Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Solvent-Switchable Regioselective 1,2- or 1,6-Addition of Quinones with Boronic Acids

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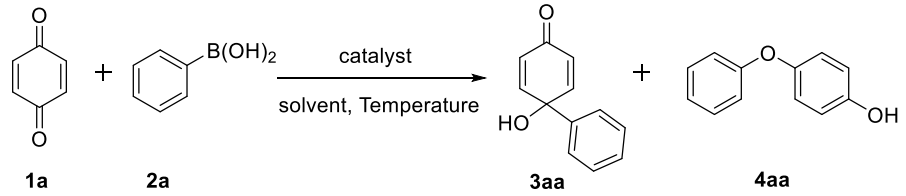
1. General information

All commercially available reagents were used without further purification unless otherwise stated. Melting points were recorded on an EZ-melt MPA120 (Stanford Research Systems, Inc., USA) and are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz and 100 MHz, respectively) with $CDCl_3$ as the solvent and TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.25 for ^{1}H and 77.05 for ^{13}C, and to DMSO-d_6 with 2.50 for ^{1}H and 39.47 for ^{13}C. Coupling constants J are reported in Hz. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized under ultraviolet light. Gas chromatography-mass spectrometry (GC-MS) was performed on Agilent 7890A/5975C and gas chromatograms (GC) were recorded on Agilent 7890A. High-resolution mass spectra were recorded under electron impact (70 eV) condition using a MicroMass GCT CA 055 instrument. High performance liquid chromatograms (HPLC) were recorded on Agilent 1260 Infinity.

2. Experimental section

2.1 Experimental optimization



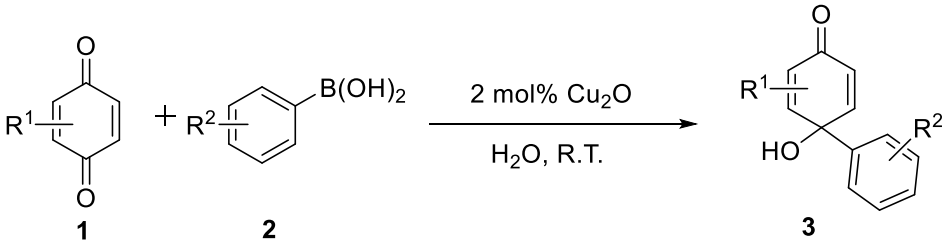
1a 2a 3aa 4aa

Entry[a]	Catalyst	Solvent	temp. (℃)	Yield[b] (%)	
				3aa	4aa
1	CuCl	H_2O	25	37	0
2	$CuCl_2·2H_2O$	H_2O	25	8	0
3	CuBr	H_2O	25	42	0
4	$CuBr_2$	H_2O	25	12	0
5	CuI	H_2O	25	35	0
6	CH_3COOCu	H_2O	25	7	0
7	$Cu(CH_3COO)_2·H_2O$	H_2O	25	< 5	0
8	$CuSO_4$	H_2O	25	< 5	0
9	$Cu(acac)_2$	H_2O	25	< 5	0
10	Cu	H_2O	25	47	0
11	CuO	H_2O	25	38	0
12	Cu_2O	H_2O	25	86	0
13	$Cu(OH)_2$	H_2O	25	80	0
14	$Cu_2(OH)_2CO_3$	H_2O	25	78	0
15	$CuFe_2O_4$	H_2O	25	0	0
16	Cu_2O	MeOH	25	8	81
17	Cu_2O	EtOH	25	< 5	12
18	Cu_2O	*t*-BuOH	25	< 5	< 5
19	Cu_2O	*i*-PrOH	25	< 5	< 5
20	Cu_2O	CH_3CN	25	0	0
21	Cu_2O	DMF	25	0	0
22	Cu_2O	DMSO	25	0	0
23	Cu_2O	Toluene	25	0	0
24	Cu_2O	1,4-Dioxane	25	0	0
25	Cu_2O	THF	25	0	0
26	Cu_2O	DCM	25	0	0
27	Cu_2O	H_2O	0	40	0
28	Cu_2O	H_2O	40	70	6
29	Cu_2O	H_2O	60	63	12
30	Cu_2O (2 mol%)	H_2O	25	88 (82)	0
31	Cu_2O (1 mol%)	H_2O	25	58	0
32	CuCl	MeOH	25	< 5	20
33	$CuCl_2·2H_2O$	MeOH	25	< 5	10

34	CuBr	MeOH	25	< 5	31
35	$CuBr_2$	MeOH	25	< 5	18
36	CuI	MeOH	25	< 5	32
37	CH_3COOCu	MeOH	25	< 5	20
38	$Cu(CH_3COO)_2·H_2O$	MeOH	25	< 5	13
39	$CuSO_4$	MeOH	25	< 5	< 5
40	$Cu(acac)_2$	MeOH	25	< 5	10
41	Cu	MeOH	25	10	65
42	CuO	MeOH	25	6	61
43	$Cu(OH)_2$	MeOH	25	6	75
44	$Cu_2(OH)_2CO_3$	MeOH	25	8	70
45	$CuFe_2O_4$	MeOH	25	0	91 (86)
46	Cu_2O	H_2O : MeOH = 3 : 1	25	70	< 5
47	Cu_2O	H_2O : MeOH = 1 : 1	25	50	< 5
48	Cu_2O	H_2O : MeOH = 1 : 3	25	38	7
49	$CuFe_2O_4$	H_2O : MeOH = 3 : 1	25	0	0
50	$CuFe_2O_4$	H_2O : MeOH = 1 : 1	25	0	0
51	$CuFe_2O_4$	H_2O : MeOH = 1 : 3	25	0	0

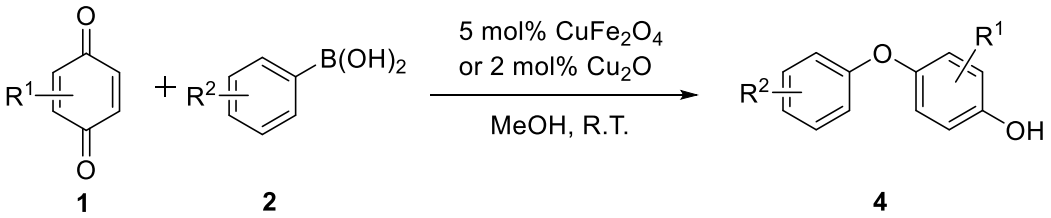
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), catalyst (0.05 mmol), solvent (2.0 mL).
[b] Yields were determined by HPLC analysis using biphenyl as internal standard; isolated yield in parenthesis.

2.2 General procedure for 1,2-addition of quinones with boronic acids



A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1** (1.0 mmol), organic boronic acid **2** (1.2 mmol), Cu_2O (2.9 mg, 0.02 mmol, 2.0 mol%) and H_2O (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24-36 h. Upon completion, the mixture was diluted with water (2.0 mL) and then extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using ethyl acetate and dichloromethane as the eluent to obtain the desired product. The products were further characterized by HRMS (EI), ^{1}H NMR, and ^{13}C NMR.

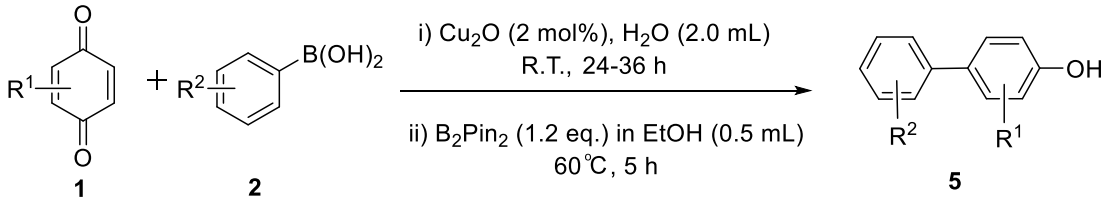
2.3 General procedure for 1,6-addition of quinones with boronic acids



1 **2** **4**

A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1** (1.0 mmol), organic boronic acid **2** (1.2 mmol), $CuFe_2O_4$ (12.0 mg, 0.05 mmol, 5.0 mol%) or Cu_2O (2.9 mg, 0.02 mmol, 2.0 mol%) and MeOH (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24-36 h. Upon completion, the mixture was diluted with 5 mL of ethyl acetate, filtered through a celite pad and washed with 10 mL of ethyl acetate. The filtrate was collected and concentrated. The residue was purified by silica gel column chromatography using ethyl acetate and petroleum ether as the eluent to obtain the desired product. The products were further characterized by HRMS (EI), ^{1}H NMR, and ^{13}C NMR.

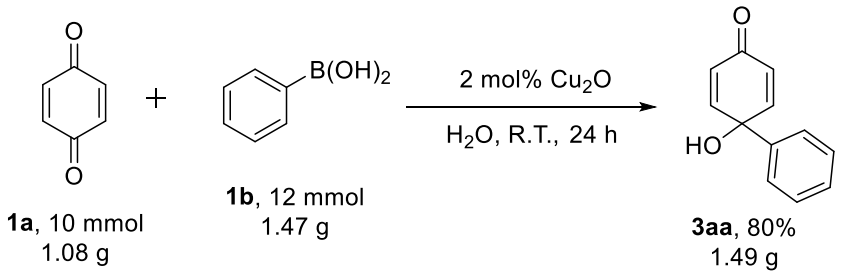
2.4 General procedure for one-pot construction of 4-phenylphenols



1 **2** **5**

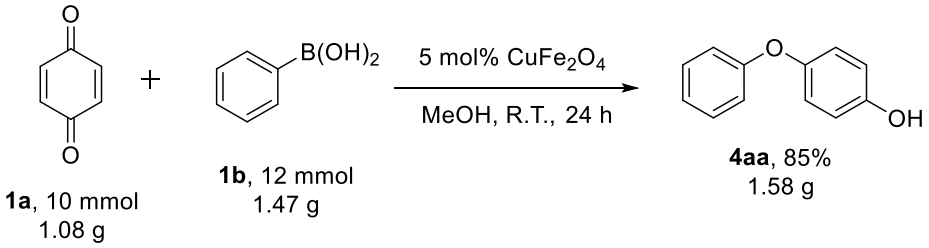
A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1** (1.0 mmol), organic boronic acid **2** (1.2 mmol), Cu_2O (2.9 mg, 0.02 mmol, 2.0 mol%) and H_2O (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24-36 h. Then B_2pin_2 (1.2 mmol) dissolved in EtOH (0.5 mL) were added, the reaction mixture was stirred at 60 ℃ for 5 h. Upon completion, the mixture was diluted with water (2.0 mL) and then extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using ethyl acetate and petroleum ether as the eluent to obtain the desired product. The products were further characterized by HRMS (EI), ^{1}H NMR, and ^{13}C NMR.

2.5 Gram scale-up and transformation of products

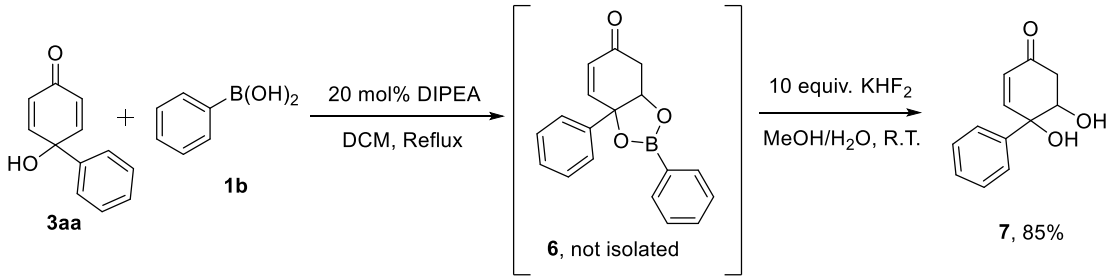


A 50 mL round-bottomed flask equipped with a stirring bar was charged with 1,4-benzoquinone **1a** (1.08 g, 10.0 mmol), phenylboronic acid **1b** (1.47 g, 12.0 mmol), Cu_2O (28.6 mg, 0.2 mmol, 2.0 mol%) and H_2O (20.0 mL). The reaction mixture was stirred at 25 ℃ for 24 h. Upon completion, the mixture was diluted with water (20.0 mL) and then extracted with ethyl acetate (25 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered,

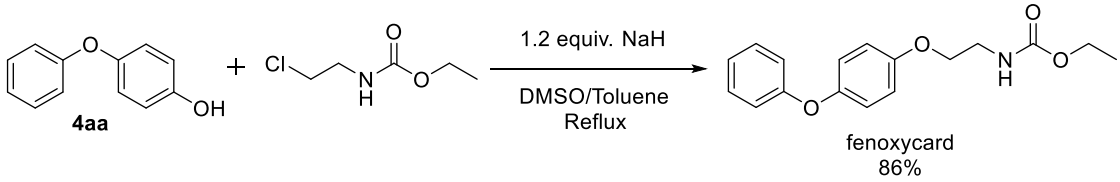
concentrated under reduced pressure, and purified by silica gel column chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent to obtain the desired product **3aa** as yellow solid (1.49 g, 80% yield). The analytical data of the gram-scale reaction of **3aa** were consistent with those of the 1.0 mmol scale experiment.



A 50 mL round-bottomed flask equipped with a stirring bar was charged with 1,4-benzoquinone **1a** (1.08 g, 10.0 mmol), phenylboronic acid **1b** (1.47 g, 12.0 mmol), $CuFe_2O_4$ (119.6 mg, 0.5 mmol, 5.0 mol%) and MeOH (20.0 mL). The reaction mixture was stirred at 25 ℃ for 24 h. Upon completion, the mixture was diluted with 25 mL of ethyl acetate, filtered through a celite pad and washed with 25 mL of ethyl acetate. The filtrate was collected and concentrated. The residue was purified by silica gel column chromatography using PE/EtOAc (5/1) as the eluent to obtain the desired product **4aa** as white solid (1.58 g, 85% yield). The analytical data of the gram-scale reaction of **4aa** were consistent with those of the 1.0 mmol scale experiment.

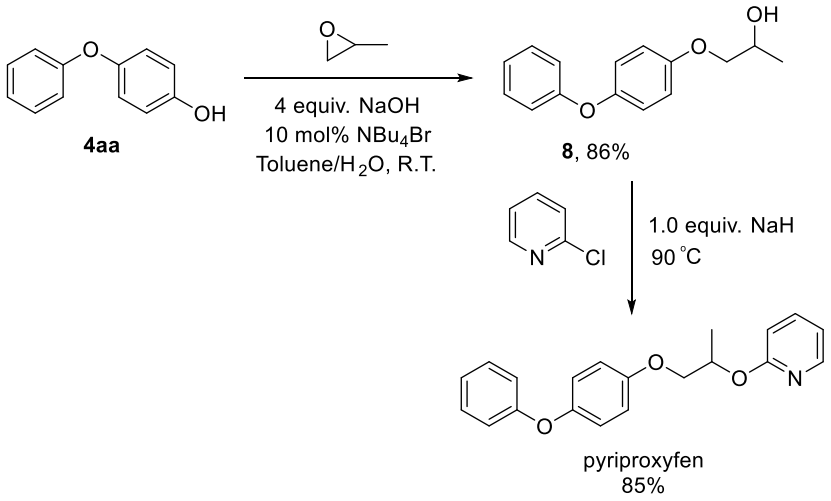


To a 10 mL round-bottomed flask was added **3aa** (93.1 mg, 0.5 mmol), phenylboronic acid **1b** (91.4 mg, 0.75 mmol), DIPEA (12.9 mg, 0.1 mmol) and DCM (1.5 mL). The mixture was kept stirring at 40 ℃ for 2 h. Upon completion, the mixture was cooled to room temperature. To the mixture was added MeOH/H_2O (1/1, 2.0 mL), and then KHF_2 (390.5 mg, 5.0 mmol, 10 eq.) was added and the mixture was stirred at 25 ℃ for 30 min. The aqueous phase was separated and collected, and the organic phase was evaporated and then re-dissolved in *n*-hexanes. The mixture was then washed MeOH/H_2O (1/1) twice and the aqueous phase was combined. The combined aqueous layers were then evaporated and purified by silica gel column chromatography using DCM/EtOAc (3/1) as the eluent to obtain the diol **7** as white oil (86.8 mg, 85% yield).



To a 10 mL round-bottomed flask was added **4aa** (186.2 mg, 1.0 mmol), 60% NaH (48.0 mg, 1.2 mmol) and DMSO/Toluene (1/1, 1.0 mL). After a solution of chloroethyl

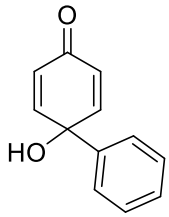
carbamate (227.4 mg, 1.5 mmol, 1.5 equiv.) in Toluene (1.0 mL) was added and the mixture was stirred at reflux temperature for 4 h. Upon completion, the mixture was cooled to room temperature. And then the mixture was diluted with water (2.0 mL) and extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using PE/EtOAc (5/1) as the eluent to obtain fenoxycard as white solid (259.2 mg, 86% yield). [1]



To a 10 mL round-bottomed flask was added **4aa** (186.2 mg, 1.0 mmol), propylene oxide (48.0 mg, 5.0 mmol), *n*Bu_4NBr (32.2 mg, 0.1 mmol), NaOH (160.0 mg, 5.0 mmol) and Toluene/H_2O (5/2, 2.0 mL). The reaction mixture was stirred at 25 ℃ for 2 d. Upon completion, the mixture was diluted with water (2.0 mL) and then extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using PE/EtOAc (5/1) as the eluent to obtain the intermediate **8** as white oil (210.1 mg, 86% yield).[1]

To a 10 mL round-bottomed flask was added **8** (122.1 mg, 0.5 mmol), 60% NaH (20.0 mg, 0.5 mmol) and 2-chloropyridin (2.0 mL) at 0 ℃. The reaction mixture was stirred at 90 ℃ for 8 h. Upon completion, the mixture was cooled to room temperature. And then the mixture was diluted with water (2.0 mL) and extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using PE/EtOAc (10/1) as the eluent to obtain pyriproxyfen as white solid (136.6 mg, 85% yield).[1]

3. Characterization of Products

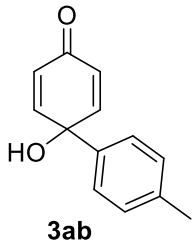


3aa

1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3aa was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3aa** was obtained in 82% yield (152.6 mg) as a yellow solid.

3aa: m.p. 107.8-108.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.30 (m, 3H), 6.90 (d, *J* = 9.6 Hz, 2H), 6.21 (d, *J* = 9.5 Hz, 2H), 2.90 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.23, 151.46 (2C), 138.71, 128.95 (2C), 128.41, 126.65 (2C), 125.32 (2C), 70.99; HRMS (EI-TOF, m/z) calcd for $C_{12}H_{10}O_2$ $[M]^+$ 186.0681, found 186.0679.

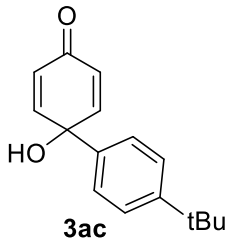


3ab

1-hydroxy-4'-methyl-[1,1'-biphenyl]-4(*1H*)-one

3ab was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3ab** was obtained in 72% yield (144.2 mg) as a white solid.

3ab: m.p. 114.2-115.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, *J* = 8.2 Hz, 2H), 7.18 (m, *J* = 8.1 Hz, 2H), 6.92 – 6.85 (m, 2H), 6.23 – 6.15 (m, 2H), 3.08 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.16, 151.47 (2C), 138.31, 135.77, 129.64 (2C), 126.54 (2C), 125.24 (2C), 70.89, 21.09. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0838.

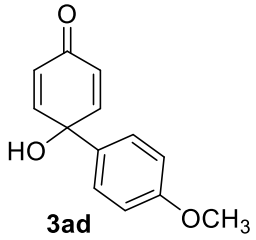


3ac

4'-(*tert*-butyl)-1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3ac was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ac** was obtained in 60% yield (145.4 mg) as a white solid.

3ac: m.p. 113.9-114.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 4H), 6.94 – 6.87 (m, 2H), 6.25 – 6.19 (m, 2H), 2.52 (s, 1H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.94, 151.59, 151.13 (2C), 135.71, 126.69 (2C), 125.92 (2C), 125.02, 70.91, 34.60, 31.27 (3C). HRMS (EI-TOF, m/z) calcd for $C_{16}H_{18}O_2$ $[M]^+$ 242.1307, found 242.1312.

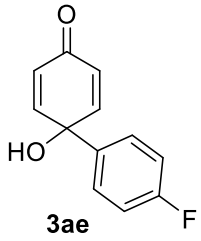


3ad

1-hydroxy-4'-methoxy-[1,1'-biphenyl]-4(*1H*)-one

3ad was synthesized following the general procedure. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent, **3ad** was obtained in 65% yield (140.6 mg) as a white solid.

3ad: m.p. 119.9-121.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, *J* = 8.4 Hz, 2H), 6.89 (m, *J* = 6.3 Hz, 4H), 6.16 (m, *J* = 9.9 Hz, 2H), 3.79 (s, 3H), 3.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.24, 159.62, 151.70 (2C), 130.66, 126.66 (2C), 126.33 (2C), 114.34 (2C), 70.63, 55.37. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_3$ $[M]^+$ 216.0786, found 216.0787.

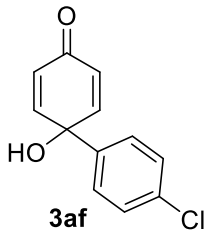


3ae

4'-fluoro-1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3ae was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3ae** was obtained in 88% yield (179.7 mg) as a white solid.

3ae: m.p. 125.4-126.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.09 – 7.02 (m, 2H), 6.92 – 6.86 (m, 2H), 6.22 – 6.14 (m, 2H), 3.55 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.00, 162.65 (d, J_{CF} = 247.6 Hz), 151.26 (2C), 134.45 (J_{CF}, *J* = 3.1 Hz), 127.25 (d, J_{CF} = 8.3 Hz, 2C), 126.66 (2C), 115.82 (d, J_{CF} = 21.7 Hz, 2C), 70.56. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9FO_2$ $[M]^+$ 204.0587, found 204.0589.

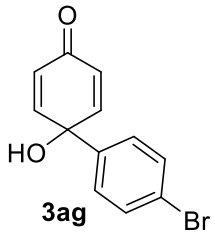


3af

4'-chloro-1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3af was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3af** was obtained in 83% yield (183.1 mg) as a white solid.

3af: m.p. 169.8-170.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.39 – 7.31 (m, 2H), 6.90 – 6.82 (m, 2H), 6.29 – 6.19 (m, 2H), 2.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.44, 150.31 (2C), 137.21, 134.43, 129.09 (2C), 127.13 (2C), 126.81 (2C), 70.67. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO_2$ $[M]^+$ 220.0291, found 220.0294; calcd for $C_{12}H_9{}^{37}ClO_2$ $[M]^+$ 222.0262, found 220.0264.

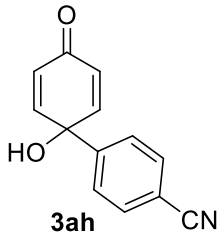


3ag

4'-bromo-1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3ag was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3ag** was obtained in 82% yield (217.4 mg) as a white solid.

3ag: m.p. 176.3-177.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.61 – 7.55 (m, 2H), 7.40 – 7.33 (m, 2H), 6.94 – 6.88 (m, 2H), 6.64 (s, 1H), 6.21 – 6.12 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.32, 152.03 (2C), 139.82, 131.49 (2C), 127.70 (2C), 125.77 (2C), 120.97, 69.75. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{79}BrO_2$ $[M]^+$ 263.9786, found 263.9791; calcd for $C_{12}H_9{}^{81}BrO_2$ $[M]^+$ 265.9765, found 265.9764.

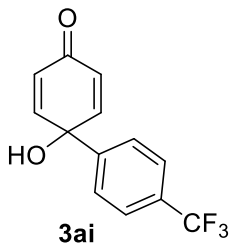


3ah

1'-hydroxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-4-carbonitrile

3ah was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ah** was obtained in 86% yield (181.6 mg) as a white solid.

3ah: m.p. 166.8-167.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 10.0 Hz, 2H), 6.80 (s, 1H), 6.20 (d, J = 10.0 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.17, 151.38 (2C), 145.92, 132.63 (2C), 126.51 (2C), 126.26 (2C), 118.57, 110.57, 69.99. HRMS (EI-TOF, m/z) calcd for $C_{13}H_9NO_2$ $[M]^+$ 211.0633, found 211.0634.

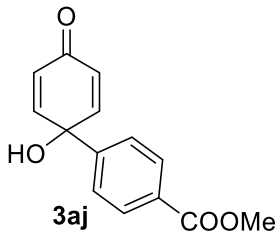


3ai

1-hydroxy-4'-(trifluoromethyl)-[1,1'-biphenyl]-4(*1H*)-one

3ai was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3ai** was obtained in 85% yield (216.1 mg) as a white solid.

3ai: m.p. 129.7-130.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (q, *J* = 8.6 Hz, 4H), 6.91 – 6.83 (m, 2H), 6.33 – 6.23 (m, 2H), 2.73 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.72, 150.51 (2C), 142.70 (d, J_{CF} = 1.1 Hz, 2C), 130.63 (q, J_{CF} = 32.4 Hz), 127.20 (2C), 125.88, 125.87 (q, J_{CF} = 3.9 Hz, 2C), 123.89 (q, J_{CF} = 272.1 Hz), 70.78. HRMS (EI-TOF, m/z) calcd for $C_{13}H_9F_3O_2$ $[M]^+$ 254.0555, found 254.0552.

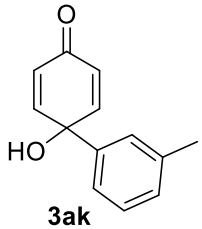


3aj

methyl 1'-hydroxy-4'-oxo-1',4'-dihydro-[1,1'-biphenyl]-4-carboxylate

3aj was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3aj** was obtained in 82% yield (200.3 mg) as a white solid.

3aj: m.p. 164.8-165.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 10.0 Hz, 2H), 6.25 (d, *J* = 10.0 Hz, 2H), 3.92 (s, 3H), 3.23 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.62, 166.70, 150.36 (2C), 143.76, 130.18 (2C), 130.10, 127.20 (2C), 125.47 (2C), 70.96, 52.30. HRMS (EI-TOF, m/z) calcd for $C_{14}H_{12}O_4$ $[M]^+$ 244.0736, found 244.0735.

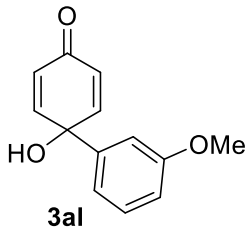


3ak

1-hydroxy-3'-methyl-[1,1'-biphenyl]-4(*1H*)-one

3ak was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ak** was obtained in 73% yield (146.2 mg) as a white solid.

3ak: m.p. 87.6-88.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 3H), 7.16 – 7.10 (m, 1H), 6.93 – 6.86 (m, 2H), 6.23 – 6.17 (m, 2H), 3.16 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.15, 151.34 (2C), 138.77, 138.65, 129.17, 128.87, 126.65 (2C), 125.87, 122.34, 70.97, 21.53. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0836.

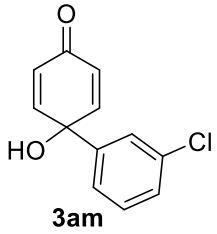


3al

1-hydroxy-3'-methoxy-[1,1'-biphenyl]-4(*1H*)-one

3al was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent, **3al** was obtained in 75% yield (162.2 mg) as a white solid.

3al: m.p. 103.6-104.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.08 – 7.05 (m, 1H), 7.03 – 6.99 (m, 1H), 6.92 – 6.87 (m, 2H), 6.22 – 6.16 (m, 2H), 3.80 (s, 3H), 3.27 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.06, 160.09, 151.08 (2C), 140.43, 129.99, 126.73 (2C), 117.59, 113.75, 111.13, 70.87, 55.36. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_3$ $[M]^+$ 216.0786, found 216.0785.

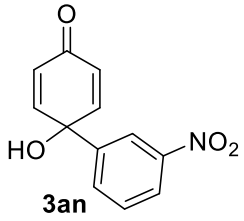


3am

3'-chloro-1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3am was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3am** was obtained in 80% yield (176.5 mg) as a white solid.

3am: m.p. 79.8-81.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 2.7, 1.4 Hz, 1H), 7.34 – 7.27 (m, 3H), 6.91 – 6.85 (m, 2H), 6.24 – 6.16 (m, 2H), 3.86 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.09, 151.03 (2C), 140.85, 134.94, 130.18, 128.56, 126.88 (2C), 125.69, 123.60, 70.59. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO_2$ $[M]^+$ 220.0291, found 220.0288; calcd for $C_{12}H_9{}^{37}ClO_2$ $[M]^+$ 222.0262, found 220.0267.



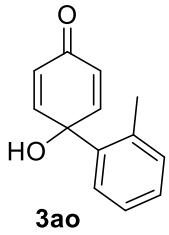
3an

1-hydroxy-3'-nitro-[1,1'-biphenyl]-4(*1H*)-one

3an was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (6/1) as the eluent, **3an** was obtained in 83% yield (191.9 mg) as a white solid.

3an: m.p. 115.6-116.8 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (t, *J* = 1.9 Hz, 1H), 8.22 – 8.16 (m, 1H), 7.82 – 7.77 (m, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 6.99 – 6.95 (m, 2H), 6.94 (s, 1H), 6.26 – 6.20 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 185.15, 151.37 (2C), 148.04,

142.87, 132.26, 130.31, 126.35 (2C), 122.82, 120.03, 69.67. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9NO_4$ $[M]^+$ 231.0532, found 231.0530.

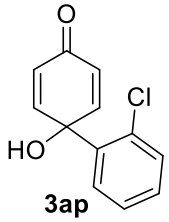


3ao

1-hydroxy-2'-methyl-[1,1'-biphenyl]-4(*1H*)-one

3ao was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ao** was obtained in 60% yield (120.1 mg) as a white solid.

3ao: m.p. 65.7-66.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.29 – 7.24 (m, 2H), 7.13 (dd, *J* = 5.8, 3.2 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.29 – 6.21 (m, 2H), 2.98 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.98, 150.24 (2C), 136.48, 135.71, 132.37, 128.63, 127.50 (2C), 126.70, 125.94, 70.26, 20.54. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0839.

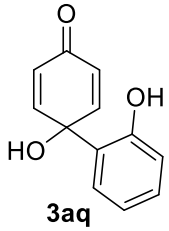


3ap

2'-chloro-1-hydroxy-[1,1'-biphenyl]-4(*1H*)-one

3ap was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ap** was obtained in 65% yield (143.4 mg) as a white solid.

3ap: m.p. 99.2-110.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.6, 4.2 Hz, 1H), 7.39 – 7.27 (m, 3H), 6.94 – 6.86 (m, 2H), 6.32 (dd, *J* = 7.1, 5.9 Hz, 2H), 3.11 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.79, 148.24 (2C), 136.17, 131.91, 131.33, 129.96, 128.52 (2C), 127.85, 127.54, 69.60. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO_2$ $[M]^+$ 220.0291, found 220.0292; calcd for $C_{12}H_9{}^{37}ClO_2$ $[M]^+$ 222.0262, found 220.0265.



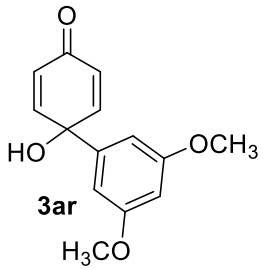
3aq

1,2'-dihydroxy-[1,1'-biphenyl]-4(*1H*)-one

3aq was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent, **3aq** was obtained in 54% yield (109.2 mg) as a white solid.

3aq: m.p. 98.3-99.7 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 9.15 (s, 1H), 6.96 – 6.91 (m, 2H), 6.80 – 6.70 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.69, 149.67, 148.59,

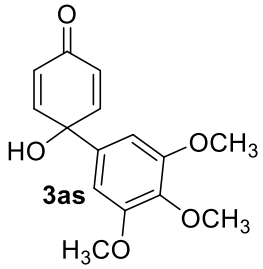
144.62, 124.02, 119.78, 119.36, 118.51 (2C), 116.98, 115.83 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_{10}O_3$ $[M]^+$ 202.0630, found 202.0629.



1-hydroxy-3',5'-dimethoxy-[1,1'-biphenyl]-4(*1H*)-one

3ar was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (6/1) as the eluent, **3ar** was obtained in 68% yield (167.5 mg) as a white solid.

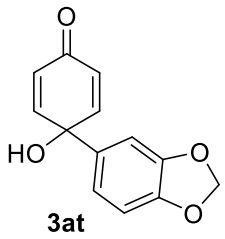
3ar: m.p. 116.8-117.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.87 (m, 2H), 6.63 (d, *J* = 2.2 Hz, 2H), 6.41 (t, *J* = 2.2 Hz, 1H), 6.22 – 6.16 (m, 2H), 3.78 (s, 6H), 3.49 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.19, 161.22 (2C), 151.10 (2C), 141.35, 126.67 (2C), 103.47 (2C), 100.19, 70.87, 55.45 (2C). HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_4$ $[M]^+$ 246.0892, found 246.0891.



1-hydroxy-3',4',5'-trimethoxy-[1,1'-biphenyl]-4(*1H*)-one

3as was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (6/1) as the eluent, **3as** was obtained in 63% yield (174.1 mg) as a white solid.

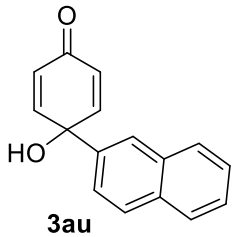
3as: m.p. 138.3-139.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 – 6.88 (m, 2H), 6.67 (s, 2H), 6.21 – 6.15 (m, 2H), 3.83 (s, 6H), 3.82 (s, 3H), 3.61 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.04, 153.49 (2C), 151.10 (2C), 137.73, 134.55, 126.57 (2C), 102.39 (2C), 70.74, 60.82, 56.16 (2C). HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_5$ $[M]^+$ 276.0998, found 276.0999.



4-(benzo[*d*][1,3]dioxol-5-yl)-4-hydroxycyclohexa-2,5-dien-1-one

3at was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent, **3at** was obtained in 66% yield (151.9 mg) as a white solid.

3at: m.p. 140.6-142.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 1.7 Hz, 1H), 6.95 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.24 – 6.16 (m, 2H), 5.97 (s, 2H), 2.54 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.61, 150.66 (2C), 148.23, 147.74, 132.60, 126.77 (2C), 118.82, 108.54, 106.03, 101.38, 70.74. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{10}O_4$ $[M]^+$ 230.0579, found 230.0580.

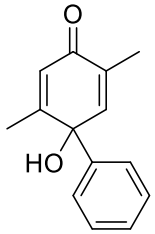


3au

4-hydroxy-4-(naphthalen-2-yl)cyclohexa-2,5-dien-1-one

3au was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent, **3au** was obtained in 70% yield (165.4 mg) as a white solid.

3au: m.p. 131.9-132.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 1.3 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.54 – 7.48 (m, 2H), 7.46 (dd, *J* = 8.7, 1.9 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.30 – 6.23 (m, 2H), 2.96 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.92, 150.93 (2C), 135.88, 133.39, 133.07, 128.79, 128.20, 127.68, 127.06 (2C), 126.63, 126.58, 124.43, 122.97, 71.21. HRMS (EI-TOF, m/z) calcd for $C_{16}H_{12}O_2$ $[M]^+$ 236.0837, found 236.0834.

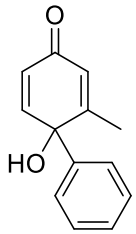


3ba

1-hydroxy-2,5-dimethyl-[1,1'-biphenyl]-4(*1H*)-one

3ba was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ba** was obtained in 90% yield (192.8 mg) as a white solid.

3ba: m.p. 118.1-119.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dt, *J* = 3.2, 1.8 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 6.61 (d, *J* = 1.4 Hz, 1H), 6.09 (d, *J* = 1.3 Hz, 1H), 3.16 (s, 1H), 1.85 (d, *J* = 1.4 Hz, 3H), 1.81 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.53, 161.65, 147.93, 139.35, 132.17, 128.71 (2C), 127.82, 126.17, 125.21 (2C), 73.51, 18.28, 15.18. HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_2$ $[M]^+$ 214.0994, found 214.0993.

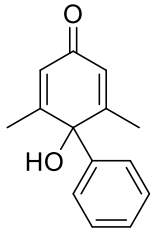


3ca

1-hydroxy-2-methyl-[1,1'-biphenyl]-4(*1H*)-one

3ca was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3ca** was obtained in 91% yield (182.2 mg) as a white solid.

3ca: m.p. 112.5-113.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.0 Hz, 1H), 6.86 (d, *J* = 9.7 Hz, 1H), 6.18 – 6.09 (m, 2H), 3.41 (s, 1H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.01, 162.20, 152.34, 138.55, 128.80 (2C), 128.04, 126.20, 125.61, 125.23 (2C), 73.23, 18.56. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0838.

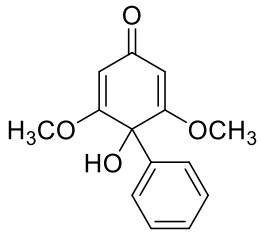


3da

1-hydroxy-2,6-dimethyl-[1,1'-biphenyl]-4(*1H*)-one

3da was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (8/1) as the eluent, **3da** was obtained in 88% yield (188.6 mg) as a white solid.

3da: m.p. 115.9-116.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.03 (s, 2H), 3.72 (s, 1H), 1.80 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.13, 163.32, 138.93, 128.60 (2C), 127.74, 125.54, 125.07 (2C), 75.35, 18.46 (2C). HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_2$ $[M]^+$ 214.0994, found 214.0997.

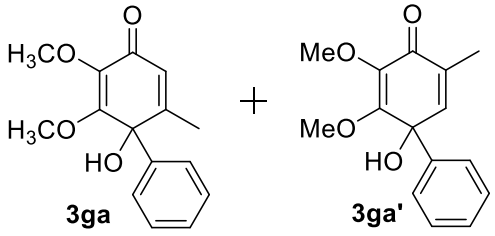


3ea

1-hydroxy-2,6-dimethoxy-[1,1'-biphenyl]-4(*1H*)-one

3ea was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent, **3ea** was obtained in 82% yield (201.9 mg) as a white solid.

3ea: m.p. 129.4-130.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.9 Hz, 2H), 7.39 – 7.29 (m, 3H), 5.52 (s, 2H), 3.66 (s, 6H), 3.60 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.74, 171.62, 139.33, 128.51 (2C), 128.32, 125.06 (2C), 100.48, 74.07, 56.54 (2C). HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_4$ $[M]^+$ 246.0892, found 246.0890.



3ga **3ga'**

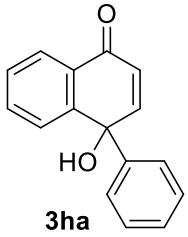
1-hydroxy-2,3-dimethoxy-6-methyl-[1,1'-biphenyl]-4(*1H*)-one (3ga)

1-hydroxy-2,3-dimethoxy-5-methyl-[1,1'-biphenyl]-4(*1H*)-one (3ga')

3ga and **3ga'** was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent. **3ga** was obtained in 72% yield (187.4 mg) as a white solid. **3ga'** was obtained in 19% yield (49.5 mg) as a white solid.

3ga: m.p. 133.5-134.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 5.96 (d, *J* = 1.4 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 3.64 (s, 1H), 1.74 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.54, 161.58, 156.47, 139.78, 135.84, 128.59 (2C), 128.03, 124.87 (2C), 124.51, 76.83, 61.02, 60.86, 17.14. HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_4$ $[M]^+$ 260.1049, found 260.1048.

3ga': m.p. 136.1-136.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dt, *J* = 8.4, 2.6 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 6.37 (d, *J* = 1.4 Hz, 1H), 4.05 (s, 3H), 3.80 (s, 3H), 3.11 (s, 1H), 1.86 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.10, 159.85, 141.43, 140.74, 136.38, 131.42, 128.77 (2C), 128.17, 125.08 (2C), 74.36, 60.97, 60.83, 15.32. HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_4$ $[M]^+$ 260.1049, found 260.1048.

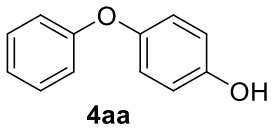


3ha

4-hydroxy-4-phenylnaphthalen-1(*4H*)-one

3ha was synthesized following the general procedure for 1,2-addition. After purification by preparative thin-layer chromatography using CH_2Cl_2/EtOAc (7/1) as the eluent, **3ha** was obtained in 48% yield (113.4 mg) as a white solid.

3ha: m.p. 124.5-125.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.48 – 7.38 (m, 4H), 7.36 – 7.30 (m, 2H), 7.30 – 7.25 (m, 1H), 6.97 (d, *J* = 10.1 Hz, 1H), 6.33 (d, *J* = 10.1 Hz, 1H), 3.05 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.94, 151.71, 146.81, 142.07, 133.59, 129.75, 128.62 (2C), 128.52, 128.27, 127.71, 126.29, 126.19, 125.65 (2C), 72.03. HRMS (EI-TOF, m/z) calcd for $C_{16}H_{12}O_2$ $[M]^+$ 236.0837, found 236.0836.



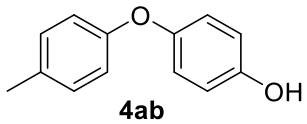
4aa

4-phenoxyphenol

4aa was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4aa** was obtained in 88% yield (163.9 mg) as a white solid. **4aa** was obtained in 79% yield (147.1 mg) using Cu_2O as a catalyst.

4aa: m.p. 83.4-84.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.07 – 7.01 (m, 1H), 6.99 – 6.89 (m, 4H), 6.85 – 6.77 (m, 2H), 4.89 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ

158.43, 151.75, 150.23, 129.66 (2C), 122.54, 121.03 (2C), 117.64 (2C), 116.38 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_{10}O_2$ [M]$^+$ 186.0681, found 186.0680.

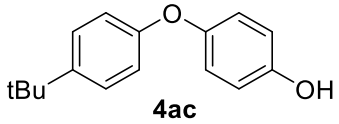


4ab

4-(*p*-tolyloxy)phenol

4ab was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ab** was obtained in 75% yield (150.2 mg) as a white solid.

4ab: m.p. 88.6-89.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.82 (m, 4H), 6.80 – 6.75 (m, 2H), 5.20 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.98, 151.45, 150.85, 132.22, 130.18 (2C), 120.54 (2C), 117.90 (2C), 116.36 (2C), 20.64. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ [M]$^+$ 200.0837, found 200.0838.

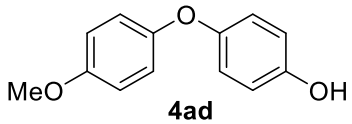


4ac

4-(4-(*tert*-butyl)phenoxy)phenol

4ac was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4ac** was obtained in 70% yield (169.6 mg) as a white solid.

4ac: m.p. 86.6-87.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 6.94 – 6.85 (m, 4H), 6.82 – 6.76 (m, 2H), 4.24 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.96, 151.55, 150.59, 145.44, 126.45 (2C), 120.80 (2C), 117.21 (2C), 116.31 (2C), 34.25, 31.52 (3C). HRMS (EI-TOF, m/z) calcd for $C_{16}H_{18}O_2$ [M]$^+$ 242.1307, found 242.1308.

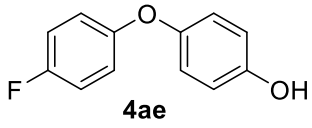


4ad

4-(4-methoxyphenoxy)phenol

4ad was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4ad** was obtained in 68% yield (147.0 mg) as a white solid. **4ad** was obtained in 61% yield (131.9 mg) using Cu_2O as a catalyst.

4ad: m.p. 94.2-95.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 – 6.89 (m, 2H), 6.88 – 6.82 (m, 4H), 6.79 – 6.74 (m, 2H), 5.31 (s, 1H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.28, 151.63, 151.55, 151.27, 119.78 (2C), 119.58 (2C), 116.29 (2C), 114.89 (2C), 55.79. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_3$ [M]$^+$ 216.0786, found 216.0788.

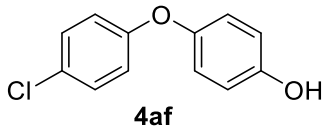


4ae

4-(4-fluorophenoxy)phenol

4ae was synthesized following the general procedure. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ae** was obtained in 95% yield (194.0 mg) as a white solid.

4ae: m.p. 97.9-98.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.95 (m, 2H), 6.93 – 6.86 (m, 4H), 6.84 – 6.75 (m, 2H), 5.08 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.42 (d, J_{CF} = 240.7 Hz), 154.10 (d, J_{CF} = 2.4 Hz), 151.60, 150.79, 120.46 (2C), 119.23 (d, J_{CF} = 8.2 Hz, 2C), 116.47 (2C), 116.17 (d, J_{CF} = 23.3 Hz, 2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_9FO_2$ $[M]^+$ 204.0587, found 204.0588.

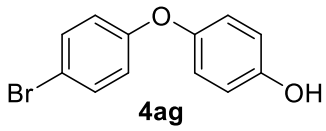


4af

4-(4-chlorophenoxy)phenol

4af was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4af** was obtained in 92% yield (203.0 mg) as a white solid.

4af: m.p.135-136.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 6.93 – 6.84 (m, 4H), 6.84 – 6.79 (m, 2H), 4.80 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.11, 152.00, 149.92, 129.59 (2C), 127.47, 121.03 (2C), 118.82 (2C), 116.49 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO_2$ $[M]^+$ 220.0291, found 220.0296; calcd for $C_{12}H_9{}^{37}ClO_2$ $[M]^+$ 222.0262, found 220.0264.

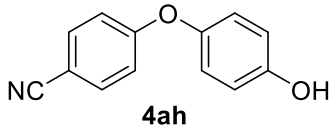


4ag

4-(4-bromophenoxy)phenol

4ag was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ag** was obtained in 93% yield (246.5 mg) as a white solid.

4ag: m.p. 158.6-160.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H), 6.93 – 6.88 (m, 2H), 6.85 – 6.78 (m, 4H), 5.10 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 152.06, 149.76, 132.54 (2C), 121.10 (2C), 119.24 (2C), 116.50 (2C), 114.83. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{79}BrO_2$ $[M]^+$ 263.9786, found 263.9797; calcd for $C_{12}H_9{}^{81}BrO_2$ $[M]^+$ 265.9765, found 265.9771.



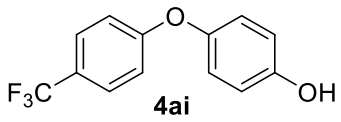
4ah

4-(4-hydroxyphenoxy)benzonitrile

4ah was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4ah** was obtained in 94% yield (198.5 mg) as a white solid.

4ah: m.p. 151.1-152.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 7.79 (d, J = 8.1 Hz, 2H), 6.99 (t, J = 8.5 Hz, 4H), 6.84 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6)

δ 162.31, 154.85, 145.89, 134.45 (2C), 121.80 (2C), 118.81, 116.89 (2C), 116.51 (2C), 104.12. HRMS (EI-TOF, m/z) calcd for $C_{13}H_9NO_2$ $[M]^+$ 211.0633, found 211.0634.

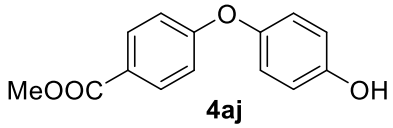


4ai

4-(4-(trifluoromethyl)phenoxy)phenol

4ai was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ai** was obtained in 92% yield (233.9 mg) as a white solid. **4ai** was obtained in 91% yield (231.3 mg) using Cu_2O as a catalyst.

4ai: m.p. 112.2-113.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.6 Hz, 2H), 6.96 (dt, J = 5.9, 3.9 Hz, 4H), 6.89 – 6.81 (m, 2H), 4.67 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.42, 152.55, 148.83, 127.05 (q, J_{CF} = 3.7 Hz, 2c), 124.32 (q, J_{CF} = 32.9 Hz), 124.27 (q, J_{CF} = 271.4 Hz), 121.76 (2C), 116.86 (2C), 116.65 (2C). HRMS (EI-TOF, m/z) calcd for $C_{13}H_9F_3O_2$ $[M]^+$ 254.0555, found 254.0556.

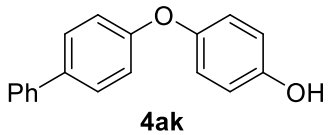


4aj

methyl 4-(4-hydroxyphenoxy)benzoate

4aj was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4aj** was obtained in 83% yield (202.7 mg) as a white solid.

4aj: m.p. 141.3-142.7 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 7.93 (d, J = 8.8 Hz, 2H), 7.00 – 6.92 (m, 4H), 6.83 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.69, 162.64, 154.63, 146.35, 131.41 (2C), 123.08, 121.73 (2C), 116.43 (2C), 116.01 (2C), 51.87. HRMS (EI-TOF, m/z) calcd for $C_{14}H_{12}O_4$ $[M]^+$ 244.0736, found 244.0735.

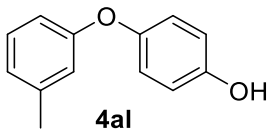


4ak

4-([1,1'-biphenyl]-4-yloxy)phenol

4ak was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ak** was obtained in 82% yield (215.1 mg) as a white solid.

4ak: m.p. 173.5-174.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 4H), 7.41 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.06 – 6.93 (m, 4H), 6.90 – 6.74 (m, 2H), 4.85 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.04, 151.84, 150.19, 140.62, 135.62, 128.79 (2C), 128.35 (2C), 126.96, 126.88 (2C), 121.12 (2C), 117.83 (2C), 116.41 (2C). HRMS (EI-TOF, m/z) calcd for $C_{18}H_{14}O_2$ $[M]^+$ 262.0994, found 262.0993.

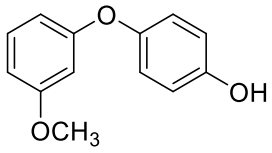


4al

4-(*m*-tolyloxy)phenol

4al was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4al** was obtained in 80% yield (160.2 mg) as a white solid.

4al: m.p. 82.3-83.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.89 (m, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.82 – 6.72 (m, 4H), 4.81 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 151.65, 150.34, 139.88, 129.41, 123.44, 121.02 (2C), 118.37, 116.40 (2C), 114.71, 21.44. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0838.

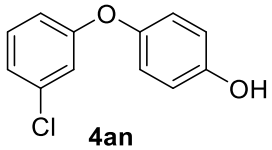


4am

4-(3-methoxyphenoxy)phenol

4am was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4am** was obtained in 84% yield (181.6 mg) as a white solid.

4am: m.p. 88.5-89.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 1H), 6.95 – 6.89 (m, 2H), 6.82 – 6.76 (m, 2H), 6.60 (ddd, *J* = 8.3, 2.2, 0.8 Hz, 1H), 6.56 – 6.47 (m, 2H), 5.41 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.81, 159.74, 151.93, 149.87, 130.14, 121.24 (2C), 116.42 (2C), 109.91, 108.16, 103.79, 55.43. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_3$ $[M]^+$ 216.0786, found 216.0785.

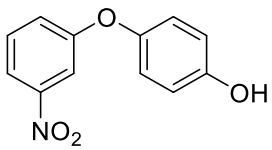


4an

4-(3-chlorophenoxy)phenol

4an was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4an** was obtained in 86% yield (189.8 mg) as a white solid.

4an: m.p. 92.9-93.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.1 Hz, 1H), 7.00 (ddd, *J* = 8.0, 1.9, 0.9 Hz, 1H), 6.95 – 6.88 (m, 3H), 6.87 – 6.79 (m, 3H), 5.48 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.37, 152.14, 149.42, 135.01, 130.46, 122.63, 121.46 (2C), 117.66, 116.63 (2C), 115.67. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO_2$ $[M]^+$ 220.0291, found 220.0293; calcd for $C_{12}H_9{}^{37}ClO_2$ $[M]^+$ 222.0262, found 220.0261.

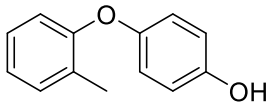


4ao

4-(3-nitrophenoxy)phenol

4ao was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (3/1) as the eluent, **4ao** was obtained in 89% yield (205.8 mg) as a white solid.

4ao: m.p. 123.9-125.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, *J* = 8.2, 2.1, 0.9 Hz, 1H), 7.71 (t, *J* = 2.3 Hz, 1H), 7.45 (t, *J* = 8.2 Hz, 1H), 7.27 (ddd, *J* = 8.2, 2.4, 0.8 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.92 – 6.87 (m, 2H), 5.15 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.54, 152.86, 149.19, 148.53, 130.27, 123.35, 121.66 (2C), 117.10, 116.88 (2C), 111.70. HRMS (EI-TOF, m/z) calcd for $C_{12}H_9NO_4$ $[M]^+$ 231.0532, found 231.0533.

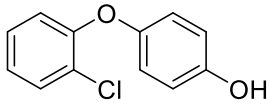


4ap

4-(*o*-tolyloxy)phenol

4ap was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ap** was obtained in 65% yield (130.2 mg) as a white solid.

4aq: m.p. 58.6-59.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 1H), 7.13 – 7.08 (m, 1H), 6.99 (td, *J* = 7.4, 1.1 Hz, 1H), 6.87 – 6.72 (m, 5H), 5.16 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.71, 151.25, 151.02, 131.38, 129.17, 127.04, 123.25, 119.49 (2C), 118.18, 116.34 (2C), 16.25. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0836.

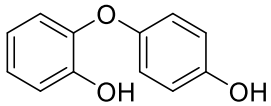


4aq

4-(2-chlorophenoxy)phenol

4aq was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4aq** was obtained in 73% yield (161.1 mg) as a white solid.

4aq: m.p. 66.4-67.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.15 (ddd, *J* = 8.2, 7.5, 1.6 Hz, 1H), 7.01 (td, *J* = 7.7, 1.5 Hz, 1H), 6.91 – 6.78 (m, 5H), 5.38 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.66, 151.77, 150.13, 130.71, 127.86, 124.74, 123.89, 120.24 (2C), 119.12, 116.48 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO_2$ $[M]^+$ 220.0291, found 220.0294; calcd for $C_{12}H_9{}^{37}ClO_2$ $[M]^+$ 222.0262, found 220.0261.

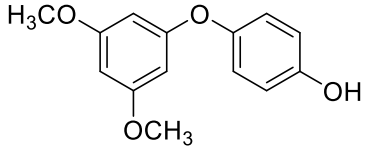


4ar

2-(4-hydroxyphenoxy)phenol

4ar was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (3/1) as the eluent, **4ar** was obtained in 65% yield (131.4 mg) as a white solid.

4ar: m.p. 70.3-71.8 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33 (s, 1H), 9.14 (s, 1H), 6.95 – 6.89 (m, 2H), 6.80 – 6.70 (m, 6H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.69, 149.68, 148.59, 144.62, 124.02, 119.78, 119.37, 118.52 (2C), 116.98, 115.83 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_{10}O_3$ $[M]^+$ 202.0630, found 202.0631.

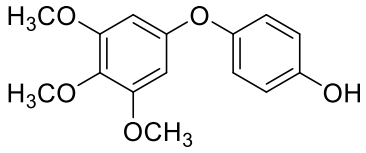


4as

4-(3,5-dimethoxyphenoxy)phenol

4as was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (3/1) as the eluent, **4as** was obtained in 83% yield (204.4 mg) as a white solid.

4as: m.p. 148.5-149..9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 – 6.89 (m, 2H), 6.81 – 6.75 (m, 2H), 6.18 (t, *J* = 2.2 Hz, 1H), 6.11 (d, *J* = 2.2 Hz, 2H), 5.93 (s, 1H), 3.72 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.48 (2C), 160.57, 152.15, 149.47, 121.42 (2C), 116.43 (2C), 96.30 (2C), 94.82, 55.48 (2C). HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_4$ $[M]^+$ 246.0892, found 246.0893.

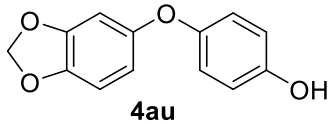


4at

4-(3,4,5-trimethoxyphenoxy)phenol

4at was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (3/1) as the eluent, **4at** was obtained in 78% yield (215.5 mg) as a white solid.

4at: m.p. 168.6-169.4 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.30 (s, 1H), 6.91 – 6.86 (m, 2H), 6.81 – 6.74 (m, 2H), 6.23 (s, 2H), 3.69 (s, 6H), 3.62 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.29, 153.56, 153.46 (2C), 148.26, 132.94, 120.32 (2C), 116.12 (2C), 95.30 (2C), 60.06, 55.78 (2C). HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_5$ $[M]^+$ 276.0998, found 276.0997.



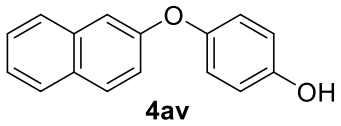
4au

4-(benzo[*d*][1,3]dioxol-5-yloxy)phenol

4au was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (3/1) as the eluent, **4au** was obtained in 80% yield (184.2 mg) as a white solid.

4au: m.p. 158.3-159.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 – 6.84 (m, 2H), 6.79 – 6.75 (m, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.93 (s, 2H), 5.40 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.88, 151.38, 151.27, 148.29,

143.19, 120.03 (2C), 116.33 (2C), 110.60, 108.23, 101.44, 101.13. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{10}O_4$ $[M]^+$ 230.0579, found 230.0578.

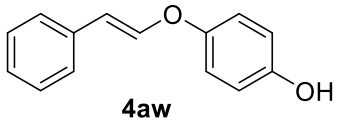


4av

4-(naphthalen-2-yloxy)phenol

4av was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4av** was obtained in 82% yield (193.7 mg) as a white solid.

4av: m.p. 79.2-80.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.38 (dtd, *J* = 16.2, 6.9, 1.2 Hz, 2H), 7.23 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.85 – 6.79 (m, 2H), 5.08 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.36, 151.92, 150.20, 134.37, 129.87, 129.86, 127.76, 127.07, 126.57, 124.49, 121.27 (2C), 119.37, 116.52 (2C), 112.40. HRMS (EI-TOF, m/z) calcd for $C_{16}H_{12}O_2$ $[M]^+$ 236.0837, found 236.0838.

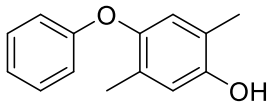


4aw

(*E*)-4-(styryloxy)phenol

4aw was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (2/1) as the eluent, **4aw** was obtained in 63% yield (133.7 mg) as a white solid.

4aw: m.p. 55.4-56.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 7.18 (ddd, *J* = 5.4, 4.1, 2.3 Hz, 1H), 7.09 (d, *J* = 12.5 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.81 – 6.77 (m, 2H), 6.24 (d, *J* = 12.5 Hz, 1H), 4.98 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.60, 151.08, 144.78, 135.32, 128.71 (2C), 126.52, 125.59 (2C), 118.66 (2C), 116.28 (2C), 112.49. HRMS (EI-TOF, m/z) calcd for $C_{14}H_{12}O_2$ $[M]^+$ 212.0837, found 212.0838.

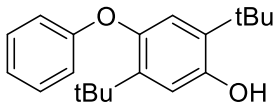


4ba

2,5-dimethyl-4-phenoxyphenol

4ba was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4ba** was obtained in 62% yield (132.8 mg) as a white solid. **4ba** was obtained in 58% yield (124.3 mg) using Cu_2O as a catalyst.

4ba: m.p. 94.6-95.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.01 – 6.96 (m, 1H), 6.86 – 6.81 (m, 2H), 6.75 (s, 1H), 6.65 (s, 1H), 4.72 (s, 1H), 2.18 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.89, 150.35, 147.03, 129.56 (2C), 129.03, 123.35, 122.47, 121.64, 117.41, 116.12 (2C), 15.82, 15.49. HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_2$ $[M]^+$ 214.0994, found 214.0993.

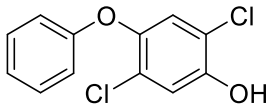


4ca

2,5-di-*tert*-butyl-4-phenoxyphenol

4ca was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4ca** was obtained in 36% yield (107.4 mg) as a white solid.

4ca: m.p. 98.5-99.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 6.99 (dd, *J* = 10.6, 4.1 Hz, 1H), 6.90 (dt, *J* = 3.3, 1.8 Hz, 2H), 6.80 (s, 1H), 6.68 (s, 1H), 4.68 (s, 1H), 1.32 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.94, 149.85, 147.51, 140.06, 134.78, 129.50 (2C), 121.57, 120.75, 117.01 (2C), 115.40, 34.23, 34.17, 30.18 (3C), 29.54 (3C). HRMS (EI-TOF, m/z) calcd for $C_{20}H_{26}O_2$ $[M]^+$ 298.1933, found 298.1932.

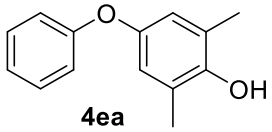


4da

2,5-dichloro-4-phenoxyphenol

4da was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **4da** was obtained in 82% yield (209.2 mg) as a white solid. **4da** was obtained in 83% yield (211.7 mg) using Cu_2O as a catalyst.

4da: m.p. 144.5-145.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.16 – 7.13 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H), 6.94 – 6.89 (m, 2H), 5.55 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.37, 148.38, 145.73, 129.86 (2C), 126.16, 123.27, 121.77, 118.56, 117.78, 117.10 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_8{}^{35}Cl_2O_2$ $[M]^+$ 253.9901, found 253.9899; calcd for $C_{12}H_8{}^{35}Cl^{37}ClO_2$ $[M]^+$ 255.9872, found 255.9871; calcd for $C_{12}H_8{}^{37}Cl_2O_2$ $[M]^+$ 257.9842, found 257.9841.

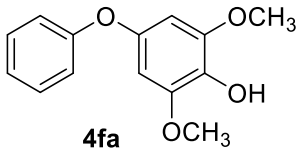


4ea

2,6-dimethyl-4-phenoxyphenol

4ea was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent, **4ea** was obtained in 63% yield (135.0 mg) as a white solid.

4ea: m.p. 89.5-90.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.5, 7.5 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.80 – 6.71 (m, 2H), 6.56 (s, 2H), 4.86 (s, 1H), 2.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.16, 152.21, 144.81, 132.72, 129.62 (2C), 121.22, 115.31 (2C), 114.54 (2C), 16.45 (2C). HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_2$ $[M]^+$ 214.0994, found 214.0993.

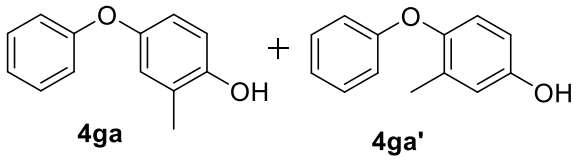


4fa

2,6-dimethoxy-4-phenoxyphenol

4fa was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (3/1) as the eluent, **4fa** was obtained in 54% yield (133.0 mg) as a white solid.

4fa: m.p. 98.8-99.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 6.96 (t, *J* = 7.3 Hz, 1H), 6.86 (dt, *J* = 3.4, 1.8 Hz, 2H), 6.15 (s, 2H), 5.26 (s, 1H), 3.69 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.69, 153.88 (2C), 153.70, 129.28 (2C), 125.82, 121.49, 114.66 (2C), 93.24 (2C), 56.16 (2C). HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O_4$ $[M]^+$ 246.0892, found 246.0893.



4ga **4ga'**

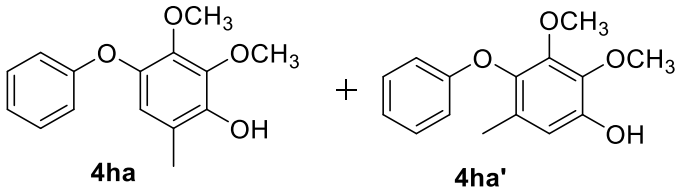
2-methyl-4-phenoxyphenol (**4ag**)

3-methyl-4-phenoxyphenol (**4ga'**)

4ga and **4ga'** was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent. **4ga** was obtained in 49% yield (98.1 mg) as a white solid. **4ga'** was obtained in 19% yield (38.0 mg) as a white solid.

4ga: m.p. 86.6-87.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.03 – 6.95 (m, 1H), 6.84 (d, *J* = 8.6 Hz, 3H), 6.72 (d, *J* = 2.9 Hz, 1H), 6.64 (dd, *J* = 8.6, 3.0 Hz, 1H), 5.10 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.72, 152.09, 147.52, 132.03, 129.62 (2C), 122.01, 121.83, 117.97, 116.20 (2C), 113.76, 16.29. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0836.

4ga: m.p. 88.1-89.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.05 – 7.01 (m, 1H), 6.96 – 6.91 (m, 2H), 6.83 (d, *J* = 2.6 Hz, 1H), 6.78 – 6.72 (m, 2H), 4.74 (s, 1H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.58, 150.05, 149.92, 129.59 (2C), 125.35, 122.39, 122.36, 118.27, 117.59 (2C), 115.74, 15.96. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0836.



4ha **4ha'**

2,3-dimethoxy-6-methyl-4-phenoxyphenol (**4ha**)

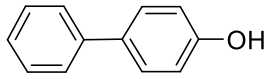
2,3-dimethoxy-5-methyl-4-phenoxyphenol (**4ha'**)

4ha and **4ha'** was synthesized following the general procedure for 1,6-addition. After purification by preparative thin-layer chromatography using PE/EtOAc (4/1) as the eluent. **4ha** was obtained in 31% yield (80.7 mg) as a white solid. **4ha'** was obtained in 19% yield (49.5 mg) as a white solid.

4ha: m.p. 168.5-169.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.00 – 6.94 (m, 1H), 6.85 – 6.80 (m, 2H), 6.60 (d, *J* = 0.6 Hz, 1H), 5.69 (s, 1H), 3.91 (s, 3H), 3.77 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.50, 146.10, 145.75, 138.91, 138.27,

129.53 (2C), 127.80, 121.59, 114.72 (2C), 111.03, 61.31, 60.84, 15.94. HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_4$ $[M]^+$ 260.1049, found 260.1048.

4ha': m.p. 170.1-171.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.03 – 6.98 (m, 1H), 6.91 (dt, *J* = 4.5, 1.8 Hz, 2H), 6.57 (d, *J* = 0.4 Hz, 1H), 5.71 (s, 1H), 3.96 (s, 3H), 3.80 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.83, 144.11, 142.83, 140.74, 139.91, 129.51 (2C), 122.03, 119.05, 118.35, 116.21 (2C), 61.27, 61.02, 15.27. HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_4$ $[M]^+$ 260.1049, found 260.1050.

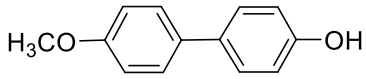


5aa

[1,1'-biphenyl]-4-ol

5aa was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5aa** was obtained in 76% yield (163.7 mg) as a white solid.

5aa: m.p. 114.4-116.0 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 7.59 – 7.54 (m, 2H), 7.51 – 7.46 (m, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 6.89 – 6.83 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.08, 140.19, 130.90, 128.75 (2C), 127.69 (2C), 126.31, 125.92 (2C), 115.68 (2C); HRMS (EI-TOF, m/z) calcd for $C_{12}H_{10}O$ $[M]^+$ 170.0732, found 170.0730.

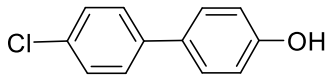


5ab

4'-methoxy-[1,1'-biphenyl]-4-ol

5ab was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **5ab** was obtained in 60% yield (120.1 mg) as a white solid.

5ab: m.p. 138.1-139.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (s, 1H), 7.52 – 7.39 (m, 4H), 7.00 – 6.92 (m, 2H), 6.87 – 6.79 (m, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.06, 156.48, 132.72, 130.70, 127.17 (2C), 126.95 (2C), 115.60 (2C), 114.17 (2C), 55.04. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0835.

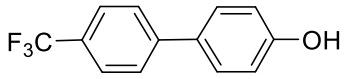


5ac

4'-chloro-[1,1'-biphenyl]-4-ol

5ac was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5ac** was obtained in 80% yield (163.7 mg) as a white solid.

5ac: m.p. 146.5-147.4 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.63 (s, 1H), 7.63 – 7.56 (m, 2H), 7.51 – 7.42 (m, 4H), 6.91 – 6.83 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.39, 138.98, 131.08, 129.49, 128.65 (2C), 127.68 (2C), 127.57 (2C), 115.77 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO$ $[M]^+$ 204.0342, found 204.0339; calcd for $C_{12}H_9{}^{37}ClO$ $[M]^+$ 206.0312, found 206.0315.

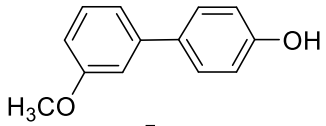


5ad

4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol

5ad was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5ad** was obtained in 81% yield (192.9 mg) as a white solid.

5ad: m.p. 118.2-119.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H), 7.81 – 7.69 (m, 4H), 7.57 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.01, 144.09 (d, J_{CF} = 1.1 Hz), 129.15, 128.13 (2C), 126.71 (q, J_{CF} = 31.8 Hz, 2C), 126.41 (2C), 125.54 (q, J_{CF} = 3.7 Hz), 124.43 (q, J_{CF} = 271.7 Hz), 115.89 (2C). HRMS (EI-TOF, m/z) calcd for $C_{13}H_9F_3O$ $[M]^+$ 238.0605, found 238.0607.

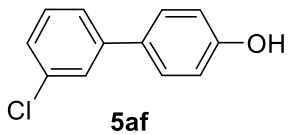


5ae

3'-methoxy-[1,1'-biphenyl]-4-ol

5ae was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **5ae** was obtained in 71% yield (142.2 mg) as a white solid.

5ae: m.p. 121.9-122.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.31 (t, J = 7.9 Hz, 1H), 7.12 (ddd, J = 7.6, 1.7, 1.0 Hz, 1H), 7.07 (dd, J = 2.6, 1.7 Hz, 1H), 6.91 – 6.83 (m, 3H), 5.74 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.83, 155.29, 142.38, 133.76, 129.82, 128.49 (2C), 119.46, 115.75 (2C), 112.59, 112.19, 55.41. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O_2$ $[M]^+$ 200.0837, found 200.0839.

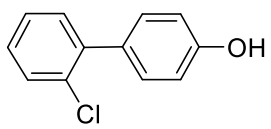


5af

3'-chloro-[1,1'-biphenyl]-4-ol

5af was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5af** was obtained in 75% yield (153.5 mg) as a white solid.

5af: m.p. 130.5-131.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, J = 1.8 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.38 (dt, J = 7.6, 1.5 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.28 – 7.23 (m, 1H), 6.93 – 6.87 (m, 2H), 5.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.48, 142.57, 134.61, 132.60, 129.99, 128.45 (2C), 126.82, 126.72, 124.84, 115.88 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO$ $[M]^+$ 204.0342, found 204.0343; calcd for $C_{12}H_9{}^{37}ClO$ $[M]^+$ 206.0312, found 206.0320.

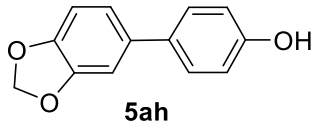


5ag

2'-chloro-[1,1'-biphenyl]-4-ol

5ag was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5ag** was obtained in 60% yield (122.8 mg) as a white solid.

5ag: m.p. 119.8-120.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 1H), 7.35 – 7.21 (m, 5H), 6.91 – 6.88 (m, 2H), 5.32 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.10, 140.08, 132.59, 132.05, 131.39, 130.88 (2C), 129.96, 128.25, 126.84, 115.03 (2C). HRMS (EI-TOF, m/z) calcd for $C_{12}H_9{}^{35}ClO$ $[M]^+$ 204.0342, found 204.0344; calcd for $C_{12}H_9{}^{37}ClO$ $[M]^+$ 206.0312, found 206.0318.

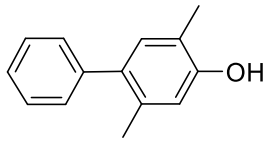


5ah

4-(benzo[*d*][1,3]dioxol-5-yl)phenol

5ah was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5ah** was obtained in 60% yield (128.5 mg) as a white solid.

5ah: m.p. 147.1-148.3 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.48 (s, 1H), 7.43 – 7.38 (m, 2H), 7.14 (d, J = 1.7 Hz, 1H), 7.03 (dd, J = 8.1, 1.8 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.85 – 6.80 (m, 2H), 6.03 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.68, 147.79, 145.93, 134.67, 130.77, 127.45 (2C), 119.22, 115.55 (2C), 108.48, 106.54, 100.87. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{10}O_3$ $[M]^+$ 214.0630, found 214.0632.

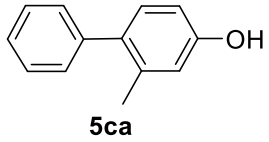


5ba

2,5-dimethyl-[1,1'-biphenyl]-4-ol

5ba was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5ba** was obtained in 85% yield (168.5 mg) as a white solid.

5ba: m.p. 126.8-127.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.31 – 7.26 (m, 3H), 6.99 (s, 1H), 6.67 (s, 1H), 4.87 (s, 1H), 2.24 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.87, 141.74, 134.66, 134.24, 132.53, 129.45 (2C), 128.05 (2C), 126.47, 121.03, 116.72, 20.10, 15.32. HRMS (EI-TOF, m/z) calcd for $C_{14}H_{14}O$ $[M]^+$ 198.1045, found 198.1043.

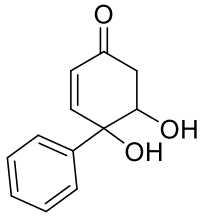


5ca

2-methyl-[1,1'-biphenyl]-4-ol

5ca was synthesized following the general procedure for one-pot construction of 4-phenylphenols. After purification by preparative thin-layer chromatography using PE/EtOAc (6/1) as the eluent, **5ca** was obtained in 88% yield (162.1 mg) as a white solid.

5ca: m.p. 124.4-125.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.27 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.77 – 6.68 (m, 2H), 4.97 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.63, 141.58, 137.05, 134.80, 131.05, 129.41 (2C), 128.04 (2C), 126.51, 116.94, 112.67, 20.58. HRMS (EI-TOF, m/z) calcd for $C_{13}H_{12}O$ $[M]^+$ 184.0888, found 184.0885.

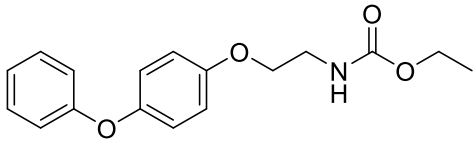


7

1,2-dihydroxy-2,3-dihydro-[1,1'-biphenyl]-4(1*H*)-one

7 was synthesized following the general procedure for transformation of products. After purification by preparative thin-layer chromatography using DCM/EtOAc (3/1) as the eluent, **7** was obtained in 85% yield (86.8 mg) as a white oil.

7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.43 – 7.31 (m, 3H), 6.79 – 6.66 (m, 1H), 6.22 (d, *J* = 10.2 Hz, 1H), 4.19 (s, 1H), 3.92 (s, 1H), 3.41 (s, 1H), 2.69 – 2.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.63, 149.46, 140.60, 129.89, 128.81 (2C), 128.54, 126.11 (2C), 74.84, 74.55, 41.76. HRMS (EI-TOF, m/z) calcd for $C_{12}H_{12}O_3$ $[M]^+$ 204.0786, found 204.0787.

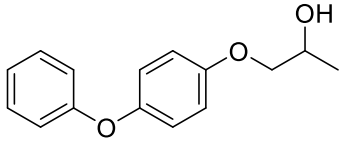


fenoxycard

ethyl (2-(4-phenoxyphenoxy)ethyl)carbamate

Fenoxycard was synthesized following the general procedure for transformation of products. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **fenoxycard** was obtained in 86% yield (259.2 mg) as a white solid.

Fenoxycard: m.p. 53.3-54.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.98 – 6.91 (m, 4H), 6.88 – 6.83 (m, 2H), 5.21 (s, 1H), 4.13 (dd, *J* = 14.0, 7.0 Hz, 2H), 4.00 (t, *J* = 5.1 Hz, 2H), 3.57 (d, *J* = 5.1 Hz, 2H), 1.24 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.35, 156.72, 154.77, 150.59, 129.65 (2C), 122.58, 120.80 (2C), 117.73 (2C), 115.55 (2C), 67.49, 60.97, 40.53, 14.65. HRMS (EI-TOF, m/z) calcd for $C_{17}H_{19}NO_4$ $[M]^+$ 301.1314, found 301.1312.

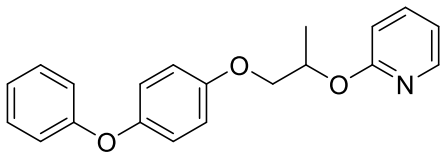


8

1-(4-phenoxyphenoxy)propan-2-ol

8 was synthesized following the general procedure for transformation of products. After purification by preparative thin-layer chromatography using PE/EtOAc (5/1) as the eluent, **8** was obtained in 86% yield (210.1 mg) as a white oil.

8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.96 (ddd, *J* = 10.8, 7.2, 5.6 Hz, 4H), 6.91 – 6.85 (m, 2H), 4.23 – 4.14 (m, 1H), 3.84 (ddd, *J* = 16.9, 9.2, 5.5 Hz, 2H), 2.41 (s, 1H), 1.28 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.38, 154.87, 150.59, 129.67 (2C), 122.58, 120.81 (2C), 117.73 (2C), 115.69 (2C), 73.90, 66.30, 18.83. HRMS (EI-TOF, m/z) calcd for $C_{15}H_{16}O_3$ $[M]^+$ 244.1099, found 244.1098.



pyriproxyfen

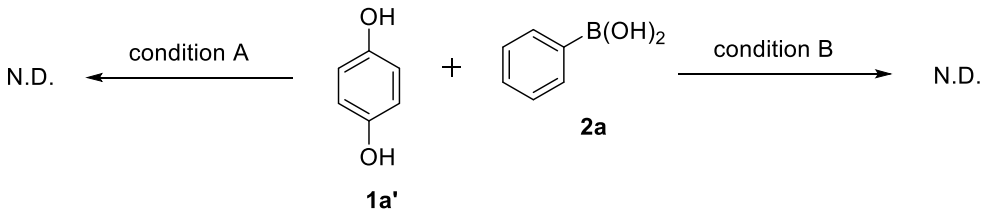
2-((1-(4-phenoxyphenoxy)propan-2-yl)oxy)pyridine

Pyriproxyfen was synthesized following the general procedure for transformation of products. After purification by preparative thin-layer chromatography using PE/EtOAc (10/1) as the eluent, **pyriproxyfen** was obtained in 85% yield (136.6 mg) as a white solid.

Pyriproxyfen: m.p. 45.8-46.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.31 – 7.25 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.98 – 6.90 (m, 6H), 6.85 (dd, *J* = 6.6, 5.5 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 5.63 – 5.55 (m, 1H), 4.13 (ddd, *J* = 46.3, 9.9, 5.1 Hz, 2H), 1.48 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.14, 158.51, 155.24, 150.31, 146.70, 138.80, 129.62 (2C), 122.44, 120.77 (2C), 117.63 (2C), 116.79, 115.82 (2C), 111.74, 71.09, 69.42, 17.02. HRMS (EI-TOF, m/z) calcd for $C_{20}H_{19}NO_3$ $[M]^+$ 321.1365, found 321.1364.

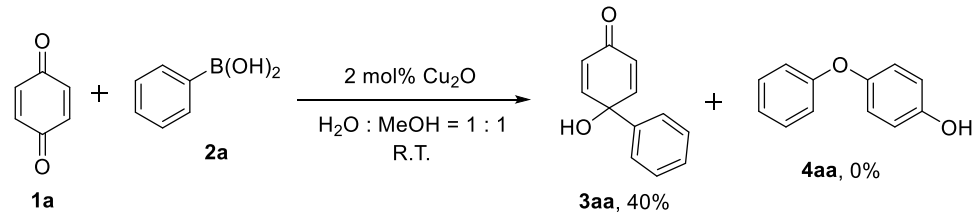
4. Mechanistic Investigations

4.1 Control experiments

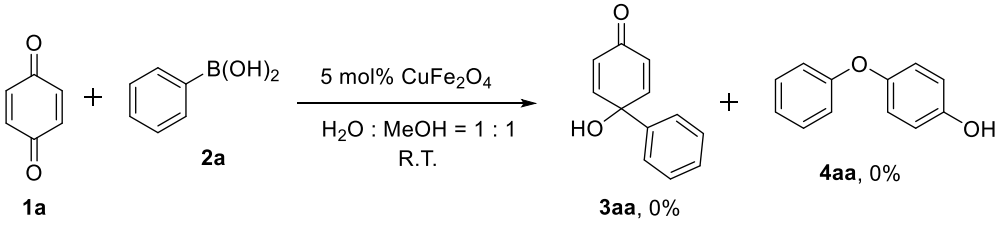


Condition A: A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1a'** (1.0 mmol), organic boronic acid **2a** (1.2 mmol), Cu_2O (2.9 mg, 0.02 mmol, 2.0 mol%) and H_2O (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24 h. Upon completion, the mixture was diluted with water (2.0 mL) and then extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent to obtain the desired product.

Condition B: A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1a'** (1.0 mmol), organic boronic acid **2a** (1.2 mmol), $CuFe_2O_4$ (12.0 mg, 0.05 mmol, 5.0 mol%) and MeOH (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24. Upon completion, the mixture was diluted with 5 mL of ethyl acetate, filtered through a celite pad and washed with 10 mL of ethyl acetate. The filtrate was collected and concentrated. The residue was purified by silica gel column chromatography using PE/EtOAc (5/1) as the eluent to obtain the desired product.



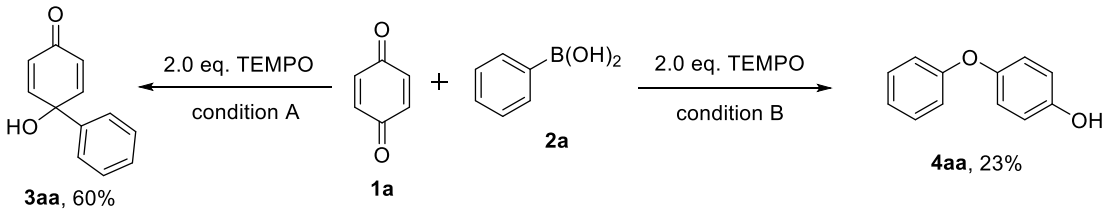
A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1a** (1.0 mmol), organic boronic acid **2a** (1.2 mmol), Cu_2O (2.9 mg, 0.02 mmol, 2.0 mol%), H_2O (1.0 mL) and MeOH (1.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24 h. Upon completion, the mixture was diluted with water (2.0 mL) and then extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using PE/EtOAc (5/1) to CH_2Cl_2/EtOAc (9/1) as the eluent to obtain the desired product.



A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1a** (1.0 mmol), organic boronic acid **2a** (1.2 mmol), $CuFe_2O_4$ (12.0 mg, 0.05 mmol, 5.0 mol%), H_2O (1.0 mL) and MeOH (1.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24 h.

Upon completion, the mixture was diluted with 5 mL of ethyl acetate, filtered through a celite pad and washed with 10 mL of ethyl acetate. The filtrate was collected and concentrated. The residue was purified by silica gel column chromatography using PE/EtOAc (5/1) to CH_2Cl_2/EtOAc (9/1) as the eluent to obtain the desired product.

4.2 Free Radical Capture Experiment



Condition A: A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1a** (1.0 mmol), organic boronic acid **2a** (1.2 mmol), Cu_2O (2.9 mg, 0.02 mmol, 2.0 mol%), TEMPO (2.0 mmol) and H_2O (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24 h. Upon completion, the mixture was diluted with water (2.0 mL) and then extracted with ethyl acetate (5 ml × 3). The combined organic layers were dried over $MgSO_4$, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography using CH_2Cl_2/EtOAc (9/1) as the eluent to obtain the desired product.

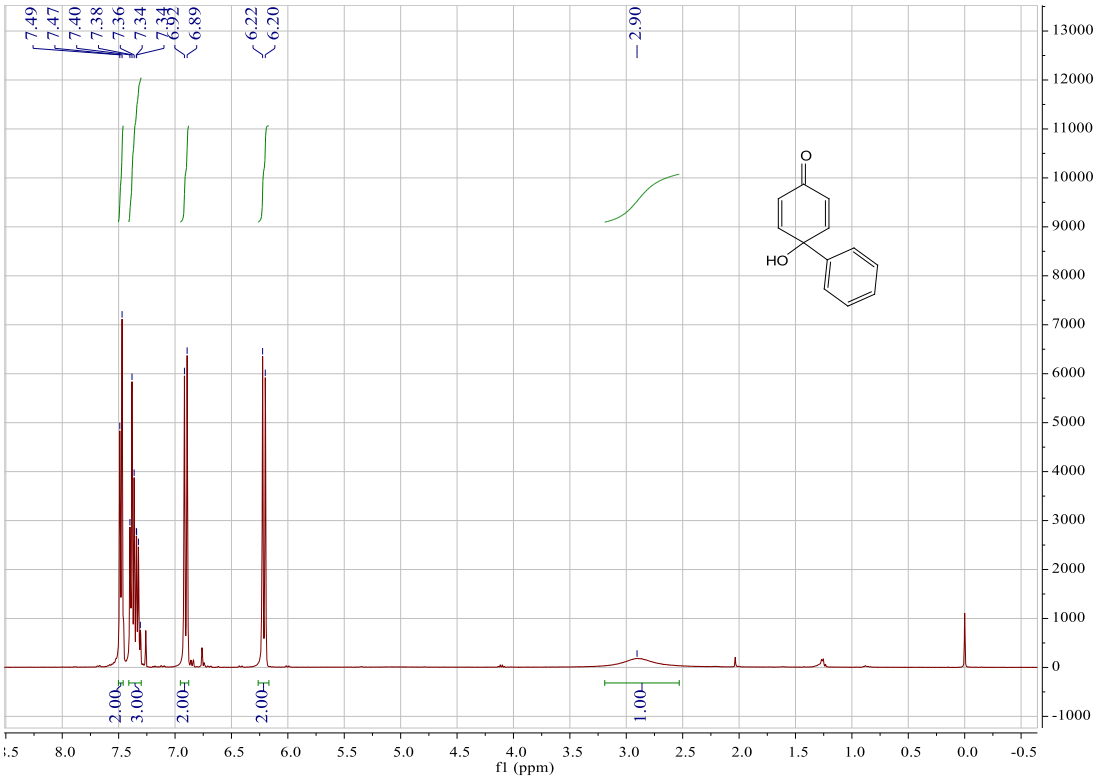
Condition B: A 10 mL sealed tube equipped with a stirring bar was charged with quinones **1a** (1.0 mmol), organic boronic acid **2a** (1.2 mmol), $CuFe_2O_4$ (12.0 mg, 0.05 mmol, 5.0 mol%), TEMPO (2.0 mmol) and MeOH (2.0 mL). The tube was tightly capped and stirred at 25 ℃ for 24. Upon completion, the mixture was diluted with 5 mL of ethyl acetate, filtered through a celite pad and washed with 10 mL of ethyl acetate. The filtrate was collected and concentrated. The residue was purified by silica gel column chromatography using PE/EtOAc (5/1) as the eluent to obtain the desired product.

5. References

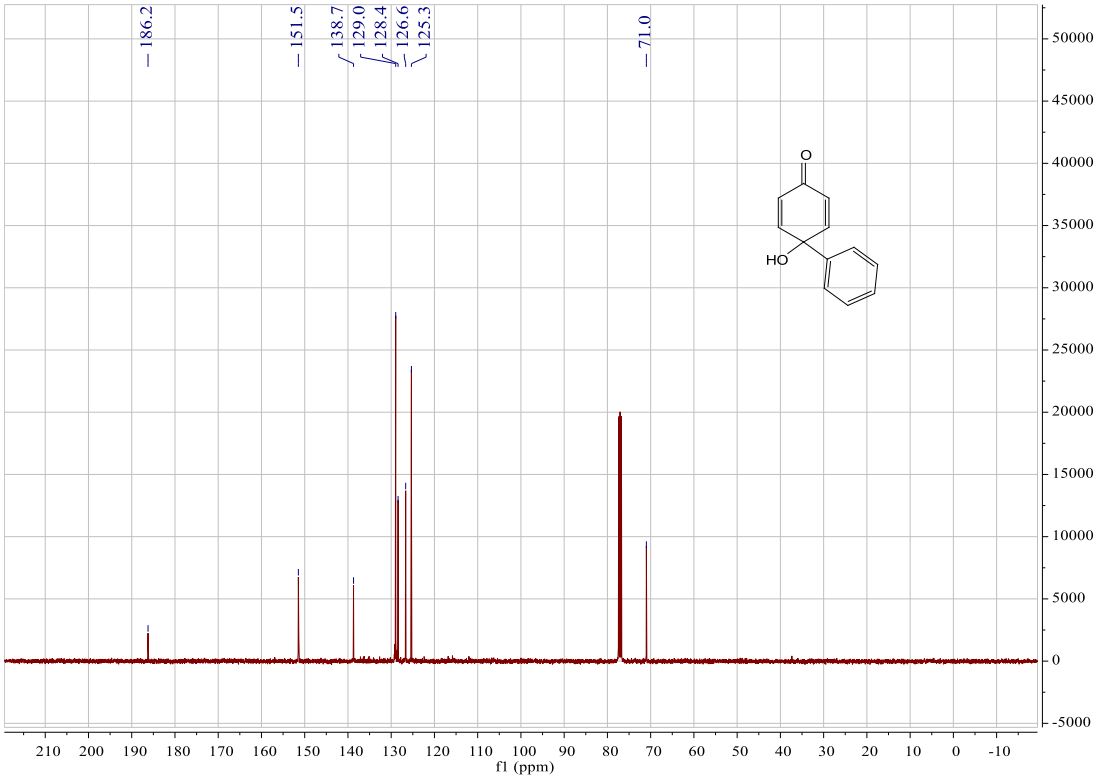
1 M. F. Boehm and G. D. Prestwich, *Journal of Labelled Compounds and Radiopharmaceuticals*, 1988, **25**, 1007-1015.

6. NMR spectra

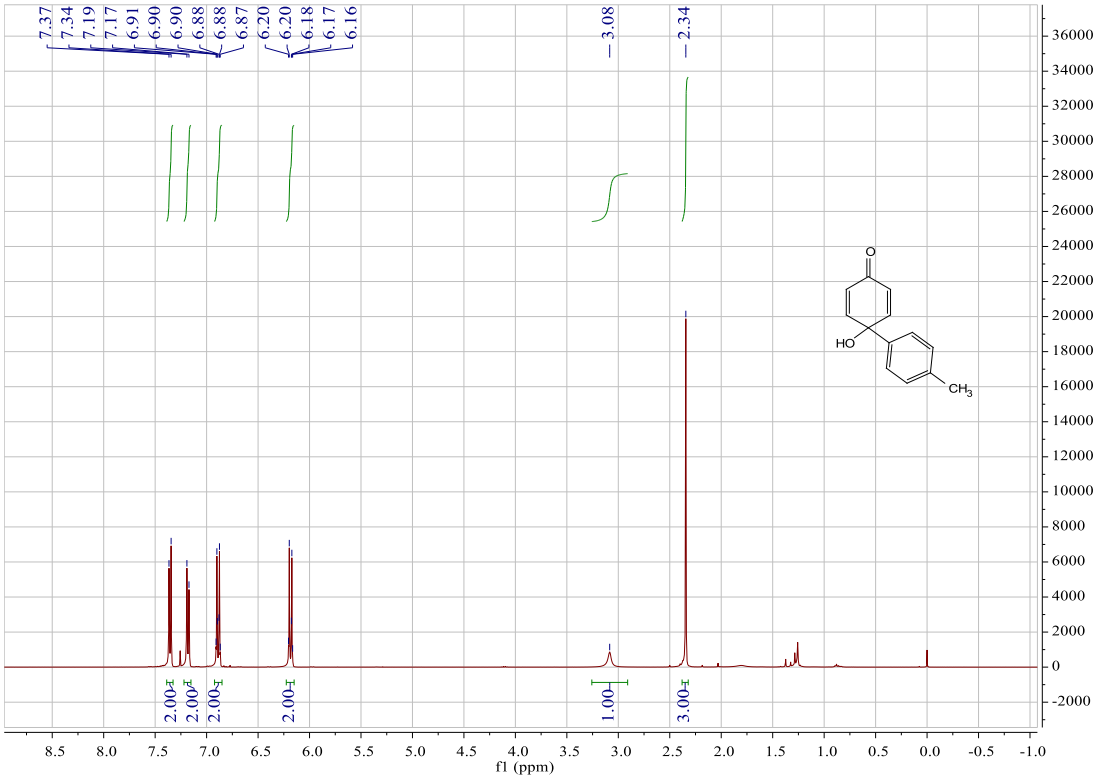
^{1}H NMR of compound **3aa**



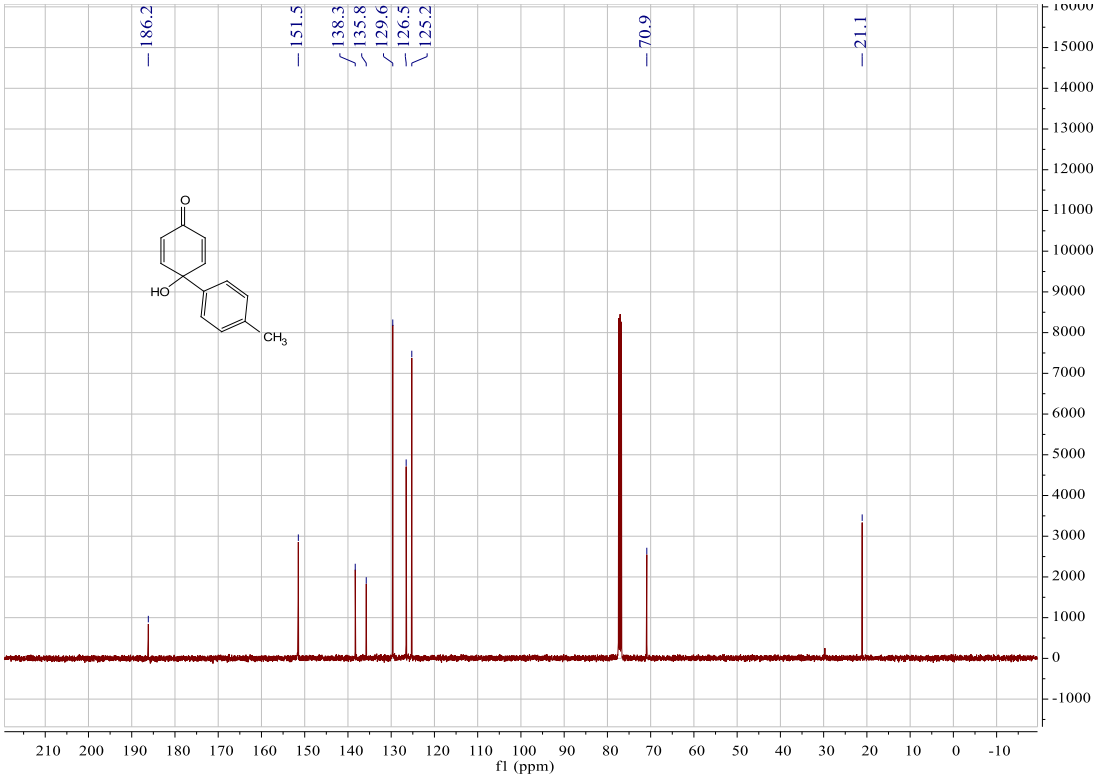
^{13}C NMR of compound **3aa**



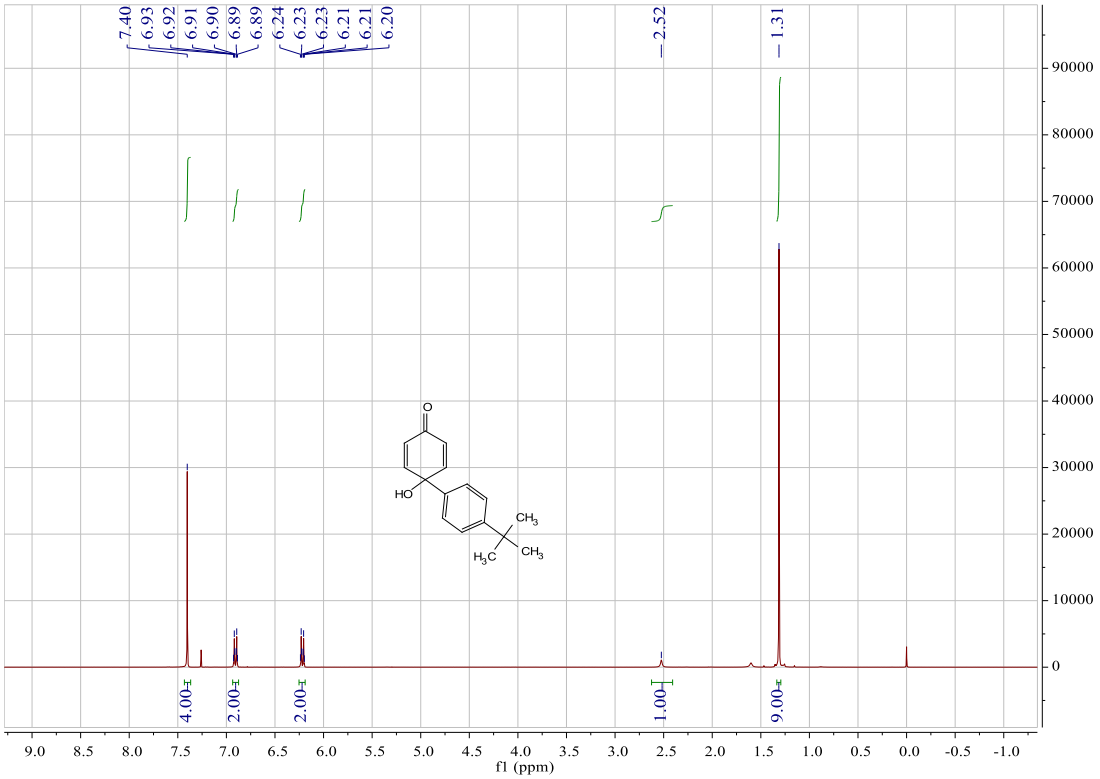
^{1}H NMR of compound **3ab**



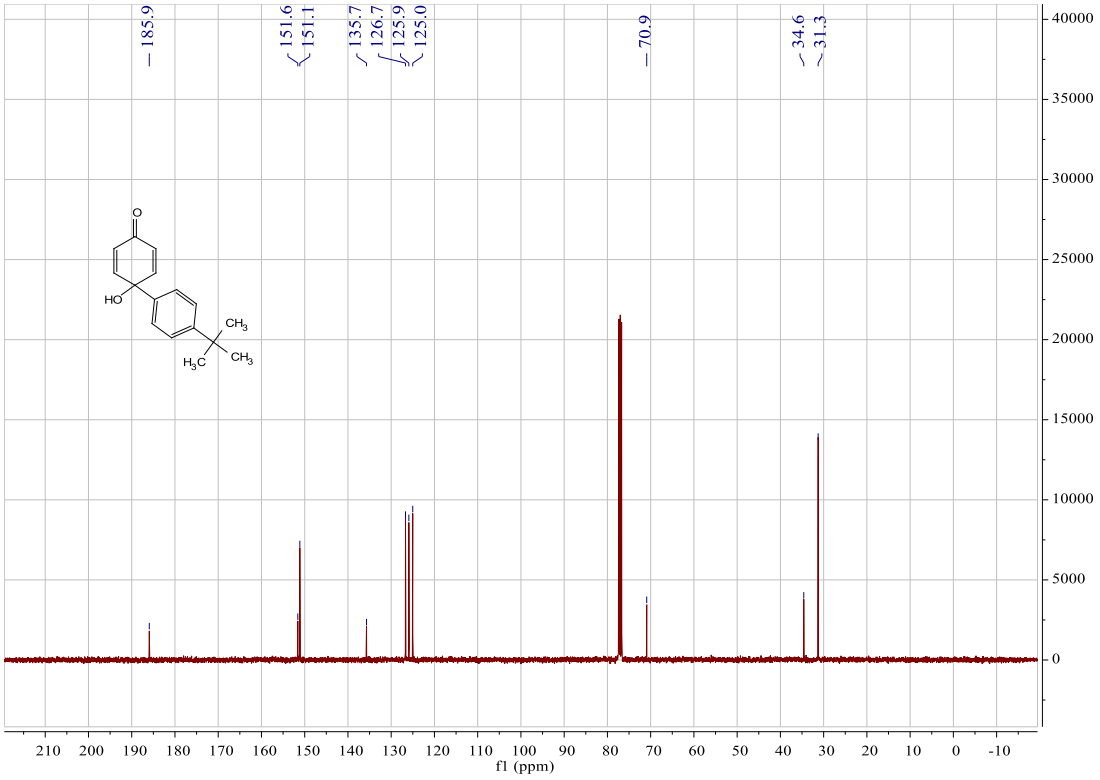
^{13}C NMR of compound **3ab**



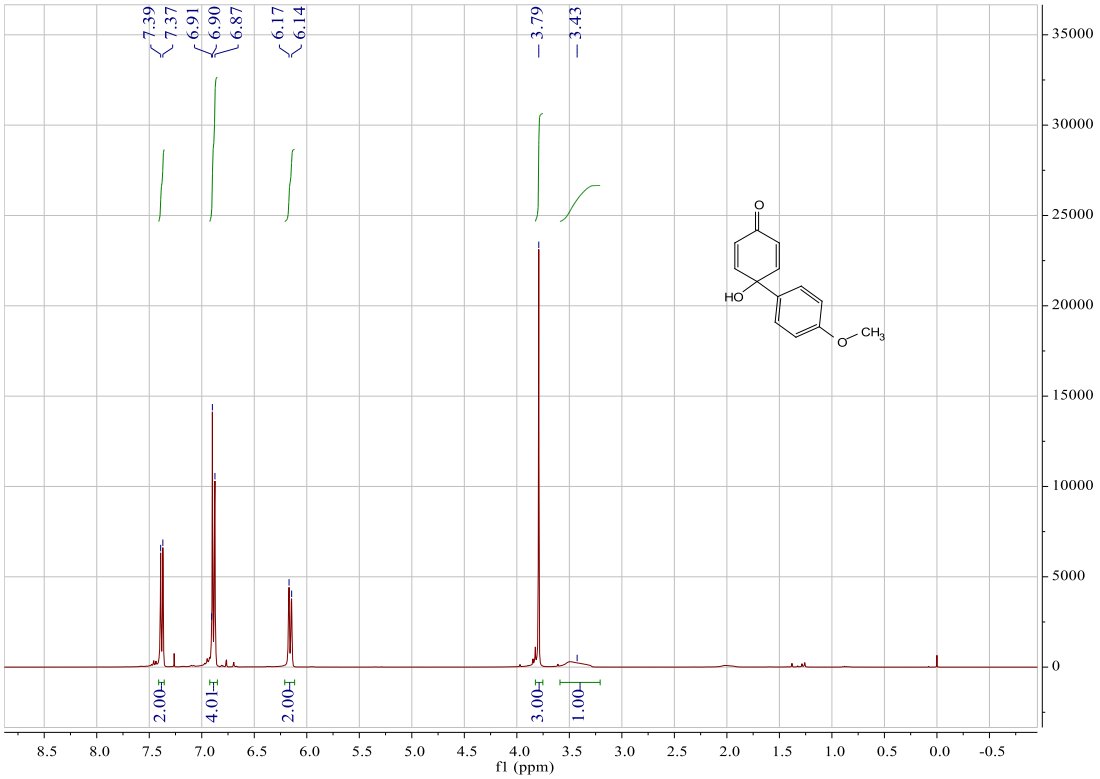
^{1}H NMR of compound **3ac**



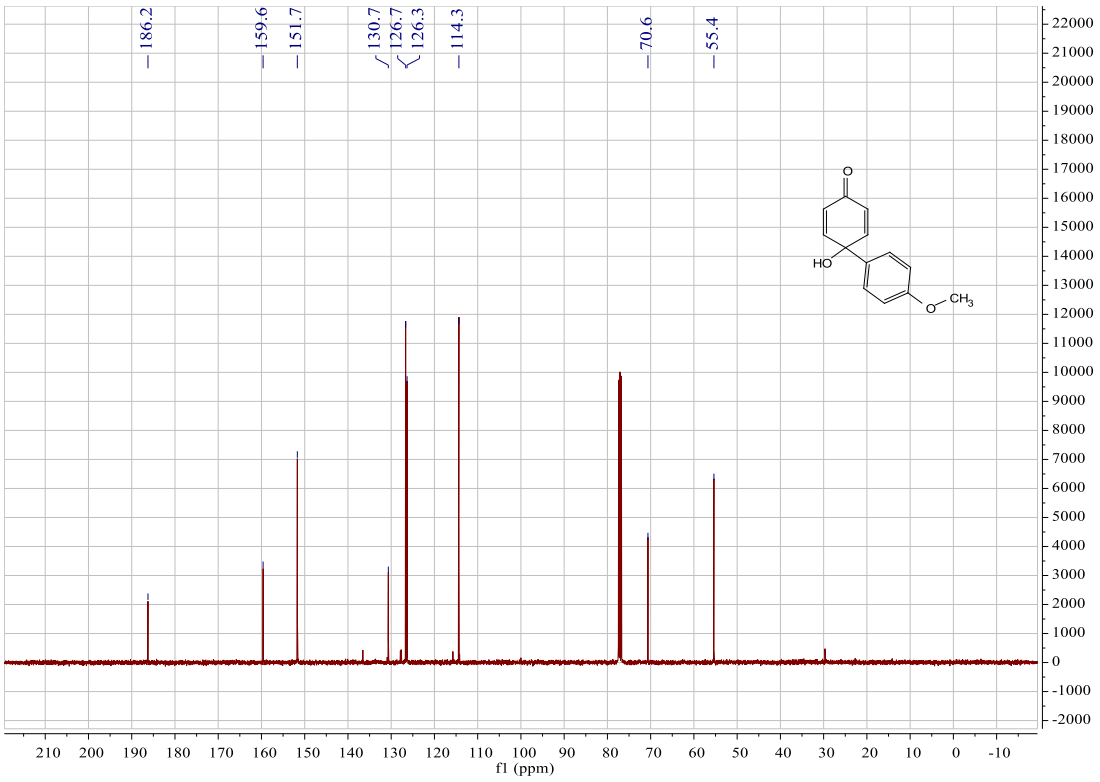
^{13}C NMR of compound **3ac**



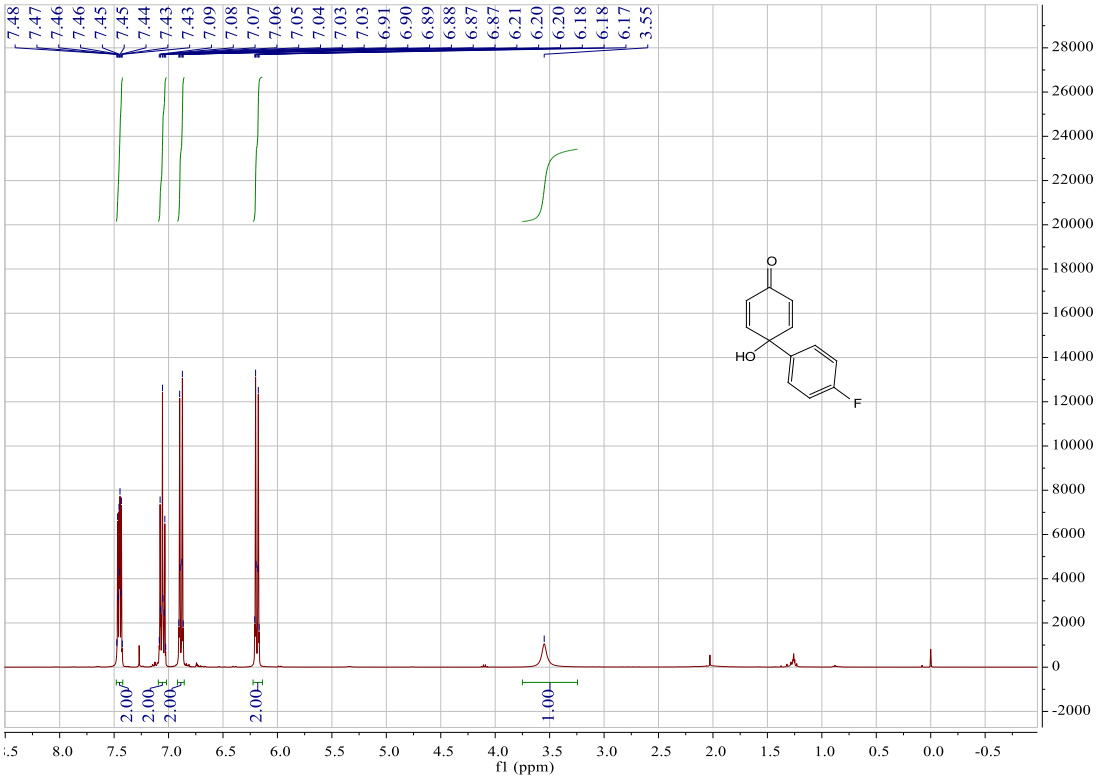
^{1}H NMR of compound **3ad**



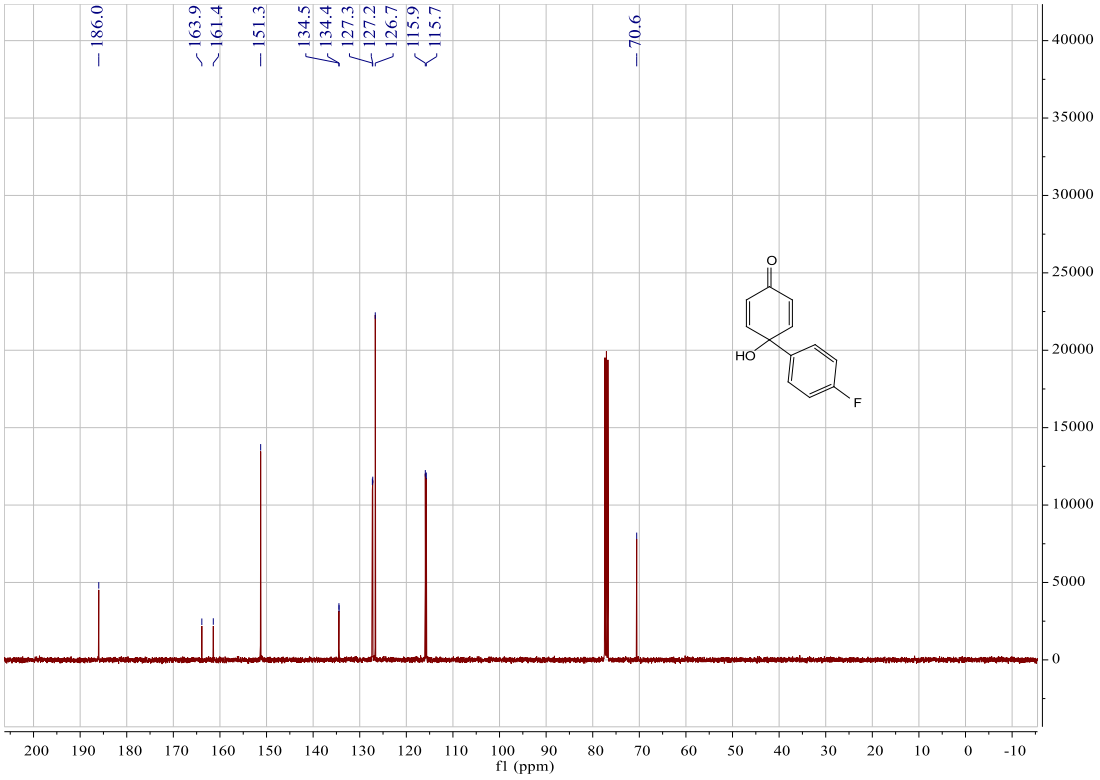
^{13}C NMR of compound **3ad**



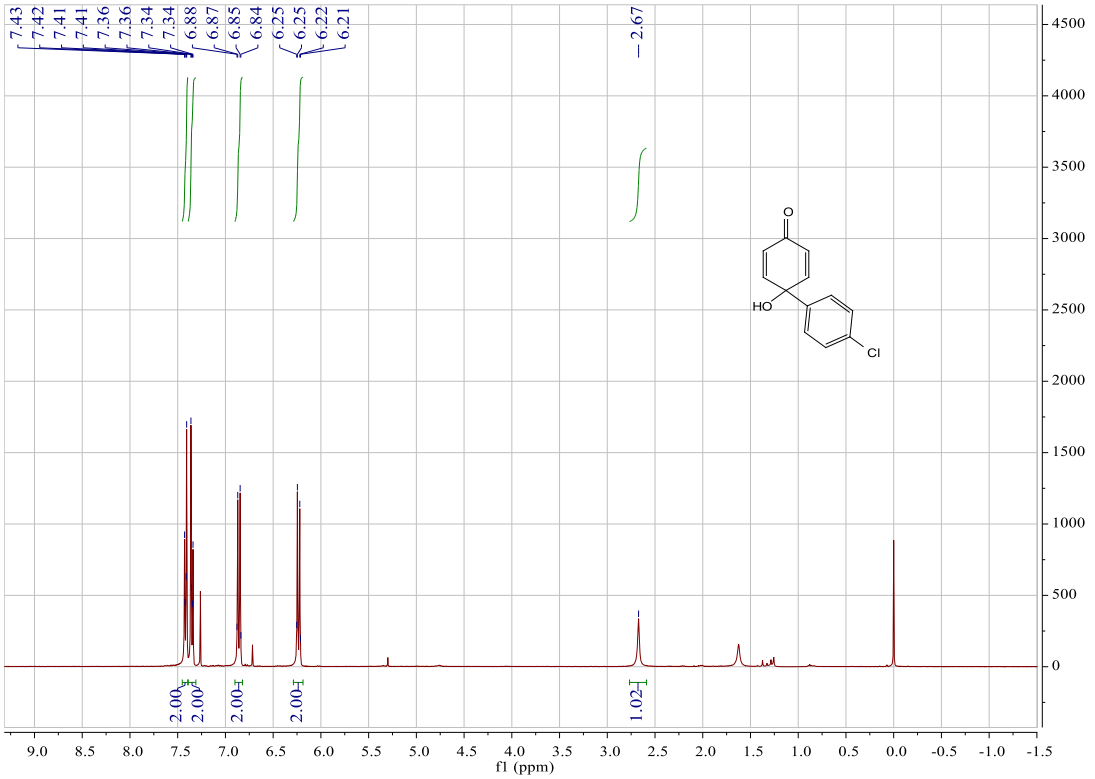
^{1}H NMR of compound **3ae**



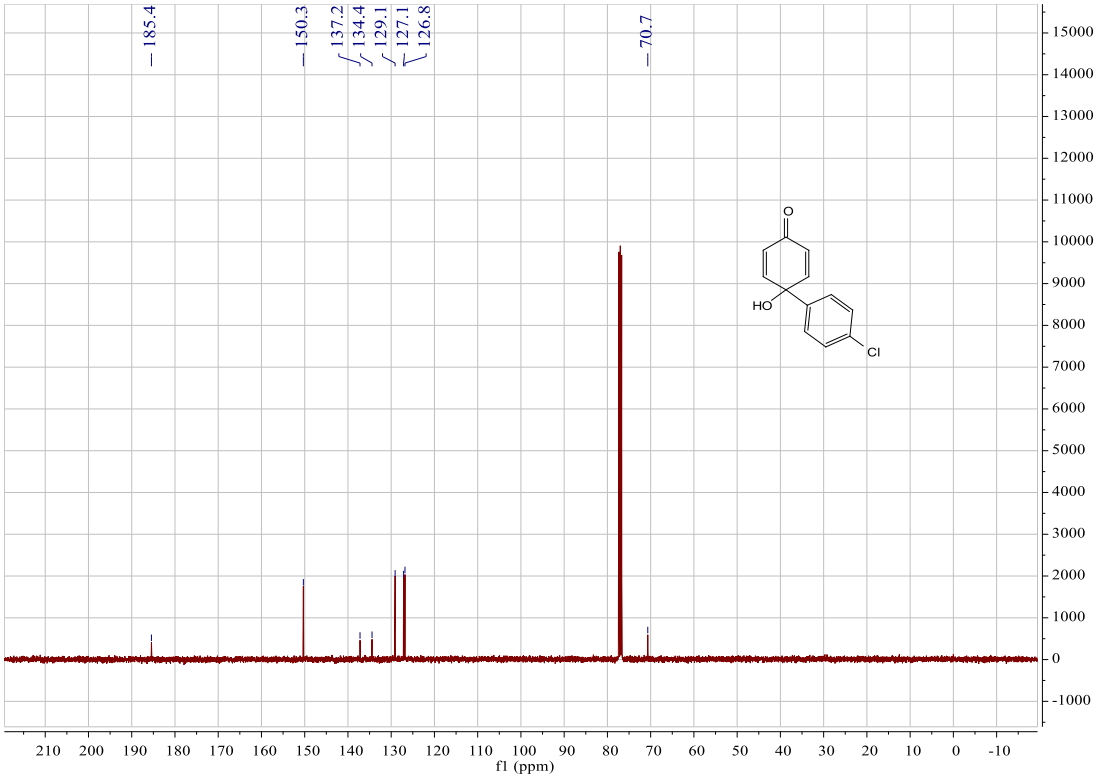
^{13}C NMR of compound **3ae**



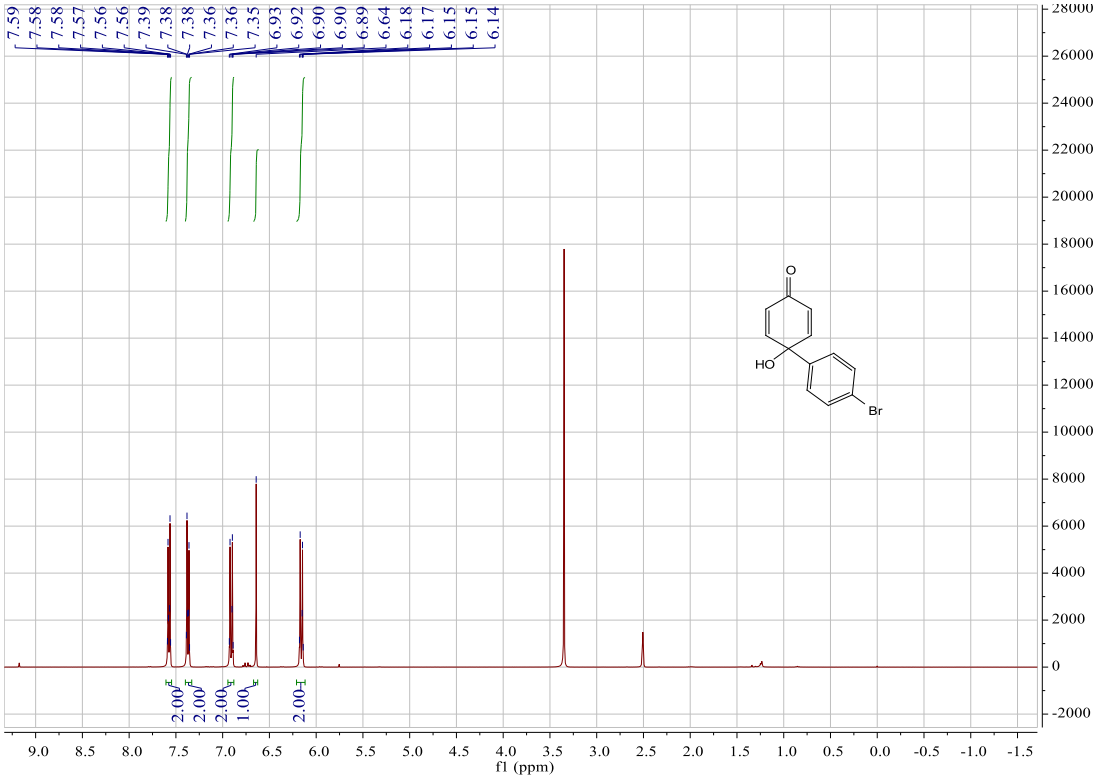
^{1}H NMR of compound **3af**



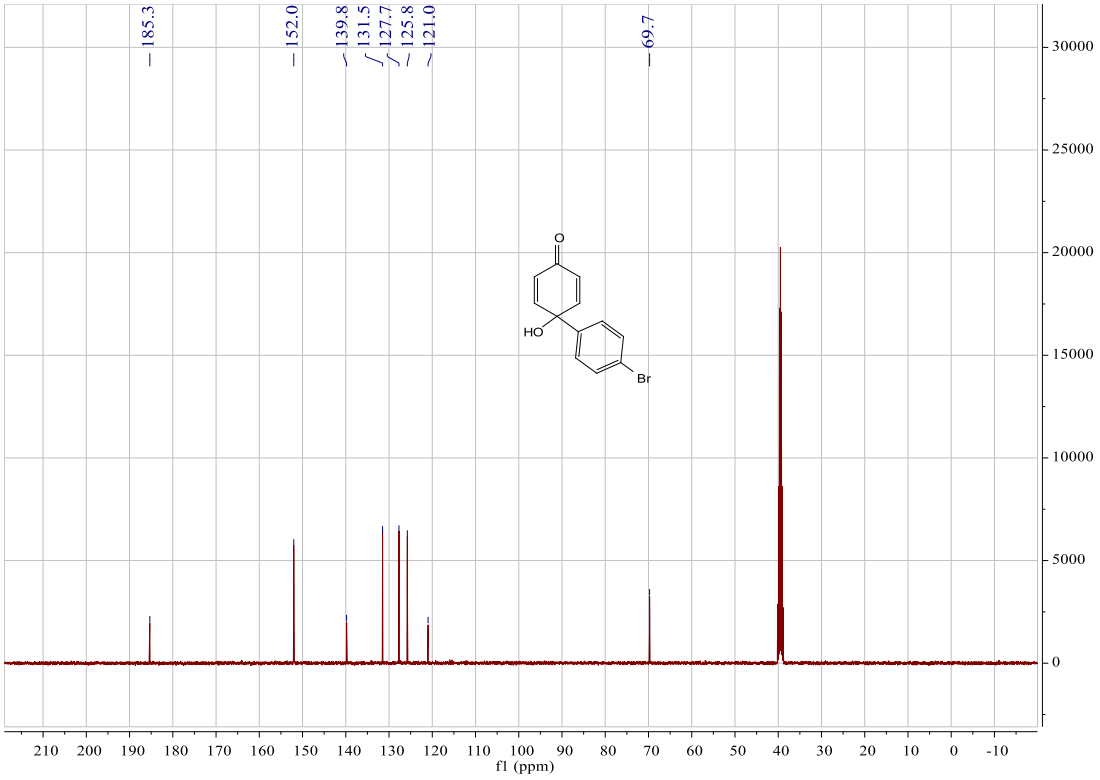
^{13}C NMR of compound **3af**



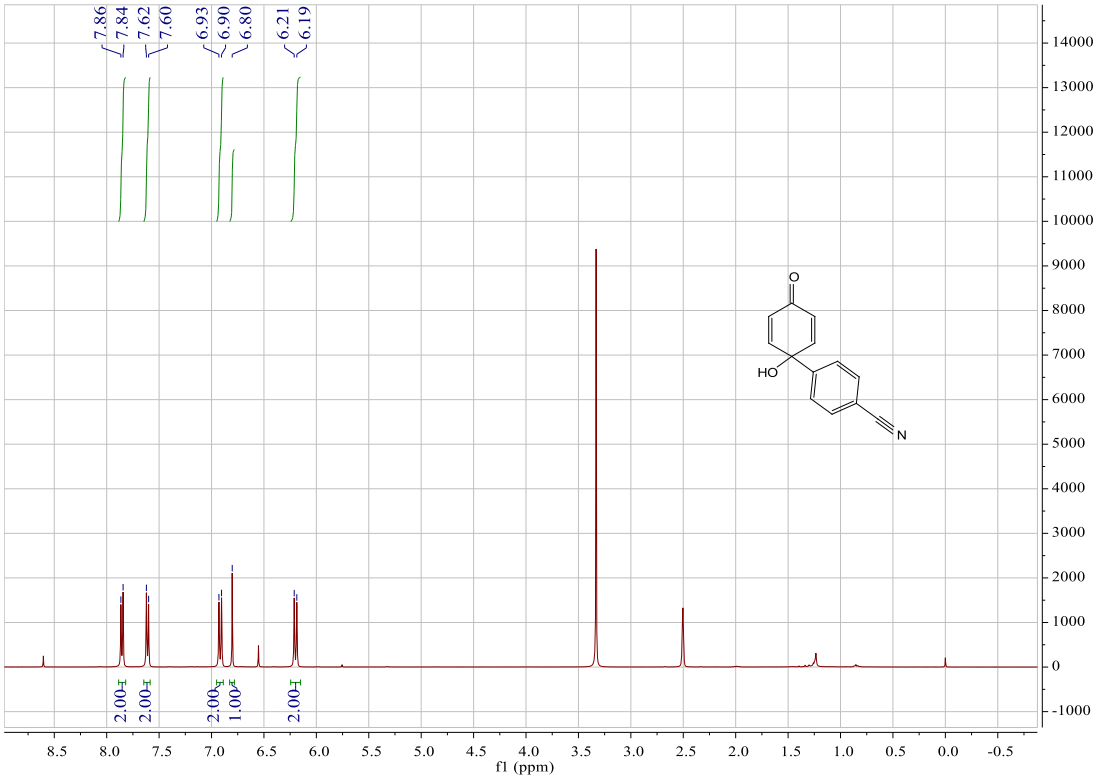
^{1}H NMR of compound **3ag**



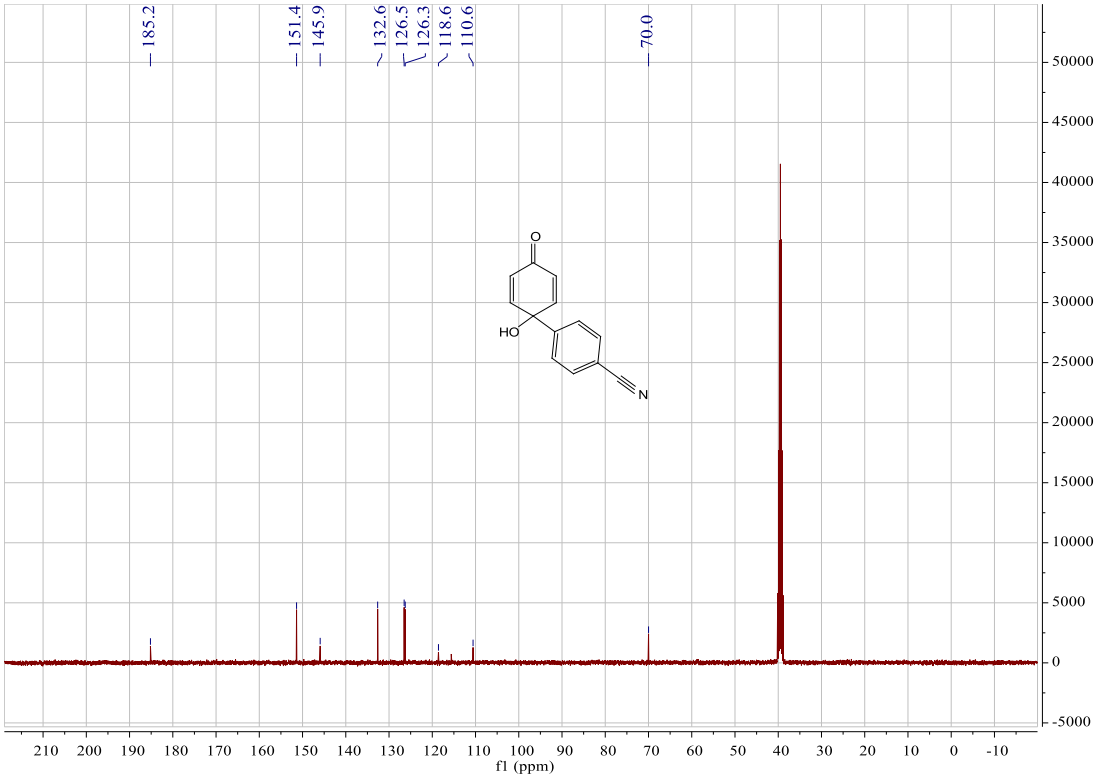
^{13}C NMR of compound **3ag**



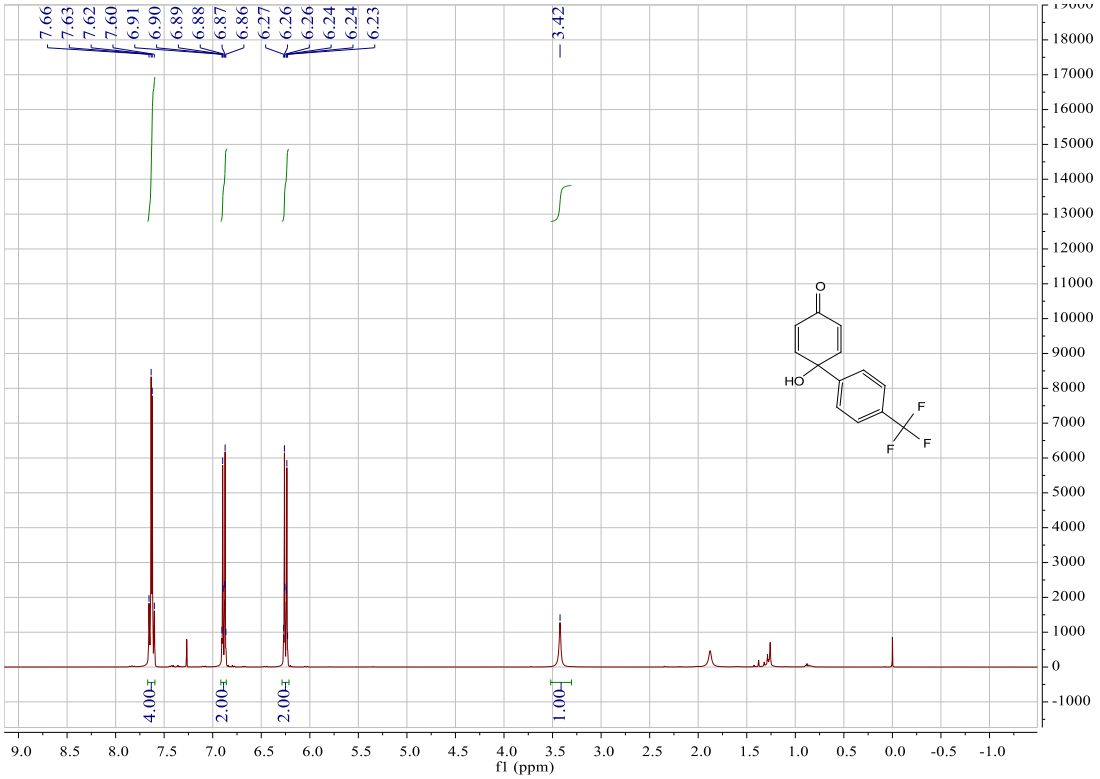
^{1}H NMR of compound **3ah**



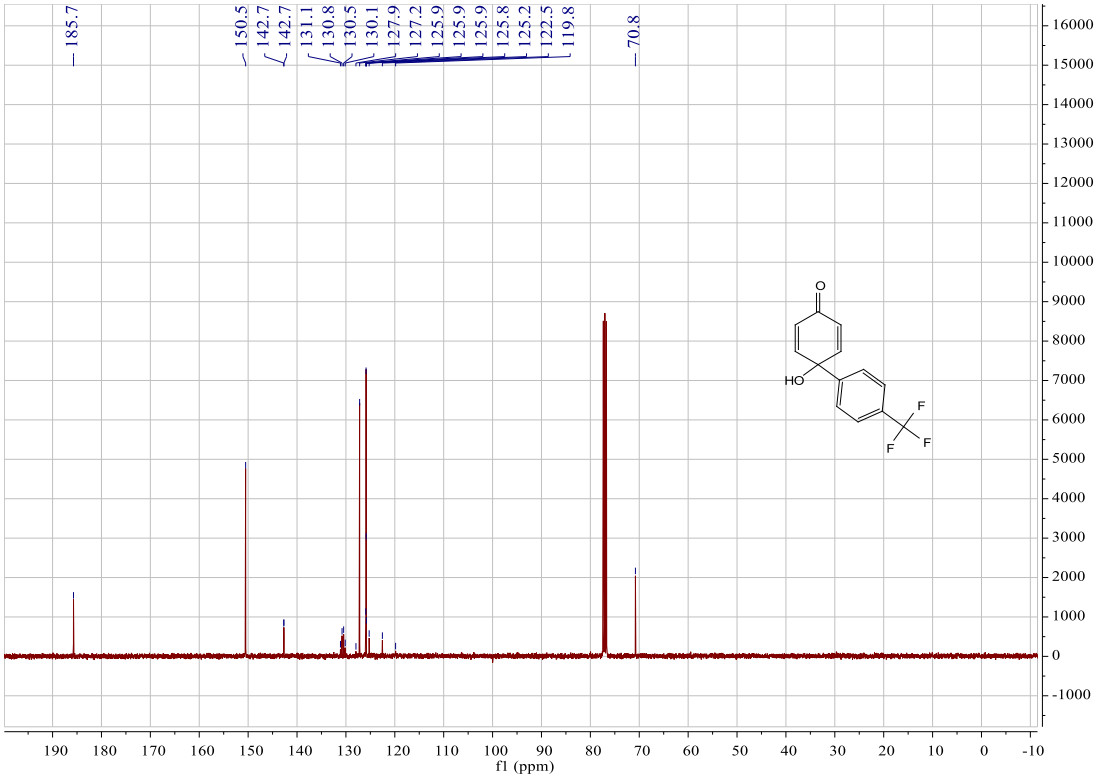
^{13}C NMR of compound **3ah**



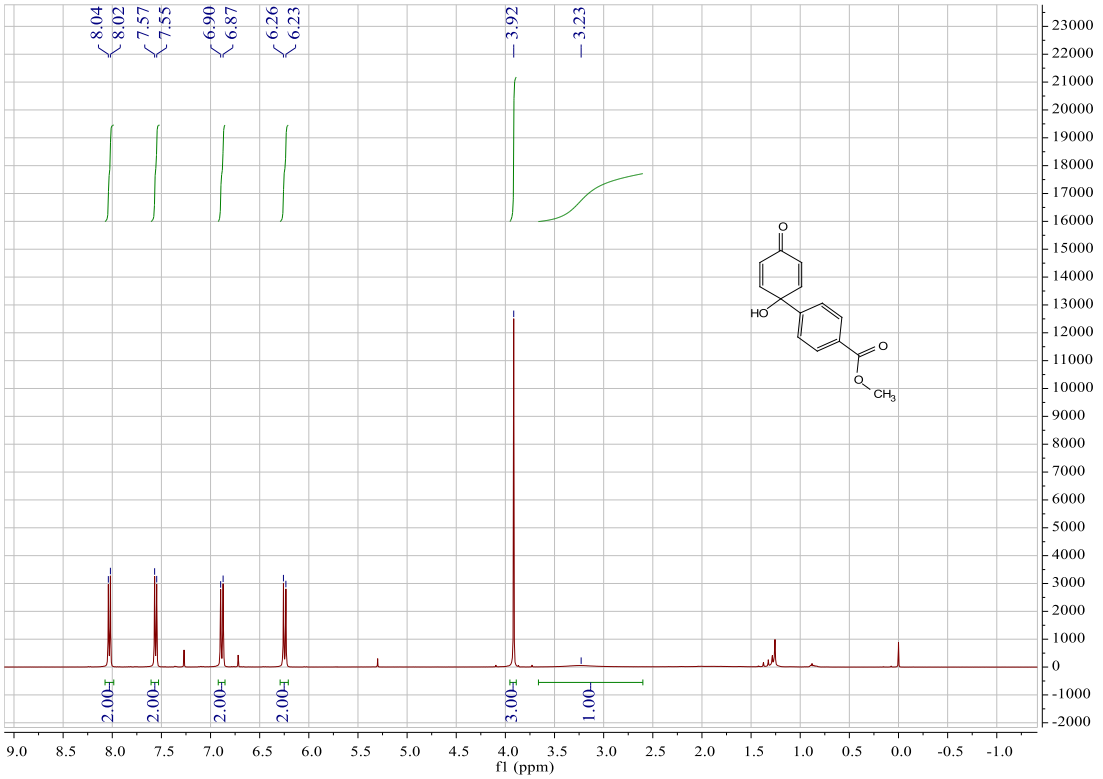
^{1}H NMR of compound **3ai**



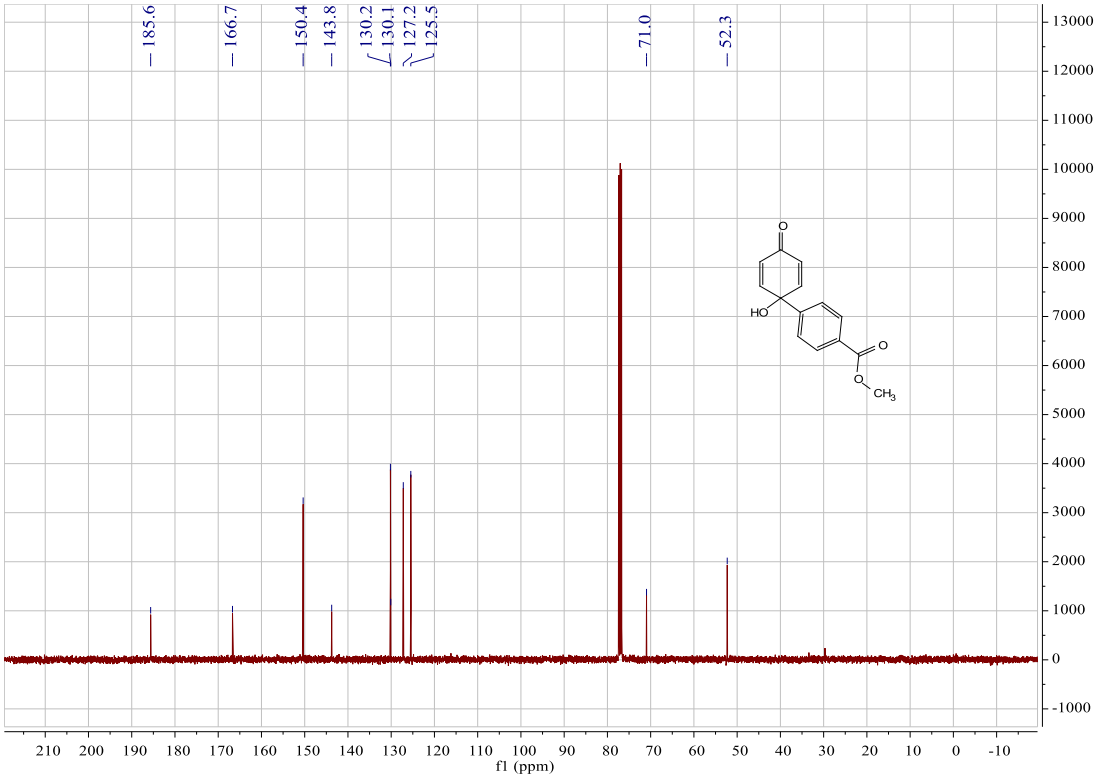
^{13}C NMR of compound **3ai**



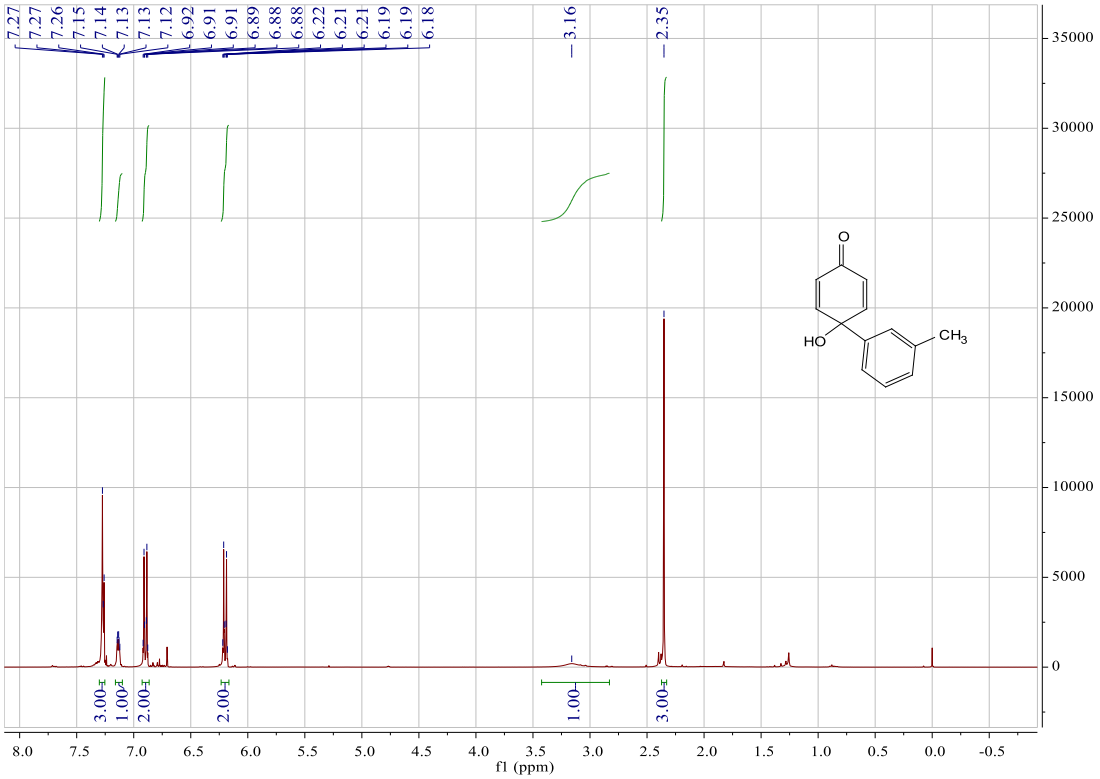
^{1}H NMR of compound **3aj**



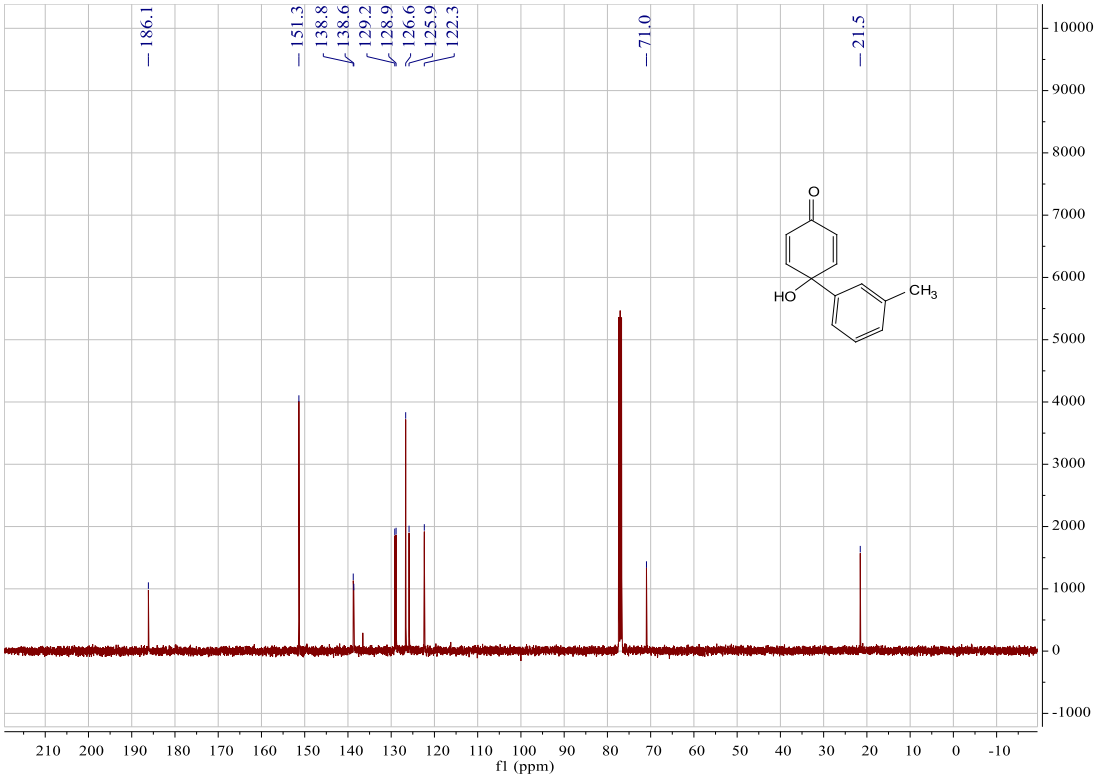
^{13}C NMR of compound **3aj**



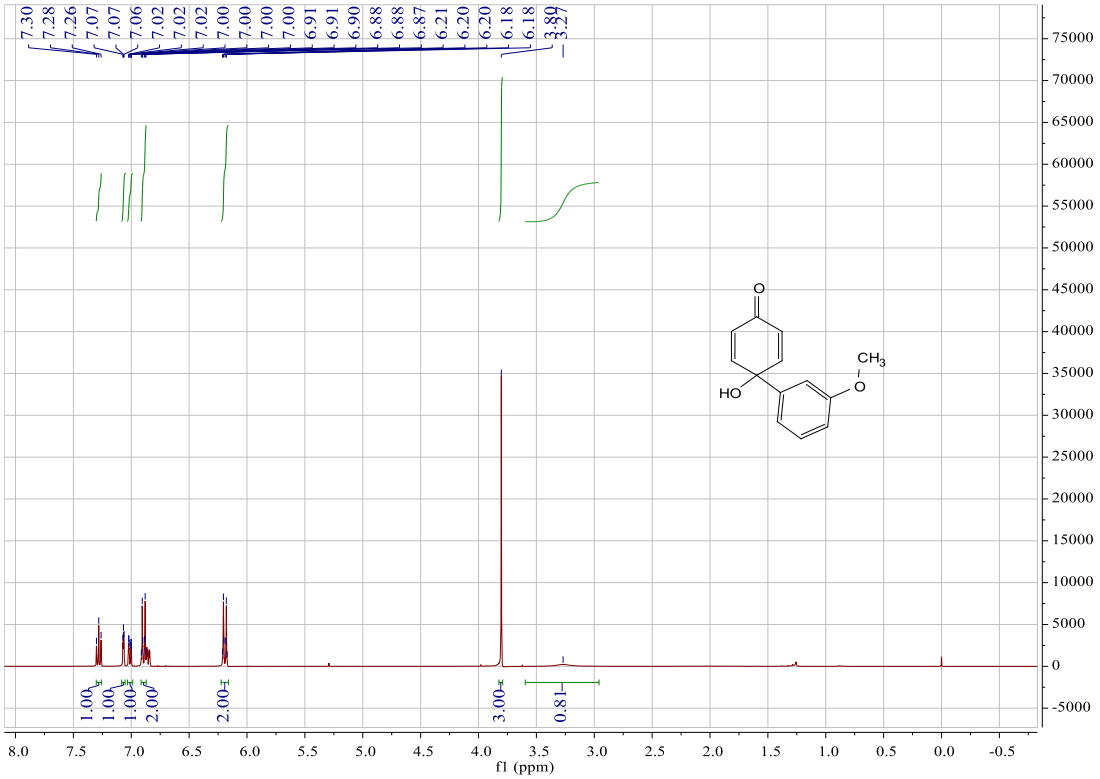
^{1}H NMR of compound **3ak**



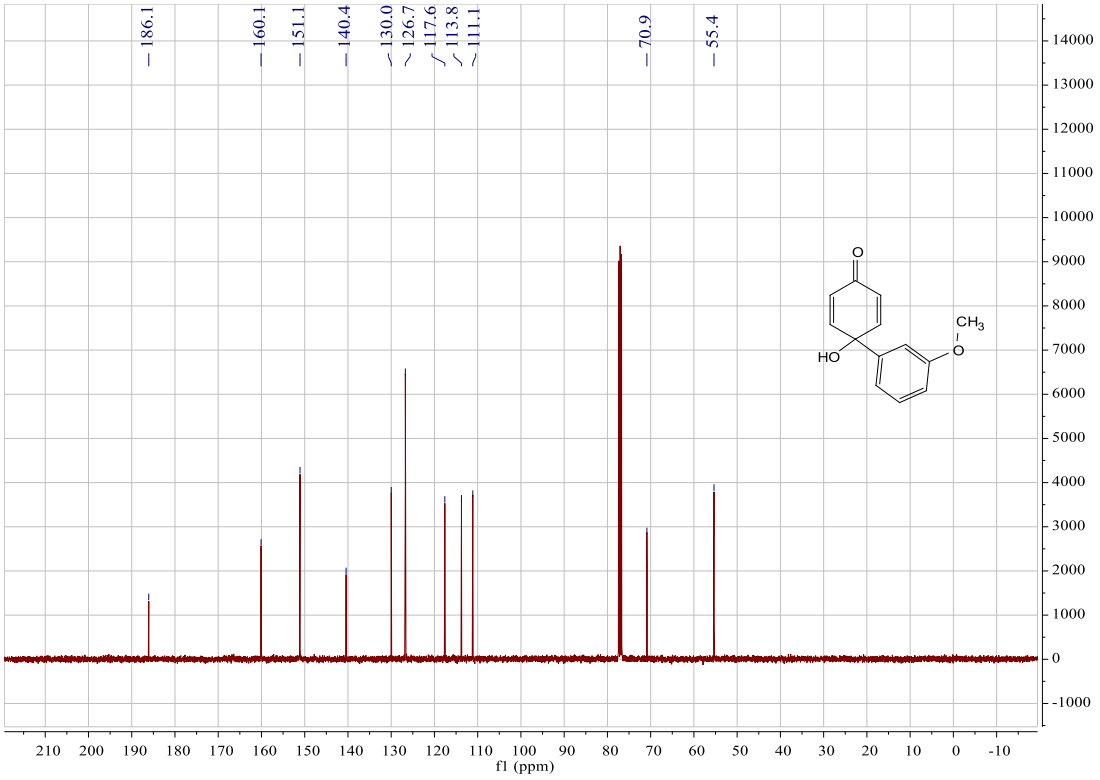
^{13}C NMR of compound **3ak**



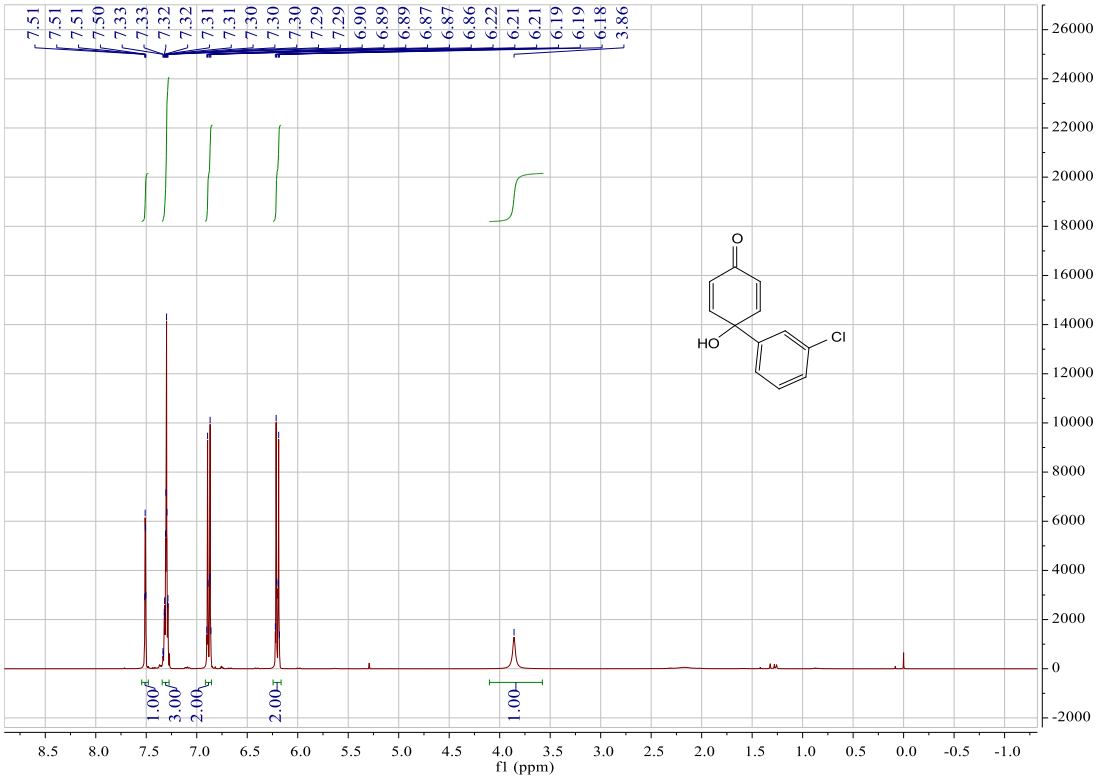
^{1}H NMR of compound **3al**



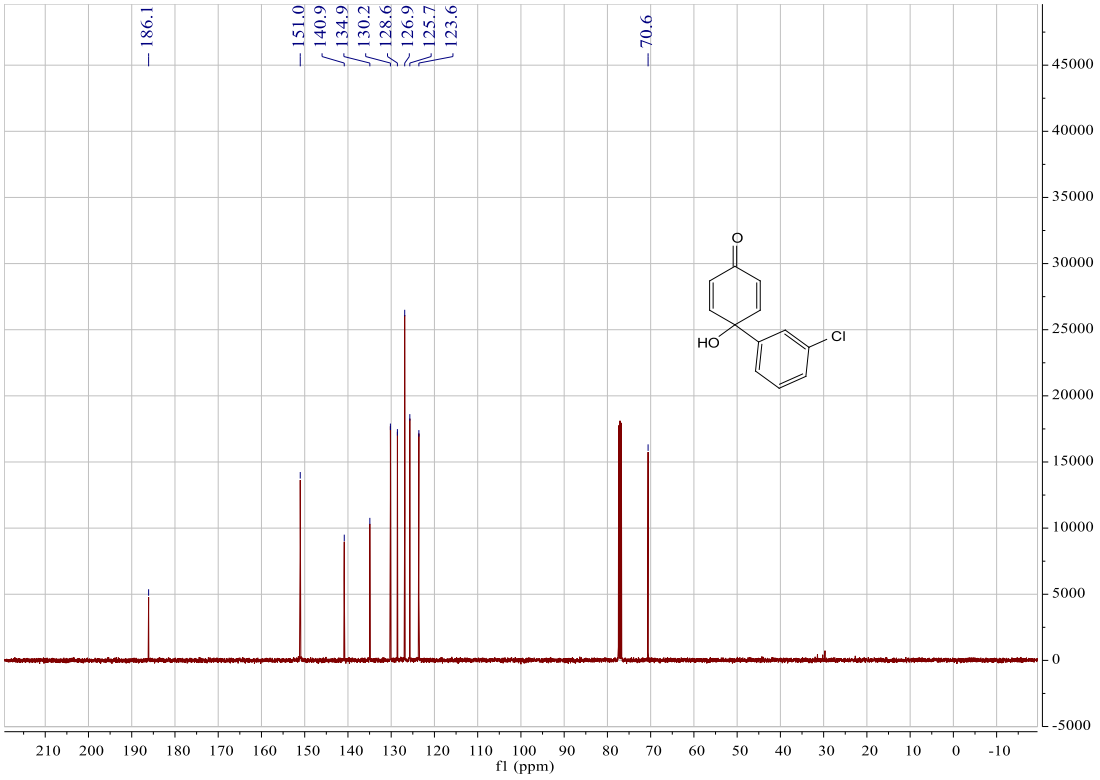
^{13}C NMR of compound **3al**



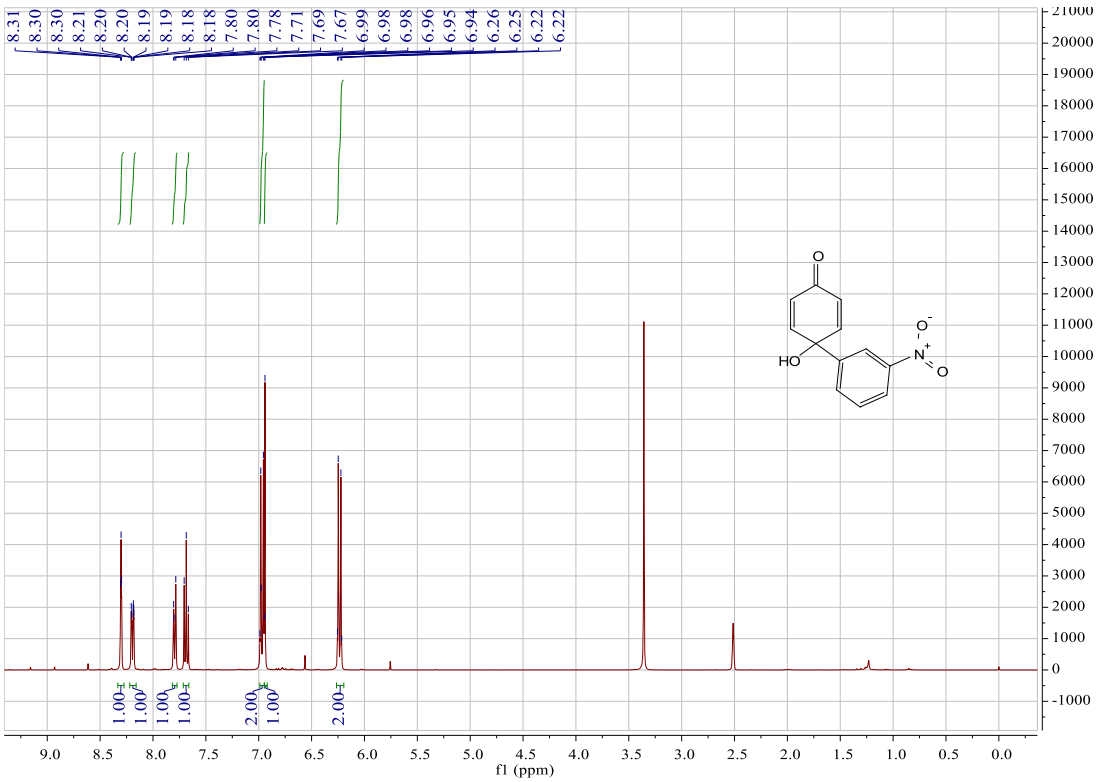
^{1}H NMR of compound **3am**



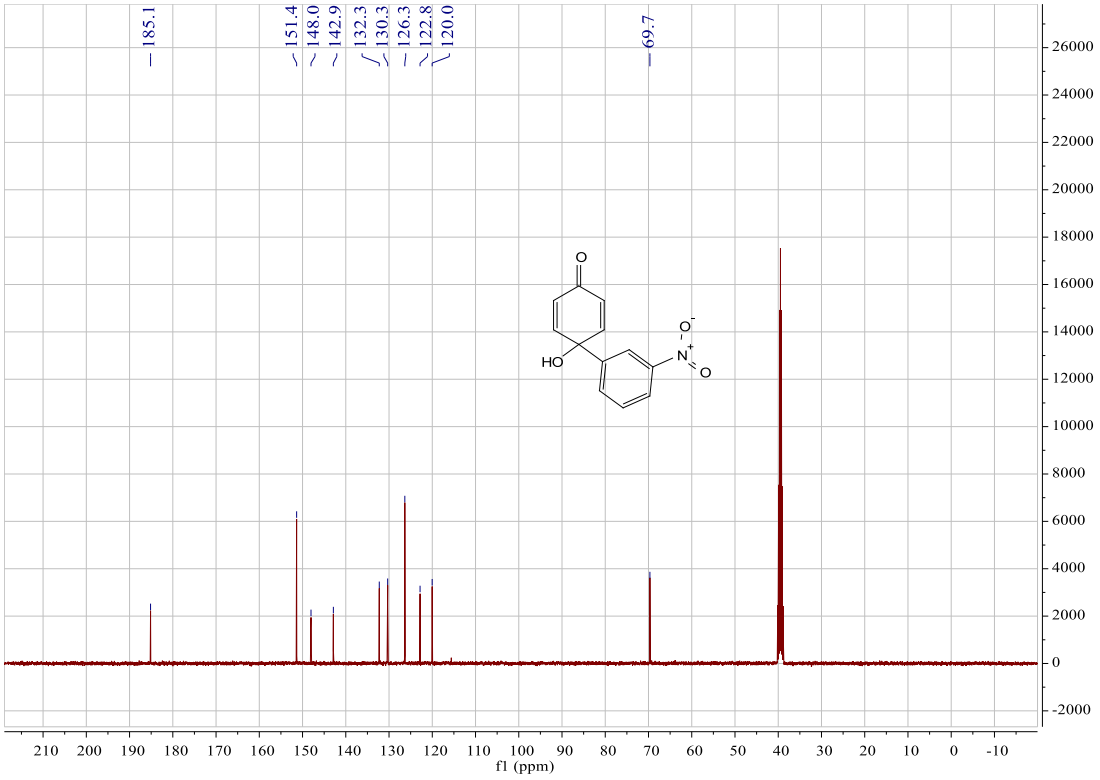
^{13}C NMR of compound **3am**



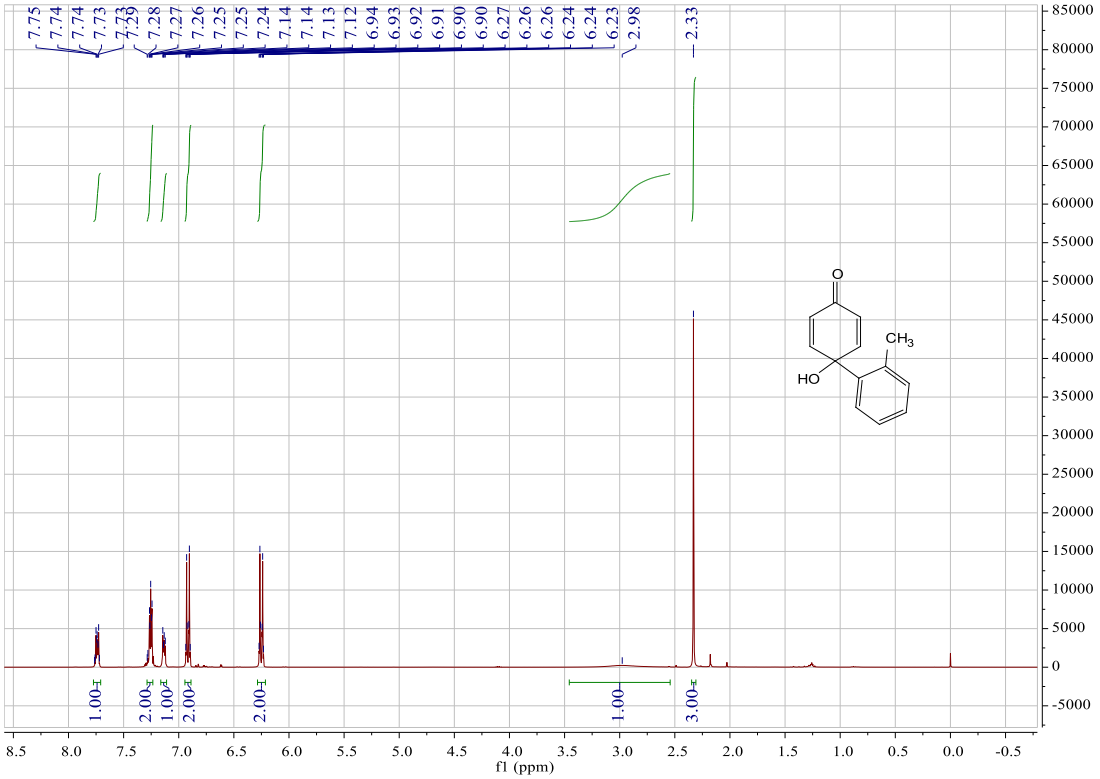
^{1}H NMR of compound **3an**



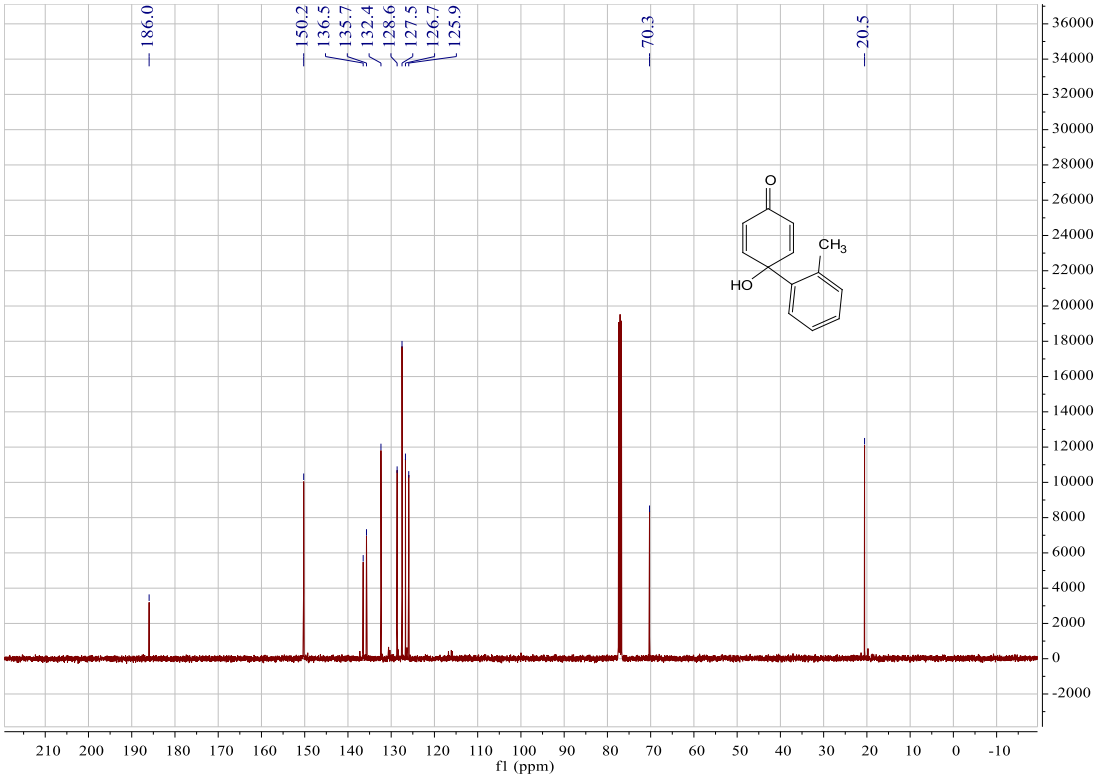
^{13}C NMR of compound **3an**



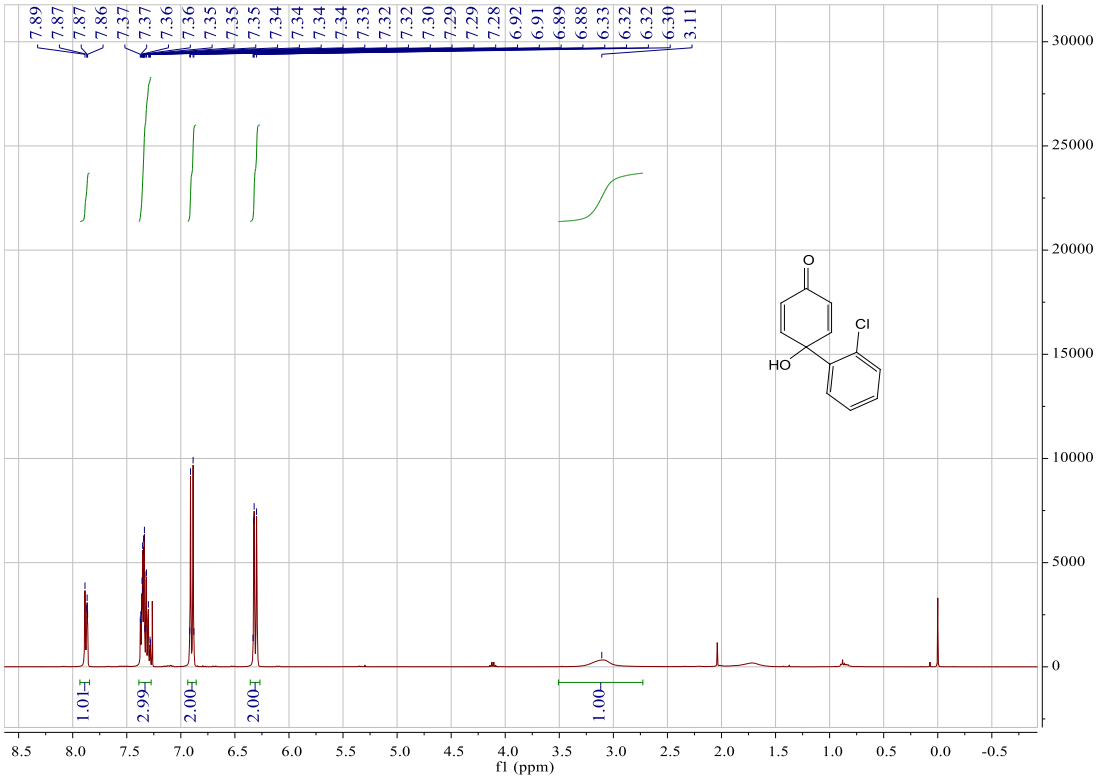
^{1}H NMR of compound **3ao**



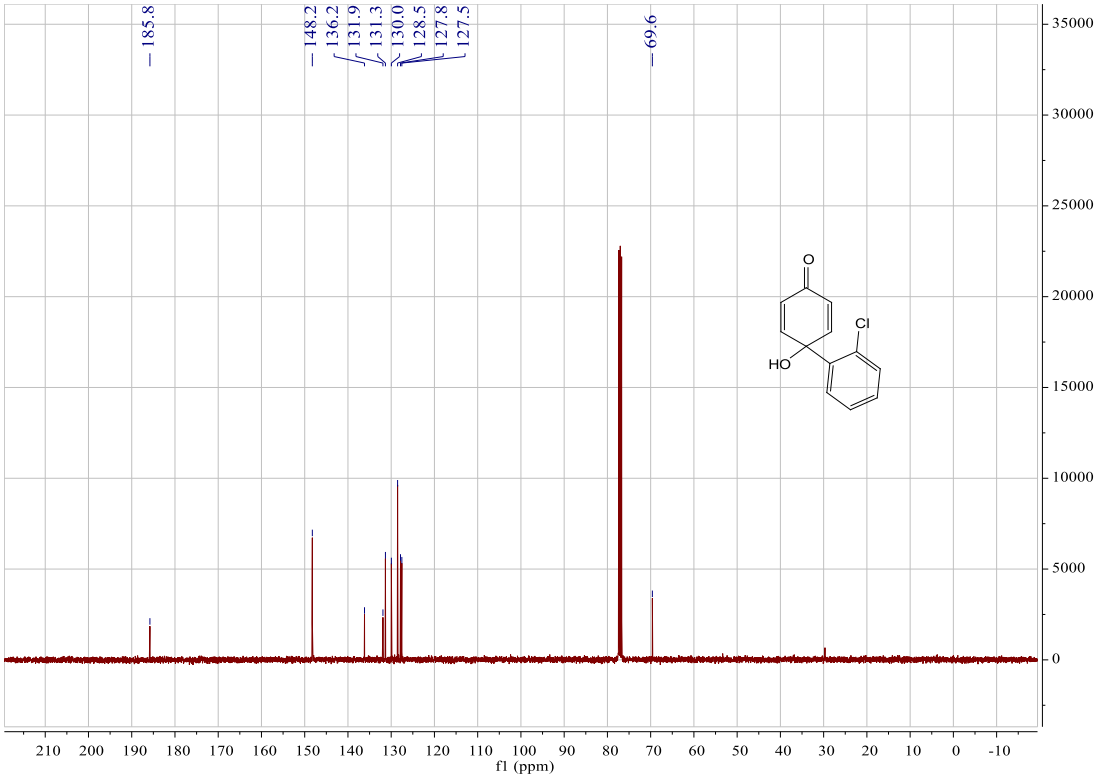
^{13}C NMR of compound **3ao**



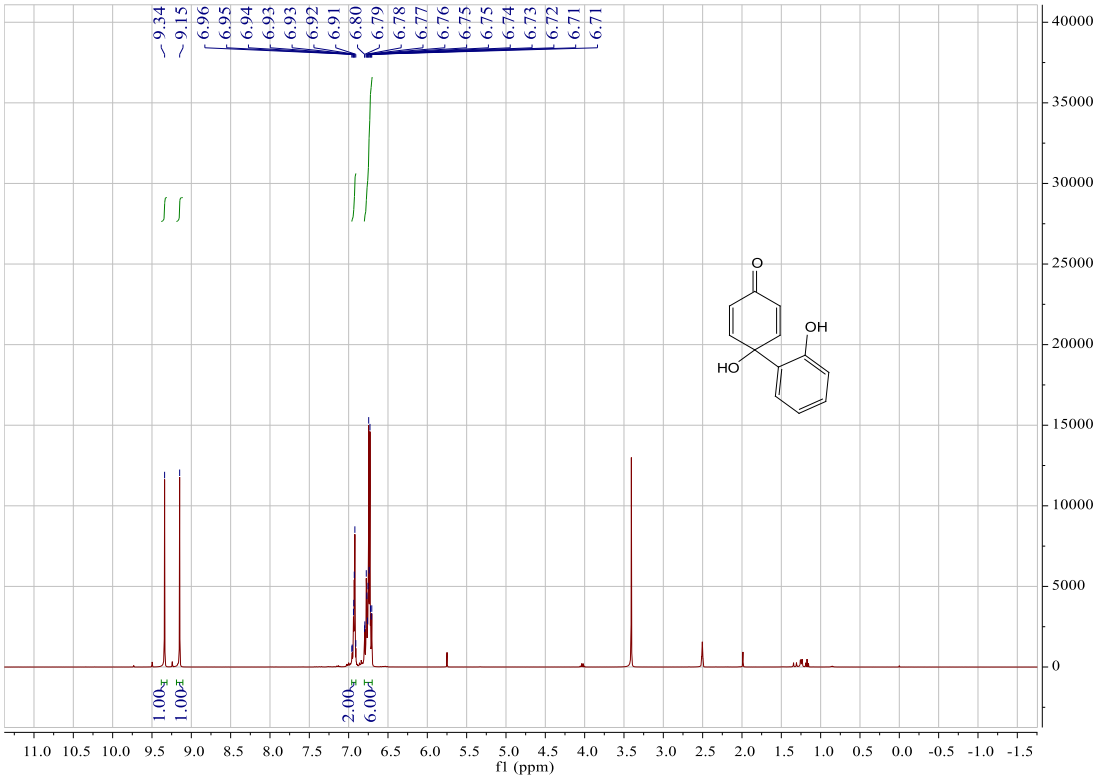
^{1}H NMR of compound **3ap**



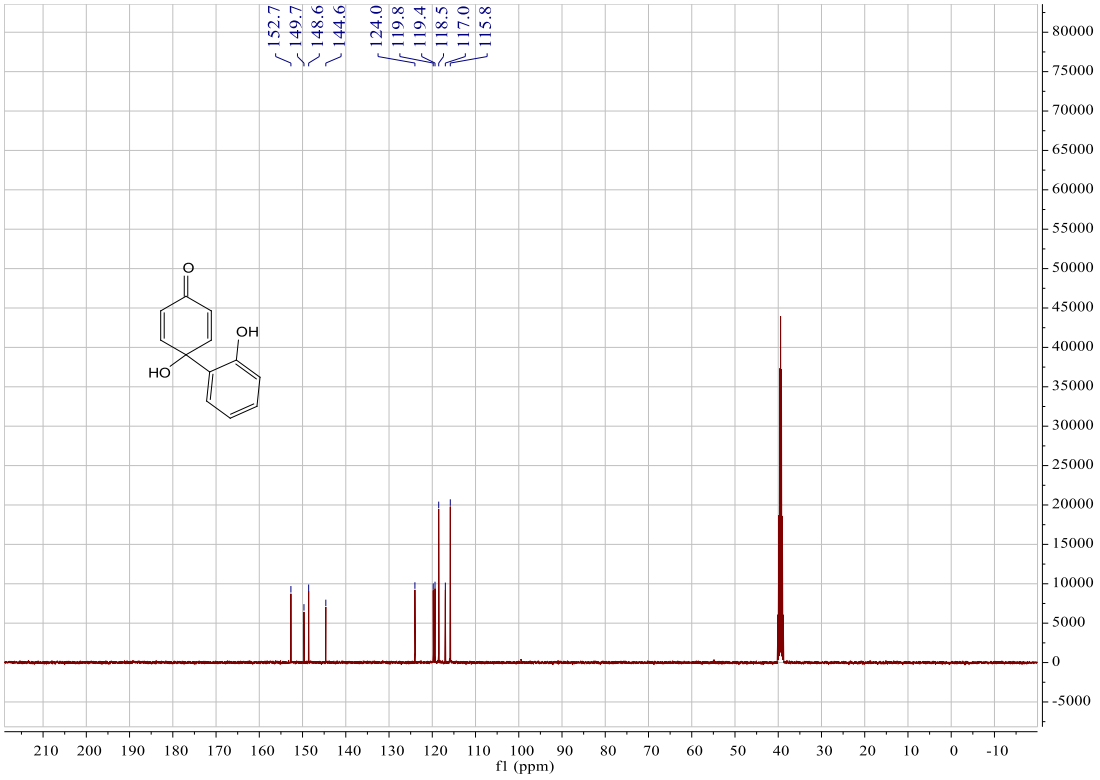
^{13}C NMR of compound **3ap**



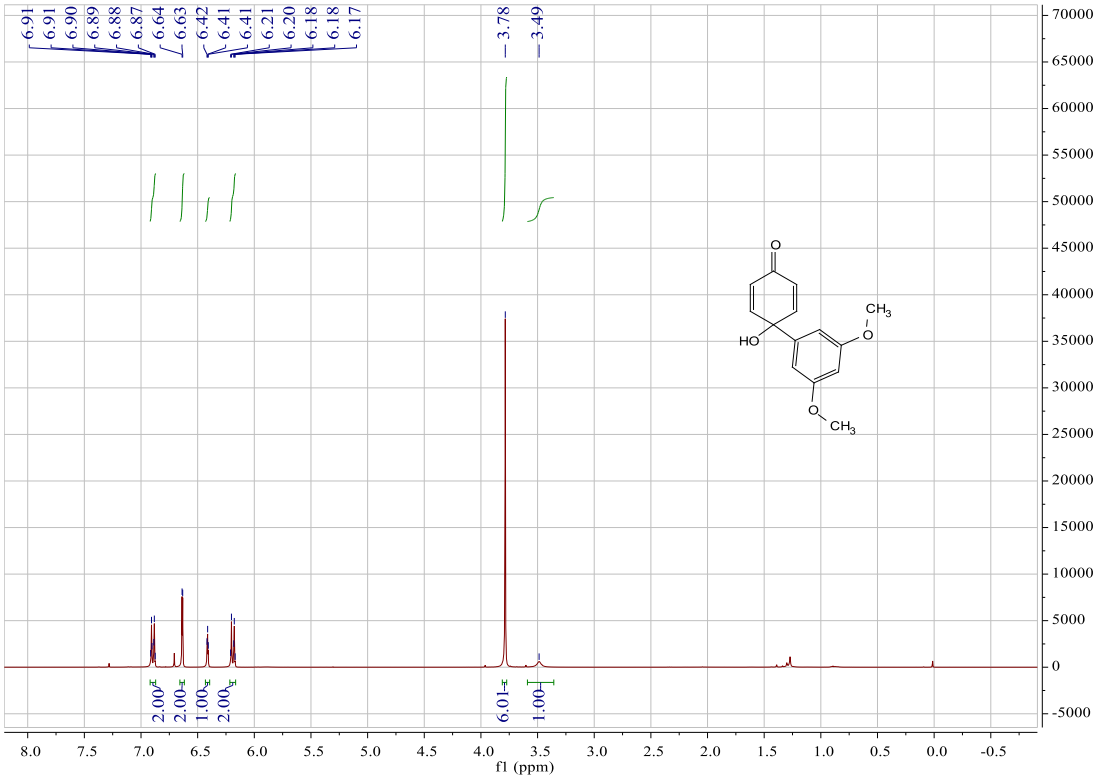
^{1}H NMR of compound **3aq**



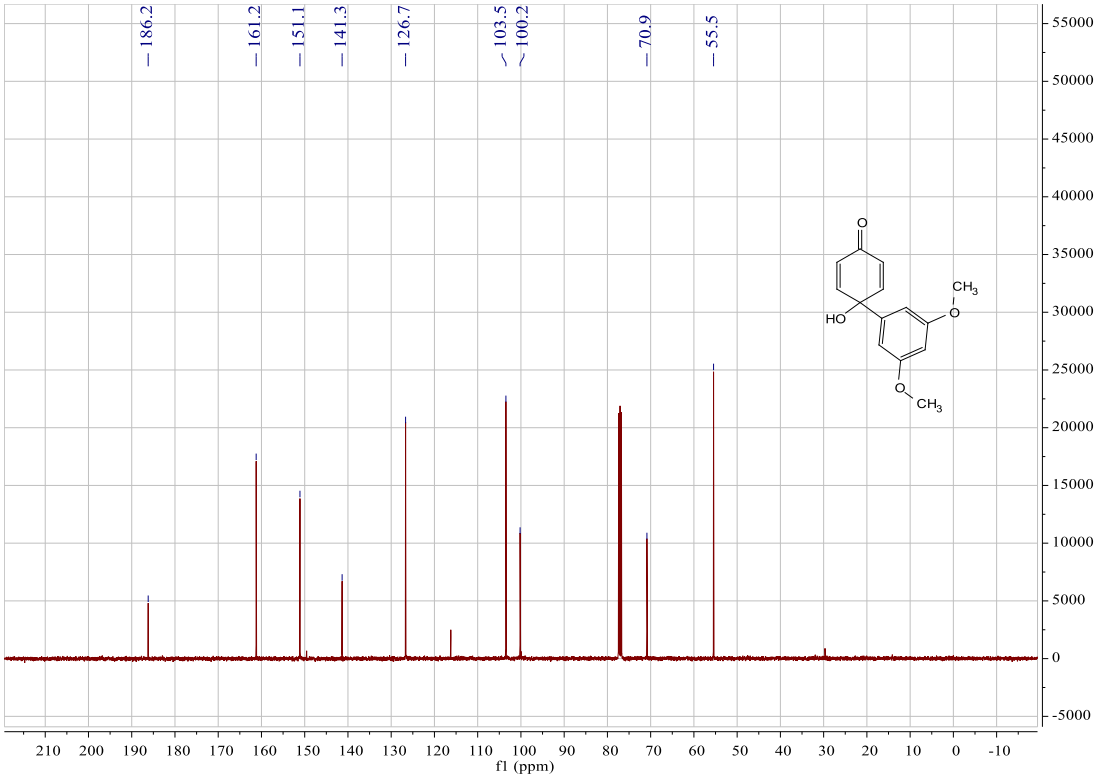
^{13}C NMR of compound **3aq**



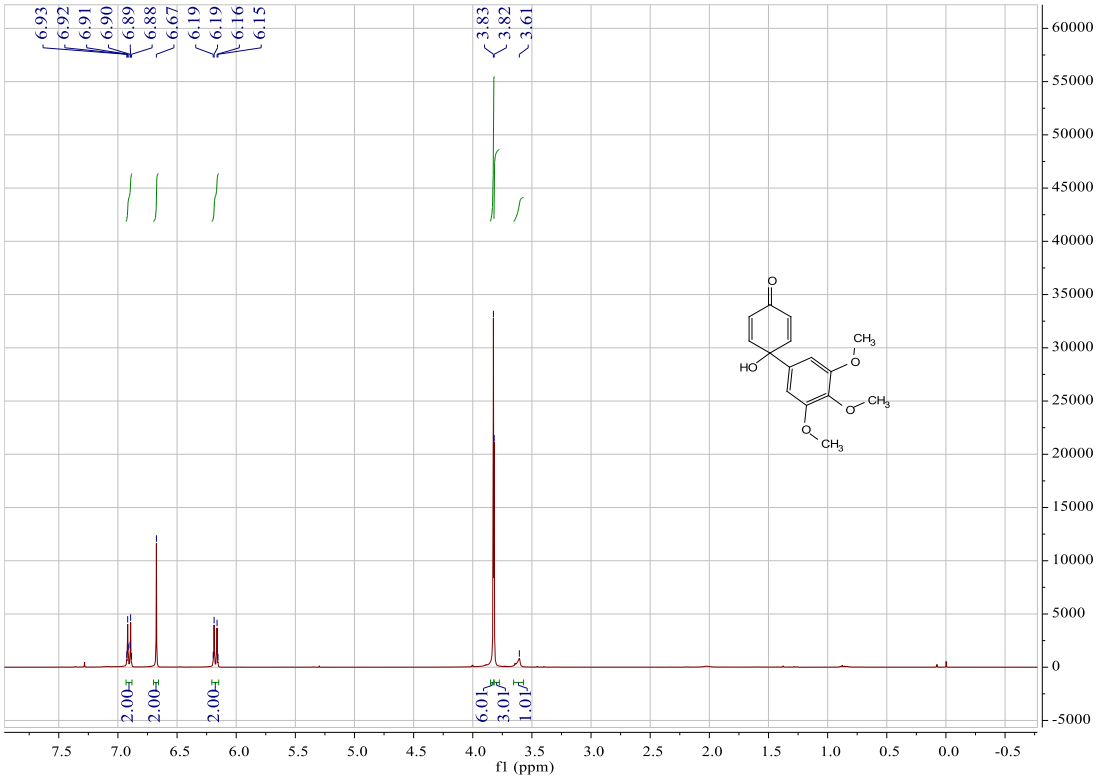
^{1}H NMR of compound **3ar**



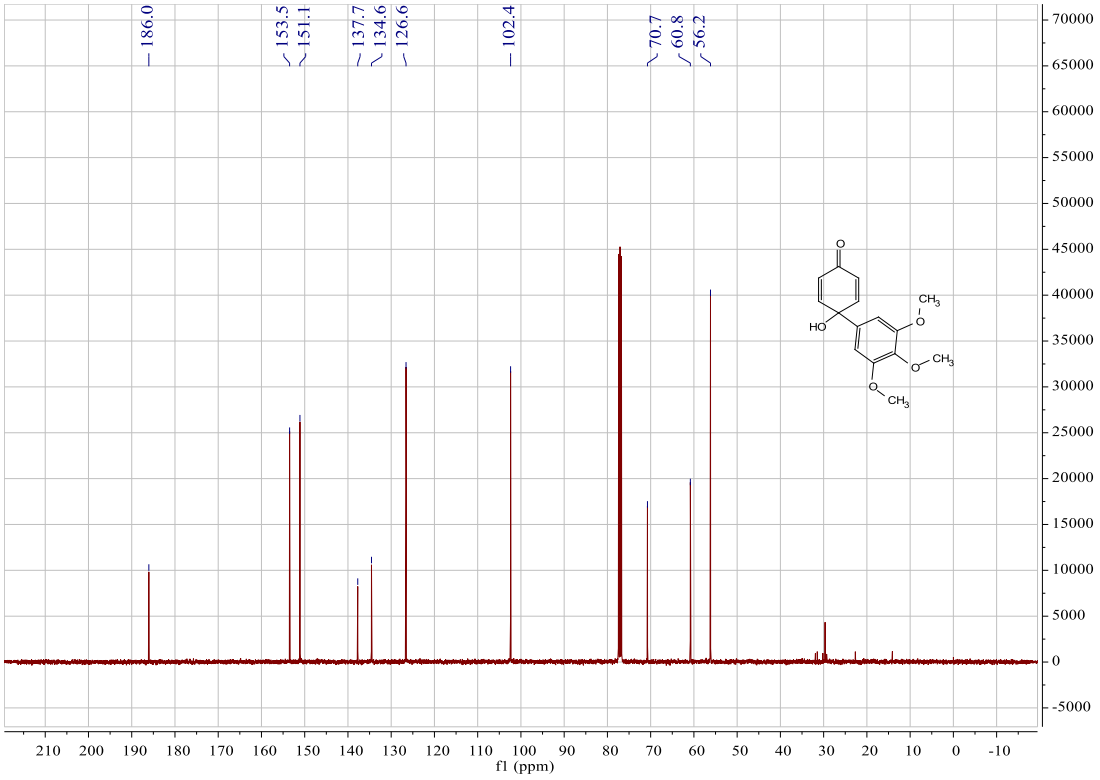
^{13}C NMR of compound **3ar**



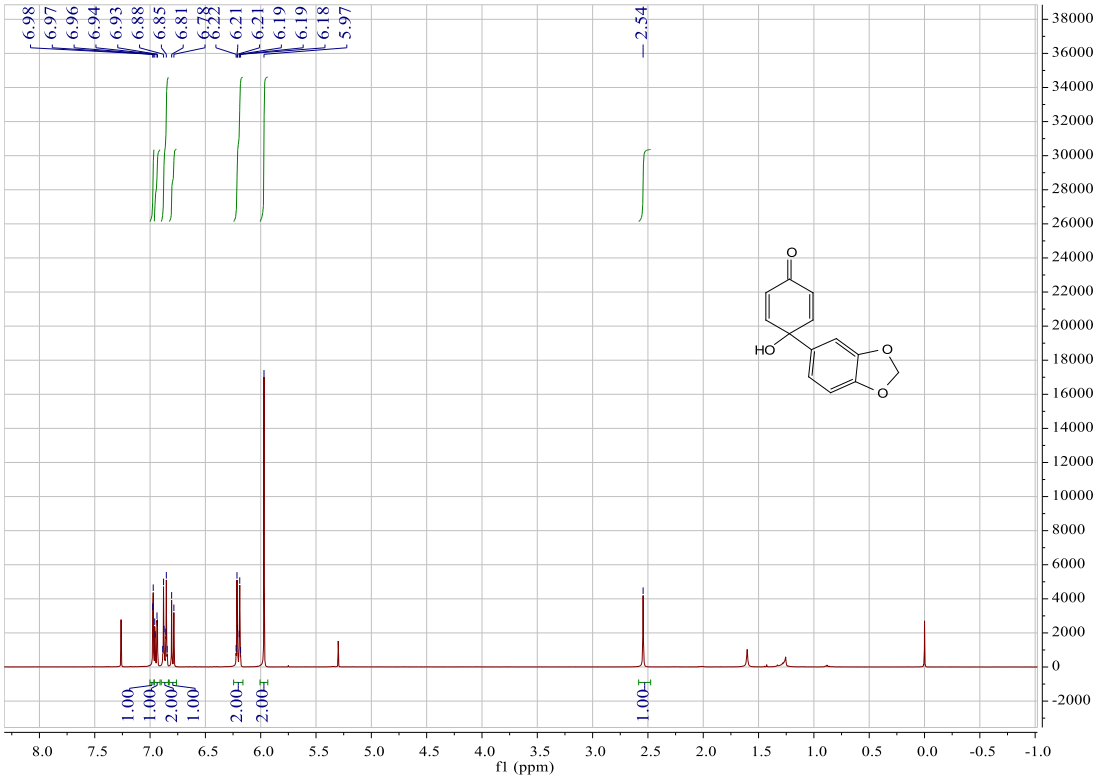
^{1}H NMR of compound **3as**



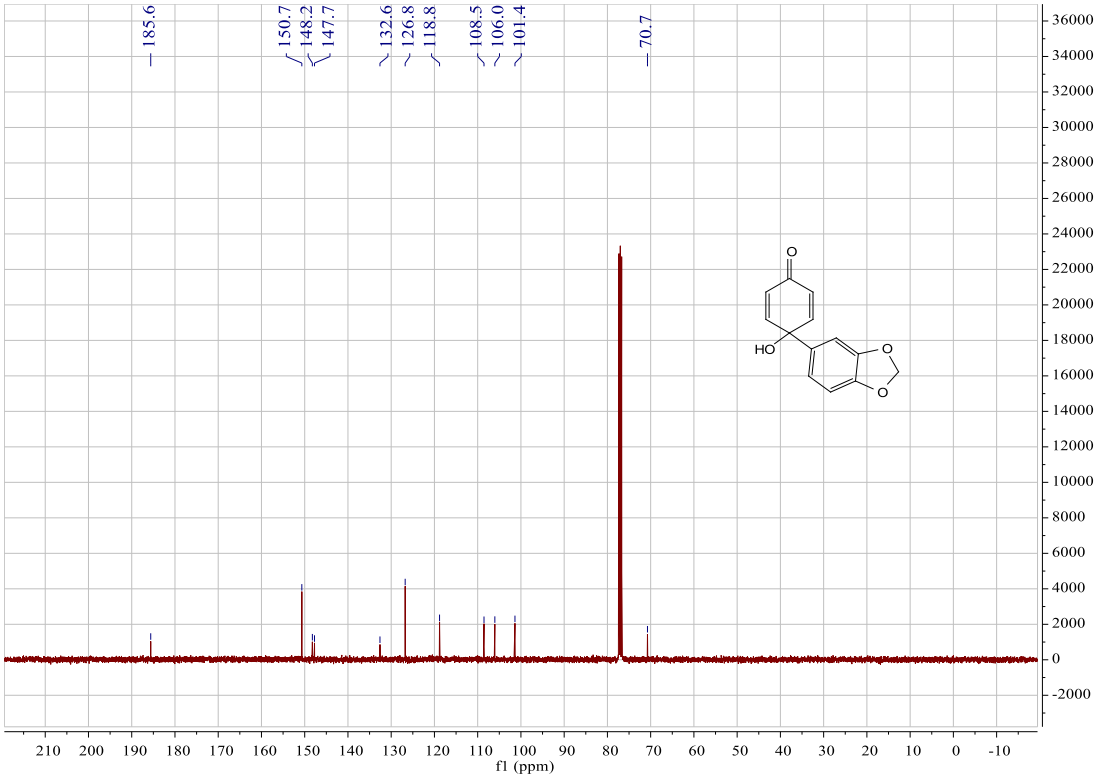
^{13}C NMR of compound **3as**



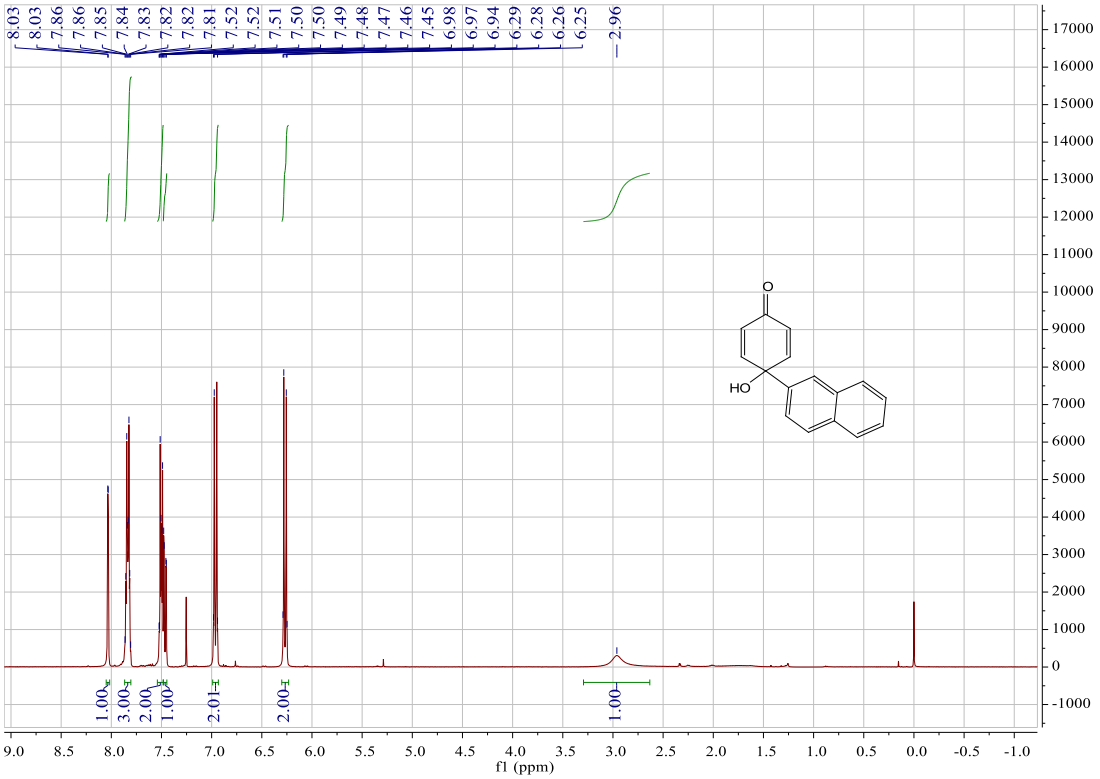
^{1}H NMR of compound **3at**



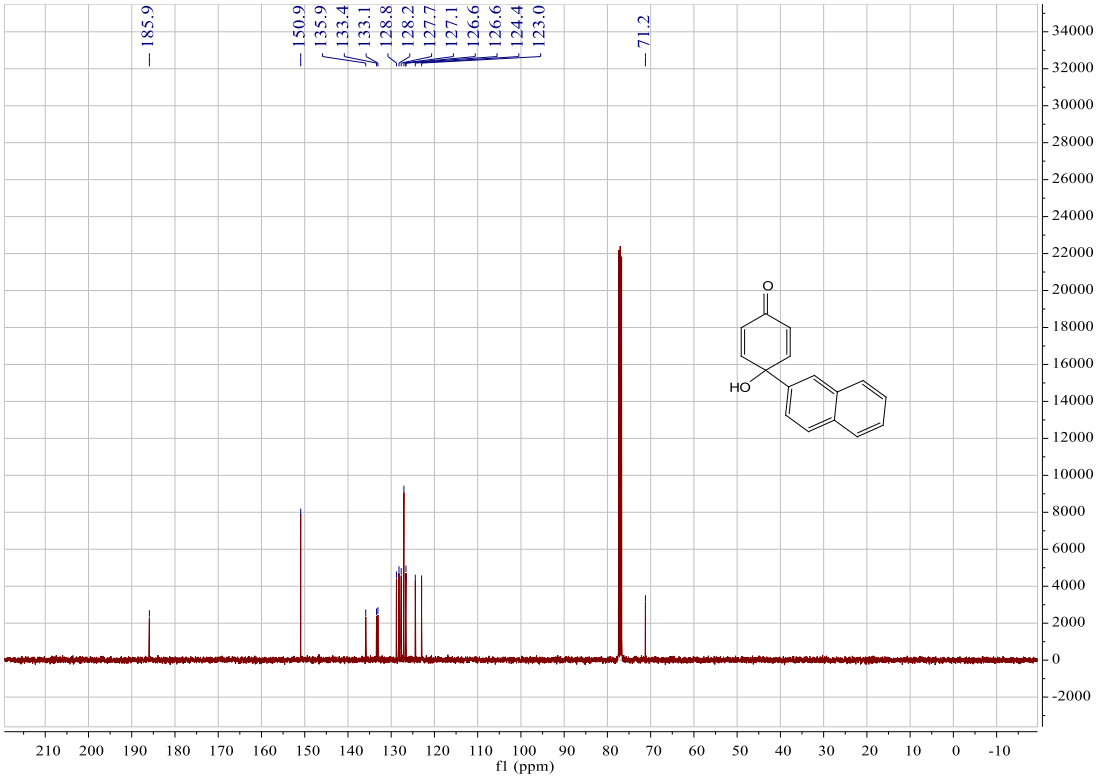
^{13}C NMR of compound **3at**



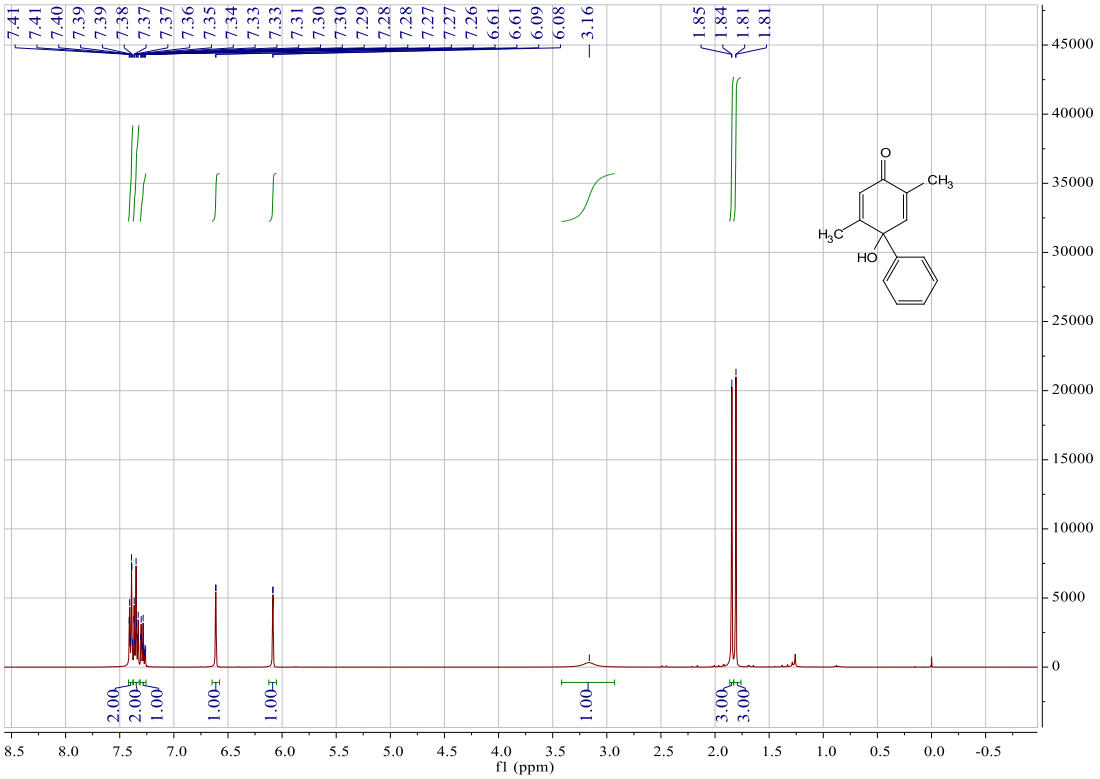
^{1}H NMR of compound **3au**



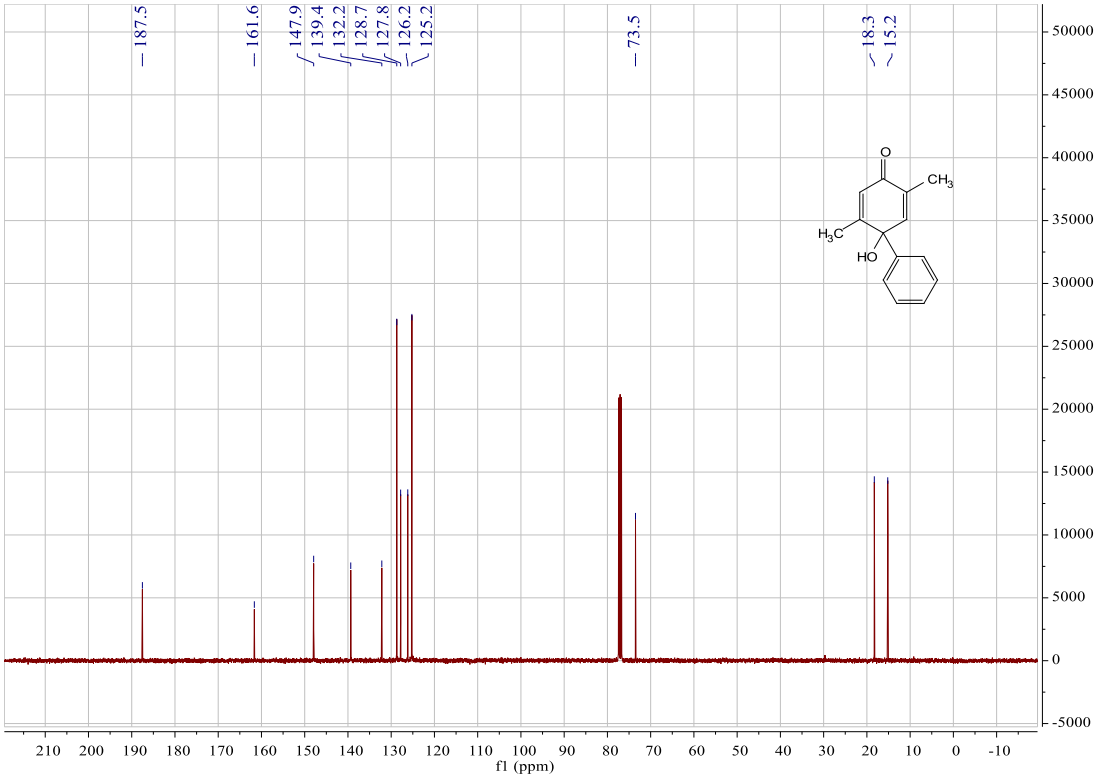
^{13}C NMR of compound **3au**



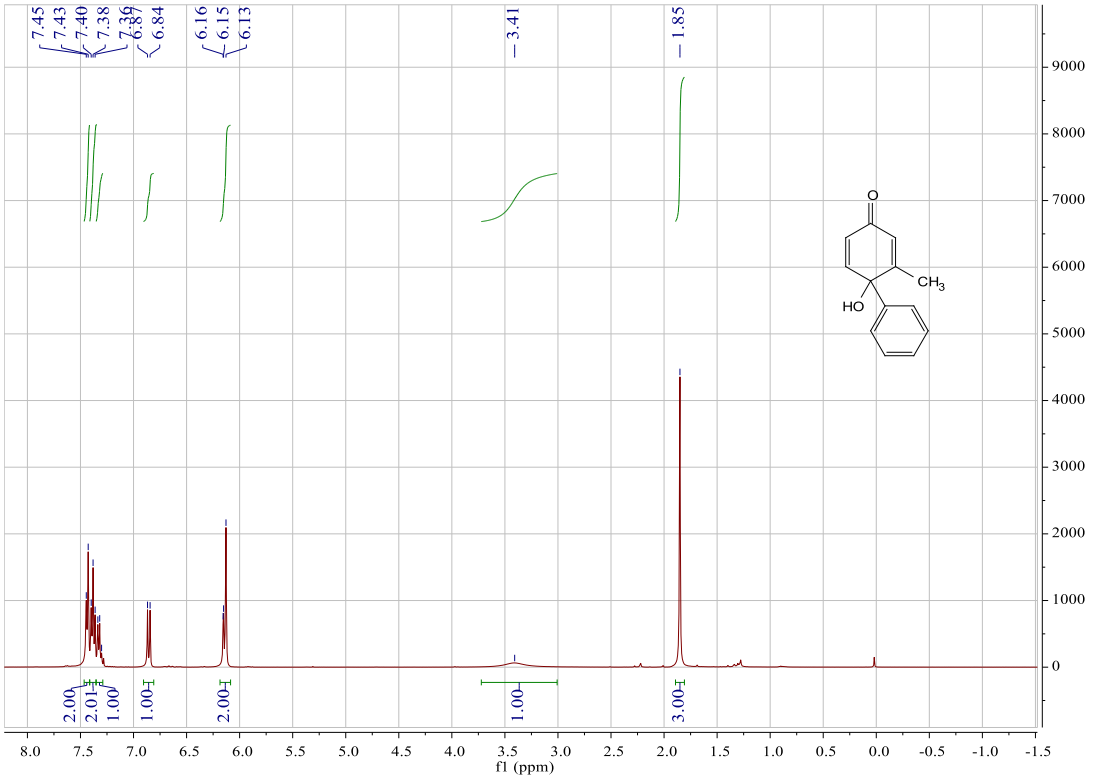
^{1}H NMR of compound **3ba**



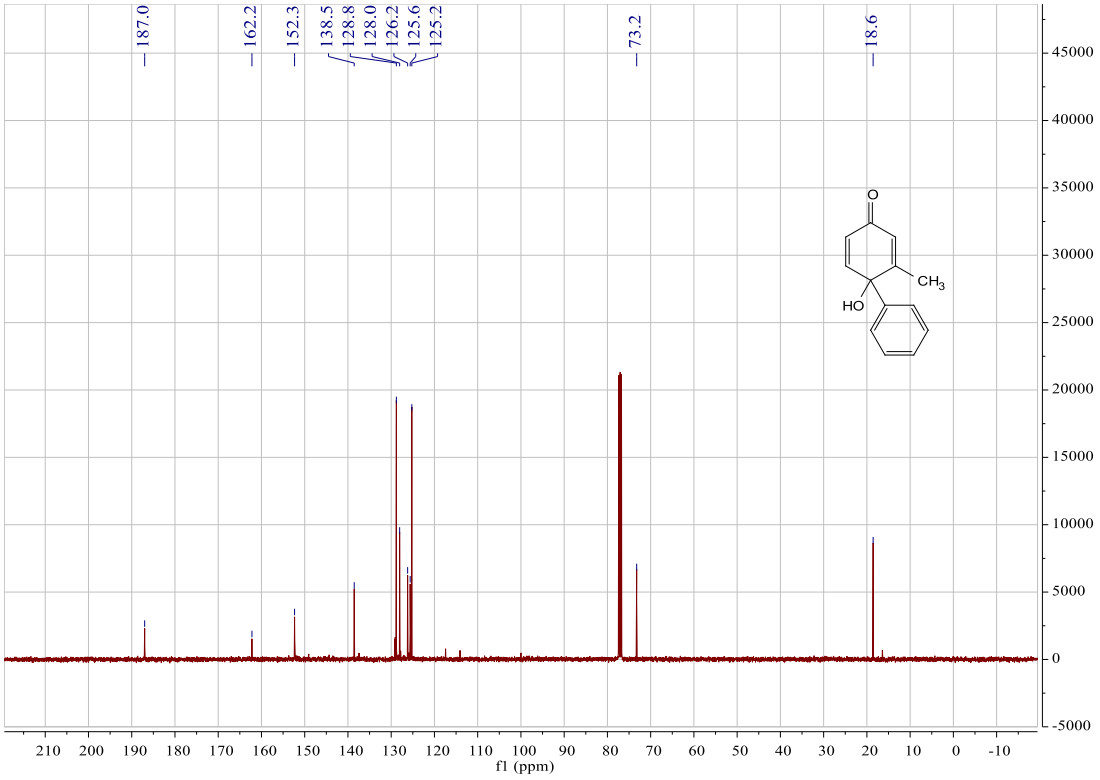
^{13}C NMR of compound **3ba**



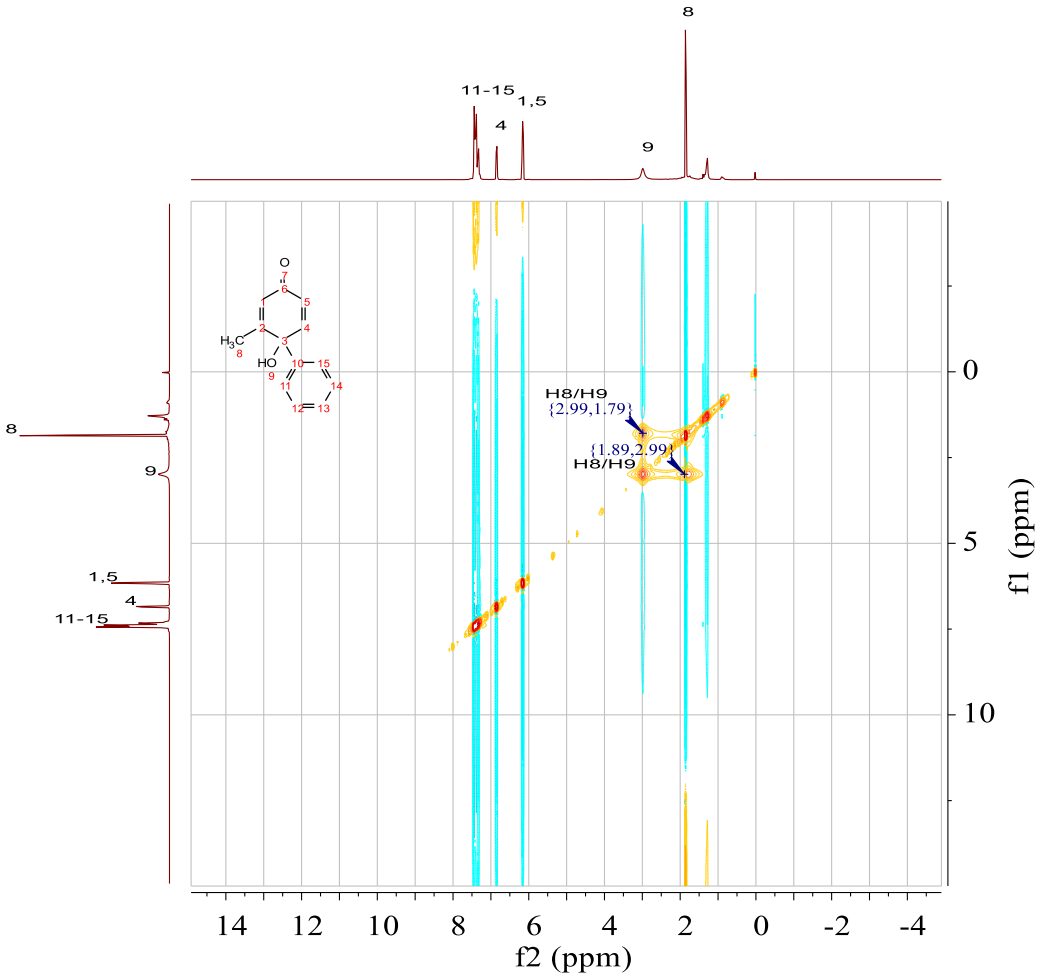
^{1}H NMR of compound **3ca**



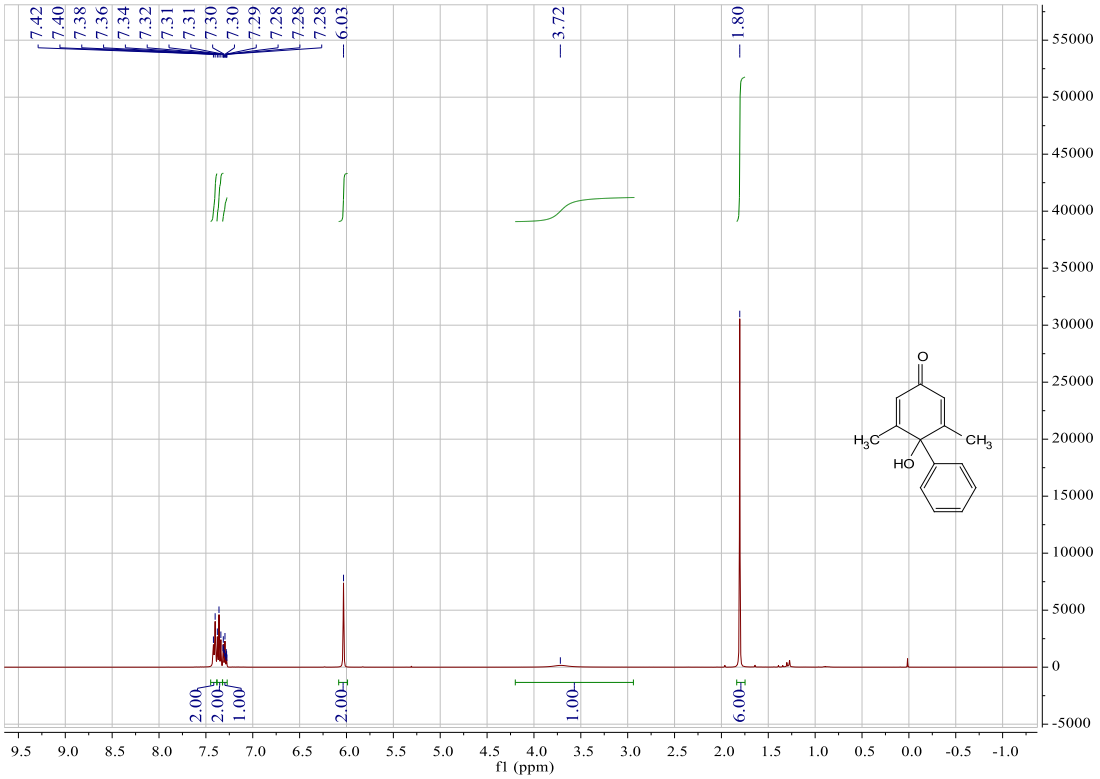
^{13}C NMR of compound **3ca**



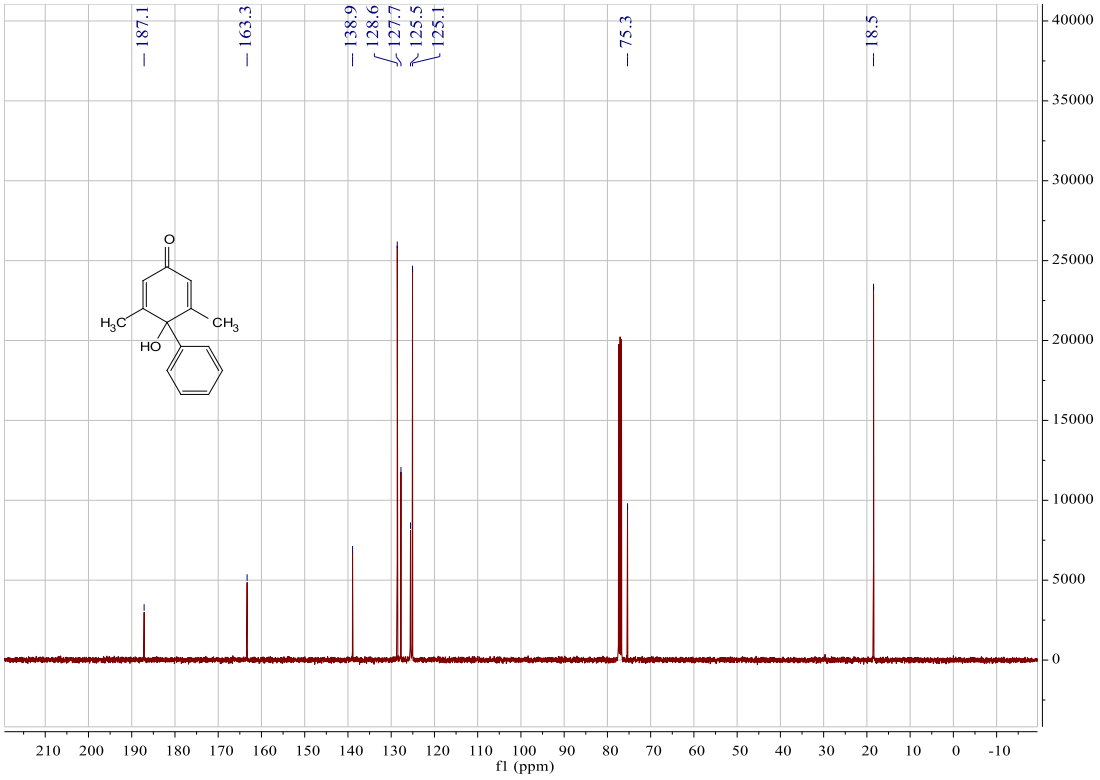
H-H NOEZY of compound **3ca**



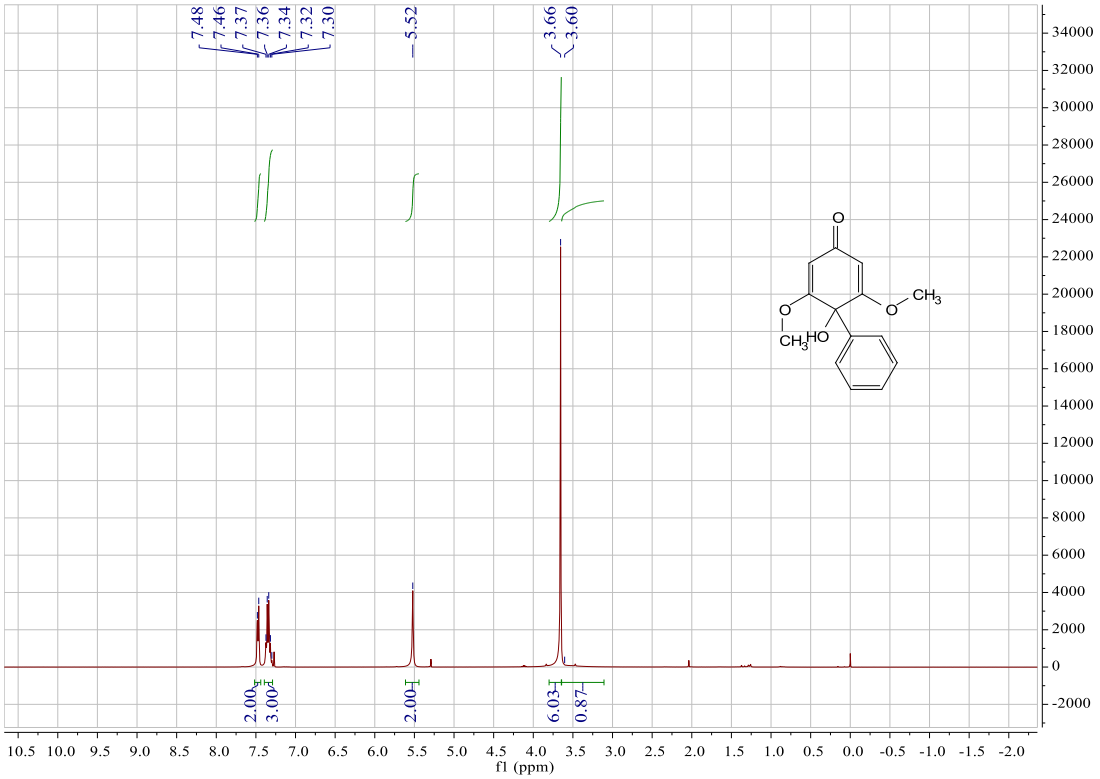
^{1}H NMR of compound **3da**



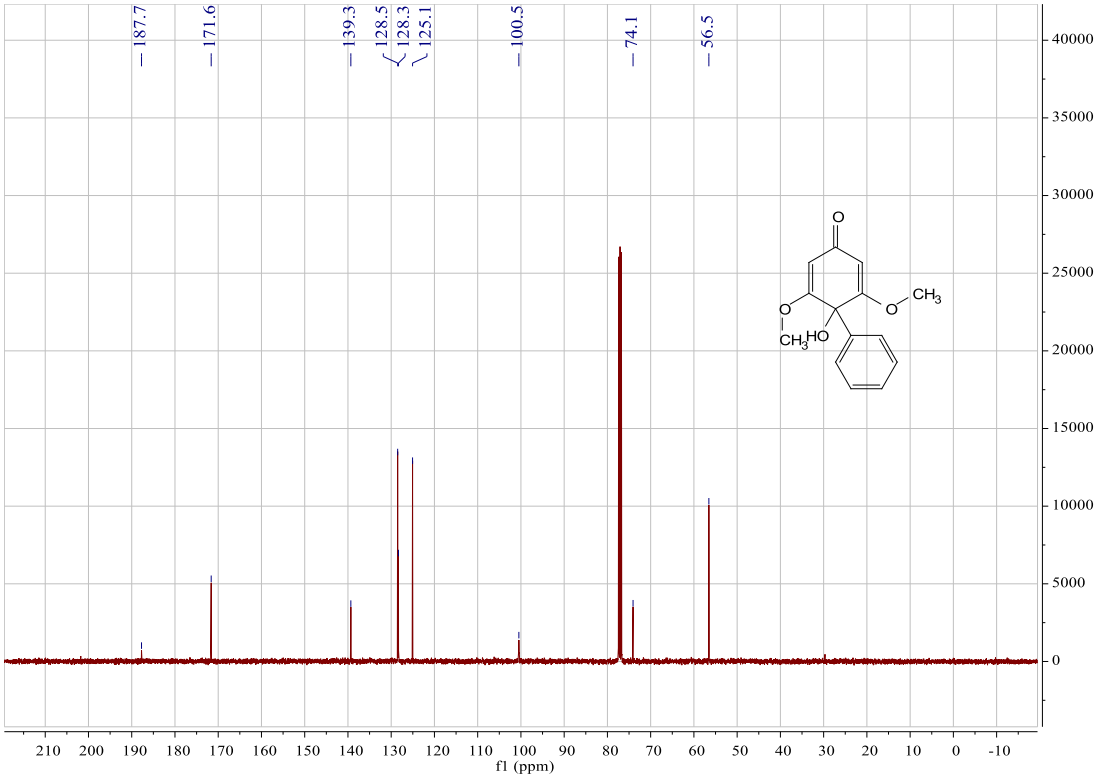
^{13}C NMR of compound **3da**



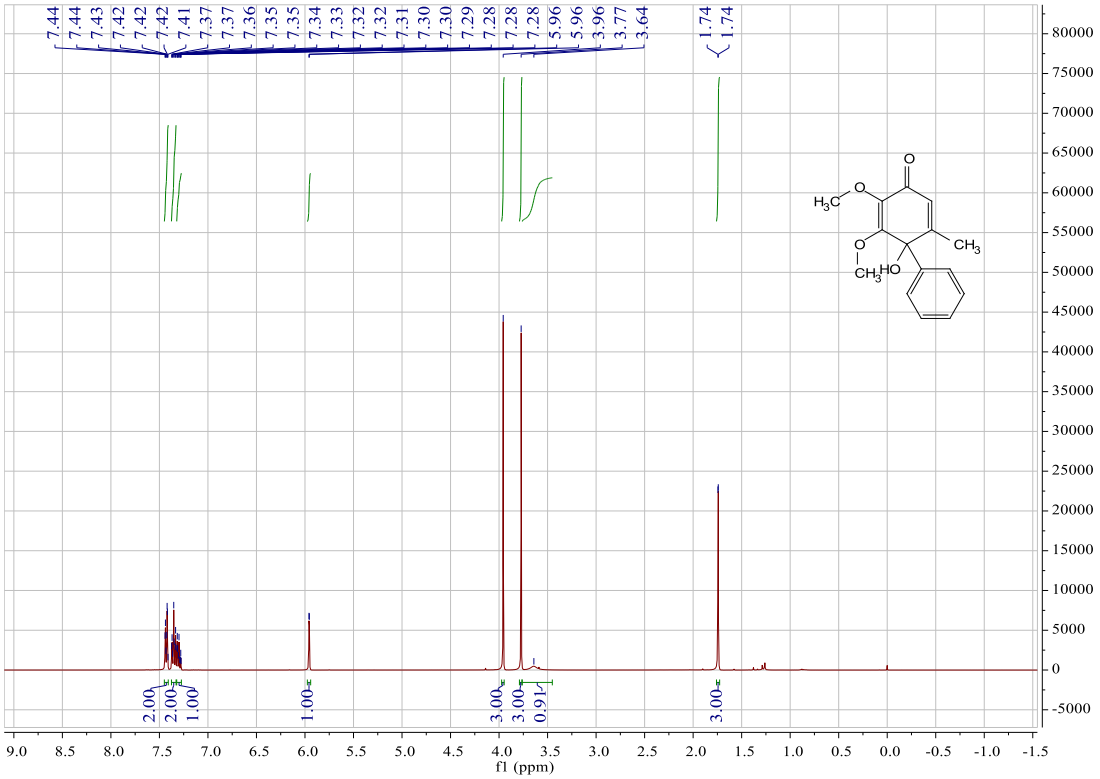
^{1}H NMR of compound **3ea**



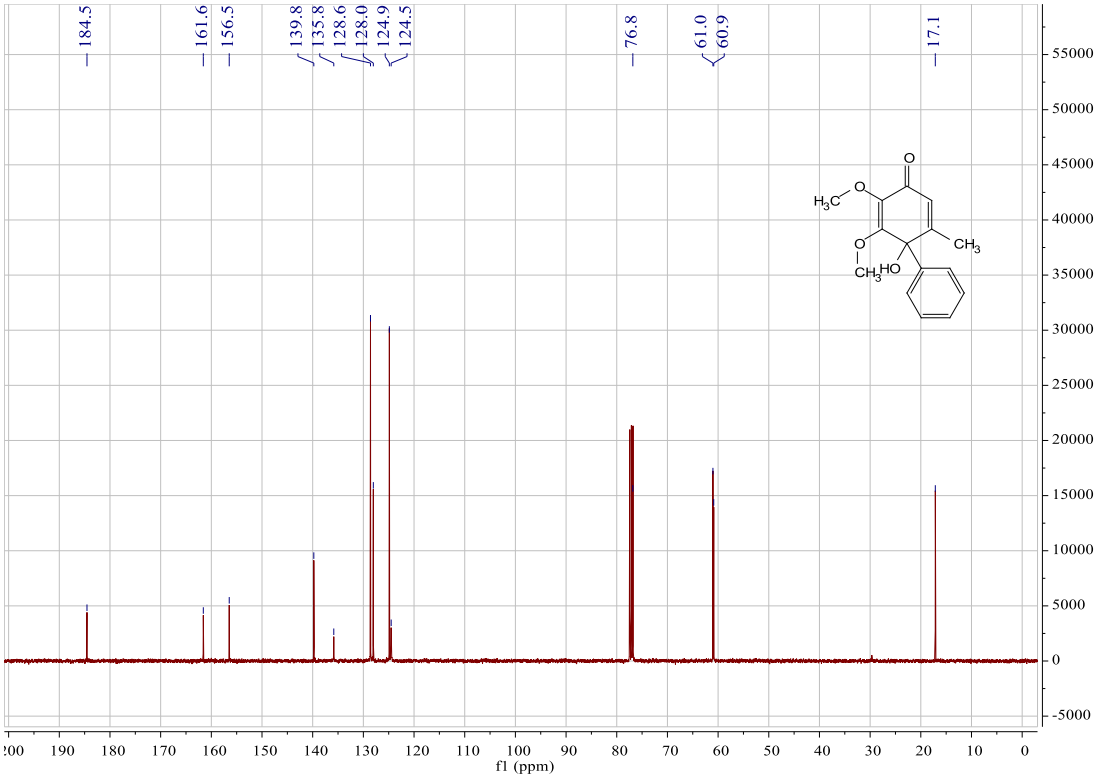
^{13}C NMR of compound **3ea**



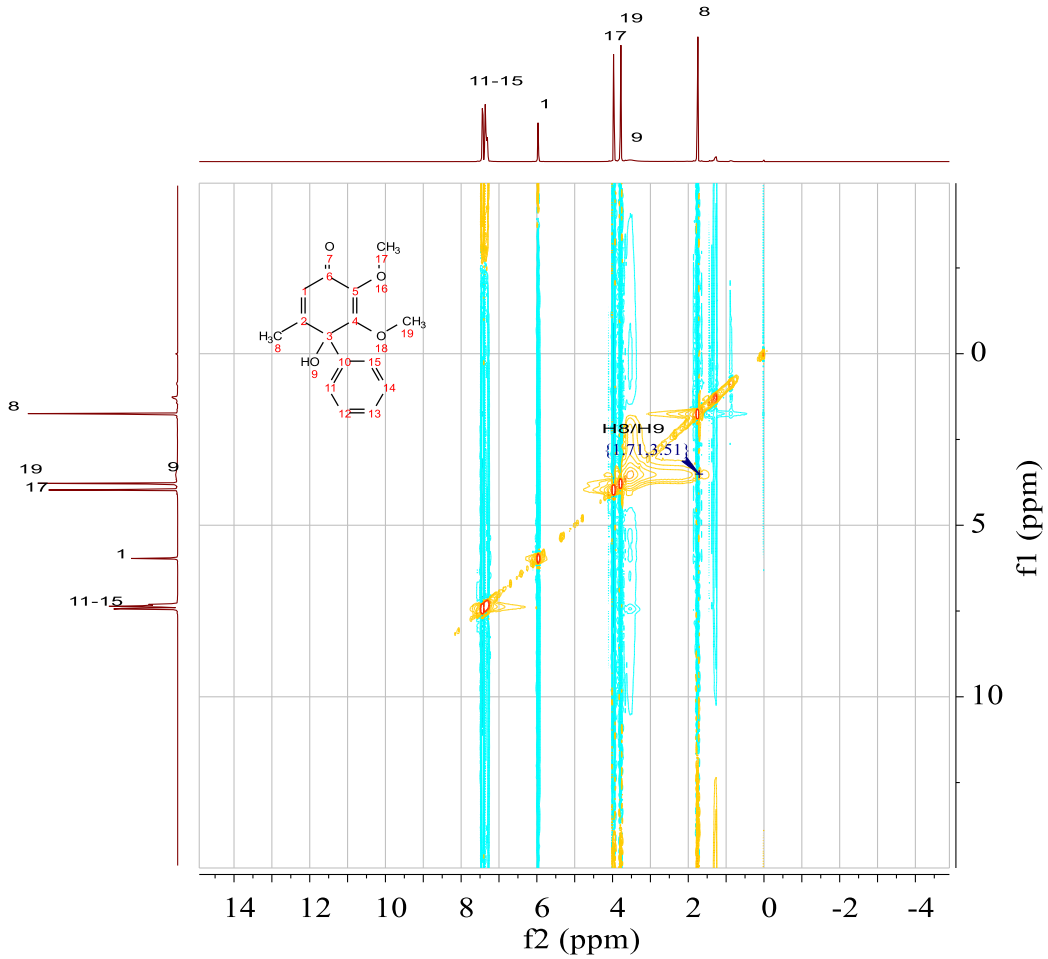
^{1}H NMR of compound **3ga**



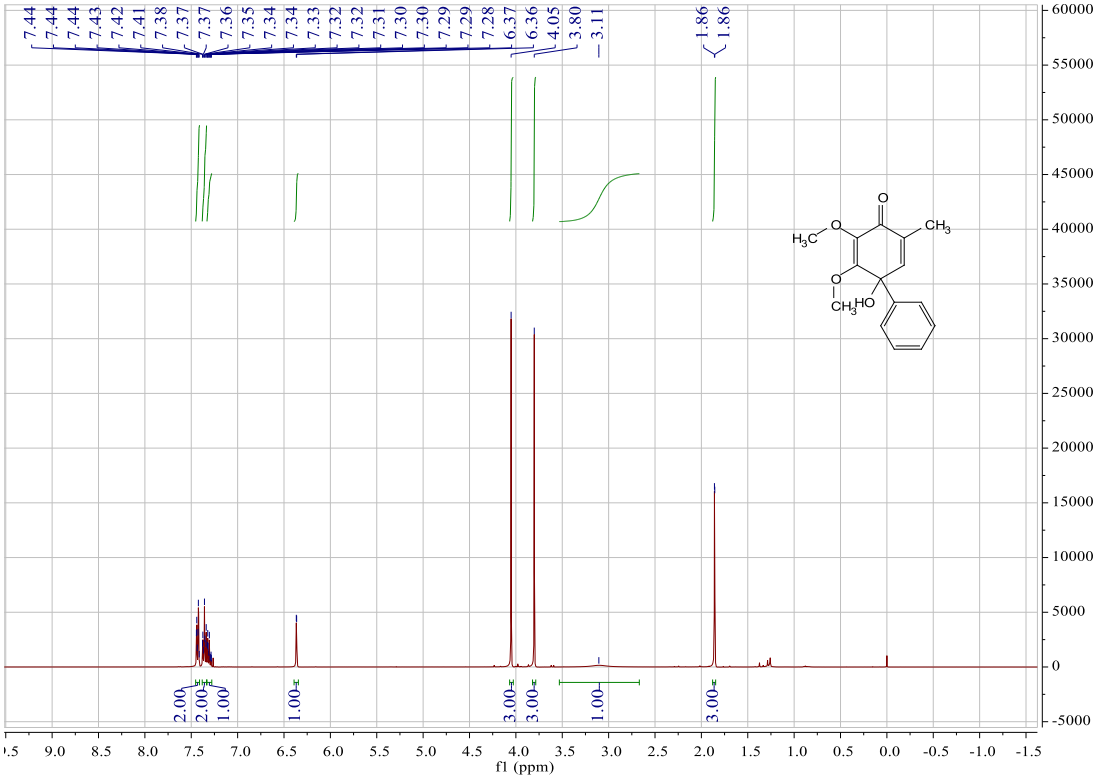
^{13}C NMR of compound **3ga**



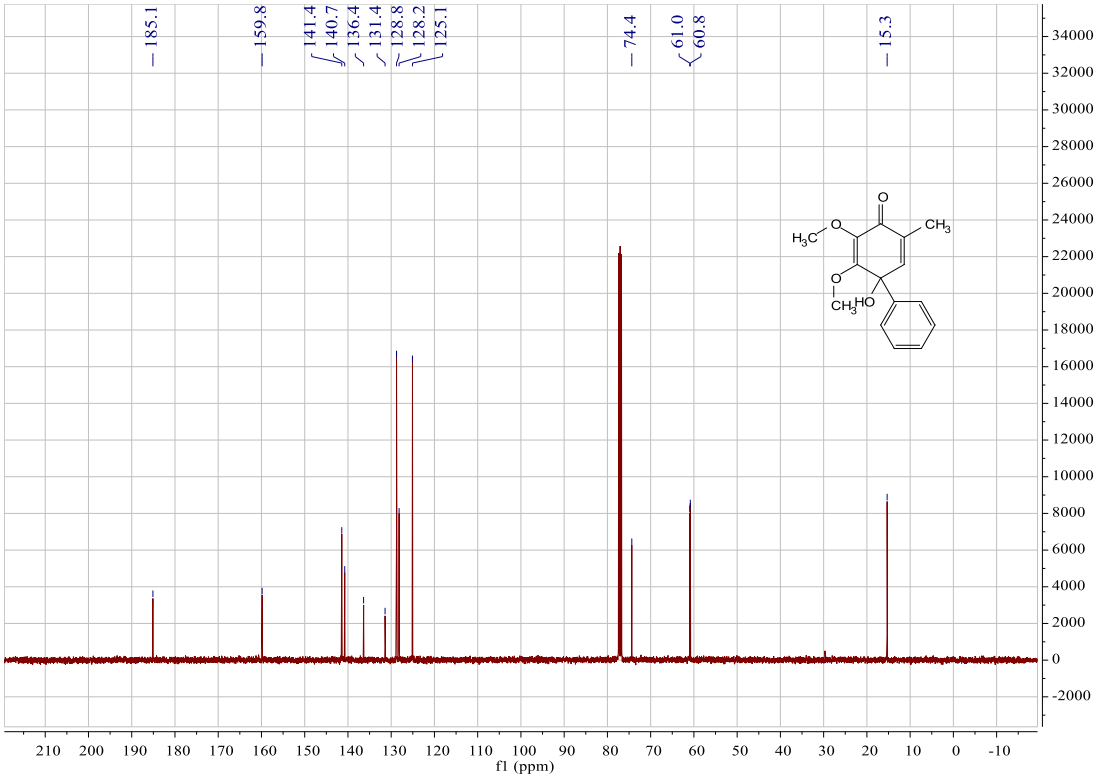
H-H NOEZY of compound **3ga**



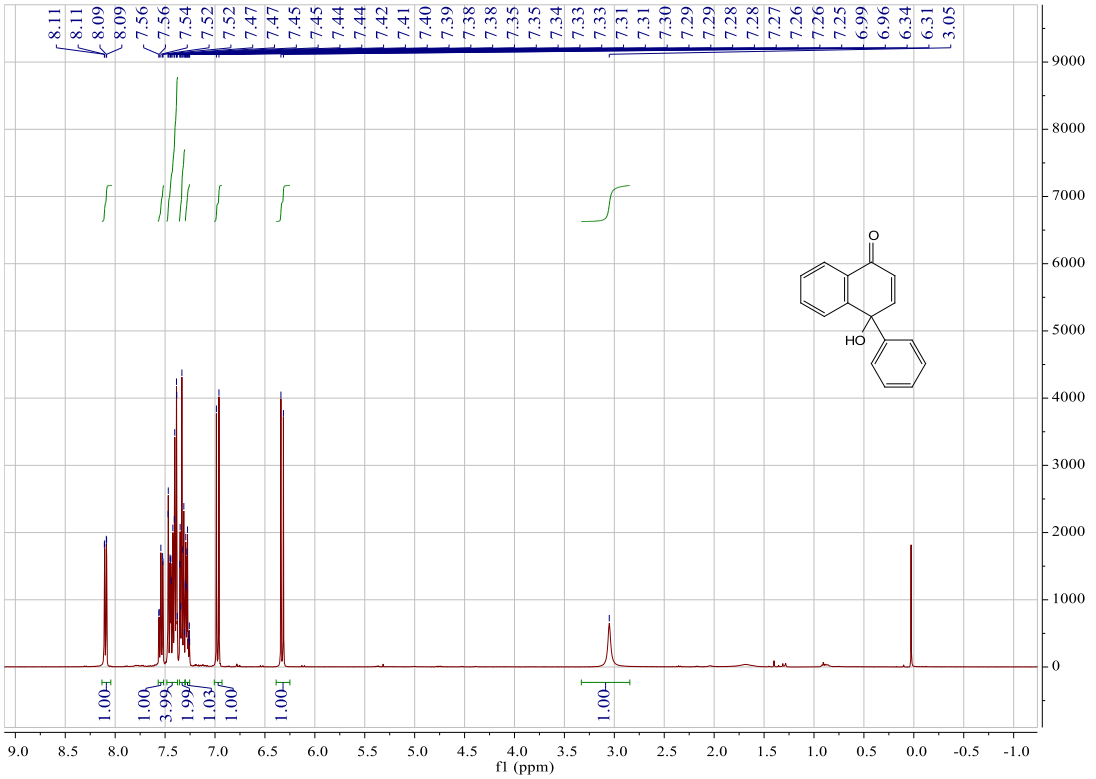
^{1}H NMR of compound **3ga'**



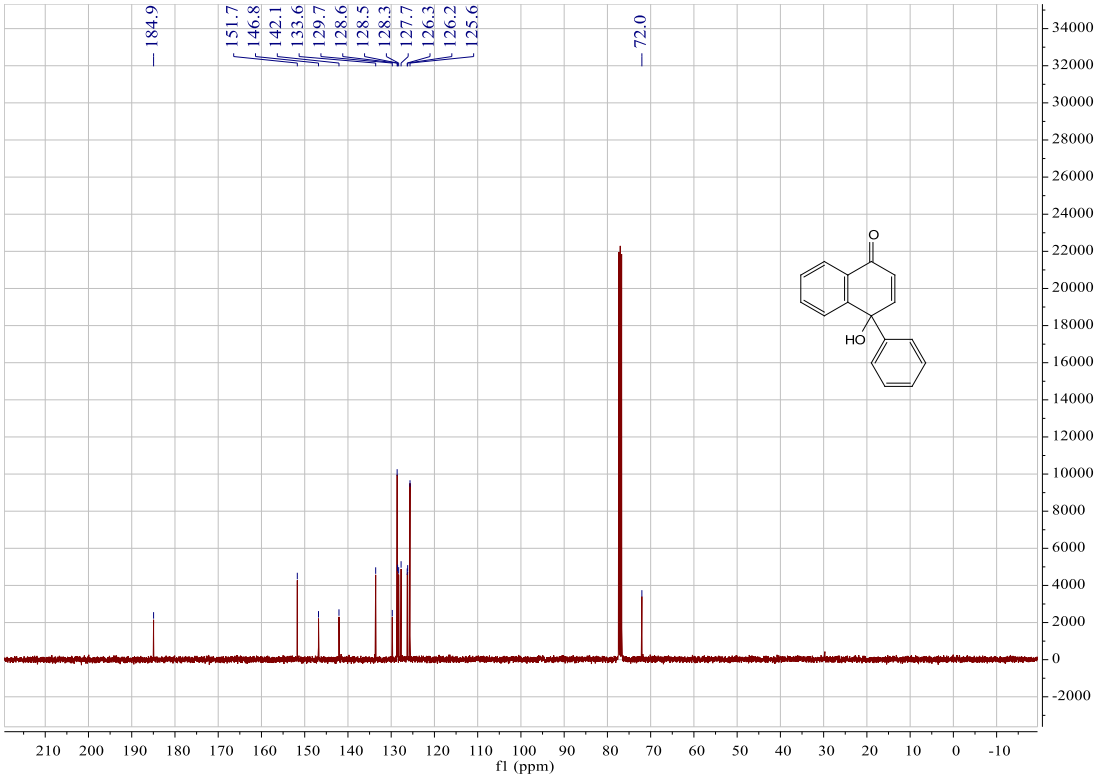
^{13}C NMR of compound **3ga'**



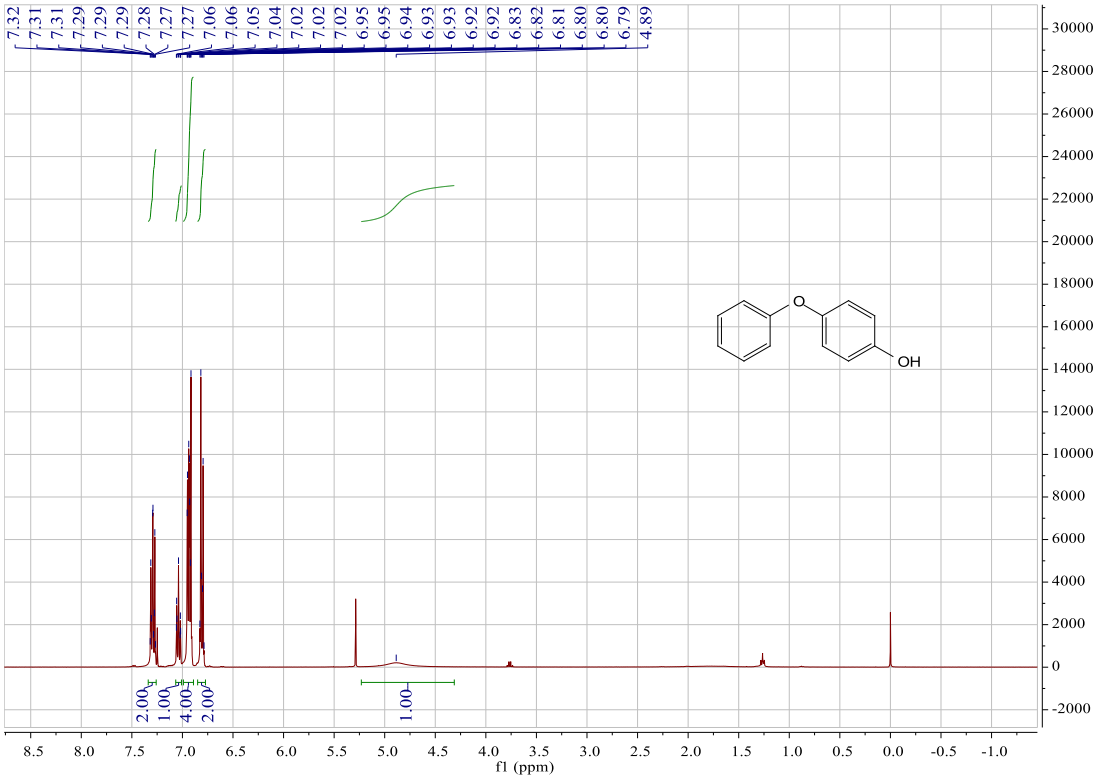
^{1}H NMR of compound **3ha**



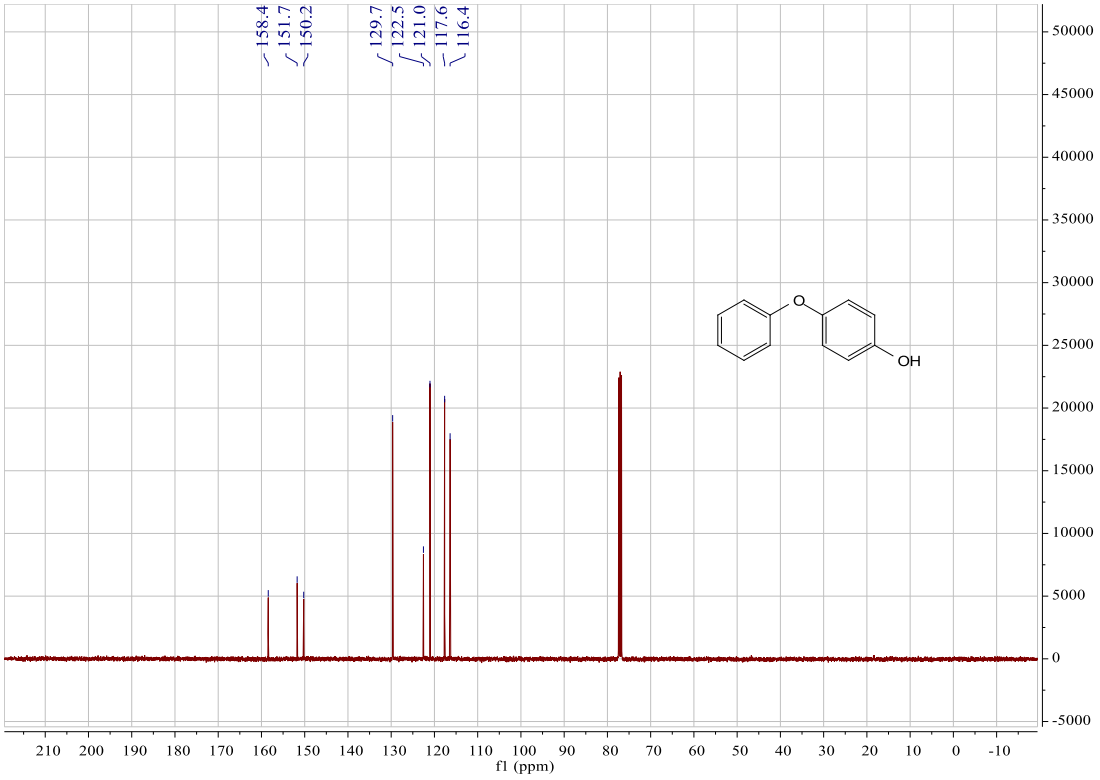
^{13}C NMR of compound **3ha**



^{1}H NMR of compound **4aa**



^{13}C NMR of compound **4aa**



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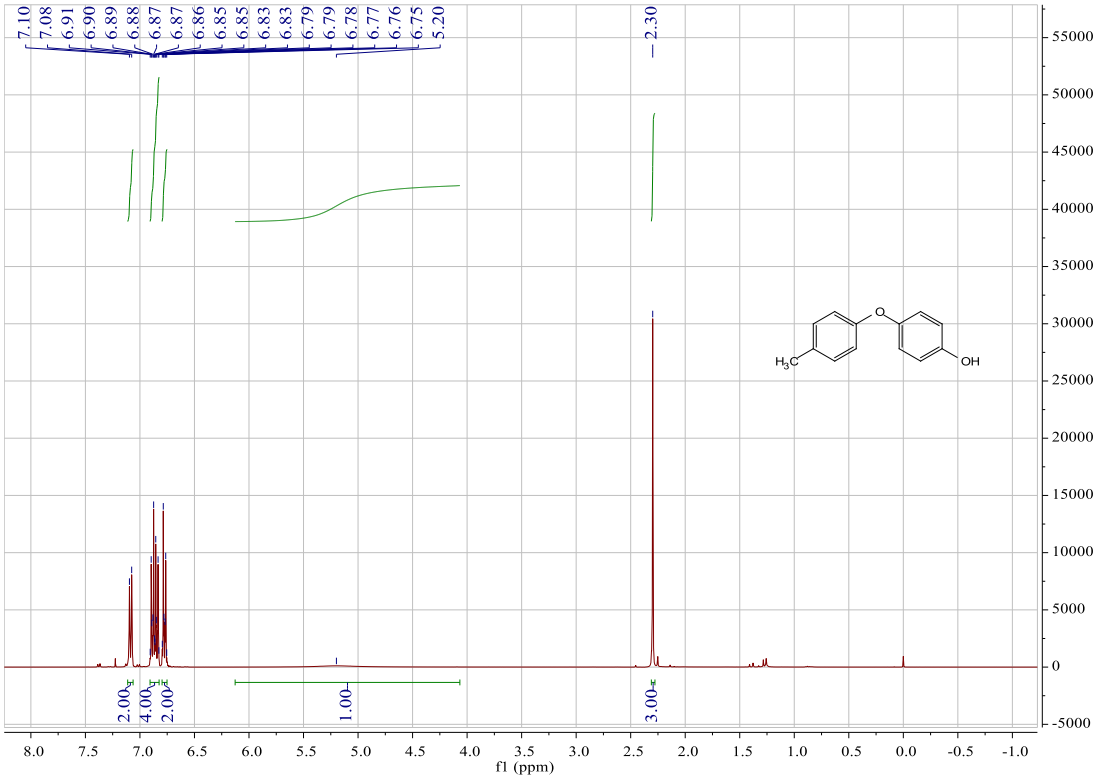
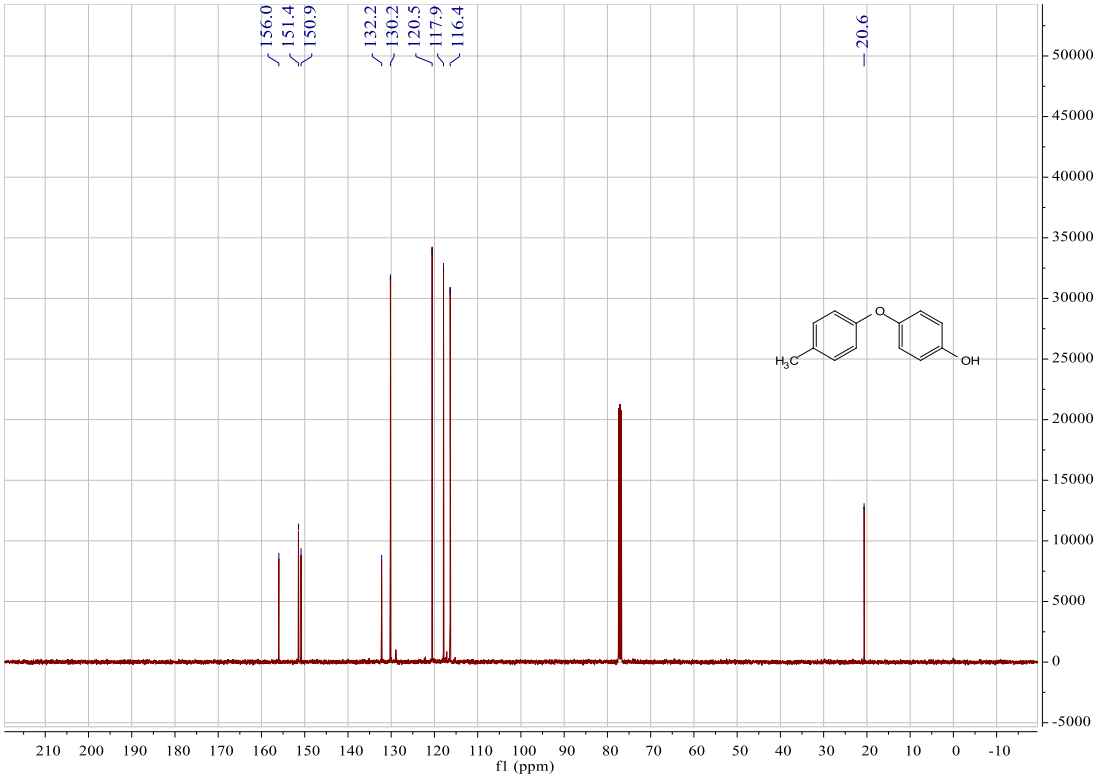
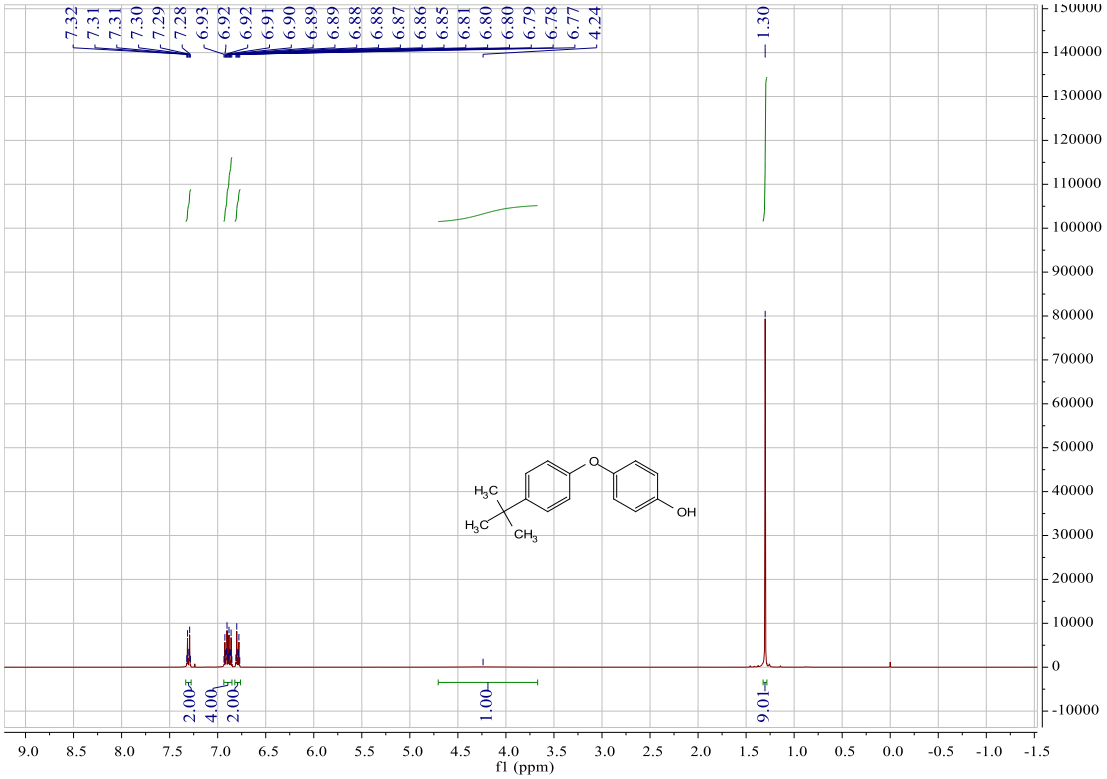


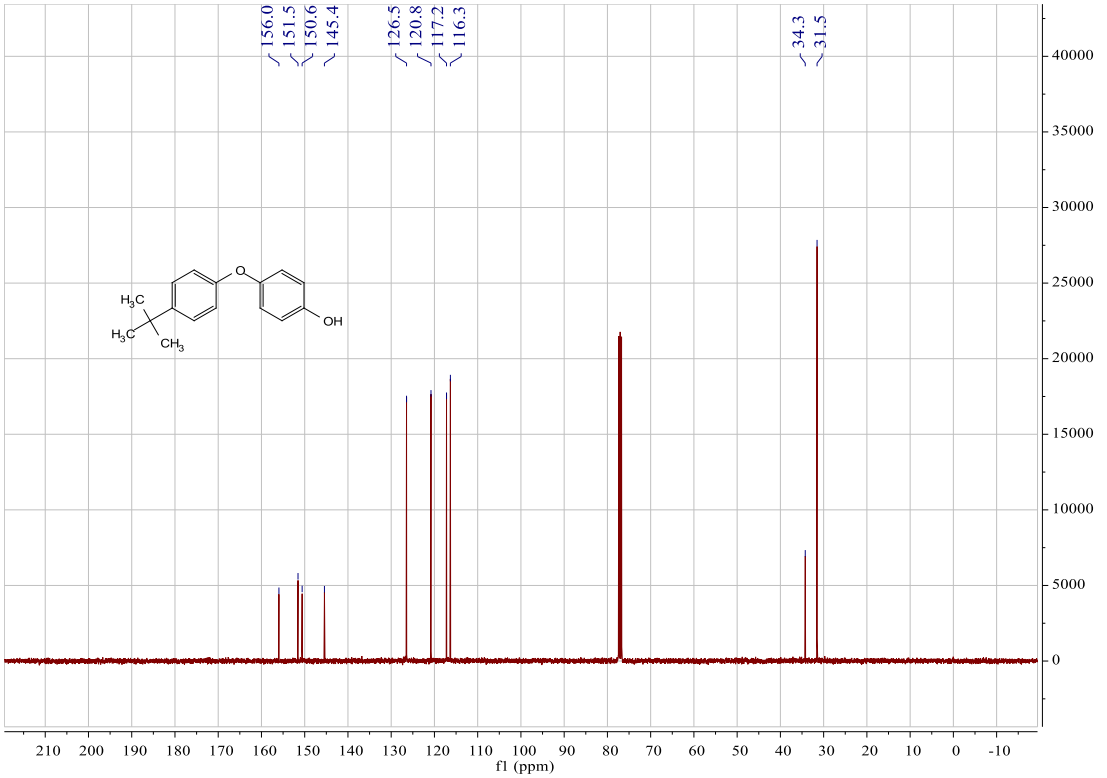
^{13}C NMR of compound **4ab**



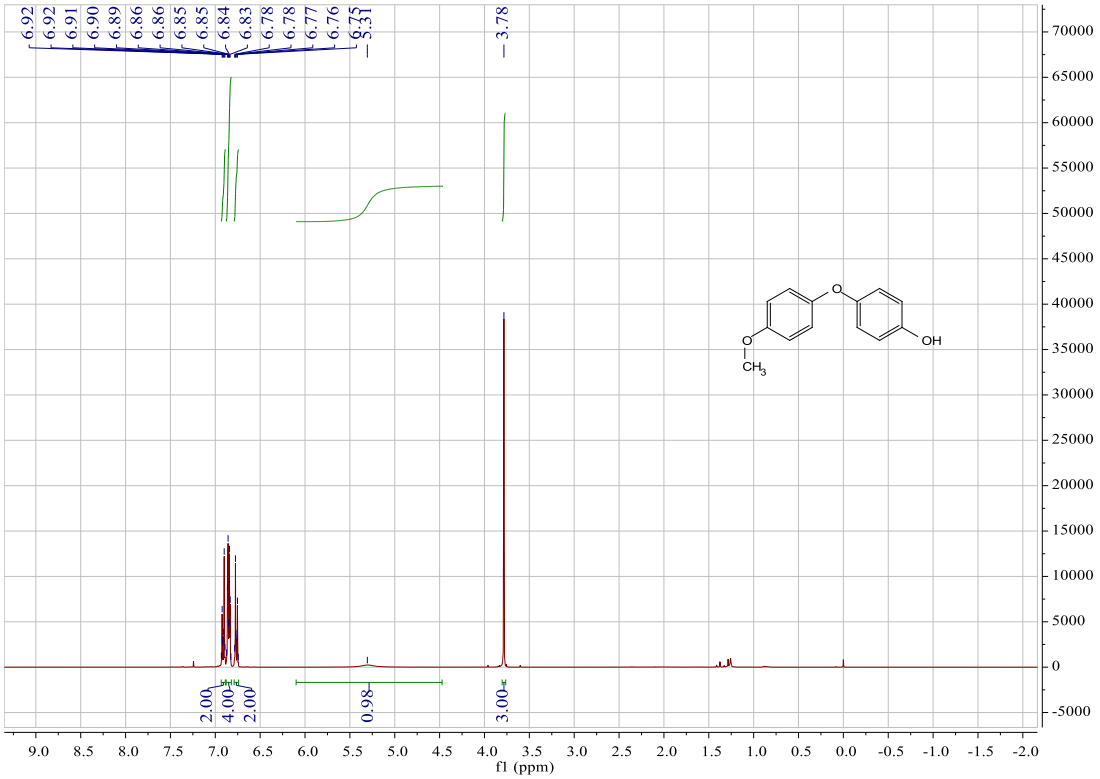
^{1}H NMR of compound **4ac**



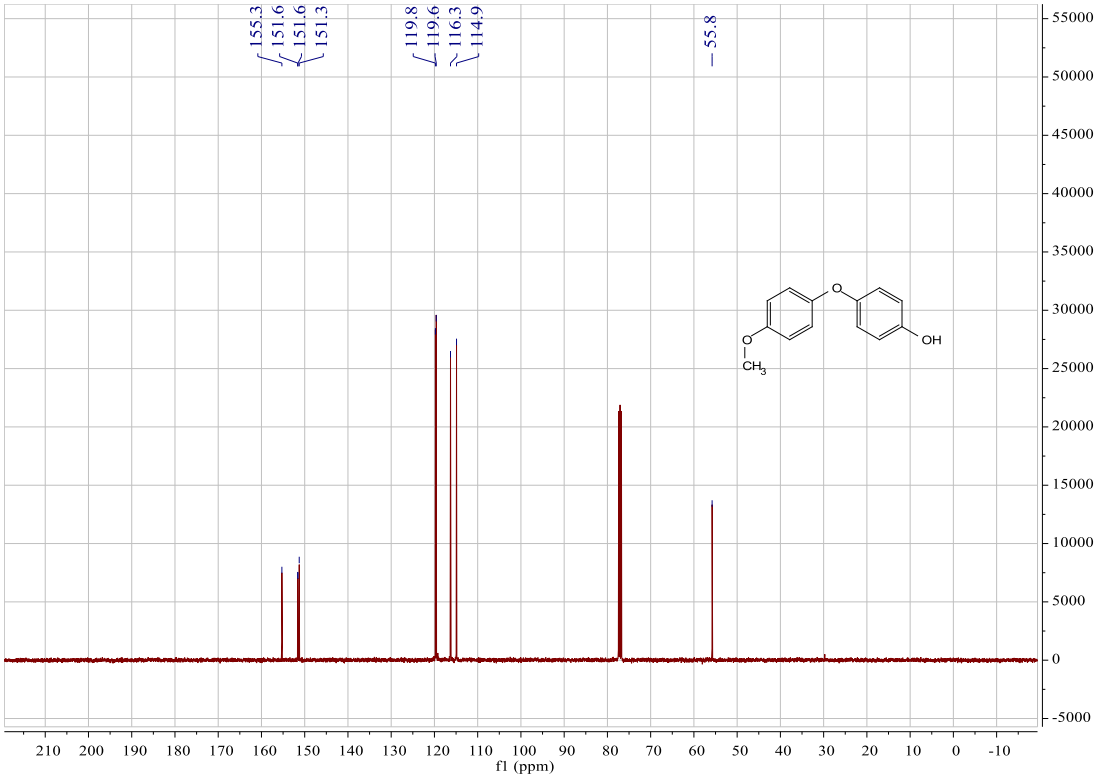
^{13}C NMR of compound **4ac**



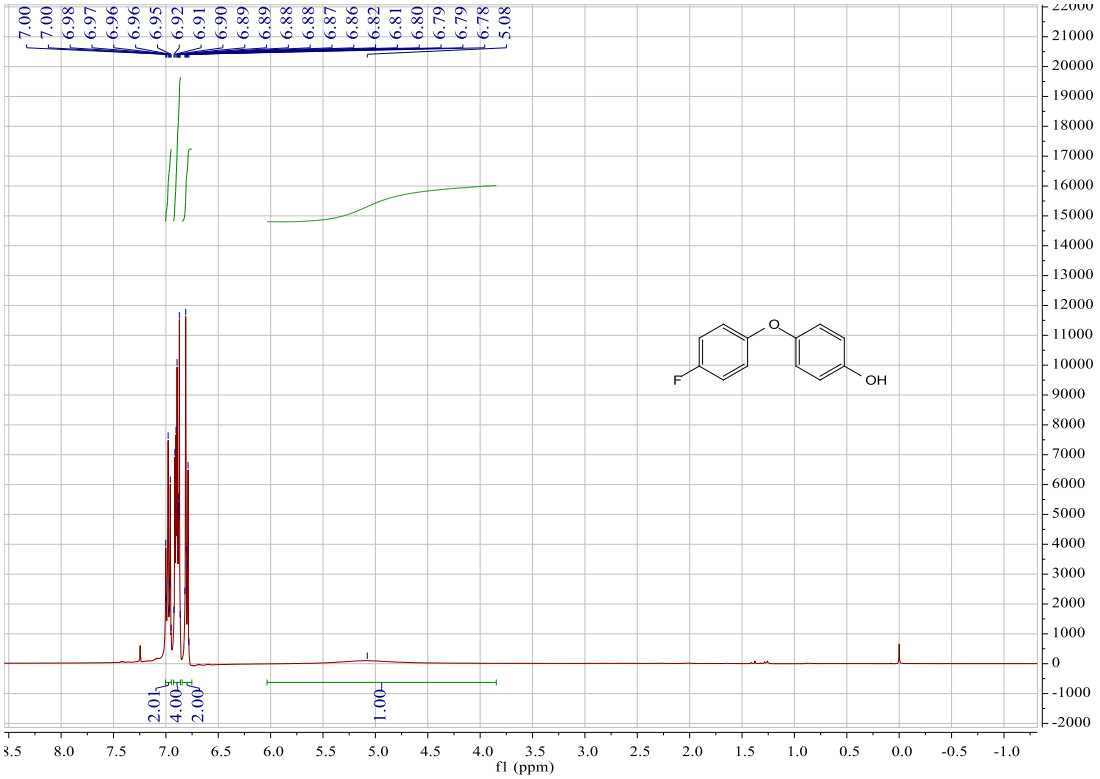
^{1}H NMR of compound **4ad**



^{13}C NMR of compound **4ad**



^{1}H NMR of compound **4ae**



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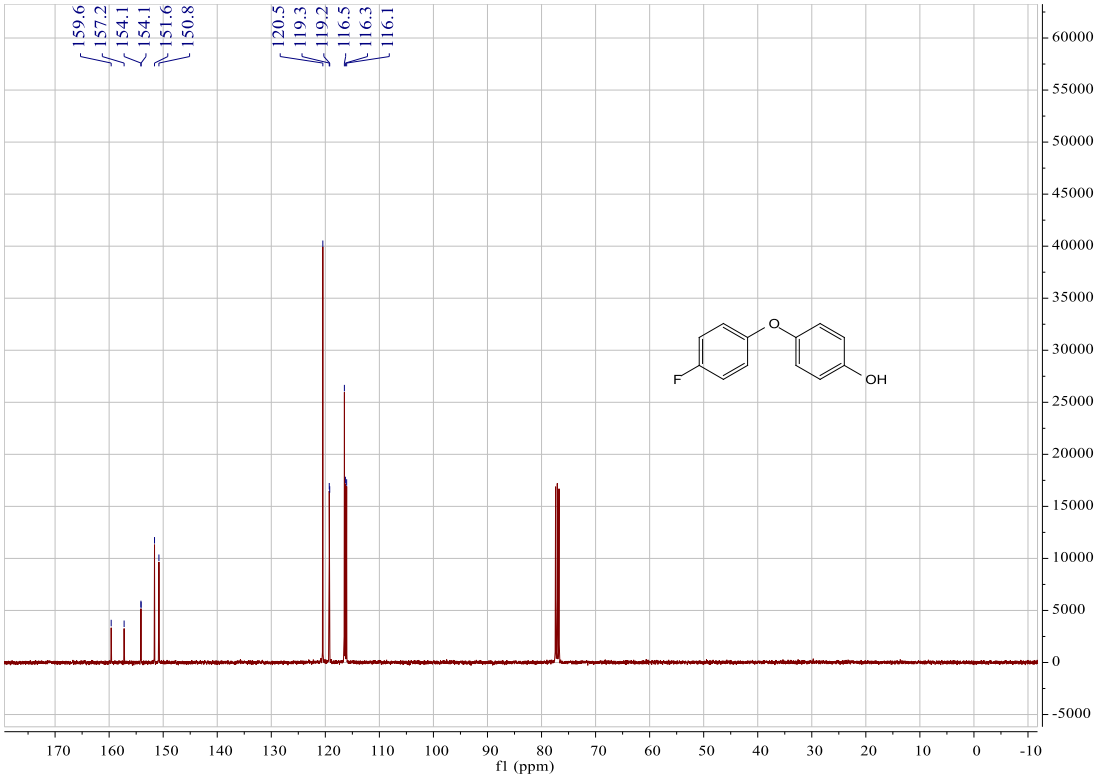

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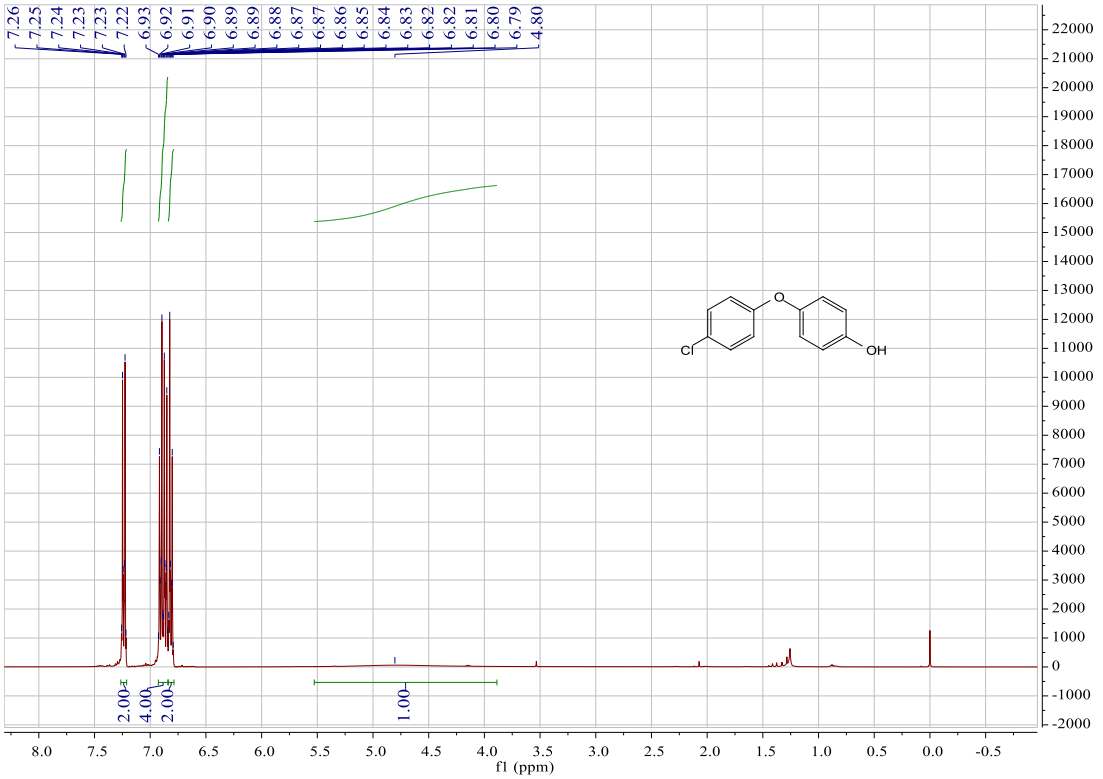

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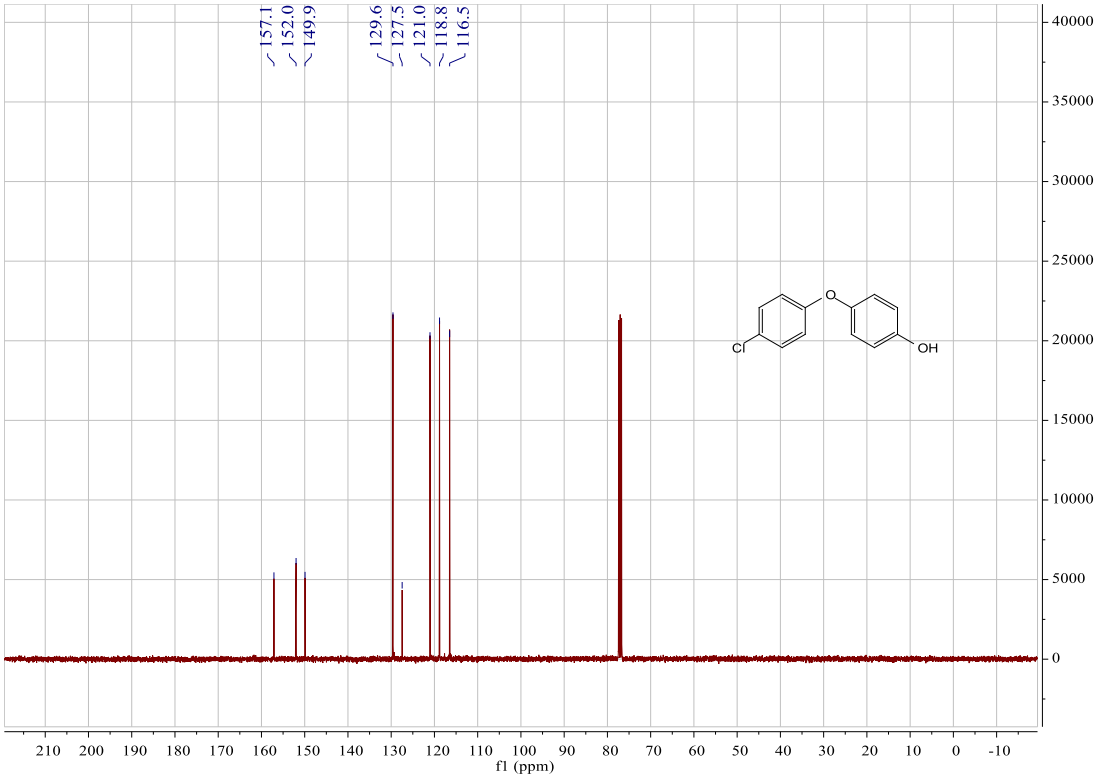
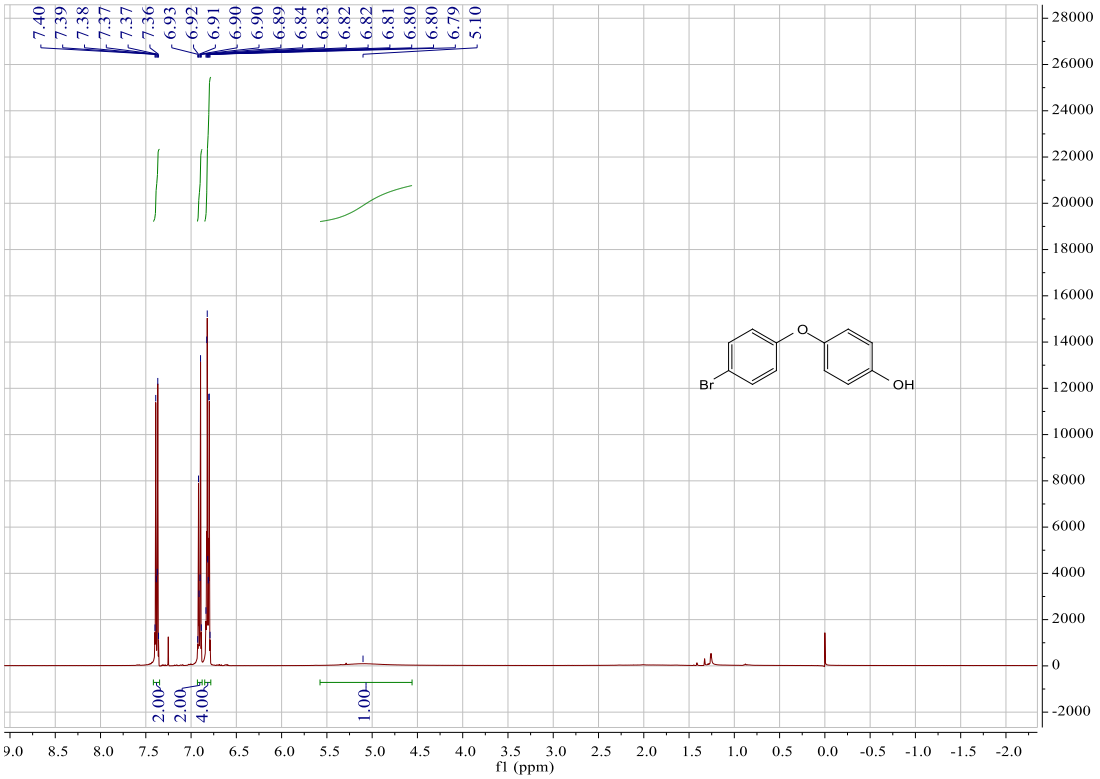
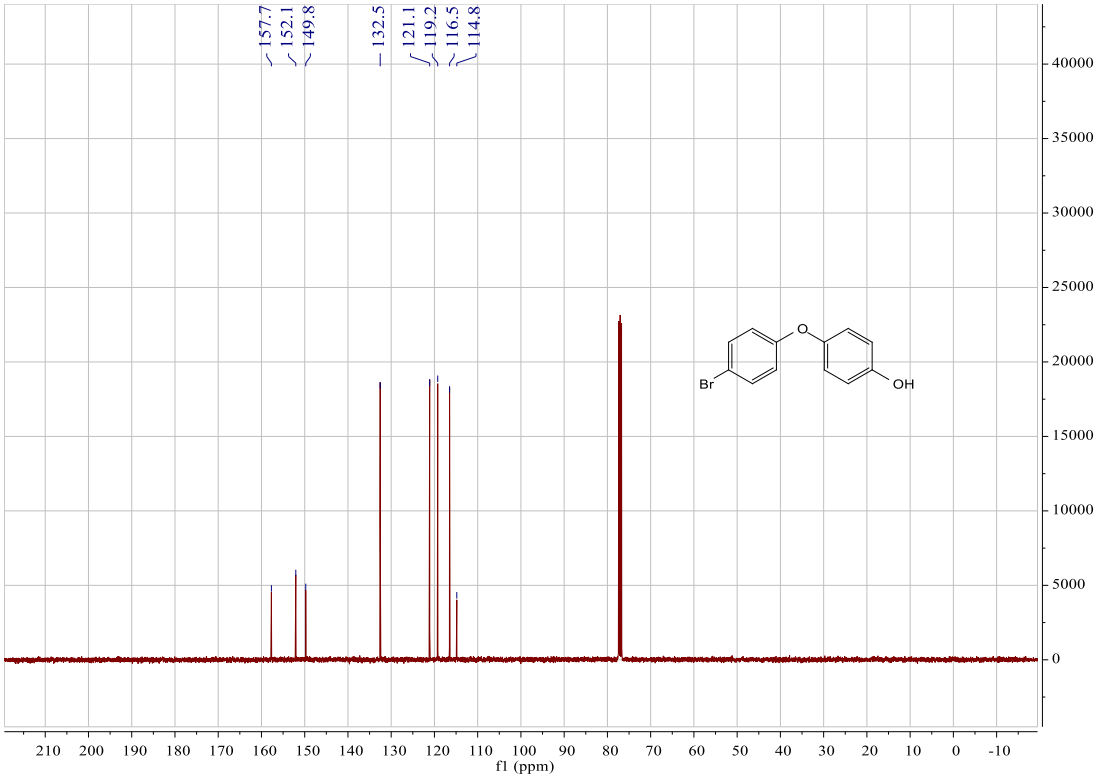


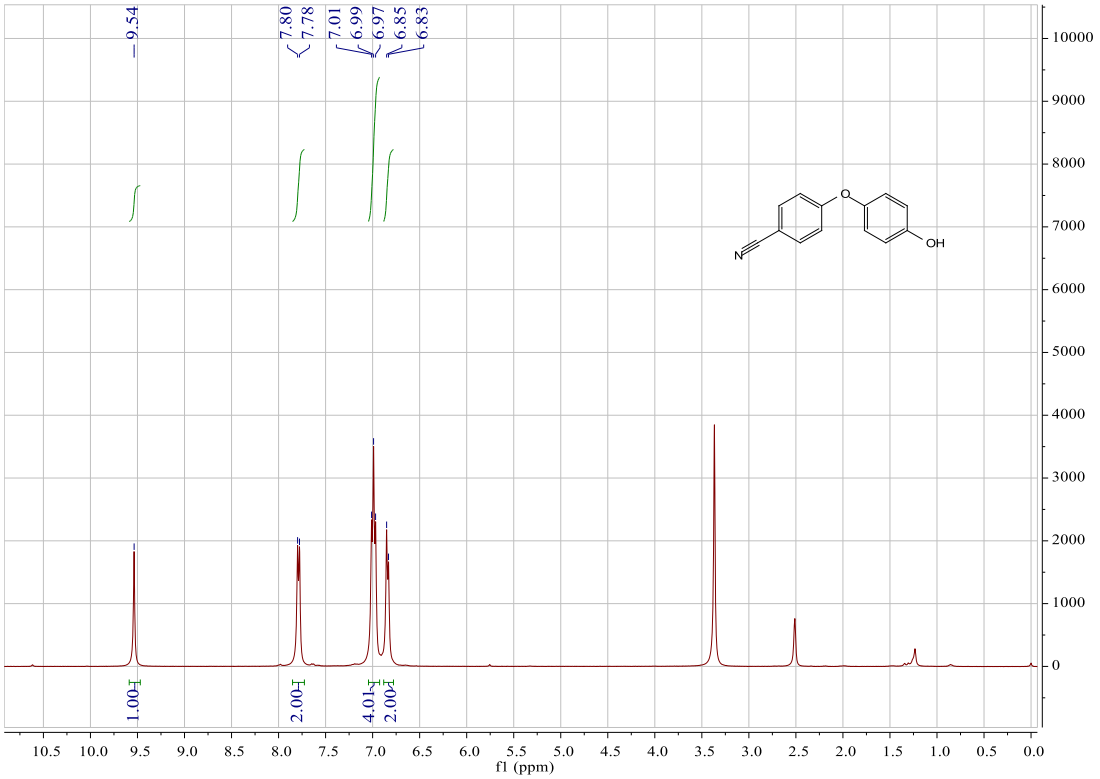
^{1}H NMR of compound **4ag**



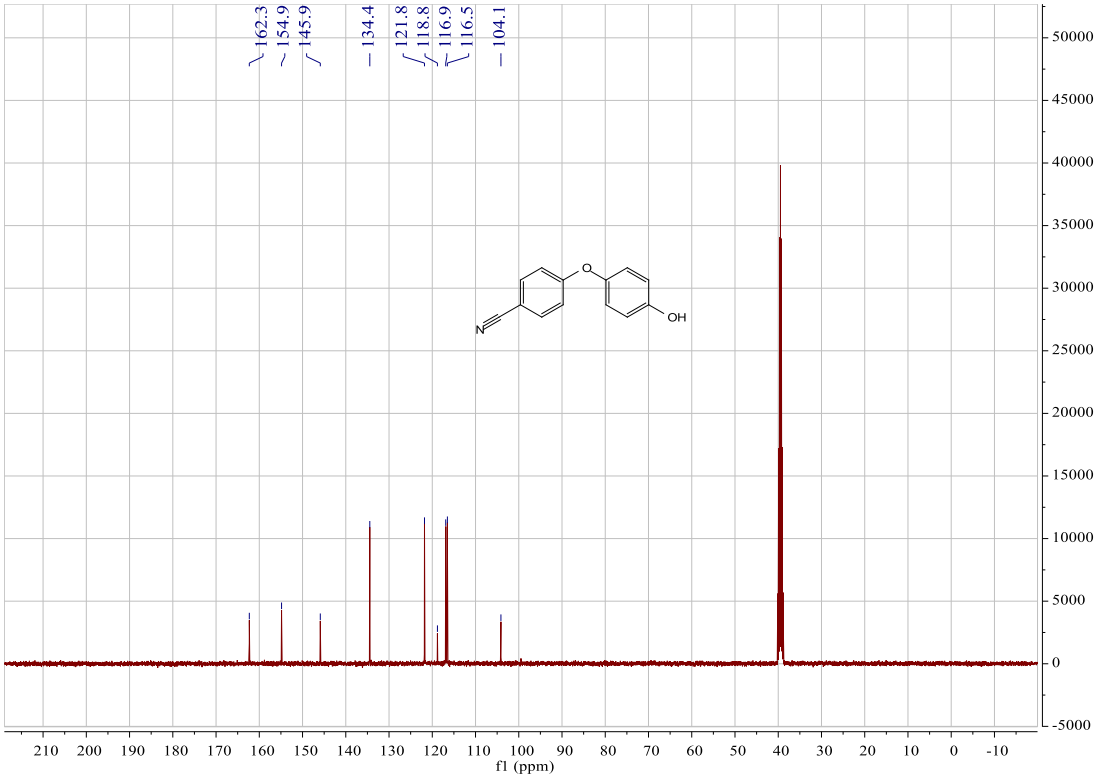
^{13}C NMR of compound **4ag**



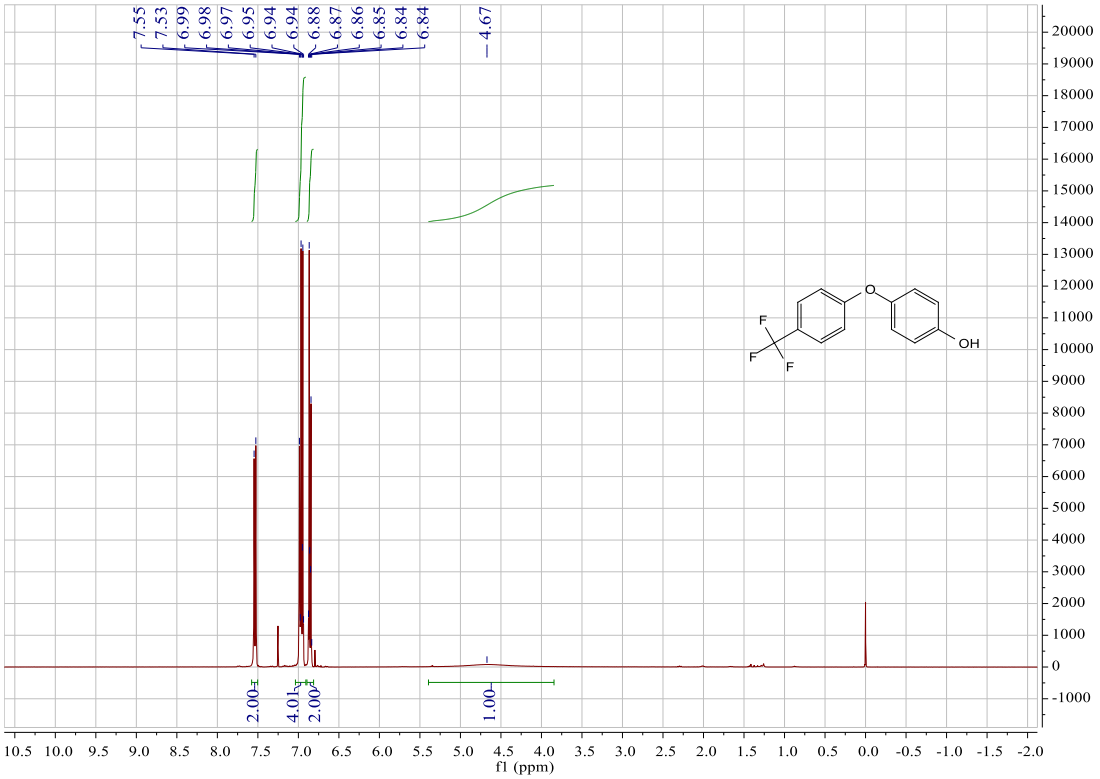
^{1}H NMR of compound **4ah**



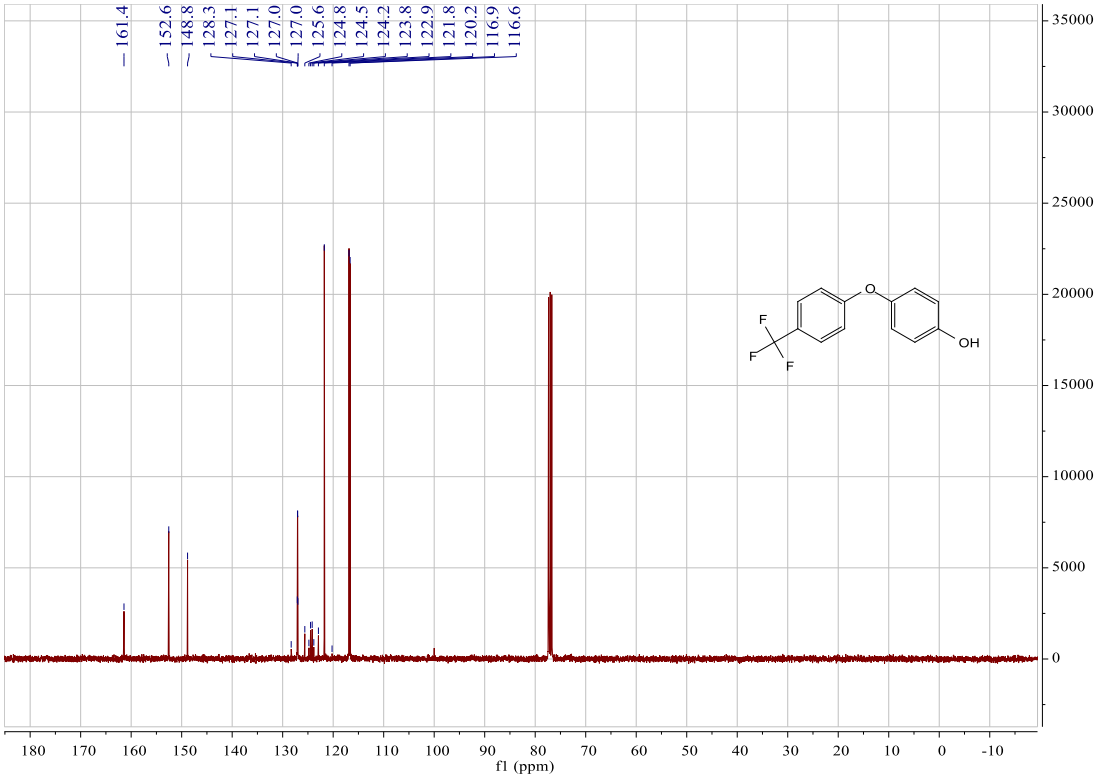
^{13}C NMR of compound **4ah**



^{1}H NMR of compound **4ai**



^{13}C NMR of compound **4ai**



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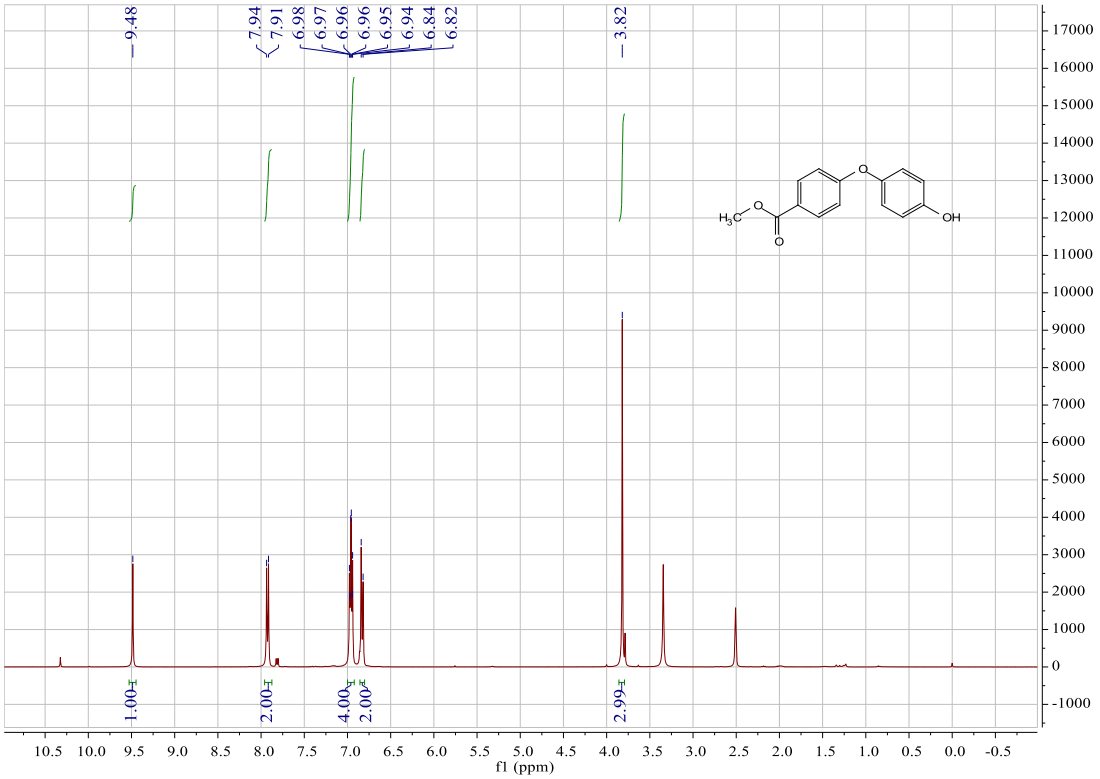

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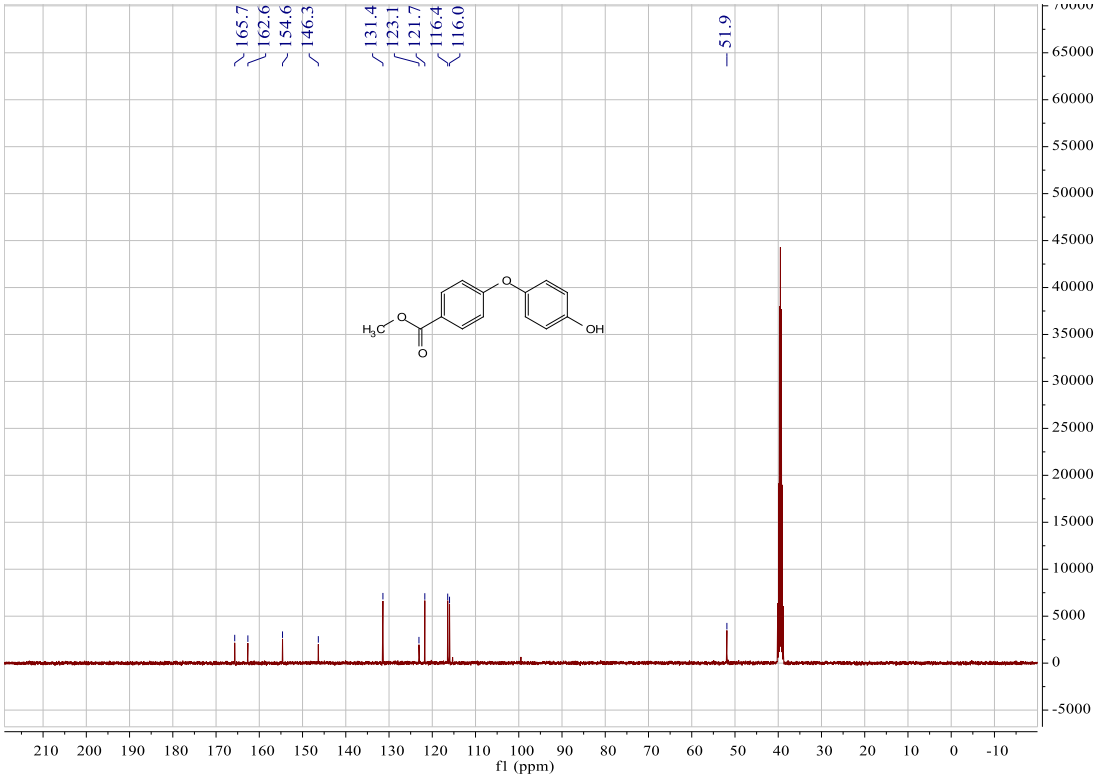
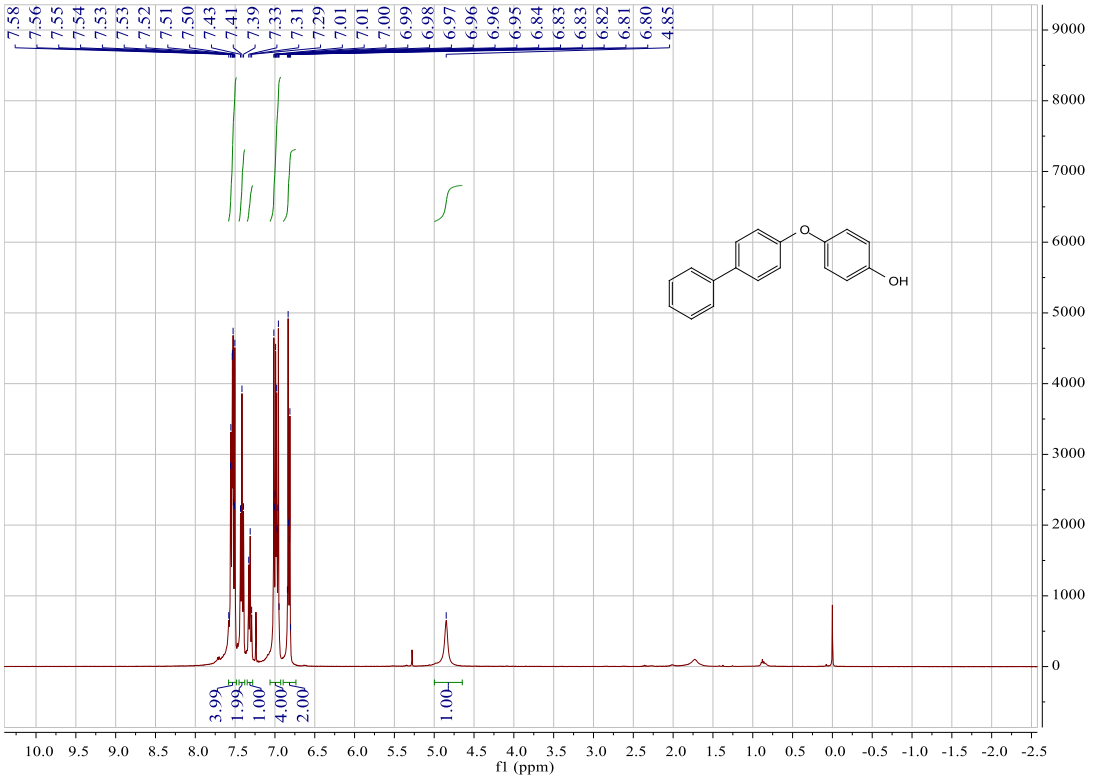
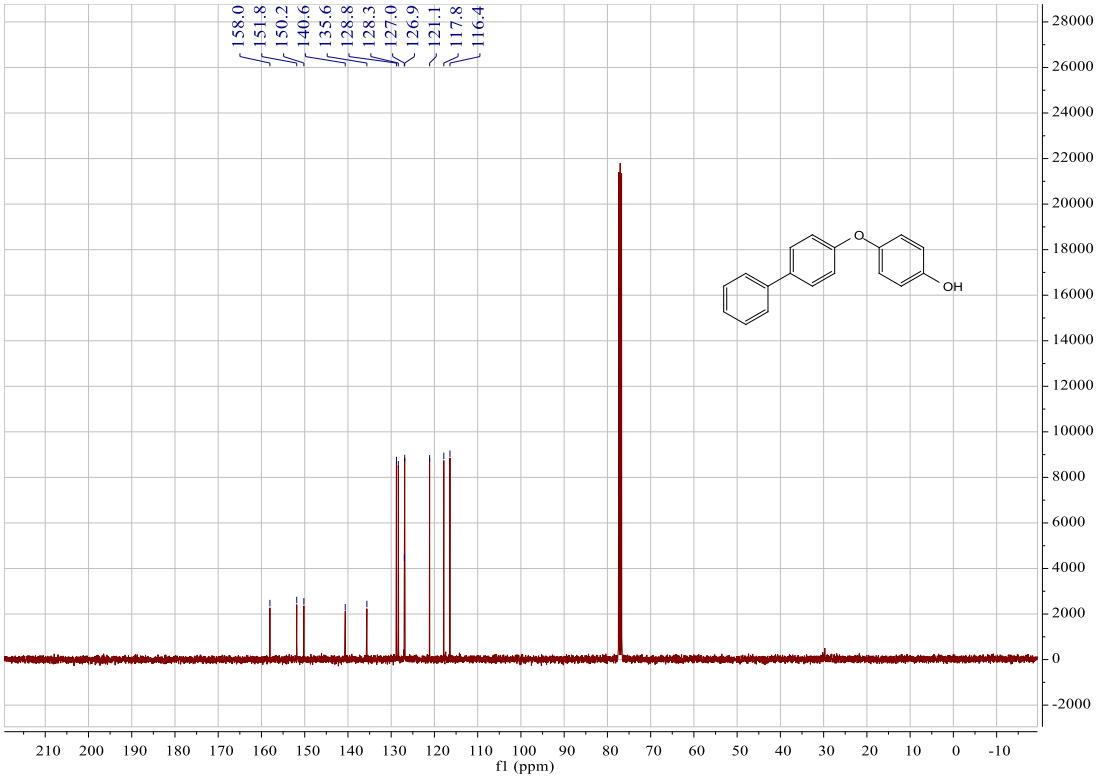


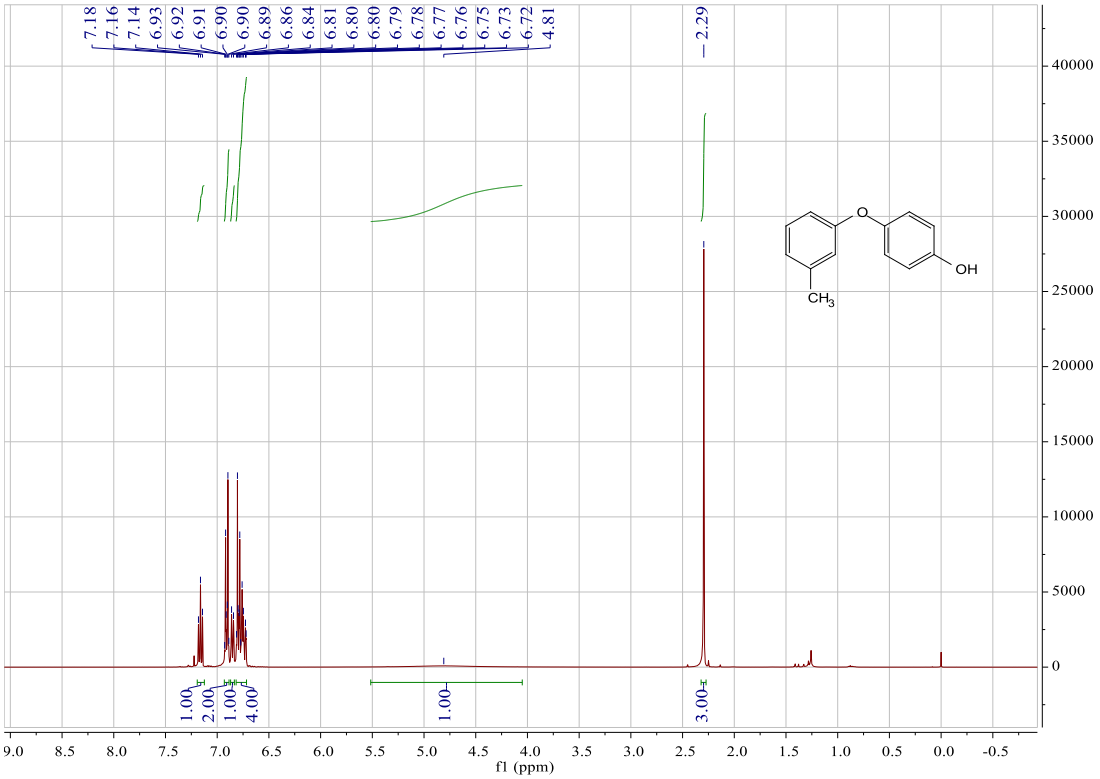
^{1}H NMR of compound **4ak**



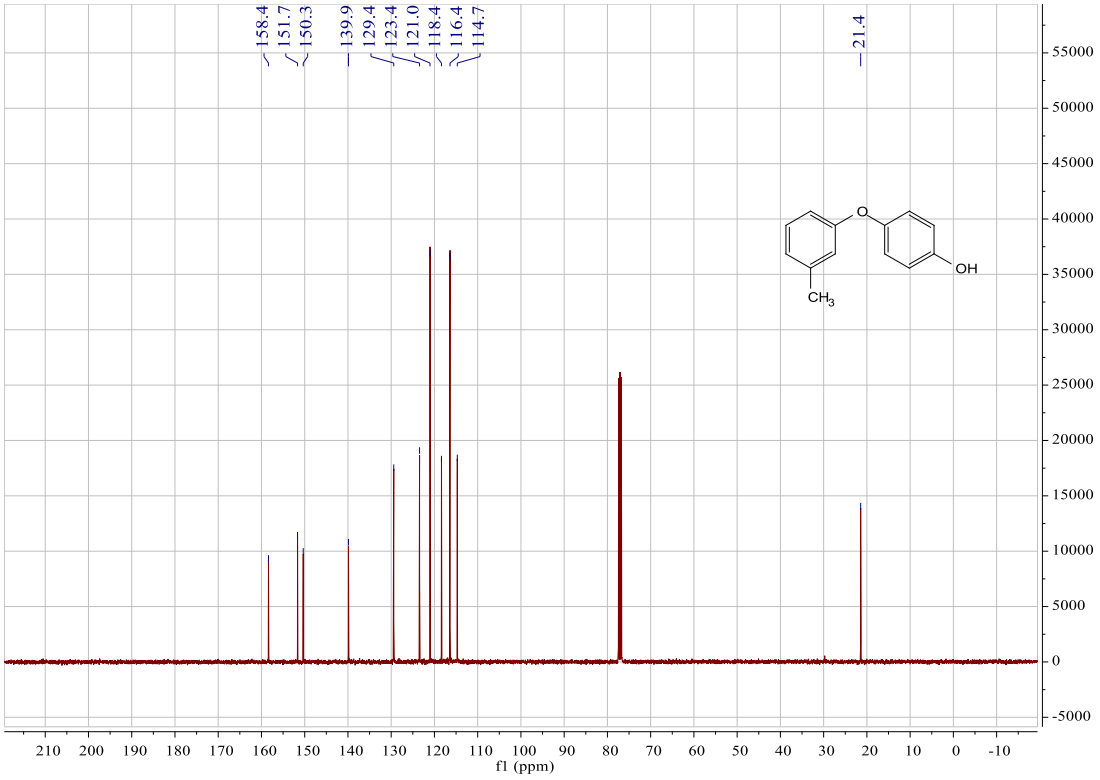
^{13}C NMR of compound **4ak**



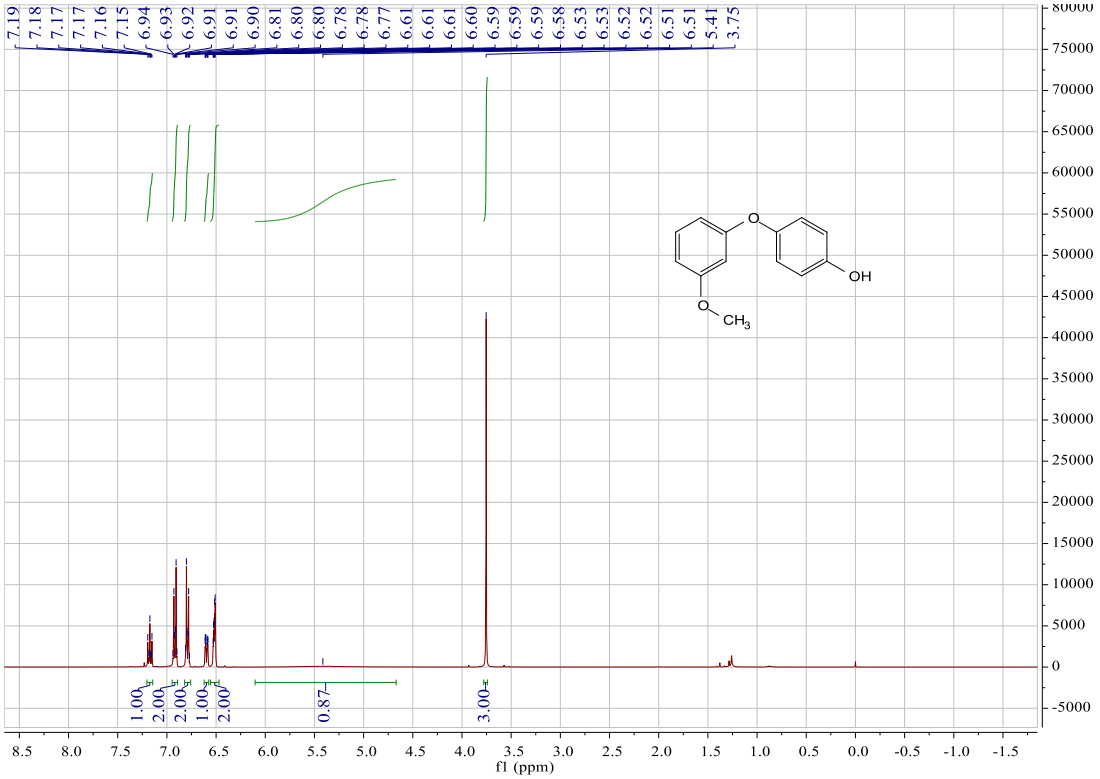
^{1}H NMR of compound **4al**



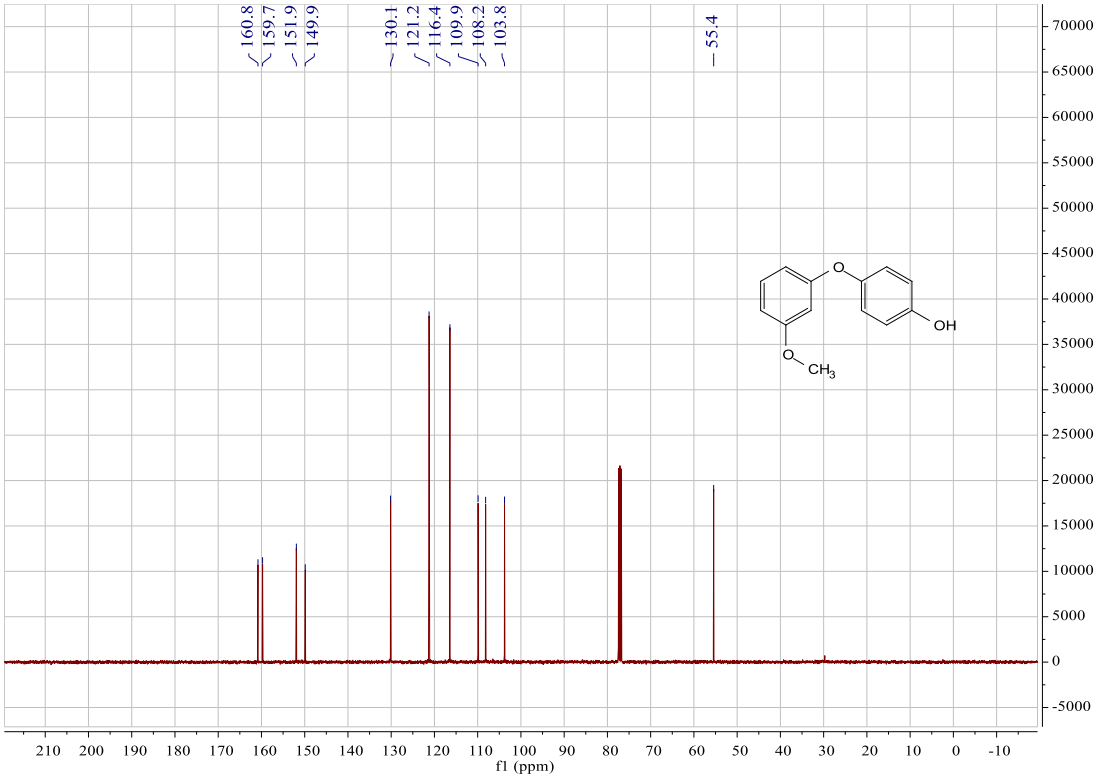
^{13}C NMR of compound **4al**



^{1}H NMR of compound **4am**



^{13}C NMR of compound **4am**



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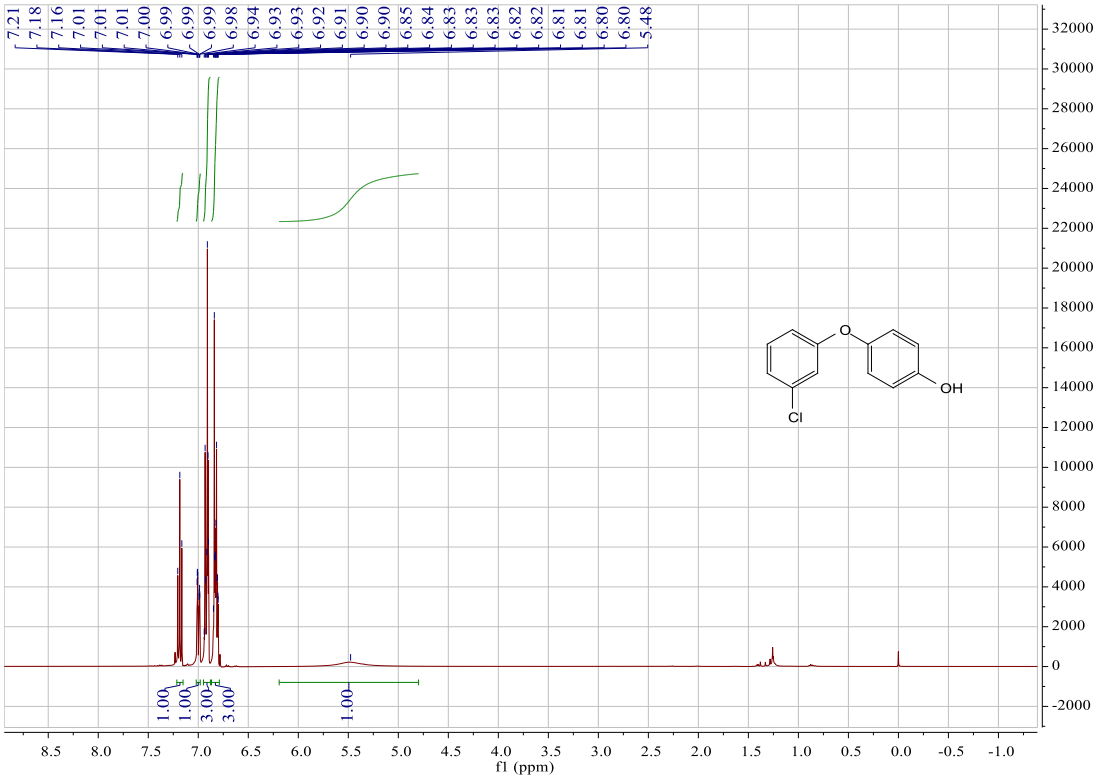

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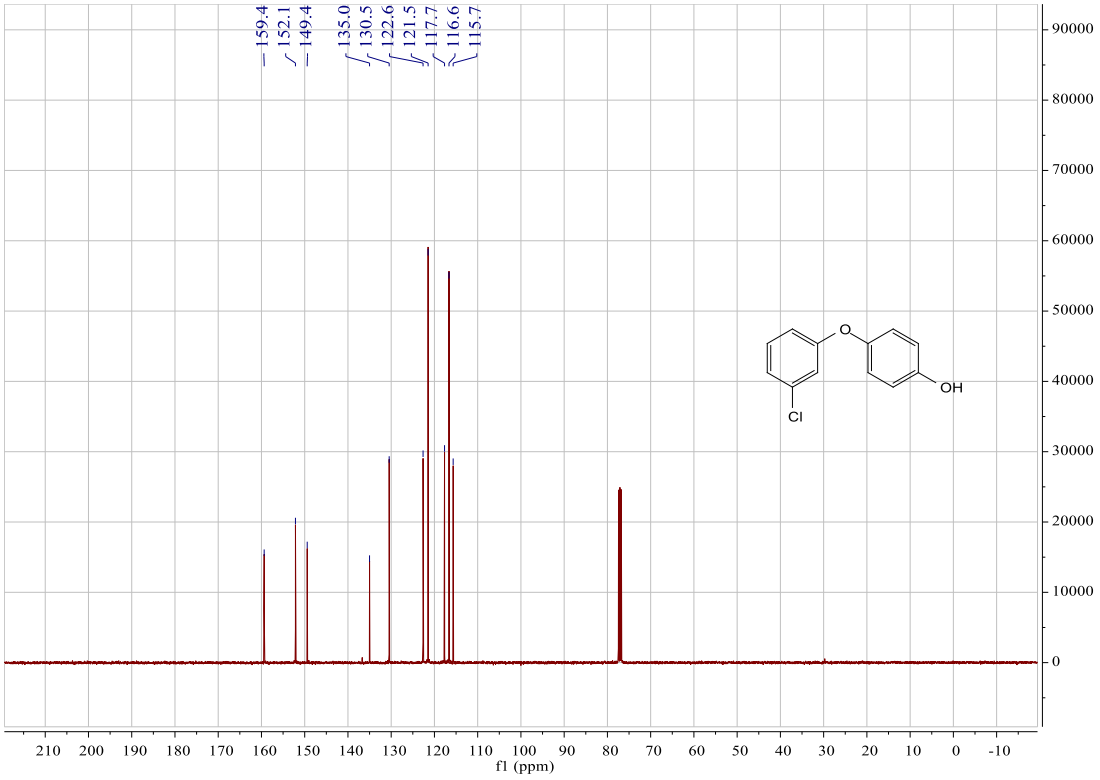
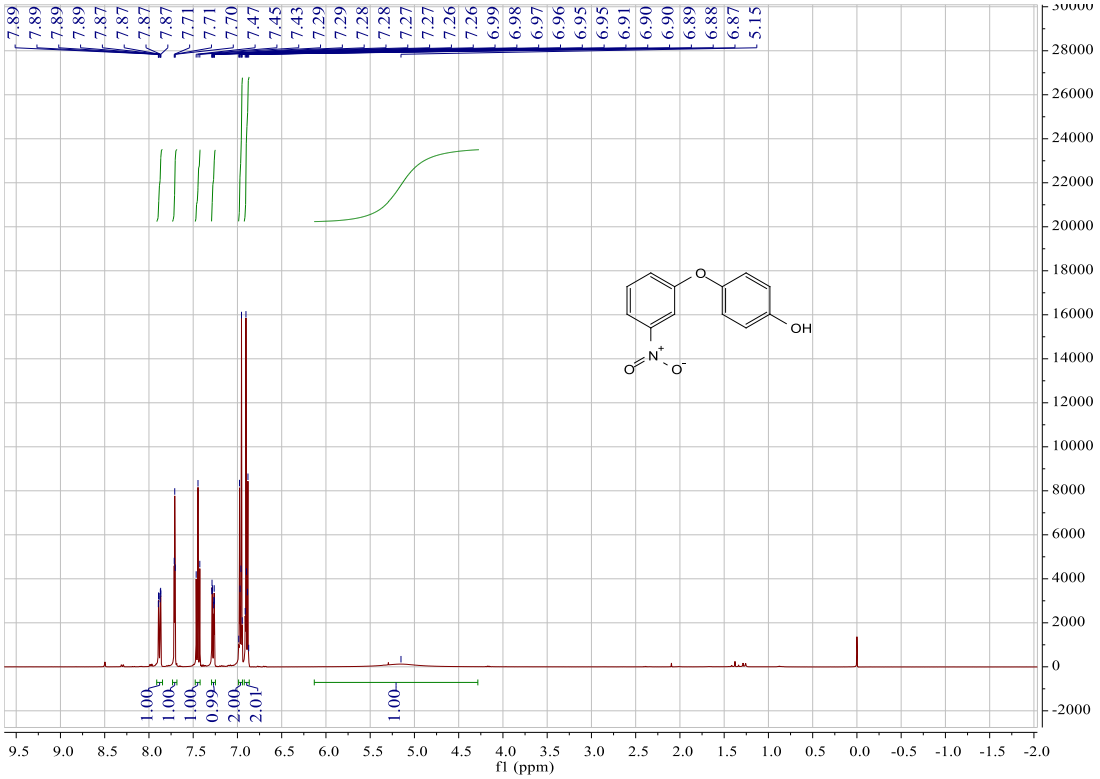
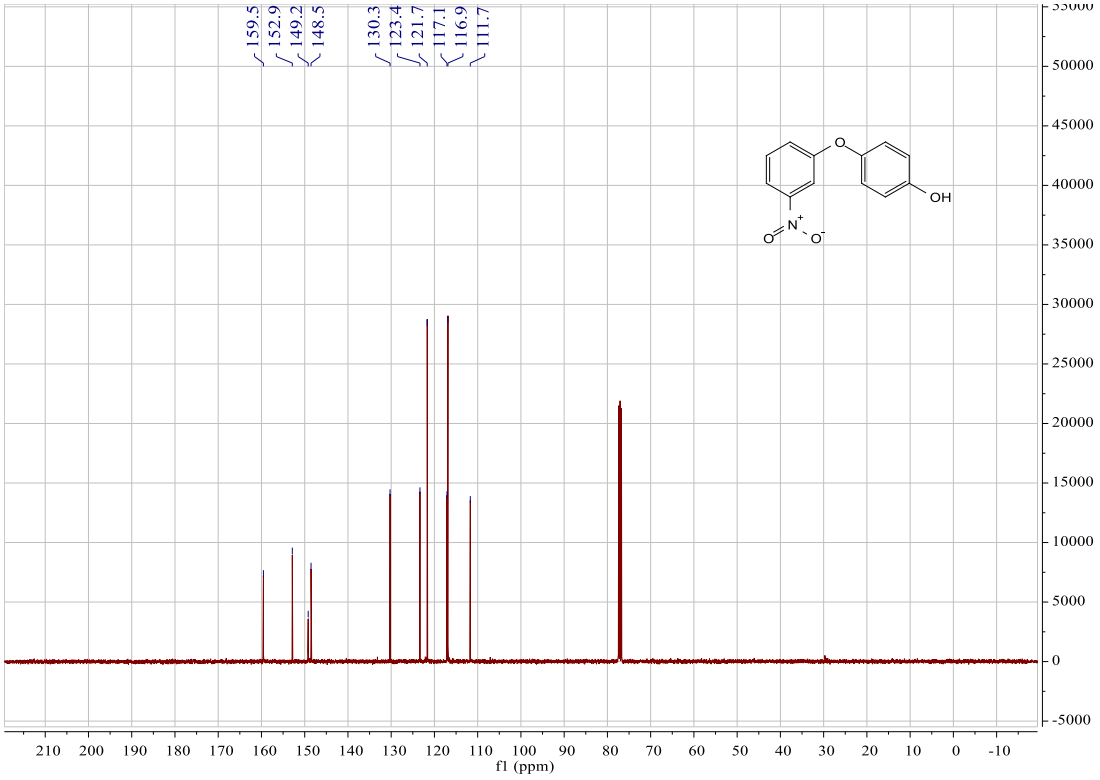


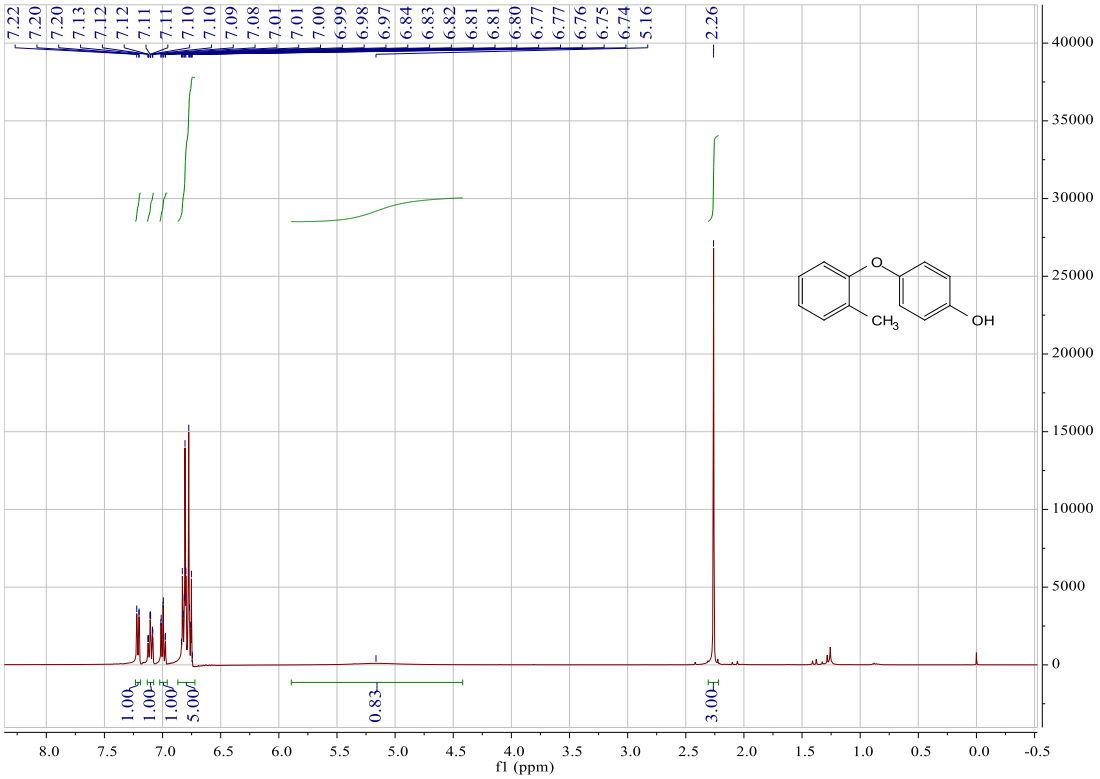
^{1}H NMR of compound **4ao**



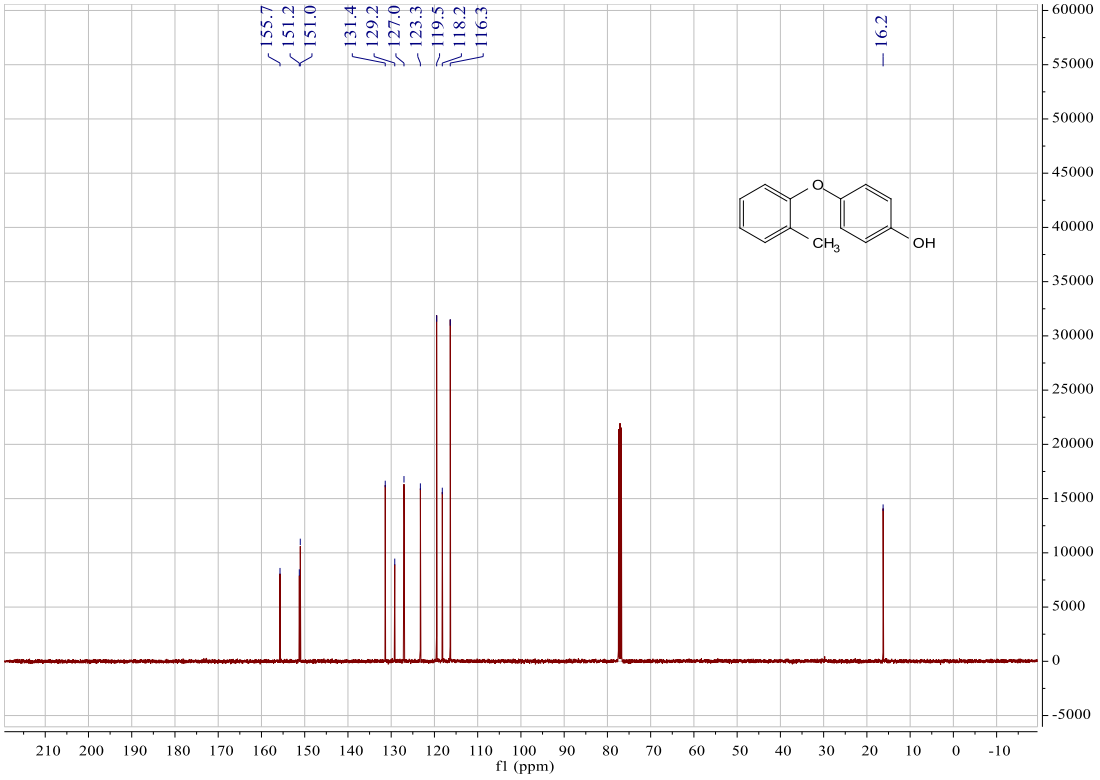
^{13}C NMR of compound **4ao**



^{1}H NMR of compound **4ap**



^{13}C NMR of compound **4ap**



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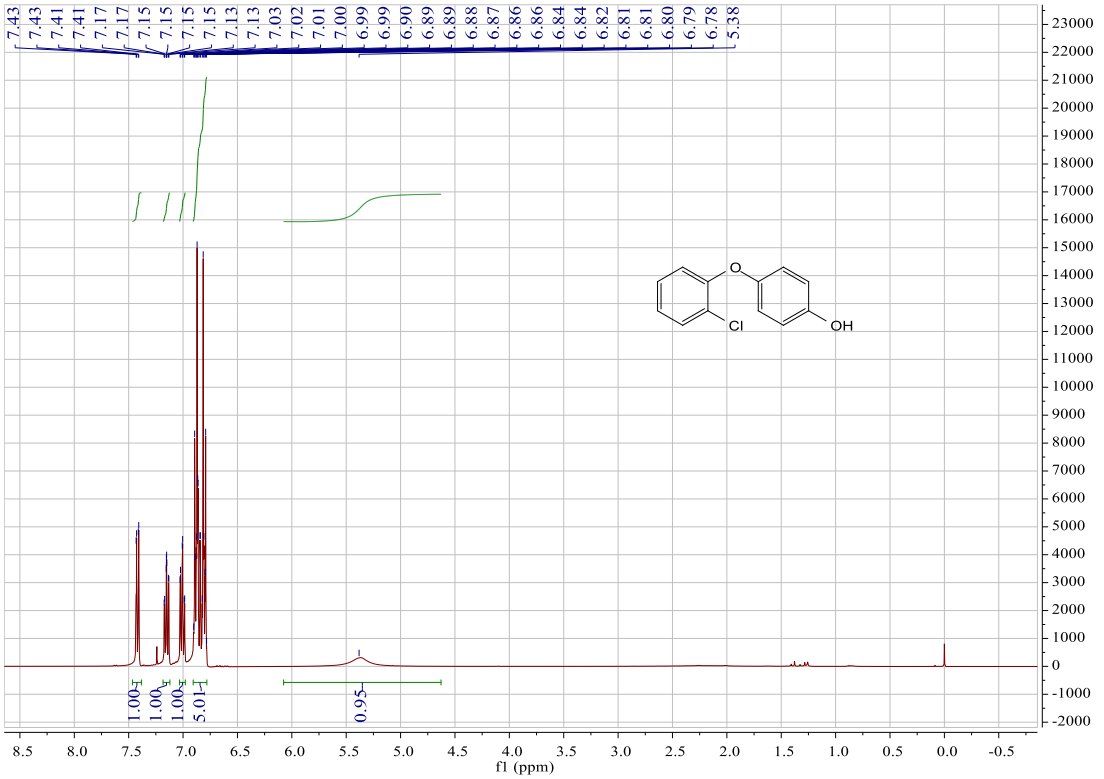

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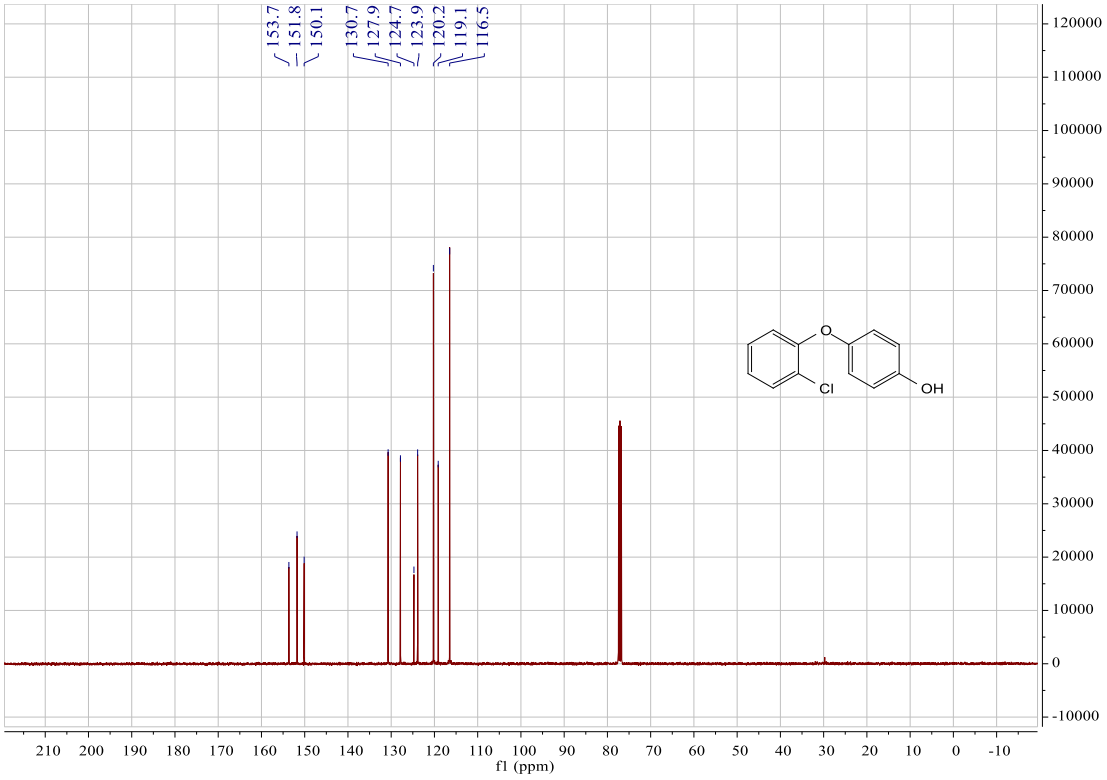

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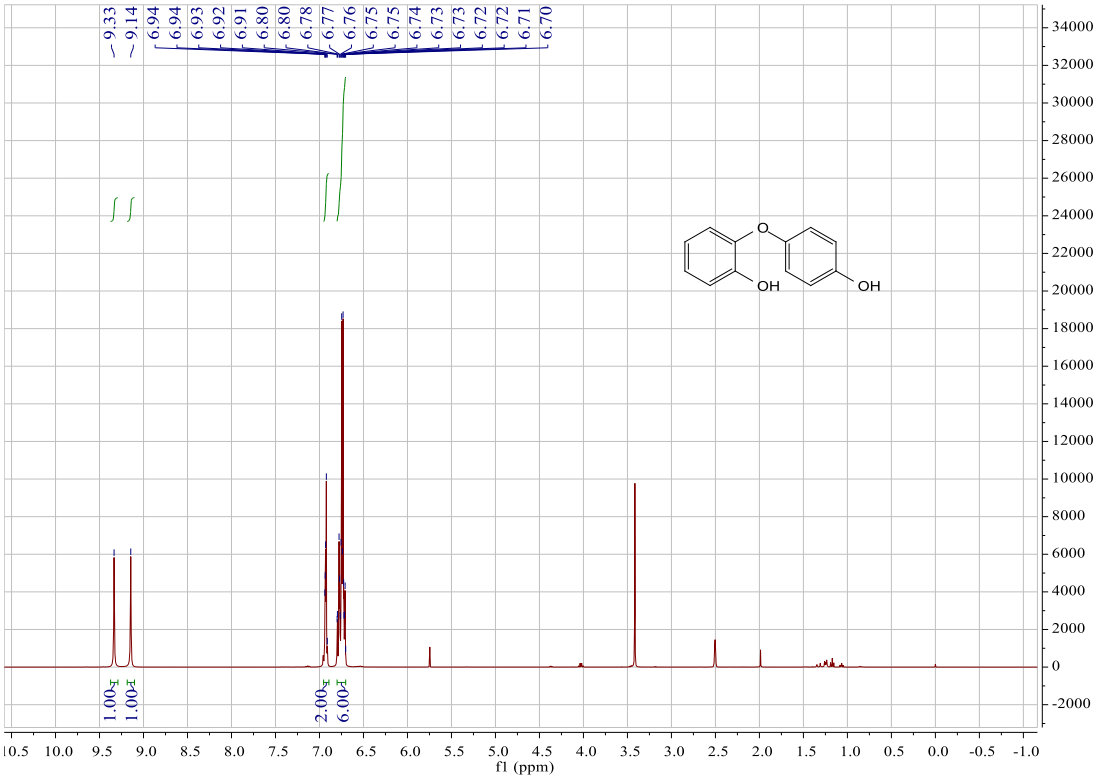
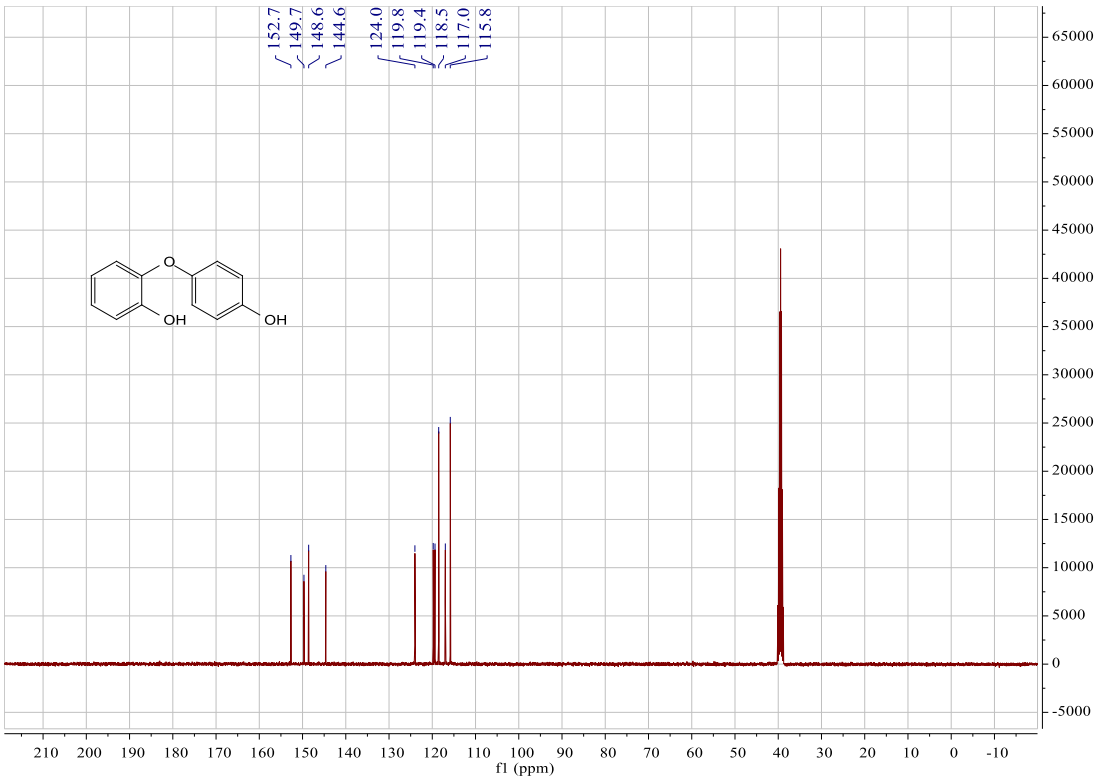
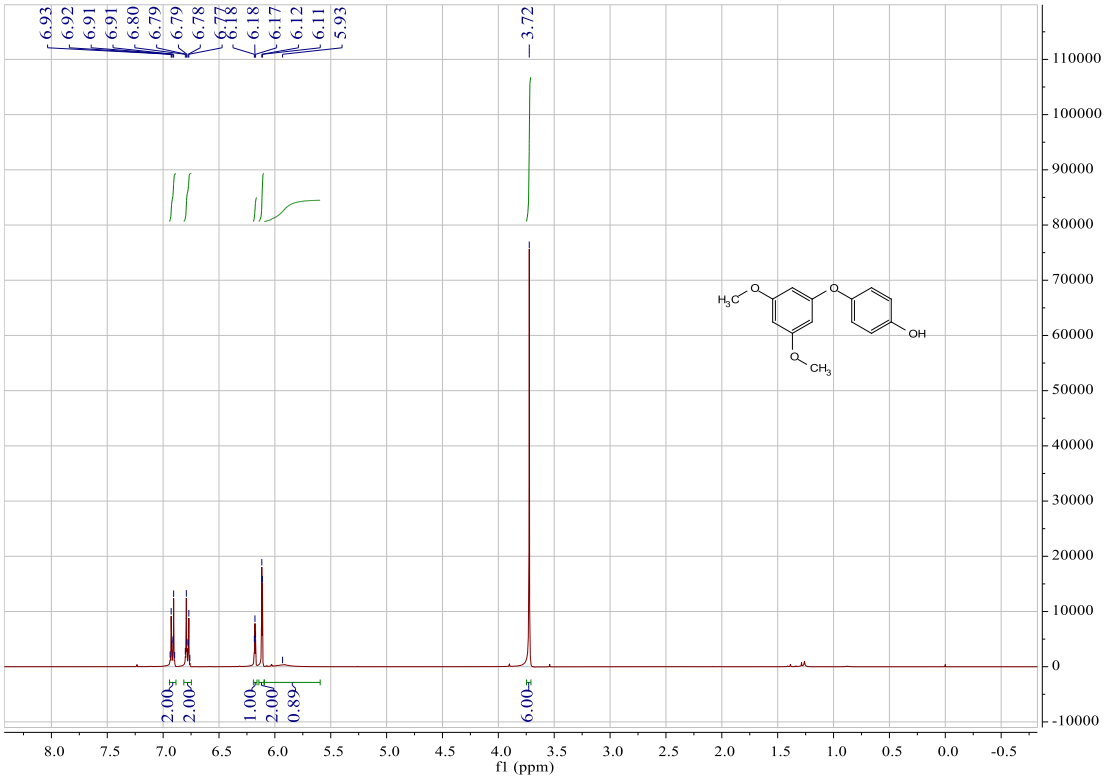


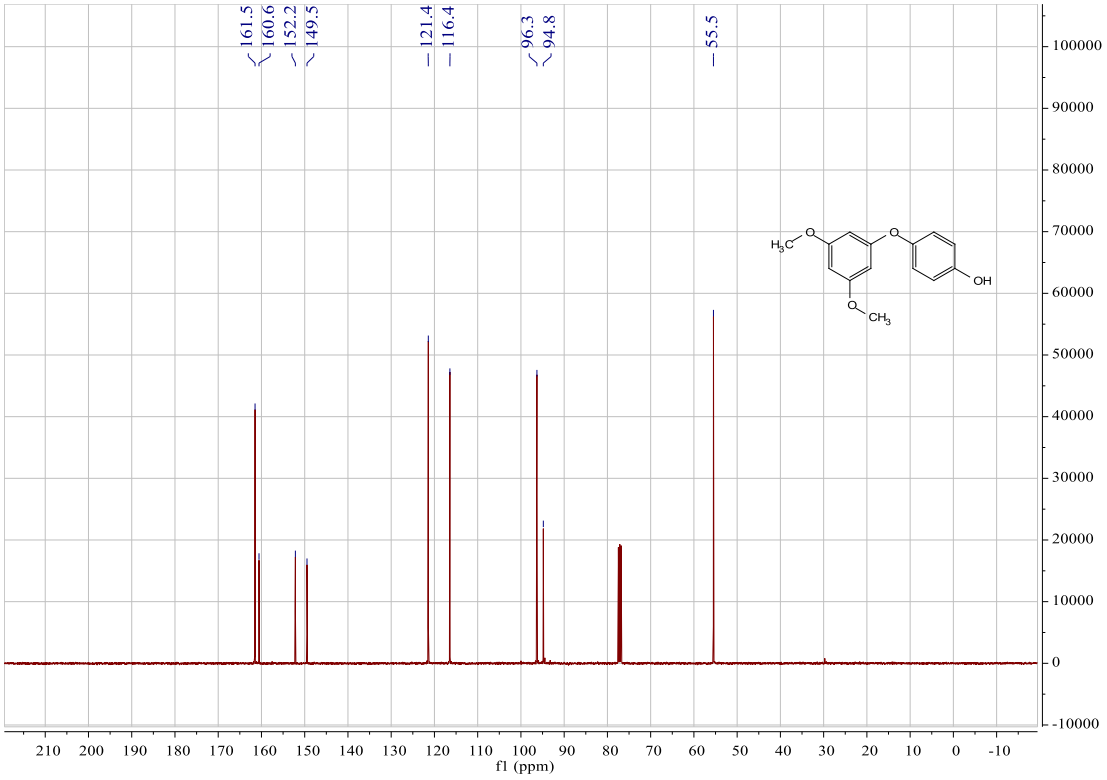
^{13}C NMR of compound **4ar**



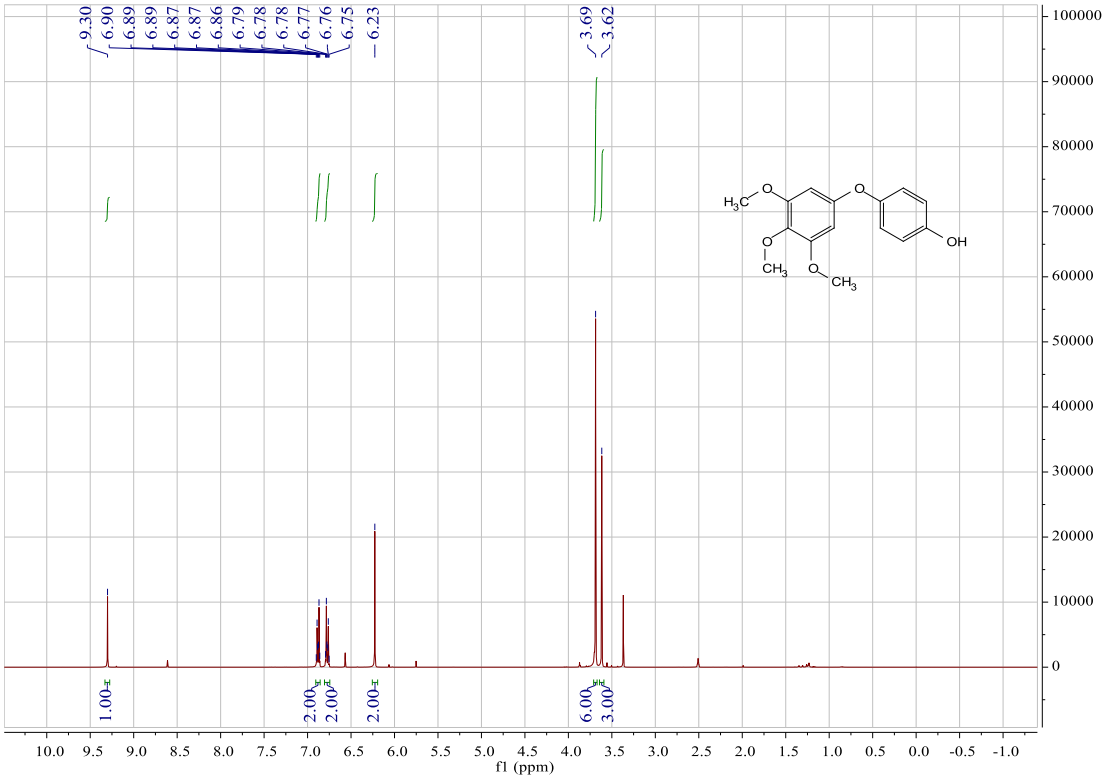
^{1}H NMR of compound **4as**



^{13}C NMR of compound **4as**



^{1}H NMR of compound **4at**



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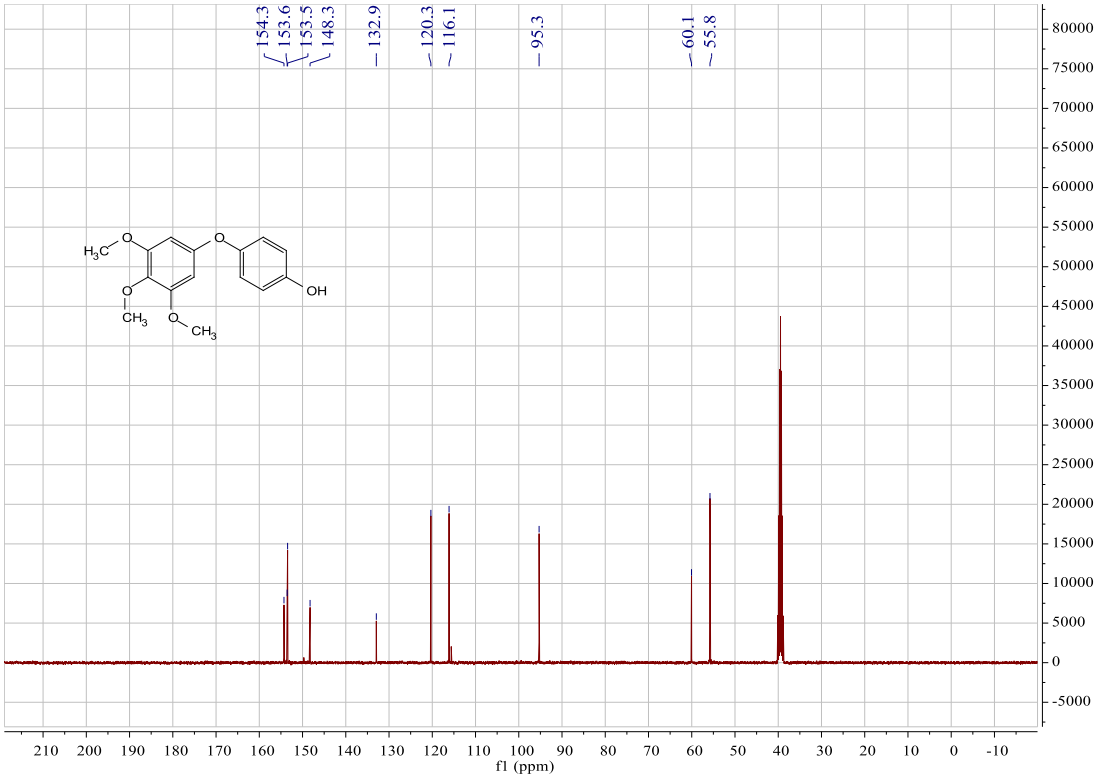
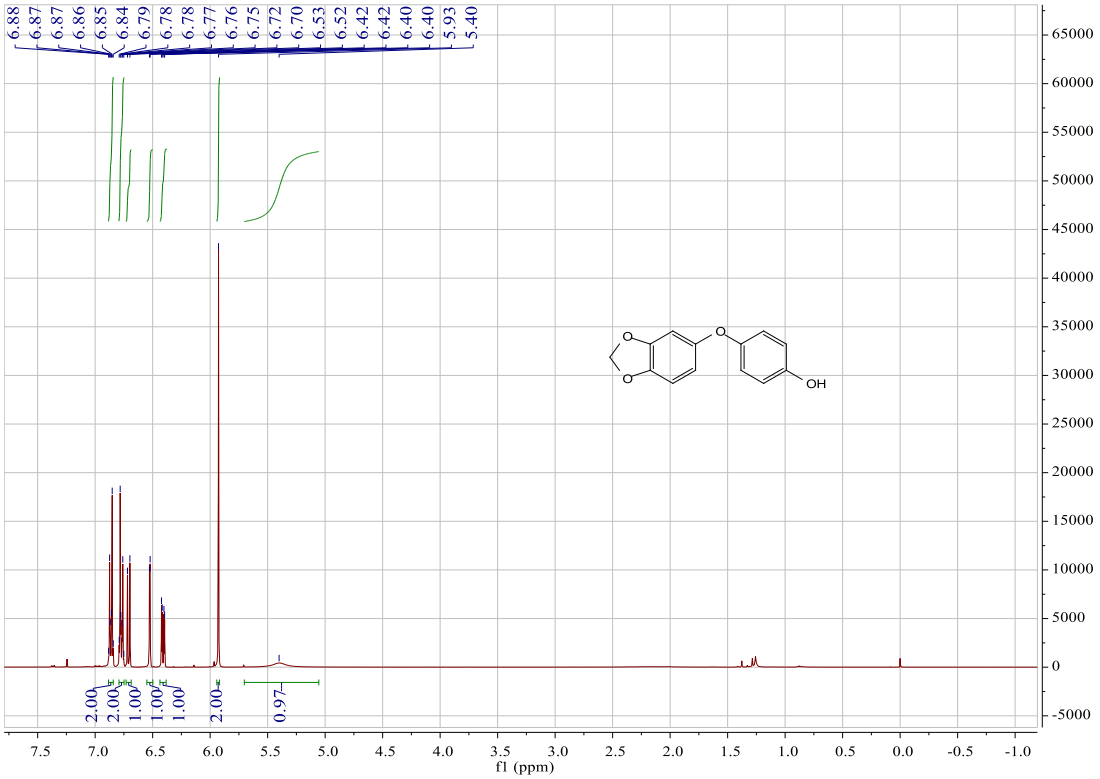


^{1}H NMR of compound **4au**



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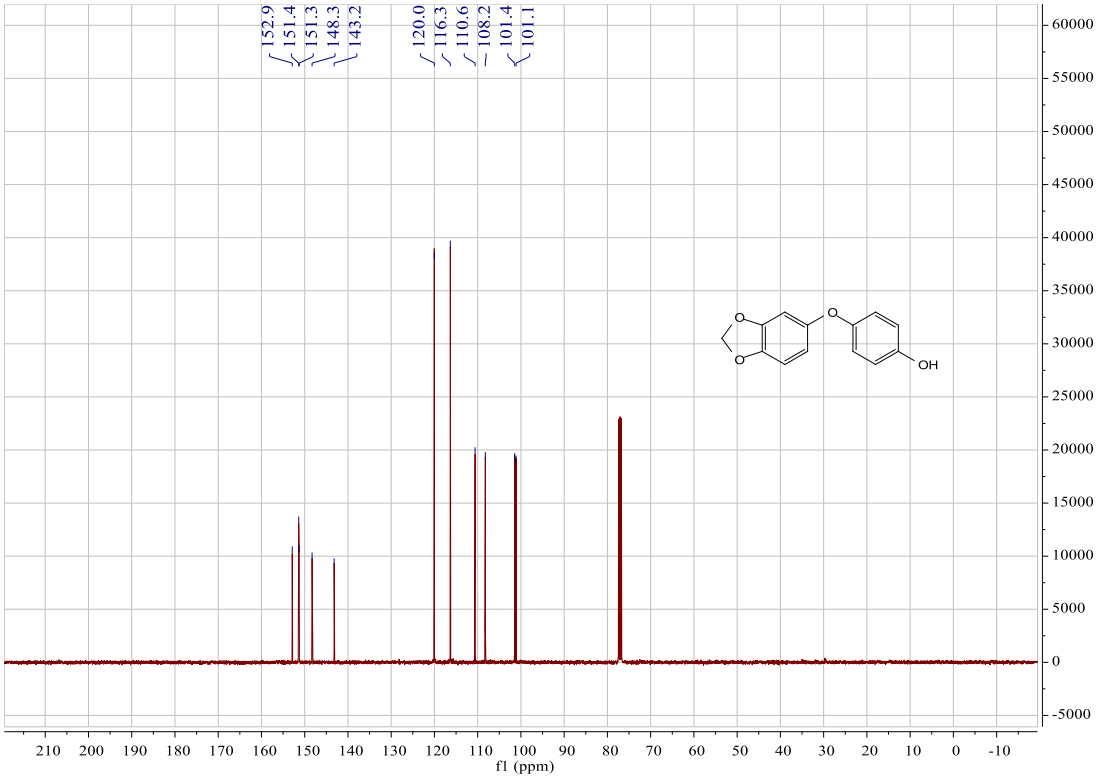
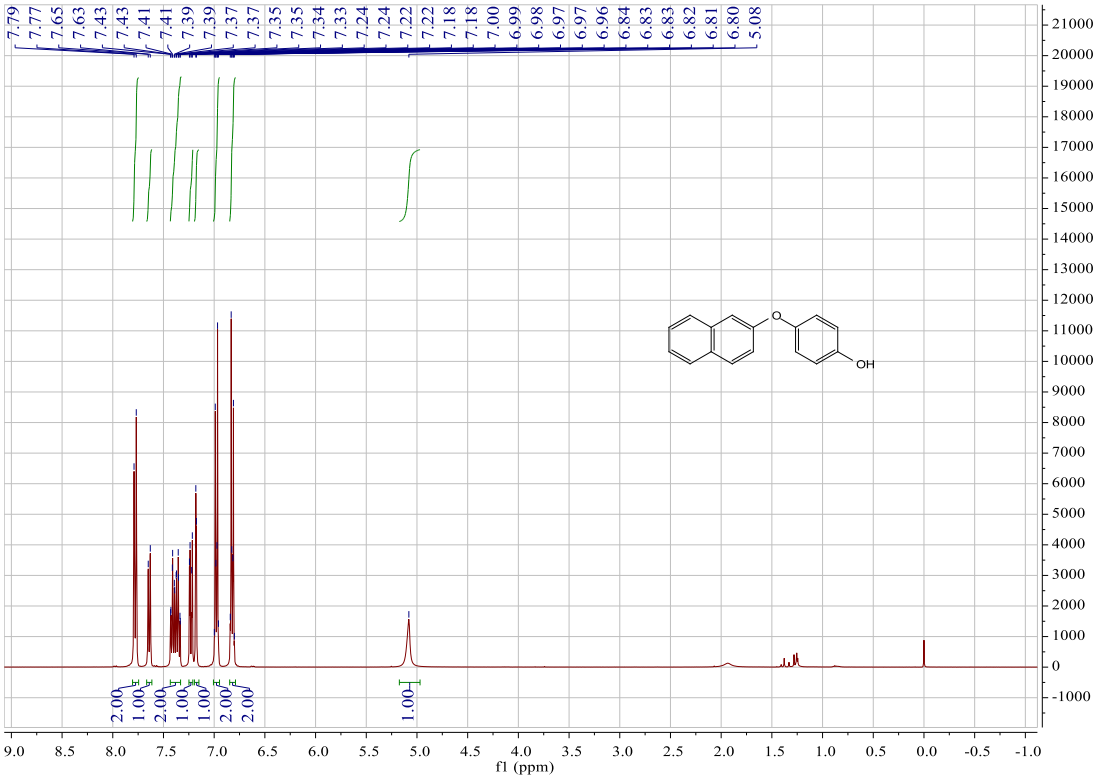


^{1}H NMR of compound **4av**



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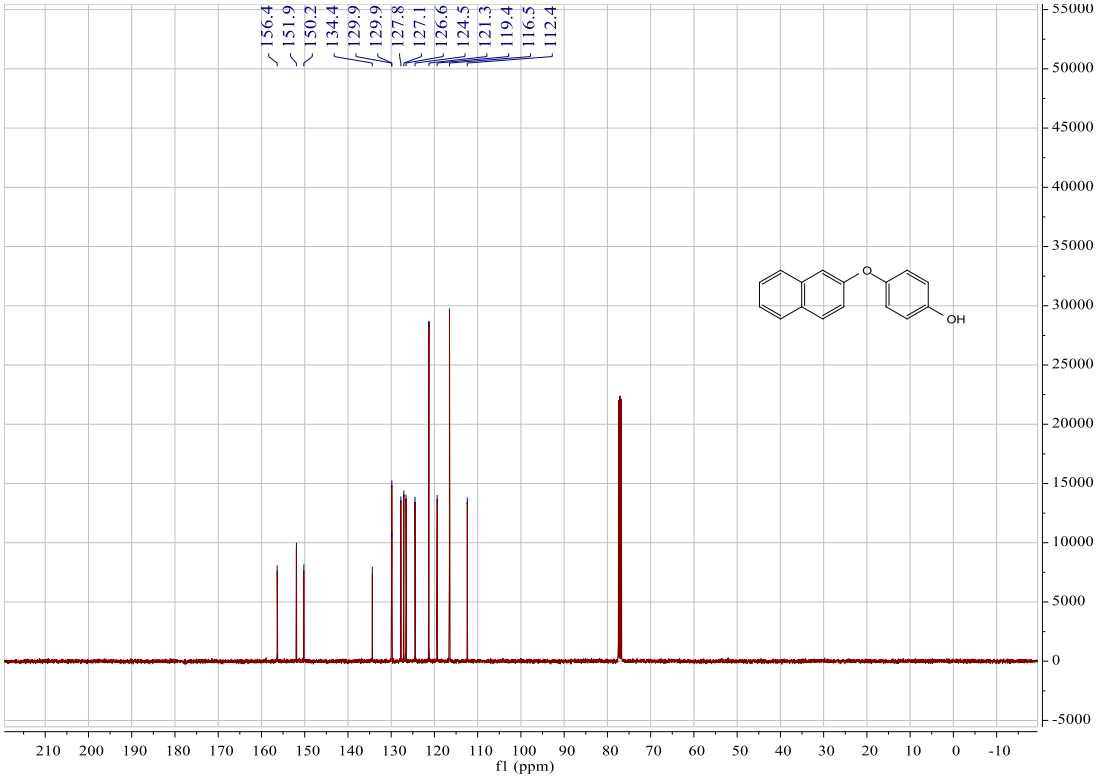

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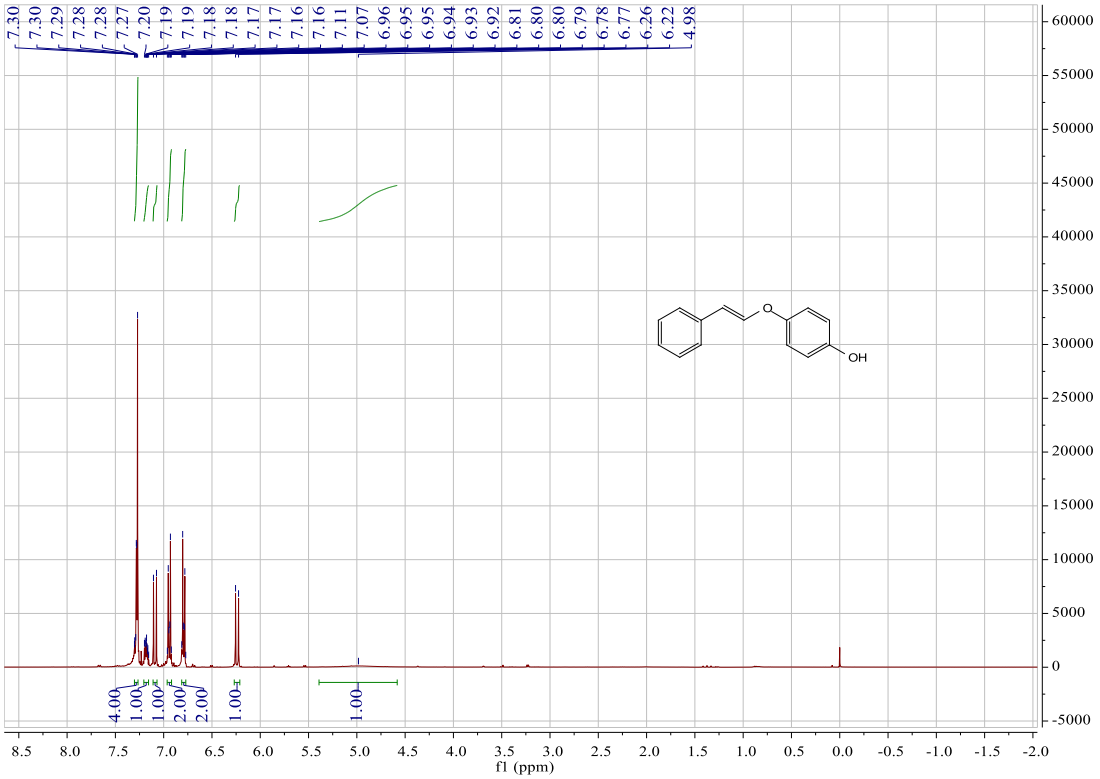

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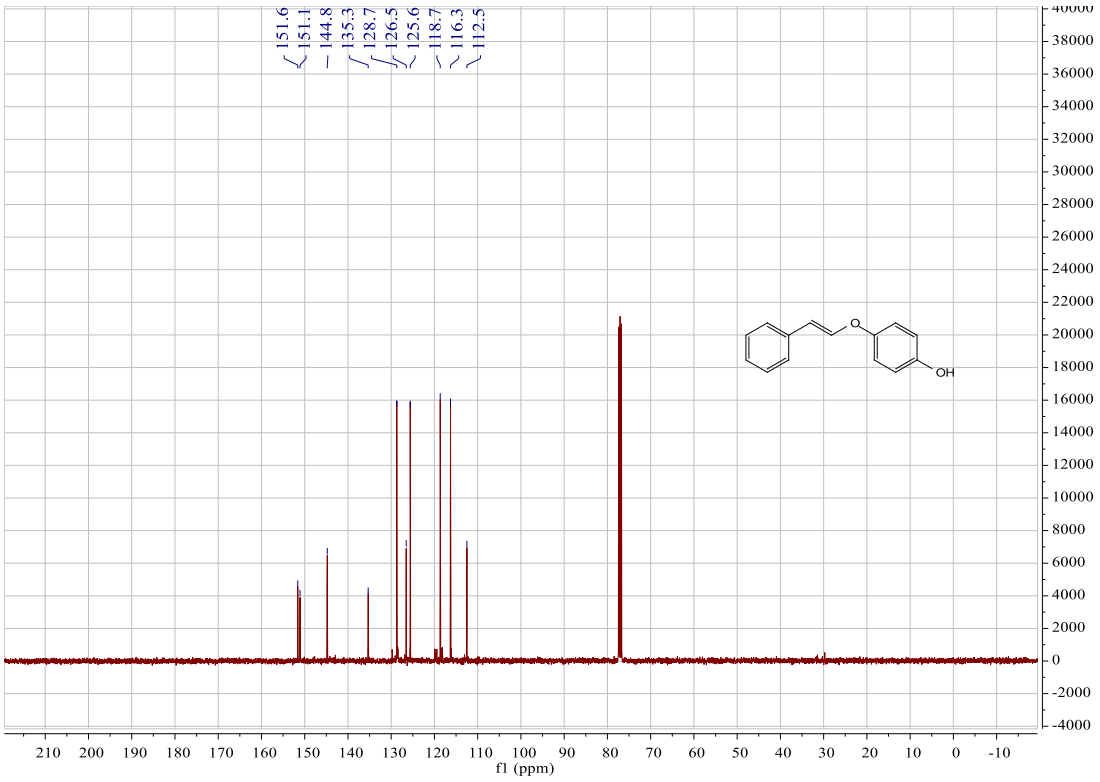
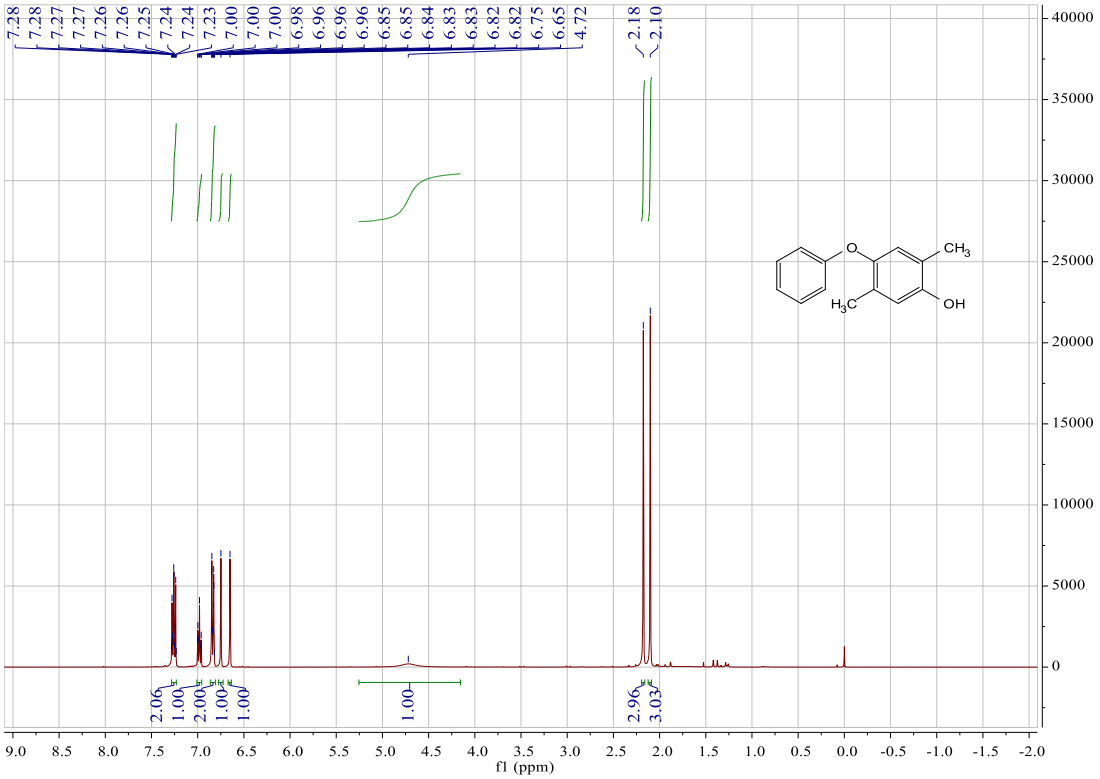
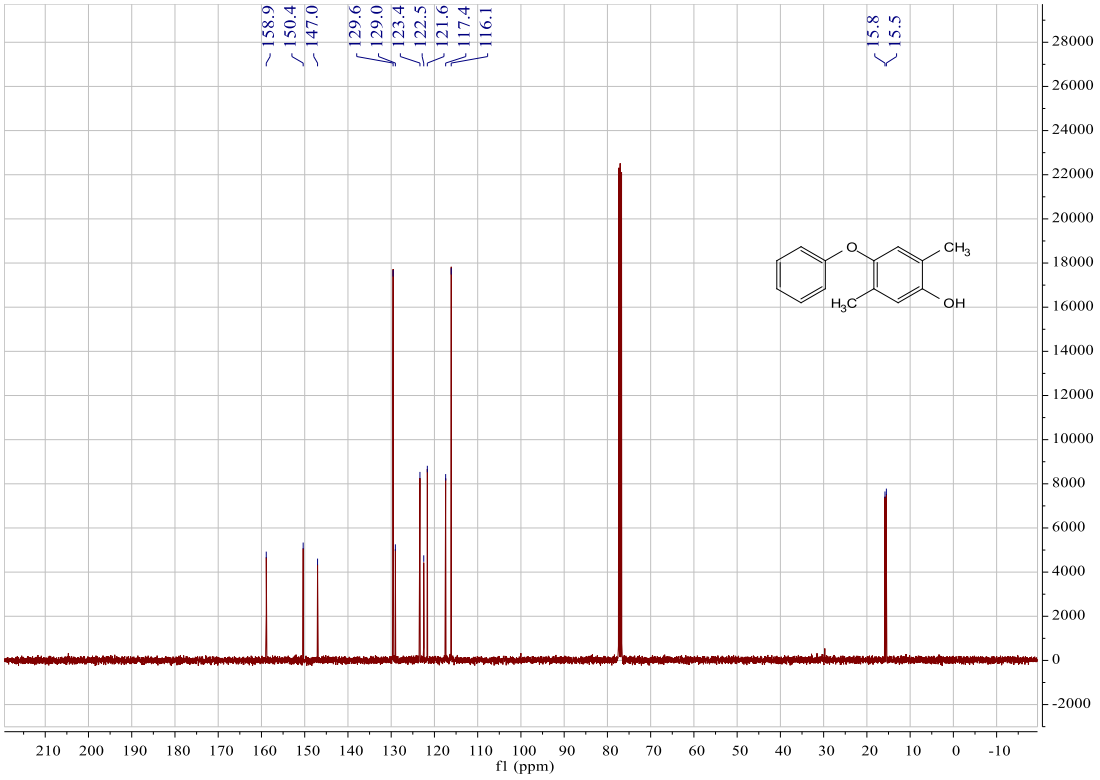


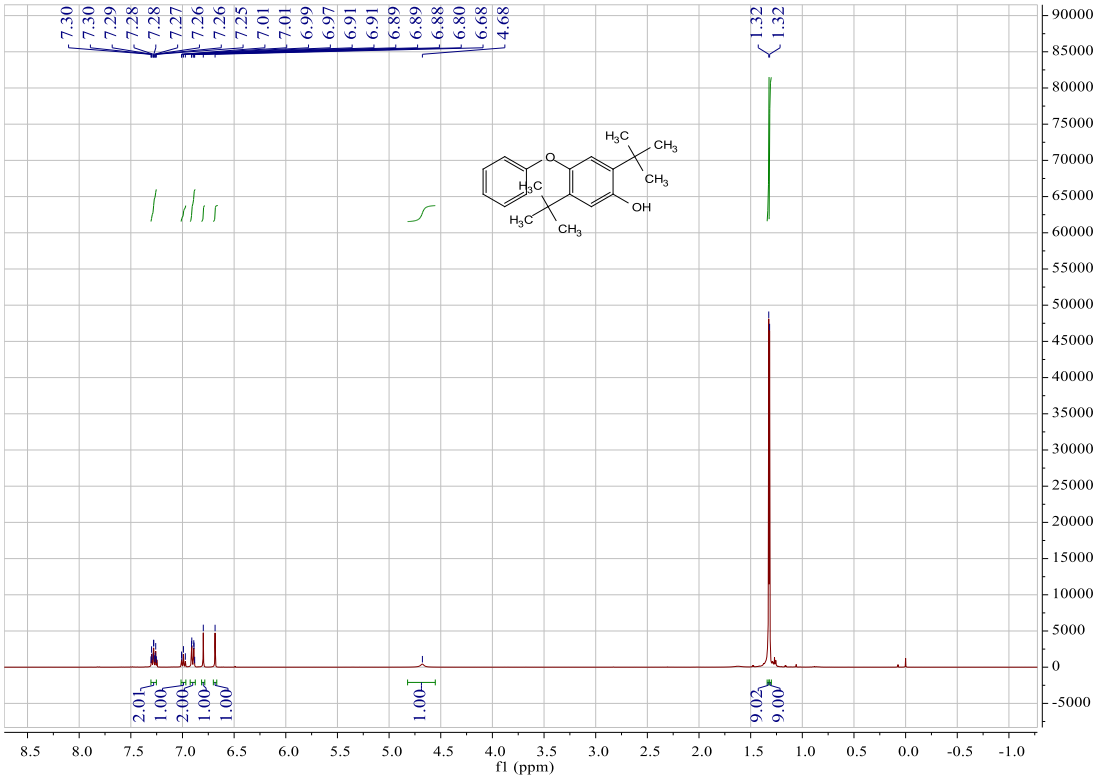
^{1}H NMR of compound **4ba**



^{13}C NMR of compound **4ba**



^{1}H NMR of compound **4ca**



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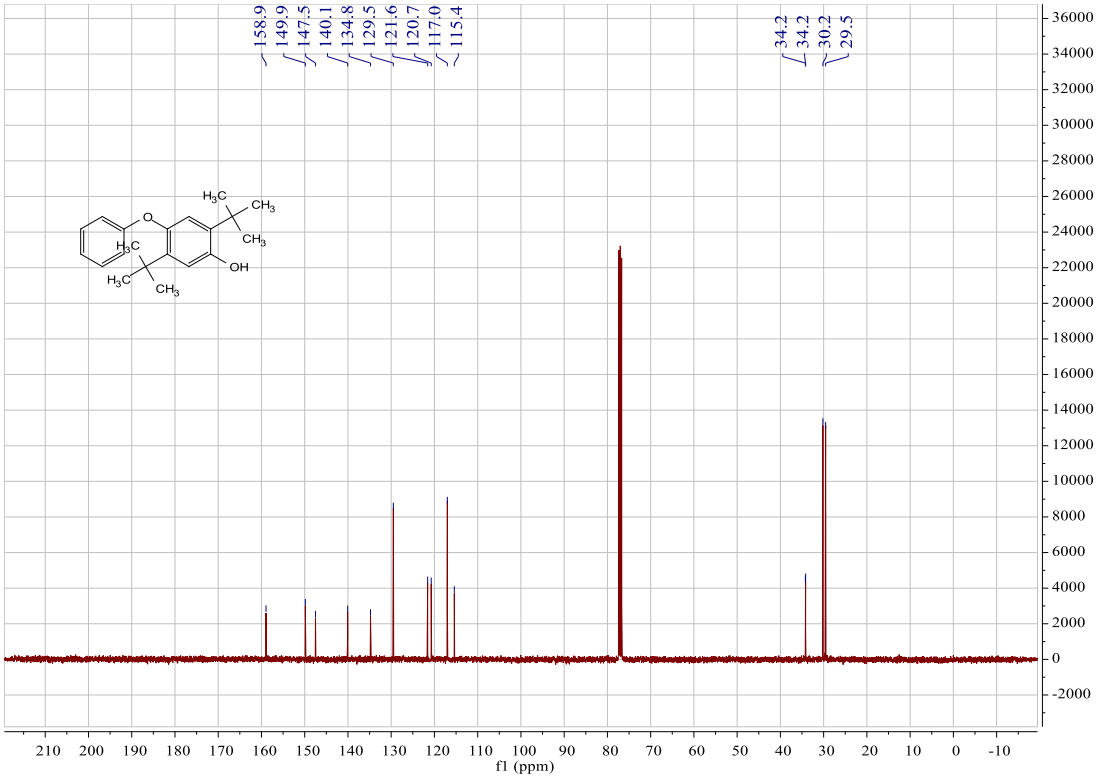
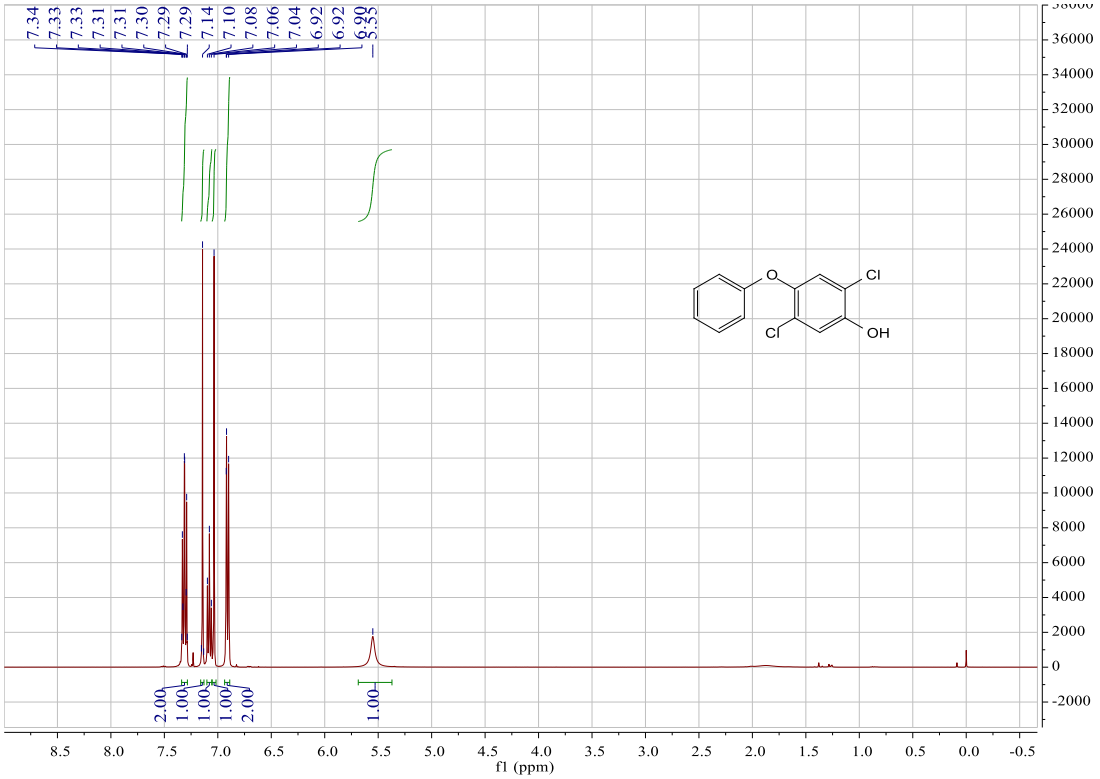


^{1}H NMR of compound **4da**



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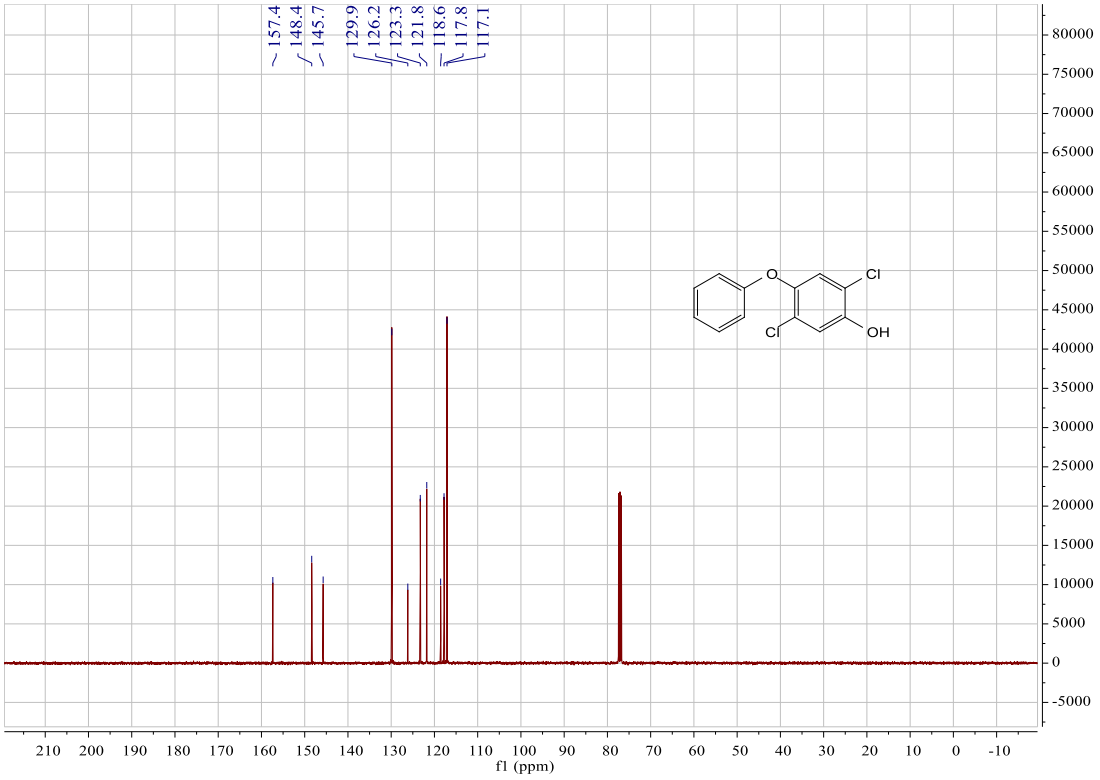

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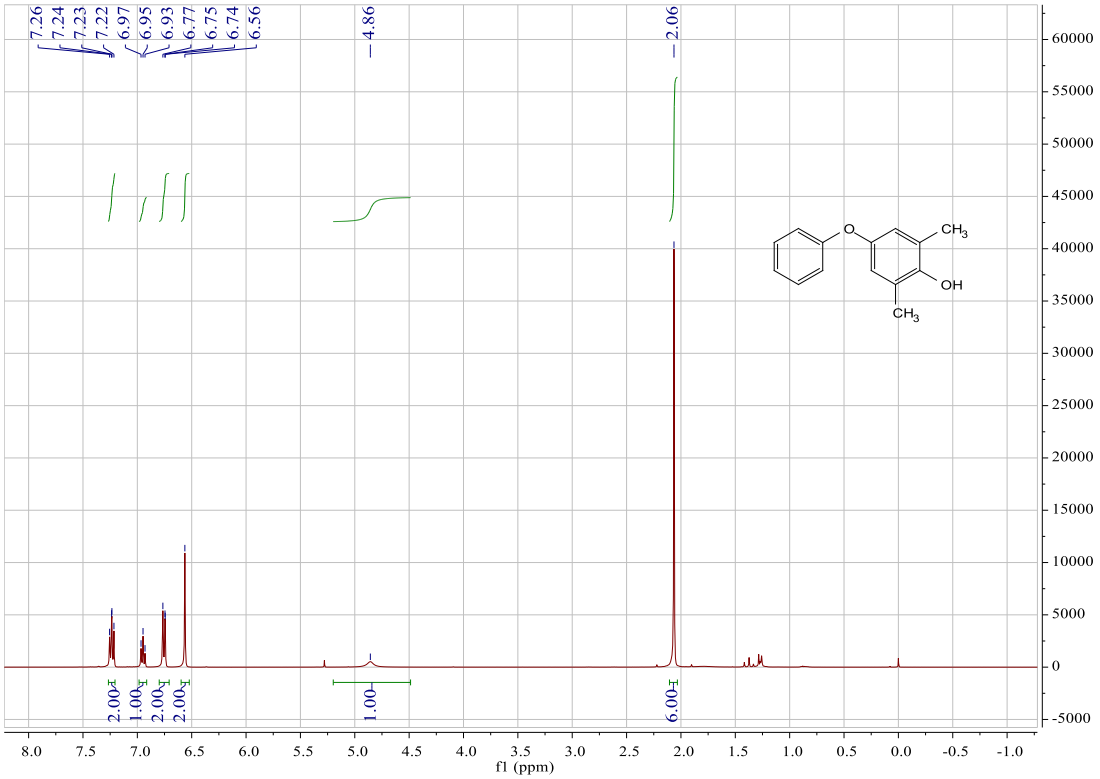
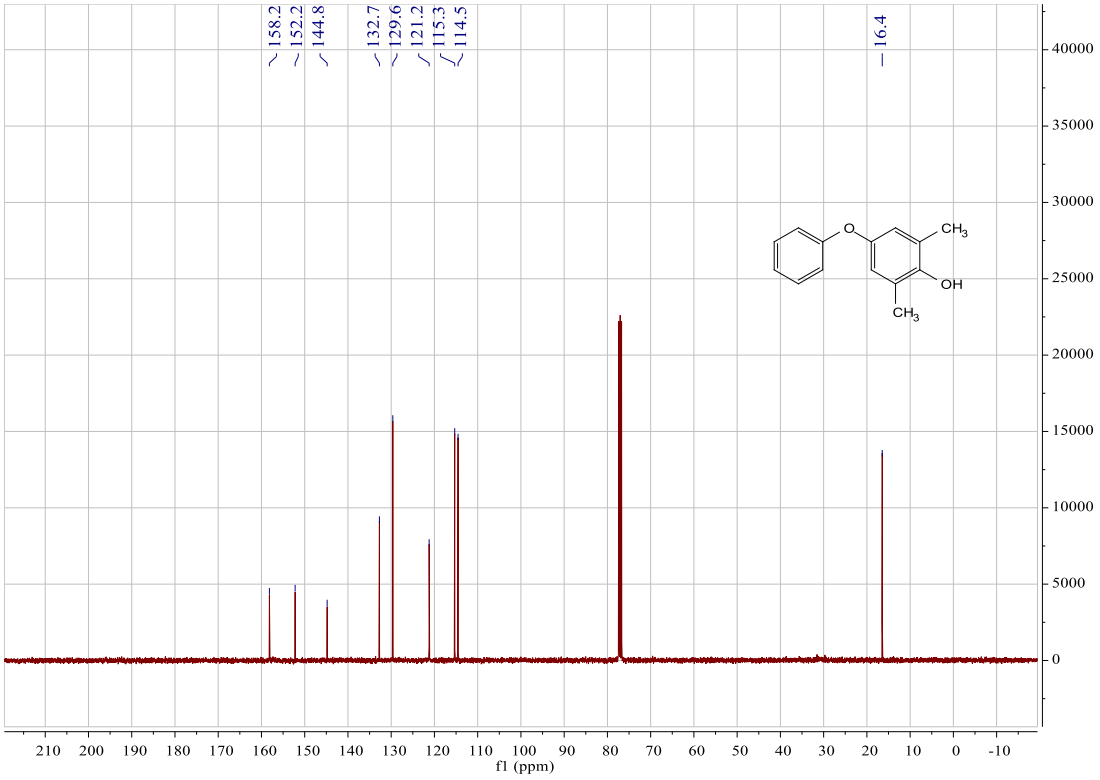
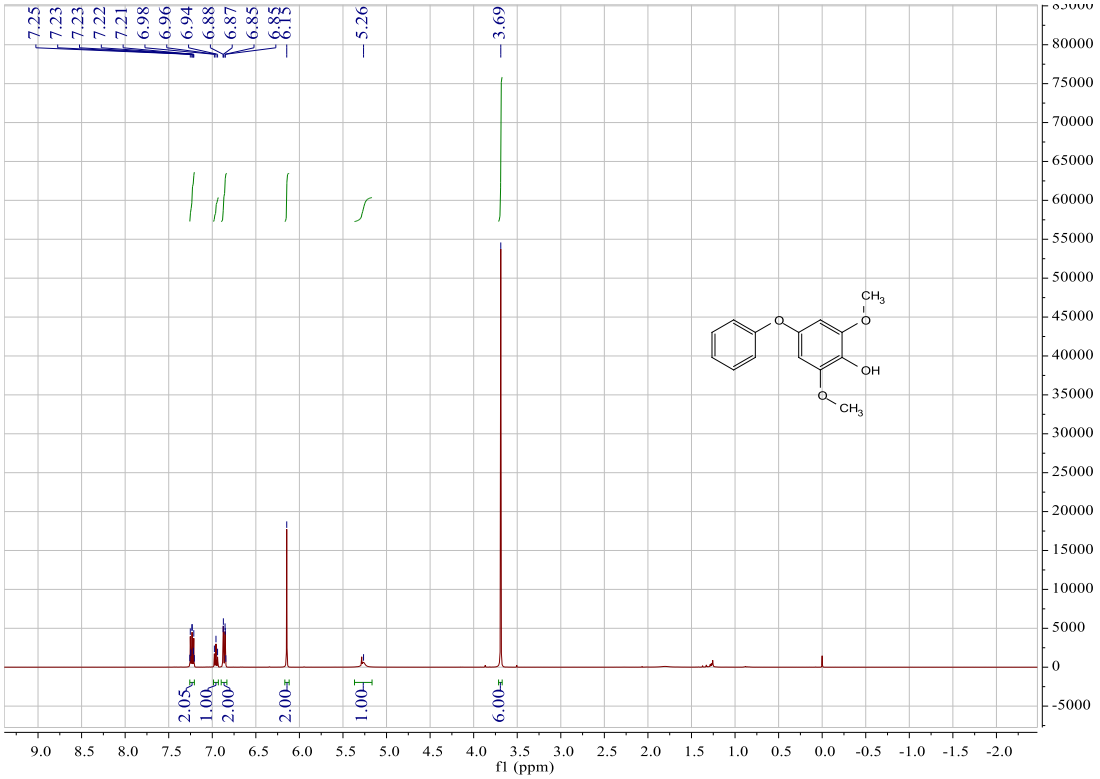


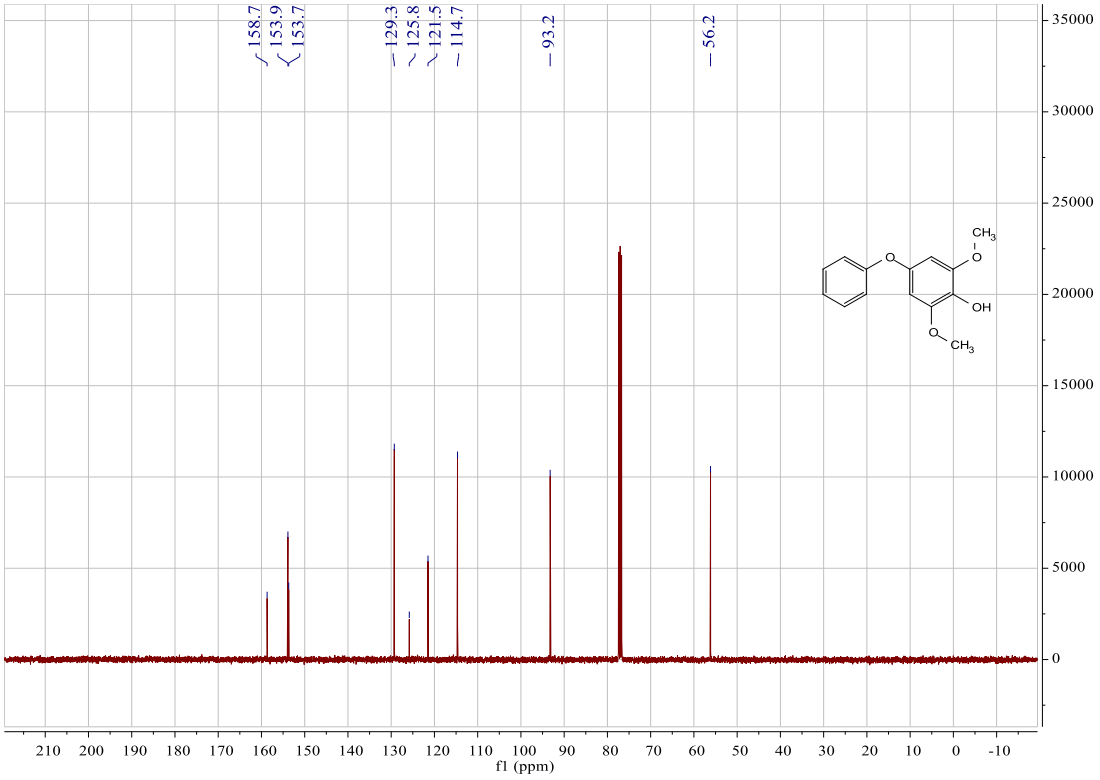
^{13}C NMR of compound **4ea**



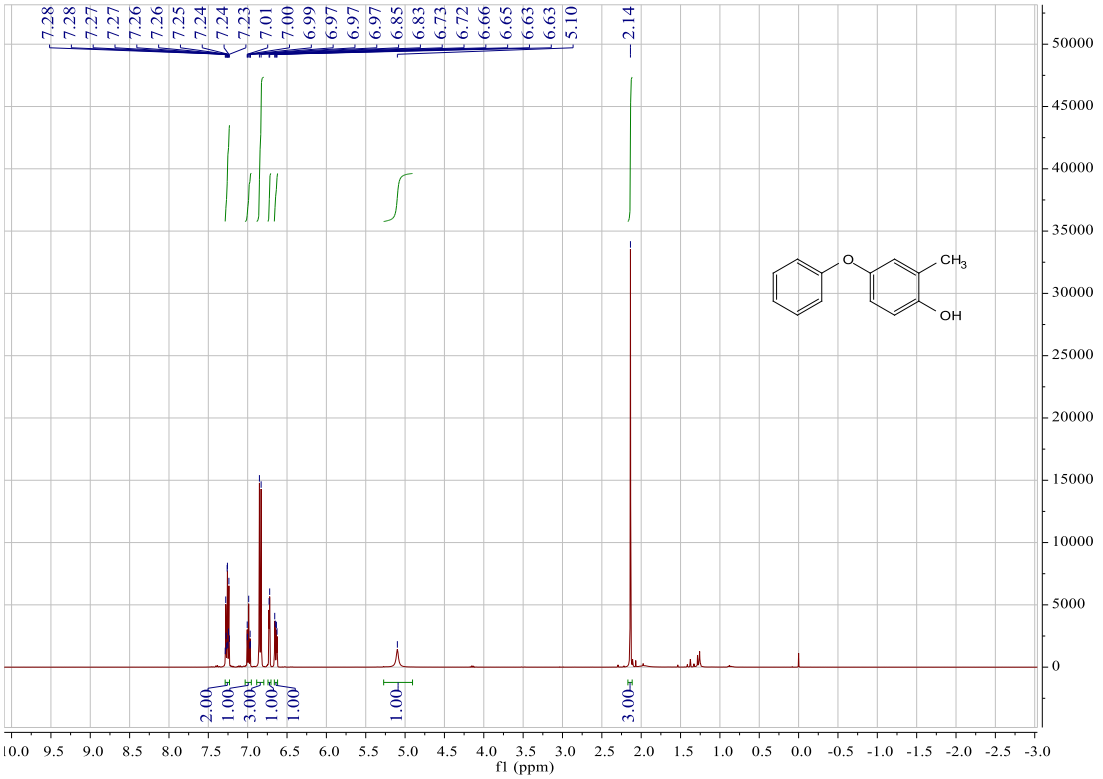
^{1}H NMR of compound **4fa**



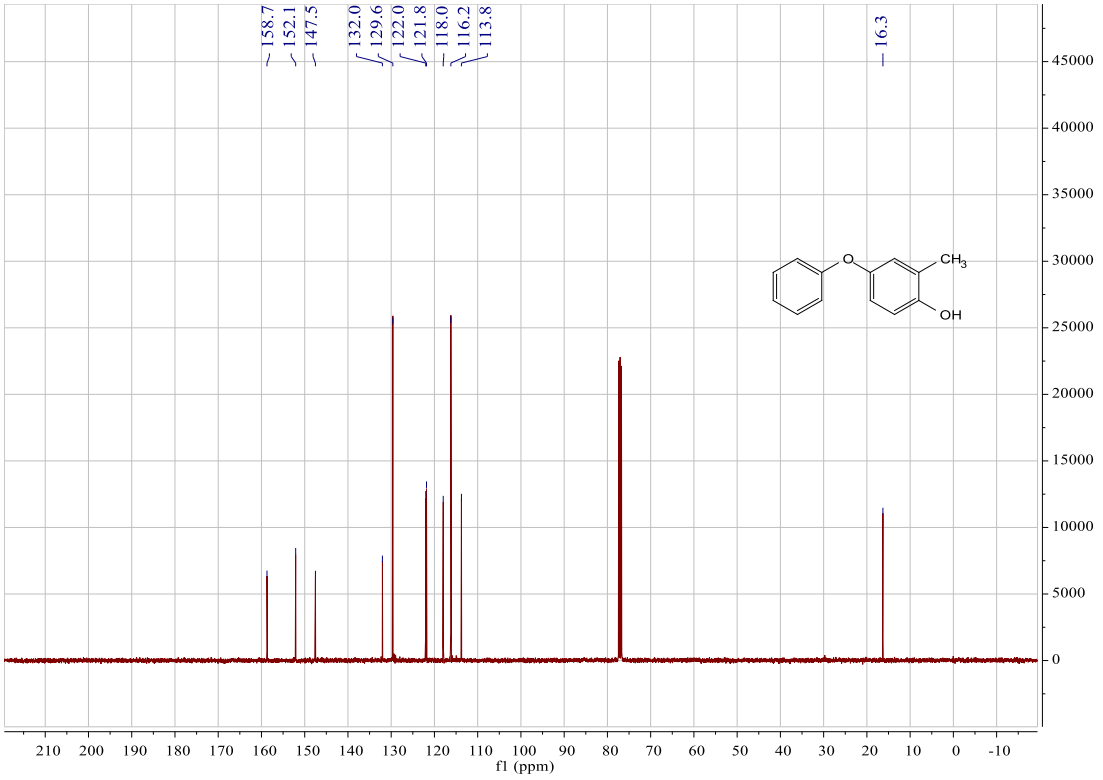
^{13}C NMR of compound **4fa**



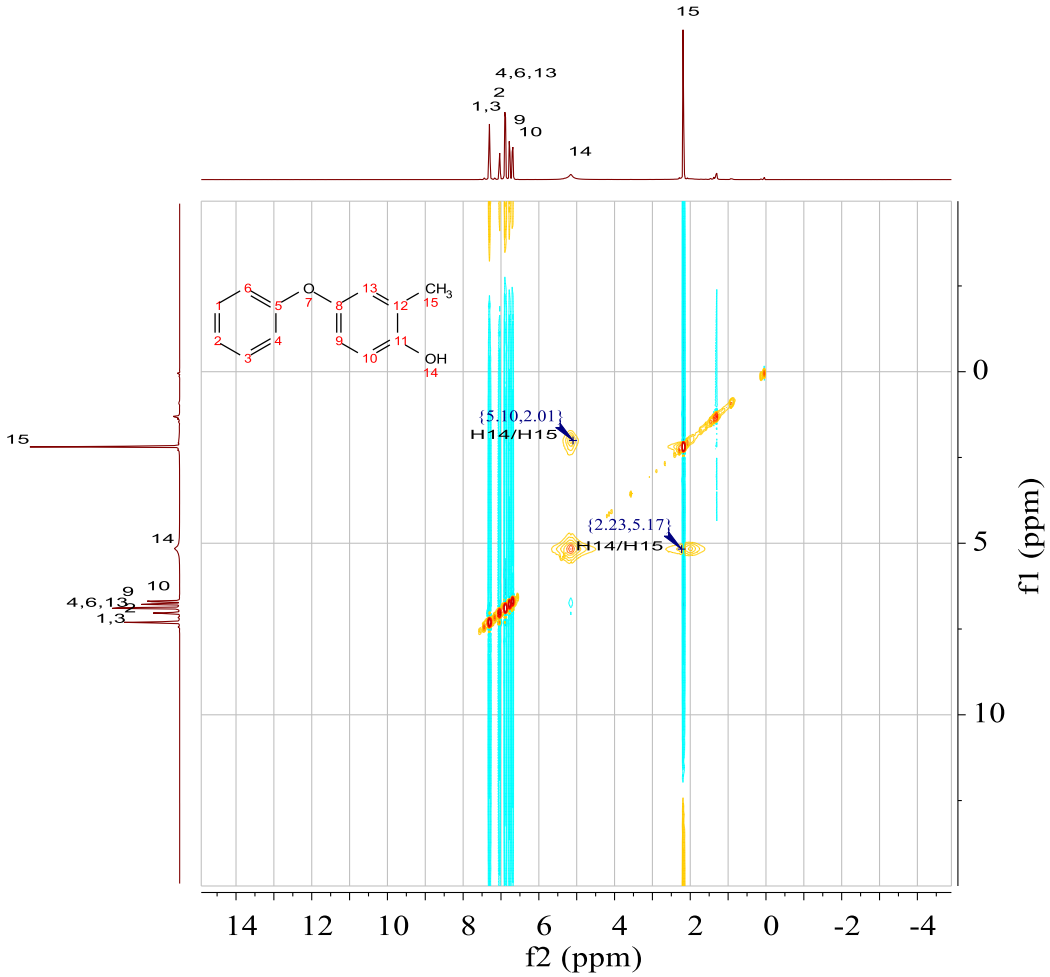
^{1}H NMR of compound **4ga**



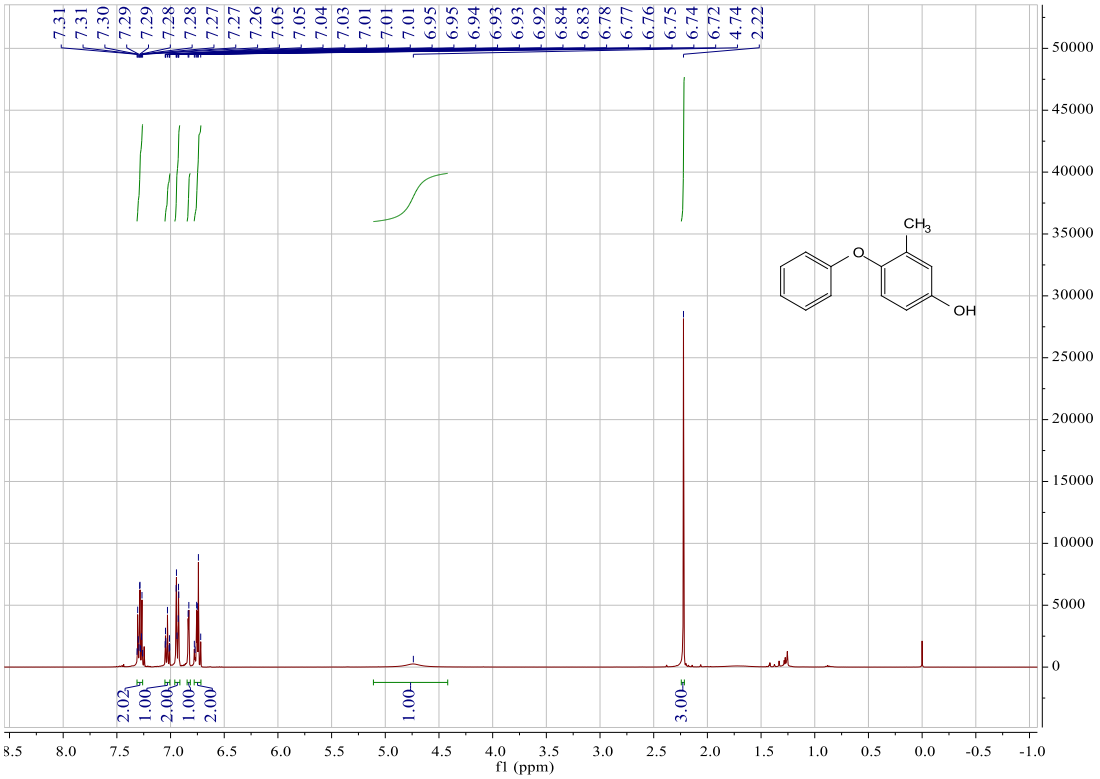
^{13}C NMR of compound **4ga**



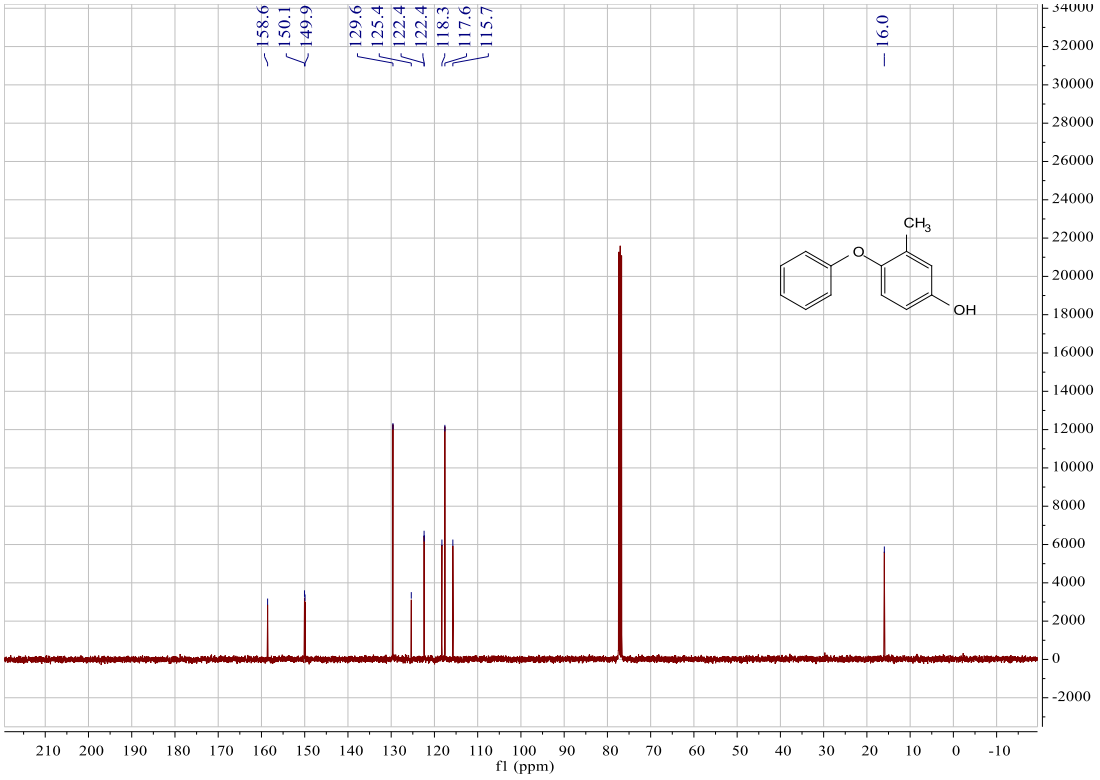
H-H NOEZY of compound **4ga**



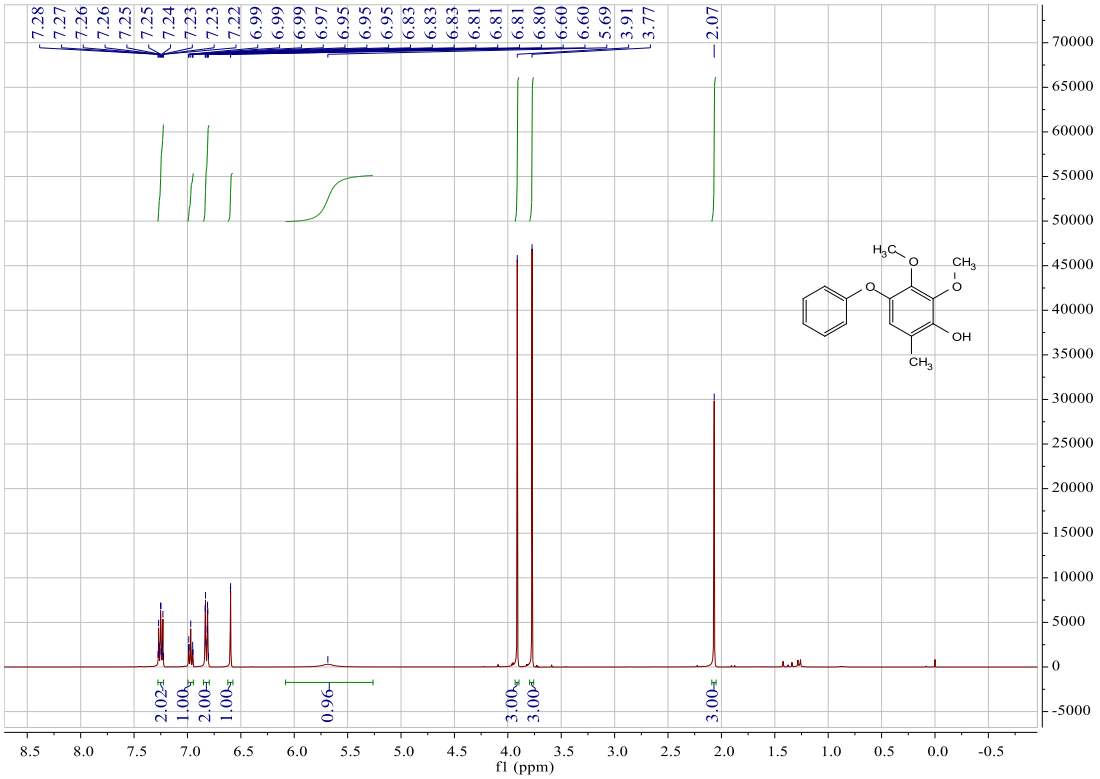
^{1}H NMR of compound **4ga'**



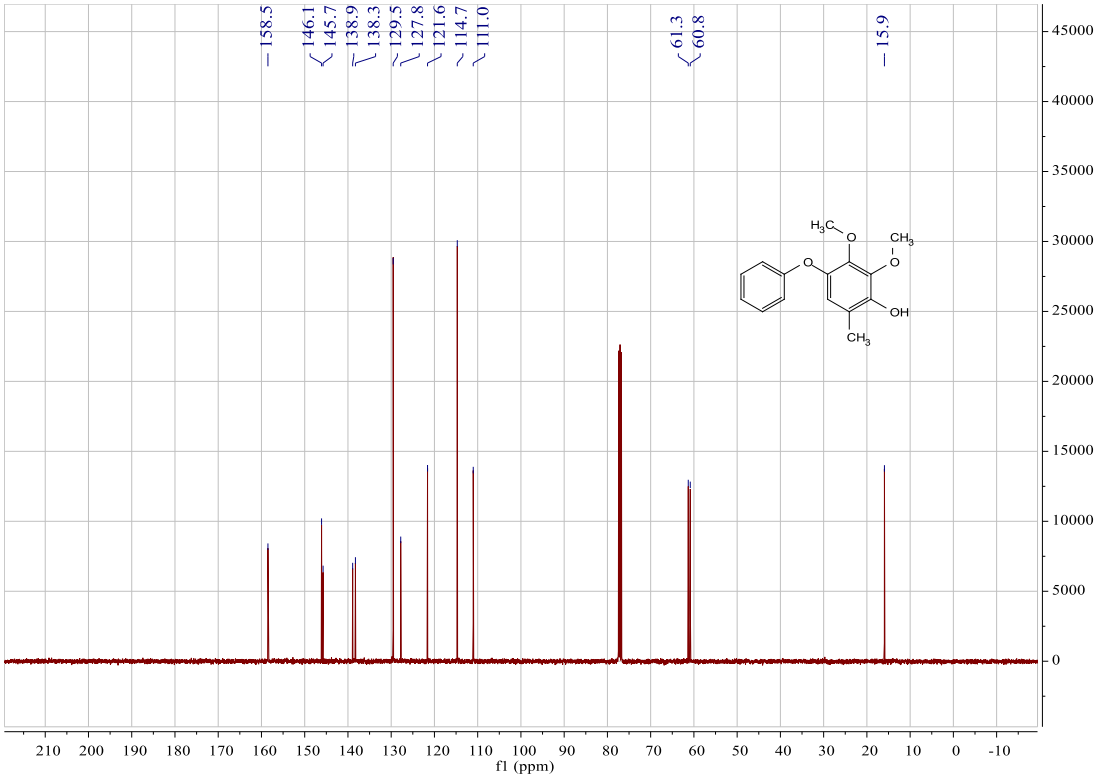
^{13}C NMR of compound **4ga'**



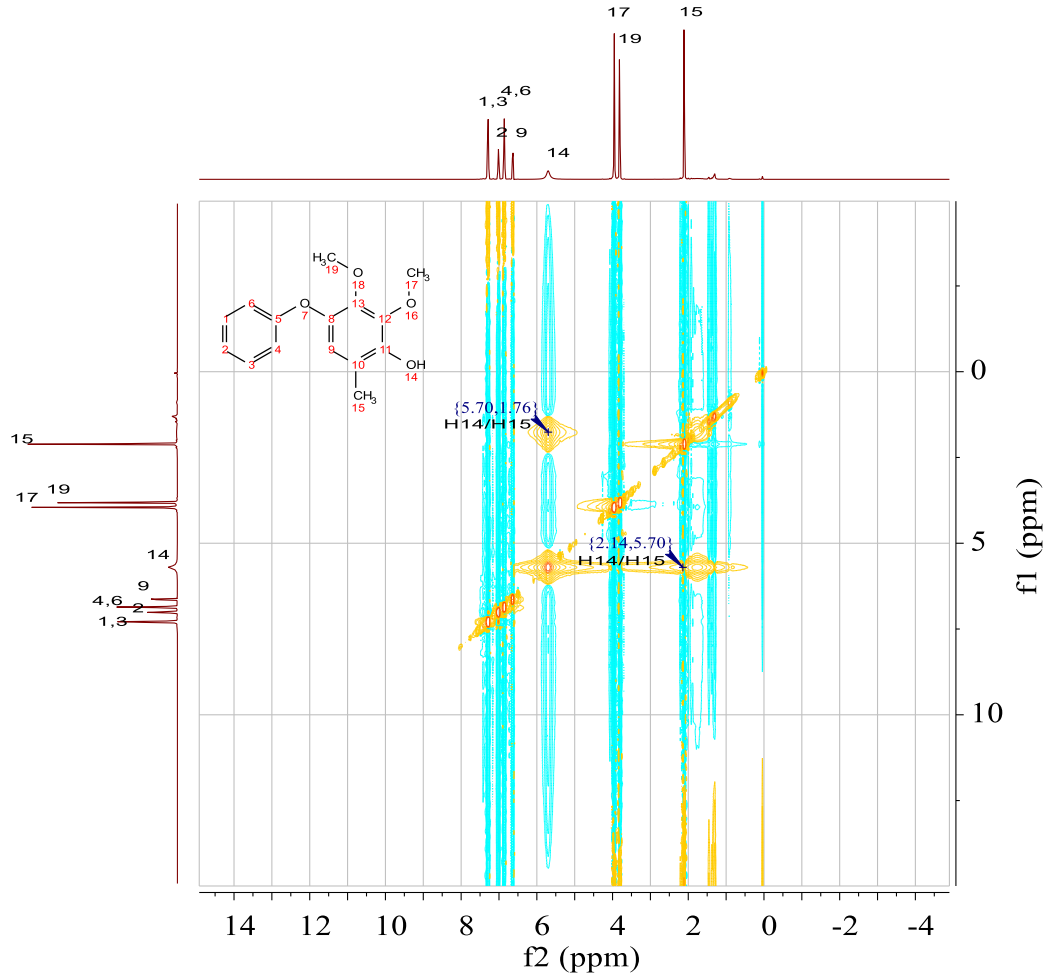
^{1}H NMR of compound **4ha**



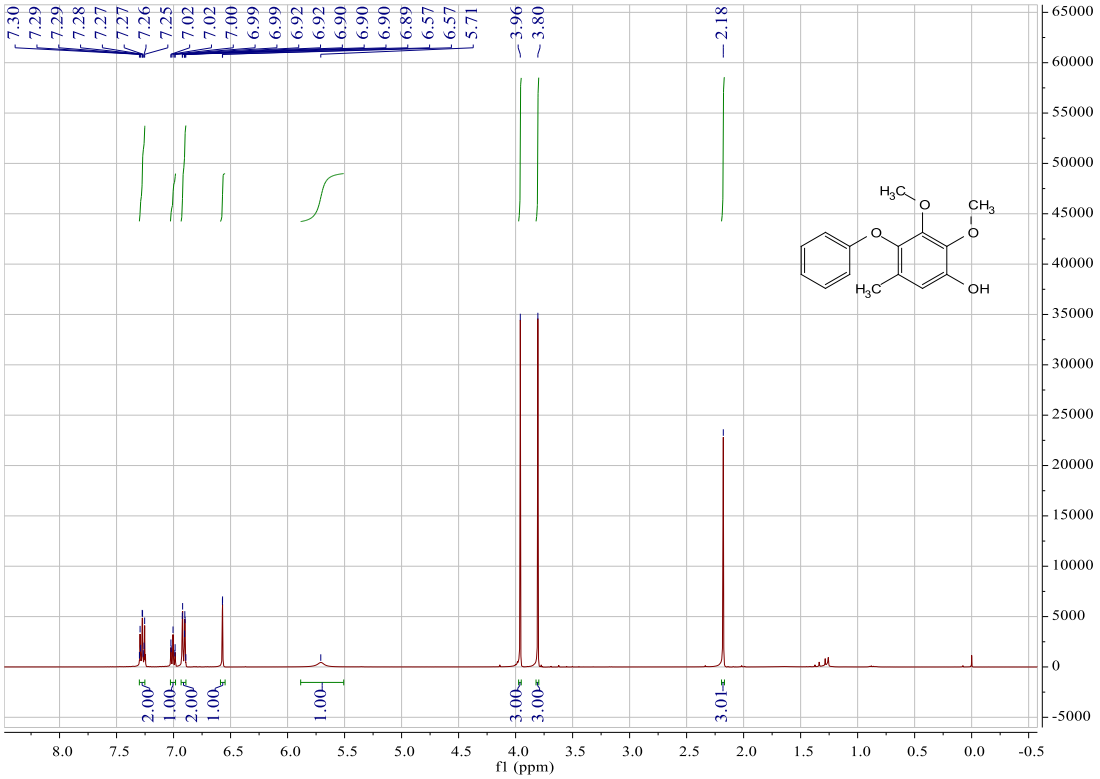
^{13}C NMR of compound **4ha**



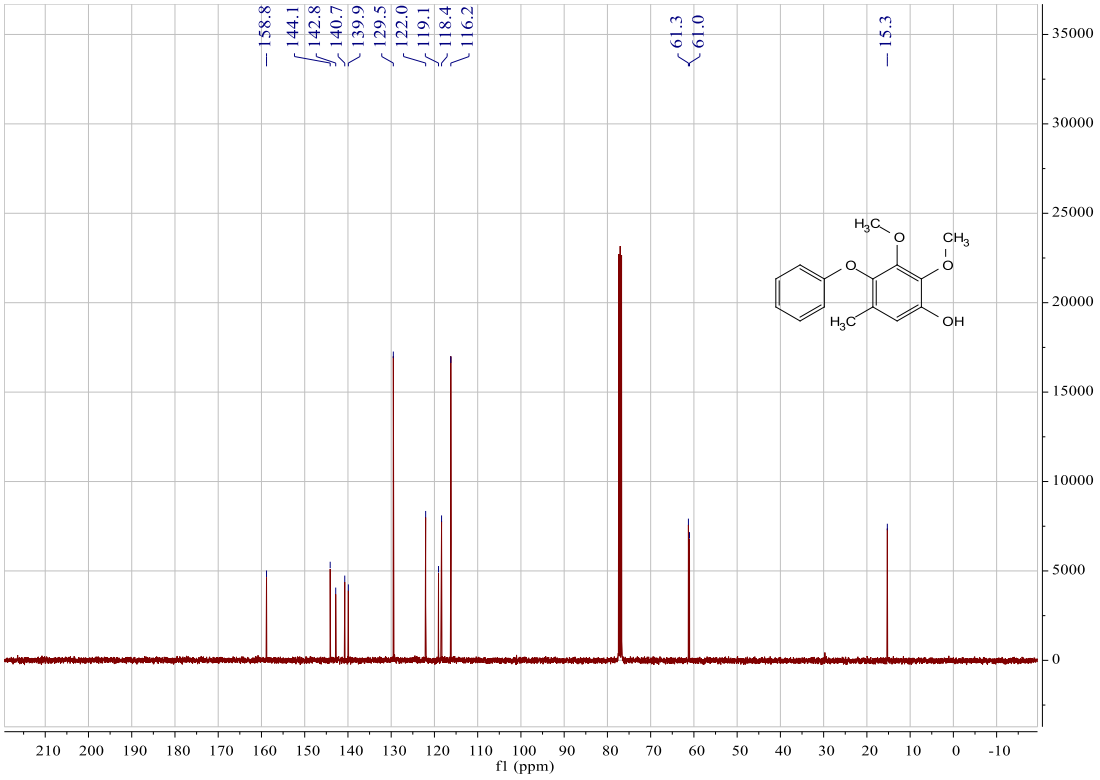
H-H NOEZY of compound **4ha**



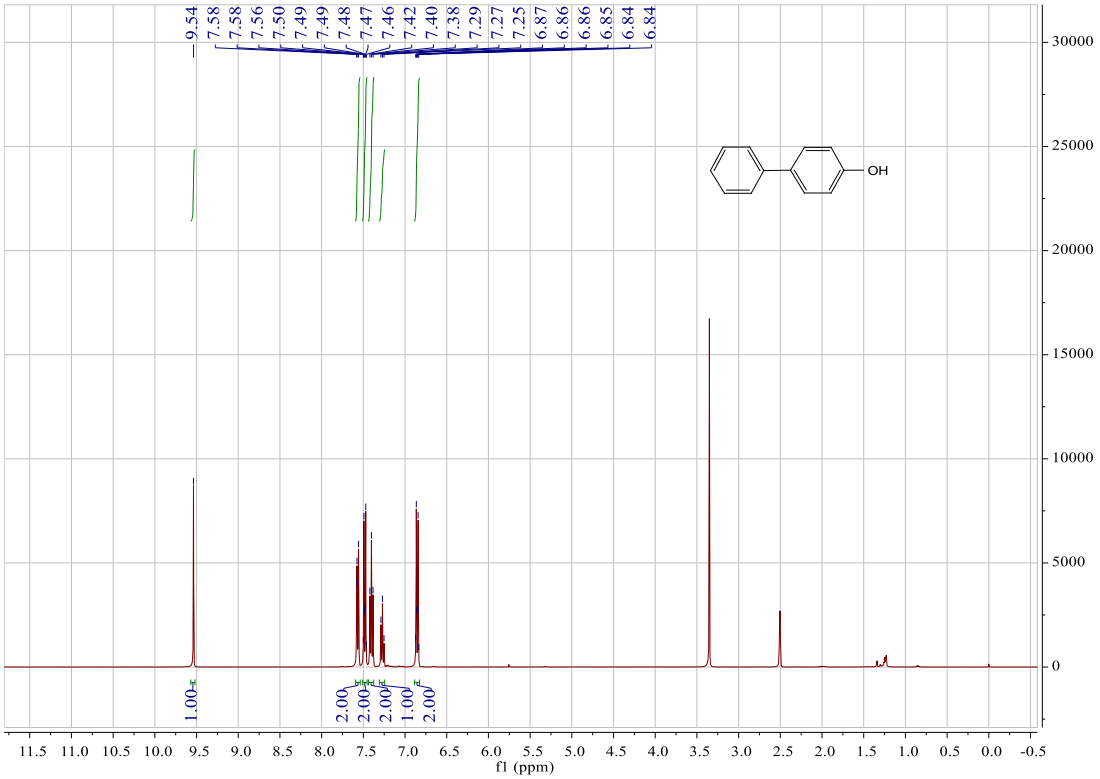
^{1}H NMR of compound **4ha'**



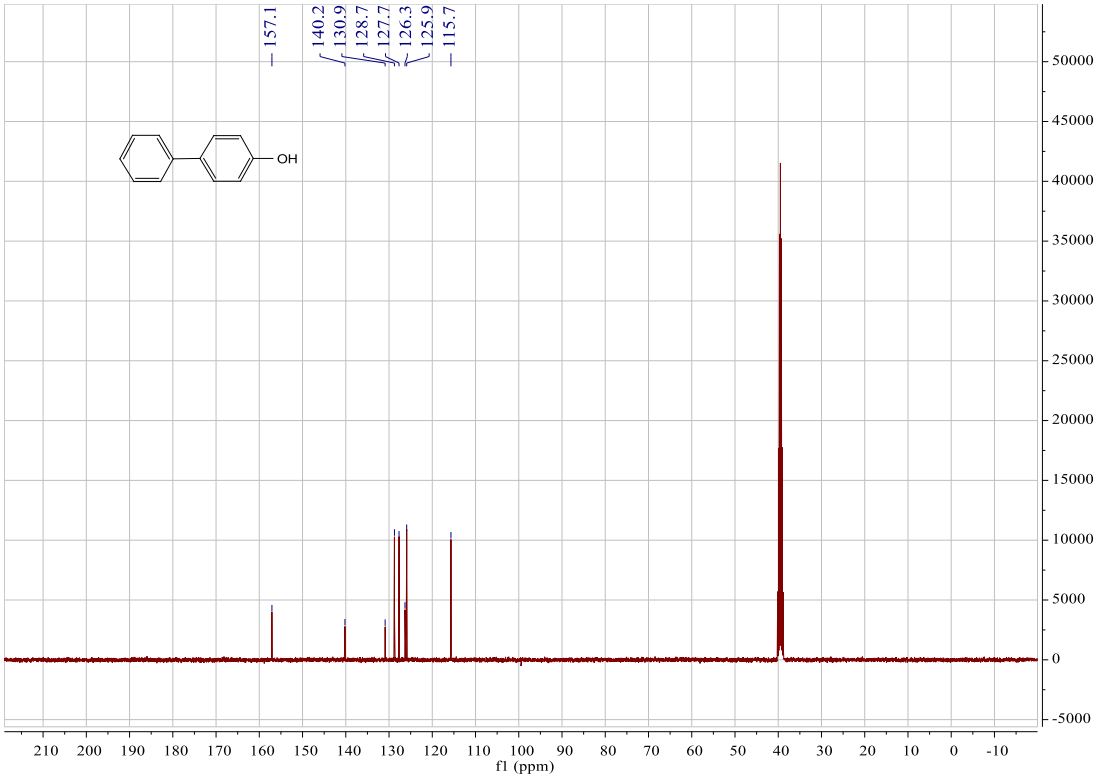
^{13}C NMR of compound **4ha'**



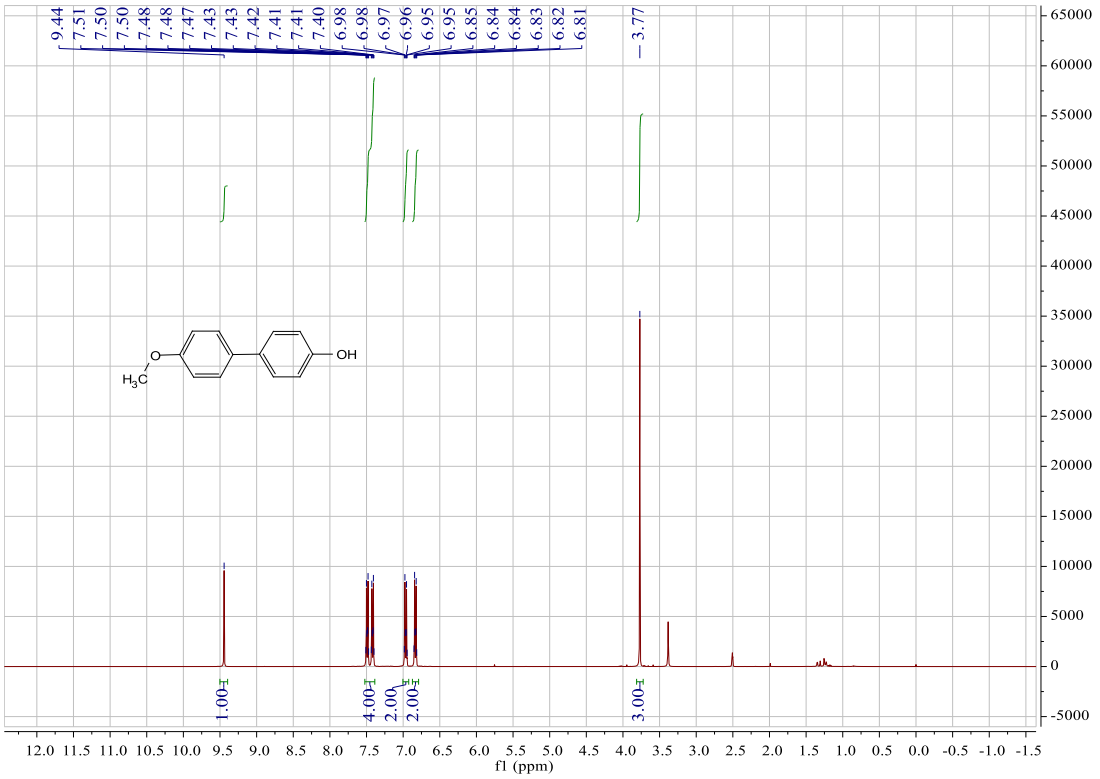
^{1}H NMR of compound **5aa**



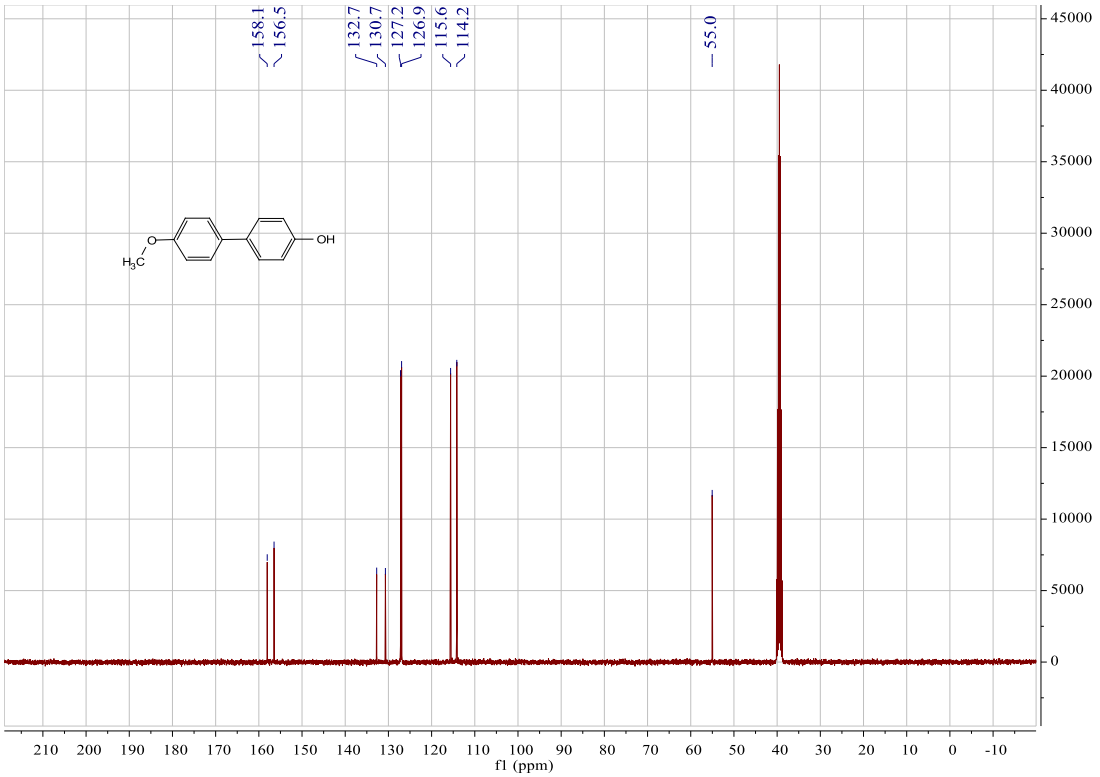
^{13}C NMR of compound **5aa**



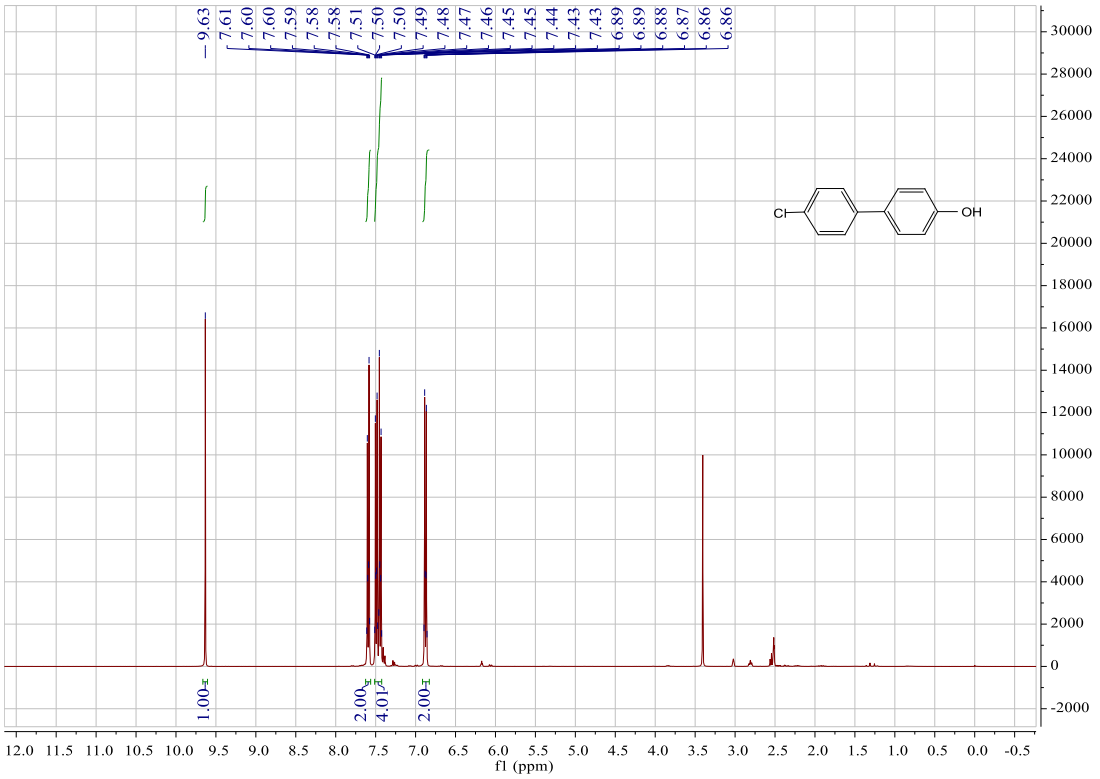
^{1}H NMR of compound **5ab**



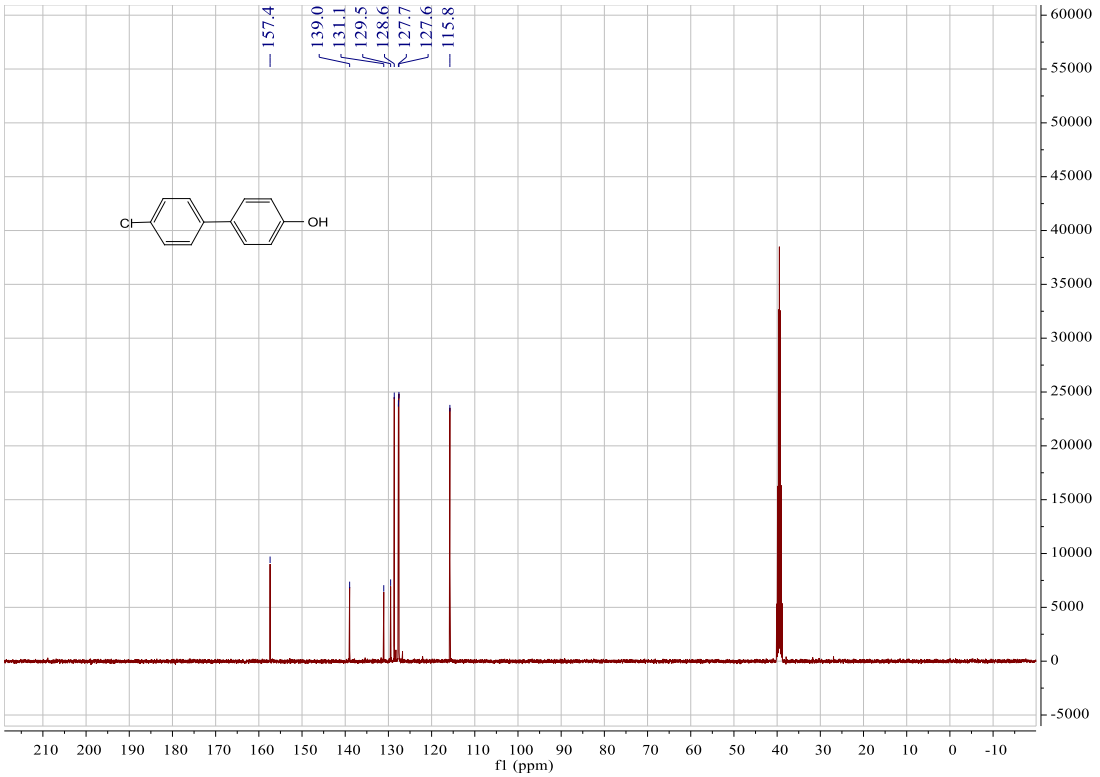
^{13}C NMR of compound **5ab**



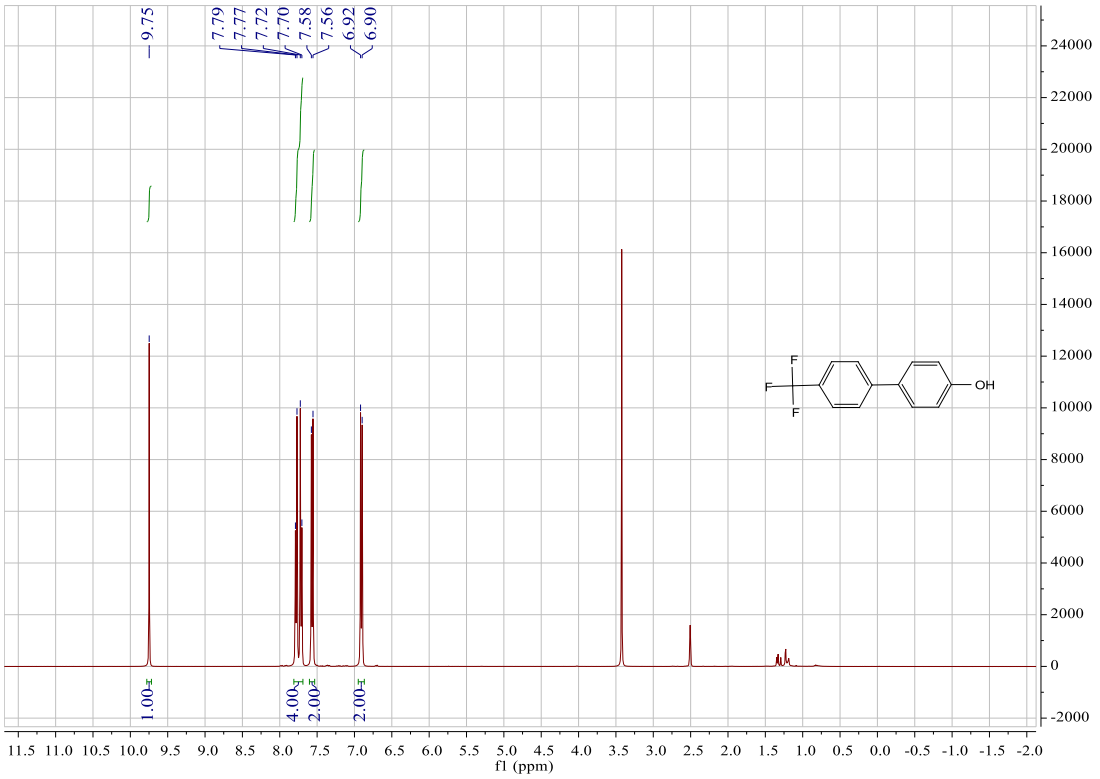
^{1}H NMR of compound **5ac**



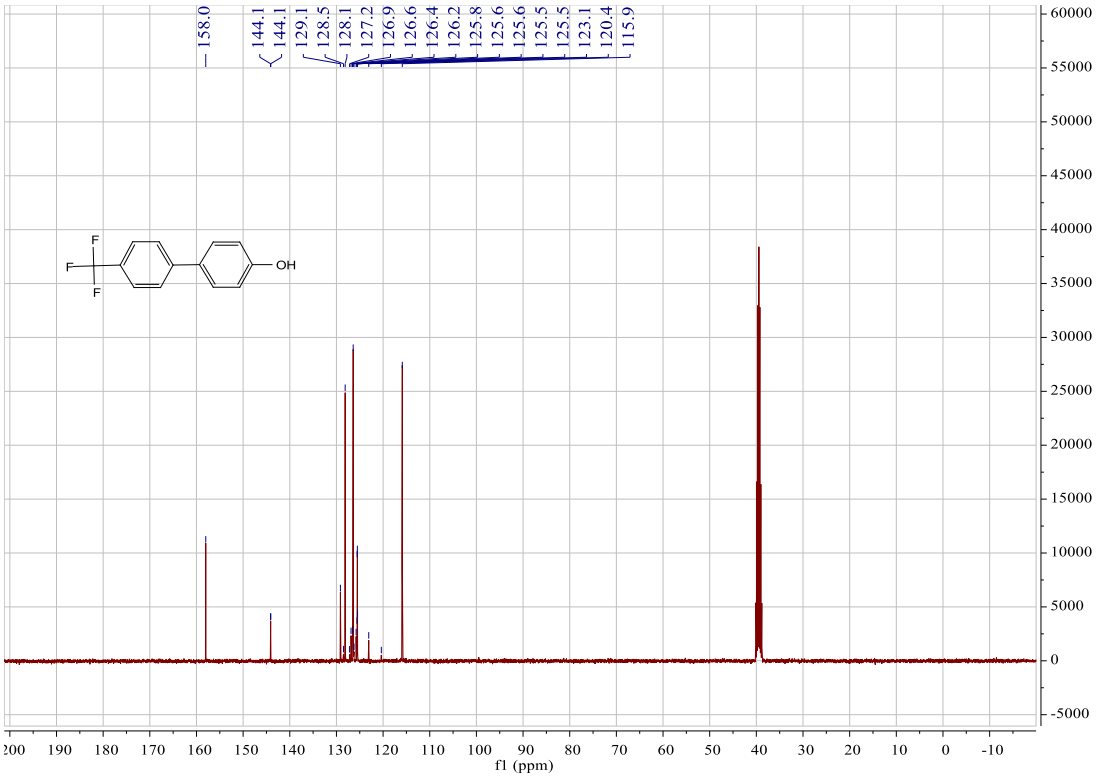
^{13}C NMR of compound **5ac**



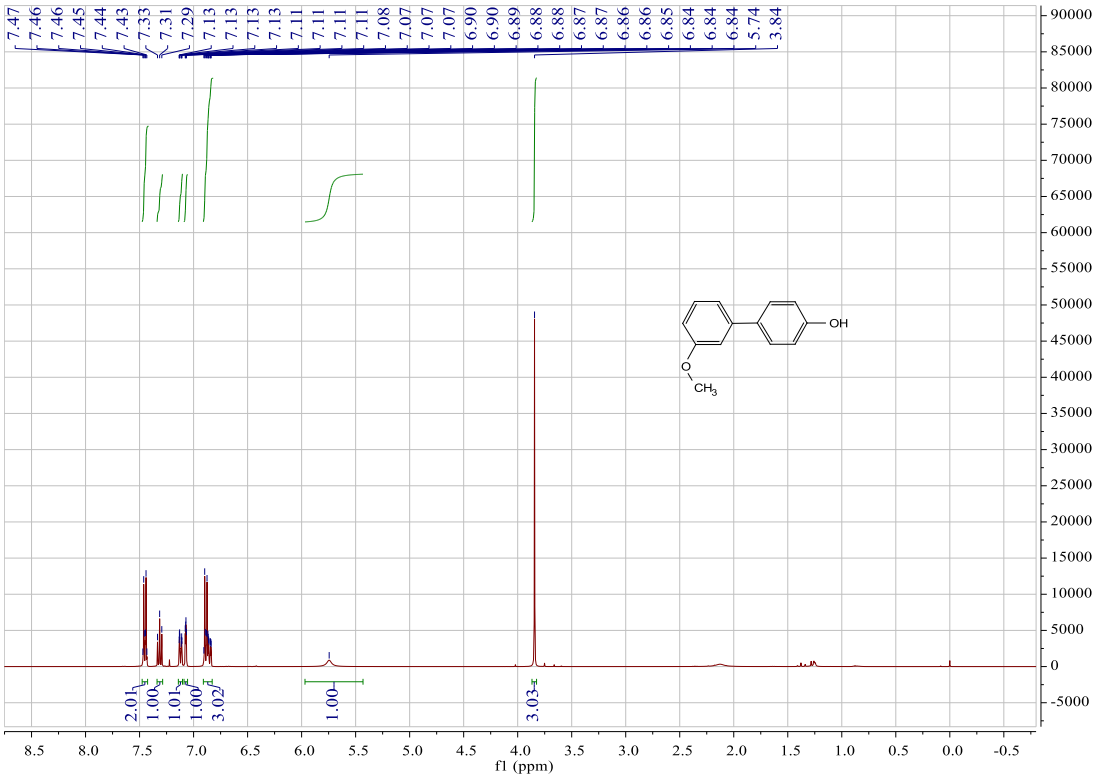
^{1}H NMR of compound **5ad**



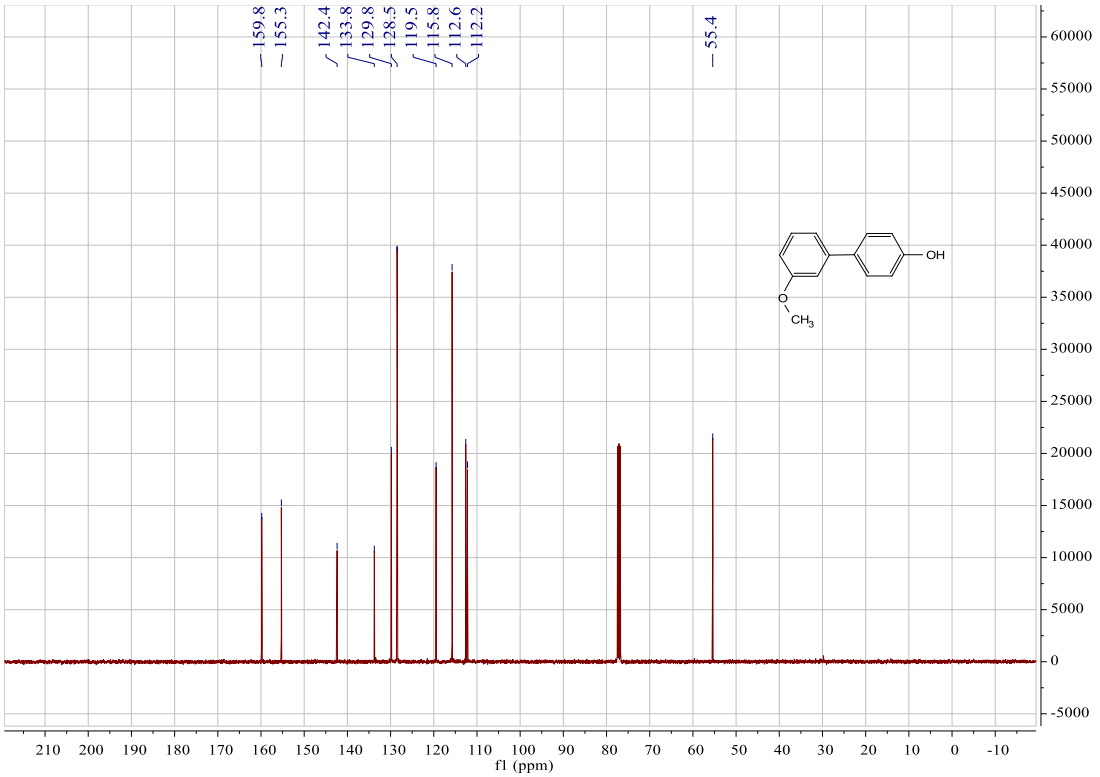
^{13}C NMR of compound **5ad**



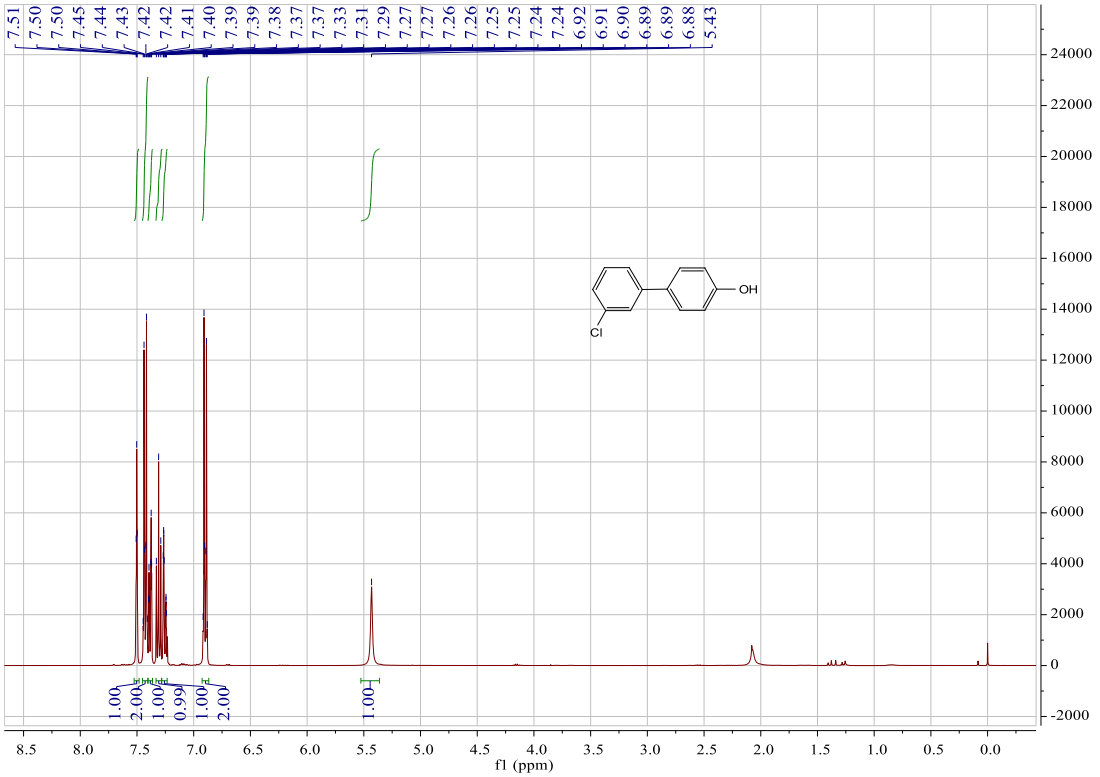
^{1}H NMR of compound **5ae**



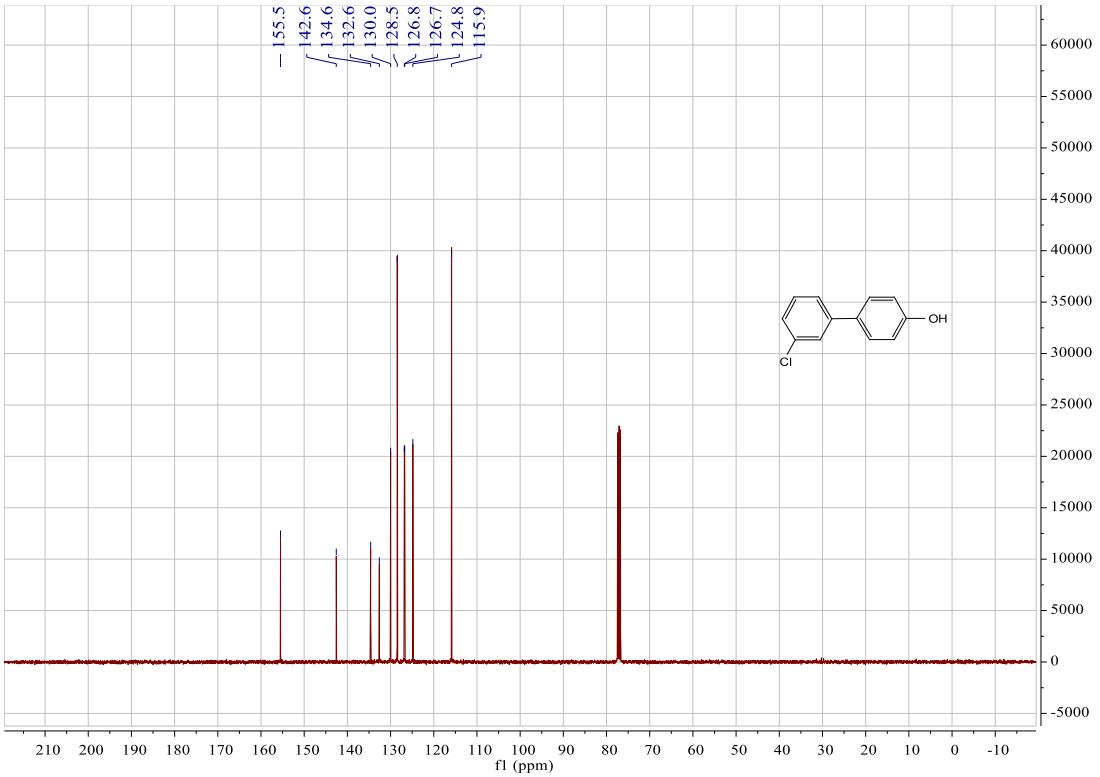
^{13}C NMR of compound **5ae**



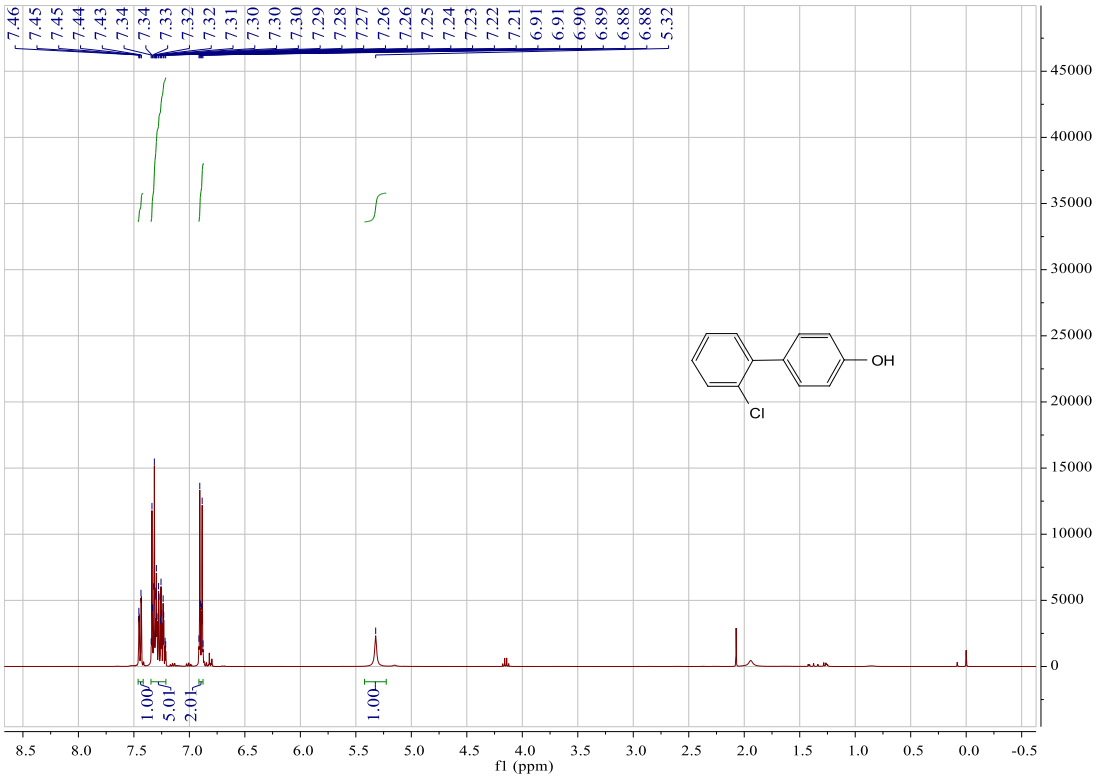
^{1}H NMR of compound **5af**



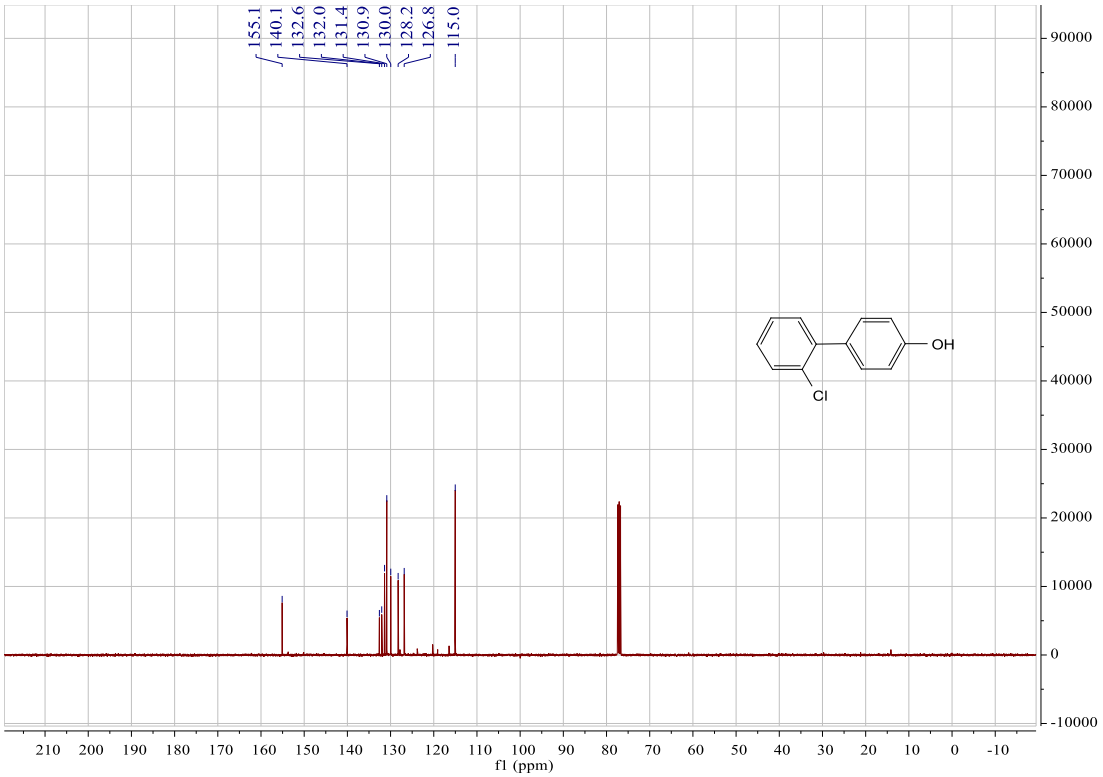
^{13}C NMR of compound **5af**



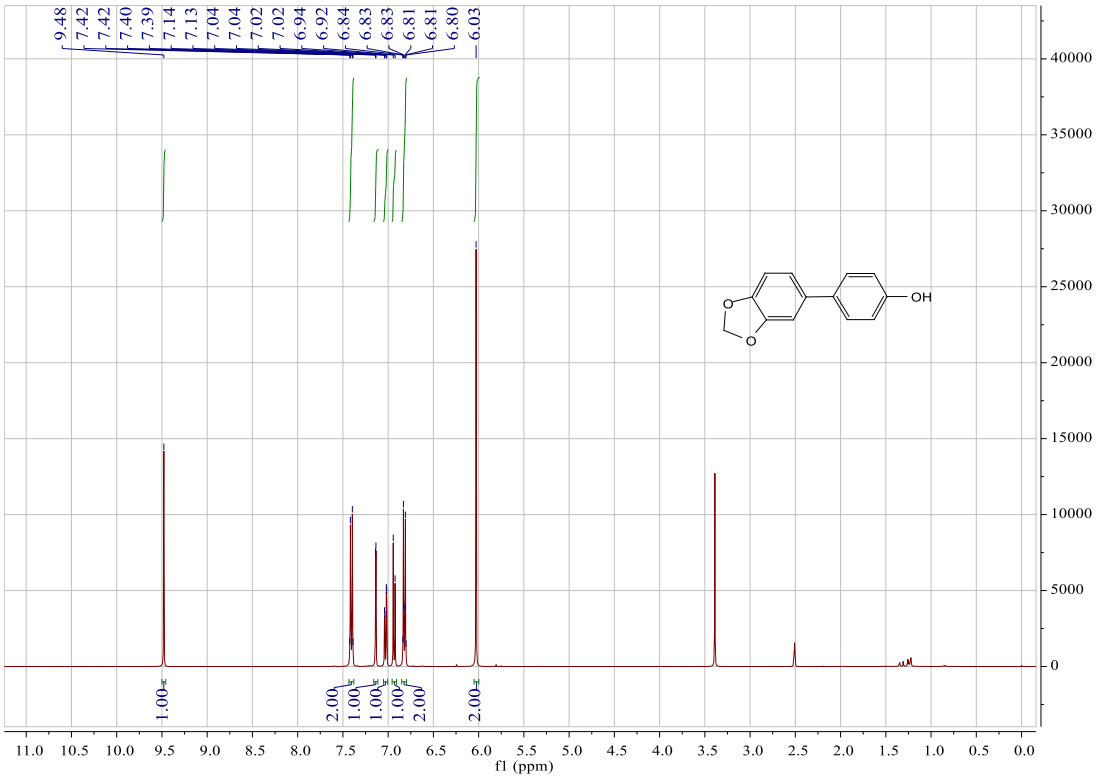
^{1}H NMR of compound **5ag**



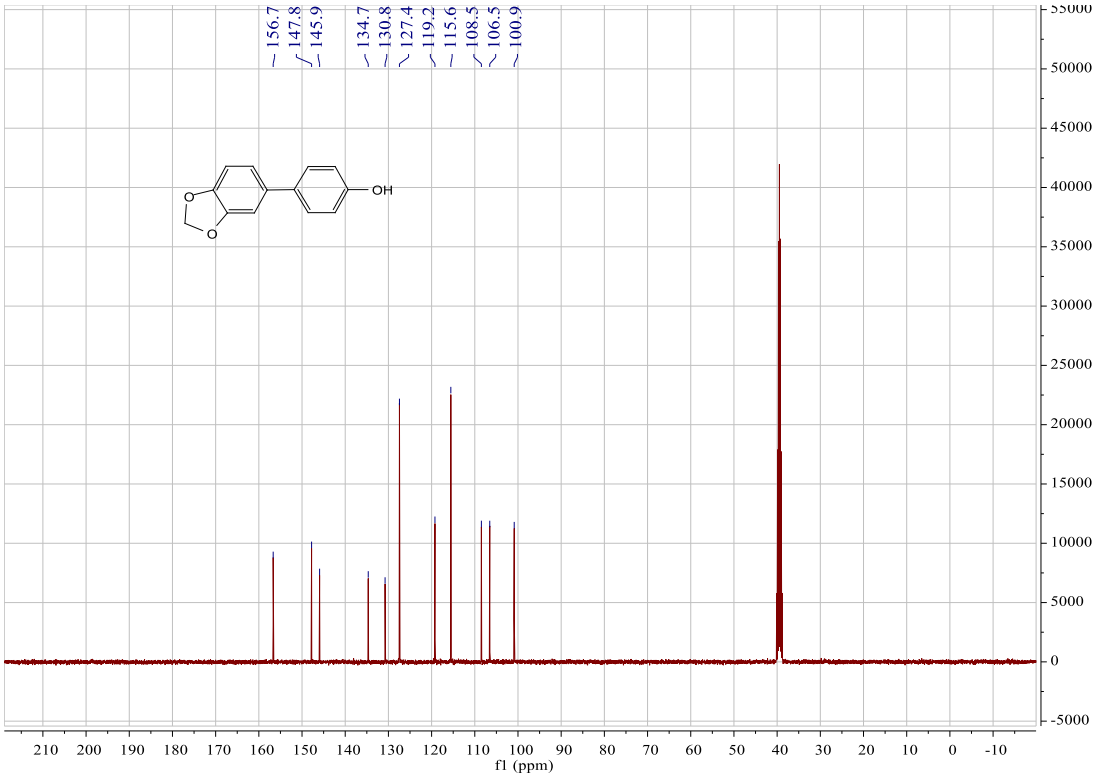
^{13}C NMR of compound **5ag**



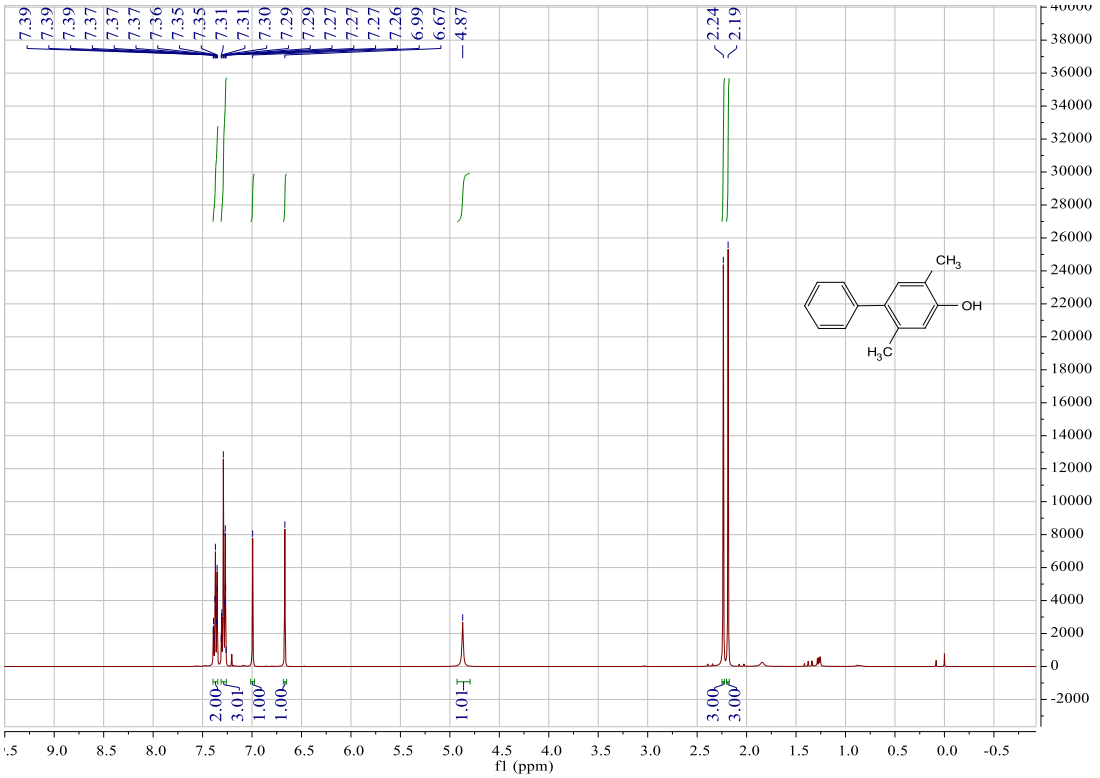
^{1}H NMR of compound **5ah**



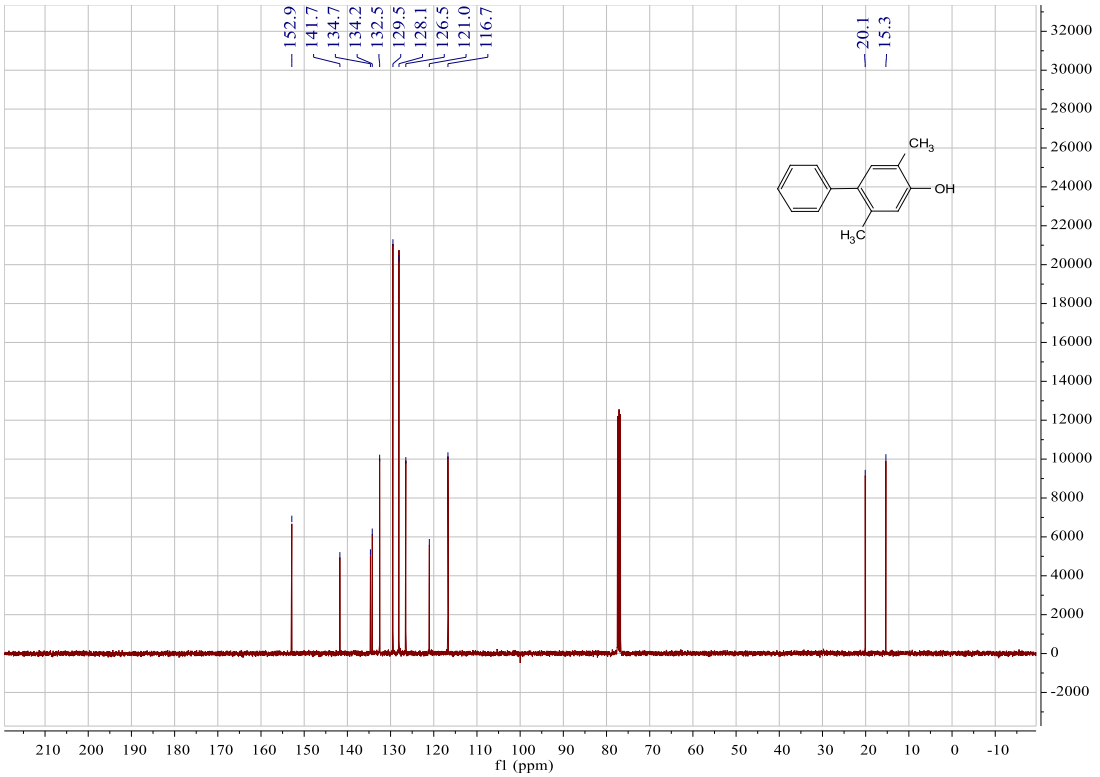
^{13}C NMR of compound **5ah**



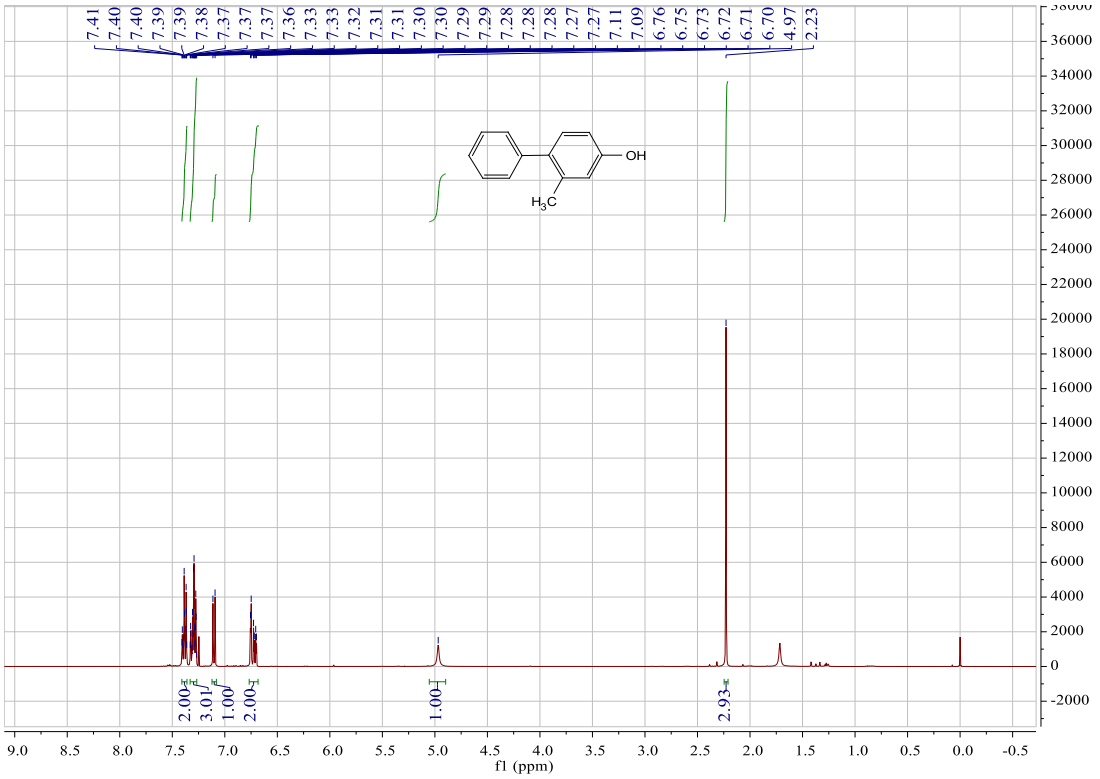
^{1}H NMR of compound **5ba**



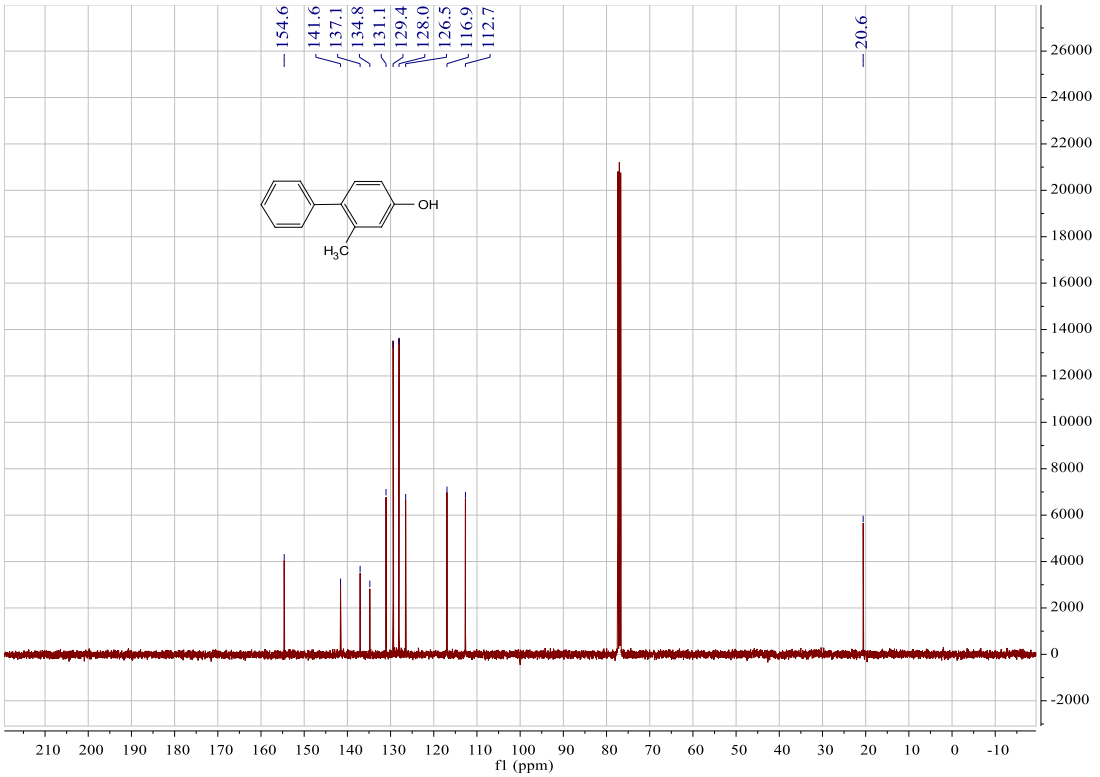
^{13}C NMR of compound **5ba**



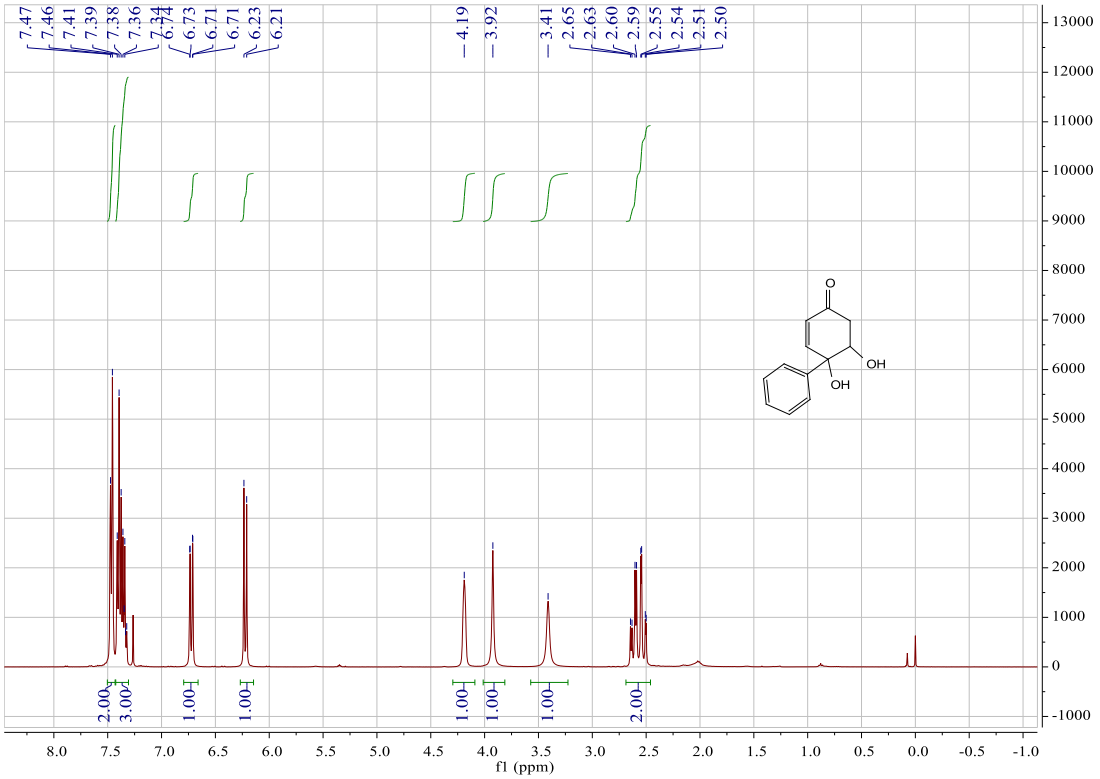
^{1}H NMR of compound **5ca**



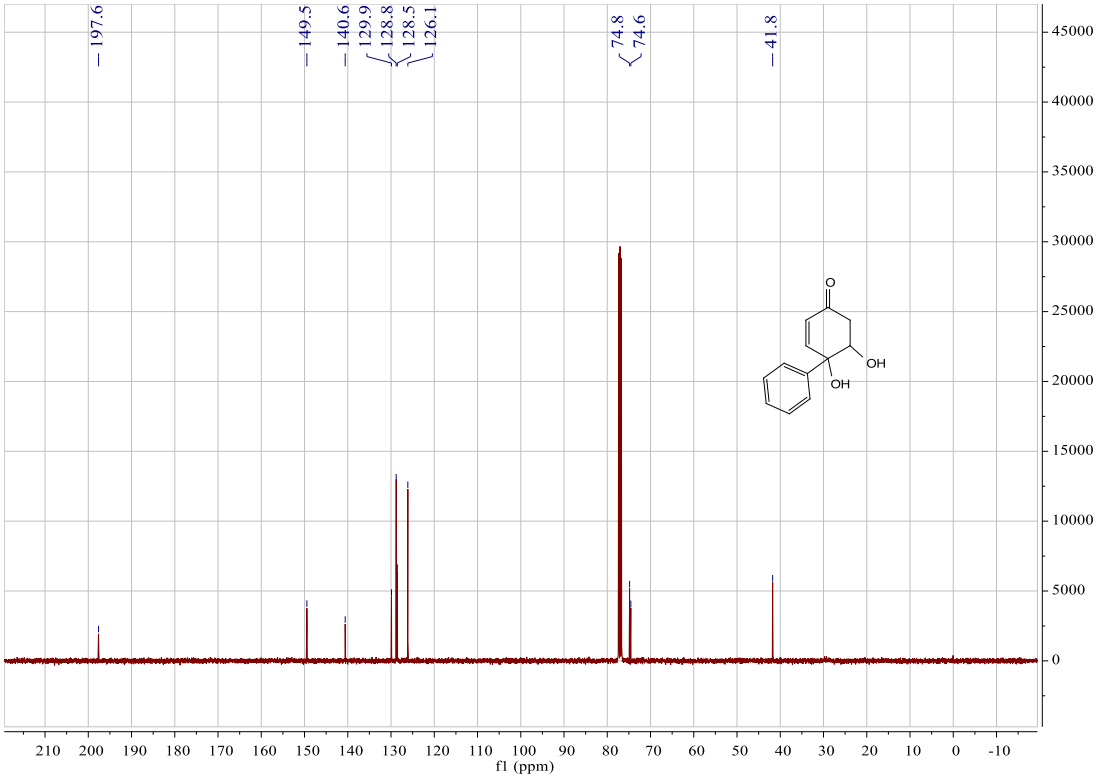
^{13}C NMR of compound **5ca**



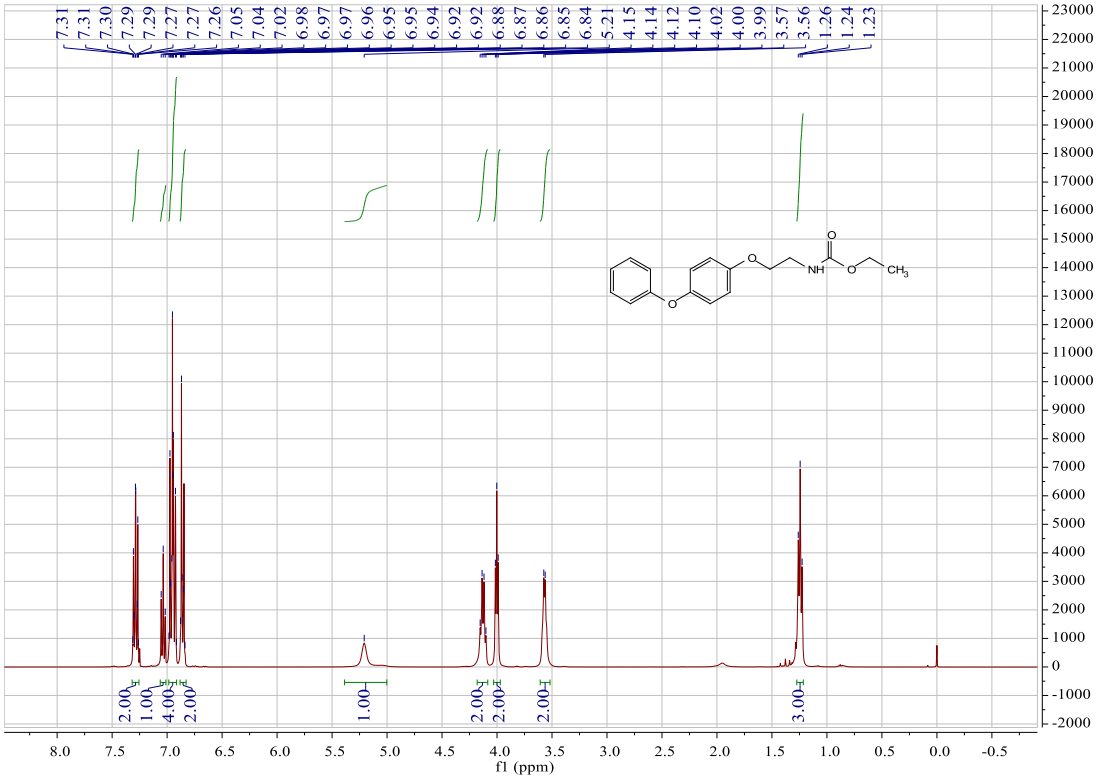
^{1}H NMR of compound **7**



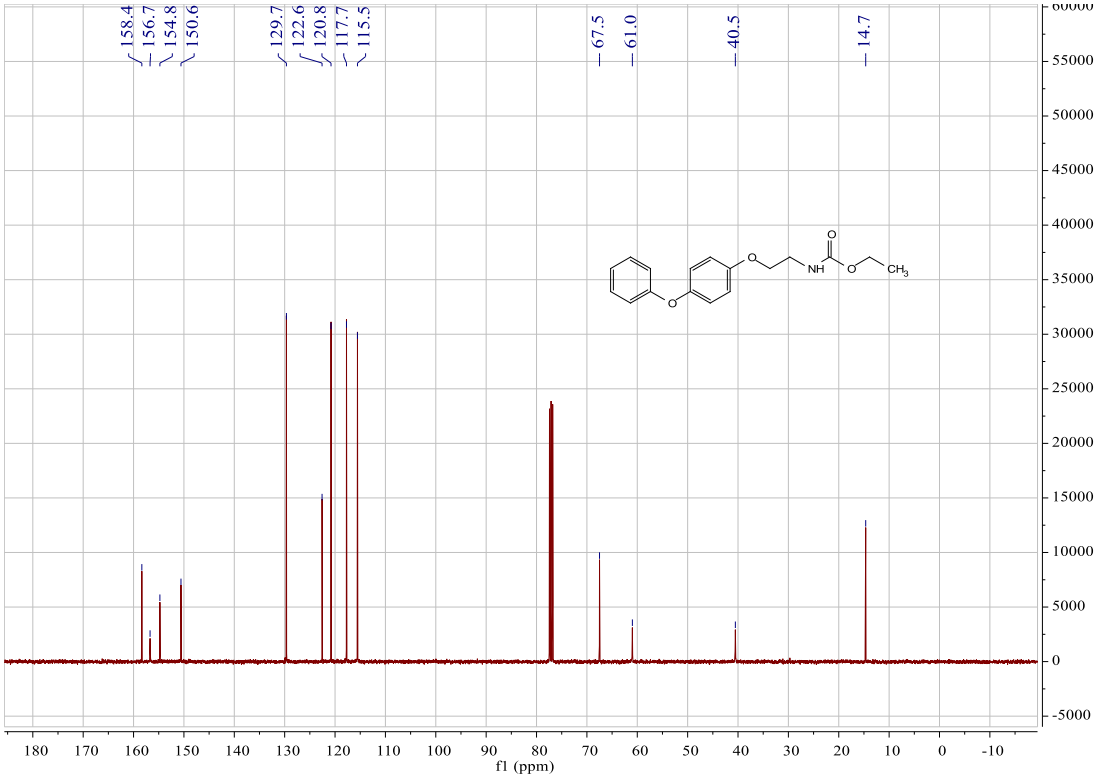
^{13}C NMR of compound **7**



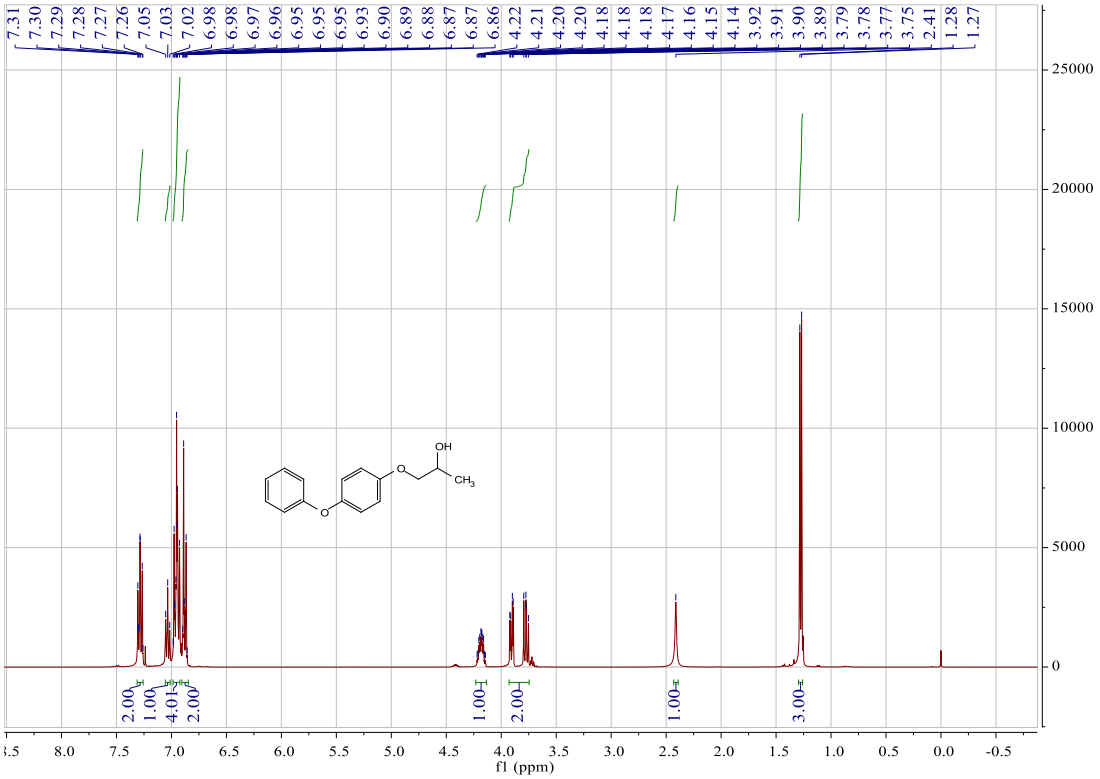
^{1}H NMR of compound **Fenoxycard**



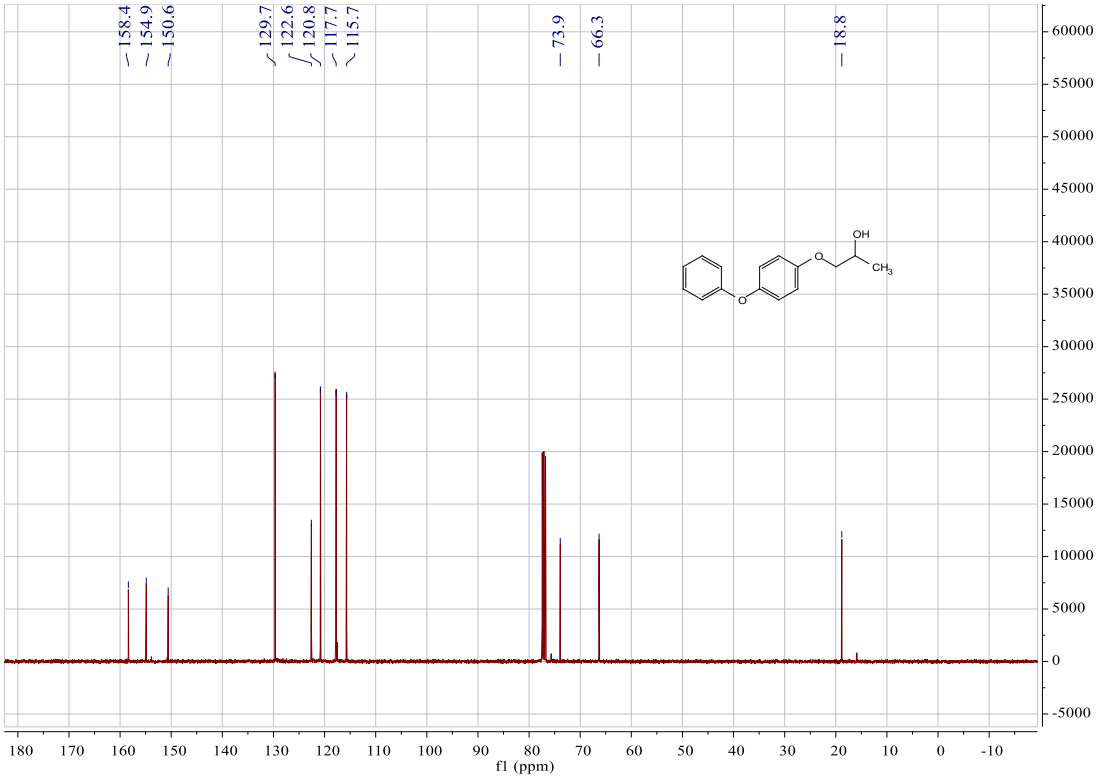
^{13}C NMR of compound **Fenoxycard**



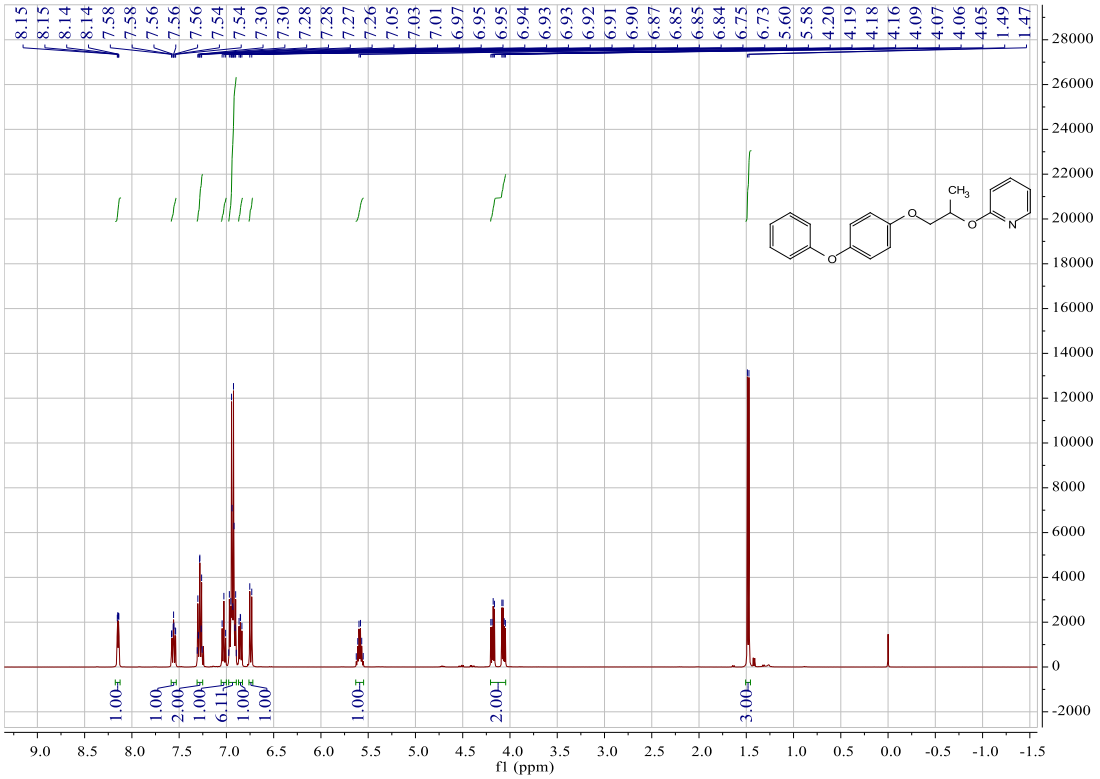
^{1}H NMR of compound **8**



^{13}C NMR of compound **8**



^{1}H NMR of compound **Pyriproxyfen**



^{13}C NMR of compound **Pyriproxyfen**