An electron-deficient MOF as efficient electron-transfer catalyst for selective oxidative carbon-carbon coupling of 2,6-di-*tert*-butylphenol

*Teng Liu, Xianfu Shen, Zhengfen Liu, Feng Zhang and Jian-Jun Liu**

College of Chemistry and Environmental Science, Qujing Normal University, Qujing 655011, China

E-mail: jjliu302@163.com

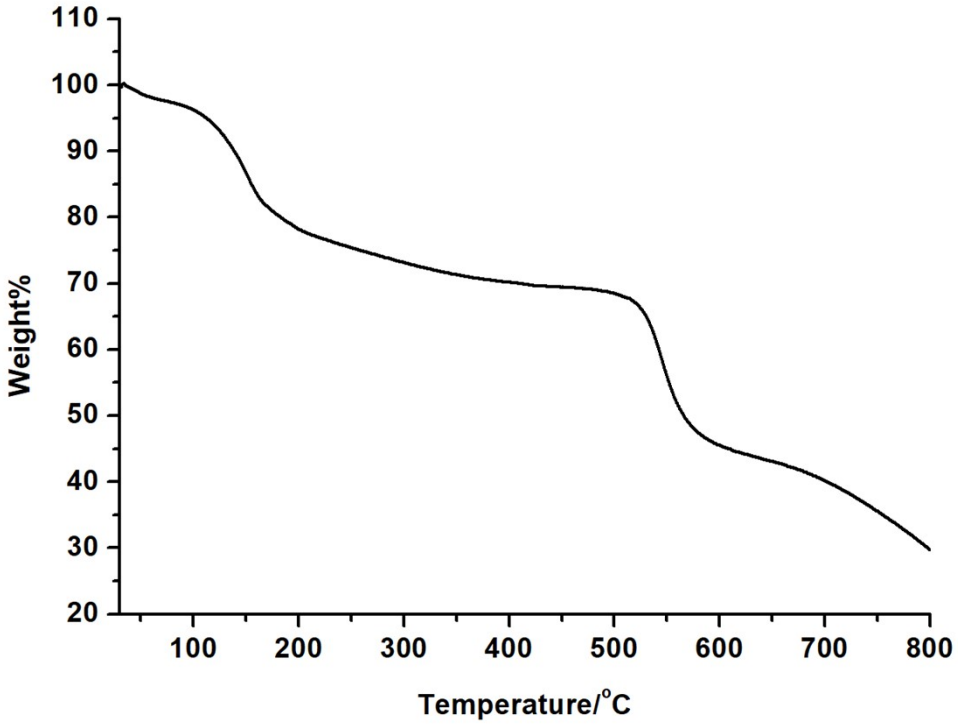


Fig. S1. TGA curve of MOF **1** under N_2 atmosphere with a heating rate of 10 °C/min.

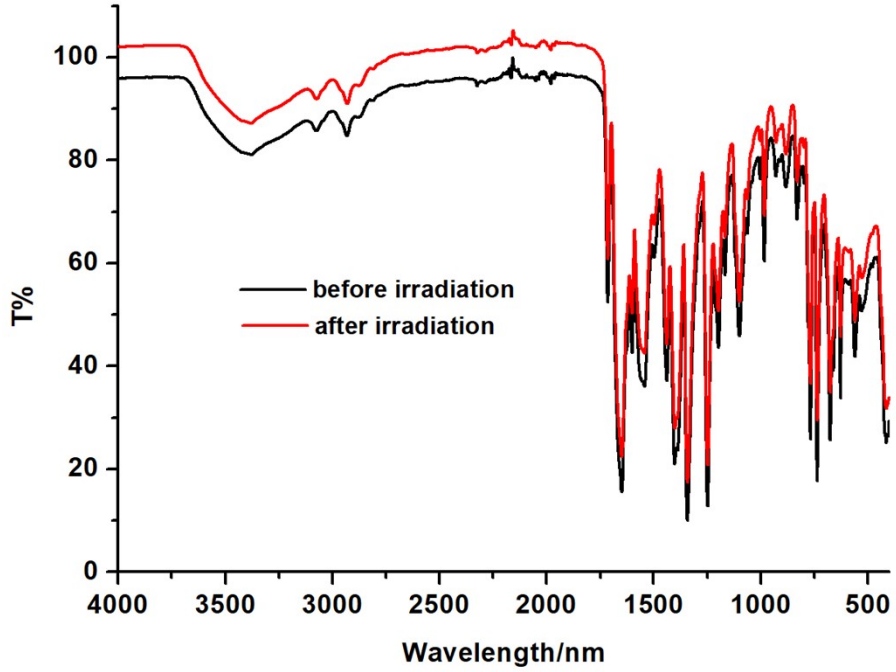


Fig. S2. Infrared spectrum of MOF 1 before and after irradiation.

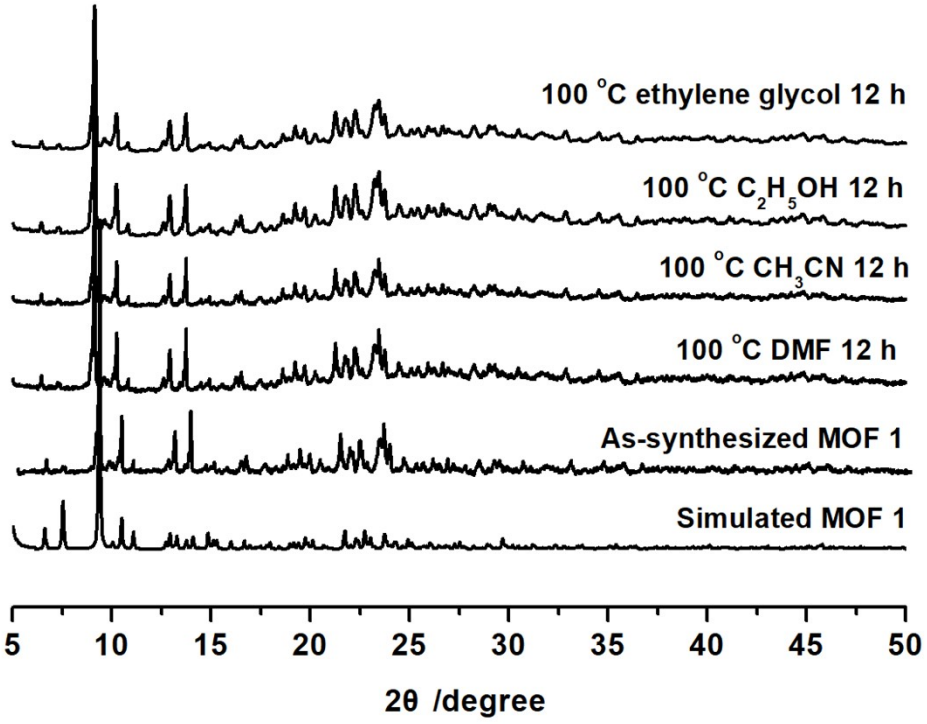
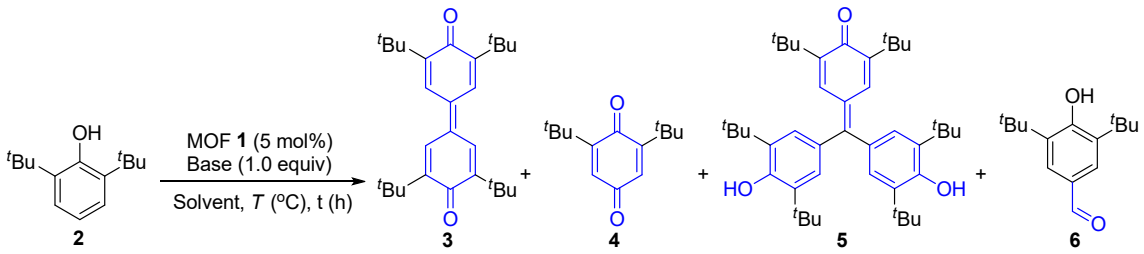


Fig. S3. XRD patterns of MOF **1** treated in different solvents.

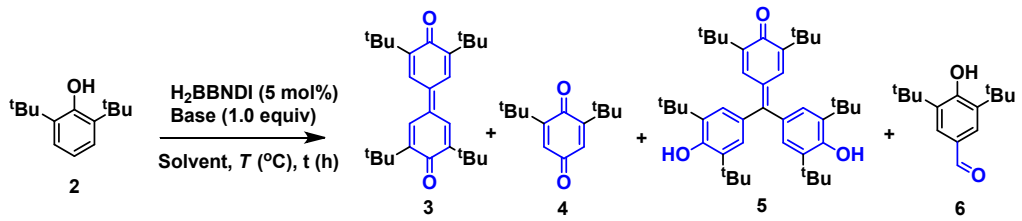
Table S1. Test the catalytic activity of MOF 1 for the transformation of 2, 6-di-*tert*-butylphenol[a]



Entry	Base	Solvent	*T* (°C)	t (h)	**3**[b]	**4**[b]	**5**[b]	**6**[b]
1	KOH	MeOH	45	24	45%	12%	-	-
2	NaOH	MeOH	45	24	38%	13%	-	-
3	KO^{t}Bu	MeOH	45	24	28%	43%	-	-
4	Cs_2CO_3	MeOH	45	24	29%	15%	-	-
5	DABCO	MeOH	45	24	31%	6%	-	-
6	DBU	MeOH	45	24	28%	25%	-	-
7	KO^{t}Bu	MeOH	65	24	21%	53%	-	-
8	KO^{t}Bu	MeOH	85	24	23%	51%	-	-
9	KO^{t}Bu	MeOH	65	36	23%	63%	-	-
10	KO^{t}Bu	MeOH	65	48	23%	72%	-	-
11	**KO^{t}Bu**	**MeOH**	**65**	**60**	**19%**	**75%**	-	-
12	KO^{t}Bu	MeOH	65	72	19%	75%	-	-
13	KOH	MeOH	65	24	53%	18%	-	-
14	KOH	MeOH	85	24	57%	19%	-	-
15	KOH	$HOCH_2CH_2OH$	120	24	71%	12%	15%	-
16	NaOH	$HOCH_2CH_2OH$	120	24	65%	16%	14%	-
17	KO^{t}Bu	$HOCH_2CH_2OH$	120	24	78%	5%	-	-
18	**DABCO**	**$HOCH_2CH_2OH$**	**120**	**24**	**93%**	**Trace**	**-**	**-**
19	DMAP	$HOCH_2CH_2OH$	120	24	91%	Trace	-	-
20	DBU	$HOCH_2CH_2OH$	120	24	91%	Trace	-	-
21	Cs_2CO_3	$HOCH_2CH_2OH$	120	24	85%	8%	-	-
22	K_2CO_3	$HOCH_2CH_2OH$	120	24	66%	-	25%	6%
23	K_2CO_3	$HOCH_2CH_2OH$	120	36	48%	-	39%	8%
24	K_2CO_3	$HOCH_2CH_2OH$	120	48	32%	-	45%	10%
25	K_2CO_3	$HOCH_2CH_2OH$	120	60	25%	-	58%	11%
26	K_2CO_3	$HOCH_2CH_2OH$	130	60	18%	-	65%	11%
27	K_2CO_3	$HOCH_2CH_2OH$	140	60	11%	-	78%	9%
28	**K_2CO_3**	**$HOCH_2CH_2OH$**	**150**	**60**	**8%**	-	**82%**	**6%**
29	K_2CO_3	$HOCH_2CH_2OH$	160	60	7%	-	82%	7%

[a]The reaction was performed with **2** (1.0 mmol), Base (1.0 mmol) and MOF 1 (5 mol%), and exposed in air. [b]Isolated yield based on the starting material **2**.

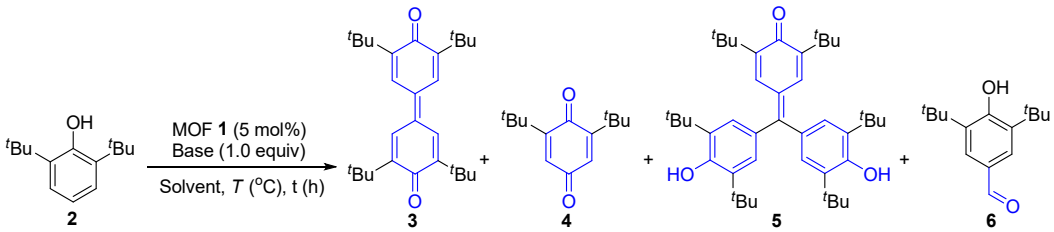
Table S2. Optimal conditions of H_2BBNDI for the transformation of 2, 6-di-*tert*-butylphenol[a]



Entry	Base	Solvent	*T* (°C)	t (h)	**3**[b]	**4**[b]	**5**[b]	**6**[b]
1	KO^{t}Bu	MeOH	65	60	12%	16%	-	-
2	DABCO	EG	120	24	<5%	<5%	-	-
3	K_2CO_3	EG	150	60	7%	<5%	12%	-

[a]The reaction was performed with **2** (1.0 mmol), Base (1.0 mmol) and H_2BBNDI (5 mol%), and exposed in air. [b]Isolated yield based on the starting material **2**.

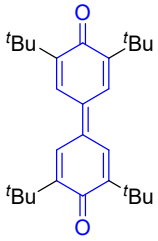
Table S3. The recycle experiments of MOF 1 for the transformation of 2, 6-di-*tert*-butylphenol.



Runs	Base	Solvent	*T* (°C)	t (h)	3[b]	4[b]	5[b]	6[b]
1	KO^{t}Bu	MeOH	65	60	23%	75%	-	-
2	KO^{t}Bu	MeOH	65	60	20%	71%	-	-
3	KO^{t}Bu	MeOH	65	60	19%	68%	-	-
1	DABCO	EG	120	24	93%	<5%	-	-
2	DABCO	EG	120	24	89%	<5%	-	-
3	DABCO	EG	120	24	86%	<5%	-	-
1	K_2CO_3	EG	150	60	8%	-	82%	6%
2	K_2CO_3	EG	150	60	<5%	-	78%	10%
3	K_2CO_3	EG	150	60	<5%	-	75%	12%

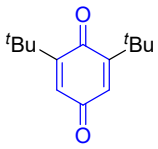
[a]The reaction was performed with **2** (1.0 mmol), Base (1.0 mmol) and MOF 1 (5 mol%), and exposed in air. [b]Isolated yield based on the starting material **2**.

3,3',5,5'-tetra-*tert*-butyl-[1,1'-bi(cyclohexylidene)]-2,2',5,5'-tetraene-4,4'-dione (3)



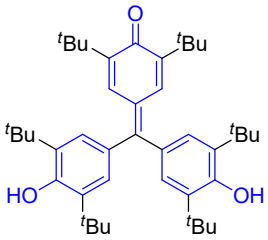
Orange solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 4H, 4CH), 1.37 (s, 36H, $12CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.5, 150.4, 136.1, 126.1, 36.0, 29.6.

2,6-di-*tert*-butylcyclohexa-2,5-diene-1,4-dione (4)



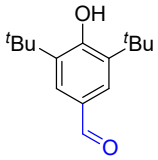
Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.43 (s, 2H, 2CH), 1.20 (s, 18H, $6CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 187.8, 157.9, 130.2, 35.6, 29.4.

4-(bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)methylene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (5)

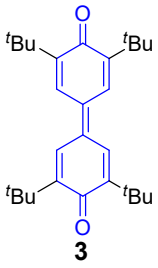


Orange solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (s, 2H, 2CH), 7.06 (s, 4H, 4ArH), 5.54 (br, 2H, 2ArOH), 1.59 (s, 36H, $12CH_3$), 1.30 (s, 18H, $6CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.01, 160.6, 155.7, 145.6, 134.9, 133.6, 131.9, 131.1, 35.3, 34.4, 30.4, 29.7.

3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (6)



Yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1H, CHO), 7.73 (s, 2H, 2ArH), 5.87 (s, 1H, ArOH), 1.48 (s, 18H, $6CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 159.7, 136.5, 128.7, 127.7, 34.4, 30.1.



3

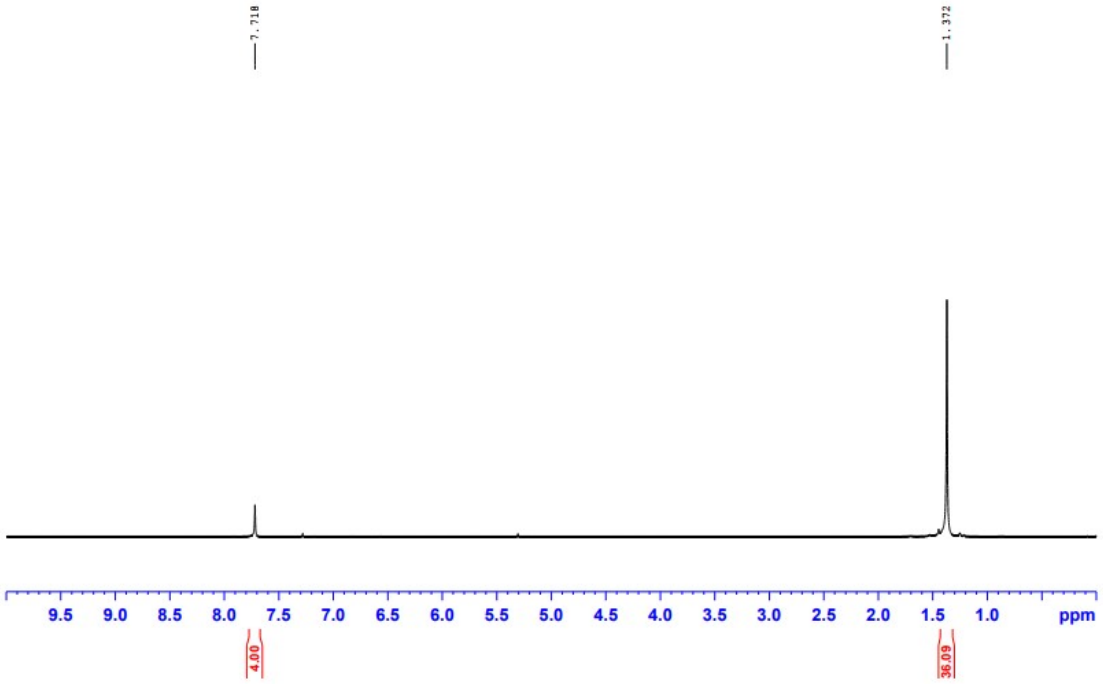


Fig. S4. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **3**

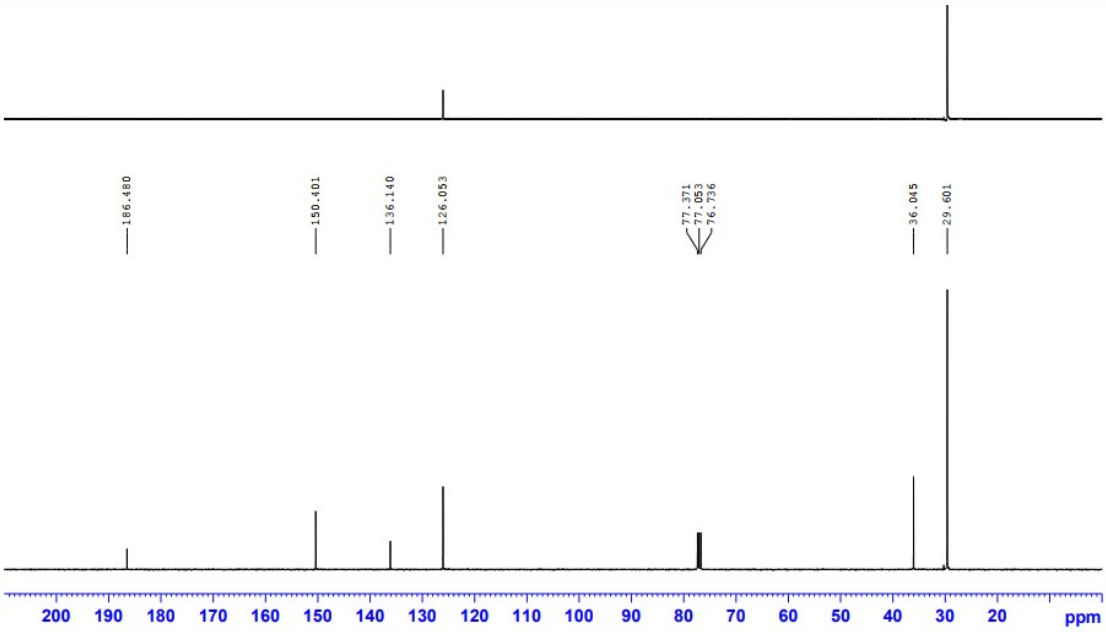
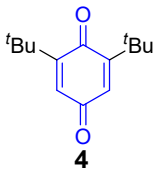


Fig. S5. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **3**



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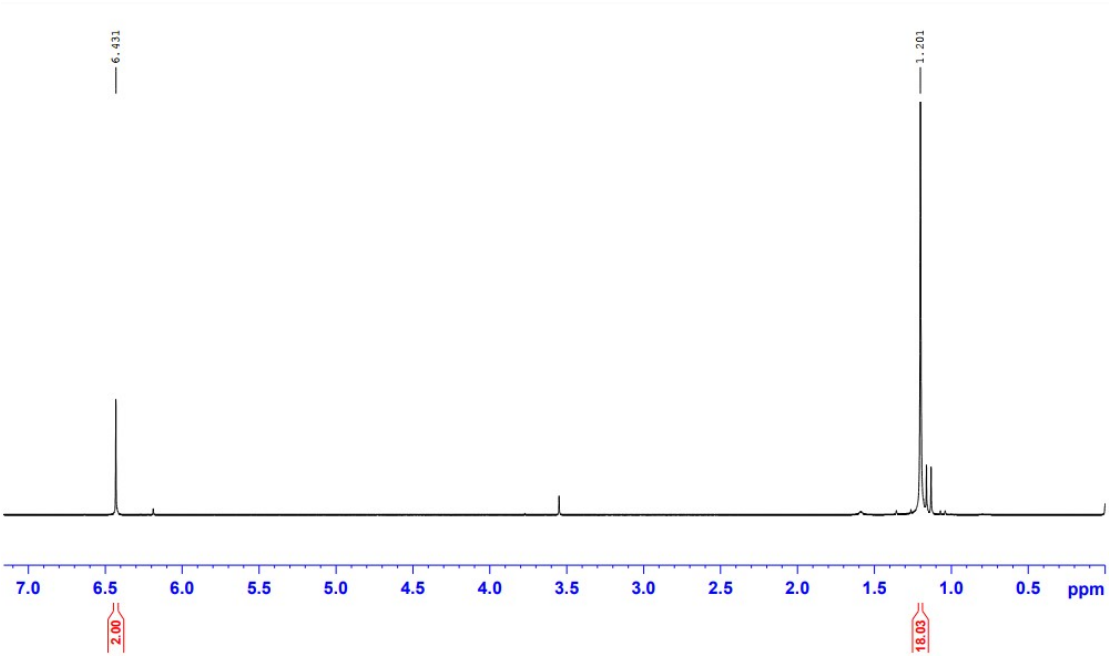


Fig. S6. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **4**

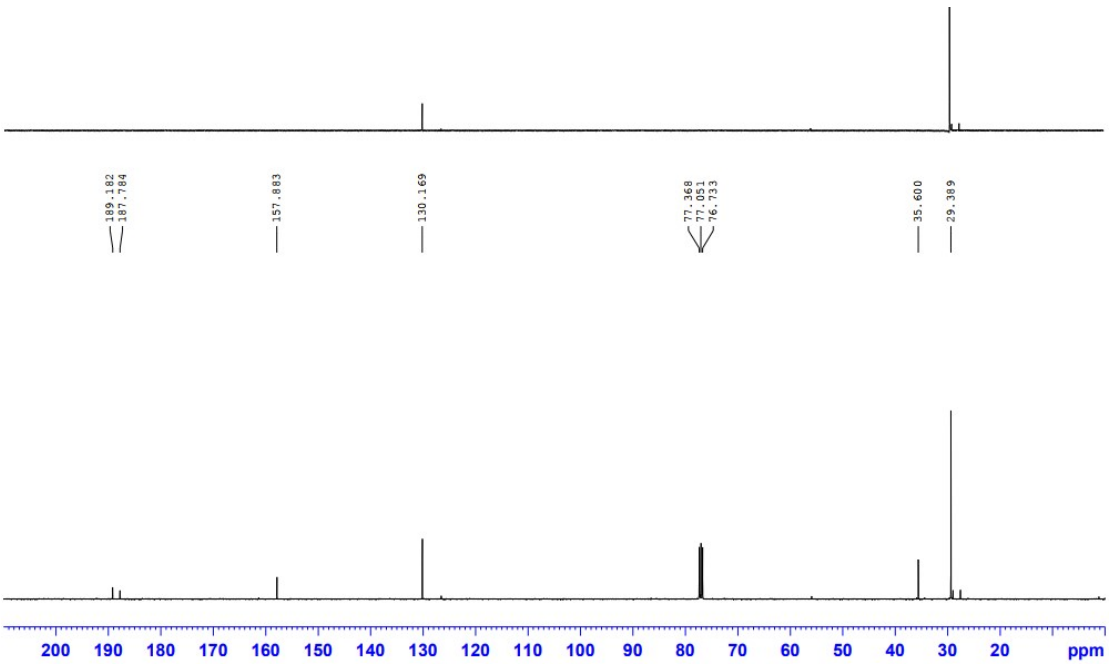
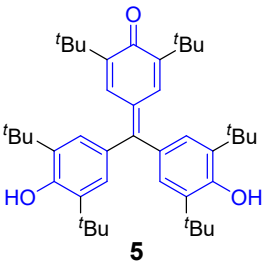


Fig. S7. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **4**



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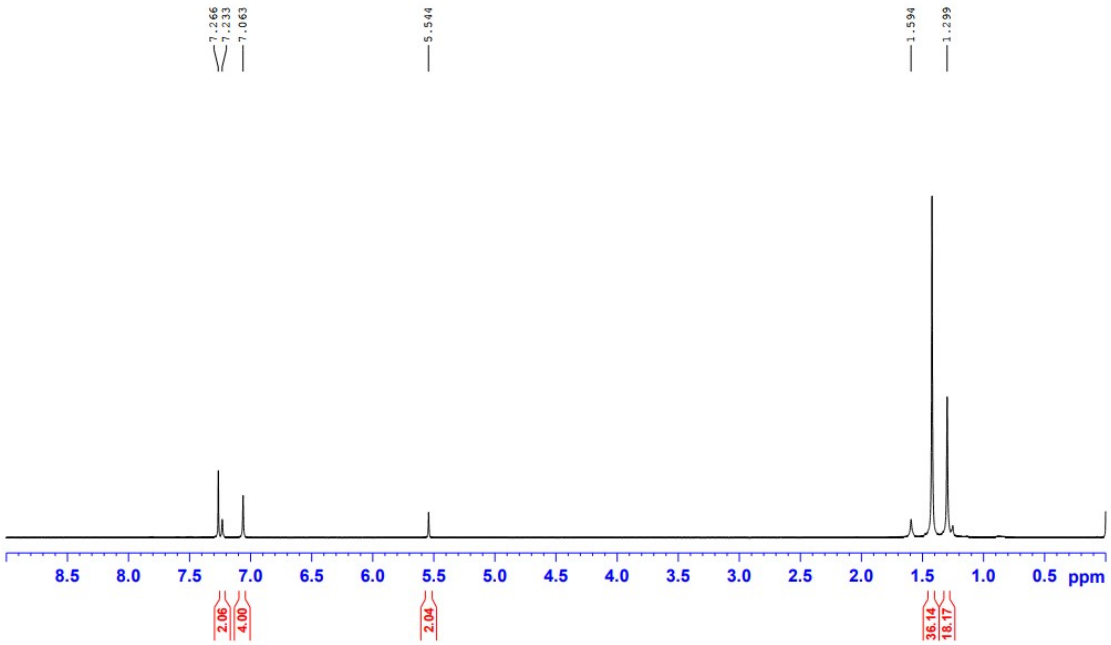

Fig. S8. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **5**

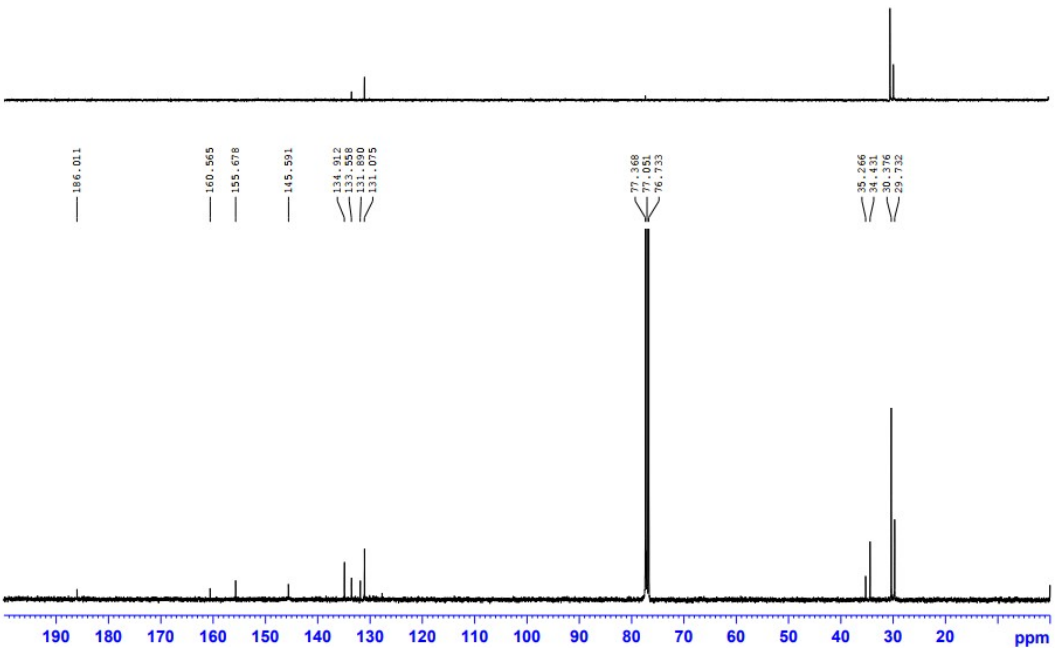

Fig. S9. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **5**

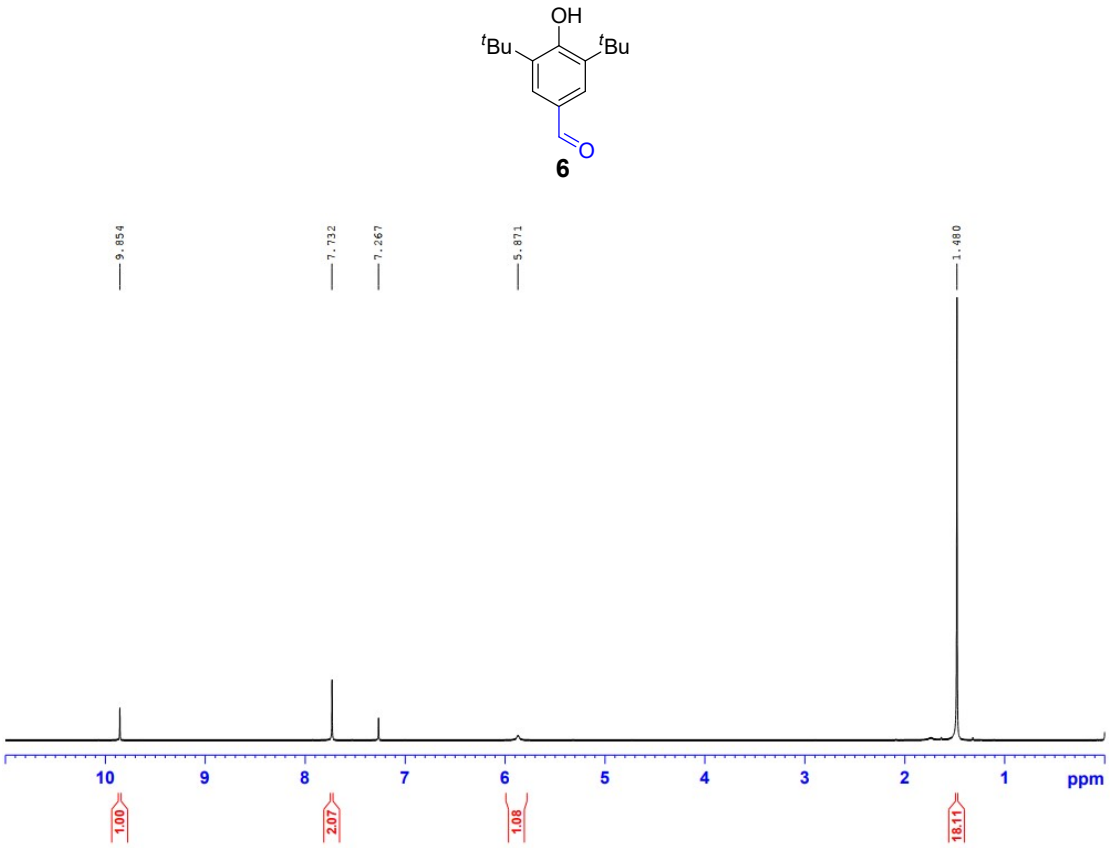

Fig. S10. ^{1}H NMR (400MHz, $CDCl_3$) spectra of compound **6**

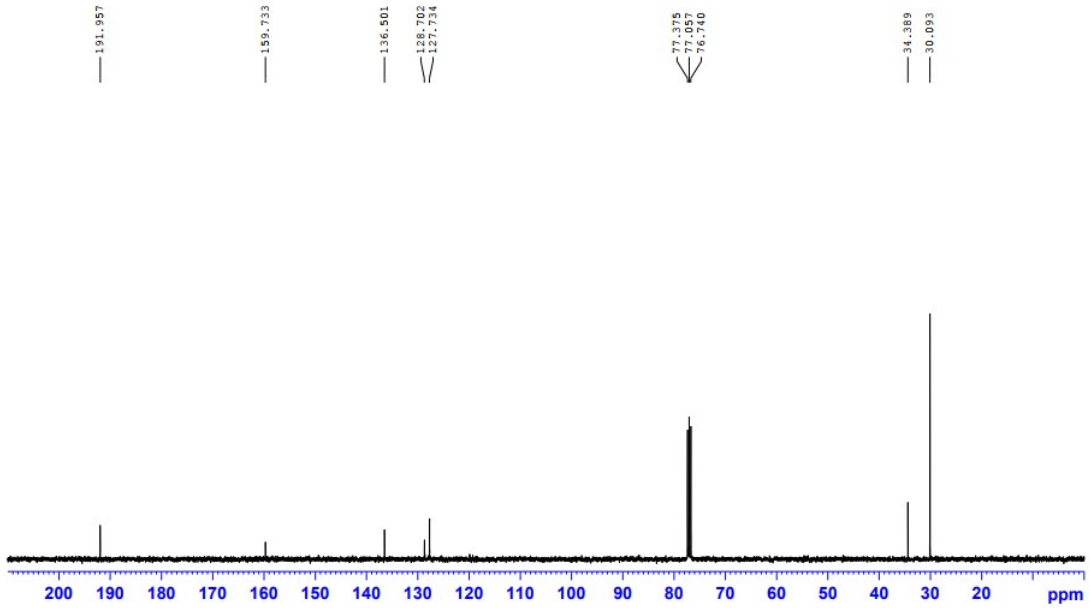

Fig. S11. ^{13}C NMR (100MHz, $CDCl_3$) spectra of compound **6**