Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Homogeneous hydrogenation of saturated bicarbonate slurry to formates using multiphase catalysis

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Supplementary Methods

All manipulations were, unless stated otherwise, performed under inert atmosphere in an argon filled glovebox (INERT) or using standard Schlenk techniques. Anhydrous solvents were either dispensed from an Inert PureSolv solvent purification system or dried using 3/4 Å molecular sieves and were degassed before use. Chemicals were purchased from Sigma-Aldrich, Strem, abcr, or TCI. Air and/or moisture sensitive materials were stored in the glovebox. Deuterated solvents were purchased from Eurisotop, dried using molecular sieves, degassed and stored in the glovebox.

NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer equipped with a 5 mm ONE NMR probe. All ^{13}C and ^{31}P NMR spectra were recorded with 1H decoupling. All chemical shifts were referenced to residual solvent peaks [D2O: 4.79 ppm (^{1}H), CDCl3: 7.26 ppm (^{1}H), 77.2 ppm (^{13}C)].

Elemental analyses were performed by Mikroanalytisches Laboratorium Kolbe, Oberhausen, Germany.

Complex **1** was prepared according to a literature procedure.[1]

General procedure for catalytic hydrogenation of CO_2 in presence of KOH

Stock solutions of **1** (0.012 M) were prepared in dimethylformamide solvent. In a typical run, potassium hydroxide, methyltrioctylammonium chloride (24 mg, 55 μmol), toluene (1 mL), water (1 mL) and appropriate amount of the stock solution of complex **1** were combined in this order in a 4 mL glass vial equipped with a rare-earth stirring bar and transferred into a stainless steel autoclave in the glovebox. The system was purged with argon (5 × 8 bar) and H_2 (7 × 10 bar), pressurized with H_2 to 3 bar, and heated to specified temperature, after which the H_2 and CO_2 were regulated to the desired pressure. After the desired reaction time, the autoclave was cooled and the pressure released, after which DMSO was added as an internal standard (100 μL, 1.408 mmol). A 100 μL aliquot of the H_2O layer was dissolved in D_2O and the yield determined by ^{1}H NMR analysis.

General procedure for catalytic hydrogenation of potassium bicarbonate

Stock solutions of **1** (0.012 M) were prepared in dimethylformamide solvent. In a typical run, potassium bicarbonate, methyltrioctylammonium chloride (24 mg, 55 μmol), toluene (1 mL), water (1 mL) and appropriate amount of the stock solution of complex **1** were combined in this order in a 4 mL glass vial equipped with a rare-earth stirring bar and transferred into a stainless steel autoclave in the glovebox. The system was purged with argon (5 × 8 bar) and H_2 (7 × 10 bar), pressurized with H_2 to 5 bar, and heated to specified temperature, after which the H_2 was regulated to the desired pressure. After the desired reaction time, the autoclave was cooled and the pressure released, after which DMSO was added as an internal standard (100 μL, 1.408 mmol). A 100 μL aliquot of the H_2O layer was dissolved in D_2O and the yield determined by ^{1}H NMR analysis.

NOTE: Reported TON and TOF values are calculated on the basis of the formate molecules produced in reaction run. Due to the low solubility, consumption of $KHCO_3$ should not be used as a main indicator of reaction progress.

Isolation of formate product:

Potassium formate product can be readily isolated from the reaction mixture in the following way:

After the catalytic reaction (Entry 5, table 4) the aqueous and toluene layers are separated. Ethanol (4 mL) is added to the water layer until no precipitation of potassium bicarbonate is observed. The resulting suspension is filtered and washed with ethanol. Removal of the solvents results in 273 mg of potassium

formate (3.25 mmol, 65% yield vs 67% in catalysis, 97% recovery). No potassium bicarbonate was observed in ^{13}C NMR, no other products are observed in ^{1}H NMR.

Elemental analysis:

ICP-MS measurements of the water and toluene layer after reaction show that more than 96% of Ru is present in toluene (96.8% in toluene, 3.2 % in water). Conditions identical to those in Table 4, Entry 1 of the manuscript

^{1}H NMR data accompanying data provided in Table 1

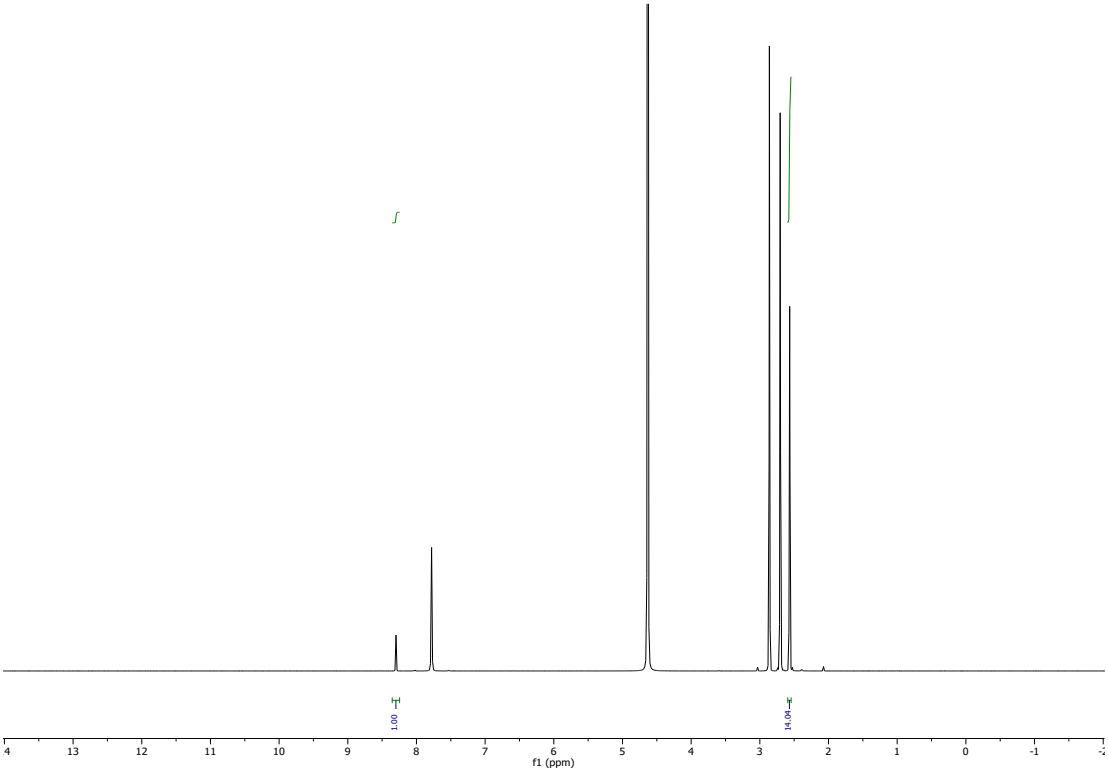

Figure S1. NMR data belonging to table 1, entry 1.

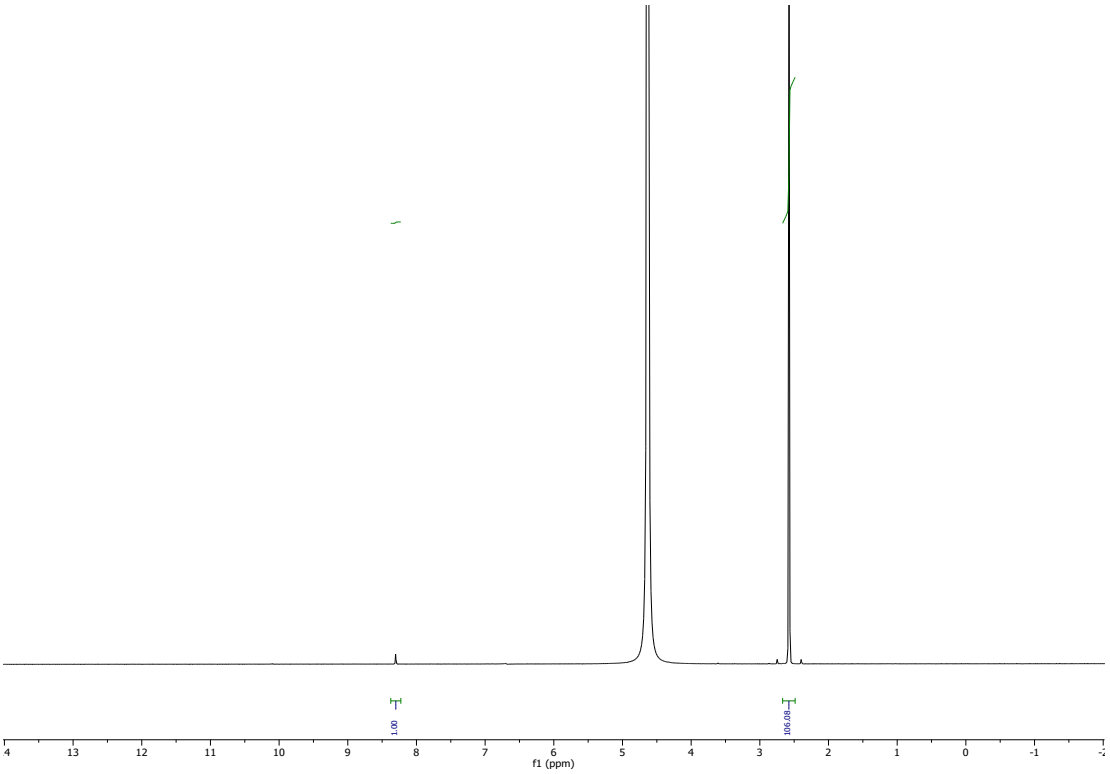

Figure S2. NMR data belonging to table 1, entry 2.

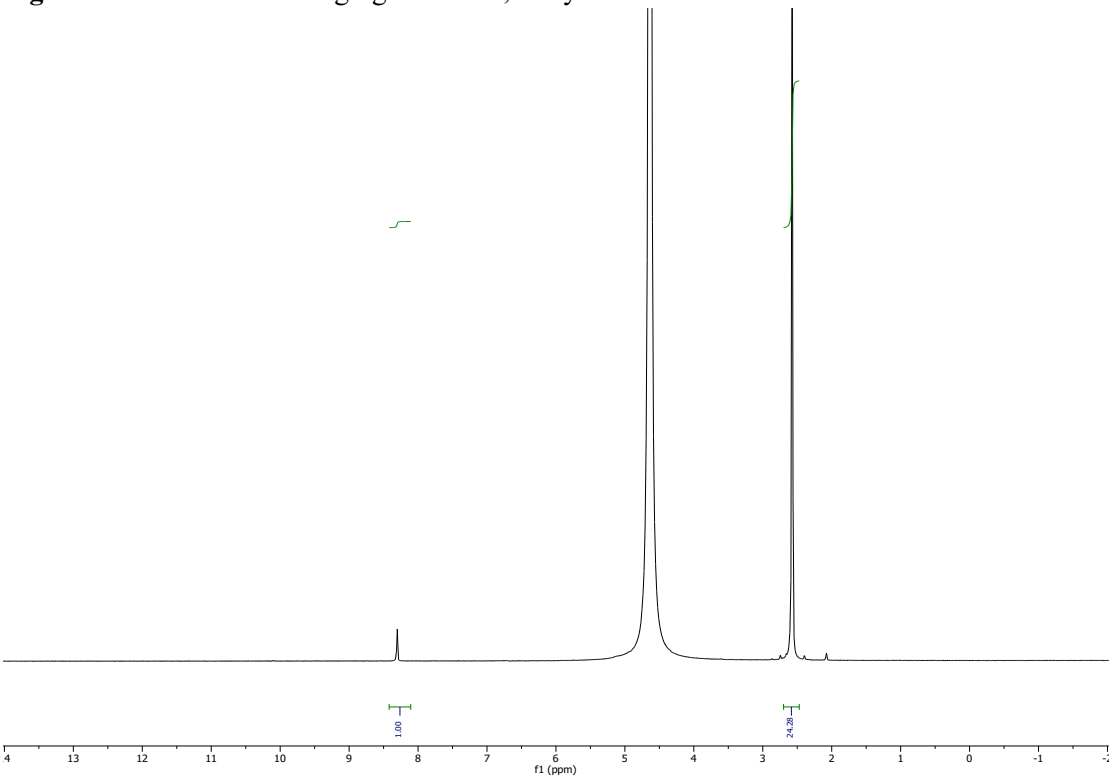

Figure S3. NMR data belonging to table 1, entry 3.

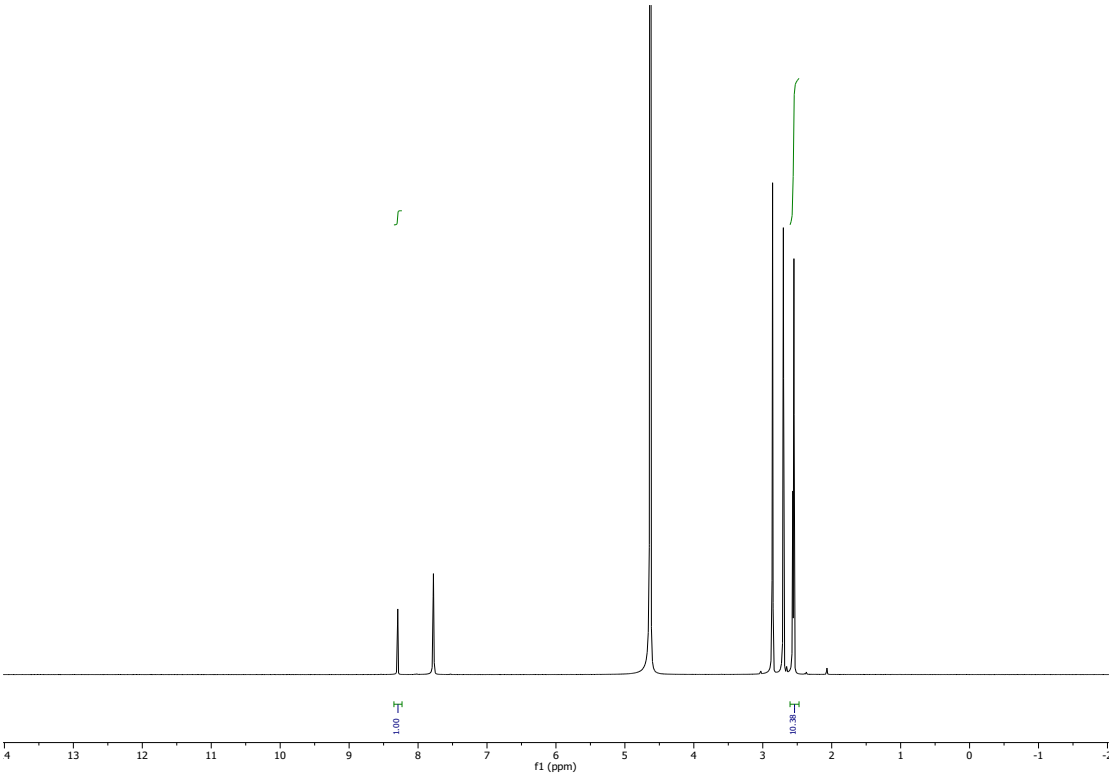

Figure S4. NMR data belonging to table 1, entry 4.

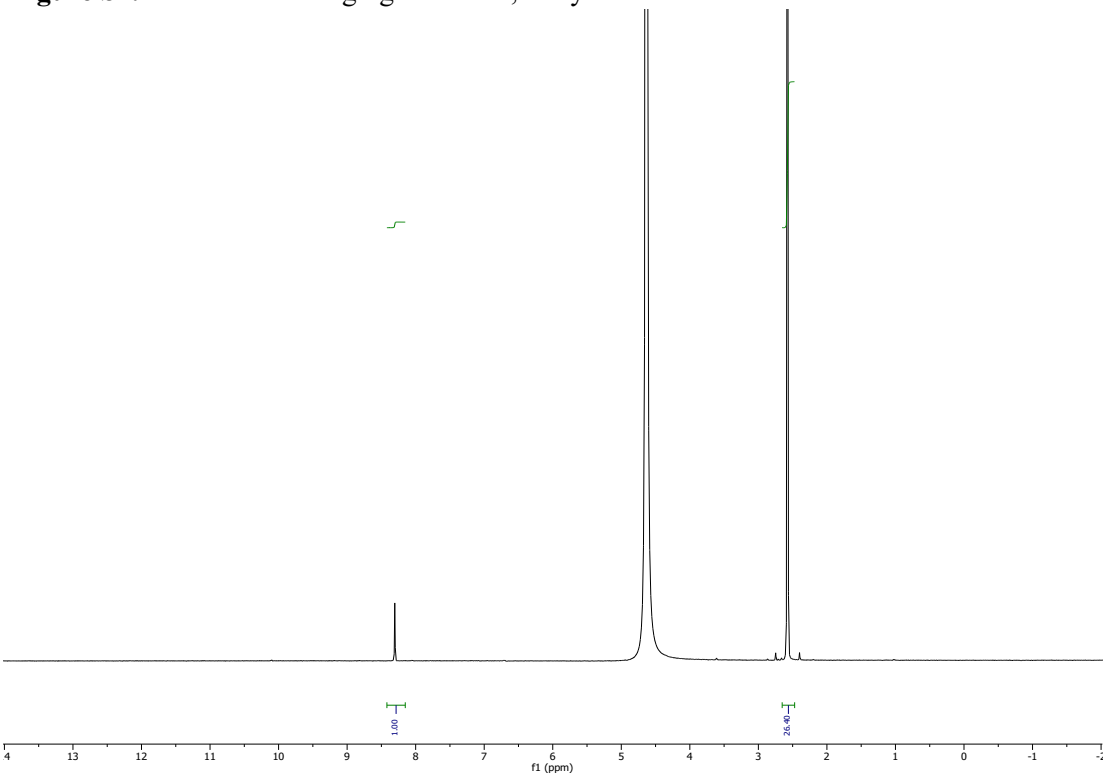

Figure S5. NMR data belonging to table 1, entry 5.

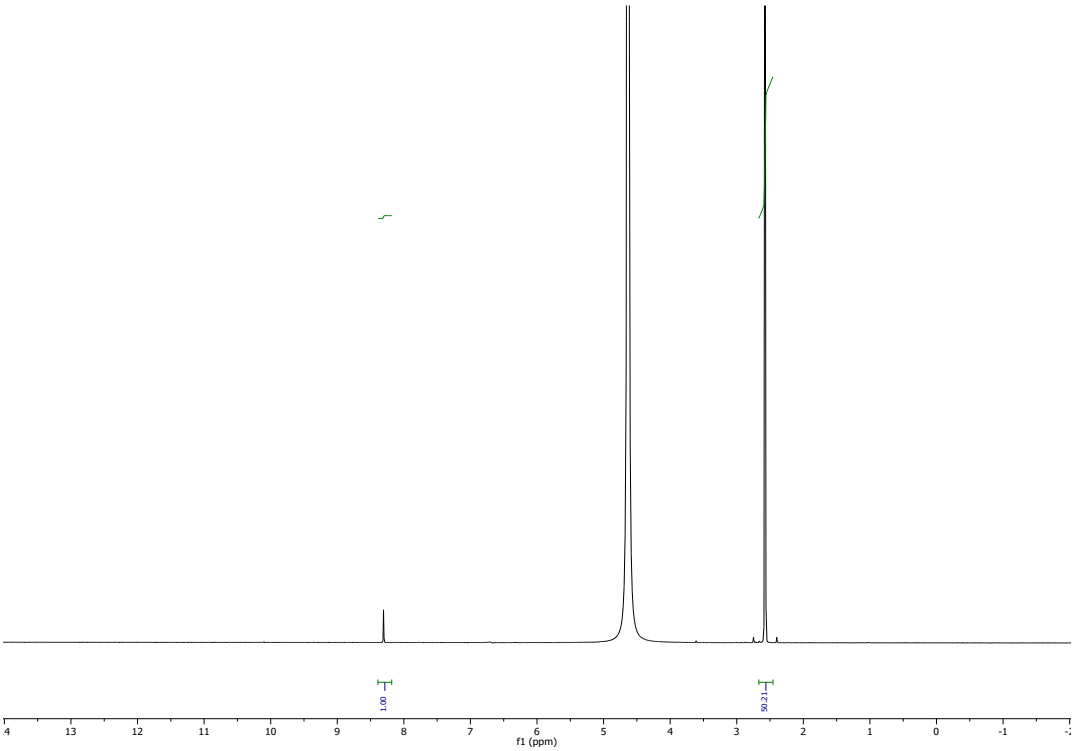

Figure S6. NMR data belonging to table 1, entry 6.

Table S1. ^{1}H NMR peak data belonging to table 1 (main text) and Figures S1-S6.

Entry	Ratio of DMSO to formate integral
1	14.04
2	24.28
3	106.08
4	10.38
5	26.40
6	50.21

^{1}H NMR data accompanying data provided in Table 2

NB: Entries 1-2 are covered in Figure S3 and Figure S6.

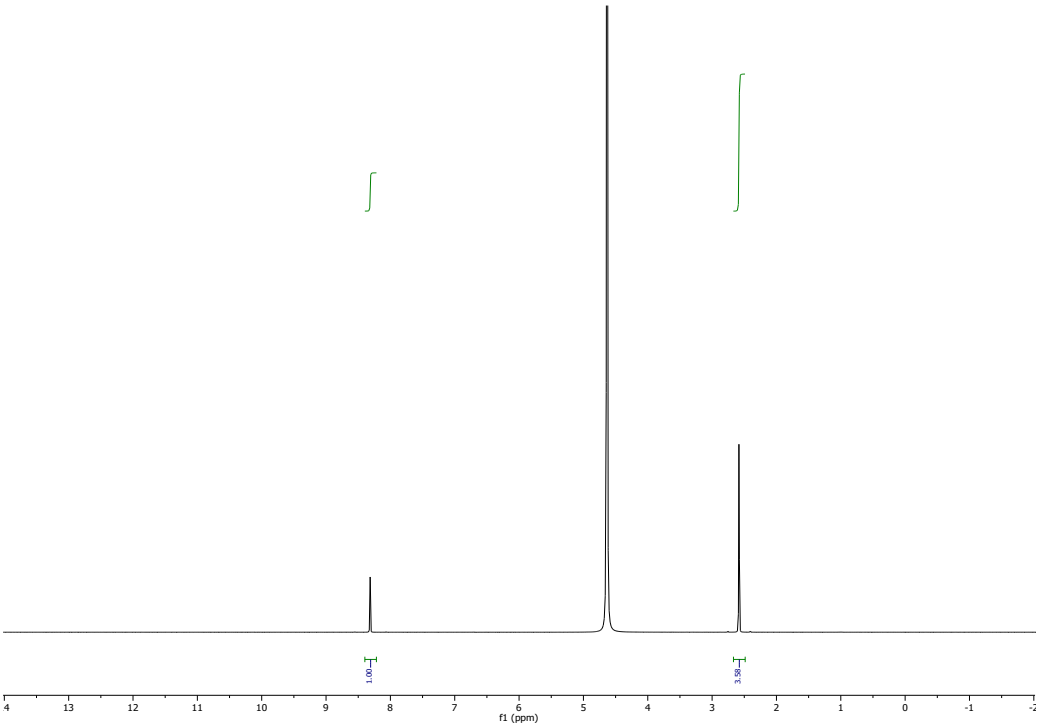

Figure S7. NMR data belonging to table 2, entry 3.

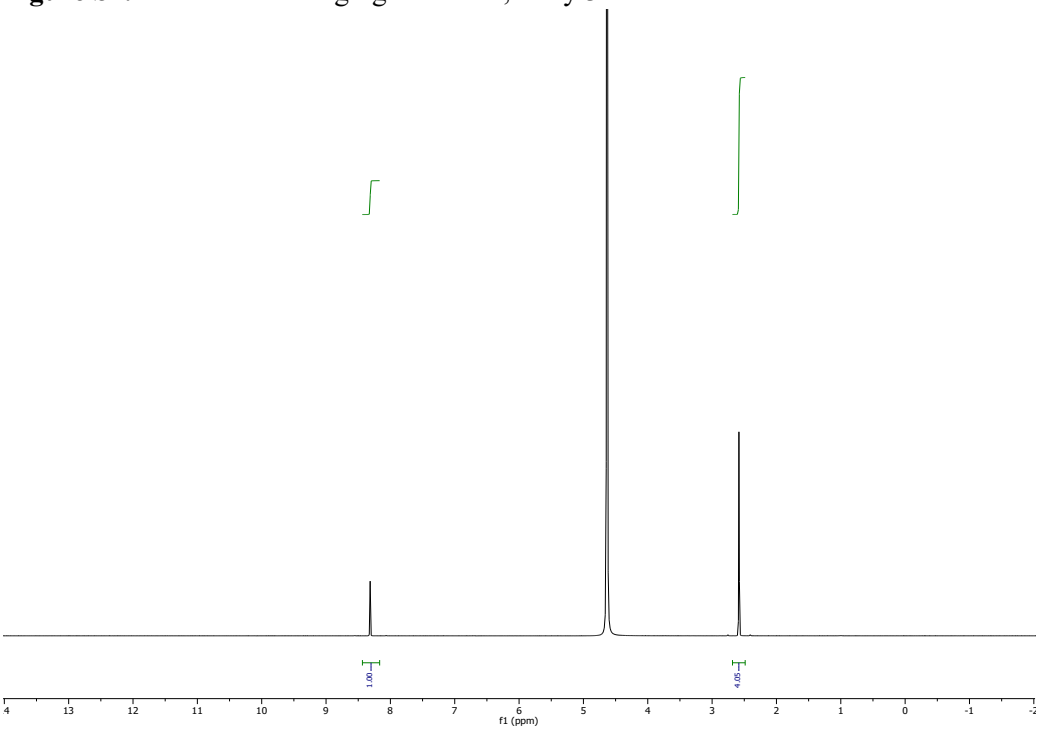

Figure S8. NMR data belonging to table 2, entry 4.

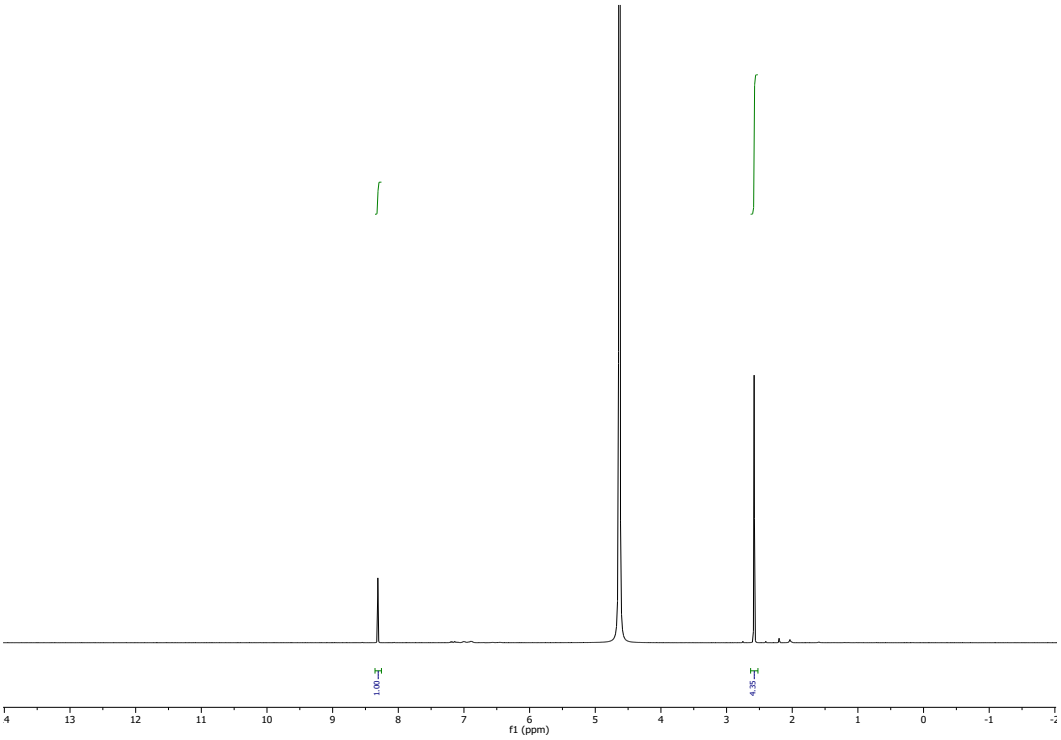

Figure S9. NMR data belonging to table 2, entry 5.

Table S2. ^{1}H NMR peak data belonging to table 2 (main text) and Figures S3 and S6-8.

Entry	Ratio of DMSO to formate integral
1	106.08
2	50.21
3	3.58
4	4.35
5	4.05

[1]H NMR Data belonging to table 3 (main text)

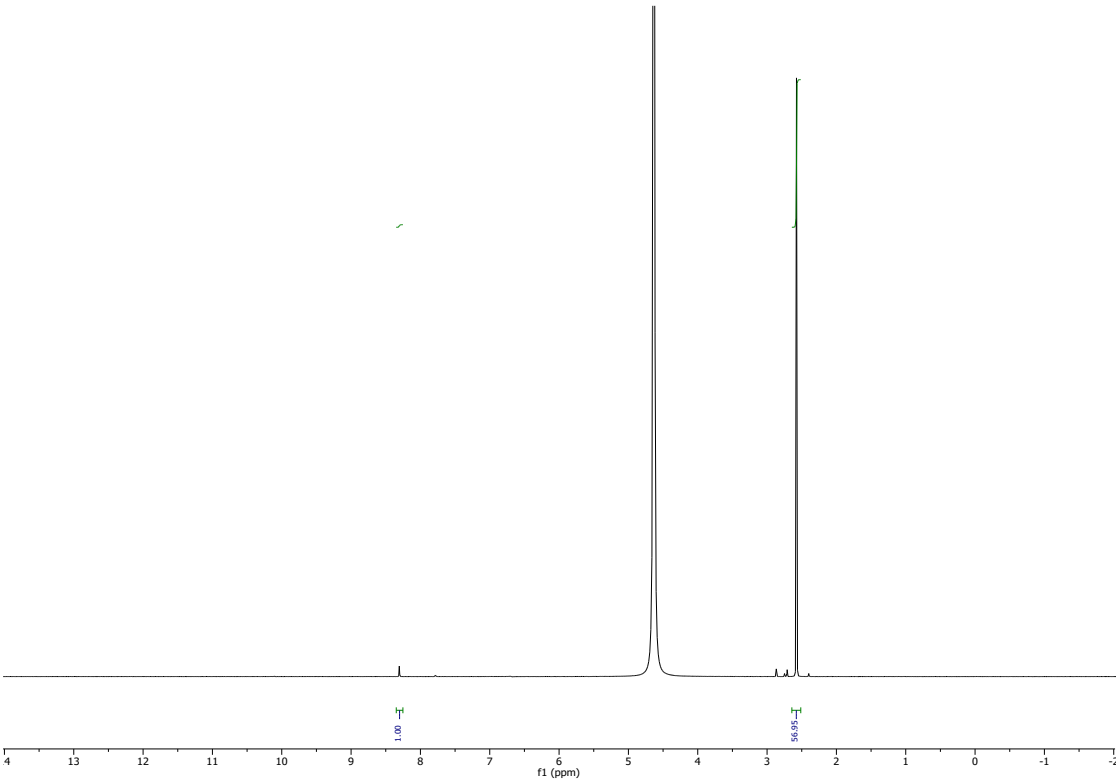

Figure S10. NMR data belonging to table 3, entry 1.

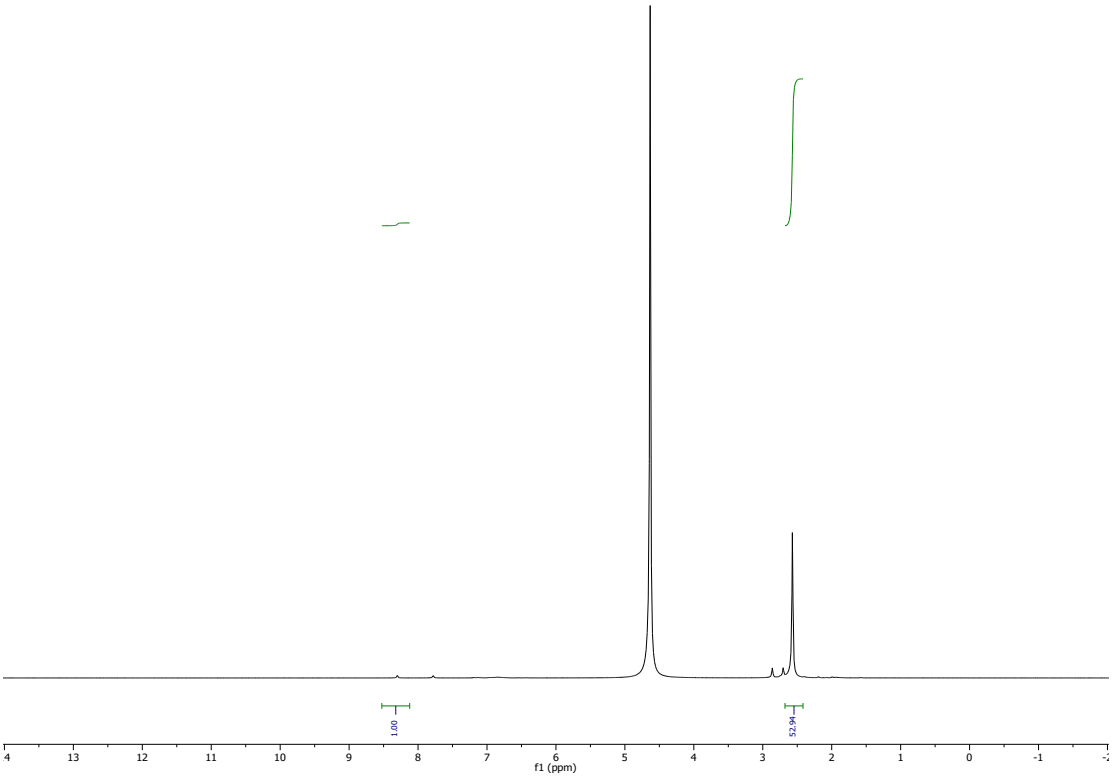

Figure S11. NMR data belonging to table 3, entry 2.

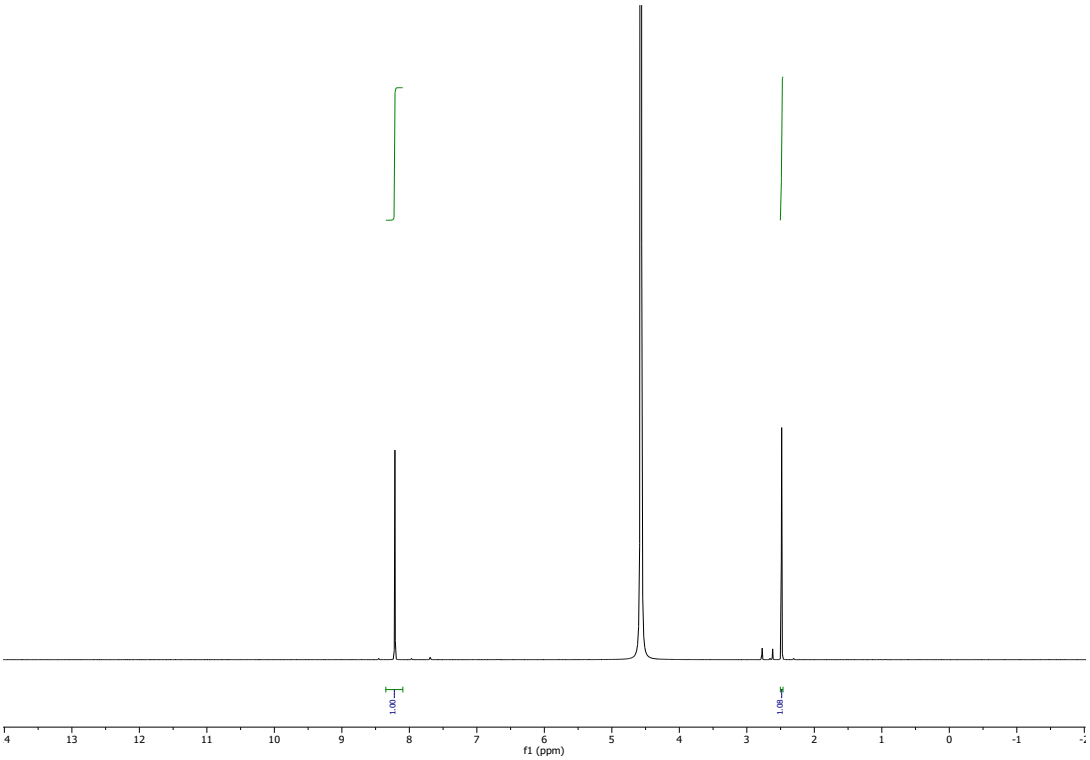

Figure S12. NMR data belonging to table 3, entry 3.

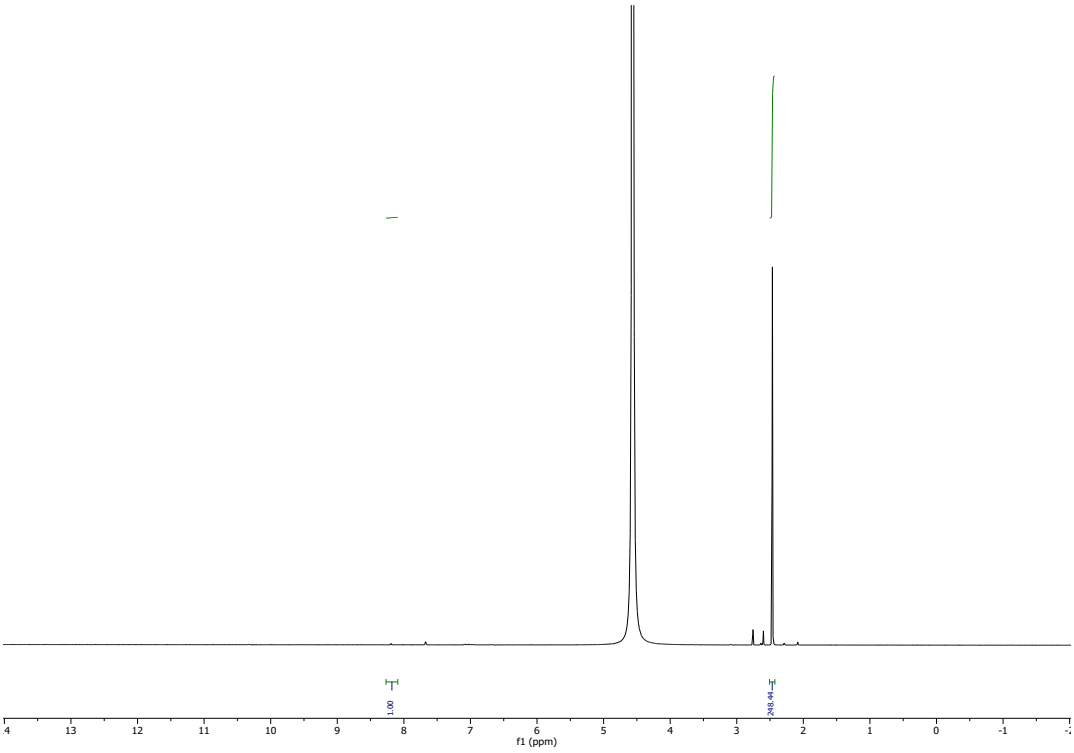

Figure S13. NMR data belonging to table 3, entry 4.

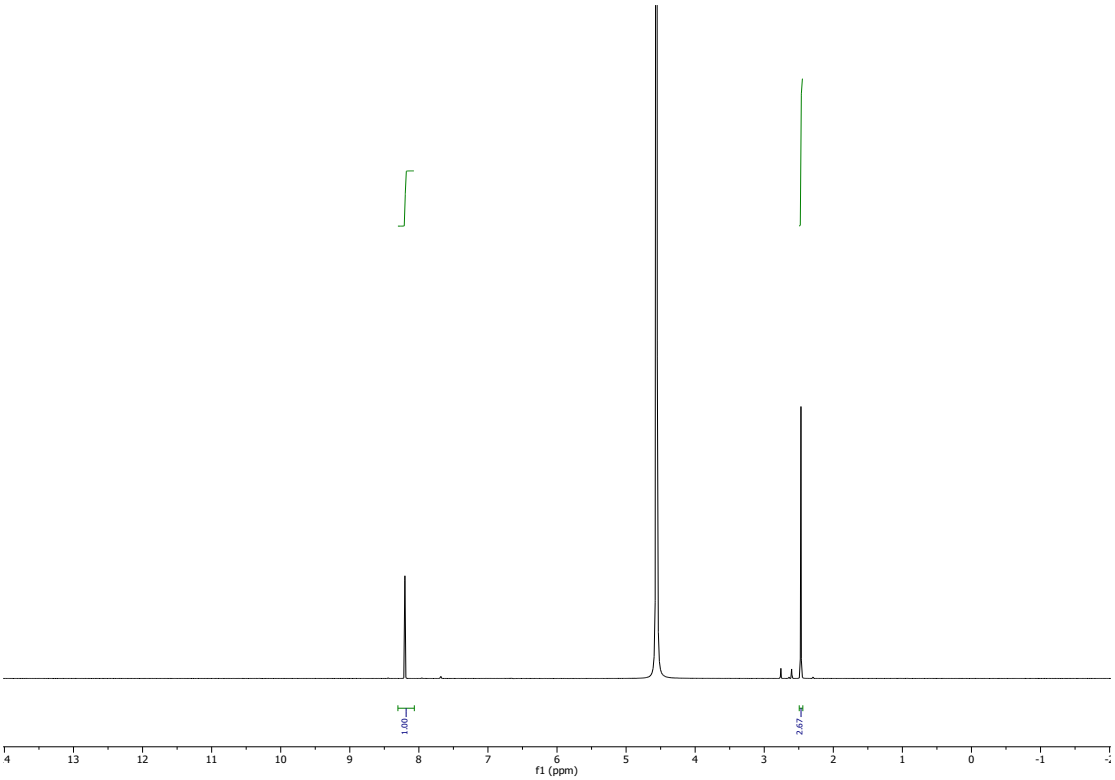

Figure S14. NMR data belonging to table 3, entry 5.

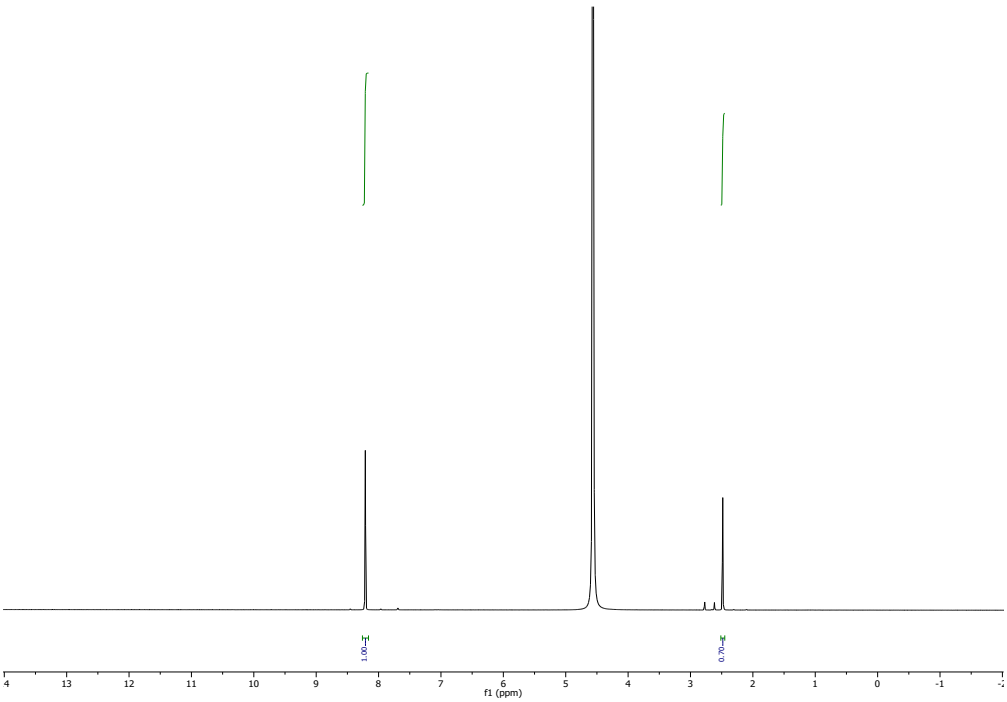

Figure S15. NMR data belonging to table 3, entry 6.

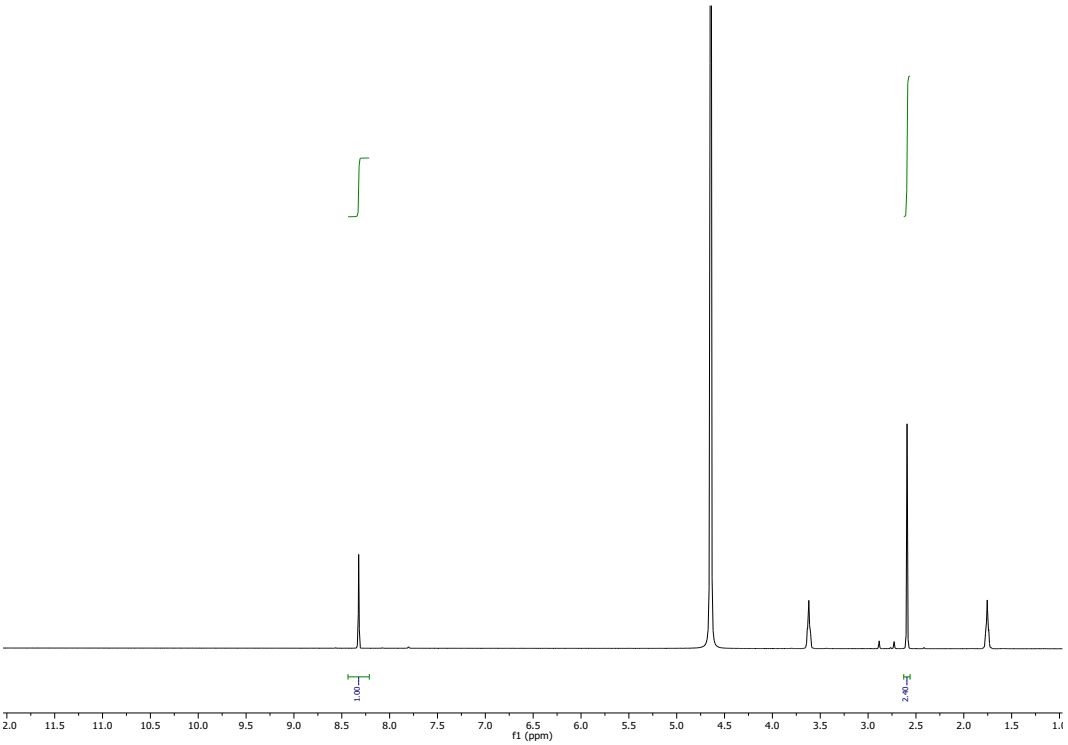

Figure S16. NMR data belonging to table 3, entry 7.

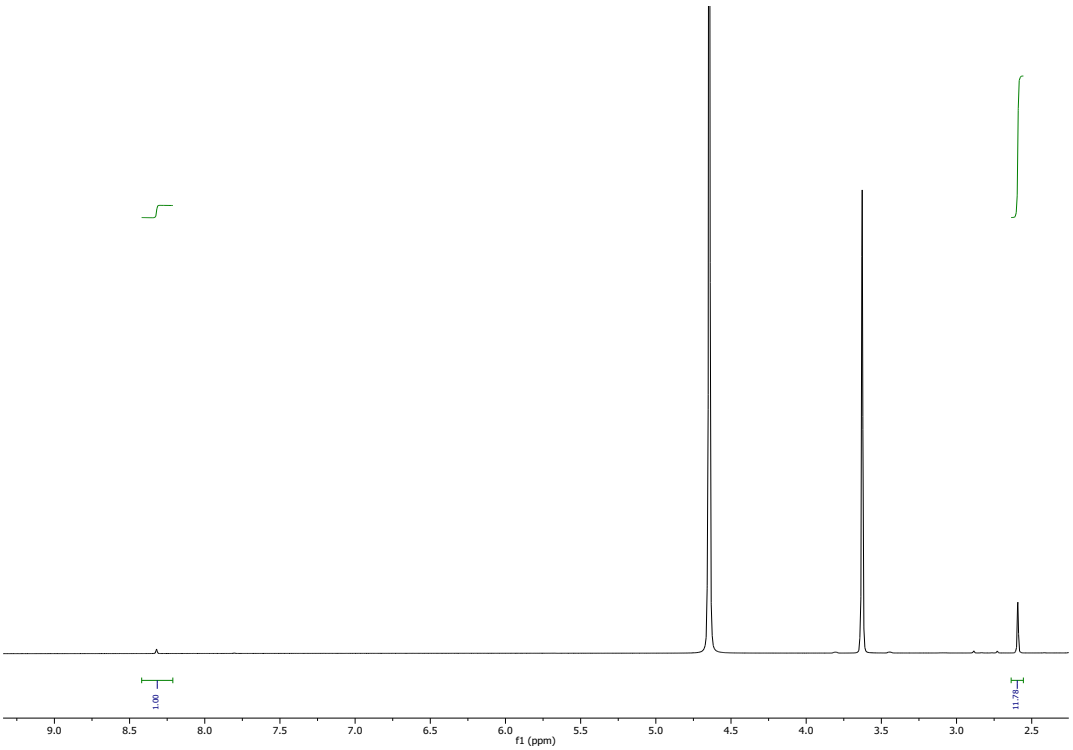

Figure S17. NMR data belonging to table 3, entry 8.

Table S3. ^{1}H NMR peak data belonging to table 3 (main text) and Figures S9-S16.

Entry	**Ratio of DMSO to formate integral**
1	56.95
2	52.94
3	1.08
4	248.44
5	2.67
6	0.70
7	2.40
8	11.78

Table S4. Data accompanying Figure 2 (main text), with $KHCO_3$ as the substrate, for the 2.5 mmol data point (the other values are found in Table 3, main text and Table S3).

Entry	$KHCO_3$ (mmol)	Ratio of DMSO to formate integral	Yield (%)	TON
1	2.5	2.80	60.3	25648

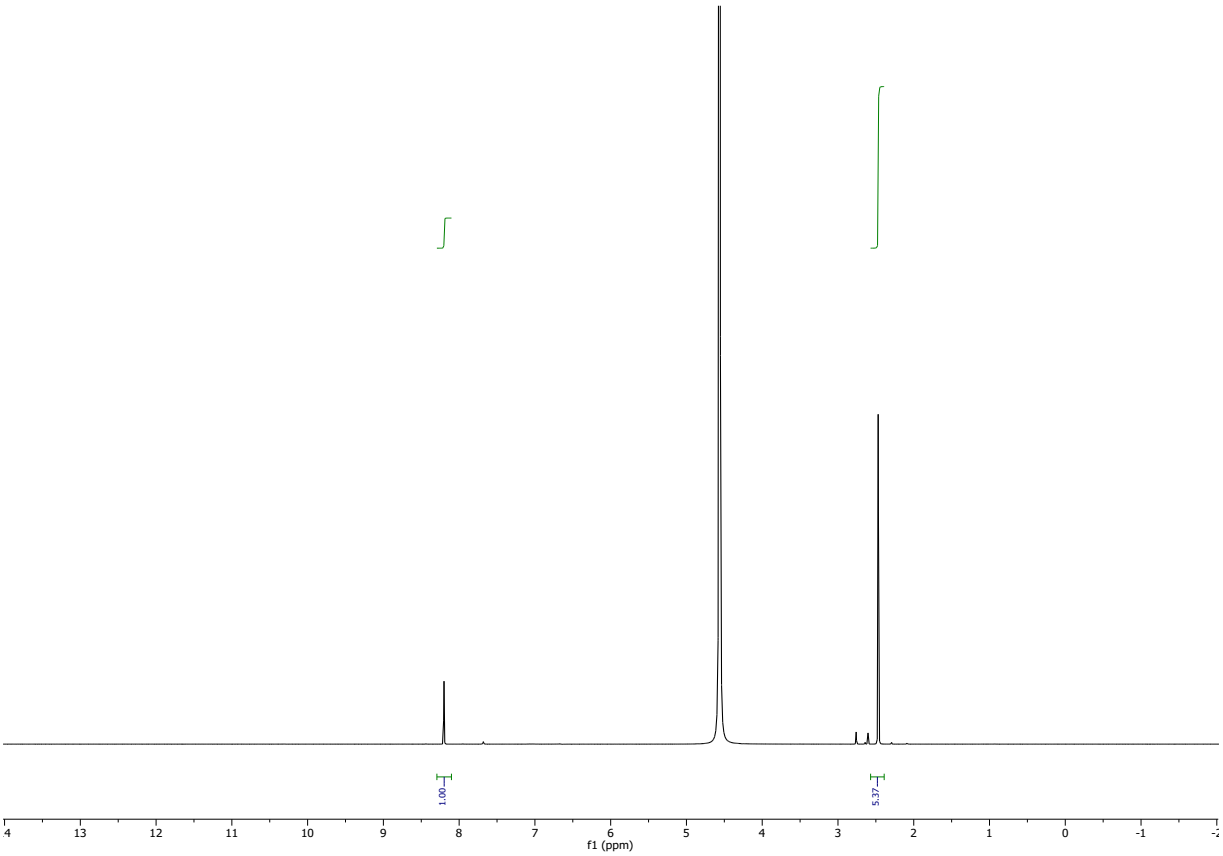

Figure S18. NMR data belonging to table S4, entry 1.

Table S5. Data accompanying Figure 2 (main text), with $NaHCO_3$ as a substrate.

Entry	$NaHCO_3$ (mmol)	Ratio of DMSO to formate integral	Yield (%)	TON
1	5	2.80	60.3	25648
2	7.5	2.26	49.8	31777
3	10	2.58	32.7	27835

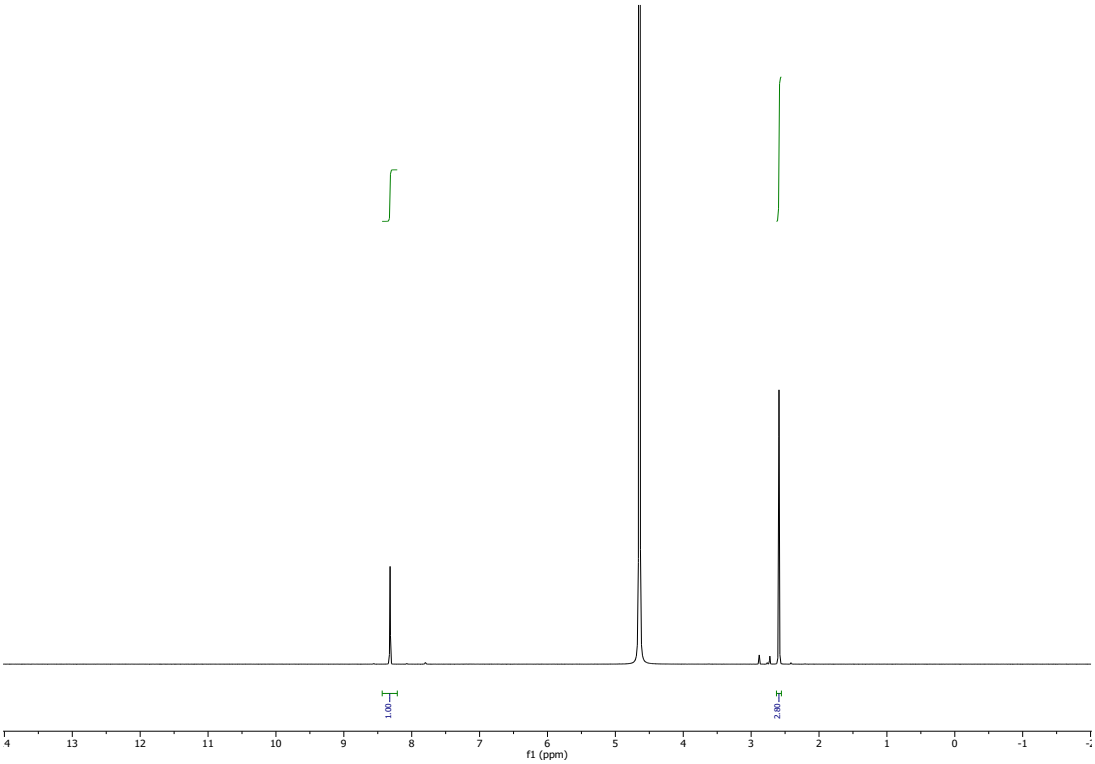

Figure S19. NMR data belonging to table S5, entry 1.

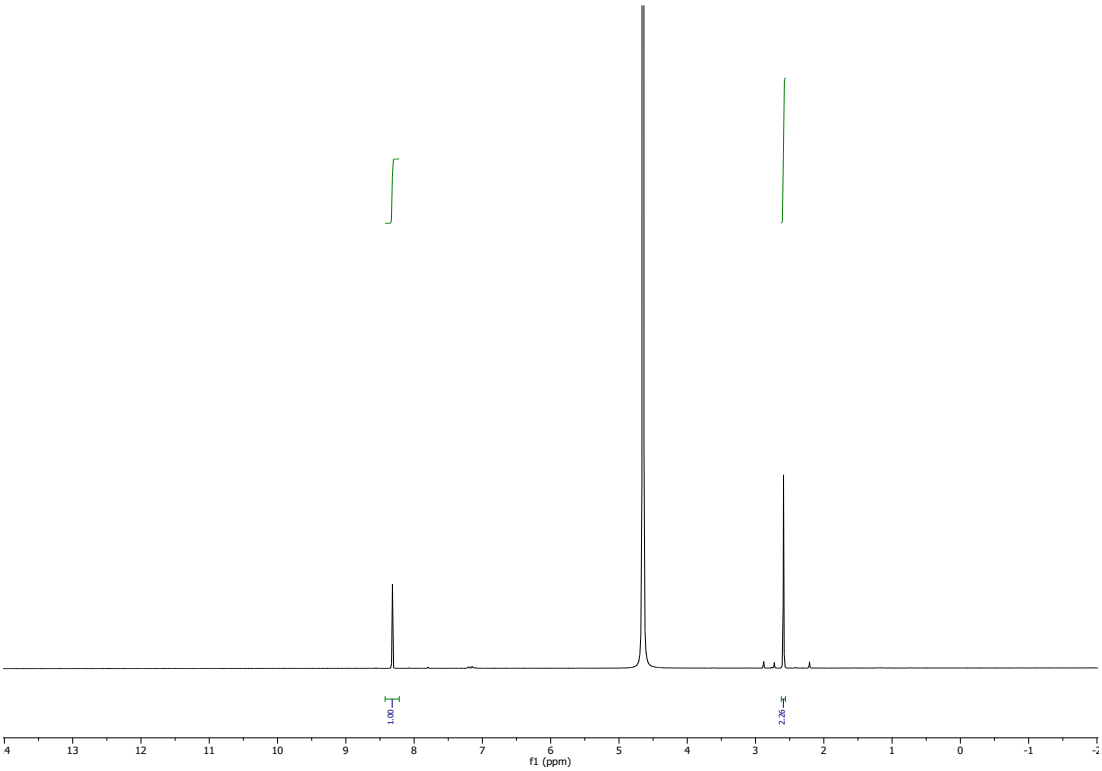

Figure S20. NMR data belonging to table S5, entry 2.

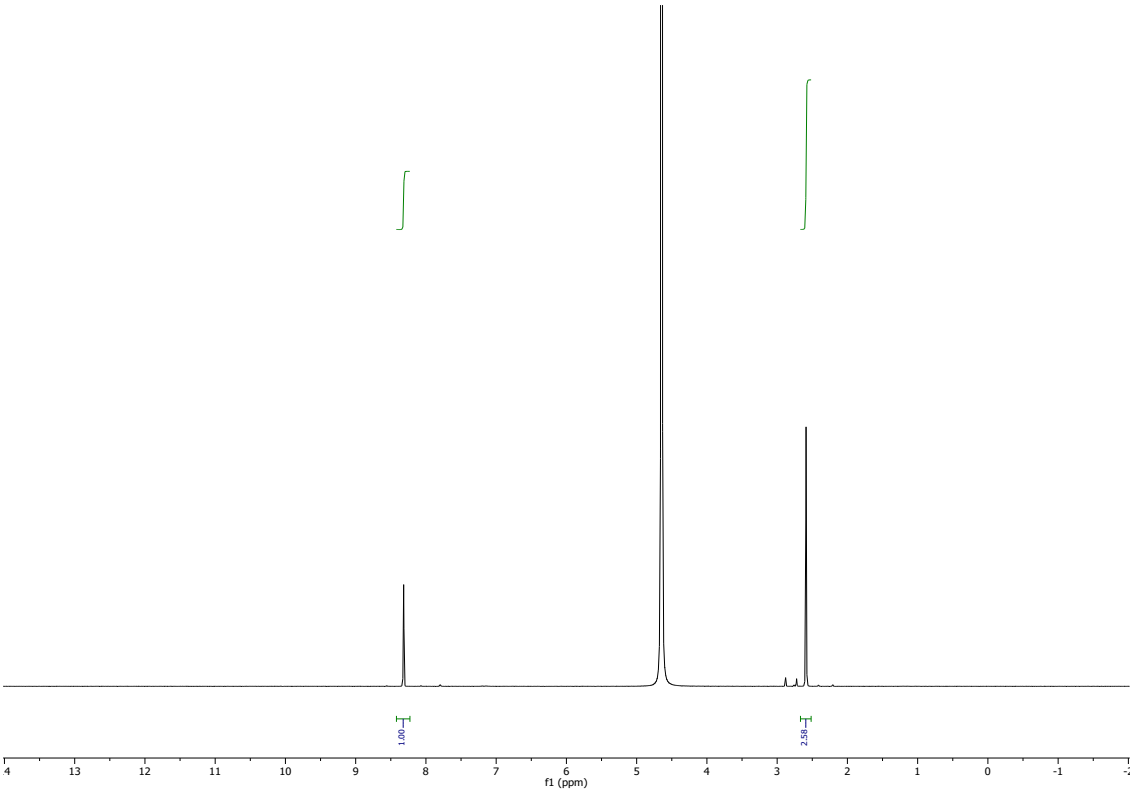

Figure S21. NMR data belonging to table S5, entry 3.

Table S6. Data accompanying Figure 3 (main text), for T = 65 °.

Entry	Pressure (bar)	Ratio of DMSO to formate integral	Yield (%)	TON
1	5	5.02	33.7	14306
2	10	3.37	50.2	21310
3	20	2.70	62.6	26598
4	40	2.31	73.2	31089
5	60	2.29	73.9	31360

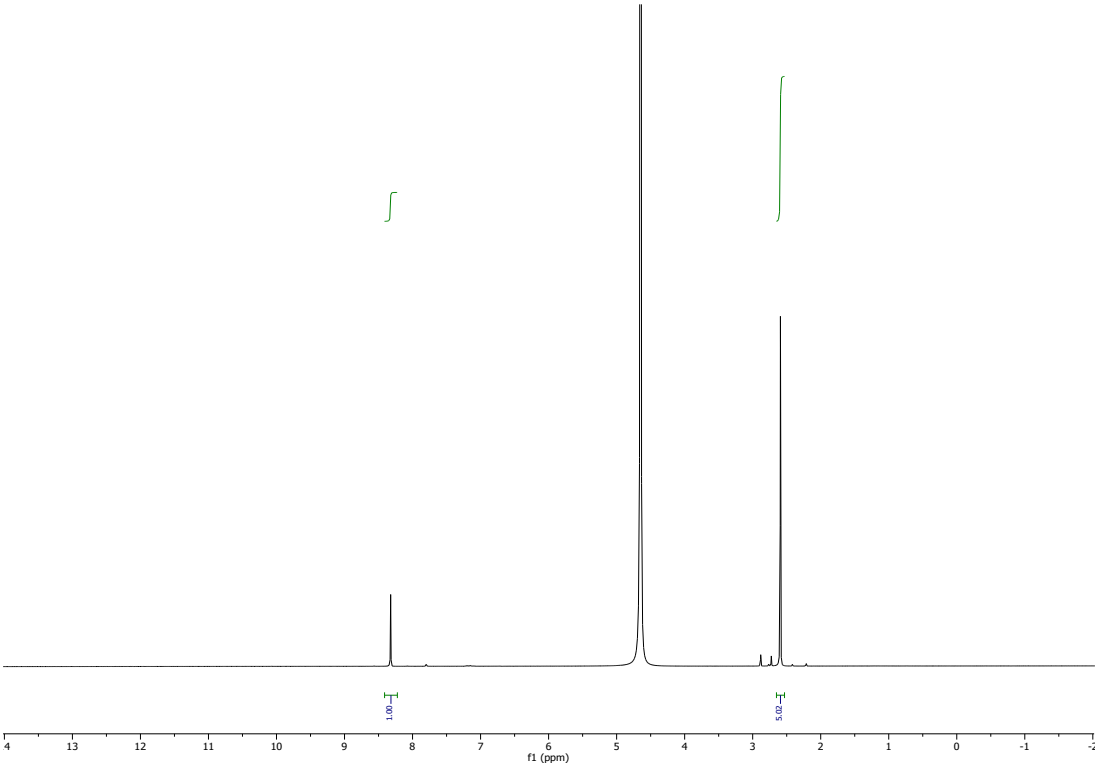

Figure S22. NMR data belonging to table S6, entry 1.

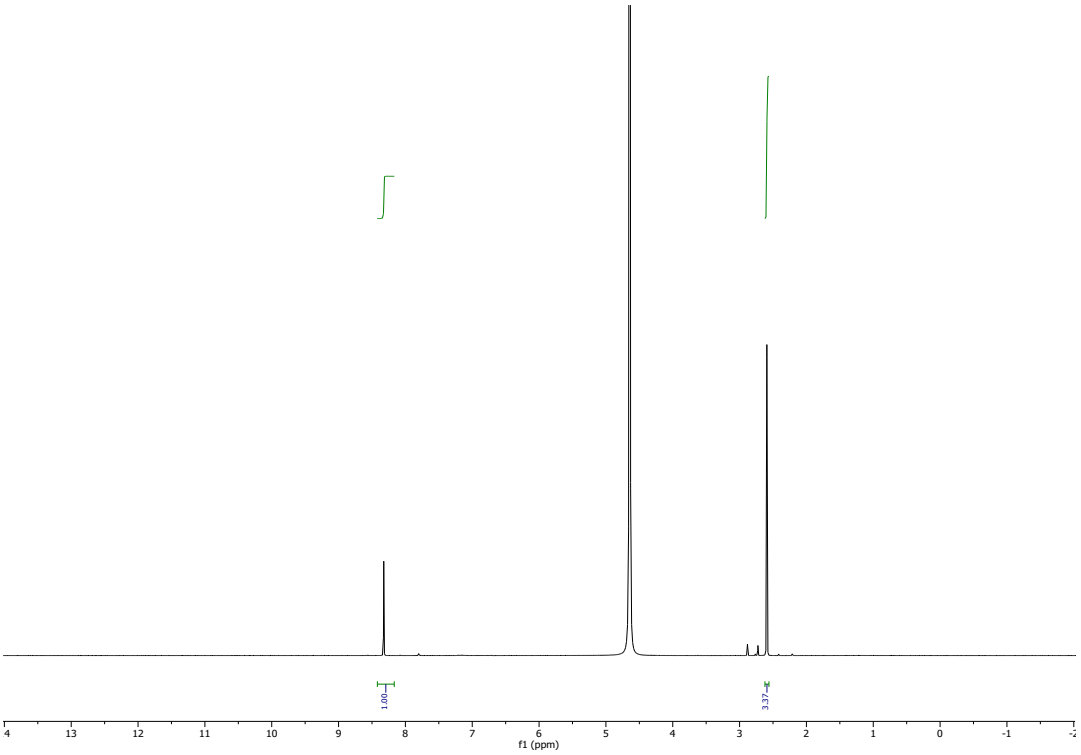

Figure S23. NMR data belonging to table S6, entry 2.

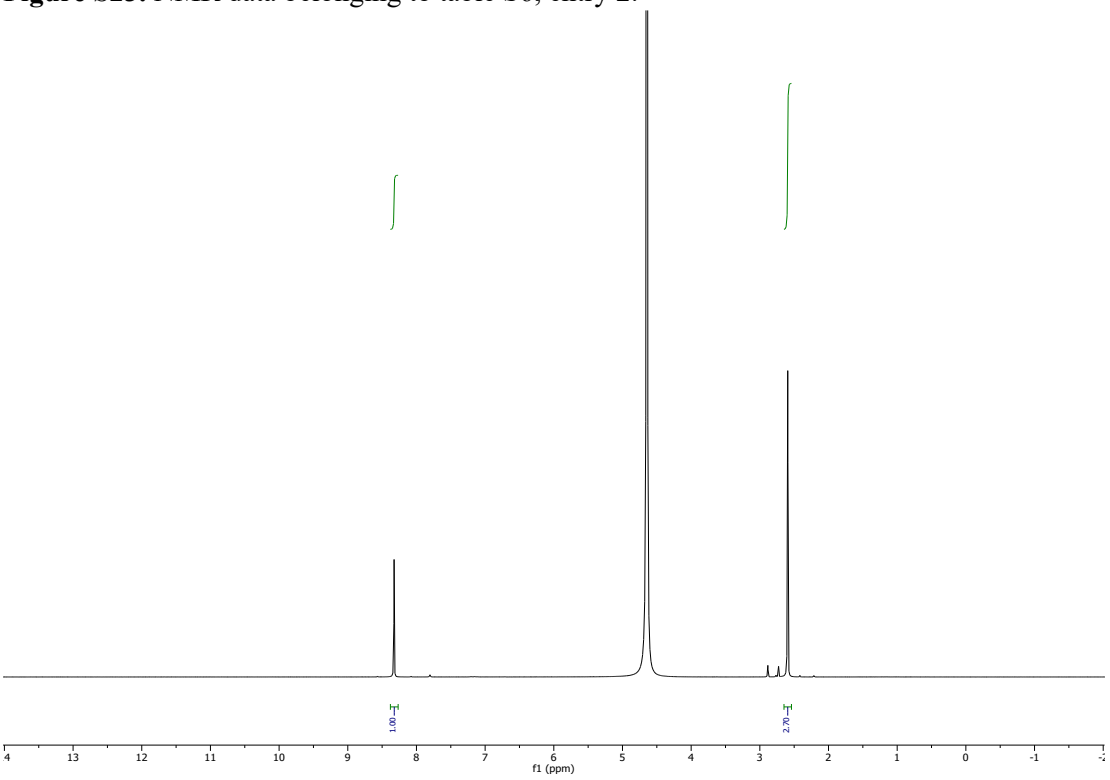

Figure S24. NMR data belonging to table S6, entry 3.

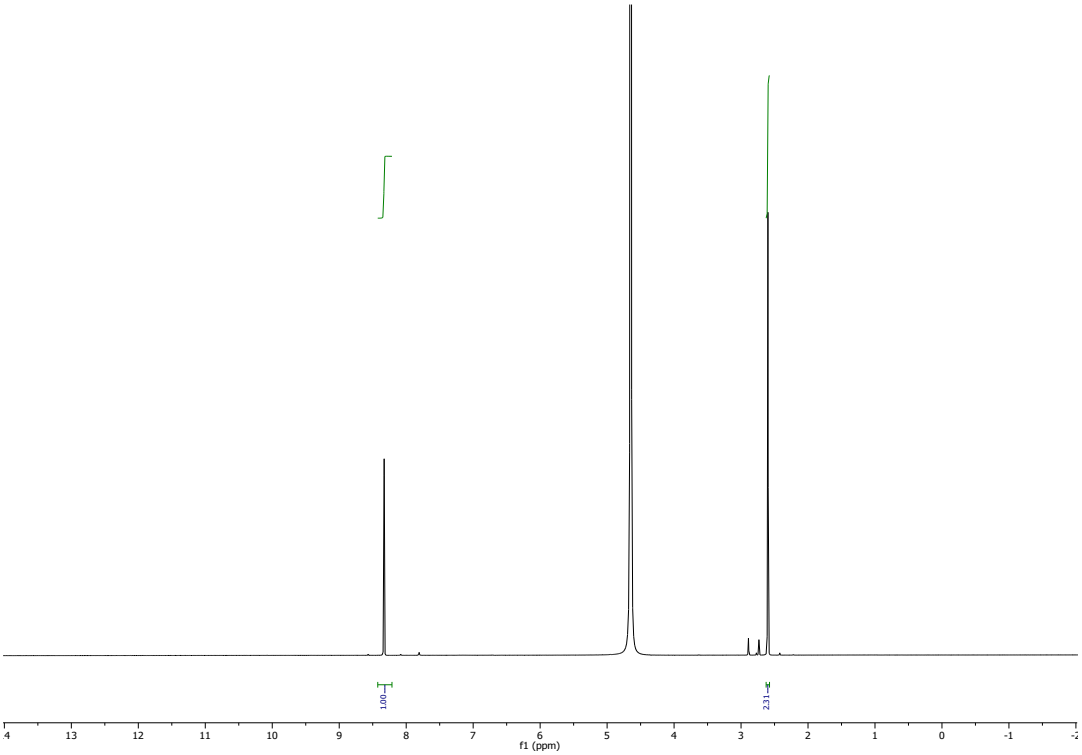

Figure S25. NMR data belonging to table S6, entry 4.

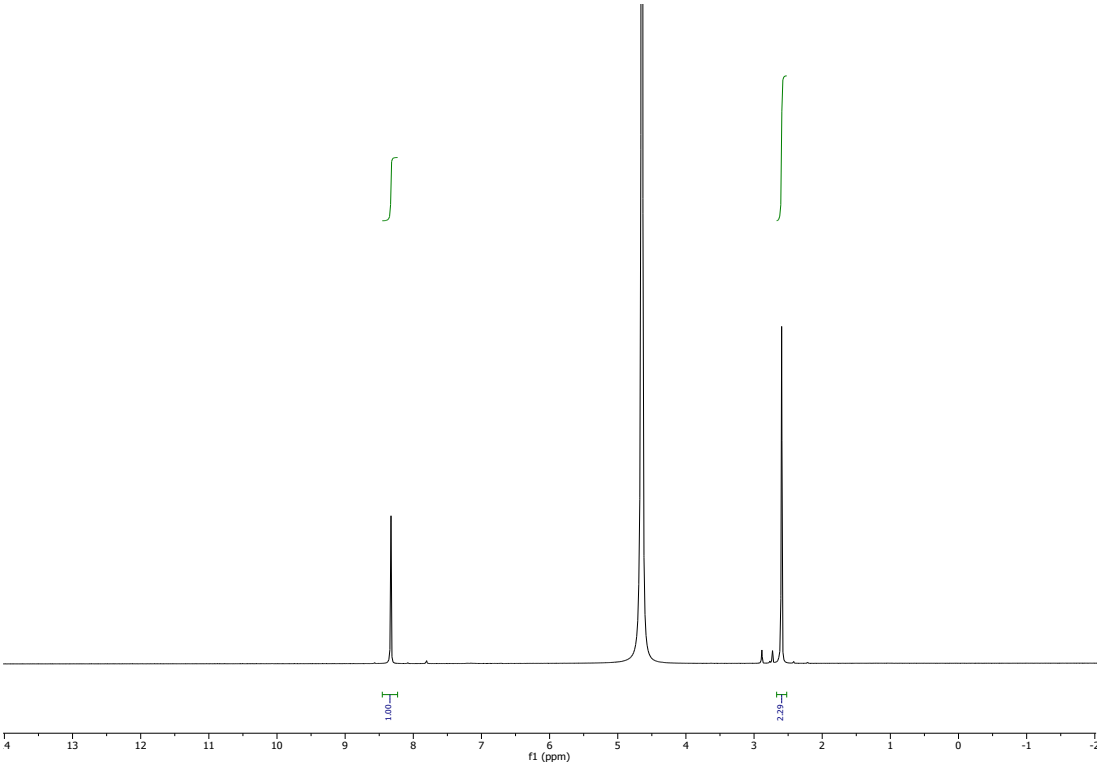

Figure S26. NMR data belonging to table S6, entry 5.

Table S7. Data accompanying Figure 3 (main text), for T = 90 °.

Entry	Pressure (bar)	Ratio of DMSO to formate integral	Yield (%)	TON
1	5	4.86	35.3	14777
2	10	4.80	35.5	14961
3	20	2.84	60.1	25287
4	40	2.32	73.4	30955
5	50	1.89	89.1	37997

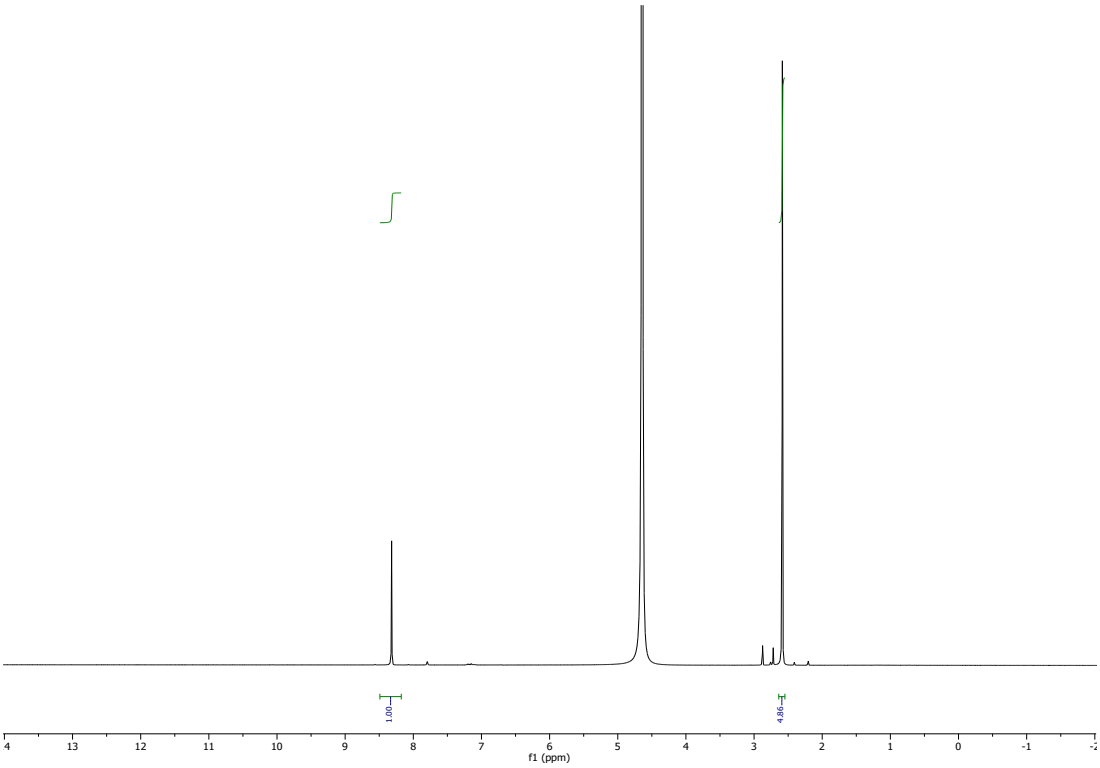

Figure S27. NMR data belonging to table S7, entry 1.

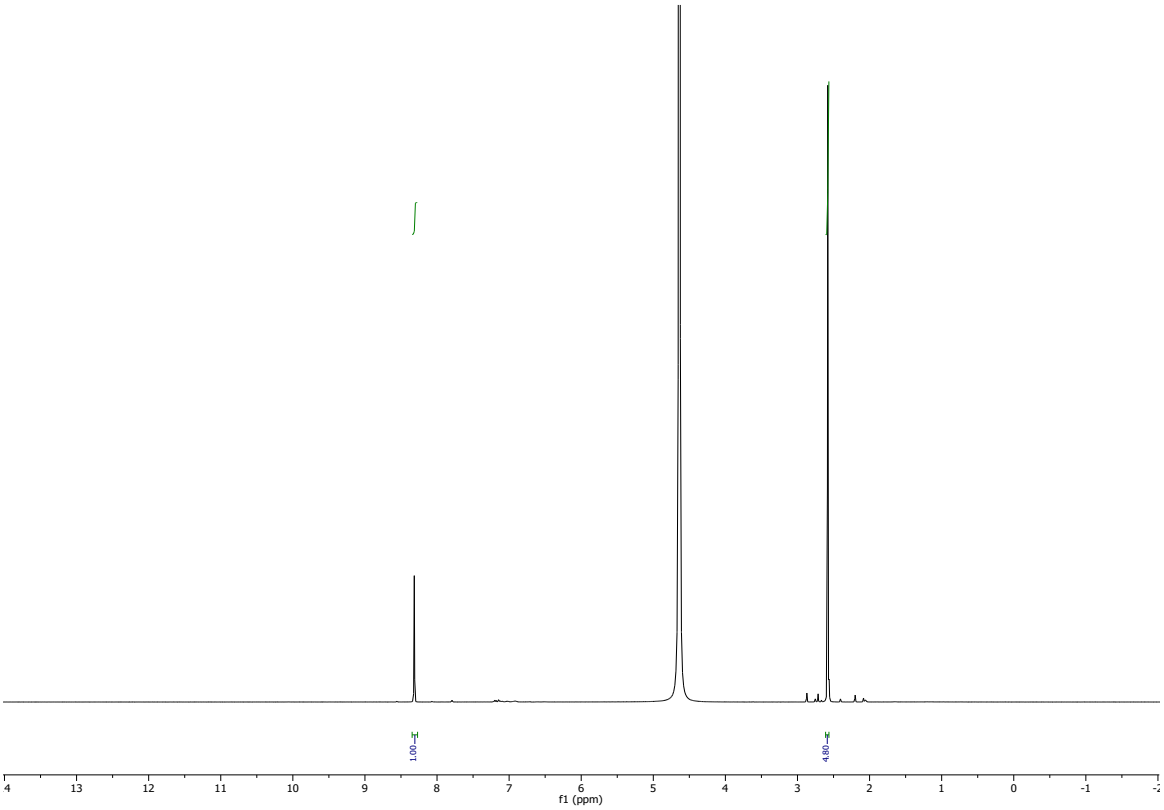

Figure S28. NMR data belonging to table S7, entry 2.

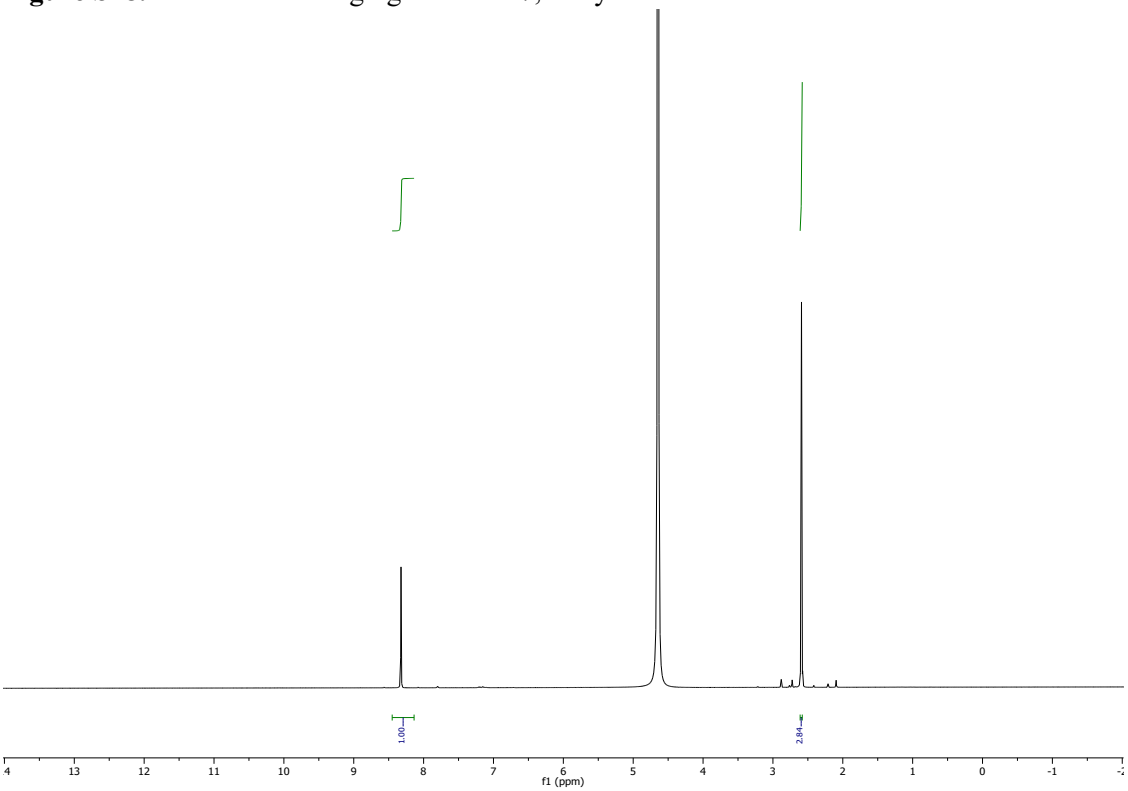

Figure S29. NMR data belonging to table S7, entry 3.

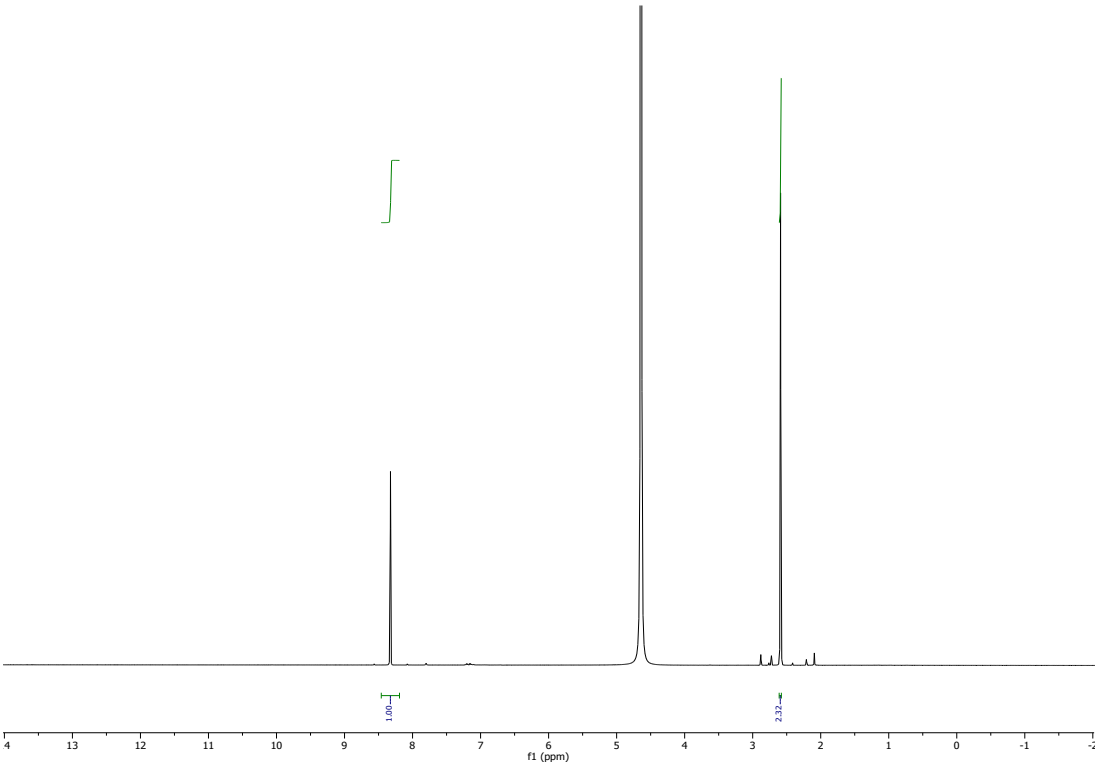

Figure S30. NMR data belonging to table S7, entry 4.

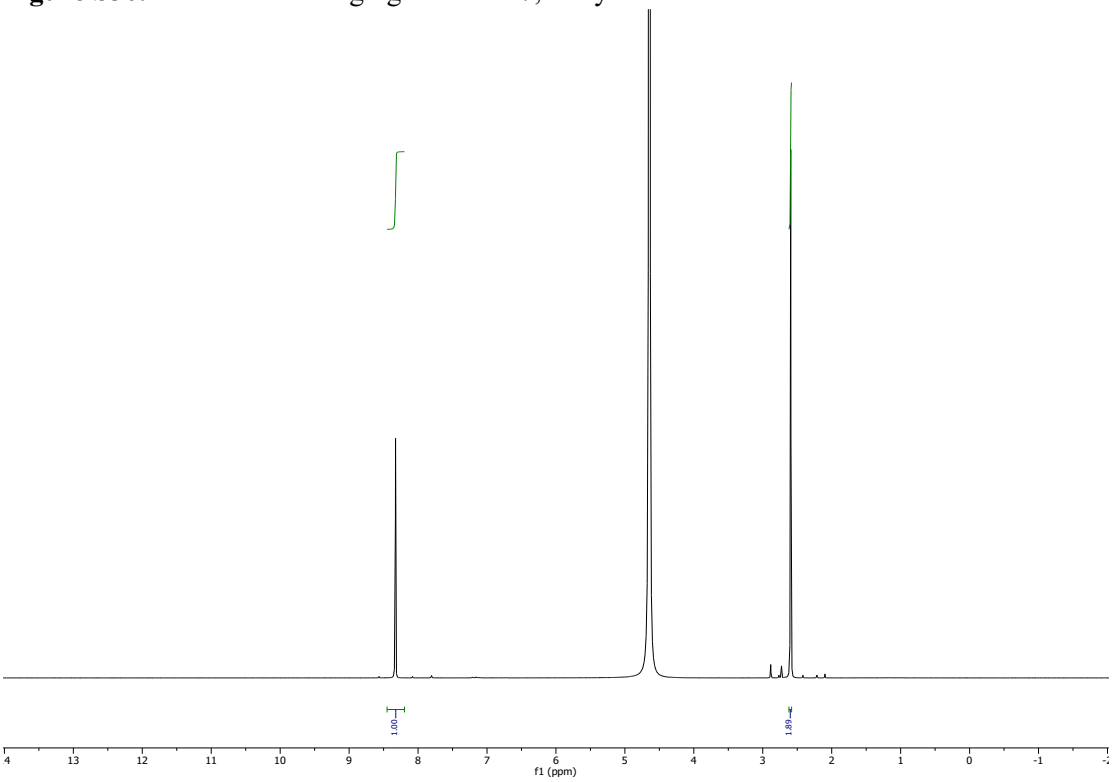

Figure S31. NMR data belonging to table S7, entry 5.

Table S8. Data accompanying Figure 3 (main text), for T = 120 °.

Entry	Pressure (bar)	Ratio of DMSO to formate integral	Yield (%)	TON
1	5	199.01	0.8	361
2	10	9.00	18.8	7979
3	20	5.00	33.8	14363
4	40	2.54	66.6	28274
5	53	2.06	82.1	34862

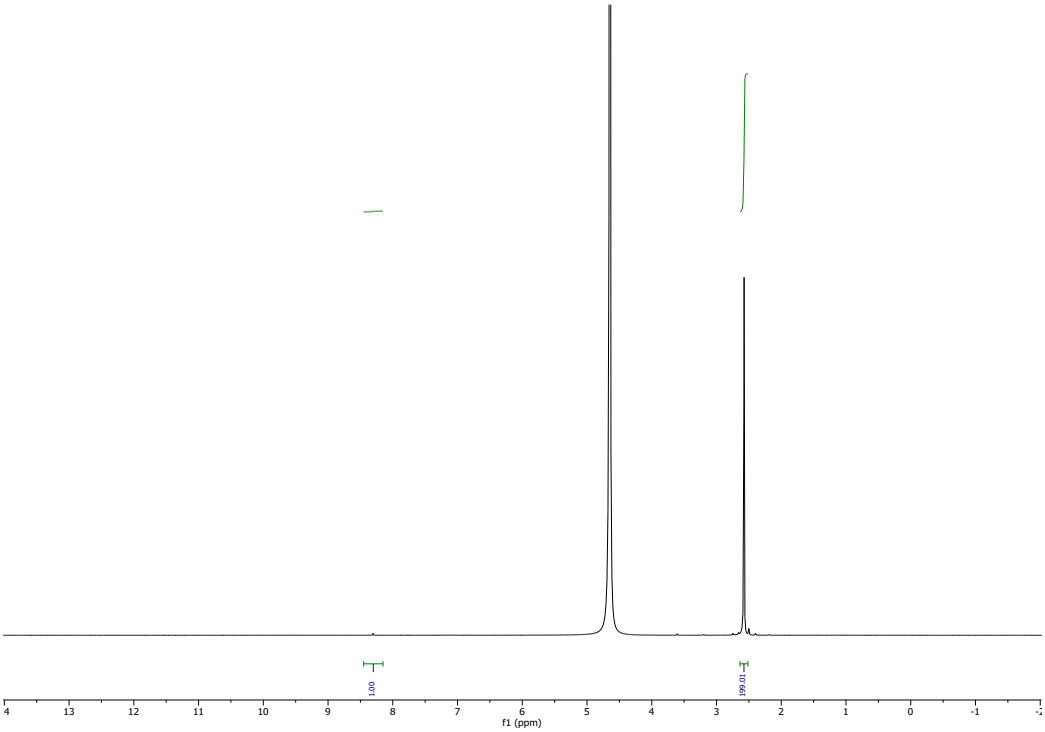

Figure S32. NMR data belonging to table S8, entry 1.

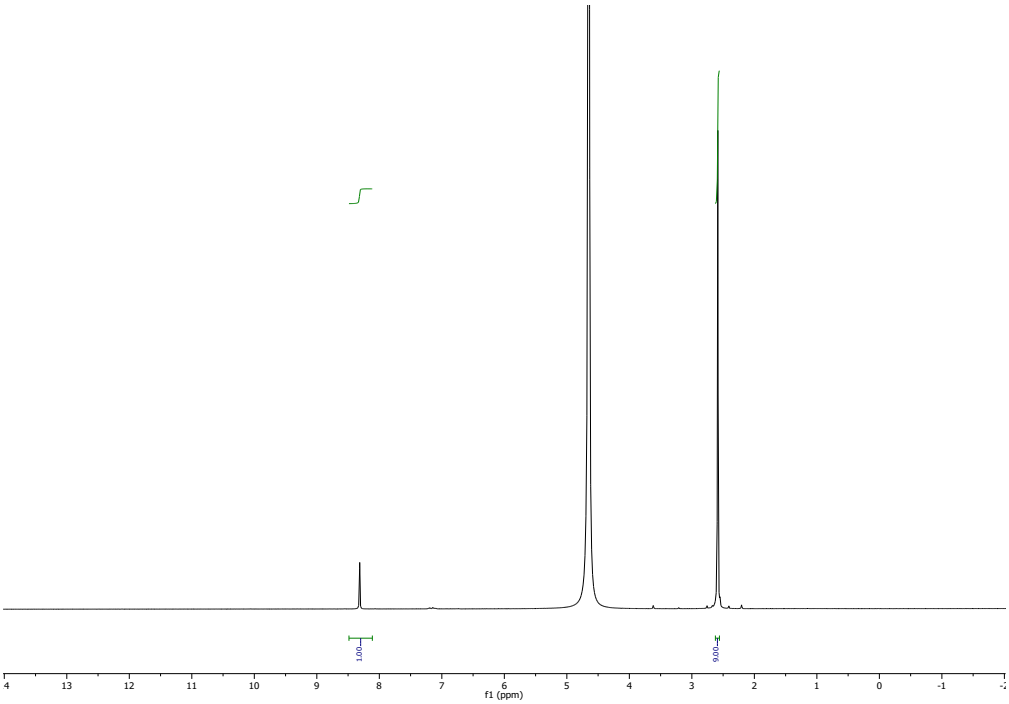

Figure S33. NMR data belonging to table S8, entry 2.

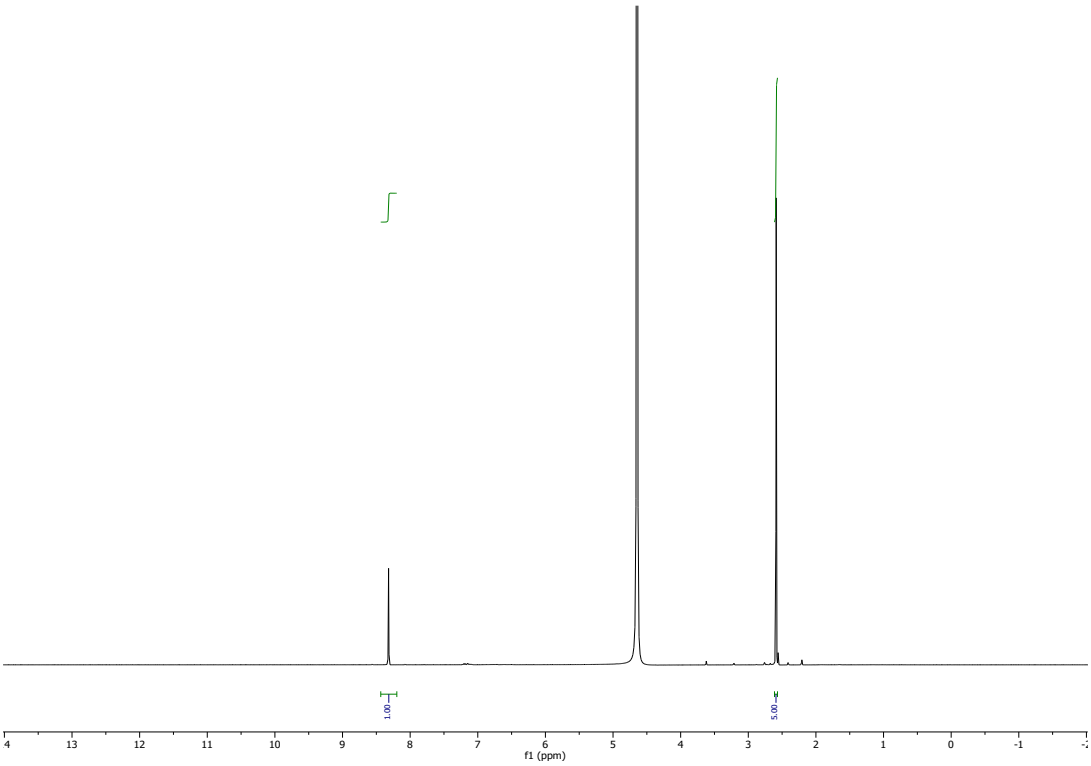

Figure S34. NMR data belonging to table S8, entry 3.

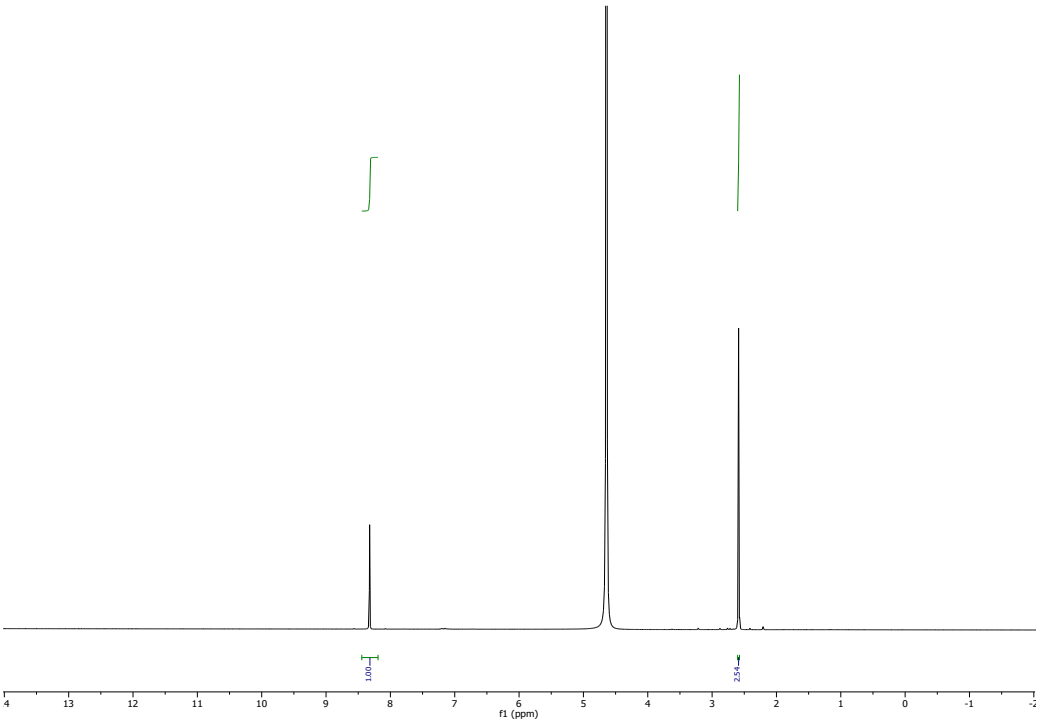

Figure S35. NMR data belonging to table S8, entry 4.

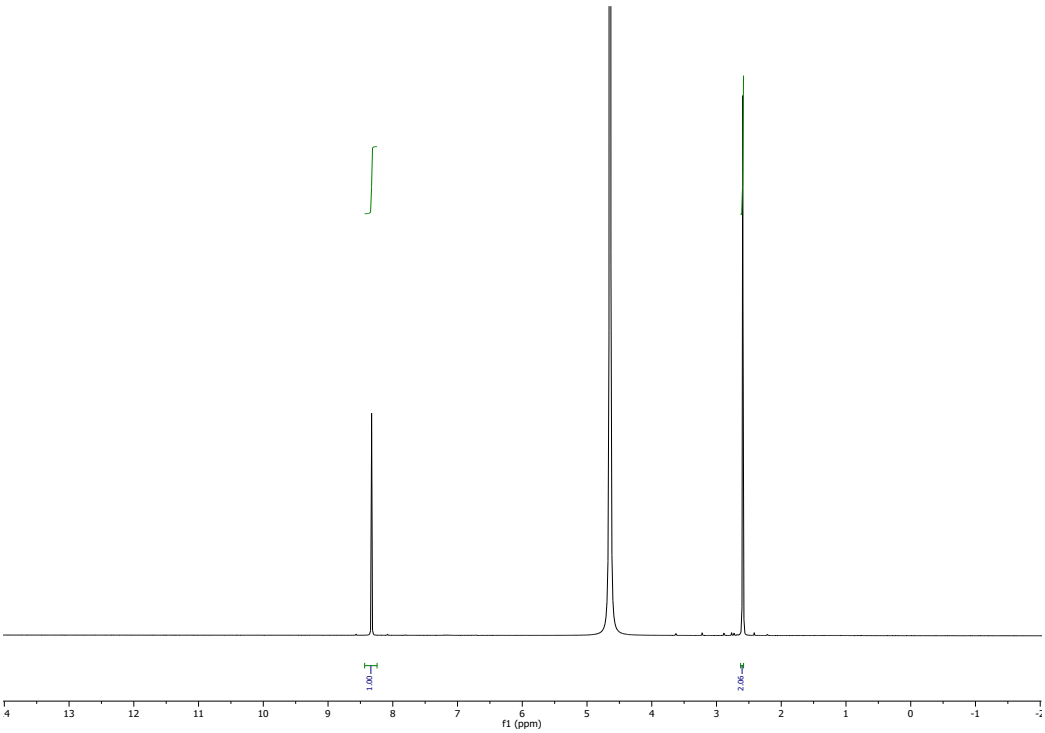

Figure S36. NMR data belonging to table S8, entry 5.

^{1}H NMR data accompanying data provided in Table 4

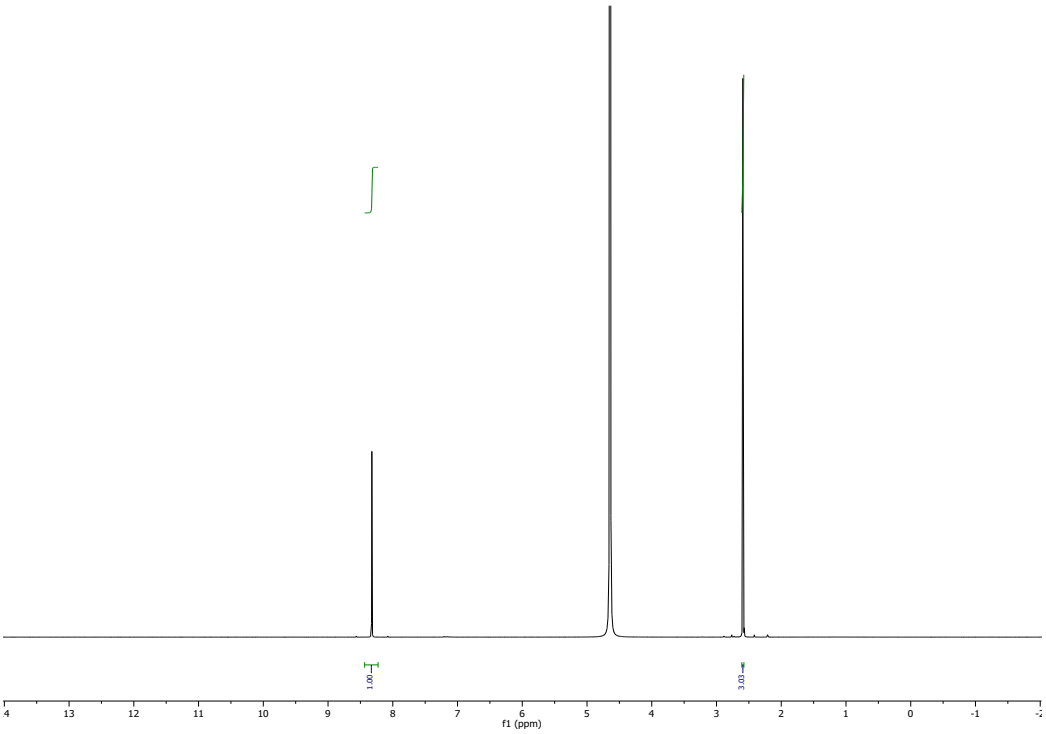

Figure S37. NMR data belonging to table S9, entry 1.

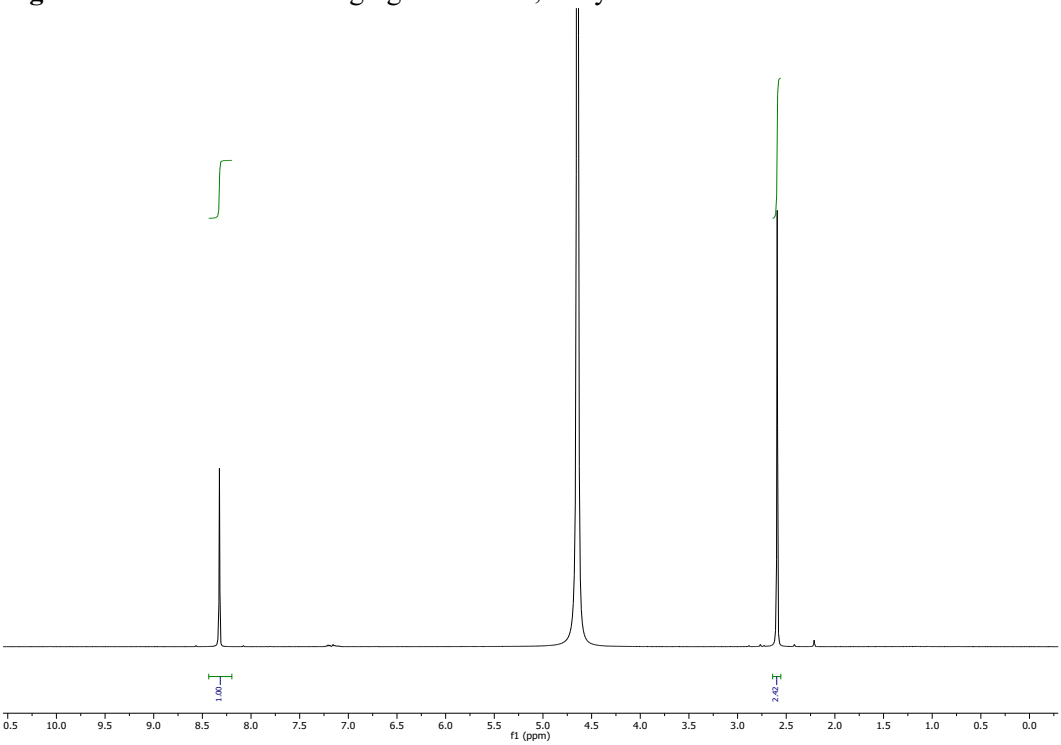

Figure S38. NMR data belonging to table S9, entry 2.

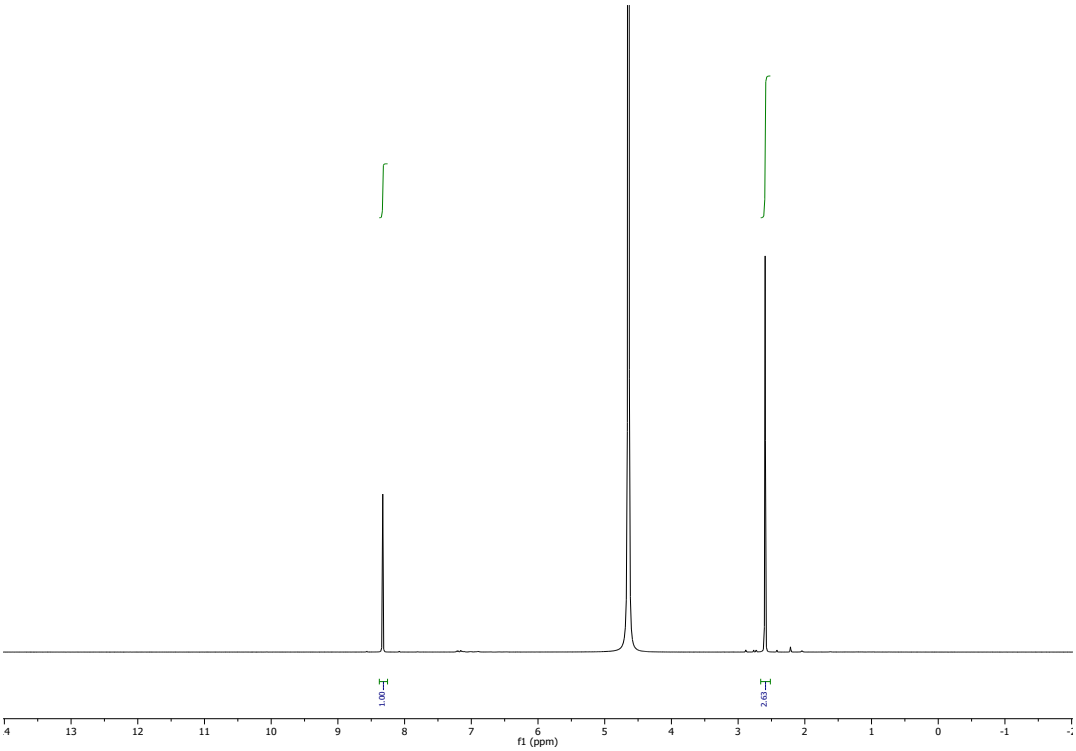

Figure S39. NMR data belonging to table S9, entry 3.

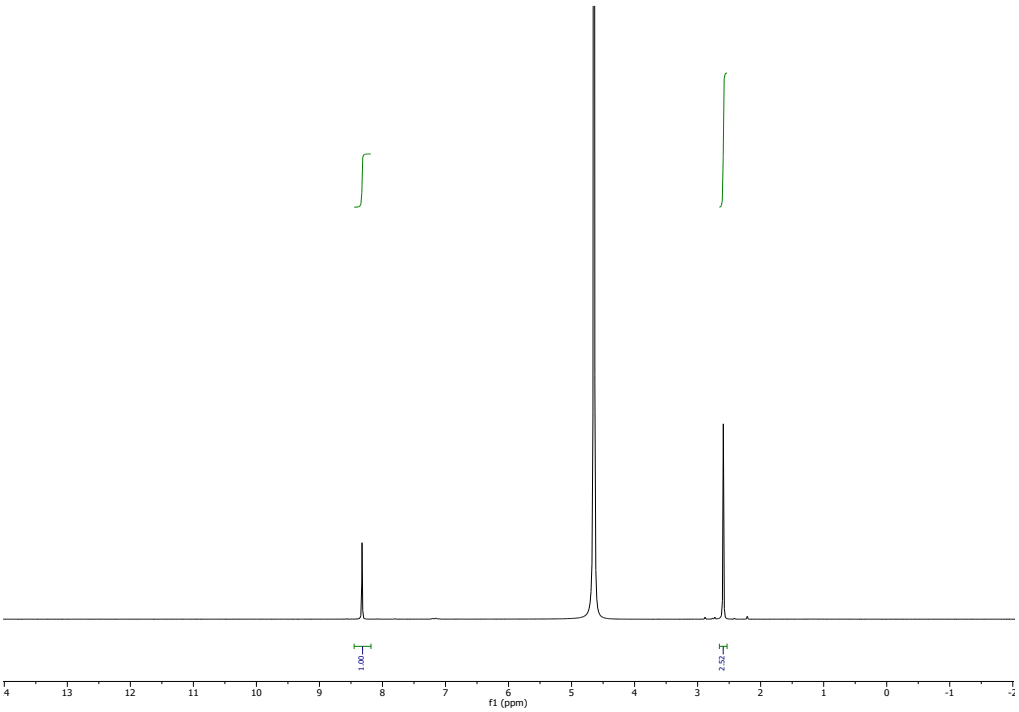

Figure S40. NMR data belonging to table S9, entry 4.

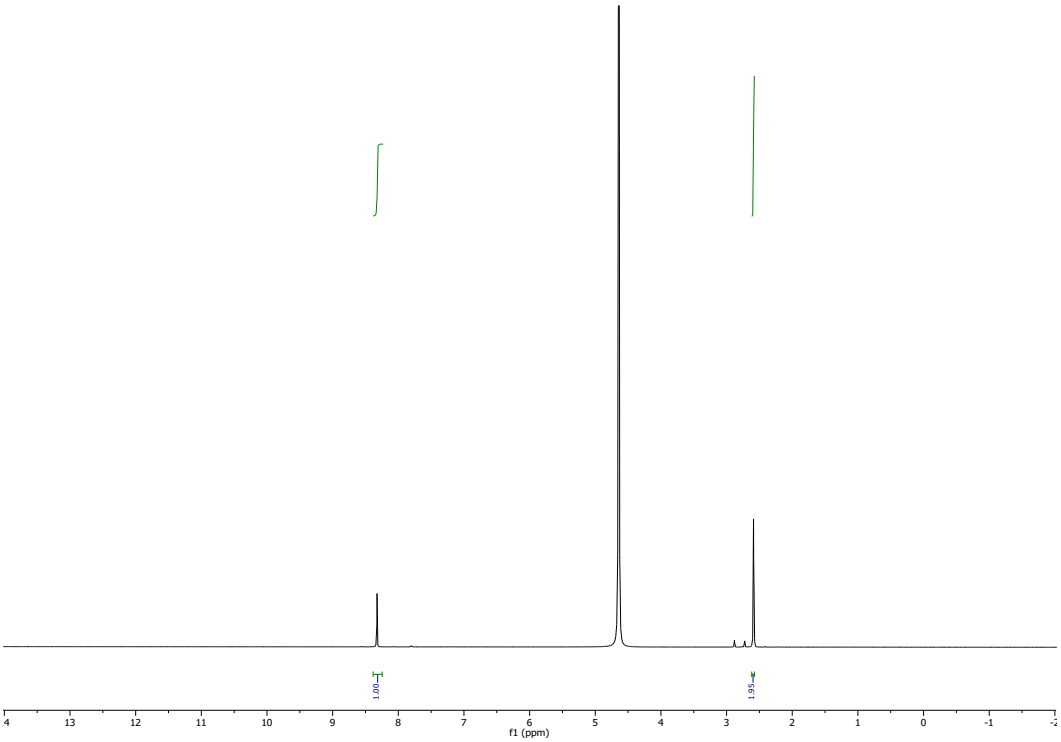

Figure S41. NMR data belonging to table S9, entry 5.

Table S9. ^{1}H NMR peak data belonging to table 4 (main text) and Figures S36-S40.

Entry	Ratio of DMSO to formate integral
1	3.03
2	2.42
3	2.63
4	2.52
5	1.95

H_2 uptake data belonging to Figure 4, main text

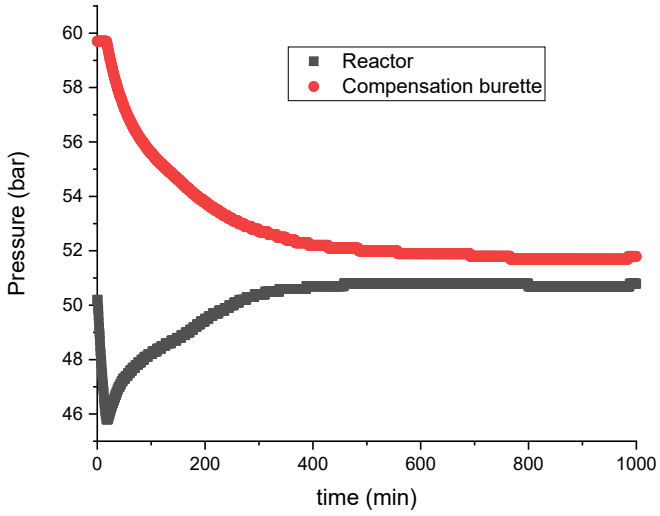

Figure S42. H_2 uptake data accompanying the experiment described in Figure 4, main text. The volume of the compensation burette is 142 mL. The volume of the headspace in the reactor is 45 mL. The compensation burette is used to keep the pressure reasonably constant during the course of the reaction.

1. Gnanaprakasam, B.; Zhang, J.; Milstein, D. *Angew. Chem. Int. Ed.*, **2010**, *49*, 1468.