Supplementary Materials

Air-stable efficient nickel catalyst for hydrogenation of organic compounds

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Method for synthesis of $Ni(cod)_2$.

The method is based on [Krysan, D. J.; Mackenzie, P. B.; A new, convenient preparation of bis (1, 5-cyclooctadiene) nickel (0). *J. Org. Chem.,* **1990**, 55 (13), 4229-4230. DOI: 10.1021/jo00300a057]

To 500-ml three-necked flask, equipped with a thermometer and dropping funnel, bis(acetylacetonate)nickel(II) (14.01 g, 54.53 mmol), cyclooctadiene (24 ml, 195.67 mmol), and 75 ml of THF were added. The mixture was backfilled with argon 3 times and cooled to -78 ºC. Then 1.0 M solution of diisobutylaluminum hydride in hexane (150 ml, 150 mmol) was introduced to the dropping funnel via a cannula. The brown suspension was slowly warmed to 0 ºC. Then 150 ml of degassed MTBE was added and temperature was decreased to 78 ºC and held for 3 hours for complete precipitation of the product. The resulting precipitate was filtered on a Schlenck filter tube under an inert atmosphere and washed with 30 ml of degassed MTBE until all colored residues are removed. The resulting light-yellow powder was dried in vacuo to obtain of $Ni(cod)_2$ (9.95 g, 66 %).

Table S1. The atomic concentrations of the elements found by XPS and calculated from the survey spectra (atomic %)

	Content of element, atomic %			
Sample	C	O	Ni	N
Ni/C-3	77.69	17.23	5.08	-
Ni/C-3 after the catalytic experiment[a)]	91.11	7.03	1.26	0.6[b)]
Ni/C-3 after 6 cycles of the catalytic experiment	89.22	7.75	1.34	1.69[b)]

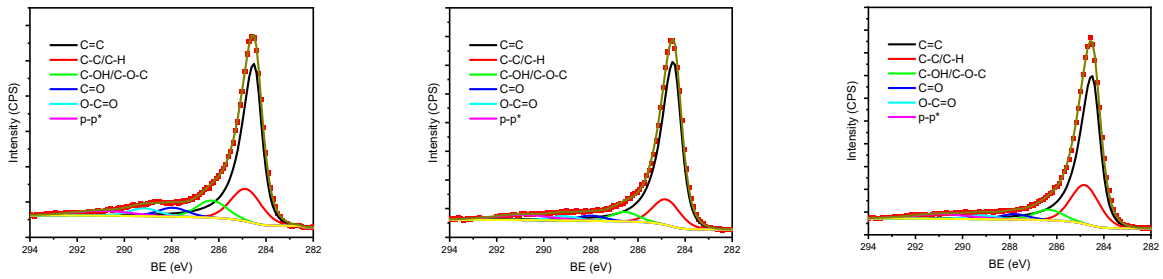
a) hydrogenation of quinoline (T = 100 °C, $p(H_2)$ = 100 atm, 24 h, methanol)

b) N of adsorbed quinoline or 1,2,3,4-tetrahydroquinoline

Table. S2 The results of analysis of the composites by CO chemisorption using extrapolation to zero pressure model

Composite	Ni content, %	S_{Ni}, $m^2/g(Ni)$	Dispersion [(a)], %	d_{Ni}, nm
Ni/C-1	0.9	863	100	0.8
Ni/C-3	2.8	341	52	2.0
Ni/C-5	4.5	362	54	1.9
Ni/C-10	9.1	82	12	8.2

[(a)] dispersion = N(adsorbing Ni atoms)/N(total Ni atoms)



(a) (b) (c)

Figure S1. 1s X-ray photoelectron spectra of Ni/C-3 composite (a), and the same sample after catalytic experiment on hydrogenation of quinoline (T = 100 °C, p(H_2) = 100 atm, 24 h, methanol) (b) and after 6 cycles of the same catalytic experiments (c).

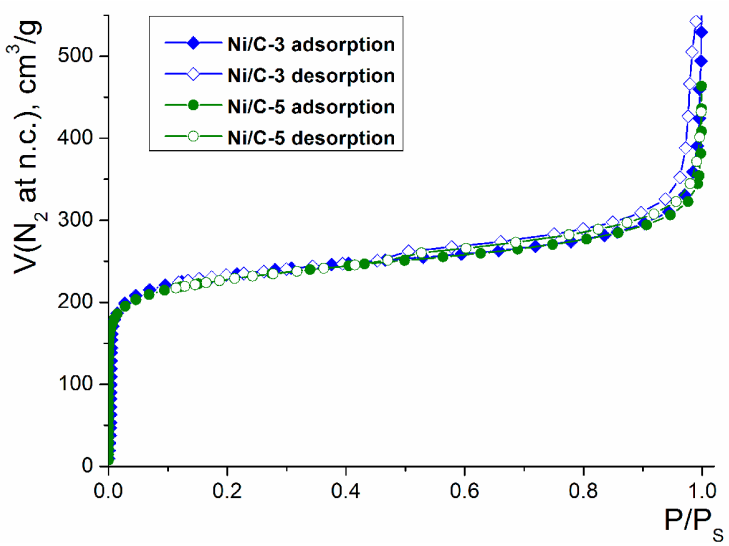


Figure S2. N_2 adsorption isotherms for samples Ni/C-3 and Ni/C-5

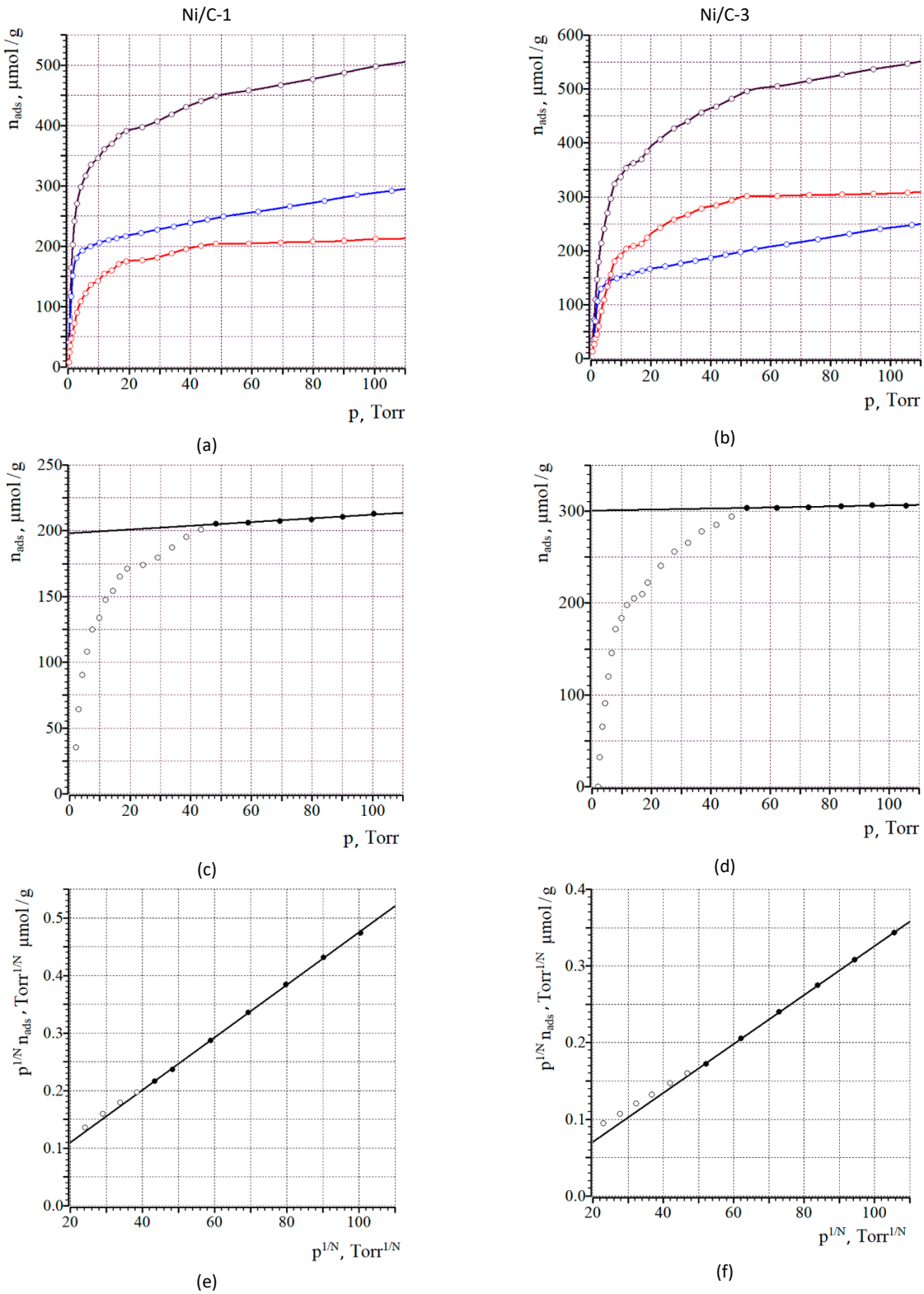


Figure S3. Isotherms of CO sorption (1st run – black, 2nd run – red, difference isotherm - blue) (a, b), the fit in the model of extrapolation to zero pressure (c, d) and the fit in the model of Langmuir adsorption, where N is the dissociation stoichiometry coefficient, N =1 for this case (e, f) for Ni/C-1 (left column) and Ni/C-3 (right column). On Figures c-f, filled symbols indicate those, which were used for linear fit.

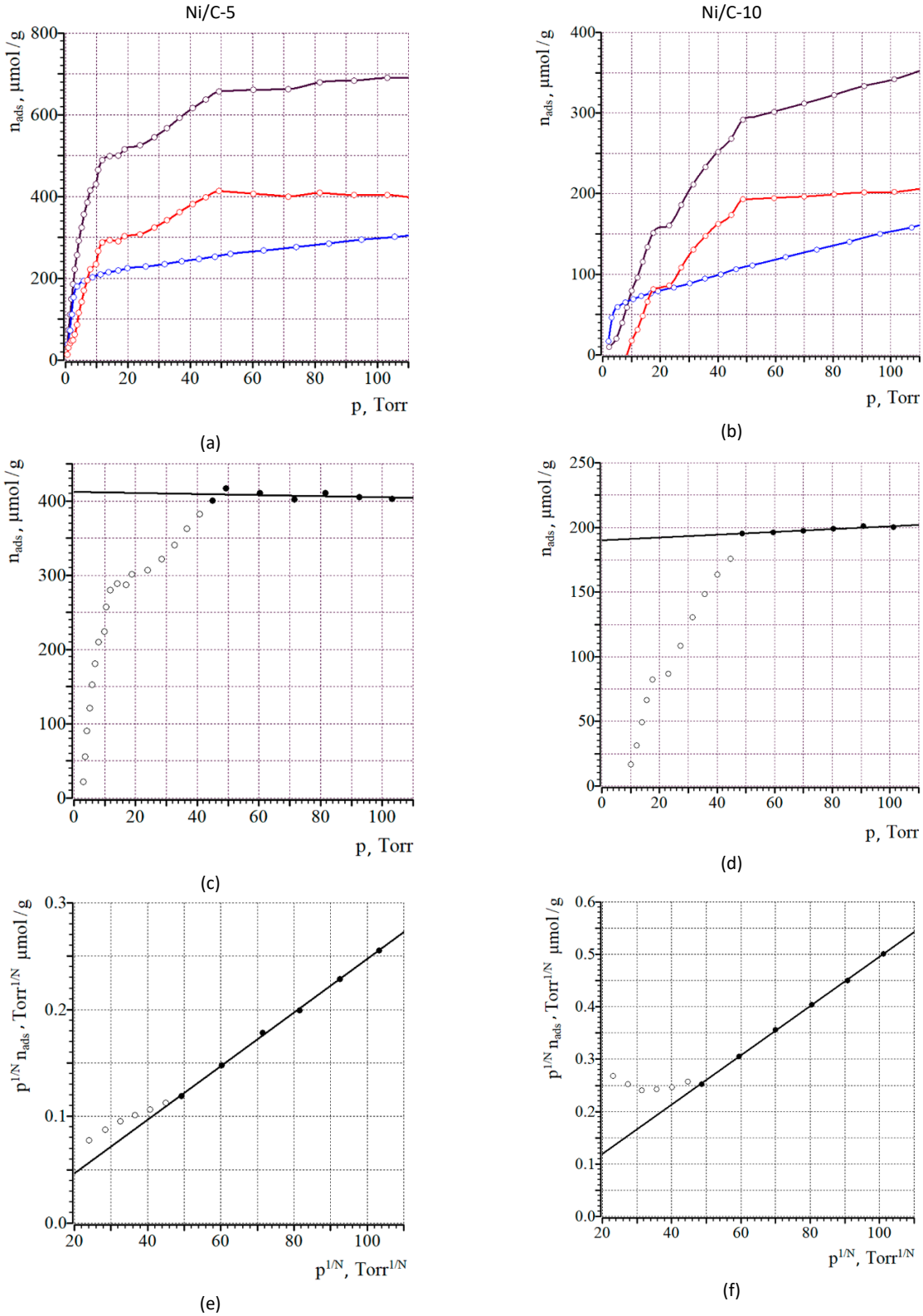
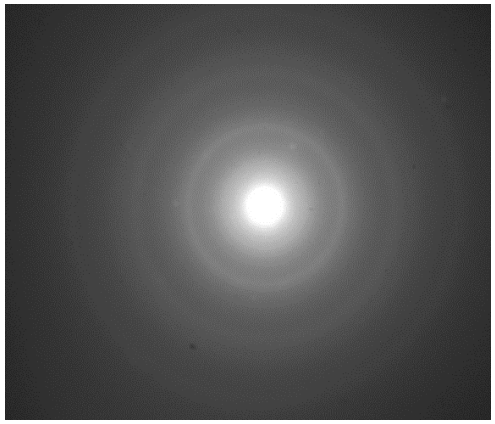


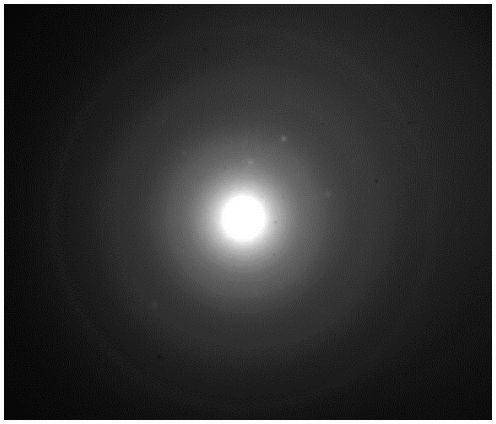
Figure S4. Isotherms of CO sorption (1st run – black, 2nd run – red, difference isotherm - blue) (a, b), the fit in the model of extrapolation to zero pressure (c, d) and the fit in the model of Langmuir adsorption, where N

is the dissociation stoichiometry coefficient, N =1 for this case (e, f) for Ni/C-5 (left column) and Ni/C-10 (right column). On Figures c-f, filled symbols indicate those, which were used for linear fit.



(a)

(b)



(c)

Figure S5. Electron diffraction patterns of composites Ni/C-3 (a), Ni/C-5 (b) and Ni/C-10 (c) after reduction with H_2 and experiments on chemisorption of CO.

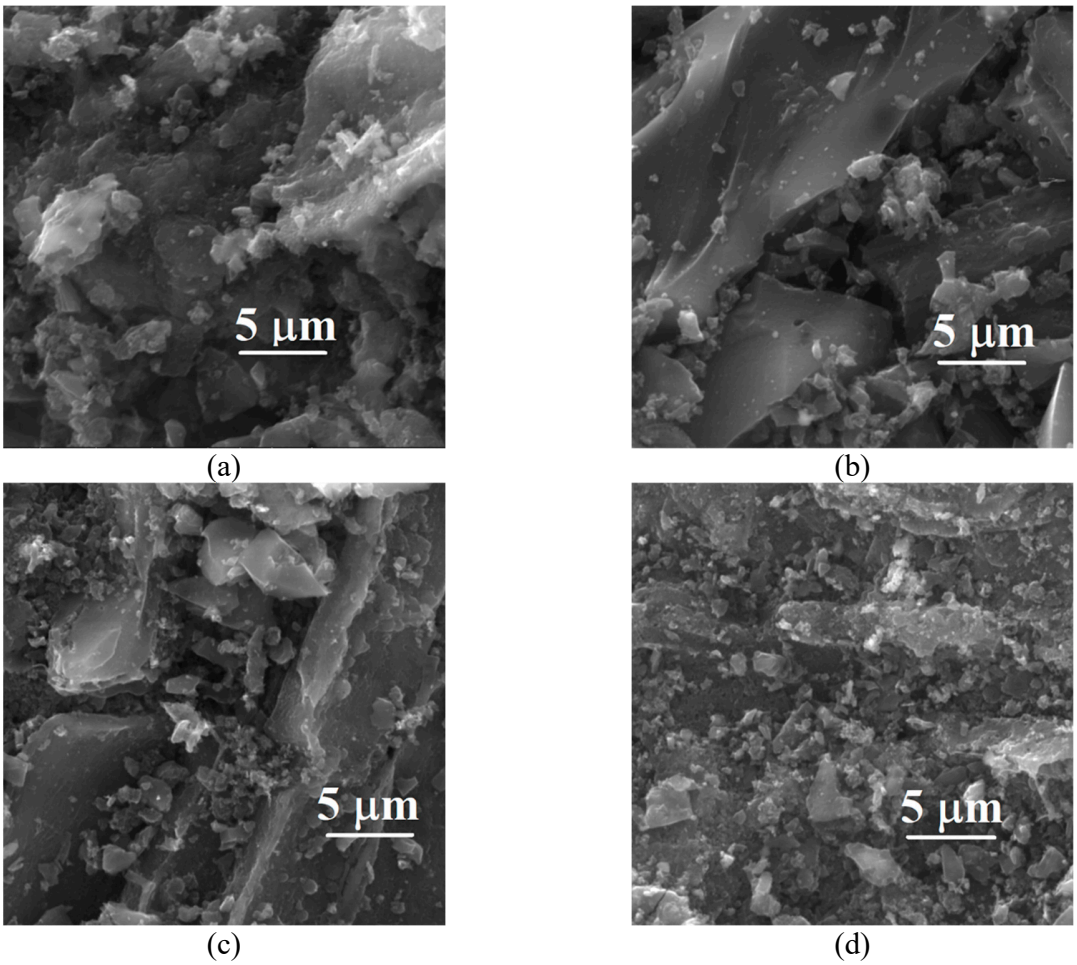
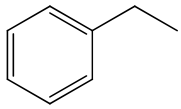


Figure S6. SEM images of Ni/C-1 (a), Ni/C-3 (b), Ni/C-5 (c) and Ni/C-10 (d) composites after catalytic hydrogenation of quinoline at 100 °C, $p(H_2)$ = 100 atm in methanol for 24 h.



DMSO-d6

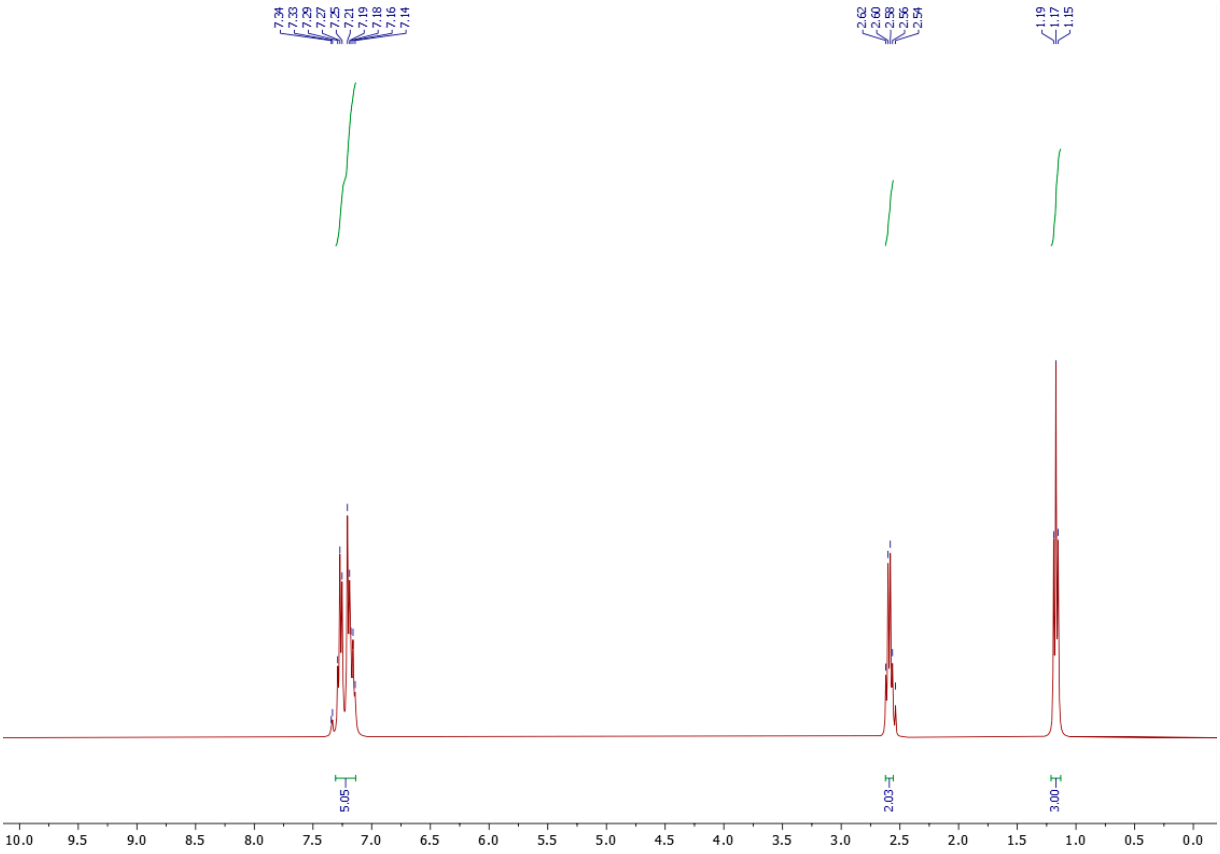


Figure S7. ^{1}H NMR spectrum of ethylbenzene

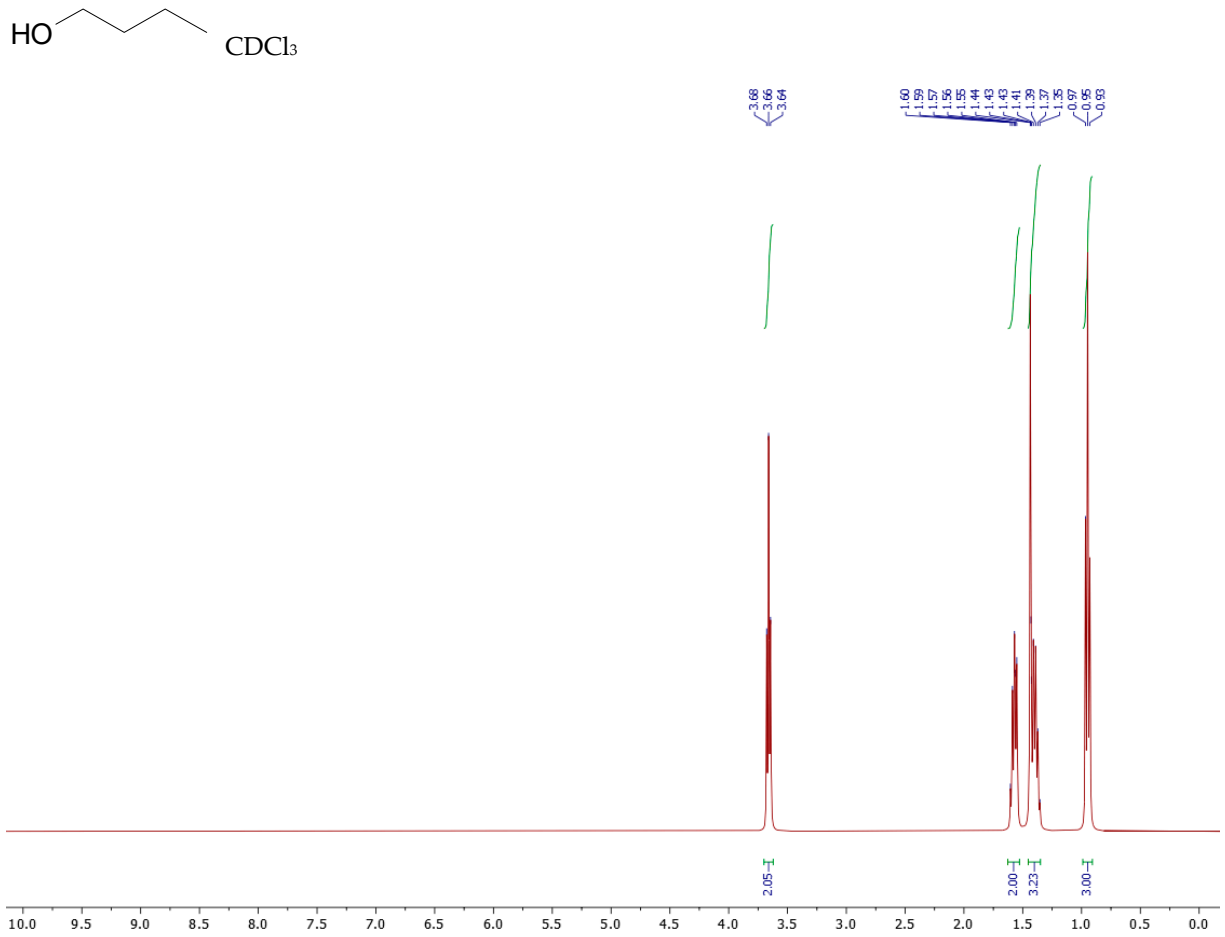


Figure S8. ^{1}H NMR spectrum of butan-1-ol

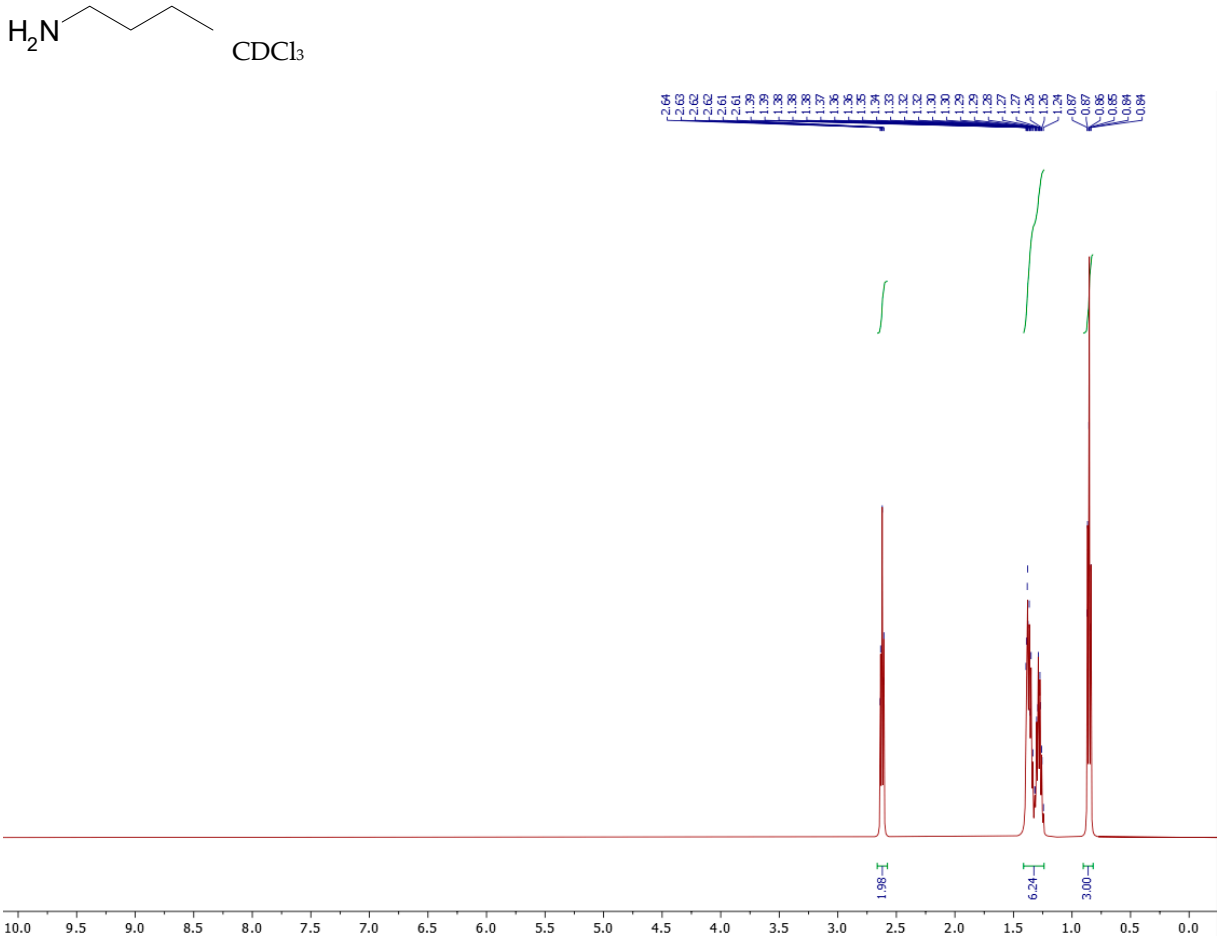


Figure S9. ^{1}H NMR spectrum of butan-1-amine

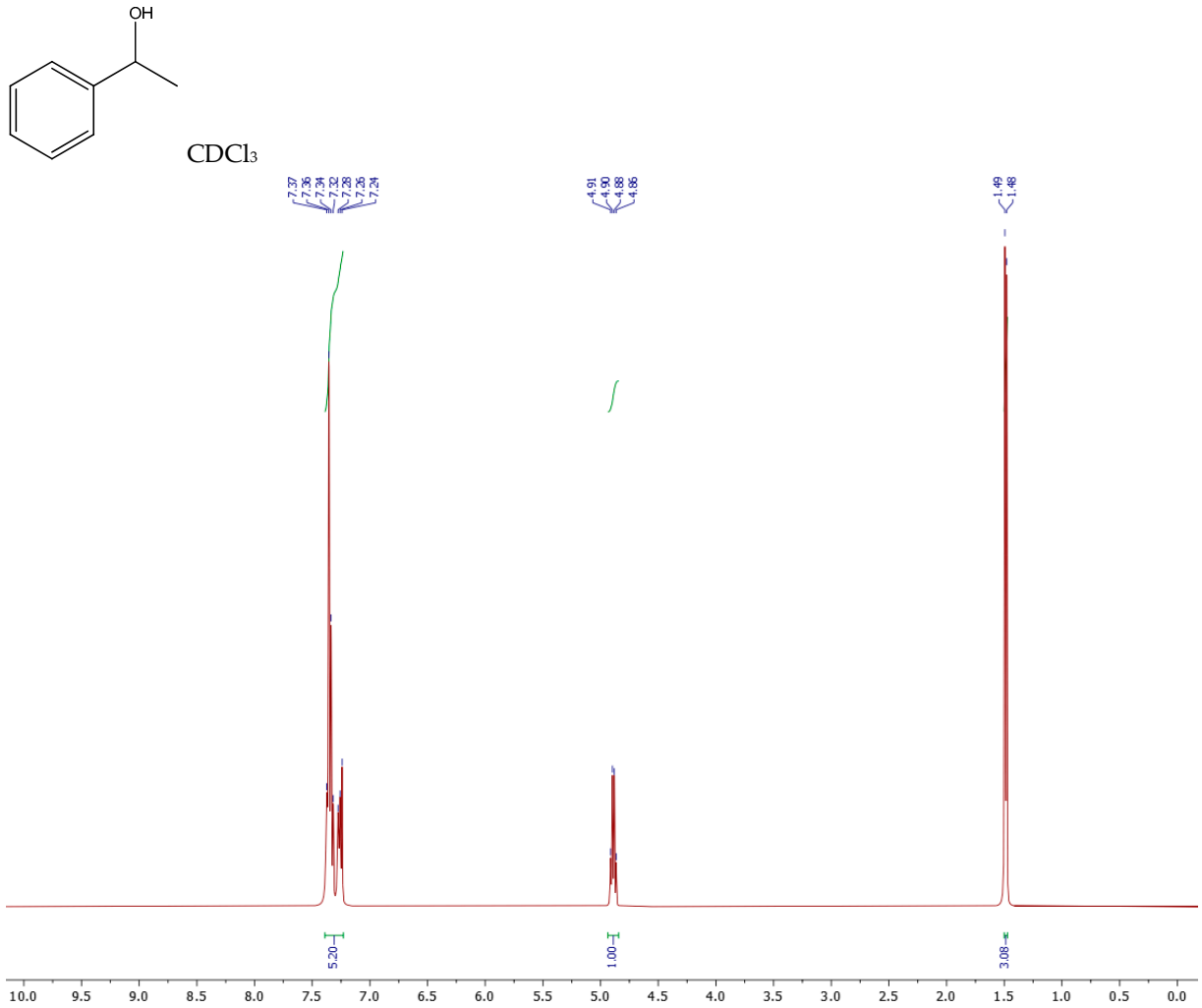


Figure S10. ^{1}H NMR spectrum of 1-phenylethanol

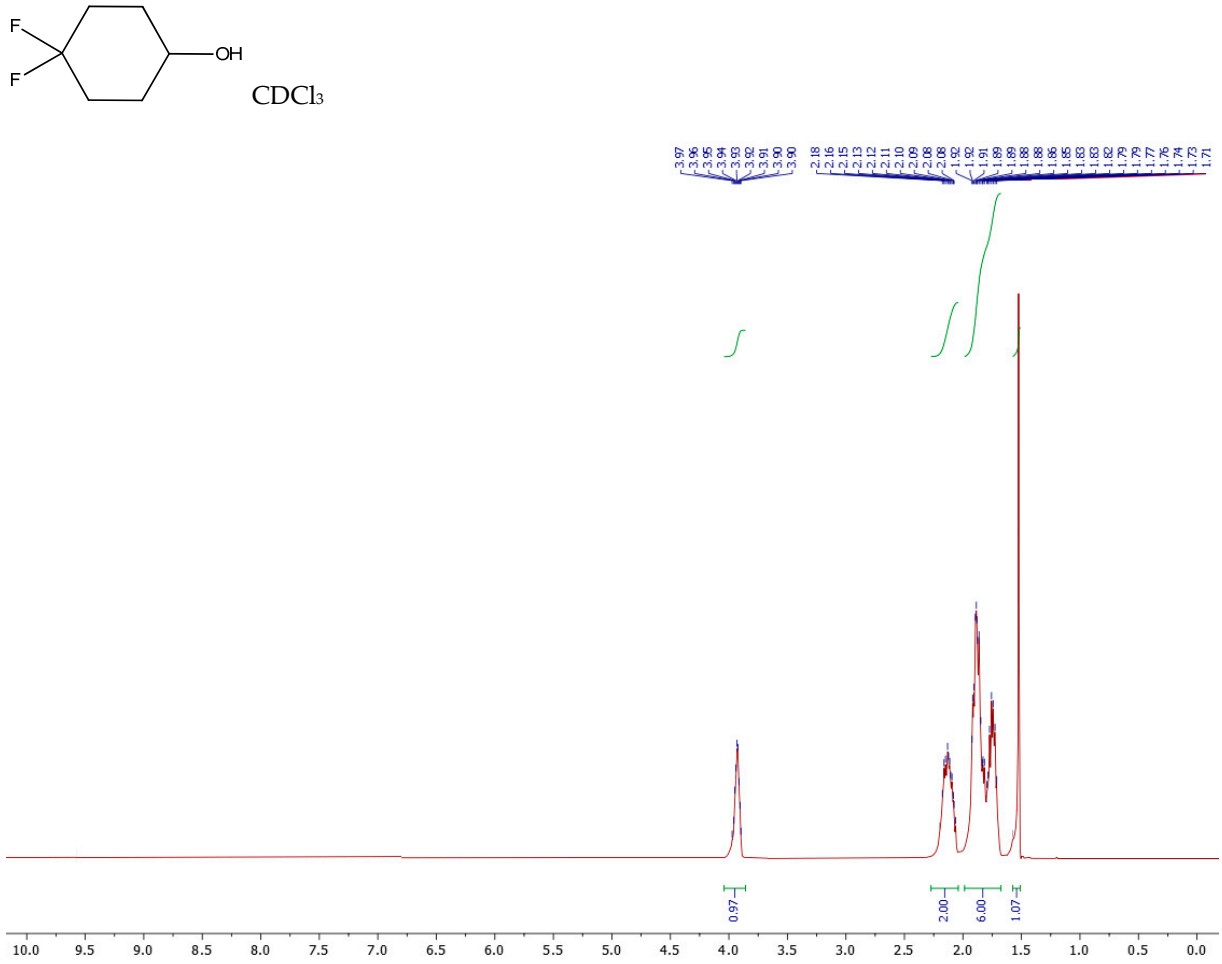


Figure S11. ^{1}H NMR spectrum of 4,4-difluorocyclohexanone

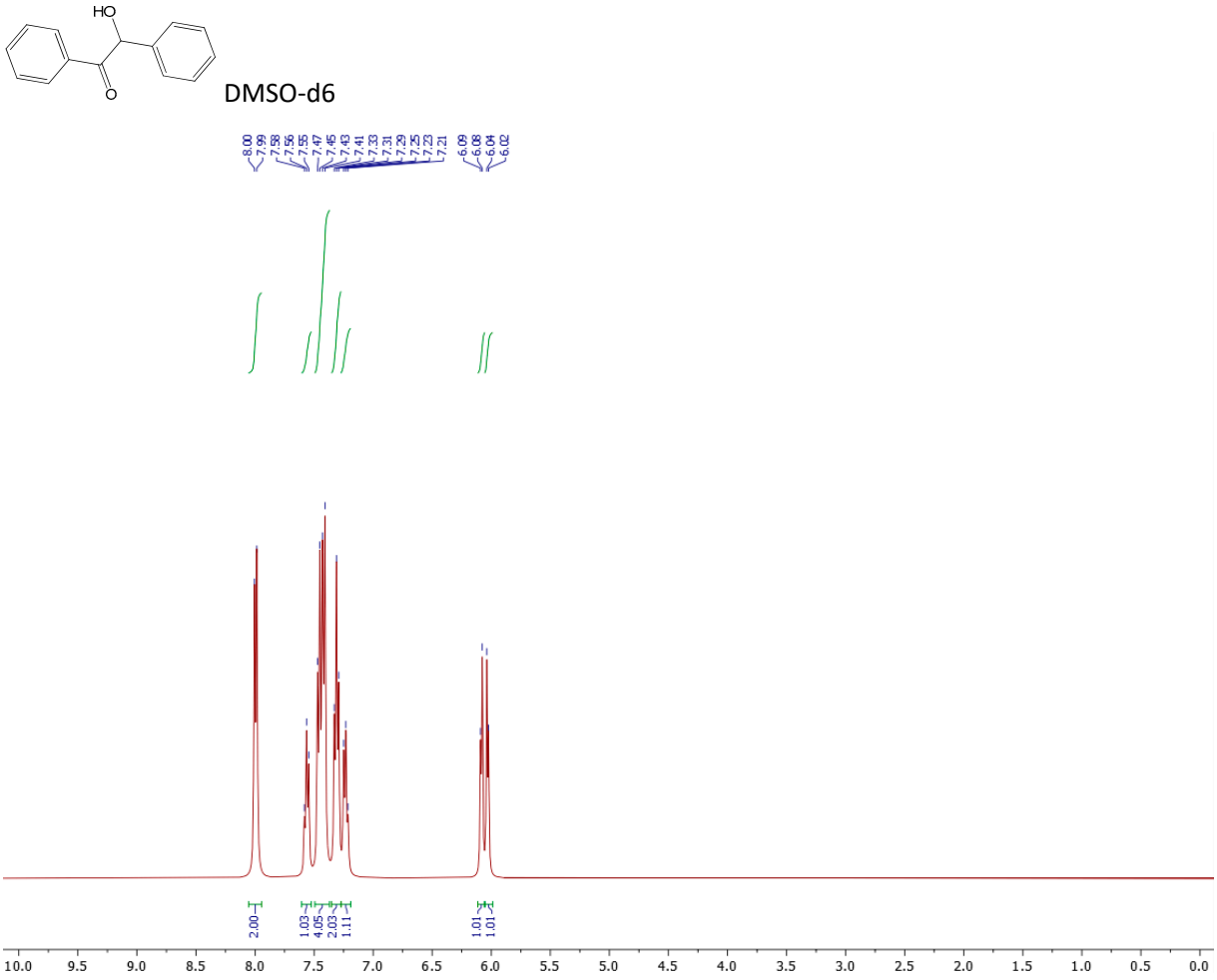


Figure S12. ^{1}H NMR spectrum of 2-hydroxy-1,2-diphenylethanone

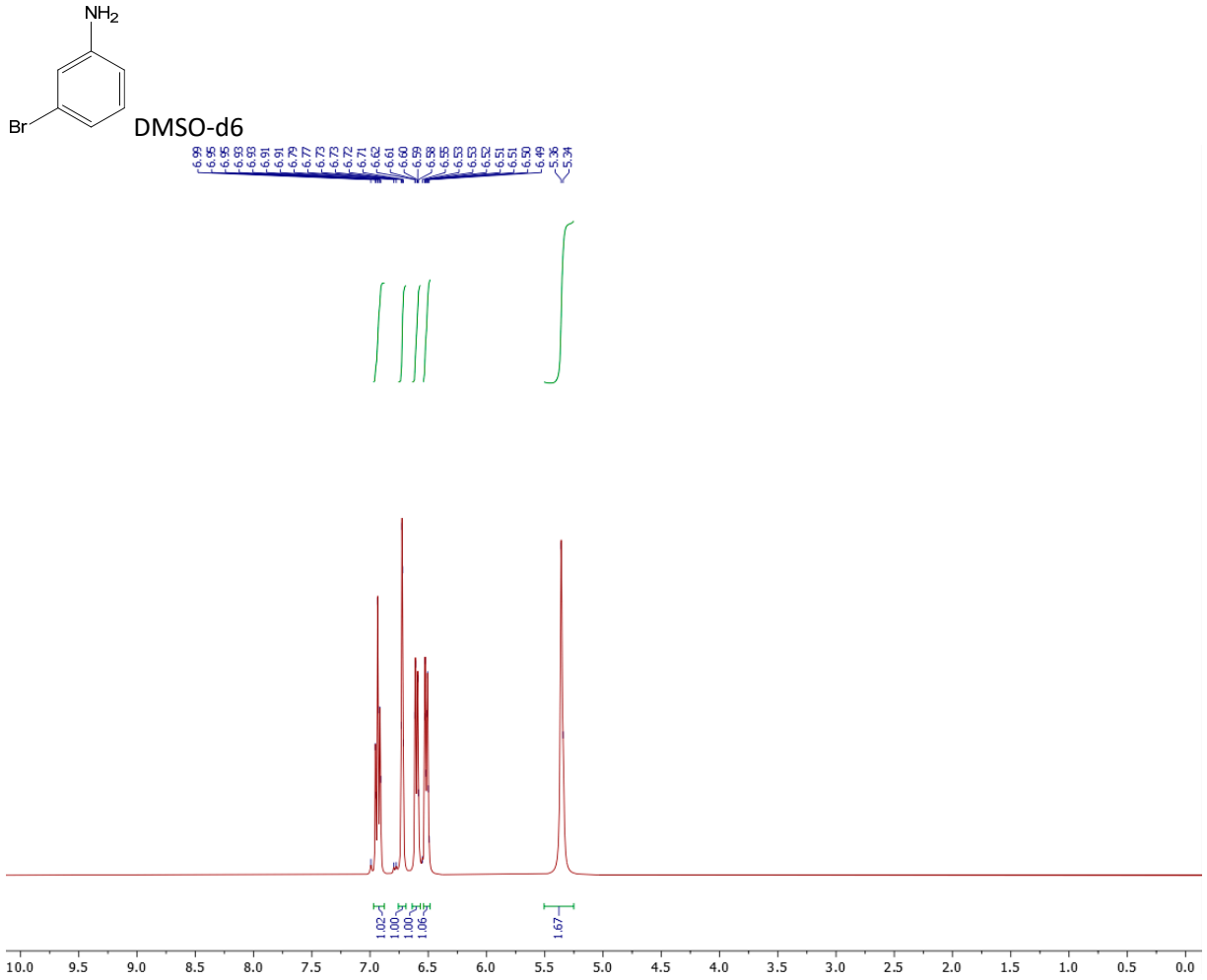


Figure S13. ^{1}H NMR spectrum of 3-bromoaniline

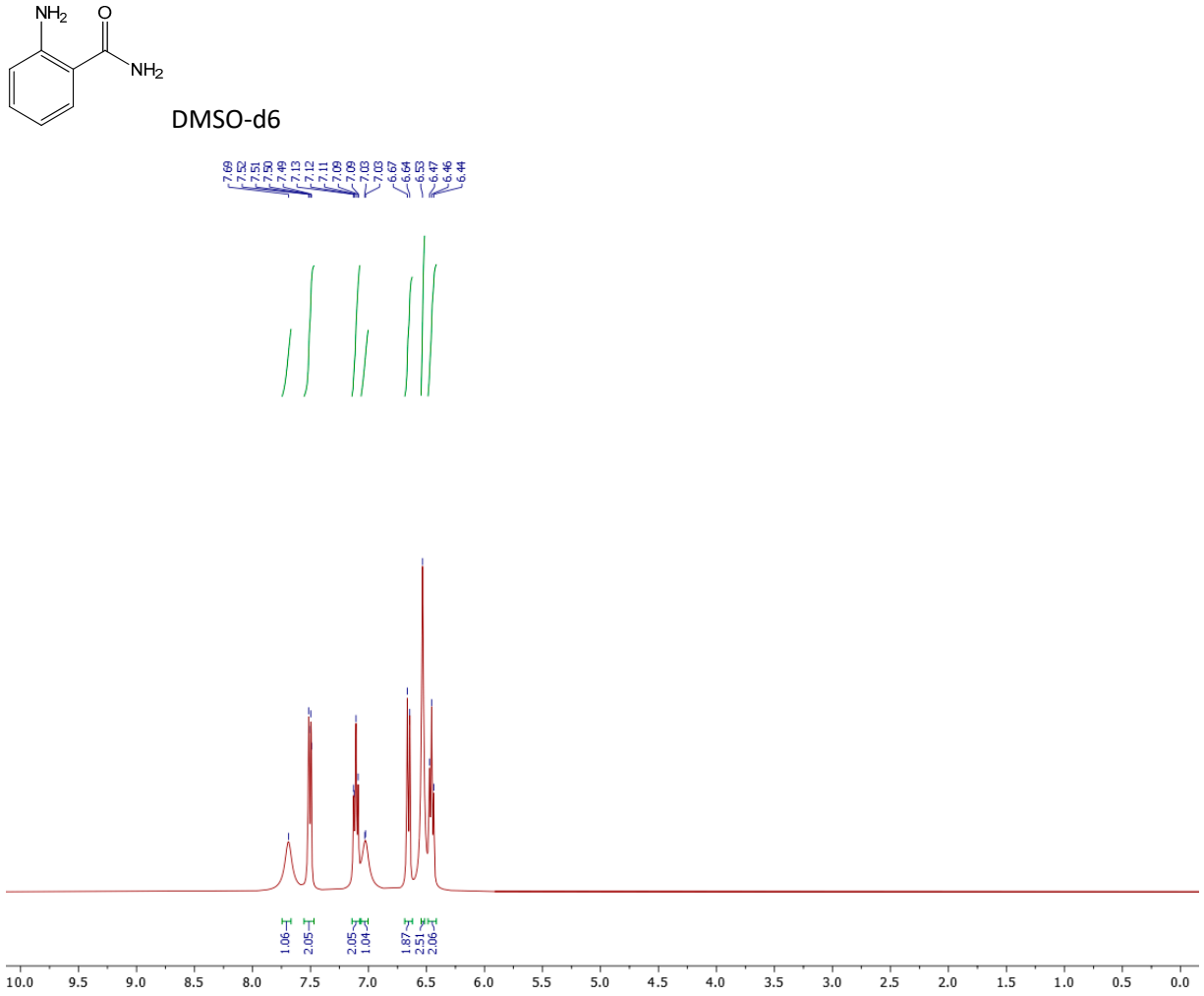
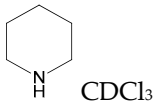


Figure S14. ^{1}H NMR spectrum of 2-aminobenzamide



$CDCl_3$

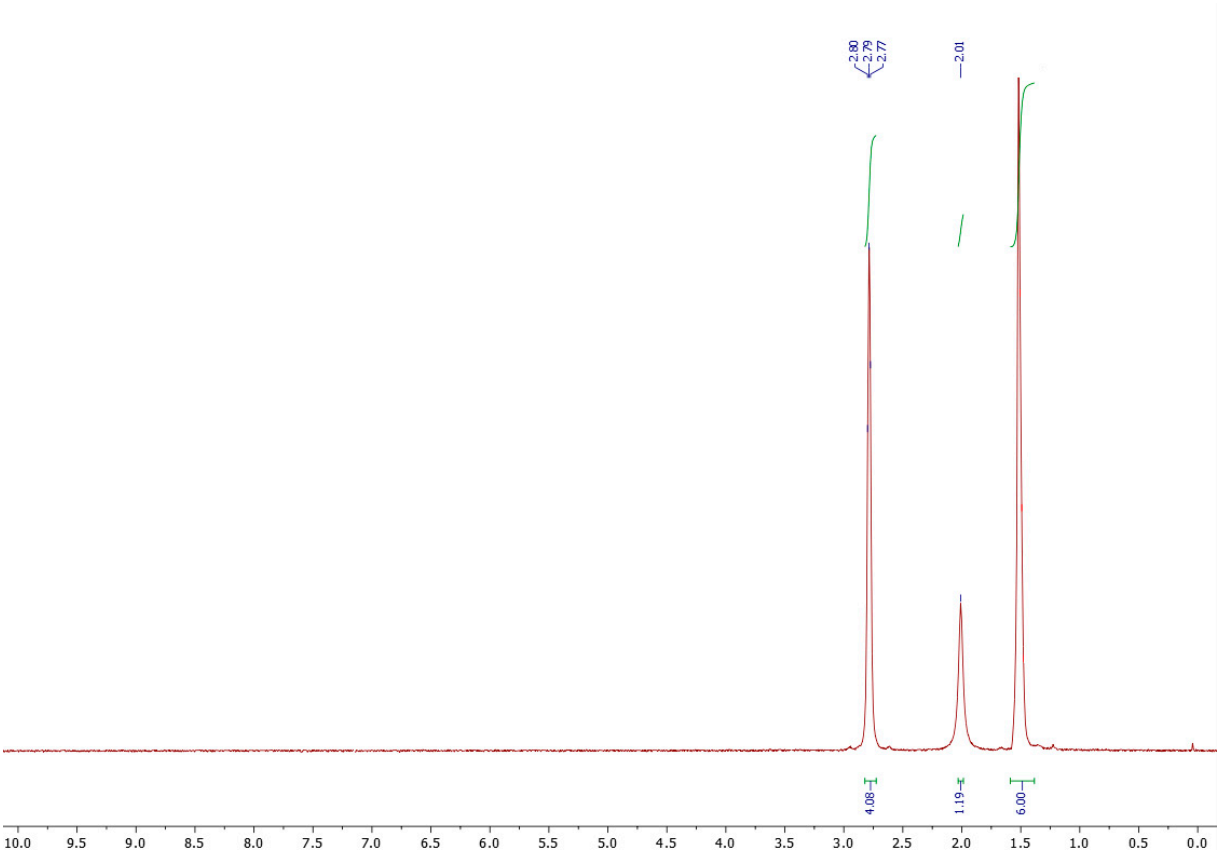
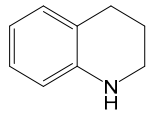


Figure S15. ^{1}H NMR spectrum of piperidine.



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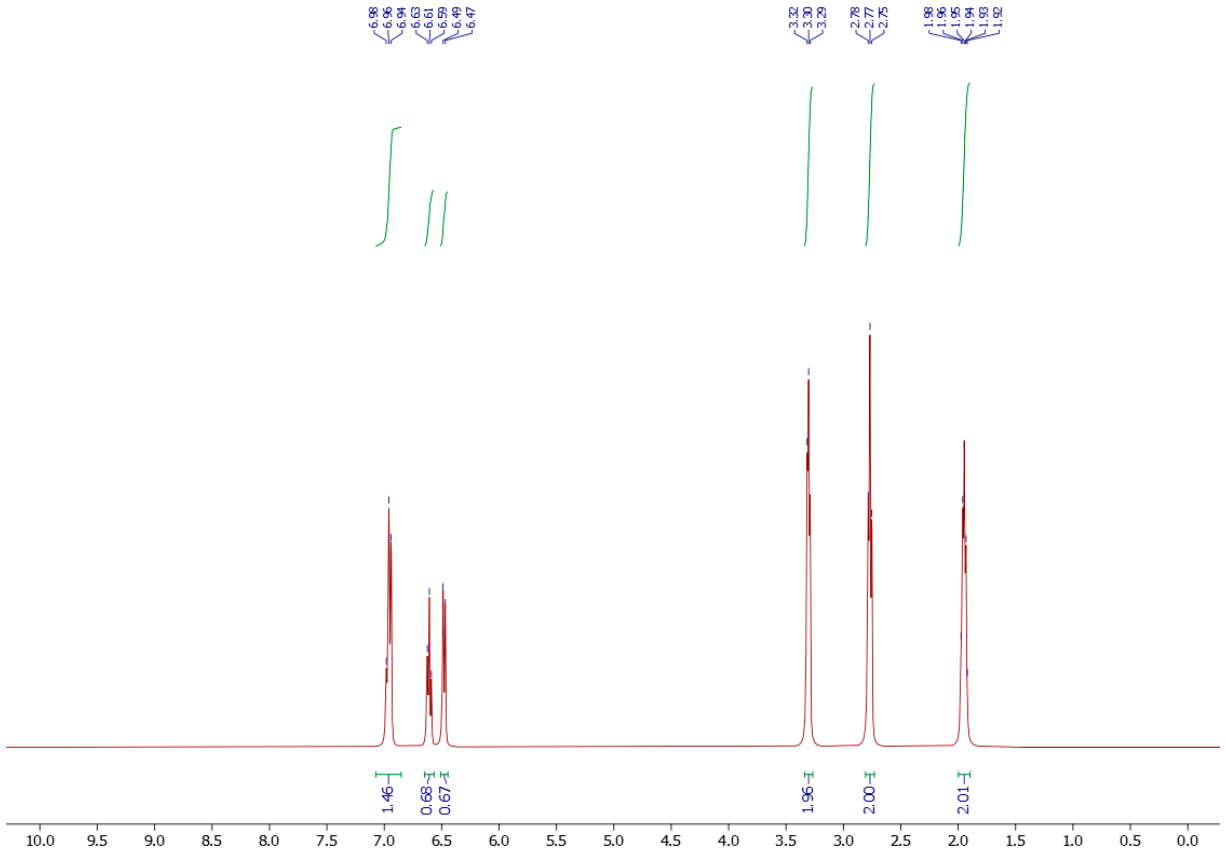


Figure S16. ^{1}H NMR spectrum of 1,2,3,4-tetrahydroquinoline

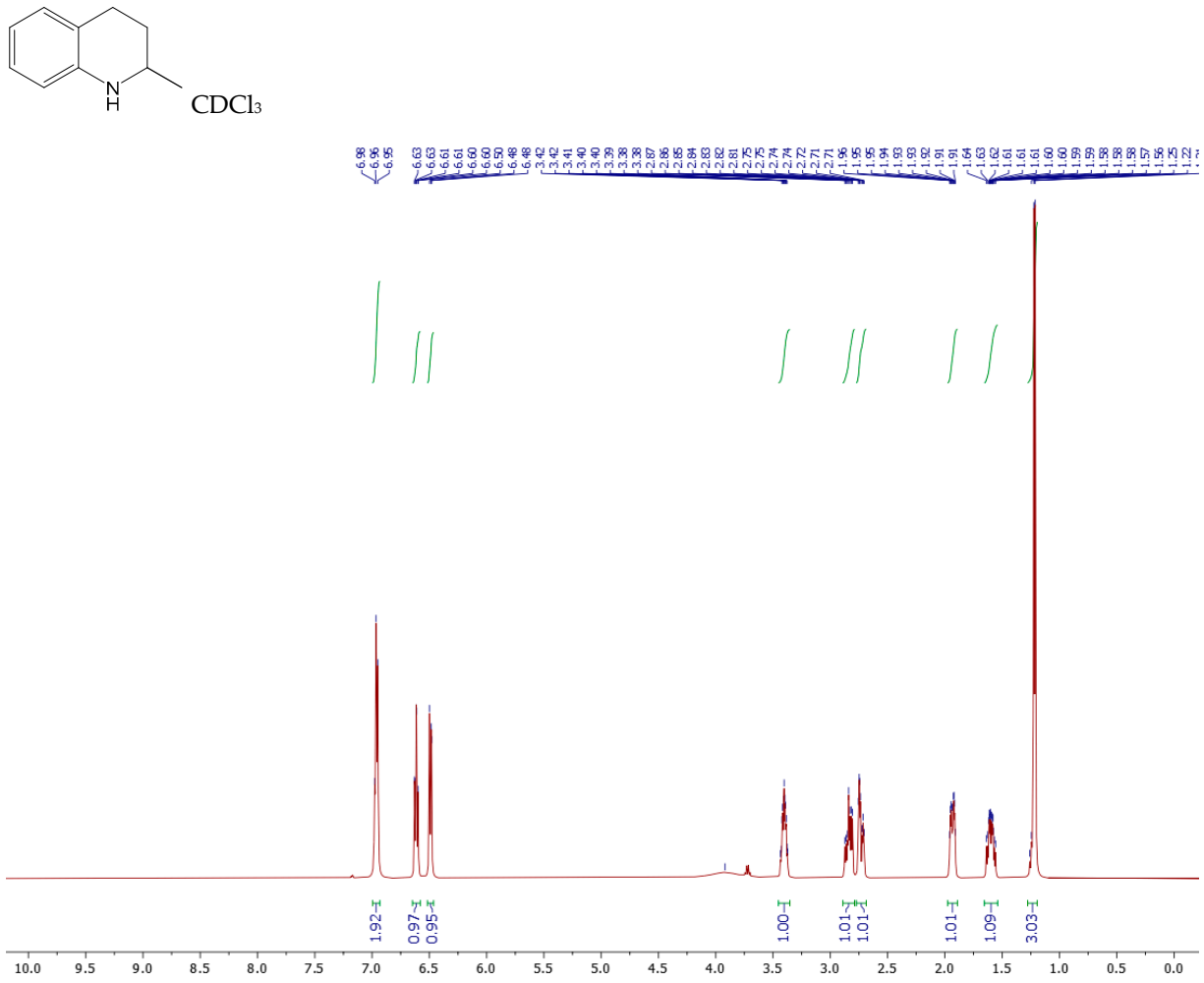
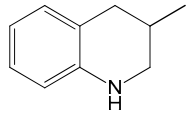


Figure S17. ^{1}H NMR spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline



$CDCl_3$

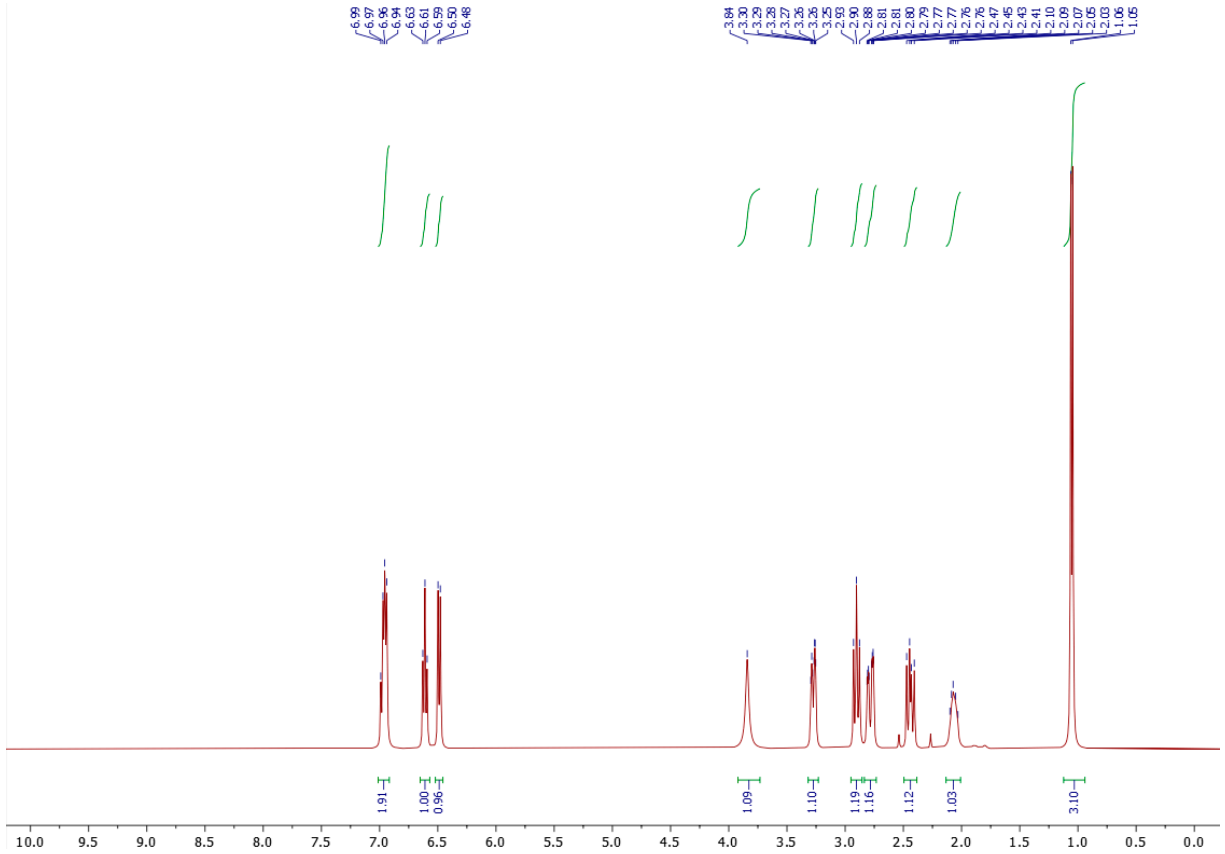


Figure S18. ^1H NMR spectrum of 3-methyl-1,2,3,4-tetrahydroquinoline

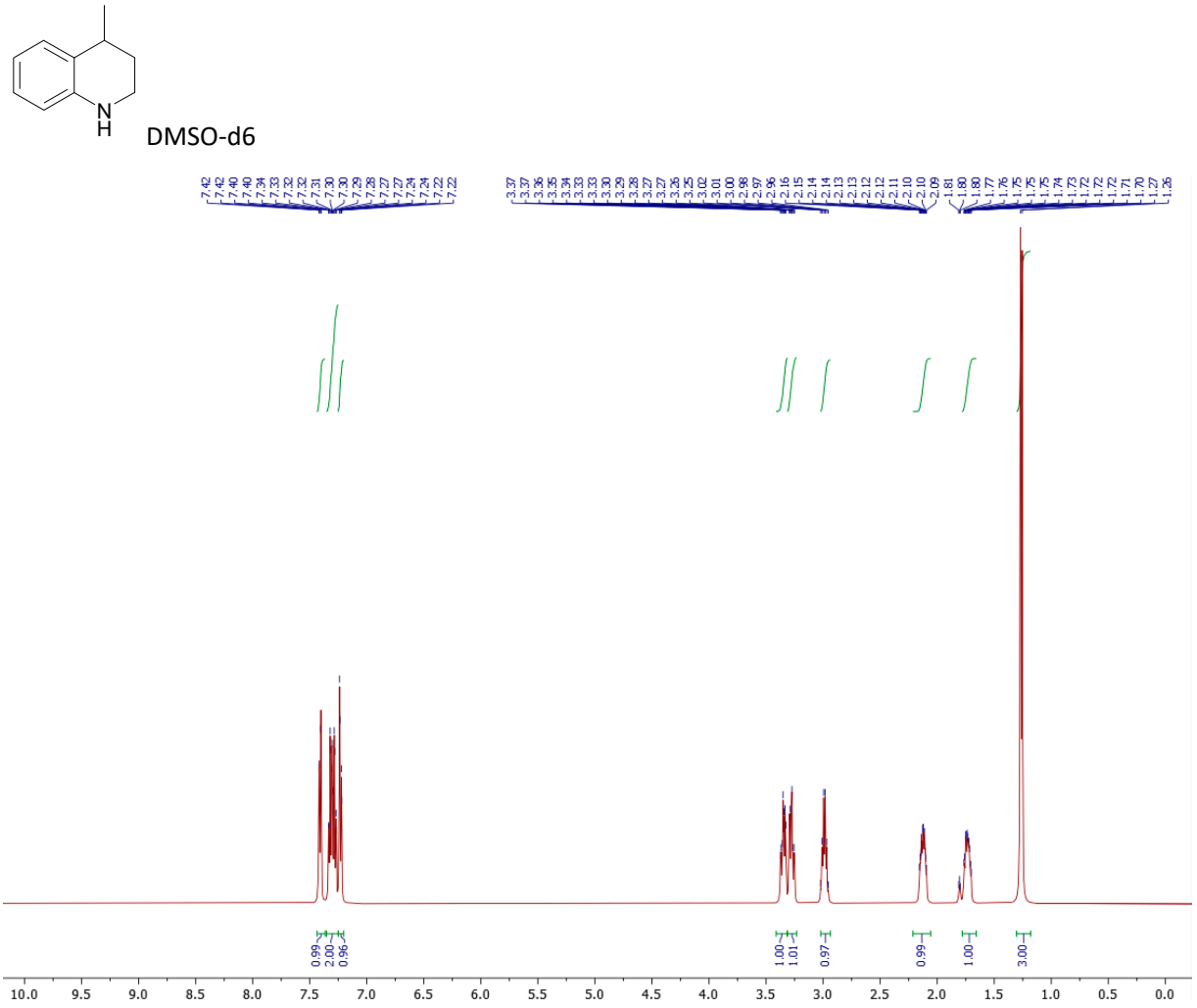
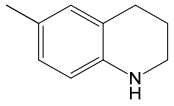


Figure S19. ^{1}H NMR spectrum of 4-methyl-1,2,3,4-tetrahydroquinoline.



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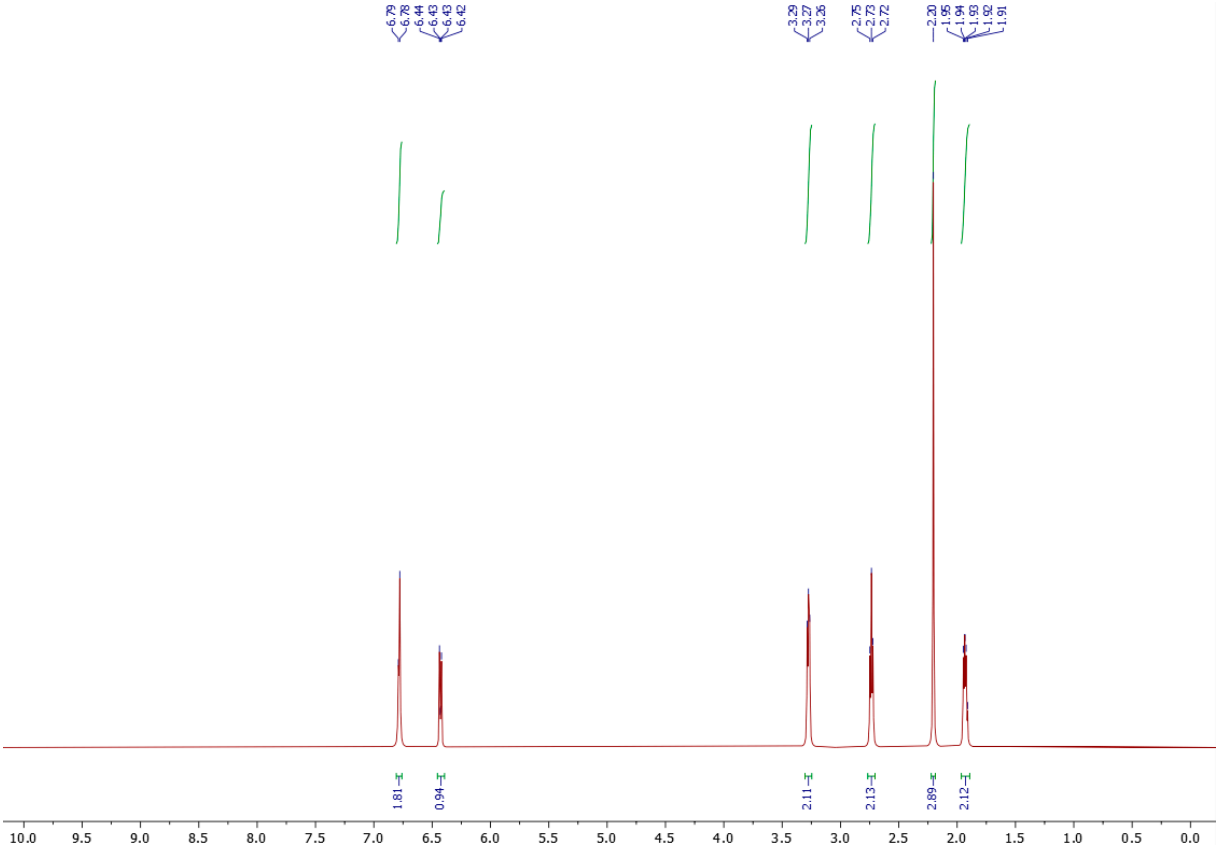


Figure S20. ^1H NMR spectrum of 6-methyl-1,2,3,4-tetrahydroquinoline

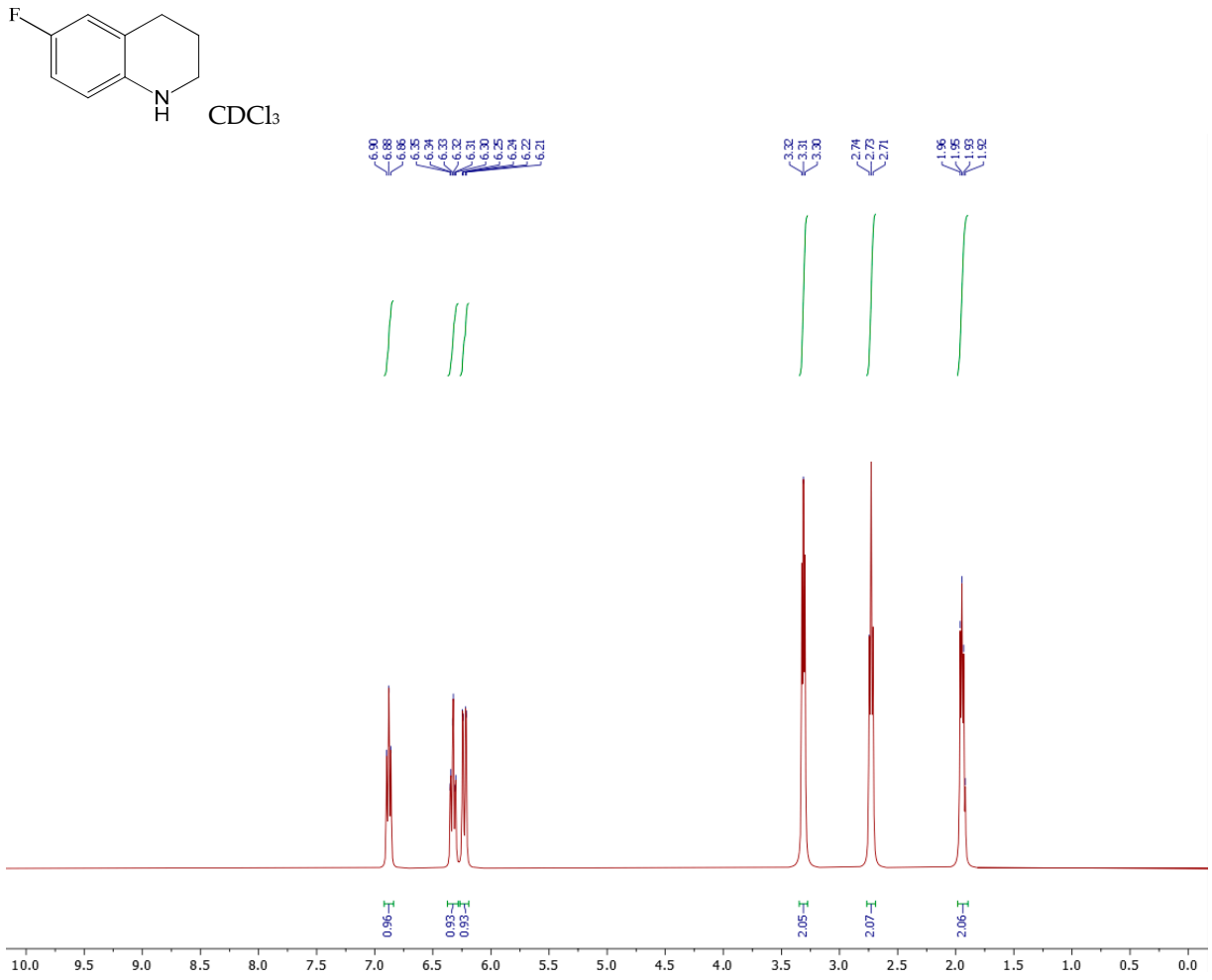


Figure S21. ^{1}H NMR spectrum of 6-fluoro-1,2,3,4-tetrahydroquinoline.

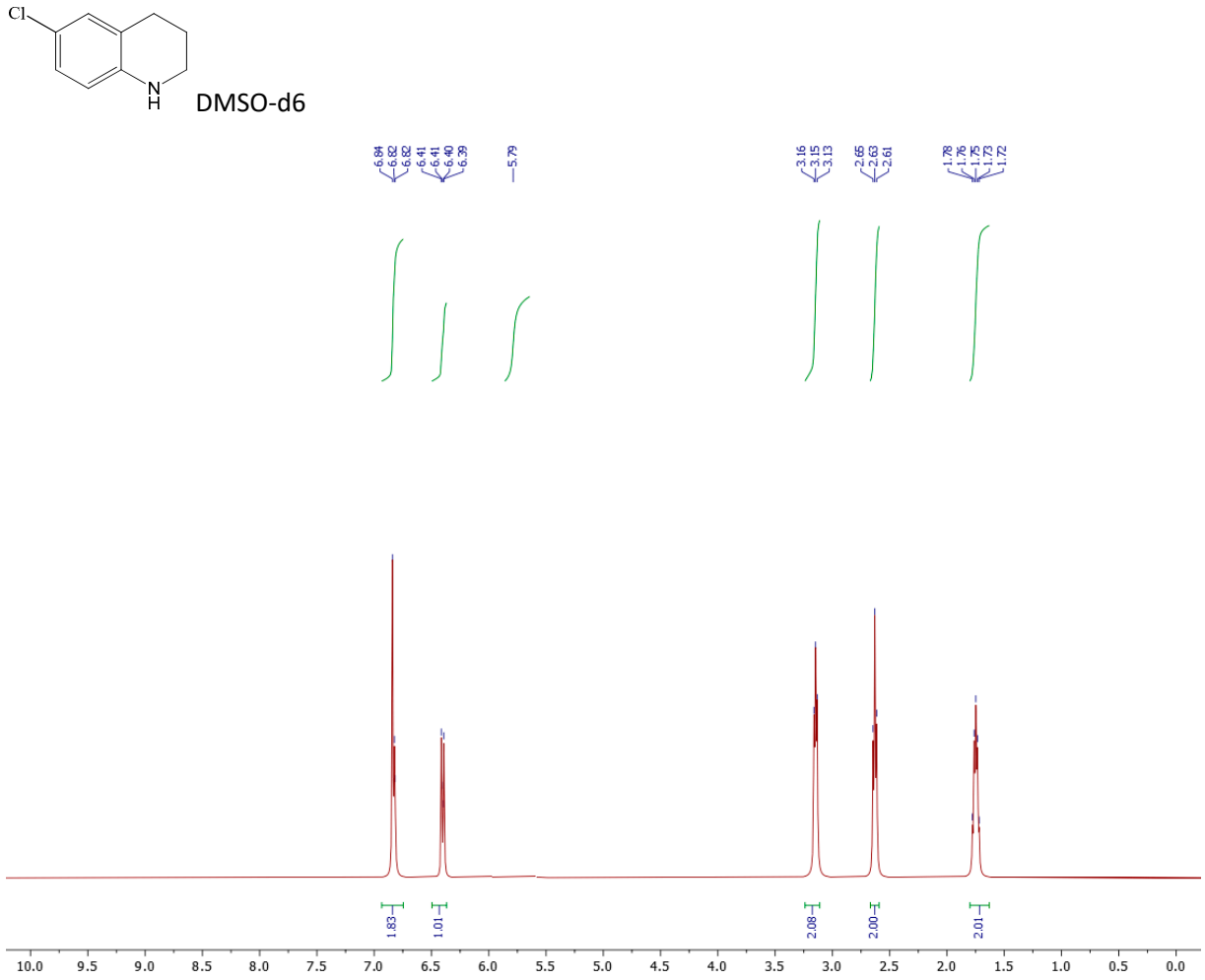


Figure S22. ^{1}H NMR spectrum of 6-chloro-1,2,3,4-tetrahydroquinoline

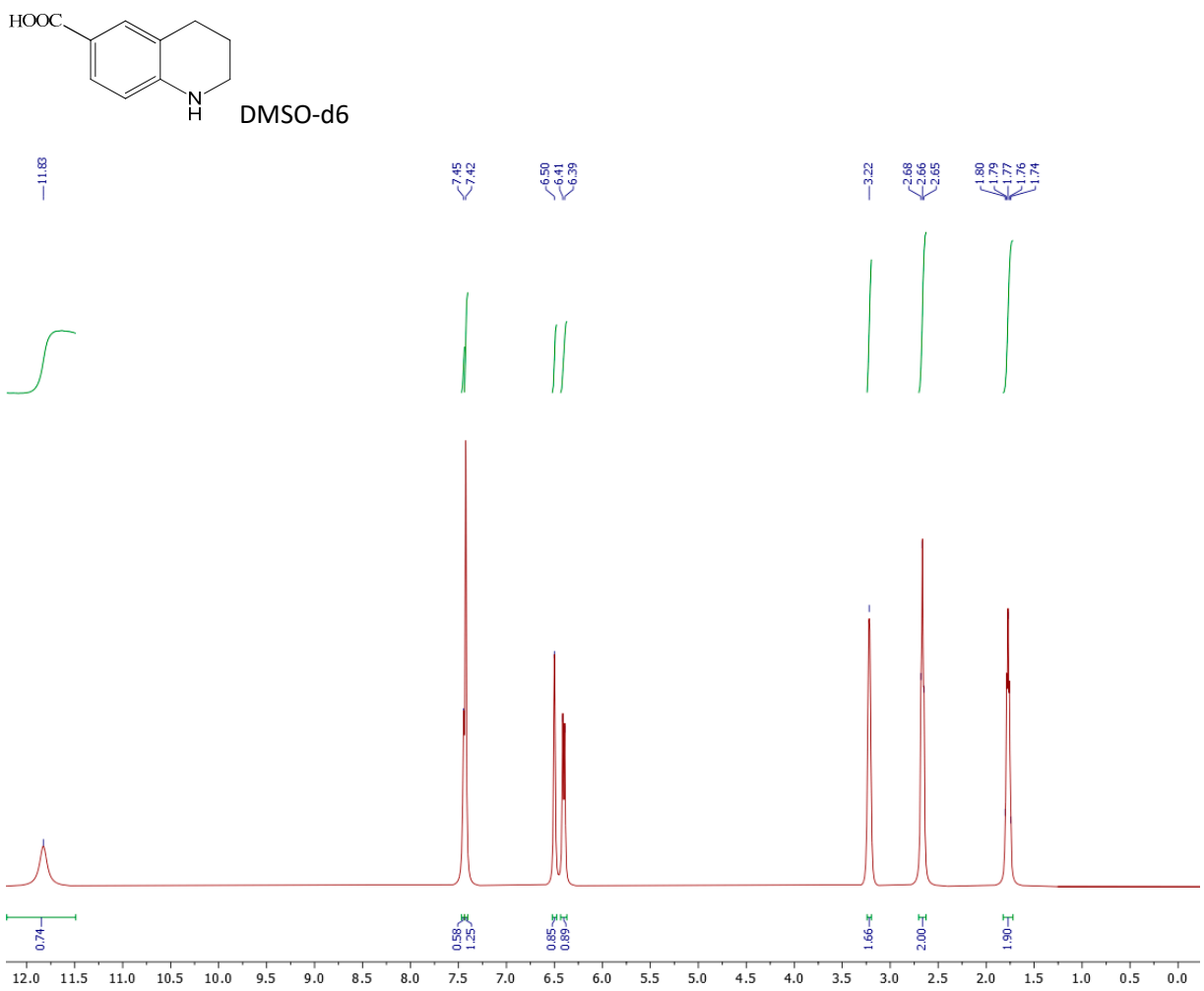
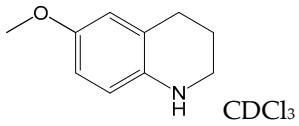


Figure S23. ^{1}H NMR spectrum of 1,2,3,4-tetrahydroquinoline-6-carboxylic acid



$CDCl_3$

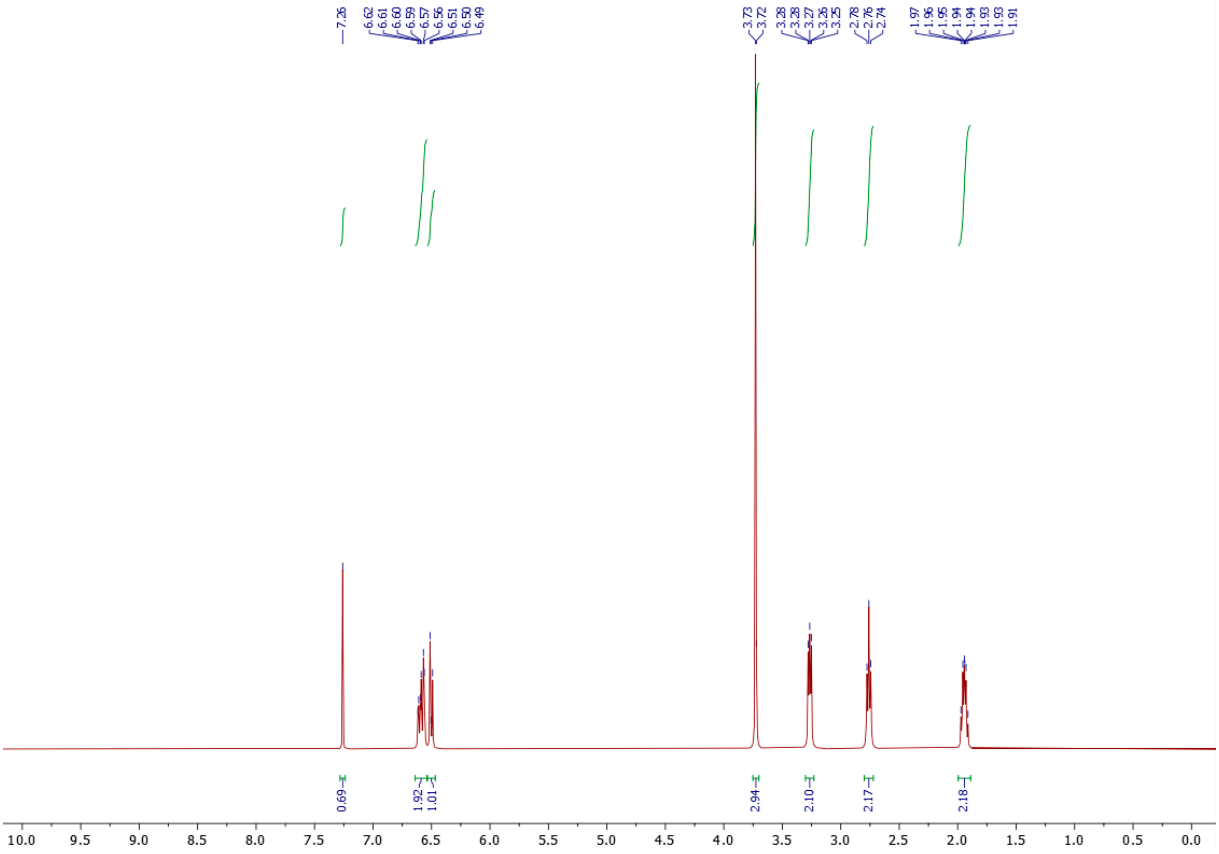


Figure S24. ^1H NMR spectrum of 6-methoxy-1,2,3,4-tetrahydroquinoline

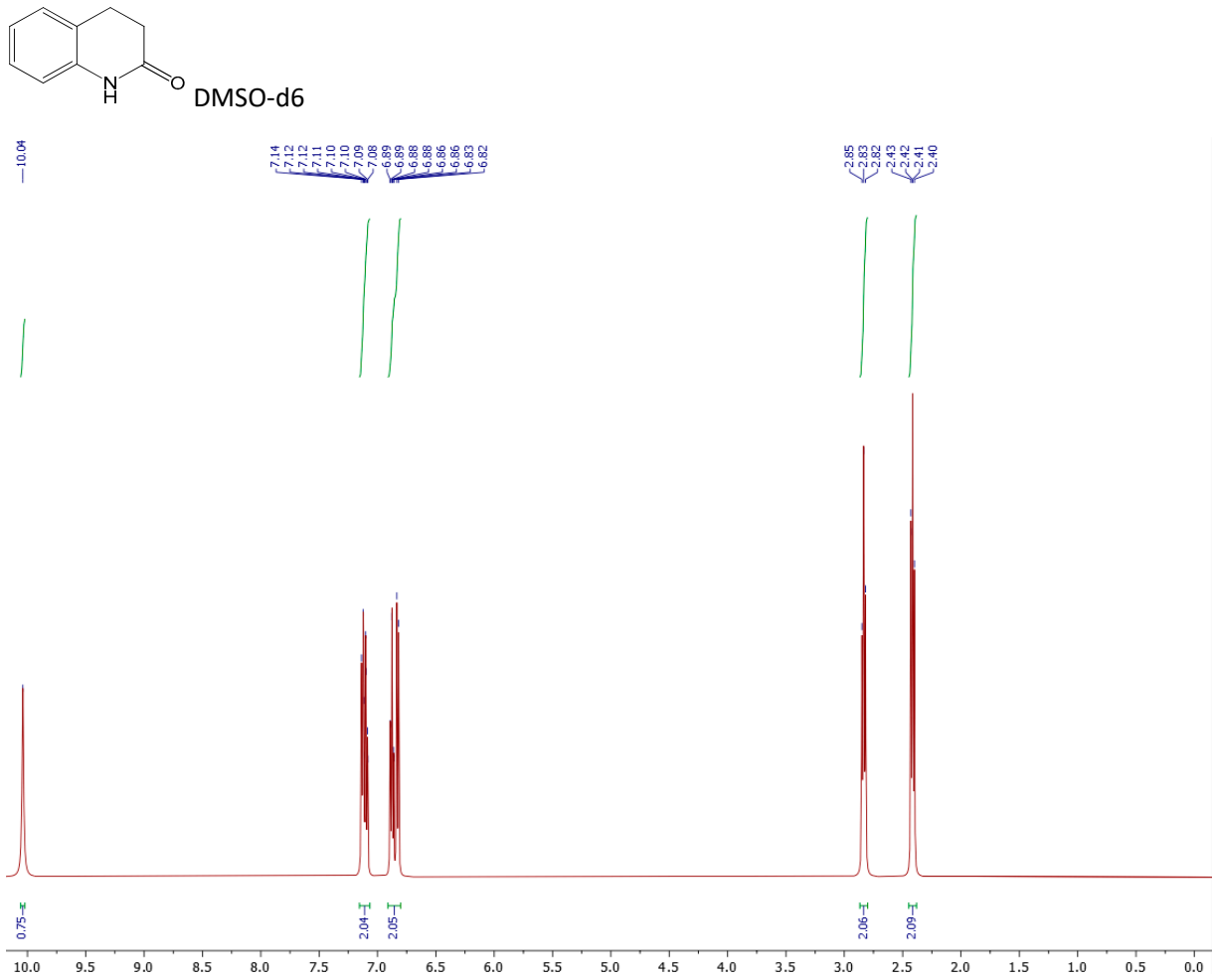


Figure S25. ^{1}H NMR spectrum of 3,4-dihydroquinolin-2(1H)-one

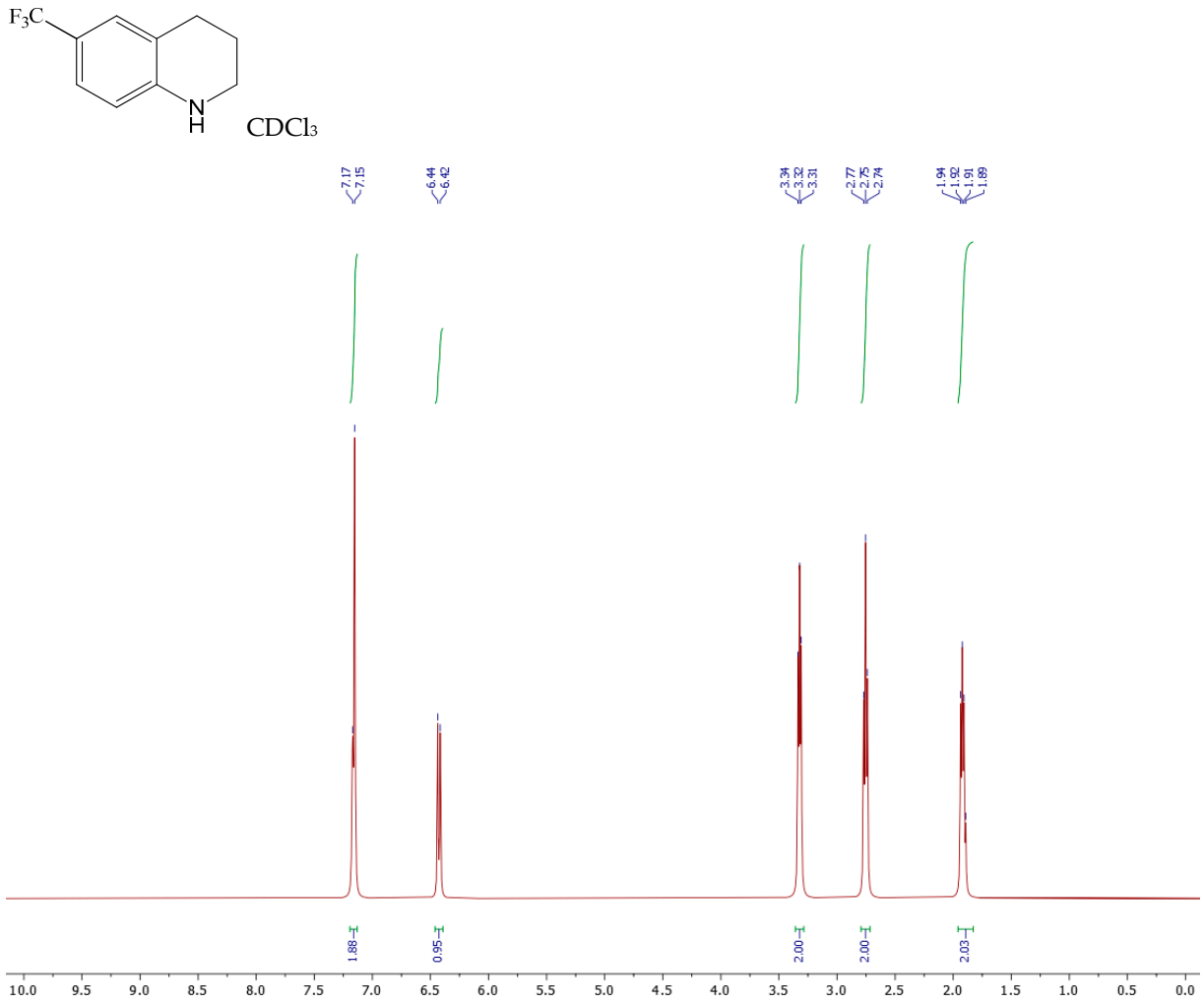


Figure S26. ^{1}H NMR spectrum of 6-(trifluoromethyl)-1,2,3,4-tetrahydroquinoline

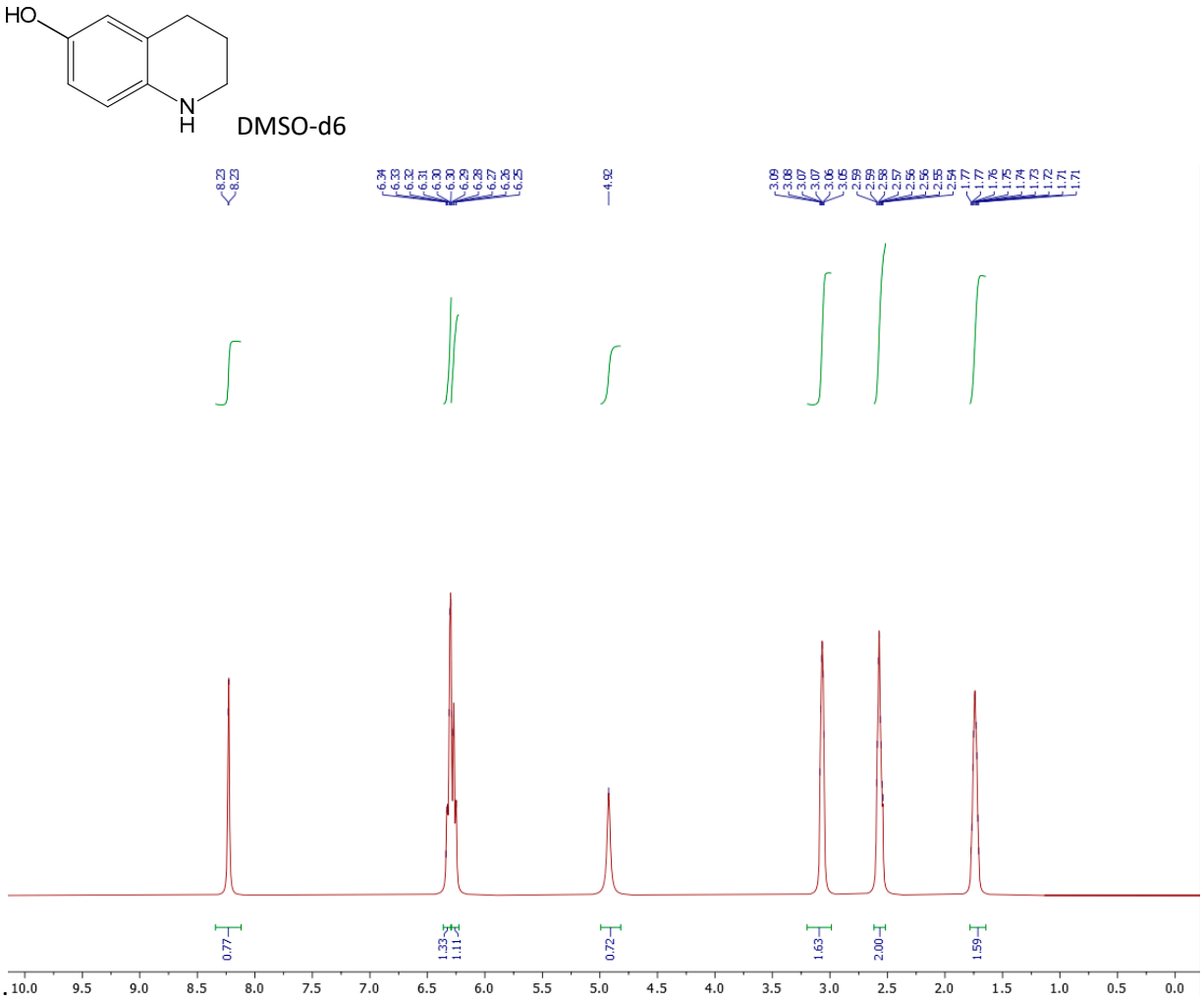


Figure S27. ^{1}H NMR spectrum of 1,2,3,4-tetrahydroquinolin-6-ol

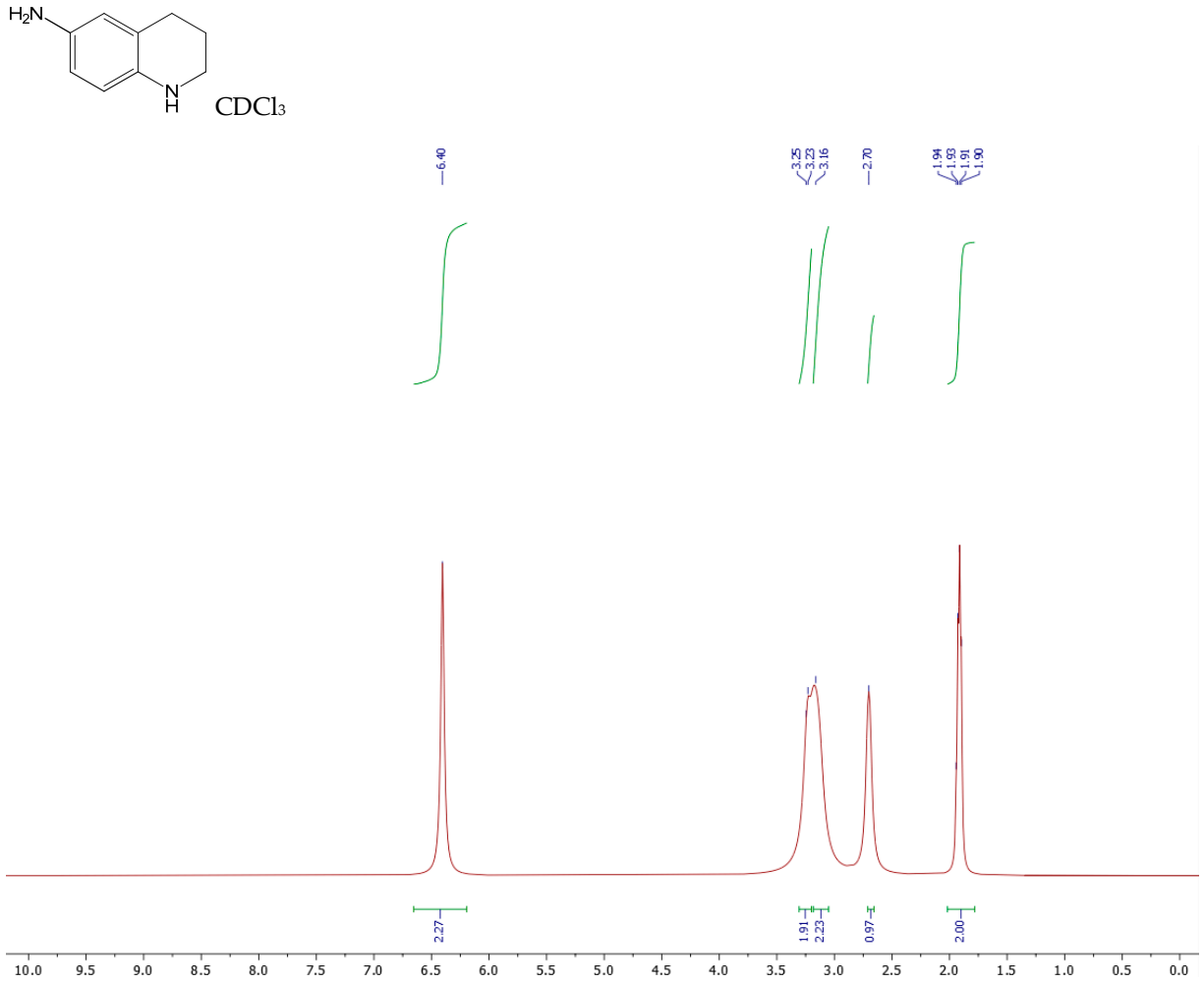


Figure S28. ^{1}H NMR spectrum of 1,2,3,4-tetrahydroquinolin-6-amine

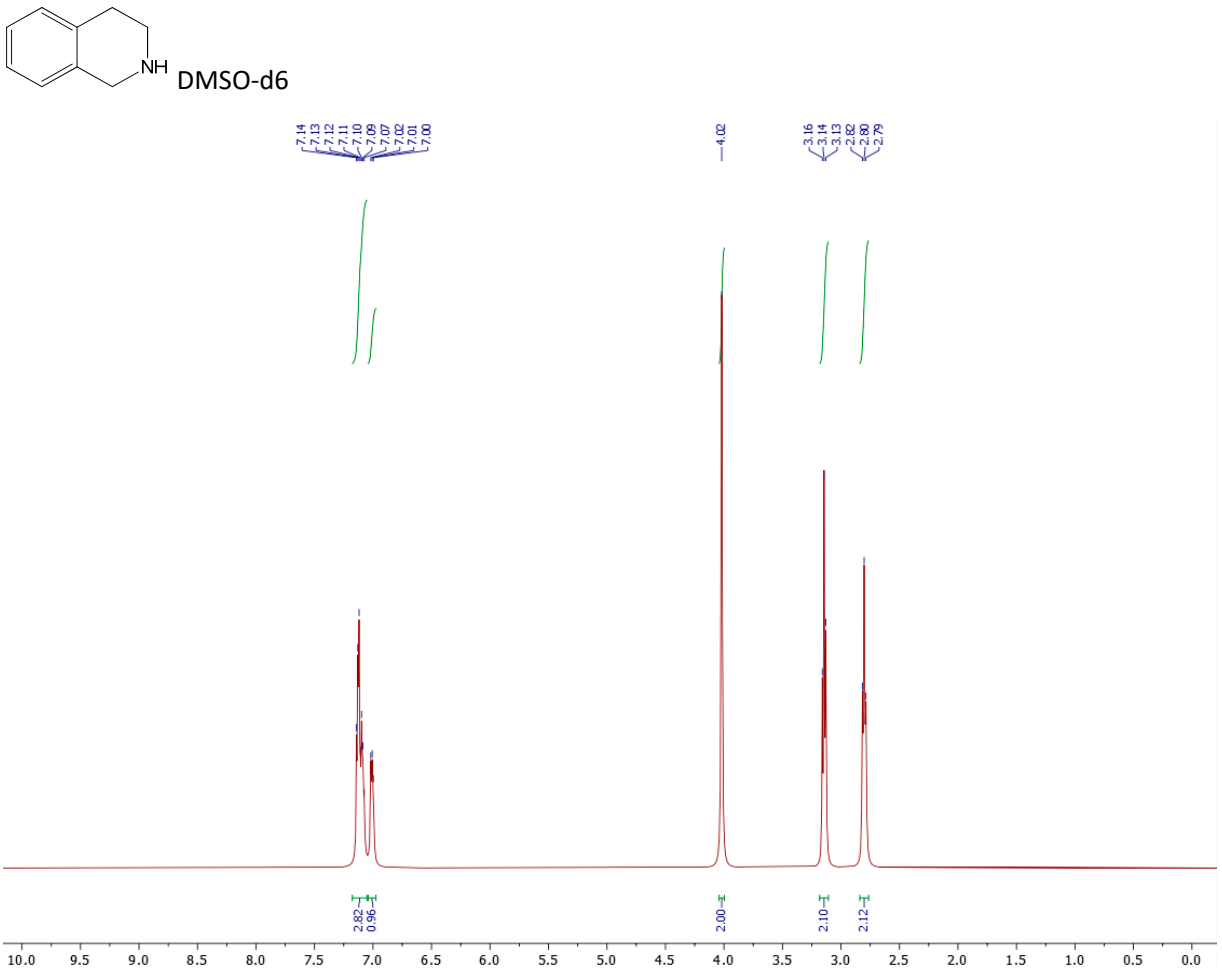


Figure S29. ^{1}H NMR spectrum of 1,2,3,4-tetrahydroisoquinoline