

Supporting Information

Acid-Promoted Metal-Free Protodeboronation of Arylboronic Acids

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1. General Information and procedure of the protodeboronation

General Information. Arylboronic acids and other species used in the reactions were analytically pure and commercial available. The reactions were conducted under air and monitored by thin-layer chromatography (TLC) using silica gel plates. All products were obtained by column chromatography using silica gel (200-300 mesh size) except several low-boiling species (**5g**, **5h**, **5j**) which were analyzed by gas chromatography using biphenyl as internal standard. The nuclear magnetic resonance spectra were recorded on a Bruker Avance III 500 MHz instrument at 500 MHz for ¹H NMR and 125 MHz for ¹³C NMR respectively. Chemical shifts were provided in ppm from tetramethyl-silane as an internal reference and CDCl₃ as the solvent. The multiplicity were described using abbreviations: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad, *J* = coupling constant. The gas chromatography mass spectrometry (GC-MS) were recorded on a Agilent 5975 C. Mass spectrometer using a EI source. The melting points of products were obtained using a Tech X-4 apparatus. Gas chromatography (GC) were analyzed on a Agilent Technologies with a flame ionization detector and a HP-5 capillary column.

General Procedure. Arylboronic acid (arylboronic acid pinacol ester or potassium aryltrifluoroborate) (0.5 mmol) was added in a 50 mL of two-necked round-bottomed flask with AcOH (10 mL). The reaction was performed at 130 °C for 1~20 h under air. The process was monitored by TLC until the original material disappeared. Then the mixture was cooled to room temperature and washed with dichloromethane and water. The organic phase was combined, washed with saturated sodium bicarbonate (3 X 20 mL) and saturated sodium chloride (1 X 20 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated on a rotary evaporator and the residue was purified by chromatography on silica gel. The products were characterized by ¹H NMR, ¹³C NMR and GC-MS except several low-boiling species (**5g**, **5h**, **5j**) which were analyzed by gas chromatography using biphenyl as internal standard and ethyl acetate as the solvent. GC conditions: injector temperature 250 °C, detector temperature 280 °C, keeping 50 °C for 3 min and then elevating to 280 °C. The split ratio was 10:1.

2. Experimental procedure and characterization of the products

Phenol (5a).¹ Following general procedure, 4-hydroxyphenylboronic acid (0.069 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5a** (0.038 g, 81%) was obtained as a white solid after purified by chromatography eluted with *n*-hexane : diethyl ether (10:1); mp: 40-41 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.27-7.23 (m, 2H), 6.95-6.92 (m, 1H), 6.85-6.82 (m, 2H), 4.75 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 155.5, 129.7, 120.8, 115.3; GC-MS (EI) *m/z* : 94 [M]⁺.

In a similar manner, 4-hydroxyphenylboronic acid pinacol ester (0.110 g, 0.5 mmol) also gave the product **5a** (0.036 g, 77%)

Anisole (5b).² Following general procedure, 4-methoxyphenylboronic acid (0.076 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5b** (0.045 g, 84%) was obtained as a colorless oil after purified by chromatography eluated with *n*-hexane : diethyl (20:1). ¹H NMR (500 MHz, CDCl₃) δ 7.34 (t, *J* = 9.8 Hz, 2H), 7.01-6.94 (m, 3H), 3.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 129.6, 120.8, 114.0, 55.1; GC-MS (EI) *m/z*: 108 [M]⁺. In a similar manner, 3-methoxyphenylboronic acid also gave the product **5b** (0.046 g, 85%).

1,3-Dimethoxybenzene (5d).³ Following general procedure, 2,6-dimethoxyphenylboronic acid (0.091 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5d** (0.061g, 88%) was obtained as a colorless oil after purified by chromatography eluated with *n*-hexane : diethyl (5:1). ¹H NMR (500 MHz, CDCl₃) δ 7.20 (t, *J* = 8.0 Hz, 1H), 6.53 (dd, *J* = 8.0 Hz, 2.5 Hz, 2H), 6.49 (t, *J* = 2.5 Hz, 1H), 3.80 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 160.9, 129.9, 106.2, 100.5, 55.3; GC-MS (EI) *m/z*:138 [M]⁺.

Biphenyl (5e).⁴ Following general procedure 4-biphenylboronic acid (0.099 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5e** (0.064 g, 83%) was obtained as a white solid after purified by chromatography eluated with *n*-hexane; mp: 153-154 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61-7.59 (m, 4H), 7.47-7.43 (m, 4H), 7.37-7.34 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 141.3, 128.8, 127.3, 127.2; GC-MS (EI) *m/z*: 154 [M]⁺.

Anthracene (5f).⁵ Following general procedure, 9-anthraceneboronic acid (0.111 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5f** (0.082 g, 92%) was obtained as a colorless crystal after purified by chromatography eluated with *n*-hexane; mp: 218-219 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.44 (s, 2H), 8.04-8.00 (m, 4H), 7.50-7.46 (m,4H); ¹³C NMR (125 MHz, CDCl₃) δ 131.7, 128.1, 126.2, 125.3; GC-MS (EI) *m/z*: 178 [M]⁺.

Toluene (5g). 4-Methylphenylboronic acid (0.068 g, 0.5 mmol) was added to AcOH (10 mL) . Then the reaction was conducted at 110 °C under air for 2 hours. The process was monitored by TLC. Then the mixture was cooled to room temperature and washed with dichloromethane and water. The organic phase was combined, washed with saturated sodium bicarbonate for three times. The organic phase was dried over anhydrous Na₂SO₄ and then analyzed by gas chromatography using biphenyl as internal standard giving a GC yield of 78%.

Bromobenzene (5h). 4-Bromophenylboronic acid (0.100 g, 0.5 mmol) was added to AcOH (10 mL). Then the reaction was conducted at 110 °C under air for 2 hours. The process was monitored by TLC. Then the mixture was cooled to room temperature and washed with dichloromethane and water. The organic phase was combined, washed with saturated sodium bicarbonate for three times. The organic phase was dried over anhydrous Na₂SO₄ and then analyzed by gas chromatography using biphenyl as internal standard giving a GC yield of 55%.

In a similar manner, 3-bromophenylboronic acid also gave the product **5h** in a GC yield of 70%.

Chlorobenzene (5j). 4-Chlorophenylboronic acid (0.078 g, 0.5 mmol) was added to AcOH (10 mL). Then the reaction was conducted at 110 °C under air for 2 hours. The process was monitored by TLC. Then the mixture was cooled to room temperature and washed with dichloromethane and water. The organic phase was combined, washed with saturated sodium bicarbonate for three times. The organic phase was dried over anhydrous Na₂SO₄ and then analyzed by gas chromatography using biphenyl as internal standard giving a GC yield of 85%.

In a similar manner, 3-chlorophenylboronic acid also gave the product **5j** in a GC yield of 71%.

Nitrobenzene (5l).⁵ Following general procedure, 3-nitrophenylboronic acid (0.083 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5l** (0.038 g, 62%) was obtained as a light yellow oil purified by chromatography eluted with *n*-hexane : diethyl (10:1). ¹H NMR (500 MHz, CDCl₃) δ 8.24-8.21 (m, 2H), 7.70 (tt, *J* = 7.3 Hz, 1.3 Hz, 1H), 7.57-7.53 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 148.2, 134.6, 129.3, 123.5; GC-MS (EI) *m/z*: 123 [M]⁺.

In a similar manner, 4-nitrophenylboronic acid also gave the protodeboronation product **5l** (0.040 g, 65%).

Acetophenone (5m).⁵ Following general procedure, 3-acetylphenylboronic acid (0.085 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5m** (0.048 g, 80%) was obtained as a colorless oil after purified by chromatography eluted with *n*-hexane : diethyl (5:1). ¹H NMR (500 MHz, CDCl₃) δ 7.98-7.95 (m, 2H), 7.57 (tt, *J* = 7.3 Hz, 1.3 Hz, 1H), 7.49-7.44 (m, 2H), 2.61 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.1, 136.1, 132.1,

127.5, 127.3, 25.6; GC-MS (EI) m/z : 120 $[M]^+$.

In a similar manner, 4-acetylphenylboronic acid also gave the product **5m** (0.039 g, 69%).

Benzaldehyde (5n).⁶ Following general procedure, 3-formylphenylboronic acid (0.075 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5n** (0.028 g, 52%) was obtained as a colorless oil after purified by chromatography eluated with *n*-hexane : diethyl (5:1). ¹H NMR (500 MHz, CDCl₃) δ 10.0 (s, 1H), 7.87 (d, J = 9.5 Hz, 2H), 7.61 (t, J = 9.3 Hz, 1H), 7.51 (t, J = 9.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 192.4, 136.4, 134.5, 129.7, 129.0; GC-MS (EI) m/z : 106 $[M]^+$.

In a similar manner, 4-formylphenylboronic acid (0.075 g, 0.5 mmol) also gave the product **5n** (0.045 g, 84%).

Benzoic acid (5r).⁵ Following general procedure, 4-carboxylphenylboronic acid (0.083 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5r** (0.039 g, 63%) was obtained as a white solid after purified by chromatography eluated with *n*-hexane : ethyl acetate (2:1). mp: 121-123 °C; ¹H NMR (500 MHz, CDCl₃) δ 12.20 (br s, 1H), 8.16-8.13 (m, 2H), 7.65-7.61 (m, 1H), 7.51-7.47 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 172.5, 133.9, 130.2, 129.3, 128.5; GC-MS (EI) m/z : 122 $[M]^+$.

In a similar manner, 2-methoxycarbonylphenylboronic acid (0.090 g, 0.5 mmol) also gave the product **5r** (0.040 g, 66%). Potassium 4-carboxyphenyltrifluoroborate (0.114 g, 0.5 mmol) also gave the product **5r** (0.022 g, 36%)

Methyl benzoate (5s).⁵ Following general procedure, 4-methoxycarbonylphenylboronic acid (0.090 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was

conducted at 130 °C under air for 2 hours. The protodeboronation product **5s** (0.047 g, 69%) as a colorless oil after purified by chromatography eluated with *n*-hexane. ¹H NMR (500 MHz, CDCl₃) δ 8.05-8.03 (m, 2H), 7.55 (tt, *J* = 7.5 Hz, 1.3 Hz, 1H), 7.43 (tt, *J* = 7.8 Hz, 1.8 Hz, 2H) 3.91 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 131.9, 129.1, 128.5, 127.3, 51.1; GC-MS (EI) *m/z*: 136 [M]⁺.

1-(2-Thienyl)ethanone (5u).⁷ Following general procedure, 5-acetylthiophene-2-boronic acid (0.085 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **5u** (0.061 g, 96%) was obtained as a colorless oil after purified by chromatography eluated with *n*-hexane : ethyl acetate (20:1). ¹H NMR (500 MHz, CDCl₃) δ 7.68-7.69 (m, 1H), 7.61-7.62 (m, 1H), 7.10-7.12 (m, 1H), 2.55 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 190.7, 144.6, 133.8, 132.5, 128.1, 26.9; GC-MS (EI) *m/z*: 126 [M]⁺.

2-Thiophenecarboxaldehyde (3).⁸ Following general procedure, 5-formyl-2-thiopheneboronic acid (0.078 g, 0.5 mmol) was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **3** (0.047 g, 84%) as a colorless oil after purified by chromatography eluated with *n*-hexane : ethyl acetate (20:1). ¹H NMR (500 MHz, CDCl₃) δ 9.94 (s, 1H), 7.75-7.78 (m, 2H), 7.21 (t, *J* = 4.3 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 183.0, 144.0, 136.3, 135.1, 128.3; GC-MS (EI) *m/z*: 112 [M]⁺.

3. The experimental procedure of the synthesis of 4-iodoanisole (8)

(1) The synthesis of 2-iodo-5-methoxyphenylboronic acid (7)⁹

A mixture of 3-methoxyphenylboronic acid (0.076g, 0.50 mmol), AgNO₃ (0.085g, 0.50 mmol) and EtOH (4 mL) was added in a 50 mL of two-necked round-bottomed flask. A solution of iodine in EtOH (0.25 M, 2 mL) was added dropwise to the mixture. Then the reaction was stirred at room temperature until the color of iodine completely disappeared. Then the mixture was filtered through a pad of celite. Water (20 mL) was added to the filtrate and the mixture was extracted with ethyl acetate (3 X 15 mL). The organic phase was combined, washed with aqueous sodium sulfite and saturated sodium chloride. The organic phase was dried over anhydrous Na₂SO₄ and concentrated on a rotary evaporator. Then the crude product was used directly in the next step without purification.

(2) The synthesis of 4-iodoanisole (**8**)

The crude product obtained above was added to AcOH (10 mL) and the mixture was conducted at 130 °C under air for 2 hours. The protodeboronation product **8** (0.071 g, total yield 61%) was obtained as a white crystal after purified by chromatography eluated with n-hexane; mp: 52-53°C; ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H).

4. Computational details of the reaction mechanism

Geometry optimizations have been performed at the M06 level of the density functional theory. The 6-31+G(d) basis set was used for all the atoms. Frequency calculations were carried out to confirm the characteristics of all of the optimized structures as minima or transition states. Calculations of intrinsic reaction coordinates (IRC) were also performed to confirm that transition states connect two relevant minima. All calculations were performed with the Gaussian 09 software packages.

Cartesian coordinates for all of the calculated structures

A1				H	3.702935	-3.349102	0.153814
C	-2.116234	0.636893	-0.745798	H	-0.807235	2.066130	-1.663526
C	-0.945337	1.389463	-0.820026	H	0.574587	0.347309	2.027291
C	0.060741	1.303922	0.151443	O	-3.417857	-0.976832	0.528495
C	-0.174198	0.439547	1.239445	C	-4.441907	-0.917363	-0.438026
C	-1.339555	-0.300981	1.345729	H	-4.081371	-1.247867	-1.423451
C	-2.316874	-0.211216	0.346683	H	-5.224650	-1.597764	-0.093698
H	-2.861883	0.729382	-1.531769	H	-4.855142	0.098628	-0.522146
H	-1.523176	-0.961269	2.191677				
B	1.367219	2.161058	0.032831	A1TS			
O	1.286951	3.356251	-0.628813	C	-2.460271	0.681746	-0.675935
H	2.155033	3.780542	-0.677934	C	-1.153772	1.073306	-0.864485
O	2.572940	1.780112	0.537532	C	-0.064954	0.313395	-0.352263
H	2.631587	0.841964	0.798007	C	-0.365868	-0.934252	0.283556
H	0.817552	-0.698827	-0.710598	C	-1.660325	-1.339963	0.464944
O	1.200679	-1.563470	-0.978494	C	-2.716601	-0.530171	-0.004347
C	2.251028	-1.828814	-0.197774	H	-3.274800	1.298575	-1.045835
O	2.663477	-1.061308	0.651598	H	-1.912510	-2.273634	0.963004
C	2.845403	-3.167086	-0.497159	B	1.002107	1.316197	0.578379
H	2.091337	-3.949820	-0.353828	O	0.917999	2.602826	0.156641
H	3.156400	-3.208822	-1.547633	H	1.587981	3.146473	0.594626

O	1.563568	0.863786	1.691757	C	-1.105291	0.821921	0.000011
H	2.021759	-0.027079	1.534345	H	-2.263071	-1.002457	0.000034
H	0.879819	0.292694	-0.961735	H	2.298015	0.968737	-0.000006
O	2.736159	0.342974	-0.832028	H	0.305532	2.447618	-0.000012
C	3.238344	-0.680761	-0.282667	H	-1.976832	1.474306	0.000008
O	2.788451	-1.223023	0.769674	H	1.997727	-1.516790	0.000020
C	4.477898	-1.275847	-0.912243	C	-0.333983	-2.856742	0.000043
H	4.632185	-2.308353	-0.582953	O	0.562538	-3.672958	0.000039
H	4.420558	-1.222153	-2.005077	H	-1.401368	-3.185887	0.000055
H	5.348101	-0.681974	-0.602351				
H	-0.937547	2.005407	-1.383435				
H	0.471218	-1.542173	0.632856	CH₃COOB(OH)₂			
O	-3.939878	-0.999396	0.230880	C	-1.143309	0.023291	0.174715
C	-5.071631	-0.258644	-0.200748	O	-0.927984	0.253697	1.342911
H	-5.072205	-0.144733	-1.292475	O	-0.148263	-0.161855	-0.711613
H	-5.942270	-0.841290	0.105587	C	-2.492238	-0.092633	-0.458986
H	-5.100137	0.727064	0.281269	H	-2.602914	0.671787	-1.237408
				H	-2.593321	-1.068209	-0.948772
				H	-3.271531	0.030762	0.296461
B1				B	1.161995	-0.040814	-0.225265
C	-1.265317	-0.560026	0.000025	O	1.774688	-1.196599	0.140627
C	-0.145690	-1.395240	0.000028	H	2.680790	-1.127782	0.460049
C	1.140708	-0.844649	0.000017	O	1.700948	1.205944	-0.250877
C	1.299796	0.533947	0.000003	H	2.595166	1.304067	0.093239
C	0.177405	1.365956	-0.000001				

A2				C	-2.519309	-0.106437	-0.162206
C	0.428363	1.191657	-0.000001	H	-2.824273	1.777949	-1.138730
C	-0.206781	-0.055615	0.000003	H	-1.937507	-1.964015	0.789542
C	0.572411	-1.218251	-0.000010	B	1.447040	1.302431	0.742181
C	1.958331	-1.137346	-0.000025	O	1.463014	2.604429	0.399566
C	2.583362	0.110131	-0.000029	H	2.168876	3.083348	0.856362
C	1.817732	1.273451	-0.000017	O	1.940705	0.668027	1.783974
H	-0.158116	2.109564	0.000008	H	2.309427	-0.250719	1.522805
H	2.557287	-2.046783	-0.000034	H	1.256319	0.409707	-0.726427
H	3.670525	0.176002	-0.000041	O	2.983256	0.258197	-0.822533
H	2.303390	2.248135	-0.000020	C	3.388460	-0.854374	-0.364590
H	0.063510	-2.180489	-0.000006	O	2.908634	-1.416525	0.662189
C	-1.692590	-0.200822	0.000019	C	4.536183	-1.529235	-1.074025
O	-2.211170	-1.304488	0.000020	H	4.509418	-1.319220	-2.148259
C	-2.540741	1.044977	0.000032	H	5.477824	-1.124024	-0.680403
H	-2.336448	1.663065	0.884618	H	4.529618	-2.607786	-0.887628
H	-2.336463	1.663073	-0.884552	H	-0.370070	2.298835	-1.245603
H	-3.594853	0.754241	0.000039	H	0.496669	-1.456273	0.682516
A2TS				C	-4.003935	-0.361147	-0.117059
C	-2.080243	1.089666	-0.743026	O	-4.771224	0.465371	-0.570963
C	-0.726857	1.369618	-0.806151	C	-4.497033	-1.642259	0.494173
C	0.210919	0.465706	-0.258472	H	-4.084470	-2.516394	-0.027326
C	-0.241610	-0.751793	0.296964	H	-4.194622	-1.718916	1.547423
C	-1.596489	-1.028595	0.350301	H	-5.588007	-1.667547	0.431499

				H	3.670525	0.176002	-0.000041
B2				H	2.303390	2.248135	-0.000020
C	0.428363	1.191657	-0.000001	H	0.063510	-2.180489	-0.000006
C	-0.206781	-0.055615	0.000003	C	-1.692590	-0.200822	0.000019
C	0.572411	-1.218251	-0.000010	O	-2.211170	-1.304488	0.000020
C	1.958331	-1.137346	-0.000025	C	-2.540741	1.044977	0.000032
C	2.583362	0.110131	-0.000029	H	-2.336448	1.663065	0.884618
C	1.817732	1.273451	-0.000017	H	-2.336463	1.663073	-0.884552
H	-0.158116	2.109564	0.000008	H	-3.594853	0.754241	0.000039
H	2.557287	-2.046783	-0.000034				

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5. Gas chromatography of the products 5g, 5h and 5j

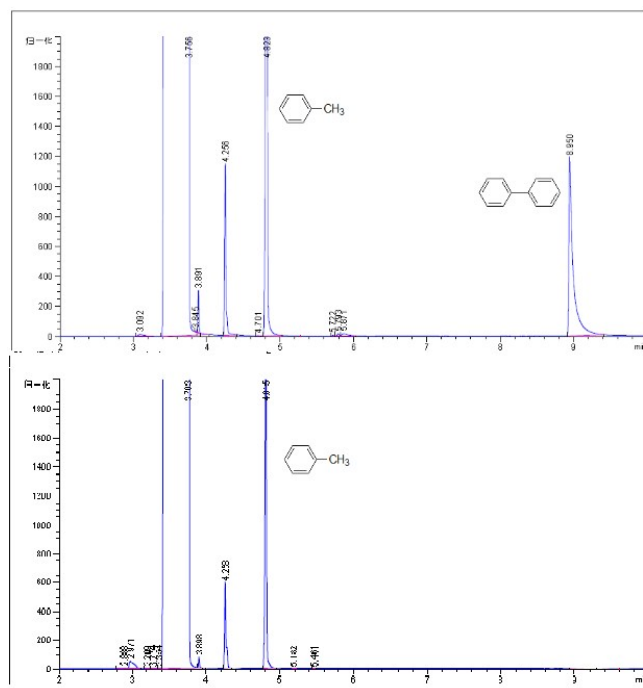


Figure above: the product Toluene (**5g**);

Figure below: the standard substance Toluene

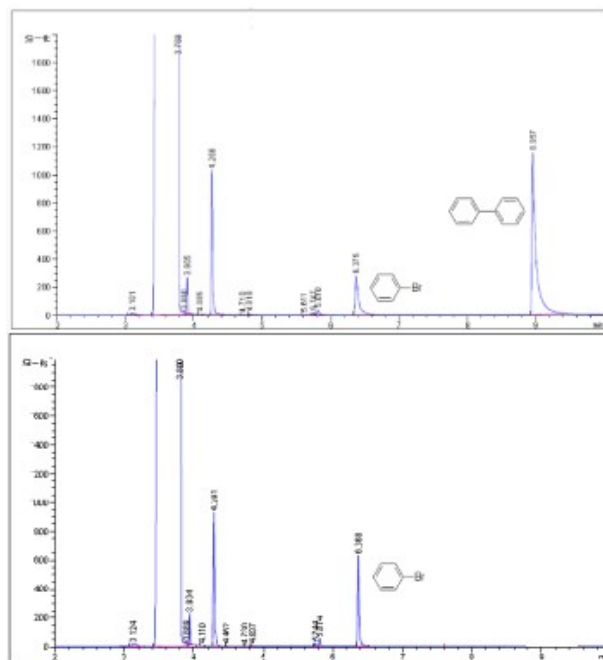


Figure above: the product Bromobenzene (**5h**) from 4-Bromophenylboronic acid;

Figure below: the standard substance Bromobenzene

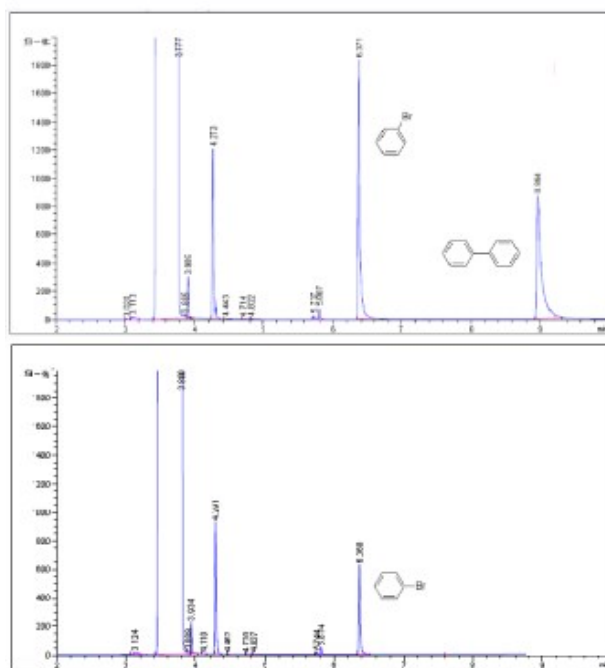


Figure above: the product Bromobenzene (**5h**) from 3-Bromophenylboronic acid

Figure below: the standard substance Bromobenzene

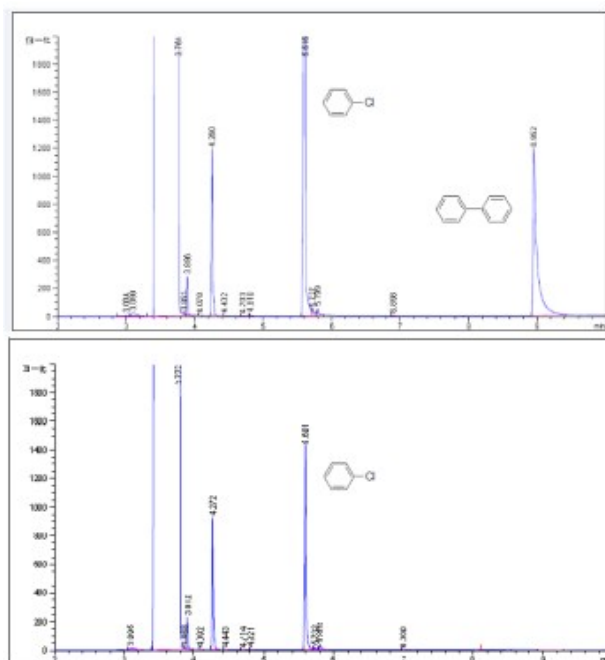


Figure above: the product Chlorobenzene (**5j**) from 4-Chlorophenylboronic acid

Figure below: the standard substance Chlorobenzene

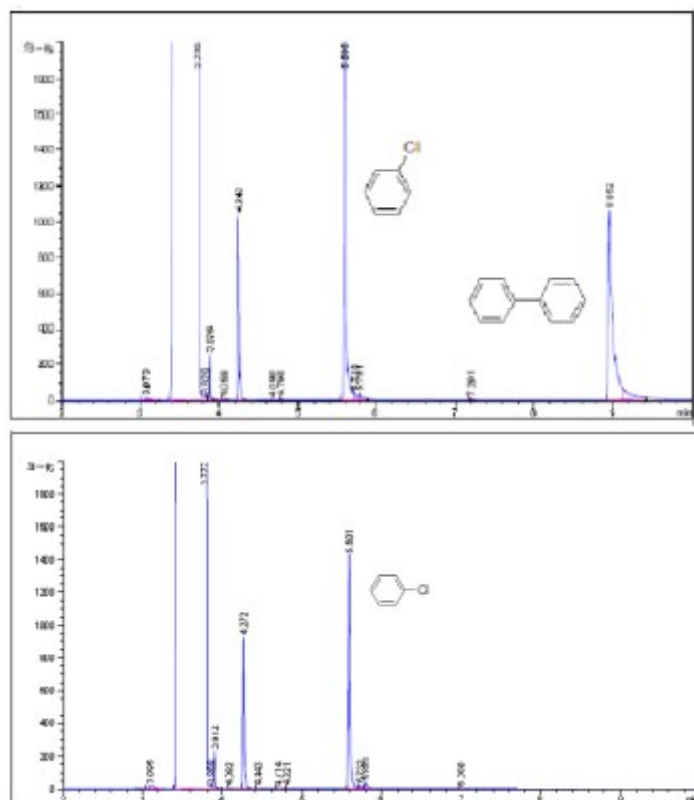
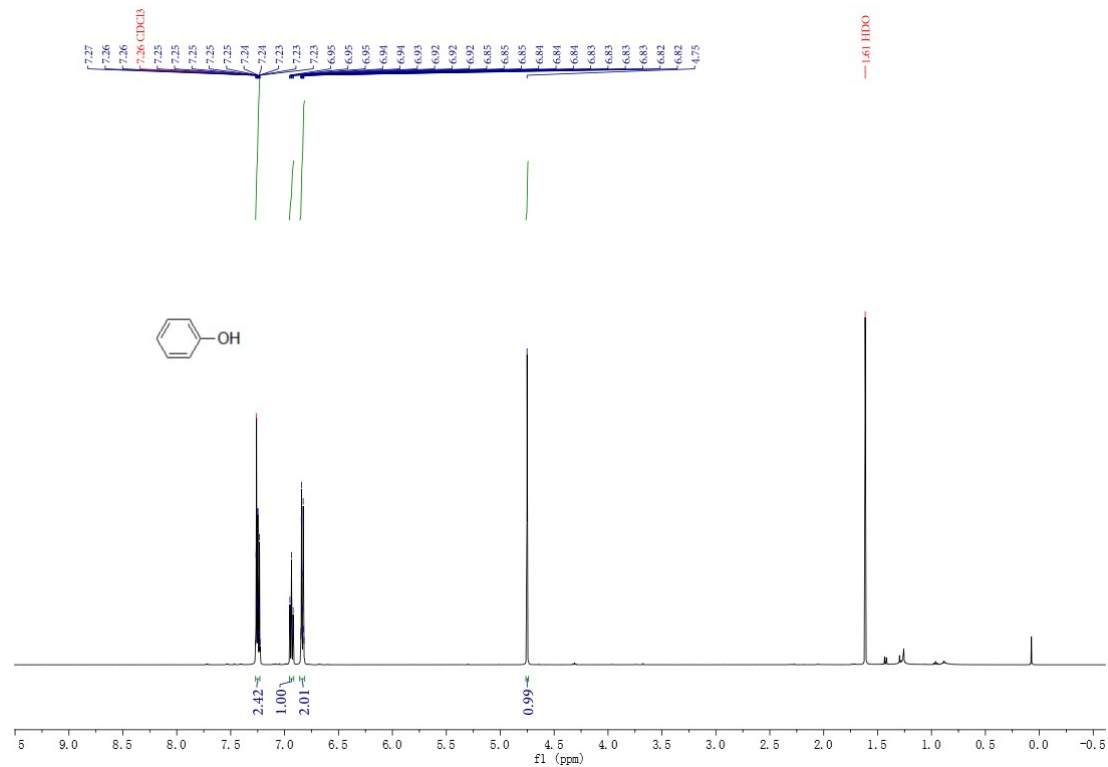


Figure above: the product Chlorobenzene (**5j**) from 3-Chlorophenylboronic acid

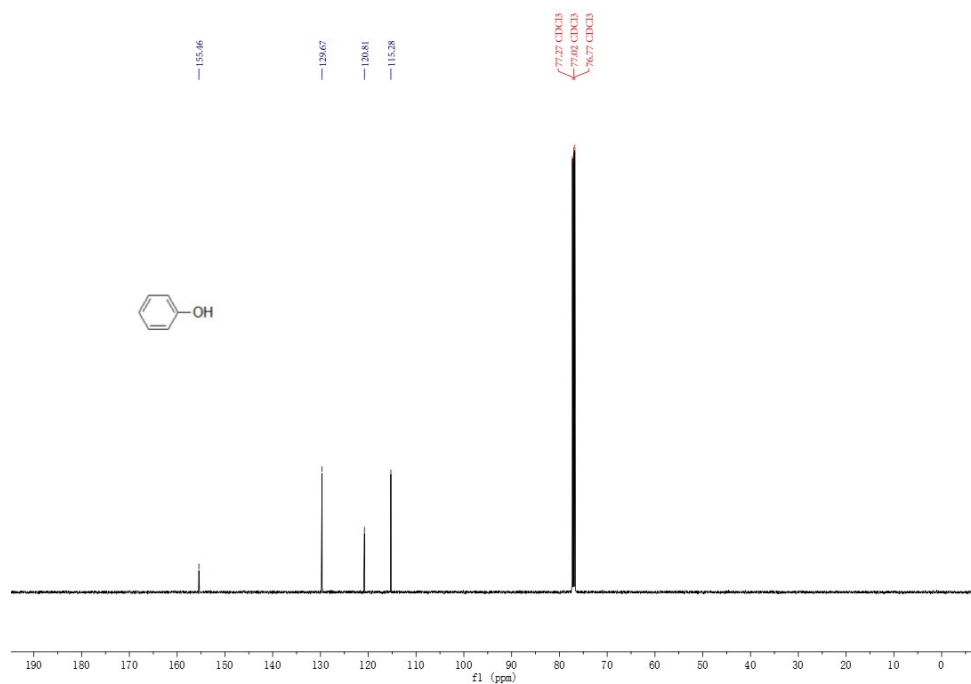
Figure below: the standard substance Chlorobenzene

6. ^1H NMR and ^{13}C NMR spectra of all products

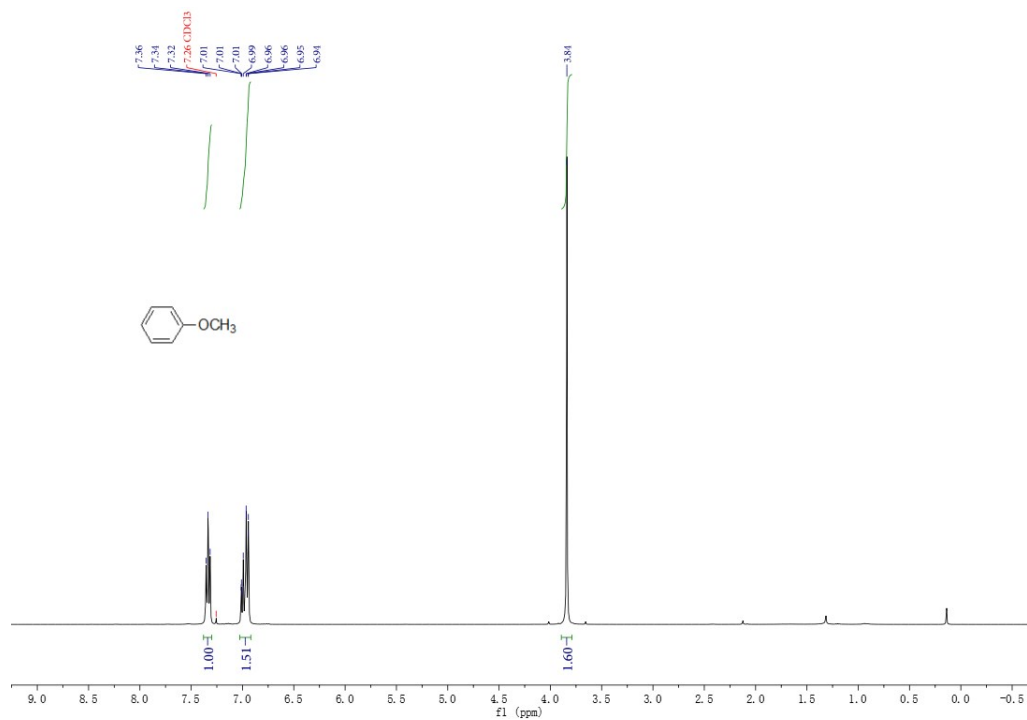
^1H NMR of Phenol (**5a**) in CDCl_3 (δ in ppm)



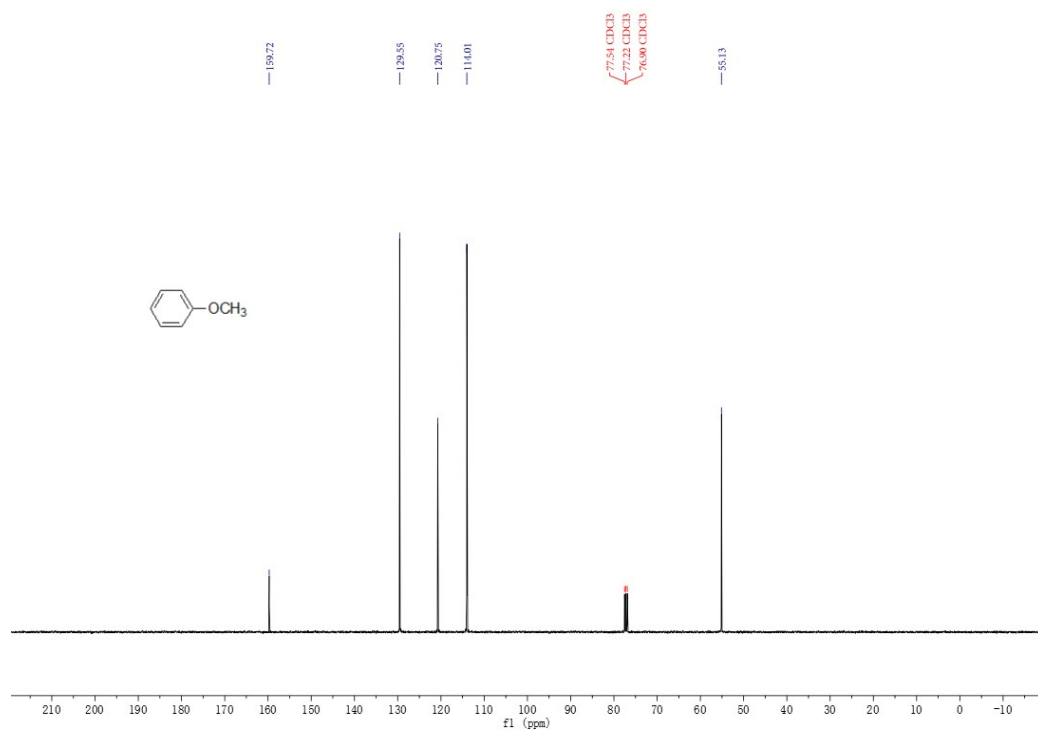
^{13}C NMR of Phenol (**5a**) in CDCl_3 (δ in ppm)



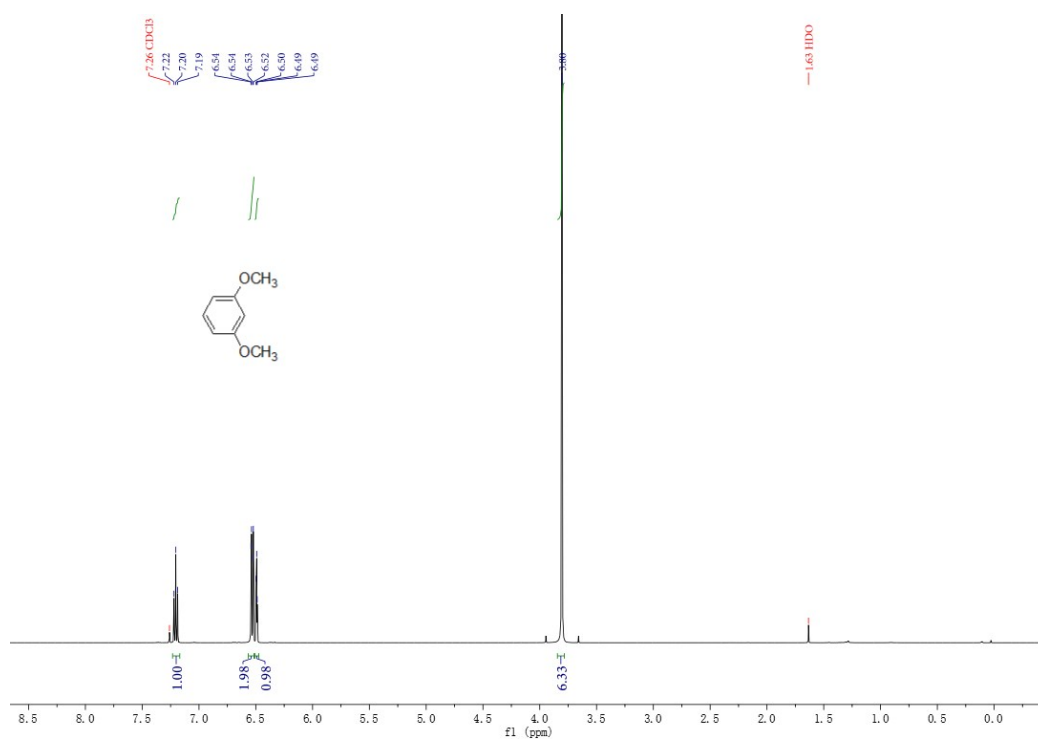
^1H NMR of Anisole (**5b**) in CDCl_3 (δ in ppm)



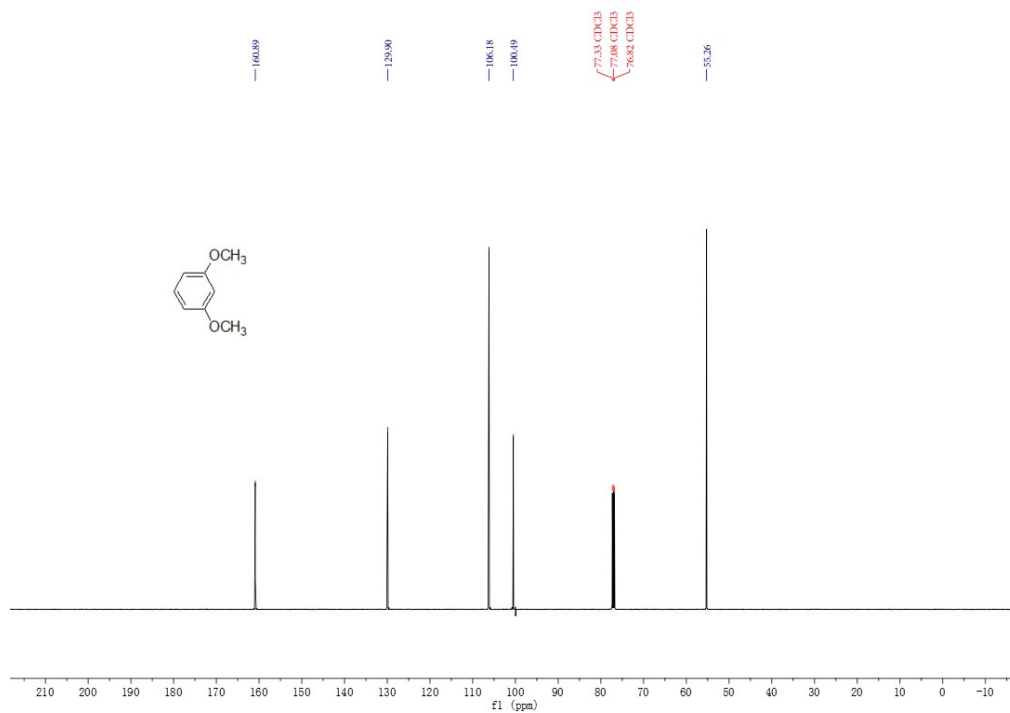
^{13}C NMR of anisole (**5b**) in CDCl_3 (δ in ppm)



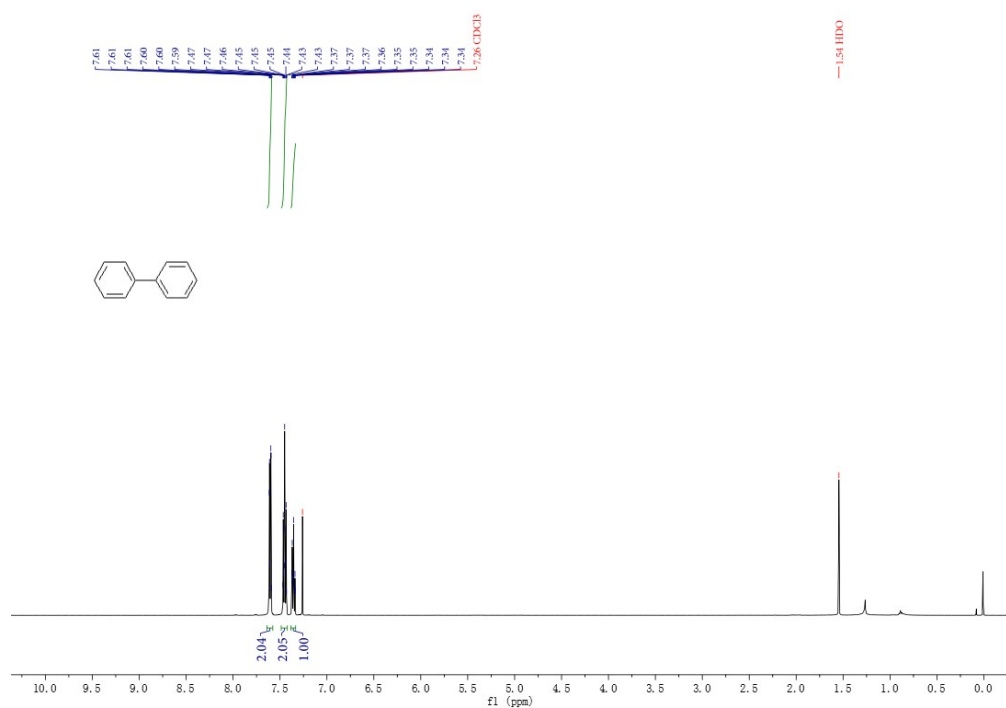
^1H NMR of 1,3-dimethoxybenzene (**5d**) in CDCl_3 (δ in ppm)



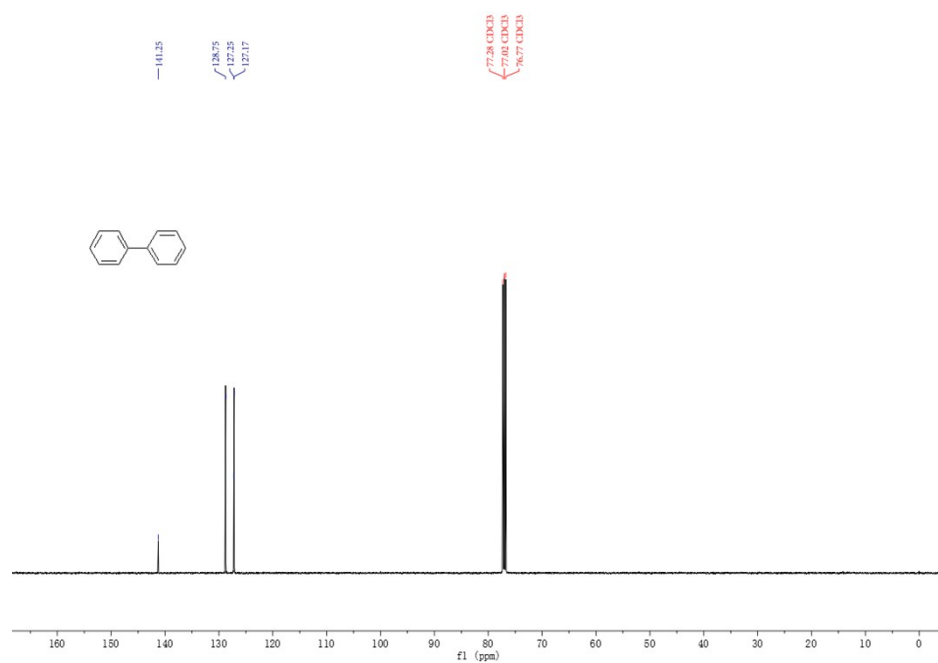
^{13}C NMR of 1,3-dimethoxybenzene (**5d**) in CDCl_3 (δ in ppm)



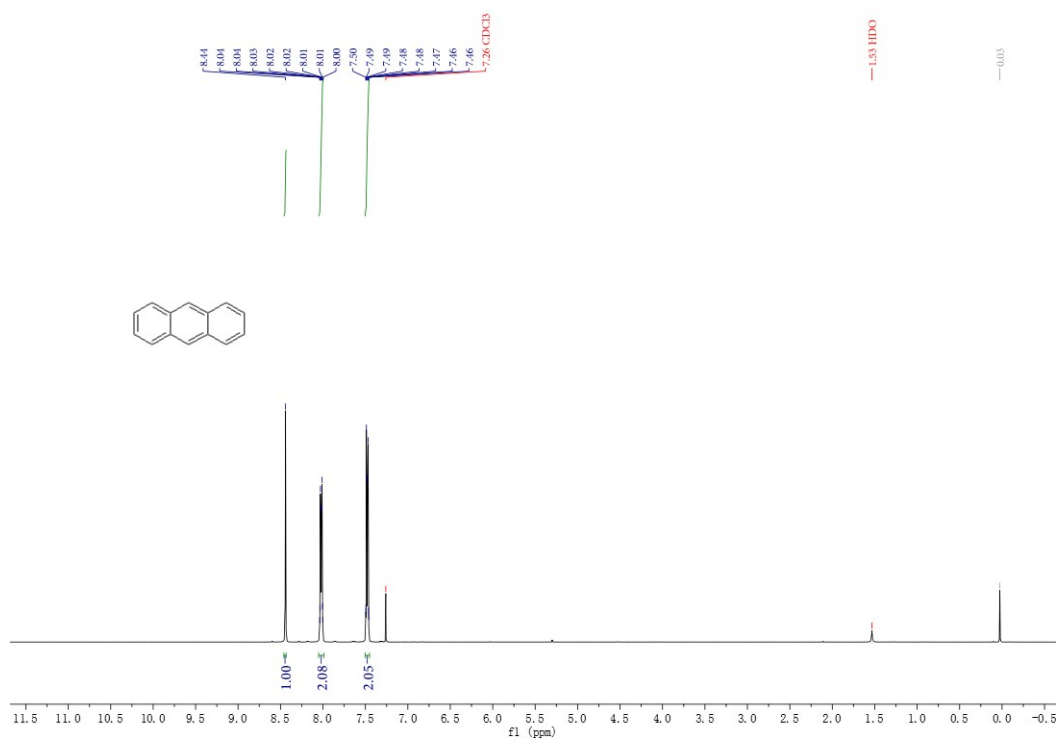
^1H NMR of biphenyl (**5e**) in CDCl_3 (δ in ppm)



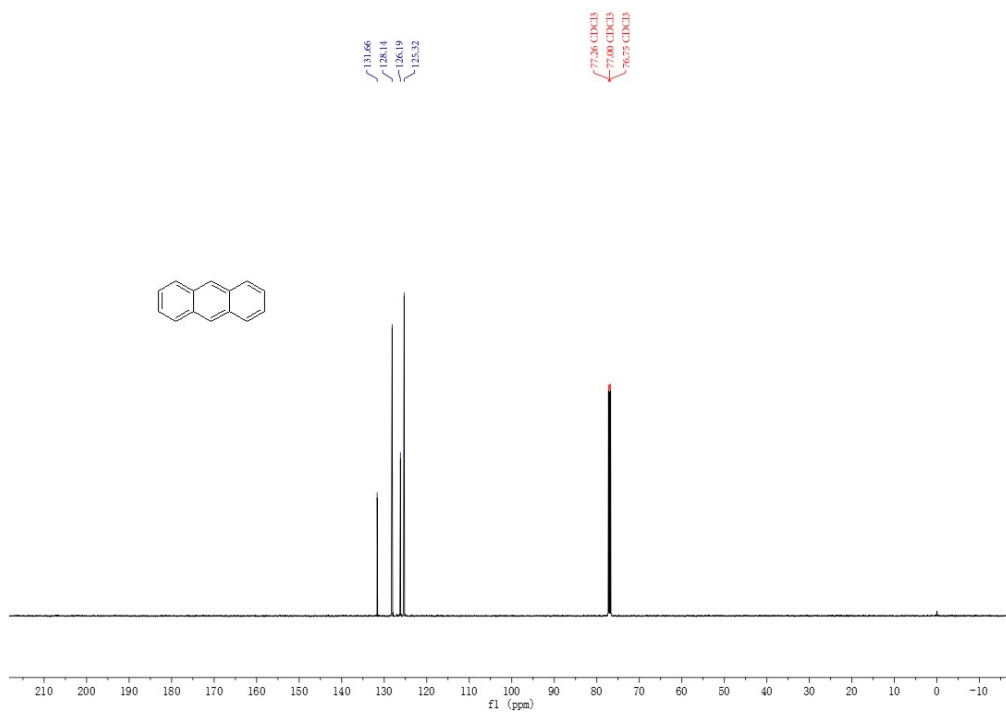
^{13}C NMR of biphenyl (**5e**) in CDCl_3 (δ in ppm)



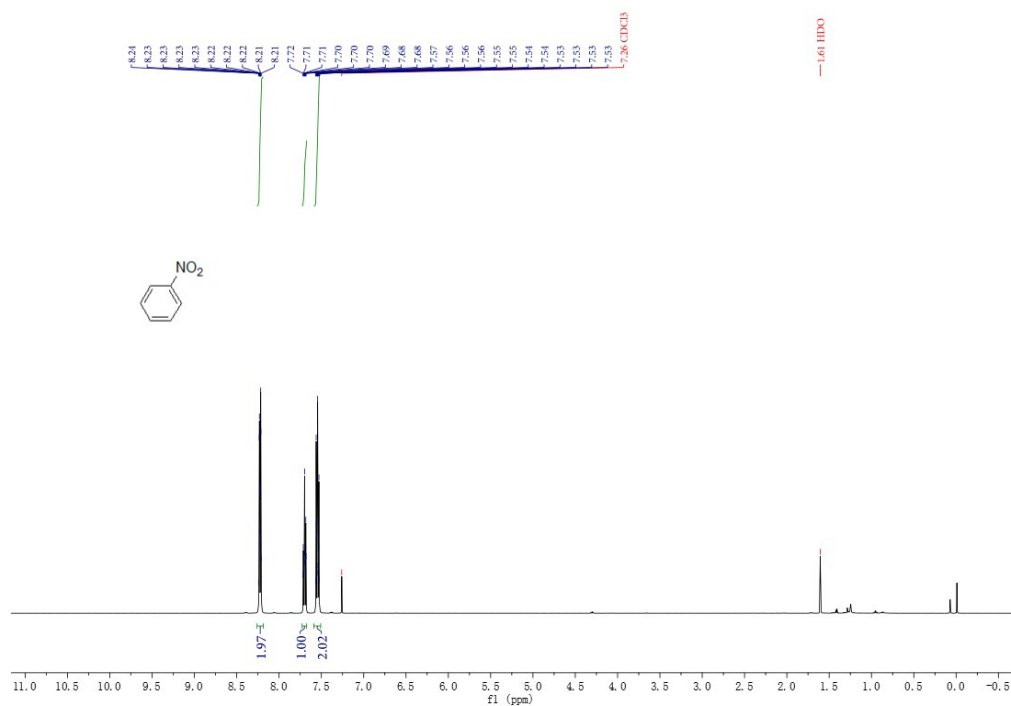
^1H NMR of anthracene (**5f**) in CDCl_3 (δ in ppm)



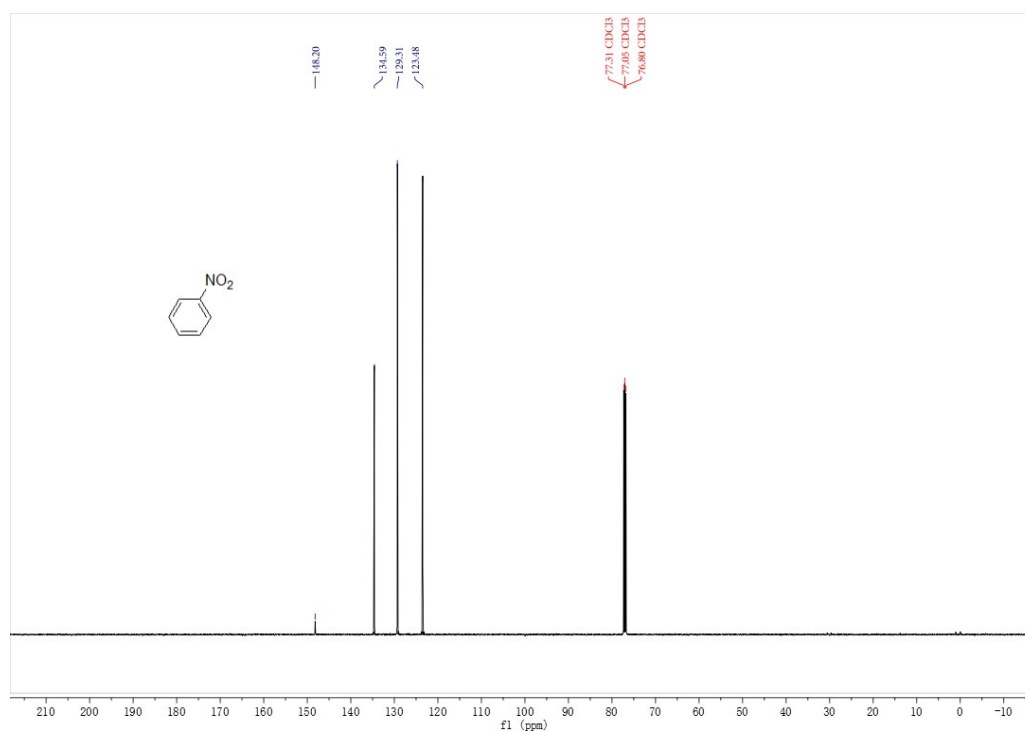
^{13}C NMR of anthracene (**5f**) in CDCl_3 (δ in ppm)



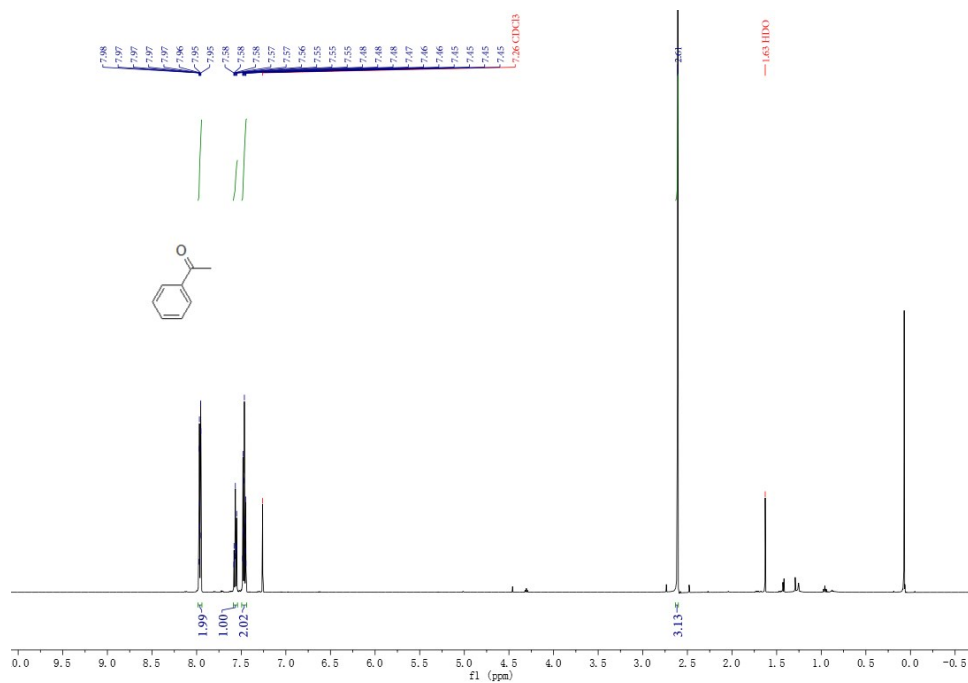
^1H NMR of nitrobenzene (**51**) in CDCl_3 (δ in ppm)



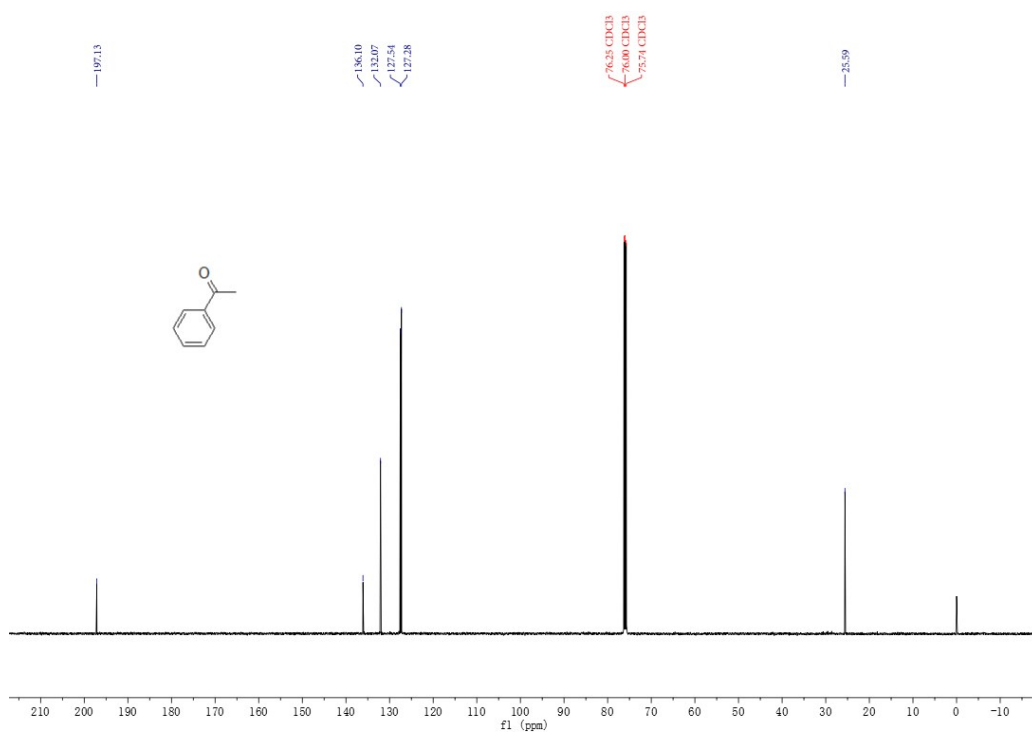
^{13}C NMR of nitrobenzene (**51**) in CDCl_3 (δ in ppm)



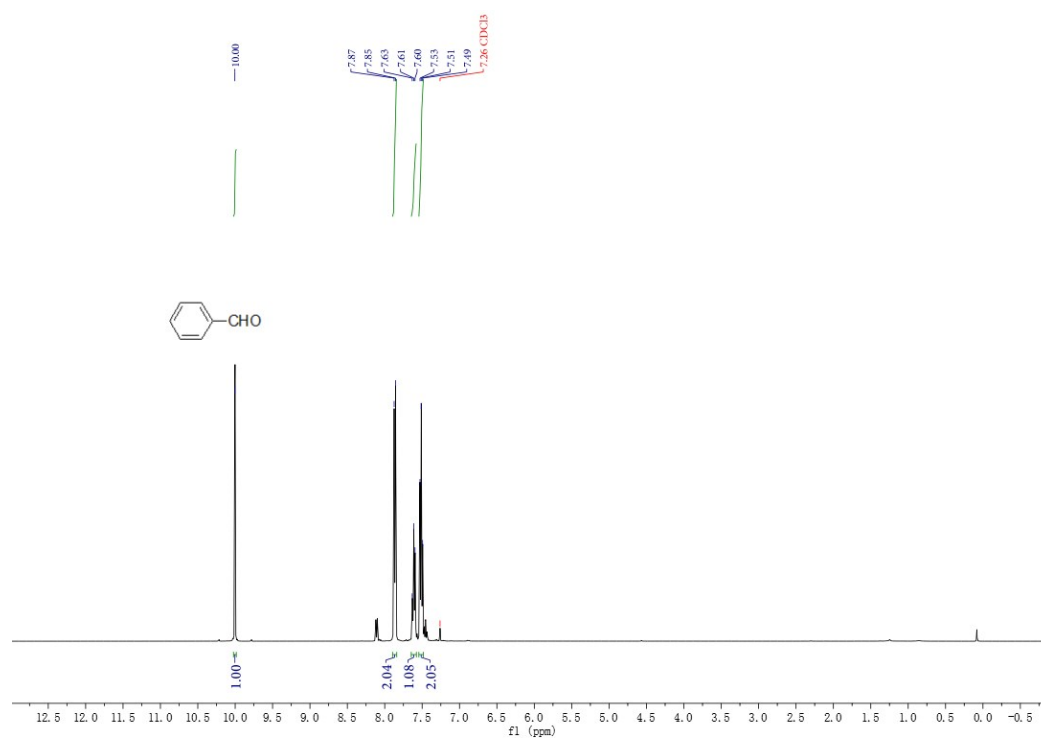
^1H NMR of Acetophenone (**5m**) in CDCl_3 (δ in ppm)



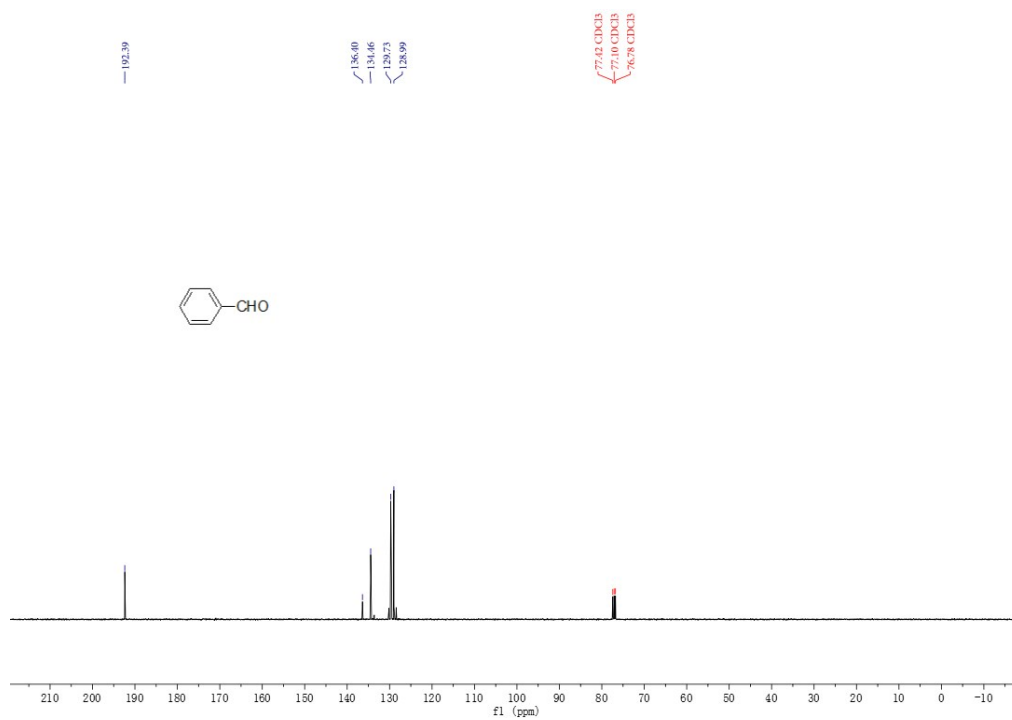
^{13}C NMR of Acetophenone (**5m**) in CDCl_3 (δ in ppm)



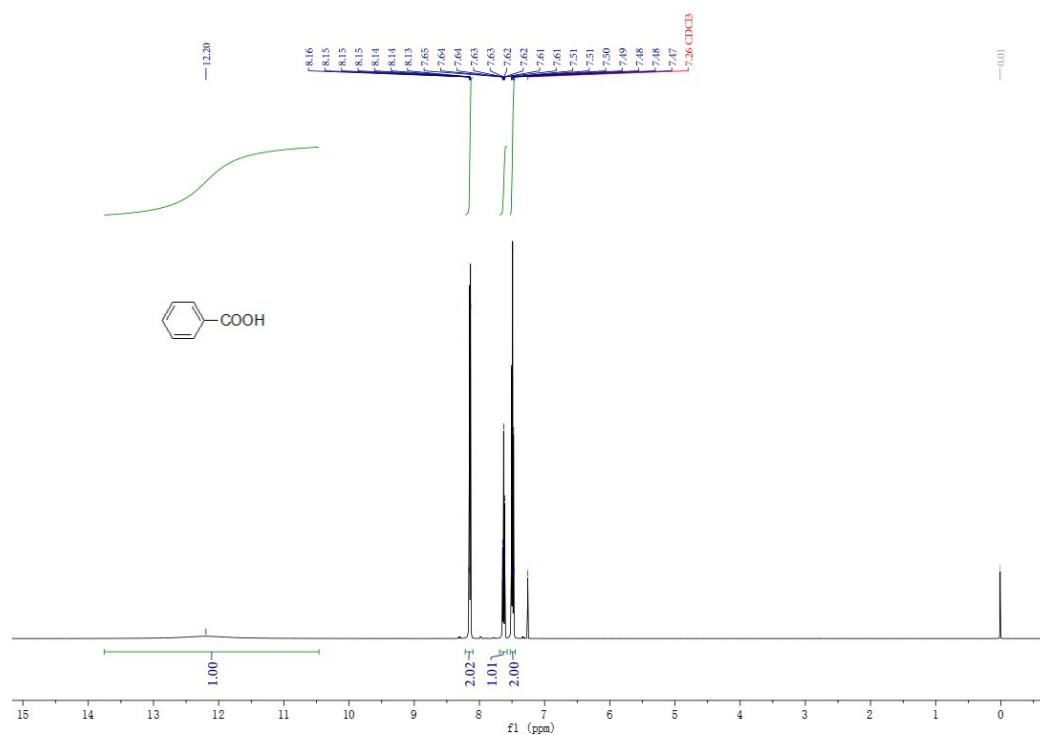
^1H NMR of Benzaldehyde (**5n**) in CDCl_3 (δ in ppm)



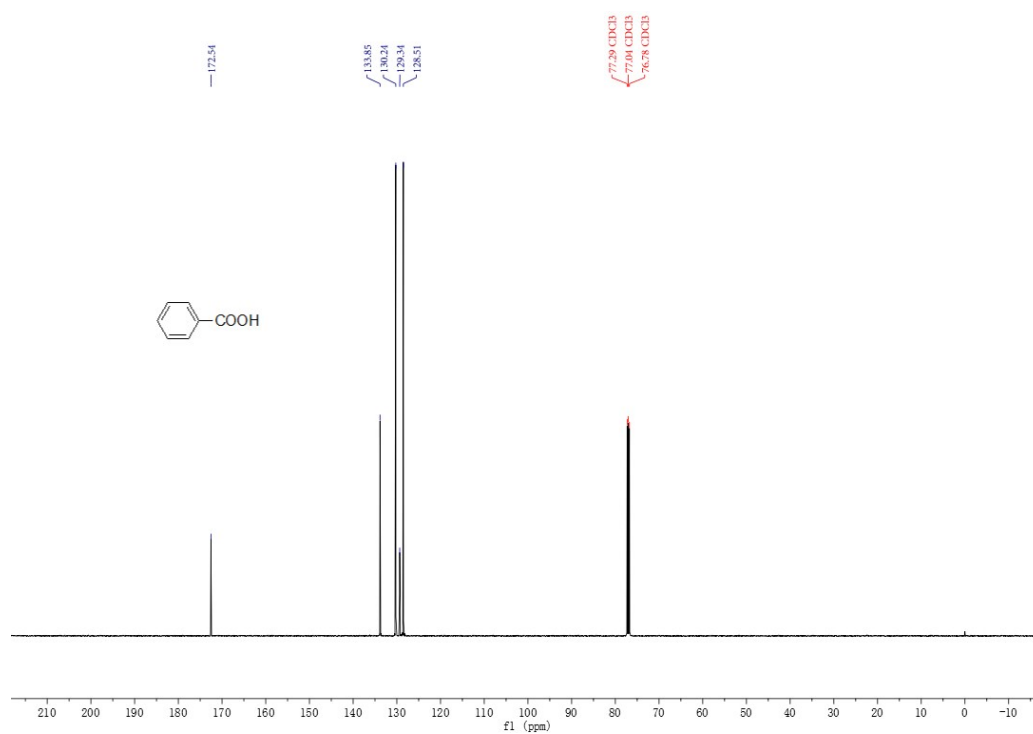
^{13}C NMR of Benzaldehyde (**5n**) in CDCl_3 (δ in ppm)



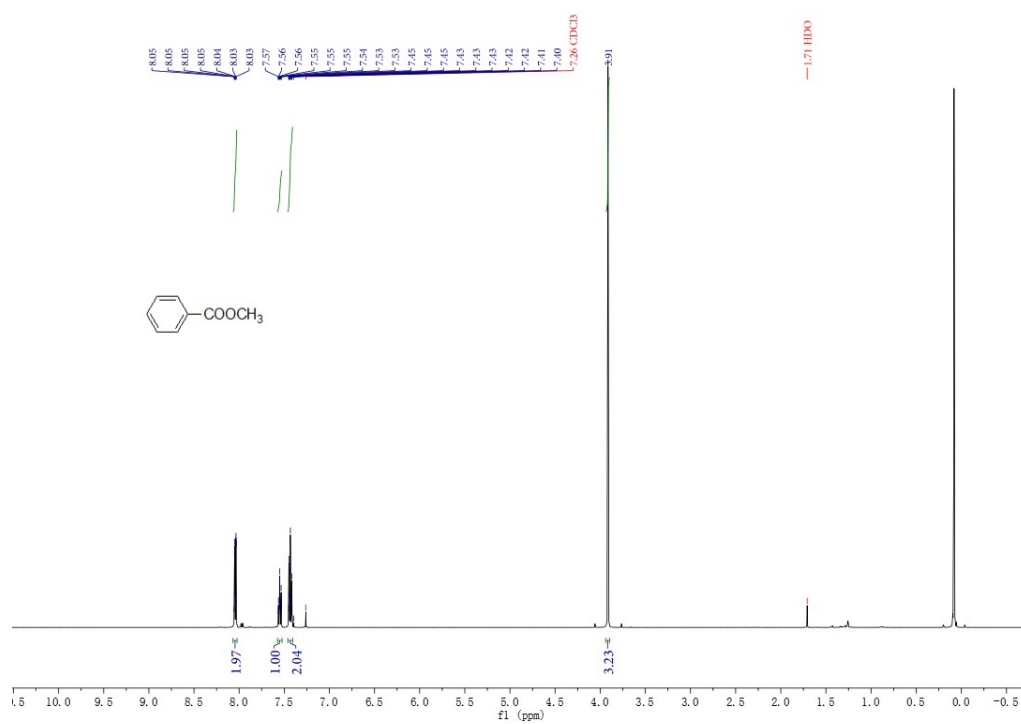
^1H NMR of Benzoic acid (**5r**) in CDCl_3 (δ in ppm)



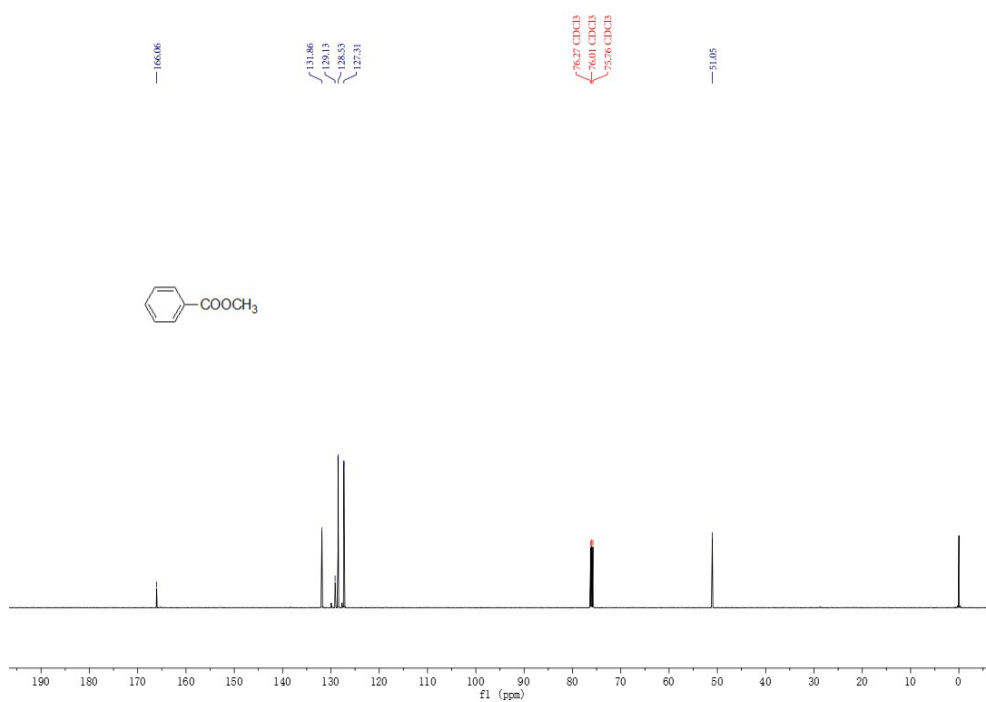
^{13}C NMR of Benzoic acid (**5r**) in CDCl_3 (δ in ppm)



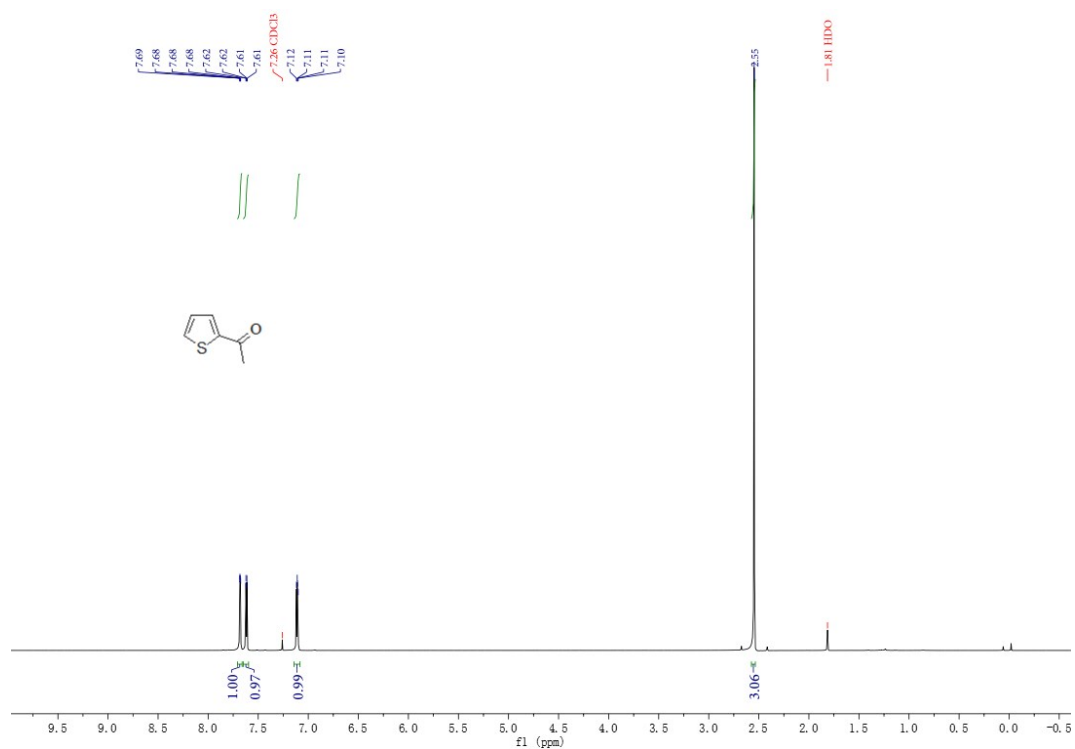
^1H NMR of Methyl benzoate (**5s**) in CDCl_3 (δ in ppm)



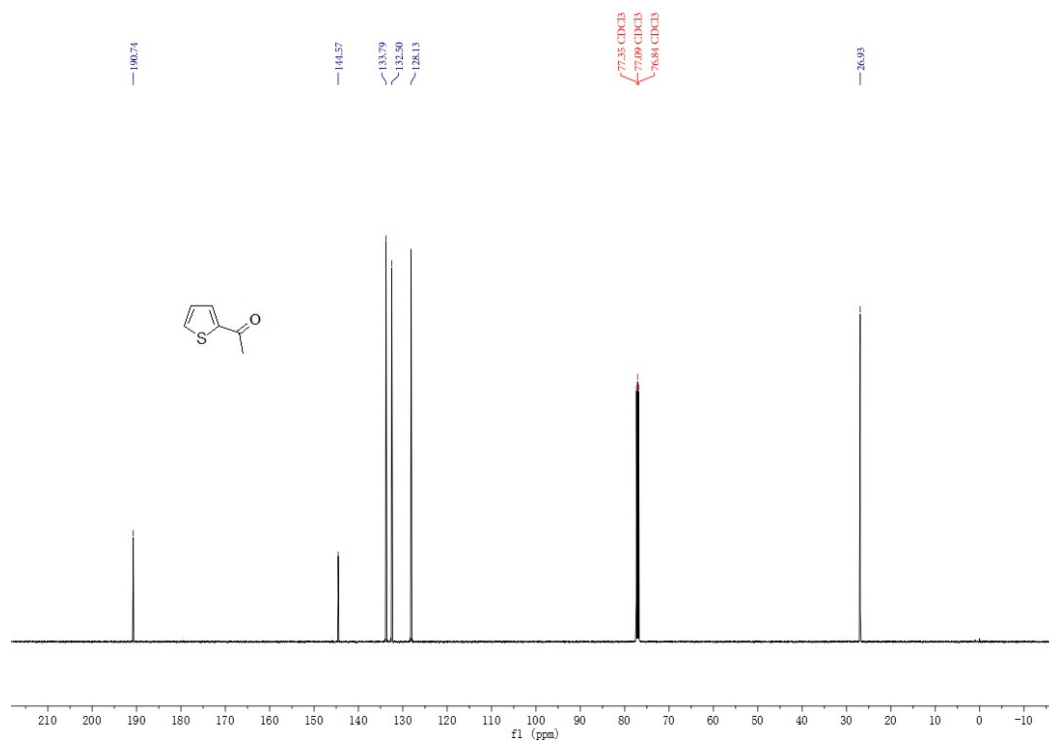
^{13}C NMR of Methyl benzoate (**5s**) in CDCl_3 (δ in ppm)



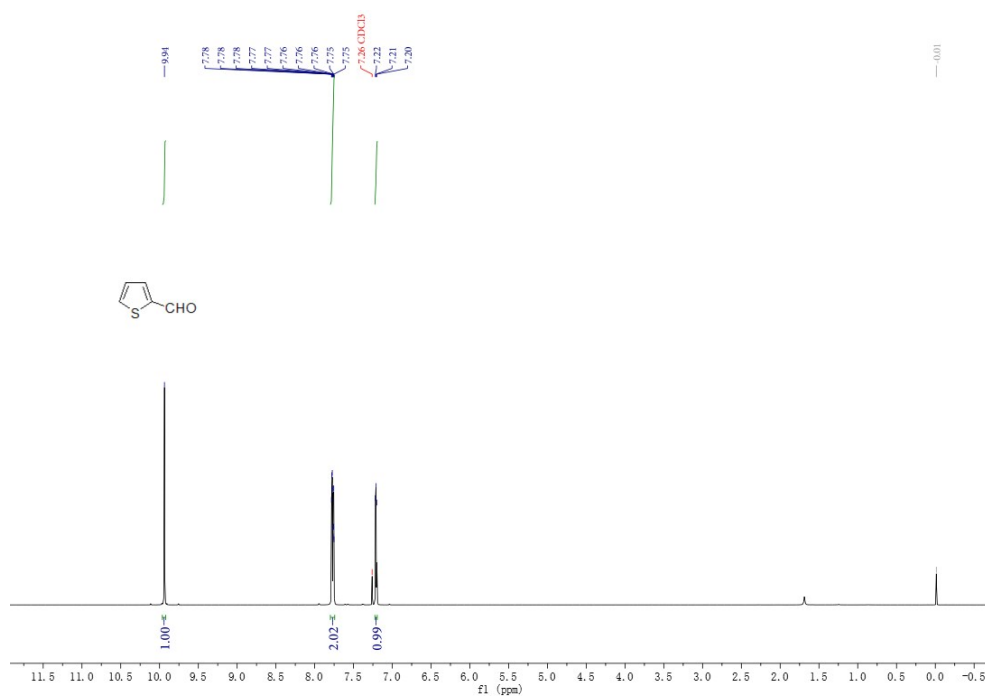
^1H NMR of 2-Acetyl thiofuran (**5u**) in CDCl_3 (δ in ppm)



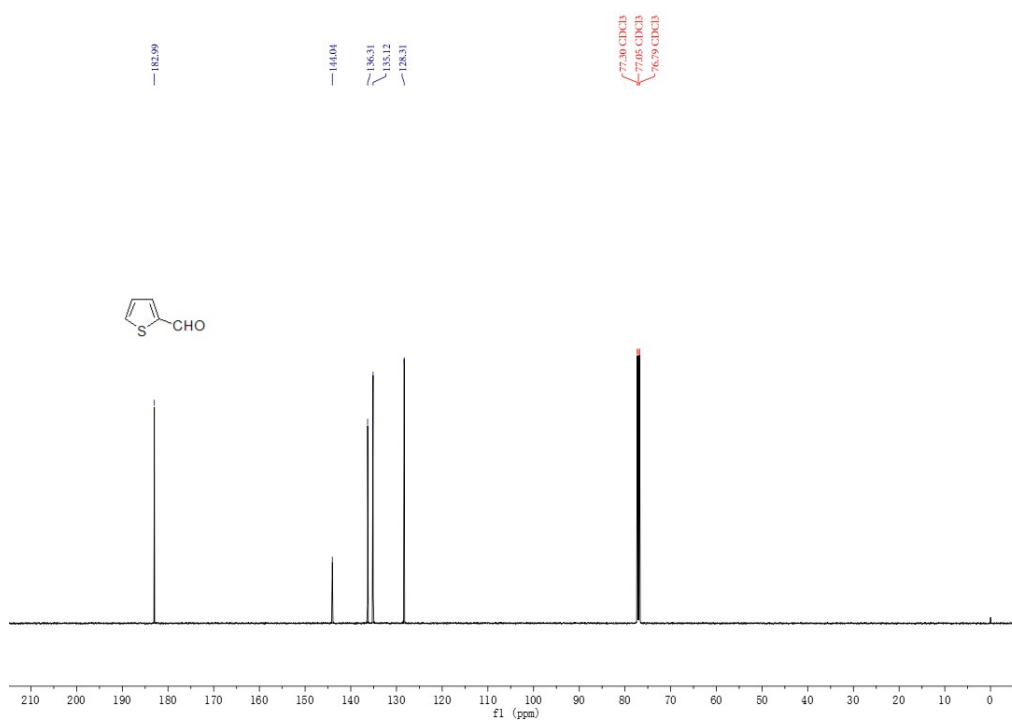
^{13}C NMR of 2-Acetyl thiofuran (**5u**) in CDCl_3 (δ in ppm)



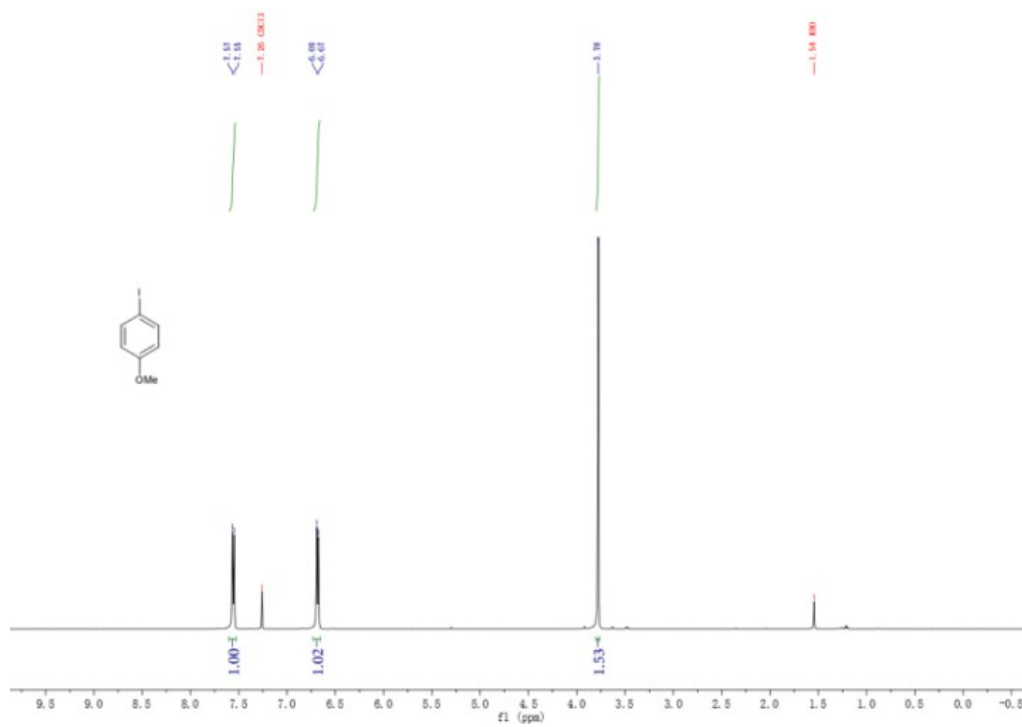
^1H NMR of 2-Formylthiophene (**3**) in CDCl_3 (δ in ppm)



^{13}C NMR of 2-Formylthiophene (**3**) in CDCl_3 (δ in ppm)

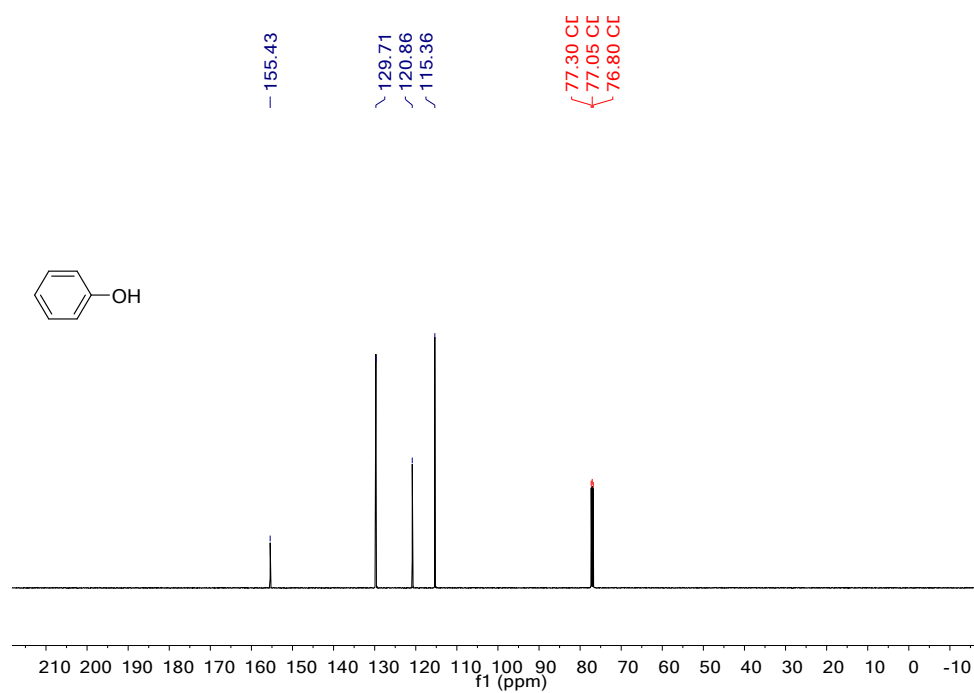
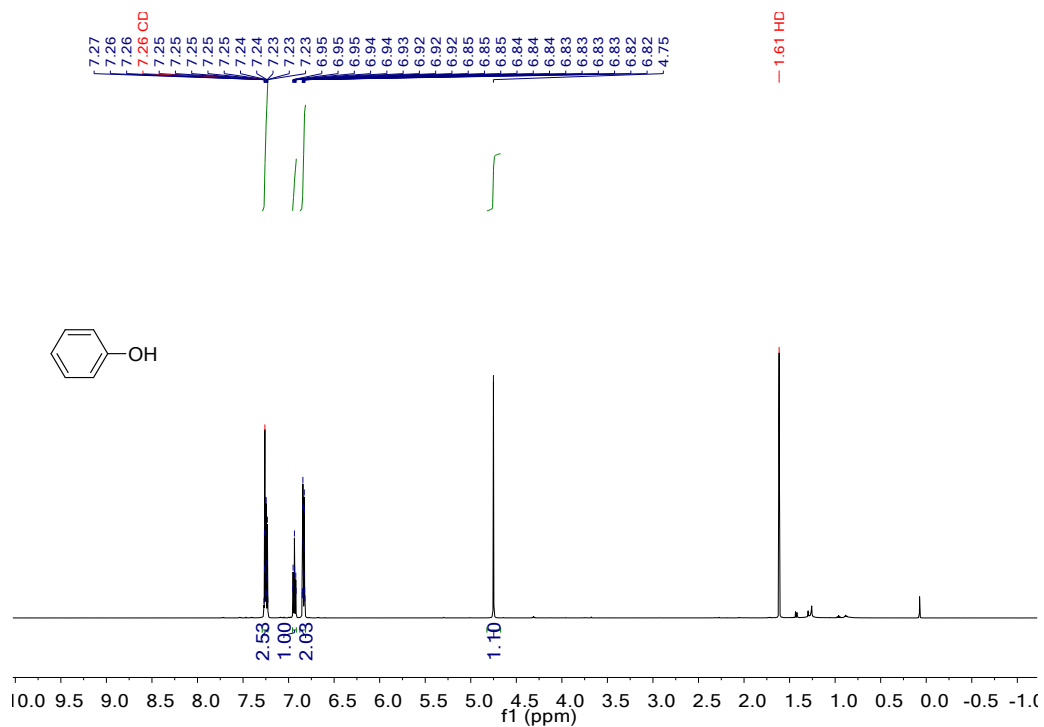


^1H NMR of 4-iodoanisole (**8**) in CDCl_3 (δ in ppm)



^1H NMR and ^{13}C NMR of Phenol (**5a**) obtained from the protodeboronation of **4v** in

CDCl_3 (δ in ppm)



^1H NMR and ^{13}C NMR of Benzoic acid (**5r**) obtained from the protodeboronation of **4w**
in CDCl_3 (δ in ppm)

