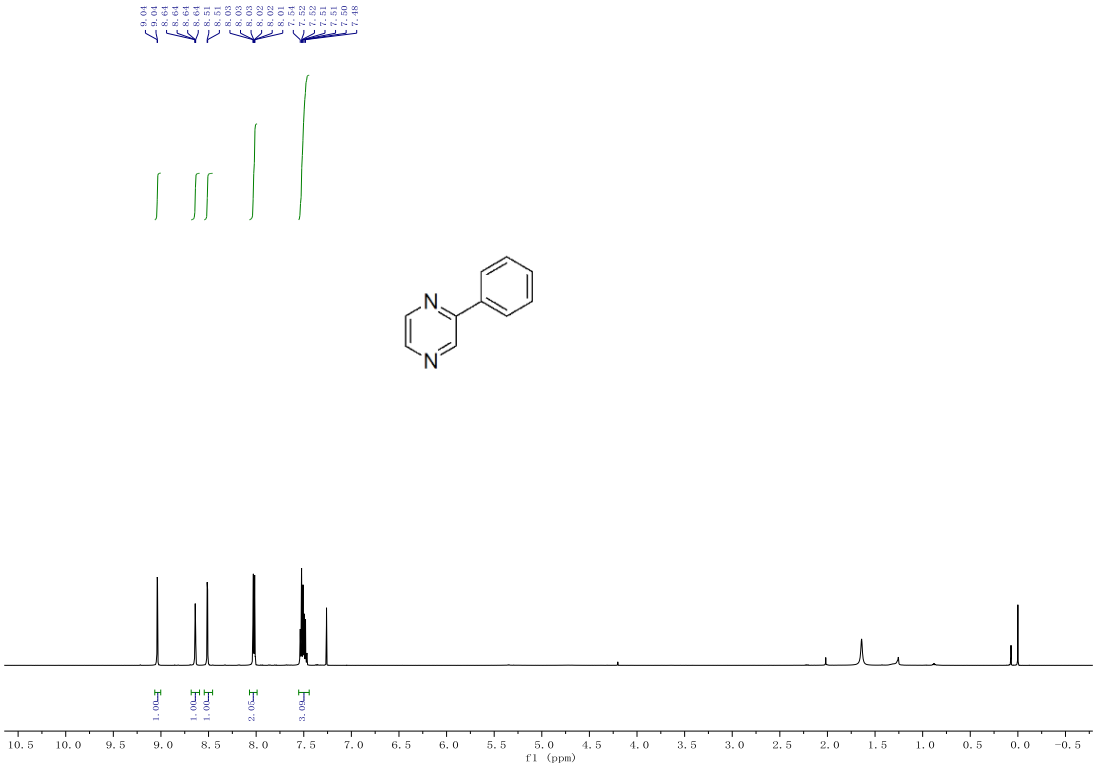
^{1}H NMR (500 MHz, Chloroform-d) δ 8.85 (d, J = 2.3 Hz, 1H), 8.58 (dd, J = 4.8, 1.6 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.57 (dd, J = 7.3, 2.0 Hz, 2H), 7.46 (dd, J = 8.6, 6.8 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.36 – 7,32 m, 1H).

^{13}C NMR spectrum of 3-Phenylpyridine



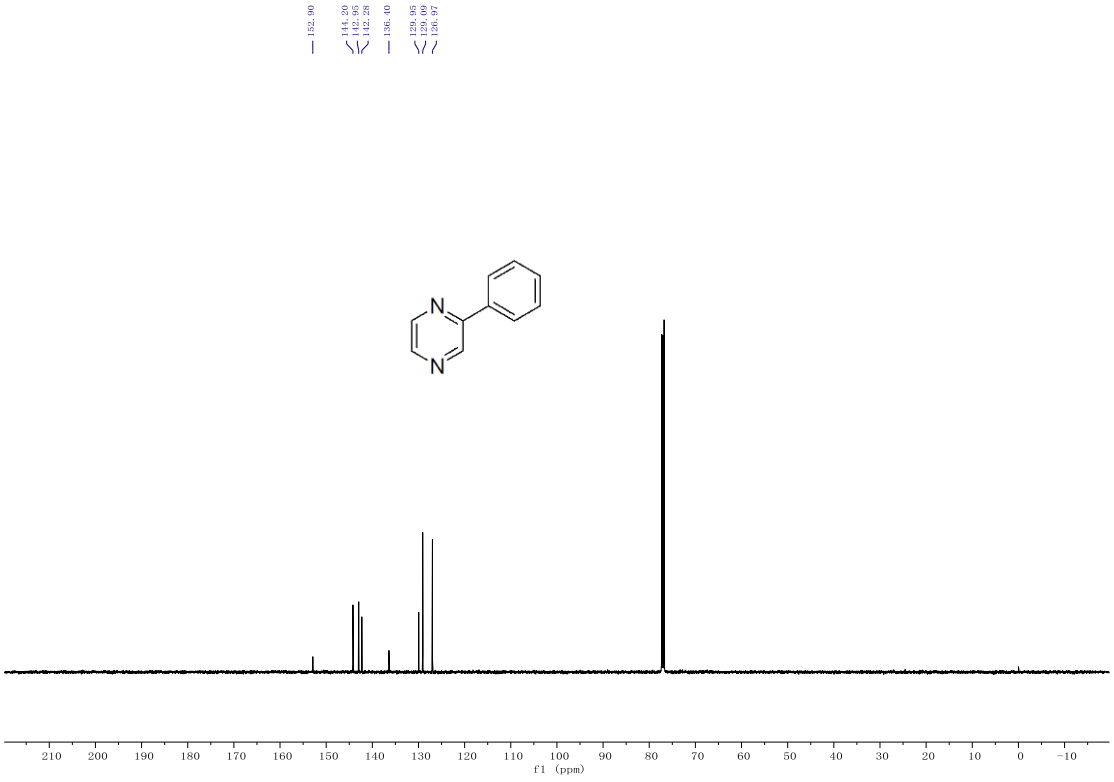
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.49, 148.37, 137.87, 136.67, 134.35, 129.10, 128.12, 127.17, 123.55.

(Table 4, entry 2) **^{1}H NMR spectrum of 2-Phenylpyrazine**



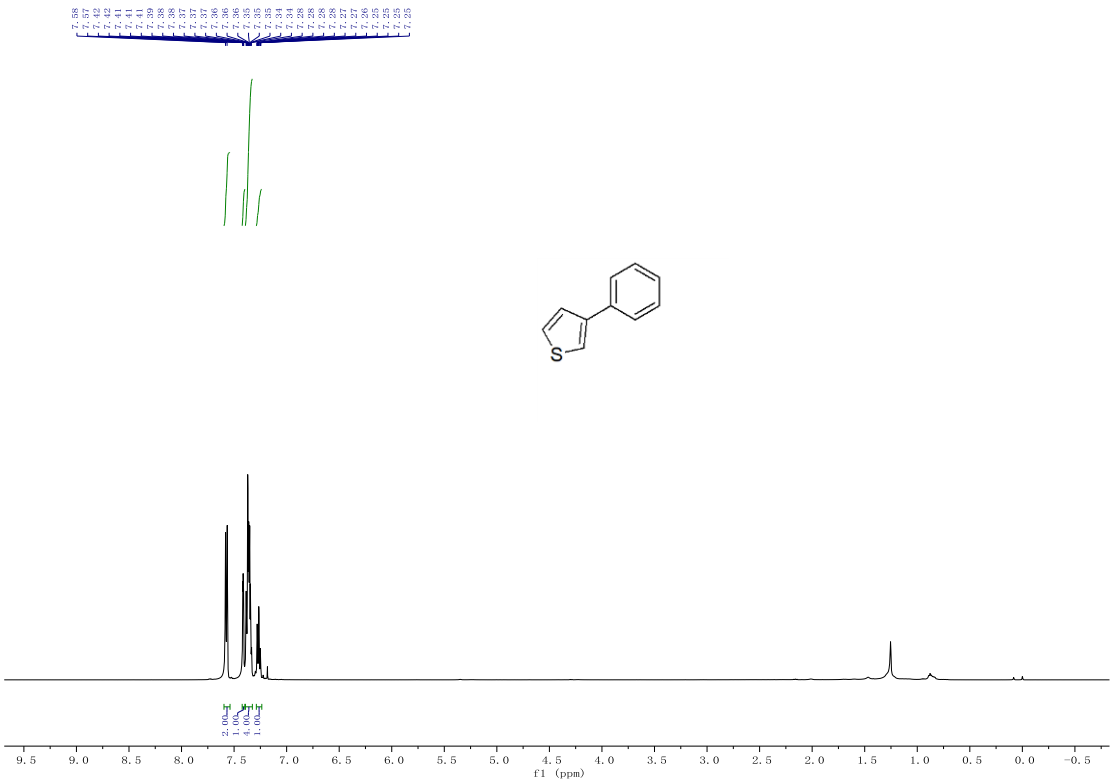
^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.04 (d, *J* = 1.6 Hz, 1H), 8.64 (dd, *J* = 2.5, 1.6 Hz, 1H), 8.51 (d, *J* = 2.5 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.54 – 7.48 (m, 3H).

^{13}C NMR spectrum of 2-Phenylpyrazine



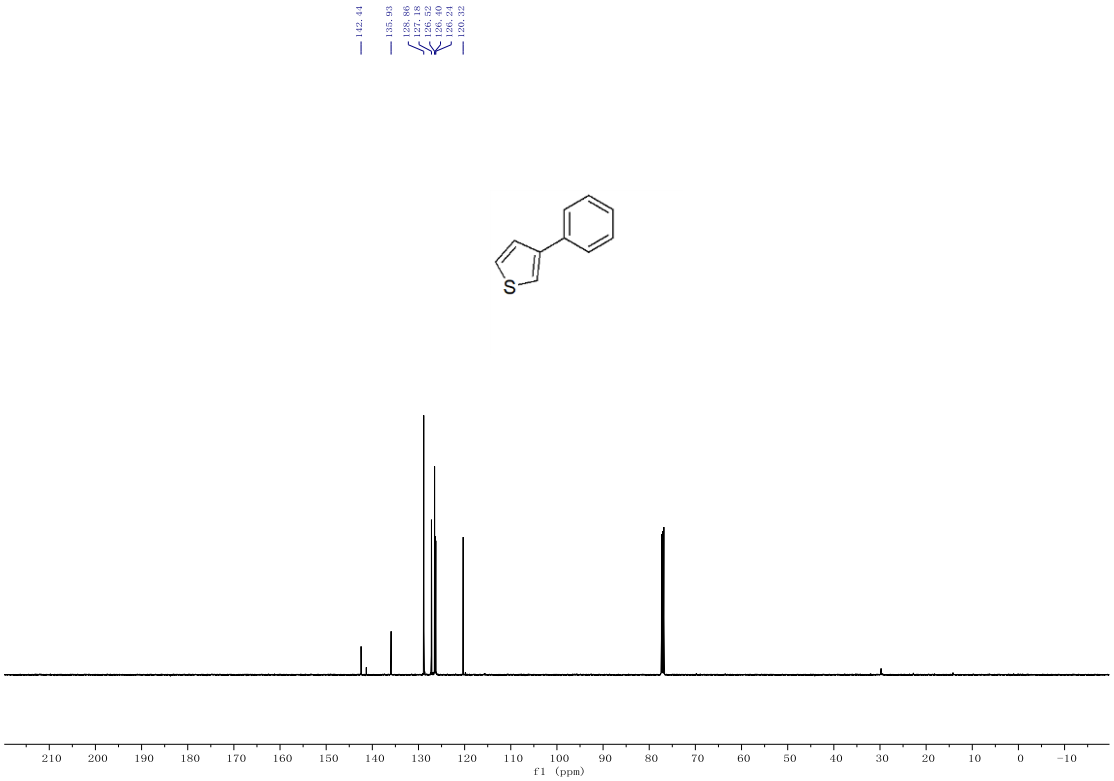
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.9, 144.2, 142.9, 142.2, 136.4, 129.9, 129.1, 126.9.

(Table 4, entry 4) **^{1}H NMR spectrum of 3-Phenylthiophene**



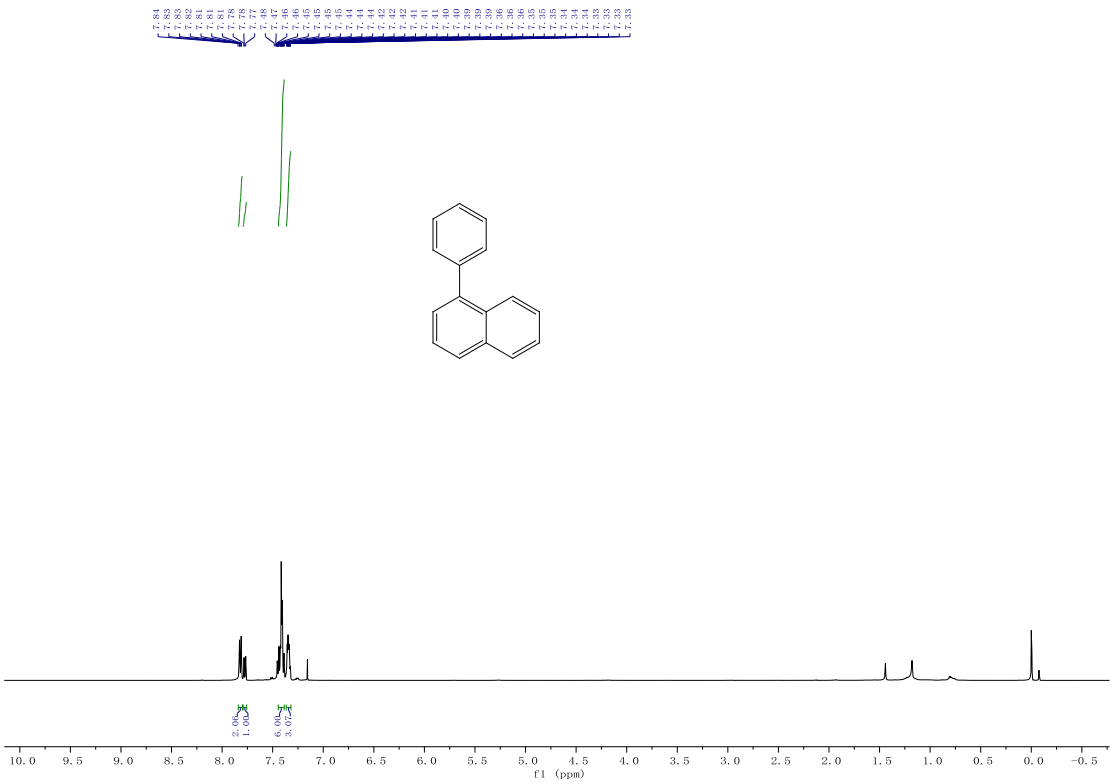
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.42 – 7.40 (m, 1H), 7.39 – 7.34 (m, 4H), 7.29 – 7.24 (m, 1H).

^{13}C NMR spectrum of 3-Phenylthiophene



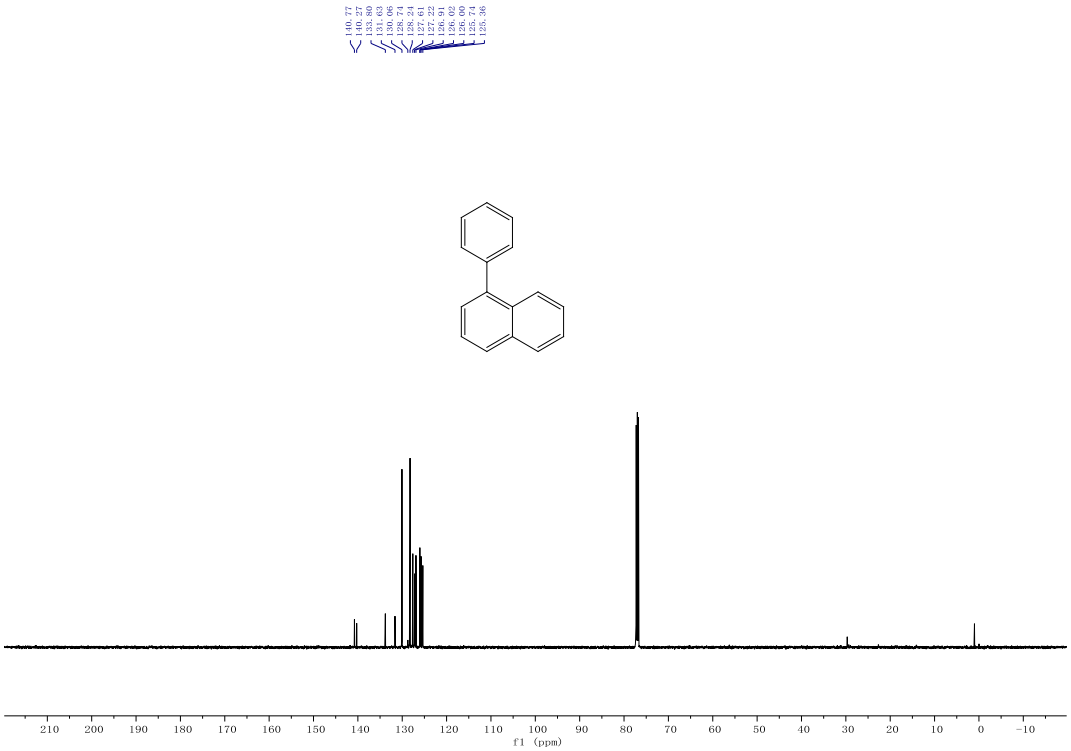
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.4, 135.9, 128.8, 127.1, 126.5, 126.4, 126.2, 120.3.

(Table 4, entry 5) **^{1}H NMR spectrum of 1-Phenylnaphthalene**



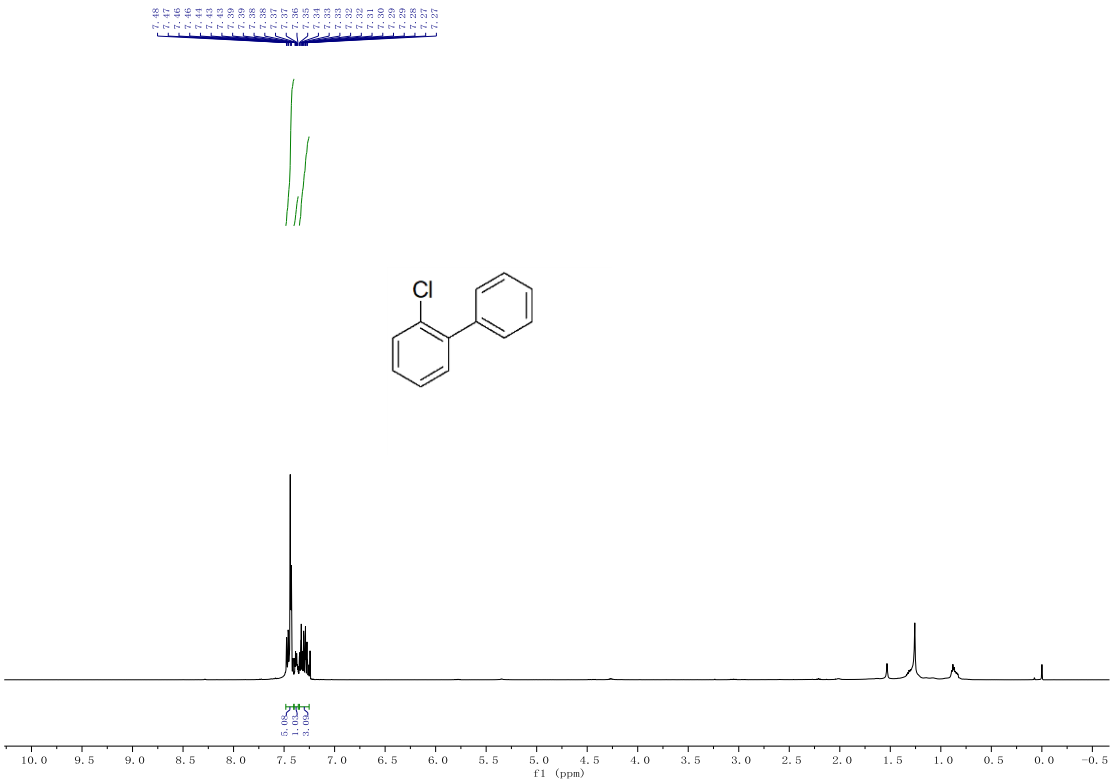
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 –7.81 (m, 2H), 7.79 – 7.76 (m, 1H), 7.44 – 7.39 (m, 6H), 7.36 – 7.33 (m, 3H).

^{13}C NMR spectrum of 1-Phenylnaphthalene



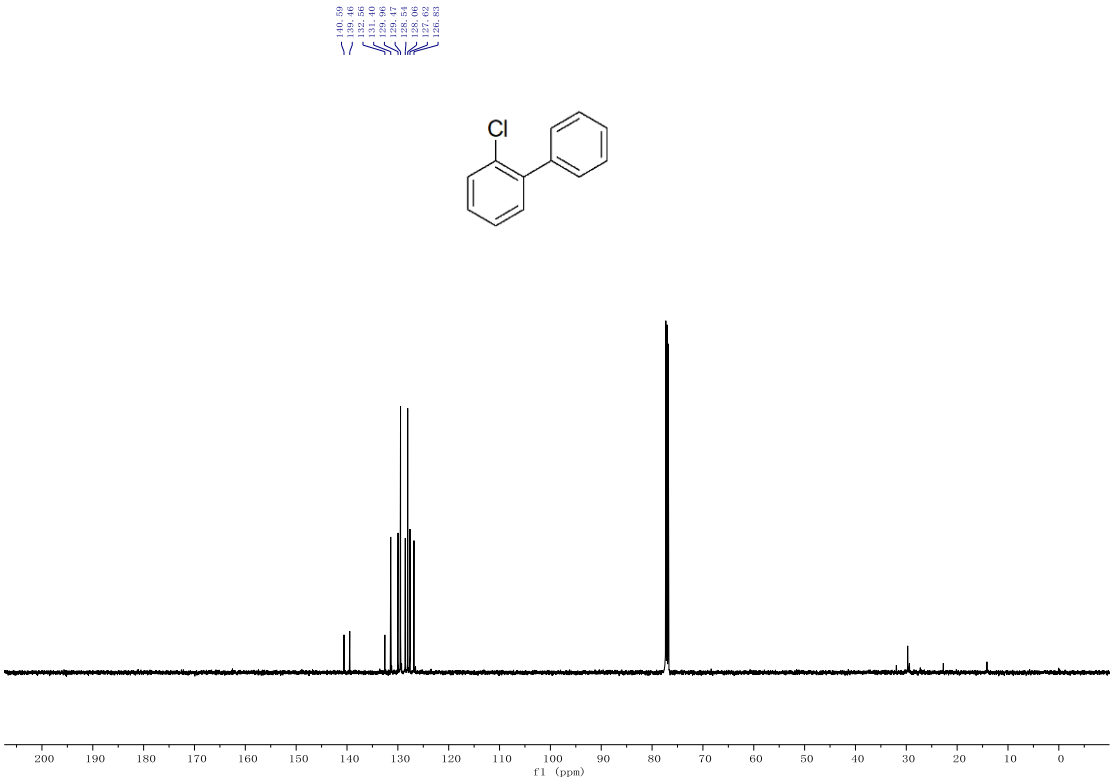
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.7, 140.2, 133.8, 131.6, 130.1, 128.7, 128.2, 127.6, 127.2, 126.9, 126.0, 126.0, 125.7, 125.3.

(Table 5, entry 6) **^{1}H NMR spectrum of 2-Chlorobiphenyl**



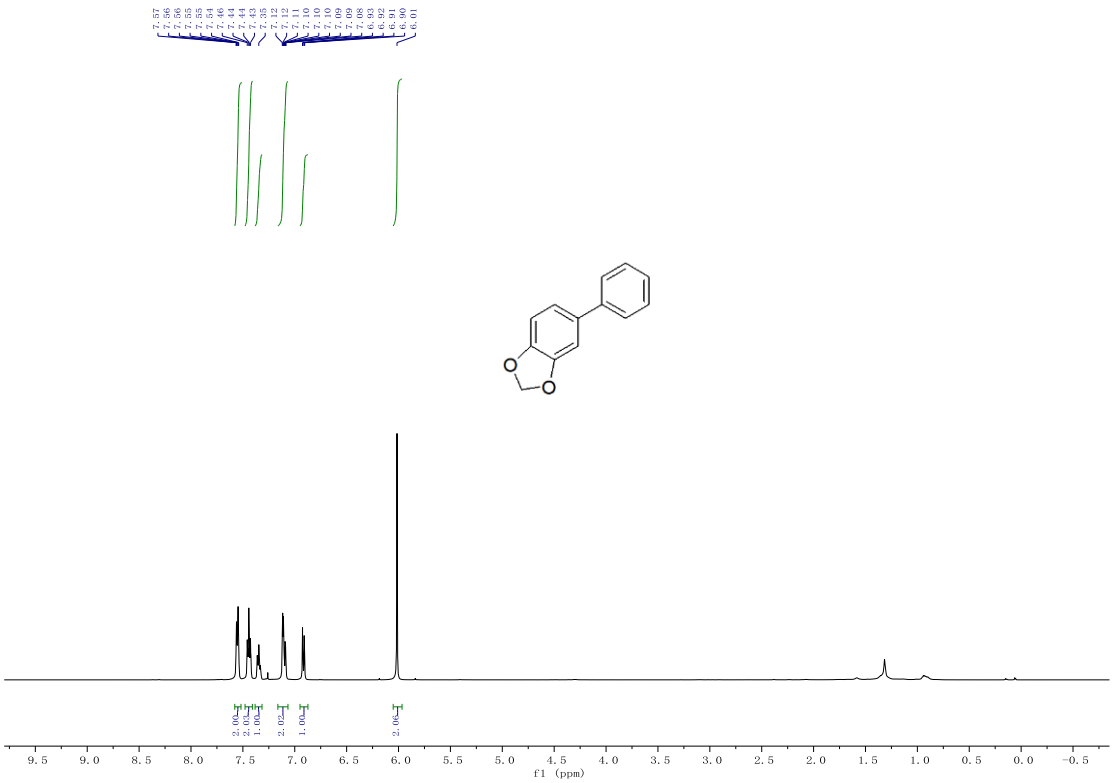
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 5H), 7.40 – 7.36 (m, 1H), 7.35 – 7.25 (m, 3H).

^{13}C NMR spectrum of 2-Chlorobiphenyl



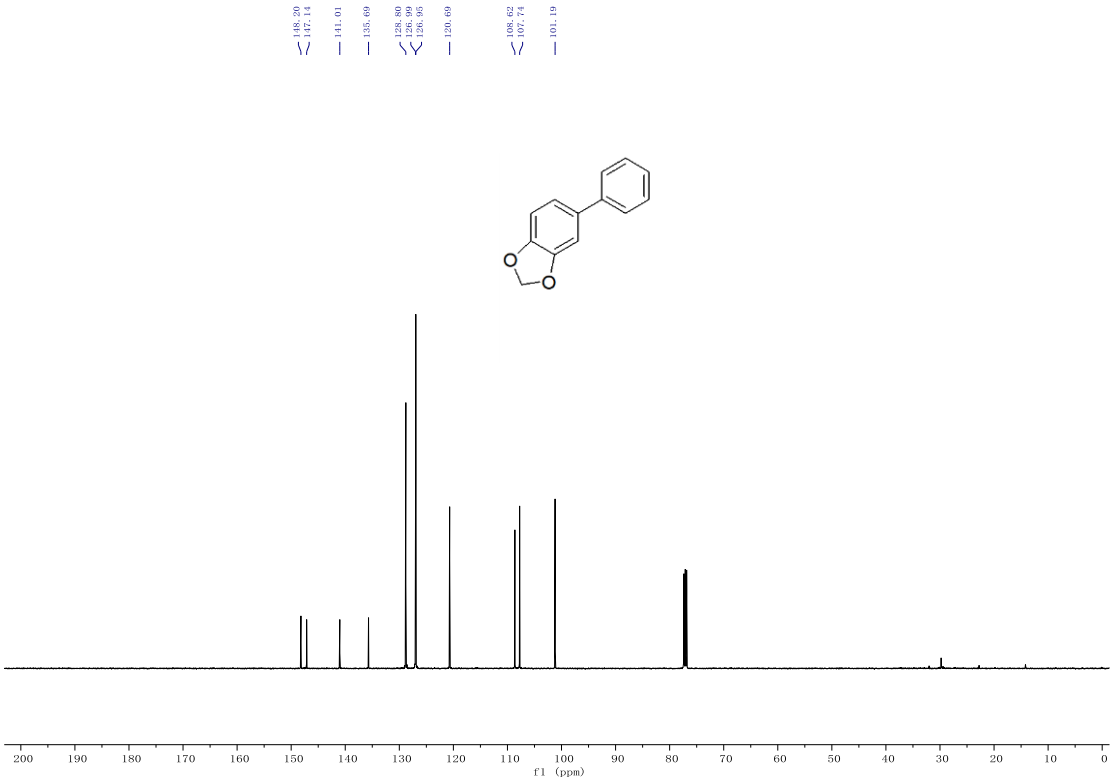
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.5, 139.4, 132.5, 131.4, 129.9, 129.4, 128.5, 128.1, 127.6, 126.8.

(Table 5, entry 9) **^{1}H NMR spectrum of 5-phenyl-1,3-benzodioxole**



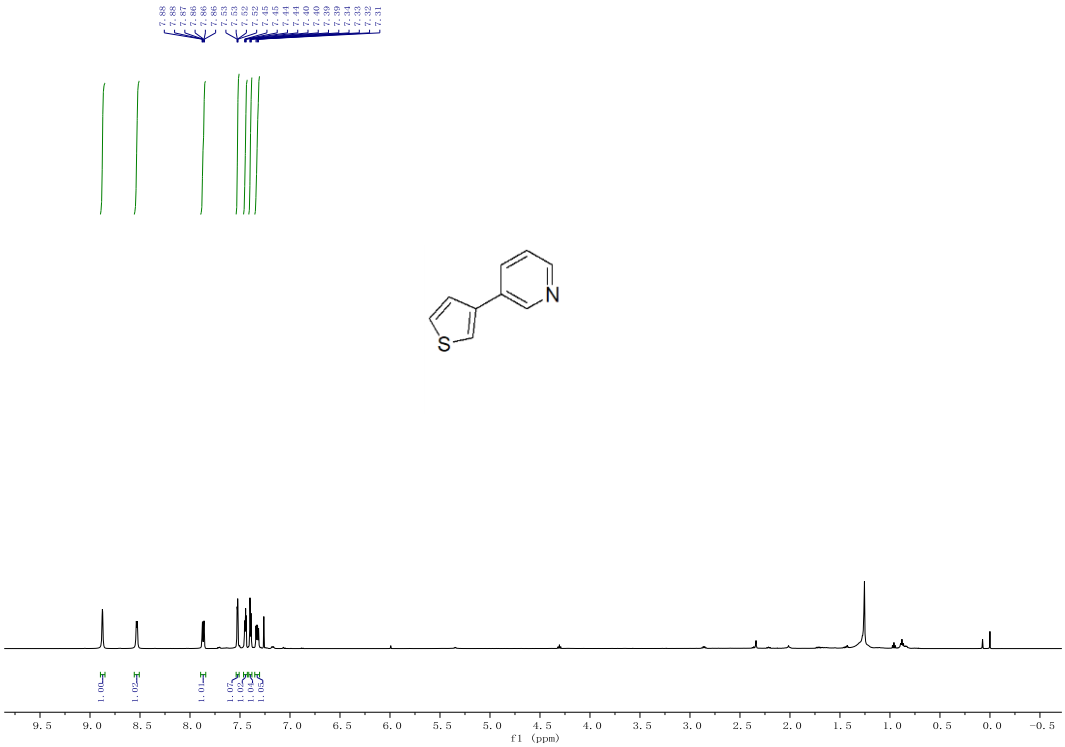
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 – 7.54 (m, 2H), 7.48 – 7.41 (m, 2H), 7.35 (s, 1H), 7.16 – 7.07 (m, 2H), 6.93 – 6.90 (m, 1H), 6.01 (s, 2H).

^{13}C NMR spectrum of 5-phenyl-1,3-benzodioxole



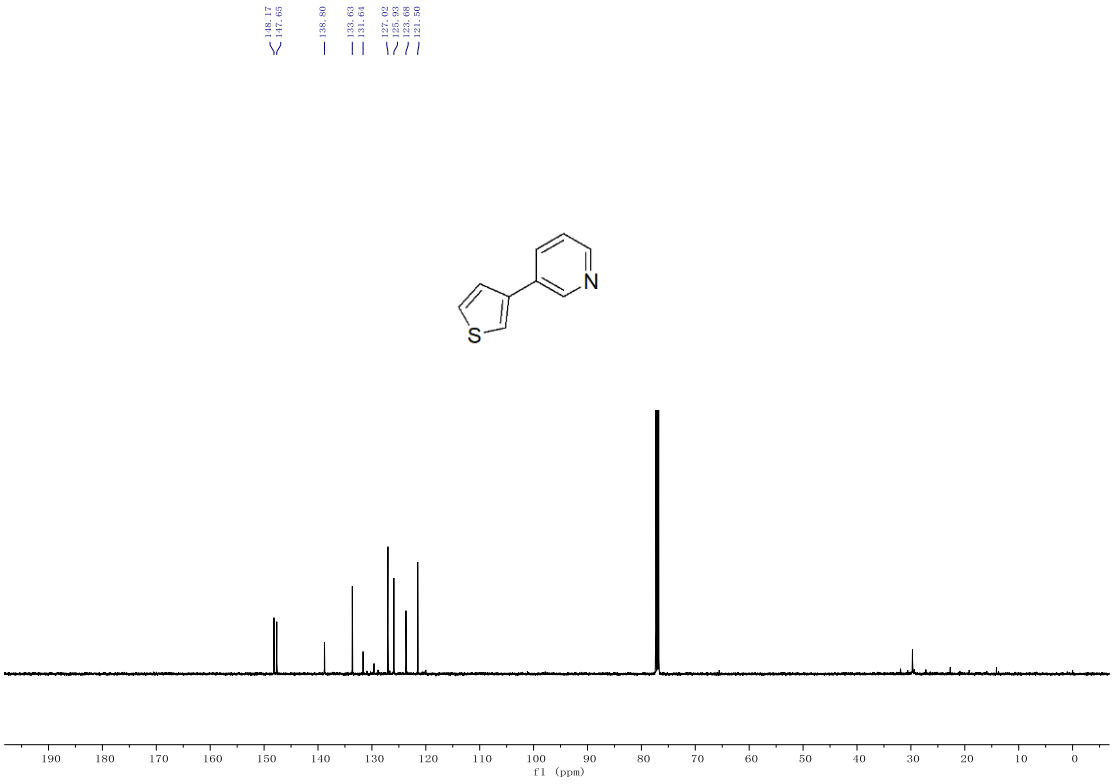
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.2, 147.1, 141.0, 135.6, 128.8, 126.9, 126.9, 120.6, 108.6, 107.7, 101.1.

(Table 5, entry 11) **^{1}H NMR spectrum of 3-(thiophen-3-yl)pyridine**



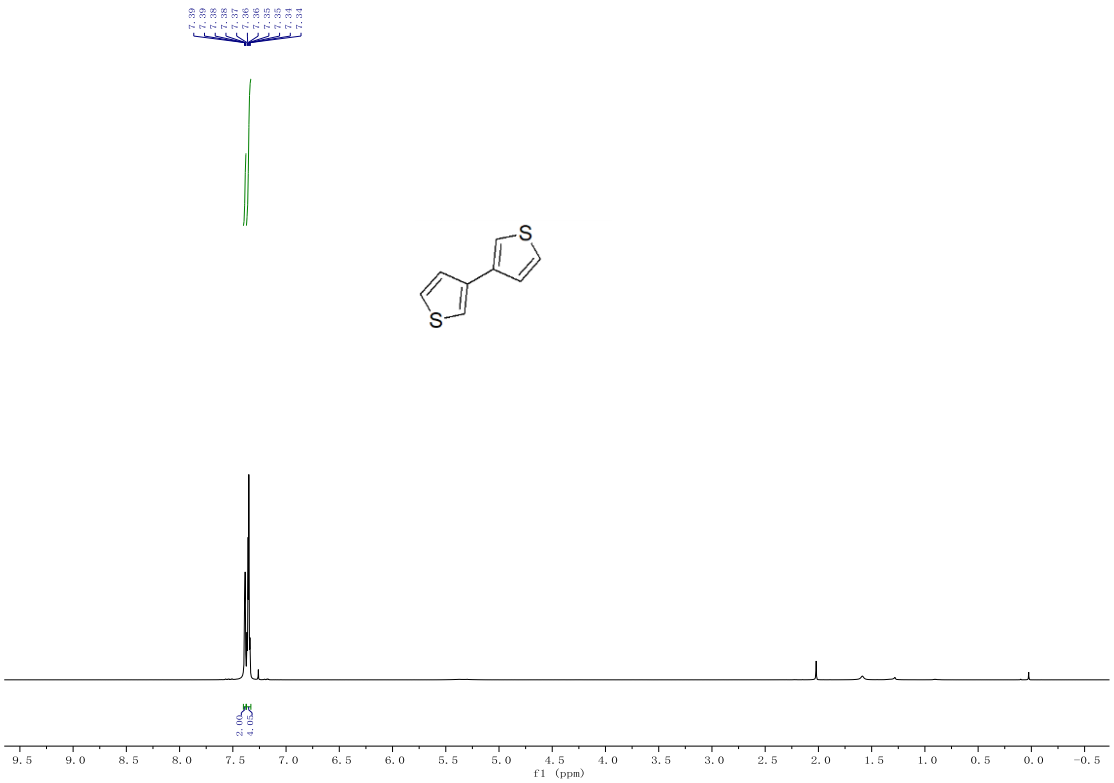
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 2.4 Hz, 1H), 8.56 – 8.51 (m, 1H), 7.88 – 7.86 (m, 1H), 7.52 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.45 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.39 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.33 (dd, *J* = 7.9, 4.8 Hz, 1H).

^{13}C NMR spectrum of 3-(thiophen-3-yl)pyridine



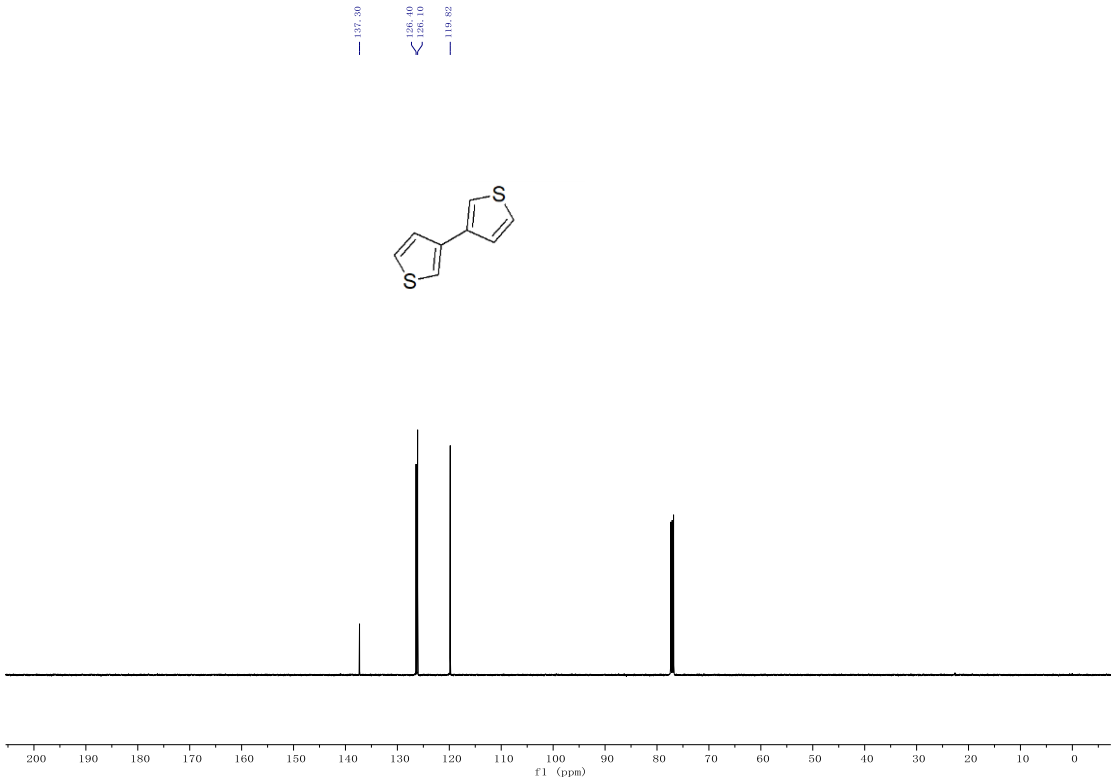
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.1, 147.6, 138.8, 133.6, 131.6, 127.0, 125.9, 123.6, 121.5.

(Table 5, entry 12) **^{1}H NMR spectrum of 3,3'-Bithiophene**



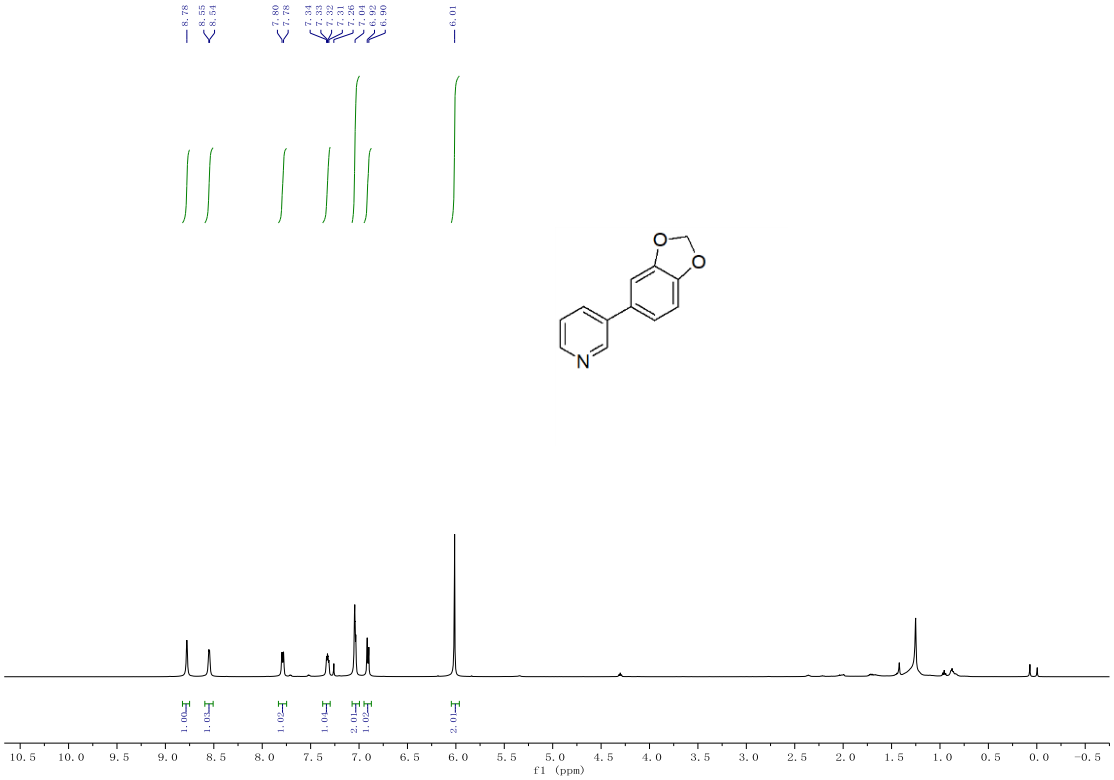
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 2.8, 1.4 Hz, 2H), 7.37 – 7.33 (m, 4H).

^{13}C NMR spectrum of 3,3'-Bithiophene



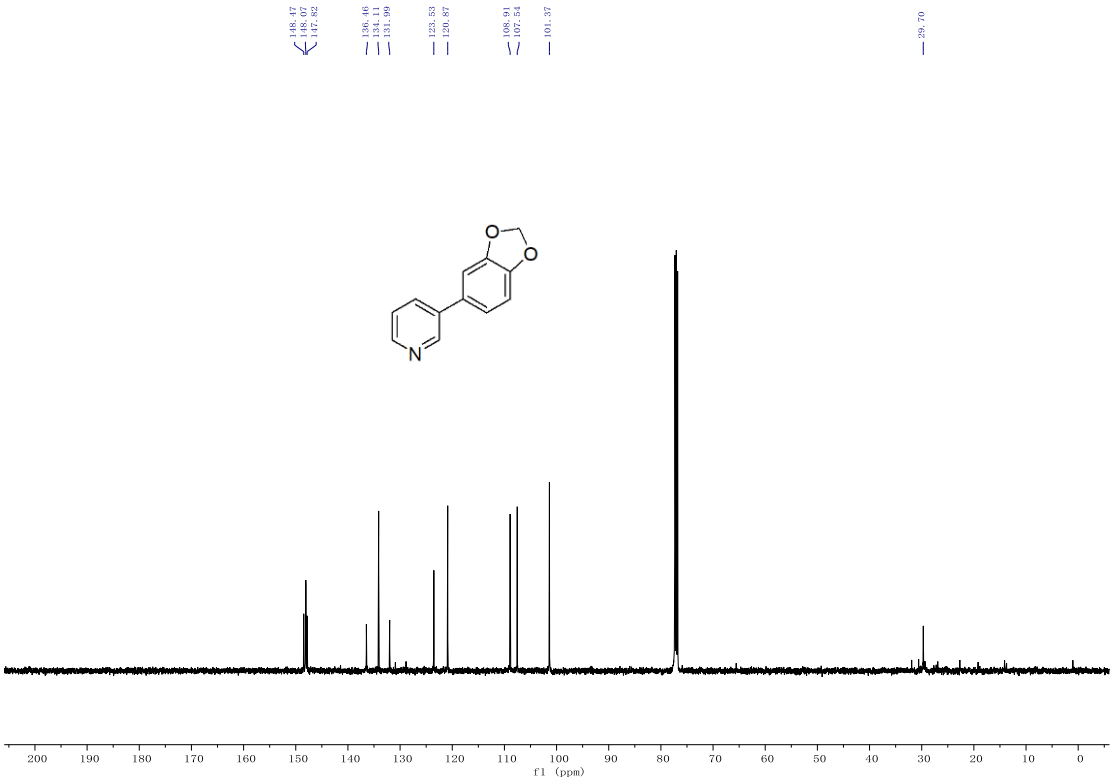
^{13}C NMR (126 MHz, Chloroform-*d*) δ 137.3, 126.4, 126.1, 119.8.

(Table 5, entry 13) **^{1}H NMR spectrum of 3-(3,4-methylenedioxyphenyl)pyridine**



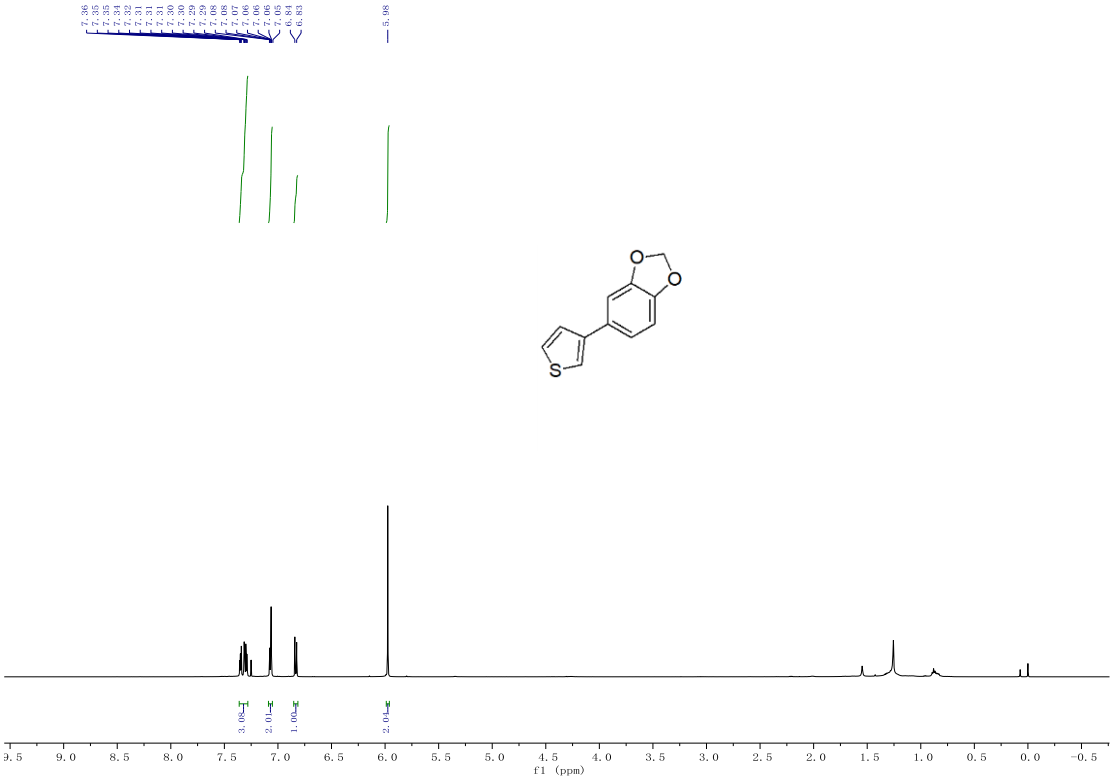
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.78 (s, 1H), 8.55 (d, *J* = 3.8 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.32 (dd, *J* = 7.5, 4.7 Hz, 1H), 7.04 (s, 2H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H).

^{13}C NMR spectrum of 3-(3,4-methylenedioxyphenyl)pyridine



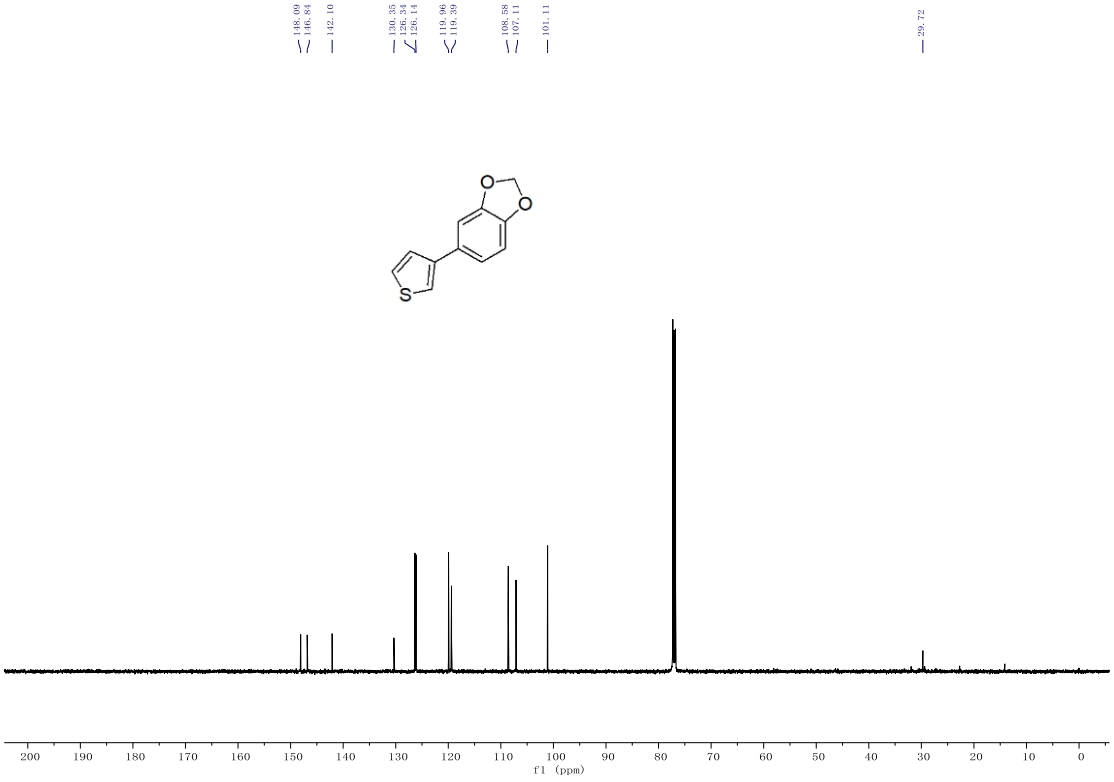
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.4, 148.1, 147.8, 136.4, 134.1, 131.9, 123.5, 120.8, 108.9, 107.5, 101.3, 29.7.

(Table 5, entry 14) **^{1}H NMR spectrum of 5-(thiophen-3-yl)benzo[d][1,3]dioxole**



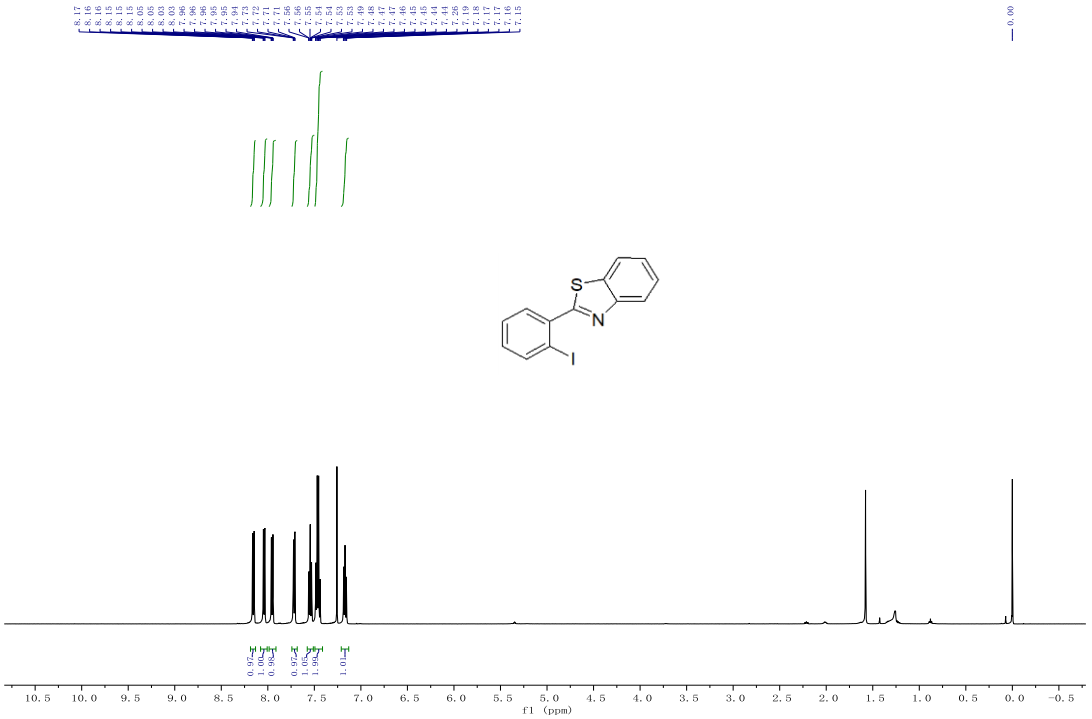
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 3H), 7.09 – 7.05 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.98 (s, 2H).

^{13}C NMR spectrum of 5-(thiophen-3-yl)benzo[d][1,3]dioxole



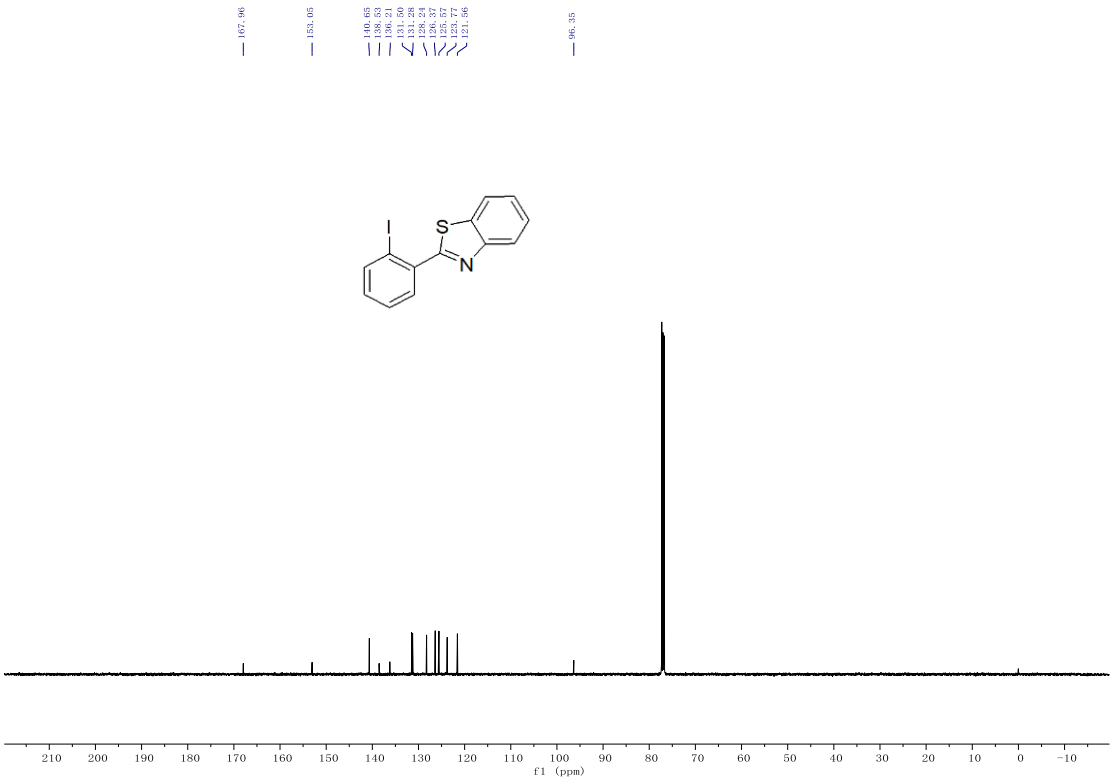
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.1, 146.8, 142.1, 130.3, 126.3, 126.1, 119.9, 119.3, 108.5, 107.1, 101.1, 29.7.

Scheme S1 **^{1}H NMR spectrum of 2-(2-Iodophenyl)benzo[*d*]thiazole**



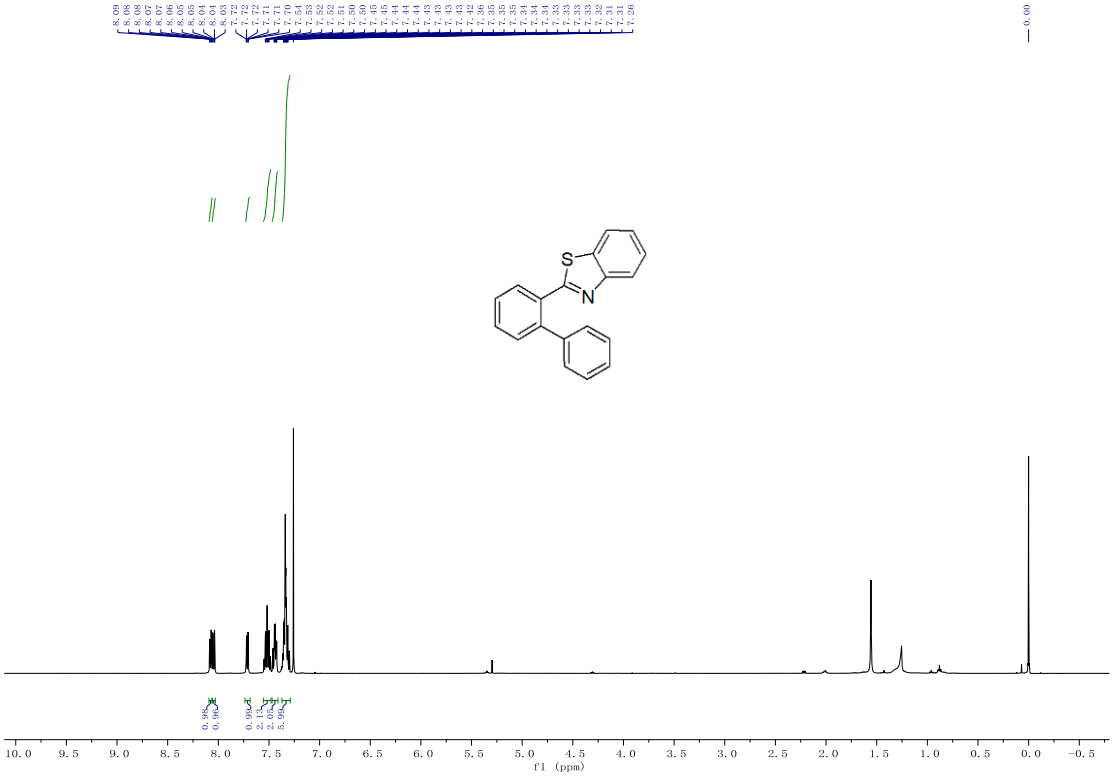
^{1}H NMR (500 MHz, Chloroform-d) δppm 8.17 – 8.15 (m, 1H), 8.04 (dd, J = 8.0, 1.2 Hz, 1H), 7.96 – 7.94 (m, 1H), 7.72 (dd, J = 7.7, 1.7 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 7.19 – 7.15 (m, 1H).

^{13}C NMR spectrum of 2-(2-Iodophenyl)benzo[*d*]thiazole



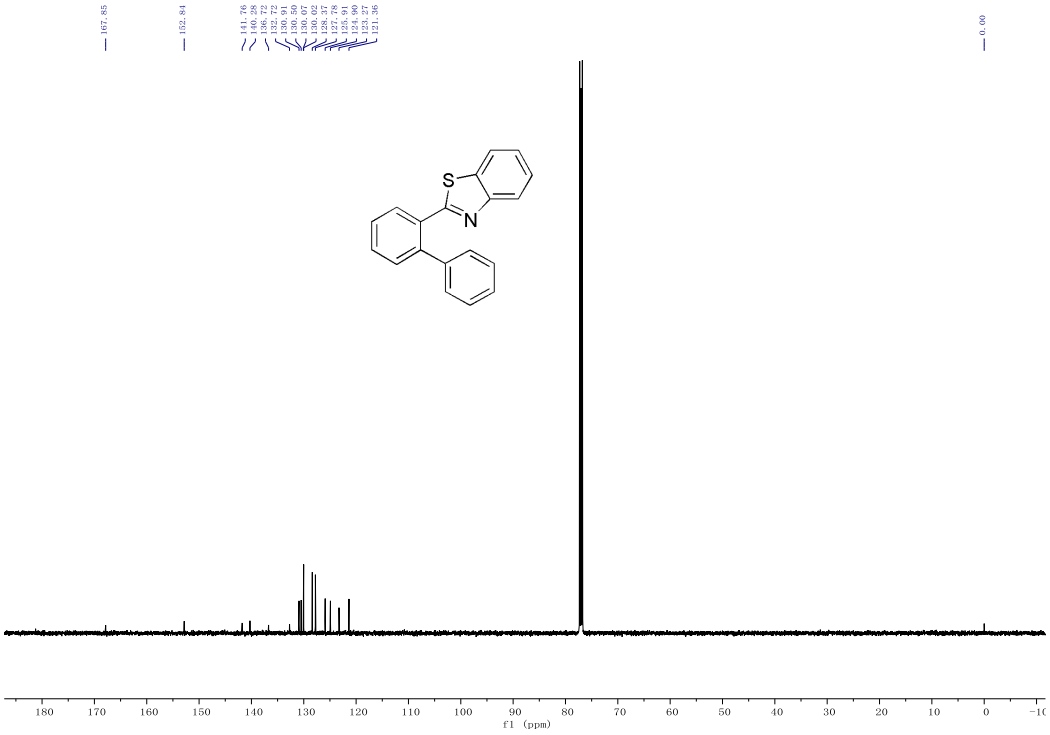
^{13}C NMR (126 MHz, Chloroform-d) δ 167.9, 153.1, 140.7, 138.5, 136.2, 131.5, 131.3, 128.2, 126.4, 125.6, 123.8, 121.6, 96.4.

Scheme 2 **^{1}H NMR spectrum of 2-[1,1'-Biphenyl]-2-ylbenzothiazole**



^{1}H NMR (500 MHz, Chloroform-d) δppm 8.09 – 8.06 (m, 1H), 8.05 – 8.03 (m, 1H), 7.72 – 7.70 (m, 1H), 7.54 – 7.50 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 -7.29 (m, 6H).

^{13}C NMR spectrum of 2-[1,1'-Biphenyl]-2-ylbenzothiazole



^{13}C NMR (126 MHz, Chloroform-d) δ 167.9, 152.8, 141.8, 140.3, 136.7, 132.7, 130.9, 130.5, 130.1, 130.0, 128.4, 127.8, 125.9, 124.9, 123.3, 121.4.

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