Supporting Information

Palladium-catalyzed Direct Arylation of Phenols with Aryl Iodides

RongrongLong,[a]XufeiYan,[a]ZhiqingWu,[a]ZhengkaiLi,[a]HaifengXiang,[a] and XianggeZhou[a,b*]

[a]Institute of Homogeneous Catalysis, College of Chemistry, Sichuan University, Chengdu 610064, China.

[b]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineeringand Materials Science, Soochow University, Suzhou 215123, China.

Email: zhouxiangge@scu.edu.cn, Fax: +86-28-85412904.

Contents

1. General methods

Analytical thin layer chromatography (TLC) was performed using Merck silica gel GF254 plates. Column chromatography was performed using silica gel (300-400mesh) eluting with ethyl acetate, petroleum andacetic acid. All products were characterized by their NMR and HRMS. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz (Bruker DPX) with $CDCl_3$ as solvent.Chemical shifts are reported in ppm using TMS as internal standard. HRMS was recorded on acommercial apparatus (ESI Source, TOF).

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification.

2. General experimental procedure

General experimental procedure for the C–H aryaltion of phenols with aryl Iodides:

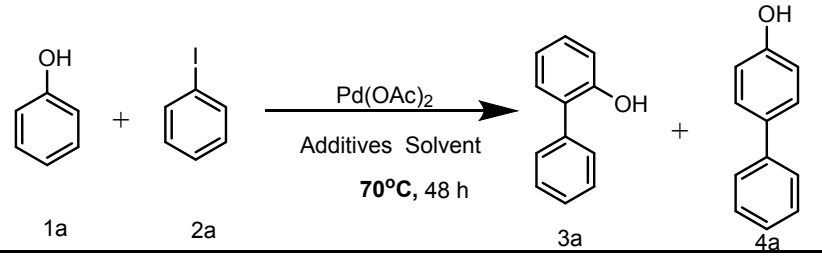
Phenols (0.5mmol),Iodobenzene (2.0mmol),$Pd(OAc)_2$ (0.05mmol), AgOAc(0.6mmol) and TsOH(1.5mmol) were combined inwater (0.3mL) and HOAc(0.3mL) in a 10mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirredin 70^{o}Coil bath for 48 hours under N_2 atmosphere. After cooled to room temperature, themixture was extracted with ethyl acetate (3 x 10mL). The organic layerwas dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified bysilica-gel column chromatography to afford the corresponding product.

3. Optimization of Reaction Conditions

Optimization of reaction conditions was carried out using phenol andiodobenzene coupling partners, and many supplement results are summarized in Table S1.Our previous observation of significant solvent effects in the C−H arylation reaction system motivated us to examine the solvent dependence of the reaction using various solvents mixed 1:1 with H_2O and AcOH. Strongly coordinating solvents such as DMF, dioxane, DMSO, and CH_3CN did not promote the desired arylation reaction, while non-coordinating solvents provided markedly higher yields. H_2O/AcOH mixtures stood out as the best-performing solvents (entry1 and 7). Apart from this, increasing the proportion of H_2O in the mixture to 2:1 decreased the yield of 53% to trace (entry 12 and 14). Similarly, if the proportion of H_2O/AcOH is 1:2, the yield of the corresponding product will turn trace (entry 13). Then, various silver salts and its amount had been explored under this perfect mixture solvent. Finally, we were pleased to obtain 3a and 4a in excellent yield (72%) by conducting the reaction with AgOAc/TsOH(entry 8 to 12).

Encouraged by the initial findings, we next started the optimization of ligands in this arylation reaction conditions. It was found that ligands, such as PPh_3, o-NO_2-PhCOOH, Proline, N-Ac-Gly, N-Ac-Ala, L-Serine, N-Ac-Leuand 2-Py-COOH, are not essential for this reaction (entry 17 to 24). Remarkably, ortho- and para-arylation products could be obtained under the best conditions (entry 16).

Table S1. Optimization of the reaction conditions[a]

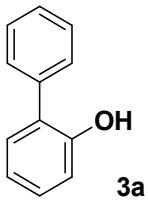


Entry	Ligand	Additives	Solvent	Yield [%][f]
1	-	AgOAc	H_2O	-
2	-	AgOAc	CH_3COOH	-
3	-	AgOAc	H_2O/CH_3CN(1:1)	-
4	-	AgOAc	H_2O/DMF(1:1)	-
5	-	AgOAc	H_2O/DMSO(1:1)	-
6	-	AgOAc	H_2O/Dioxane(1:1)	-
7	-	AgOAc	H_2O/CH_3COOH(1:1)	38(1:5)
8	-	AgOAc (2)/TsOH (3)	H_2O/CH_3COOH(1:1)	36(1:4)
9	-	AgOAc (1.2)/TsOH (3)	H_2O/CH_3COOH(1:1)	54(1:4)
10	-	Ag_2O (0.6)/TsOH (3)	H_2O/CH_3COOH(1:1)	-
11	-	Ag_2CO_3 (0.6)/TsOH (3)	H_2O/CH_3COOH(1:1)	-
12	-	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	53(1:10)
13[b]	-	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:2)	trace
14[c]	-	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(2:1)	trace
15[d]	-	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	61(1:5)
16[e]	-	**AgOAc (0.6)/TsOH (1.5)**	**H_2O/CH_3COOH(1:1)**	**76(1:17)**
17[e]	PPh_3	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
18[e]	*o*-NO_2-PhCOOH	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
19[e]	2-Py-COOH	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
20[e]	Proline	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
21[e]	*L*-Serine	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
22[e]	N-Ac-Gly	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
23[e]	N-Ac-Ala	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-
24[e]	N-Ac-Leu	AgOAc (0.6)/TsOH (1.5)	H_2O/CH_3COOH(1:1)	-

[a]Reactions conditions:**1a**(0.5 mmol),**2a** (2mmol), $Pd(OAc)_2$(0.05 mmol), AgOAc (0.6mmol), TsOH(1.5 mmol).[b]0.1 mL H_2O, 0.2 mLHOAc. [c]0.2 mL H_2O, 0.1 mLHOAc. [d]0.2 mL H_2O, 0.2 mLHOAc. [e]0.3 mL H_2O, 0.3 mL HOAc.[f]Isolated yields.

4. Characterization data

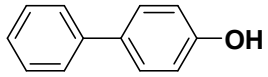
2-Phenylphenol (3a)[1]



3a

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp58-59°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.52 (s, 2H), 7.44 (s, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 7.04 (s, 1H), 7.03 (d, *J* = 7.7 Hz, 2H), 5.29 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 152.42, 137.10, 130.26, 129.29, 129.18, 129.12, 128.14, 127.89, 120.87, 115.84; MS (EI): m/z = 170(M^+).

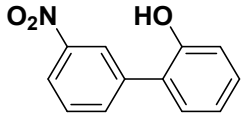
4-Phenylphenol (4a)[2]



4a

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp164-165 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.1 Hz, 2H), 7.63 – 7.48 (m, 3H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.36 (m, 3H), 7.36 (d, *J* = 44.1 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.97 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.86, 140.54, 133.82, 128.51, 128.19, 126.51, 115.44; MS (EI): m/z = 170(M^+).

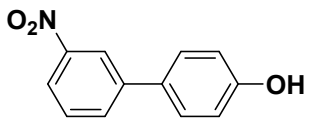
3'-Nitro-[1,1'-biphenyl]-2-ol (3b) [3]



3b

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), yellow solid,mp99.5-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 96.2 Hz, 2H), 8.19 (s, 1H), 8.31 – 7.53 (m, 3H), 7.99 – 7.28 (m, 3H), 7.78 – 7.21 (m, 3H), 7.16 (d, *J* = 83.5 Hz, 1H), 7.00 (d, *J* = 37.2 Hz, 2H), 5.22 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 152.76, 148.33, 139.68, 135.40, 130.59, 129.93, 129.31, 126.04, 124.31, 122.02, 121.23, 116.39;MS (EI): m/z = 215(M^+).

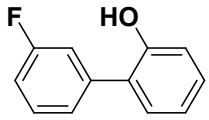
3'-Nitro-[1,1'-biphenyl]-4-ol(4b) [4]



4b

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1),yellow solid,mp108-108.5 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.17 (d, *J* = 102.0 Hz, 2H), 7.90 (d, *J* = 115.0 Hz, 2H), 7.48 (s, 1H), 7.44 (t, *J* = 14.8 Hz, 3H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.57 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 156.33, 148.66, 142.45, 132.58, 131.20, 131.11, 129.66, 128.92, 128.49, 121.40, 121.36, 116.13;MS (EI): m/z = 215(M^+).

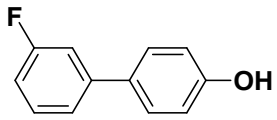
3'-Fluoro-[1,1'-biphenyl]-2-ol (3c) [5]



3c

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.27 (s, 1H), 7.26 (s, 1H), 7.25 (s, 1H), 7.23 (s, 1H), 7.07 (s, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 5.26 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 167.25, 164.79, 155.23, 142.43, 142.35, 133.51, 133.42, 133.11, 132.40, 129.89, 127.58, 127.56, 123.89, 119.23, 119.02, 118.98, 117.62, 117.41; MS (EI): m/z = 188(M^+).

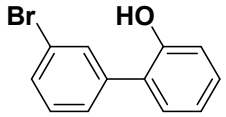
3'-Fluoro-[1,1'-biphenyl]-4-ol (4c) [6]



4c

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp122-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.44 (s, 1H), 7.34 (s, 1H), 7.31 (s, 1H), 7.24 (s, 1H), 6.98 (s, 1H), 6.92 (s, 1H), 6.90 (s, 1H), 5.60 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 164.43, 161.99, 155.68, 143.11, 143.03, 132.60, 132.57, 130.19, 130.10, 128.37, 122.27, 122.25, 115.79, 113.61, 113.51, 113.39, 113.30;MS (EI): m/z = 188(M^+).

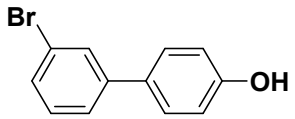
3'-Bromo-[1,1'-biphenyl]-2-ol (3d)



3d

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), colourlessoil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.45 (s, 1H), 7.31 (s, 2H), 7.25 (s, 1H), 6.98 (s, 1H), 6.95 – 6.87 (m, 2H), 4.99 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 152.40, 139.47, 132.23, 130.72, 130.46, 130.30, 129.58, 127.72, 126.81, 123.09, 121.03, 116.11; ESI-MS: calculated[$C_{12}H_8BrO$]$^-$: 246.9764, found: 246.9777.

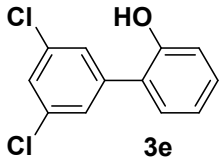
3'-Bromo-[1,1'-biphenyl]-4-ol (4d)



4d

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.45 (s, 1H), 7.44 (s, 1H), 7.41 (d, J = 5.9 Hz, 2H), 7.25 (s, 1H), 6.90 (d, J = 8.6 Hz, 2H), 5.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.70, 142.93, 132.37, 130.24, 129.74, 129.59, 128.42, 125.29, 122.88, 115.85; ESI-MS: calculated [$C_{12}H_8BrO$]$^-$: 246.9764, found: 246.9777.

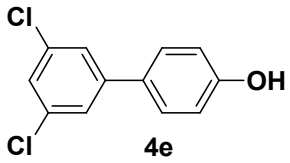
3',5'-dichloro-[1,1'-Biphenyl]-2-ol (3e)



3e

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.8 Hz, 1H), 7.42 (s, 1H), 7.40 (s, 1H), 7.26 (s, 1H), 7.03 (s, 1H), 5.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.57, 138.70, 138.31, 136.07, 135.87, 135.57, 134.16, 129.57, 129.29, 124.69;ESI-MS: calculated[$C_{12}H_7Cl_2O$]$^-$: 236.9979, found:236.9896.

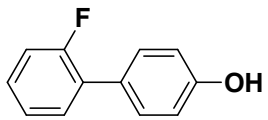
3',5'-dichloro-[1,1'-Biphenyl]-4-ol (4e)



4e

Purification by flash chromatography (petroleum ether/ethyl acetate100:1), white solid, mp108-109 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 1.8 Hz, 2H), 7.27 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.12, 142.81, 134.30, 130.34, 127.52, 125.62, 124.23, 115.05; ESI-MS: calculated [$C_{12}H_7Cl_2O$]$^-$: 236.9879, found: 236.9855.

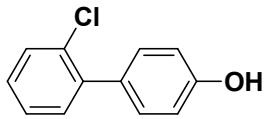
2'-Fluoro-[1,1'-biphenyl]-4-ol(4f)[5]



4f

Purification by flash chromatography (petroleum ether/ethyl acetate100:1), white solid, mp124-126°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.42 (s, 2H), 7.38 (s, 1H), 7.23 (s, 1H), 7.18 (s, 1H), 7.16 (s, 1H), 6.91 (s, 1H), 6.89 (s, 1H), 5.33 (s, 1H);^{13}C NMR (101 MHz, $CDCl_3$) δ 162.25 (d, *J* = 246.9 Hz), 157.78 (s), 134.50 (d, *J* = 3.4 Hz), 133.02 (s), 132.98 (s), 132.90 (s), 132.87 (s), 130.95 (d, *J* = 8.2 Hz), 126.82 (d, *J* = 3.7 Hz); MS (EI): m/z = 188(M^+).

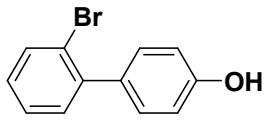
2'-chloro-[1,1'-biphenyl]-4-ol (4g)[6]



4g

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1),yellow solid, mp 54-56 °C;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 6.89 (d, J = 8.3 Hz, 1H), 5.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.09, 140.08, 132.59, 132.05, 131.39, 130.87, 129.96, 128.25, 126.84, 115.01; MS (EI): m/z = 204(M^+).

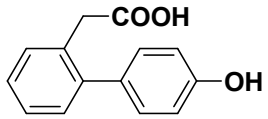
2'-Bromo-[1,1'-biphenyl]-4-ol (4h)



4h

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), yellow solid; mp98-100 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.29 (s, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.01 (s, 1H), 6.99 (s, 1H), 6.96 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.25, 142.19, 133.74, 133.12, 131.35, 130.78, 128.44, 127.38, 122.89, 114.93; ESI-MS: calculated $[C_{12}H_8BrO]^-$: 246.9764, found: 246.9777.

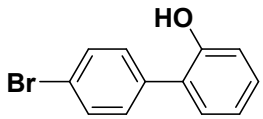
4'-hydroxy-[1,1'-Biphenyl]-2-acetic acid (4i)



4i

Purification by flash chromatography (petroleum ether/ethyl acetate/ acetic acid 100:1:1), white solid, mp105-107 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.83 (s, 1H), 7.83 (s, 1H), 7.30 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.28 (s, 1H), 6.96 (s, 1H), 6.95 (s, 1H), 3.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.99, 139.60, 137.08, 133.28, 130.80, 129.45, 129.19, 128.70, 128.54, 127.40, 101.13, 46.07;ESI-MS: calculated $[C_{14}H_{11}O_3]^-$: 227.0714, found: 227.0708.

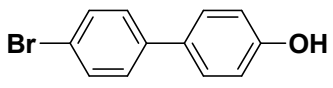
4'-bromo-[1,1'-Biphenyl]-2-ol (3j)[8]



3j

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp64-65 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.4 Hz, 3H), 7.40 (d, *J* = 6.4 Hz, 2H), 7.27 (d, *J* = 10.4 Hz, 3H), 7.35 – 6.98 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 5.22 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 152.63, 132.15, 131.90, 130.84, 130.23, 129.40, 129.27, 121.05, 120.87, 116.08; MS (EI): m/z = 188(M+).

4'-bromo-[1,1'-Biphenyl]-4-ol(4j)[9]

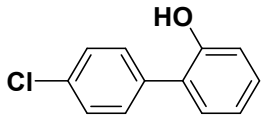


4j

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp 166-167 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.37,

139.67, 132.77, 131.80, 128.29, 128.24, 120.85, 115.80;MS (EI): m/z = 188(M+).

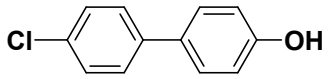
4'-chloro-[1,1'-Biphenyl]-2-ol (3k)[10]



3k

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp53.0-53.5 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.2 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 3H), 7.27 (s, 1H), 7.25 (s, 1H), 7.03 (s, 1H), 7.00 (s, 1H), 5.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.39, 135.75, 135.73, 133.79, 130.52, 130.29, 129.38, 129.21, 129.20, 127.09, 121.05, 116.07. MS (EI): m/z = 188(M+).

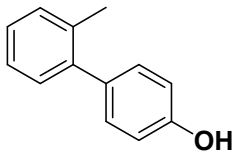
4'-chloro-[1,1'-Biphenyl]-4-ol (4k)[2]



4k

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp 146-147 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.46 (d, *J* = 8.3 Hz, 3H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.39 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 5.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.33, 139.21, 132.78, 132.74, 128.85, 128.27, 127.93, 115.81. MS (EI): m/z = 204(M^+).

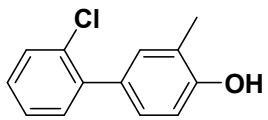
2'-methyl-[1,1'-Biphenyl]-4-ol (4l)[11]



4l

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), light yellow solid, mp80-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 4.7 Hz, 1H), 7.14 – 7.12 (m, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 7.10 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.22 (s, 1H), 2.19 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 153.47, 140.49, 134.48, 133.52, 129.45, 129.31, 128.89, 126.00, 124.76, 113.97, 19.54.MS (EI): m/z = 184(M^+).

2'-chloro-3-methyl-[1,1'-Biphenyl]-4-ol (4m)

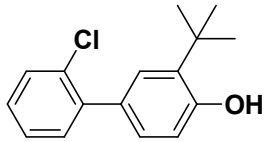


4m

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), white solid, mp84-85°C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 7.29 – 7.23 (m, 2H),

7.25 (d, *J* = 2.2 Hz, 1H), 7.24 (t, *J* = 9.7 Hz, 3H), 6.84 (s, 1H), 4.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.14, 134.42, 133.98, 133.26, 131.75, 130.11, 129.97, 128.62, 116.38, 17.71.ESI-MS: calculated $[C_{13}H_9ClO]^-$: 217.0426, found:217.0429.

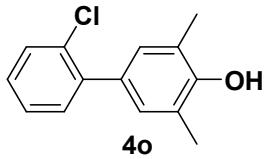
2'-chloro-3-(1,1-dimethylethyl)-[1,1'-Biphenyl]-4-ol(4n)



4n

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), deep yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.35 (d, *J* = 15.6 Hz, 1H), 7.25 (d, *J* = 20.7 Hz, 1H), 7.18 (s, 1H), 6.72 (s, 1H), 4.99 (s, 1H), 1.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.84, 140.63, 135.64, 132.59, 131.57, 131.46, 129.98, 128.69, 128.02, 127.93, 126.80, 116.13, 34.69, 29.65;ESI-MS: calculated $[C_{16}H_{16}ClO]^-$: 259.0895, found: 259.0913.

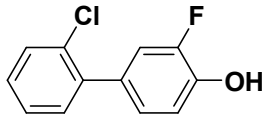
2'-chloro-3,5-dimethyl-[1,1'-Biphenyl]-4-ol (4o)



4o

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), yellowoil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.33 (d, *J* = 46.3 Hz, 1H), 7.27 (d, *J* = 4.5 Hz, 1H), 7.23 (d, *J* = 27.1 Hz, 1H), 7.19 (s, 1H), 7.03 (s, 1H), 6.61 (s, 1H), 2.10 (s, 1H), 2.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.39, 146.19, 143.56, 142.62, 133.75, 133.63, 132.93, 130.83, 130.43, 130.07, 127.18, 14.23; ESI-MS: calculated $[C_{14}H_{12}ClO]^-$: 231.0582, found: 231.0561.

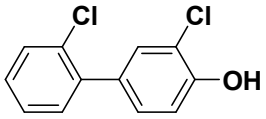
2'-chloro-3-Fluoro-[1,1'-Biphenyl]-4-ol(4p)



4p

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1),colourlessoil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.34 (d, *J* = 2.9 Hz, 1H), 7.33 (d, *J* = 1.7 Hz, 1H), 7.32 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 18.2 Hz, 2H), 5.76 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 150.48 (d, *J* = 237.7 Hz), 143.11 (d, *J* = 14.3 Hz), 132.26 (d, *J* = 6.2 Hz), 131.31 (s), 130.02 (d, *J* = 5.8 Hz), 128.70 (d, *J* = 9.7 Hz), 126.90 (d, *J* = 7.0 Hz), 126.04 (d, *J* = 3.1 Hz), 126.04 (d, *J* = 3.1 Hz); ESI-MS: calculated $[C_{12}H_7ClFO]^-$: 221.0175, found: 221.0176.

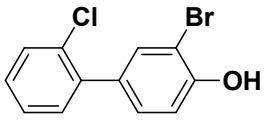
2',3-dichloro-[1,1'-Biphenyl]-4-ol (4q)



4q

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), dark green solid,mp44-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.1 Hz, 3H), 7.28 (s, 1H), 7.27 (d, *J* = 1.6 Hz, 2H), 7.25 (s, 1H), 7.07 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.92, 138.86, 132.82, 132.54, 131.27, 130.05, 129.95, 129.69, 128.72, 126.95, 119.55, 115.88. ESI-MS: calculated $[C_{12}H_7Cl_2O]^{-}$: 236.9879, found: 236.9863.

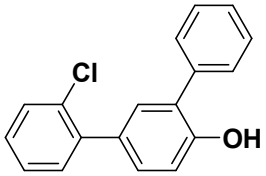
2'-chloro-3-Bromo-[1,1'-Biphenyl]-4-ol (4r)



4r

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), pale yellow solid; mp53-55 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.93 (s, 1H), 6.78 (s, 1H), 6.78 (s, 1H), 6.77 (s, 1H), 6.77 (s, 1H), 6.57 (s, 1H), 5.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.85, 138.72, 133.20, 132.85, 132.55, 131.28, 130.44, 130.04, 128.72, 126.93, 115.64, 109.81; ESI-MS: calculated $[C_{12}H_8BrClO]^{-}$: 280.9374, found: 280.9366.

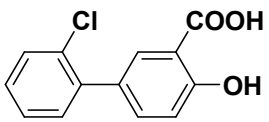
2'-chloro-3-phenyl-[1,1'-Biphenyl]-4-ol (4s)



4s

Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.1 Hz, 3H), 7.34 (s, 2H), 7.32 (s, 1H), 7.30 (s, 1H), 7.22 (d, *J* = 1.4 Hz, 2H), 7.20 (s, 2H), 7.14 (s, 2H), 7.09 (s, 1H), 6.90 (s, 2H), 5.21 (s, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 154.63, 142.51, 135.17, 134.63, 133.97, 132.80, 132.56, 131.90, 131.71, 130.84, 130.56, 130.31, 129.42, 118.14. ESI-MS: calculated $[C_{18}H_{12}ClO]^{-}$: 279.0582, found: 279.0552.

2'-chloro-4-hydroxy-[1,1'-Biphenyl]-3-carboxylic acid (4t)

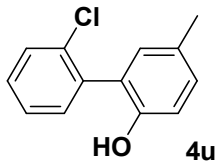


4t

Purification by flash chromatography (petroleum ether/ethyl acetate/ acetic acid 100:1:1), white solid, mp158-160°C;^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.04 (s, 1H), 7.65 (s, 1H), 7.51

(s, 1H), 7.50 (s, 1H), 7.36 (s, 2H), 7.11 (s, 1H), 7.09 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.62, 138.03, 131.63, 131.21, 130.05, 129.73, 128.94, 128.74, 128.58, 127.01, 126.39, 122.89, 117.53; ESI-MS: calculated $[C_{13}H_8ClO_3]^-$: 247.0167, found: 247.0153.

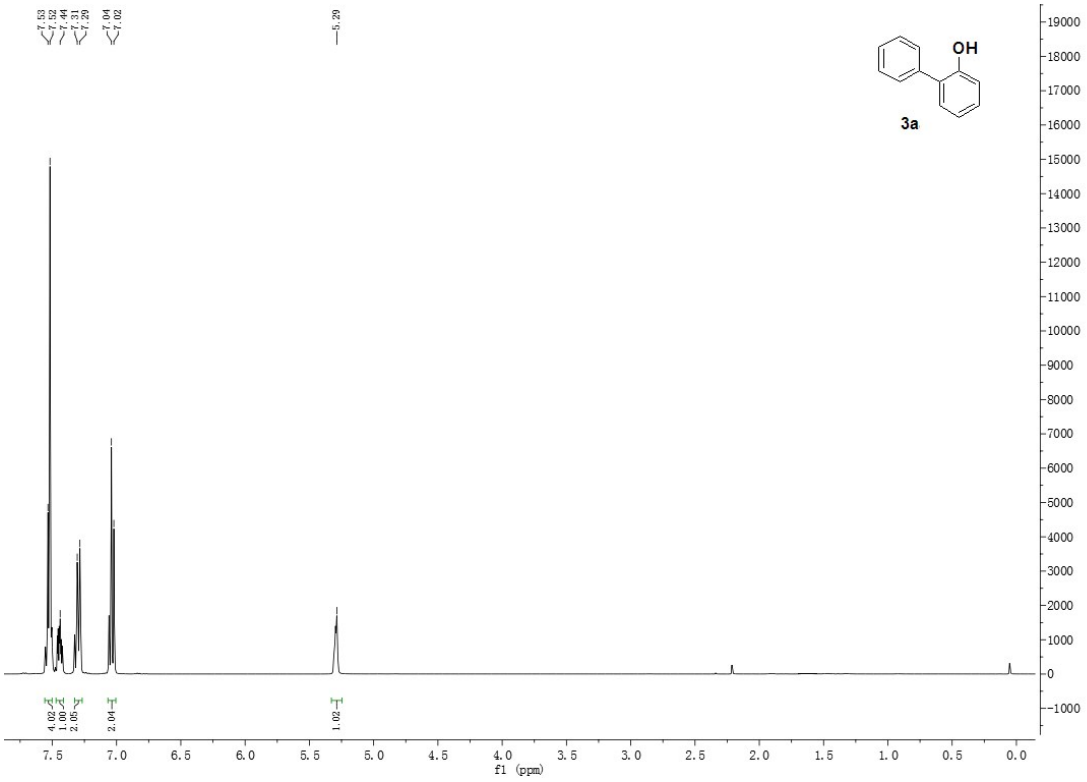
2'-chloro-5-methyl-[1,1'-Biphenyl]-2-ol (4u)

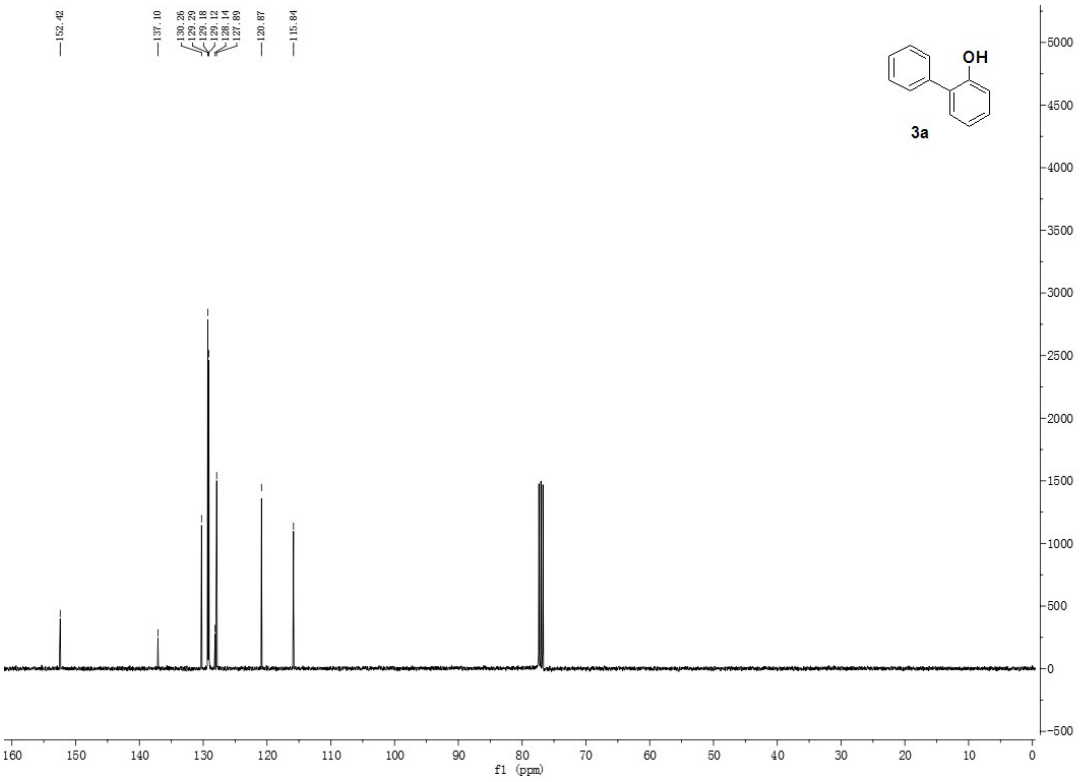


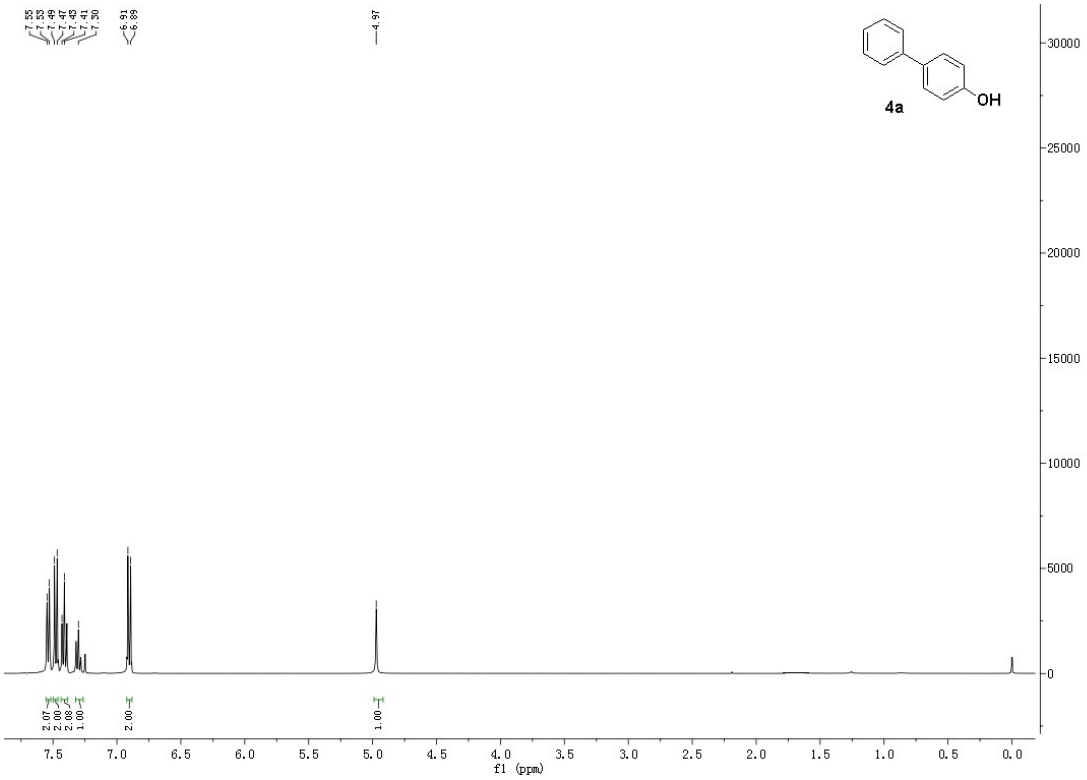
4u

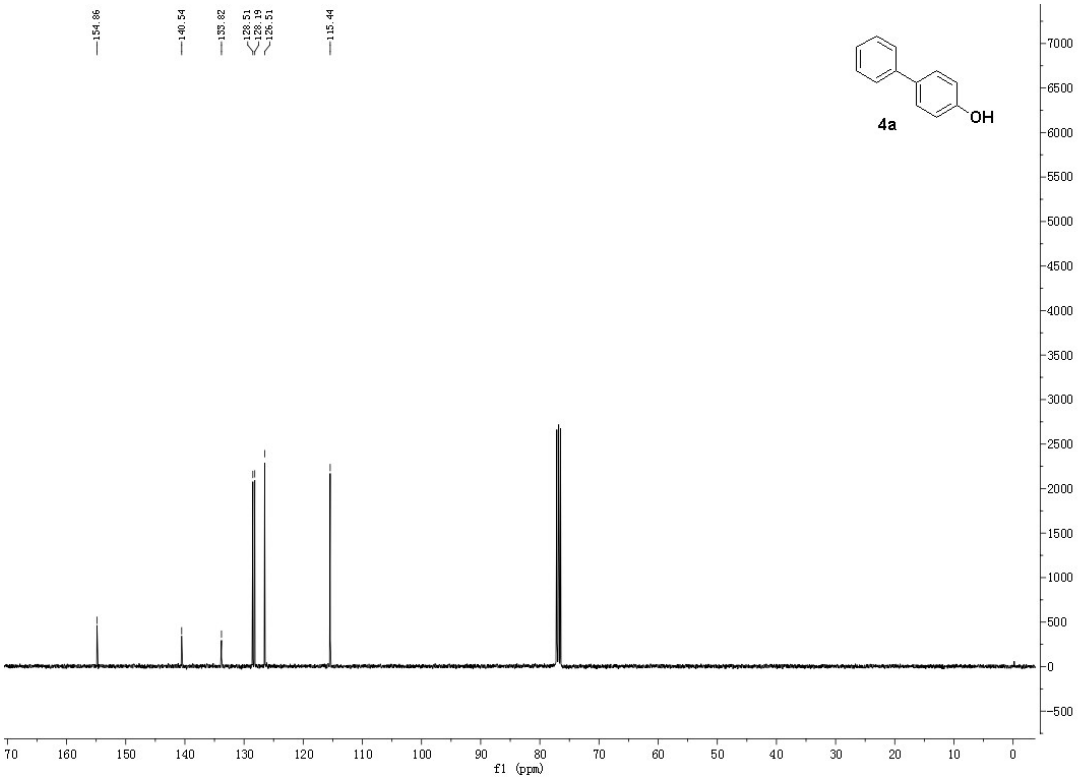
Purification by flash chromatography (petroleum ether/ethyl acetate 100:1), colourless oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.39 (dd, *J* = 36.0, 35.0 Hz, 2H), 7.41 – 7.17 (m, 1H), 6.96 (t, *J* = 43.9 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.71 (s, 1H), 2.32 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.34, 135.94, 133.99, 132.14, 130.99, 130.33, 130.01, 129.52, 128.85, 127.26, 125.73, 115.70, 13.75; ESI-MS: calculated $[C_{13}H_{10}ClO]^-$: 217.0426, found: 217.0410.

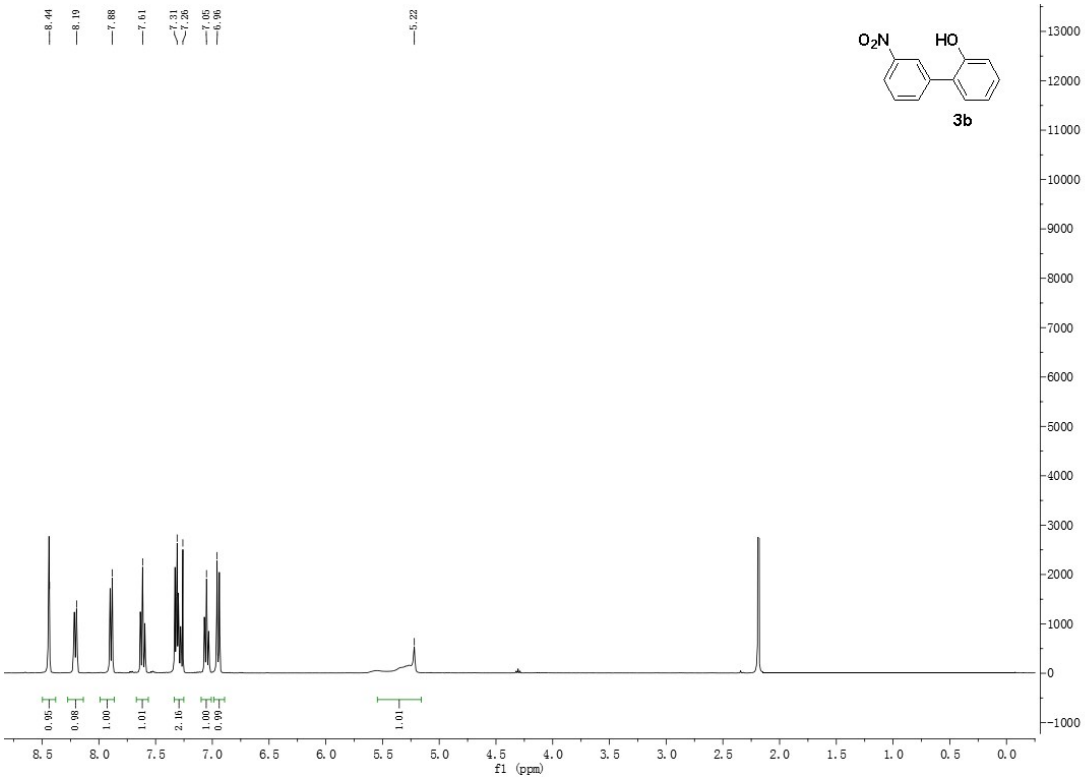
5. NMR Spectra

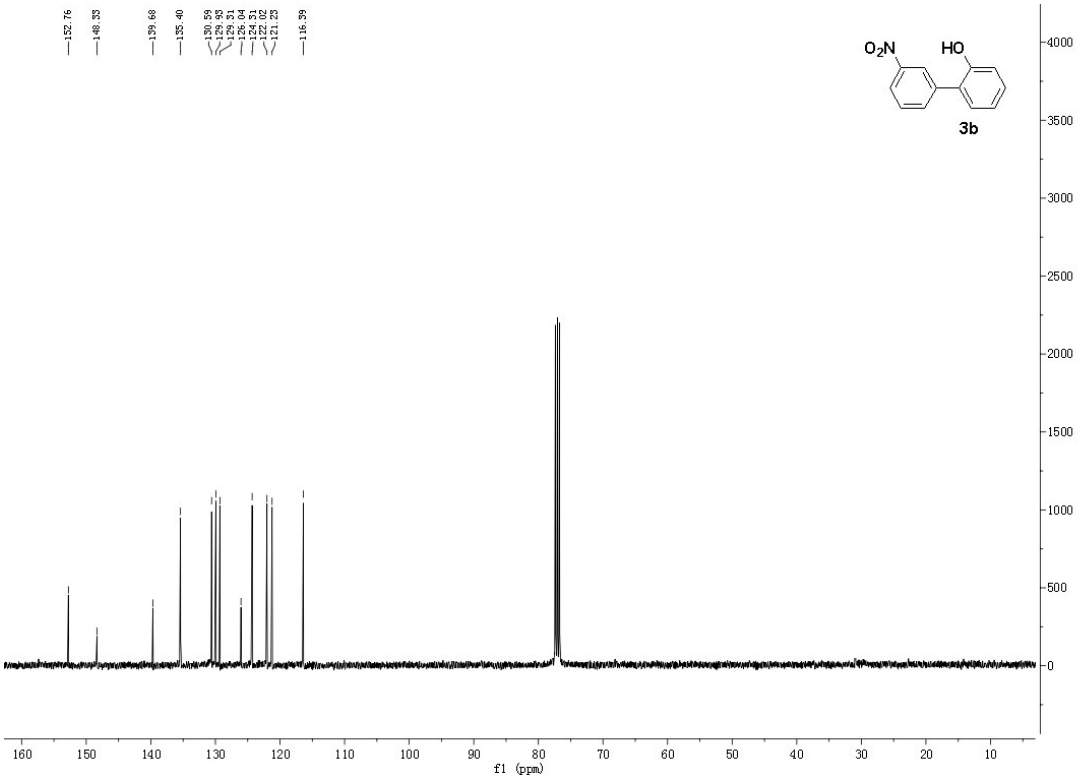


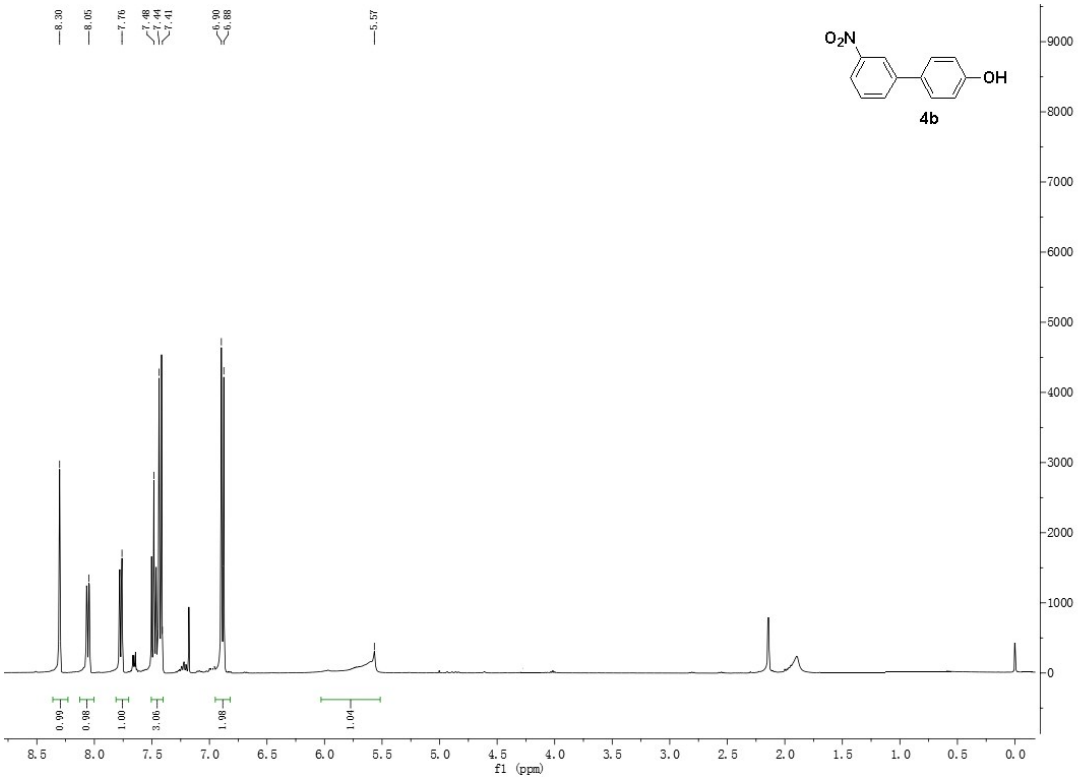


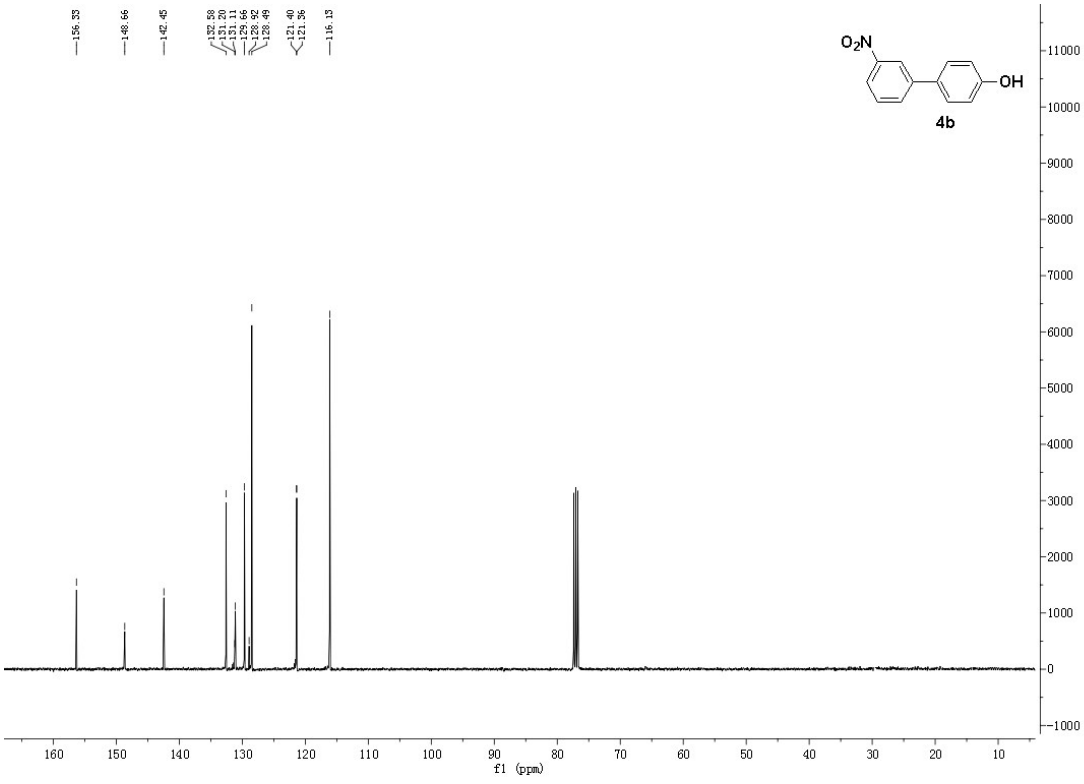

7.55
7.53
7.49
7.47
7.45
7.41
7.30
6.91
6.89
4.97
OH
4a
2.07
2.00
2.08
1.00
2.00
1.00
f1 (ppm)

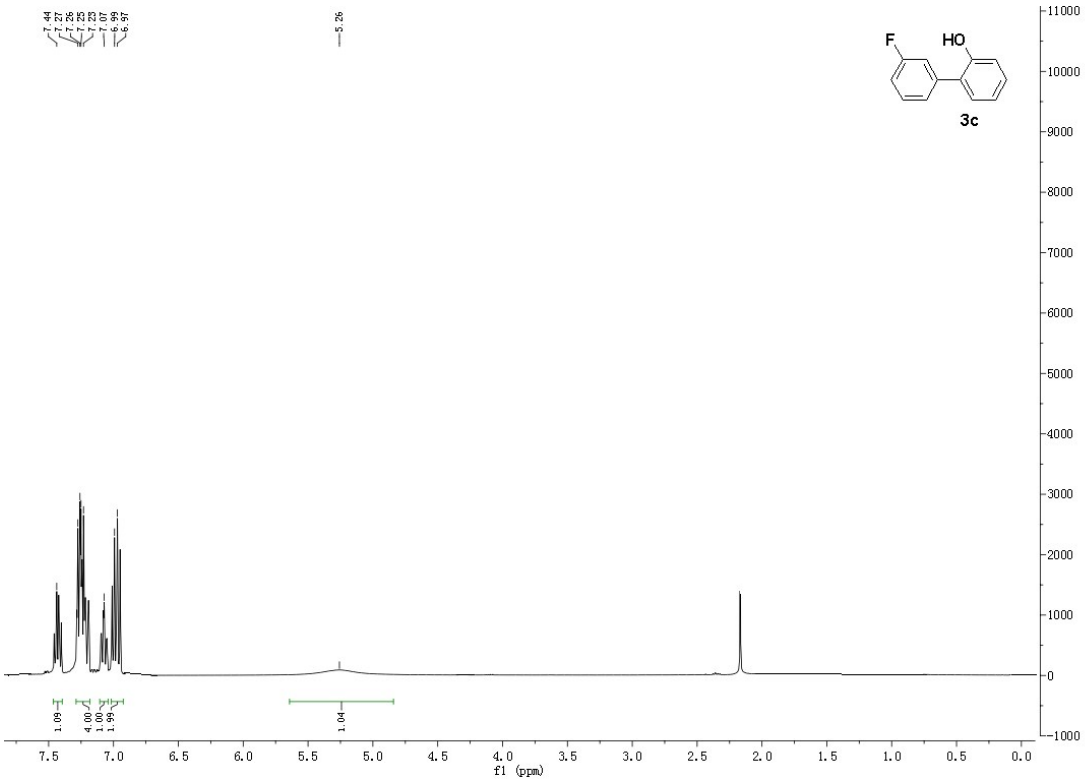

154.86
140.54
133.82
128.51
128.19
126.51
115.44
OH
4a
f1 (ppm)

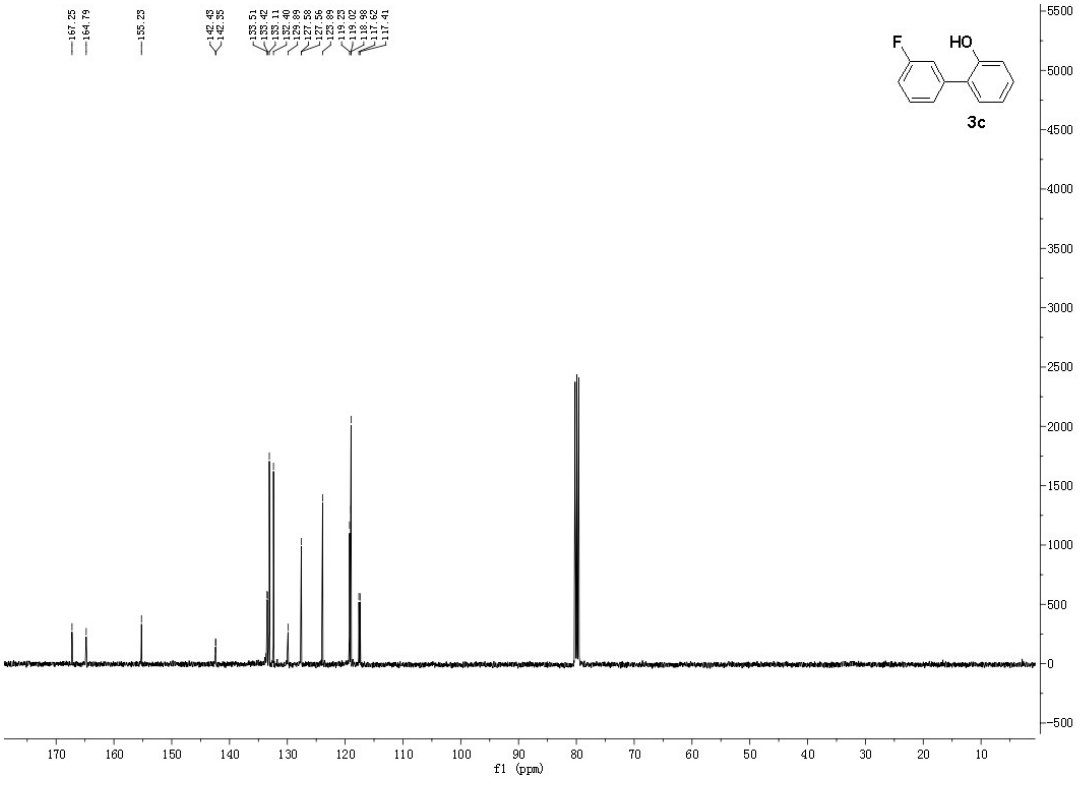

8.44
8.19
7.88
7.61
7.31
7.26
7.05
6.96
5.22
O2N
HO
3b
0.99
0.98
1.00
1.01
2.16
1.00
0.99
1.01
f1 (ppm)

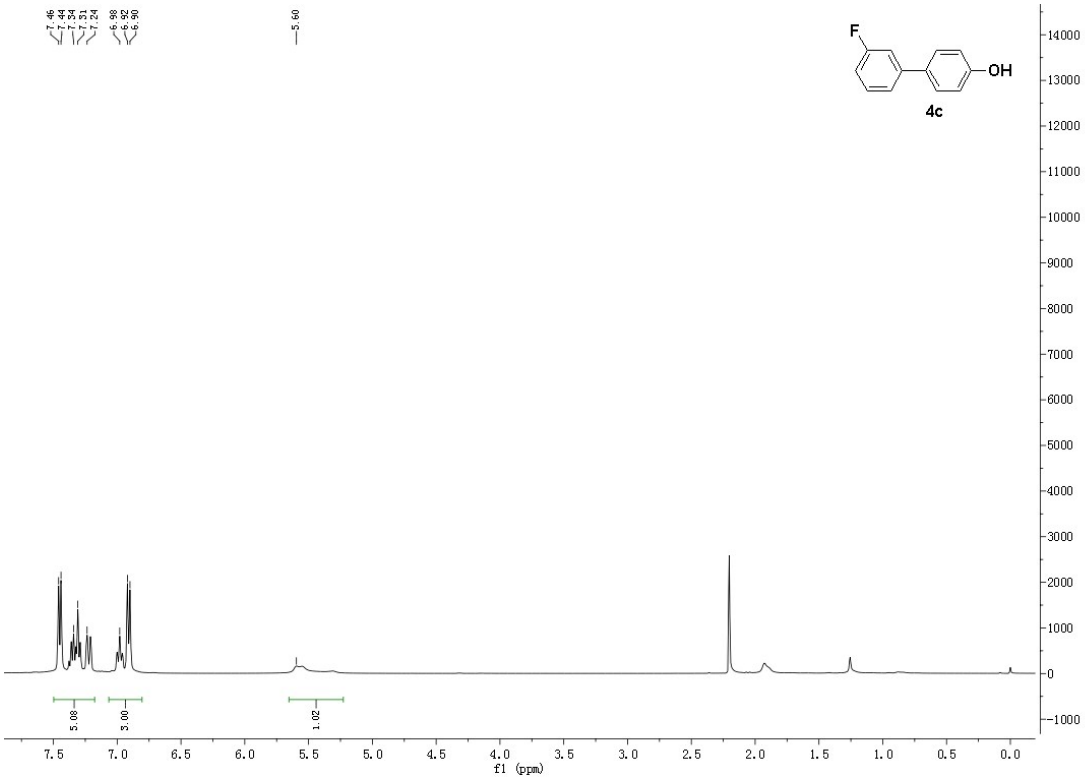

152.76
148.33
139.68
135.40
130.59
129.93
129.51
126.94
124.31
122.02
121.23
116.39
O2N
HO
3b
f1 (ppm)

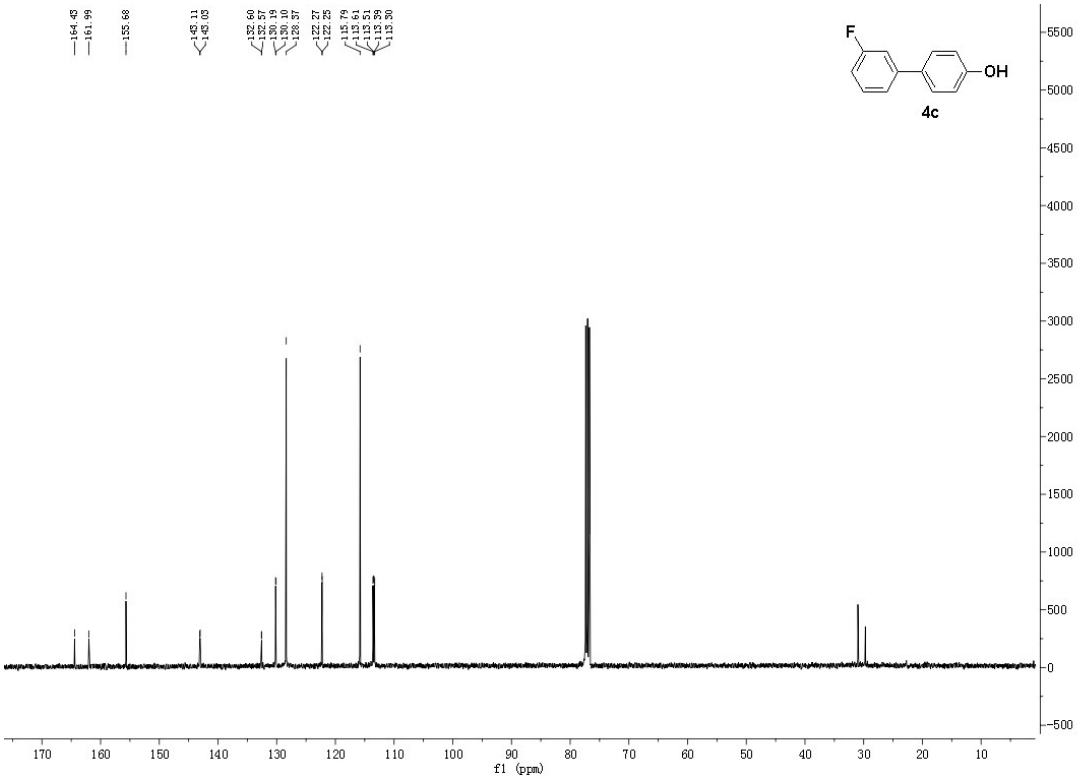

8.30
8.05
7.76
7.48
7.44
7.41
6.90
6.88
5.57
O2N
OH
4b
0.99
0.98
1.00
3.00
1.98
1.04
f1 (ppm)

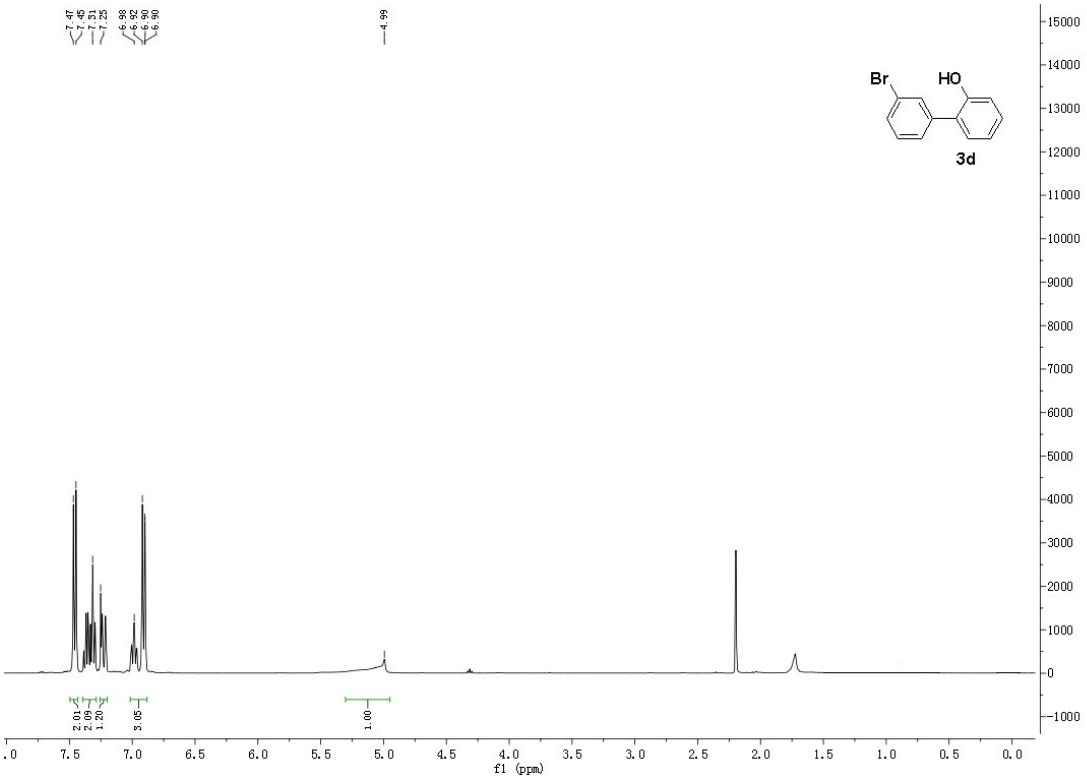

156.53
148.66
142.45
132.58
131.20
131.11
129.66
128.92
128.49
121.40
121.36
116.13
O2N
OH
4b
f1 (ppm)

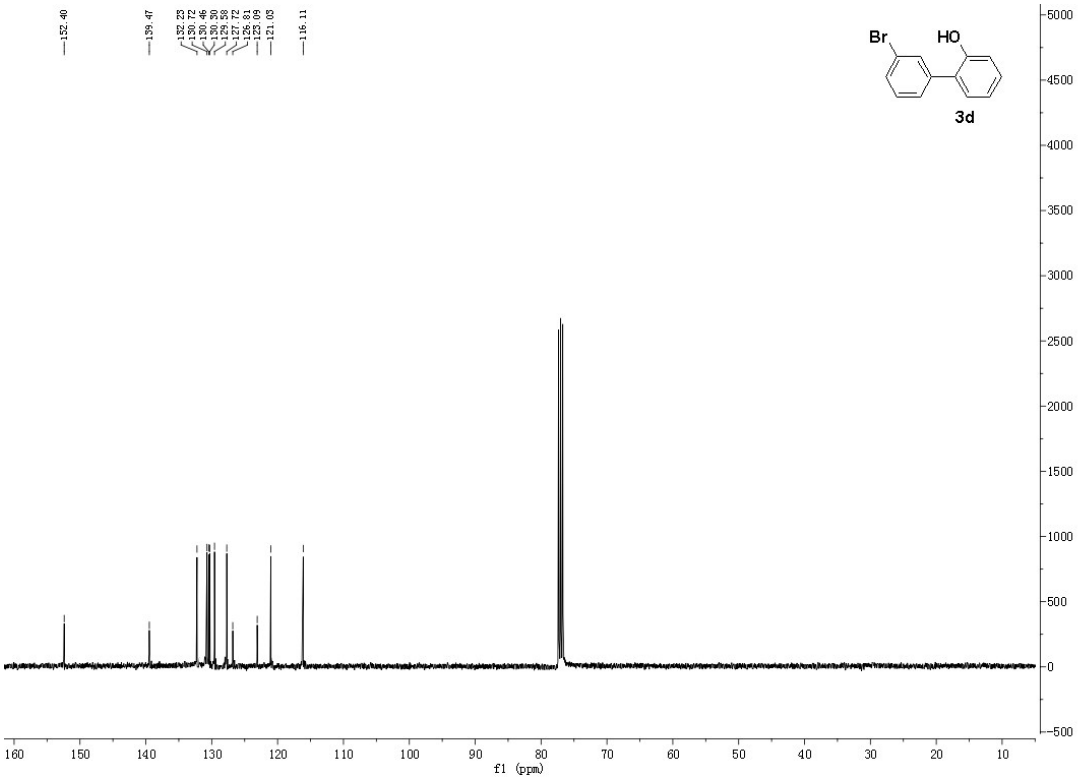

7.44
7.27
7.26
7.25
7.23
7.07
6.99
6.97
5.26
F
HO
3c
1.09
4.00
1.00
1.99
1.04
f1 (ppm)

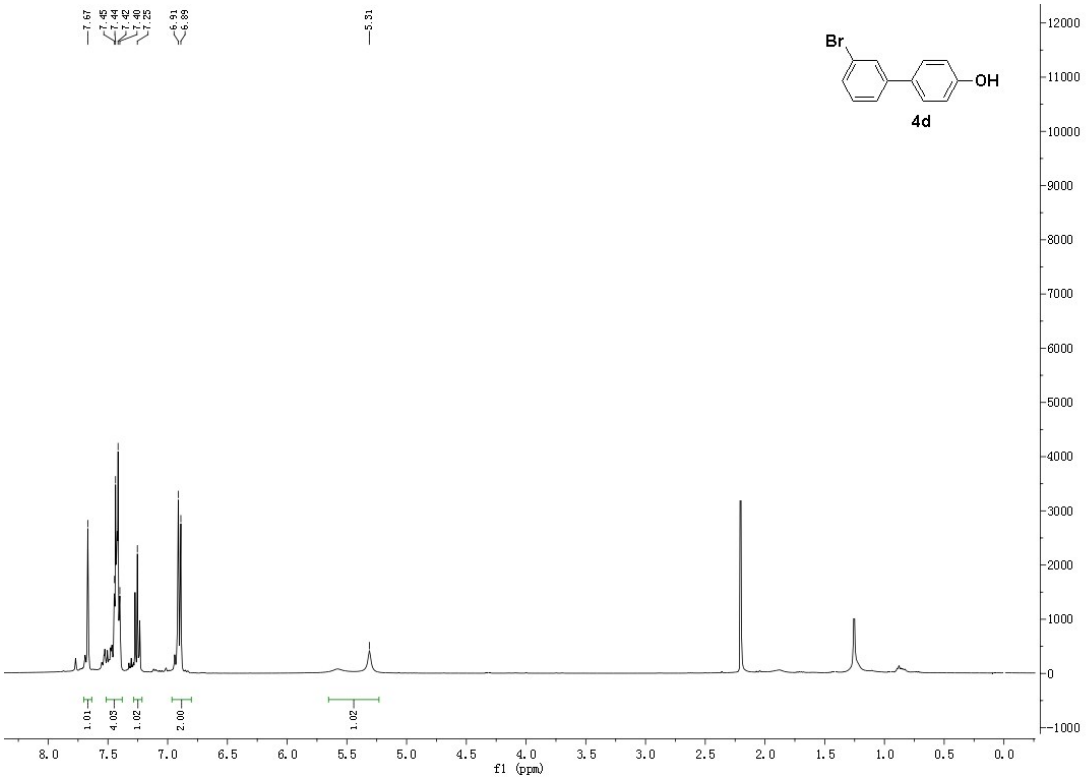

167.25
164.79
155.23
142.43
142.35
133.51
133.42
133.11
132.40
129.88
127.58
127.56
123.89
119.23
119.07
118.98
118.96
117.62
117.41
F
HO
3c
f1 (ppm)

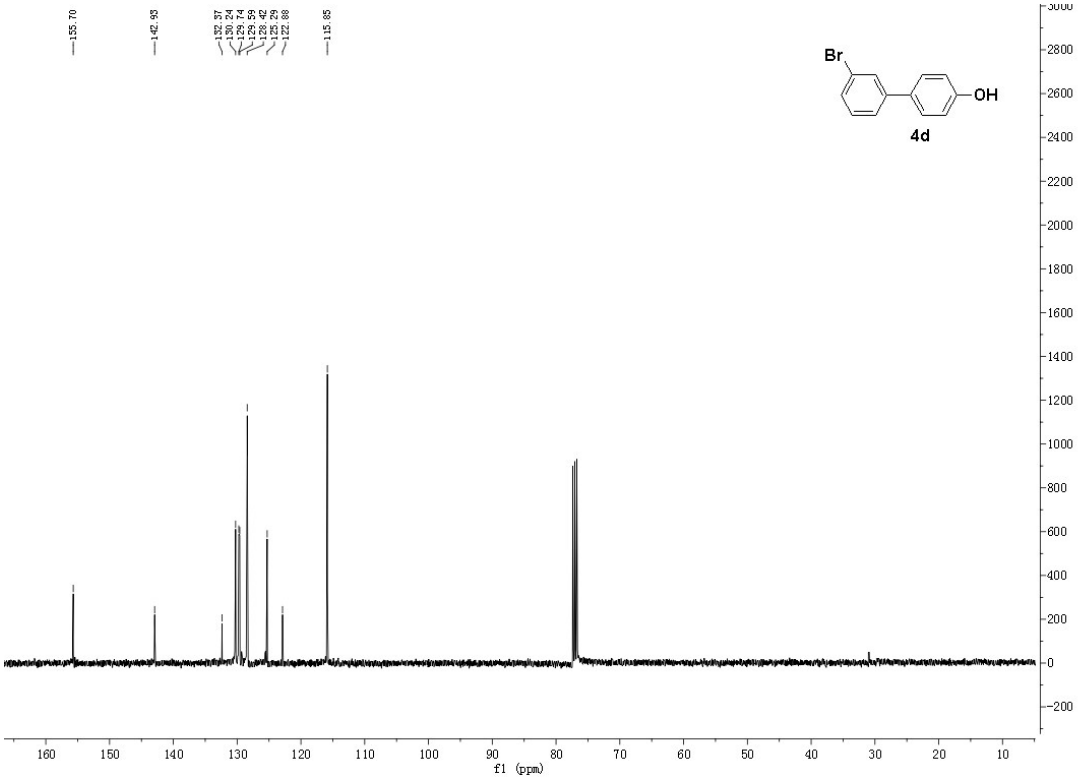

7.46
7.44
7.34
7.31
7.24
6.98
6.92
6.90
5.60
F
OH
4c
5.08
3.00
1.02
f1 (ppm)

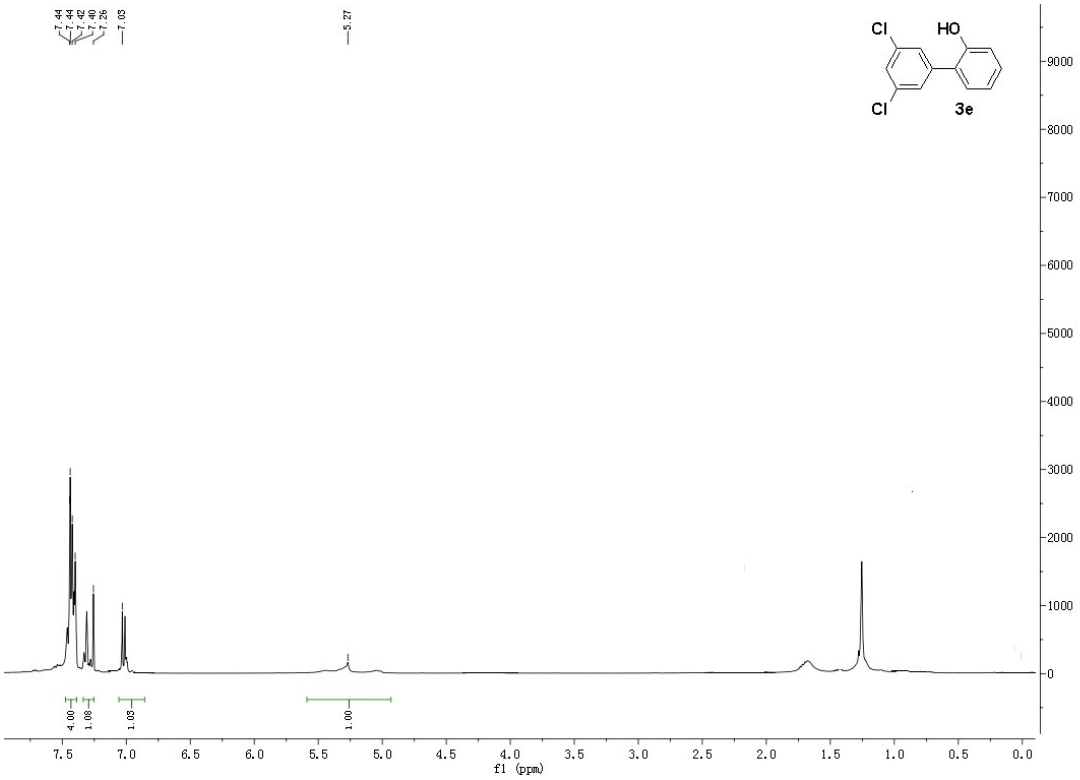

164.45
161.99
155.68
145.11
145.03
132.60
132.57
130.19
130.10
128.37
122.27
122.25
115.79
115.61
115.51
115.34
115.30
F
OH
4c
f1 (ppm)


7.47
7.45
7.31
7.25
6.98
6.92
6.90
6.90
4.99
Br
HO
3d
2.01
2.09
1.20
3.05
1.00
f1 (ppm)


152.40
139.47
132.23
130.72
130.46
130.30
129.88
127.72
126.81
123.09
121.03
116.11
Br
HO
3d
f1 (ppm)


7.67
7.45
7.44
7.42
7.40
7.25
6.91
6.89
5.31
Br
OH
4d
1.01
4.03
1.02
2.00
1.02
f1 (ppm)


155.70
142.93
132.37
130.24
129.74
129.59
128.42
125.29
122.88
115.85
Br
OH
4d
f1 (ppm)


7.44
7.44
7.42
7.40
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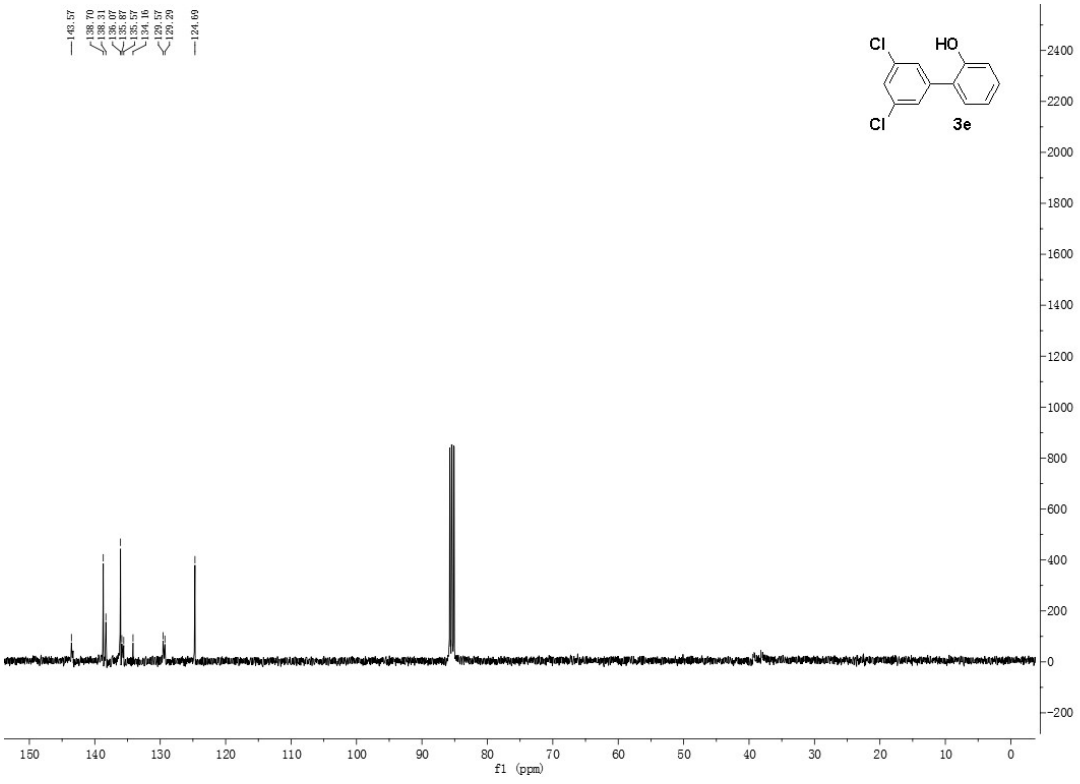
7.03
5.27
Cl
HO
Cl
3e
4.00
1.08
1.03
1.00
f1 (ppm)


143.57
138.70
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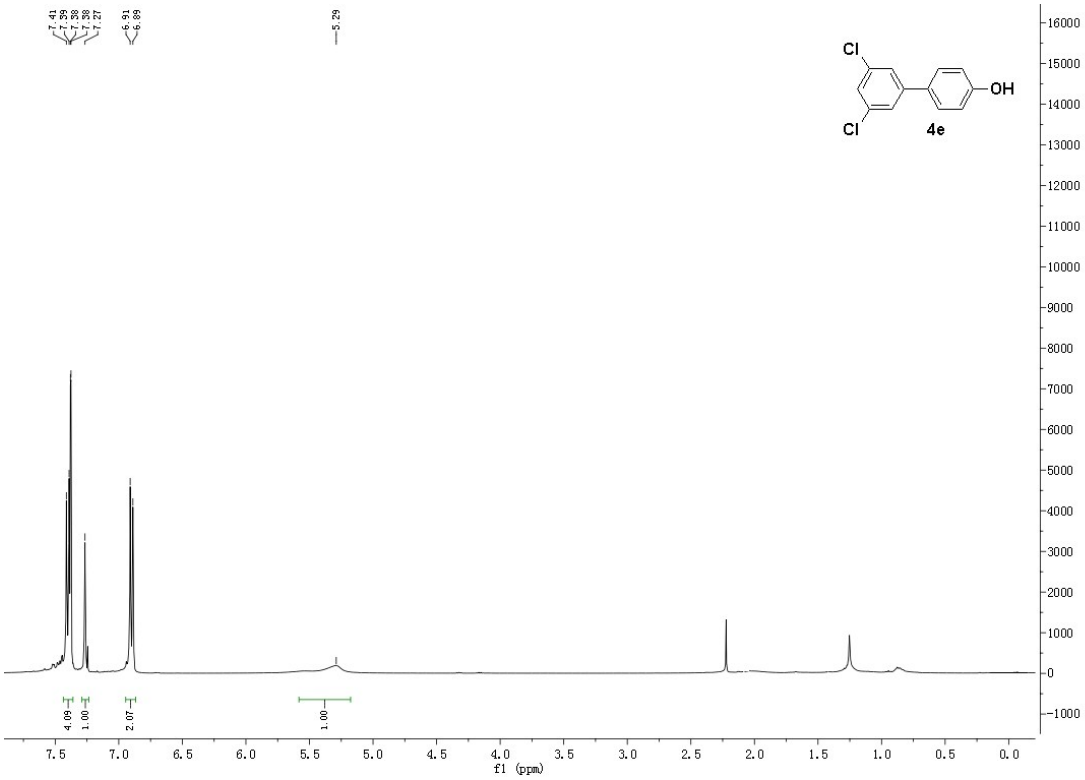
135.87
135.57
134.16
129.57
129.29
124.69
Cl
HO
Cl
3e
f1 (ppm)


7.41
7.39
7.38
7.30
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6.91
6.89
5.29
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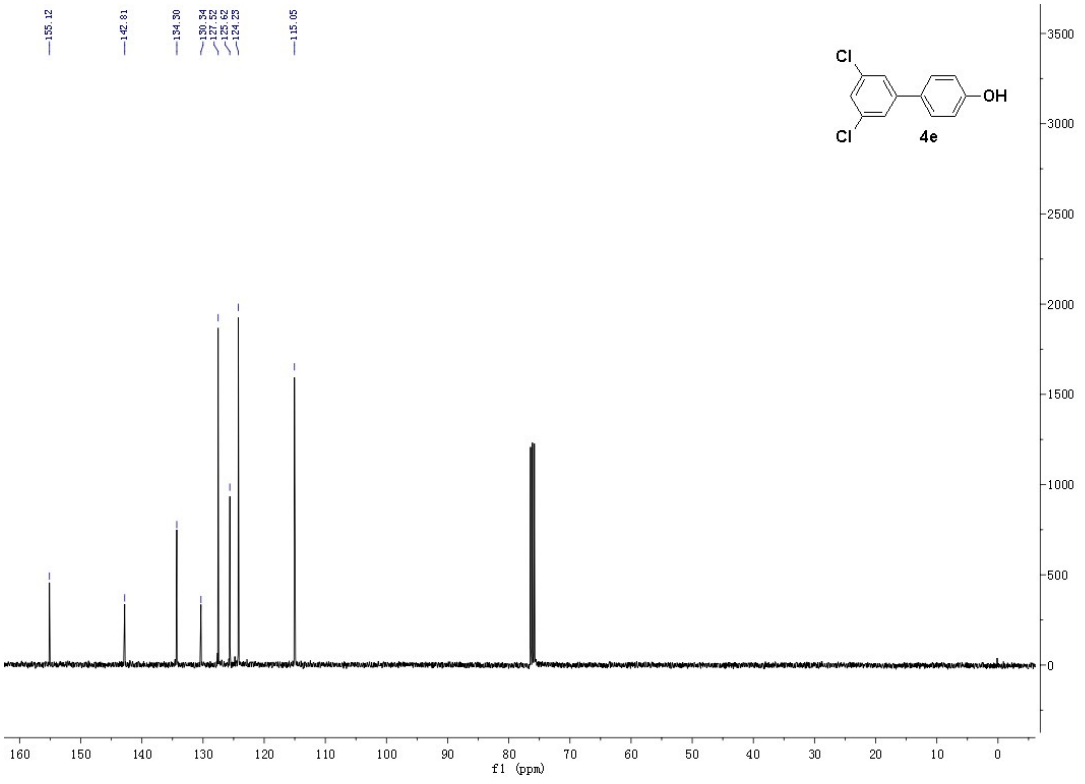
Cl
OH
4e
4.09
1.00
2.07
1.00
f1 (ppm)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115.05
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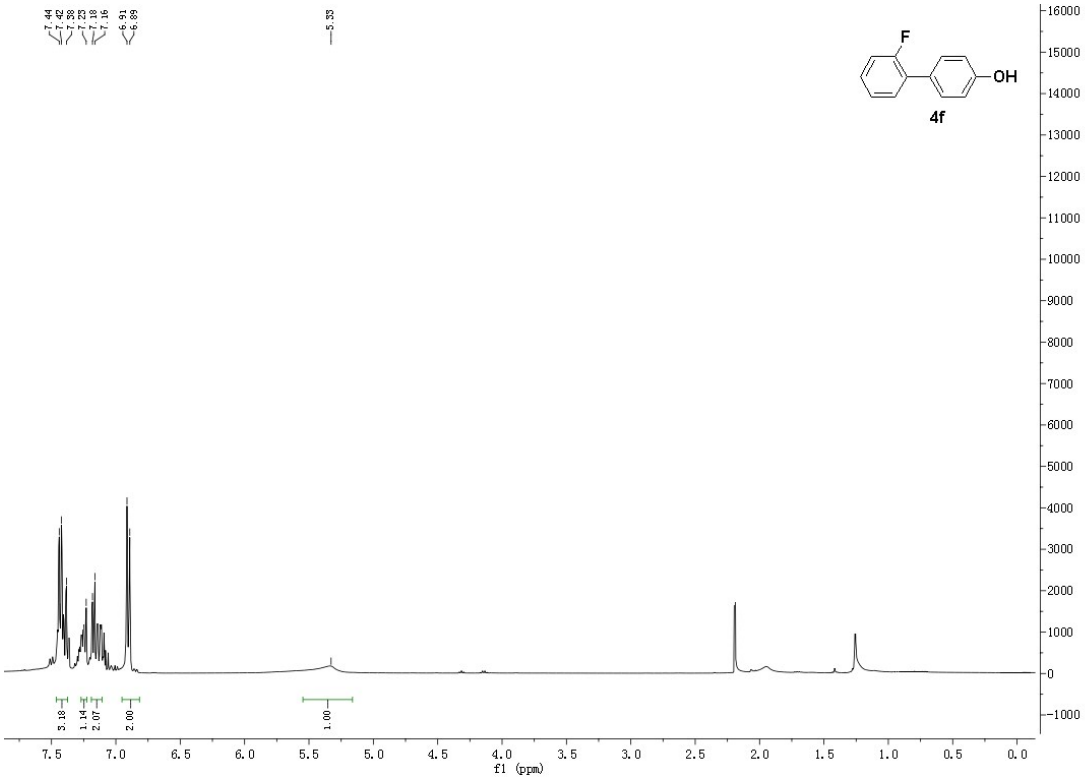
OH
4e
f1 (ppm)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7.23
7.18
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4f
3.18
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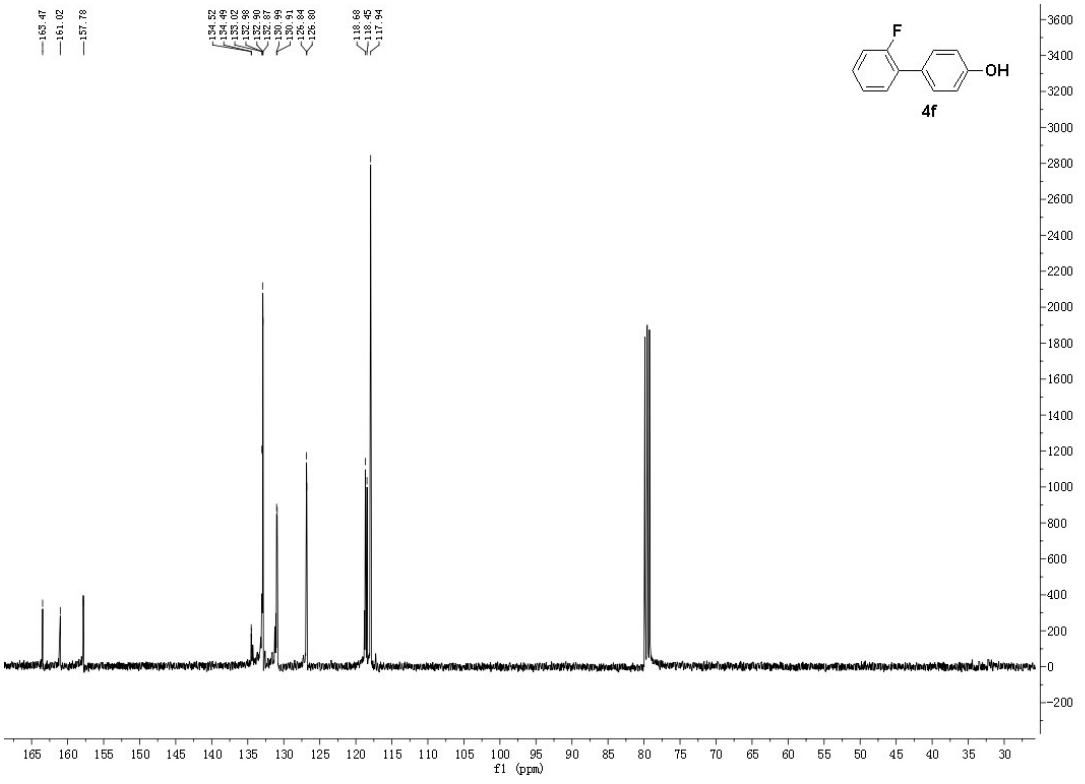
2.07
2.00
1.00
f1 (ppm)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157.78
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133.02
132.98
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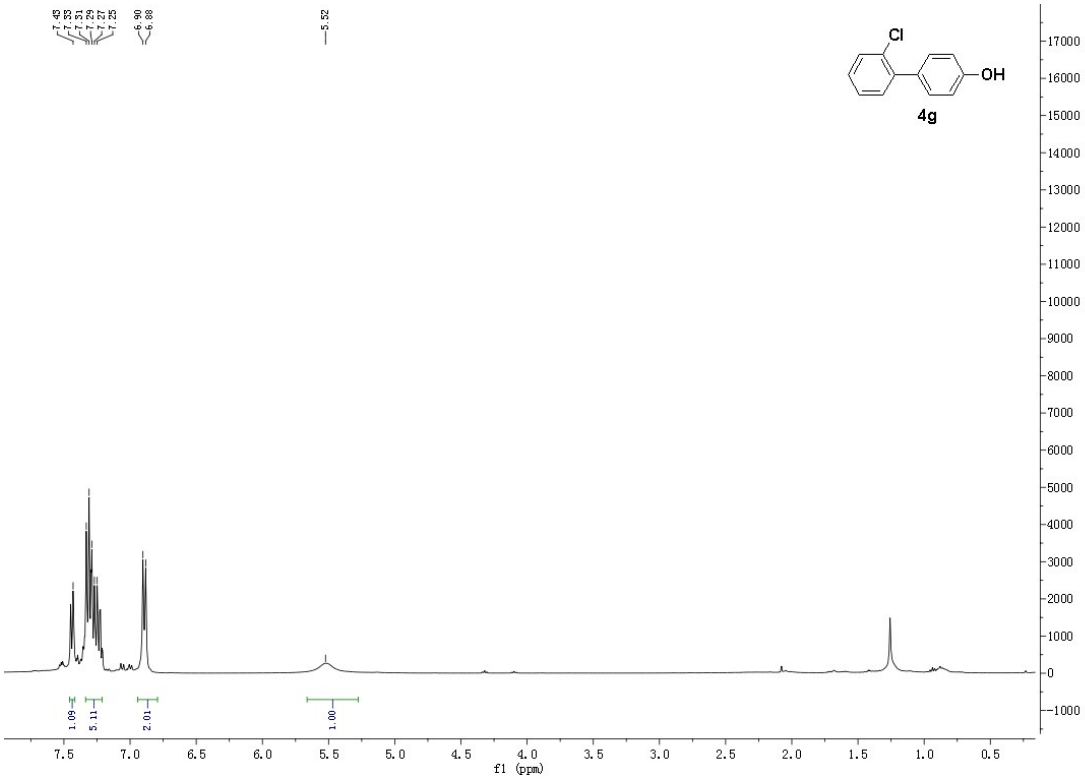
117.94
F
OH
4f
f1 (ppm)


7.43
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7.31
7.29
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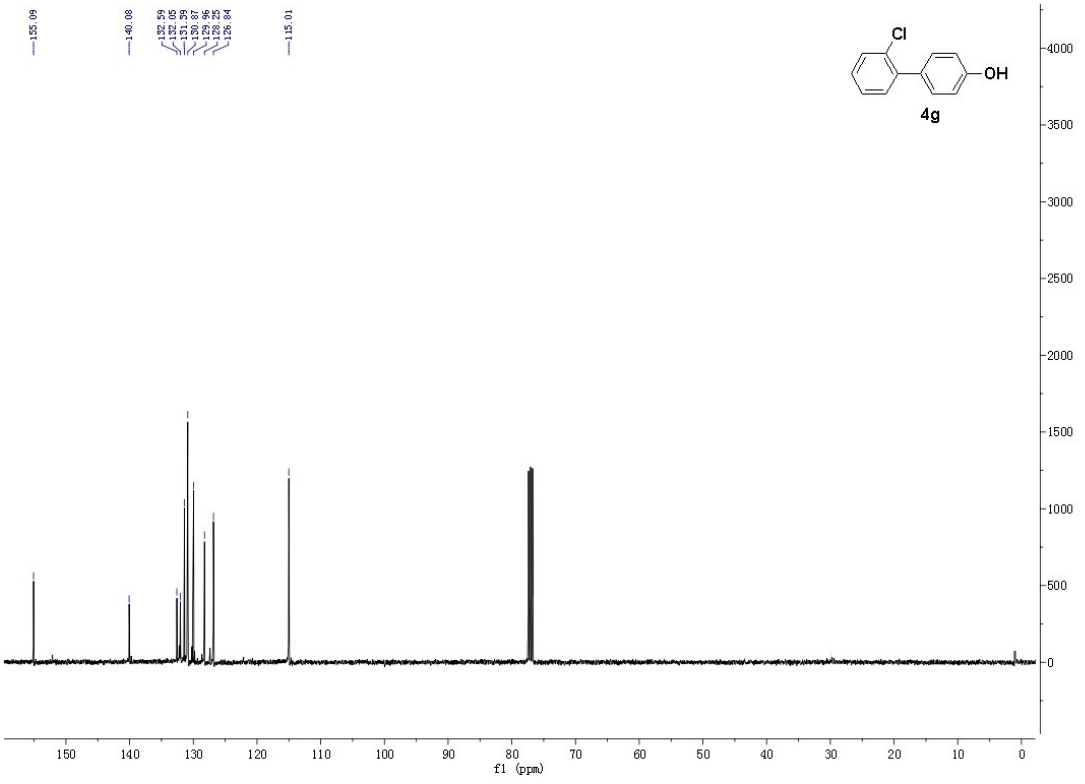
2.01
1.00
f1 (ppm)


155.09
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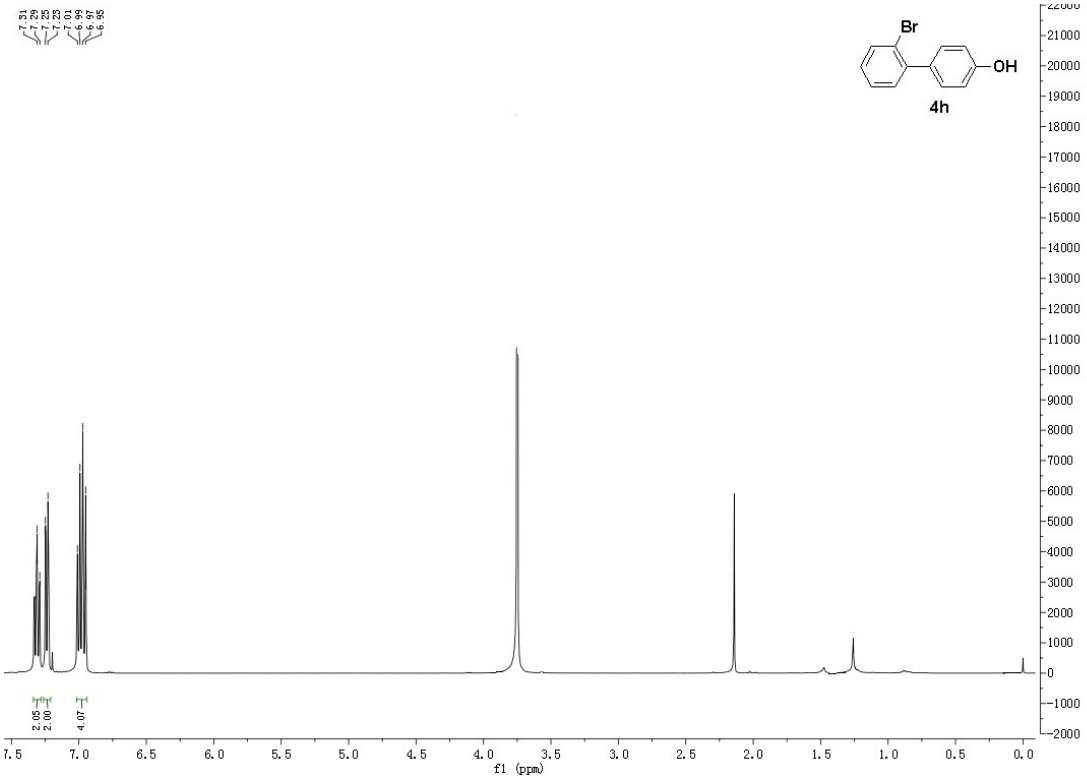
130.87
129.96
128.25
126.84
115.01
Cl
OH
4g
f1 (ppm)


7.31
7.29
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6.95
Br
OH
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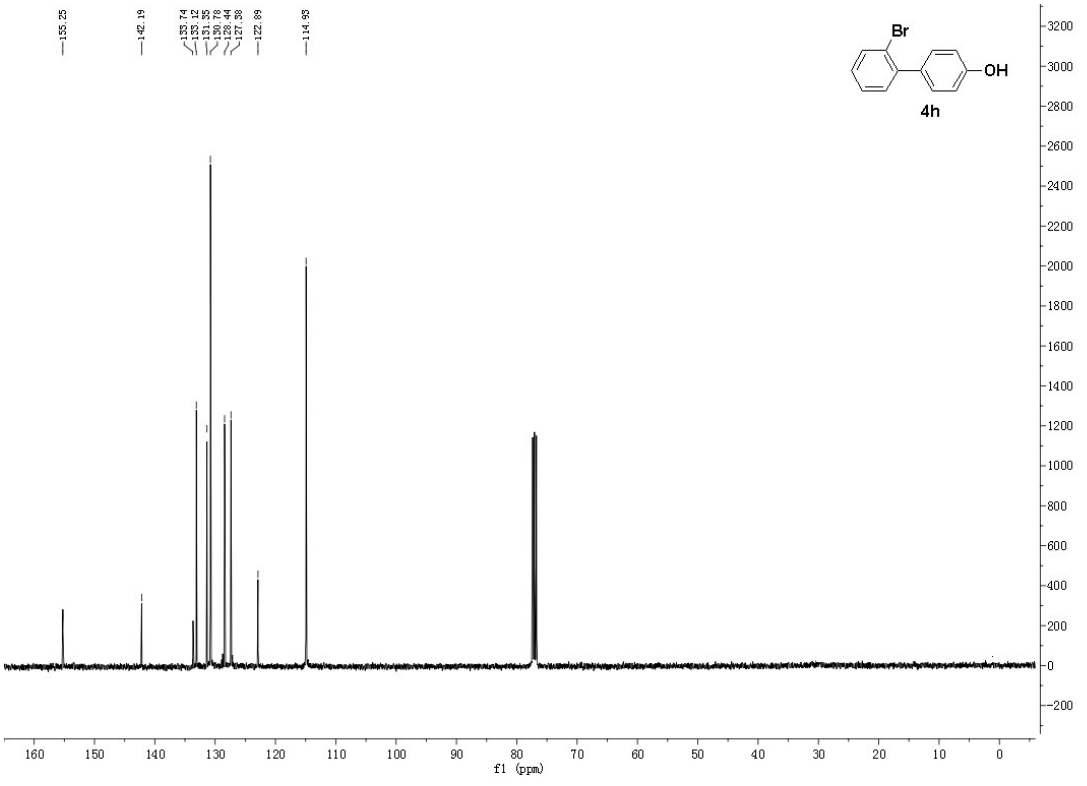
2.05
2.00
4.07
f1 (ppm)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127.38
122.89
114.93
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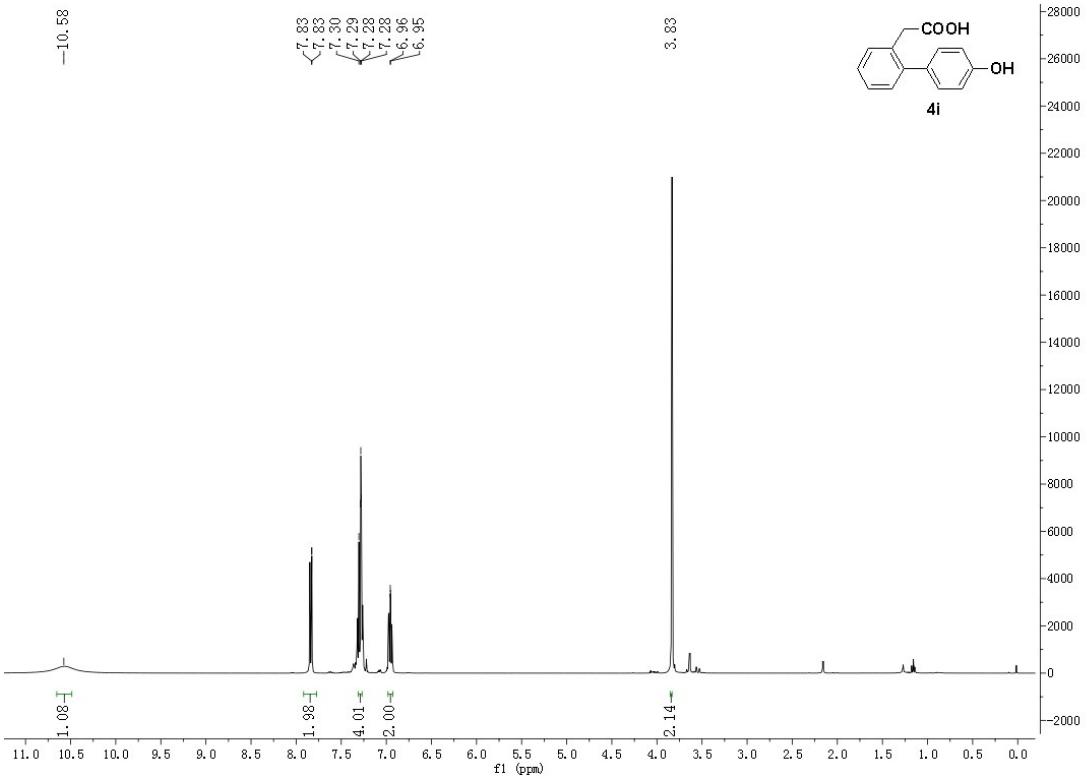
OH
4h
f1 (ppm)


10.58
7.83
7.83
7.30
7.29
7.28
7.28
6.96
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COOH
OH
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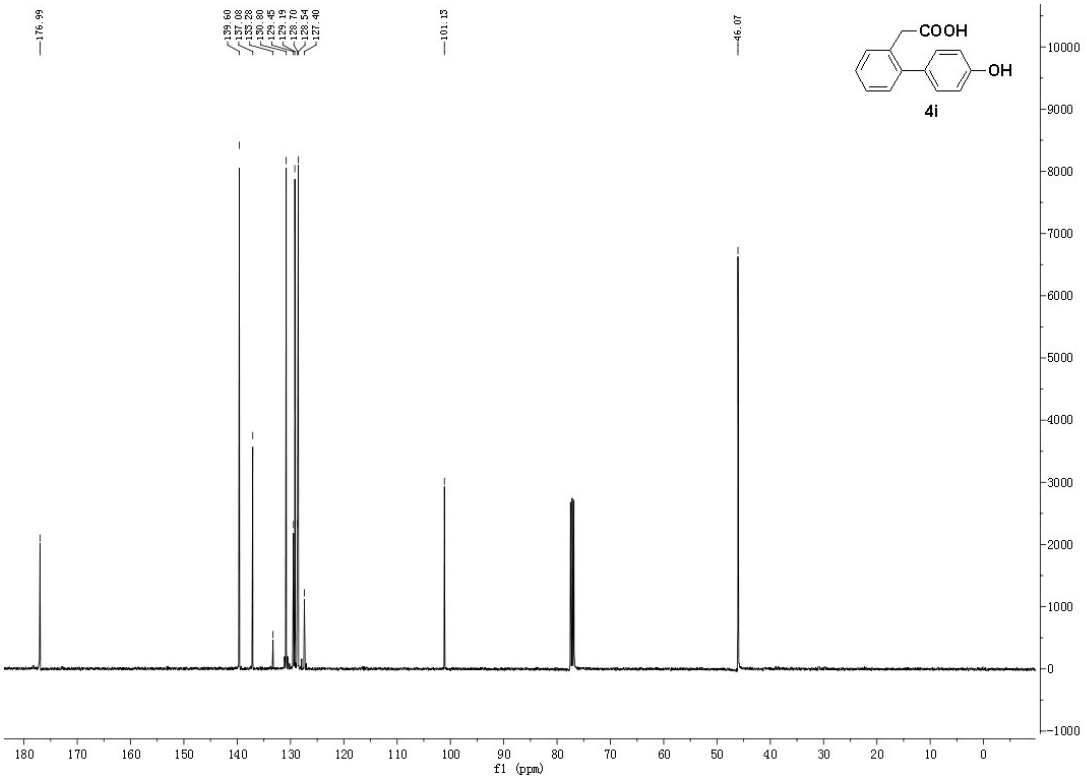
1.98
4.01
2.00
2.14
f1 (ppm)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137.88
133.28
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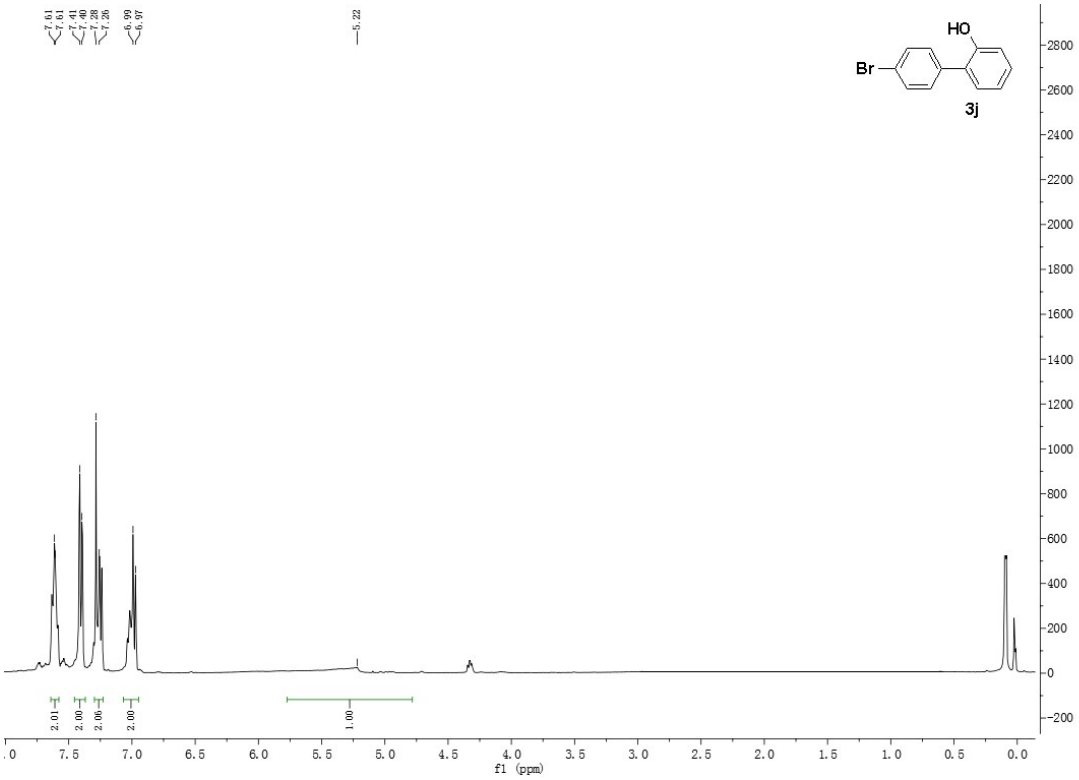
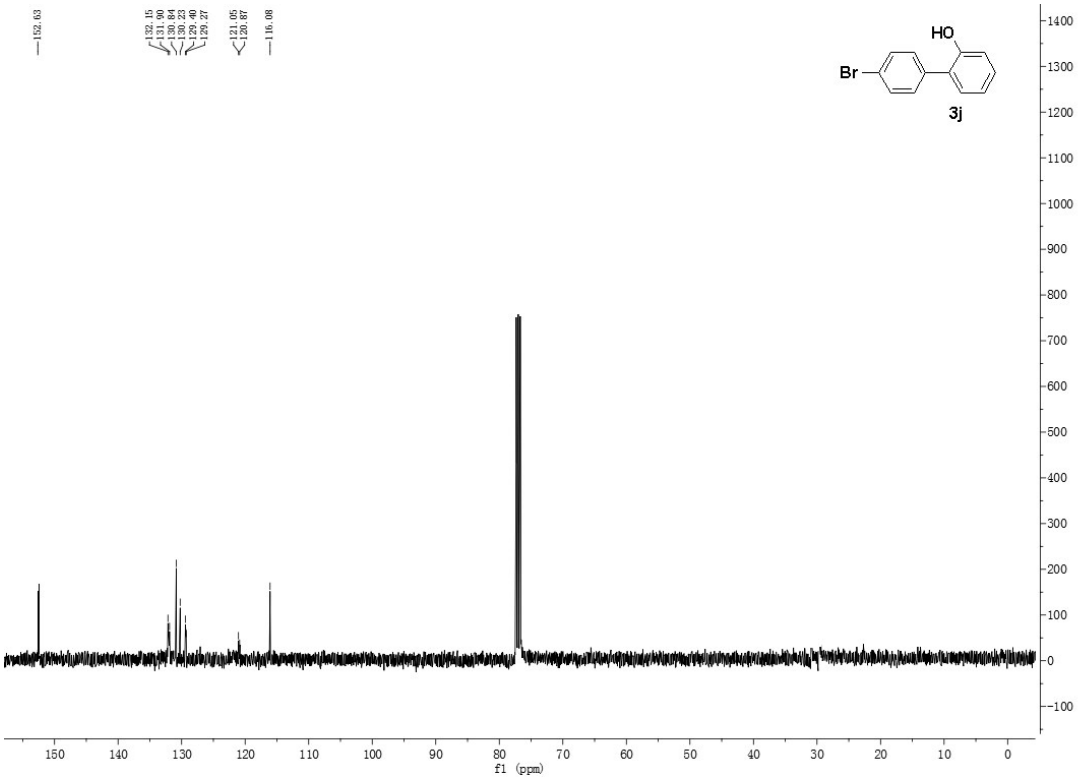
128.99
128.70
128.54
127.40
101.13
46.07
COOH
OH
4i
f1 (ppm)


7.61
7.61
7.41
7.40
7.28
7.26
6.99
6.97
5.22
HO
Br
3j
2.01
2.00
2.06
2.00
1.00
f1 (ppm)


152.63
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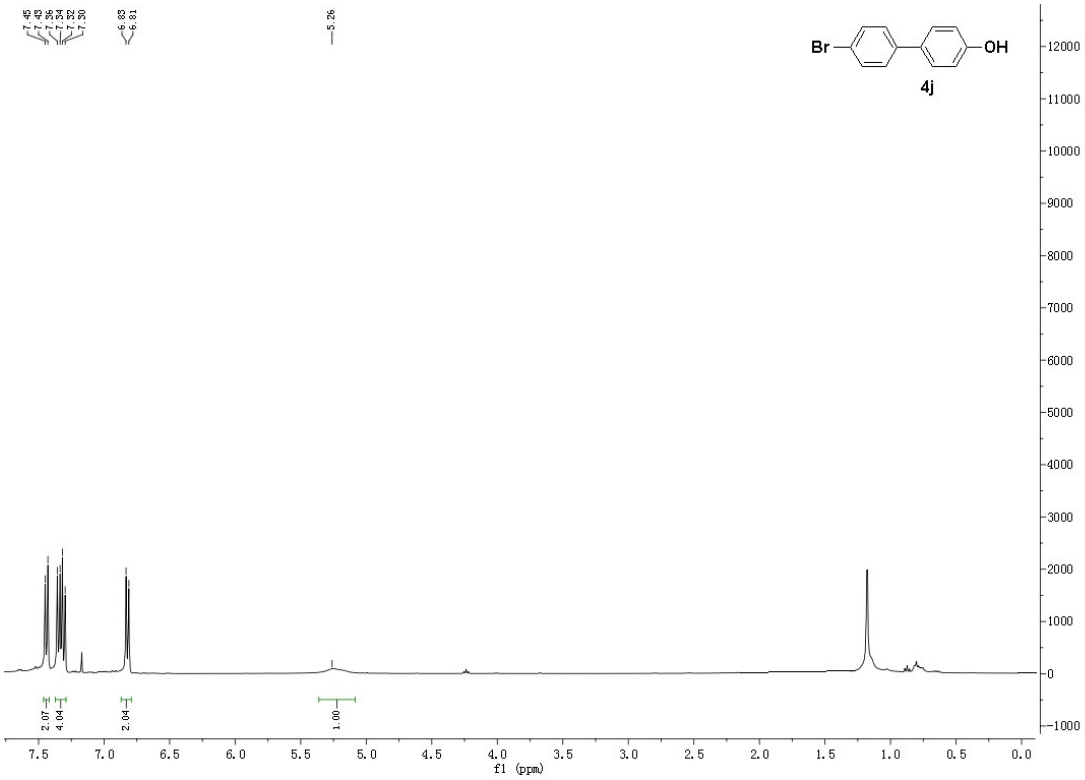
130.23
129.40
129.27
121.05
120.87
116.08
HO
Br
3j
f1 (ppm)


7.45
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7.34
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7.30
6.83
6.81
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Br
OH
4j
2.07
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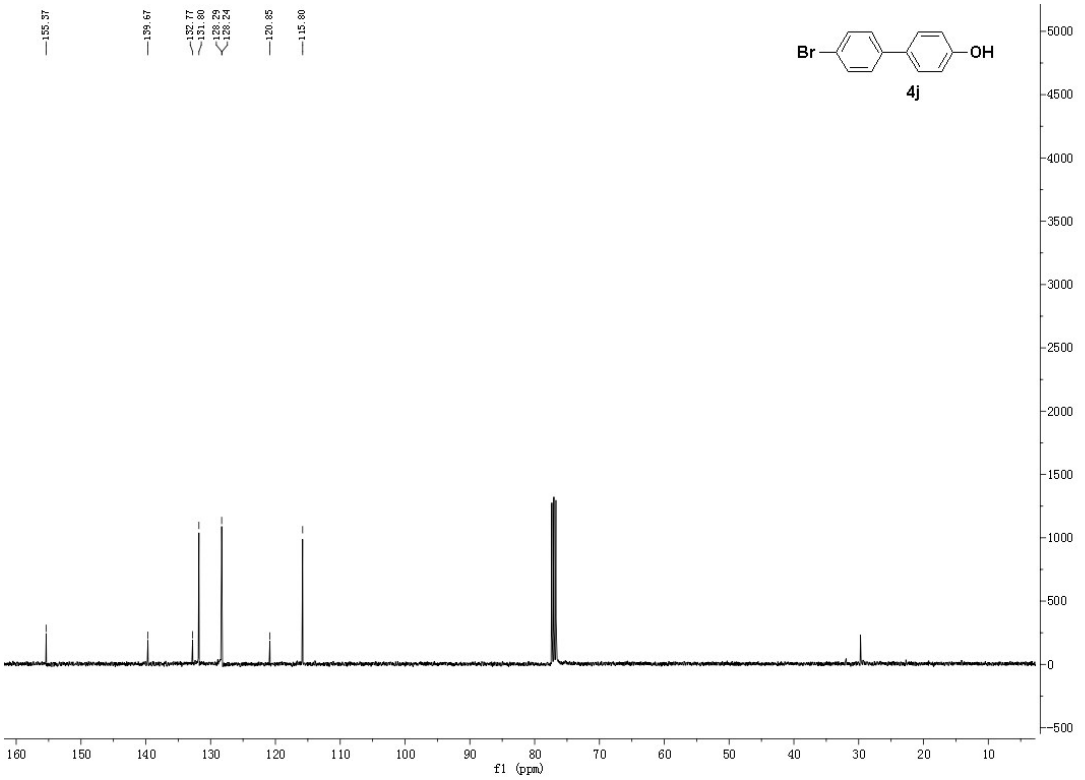
2.04
1.00
f1 (ppm)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120.65
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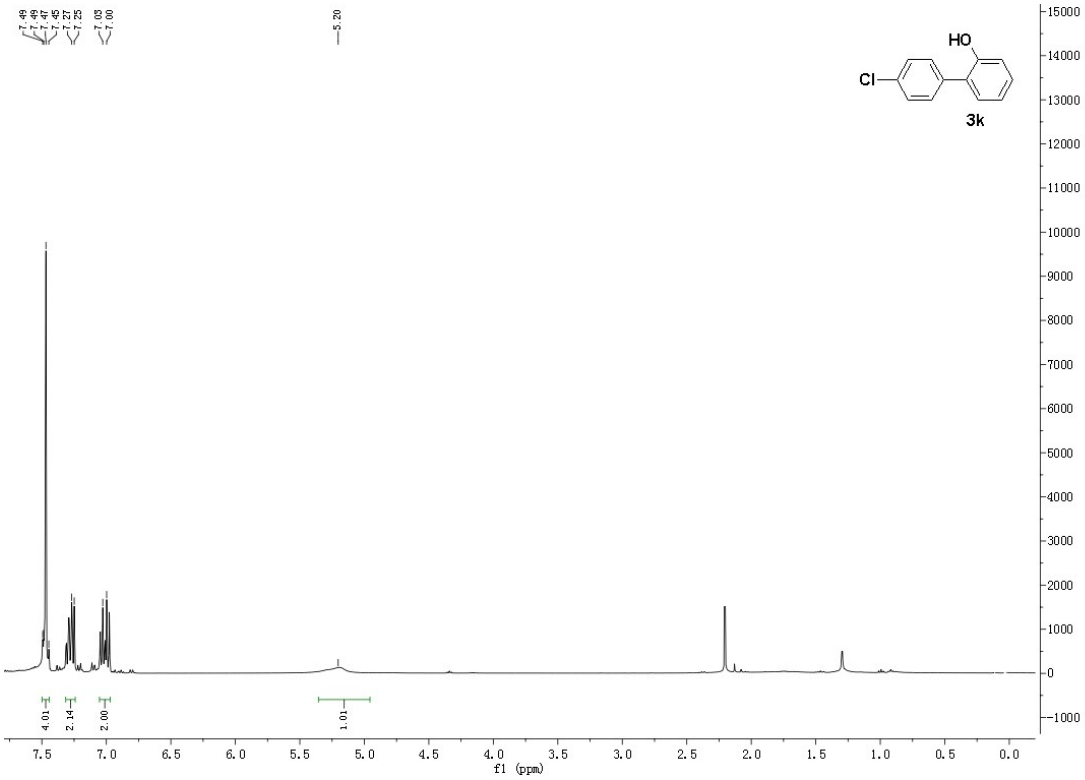
OH
4j
f1 (ppm)


7.49
7.49
7.47
7.47
7.27
7.25
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7.00
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Cl
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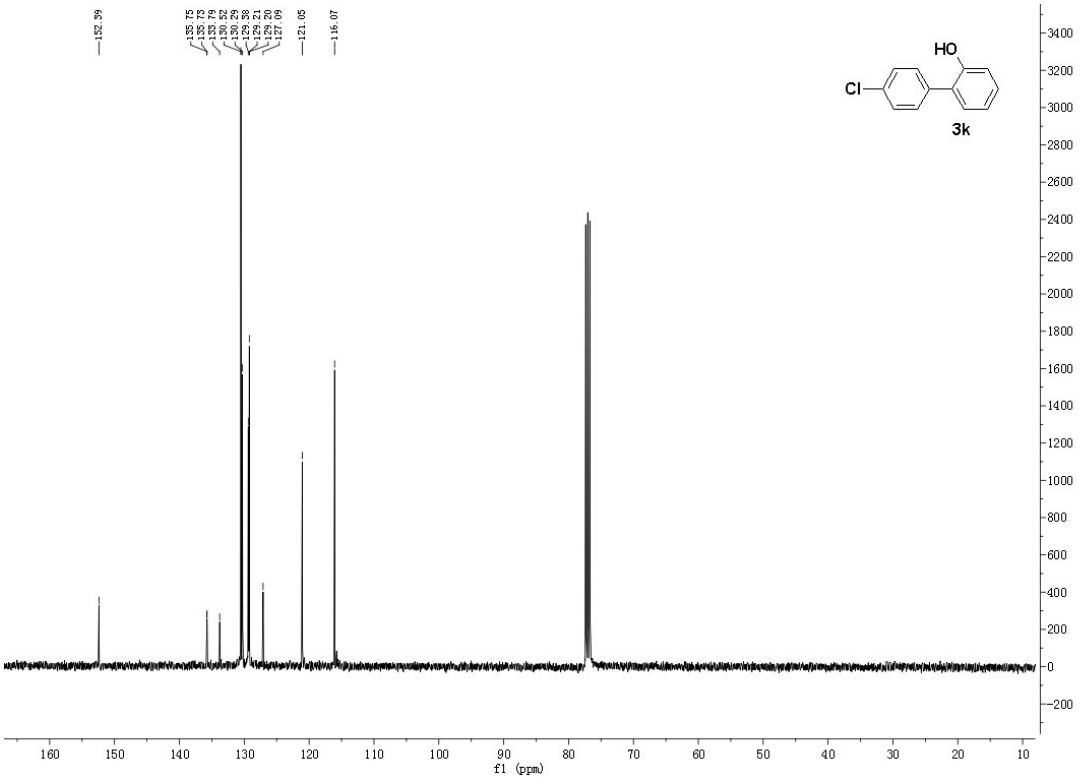
4.01
2.14
2.00
1.01
f1 (ppm)


152.39
135.75
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130.52
130.29
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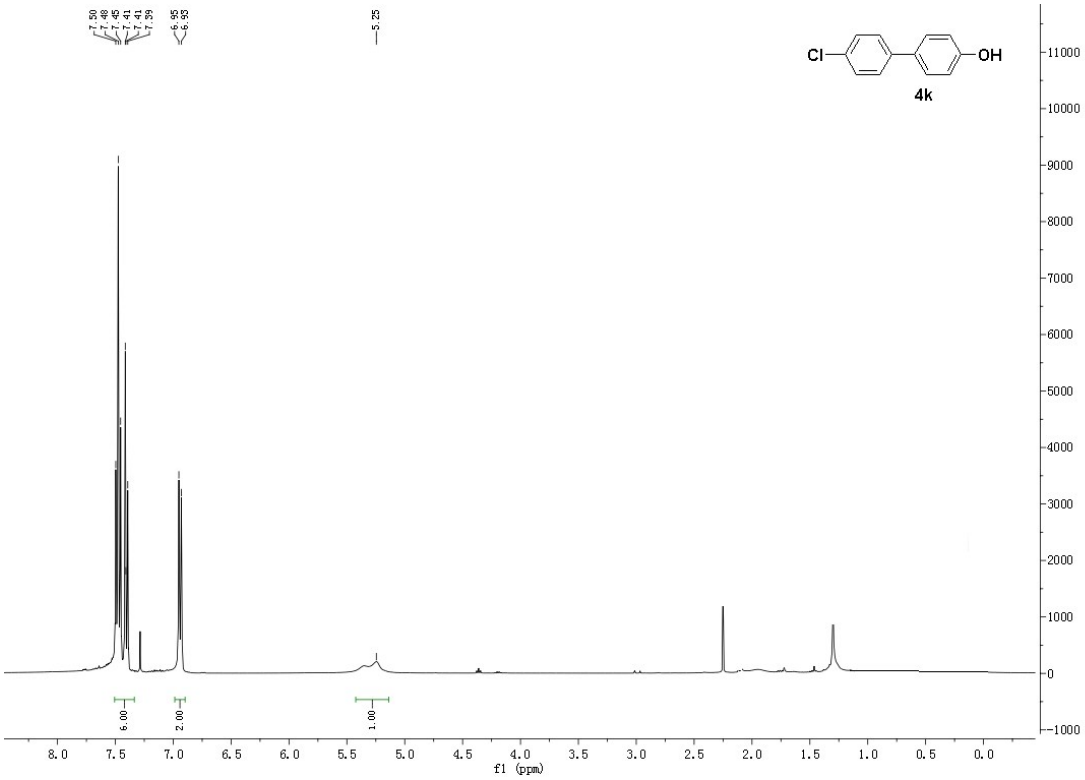
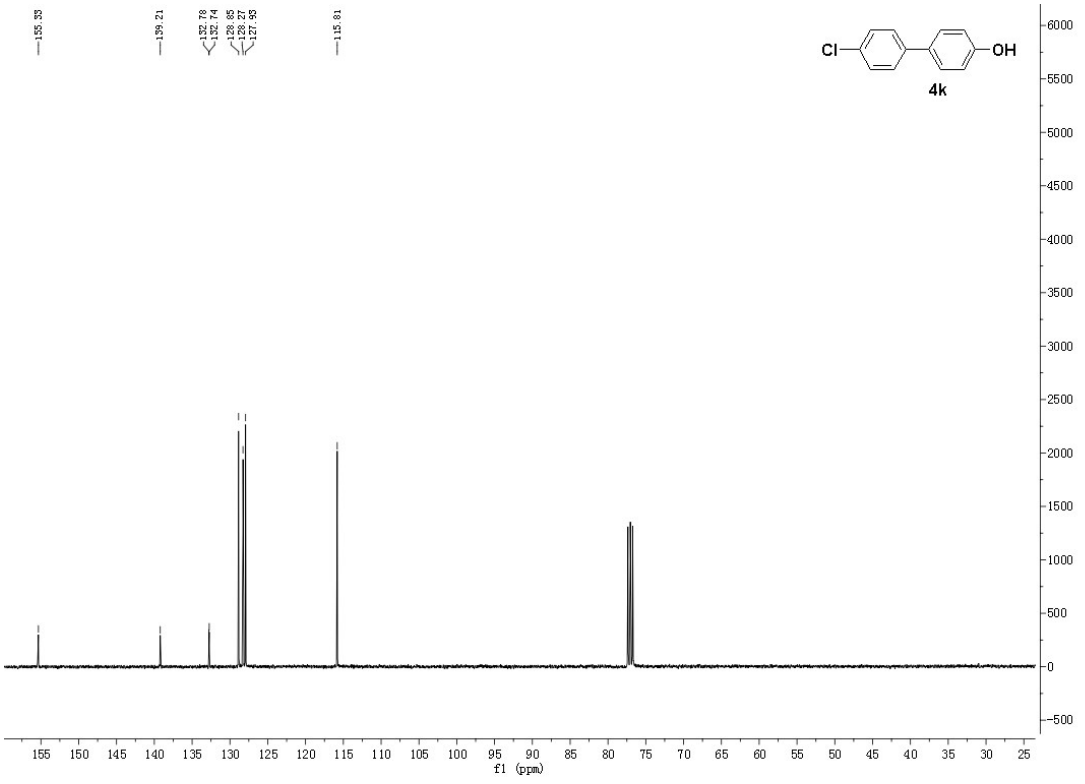
129.21
128.80
127.09
121.05
116.07
HO
Cl
3k
f1 (ppm)


7.50
7.48
7.45
7.41
7.41
7.39
6.95
6.93
5.25
Cl
OH
4k
6.00
2.00
1.00
f1 (ppm)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127.58
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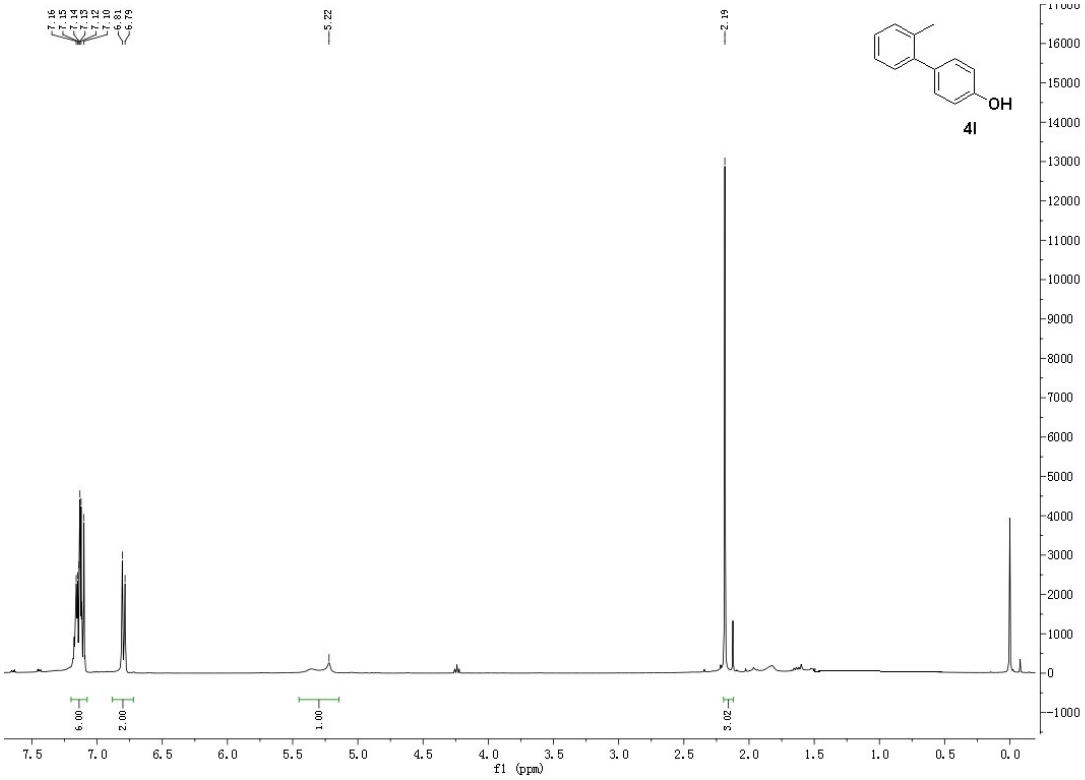
Cl
OH
4k
f1 (ppm)


7.16
7.15
7.14
7.13
7.12
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4l
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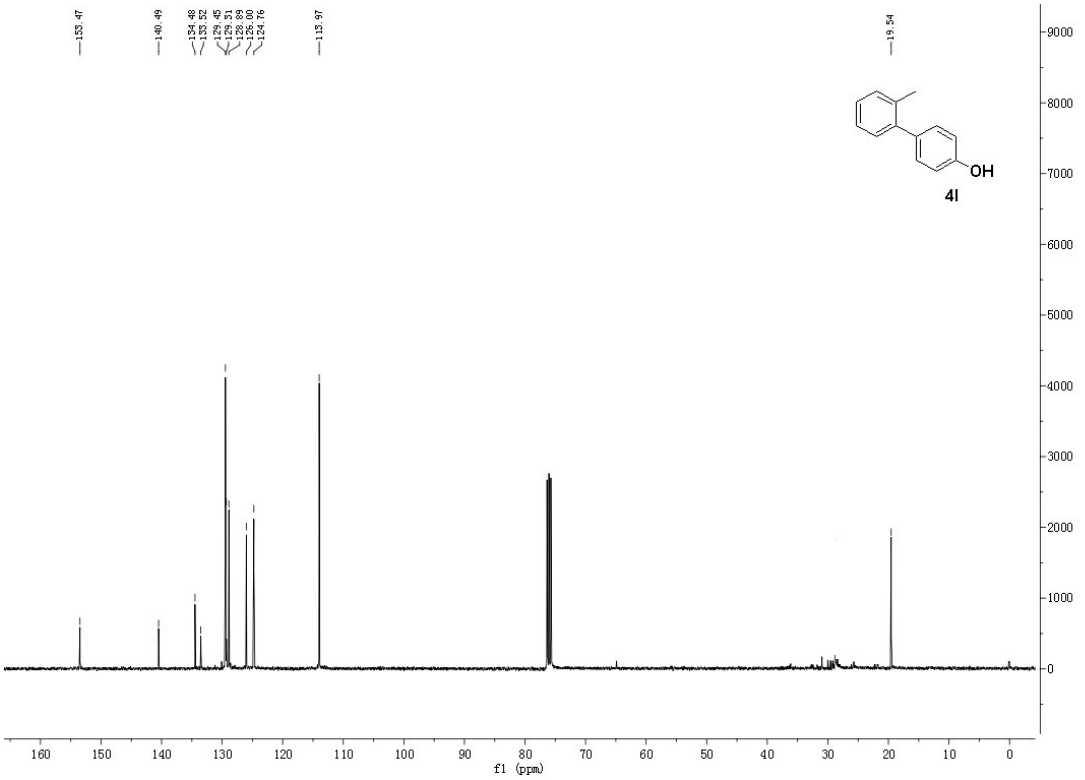
2.00
1.00
3.02
f1 (ppm)


153.47
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129.31
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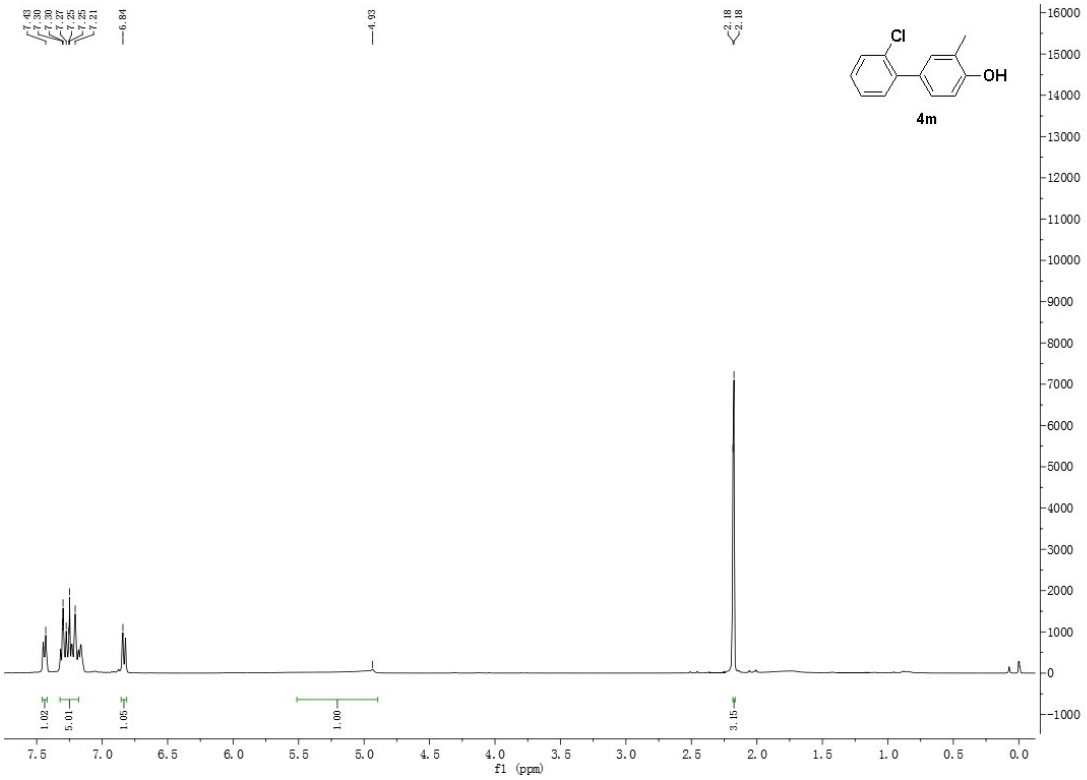
126.00
124.76
115.97
19.54
OH
4l
f1 (ppm)


7.43
7.30
7.30
7.27
7.25
7.25
7.21
6.84
4.93
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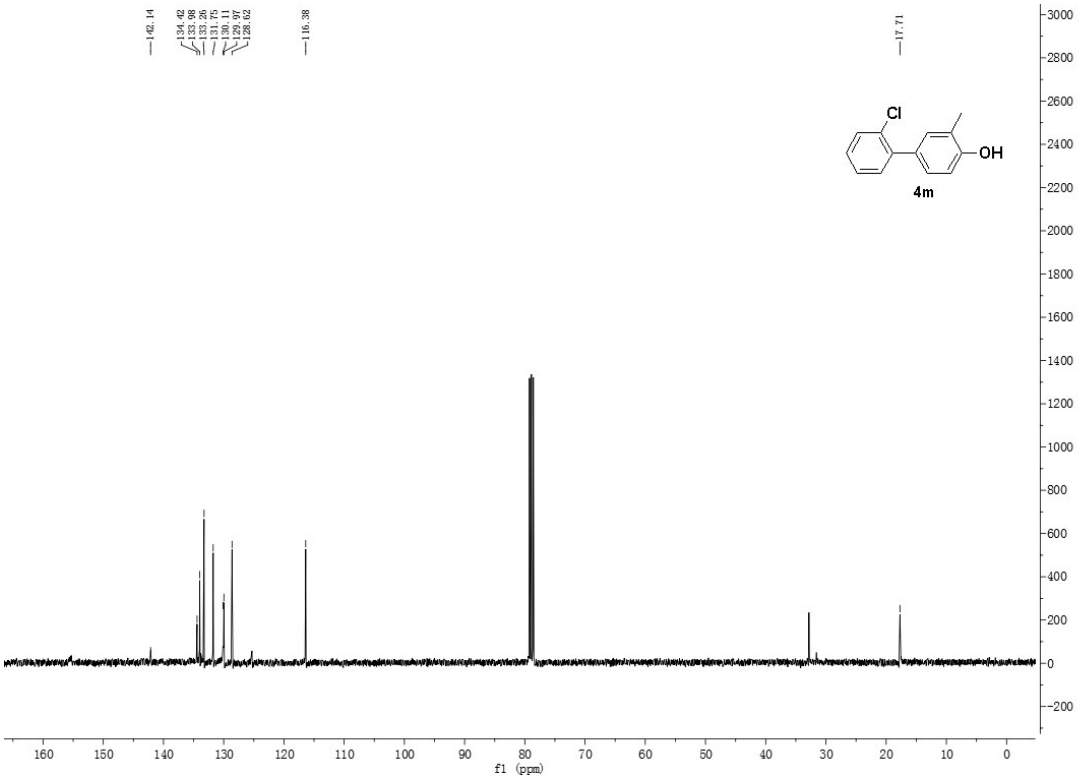
2.18
Cl
OH
4m
1.02
5.01
1.05
1.00
3.15
f1 (ppm)


142.14
134.42
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131.75
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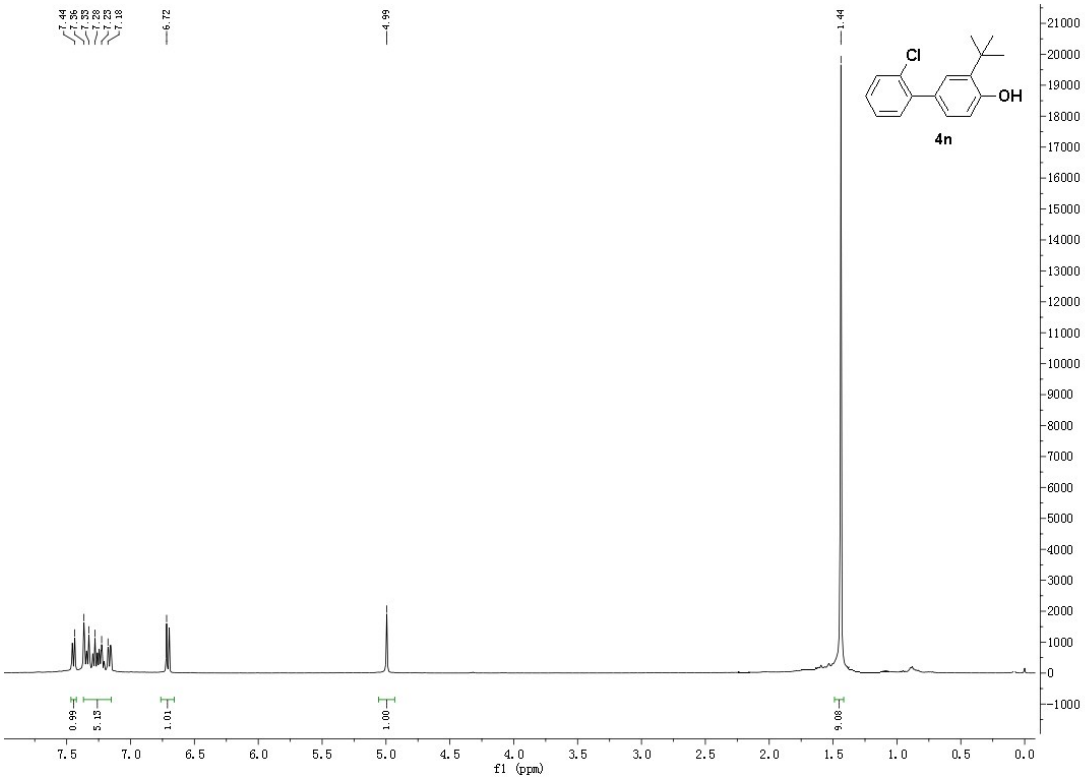
128.62
116.38
17.71
Cl
OH
4m
f1 (ppm)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7.36
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7.28
7.23
7.18
6.72
4.99
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OH
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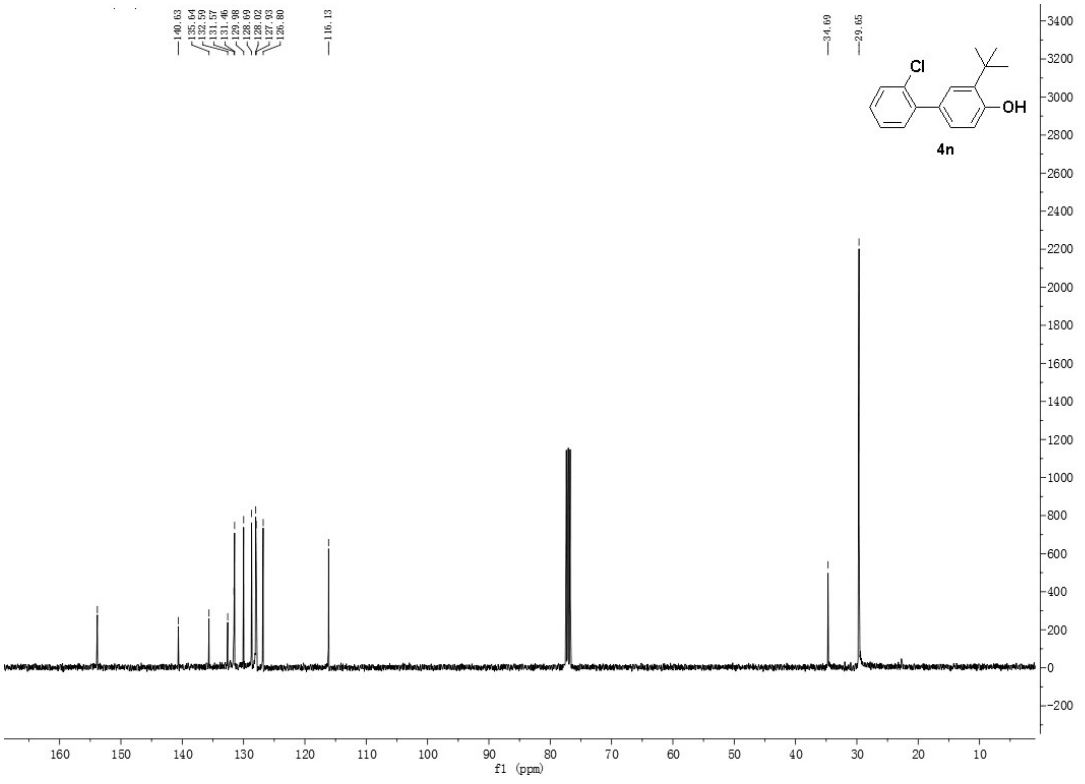
9.08
f1 (ppm)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135.64
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116.13
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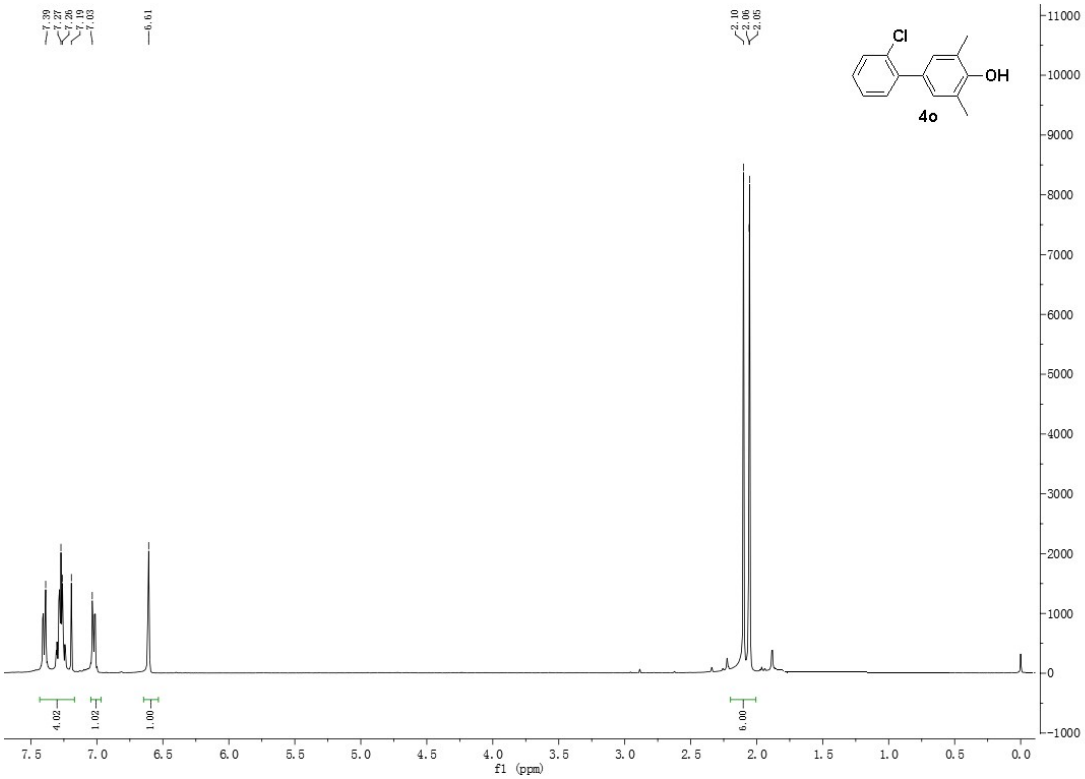
Cl
OH
4n
f1 (ppm)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7.27
7.26
7.19
7.03
6.61
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2.06
2.05
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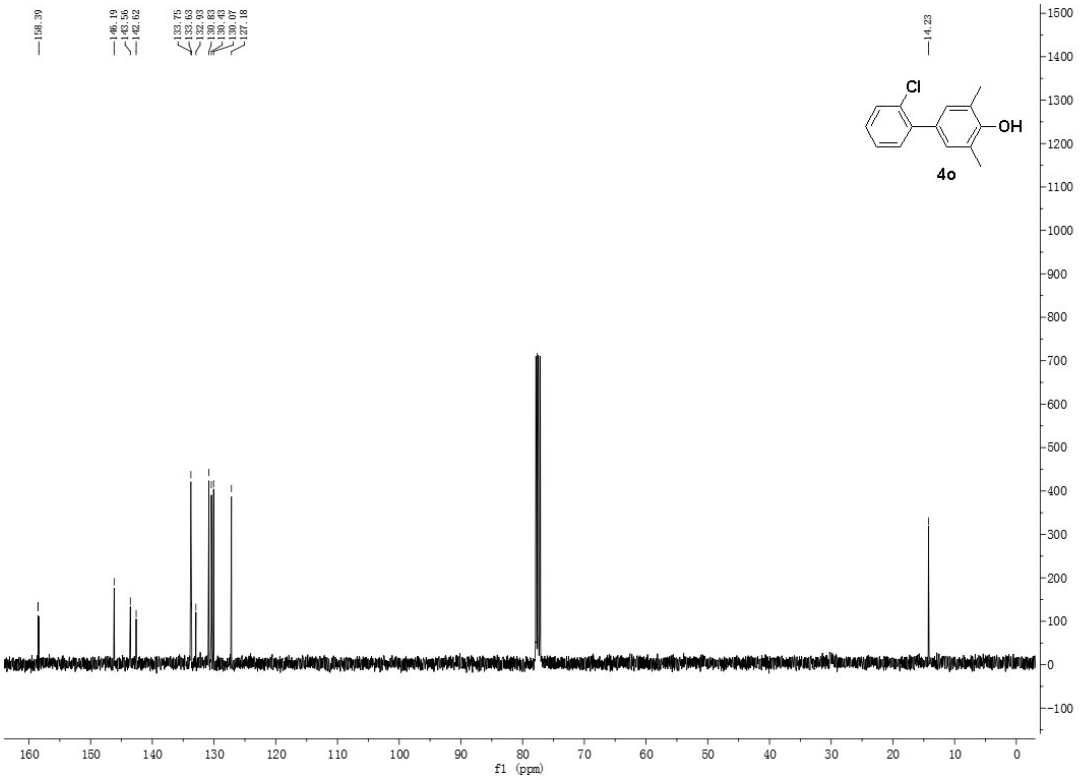
OH
4o
4.02
1.02
1.00
6.00
f1 (ppm)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146.19
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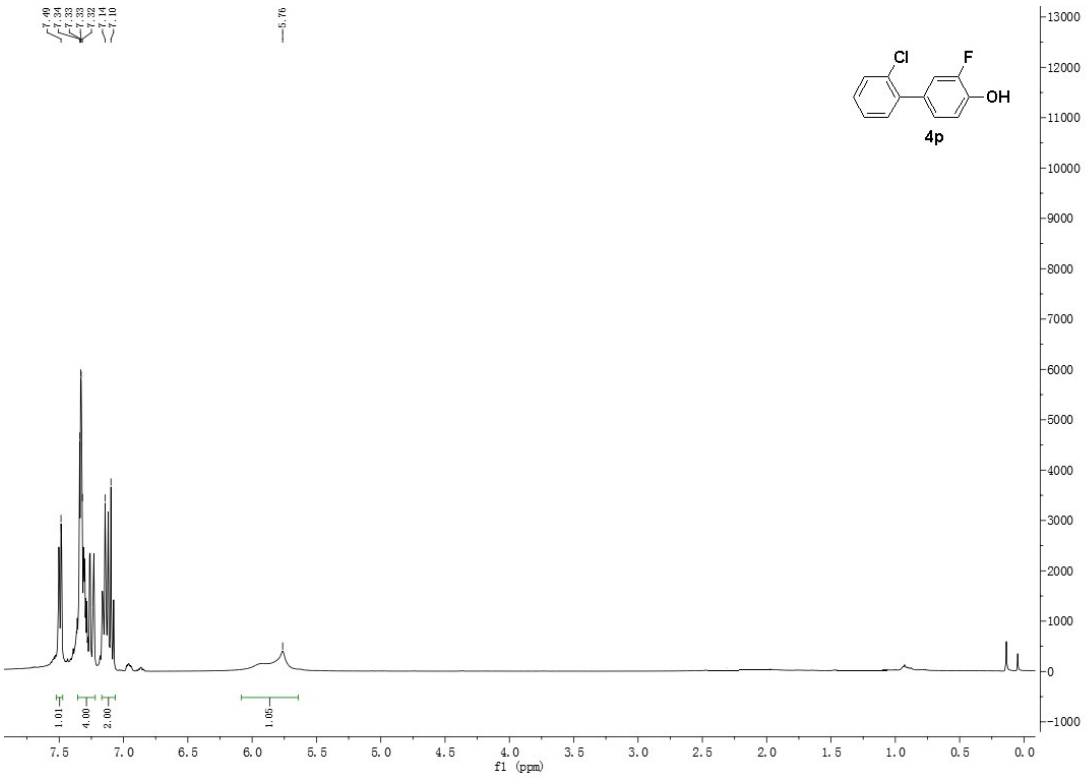
Cl
OH
4o
f1 (ppm)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7.34
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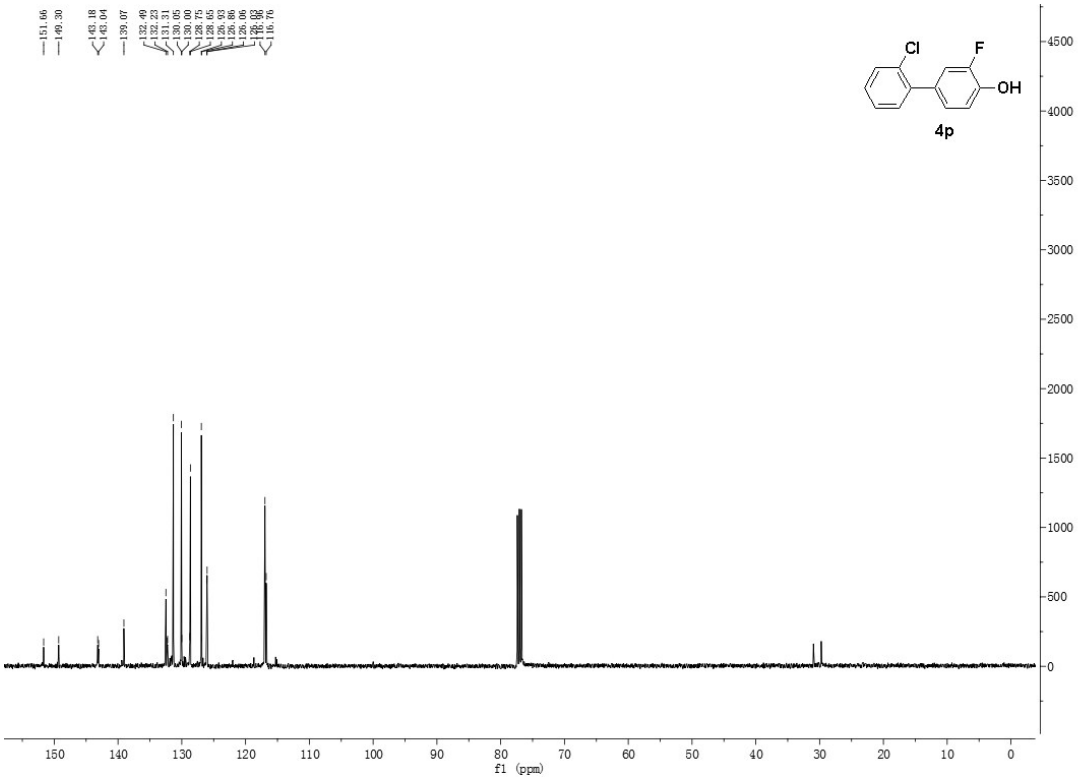
Cl
F
OH
4p
1.01
4.00
2.00
1.05
f1 (ppm)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132.49
132.23
131.31
130.05
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128.55
126.93
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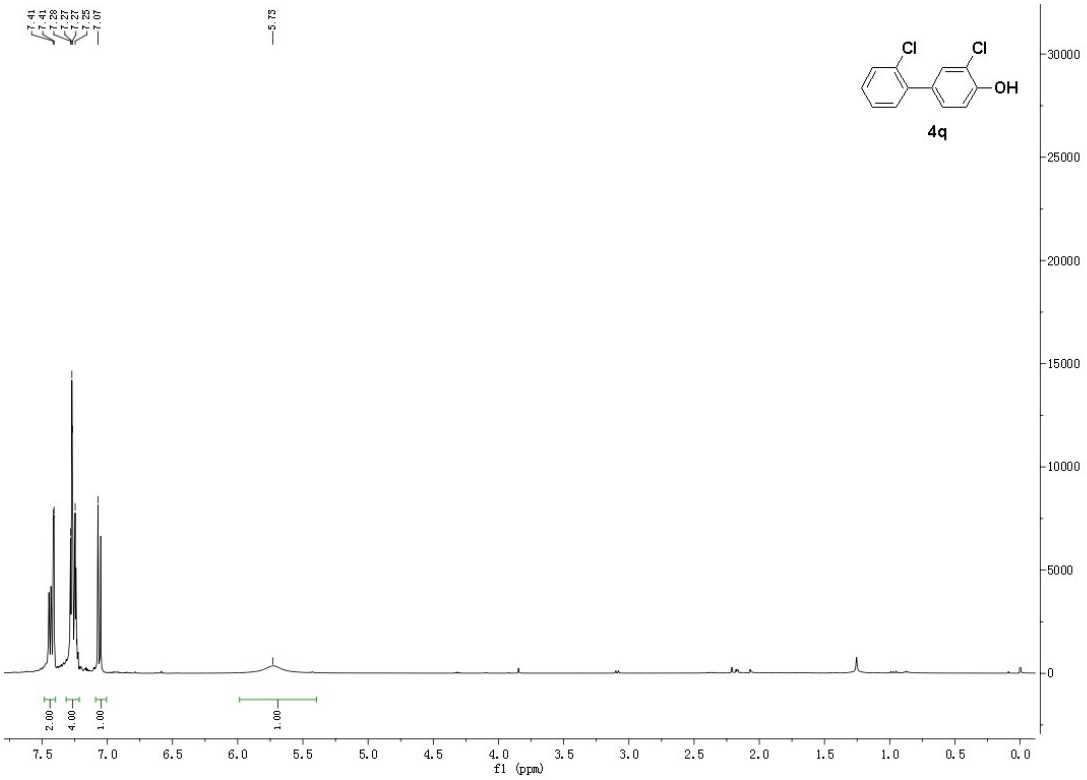
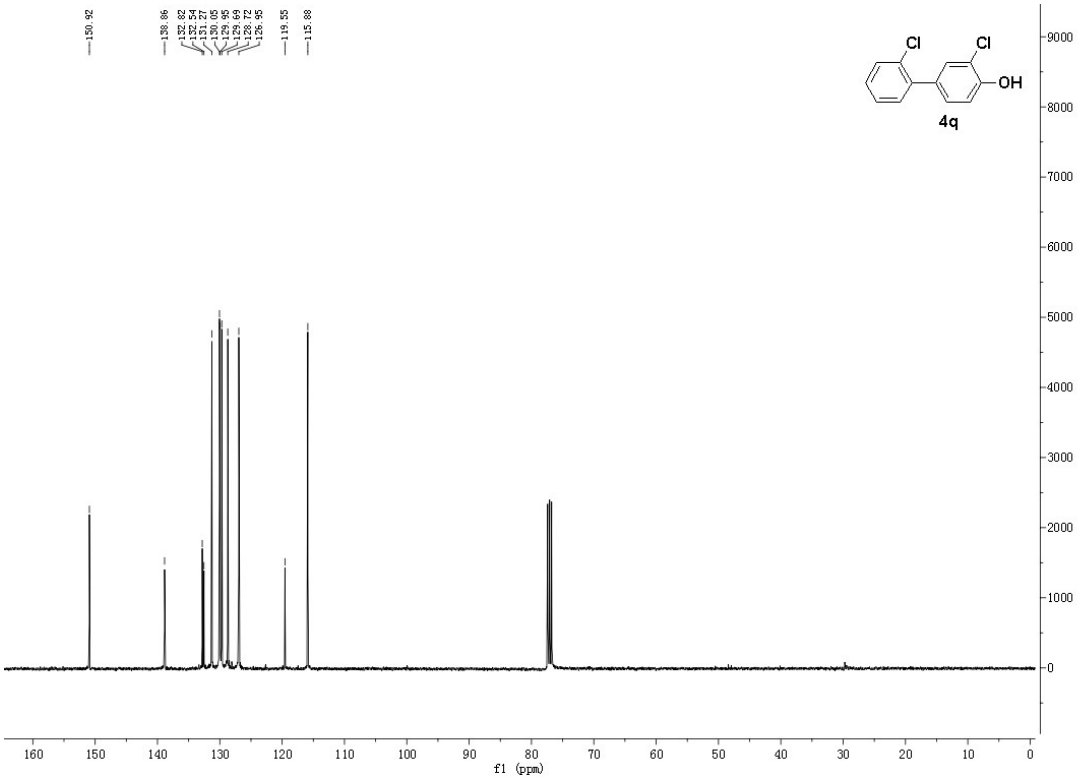
116.76
Cl
F
OH
4p
f1 (ppm)


7.41
7.41
7.28
7.27
7.27
7.25
7.07
5.73
Cl
Cl
OH
4q
2.00
4.00
1.00
1.00
f1 (ppm)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132.54
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129.95
129.69
128.72
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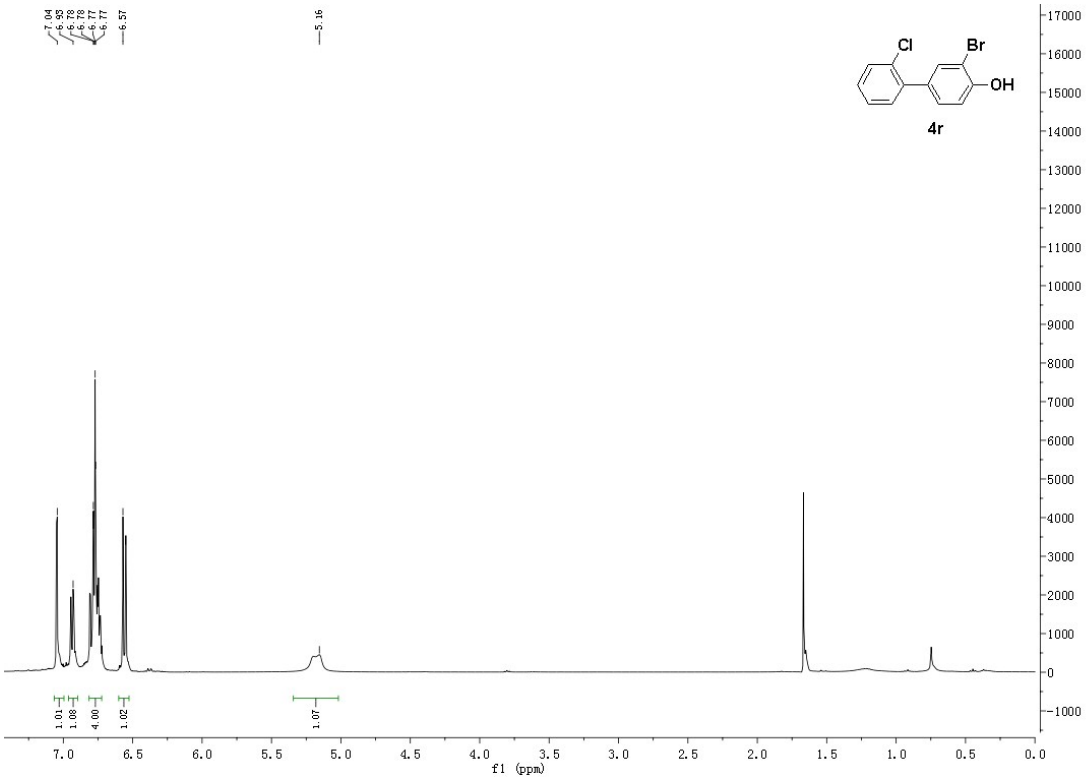
119.55
115.88
Cl
Cl
OH
4q
f1 (ppm)


7.04
6.93
6.78
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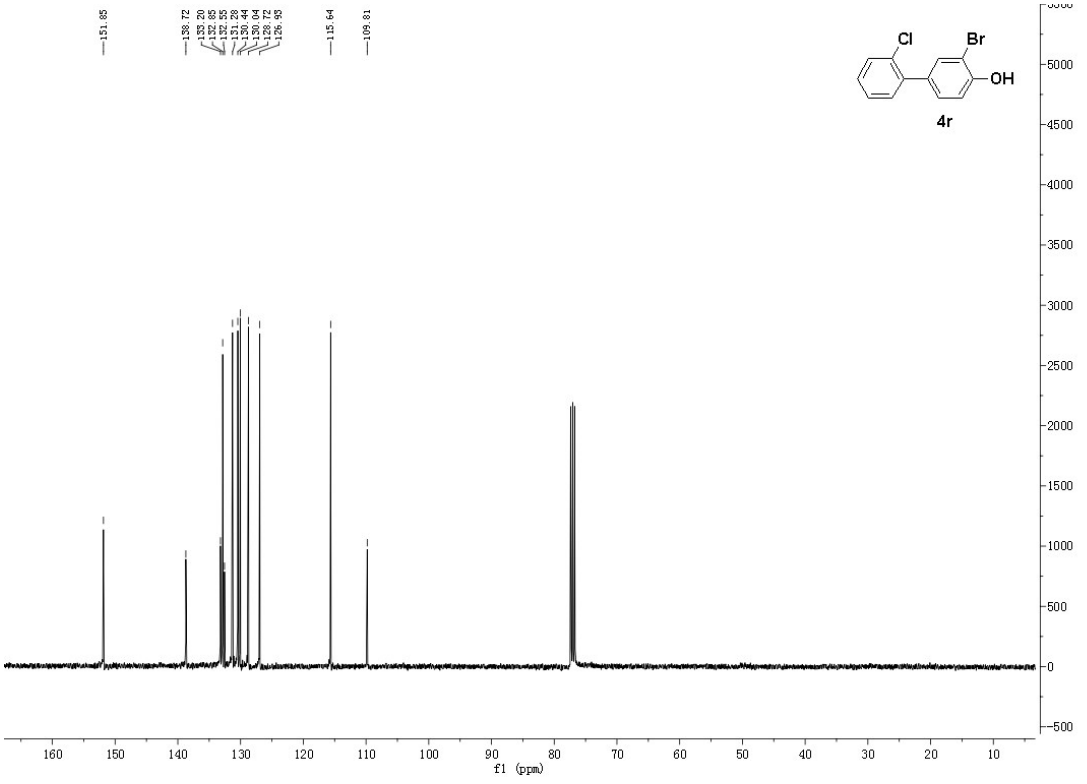
Cl
Br
OH
4r
1.01
1.08
4.00
1.02
1.07
f1 (ppm)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138.72
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130.04
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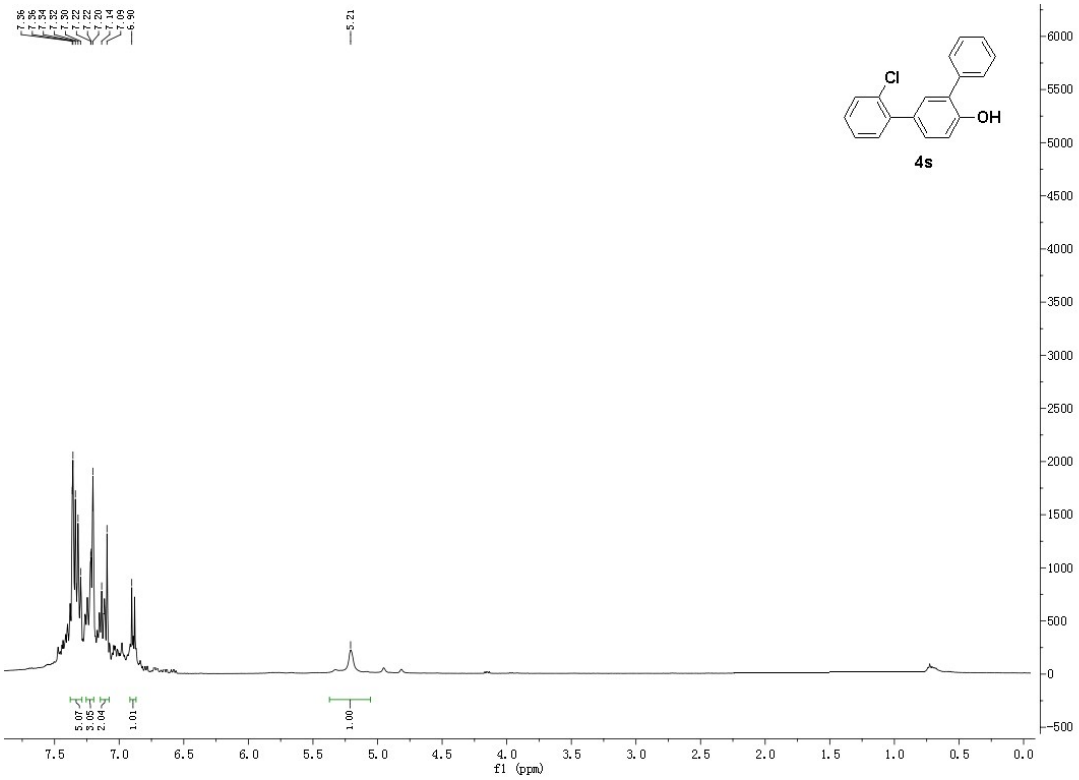
109.81
Cl
Br
OH
4r
f1 (ppm)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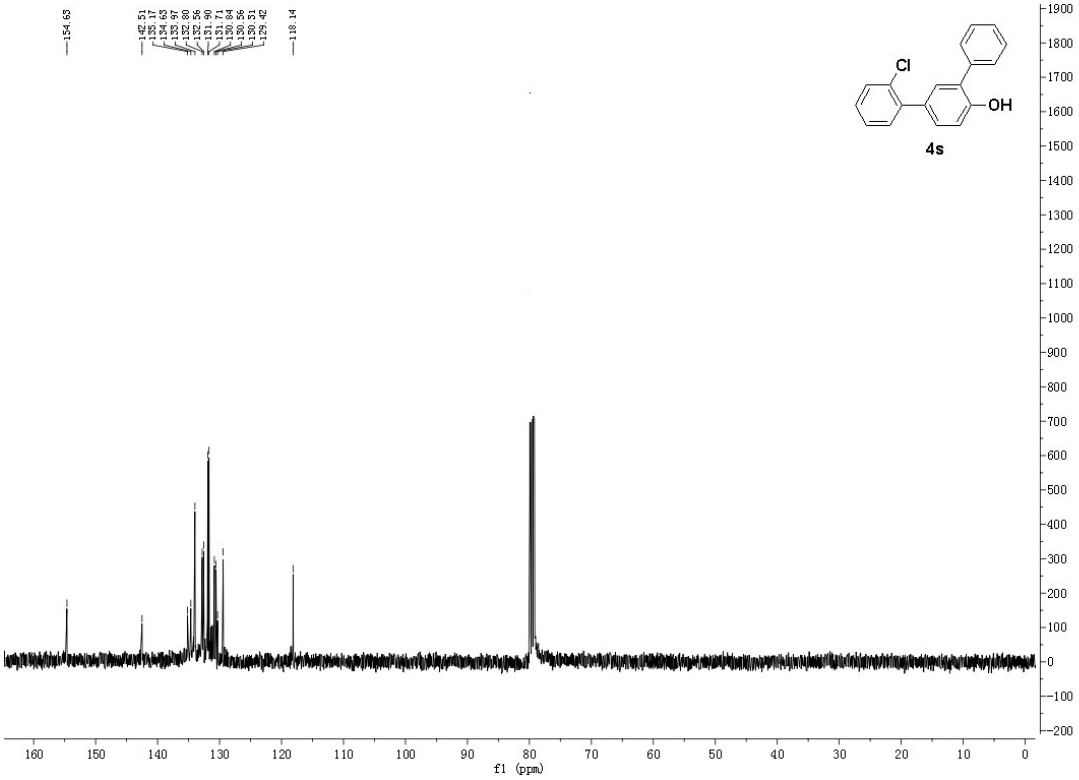
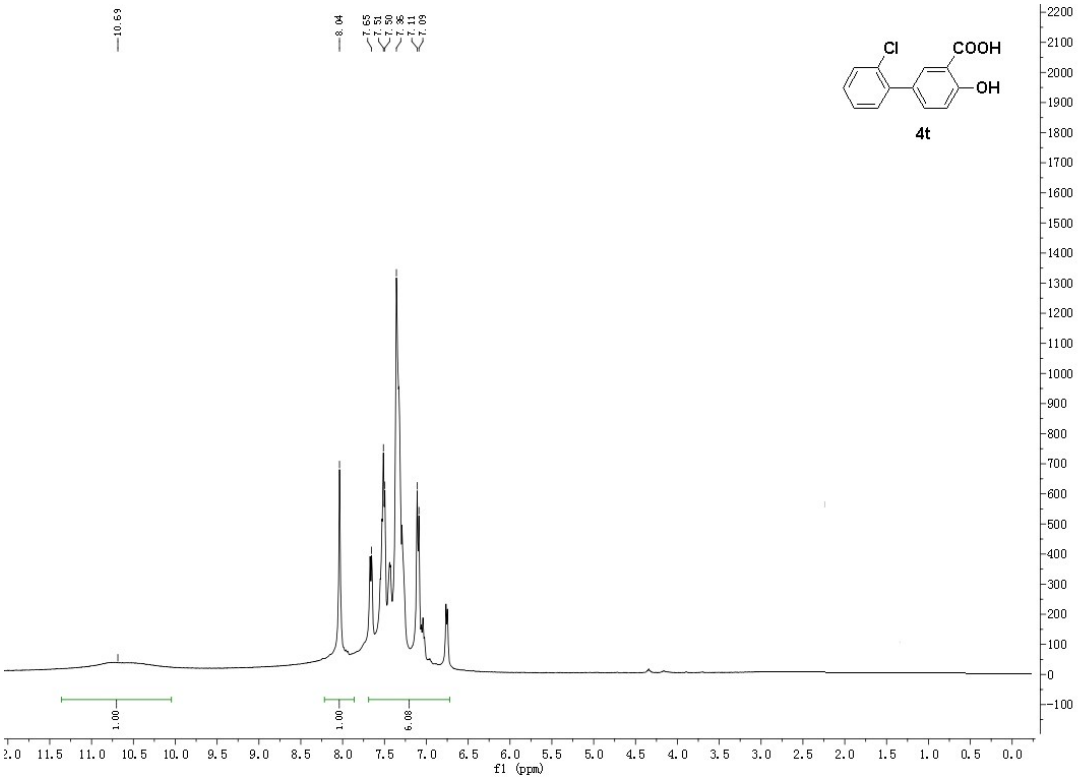
OH
4s
f1 (ppm)


Cl
OH
4s
f1 (ppm)


10.69
8.04
7.65
7.51
7.50
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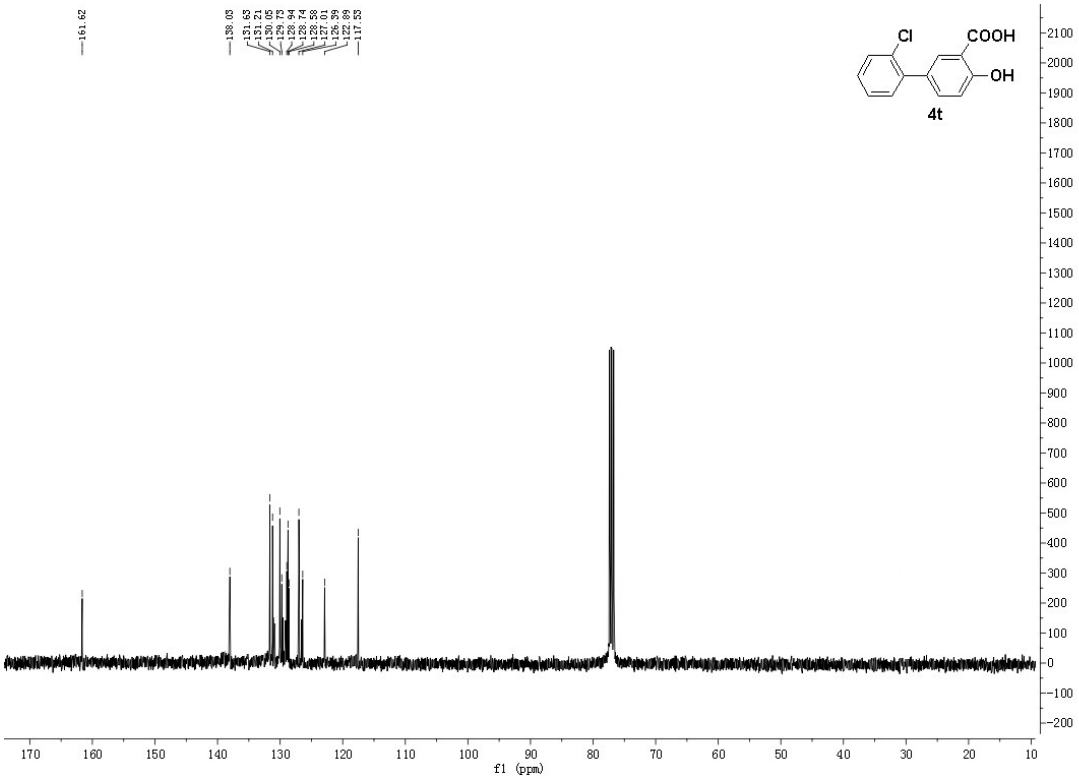
7.11
7.09
Cl
COOH
OH
4t
1.00
1.00
6.08
f1 (ppm)


161.62
138.05
131.63
131.21
130.05
129.73
128.94
128.74
128.58
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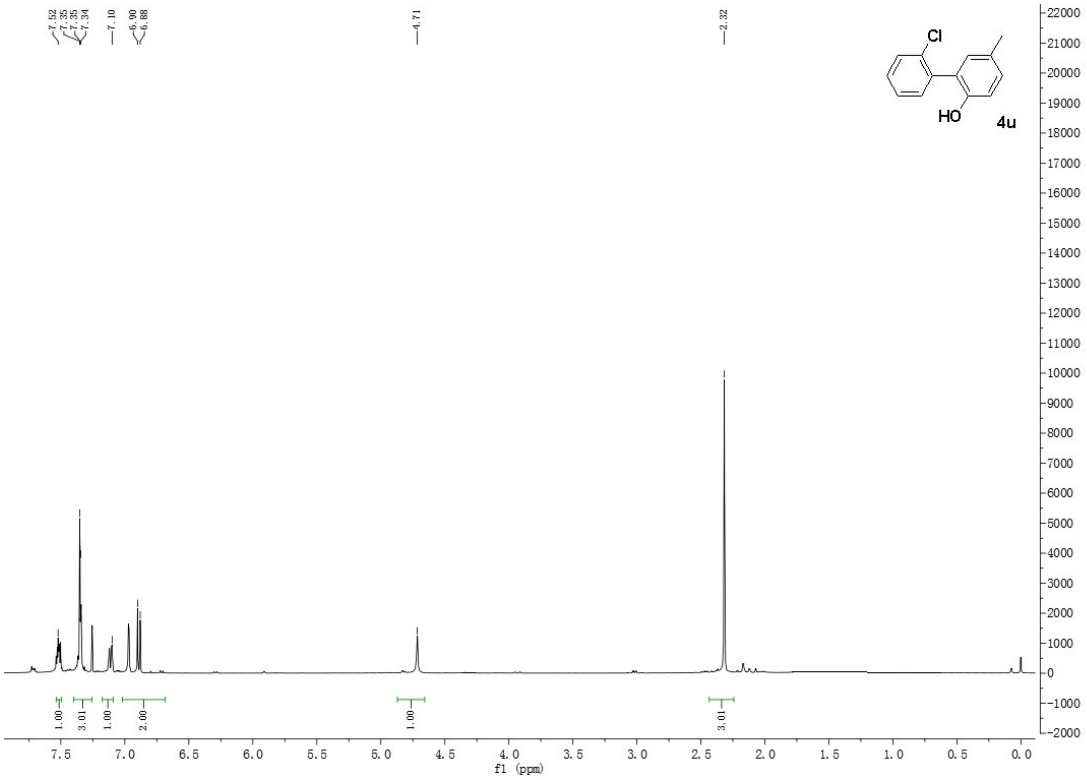
122.89
117.53
Cl
COOH
OH
4t
f1 (ppm)


7.52
7.35
7.35
7.34
7.10
6.90
6.88
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Cl
HO
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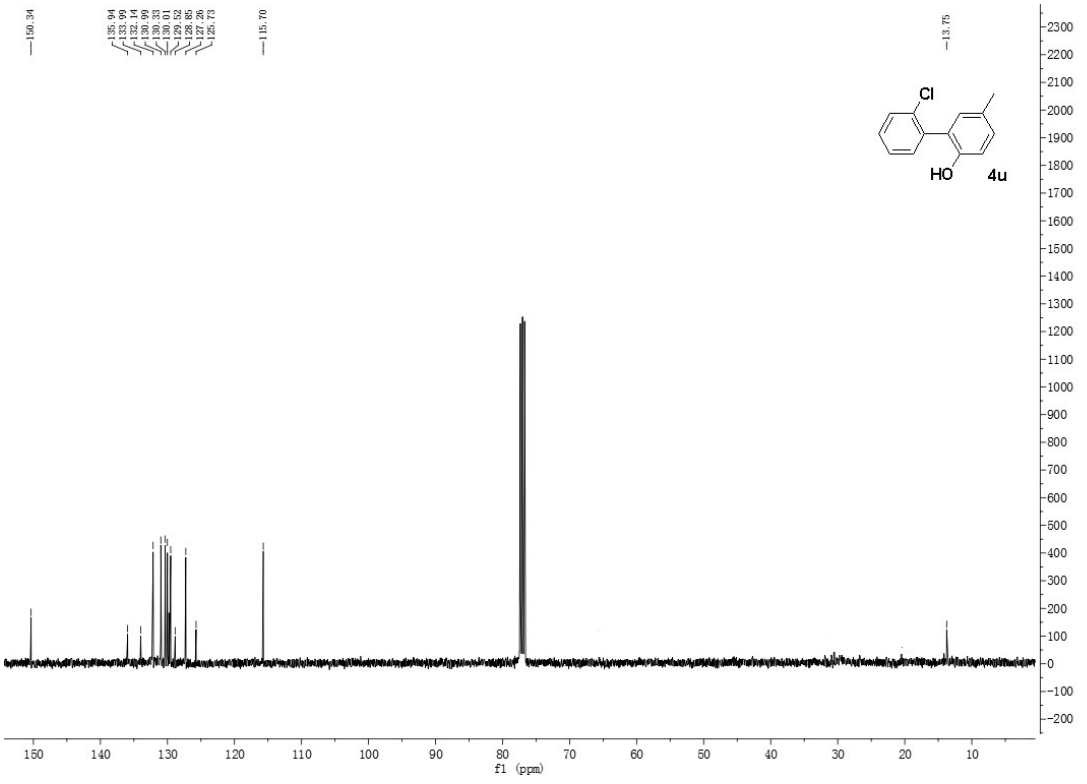
1.00
2.00
1.00
3.01
f1 (ppm)


160.34
135.94
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132.14
130.99
130.93
130.01
129.52
128.85
127.26
125.79
115.70
13.75
Cl
HO
4u
f1 (ppm)

6. References

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