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SUPPORTING INFORMATION

The first report of hercynite as a solid support, L-methionine-pd complex supported on hercynite as highly efficient reusable nanocatalyst for C-C cross coupling reactions

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Experimental

Preparation of L-Methionine-Pd heterogenized complex supported on the surface of hercynite magnetic nanoparticles (Hercynite@L-Methionine-Pd)

The hercynite magnetic nanoparticles were prepared by the coprecipitation technique as it was previously reported [68]. A mixture of $Al(NO_3)_3 \cdot 9H_2O$ (2 mmol) and $FeCl_2 \cdot 4H_2O$ (4 mmol) was dissolved in 100 mL of water and stirred at 80 °C under N_2 protection. In the next step, 10 mL of aqueous NaOH solution (0.2 M) was added to the reaction mixture (the pH of solution was found to be 12). After 30 min of stirring the mixture, an external magnet collected the prepared hercynite MNPs which were washed with deionized water and ethanol few times and, then, dried at 75 °C in an oven for 4 h. For the immobilization of the L-Methionine amino acid on the surface of hercynite heterogeneous support, 1 g of the prepared hercynite nanoparticles was dispersed in 50 mL water by sonication for 30 min. and, then, L-Methionine (2.5 mmol) was added to the reaction mixture which was stirred

under the N_2 atmosphere at reflux conditions for 24 h. Afterwards, the obtained Hercynite@L-Methionine MNPs were washed with hot deionized water and hot ethanol few times and, then, dried at 75 °C in an oven for 4 h. Finally, in order to synthesize the target Hercynite@L-Methionine-Pd heterogenized complex, 0.5 g of Hercynite@L-Methionine MNPs was dispersed in 30 mL ethanol by sonication for 30 min and, then, $Pd(OAc)_2$ (0.25 g) was added to the reaction mixture. Then, it was stirred under the N_2 atmosphere at 80 ºC for 24 h. In the next step, 3 mmol of $NaBH_4$ was added to the reaction and stirred for 2 more hours. Then, the obtained Hercynite@L-Methionine-Pd MNPs was separated using an external magnet, washed with water and ethanol and dried at 80 °C in an oven for 12h.

2.2 | General procedure for the Suzuki reaction

A mixture of Phenylboronic acid (1 mmol), aryl halide (1 mmol), K_2CO_3 (3 mmol) and Hercynite@L-Methionine-Pd (0.1 mol %) was dissolved in 3 mL ethanol and stirred at 80 ºC under reflux conditions. The progress of the reaction was monitored by TLC. Upon the completion of the reaction, the mixture was cooled down to room temperature

and the catalyst was separated by magnetic separation technique, and washed with EtOAc. Finally, the reaction mixture was extracted with H_2O and EtOAc. The organic layer was dried over Na_2SO_4. Finally, the solvent was evaporated, and the corresponding pure products were obtained in excellent yields.

General procedure for the Heck reaction

A mixture of buthyl acrylate (1.2 mmol), aryl halide (1 mmol) and K_2CO_3 (3 mmol) was dissolved in 2 mL PEG-400 and ,then, Hercynite@L-Methionine-Pd (0.125 mol %) was added to the flask and, finally, the mixture was stirred at 80 ºC under reflux conditions. The progress of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated from the reaction mixtire via magnetic separation technique; the reaction mixture was extracted with ethyl acetate and water. The organic layer was dried over Na_2SO_4. Then, the solvent was evaporated and the corresponding pure products were consequently obtained.

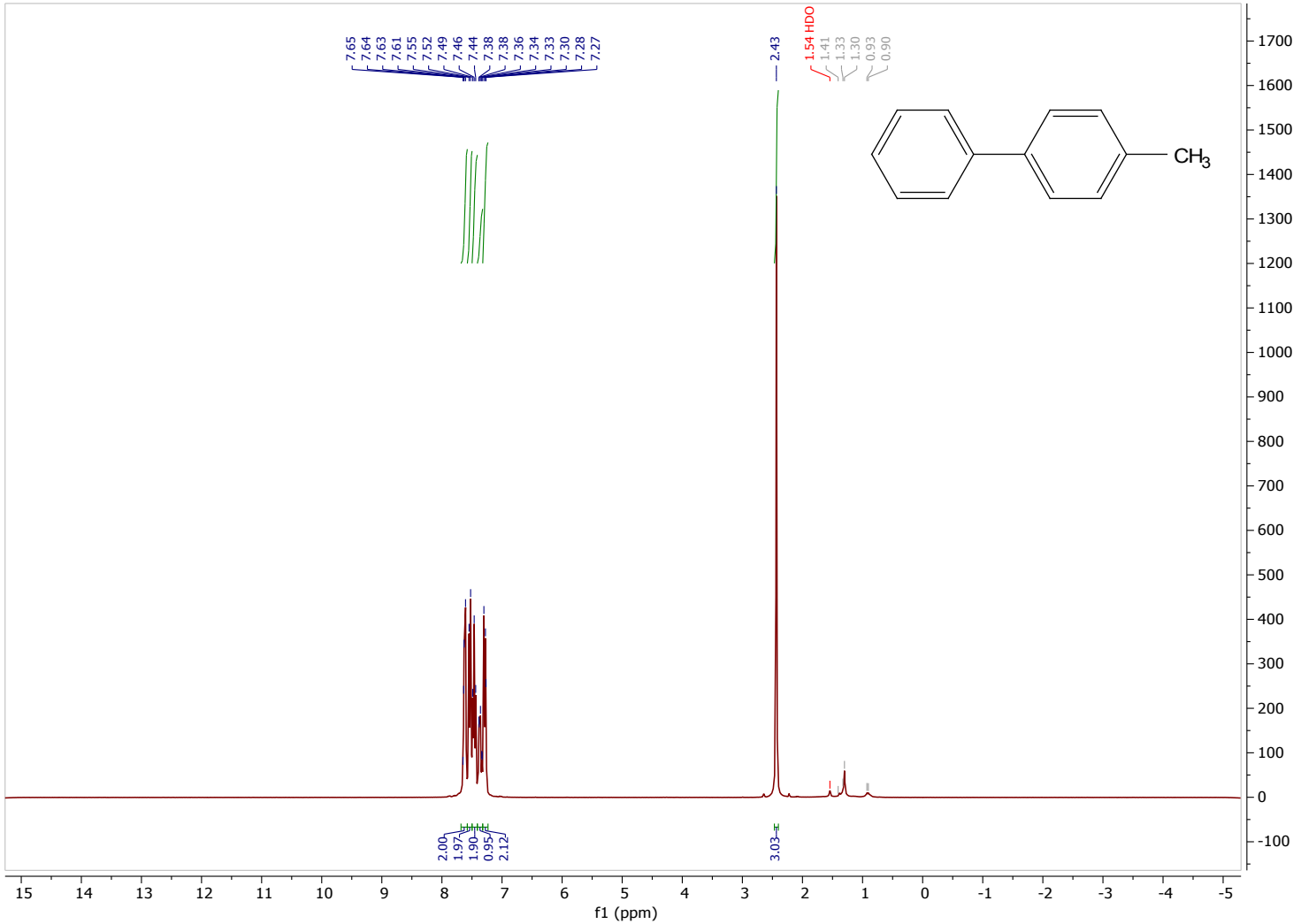
Selected spectral data

4-methylbiphenyl: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.66-7.61 (m,2H), 7.55-7.52 (m, 2H), 7.49-7.44 (m, 2H), 7.38-7.333 (m,1H), 7.30- 7.227 (m,2H), 2.43(s, 3H, Me).

3-methoxybiphenyl: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.63-7.55(m, 2H), 7.48-7.34(m, 2H), 7.21-7.18(m, 2H),7.22-7.14(t, J=2, 1H), 6.94-6.90(m, 1H), 3.01(s,1H)

4-methoxybiphenyl: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.60-7.53(m, 4H), 7.45(t, J=7.5, 2H), 7.35(t, J=7.2, 1H), 7.03-6.98(m, 2H), 3.88(s, 3H)

4-Nitro-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 8.34-8.31 (d, J = 8 Hz, 2H), 7.78–7.75 (d, J = 12 Hz, 2H), 7.67–7.65 (d, J = 12Hz, 2H), 7.55-7.51 (m, 2H) 7.50-7.45 (m, 1H).


7.65
7.64
7.63
7.61
7.55
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7.49
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7.38
7.38
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7.34
7.33
7.30
7.28
7.27
2.43
1.54 HDO
1.41
1.33
1.30
0.93
0.90
CH3
2.00
1.97
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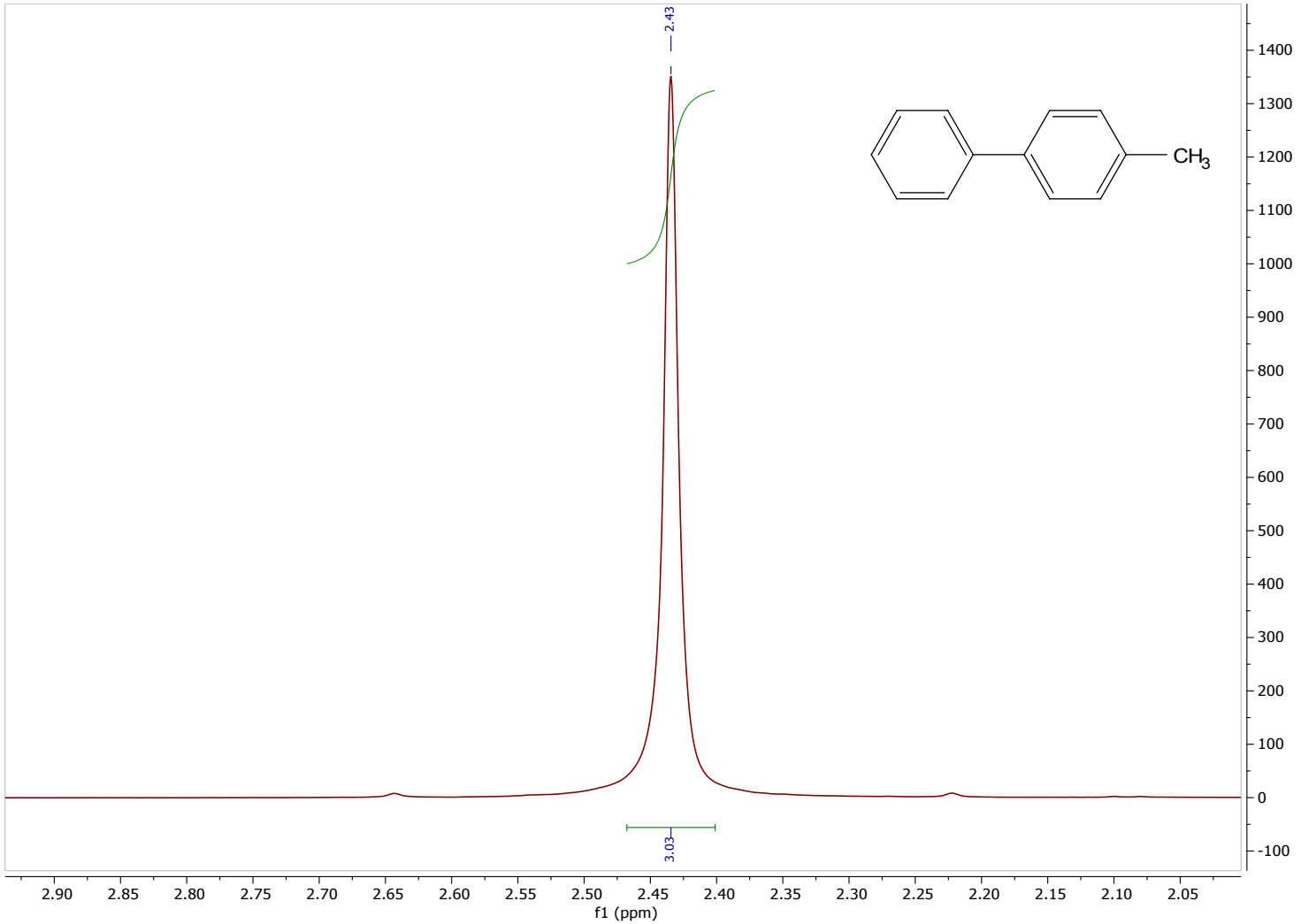
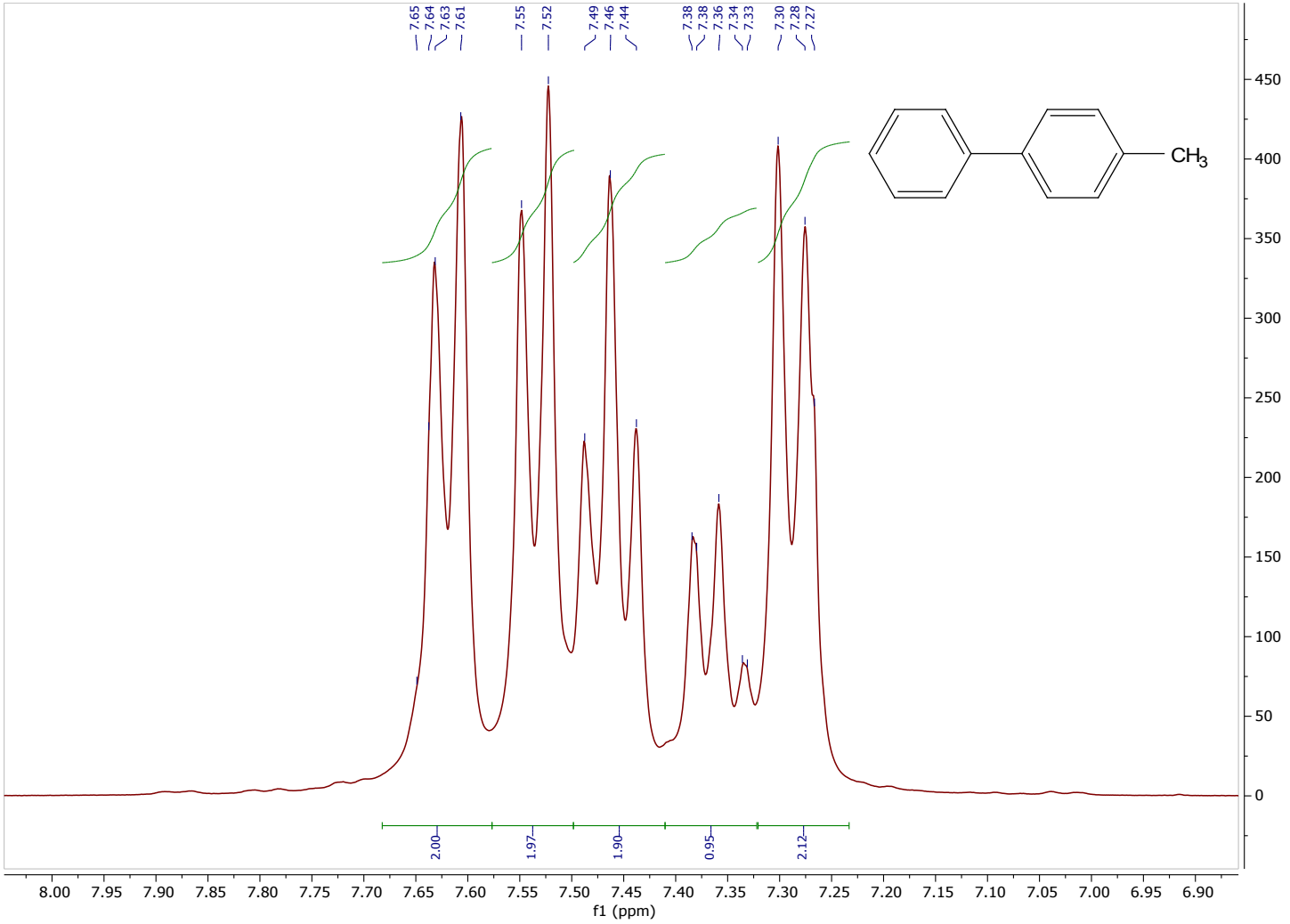
2.12
3.03
f1 (ppm)

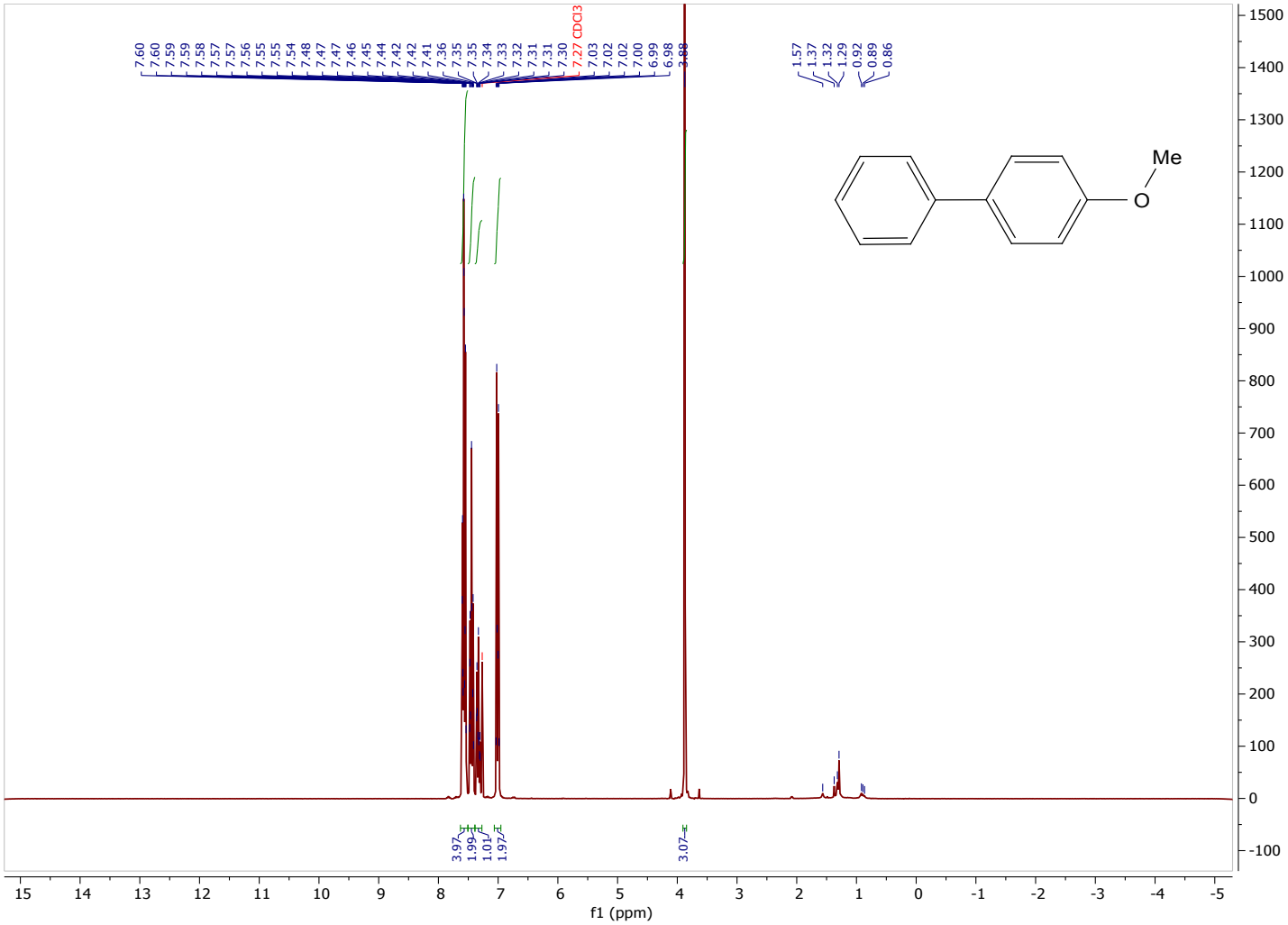
4-Methyl-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



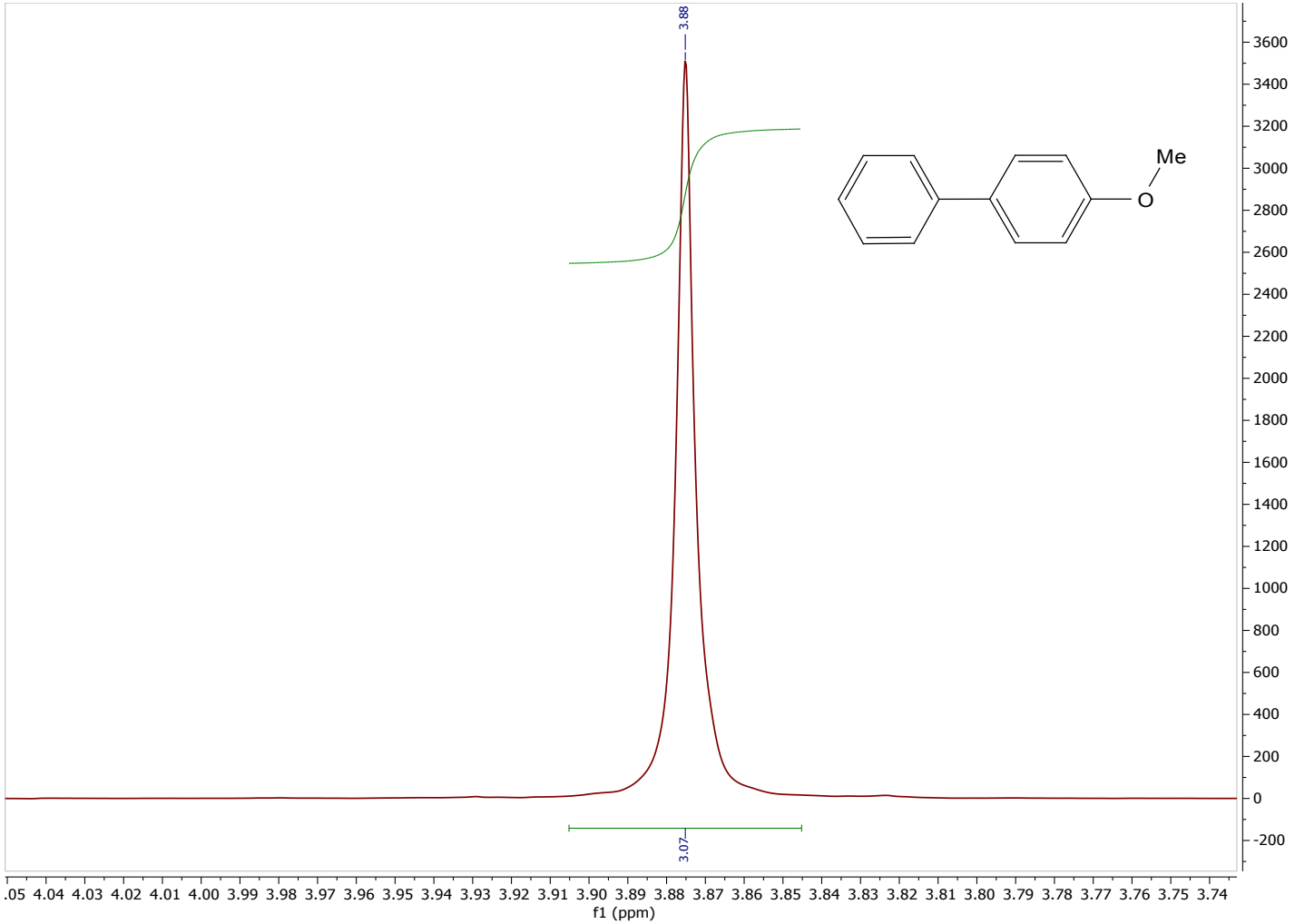
4-Methyl-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



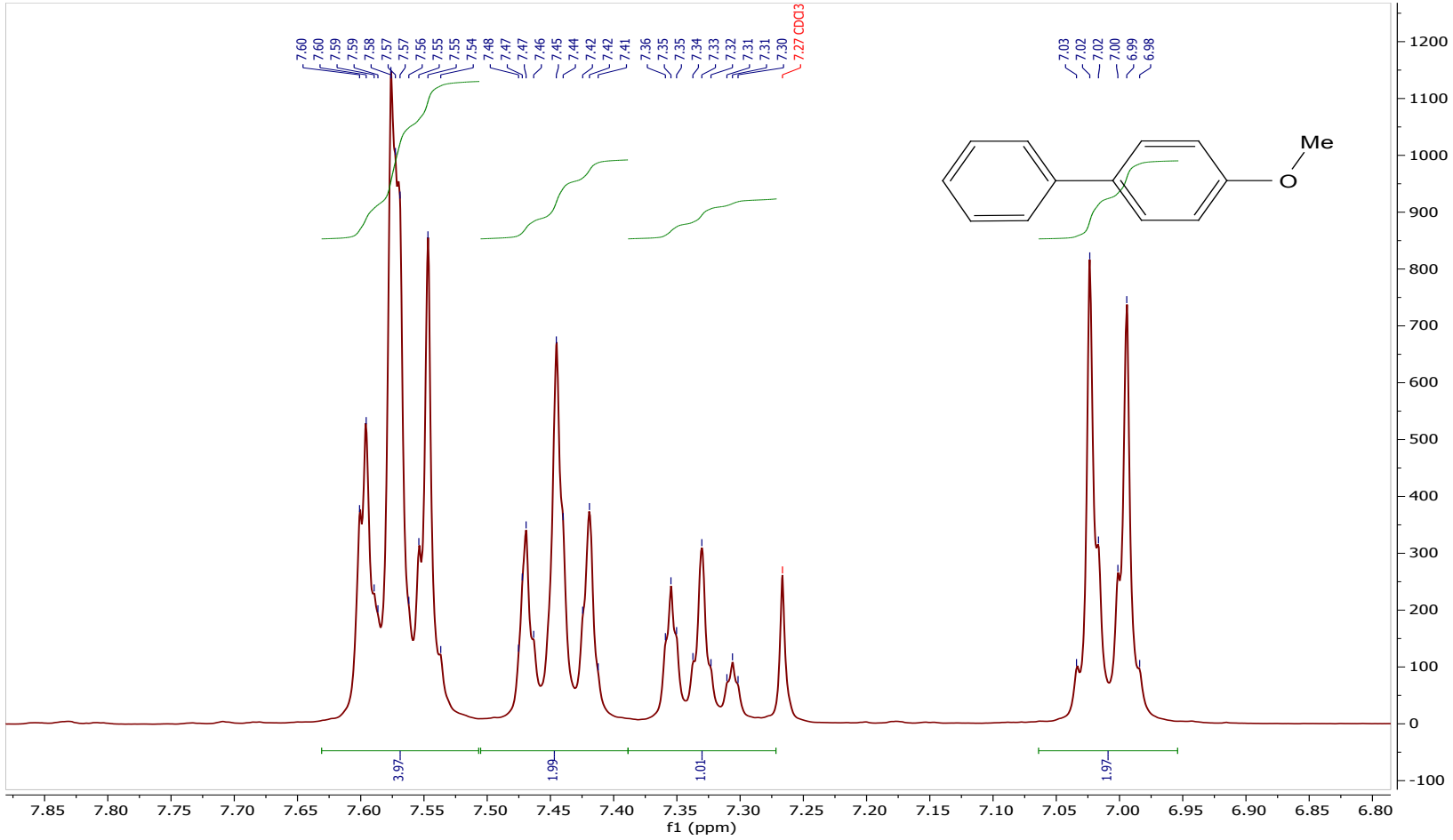
4-Methyl-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



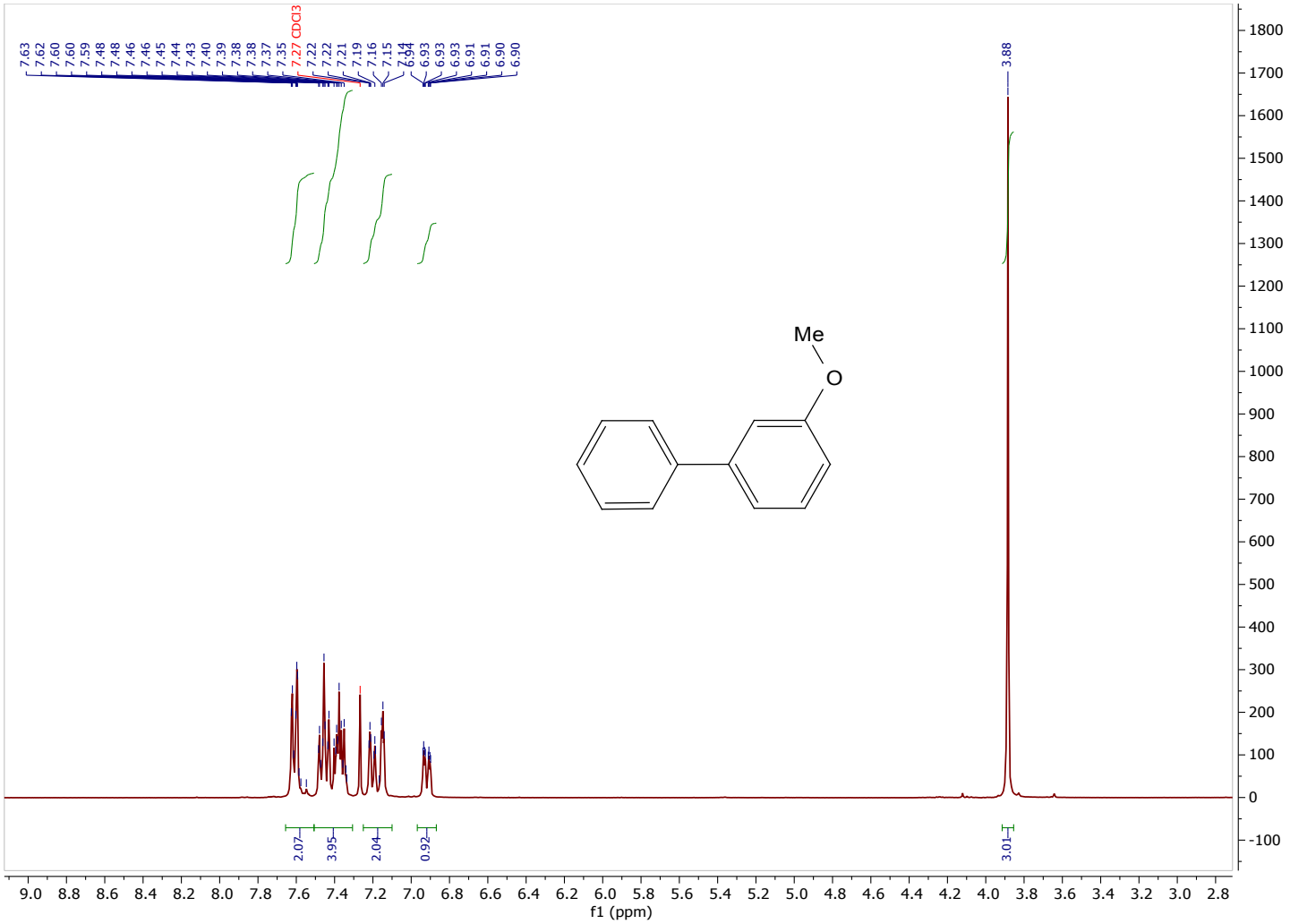
4-Methoxy-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



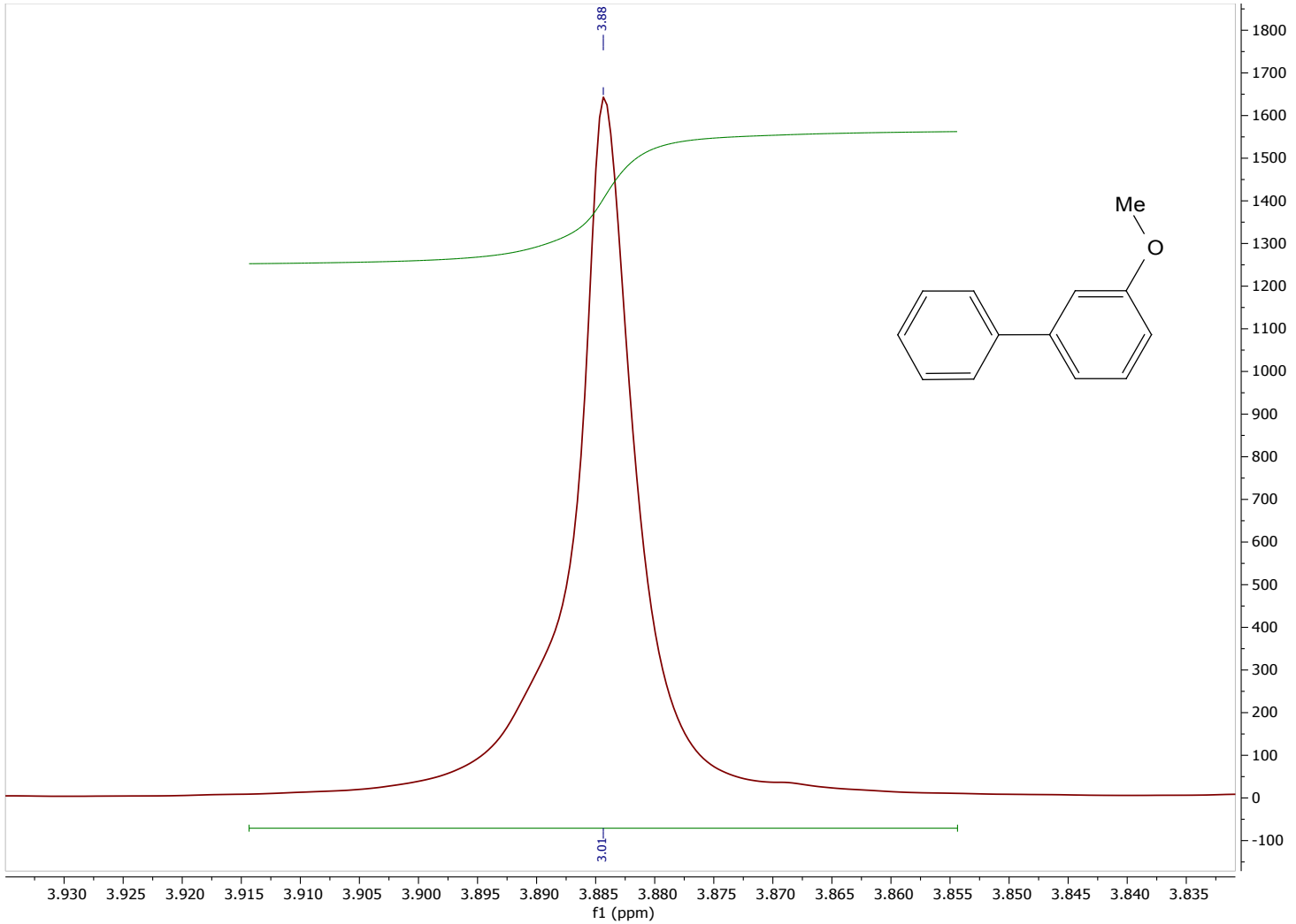
4-Methoxy-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



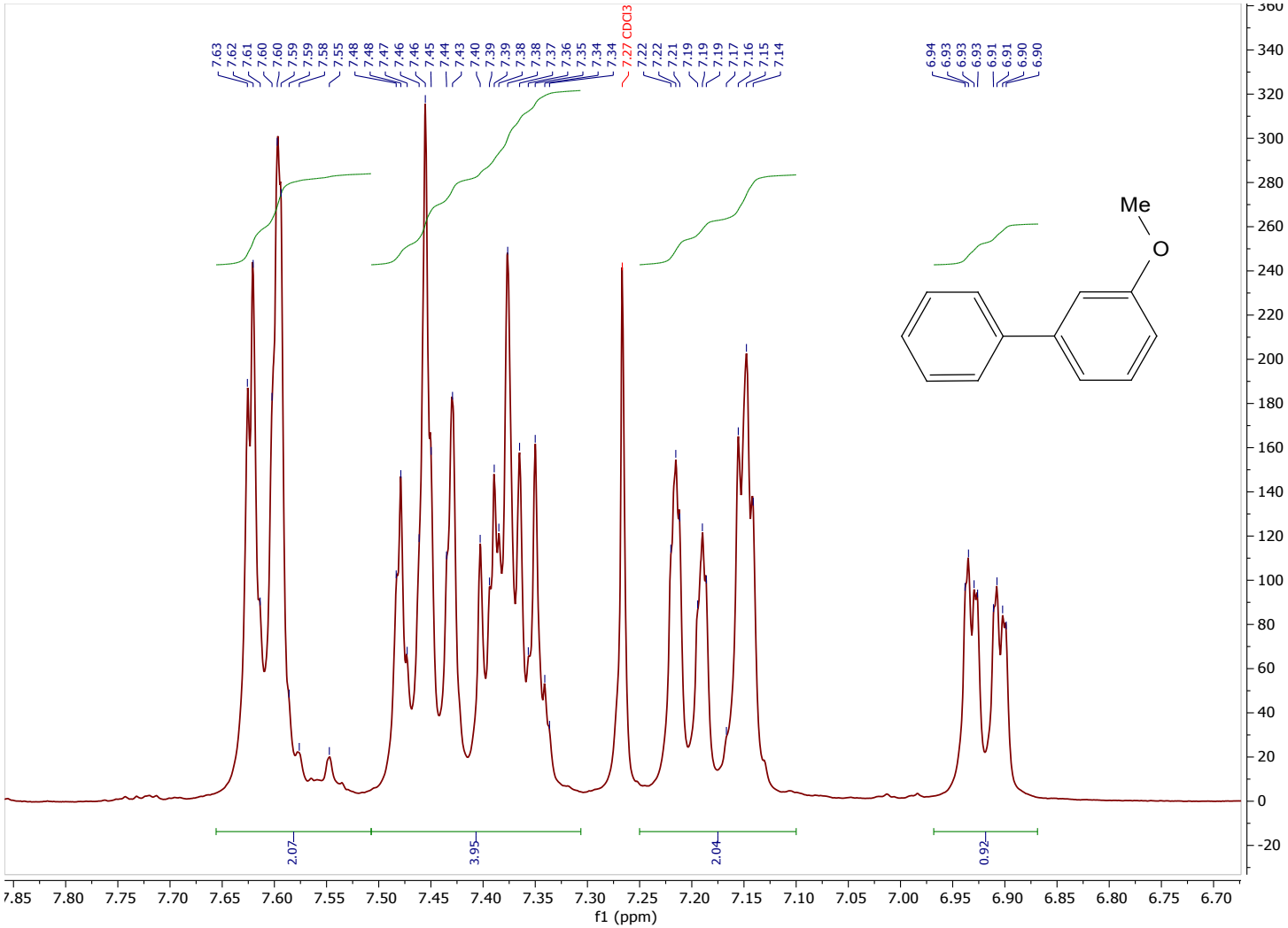
4-Methoxy-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



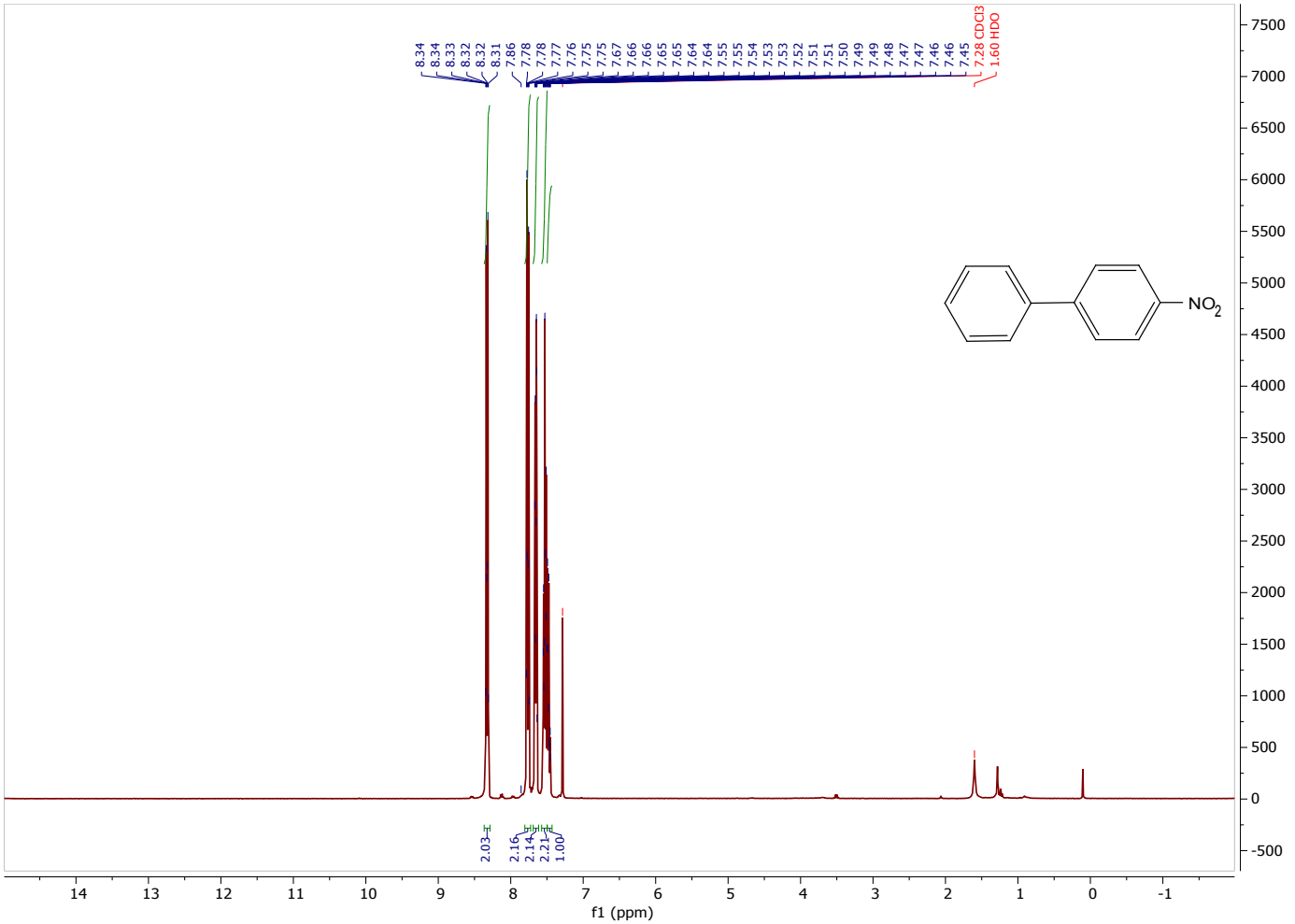
3-Methoxy-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



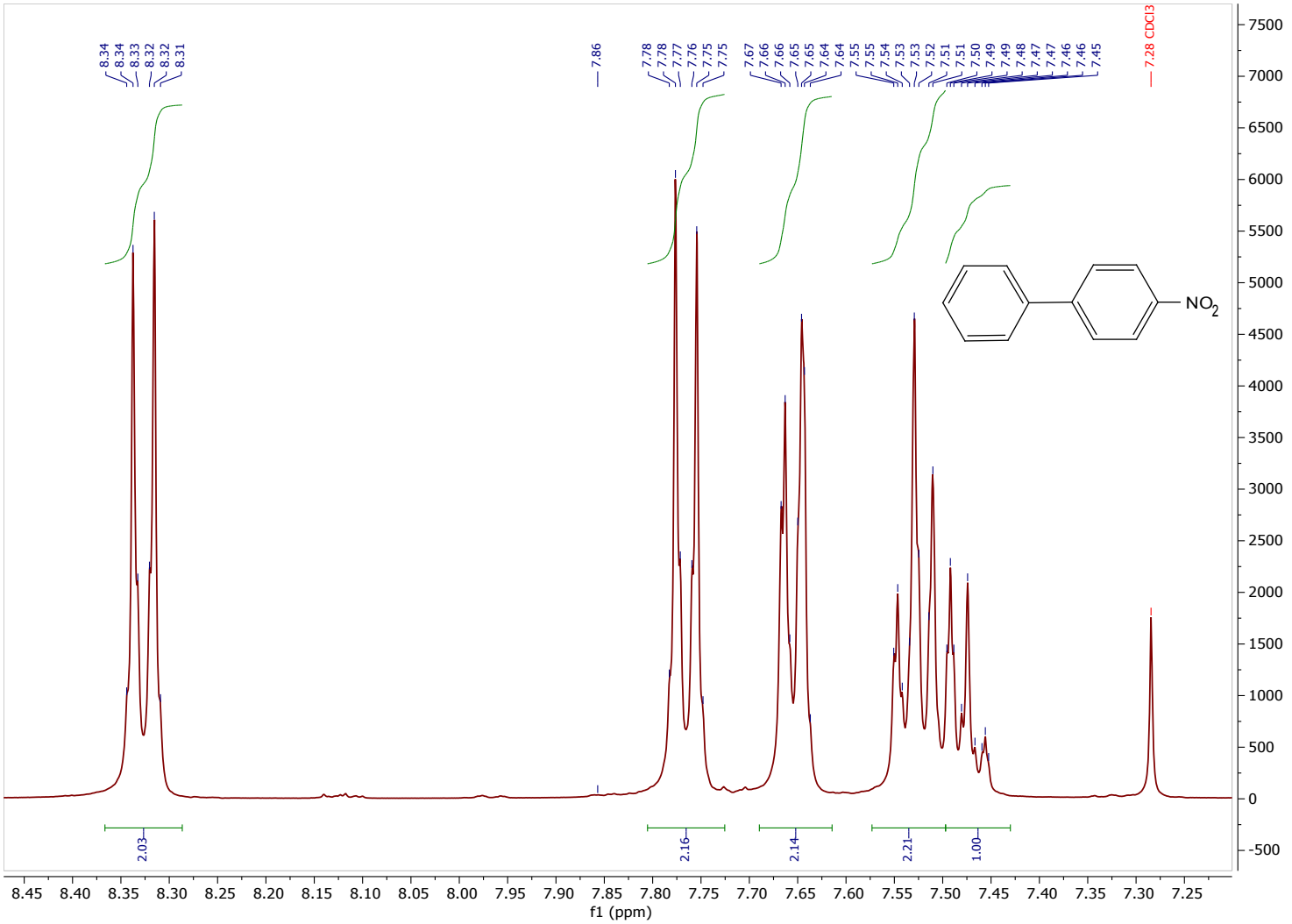
3-Methoxy-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



3-Methoxy-1,1'-biphenyl: ^{1}H NMR (300 MHz, $CDCl_3$)



4-Nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$)



4-Nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$)