Supporting Information

Methanol production from CO_2 via an integrated, formamide-assisted approach

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S1. Reduction of formamides

S1.1 Reduction of *N,N*-diphenylformamide in different solvents

N,N-diphenylformamide (0.17 mmol, 33 mg, 1.0 Equiv.) and sodium borohydride (0.50 mmol, 19 mg, 3.0 Equiv.) were added to a glass vial and dissolved in the appropriate solvent (1 mL). The vial was then closed, and the reaction mixture was stirred at 50°C for 1 h. Next, the vial was cooled to room temperature, and the pressure carefully released with a needle. ^{1}H NMR spectra were recorded using the reaction mixture (0.1 mL) diluted in DMSO-d_6 (0.3 mL).

Solvent	Yield[a] [%]
DMSO (dry)	0
Methanol	41
Ethanol	78[b]
tert-Butanol	75[b]
Diethylene glycol	100[b]
DMSO/water (9:1)	30
THF/water (1:1)	38
Acetonitrile/water (3:1)	41

Table S1. [a] Yield was determined by comparing the *N,N*-diphenylformamide formyl ^{1}H NMR peak (1H, s, 8.6 ppm) with the aromatic peak of N,N-diphenylamine (4H, d, 7.2 ppm); [b] Complete consumption of $NaBH_4$ was observed.

Higher conversions were observed using diethylene glycol, ethanol and tert-butanol as proton sources. However, these reactions showed complete consumption of $NaBH_4$ and a large excess of borohydride was required because the competing alcoholysis reaction becomes fast (see Figure S1-a). Different mixtures between organic solvents and water were also tested which yielded more selectivity towards formamide reduction than solvolysis (Figure S1-c). Among these solvent mixtures, DMSO/water system was selected due to the higher substrate solubility and higher boiling point, although the reaction proceeds slowly. As shown in Figure S1-b, the absence of water leads to an unreactive substrate. Thus, further optimization was performed by varying the water/DMSO ratios (see S.1.2 section).

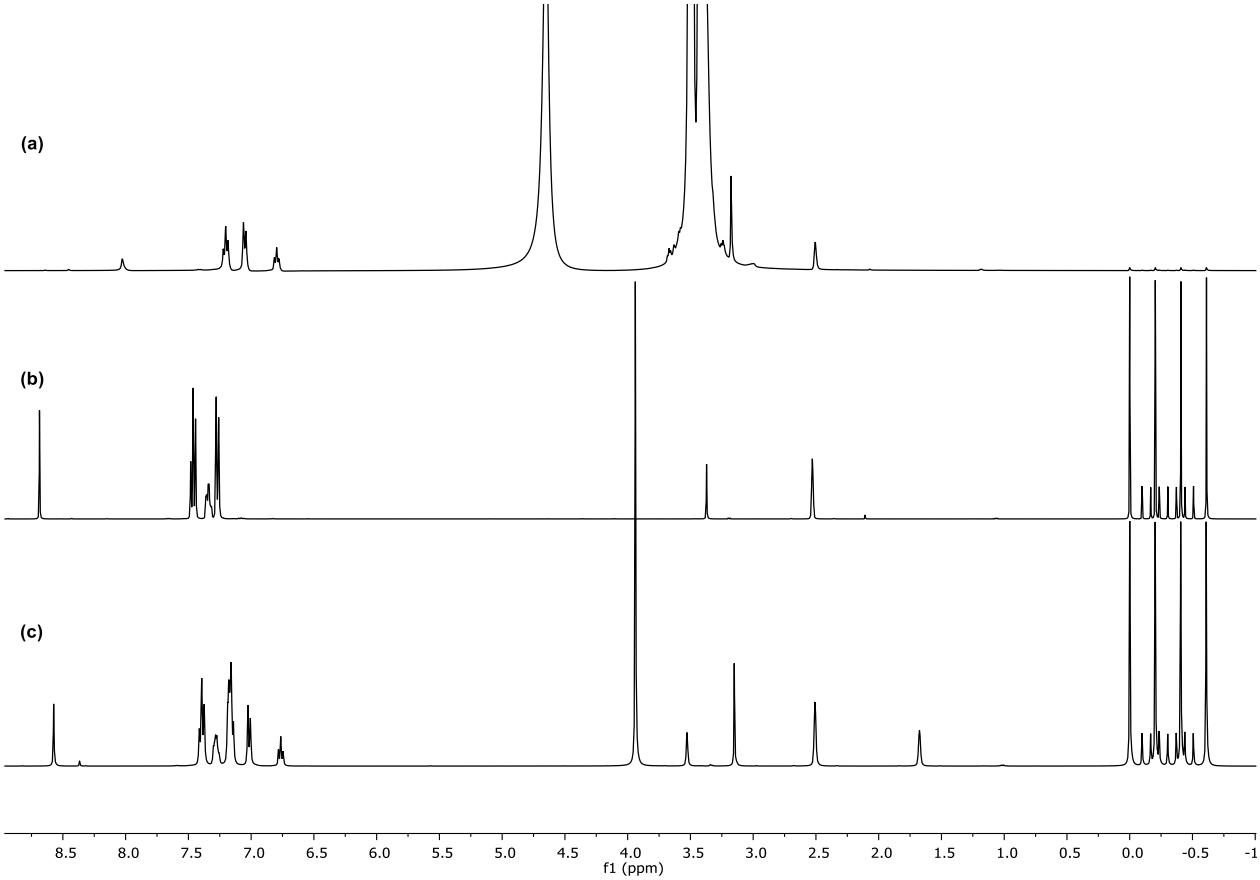


Figure S1. Stacked ^{1}H NMR (400 MHz in dry DMSO-d_6) spectra showing the reduction of *N,N*-diphenylformamide in (a) diethylene glycol, (b) DMSO and (c) water/THF mixture (1:1 ratio). Reaction conditions: $NaBH_4$ (3 equivalents), 50^{o}C, 1 h. The consumption of $NaBH_4$ is near quantitative (~0 ppm) and complete reduction of the substrate is also observed in diethylene glycol (a). No reaction was observed in DMSO (b) and approximately 38% substrate reduction was observed for the water/THF mixture (c).

S1.2 Reduction of *N*-methylformanilide with different DMSO/water ratios

N-methylformanilide (0.50 mmol, 1.0 Equiv.) and sodium borohydride (0.50 mmol, 1.0 Equiv.) were added to a glass vial and dissolved in different DMSO/water mixtures (see Table 2). The vial was then sealed, and the reaction mixture was stirred for 12 h at 90°C. The vial was cooled to room temperature, and the pressure was carefully released with a needle. ^{1}H NMR spectra were recorded using the reaction mixture (0.1 mL) diluted in DMSO-d6 (0.3 mL).

DMSO/water ratio	DMSO [ml]	Water [ml]	Yield[a] [%]
90/10	1.8	0.20	49
85/15	1.7	0.30	66
80/20	1.6	0.40	64
75/25	1.5	0.50	66

Table S2. [a] Yield was estimated by comparing the *N*-methylformanilide formyl ^{1}H NMR peaks (1H, t,~8.4 – 8.5 ppm) with the aromatic peak of *N*-methylamine (3H, t, ~6.5 ppm).

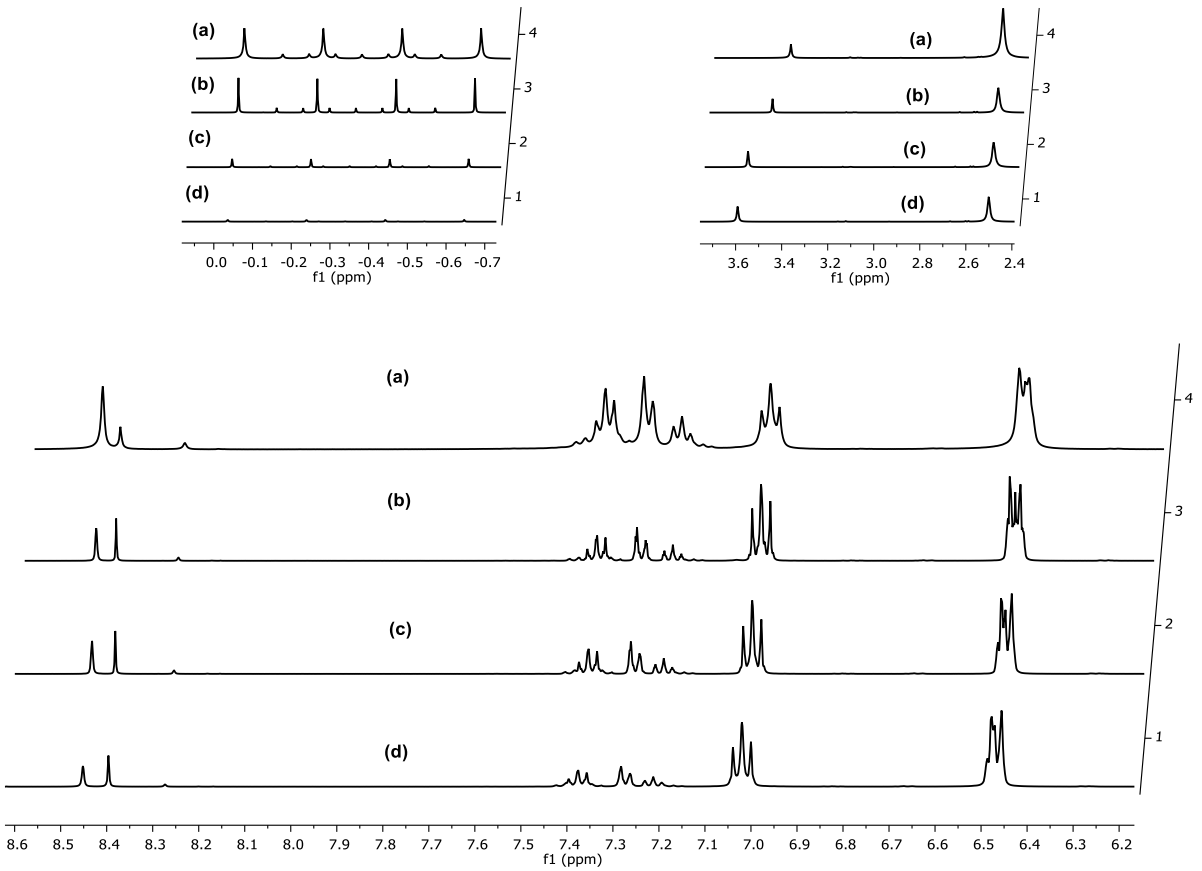


Figure S2. Stacked ^{1}H NMR (400 MHz in dry DMSO-d_6) spectra showing the reduction of *N*-methylformanilide in DMSO-d_6/water: (a) 10 vol% water, (b) 15 vol% water, (c) 20 vol% water and (d) 25 vol% water. Reaction conditions: *N*-methylformanilide (100 mg), $NaBH_4$ (20 mg), 90^{o}C, 12 h. The ^{1}H NMR chemical shifts for $NaBH_4$ is shown in the top-left inset and for DMSO and water in the top-right inset.

Although the product yield is similar at higher quantities of water, the consumption of $NaBH_4$ significantly increases due to hydrolysis (the same problem that was observed when alcohols were used as solvent) (see top-left inset in Figure S2). The yield obtained is a "compromise" between the amount of water needed as a proton donor and the amount of $NaBH_4$ consumed by this co-solvent. For this reason, the DMSO/water (85/15) ratio was selected as the best solvent mixture for the reduction of amines.

S1.3 Reduction of *N*-methylformanilide at different temperatures

N-methylformanilide (0.50 mmol, 1.0 equiv.) and sodium borohydride (0.50 mmol, 1.0 equiv.) were added to a glass vial and dissolved in DMSO/water (2 mL, 85/15) mixture. The vial was then sealed, and the reaction mixture was stirred for 12 h at different temperatures. The vial was then cooled to room temperature, and the pressure was carefully released with a needle. ^{1}H NMR spectra were recorded using the reaction mixture (0.1 mL) diluted in DMSO-d6 (0.3 mL).

Temperature [°C]	Yield [%]
90	66[a]
70	18[b]
50	4[b]

Table S3. [a] Yield was previously estimated in section S1.2. [b] Yields were determined from the integrals of the *N*-methylformanilide formyl ^{1}H NMR peaks (1H, t, ~8.4 – 8.5 ppm) and the aromatic peak of *N*-methylamine (3H, t, ~6.5 ppm) relative to the aromatic mesitylene singlet at ~6.7 ppm.

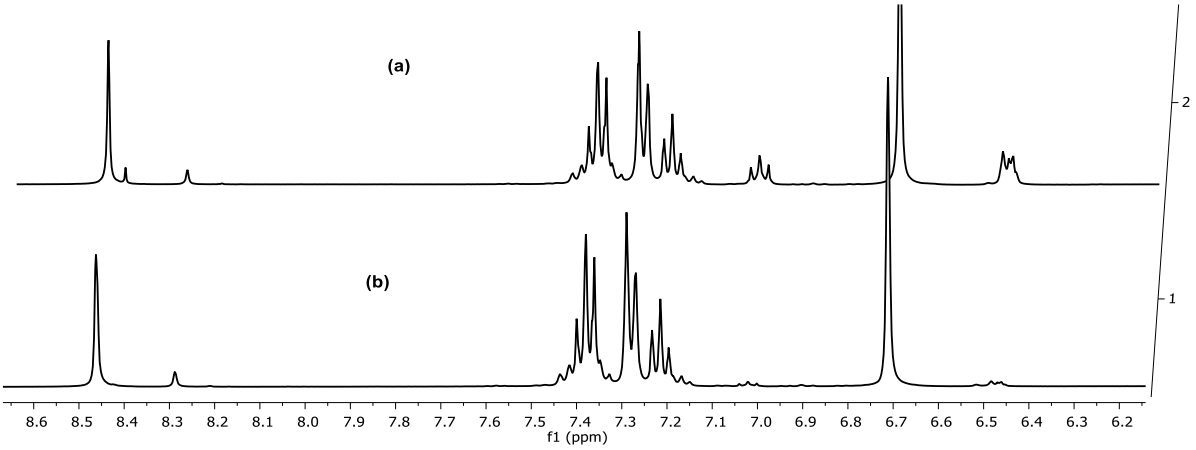


Figure S3. Stacked ^{1}H NMR (400 MHz in dry DMSO-d_6) spectra showing the reduction of *N*-methylformanilide at lower temperatures: (a) 70°C, (b) 50°C. Reaction conditions: *N*-methylformanilide (0.5 mmol), $NaBH_4$ (0.5 mmol), dissolved in DMSO/water (2 mL, 85/15) mixture, 12 h.

As shown in Table S3, the product yield is temperature-dependent. At lower temperatures the yield obtained is reduced and for this reason reactions were carried out at 90°C.

S1.4 Representative ^{1}H NMR spectra for the quantification of amines after formamide reduction

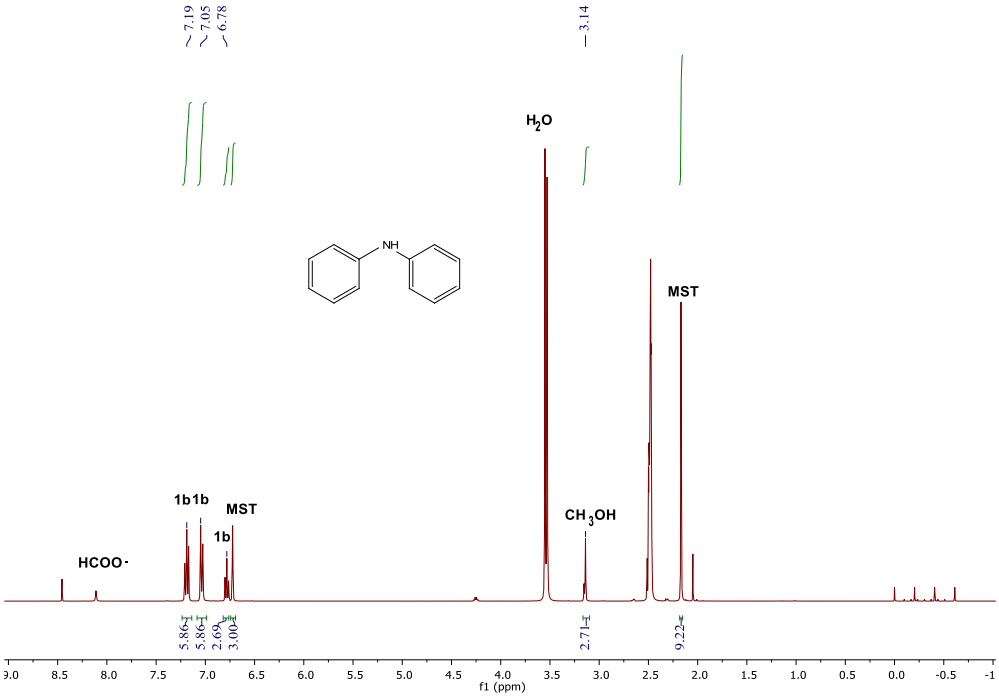


Figure S4. ^{1}H NMR spectrum of the crude reaction mixture for the reduction of substrate **1a**. Diphenylamine (**1b**) and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aromatic mesitylene singlet at ~6.7 ppm. Complete conversion was observed.

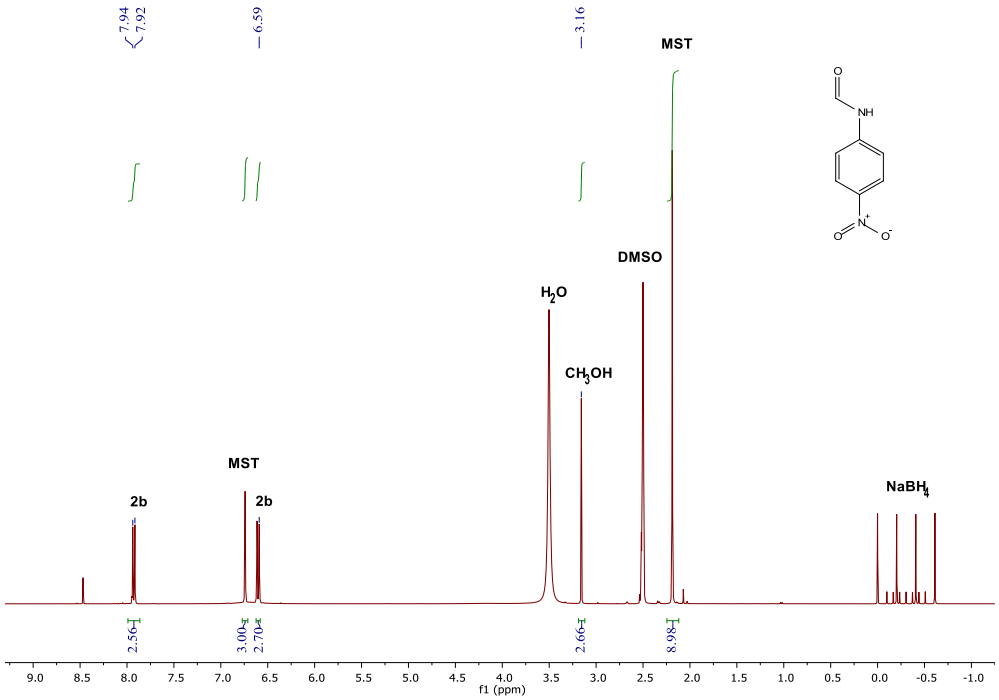


Figure S5. ^{1}H NMR spectrum of the crude reaction mixture for the reduction of substrate **2a**. Amine (**2b**) and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aromatic mesitylene singlet at ~6.7 ppm. Complete conversion was observed.

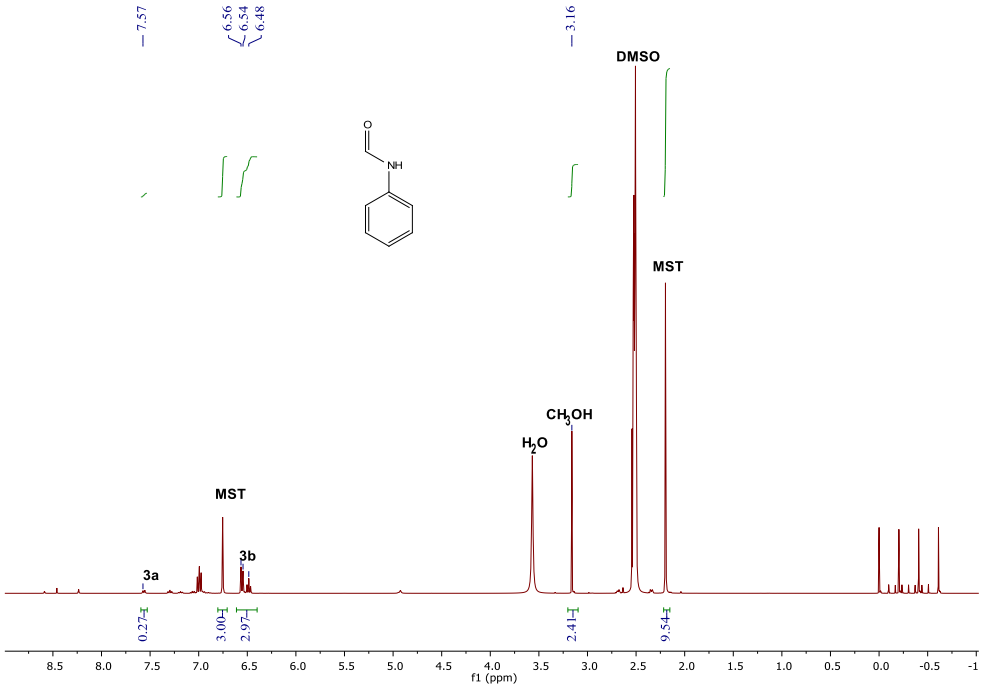


Figure S6. ^{1}H NMR spectrum of the crude reaction mixture for the reduction of substrate **3a**. Amine (**3b**) and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aromatic mesitylene singlet at ~6.7 ppm.

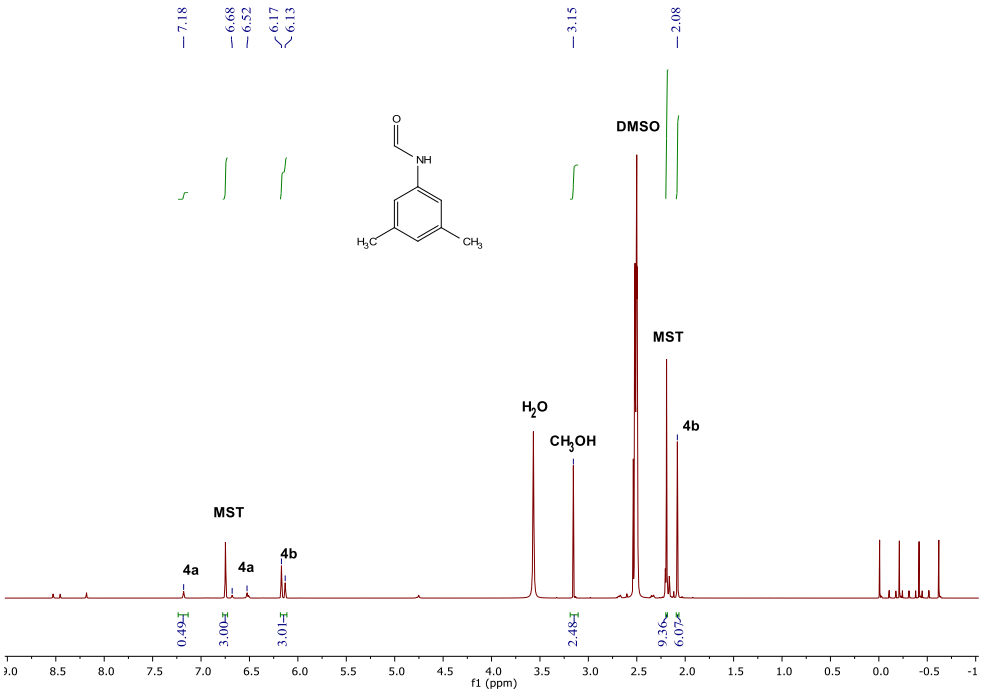


Figure S7. ^{1}H NMR spectrum of the crude reaction mixture for the reduction of substrate **4a**. Amine (**4b**) yield and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aromatic mesitylene singlet at ~6.7 ppm.

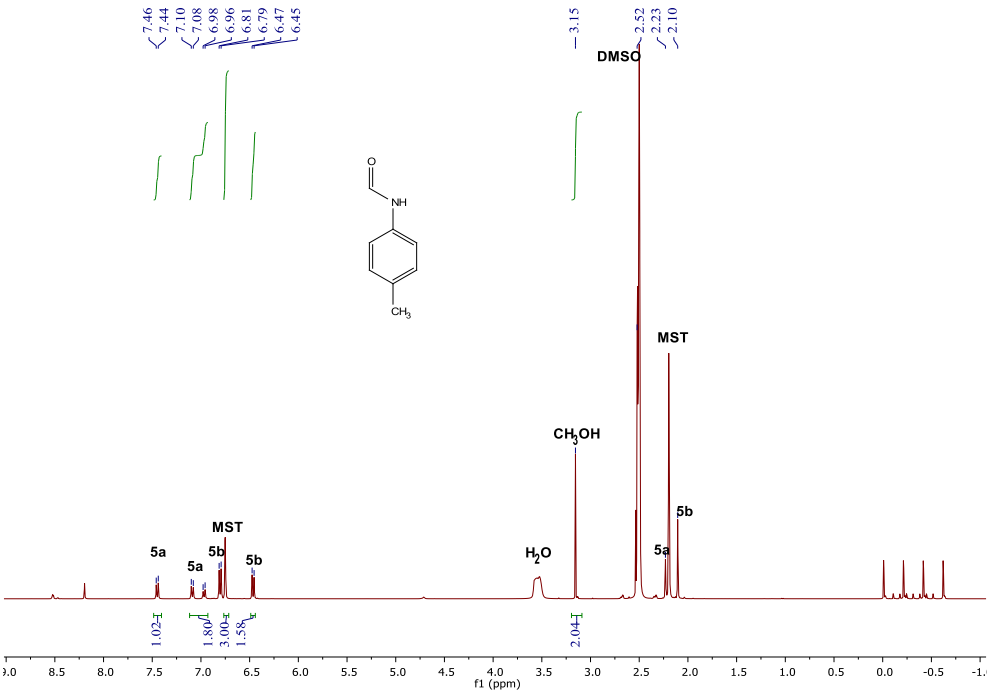


Figure S8. ^{1}H NMR spectrum of the crude reaction mixture for the reduction of substrate **5a**. Amine (**5b**) yield and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aromatic mesitylene singlet at ~6.7 ppm.

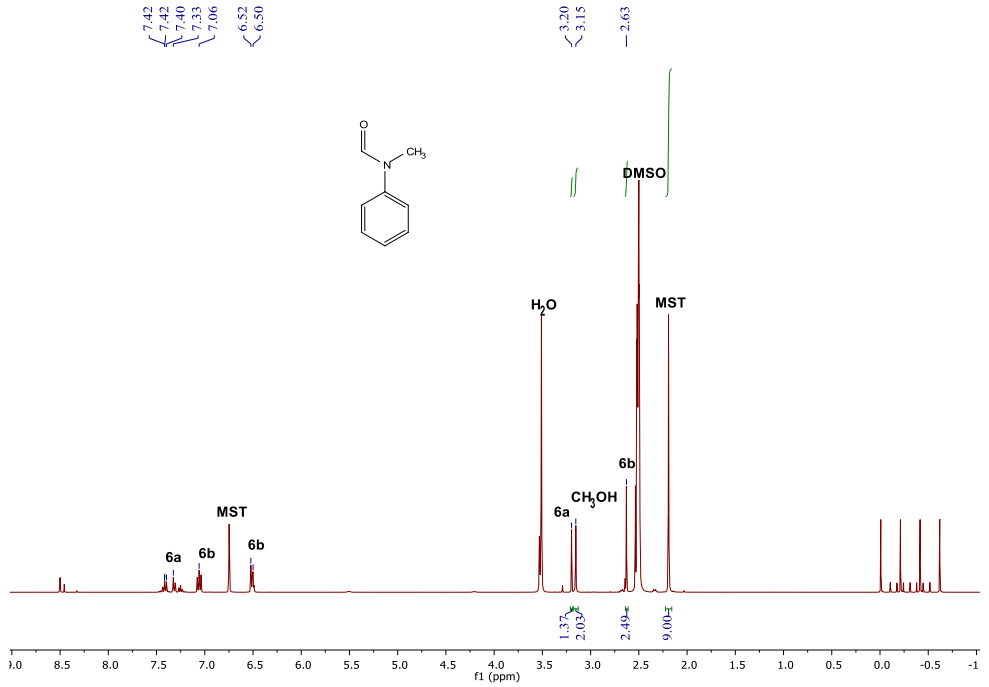


Figure S9. ^{1}H NMR spectrum of the crude reaction mixture for the reduction of substrate **6a**. Amine (**6b**) yield and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aliphatic mesitylene singlet at ~2.2 ppm.

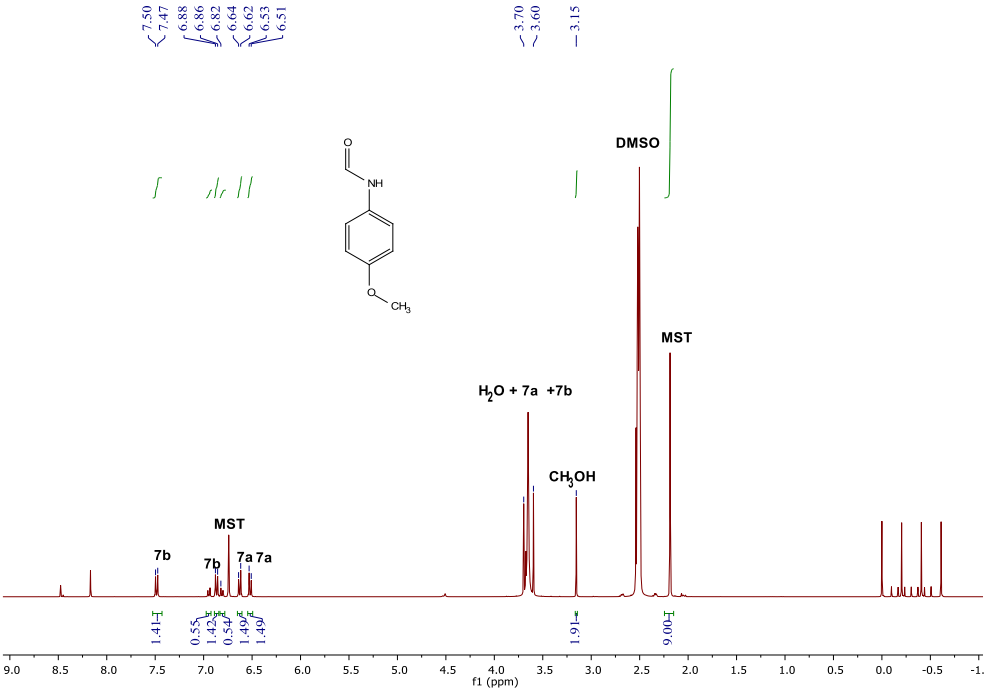


Figure S10. [1]H NMR spectrum of the crude reaction mixture for the reduction of substrate **7a**. Amine (**7b**) yield and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aliphatic mesitylene singlet at ~2.2 ppm.

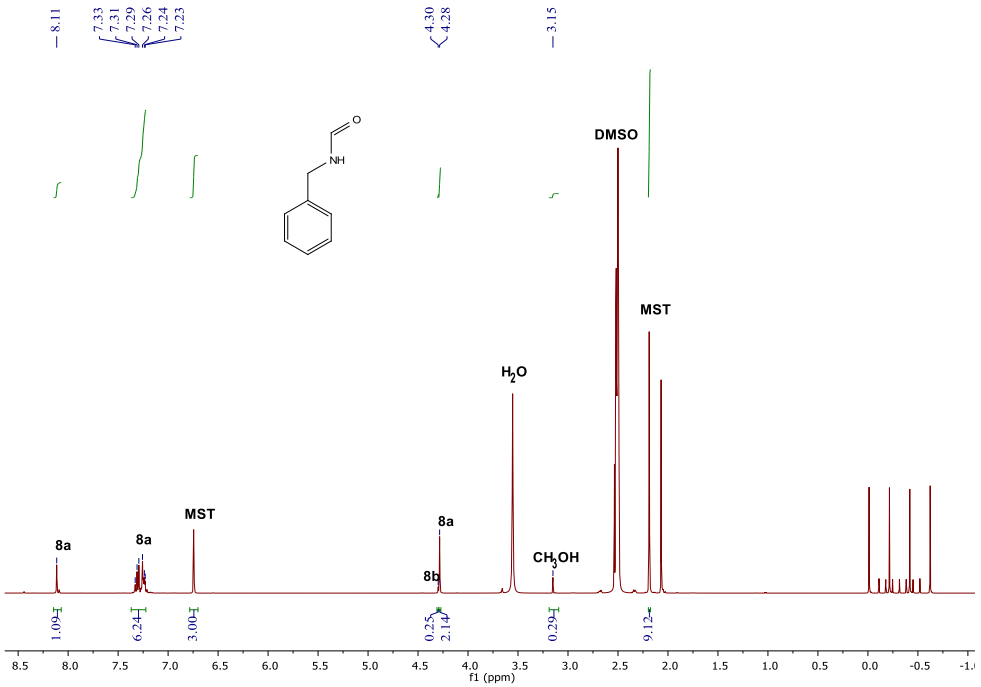


Figure S11. [1]H NMR spectrum of the crude reaction mixture for the reduction of substrate **7a**. Amine (**7b**) yield and methanol yields were determined from the integration ratios between the amine and methanol peaks relative to the aliphatic mesitylene singlet at ~2.2 ppm.

S1.5 Boron analysis

Boron analysis was carried out by ^{11}B NMR spectroscopy and the resulting spectra were compared with literature data.

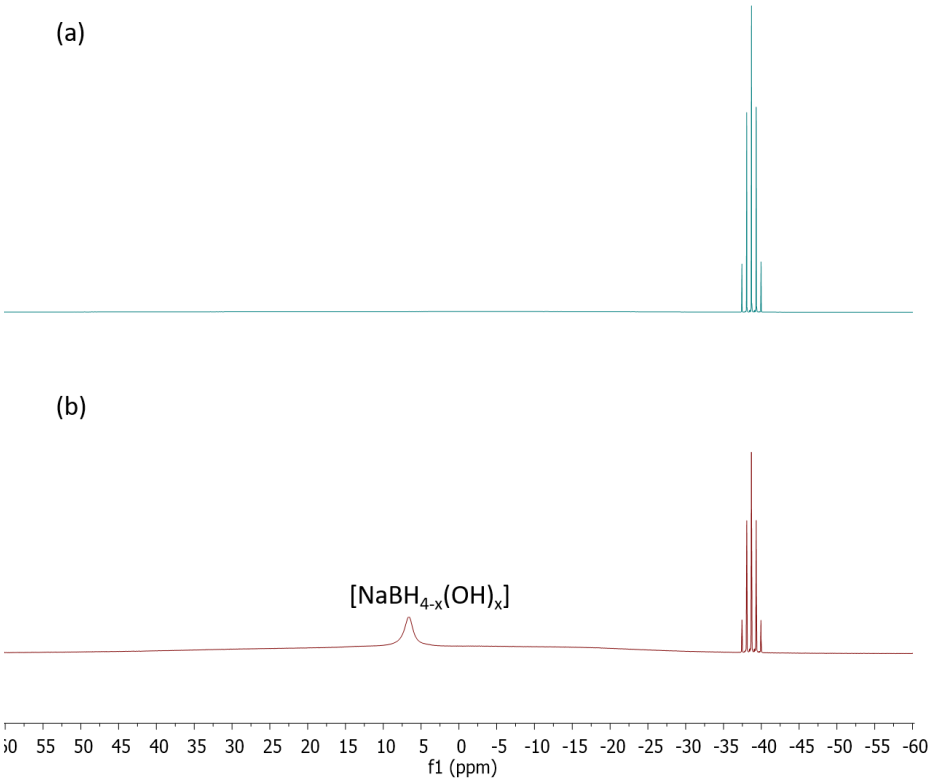


Figure S12. ^{11}B NMR spectrum of the crude reaction mixture (a) before the reduction, and (b) after the reduction of substrate **6a** in DMSO-d6 using the optimized reaction conditions described in section S1. The observed broad peak in (b) appearing at ~5 ppm is consistent with the hydroxyborate compound $[NaBH_{4-x}(OH)_x]$ as previously described.[1] In addition, remaining $NaBH_4$ was also detected as a characteristic quintet at ~-40 ppm.

S2. Formylation of amines

S2.1 ^{1}H NMR spectra for the crude mixtures of formylation reaction

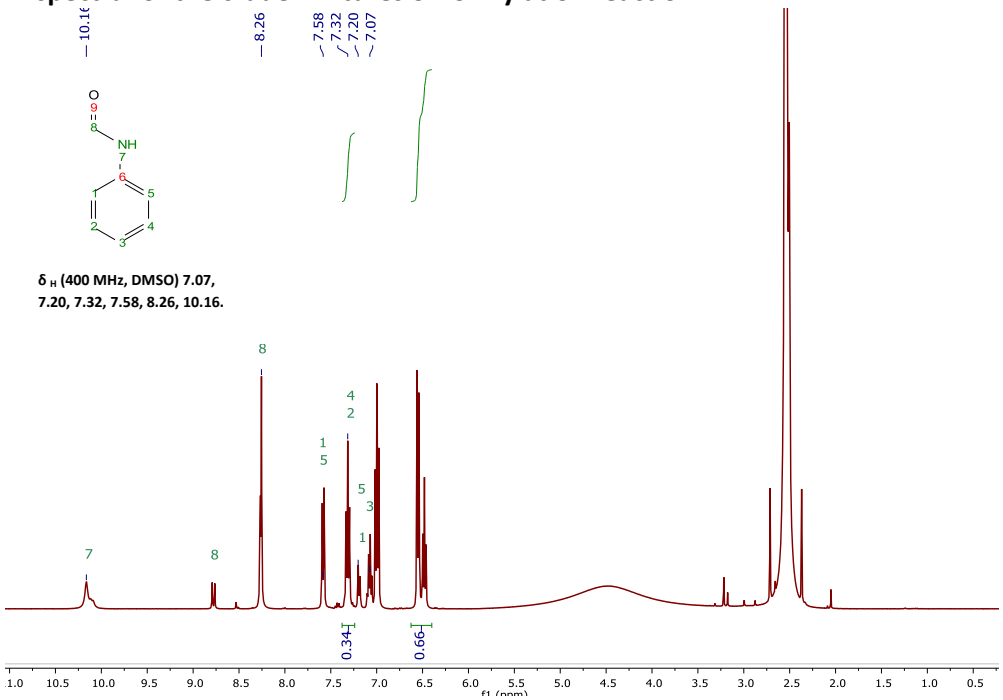


Figure S13. ^{1}H NMR spectrum of the crude reaction mixture for the formylation of substrate **3a** in DMSO-d6. Reaction conditions: aniline (1 mmol), triformatoborohydride (1 mmol) in DMSO (1 mL), 70ºC, 4 h. Formylation product **3b**, yield = 43%.

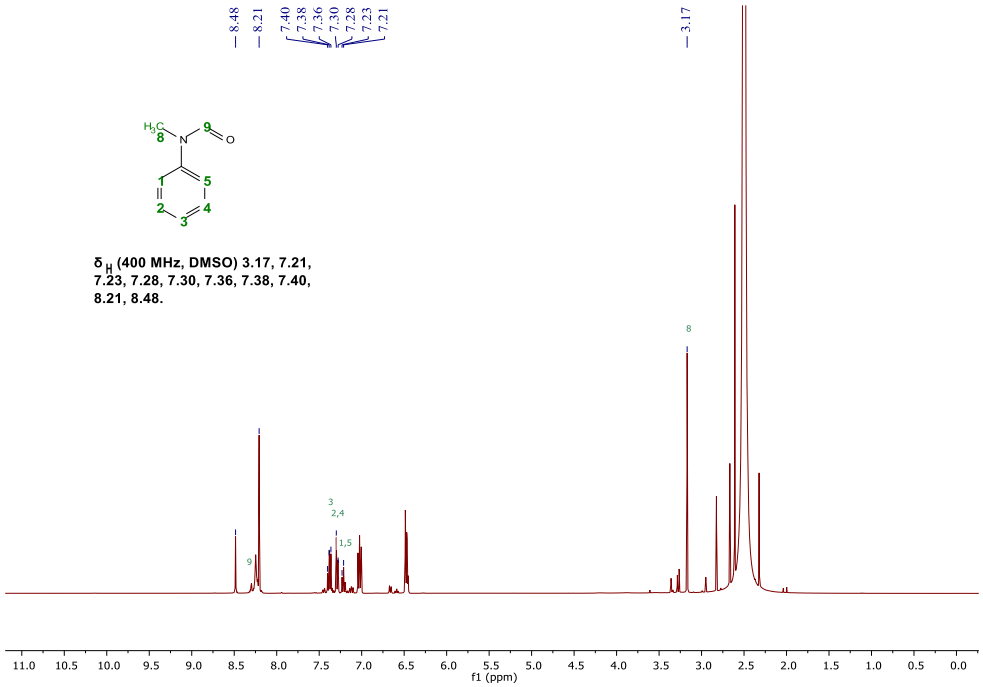


Figure S14. ^{1}H NMR spectrum of the crude reaction mixture for the formylation of substrate **6a** in DMSO-d6. Reaction conditions: *N*-methylaniline (1 mmol), triformatoborohydride (1 mmol) in DMSO (1 mL), 70ºC, 4 h. Formylation product **6b** yield = 46%.

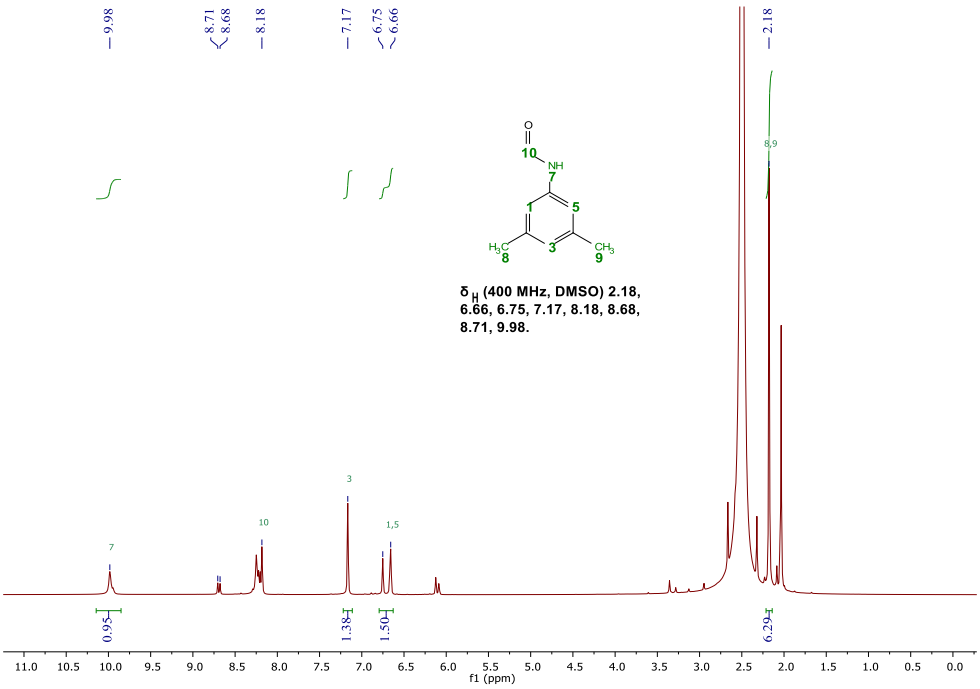


Figure S15. ^{1}H NMR spectrum of the crude reaction mixture for the formylation of substrate **4a** in DMSO-d6. Reaction conditions: 3,5-dimethylformanilide (1 mmol), triformatoborohydride (1 mmol) in DMSO (1 mL), 70^{o}C, 4 h. Formylation product **4b** yield = 88%.

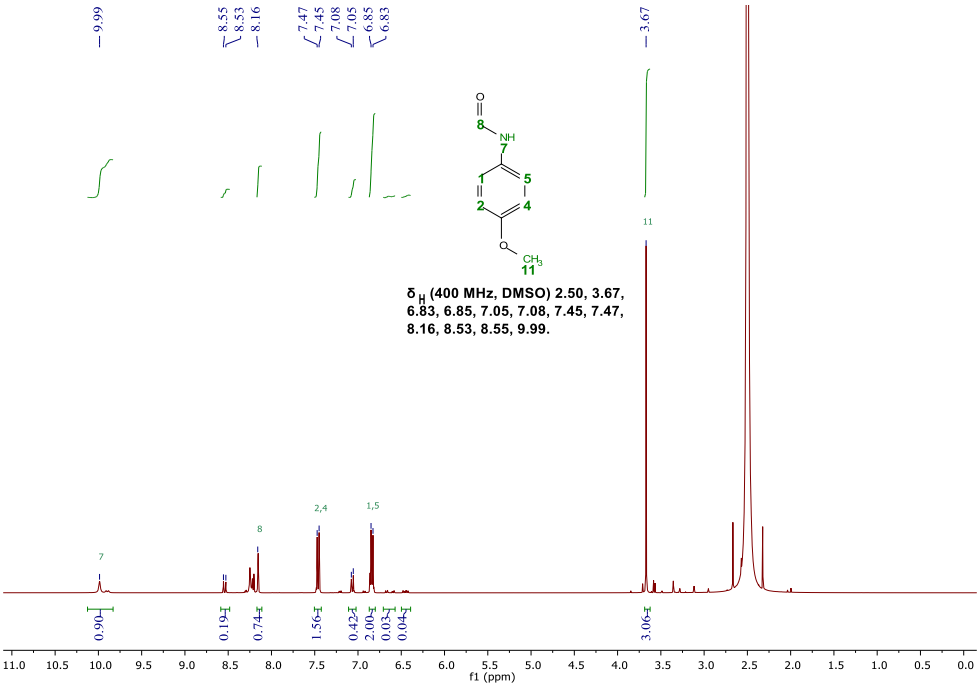


Figure S16. ^{1}H NMR spectrum of the crude reaction mixture for the formylation of substrate **7a** in DMSO-d6. Reaction conditions: 4-methoxyformanilide (1 mmol), triformatoborohydride (1 mmol) in DMSO (1 mL), 70^{o}C, 4 h. Formylation product **7b** yield = 96%.

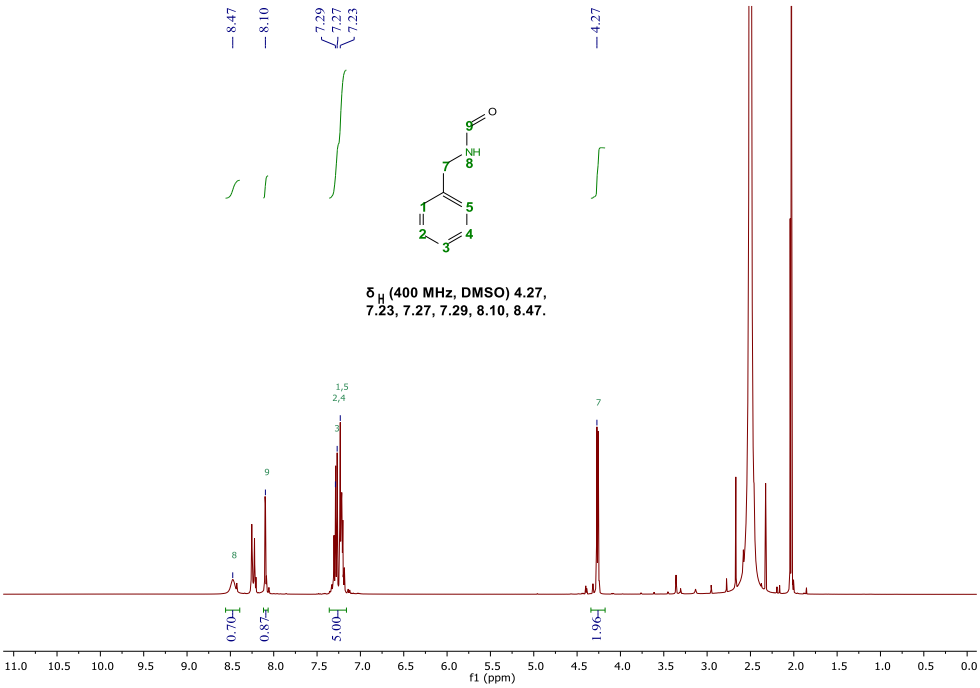


Figure S17. ^{1}H NMR spectrum of the crude reaction mixture for the formylation of substrate **8a** in DMSO-d6. Reaction conditions: Benzylformanilide (1 mmol), triformatoborohydride (1 mmol) in DMSO (1 mL), 70^{o}C, 4 h. Formylation product **8b** yield = 97%.

S2.2 ^{1}H and ^{13}C NMR spectra of the isolated formamides

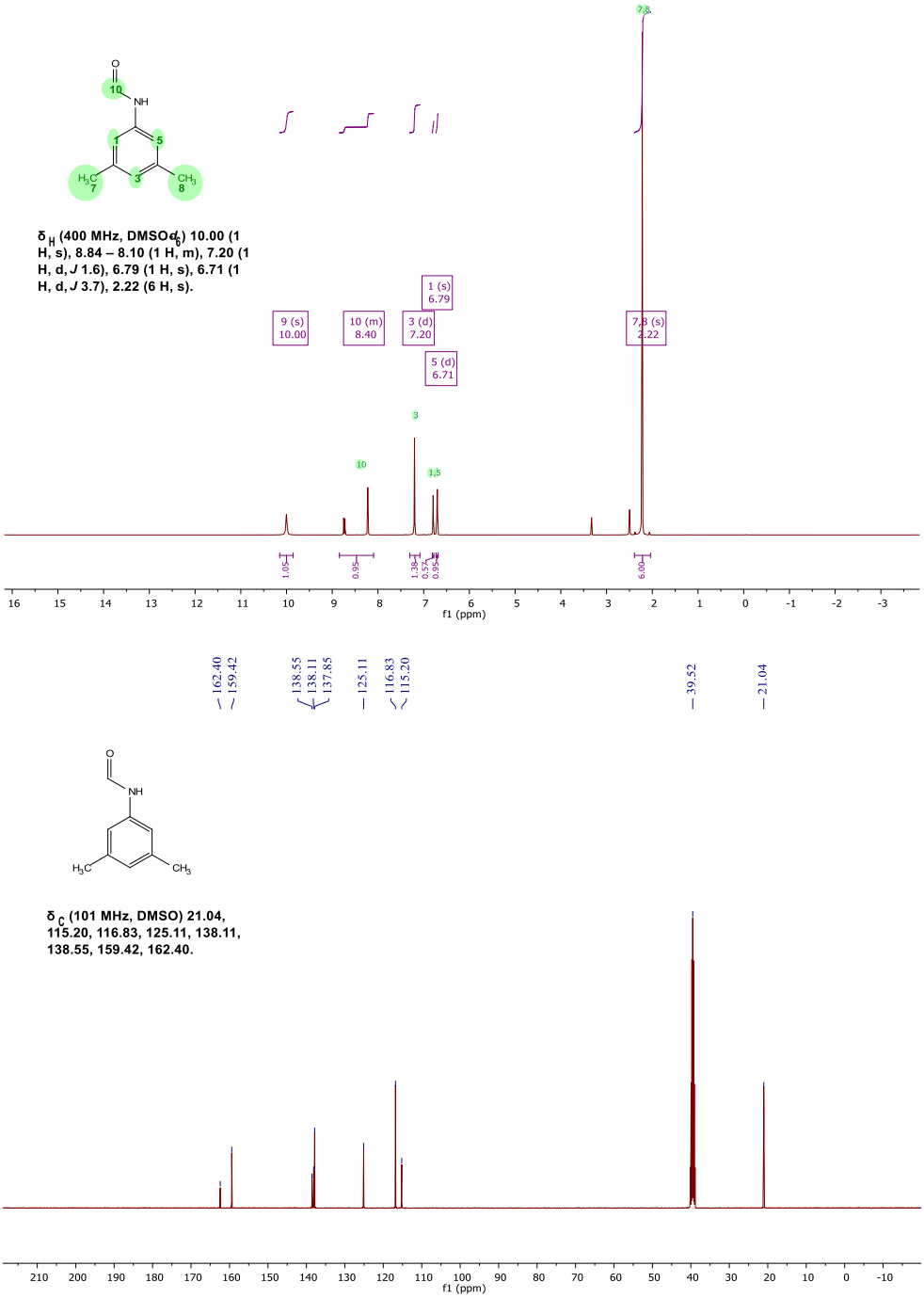


Figure S18. ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of 3,5-dimethylformanilide.

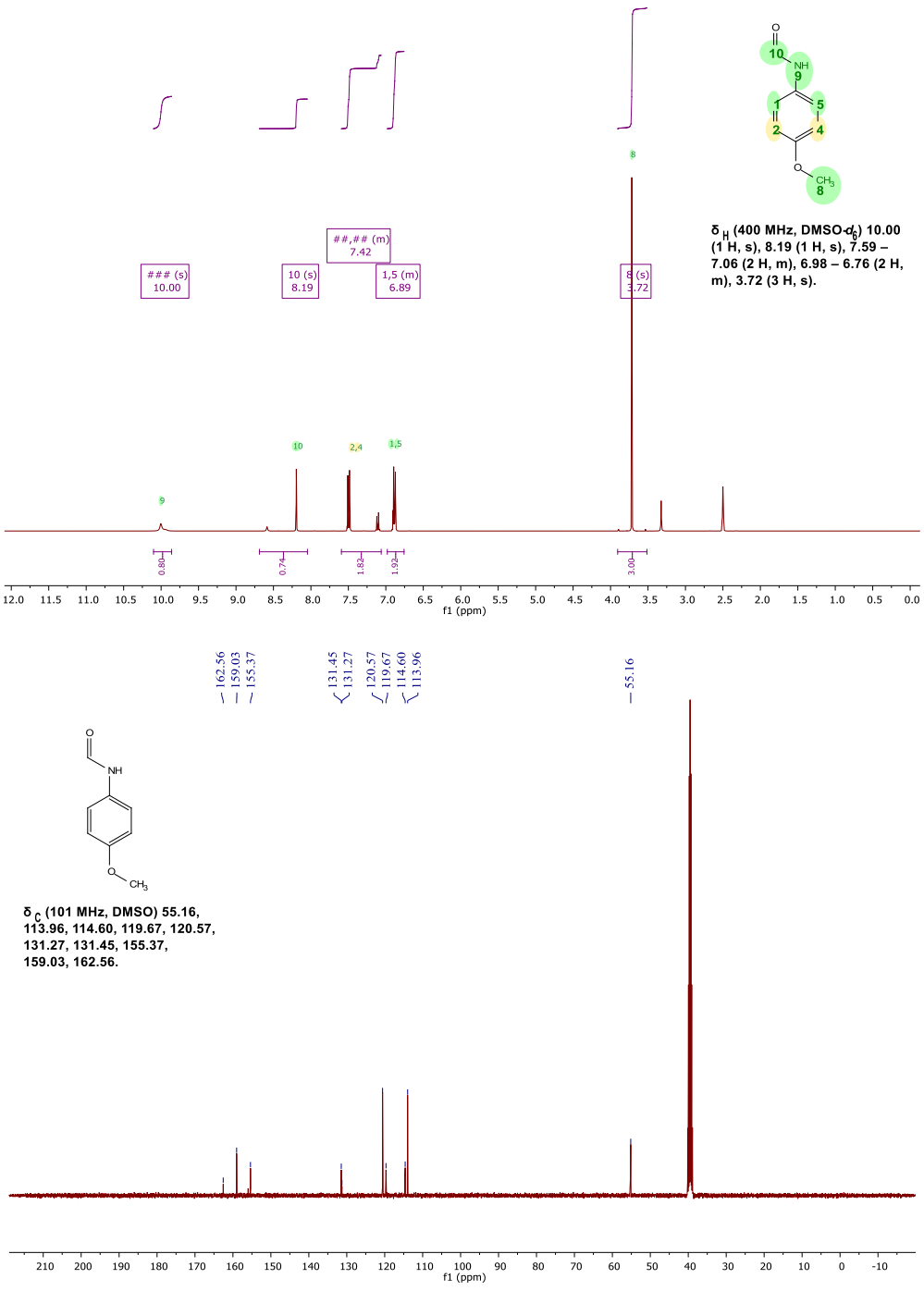


Figure S19. ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of 4-methoxyformanilide.

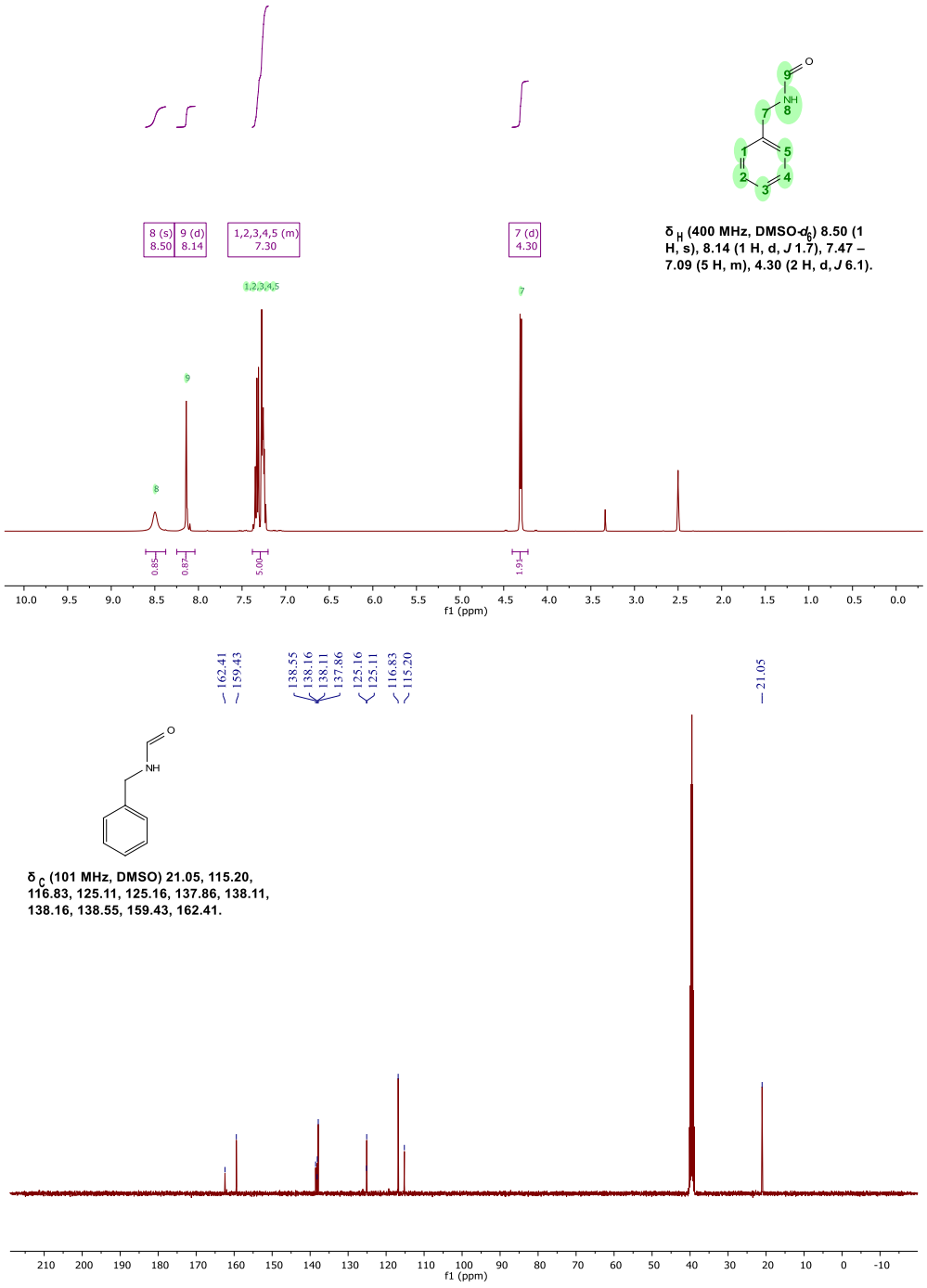


Figure S20. ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of *N*-benzylformanilide.

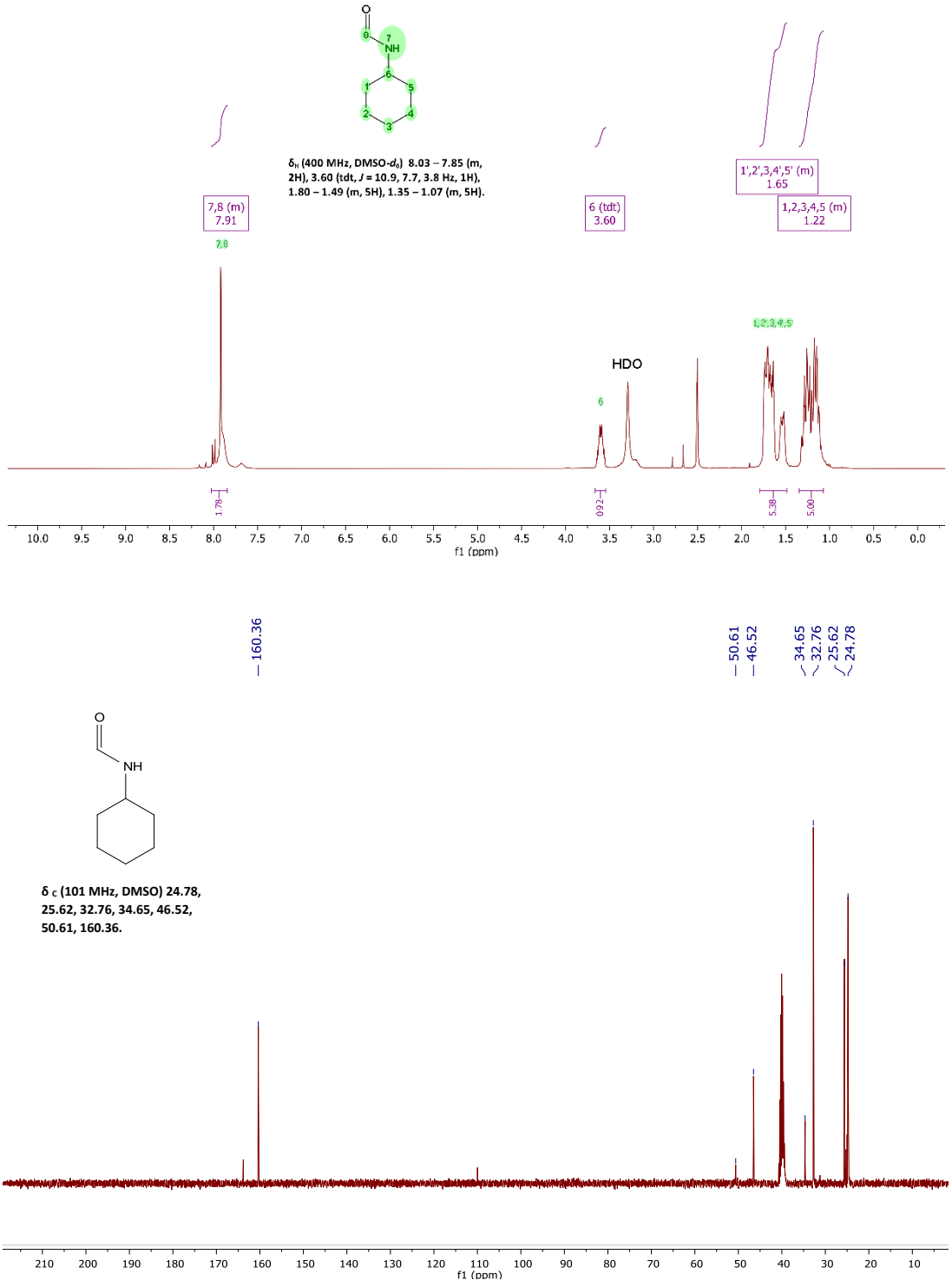


Figure S21. ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of *N*-cyclohexylformamide.

S3. Reactivity analysis

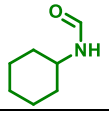
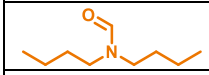
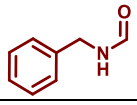
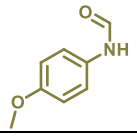
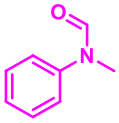
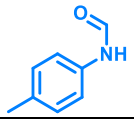
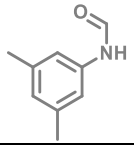
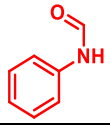
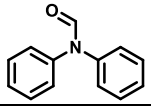
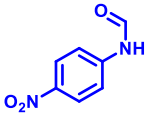
Formamide	Atomic charge Oxygen in atomic units	Bond order C-N	Bond order C-O	Bond distance in Angstroms C-N	Bond distance in Angstroms C-O	Average ^{1}H NMR chemical shift C(O)H in ppm	C-O stretching IR band (cm^{-1})
	-0.718	1.061	1.232	1.345	1.238	**8.01; 7.92 (7.96)**	1674
	-0.717	1.064	1.211	1.348	1.239	**8.00 (8.00)**	1663
	-0.707	1.049	1.237	1.348	1.235	**8.50; 8.14 (8.32)**	1679
	-0.690	1.019	1.244	1.356	1.233	**8.60; 8.21 (8.40)**	1686
	-0.688	1.026	1.233	1.361	1.233	**8.53; 8.35 (8.44)**	1671
	-0.686	1.015	1.245	1.357	1.233	**8.70; 8.23 (8.46)**	1688
	-0.686	1.014	1.245	1.357	1.232	**8.74;8.22 (8.48)**	1689
	-0.682	1.011	1.247	1.359	1.232	**8.78; 8.26(8.52)**	1692
	-0.670	1.009	1.239	1.371	1.229	**8.68 (8.68)**	1683
	-0.649	0.979	1.260	1.368	1.226	**9.05; 8.41 (8.73)**	1698

Table S4. Summary of spectroscopic and electronic properties of the formamides.

S3.1 Stacked IR spectra of secondary and tertiary formamides

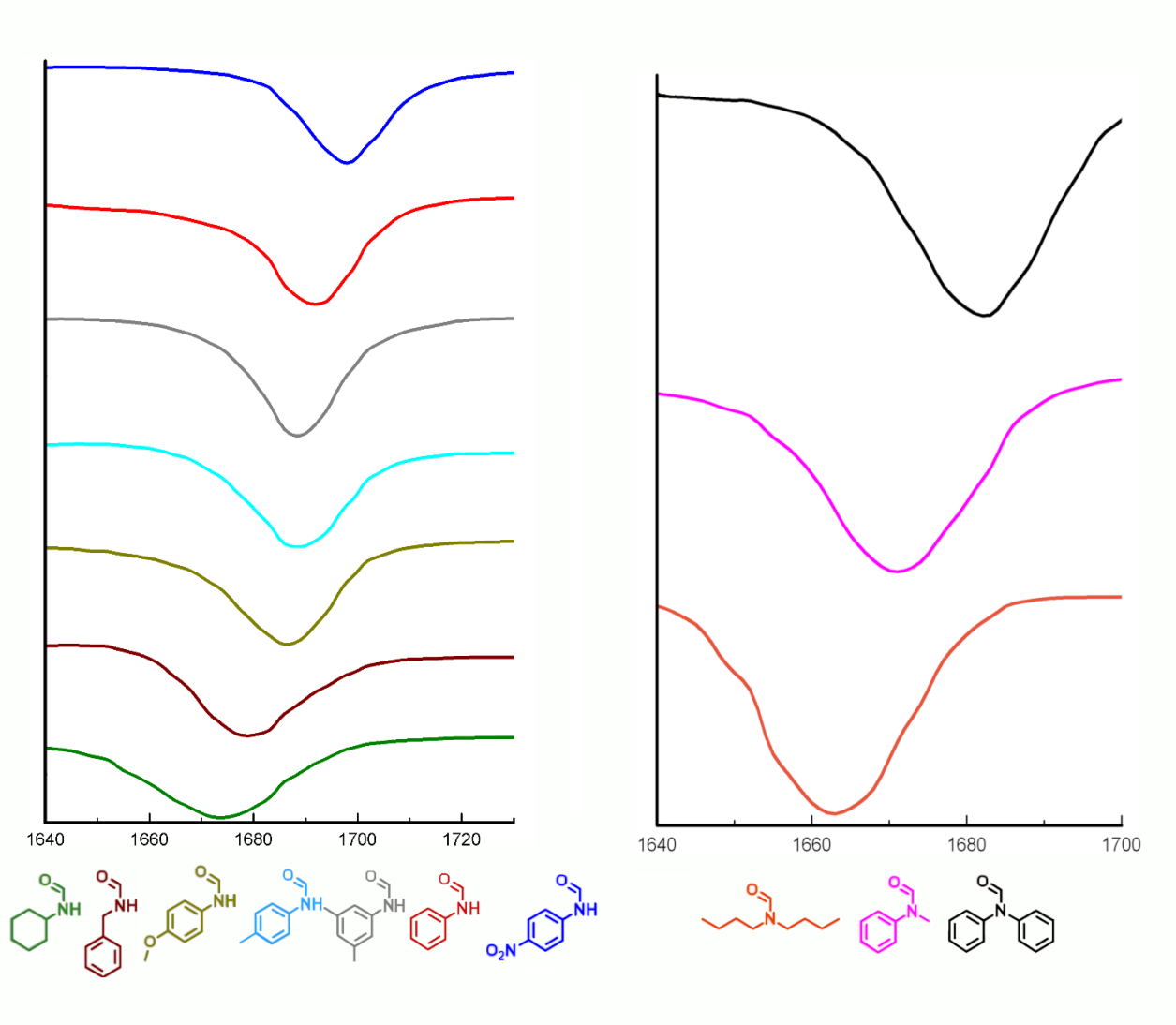


Figure S22. IR spectra for the secondary (a) and tertiary formamides (b). The C=O band fit with the reactivity trend when the comparison is made between the formamides having the same degree of substitutions (i.e., secondary and tertiary formamides). Notably, the comparison of formamide with the same degree of substitution follows the experimentally observed reactivity trend.

S3.2 Computational details

Electronic structure calculations were carried out at the B3LYP/6-31+G* level using the Gaussian 09 suite of programs [2]. The compounds were fully optimized resulting in a planar N-C-O conformation, and all structures were confirmed as minima by Hessian matrix analysis. The solvent effect was included using the IEFPCM model [3] using DMSO parameters. Natural Population analysis was performed with the NBO[4] model as implemented in the g09 package.

S3.3 Effect of conjugation

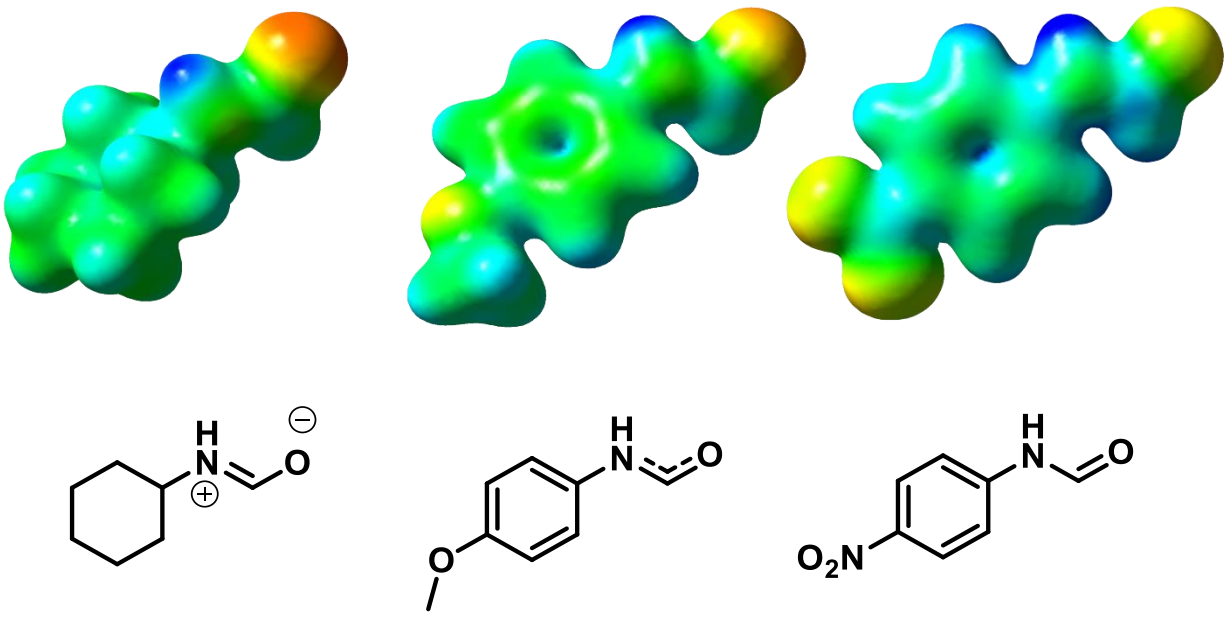


Figure S23. Electrostatic potential (ESP) maps of the formamides showing the conjugation effect induced by different substituent groups (top). Graphical representations of the formamides (bottom) are shown for clarity.

The ESP maps show the effect of conjugation on the carbonylic oxygen partial charge. Notably, in *N*-cyclohexylformamide, the carbonyl group exhibits a high negative charge on the oxygen, 4-methoxyformanilide shows an intermediate atomic charge and 4-nitroformanilide has a much lower charge.

S3.4 Optimized geometries in Cartesian coordinates

N,*N*-diphenylformamide (**1a**)

C	-2.752664	-1.419469	1.050122
C	-3.776094	-1.038380	0.176736
C	-3.546321	-0.028133	-0.757476
C	-2.299071	0.596933	-0.827515
C	-1.282852	0.226652	0.060964
C	-1.512251	-0.787021	1.000877
H	-4.743350	-1.530377	0.222334
N	-0.012629	0.892164	0.025656
C	1.192030	0.114173	-0.042529
H	-4.330952	0.267032	-1.448312
H	-2.108177	1.357112	-1.578943
H	-0.720679	-1.069589	1.687876
H	-2.923822	-2.204756	1.781036
C	0.021840	2.272215	0.036545
C	1.260619	-0.966295	-0.930661
C	2.419639	-1.738298	-1.000278
C	3.518831	-1.433227	-0.194504

C	3.448104	-0.352388	0.686986
C	2.289175	0.419613	0.771484
H	0.408633	-1.197563	-1.562250
H	2.463540	-2.575110	-1.691809
H	4.422616	-2.033059	-0.252782
H	4.296543	-0.108982	1.320484
H	2.236798	1.256938	1.456630
O	1.023749	2.961866	-0.055842
H	-0.988651	2.700019	0.148365

4-nitroformanilide (**2a**)

C	0.018655	-0.008371	0.007211
C	-0.003845	0.061168	1.390442
C	1.203299	0.020721	2.092550
C	2.425240	-0.081606	1.424014
C	2.446698	-0.145396	0.038775
C	1.239573	-0.116197	-0.687072
N	1.187760	0.090134	3.544134
O	0.095418	0.187596	4.114010
N	1.189982	-0.180219	-2.081815
C	2.206732	-0.426446	-2.970903
O	2.032575	-0.462161	-4.178114
O	2.267195	0.048333	4.144581
H	0.278438	-0.066805	-2.515461
H	3.348028	-0.103439	1.989681
H	3.403823	-0.208313	-0.463654
H	-0.914710	0.016513	-0.547097
H	-0.940216	0.142449	1.927599
H	3.187192	-0.594730	-2.504689

Formanilide (**3a**)

C	0.000914	0.006749	-0.001043
C	-0.001863	-0.005937	1.401644
C	1.205508	-0.009727	2.102436
C	2.423847	-0.017551	1.414828
C	2.422366	-0.001317	0.016764
C	1.219845	0.026650	-0.694828
N	-1.242505	0.018896	-0.683815
C	-1.506700	-0.528585	-1.898254
O	-2.610498	-0.485750	-2.443400
H	3.361377	0.010714	-0.529994
H	1.238051	0.085472	-1.778399
H	-0.946458	-0.020289	1.939537
H	1.190541	-0.016441	3.188971
H	-0.645913	-1.030845	-2.362762
H	-2.044707	0.403080	-0.191948
H	3.362296	-0.026882	1.961867

3,5-dimethylformanilide (**4 a**)

C	-0.014541	-0.025077	-0.008872
C	-0.021049	-0.033924	1.391523
C	1.181759	0.005687	2.107160
C	2.388843	0.028972	1.393942
C	2.413004	0.036616	-0.007855
C	1.198609	0.028715	-0.707361
N	-1.259731	-0.052703	-0.690842
C	-1.510107	-0.612606	-1.901396
O	-2.616660	-0.607007	-2.444338
C	3.725641	0.045780	-0.758582
H	1.207013	0.085074	-1.791985
H	-0.968615	-0.076696	1.924146
C	1.172411	0.041085	3.618851
H	-0.635026	-1.088746	-2.366599
H	-2.072354	0.307073	-0.197683
H	3.329101	0.050712	1.941464
H	2.098376	-0.371279	4.033088
H	1.079109	1.072102	3.985746
H	0.330001	-0.527038	4.028131
H	3.634091	0.562081	-1.720254
H	4.514127	0.536560	-0.178373
H	4.062992	-0.978166	-0.968725

4-methylformanilide (**5a**)

C	-0.002184	0.013587	-0.002668
C	-0.001635	0.010350	1.397168
C	1.221967	0.002628	2.082791
C	2.421547	-0.012093	1.373071
C	2.441960	-0.038031	-0.031631
C	1.209960	-0.026295	-0.698940
N	-1.209130	0.032524	2.144474
C	-2.382593	-0.553755	1.797546
O	-3.406552	-0.500918	2.481611
C	3.750704	-0.070133	-0.787539
H	1.188772	-0.027315	-1.786221
H	-0.935143	0.068370	-0.555132
H	1.232502	0.002477	3.169976
H	3.359624	-0.013900	1.923944
H	-2.346396	-1.097948	0.842346
H	-1.185475	0.460151	3.066196
H	3.586625	-0.039731	-1.869496
H	4.388144	0.781388	-0.518948
H	4.319035	-0.981061	-0.560130

N-methylfomanilide (**6a**)

C	-0.000080	-0.026088	-0.001116
C	0.000342	-0.022272	1.395732
C	1.205673	0.005982	2.104837
C	2.414709	0.046581	1.404067
C	2.423388	0.064035	0.006626
C	1.213984	0.010807	-0.702743
N	1.212886	0.009075	-2.131612
C	0.211190	0.795250	-2.861266
C	2.071727	-0.784742	-2.827827
O	2.127979	-0.853328	-4.058181
H	3.357714	0.086863	1.942590
H	3.365430	0.141699	-0.527733
H	-0.940761	-0.067157	-0.541348
H	-0.946351	-0.051072	1.928545
H	1.202072	0.005265	3.191254
H	0.614467	1.042493	-3.843974
H	-0.719594	0.232362	-2.995204
H	0.003109	1.712495	-2.307320
H	2.728677	-1.387374	-2.183827

4-methoxyformanilide (**7a**)

C	0.058745	1.319668	-0.332080
C	-1.329702	1.378587	-0.359350
C	-2.094610	0.235456	-0.073229
C	-1.447034	-0.960187	0.261423
C	-0.048640	-1.005811	0.314470
C	0.713199	0.123270	0.002406
N	2.135237	0.093106	0.030183
C	2.919382	-0.932807	-0.382700
O	4.151268	-0.927004	-0.327874
H	-2.008737	-1.854369	0.505431
H	0.435847	-1.928570	0.618900
H	0.640578	2.204721	-0.575970
H	-1.838205	2.303873	-0.613792
O	-3.451138	0.391440	-0.139337
H	2.356265	-1.788686	-0.785009
C	-4.281612	-0.738525	0.138318
H	-5.307072	-0.387960	0.016155
H	-4.085312	-1.554500	-0.567249
H	-4.134473	-1.092906	1.165366
H	2.622616	0.934266	0.326599

N-Benzylformamide (**8a**)

C	0.106383	0.097723	-0.257670
C	-0.027961	0.555037	1.062859
C	1.055228	0.511673	1.943222
C	2.290848	0.010557	1.514017
C	2.433960	-0.445755	0.201197

C	1.345188	-0.402578	-0.678004
H	-0.984147	0.945268	1.404530
H	0.937678	0.870750	2.962481
H	3.133770	-0.022728	2.199426
H	3.388567	-0.837679	-0.140340
H	1.461423	-0.760569	-1.698735
C	-1.065710	0.151550	-1.222286
N	-2.203025	-0.661354	-0.788827
C	-3.440625	-0.190788	-0.537969
H	-2.059599	-1.660957	-0.674109
O	-4.402203	-0.881402	-0.184499
H	-3.530230	0.899753	-0.677645
H	-0.743740	-0.180582	-2.215313
H	-1.430548	1.179052	-1.327979

N-cyclohexylformamide (**9a**)

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.538994
C	1.432890	0.000000	2.100538
C	2.262673	-1.162401	1.529959
C	2.265640	-1.155829	-0.006503
C	0.834034	-1.162394	-0.564381
N	-0.766777	1.136153	2.062055
C	-1.875360	1.048908	2.818495
O	-2.516927	2.012965	3.256206
H	-0.515940	-0.902741	1.890929
H	1.913906	0.955256	1.841440
H	1.394603	-0.052276	3.195802
H	3.288371	-1.105813	1.915911
H	1.844922	-2.115375	1.887921
H	2.791876	-0.258464	-0.365466
H	2.823087	-2.021623	-0.386765
H	0.848953	-1.105808	-1.660189
H	0.348319	-2.115368	-0.306048
H	0.416746	0.955255	-0.353314
H	-1.033723	-0.052275	-0.363989
H	-0.440093	2.073234	1.839086
H	-2.181659	0.010167	3.027602

Di n-buthylformamide (**10a**)

N	-0.031336	0.919659	-0.096956
C	-1.151431	0.223934	-0.744219
C	2.117209	-0.360310	-0.255591
C	0.967244	0.130651	0.636029
H	1.709916	-0.958022	-1.082958
H	1.357234	0.755809	1.444118
C	0.088415	2.259957	-0.183620
O	0.986738	2.941681	0.330025
H	-0.716046	2.727981	-0.775712

H	2.613408	0.509686	-0.706021
H	-0.755592	-0.673538	-1.234349
C	-2.285613	-0.151517	0.219630
H	-2.673038	0.765314	0.685472
H	-1.891313	-0.776873	1.032122
H	-1.537763	0.873752	-1.537085
H	0.452202	-0.720822	1.093262
C	3.141930	-1.196505	0.523283
H	3.543604	-0.597311	1.352917
H	2.635559	-2.058420	0.981331
C	4.297380	-1.691918	-0.354700
H	5.013245	-2.284304	0.227712
H	3.928930	-2.322695	-1.173869
H	4.843377	-0.850895	-0.801061
C	-3.425670	-0.896108	-0.489095
H	-3.027247	-1.805648	-0.961076
H	-3.816191	-0.270480	-1.304423
C	-4.570963	-1.273051	0.458258
H	-5.013904	-0.380538	0.918389
H	-4.216438	-1.924518	1.267221
H	-5.367965	-1.804966	-0.074950

S4. Tandem protocol

S4.1 ^{1}H NMR spectra for the integrated procedure

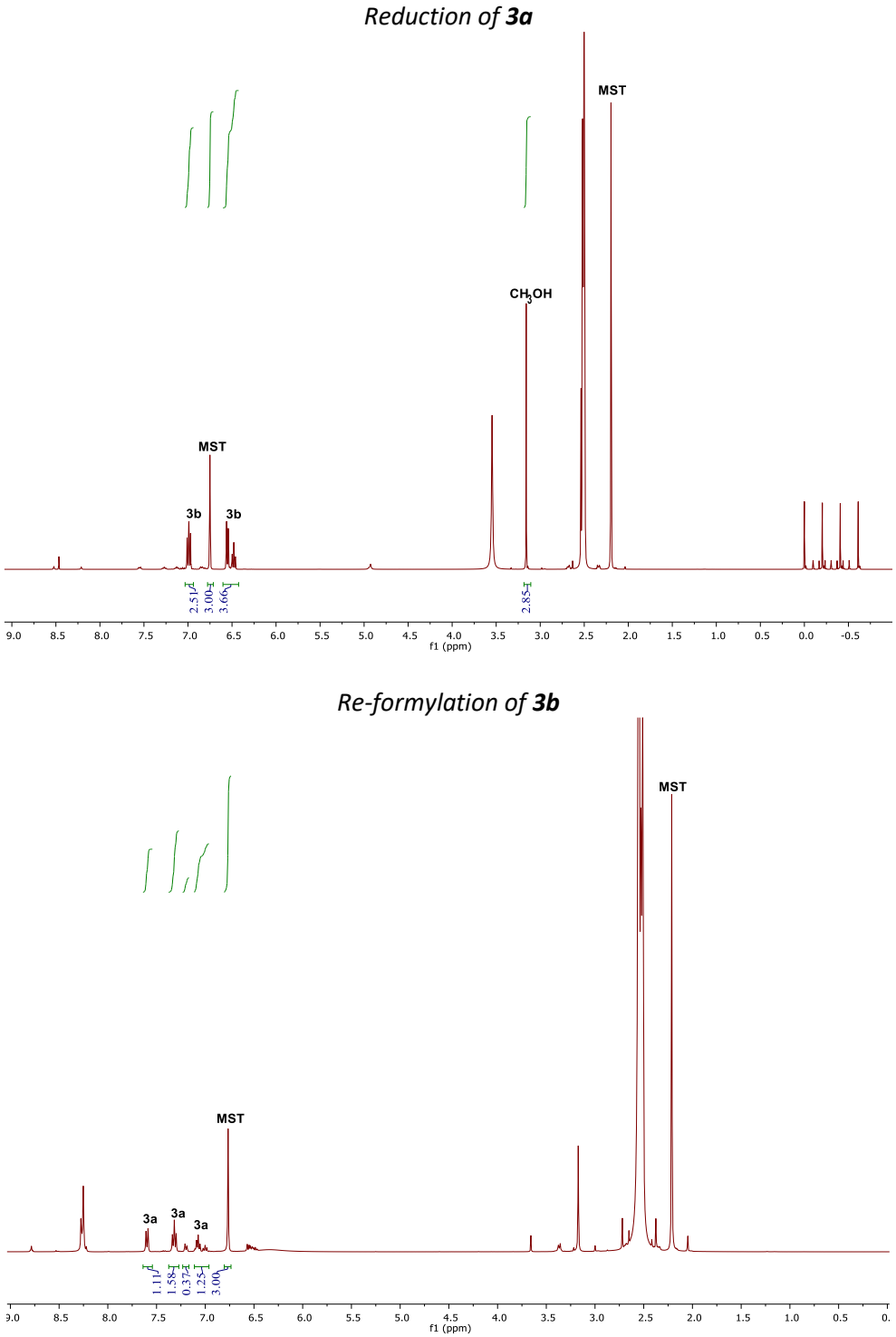


Figure S24. ^{1}H NMR spectra of the crude reaction mixture for the reduction of substrate **3a** (top) and its re-formylation product (bottom).

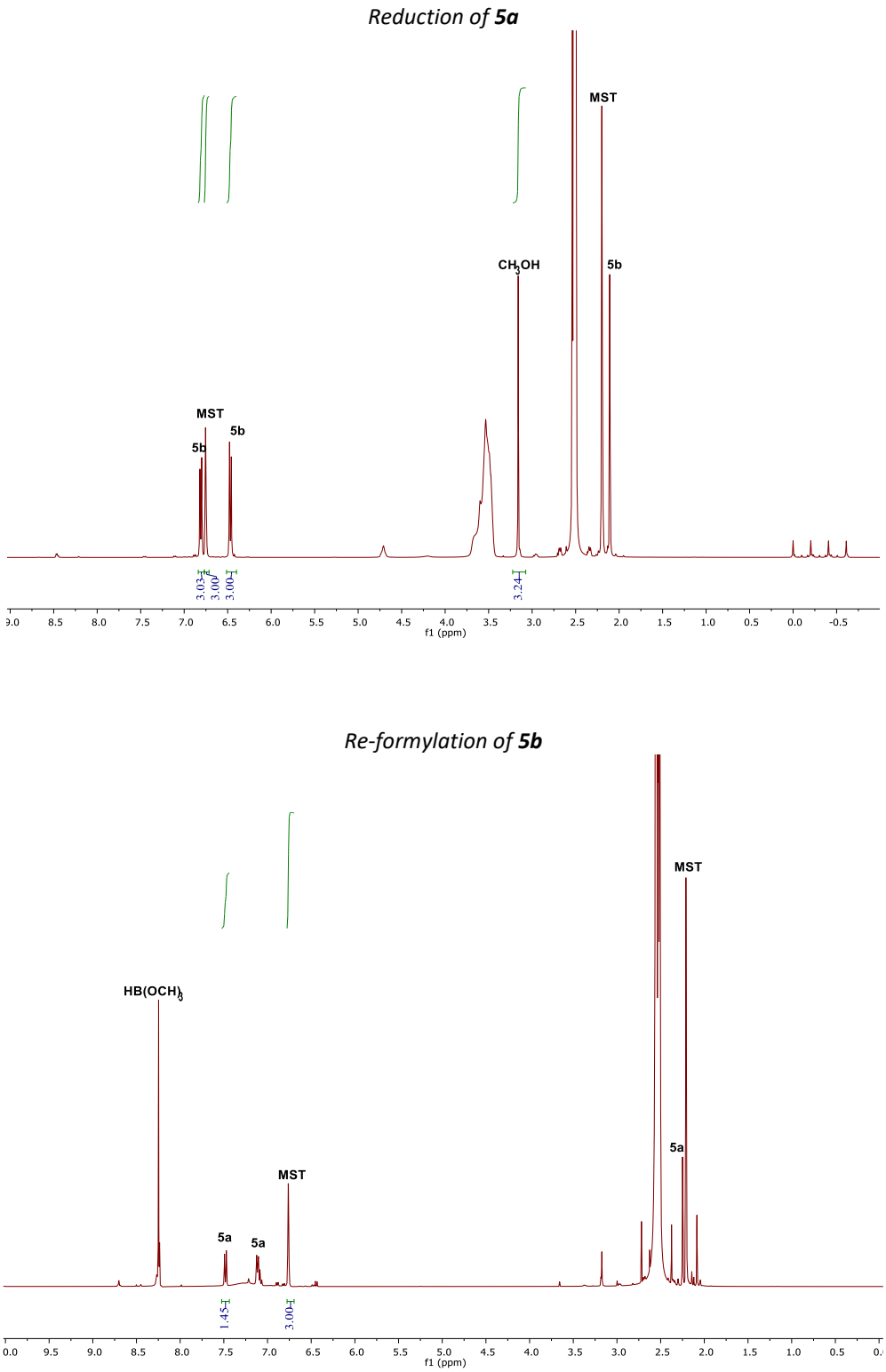


Figure S25. ^{1}H NMR spectra of the crude reaction mixture for the reduction of substrate **5a** (top) and its re-formylation product (bottom).

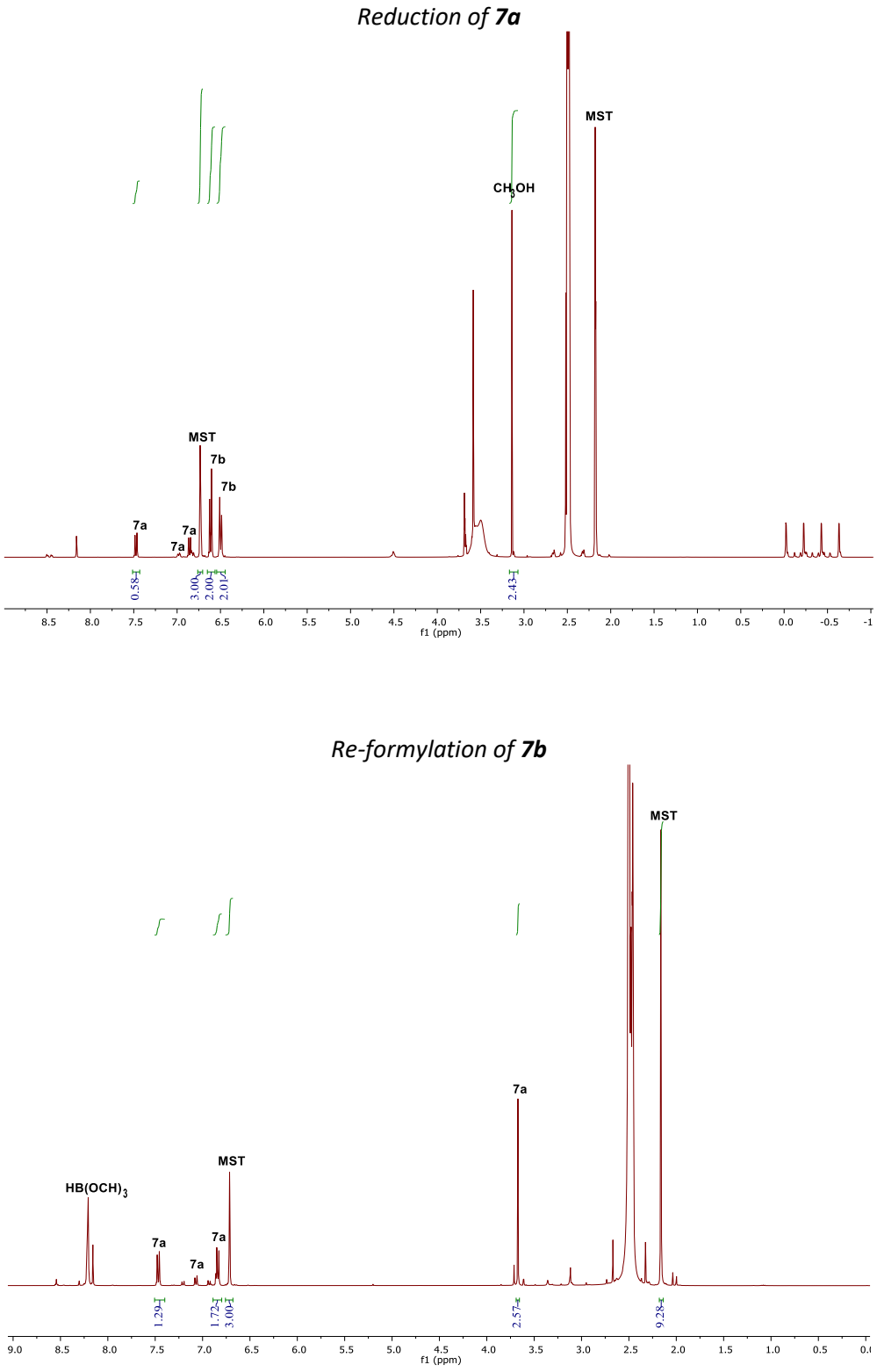


Figure S26. ^{1}H NMR spectra of the crude reaction mixture for the reduction of substrate **7a** (top) and its re-formylation product (bottom).

S5. References

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