Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium Catalyzed C_{sp2}-H Activation for Direct Aryl Hydroxylation: Unprecedented Role of 1,4-Dioxane as Source of Hydroxyl Radical

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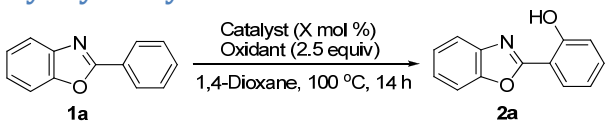
1. The standardisation of various reaction parameters such as the effect of catalyst, oxidant, solvent, reaction temperature and time etc. on the aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.

Table 1A. The effect of various Pd-compounds and oxidants on the aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.[a]

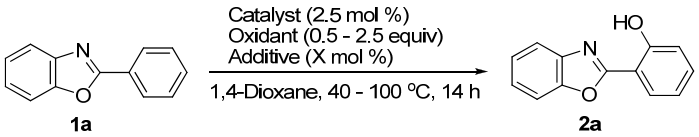


Entry	Catalyst (X)	Oxidant	Yield (%)[b,c]
1	$Pd(OAc)_2$ (15)	Oxone	56
2	$Pd(acac)_2$ (15)	Oxone	49
3	$Pd(TFA)_2$ (15)	Oxone	41
4	$Pd(Piv)_2$ (15)	Oxone	45
5	$PdCl_2$ (15)	Oxone	trace
6	Na_2PdCl_4 (15)	Oxone	trace
7	$[PdCl_2(PPh_3)_2]$ (15)	Oxone	18
8	$Pd(PPh_3)_4$ (15)	Oxone	19
9	$Pd(dba)_2$ (15)	Oxone	33
10	$Pd_2(dba)_3$ (15)	Oxone	30
11	Pd/C (15)	Oxone	trace
12	$Pd(OAc)_2$ (10)	Oxone	54
13	$Pd(OAc)_2$ (5)	Oxone	50
14	$Pd(OAc)_2$ (2.5)	Oxone	49
15	$Pd(OAc)_2$ (1)	Oxone	42
16	$Pd(OAc)_2$ (0.5)	Oxone	trace
17	$Pd(OAc)_2$ (0.1)	Oxone	0
18	None	Oxone	0
19	$Pd(OAc)_2$ (2.5)	TBHP	0
20	$Pd(OAc)_2$ (2.5)	H_2O_2	0
21	$Pd(OAc)_2$ (2.5)	$(PhCO_2)_2$	0
22	$Pd(OAc)_2$ (2.5)	*m*CPBA	21
23	$Pd(OAc)_2$ (2.5)	BQ	0
24	$Pd(OAc)_2$ (2.5)	BQ + O_2	0[d]
25	$Pd(OAc)_2$ (2.5)	$NaIO_4$	0
26	$Pd(OAc)_2$ (2.5)	HIO_4	0
27	$Pd(OAc)_2$ (2.5)	$Ce(SO_4)_2$	0
28	$Pd(OAc)_2$ (2.5)	CAN	0
29	$Pd(OAc)_2$ (2.5)	$PhI(OAc)_2$	30
30	$Pd(OAc)_2$ (2.5)	$PhI(TFA)_2$	31
31	**$Pd(OAc)_2$ (2.5)**	**$Na_2S_2O_8$**	**63**
32	$Pd(TFA)_2$ (2.5)	$Na_2S_2O_8$	50
33	$Pd(TFA)_2$ (2.5)	$Na_2S_2O_8$	12[e]
34	$Pd(TFA)_2$ (2.5)	$Na_2S_2O_8$	0[f]

35	$Pd(TFA)_2$ (2.5)	$Na_2S_2O_8$	0[f]
36	$Pd(acac)_2$ (2.5)	$Na_2S_2O_8$	60
37	$Pd(acac)_2$ (2.5)	$Na_2S_2O_8$	0[e]
38	$Pd(acac)_2$ (2.5)	$Na_2S_2O_8$	0[f]
39	$Pd(dba)_2$ (2.5)	$Na_2S_2O_8$	45
40	$Pd(dba)_2$ (2.5)	$Na_2S_2O_8$	0[e]
41	$Pd(dba)_2$ (2.5)	$Na_2S_2O_8$	0[e]
42	$Pd_2(dba)_3$ (2.5)	$Na_2S_2O_8$	47
43	$Pd_2(dba)_3$ (2.5)	$Na_2S_2O_8$	0[e]
44	$Pd_2(dba)_3$ (2.5)	$Na_2S_2O_8$	0[f]
45	$Pd(OAc)_2$ (2.5)	None	0
46	None	$Na_2S_2O_8$	0

[a]2-Phenylbenzoxazole **1a** (1 mmol) in 1,4-dioxane (6 mL) was treated with the oxidant (2.5 mmol, 2.5 equiv) at 100 °C for 14 h in the presence of the Pd-compound. [b]The isolated yield of **2a**. [c]The unreacted **1a** could be recovered. [d]Under O_2 bubbling. [e]The reaction was performed in AcOH:DCE (1:1). [f]The reaction was performed in $CHCl_3$:DCE (1:1). [BQ = 1,4-Benzoquinone; TBHP = *tert*-Butyl hydroperoxide; CAN = Ceric ammonium nitrate].

Table 1B. The effect of various Pd-based catalyst, oxidant, additive, and other reaction parameters on the aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.[a]

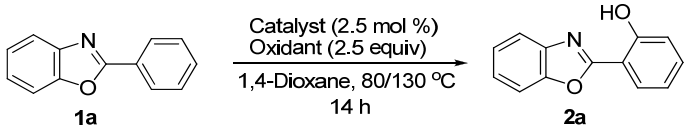


Entry	Catalyst	Oxidant(equiv)	Temp (°C)	Yield (%)[b]
1	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	100	63
2	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	80	62
3	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	80	40[c]
4	$Pd(OAc)_2$	$Na_2S_2O_8$ (1)	80	38
5	$Pd(OAc)_2$	$Na_2S_2O_8$ (0.5)	80	20
6	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	80	23[d]
7	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	80	44[e]
8	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	60	23
9	$Pd(OAc)_2$	$Na_2S_2O_8$ (2.5)	40	0
10	None	$Na_2S_2O_8$ (2.5)	80	0
11	$Pd(OAc)_2$	$K_2S_2O_8$ (2.5)	80	53
12	$PdCl_2$	$K_2S_2O_8$ (2.5)	80	trace
13	$[PdCl_2(PPh_3)_2]$	$K_2S_2O_8$ (2.5)	80	trace
14	$Pd(PPh_3)_4$	$K_2S_2O_8$ (2.5)	80	trace
15	$Pd(OAc)_2$	$Na_2S_2O_8$ (1) + O_2	80	40[f]
16	$Pd(OAc)_2$	O_2	80	0[g]
17	$Pd(OAc)_2$	$Na_2S_2O_8$ (1.5)	80	62
18	**$Pd(OAc)_2$**	**$Na_2S_2O_8$ (1.25)**	**80**	**62**
18	$Pd(piv)_2$	$Na_2S_2O_8$ (1.25)	80	42

19	$Pd(TFA)_2$	$Na_2S_2O_8$ (1.25)	80	31
20	$Pd(OAc)_2$	Oxone (1.25)	80	46
21	$Pd(acac)_2$	$Na_2S_2O_8$ (1.25)	80	50
22	$Pd(dba)_2$	$Na_2S_2O_8$ (1.25)	80	40
23	$Pd_2(dba)_3$	$Na_2S_2O_8$ (1.25)	80	40
24	$Pd(OAc)_2$	$Na_2S_2O_8$ (1.0) + BQ (0.25)	80	35
25	$Pd(OAc)_2$	$Na_2S_2O_8$ (1.0) + BQ (0.25) + O_2	80	34[h]
26	$Pd(OAc)_2$	$Na_2S_2O_8$ (0.25) + BQ (1)	80	20
27	$Pd(OAc)_2$	$Na_2S_2O_8$ (0.25) + BQ (1) + O_2	80	16[h]
28	$Pd(OAc)_2$	$Na_2S_2O_8$ (1.25)+ O_2	80	58[g]
29	$Pd(OAc)_2$	DDQ (1.25)	80	0
30	$Pd(TFA)_2$	PIFA (1.25)	60	21[i]
31	$Pd(OAc)_2$	$Na_2S_2O_8$ (1.25) + HOBT (0.2)	80	0
32	$Pd(OAc)_2$	$Na_2S_2O_8$ (1.25) + HOBT (0.2) + O_2	80	0[g]

[a]**1a** (1 mmol) in 1,4-dioxane (6 mL) was treated with the oxidant (0.5 - 2.5 equiv) at 40 - 100 °C for 14 h in the presence of the Pd-compound (2.5 mol %). [b]The isolated yield of **2a**. [c]1 mol % of $Pd(OAc)_2$ was used. [d]Reaction performed for 6 h. [e]Reaction performed for 10 h. [f]The reaction was performed separately under O_2 atmosphere (balloon) as well as by bubbling O_2 into the reaction mixture. [g]The reaction was performed separately under O_2 atmosphere (balloon) as well as by bubbling O_2 into the reaction mixture. [h]The reaction was performed by O_2 bubbling into the reaction mixture. [i]The reaction was performed in nitrometahne.

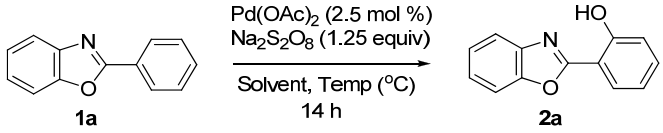
Table 1C. The effect of various transition metal-based catalyst on the aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.[a]



Entry	Catalyst	Oxidant	Temp (°C)	Yield (%)[b]
1	$Pd(OAc)_2$	$Na_2S_2O_8$	80	62
2	**$Pd(OAc)_2$**	**$Na_2S_2O_8$**	**80**	**62[c]**
3	$NiCl_2 \cdot 6H_2O$	$Na_2S_2O_8$	80	0
4	$[NiCl_2(PPh_3)_2]$	$Na_2S_2O_8$	80	0
5	$Cu(OAc)_2 \cdot H_2O$	$Na_2S_2O_8$	80	0
6	$Cu(OAc)_2 \cdot H_2O$	O_2	130	13[d]
7	$CoCl_2 \cdot 6H_2O$	$Na_2S_2O_8$	80	0
8	$Co(OAc)_2$	$Na_2S_2O_8$	80	26
9	$Fe(OAc)_2$	$Na_2S_2O_8$	80	0
10	AgOAc	$Na_2S_2O_8$	80	trace
11	$Mn(OAc)_2 \cdot 4H_2O$	$Na_2S_2O_8$	80	0
12	$Mn(OAc)_3 \cdot 2H_2O$	$Na_2S_2O_8$	80	0
13	$RuCl_3 \cdot xH_2O$	$Na_2S_2O_8$	80	0[e]
14	$[RuCl_2(p\text{-}cym)_2]_2$	$Na_2S_2O_8$	80	0[e]

[a]**1a** (1 mmol) in 1,4-dioxane (6 mL) (except entry 6) was treated with the oxidant (2.5 mmol, 2.5 equiv) at 100 °C for 14 h in the presence of the Pd-compound (2.5 mol %). [b]The isolated yield of **2a**. [c]1.25 equiv $Na_2S_2O_8$ was used. [d]The reaction was performed in Ac_2O-HOAc under O_2 bubbling. [e]$Na_2S_2O_8$ (1 equiv) was used under O_2 bubbling.

Table 1D. The evaluation of the critical role of the solvent as the oxygen source during the $Pd(OAc)_2$-catalysed aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.[a]

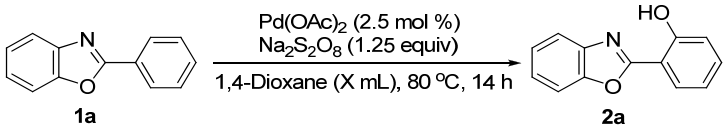


Entry	Solvent	Oxidant	Yield (%)[b]
1	DMF	$Na_2S_2O_8$	0
2	DMA	$Na_2S_2O_8$	0
3	NMP	$Na_2S_2O_8$	0
4	NMO	$Na_2S_2O_8$	0
5	DMSO	$Na_2S_2O_8$	0
6	DMSO	-	0
7	**1,4-Dioxane**	**$Na_2S_2O_8$**	**62**
8	1,4-Dioxane (dry & air/oxygen free)	$Na_2S_2O_8$	62
9	1,4-Dioxane (dry & air/oxygen free)	$Na_2S_2O_8$	62[c]
10	1,4-Dioxane (dry)	O_2	0[d]
11	NMM	$Na_2S_2O_8$	0
12	$MeNO_2$	$Na_2S_2O_8$	0[e]
13	THF	O_2	13[d]
14	THP	$Na_2S_2O_8$	trace
15	DCE	O_2	0[d]
16	$CHCl_3$	$Na_2S_2O_8$	0[e]
17	MeCN	O_2	27[d]
18	EG	$Na_2S_2O_8$	0
19	^{i}PrOH	$Na_2S_2O_8$	0
20	^{t}BuOH	$Na_2S_2O_8$	0
21	PEG-2000/^{t}BuOH	$Na_2S_2O_8$	0
22	H_2O	$Na_2S_2O_8$	0
23	1,4-Dioxane:H_2O (1:1)	$Na_2S_2O_8$	0
24	1,4-Dioxane:MeOH (1:1)	$Na_2S_2O_8$	41
25	Toluene	$Na_2S_2O_8$	0
26	Toluene	$Na_2S_2O_8$ + BQ	0[f]
27	Toluene	$Na_2S_2O_8$ + $(PhCO_2)_2$	0[g]
28	Toluene	$Na_2S_2O_8$ + O_2	0[h]
29	Hexane	$Na_2S_2O_8$	0
30	THF	O_2	0[i]
31	THF	O_2	0[j]

32	THF	$Na_2S_2O_8 + O_2$	trace[k]
33	THF	$Na_2S_2O_8 + O_2$	trace[l]
34	DCE	O_2	0[i]
35	DCE	O_2	0[j]
36	DCE	$Na_2S_2O_8 + O_2$	0[k]
37	DCE	$Na_2S_2O_8 + O_2$	0[l]
38	MeCN	O_2	0[i]
39	MeCN	O_2	0[j]
40	MeCN	$Na_2S_2O_8 + O_2$	16[k]
41	MeCN	$Na_2S_2O_8 + O_2$	14[l]
42	H_2O	O_2	0[i]
43	H_2O	O_2	0[j]
44	H_2O	$Na_2S_2O_8 + O_2$	0[k]
45	H_2O	$Na_2S_2O_8 + O_2$	0[l]

[a]**1a** (1 mmol) in 1,4-dioxane (6 mL) (unless otherwise mentioned) was treated with $Na_2S_2O_8$ (1.25 mmol, 1.25 equiv) at 80 °C for 14 h. [b]Isolated yield of **2a**. [c]The reaction was performed under N_2 atmosphere. [d]The reaction was performed under O_2 atmosphere in the absence of $Na_2S_2O_8$. [e]Reflux temperature. [f]BQ (1 equiv) was used as additive. [g]Benzoyl peroxide (1 equiv) was used as additive. [h]Under O_2 bubbling. [i]No $Na_2S_2O_8$ was used and under O_2 atmosphere (balloon). [j]No $Na_2S_2O_8$ was used and under O_2 bubbling. [k]$Na_2S_2O_8$ (1.25 equiv) has been used under O_2 balloon. [l]$Na_2S_2O_8$ (1.25 equiv) has been used under O_2 bubbling.

Table 1E. The evaluation of the amount of dioxane as the solvent/cosolvent during the $Pd(OAc)_2$-catalysed aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.[a]



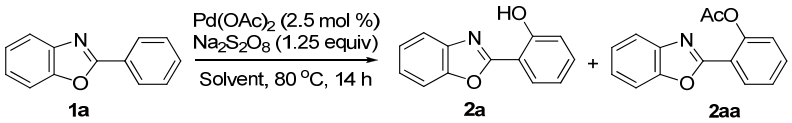
Entry	Solvent	Amt (mL)	Co-solvent	Amt (equiv)	Yield (%)[b]
1	1,4-Dioxane	0.5	---	---	trace
2	1,4-Dioxane	1	---	---	16
3	1,4-Dioxane	2	---	---	30
4	1,4-Dioxane	4	---	---	44
5	1,4-Dioxane	**6**	---	---	**62**
6	1,4-Dioxane	8	---	---	63
7	1,4-Dioxane	10	---	---	63
8	PhMe	6	1,4-Dioxane	1	trace
9	PhMe	6	1,4-Dioxane	2.5	trace
10	PhMe	6	1,4-Dioxane	5	12
11	PhMe	6	1,4-Dioxane	10	19
12	DCE	6	1,4-Dioxane	1	0
13	DCE	6	1,4-Dioxane	2.5	0
14	DCE	6	1,4-Dioxane	5	trace

15	DCE	6	1,4-Dioxane	10	13

[a]**1a** (1 mmol) in varying amount of 1,4-dioxane (dry and air/oxygen free) was treated with $Na_2S_2O_8$ (1.25 mmol, 1.25 equiv) at 80 °C for 14 h in the presence of $Pd(OAc)_2$ (2.5 mol %). [b]Isolated yield of **2a**.

2. Evidences for direct formation of hydroxyarenes under the conditions developed in the present study and indirect aryl hydroxylation under reported conditions:

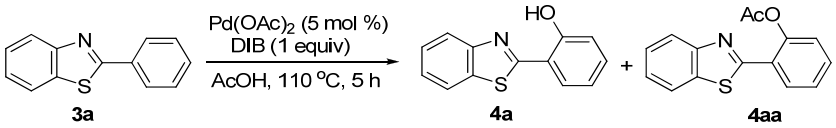
Table 2A. The reaction of 1a in Ac_2O, AcOH-Ac_2O, AcOH-H_2O during the $Pd(OAc)_2$-catalysed C_{sp2}-H activation for direct aryl hydroxylation.[a]



Entry	Solvent	Aq. workup Yield (%)[b]		Without aq. workup Yield (%)[b]	
		2a	**2aa**	**2a**	**2aa**
1	Ac_2O	49	0	0	55
2	HOAc/Ac_2O (1:1)	47	0	0	53
3	HOAc/H_2O (1:1)	0	0	0	0

[a]**1a** (1 mmol) was treated with $Pd(OAc)_2$ (2.5 mol %) and $Na_2S_2O_8$ (1.25 mmol, 1.25 equiv) at 80 °C in different solvents (6 mL) for 14 h. [b]Isolated yield.

Table 2B. The reaction of 2-phenylbenzothiazole 3a under the reported condition[1] following aqueous workup and without aqueous workup.[a]

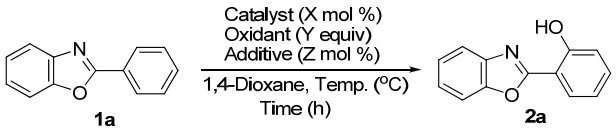


Entry	Aq. workup Yield (%)[b]		Without aq. workup Yield (%)[b]	
	4a	**4aa**	**4a**	**4aa**
1	76	0	0	81

[a]2-Phenylbenzothiazole **3a** (1 mmol) was treated with $Pd(OAc)_2$ (5 mol %) and DIB (1 mmol, 1 equiv) at 110 °C in AcOH (2 mL) for 5 h. [b]Isolated yield.

3. Comparison of the direct aryl hydroxylation developed under the present investigation with some of the reported aryl hydroxylation protocols.

Table 3A. Comparison of the direct aryl hydroxylation of 1a to from 2a developed under the present investigation with some of the reported aryl hydroxylation protocols.



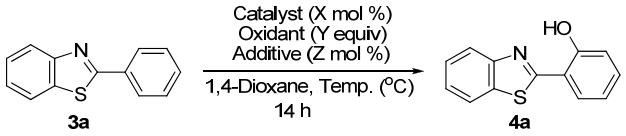
Previous Report	Catalyst system	Condition	T (°C)	Time (h)	Yield (%)[a]
1. Angew. Chem. Int. Ed. **2014**, *53*, 11285-11288					
A)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $PhI(OTFA)_2$ (1.5 equiv), DCE	original	100	8	0
B)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $PhI(OTFA)_2$ (1.5 equiv), 1,4-Dioxane	modified	80	14	0
2. Tetrahedron Lett. **2008**, *49*, 5863-5866					
A)	$Pd(OAc)_2$ (10 mol %), oxone (5 equiv), PEG-4600 (2 gm), ^tBuOH (4 mL)	original	90	2	11
B)	$Pd(OAc)_2$ (10 mol %), $Na_2S_2O_8$ (1.25 equiv), PEG-4600 (2 gm), 1,4-Dioxane	modified	80	14	0
3. J. Am. Chem. Soc. **2009**, *131*, 14654-14655					
A)	$Pd(OAc)_2$ (10 mol %), KOAc (2 equiv), BQ (1 equiv), O_2 (1 atm), DMA	original	115	15	12
B)	$Pd(OAc)_2$ (10 mol %), KOAc (2 equiv), BQ (1 equiv), O_2 (1 atm), 1,4-Dioxane	modified	80	14	0
4. Org. Lett. **2012**, *14*, 2874-2877					
A)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), selectfluor (1.1 equiv), TFA/TFAA (7:3)	original	80	12	0
B)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), selectfluor (1.1 equiv), 1,4-Dioxane	modified	80	14	0
5. Org. Lett. **2012**, *14*, 4210-4213					
A)	$[RuCl_2(p\text{-cym})]_2$ (1 mol %), $PhI(OAc)_2$ (1.2 equiv), TFA/TFAA (3:2)	original	120	12	0
B)	$[RuCl_2(p\text{-cym})]_2$ (1 mol %), $PhI(OAc)_2$ (1.2 equiv), 1,4-Dioxane	modified	80	14	11
6. Org. Lett. **2012**, *14*, 6206-6209					
A)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $PhI(OAc)_2$ (1.2 equiv), TFA/TFAA (3:2)	original	120	22	0
B)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %),	modified	80	14	14

	$PhI(OAc)_2$ (1.2 equiv), 1,4-Dioxane				
7. Angew. Chem. Int. Ed. **2012**, *51*, 13070-13074					
A)	$Pd(OAc)_2$ (5 mol %), selectfluor (1.1 equiv), TFA/TFAA (9:1)	original	100	3.5	0
B)	$Pd(OAc)_2$ (5 mol %), selectfluor (1.1 equiv), 1,4-Dioxane	modified	80	14	0
8. Angew. Chem. Int. Ed. **2012**, *51*, 13075-13079					
A)	$Pd(TFA)_2$ (2 mol %), PIFA (2 equiv), DCE	original	80	3	0
B)	$Pd(TFA)_2$ (2 mol %), PIFA (2 equiv), 1,4-Dioxane	modified	80	14	23
C)	$Pd(OAc)_2$ (5 mol %), $K_2S_2O_8$ (2 equiv), TFA	original	50	3	0
D)	$Pd(OAc)_2$ (5 mol %), $K_2S_2O_8$ (2 equiv), 1,4-Dioxane	modified	80	14	47
9. Tetrahedron Lett. **2013**, *69*, 2175-2183					
A)	$Pd(OAc)_2$ (5 mol %), DIB (1 equiv), AcOH (2 mL)	original	110	5	17
B)	$Pd(OAc)_2$ (5 mol %), DIB (1 equiv), 1,4-Dioxane	modified	80	14	21
10. Angew. Chem. Int. Ed. **2013**, *52*, 5827-5831					
A)	$PdCl_2$ (5 mol %), NHSI (10 mol %), O_2 (1 atm), Toluene	original	100	15	16
B)	$PdCl_2$ (5 mol %), NHSI (10 mol %), O_2 (1 atm), 1,4-Dioxane	modified	80	14	13
11. Org. Lett. **2013**, *15*, 270-273					
A)	$Pd(OAc)_2$ (5 mol %), PIFA (2 equiv), DCE	original	80	20	
B)	$Pd(OAc)_2$ (5 mol %), PIFA (2 equiv), 1,4-Dioxane	modified	80	14	26
12. Org. Lett. **2013**, *15*, 718-720					
A)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $PhI(OAc)_2$ (1 equiv), TFA/TFAA (3:1)	original	50	16	0
B)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $PhI(OAc)_2$ (1 equiv), 1,4-Dioxane	modified	80	14	14
13. Org. Lett. **2013**, *15*, 2334-2337					
A)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $K_2S_2O_8$ (1.2 equiv), TFA/TFAA (3:1)	original	80	12	0
B)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), $K_2S_2O_8$ (1.2 equiv), 1,4-Dioxane	modified	80	14	17
14. Org. Lett. **2013**, *15*, 3484-3486					
A)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %), PIFA (2 equiv), DCE	original	80	12	0
B)	$[RuCl_2(p\text{-cym})]_2$ (2.5 mol %),	modified	80	14	0

	PIFA (2 equiv), 1,4-Dioxane				
15. J. Am. Chem. Soc. **2013**, *135*, 9350-9353					
A)	$Cu(OAc)_2·H_2O$ (5 mol %) $[(PhCO)_2]_2$ (1.25 equiv), HFIP	original	75	12	0
B)	$Cu(OAc)_2·H_2O$ (5 mol %) $[(PhCO)_2]_2$ (1.25 equiv), 1,4-Dioxane	modified	80	14	0
16. Asian J. Org. Chem. **2014**, *3*, 68-76					
A)	$Pd(OAc)_2$ (10 mol %) oxone (2 equiv), Cs_2CO_3 (2 equiv), DMF	original	120	12	0
B)	$Pd(OAc)_2$ (10 mol %) oxone (2 equiv), Cs_2CO_3 (2 equiv), 1,4-Dioxane	modified	80	14	22
17. Org. Lett. **2014**, *16*, 3904-3907					
A)	$Cu(OAc)_2·H_2O$ (1 equiv), Ag_2CO_3 (2 equiv), TBAI (2 equiv), DMF	original	100	1	0
B)	$Cu(OAc)_2·H_2O$ (1 equiv), Ag_2CO_3 (2 equiv), TBAI (2 equiv), 1,4-Dioxane	modified	80	14	14

[a]Isolated yield of **2a**.

Table 3B. Comparison of the direct aryl hydroxylation of 3a to from 4a developed under the present investigation with some of the reported aryl hydroxylation protocols.



Previous Report	Catalysts system	Condition	T (°C)	Time (h)	Yield (%)[a]
1. Asian J. Org. Chem. **2014**, *3*, 68-76					
A)	$Pd(OAc)_2$ (10 mol %) oxone (2 equiv), Cs_2CO_3 (2 equiv), DMF	original	120	12	0
B)	$Pd(OAc)_2$ (10 mol %) oxone (2 equiv), Cs_2CO_3 (2 equiv), 1,4-Dioxane	modified	80	14	28

[a]Isolated yield of **4a**.

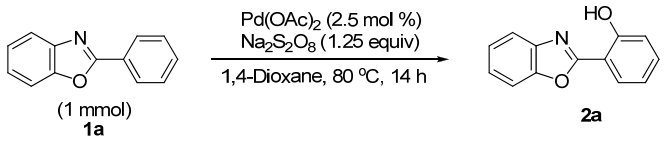
4. Experimental Procedure

General Information

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 MHz NMR spectrometer in $CDCl_3$ with residual undeuterated solvent ($CDCl_3$: 7.26/77.0) using Me_4Si as an internal standard. Chemical shifts (δ) are given in ppm and *J* values are given in Hz. The IR spectra were recorded either on KBr pellets (for solids) or neat (for liquids) on a Nicolet Impact 410 FTIR spectrometer. The HRMS spectra were recorded on Bruker Maxis instrument. Melting points were measured with Gupta scientific, India melting point apparatus. Flash column

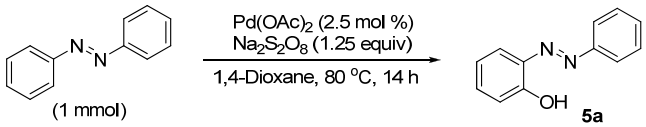
chromatography, thin layer chromatography (TLC) was performed on Silica gel [Fisher Scientific silica gel 230-400 mesh, F254 and Merck® silica gel respectively]. Flash column chromatography was done on Biotage 'Isolera One' instruement. Evaporation of solvents was performed at reduced pressure, using a Bűchi rotary evaporator. All chemicals were purchased from Aldrich, Lancaster, Alfa Aesar and Fluka Chemicals and used as received.

Typical procedure for the $Pd(OAc)_2$ catalyzed direct hydroxylation of benzoxazole scaffold by C_{sp2}-H activation (1a to 2a):-



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added **1a** (195 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (14 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered, and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane (300 mL) afforded the unreacted **1a** (67 mg, 34%) and 2-benzoxazol-2-yl-phenol[2] **2a** as light yellow solid (131 mg, 62%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst (5.6 mg). The recovered Pd catalyst (1.9 mg, 2.5 mol %) was charged with 1,4-dioxane (2 mL), $Na_2S_2O_8$ (121 mg, 0.51 mmol, 1.25 equiv) and the recovered **1a** (67 mg) and the mixture was magnetically stirred at 80 °C for 14 h to obtain **2a** (43 mg, 60%) after usual workup and purification. The total/overall isolated yield of **2a** is 174 mg (82%). mp: 121-123 °C. TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.05 (dt, 1H, J = 1.0 Hz, 7.4 Hz), 7.16 (dd, 1H, J = 1.0 Hz, 8.3 Hz), 7.38 – 7.44 (m, 2H), 7.45 – 7.50 (m, 1H), 7.62 – 7.66 (m, 1H), 7.74 – 7.79 (m, 1H), 8.06 (dd, 1H, J = 1.7 Hz, 7.9 Hz), 11.51 (s, 1H); IR (KBr) ν_{max}: 3397, 2925, 1277, 1260, 1031 cm^{-1}; MS (ESI) $(M + H)^+$ = 212.3.

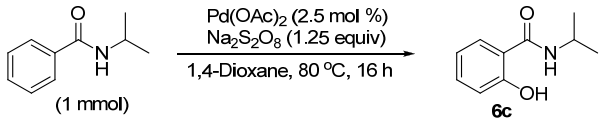
Typical procedure for the $Pd(OAc)_2$ catalyzed direct hydroxylation of azo scaffold by C_{sp2}-H activation to form 2-phenylazo-phenol 5a:-



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added

azobenzene (182 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (14 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane (300 mL) afforded the unreacted azobenzene (65 mg, 36%) and the 2-phenylazo-phenol **5a** as reddish solid, (121 mg, 61%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst (5.6 mg). The recovered Pd catalyst (2 mg, 2.5 mol %) was charged with 1,4-dioxane (2.2 mL), $Na_2S_2O_8$ (128 mg, 0.54 mmol, 1.25 equiv) and the recovered azobenzene (65 mg) and the mixture was magnetically stirred at 80 °C for 14 h to obtain **5a** (43 mg, 61%) after usual workup and purification. The total/overall isolated yield of **5a** is 164 mg (83%). mp: 82-84 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.02 – 7.10 (m, 2H), 7.34 – 7.41 (m, 1H), 7.44 – 7.58 (m, 3H), 7.87 – 7.89 (m, 2H), 7.93 – 7.96 (m, 1H), 12.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 118.2, 120.0, 122.3, 129.4, 131.2, 133.3, 133.3, 137.4, 150.6, 152.8; IR (KBr) ν_{max}: 3478, 2923, 2857, 1733, 1613, 1459, 1225, 1144 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_{10}N_2ONa$, 221.0691; found, 221.0687.

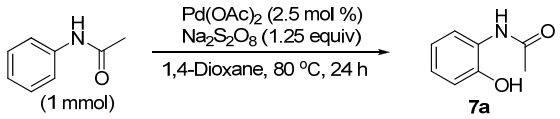
Typical procedure for the $Pd(OAc)_2$ catalyzed direct hydroxylation of benzamide scaffold by C_{sp2}-H activation to form 2-hydroxy *N*-isopropyl benzamide 6c:-



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added *N*-isopropyl benzamide (163 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (16 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane/EtOAc (400 mL) afforded 2-hydroxy *N*-isopropyl benzamide **6c** as yellowish liquid, (142 mg, 70%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst (5.6 mg). **6c**: TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.29 (d, 6H, J = 6.6 Hz), 4.26 – 4.32 (m, 1H), 6.30 (bs, 1H, D_2O exchangeable), 6.83 (t, 1H, J = 7.2 Hz), 6.97 – 6.99 (m, 1H), 7.36 – 7.40 (m, 2H), 12.52 (bs, 1H, D_2O exchangeable); ^{13}C NMR ($CDCl_3$, 100

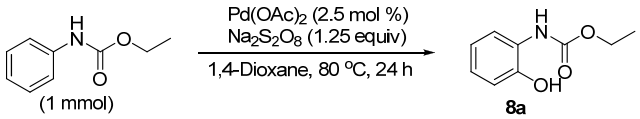
MHz) δ (ppm): 22.6, 41.8, 114.4, 118.5, 118.6, 125.4, 134.1, 161.5, 169.2; IR (Neat) ν_{max}: 3734, 2976, 1539, 1361, 1275 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{10}H_{13}NO_2Na$, 202.0844; found, 202.0844.

Typical procedure for the $Pd(OAc)_2$ catalyzed direct hydroxylation of acetanilide scaffold by C_{sp2}-H activation to form *N*-(2-hydroxyphenyl)-acetamide 7a:-



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added *N*-phenylacetamide (135 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (24 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane/EtOAc (350 mL) afforded the unreacted *N*-phenylacetamide (98 mg, 73%) and the *N*-(2-hydroxyphenyl)-acetamide[3] **7a** as light brown solid, (35 mg, 23%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst (5.6 mg). The recovered Pd catalyst (4.1 mg, 2.5 mol %) was charged with 1,4-dioxane (4.4 mL), $Na_2S_2O_8$ (261 mg, 1.09 mmol, 1.25 equiv) and the recovered *N*-phenylacetamide (98 mg) and the mixture was magnetically stirred at 80 °C for 24 h to obtain **7a** (24 mg, 20%) after usual workup and purification. The total/overall yield of **7a** is 59 mg (39%). mp: 206-208 °C; TLC (Hexane:EtOAc, 80:20 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.31 (s, 3H), 6.89 (t, 1H, J = 7.4 Hz), 6.99 – 7.07 (m, 2H), 7.15 – 7.19 (m, 1H), 7.41 (bs, 1H, D_2O exchangeable), 8.69 (bs, 1H, D_2O exchangeable); IR (Neat) ν_{max}: 3405, 2925, 1656, 1454, 1275, 1260 cm^{-1}; MS (ESI) $(M + H)^+$ = 152.4.

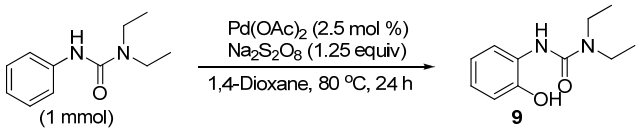
Typical procedure for the $Pd(OAc)_2$ catalyzed direct hydroxylation of carbamate scaffold by C_{sp2}-H activation to form ethyl-2-hydroxyphenylcarbamate 8a:-



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added ethyl phenylcarbamate (165 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (24 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts

were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane/EtOAc (400 mL) afforded the unreacted ethyl phenylcarbamate (130 mg, 79%) and the ethyl-2-hydroxyphenylcarbamate[4] **8a** as light yellow solid, (34 mg, 19%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst (5.6 mg). The recovered Pd catalyst (4.4 mg, 2.5 mol %) was charged with 1,4-dioxane (4.7 mL), $Na_2S_2O_8$ (282 mg, 1.18 mmol, 1.25 equiv) and the recovered ethyl phenylcarbamate (130 mg) and the mixture was magnetically stirred at 80 °C for 24 h to obtain **8a** (27 mg, 19%) after usual workup and purification. The total/overall yield of **8a** is 61 mg (34%). mp: 80-82 °C; TLC (Hexane:EtOAc, 80:20 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.36 (t, 3H, J = 7.1 Hz), 4.28 (q, 2H, J = 7.1 Hz), 6.88 – 6.92 (m, 1H), 6.96 – 6.99 (m, 1H), 7.04 – 7.08 (m, 1H), 7.25 – 7.28 (m, 1H), 7.81 (bs, 1H, D_2O exchangeable); IR (Neat) ν_{max}: 3409, 2927, 1710, 1661, 1455, 1274, 1261 cm^{-1}; MS (ESI) $(M + H)^+$ = 182.3.

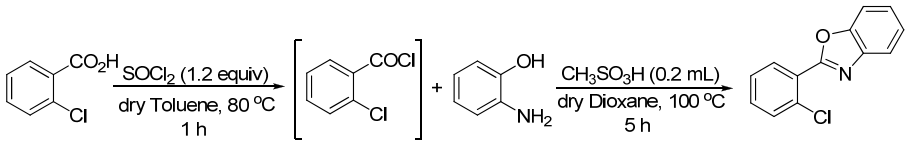
Typical procedure for the $Pd(OAc)_2$ catalyzed direct hydroxylation of urea scaffold by C_{sp2}-H activation to form 1,1-diethyl-3-(2-hydroxyphenyl)urea 9:-



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added 1,1-diethyl-3-phenylurea (192 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (24 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane/EtOAc (400 mL) afforded the unreacted 1,1-diethyl-3-phenylurea (143 mg, 74%) and 1,1-diethyl-3-(2-hydroxyphenyl)urea **9** as brown solid, (46 mg, 22%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst (5.6 mg). The recovered Pd catalyst (4.2 mg, 2.5 mol %) was charged with 1,4-dioxane (4.4 mL), $Na_2S_2O_8$ (264 mg, 1.11 mmol, 1.25 equiv) and the recovered 1,1-diethyl-3-phenylurea (143 mg) and the mixture was magnetically stirred at 80 °C for 24 h to obtain **9** (34 mg, 22%) after usual workup and purification. The total/overall yield of **9** is 80 mg (38%). mp: 126-128 °C; TLC (Hexane:EtOAc, 60:40 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.30 (t, 6H, J = 7.2 Hz), 3.44 (q, 4H, J = 7.2 Hz), 6.32 (bs, 1H, D_2O

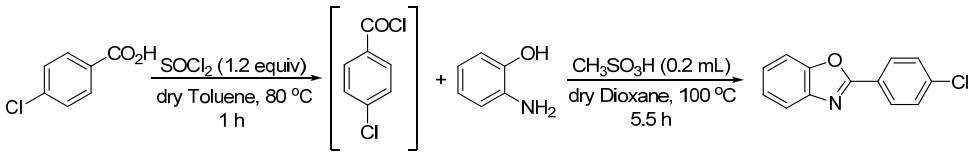
exchangeable), 6.83 – 6.85 (m, 1H), 6.88 – 6.91 (m, 1H), 7.02 – 7.08 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.6, 42.3, 119.9, 120.0, 122.1, 125.9, 126.7, 149.5, 156.3; HRMS (M + Na)$^+$ Calcd. for $C_{11}H_{16}N_2O_2Na$, 231.1109; found, 231.1122.

Preparation of 2-(2-chlorophenyl)-benzoxazole[5a] (starting benzoxazole of 2b):-



2-Chlorobenzoic acid (1.565 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-aminophenol (1.09 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-aminophenol (5 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-(2-chlorophenyl)-benzoxazole as light yellow solid, (1.516 g, 66%), mp: 61-63 °C; TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.36 – 7.47 (m, 4H), 7.56 – 7.58 (m, 1H), 7.60 – 7.64 (m, 1H), 7.83 – 7.87 (m, 1H), 8.14 – 8.16 (m, 1H); IR (KBr) ν_{max}: 2923, 1276, 1260, 1058, 1029 cm^{-1}; MS (ESI) (M + H)$^+$ = 230.8.

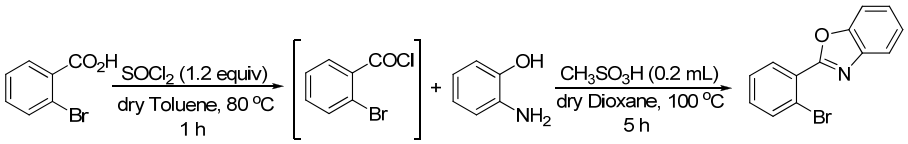
Preparation of 2-(4-chlorophenyl)-benzoxazole[5a] (starting benzoxazole of 2c):-



4-Chlorobenzoic acid (1.565 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-aminophenol (1.09 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-aminophenol (5.5 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-

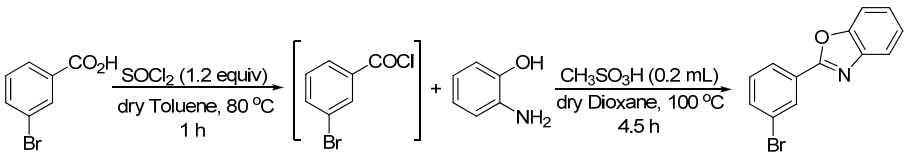
(4-chlorophenyl)-benzoxazole as off white solid, (1.608 g, 70%), mp: 147-149 °C; TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.34 – 7.39 (m, 2H), 7.48 – 7.52 (m, 2H), 7.57 – 7.59 (m, 1H), 7.75 – 7.78 (m, 1H), 8.17 – 8.21 (m, 2H); IR (KBr) ν_{max}: 2926, 1270, 1261, 1060, 1031 cm^{-1}; MS (ESI) $(M + H)^+ = 230.7$.

Preparation of 2-(2-bromophenyl)-benzoxazole[5] (starting benzoxazole of 2e):-



2-Bromobenzoic acid (2.01 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-aminophenol (1.09 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-aminophenol (5 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-(2-bromophenyl)-benzoxazole as off white solid, (2.056 g, 75%), mp: 51-53 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.35 – 7.43 (m, 3H), 7.47 (dd, 1H, J = 1.2 Hz, 7.5 Hz), 7.60 – 7.65 (m, 1H), 7.78 (dd, 1H, J = 1.1 Hz, 6.8 Hz),7.84 – 7.88 (m, 1H), 8.08 (dd, 1H, J = 1.7 Hz, 7.8 Hz); IR (KBr) ν_{max}: 2929, 1279, 1270, 1051, 1030 cm^{-1}; MS (ESI) $(M + H)^+ = 275.4$.

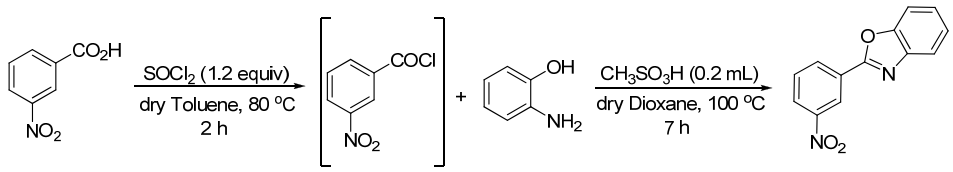
Preparation of 2-(3-bromophenyl)benzo[*d*]oxazole (starting benzoxazole of 2f):-



3-Bromobenzoic acid (2.01 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-aminophenol (1.09 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-aminophenol (4.5 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were

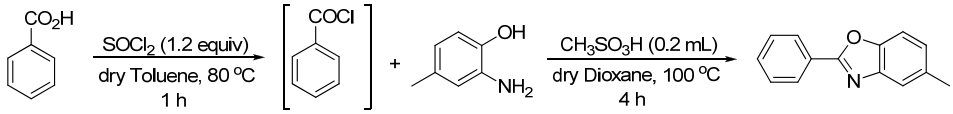
washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-(3-bromophenyl)benzo[*d*]oxazole[6] as white solid, (2.111 g, 77%), mp: 111-114 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.35 - 7.41 (m, 3H), 7.57 – 7.61 (m, 1H), 7.64 – 7.69 (m, 1H), 7.75 – 7.80 (m, 1H), 8.17 - 8.19 (m, 1H), 8.41 (d, 1H, J = 1.5 Hz); IR (KBr) ν_{max}: 2979, 1640, 1545, 1278, 1250 cm^{-1}; MS (ESI) $(M + H)^+$ = 275.3.

Preparation of 2-(3-nitrophenyl)-benzoxazole (starting benzoxazole of 2g):-



3-Nitrobenzoic acid (1.671 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (2 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-aminophenol (1.09 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-aminophenol (7 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-(3-nitrophenyl)-benzoxazole[6] as off white solid, (1.369 g, 57%), mp: 204-206 °C; TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.42 – 7.46 (m, 2H), 7.65 – 7.67 (m, 1H), 7.76 (t, 1H, J = 8.1 Hz), 7.83 – 7.85 (m, 1H), 8.39 – 8.42 (m, 1H), 8.60 – 8.62 (m, 1H), 9.12 – 9.13 (m, 1H); IR (KBr) ν_{max}: 2978, 1630, 1525, 1347 cm^{-1}; MS (ESI) $(M + H)^+$ = 241.4.

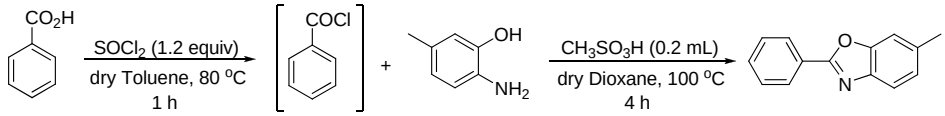
Preparation of 5-methyl-2-phenyl-benzoxazole[5a] (starting benzoxazole of 2h):-



Benzoic acid (1.221 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-hydroxy 5-methyl aniline (1.231 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-hydroxy 5-methyl aniline (4 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was

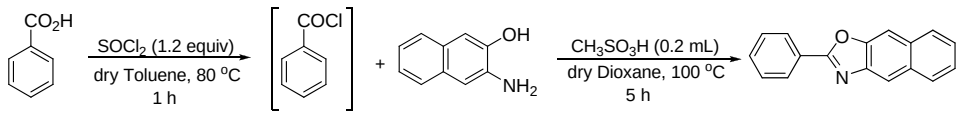
diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 5-methyl-2-phenyl-benzoxazole as yellow solid, (1.548 g, 74%), mp: 101-103 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.49 (s, 3H), 7.15 – 7.17 (m, 1H), 7.45 (d, 1H, J = 8.3 Hz), 7.51 – 7.53 (m, 3H), 7.56 – 7.57 (m, 1H), 8.23 – 8.26 (m, 2H); IR (KBr) ν_{max}: 2929, 1621, 1450, 1245, 1021 cm^{-1}; MS (ESI) $(M + H)^+$ = 210.3.

Preparation of 6-methyl-2-phenyl-benzoxazole (starting benzoxazole of 2i):-



Benzoic acid (1.221 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-hydroxy 4-methyl aniline (1.231 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-hydroxy 4-methyl aniline (4 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 6-methyl-2-phenyl-benzoxazole as off white solid, (1.590 g, 76%), mp: 87-89 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.50 (s, 3H), 7.16 (dd, 1H, J = 0.9 Hz, 8.1 Hz), 7.38 (s, 1H), 7.50 – 7.52 (m, 3H), 7.64 (d, 1H, J = 8.1 Hz), 8.22 – 8.25 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 21.8, 110.8, 119.4, 125.8, 127.4, 127.5, 128.9, 131.3, 135.6, 139.9, 151.1, 162.6; IR (KBr) ν_{max}: 2927, 1617, 1445, 1247, 1021 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{14}H_{11}NONa$, 232.0738; found, 232.0747.

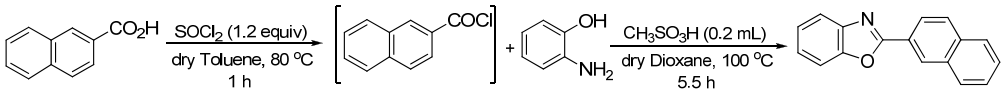
Preparation of 2-phenyl-naphtho[2,3-*d*]oxazole[5a] (starting benzoxazole of 2k):-



Benzoic acid (1.221 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 3-amino 2-naphthol (1.591 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture

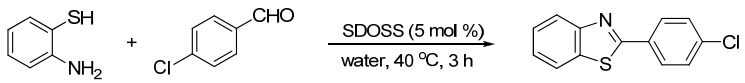
was stirred magnetically at 100 °C. After complete consumption of 3-amino 2-naphthol (5 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-phenyl-naphtho[2,3-*d*]oxazole as deep brown solid, (1.864 g, 76%), mp: 189-191 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.47 – 7.51 (m, 2H), 7.53 – 7.59 (m, 3H), 7.95 – 7.97 (m, 2H), 7.99 – 8.01 (m, 1H), 8.20 (s, 1H), 8.33 – 8.35 (m, 2H); IR (KBr) ν_{max}: 2925, 1618, 1450, 1248 cm^{-1}; MS (ESI) $(M + H)^+ = 246.4$.

Preparation of 2-naphthalen-2-yl-benzoxazole[5a] (starting benzoxazole of 2l):-



2-Naphthoic acid (1.721 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1 h). The excess $SOCl_2$ was distilled off and the reaction mixture was treated with 2-aminophenol (1.09 g, 10 mmol) in dry 1,4-dioxane (20 mL) followed by addition of CH_3SO_3H (2 mL) and the mixture was stirred magnetically at 100 °C. After complete consumption of 2-aminophenol (5.5 h, TLC), 1,4-dioxane was distilled off in rotary evaporator and the residue was diluted with EtOAc (20 mL) followed by saturated aq. $NaHCO_3$ (20 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined EtOAc extracts were washed with H_2O (3 × 10 mL), dried (anh Na_2SO_4) and purified by flash column chromatography (silica-gel: 230-400 mesh) using hexane/EtOAc solvent system to afford the 2-naphthalen-2-yl-benzoxazole as off white solid, (1.741 g, 71%), mp: 115-117 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.38 – 7.42 (m, 2H), 7.56 – 7.66 (m, 3H), 7.82 – 7.84 (m, 1H), 7.91 – 7.93 (m, 1H), 7.99 – 8.02 (m, 2H), 8.34 (dd, 1H, J = 1.6 Hz, 8.6 Hz), 8.80 (s, 1H); IR (KBr) ν_{max}: 2976, 1630, 1343, 1270 cm^{-1}; MS (ESI) $(M + H)^+ = 246.6$.

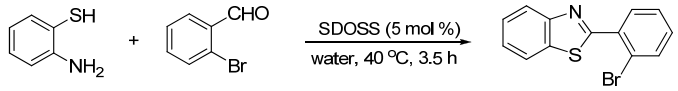
Preparation of 2-(4-chlorophenyl)-benzothiazole[7] (starting benzothiazole of 4b):-



To a magnetically stirred suspension of SDOSS (222 mg, 0.5 mmol, 5 mol %) in water (50 mL) were added 4-chloro benzaldehyde (1.405 g, 10 mmol) and 2-aminothiophenol (1.502 g, 12 mmol, 1.2 equiv) and the mixture was stirred magnetically at 40 °C. After completion of the reaction (3 h, TLC), the mixture was extracted with EtOAc (2 × 20 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg). The residue was purified by the recrystallization from distilled

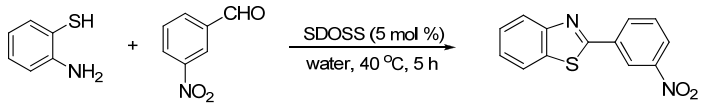
methanol to afford the 2-(4-chlorophenyl)-benzothiazole as off white solid, (1.966 g, 80%). mp: 116-118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.40 (t, 1H, *J* = 7.8 Hz), 7.46 – 7.52 (m, 3H), 7.90 (d, 1H, *J* = 8.0 Hz), 8.02 – 8.08 (m, 3H); IR (KBr) ν_{max}: 2927, 1635, 1494 cm^{-1}; MS (ESI) $(M + H)^+$ = 246.8.

Preparation of 2-(2-bromophenyl)-benzothiazole (starting benzothiazole of 4c):-



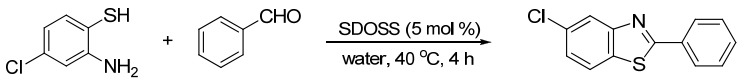
To a magnetically stirred suspension of SDOSS (222 mg, 0.5 mmol, 5 mol %) in water (50 mL) were added 2-bromo benzaldehyde (1.85 g, 10 mmol) and 2-aminothiophenol (1.502 g, 12 mmol, 1.2 equiv) and the mixture was stirred magnetically at 40 °C. After completion of the reaction (3.5 h, TLC), the mixture was extracted with EtOAc (2 × 20 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg). The residue was purified by the recrystallization from distilled methanol to afford the 2-(2-bromophenyl)-benzothiazole[8] as off white solid, (2.263 g, 78%). mp: 63-65 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.32 (dt, 1H, *J* = 1.4 Hz, 9.0 Hz), 7.42 – 7.46 (m, 2H), 7.53 (dt, 1H, *J* = 1.1 Hz, 8.2 Hz), 7.74 (d, 1H, *J* = 8.0 Hz), 7.94 (d, 1H, *J* = 8.0 Hz), 8.00 (dd, 1H, *J* = 1.7 Hz, 7.8 Hz), 8.14 (d, 1H, *J* = 8.1 Hz); IR (KBr) ν_{max}: 2928, 1633, 1496, 1240 cm^{-1}; MS (ESI) $(M + H)^+$ = 291.3.

Preparation of 2-(3-nitrophenyl)benzo[*d*]thiazole (starting benzothiazole of 4d):-



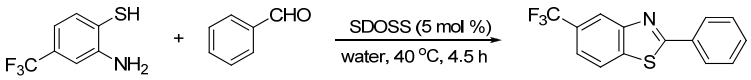
To a magnetically stirred suspension of SDOSS (222 mg, 0.5 mmol, 5 mol %) in water (50 mL) were added 3-nitrobenzaldehyde (1.511 g, 10 mmol) and 2-aminothiophenol (1.502 g, 12 mmol, 1.2 equiv) and the mixture was further stirred magnetically at 40 °C. After completion of the reaction (5 h, TLC), the mixture was extracted with EtOAc (2 × 20 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg). The residue was purified by the recrystallization from distilled methanol to afford the 2-(3-nitrophenyl)benzo[*d*]thiazole[6] as off white solid, (1.717 g, 67%). mp: 180-182 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.46 (t, 1H, *J* = 7.8 Hz), 7.55 (t, 1H, *J* = 7.8 Hz), 7.70 (t, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 8.12 (d, 1H, *J* = 8.2 Hz), 8.34 (d, 1H, *J* = 8.0 Hz), 8.43 (d, 1H, *J* = 7.7 Hz), 8.94 (s, 1H); IR (KBr) ν_{max}: 2971, 1644, 1540, 1277, 1252 cm^{-1}; MS (ESI) $(M + H)^+$ = 257.4.

Preparation of 5-chloro-2-phenylbenzo[*d*]thiazole (starting benzothiazole of 4e):-



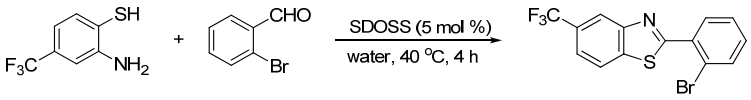
To a magnetically stirred suspension of SDOSS (222 mg, 0.5 mmol, 5 mol %) in water (50 mL) were added benzaldehyde (1.061 g, 10 mmol) and 2-amino-4-chloro thiophenol (1.756 g, 11 mmol, 1.1 equiv) and the mixture was further stirred magnetically at 40 °C. After completion of the reaction (4 h, TLC), the mixture was extracted with EtOAc (2 × 20 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg). The residue was purified by the recrystallization from distilled methanol to afford the 5-chloro-2-phenylbenzo[*d*]thiazole[8] as light green solid, (1.892 g, 77%). mp: 134-136 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.39 (dd, 1H, *J* = 2.0 Hz, 8.5 Hz), 7.52 – 7.55 (m, 3H), 7.84 (d, 1H, *J* = 8.5 Hz), 8.08 – 8.12 (m, 3H); IR (KBr) ν_{max}: 2972, 1649, 1541, 1275, 1250 cm^{-1}; MS (ESI) $(M + H)^+$ = 246.8.

Preparation of 2-phenyl-5-trifluoromethyl-benzothiazole (starting benzothiazole of 4f):-



To a magnetically stirred suspension of SDOSS (222 mg, 0.5 mmol, 5 mol %) in water (50 mL) were added benzaldehyde (1.061 g, 10 mmol) and 2-amino-4-(trifluoromethyl)benzenethiol (2.13 g, 11 mmol, 1.1 equiv) and the mixture was stirred magnetically at 40 °C. After completion of the reaction (4.5 h, TLC), the mixture was extracted with EtOAc (2 × 20 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg). The residue was purified by the recrystallization from distilled methanol to afford the 2-phenyl-5-trifluoromethyl-benzothiazole[9] as light green solid, (2.29 g, 82%). mp: 131-133 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.48 – 7.52 (m, 3H), 7.60 (dd, 1H, *J* = 1.2 Hz, 8.4 Hz), 7.97 (d, 1H, *J* = 8.4 Hz), 8.06 – 8.09 (m, 2H), 8.32 (s, 1H); IR (KBr) ν_{max}: 2925, 1630, 1490, 1237 cm^{-1}; MS (ESI) $(M + H)^+$ = 280.4.

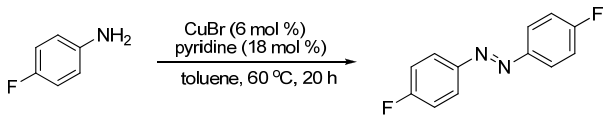
Preparation of 2-(2-bromophenyl)-5-(trifluoromethyl)benzo[*d*]thiazole (starting benzothiazole of 4g):-



To a magnetically stirred suspension of SDOSS (222 mg, 0.5 mmol, 5 mol %) in water (50 mL) were added 2-bromobenzaldehyde (1.850 g, 10 mmol) and 2-amino-4-(trifluoromethyl)benzenethiol (2.13 g, 11 mmol, 1.1 equiv) and the mixture was stirred magnetically at 40 °C. After completion of the reaction (4 h, TLC), the mixture was extracted with EtOAc (2 × 20 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg). The residue was purified by the recrystallization from distilled methanol to afford the 2-(2-bromophenyl)-5-(trifluoromethyl)benzo[*d*]thiazole as off white solid, (3.009 g, 84%). mp: 110-112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.39 (dt, 1H, *J* = 1.8 Hz, 8.0 Hz), 7.50 (dt, 1H, *J* = 1.2 Hz, 7.6 Hz),

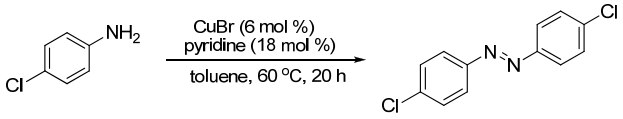
7.70 (dd, 1H, J = 1.2 Hz, 8.4 Hz), 7.78 (dd, 1H, J = 1.1 Hz, 8.0 Hz), 8.06 – 8.09 (m, 2H), 8.43 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 120.1, 120.8, 120.8, 120.9, 121.8, 121.8, 121.8, 121.9, 122.1, 122.2, 122.8, 125.6, 127.8, 128.8, 129.2, 129.5, 131.8, 132.2, 133.8, 134.3, 139.4, 152.2, 167.7; IR (KBr) ν_{max}: 2973, 1647, 1545, 1279, 1250 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{14}H_7BrF_3NSNa$, 379.9332; found, 379.9344.

Preparation of bis-(4-fluorophenyl)-diazene[10] (starting azo compound of 5b):-



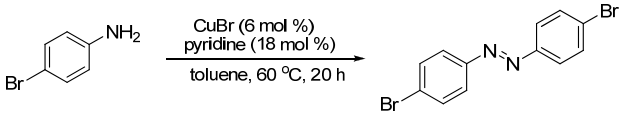
To a magnetically stirred mixture of CuBr (25.8 mg, 0.18 mmol, 6 mol %) and pyridine (42.7 mg, 0.54 mmol, 18 mol %) in toluene (6 mL) was added 4-fluoro aniline (666 mg, 6 mmol, 2 equiv) and the mixture was further stirred magnetically at 60 °C under air. After completion of the reaction (20 h, TLC), the mixture was cooled to rt and the solvent was evaporated to dryness under vacuum (30 mm Hg). The residue was passed through flash chromatography column (silica-gel: 230-400 mesh) and eluted with hexane to afford the bis-(4-fluorophenyl)-diazene as yellow solid, (622 mg, 95%). mp: 99-101 °C; TLC (Hexane:EtOAc, 96:4 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20 (t, 4H, J = 8.5 Hz), 7.91 – 7.94 (m, 4H); IR (KBr) ν_{max}: 2922, 1276, 1260, 1051, 1030 cm^{-1}; MS (ESI) $(M + H)^+$ = 219.3.

Preparation of bis-(4-chlorophenyl)-diazene[10] (starting azo compound of 5d):-



To a magnetically stirred mixture of CuBr (25.8 mg, 0.18 mmol, 6 mol %) and pyridine (42.7 mg, 0.54 mmol, 18 mol %) in toluene (6 mL) was added 4-chloro aniline (765 mg, 6 mmol, 2 equiv) and the mixture was further stirred magnetically at 60 °C under air. After completion of the reaction (20 h, TLC), the mixture was cooled to rt and the solvent was evaporated to dryness under vacuum (30 mm Hg). The residue was passed through flash chromatography column (silica-gel: 230-400 mesh) and eluted with hexane to afford the bis-(4-chlorophenyl)-diazene as yellow solid, (678 mg, 90%). mp: 185-187 °C; TLC (Hexane:EtOAc, 96:4 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.47 – 7.51 (m, 4H), 7.85 – 7.88 (m, 4H); IR (KBr) ν_{max}: 2920, 1272, 1262, 1059, 1031 cm^{-1}; MS (ESI) $(M + H)^+$ = 252.3.

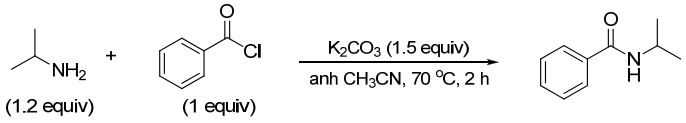
Preparation of bis-(4-bromophenyl)-diazene[10] (starting azo compound of 5f):-



To a magnetically stirred mixture of CuBr (25.8 mg, 0.18 mmol, 6 mol %) and pyridine (42.7 mg, 0.54 mmol, 18 mol %) in toluene (6 mL) was added 4-bromo aniline (1.032 g, 6 mmol, 2

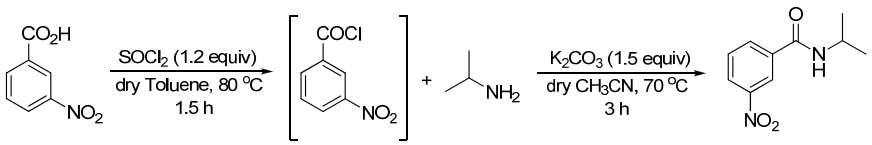
equiv) and the mixture was further stirred magnetically at 60 °C under air. After completion of the reaction (20 h, TLC), the mixture was cooled to rt and the solvent was evaporated to dryness under vacuum (30 mm Hg). The residue was passed through flash chromatography column (silica-gel: 230-400 mesh) and eluted with hexane to afford the bis-(4-bromophenyl)-diazene as reddish solid, (612 mg, 60%). mp: 205-207 °C; TLC (Hexane:EtOAc, 96:4 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.64 – 7.67 (m, 4H), 7.78 – 7.81 (m, 4H); IR (KBr) ν_{max}: 2921, 1270, 1260, 1057, 1030 cm^{-1}; MS (ESI) $(M + H)^+ = 341.2$.

Preparation of *N*-isopropyl benzamide (starting benzamide derivative of 6c):-



To a magnetically stirred solution of K_2CO_3 (2.073 g, 15 mmol, 1.5 equiv) and isopropylamine (709 mg, 12 mmol, 1.03 mL, 1.2 equiv) in anh CH_3CN (20 mL) was added benzoyl chloride (1.405 g, 10 mmol, 1.16 mL, 1 equiv) and the mixture was stirred magnetically at 70 °C. After completion of the reaction (2 h, TLC), the reaction mixture was cooled to rt; filtered off and the solvent was evaporated to dryness under vacuum (30 mm Hg) to afford the *N*-isopropyl benzamide[11] as off white solid, (1.583 g, 97%). mp: 99-101 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.26 (d, 6H, J = 6.6 Hz), 4.26 – 4.31 (m, 1H), 6.08 (bs, 1H, D_2O exchangeable), 7.38 – 7.42 (m, 2H), 7.45 – 7.49 (m, 1H), 7.74 – 7.76 (m, 2H); IR (KBr) ν_{max}: 3734, 3296, 2971, 1634, 1539, 1275, 1260 cm^{-1}; MS (ESI) $(M + H)^+ = 164.3$.

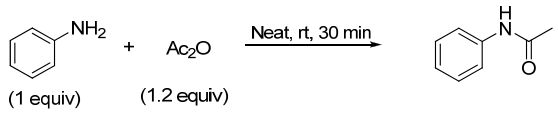
Preparation of *N*-isopropyl-3-nitro-benzamide (starting benzamide derivative of 6d):-



3-Nitrobenzoic acid (1.671 g, 10 mmol) was treated with $SOCl_2$ (1.427 g, 12 mmol, 0.88 mL, 1.2 equiv) in dry toluene (20 mL) at 80 °C until quenching of an aliquot with few drops of MeOH revealed the complete consumption of acid and appearance of new spot in TLC (1.5 h). The excess $SOCl_2$ was distilled off and the reaction mixture was charged with K_2CO_3 (2.073 g, 15 mmol, 1.5 equiv) and isopropylamine (709 mg, 12 mmol, 1.03 mL, 1.2 equiv) in anh CH_3CN (20 mL) and the mixture was stirred magnetically at 70 °C. After completion of the reaction (3 h, TLC), the reaction mixture was cooled to rt; filtered off and the solvent was evaporated to dryness under vacuum (30 mm Hg). The residue was passed through flash chromatography column (silica-gel: 230-400 mesh) and eluted with hexane/EtOAc solvent system to afford the *N*-isopropyl-3-nitro-benzamide[12] as off white solid, (1.312 g, 63%). mp: 210-212 °C; TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.31 (d, 6H, J = 6.6 Hz), 4.29 – 4.34 (m, 1H), 6.15 (bs, 1H, D_2O exchangeable), 7.64 (t, 1H, J = 8.0 Hz), 8.15 – 8.17

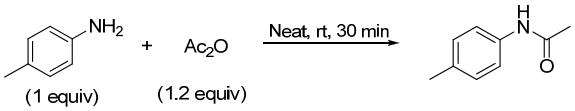
(m, 1H), 8.34 – 8.36 (m, 1H), 8.56 – 8.57 (m, 1H); IR (KBr) ν_{max}: 3292, 2975, 1637, 1527, 1346 cm^{-1}; MS (ESI) $(M + H)^+ = 209.4$.

Preparation of *N*-phenylacetamide (starting acetanilide derivative of 7a):-



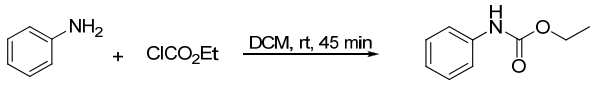
Aniline (279 mg, 3 mmol) was treated with Ac_2O (367 mg, 3.6 mmol, 0.34 mL, 1.2 equiv) under neat condition at rt. After completion of the reaction (30 min, TLC), the reaction mixture was diluted with H_2O (10 mL) and extracted with EtOAc (2 × 5 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg) to afford the *N*-phenylacetamide[13] as off white solid, (397 mg, 98%), mp: 112-114 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.26 (s, 3H), 7.09 (t, 1H, J = 7.4 Hz), 7.30 (t, 2H, J = 7.8 Hz), 7.49 – 7.51 (m, 2H), 7.75 (bs, 1H, D_2O exchangeable); IR (KBr) ν_{max}: 3292, 2946, 1668, 1511, 1320, 823 cm^{-1}; MS (ESI) $(M + H)^+ = 136.3$.

Preparation of *N*-*p*-tolyl-acetamide (starting acetanilide derivative of 7b):-



p-Toluidine (428 mg, 3 mmol) was treated with Ac_2O (367 mg, 3.6 mmol, 0.34 mL, 1.2 equiv) under neat condition at rt. After completion of the reaction (30 min, TLC), the reaction mixture was diluted with H_2O (10 mL) and extracted with EtOAc (2 × 5 mL). The EtOAc layer was separated from the aqueous layer, dried (anh Na_2SO_4); filtered off and evaporated to dryness under vacuum (30 mm Hg) to afford the *N*-*p*-tolyl-acetamide[13] as off white solid, (434 mg, 97%), mp: 145-147 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.18 (s, 3H), 2.32 (s, 3H), 7.13 (d, 2H, J = 8.2 Hz), 7.38 (d, 2H, J = 8.2 Hz); IR (KBr) ν_{max}: 3290, 2944, 1661, 1510, 1321, 820 cm^{-1}; MS (ESI) $(M + H)^+ = 150.4$.

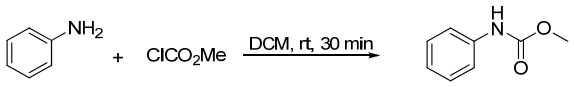
Preparation of ethyl phenylcarbamate (starting carbamate derivative of 8a):-



Aniline (279 mg, 3 mmol) was treated with ethyl chloroformate (326 mg, 3 mmol, 0.29 mL, 1 equiv) in DCM (6 mL) at rt. After completion of the reaction (45 min, TLC), the solvent was evaporated to dryness under vacuum (30 mm Hg). The residue was passed through flash chromatography column (silica-gel: 230-400 mesh) and eluted with hexane/EtOAc solvent system to afford the ethyl phenylcarbamate[14] as off white liquid, (481 mg, 97%). TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.28 (t, 3H, J = 7.1 Hz), 4.21 (q, 2H, J = 7.1 Hz), 6.92 (bs, 1H), 7.01 – 7.05 (m, 1H), 7.24 – 7.29 (m, 2H), 7.35 –

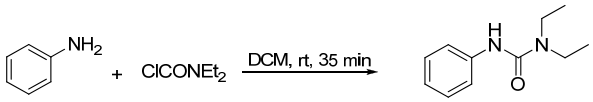
7.39 (m, 2H); IR (Neat) ν_{max}: 3290, 2947, 1724, 1671, 1513, 1323 cm^{-1}; MS (ESI) $(M + H)^+$ = 166.3.

Preparation of methyl phenylcarbamate (starting carbamate derivative of 8b):-



Aniline (279 mg, 3 mmol) was treated with methyl chloroformate (340 mg, 3.6 mmol, 0.28 mL, 1.2 equiv) in DCM (6 mL) at rt. After completion of the reaction (30 min, TLC), the solvent was evaporated to dryness under vacuum (30 mm Hg) to afford the methyl phenylcarbamate[15] as light yellow solid, (431 mg, 95%). mp: 49-51 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.81 (s, 3H), 6.67 (bs, 1H, D_2O exchangeable), 7.08 – 7.12 (m, 1H), 7.31 – 7.35 (m, 2H), 7.40 – 7.42 (m, 2H); IR (KBr) ν_{max}: 3289, 2949, 1722, 1682, 1510, 1321 cm^{-1}; MS (ESI) $(M + H)^+$ = 152.3.

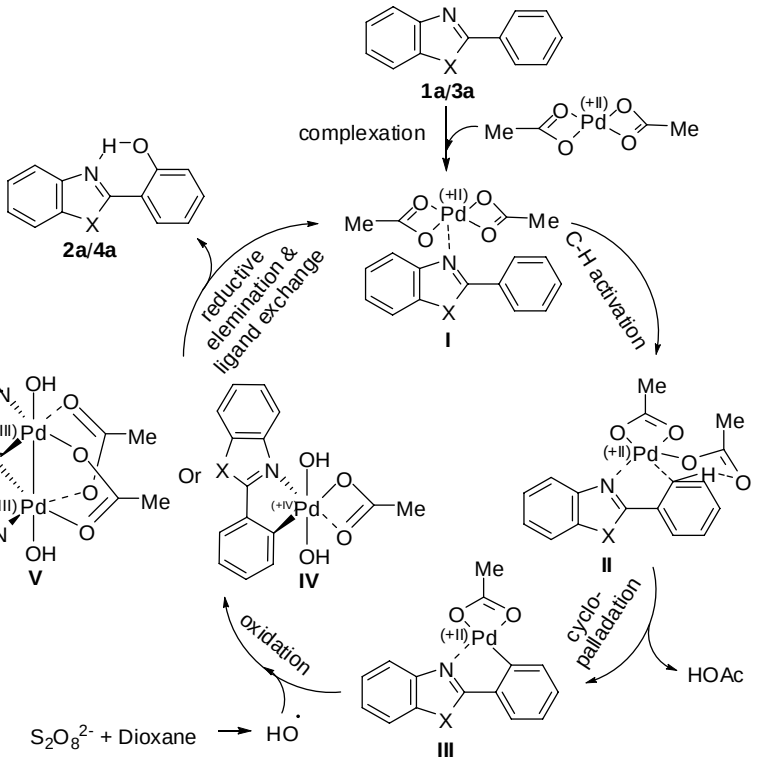
Preparation of 1,1-diethyl-3-phenylurea (starting urea derivative of 9):-



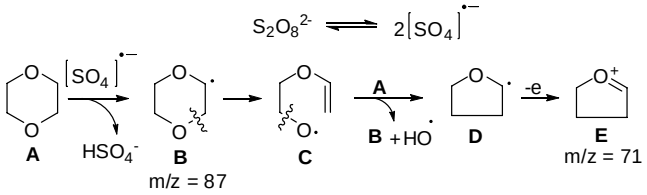
Aniline (279 mg, 3 mmol) was treated with diethylcarbamoyl chloride (407 mg, 3 mmol, 0.38 mL, 1 equiv) in DCM (6 mL) at rt. After completion of the reaction (35 min, TLC), the solvent was evaporated to dryness under vacuum (30 mm Hg). The residue was passed through flash chromatography column (silica-gel: 230-400 mesh) and eluted with hexane/EtOAc solvent system to afford the 1,1-diethyl-3-phenylurea[16] as deep brown solid, (461 mg, 80%). mp: 79-81 °C; TLC (Hexane:EtOAc, 70:30 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.24 (t, 6H, J = 7.2 Hz), 3.39 (q, 4H, J = 7.2 Hz), 6.35 (bs, 1H, D_2O exchangeable), 7.01 – 7.06 (m, 1H), 7.27 – 7.31 (m, 2H), 7.40 – 7.42 (m, 2H); IR (Neat) ν_{max}: 3287, 2948, 1724, 1711, 1510, 1312 cm^{-1}; MS (ESI) $(M + H)^+$ = 193.4.

5. Proposed Mechanistic Pathway and Relevant Studies:

Scheme 5A. Plausible mechanistic pathway for the C_{sp2}-H activation mediated direct aryl hydroxylation.



Scheme 5B. In situ generation of hydroxyl radical by oxidative degradation of 1,4-dioxane in the presence of persulfate anion.



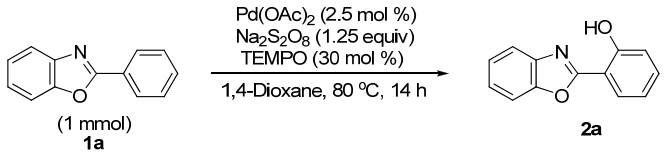
5.1. Rational for consideration of hydroxyl radical generation from 1,4-dioxane: The dissociation of 1,4-dioxane is complex and neither the theoretical nor experimental work alone would provide a satisfactory, quantitative description of the reaction mechanism. The homolytic cleavage for the ring opening (C-O bond cleavage) of 1,4-dioxane (**A**) followed by isomerisation and dissociation of the linear species generate the hydroxyl radical (Phys. Chem. Chem. Phys. 2011, **13**, 3686). However, high temperature (1550-2100 K) is required to generate the hydroxyl radical by ring opening (C-O homolytic cleavage). We reasoned that the hydroxyl radical generation from 1,4-dioxane may be achieved under milder condition in the presence of an oxidant that would abstract H from 1,4-dioxane and facilitate its dissociation by ring opening C-O cleavage involving free radical mechanism. The following mechanism is proposed for the

generation of hydroxyl radical from $Na_2S_2O_8$ and 1,4-dioxane but under milder reaction condition. Decomposition of the persulfate anion generates the sulfate anion radical (J. Phys. Chem. 1967, **71**, 1472; J. Phys. Chem. 1967, **71**, 2511; J. Org. Chem. 1987, **52**, 4689; J. Am. Chem. Soc. 1996, **118**, 13111). Sulfate anion radical has the ability to abstract C-H hydrogen (J. Am. Chem. Soc. 1996, **118**, 13111) and undergoes H-abstraction from 1,4-dioxane (**A**) to form the 1,4-dioxan-2yl radical (**B**). The radical **B** undergoes homolytic ring C-O cleavage (Phys. Chem. Chem. Phys. 2011, **13**, 3686) to produce the ethylene glycol vinyl ether (EGVE) radical **C**. On further homolytic C-O cleavage, **C** is converted to the tetrahydrofuran-2yl radical (**D**) and oxygen diradical. H-Abstraction by the oxygen diradical from another molecule of **A** forms the hydroxyl radical and the radical **B** to propagate the radical chain process.

To substantiate this mechanistic proposal we performed GC-MS and MS-MS (ms^2) studies to identify the relevant ion species. When aliquot portions (at an interval of 2 h) of the reaction mixture during the treatment of 1,4-dioxane (**A**) with $Na_2S_2O_8$ at 80 °C was subjected to GC-MS analyses the ion peak corresponding to **B** (m/z 87) and **D**/**E** (m/z 71) were detected. The GC-MS of **A** (in the absence of $Na_2S_2O_8$) exhibits the ion at m/z 89 ($\mathbf{A}H^+$) and 88 ($\mathbf{A}^+$) but no ion peak at m/z 87 and 71 could be detected. Some of the daughter ions observed in the ms^2 of the ion at m/z 71 were also observed in the ms^2 of the ion at m/z 87 (e.g. 70.81 vs 70.82; 42.93 vs 42.87) suggesting that the ion at m/z 71 is derived from the ion at m/z 87 through loss of active oxygen species. Further mass fragmentation (ms^2) of the ions at m/z 87 and 71 were supportive to their structures as **B** and **D**/**E**, respectively. The identity of **D**/**E** was further confirmed by comparison with the GC-MS and ms^2 (of the ion at m/z 71) spectra of an authentic sample of THF. The GC-MS spectra of the aliquots of the reaction mixture during the treatment of 2-phenylbenzoxazole (**1a**) with $Na_2S_2O_8$ and 1,4-dioxane at 80 °C also revealed the presence of the ion peak m/z 87 and 71 corresponding to **B** and **D**/**E**, respectively (ms^2 spectra of these ion were found to be similar to those derived from the reaction mixture for the treatment of **A** with $Na_2S_2O_8$ at 80 °C).

5.2. Evidence for radical formation:

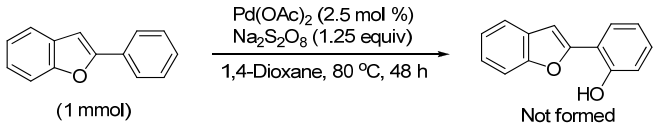
Scheme 5C. Effect of radical scavenger.



To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in 1,4-dioxane (6 mL) under N_2 was added **1a** (195 mg, 1 mmol) and TEMPO (46.8 mg, 30 mol %) and the resultant mixture was treated at 80 °C. After completion of the reaction (14 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane (200 mL) afforded the **2a** as light yellow solid, (35.9 mg, 17%).

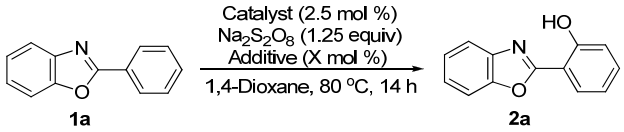
5.3. Relevance/importance of the complex formation via coordination of the nitrogen atom of the directing group with the Pd catalyst:

Scheme 5D. Reaction with 2-phenyl benzofuran.



5.4. Relevance/importance of the ligand assisted intramolecular aryl C-H proton abstraction:

Table 5A. The role of the ligand for intramolecular proton abstraction during the aryl C_{sp2}-H activation for direct aryl hydroxylation of 1a to form 2a.[a]

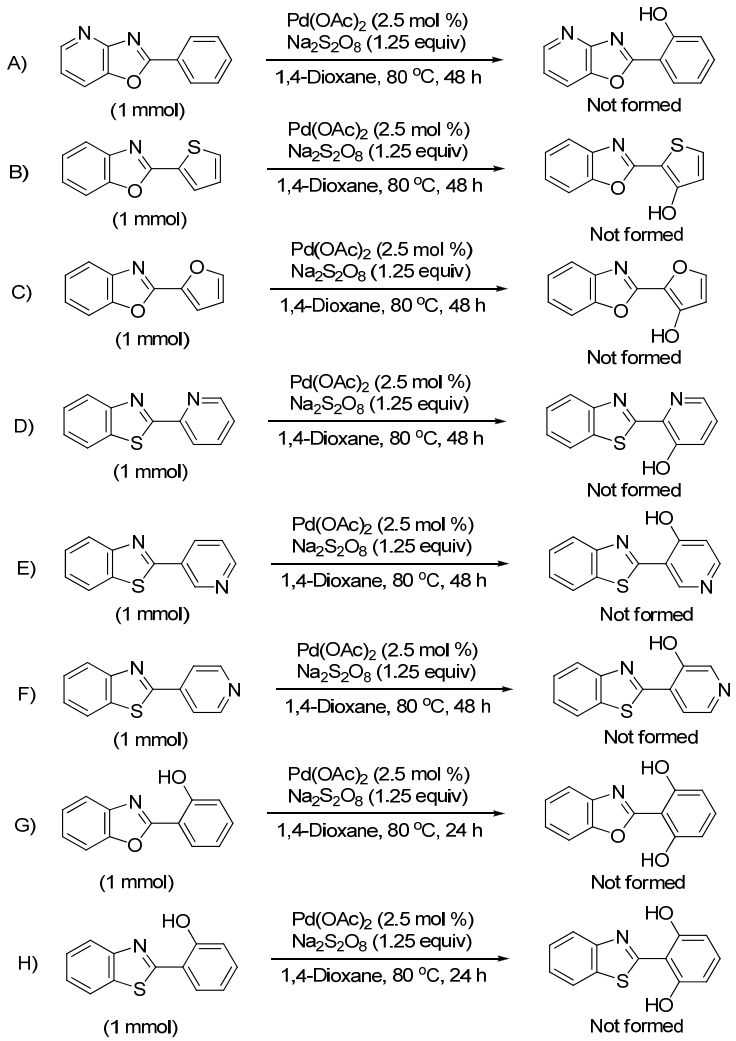


Entry	Catalyst	Additive (mol%)	Yield (%)[b]
1	$Pd(OAc)_2$	None	62
2	$Pd(OAc)_2$	NaOAc (5)	60
3	$Pd(OAc)_2$	KOAc (5)	61
4	$Pd(TFA)_2$	NH_4OAc (5)	39
5	$Pd(TFA)_2$	KOAc (5)	40
6	$Pd(TFA)_2$	KOAc (5) + 18-C-6 (5)	42
7	$PdCl_2$	NaOAc (5)	28
8	$PdCl_2$	KOAc (5)	37
9	$PdCl_2$	NH_4OAc (5)	trace
10	$PdCl_2$	KOAc (5) + 18-C-6 (5)	35
11	Na_2PdCl_4	NaOAc (5)	19
12	Na_2PdCl_4	KOAc (5)	22
13	Na_2PdCl_4	NH_4OAc (5)	trace
14	Na_2PdCl_4	KOAc (5) + 18-C-6 (5)	20
15	$[PdCl_2(PPh_3)_2]$	NaOAc (5)	27
16	$[PdCl_2(PPh_3)_2]$	KOAc (5)	26
17	$[PdCl_2(PPh_3)_2]$	NH_4OAc (5)	trace
18	$[PdCl_2(PPh_3)_2]$	KOAc (5) + 18-C-6 (5)	28
19	$Pd(PPh_3)_4$	NaOAc (5)	24
20	$Pd(PPh_3)_4$	KOAc (5)	26
21	$Pd(PPh_3)_4$	NH_4OAc (5)	trace
22	$Pd(PPh_3)_4$	KOAc (5) + 18-C-6 (5)	29

[a]**1a** (1 mmol) in 1,4-dioxane (6 mL) was treated with $Na_2S_2O_8$ (1.25 mmol, 1.25 equiv) at 80 °C for 14 h in the presence of the Pd-compound (2.5 mol %) and the additive. [b]The isolated yield of **2a**.

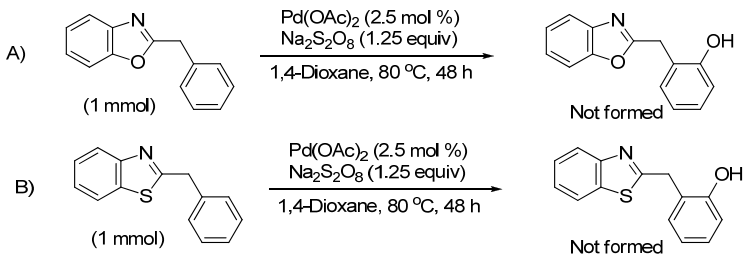
5.5. Relevance/importance of the formation of the complex II for C-H activation.

Scheme 5E. Reactions with substrates containing additional donor centre.

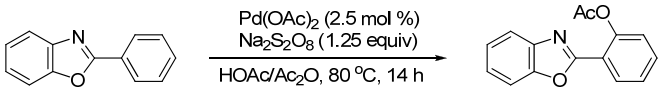


5.6. Relevance/importance of the formation of the complex II for C-H activation.

Scheme 5F. Effect of the presence of methylene spacer between the DG and the aryl moiety.



6. Typical procedure for the formation of *O*-acetoxylation product, 2-(benzo[*d*]oxazol-2-yl)phenyl acetate 2aa, from 1a without the aqueous workup:-



(1 mmol) **1a** **2aa**

To a magnetically stirred mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 2.5 mol %) and $Na_2S_2O_8$ (298 mg, 1.25 mmol, 1.25 equiv) in HOAc-Ac_2O (1:1) (6 mL) under N_2 atmosphere was added **1a** (195 mg, 1 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (24 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The EtOAc extracts were combined with the above supernatant liquid, dried (anh Na_2SO_4), filtered and concentrated under vacuum (30 mm Hg) to afford the crude product which on passing through flash chromatography column (silica-gel: 230-400 mesh) and elution with hexane/EtOAc (400 mL) afforded the **2aa** as light yellow solid, (139 mg, 55%), mp: 78-80 °C. TLC (Hexane:EtOAc, 80:20 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.52 (s, 3H), 7.26 (dd, 1H, J = 1.0 Hz, 8.1 Hz), 7.36 – 7.42 (m, 2H), 7.45 (dt, 1H, J = 1.1 Hz, 7.8 Hz), 7.57 – 7.62 (m, 2H), 7.77 – 7.80 (m, 1H), 8.33 (dd, 1H, J = 1.6 Hz, 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 21.4, 110.5, 120.4, 120.4, 124.1, 124.6, 125.5, 126.5, 130.3, 132.5, 142.0, 149.3, 150.2, 159.8, 170.0; IR (KBr) ν_{max}: 2979, 1742, 1647, 1539, 1270, 1250 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{15}H_{11}NO_3Na$, 276.0637; found, 276.0652.

7. Characterization of compounds

2-Benzoxazol-2-yl-phenol[2] (2a, Table 1):- Light yellow solid, mp: 121-123 °C. TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.05 (dt, 1H, J = 1.0 Hz, 7.4 Hz), 7.16 (dd, 1H, J = 1.0 Hz, 8.3 Hz), 7.38 – 7.44 (m, 2H), 7.45 – 7.50 (m, 1H), 7.62 – 7.66 (m, 1H), 7.74 – 7.79 (m, 1H), 8.06 (dd, 1H, J = 1.7 Hz, 7.9 Hz), 11.51 (s, 1H); IR (KBr) ν_{max}: 3397, 2925, 1277, 1260, 1031 cm^{-1}; MS (ESI) $(M + H)^+$ = 212.3.

2-Benzoxazol-2-yl-3-chloro-phenol (2b, Table 1):- Off white solid; mp: 155-157 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.94 (d, 2H, J = 8.2 Hz), 7.18 (t, 1H, J = 8.2 Hz),7.27 – 7.32 (m, 2H), 7.55 – 7.57 (m, 1H), 7.62 – 7.64 (m, 1H), 12.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 109.7, 111.1, 116.4, 119.1, 122.4, 125.3, 125.8, 132.6, 133.0, 138.3, 149.1, 161.0, 161.9; IR (KBr) ν_{max}: 3395, 2923, 1270, 1264, 1052, 1027 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{13}H_8ClNO_2Na$, 268.0141; found 268.0150.

2-Benzoxazol-2-yl-5-chloro-phenol (2c, Table 1):- Off white solid; mp: 165-167 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.00 (dd, 1H, J = 2.0 Hz, 8.5 Hz), 7.15 (d, 1H, J = 2.0 Hz), 7.39 – 7.41 (m, 2H), 7.60 – 7.62 (m, 1H), 7.72 – 7.74 (m, 1H), 7.95 (d, 1H, J = 8.4 Hz), 11.65 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 109.3, 110.7, 117.7, 119.3, 120.2, 125.2, 125.6, 128.0, 139.2, 139.8, 149.1, 159.3, 162.2; IR (KBr) ν_{max}: 3396,

2921, 1277, 1260, 1053, 1029 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{13}H_8ClNO_2Na$, 261.0141; found 268.0138.

2-(Benzo[*d*]oxazol-2-yl)-4-chlorophenol (2d, Table 1):- Off white solid; mp: 156-159 ^oC; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.07 (d, 1H, J = 8.8 Hz), 7.37 – 7.44 (m, 3H), 7.61 – 7.64 (m, 1H), 7.73 – 7.76 (m, 1H), 8.01 (d, 1H, J = 2.6 Hz), 11.46 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 110.8, 111.6, 119.0, 119.5, 124.4, 125.3, 125.8, 126.4, 133.4, 139.8, 149.2, 157.2, 161.7; IR (KBr) ν_{max}: 2976, 1643, 1547, 1279, 1253 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{13}H_8ClNO_2Na$, 268.0141; found 268.0152.

2-Benzoxazol-2-yl-3-bromo-phenol (2e, Table 1):- White solid; mp: 137-139 ^oC; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.08 – 7.10 (m, 1H), 7.18 – 7.22 (m, 1H), 7.25 – 7.29 (m, 1H), 7.38 – 7.44 (m, 2H), 7.66 – 7.68 (m, 1H), 7.74 – 7.76 (m, 1H), 12.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 111.1, 111.3, 117.0, 119.1, 120.6, 125.3, 125.9, 126.1, 133.0, 138.5, 149.0, 161.1, 161.8; IR (KBr) ν_{max}: 3394, 2922, 1272, 1260, 1057, 1030 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{13}H_8BrNO_2Na$, 311.9636; found 311.9644.

2-(Benzo[*d*]oxazol-2-yl)-4-bromophenol[17] (2f, Table 1):- Off white solid; mp: 167-169 ^oC; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.05 (d, 1H, J = 8.8 Hz), 7.40 – 7.46 (m, 2H), 7.54 (dd, 1H, J = 2.5 Hz, 8.8 Hz), 7.63 – 7.66 (m, 1H), 7.75 – 7.78 (m, 1H), 8.18 (d, 1H, J = 2.5 Hz), 11.50 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 110.8, 111.3, 112.2, 119.4, 119.5, 125.3, 125.9, 129.4, 136.2, 149.2, 157.7, 161.6; IR (KBr) ν_{max}: 2978, 1640, 1541, 1277, 1255 cm^{-1}; MS (ESI) $(M + H)^+$ = 291.4.

2-Benzoxazol-2-yl-4-nitro-phenol (2g, Table 1):- Off white solid; mp: 184-186 ^oC; TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.25 (d, 1H, J = 9.2 Hz), 7.46 – 7.52 (m, 2H), 7.69 – 7.74 (m, 1H), 7.78 – 7.83 (m, 1H), 8.35 (dd, 1H, J = 2.8 Hz, 9.2 Hz), 9.01 (d, 1H, J = 2.8 Hz), 12.32 (bs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 110.6, 111.1, 118.3, 119.6, 123.6, 125.7, 126.5, 128.6, 139.3, 140.5, 149.2, 160.9, 163.4; IR (KBr) ν_{max}: 3294, 2972, 1637, 1535, 1277, 1260 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{13}H_8N_2O_4Na$, 279.0379; found 279.0382.

2-(5-Methyl-benzoxazol-2-yl)-phenol[18] (2h, Table 1):- Yellowish solid; mp: 141-143 ^oC; TLC (Hexane:EtOAc, 100:0 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.50 (s, 3H), 6.99 – 7.01 (m, 1H), 7.12 (dd, 1H, J = 0.8 Hz, 8.4 Hz), 7.18 – 7.20 (m, 1H), 7.42 – 7.44 (m, 1H), 7.46 – 7.50 (m, 1H), 7.52 – 7.53 (m, 1H), 8.02 (dd, 1H, J = 1.6 Hz, 7.9 Hz), 11.53 (s, 1H); IR (KBr) ν_{max}: 3395, 2923, 1274, 1262, 1055, 1031 cm^{-1}; MS (ESI) $(M + H)^+$ = 226.4.

2-(6-Methyl-benzoxazol-2-yl)-phenol[19] (2i, Table 1):- Light yellow solid; mp: 123-125 ^oC; TLC (Hexane:EtOAc, 100:0 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.48 (s, 3H), 6.97 (t, 1H, J = 7.4 Hz), 7.10 (d, 1H, J = 8.3 Hz), 7.15 (d, 1H, J = 8.0 Hz), 7.36 (s, 1H), 7.40 (t, 1H, J = 7.8 Hz), 7.55 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 7.8 Hz), 11.46 (s, 1H); IR (KBr) ν_{max}: 3392, 2921, 1275, 1260, 1052, 1030 cm^{-1}; MS (ESI) $(M + H)^+$ = 226.5.

2-(6-Chlorobenzo[*d*]oxazol-2-yl)phenol[19] (2j, Table 1):- Off white solid; mp: 146-148 ^oC; TLC (Hexane:EtOAc, 93:7 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.02 (dt, 1H, J = 1.0 Hz, 7.4 Hz), 7.13 (dd, 1H, J = 1.0 Hz, 8.4 Hz), 7.38 (dd, 1H, J = 2.0 Hz, 8.5 Hz), 7.46 (dt,

1H, J = 1.6 Hz, 7.3 Hz), 7.63 – 7.66 (m, 2H), 8.01 (dd, 1H, J = 1.7 Hz, 8.0 Hz), 11.24 (s, 1H); IR (KBr) ν_{max}: 3323, 2974, 1645, 1538, 1277, 1250 cm^{-1}; MS (ESI) $(M + H)^+$ = 246.8.

2-Naphtho[2,3-*d*]oxazol-2-yl-phenol (2k, Table 1):- Light yellow solid; mp: 225-227 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.07 (dt, 1H, J = 1.1 Hz, 7.4 Hz), 7.18 (d, 1H, J = 1.0 Hz, 8.3 Hz), 7.49 – 7.57 (m, 3H), 7.99 – 8.04 (m, 3H), 8.12 (dd, 1H, J = 1.7 Hz, 7.9 Hz), 8.18 (s, 1H), 11.62 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 106.6, 110.3, 116.6, 117.5, 119.7, 125.1, 125.8, 127.6, 128.0, 128.5, 131.6, 131.7, 134.2, 139.8, 148.0, 159.4, 165.0; IR (KBr) ν_{max}: 2922, 1275, 1260, 1054, 1033 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{17}H_{11}NO_2Na$, 284.0687; found 284.0689.

3-Benzoxazol-2-yl-naphthalen-2-ol[20] (2l, Table 1):- Off white solid; mp: 160-162 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.34 – 7.38 (m, 1H), 7.42 – 7.46 (m, 3H), 7.48 – 7.52 (m, 1H), 7.66 – 7.68 (m, 1H), 7.74 (d, 1H, J = 8.3 Hz), 7.78 – 7.80 (m, 1H), 7.89 (d, 1H, J = 8.3 Hz), 8.64 (s, 1H), 11.29 (bs, 1H); IR (KBr) ν_{max}: 3321, 2975, 1632, 1345 cm^{-1}; MS (ESI) $(M + H)^+$ = 262.4.

2-Benzothiazol-2-yl-phenol[1] (4a, Table 1):- Off white solid; mp: 129-131 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.96 (t, 1H, J = 7.6 Hz), 7.11 (d, 1H, J = 8.3 Hz), 7.36 – 7.42 (m, 2H), 7.50 (t, 1H, J = 7.5 Hz), 7.69 (d, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 8.1 Hz), 12.52 (s, 1H); IR (KBr) ν_{max}: 3394, 2921, 1277, 1260, 1056, 1030 cm^{-1}; MS (ESI) $(M + H)^+$ = 228.4.

2-Benzothiazol-2-yl-5-chloro-phenol[1] (4b, Table 1):- Off white solid; mp: 106-108 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.97 (dd, 1H, J = 2.1 Hz, 8.5 Hz), 7.15 (d, 1H, J = 2.0 Hz), 7.44 – 7.49 (m, 1H), 7.53 – 7.57 (m, 1H), 7.64 (d, 1H, J = 8.4 Hz), 7.92 – 7.97 (m, 1H), 8.00 – 8.04 (m, 1H), 12.77 (s, 1H); IR (KBr) ν_{max}: 3779, 3440, 2922, 1251, 1051 cm^{-1}; MS (ESI) $(M + H)^+$ = 262.7.

2-Benzothiazol-2-yl-3-bromo-phenol (4c, Table 1):- Light yellow solid; mp: 129-131 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.10 (dd, 1H, J = 1.5 Hz, 8.3 Hz), 7.16 (t, 1H, J = 8.2 Hz), 7.27 (dd, 1H, J = 1.4 Hz, 7.9 Hz), 7.45 (dt, 1H, J = 1.1 Hz, 7.1 Hz), 7.54 (dt, 1H, J = 1.2 Hz, 7.2 Hz), 7.93 – 7.96 (m, 1H), 8.01 – 8.03 (m, 1H), 14.59 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 117.1, 117.9, 121.0, 121.8, 122.1, 125.3, 125.9, 126.8, 131.9, 133.3, 148.7, 161.0, 167.2; IR (KBr) ν_{max}: 3373, 2921, 2853, 1275, 1260, 1046 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{13}H_8BrNOSNa$, 327.9408; found 327.9420.

2-(Benzo[*d*]thiazol-2-yl)-4-nitrophenol[1] (4d, Table 1):- Yellow solid; mp: 215-217 °C; TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20 (d, 1H, J = 5.9 Hz), 7.51 (dt, 1H, J = 1.2 Hz, 7.4 Hz), 7.58 (dt, 1H, J = 1.2 Hz, 7.3 Hz), 7.97 – 8.00 (m, 1H), 8.04 – 8.11 (m, 1H), 8.28 (dd, 1H, J = 2.6 Hz, 9.1 Hz), 8.66 (d, 1H, J = 2.6 Hz), 13.66 (bs, 1H); IR (KBr) ν_{max}: 3323, 2981, 1633, 1527, 1349 cm^{-1}; MS (ESI) $(M + H)^+$ = 273.4.

2-(5-Chlorobenzo[*d*]thiazol-2-yl)phenol[1] (4e, Table 1):- Deep brown solid; mp: 193-195 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.98-7.02 (m, 1H), 7.14 (dd, 1H, J = 1.0 Hz, 8.4 Hz), 7.41 – 7.45 (m, 2H), 7.71 (dd, 1H, J = 1.5 Hz, 7.9

Hz), 7.84 (d, 1H, J = 8.5 Hz), 8.02 (d, 1H, J = 1.9 Hz), 12.28 (s, 1H, D_2O exchangeable); IR (KBr) ν_{max}: 3324, 2970, 1641, 1539, 1276, 1251 cm^{-1}; MS (ESI) $(M + H)^+$ = 362.7.

2-(5-Trifluoromethyl-benzothiazol-2-yl)-phenol (4f, Table 1):- Off white solid; mp: 175-177 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.96 (dt, 1H, J = 1.1 Hz, 8.2 Hz), 7.10 (dd, 1H, J = 1.0 Hz, 8.4 Hz), 7.38 – 7.43 (m, 1H), 7.62 – 7.68 (m, 2H), 7.99 (d, 1H, J = 8.4 Hz), 8.23 (d, 1H, J = 1.0 Hz), 12.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 116.2, 118.1, 119.2, 119.2, 119.3, 119.3, 119.8, 120.0, 121.9, 121.9, 121.9, 122.0, 122.2, 122.7, 125.4, 128.1, 128.6, 129.0, 129.3, 129.6, 129.9, 133.5, 136.0, 151.6, 158.1, 171.4; IR (KBr) ν_{max}: 3374, 2920, 1276, 1262, 1050, 1030 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{14}H_8F_3NOSNa$, 318.0176; found 318.0172.

3-Bromo-2-(5-(trifluoromethyl)benzo[*d*]thiazol-2-yl)phenol (4g, Table 1):- Yellow solid; mp: 163-165 °C; TLC (Hexane:EtOAc, 97:3 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.03 (dd, 1H, J = 1.3 Hz, 8.3 Hz), 7.11 (t, 1H, J = 8.2 Hz), 7.20 (dd, 1H, J = 1.3 Hz, 7.8 Hz), 7.60 (dd, 1H, J = 1.0 Hz, 8.2 Hz), 7.97 (d, 1H, J = 8.4 Hz), 8.21 (s, 1H), 14.04 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 116.6, 118.1, 119.0, 119.1, 121.8, 122.1, 122.2, 122.2, 122.3, 122.6, 125.4, 125.5, 127.7, 129.4, 129.7, 131.7, 132.2, 132.6, 134.3, 136.5, 148.4, 161.0, 169.3; IR (KBr) ν_{max}: 3347, 2976, 1649, 1541, 1277, 1252 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{14}H_7BrF_3NOSNa$, 395.9282; found 395.9286.

2-Phenylazo-phenol (5a, Table 2):- Reddish solid, mp: 82-84 °C. TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.02 – 7.10 (m, 2H), 7.34 – 7.41 (m, 1H), 7.44 – 7.58 (m, 3H), 7.87 – 7.89 (m, 2H), 7.93 – 7.96 (m, 1H), 12.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 118.2, 120.0, 122.3, 129.4, 131.2, 133.3, 133.3, 137.4, 150.6, 152.8; IR (KBr) ν_{max}: 3478, 2923, 2857, 1733, 1613, 1459, 1225, 1144 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_{10}N_2ONa$, 221.0691; found, 221.0687.

5-Fluoro-2-(4-fluoro-phenylazo)-phenol (5b, Table 2):- Reddish solid; mp: 91-93 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.71 (dd, 1H, J = 2.6 Hz, 10.2 Hz), 6.76 – 6.81 (m, 1H), 7.17 – 7.23 (m, 2H), 7.84 – 7.88 (m, 1H), 7.89 – 7.94 (m, 2H), 13.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 104.8, 105.1, 107.9, 108.2, 116.0, 116.2, 116.4, 116.6, 124.1, 124.1, 124.8, 124.9, 135.1, 135.2, 146.8, 149.0, 155.0, 155.1, 163.1, 165.6; IR (KBr) ν_{max}: 3321, 2920, 1270, 1267, 1057, 1035 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_8F_2N_2ONa$, 257.0502; found, 257.0504.

***N,N′*-Bis-(4-fluoro-phenyl)-diazene *N*-oxide (5c, Table 2):-** Yellowish solid; mp: 83-85 °C; TLC (Hexane:EtOAc, 92:8 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.14 – 7.21 (m, 4H), 8.24 – 8.28 (m, 2H), 8.31 – 8.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 115.6, 115.6, 115.8, 115.9, 124.1, 124.5, 124.6, 124.9, 128.0, 128.1, 140.3, 144.3, 161.3, 163.3, 163.8, 165.8; IR (KBr) ν_{max}: 2922, 1270, 1268, 1057, 1029 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_8F_2N_2ONa$, 257.0502; found, 257.0502.

5-Chloro-2-(4-chloro-phenylazo)-phenol (5d, Table 2):- Reddish solid; mp: 167-169 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.04 – 7.06 (m, 2H), 7.47 – 7.52 (m, 2H), 7.79 – 7.83 (m, 2H), 7.84 – 7.87 (m, 1H), 12.92 (s, 1H); ^{13}C NMR

($CDCl_3$, 100 MHz) δ (ppm): 118.4, 120.8, 123.5, 124.2, 129.4, 129.7, 134.2, 148.8, 153.5; IR (KBr) ν_{max}: 3430, 2920, 1274, 1266, 1056, 1030 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_8Cl_2N_2ONa$, 288.9911; found, 288.9904.

***N,N′*-Bis-(4-chloro-phenyl)-diazene *N*-oxide (5e, Table 2):-** Yellow solid; mp: 147-149 °C; TLC (Hexane:EtOAc, 92:8 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.44 – 7.49 (m, 4H), 8.15 – 8.17 (m, 2H), 8.24 – 8.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 123.7, 127.1, 129.0, 129.1, 135.3, 138.1, 142.2, 146.6; IR (KBr) ν_{max}: 2925, 1270, 1261, 1057, 1034 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_8Cl_2N_2ONa$, 288.9911; found, 288.9902.

5-Bromo-2-(4-bromo-phenylazo)-phenol (5f, Table 2):- Yellow solid; mp: 189-191 °C; TLC (Hexane:EtOAc, 95:5 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.19 – 7.22 (m, 2H), 7.64 – 7.67 (m, 2H), 7.72 – 7.80 (m, 3H), 12.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 121.5, 123.7, 123.7, 125.9, 127.8, 132.4, 132.7, 134.3, 149.2, 153.3; IR (KBr) ν_{max}: 3433, 2921, 1273, 1262, 1056, 1037 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{12}H_8Br_2N_2ONa$, 376.8901; found, 376.8900.

2-Hydroxy-benzamide[21] (6a, Table 2):- Off white solid; mp: 140-142 °C; TLC (Hexane:EtOAc, 55:45 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.12 (bs, 2H, D_2O exchangeable), 6.85 – 6.89 (m, 1H), 7.00 (dd, 1H, J = 1.1 Hz, 8.3 Hz), 7.38 (dd, 1H, J = 1.6 Hz, 8.0 Hz), 7.42 – 7.46 (m, 1H), 12.17 (s, 1H); IR (KBr) ν_{max}: 3446, 3197, 2906, 1677, 1591, 1499, 1369, 1257, 1119 cm^{-1}; MS (ESI) $(M + H)^+$ = 138.2.

***N*-Hydroxy-4-methoxy-benzamide[22] (6b, Table 2):-** Off white solid; mp: 189-191 °C; TLC (Hexane:EtOAc, 70:30 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.91 (s, 3H), 7.00 – 7.04 (m, 2H), 7.90 – 7.93 (m, 2H), 9.36 (s, 1H); IR (KBr) ν_{max}: 3737, 2978, 1681, 1541, 1360, 1277 cm^{-1}; MS (ESI) $(M + H)^+$ = 168.4.

2-Hydroxy *N*-isopropyl benzamide (6c, Table 2):- Yellowish liquid, TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.29 (d, 6H, J = 6.6 Hz), 4.26 – 4.32 (m, 1H), 6.30 (bs, 1H, D_2O exchangeable), 6.83 (t, 1H, J = 7.2 Hz), 6.97 – 6.99 (m, 1H), 7.36 – 7.40 (m, 2H), 12.52 (bs, 1H, D_2O exchangeable); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 22.6, 41.8, 114.4, 118.5, 118.6, 125.4, 134.1, 161.5, 169.2; IR (Neat) ν_{max}: 3734, 2976, 1539, 1361, 1275 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{10}H_{13}NO_2Na$, 202.0844; found, 202.0844.

2-Hydroxy-*N*-isopropyl-5-nitro-benzamide (6d, Table 2):- Yellow solid; mp: 150-152 °C; TLC (Hexane:EtOAc, 90:10 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.35 (d, 6H, J = 4.4 Hz), 4.29 – 4.35 (m, 1H), 7.02 (d, 1H, J = 9.2 Hz), 8.24 (dd, 1H, J = 2.7 Hz, 9.2 Hz), 8.48 (d, 1H, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 22.5, 42.3, 114.4, 119.5, 123.1, 129.0, 138.6, 167.5, 168.0; IR (KBr) ν_{max}: 3396, 2920, 1598, 1341, 1294 cm^{-1}; HRMS $(M + Na)^+$ Calcd. for $C_{10}H_{12}N_2O_4Na$, 247.0695; found, 247.0702.

***N*-(2-Hydroxy-phenyl)-acetamide[3] (7a, Table 2):-** Light brown solid; mp: 206-208 °C; TLC (Hexane:EtOAc, 80:20 v/v): $R_f \approx 0.5$; ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.31 (s, 3H), 6.89 (t, 1H, J = 7.4 Hz), 6.99 – 7.07 (m, 2H), 7.15 – 7.19 (m, 1H), 7.41 (bs, 1H, D_2O exchangeable), 8.69 (bs, 1H, D_2O exchangeable); IR (KBr) ν_{max}: 3405, 2925, 1656, 1454, 1275, 1260 cm^{-1}; MS (ESI) $(M + H)^+$ = 152.4.

***N*-(2-Hydroxy-4-methyl-phenyl)-acetamide (7b, Table 2):-** Off white solid; mp: 163-165 °C; TLC (Hexane:EtOAc, 85:15 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.27 (s, 3H), 2.30 (s, 3H), 6.67 – 6.69 (m, 1H), 6.83 – 6.85 (m, 2H), 7.42 (bs, 1H, D_2O exchangeable), 8.73 (bs, 1H, D_2O exchangeable); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 20.8, 23.7, 120.5, 121.2, 121.9, 122.9, 137.6, 148.6, 170.3; IR (KBr) ν_{max}: 3273, 2867, 1641, 1551, 1294 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_9H_{11}NO_2Na$, 188.0687; found 188.0687.

Ethyl-2-hydroxyphenylcarbamate[4] (8a, Table 2):- Light yellow solid, mp: 80-82 °C; TLC (Hexane:EtOAc, 80:20 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.36 (t, 3H, J = 7.1 Hz), 4.28 (q, 2H, J = 7.1 Hz), 6.88 – 6.92 (m, 1H), 6.96 – 6.99 (m, 1H), 7.04 – 7.08 (m, 1H), 7.25 – 7.28 (m, 1H), 7.81 (bs, 1H, D_2O exchangeable); IR (Neat) ν_{max}: 3409, 2927, 1710, 1661, 1455, 1274, 1261 cm^{-1}; MS (ESI) $(M + H)^+$ = 182.3.

Methyl-2-hydroxyphenylcarbamate[23] (8b, Table 2):- Off white solid; mp: 118-120 °C; TLC (Hexane:EtOAc, 82:18 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 3.85 (s, 3H), 6.91 (dt, 2H, J = 1.5 Hz, 7.8 Hz, 1H, D_2O exchangeable), 6.97 (dd, 1H, J = 1.4 Hz, 8.0 Hz), 7.05 – 7.09 (m, 1H), 7.28 – 7.30 (m, 1H,), 7.48 (bs, 1H, D_2O exchangeable); IR (Neat) ν_{max}: 3401, 2973, 1701, 1633, 1345, 1272 cm^{-1}; MS (ESI) $(M + H)^+$ = 168.3.

1,1-Diethyl-3-(2-hydroxyphenyl)urea (9, Table 2):- Brown solid; mp: 126-128 °C; TLC (Hexane:EtOAc, 60:40 v/v): $R_f \approx 0.5$; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.30 (t, 6H, J = 7.2 Hz), 3.44 (q, 4H, J = 7.2 Hz), 6.32 (bs, 1H), 6.83 – 6.85 (m, 1H), 6.88 – 6.91 (m, 1H), 7.02 – 7.08 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 13.6, 42.3, 119.9, 120.0, 122.1, 125.9, 126.7, 149.5, 156.3; IR (KBr) ν_{max}: 3392, 2978, 1680, 1633, 1346, 1274 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{11}H_{16}N_2O_2Na$, 231.1109; found 231.1122.

2-(Benzo[*d*]thiazol-2-yl)phenyl acetate, 4aa :- Light yellow semi-solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.49 (s, 3H), 7.27 (dd, 1H, J = 1.1 Hz, 7.9 Hz), 7.41 – 7.44 (m, 2H), 7.51 (dt, 2H, J = 1.1 Hz, 7.6 Hz), 7.95 (d, 1H, J = 7.7 Hz), 8.11 (d, 1H, J = 8.2 Hz), 8.33 (dd, 1H, J = 1.6 Hz, 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 21.7, 121.4, 123.4, 123.7, 125.4, 126.1, 126.3, 126.5, 130.3, 131.4, 135.4, 148.2, 153.0, 162.5, 169.2; IR (KBr) ν_{max}: 2981, 1740, 1649, 1538, 1277, 1251 cm^{-1}; HRMS (ESI) $(M + Na)^+$ Calcd. for $C_{15}H_{11}NO_2SNa$, 292.0408; found 292.0419.

8. Typical procedure for the recovery and recyclability of catalyst for the direct hydroxylation of 1a to form 2a:- To a magnetically stirred mixture of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 2.5 mol %) and $Na_2S_2O_8$ (595 mg, 2.5 mmol, 1.25 equiv) in 1,4-dioxane (12 mL) under N_2 atmosphere was added **1a** (390 mg, 2 mmol) and the resultant mixture was treated at 80 °C. After completion of the reaction (14 h, TLC), the reaction mixture was cooled to rt and the supernatant liquid (organic layer) was decanted off. The residue was extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried (anh Na_2SO_4) and concentrated under reduced pressure to afford the crude product which upon subjected to flash chromatography afforded **2a** (262 mg, 62%). The residue that remained in the reaction flask was washed with H_2O (3 × 5 mL). During each washing after the addition of water the mixture was stirred, the catalyst was allowed to settle down for ~ 10 min, and the aqueous layer was decanted off to obtain the recovered Pd catalyst. The flask containing the recovered Pd catalyst was charged with 1,4-

dioxane (12 mL), $Na_2S_2O_8$ (2.5 mmol, 1.25 equiv) and **1a** (2 mmol) and the mixture was magnetically stirred at 80 °C for 14 h to obtain **2a** in 62% yield after usual workup and purification. The fresh batches of reaction involving **1a** (2 mmol) were repeated for five consecutive times with the recovered Pd catalyst after each fresh reaction to obtain **2a** in 62, 61, 61, 60, and 57% yields.

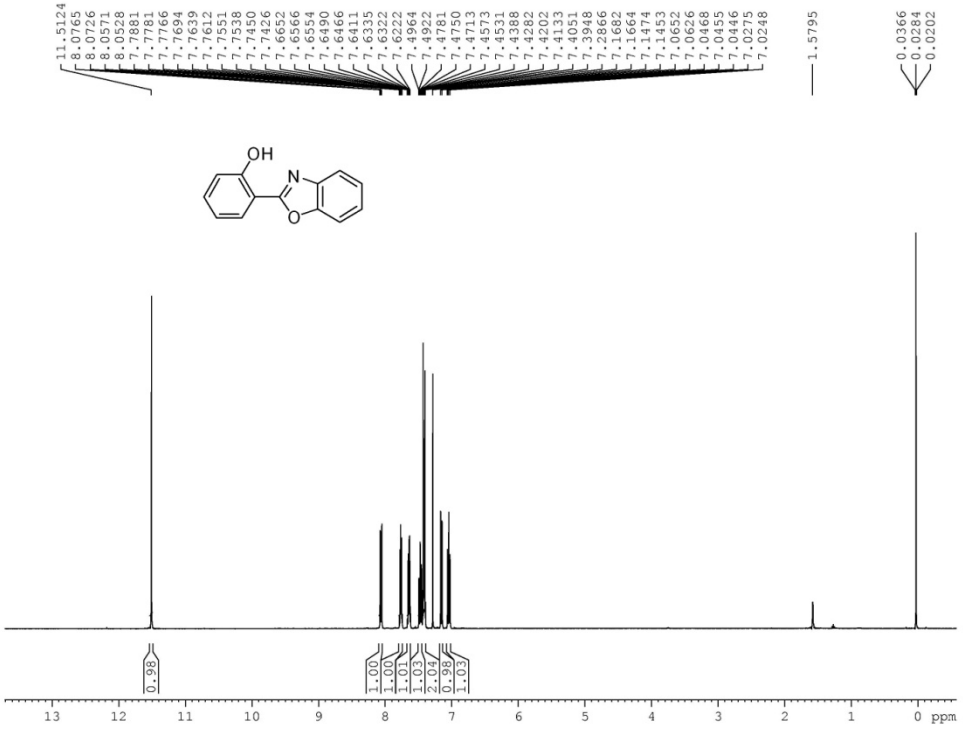
Table 8A. Catalyst recovery and reuse.[a]

Entry	No. of Runs	Yield (%)[b]
1	Fresh	62
2	1st reuse	62
3	2nd reuse	61
4	3rd reuse	61
5	4th reuse	60
6	5th reuse	57

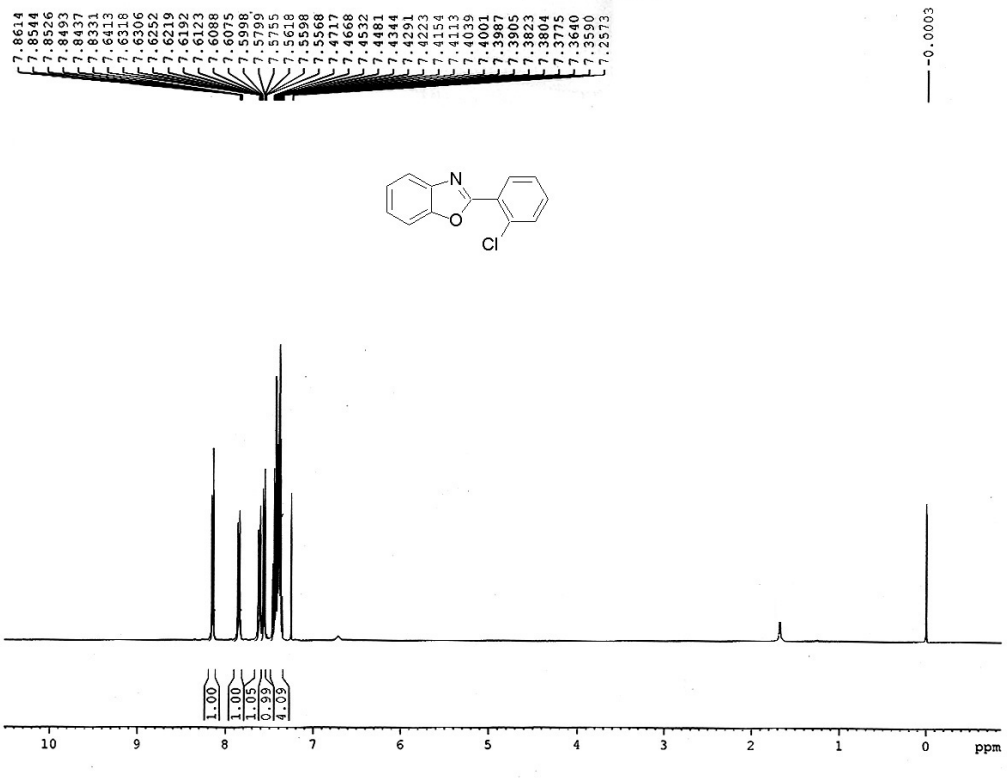
[a]**1a** (390 mg, 2 mmol) was treated with $Na_2S_2O_8$ (2.5 mmol, 1.25 equiv) in 1,4-dioxane (12 mL) with the recovered catalyst for each cycle. [b]The isolated yield of **2a**.

9. Scanned NMR Spectra

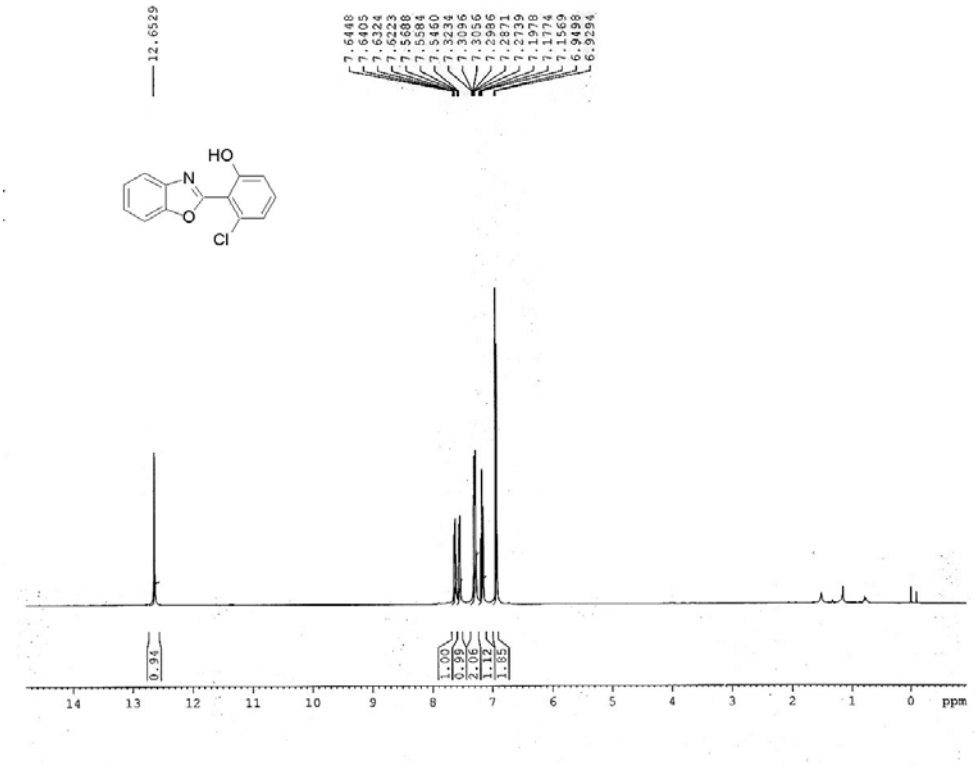
^{1}H NMR of 2-Benzoxazol-2-yl-phenol (2a, Table 1):-



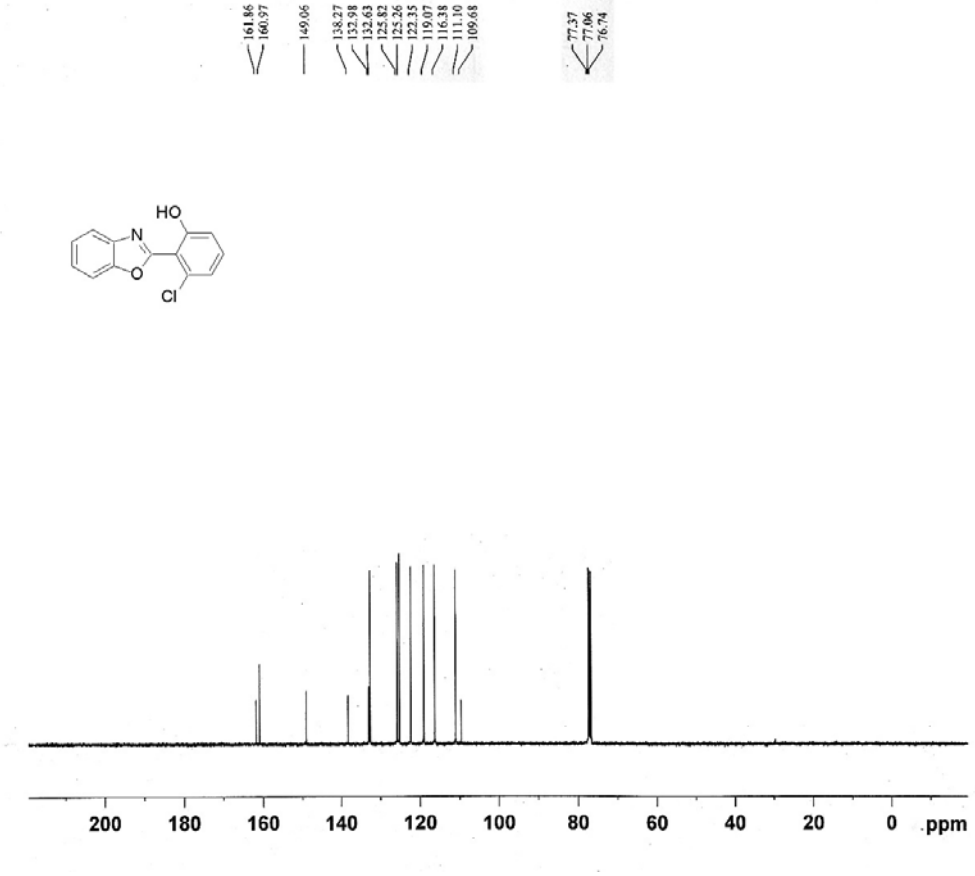
^{1}H NMR of 2-(2-Chlorophenyl)-benzoxazole (starting benzoxazole of 2b, Table 1):-



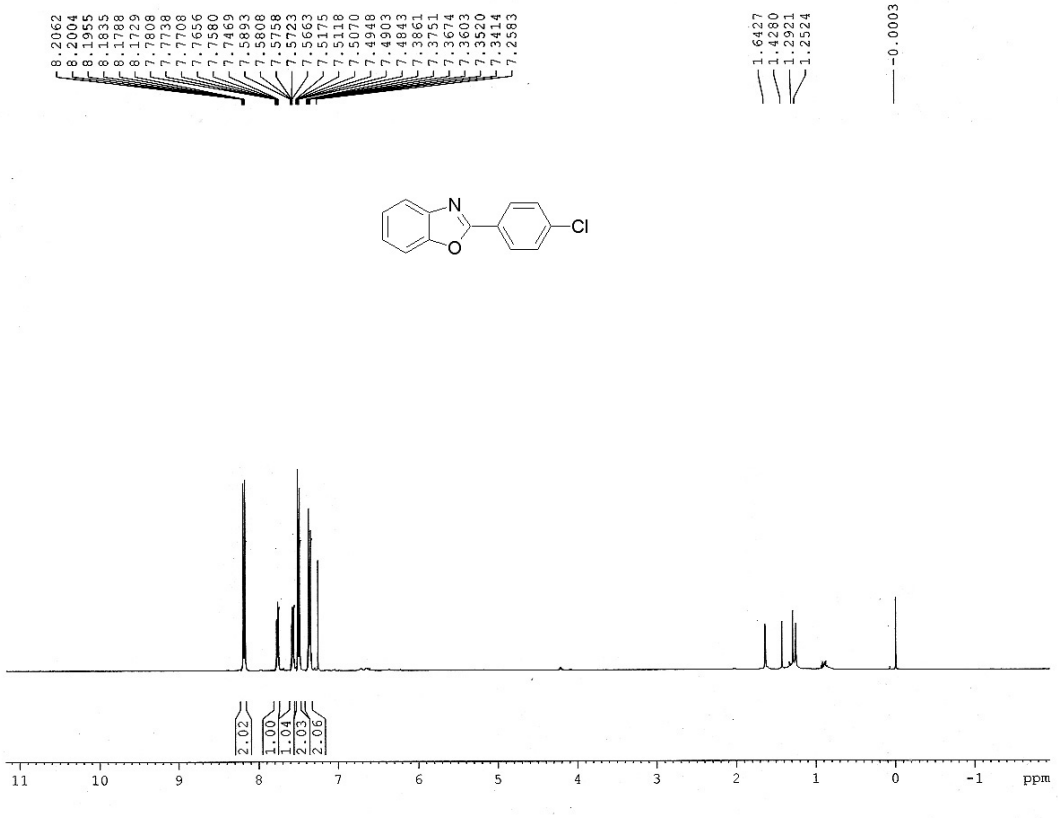
^{1}H NMR of 2-Benzoxazol-2-yl-3-chloro-phenol (2b, Table 1):-



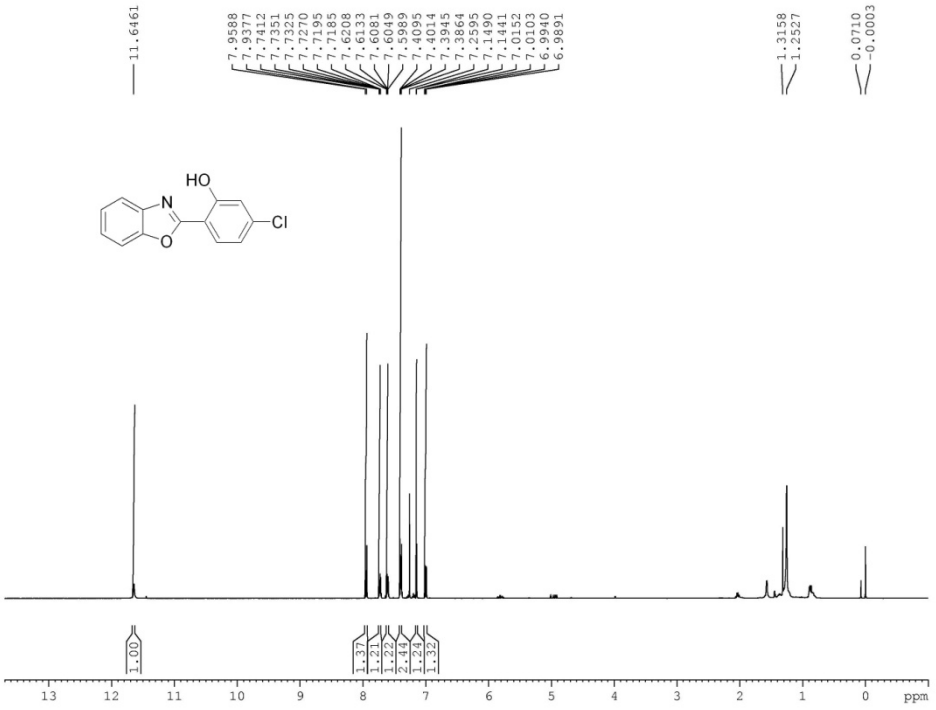
^{13}C NMR of 2-Benzoxazol-2-yl-3-chloro-phenol (2b, Table 1):-



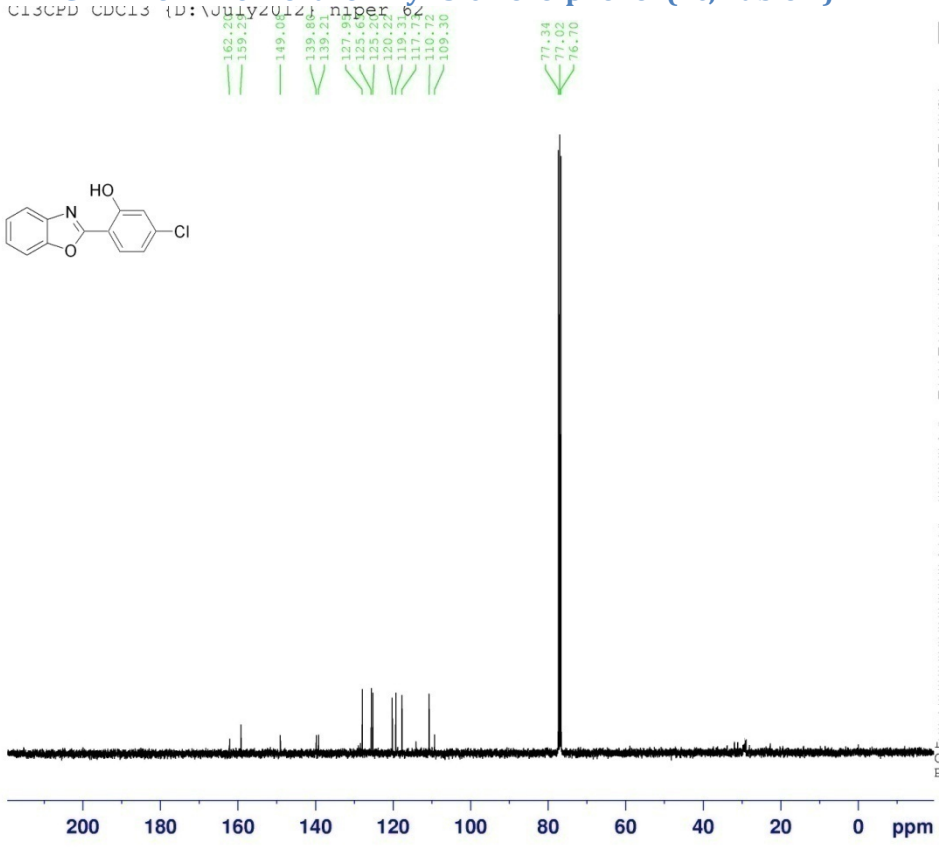
^{1}H NMR of 2-(4-Chlorophenyl)-benzoxazole (starting benzoxazole of 2c, Table 1):-



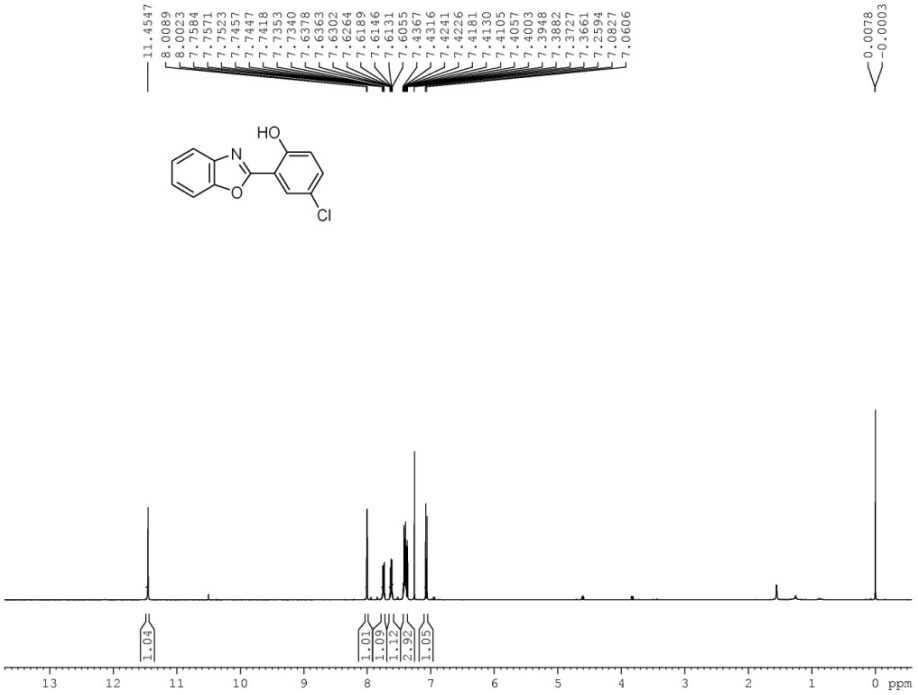
^{1}H NMR of 2-Benzoxazol-2-yl-5-chloro-phenol (2c, Table 1):-



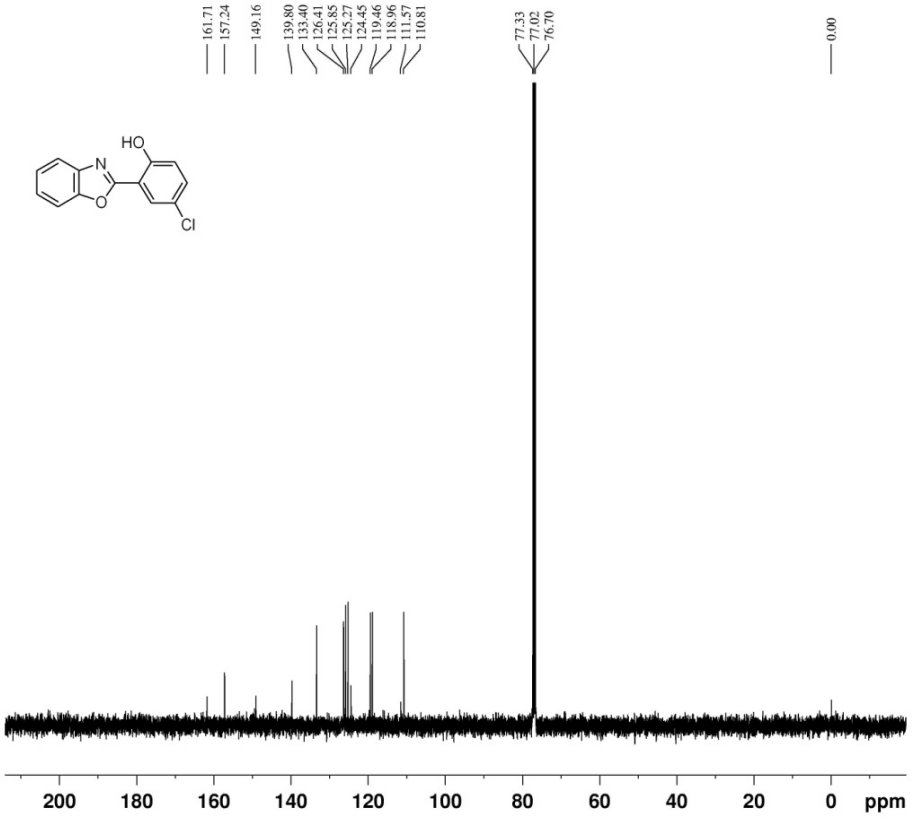
^{13}C NMR of 2-Benzoxazol-2-yl-5-chloro-phenol (2c, Table 1):-



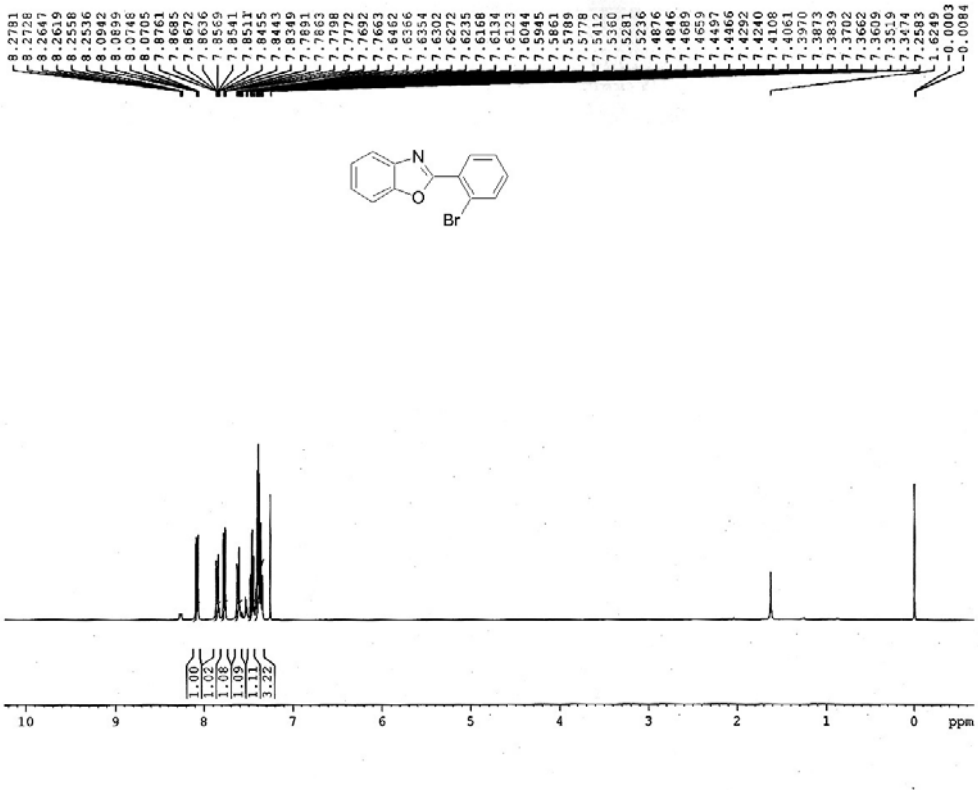
^{1}H NMR of 2-(Benzo[*d*]oxazol-2-yl)-4-chlorophenol (2d, Table 1):-



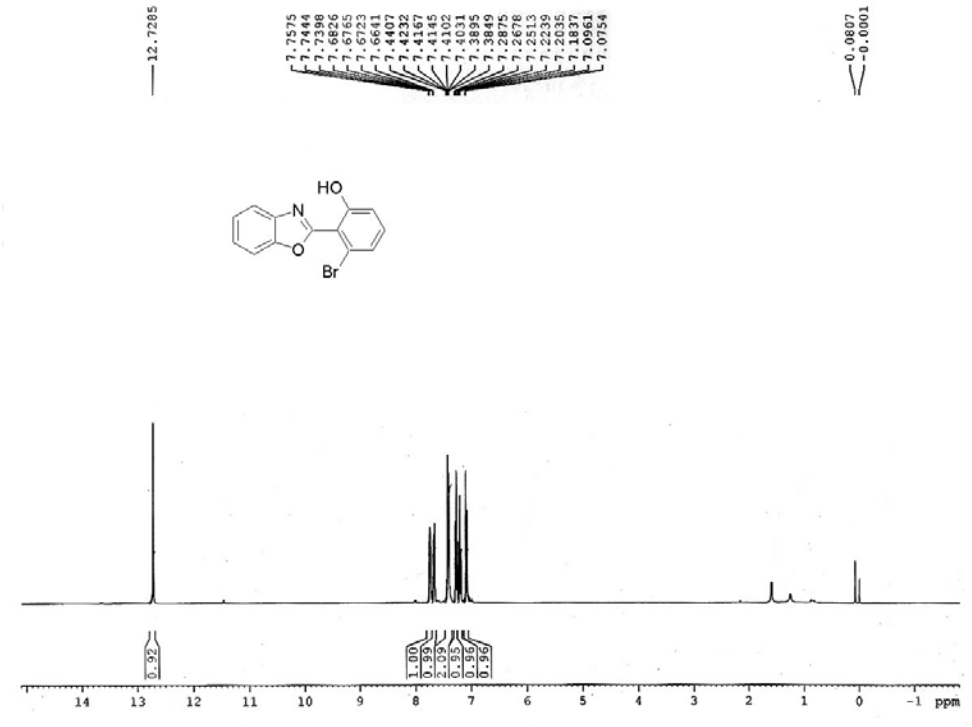
^{13}C NMR of 2-(Benzo[*d*]oxazol-2-yl)-4-chlorophenol (2d, Table 1):-



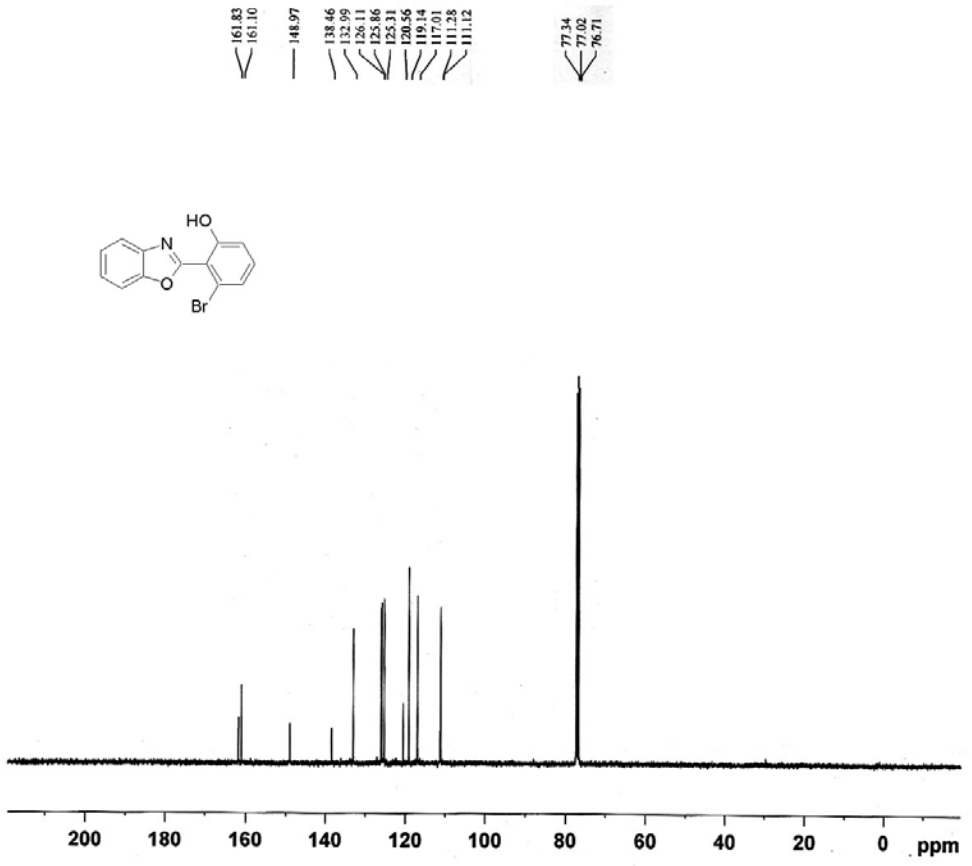
^{1}H NMR of 2-(2-Bromophenyl)-benzoxazole (starting benzoxazole of 2e, Table 1):-



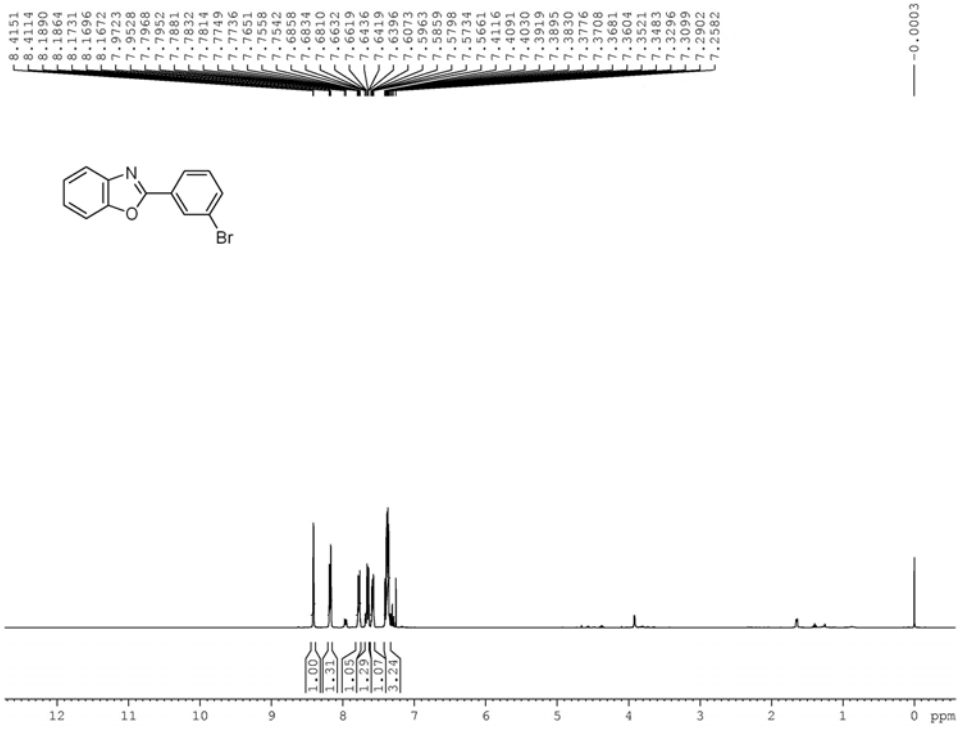
^{1}H NMR of 2-Benzoxazol-2-yl-3-bromo-phenol (2e, Table 1):-



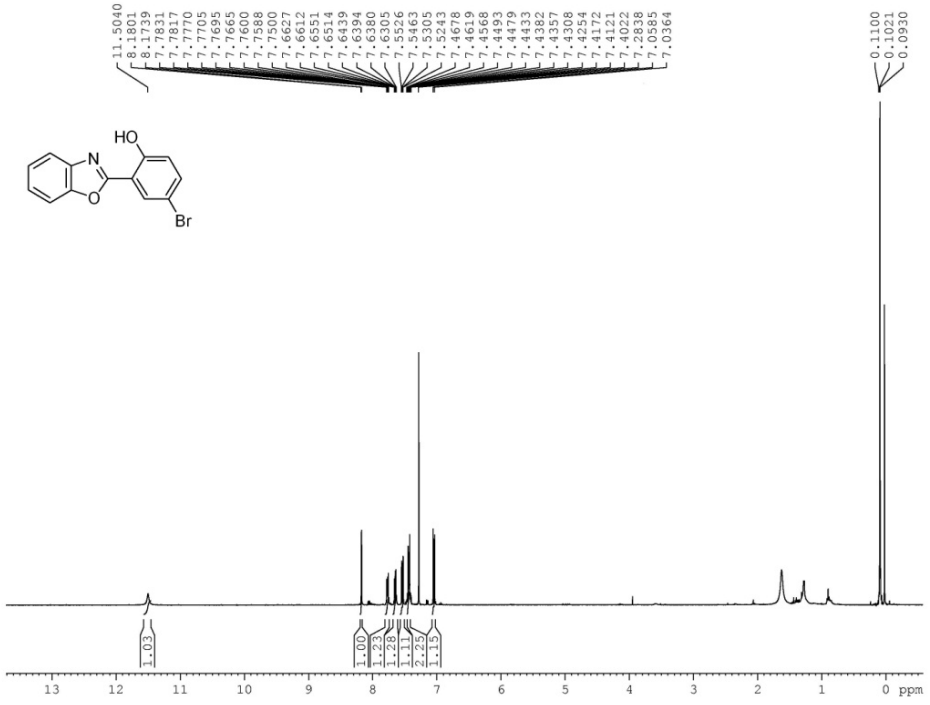
^{13}C NMR of 2-Benzoxazol-2-yl-3-bromo-phenol (2e, Table 1):-



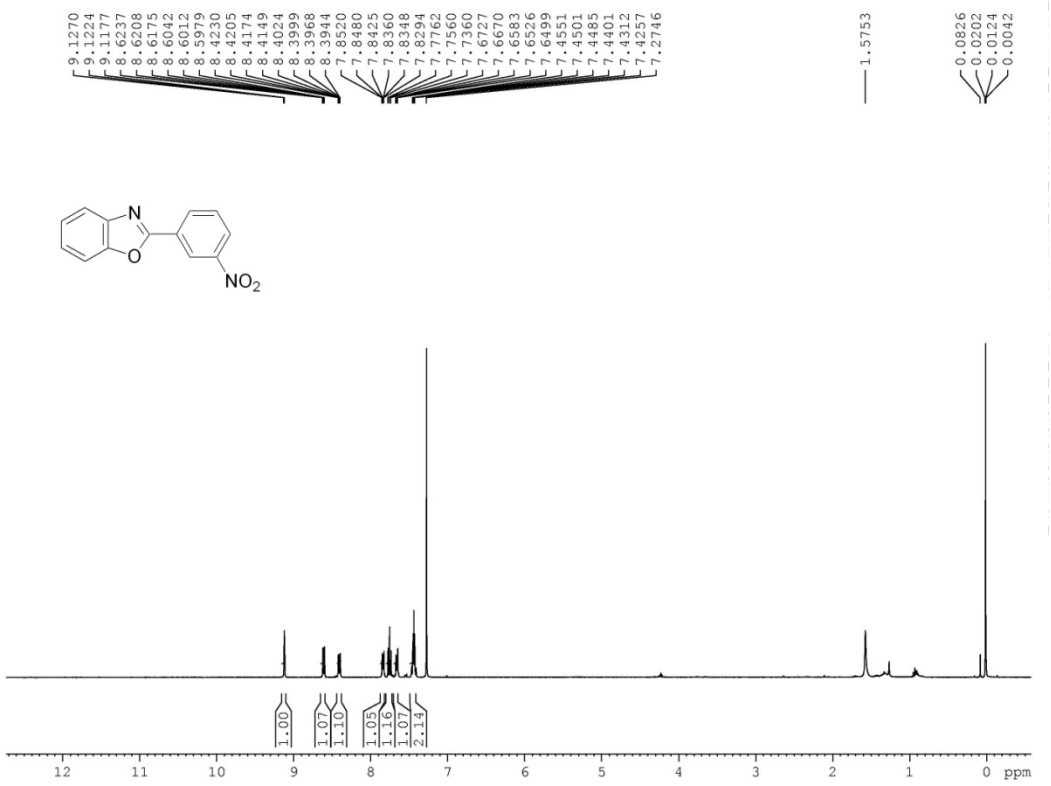
^{1}H NMR of 2-(3-Bromophenyl)benzo[*d*]oxazole (starting benzoxazole of 2f, Table 1):-



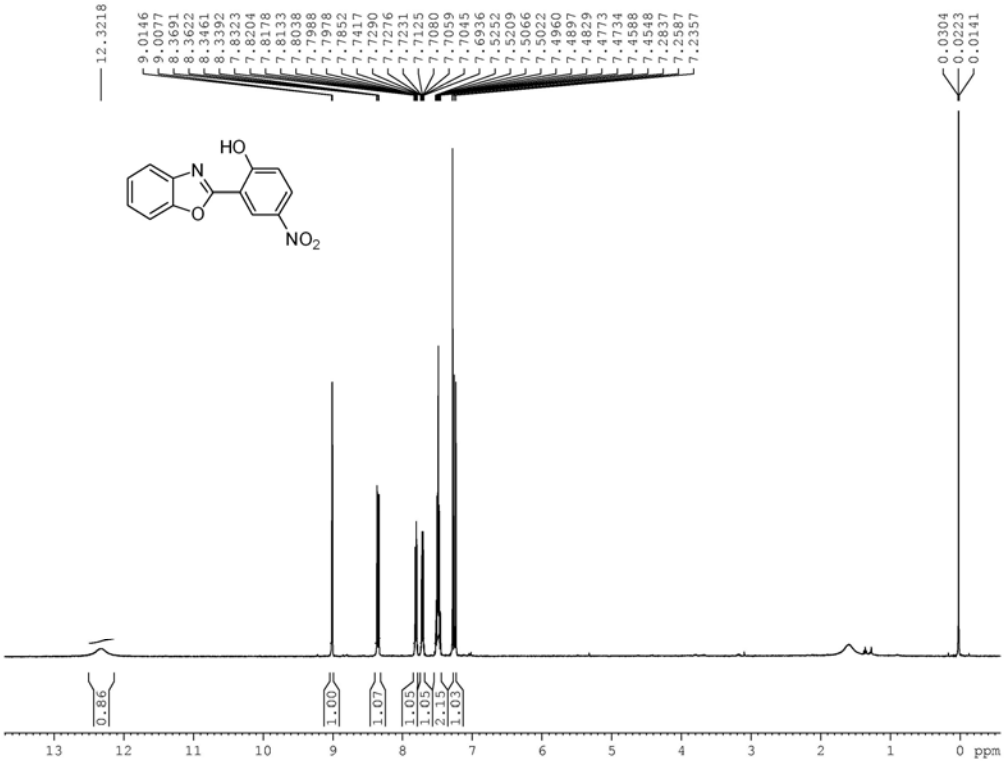
^{1}H NMR of 2-(Benzo[*d*]oxazol-2-yl)-4-bromophenol (2f, Table 1):-



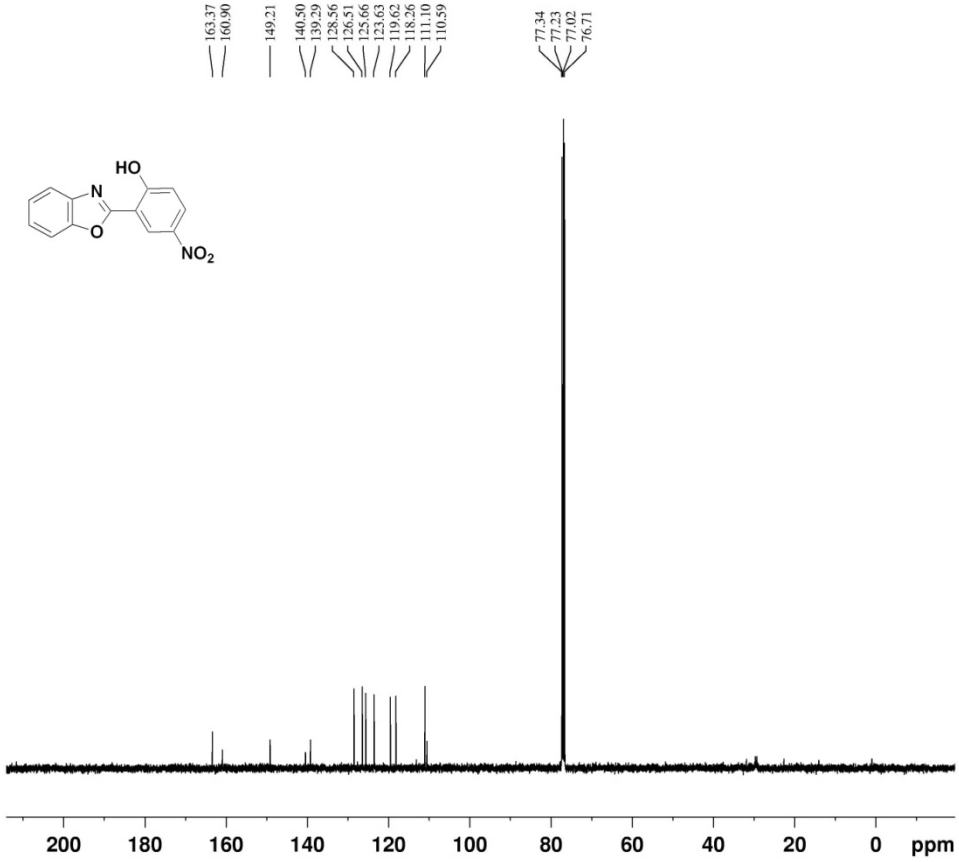
^{1}H NMR of 2-(3-Nitrophenyl)-benzoxazole (starting benzoxazole of 2g, Table 1):-



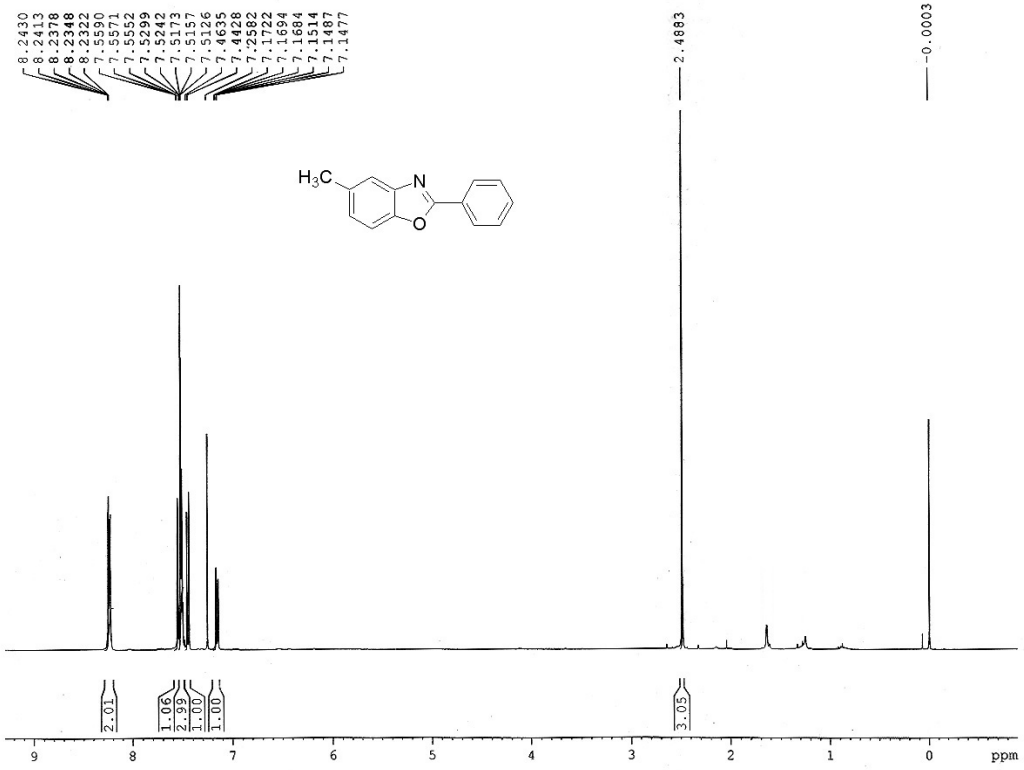
^{1}H NMR of 2-Benzoxazol-2-yl-4-nitro-phenol (2g, Table 1):-



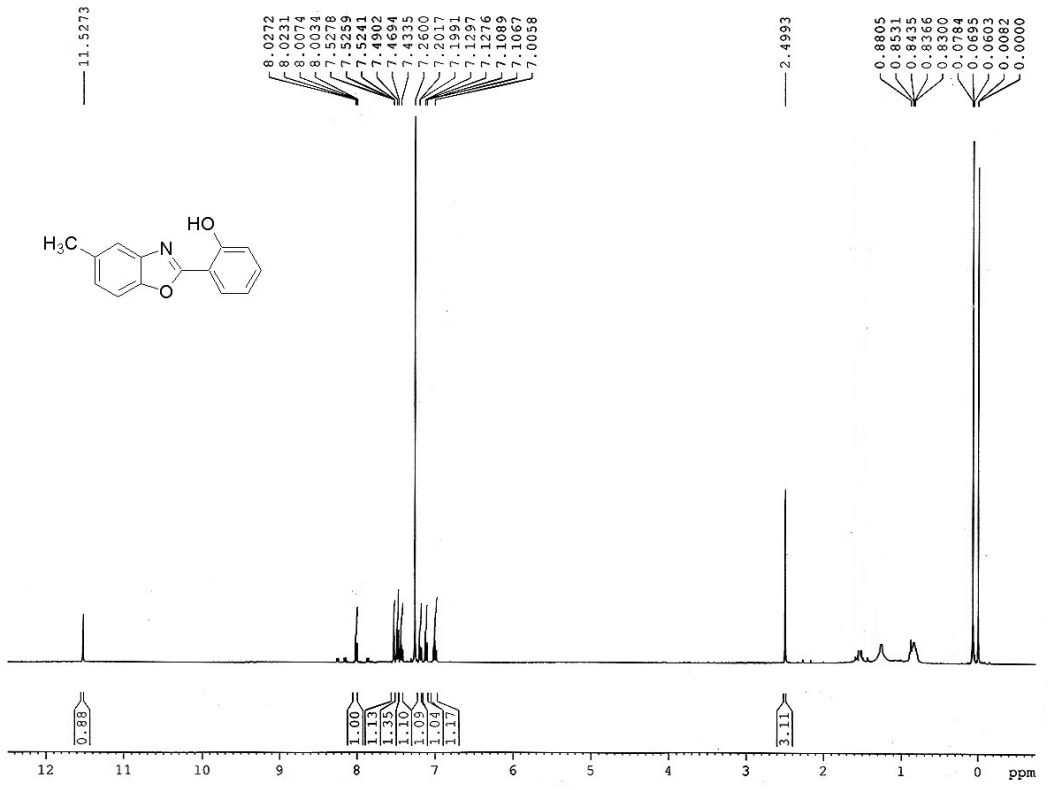
^{13}C NMR of 2-Benzoxazol-2-yl-4-nitro-phenol (2g, Table 1):-



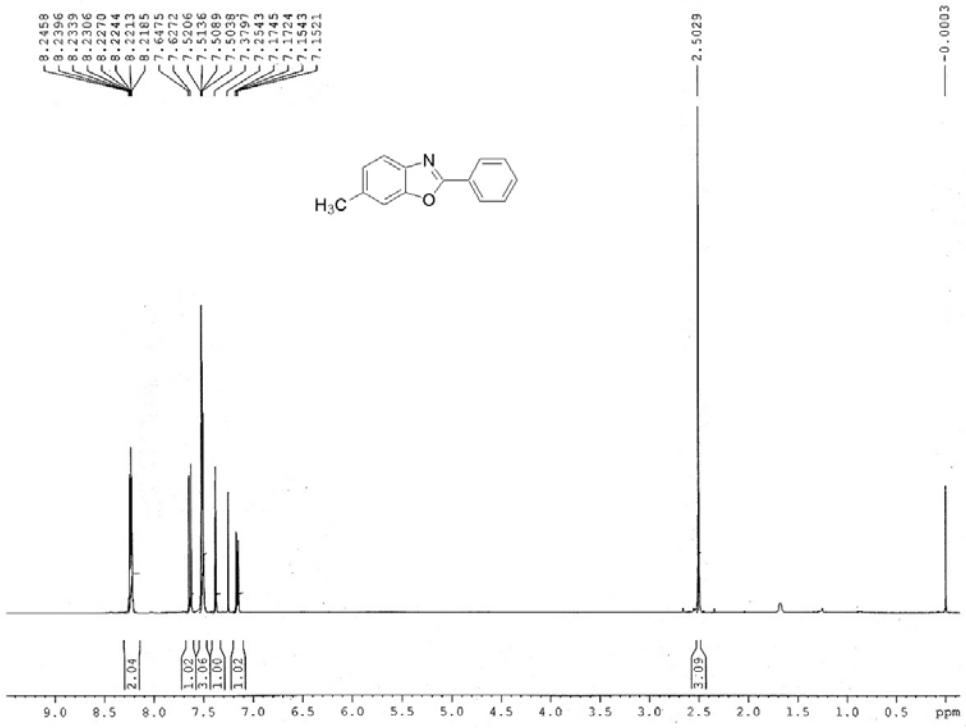
^{1}H NMR of 5-Methyl-2-phenyl-benzoxazole (starting benzoxazole of 2h, Table 1):-



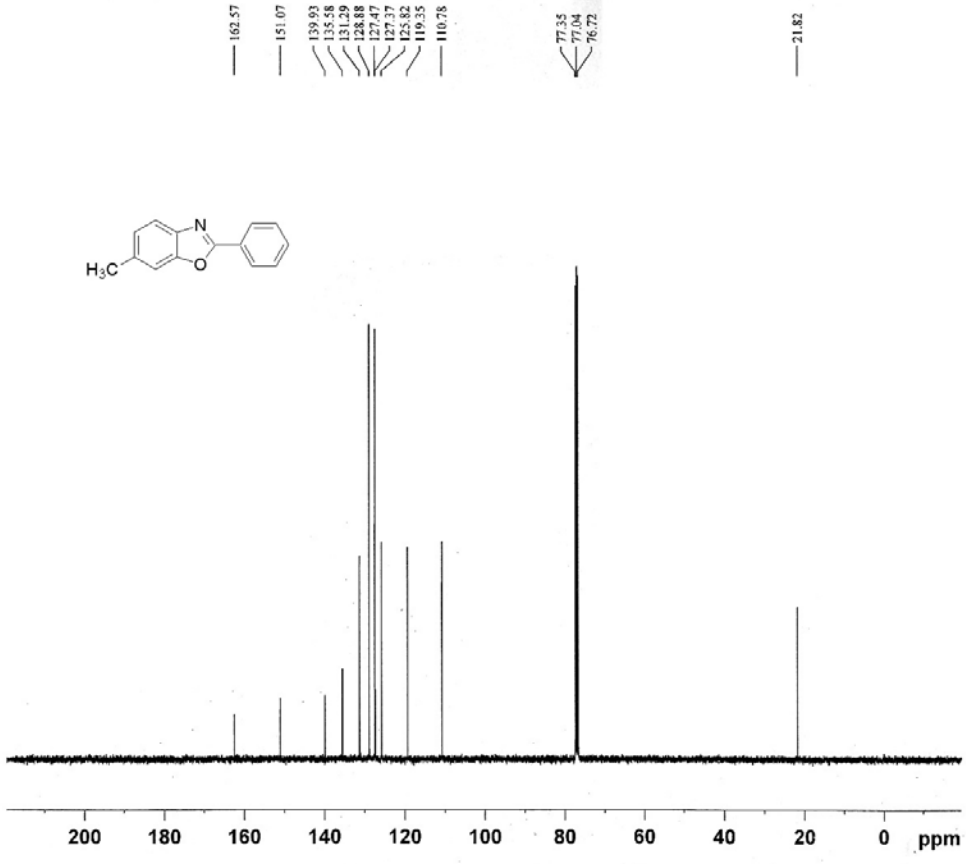
^{1}H NMR of 2-(5-Methyl-benzoxazol-2-yl)-phenol (2h, Table 1):-



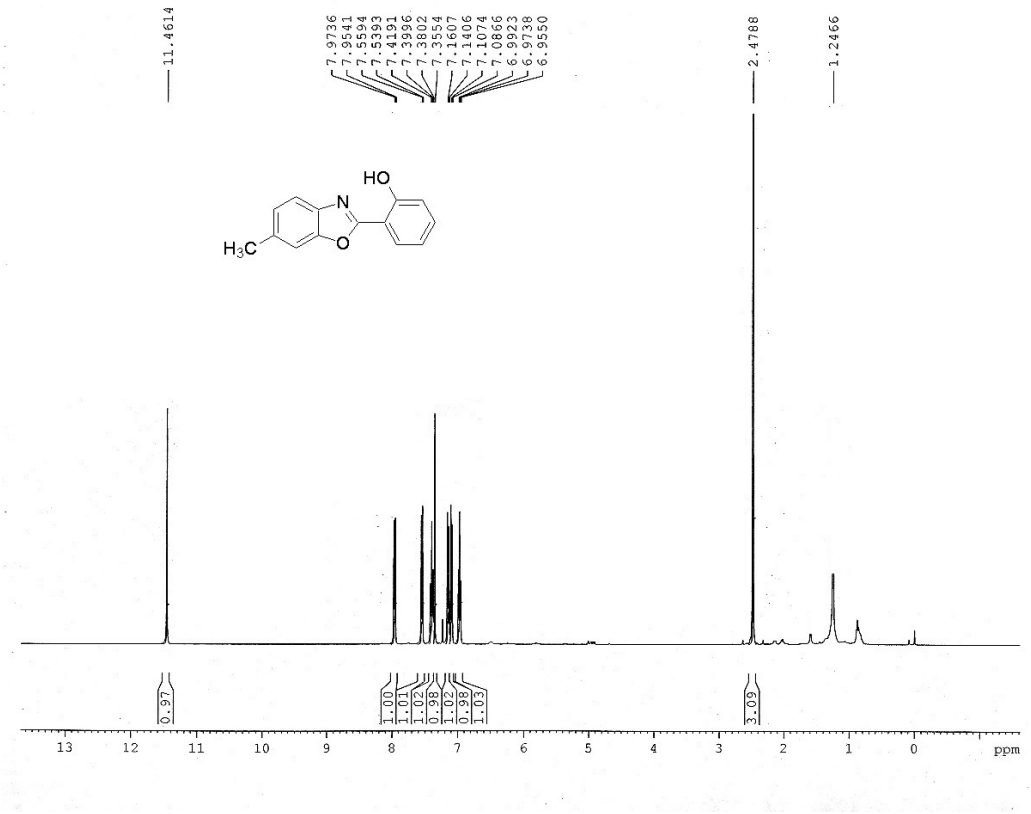
^{1}H NMR of 6-Methyl-2-phenyl-benzoxazole (starting benzoxazole of 2i, Table 1):-



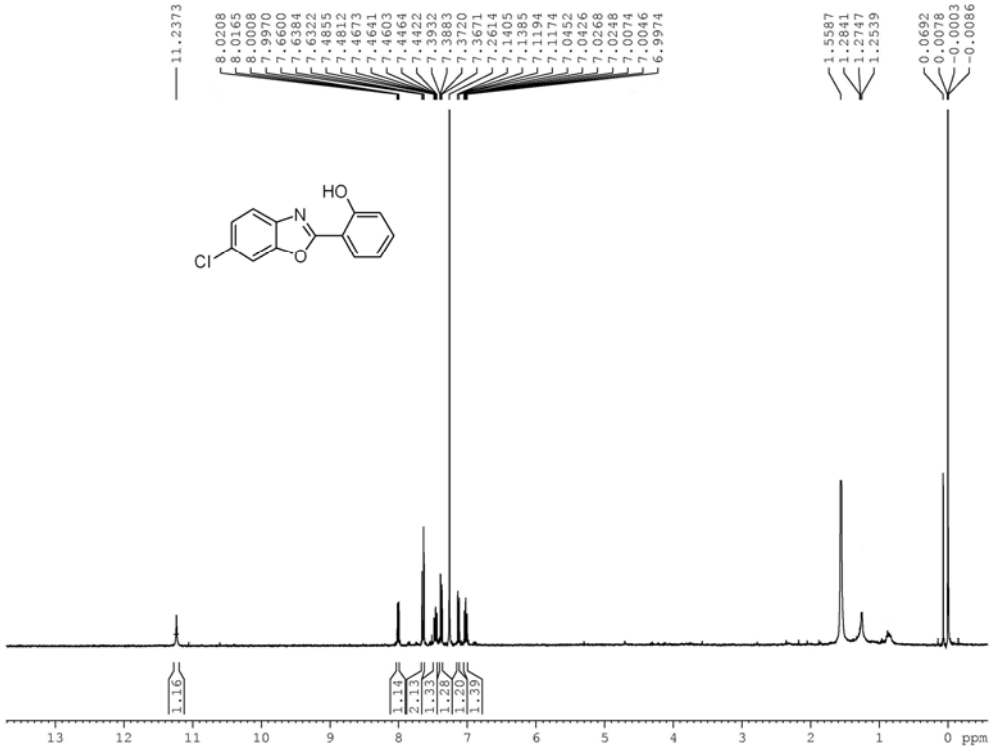
^{13}C NMR of 6-Methyl-2-phenyl-benzoxazole (starting benzoxazole of 2i, Table 1):-



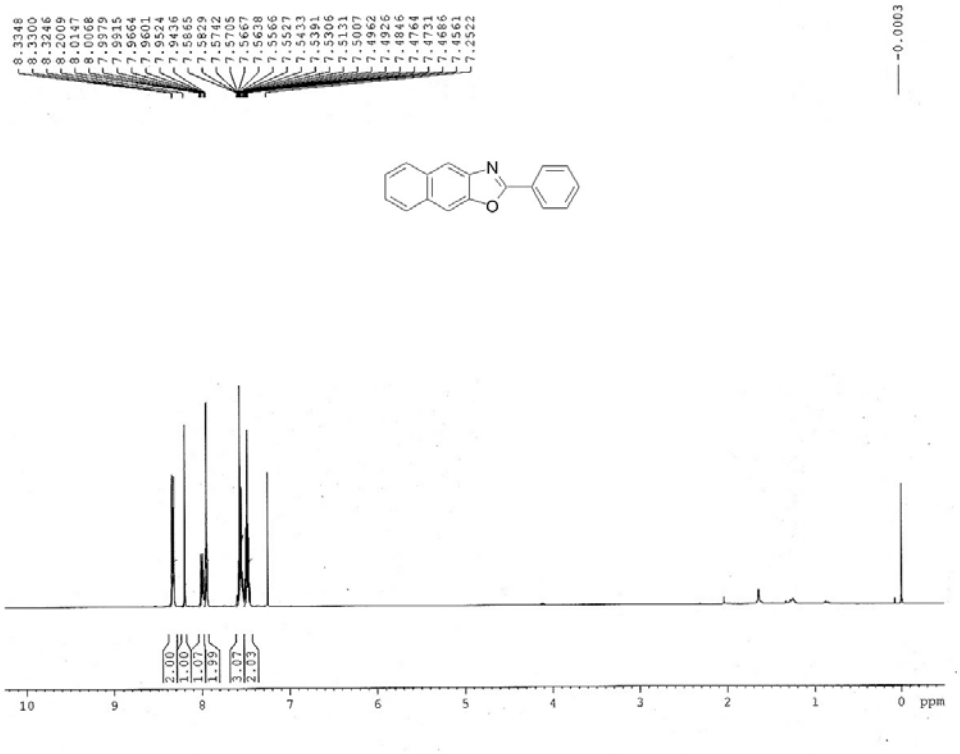
^{1}H NMR of 2-(6-Methyl-benzoxazol-2-yl)-phenol (2i, Table 1):-



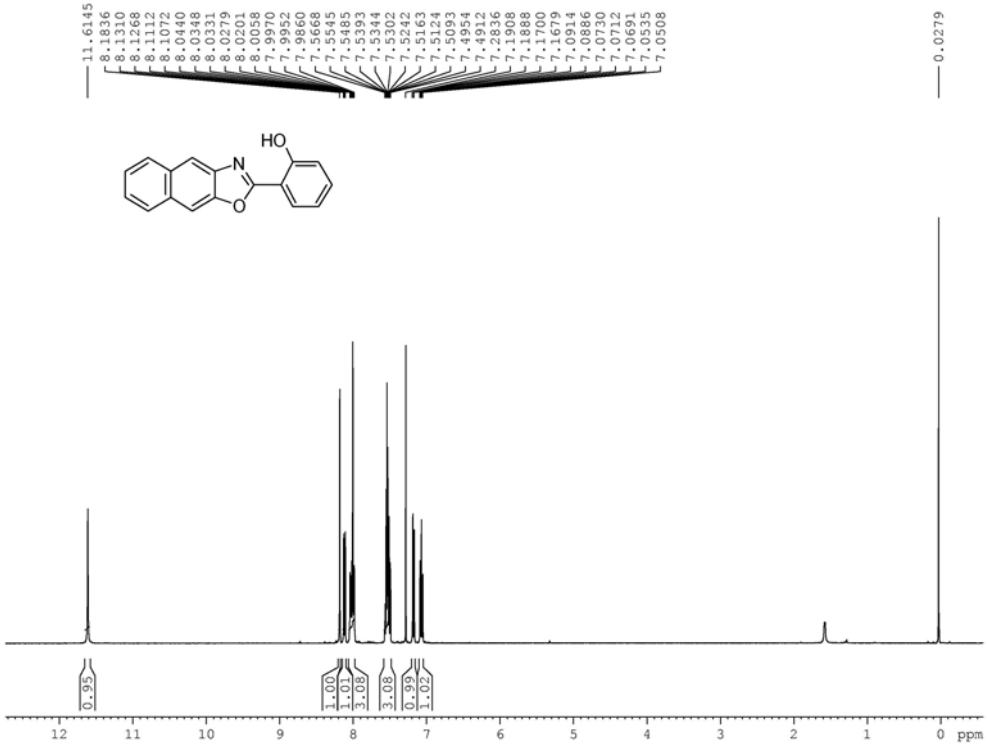
^{1}H NMR of 2-(6-Chlorobenzo[*d*]oxazol-2-yl)phenol (2j, Table 1):-



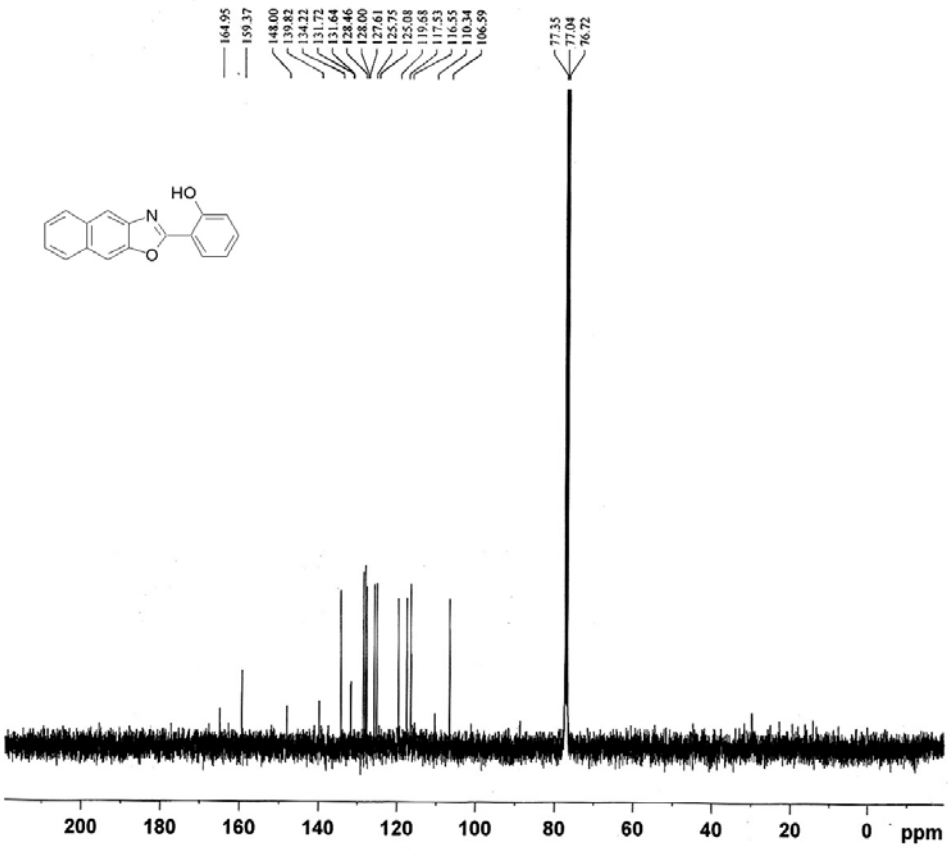
^{1}H NMR of 2-Phenyl-naphtho[2,3-*d*]oxazole (starting benzoxazole of 2k, Table 1):-



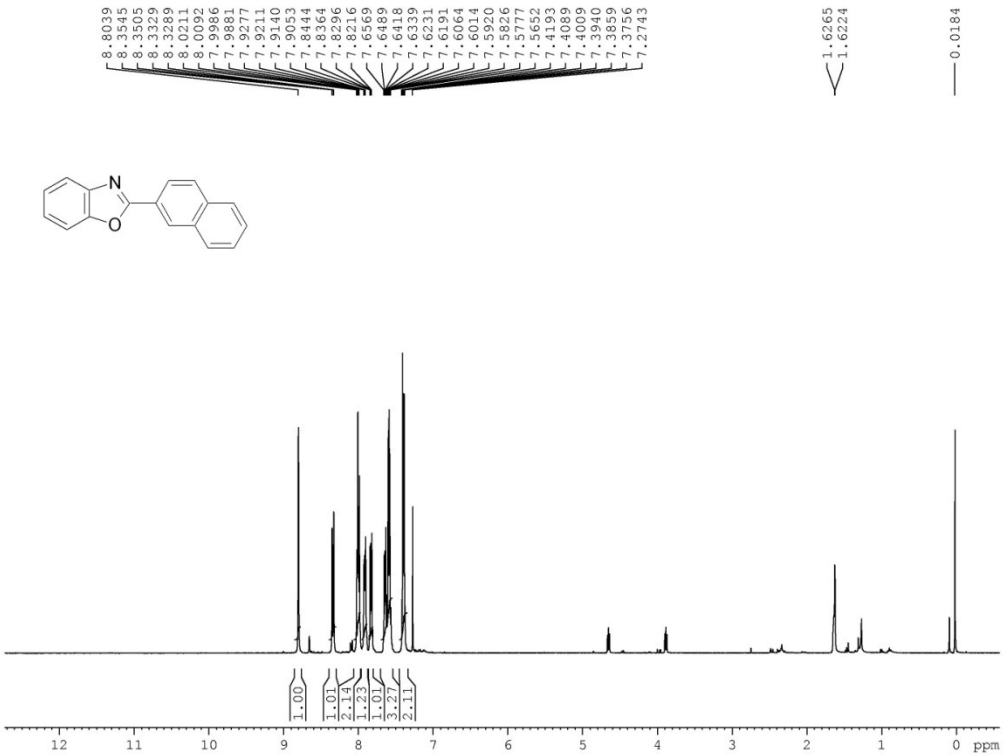
^{1}H NMR of 2-Naphtho[2,3-*d*]oxazol-2-yl-phenol (2k, Table 1):-



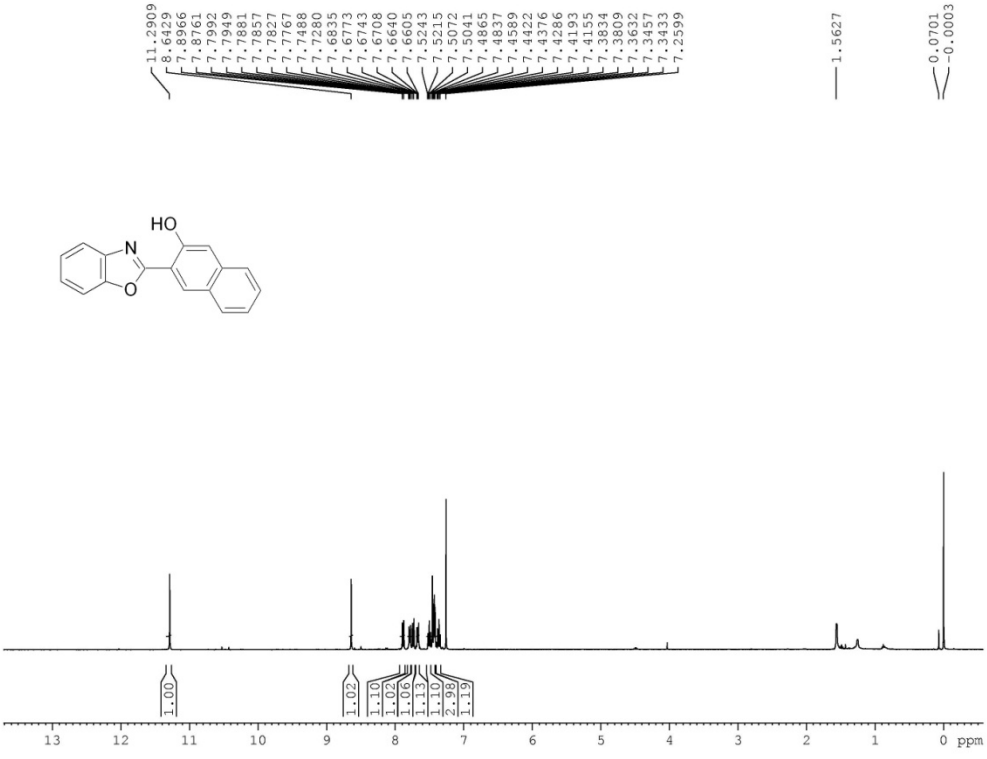
^{13}C NMR of 2-Naphtho[2,3-*d*]oxazol-2-yl-phenol (2k, Table 1):-



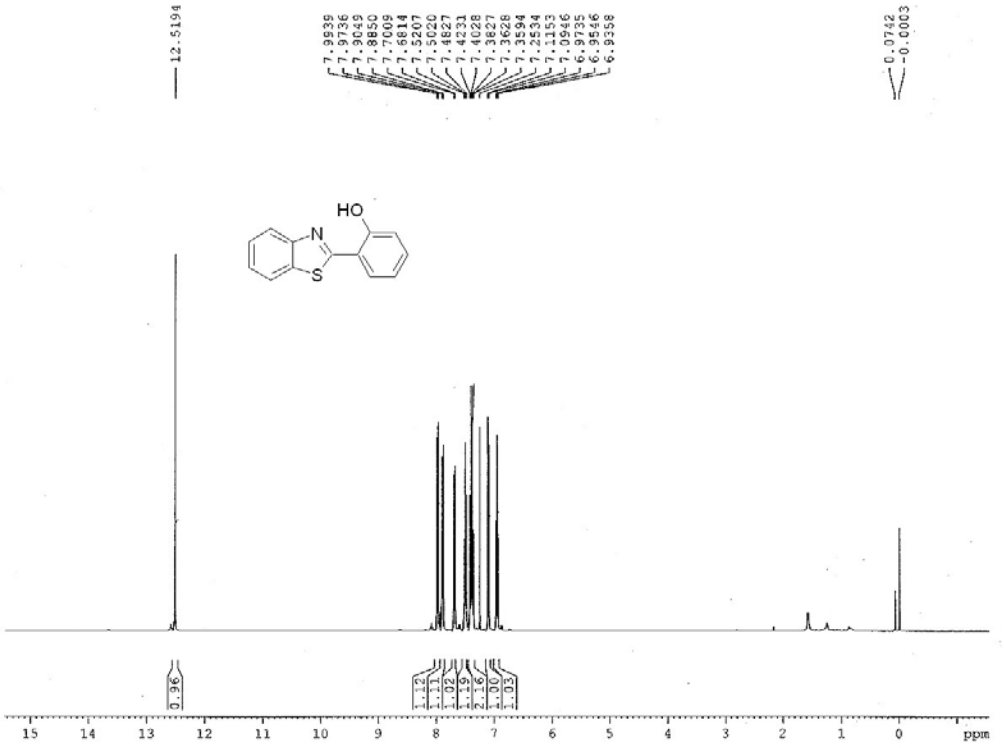
^{1}H NMR of 2-Naphthalen-2-yl-benzoxazole (starting benzoxazole of 2l, Table 1):-



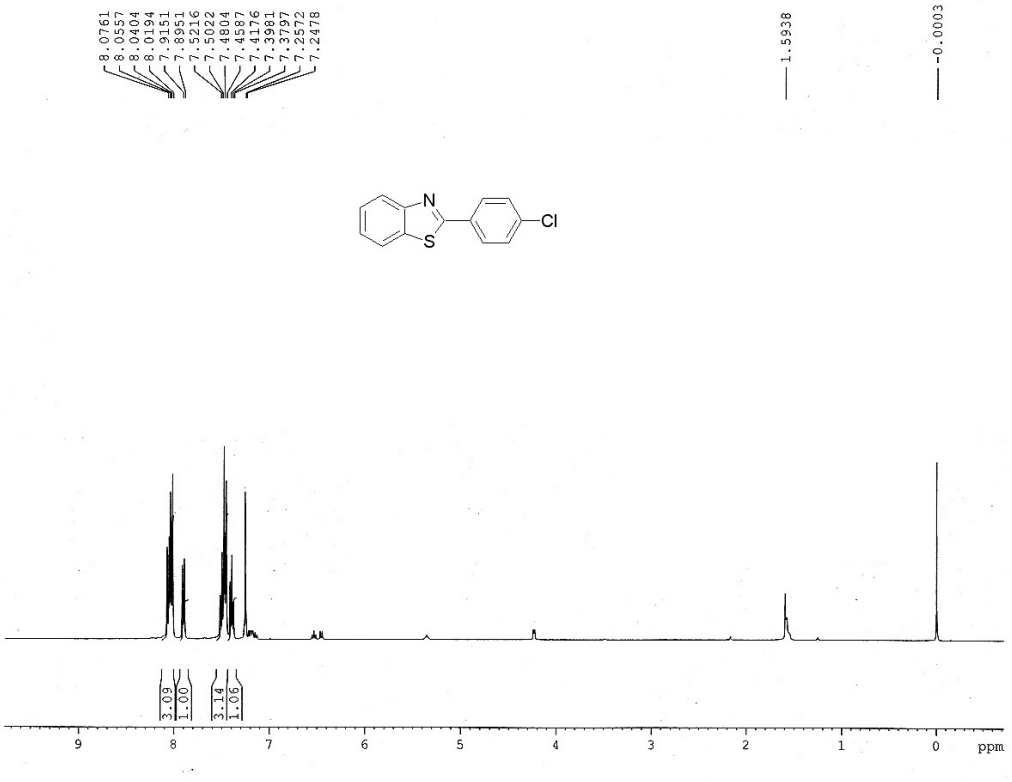
^{1}H NMR of 3-Benzoxazol-2-yl-naphthalen-2-ol (2l, Table 1):-



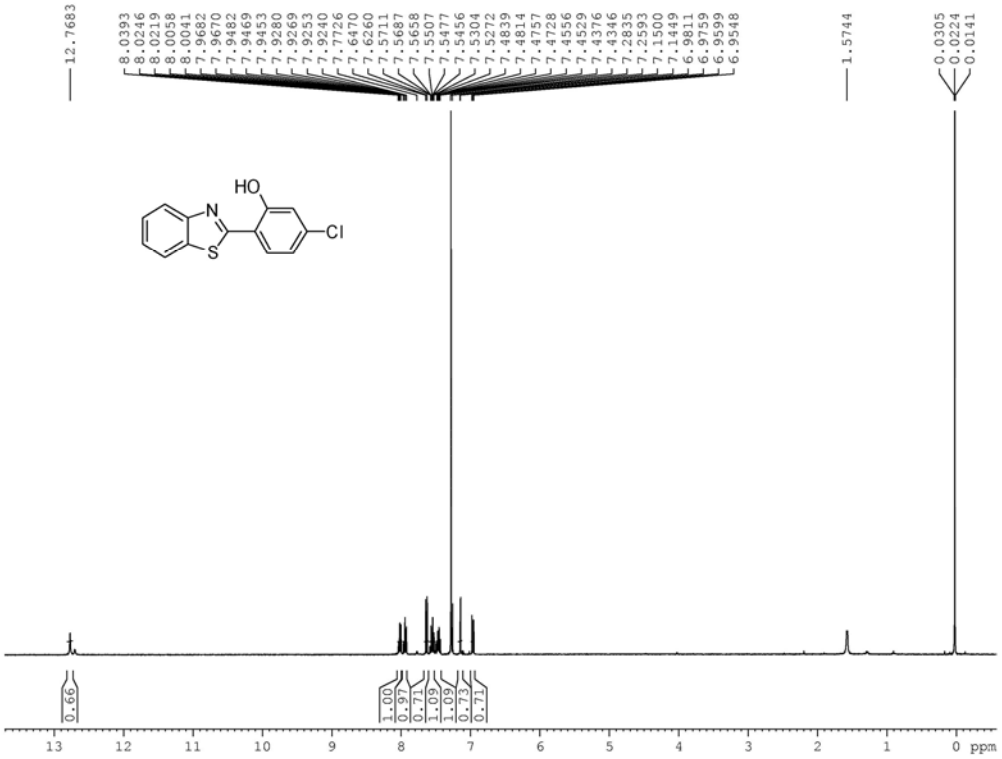
^{1}H NMR of 2-Benzothiazol-2-yl-phenol (4a, Table 1):-



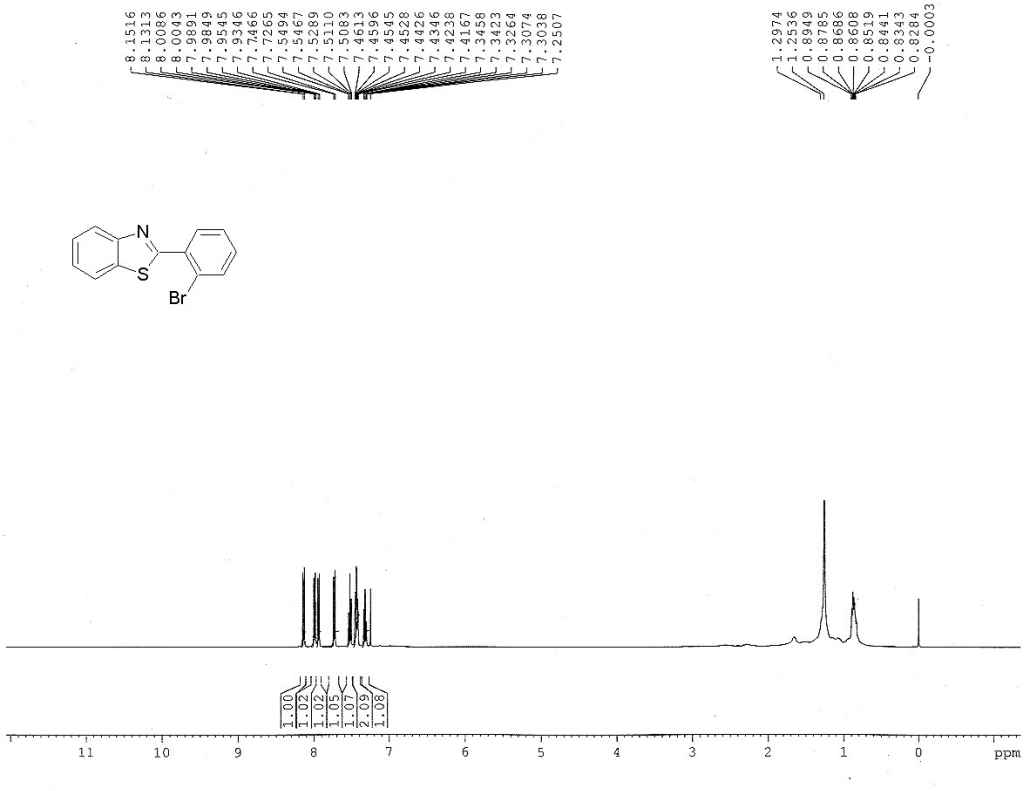
^{1}H NMR of 2-(4-Chlorophenyl)-benzothiazole (starting benzothiazole of 4b, Table 1):-



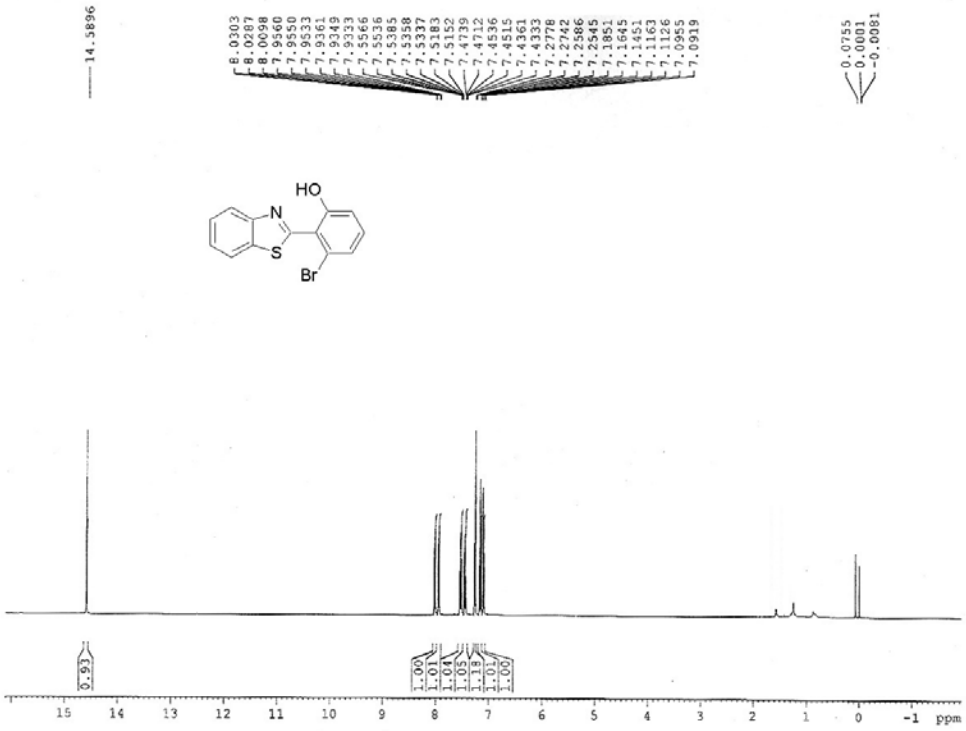
^{1}H NMR of 2-Benzothiazol-2-yl-5-chloro-phenol (4b, Table 1):-



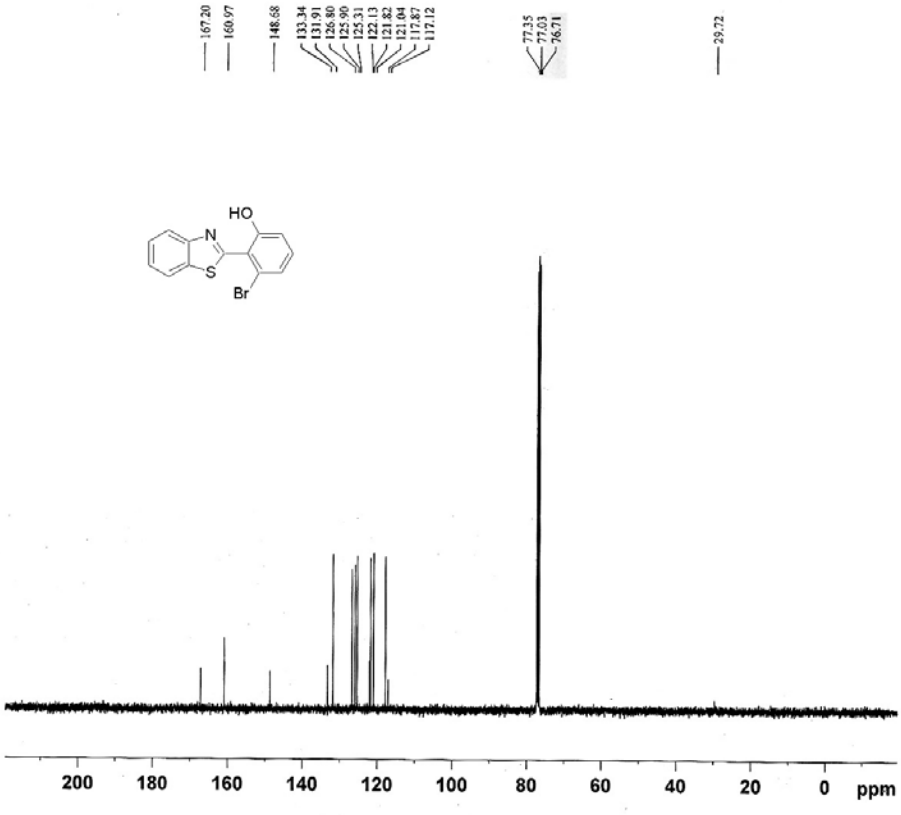
^{1}H NMR of 2-(2-Bromophenyl)-benzothiazole (starting benzothiazole of 4c, Table 1):-



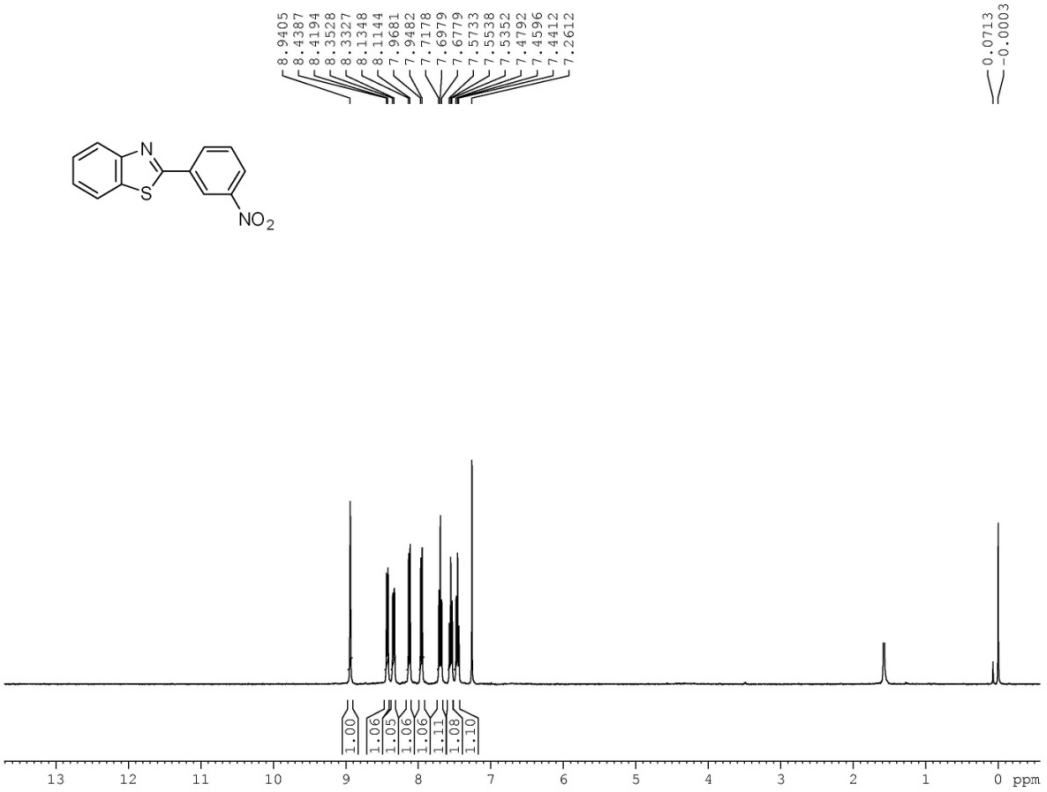
^{1}H NMR of 2-Benzothiazol-2-yl-3-bromo-phenol (4c, Table 1):-



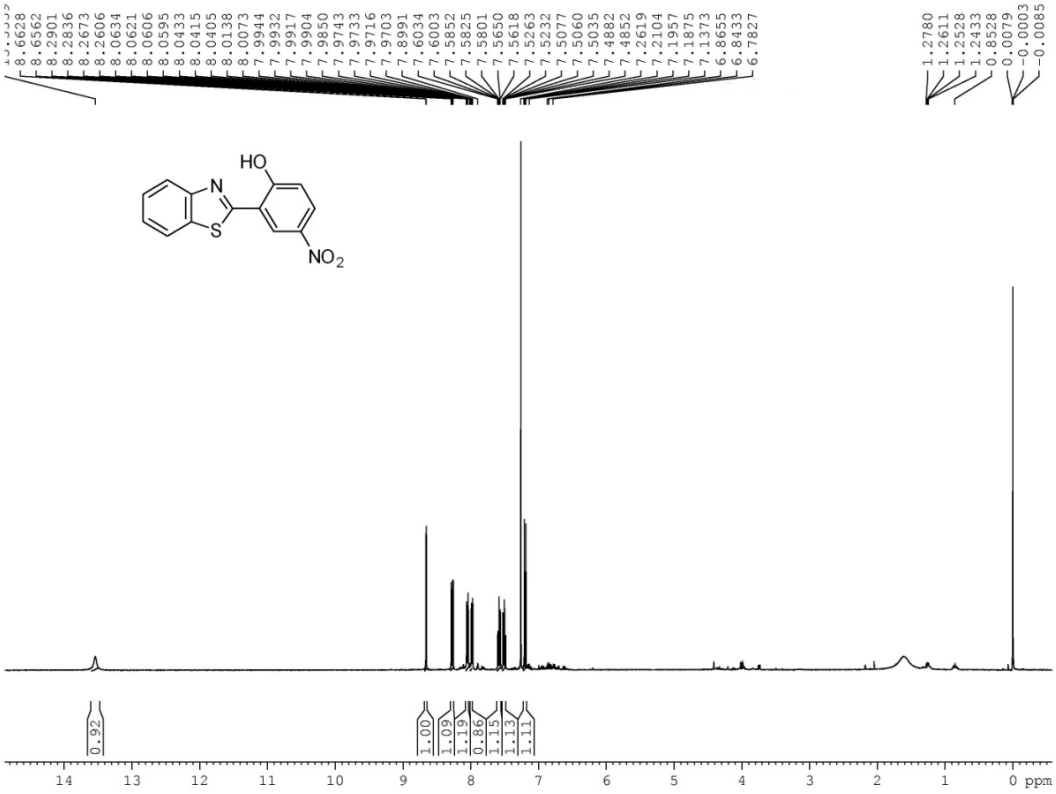
^{13}C NMR of 2-Benzothiazol-2-yl-3-bromo-phenol (4c, Table 1):-



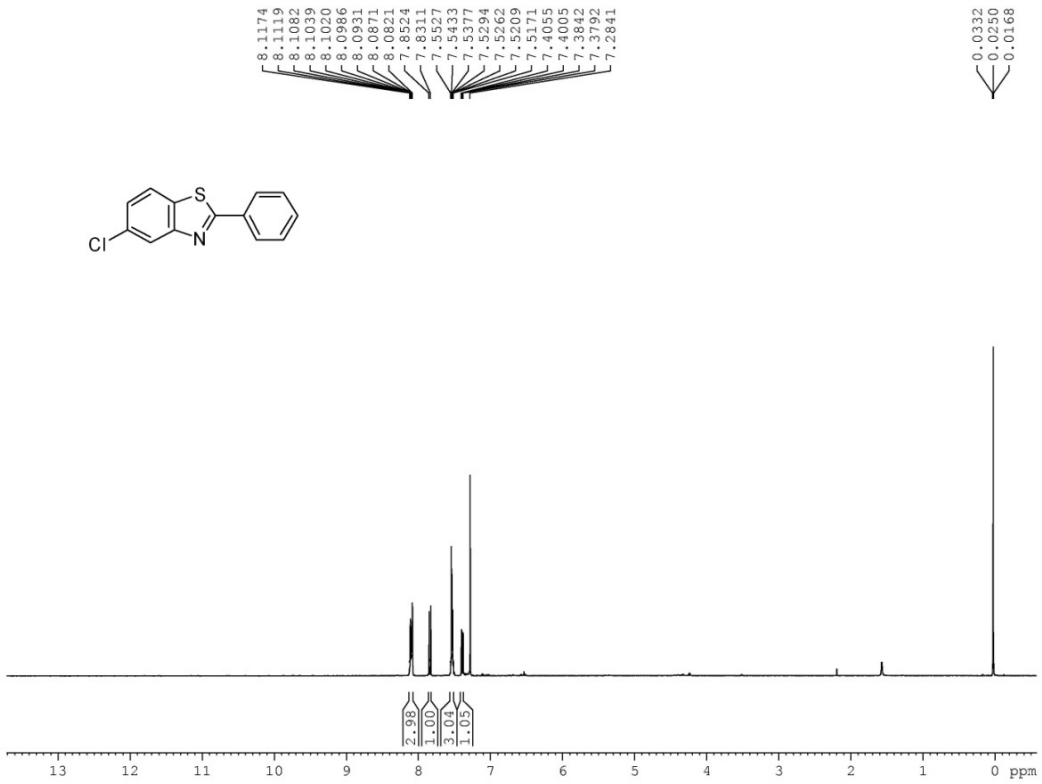
^{1}H NMR of 2-(3-Nitrophenyl)benzo[*d*]thiazole (starting benzothiazole of 4d, Table 1):-



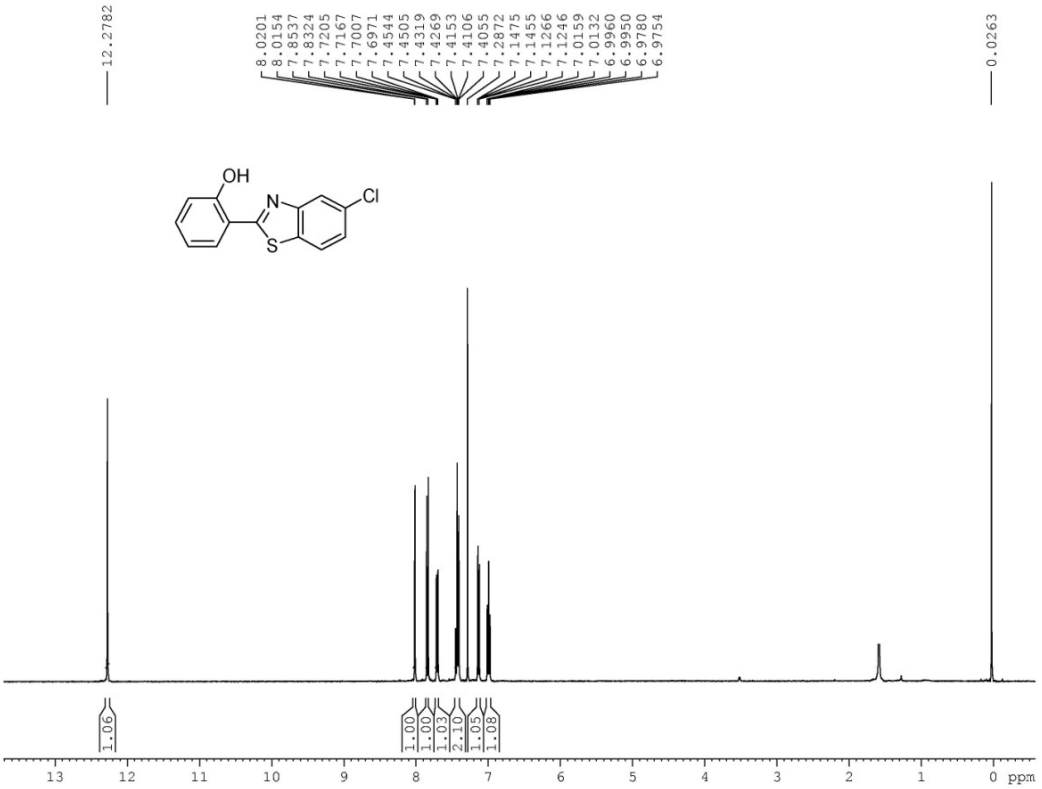
^{1}H NMR of 2-(Benzo[*d*]thiazol-2-yl)-4-nitrophenol (4d, Table 1):-



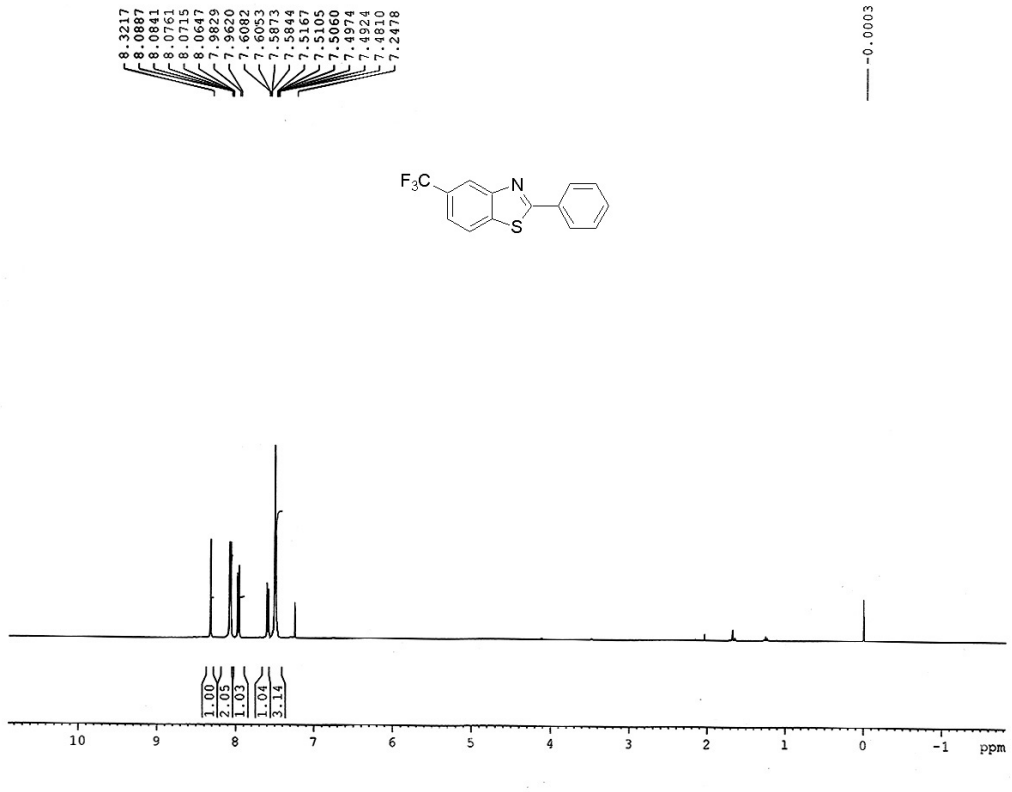
^{1}H NMR of 5-Chloro-2-phenylbenzo[*d*]thiazole (starting benzothiazole of 4e, Table 1):-



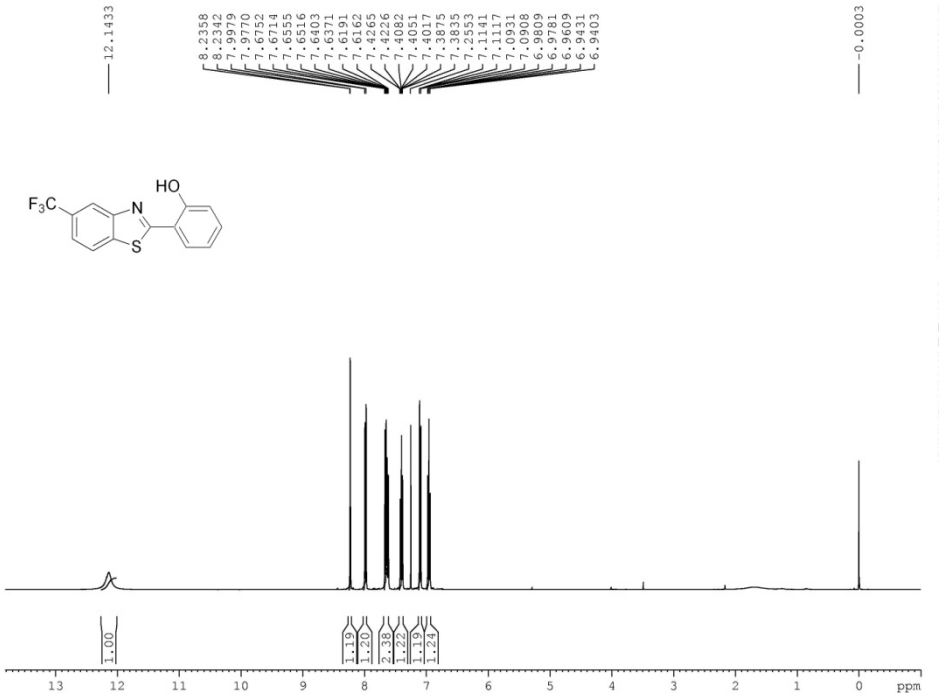
^{1}H NMR of 2-(5-Chlorobenzo[*d*]thiazol-2-yl)phenol (4e, Table 1):-



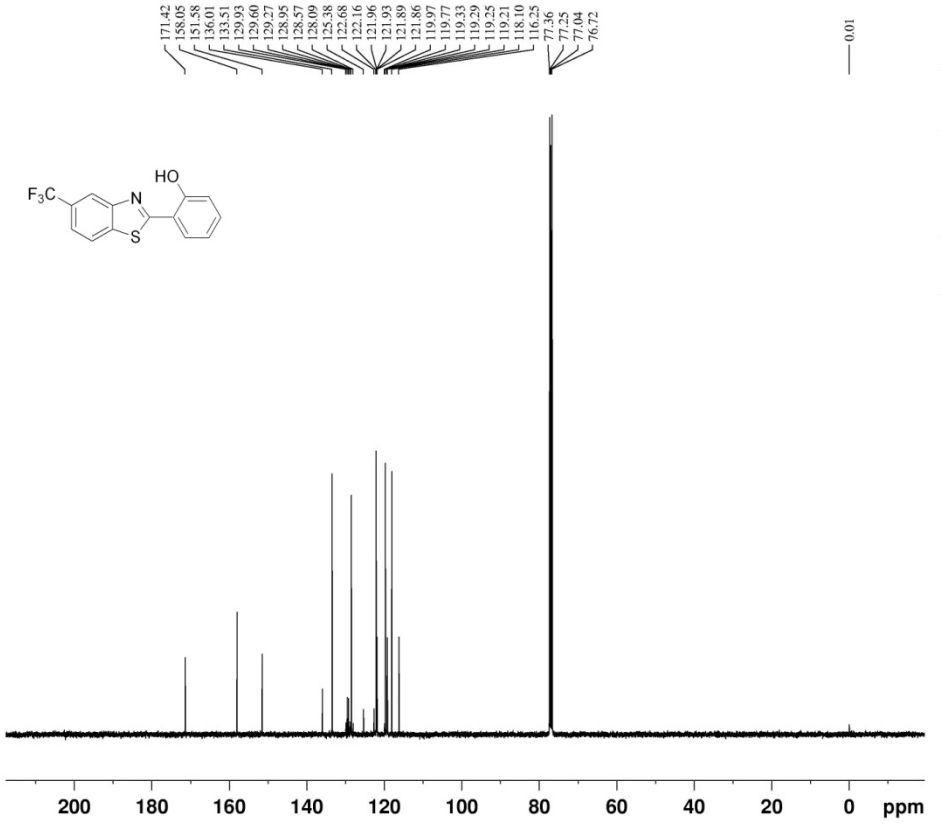
^{1}H NMR of 2-Phenyl-5-trifluoromethyl-benzothiazole (starting benzothiazole of 4f, Table 1):-



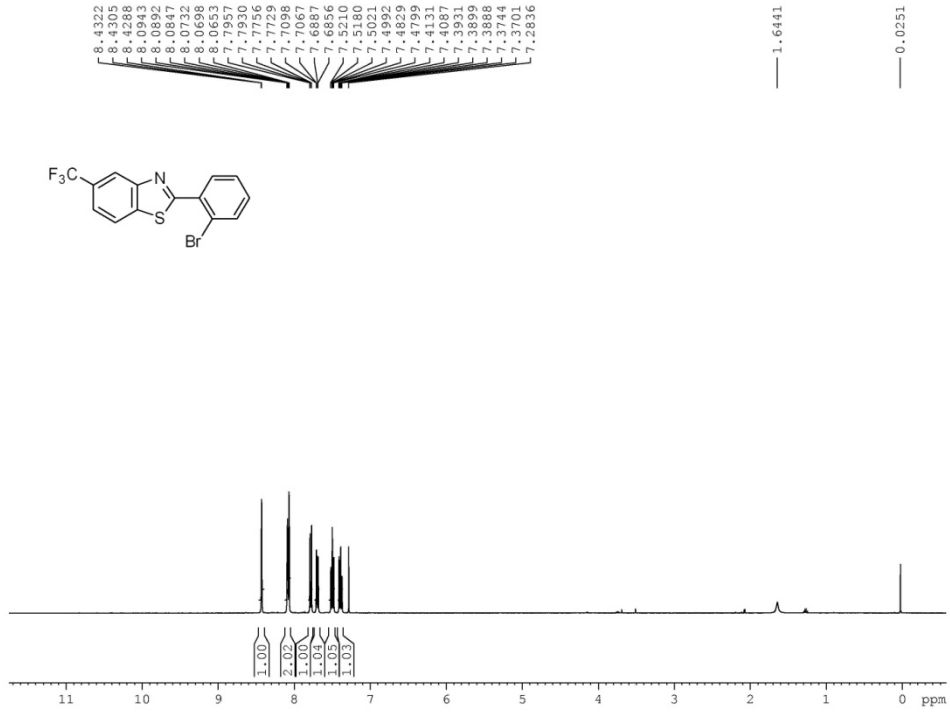
^{1}H NMR of 2-(5-Trifluoromethyl-benzothiazol-2-yl)-phenol (4f, Table 1):-



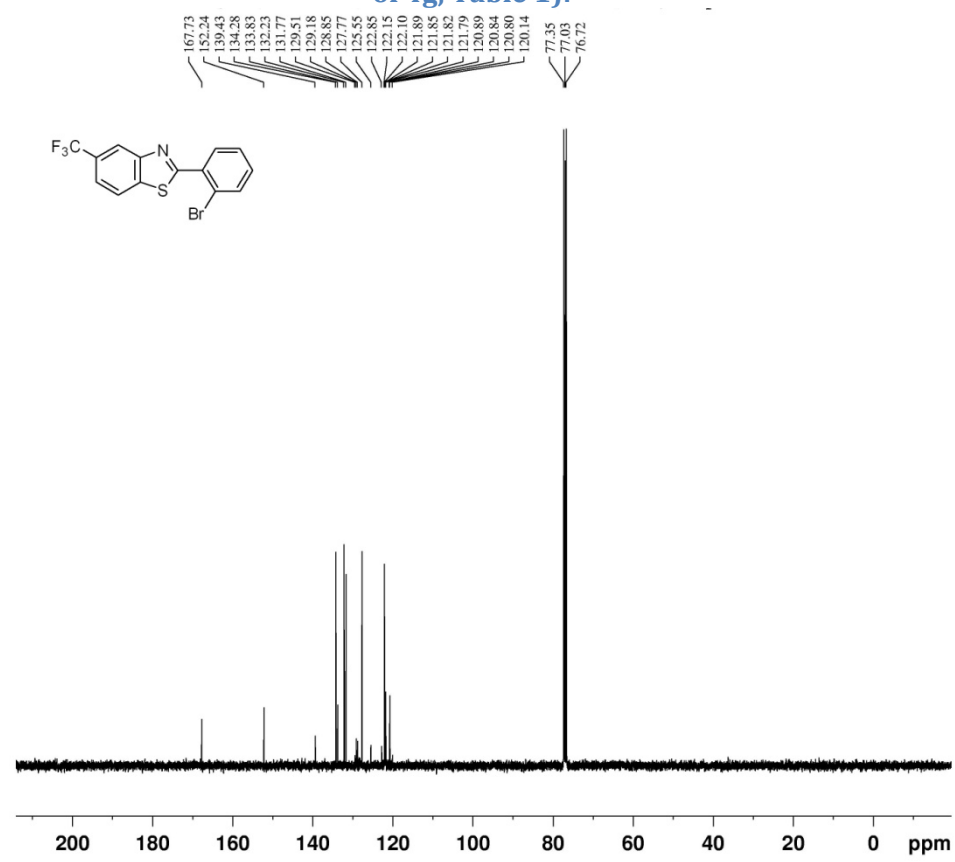
^{13}C NMR of 2-(5-Trifluoromethyl-benzothiazol-2-yl)-phenol (4f, Table 1):-



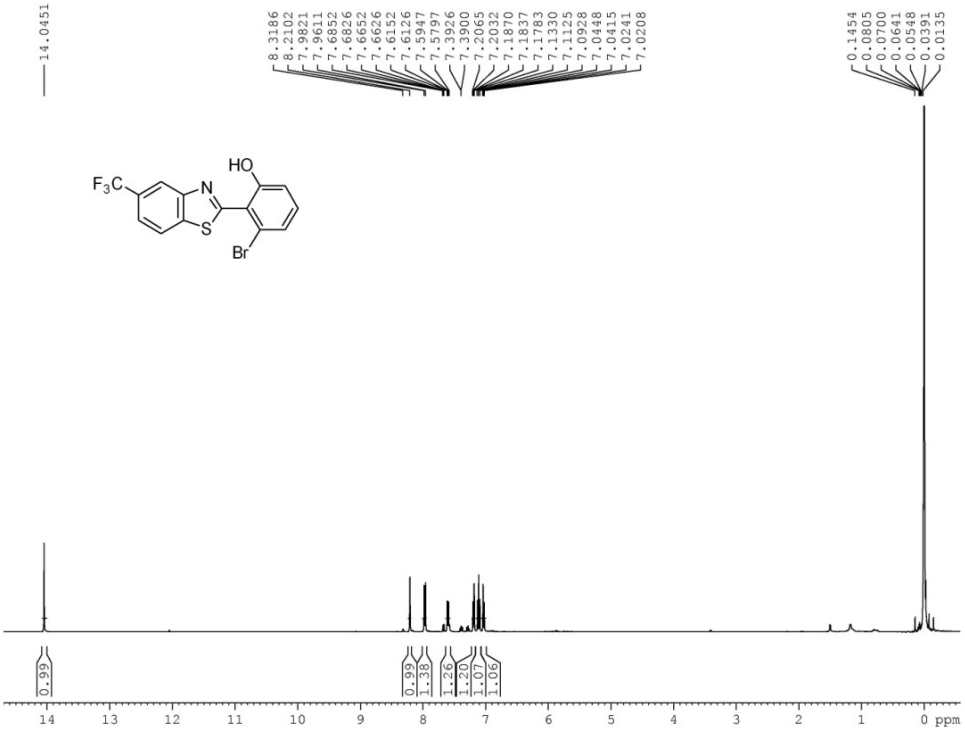
^{1}H NMR of 2-(2-Bromophenyl)-5-(trifluoromethyl)benzo[*d*]thiazole (starting benzothiazole of 4g, Table 1):-



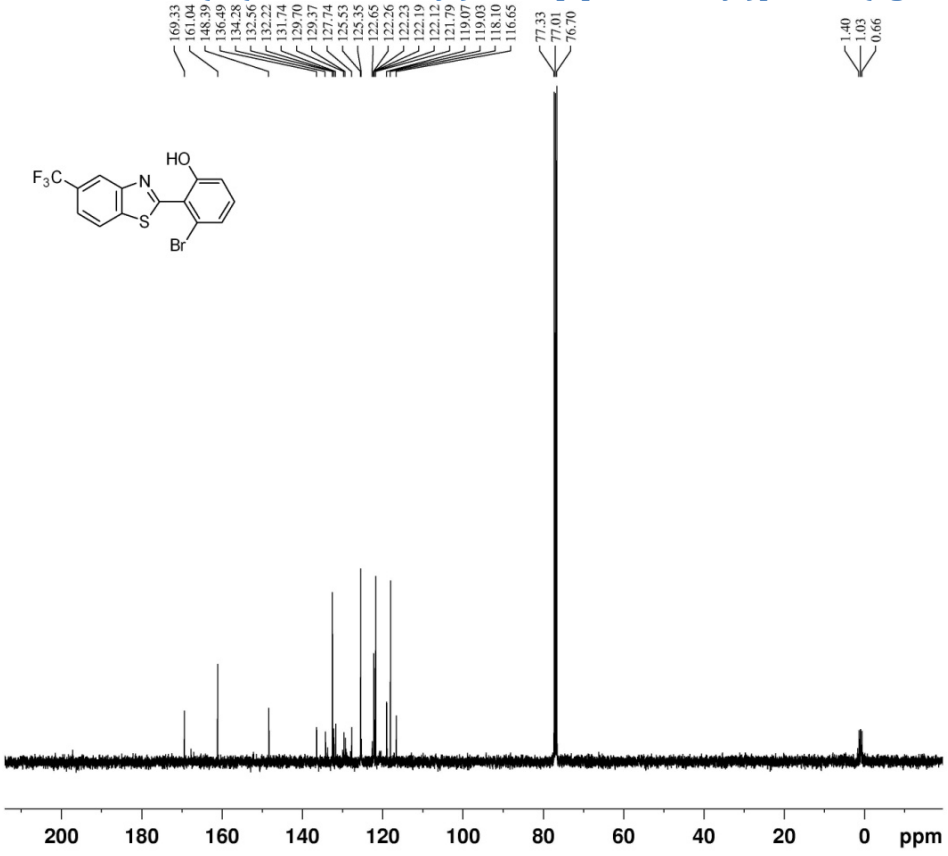
^{13}C NMR of 2-(2-Bromophenyl)-5-(trifluoromethyl)benzo[*d*]thiazole (starting benzothiazole of 4g, Table 1):-



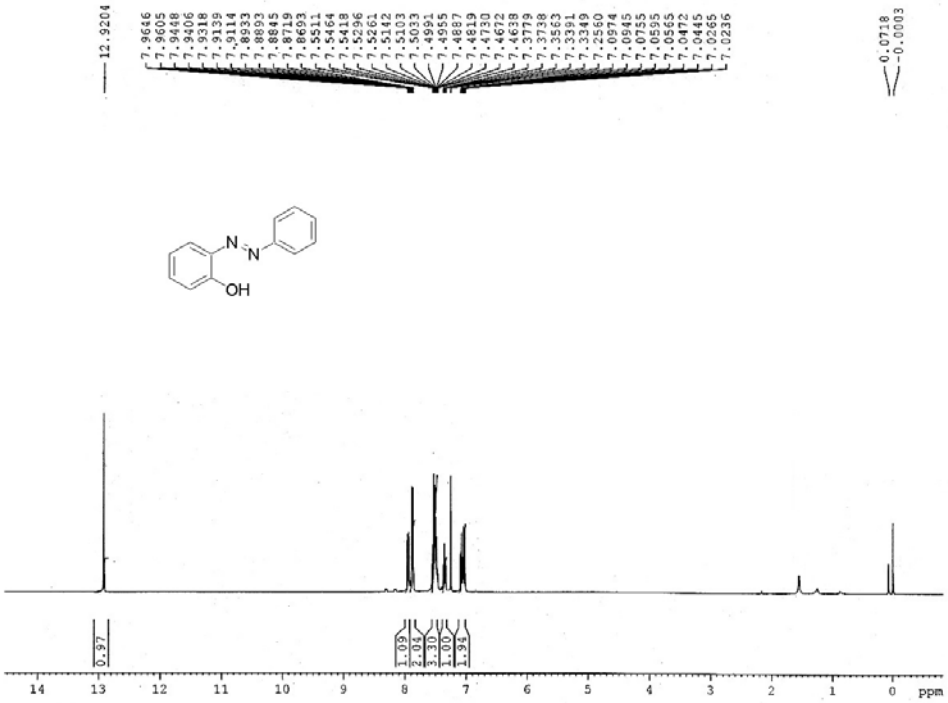
^{1}H NMR of 3-Bromo-2-(5-(trifluoromethyl)benzo[*d*]thiazol-2-yl)phenol (4g, Table 1):-



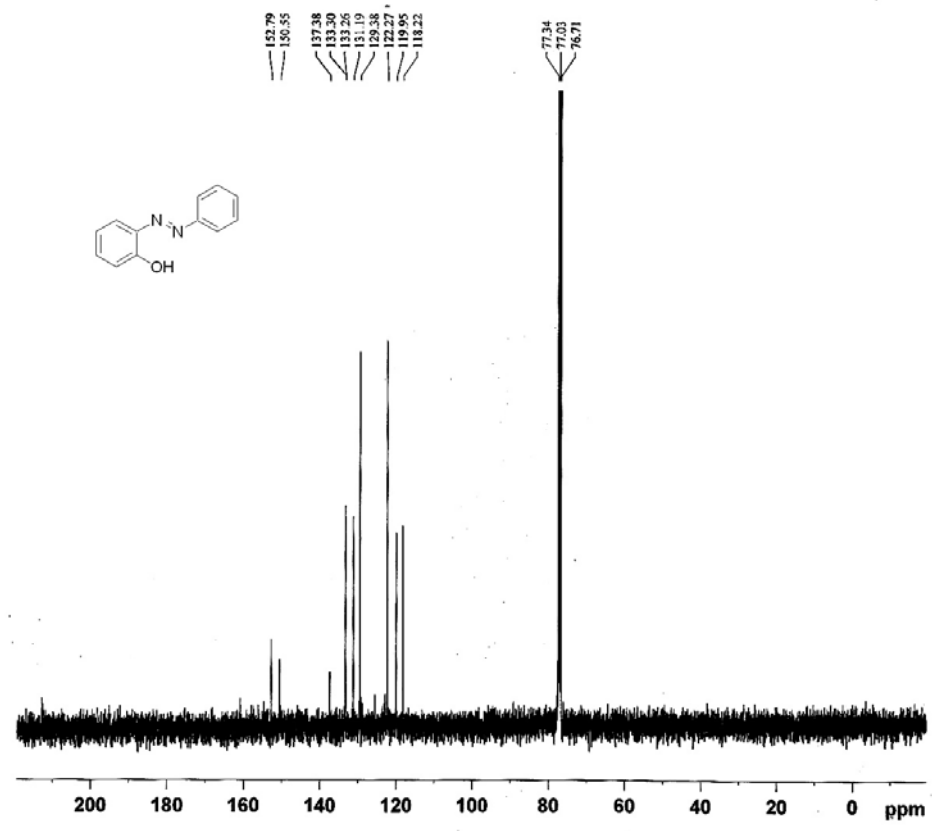
^{13}C NMR of 3-Bromo-2-(5-(trifluoromethyl)benzo[*d*]thiazol-2-yl)phenol (4g, Table 1):-



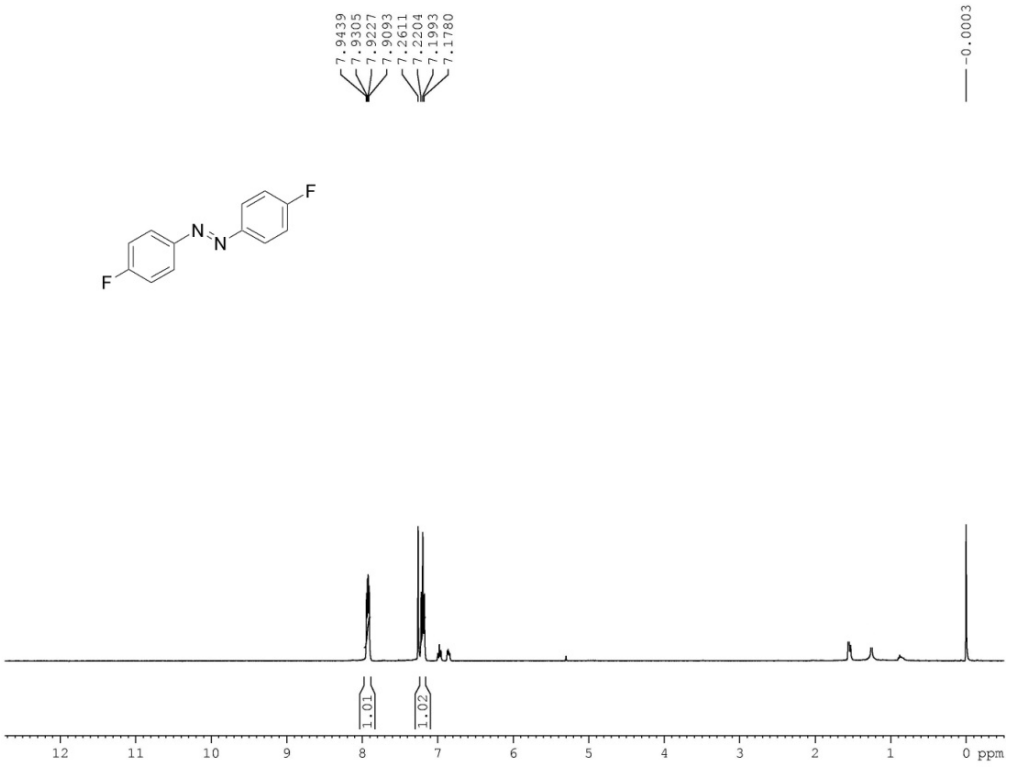
^{1}H NMR of 2-Phenylazo-phenol (5a, Table 2):-



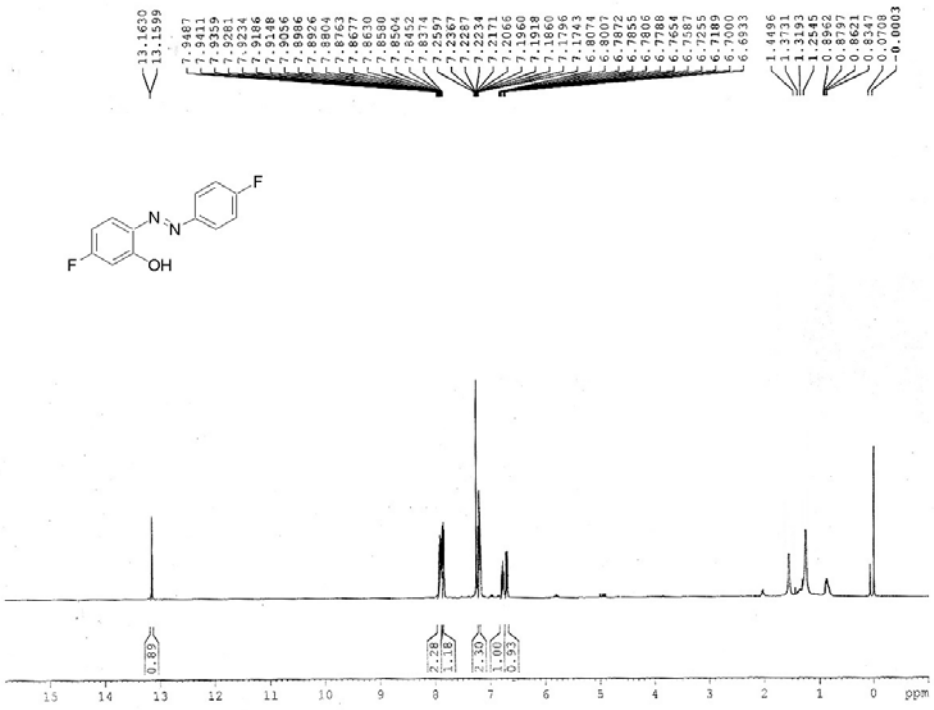
^{13}C NMR of 2-Phenylazo-phenol (5a, Table 2):-



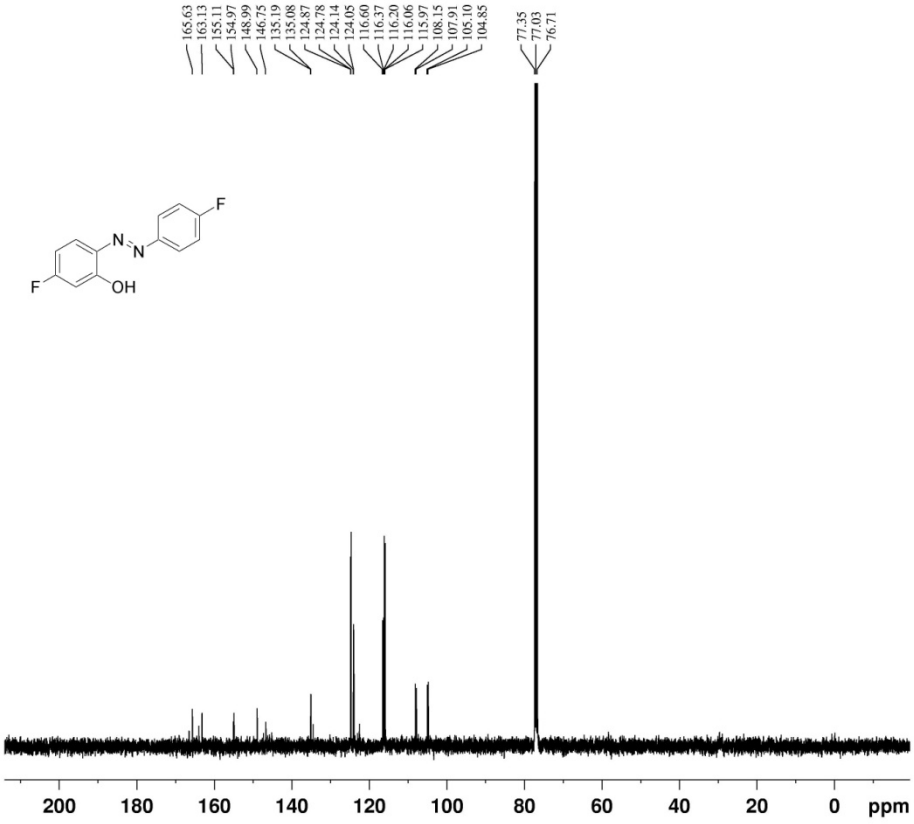
^{1}H NMR of Bis-(4-fluorophenyl)-diazene (starting azo compound of 5b, Table 2):-



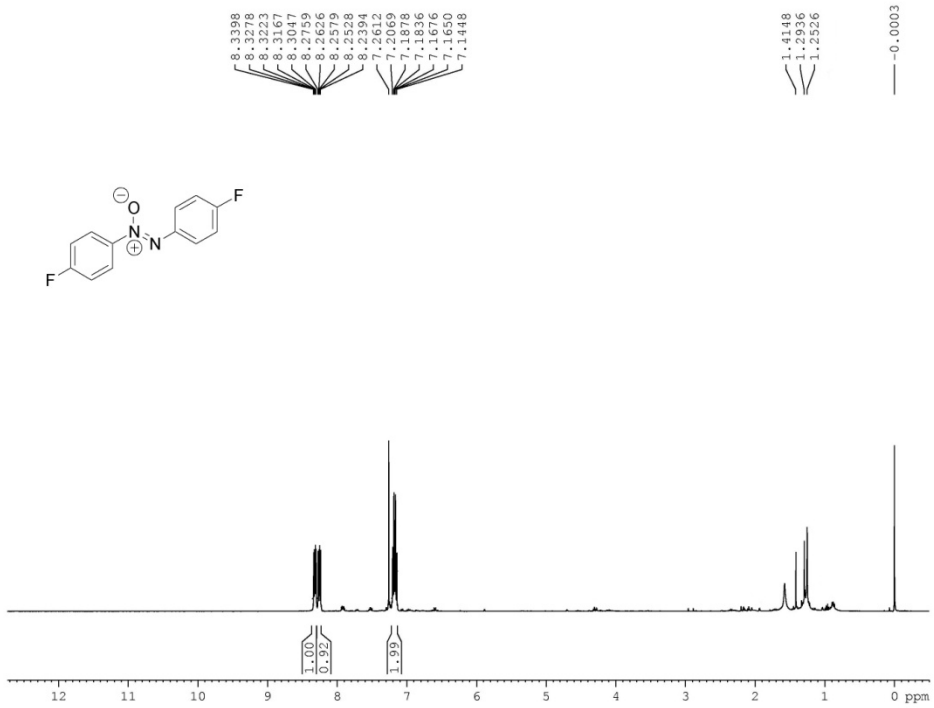
^{1}H NMR of 5-Fluoro-2-(4-fluoro-phenylazo)-phenol (5b, Table 2):-



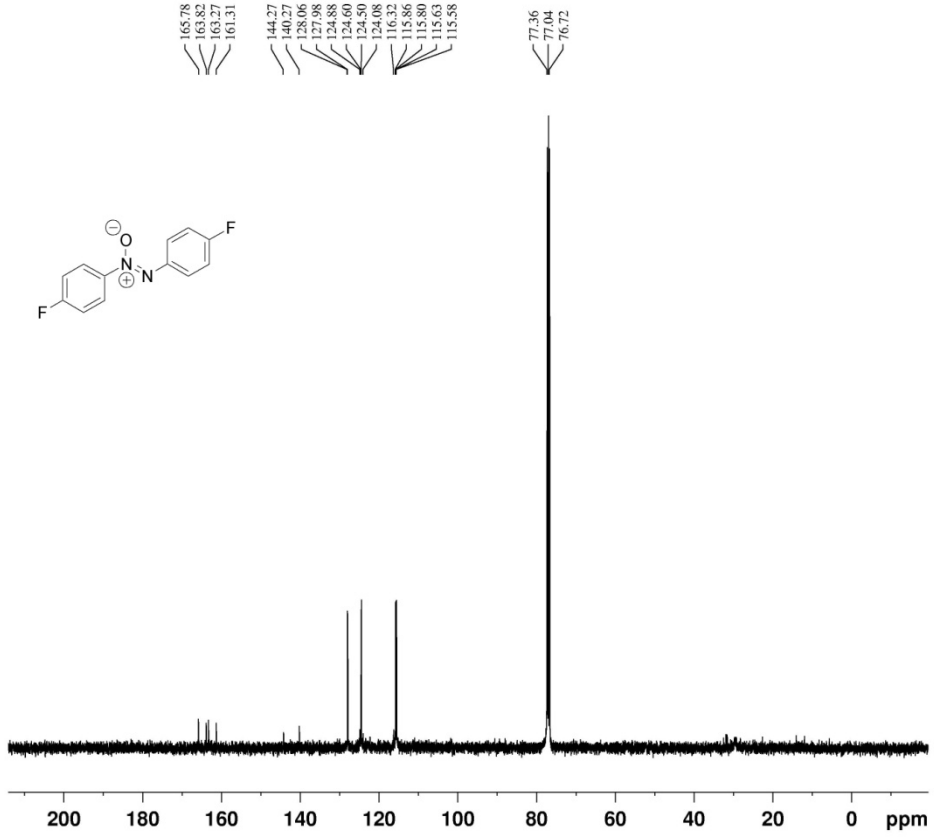
^{13}C NMR of 5-Fluoro-2-(4-fluoro-phenylazo)-phenol (5b, Table 2):-



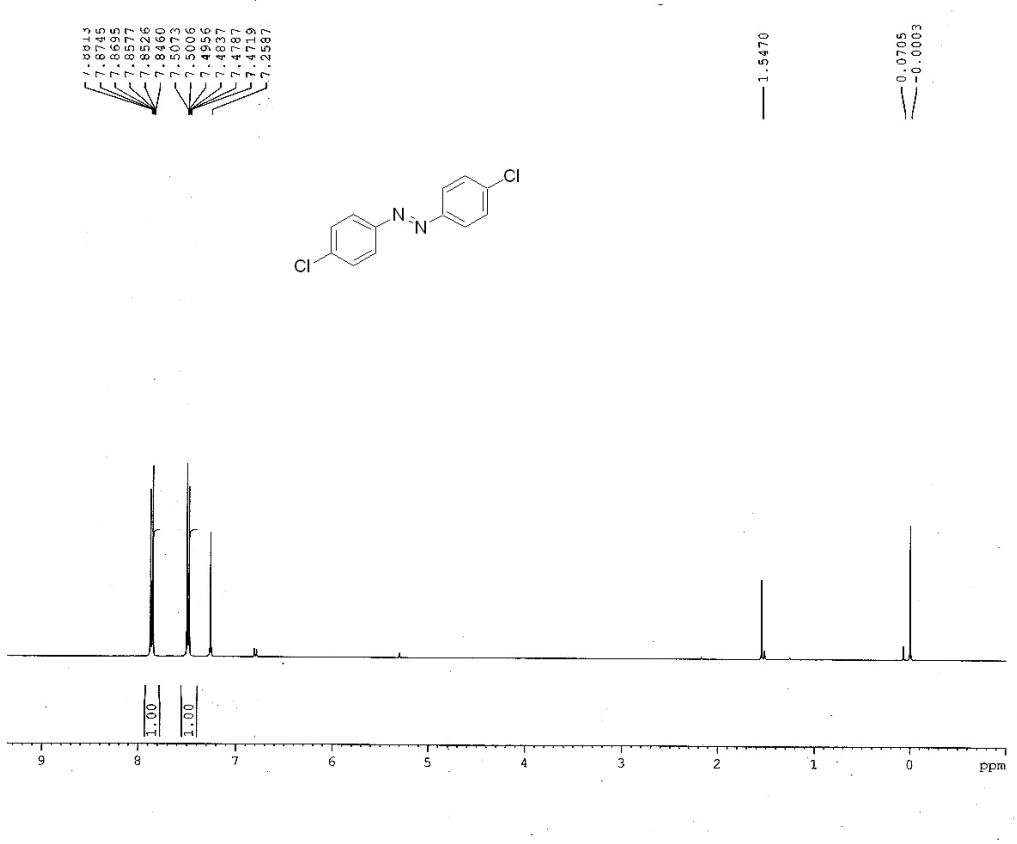
^{1}H NMR of *N,N′*-Bis-(4-fluoro-phenyl)-diazene *N*-oxide (5c, Table 2):-



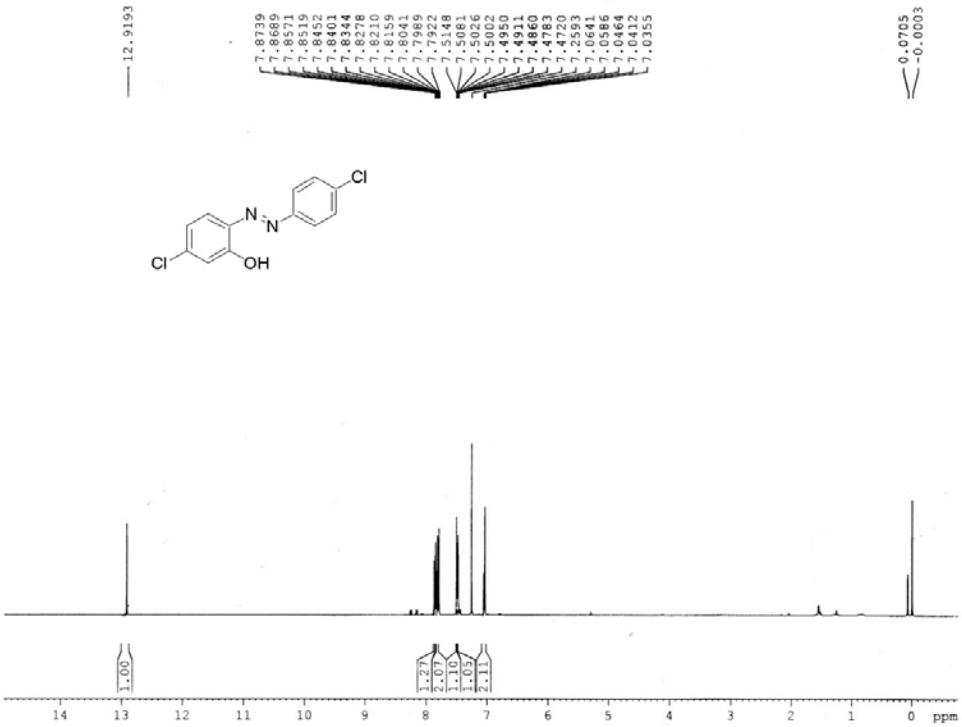
^{13}C NMR of *N,N′*-Bis-(4-fluoro-phenyl)-diazene *N*-oxide (5c, Table 2):-



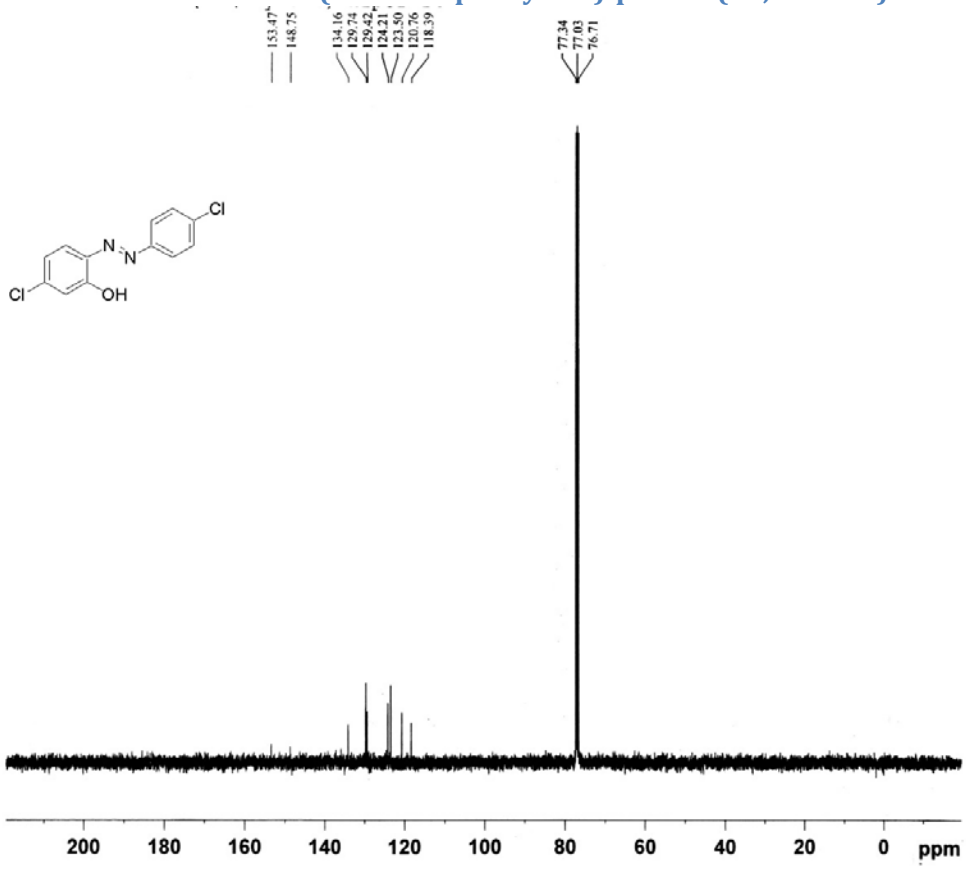
^{1}H NMR of Bis-(4-chlorophenyl)-diazene (starting azo compound of 5d, Table 2):-



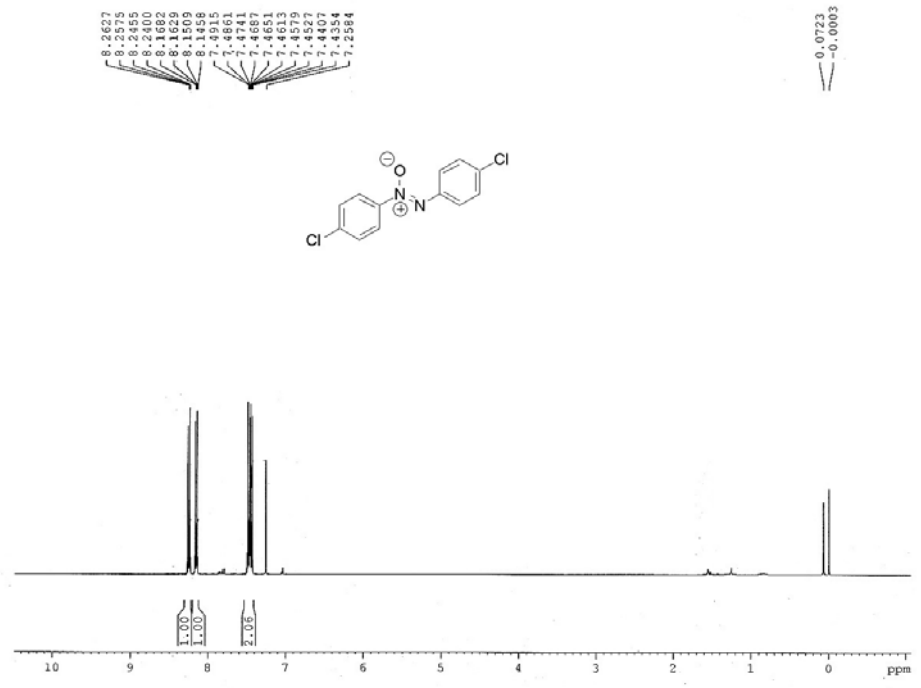
^{1}H NMR of 5-Chloro-2-(4-chloro-phenylazo)-phenol (5d, Table 2):-



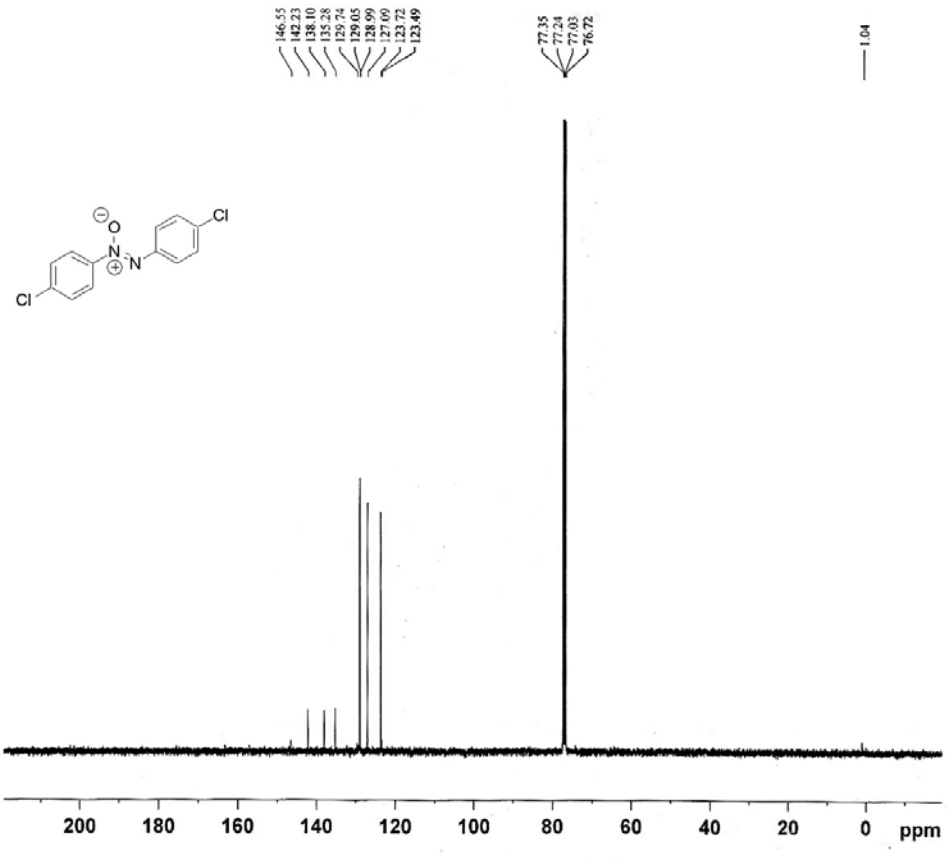
^{13}C NMR of 5-Chloro-2-(4-chloro-phenylazo)-phenol (5d, Table 2):-



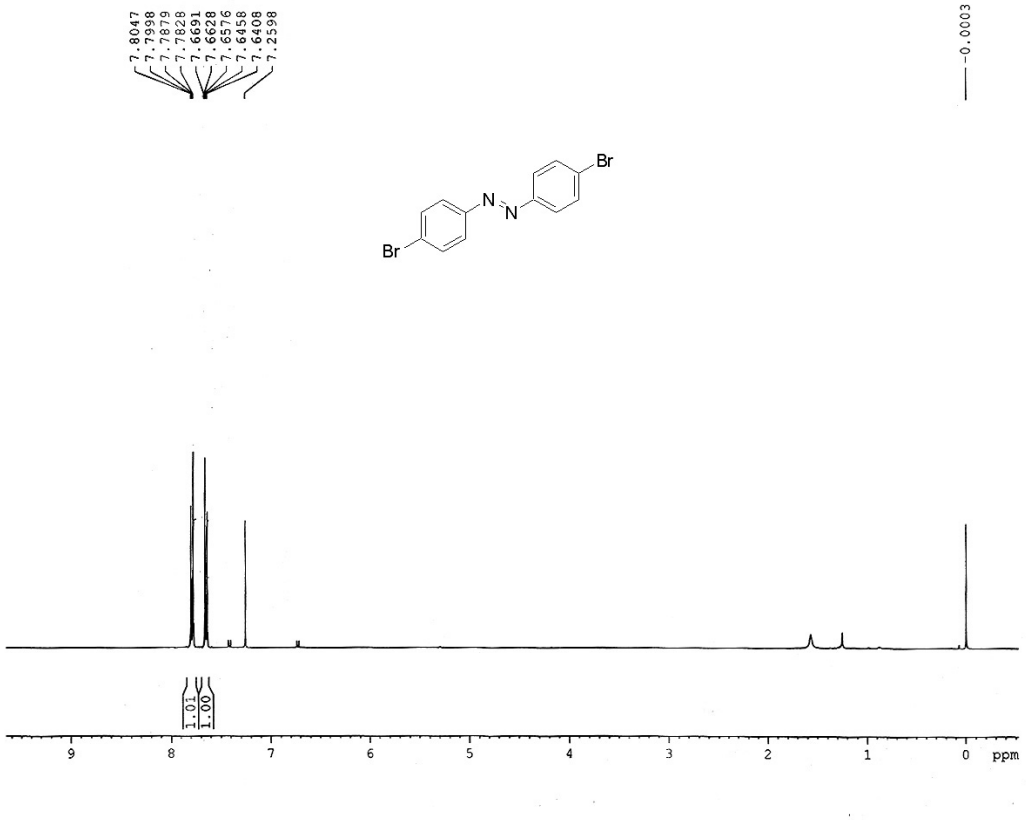
^{1}H NMR of *N,N′*-Bis-(4-chloro-phenyl)-diazene *N*-oxide (5e, Table 2):-



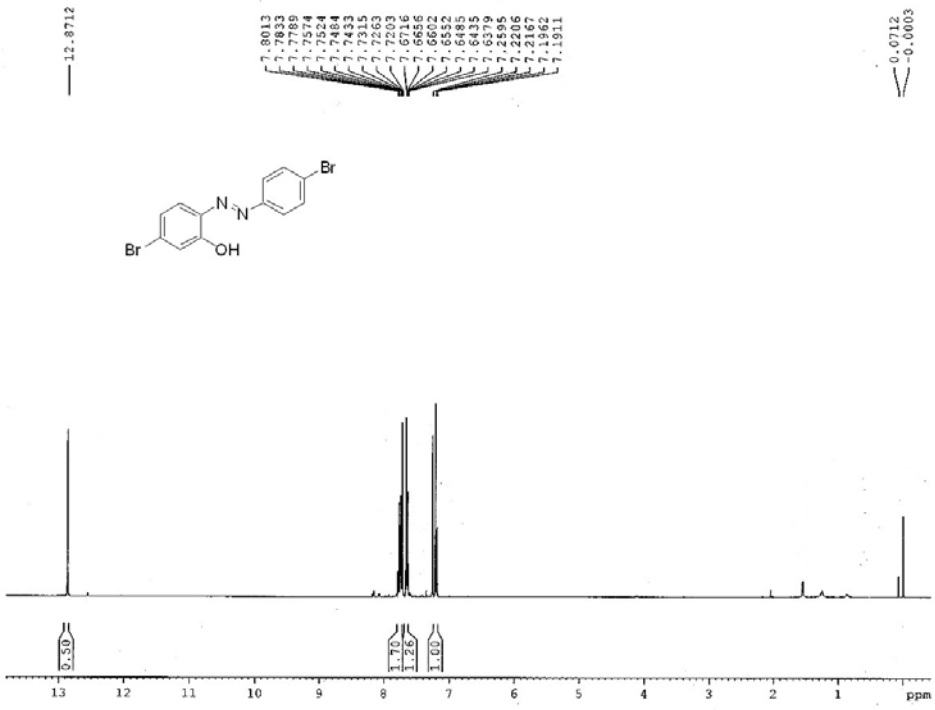
^{13}C NMR of of *N,N′*-Bis-(4-chloro-phenyl)-diazene *N*-oxide (5e, Table 2):-



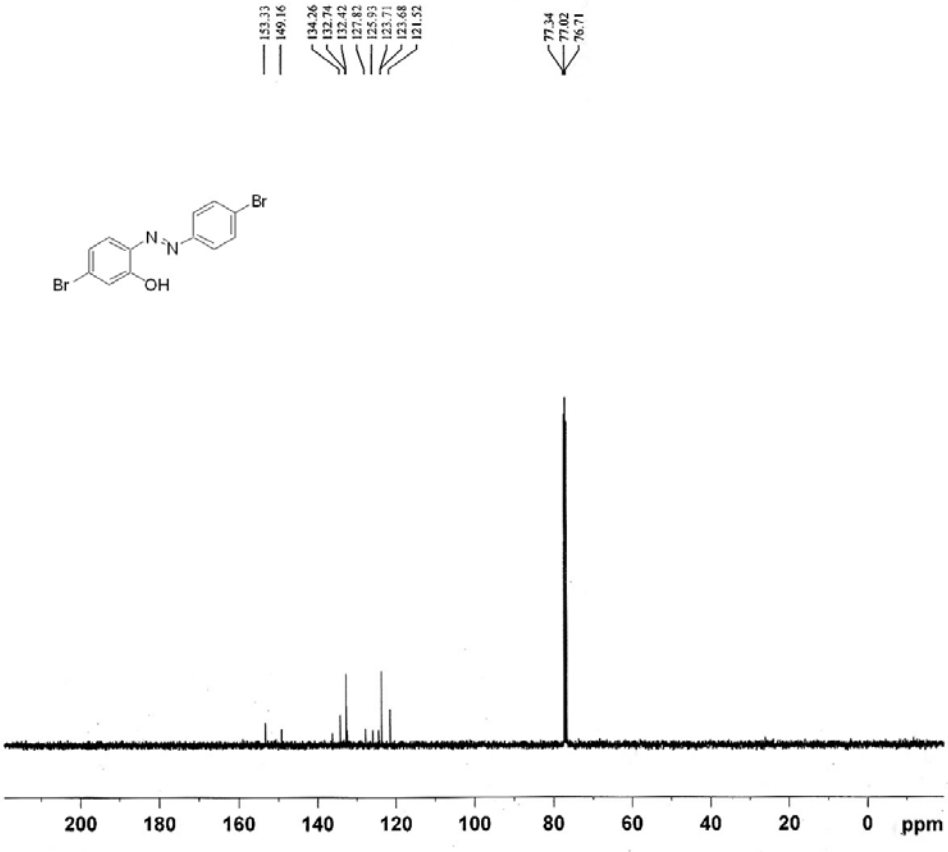
^{1}H NMR of Bis-(4-bromophenyl)-diazene (starting azo compound of 5f, Table 2):-



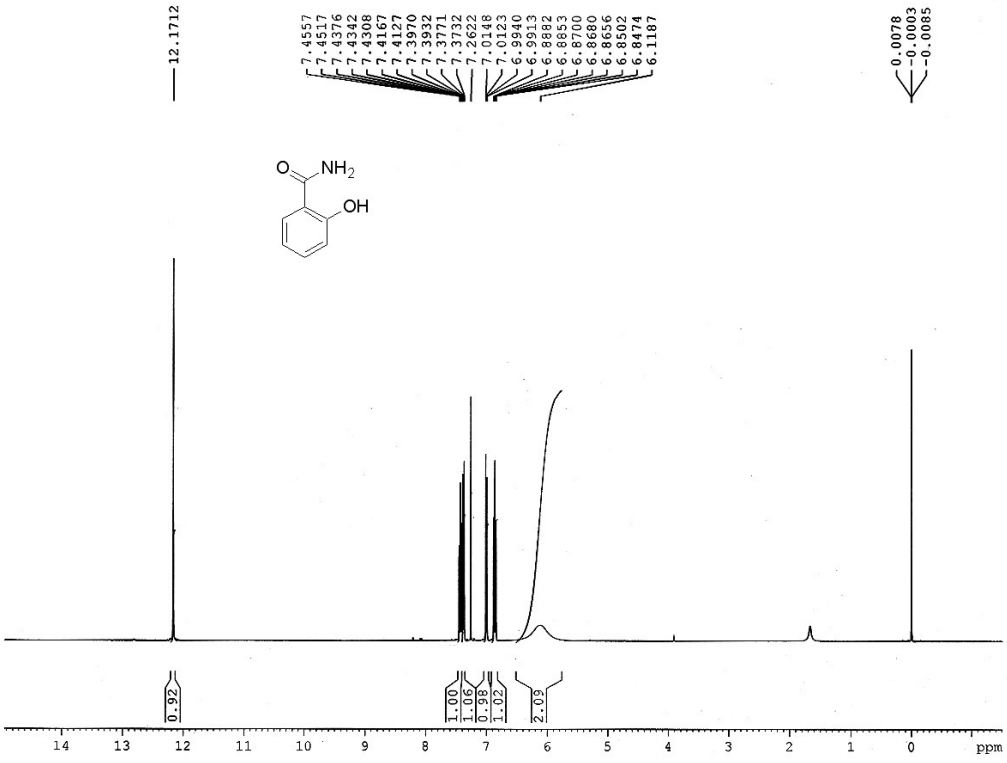
^{1}H NMR of 5-Bromo-2-(4-bromo-phenylazo)-phenol (5f, Table 2):-



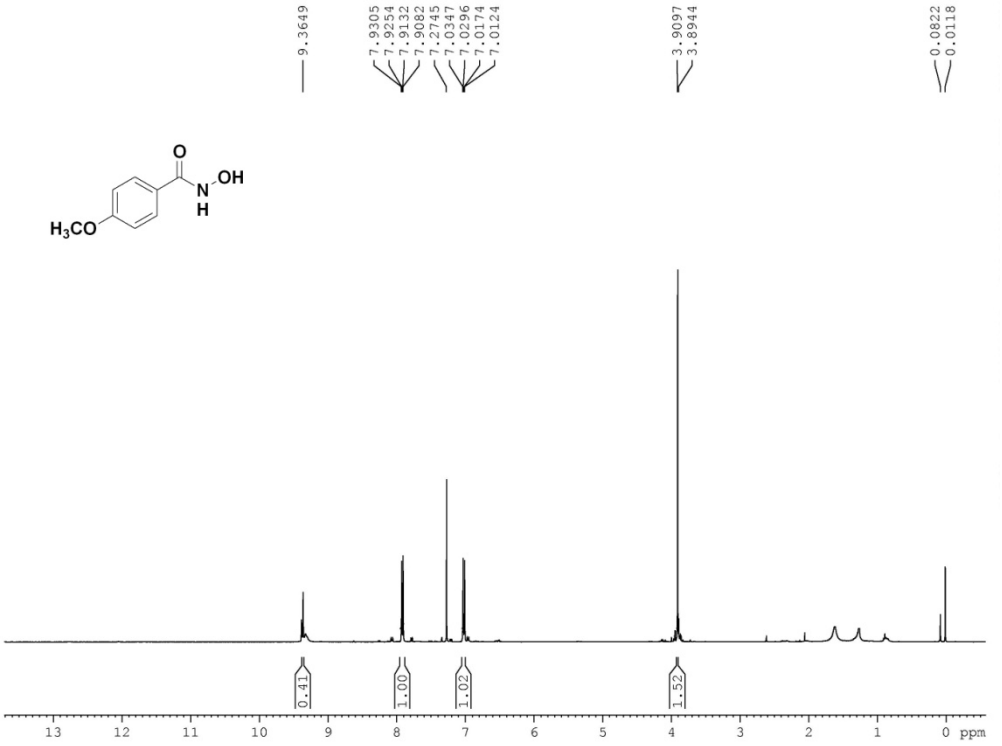
^{13}C NMR of 5-Bromo-2-(4-bromo-phenylazo)-phenol (5f, Table 2):-



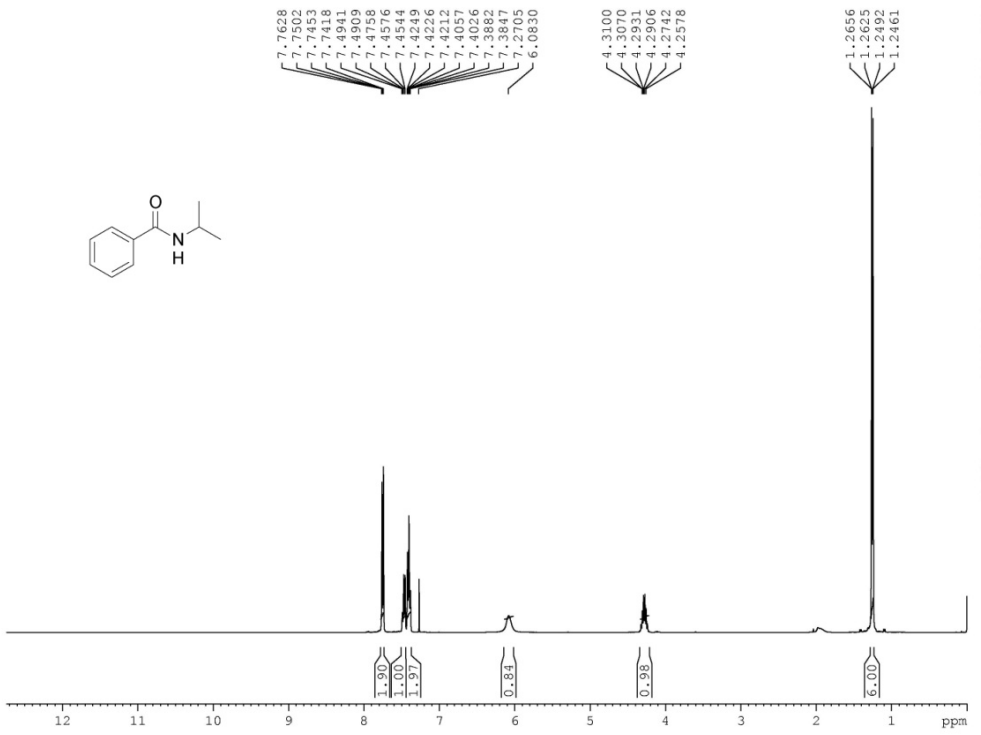
^{1}H NMR of 2-Hydroxy-benzamide (6a, Table 2):-



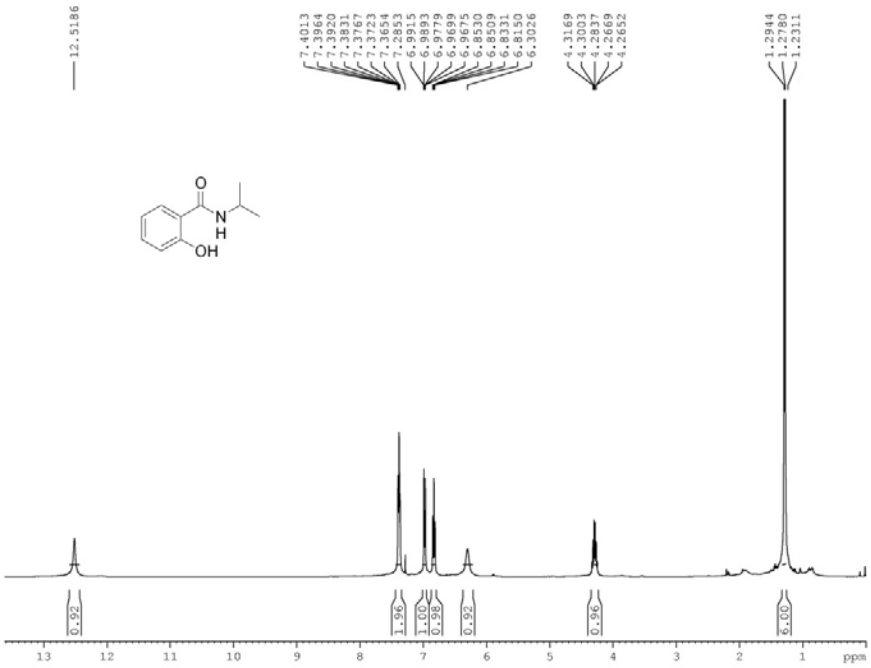
^{1}H NMR of *N*-Hydroxy-4-methoxy-benzamide (6b, Table 2):-



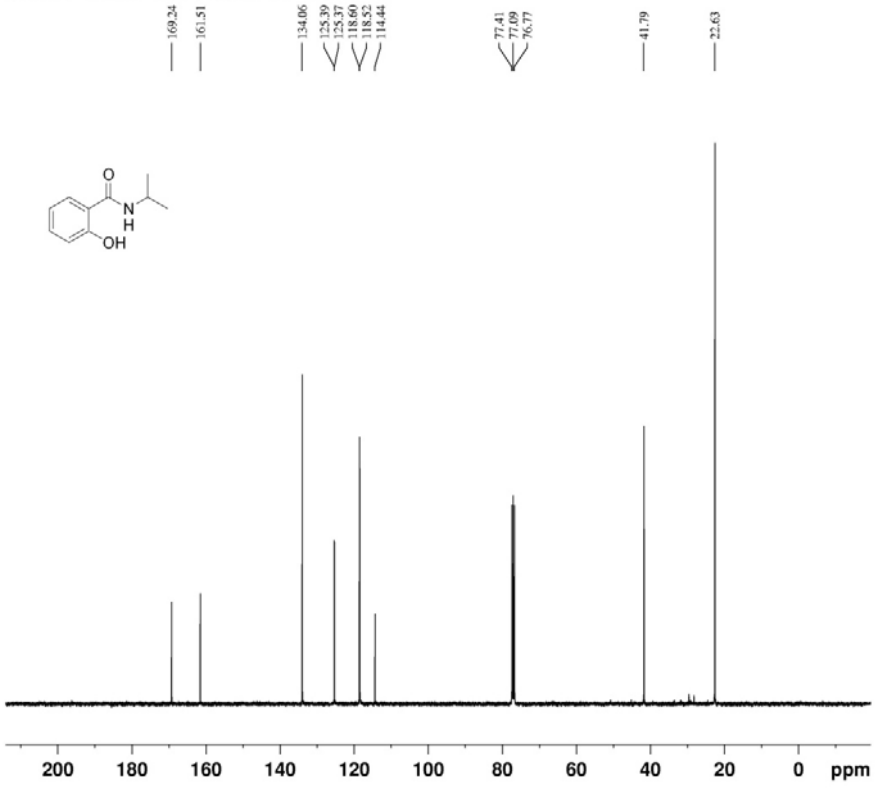
^{1}H NMR of *N*-Isopropyl benzamide (starting benzamide of 6c, Table 2):-



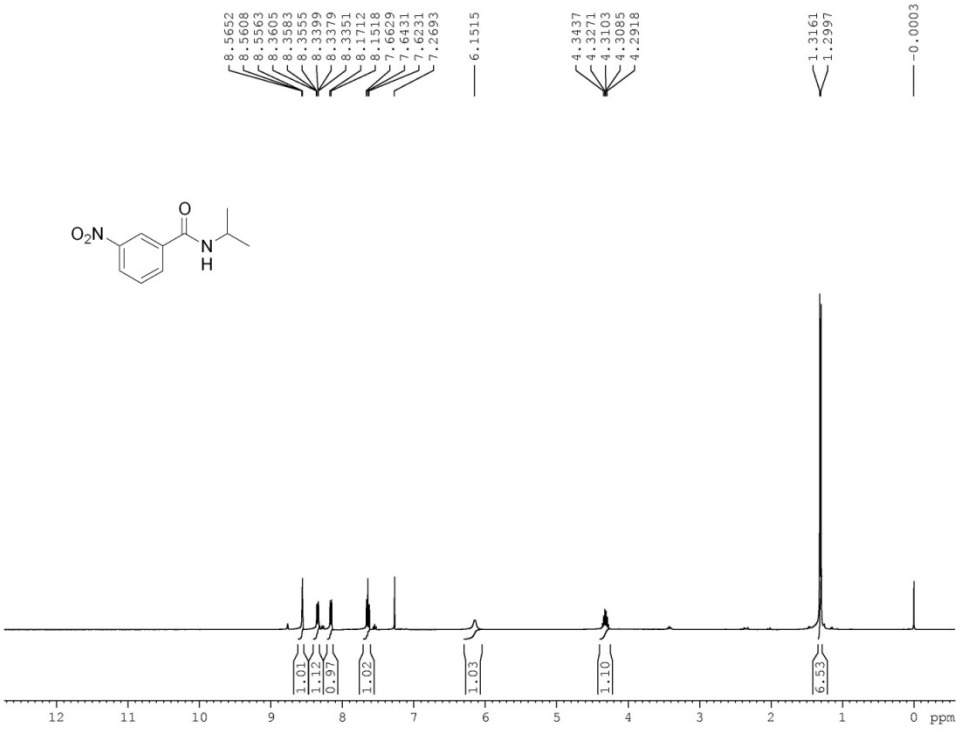
^{1}H NMR of 2-Hydroxy *N*-isopropyl benzamide (6c, Table 2):-



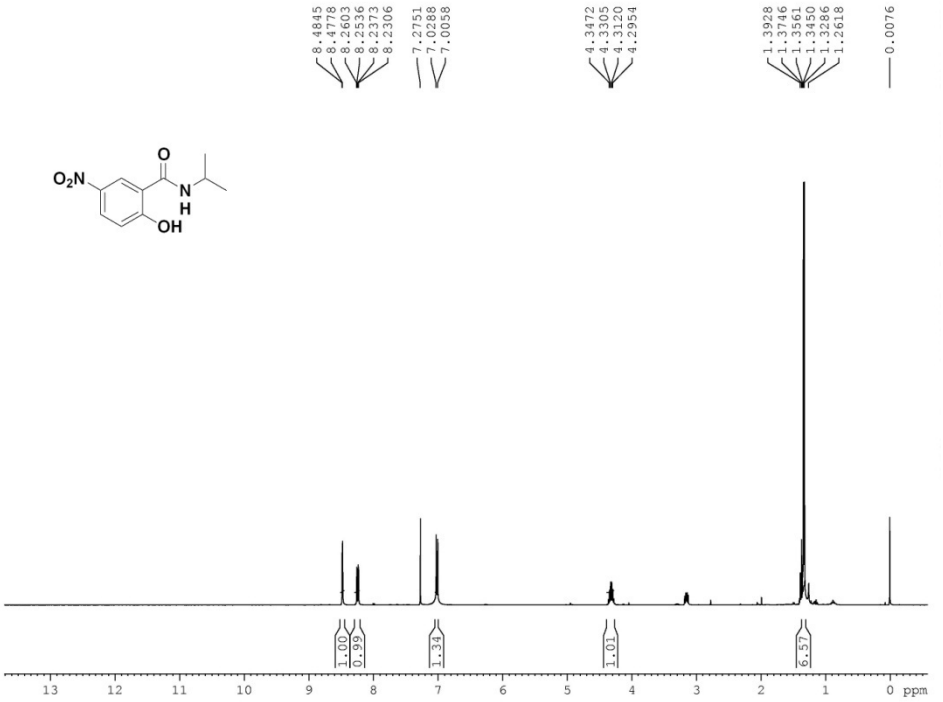
^{13}C NMR of 2-Hydroxy *N*-isopropyl benzamide (6c, Table 2):-



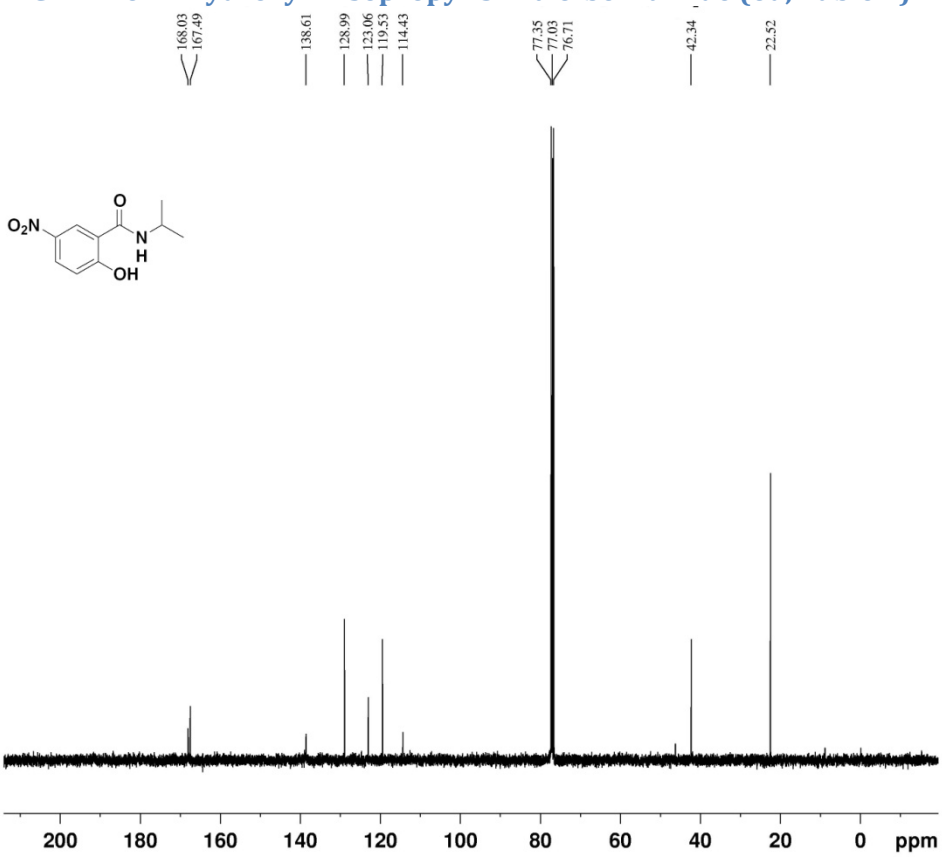
^{1}H NMR of *N*-Isopropyl-3-nitro-benzamide (starting benzamide of 6d, Table 2):-



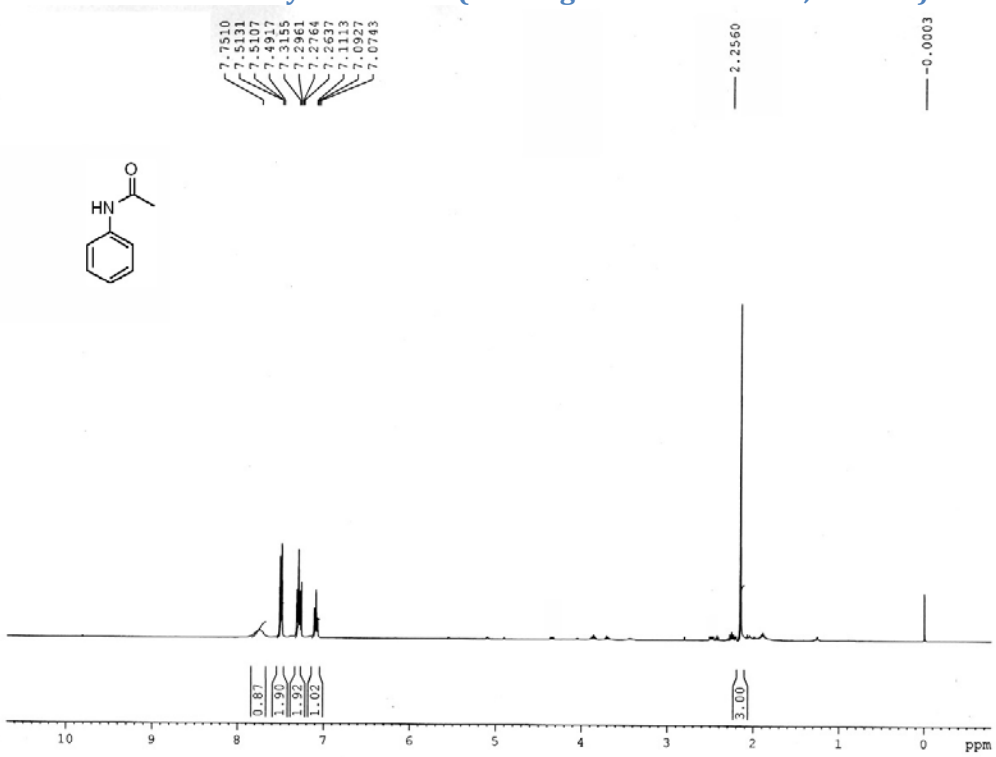
^{1}H NMR of 2-Hydroxy-*N*-isopropyl-5-nitro-benzamide (6d, Table 2):-



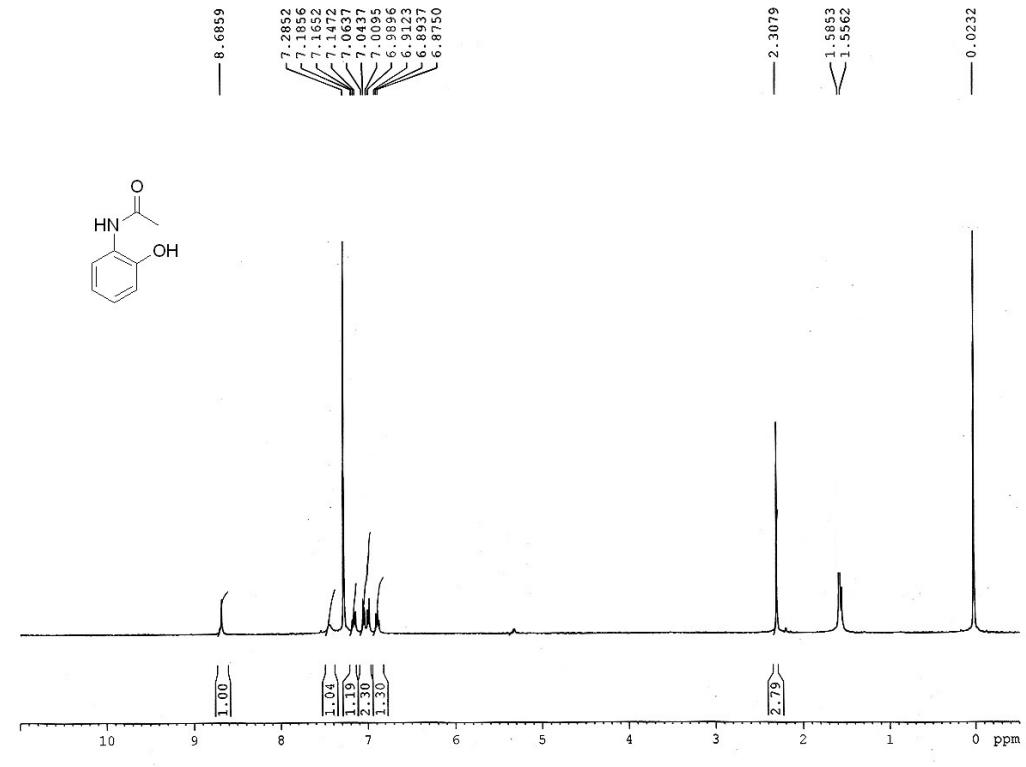
^{13}C NMR of 2-Hydroxy-*N*-isopropyl-5-nitro-benzamide (6d, Table 2):-



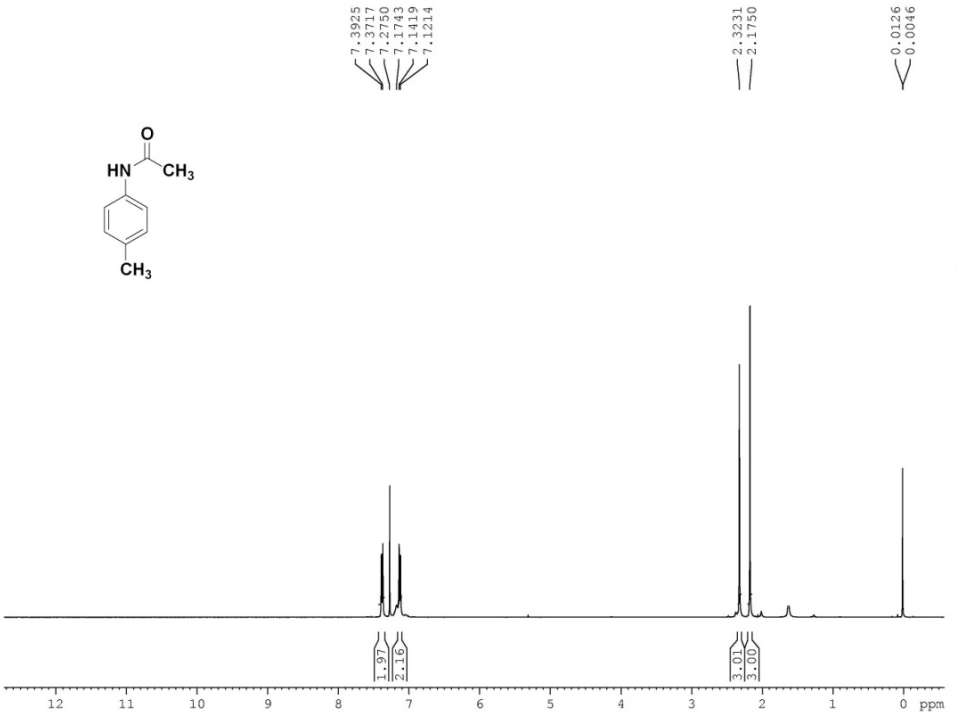
^{1}H NMR of *N*-Phenylacetamide (starting acetanilide of 7a, Table 2):-



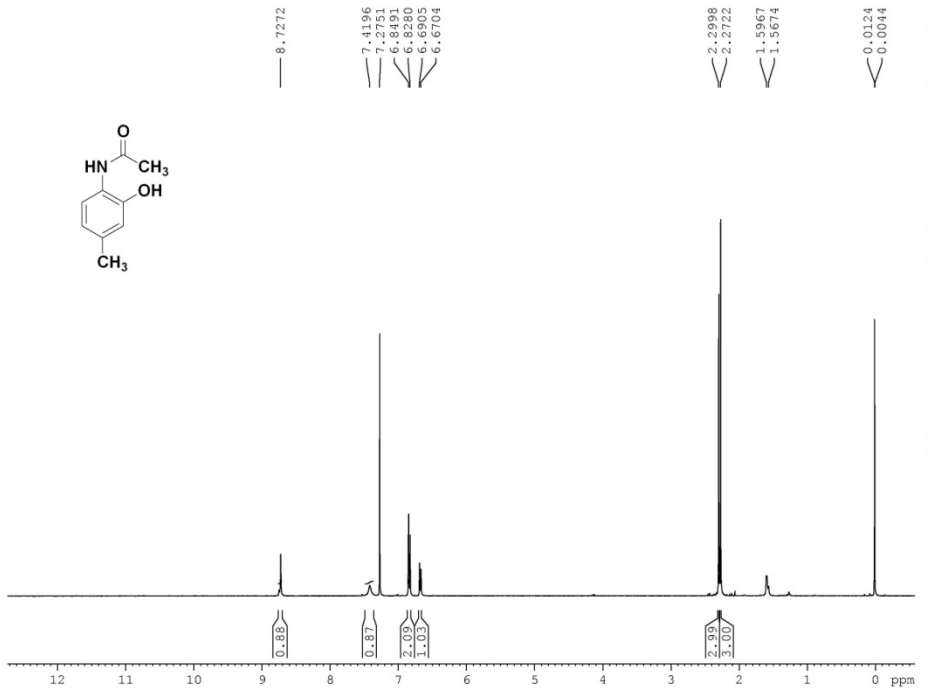
^{1}H NMR of *N*-(2-Hydroxyphenyl)-acetamide (7a, Table 2):-



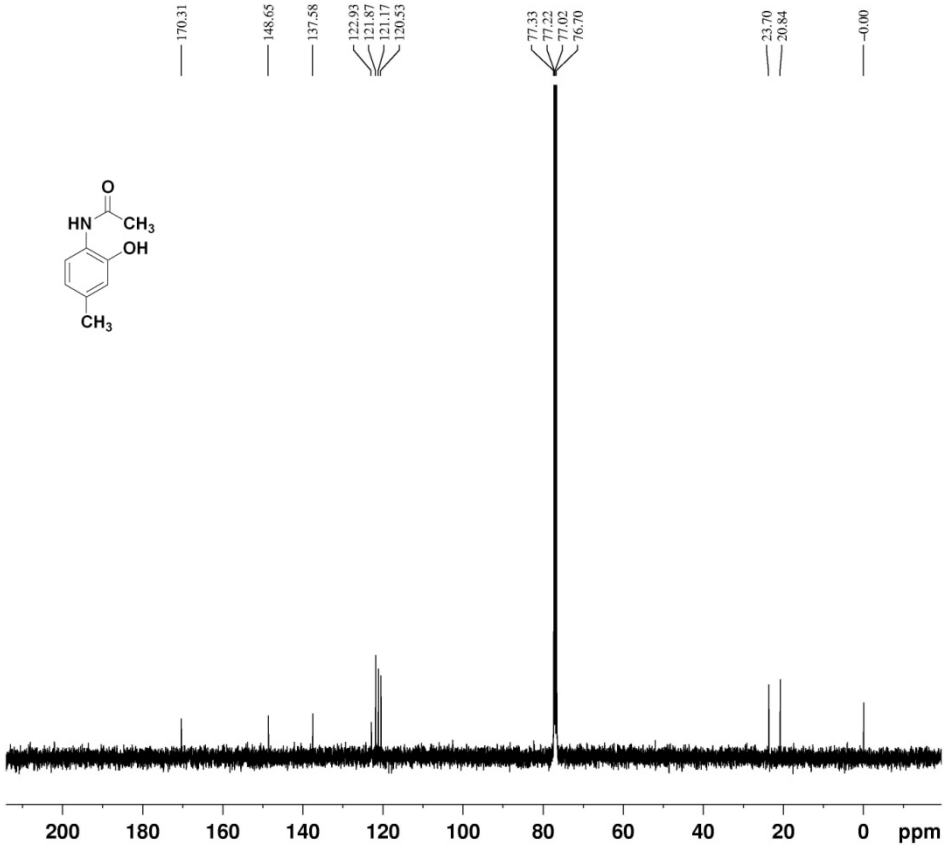
^{1}H NMR of *N*-*p*-Tolyl-acetamide (starting acetanilide of 7b, Table 2):-



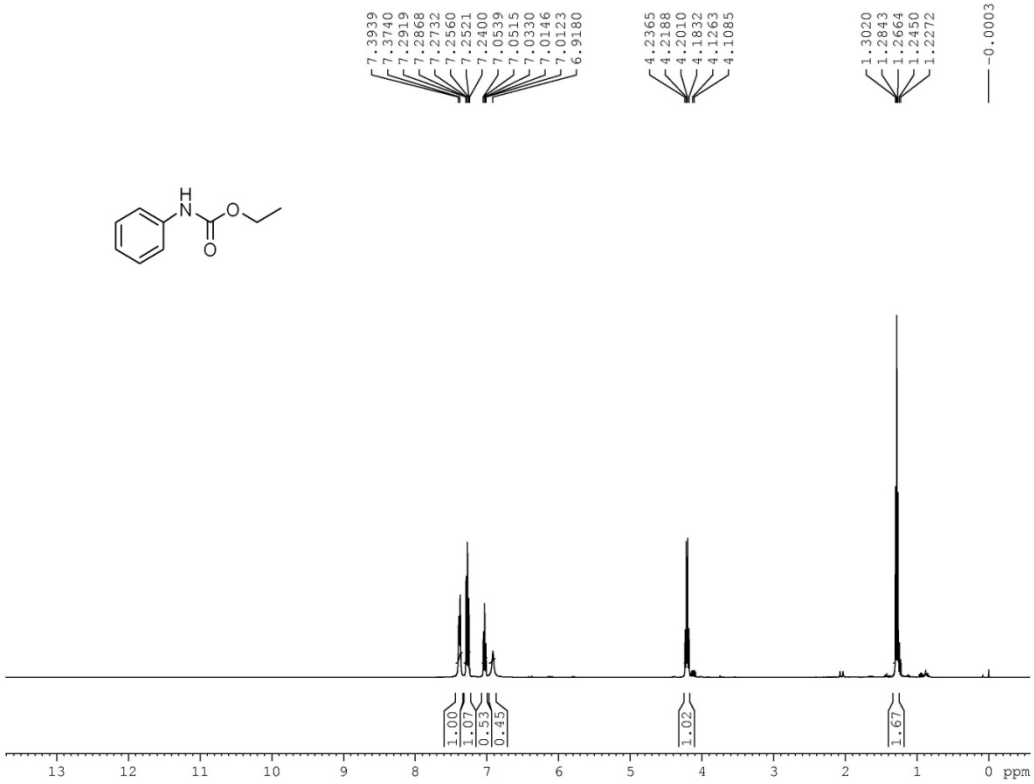
^{1}H NMR of *N*-(2-Hydroxy-4-methyl-phenyl)-acetamide (7b, Table 2):-



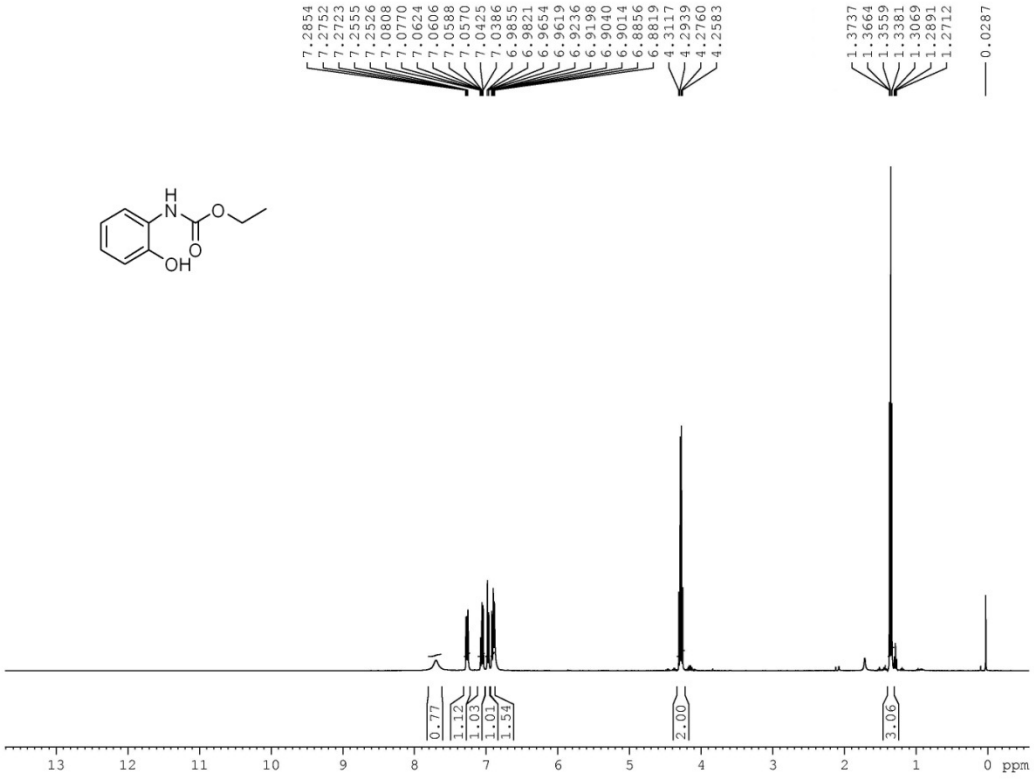
^{13}C NMR of *N*-(2-Hydroxy-4-methyl-phenyl)-acetamide (7b, Table 2):-



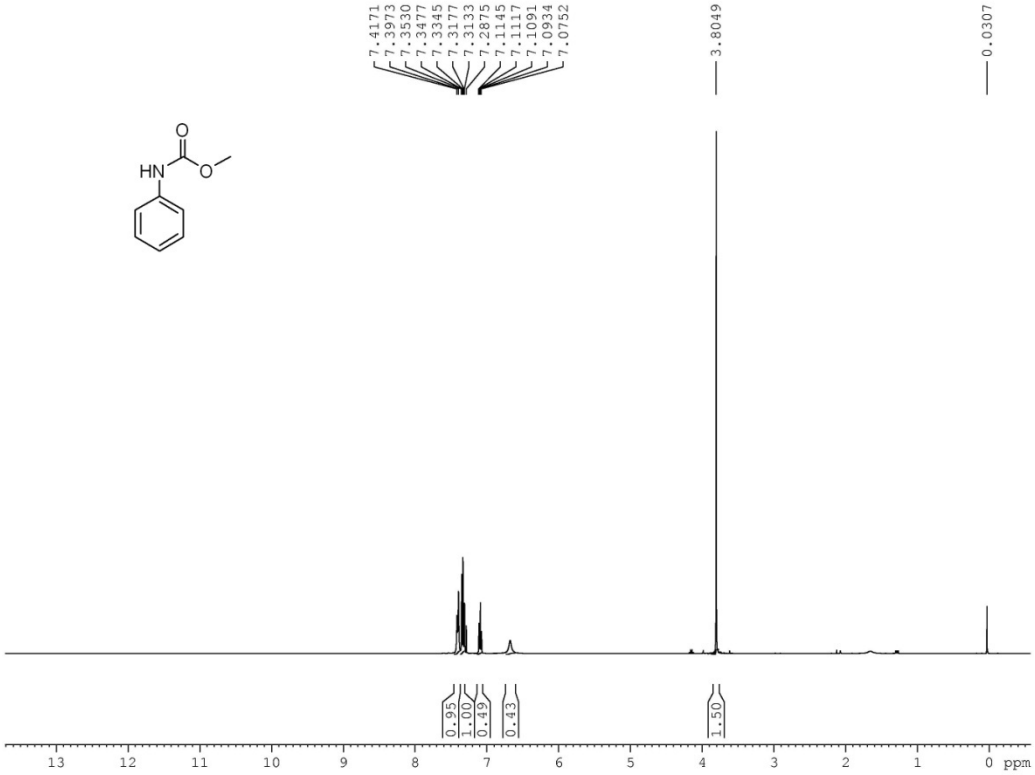
^{1}H NMR of Ethyl phenylcarbamate (starting carbamate of 8a, Table 2):-



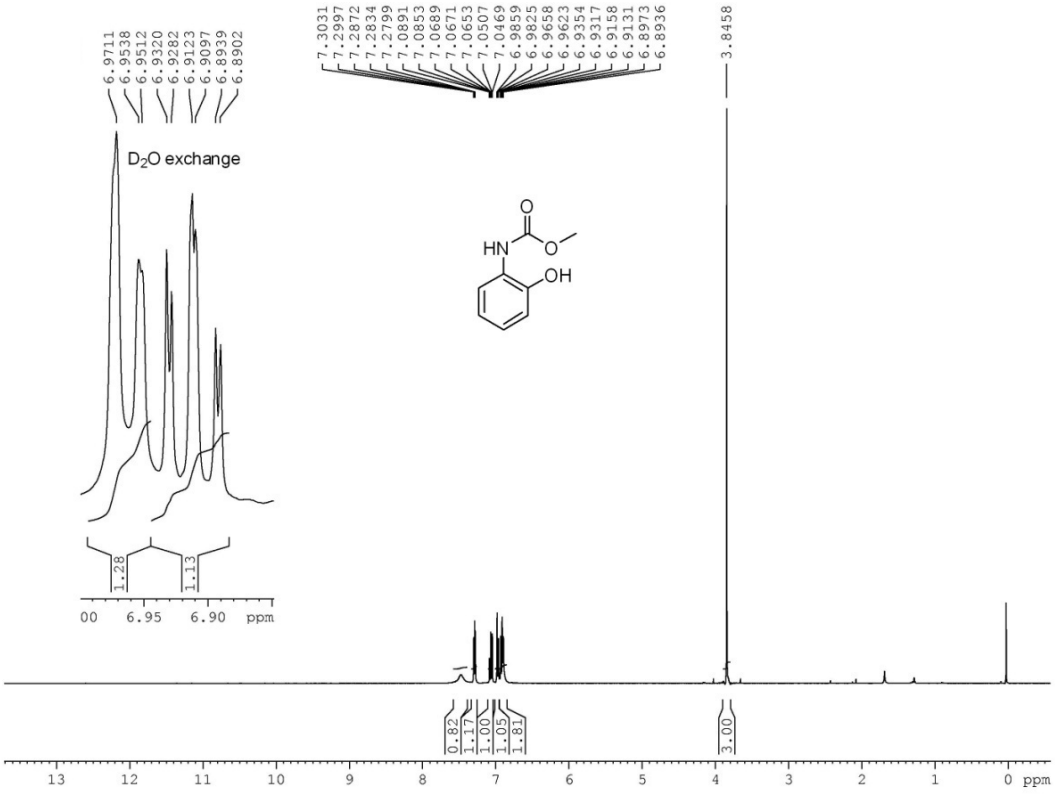
^{1}H NMR of Ethyl-2-hydroxyphenylcarbamate (8a, Table 2):-



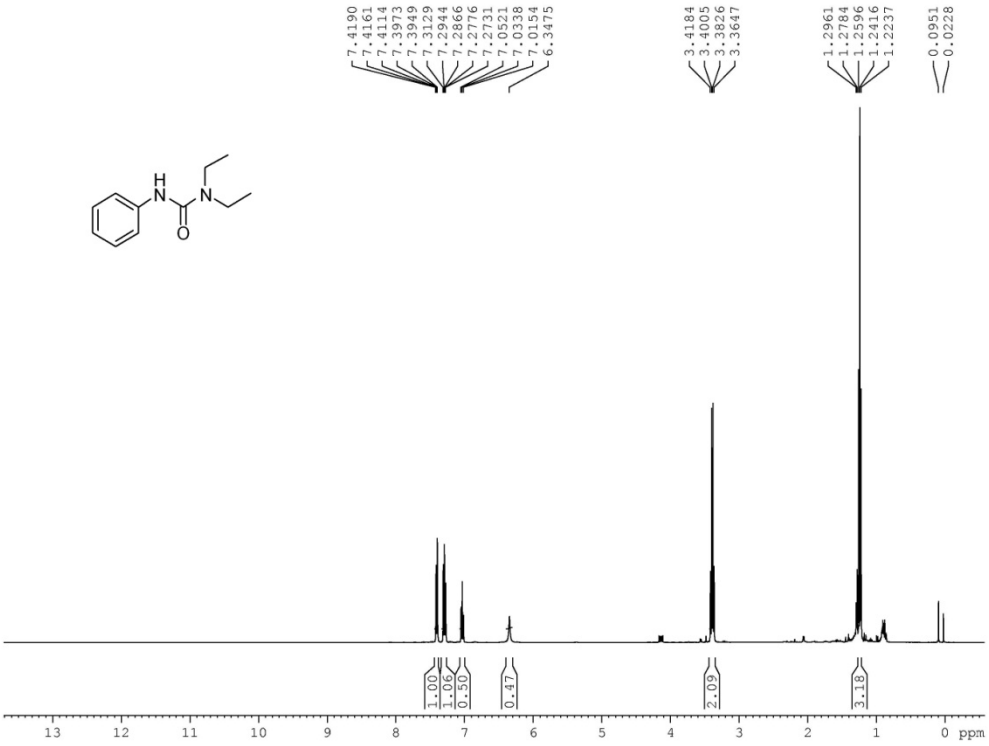
^{1}H NMR of Methyl phenylcarbamate (starting carbamate of 8b, Table 2):-



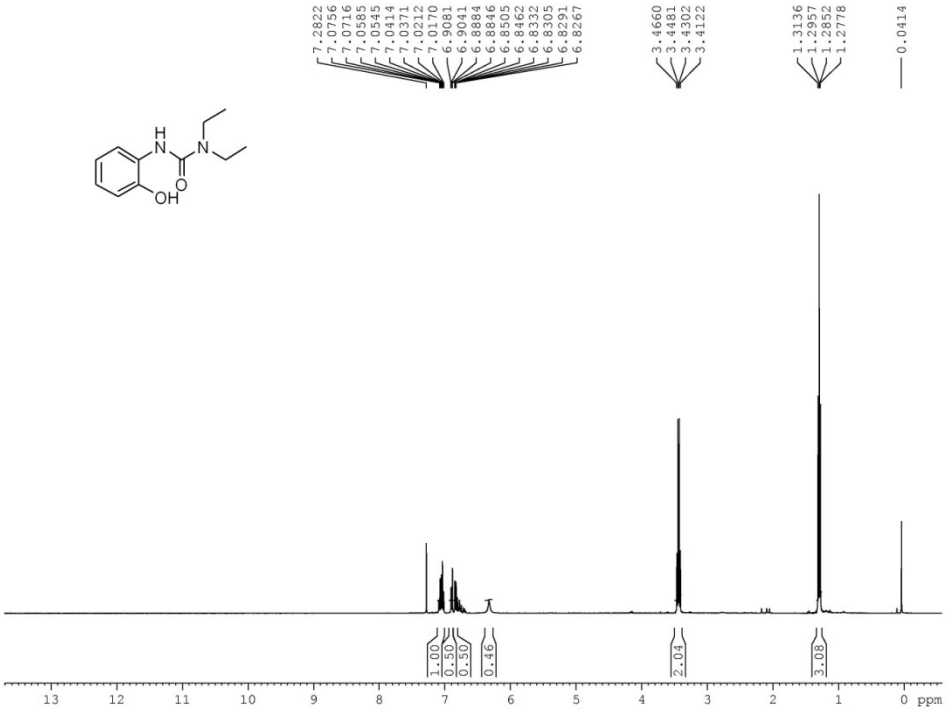
^{1}H NMR of Methyl-2-hydroxyphenylcarbamate (8b, Table 2):-



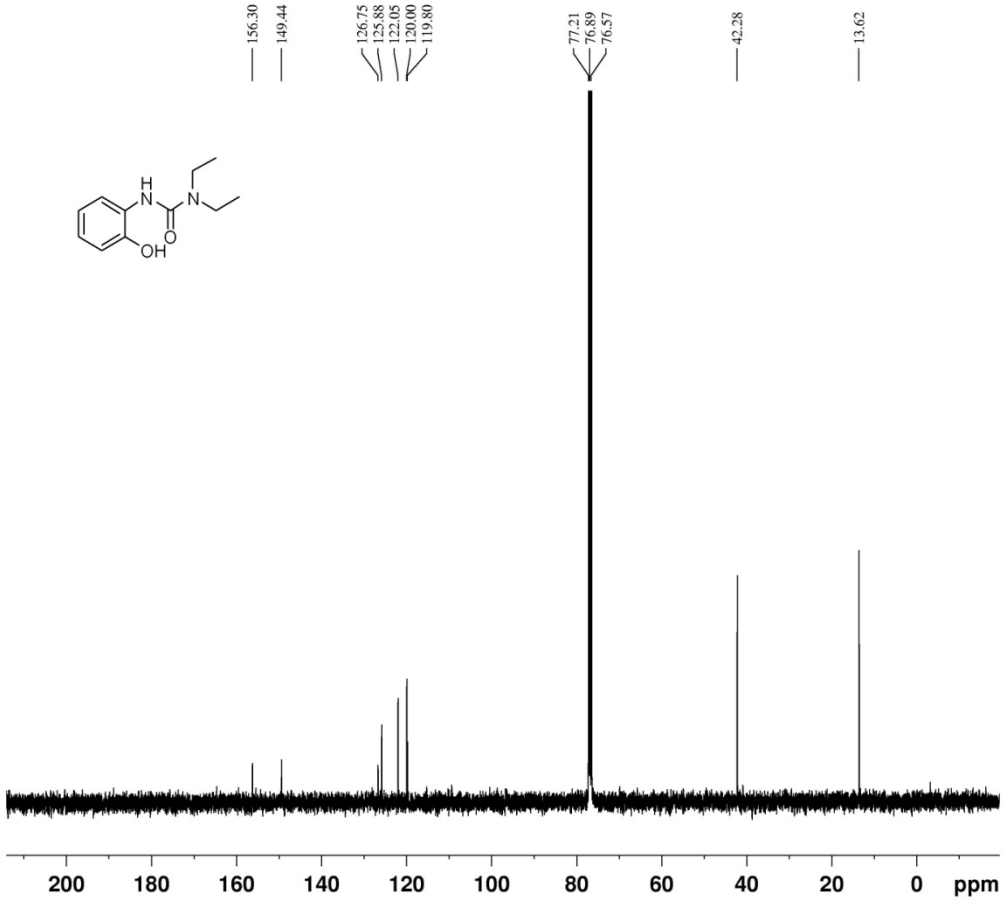
^{1}H NMR of 1,1-Diethyl-3-phenylurea (starting urea derivative of 9, Table 2):-



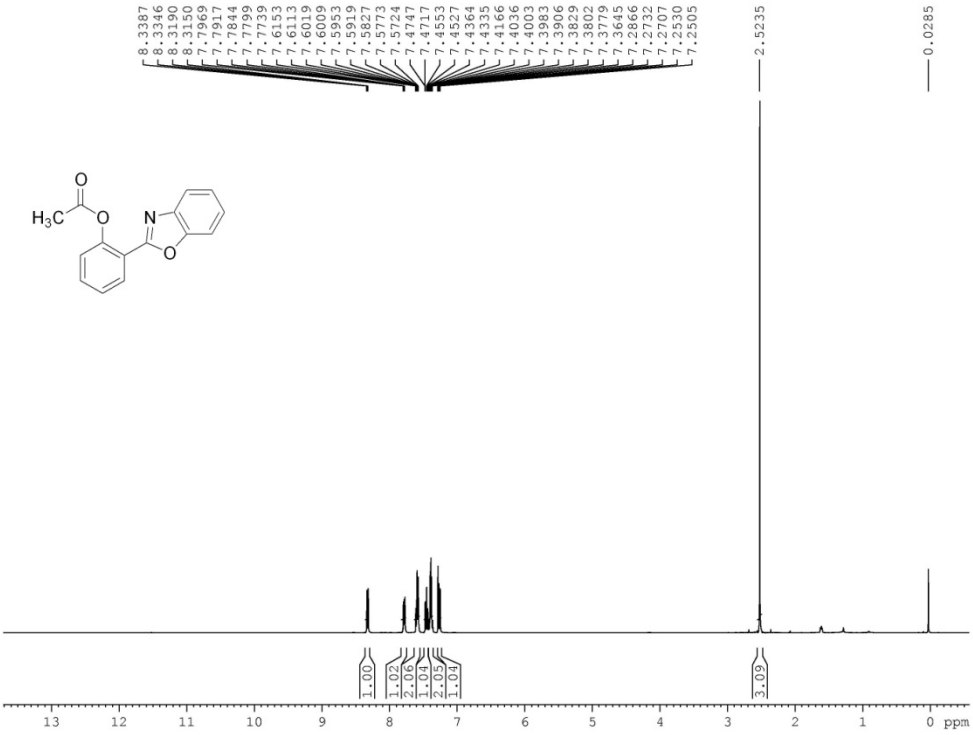
^{1}H NMR of 1,1-Diethyl-3-(2-hydroxyphenyl)urea (9, Table 2):-



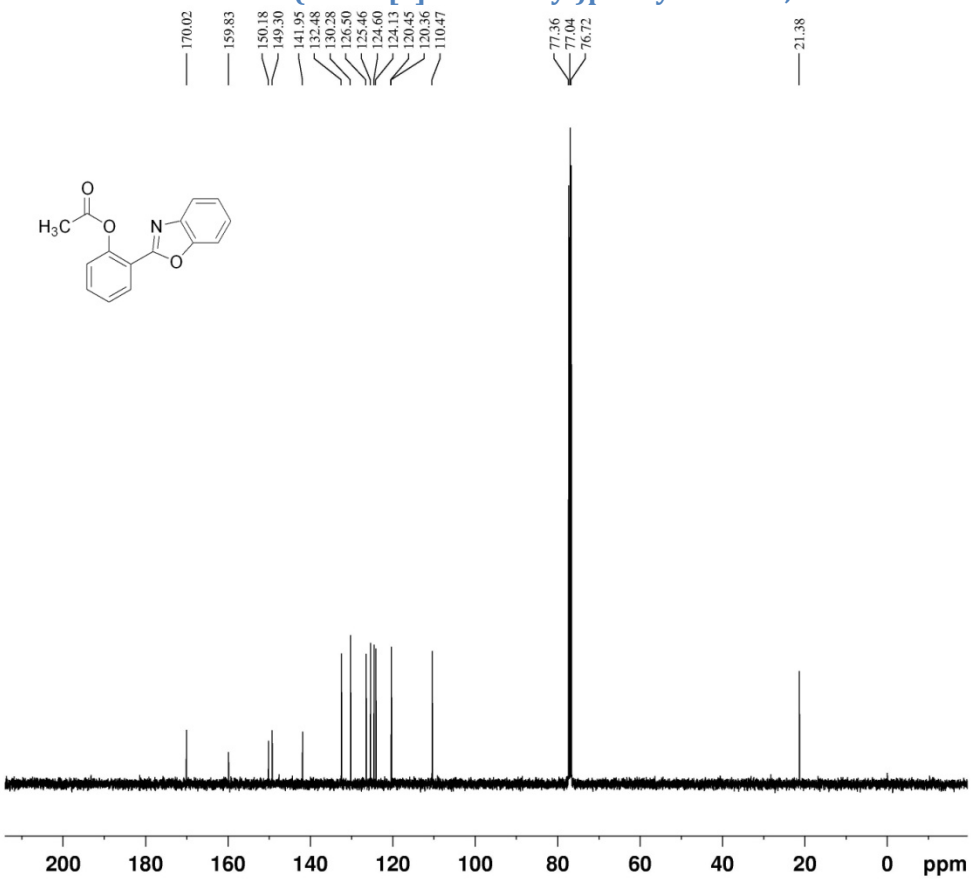
^{13}C NMR of 1,1-Diethyl-3-(2-hydroxyphenyl)urea (9, Table 2):-



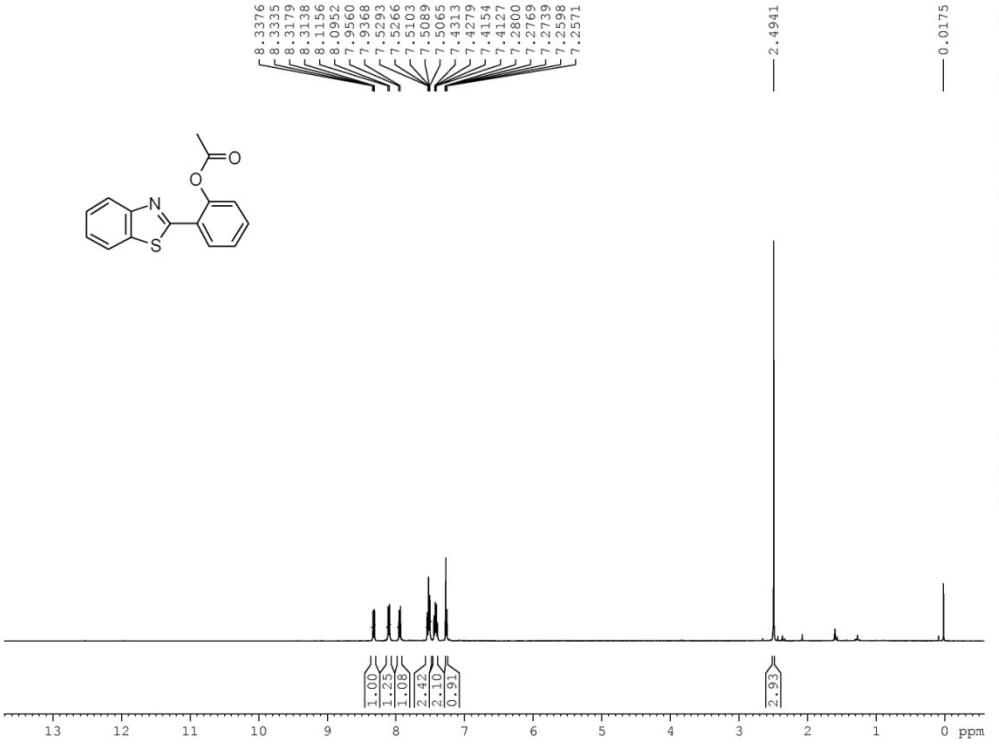
^{1}H NMR of 2-(Benzo[*d*]oxazol-2-yl)phenyl acetate, 2aa



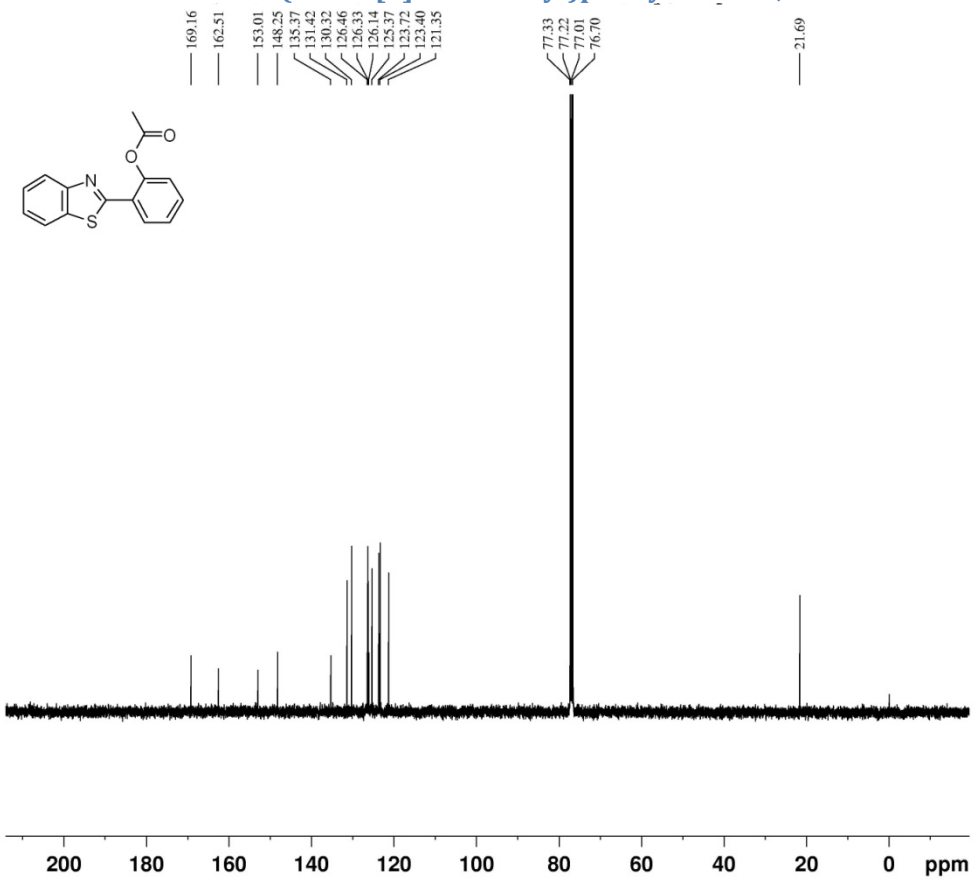
^{13}C NMR of 2-(Benzo[*d*]oxazol-2-yl)phenyl acetate, 2aa



^{1}H NMR of 2-(Benzo[*d*]thiazol-2-yl)phenyl acetate, 4aa :-

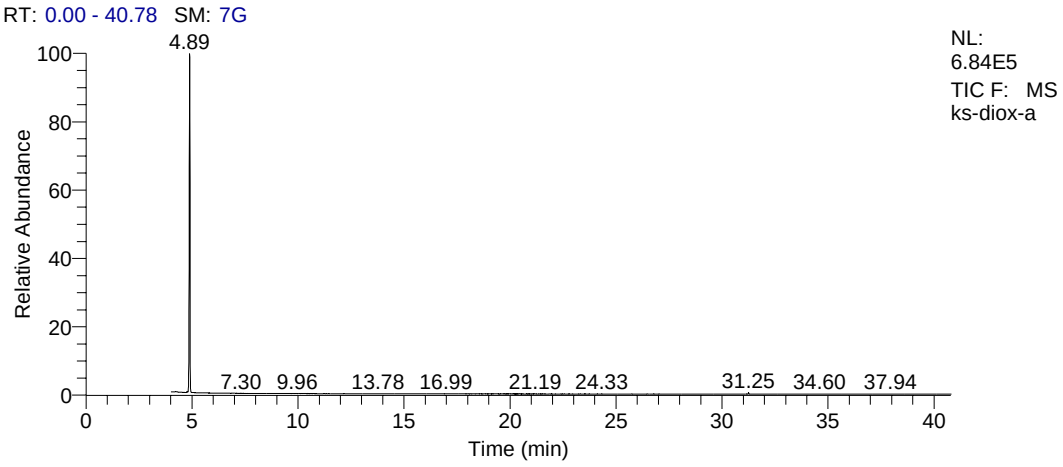


^{13}C NMR of 2-(Benzo[*d*]thiazol-2-yl)phenyl acetate, 4aa :-



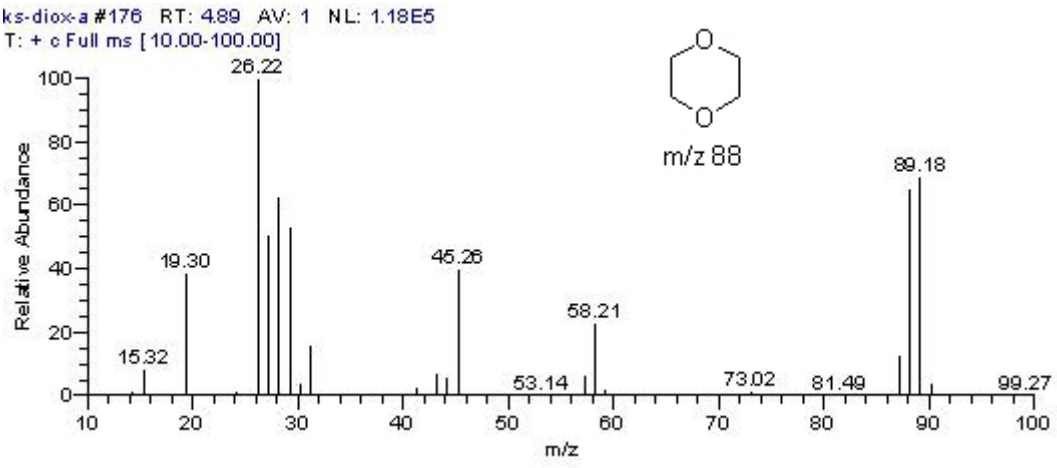
10. GCMS and MS-MS Spectra in Support of the Mechanistic Proposal for Hydroxyl Radical Generation from the Reaction of 1,4-Dioxane with Persulfate Anion:

10.1. TIC of an authentic sample of 1,4-dioxane (in the absence of $Na_2S_2O_8$):

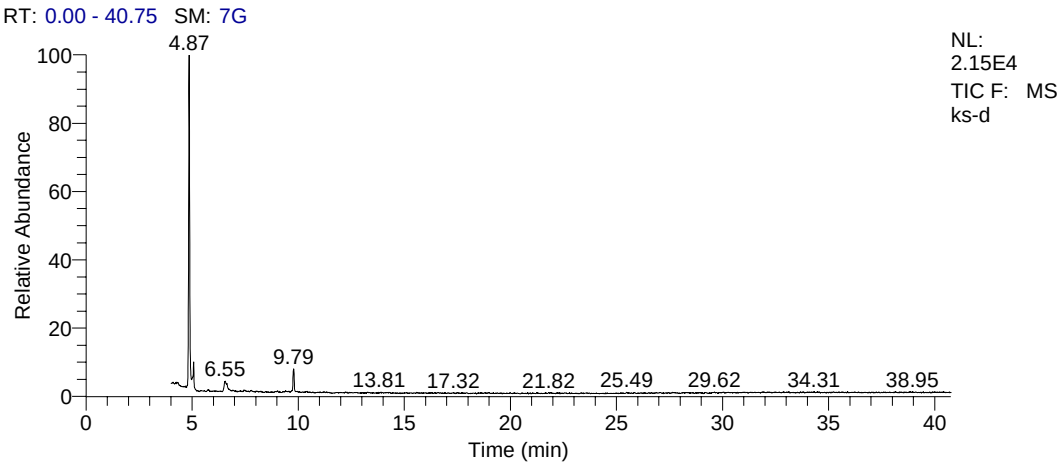


RT	Area %	Peak Area	Peak Height
4.77	0.15	1920	965
4.89	99.61	1299900	519243
31.25	0.24	3116	1452

10.1.1 Mass spectrum of the peak/ion at RT 4.89:

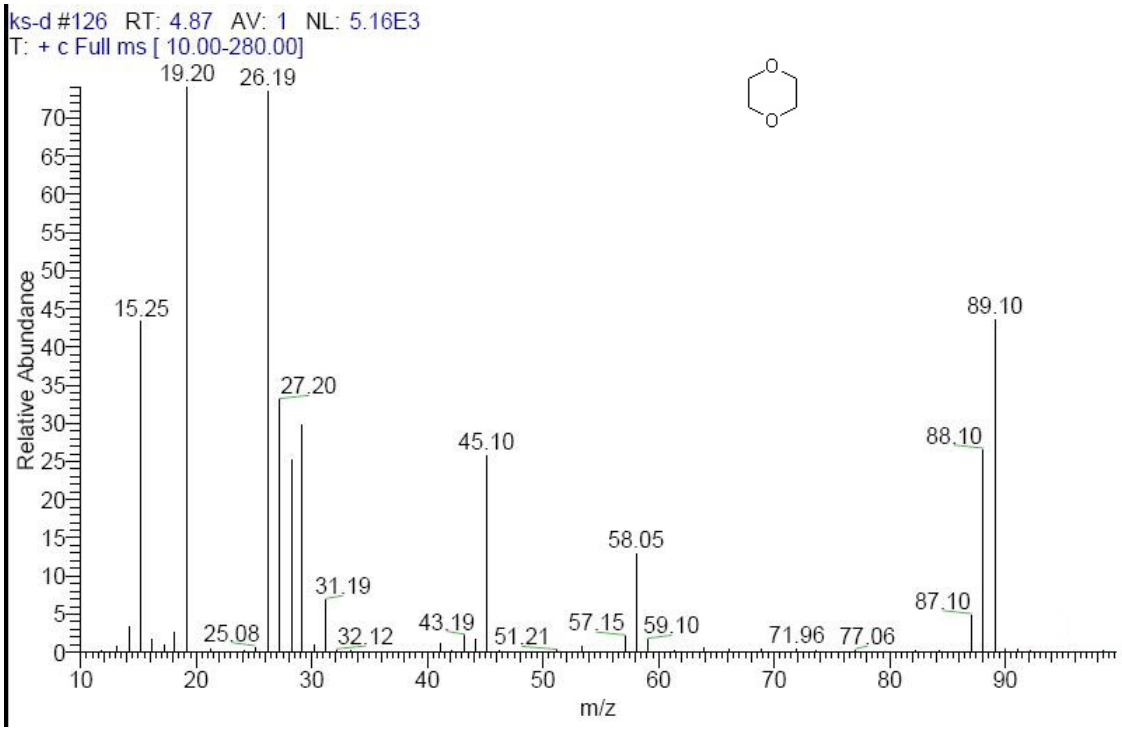


10.2. TIC of aliquot portions (at an interval of 2 h) of the reaction mixture during the treatment of 1,4-dioxane with $Na_2S_2O_8$ at 80 °C:

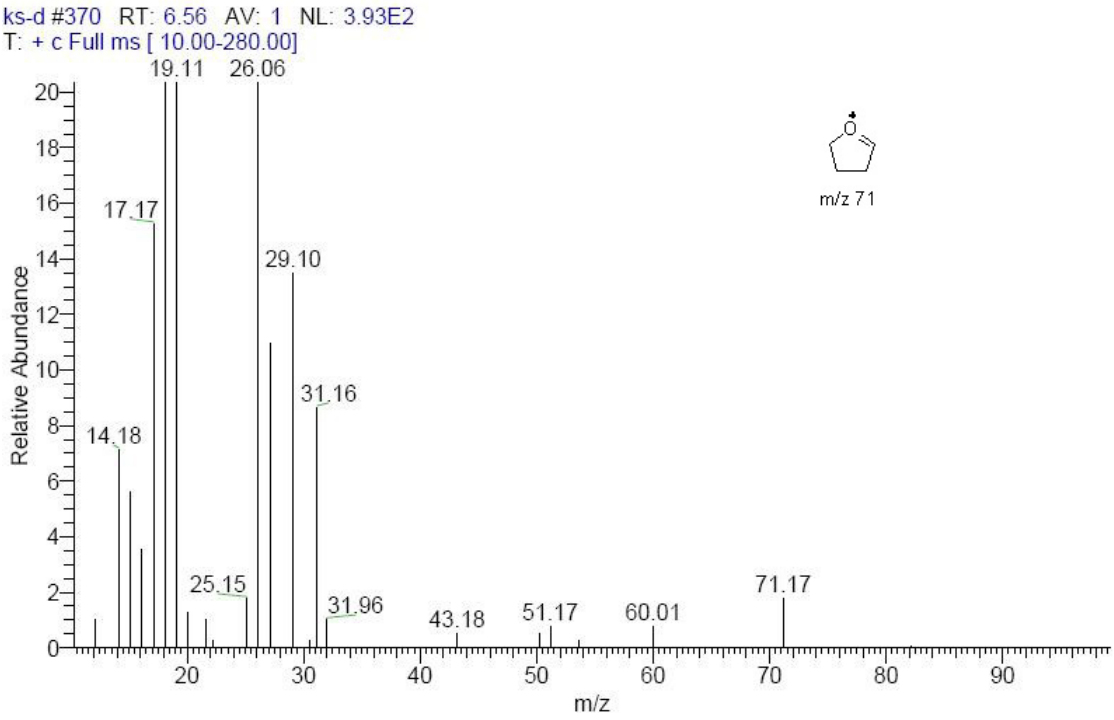


RT	Area %	Peak Area	Peak Height
4.87	87.45	47279	13656
6.56	5.83	3152	435
9.79	6.72	3634	982

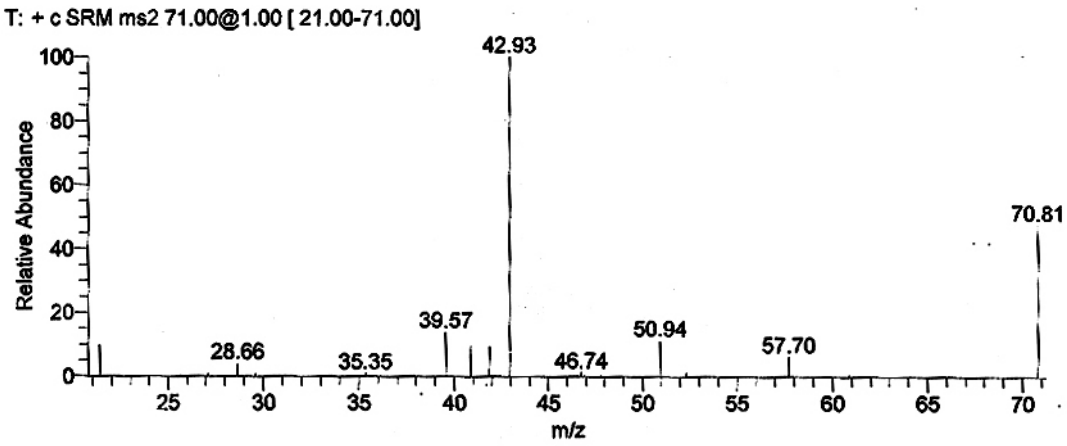
10.2.1. Mass spectrum of the peak/ion at RT 4.87:



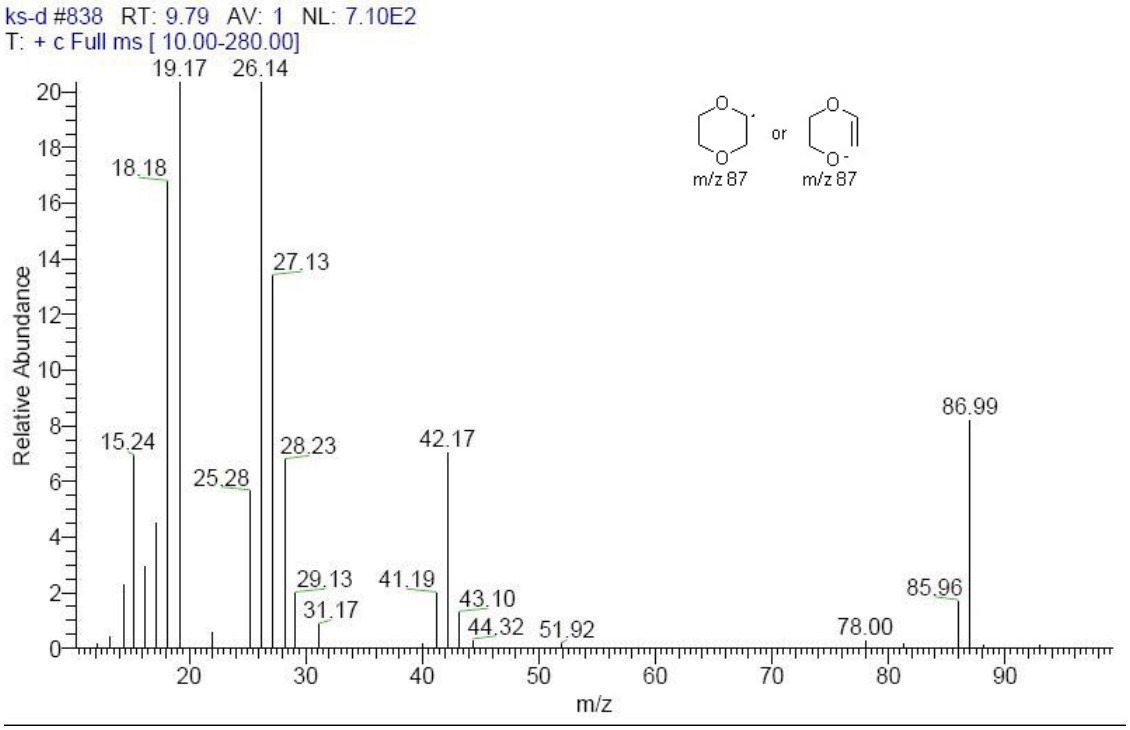
10.2.2. Mass spectrum of the peak/ion at RT 6.56:



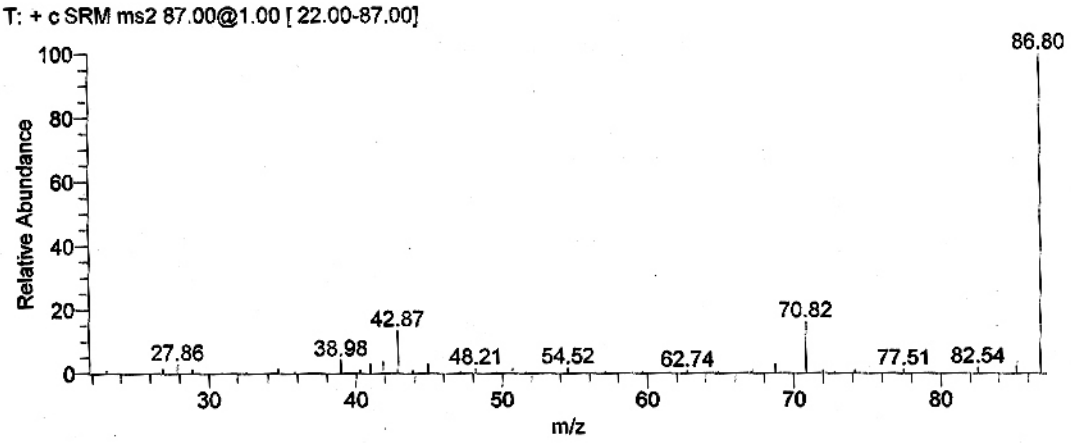
10.2.2.1. The ms-ms (ms^2) spectrum of the ion at *m/z* 71:



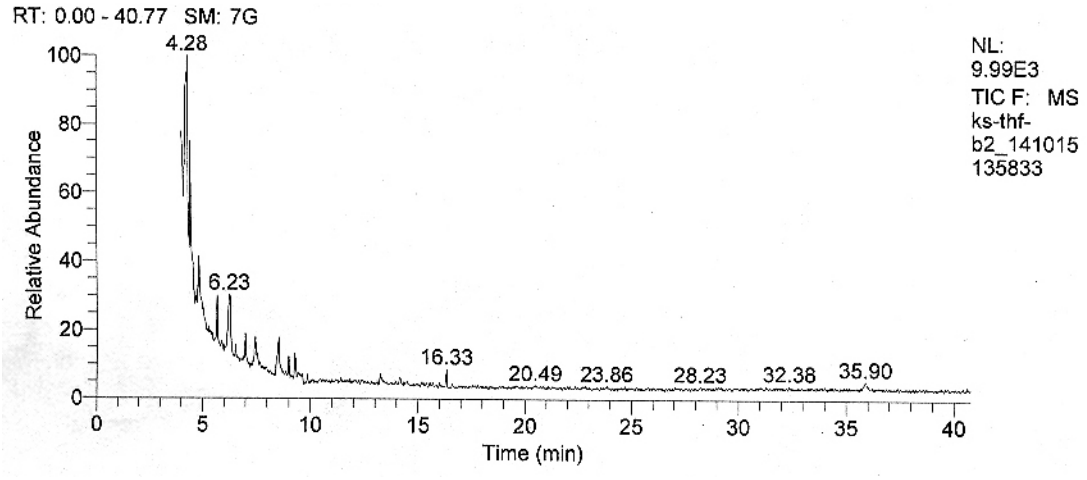
10.2.3. Mass spectrum of the peak/ion at RT 9.79:



10.2.3.1. The ms-ms (ms^2) spectrum of the ion at *m/z* 87:

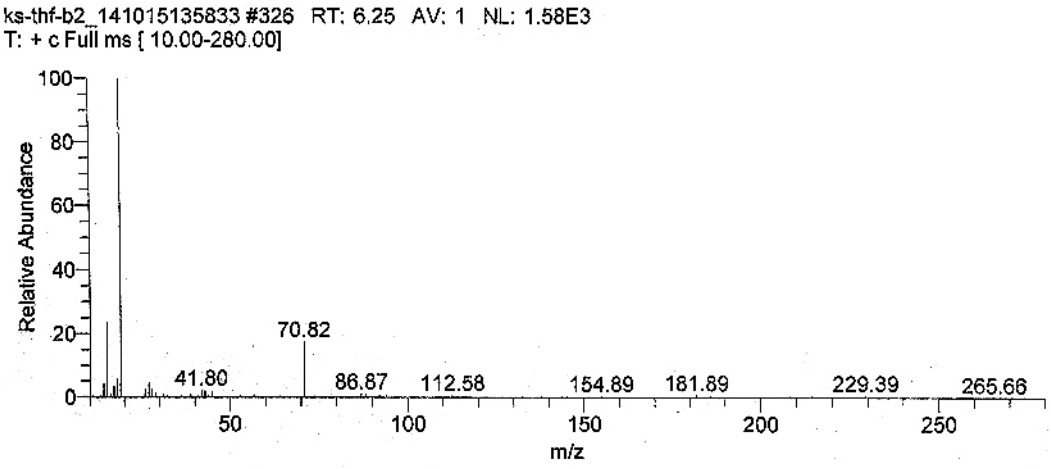


10.3. TIC of an authentic sample of THF (in the absence of $Na_2S_2O_8$):

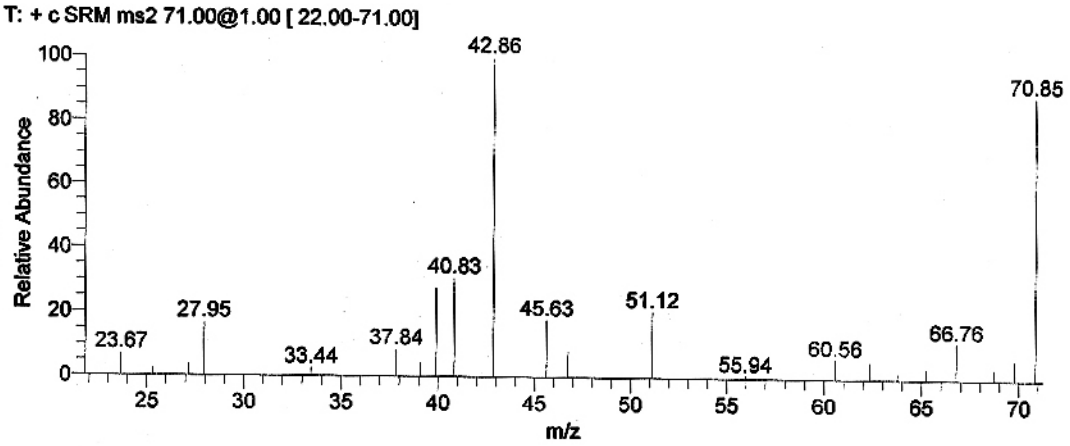


RT	Area %	Peak Area	Peak Height
4.27	57.62	27025	3687
4.42	12.60	5911	1861
4.82	6.60	3098	760
6.25	13.78	6464	1007

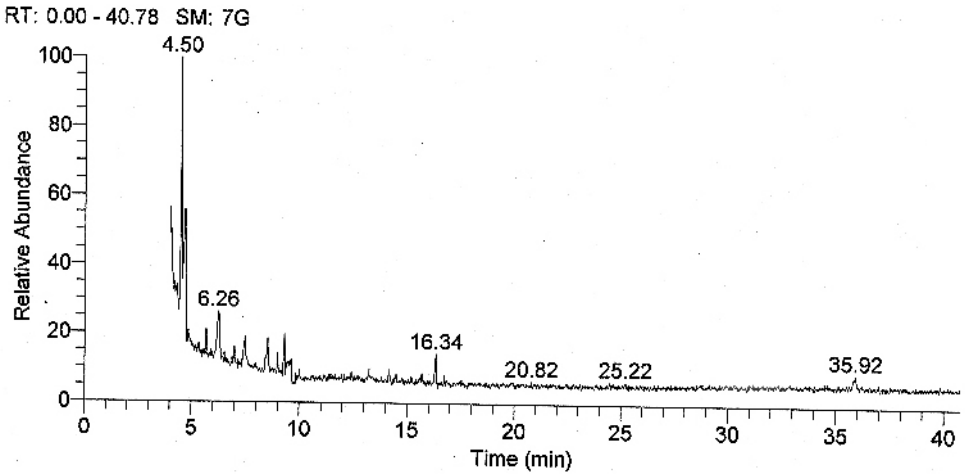
10.3.1 Mass spectrum of the peak/ion at RT 6.25:



10.3.1.1. The ms-ms (ms^2) spectrum of the ion at *m/z* 71:

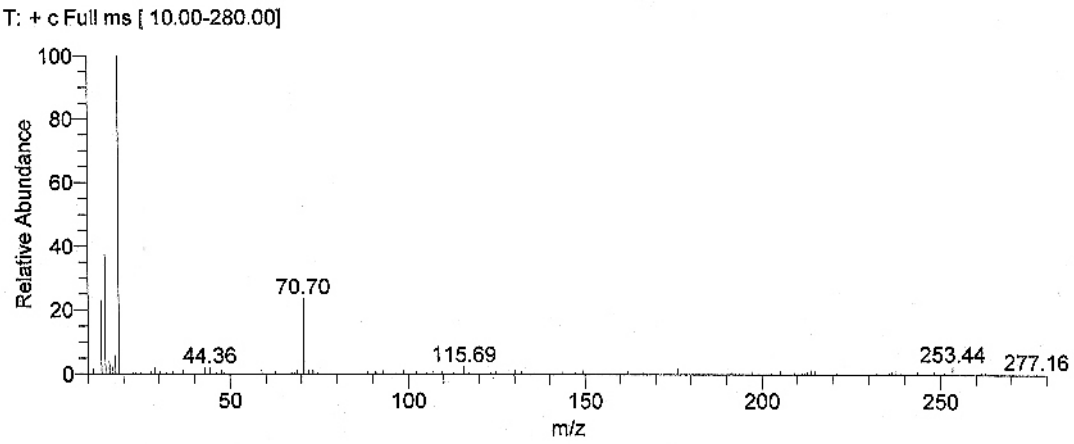


10.4. TIC of aliquot portions of the mixture (during the treatment of THF with $Na_2S_2O_8$ at 80 °C):

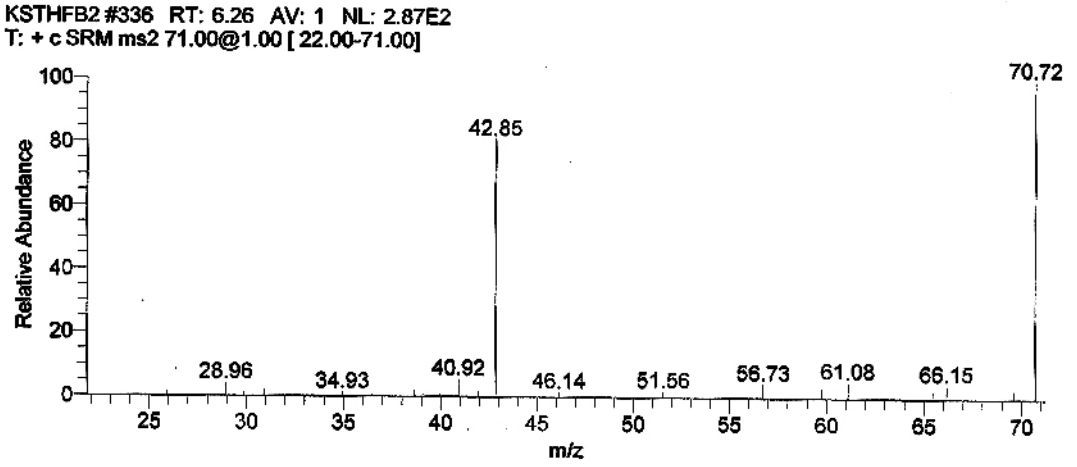


RT	Area %	Peak Area	Peak Height
4.50	41.16	8116	2256
4.69	28.34	5589	1115
6.26	16.13	3181	431

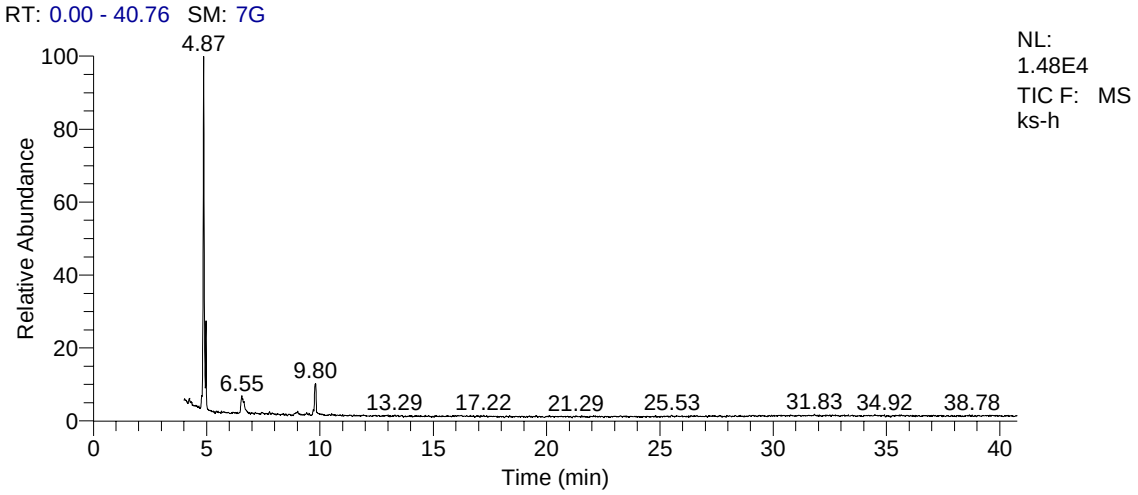
10.4.1 Mass spectrum of the peak/ion at RT 6.26:



10.4.1.1. The ms-ms (ms^2) spectrum of the ion at *m/z* 71:

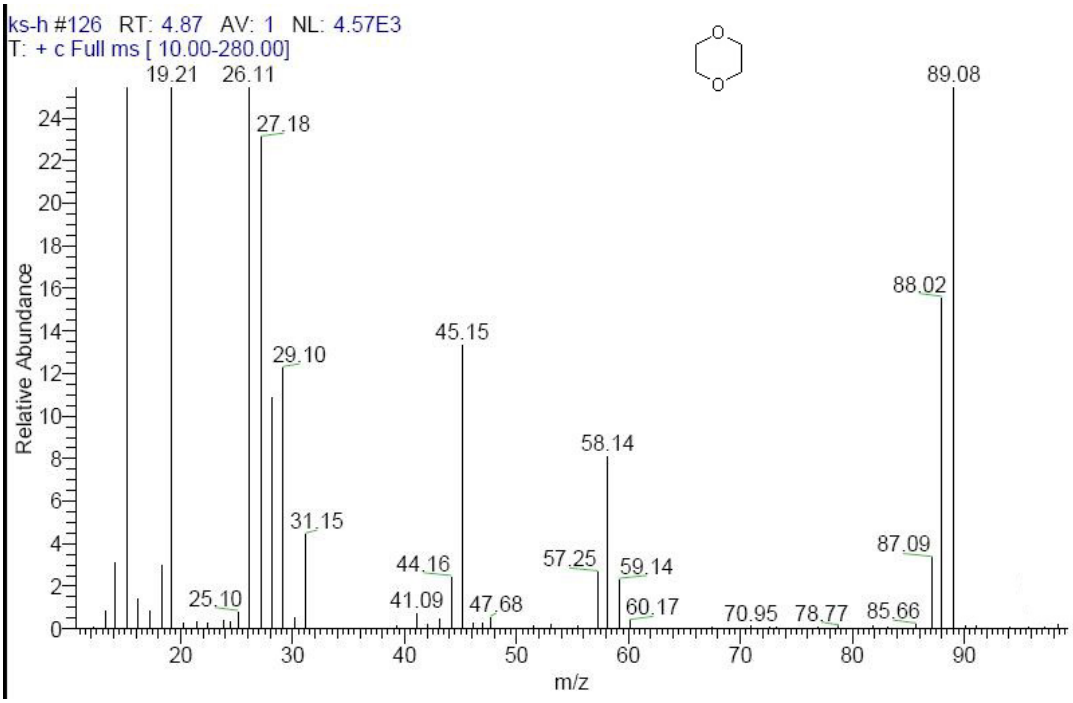


10.5. TIC of aliquot portions (at an interval of 2 h) of the reaction mixture during the treatment of 2-phenylbenzoxazole (1a) with $Na_2S_2O_8$ and 1,4-dioxane at 80 °C:

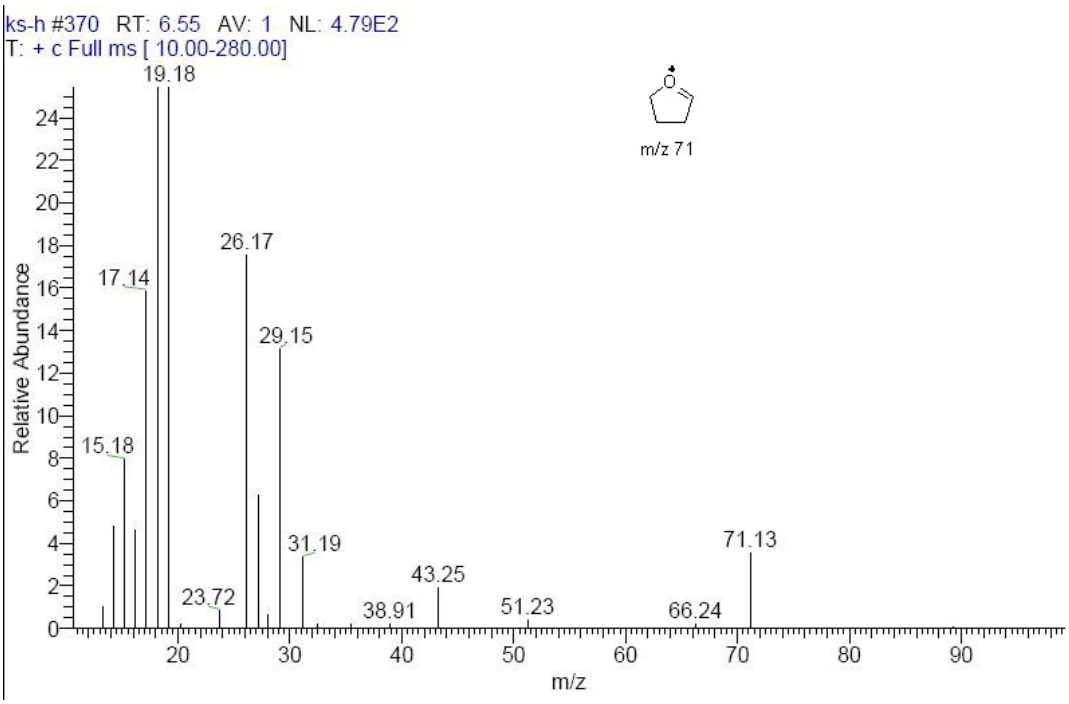


RT	Area %	Peak Area	Peak Height
4.87	81.50	30657	8823
6.55	9.15	3440	462
9.80	9.35	3518	869

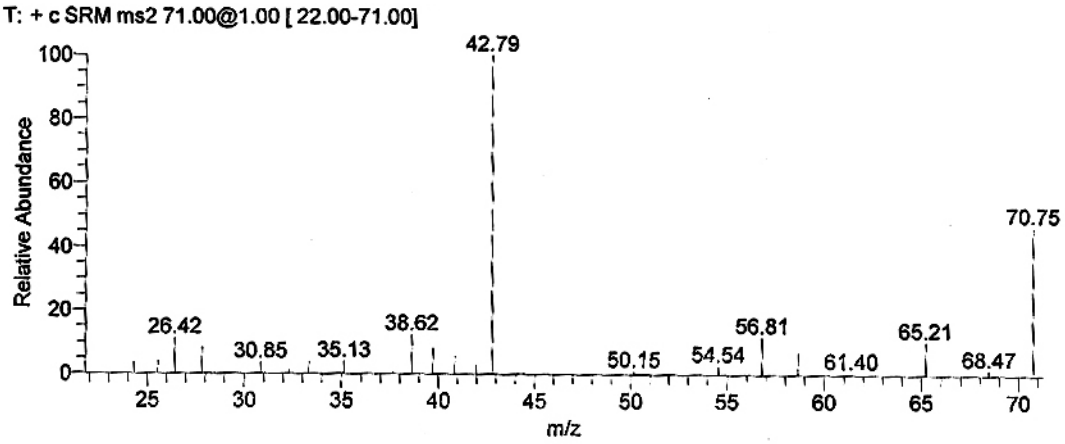
10.5.1. Mass spectrum of the peak/ion at RT 4.87:



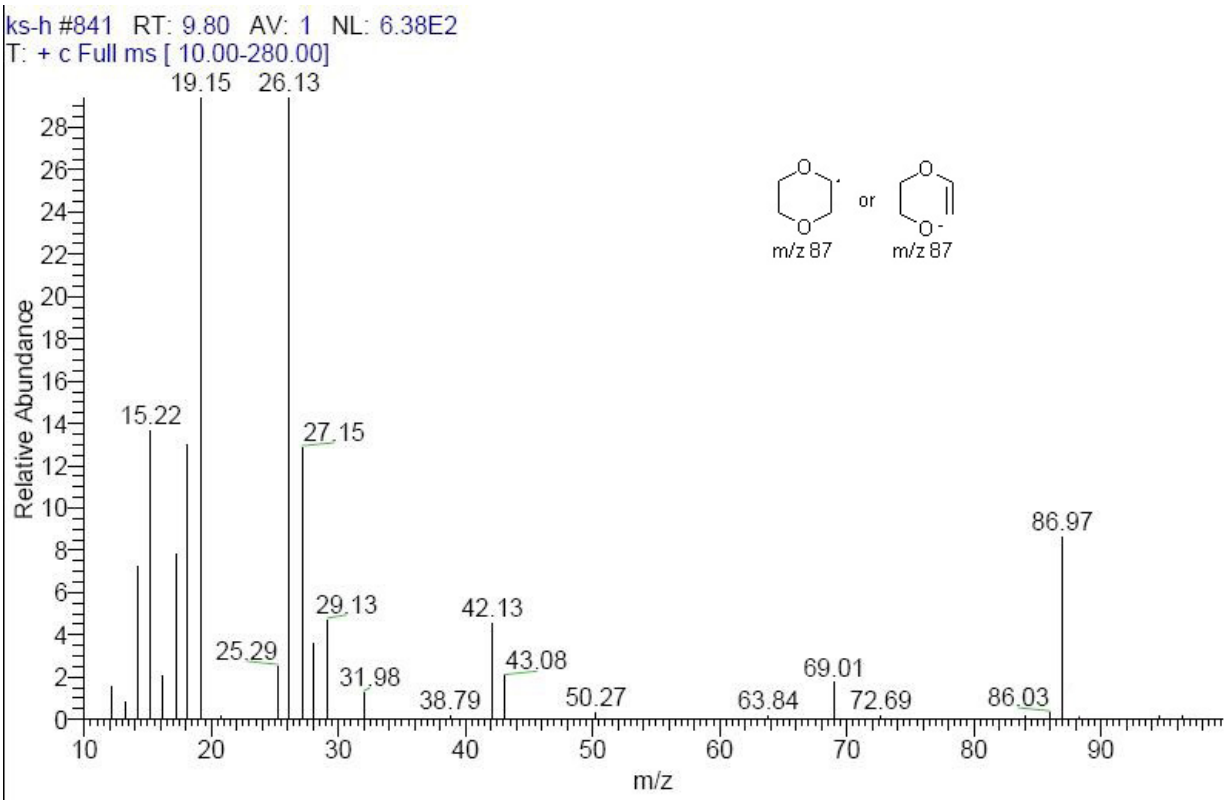
10.5.2. Mass spectrum of the peak/ion at RT 6.55:



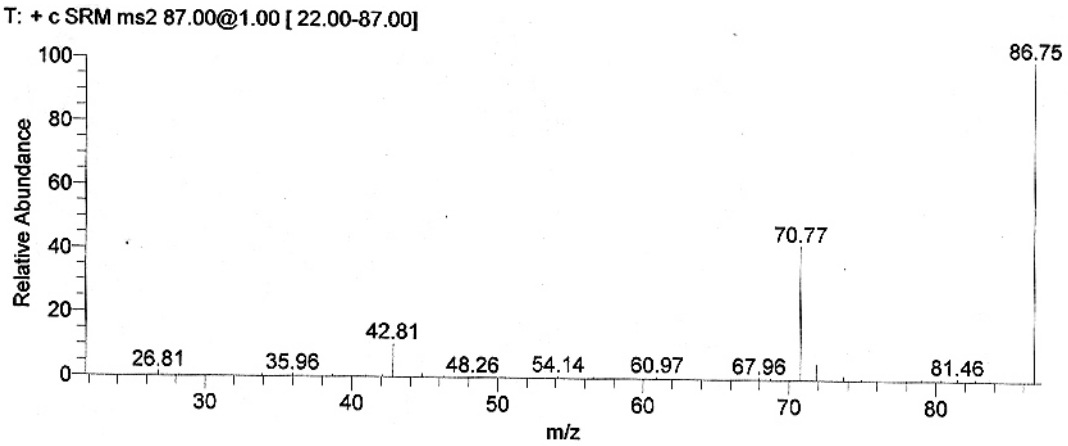
10.5.2.1. The ms-ms (ms^2) spectrum of the ion at *m/z* 71:



10.5.3. Mass spectrum of the peak/ion at RT 9.80:



10.5.3.1. The ms-ms (ms^2) spectrum of the ion at *m/z* 87:



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