Supporting Information

Protic Tris(pyrazol-3-ylmethyl)amine Ruthenium Complexes Featuring Hydrogen Bonding Network in the Second Coordination Sphere

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Experimental Details

General procedures. All manipulations were performed under an atmosphere of argon using standard Schlenk technique unless otherwise specified. Solvents and reagents were dried by refluxing over sodium benzophenone ketyl (THF, 1,4-dioxane, toluene, diethyl ether, and hexane), CaH_2 (dichloromethane and 1,2-dichloroethane), P_2O_5 (CD_2Cl_2) and distilled before use. 1,2-Diphenylhydrazine was used after recrystallization from hot hexane. $[(C_6H_6)RuCl_2]_2$,[S1] $NaBAr^F{}_4$,[S2] and $[Ru(tpa)(MeCN)_2](SbF_6)_2$[S3] were prepared according to the literature. Other reagents were used as received. ^1H (399.78 MHz) and $^{31}P\{^1H\}$ (161.83 MHz) NMR spectra were obtained on a JEOL JNM-ECX-400 spectrometer. ^1H NMR shifts are relative to the signal of the residual $CHDCl_2$ (δ 5.32) and $CHCl_3$ (δ 7.26), while $^{13}C\{^1H\}$ NMR shifts are relative to the signal of the solvent ($CDCl_3$, δ 77.0) $^{31}P\{^1H\}$ NMR shifts are referenced to phosphoric acid (δ 0.0). Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyzer. ESI-TOF mass spectra were recorded on a JEOL JMS-T 100LC with positive ionization mode.

Synthesis of LH_3. To a suspension of NaH (60 wt% in mineral oil, 1.6369 g, 40.9 mmol) in THF (12 mL) was added 2',4',6'-trimethylacetophenone (6.0 mL, 36 mmol), and the mixture was allowed to reflux for 1.5 h. To the boiling mixture was added 2,2',2"-nitrilotriacetic acid triethyl ester (2.960 g, 10.8 mmol) in THF (40 mL) over the course of 10 min, and the mixture was allowed to reflux for additional 3 h. The mixture was treated with 1M HCl solution at 0 °C in open air until pH 7–8 and extracted with THF (20 mL × 3). The combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4. Evaporation of the solvent afforded orange oil. To a suspension of this crude hexaketone in ethanol (40 mL) was added an ethanol (40 mL) solution of hydrazine monohydrate (10 mL, 0.21 mol) over the course of 20 min. The mixture was stirred for additional 30 min at room temperature and then allowed to reflux for additional 5 h. The solvent was evaporated, washed with H_2O (20 mL), acetone, and hexane. The resultant pale white solid was dissolved in THF (25 mL). Slow addition of hexane afforded $LH_3 \cdot 0.5H_2O$ (1.9265 g, 3.10 mmol, 29%) as pale white crystals. The presence of the solvating water has been confirmed by ^1H NMR spectroscopy as well as elemental analysis. ^1H NMR ($CDCl_3$) 2.05 (s, 18H, *o*-Me), 2.31 (s, 9H, *p*-Me), 3.79 (brs, 6H, CH_2), 6.15 (brs, 3H, pyrazole CH), 6.85 (s, 6H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 20.4 and 21.3 (Me), 50.5 (CH_2), 106.0 and 137.3 (pyrazole), 128.3 and 137.6 ($C_6H_2Me_3$). Signals of some

quaternary carbon atoms could not be assigned. Anal. Calcd for $C_{39}H_{46}N_7O_{0.5}$: C, 75.45; H, 7.47; N, 15.79. Found: C, 75.37; H, 7.71; N, 15.70.

Synthesis of [{RuCl(LH$_3$)}$_2$(μ$_2$-Cl)]Cl (2). A mixture of $[(C_6H_6)RuCl_2]_2$ (100.0 mg, 0.200 mmol) and $LH_3 \cdot 0.5H_2O$ (244.8 mg, 0.394 mmol) in 1,4-dioxane (20 mL) was allowed to reflux for 16 h. After cooling the yellow suspension to the room temperature, diethyl ether (60 mL) was added. The yellow powder that formed was washed with diethyl ether (50 mL) and dried in vacuo (255.9 mg, 0.163 mmol, 83%). ^{1}H NMR (CD_2Cl_2, [Ru] = 0.01 M): δ 1.91, 1.96, 1.98, 2.28 (s, 6H each, *o*- and *p*-Me), 2.32 (s, 3H, *p*-Me), 3.26 (br, 2H, CH_2), 4.13 (br, 4H, CH_2), 5.71 (brs, 1H, pyrazole CH), 5.99 (brs, 2H, pyrazole CH), 6.84 (brs, 4H, C_6H_2), 6.91 (brs, 2H, C_6H_2), 12.65, 13.64, 13.86 (brs, 1H each, NH). The NH resonances are broadened in lower concentrations. The signals for the mesityl and pyrazole CH groups, with apparent local C_s symmetry around the Ru atoms, are also broad and dependent on the concentration, suggesting dynamic behavior of **2** in solution. Anal. Calcd for $C_{78}H_{90}Cl_4N_{14}Ru_2$: C, 59.76; H, 5.79; N, 12.51. Found: C, 57.61; H, 6.27; N, 11.79.[S4] ESI-MS (in methanol): *m*/*z* = 1533.46573 (calcd for [**2**–Cl]$^+$ 1533.46402). Crystals suitable for X-ray analysis were obtained by recrystallization from 1,2-dichloroethane–diethyl ether.

Synthesis of [RuCl(PPh$_3$)(LH$_3$)]Cl (3). A mixture of **2** (48.0 mg, 0.0306 mmol) and triphenylphosphine (48.2 mg, 0.184 mmol) in toluene (5 mL) was stirred at 100 °C for 14 h. After removal of the solvent in vacuo, residual solid was washed with hexane (5 mL × 3). Subsequent recrystallization from dichloromethane–diethyl ether (1.5 mL/18 mL) afforded **3** as yellow-green crystals (32.2 mg, 0.0308 mmol, 50%). ^{1}H NMR (CD_2Cl_2): δ 1.54, 2.27 (s, 6H each, *o*- and *p*-Me), 1.87 (s, 12H, *o*-Me), 2.29 (s, 3H, *p*-Me), 4.78 (s, 2H, CH_2), 4.89 (dd, 2H, $^2J_{HH}$ = 13.8 Hz, $^5J_{HP}$ = 4.1 Hz, CH_2), 5.85 (d, 1H, $^4J_{HH}$ = 1.8 Hz, pyrazole CH), 5.97 (d, 2H, $^2J_{HH}$ = 13.8 Hz, CH_2), 6.34 (d, 2H, $^4J_{HH}$ = 1.9 Hz, pyrazole CH), 6.81 (s, 2H, C_6H_2), 6.86 (s, 4H, C_6H_2), 7.16–7.20 (m, 3H, PPh_3), 7.27–7.31, 8.12–8.15 (m, 6H each, PPh_3), 7.54 (br, 1H, NH), 9.67 (br, 2H, NH). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 58.3 (s). Anal. Calcd for $C_{57}H_{60}Cl_2N_7PRu$: C, 65.45; H, 5.78; N, 9.37. Found: C, 65.27; H, 5.90; N, 9.10.

Synthesis of [RuCl(PPh$_3$)(LH$_2$)] (4). To a solution of **3** (52.3 mg, 0.0500 mmol)

in THF (3 mL) was added a 0.5 M solution of $KN(SiMe_3)_2$ (0.1 mL, 0.05 mmol) in toluene at –78°C. The mixture was gradually warmed to room temperature over the course of 6 h. After removal of the solvent in vacuo, the residue was extracted with toluene (5 mL × 2). The extract was concentrated to ca. 2.5 mL. Slow addition of hexane (18 mL) afforded **4** as green crystals (34.2 mg, 0.0339 mmol, 68%). ^{1}H NMR (CD_2Cl_2): δ 1.64, 2.26 (s, 6H each, *o*- and *p*-Me), 1.89 (s, 12H, *o*-Me), 2.24 (s, 3H, *p*-Me), 4.42 (dd, 2H, $^2J_{HH}$ = 13.1 Hz, $^5J_{HP}$ = 3.5 Hz, CH_2), 4.57 (s, 2H, CH_2), 5.70 (s, 1H, pyrazole CH), 5.80 (d, 2H, $^2J_{HH}$ = 13.3 Hz, CH_2), 6.07 (s, pyrazole CH), 6.77 (s, 2H, C_6H_2), 6.82, (s, 4H, C_6H_2), 7.05–7.08 (m, 3H, PPh_3), 7.17–7.20, 8.21–8.25 (m, 6H each, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.3 (s). Anal. Calcd for $C_{57}H_{59}ClN_7PRu$: C, 67.81; H, 5.89; N, 9.71. Found: C, 67.82; H, 5.59; N, 9.69.

Protonation of 4 To Give 3. The mixture of **4** (13.5 mg, 0.0134 mmol) and diphenylammonium chloride (2.8 mg, 0.0136 mmol) in THF (2.5 mL) was stirred at room temperature for 15 h. After removal of the solvent in vacuo, the residue was dissolved in CH_2Cl_2 (1 mL). Slow addition of diethyl ether (4 mL) and hexane (4 mL) afforded **3** (5.6 mg, 0.0054 mmol, 40%).

Synthesis of [RuCl(PhNH$_2$)(LH$_3$)]Cl (5). A mixture of **2** (19.8 mg, 0.0253 mmol) and 1,2-diphenylhydrazine (13.8 mg, 0.0750 mmol) in dichloromethane (2 mL) was stirred for 14 h. The resultant mixture was concentrated to ca. 1.5 mL under reduced pressure. Slow addition of diethyl ether (15 mL) afforded **5**·0.5Et_2O as red crystals (14.2 mg, 0.0155 mmol, 61%). ^{1}H NMR (CD_2Cl_2) 1.94 (s, 12H, *o*-Me), 1.97, 2.29 (s, 6H each, *o*- and *p*-Me), 2.30 (s, 3H, *p*-Me), 4.11 (s, 2H, CH_2), 4.32, 5.30 (d, 2H each, CH_2), 5.84 (d, 1H, pyrazole CH), 6.15 (d, 2H, pyrazole CH), 6.88 (s, 4H, aryl), 6.91 (s, 4H, aryl), 6.78–6.81 (m, 1H, Ph), 7.15–7.19, 7.56–7.58 (m, 2H each, Ph), 13.24 (br, 1H, NH). The signals for the rest NH groups could not be assigned. Anal. Calcd for $C_{47}H_{57}Cl_2N_8O_{0.5}Ru$: C, 61.76; H, 6.29; N, 12.26. Found: C, 61.42; H, 6.31; N, 12.16. Integration of the ^{1}H NMR signals of the crude product, containing 1,3,5-methoxybenzene (3.2 mg, 0.019 mmol) as an internal standard, revealed the formation of aniline (145% per Ru atom in **2**) and azobenzene (132% per Ru atom in **2**) during the reaction (Figure S8). The yields are more than one equivalent per Ru atom in **2** due to addition of a slight excess of 1,2-diphenylhydrazine to accelerate the reaction.

Catalytic Disproportionation of 1,2-Diphenylhydrazine. A mixture of **2** (19.8 mg, 0.0126 mmol), 1,2-diphenylhydrazine (93.1 mg, 0.505 mmol), and 1,3,5-trimethoxybenzene (17.8 mg, 0.106 mmol) as an internal standard in dichloromethane (2 mL) was stirred for 18 h at room temperature. After removal of the solvent in vacuo, the mixture was dissolved in $CDCl_3$ and subjected to NMR analysis as described in the stoichiometric reaction. Table S1 summarizes the results.

X-ray Diffraction Studies. Single crystals suitable for X-ray analyses were mounted on a fiber loop. Diffraction experiments were performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation (λ = 0.710 70 Å). Intensity data were corrected for Lorentz–polarization effects and for absorption.

Structure solution and refinements were carried out by using the CrystalStructure program package.[S5] The heavy-atom positions were determined by a direct methods program (SIR2002[S6] for **2**·H_2O·$3C_2H_4Cl_2$·$3Et_2O$; SIR92[S7] for the rest crystals) and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. Two of the three solvated diethyl ether molecules in **2**·H_2O·$3C_2H_4Cl_2$·$3Et_2O$ were disordered. One molecule was placed at two disordered positions with 50% occupancy and refined with restraint geometries and fixed thermal parameters except for the O3 and C98–C100 atoms, which were refined isotropically. The other molecule, as well as the solvating diethyl ether molecule in **5**·$0.5Et_2O$, was refined with restraint geometries and fixed thermal parameters due to the partial disorder. The chloride ion in **5**·$0.5Et_2O$ was placed at three disordered positions with 0.8/0.1/0.1 occupancies. The rest non-hydrogen atoms were refined anisopropically by full-matrix least-squares techniques based on F^2. The hydrogen atoms in the disordered diethyl ether molecules were not included in the refinements, while the NH hydrogen atoms in the aniline ligand in **5**·$0.5Et_2O$ were found in the difference Fourier map and refined with a riding model. The rest hydrogen atoms were placed at calculated positions and included in the refinements with a riding model. The maximum residual peak (5.58 e·Å^{-3} in **2**·H_2O·$3C_2H_4Cl_2$·$3Et_2O$ and 4.41 e·Å^{-3} in **5**·$0.5Et_2O$) around the solvating Et_2O molecules was larger than normally expected (Alert B level) due to the severe disorder of these solvating molecules.

References and Notes

(S1) Bennett, M. A.; Smith, A. K. *J. Chem. Soc. Dalton Trans.* **1974**, 233–241.

(S2) Smith, C. R.; Zhang, A.; Mans, D. J.; RajanBabu, T. V. *Org. Synth.* **2008**, *85*, 248–266.
(S3) Whiteoak, C. J.; Nobbs, J. D.; Kiryushchenkov, E.; Pagano, S.; White, A. J. P.; Britovsek, G. J. P. *Inorg. Chem.* **2013**, *52*, 7000–7009.
(S4) The results of the analysis were reproducible, even for the thoroughly dried X-ray-quality crystals obtained by recrystallization from 1,2-dichloroethane–diethyl ether. The low value for carbon may be due to incomplete combustion of the complex during the analysis.
(S5) *CrystalStructure 4.0: Crystal Structure Analysis Package*, Rigaku Corporation, Tokyo 196-8666, Japan, **2000**–**2010**.
(S6) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2003**, *36*, 1103.
(S7) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.

Table S1. Catalytic disproportionation of 1,2-diphenylhydrazine with tris(pyrazolylmethyl)amine ruthenium complex **2**.[a]

			Yield (TON)[b]	
Entry	PhNHNHPh charged, mmol	S/C[c]	azobenzene, mmol	aniline, mmol
1	0.505	20	0.087 (3.5)	0.115 (2.3)
2[d]	0.506	20	0.150 (6.0)	0.234 (4.6)
3	0.126	5	0.059 (2.3)	0.053 (1.0)
4[e]	0.126	5	0.0038 (0.15)	0.0046 (0.09)
5[e,f]	0.126	5	0.0012 (0.05)	0.0015 (0.03)

[a] Conditions: **2**, 0.0126 mmol, CH_2Cl_2 (2 mL), room temp., 18 h, under Ar. [b] Determined by ^{1}H NMR spectroscopy by using a known amount of 1,3,5-trimethoxybenzene as an internal standard. The TON is calculated by (moles of azobenzene)/(moles of Ru in **2**) and [(moles of aniline)/(moles of Ru in **2**)]/2. [c] (Moles of 1,2-diphenylhydrazine charged)/(moles of Ru in **2**). [d] In the presence of $NaBAr^F_4$ (0.0259 mmol). [e] $[Ru(tpa)(MeCN)_2](SbF_6)_2$ (0.0253 mmol) instead of **2** was used. [d] Pyrazole (1 equiv/Ru, 0.0250 mmol) wad added.

Figure S1. ^{1}H NMR spectrum of 1

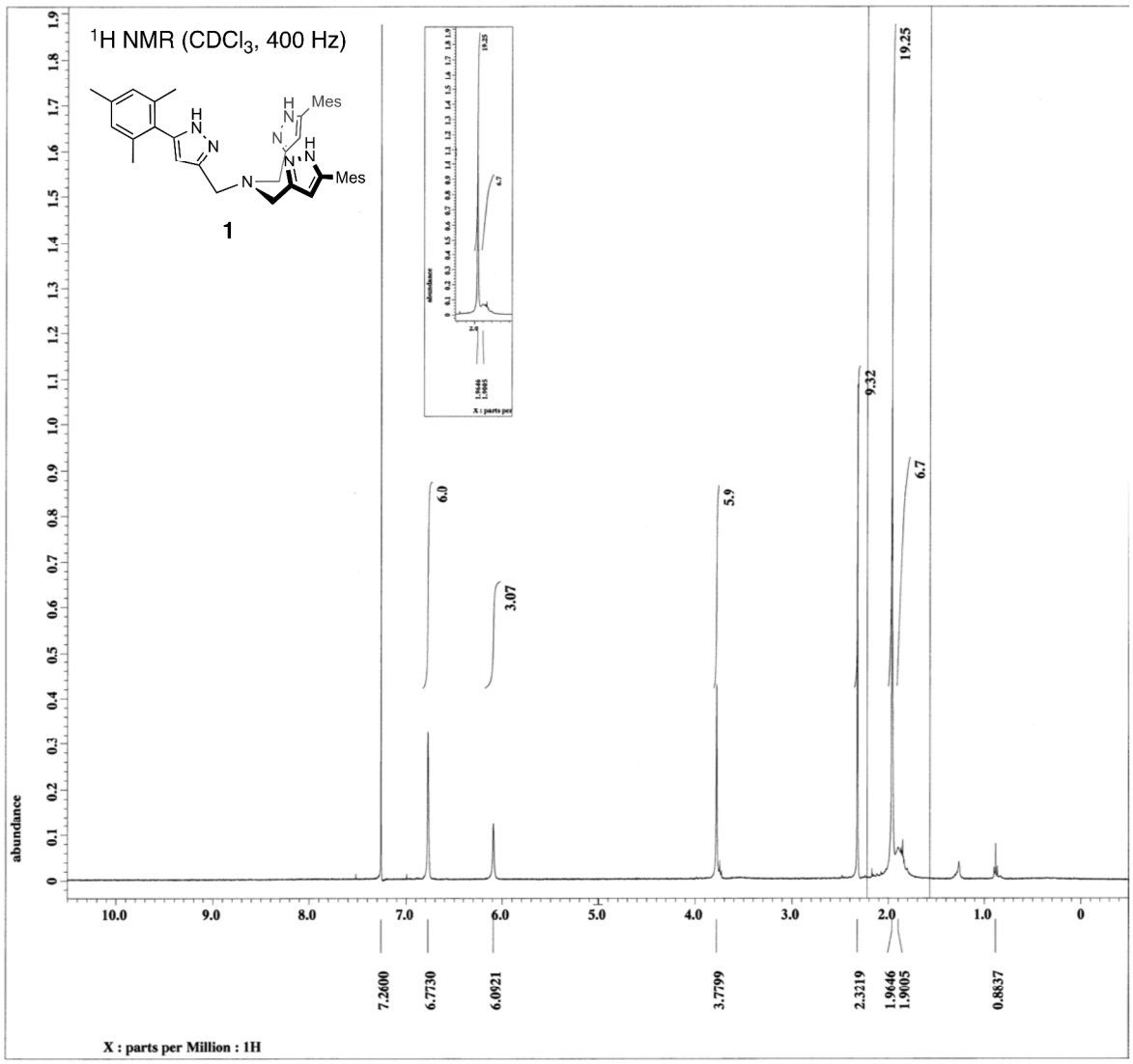


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of 1

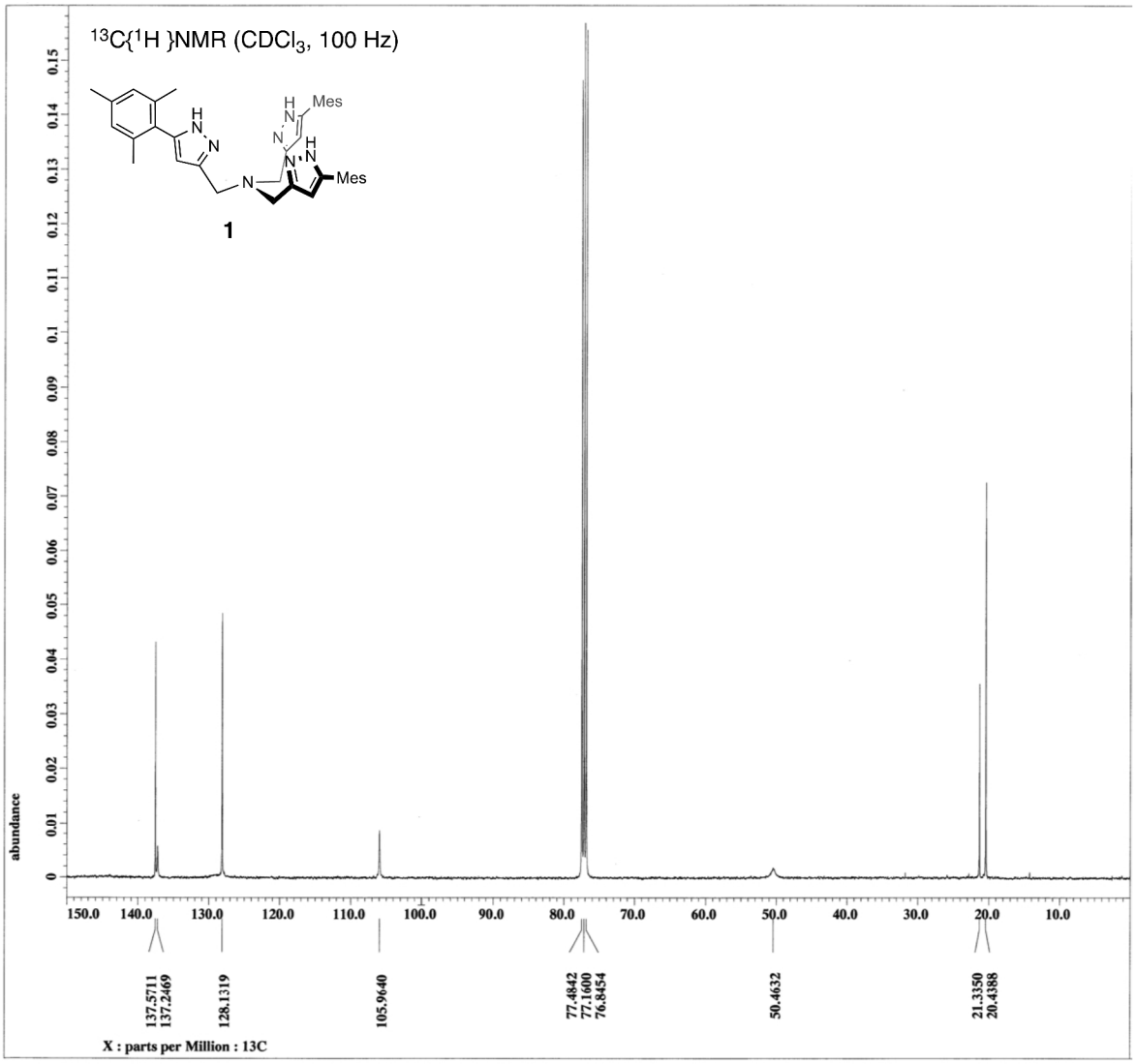


Figure S3. ^{1}H NMR spectrum of 2

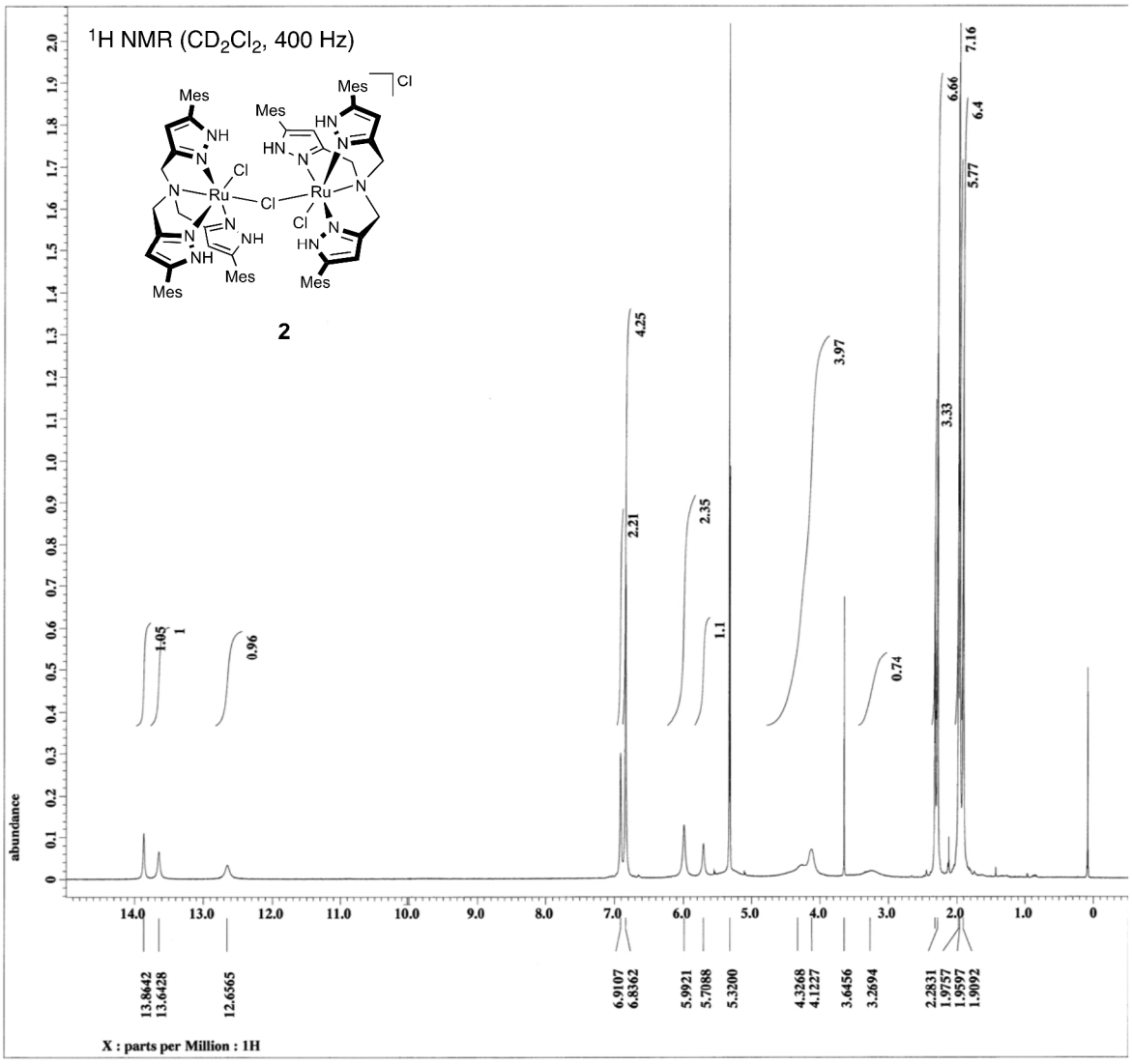


Figure S4. ^{1}H NMR spectrum of 3

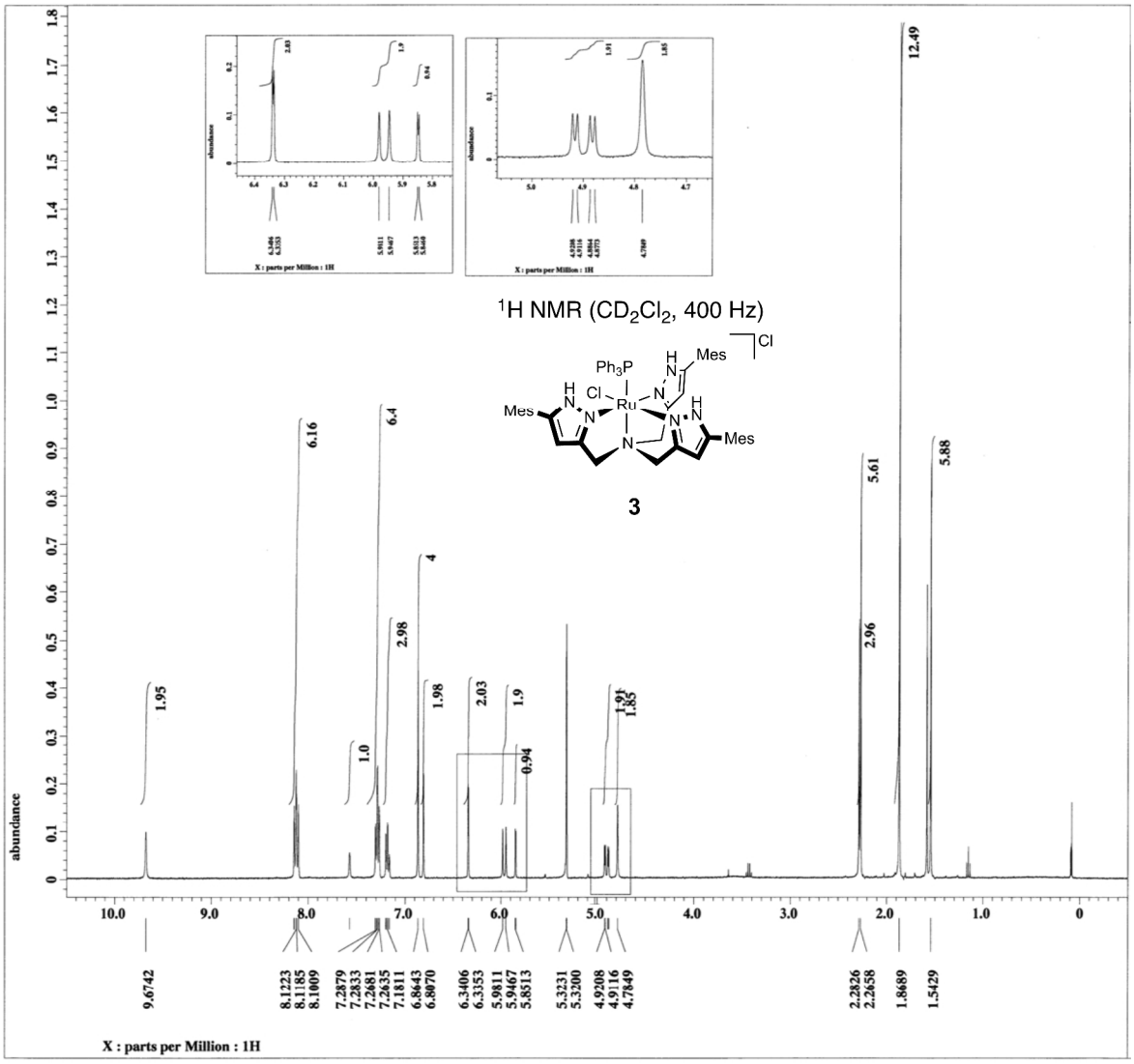


Figure S5. ^{1}H NMR spectrum of 4

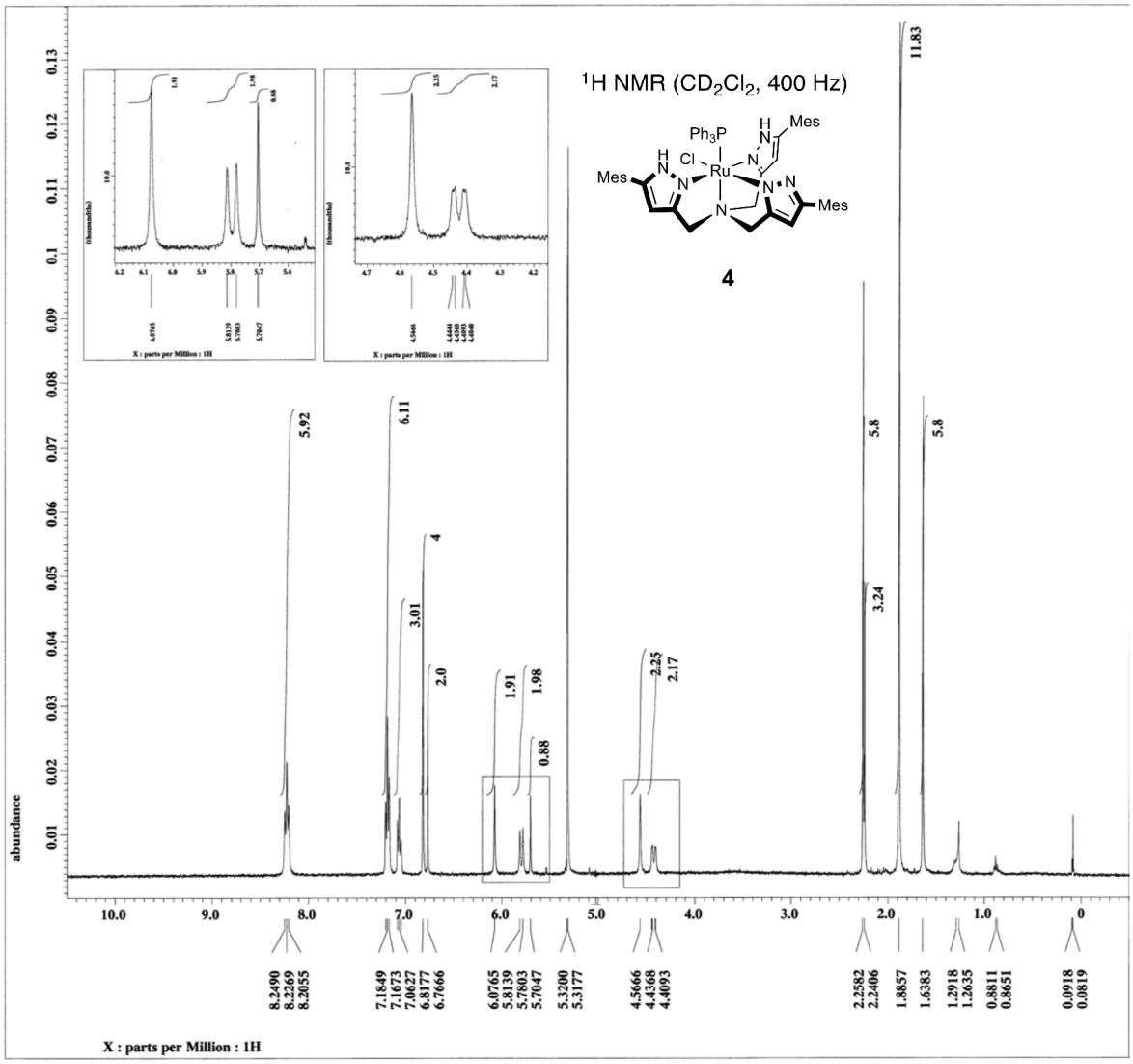


Figure S6. ^{1}H NMR spectrum of 5

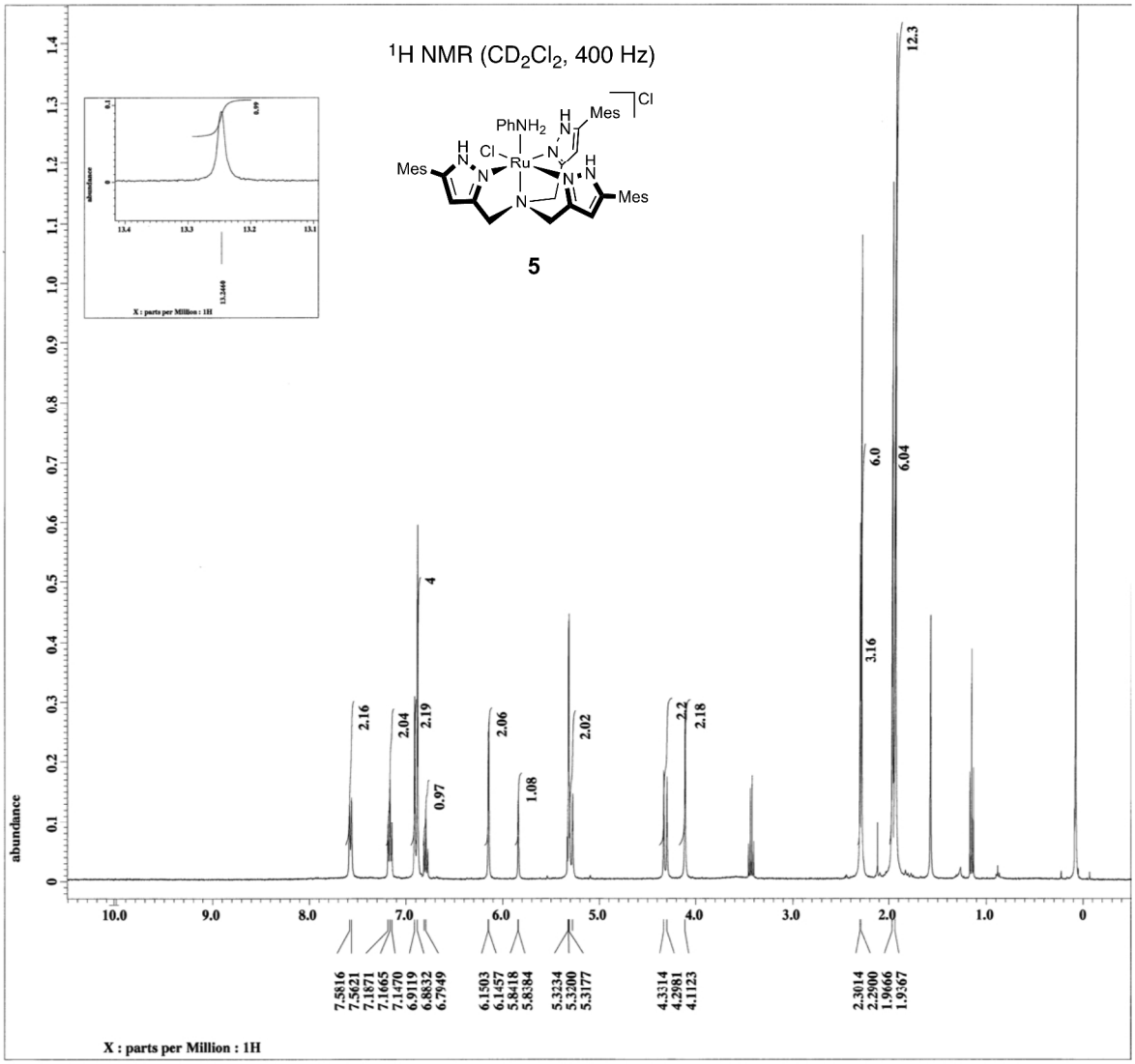


Figure S7. ESI-TOF mass spectrum of 2

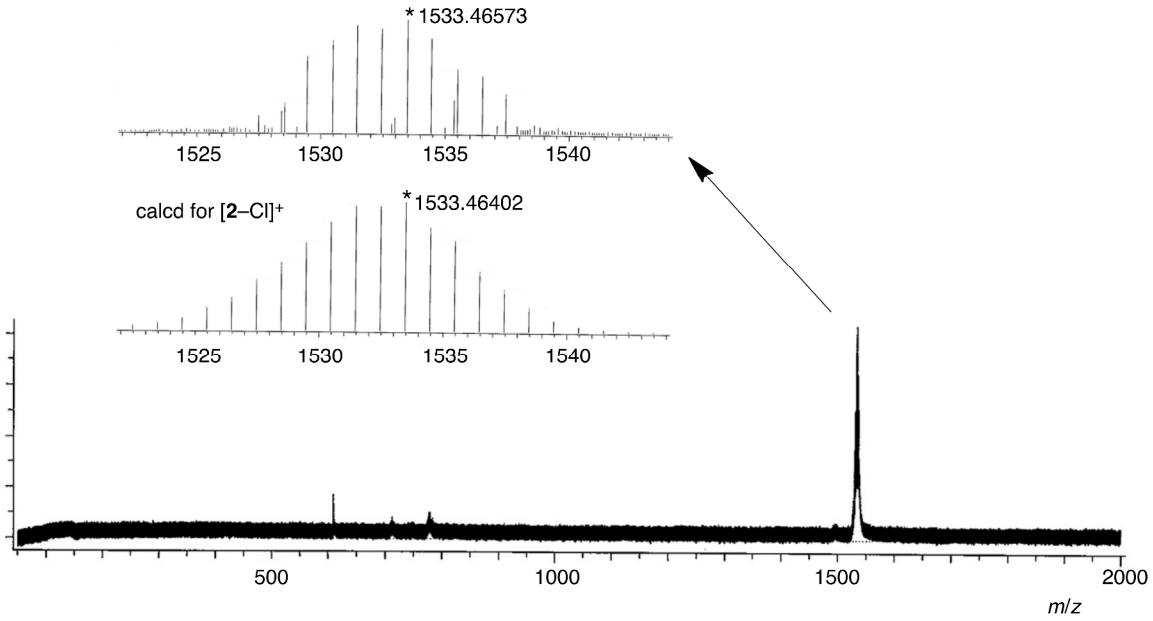
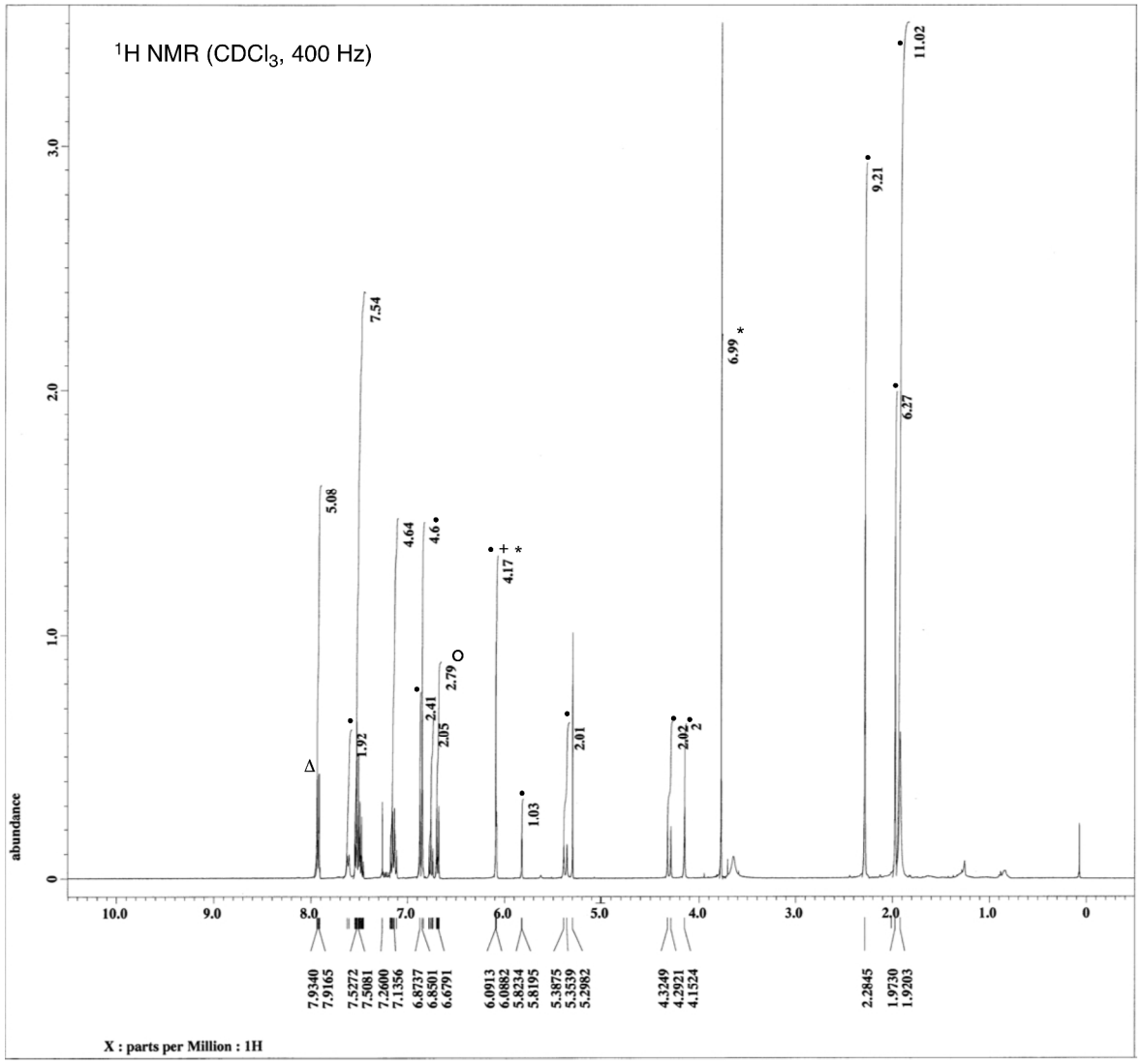


Figure S8. **^{1}H NMR spectrum of the crude product obtained from a stoichiometric reaction of 2 and 1,2-diphenylhydrazine** [a]



[a] solid circles: signal of aniline complex **5**, open circle: signal of aniline, open triangle: signal of azobenzene, asterisk: signal of the internal standard (1,3,5-trimethoxybenzene).