

Manganese Catalyzed Formate Synthesis via Coupled Methanol Dehydrogenation and Bicarbonate Transfer hydrogenation

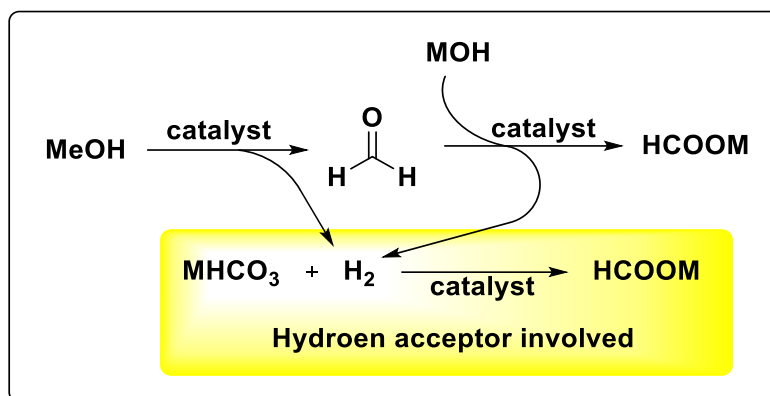
4.1. History, Background and Objective

In recent years, the quest for development of atom-economic, environmentally benign, and energy-efficient sustainable methodologies have garnered appreciable attention among the scientific community.^{77,211} Utilization of readily available raw-materials, evading consumption of noxious reagents, additives, and solvents, eliminating the possibility of copious waste generation forms the basis of sustainable chemical processes.^{212,213} Within this framework, homogeneous hydrogenation and dehydrogenation reactions emerged as attractive protocols for the construction of legions of molecules with diverse functionalization via greener catalytic routes.^{33,84,214}

Formic acid/formate constitutes an essential material having multitude of applications in industrial processes like, printing, fabric dyeing, food additive, silage production, buffering agent for strong mineral acids, reducing agent in synthetic industries, and in pharmaceuticals. Formic acid is also used as a coagulating agent in the manufacture of latex rubber, electroplating of various materials, and for the production of resins, varnishes, plasticizers, and glass.²¹⁵ Lately formic acid (FA) has drawn paramount attention as a potential renewable hydrogen storage material^{216,217} because of various advantages; it is kinetically stable liquid at room temperature, has low toxicity, can be handled, and stored easily. As of now, the current method for production of formic acid/formate salt on commercial scale involves the utilization of harmful and flammable carbon monoxide under pressure in the presence of solid sodium hydroxide at high temperature.^{16,218}

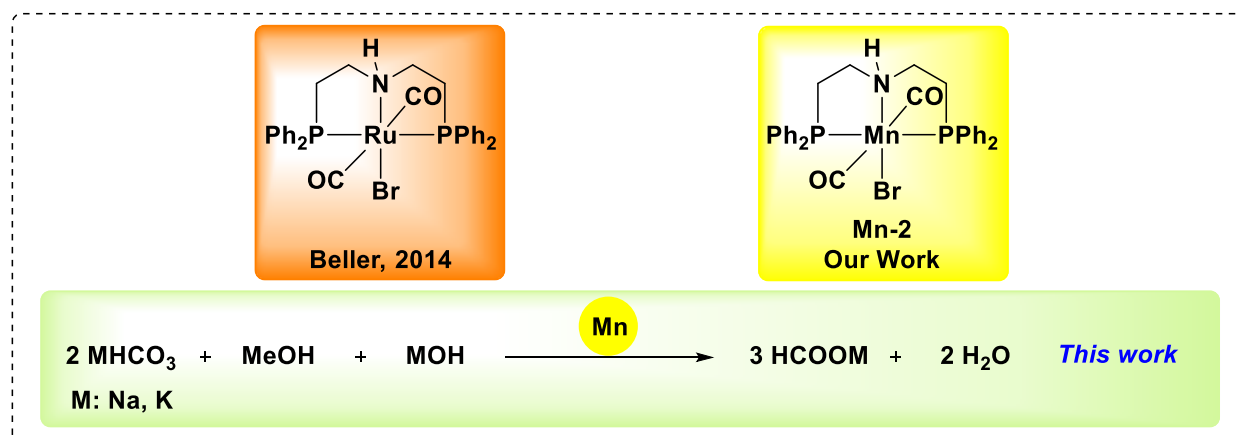
Recently hydrogenation of readily available, cheap, earth-abundant carbon dioxide has attracted considerable attention.^{35,219–228} Indirect hydrogenation of carbon dioxide is also gaining prominence owing to their ease of handling and potential application for a closed cycle economy.^{229–234} However, these processes have their own limitations. Hydrogenation strategies deal with high pressure of hydrogen invoking safety issues. In this context, ‘transfer hydrogenation’ strategy^{235–238} employing readily accessible biomass derived feedstock alcohols as hydrogen source is gaining momentum.^{239–242} Transfer hydrogenation of CO₂ and its derivatives for the formation of methanol or formate have been reported.^{243–251} In 2022 a comprehensive review by Choudhury compiled the developments of CO₂ transfer hydrogenation reactions.²⁵² However, reports on indirect CO₂ transfer hydrogenation to formate are rare and moreover this methodology generates stoichiometric byproducts from the hydrogen source. In 2021 Werner and co-workers have documented indirect reduction of CO₂ to methanol by transfer hydrogenation of amides, carbamates, urea derivatives and polyurethanes using Mn-based catalysts.²⁵³ We have recently developed a chromium catalyst for transfer hydrogenation of CO₂ and bicarbonate under ambient condition.²⁵⁴ Therefore, it is still demanding to find novel and better routes to synthesize formate in a sustainable manner.

In this context a combined homogeneous (de)hydrogenative approach for formate synthesis from methanol and bicarbonate would be an attractive, sustainable, atom efficient protocol compared to existing routes as well as from the perspective of closed-cycle economy (Scheme 4.1).



Scheme 4.1. General reaction pathway.

Methanol is cheap, earth-abundant, biodegradable feedstock.²⁵⁵ Although methanol is commonly produced from non-renewable syngas sources, Recently, sustainable methanol synthesis via innovative and efficient catalytic processes attracted considerable attention focusing on “methanol economy”.²⁵⁶ However, catalytic dehydrogenation of methanol to the aldehyde is considerably more problematic for methanol ($\Delta H = 84 \text{ kJmol}^{-1}$) than for higher alcohols, such as ethanol ($\Delta H = 68 \text{ kJmol}^{-1}$),²⁵⁷ and the generated formaldehyde is very unstable towards decomposition to CO and hydrogen, making subsequent dehydrogenative reactions challenging and less explored. Despite these difficulties, methanol has been explored as hydrogen source for transfer hydrogenation reactions and as C1 source in dehydrogenative coupling reactions.^{258–260}



Scheme 4.2. Reports on coupled methanol dehydrogenation and bicarbonate transfer hydrogenation for formate synthesis.

Biologically relevant bicarbonate is an alternative source of carbon dioxide and reduction of bicarbonate to formate would be a valuable route for indirect carbon dioxide reduction relevant for a closed cycle bicarbonate/formate cycle.^{261–263} Recently, Beller highlighted the utilization of bicarbonate/formate salt combination for green hydrogen production.²⁶⁴ There are several reports on hydrogenation of bicarbonates, however transfer hydrogenation of bicarbonate to formate is elusive.²⁶⁵

Nevertheless, despite the challenges associated with methanol dehydrogenation and transfer hydrogenation of bicarbonate, the seminal elegant report for the combined dehydrogenation of methanol and transfer hydrogenation of bicarbonate strategy was disclosed by Beller group using Ru complexes furnishing a TON of 18422.²⁴⁷ Hence this simultaneous dehydrogenation and hydrogenation approach is highly praiseworthy to achieve a sustainable synthesis of chemicals. (Scheme 4.2). Nonetheless, high cost, low abundance, and quite often toxicity issues of the heavy late transition metals prompted scientific community to delve into inexpensive, earth-abundant, bio-relevant base metals instead.^{7,13,88–92,94,183} Manganese being the third most earth-abundant

transition metal, preceded only by iron and titanium, serves to be an unambiguous surrogate to expensive metals in the exploration of various (de)hydrogenative coupling reactions.^{34,104–110,266}

Table 4.1. Sodium formate synthesis from sodium bicarbonate, sodium hydroxide and methanol.

$\text{NaHCO}_3 + \text{MeOH} + \text{NaOH} \xrightarrow[\text{H}_2\text{O, 100 } ^\circ\text{C, 24 h}]{\text{Mn-2}} \text{HCOONa} + \text{H}_2\text{O}$					
S. No.	NaHCO ₃ (mmol)	NaOH (mmol)	Mn-1 μmol	MeOH / H ₂ O (mL)	TON ^b
1	0	0	10	15 / 0	trace
2	0	15	10	15 / 0	80
3	10	15	10	15 / 0	140
4	10	15	10	12 / 3	300
5	7.5	15	10	12 / 3	180
6	10	15	10	7 / 7	130
7	10	15	10	12 / 3	460 ^c
8	10	15	10	7 / 7	270 ^d
9	10	15	10	12 / 3	580 ^d
10	10	15	5	7 / 7	480 ^{d,e}
11	10	15	5	12 / 3	840 ^{d,f}

^aReaction conditions unless otherwise stated: Under N₂ atmosphere, **Mn-2** complex (10 μmol), respective amount of methanol/water solution added to 15 mL autoclave and respective amount of NaHCO₃ and NaOH added and stirred at 100 °C for 24 h. TON calculated with respect to 10 mmol of N,N-Dimethylformamide as internal standard. ^bTON = HCOONa/mmol of Mn catalyst. ^cReaction performed at 125 °C. ^dReaction performed at 150 °C. ^eReaction performed for 36 h. ^fReaction performed for 36 h.

In fact, hydrogenation of CO₂ and its derivatives have been also explored with manganese pincer catalysts.^{16,44,60} In addition, manganese pincer catalyzed dehydrogenative coupling of methanol have also been demonstrated by several groups.^{48,52,53,112,115,117,195,267–272}

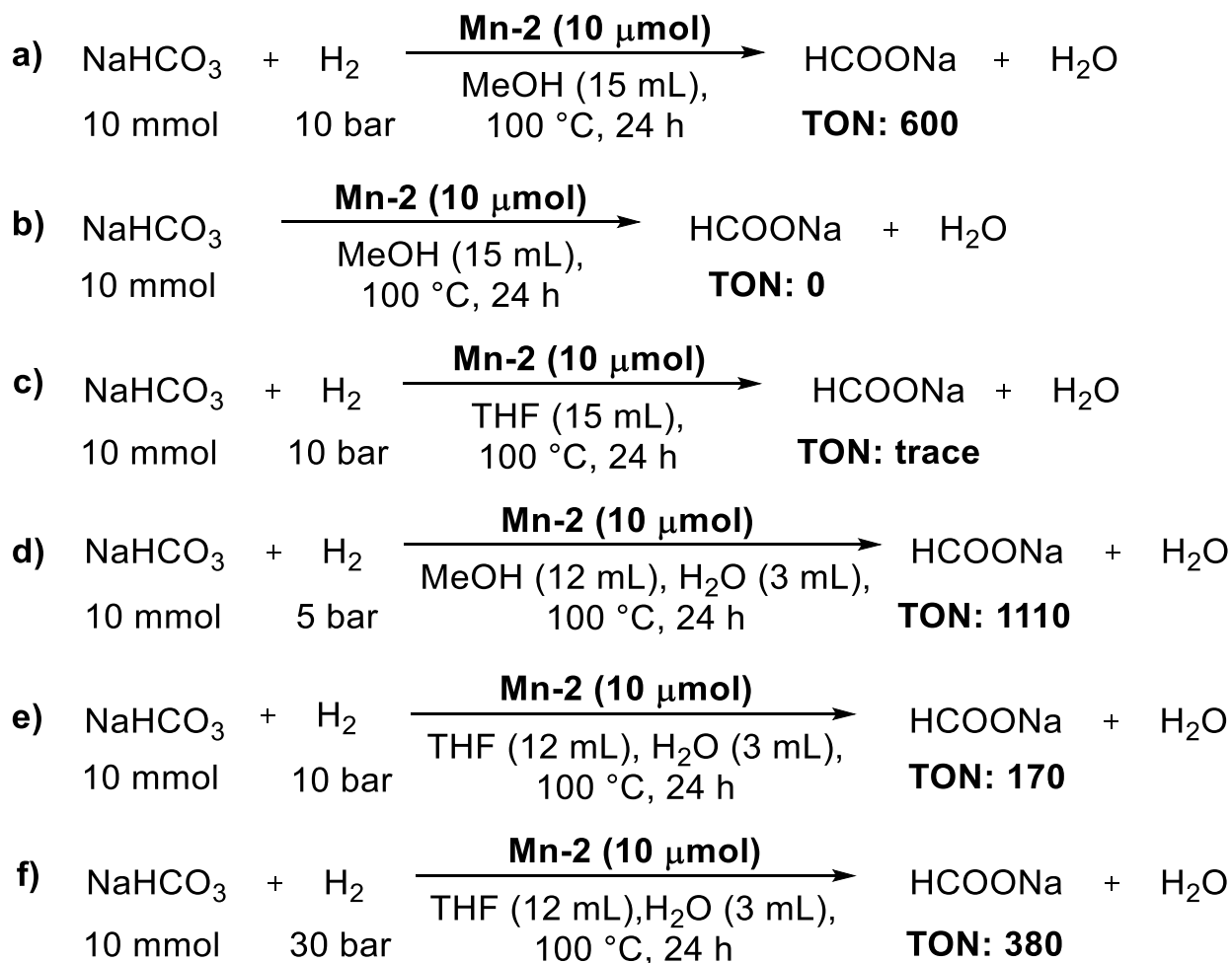
4.2. Results and Discussion

Inspired by these transformations and our recent discovery²⁵⁴ on Cr catalysed ambient pressure transfer hydrogenation of CO₂ and bicarbonate, we reckoned that combined transfer hydrogenation of bicarbonate with methanol is feasible with Mn pincer complexes. Herein, we demonstrate the first report from base metals based on pincer Mn catalyzed combined reaction for methanol dehydrogenation and bicarbonate hydrogenation to give formate in a greener way.

We commenced our investigation by utilizing Mn-PN^{HP} complex **Mn-2**,¹⁹¹ (PNP = bis(2-(diphenylphosphaneyl)ethyl)amine) for the dehydrogenation of methanol under basic conditions. The dehydrogenation of methanol was examined in a closed system (50 mL autoclave) at 100 °C in the presence of sodium hydroxide. A TON of 80, for sodium formate formation was noticed (Table 4.1, entry 2). A trace amount of methanol dehydrogenation in the absence of sodium bicarbonate and NaOH took place (Table 4.1, entry 1).

This clearly indicates the importance of base to facilitate the dehydrogenation reaction of methanol. Furthermore, when sodium bicarbonate was introduced in the reaction as hydrogen acceptor, the TON increases to 140 (Table 4.1, entry 3). When water was used in the reaction mixture, the catalytic efficiency was improved giving a TON of 300. This could be due to enhanced solubility of the substrate in water (Table 4.1, entry 4). However, increasing the amount of water led to decreased TON of the reaction (130, Table 4.1, entry 6). Furthermore, decrease in

sodium bicarbonate also resulted in decrease of the TON (Table 4.1, entry 5). In order to optimize the efficiency of the transformation process and increase the TON, we examined a diverse array of reaction parameters. Increasing the temperature to 125 °C resulted in the increase in TON to 460 (Table 4.1 entry 7). Furthermore, A TON of 580 was achieved at 150 °C (Table 4.1, entry 9). Additionally, TON decreased to 270 when MeOH/H₂O mixture changed to (7 mL and 7 mL) (Table 4.1, entry 8). When catalyst loading was reduced to 5 μmol with same solvent mixture of MeOH/H₂O (7 mL and 7 mL) the TON achieved was 480 for 36 h of reaction time (Table 4.1, entry 10). Surprisingly, when we used the standard solvent mixture for 5 μmol catalyst loading at 150 °C, a TON of 840 was achieved for 36 h reaction time (Table 4.1 entry 11). In order, to further demonstrate that sodium bicarbonate can function as a hydrogen acceptor and produce sodium formate in this reaction, the **Mn-2** catalyzed hydrogenation of sodium bicarbonate in methanol was conducted at 100 °C under 10 bar of H₂ (Scheme 4.3). A TON of 600 was achieved after 24 h under the reaction condition. A TON of 1110 was achieved when reaction is carried out in methanol water mixture (Scheme 4.3). Additionally, no formate was formed in the absence of H₂ under the same conditions (Scheme 4.3). When THF is employed as the solvent in place of methanol, a trace amount of product obtained (Scheme 4.3). Furthermore, when THF and water mixture is used with 10 bar H₂ a TON of 170 is achieved. Additionally, when H₂ pressure is increased to 30 bar TON increased to 380 (Scheme 4.3), which suggests that the hydrogenation of sodium bicarbonate proceeds smoothly in our sodium formate synthesis.

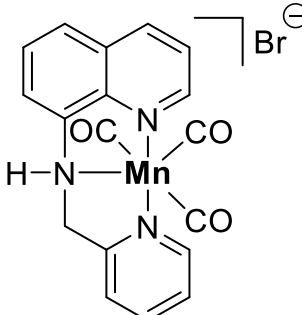
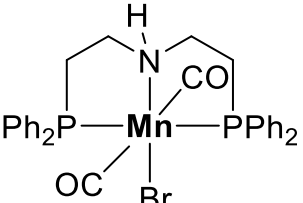
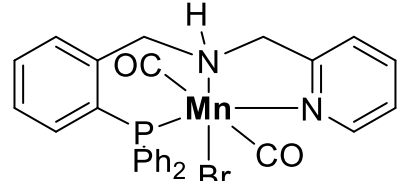
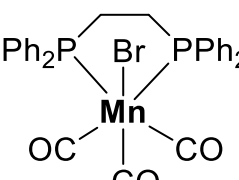
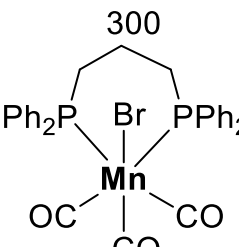


Scheme 4.3. Bicarbonate hydrogenation reactions.

In recent years, a variety of manganese pincer complexes have been proven to be efficient catalysts for the dehydrogenation of alcohols. Therefore, different manganese pincer complexes were probed for their activities towards the target reaction. A variety of potential catalysts (**Mn-1** (trace), **Mn-3** (150), **Mn-4** (60), **Mn-5** (80), **Mn(CO)₅Br** (trace), **MnBr₂** (trace)) (Table 4.2, entries 1–7) were screened for this transformation and the results are summarized in Table 4.2.

As a result of our tests, we found that **Mn-2**, exhibited better catalytic efficiency towards the transfer hydrogenation of bicarbonate at 100 °C for 24 h (Table 4.2, entry 1). Other manganese catalysts had much lower activity towards this transformation. The blank reaction without manganese catalyst did not lead to any conversion under the given reaction conditions (Table 4.2, entry 8).

Table 4.2. Catalyst screening for sodium formate synthesis from sodium bicarbonate, sodium hydroxide and methanol.

NaHCO_3 + MeOH + NaOH			$\xrightarrow[\text{H}_2\text{O (3 mL), 100 }^\circ\text{C, 24 h}]{\text{Mn (10 } \mu\text{mol)}} $	$\text{HCOONa} + \text{H}_2\text{O}$	
10 mmol	12 mL	15 mmol			
 Mn-1 trace  Mn-2 300  Mn-3 150					
 Mn-4 60  Mn-5 80 Mn(CO)₅Br trace					
MnBr₂			no catalyst		
trace			0		

^aReaction conditions unless otherwise stated: Under N_2 atmosphere, **Manganese complex** (10 μmol), methanol (12 mL), water (3 mL) to 15 mL autoclave and 10 mmol amount of NaHCO_3 and 15 mmol of NaOH added and stirred at 100 °C for 24 h. TON calculated with respect to 10 mmol of *N,N*-Dimethylformamide as internal standard. ^bTON = $\text{HCOONa}/\text{mmol}$ of Mn catalyst.

Furthermore, the catalyst TON was significantly increased to 1820, when potassium bicarbonate and KOH used for potassium formate synthesis reaction (Table 4.3, entry 1). A TON of 1060 was achieved when reaction was stopped after 12 h (Table 4.3, entry 2). The TON and yield were significantly reduced to 1380 when the reaction temperature was lowered (Table 4.3, entry 3). Reducing the amount of potassium bicarbonate resulted in lower TON (Table 4.3, entry 4), demonstrating its significant role as a hydrogen acceptor to facilitate this transformation. Nevertheless, as previously stated, the reaction efficiency was also reduced with increasing amounts of potassium bicarbonate because the reaction system had a lower pH (Table 4.3, entries 6 and 7). Table 4, entry 5 shows that the most significant result was a TON of 2040 in aqueous methanol, which was achieved by combining 10 mmol potassium bicarbonate with 40 mmol potassium hydroxide. Additionally, when reaction time is increased to 48 h a significant increase in TON was observed to 2640 (Table 4.3, entry 8). Our research indicates that this outcome

outperforms all previously documented instances of direct catalytic hydrogenation of bicarbonates to formates, even when subjected to elevated hydrogen gas pressure.

Table 4.3. Potassium formate synthesis from potassium bicarbonate, potassium hydroxide and methanol at various parameters.

$\text{KHCO}_3 + \text{MeOH} + \text{KOH} \xrightarrow[\text{H}_2\text{O (3 mL), 150 }^\circ\text{C, 24 h}]{\text{Mn-2 (5 } \mu\text{mol)}} \text{HCOOK} + \text{H}_2\text{O}$					
S. No.	KHCO ₃ (mmol)	KOH (mmol)	Mn-1 μmol	MeOH / H ₂ O (mL)	TON ^b
1	10	30	5	12 / 3	1820
2	10	30	5	12 / 3	1060 ^c
3	10	30	5	12 / 3	1380 ^d
4	0	30	5	12 / 3	640
5	5	30	5	12 / 3	2040
6	20	30	5	12 / 3	940
7	30	30	5	12 / 3	560
8	10	30	5	12 / 3	2640 ^e
9	10	0	5	12 / 3	trace
10	10	30	0	12 / 3	trace

^aReaction conditions unless otherwise stated: Under N₂ atmosphere, **Mn-2** complex (5 μmol), methanol (12 mL), water (3 mL) to 15 mL autoclave and 10 mmol amount of KHCO₃ and 15 mmol of KOH added and stirred at 150 $^\circ\text{C}$ for 24 h. TON calculated with respect to 10 mmol of *N, N*-Dimethylformamide as internal standard. ^bTON = HCOONa/mmol of Mn catalyst. ^cReaction performed for 12 h. ^dReaction performed at 125 $^\circ\text{C}$. ^eReaction performed for 48 h.

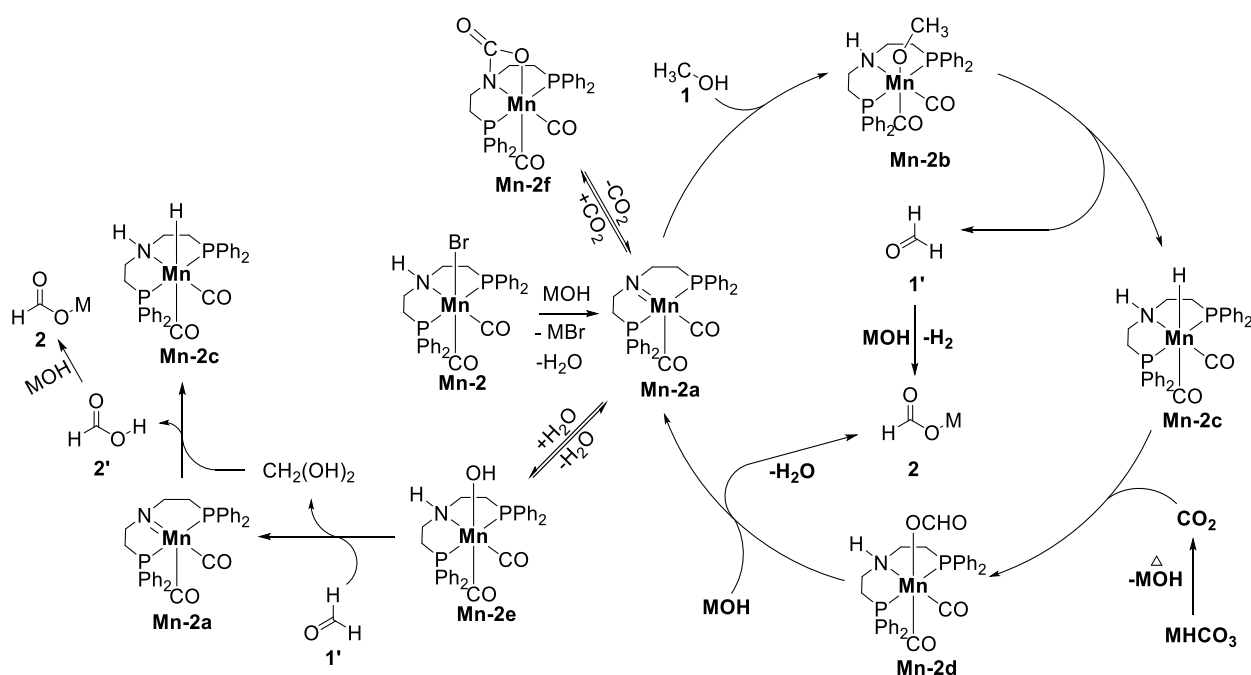
Furthermore, In the absence of CO₂ we got the TON of 1200 (Table 4.4, entry 1). When pressure of CO₂ was increased to 5 bar under identical conditions the TON of formate decreased to 1000 (Table 4.4, entry 2). Further increase in CO₂ pressure to 10 bar shut down the reaction (Table 4.4, entry 3). Additionally, without catalyst no reaction happened.

Table 4.4. Effect of CO₂ pressure for formate synthesis

$\text{CO}_2 + \text{MeOH} + \text{KOH} \xrightarrow[\text{H}_2\text{O (3 mL), 150 }^\circ\text{C, 24 h}]{\text{Mn-2 (5 } \mu\text{mol)}} \text{HCOOK} + \text{H}_2\text{O}$				
S. No.	CO ₂ (bar)	KOH (mmol)	MeOH / H ₂ O (mL)	TON ^b
1	0	40	12 / 3	1200
2	5	40	12 / 3	1000
3	10	40	12 / 3	trace
4	0	40	12 / 3	0 ^c

^aReaction conditions unless otherwise stated: **Mn-2** complex (5 μmol), methanol (12 mL), water (3 mL) to 15 mL autoclave and 40 mmol of KOH added and stirred at 150 $^{\circ}\text{C}$, 24 h. TON calculated with respect to 10 mmol of *N,N*-Dimethylformamide as internal standard. ^bTON = $\text{HCOONa}/\text{mmol}$ of Mn catalyst. ^cWithout catalyst.

Based on our experimental observations, we concluded that the **Mn-2** in presence of base converts into highly active amido complex **Mn-2a**, which then interacts with methanol through metal-ligand cooperative mechanism and leads to the formation of methoxy complex **Mn-2b**. Further, formaldehyde formation occurs via β -hydride elimination (dehydrogenation of methanol to formaldehyde and hydrogen). Furthermore, base promoted dehydrogenation of formaldehyde yields formate salt and H_2 . In addition, sodium carbonate at high temperature releases CO_2 which in situ forms formate complex, which further interaction with base produces corresponding formate salt. Additionally, hydrogen addition to amido complex **Mn-2a** forms Mn-hydride complex **Mn-2c** which reacts in situ generated CO_2 to give a formate complex **Mn-2d** (scheme 4.4). Meanwhile, bicarbonate acts as a hydrogen acceptor or undergoes transfer hydrogenation with methanol to afford the formate product as well, which also facilitates the methanol dehydrogenation process.



Scheme 4.4. Proposed reaction mechanism.

4.3. Summary

In conclusion, we have developed a base metal pincer complex based on earth-abundant Mn for combined catalytic transfer hydrogenation of bicarbonate and dehydrogenation of methanol to produce formate salts. Formate salts can be synthesized through this methodology, which has practical applications in industry.

4.4. Experimental procedures and supporting data

All experiments were conducted under inert atmosphere in high pressure reactor (50 mL) from Amar Equipments or in nitrogen glove box, unless stated otherwise. Tetrahydrofuran (THF) and methanol (MeOH) were heated under reflux over suitable drying agent (sodium/benzophenone for THF; 3 $\text{\AA}$ molecular sieves for MeOH), distilled and stored under nitrogen atmosphere. Degassed distilled water was stored in the the nitrogen atmosphere. Deuterated (D_2O) solvents were stored under nitrogen atmosphere. Unless otherwise stated, commercial reagents were used without purification. Pentacarbonyl manganese bromide ($\text{Mn}(\text{CO})_5\text{Br}$) was purchased from Sigma- Aldrich, Bis(2-(diphenylphosphino)ethyl)amine hydrochloride was purchased from BLD pharma, and all other materials were purchased from Avra, BLDpharma and Sigma- Aldrich, stored under nitrogen and used as received. All the

reaction were monitored by NMR. ^1H NMR were taken from Bruker 500 MHz spectrometer. All spectra were recorded at room temperature, unless otherwise noted.

Synthesis of $\text{NN}^{\text{H}}\text{Mn}(\text{CO})_3\text{Br}$ (**Mn-1**):

Catalyst was synthesised as reported in our last literature,¹⁹⁸ In the glovebox, A 100ml schlenk tube is charged with $\text{Mn}(\text{CO})_5\text{Br}$ (137.5 mg, 0.5 mmol, 1.0 equiv.) in 5 ml THF and stirred for 5 minutes. To the stirring solution, *N*-(pyridin-2-ylmethyl)quinolin-8-amine (117.5 mg, 0.5 mmol) in 5 ml THF added dropwise with vigorous stirring. After addition of ligand, schenk was closed and kept for stirring at 90 °C for stirring overnight. A yellow-coloured precipitates appeared at the bottom of the schlenk. Then, the solvent was decanted and solid washed with *n*-hexane (3*5ml) and bright yellow to reddish coloured precipitates collected and dried under vacuo (84% yield).

Synthesis of $\text{PN}^{\text{H}}\text{P-Mn}(\text{CO})_2\text{Br}$ catalyst (**Mn-2**):

Catalyst was synthesised as reported in literature,¹⁹¹ A flame dried Schlenk tube was charged with ligand bis(2-(diphenylphosphanyl)ethyl)amine hydrochloride (478 mg, 1.0 mmol, 1.0 equiv.), toluene (8 mL), water (2 mL) and NaOH (120 mg, 3.0 mmol, 3.0 equiv.). The reaction mixture was stirred at room temperature for 30 min. The two phases were separated, and the organic layer was washed with water (3 × 5 mL). The organic layer was concentrated under reduced pressure. Subsequently, toluene (12 mL) and $\text{Mn}(\text{CO})_5\text{Br}$ precursor (275 mg, 1.0 mmol, 1.0 equiv.) were added to the Schlenk tube. The reaction mixture was heated up to 110 °C and the atmosphere was exchanged three times by evacuating and backfilled with nitrogen. After the mixture was stirred for 20 h at reflux temperature, it was cooled to room temperature and concentrated in vacuo. The crude precipitate was washed with pentane and extracted with dichloromethane/diethylether to remove insoluble inorganic side products. The solution was concentrated under reduced pressure and dried to afford the complex **Mn-1** as a yellow powder in 87%. ^{31}P NMR also Matched as reported in literature.

Synthesis of $(\text{PN}^{\text{H}}\text{N})\text{Mn}(\text{CO})_2\text{Br}$ catalyst (**Mn-3**):

Catalyst was synthesised as reported in literature,²¹⁰ Under N_2 atmosphere, A 100 mL young Schlenk tube was charge with $\text{PN}^{\text{H}}\text{N}$ ligand { $\text{PN}^{\text{H}}\text{N}$ = *N*-(2-(diphenylphosphanyl)benzyl)-1-(pyridin-2-yl)methanamine} (95.67 mg, 0.25 mmol, 1.0 equiv.), $\text{Mn}(\text{CO})_5\text{Br}$ (68.63 mg, 0.25 mmol) and dry THF (5 mL) and stirred for overnight at 80 °C. The reaction mixture cooled and concentrated in *vacuo*. The residue was thoroughly washed with *n*-pentane and dried under *vacuo*, affording light yellow powder (126 mg, 85%). The product was confirmed by analysing the complex by ^{31}P NMR, which matched with the literature reported data.

Synthesis of $\text{DPPE-Mn}(\text{CO})_3\text{Br}$ (**Mn-4**) and $\text{DPPP-Mn}(\text{CO})_3\text{Br}$ (**Mn-5**):

Catalyst was synthesised with slight modifications as reported in literature,²⁷³ In the glovebox, A 100ml schlenk tube is charged with $\text{Mn}(\text{CO})_5\text{Br}$ (137.5 mg, 0.5 mmol, 1.0 equiv.) in 5 ml THF and stirred for 5 minutes. To the stirring solution, DPPE or DPPP ligand (0.5 mmol, 1.0 equiv.) in 5 ml THF added dropwise with vigorous stirring. After addition of ligand, Schenk was closed and kept for stirring at 90 °C for stirring overnight. After completion of reaction whole liquid was dried under vacuo and solid precipitates were washed with *n*-hexane (3*5ml) and yellowish-coloured precipitates collected and dried under vacuo (87% for DPPE and 89% for DPPP yield). The product was confirmed by analysing the complex by ^{31}P NMR, which matched with the literature reported data.

General procedure for formate salt synthesis:

Synthesis of sodium formate from sodium bicarbonate, sodium hydroxide and methanol:

In the glovebox, sodium bicarbonate (10 mmol), sodium hydroxide (15 mmol) and **Mn-2** complex (10 μmol) were added to autoclave (50 mL) and Methanol (12 mL)/ H_2O (3 mL) were transferred into it under N_2 atmosphere. Autoclave was packed properly inside the glovebox and reaction was stirred at 100 °C for 24 h. After completion of the reaction, autoclave was cooled and slowly pressure was released. Solid was dissolved in 15 mL H_2O and DMF (10 mmol) was added as

internal standard and aliquot was taken out of it, which is diluted in D₂O (0.5 mL and characterised by ¹H NMR and yield was calculate with respect to 10 mmol of *N, N*-Dimethylformamide as internal standard.

Screening of Mn catalysts for sodium formate synthesis from sodium bicarbonate, sodium hydroxide and methanol:

In the glovebox, sodium bicarbonate (10 mmol), sodium hydroxide (15 mmol) and **Mn** complex (10 μmol) were added to autoclave (50 mL) and Methanol (12 mL)/H₂O (3 mL) were transferred into it under N₂ atmosphere. Autoclave was packed properly inside the glovebox and reaction was stirred at 100 °C for 24 h. After completion of the reaction, autoclave was cooled and slowly pressure was released. Solid was dissolved in 15 mL H₂O and DMF (10 mmol) was added as internal standard and aliquot was taken out of it, which is diluted in D₂O (0.5 mL and characterised by ¹H NMR and yield was calculate with respect to 10 mmol of *N, N*-Dimethylformamide as internal standard.

Synthesis of potassium formate from potassium bicarbonate, potassium hydroxide and methanol:

In the glovebox, potassium bicarbonate (10 mmol), potassium hydroxide (30 mmol) and **Mn-2** complex (5 μmmol) were added to autoclave (50 mL) and Methanol (12 mL)/H₂O (3 mL) were transferred into it under N₂ atmosphere. Autoclave was packed properly inside the glovebox and reaction was stirred at 150 °C for 24 h. After completion of the reaction, autoclave was cooled and slowly pressure was released. Solid was dissolved in 15 mL H₂O and DMF (10 mmol) was added as internal standard and aliquot was taken out of it, which is diluted in D₂O (0.5 mL and characterised by ¹H NMR and yield was calculate with respect to 10 mmol of *N, N*-Dimethylformamide as internal standard.

Synthesis of formate salts from CO₂ hydroxides and methanol:

In the glovebox, potassium hydroxide (40 mmol) and **Mn-2** complex (5 μmmol) were added to autoclave (50 mL) and Methanol (12 mL)/H₂O (3 mL) were transferred into it under N₂ atmosphere. Autoclave was packed properly inside the glovebox, then autoclave was purged with CO₂ gas three times and reactor was filled with respective pressure of CO₂. The reaction was stirred at 150 °C for 24 h. After completion of the reaction, autoclave was cooled and slowly pressure was released. Solid was dissolved in 15 mL H₂O and DMF (10 mmol) was added as internal standard and aliquot was taken out of it, which is diluted in D₂O (0.5 mL and characterised by ¹H NMR and yield was calculate with respect to 10 mmol of *N, N*-Dimethylformamide as internal standard.

General procedure for sodium bicarbonate hydrogenation:

Under nitrogen protection, 10 mmol of NaHCO₃ and 10 μmol of **Mn-2** complex were added to 50 mL of autoclave, followed by the addition of 15 mL of MeOH. A pressure of 10 bar H₂ was applied to the autoclave. We stirred the reaction mixture at 100 °C for 24 hours. Pressure was gradually released from the autoclave after cooling it down after the reaction time. The autoclave was cooled, and the pressure was gradually released after the reaction was complete. The solid was dissolved in 15 mL of water, while 10 mmol of dimethylformamide (DMF) was added as an internal standard. An aliquot was then extracted and diluted in half a millilitre of water. The mixture was then analysed using ¹H NMR, and yield was calculated with respect to 10 mmol of *N, N*-Dimethylformamide as internal standard.

General procedure for the stoichiometric Reaction for intermediate trapping in the reaction mixture:

A flame-dried Schlenk tube (25 mL) under a nitrogen atmosphere was charged with **Mn-2** (12 mg, 0.02 mmol) and sodium hydroxide (20.0 mg, 0.5 mmol) dissolved in 1.0 mL of methanol and the mixture was stirred for 5 min. Then, the Schlenk flask was closed tightly and kept at 80 °C for

4 h. After the reaction had stopped, the Schlenk flask was cooled to room temperature, and an aliquot was taken in benzene- d_6 for analysis of intermediates by NMR.

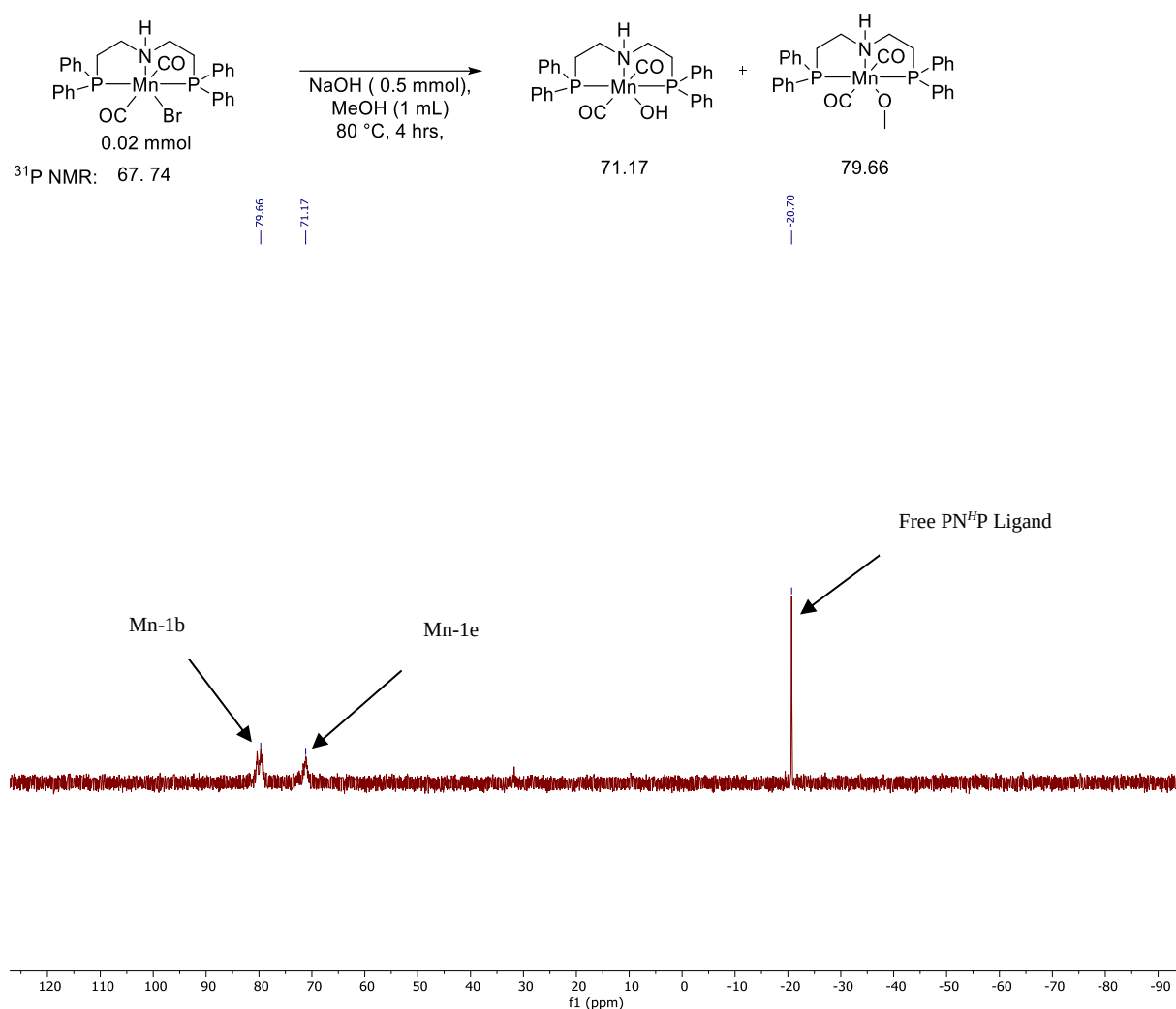
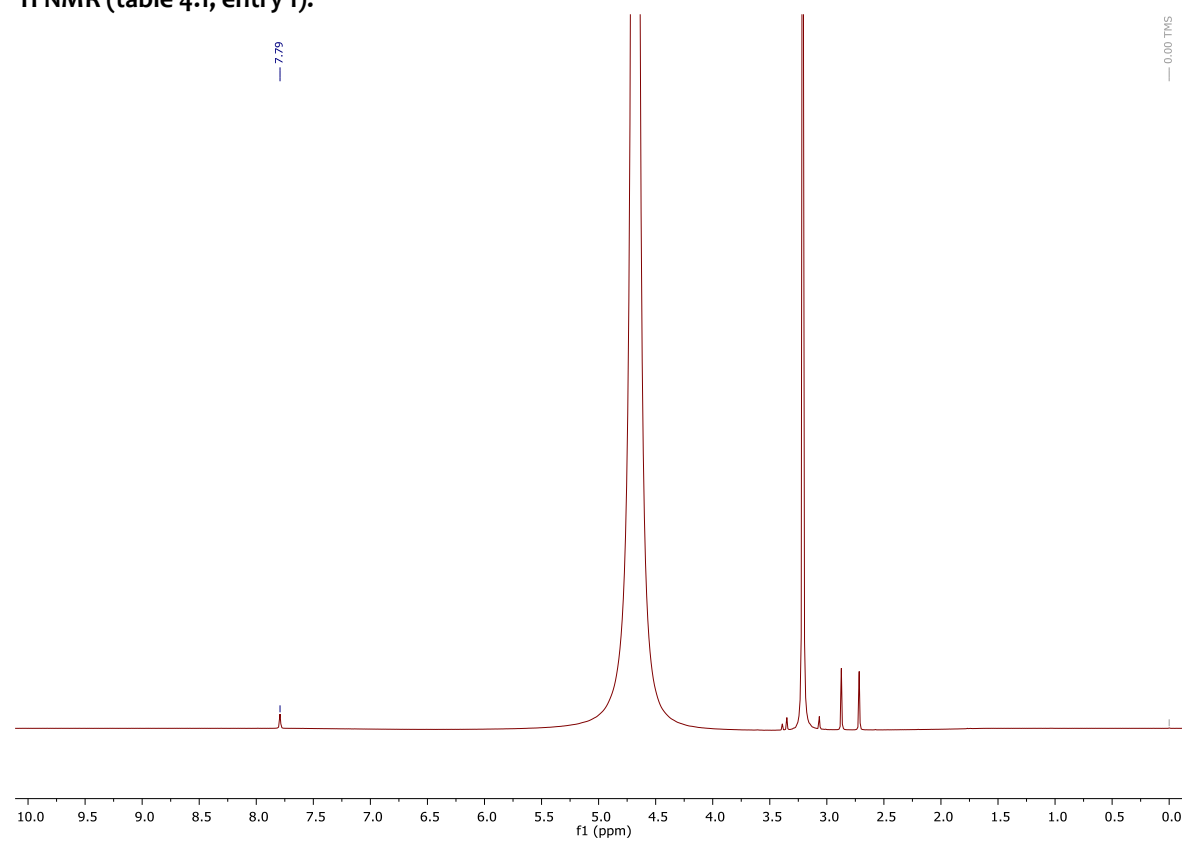


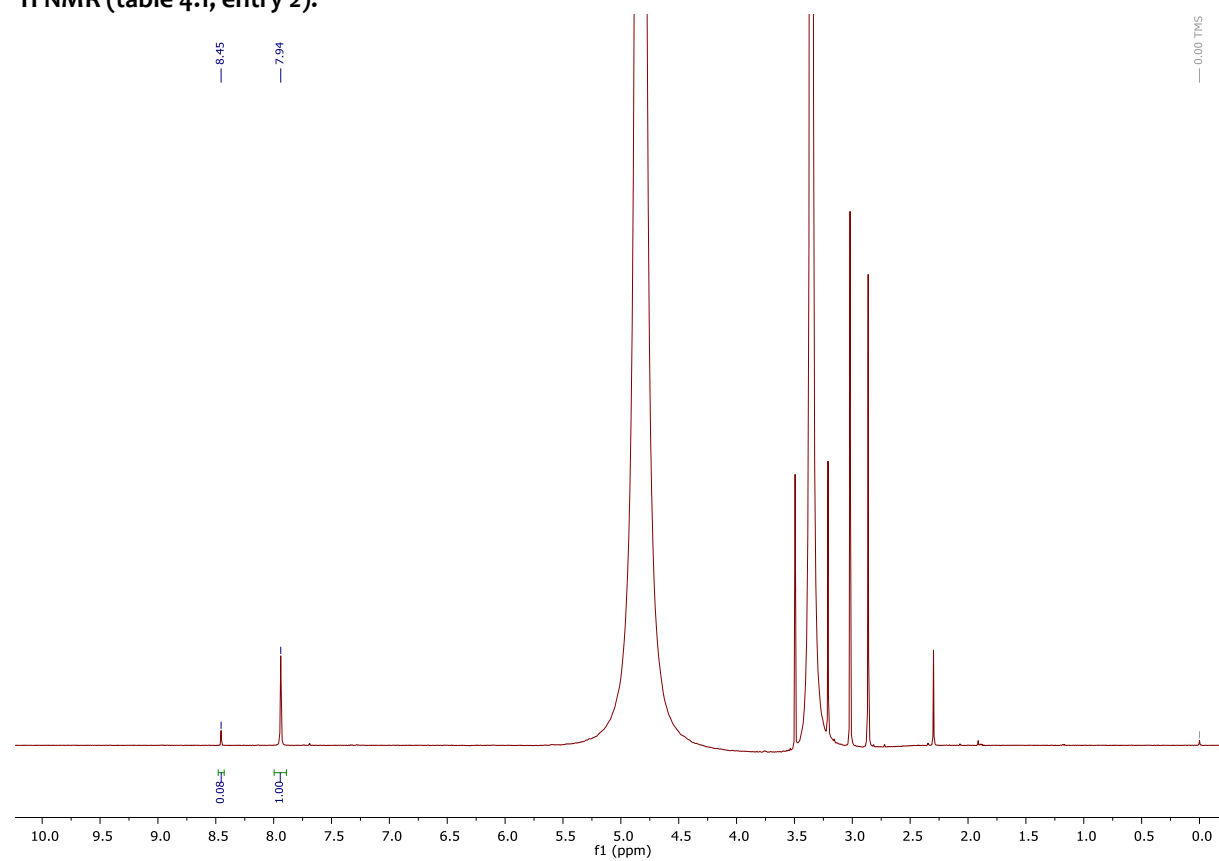
Figure S4.1. ^{31}P NMR of the stoichiometric reaction of **Mn-2** with methanol and NaOH.

NMR Spectra

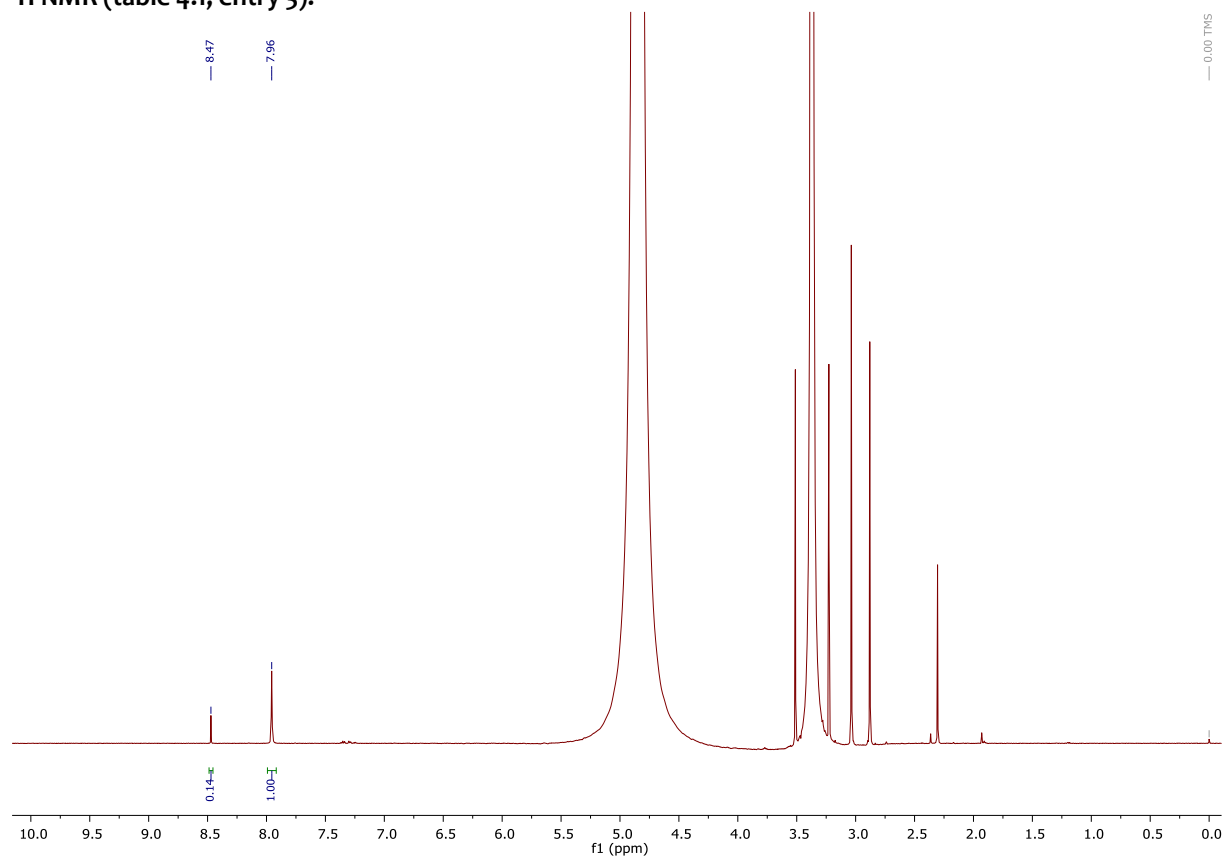
¹H NMR (table 4.1, entry 1):



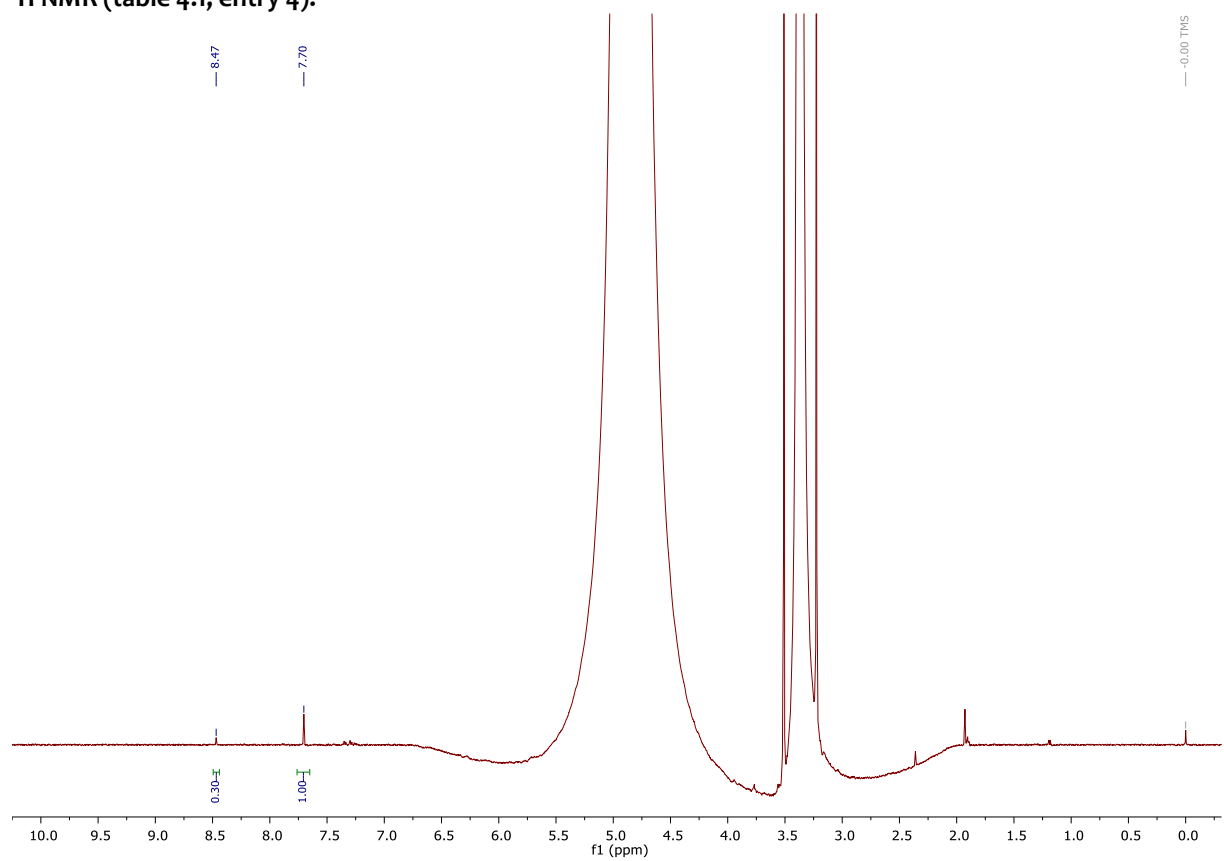
¹H NMR (table 4.1, entry 2):



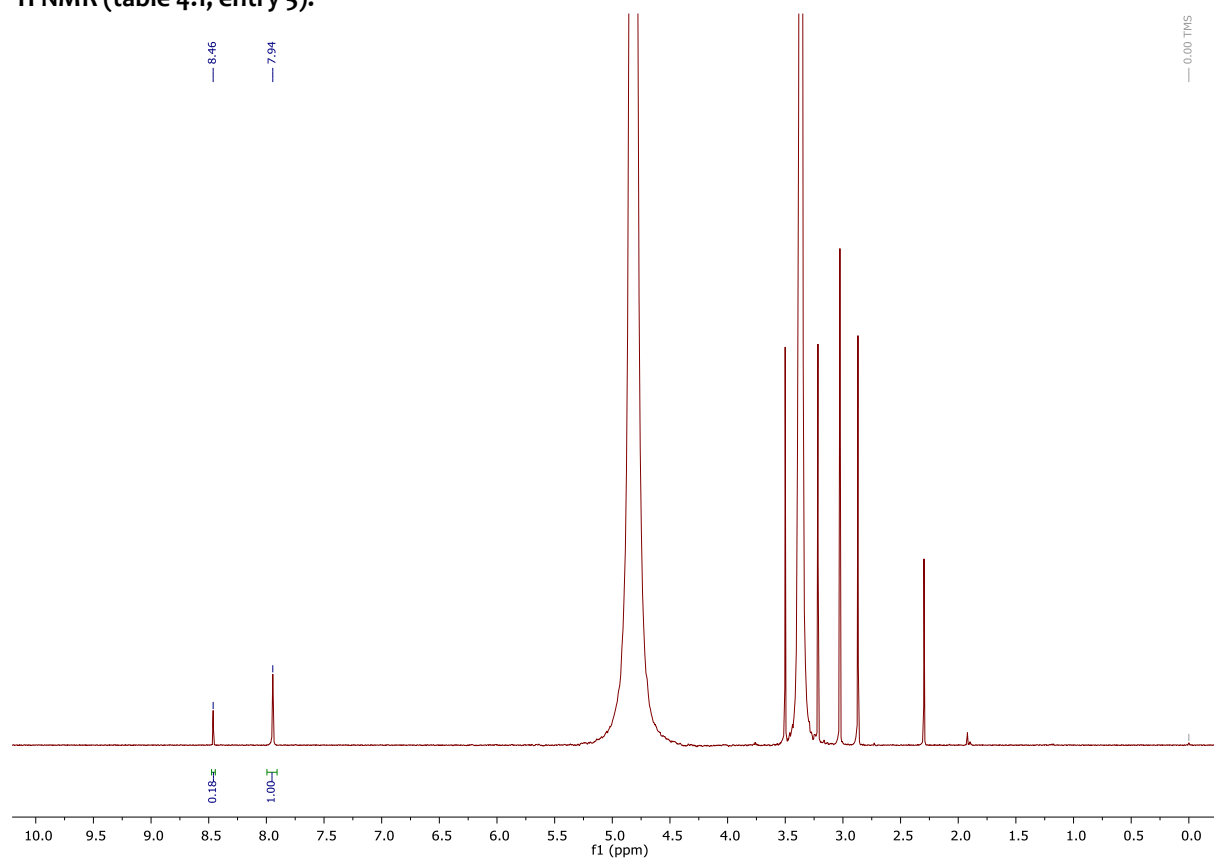
¹H NMR (table 4.1, entry 3):



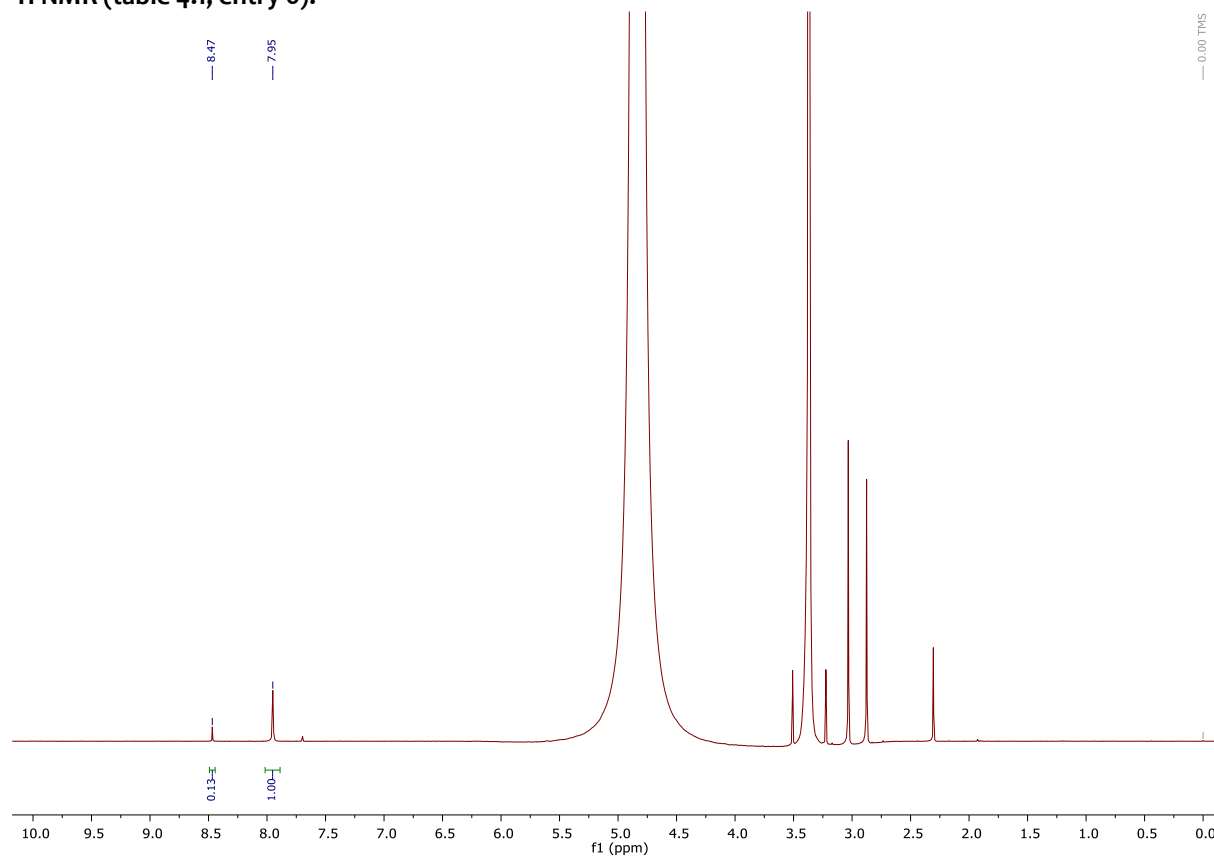
¹H NMR (table 4.1, entry 4):



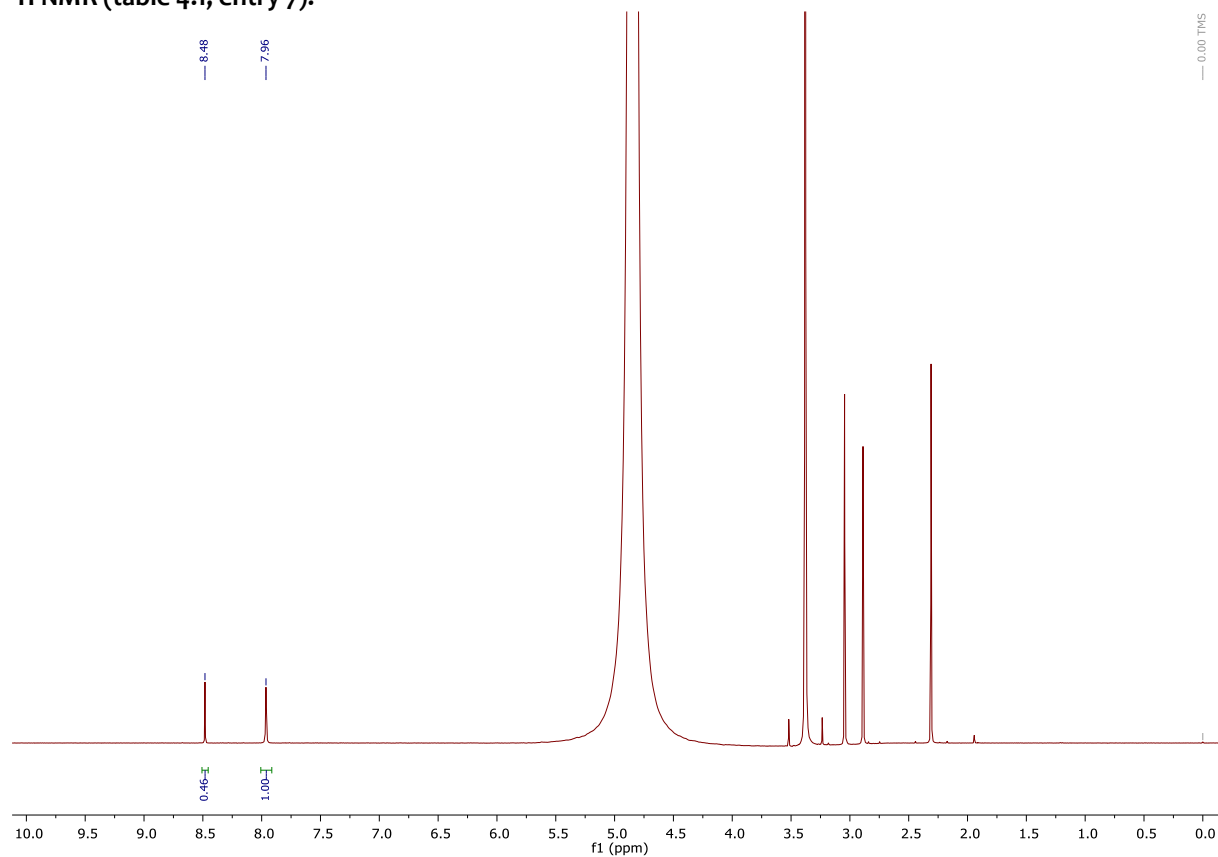
¹H NMR (table 4.1, entry 5):



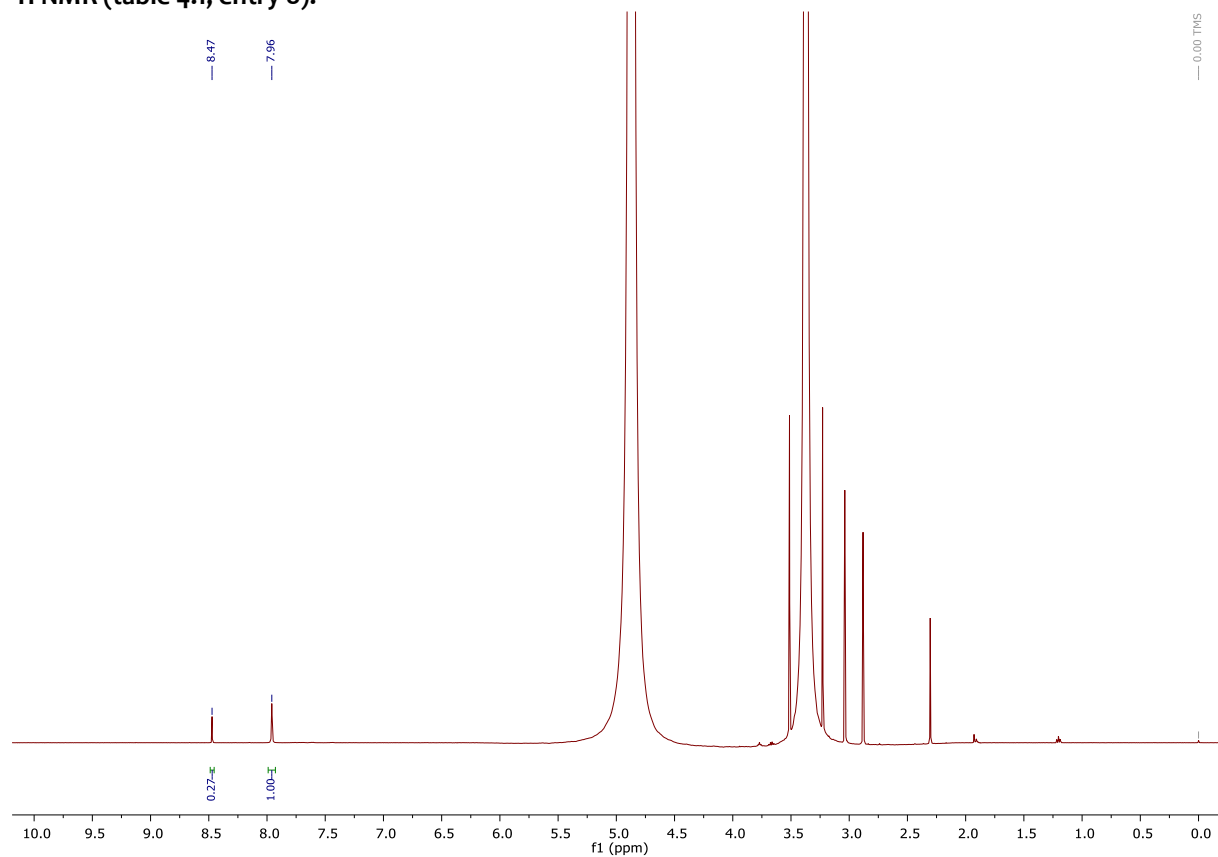
¹H NMR (table 4.1, entry 6):



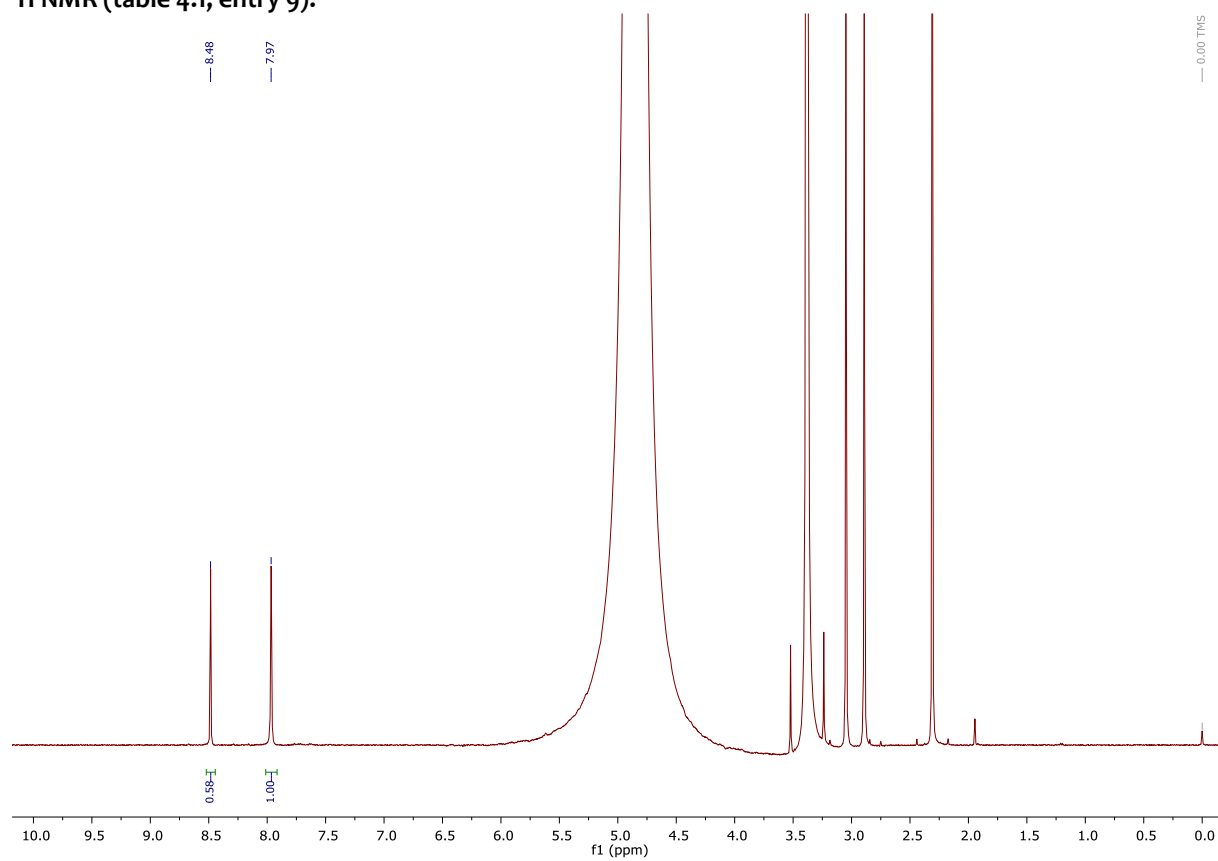
¹H NMR (table 4.1, entry 7):



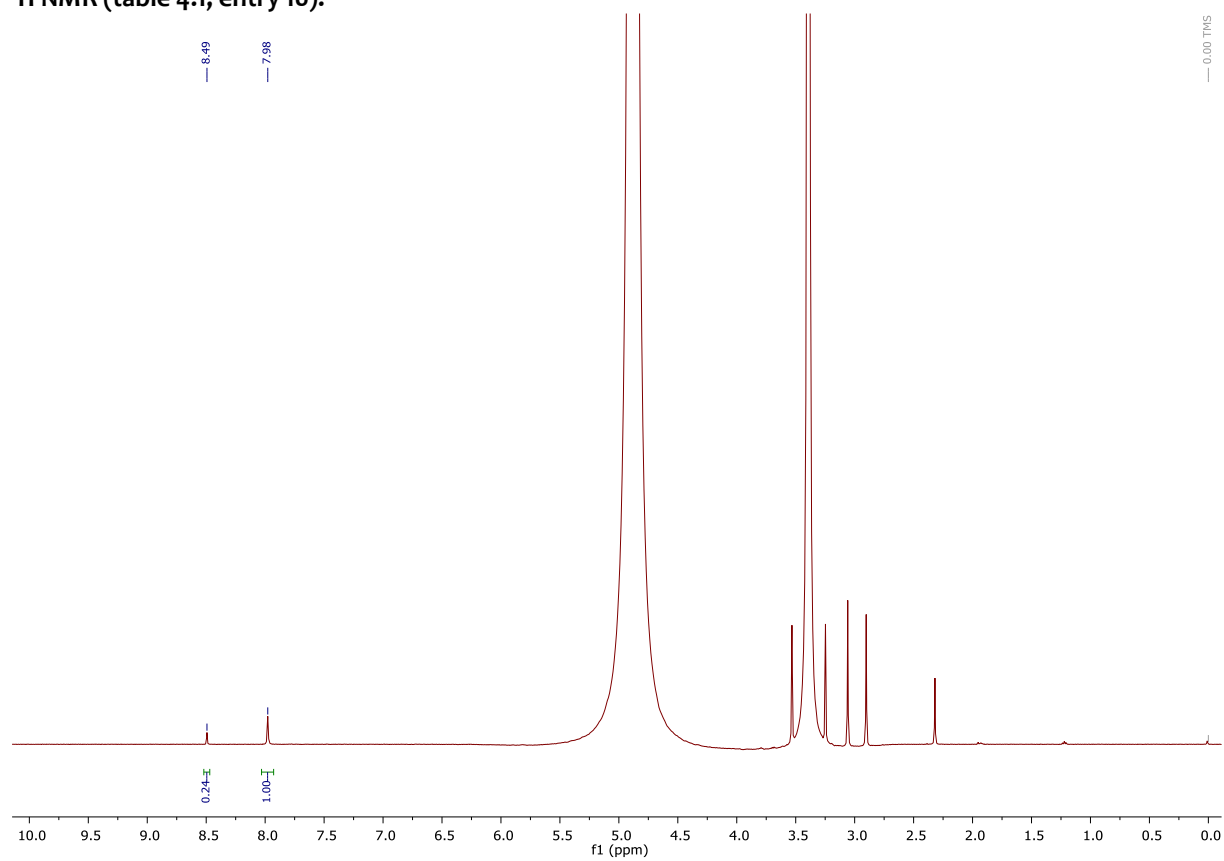
¹H NMR (table 4.1, entry 8):



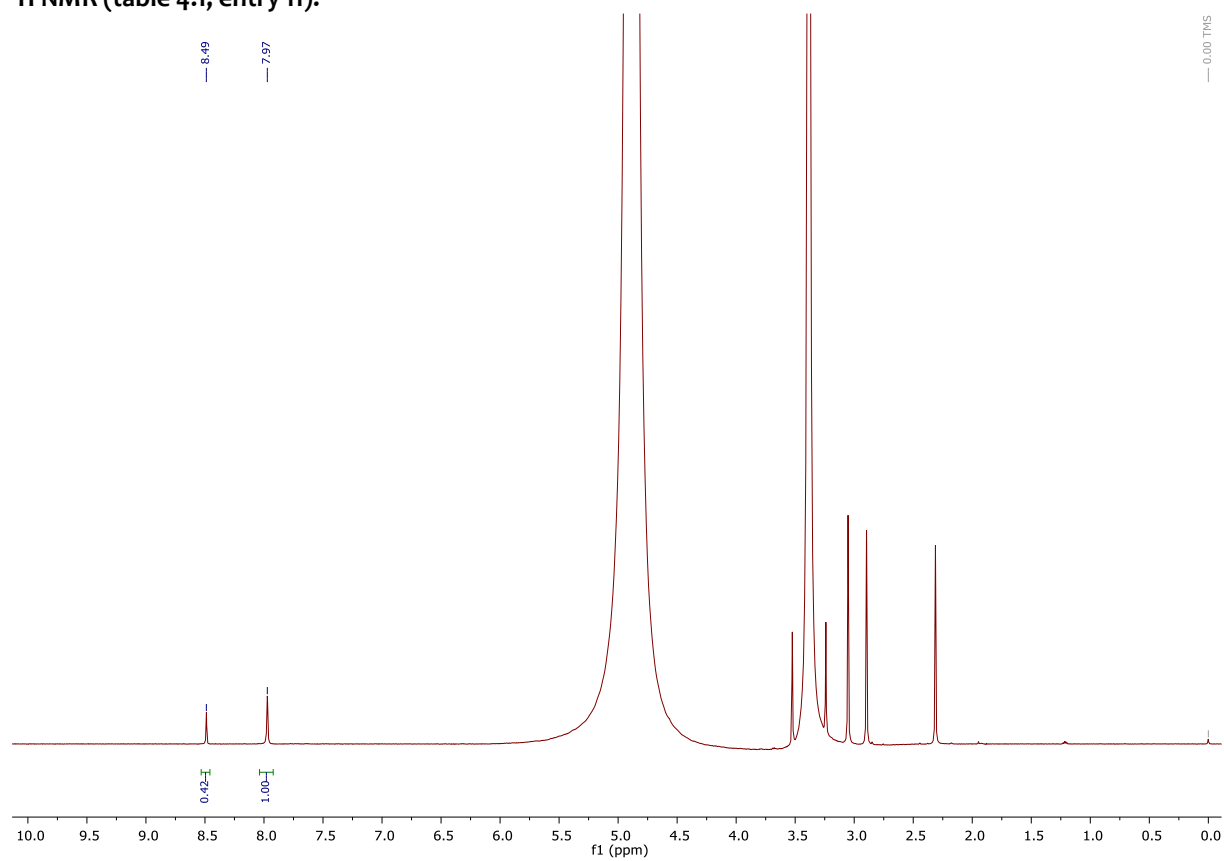
¹H NMR (table 4.1, entry 9):



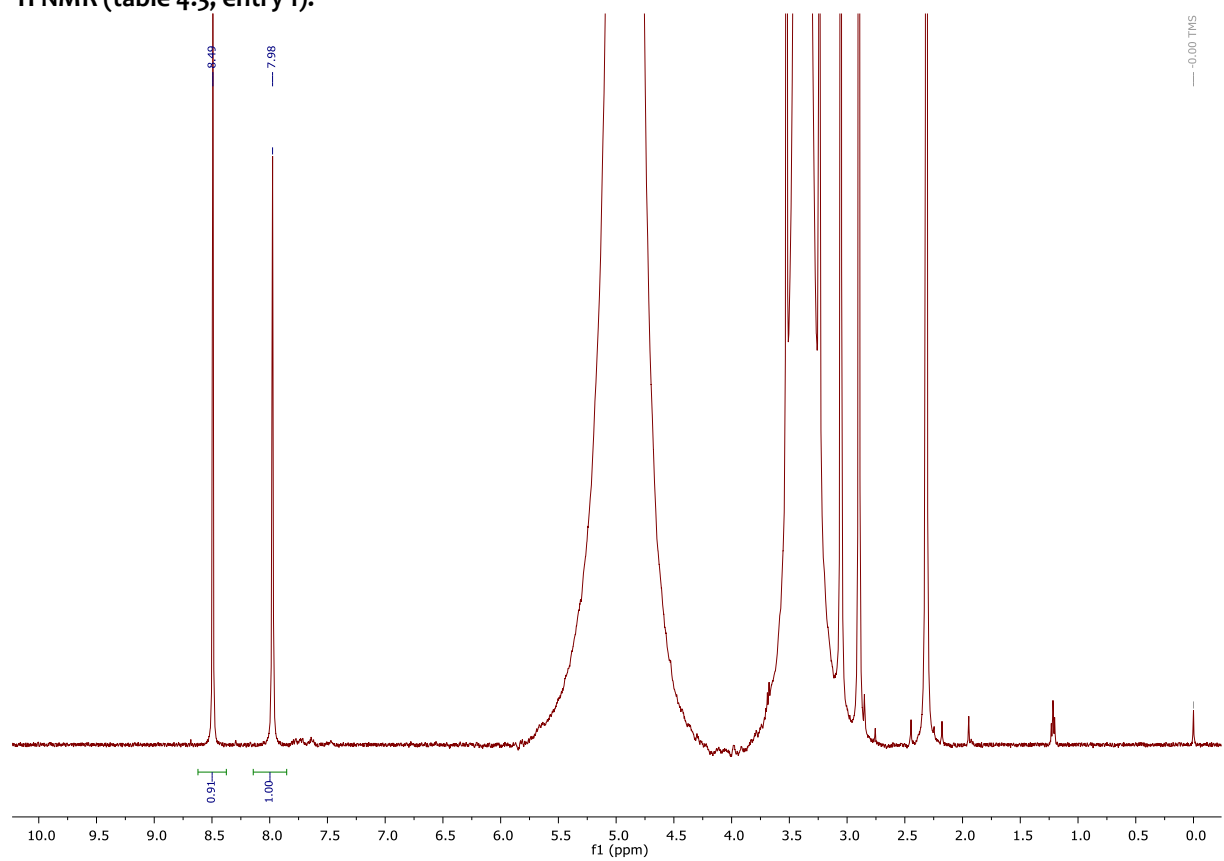
¹H NMR (table 4.1, entry 10):



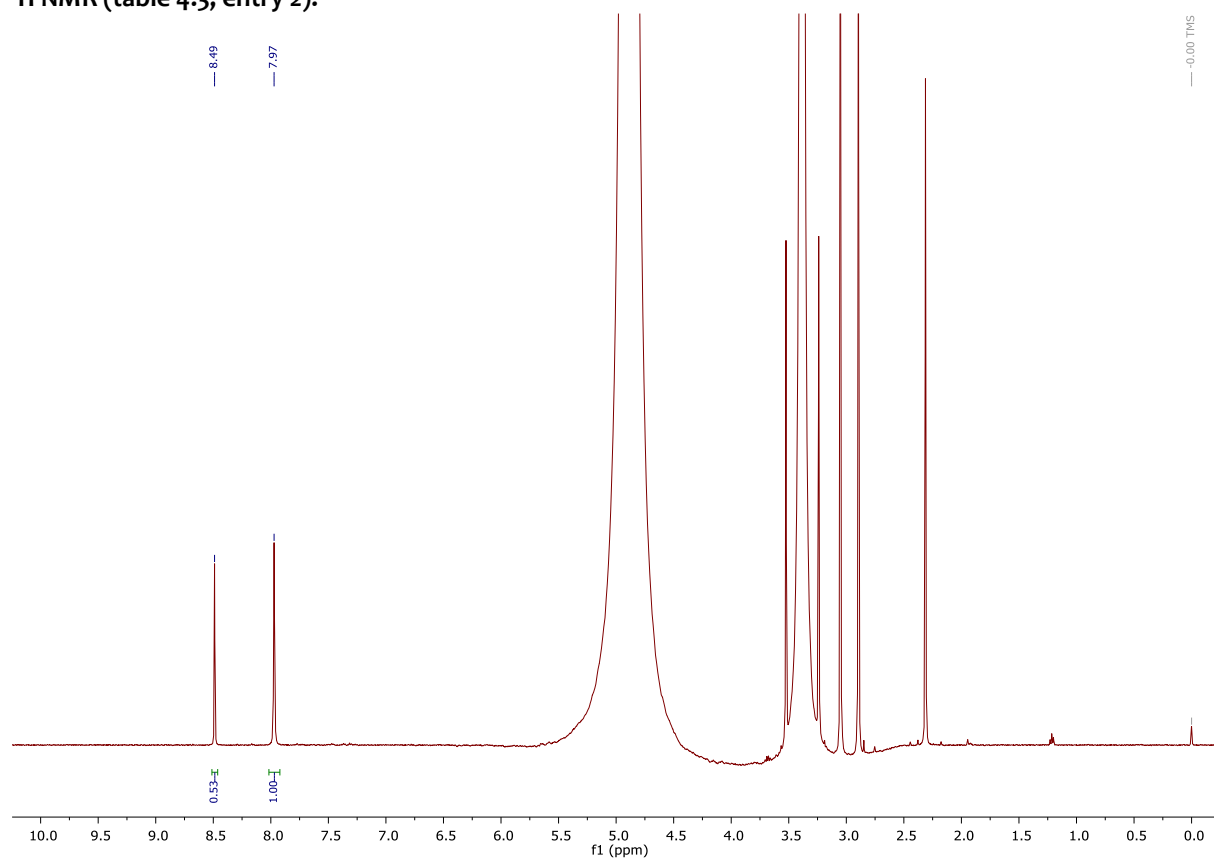
¹H NMR (table 4.1, entry 11):



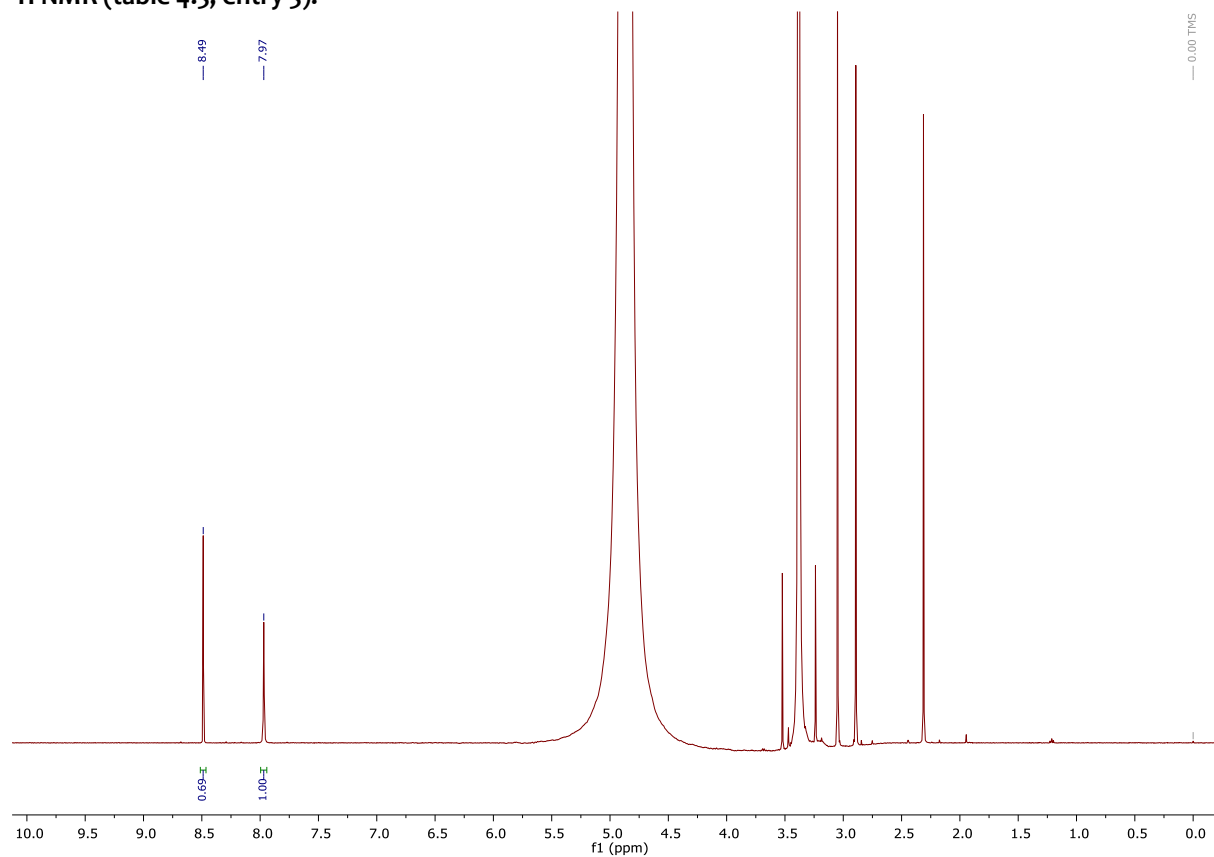
¹H NMR (table 4.3, entry 1):



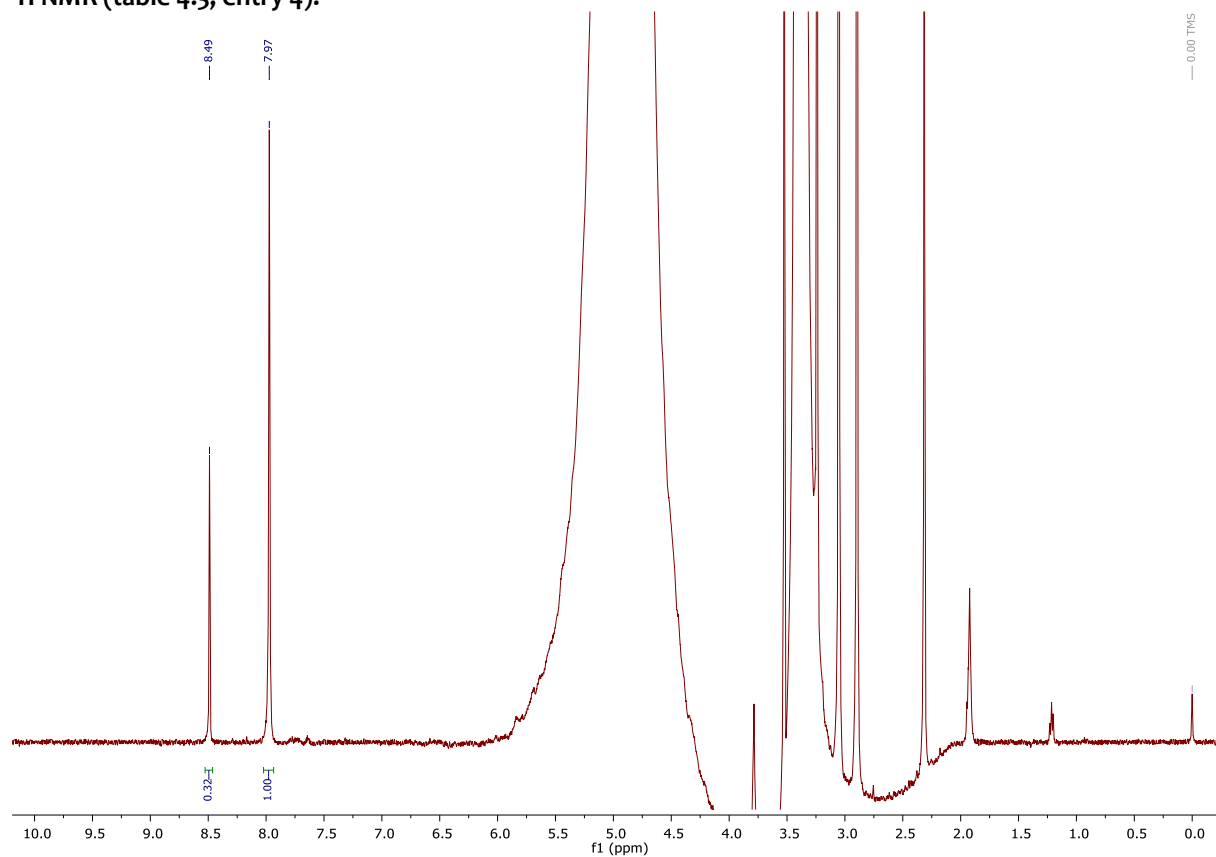
¹H NMR (table 4.3, entry 2):



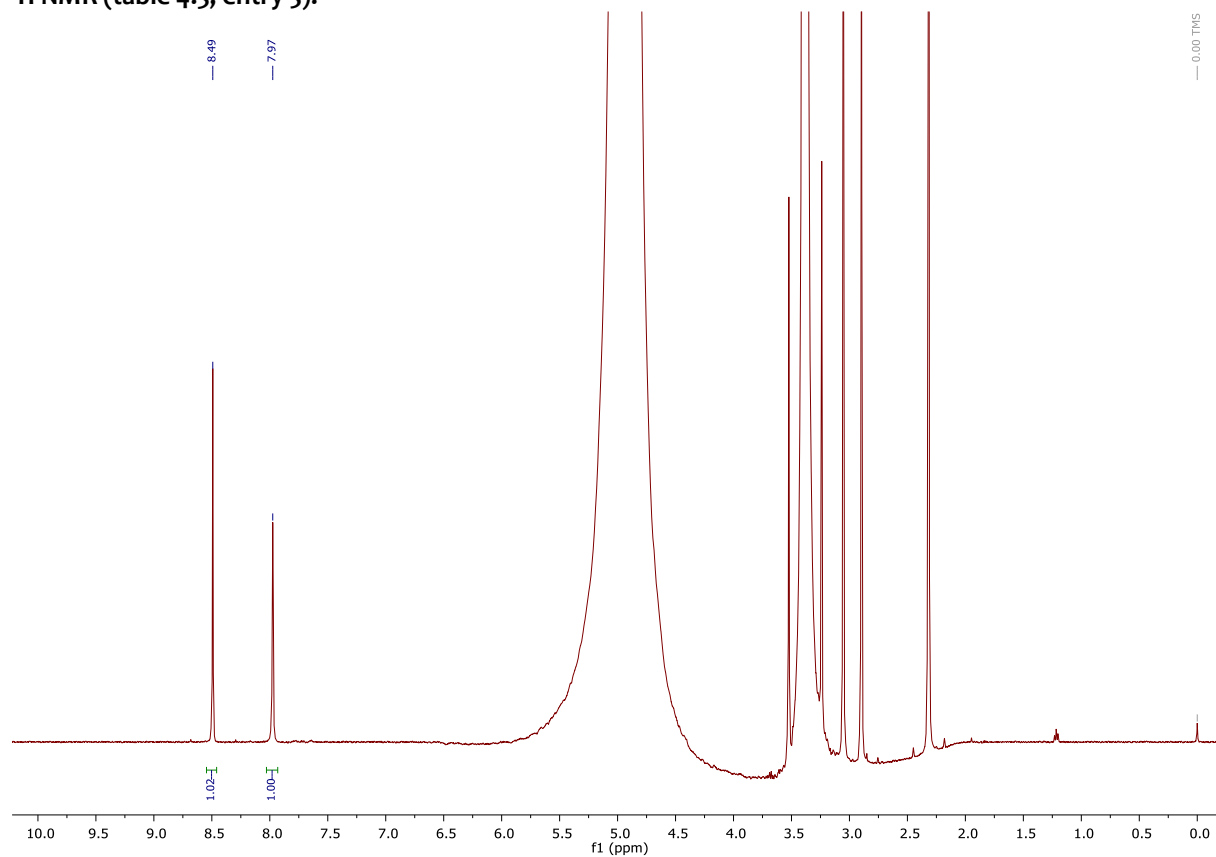
¹H NMR (table 4.3, entry 3):



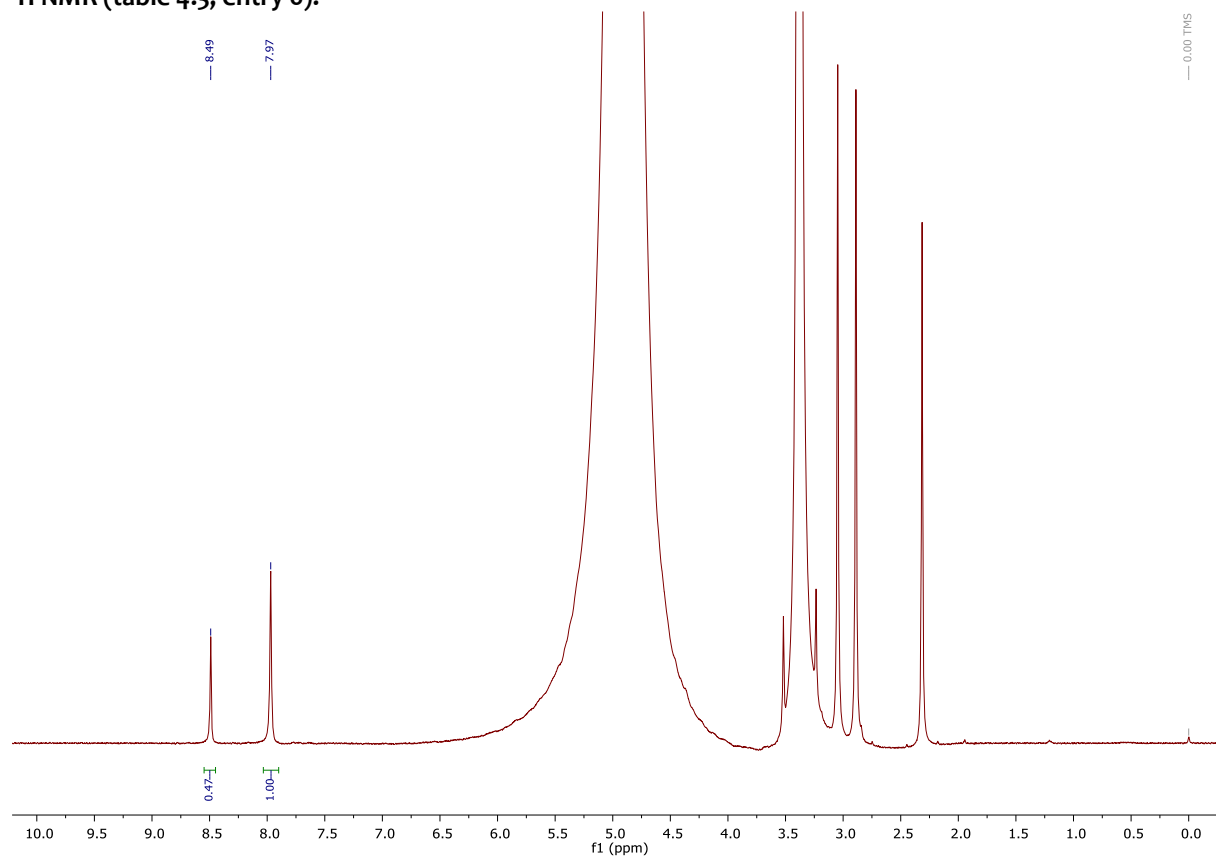
¹H NMR (table 4.3, entry 4):



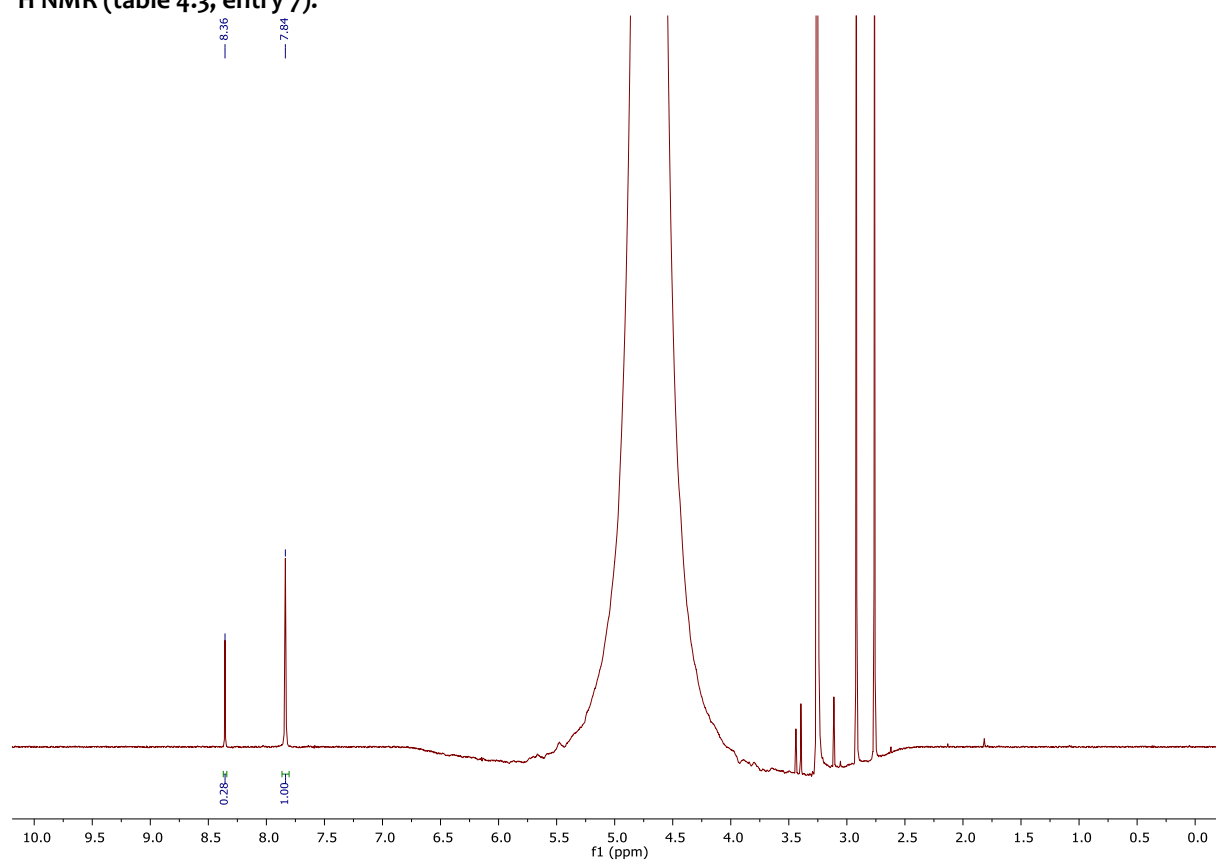
¹H NMR (table 4.3, entry 5):



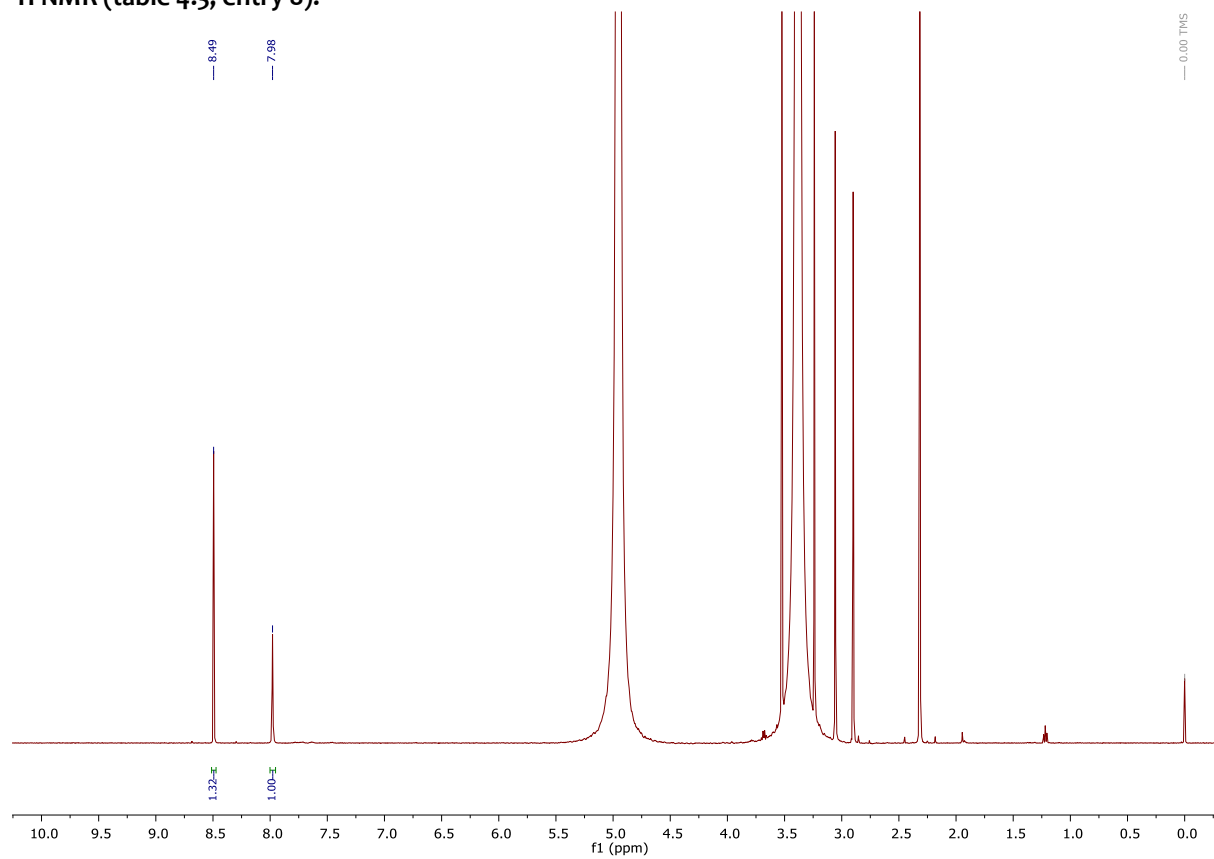
¹H NMR (table 4.3, entry 6):



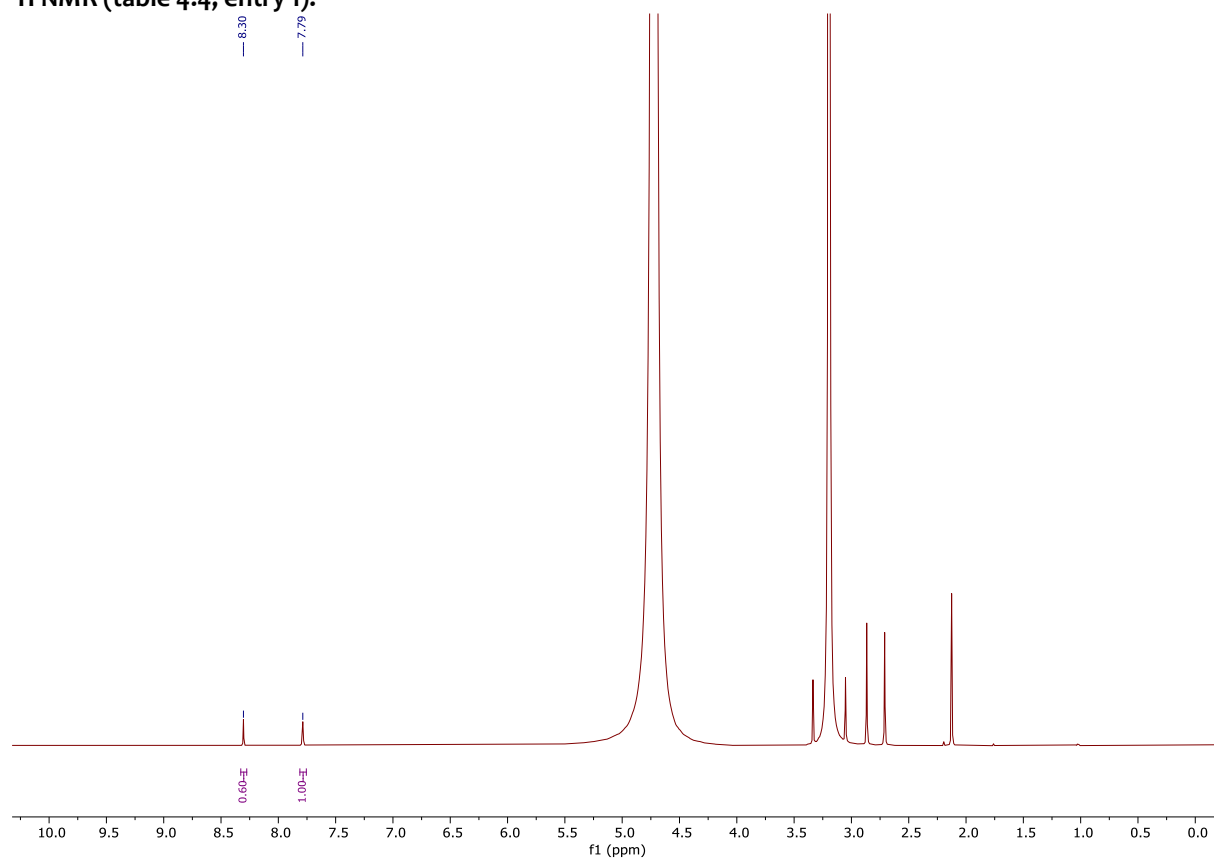
¹H NMR (table 4.3, entry 7):



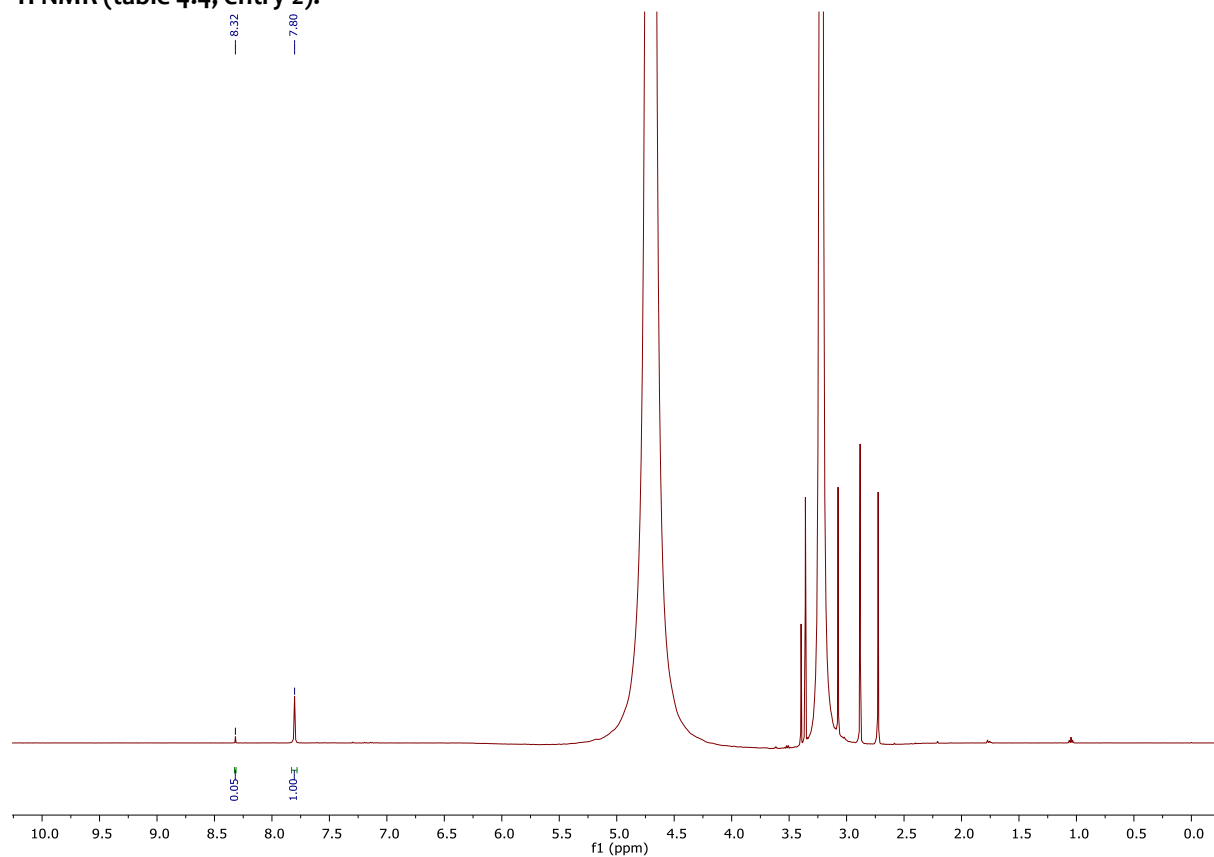
¹H NMR (table 4.3, entry 8):



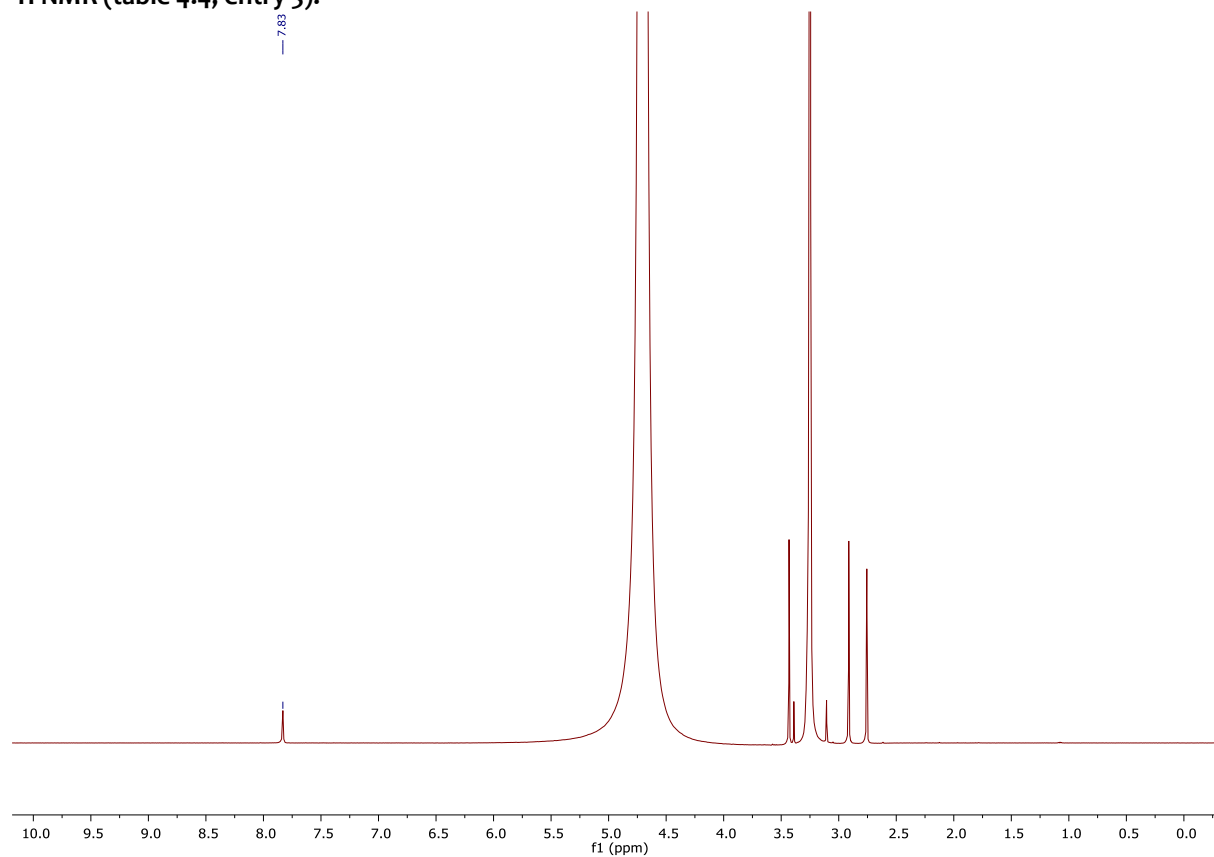
¹H NMR (table 4.4, entry 1):



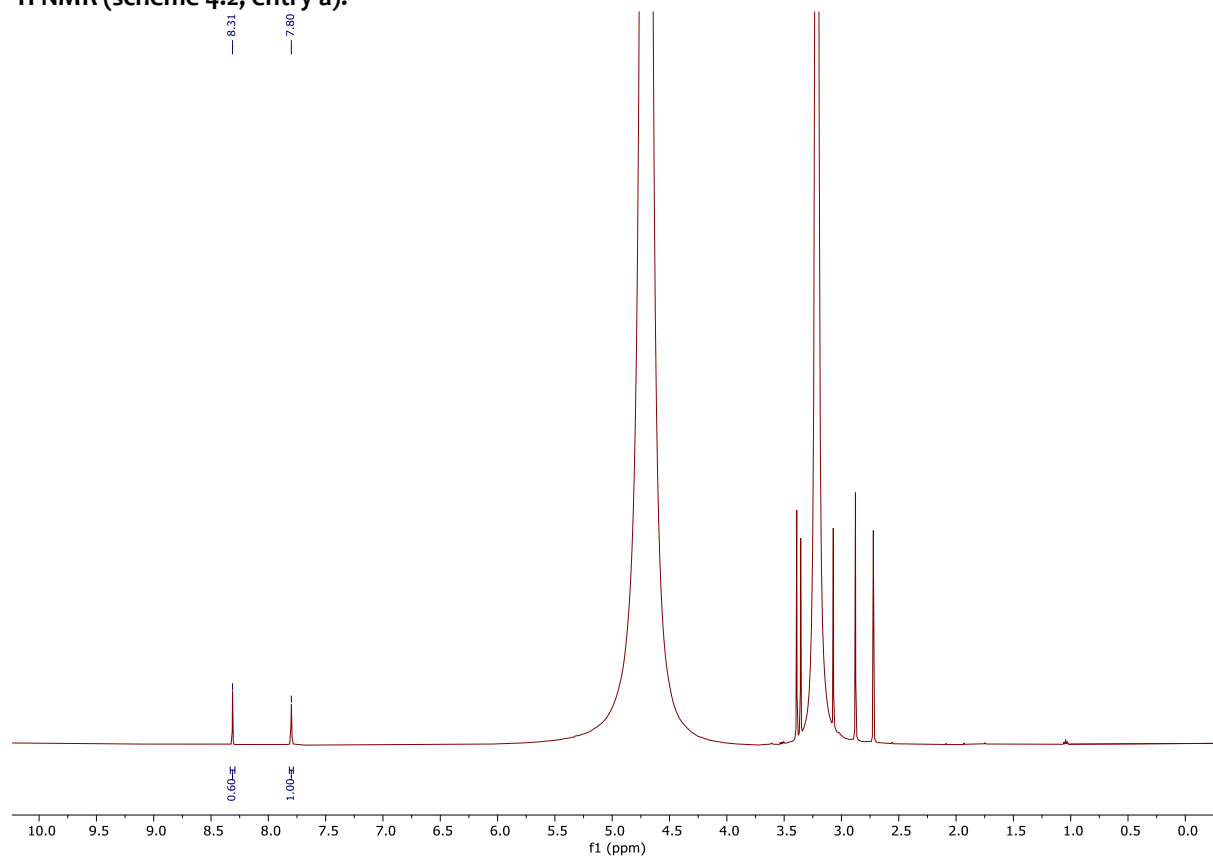
¹H NMR (table 4.4, entry 2):



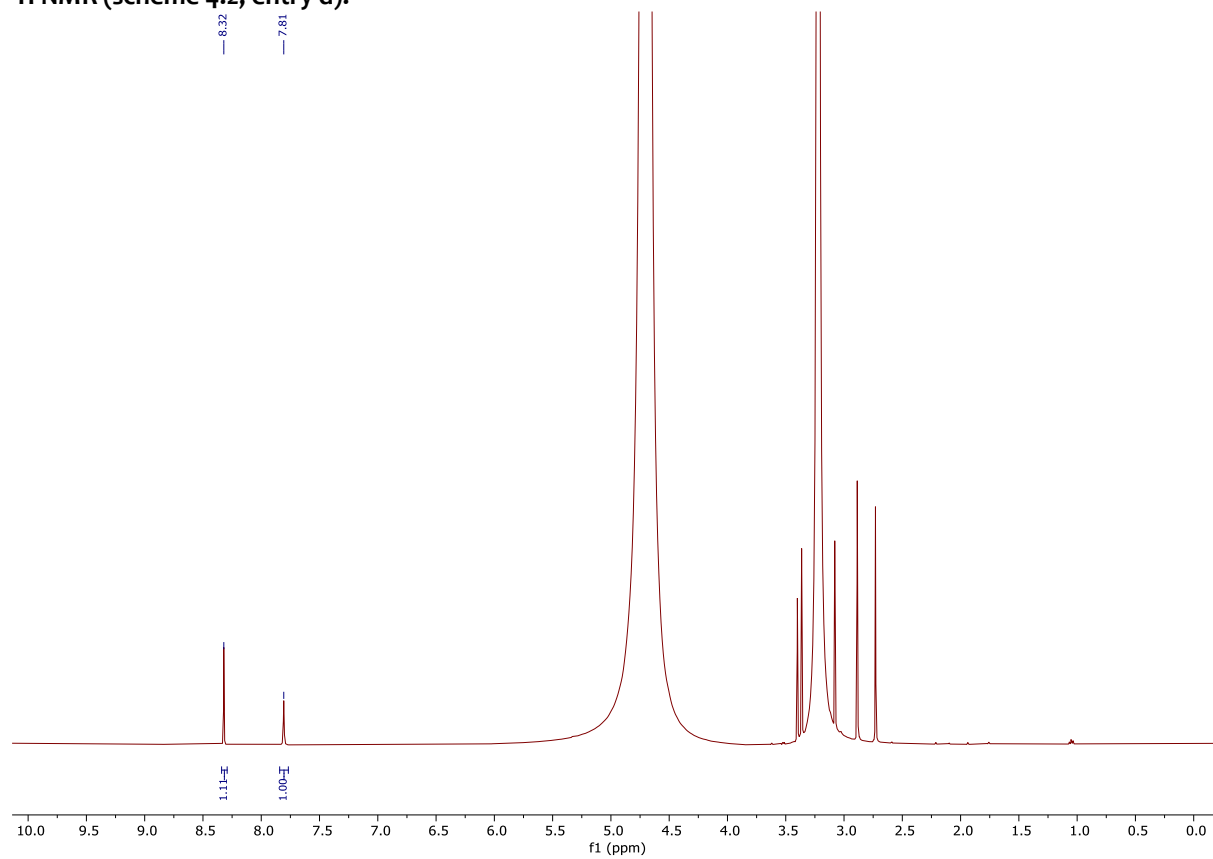
¹H NMR (table 4.4, entry 3):



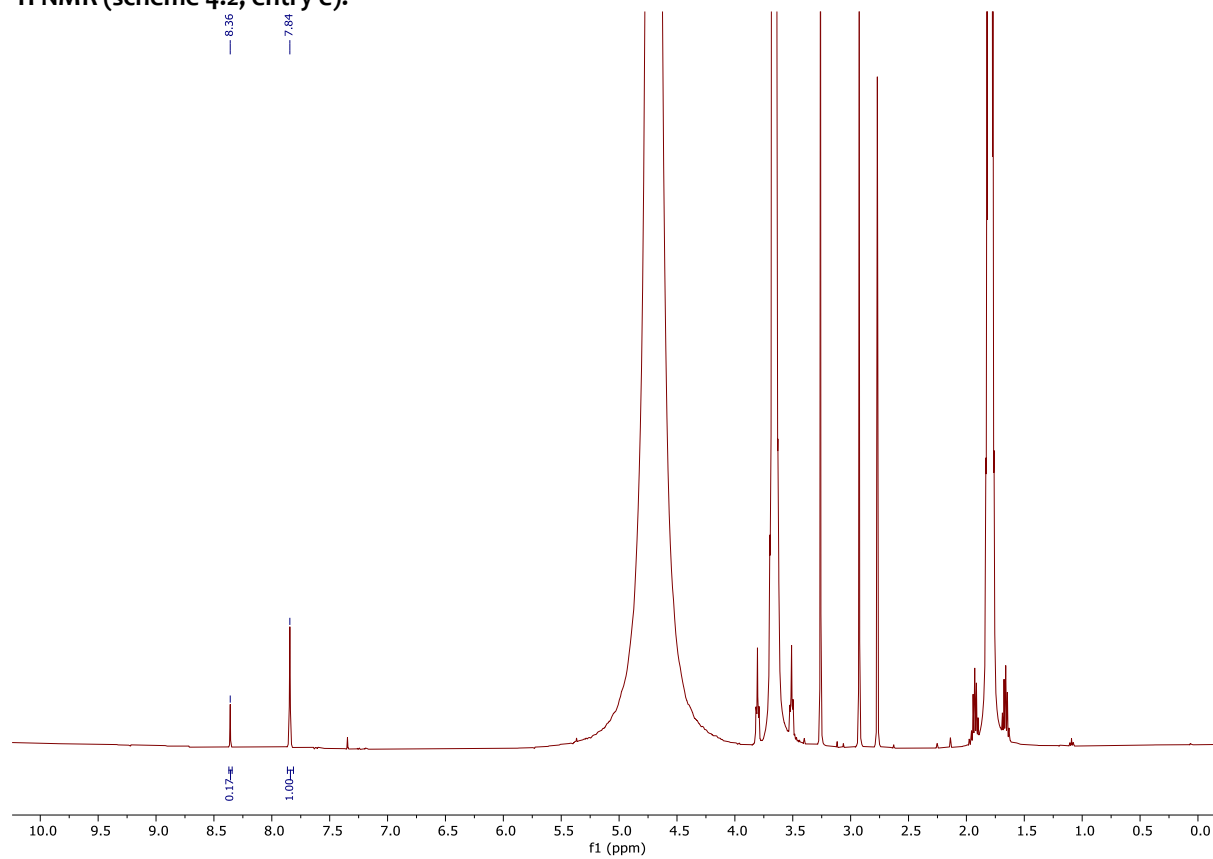
¹H NMR (scheme 4.2, entry a):



¹H NMR (scheme 4.2, entry d):



¹H NMR (scheme 4.2, entry e):



¹H NMR (scheme 4.2, entry f):

