Supporting Information:

Bio-based green solvent for the catalyst free oxidation of arylboronic acids into phenols

Surabhi Gupta,[a#] Priyanka Chaudhary,[a#] Lavudi Seva,[b] Shahulhameed Sabiah[b] and Jeyakumar Kandasamy[a]*

[a]*Department of chemistry, Indian Institute of Technology (BHU), Varanasi, Uttar Pradesh-221005; Email: jeyakumar.chy@iitbhu.ac.in.* [b]*Department of chemistry, Pondicherry University, Pondicherry-605014.*
[#]*Both authors contributed equally to this work*

Experimental section:

All reactions were performed under open air atmosphere at room temperature (~30°C). Solvents and chemicals were purchased from commercial sources and used without further purifications. The NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer and JEOL 300 MHz NMR Spectrometer. The column chromatography was performed on silica gel (60-120 mesh) using a mixture of ethylacetate and hexane as eluent. Thin layer chromatography was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F254). The proton NMR was recorded for the phenols and compared with literature reports.[1-4]

A general experimental procedure for the oxidation reaction:

To a stirred solution of aryl boronic acid (or) aliphatic boronic acid (0.5 mmol) in lactic acid (or) acetic acid (1.0 mL) was added 1.0 equivalent of 30% aqueous hydrogen peroxide at room temperature and the progress of the reaction was monitored by TLC. *In case of acetic acid,* after completion of the reaction (as seen by TLC), solvent was evaporated to dryness and the residue was subjected to column chromatography to obtain pure phenols. *In case of lactic acid,* after completion, the reaction mixture was diluted with water and extracted with petroleum ether-ethyl acetate mixture (2:1, 5x5mL).[6] The companied organic layer was dried over sodium sulphate (Na_2SO_4), evaporated and subjected to chromatography to obtain pure products.

Analytical data for the products:

2a: Phenol was obtained as brown oil (Yield: 45 mg (95%) in both lactic acid and acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.27 (m, 2H), 6.97 (m, 1H), 6.87 (m, 2H), 6.16 (br, 1H).

2b: 1-Naphthol was obtained as a white solid (Yield: 67 mg (93%) in lactic acid; 68 mg (95%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 8.20 (m, 1H), 7.80 (m, 1H), 7.57-7.42 (m, 3H), 7.32 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 7.3 Hz, 1H), 5.40 (br, OH).

2c: 2-Naphthol was obtained as a white solid (Yield: 68 mg (94%) in lactic acid; 69 mg (96%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.77 (t, J = 9.2 Hz, 2H), 7.67 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.3 Hz, 1H), 7.35 (t, J = 8.2 Hz, 1H), 7.17-7.08 (m, 2H).

2d: 4-Methoxyphenol was obtained as colorless oil. (Yield: 56 mg (90%) in lactic acid; 59 mg (95%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 6.82-6.75 (m, 4H), 3.77 (s, 3H).

2e: 4-Methylphenol was obtained as colorless oil (Yield: 51 mg (95%) in lactic acid; 50 mg (93%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.05 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 2.31 (s, 3H).

2f: 2-Methylphenol was obtained as colorless oil (Yield: 51 mg (95%) in lactic acid; 51 mg (95%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[2]: δ 7.27 (m, 2H), 7.10-6.85 (m, 2H), 5.80 (br, OH), 2.42 (3H, s).

2g: 4-Ethylphenol was obtained as a white solid (Yield: 57 mg (93%) in lactic acid; 58 mg (95%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[3]: δ 7.03 (d, J = 8.4, 2H), 6.73 (d, J = 8.8 Hz, 2H), 4.89 (br, OH), 2.58 (q, J= 7.59 Hz, 2H), 1.22 (t, J = 7.6 Hz, 3H).

2h: 4-tert-Butylphenol was obtained as a colourless solid (Yield: 72 mg (96%) in lactic acid; 70 mg (93%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.27-7.23 (m, 2 H), 6.79-6.74 (m, 2 H), 4.84 (br, OH), 1.29 (s, 9 H).

2i: 4-Phenylphenol was obtained as a white solid (Yield: 79 mg (93%) in lactic acid; 83 mg (97%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[2]: δ 7.56–7.53 (m, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 5.00 (br, OH).

2j: 2,4,6-Trimethyl phenol was obtained as a white solid (Yield: 64 mg (94%) in both lactic acid and acetic acid). ^{1}HNMR (400 MHz, $CDCl_3$)[4]: δ 6.79 (s, 2H), 4.47 (s, 1H), 2.22 (m, 9H).

2k: 3-Nitrophenol was obtained as a pale yellow solid (Yield: 63 mg (91%) in lactic acid; 66 mg (95%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[2]: δ 7.81-7.78 (m, 1H), 7.72 (t, J = 2.3 Hz, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.21–7.17 (m, 1H), 5.96 (br, OH).

2l: 4-Nitrophenol was obtained as a yellow solid (Yield: 64 mg (92%) in lactic acid; 65 mg (94%) in acetic acid). ^{1}HNMR (400 MHz, $CDCl_3$) [1]: δ 8.19-8.15 (m, 2H), 6.96-6.91 (m, 2H), 6.57 (s, OH).

2m: 4-Fluorophenol was obtained as a white solid (Yield: 52 mg (92 %) in both lactic acid and acetic acid). ^{1}H NMR (400MHz, $CDCl_3$)[1]: δ 6.95-6.88 (m, 2H), 6.80-6.75 (m, 2H).

2n: 4-Chlorophenol was obtained as a white solid (Yield: 61 mg (95%) in both lactic acid and acetic acid). ^{1}H NMR (400MHz, CDCl3)[2]: δ 7.21-7.17 (m, 2H), 6.79-6.74 (m, 2H), 5.58 (br, OH).

2o: 2,4-Dichlorophenol was obtained as a white solid (Yield: 76 mg (93%) in lactic acid; 73 mg (90%) in acetic acid). ^{1}H NMR ($CDCl_3$, 400 MHz)[3]: δ 7.33 (s, 1H), 7.18 (d, J=8.0 Hz, 1H), 6.95 (d, 1H, J=8.0 Hz), 5.57 (br, OH).

2p: 4-Bromophenol was obtained as a semisolid (Yield: 81 mg (94%) in lactic acid; 83 mg (96%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.32 (m, 2H), 6.72 (m, 2H), 5.36 (br, OH).

2q: 4-Iodophenol was obtained as a semisolid (Yield: 103 mg (94%) in lactic acid; 100 mg (91%) in acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.51 (m, 2H), 6.62 (m, 2H), 5.15 (br, OH).

2r: 4-Hydroxyphenol was obtained as a white solid (Yield: 52 mg (95%) in both lactic acid and acetic acid). ^{1}HNMR (400 MHz, $CDCl_3$)[3]: δ 6.72 (4H, s), 3.47 (2H, s).

2s: 4-Hydroxyacetophenone was obtained as white solid. (Yield: 65mg (95%) in both lactic acid and acetic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[1]: δ 7.91 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 2.57 (s, 3H).

2t: 2-Phenylethanol was obtained as colorless oil (Yield: 57 mg (94%) in lactic acid). ^{1}H NMR (300 MHz, $CDCl_3$)[5]: δ 7.30-7.34 (m, 3H), 7.24 (t, J = 7.4 Hz, 2H), 3.85 (t, J = 6.4 Hz, 2H), 2.87 (t, J = 6.4 Hz, 2H).

2u: Cyclohexanol was obtained as colorless oil (Yield: 43 mg (86%) in lactic acid). ^{1}H NMR (400 MHz, $CDCl_3$)[5]: δ 3.61 (m, 1H), 2.00-1.50 (m, 6H), 1.35-1.10 (m, 4H).

References

1. Xu, J. M.; Wang, X. Y.; Shao, C. W.; Su, D. Y.; Cheng, G. L.; Hu, Y. F. *Org. Lett.* **2010,** *12*, 1964-1967.

2. Zhu, C.; Wang, R.; Falck, J. R. *Org. Lett.* **2012,** *14*, 3494-3497.

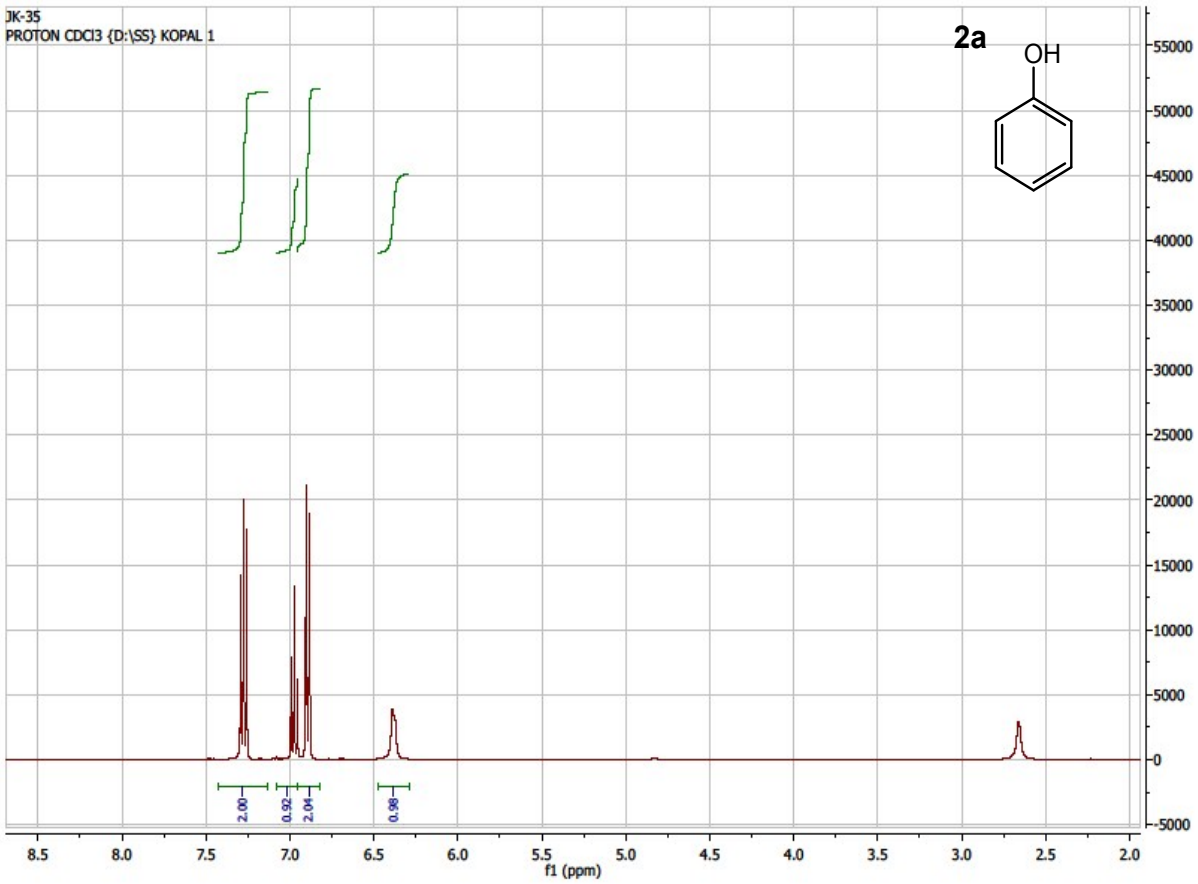
3. Zou, Y. Q.; Chen, J. R.; Liu, X. P.; Lu, L. Q.; Davis, R. L.; Jorgensen, K. A.; Xiao, W. J. *Angew. Chem. Int. Ed. Engl.* **2012,** *51*, 784-8.

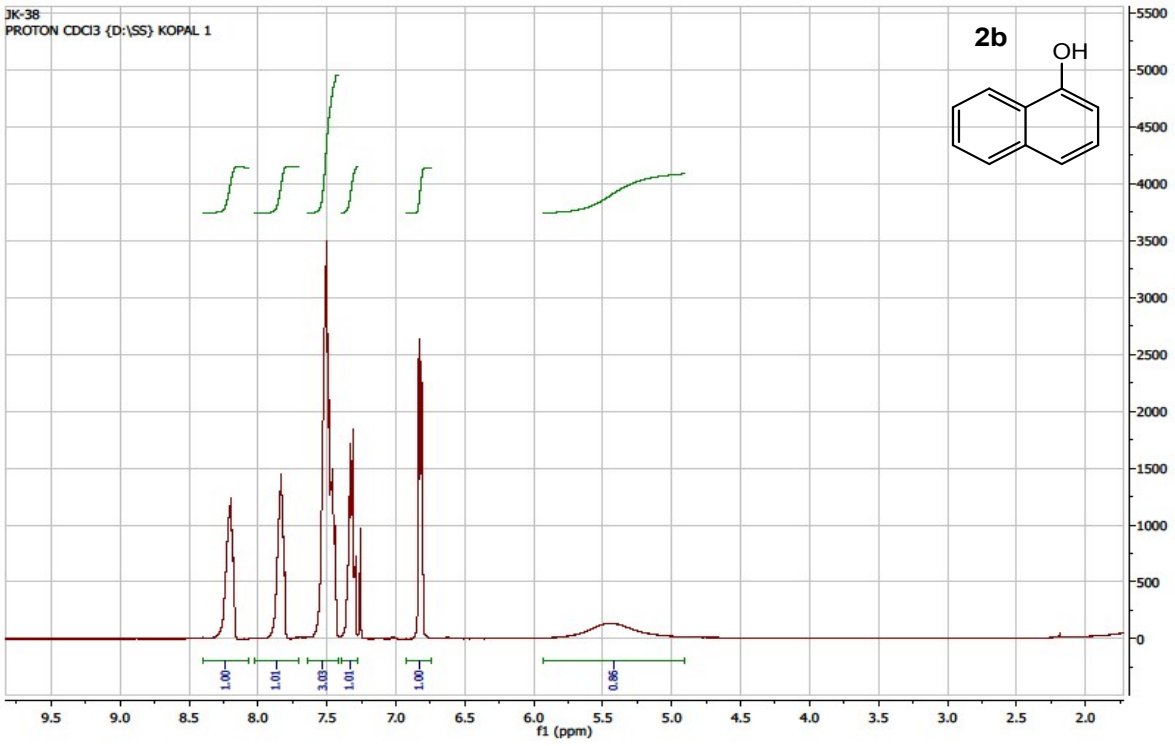
4. Jiang, M.; Li, Y.; Yang, H.; Zong, R.; Jinb, Y.; Fub H. RSC Adv., **2014**, *4*, 12977–12980.

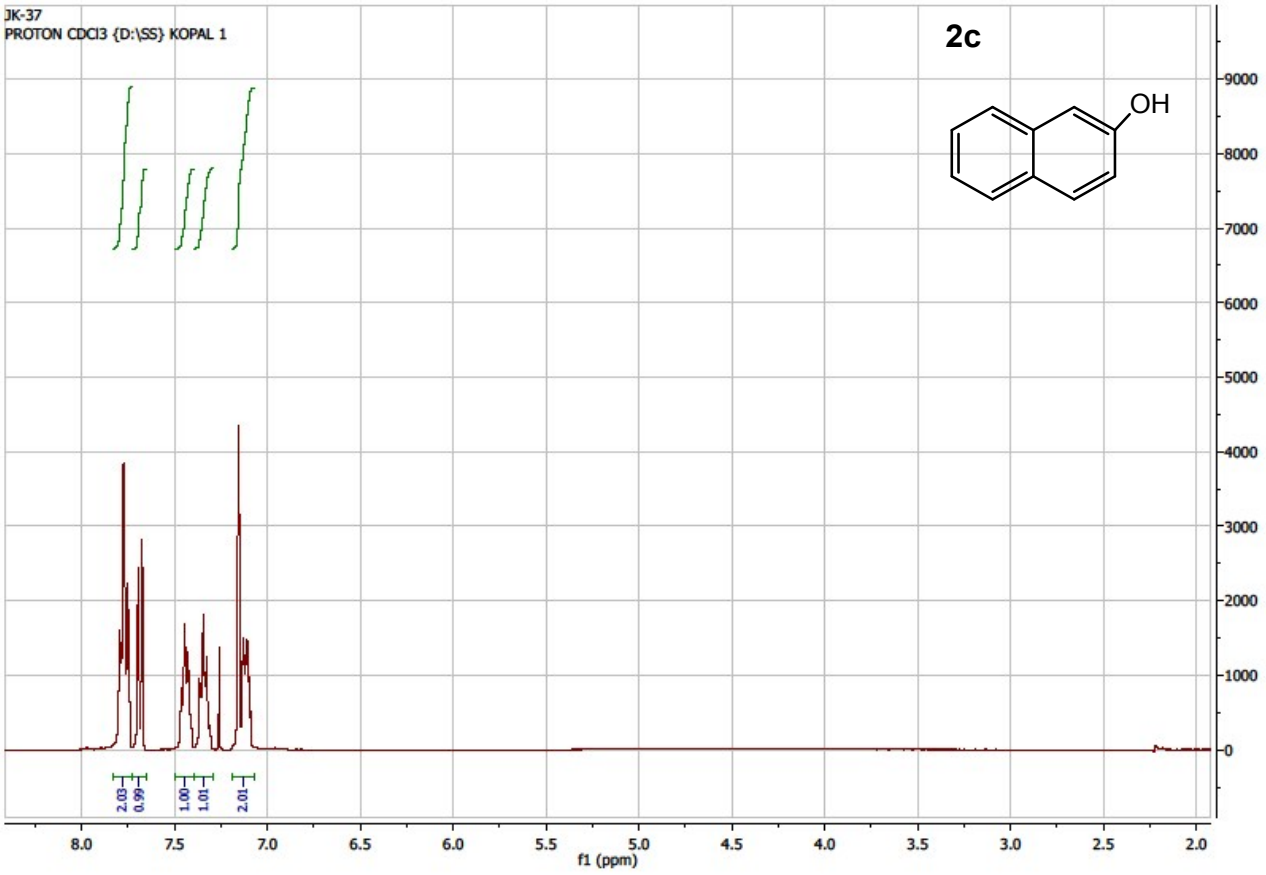
5. Chatterjee, N.; Chowdhury, H.; Sneh, K.; Goswami, A. *Tetrahedron Lett* **2015,** *56*, 172-174.

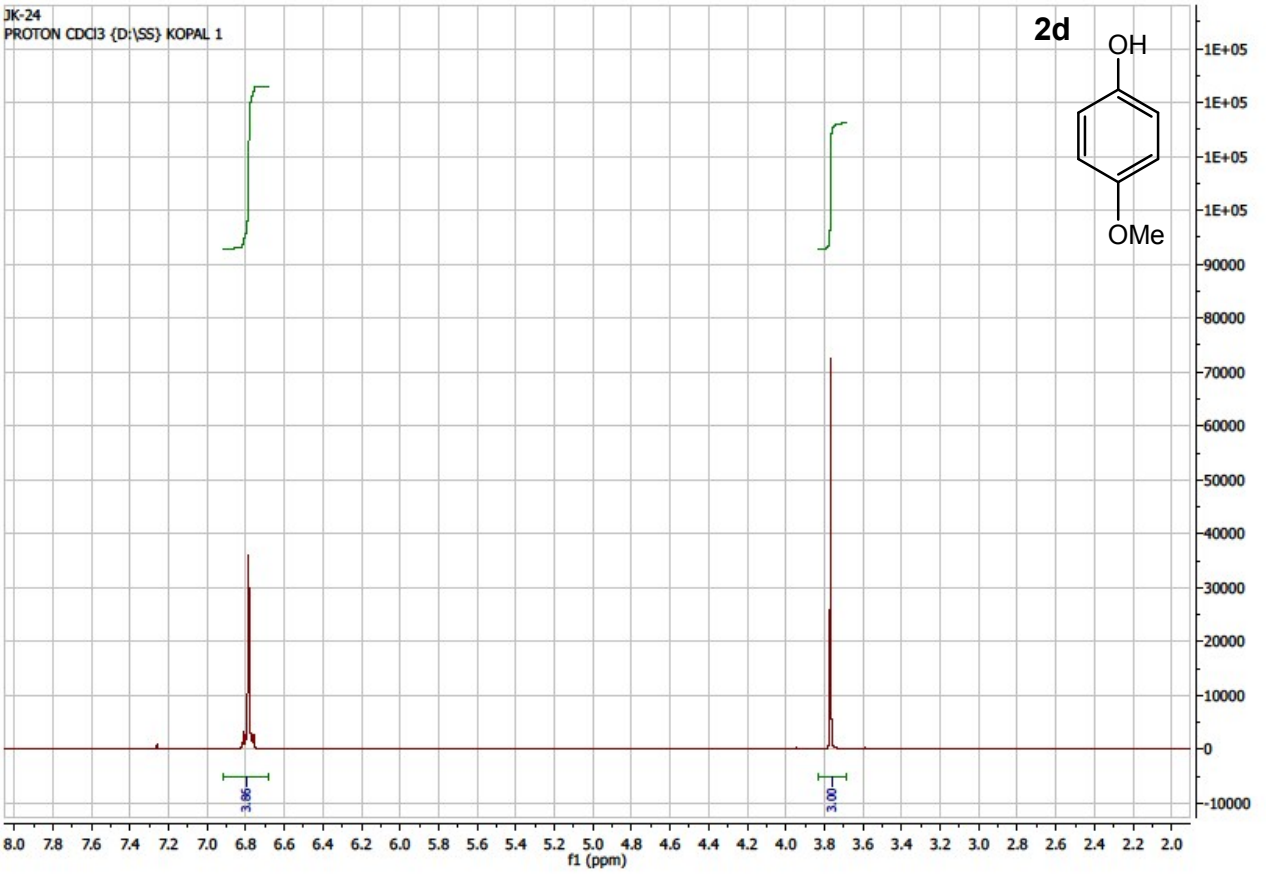
6. Yang, J.; Tan, J. N.; Gu, Y. L. *Green Chem* **2012,** *14*, 3304-3317.

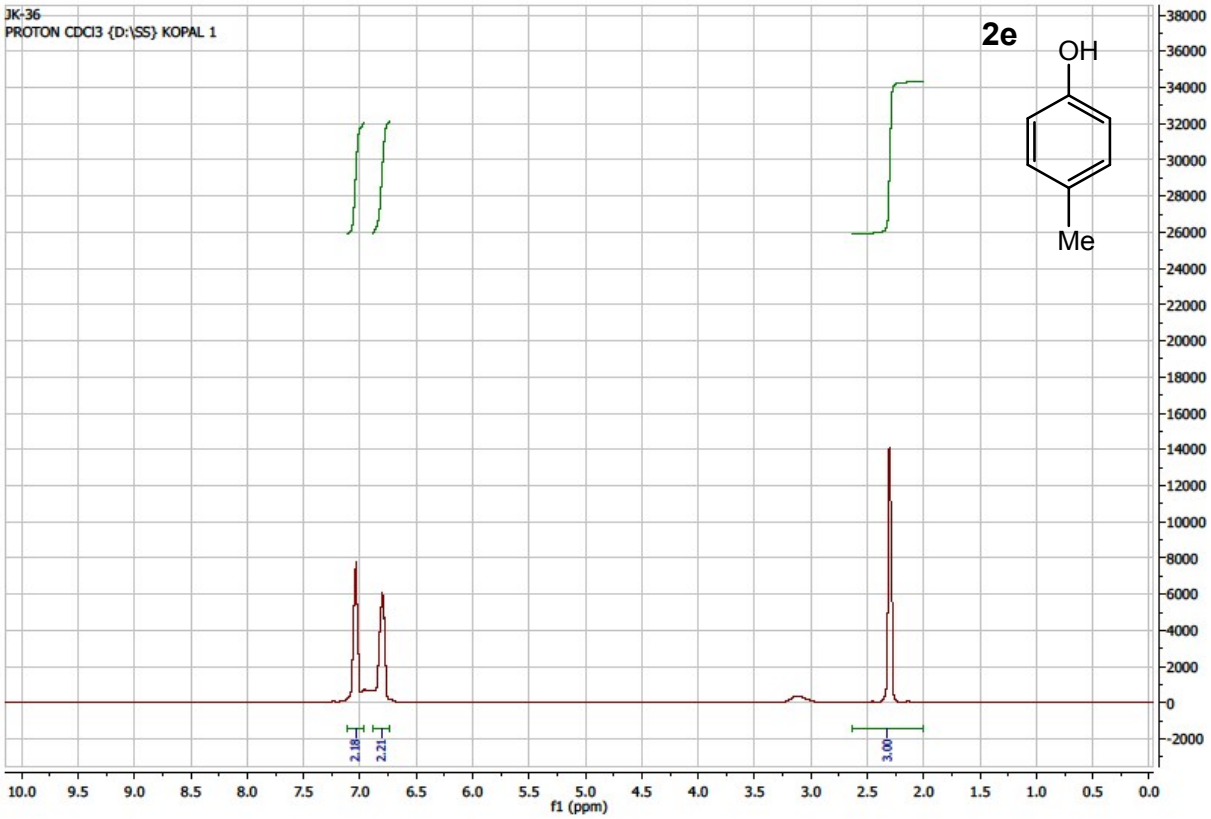
1H NMR Spectrum of Phenols and aliphatic alcohols

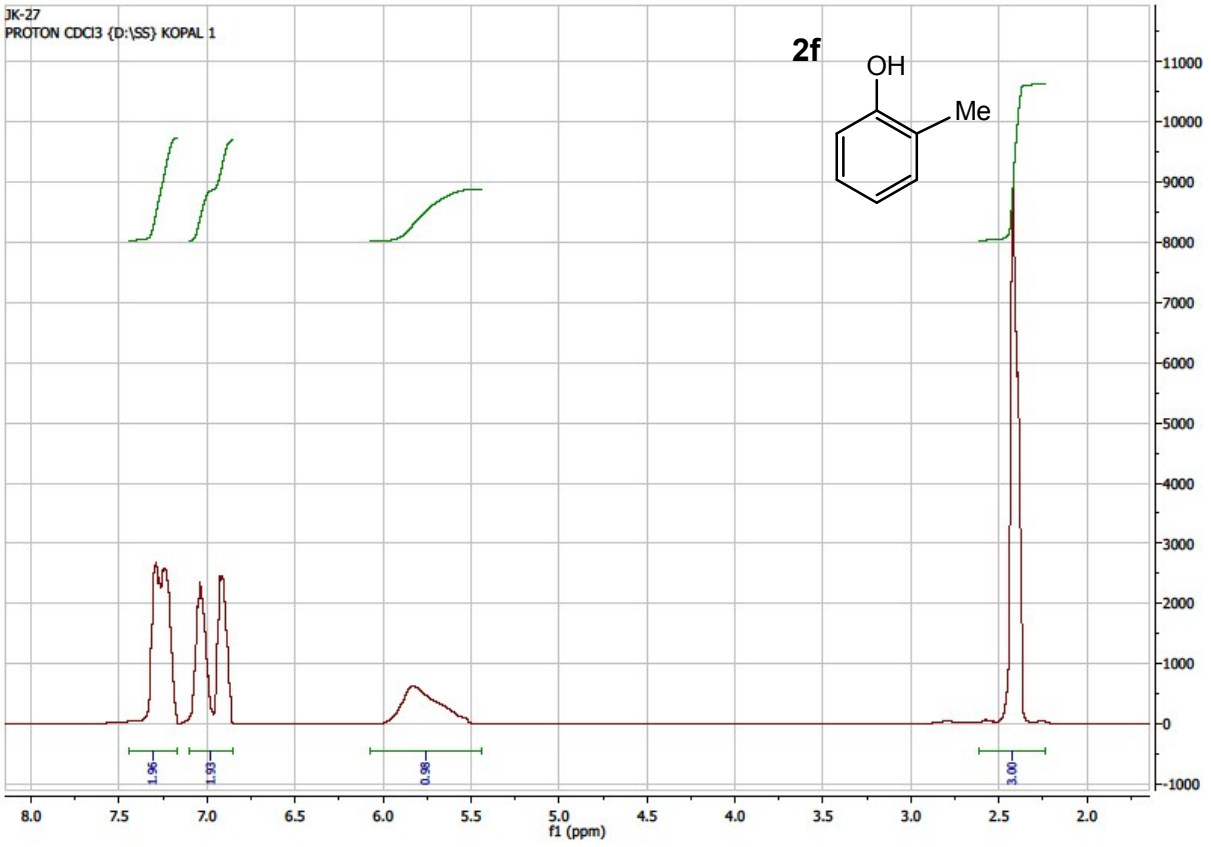

JK-35
PROTON CDCl3 {D:\SS} KOPAL 1
2a
OH
2.00
0.92
2.04
0.98
f1 (ppm)

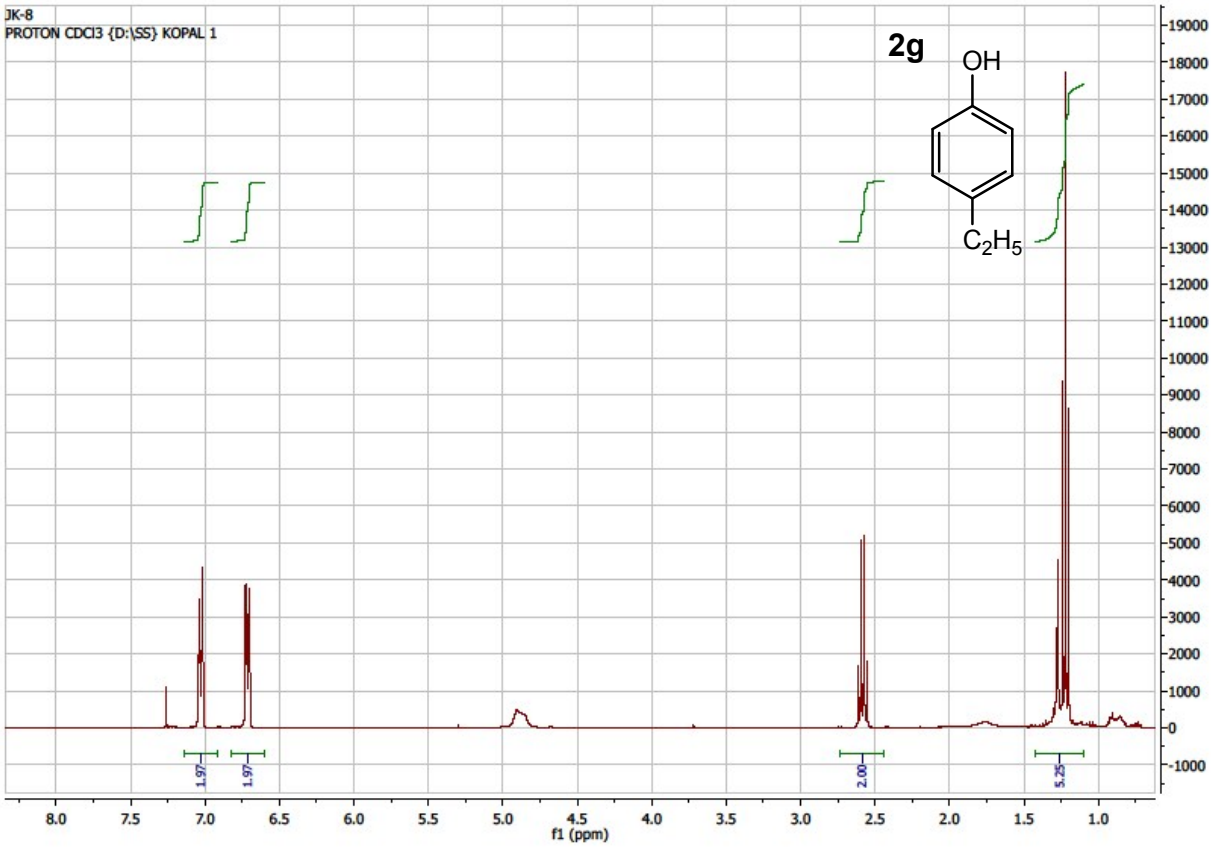

JK-38
PROTON CDCl3 {D:\SS} KOPAL 1
2b
OH
1.00
1.01
3.03
1.01
1.00
0.86
f1 (ppm)

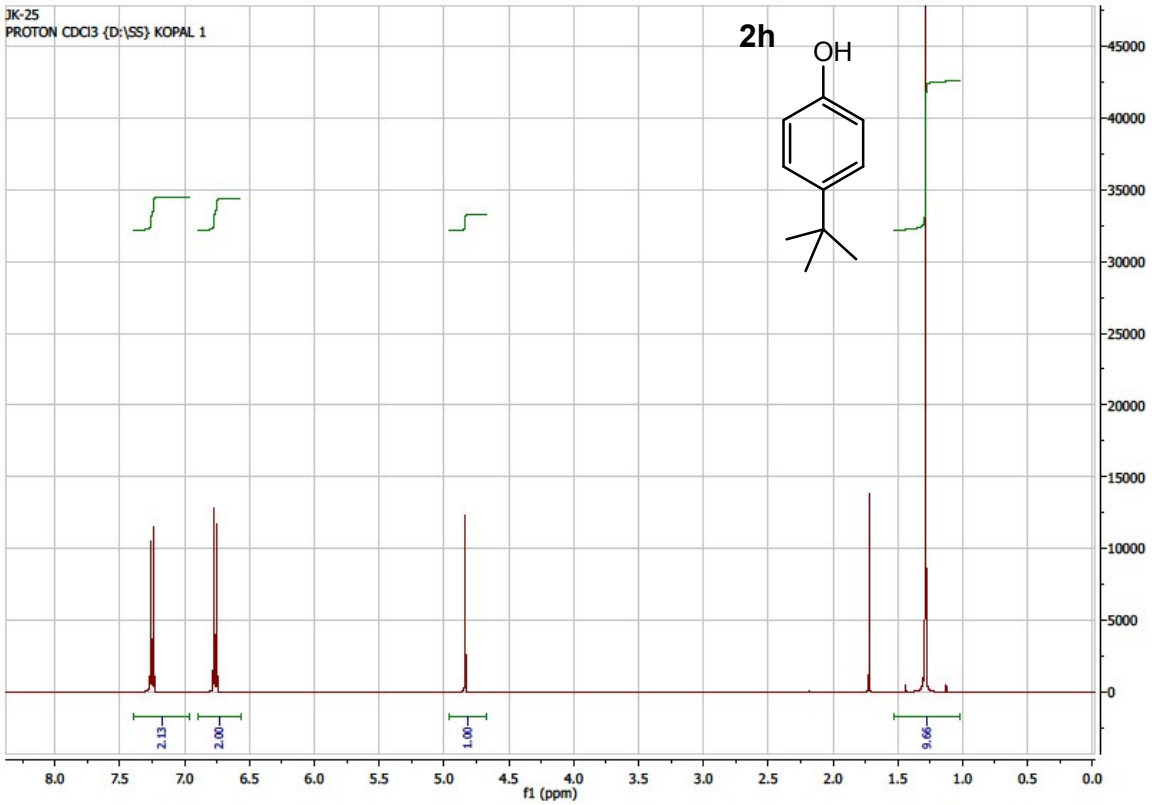

JK-37
PROTON CDCl3 {D:\SS} KOPAL 1
2c
OH
2.03
0.99
1.00
1.01
2.01
f1 (ppm)

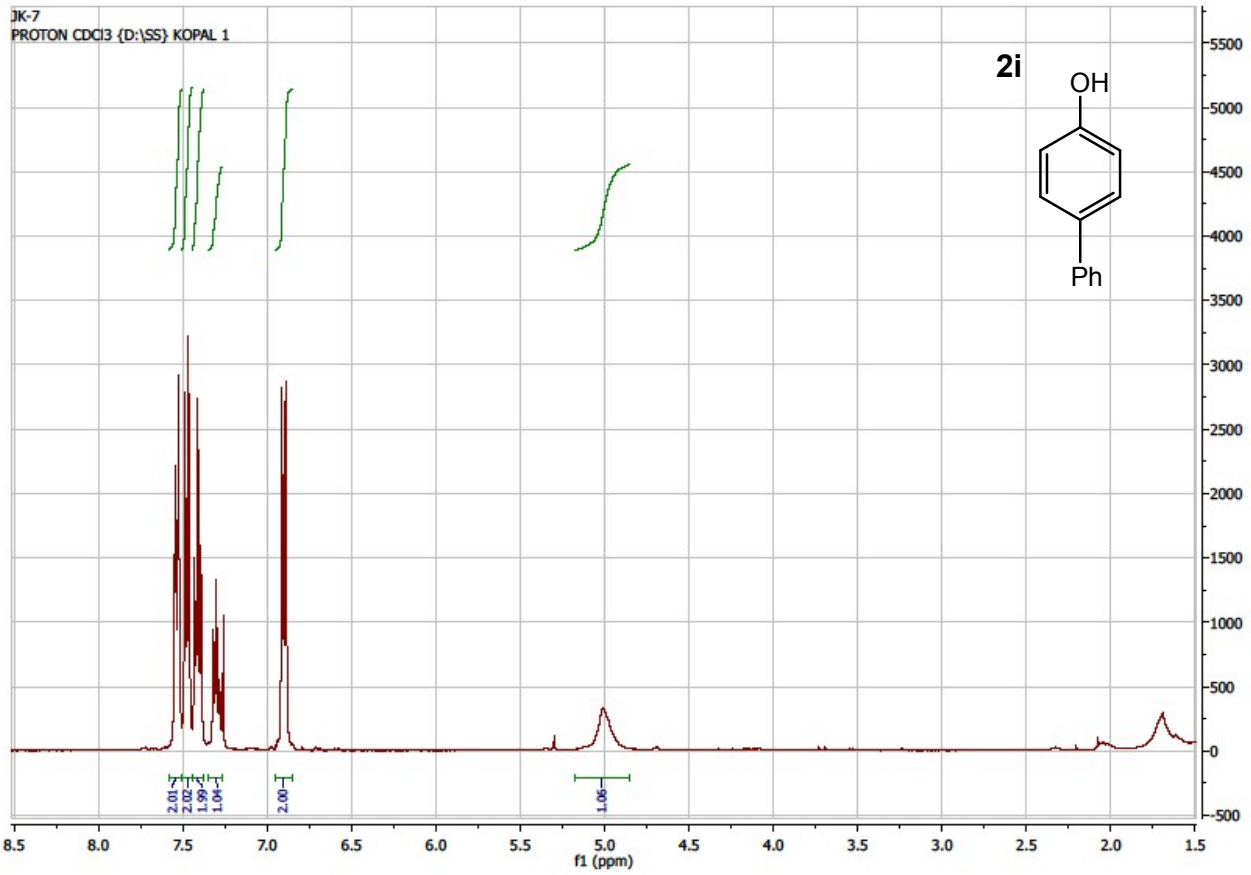

JK-24
PROTON CDCl3 {D:\SS} KOPAL 1
2d
OH
OMe
3.86
3.00
f1 (ppm)

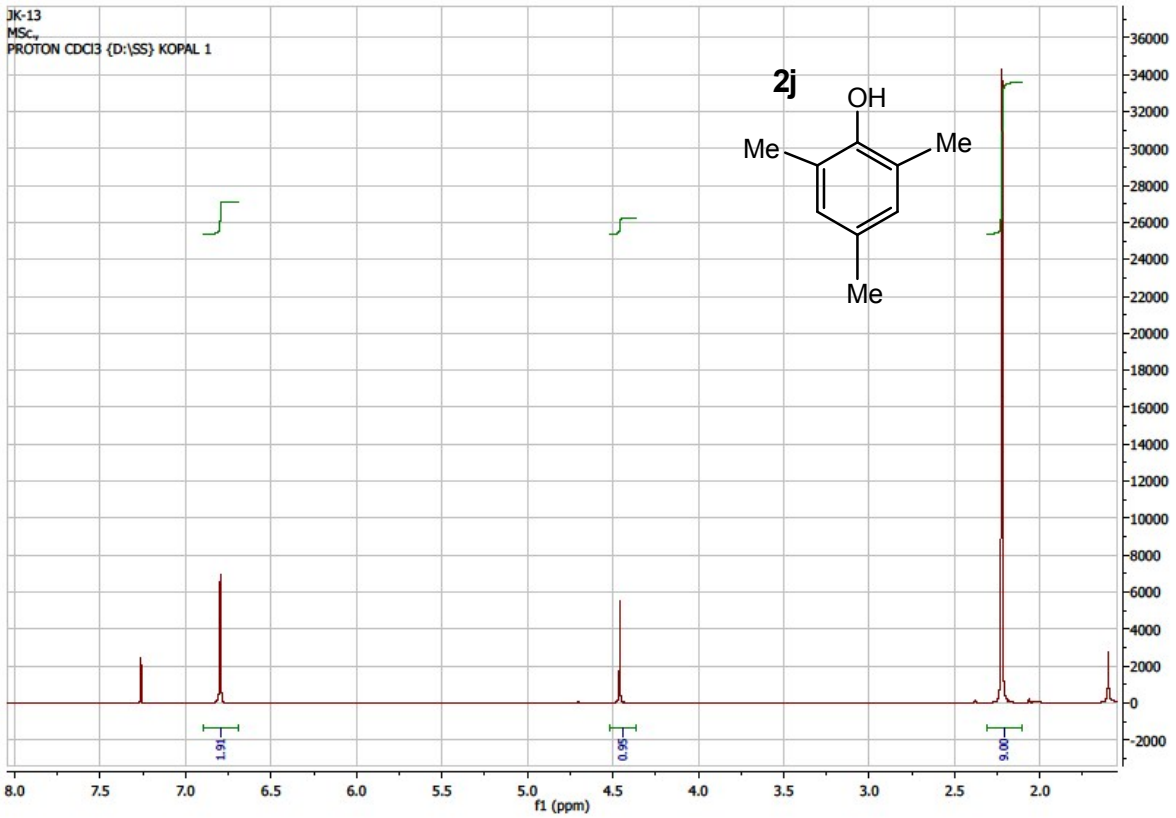

JK-36
PROTON CDCl3 {D:\SS} KOPAL 1
2e
OH
Me
2.18
2.21
3.00
f1 (ppm)

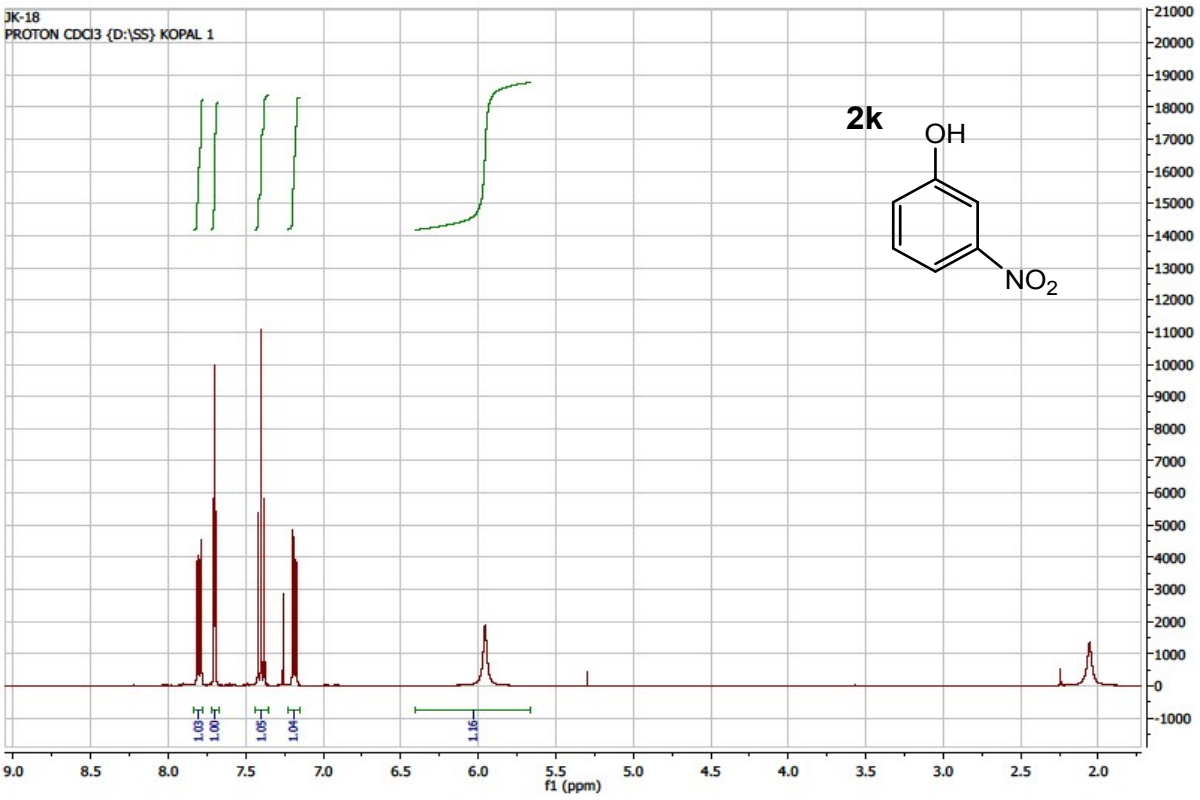

JK-27
PROTON CDCl3 {D:\SS} KOPAL 1
2f
OH
Me
1.96
1.93
0.98
3.00
f1 (ppm)

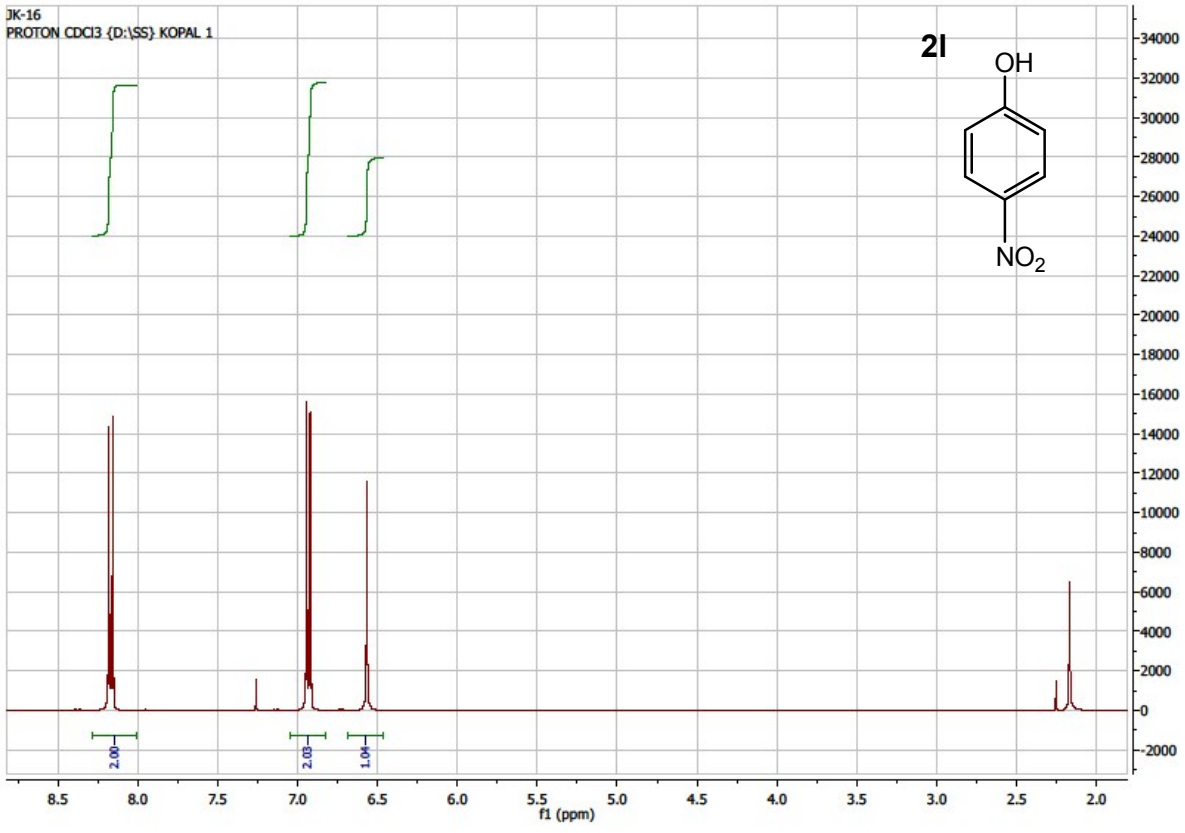

JK-8
PROTON CDCl3 {D:\SS} KOPAL 1
2g
OH
C_2H_5
1.97
1.97
2.00
5.25
f1 (ppm)

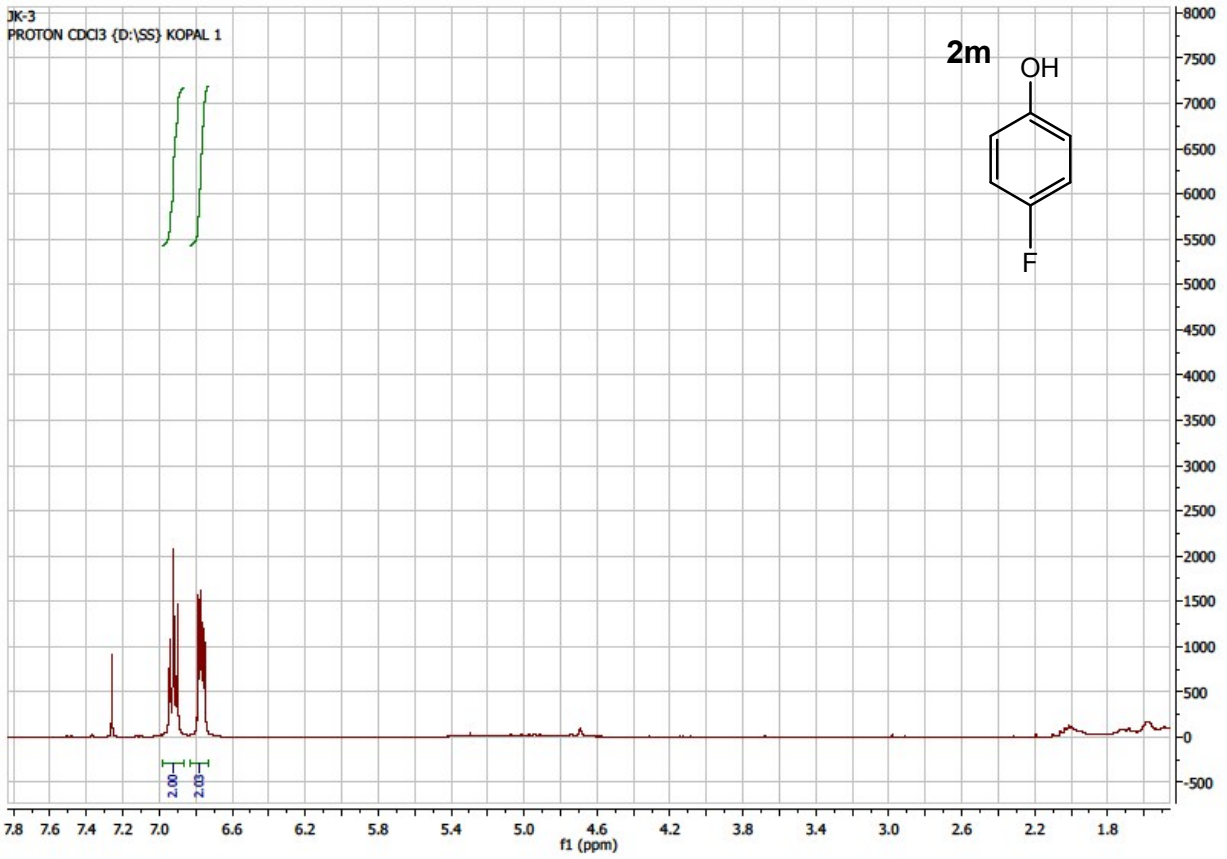

JK-25
PROTON CDCl3 {D:\SS} KOPAL 1
2h
OH
2.13
2.00
1.00
9.66
f1 (ppm)

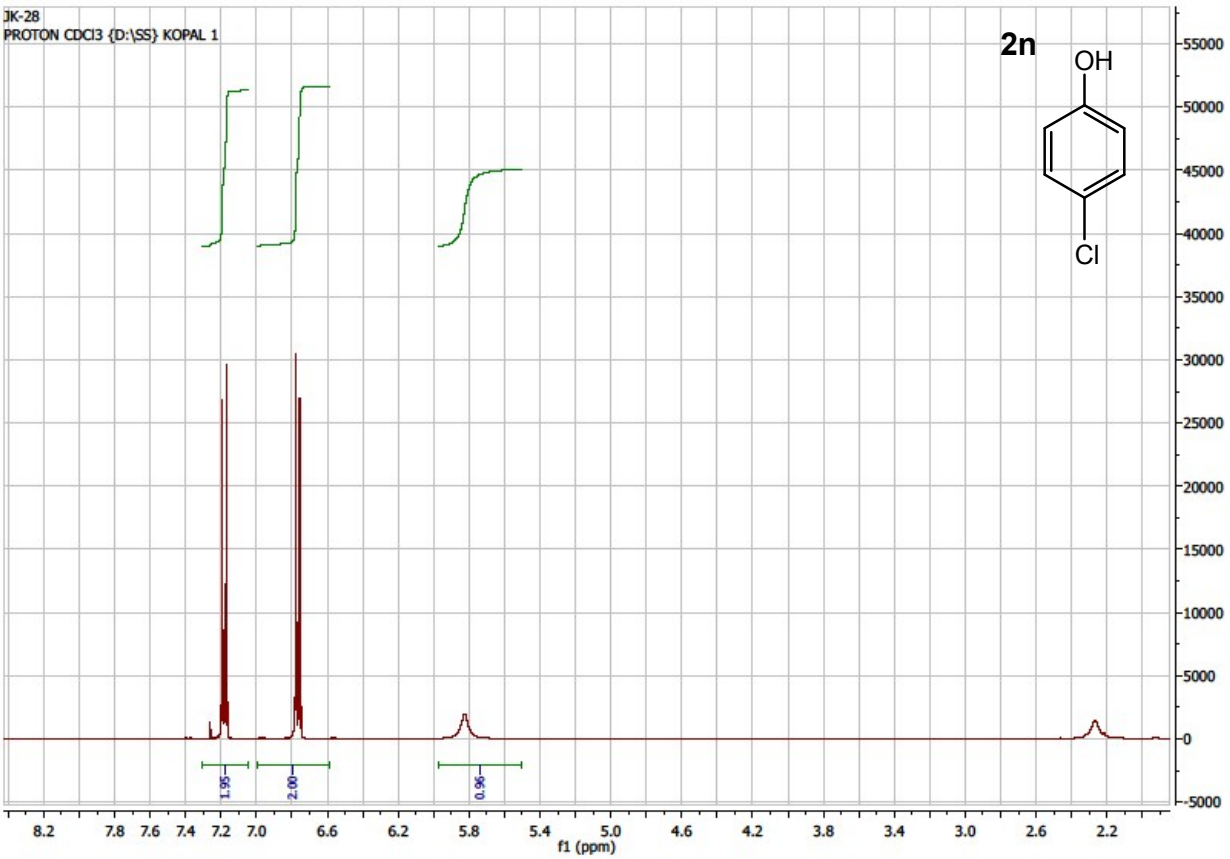

JK-7
PROTON CDCl3 {D:\SS} KOPAL 1
2i
OH
Ph
2.01
2.02
1.99
1.04
2.00
1.06
f1 (ppm)

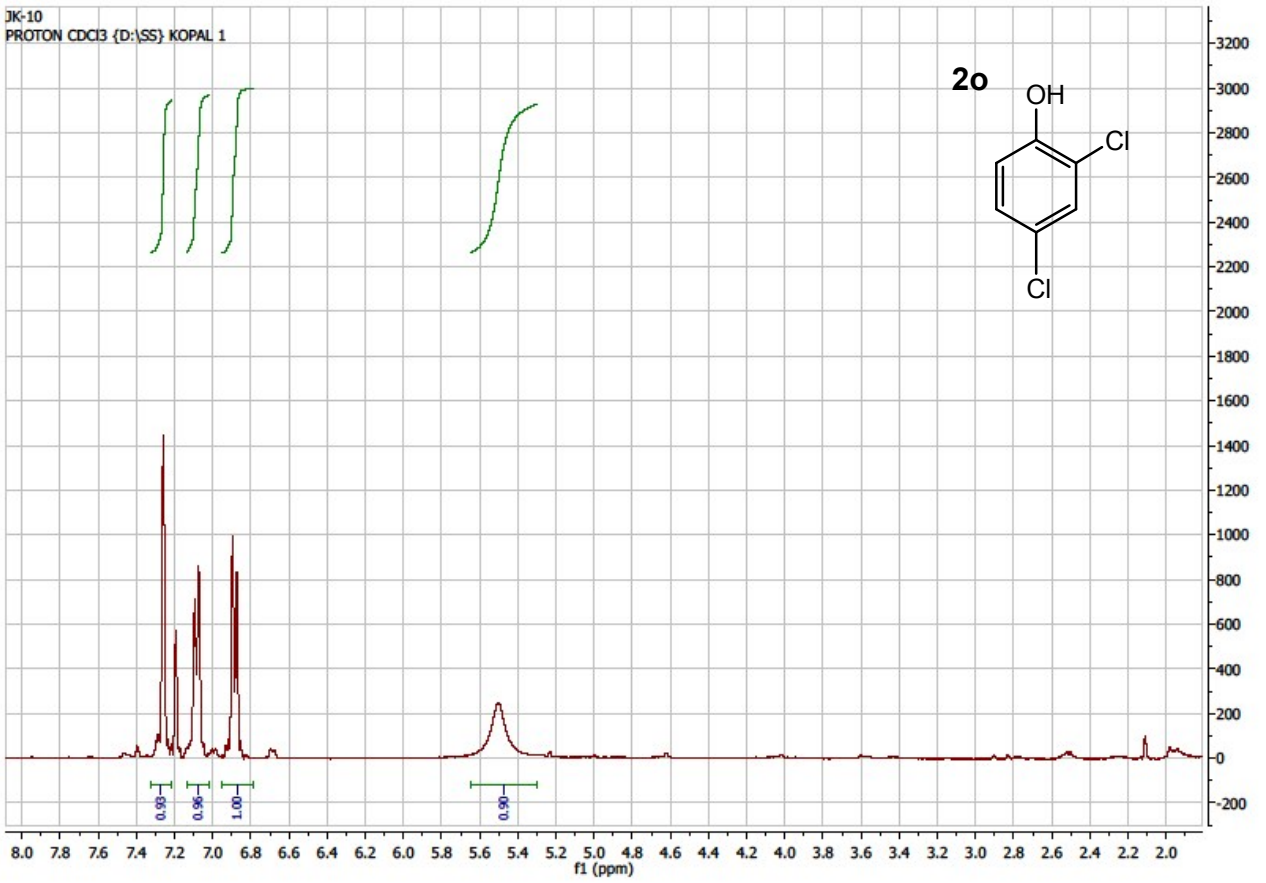

JK-13
MSc,,
PROTON CDCl3 {D:\SS} KOPAL 1
2j
OH
Me
Me
Me
1.91
0.95
9.00
f1 (ppm)

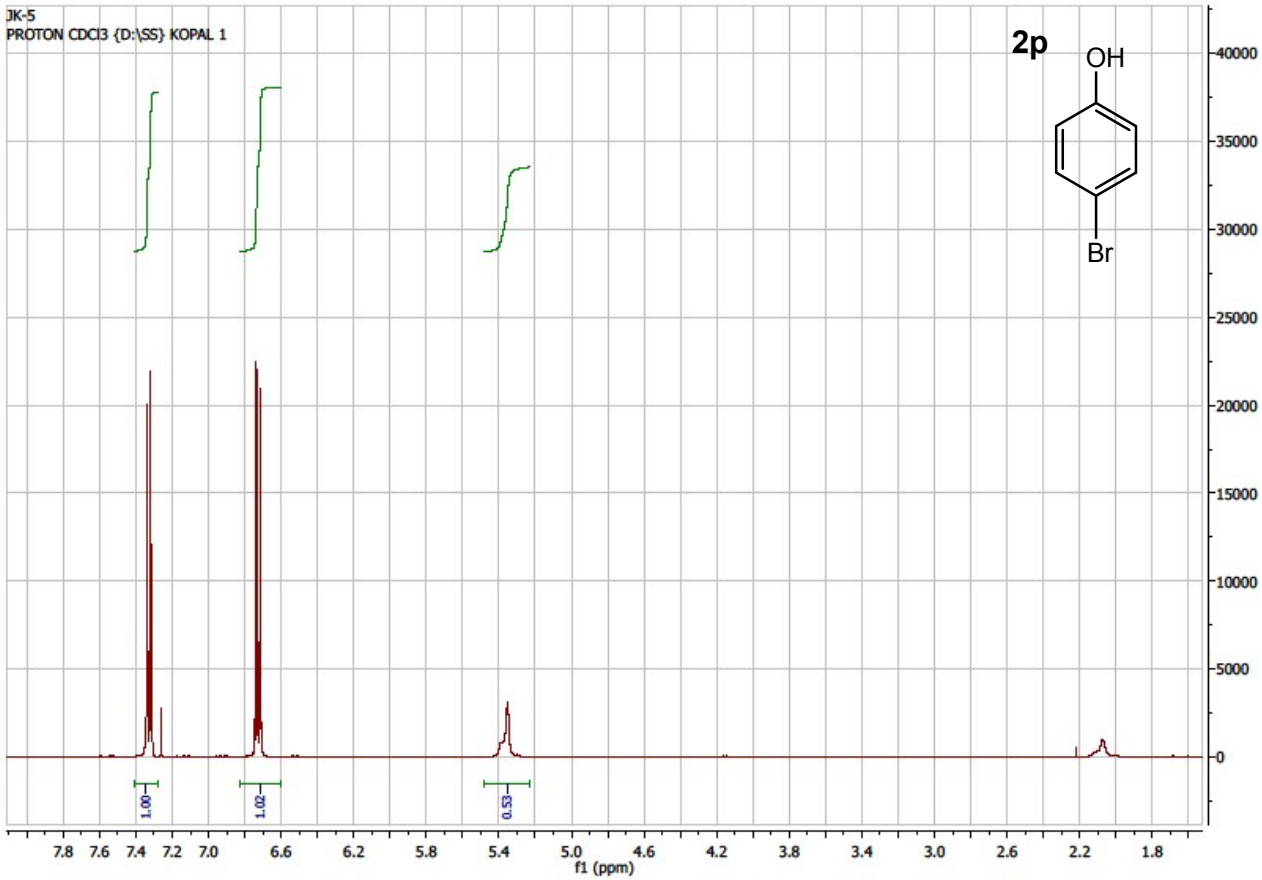

JK-18
PROTON CDCl3 {D:\SS} KOPAL 1
2k
OH
NO2
1.03
1.00
1.05
1.04
1.16
f1 (ppm)

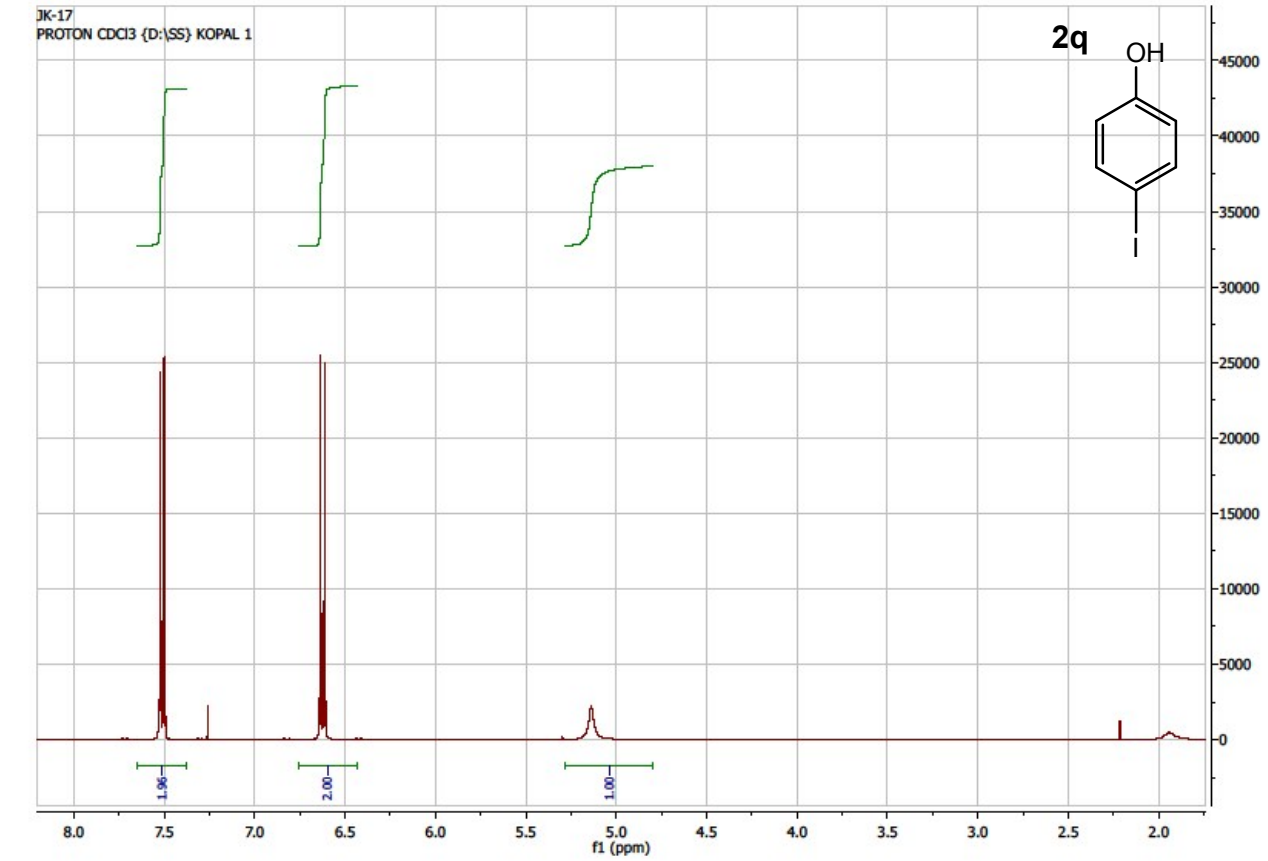

JK-16
PROTON CDCl3 {D:\SS} KOPAL 1
2l
OH
NO2
2.00
2.03
1.04
f1 (ppm)

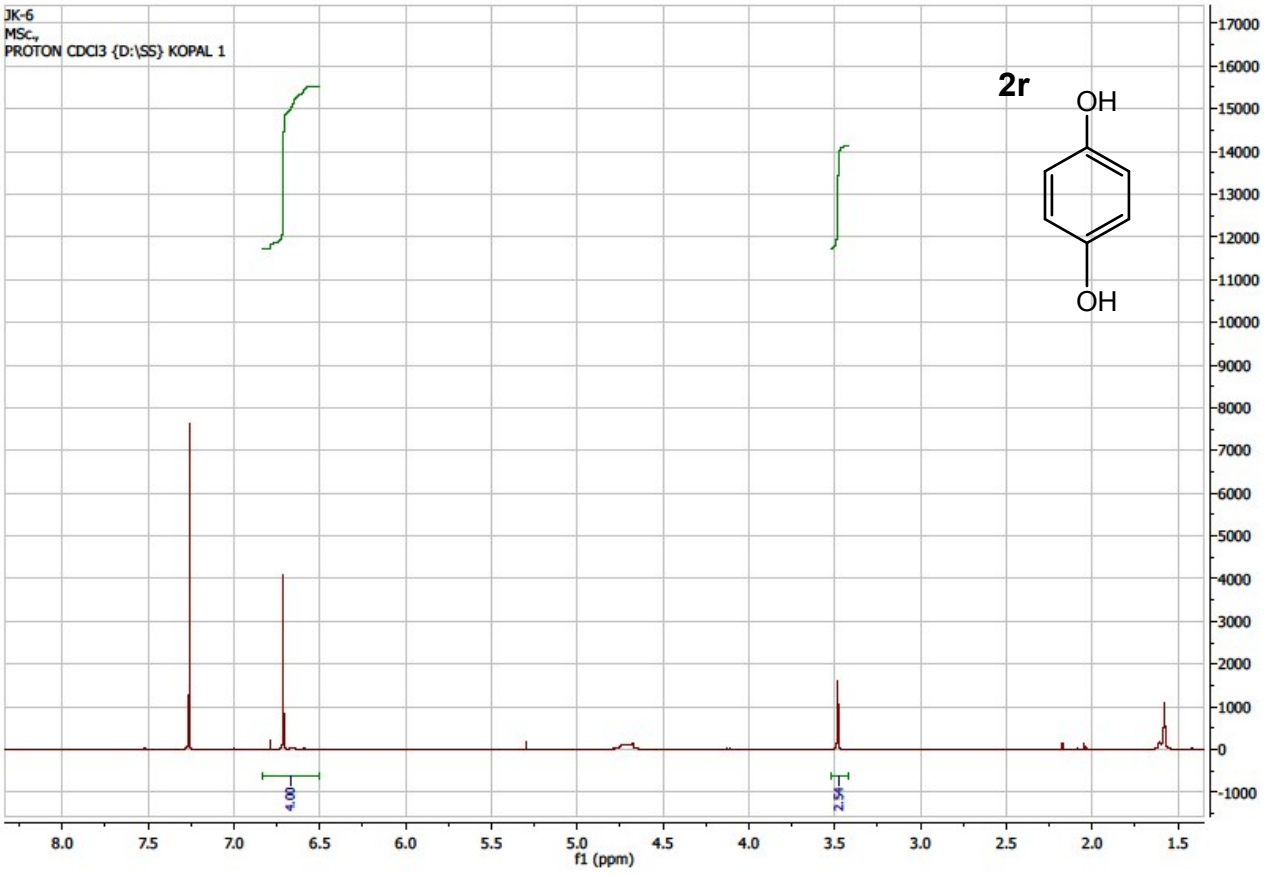

JK-3
PROTON CDCl3 {D:\SS} KOPAL 1
2m
OH
F
2.00
2.03
f1 (ppm)

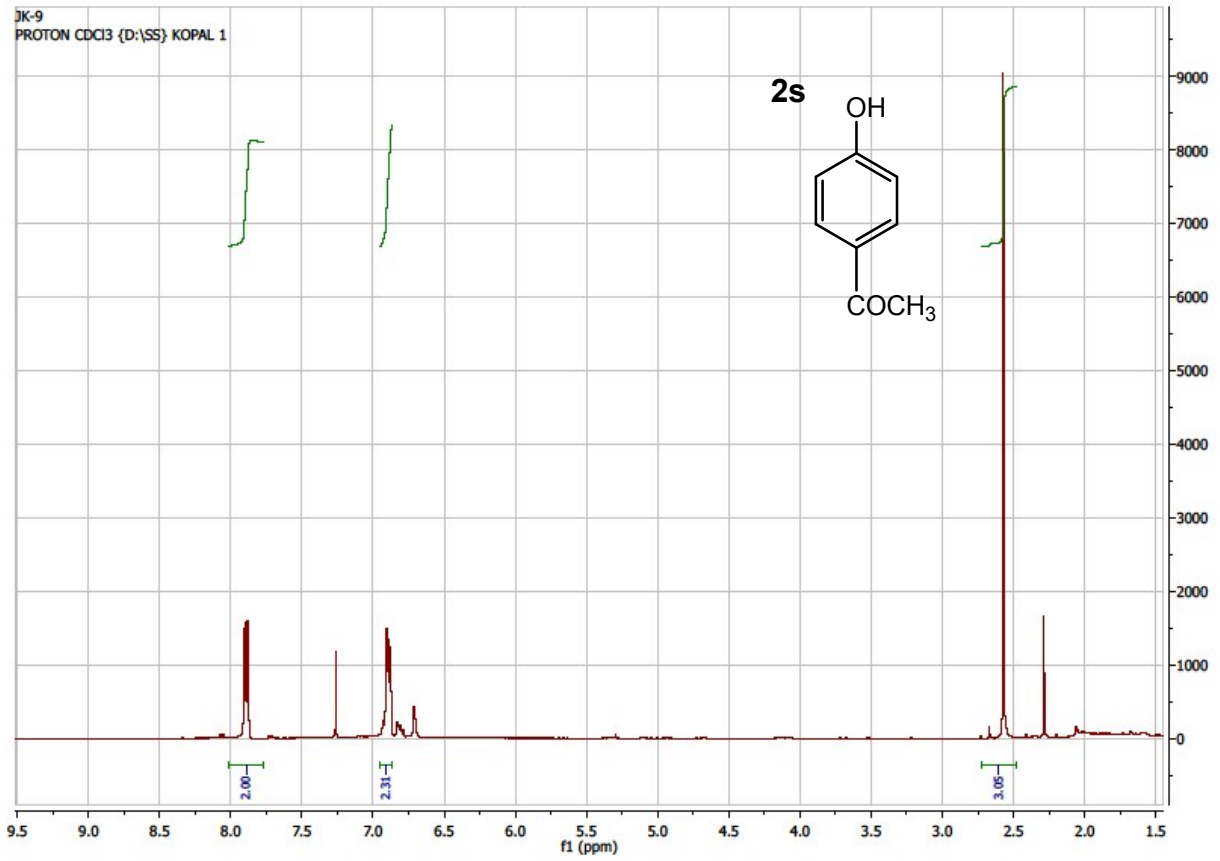

JK-28
PROTON CDCl3 {D:\SS} KOPAL 1
2n
OH
Cl
1.95
2.00
0.96
f1 (ppm)

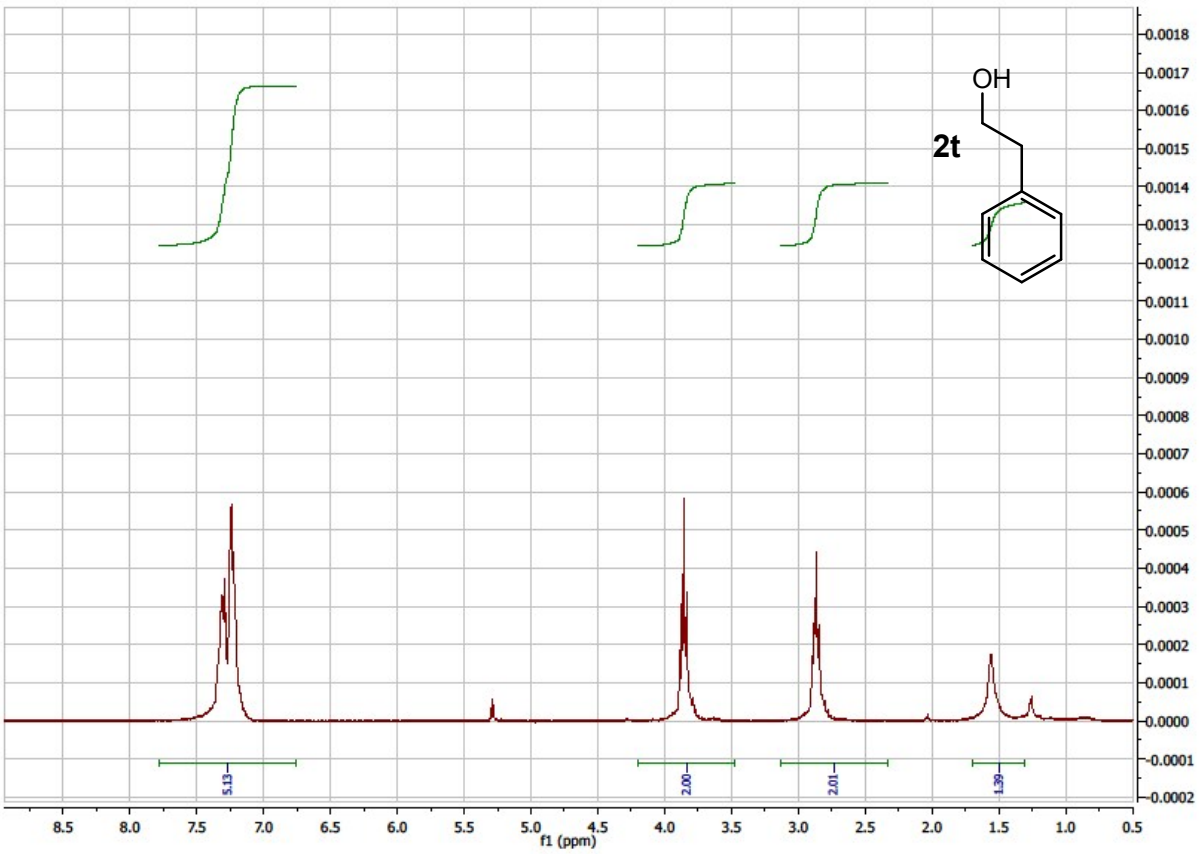

JK-10
PROTON CDCl3 {D:\SS} KOPAL 1
2o
OH
Cl
Cl
0.93
0.96
1.00
0.90
f1 (ppm)

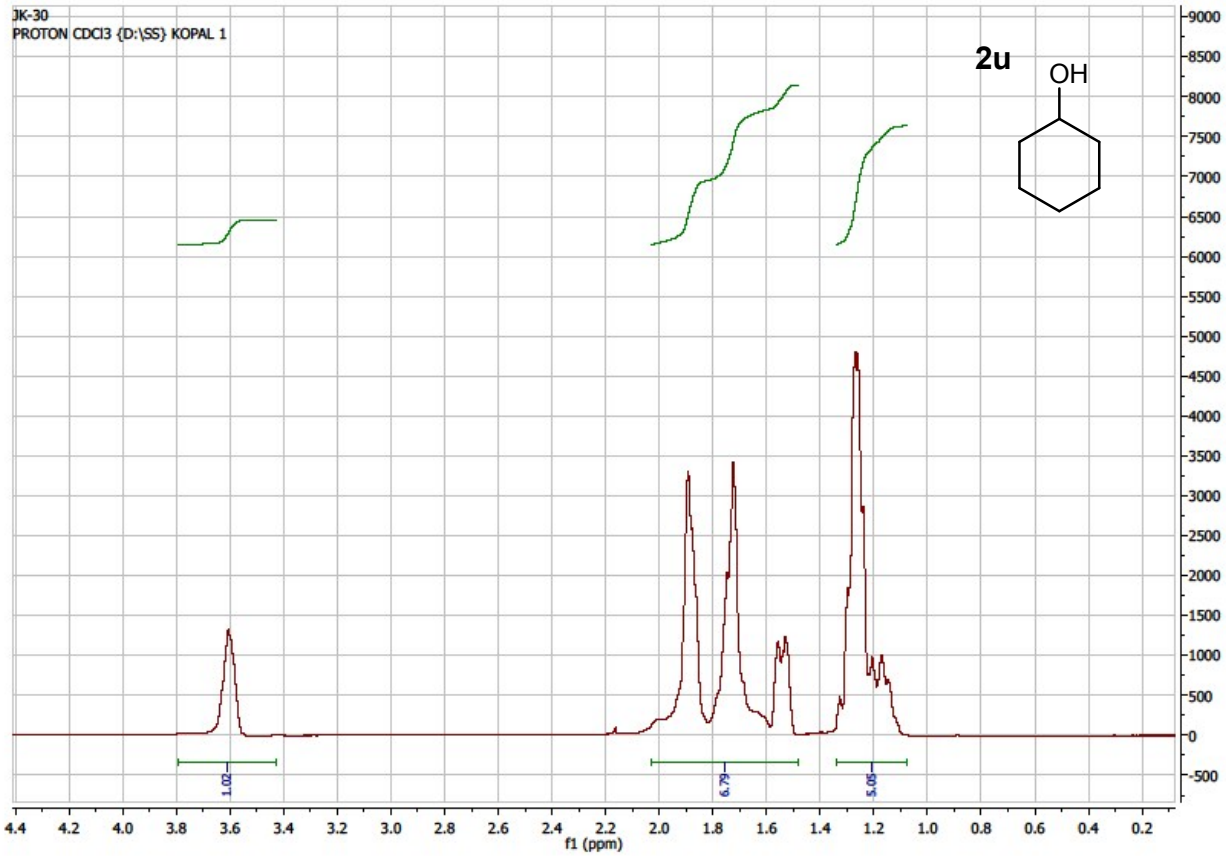

JK-5
PROTON CDCl3 {D:\SS} KOPAL 1
2p
OH
Br
1.00
1.02
0.53
f1 (ppm)


JK-17
PROTON CDCl3 {D:\SS} KOPAL 1
2q
OH
I
1.96
2.00
1.00
f1 (ppm)


JK-6
MSc,
PROTON CDCl3 {D:\SS} KOPAL 1
2r
OH
OH
4.00
2.54
f1 (ppm)


JK-9
PROTON CDCl3 {D:\SS} KOPAL 1
2s
OH
COCH3
2.00
2.31
3.05
f1 (ppm)


2t
OH
5.13
2.00
2.01
1.39
f1 (ppm)


JK-30
PROTON CDCl3 {D:\SS} KOPAL 1
2u
OH
1.02
6.79
5.05
f1 (ppm)