Copper Nanoparticles Supported on Highly Nitrogen-Rich Containing Covalent Organic Polymers as Heterogeneous Catalyst for *ipso*-Hydroxylation of Phenyl boronic acid to Phenol

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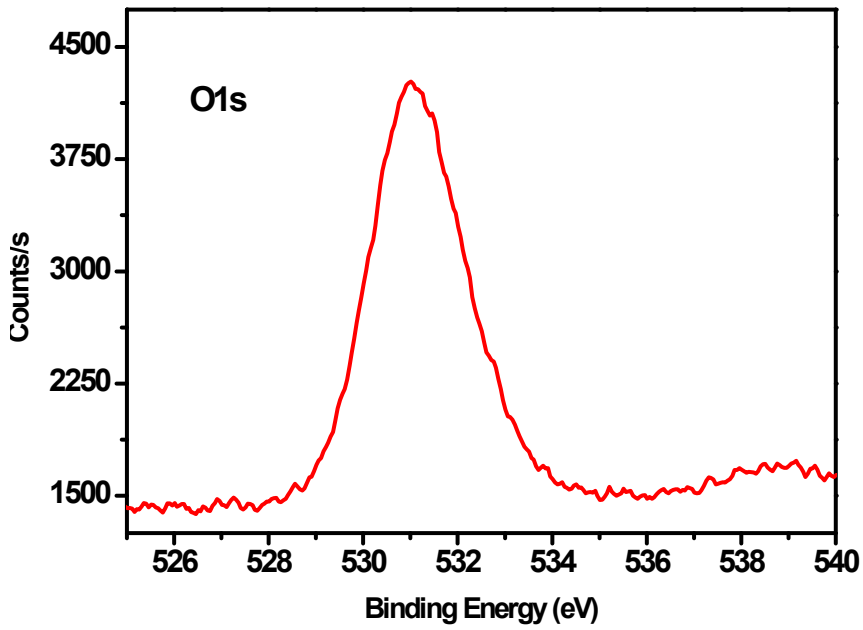


Figure S1. XP spectra of compound Cu@TCOP for O1s.

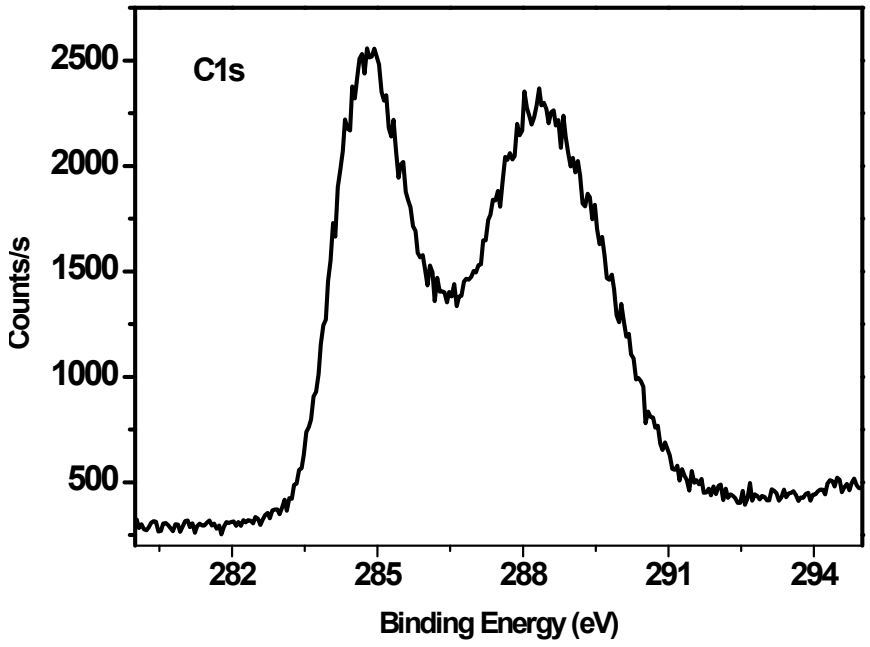


Figure S2. XP spectra of compound Cu@TCOP for C1s.

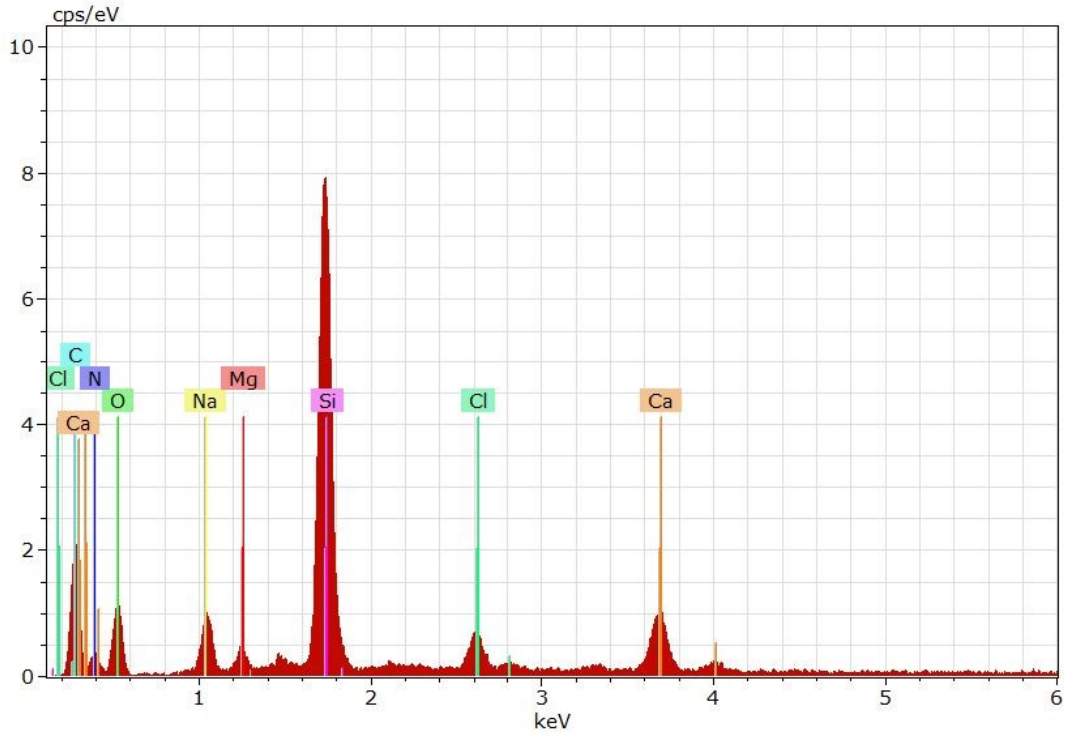


Figure S3. EDS spectra of compound TCOP.

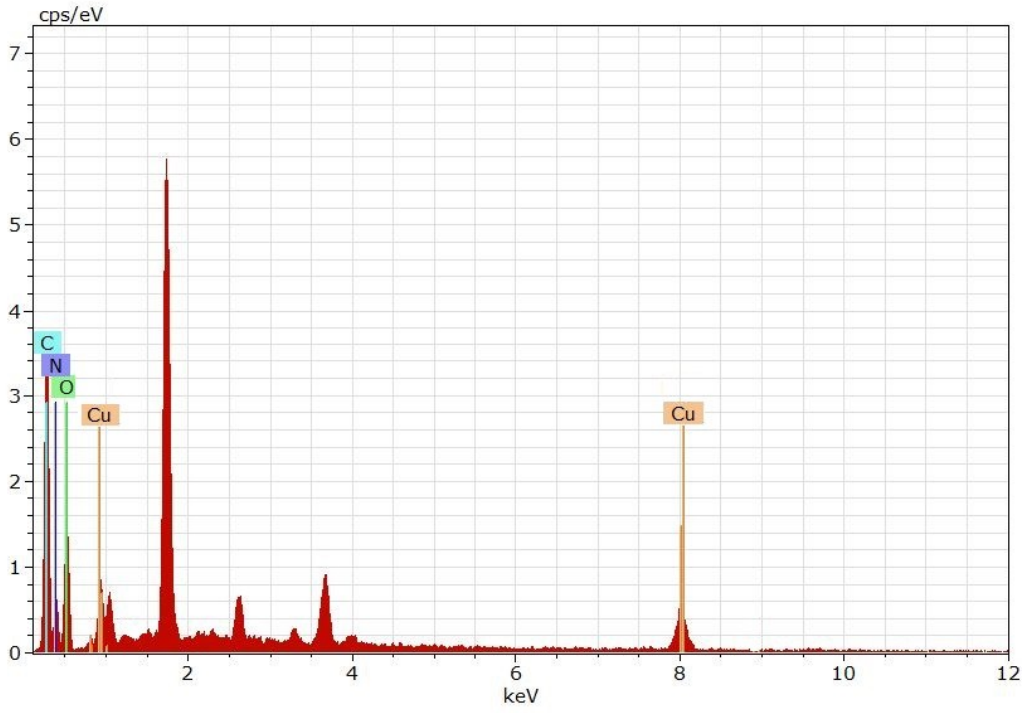


Figure S4. EDS spectra of compound Cu@TCOP.

Table 1. Elemental atomic weight % of compound TCOP.

Elem: At No	Series	Unn. C [Wt %]	Norm. C [Wt %]	Atom. C [at. %]	(1 Sigma) [Wt %]
C-6	K- Series	39.90	39.95	49.74	7.06
N-7	K-Series	25.65	25.68	24.00	5.03
O-8	K-Series	14.86	14.88	15.89	4.19
Si-14	K-Series	12.09	12.11	6.45	0.58
Na-11	K-Series	3.37	3.38	2.20	0.30
Mg-12	K-Series	2.10	2.02	0.84	0.08
Ca-20	K-Series	2.03	2.00	0.88	0.05
Total		**100.00**	**100.00**	**100.00**	

Table 2. Elemental atomic weight % of compound Cu/TCOP.

Elem: At No	Series	Unn. C [Wt %]	Norm. C [Wt %]	Atom. C [at. %]	(1 Sigma) [Wt %]
C-6	K- Series	44.10	43.84	52.76	8.54
N-7	K-Series	31.15	29.98	25.17	5.92
O-8	K-Series	21.51	20.71	19.11	5.39
Cu -29	K-series	3.34	3.29	0.71	0.12
Total		**100.00**	**100.00**	**100.00**	

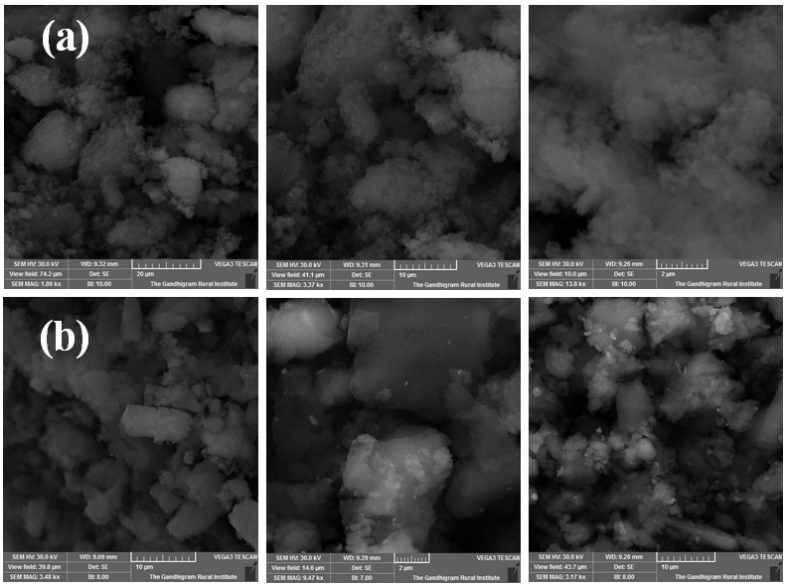


Figure S5. SEM images of compound (a) TCOP (b) Cu/TCOP.

[1]H NMR characterization data for all the biphenyl coupled products.

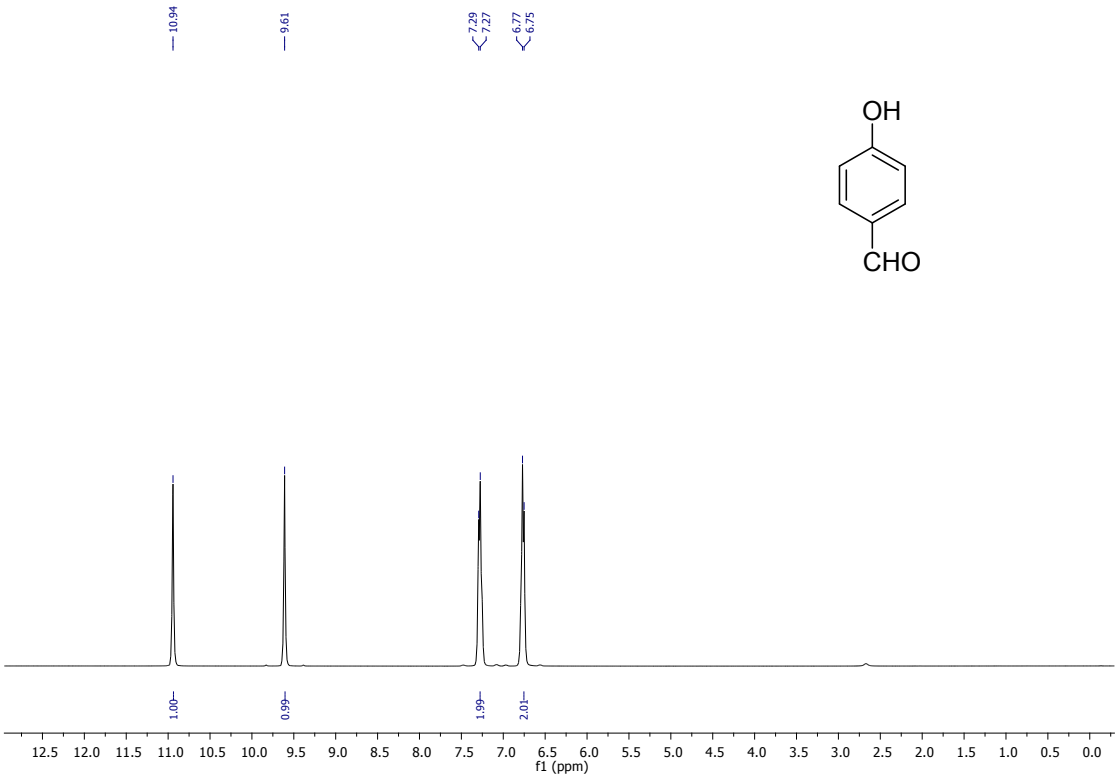


Figure S6: [1]H NMR spectrum of compound 4-hydroxy benzaldehyde.

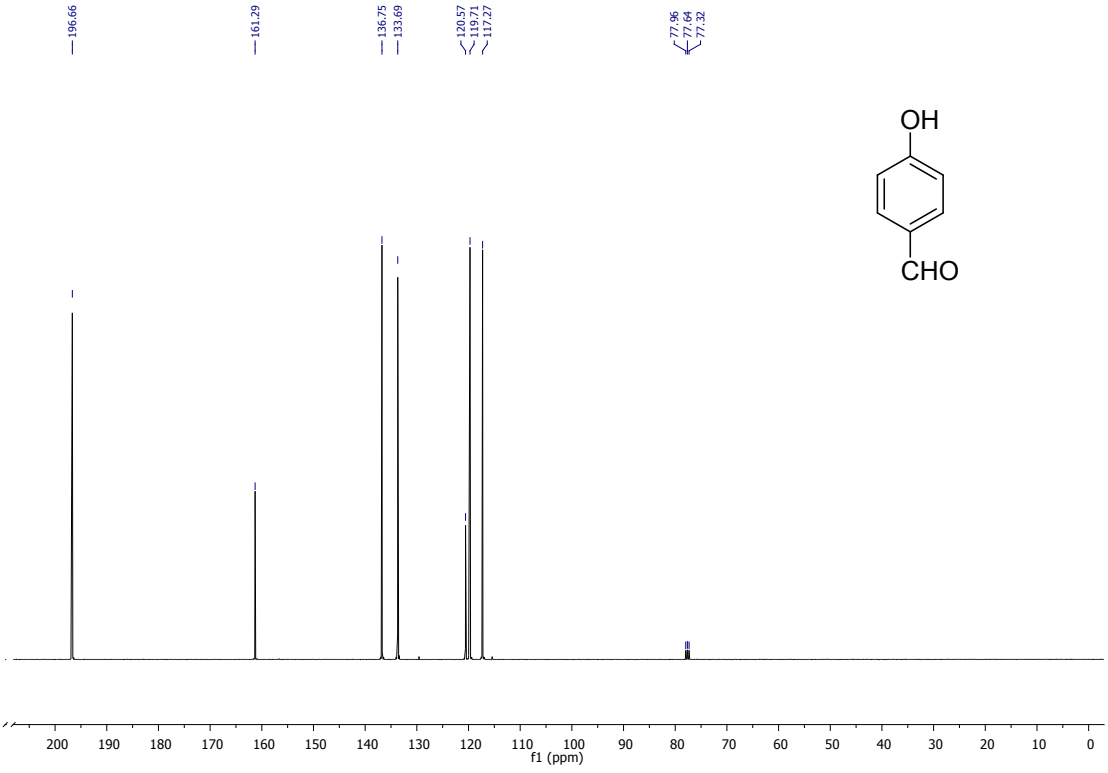


Figure S7: [13]C NMR spectrum of compound 4-hydroxy benzaldehyde.

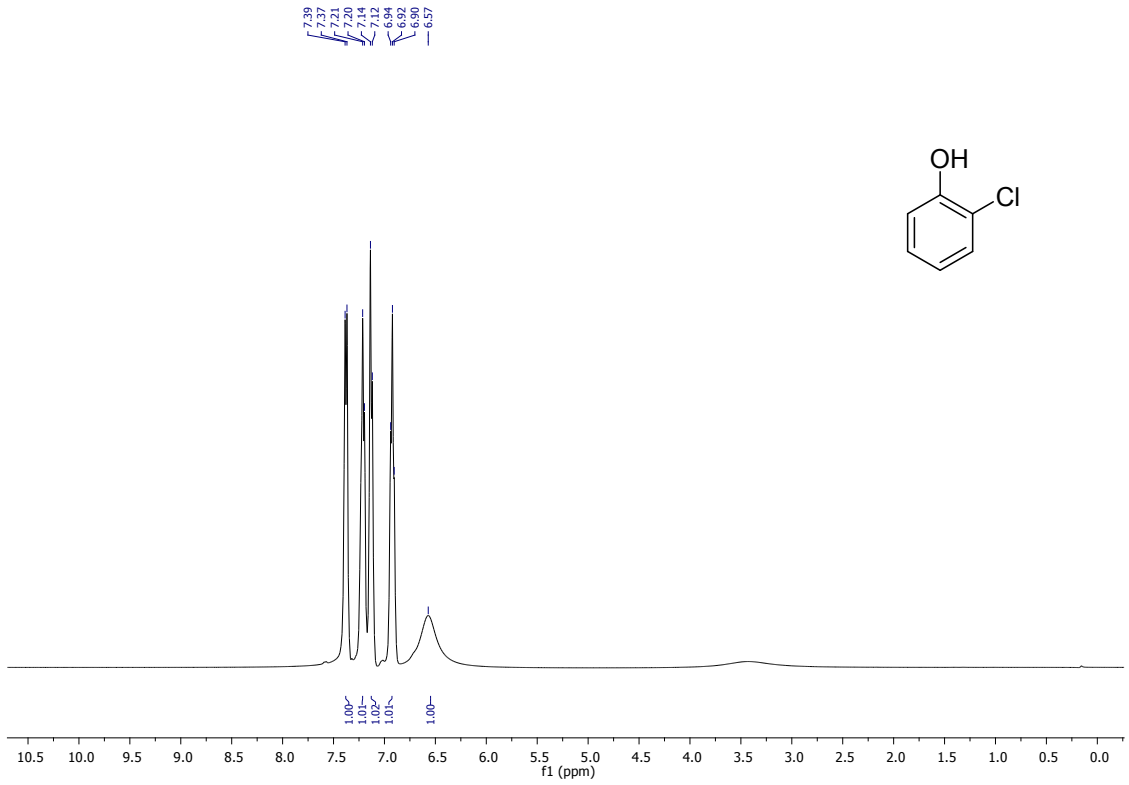


Figure S8: ^{1}H NMR spectrum of compound 2-chloro phenol.

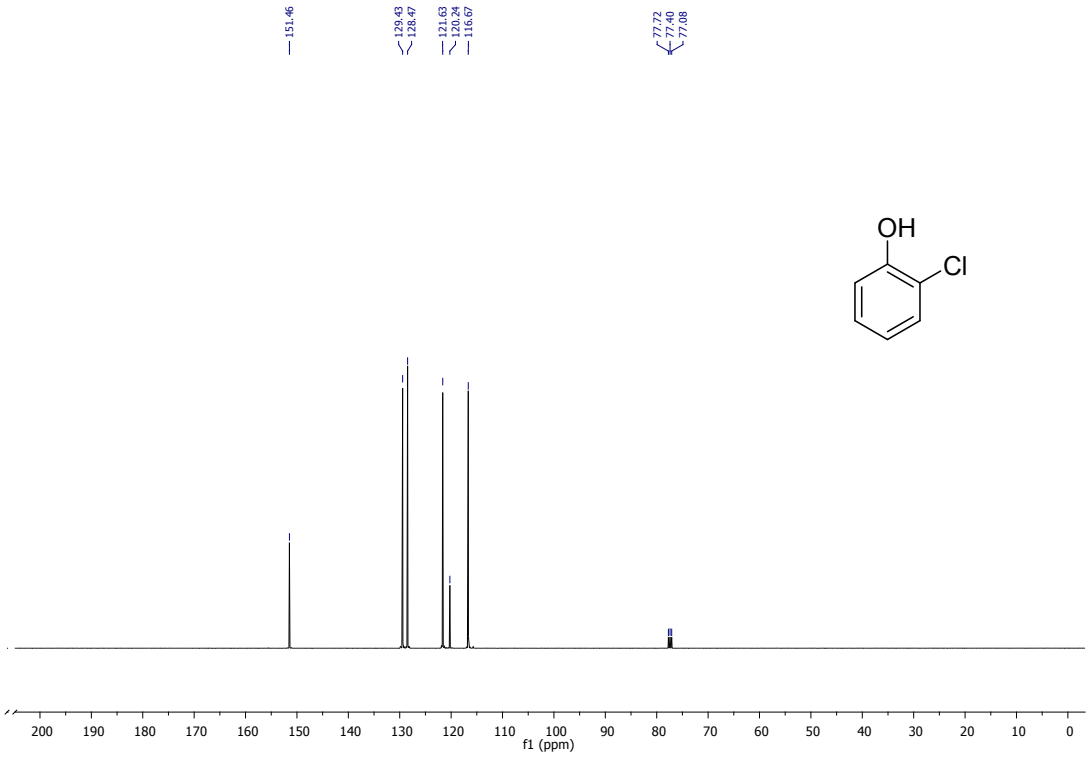


Figure S9: ^{13}C NMR spectrum of compound 4-chloro phenol.

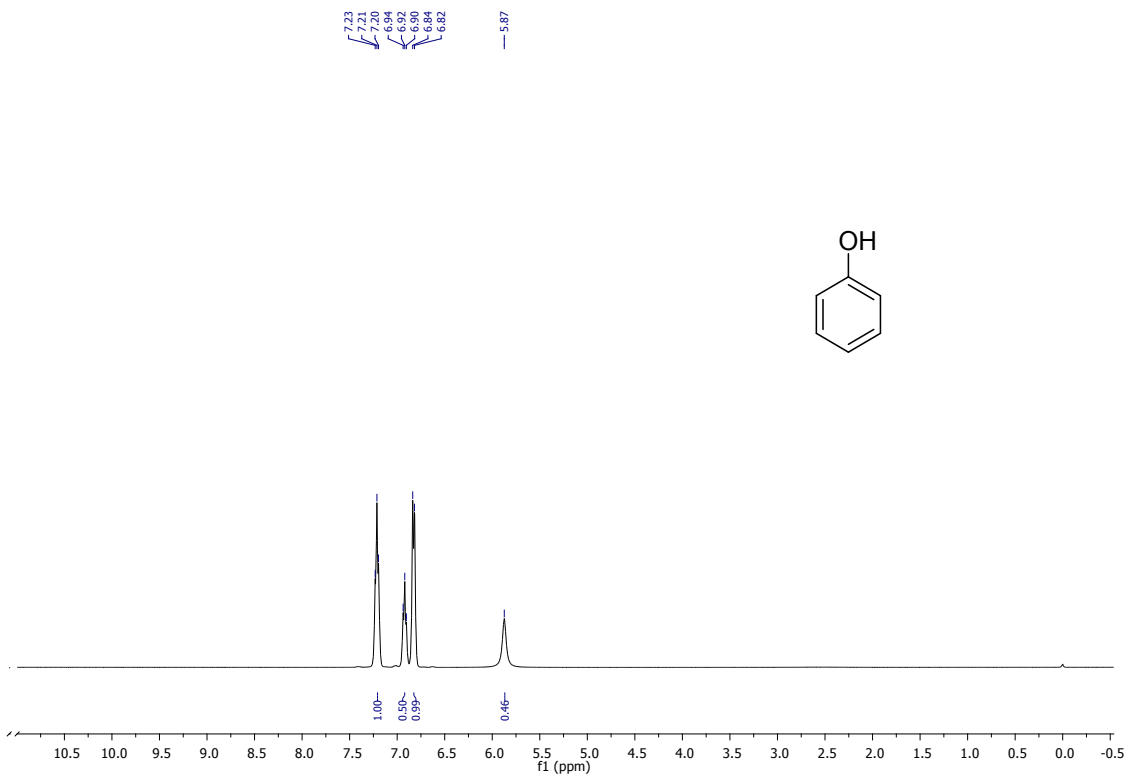


Figure S10: ^{1}H NMR spectrum of compound phenol.

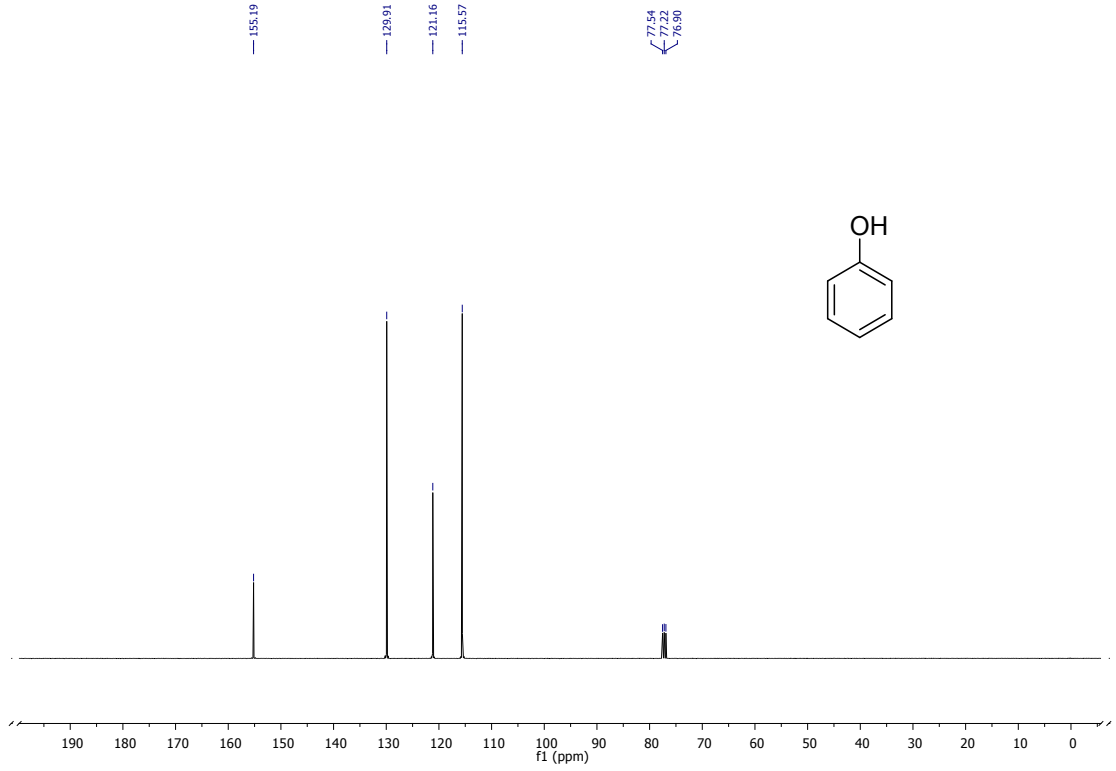


Figure S11: ^{13}C NMR spectrum of compound phenol.

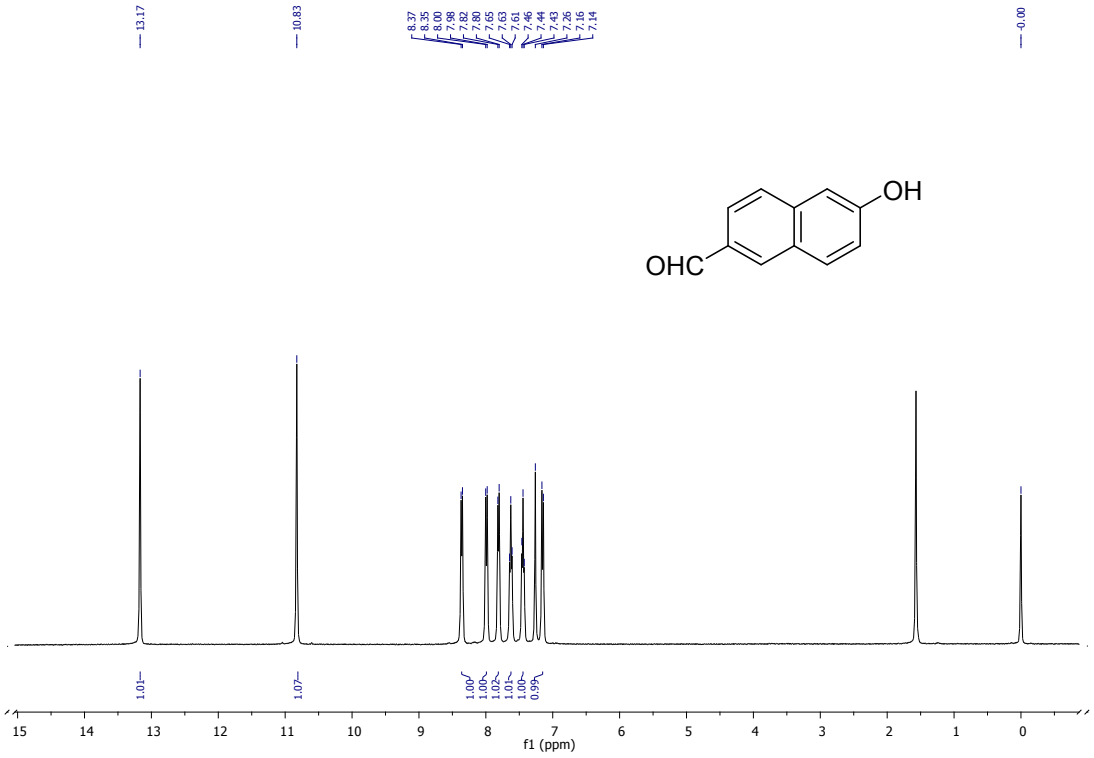


Figure S12: ^{1}H NMR spectrum of compound 2-Napthol.

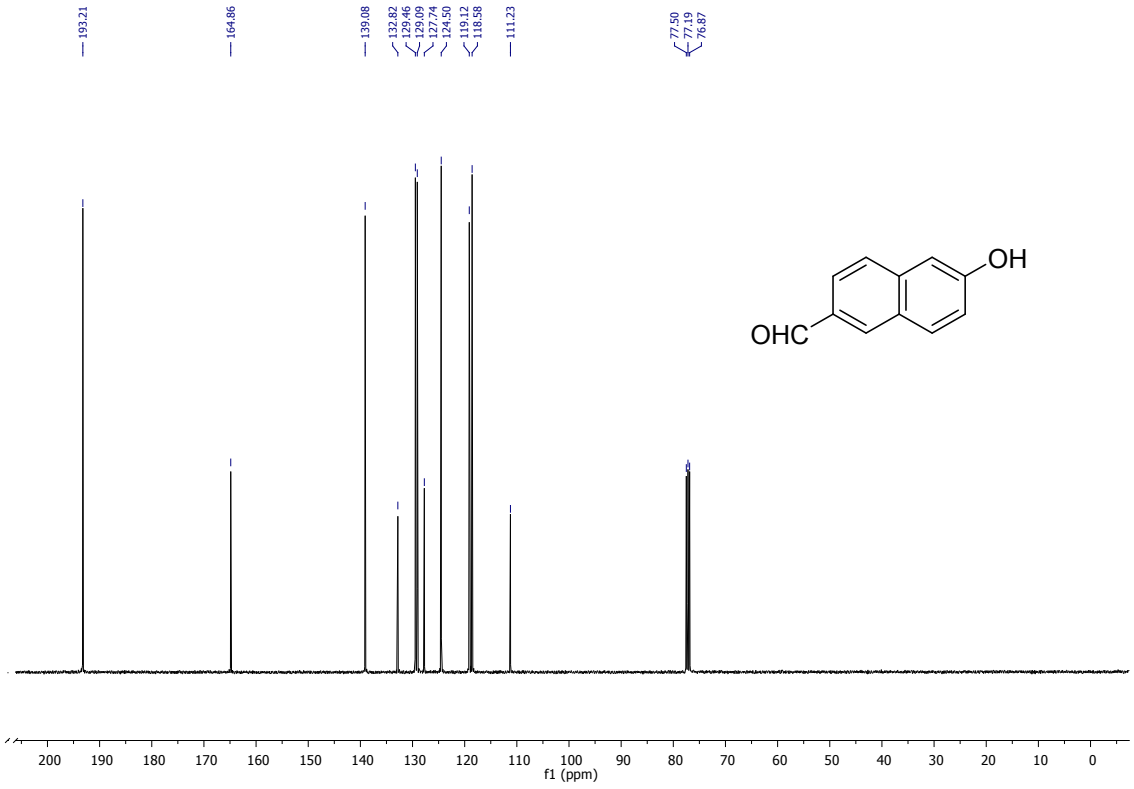


Figure S13: ^{13}C NMR spectrum of compound 2-Napthol.

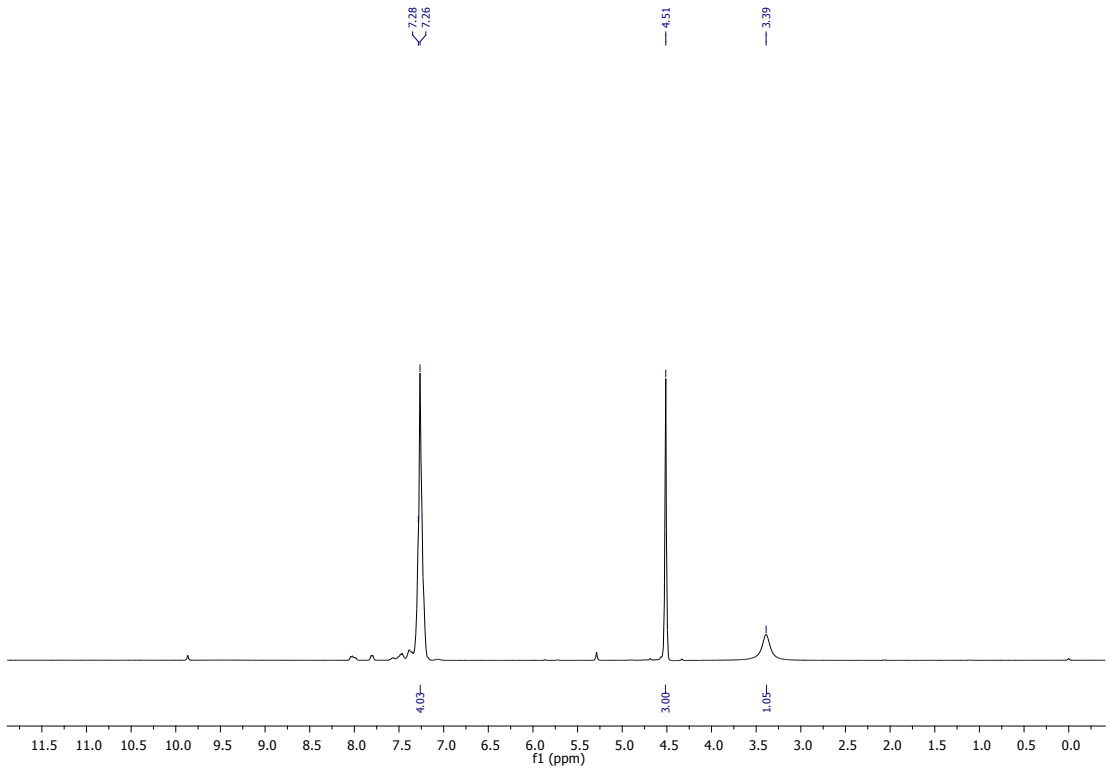


Figure S14: ^{13}C NMR spectrum of compound 4-Methoxy Phenol.

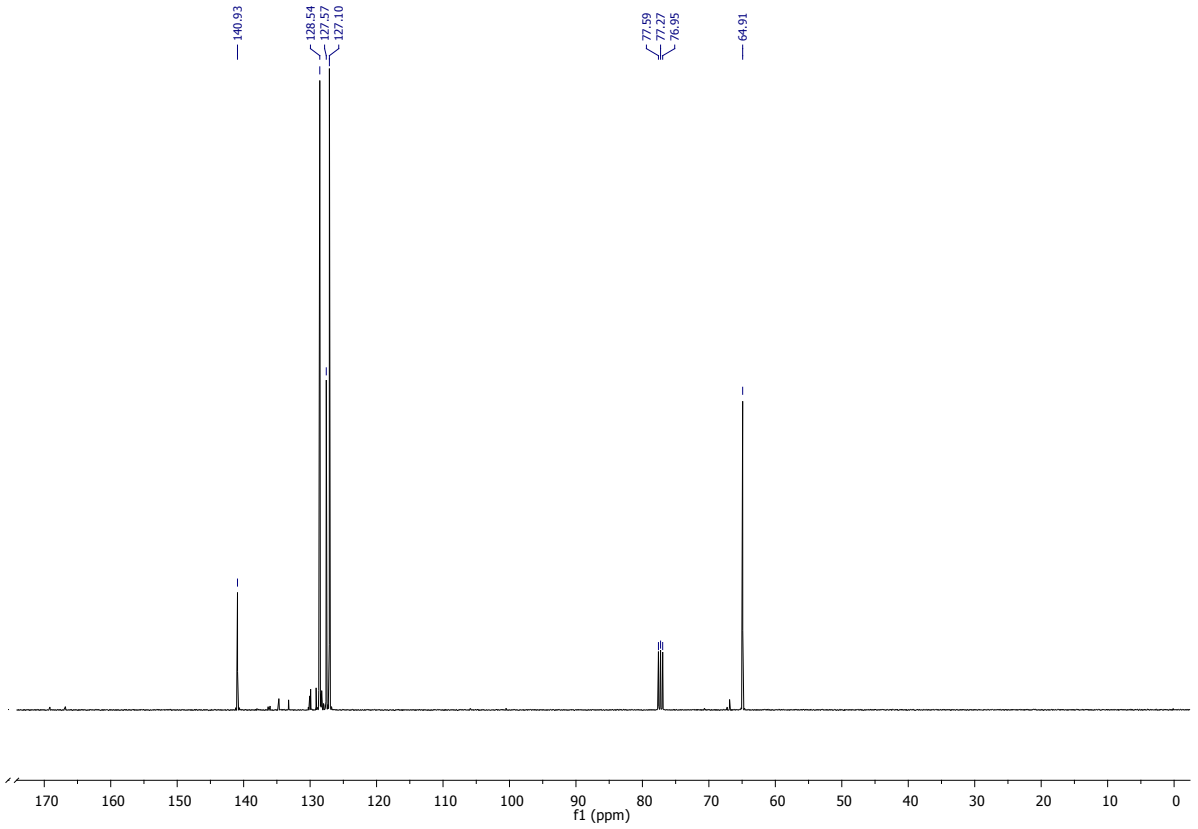


Figure S15: ^{13}C NMR spectrum of compound 4-Methoxy Phenol.

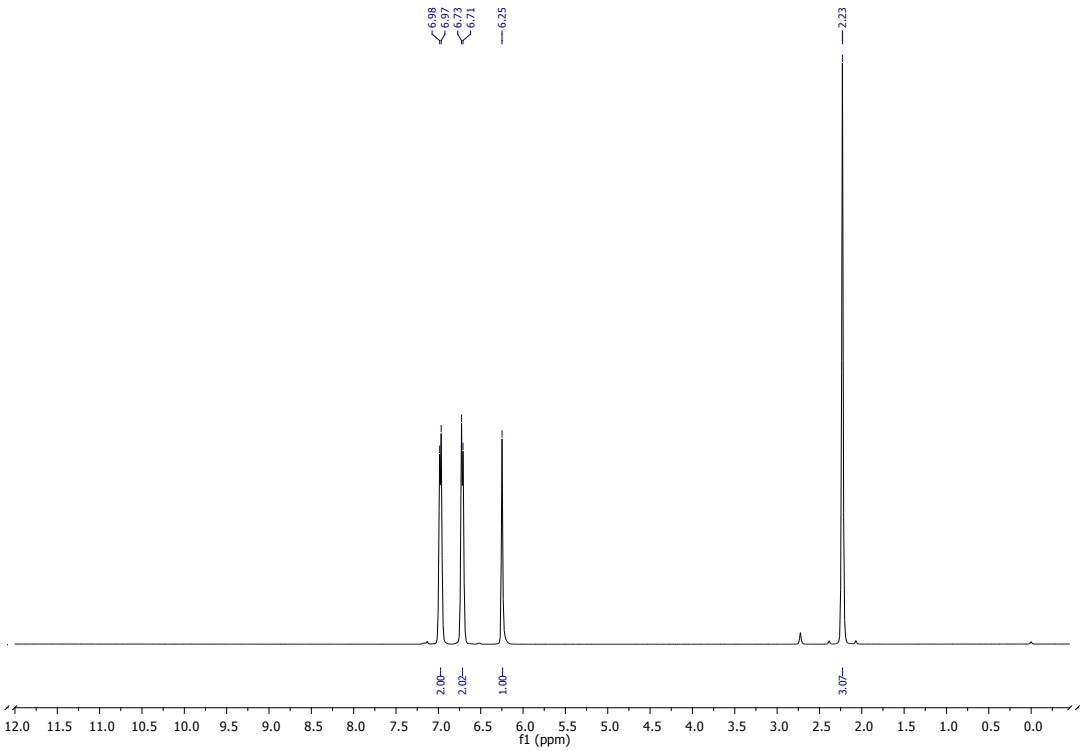


Figure S16: ^{1}H NMR spectrum of compound 4-Methyl Phenol.

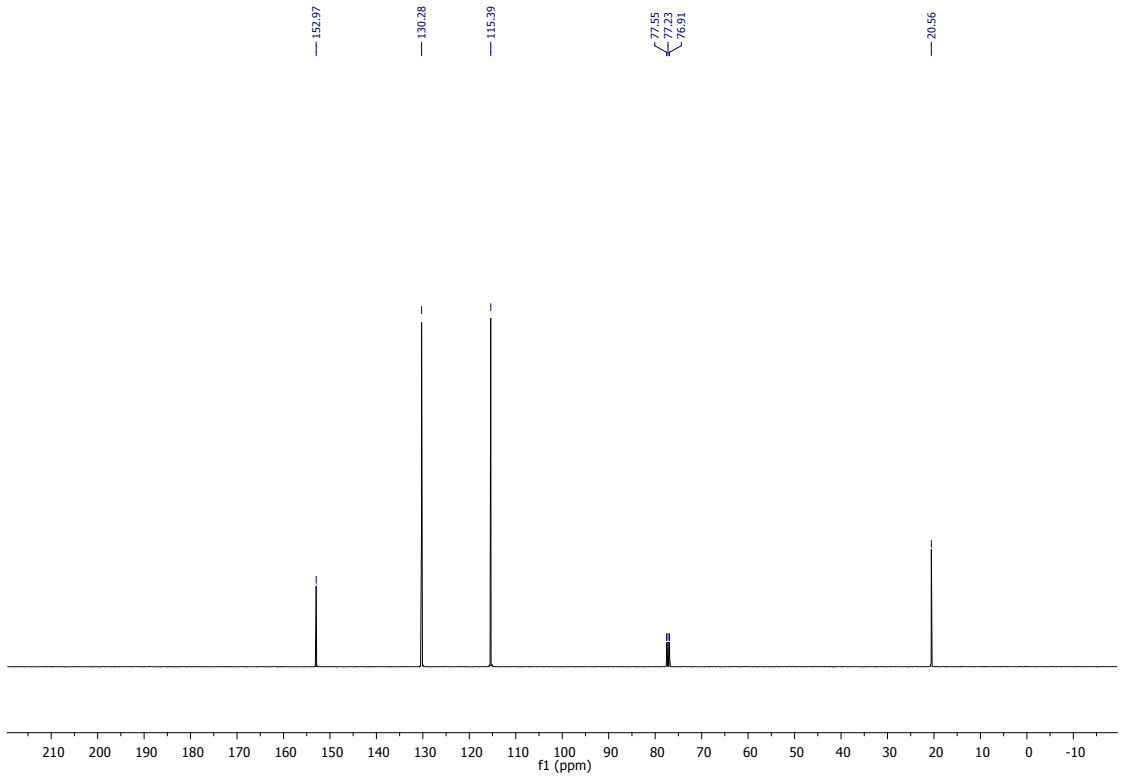


Figure S17: ^{13}C NMR spectrum of compound 4-Methyl Phenol.

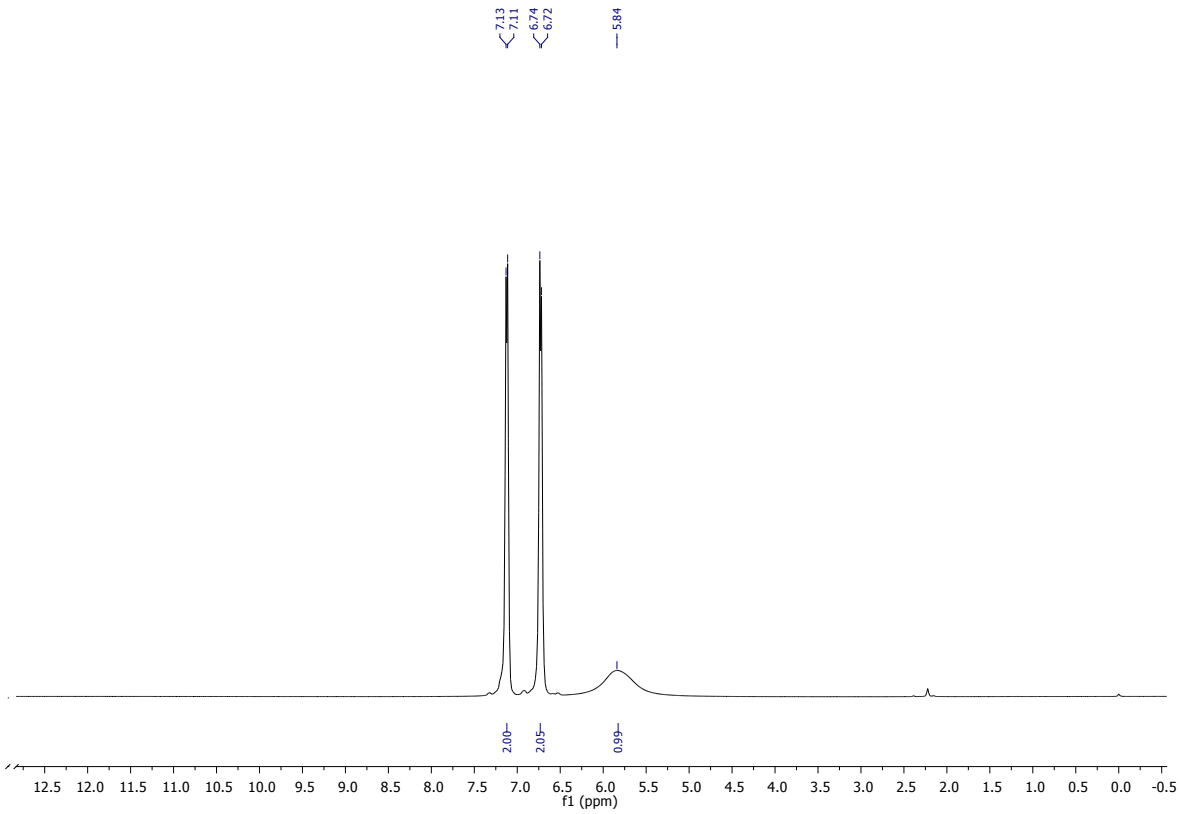


Figure S18: ^{1}H NMR spectrum of compound 4-Chlorophenol.

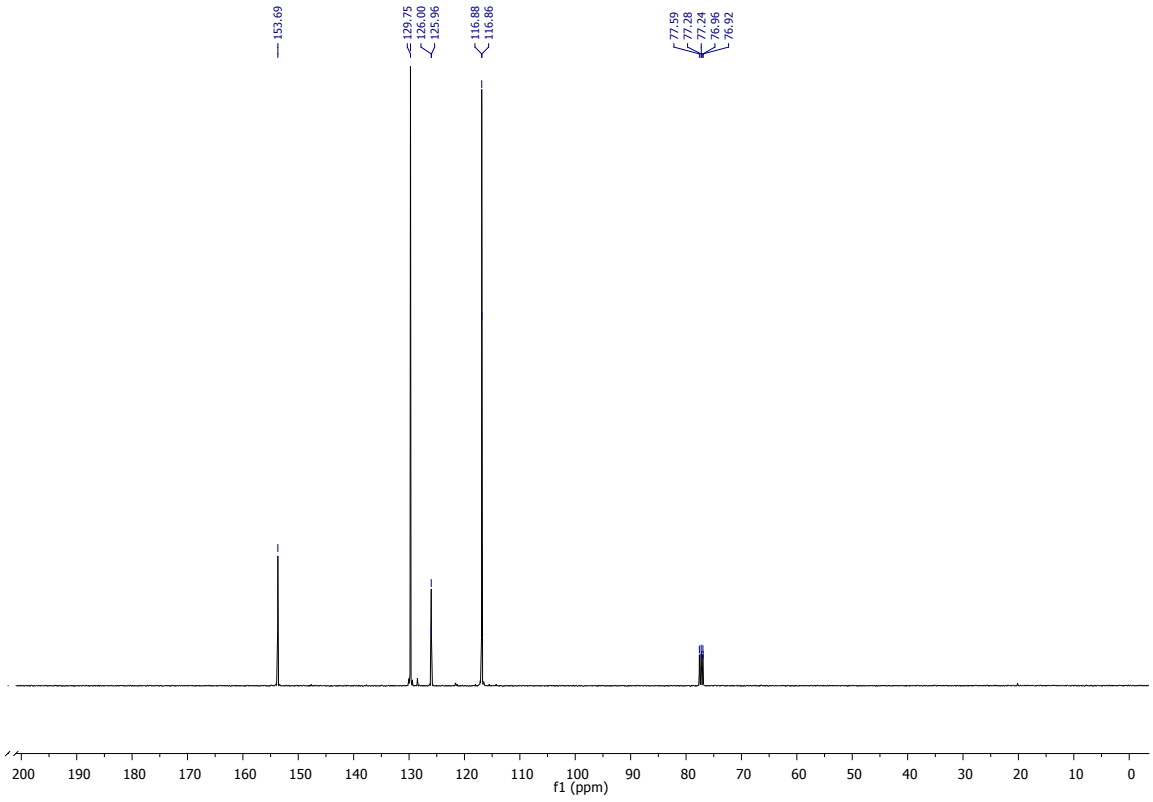


Figure S19: ^{13}C NMR spectrum of compound 4-ChloroPhenol.

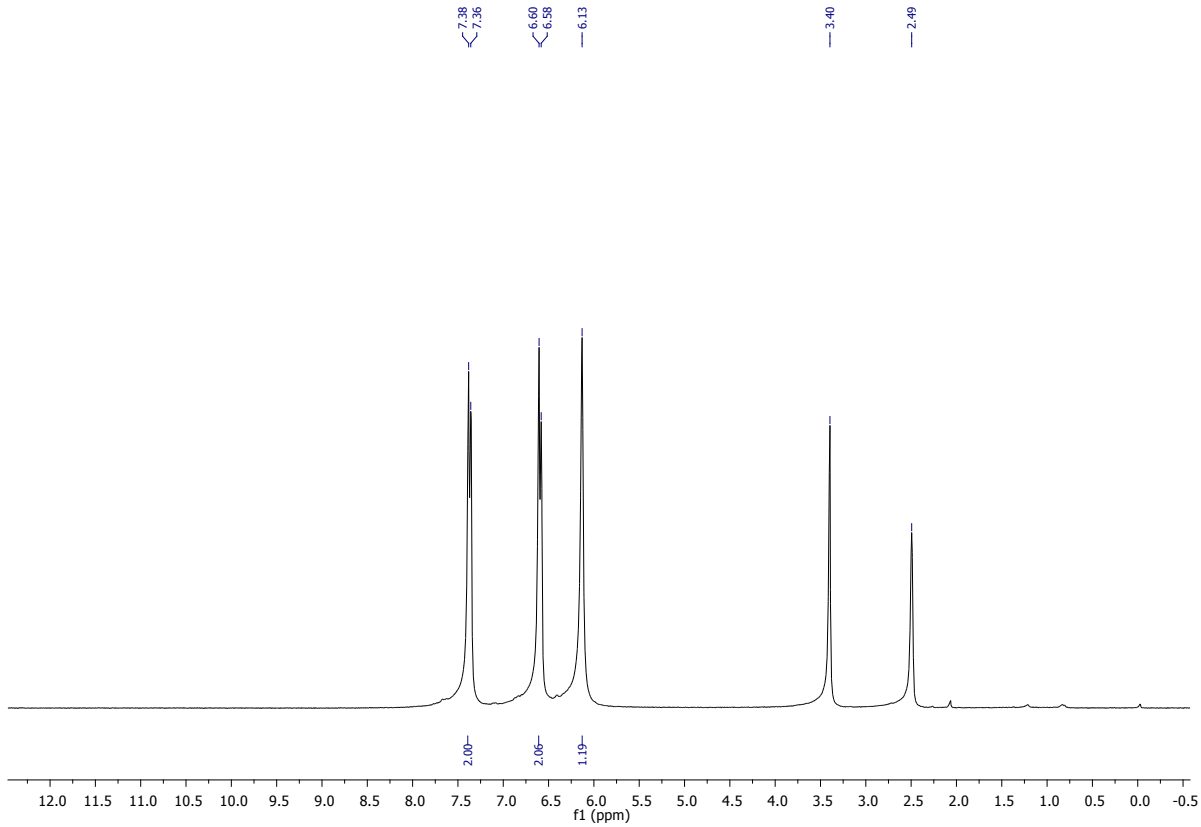
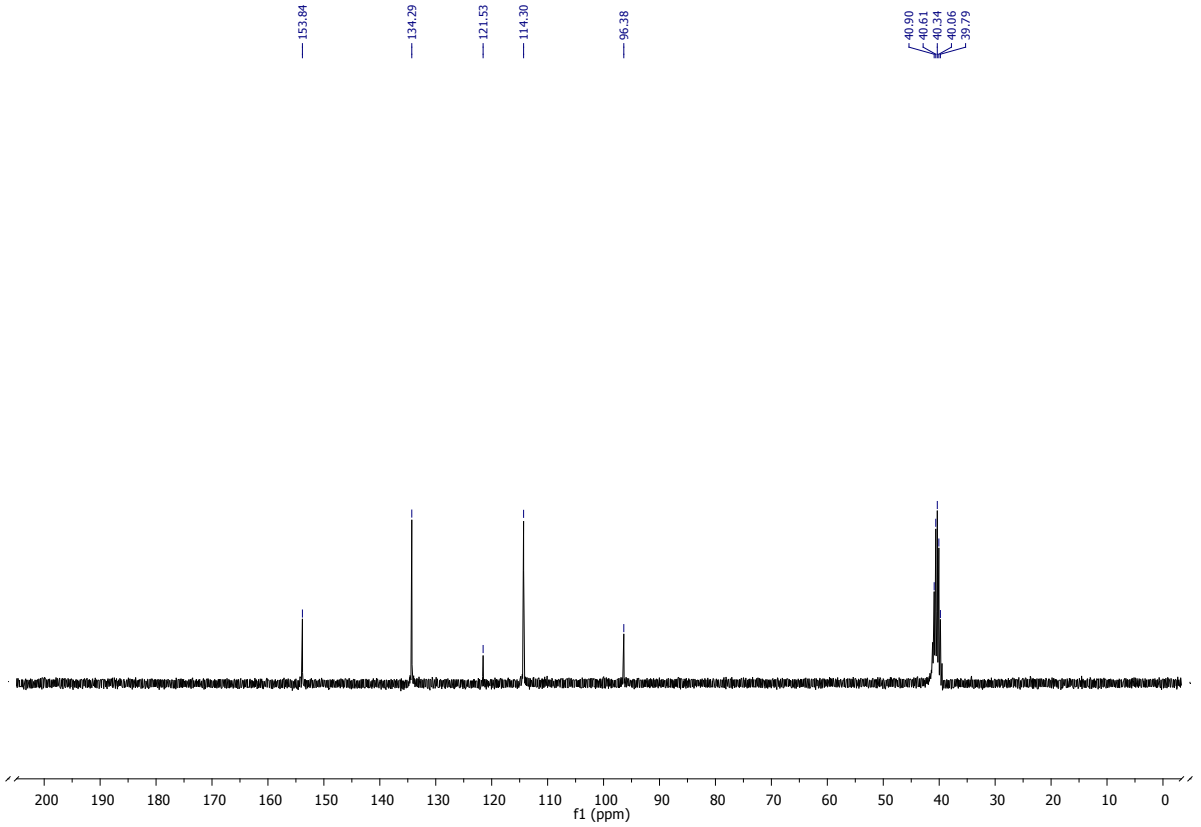


Figure S20: [1]H NMR spectrum of compound 4-hydroxyl benzonitrile.



. **Figure S21**: [13] C NMR spectrum of compound 4-hydroxyl benzonitrile.

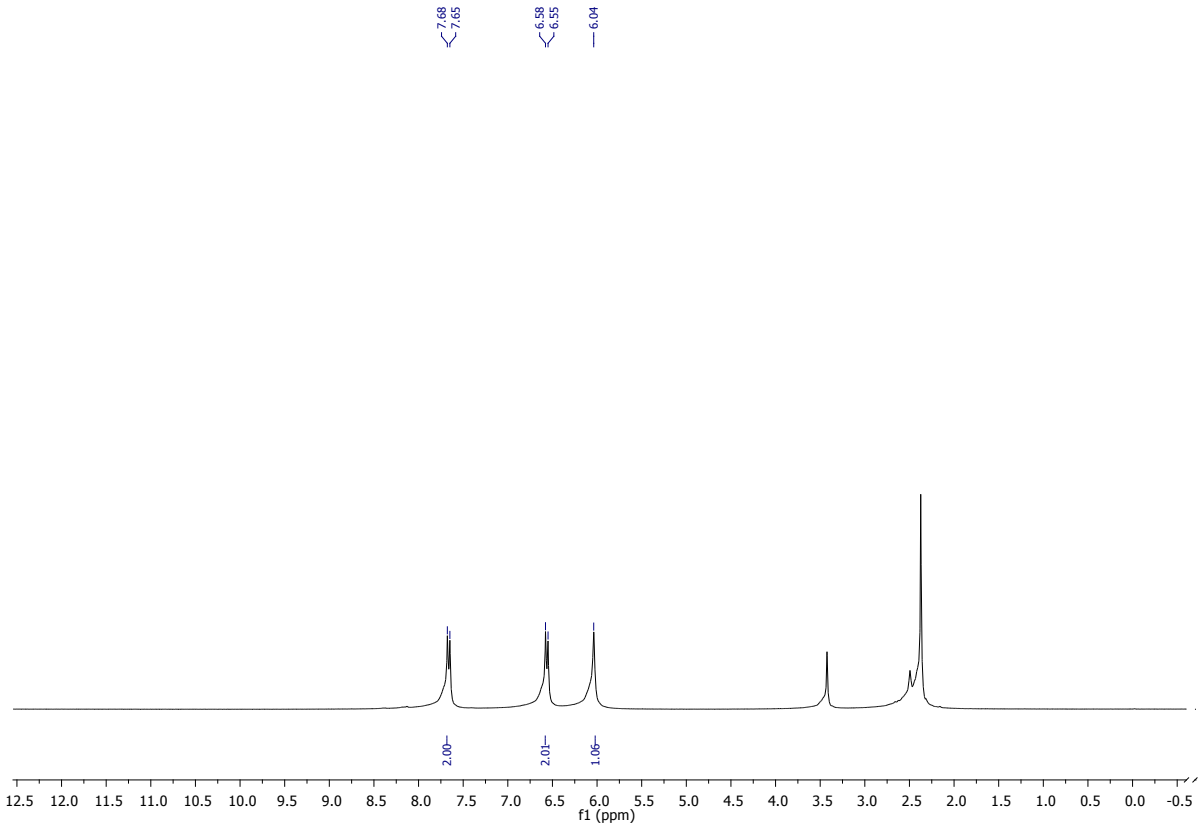


Figure S22: [1]H NMR spectrum of compound 4-hydroxylacetophenone.

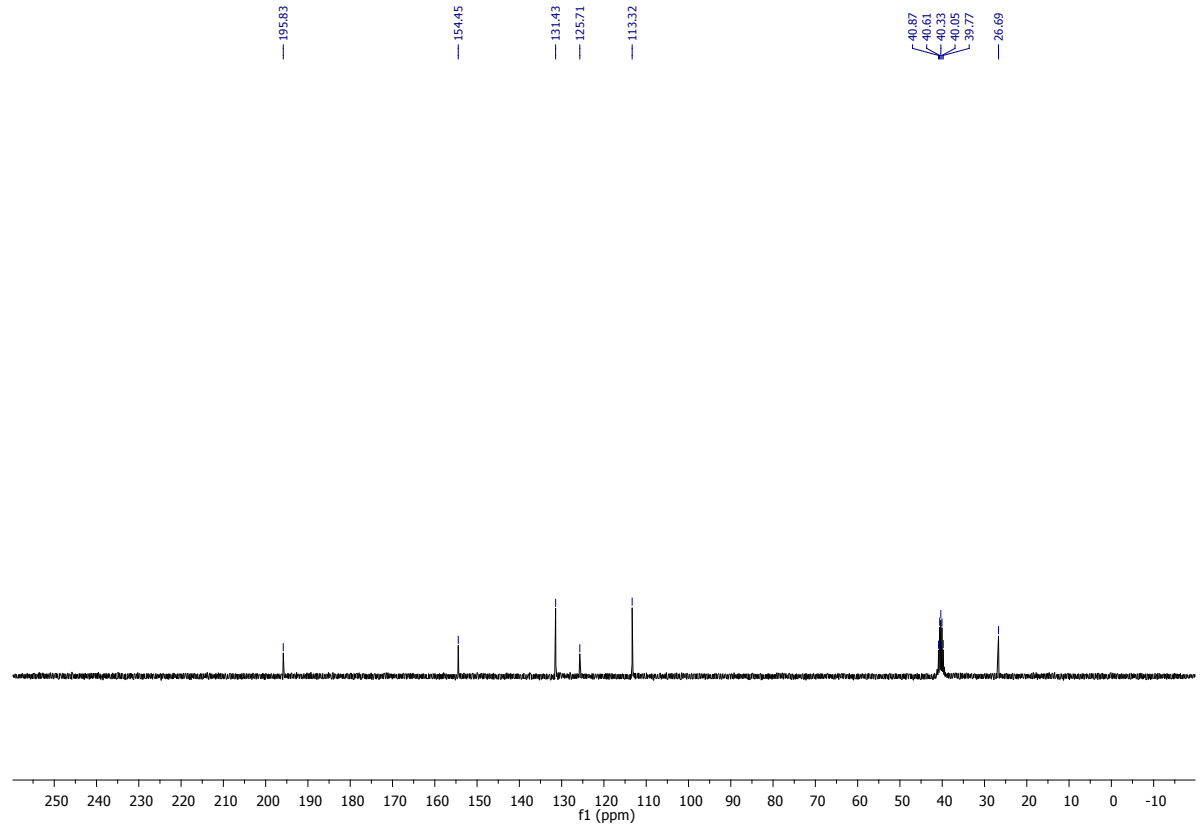
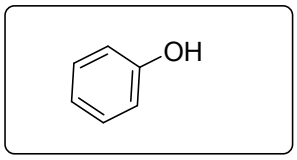
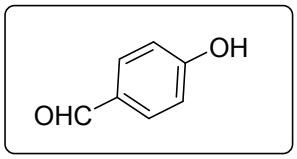


Figure S23: [1]H NMR spectrum of compound 4-hydroxylacetophenone.

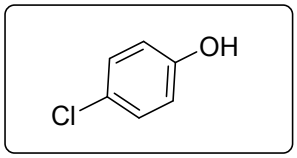
^{1}H and ^{13}C NMR data for all the derivatives



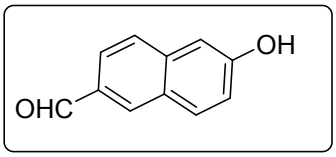
Phenol 1a Compound **1a** was prepared according to the general procedure to give a colourless viscous liquid with 99% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.0 Hz, 2H), 6.92 (t, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 2H), 5.87 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.19 (s), 129.91 (s), 121.16 (s), 115.57 (s), 77.54 (s), 77.22 (s), 76.90 (s).



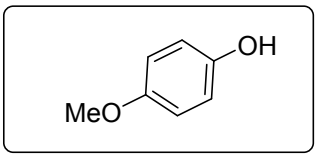
4-hydroxyl benzaldehyde (1b) Compound **1b** was prepared according to the general procedure to give a colourless solid with 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.94 (s, 1H), 9.61 (s, 1H), 7.28 (d, *J* = 7.4 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.66 (s), 161.29 (s), 136.75 (s), 133.69 (s), 120.57 (s), 119.71 (s), 117.27 (s), 77.96 (s), 77.64 (s), 77.32 (s).



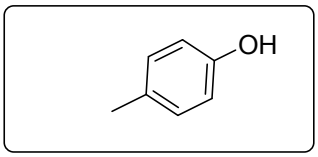
4-chlorophenol (1c) Compound **1c** was prepared according to the general procedure to give a light brown solid with 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 7.4 Hz, 2H), 6.73 (d, *J* = 7.5 Hz, 2H), 5.84 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.69 (s), 129.75 (s), 125.98 (d, *J* = 4.0 Hz), 116.87 (d, *J* = 2.5 Hz), 77.59 (s), 77.26 (d, *J* = 4.0 Hz), 76.94 (d, *J* = 3.9 Hz).



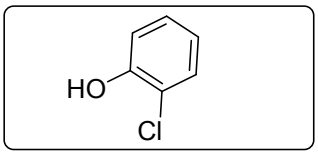
6-hydroxy-2-naphthaldehyde (1d) Compound **1d** was prepared according to the general procedure to give a colourless solid with 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.17 (s, 1H), 10.83 (s, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.21 (s), 164.86 (s), 139.08 (s), 132.82 (s), 129.46 (s), 129.09 (s), 127.74 (s), 124.50 (s), 119.12 (s), 118.58 (s), 111.23 (s), 77.50 (s), 77.19 (s), 76.87 (s).



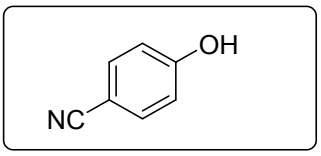
4-methoxyphenol (1e) Compound **1e** was prepared according to the general procedure to give a colourless solid with 85% yield^{13}C NMR (101 MHz, $CDCl_3$) δ 140.93 (s), 128.54 (s), 127.57 (s), 127.10 (s), 77.59 (s), 77.27 (s), 76.95 (s), 64.91 (s).



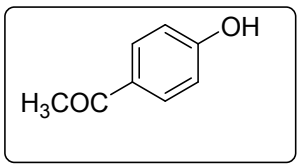
p-cresol (1f) Compound **1f** was prepared according to the general procedure to give a colourless viscous liquid with 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 7.2 Hz, 2H), 6.72 (d, *J* = 6.8 Hz, 2H), 6.25 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.97 (s), 130.28 (s), 115.39 (s), 20.56 (s).



2-chlorophenol (1g) Compound **1g** was prepared according to the general procedure to give a colourless solid with 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 6.9 Hz, 1H), 6.57 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.46 (s), 129.43 (s), 128.47 (s), 121.63 (s), 120.24 (s), 116.67 (s), 77.72 (s), 77.40 (s), 77.08 (s).

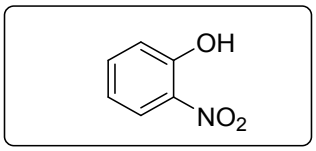


4-hydroxybenzonitrile (1h) Compound **1h** was prepared according to the general procedure to give a light brown colour solid with 78% yield. ^{1}H NMR (300 MHz, DMSO) δ 7.37 (d, *J* = 7.0 Hz, 2H), 6.59 (d, *J* = 7.0 Hz, 2H), 6.13 (s, 1H). ^{13}C NMR (75 MHz, DMSO) δ 153.84 (s), 134.29 (s), 121.53 (s), 114.30 (s), 96.38 (s), 44.93 – 42.02 (m), 41.18 (s), 40.76 (d, *J* = 21.4 Hz), 40.20 (d, *J* = 20.9 Hz), 39.79 (s).



1-(4-hydroxyphenyl)ethan-1-one (1i) Compound **1i** was prepared according to the general procedure to give a light yellow solid with 72% yield. ^{1}H NMR (300 MHz, DMSO) δ 7.66 (d, *J* = 8.5 Hz, 2H), 6.56 (d, *J* = 8.6 Hz, 2H), 6.04 (s, 1H). ^{13}C NMR (75 MHz, DMSO) δ 195.83 (s), 154.45 (s), 131.43 (s),

125.71 (s), 113.32 (s), 40.87 (s), 40.47 (d, J = 20.8 Hz), 39.91 (d, J = 21.4 Hz), 39.71 – 39.53 (m), 26.69 (s).



2-Nitro phenol 1j Compound **1j** was prepared according to the general procedure to give a light yellow solid with 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.11 (d, J = 8.3 Hz, 1H), 7.59 (dd, J = 10.8, 4.2 Hz, 1H), 7.16 (d, J = 8.2 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.13 (s), 137.57 (s), 133.69 (s), 125.07 (s), 120.24 (s), 119.97 (s), 77.39 (s), 77.07 (s), 76.75 (s).