Supporting Information

Facile Hydrogenative Deprotection of *N*-Benzyl Groups Using a Mixed Catalyst of Palladium and Niobic Acid on Carbon

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Contents

1. EPMA spectrum of Nb_2O_5/C.

The electron probe micro analyzer (EPMA) spectrum of Nb_2O_5/C is shown in Figure S1. Nb_2O_5 was mainly dispersed at the surface of the carbon support.

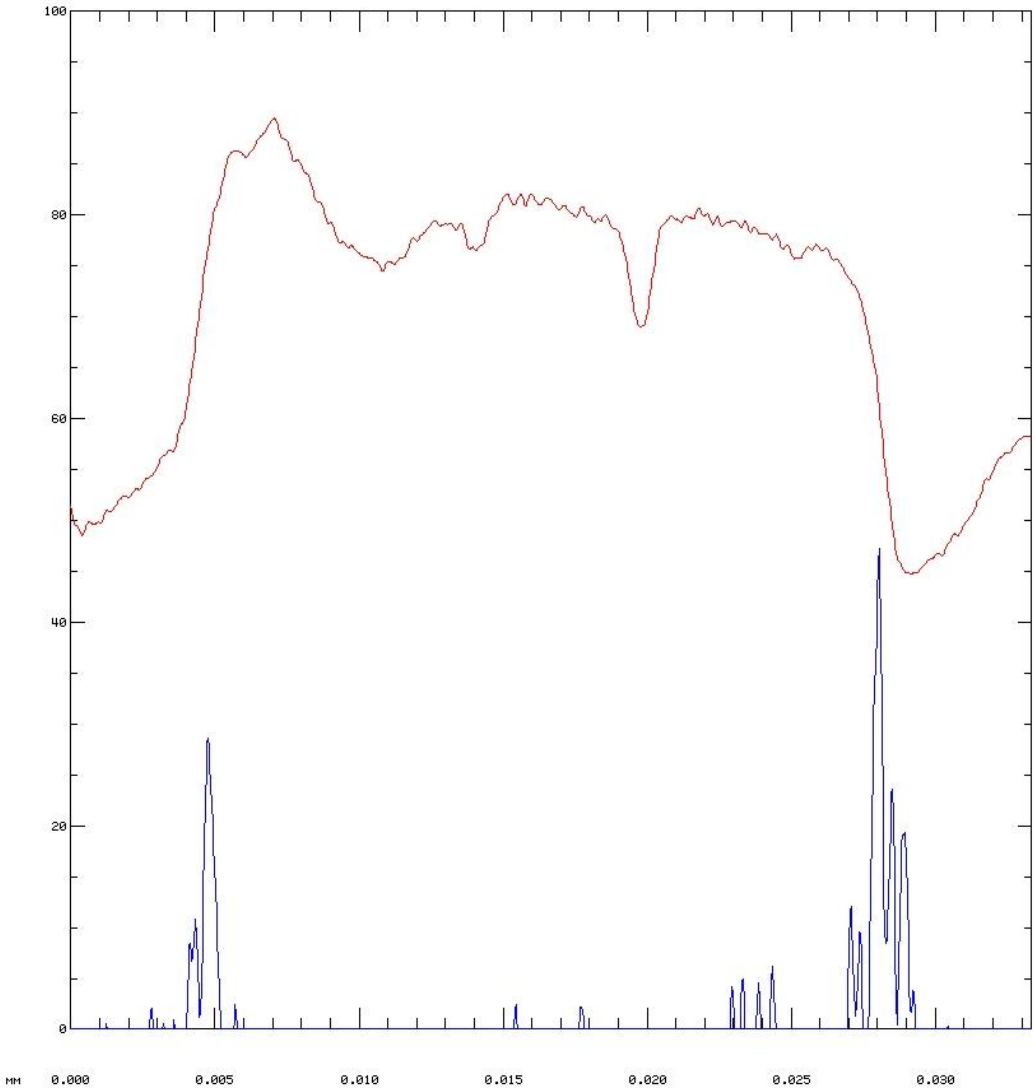


Figure S1. EPMA spectrum of Nb_2O_5/C.

2. XRD spectra of the mixture of used Pd/C and Nb_2O_5/C.

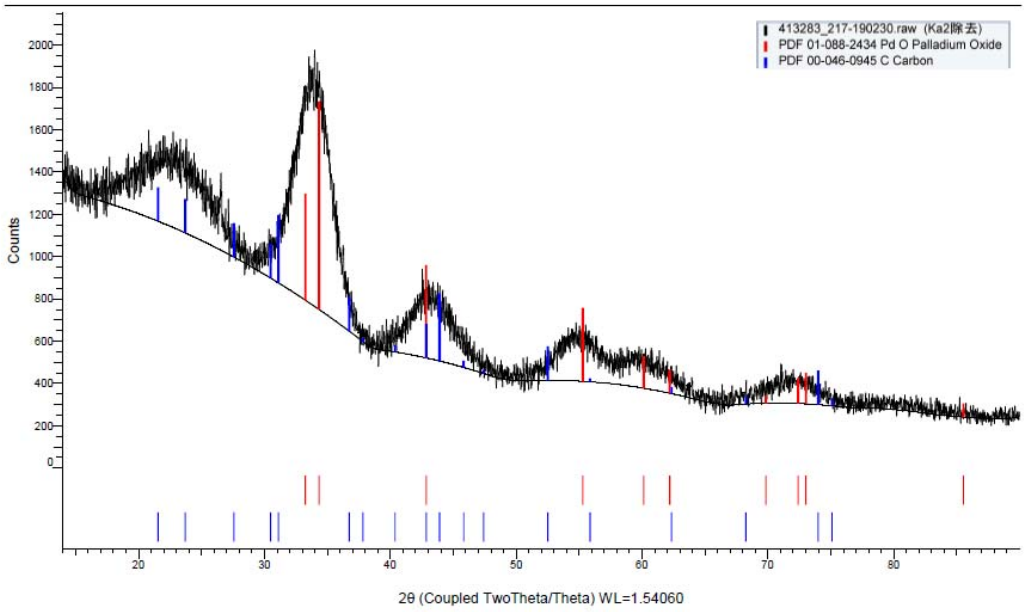


Figure S2. XRD spectrum of Pd/C. [The broad peaks (2θ = 22 º, 43 º) in XRD were derived from carbon. These peaks exist in Figure S3 and Figure 2 in the manuscript. Other peaks are derived from Pd.)]

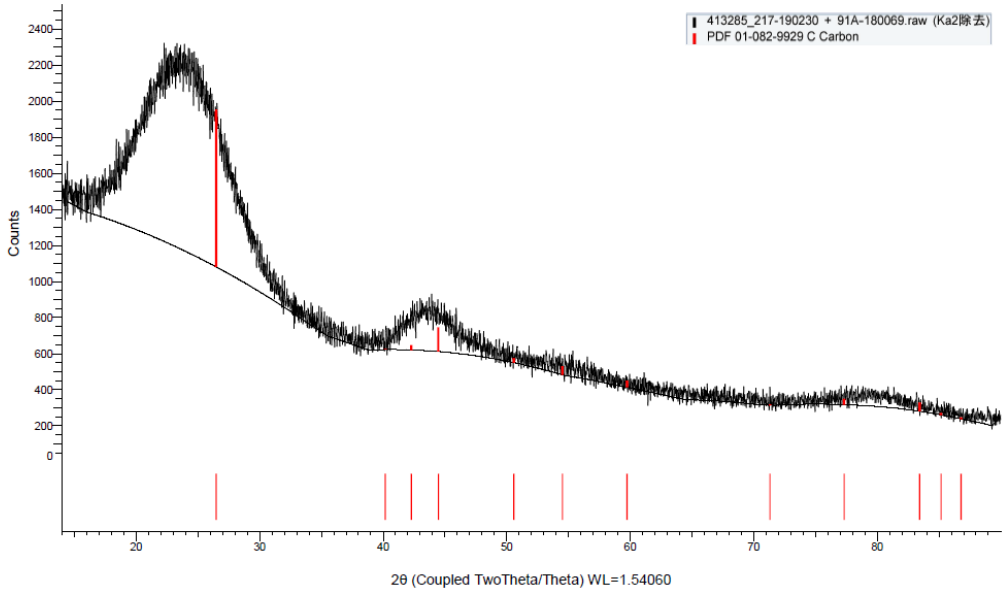
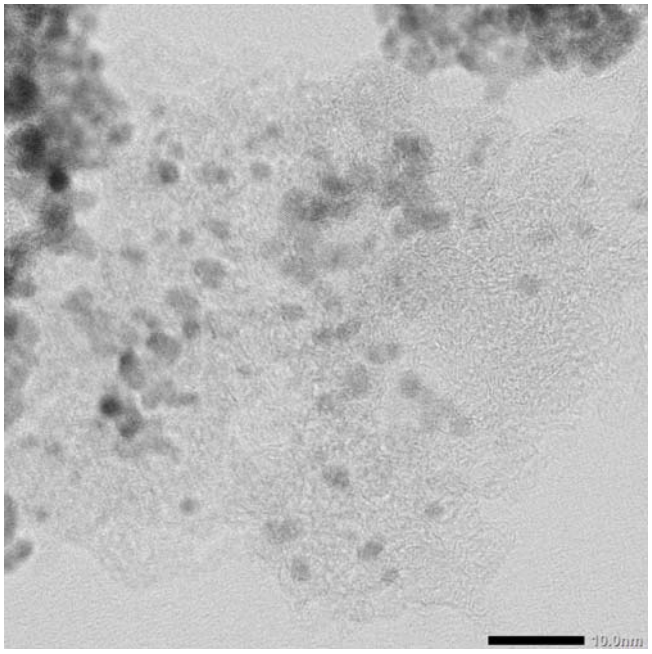


Figure S3. XRD spectrum of the mixture of Pd/C (1 mol) and Nb_2O_5/C (1 mol). (The weight of amorphous Nb_2O_5 is 4 times larger than that of Pd. Therefore, the peaks derived from Pd was too small to be detected.)

3. STEM images of Pd/C.

Scanning transmission electron microscope (STEM) images of Pd/C before and after reaction are shown in Figure S3. The particle size of Pd did not change before and after the reaction.

Before reaction



After reaction

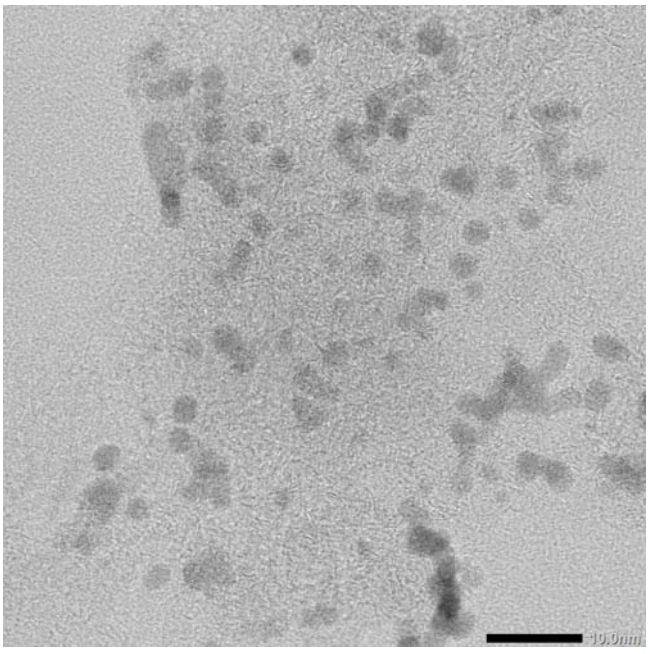
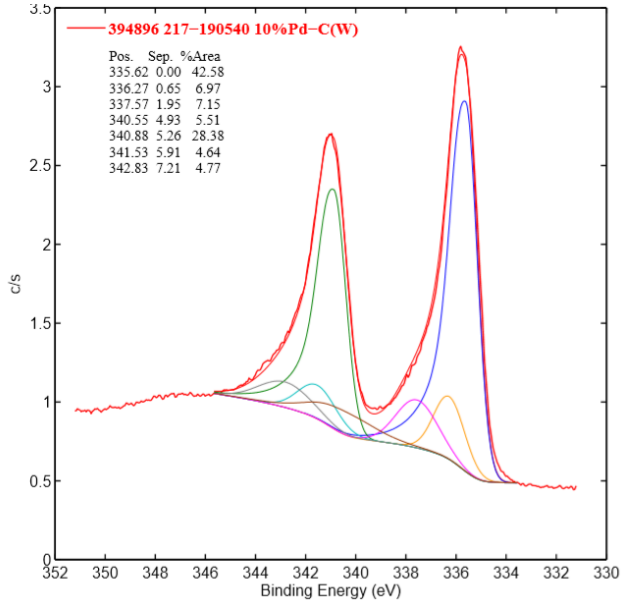


Figure S4. STEM images of Pd/C.

4. XPS spectra of Pd/C.

XPS spectra of Pd before and after the reaction are shown in Figure S5. Zero valent of Pd and the oxidized state of Pd was mixed before and after the reaction.

Before reaction



After reaction

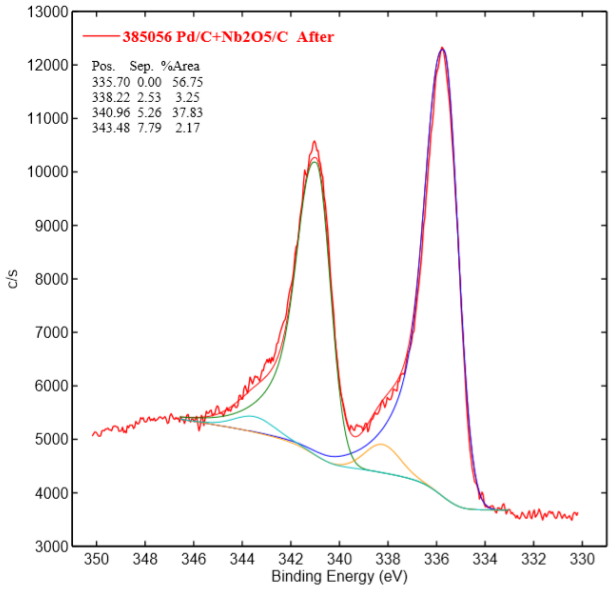
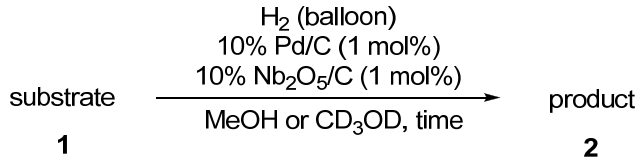
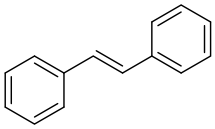
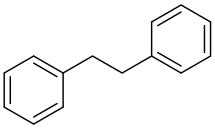
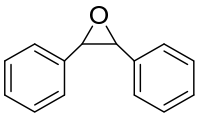
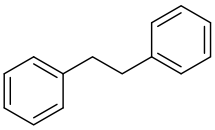
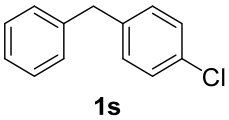
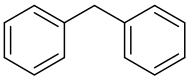
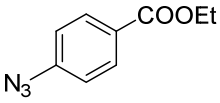
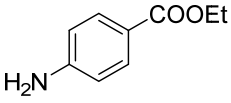
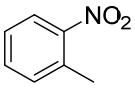
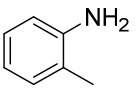
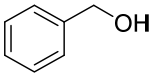


Figure S5. XPS spectra of Pd/C.

5. Hydrogenation using Pd/C and Nb_2O_5/C.

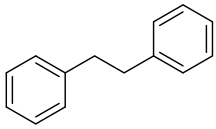
Table S1. Heterogeneous hydrogenation using Pd/C and Nb_2O_5/C.



entry	substrate	product	time (h)	yield (%)
1	 **1q**	 **2q**	1.5	quant.
2	 **1r**	 **2q**	2	86
3	 **1s**	 **2s**	19	90
4	 **1t**	 **2t**	1.5	quant.[a]
5	 **1u**	 **2u**	4.5	quant.[a]
6	 **1v**	 **2v**	0.5	92[a]

[a] Reaction was carried out in CD_3OD, and the yield was determined by ^1H NMR using 1, 2-methylenedioxybenzene as an internal standard.

diphenylethane (2q)



2q

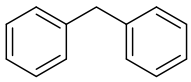
When using **1q** (36.2 mg, 0.2 mmol) according to Method A, diphenylethane (**2q**: 37 mg, 0.2 mmol) was obtained for 1.5 h in quantitative yield without further colum chromatography purification.

When using **1r** (39.5 mg, 0.2 mmol) according to Method A, diphenylethane (**2q**: 0.172 mmol) was obtained for 2.5 h in 86% yield without further colum chromatography purification. The yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as an internal standard.

Colorless oil; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.31–7.17 (m, 10H), 2.93 (s, 4H).

Spectroscopic data of ^{1}H NMR was identical to those reported in reference 1.

diphenylmethane (2s)



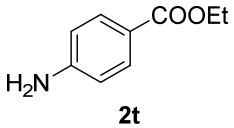
2s

When using **1s** (40.8 mg, 0.2 mmol) according to Method A, diphenylmethane (**2s**: 30.3 mg, 0.18 mmol) was obtained for 19 h in 90% yield without further colum chromatography purification.

Colorless oil; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.30–7.18 (m, 10H), 3.98 (s, 2H).

Spectroscopic data of ^{1}H NMR was identical to those reported in reference 2.

***p*-amino ethylbenzoate (2t)**



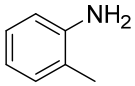
2t

When using **1t** (38.3 mg, 0.2 mmol) according to Method B, *p*-amino ethylbenzoate (**2t**: 0.2 mmol) was obtained for 4.5 h in quantitative yield without further colum chromatography purification.

^{1}HNMR (400 MHz, CD_3OD): δ 7.73 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.8 Hz, 2H), 4.27 (q, J = 7.2 Hz, 2H), 1.33 (t, J = 7.2 Hz, 3H).

Spectroscopic data of ^{1}H NMR of the product was identical to that of the commercially available authentic sample.

***o*-toluidine (2u)**



2u

When using **1u** (27.4 mg, 0.2 mmol) according to Method B, *o*-toluidine (**2u**: 0.2 mmol) was obtained for 1.5 h in quantitative yield without further colum chromatography purification.

^{1}HNMR (400 MHz, CD_3OD): δ 6.96 (m, 2H), 6.72 (d, J = 7.0 Hz, 1H), 6.64 (t, J = 7.0 Hz, 1H), 2.15 (s, 3H).

Spectroscopic data of ^{1}H NMR of the product was identical to that of the commercially available authentic sample.

toluene (2v)

2v

When using **1v** (21.9 mg, 0.2 mmol) according to Method B, toluene (**2v**: 0.184 mmol) was obtained for 0.5 h in 92% yield without further colum chromatography purification.

^{1}HNMR (500 MHz, CD_3OD): δ 7.22–7.19 (m, 2H), 7.14 (d, J = 3.5 Hz, 2H), 7.10 (t, J = 4.0 Hz, 1H), 2.31 (s, 3H).

Spectroscopic data of ^{1}H NMR of the product was identical to that of the commercially available authentic sample.

6. References.

(1) Lamani, M.; Ravikumara, G. S.; Prabhu, K. R. Iron(III) Chloride‐Catalysed Aerobic Reduction of Olefins using Aqueous Hydrazine at Ambient Temperature. *Adv. Synth. Catal*., **2012**, *354*, 1437–1442.

(2) Sangeun, Y.; Chan, H. M.; Hakjune, R. Palladium-Catalyzed Benzylation of Arylboronic Acids with *N,N*-Ditosylbenzylamines. *J. Org. Chem*., **2014**, *79*, 4206–4211.

7. ^{1}H NMR spectra of the substrates and products.

Figure S6. ^{1}H NMR spectra of *N*-benzyldioctylamine (**1a**).

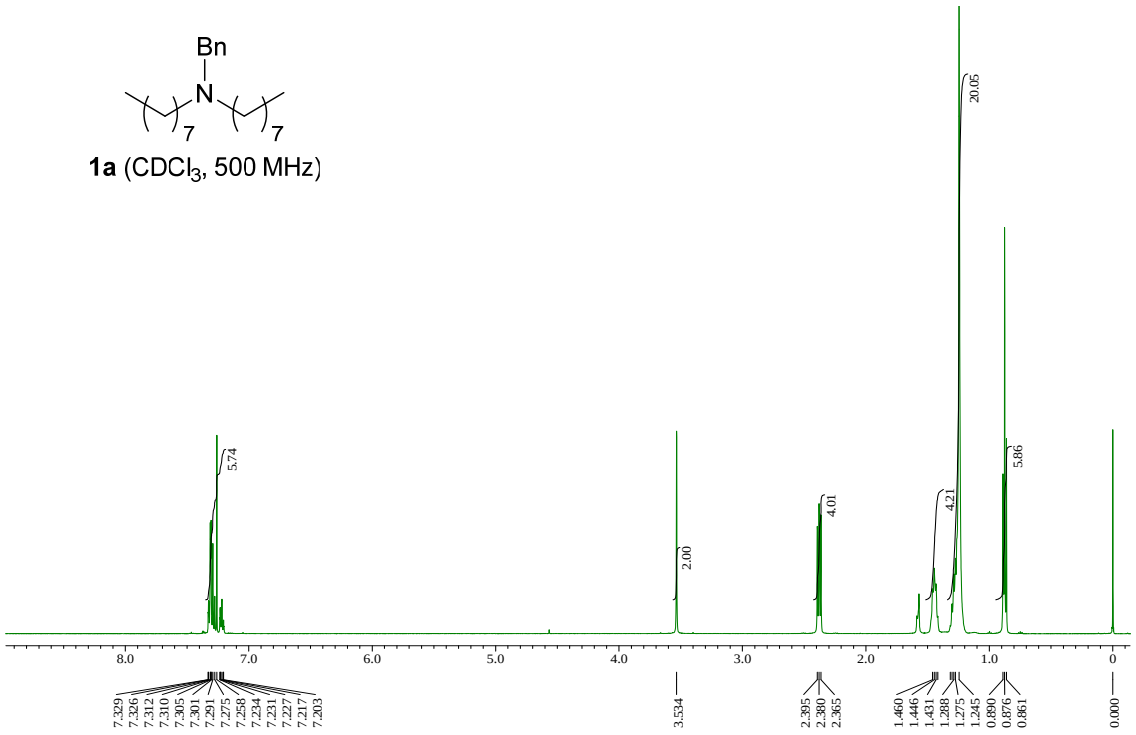


Figure S7. ^{1}H NMR spectra of *N*-benzyl-*N*-methylaniline (**1c**).

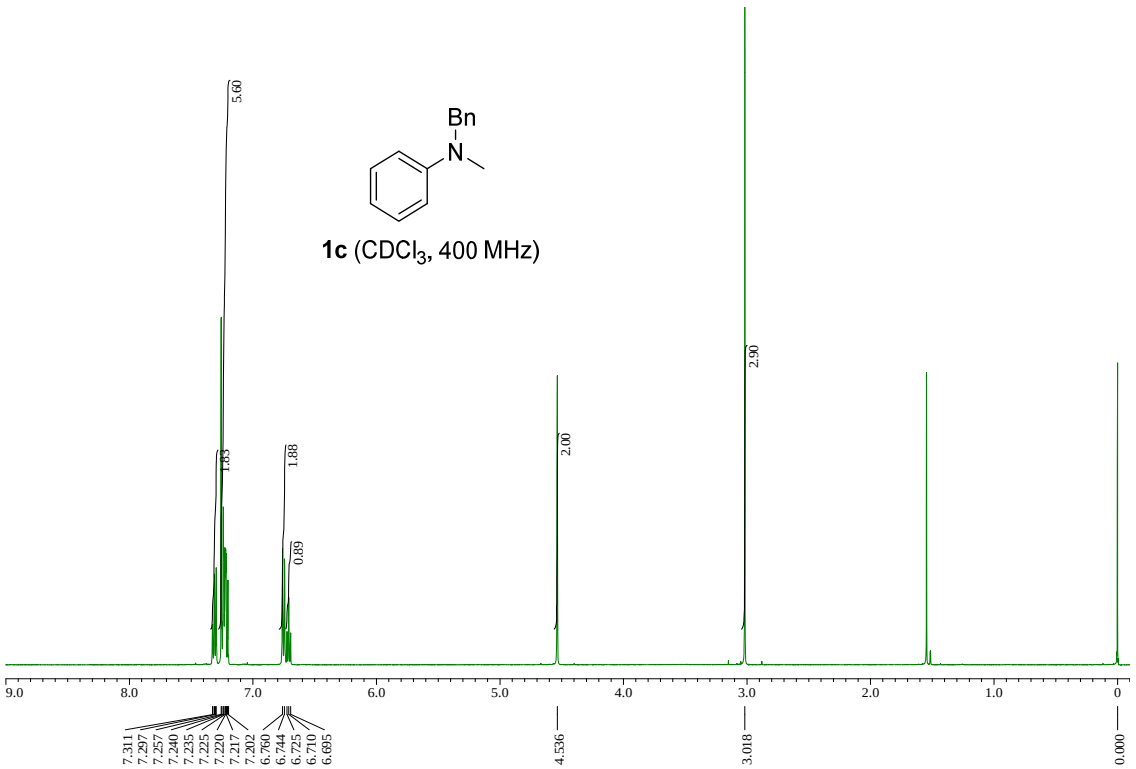


Figure S8. [1]H NMR spectra of *N*-benzyl-3-phenylpropan-1-amine (**1g**).

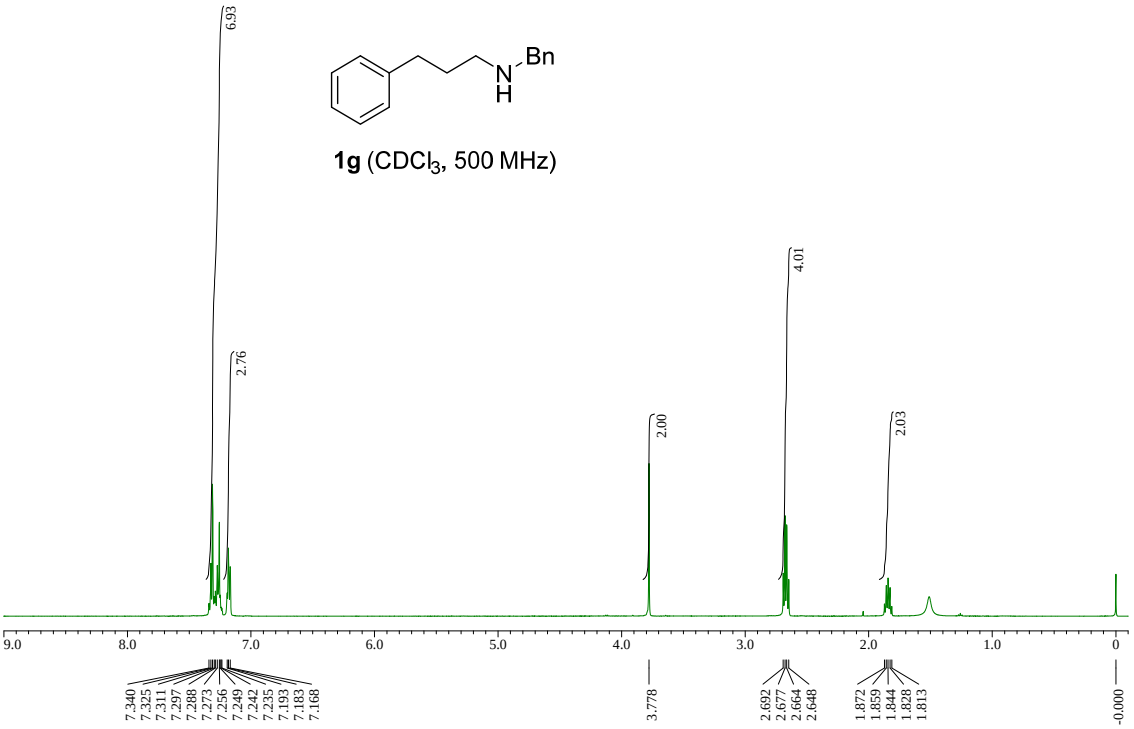


Figure S9. [1]H NMR spectra of *N*-benzyl-4-phenylpiperazine (**1h**).

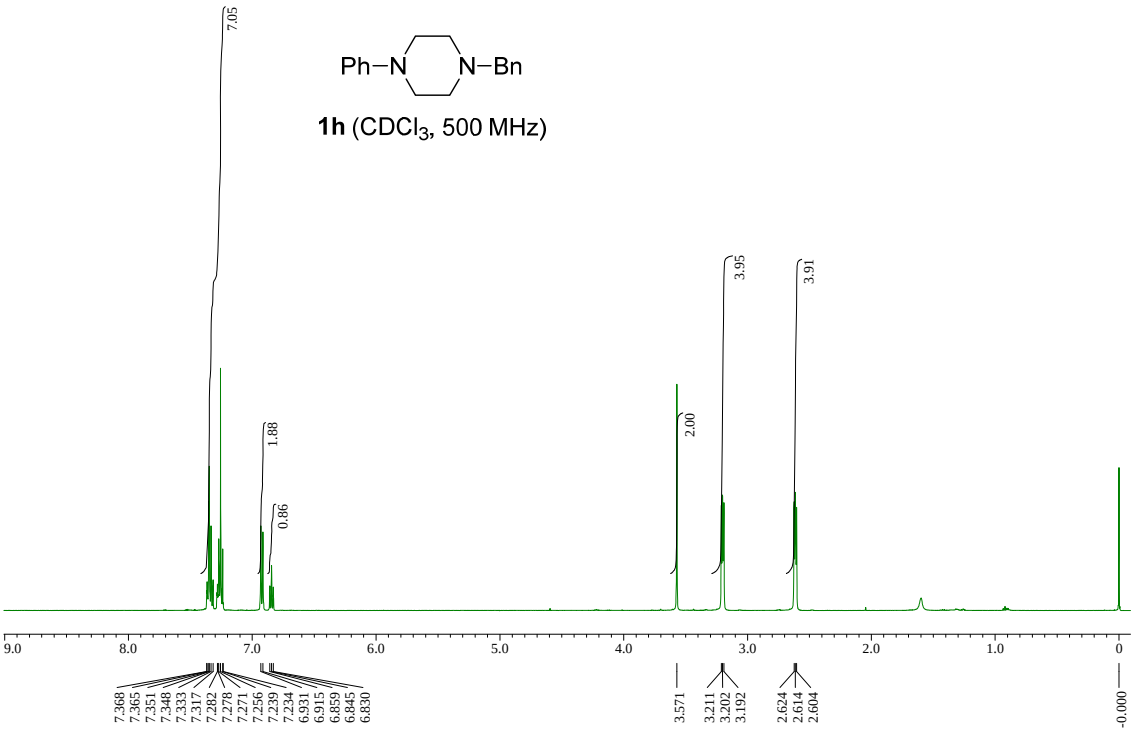


Figure S10. ^{1}H NMR spectra of *N*-benzyl-2-aminopirimidine (**1j**).

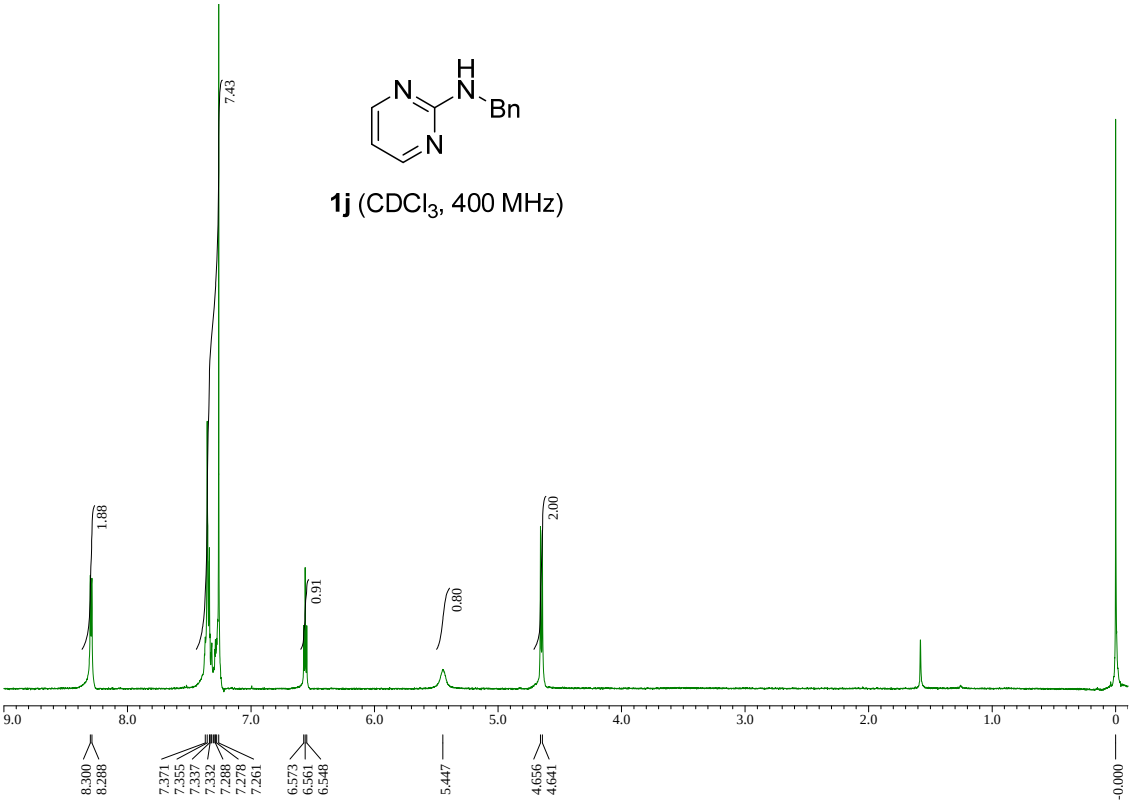


Figure S11. ^{1}H NMR spectra of *N*- benzyloxycarbonyl-2-aminopyrimidine (**1k**).

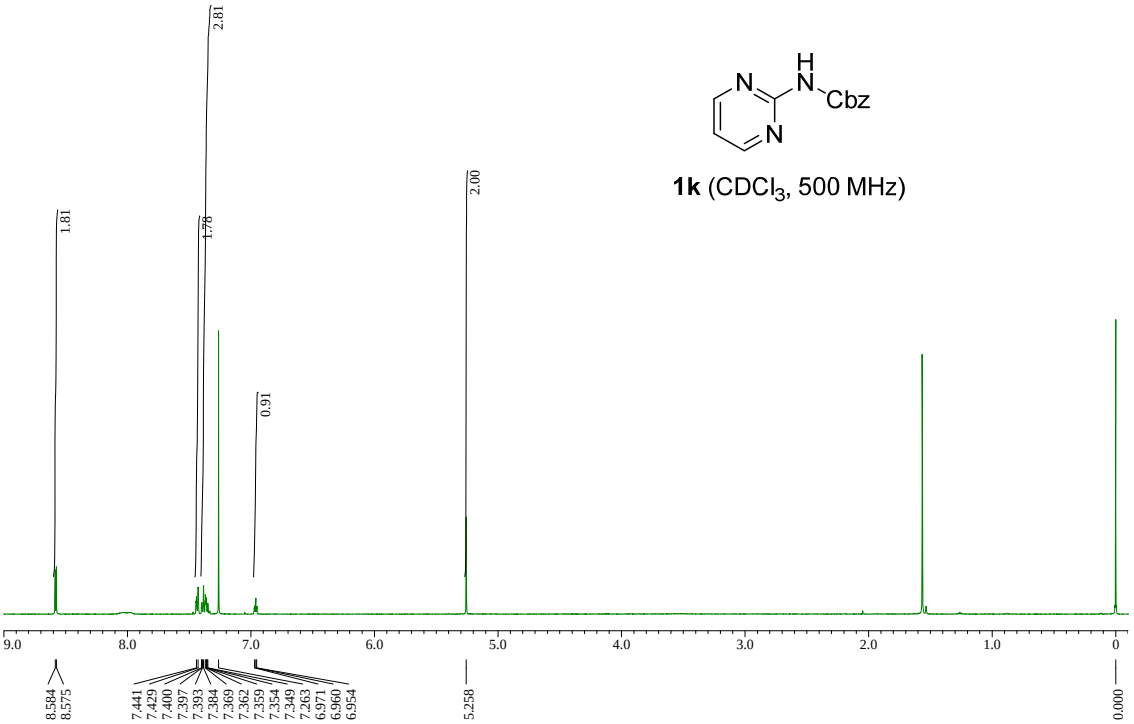


Figure S12. ^{1}H NMR spectra of *N*- benzyloxycarbonyldioctylamine (**1l**).

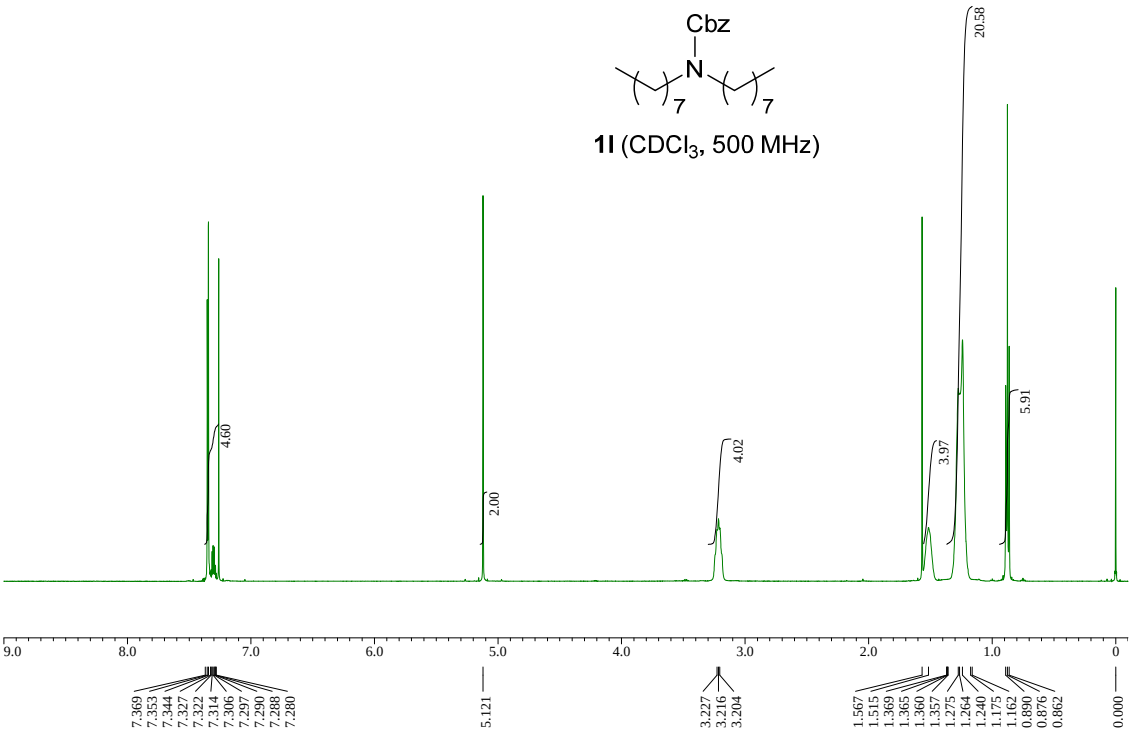


Figure S13. ^{1}H NMR spectra of *N*-benzyl-2-((*tert*-butyldimethylsilyl)oxy)ethan-1-amine (**1o**).

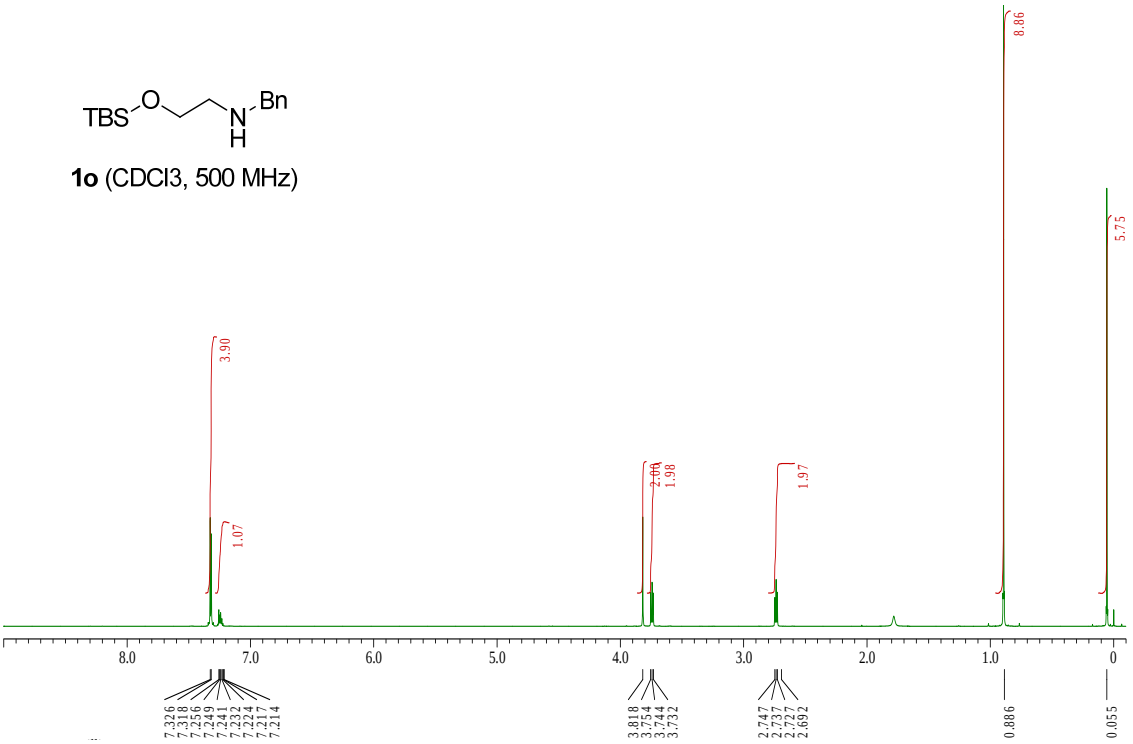


Figure S14. ^{1}H NMR spectra of *O-(tert*-butyldimethylsilyl)benzyloxyphenol (**1p**).

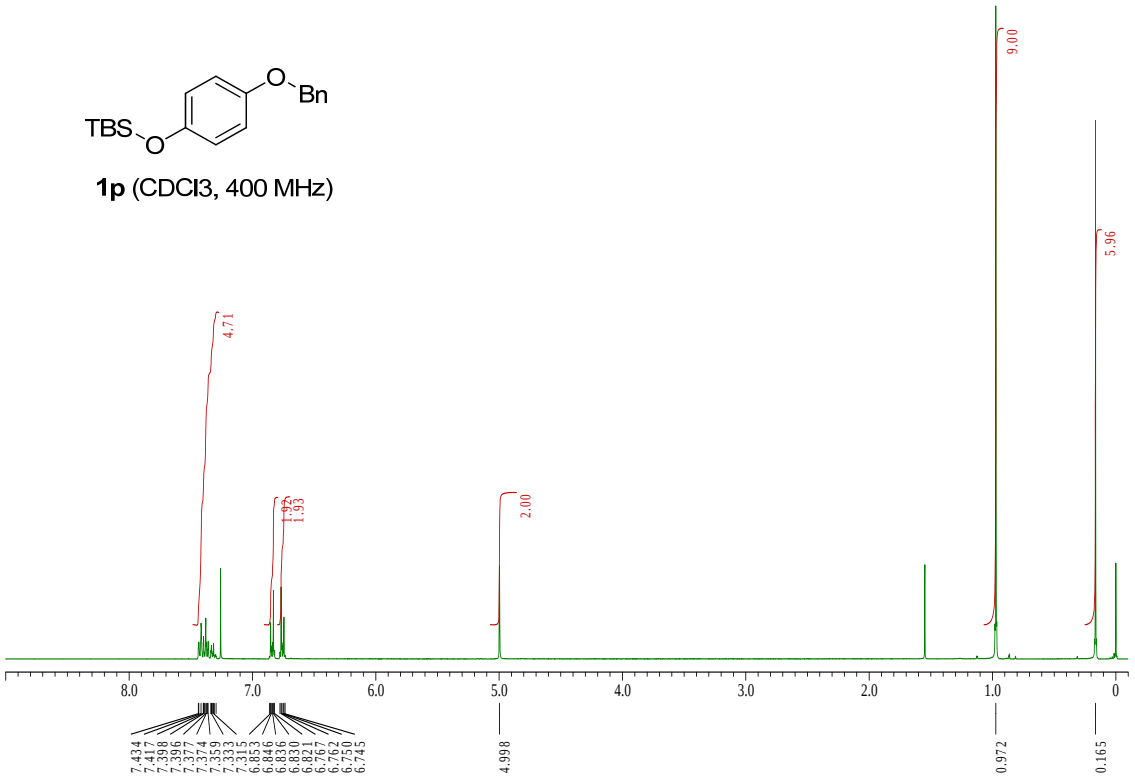


Figure S15. ^{1}H NMR spectra of dioctylamine (**2a**).

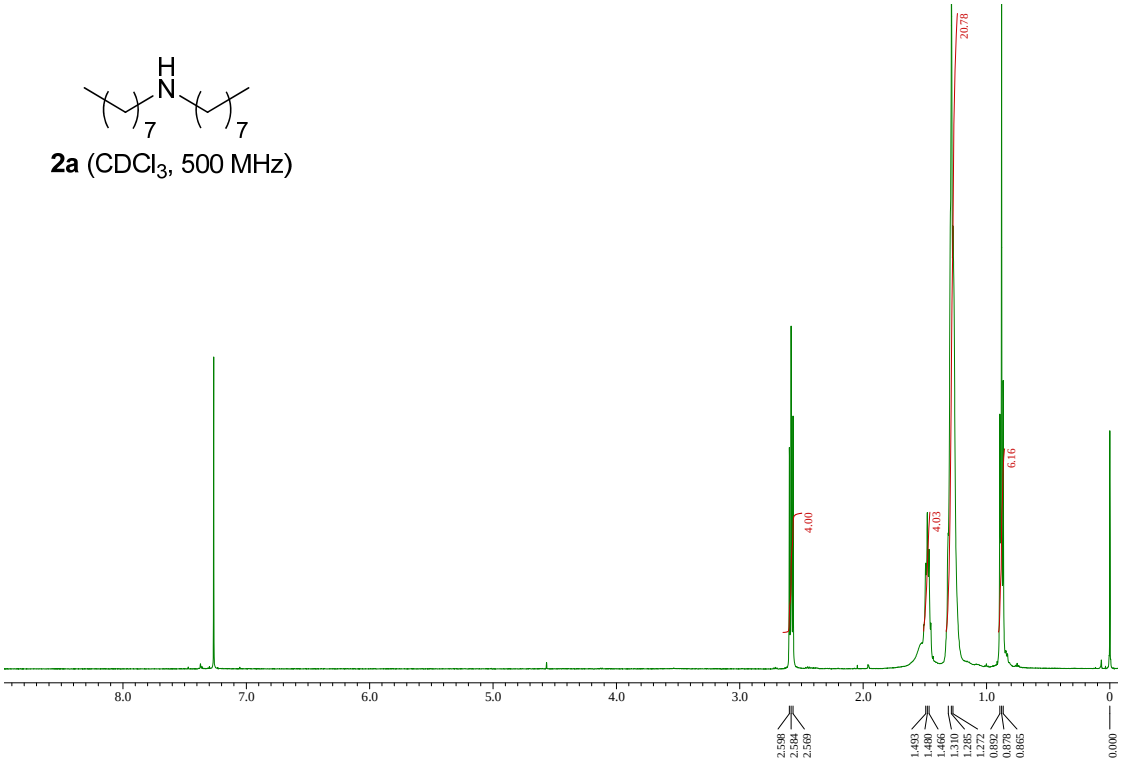


Figure S16. ^{1}H NMR spectra of *N*-butyl-*m*-toluidine (**2b**).

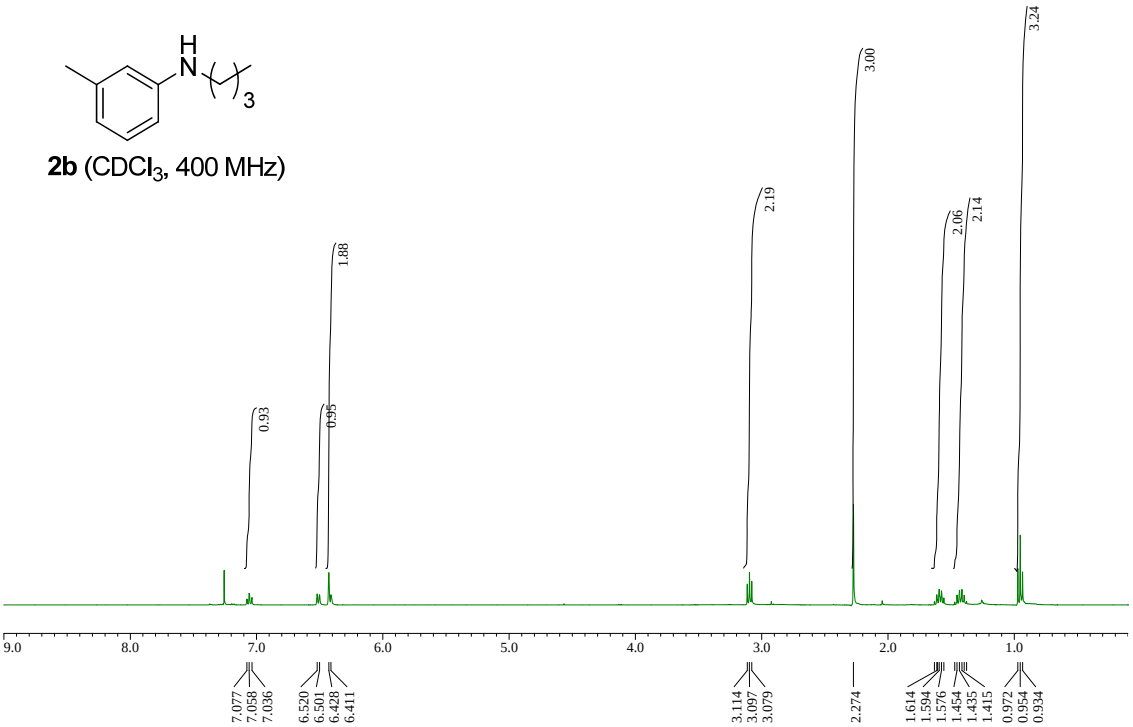


Figure S17. ^{1}H NMR spectra of *N*-methylaniline (**2c**).

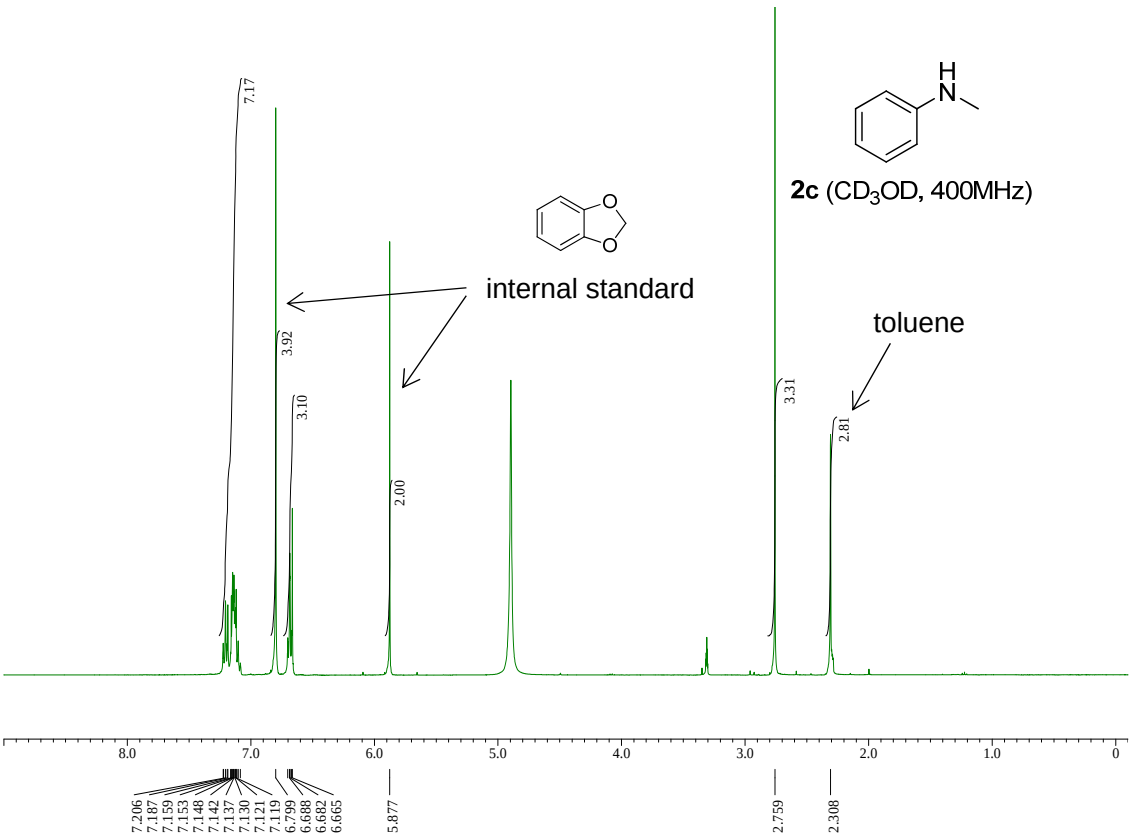


Figure S18. ^{1}H NMR spectra of aniline (**2d**).

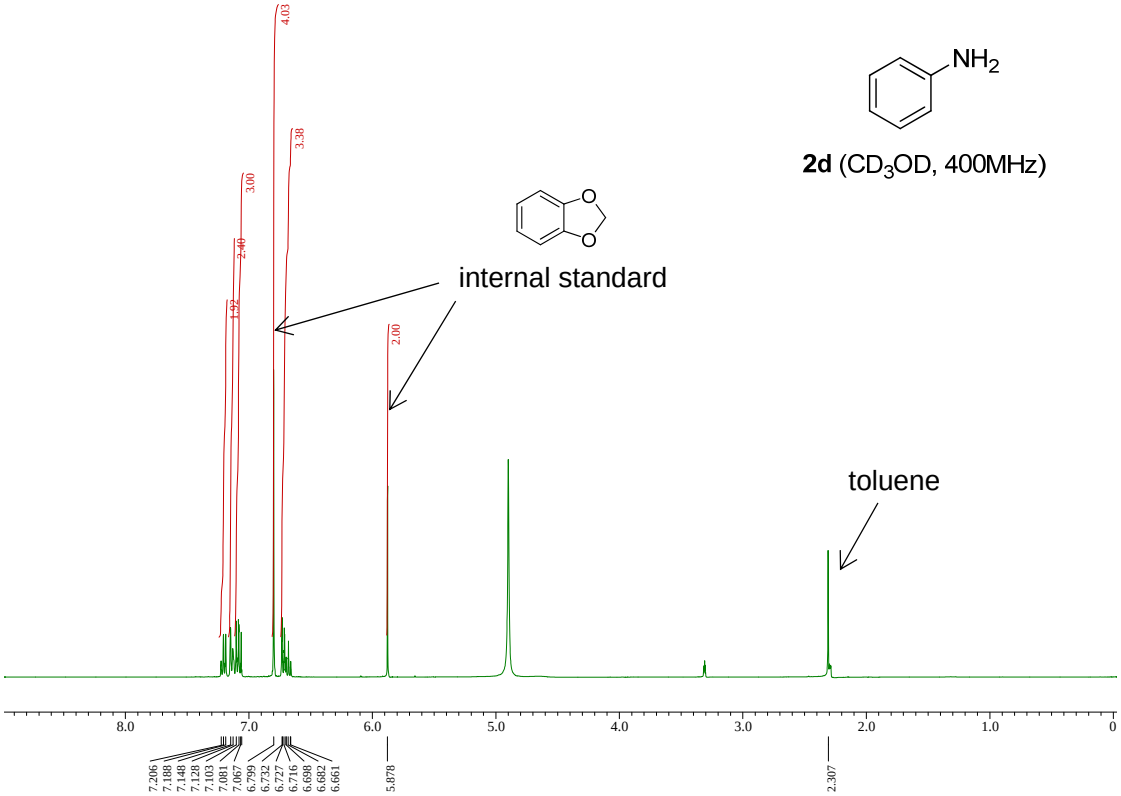


Figure S19. ^{1}H NMR spectra of 2-aminoethanol (**2f**).

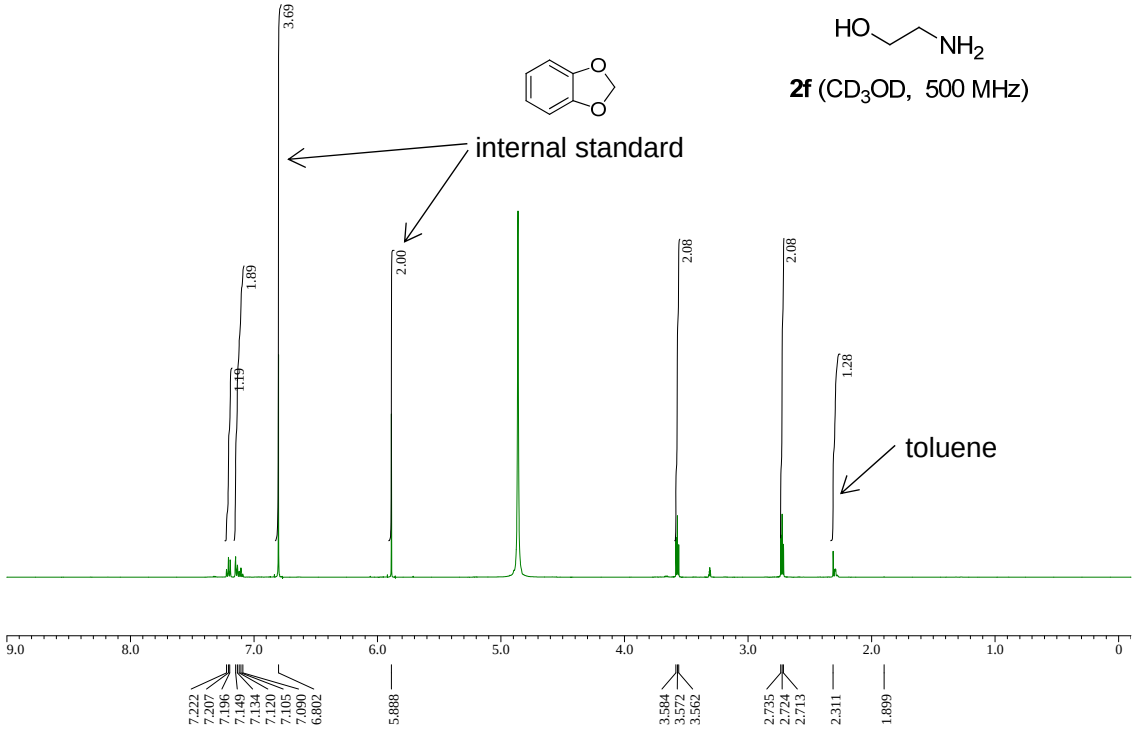


Figure S20. ^{1}H NMR spectra of 3-phenylpropan-1-amine (**2g**).

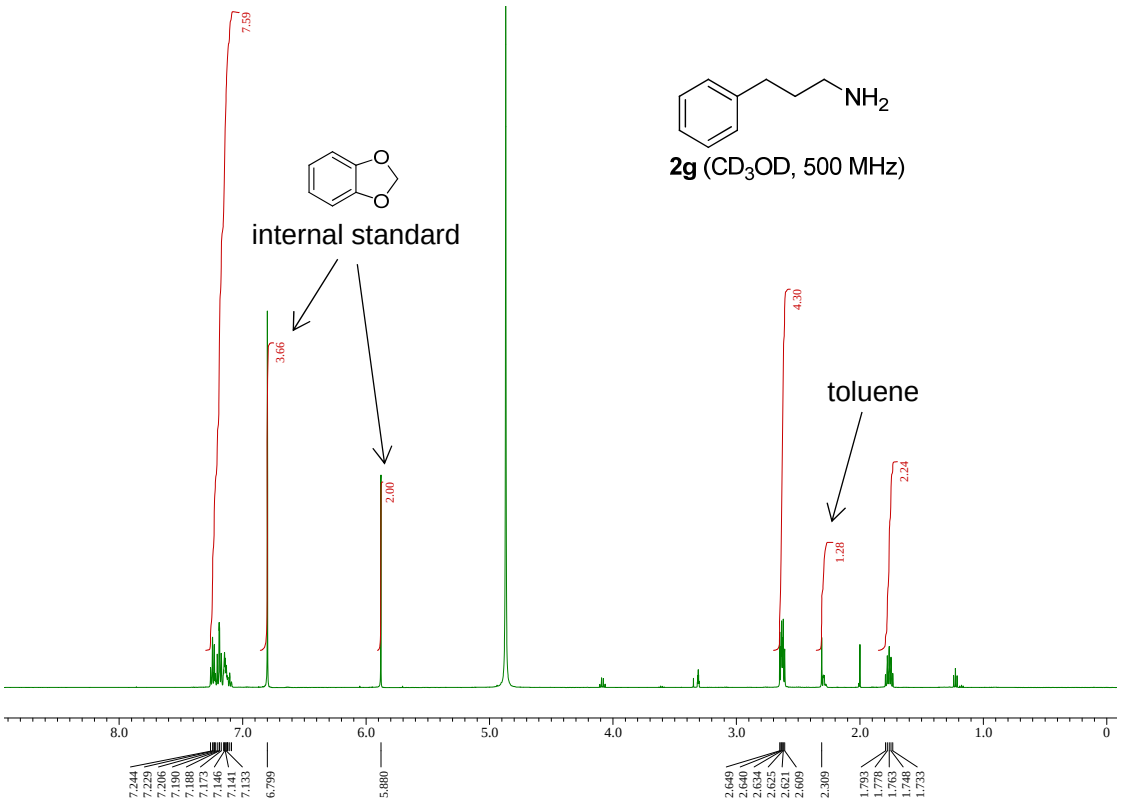


Figure S21. ^{1}H NMR spectra of 1-phenylpiperazine (**2h**).

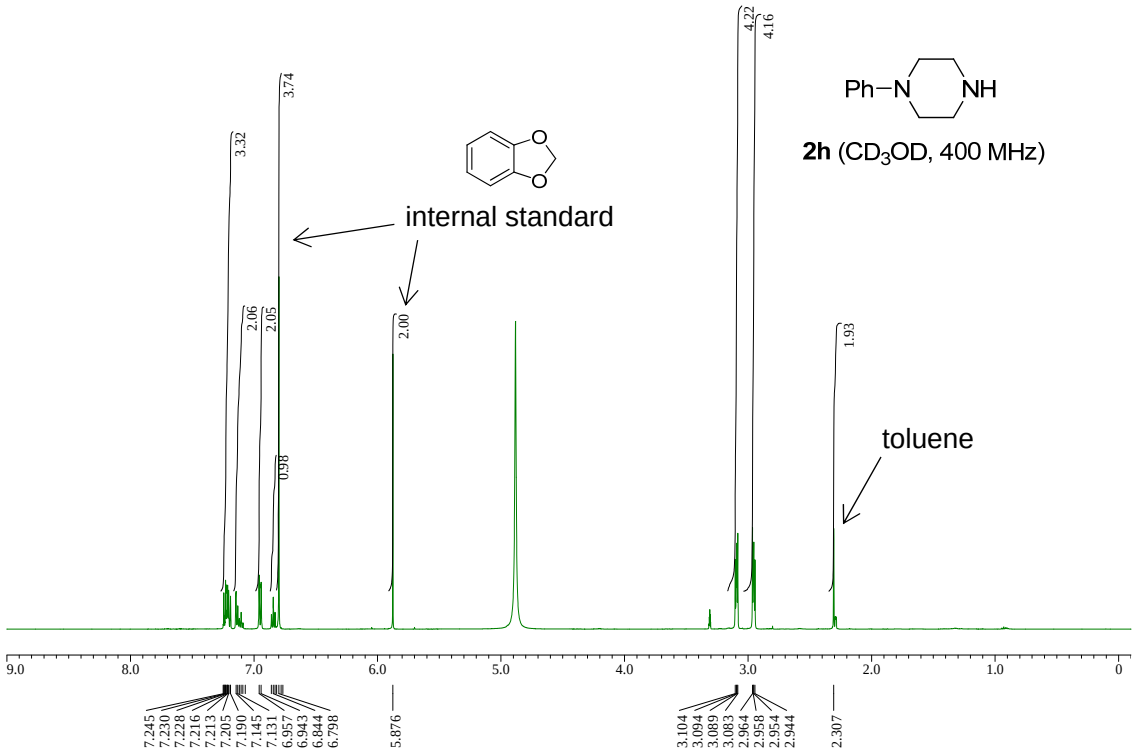


Figure S22. ^{1}H NMR spectra of 2-aminopyrimidine (**2j**).

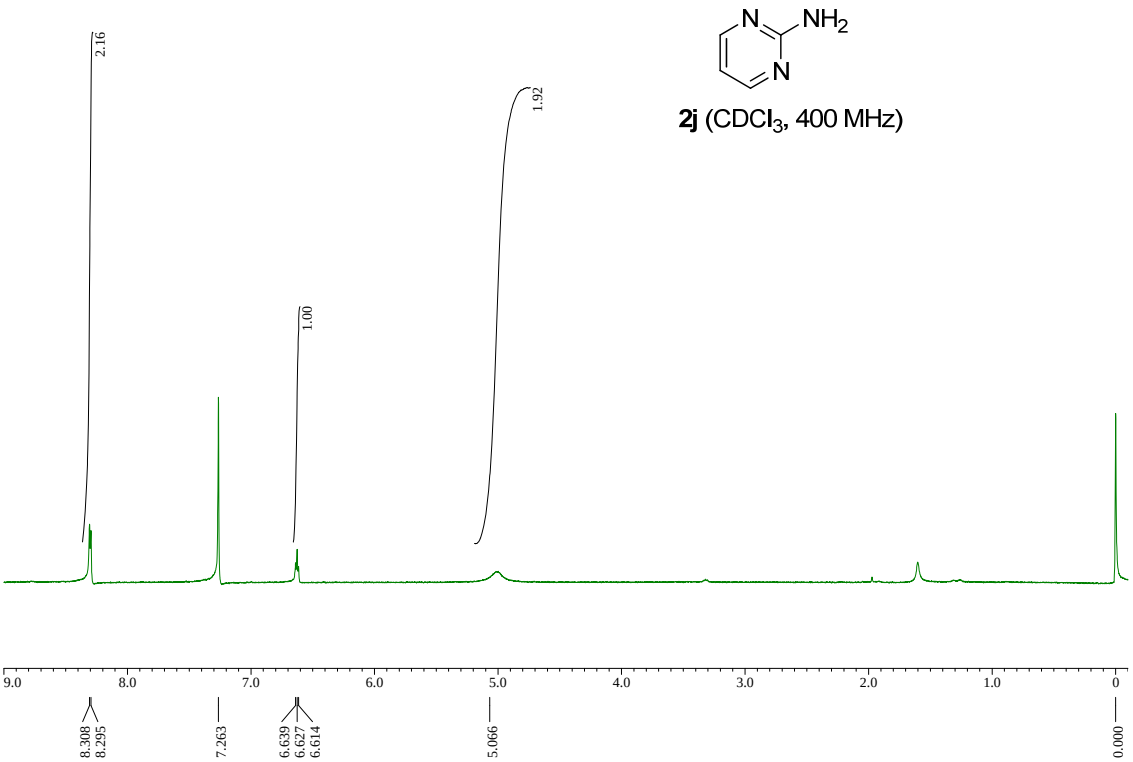


Figure S23. ^{1}H NMR spectra of phenol (**2m**).

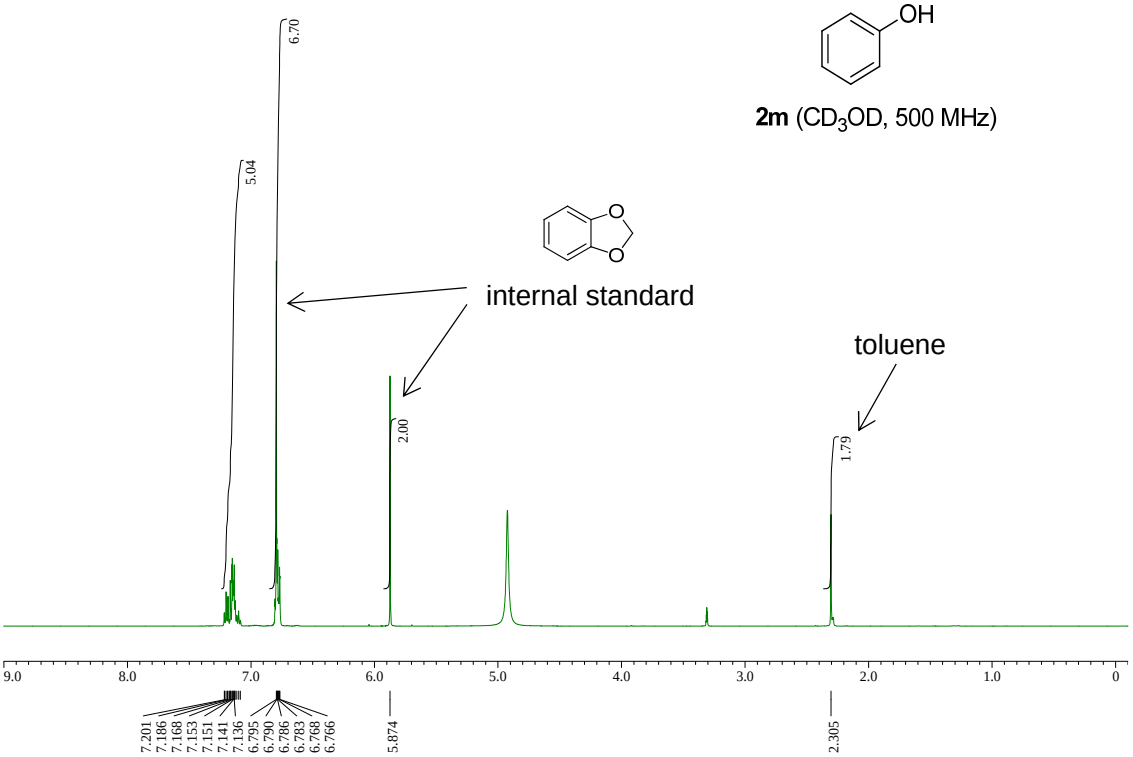


Figure S24. ^{1}H NMR spectra of ethylene glycol (**2n**).

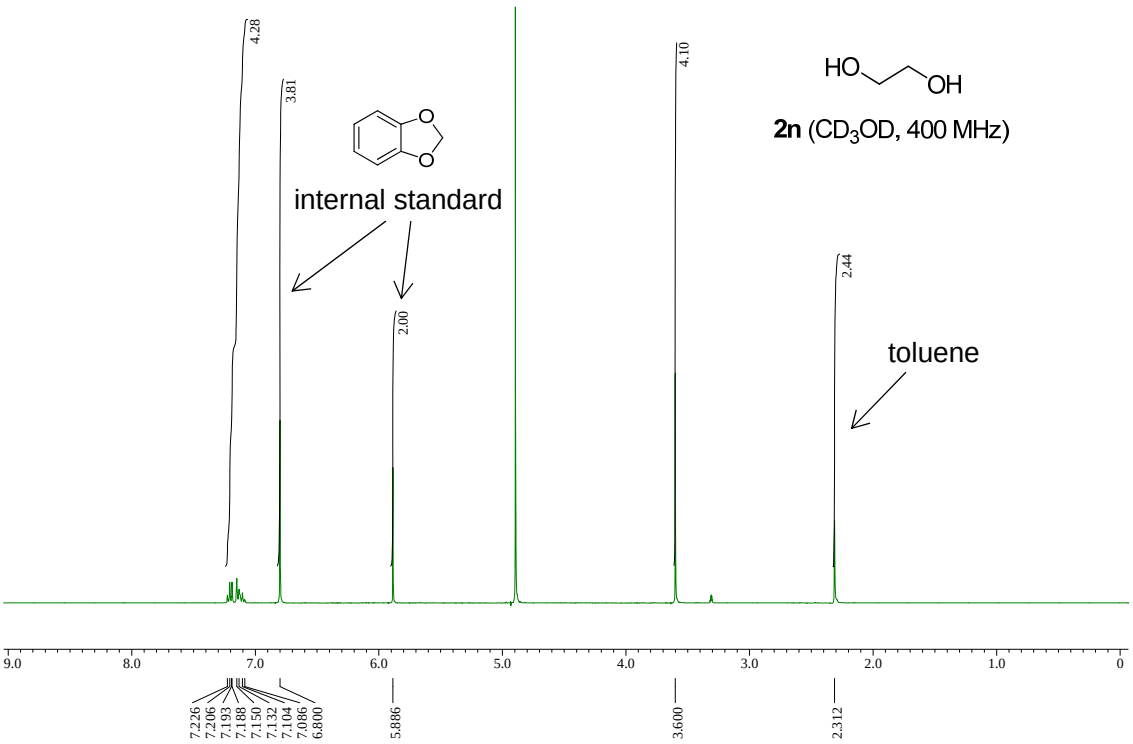


Figure S25. ^{1}H NMR spectra of 2-amino-1-(*tert*-butyldimethylsilyloxy)ethanol (**2o**).

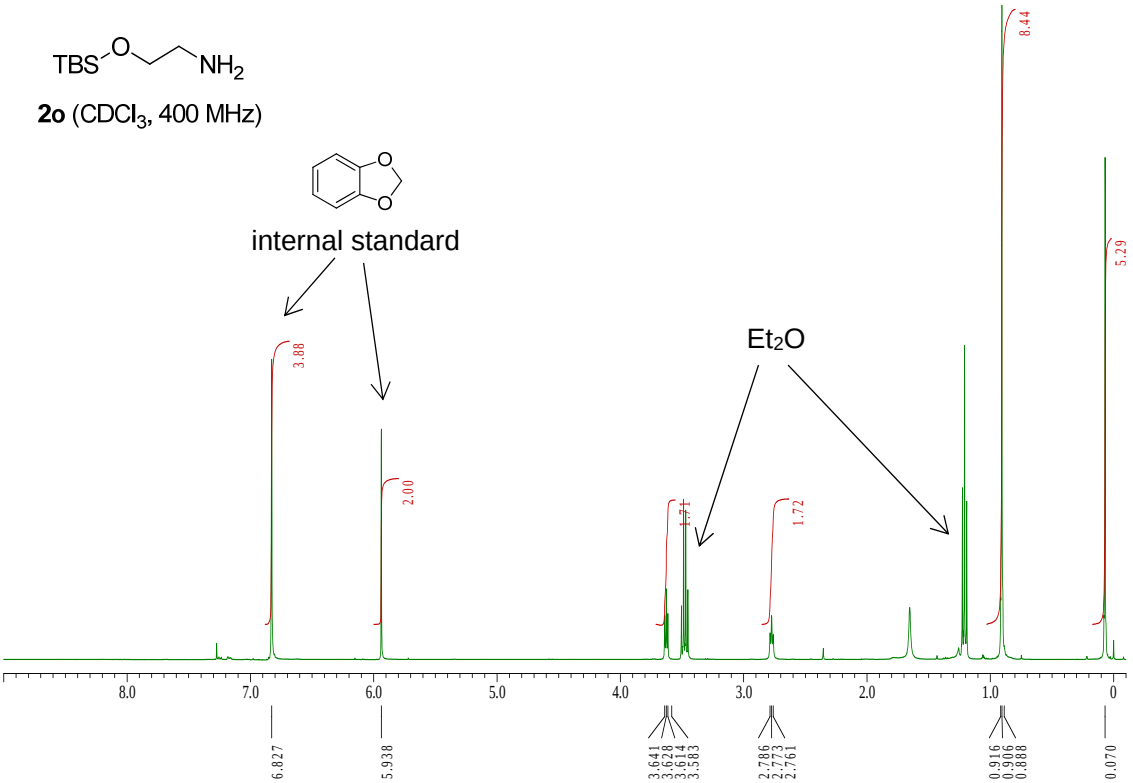


Figure S26. [1]H NMR spectra of 4-(*tert*-butyldimethylsilyloxy)phenol (**2p**).

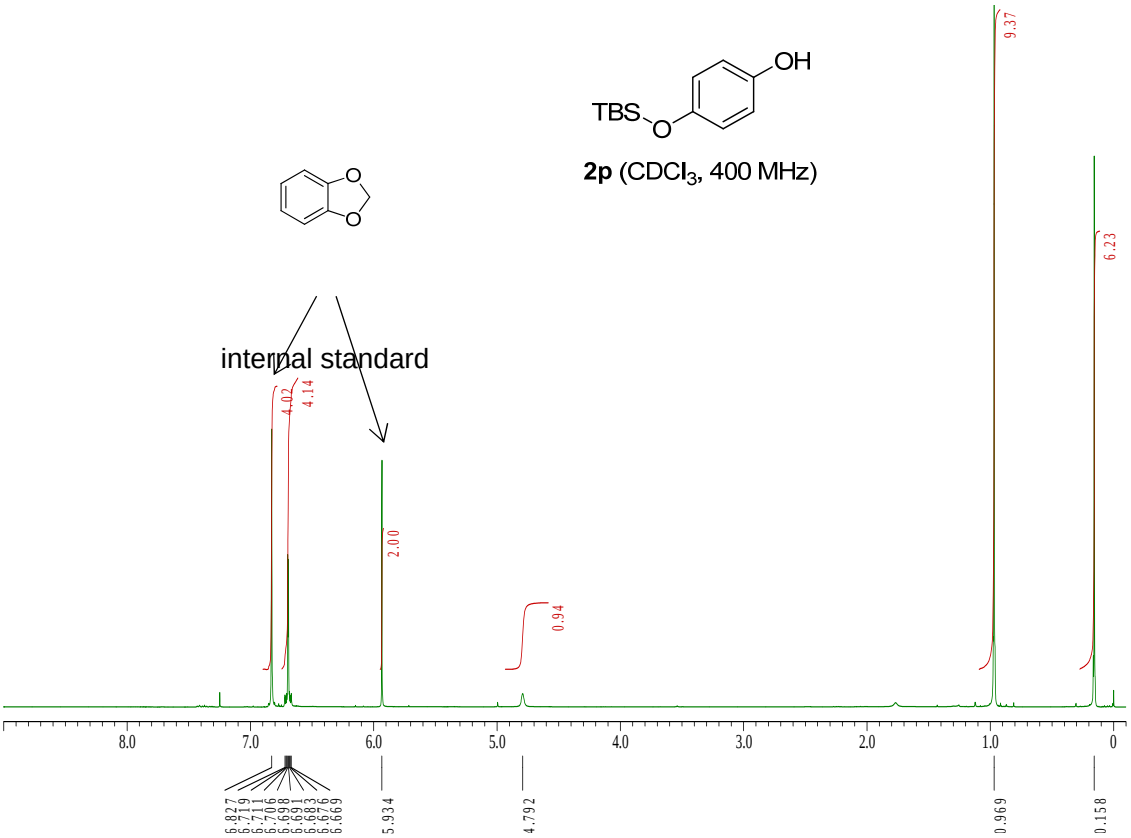


Figure S27. [1]H NMR spectra of hydroquinone (**2p'**).

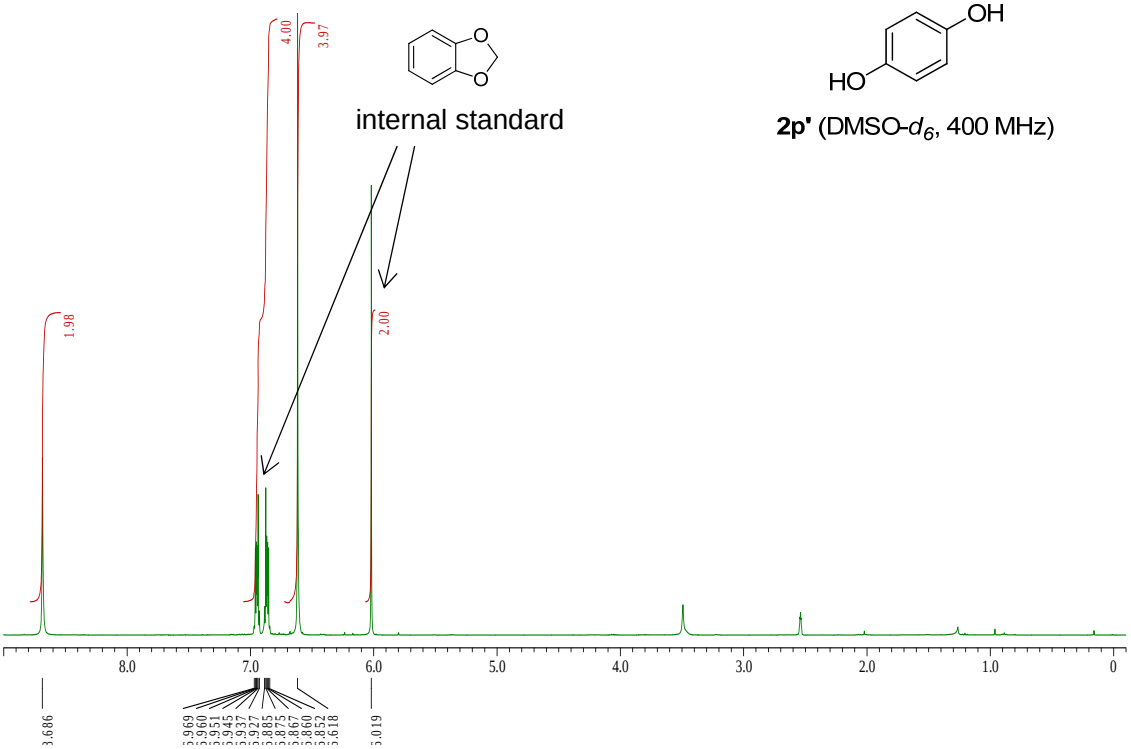


Figure S28. ^{1}H NMR of diphenylethane (**2q**).

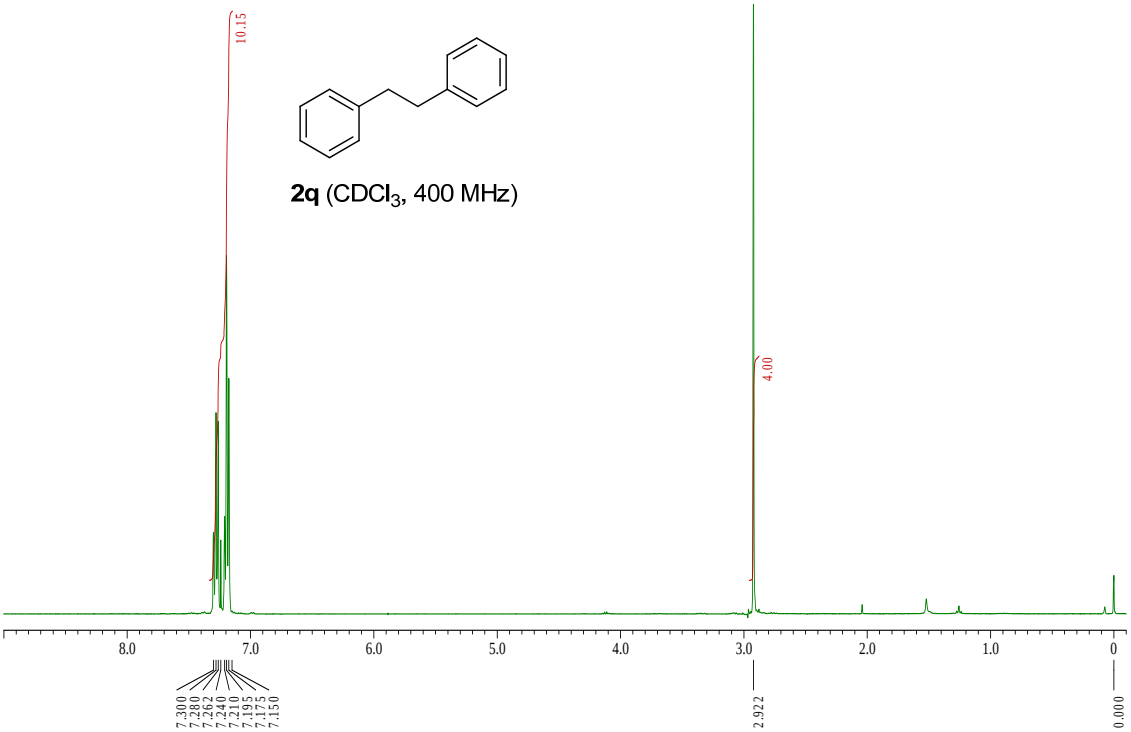


Figure S29. ^{1}H NMR of diphenylmethane (**2s**).

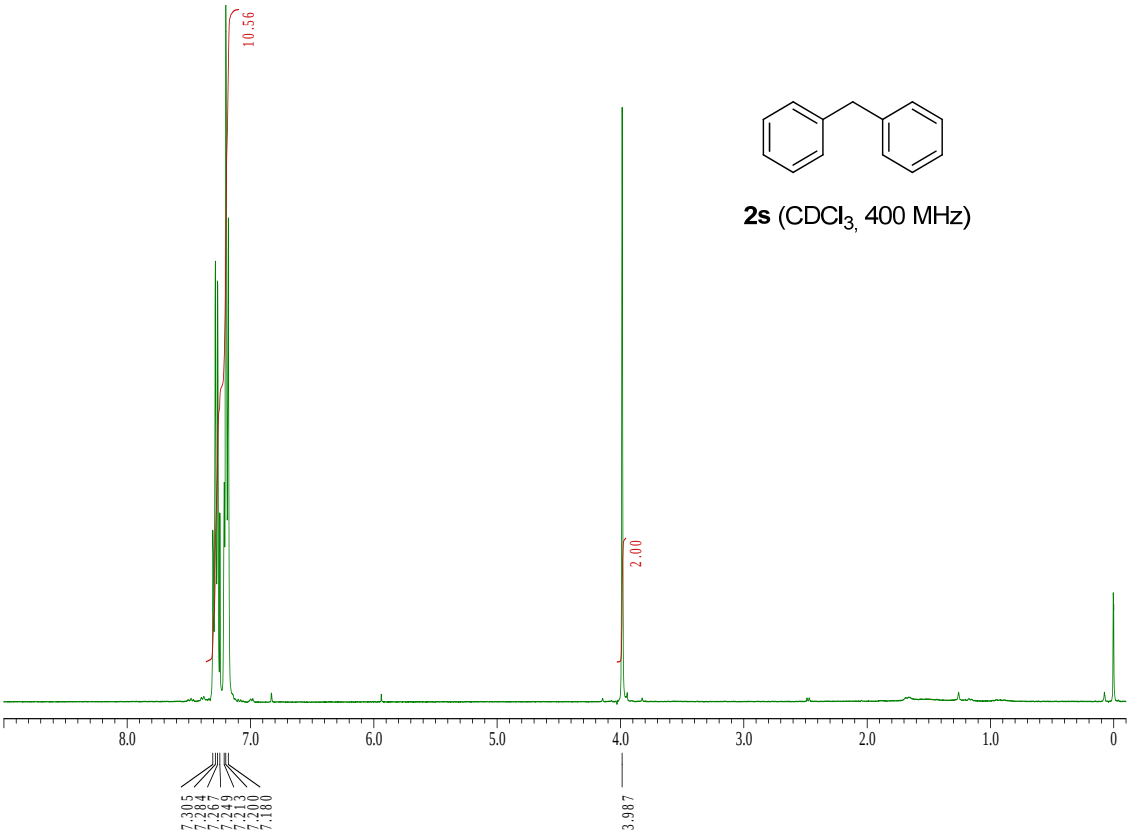


Figure S30. ^{1}H NMR of *p*-amino ethylbenzoate (**2t**).

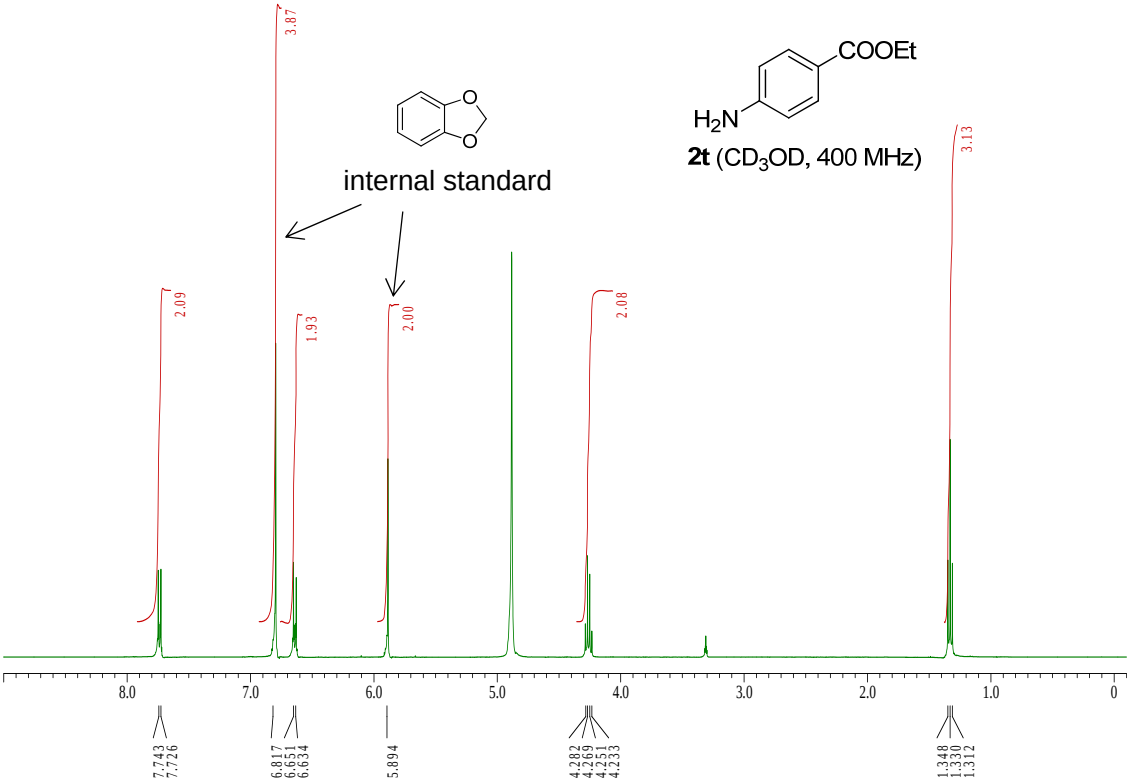


Figure S31. ^{1}H NMR of *o*-toluidine (**2u**).

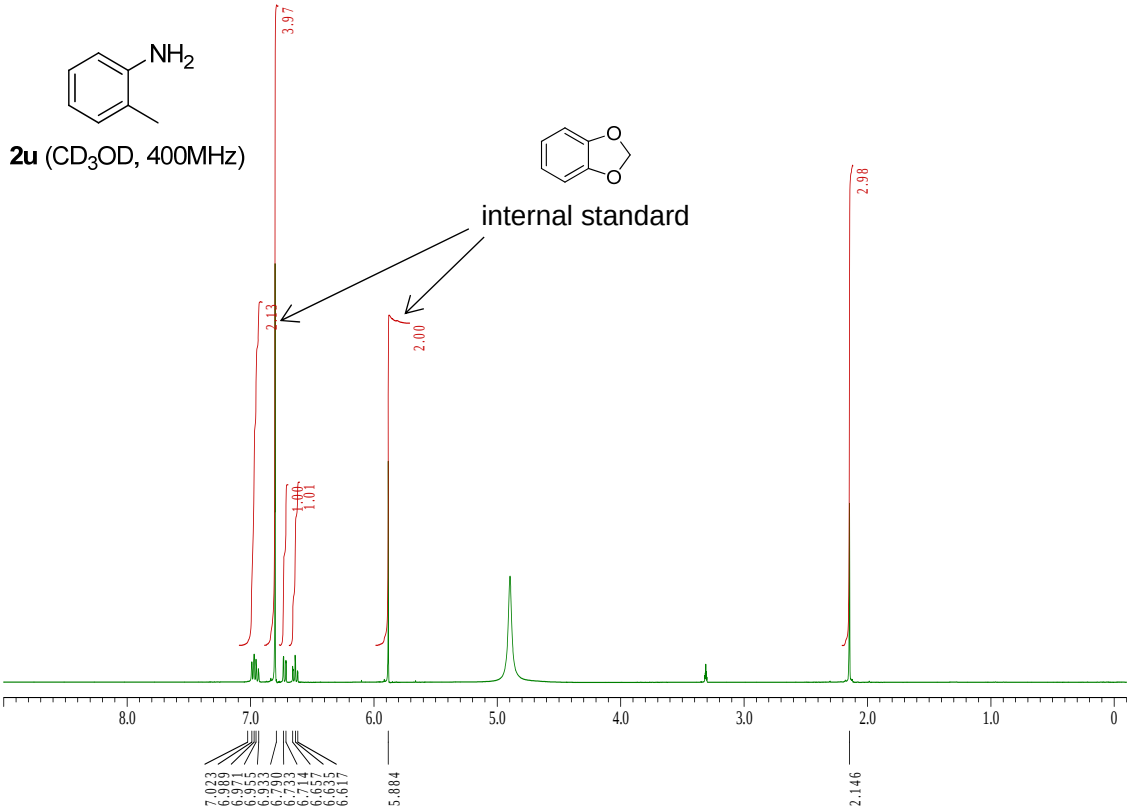
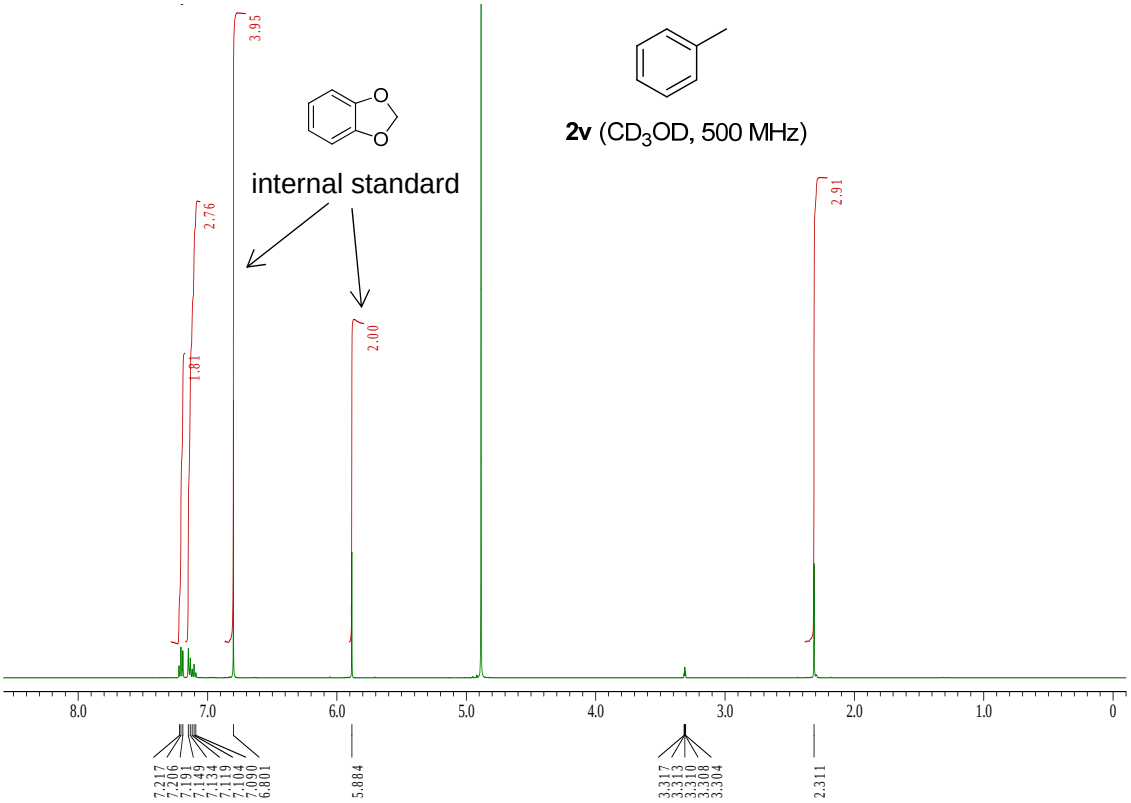


Figure S32. ^{1}H NMR of toluene (**2v**).



9. ^{1}H and ^{13}C NMR spectra of the newly synthesized substrates.

Figure S33. ^{1}H NMR of *N*-benzyl-*N*-butyl-*m*-toluidine (**1b**).

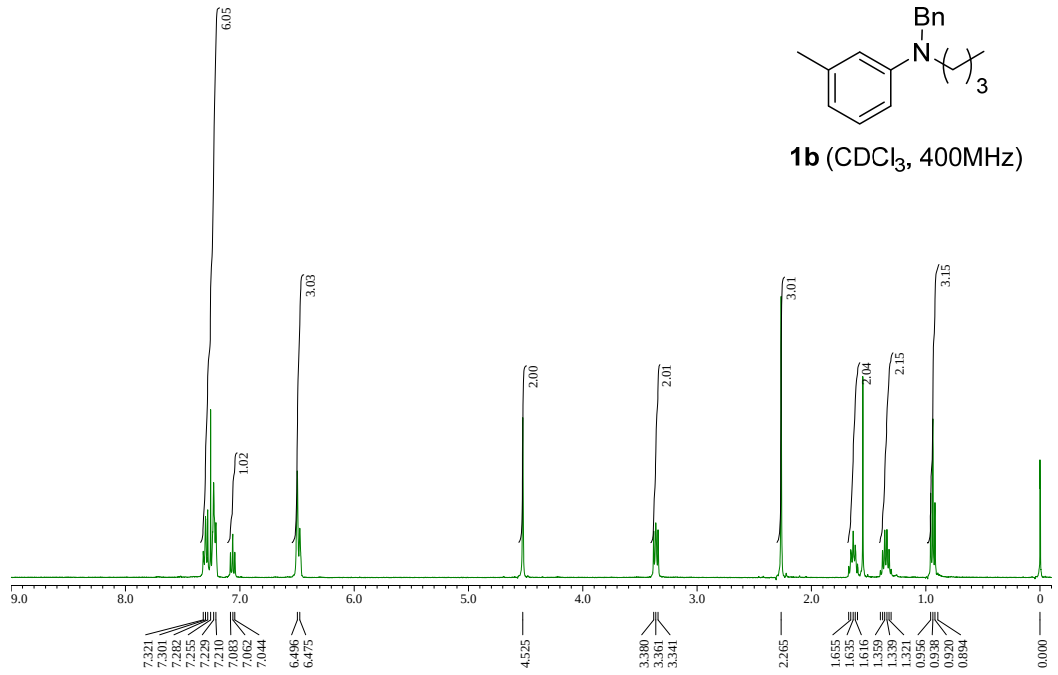


Figure S34. ^{13}C NMR of *N*-benzyl-*N*-butyl-*m*-toluidine (**1b**).