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Supporting Information

Photocatalytic conversion of arylboronic acids to phenols by a new 2D donor–acceptor Covalent Organic Framework

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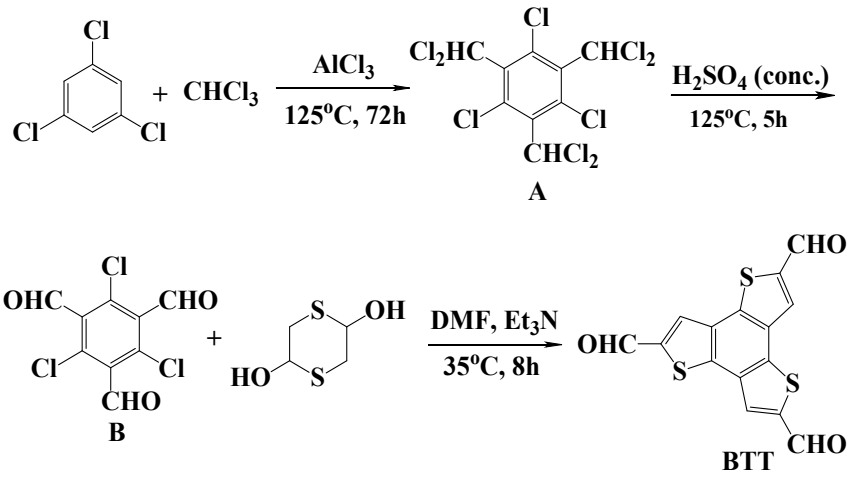
Contents

Synthesis of benzo[1,2-b:3,4-b':5,6-b']trithiophene-2,5,8-trialdehyde (BTT)



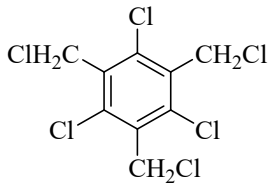
Scheme S1. Synthetic route approach to **BTT**

Synthesis of **A.** 1,3,5-trichlorobenzene (3 g, 16.6 mmol) and $AlCl_3$ (2.6 g, 19.6 mmol) dissolved in 60 mL of $CHCl_3$, reacted in the reactor at 125 °C for 3 days. Then the reaction mixture was cooled to room temperature and transferred to an ice-water mixture containing 60 mL $CHCl_3$ and 20 mL HCl, and stirred for 1 hour. Subsequently, it was extracted with a 5% $NaHCO_3$ aqueous solution, the collected organic phase was dried over anhydrous $MgSO_4$, and the solvent was distilled off under reduced pressure to obtain a brown solid. Compound **A** was further purified by silica gel column (eluent: PE/EA=5/1).

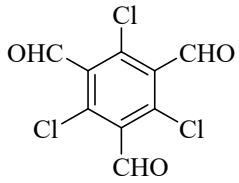
Synthesis of **B.** Compound **A** (2.2 g, 5.1 mmol) and $FeSO_4$ (0.1 g, 0.7 mmol) were added to 12 mL of concentrated H_2SO_4 and reacted at 125 °C for 5 hours. Then the reaction mixture was cooled to room temperature, poured into ice water and extracted with dichloromethane. After the collected organic phase was dried over anhydrous $MgSO_4$, the organic phase solution was concentrated and purified by silica gel chromatography to obtain compound **B**.

Synthesis of **BTT.** At room temperature, compound **B** (1.17 g, 4.4 mmol), p-dithiophene-2,5-diol (1 g, 6.6 mmol) were dispersed in 15 mL DMF, and then triethylamine (3.67 mL, 26.4 mmol) was added to it. Subsequently, the above mixture was stirred at 35 °C for 8 hours. Then the reaction mixture was poured into ice water, the precipitate was separated by centrifugation, and washed several times with water, THF and ethanol, respectively, to obtain a dark yellow solid (**BTT**). The solubility of

BTT in various solvents is very poor, so no further characterization was performed. m.p.＞300 °C.

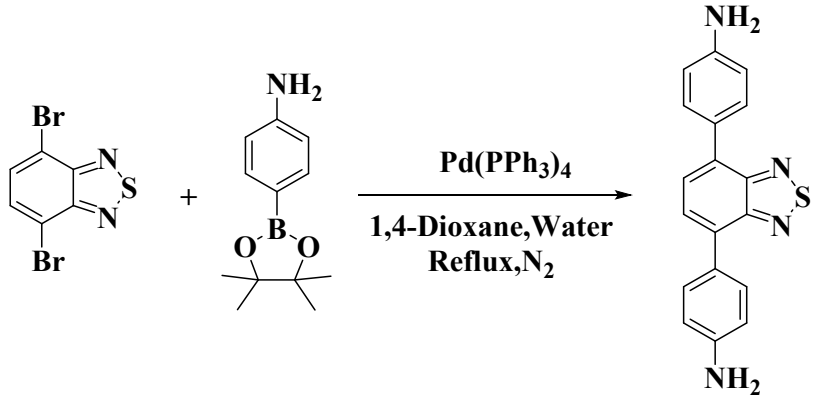


A.1,3,5-trichloro-2,4,6-tris(chloromethyl)benzene: ^{1}H NMR(δ, $CDCl_3$, 25℃): 7.75(s, 2H).



B.2,4,6-Trichloro-benzene-1,3,5-tricarbaldehyde: ^{1}H NMR (δ, $CDCl_3$): 10.41 (s).

Synthesis of 4,4'-(benzothiadiazole-4,7-diyl)dianiline (BTDDA)



Scheme S2 Synthesis of 4,4'-(benzothiadiazole-4,7-diyl)dianiline (**BTDDA**).

4,7-dibromobenzo[*c*][1,2,5]thiadiazole (2 g，6.82 mmol), 4-aminophenylborate (3.59 g, 16.39 mmol), $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol) and K_2CO_3 (4.5 g, 32.45 mmol) were added into a round-bottom flask with 1, 4-dioxane (100 mL) and water (20 mL). After refluxing for 72 hours under nitrogen atmosphere, the precipitate was cooled to room temperature, extracted with ethyl acetate, and then washed with salt water. The crude product was purified by silica gel column chromatography to obtain red solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 – 7.72 (m, 2H), 7.73 – 7.68 (m, 1H), 6.70 (d, J = 5.9 Hz, 2H), 5.39 (s, 2H).^{13}C NMR (150 MHz, DMSO-d_6) δ 154.11, 149.37, 131.43, 130.18, 126.57, 124.80, 114.16.

Synthesis of BTT-BTDDA-COF

BTT (66.1 mg, 0.2 mmol) and **BTDDA** (95.5 mg, 0.3 mmol) were placed in a heat-resistant glass bottle, and 1, 4-dioxane (3 mL), trimethylbenzene (3 mL), and 6 M AcOH (0.3 mL) were added, respectively. After ultrasonic dispersion for 5 min, the mixture was sealed in N_2 atmosphere and heated at 120 °C for 3 days. After cooling to room temperature, the products were separated by centrifugation, washed with DMF, methanol and ethanol for several times successively, and then Soxhlet extracted with THF for 24 h. Finally, the obtained solids were dried at 100 °C for 12 h in vacuum to obtain red **BTT-BTDDA-COF**.

Surface morphology analysis

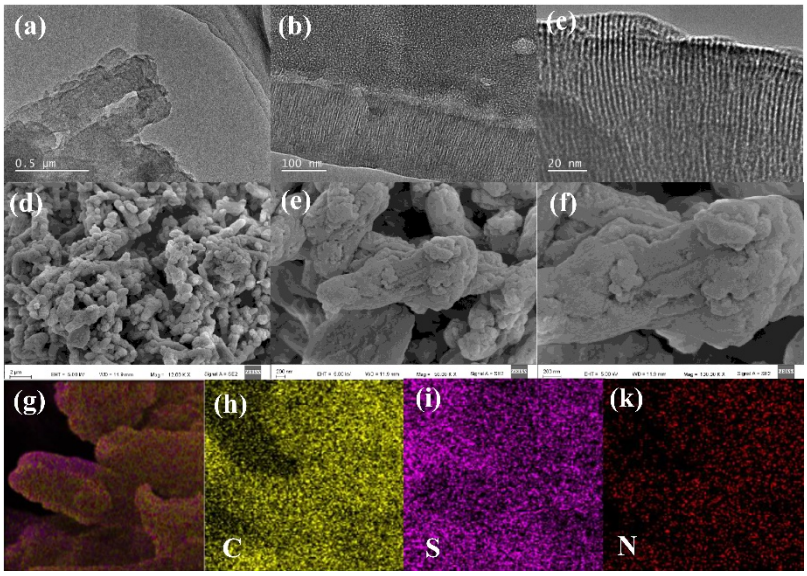


Fig. S1 TEM image of BTT-BTDDA-COF COFs，scales are 0.5 μm **(a)**、100 nm **(b)** and 20 nm **(c)**；SEM image of BTT-BTDDA-COF, scales are 2 μm **(d)**、200 nm **(e)**、 and 202 nm **(f)**；EDS mapping image of BTT- BTDDA -COF: EDS scanning area; **(g)**，C **(h)**、S **(i)**、N **(k)** element EDS mapping.

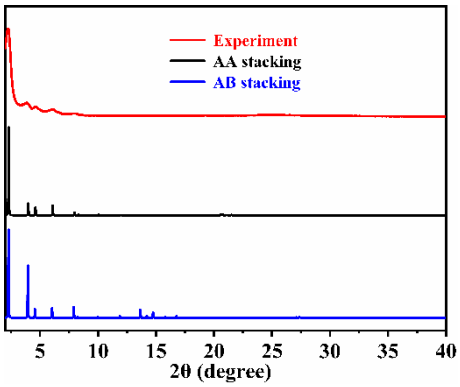


Fig. S2 BTT-BTDDA-COF experiment (red), predicted AA stacking (black) and AB stacking (blue) PXRD patterns;

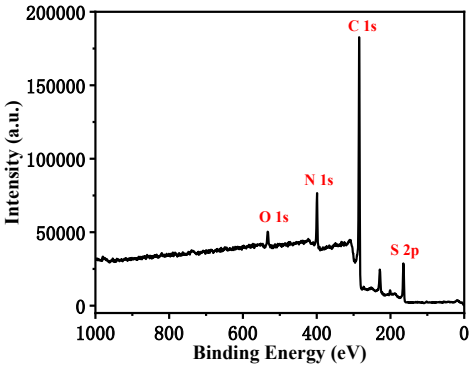
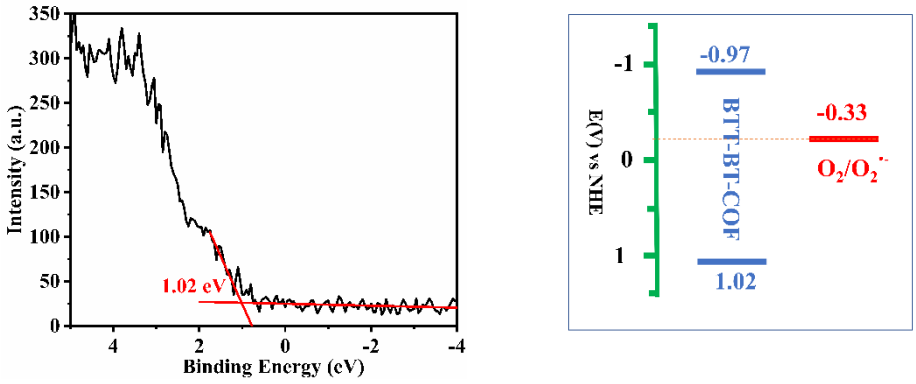


Fig. S3 XPS full spectrum of BTT-BTDDA-COF.



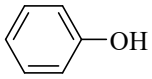
(a) (b)

Fig. S4 (a) VB-XPS spectrum of BTT-BTDDA-COF; (b) Schematic diagram of band structure of BTT-BTDDA-COF.

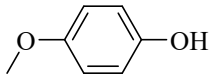
Photocatalytic conversion of arylboronic acids to phenols

Scheme S3. Photocatalytic reaction for oxidative hydroxylation of 4-formylphenylboronic acid.

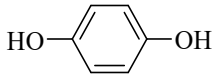
Phenylboric acid (0.1 mmol), triethylamine (0.3 mmol), and BTT-BTDDA-COF (2 mg) were added to a translucent glass bottle containing 3 mL acetonitrile. The reaction was irradiated by 36 W blue LED lamp and stirred at room temperature. The reaction process was detected by TLC. The catalyst was removed by centrifugation from the reacted mixed solution. The solvent was removed by rotary evaporation to obtain the crude product, and the product was purified by column chromatography to obtain phenol (eluent: petroleum ether/ethyl acetate =5:1).



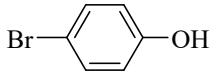
1. Phenol: white solid,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 6.95 (t, J = 7.4 Hz, 1H), 6.88 – 6.83 (m, 2H), 4.99 (s, 1H). ^{13}CNMR (150 MHz, $CDCl_3$) δ 155.38, 129.70, 120.86, 115.32.



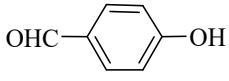
2. 4-Methoxyphenol: white solid,^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J = 2.9 Hz, 4H), 5.26 (s, 1H), 3.76 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 153.62, 153.58, 149.54, 116.24, 116.17, 116.14, 115.07, 114.97, 55.89.



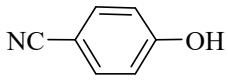
3. Hydroquinone: white solid,^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (d, J = 2.6 Hz, 1H), 6.55 (d, J = 3.0 Hz, 2H).^{13}C NMR (150 MHz, DMSO-d_6) δ 150.17, 116.10.



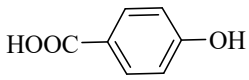
4. 4-Bromophenol: white solid,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 4.86 (s, 1H).13C NMR (150 MHz, $CDCl_3$) δ 154.58, 132.47, 117.18, 112.89.



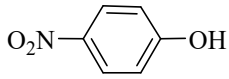
5. *p*-Hydroxybenzaldehyde: light yellow, ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 9.77 (s, 1H), 7.74 (d, J = 4.9 Hz, 2H), 6.93 (d, J = 4.9 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 191.37, 163.80, 132.52, 128.84, 116.29.



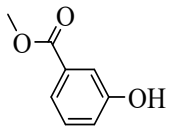
6. 4-Cyanophenol: white solid ,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 2H), 6.94 (d, *J* = 7.0 Hz, 2H), 6.86 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 160.04, 134.31, 119.21, 116.42, 103.27.



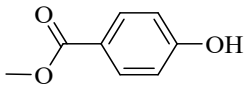
7. 4-Hydroxybenzoic acid: white solid,^{1}H NMR (400 MHz, DMSO-d_6) δ 12.40 (s, 1H), 10.19 (s, 1H), 7.77 (d, *J* = 7.0 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 167.60, 162.03, 131.96, 121.79, 115.55.



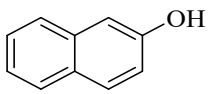
8. 4-Nitrophenol: Light yellow,^{1}H NMR (400 MHz, DMSO-d_6) δ 11.03 (s, 1H), 8.09 (d, *J* = 6.7 Hz, 2H), 6.90 (d, *J* = 6.8 Hz, 2H).^{13}C NMR (150 MHz, DMSO-d_6) δ 164.34, 140.04, 126.60, 116.21.



9. Methyl 3-hydroxybenzoate: white solid,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.61 – 7.58 (m, 1H), 7.31 (t, J = 8.2 Hz, 1H), 7.14 – 7.05 (m, 1H), 6.13 (s, 1H), 3.92 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 167.50, 155.97, 131.23, 129.73, 121.83, 120.41, 116.38, 52.39.



10. Methylparaben: white solid,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.47, 160.30, 131.95, 122.23, 115.28, 52.08.



11. 2-Naphthol: white solid,^{1}H NMR (400 MHz, CDCl3) δ 7.78 (t, J = 8.6 Hz, 2H), 7.69 (d, J = 8.2 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.35 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.18 – 7.09 (m, 2H), 5.15 (s, 1H). 13C NMR (150 MHz, CDCl3) δ 153.29, 129.86, 129.85, 128.95, 127.77, 126.54, 126.37, 123.64, 117.72, 109.51.

Table S1 Fractional atomic coordinates for the unit cell of **BTT-BTDDA-COF**

BTT-BTDDA-COF: Space group: P6 (C3H-1) a = 44.277 Å, b = 44.277 Å, c = 4.3087 Å α = 90°, β = 90°, γ = 120°				
Sequence number	atom	x	y	z
1	C	18.234	33.088	2.154
2	C	18.790	31.808	2.154
3	C	20.186	31.722	2.154
4	C	17.897	30.629	2.154
5	C	16.513	30.802	2.154
6	C	15.659	29.711	2.154
7	C	16.170	28.423	2.154
8	C	17.550	28.237	2.154
9	C	18.401	29.331	2.154
10	N	15.269	27.325	2.154
11	S	12.907	25.296	2.154
12	C	14.693	25.017	2.154
13	C	15.657	26.100	2.154
14	C	15.084	23.758	2.154
15	C	13.957	22.864	2.154
16	C	12.750	23.522	2.154
17	S	22.545	30.885	2.154
18	N	20.892	30.593	2.154
19	C	21.278	5.709	2.154
20	C	22.024	6.885	2.154
21	C	21.388	8.115	2.154
22	C	19.996	8.200	2.154
23	C	19.261	7.017	2.154
24	C	19.894	5.785	2.154
25	N	21.897	4.432	2.154
26	C	23.172	4.270	2.154
27	C	25.058	2.768	2.154
28	C	23.751	2.941	2.154
29	S	22.749	1.437	2.154
30	C	24.295	0.550	2.154
31	C	25.398	1.371	2.154
32	H	17.110	33.216	2.154
33	H	16.074	31.845	2.154
34	H	14.540	29.875	2.154
35	H	17.979	27.191	2.154
36	H	19.521	29.175	2.154
37	H	16.765	25.871	2.154
38	H	16.136	23.342	2.154

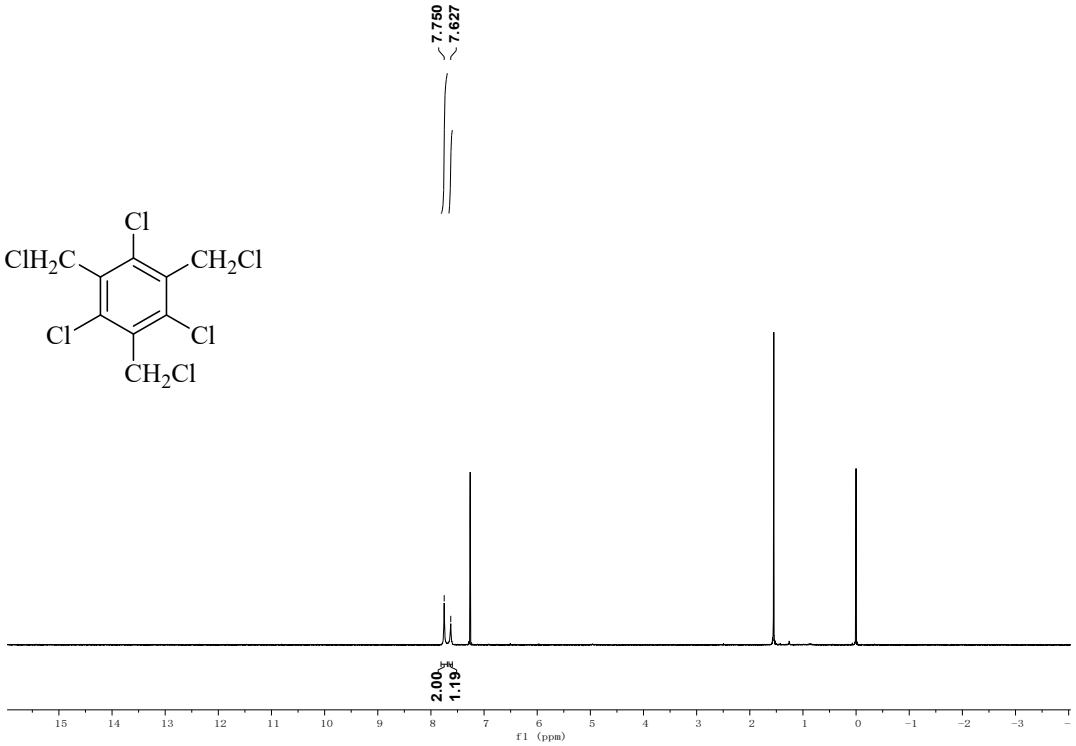
39	H	23.154	6.834	2.154
40	H	22.002	9.065	2.154
41	H	18.130	7.060	2.154
42	H	19.281	4.834	2.154
43	H	23.848	5.177	2.154
44	H	25.748	3.666	2.154
45	C	20.430	-10.156	2.154
46	C	19.038	-10.055	2.154
47	C	20.974	-11.445	2.154
48	N	22.273	-11.737	2.154
49	H	18.544	-9.038	2.154
50	C	22.762	-6.567	2.154
51	C	21.371	-6.508	2.154
52	C	20.624	-7.674	2.154
53	C	21.246	-8.922	2.154
54	C	22.638	-8.967	2.154
55	C	23.389	-7.802	2.154
56	N	23.559	-5.391	2.154
57	C	23.061	-4.207	2.154
58	C	23.419	-1.822	2.154
59	C	23.923	-3.040	2.154
60	S	25.727	-3.156	2.154
61	C	25.721	-1.374	2.154
62	C	24.459	-0.829	2.154
63	H	20.850	-5.504	2.154
64	H	19.494	-7.617	2.154
65	H	23.167	-9.968	2.154
66	H	24.519	-7.858	2.154
67	H	21.938	-4.075	2.154
68	H	22.297	-1.674	2.154
69	C	0.574	21.386	2.154
70	C	1.405	22.507	2.154
71	C	0.781	23.760	2.154
72	C	2.872	22.323	2.154
73	C	3.414	21.039	2.154
74	C	4.786	20.844	2.154
75	C	5.646	21.931	2.154
76	C	5.116	23.219	2.154
77	C	3.744	23.409	2.154
78	N	7.047	21.700	2.154
79	S	9.985	20.668	2.154
80	C	9.334	22.355	2.154
81	C	7.914	22.648	2.154
82	C	10.229	23.323	2.154

83	C	11.566	22.794	2.154
84	C	11.600	21.420	2.154
85	S	0.326	26.221	2.154
86	N	1.405	24.936	2.154
87	H	1.024	20.348	2.154
88	H	2.730	20.137	2.154
89	H	5.203	19.793	2.154
90	H	5.808	24.114	2.154
91	H	3.318	24.457	2.154
92	H	7.558	23.722	2.154
93	H	10.063	24.442	2.154
94	C	36.926	0.632	2.154
95	C	37.535	-0.624	2.154
96	C	37.770	1.747	2.154
97	N	37.374	3.018	2.154
98	H	36.901	-1.560	2.154
99	C	19.335	9.524	2.154
100	C	20.118	10.679	2.154
101	C	19.538	11.943	2.154
102	C	18.151	12.102	2.154
103	C	17.379	10.935	2.154
104	C	17.947	9.697	2.154
105	C	17.577	13.464	2.154
106	C	18.419	14.576	2.154
107	C	17.901	15.861	2.154
108	C	16.530	16.063	2.154
109	C	15.679	14.960	2.154
110	C	16.201	13.677	2.154
111	N	16.030	17.392	2.154
112	S	15.454	20.452	2.154
113	C	14.319	19.045	2.154
114	C	14.775	17.668	2.154
115	C	13.033	19.336	2.154
116	C	12.822	20.758	2.154
117	C	13.995	21.475	2.154
118	N	17.045	8.719	2.154
119	S	15.474	9.310	2.154
120	N	16.048	10.888	2.154
121	H	21.247	10.598	2.154
122	H	20.211	12.852	2.154
123	H	19.542	14.435	2.154
124	H	18.603	16.748	2.154
125	H	14.558	15.112	2.154
126	H	15.506	12.784	2.154

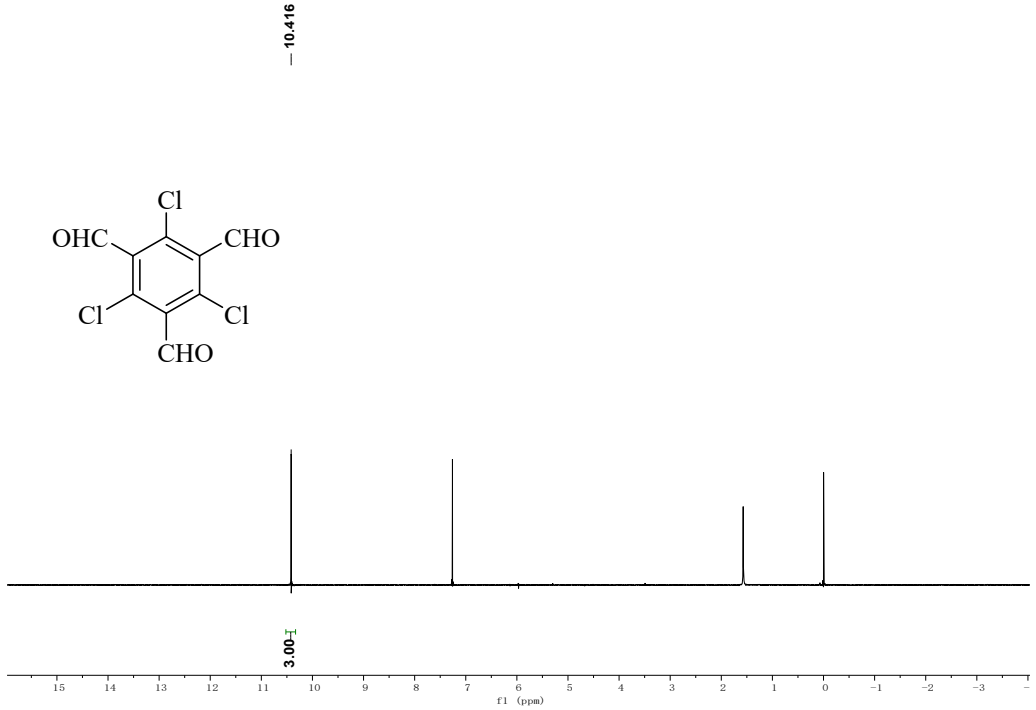
127	H	14.023	16.824	2.154
128	H	12.147	18.632	2.154
129	C	32.651	0.857	2.154
130	C	33.296	-0.377	2.154
131	C	34.680	-0.441	2.154
132	C	35.449	0.722	2.154
133	C	34.792	1.950	2.154
134	C	33.408	2.018	2.154
135	N	31.235	0.959	2.154
136	C	30.458	-0.064	2.154
137	C	28.214	-0.947	2.154
138	C	29.017	0.099	2.154
139	S	28.215	1.719	2.154
140	C	26.675	0.824	2.154
141	C	26.834	-0.542	2.154
142	H	32.687	-1.330	2.154
143	H	35.195	-1.448	2.154
144	H	35.395	2.908	2.154
145	H	32.891	3.024	2.154
146	H	30.905	-1.103	2.154
147	H	28.646	-1.992	2.154

NMR Spectra of Some Compounds

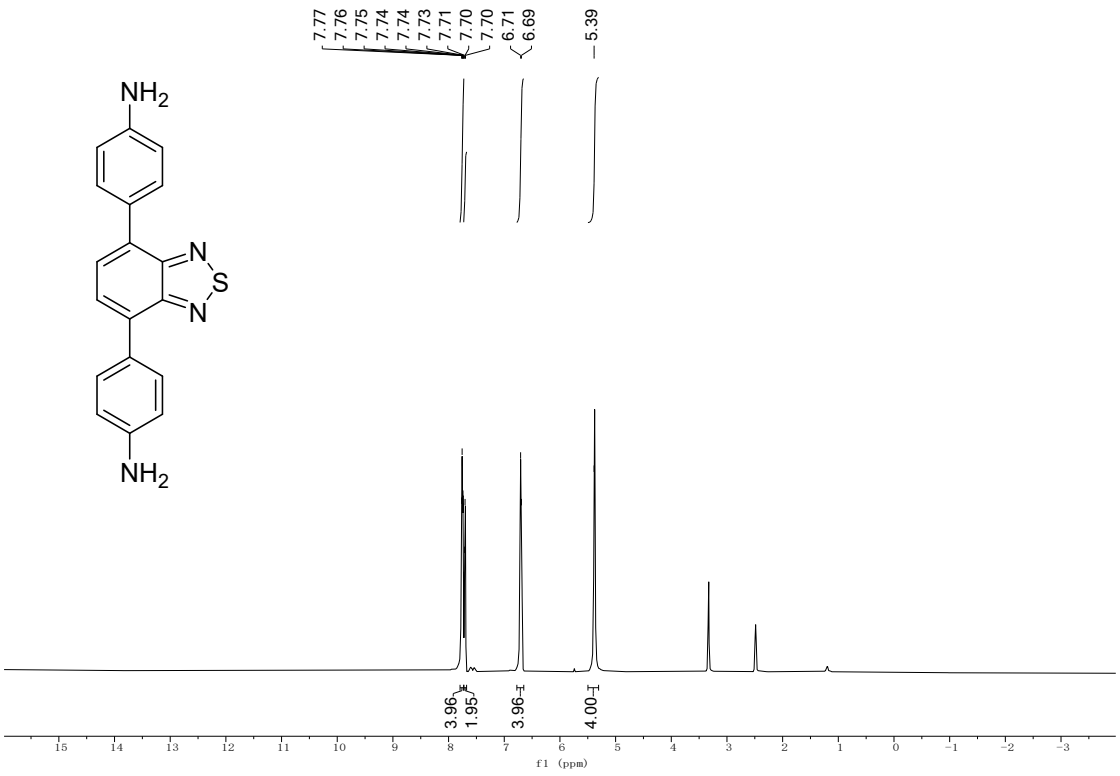
1H of compound A ($CDCl_3$)

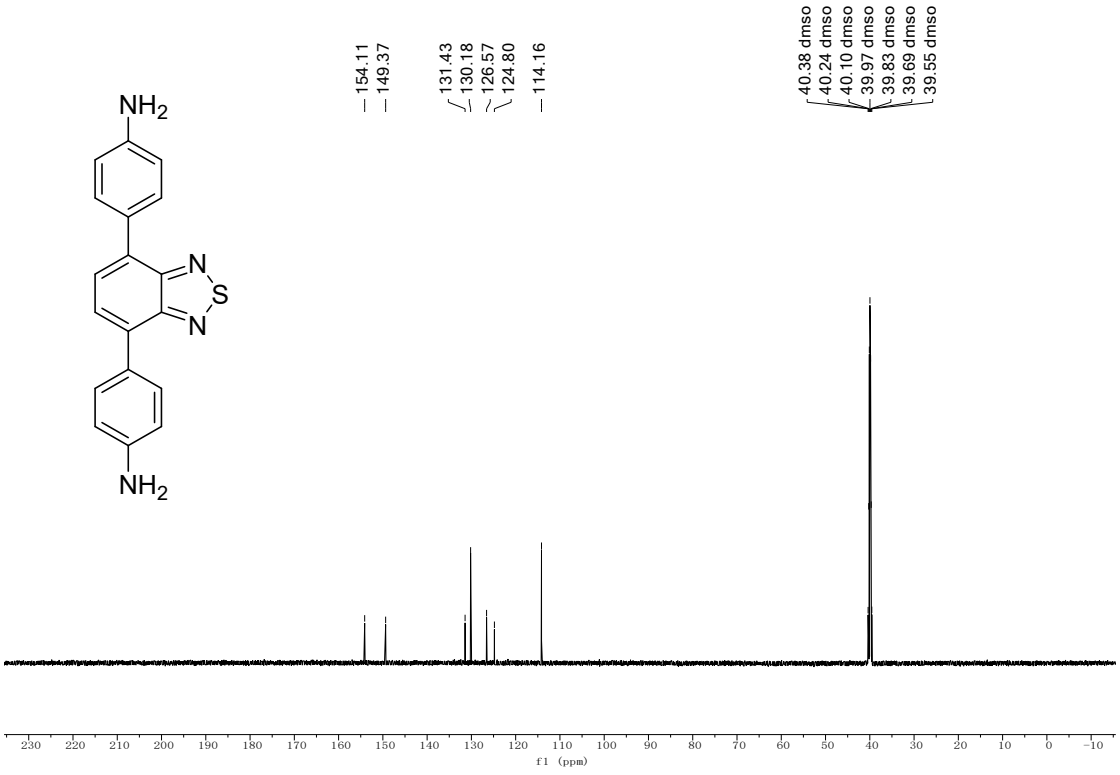


1H of compound B ($CDCl_3$)

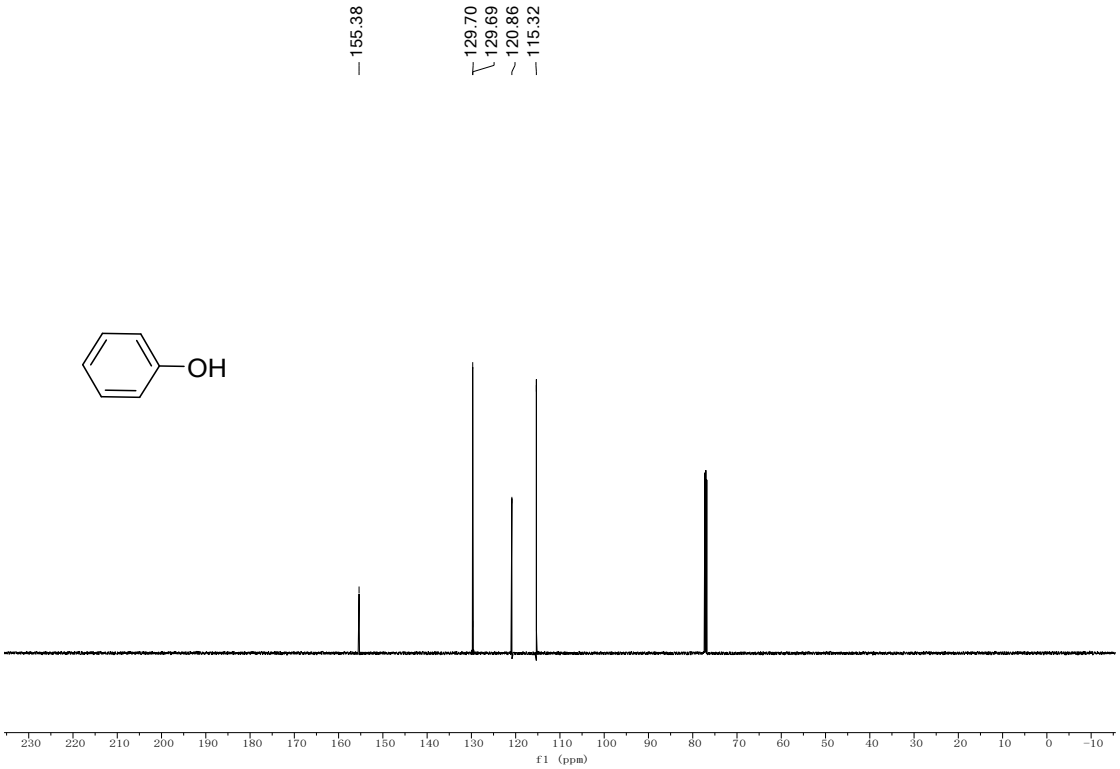


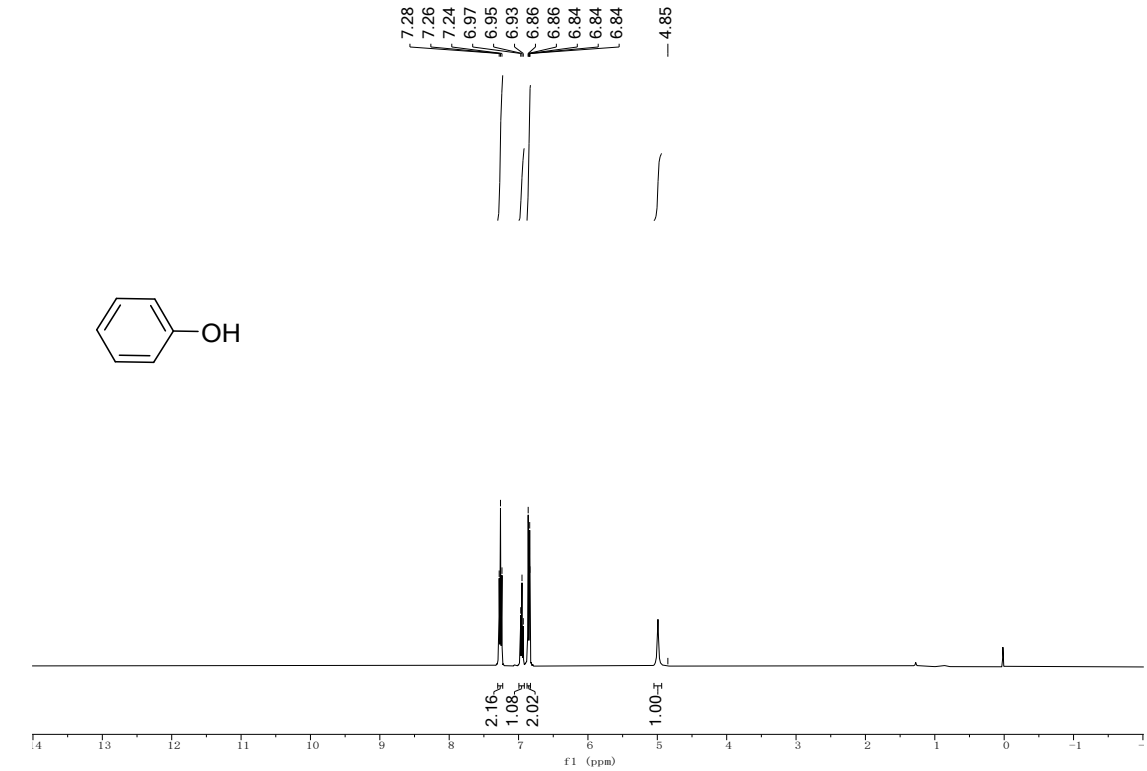
1H and 13C Spectra of compound BT (DMSO)



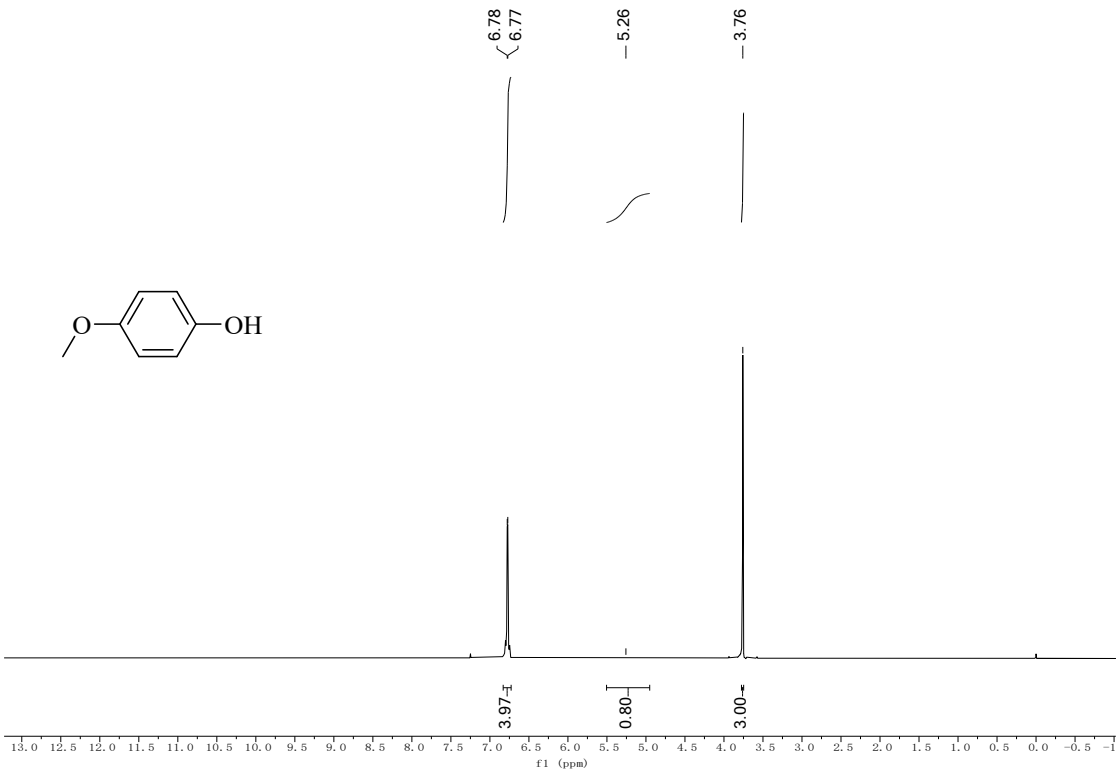


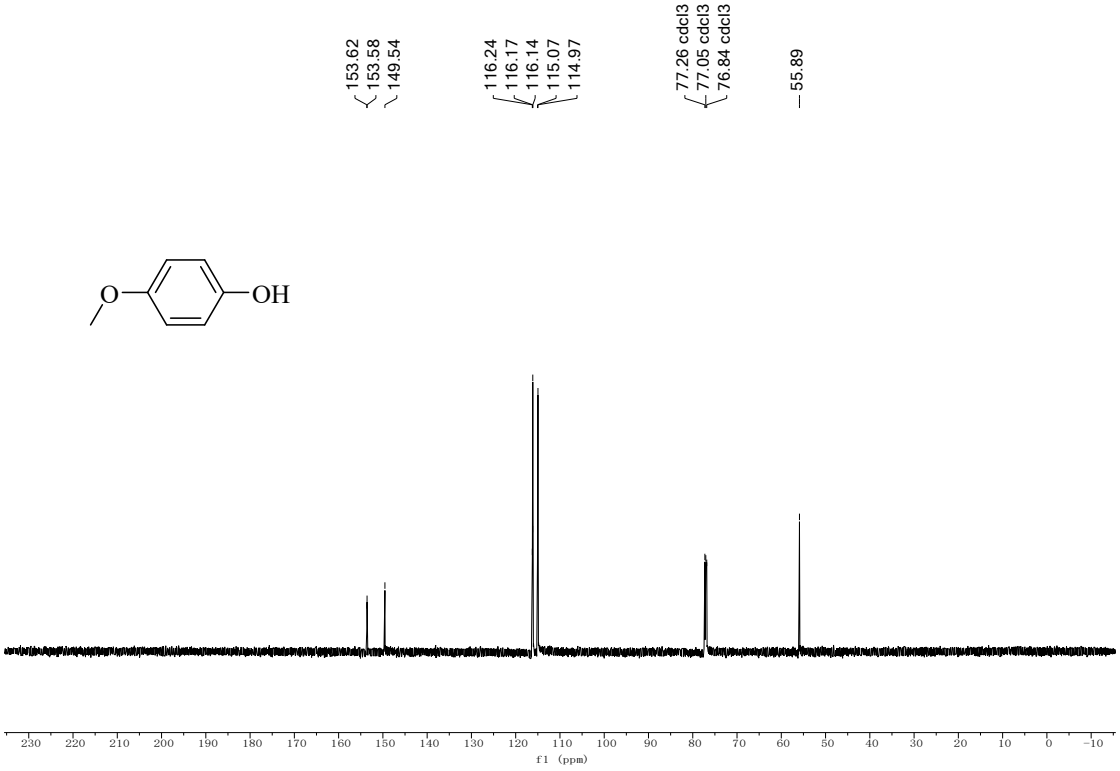
1H and 13C Spectra of compound 1 ($CDCl_3$)



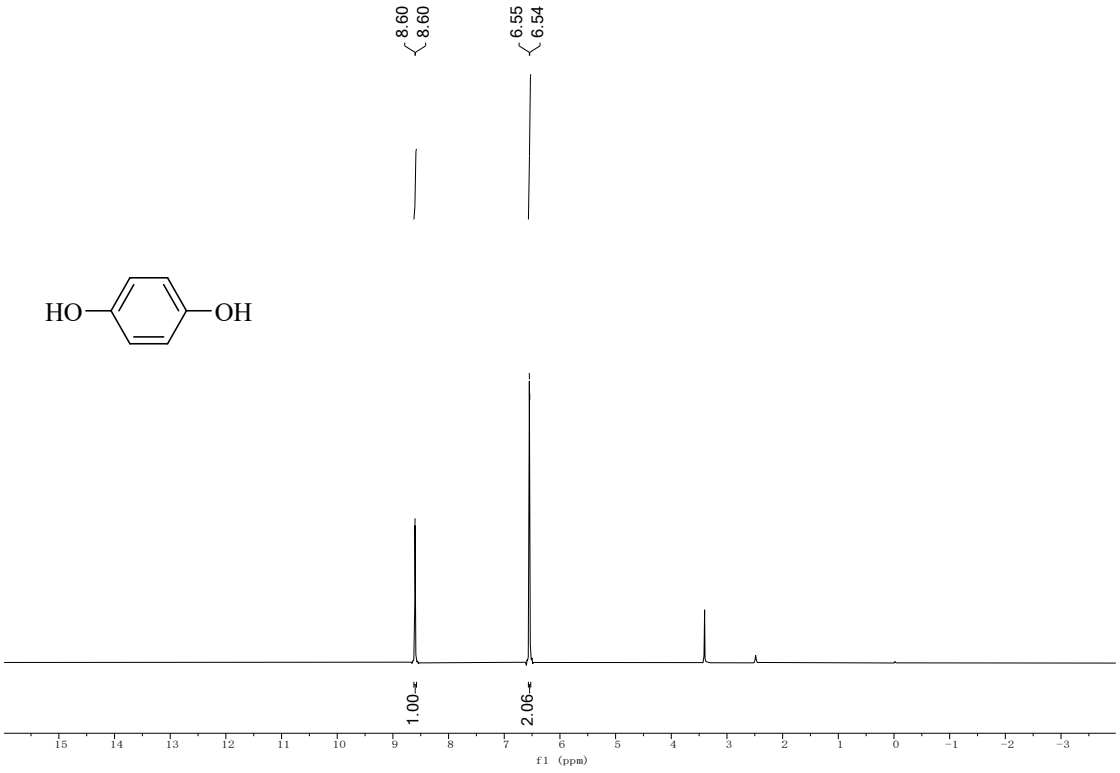


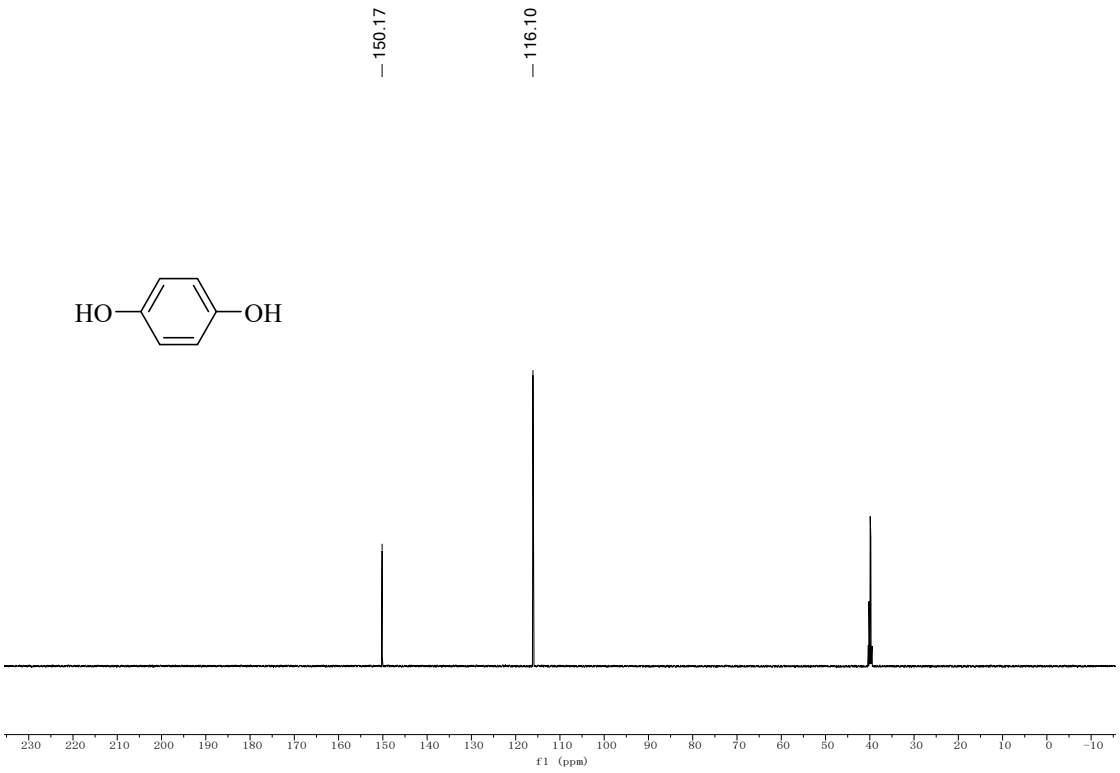
1H and 13C Spectra of compound 2 ($CDCl_3$)



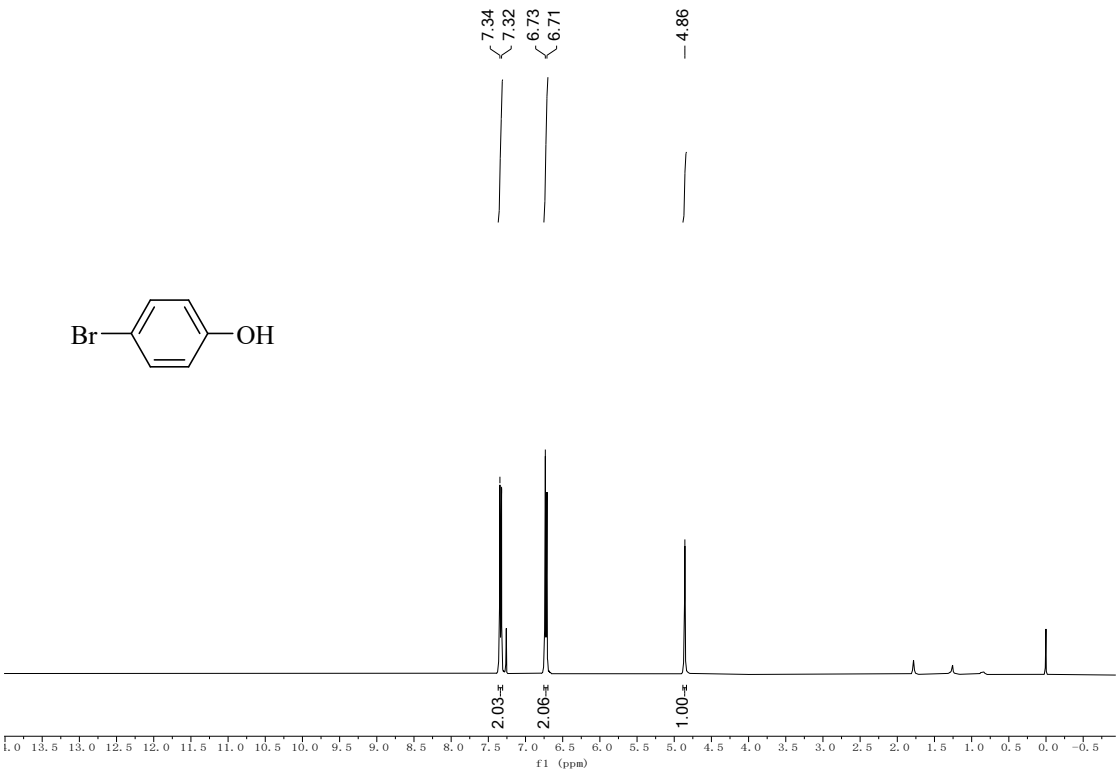


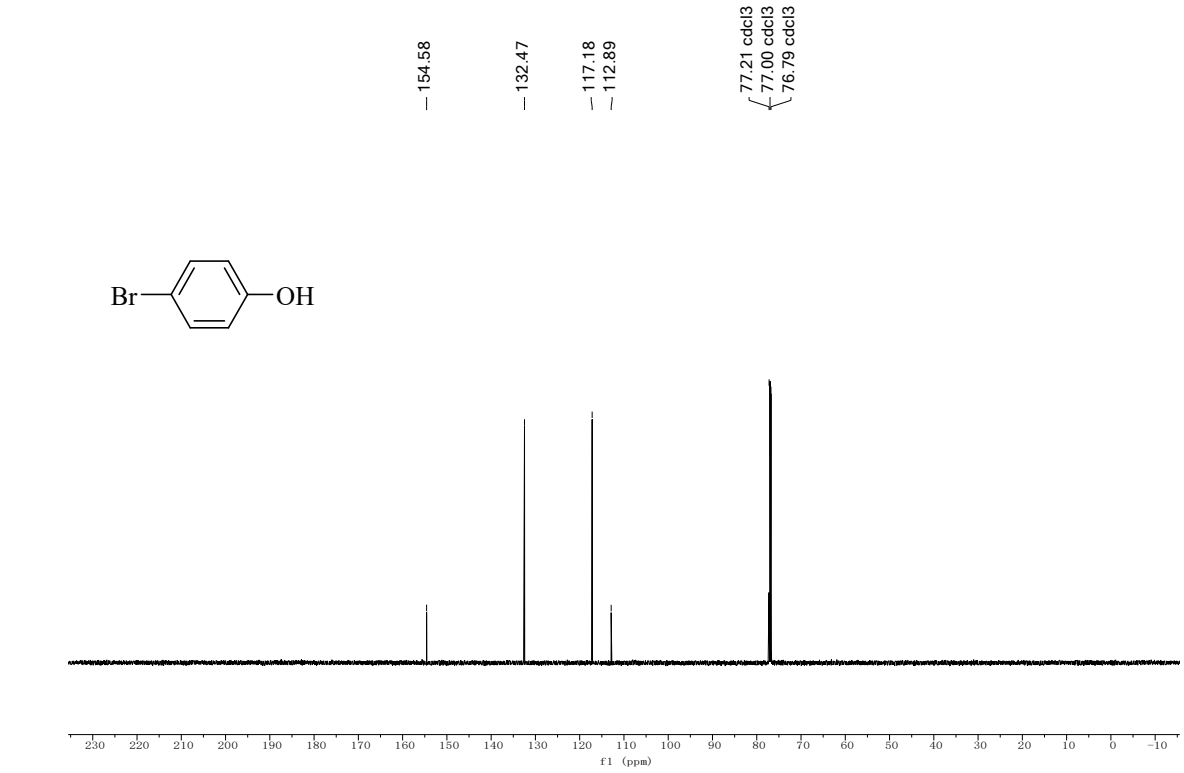
1H and 13C Spectra of compound 3 (DMSO)



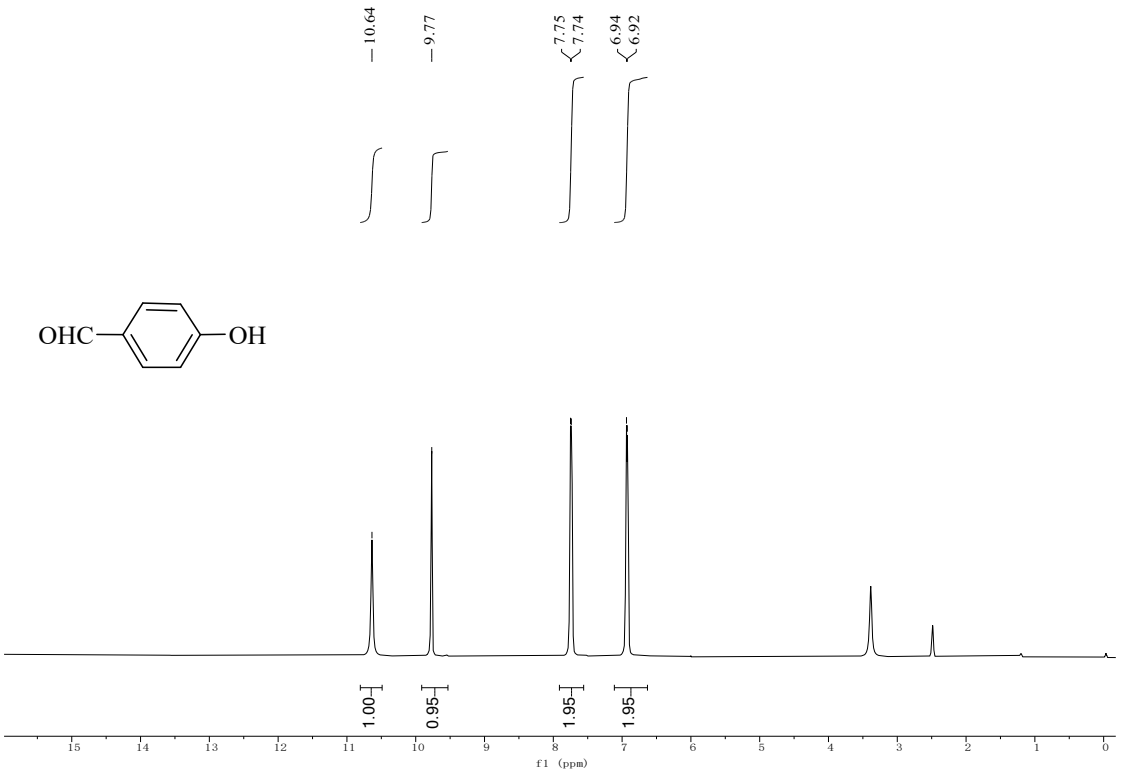


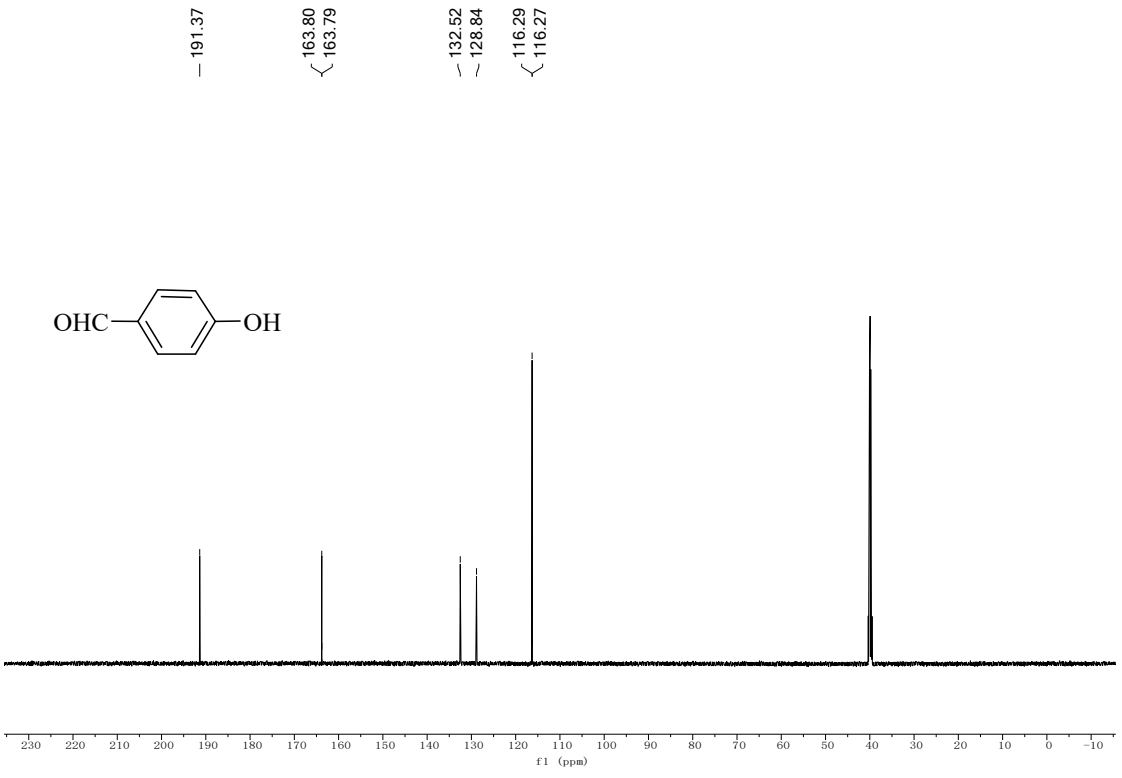
1H and 13C Spectra of compound 4 ($CDCl_3$)



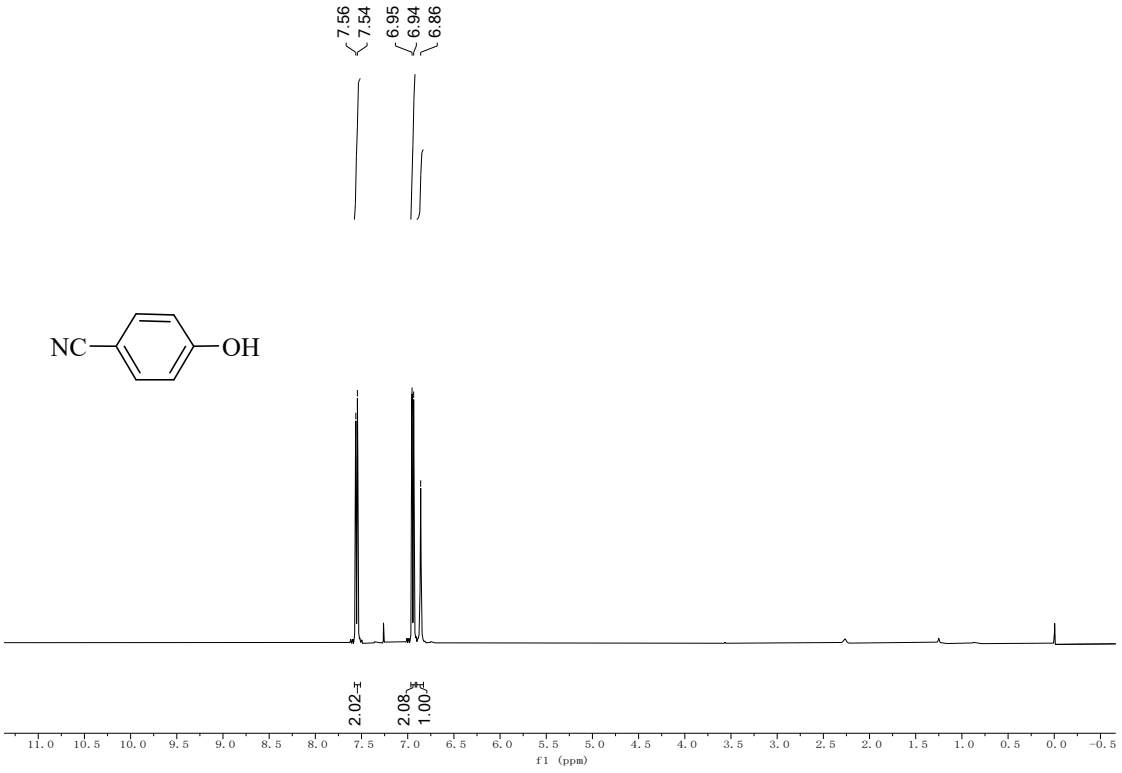


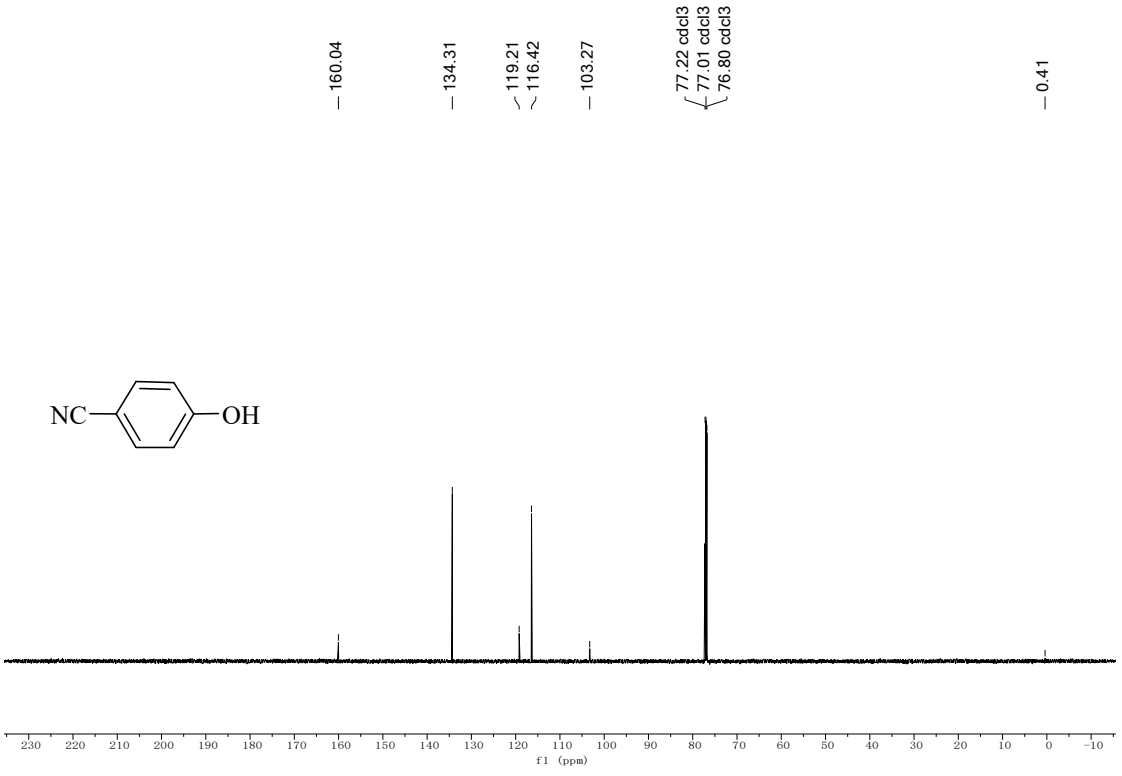
1H and 13C Spectra of compound 5 (DMSO)



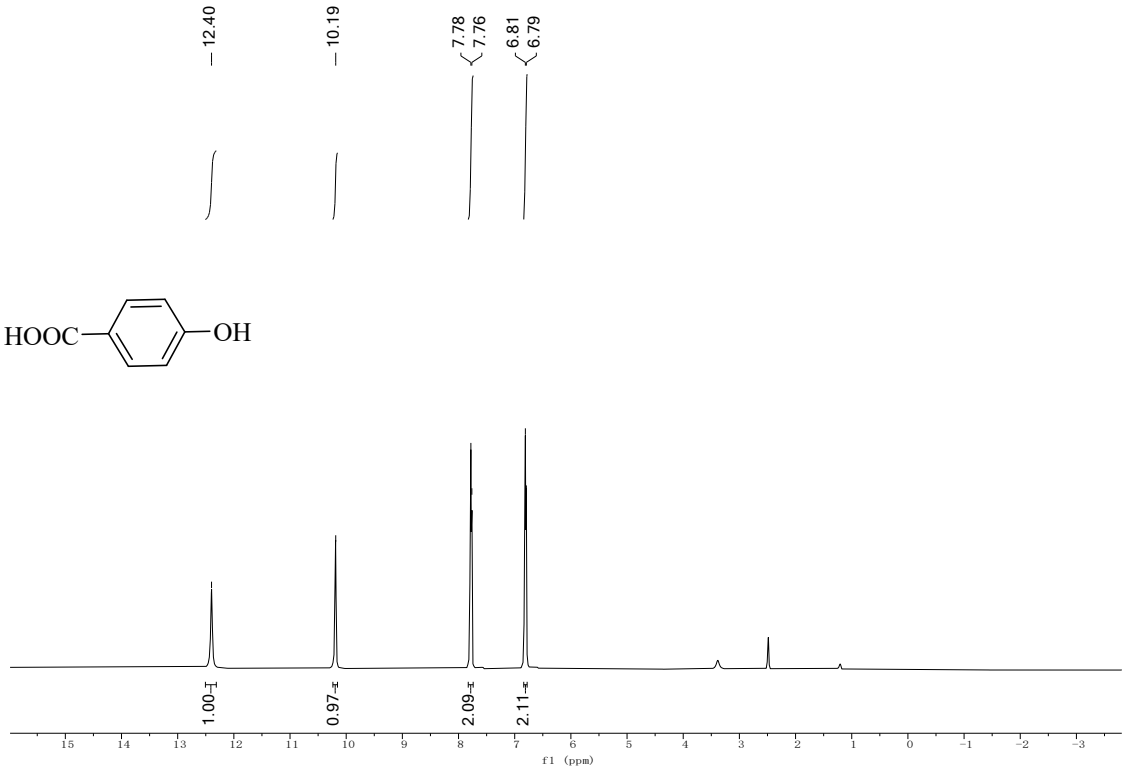


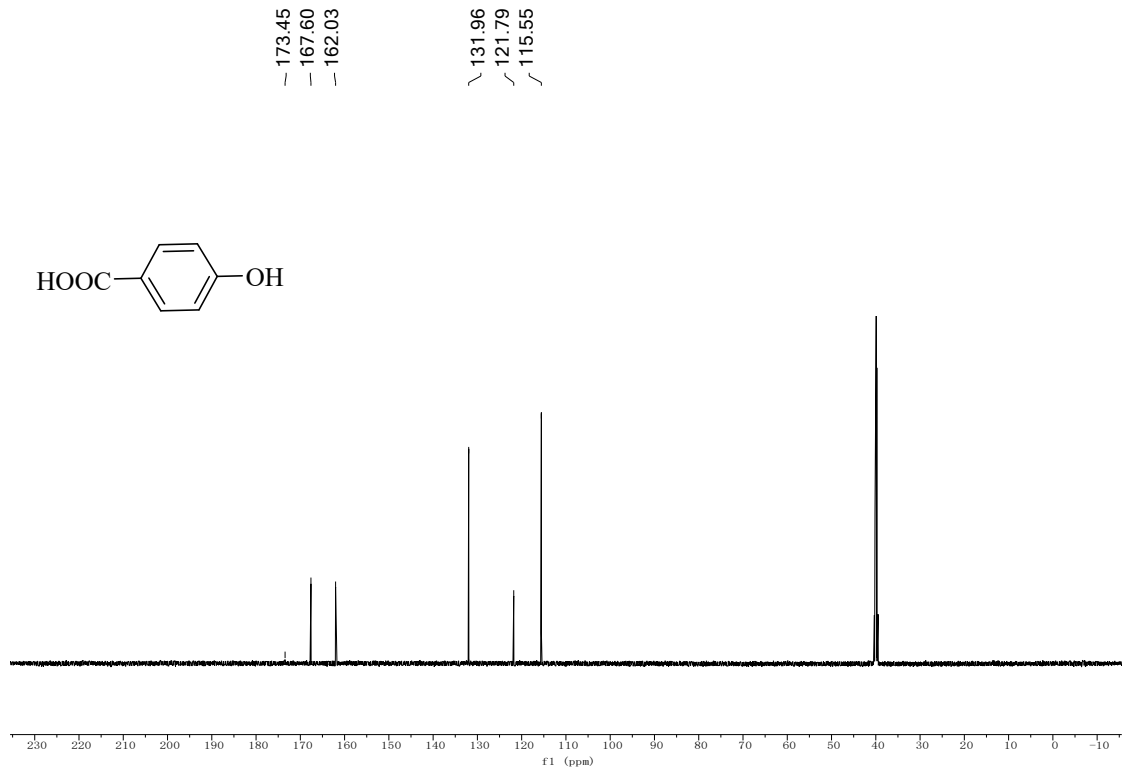
1H and 13C Spectra of compound 6 ($CDCl_3$)



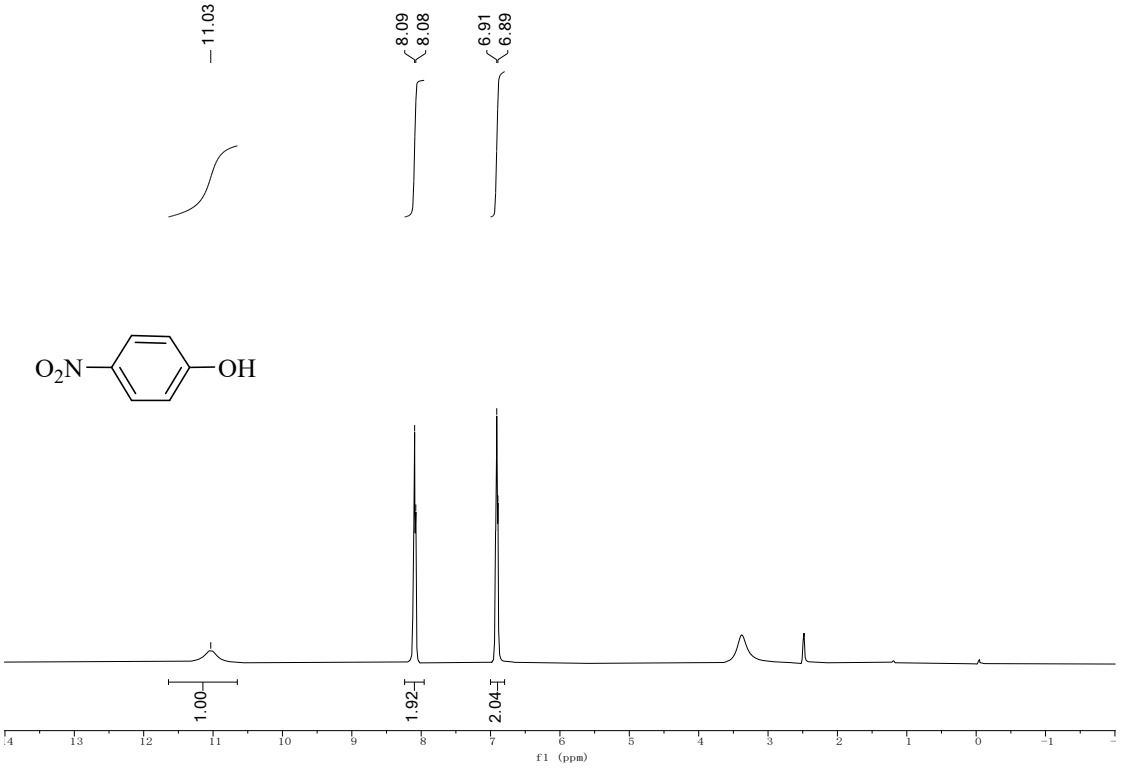


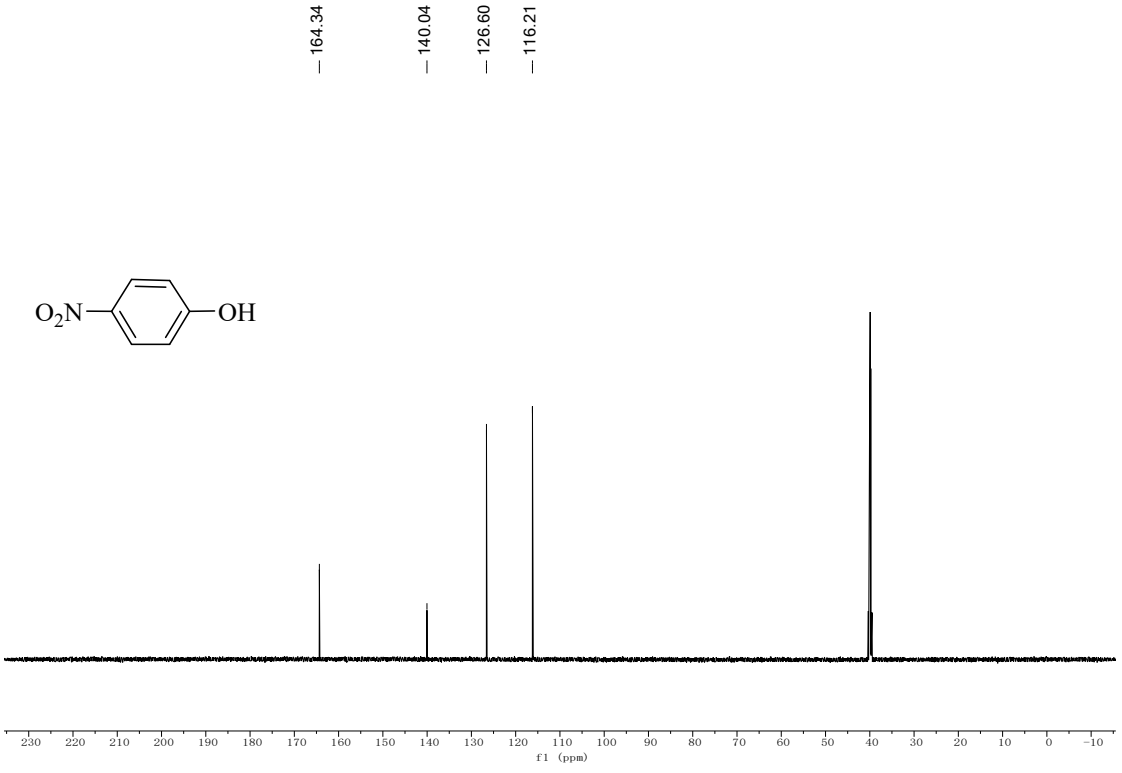
1H and 13C Spectra of compound 7 (DMSO)



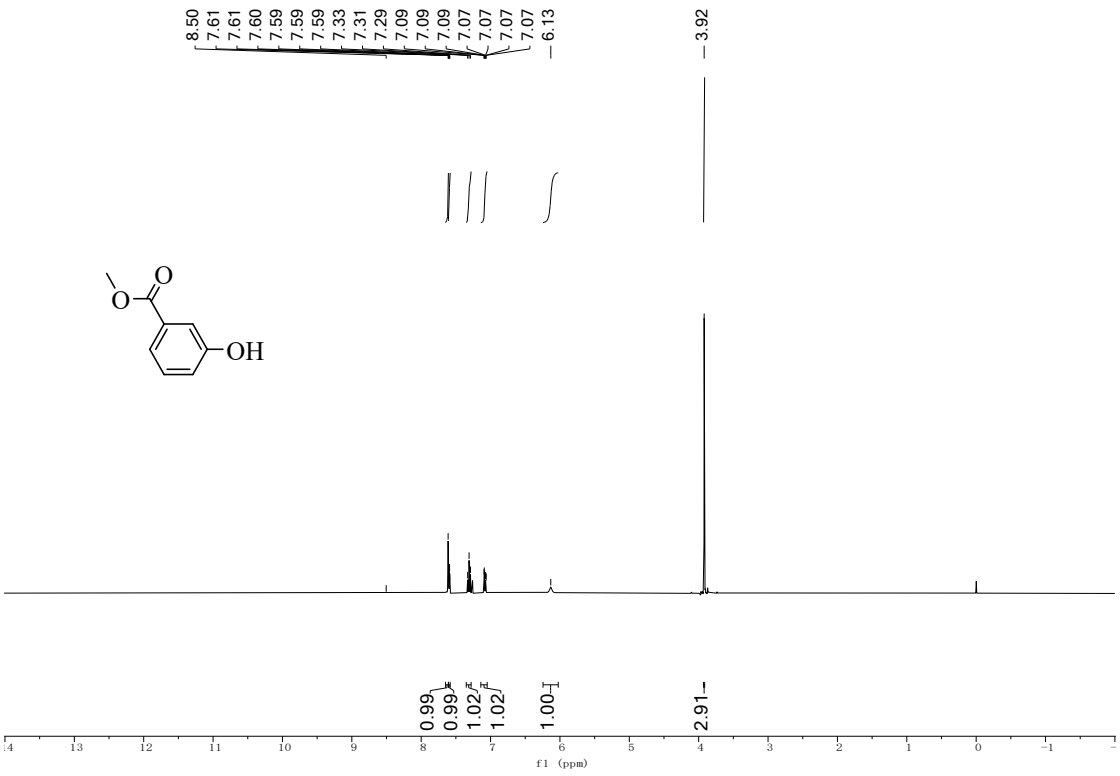


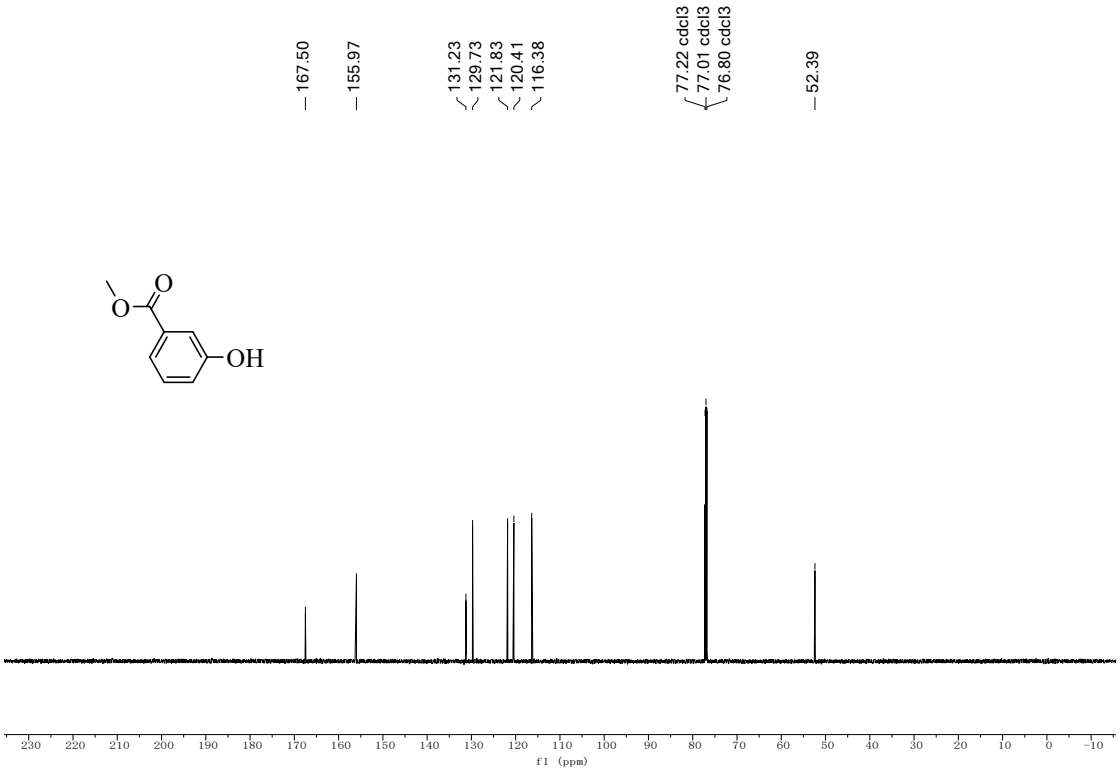
1H and 13C Spectra of compound 8 (DMSO)



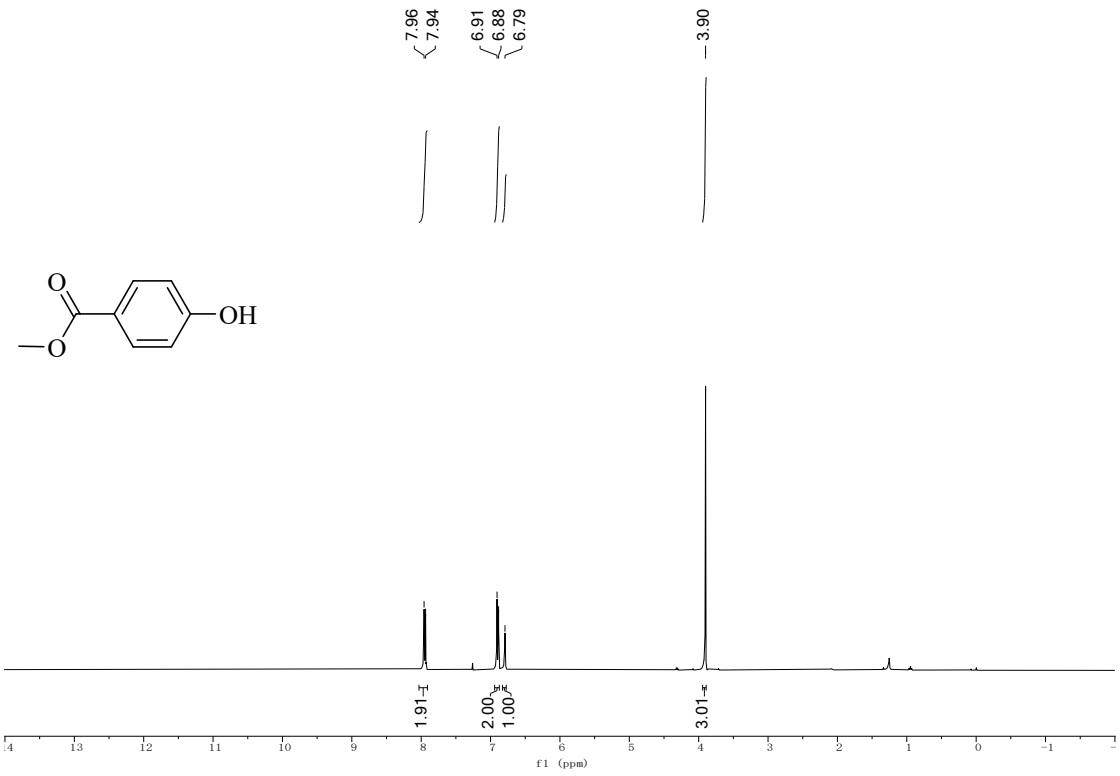


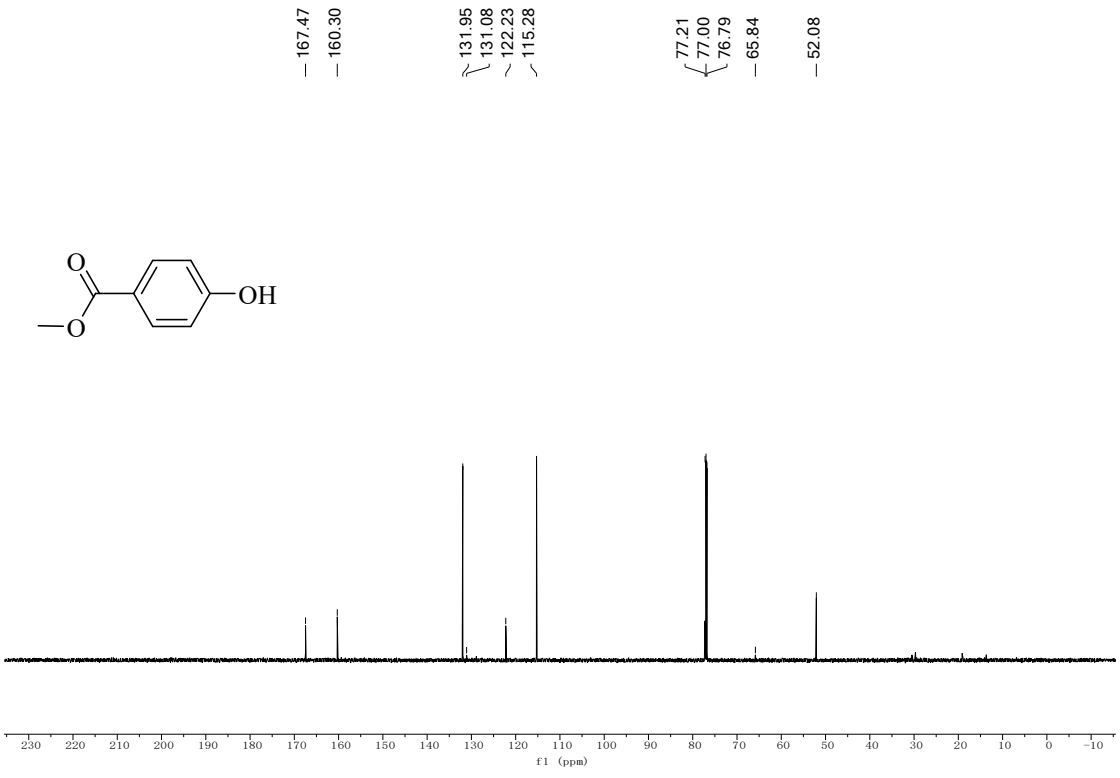
1H and 13C Spectra of compound 9 ($CDCl_3$)



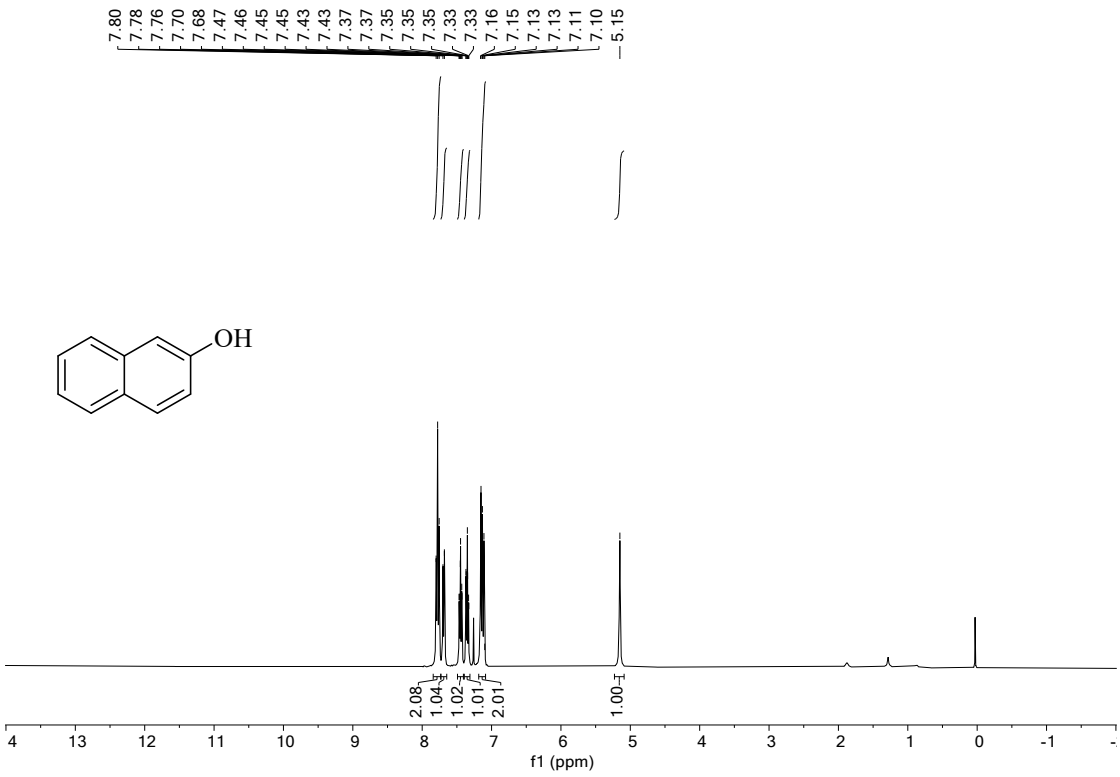


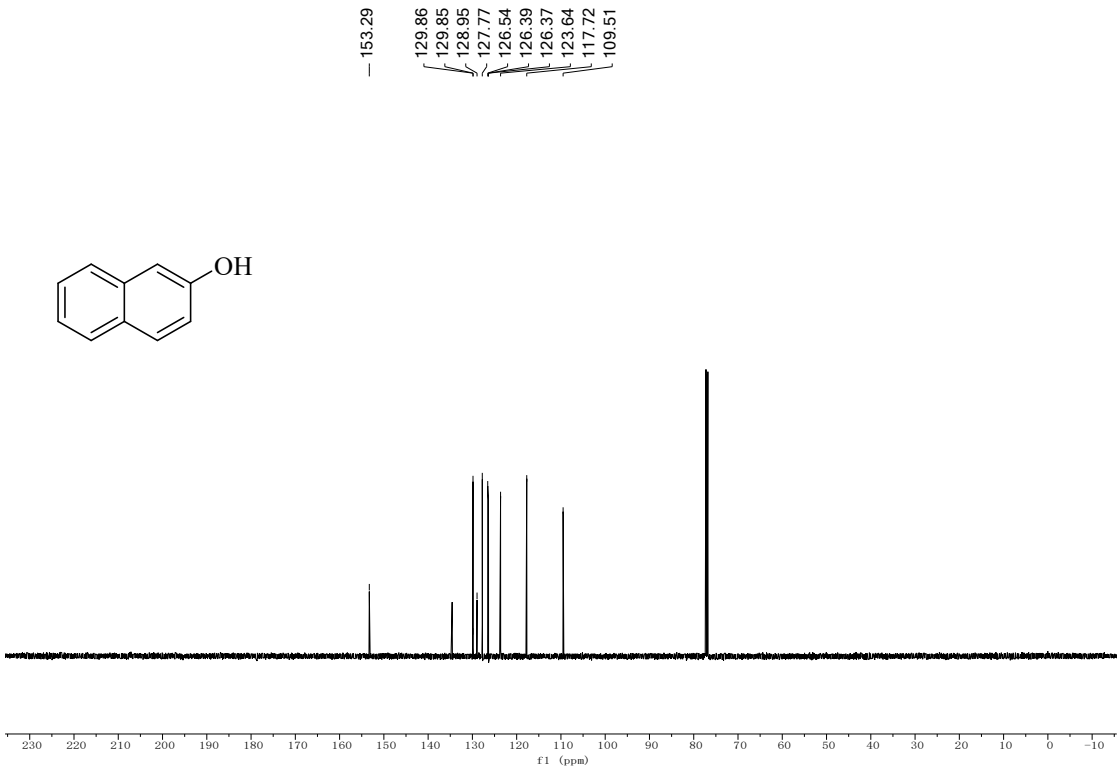
1H and 13C Spectra of compound 10 ($CDCl_3$)





1H and 13C Spectra of compound 11 ($CDCl_3$)





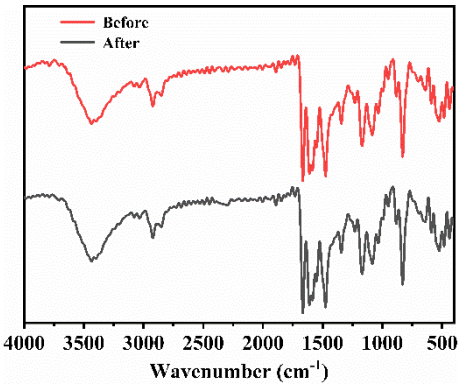


Fig. S5 FT-IR diagram before and after the reaction.

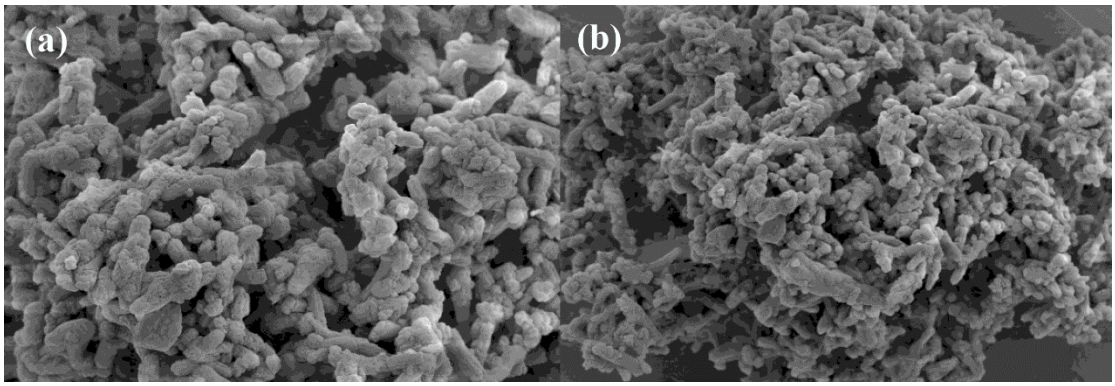


Fig. S6 SEM before **(a)** and **(b)** SEM after the reaction.