

Supporting Information

Highly recyclable $\text{Ti}_{0.97}\text{Ni}_{0.03}\text{O}_{1.97}$ catalyst coated on cordierite monolith for efficient transformation of arylboronic acids to phenols and reduction of 4-nitrophenol

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1 General information

X-ray diffraction pattern of catalyst was recorded on a Philips X'Pert Diffractometer. IR spectra is recorded in Perkin Elmer spectrometer. NMR spectra were recorded on Bruker-AV400 spectrometer in CDCl_3 and D_2O , tetramethylsilane (TMS; $\delta = 0.00$ ppm) served as an internal standard for ^1H NMR. The corresponding residual non-deuterated solvent signal (CDCl_3 ; $\delta = 77.00$ ppm) was used as an internal standard for ^{13}C NMR. Column chromatography was carried out by packing glass columns with silica gel 100 – 200 mesh and thin-layer chromatography was carried out using SILICA GEL GF-254. All reagents and reactants were procured from Sigma-Aldrich and SD-Fine chemicals. Solvents used for workup and chromatographic procedures were purchased from commercial suppliers and used without further purification.

2 Procedure for *ipso*-hydroxylation reaction

Screening reactions were carried out in a 10 mL screw-cap vial. 1 equivalent of Phenylboronic acid (122 mg, 1 mmol), 2 equivalents of 30% H_2O_2 (227 mg, 2 mmol) and 10 mg of catalyst were mixed in 3 mL of water and stirred at room temperature. The reaction was monitored by TLC. The product was extracted with diethyl ether and water workup. The product was isolated by column chromatography using 5% ethyl acetate in petroleum ether followed by rotary evaporation under vacuum to evaporate the solvents and then calculated the percentage yield.

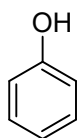
Various substrates of aryl halides were synthesized using a 10 mL screw cap vial. 10 mg of powder catalyst was used in these reactions. Aryl boronic acid (122 mg, 1 mmol), 30% H_2O_2 (227 mg, 2 mmol), and 3 mL water were taken in the vial. Reactions were performed under an open atmosphere at room temperature. Reactions were monitored by TLC. The product was

extracted with diethyl ether and water workup. The aqueous layer was discarded and the organic layer was dried under vacuum. Desired phenol derivatives were isolated by column chromatography using petroleum ether and ethyl acetate. The ratio was standardized by using TLC according to the polarity of the products. The products were characterized by ^1H NMR and ^{13}C NMR.

In the scale-up reaction with recycling of the catalyst, phenylboronic acid (500 mg, 4.1 mmol), 30% H_2O_2 (931 mg, 8.2 mmol) and 25 mg of 3%Ni/TiO₂ was coated on cordierite monolith were employed. After each cycle, the products were isolated by column chromatography and the used monolith was taken out from the specially designed flask. Washed the monolith with distilled water to remove excess H_2O_2 , and then washed with hexane to remove organic impurities. Washed monolith was dried in a furnace at 350 °C for 20 minutes. Dried monolith was reused for another reaction. The honeycomb catalyst used in the reactions was taken out and washed with water (3×10 mL) to remove inorganic salts, and then washed with hexane (3×10 mL) to remove organic compounds. Washed honeycomb was dried in a furnace at 350 °C for 2 h and it was used for another cycle. In this way, several cycles of reaction were carried.

3 Characterization data for phenol derivatives

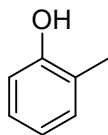
2a Phenol¹



Obtained as a white solid; **Yield:** 100% (94 mg); **R_f** = 0.35 (10% ethyl acetate in petroleum ether); **M. p** = 41 °C; **^1H NMR** (CDCl_3 , 400 MHz) δ (ppm): 7.32 - 7.29 (m, 2H), 7.03 - 6.99

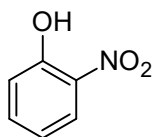
(m, 1H), 6.96 – 6.91 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 155.39, 129.82, 120.93, 115.51.

2b 2-methylphenol²



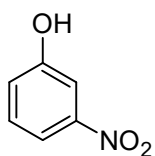
Obtained as a brown liquid; **Yield:** 100% (108 mg); R_f = 0.43 (10% ethyl acetate in petroleum ether); ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.15 – 7.09 (m, 2H), 6.89 – 6.73 (m, 2H), 5.18 (s, br, 1H), 2.28 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 153.8, 131.02, 127.11, 123.73, 120.7, 114.87.

2c 2-nitrophenol¹



Obtained as yellow solid; **Yield:** 100% (139 mg); R_f = 0.6 (30% ethyl acetate in petroleum ether); **M. p** = 45 °C; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 10.62 (s, 1H), 8.15 – 8.13 (d, J = 8 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.20 – 7.18 (d, J = 8 Hz, 1H), 7.04 – 7.00 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 155.16, 137.55, 125.10, 120.23, 119.99.

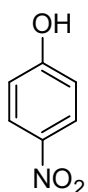
2d 3-nitrophenol²



Obtained as a yellow solid; **Yield:** 100% (139 mg); R_f = 0.58 (30% ethyl acetate in petroleum ether); **M. p** = 94 - 96 °C; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.84 - 7.82 (d, J = 8 Hz, 1H),

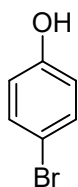
7.73 – 7.72 (t, $J = 2$ Hz, 1H), 7.45 – 7.41 (t, $J = 8$ Hz, 1H), 7.22 – 7.19 (dd, $J = 12$ Hz, 6 Hz, 1H), 6.05 (s, br, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 156.43, 130.27, 121.96, 115.80, 110.52.

2e 4-nitrophenol¹



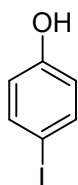
Obtained as yellow solid; **Yield:** 100% (139 mg); $R_f = 0.6$ (30% ethyl acetate in petroleum ether); **M. p** = 112 °C; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 8.21 – 8.19 (d, $J = 8$ Hz, 2H), 6.97 – 6.95 (d, $J = 8$ Hz, 2H), 6.34 (s, br, 1H); ^{13}C NMR (D_2O , 100 MHz) δ (ppm): 162.51, 140.42, 126.41, 115.57.

2f 4-bromophenol¹



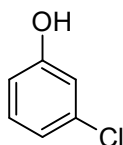
Obtained white solid; **Yield:** 100% (173 mg); $R_f = 0.42$ (10% ethyl acetate in petroleum ether); **M. p** = 65 °C; ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.37 – 7.35 (d, $J = 8$ Hz, 2H), 6.77 – 6.74 (d, $J = 12$ Hz, 2H), 5.15 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 154.60, 132.51, 117.23, 112.93.

2g 4-iodophenol³



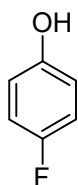
Obtained as light-yellow solid; **Yield:** 100% (220 mg); $R_f = 0.3$ (10% ethyl acetate in petroleum ether); **M. p** = 91 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.55 – 7.53 (d, $J = 8$ Hz, 2H), 6.66 – 6.64 (d, $J = 8$ Hz, 2H), 5.51 (s, br, 1H); $^{13}\text{CNMR}$ (CDCl_3 , 100 MHz) δ (ppm): 155.25, 138.62, 117.89, 82.88.

2h 3-chlorophenol²



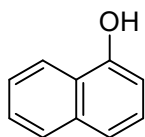
Obtained as white solid; **Yield:** 100% (128 mg); $R_f = 0.3$ (10% ethyl acetate in petroleum ether); **M. p** = 33 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.20 – 7.16 (t, $J = 8$ Hz, 1H), 6.95 – 6.89 (m, 2H), 6.82 – 6.74 (m, 1H), 5.65 (s, br, 1H); $^{13}\text{CNMR}$ (CDCl_3 , 100 MHz) δ (ppm): 156.43, 134.90, 130.45, 120.96, 115.93, 113.78.

2i 4-fluorophenol¹



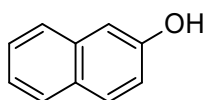
Obtained as white solid; **Yield:** 100% (112 mg); $R_f = 0.29$ (10% ethyl acetate in petroleum ether); **M. p** = 45 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.04 – 6.92 (m, 2H), 6.84 – 6.74 (m, 2H), 5.35 (s, br, 1H); $^{13}\text{CNMR}$ (CDCl_3 , 100 MHz) δ (ppm): 158.41, 156.06, 151.57, 116.27, 115.86.

2j 1-naphthol¹



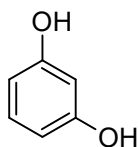
Obtained as colourless liquid; **Yield:** 100% (144 mg); **R_f** = 0.42 (10% ethyl acetate in petroleum ether); **M. p:** 96 °C; **¹H NMR** (CDCl₃, 400 MHz): δ 8.28 – 8.25 (t, *J* = 6 Hz, 1H), 7.90 – 7.88 (t, *J* = 4 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.39 – 7.35 (t, *J* = 8 Hz, 1H), 6.86 – 6.84 (d, *J* = 8 Hz, 1H) 5.58 (s, br, 1H); **¹³C NMR** (CDCl₃, 100 MHz): δ 151.38, 134.84, 127.77, 125.93, 125.37, 121.59, 120.80, 108.78.

2k 2-naphthol¹



Obtained as white solid; **Yield:** 100% (144 mg); **R_f** = 0.37 (10% ethyl acetate in petroleum ether); **M. p:** 122 °C ; **¹H NMR** (CDCl₃, 400 MHz): δ 7.83-7.79 (t, *J* = 8 Hz, 2H), 7.73 – 7.71 (d, *J* = 8 Hz, 1H), 7.50 – 7.46 (t, *J* = 8 Hz, 1H), 7.40 – 7.36 (t, *J* = 8 Hz, 1H), 7.19 – 7.14 (m, 2H), 5.20 (s, br, 1H); **¹³C NMR** (CDCl₃, 100 MHz): δ 153.32, 134.62, 129.92, 127.82, 126.59, 126.43, 123.70, 117.79, 109.60.

2l Resorcinol¹



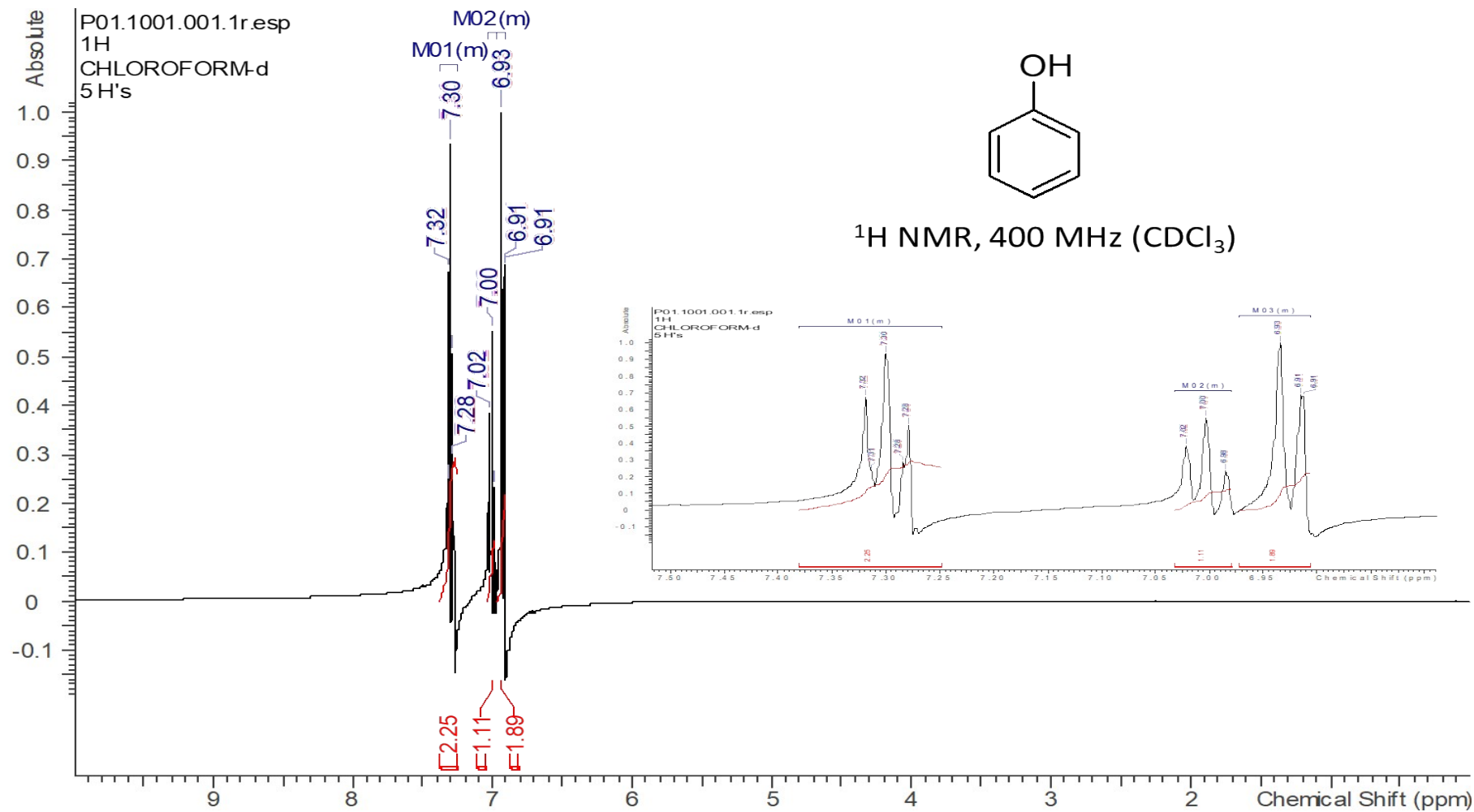
Obtained as light brown solid; **Yield:** 100% (110 mg); **R_f** = 0.53 (30% ethyl acetate - petroleum ether); **Melting Point:** 110 °C ; **¹H NMR** (D₂O, 400 MHz): δ 6.95-6.91 (t, *J* = 8 Hz, 1H), 6.28 – 6.22 (m, 3H), 4.66 (s, br, 2H); **¹³C NMR** (D₂O, 100 MHz): δ 156.66, 130.65, 107.47, 102.49.

4 References

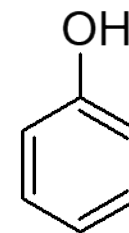
1. Lingxian Liu, Zengguang Li, Changjun Chen, Huanrong Li, Lijin Xu, Zhiyong Yu, *Tetrahedron*, 2018, **74**, 2447.
2. Hong-Yan Xie, Li-Shuai Han, Shan Huang, Xiantao Lei, Yong Cheng, Wenfeng Zhao, Hongbin Sun, Xiaoan Wen, Qing-Long Xu, *J. Org. Chem.*, 2017, **82**, 5236.
3. Yuanding Fang, Rong Zhao, Yuan Yao, Yang Liu, Denghu Chang, Ming Yaoa, Lei Shi, *Org. Biomol. Chem.*, 2019, **17**, 7558.

5 Copies of NMR spectra

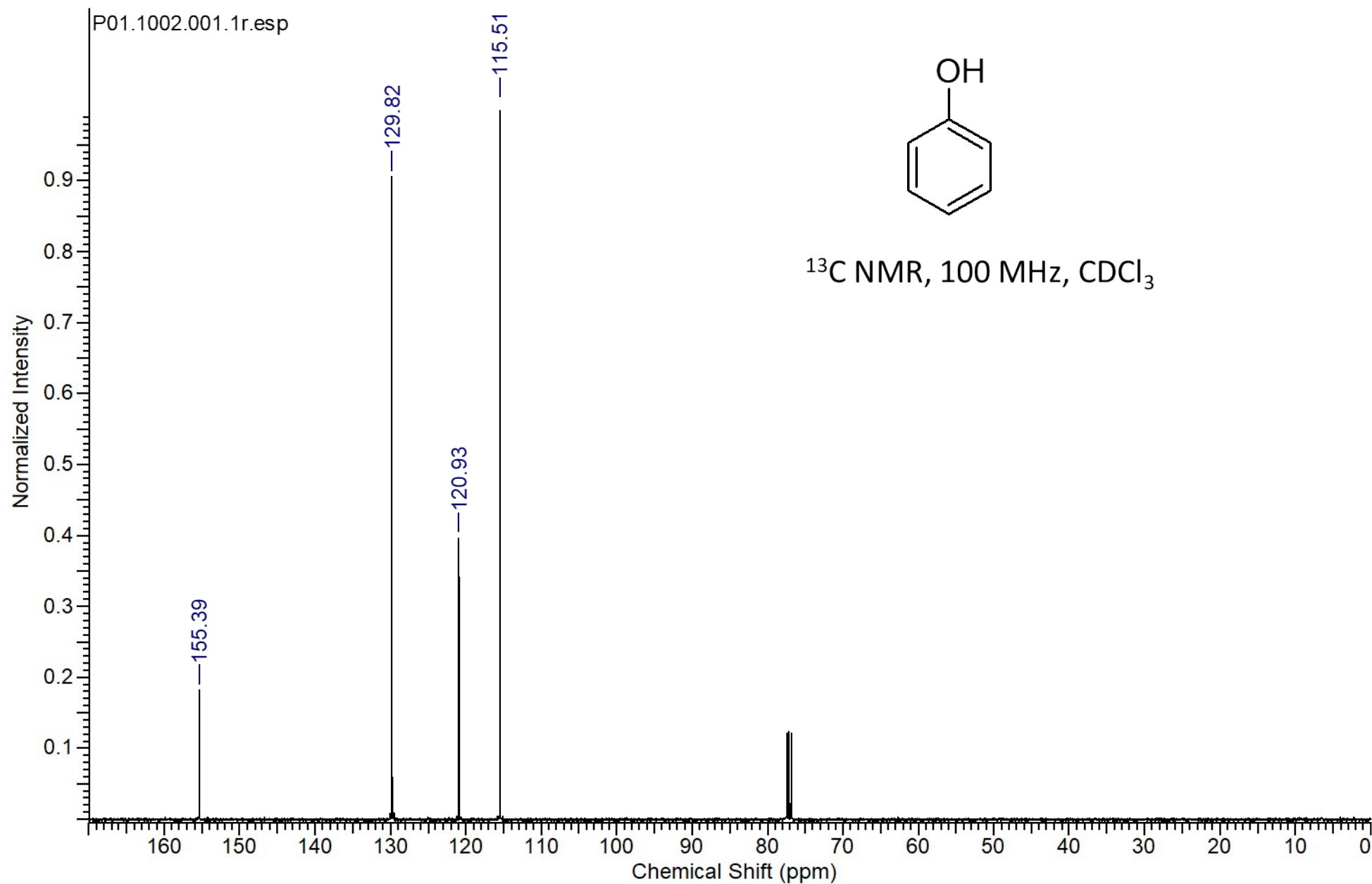
^1H and ^{13}C NMR spectra of the products

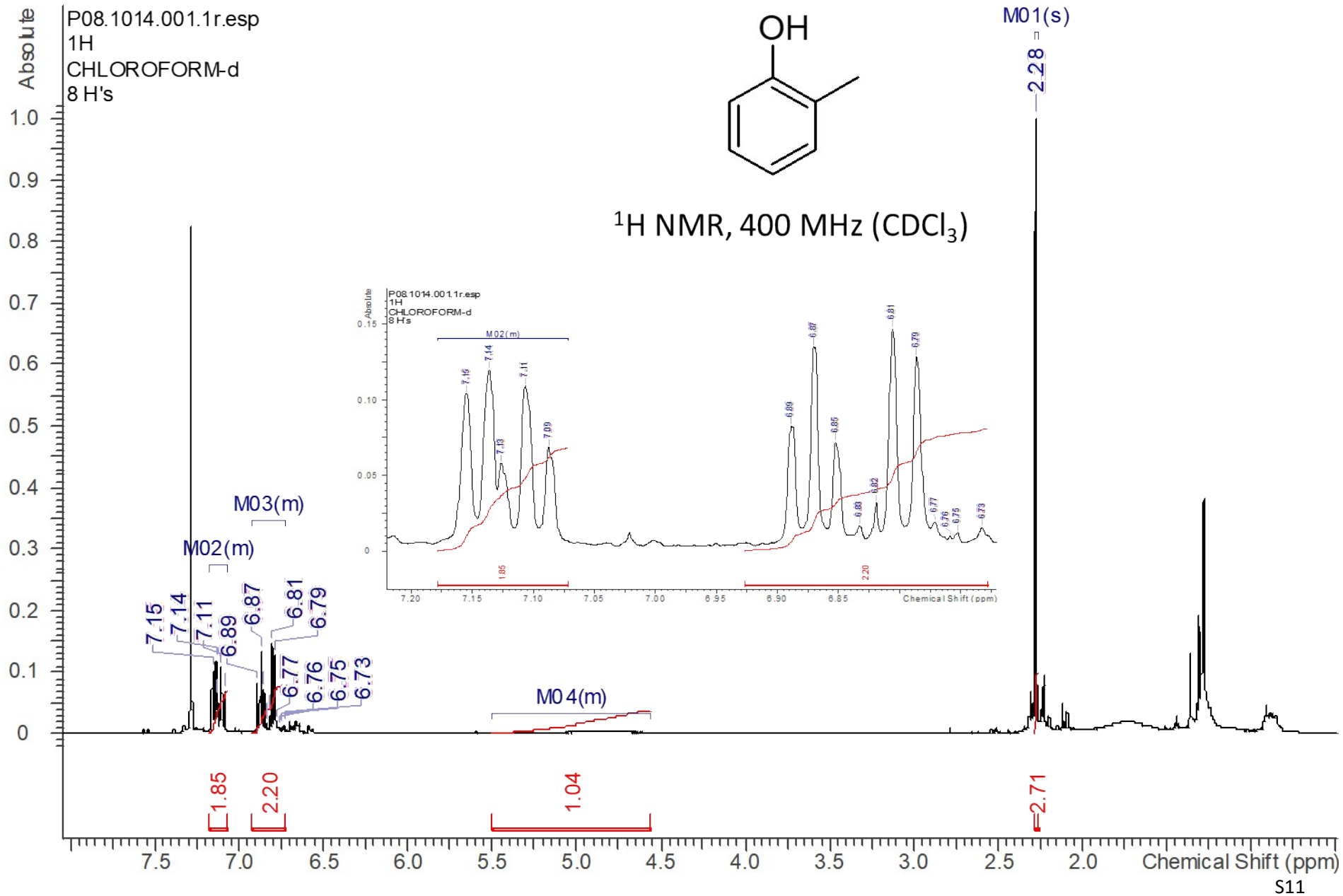


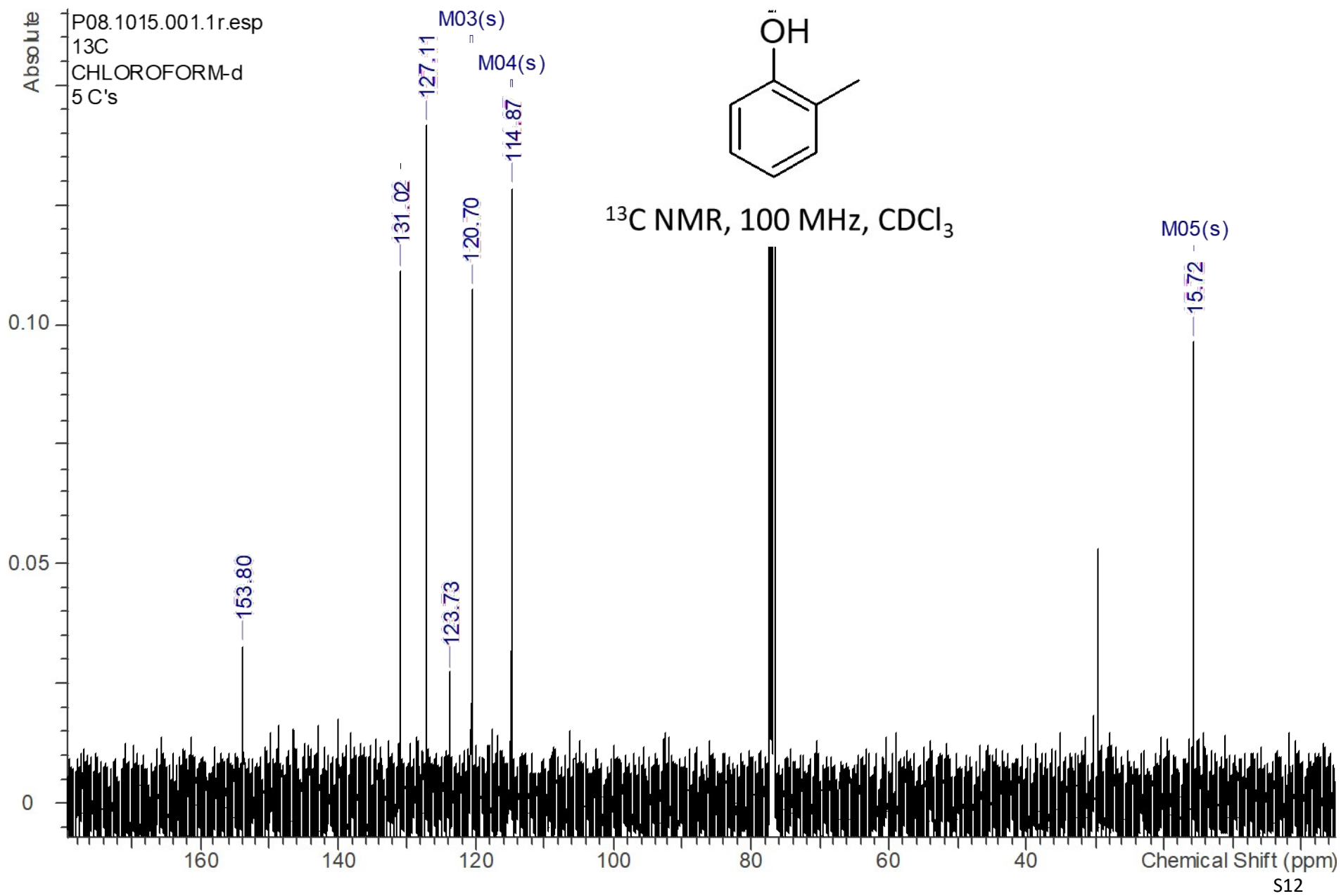
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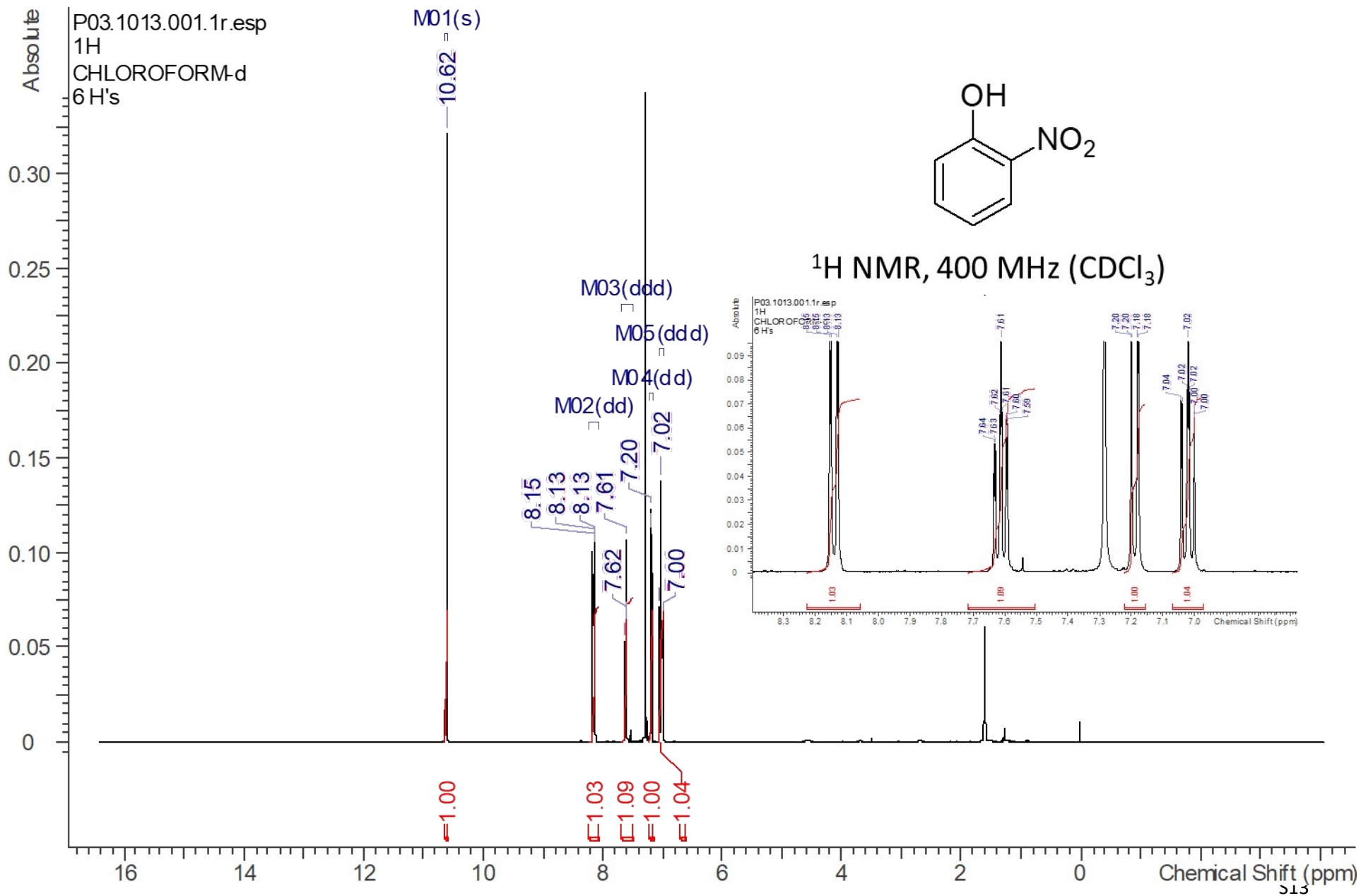


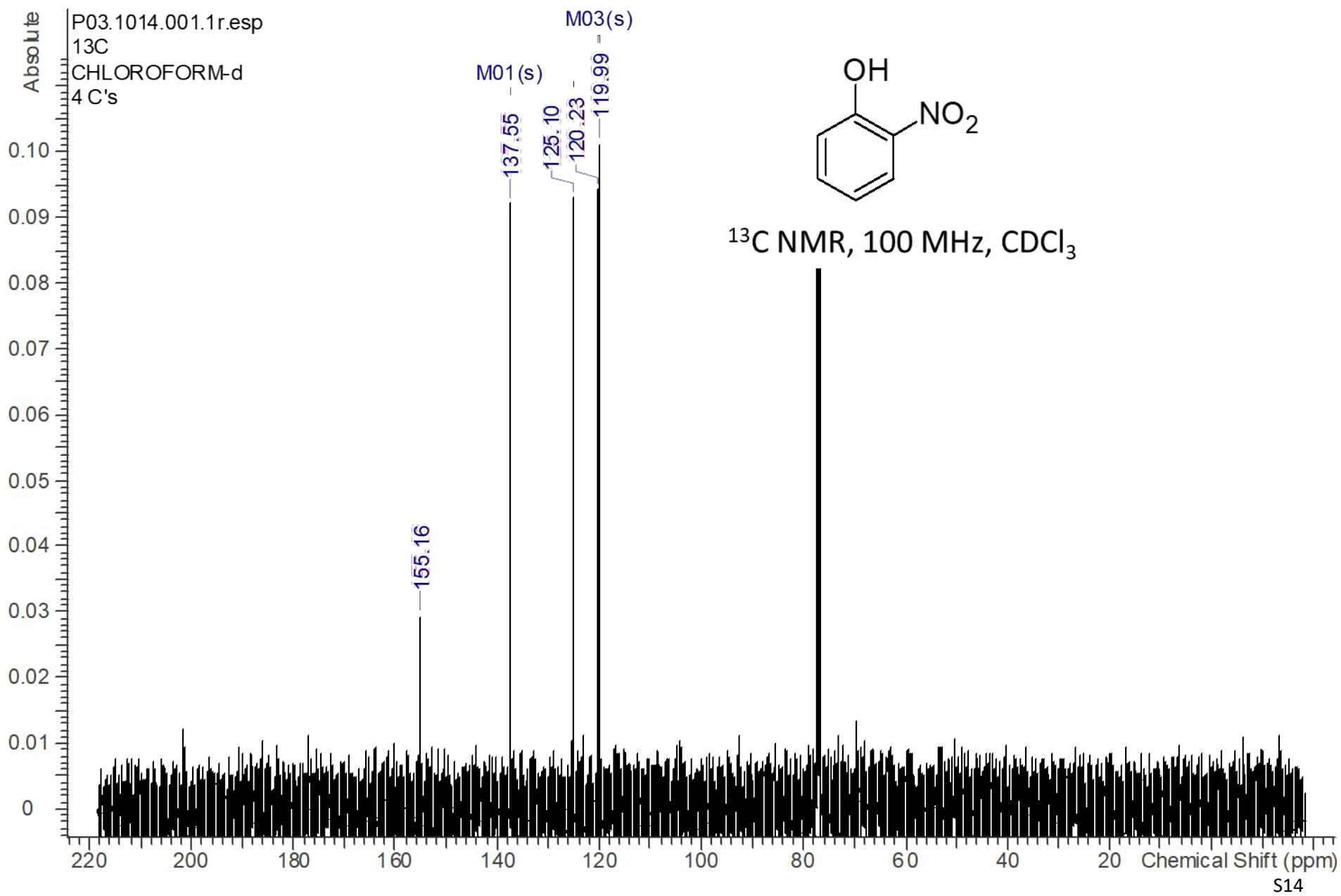
^{13}C NMR, 100 MHz, CDCl_3

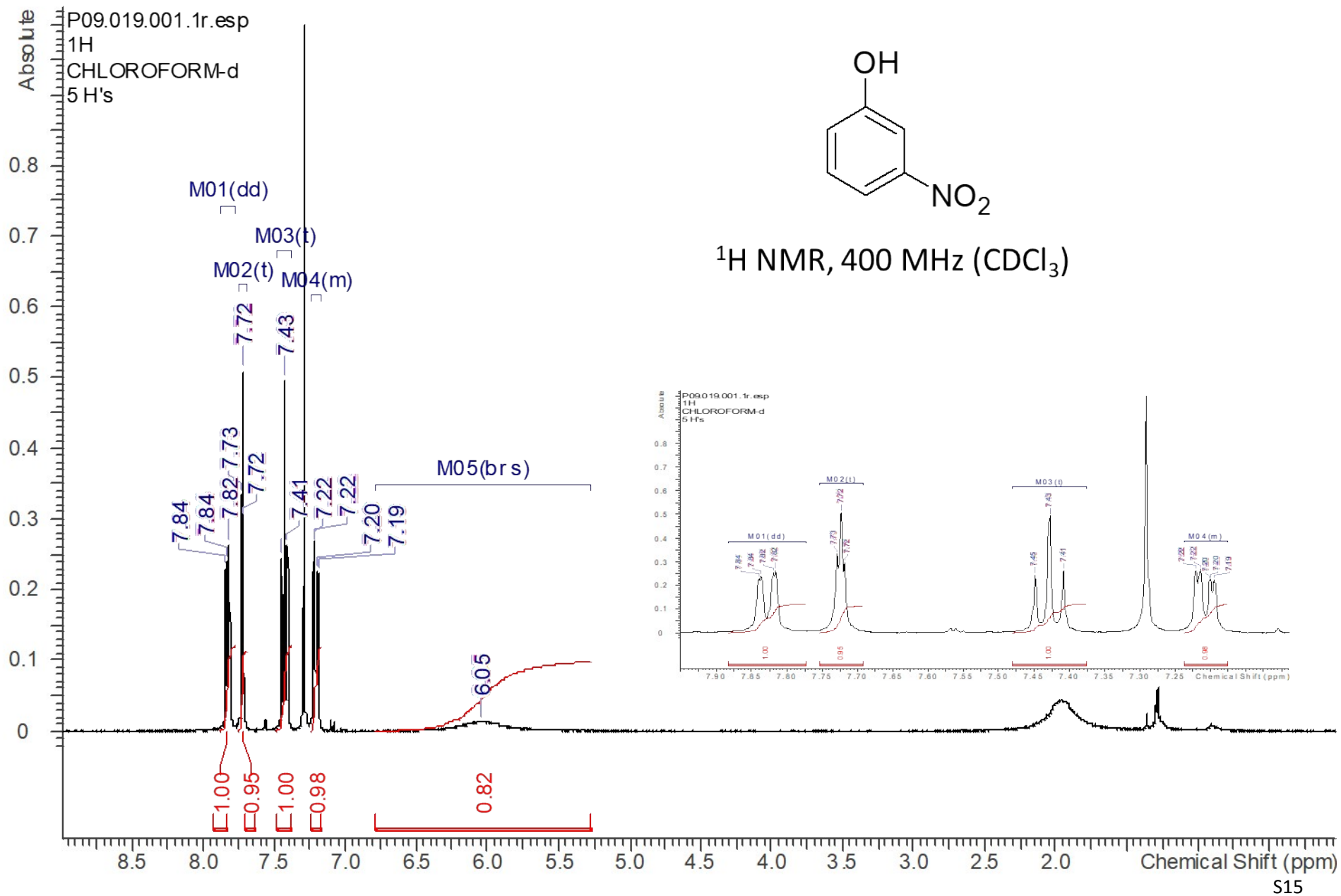




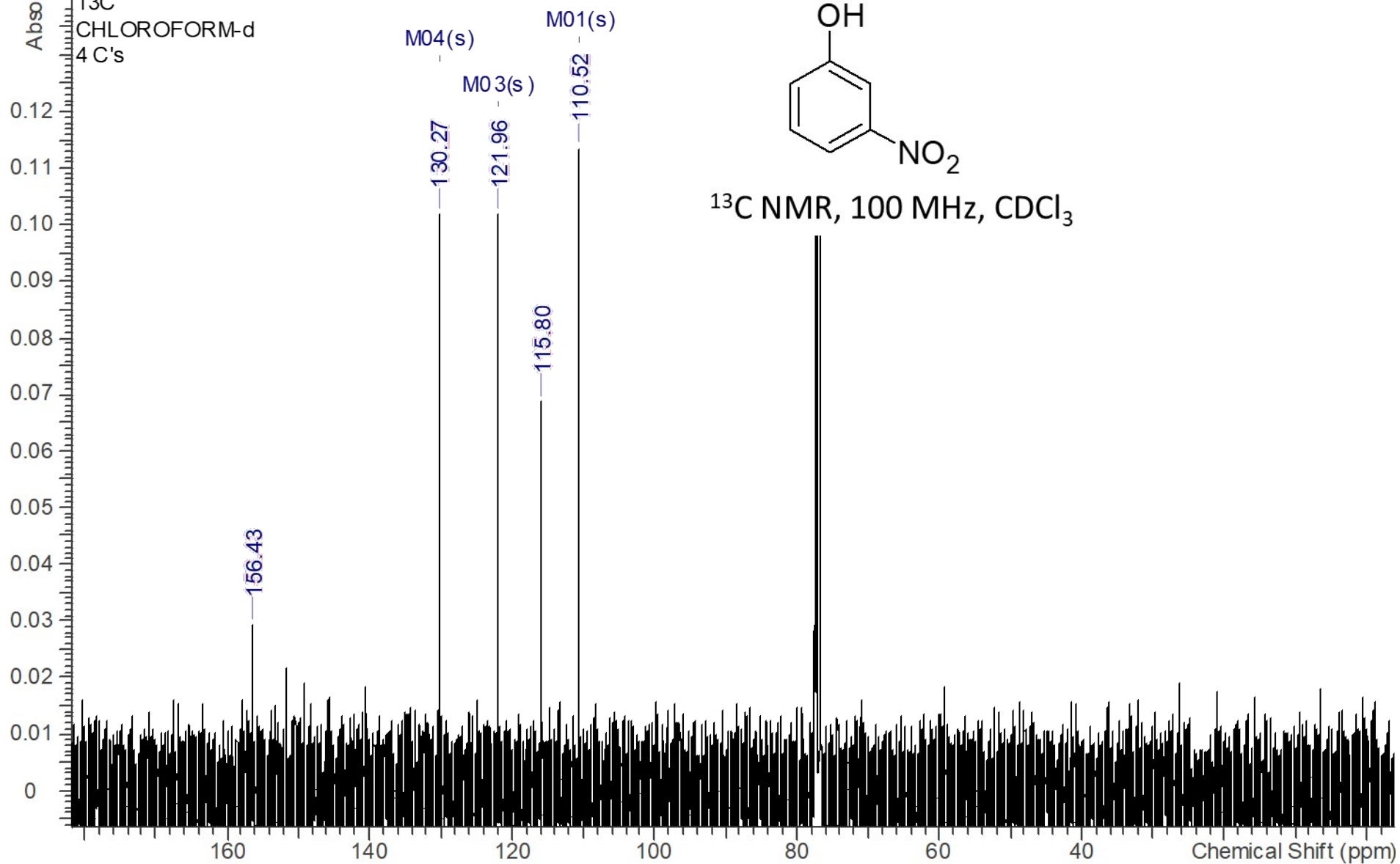


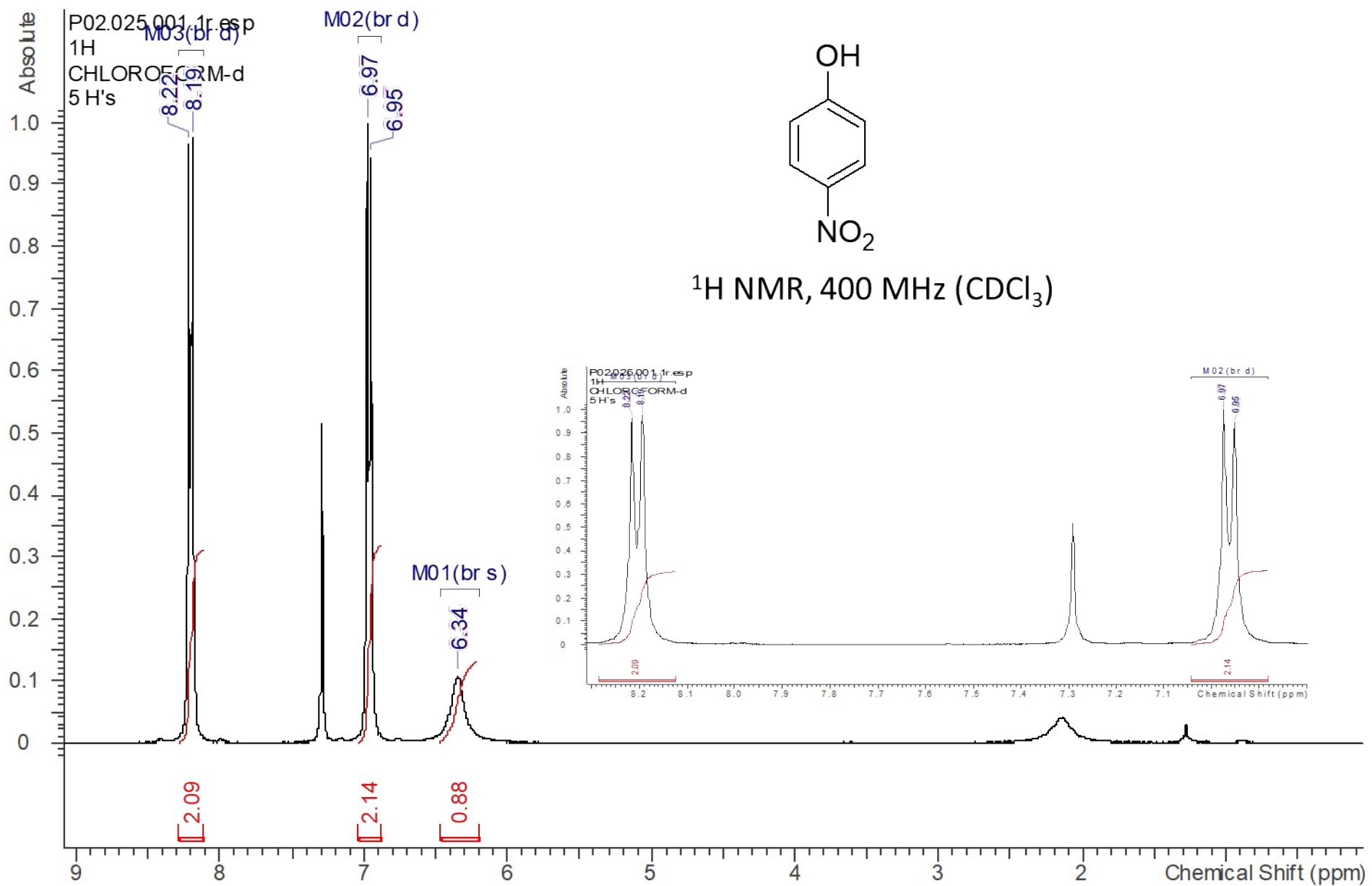


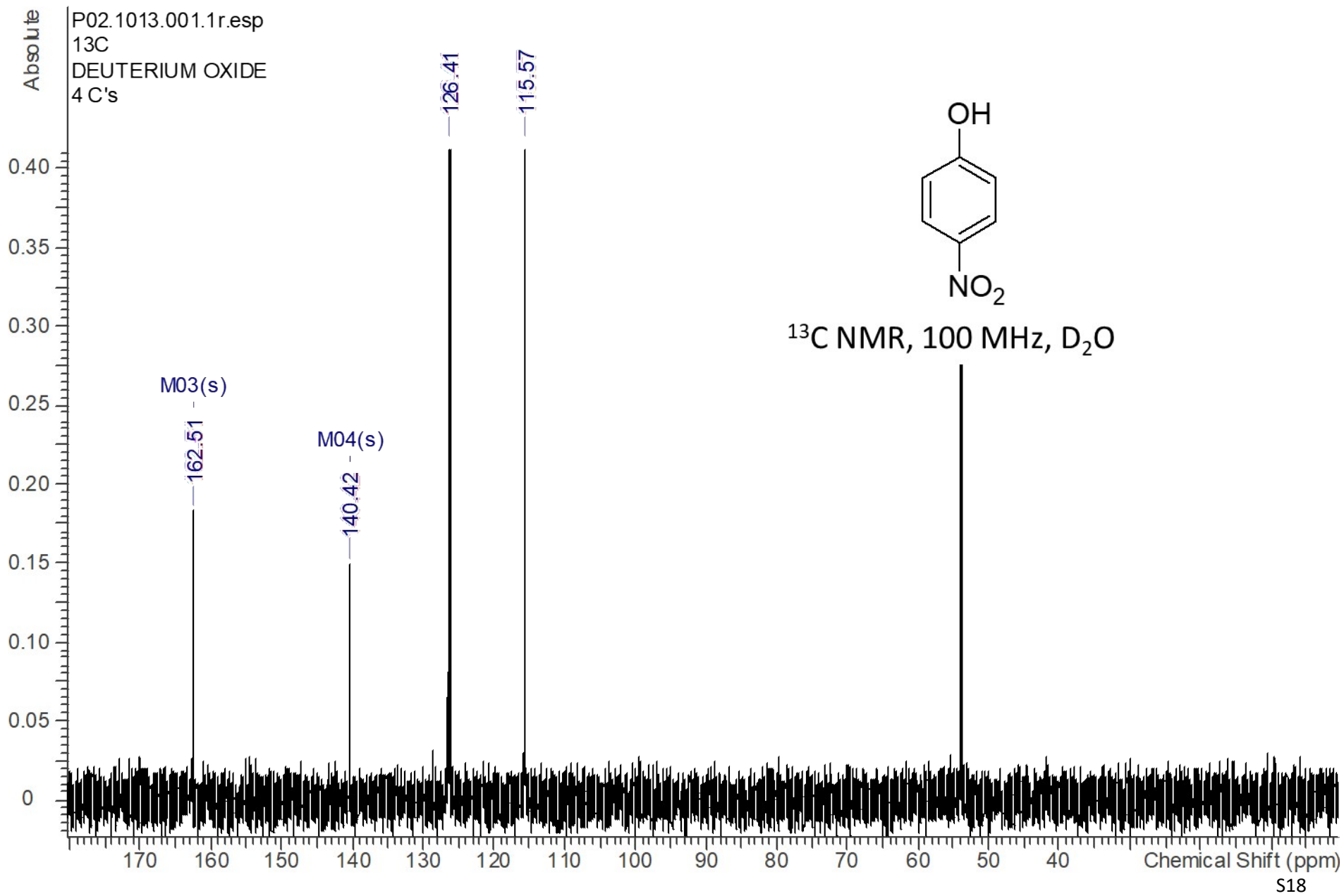


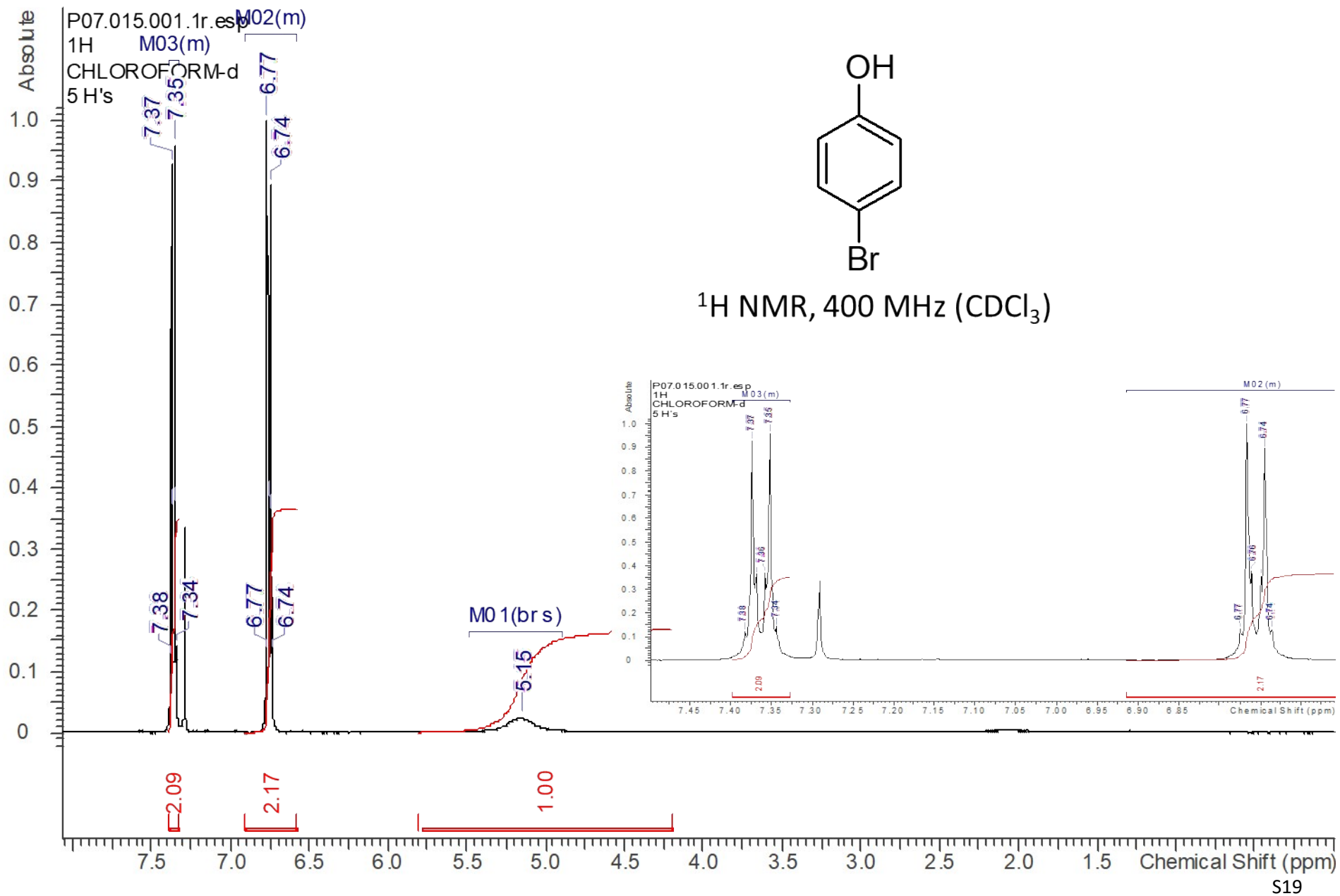


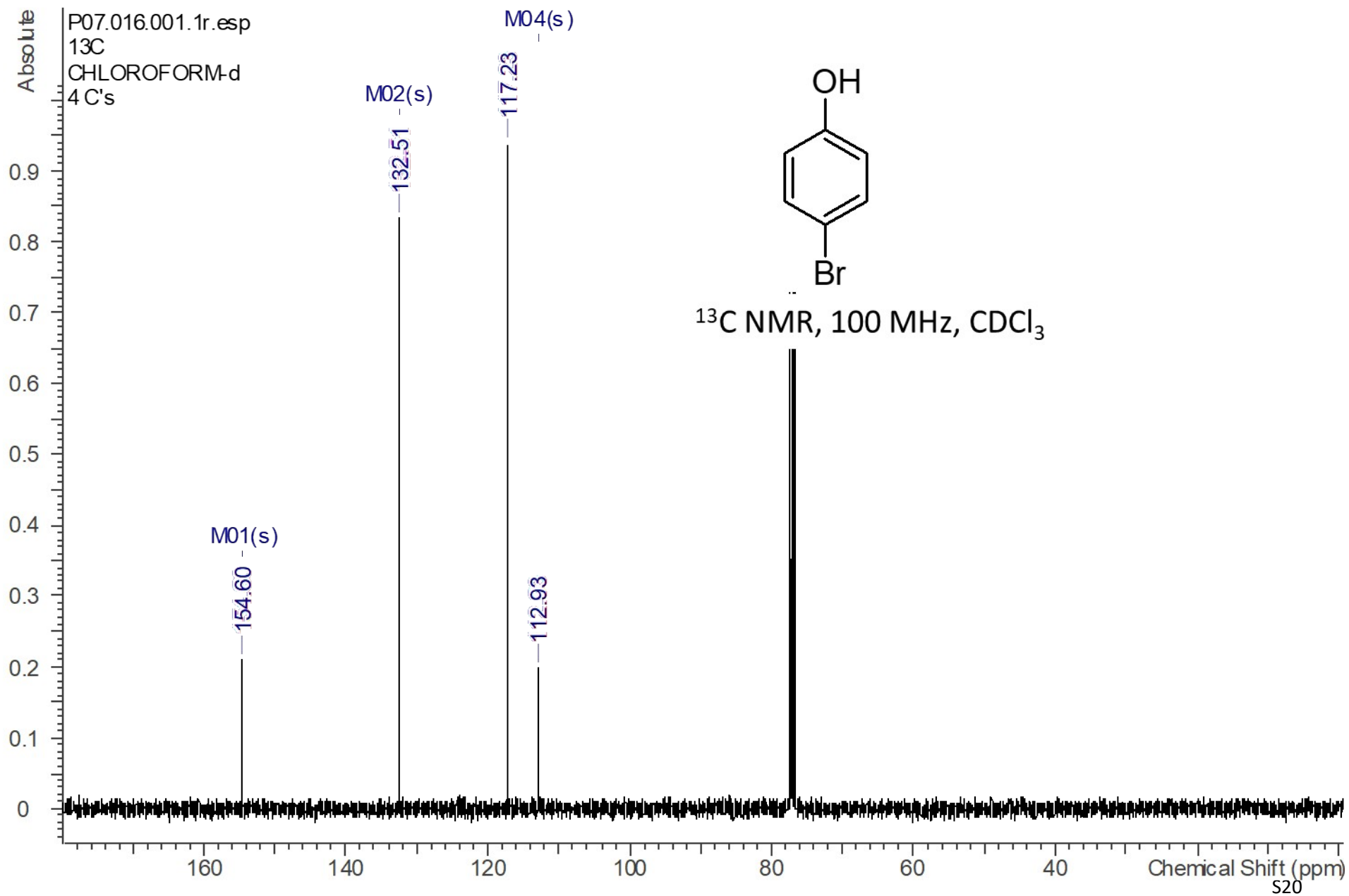
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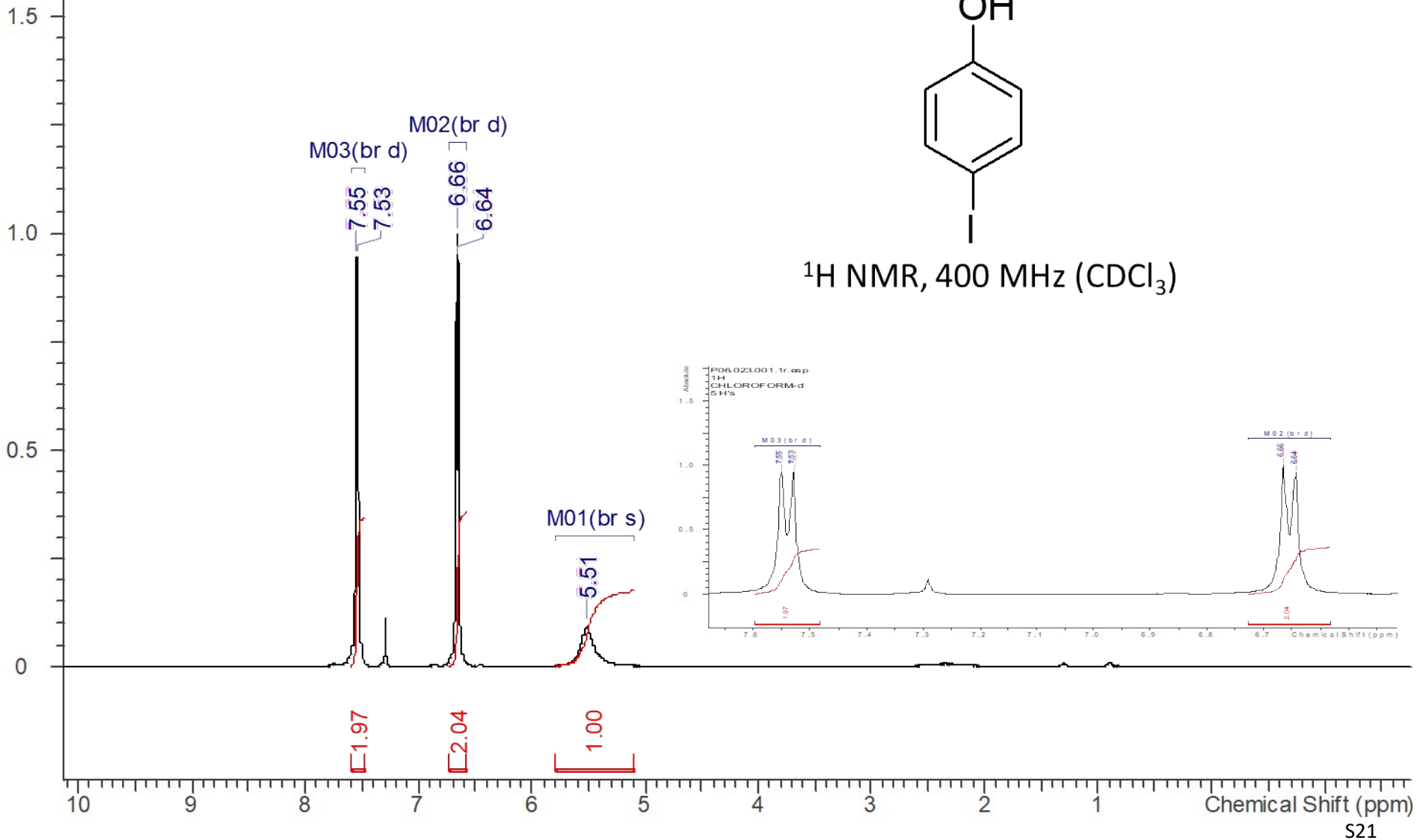


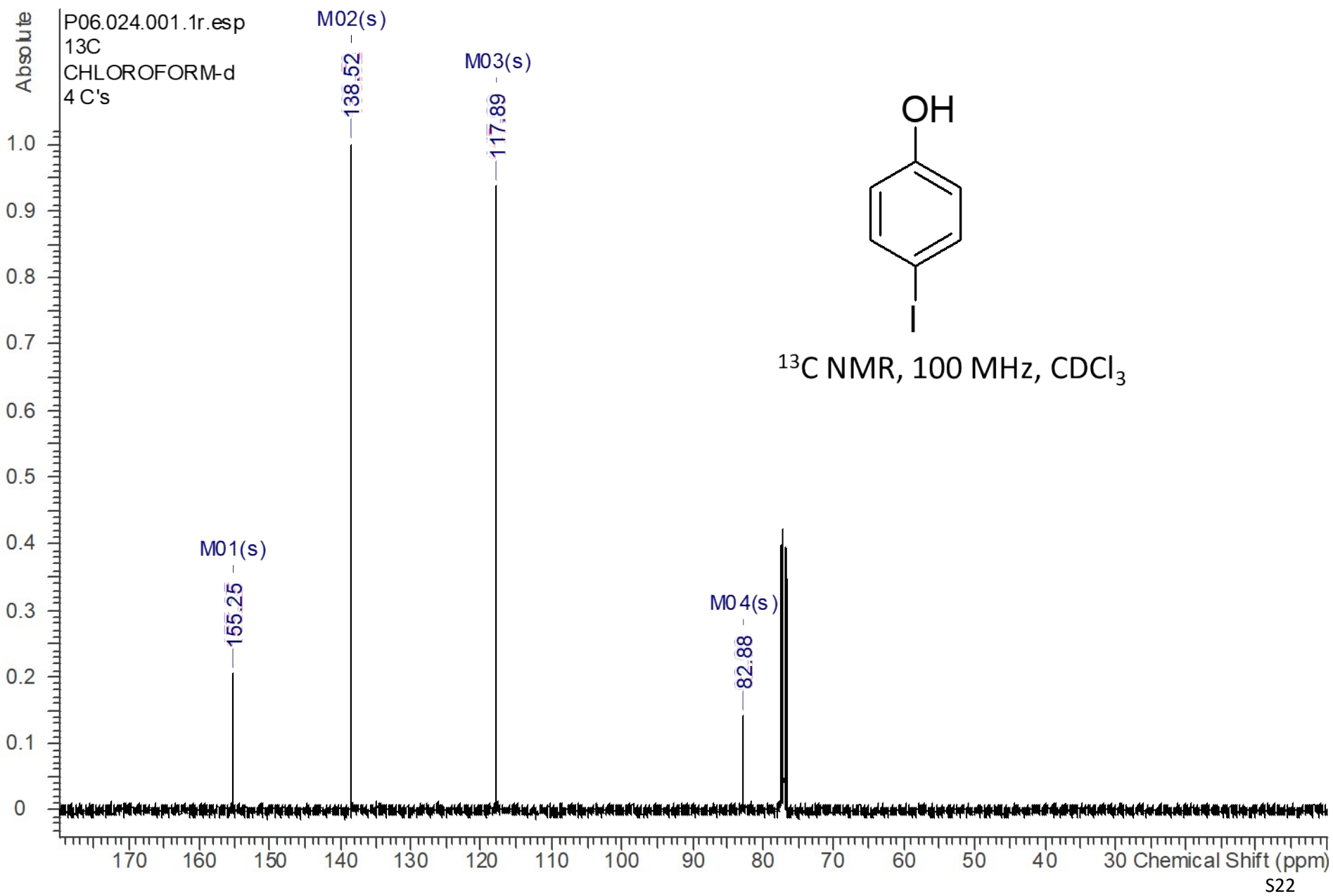




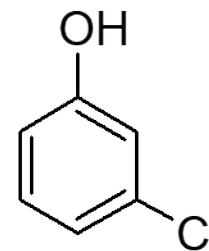


P06.023.001.1r.esp
1H
CHLOROFORM-d
5 H's





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1H
CHLOROFORM-d
5 H's



¹H NMR, 400 MHz (CDCl₃)

