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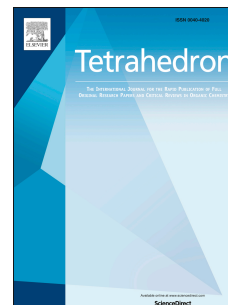
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Graphical Abstract

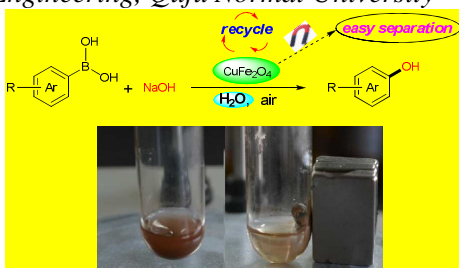
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A Novel Sustainable Strategy for the Synthesis of Phenols by Magnetic CuFe_2O_4 -Catalyzed Oxidative Hydroxylation of Arylboronic Acids under Mild Conditions in Water

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A Novel Sustainable Strategy for the Synthesis of Phenols by Magnetic CuFe₂O₄-Catalyzed Oxidative Hydroxylation of Arylboronic Acids under Mild Conditions in Water

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ABSTRACT

A novel sustainable strategy for the synthesis of phenols has been developed using inexpensive, readily available, air-stable and recyclable CuFe₂O₄ nanoparticles as the catalyst, and the corresponding substituted phenols were obtained in moderate to good yields by oxidative hydroxylation of arylboronic acids in water. Importantly, a ligand or an additive was not necessary. The catalyst was completely recoverable with an external magnet and could be reused six times without significant loss of catalytic activity.

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1. Introduction

Phenols widely occur in natural products, biologically and pharmaceutically active molecules.¹ They also serve as important synthetic intermediates in constructing aryl ethers and *O*-heterocycles. In industry-scale production, phenols are prepared by the cumene-phenol process (Hock process).² Unfortunately, the method shows low efficiency (only 5% overall yield). The traditional non-oxidative methods for the synthesis of phenols involve transformation of arene diazonium salts in the presence of copper salts and nucleophilic aromatic substitution of activated aryl halides. These methods, however, have some shortcomings. For example, the former method requires the conversion of amino groups to diazonium salts, which is often suffered from the low tolerance of other functional groups. The latter one is often performed under harsh reaction conditions. Transition-metal-catalyzed transformations are useful tools in synthetic organic chemistry.³ The direct hydroxylation of readily available aryl halides to substituted phenols is an appealing approach.⁴ Up to now, considerable progress in the transition-metal-catalyzed synthesis of phenols from aryl halides has been achieved by many groups.⁵

Arylboronic acids are important and common building blocks, and they are easily prepared from readily available aryl halides,⁶ tosylates⁷ and arylamines,⁸ or by iridium-catalyzed direct borylations of arenes via C-H bond activation.⁹ The arylboronic acids have been used as the starting materials to convert into phenols by oxidative hydroxylation,¹⁰ in which several equivalents of oxidants are needed. Despite these approaches to phenols are efficient, the amount of oxidants needs to be controlled carefully because the products are sensitive to the oxidants. Recently, Hu and Inamoto respectively reported an efficient copper-catalyzed oxidative hydroxylation of arylboronic acids at room temperature under air and O₂ conditions.^{11, 12} In 2012, Jørgensen and co-workers successfully developed a Ru-catalyzed visible-light-initiated aerobic oxidative hydroxylation of arylboronic acids.¹³ Despite their excellent works, removal of the trace amounts of metal-catalyst from the end products could be difficult due to the homogeneous reaction system. Hence, there remains an urgent need for economical and green method for the synthesis of phenols.

In modern organic synthesis, efforts to develop of practical methods, reaction conditions, highly efficient and recyclable catalyst systems, media, and the use of chemicals based on the principles of green chemistry are the central contents of the sustainable chemistry.¹⁴ As one of the vital participants in the

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green organic synthesis chemistry, magnetic nanoparticles have been extensively used in organic transformations because of their easy preparation, low toxicity, efficient separation by using an external magnet and without the need for filtration step.^[15] Among all the magnetic nanoparticles, CuFe₂O₄ nanoparticles have emerged as a powerful and excellent catalyst for many organic transformations,^[16] and water is the most economical and environmentally friendly solvent in the world.^[17] Herein, we report a simple, practical and efficient CuFe₂O₄-catalyzed synthesis of substituted phenols from arylboronic acids by using environmentally benign water as the solvent under mild conditions. Notably, when we were performing these studies, Sawant and his coworkers reported the elegant example of the direct oxidation of arylboronic acids to phenols using iron(III) oxide as the catalyst under ligand- and base free condition in solar VIS-light irradiation.^[18]

2. Results and discussion

The CuFe₂O₄ nanoparticles were prepared according to the literature procedure^[19] and characterized by X-ray diffraction (Fig 1), the diffraction patterns of all the peaks matched well with the standard XRD pattern (JCPDS34-0425). As can be seen from the SEM and TEM images, the CuFe₂O₄ nanoparticles could remain well in the same state, even after six cycles. (Fig 1, Fig 2, ESI†). Moreover, the EDX spectrum shows that the spheres are composed of Cu, Fe and O, as expected. (Fig 3, ESI†).

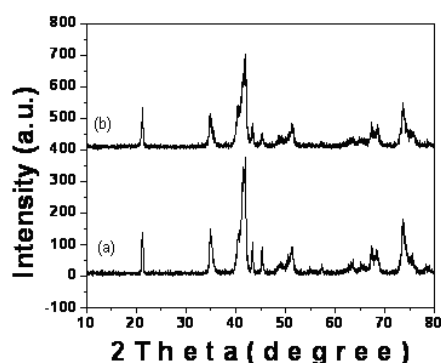


Figure 1. XRD spectrum of native CuFe₂O₄ catalyst. (b) XRD spectrum of reused CuFe₂O₄ catalyst after 6th cycle

At first, phenylboronic acid (1a) was chosen as the model substrate to optimize reaction conditions including the bases, ligands and reaction temperatures under air atmosphere in water. Firstly, a range of bases such as NaOH, KOH, Na₂CO₃, K₂CO₃, Cs₂CO₃ and K₃PO₄ were investigated by using 0.1 equiv of CuFe₂O₄ nanoparticles as the catalyst (relative to amount of 1a) in water, NaOH and KOH provided almost the same yields, but the others were bad bases, and we chose NaOH as the base (entries 1–7). Interestingly, the reaction gave low yield when proline or 1,10-Phenanthroline was added as the ligand (entry 10 and 11). The effect of reaction temperature was also investigated, and it was found that performing the reaction at 40 °C in the presence of the promoter was optimal for the reaction and the reaction provided phenol (2a) in 25% yield with the corresponding symmetric Biphenyl appearing in 15% yield. (Table 1, entries 1, 7 and 13). Control experiments indicated that the desired phenol was formed in the absence of the catalyst, but the yield was low and only 10% phenol was obtained (entries 12). Therefore, the CuFe₂O₄-catalyzed optimum conditions are as follows: 10 mol % CuFe₂O₄ nanoparticles as the catalyst, 3.0 equiv of NaOH as the base (relative to phenylboronic acid) and H₂O as the solvent at 40 °C under air atmosphere.

Table 1. Magnetic CuFe₂O₄-catalyzed oxidative hydroxylation of phenylboronic acid (1a) leading to phenol (2a): optimization of conditions.^a

Entry	Base	Temp. [°C]	Yield [%] ^[b]
1	NaOH	25	70
2	KOH	25	71
3	K ₂ CO ₃	25	trace
4	Cs ₂ CO ₃	25	trace
5	K ₃ PO ₄	25	trace
6	Na ₂ CO ₃	25	trace
7	NaOH	40	97
8	KOH	40	98
9	NaOH	60	75
10	NaOH	40	65 ^[c]
11	NaOH	40	70 ^[d]
12	NaOH	40	10 ^[e]
13	NaOH	60	25

^[a] Reaction conditions: phenylboronic acid (1a) (1.0 mmol) catalyst (0.1 mmol),

base (2.0 mmol), solvent (1 mL) under air atmosphere.

^[b] Isolated yield.

^[c] L-Proline (0.2 mmol) as the ligand was added

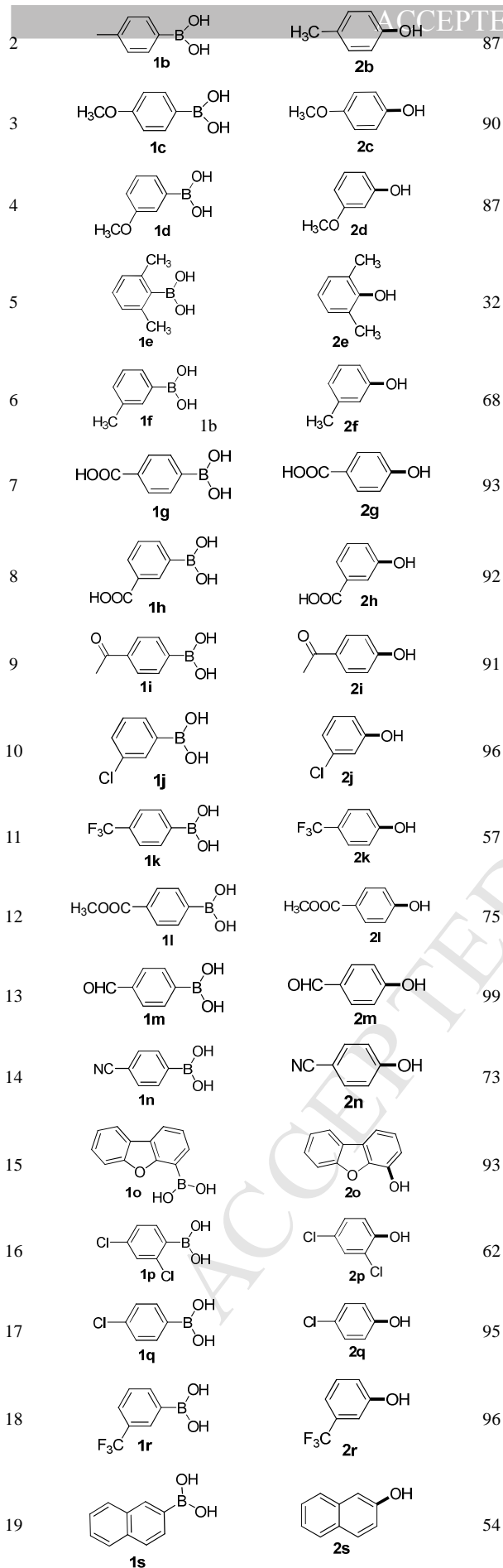
^[d] 1,10-Phenanthroline (0.2 mmol) as the ligand was added

^[e] In the absence of catalyst

We then investigated the scope of the CuFe₂O₄-catalyzed reaction with respect to the aromatic boronic acid.²⁰ As shown in Table 2, most of the substrates examined provided moderate to excellent yields under similar conditions. The electronic effect of the substituted groups in the arylboronic acids including electron-rich, -neutral, and -deficient substituents did not display evident difference in reactivity (comparing entry 11, 13 and 14 with entries 1-3 in Table 2). Phenylboronic acids bearing bulky substituents, such as 2, 6-dimethylphenylboronic acid and 2, 4-dichlorophenylboronic acid were also examined, and moderate yields of the reactions were obtained (entries 5 and 16). The reactions showed good tolerance of functional groups on the aryl ring including ester groups (entries 12), C-Cl bonds (entries 16, 17), aldehyde groups (entries 13), carboxyl groups (entry 9) and heterocycle (entry 15). The target products containing ester or cyanyl groups, are favorable for their further modifications.

Table 2. Magnetic CuFe₂O₄-catalyzed oxidative hydroxylation of phenylboronic acid (1a) leading to phenol (2a).^a

entry	1	2	yield (%) ^b
1			98



NaOH (2.0 mmol), solvent (1 mL) under air atmosphere.

^[b] Isolated yield.

The reusability of the catalyst were also studied. For this, we investigated the CuFe₂O₄-catalyzed oxidative hydroxylation of phenylboronic acid under the optimized conditions (Fig. 2). After completion of the reaction, the catalyst was magnetically separated from the reaction mixture, washed with deionized water and acetone, air dried and then used directly for further catalytic reactions. No significant loss of catalyst activity was found (95%), even up to six cycles.

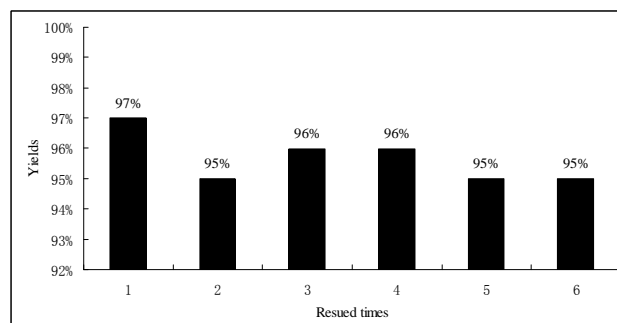
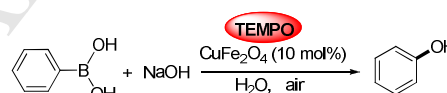


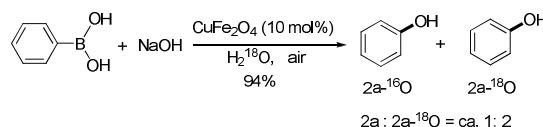
Figure 2. Recycling of the CuFe₂O₄ catalyst.

As shown in Scheme 1, when one equivalent of TEMPO (2, 2, 6, 6-tetramethyl-1-piperidinyloxy, a well known radical-capturing species) was added to the reaction system, no significant difference was observed in the yield, ruling out the presence of radicals during the reaction.



Scheme 1. Reactions of phenylboronic acid in the presence of TEMPO under the optimized reaction condition.

When the reaction of boronic acid **1a** with NaOH was performed employing H₂¹⁸O as a solvent under the optimal reaction conditions, 63% ¹⁸O-**2a** and 31% ¹⁶O-**2a** products were detected (Scheme 2, HRMS, see ESI[†]), indicating that the oxygen source for the phenol formation is water as previously hypothesized by Evans et al²¹ and Lam et al.²²



Scheme 2. Reactions of phenylboronic acid using H₂¹⁸O as the solvent under the optimized reaction condition.

3. Conclusion

In summary, a simple, green and efficient strategy for the synthesis of phenols in water has been successfully developed using strongly magnetic CuFe₂O₄ as the catalyst and arylboronic acids as the starting materials. CuFe₂O₄ nanoparticles, which are cost-effective, readily available, air-stable and recyclable materials, have been initially demonstrated as an excellent catalyst for the oxidative hydroxylation of arylboronic acids in water, importantly, a ligand, or an additive was not necessary. Such a novel sustainable strategy for the synthesis of phenols will attract much attention in industrial and academic researches. Further applications of CuFe₂O₄ magnetic nanoparticles in organic transformations are in progress in our laboratory.

^[a] Reaction conditions: arylboronic acid (**1**) (1.0 mmol) catalyst (0.1 mmol),

4. Experimental section

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4.1. General remarks

All reagents and solvents were obtained from commercial suppliers and used without further purification. Flash chromatography was performed on silica gel (200 ~ 300 mesh). ^1H , and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl_3 as the internal standard (1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.28 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm).

4.2. General procedure for synthesis of substituted phenols

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with CuFe_2O_4 nanoparticles (0.1 mmol, 24 mg), substituted arylboronic acids (**1**) (1.0 mmol), NaOH (3.0 mmol, 120 mg), and H_2O (2.0 mL) was added to the tube under air atmosphere. The flask was not sealed in order that air could enter the flask, and the mixture was allowed to stir for 24 h under air at 40 °C. After completion of the reaction, the resulting solution was cooled to room temperature, HCl (2N, 1 mL) was added to acidify the solution (pH 5-7), and the target product was extracted with ethyl acetate (4-6 mL). The combined organic phase was dried over anhydrous MgSO_4 and filtered, and the solvent of the filtrate was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as an eluent to provide the desired product (**2**).

4.2.1. *Phenol (2a)*.^[23] Eluent petroleum ether/ethyl acetate (5:1). Yield 95% (89 mg). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.21 (t, 2H, $J = 5.5\text{Hz}$), 6.93 (t, 1H, $J = 4.9\text{Hz}$), 6.83(d, 2H, $J = 5.1\text{Hz}$), 6.03(s, br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm) δ 155.3, 129.9, 121.1, 115.6. ESI-MS [M-H]⁻ m/z 93.1.

4.2.2 *p-Cresol (2b)*.^[24] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.06 (d, 2H, $J = 7.9\text{Hz}$), 6.78 (d, 2H, $J = 7.9\text{Hz}$), 5.3 (s, br, 1H), 2.31 (s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 153.3, 130.1, 130.0, 115.2, 20.5. ESI-MS [M-H]⁻ m/z 107.6.

4.2.3. *4-methoxyphenol (2c)*.^[25] Eluent petroleum ether/ethyl acetate (5:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 6.83-6.78(m, 4H), 4.5(s, br, 1H), 3.8(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 153.8, 149.5, 55.6. ESI-MS [M-H]⁻ m/z 123.4.

4.2.4. *3-methoxyphenol (2d)*.^[25] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.16(d, 1H, $J = 8.0\text{Hz}$), 6.52(d, 1H, $J = 7.6\text{Hz}$), 6.45(d, 1H, $J = 8.0\text{Hz}$), 3.8(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 161.0, 156.8, 130.2, 107.8, 106.4, 101.6, 55.3. ESI-MS [M-H]⁻ m/z 123.7.

4.2.5. *2,6-dimethylphenol (2e)*.^[26] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.07(d, 2H, $J = 8.0\text{ Hz}$), 6.86(t, 1H, $J = 7.6\text{ Hz}$), 4.48(s, br, 1H), 2.33(s, 6H). ^{13}C NMR (CDCl_3 , 200MHz, ppm) δ 152.1, 128.5, 123.0, 120.2, 15.8. ESI-MS [M-H]⁻ m/z 121.7.

4.2.6. *m-cresol (2f)*.^[26] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.15(t, 1H, $J = 7.9\text{Hz}$), 6.77(s, 1H, $J = 7.9\text{Hz}$), 6.67(d, 1H, $J = 8.0\text{Hz}$), 2.33(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 155.5, 139.8.8, 129.4, 121.6, 116.0, 112.2, 21.3. ESI-MS [M-H]⁻ m/z 107.5.

4.2.7. *4-hydroxybenzoic acid (2g)*.^[27] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ^1H NMR (CDCl_3 , 400

MHz, ppm) 7.15(t, 1H, $J = 7.9\text{Hz}$), 6.77(s, 1H, $J = 7.9\text{Hz}$), 6.67(d, 1H, $J = 8.0\text{Hz}$), 2.33(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 155.5, 139.8.8, 129.4, 121.6, 116.0, 112.2, 21.3. ESI-MS [M-H]⁻ m/z 107.5.

4.2.8. *3-hydroxybenzoic acid (2h)*.^[28] Eluent petroleum ether/ethyl acetate (3:1). White solid. ^1H NMR (DMSO-d_6 , 400 MHz, ppm) 12.72(s, br, 1H), 9.68 (s, br, 1H), 7.38-7.33(m, 2H), 6.70(s, 1H). ^{13}C NMR (DMSO-d_6 , 200 MHz, ppm) δ 167.8, 157.8, 132.5, 129.9, 120.3, 116.3. ESI-MS [M-H]⁻ m/z 137.2.

4.2.9. *1-(4-hydroxyphenyl)ethanone (2i)*.^[26] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 8.57(s, br, 1H), 7.93(d, 2H, $J = 8.0\text{Hz}$), 6.98(d, 1H, $J = 8.0\text{Hz}$), 2.61(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 199.2, 161.8, 131.3, 129.3, 115.7, 26.3. ESI-MS [M-H]⁻ m/z 135.4.

4.2.10. *3-chlorophenol (2j)*.^[29] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.17(m, 1H), 6.90(m, 2H), 6.76(d, 1H, $J = 8.0\text{Hz}$), 6.03(s, br, 1H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 172.7, 156.5, 134.9, 130.5, 120.9, 116.0, 113.8. ESI-MS [M-H]⁻ m/z 127.4.

4.2.11. *4-(trifluoromethyl)phenol (2k)*.^[30] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.54(d, 1H, $J = 8.0\text{Hz}$), 6.94(d, 1H, $J = 8.0\text{Hz}$), 5.63(s, br, 1H). ^{13}C NMR (CDCl_3 , 200MHz, ppm) δ 157.8, 127.3, 123.9(q, $^1J = 360.0\text{Hz}$), 123.0(q, $^1J = 48.0\text{Hz}$), 115.4. [M-H]⁻ m/z 161.4.

4.2.12. *methyl 4-hydroxybenzoate (2l)*.^[31] Eluent petroleum ether/ethyl acetate (5:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.99(d, 1H, $J = 8.0\text{Hz}$), 6.90(d, 1H, $J = 8.0\text{Hz}$), 6.05(s, br, 1H), 3.92(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 167.3, 160.1, 132.0, 122.5, 115.3, 52.1. ESI-MS [M-H]⁻ m/z 151.4.

4.2.13. *4-hydroxybenzaldehyde (2m)*.^[32] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 9.88(s, 1H), 7.83(d, 2H, $J = 8.0\text{Hz}$), 7.00 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 191.1, 161.9, 132.5, 129.7, 116.0. ESI-MS [M-H]⁻ m/z 121.3.

4.2.14. *4-hydroxybenzonitrile (2n)*.^[33] Eluent petroleum ether/ethyl acetate (15:1). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.57(d, 2H, $J = 8.0\text{Hz}$), 6.93(d, 2H, $J = 8.0\text{Hz}$), 7.00 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 160.0, 134.3, 119.5, 116.4. ESI-MS [M-H]⁻ m/z 118.3.

4.2.15. *dibenzo[b,d]furan-4-ol (2o)*.^[34] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.95(d, 2H, $J = 7.2\text{ Hz}$), 7.60(d, 2H, $J = 8.0\text{Hz}$), 7.56-7.47(m, 2H), 7.40(t, 1H, $J = 8.0\text{Hz}$), 7.28(t, 1H, $J = 8.0\text{Hz}$), 7.05(d, 1H, $J = 8.0\text{Hz}$), 5.53(s, br, 1H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 156.1, 144.1, 141.2, 127.3, 125.8, 124.6, 123.7, 123.0, 121.0, 113.6, 112.8, 111.8. ESI-MS [M-H]⁻ m/z 183.3.

4.2.16. *2,4-dichlorophenol (2p)*.^[35] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.33(d, 2H, $J = 2.4\text{Hz}$), 7.18(d, 2H, $J = 8.0\text{Hz}$), 6.97(d, 1H, $J = 8.0\text{Hz}$), 5.57(s, br, 1H). ^{13}C NMR (CDCl_3 , 200MHz, ppm) δ 150.2, 128.6, 128.5, 125.6, 120.4, 117.1. ESI-MS [M-H]⁻ m/z 160.8.

4.2.17. *4-chlorophenol (2q)*.^[36] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.21(d, 2H, $J = 8.0\text{Hz}$), 6.80 (d, 2H, $J = 8.0\text{Hz}$), 5.60(s, br, 1H). ^{13}C NMR (CDCl_3 , 200MHz, ppm) δ 154.2, 129.5, 125.6, 116.7. ESI-MS [M-H]⁻ m/z 127.3.

4.2.18. 3-(trifluoromethyl)phenol (**2r**).^[37] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.36(d, 2H, *J* = 8.0Hz), 7.20 (d, 2H, *J* = 8.0Hz), 7.12(s, 1H), 7.04(d, 2H, *J* = 8.0Hz), 6.0(s, br, 1H). ¹³C NMR (CDCl₃, 200MHz, ppm) δ 156.0, 131.2(q, ²*J* = 64.0Hz), 130.2, 123.6(q, ¹*J* = 542.0Hz), 118.0, 117.0, 112.3. ESI-MS [M-H]⁺m/z 161.3.

4.2.19. naphthalen-2-ol (**2s**).^[34] Eluent petroleum ether/ethyl acetate (15:1). White solid. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.82-7.78(m, 2H), 7.11 (d, 2H, *J* = 8.0Hz), 7.49-7.45(m, 1H), 7.39-7.35(m, 1H), 7.18-7.13(m, 2H), 5.11(s, br, 1H). ¹³C NMR (CDCl₃, 200MHz, ppm) δ 153.2, 134.6, 129.9, 129.0, 127.8, 126.6, 126.4, 123.7, 117.4, 109.6. ESI-MS [M-H]⁺m/z 143.3.

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Supplementary Material

Supplementary data associated with this article can be found at <http://>

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Supporting Information

A Novel Sustainable Strategy for the Synthesis of Phenols by Magnetic CuFe₂O₄-Catalyzed Oxidative Hydroxylation of Arylboronic Acids under Mild Conditions in Water

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Table of Contents

Characterisation of the CuFe ₂ O ₄ nano Catalyst:	P2
General experimental procedures	P7
General procedure for synthesis of compounds 2a-s	P7
The characterization data of compounds 2a-s	P7
References	P11
The ¹ H and ¹³ C NMR spectra of compounds 2a-q 4 and 6	P13

Characterisation of the CuFe_2O_4 nano Catalyst:

From SEM, XRD spectral studies, it is revealed that the CuFe_2O_4 nanoparticles remained in the same state, even after six cycles.

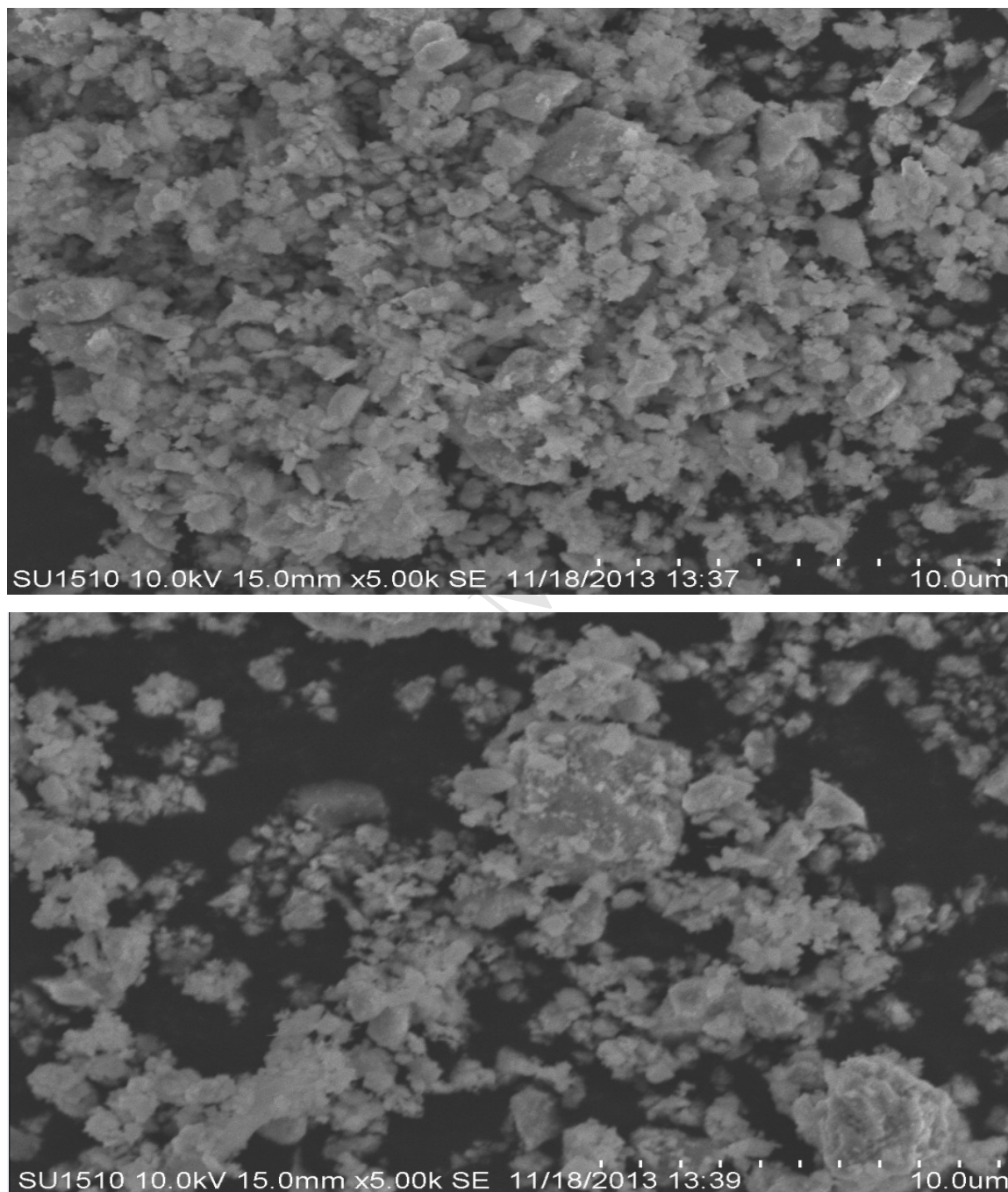


Fig. 1 SEM-analysis of (a) native CuFe_2O_4 catalyst and (b) reused catalyst after six cycle.

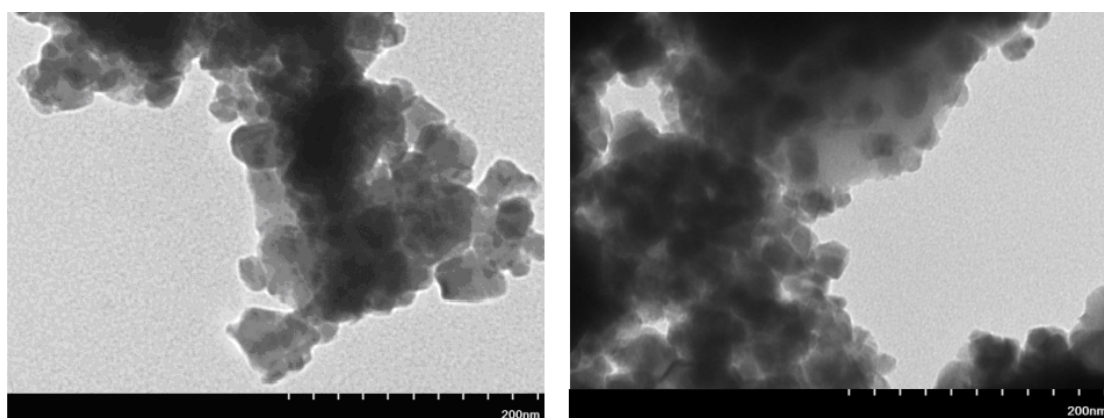
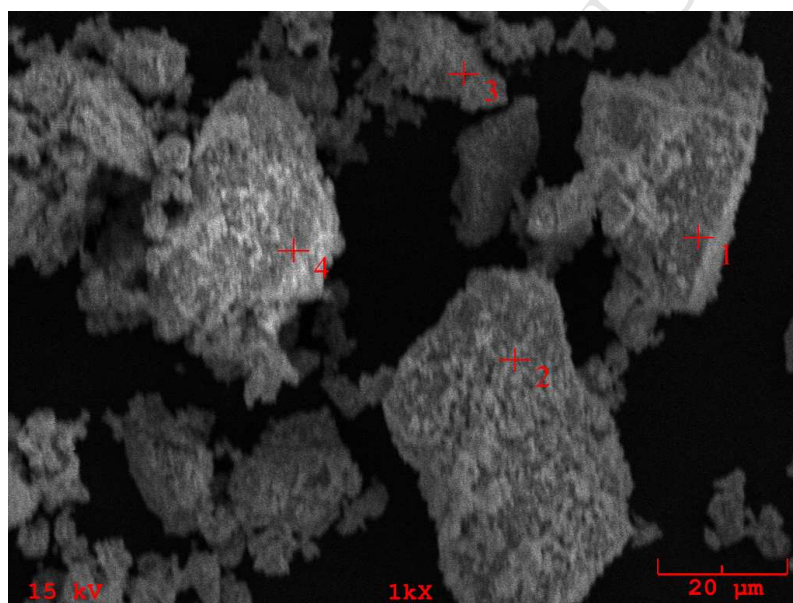
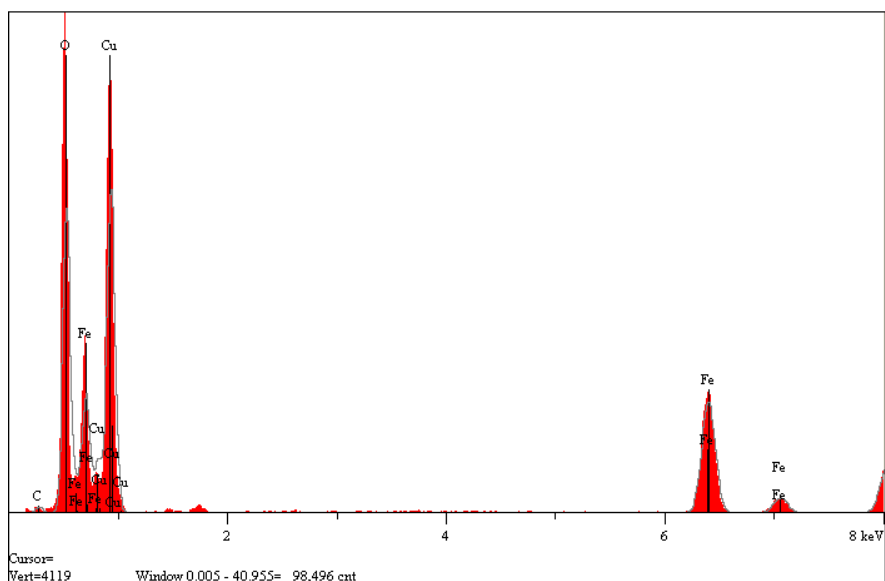


Fig. 2 TEM-analysis of (a) native CuFe_2O_4 catalyst and (b) reused catalyst after six cycle.



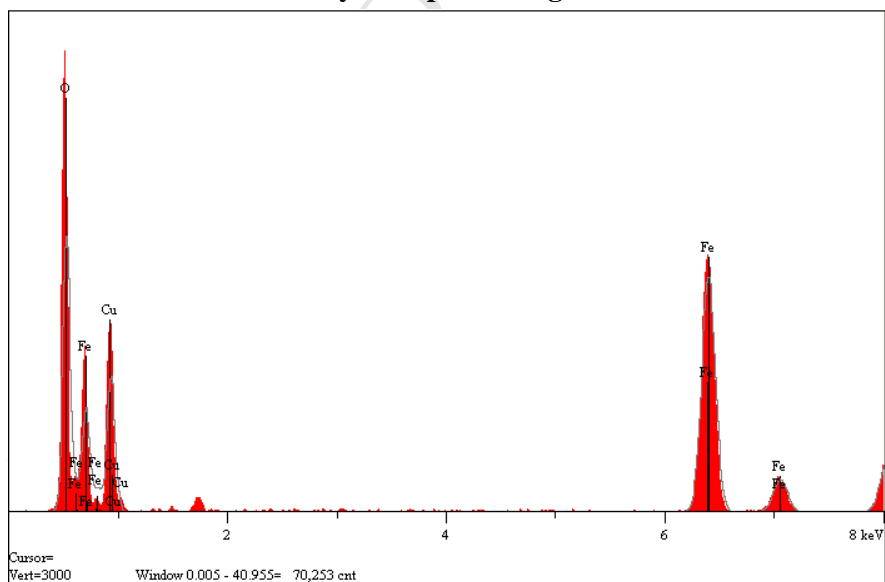


Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	Error 2-sig	
C	Ka	14.24	3.265	1.113	wt.%	0.263	
O	Ka	700.56	52.453	23.811	wt.%	0.349	
Fe	Ka	472.48	21.807	34.553	wt.%	0.607	
Cu	Ka	230.44	22.476	40.524	wt.%	1.030	
			100.000	100.000	wt.%		Total

kV 15.0

Takeoff Angle 35.0°

Elapsed Livetime 30.0

Analysis Report: Image2-2

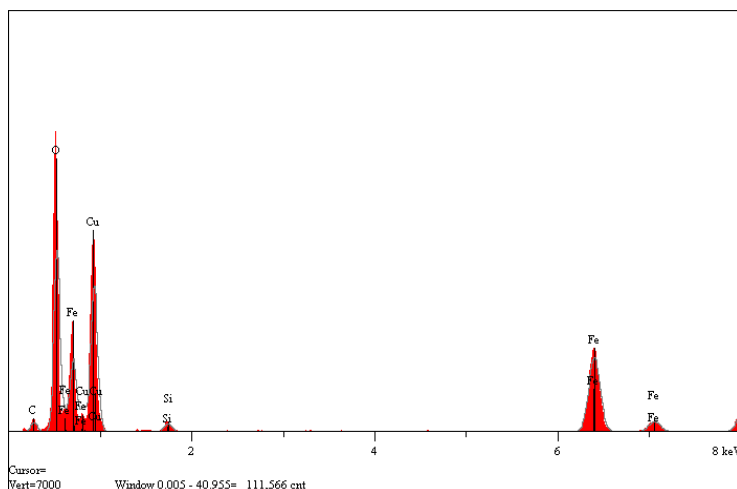
Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	Error 2-sig	
O	Ka	463.08	39.626	15.226	wt.%	0.274	
Fe	Ka	732.18	39.800	53.377	wt.%	0.745	
Cu	Ka	183.12	20.574	31.398	wt.%	0.917	
			100.000	100.000	wt.%		Total

kV 15.0

Takeoff Angle 35.0°

Elapsed Livetime 30.0

Analysis Report: Image2-3



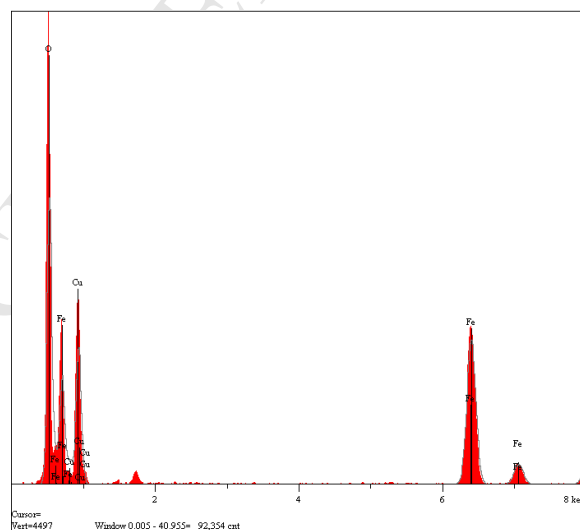
Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	Error 2-sig	
C	Ka	47.10	8.175	2.933	wt.%	0.276	
O	Ka	843.01	49.745	23.770	wt.%	0.316	
Si	Ka	47.66	1.106	0.928	wt.%	0.089	
Fe	Ka	643.08	23.439	39.093	wt.%	0.585	
Cu	Ka	230.81	17.534	33.277	wt.%	0.855	
			100.000	100.000	wt.%		Total

kV 15.0

Takeoff Angle 35.0°

Elapsed Livetime 30.0

Analysis Report: Image2-4

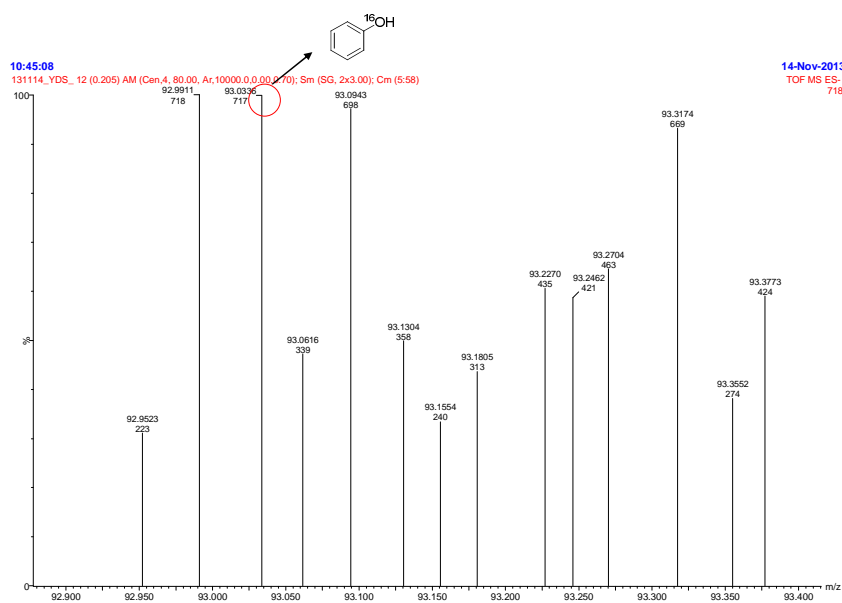
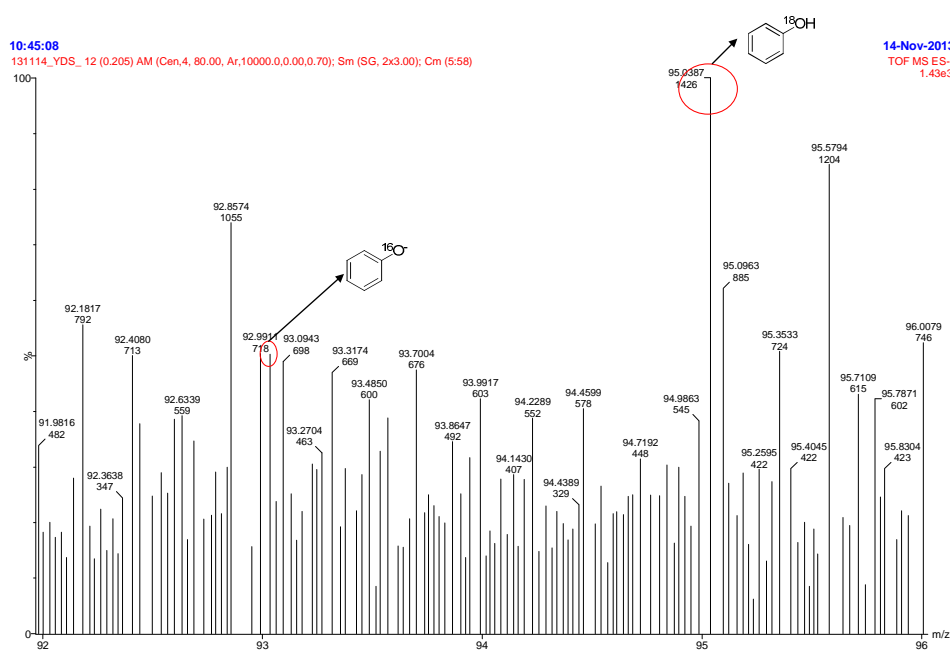


Elt.	Line	Intensity (c/s)	Atomic %	Conc	Units	Error 2-sig	
O	Ka	762.54	51.557	22.553	wt.%	0.315	
Fe	Ka	713.15	31.907	48.718	wt.%	0.689	
Cu	Ka	179.06	16.536	28.729	wt.%	0.846	
			100.000	100.000	wt.%		Total

kV 15.0

Takeoff Angle 35.0°

Elapsed Livetime 30.0

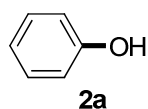
Fig. 3. EDX-analysis of CuFe_2O_4 catalyst**Fig. 4** Reactions of phenylboronic acid using H_2^{18}O as the solvent under the optimized reaction condition.

General experimental procedures

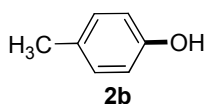
All reagents and solvents were obtained from commercial suppliers and used without further purification. Flash chromatography was performed on silica gel (200 ~ 300 mesh). ^1H , and ^{13}C NMR data were recorded at 400 and 100 MHz on a BRUKER 400 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) coupling constants (J) are in Hz. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl_3 as the internal standard (^1H NMR: TMS at 0.00 ppm, CDCl_3 at 7.28 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm).

General procedure for synthesis of substituted phenols:

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with CuFe_2O_4 nanoparticles (0.1 mmol, 24 mg), substituted substituted arylboronic acids (**1**) (1.0 mmol), NaOH (3.0 mmol, 120 mg), and H_2O (2.0 mL) was added to the tube under air atmosphere. The flask was not sealed in order that air could enter the flask, and the mixture was allowed to stir for 24 h under air at 40 °C. After completion of the reaction, the resulting solution was cooled to room temperature, HCl (2N, 1 mL) was added to acidify the solution (pH 5-7), and the target product was extracted with ethyl acetate (4-6 mL). The combined organic phase was dried over anhydrous MgSO_4 and filtered, and the solvent of the filtrate was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product (**2**).

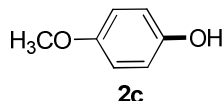


Phenol (2a):^[1] Eluent petroleum ether/ethyl acetate (5:1). Yield 95% (89 mg). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 7.21 (t, 2H, $J = 5.5\text{Hz}$), 6.93 (t, 1H, $J = 4.9\text{Hz}$), 6.83(d, 2H, $J = 5.1\text{Hz}$), 6.03(s, br, 1H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm) δ 155.3, 129.9, 121.1, 115.6. ESI-MS $[\text{M}-\text{H}]$ m/z 93.1.

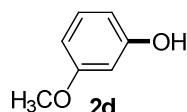


p-Cresol (2b):^[2] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ^1H NMR

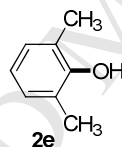
(CDCl₃, 400 MHz, ppm) 7.06 (d, 2H, $J = 7.9$ Hz), 6.78 (d, 2H, $J = 7.9$ Hz), 5.3 (s, br, 1H), 2.31 (s, 3H). ¹³C NMR (CDCl₃, 200 MHz, ppm) δ 153.3, 130.1, 130.0, 115.2, 20.5. ESI-MS [M-H]⁻m/z 107.6



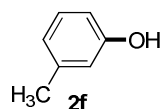
4-methoxyphenol (2c):^[3] Eluent petroleum ether/ethyl acetate (5:1). White solid. ¹H NMR (CDCl₃, 400 MHz, ppm) 6.83-6.78(m, 4H), 4.5(s, br, 1H), 3.8(s, 3H). ¹³C NMR (CDCl₃, 200 MHz, ppm) δ 153.8, 149.5, 55.6. ESI-MS [M-H]⁻m/z 123.4.



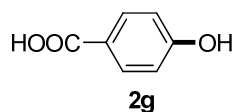
3-methoxyphenol (2d):^[3] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.16(d, 1H, $J = 8.0$ Hz), 6.52(d, 1H, $J = 7.6$ Hz), 6.45(d, 1H, $J = 8.0$ Hz), 3.8(s, 3H). ¹³C NMR (CDCl₃, 200 MHz, ppm) δ 161.0, 156.8, 130.2, 107.8, 106.4, 101.6, 55.3. ESI-MS [M-H]⁻m/z 123.7.



2,6-dimethylphenol (2e):^[4] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.07(d, 2H, $J = 8.0$ Hz), 6.86(t, 1H, $J = 7.6$ Hz), 4.48(s, br, 1H), 2.33(s, 6H). ¹³C NMR (CDCl₃, 200MHz, ppm) δ 152.1, 128.5, 123.0, 120.2,15.8. ESI-MS [M-H]⁻m/z 121.7.

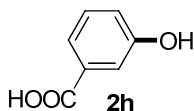


m-cresol (2f):^[4] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.15(t, 1H, $J = 7.9$ Hz), 6.77(s, 1H, $J = 7.9$ Hz), 6.67(d, 1H, $J = 8.0$ Hz), 2.33(s, 3H). ¹³C NMR (CDCl₃, 200 MHz, ppm) δ 155.5, 139.8.8, 129.4, 121.6, 116.0, 112.2, 21.3. ESI-MS [M-H]⁻m/z 107.5.

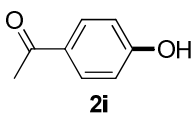


4-hydroxybenzoic acid (2g):^[5] Eluent petroleum ether/ethyl acetate (3:1). White

solid.. ^1H NMR (DMSO- d_6 , 400 MHz, ppm) 12.37(s, br, 1H), 10.17 (s, br, 1H), 7.78(d, 1H, $J = 8.8$ Hz), 6.81(d, 1H, $J = 8.8$ Hz). ^{13}C NMR (DMSO- d_6 , 200 MHz, ppm) δ 167.6, 162.0, 121.8, 115.5, . ESI-MS $[\text{M-H}]^-$ m/z 137.2.



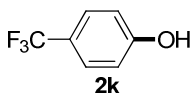
3-hydroxybenzoic acid (2h): ^[6] Eluent petroleum ether/ethyl acetate (3:1). White solid. ^1H NMR (DMSO- d_6 , 400 MHz, ppm) 12.72(s, br, 1H), 9.68 (s, br, 1H), 7.38-7.33(m, 2H), 6.70(s, 1H). ^{13}C NMR (DMSO- d_6 , 200 MHz, ppm) δ 167.8, 157.8, 132.5, 129.9, 120.3, 116.3,. ESI-MS $[\text{M-H}]^-$ m/z 137.2.



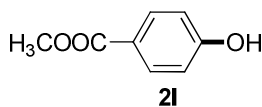
1-(4-hydroxyphenyl)ethanone (2i): ^[4] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 8.57(s, br, 1H), 7.93(d, 2H, $J = 8.0$ Hz), 6.98(d, 1H, $J = 8.0$ Hz), 2.61(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 199.2, 161.8, 131.3, 129.3, 115.7, 26.3. ESI-MS $[\text{M-H}]^-$ m/z 135.4.



3-chlorophenol (2j): ^[7] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.17(m, 1H), 6.90(m, 2H), 6.76(d, 1H, $J = 8.0$ Hz), 6.03(s, br, 1H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 172.7, 156.5, 134.9, 130.5, 120.9, 116.0, 113.8. ESI-MS $[\text{M-H}]^-$ m/z 127.4.

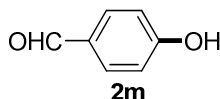


4-(trifluoromethyl)phenol (2k): ^[8] Eluent petroleum ether/ethyl acetate (5:1). Yellow oil. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.54(d, 1H, $J = 8.0$ Hz), 6.94(d, 1H, $J = 8.0$ Hz), 5.63(s, br, 1H). ^{13}C NMR (CDCl_3 , 200MHz, ppm) δ 157.8, 127.3, 123.9(q, $^1J = 360.0$ Hz), 123.0(q, $^1J = 48.0$ Hz), 115.4. $[\text{M-H}]^-$ m/z 161.4.

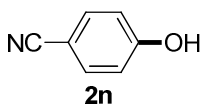


methyl 4-hydroxybenzoate (2l): ^[9] Eluent petroleum ether/ethyl acetate (5:1). White

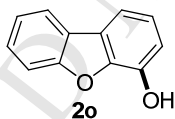
solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.99(d, 1H, $J = 8.0\text{Hz}$), 6.90(d, 1H, $J = 8.0\text{Hz}$), 6.05(s, br, 1H), 3.92(s, 3H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 167.3, 160.1, 132.0, 122.5, 115.3, 52.1. ESI-MS $[\text{M-H}]^-$ m/z 151.4.



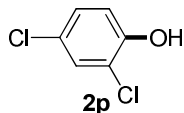
4-hydroxybenzaldehyde (2m): ^[10] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 9.88(s, 1H), 7.83(d, 2H, $J = 8.0\text{Hz}$), 7.00 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 191.1, 161.9, 132.5, 129.7, 116.0. ESI-MS $[\text{M-H}]^-$ m/z 121.3.



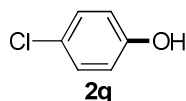
4-hydroxybenzonitrile (2n): ^[11] Eluent petroleum ether/ethyl acetate (15:1). Yellow solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.57(d, 2H, $J = 8.0\text{Hz}$), 6.93(d, 2H, $J = 8.0\text{Hz}$), 7.00 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 160.0, 134.3, 119.5, 116.4. ESI-MS $[\text{M-H}]^-$ m/z 118.3.



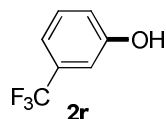
dibenzo[b,d]furan-4-ol (2o): ^[12] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.95(d, 2H, $J = 7.2\text{ Hz}$), 7.60(d, 2H, $J = 8.0\text{Hz}$), 7.56-7.47(m, 2H), 7.40(t, 1H, $J = 8.0\text{Hz}$), 7.28(t, 1H, $J = 8.0\text{Hz}$), 7.05(d, 1H, $J = 8.0\text{Hz}$), 5.53(s, br, 1H). ^{13}C NMR (CDCl_3 , 200 MHz, ppm) δ 156.1, 144.1, 141.2, 127.3, 125.8, 124.6, 123.7, 123.0, 121.0, 113.6, 112.8, 111.8. ESI-MS $[\text{M-H}]^-$ m/z 183.3.



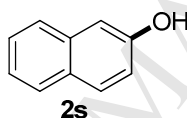
2,4-dichlorophenol (2p): ^[13] Eluent petroleum ether/ethyl acetate (15:1). White solid. ^1H NMR (CDCl_3 , 400 MHz, ppm) 7.33(d, 2H, $J = 2.4\text{Hz}$), 7.18(d, 2H, $J = 8.0\text{Hz}$), 6.97(d, 1H, $J = 8.0\text{Hz}$), 5.57(s, br, 1H). ^{13}C NMR (CDCl_3 , 200MHz, ppm) δ 150.2, 128.6, 128.5, 125.6, 120.4, 117.1,. ESI-MS $[\text{M-H}]^-$ m/z 160.8.



4-chlorophenol (2q): ^[14] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.21(d, 2H, *J* = 8.0Hz), 6.80 (d, 2H, *J* = 8.0Hz), 5.60(s, br, 1H). ¹³C NMR (CDCl₃, 200MHz, ppm) δ 154.2, 129.5, 125.6, 116.7. ESI-MS [M-H]⁻m/z 127.3.



3-(trifluoromethyl)phenol (2r): ^[15] Eluent petroleum ether/ethyl acetate (15:1). Yellow oil. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.36(d, 2H, *J* = 8.0Hz), 7.20 (d, 2H, *J* = 8.0Hz), 7.12(s, 1H), 7.04(d, 2H, *J* = 8.0Hz), 6.0(s, br, 1H). ¹³C NMR (CDCl₃, 200MHz, ppm) δ 156.0, 131.2(q, ²*J* = 64.0Hz), 130.2, 123.6(q, ¹*J* = 542.0Hz), 118.0, 117.0, 112.3. ESI-MS [M-H]⁻m/z 161.3.



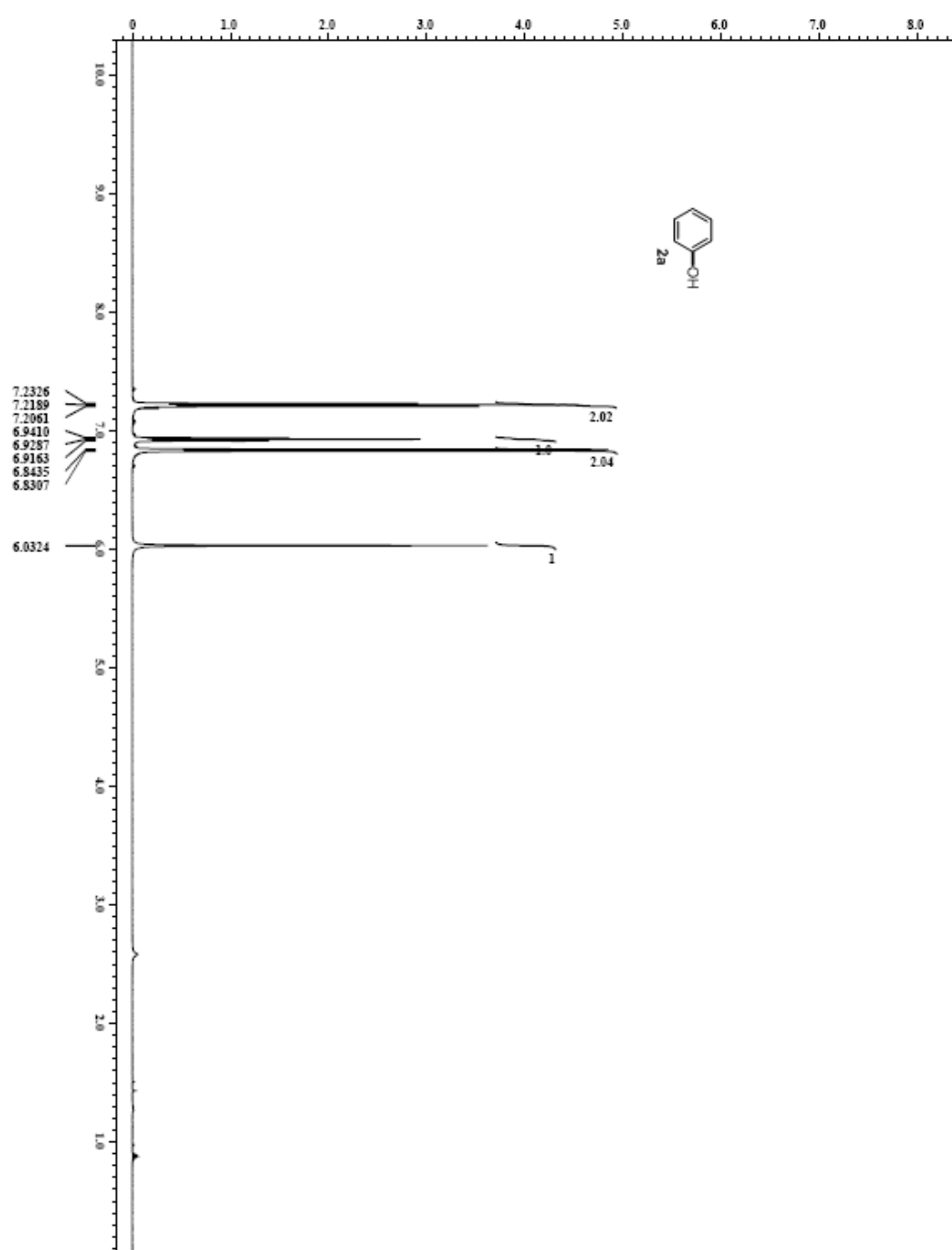
naphthalen-2-ol (2s): ^[12] Eluent petroleum ether/ethyl acetate (15:1). White solid. ¹H NMR (CDCl₃, 400 MHz, ppm) 7.82-7.78(m, 2H), 7.11 (d, 2H, *J* = 8.0Hz), 7.49-7.45(m, 1H), 7.39-7.35(m, 1H), 7.18-7.13(m, 2H), 5.11(s, br, 1H). ¹³C NMR (CDCl₃, 200MHz, ppm) δ 153.2, 134.6, 129.9, 129.0, 127.8, 126.6, 126.4, 123.7, 117.4, 109.6. ESI-MS [M-H]⁻m/z 143.3.

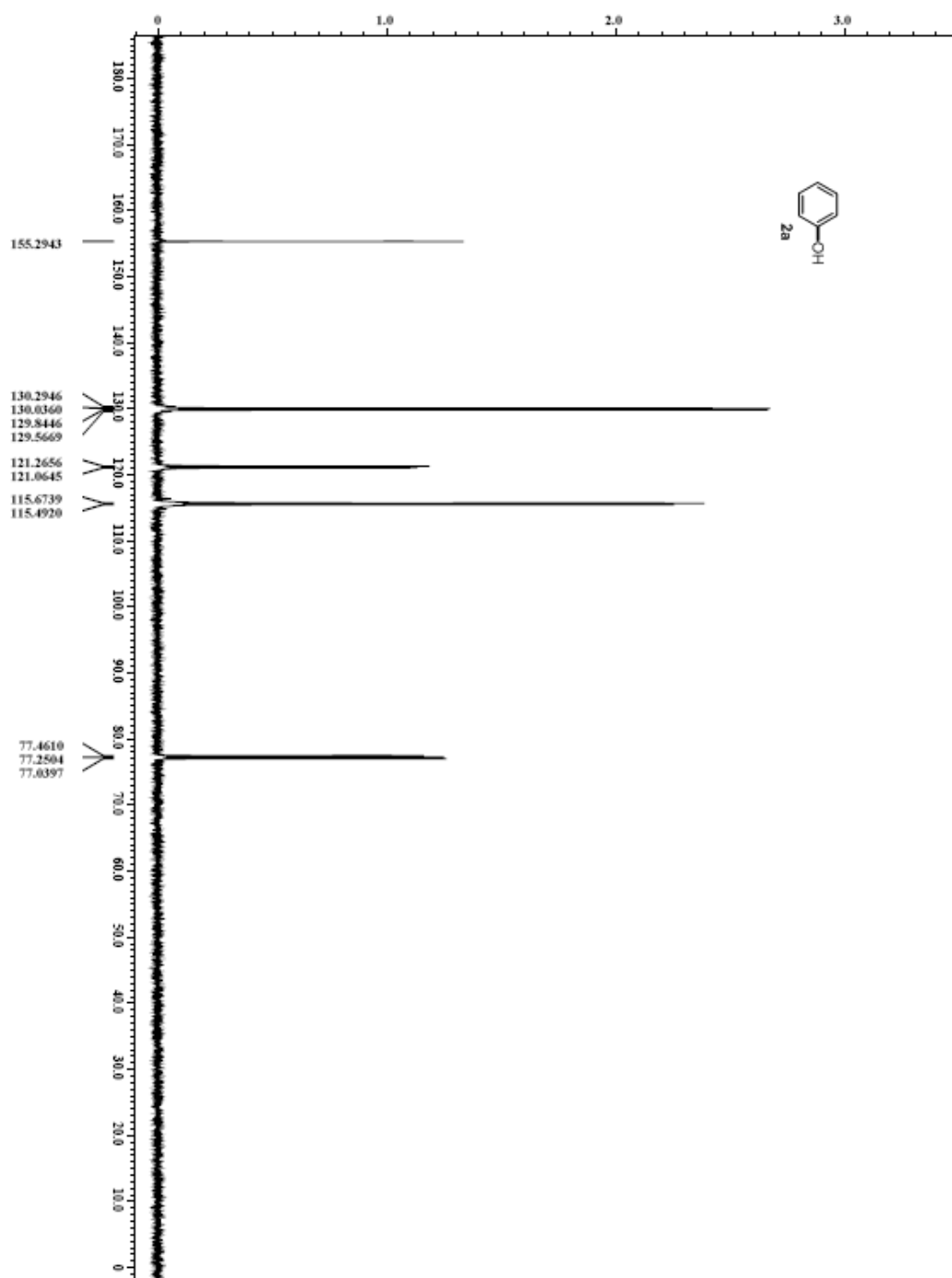
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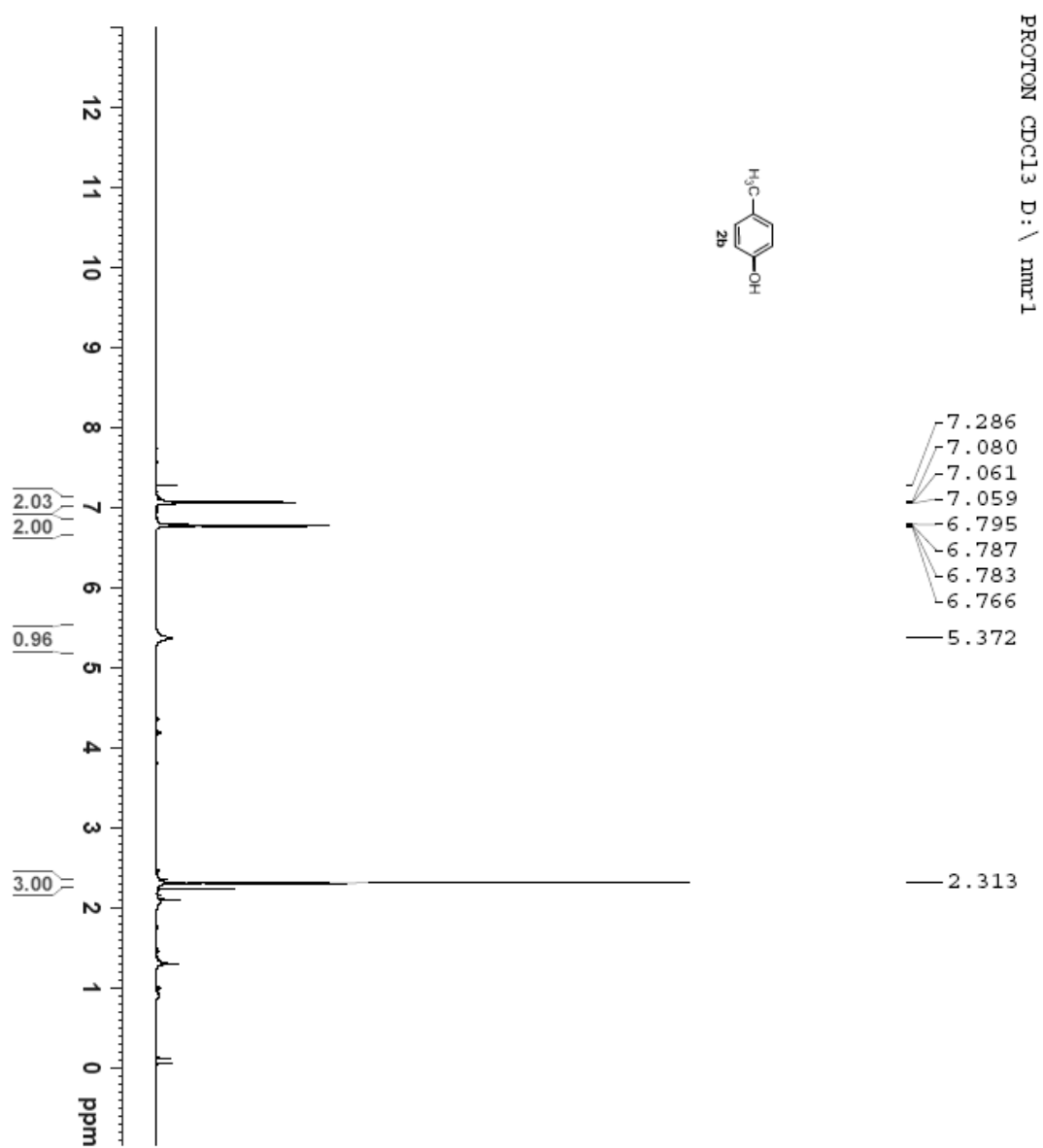
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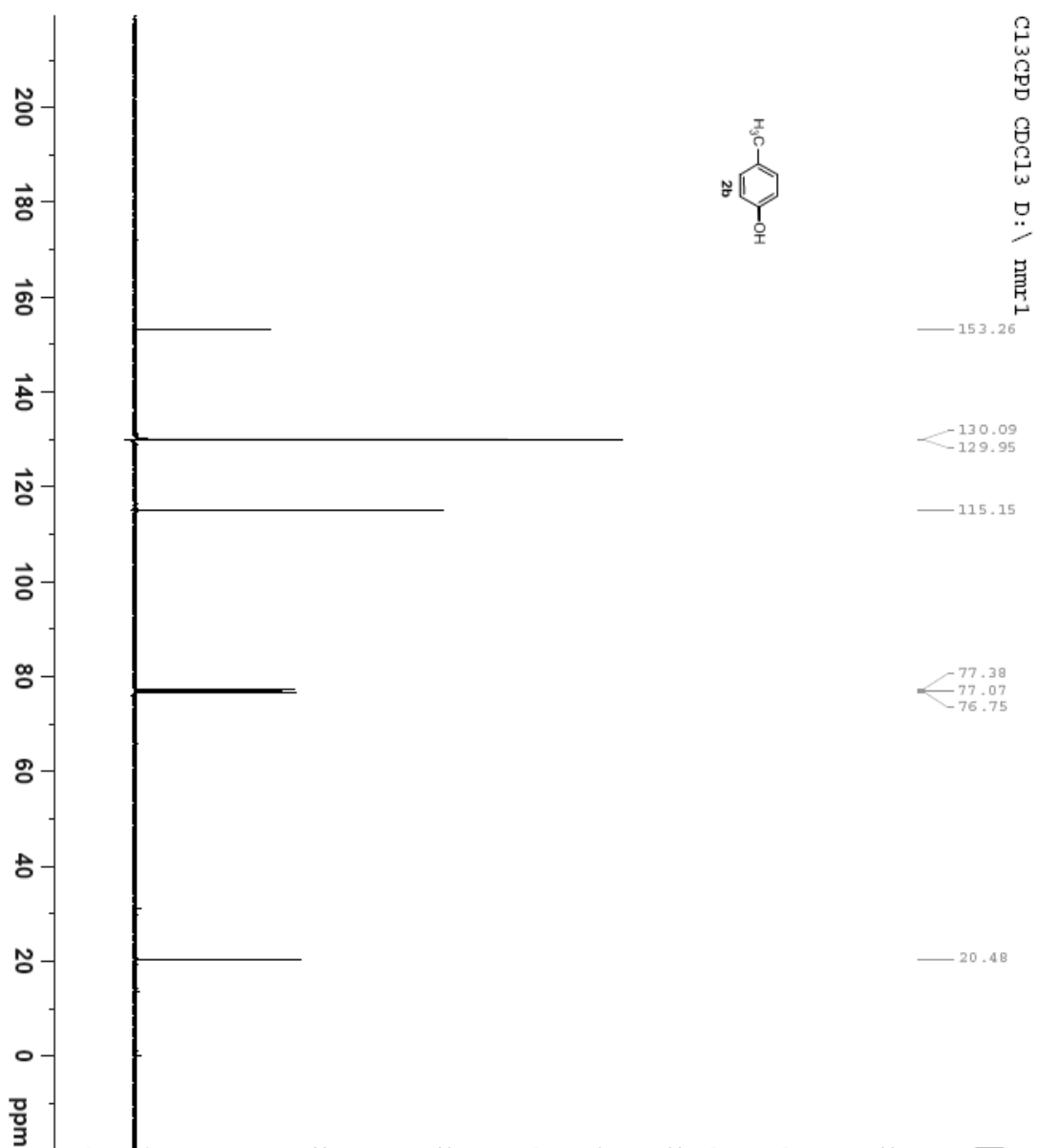
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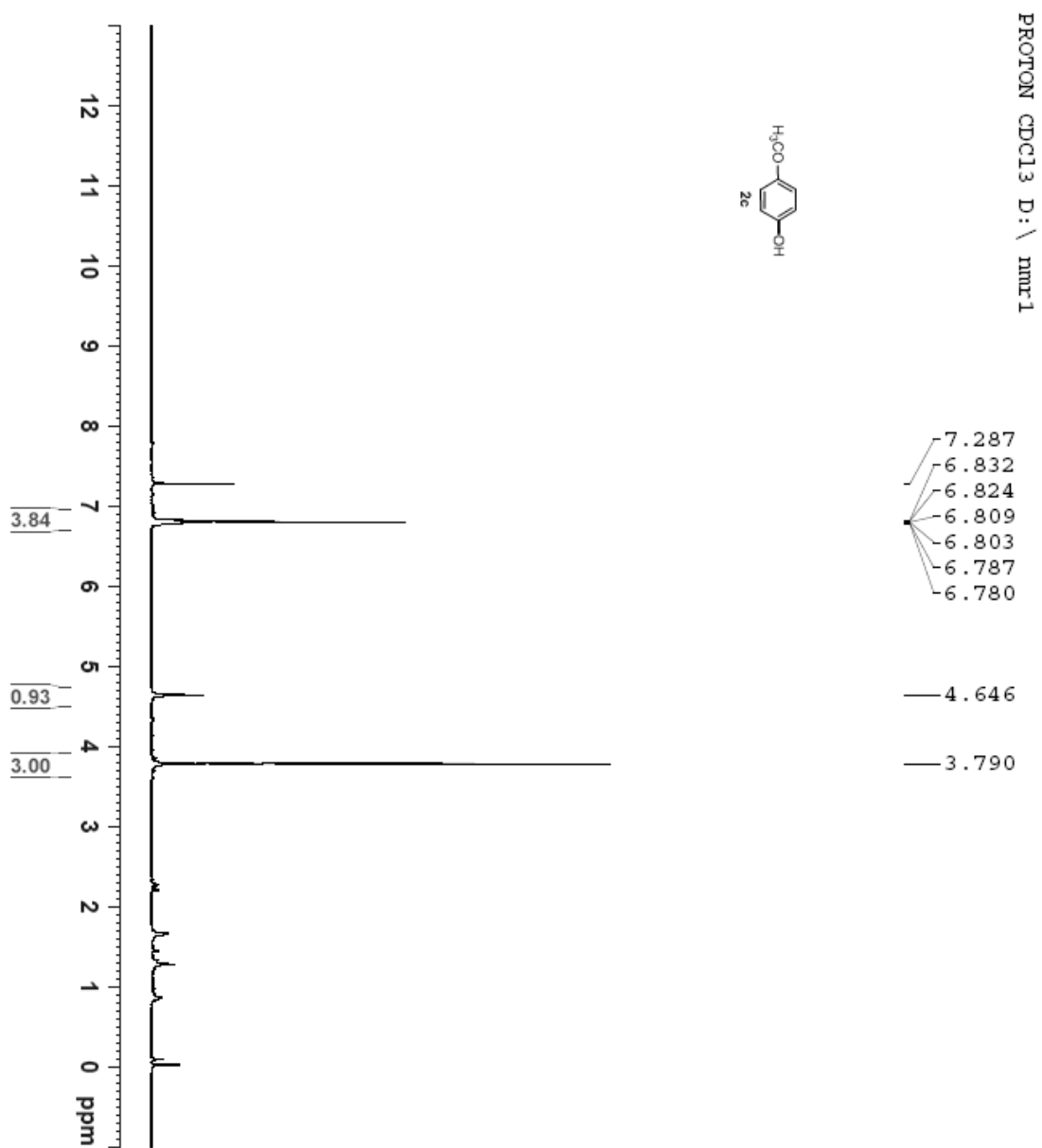
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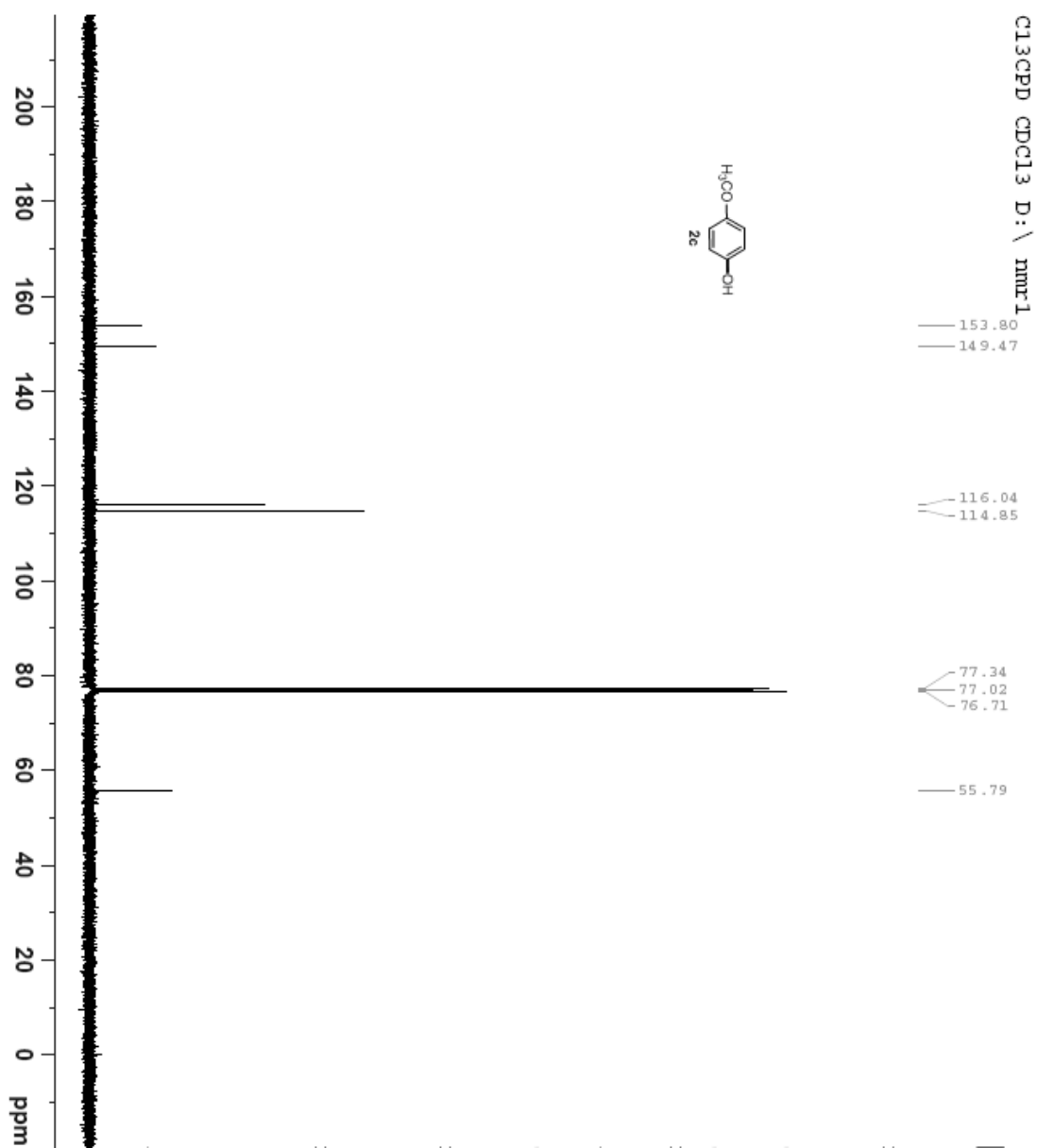


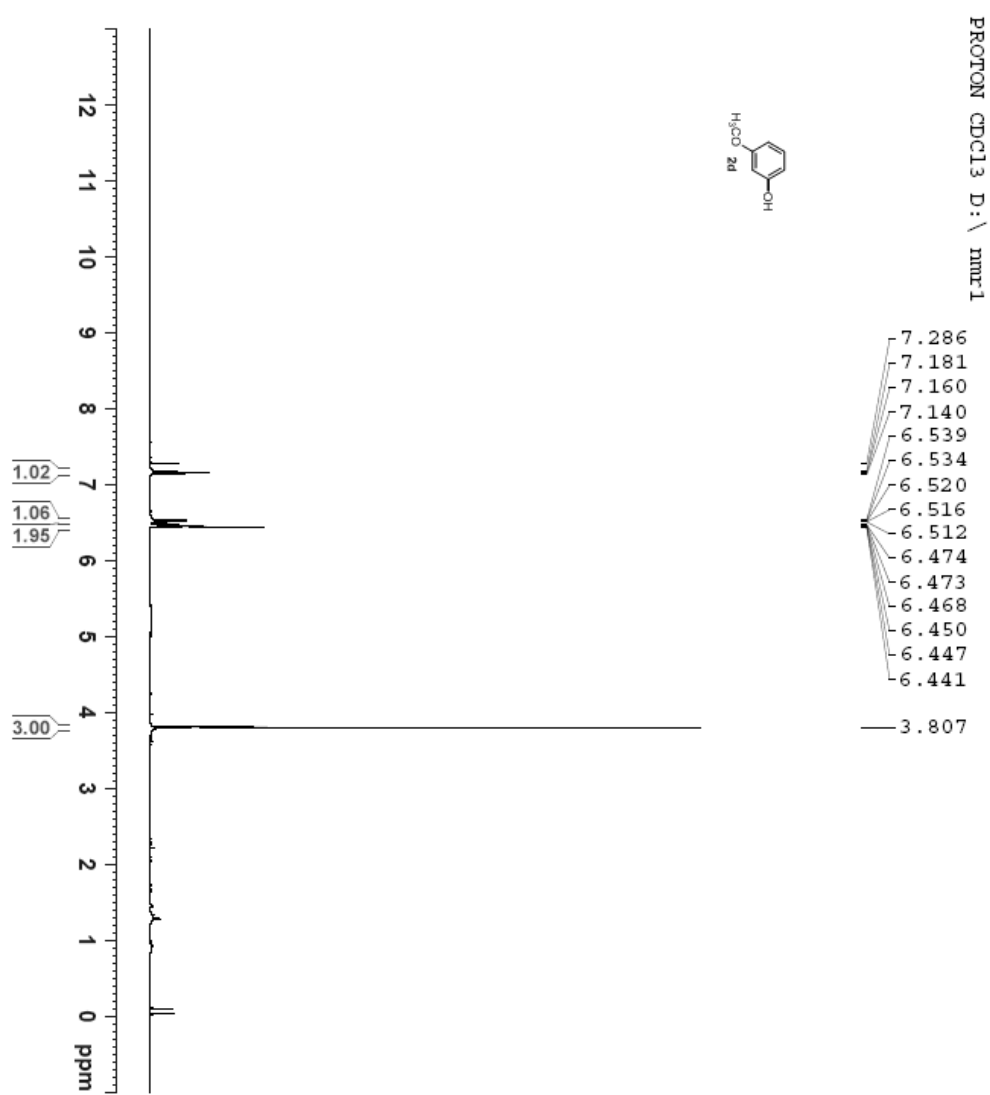


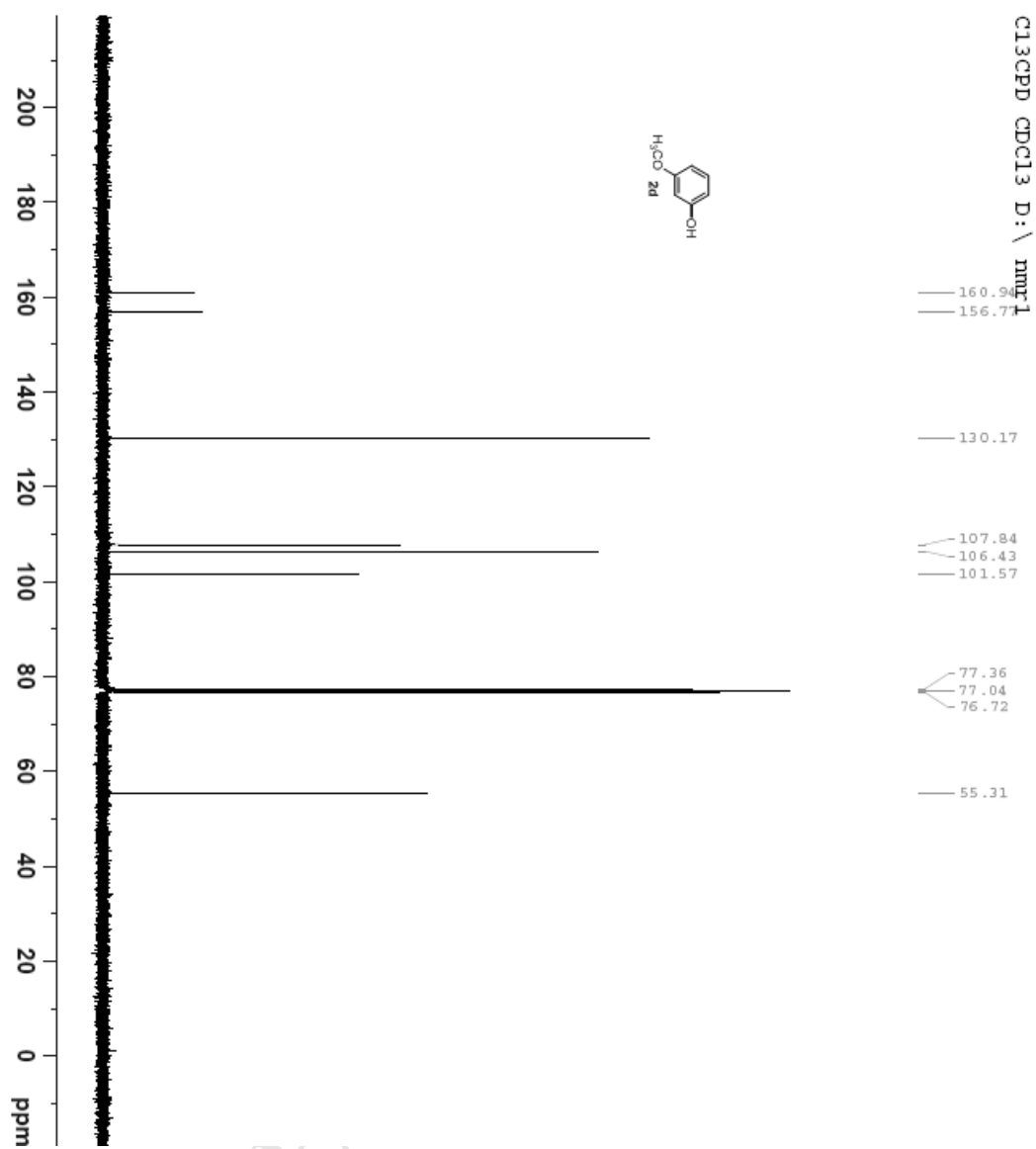


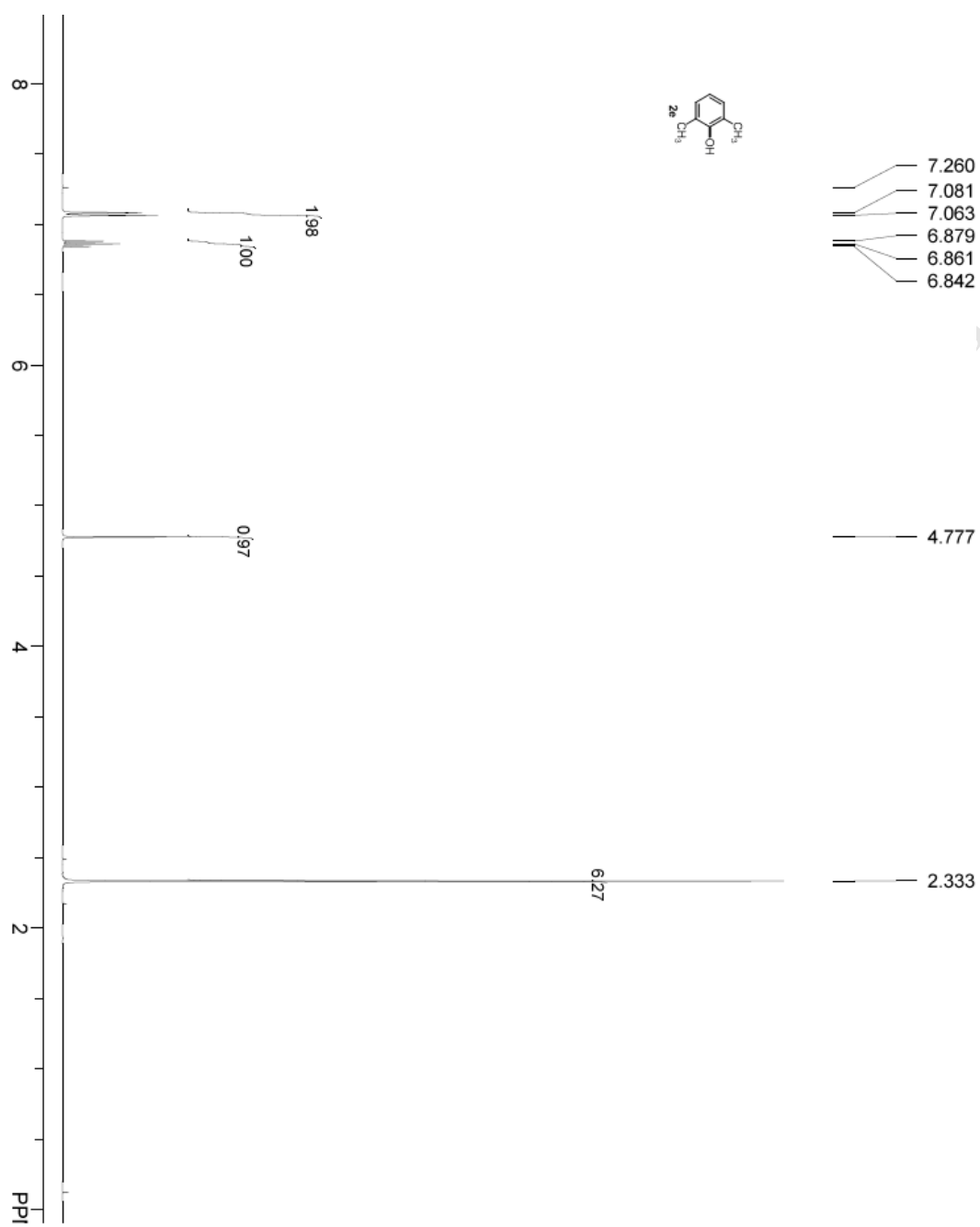


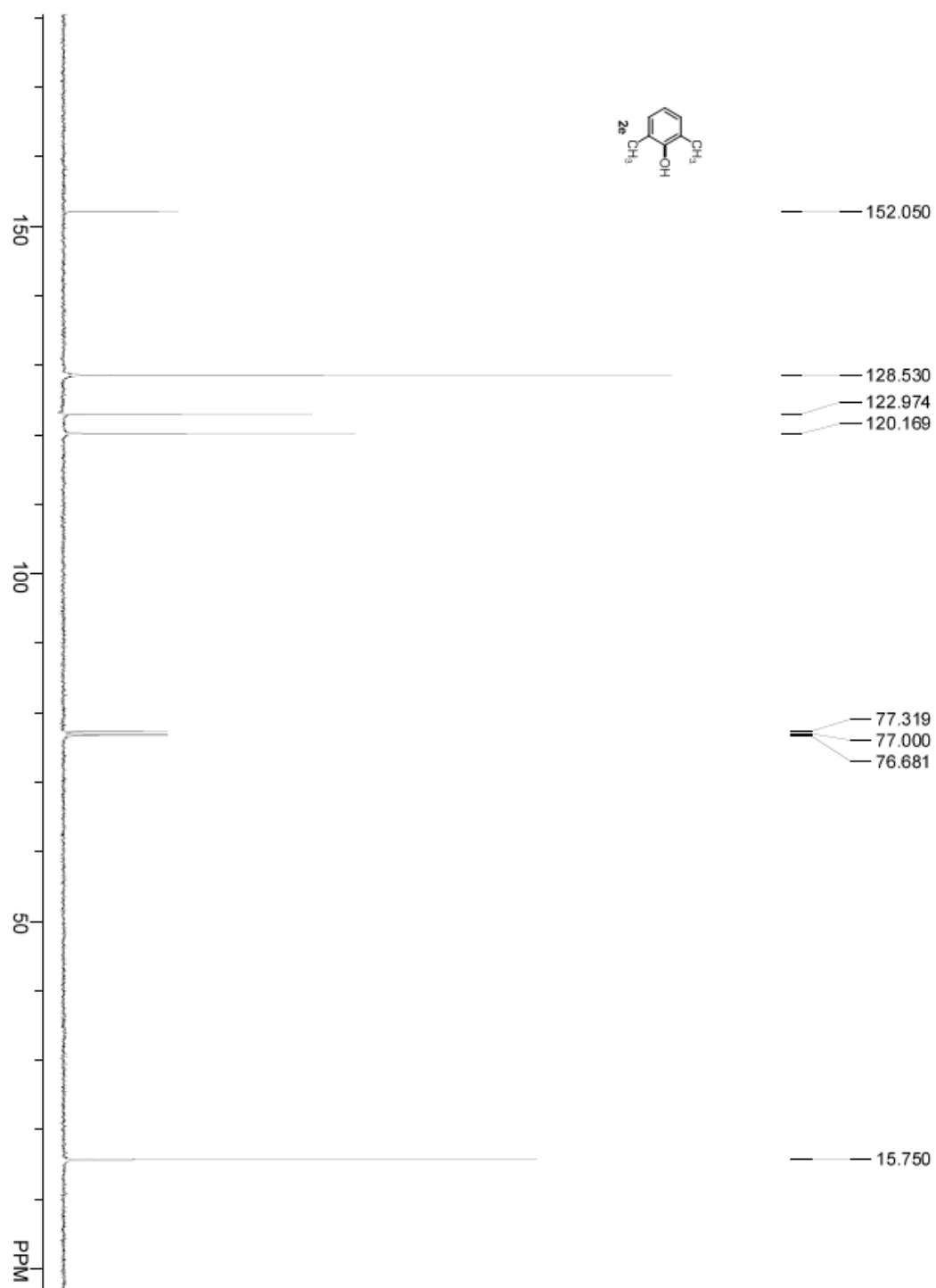


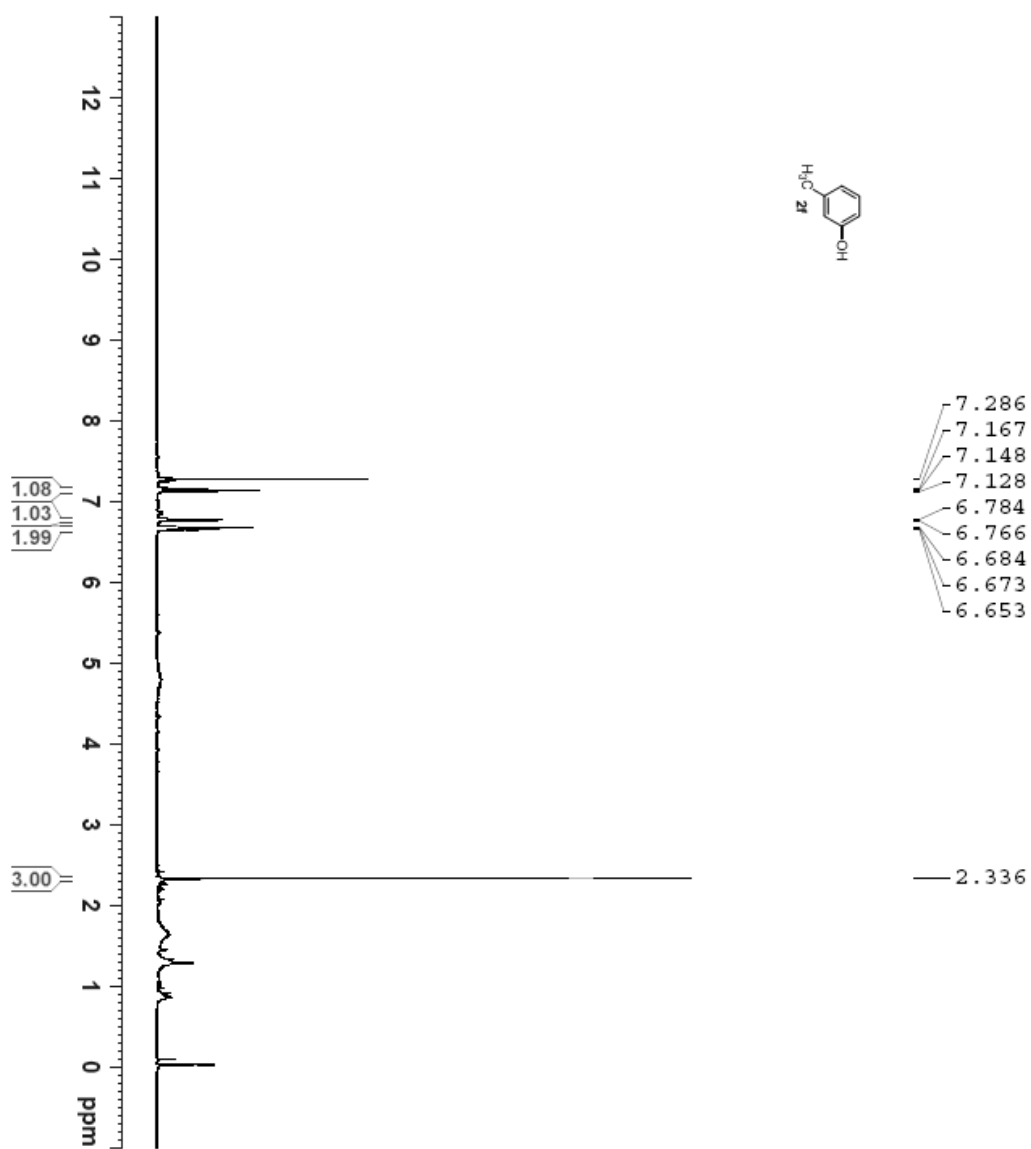


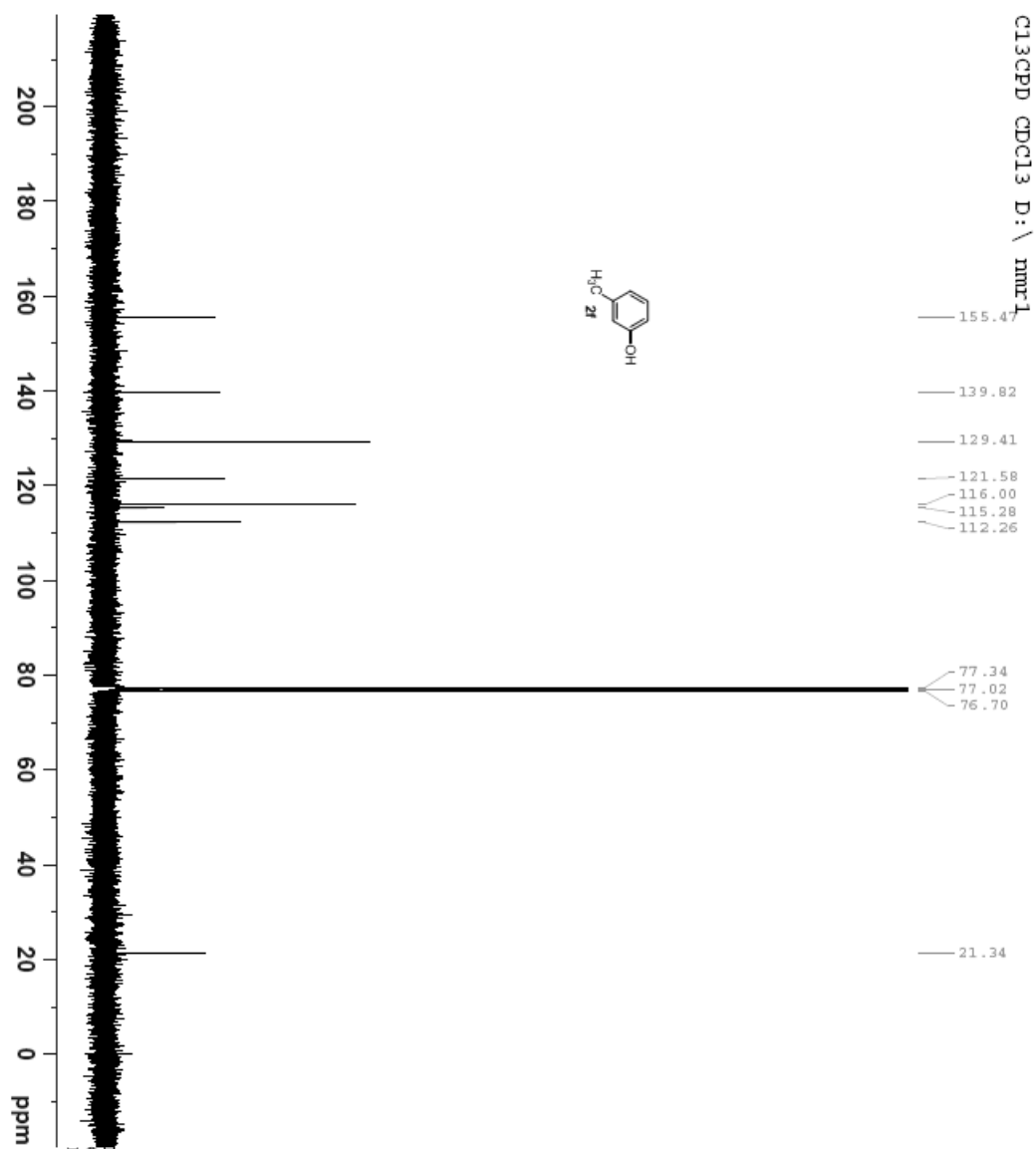


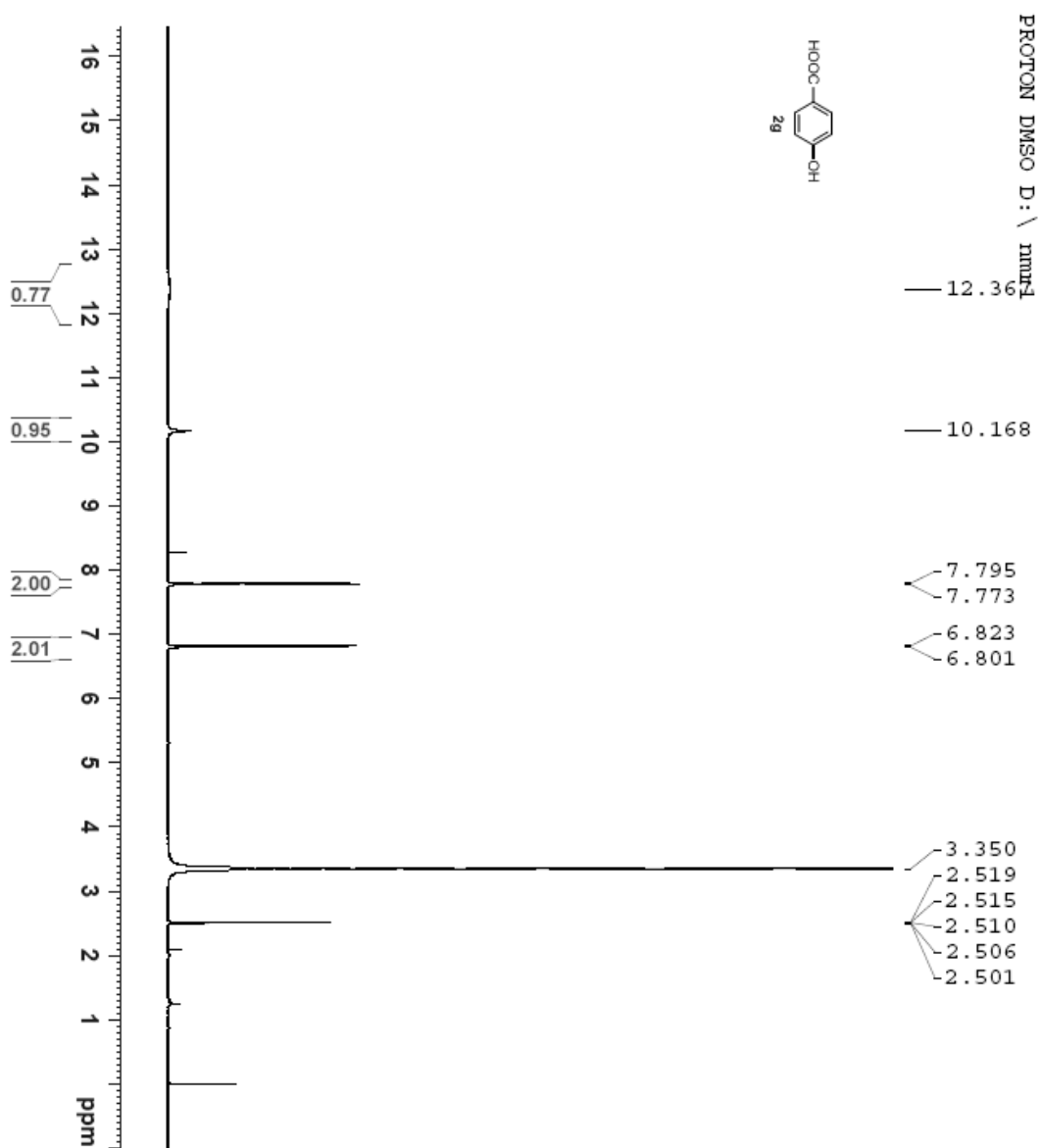


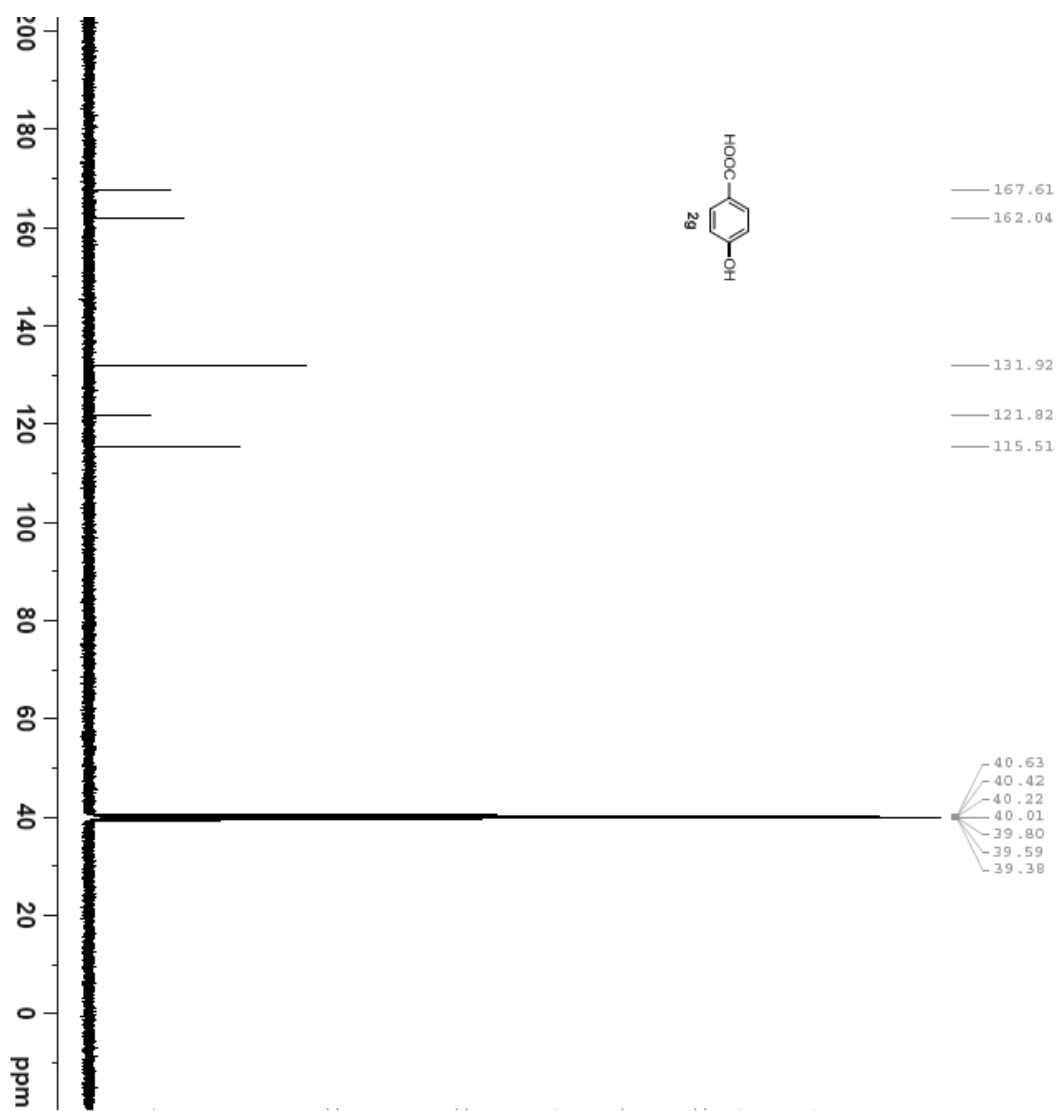


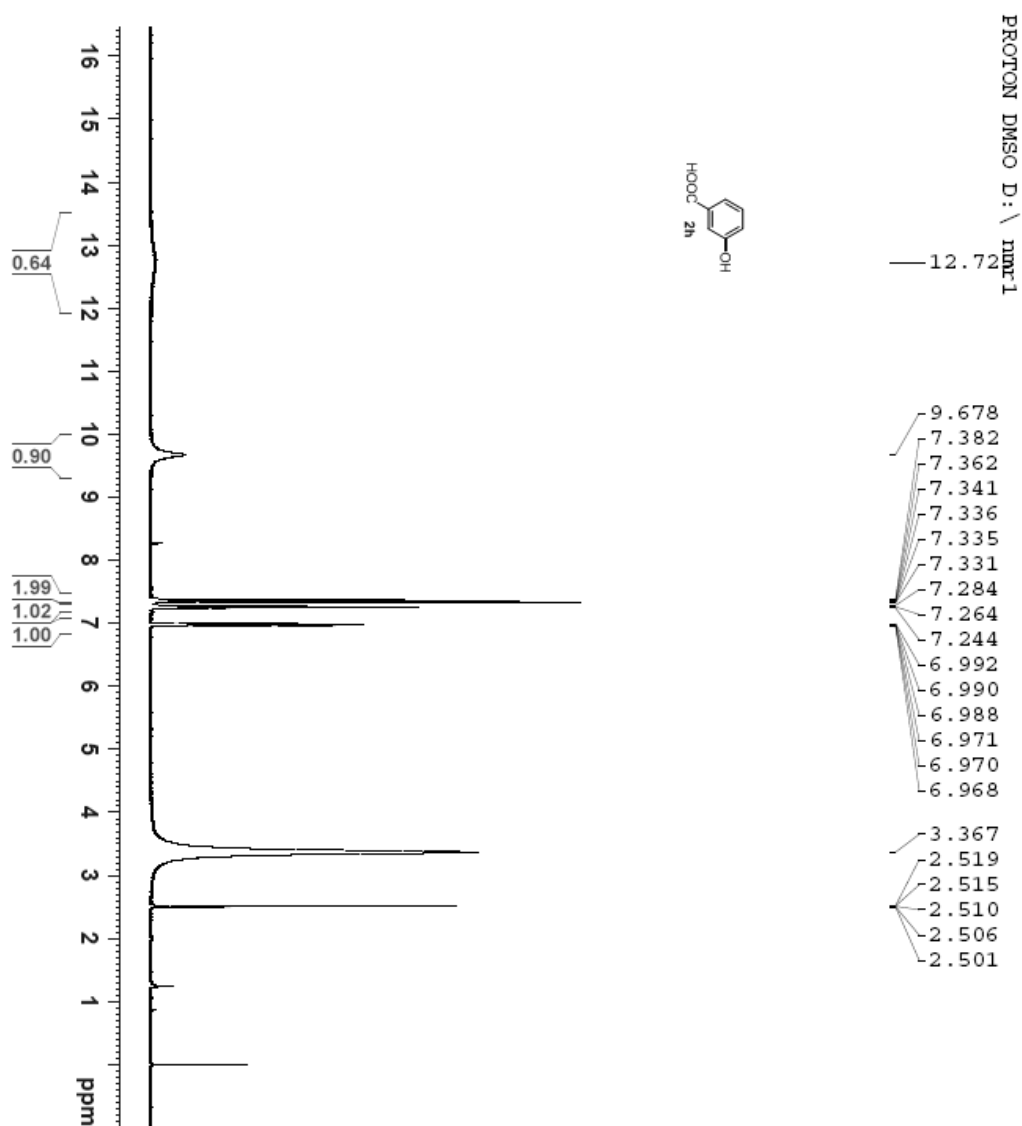




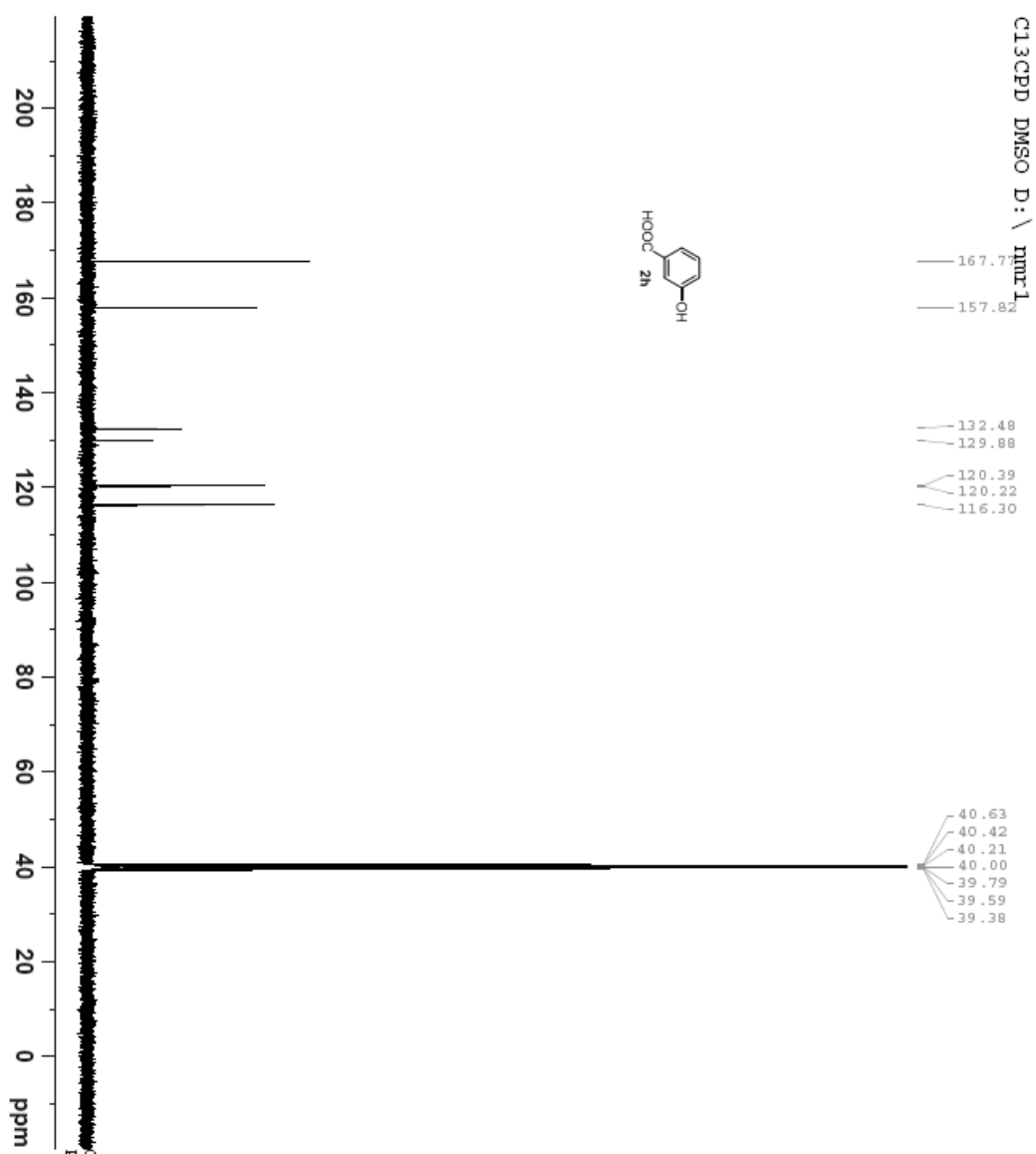


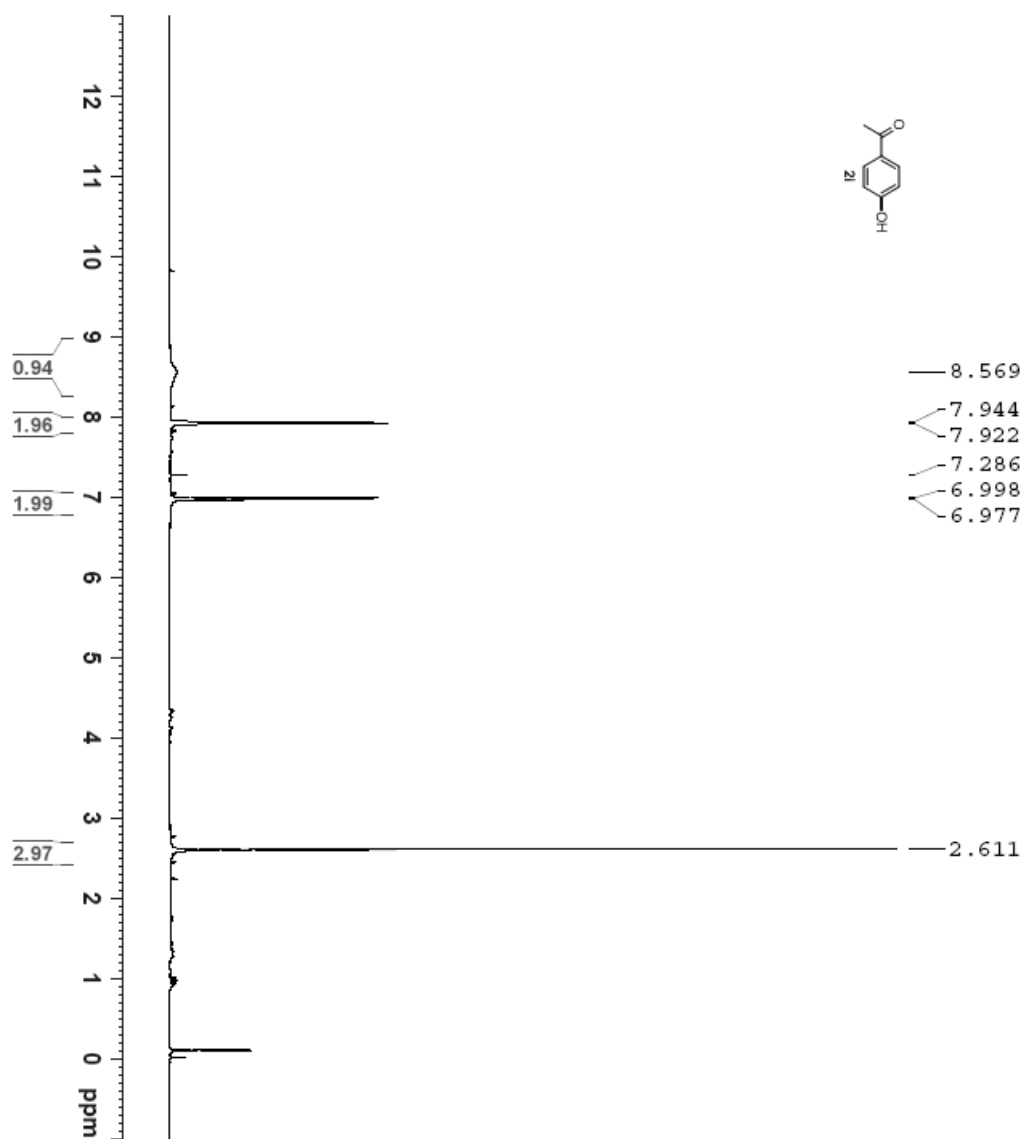


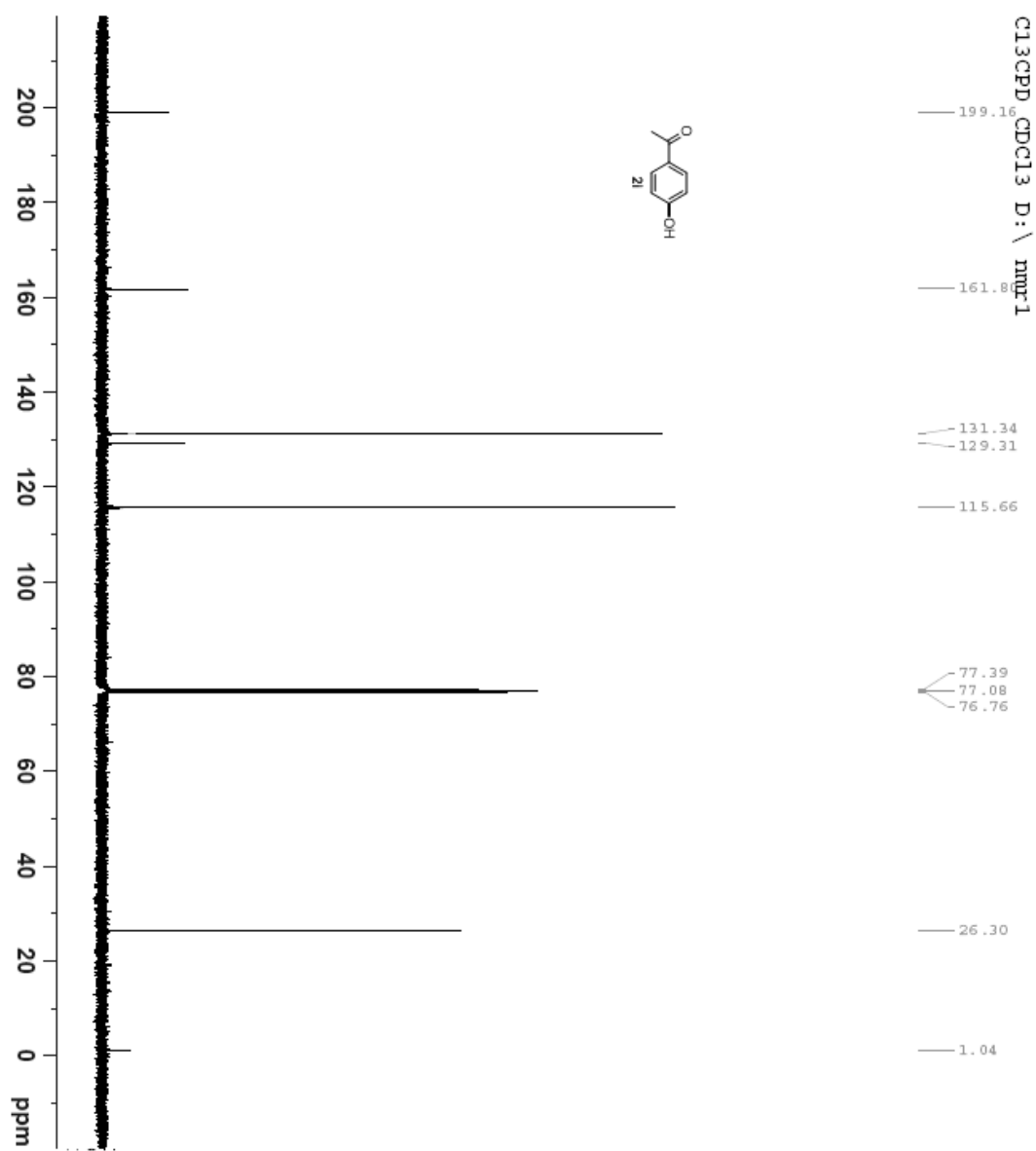


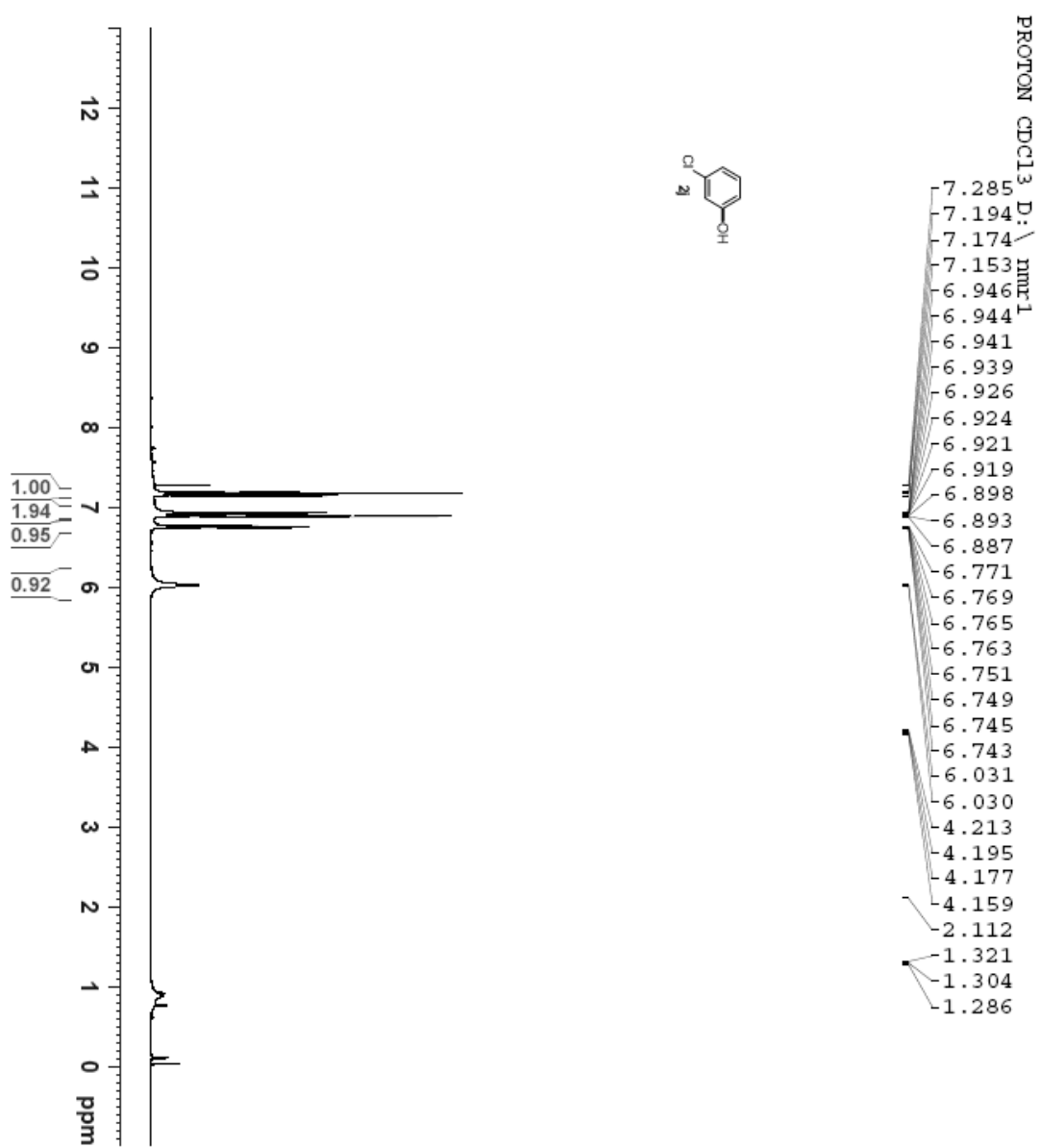


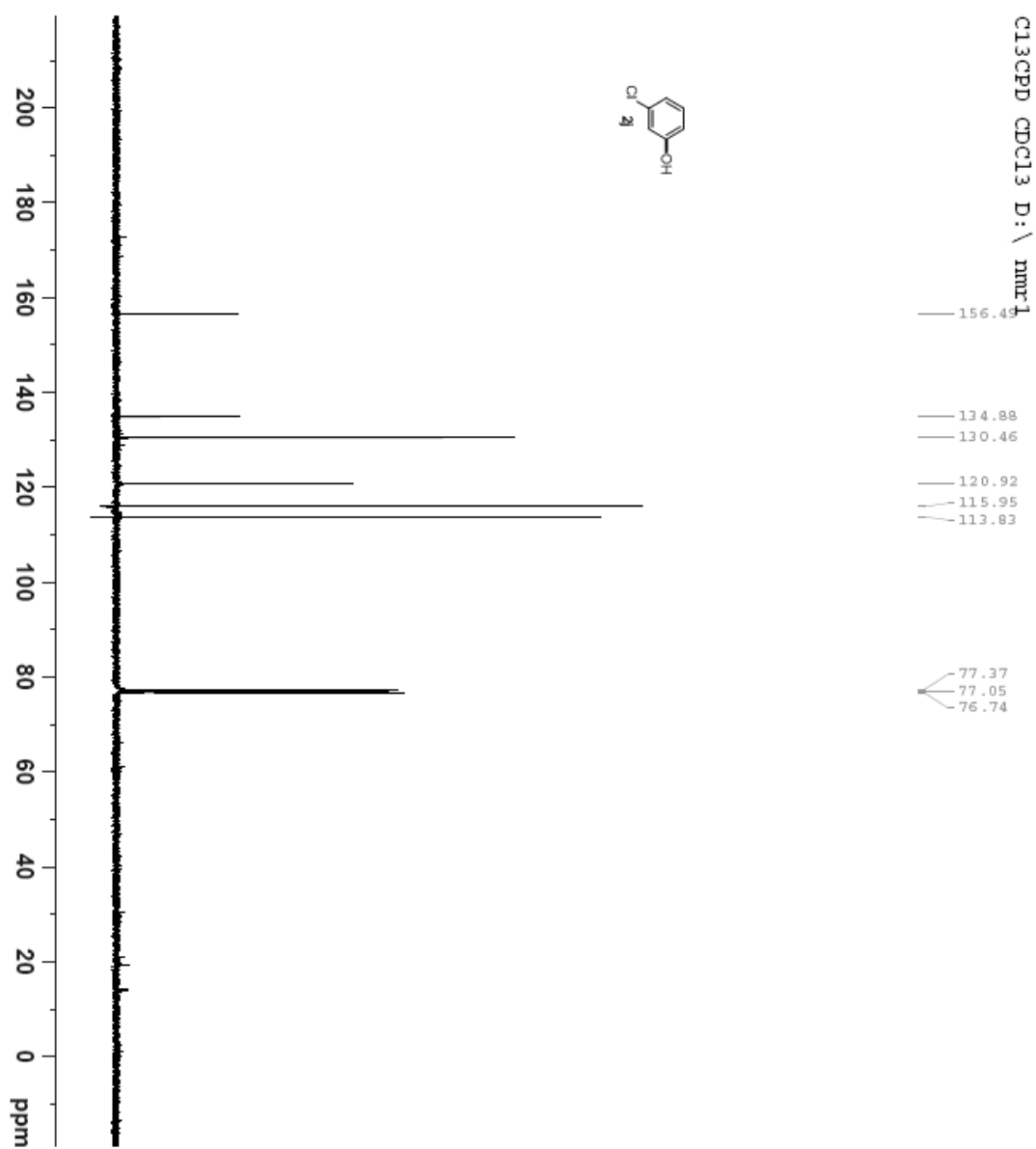
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