Electronic Supplementary Material (ESI) for Organic .

Electronic Supplementary Information for

Biomimetic aerobic oxidative hydroxylation of arylboronic acids to phenols catalysed by a flavin derivative

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Content:

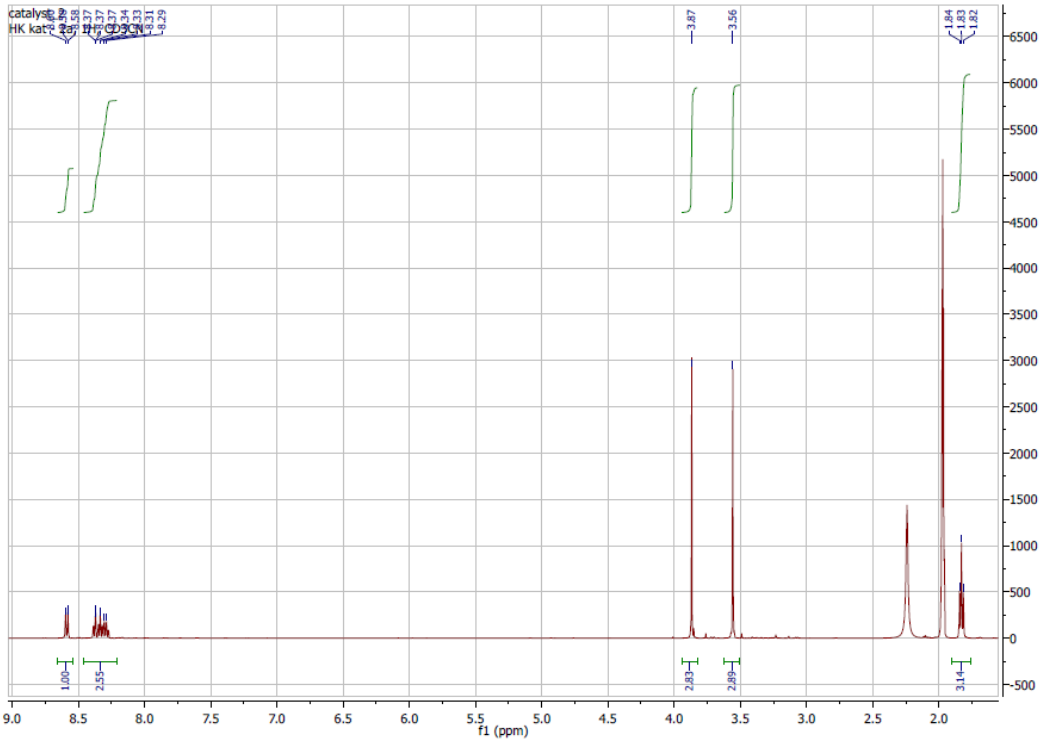
S1 Synthesis and characterization of catalyst 2

5-Ethyl-1,3-dimethylalloxazinium perchlorate (2)

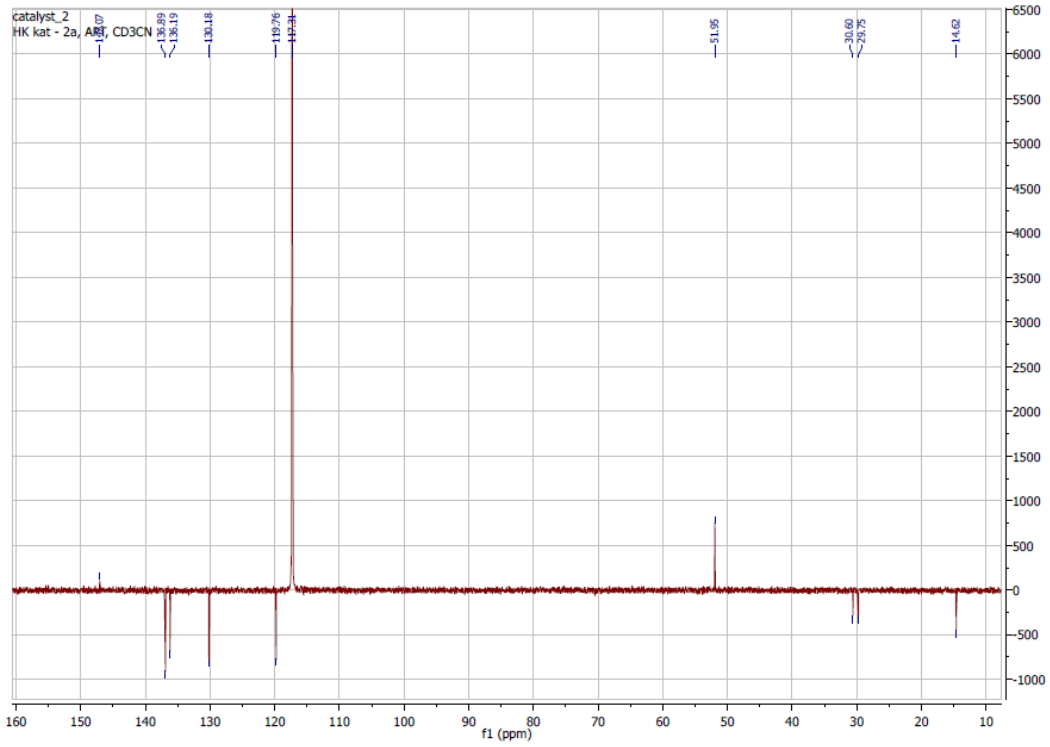
Acetaldehyde (1.55 mL, 27.8 mmol) and palladium on carbon (10%, 88.8 mg) were added to a suspension of 1,3-dimethylalloxazine (223 mg, 0.92 mmol) in acetic acid (15.5 mL) and water (1.55 mL). The resulting mixture was stirred for 56 hours in an autoclave under hydrogen atmosphere (0.6 MPa) at room temperature. The catalyst was removed by filtration, the solvents were evaporated under reduced pressure, and the remaining solid was dried in vacuo. The residue was suspended in perchloric acid (2M, 10.0 mL) and cooled to 0 °C. Then, sodium nitrite (510 mg, 7.39 mmol) was added and the mixture was stirred at room temperature. After 1.5 hour sodium perchlorate (1.332 g, 10.88 mmol) was added and stirred for 30 minutes. The precipitated solid was collected by filtration, washed with 2M perchloric acid and dried in vacuo to give **2** as dark orange powder (160 mg, 64 %). M.p. 226-229 °C.

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 1.83 (t, J = 7.2 Hz, 3H, $N^{+}CH_2CH_3$), 3.56 (s, 3H, 3-NCH_3), 3.87 (s, 3H, 1-NCH_3), 8.41 – 8.26 (m, 3H, ArH), 8.59 (d, J = 8.9 Hz, 1H, 6-ArH) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ 14.6 ($N^{+}CH_2CH_3$), 29.8 (3-NCH_3), 30.6 (1-NCH_3) 51.9 ($N^{+}CH_2CH_3$), 119.8 (CH), 130.2 (CH) 136.2 (CH), 136.9 (CH), 147.1 (C_{ar}), 147.7 (C_{Ar}) 148.8 (2-CO) 155.38 (4-CO) ppm. $C_{14}H_{15}ClN_4O_6 \cdot H_2O$ (388.77): calcd. C 43.25, H 4.41, N 14.41, Cl 9.12; found C 43.52, H 4.19, N 14.34, Cl 9.27. HRMS (ESI): calcd. for $C_{14}H_{15}N_4O_2$ $[M]^{+}$ 271.11895; found 271.11880.

^{1}H NMR of catalyst **2**



^{13}C NMR of catalyst **2**



S2 Synthesis and characterization of phenols 4 and 5 and alcohols 7

Phenol (4a) was prepared according to general procedure B (see main text), reaction time 1h, mobile phase hexane – ethyl acetate (5 : 1), yield (70 mg, 94 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.85 – 6.68 (m, 3H), 7.23 – 7.08 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 116.12, , 120.76, 130.52, 157.83 ppm.
HRMS (ESI): calcd. for C_6H_6O $[M - H]^-$ 93.03459; found 93.03429.

2-Naphtol (4b) was prepared according to general procedure B (see main text), reaction time 1h, mobile phase hexane – ethyl acetate (5 : 1), yield (112 mg, 99 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 7.13 – 6.99 (m, 2H), 7.23 (ddd, J = 8.1, 6.8, 1.3 Hz, 1H), 7.40 – 7.29 (m, 1H), 7.65 – 7.58 (m, 1H), 7.77 – 7.65 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 109.85, 119.06, 124.10, 127.10, 127.31, 128.55, 129.47, 130.47, 130.48, 135.83 ppm.
HRMS (ESI): calcd. for $C_{10}H_8O$ $[M - H]^-$143.05024; found 143.05046.

2,6-Dimethylphenol (4c) was prepared according to general procedure B (see main text), reaction time 4h, mobile phase hexane – ethylacetate (5 : 1), yield (80 mg, 82 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 2.18 (d, J = 0.6 Hz, 3H), 2.33 (d, J = 0.6 Hz, 3H), 6.63 (t, J = 7.5 Hz, 1H), 6.97 – 6.80 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 16.54, 22.33, 120.73, 124.67, 126.80, 128.96, 129.36, 139.97 ppm.
HRMS (ESI): calcd. for $C_8H_{10}O$ $[M - H]^-$ 121.06589; found 121.06586.

4-Methylphenol (4d) was prepared according to general procedure B (see main text), reaction time 1h, mobile phase hexane – ethyl acetate (5 : 1), yield (79 mg, 93 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 2.21 (s, 3H), 6.65 (d, J = 8.5 Hz, 2H), 7.07 – 6.86 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ, 20.49, 115.92, 129.79 130.84, 130.87, 155.55 ppm
HRMS (ESI): calcd. for C_7H_8O $[M - H]^-$ 107.05024; found 107.05008.

3-Methylphenol (4e) was prepared according to general procedure B (see main text), reaction time 1h, mobile phase hexane – ethyl acetate (5 : 1), yield (80 mg, 94 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 2.24 (s, 3H), 6.76 – 6.43 (m, 3H), 7.16 – 6.90 (m, 1H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 21.42, 113.14, 116.77, 121.54, , 130.29, 140.58 , 157.81 ppm.
HRMS (ESI): calcd. for C_7H_8O $[M - H]^-$ 107.05024; found 107.05003.

2-Methylphenol (4f) was prepared according to general procedure B (see main text), reaction time 2h, mobile phase hexane – ethyl-acetate (5 : 1), yield (71 mg, 84 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 2.16 (s, 3H), 6.79 – 6.62 (m, 2H), 7.11 – 6.88 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 16.15, 115.59, 115.60, 120.80, 125.17, 127.77, 127.80, 131.79, 155.83 ppm.
HRMS (ESI): calcd. for C_7H_8O $[M - H]^-$ 107.05024; found 107.05006.

4-Nitrophenol (4g) was prepared according to general procedure B (see main text), reaction time 4h, mobile phase hexane – ethylacetate (3 : 1), yield (63 mg, 57 %) or according to general procedure D (see main text), reaction time 2h, mobile phase hexane – acetate (3 : 1), yield (92 mg, 84%)
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.93 – 6.83 (m, 2H), 8.17 – 8.06 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 116.50, 127.01, 163.82 ppm.
HRMS (ESI): calcd. $C_6H_5NO_3$ $[M - H]^-$ 138.01967; found 138.01971.

3-Nitrophenol (4h) was prepared according to general procedure B (see main text), reaction time 4h, mobile phase hexane – ethyl acetate (5 : 1), yield (101 mg, 92 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 7.15 (ddd, J = 8.2, 2.5, 0.9 Hz, 1H), 7.39 (td, J = 8.2, 0.3 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.67 (ddd, J = 8.2, 2.2, 0.9 Hz, 1H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 110.89, , 115.67, 122.89, 131.33, 150.20, 158.54 ppm.
HRMS (ESI): calcd. $C_6H_5NO_3$ $[M - H]^-$ 138.01967; found 138.01973.

2-Nitrophenol (4i) was prepared according to general procedure B (see main text), reaction time 4h, mobile phase hexane – ethyl acetate (2 : 1), yield (25 mg, 23 %) or according to general procedure C (see main text), reaction time 4h, mobile phase hexane – ethyl acetate (2 : 1), yield (55 mg, 49 %) or according to general procedure D (see S3), reaction time 2h, mobile phase hexane – acetate (2 : 1), yield (64 mg, 56%).
^{1}H NMR (300 MHz, Methanol-d_4) δ 7.01 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.17 – 7.08 (m, 1H), 7.59 (ddd, J = 8.4, 7.2, 1.7 Hz, 1H) 8.10 – 8.02 (m, 1H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 120.61., 121.25, 125.94, 138.58, 155.56 ppm.
HRMS (ESI): calcd. $C_6H_5NO_3$ $[M - H]^-$ 138.01967; found 138.01988.

4-Chlorophenol (4j) was prepared according to general procedure B (see main text), reaction time 1h, mobile phase hexane – ethyl acetate (5 : 1), yield (96 mg, 95 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.79 – 6.66 (m, 2H), 7.18 – 7.06 (m, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 117.72, 124.91, 130.23, 156.75, 171.78 ppm.
HRMS (ESI): calcd. C_6H_5ClO $[M - H]^-$ 126.99562; found 126.99575.

3-Chlorophenol (4k) was prepared according to general procedure B (see main text), reaction time 2h, mobile phase hexane – ethyl-acetate (5 : 1), yield (85 mg, 84 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.68 (ddd, J = 8.2, 2.1, 1.2 Hz, 1H), 6.83 – 6.74 (m, 2H), 7.18 – 7.07 (m, 1H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 114.91, 116.40, 120.76, 131.65, 135.18, 158.84 ppm.
HRMS (ESI): calcd. C_6H_5ClO $[M - H]^-$ 126.99562; found 126.99564.

2-Chlorophenol (4l) was prepared according to general procedure B (see main text), reaction time 1h, mobile phase hexane – ethyl acetate (5 : 1), yield (102 mg, 98 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.78 (ddd, J = 7.9, 7.3, 1.5 Hz, 1H), 6.93 – 6.85 (m, 1H), 7.10 (ddd, J = 8.2, 7.4, 1.6 Hz, 1H), 7.26 (dd, J = 8.0, 1.6 Hz, 1H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 117.58, 120.95, 121.93, 129.07, 130.66, 153.20 ppm.
HRMS (ESI): calcd. C_6H_5ClO $[M - H]^-$ 126.99562; found 126.99562.

4-Vinylphenol (4m) was prepared according to general procedure C (see main text), reaction time 2h, mobile phase hexane – ethyl acetate (2 : 1), yield (72 mg, 76 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 5.02 (d, J = 10.9 Hz, 1H), 5.68 – 5.45 (m, 1H), 6.62 (dd, J = 17.6, 10.9 Hz, 1H), 6.73 (d, J = 8.6 Hz, 2H), 7.48 – 7.06 (m, 2H) ppm.
^{13}C NMR (126 MHz, Methanol-d_4) δ 16.55, 28.97, 116.05, 156.14, 129.62, 136.39 ppm
HRMS (ESI): calcd. C_8H_8O $[M - H]^-$ 119.05024; found 119.05036.

3-Hydroxypyridine (4n) was prepared according to general procedure B (see main text), reaction time 2h, mobile phase ethyl acetate, yield (52 mg, 69 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 7.34 – 7.19 (m, 2H), 8.00 (dd, J = 4.2, 2.0 Hz, 1H), 8.15 – 8.05 (m, 1H) ppm.
^{13}C NMR (126 MHz, Methanol-d_4) δ 124.46, 125.85, 138.26, 140.82, 155.94 ppm.
HRMS (ESI): calcd. C_5H_5NO $[M - H]^-$ 94.02984; found 94.02971.

4-(Hydroxymethyl)phenol (4o) was prepared according to general procedure B (see main text), reaction time 2h, mobile phase hexane – ethyl acetate (1 : 1), yield (73 mg, 74 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 4.48 (s, 2H), 6.75 (d, J = 8.5 Hz, 1H), 7.24 – 7.10 (m, 1H) ppm.
^{13}C NMR (126 MHz, Methanol-d_4) δ 65.07, 116.05, 129.80, 133.43, 157.81 ppm.
HRMS (ESI): calcd. $C_7H_8O_2$ $[M - H]^-$ 123.04515; found 123.04531

4-Hydroxybenzaldehyde (**4p)** was prepared according to general procedure C (see S3), mobile phase hexane – ethyl acetate (2 : 1), yield (75 mg, 77 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.68 (ddd, J = 8.2, 2.1, 1.2 Hz, 1H), 6.83 – 6.74 (m, 2H), 7.18 – 7.07 (m, 1H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 116.69, 130.56, 132.95, 163.47, 191.80 ppm.
HRMS (ESI): calcd. $C_6H_5O_2$: $[M - H]^-$ 121.02950; found 121.02954.

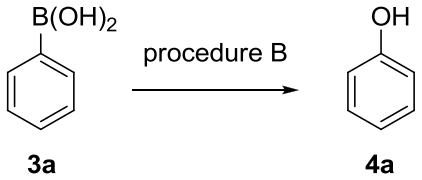
Bis(4-hydroxybenzylidene)hydrazine (**5**) was prepared according to general procedure B (see S3), reaction time 1h, mobile phase hexane – ethyl acetate (1 : 1), yield (91 mg, 96 %).
^{1}H NMR (300 MHz, Methanol-d_4) δ 6.86 (d, J = 8.6 Hz, 4H), 7.69 (d, J = 8.7 Hz, 4H), 8.52 (s, 2H) ppm.
^{13}C NMR (126 MHz, Dimethyl Sulfoxide-d_6) δ 115.73, 125.10, 130.04, 130.05, 160.25, 160.34 ppm.
HRMS (ESI): calcd. for $C_{14}H_{12}N_2O_2$ $[M - H]^-$ 238.07533; found 239.08360.

Cyclohexanol (7a) was prepared according to general procedure B (see S3), reaction time 2h, mobile phase hexane – ethyl acetate (2 : 1), yield (30 mg, 38 %).
^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 1.20 (dd, J = 19.9, 11.4 Hz, 4H), 1.51 (d, J = 12.2 Hz, 2H), 1.69 (dd, J = 9.0, 3.3 Hz, 2H), 1.79 (d, J = 11.3 Hz, 1H), 2. 89 (s, 1H), 3.50 (d, J = 32.5 Hz, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 25.21, 26.60, 36.44, 70.45, 118.26 ppm.
HRMS (ESI): calcd. for $C_6H_{12}O$ $[M +Na]^+$ 123.07858; found 123.07804

Dodecanol (7b) was prepared according to general procedure B (see S3), reaction time 2h, mobile phase hexane – ethyl acetate (5 : 1), yield (101 mg, 69%).
^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 0.88 (t, J = 6.7 Hz, 3H), 1.28 (s, 18H), 1.46 (d, J = 6.2 Hz, 2H), 2.17 (s, 1H), 2.49 (t, J = 5.4 Hz, 2H), 3.47 (q, J = 6.5 Hz, 2H) ppm.
^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 14.42, 23.43, 26.68, 30.12, 30.26, 30.40, 30.43, 32.68, 62.64, 118.26 ppm.
HRMS (ESI): calcd. for $C_{12}H_{26}O$ $[M +Na]^+$ 209.18813; found 209.18759

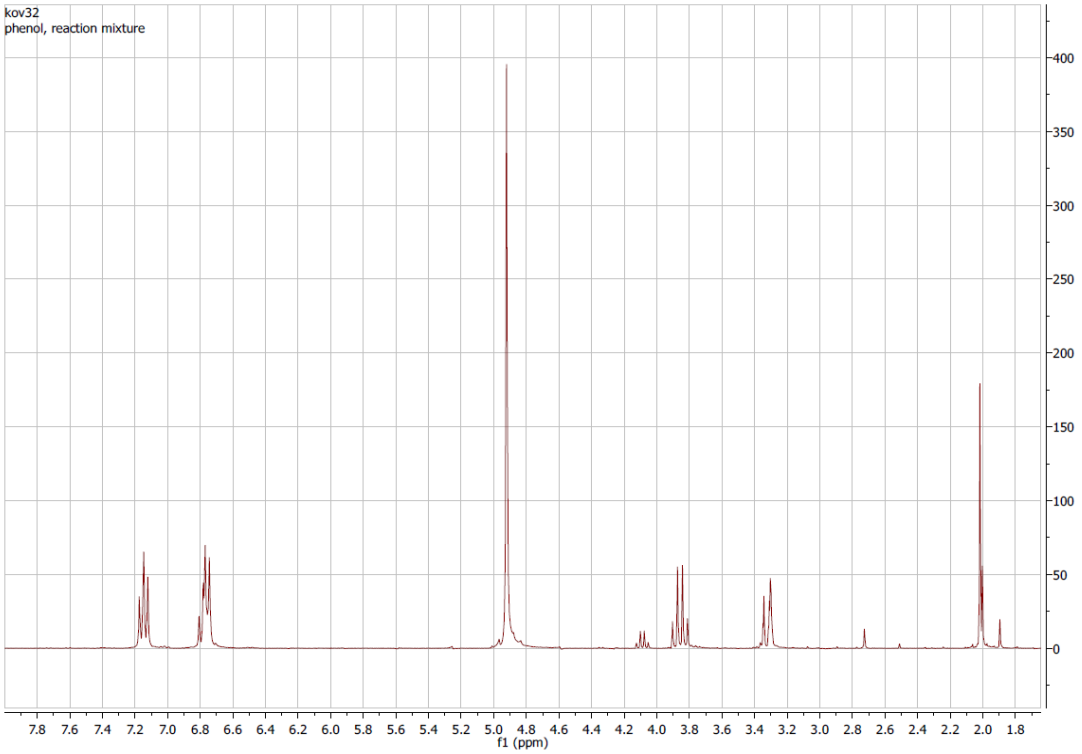
S3 ^{1}H NMR and ^{13}C NMR spectra of products 4, 5 and 7

Phenol (4a)

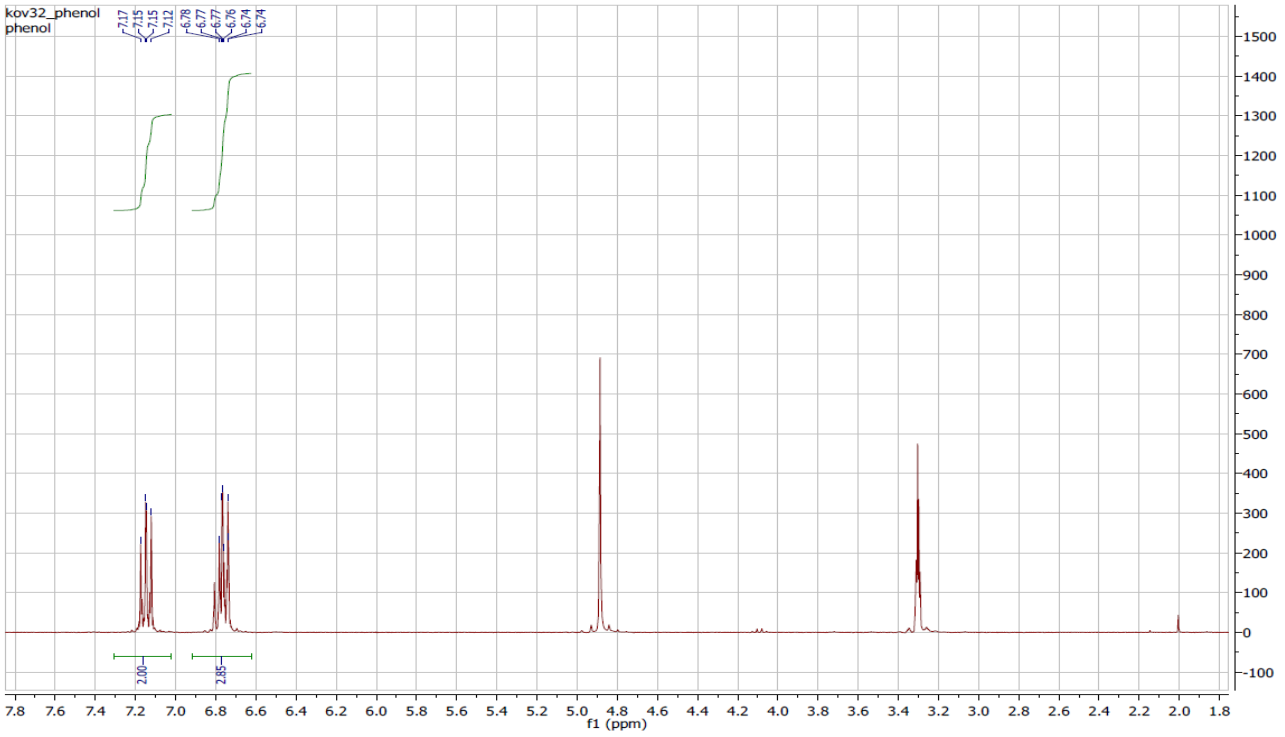


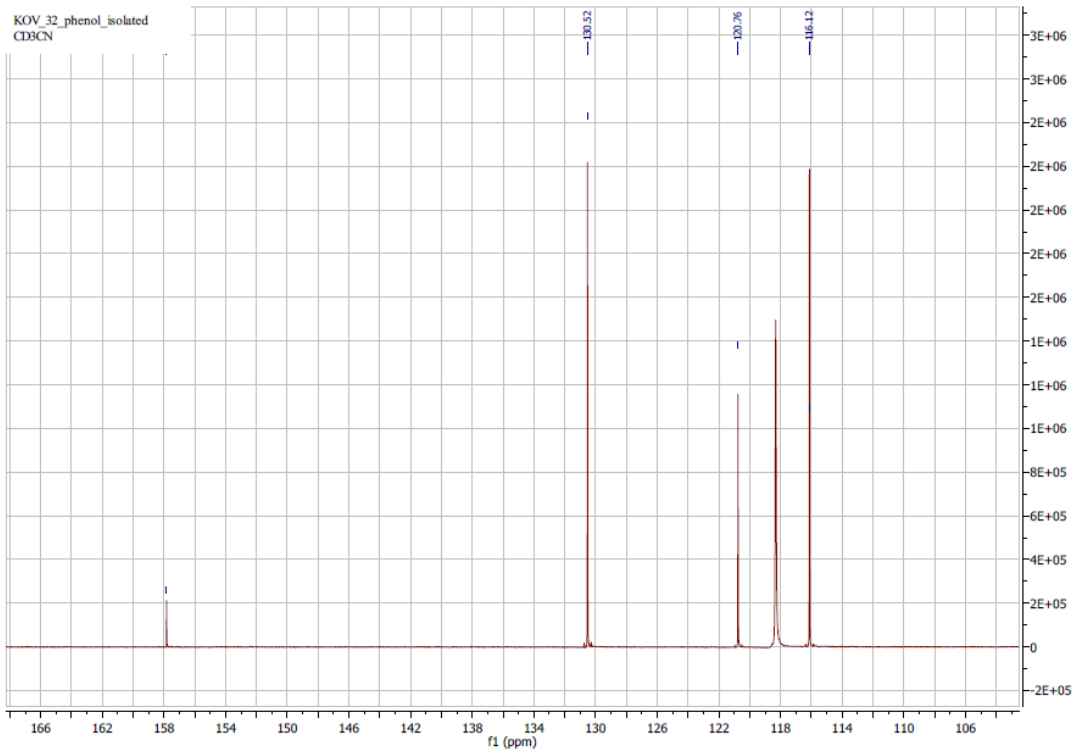
3a **4a**

Reaction mixture

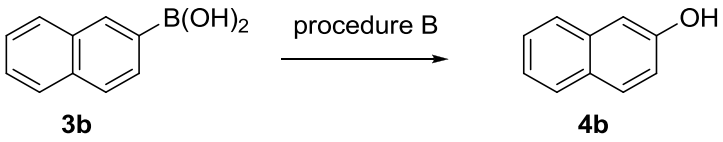


Isolated phenol **4a** (^{1}H and ^{13}C NMR)



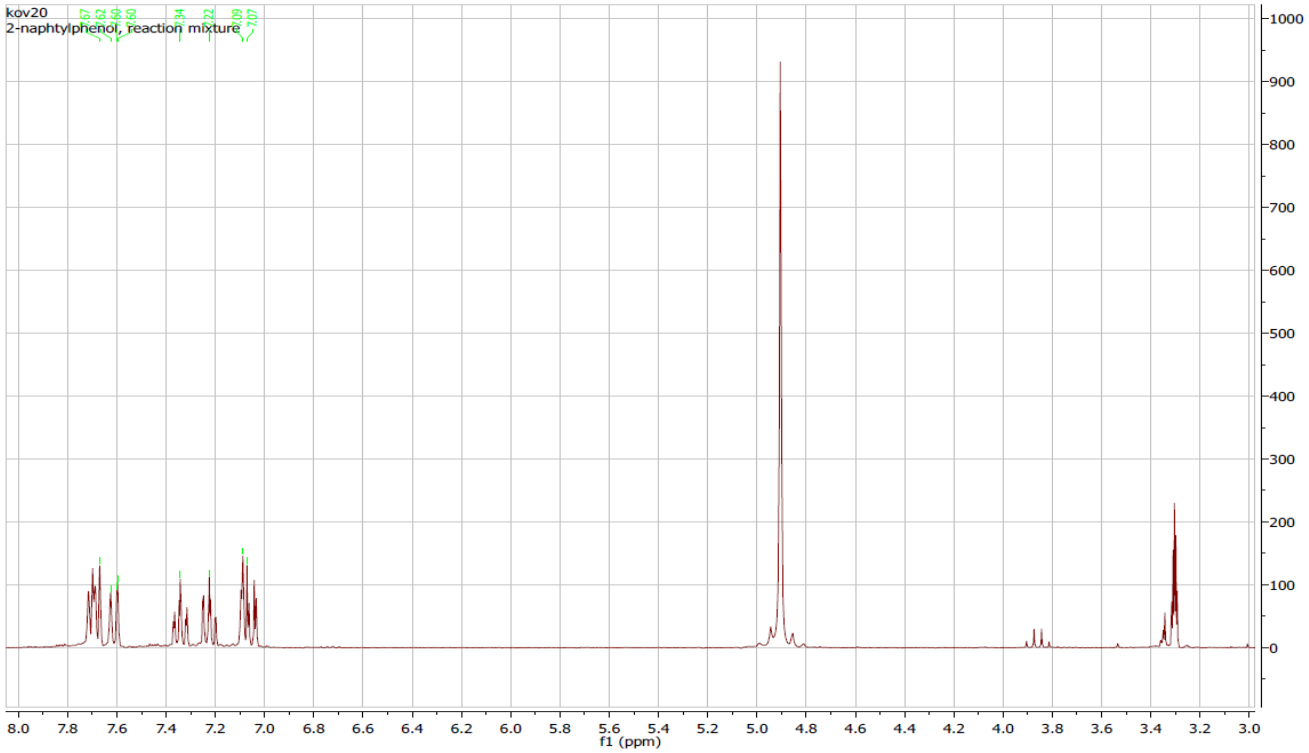


2-Naphtol (4b)

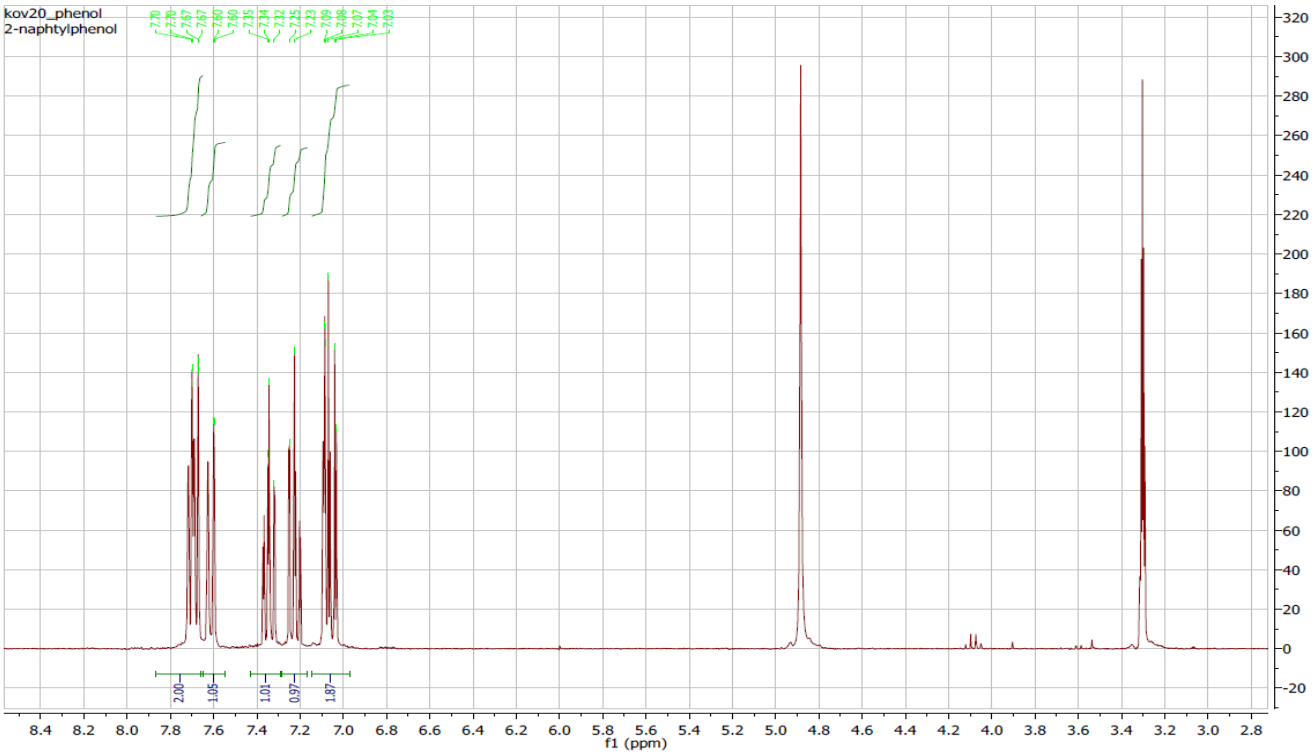


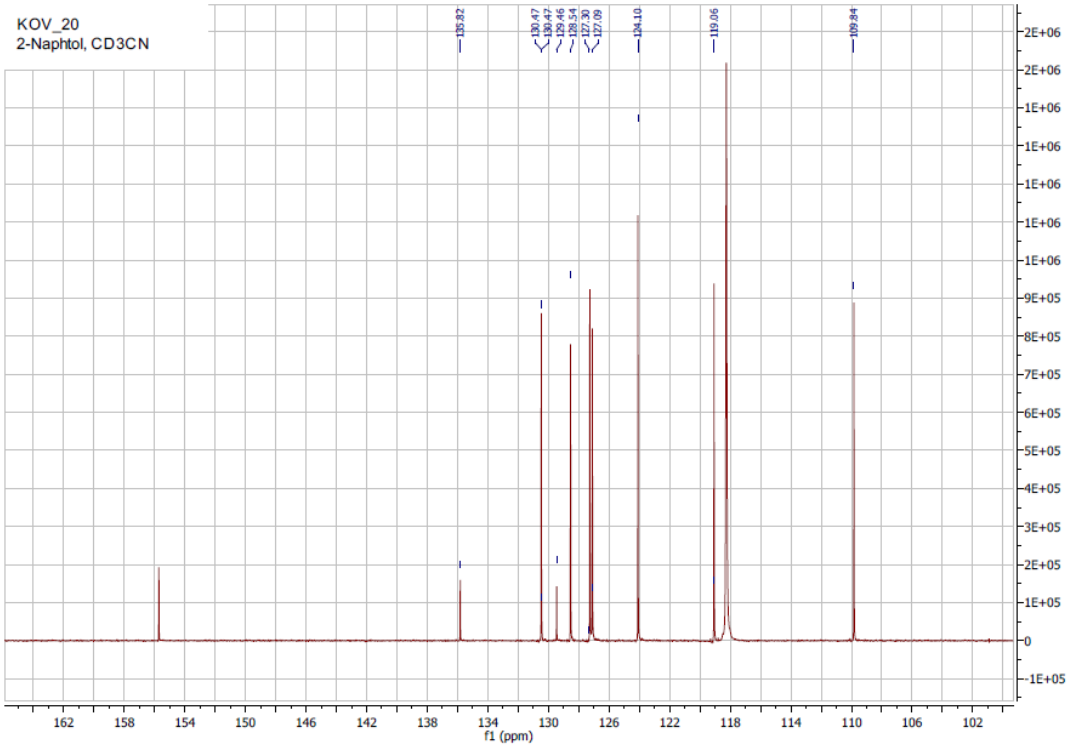
3b **4b**

Reaction mixture

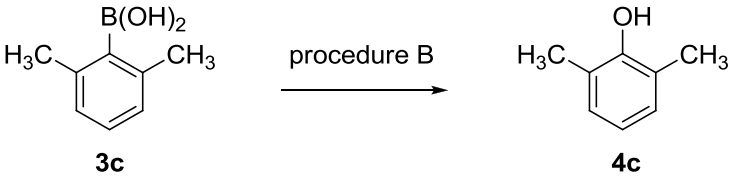


Isolated naphtol **4b** (^{1}H and ^{13}C NMR)



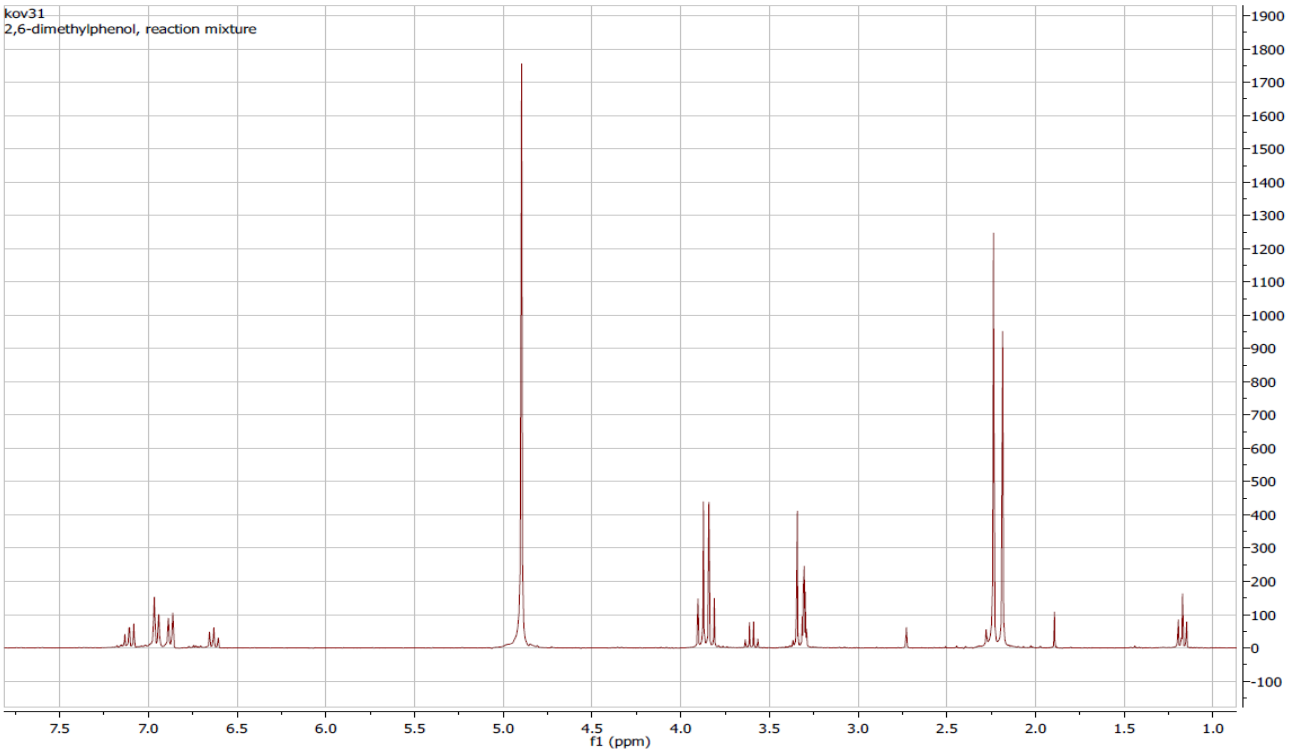


2,6-Dimethylphenol (4c)

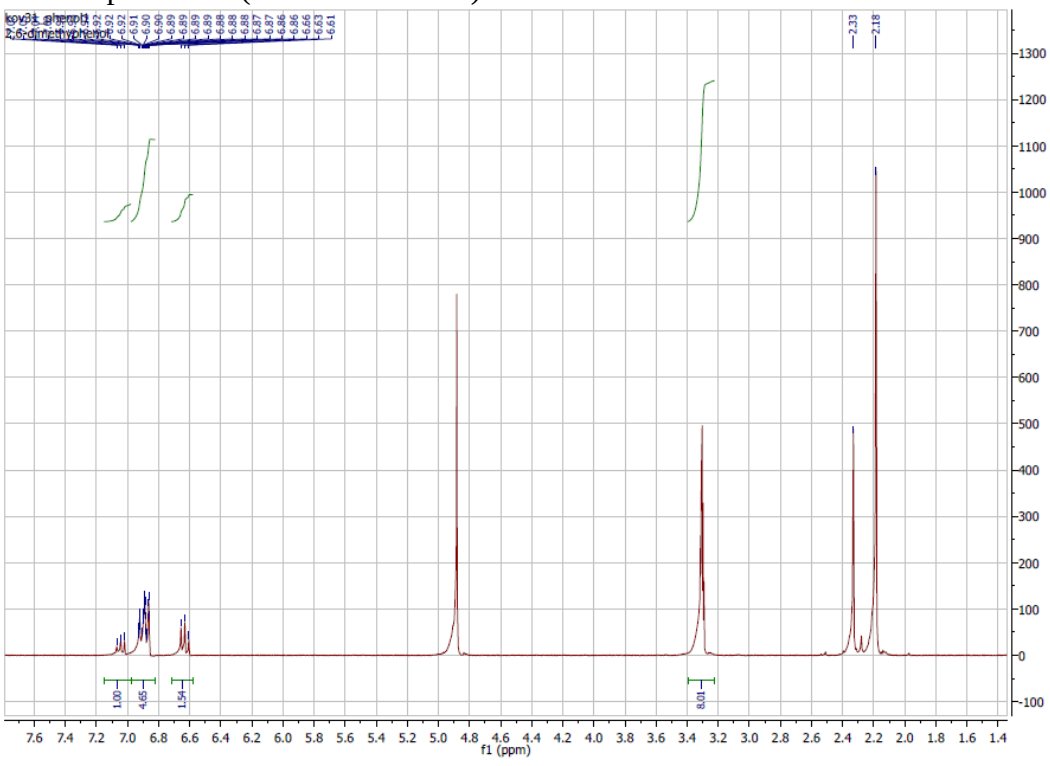


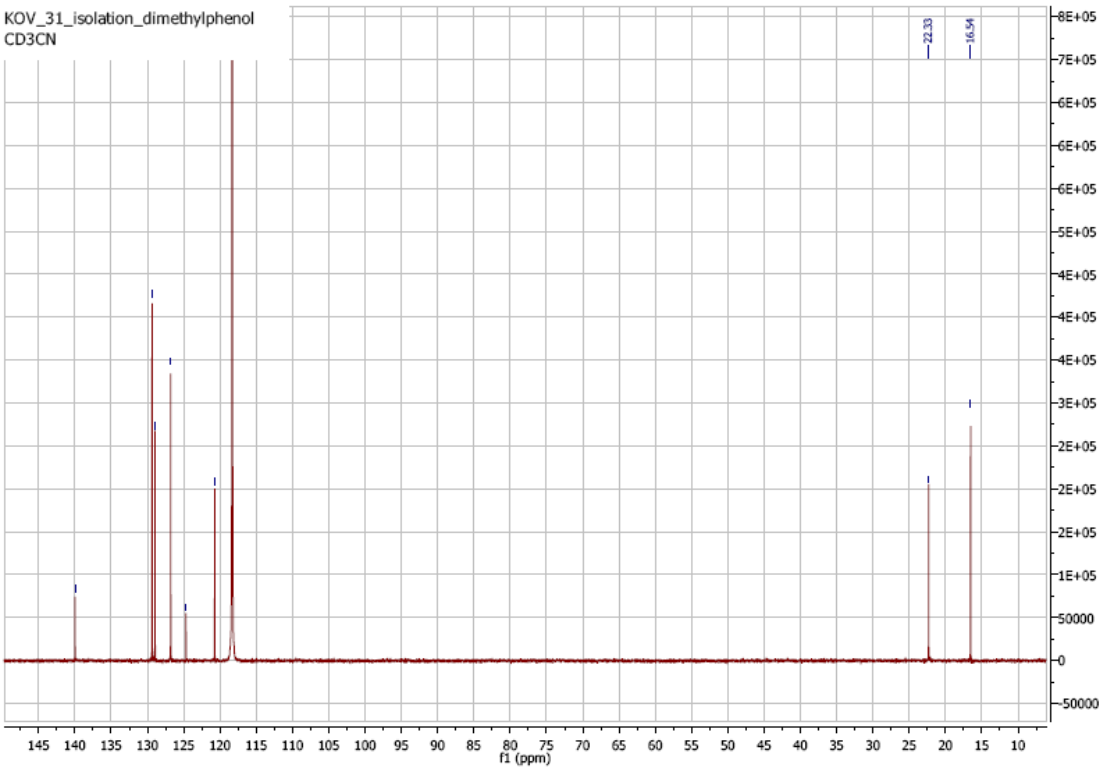
3c **4c**

Reaction mixture

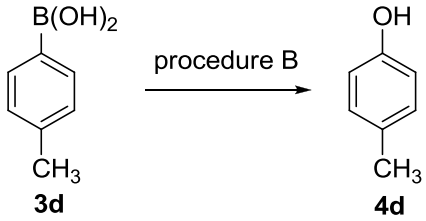


Isolated phenol **4c** (^{1}H and ^{13}C NMR)



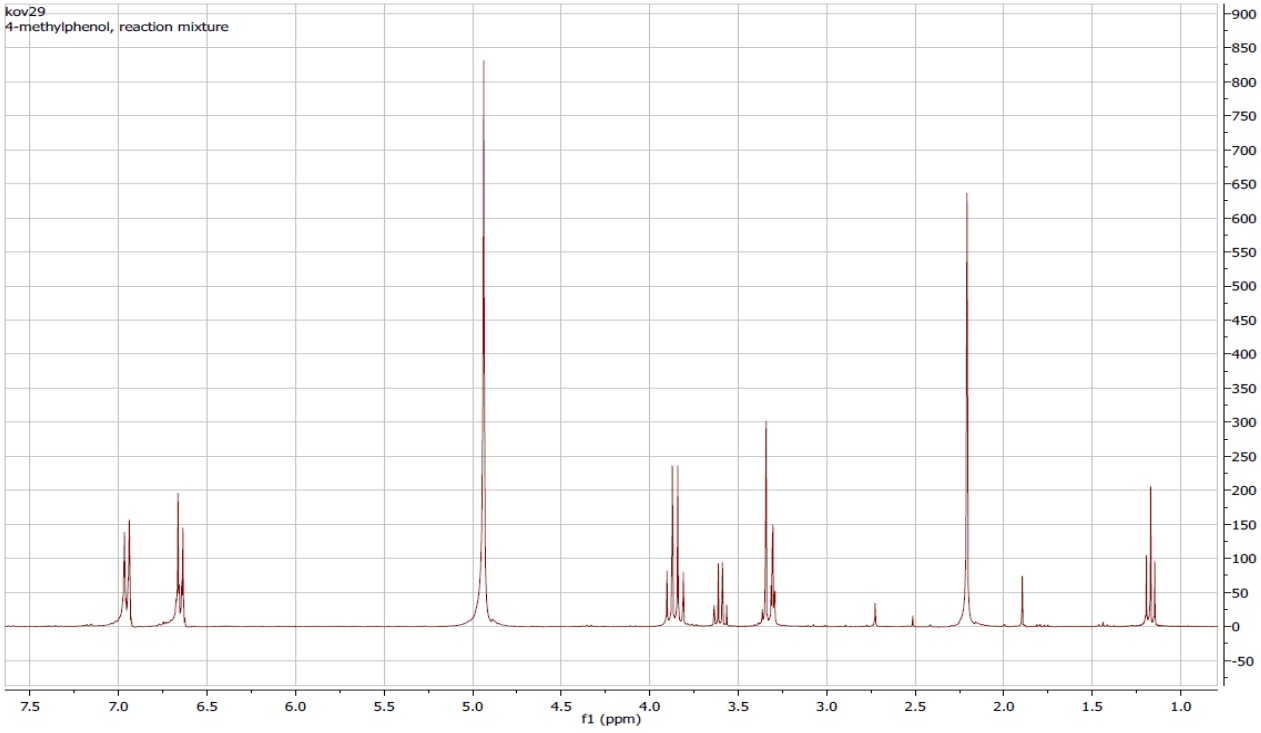


4-Methylphenol (4d)

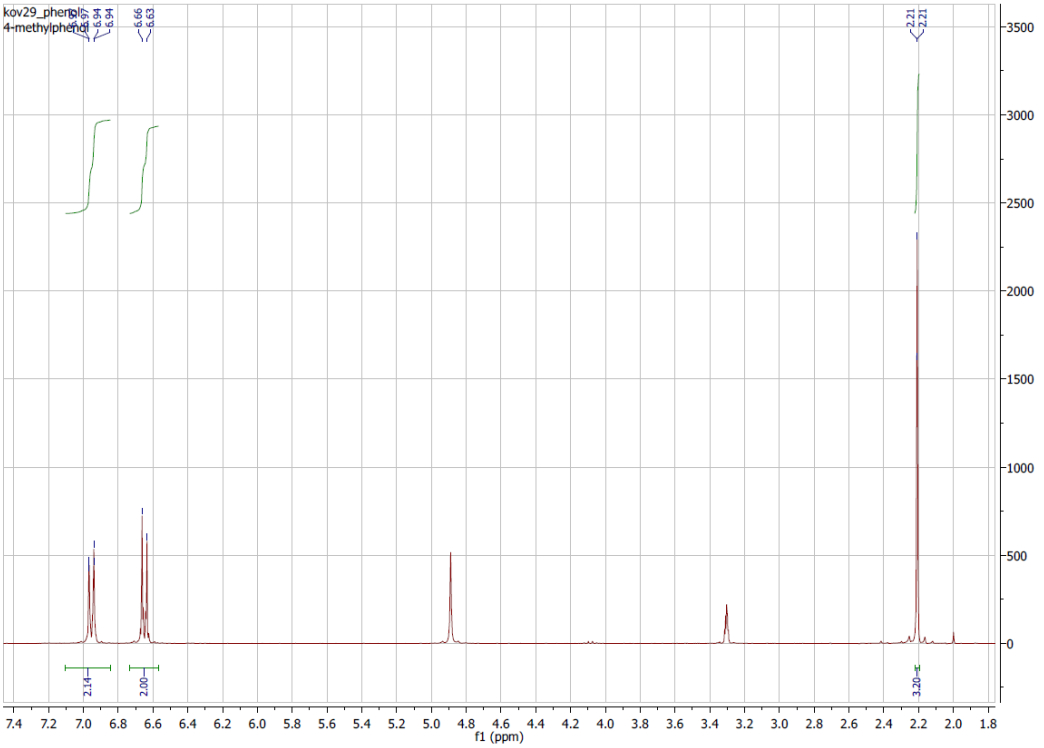


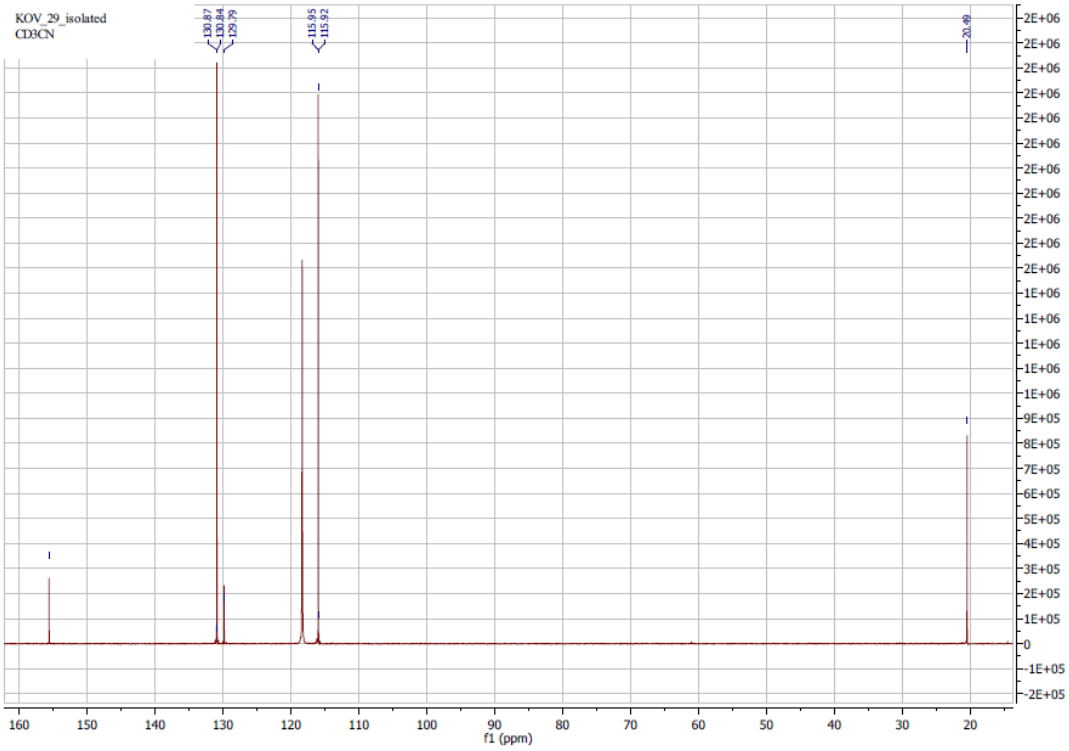
3d **4d**

Reaction mixture

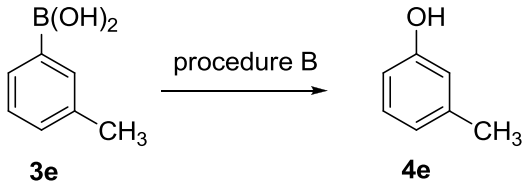


Isolated phenol **4d** (^{1}H and ^{13}C NMR)



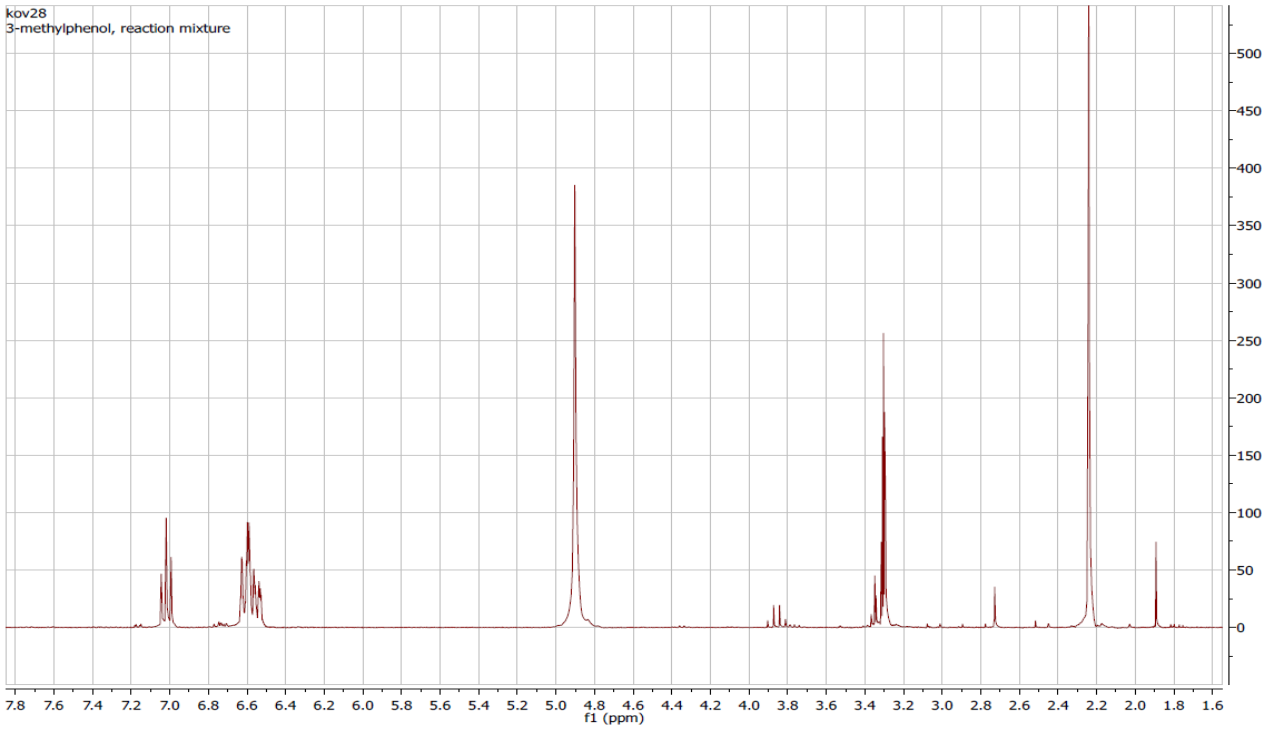


3-Methylphenol (4e)

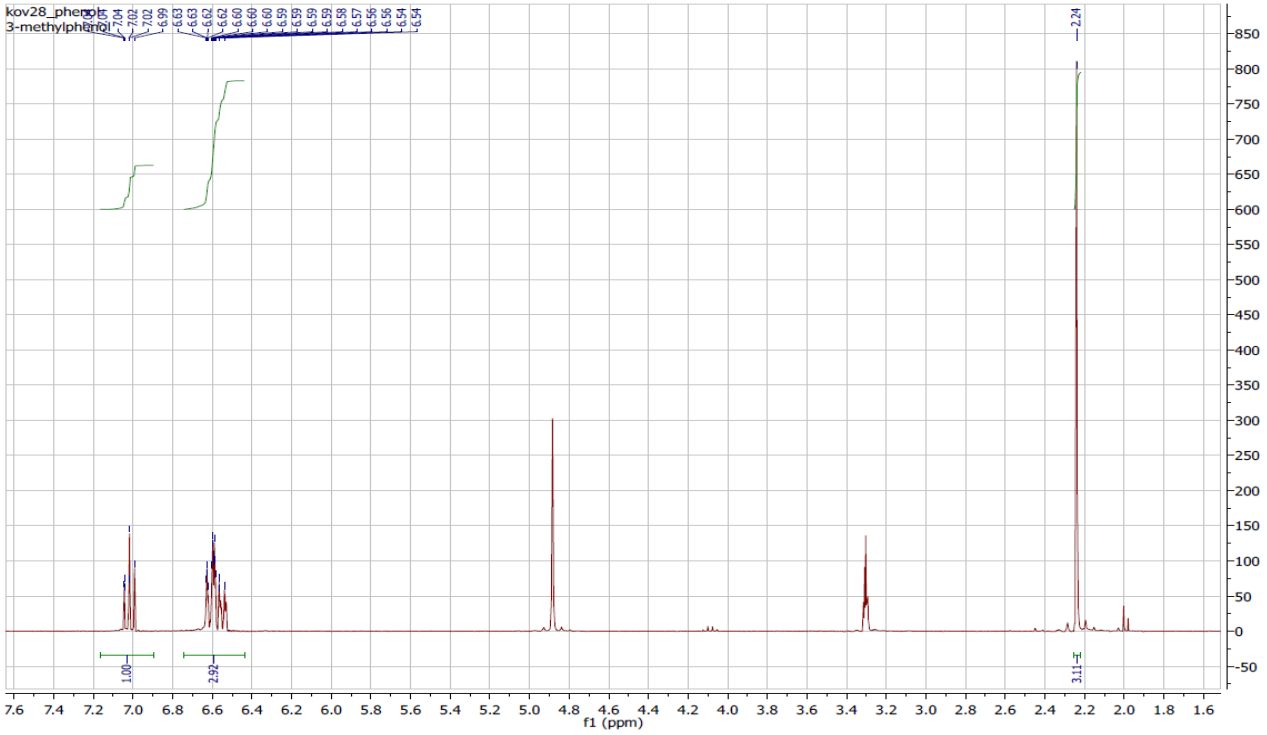


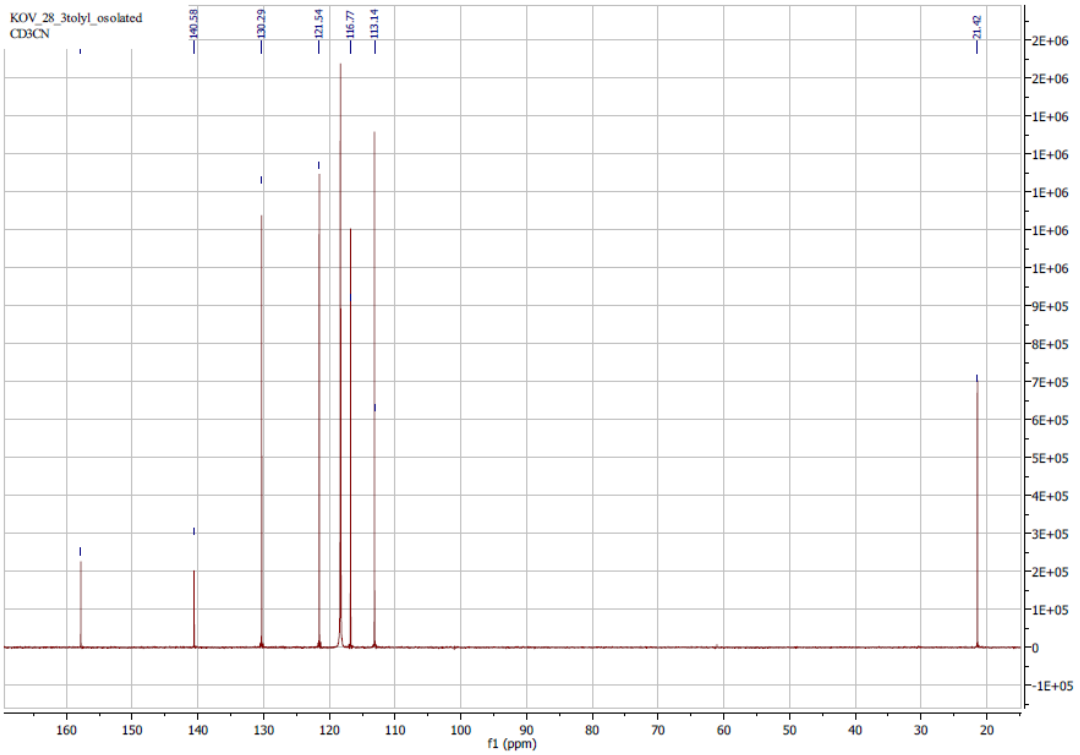
3e **4e**

Reaction mixture

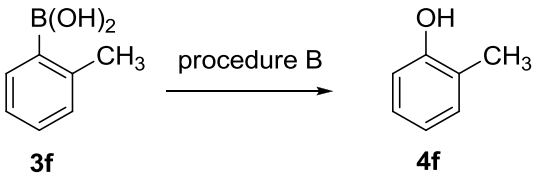


Isolated phenol **4e** (^{1}H and ^{13}C NMR)



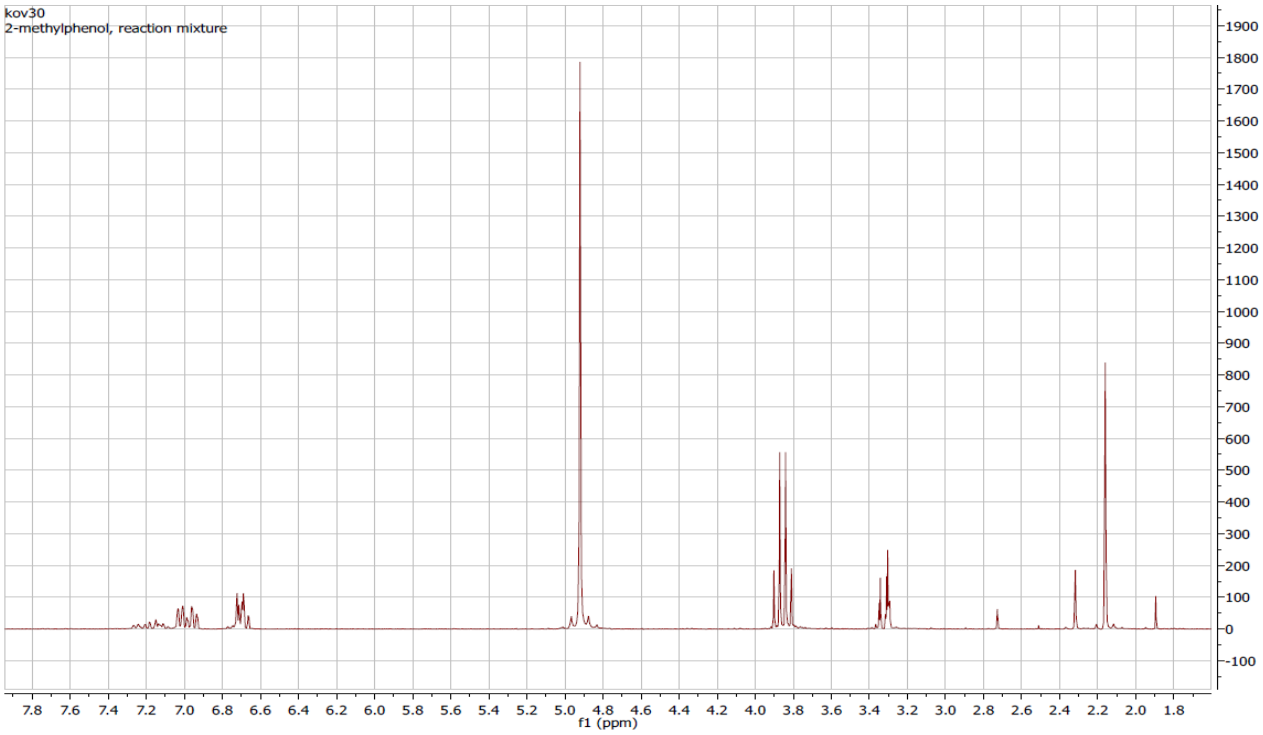


2-Methylphenol (4f)

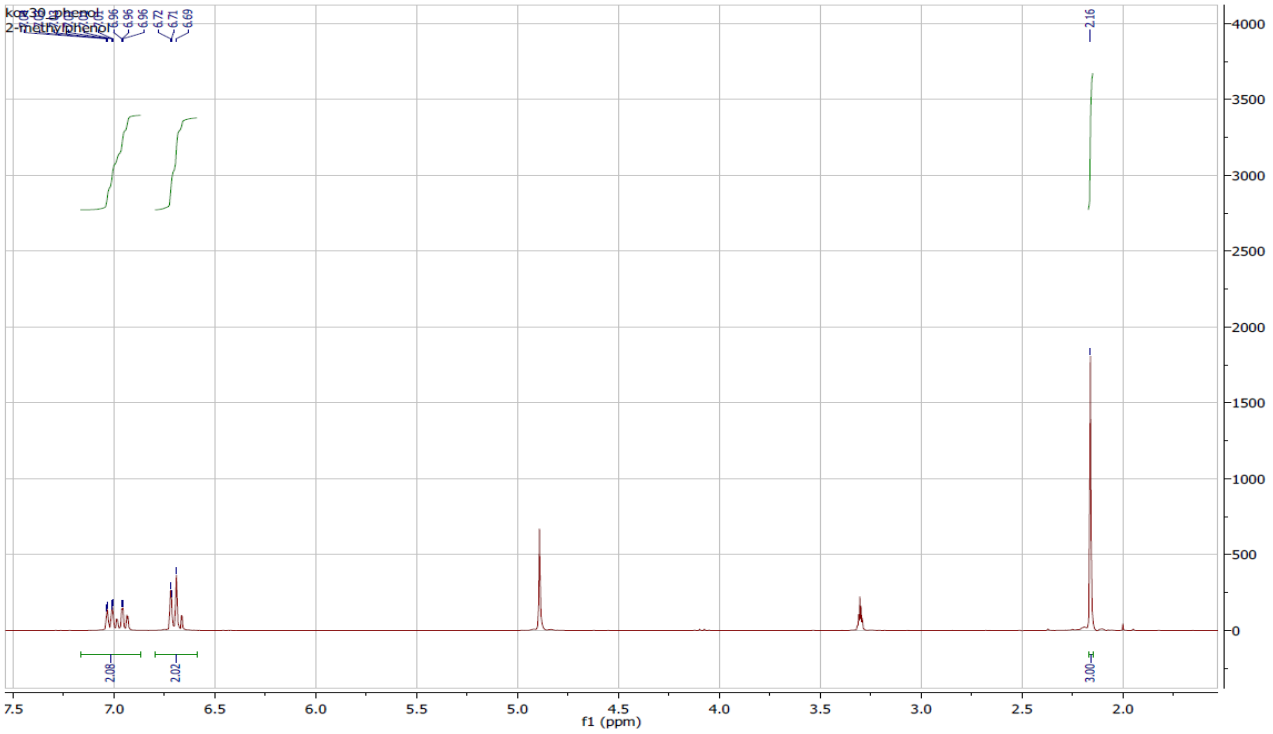


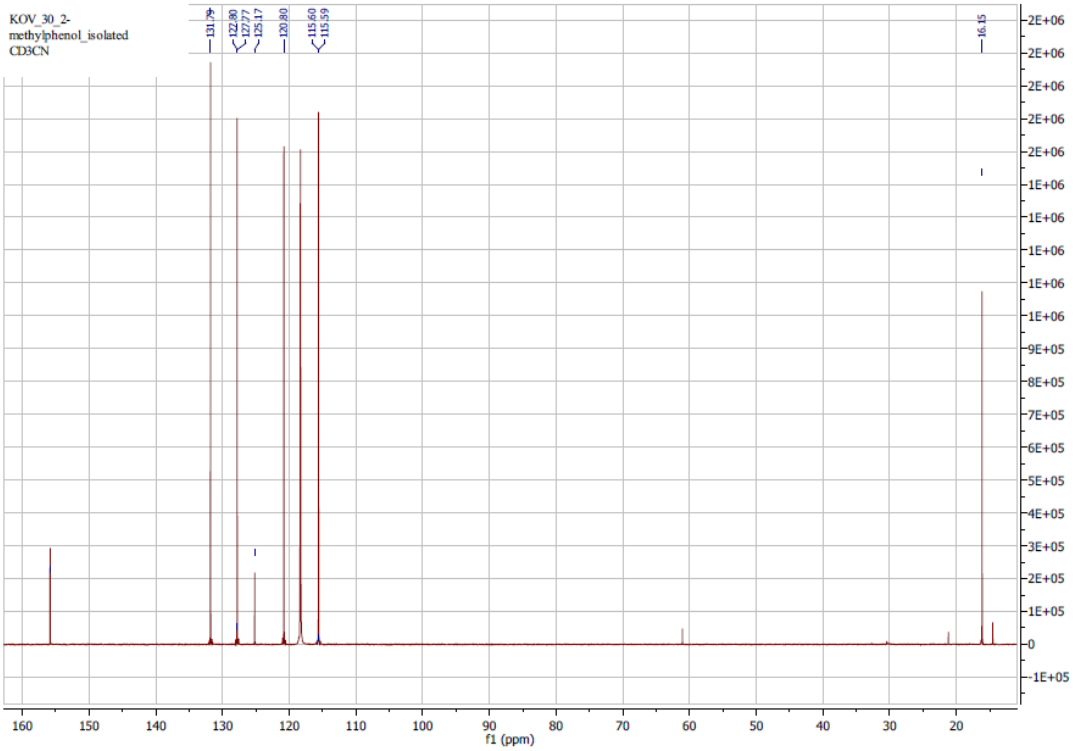
3f **4f**

Reaction mixture

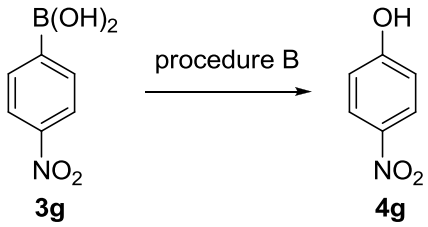


Isolated phenol **4f** (^{1}H and ^{13}C NMR)

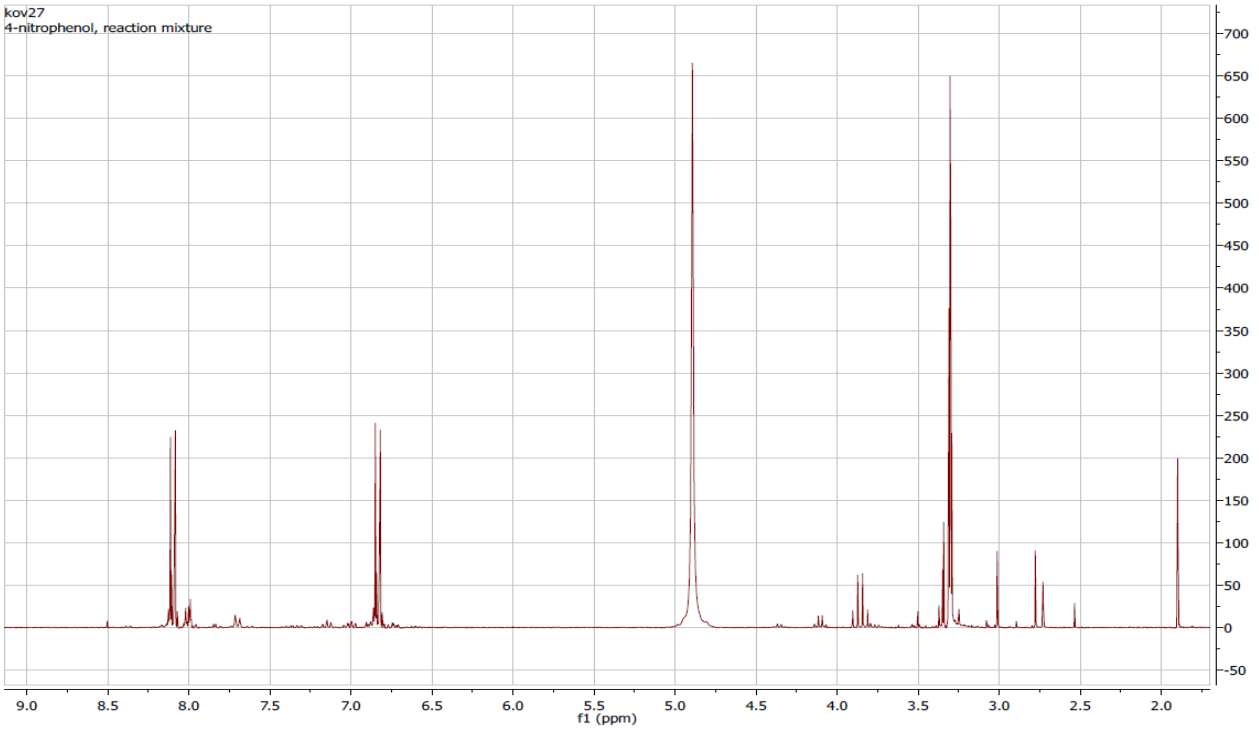




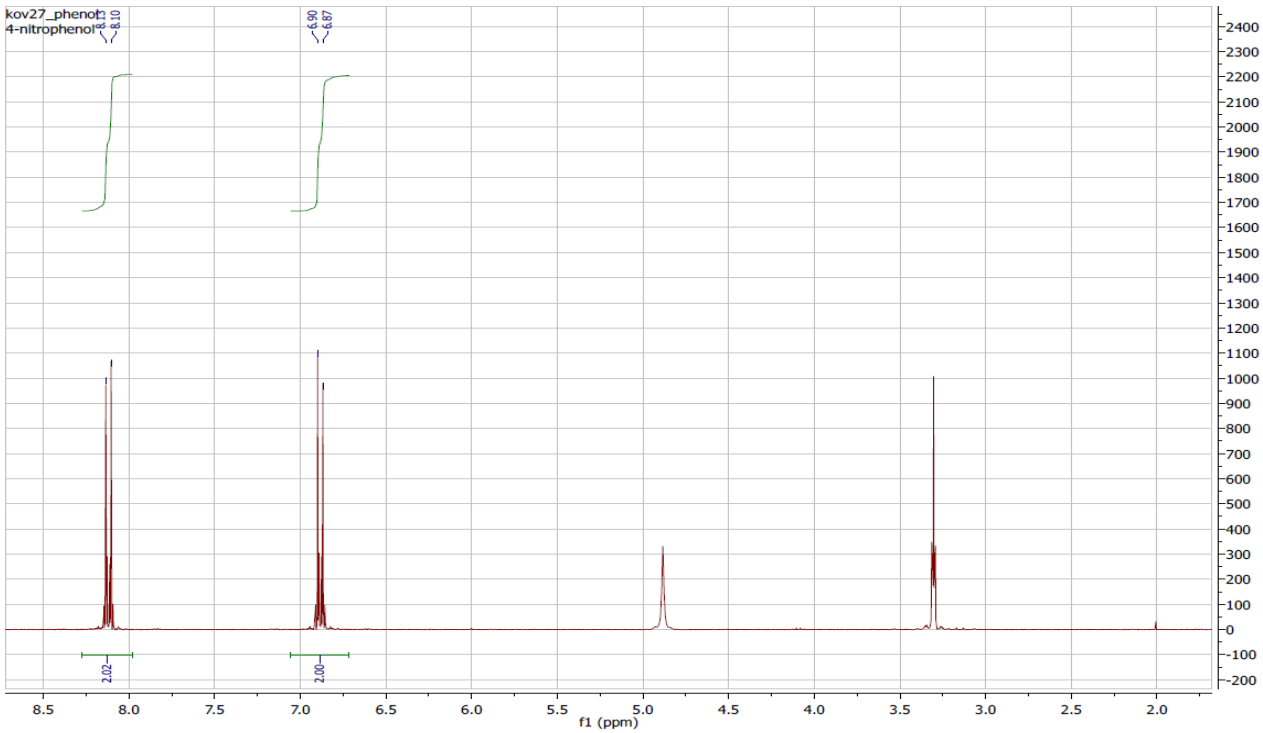
4-Nitrophenol (4g)

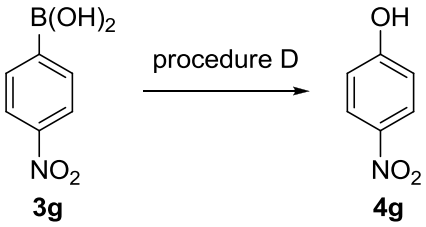


Reaction mixture – procedure B



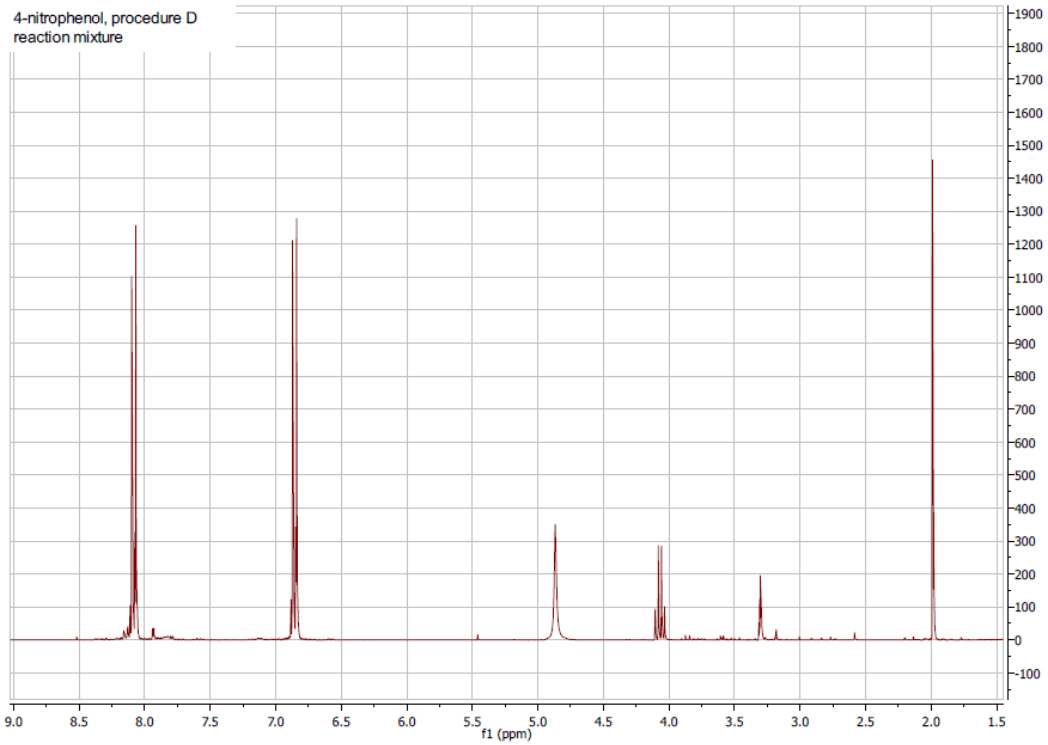
Isolated phenol **4g –** procedure B



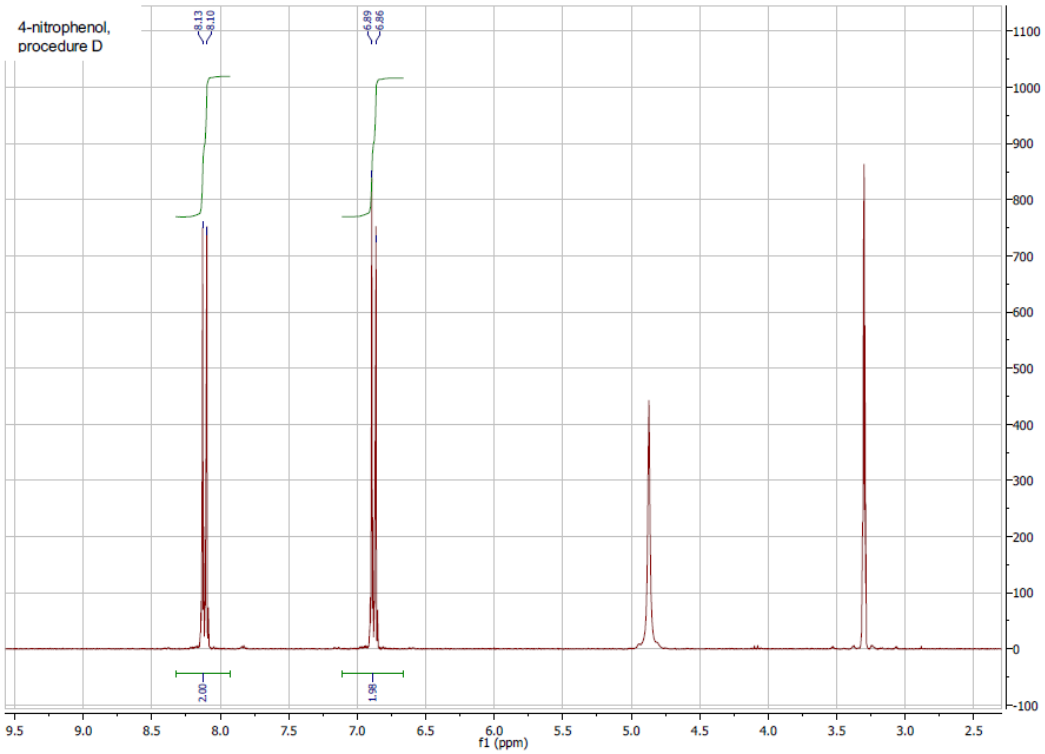


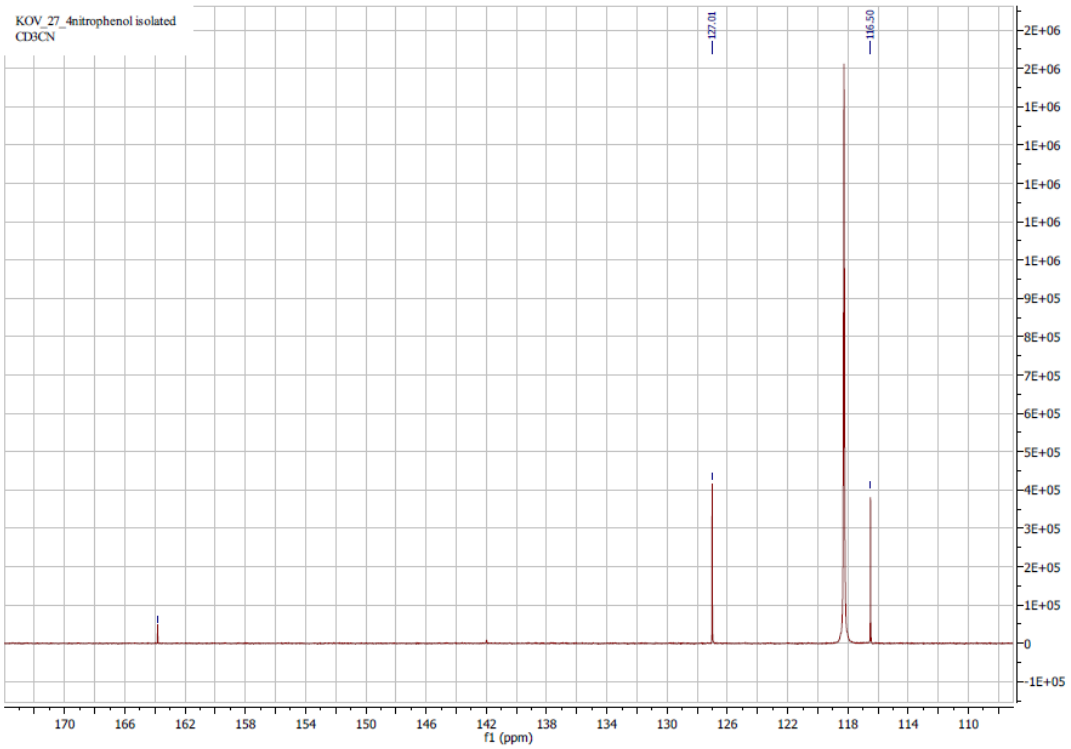
3g **4g**

Reaction mixture – procedure D

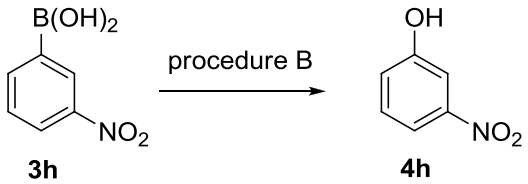


Isolated phenol **4g** – procedure D (^{1}H and ^{13}C NMR)



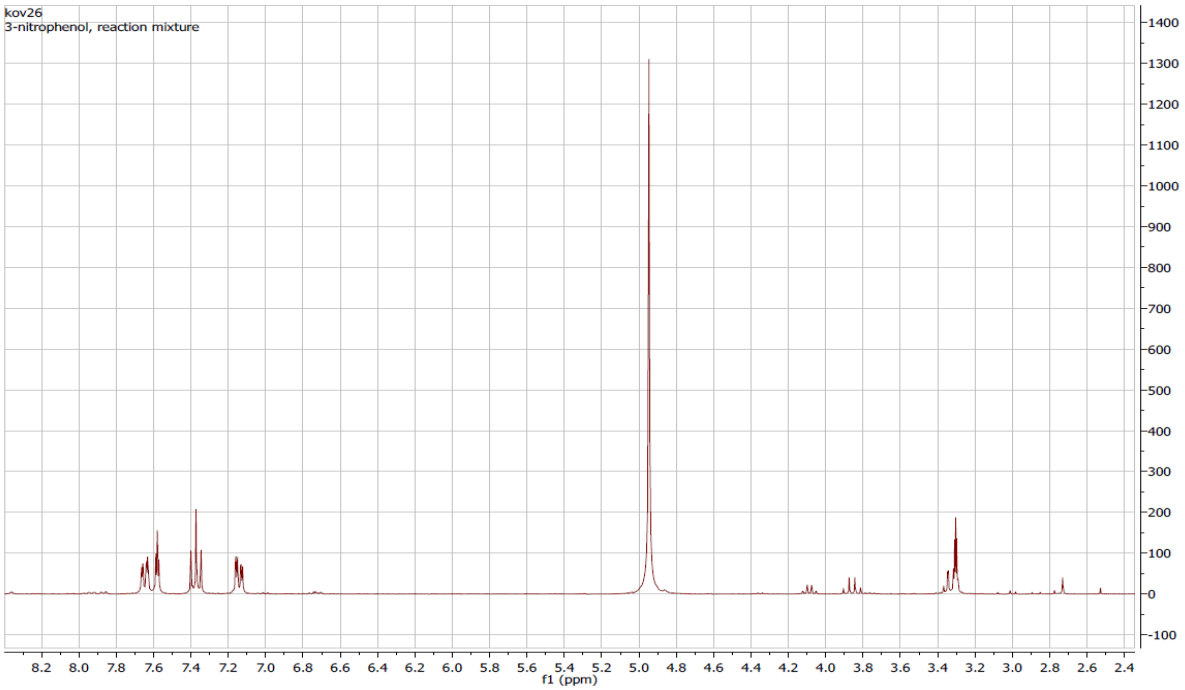


3-Nitrophenol (4h)

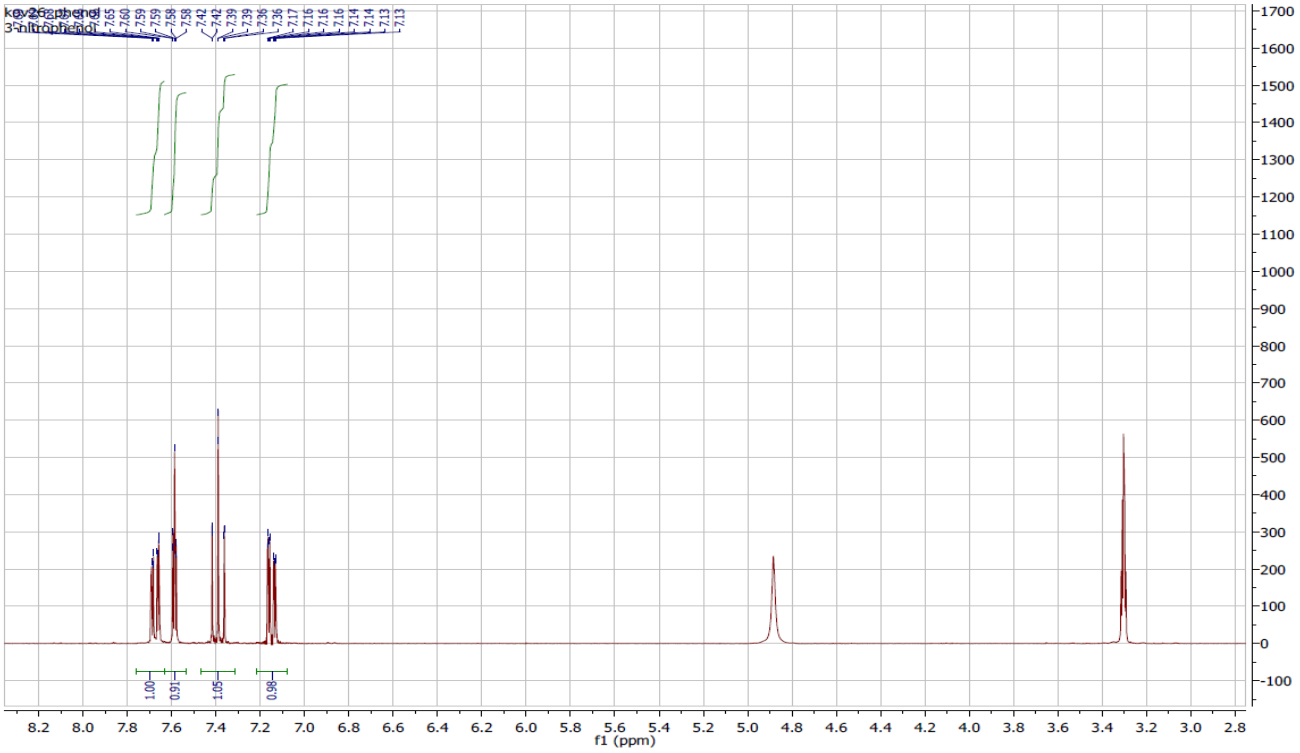


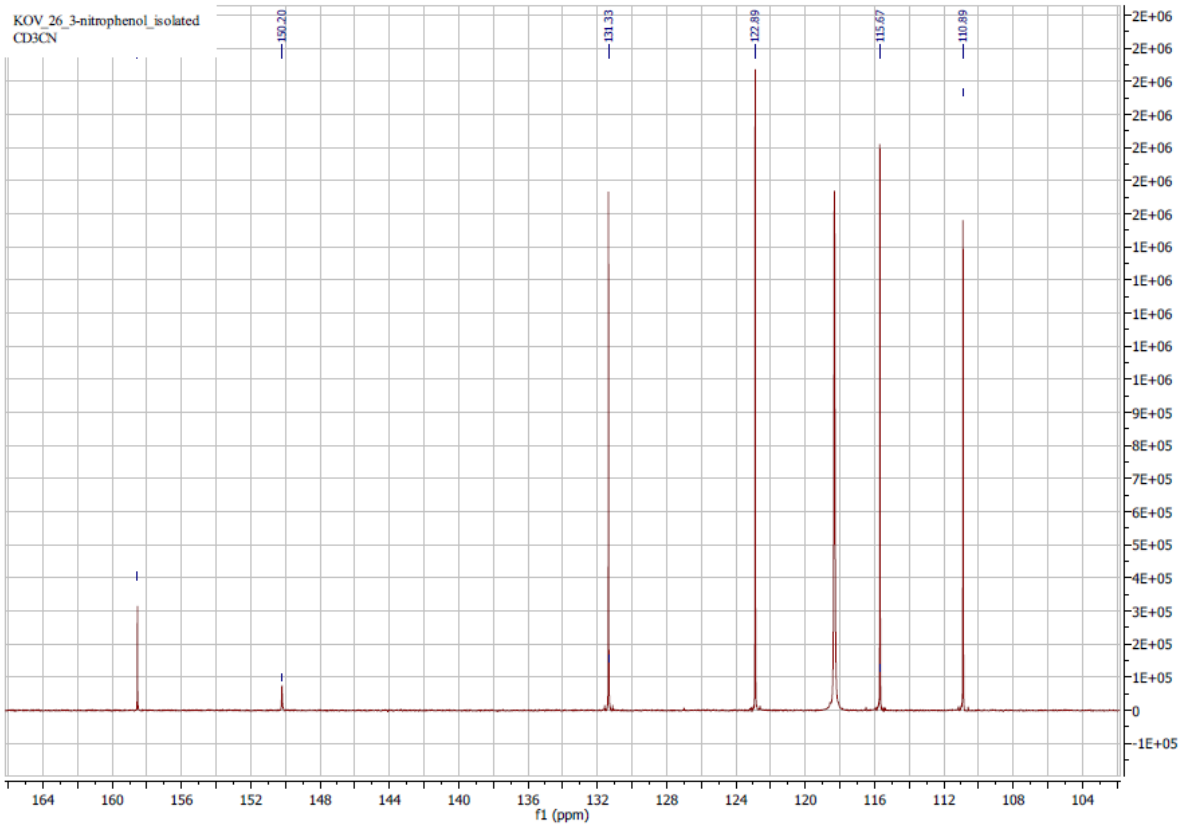
3h **4h**

Reaction mixture

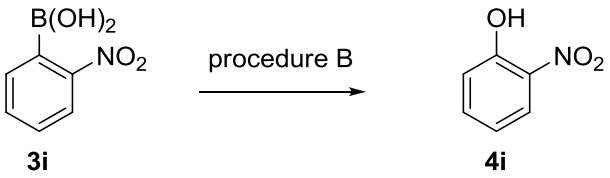


Isolated phenol **4h** (^{1}H and ^{13}C NMR)



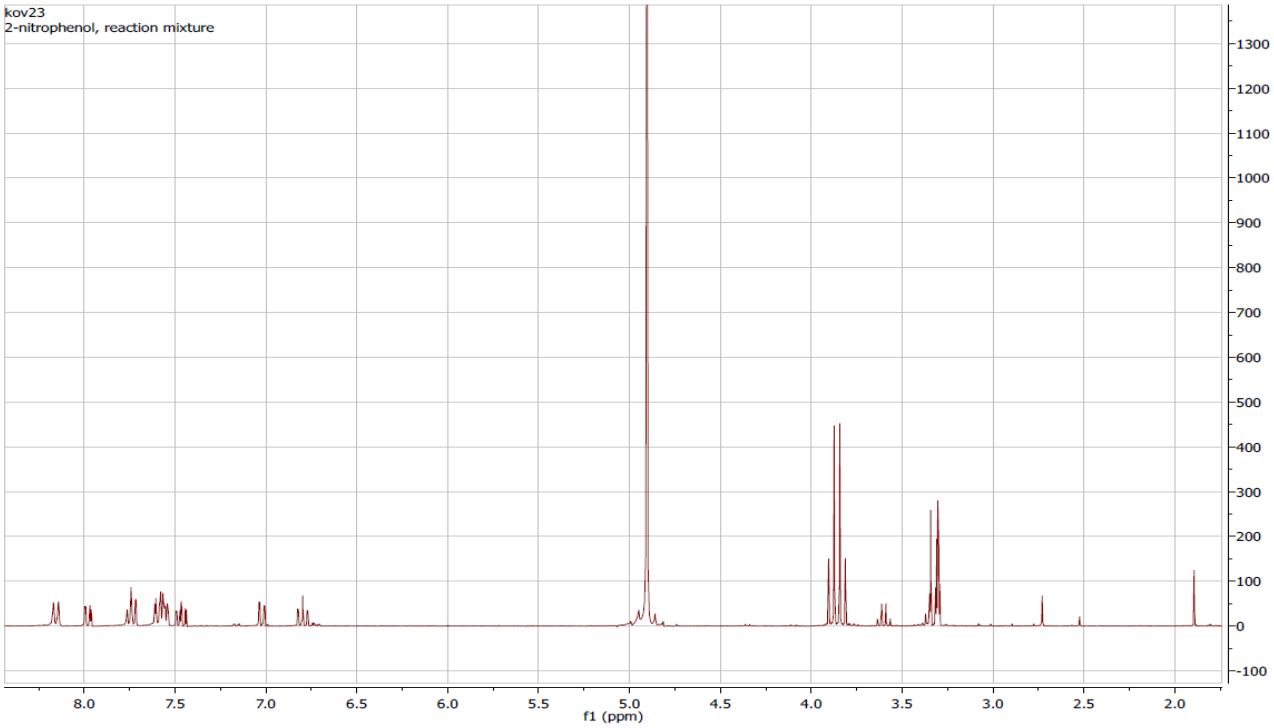


2-Nitrophenol (4i)

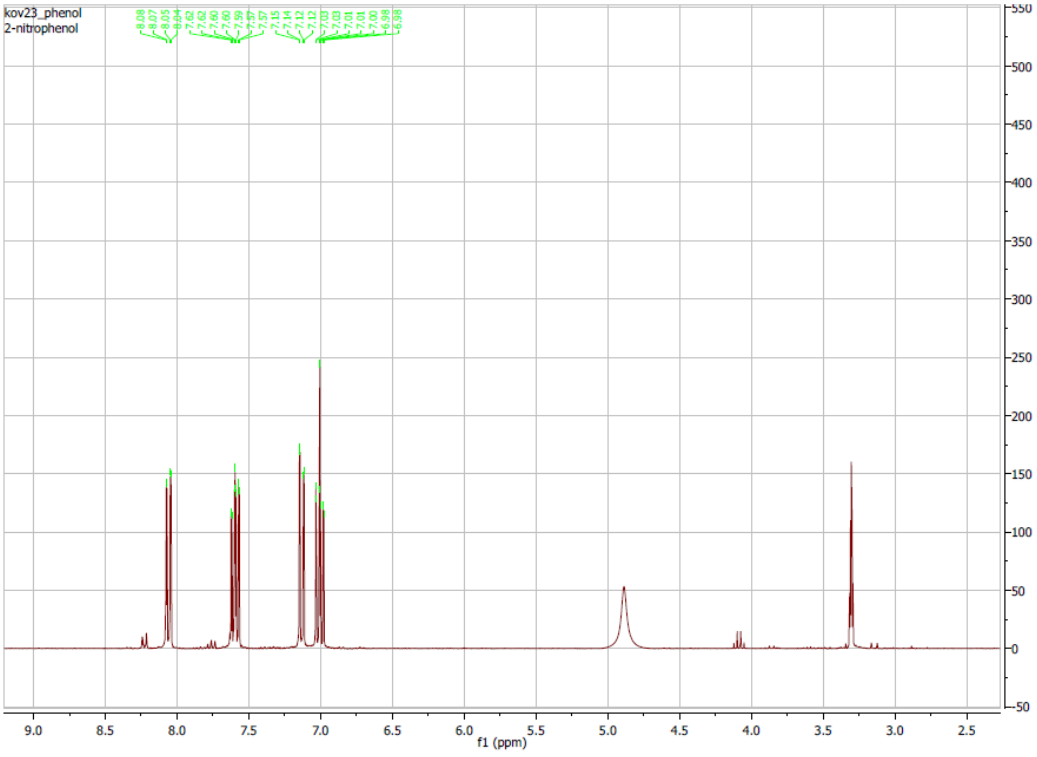


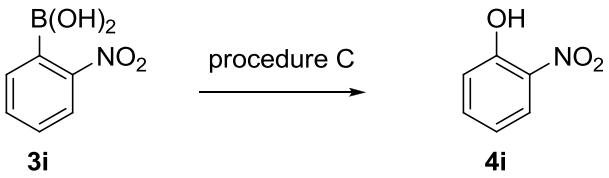
3i **4i**

Reaction mixture – procedure B



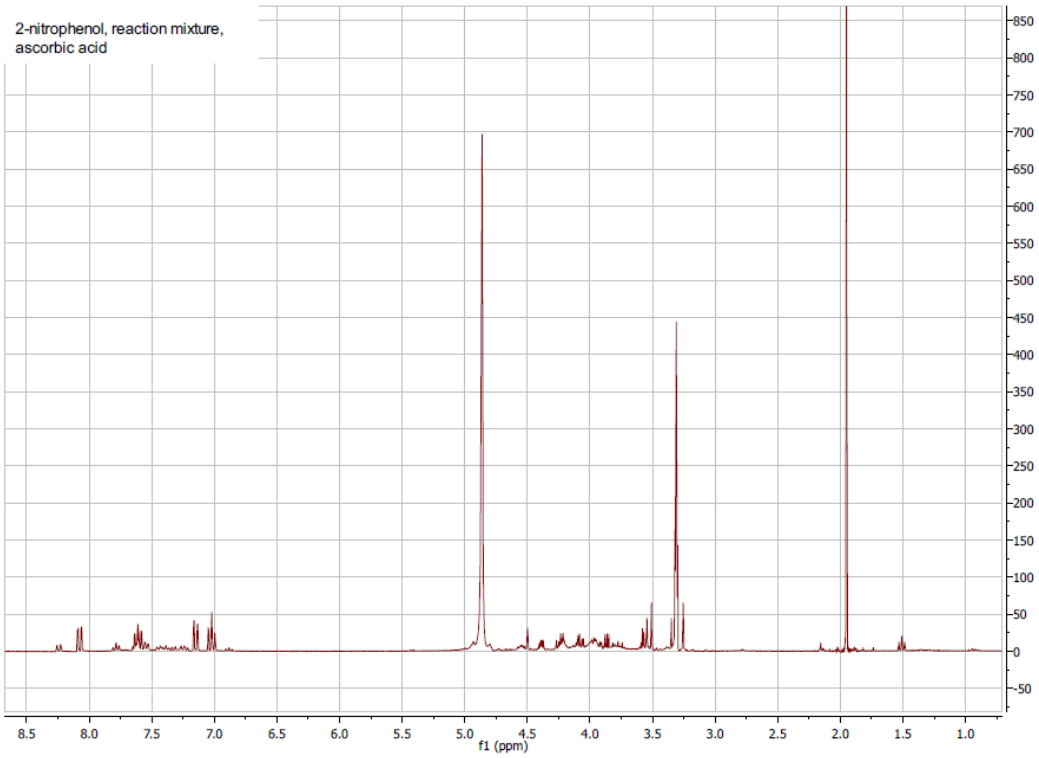
Isolated phenol **4i** – procedure B



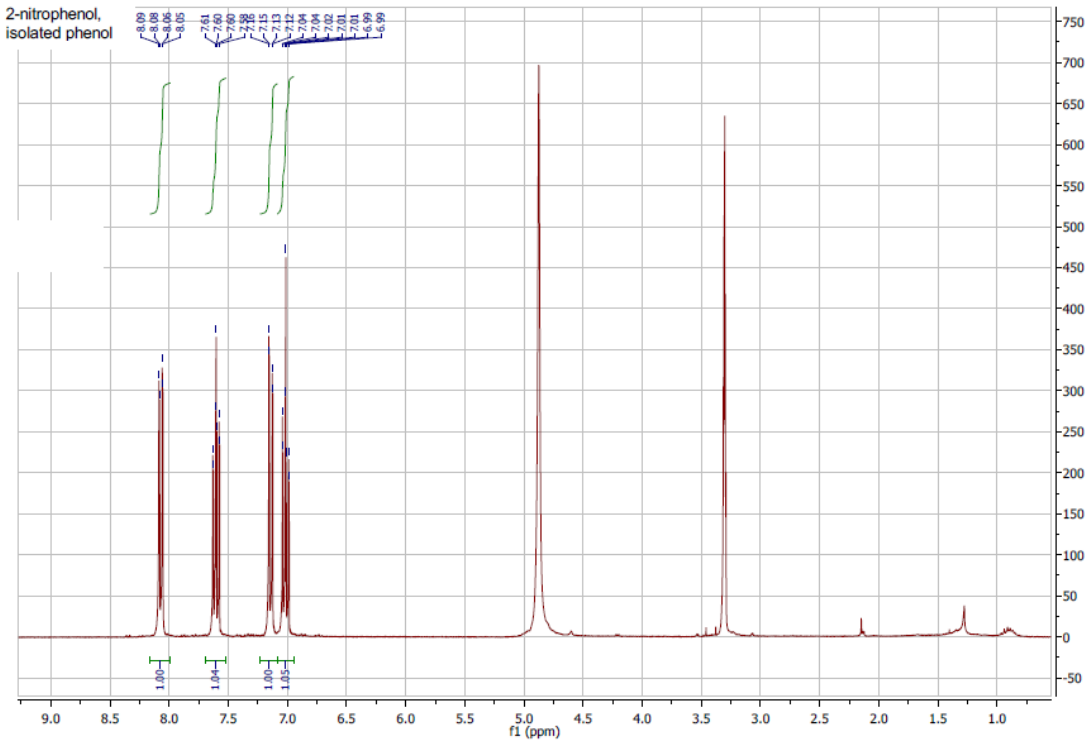


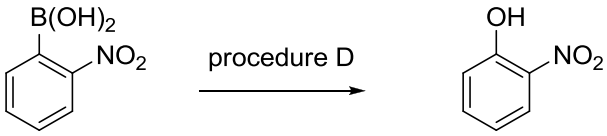
3i **4i**

Reaction mixture – procedure C



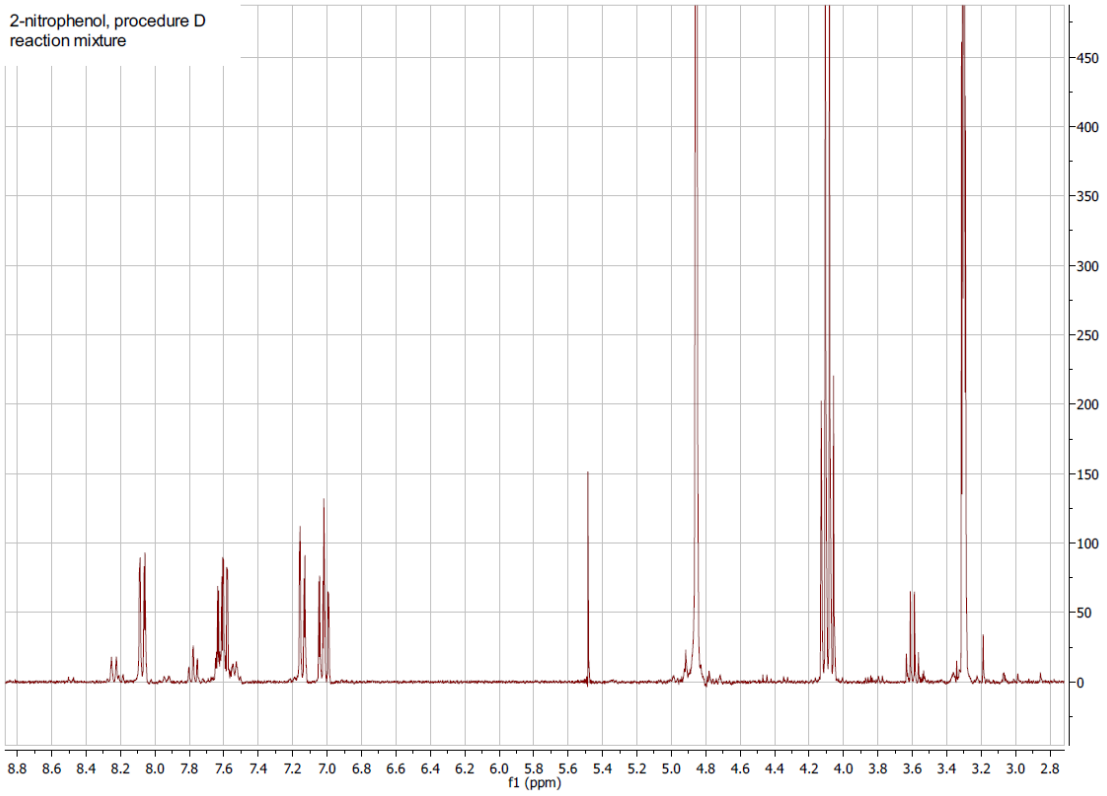
Isolated phenol **4i** – procedure C



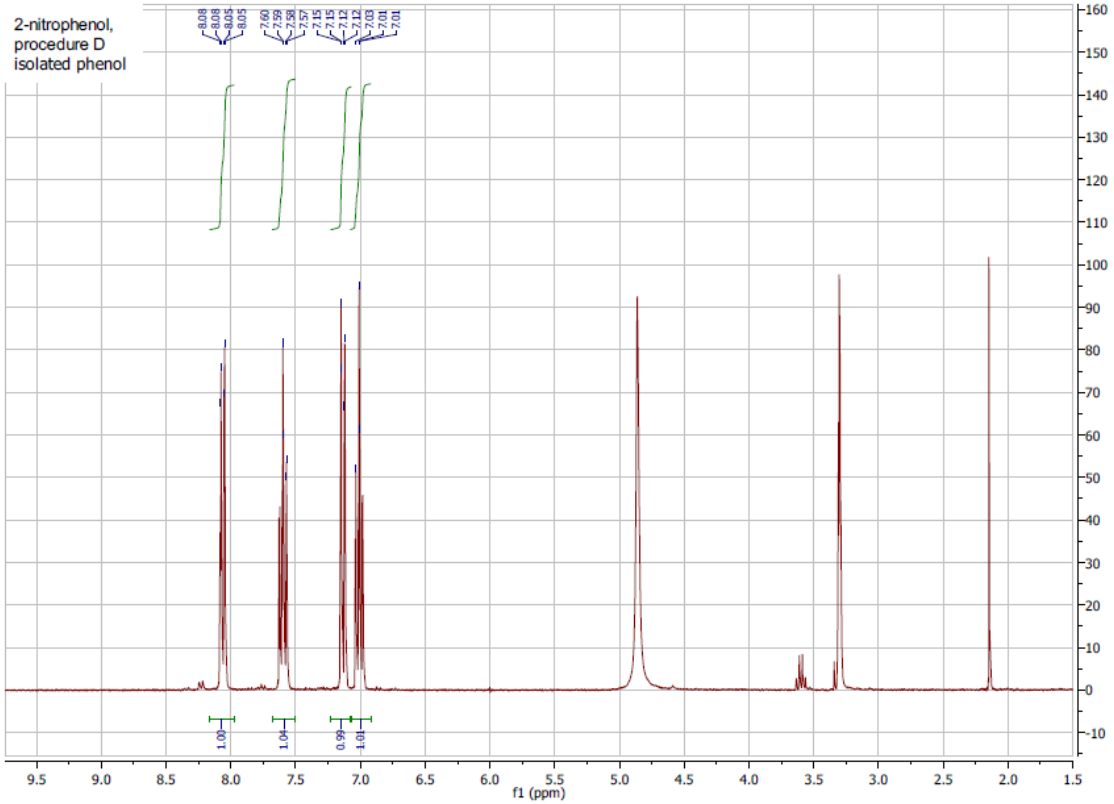


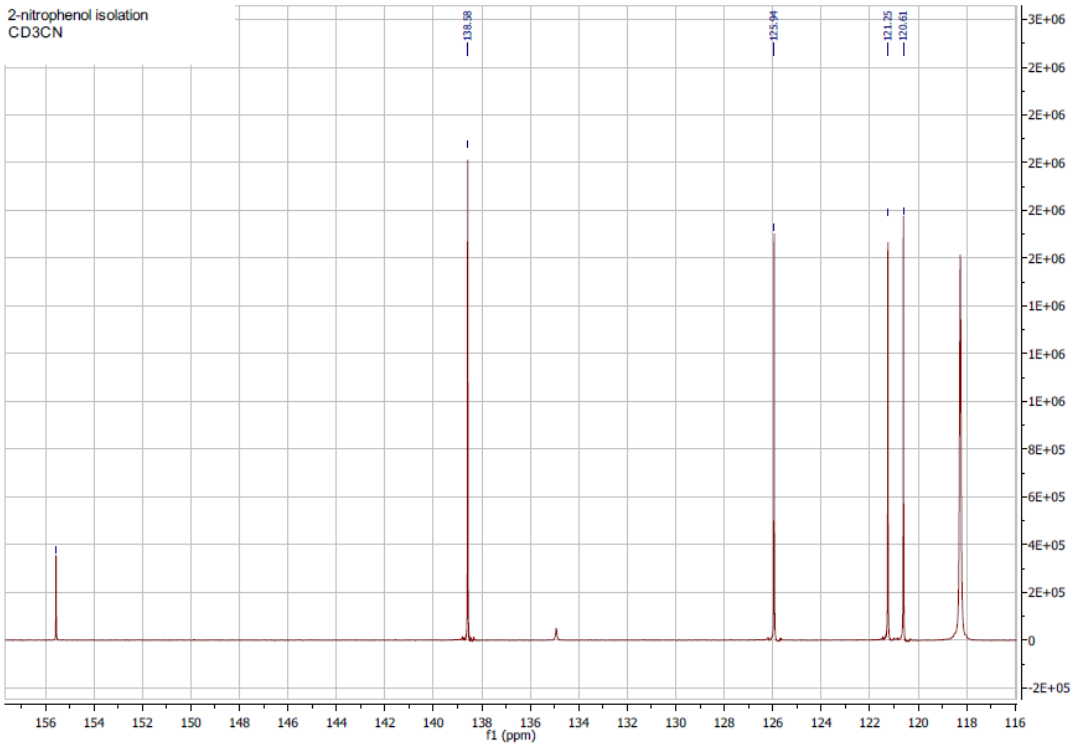
3i **4i**

Reaction mixture – procedure D

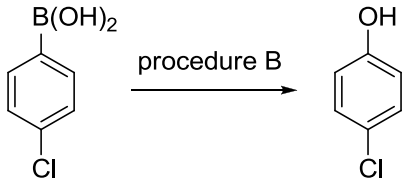


Isolated phenol **4i** – procedure D (^{1}H and ^{13}C NMR)



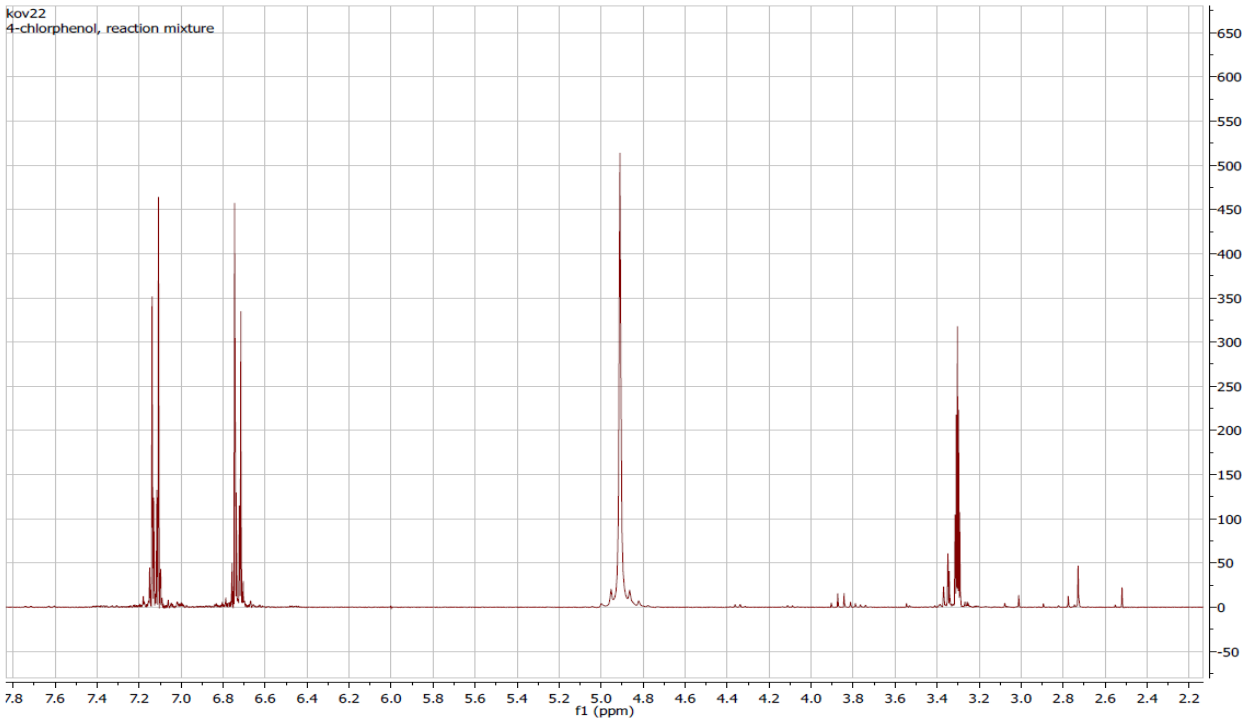


4-Chlorophenol (4j)

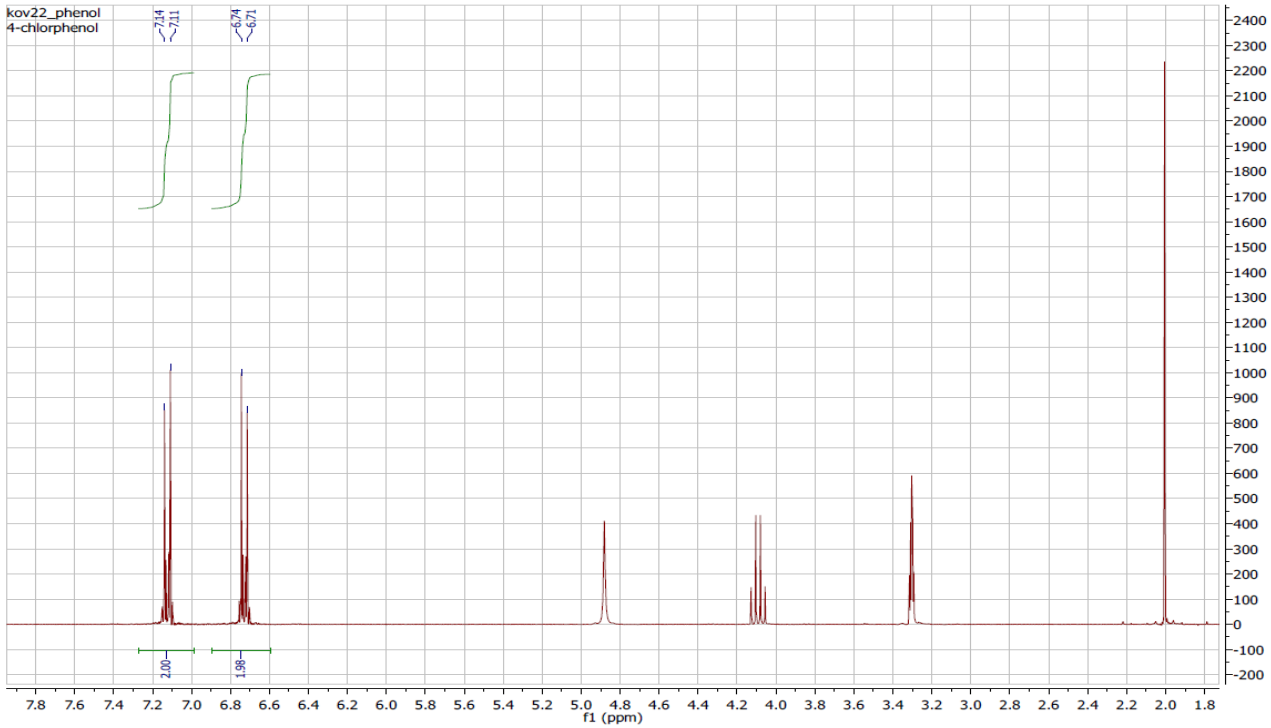


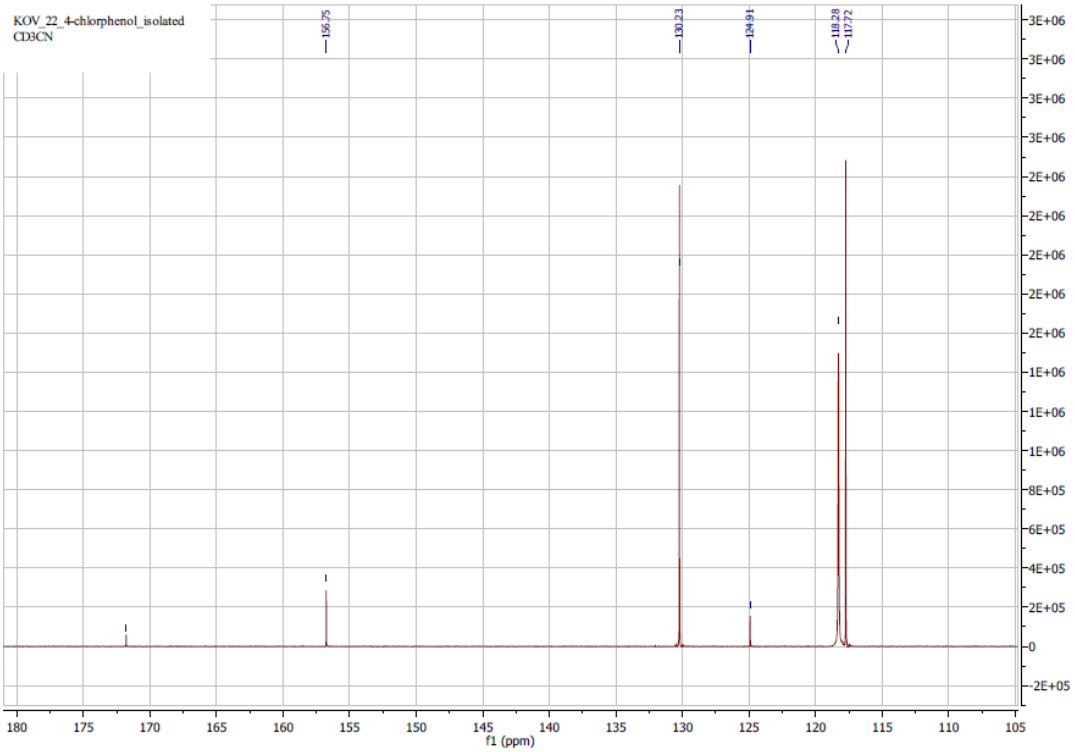
3j **4j**

Reaction mixture

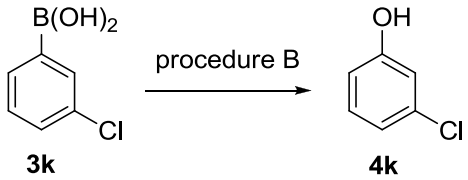


Isolated phenol **4j** (^{1}H and ^{13}C NMR)



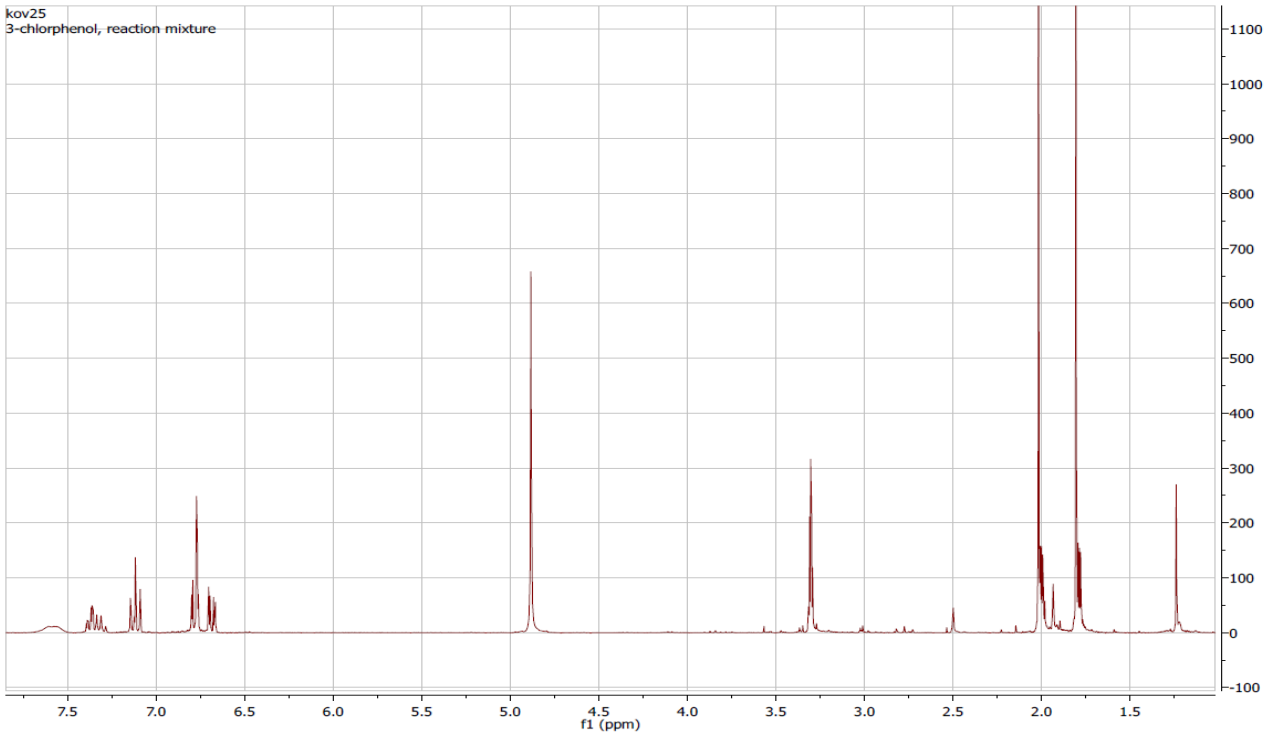


3-Chlorophenol (4k)

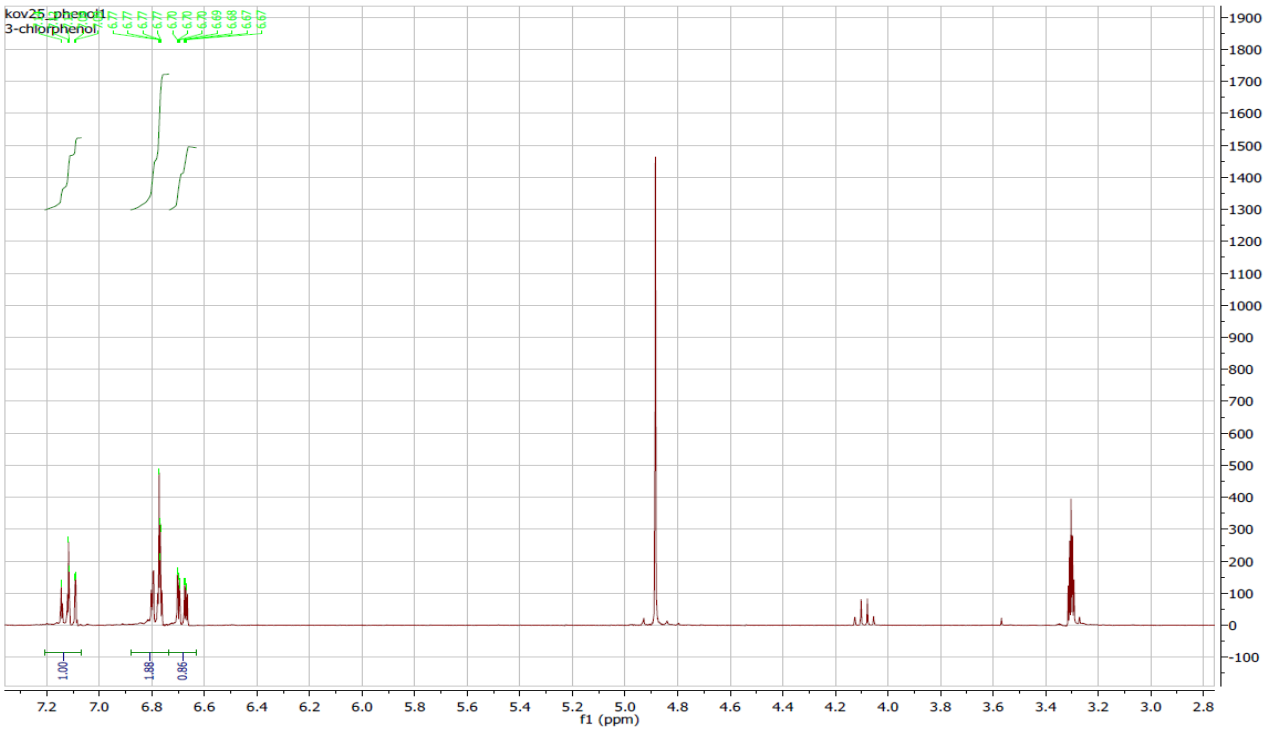


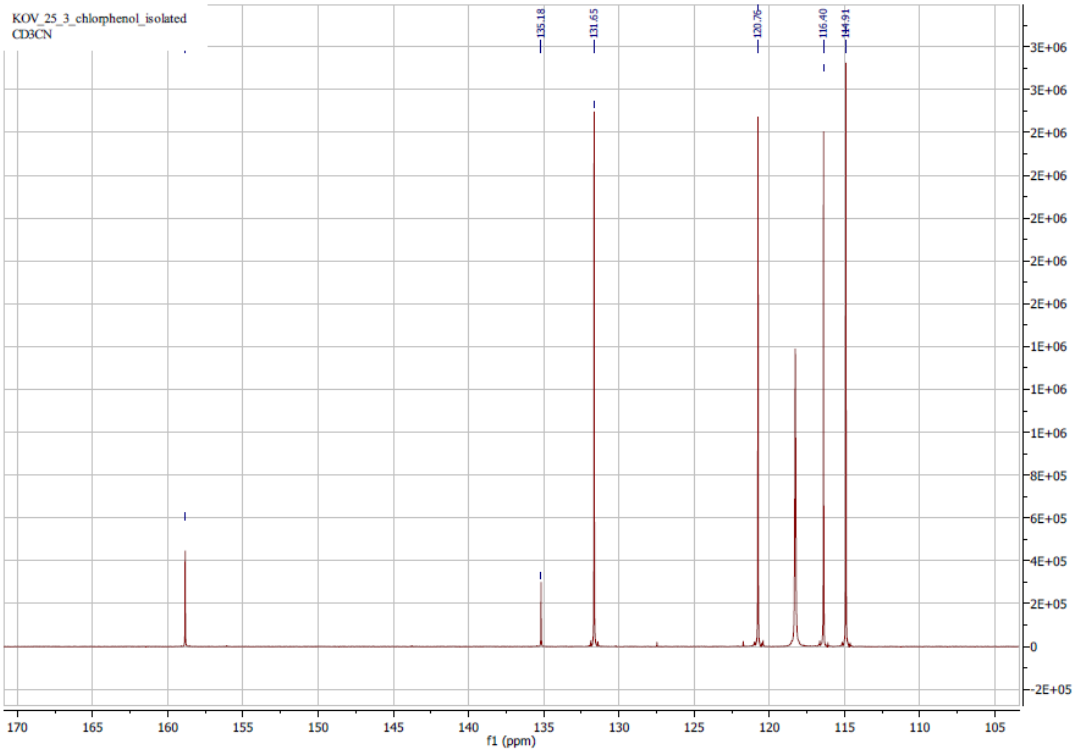
3k **4k**

Reaction mixture

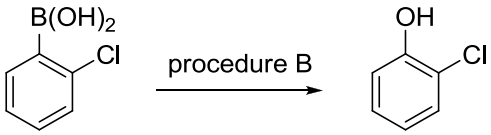


Isolated phenol **4k** (^{1}H and ^{13}C NMR)



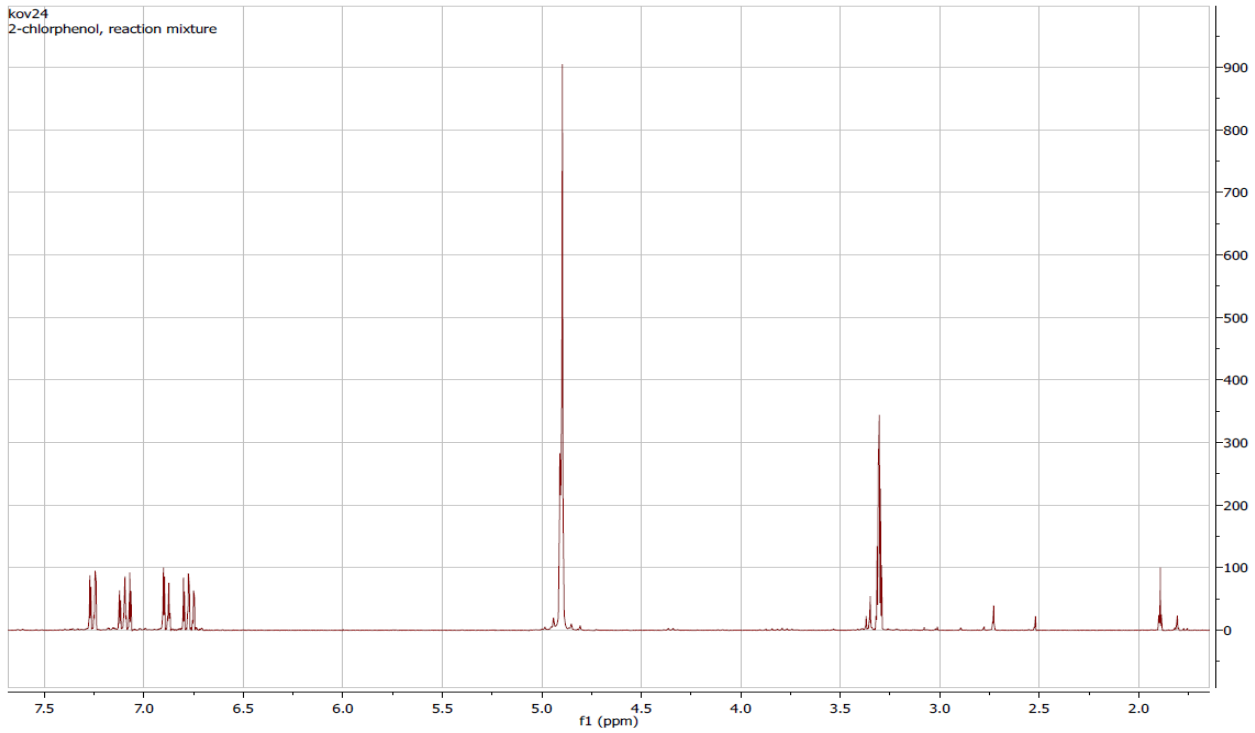


2-Chlorophenol (4l)

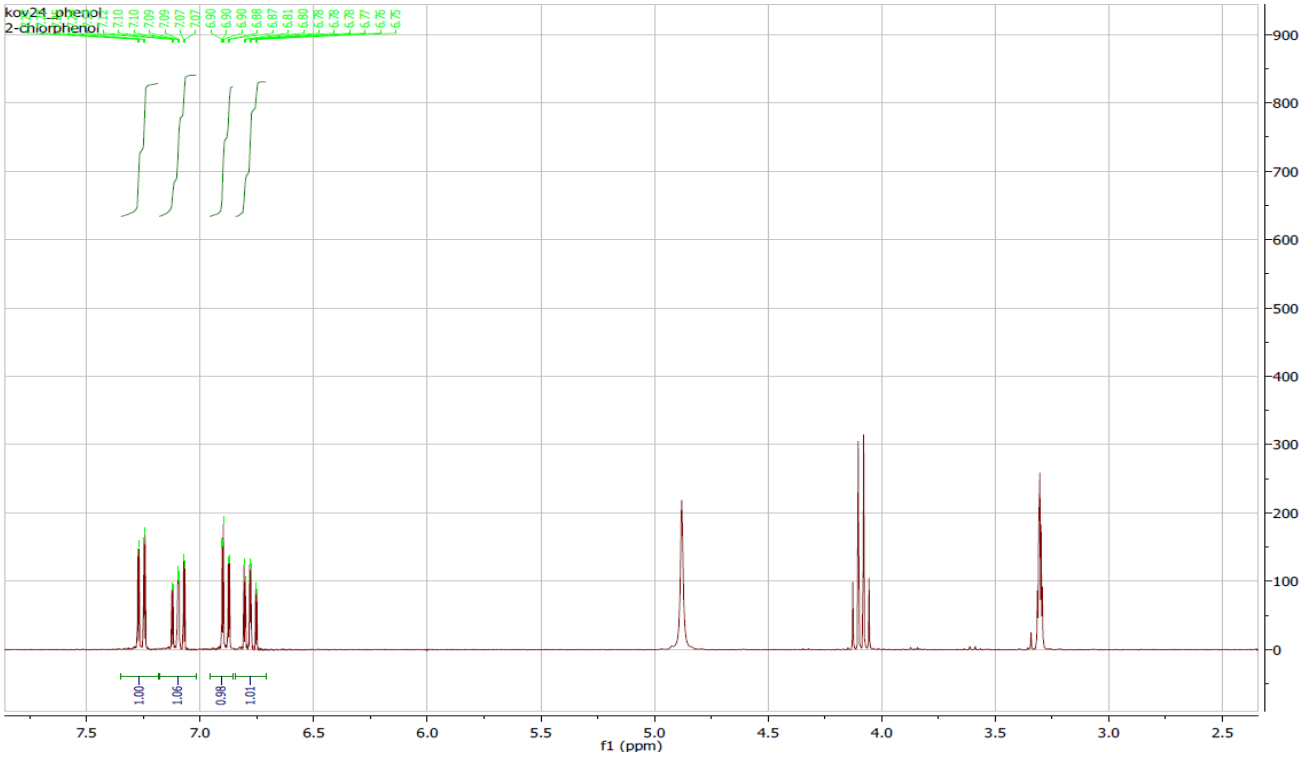


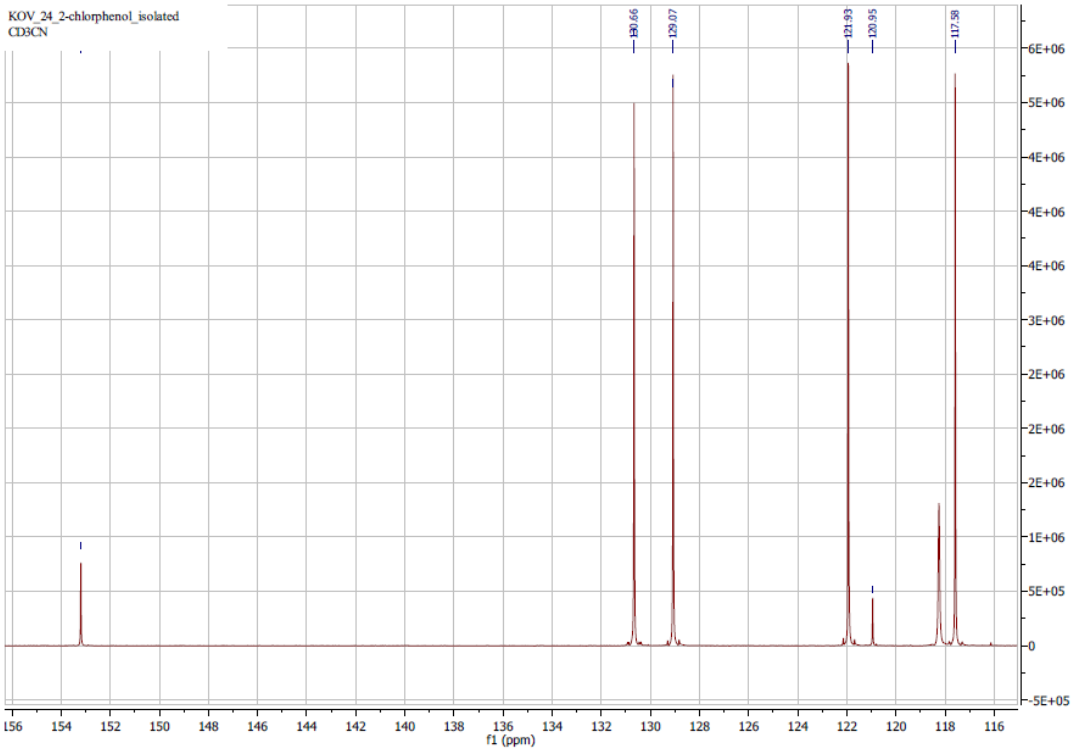
3l **4l**

Reaction mixture

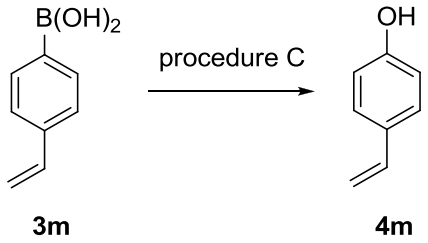


Isolated phenol **4l** (^{1}H and ^{13}C NMR)



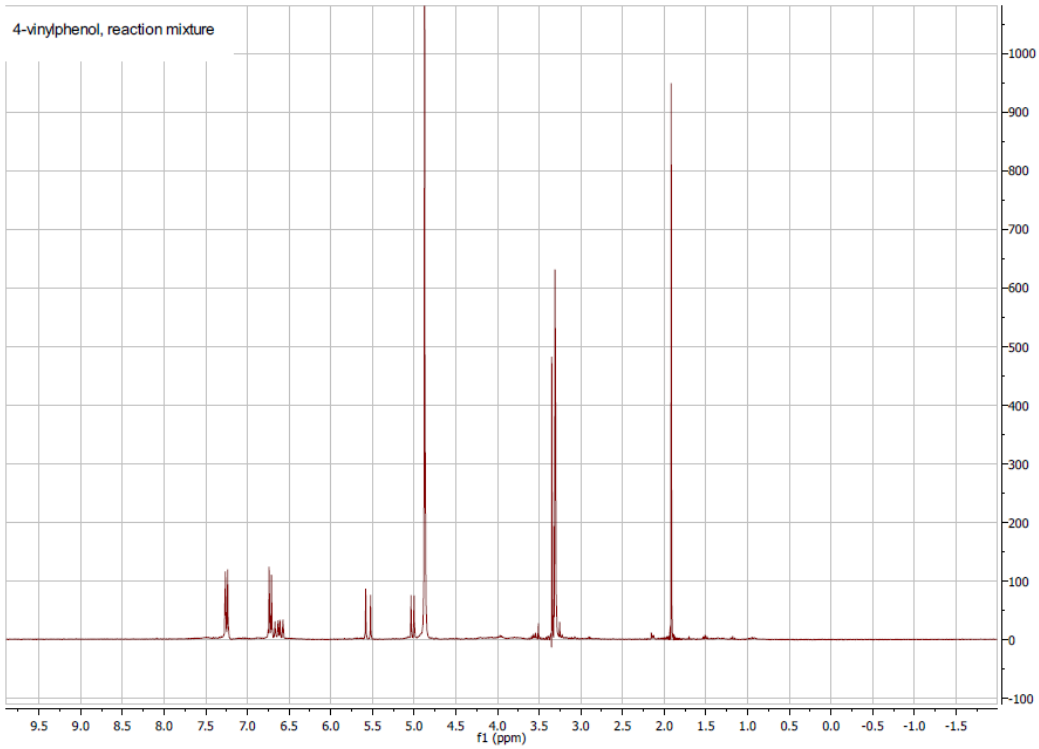


4-Vinylphenol (4m)

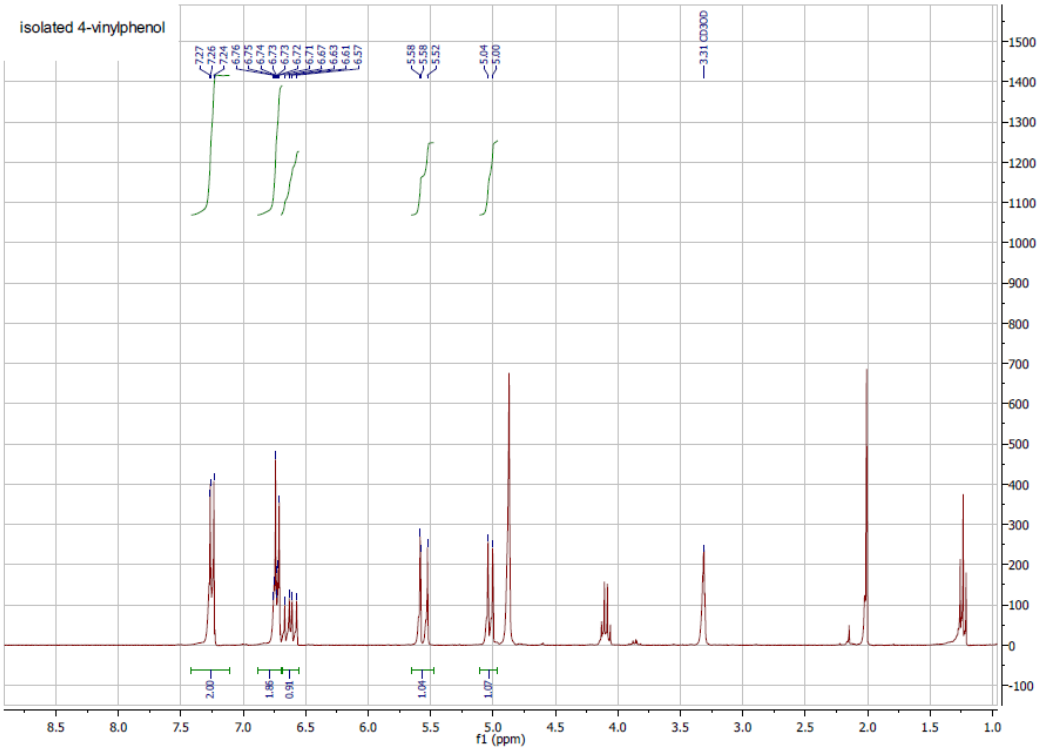


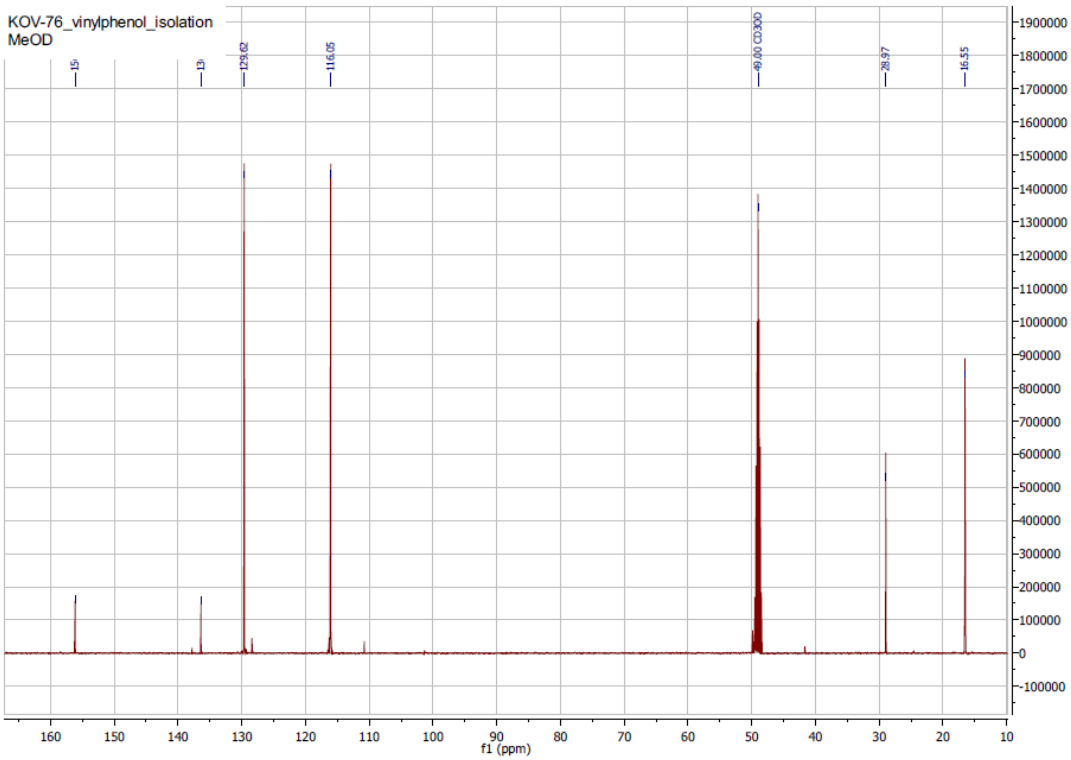
3m **4m**

Reaction mixture

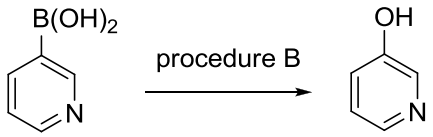


Isolated phenol **4m** (^{1}H and ^{13}C NMR)



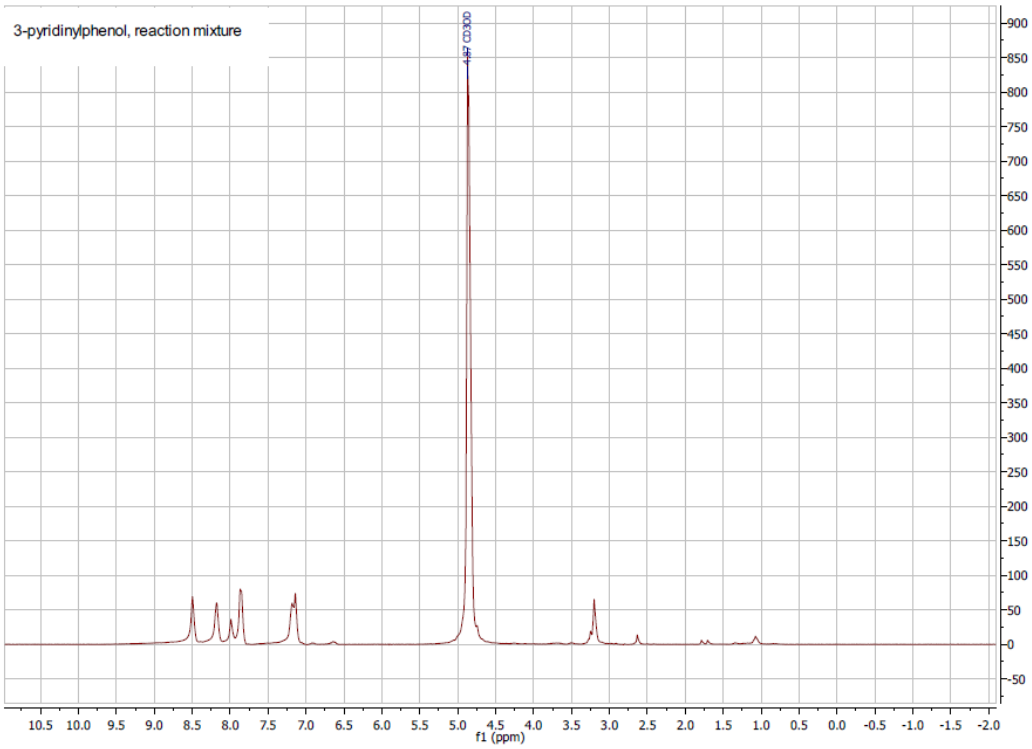


3-Pyridinylphenol (4n)

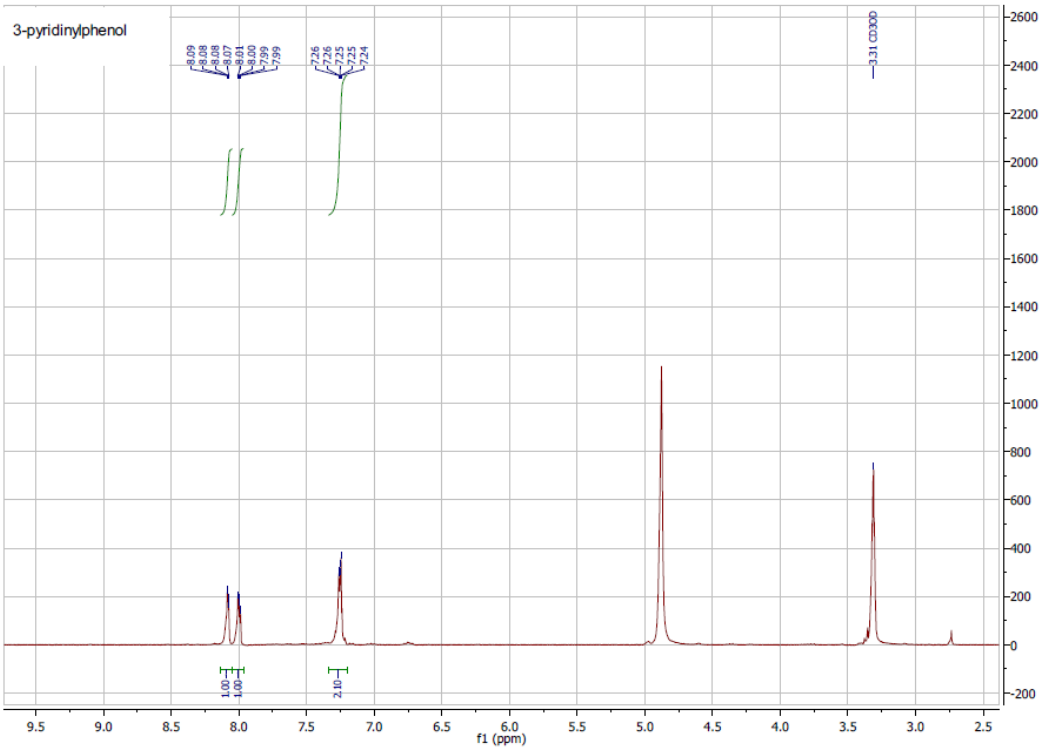


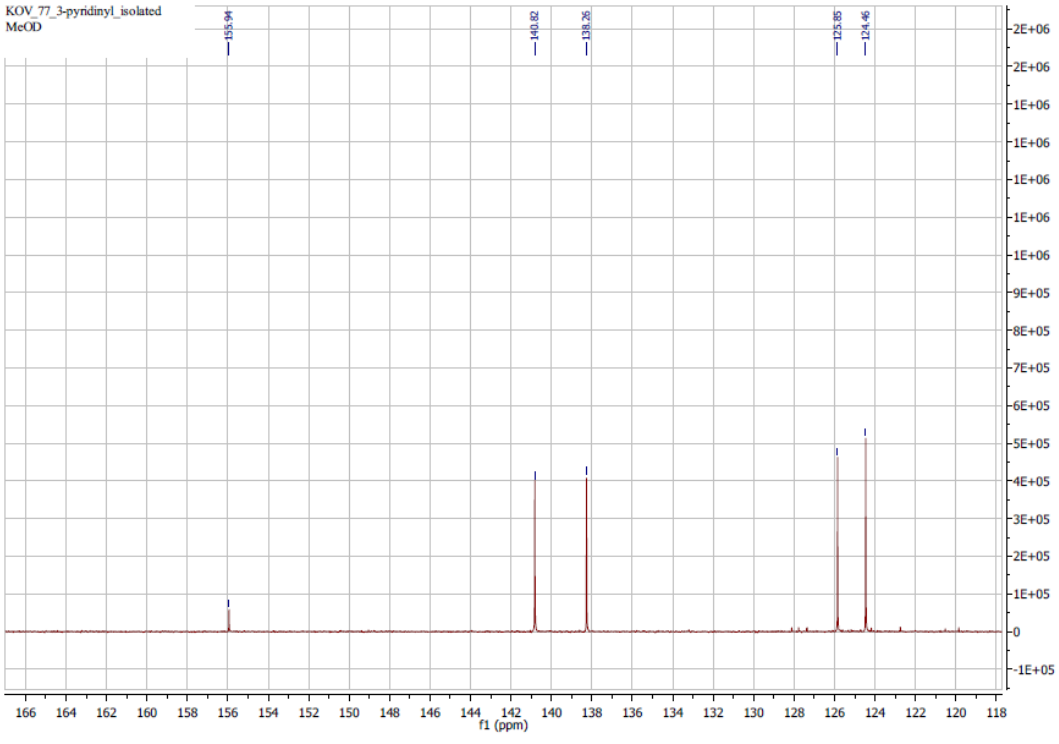
3n **4n**

Reaction mixture

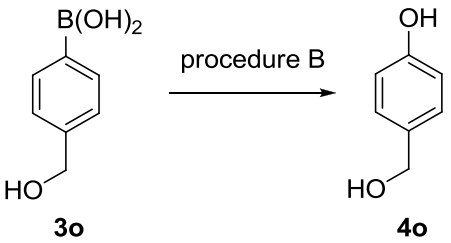


Isolated phenol **4n** (^{1}H and ^{13}C NMR)



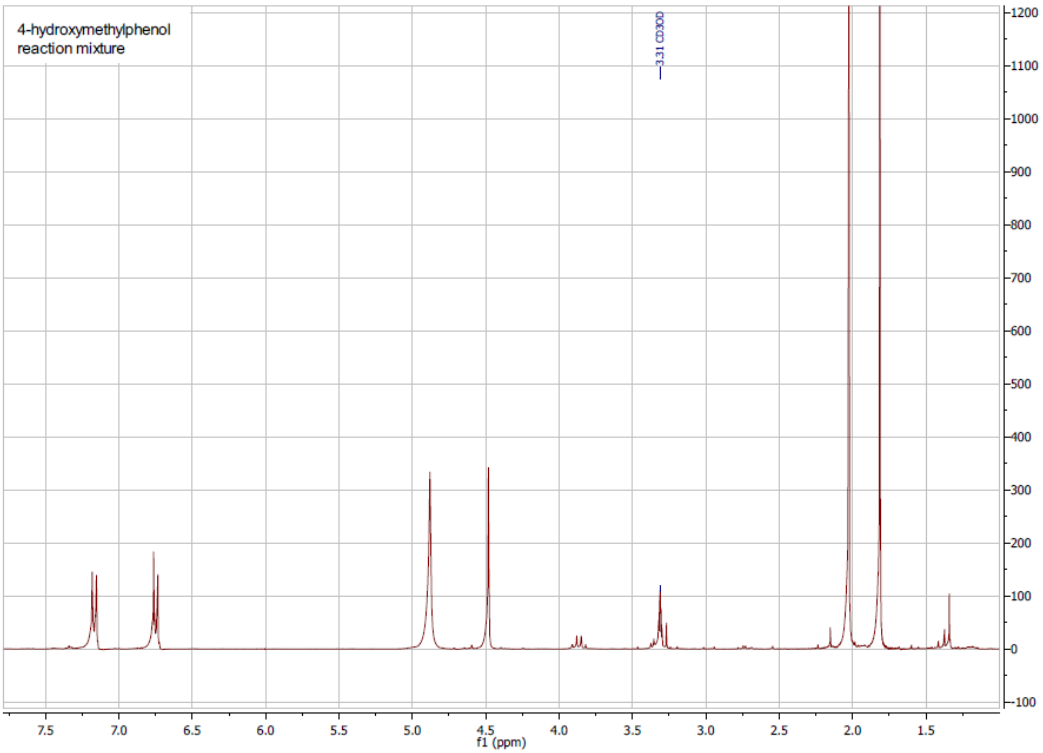


4-(Hydroxymethyl)phenol (4o)

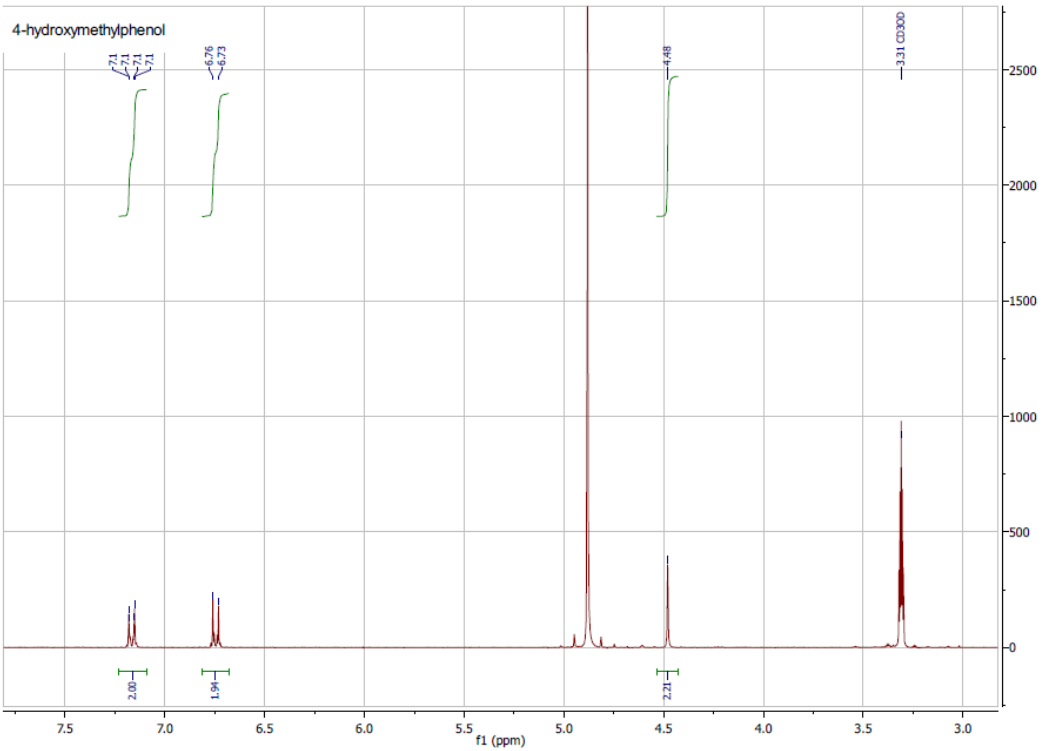


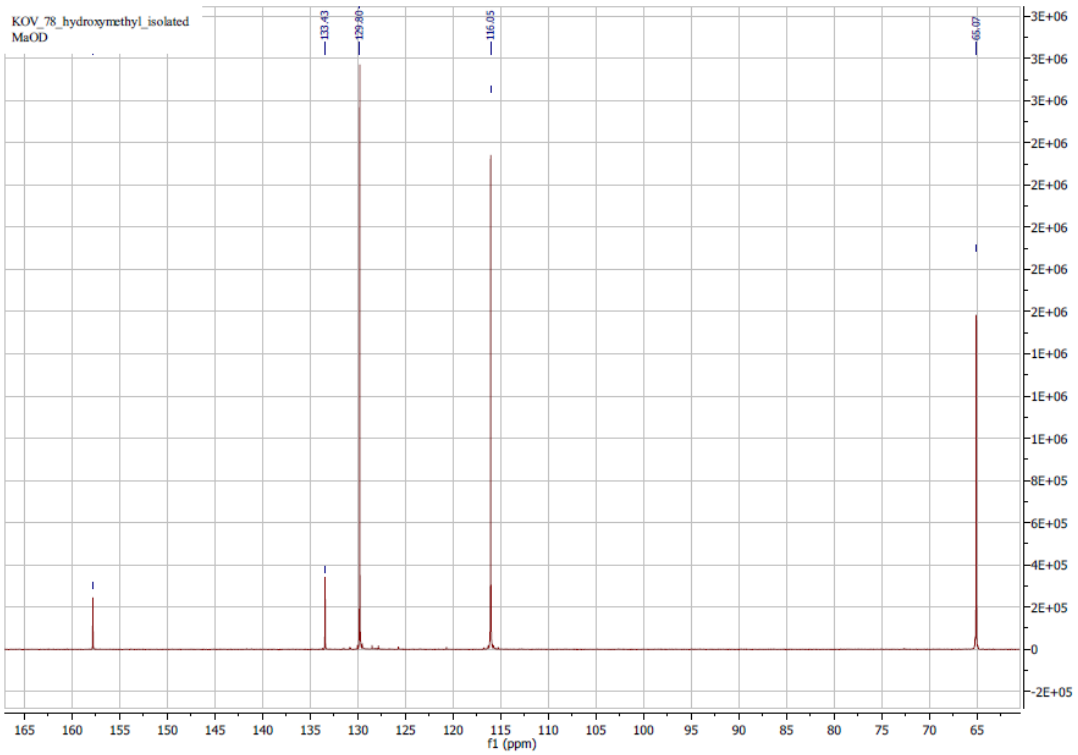
3o **4o**

Reaction mixture

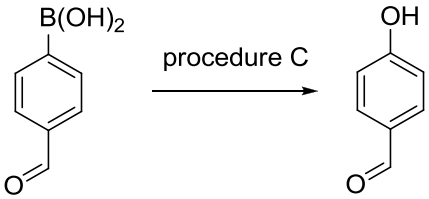


Isolated phenol **4o** (^{1}H and ^{13}C NMR)



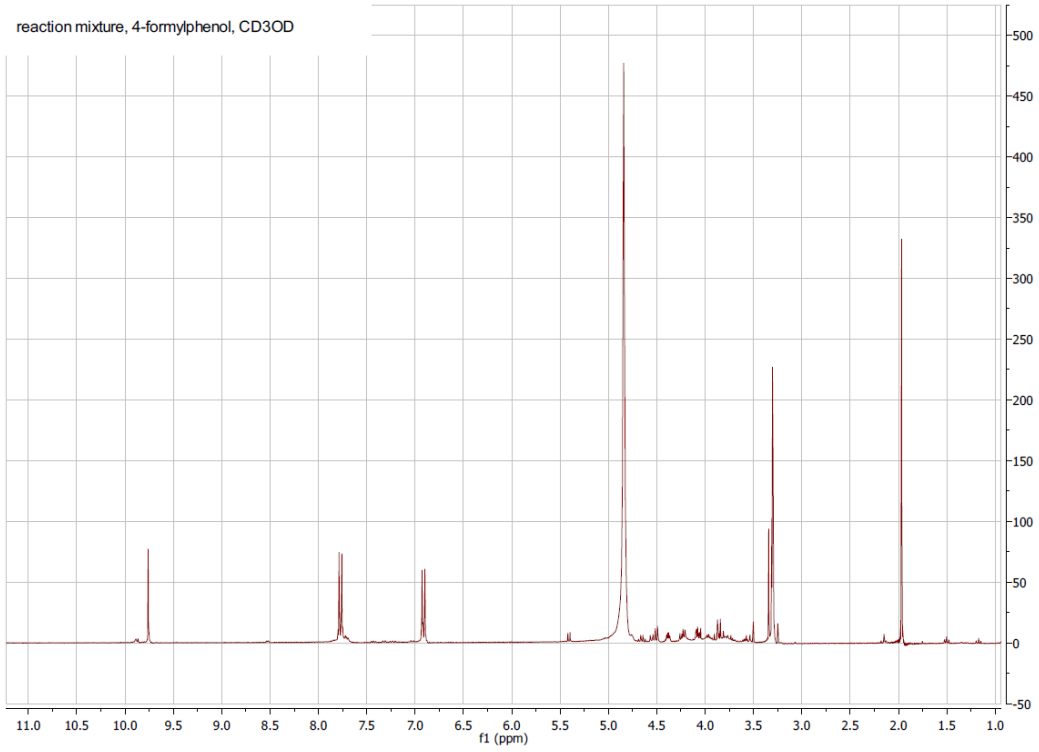


4-Hydroxybenzaldehyde (4p)

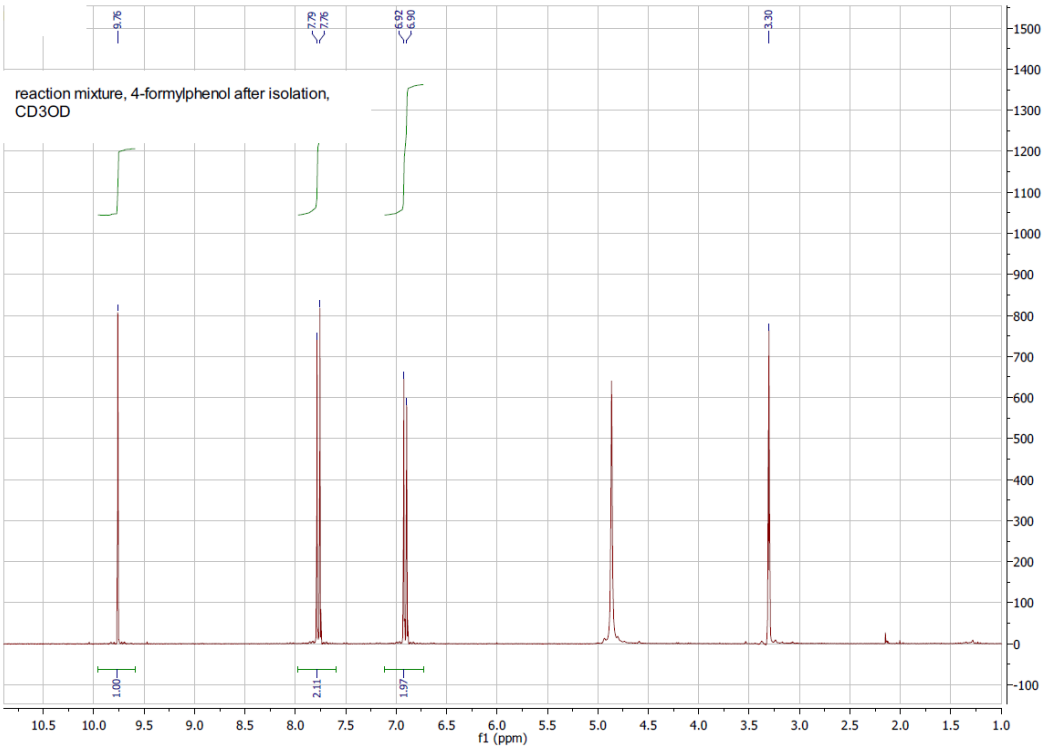


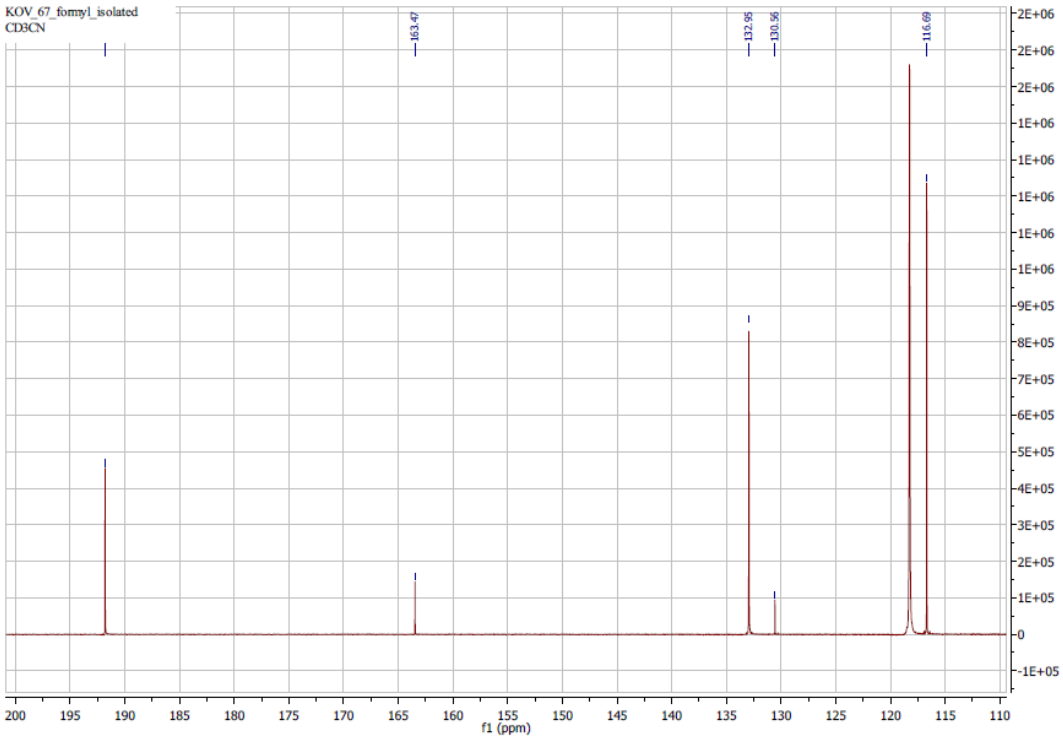
3p **4p**

Reaction mixture

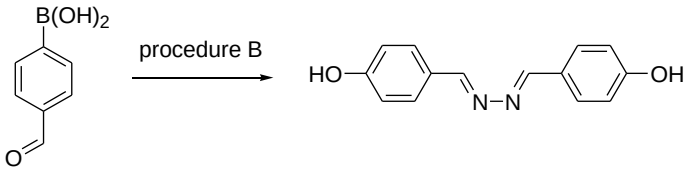


Isolated phenol **4p** (^{1}H and ^{13}C NMR)



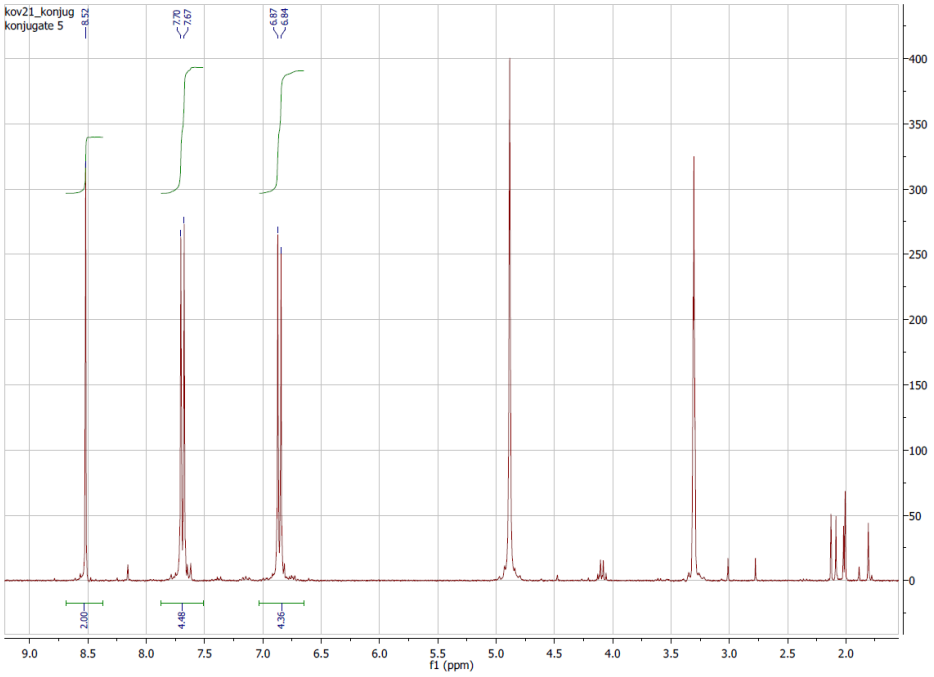


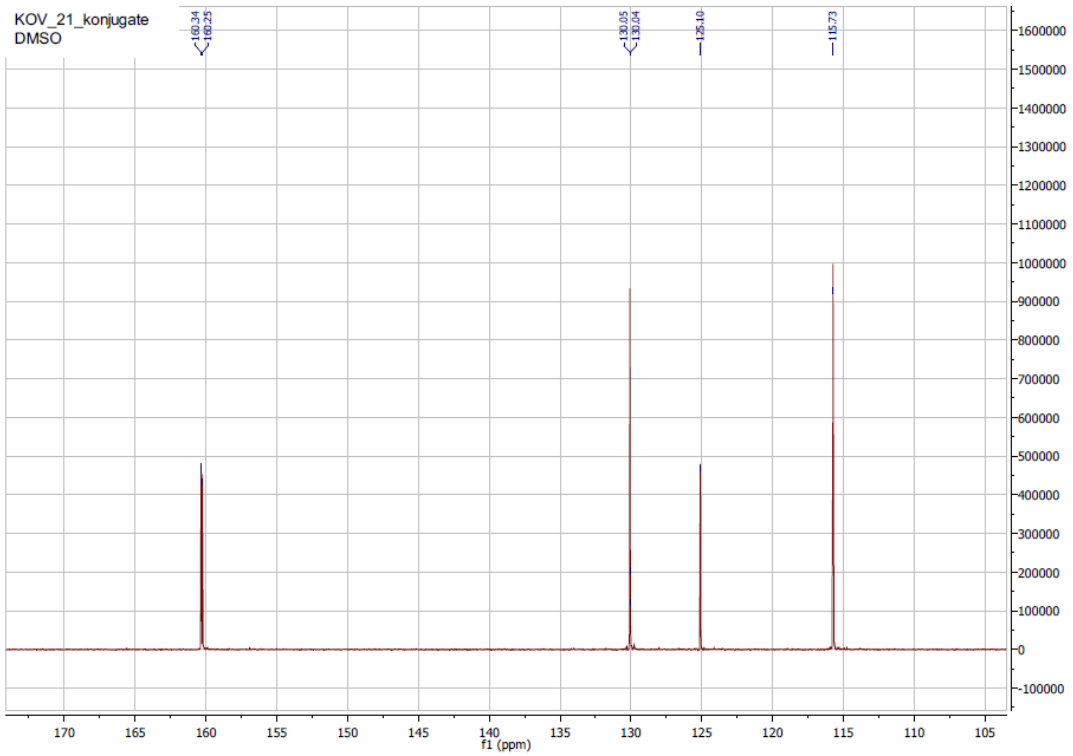
Bis(4-hydroxybenzylidene)hydrazine (5)



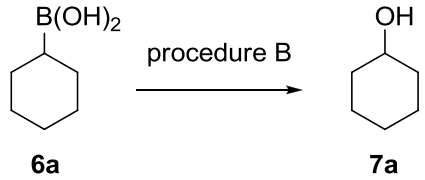
3l **5**

Isolated conjugate **5** (^{1}H and ^{13}C NMR)

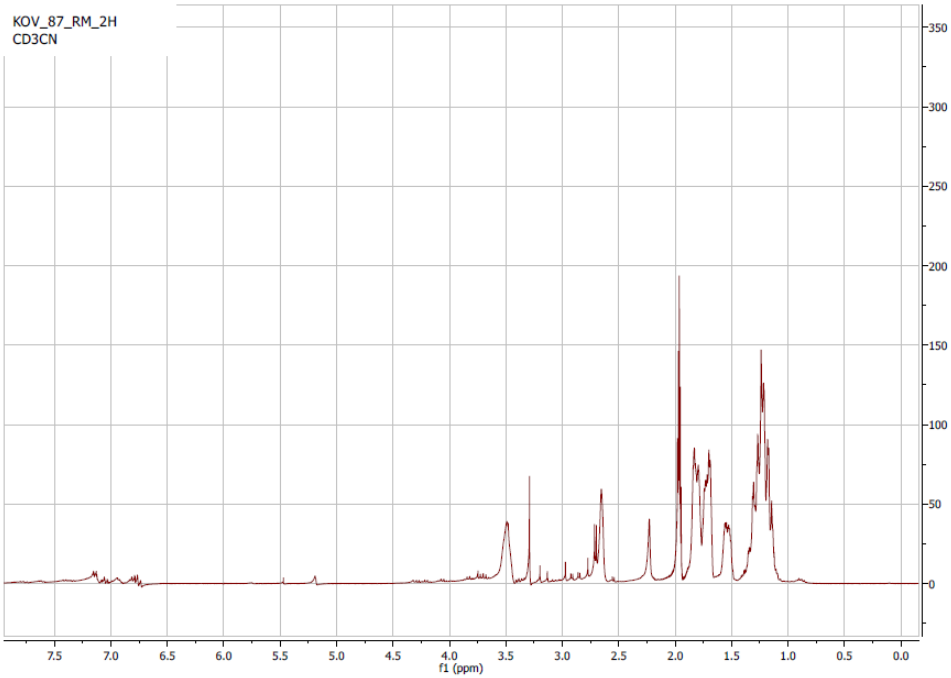




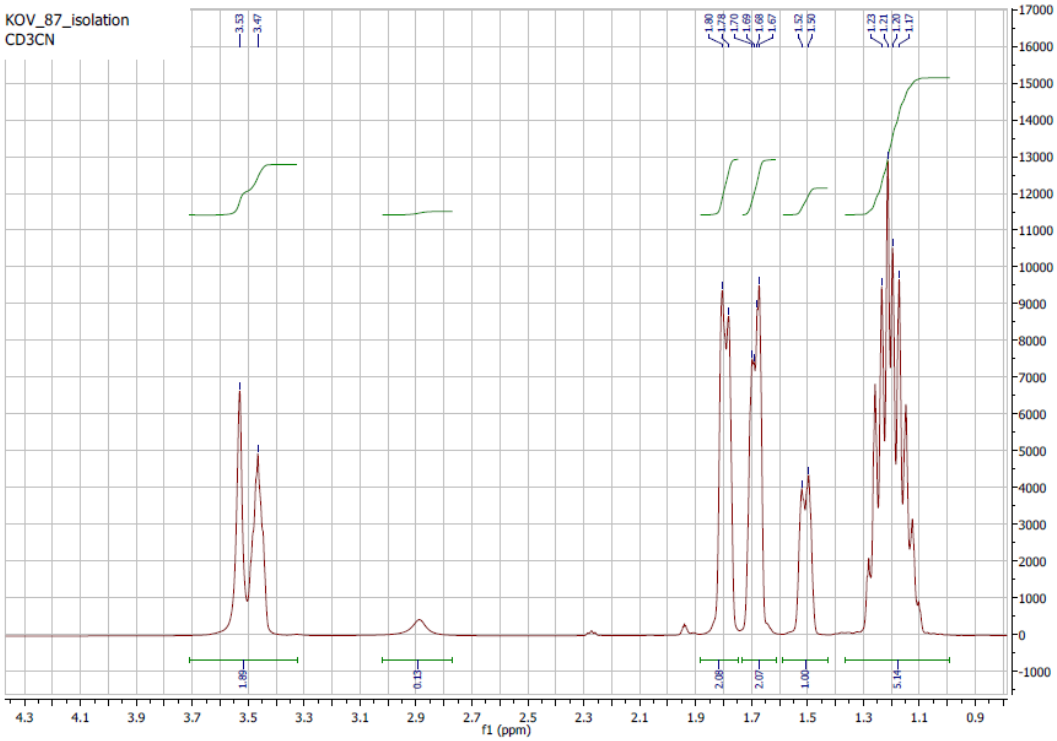
Cyclohexanol (7a)

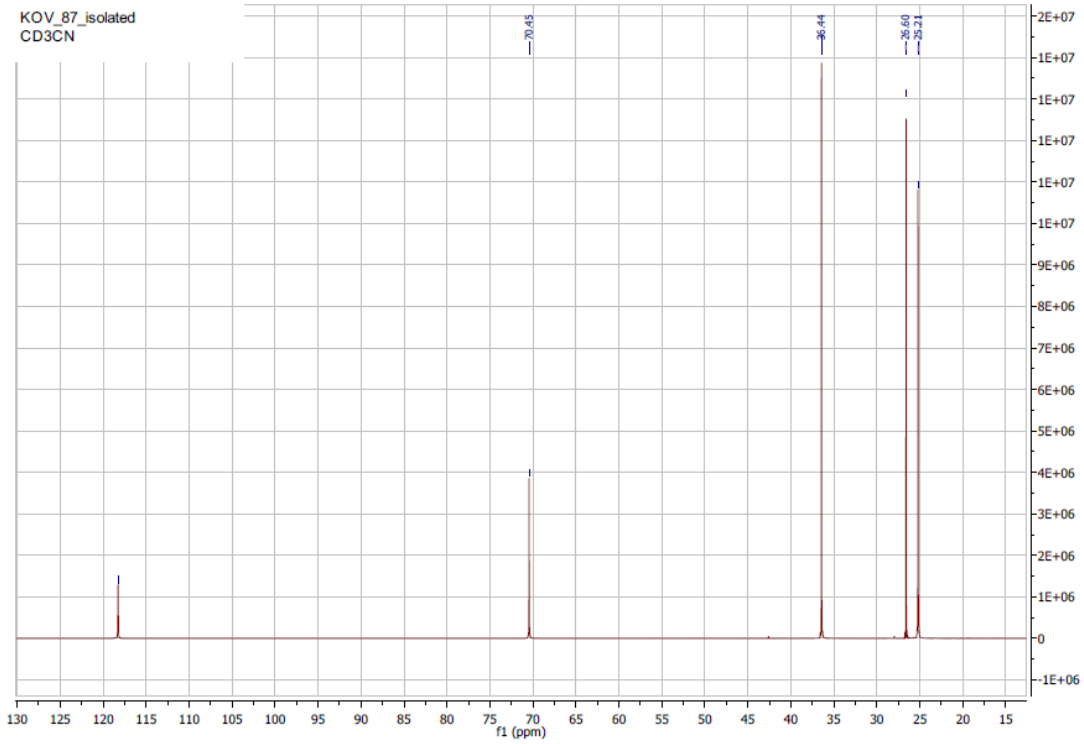


Reaction mixture

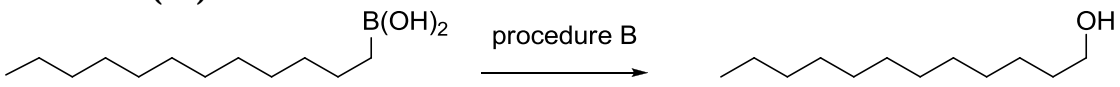


Isolated alcohol **7a** (^{1}H and ^{13}C NMR)



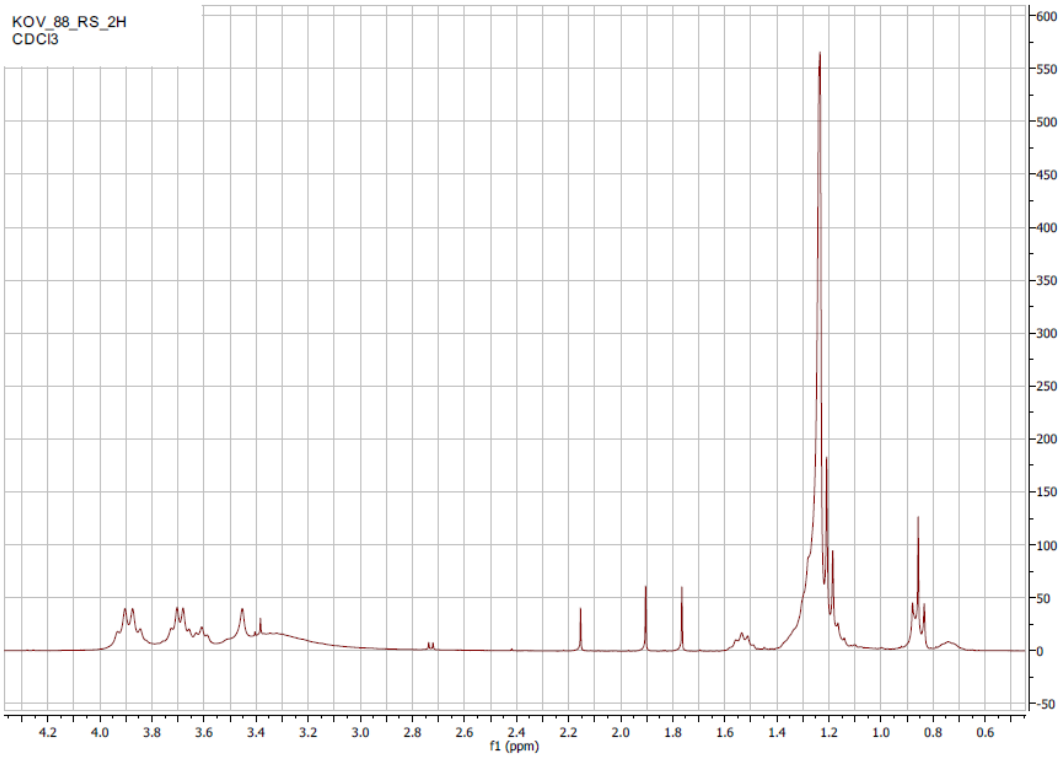


Dodecanol (7b)

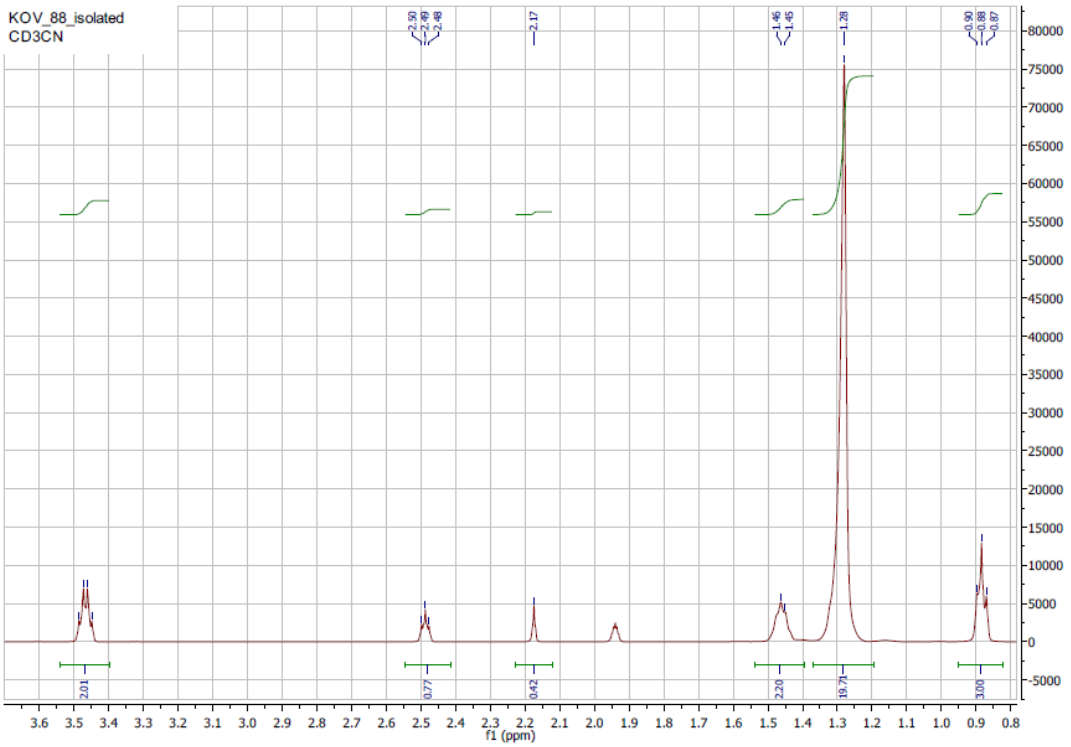


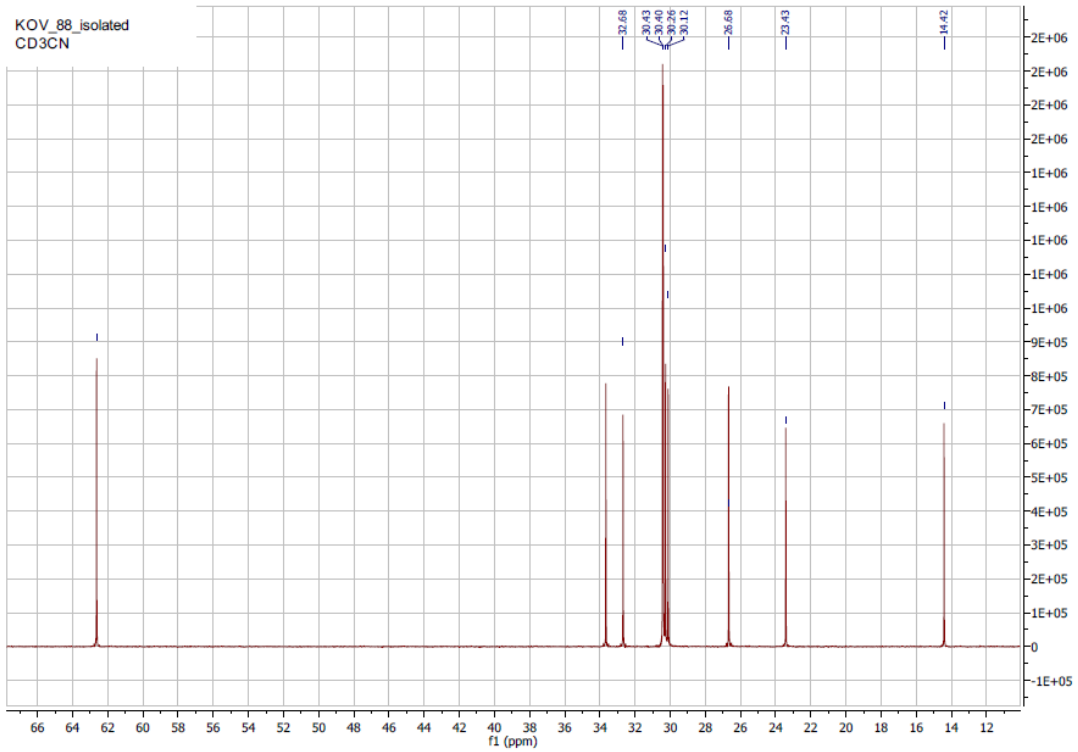
6b **7b**

Reaction mixture



Isolated alcohol **7b** (^{1}H and ^{13}C NMR)





S4 Course of oxidative hydroxylations monitored by ^{1}H and ^{11}B NMR

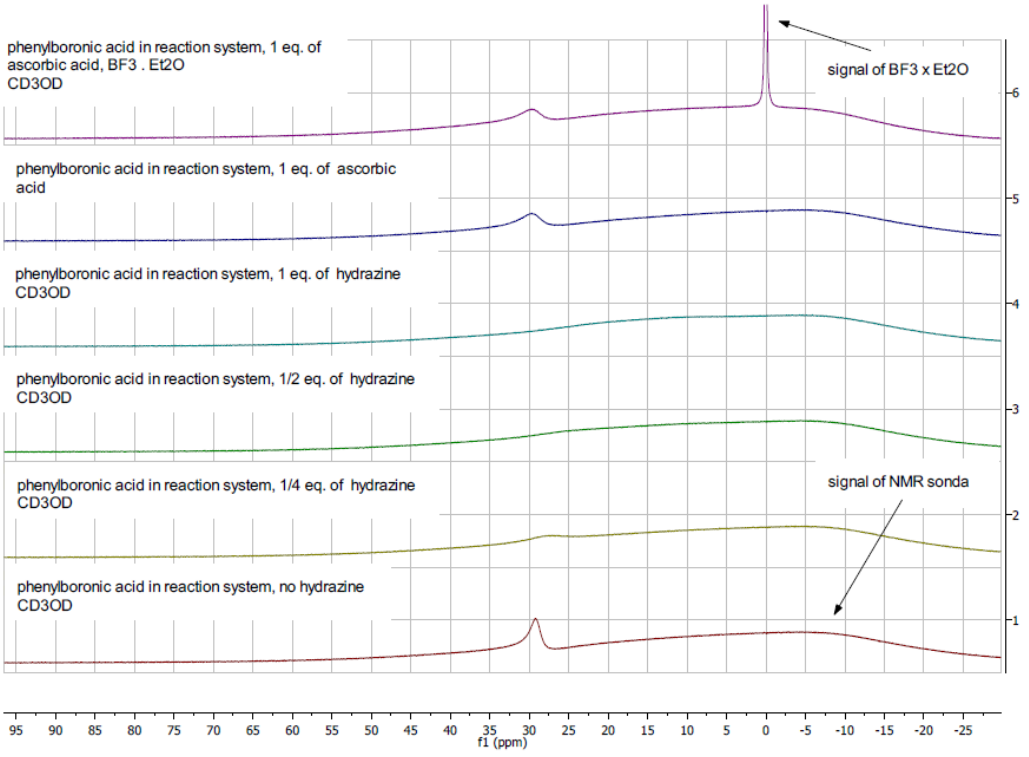
Hydroxylations carried out on analytical scale – general procedure E

Boronic acid (7.9 x 10^{-5} mol) and reducing agent (10.6 x 10^{-5} mol) and other additives were dissolved or suspended in 0.6 mL of solvent and starting ^{1}H NMR and ^{11}B NMR (blank) was measured. Then catalyst **2** (0.4 x 10^{-5}mol) was added and reaction mixture was transferred to small flask under balloon with oxygen and shaken. Spectra for kinetic studies were performed in defined times and the reaction mixture was every time transported from flask to NMR cell and after measurement again to flask to continue the reaction. D_2O, CD_3CN or methanol-d_4 were used as deuterated solvents.

Effect of hydrazine and ascorbic acid on ^{11}B NMR spektra.

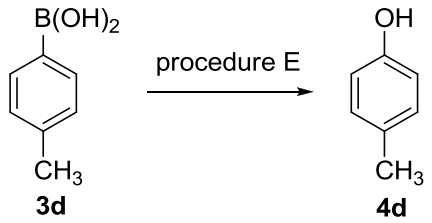
Phenylboronic acid **3a** was dissolved in the mixture of CF_3CH_2OH (400 uL) and CD_3OD (200 uL). Hydrazine hydrate or ascorbic acid (full amount 7.92 uL; 1.3 eq.) was added by parts to this solution into NMR cell and the broadening of boron signal in ^{11}B NMR spectra was observed. No change of ^{11}B NMR spectra was observed after addition of ascorbic acid. See below.

^{11}B NMR spectra, CD_3OD, hydrazine hydrate adding



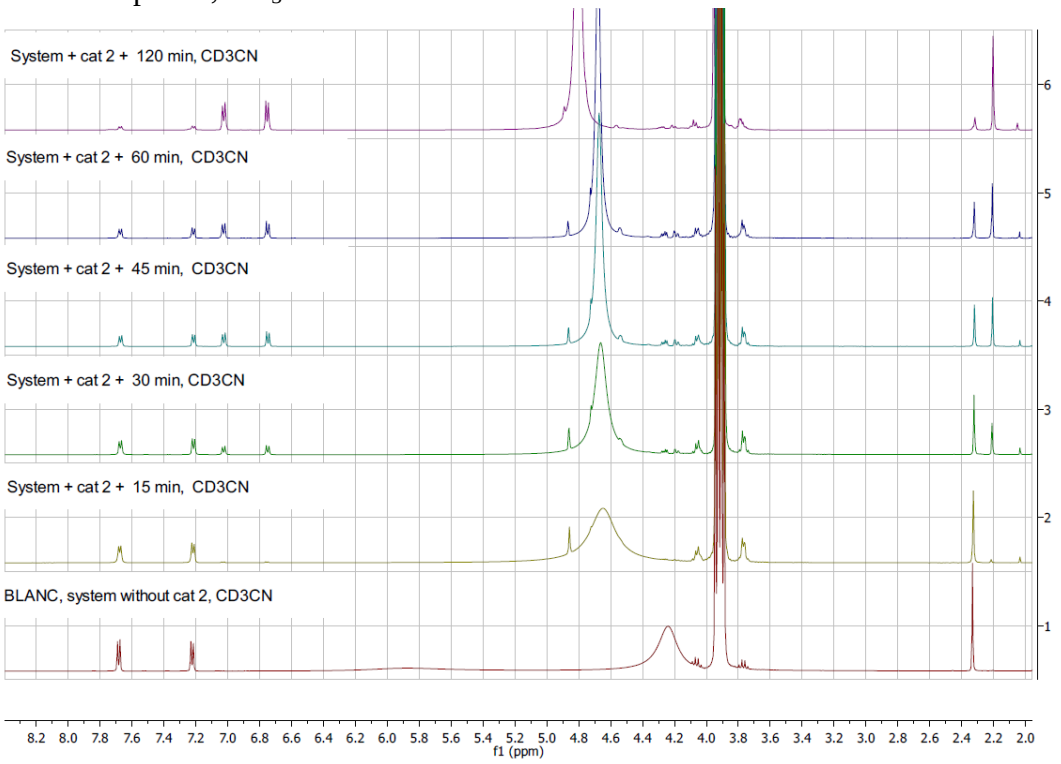
Monitoring of oxidation of 4-tolylboronic acid (3d) to 4-methylphenol (4d) in the mixture of organic solvents

Reaction was carried out according to general procedure E, CF_3CH_2OH (350 uL), CD_3CN (200 uL), D_2O (150 uL), ascorbic acid (18.31 mg; 10.4 x 10^{-5} mol), natrium acetate (0.34 mg; 10.4 x 10^{-5} mmol). (Aromatic part of spectra is shown in the main text as Figure 1)

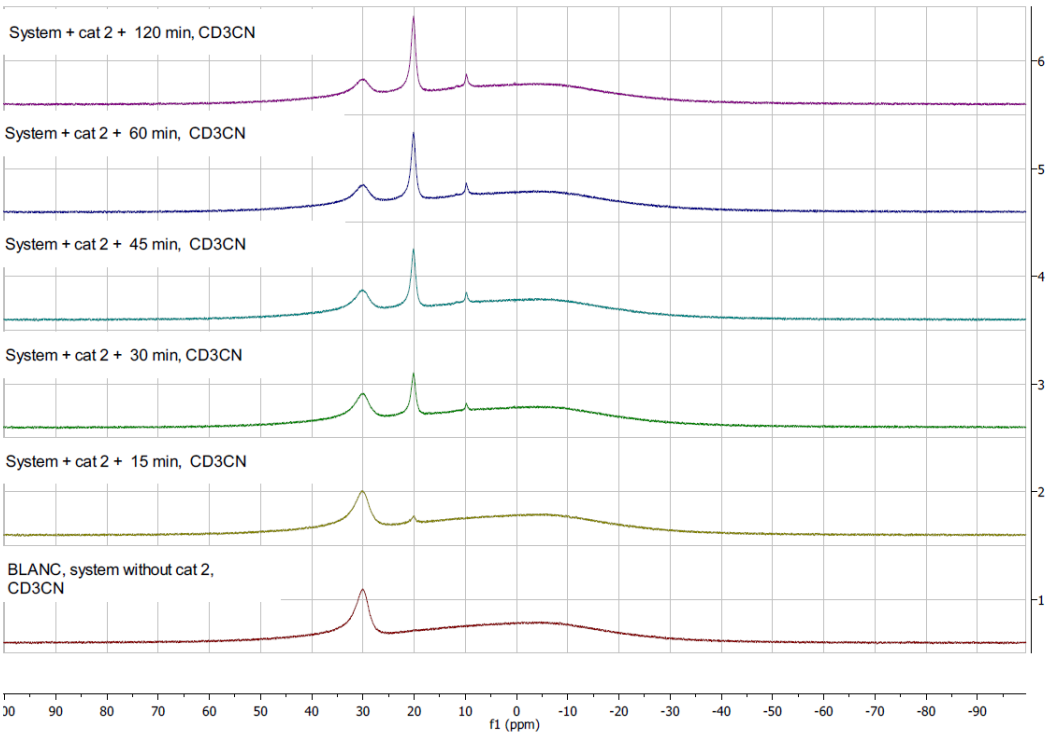


3d **4d**

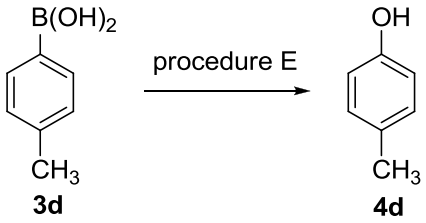
^{1}H NMR spectra, CD_3CN – full screen



^{11}B NMR spectra, CD_3CN – full screen

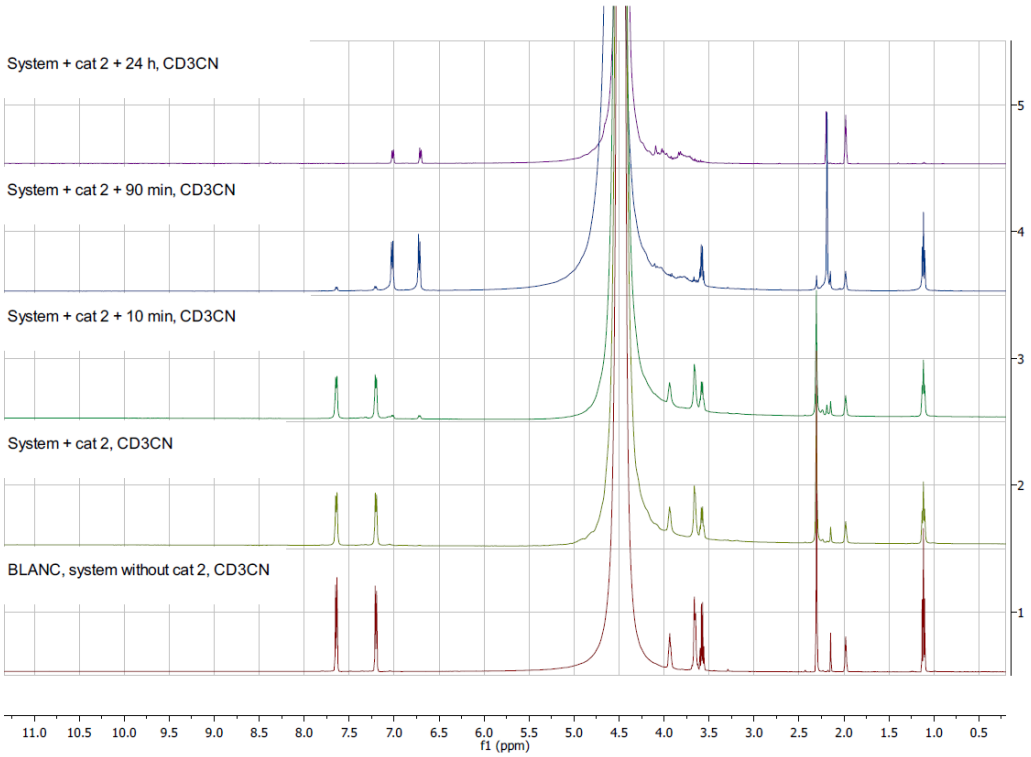


Monitoring of oxidation of 4-tolylboronic acid (3d) to 4-methylphenol (4d) in aqueous solution
Reaction was carried out according to general procedure E, phosphate buffer pH = 7.5 (400 uL), CD_3CN (200 uL), ascorbic acid (18.31 mg; 10.4 x 10^{-5} mol), natrium acetate (0.34 mg; 10.4 x 10^{-5} mmol)

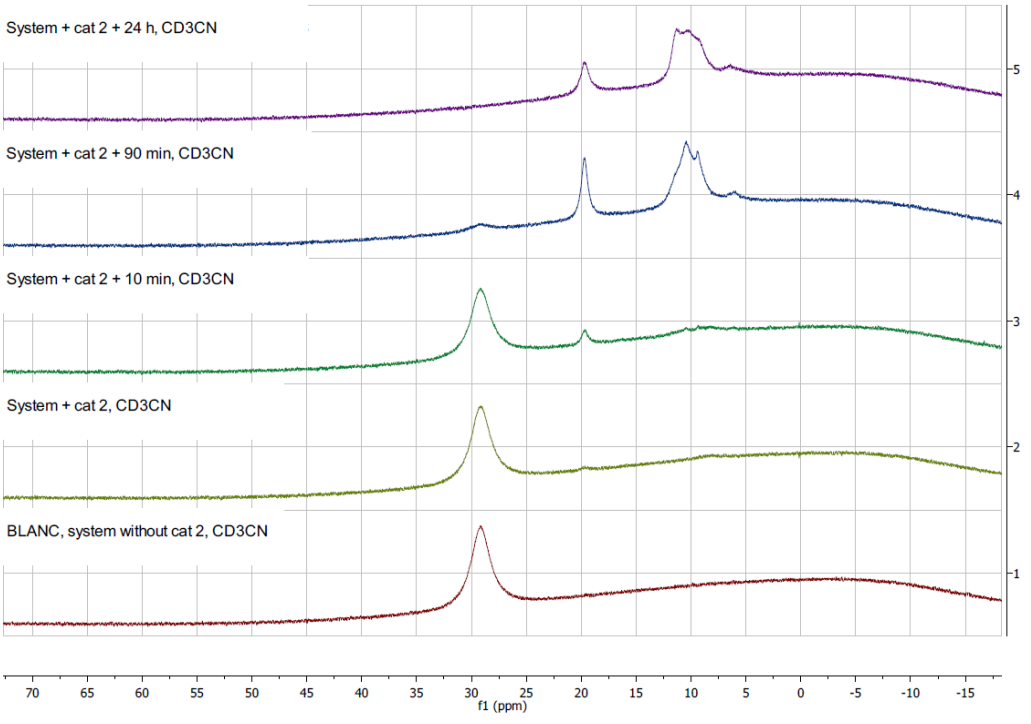


3d **4d**

^1H NMR spectra, CD_3CN – full screen

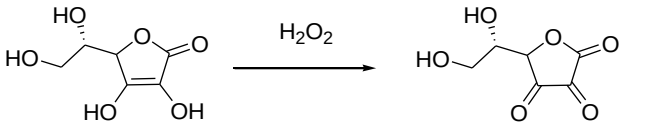


^{11}B NMR spectra, CD_3CN – full screen (unexpected peak at 10 ppm corresponds to complex between boric acid and dehydroascorbic acid, see explanation bellow)



Explanation of unexpected peaks in ^{11}B NMR spectra –generation of dehydroascorbic acid from ascorbic acid and its interaction with boric acid

Ascorbic acid (14.09 mg; 7.9×10^{-5} mol) and natrium acetate (0.34 mg; 10.4×10^{-5} mol) were dissolved in the mixture of trifluoroethanol (350 uL), D_2O (150 uL) and CD_3OD (100 uL) in NMR cell. After blank measurement boric acid (4.88 mg; 7.9×10^{-5} mol) and hydrogen peroxide (2.42 mL 30% water solution; 7.9×10^{-5} mol) were added. After 10 min ^{11}B NMR spectra were measured. Control measurement was performed with commercial dehydroascorbic acid (13.75 mg; 7.9×10^{-5} mol), boric acid (4.88 mg; 7.9×10^{-5} mol) and natrium acetate (0.34 mg; 10.4×10^{-5} mol) in trifluoroethanol (350 uL), D_2O (150 uL) and CD_3OD (100 uL).



ascorbic acid dehydroascorbic acid

^{11}B NMR spectra, CD_3OD – interaction of boric acid and dehydroascorbate