

Supporting Information

Reductive Cleavage of C–X (F, Cl, Br, I) Bonds Catalyzed by Cheap and Abundant Raney Nickel in Water

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1. General Information

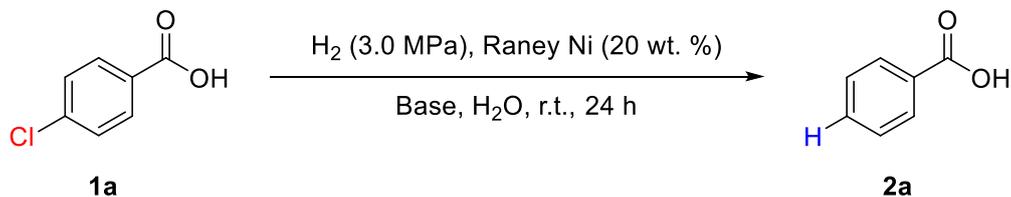
All reactions were carried out in dried stainless-steel high-pressure reactors, which were purchased from Anhui Kemi Instrument Co., LTD., with built-in magnetic stirring or mechanical stirring paddle, and total volume of 20 mL (Six parallel reactors, dimensions 260 x 260 x 900 mm, wall-thickness of 100 mm) or 100 mL (dimensions 550 x 550 x 850 mm, wall-thickness of 150 mm). For reactions that require heating, the heating mantle was used for the heat source. A 50 μm Raney nickel catalyst used in this study was purchased from Meryer Technologies Co., LTD.

Unless otherwise specified, Nuclear magnetic resonance (NMR) spectra were recorded in CDCl_3 or DMSO-d_6 on a 500 MHz (for ^1H) spectrometers. All chemical shifts were reported in ppm relative to tetramethylsilane (TMS) (^1H NMR, 0 ppm or ^1H NMR, 2.5 ppm) as the internal standard. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm , 4.6 \times 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. The coupling constants were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Caution: *Raney nickel catalyst is prone to spontaneous combustion in air, and hydrogen gas is highly explosive when exposed to an open flame. It is imperative to ensure that Raney nickel is always kept in a solvent and to utilize high-purity hydrogen gas.*

2. Optimization of the Reaction Conditions

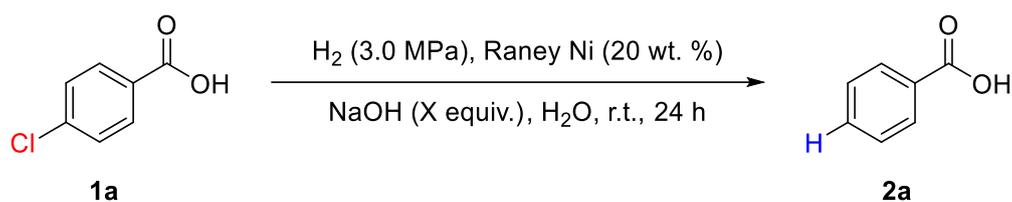
Table S1. Screening the base^a



Entry	Base	Yield ^b /%
1	KOH	71
2	NaOH	99
3	K ₂ CO ₃	12
4	Na ₂ CO ₃	15
5	KHCO ₃	14
6	NaHCO ₃	17

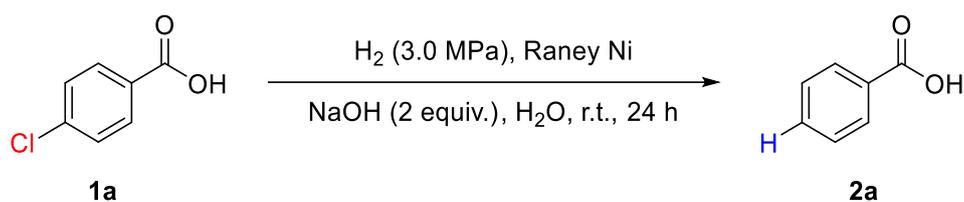
^a Reaction conditions: 4-chlorobenzoic acid (**1a**, 156 mg, 1 mmol), Raney nickel (20 wt.%), Base (2 mmol, 2.0 equiv.) and H₂O (5 mL, 0.2 M) were stirred at room temperature for 24 h under H₂ (3.0 MPa) in dried stainless-steel high-pressure reactors.

^b The yield was determined by HPLC using pure **2a** as the external standard ($t_{R,2a} = 2.1$ min, $\lambda_{max} = 226.4$ nm; water/acetonitrile = 30:70 (v/v)).

Table S2. Screening the Loading of NaOH^a

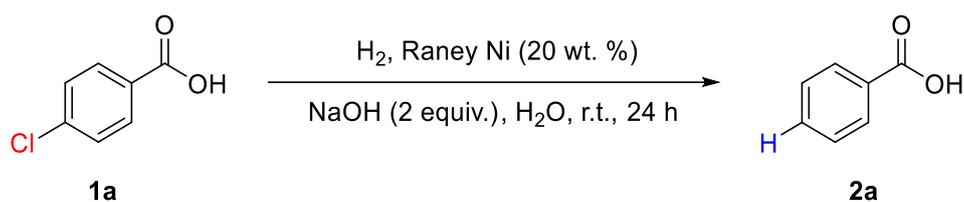
Entry	NaOH (X equiv.)	Yield ^b /%
1	1	11
2	1.25	26
3	1.5	35
4	1.75	60
5	2	99

^a Reaction conditions: 4-chlorobenzoic acid (**1a**, 156 mg, 1 mmol), Raney nickel (20 wt.%), NaOH (X equiv.) and H₂O (5 mL, 0.2 M) were stirred at room temperature for 24 h under H₂ (3.0 MPa) in dried stainless-steel high-pressure reactors. ^b The yield was determined by HPLC using pure **2a** as the external standard ($t_{R,2a} = 2.1$ min, $\lambda_{max} = 226.4$ nm; water/acetonitrile = 30:70 (v/v)).

Table S3. Screening the loading of Raney Ni^a

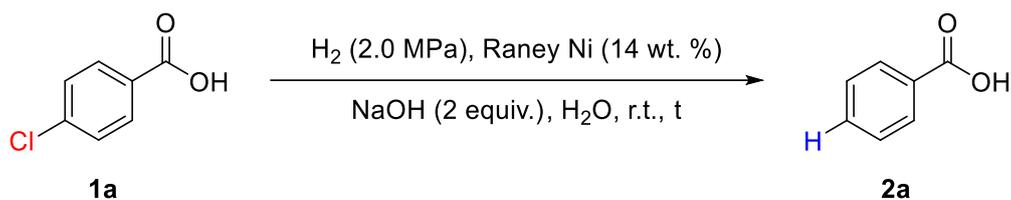
Entry	Raney Ni (wt. %)	Yield ^b /%
1	2	8
2	4	23
3	6	33
4	8	52
5	10	75
6	12	84
7	14	99
8	16	99
9	18	99
10	20	99

^aReaction conditions: 4-chlorobenzoic acid (**1a**, 156 mg, 1 mmol), Raney nickel, NaOH (2 mmol, 2.0 equiv.) and H₂O (5 mL, 0.2 M) were stirred at room temperature for 24 h under H₂ (3.0 MPa) in dried stainless-steel high-pressure reactors. ^b The yield was determined by HPLC using pure **2a** as the external standard ($t_{R,2a} = 2.1$ min, $\lambda_{max} = 226.4$ nm; water/acetonitrile = 30:70 (v/v)).

Table S4. Screening the H₂ pressures^a

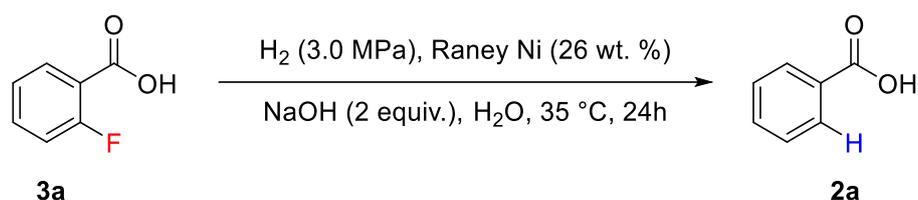
Entry	H ₂ pressures (MPa)	Yield ^b /%
1	1	86
2	2	99
3	3	99

^a Reaction conditions: 4-chlorobenzoic acid (**1a**, 156 mg, 1 mmol), Raney nickel (14 wt.%), NaOH (2 equiv.) and H₂O (5 mL, 0.2 M) were stirred at room temperature for 24 h under H₂ in dried stainless-steel high-pressure reactors. ^b The yield was determined by HPLC using pure **2a** as the external standard ($t_{R,2a} = 2.1$ min, $\lambda_{max} = 226.4$ nm; water/acetonitrile = 30:70 (v/v)).

Table S5. Screening the reaction time^a

Entry	Time (h)	Yield ^b /%
1	18	88
2	20	93
3	22	97
4	24	99

^a Reaction conditions: 4-chlorobenzoic acid (**1a**, 156 mg, 1 mmol), Raney nickel (14 wt.%), NaOH (2 equiv.) and H₂O (5 mL, 0.2 M) were stirred at room temperature under H₂(2.0 MPa) in dried stainless-steel high-pressure reactors. ^b The yield was determined by HPLC using pure **2a** as the external standard ($t_{R,2a} = 2.1$ min, $\lambda_{max} = 226.4$ nm; water/acetonitrile = 30:70 (v/v)).

Table S6. The result of Raney Ni recycling^a

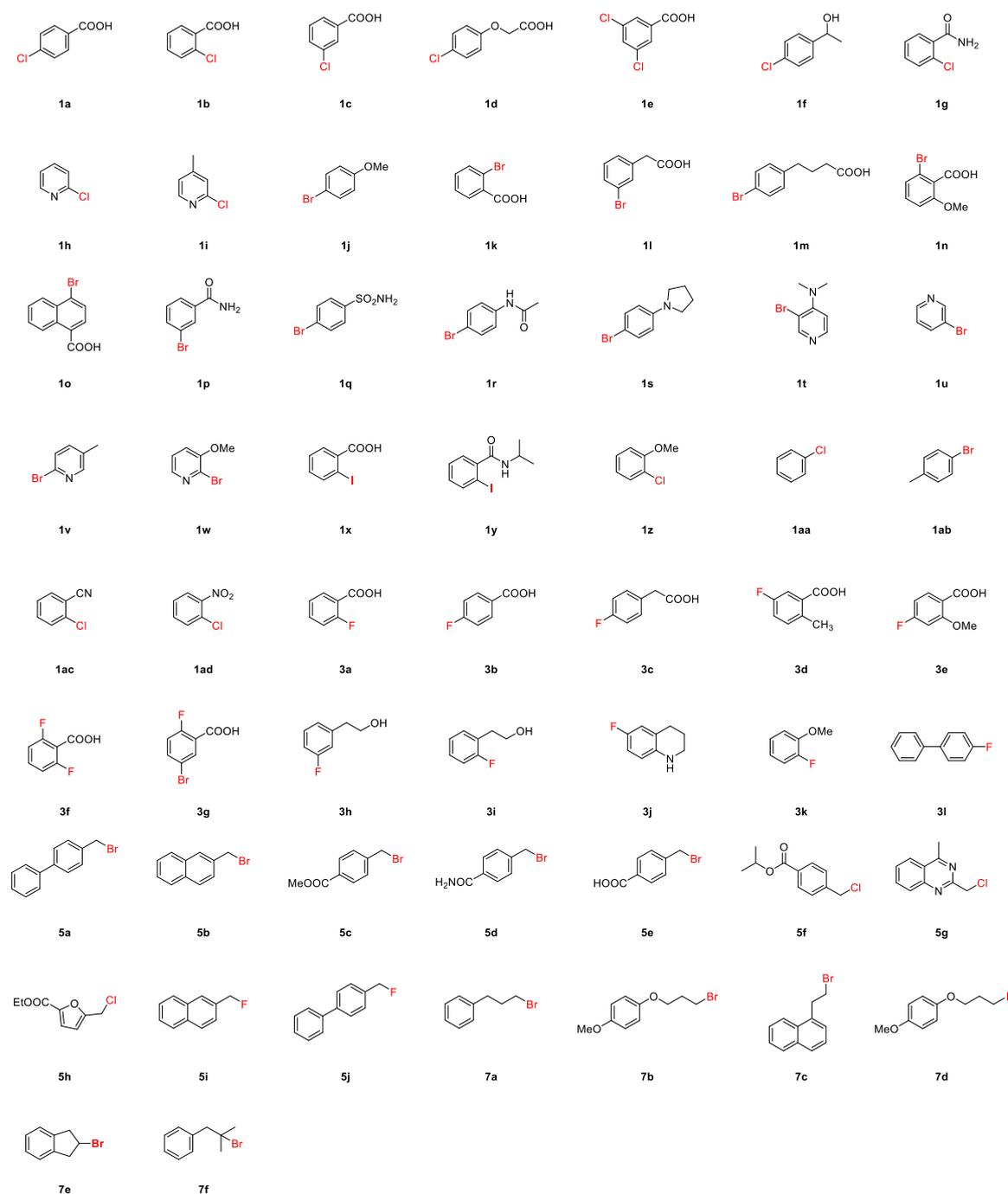
Entry	Number of reuses	Yield ^b /%		
		1	2	3
1	1	98	99	98
2	2	97	98	99
3	3	98	96	97
4	4	96	95	93
5	5	95	93	92
6	6	94	96	93
7	7	93	94	92
8	8	90	94	91
9	9	85	84	90
10	10	75	71	69
11	11	62	65	61
12	12	50	55	53
13	13	46	41	42
14	14	32	33	35
15	15	30	26	31

^a Reaction conditions: 2-fluorobenzoic acid (**3a**, 140 mg, 1 mmol), Raney nickel (26 wt.%), NaOH (2 equiv.) and H₂O (5 mL, 0.2 M) were stirred at 35 °C for 24 h under H₂ (3.0 MPa) in dried stainless-steel high-pressure reactors. ^b The yield was determined by HPLC using pure **2a** as the external standard ($t_{R,2a} = 2.1$ min, $\lambda_{max} = 226.4$ nm; water/acetonitrile = 30:70 (v/v)).

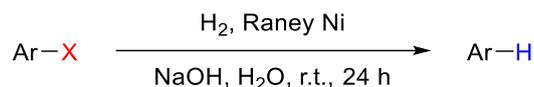
3. Experimental Procedures

3.1 Preparation of halides

1a-1q, **1u-1x**, **1z-1ad**, **3a-3l**, **5a**, **5b**, **5e**, **5g**, **5h** and **7a** are received from commercial suppliers. **1r**,¹ **1s**,² **1t**,³ **1y**,⁴ **5c**,⁵ **5d**,⁶ **5f**,⁵ **5i**,⁷ **5j**,⁸ **7b**,⁹ **7c**,¹⁰ **7d**,¹¹ **7e**¹² and **7f**¹³ are known compounds and were synthesized according to the literature.

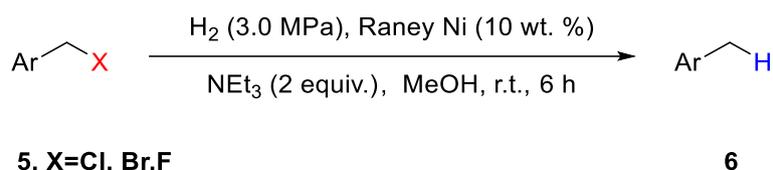


3.2 General procedures for synthesis of the compounds 2 and 4 (GP 1)



Aryl halides **1** or **3** (2.0 mmol), Raney nickel (14 wt.% or 26 wt.%), H₂ (2.0 or 3.0 MPa), NaOH (2 equiv.) and H₂O (10 mL) were added to a high-pressure reactor equipped with a magnetic stirrer, which total volume of 100 mL. Hydrogen was charged into the reactor through the inlet, and the gas inside was replaced three times. The reaction kettle was filled with hydrogen to 2.0 or 3.0 MPa, followed by vigorous stirring of the reaction mixture at 35 °C for 24 hours. Then, the hydrogen in the reactor was released in a fume hood upon completion of the reaction. After filtering the reaction mixture to remove Raney nickel, the filter residue was washed with ethyl acetate. (For organic compounds containing carboxyl groups used as substrates, add 1 M HCl dropwise to adjust the pH to the range of 2–3.) Then the filtered filtrate was washed with ethyl acetate (3 × 10 mL). The combined organic extracts were dried by adding anhydrous sodium sulfate to completely remove residual moisture. After filtering out the drying agent, the filtrate was rotary evaporated under reduced pressure and concentrated to dryness to obtain the product **2** or **4**.

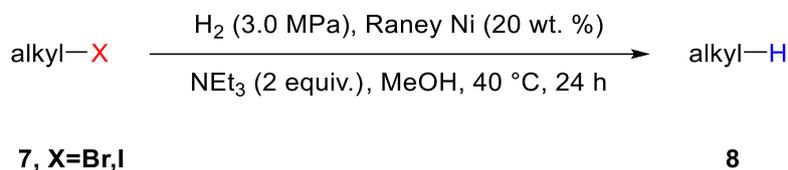
3.3 General procedures for synthesis of the compounds 6 (GP 2)



Benzyl halides **5** (2.0 mmol), Raney nickel (10 wt.%), H₂ (3.0 MPa), NEt₃ (2 equiv.) and MeOH (10 mL) were added to a high-pressure reactor equipped with a magnetic stirrer, which total volume of 100 mL. Hydrogen was charged into the reactor through the inlet, and the gas inside was replaced three times. The reaction kettle was filled with hydrogen to 3.0 MPa, followed by vigorous stirring of the reaction mixture at room temperature for 6 hours. Then, the hydrogen in the reactor was released in a fume hood upon completion of the reaction. After filtering the reaction mixture to remove Raney nickel, the filter residue was washed with ethyl acetate. Then the filtered filtrate was

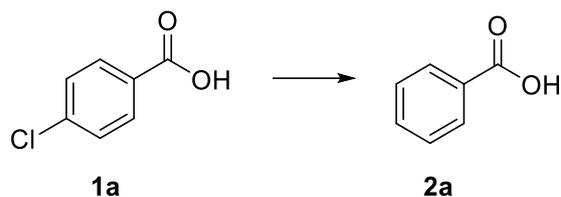
washed with ethyl acetate (3 × 10 mL). The combined organic extracts were dried by adding anhydrous sodium sulfate to completely remove residual moisture. Product **6** was obtained through column chromatography purification.

3.4 General procedures for synthesis of the compounds **8** (GP 3)

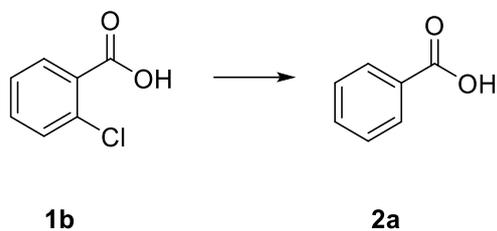


Primary alkyl halides **7** (1.0 mmol), Raney nickel (20 wt.%), H₂ (3.0 MPa), NEt₃ (2 equiv.) and MeOH (5 mL) were added to a high-pressure reactor that was equipped with a mechanical stirring paddle, which total volume of 100 mL. Hydrogen was charged into the reactor through the inlet, and the gas inside was replaced three times. The reaction kettle was filled with hydrogen to 3.0 MPa, followed by vigorous stirring of the reaction mixture at 40 °C for 24 hours. Then, the hydrogen in the reactor was released in a fume hood upon completion of the reaction. After filtering the reaction mixture to remove Raney nickel, the filter residue was washed with ethyl acetate. Then the filtered filtrate was washed with ethyl acetate (3 × 10 mL). The combined organic extracts were dried by adding anhydrous sodium sulfate to completely remove residual moisture. Product **8** was obtained through column chromatography purification.

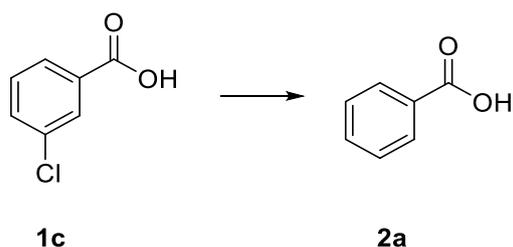
4. Characterization



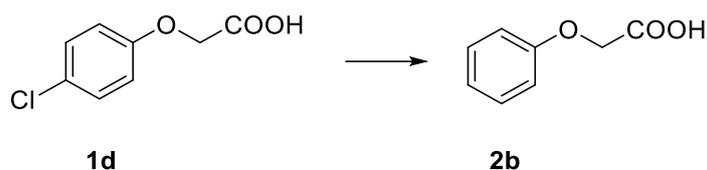
Benzoic acid (2a). White solid, 234 mg, 96% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 12.25 (s, 1H), 8.14-8.15 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48-7.51 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.51, 133.85, 130.25, 129.36, 128.51.



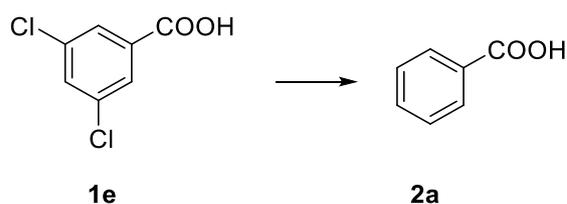
Benzoic acid (2a). White solid, 232 mg, 95% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 12.25 (s, 1H), 8.14-8.15 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48-7.51 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.51, 133.85, 130.25, 129.36, 128.51.



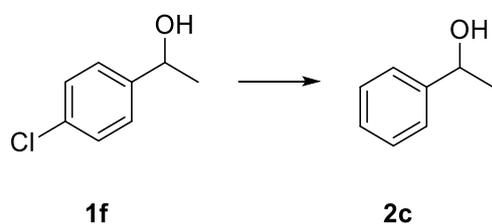
Benzoic acid (2a). White solid, 239 mg, 98% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 12.25 (s, 1H), 8.14-8.15 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48-7.51 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.51, 133.85, 130.25, 129.36, 128.51.



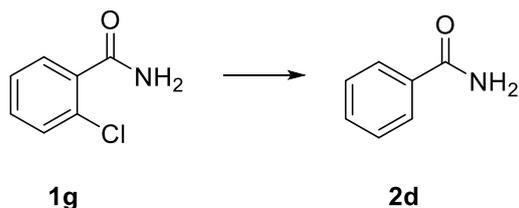
2-Phenoxyacetic acid (2b). White solid, 301mg, 99% yield. M.p. 98–100 °C. Compound **2b** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.96 (s, 1H), 7.30-7.33 (t, $J = 7.8$ Hz, 2H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.93 (d, $J = 8.1$ Hz, 2H), 4.69 (s, 2H).



Benzoic acid (2a). White solid, 224 mg, 92% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 12.25 (s, 1H), 8.14-8.15 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48-7.51 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.51, 133.85, 130.25, 129.36, 128.51.

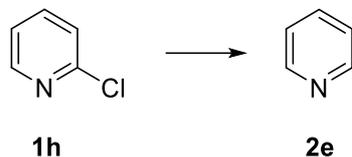


1-Phenylethanol (2c). Colorless liquid, 229 mg, 94% yield. Compound **2c** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁶ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34-7.40 (m, 4H), 7.27-7.30 (m, 1H), 4.89 (q, $J = 6.5$ Hz, 1H), 2.01 (s, 1H), 1.50 (d, $J = 6.3$ Hz, 3H).

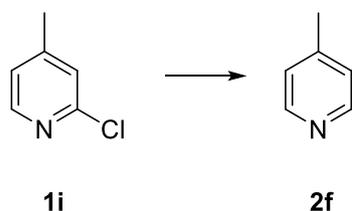


Benzamide (2d). White solid, 240 mg, 99% yield. M.p. 126-128 °C. Compound **2d** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁷

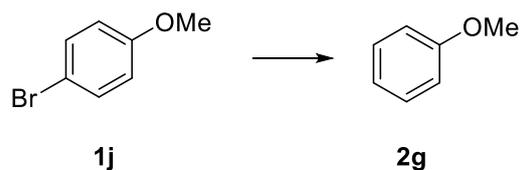
^1H NMR (500 MHz, DMSO-*d*₆) δ 7.97 (s, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-*d*₆) δ 173.15, 139.48, 136.42, 133.41, 132.67.



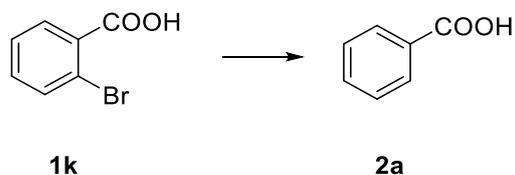
Pyridine (2e). Colorless liquid, 96% yield. Compound **2e** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in literature.¹⁸ ^1H NMR (500 MHz, CDCl₃) δ 8.55-8.57 (m, 2H), 7.60 (tt, *J* = 7.6, 1.9 Hz, 1H), 7.20 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl₃) δ 149.85, 136.09, 123.69.



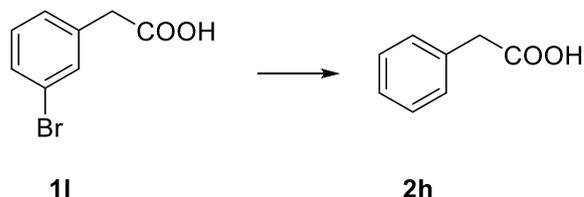
4-Methylpyridine (2f). Colorless liquid, 98% yield. Compound **2f** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in literature.¹⁹ ^1H NMR (500 MHz, CDCl₃) δ 8.45 (d, *J* = 6.1 Hz, 2H), 7.09 (d, *J* = 5.1 Hz, 2H), 2.34 (s, 3H).



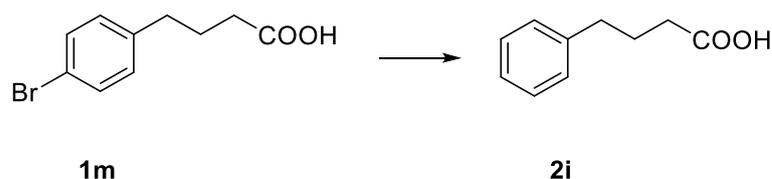
Anisole (2g). Colorless liquid, 91% yield. Compound **2g** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in literature.¹⁸ ^1H NMR (500 MHz, CDCl₃) δ 7.29-7.33 (m, 2H), 6.92-6.98 (m, 3H), 3.80 (s, 3H).



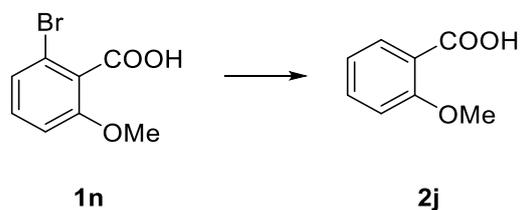
Benzoic acid (2a). White solid, 232 mg, 95% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ ^1H NMR (500 MHz, CDCl_3) δ 12.25 (s, 1H), 8.14-8.15 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48-7.51 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.51, 133.85, 130.25, 129.36, 128.51.



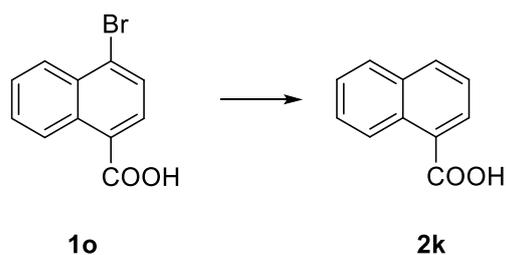
2-Phenylacetic acid (2h). White solid, 259 mg, 95% yield. M.p. 76-78 °C. Compound **2h** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²⁰ ^1H NMR (500 MHz, CDCl_3) δ 10.66 (s, 1H), 7.27-7.34 (m, 5H), 3.64 (s, 2H).



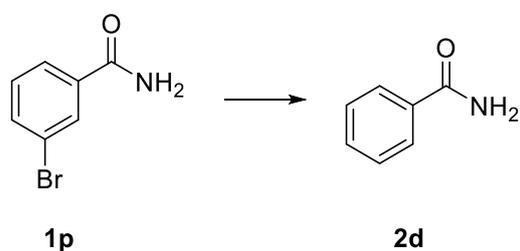
4-Phenylbutanoic acid (2i). White solid, 309 mg, 94% yield. M.p. 49-51 °C. Compound **2i** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²¹ ^1H NMR (500 MHz, CDCl_3) δ 11.45 (s, 1H), 7.28-7.31 (m, 2H), 7.19-7.21 (m, 3H), 2.69 (t, $J = 7.5$ Hz, 2H), 2.39 (t, $J = 7.6$ Hz, 2H), 1.98 (m, 2H).



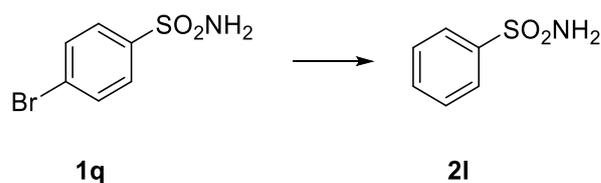
2-Methoxybenzoic acid (2j). White solid, 292 mg, 96% yield. M.p. 101-103 °C. Compound **2j** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²² ^1H NMR (500 MHz, CDCl_3) δ 10.85 (s, 1H), 8.16 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.52-7.60 (m, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 1H), 4.07 (s, 3H).



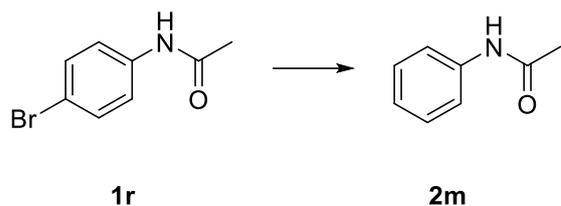
1-Naphthoic acid (2k). White solid, 331 mg, 96% yield. M.p. 159-161 °C. Compound **2k** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²² **¹H NMR (500 MHz, CDCl₃)** δ 12.20 (s, 1H), 9.11 (d, *J* = 8.7 Hz, 1H), 8.44 (d, *J* = 7.2 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.57 (q, *J* = 7.9 Hz, 2H).



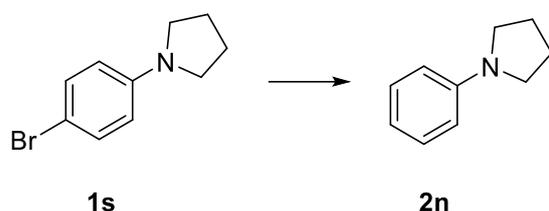
Benzamide (2d). White solid, 240 mg, 99% yield. M.p. 126-128 °C. Compound **2d** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁷ **¹H NMR (500 MHz, DMSO-*d*₆)** δ 7.97 (s, 1H), 7.88 (d, *J* = 7.1 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (s, 1H). **¹³C{¹H} NMR (126 MHz, DMSO-*d*₆)** δ 173.15, 139.48, 136.42, 133.41, 132.67.



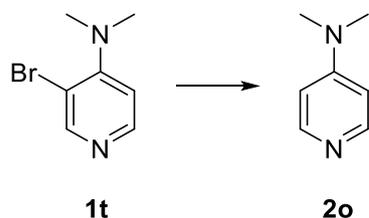
Benzenesulfonamide (2l). White solid, 302 mg, 96% yield. M.p. 150-152 °C. Compound **2l** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²³ **¹H NMR (500 MHz, DMSO-*d*₆)** δ 7.81 -7.87 (m, 2H), 7.58 (m, 3H), 7.36 (s, 2H).



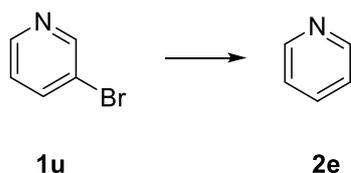
N-Phenylacetamide (**2m**). White solid, 249 mg, 92% yield. M.p. 112-114 °C. Compound **2m** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.97 (s, 1H), 7.54 (d, $J = 7.9$ Hz, 2H), 7.31 (t, $J = 7.8$ Hz, 2H), 7.11 (t, $J = 7.4$ Hz, 1H), 2.17 (s, 3H).



1-Phenylpyrrolidine (**2n**). Yellow oil, 265 mg, 90% yield. Compound **2n** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.25-7.33 (t, $J = 8.1$ Hz, 2H), 6.71 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 8.0$ Hz, 2H), 3.30-3.35 (m, 4H), 2.00-2.10 (m, 4H).

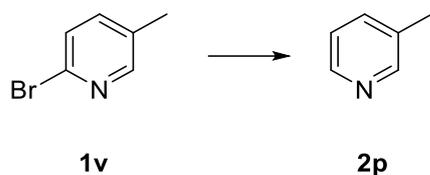


N,N-dimethylpyridin-4-amine (**2o**). White solid, 239 mg, 98% yield. M.p. 110-112 °C. Compound **2o** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²⁶ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.15-8.27 (m, 2H), 6.41-6.58 (m, 2H), 2.99 (s, 6H).

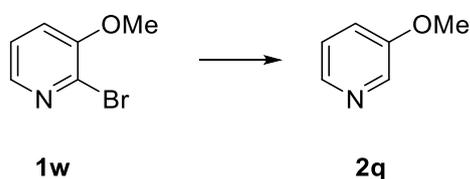


Pyridine (**2e**). Colorless liquid, 98% yield. Compound **2e** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in

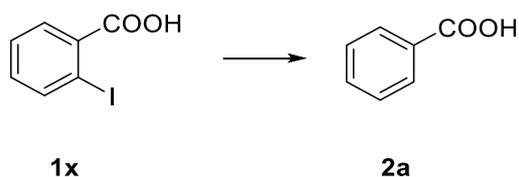
literature.¹⁸ ^1H NMR (500 MHz, CDCl_3) δ 8.55-8.57 (m, 2H), 7.60 (tt, $J = 7.6, 1.9$ Hz, 1H), 7.20 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 149.85, 136.09, 123.69



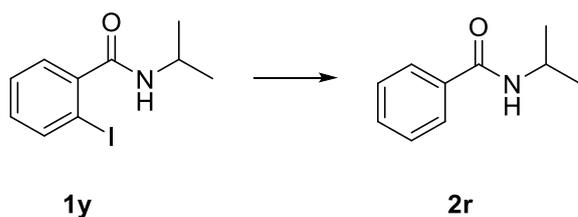
3-Methylpyridine (2p). Colorless liquid, 95% yield. Compound **2p** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in literature.²⁷ ^1H NMR (500 MHz, CDCl_3) δ 8.35-8.40 (m, 2H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.11-7.14 (dd, $J = 7.8, 4.7$ Hz, 1H), 2.28 (s, 3H).



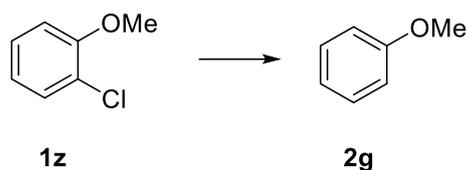
3-Methoxypyridine (2q). Colorless liquid, 214 mg, 98% yield. Compound **2q** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²⁸ ^1H NMR (500 MHz, CDCl_3) δ 8.28 (d, $J = 2.6$ Hz, 1H), 8.15-8.21 (m, 1H), 7.11-7.27 (m, 2H), 3.82 (s, 3H).



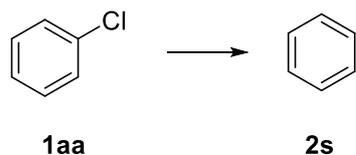
Benzoic acid (2a). White solid, 234 mg, 96% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ ^1H NMR (500 MHz, CDCl_3) δ 12.25 (s, 1H), 8.14-8.15 (d, $J = 7.7$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.48-7.51 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 172.51, 133.85, 130.25, 129.36, 128.51.



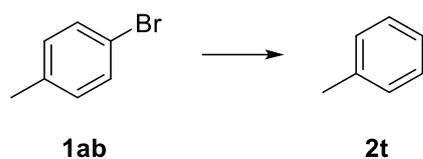
N-Isopropylbenzamide (**2r**). White solid, 323 mg, 99% yield. M.p. 100-102 °C. Compound **2r** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²⁹ ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.44-7.48 (t, *J* = 7.3 Hz, 1H), 7.36-7.42 (t, *J* = 7.6 Hz, 2H), 6.05 (s, 1H), 4.24-4.35 (m, 1H), 1.25 (d, *J* = 6.6 Hz, 6H).



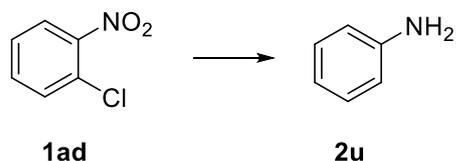
Anisole (**2g**). Colorless liquid, 75% yield. Compound **2g** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in literature.¹⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.29-7.33 (m, 2H), 6.92-6.98 (m, 3H), 3.80 (s, 3H).



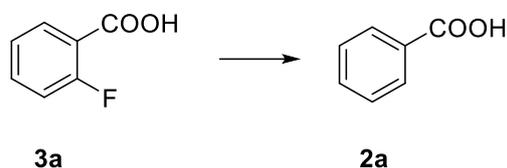
Benzene(**2s**). Product **2s** was prepared according to **GP1** and obtained in 42% yield. Its identity was confirmed by HPLC, and the yield was determined by quantitative HPLC analysis using a response factor obtained with commercially available benzene (CAS No. 71-43-2).



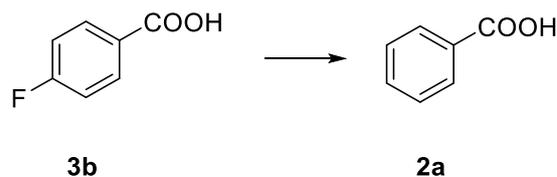
Toluene (**2t**). Product **2t** was prepared according to **GP1** and obtained in 28% yield. Its identity was confirmed by HPLC, and the yield was determined by quantitative HPLC analysis using a response factor obtained with commercially available toluene (CAS No. 108-88-3).



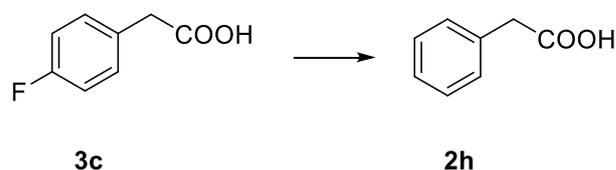
Aniline (2u). Yellow liquid, 167 mg, 90% yield. Compound **2u** was prepared according to **GPI**. The NMR data is identical to that reported in literature.³⁰ **¹H NMR (500 MHz, CDCl₃)** δ 7.18 (t, *J* = 7.5 Hz, 2H), 6.78 (t, *J* = 7.0 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 2H), 3.65 (s, 2H).



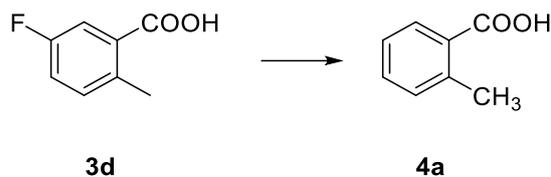
Benzoic acid (2a). White solid, 242 mg, 99% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GPI**. The NMR data is identical to that reported in literature.¹⁴ **¹H NMR (500 MHz, CDCl₃)** δ 12.25 (s, 1H), 8.14-8.15 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48-7.51 (t, *J* = 7.6 Hz, 2H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 172.51, 133.85, 130.25, 129.36, 128.51.



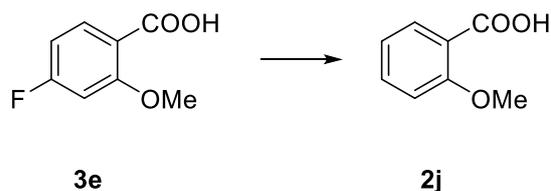
Benzoic acid (2a). White solid, 239 mg, 98% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GPI**. The NMR data is identical to that reported in literature.¹⁴ **¹H NMR (500 MHz, CDCl₃)** δ 12.25 (s, 1H), 8.14-8.15 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48-7.51 (t, *J* = 7.6 Hz, 2H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 172.51, 133.85, 130.25, 129.36, 128.51.



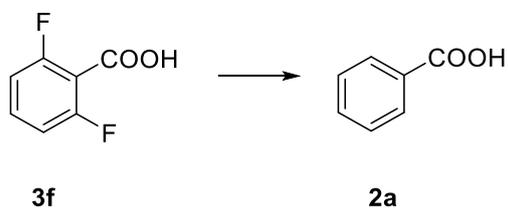
2-Phenylacetic acid (2h). White solid, 264 mg, 97% yield. M.p. 76-78 °C. Compound **2h** was prepared according to **GPI**. The NMR data is identical to that reported in literature.²⁰ **¹H NMR (500 MHz, CDCl₃)** δ 10.66 (s, 1H), 7.27-7.34 (m, 5H), 3.64 (s, 2H).



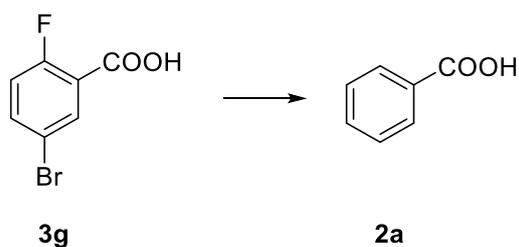
2-Methylbenzoic acid (4a). White solid, 259 mg, 95% yield. M.p. 101-103°C. Compound **4a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.³¹ **¹H NMR (500 MHz, CDCl₃)** δ 11.78 (s, 1H), 8.08-8.12 (m, 1H), 7.44-7.53 (m, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 2.68 (s, 3H).



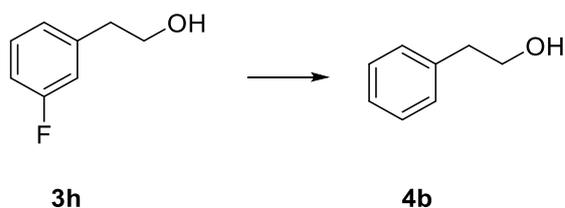
2-Methoxybenzoic acid (2j). White solid, 277 mg, 91% yield. M.p. 101-103 °C. Compound **2j** was prepared according to **GP1**. The NMR data is identical to that reported in literature.²² **¹H NMR (500 MHz, CDCl₃)** δ 10.85 (s, 1H), 8.16 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.52-7.60 (m, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.07 (s, 3H).



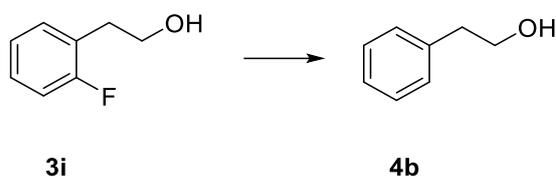
Benzoic acid (2a). White solid, 237 mg, 97% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ **¹H NMR (500 MHz, CDCl₃)** δ 12.25 (s, 1H), 8.14-8.15 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48-7.51 (t, *J* = 7.6 Hz, 2H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 172.51, 133.85, 130.25, 129.36, 128.51.



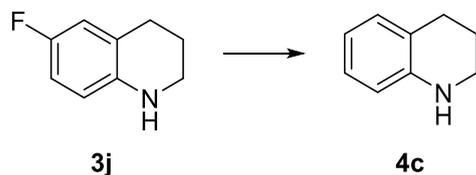
Benzoic acid (2a). White solid, 224 mg, 92% yield. M.p. 121-123 °C. Compound **2a** was prepared according to **GP1**. The NMR data is identical to that reported in literature.¹⁴ **¹H NMR (500 MHz, CDCl₃)** δ 12.25 (s, 1H), 8.14-8.15 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.48-7.51 (t, *J* = 7.6 Hz, 2H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 172.51, 133.85, 130.25, 129.36, 128.51.



2-Phenylethan-1-ol (4b). Colorless liquid, 230 mg, 94% yield. Compound **4b** was prepared according to **GP1**. The NMR data is identical to that reported in literature.³² **¹H NMR (500 MHz, CDCl₃)** δ 7.31-7.38 (t, *J* = 7.5 Hz, 2H), 7.22-7.28 (d, *J* = 7.5 Hz, 3H), 3.85 (t, *J* = 6.6 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 1.78 (s, 1H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 138.53, 129.06, 128.60, 126.49, 63.68, 39.22.

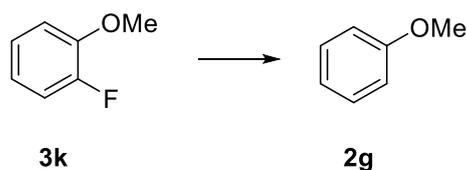


2-Phenylethan-1-ol (4b). Colorless liquid, 239 mg, 98% yield. Compound **4b** was prepared according to **GP1**. The NMR data is identical to that reported in literature.³² **¹H NMR (500 MHz, CDCl₃)** δ 7.31-7.38 (t, *J* = 7.5 Hz, 2H), 7.22-7.28 (d, *J* = 7.5 Hz, 3H), 3.85 (t, *J* = 6.6 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 1.78 (s, 1H). **¹³C{¹H} NMR (126 MHz, CDCl₃)** δ 138.53, 129.06, 128.60, 126.49, 63.68, 39.22.

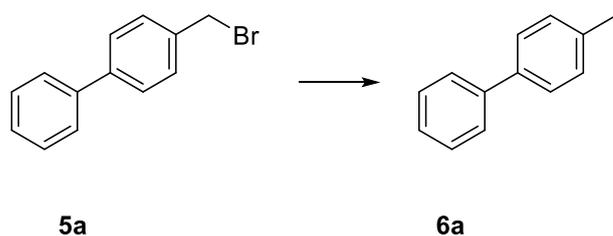


1,2,3,4-Tetrahydroquinoline (4c). Yellow oil, 240 mg, 90% yield. Compound **4c** was prepared according to **GP1**. The NMR data is identical to that reported in literature.³³ **¹H NMR (500 MHz, CDCl₃)** δ 6.94-7.02 (m, 2H), 6.63 (t, *J* = 7.4 Hz, 1H), 6.48 (d, *J* = 7.9 Hz, 1H), 3.81 (s, 1H), 3.32 (t, *J* = 5.5 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 1.95-2.01

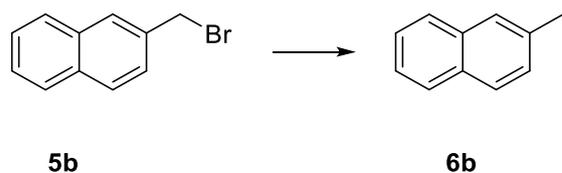
(m, 2H).



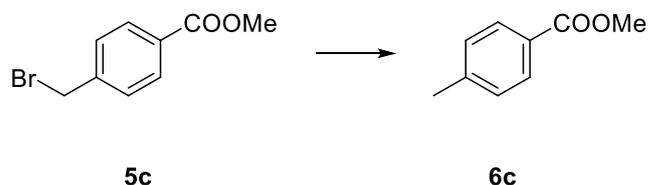
Anisole (2g). Colorless liquid, 51% yield. Compound **2g** was prepared according to **GP1** and determined by HPLC. The NMR data is identical to that reported in literature.¹⁸ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.29-7.33 (m, 2H), 6.92-6.98 (m, 3H), 3.80 (s, 3H)



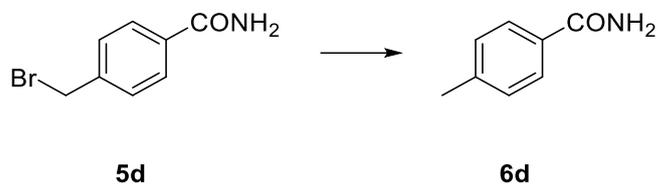
4-Methyl-1,1'-biphenyl (6a). White solid, 289 mg, 86% yield. M.p. 45-47 °C. Compound **6a** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 (d, $J = 7.6$ Hz, 2H), 7.54 (d, $J = 6.9$ Hz, 2H), 7.46 (t, $J = 7.9$ Hz, 2H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.29 (d, $J = 7.7$ Hz, 2H), 2.43 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 141.22, 138.41, 137.05, 129.52, 128.75, 128.54, 127.04, 127.01, 21.14.



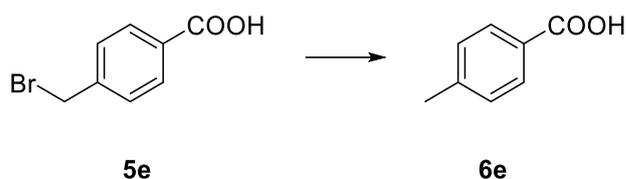
2-Methylnaphthalene (6b). Colorless oil, 230 mg, 81% yield. Compound **6b** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.64-7.85 (m, 3H), 7.64 (s, 1H), 7.41-7.48 (m, 2H), 7.35 (d, $J = 10.1$ Hz, 1H), 2.54 (s, 3H).



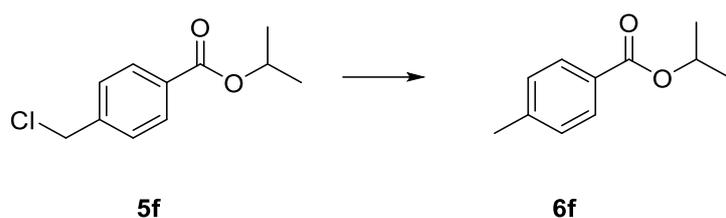
Methyl 4-methylbenzoate (6c). Colorless oil, 291 mg, 97% yield. Compound **6c** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁶ ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 6.2 Hz, 2H), 7.22 (d, *J* = 6.0 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H).



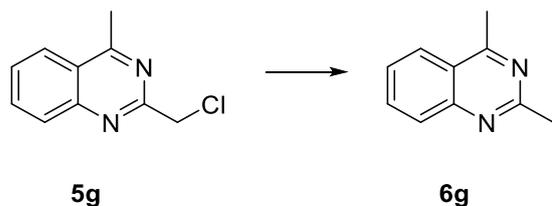
4-Methylbenzamide (6d). White solid, 260 mg, 96% yield. Compound **6d** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁷ ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.11 (s, 2H), 2.39 (s, 3H).



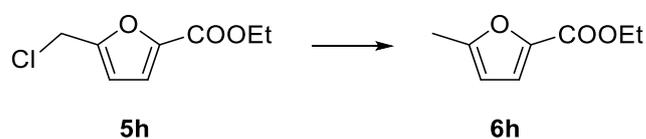
4-Methylbenzoic acid (6e). White solid, 190 mg, 70% yield. M.p. 180-182 °C. Compound **6e** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁸ ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H).



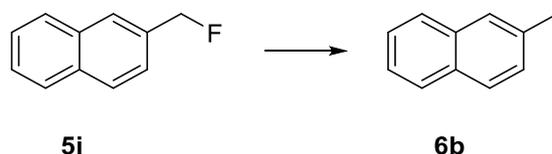
Isopropyl 4-methylbenzoate (6f). Colorless oil, 324 mg, 91% yield. Compound **6f** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁹ ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.24 (p, *J* = 6.3 Hz, 1H), 2.40 (s, 3H), 1.35 (d, *J* = 6.3 Hz, 6H).



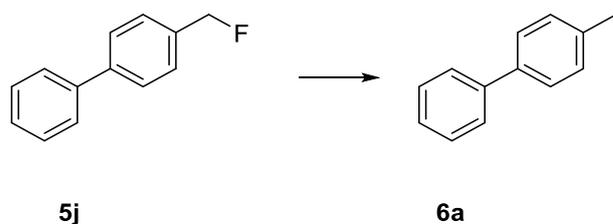
2,4-Dimethylquinazoline (6g). Yellow solid, 285 mg, 90% yield. M.p. 288-290 °C. Compound **6g** was prepared according to **GP2**. The NMR data is identical to that reported in literature.⁴⁰ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.03 (d, $J = 8.3$ Hz, 1H), 7.90 (d, $J = 8.5$ Hz, 1H), 7.81 (t, $J = 7.6$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 2.89 (s, 3H), 2.82 (s, 3H).



Ethyl 5-methylfuran-2-carboxylate (6h). Colorless oil, 284 mg, 92% yield. Compound **6h** was prepared according to **GP2**. The NMR data is identical to that reported in literature.⁴¹ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.06 (d, $J = 2.9$ Hz, 1H), 6.10 (d, $J = 2.3$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.37 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H).

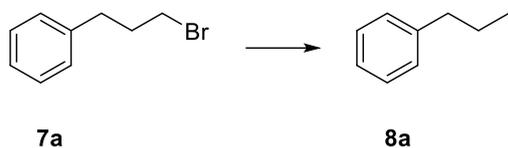


2-Methylnaphthalene (6b). Colorless oil, 262 mg, 92% yield. Compound **6b** was prepared according to **GP2**. The NMR data is identical to that reported in literature.³⁵ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.74-7.90 (m, 3H), 7.67 (s, 1H), 7.42-7.53 (m, 2H), 7.37 (d, $J = 10.1$ Hz, 1H), 2.57 (s, 3H).

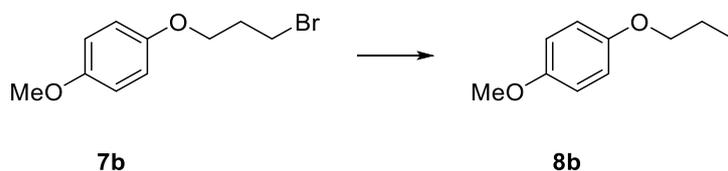


4-Methyl-1,1'-biphenyl (6a). White solid, 313 mg, 93% yield. M.p. 45-47 °C. Compound **6a** was prepared according to **GP2**. The NMR data is identical to that

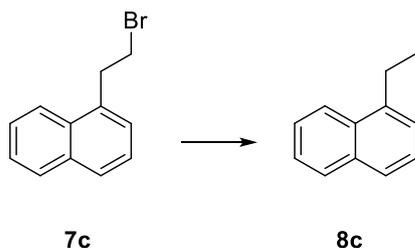
reported in literature.³⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.64 (d, $J = 7.6$ Hz, 2H), 7.56 (d, $J = 6.9$ Hz, 2H), 7.49 (t, $J = 7.9$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 1H), 7.31 (d, $J = 7.7$ Hz, 2H), 2.46 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ 141.22, 138.41, 137.05, 129.52, 128.75, 128.54, 127.04, 127.01, 21.14.



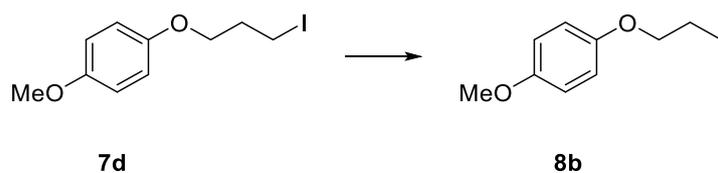
Propylbenzene (8a). Colorless oil, 100 mg, 83% yield. Compound **8a** was prepared according to **GP3**. The NMR data is identical to that reported in literature.⁴² $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.16-7.32 (m, 5H), 2.61 (t, $J = 7.7$ Hz, 2H), 1.69 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H).



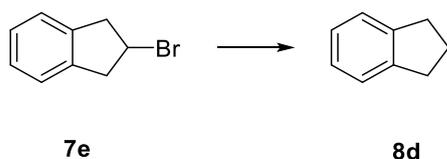
1-Methoxy-4-propoxybenzene (8b). Colorless oil, 158 mg, 95% yield. Compound **8b** was prepared according to **GP3**. The NMR data is identical to that reported in literature.⁴³ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.84 (s, 4H), 3.88 (t, $J = 6.7$ Hz, 2H), 3.77 (s, 3H), 1.79 (m, 2H), 1.03 (t, $J = 6.6$ Hz, 3H).



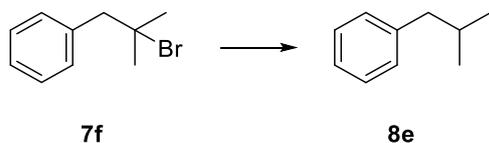
1-Ethyl-1-naphthalene (8c). Colorless oil, 142 mg, 91% yield. Compound **8c** was prepared according to **GP3**. The NMR data is identical to that reported in literature.⁴⁴ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.11 (d, $J = 8.2$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.50-7.57 (m, 2H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.39 (d, $J = 7.0$ Hz, 1H), 3.15 (q, $J = 7.5$ Hz, 2H), 1.43 (t, $J = 6.8$ Hz, 3H).



1-Methoxy-4-propoxybenzene (8b). Colorless oil, 136mg, 82% yield. Compound **8b** was prepared according to **GP3**. The NMR data is identical to that reported in literature.⁴³ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.84 (s, 4H), 3.88 (t, $J = 6.7$ Hz, 2H), 3.77 (s, 3H), 1.79 (m, 2H), 1.03 (t, $J = 6.6$ Hz, 3H).



2,3-Dihydro-1H-indene (8d). Yellow oil, 83mg, 70% yield. Compound **8d** was prepared according to **GP3**. The NMR data is identical to that reported in literature.⁴⁵ $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 7.21-7.23 (m, 2H), 7.11-7.13 (m, 2H), 2.85 (t, $J = 7.4$ Hz, 4H), 2.00 (p, $J = 7.4$ Hz, 2H).



Isobutylbenzene (8e). Colorless oil, 101mg, 75% yield. Compound **8e** was prepared according to **GP3**. The NMR data is identical to that reported in literature.⁴⁶ $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.16-7.31 (m, 5H), 2.50 (d, $J = 7.2$ Hz, 2H), 1.84-1.94 (m, 1H), 0.94 (d, $J = 6.7$ Hz, 6H).

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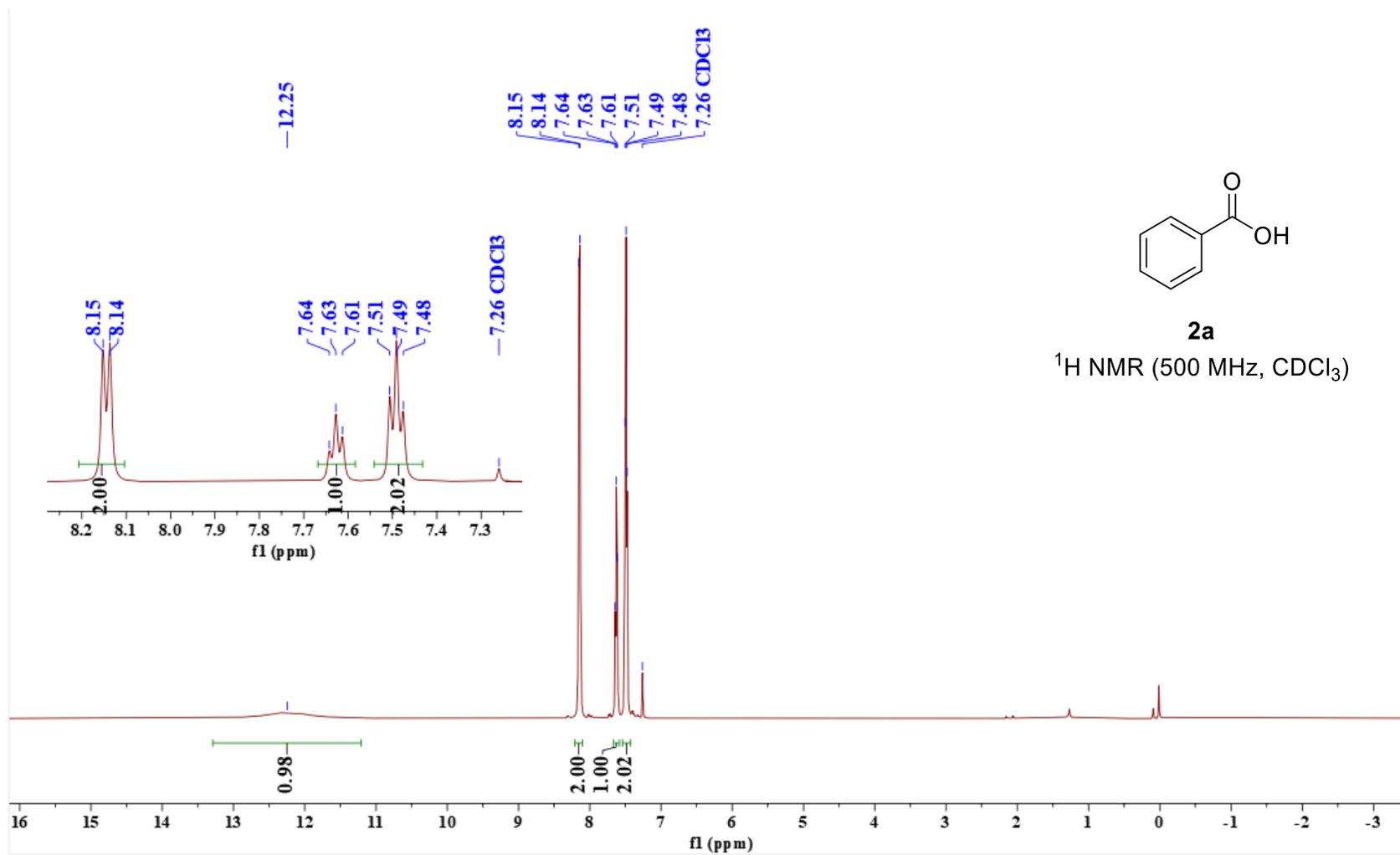
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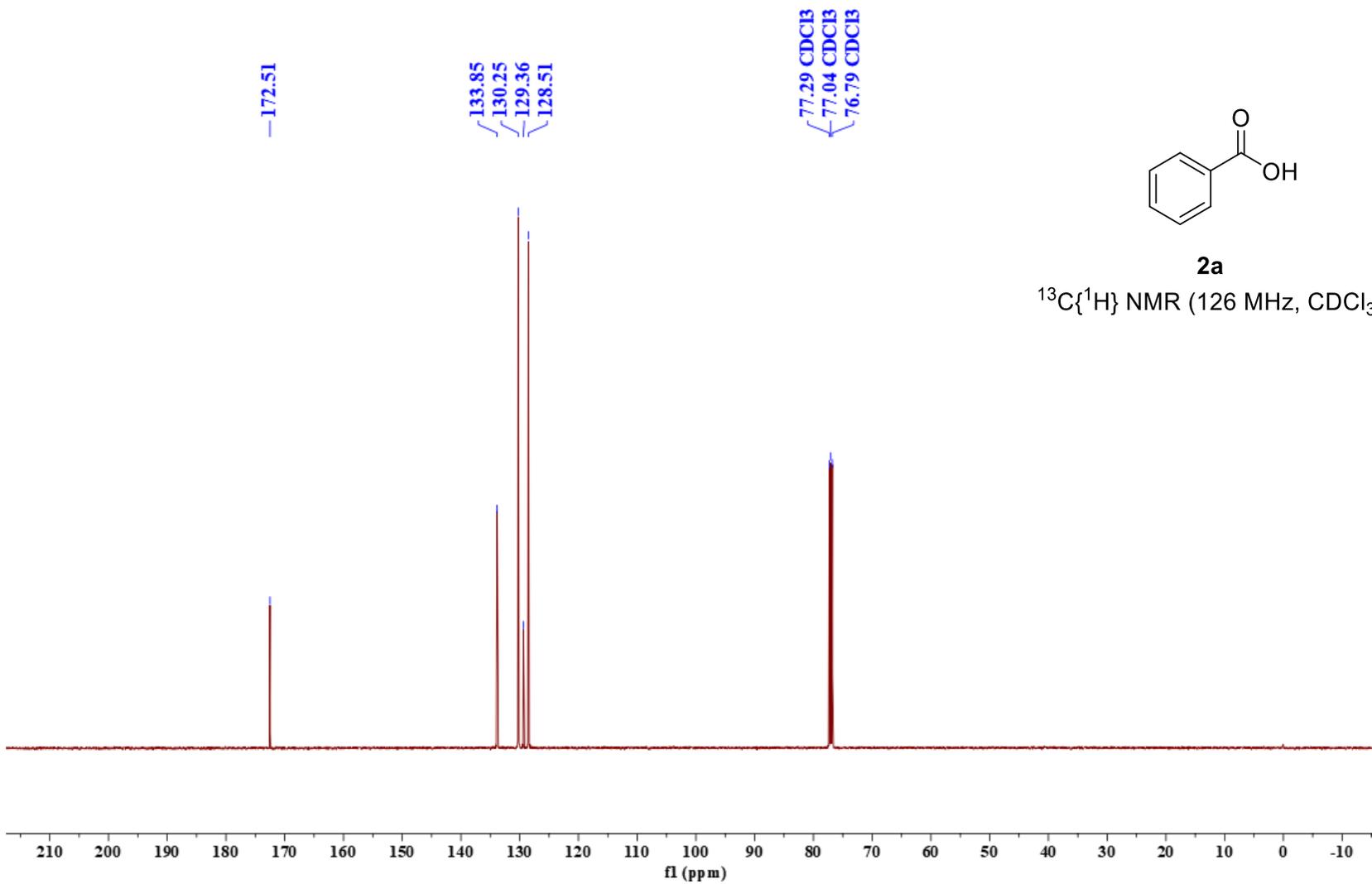
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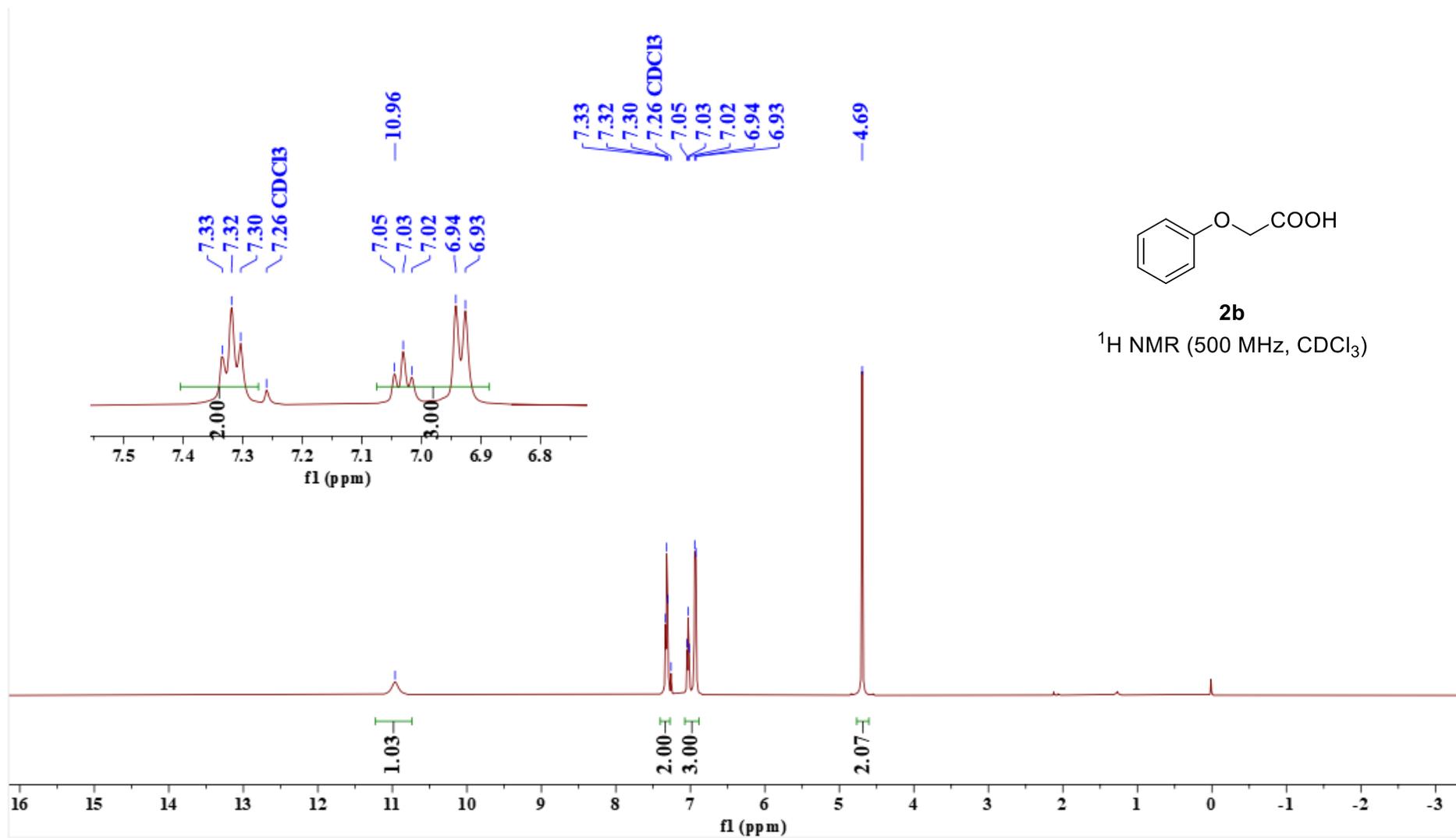
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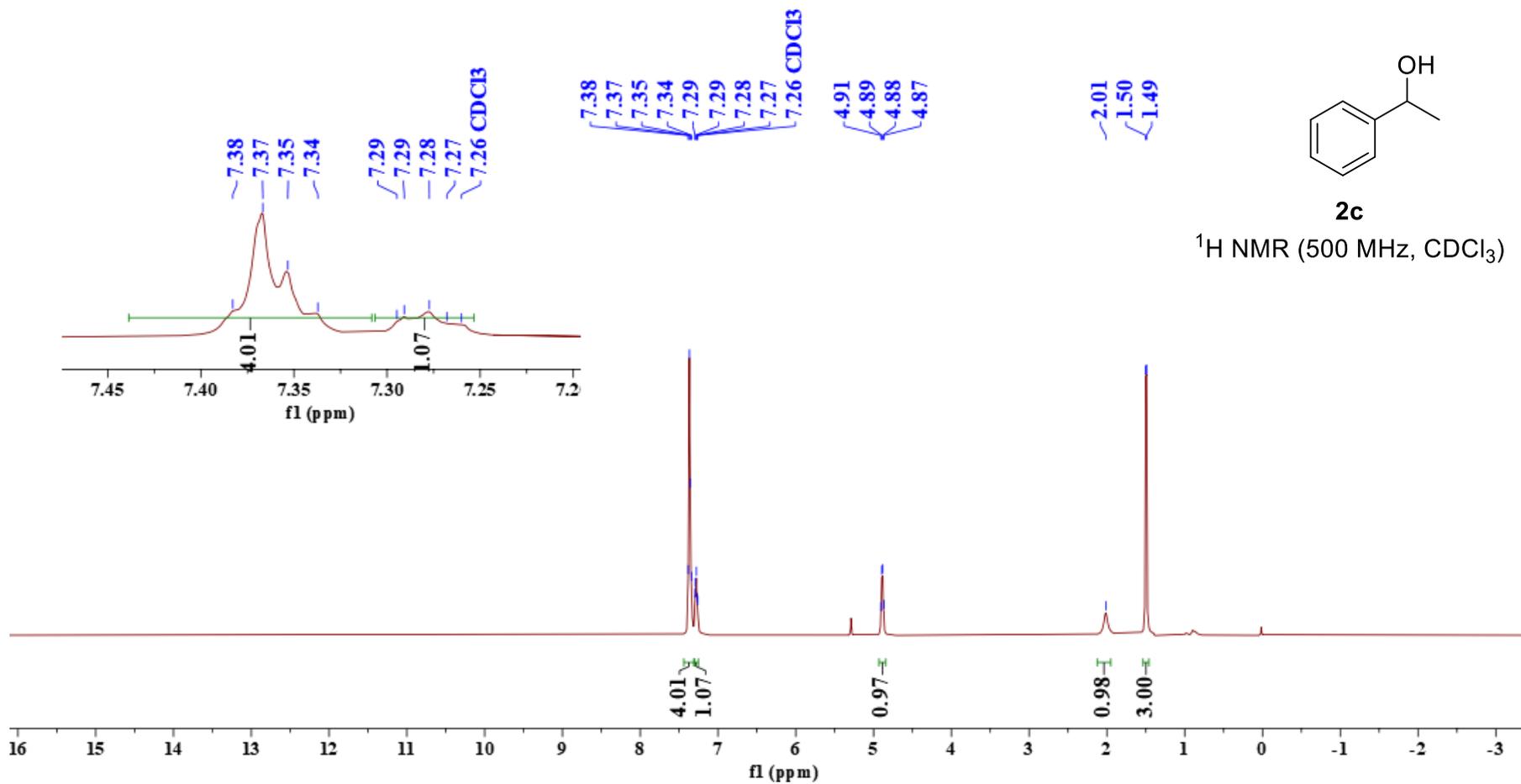
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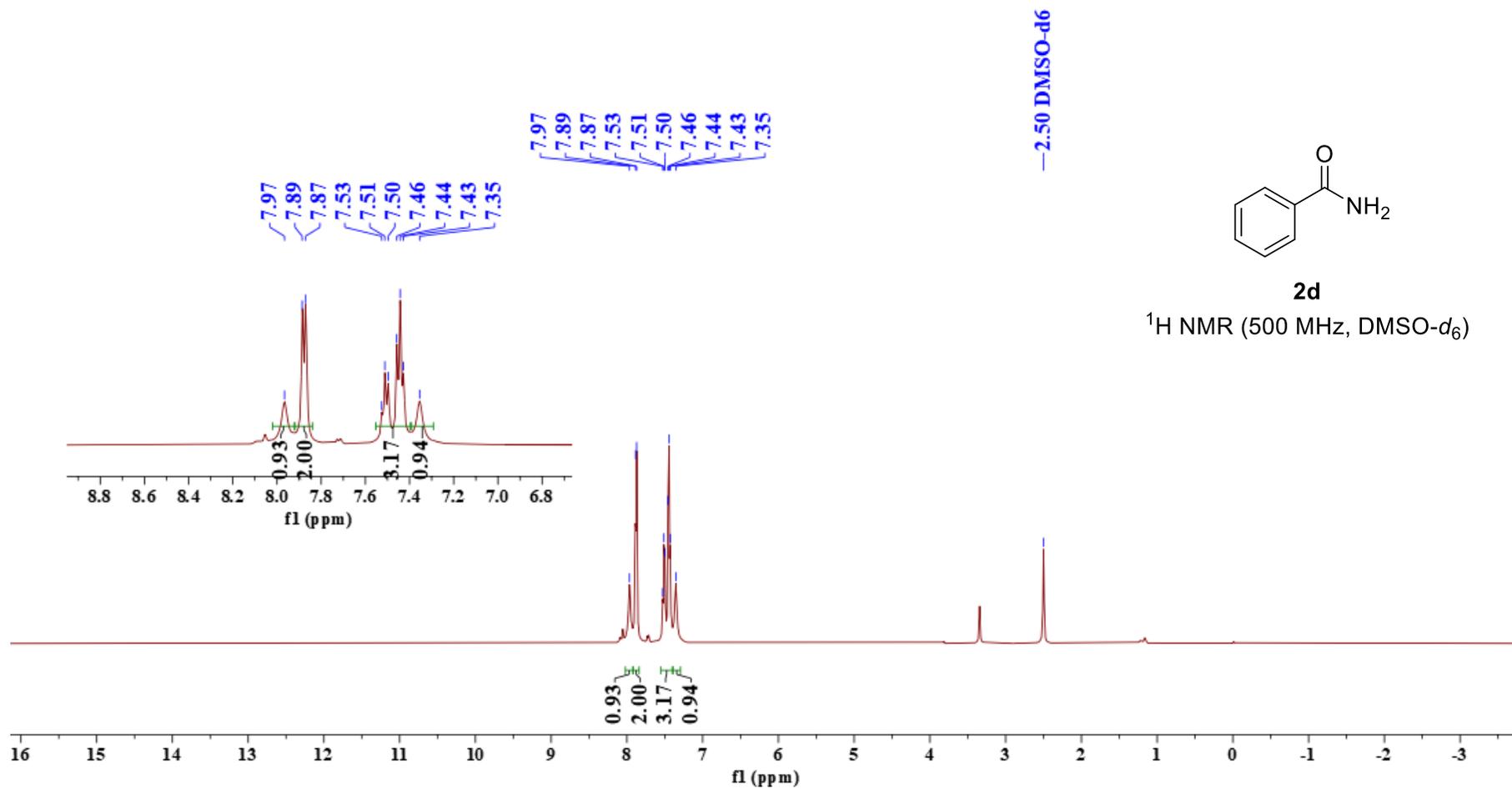
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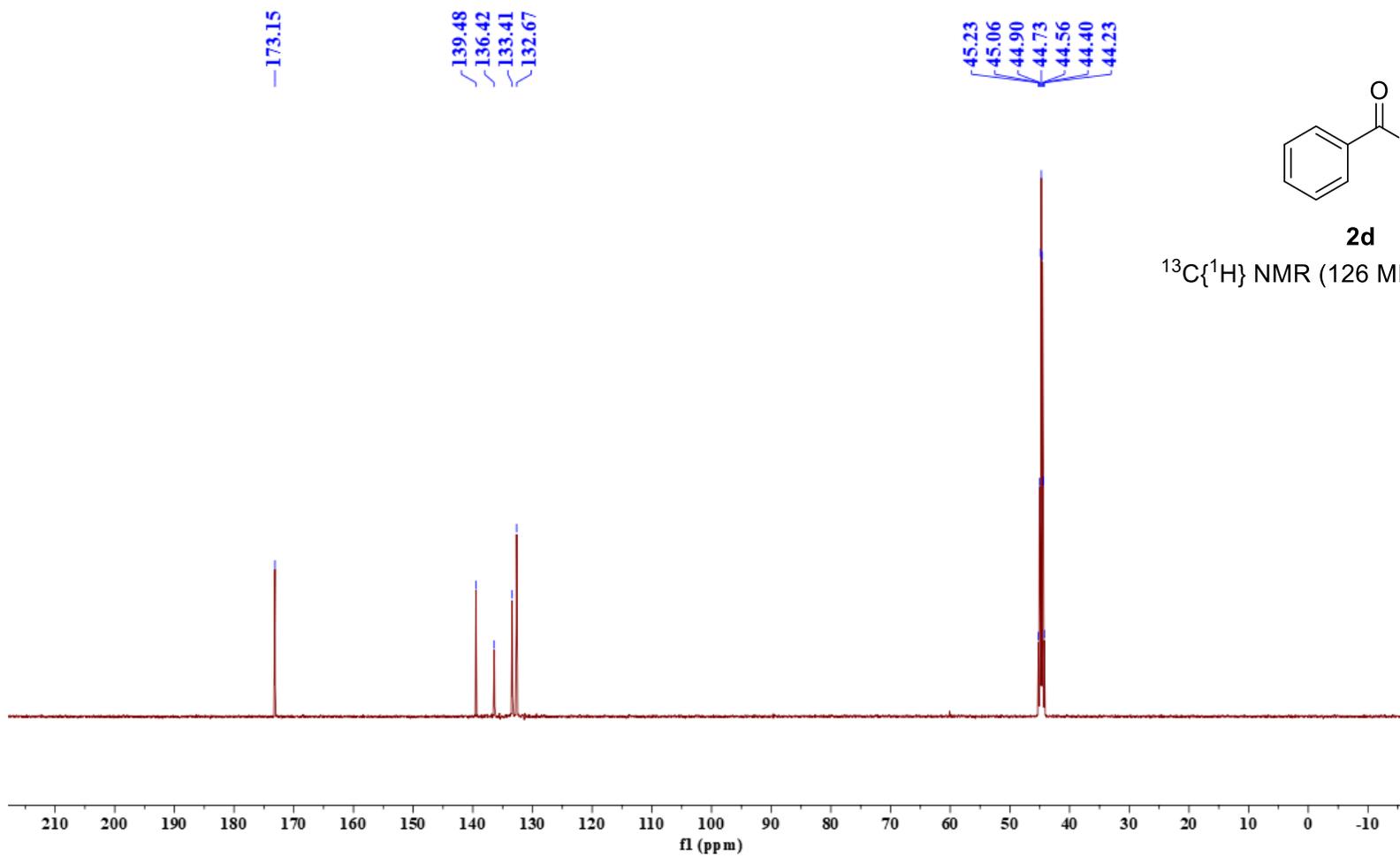


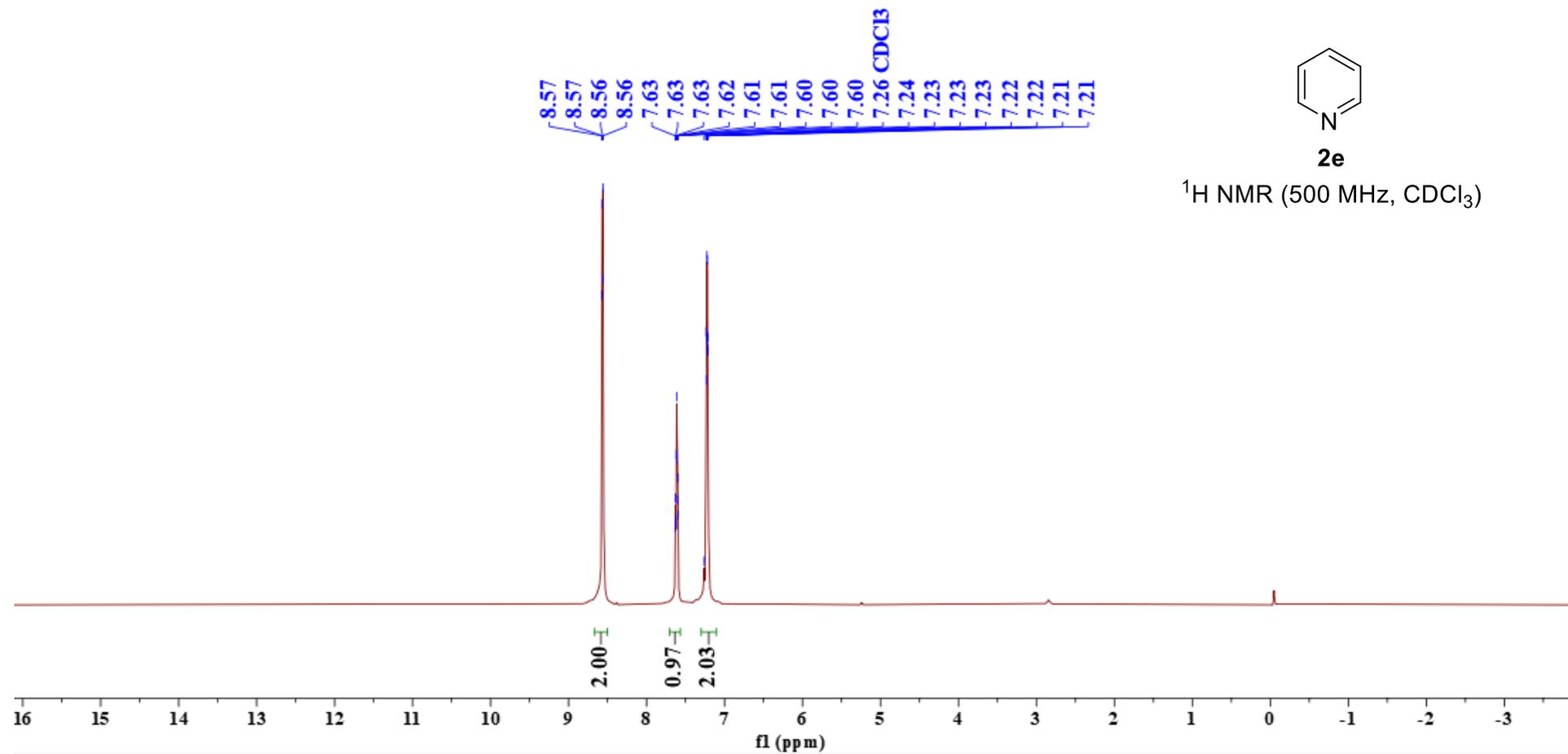


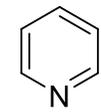
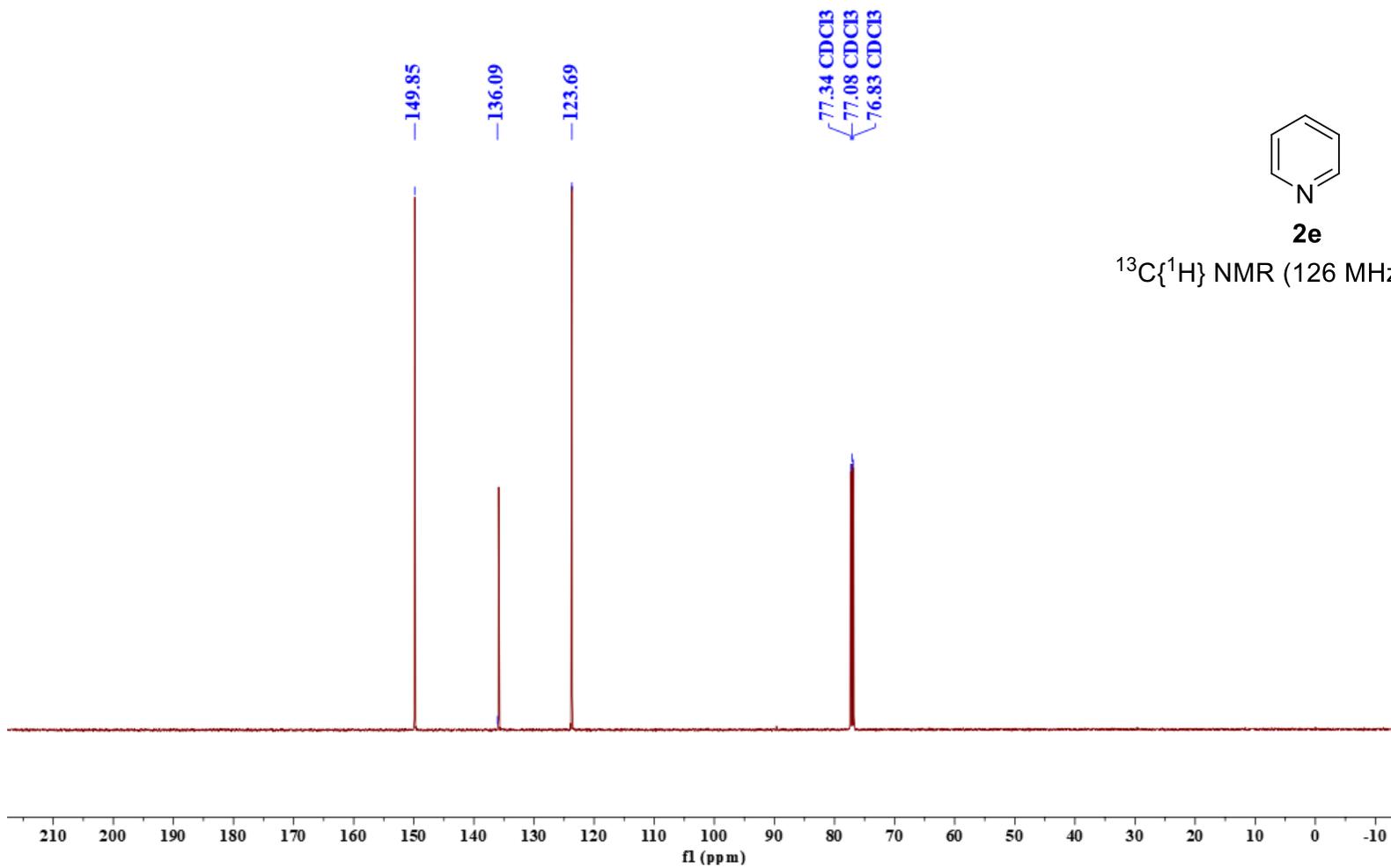




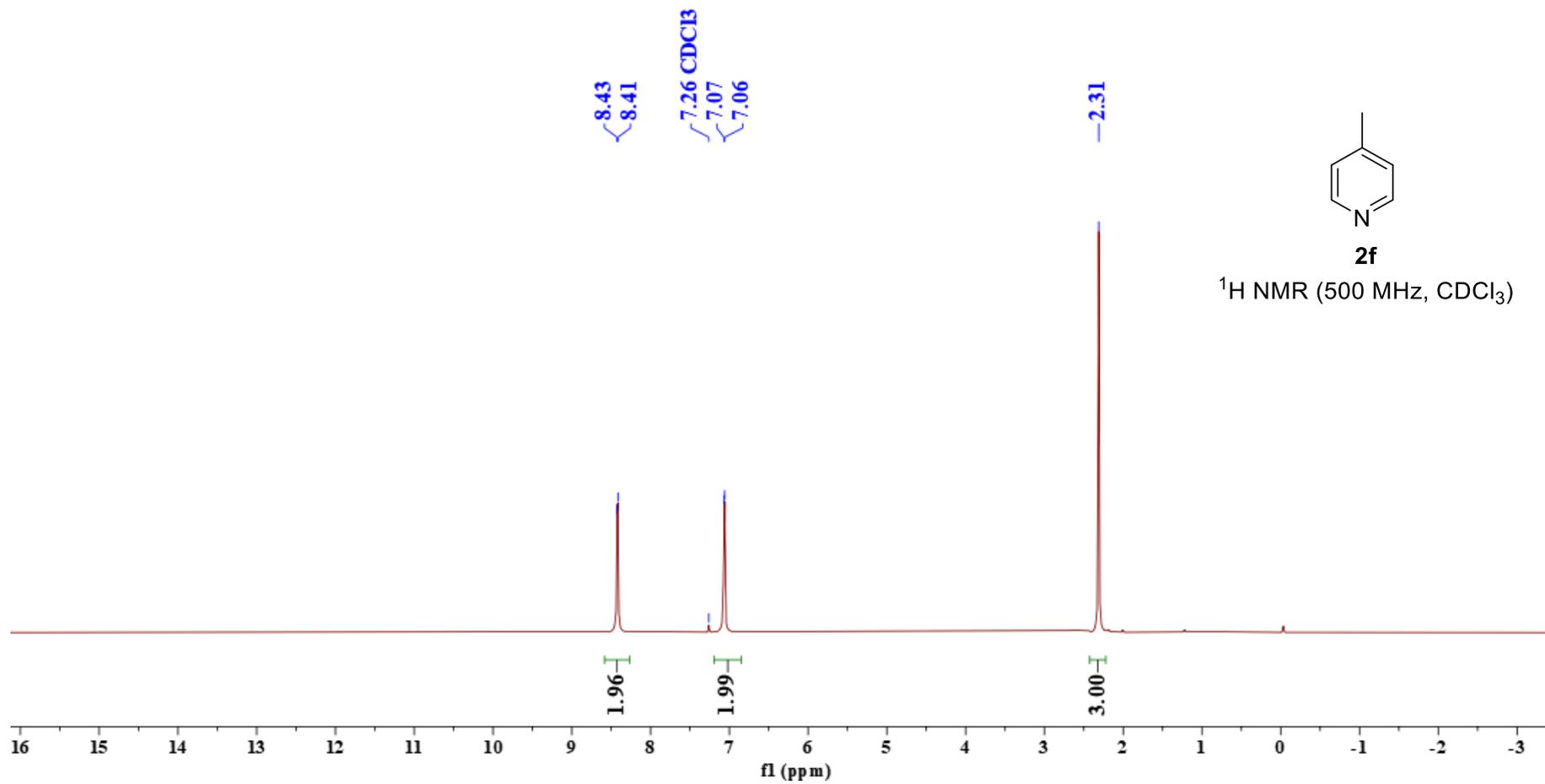


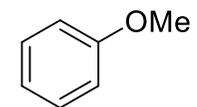






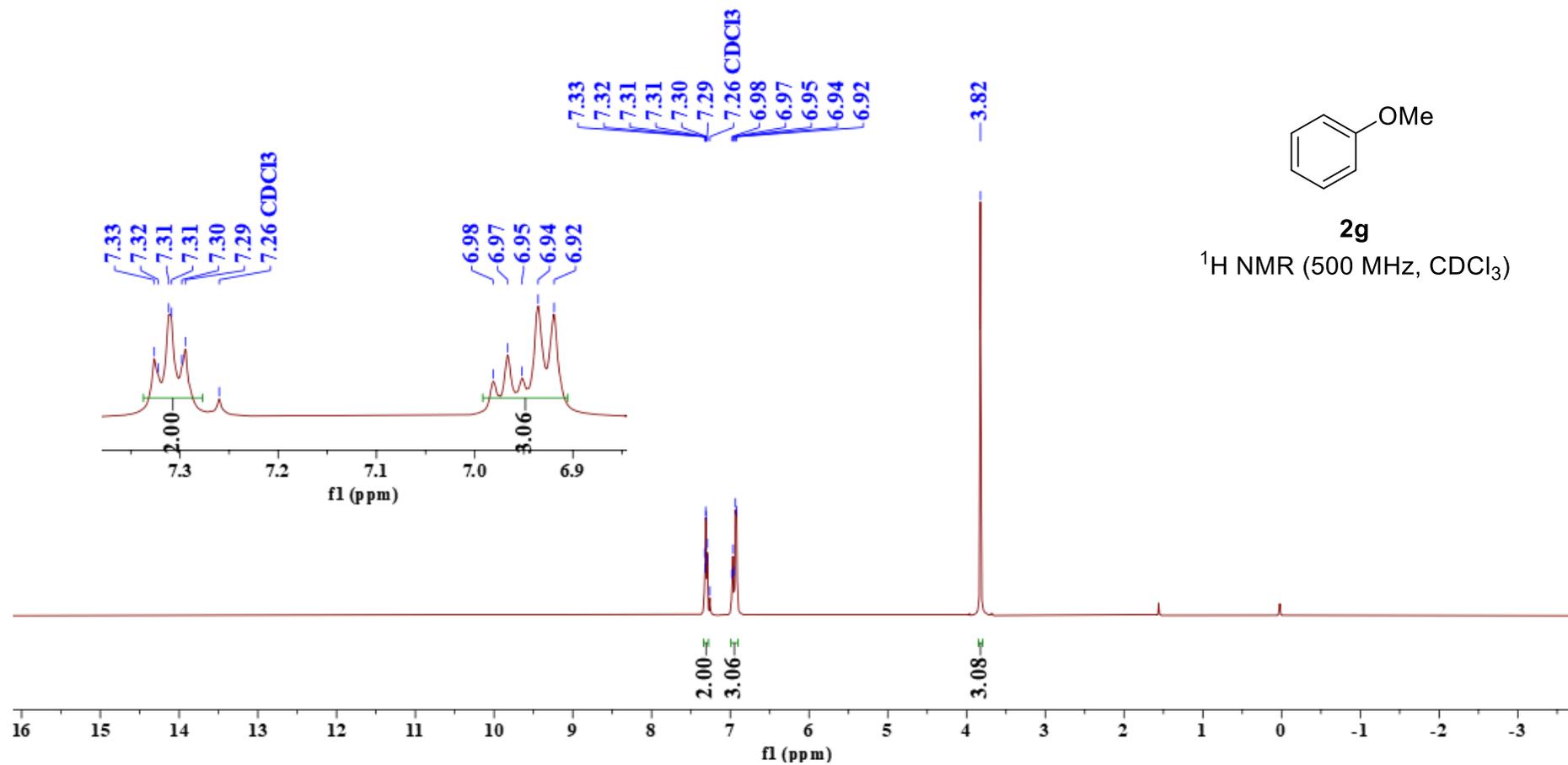
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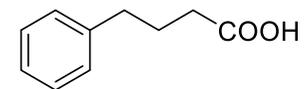




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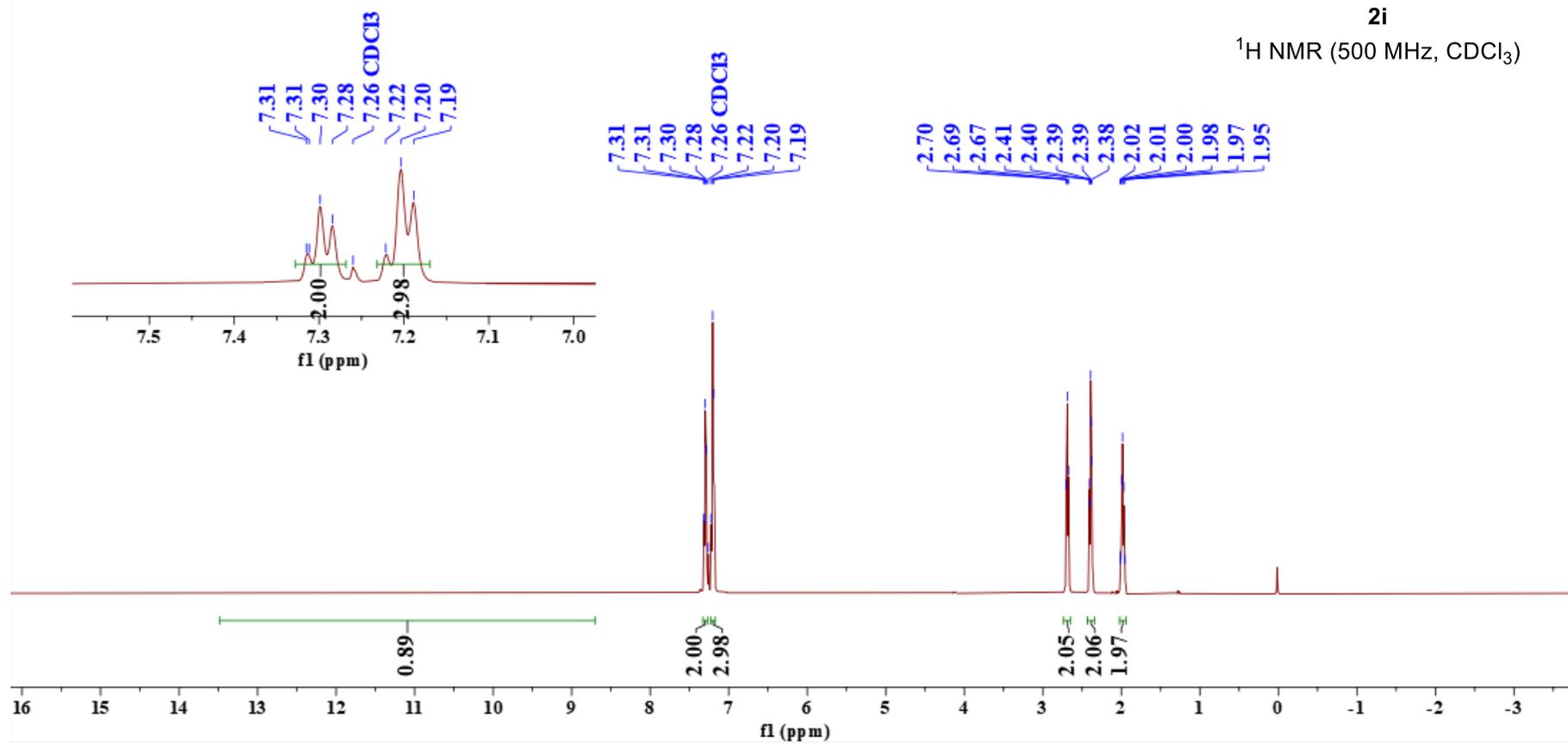
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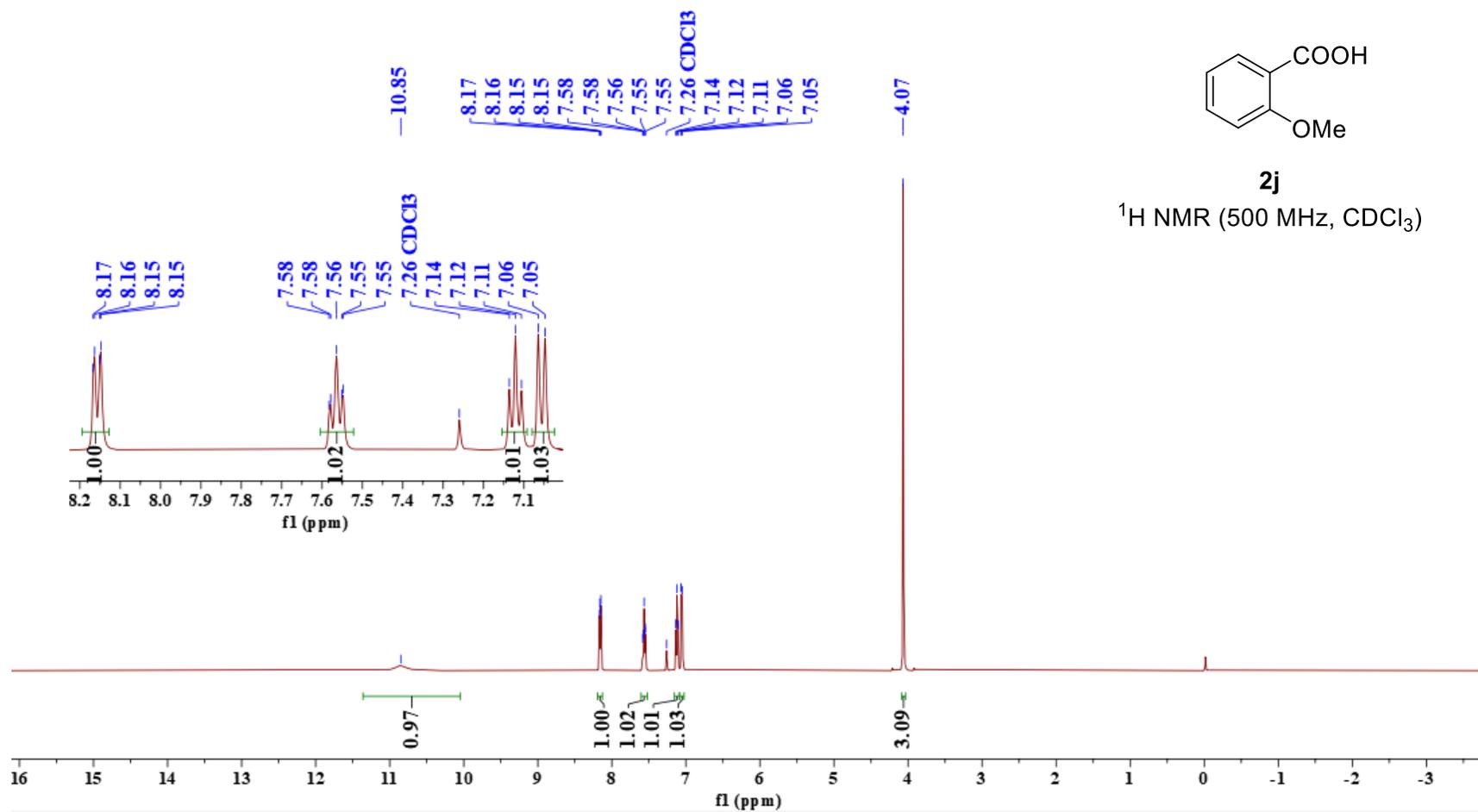


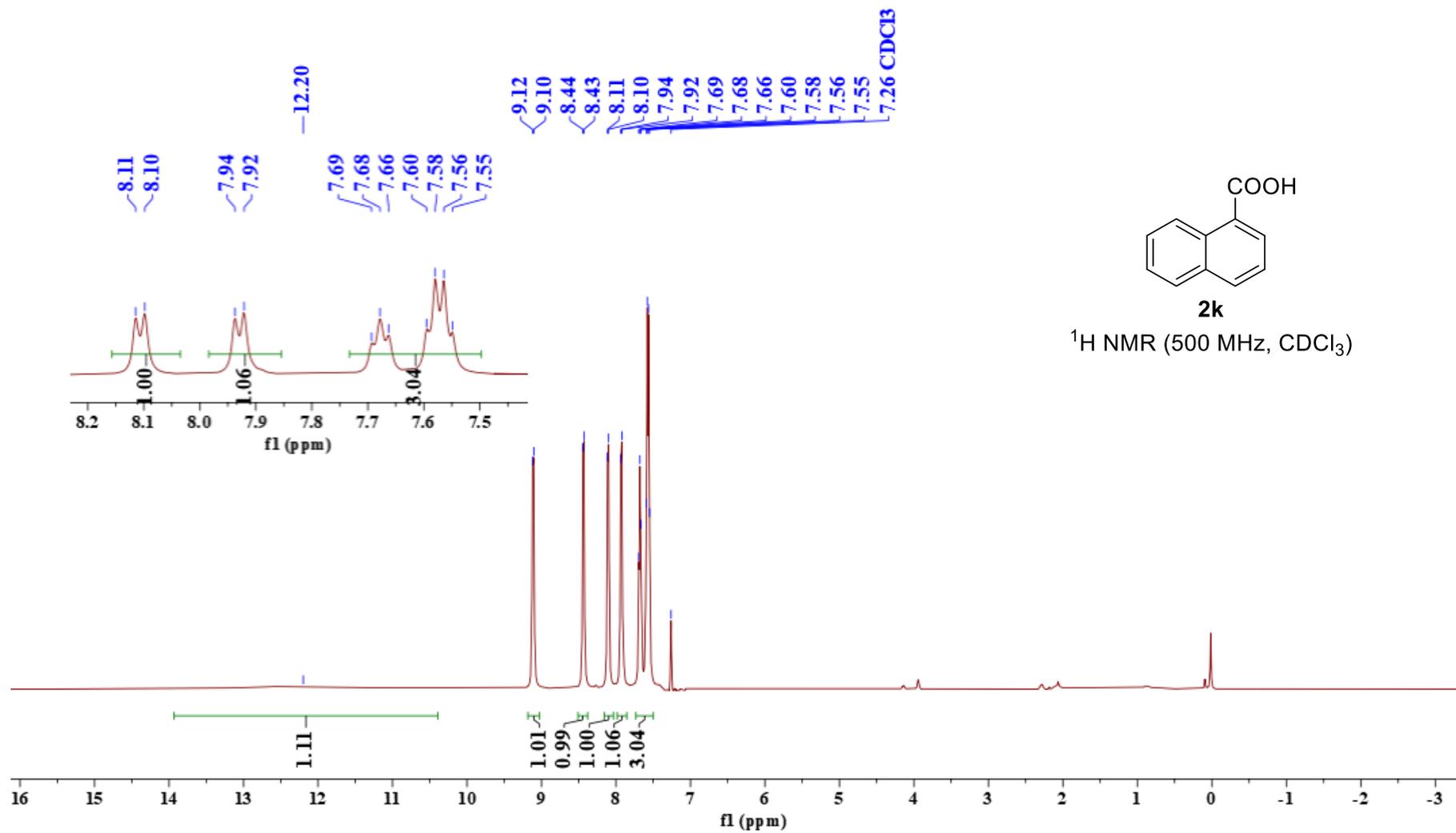


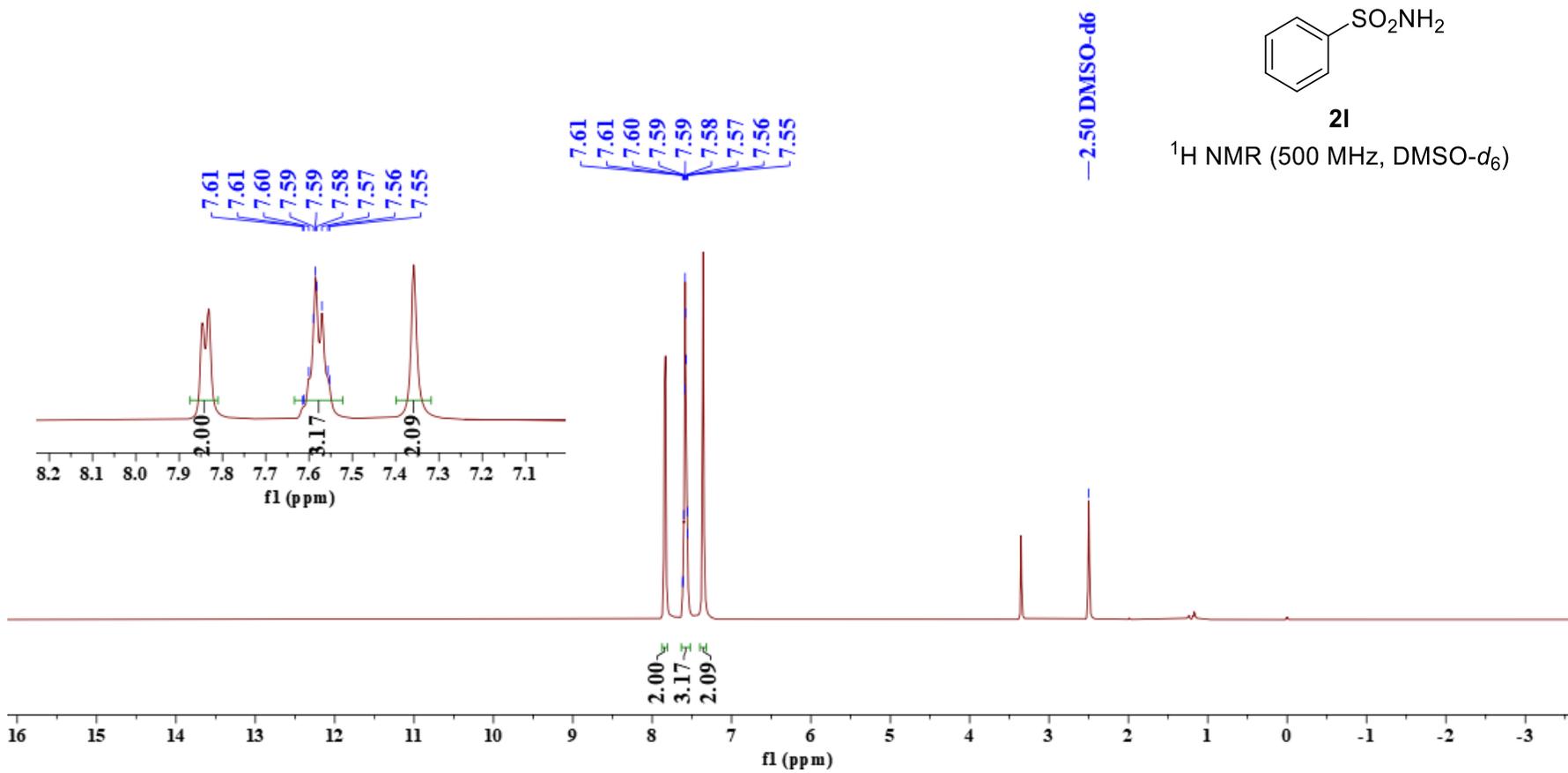
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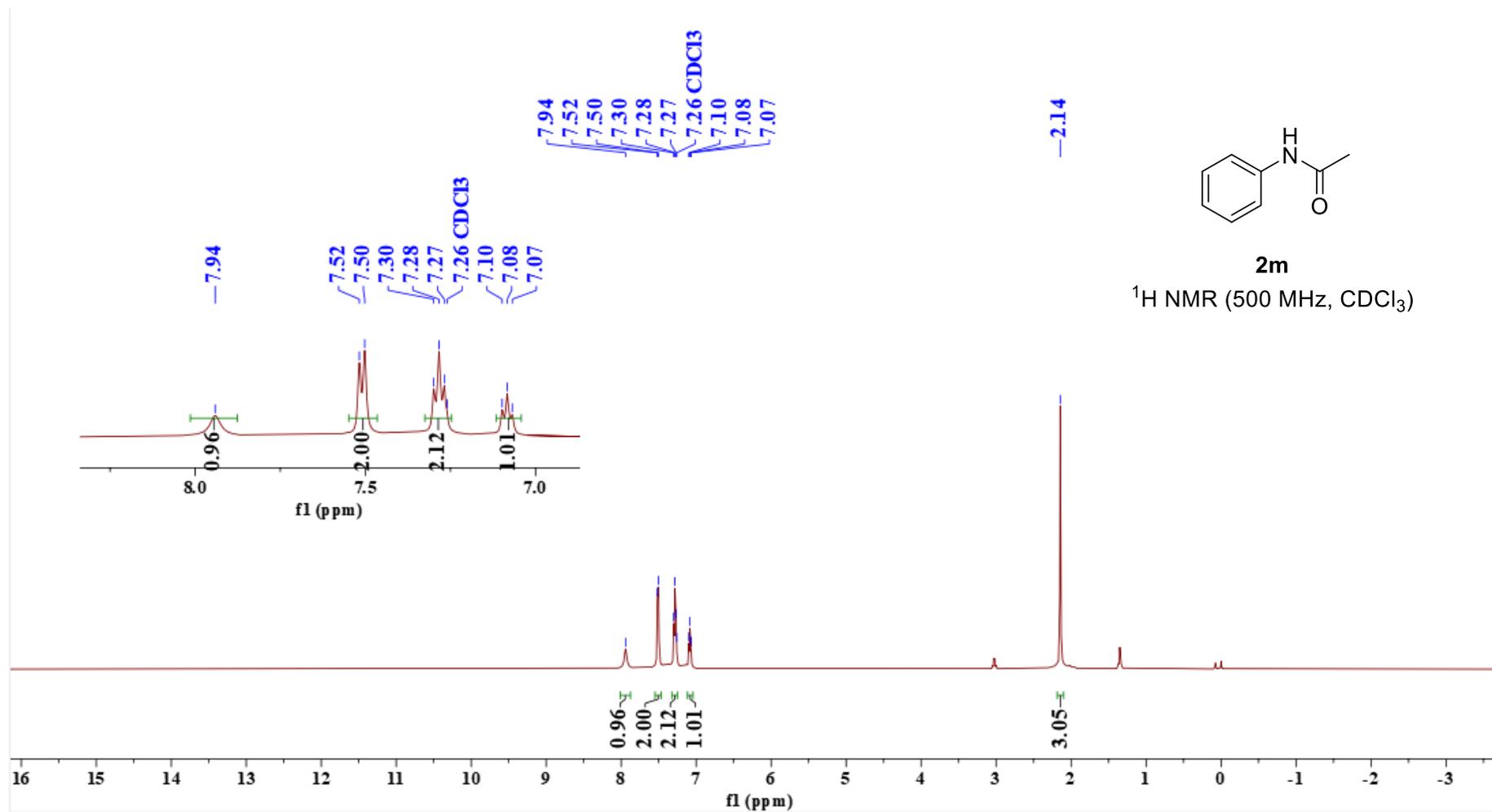
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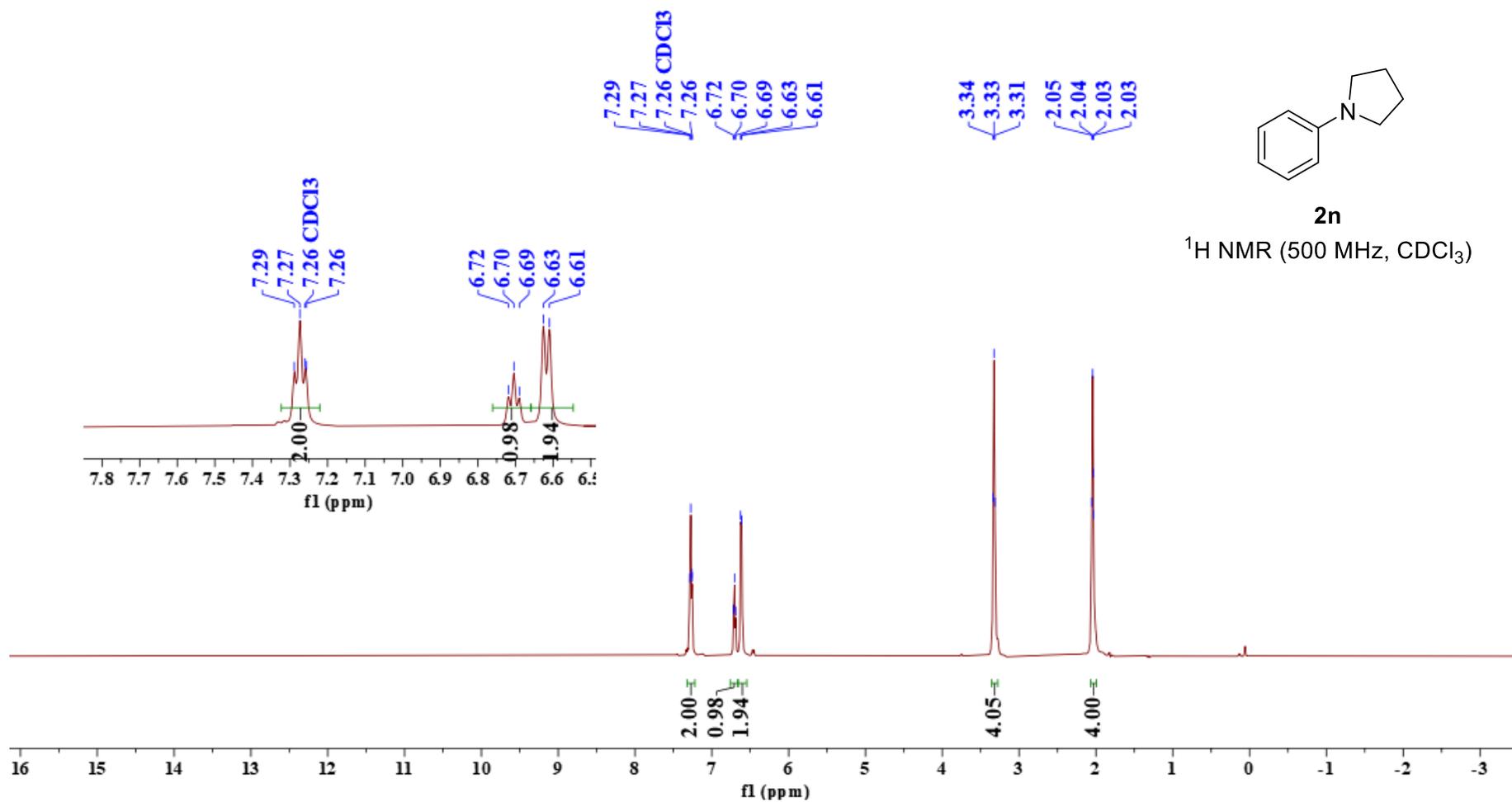


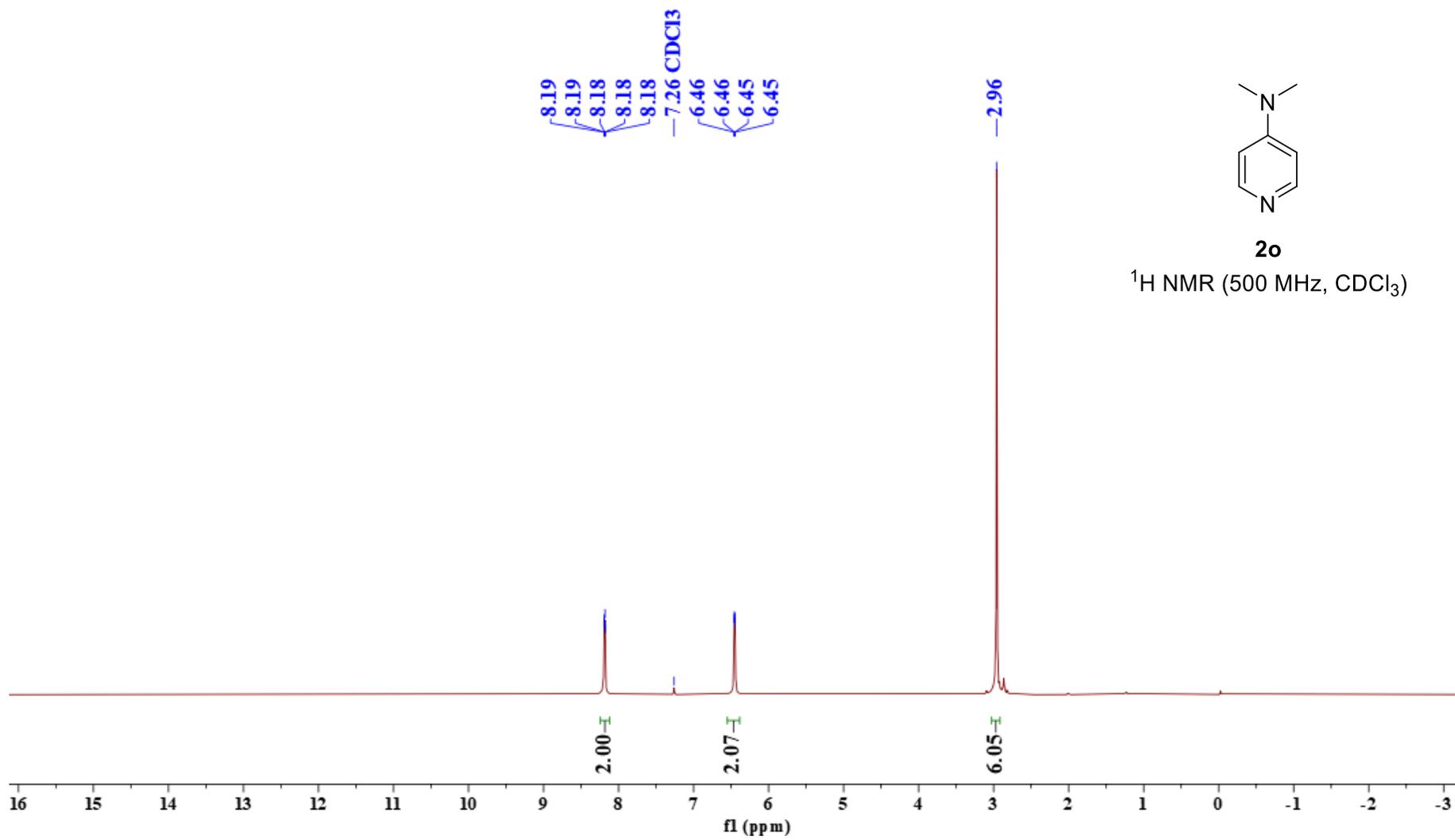


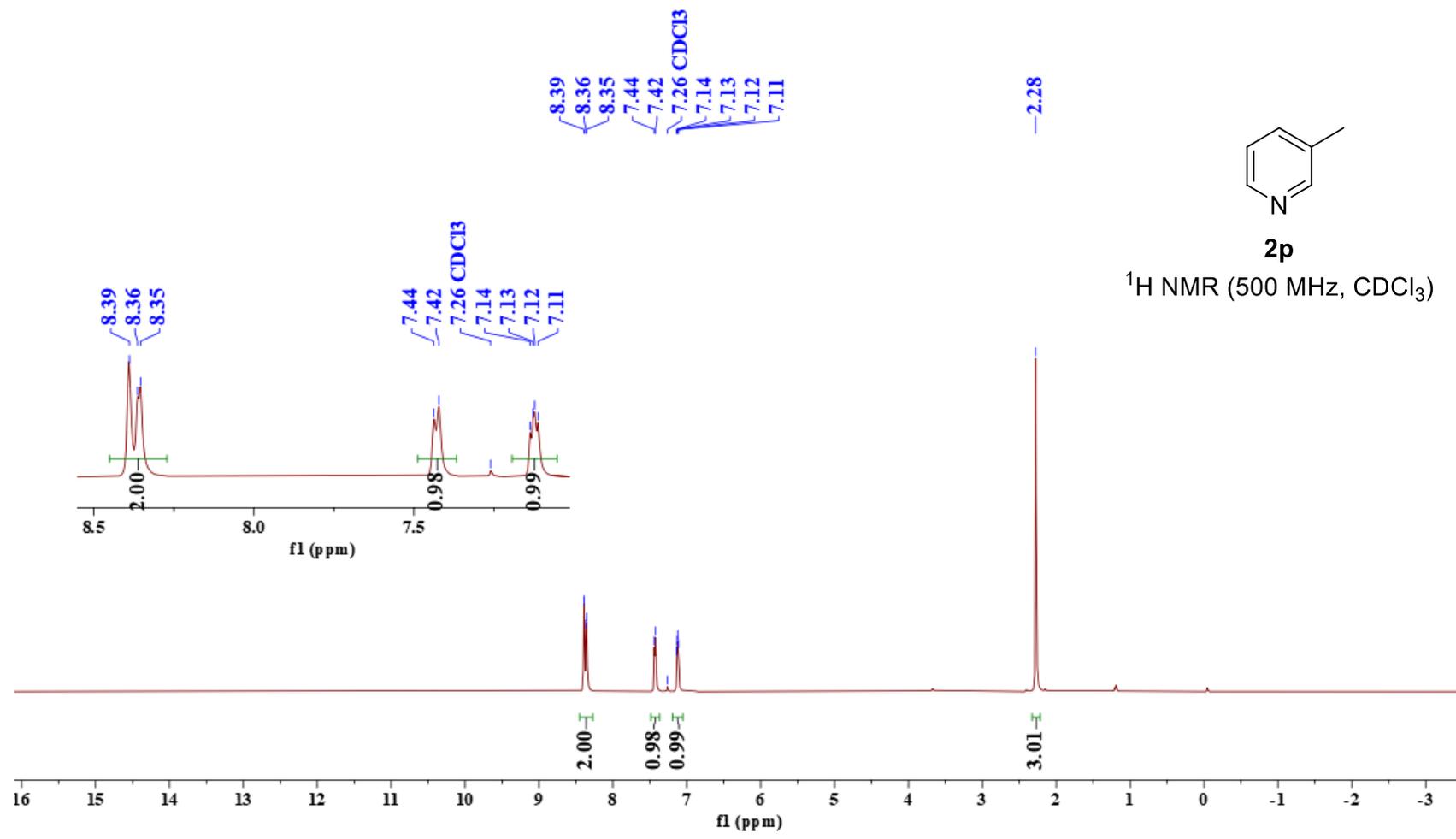


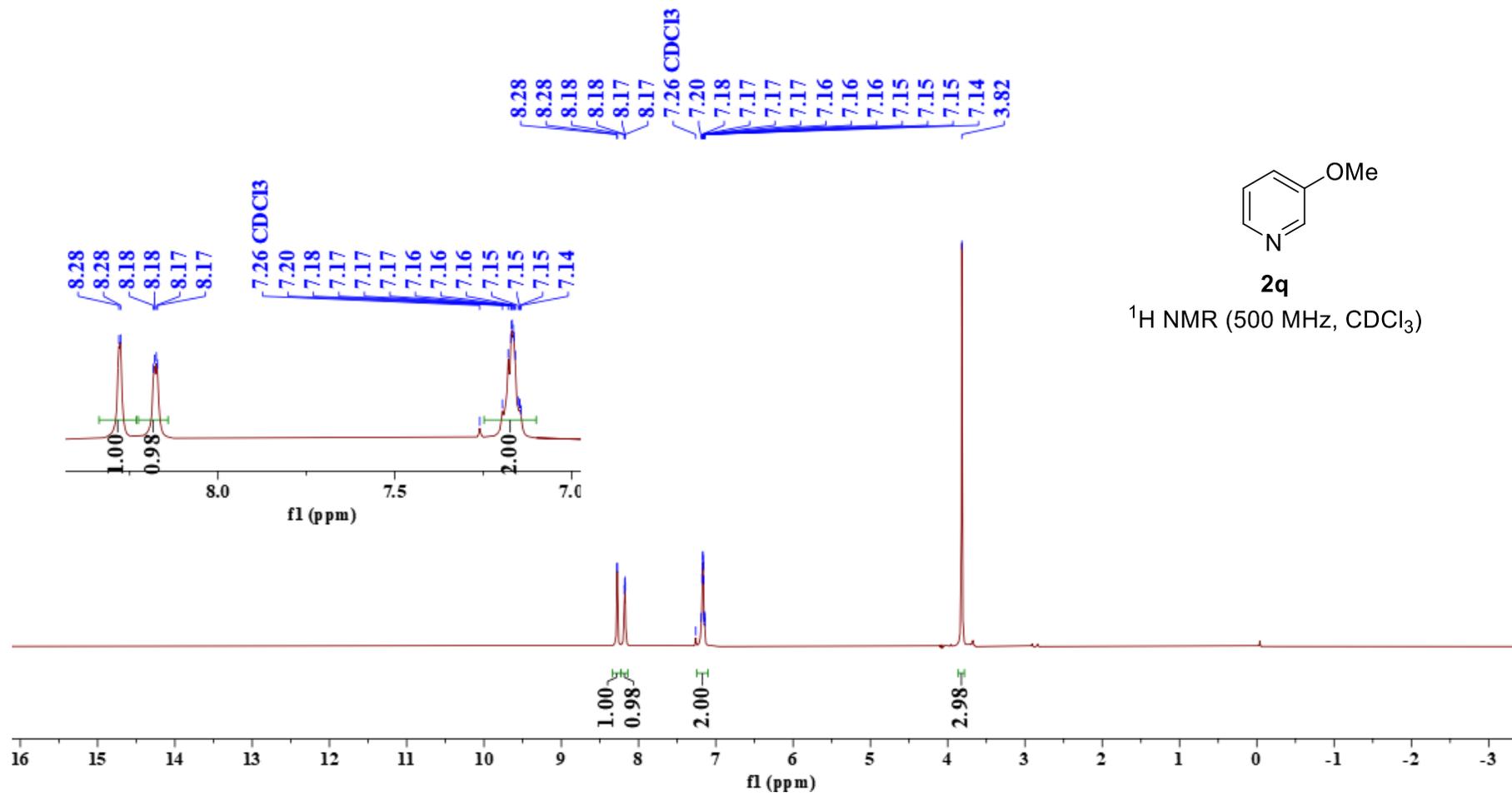


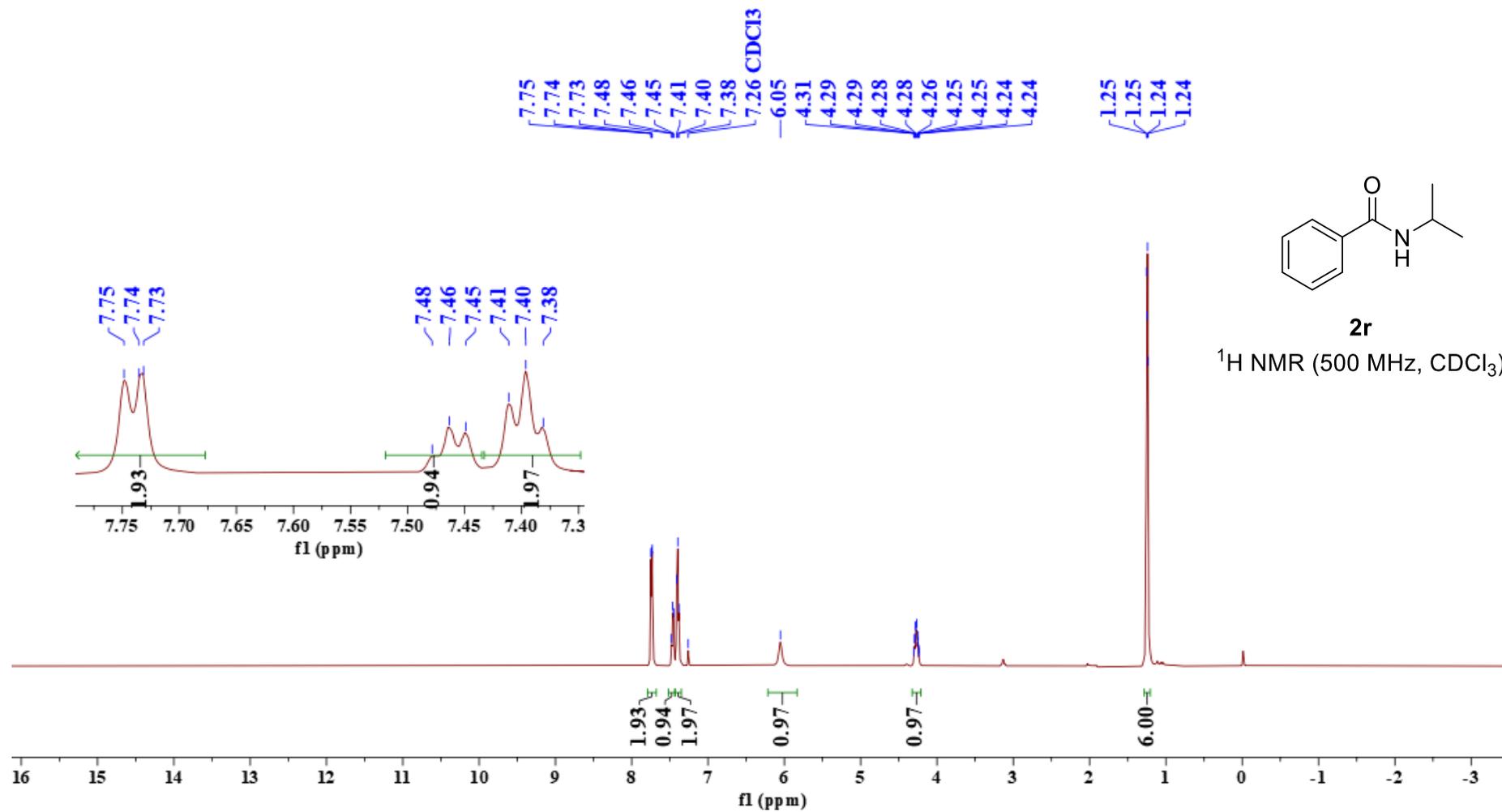


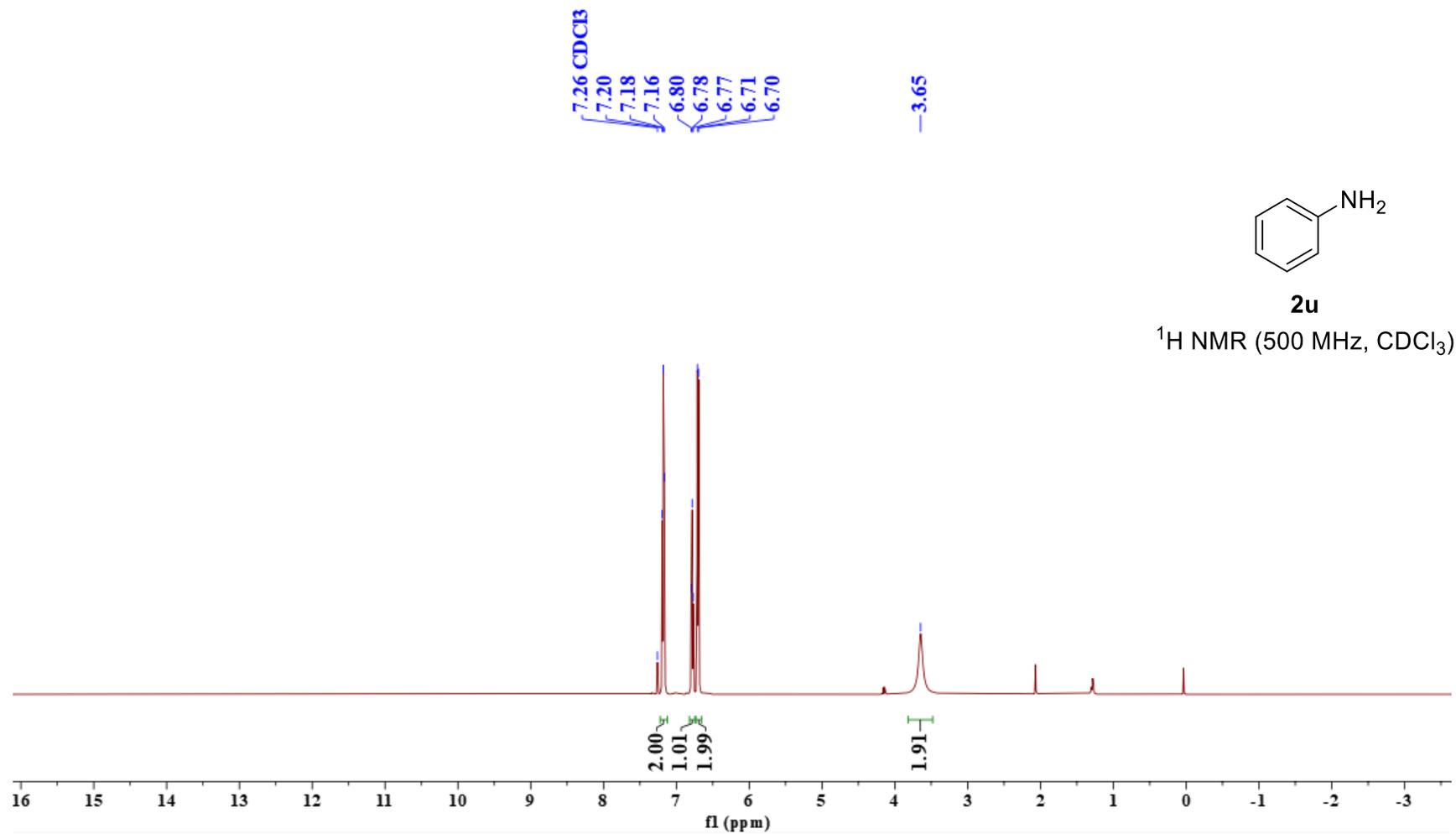




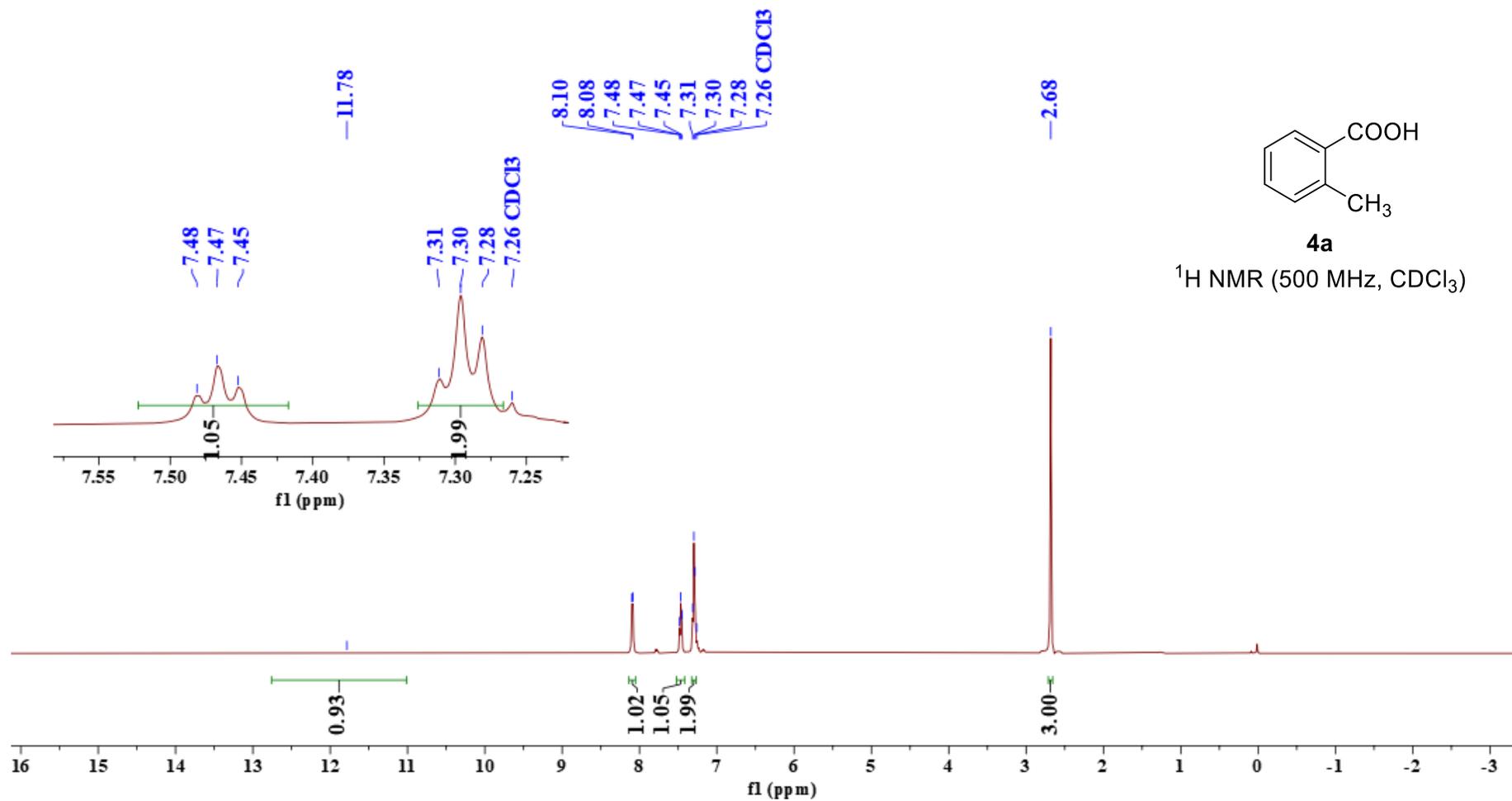


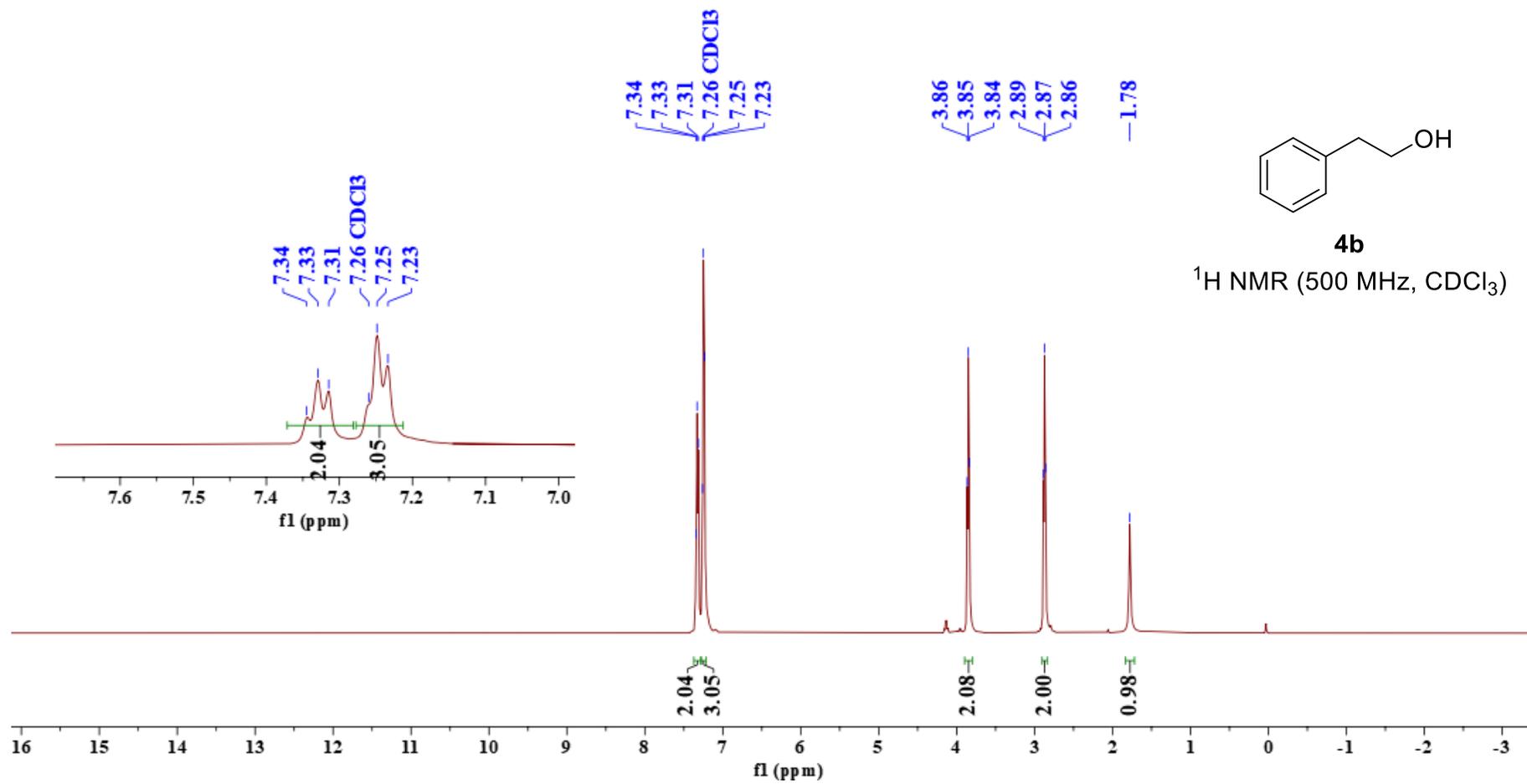


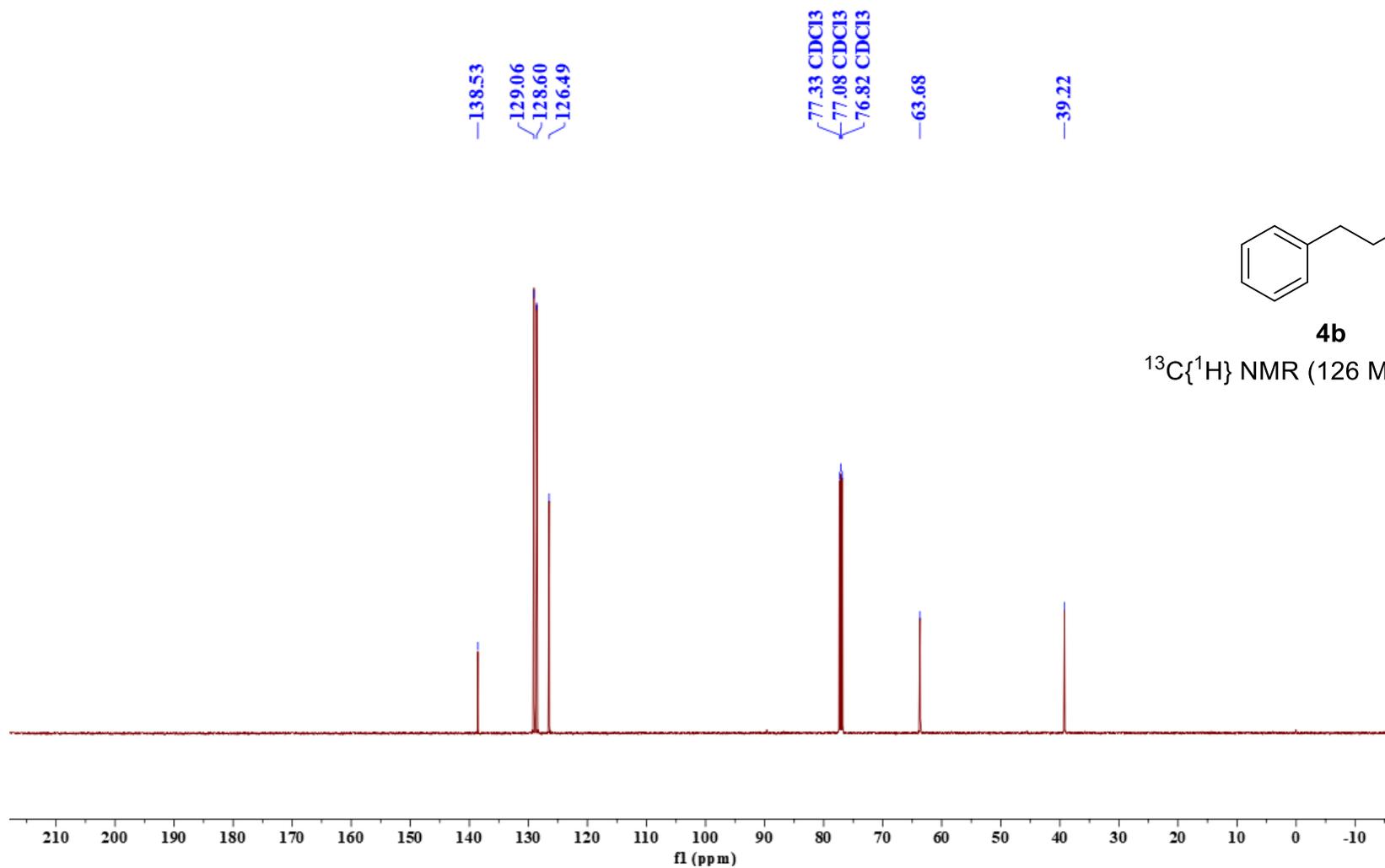


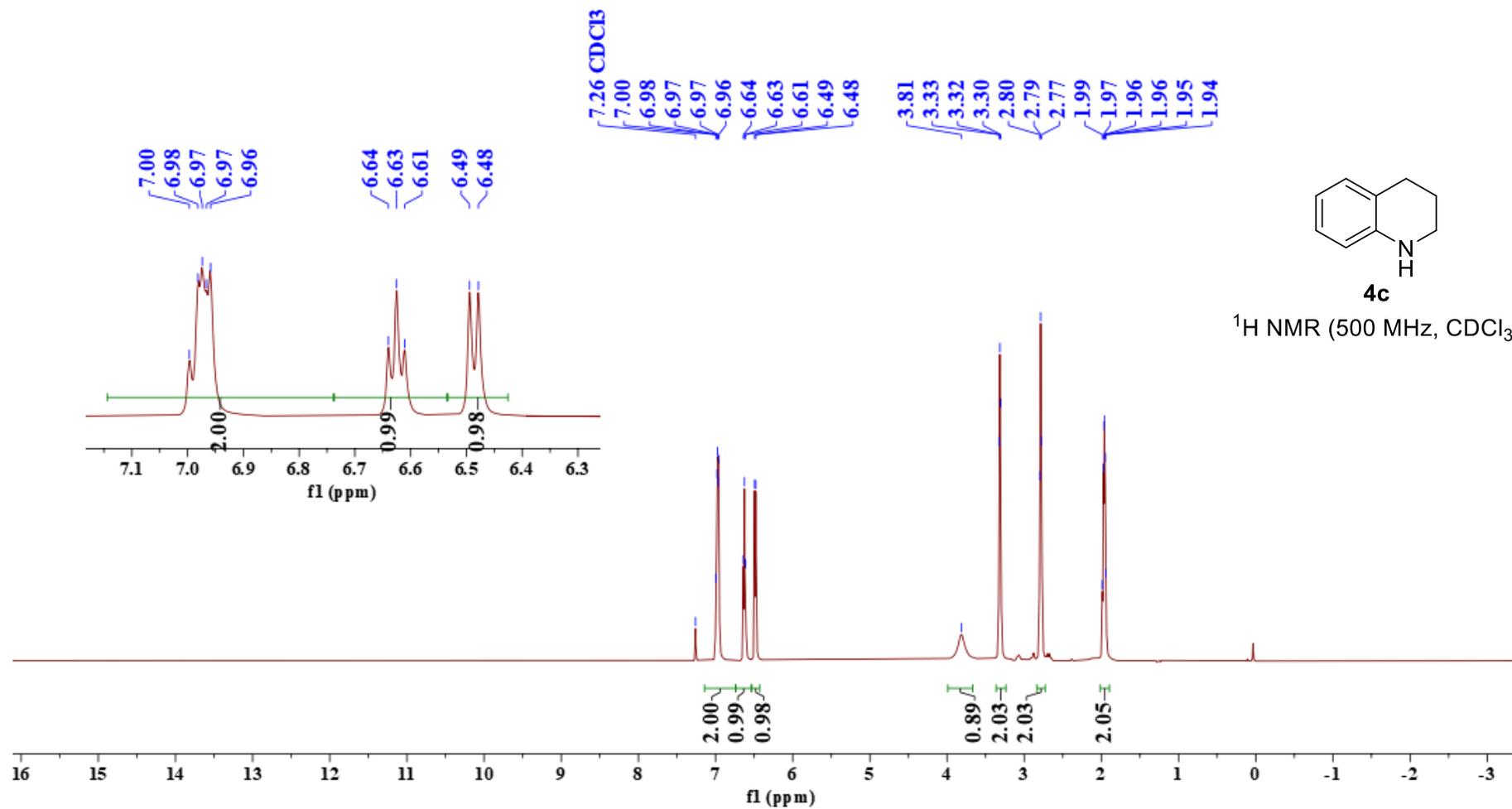


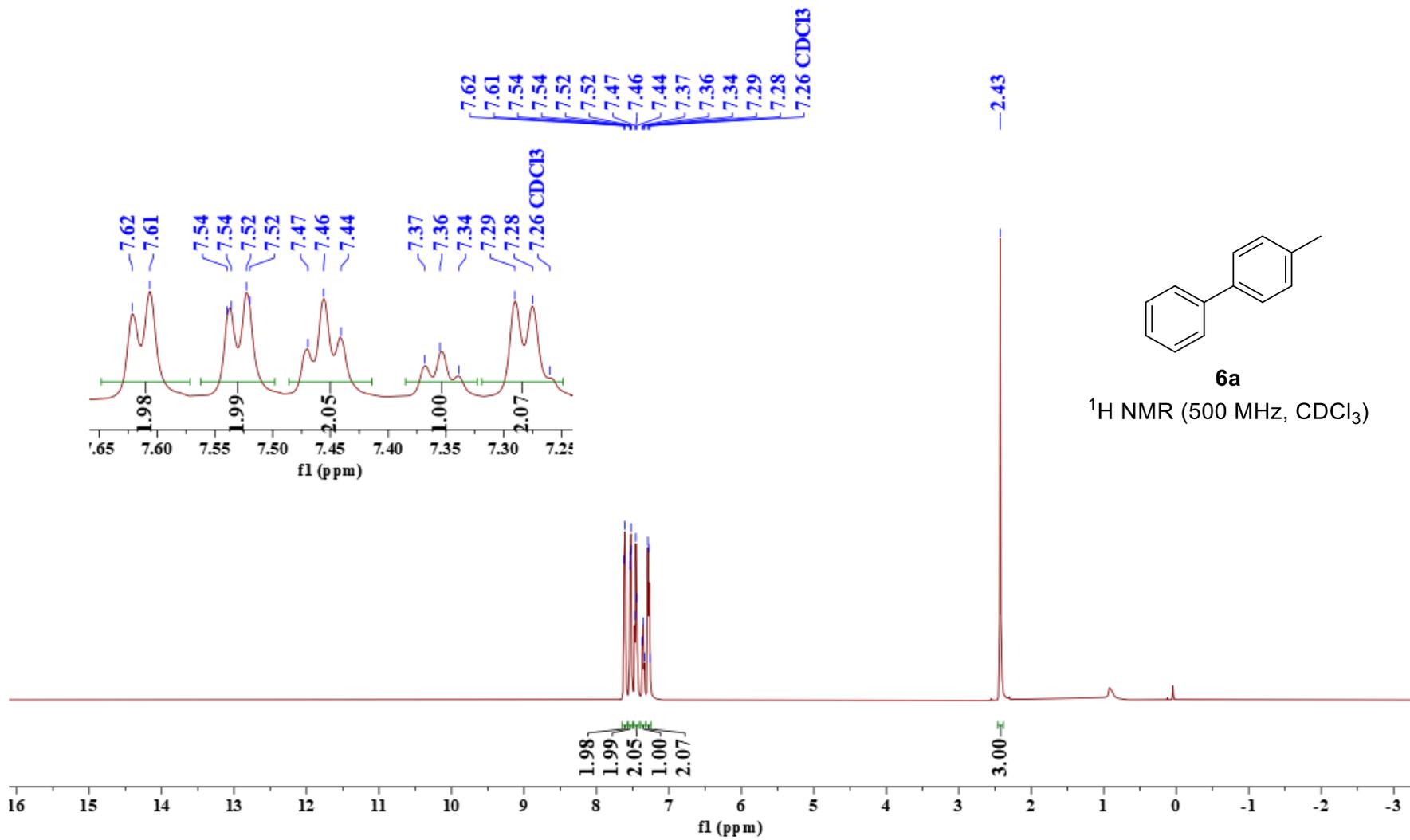
S53

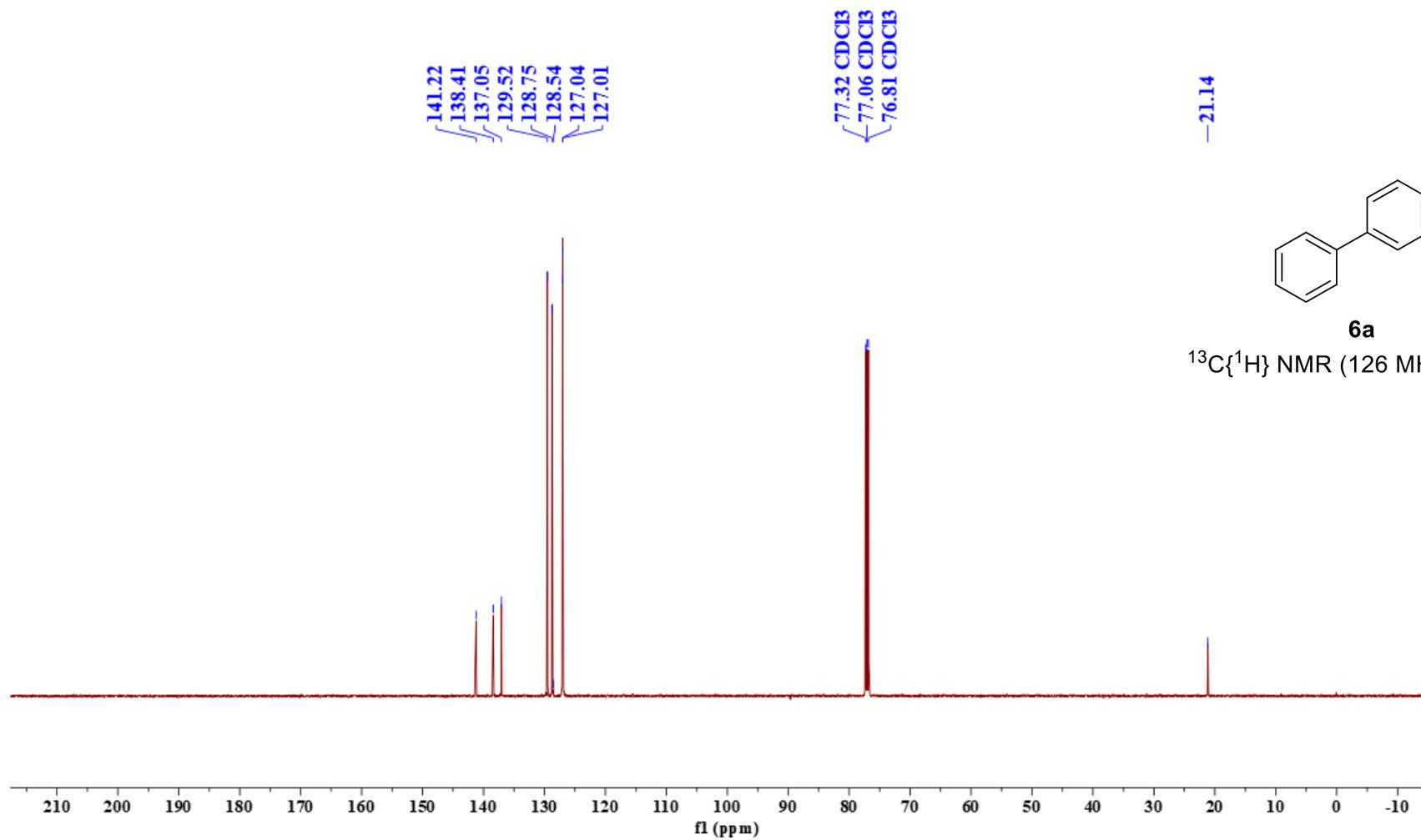


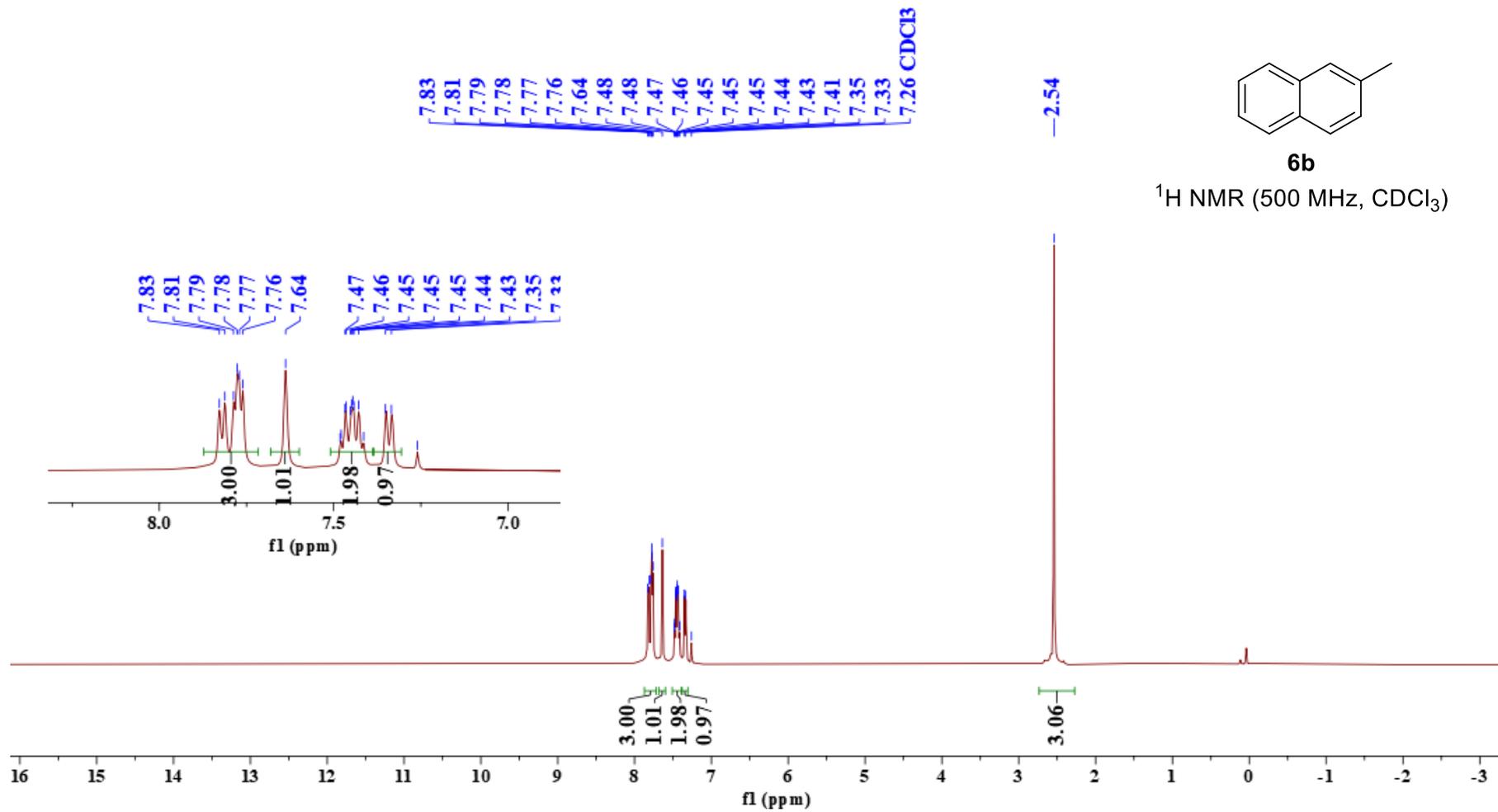


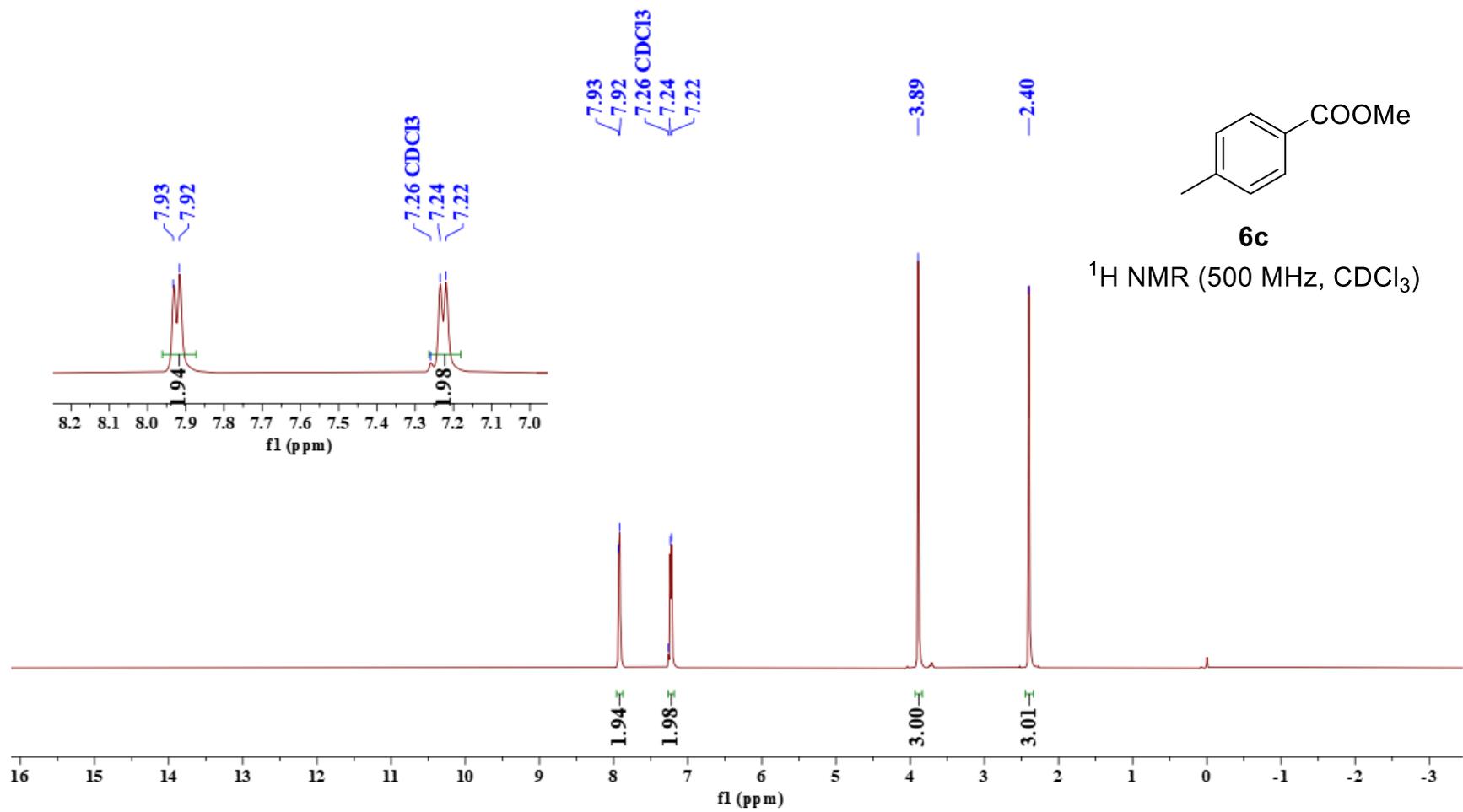


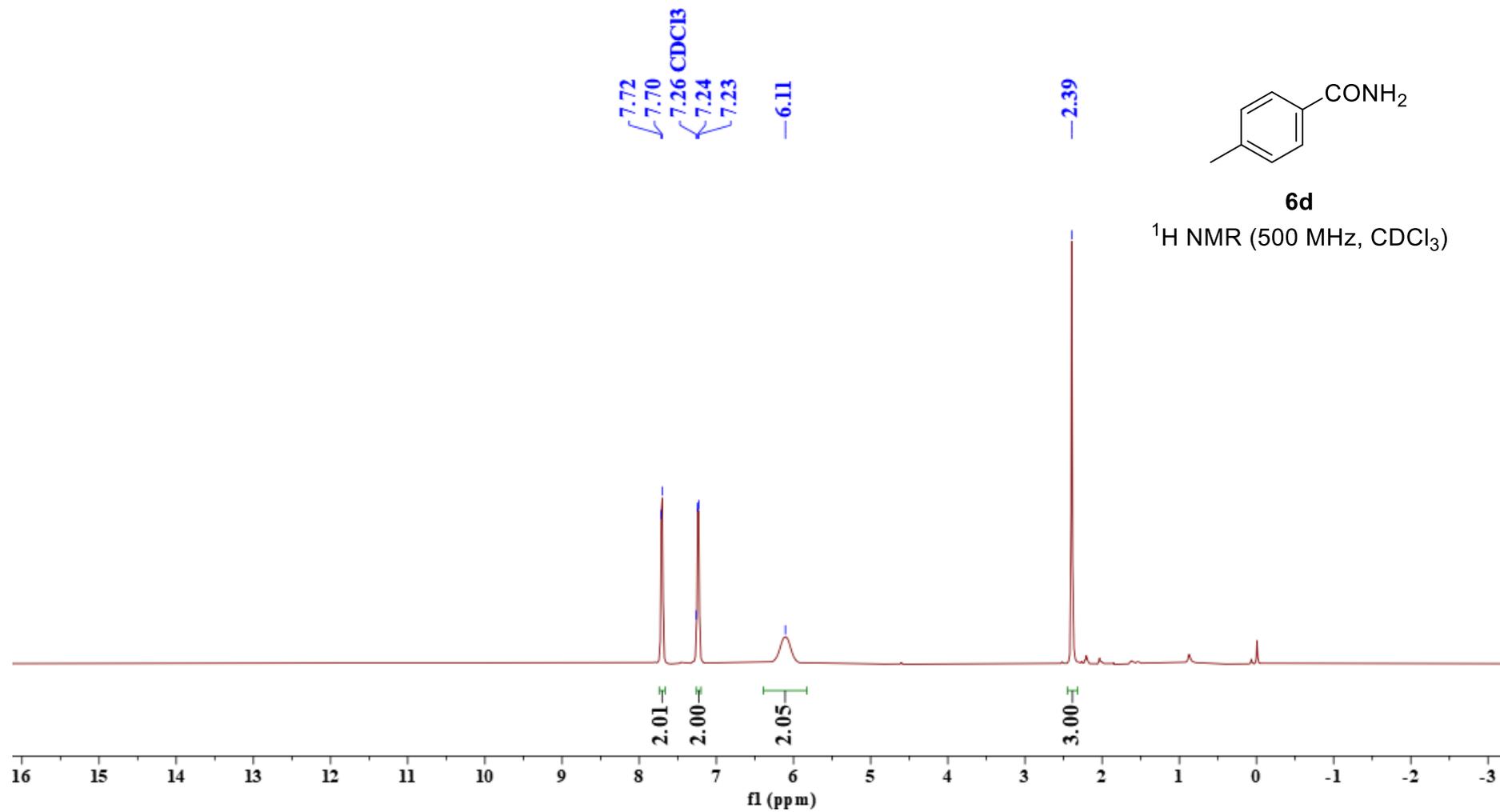


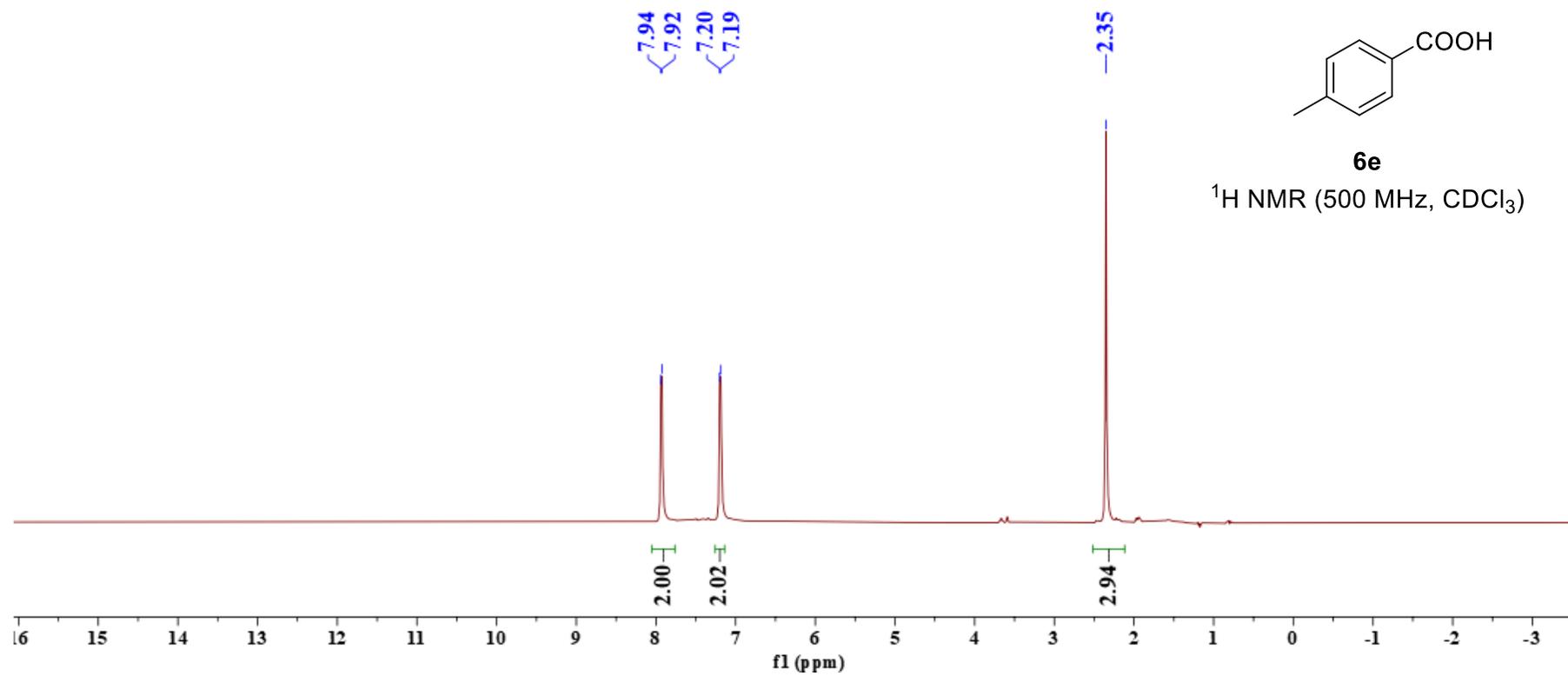


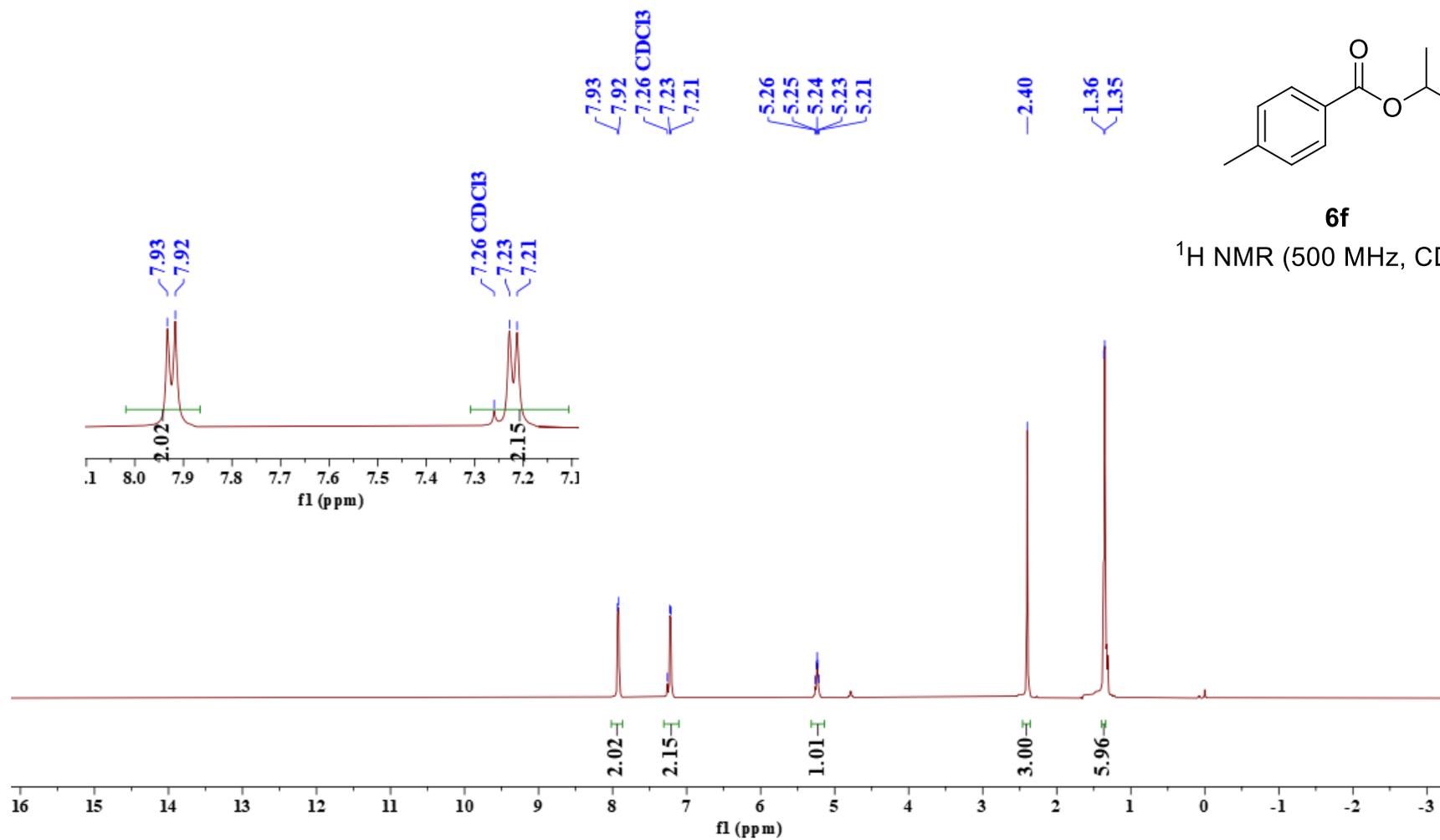


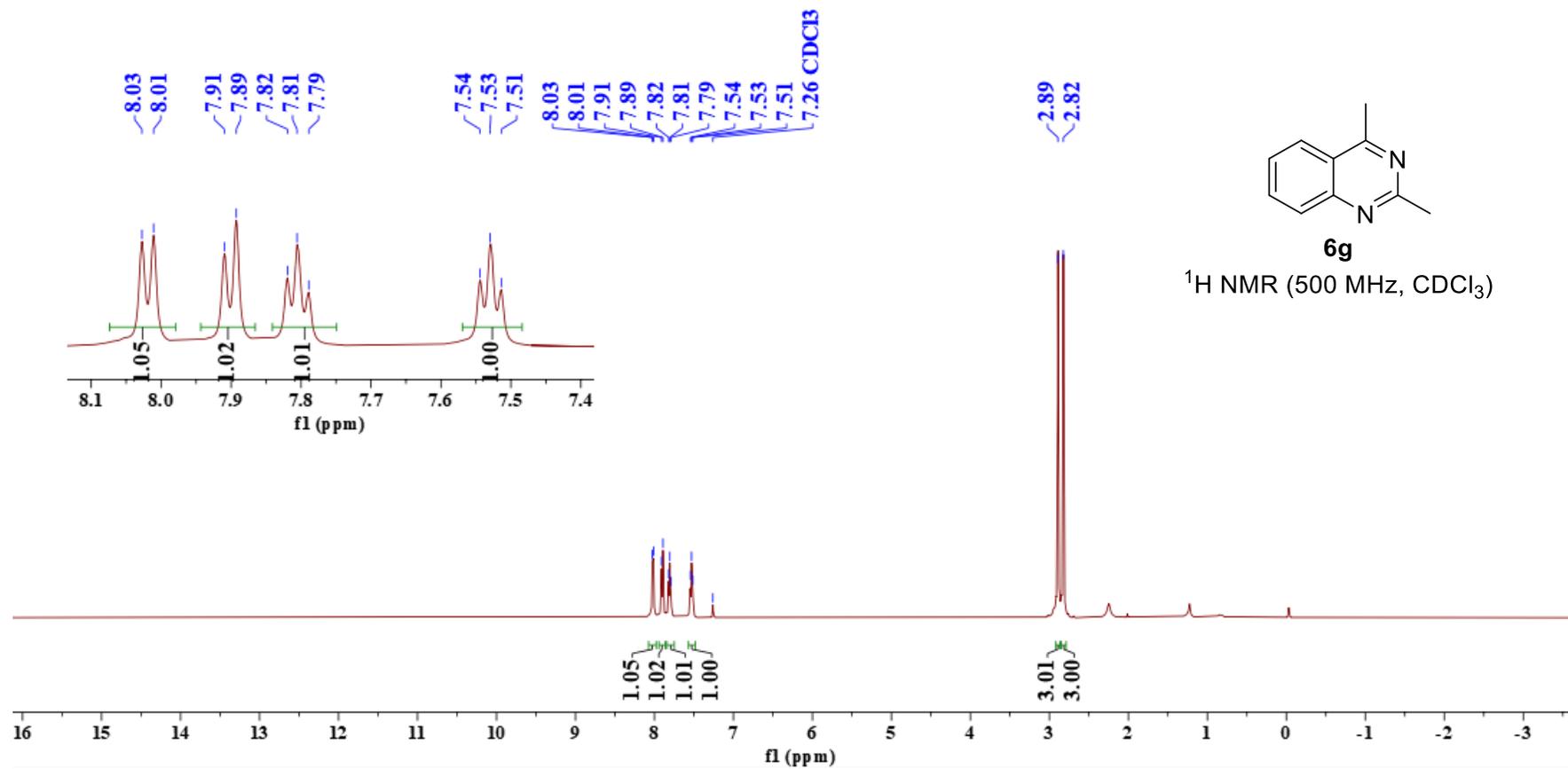


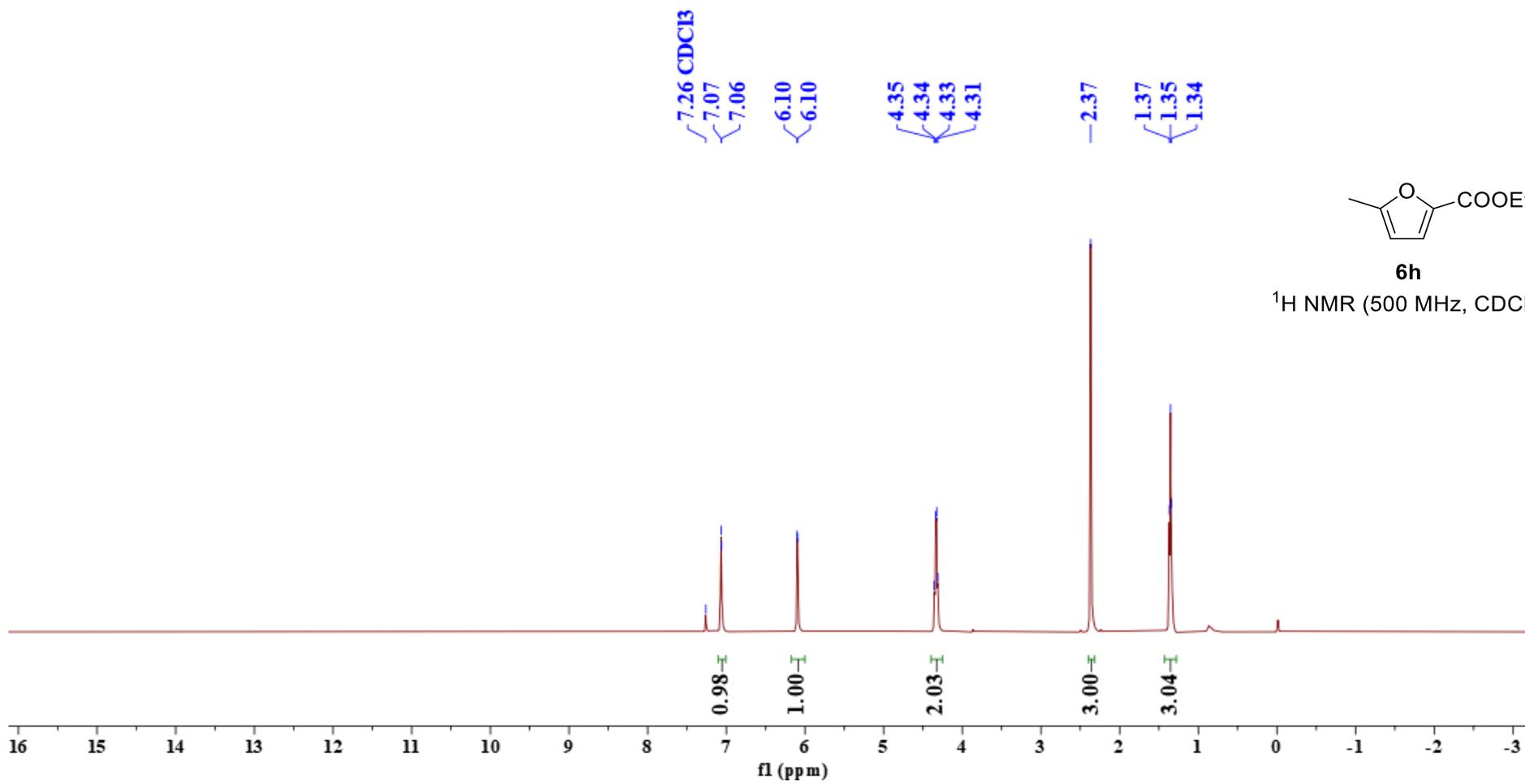


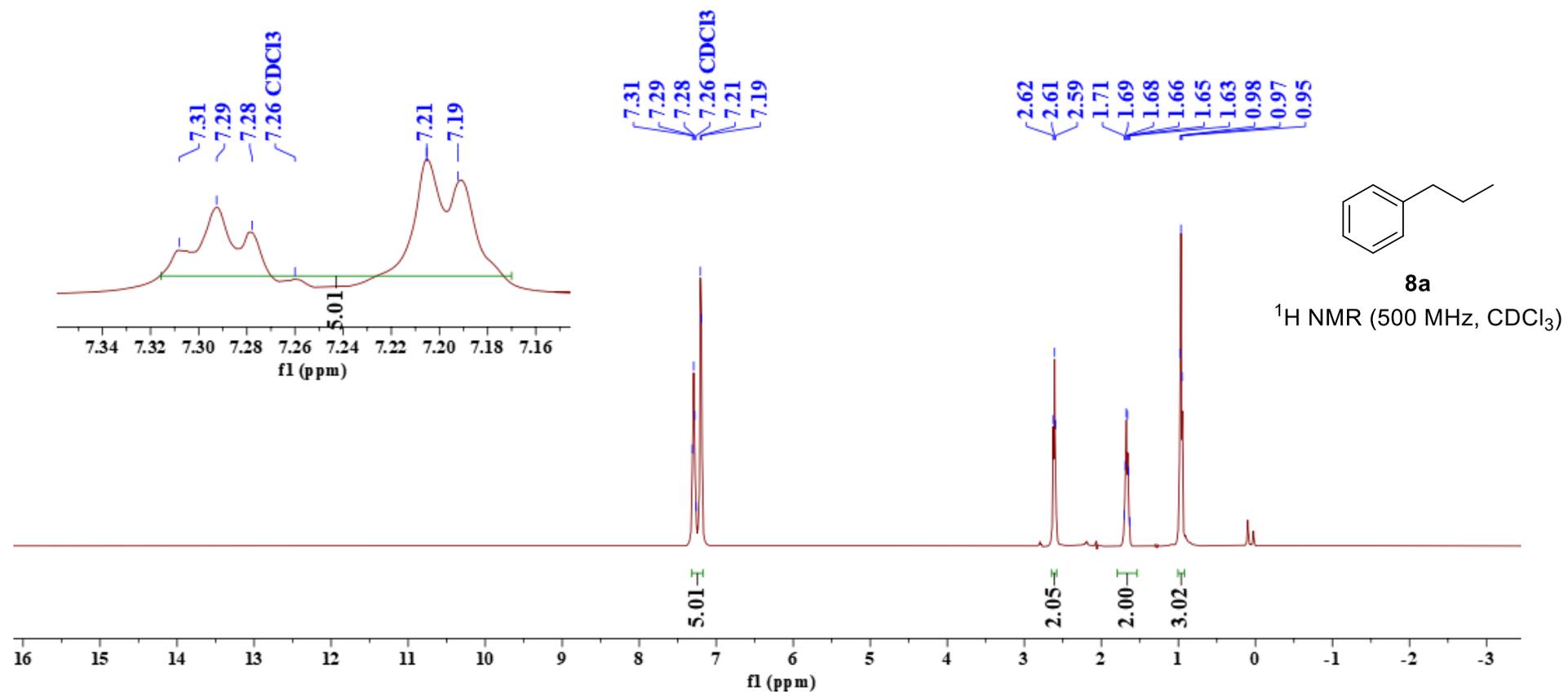


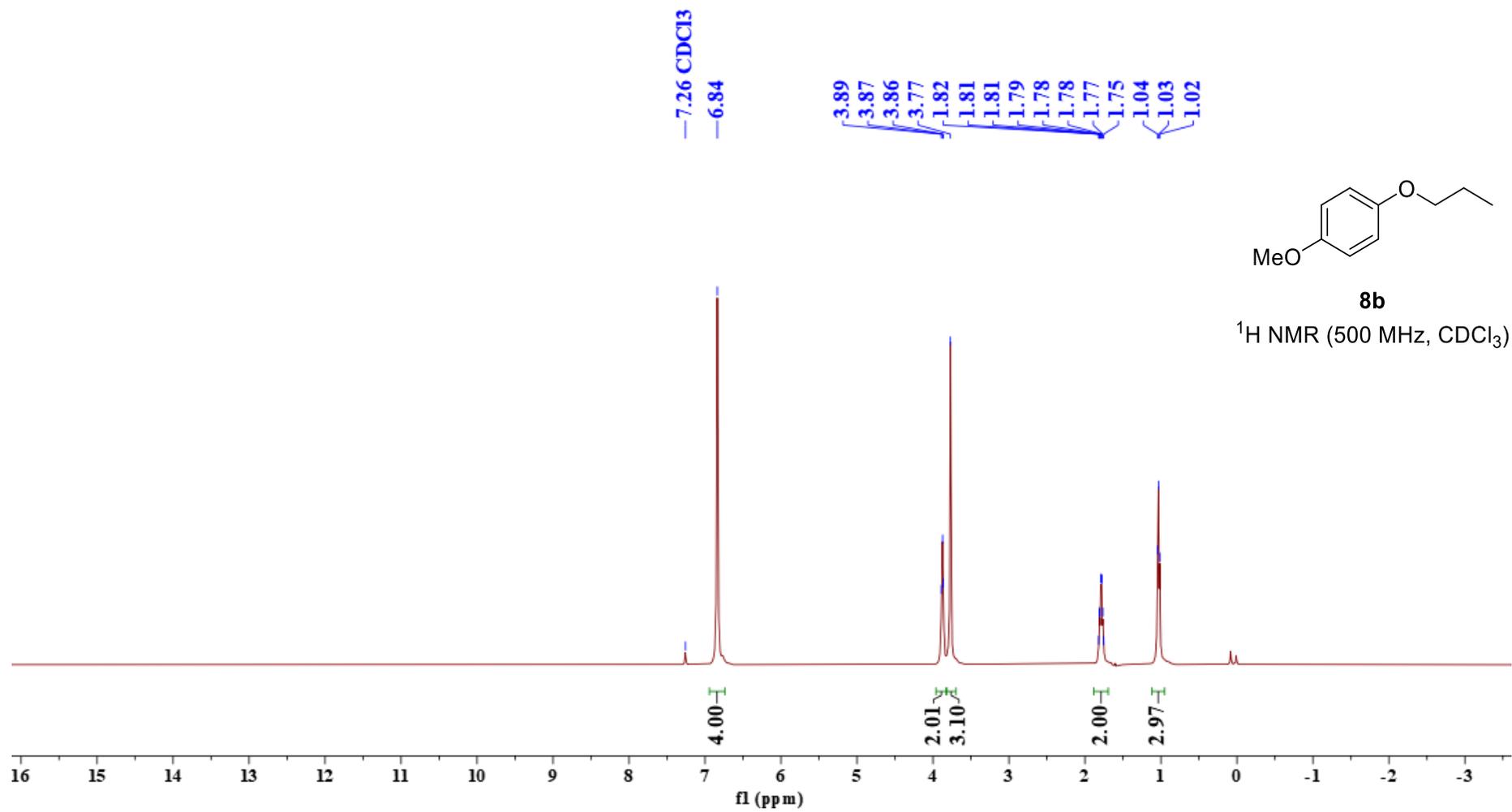


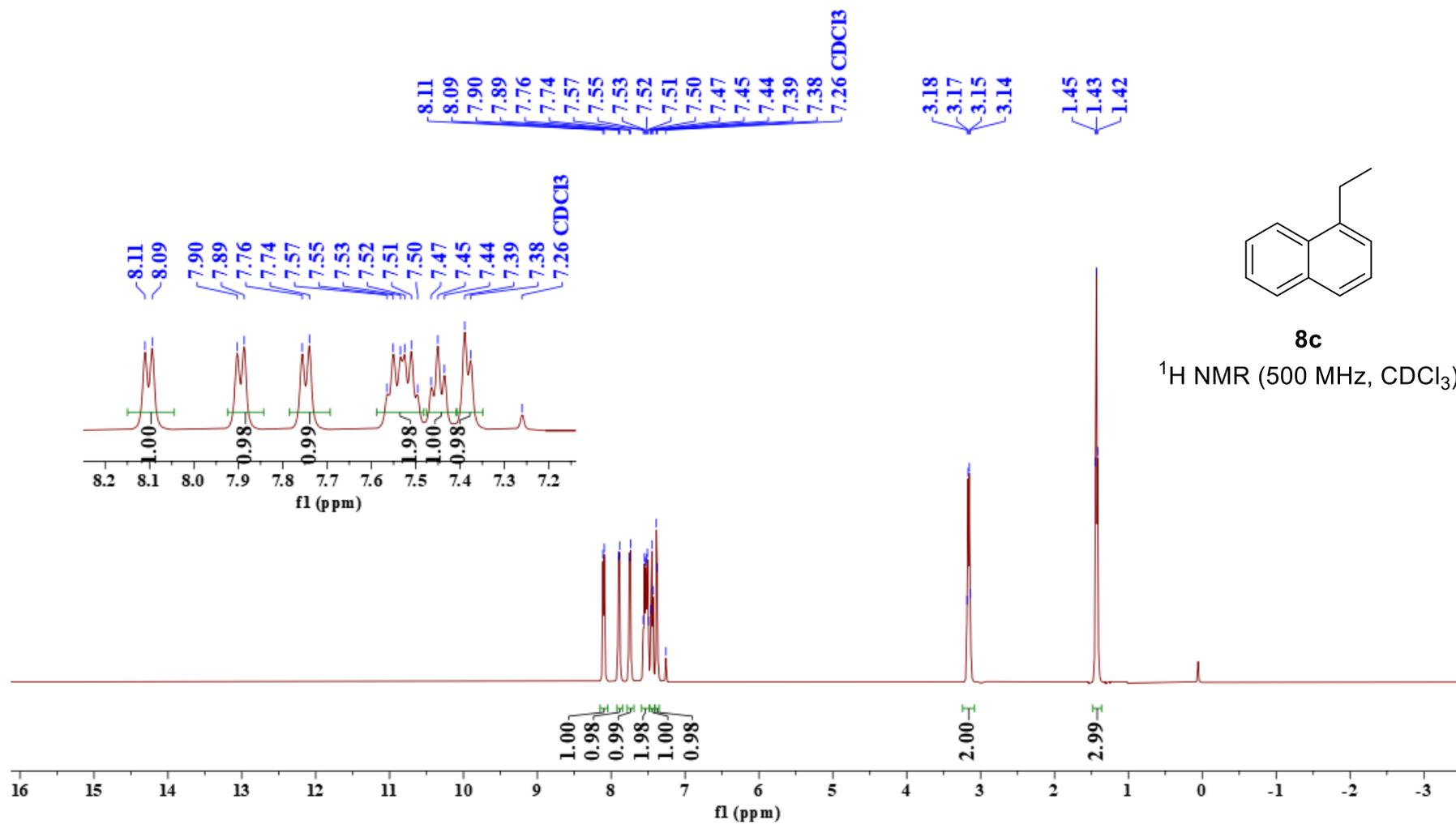


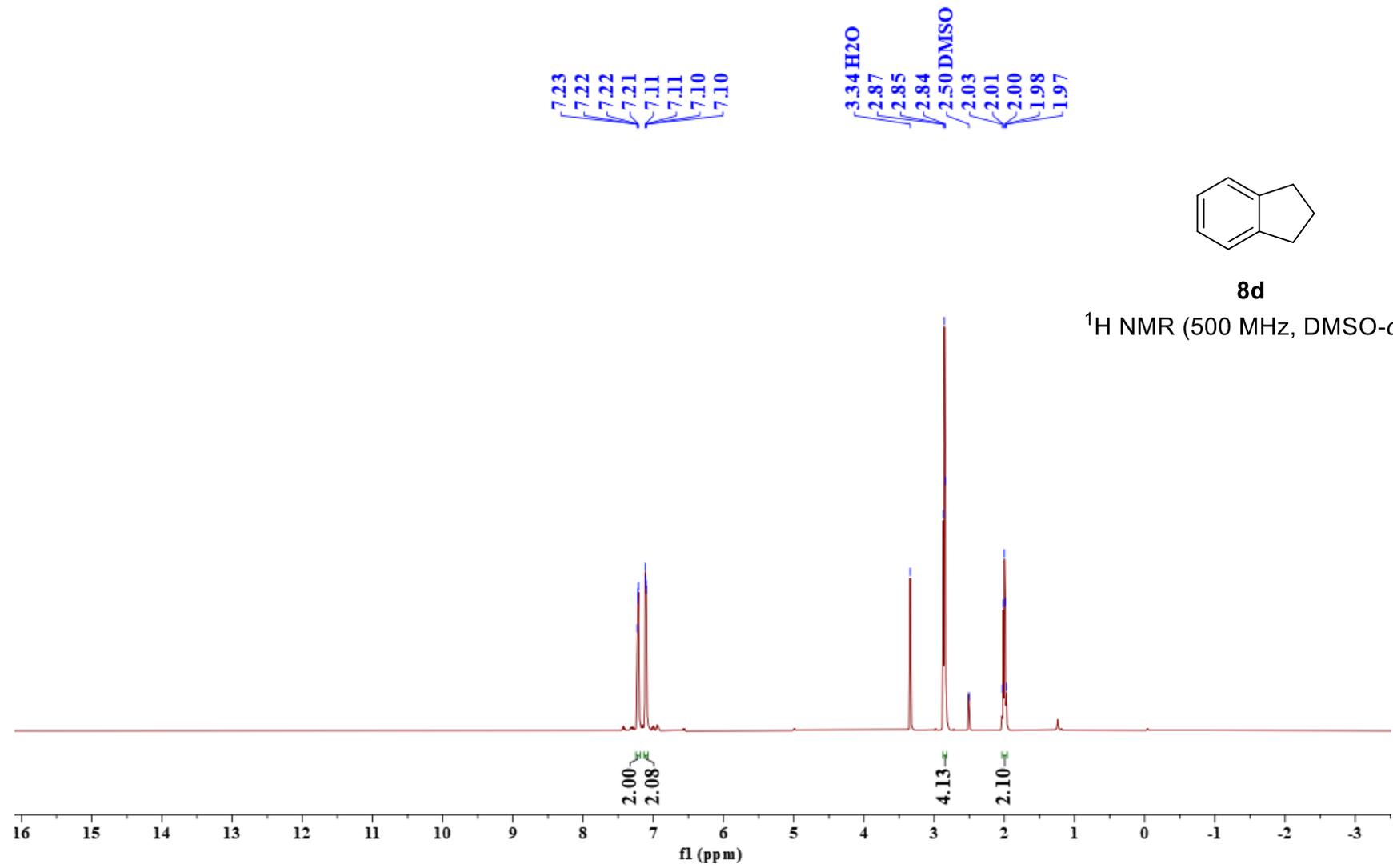






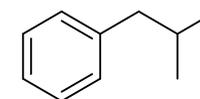






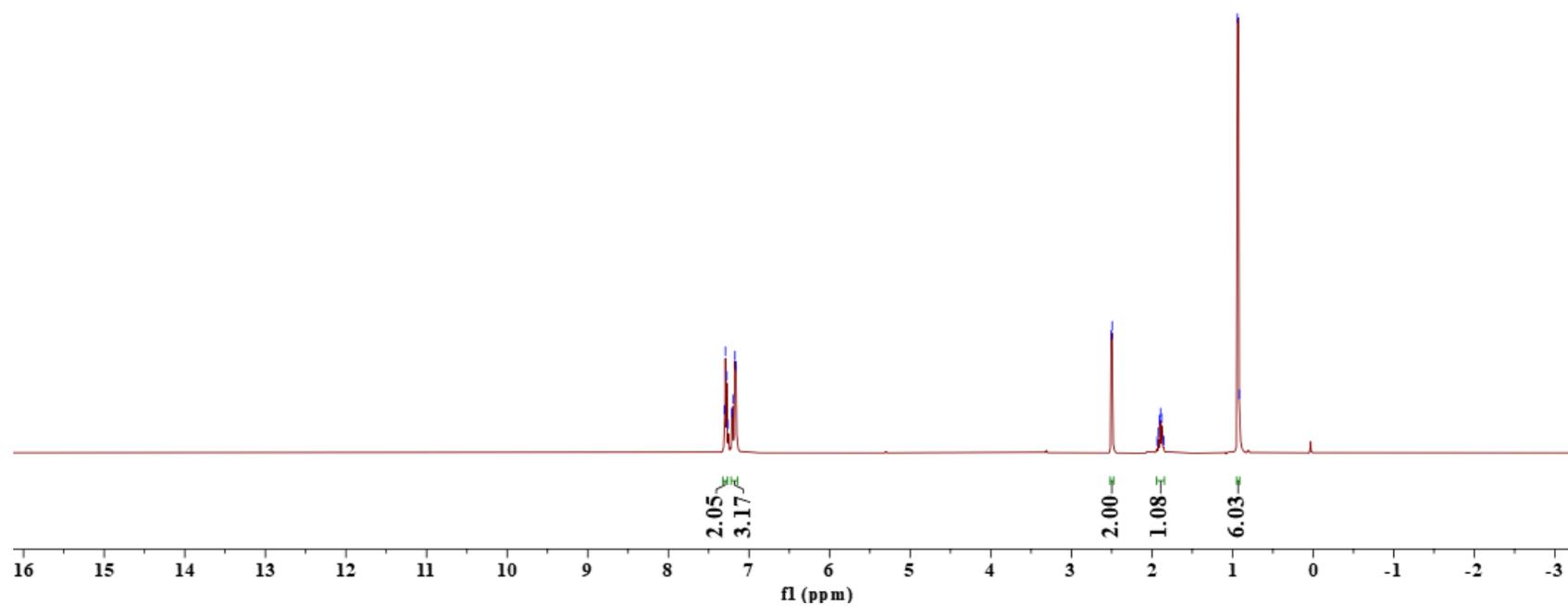
7.31
7.29
7.28
7.26 CDCl₃
7.21
7.20
7.17
7.16

2.51
2.49
1.93
1.92
1.91
1.89
1.88
1.85
0.94
0.92



8e

¹H NMR (500 MHz, CDCl₃)



S71