Supporting Information

n-$Bu_4NI/K_2S_2O_8$-Mediated C–N Coupling between Aldehydes and Amides

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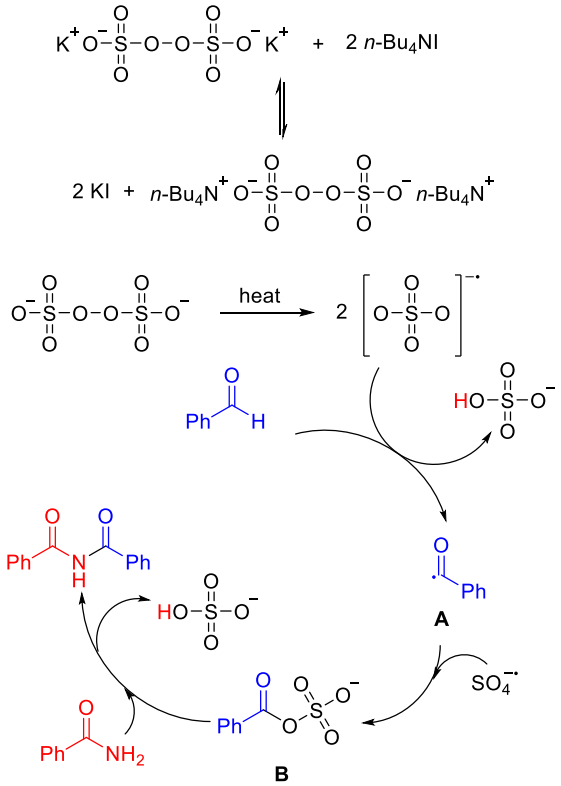
1. Density Functional Theory (DFT) Thermochemistry Calculations for the Proposed Mechanisms of the *n*-$Bu_4NI/K_2S_2O_8$-Mediated Cross Dehydrogenative Coupling between Benzaldehyde and Benzamide and the Transformylation from *p*-Anisaldehyde to Benzamide.

Computational Methods

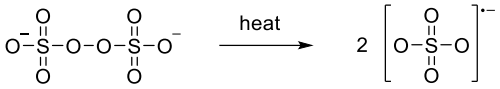
DFT electronic structure calculations were performed using the ωB97XD[1] functional coupled with the 6-31+G(d,p) basis set, except for the reactions involving the iodine species for which the LANL2DZ basis set (which uses D95V on first row[2] and Los Alamos ECP plus DZ on Na-La and Hf-Bi[3]) was used. Geometries of reactants and products were fully optimized by calculating force constants at every step. Thermal corrections, reaction enthalpies (ΔH) and changes of Gibbs free energy (ΔG) were calculated by the standard statistical thermodynamical methods using the unscaled ωB97XD vibrational frequencies and the rigid rotor and harmonic oscillator approximations. All reactions were calculated in the acetonitrile solvent using the SMD solvation model.[4] Reaction enthalpy and change of Gibbs free energy reported for each product pathway include zero-point energies (ZPEs) and thermal corrections to 298 K.

The calculations were accomplished at a Linux computational cluster equipped with 20 nodes of dual Intel Xeon 28-core 2.7 GHz processors and using the Gaussian 16 suite of program.[5]

Scheme SI.1. Proposed Mechanism of the *n*-$Bu_4NI/K_2S_2O_8$-Mediated Cross Dehydrogenative Coupling between Benzaldehyde and Benzamide.



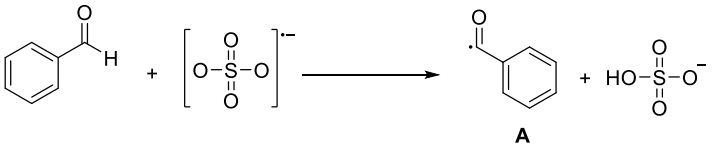
Elementary reaction (1)



ΔH (298 K) = 93 kJ/mol

ΔG (298 K) = 38 kJ/mol

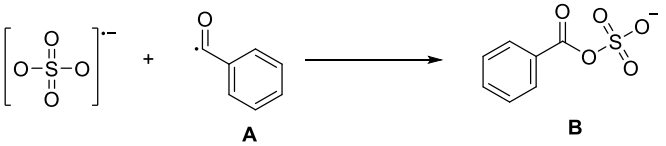
Elementary reaction (2)



ΔH (298 K) = - 40 kJ/mol

ΔG (298 K) = - 42 kJ/mol

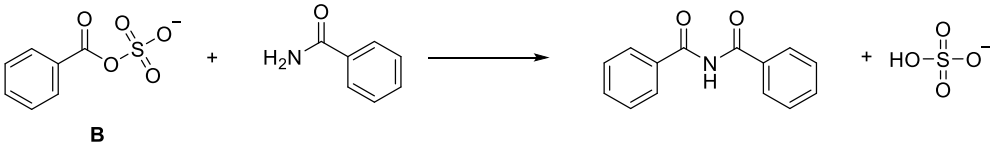
Elementary reaction (3)



ΔH (298 K) = -374 kJ/mol

ΔG (298 K) = -318 kJ/mol

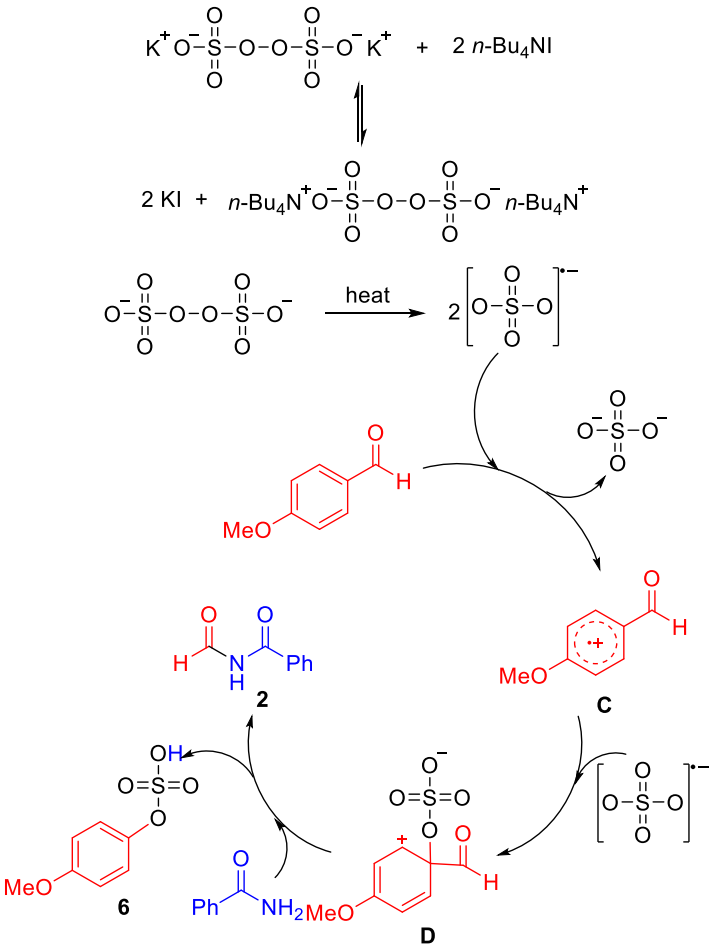
Elementary reaction (4)



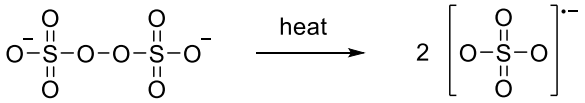
ΔH (298 K) = 18 kJ/mol

ΔG (298 K) = 22 kJ/mol

Scheme SI.2. Proposed Mechanism for the *n*-$Bu_4NI/K_2S_2O_8$-Mediated Transformylation from *p*-Anisaldehyde to Benzamide.



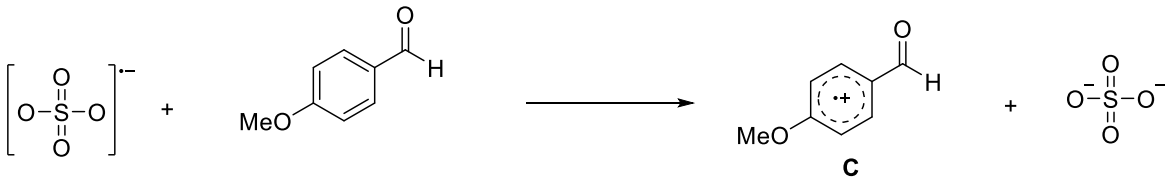
Elementary reaction (1)



ΔH (298 K) = 93 kJ/mol

ΔG (298 K) = 38 kJ/mol

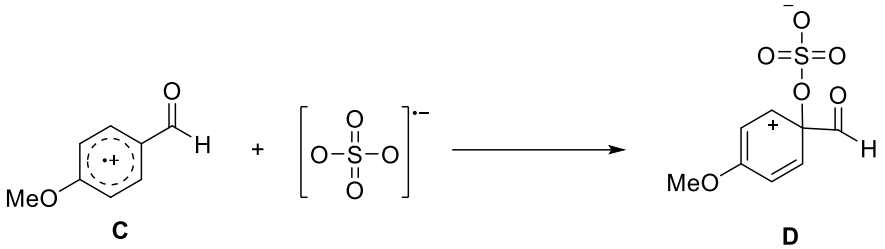
Elementary reaction (2)



ΔH (298 K) = 98 kJ/mol

ΔG (298 K) = 104 kJ/mol

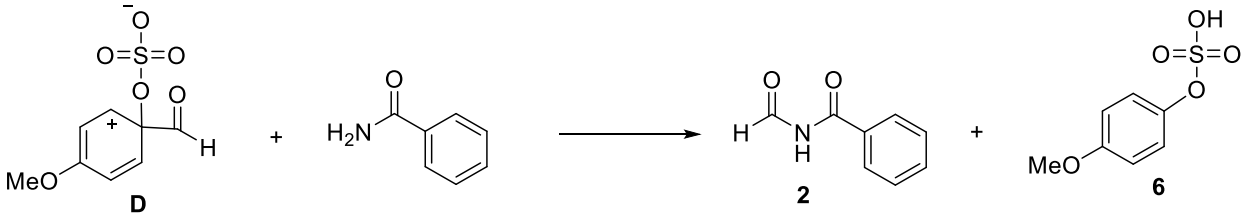
Elementary reaction (3)



ΔH (298 K) = -194 kJ/mol

ΔG (298 K) = -137 kJ/mol

Elementary reaction (4)



ΔH (298 K) = -100 kJ/mol

ΔG (298 K) = -101 kJ/mol

2. General Information. All reactions were carried out in sealed 20 mL glass reaction vials sealed with pressure relief caps, unless otherwise indicated. All commercially available chemicals were used as received without further purification, unless otherwise noted. Acetonitrile was dried over 4Å molecular sieves overnight before use. Molecular sieves (4Å) were activated at 200 °C at 0.5 mmHg for a week before use. All ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 400 or 500 MHz and 100 or 125 MHz, respectively, using $CDCl_3$ or DMSO-d_6 as solvent. The chemical shifts of all ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm for the ^{1}H NMR spectra and δ 77.23 ppm for the $^{13}C\{^{1}H\}$ NMR spectra) and the residual signal of DMSO-d_6 (δ 2.50 ppm for the ^{1}H NMR spectra). The high-resolution mass analysis was carried out on

high resolution mass spectrometers using electrospray ionization (ESI-TOF) method. Samples were dissolved in acetonitrile and analyzed via flow injection into the mass spectrometer at a flow rate of 200 μL/min. The mobile phase was 90:10 methanol:water, with 0.1% formic acid. The melting points are uncorrected.

3. General Procedure for the Preparation of Imides (1) via *n*-$Bu_4NI/K_2S_2O_8$-Mediated Cross Dehydrogenative Coupling between Amides and Aldehydes.

An oven dried 20 mL glass reaction vial was charged with amide (1.0 mmol, 1.0 equiv), aldehyde (1.2 mmol, 1.2 equiv), tetrabutylammonium iodide (36.9 mg, 0.1 mmol, 10 mol%), potassium persulfate (540.6 mg, 2.0 mmol, 2.0 equiv), and anhydrous acetonitrile (7 mL). The reaction mixture was sealed with a pressure relief cap and stirred at 80 °C for 20 h. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with saturated aqueous $NaHCO_3$ solution (20 mL). The aqueous phase was extracted with diethyl ether (2 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator under reduced pressure (20 mmHg). The residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the corresponding product.

N-acetylbenzamide (**1a**)

This product was obtained as a white solid (123.9 mg, 76% yield): m.p. 114.2-115.6 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, $R_f = 0.20$; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.62–7.59 (m, 1H), 7.52–7.48 (m, 2H), 2.61 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[6]

methyl 4-(acetylcarbamoyl)benzoate (**1b**)

This product was obtained as a white solid (177.0 mg, 80% yield): m.p. 166.3-167.5 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, $R_f = 0.15$; ^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.73 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 3H), 2.63 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[7]

N-acetyl-4-nitrobenzamide (**1c**)

This product was obtained as a yellow solid (93.6 mg, 45% yield): m.p. 223.3-224.5 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.19; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 2H), 2.64 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[7]

N-acetylpicolinamide (**1d**)

This product was obtained as a black solid (52.5 mg, 32% yield): m.p. 62.9-64.1 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.61 (d, *J* = 5.2 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.92 (td, *J* = 7.7, 1.8 Hz, 1H), 7.55–7.52 (m, 1H), 2.61 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[7]

N-propionylbenzamide (**1e**)

This product was obtained as a white solid (90.4 mg, 51% yield): m.p. 96.0-96.5 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.25; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.90 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 3.03 (q, *J* = 7.3 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[6]

N-(3-phenylpropanoyl)benzamide (**1f**)

This product was obtained as a white solid (202.6 mg, 80% yield): m.p. 105.7-106.3 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.31; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.32–

7.28 (m, 4H), 7.23–7.20 (m, 1H), 3.35 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.3 Hz, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[8]

N-(2-phenylacetyl)benzamide (**1g**)

This product was obtained as a white solid (148.3 mg, 62% yield): m.p. 132.1-132.9 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.36–7.30 (m, 5H), 4.33 (s, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[6]

N-(2-(naphthalen-2-yl)acetyl)benzamide (**1h**)

This product was obtained as a white solid (153.2 mg, 53% yield): m.p. 175.0-175.3 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 7.95–7.89 (m, 2H), 7.86–7.84 (m, 1H), 7.74 (d, *J* = 7.7 Hz, 2H), 7.58–7.46 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 2H), 4.74 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 165.8, 134.1, 133.5, 132.7, 132.5, 130.5, 129.1, 129.0, 128.6, 128.5, 127.9, 126.7, 126.1, 125.7, 124.0, 42.2; HRMS (ESI-TOF) calcd for $(C_{19}H_{15}NO_2+Na)^+$ $[M+Na]^+$ 312.0995, found 312.0986.

N-(cyclopropanecarbonyl)benzamide (**1i**)

This product was obtained as a beige solid (111.6 mg, 59% yield): m.p. 135.6-135.8 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.36; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.88–7.86 (m, 2H), 7.61–7.58 (m, 1H), 7.51–7.48 (m, 2H), 3.11–3.08 (m, 1H), 1.22–1.20 (m, 2H), 1.07–1.04 (m, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[9]

N-benzoyl-2-bromobenzamide (**1j**)

This product was obtained as a white solid (182.4 mg, 60% yield): m.p. 161.1-162.6 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.30; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.54–7.51 (m, 3H), 7.44 (td, *J* = 7.6, 1.2 Hz, 1H), 7.37 (td, *J* = 7.9, 1.7 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.4, 165.0, 137.3, 133.7, 133.3, 132.5, 132.0, 129.4, 129.3, 128.1, 127.9, 118.9; HRMS (ESI-TOF) calcd for $(C_{14}H_{10}BrNO_2+Na)^+$ $[M+Na]^+$ 325.9787, found 325.9771.

N-benzoyl-3-methoxybenzamide (**1k**)

This product was obtained as a yellow solid (53.6 mg, 21% yield): m.p. 121.1–121.9 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.50; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.87–7.84 (m, 2H), 7.62–7.58 (m, 1H), 7.49 (t, *J* = 7.9 Hz, 2H), 7.42–7.39 (m, 3H), 7.14–7.11 (m, 1H), 3.85 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[10]

N-benzoylbenzamide (**1l**)

This product was obtained as a white solid (177.8 mg, 79% yield): m.p. 140.5-141.2 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.3; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.87 (d, *J* = 7.4 Hz, 4H), 7.62 (t, *J* = 6.5 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 4H). The ^{1}H NMR spectral data are in good agreement with the literature data.[6]

N-benzoyl-4-methoxybenzamide (**1m**)

This product was obtained as a yellow solid (155.7 mg, 61% yield): m.p. 102.6-103.6 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.29; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.86–7.84 (m, 4H), 7.61–7.57 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[10]

N-benzoyl-4-methylbenzamide (**1n**)

This product was obtained as a yellow solid (184.0 mg, 77% yield): m.p. 104.0-105.6 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.28; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 2H), 2.44 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[11]

N-benzoyl-4-fluorobenzamide (**1o**)

This product was obtained as a white solid (136.2 mg, 56% yield): m.p. 126.6-127.3 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.21; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.91–7.86 (m, 4H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.50 (t, *J* = 8.2 Hz, 2H), 7.17 (t, *J* = 8.6 Hz, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[11]

N-acryloylbenzamide (**1p**)

This product was obtained as a white solid (85.8 mg, 49% yield): m.p. 114.3-114.9 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.31; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 16.4, 10.8 Hz, 1H), 6.61 (dd, *J* = 17.4, 1.7 Hz, 1H), 5.97 (dd, *J* = 10.6, 1.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.3, 165.8, 133.6, 133.0, 132.2, 129.8, 129.3, 127.9; HRMS (ESI-TOF) calcd for $(C_{10}H_9NO_2+Na)^+$ $[M+Na]^+$ 198.0525, found 198.0525.

N-cinnamoylbenzamide (**1q**)

This product was obtained as a white solid (113.0 mg, 45% yield): m.p. 139.6-140.2 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.94–7.84 (m, 4H), 7.66–7.61 (m, 3H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.43–7.40 (m, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[10]

1-benzoylpyrrolidin-2-one (**1r**)

This product was obtained as a white solid (117.3 mg, 62% yield): m.p. 85.7-86.4 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.36; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.53–7.49 (m, 1H), 7.43–7.39 (m, 2H), 3.96 (t, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 2.14 (quint, *J* = 7.6 Hz, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[10]

N-formylbenzamide (**2**)

This product was obtained as a yellow solid (23.9 mg, 16% yield) alongside with **1k** in the coupling between *m*-anisaldehyde and benzamide: m.p. 98.2-100.3 °C; flash column chromatography eluent: 1/3 ethyl acetate/hexanes, R_f = 0.46; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 9.40 (d, *J* = 9.4 Hz, 1H), 7.99–7.97 (m, 2H), 7.68–7.64 (m, 1H), 7.57–7.53 (m, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[12]

4. General Procedure for the Preparation of Quinazolinones (3)

An oven dried 20 mL glass reaction vial was charged with 2-aminobenzamide (136.2 mg, 1.0 mmol, 1.0 equiv), aldehydes (1.2 mmol, 1.2 equiv), tetrabutylammonium iodide (36.9 mg, 0.1 mmol, 10 mol%), potassium persulfate (540.6 mg, 2.0 mmol, 2.0 equiv) and anhydrous acetonitrile (7 mL). The reaction mixture was sealed with a pressure relief cap, and stirred at 80 °C for 20 h. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine (20 mL). The aqueous phase was extracted with diethyl ether (2 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator under reduced pressure (20 mmHg). The subsequent residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the corresponding product.

2-phenylquinazolin-4(3H)-one (**3a**)

This product was obtained as a yellow solid (219.8 mg, 99% yield): m.p. 232.0-232.7 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.32; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.34 (d, *J* = 7.8 Hz, 1H), 8.29–8.27 (m, 2H), 7.86–7.80 (m, 2H), 7.60 (t, *J* = 3.1 Hz, 3H), 7.52 (t, *J* = 7.4 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[13]

2-(2-bromophenyl)quinazolin-4(3H)-one (**3b**)

This product was obtained as a white solid (249.8 mg, 83% yield): m.p. 167.4-168.2 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 3.2 Hz, 2H), 7.76 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.72 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.57–7.53 (m, 1H), 7.50 (td, *J* = 7.5, 1.1 Hz, 1H), 7.41 (td, *J* = 7.4, 1.9 Hz, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[13]

2-phenethylquinazolin-4(3H)-one (**3c**)

This product was obtained as a white solid (175.0 mg, 70% yield): m.p. 205.0-205.9 °C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.29 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.79–7.77 (m, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.51–7.47 (m, 1H), 7.31–7.28 (m, 4H), 7.25–7.23 (m, 1H), 3.21–3.17 (m, 2H), 3.06–3.02 (m, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[14]

2-(4-methoxyphenyl)quinazolin-4(3H)-one (**3d**)

This product was obtained as a white solid (163.8 mg, 65% yield): m.p. 188.5-189.3°C; flash column chromatography eluent: 1/3 ethyl acetate / hexanes, R_f = 0.38; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.43 (s, 1H), 8.20 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 7.1 Hz, 1H), 7.82 (t, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H). The ^{1}H NMR spectral data are in good agreement with the literature data.[14]

5. Procedure for the Preparation of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (4)

An oven dried 4-dram vial was charged with 2-aminobenzamide (136.2 mg, 1.0 mmol, 1.0 equiv), benzaldehyde (127.3 mg, 1.2 mmol, 1.2 equiv) and anhydrous acetonitrile (7 mL). The reaction mixture was stirred at 80 ℃ for 20 h. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine (20 mL). The aqueous phase was extracted with diethyl ether (2 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator under reduced pressure (20 mmHg). The subsequent residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the corresponding product.

2-phenyl-2,3-dihydroquinazolin-4(1H)-one (**4**)

This product was obtained as a white solid (144.0 mg, 64% yield): m.p. 227.0-227.6 °C; flash column chromatography eluent: 1/5 ethyl acetate / hexanes, R_f = 0.50; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.7 Hz, 1H), 7.61–7.59 (m, 2H), 7.46–7.44 (m, 3H), 7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 6.91 (td, *J* = 7.5, 0.8 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 1H), 5.77(s, 1H), 4.39(s, 1H). The ^{1}H NMR spectral data are in good agreement with the literature data.[14]

6. Procedure for the Preparation of 2,2,6,6-tetramethylpiperidin-1-yl benzoate (5)

An oven dried 20 mL glass reaction vial was charged with benzamide (121.1 mg, 1.0 mmol, 1.0 equiv), benzaldehyde (127.3 mg, 1.2 mmol, 1.2 equiv), tetrabutylammonium iodide (36.9 mg, 0.1 mmol, 10 mol%), potassium persulfate (540.6 mg, 2.0 mmol, 2.0 equiv), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (468.8 mg, 3.0 mmol, 3.0 equiv) and anhydrous acetonitrile (7 mL). The reaction mixture was stirred at 80 °C for 24 h. The reaction mixture was diluted with 20 mL of ethyl acetate and washed with brine (20 mL). The aqueous phase was extracted with ethyl acetate (2 × 15 mL). The combined organic layers were dried over anhydrous

$MgSO_4$ and concentrated using a rotary evaporator under reduced pressure (20 mmHg). The subsequent residue was purified by flash column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the corresponding product.

2,2,6,6-tetramethylpiperidin-1-yl benzoate (**5**)

This product was obtained as an orange solid (28.7 mg, 11% yield): m.p. 65.6-67.6 °C; flash column chromatography eluent: hexanes, R_f = 0.15; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 6.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 1.79–1.71 (m, 3H), 1.61–1.58 (m, 2H), 1.48–1.44 (m, 1H), 1.28 (s, 6H), 1.12 (s, 6H). The ^{1}H NMR spectral data are in good agreement with the literature data.[15]

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8. Copies of ^{1}H, ^{13}C NMR spectra

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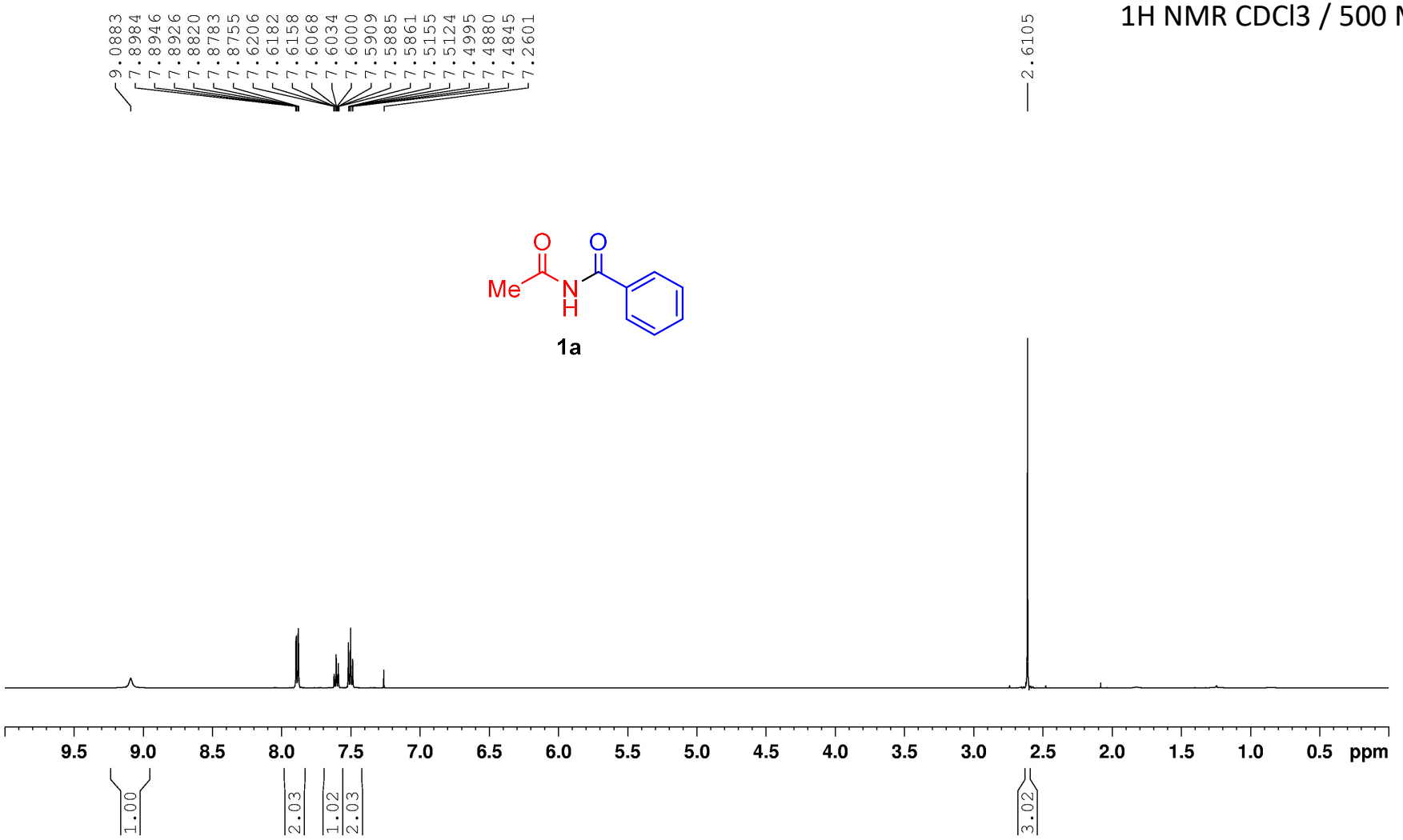

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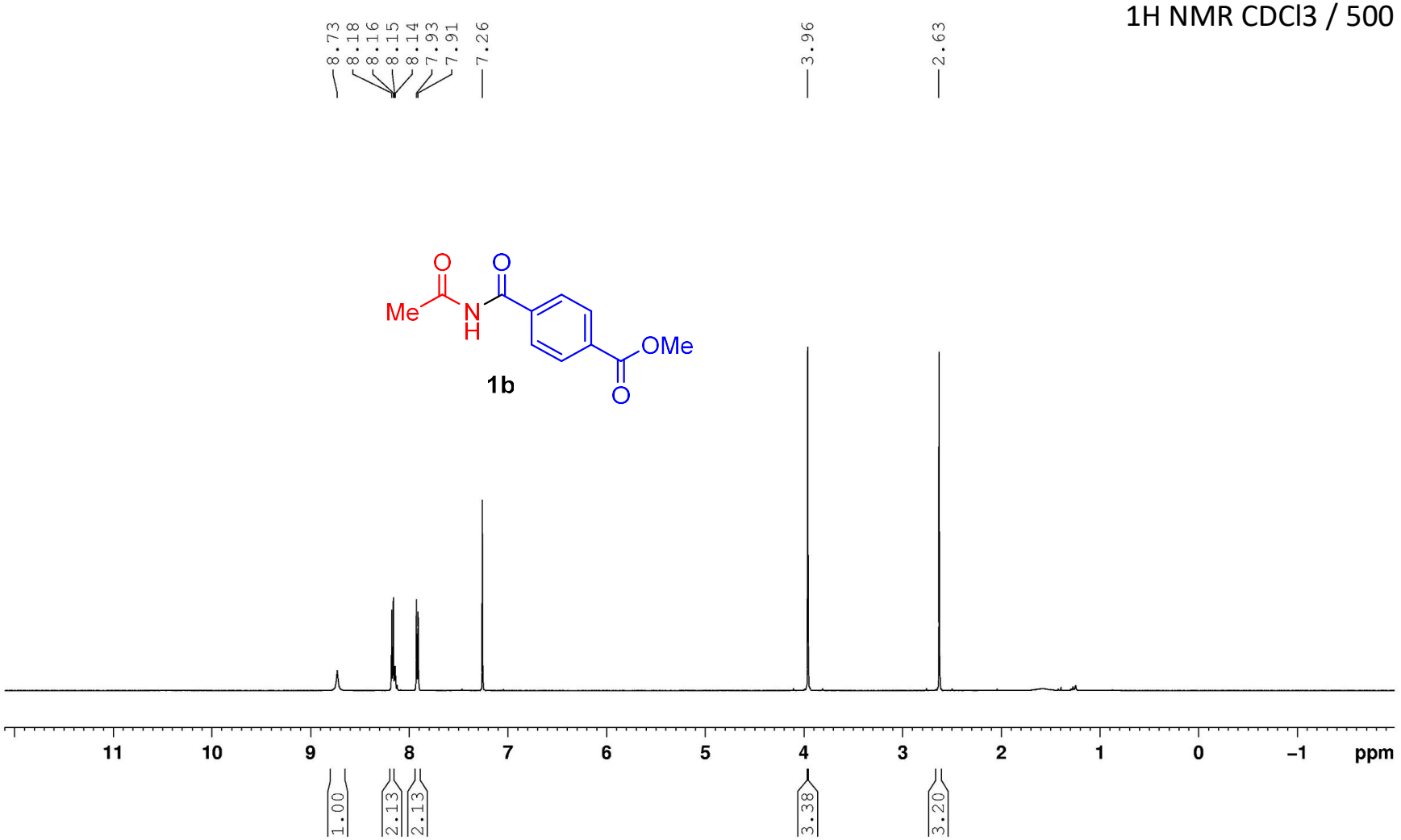

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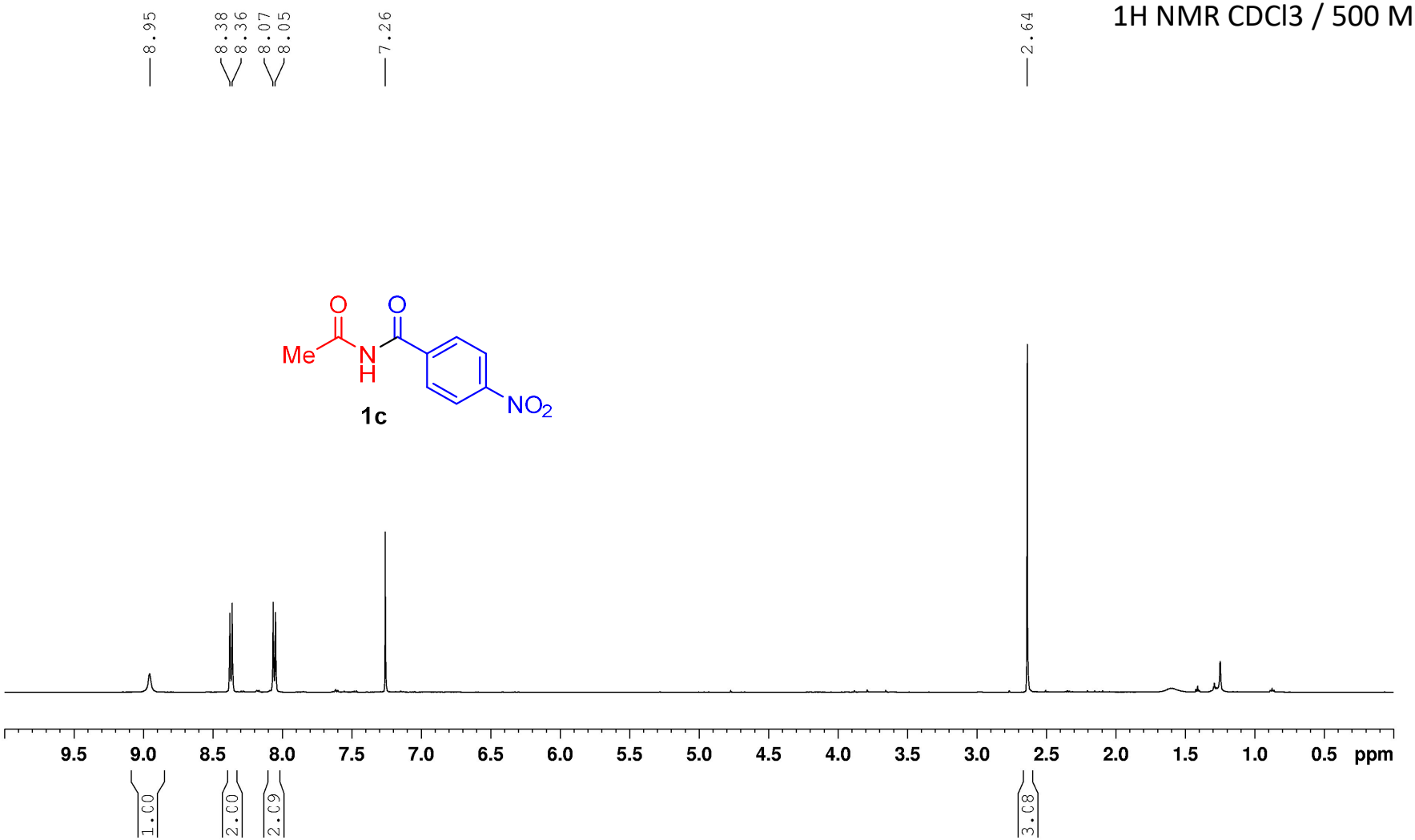

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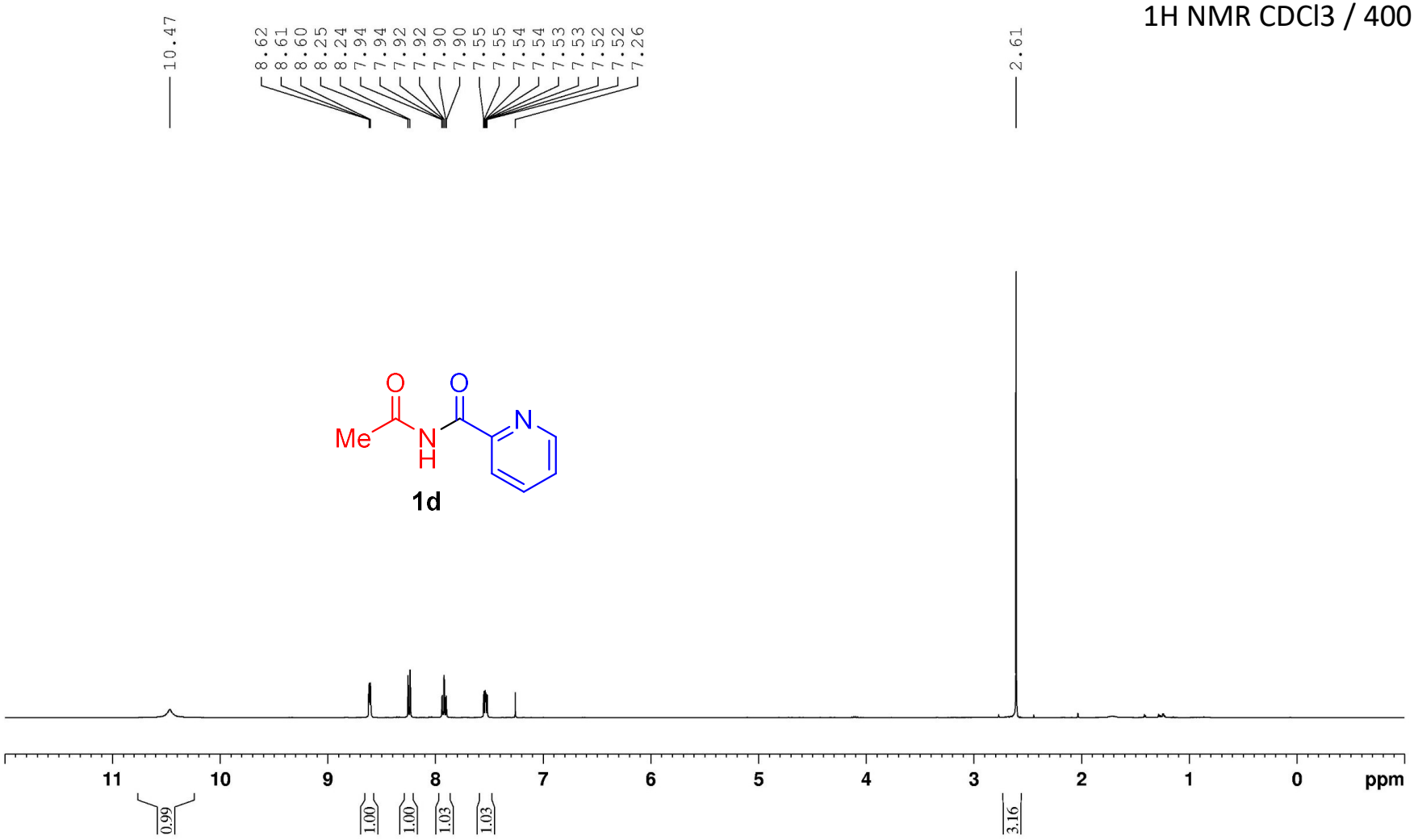

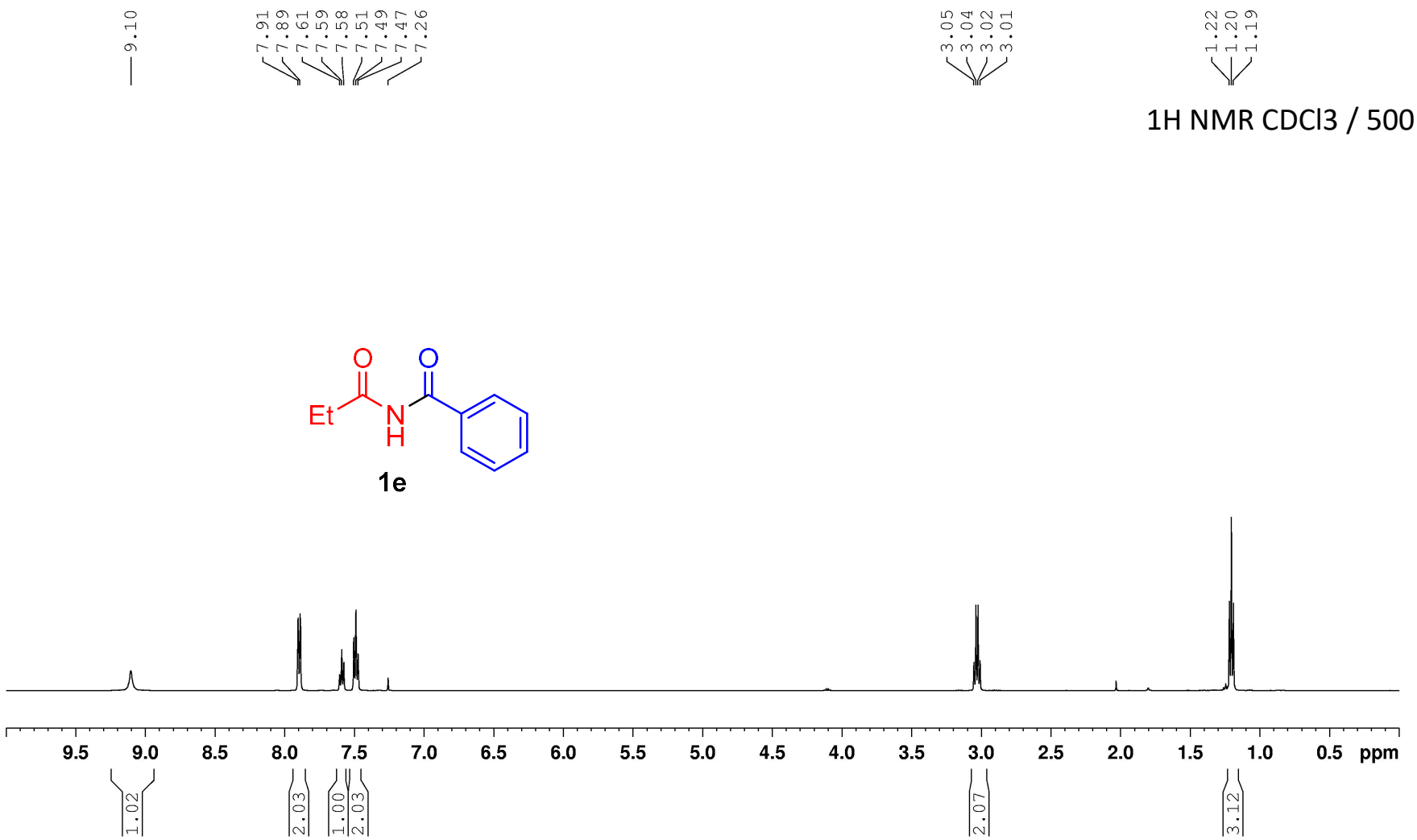

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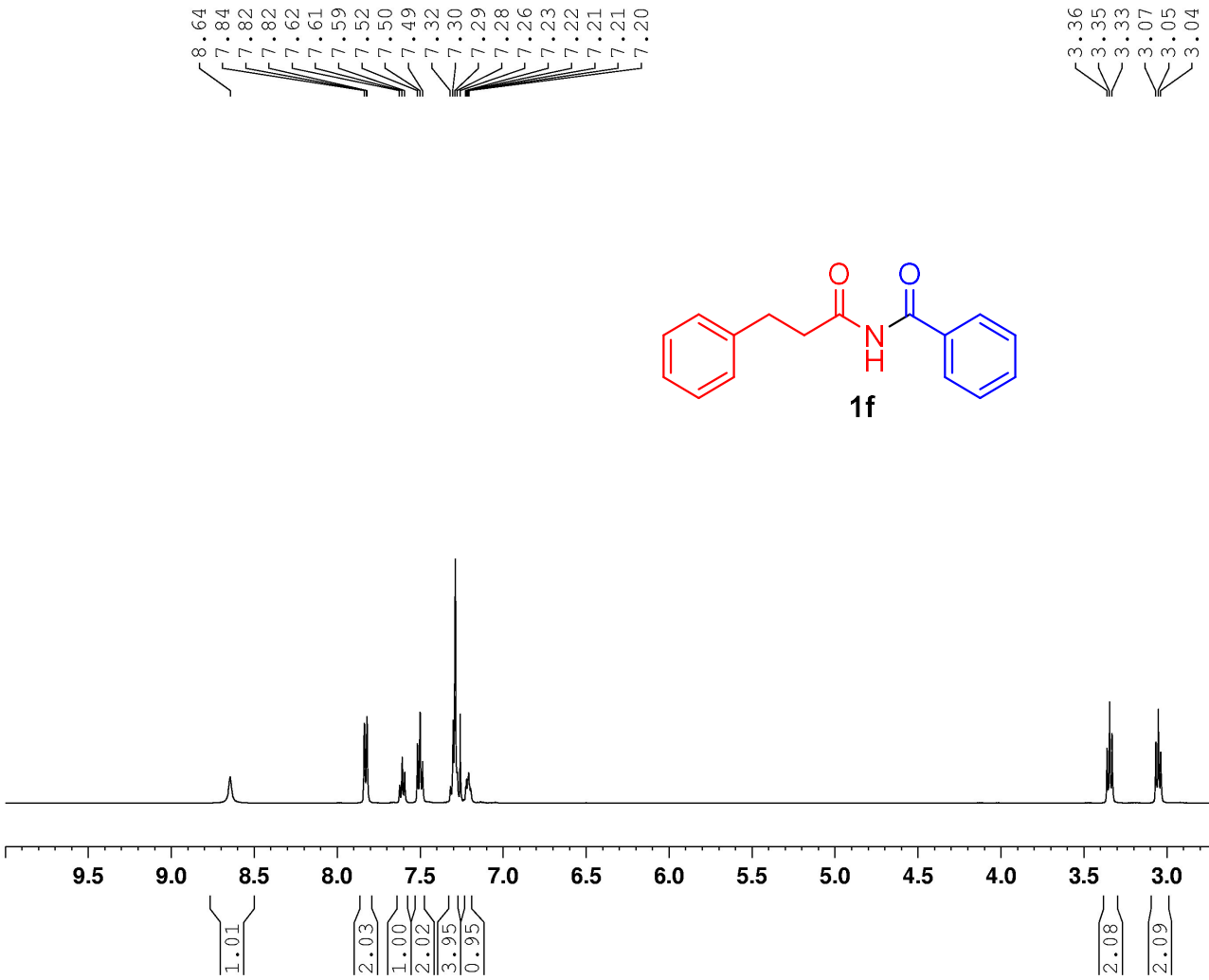

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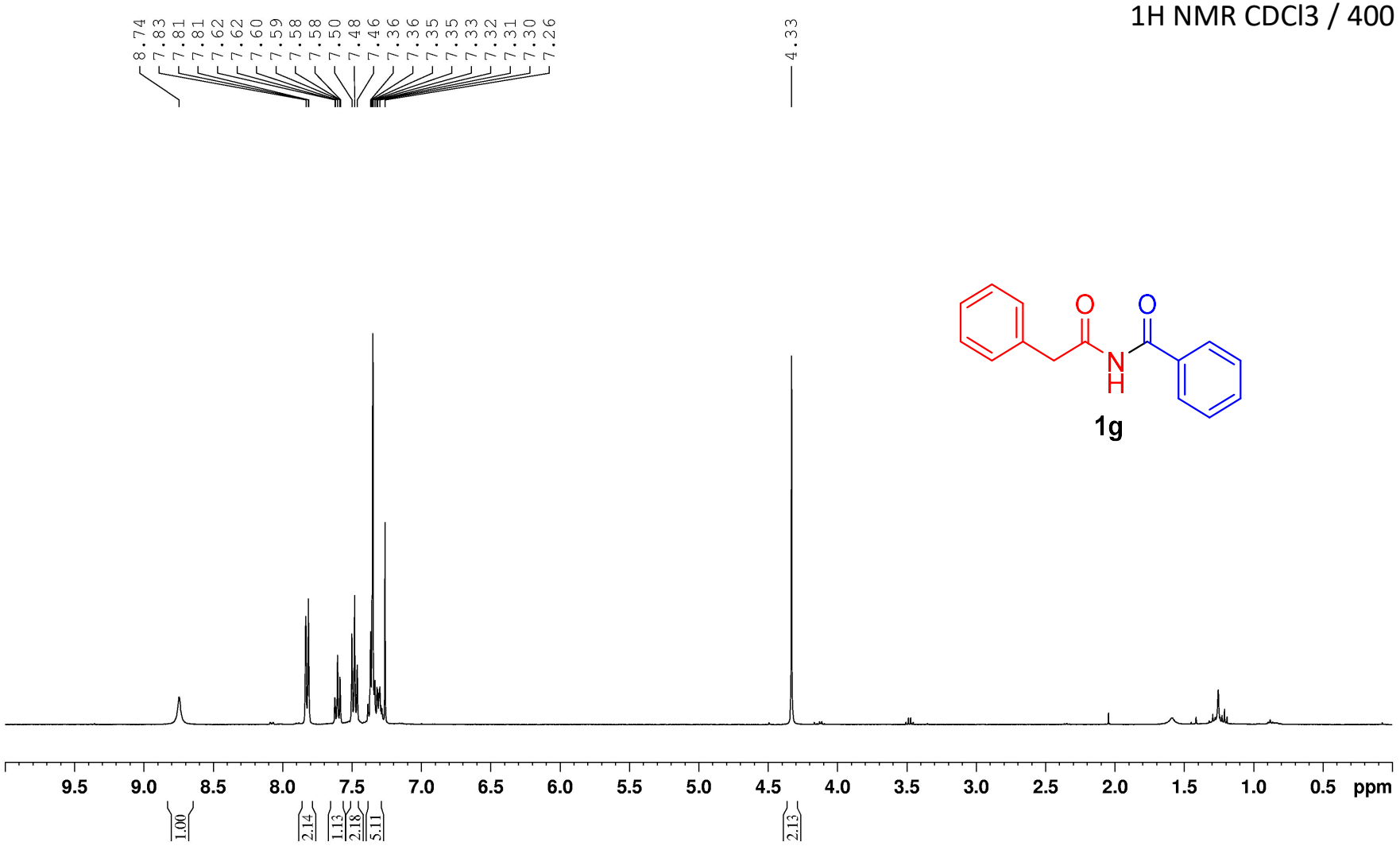

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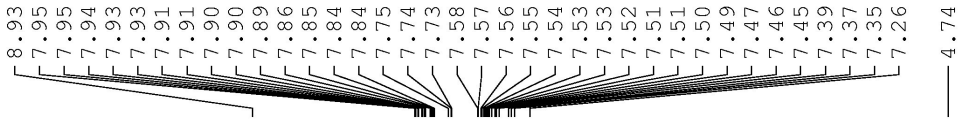

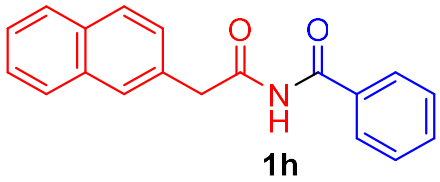

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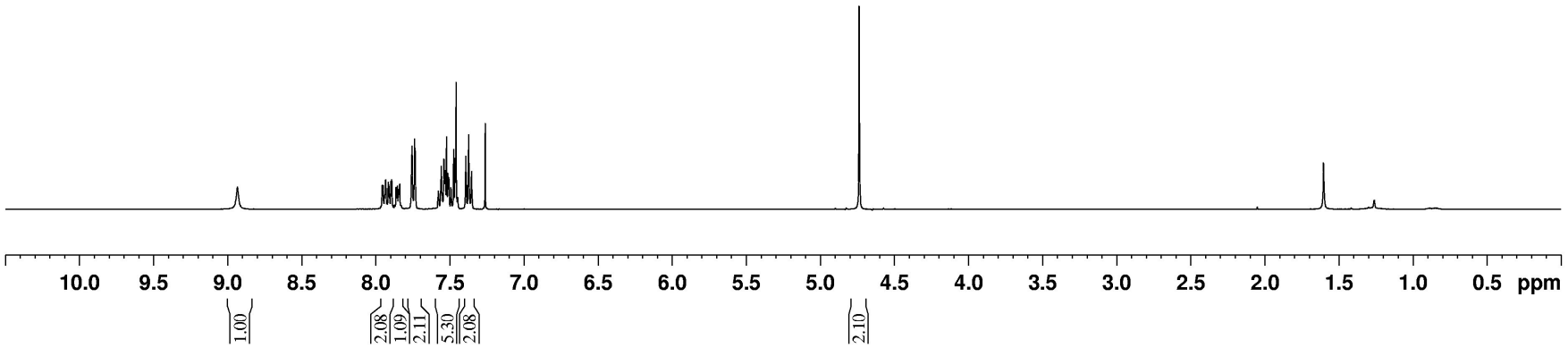

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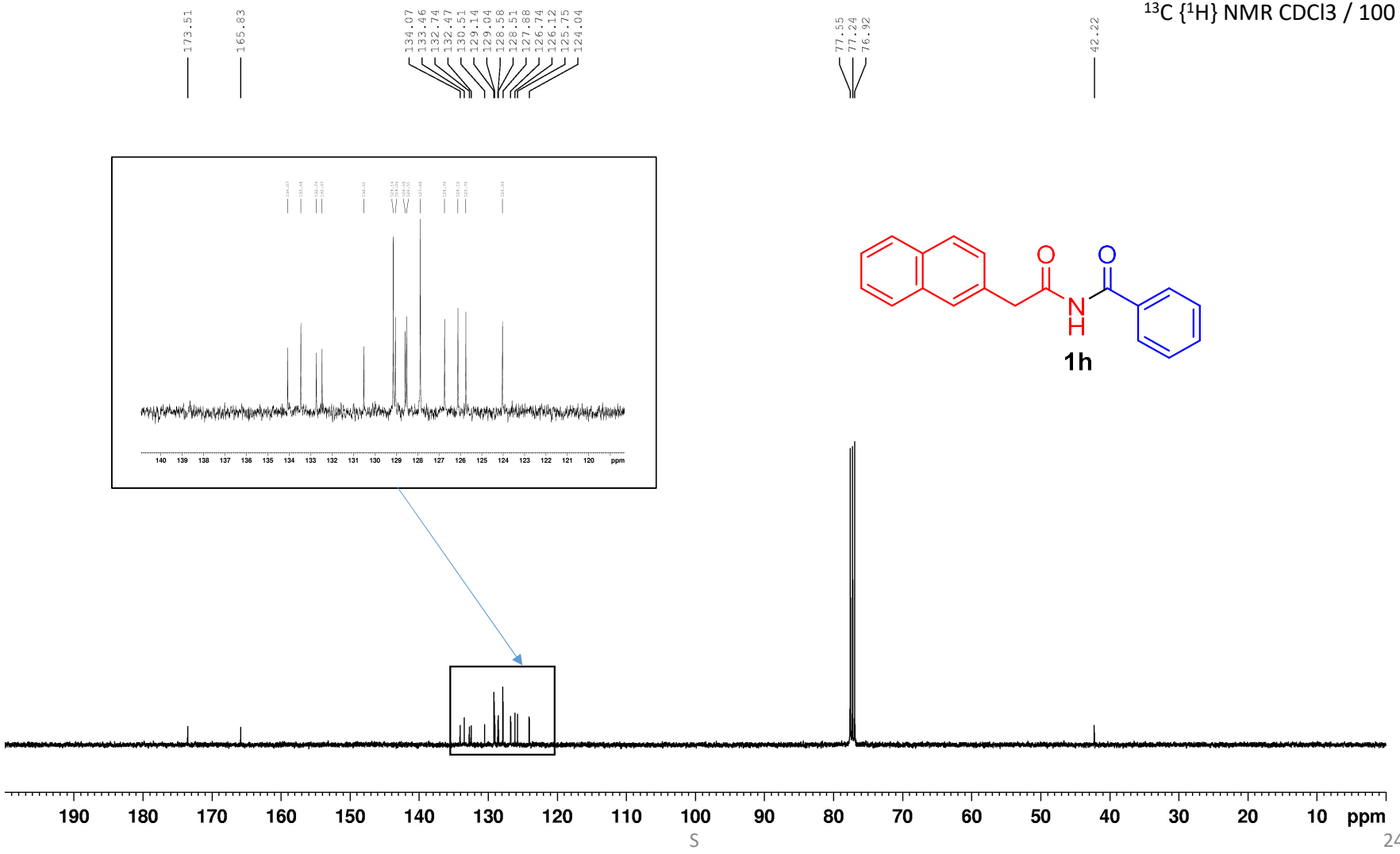

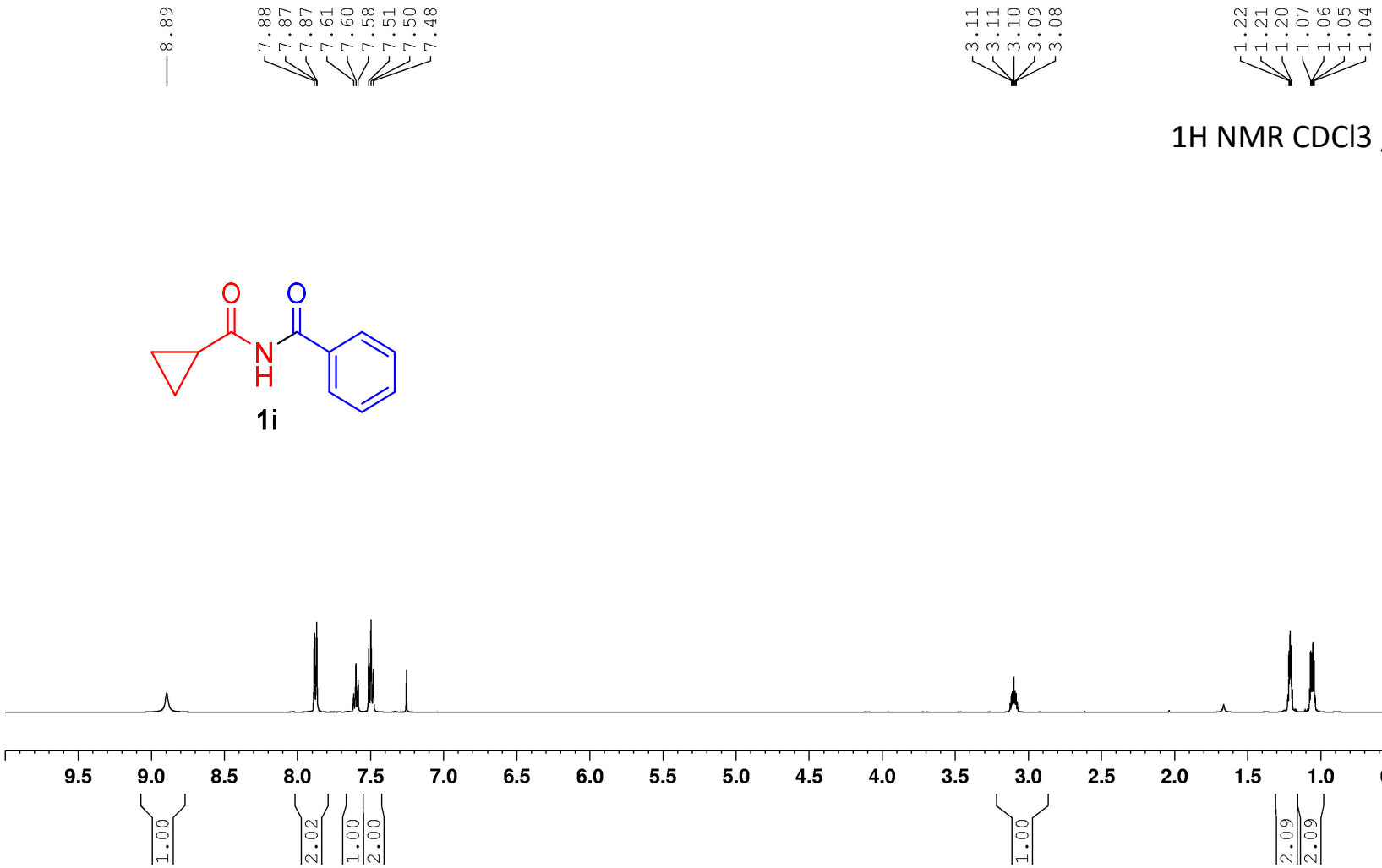

1H NMR CDCl3 / 500 MHz

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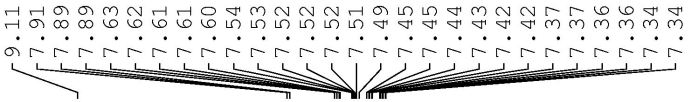

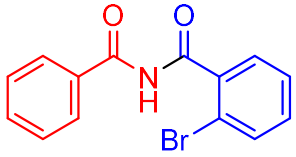

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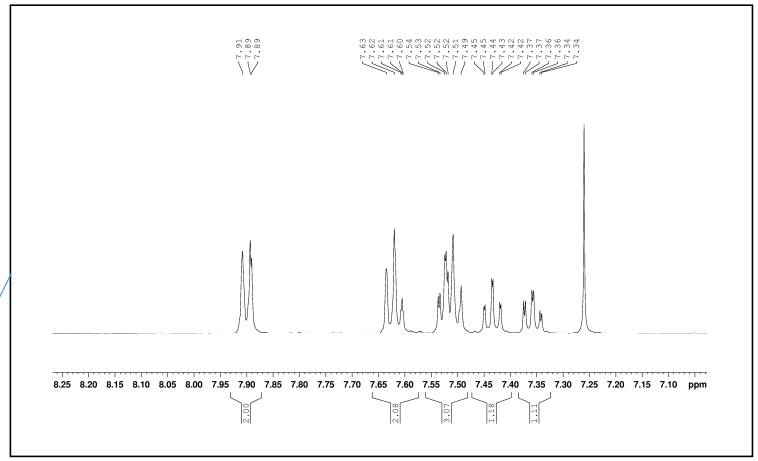

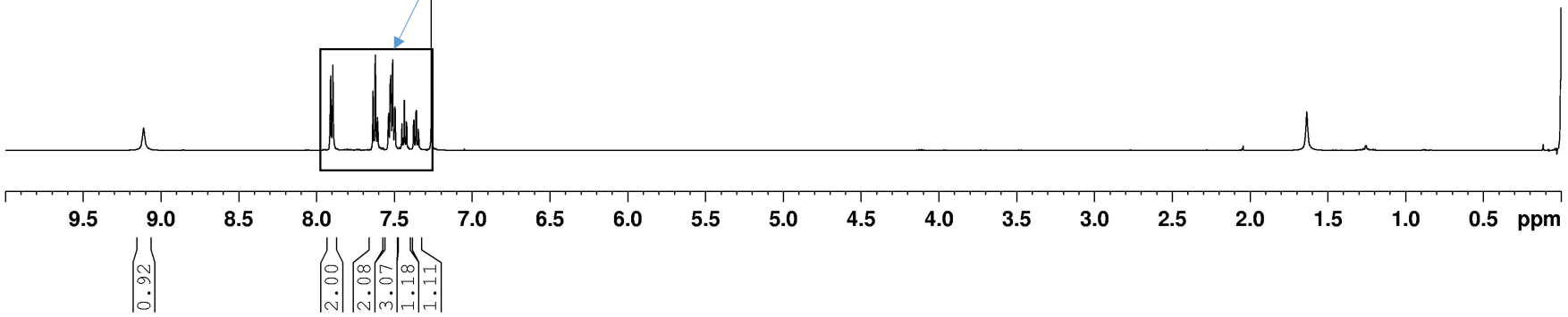

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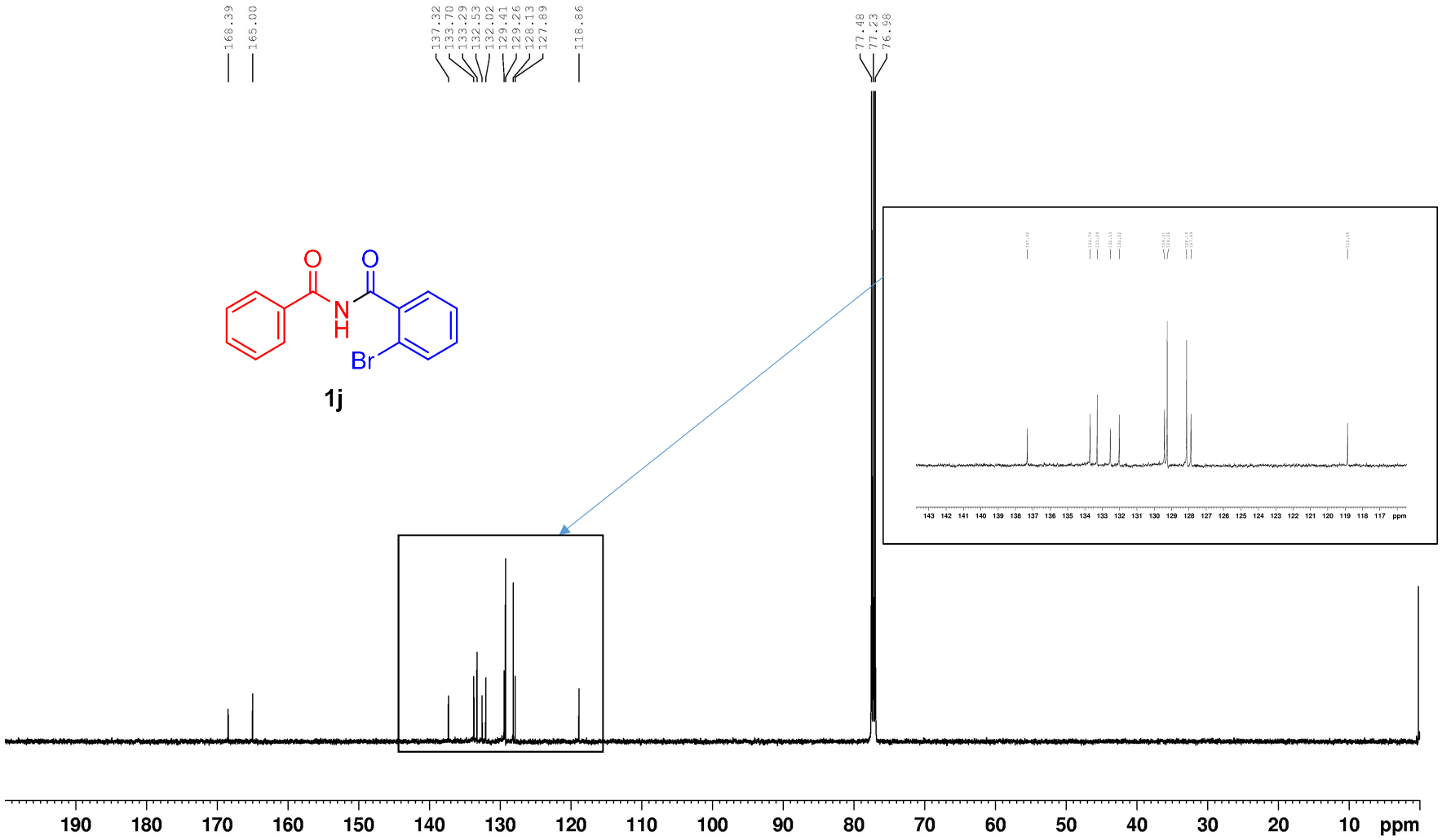

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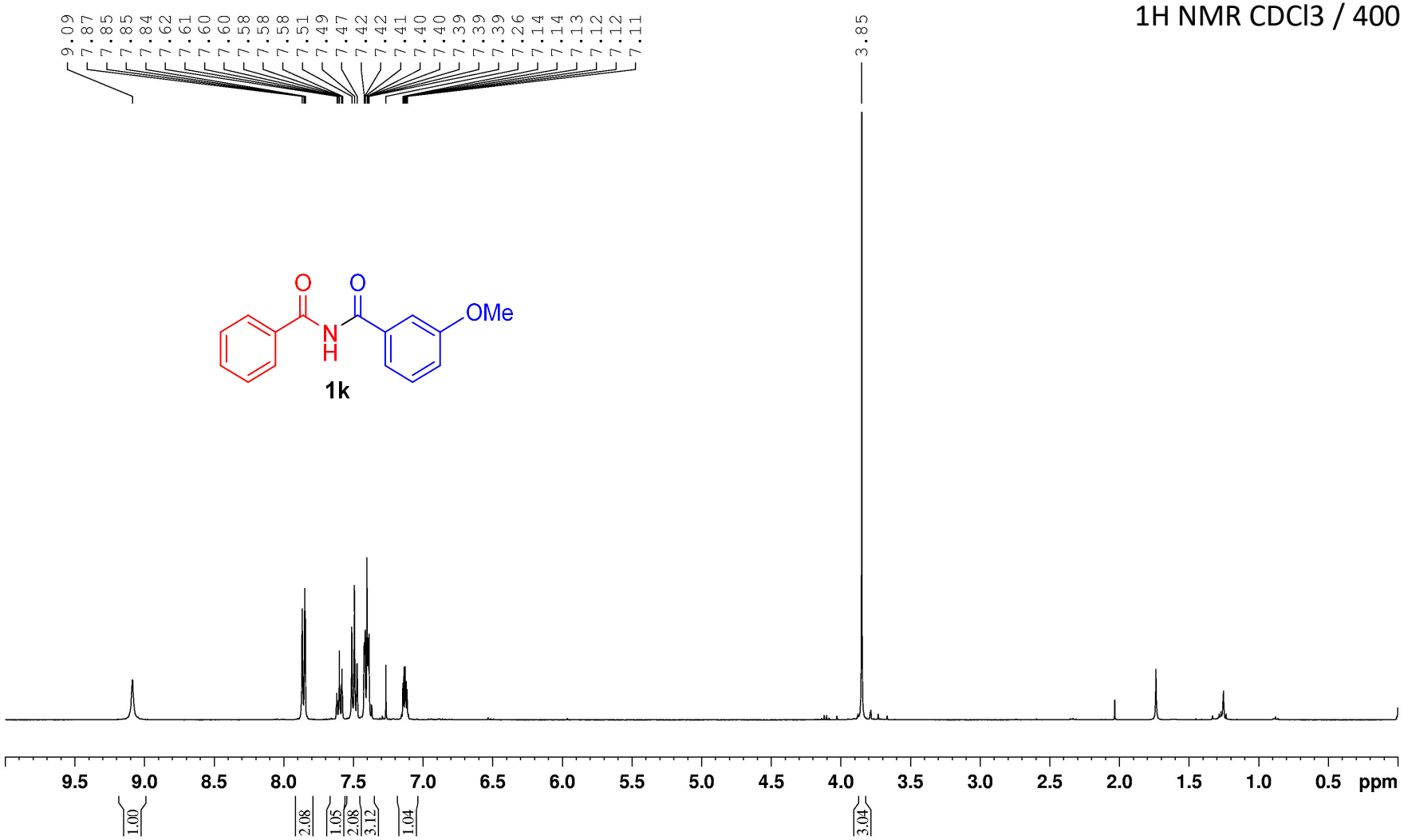

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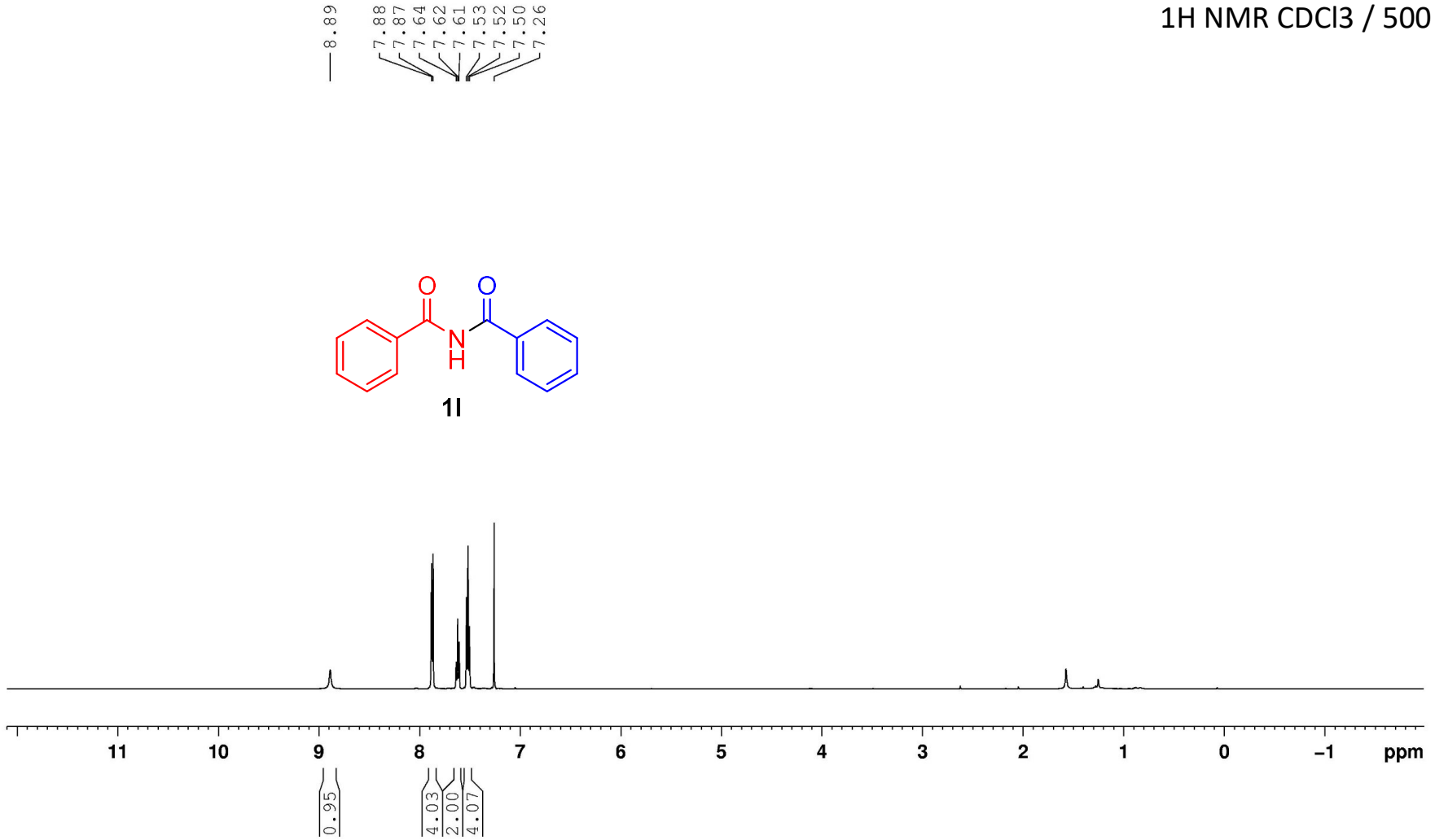

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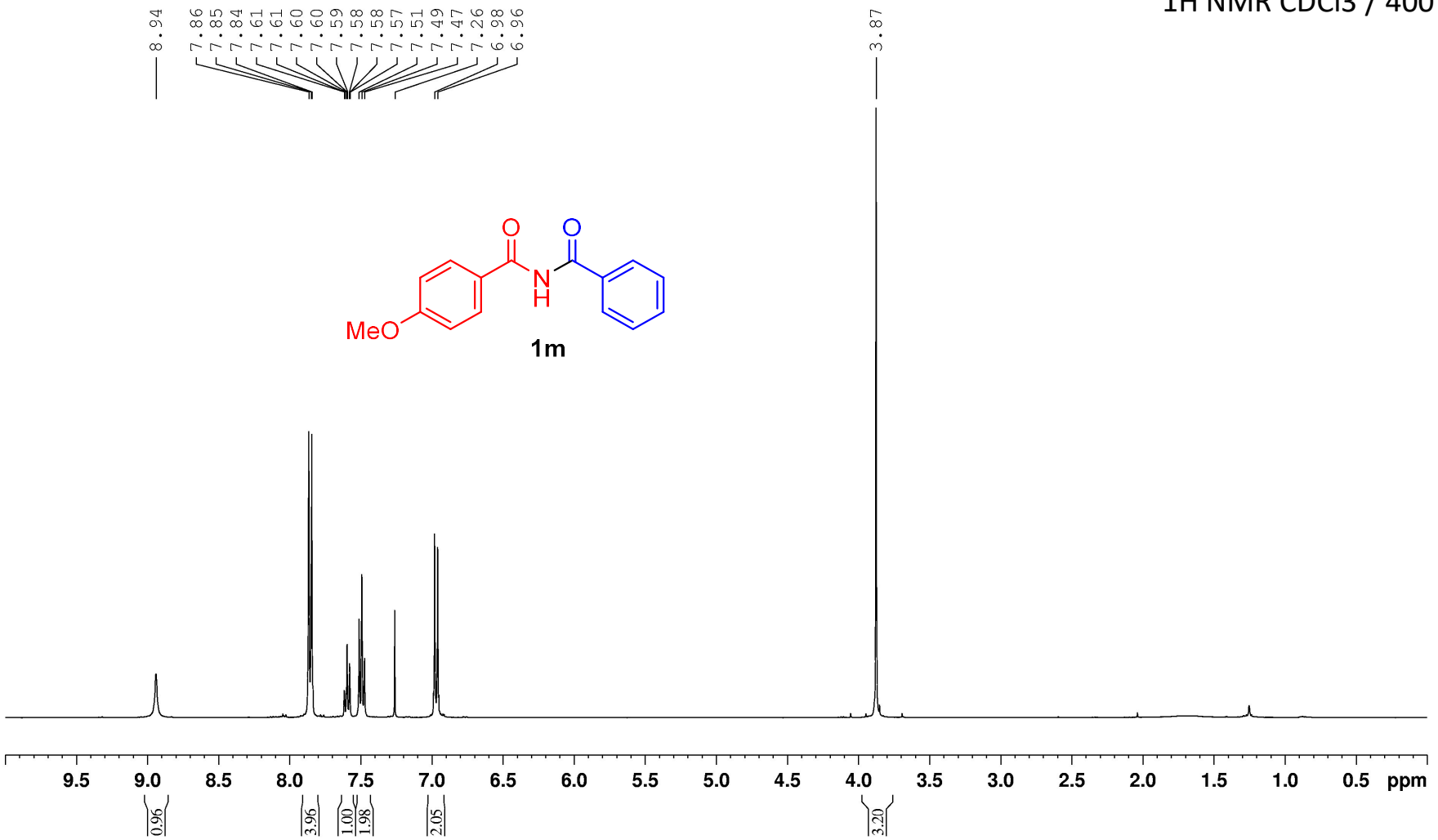

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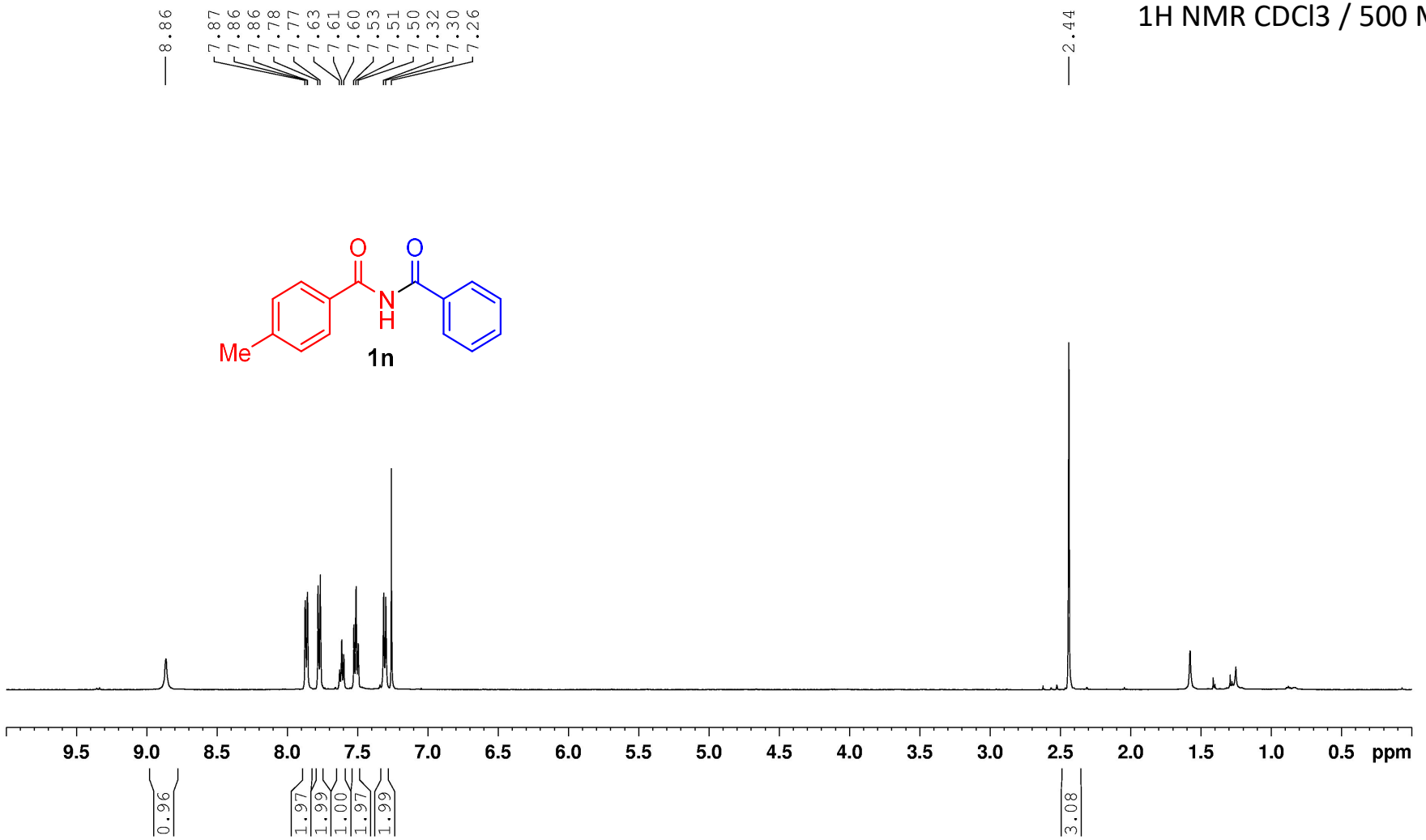

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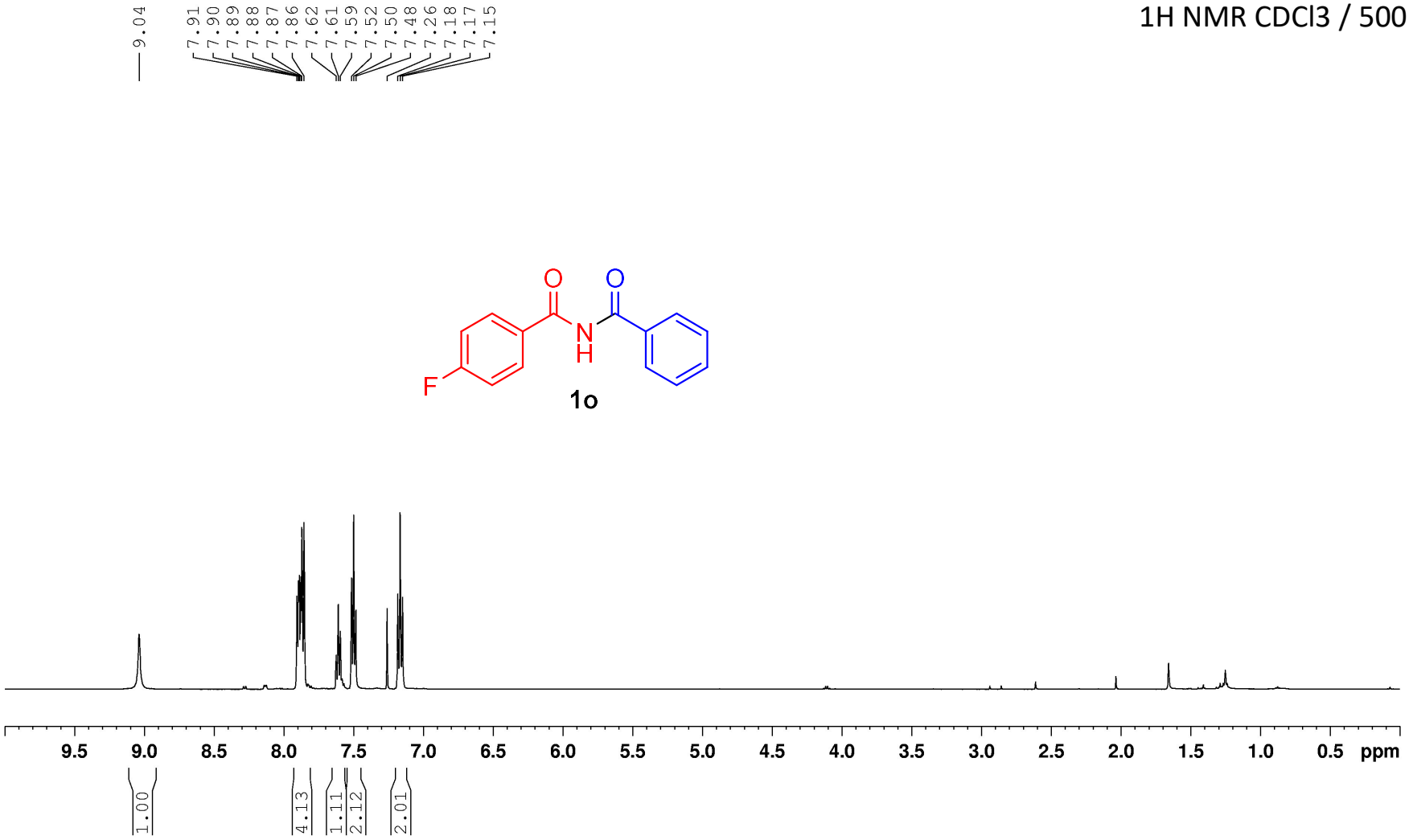

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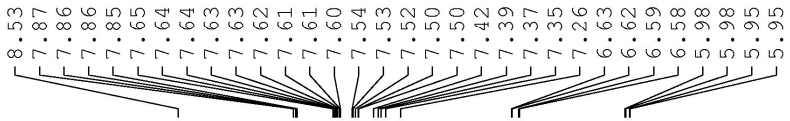

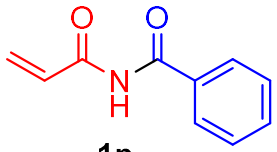

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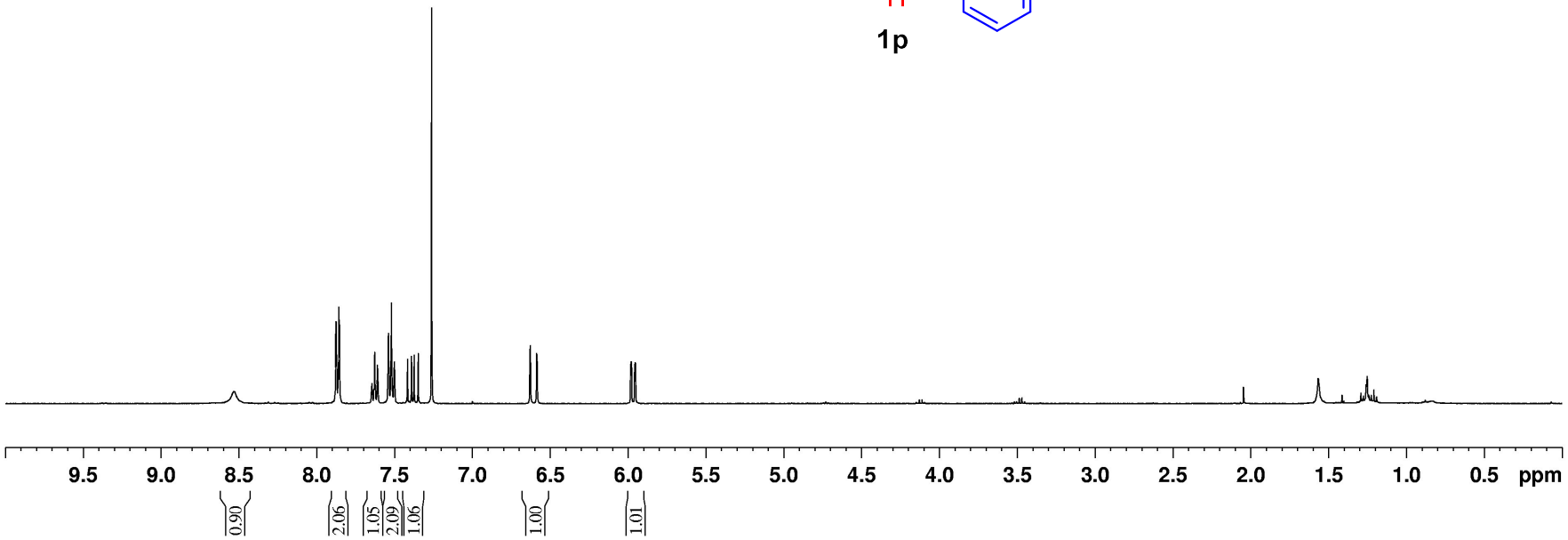

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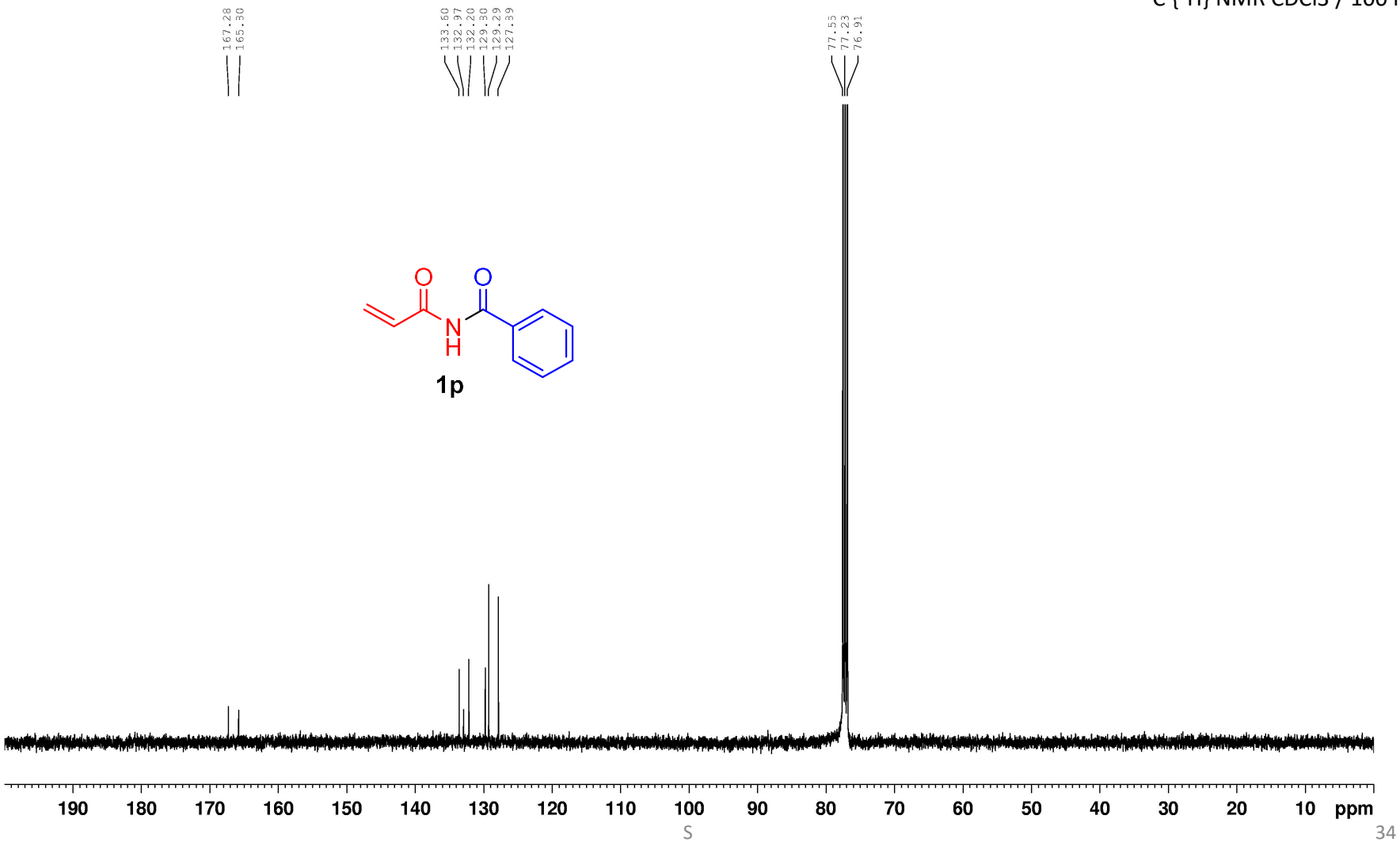

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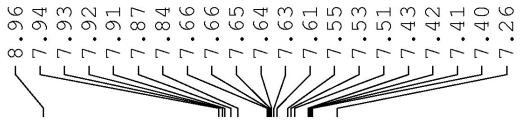

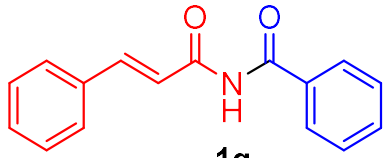

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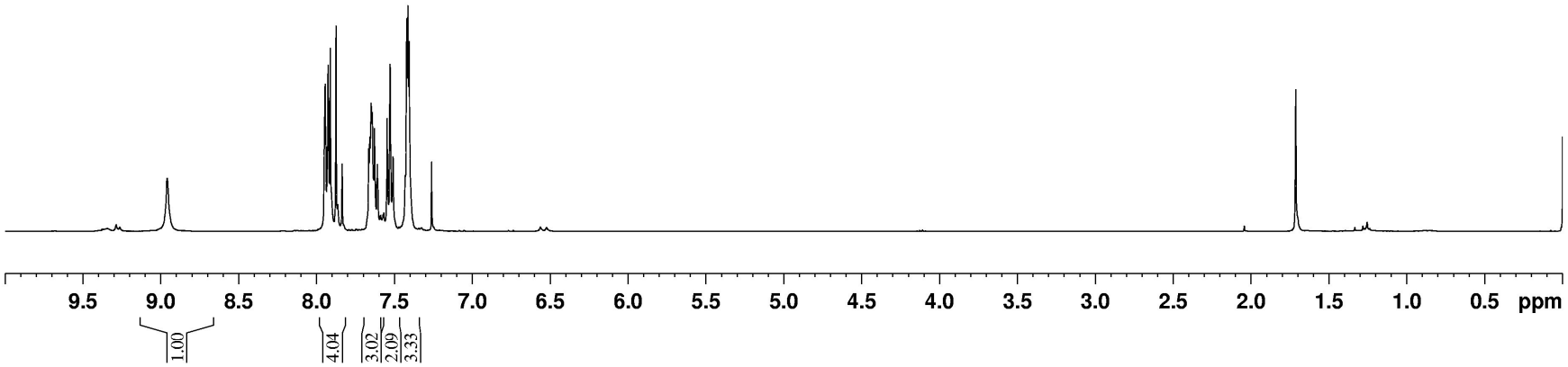

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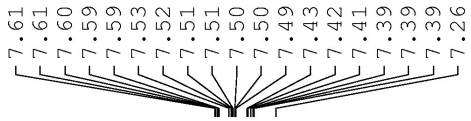

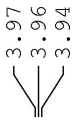

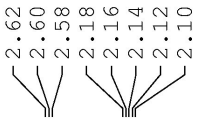

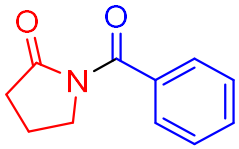

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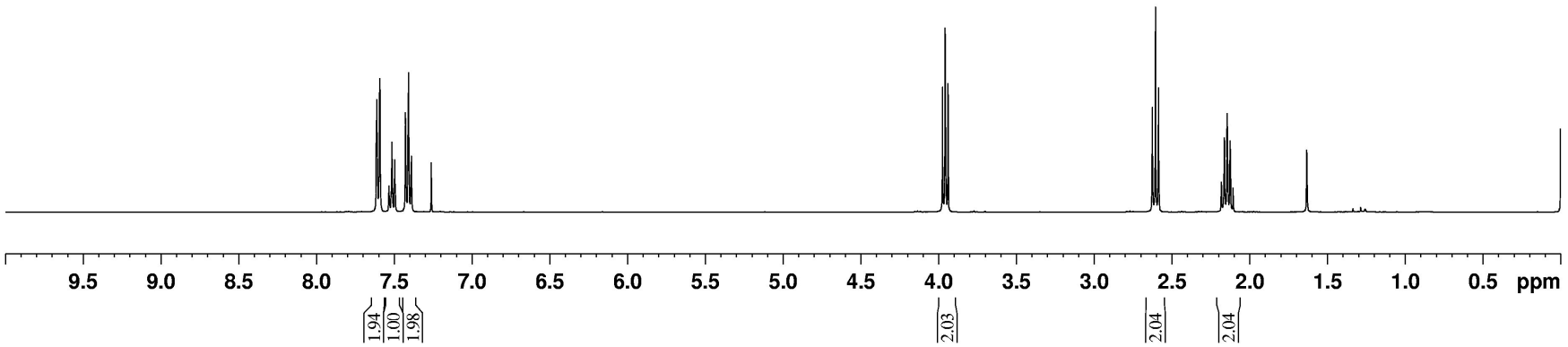

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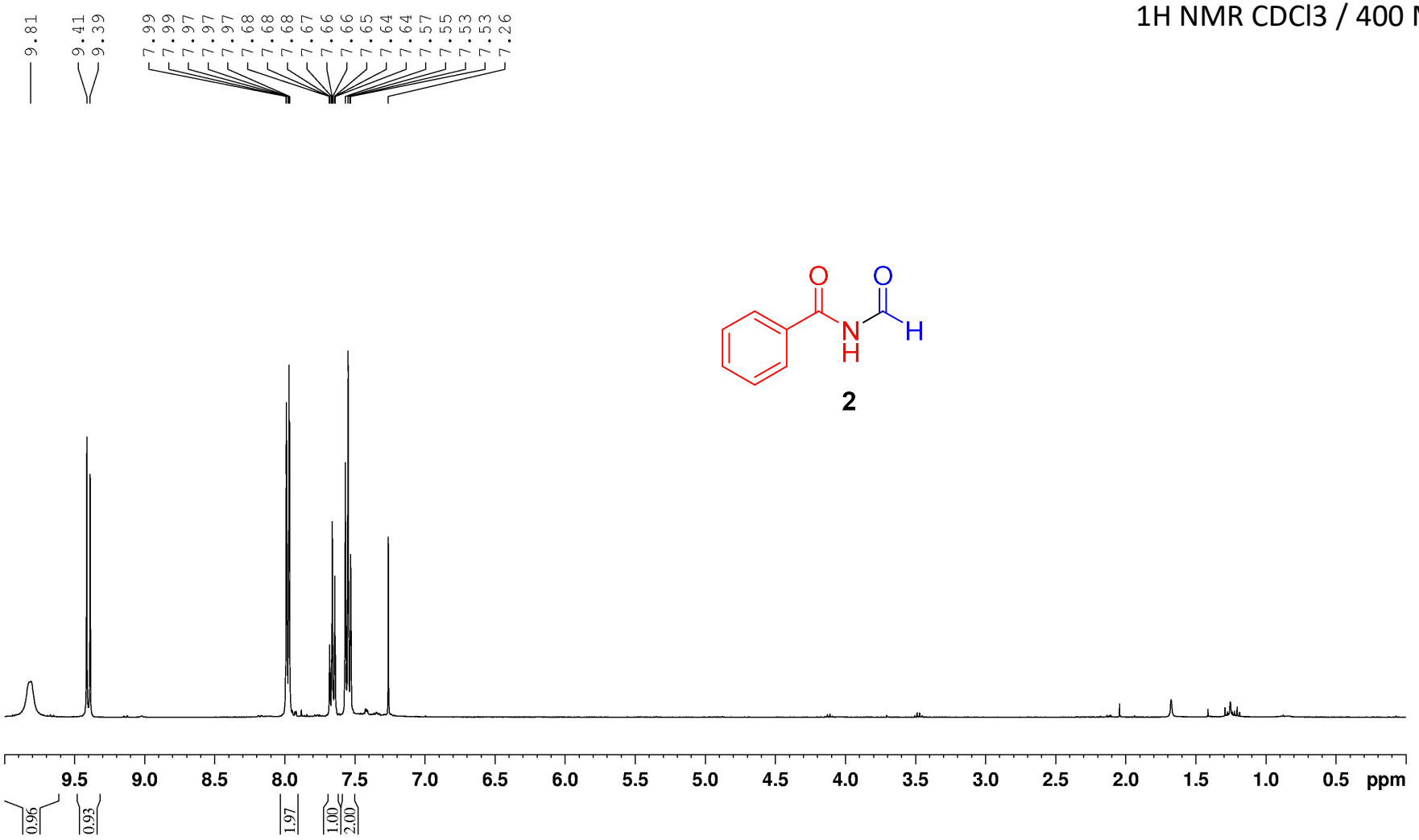

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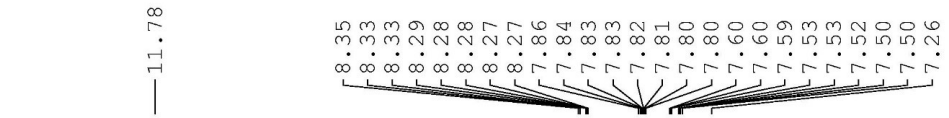

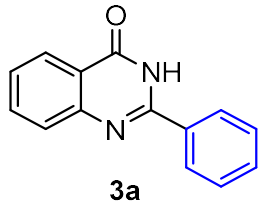

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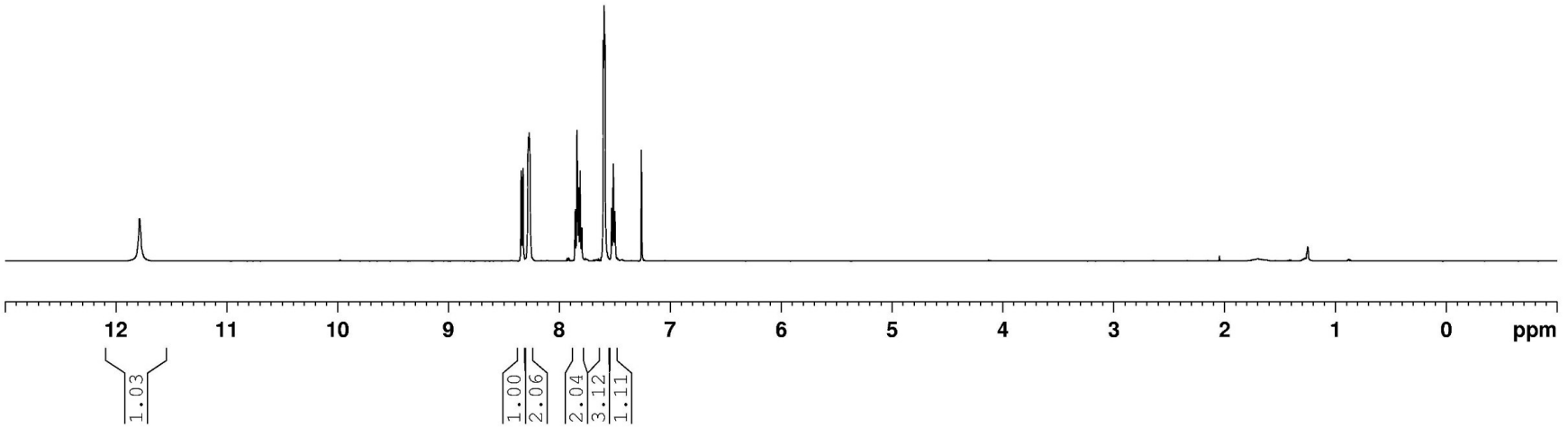

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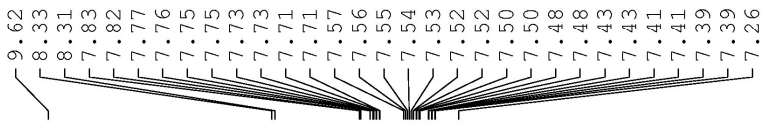

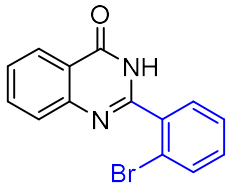

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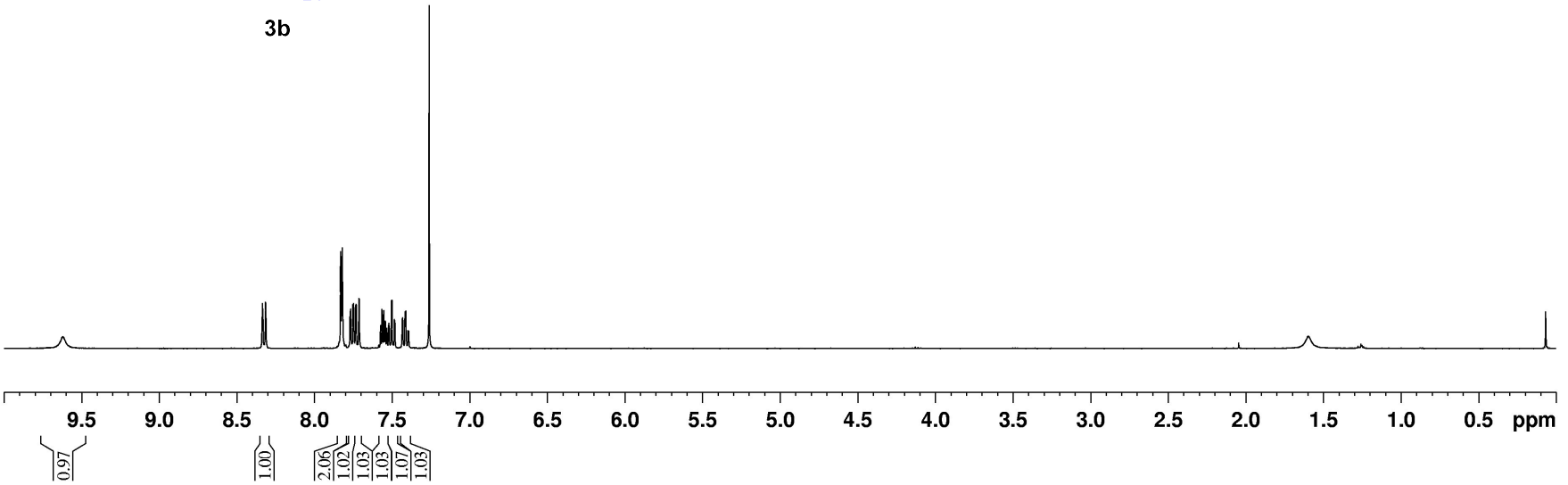

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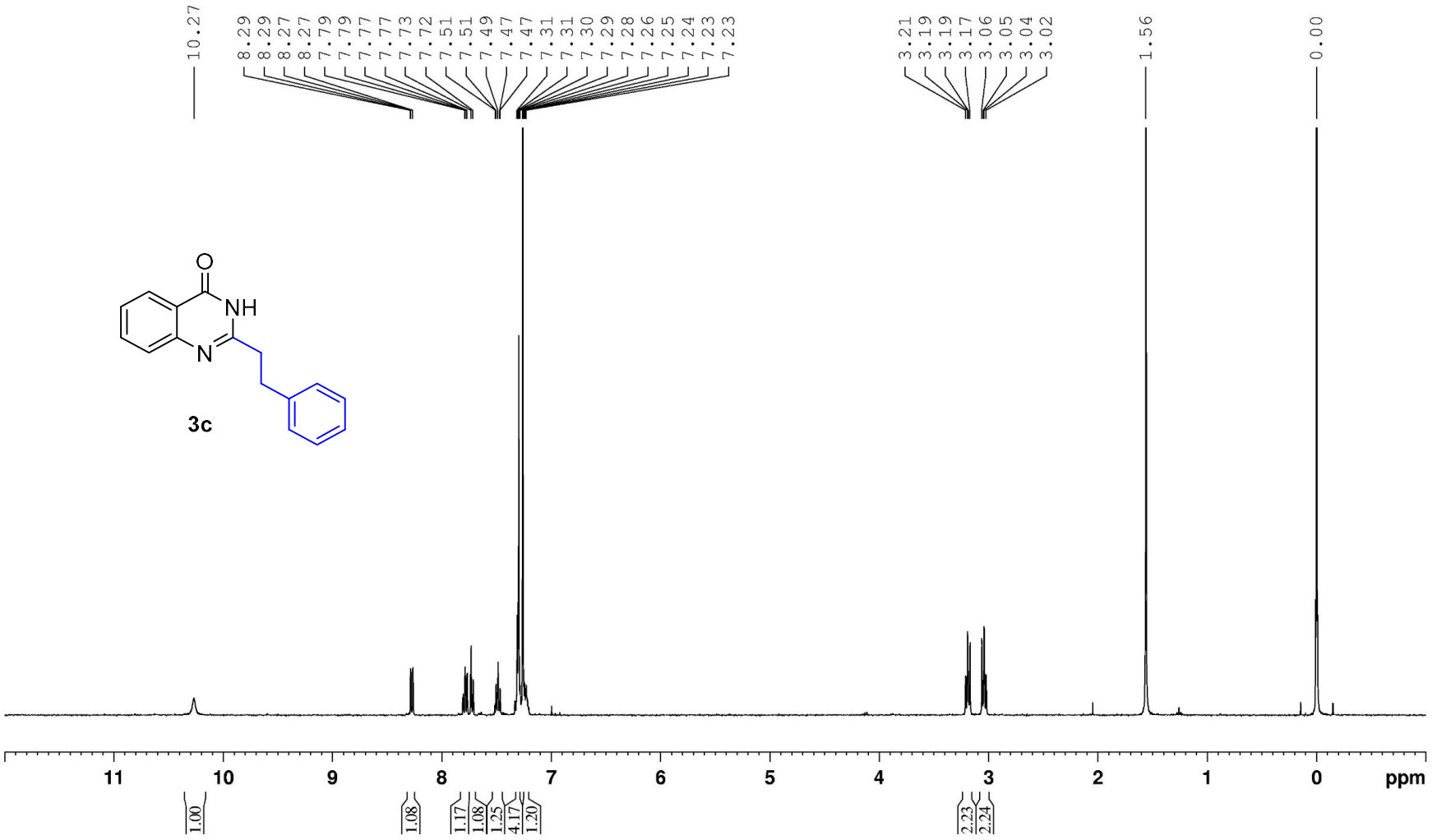
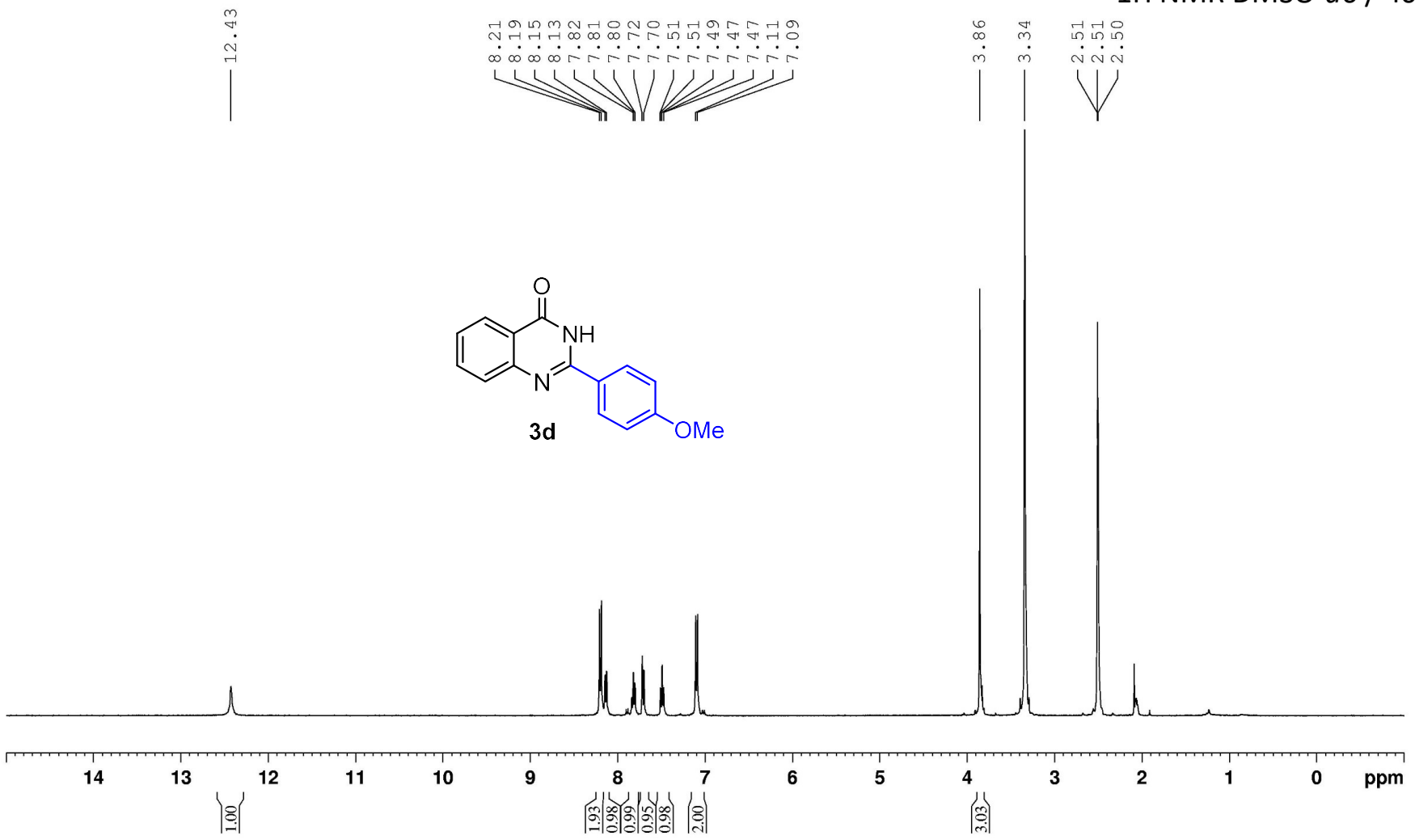
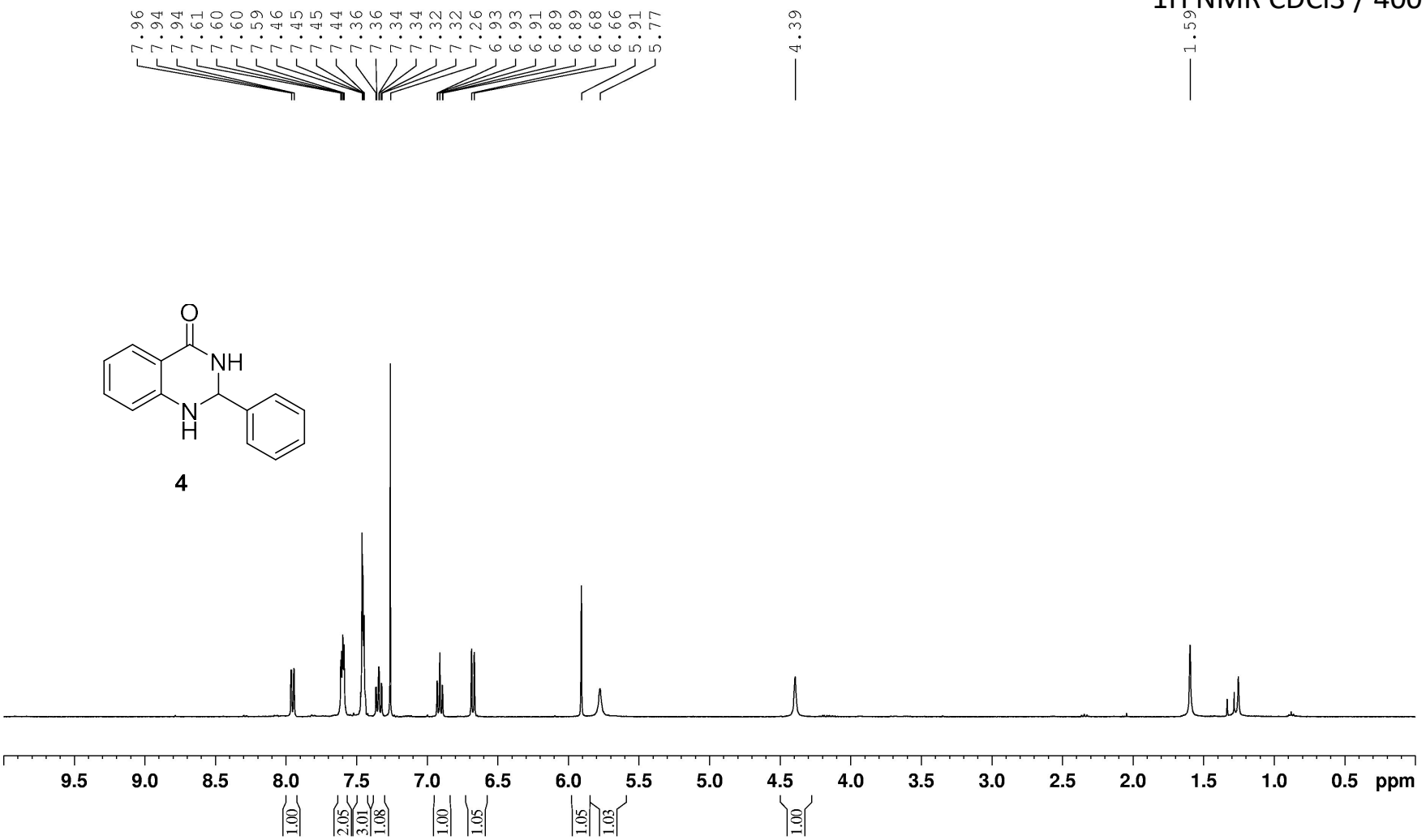


1H NMR DMSO-*d*6 / 400 MHz



1H NMR CDCl3 / 400 MHz



1H NMR CDCl3 / 400 MHz