ELECTRONIC SUPPLEMENTARY INFORMATION

FOR

Catalytic methylation of aromatic amines with formic acid as the unique carbon and hydrogen source

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General considerations

All the syntheses were conducted under ultra high purity argon atmosphere with rigorous exclusion of air and water, using Schlenk-vessel and vacuum-line techniques and a MBraun LabMaster DP recycling inert atmosphere (Ar) gloves box. Glassware was dried overnight at 60 ºC before use. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 23°C on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0).

Tetrahydrofuran (THF), d_8-tetrahydrofuran (d_8-THF), d_6-benzene and d_8-toluene were dried over a sodium/benzophenone mixture and distilled before use. Deuterated chloroform ($CDCl_3$) was dried over calcium hydride and distilled before use.

1,1,1-tris(diphenylphosphinomethyl)ethane (triphos) was purchased from Aldrich and Ru(COD)(methylallyl)$_2$ from Strem and were used as received. All the other reagents (HNTf, MSA, HCOOH (99%) and aqueous HCl 1.0 M, K_2CO_3) are commercial available (Aldrich) and were degassed and stored under argon.

Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLBTM-ms fused silica capillary.

Procedures for catalytic reactions

Caution! *Full decomposition of formic acid generates high pressure in a sealed tube!*

Reaction in Sapphire NMR tube: In a typical reaction Ru(COD)(2-methylallyl)$_2$ (1 mg, 3.13 μmol), triphos (2 mg, 3.23 μmol), the desired amine (0.39 mmol) and mesitylene (as internal standard) (11 μL, 0.08 mmol) were introduced in a Sapphire NMR tube with 0.3 mL d_8-tetrahydrofuran. After dissolution, formic acid (90 μL, 2.38 mmol) and the acid (MSA or $HNTf_2$) (1.5 mol%) were introduced to the pale yellow solution and the reaction mixture was heated at 150 °C for 17 h. Reactions were periodically cooled down to room temperature and monitored by NMR spectroscopy.

Reaction in a 50 mL Parr autoclave: In a typical reaction Ru(COD)(2-methylallyl)$_2$ (24 mg, 75 μmol), triphos (50 mg, 80 μmol), the desired amine (8.33 mmol) and hexamethylbenzene as internal standard were weighted in the autoclave with 10 mL tetrahydrofuran. After dissolution, formic acid (1.9 mL, 50 mmol) and the acid (MSA or $HNTf_2$) (1.5 mol%) were added to the pale

yellow solution and the reaction mixture was heated at 150 °C for 24 h. Reaction was periodically monitored by GC/MS chromatography.

Definitions: Turn over number (TON) is the moles of methylated amines divided by the moles of catalyst. Turnover frequency (TOF) is TON divided by time in hours. Conversion is the moles of substrate consumed divided by the initial moles of substrate. C-H yield is the moles of products formed multiply by the number of C-H bonds in the product divided by the initial moles of formic acid.

Synthesis and purification of anilines 3 from the methylation of anilines 2.

Under argon inert atmosphere, a 50 mL Parr autoclave, equipped with a magnetic stir bar was charged successively with Ru(COD)(2-methylallyl)$_2$ (12 mg, 37 μmol), triphos (25 mg, 40 μmol) and the desired amine (3.7 mmol) with 10 mL tetrahydrofuran. After dissolution, formic acid (1 mL, 25 mmol) and the additive $HNTf_2$ (1.5 mol%) were added to the pale yellow solution and the reaction mixture was heated at 150 °C for 24 h. The reaction was then cooled down to room temperature and CH_2Cl_2 (10.0 mL) was added. The solution was extracted with an aqueous solution of HCl (2x20 mL, 1.0 M) the aqueous phase was removed and its pH was adjusted to 12 with the addition K_2CO_3. The free amines were extracted from the aqueous phase with Et_2O (2x20 mL). The ethereal organic phases were combined and dried over $MgSO_4$, then filtrated, and Et_2O was evaporated off under vacuum leaving a brown oil residue. The amine **3** was separated by flash chromatography on silica gel (0.069-0.200 mm, standard grade) by elution with a mixture of *n*-pentane and ethyl acetate (98:2). The desired anilines were recovered as oil.

Synthesis and purification of anilines 2 and 3 from the methylation of anilines 1.

Under argon inert atmosphere, a 50 mL Parr autoclave, equipped with a magnetic stir bar was charged successively with Ru(COD)(2-methylallyl)$_2$ (12 mg, 37 μmol), triphos (25 mg, 40 μmol) and the desired amine (3.7 mmol) with 10 mL tetrahydrofuran. After dissolution, formic acid (1 mL, 25 mmol) and the additive MSA (1.5 mol%) were added to the pale yellow solution and the reaction mixture was heated at 150 °C for 24 h. The reaction was then cooled down to room temperature and CH_2Cl_2 (10.0 mL) was added. The solution was extracted with an aqueous solution of HCl (2x20 mL, 1.0 M) the aqueous phase was removed and its pH was adjusted to 12 with the addition K_2CO_3. The free amines were extracted from the aqueous phase with Et_2O (2x20 mL). The ethereal organic phases were combined and dried over $MgSO_4$, then filtrated, and Et_2O was evaporated off under vacuum leaving a brown oil residue. The amines **2** and **3** were separated by flash chromatography on silica gel (0.069-0.200 mm, standard grade) by elution with a mixture of *n*-pentane and ethyl acetate (98:2). The desired anilines were recovered as oil.

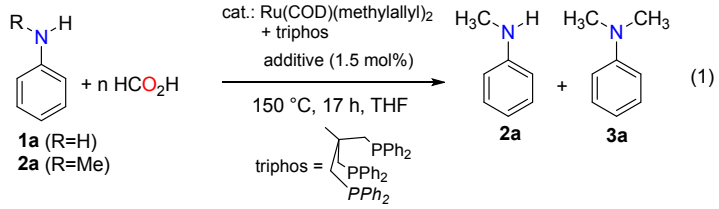
Synthesis of 4-Amino-*N*,*N*-diethylbenzamide (1v).[18]

A solution of *p*-nitrobenzoylchloride (3.0 g, 16.1 mmol) in 50 ml CH_2Cl_2 was introduced dropwise to a solution of diethylamine (6 ml, 64 mmol) in 50 ml CH_2Cl_2 at 0°C. The yellow solution was stirred 2h at room temperature and concentrated. Pentane was then added utile a white precipitate formed. The solution was filtered and the filtrate was concentrated to afford pure *p*-nitro-*N,N*-diethylbenzamide (2.5 g 70% yield) as a yellow powder.
^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.06 (t, 3H), 2.12 (t, 3H), 3.13 (q, 2H), 3.53 (q, 2H), 7.46 (d, J = 8.7 Hz, 2H), 8.26 (d, J = 8.7 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.58, 14.94, 40.22, 44.01, 124.61, 128.09, 144.17, 148.50, 169.61.

p-nitro-*N,N*-diethylbenzamide (4.5 mmol) was dissolved in ethanol (5 mL) in a two-necked flask. A mixture of $SnCl_2$/2 H_2O (12 mmol, 2.3 g) and concentrated hydrochloric acid (36%, 52.5 mmol, 4 ml) was added dropwise to the flask at room temperature. The whole mixture was allowed to react at 70 °C for 6 h. Reaction followed with TLC. The pH was then adjusted to 6–7 with sodium hydroxide aqueous solution (10%). The mixture was filtered off to remove impurities. The filtrate was then evaporated under vacuum to obtain the 4-Amino-*N*,*N*-diethylbenzamide as a yellow powder (50% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.14 (m , 6H), 3.39 (m, 2H), 3.85 (m, 2H), 6.61 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H);

Products identification: ^{1}H NMR and ^{13}C NMR of the following methylated products **2b**[1], **2c**[2], **2g**[3], **2h**[4], **2j**[5], **3b**[6], **3d**[7], **3e (3o)**[8], **3f (3p)**[9], **3h**[10], **3i**[11], **3j**[12],**3n**[13],**1w**[15], **2w**[16], **3w**[17] are identical to reported data.
^{1}H NMR and **^{13}C NMR** of the following products were compared with commercial samples purchased from Aldrich: **2a**, **2f**, **2d**, **3i (3q)**, **2e**, **3a**, **3m.**
2v was identified by GC/MS chromatography and by ^{1}H NMR and ^{13}C NMR from the crude mixture.

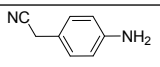
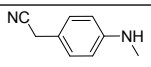
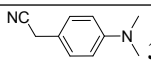
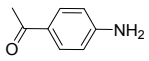
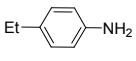
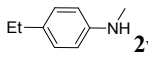
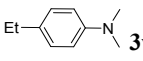
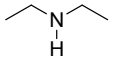
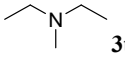
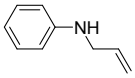
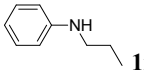
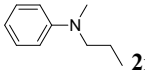
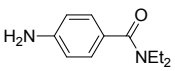
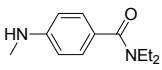
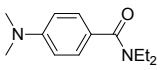
Table S1. Ruthenium catalyzed methylation of **2a** with formic acid



Entry	Sub.	Cat. (mol%)	Ligand (mol%)	Add. (1.5 mol%)	HCOOH (equiv.)	T (°C)	Conv.(%)	Yield (%) 2a	Yield (%) 3a
1	**2a**	0.4	triphos (0.4)	$HNTf_2$	6	150	80	-	<1
2	**2a**	0.8	triphos (0.8)	$HNTf_2$	6	150	>99	-	>99
3	**2a**	1.4	triphos (1.4)	$HNTf_2$	6	150	>99	-	>99
4	**2a**	3.0	triphos (3.0)	$HNTf_2$	6	150	93	-	93
5	**2a**	0.4	triphos (1.6)	$HNTf_2$	6	150	60	-	46
6[a]	**2a**	1.0	triphos (1.0)	MSA	6	150	64	-	39
7[a]	**2a**	1.0	triphos (1.0)	$HNTf_2$	6	150	85	-	85
8[a]	**2a**	1.0	triphos (1.0)	$HNTF_2$	6	80	>99	-	47
9[a]	**1a**	1.0	triphos (1.0)	MSA	9	150	86	67	19
10[a]	**1a**	1.0	PP_3 (1.0)[c]	MSA	6	150	32	20	<1
11[a]	**1a**	1.0	dppe (1.0)[d]	MSA	6	150	37	23	<1
12[a]	**1a**	1.0	triphos (1.0)	MSA	6	125	94	61	33
14[a]	**1a**	1.0	-	MSA	6	150	>99	-	-

Reaction conditions: substrate (0.4 mmol), $Ru(COD)(methylallyl)_2$, triphos, HCOOH, add. (1.5 mol%), THF (0.3 mL), 150°C, 17 h in a Sapphire tube. Yields determined by ^1H NMR spectroscopy with mesitylene as an internal standard. a) Substrate (8.33 mmol), $Ru(COD)(methylallyl)_2$, triphos, HCOOH, add. (1.5 mol%), 150°C, 17 h. Yield determined by GC/MS chromatography with hexamethylbenzene as an internal standard c) PP_3 : Tris[2-(diphenylphosphino)ethyl]phosphine d) dppe: Ethylenebis(diphenylphosphine). Note: Unless otherwise noted, formamide derivatives were observed as the only side-products when the yields of **2** and **3** don't add up to the conversion of **1**.

Table S2. Ruthenium-catalyzed methylation of substituted amines with formic acid.

Entry	Substrate		Conversion (%)	Products distribution (%)
1		**1r**	70[a]	 **2r**, <1  **3r**, <1
2		**1s**	>99	 **1w**, 28  **2w** , 51  **3w**, 10
3		**2t**	<1	 **3t**, <1
4		**2u**	>99	 **1x**, 35 (26)  **2x**, 27 (15)
5		**1v**	52	 **2v**, 8  **3v**, <1

Substrate (8.33 mmol), Ru(COD)(methylallyl)$_2$, triphos, formic acid, add. (1.5 mol%), 150°C, 17 h. Yield determined by GC/MS chromatography with hexamethylbenzene as an internal standard. Isolated yields in parenthesis. a) **1r** was decomposed into unidentified products. Note: Unless otherwise noted, formamide derivatives were observed as the only side-products when the yields of **2** and **3** don't add up to the conversion of **1**.

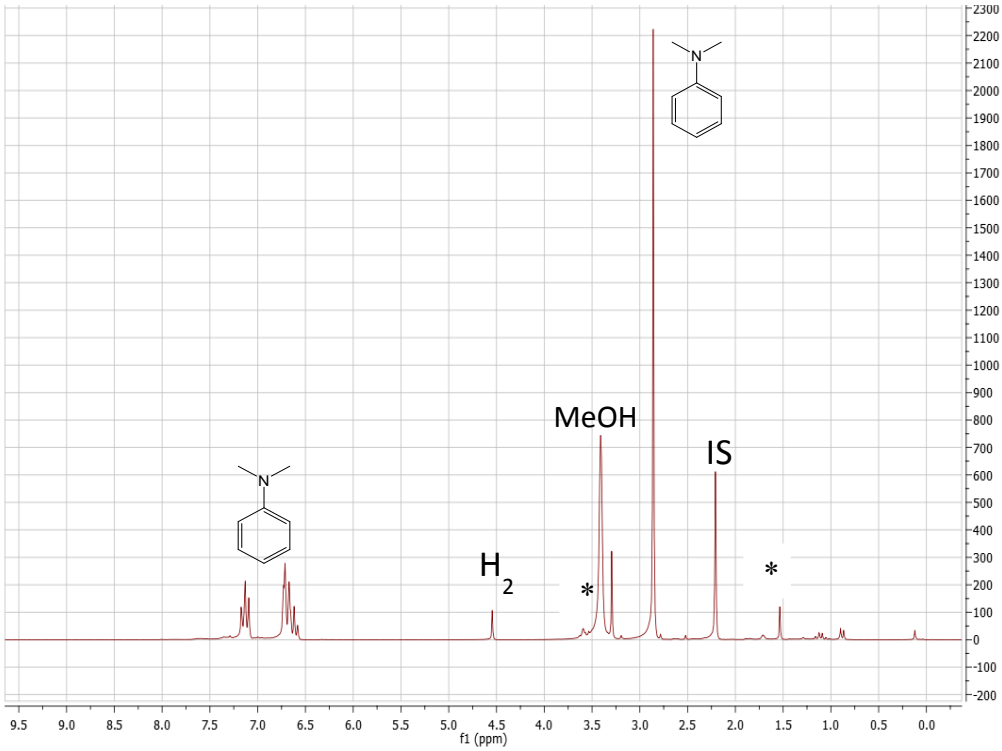


Figure S1. ^{1}H NMR spectrum of the crude mixture for the methylation of *N*-methylaniline (**2a**) after 17 h at 150 °C. Reaction conditions: substrate (0.4 mmol), d_8-THF (0.3 mL), Ru(COD)(methylallyl)$_2$, (1 mol%), triphos (1 mol%), formic acid (6 equiv.), $HNTf_2$ (1.5 mol%) in a Sapphire tube. IS = internal standard (mesitylene), THF (*)

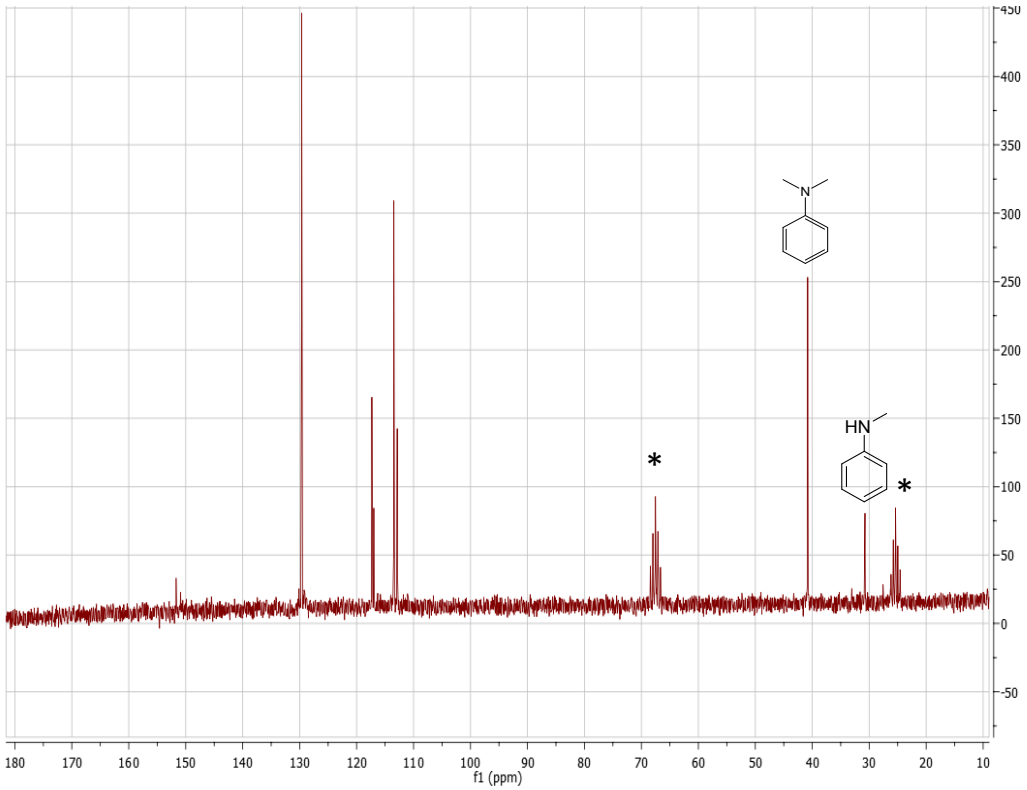


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Figure S2. ^{13}C NMR spectrum of the degassed crude mixture for the methylation of *N*-methylaniline (**2a**) after 12 h at 150 °C. Reaction conditions in the autoclave : substrate (8.3 mmol), Ru(COD)(methylallyl)$_2$ (1 mol%), triphos (1 mol%), formic acid (6 equiv.), $HNTf_2$ (1.5 mol%). THF (*)

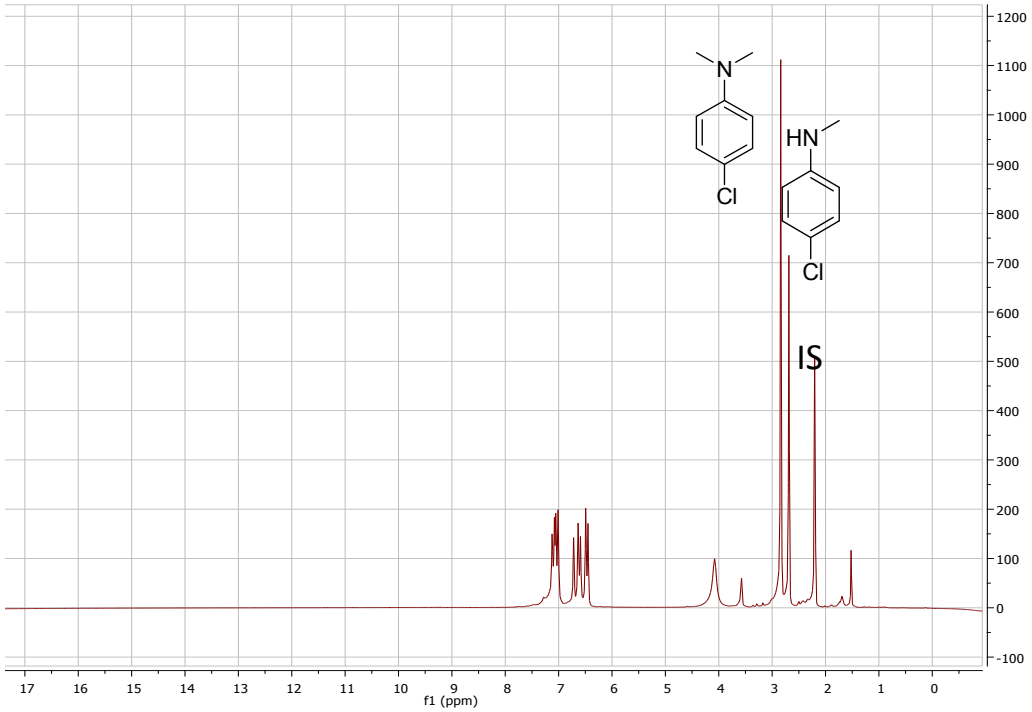
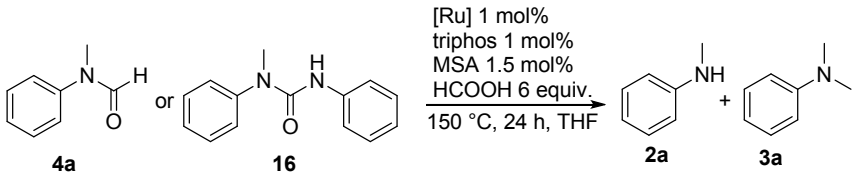


Figure S3. ^{1}H NMR spectrum of the degassed crude mixture for the methylation of *N*-methyl-4-chloroaniline (**2a**) after 17 h at 150 °C. Reaction conditions in the autoclave : substrate (8.3 mmol), Ru(COD)(methylallyl)$_2$ (1 mol%), triphos (1 mol%), formic acid (6 equiv.), $HNTf_2$ (1.5 mol%). THF (*)

Organic intermediates

Formamide **4a** and urea **16** were studied as intermediates in the methylation of amine. Heating **4** for 24 h at 150 °C with 1 mol% of the mixture Ru(COD)(methylallyl)$_2$ / MSA+ triphos and 6 equiv. of formic acid afforded **3a** in 67% yield. In the same conditions **16** showed a lower reactivity than **4** and only 3% of **3a** was formed in solution. The low reactivity of urea should suggest that it is not the predominant intermediate in the reaction.



4a **16** **2a** **3a**

4a	17%	67%
16	20%	3%

Figure S3. Control experiments: methylation of **4a** and **16**. Reaction conditions in a 50 mL autoclave : substrate (8.3 mmol), Ru(COD)(methylallyl)$_2$ (1 mol%), triphos (1 mol%), formic acid (6 equiv.), MSA (1.5 mol%), THF 10mL.

Control experiment with methanol

Ru(COD)(2-methylallyl)$_2$ (1 mg, 3.13 µmol), triphos (2 mg, 3.23 µmol), *N*-methylaniline (0.39 mmol) and mesitylene (as internal standard) (11 µL, 0.08 mmol) were introduced in a Sapphire NMR tube with 0.3 mL d_8-tetrahydrofuran. After complete dissolution, methanol (16 µL, 0.4 mmol) was added to the pale yellow solution and the reaction mixture was heated at 150 °C for 24 h. No trace of the desired *N,N*-dimethylaniline was observed by ^{1}H NMR spectroscopy.

Kinetic studies

Kinetic experiments: In a typical reaction Ru(COD)(2-methylallyl)$_2$ (1 mg, 3.13 µmol), triphos (2 mg, 3.23 µmol), the desired amine (0.39 mmol) and mesitylene (as internal standard) (11 µL, 0.08 mmol) were introduced in a Sapphire NMR tube with 0.3 mL d_8-tetrahydrofuran. After complete dissolution, formic acid (90 µL, 2.38 mmol) was added to the pale yellow solution and the reaction mixture was heated at 150 °C for 24 h. Reactions were periodically cooled down to room temperature and monitored by NMR spectroscopy.

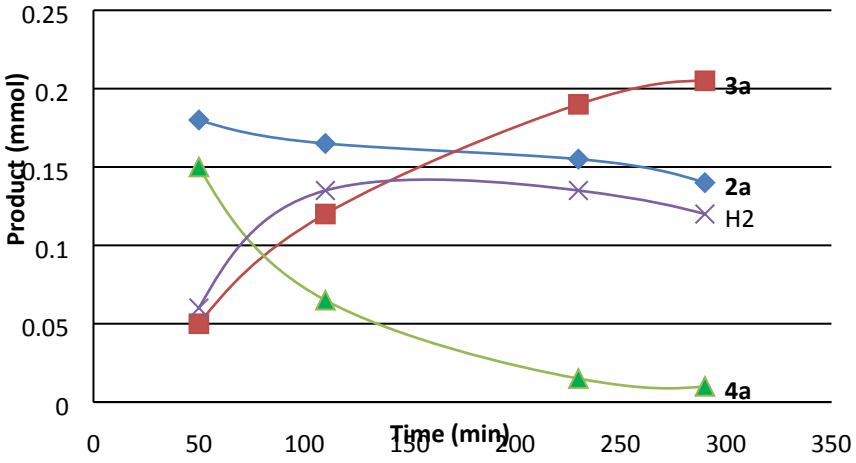


Figure S4: Kinetic profile determined by ^{1}H NMR of the ruthenium-catalyzed methylation of N-methylaniline (**2a**) to *N,N*-dimethylaniline (**3a**). Reaction conditions: Ru(COD)(methylallyl)$_2$ (1.0 mg, 3.1 µmol), triphos (2.0 mg, 3.2 µmol), THF, HCOOH (90 µL, 2.4 mmol), $HNTf_2$ (1.5 mol%), *N*-methylaniline (0.39 mmol). *N*-methylaniline (blue diamonds), *N*-methylformanilide (**4a**) (green triangles), hydrogen in solution (purple cross), *N,N*-dimethylaniline (red squares).

Computed pathways

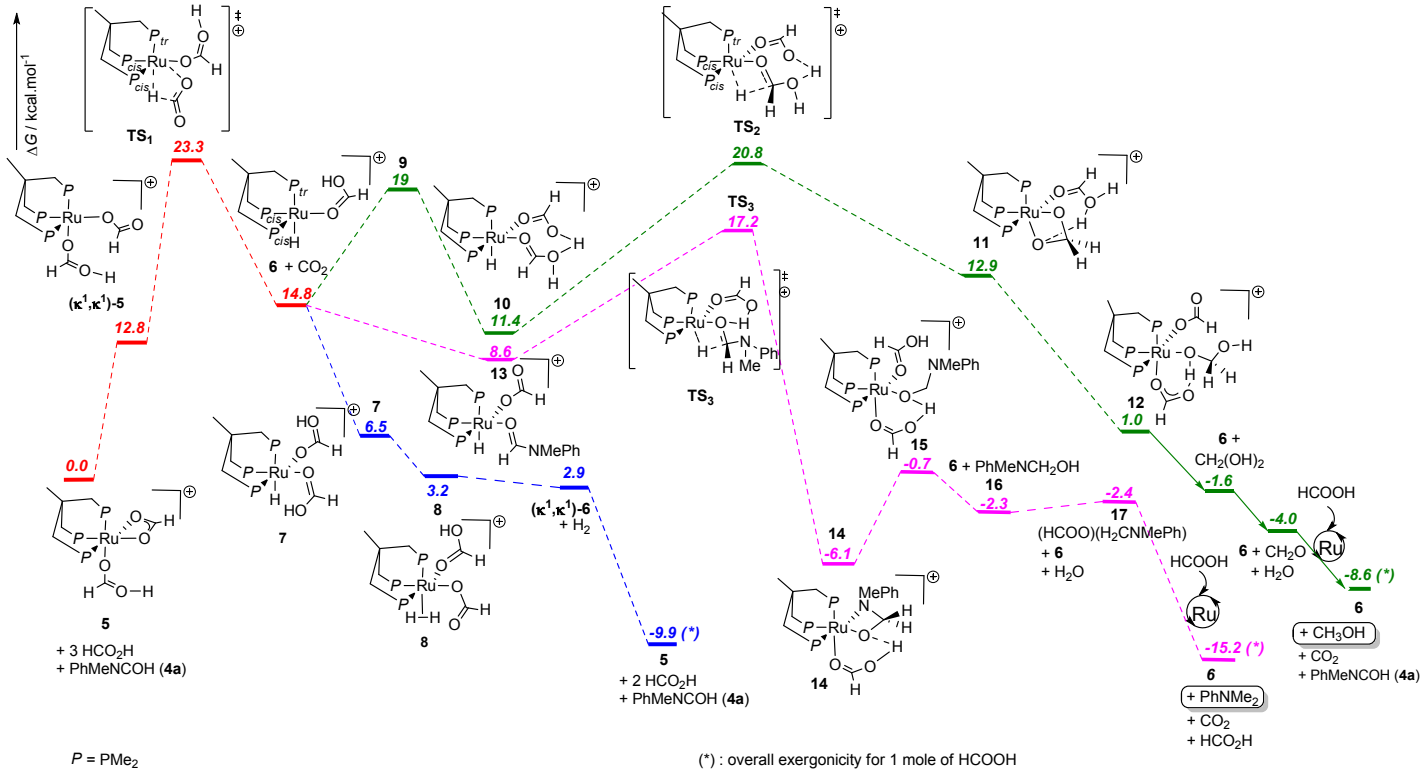


Figure S5. Computed pathways for the catalytic methylation of N-methylaniline with HCOOH, disproportionation of HCOOH to methanol and HCOOH dehydrogenation to H_2 and CO_2 (at the M06/6-31+G* (H, C, O, P) + SDD (Ru) level of theory using the PCM model to take into account the polarity of THF).

Computational Details

Density functional theory[14a] was applied to determine the structural and energetic features of the complexes described herein. Calculations were performed using Gaussian09 code.[14b] The 6-31+G(d) basis set[14c,d] was used for atoms C, H , P, O; Ru was treated using the Stuttgart pseudopotential and associated basis set,[14e] The hybrid exchange correlation functional M06 was used.[14f] All structures were calculated without geometrical constraint; stationary points were characterized by frequency calculations (one negative frequency for a transition state, no negative frequency for minima). Solvent effects were included in structure-optimization and frequency calculations using the PCM model implemented in the Gaussian code.[14g,h]

Computed stuctures

5

C	2.558328000	-1.529993000	0.289830000
H	3.475340000	-2.127507000	0.407132000
C	2.136745000	-1.692016000	-1.181560000
H	2.849679000	-1.162942000	-1.832257000
H	2.188976000	-2.753088000	-1.468207000
C	1.537982000	-2.128971000	1.272913000
H	1.241826000	-3.132535000	0.931203000
H	2.008706000	-2.266733000	2.258191000
C	2.949403000	-0.086458000	0.646414000
H	3.149280000	-0.015281000	1.726787000
H	3.890974000	0.179791000	0.142290000
P	0.002774000	-1.117507000	1.518031000
P	1.694001000	1.202784000	0.202997000
P	0.428931000	-1.085732000	-1.569832000
Ru	-0.394329000	0.409747000	-0.093239000
O	-0.988807000	2.245856000	-1.273529000
O	-1.363645000	2.201134000	0.897983000
C	-1.435642000	2.781757000	-0.223309000
H	-1.902038000	3.781298000	-0.283480000
O	-2.502769000	-0.295197000	-0.478232000
C	-3.485745000	0.082299000	0.133808000
H	-3.431255000	0.788884000	0.977219000
C	2.438573000	2.058085000	-1.237375000
H	1.729051000	2.798464000	-1.626131000
H	3.362615000	2.565199000	-0.928645000
H	2.683886000	1.352895000	-2.039080000
C	1.879208000	2.488508000	1.491718000
H	2.943320000	2.695979000	1.666901000
H	1.389245000	3.406666000	1.145380000
H	1.404103000	2.184083000	2.430478000
C	0.516055000	-0.445086000	-3.281741000
H	1.031952000	0.520500000	-3.320074000
H	1.028612000	-1.160695000	-3.938455000
H	-0.508436000	-0.295858000	-3.646158000

C	-0.522886000	-2.630922000	-1.829692000
H	-1.573151000	-2.387035000	-2.028165000
H	-0.110739000	-3.177446000	-2.688466000
H	-0.474005000	-3.283572000	-0.950324000
C	-1.318365000	-2.351714000	1.820659000
H	-0.951915000	-3.149677000	2.480139000
H	-2.162168000	-1.852387000	2.314322000
H	-1.679624000	-2.787429000	0.882748000
C	0.211303000	-0.421878000	3.202290000
H	-0.599362000	0.288529000	3.409347000
H	0.186393000	-1.226895000	3.949221000
H	1.167843000	0.104683000	3.294955000
O	-4.681038000	-0.360962000	-0.199217000
H	-5.373933000	0.021785000	0.367930000

Sum of electronic and thermal Energies=-1893.010080
Sum of electronic and thermal Enthalpies=-1893.009136
Sum of electronic and thermal Free Energies=-1893.092017
Lowest vibration frequencies (/ cm^–1): 49.7604 52.7396 63.8654

(κ^1,κ^1)-5

C	-2.794268000	-0.127563000	1.147111000
H	-3.771181000	-0.162487000	1.652965000
C	-2.802356000	1.155648000	0.301564000
H	-3.491600000	1.035552000	-0.547592000
H	-3.198204000	1.990631000	0.898914000
C	-1.744676000	-0.087182000	2.268188000
H	-1.796452000	0.878804000	2.792587000
H	-1.970311000	-0.858303000	3.020138000
C	-2.712179000	-1.407357000	0.300102000
H	-2.622625000	-2.282866000	0.961213000
H	-3.648861000	-1.544035000	-0.261270000
P	0.003285000	-0.355449000	1.724613000
P	-1.311503000	-1.443085000	-0.914949000
P	-1.146558000	1.682496000	-0.350177000
Ru	0.386319000	0.016481000	-0.429401000
O	1.926270000	-1.609663000	-0.661305000
C	3.100165000	-1.439858000	-0.367028000
O	2.120319000	1.236403000	-0.075677000
C	2.433661000	2.313105000	-0.699942000
O	3.487904000	2.933315000	-0.583507000
H	1.658790000	2.694063000	-1.411315000
H	3.473649000	-0.484053000	0.035665000
C	-1.524507000	2.467014000	-1.963625000
H	-2.410305000	3.108772000	-1.866744000
H	-0.676956000	3.089022000	-2.275802000
H	-1.706224000	1.717499000	-2.741735000
C	-0.767119000	3.158475000	0.671678000
H	0.197925000	3.591476000	0.384346000
H	-1.551032000	3.913513000	0.523847000
H	-0.729737000	2.906770000	1.737731000
C	1.026045000	0.642428000	2.859564000
H	0.970920000	1.709511000	2.623326000
H	0.697444000	0.472677000	3.893567000
H	2.071599000	0.327323000	2.755281000
C	0.386147000	-2.048992000	2.307350000
H	1.400551000	-2.333393000	2.004848000
H	0.322888000	-2.071109000	3.403649000
H	-0.318767000	-2.784610000	1.905217000
C	-2.156903000	-1.189649000	-2.525950000

H	-2.821119000	-2.040255000	-2.729729000
H	-2.761705000	-0.275641000	-2.524124000
H	-1.415193000	-1.119795000	-3.330923000
C	-0.872452000	-3.216291000	-1.053961000
H	-1.785027000	-3.824595000	-1.107684000
H	-0.292816000	-3.365674000	-1.972863000
H	-0.258834000	-3.550714000	-0.210950000
O	3.961736000	-2.421175000	-0.532138000
H	4.857598000	-2.152371000	-0.260499000

Sum of electronic and thermal Energies=-1892.988662
Sum of electronic and thermal Enthalpies=-1892.987718
Sum of electronic and thermal Free Energies=-1893.071668
Lowest vibration frequencies (/ cm^–1): 36.7894 41.3358 66.8871

TS1

C	-2.429731000	-1.681450000	-0.447050000
H	-3.314543000	-2.313174000	-0.622268000
C	-2.120529000	-1.812670000	1.053603000
H	-2.940375000	-1.358993000	1.632038000
H	-2.100629000	-2.875774000	1.338484000
C	-1.326900000	-2.257526000	-1.347088000
H	-1.004108000	-3.231941000	-0.948267000
H	-1.728088000	-2.453347000	-2.353244000
C	-2.852434000	-0.258903000	-0.842647000
H	-2.957085000	-0.192773000	-1.936233000
H	-3.848477000	-0.040665000	-0.428540000
P	0.175645000	-1.185586000	-1.519324000
P	-1.723521000	1.102109000	-0.281065000
P	-0.524073000	-1.052440000	1.628026000
Ru	0.375701000	0.430097000	0.189785000
O	1.513223000	2.118248000	-0.862031000
C	1.134162000	2.762938000	0.093558000
O	2.485714000	-0.217195000	0.695424000
C	3.493195000	0.021725000	0.057777000
H	3.492871000	0.618326000	-0.869183000
H	0.518954000	1.587057000	1.413646000
O	0.986984000	3.780622000	0.673627000
C	-1.874818000	2.358210000	-1.609124000
H	-2.919957000	2.424788000	-1.940922000
H	-1.572148000	3.338803000	-1.220974000
H	-1.237387000	2.114279000	-2.466543000
C	-2.683202000	1.908615000	1.055235000
H	-2.090084000	2.719817000	1.495781000
H	-3.617345000	2.320427000	0.650448000
H	-2.936957000	1.193542000	1.846647000
C	1.538562000	-2.394057000	-1.765994000
H	1.193918000	-3.232570000	-2.386206000
H	2.365503000	-1.895513000	-2.288630000
H	1.917304000	-2.782796000	-0.813417000
C	0.039834000	-0.506891000	-3.221671000
H	0.114464000	-1.313852000	-3.963601000
H	-0.916821000	0.008455000	-3.367520000
H	0.852229000	0.212265000	-3.392274000
C	0.541621000	-2.499179000	1.983461000
H	1.522366000	-2.154657000	2.329858000
H	0.078104000	-3.116415000	2.764606000
H	0.683665000	-3.114525000	1.087595000
C	-0.900752000	-0.478117000	3.322368000

H	-1.429299000	-1.260423000	3.883552000
H	0.044506000	-0.246568000	3.828461000
H	-1.509310000	0.432614000	3.304074000
O	4.658194000	-0.441664000	0.466667000
H	5.380153000	-0.168143000	-0.126503000

Sum of electronic and thermal Energies= -1892.973894
Sum of electronic and thermal Enthalpies= -1892.972949
Sum of electronic and thermal Free Energies= -1893.054940
Lowest vibration frequencies (/cm^{-1}): -456.2316 -88.3144 (rotation of a Me group) -48.5044 (global rotation)

6

C	-1.970677000	0.416711000	1.774223000
H	-2.739027000	0.559547000	2.550620000
C	-1.578501000	-1.070399000	1.843695000
H	-0.977134000	-1.253580000	2.747569000
H	-2.484390000	-1.687045000	1.948479000
C	-2.652591000	0.788574000	0.447332000
H	-3.450860000	0.061323000	0.232181000
H	-3.148017000	1.766709000	0.545521000
C	-0.817605000	1.363132000	2.150594000
H	-1.122412000	2.404242000	1.959586000
H	-0.618713000	1.294990000	3.231440000
P	-1.534452000	0.865297000	-1.036427000
P	0.781274000	1.053035000	1.254063000
P	-0.635987000	-1.721791000	0.378728000
Ru	0.437525000	-0.167239000	-0.760090000
H	0.130487000	-1.049230000	-2.154612000
O	2.468521000	-1.135702000	-0.633441000
C	3.461420000	-0.640525000	-1.128977000
H	4.443327000	-1.131786000	-1.092546000
C	0.449522000	-3.018478000	1.078947000
H	-0.121542000	-3.658219000	1.765330000
H	0.841303000	-3.631933000	0.258640000
H	1.298496000	-2.572770000	1.608661000
C	-1.890651000	-2.746740000	-0.477773000
H	-1.449314000	-3.177592000	-1.383908000
H	-2.227886000	-3.554201000	0.186583000
H	-2.764415000	-2.149536000	-0.763967000
C	-2.634657000	0.374699000	-2.416856000
H	-2.829181000	-0.703410000	-2.400366000
H	-3.587574000	0.919186000	-2.368739000
H	-2.131505000	0.612192000	-3.362374000
C	-1.391307000	2.669430000	-1.360109000
H	-0.749453000	2.837891000	-2.233688000
H	-2.381872000	3.101052000	-1.559082000
H	-0.951161000	3.187768000	-0.500459000
C	1.816924000	0.267604000	2.559079000
H	2.807872000	0.036721000	2.147906000
H	1.933211000	0.941489000	3.418962000
H	1.366893000	-0.668512000	2.911480000
C	1.556231000	2.722393000	1.230466000
H	1.494214000	3.195531000	2.220306000
H	2.613614000	2.618014000	0.955965000
H	1.076690000	3.375210000	0.491973000
O	3.401416000	0.532593000	-1.738142000
H	4.266562000	0.802836000	-2.094014000

Sum of electronic and thermal Energies=-1704.477968
Sum of electronic and thermal Enthalpies=-1704.477024
Sum of electronic and thermal Free Energies=-1704.551189
Lowest vibration frequencies (/ cm^–1): -24.4816 (global rotation of HCOOH moiety around the (RuO) axis)
69.301 81.8768

7

C	-2.989577000	-0.356388000	-0.010299000
H	-4.082170000	-0.495883000	-0.020832000
C	-2.726542000	0.907660000	-0.844045000
H	-2.978291000	0.708115000	-1.897617000
H	-3.399922000	1.714930000	-0.517191000
C	-2.605891000	-0.192635000	1.471649000
H	-2.967812000	0.782589000	1.833688000
H	-3.124187000	-0.954875000	2.073868000
C	-2.400525000	-1.623995000	-0.654333000
H	-2.512129000	-2.472042000	0.038678000
H	-2.980253000	-1.885296000	-1.553072000
P	-0.788419000	-0.305522000	1.843342000
P	-0.611346000	-1.509456000	-1.155571000
P	-0.990600000	1.569848000	-0.785756000
Ru	0.532903000	0.089108000	-0.064099000
O	2.093663000	-1.322047000	0.805800000
C	3.184001000	-1.660187000	0.388578000
O	1.748515000	1.622275000	1.068321000
C	2.614385000	2.265655000	0.476036000
O	2.900188000	2.144149000	-0.786465000
H	3.219680000	3.018796000	0.995389000
H	3.848007000	-2.306493000	0.981727000
C	-0.649032000	-1.951290000	2.652695000
H	0.395061000	-2.128193000	2.936819000
H	-1.280176000	-1.991992000	3.550982000
H	-0.960317000	-2.753889000	1.972938000
C	-0.594494000	0.781144000	3.310152000
H	-1.366246000	0.567302000	4.061879000
H	0.394794000	0.601854000	3.749868000
H	-0.646055000	1.838471000	3.026158000
C	-0.714530000	-1.452253000	-2.986463000
H	0.299203000	-1.395432000	-3.401067000
H	-1.214560000	-2.354890000	-3.363473000
H	-1.278937000	-0.577712000	-3.330681000
C	0.012591000	-3.219129000	-0.928963000
H	-0.685705000	-3.943236000	-1.369969000
H	0.982177000	-3.310215000	-1.435647000
H	0.154171000	-3.450157000	0.132835000
C	-1.164726000	3.082929000	0.240584000
H	-0.212088000	3.625753000	0.267233000
H	-1.933576000	3.740212000	-0.187589000
H	-1.445775000	2.830093000	1.269594000
C	-0.781923000	2.334353000	-2.438150000
H	-1.654865000	2.952022000	-2.689901000
H	0.112395000	2.970787000	-2.421640000
H	-0.639817000	1.570690000	-3.210860000
H	1.414532000	0.307829000	-1.516983000
H	2.294998000	1.393668000	-1.157160000
O	3.636255000	-1.281813000	-0.791324000
H	4.524235000	-1.642327000	-0.963162000

Sum of electronic and thermal Energies=-1894.152430
Sum of electronic and thermal Enthalpies=-1894.151486
Sum of electronic and thermal Free Energies=-1894.234217
Lowest vibration frequencies (/ cm^–1): 30.5323 64.0697 69.5622

8

C	-2.748337000	-0.144785000	1.278899000
H	-3.703539000	-0.194425000	1.823383000
C	-2.818192000	1.134709000	0.429522000
H	-3.551961000	1.000137000	-0.379672000
H	-3.191380000	1.968414000	1.043424000
C	-1.656118000	-0.081717000	2.358550000
H	-1.699596000	0.890530000	2.872045000
H	-1.847883000	-0.844438000	3.128135000
C	-2.679696000	-1.427882000	0.434283000
H	-2.525150000	-2.296120000	1.092559000
H	-3.645722000	-1.594462000	-0.065429000
P	0.074280000	-0.333333000	1.752860000
P	-1.370602000	-1.450901000	-0.878775000
P	-1.218263000	1.685529000	-0.328315000
Ru	0.335477000	0.049382000	-0.502791000
O	1.933048000	-1.555431000	-0.691208000
C	3.095611000	-1.384702000	-0.362698000
O	2.019508000	1.291464000	0.016302000
C	2.606452000	2.134091000	-0.756219000
O	3.713495000	2.629046000	-0.561635000
H	2.035030000	2.422446000	-1.674758000
H	3.459229000	-0.431529000	0.056648000
C	0.490885000	-2.023594000	2.325104000
H	1.500520000	-2.295848000	1.996098000
H	0.454834000	-2.050360000	3.422222000
H	-0.213530000	-2.767969000	1.938482000
C	1.111412000	0.673363000	2.865270000
H	0.827887000	0.473473000	3.906941000
H	2.161497000	0.397421000	2.713725000
H	1.013128000	1.742053000	2.651416000
C	-2.346233000	-1.254405000	-2.418804000
H	-1.677502000	-1.268973000	-3.288169000
H	-3.064257000	-2.080340000	-2.508129000
H	-2.905041000	-0.311256000	-2.423890000
C	-0.889800000	-3.210904000	-1.014890000
H	-1.787966000	-3.842090000	-1.040347000
H	-0.327832000	-3.352141000	-1.946152000
H	-0.248321000	-3.520955000	-0.183544000
C	-0.741966000	3.144398000	0.672055000
H	0.222790000	3.534942000	0.328440000
H	-1.506523000	3.924718000	0.560042000
H	-0.655830000	2.896675000	1.735835000
C	-1.715959000	2.496102000	-1.892385000
H	-2.541592000	3.196079000	-1.707148000
H	-0.861301000	3.058420000	-2.289631000
H	-2.027129000	1.763966000	-2.645940000
H	0.366206000	-0.025075000	-2.364853000
H	0.750935000	0.676043000	-2.222674000
O	3.964983000	-2.364555000	-0.501356000
H	4.851174000	-2.093769000	-0.201764000

Sum of electronic and thermal Energies=-1894.155339

Sum of electronic and thermal Enthalpies=-1894.154395
Sum of electronic and thermal Free Energies=-1894.239371
Lowest vibration frequencies (/cm^{-1}): 32.6622 57.0031 63.9339

9

C	3.005985000	0.387644000	1.282098000
H	3.951656000	0.547290000	1.824257000
C	2.616755000	1.763940000	0.711121000
H	2.278401000	2.420216000	1.527595000
H	3.507023000	2.247120000	0.280247000
C	3.334807000	-0.634848000	0.181543000
H	4.029573000	-0.179161000	-0.541472000
H	3.866680000	-1.494668000	0.617725000
C	2.013728000	-0.144726000	2.330765000
H	2.299844000	-1.170043000	2.613937000
H	2.085748000	0.459167000	3.248813000
P	1.884674000	-1.298864000	-0.770943000
P	0.234127000	-0.174432000	1.793744000
P	1.301404000	1.723214000	-0.604768000
Ru	0.033742000	-0.116908000	-0.570496000
H	-0.058570000	-0.029593000	-2.244769000
O	-2.576049000	0.143555000	-0.370879000
O	-1.550050000	-1.773015000	-0.598825000
C	-2.604280000	-1.165555000	-0.500812000
H	-3.591607000	-1.648708000	-0.512175000
C	0.346357000	3.269125000	-0.350583000
H	1.022707000	4.122025000	-0.202301000
H	-0.264161000	3.452207000	-1.243763000
H	-0.324125000	3.185281000	0.512679000
C	2.244670000	2.169909000	-2.114216000
H	1.564356000	2.179072000	-2.974078000
H	2.699408000	3.162991000	-1.995992000
H	3.045072000	1.447432000	-2.312455000
C	2.573079000	-1.599017000	-2.439434000
H	2.717516000	-0.655852000	-2.977295000
H	3.530089000	-2.134123000	-2.371228000
H	1.857592000	-2.207220000	-3.006226000
C	1.709599000	-3.020676000	-0.159671000
H	0.840554000	-3.490042000	-0.636663000
H	2.610278000	-3.602273000	-0.400282000
H	1.563501000	-3.036114000	0.926293000
C	-0.485453000	1.227576000	2.749880000
H	-1.548778000	1.337769000	2.500217000
H	-0.387516000	1.050638000	3.829797000
H	0.022506000	2.168707000	2.507984000
C	-0.459043000	-1.579237000	2.757695000
H	-0.177765000	-1.505873000	3.817191000
H	-1.553963000	-1.555275000	2.680648000
H	-0.114288000	-2.541221000	2.360386000
H	-3.483526000	0.558381000	-0.291953000
O	-5.025127000	1.241890000	-0.117379000
C	-6.018796000	0.564357000	-0.270207000
H	-7.037993000	0.972118000	-0.201782000
O	-5.924249000	-0.731127000	-0.530126000
H	-6.798572000	-1.146456000	-0.635392000

Sum of electronic and thermal Energies= -1894.128908
Sum of electronic and thermal Enthalpies= -1894.127963
Sum of electronic and thermal Free Energies= -1894.214228

Lowest vibration frequencies (/cm^{-1}): -1.74 20.83 29.76

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C	-2.728423000	0.185196000	1.291925000
H	-3.688853000	0.247062000	1.828194000
C	-2.440466000	1.611628000	0.797061000
H	-3.180559000	1.883880000	0.028125000
H	-2.579612000	2.328180000	1.621259000
C	-1.708952000	-0.319657000	2.327718000
H	-1.526303000	0.469292000	3.074502000
H	-2.140243000	-1.168452000	2.880934000
C	-2.956241000	-0.805720000	0.136427000
H	-3.031483000	-1.827609000	0.538892000
H	-3.922652000	-0.594243000	-0.346628000
P	-0.060423000	-0.861257000	1.648766000
P	-1.651497000	-0.798730000	-1.184509000
P	-0.745982000	1.896301000	0.083694000
Ru	0.322104000	0.020305000	-0.523280000
O	1.406054000	-1.873131000	-1.211810000
C	2.459594000	-2.383556000	-0.869648000
O	2.440467000	0.747005000	-0.021927000
C	3.040868000	1.610264000	-0.644766000
H	2.531026000	2.295497000	-1.338728000
H	2.774318000	-3.371243000	-1.229637000
O	3.339730000	-1.860124000	-0.043387000
C	-0.146540000	-2.690400000	1.854449000
H	0.798429000	-3.143847000	1.529970000
H	-0.320742000	-2.952457000	2.907123000
H	-0.956261000	-3.117862000	1.250744000
C	1.080168000	-0.463164000	3.039152000
H	0.661911000	-0.800711000	3.997729000
H	2.039408000	-0.972428000	2.878152000
H	1.276217000	0.614241000	3.091627000
C	-2.511373000	0.002647000	-2.593438000
H	-1.835559000	0.024488000	-3.456646000
H	-3.419533000	-0.558035000	-2.854042000
H	-2.798392000	1.032975000	-2.352967000
C	-1.625786000	-2.535162000	-1.769350000
H	-2.647425000	-2.876312000	-1.984509000
H	-1.025466000	-2.590893000	-2.685278000
H	-1.170443000	-3.195431000	-1.023035000
C	0.074011000	2.886581000	1.398562000
H	1.089722000	3.164563000	1.092282000
H	-0.497365000	3.804864000	1.589693000
H	0.140262000	2.316478000	2.332476000
C	-1.044906000	3.206552000	-1.163777000
H	-1.652610000	4.018756000	-0.741743000
H	-0.078570000	3.613448000	-1.487777000
H	-1.547160000	2.794629000	-2.046175000
H	0.502995000	0.671832000	-2.063836000
H	3.072643000	-0.938809000	0.199722000
O	4.337045000	1.747535000	-0.497980000
H	4.690148000	2.468479000	-1.050407000

Sum of electronic and thermal Energies=-1894.143070
Sum of electronic and thermal Enthalpies=-1894.142126
Sum of electronic and thermal Free Energies=-1894.226310
Lowest vibration frequencies (/cm^{-1}): 39.1418 56.4881 63.7118

TS2

C	-2.926804000	-0.812460000	-0.270886000
H	-3.976908000	-1.124368000	-0.384211000
C	-2.566860000	-1.093257000	1.196544000
H	-3.126562000	-0.402037000	1.845810000
H	-2.896402000	-2.106456000	1.473369000
C	-2.126560000	-1.667436000	-1.268196000
H	-2.088188000	-2.708231000	-0.910579000
H	-2.648266000	-1.694756000	-2.237209000
C	-2.900555000	0.686011000	-0.610689000
H	-3.075581000	0.825532000	-1.688490000
H	-3.731107000	1.195754000	-0.098948000
P	-0.386208000	-1.097142000	-1.569111000
P	-1.344380000	1.590730000	-0.152476000
P	-0.762667000	-0.948463000	1.621369000
Ru	0.447366000	0.266058000	0.131376000
O	1.779598000	1.617487000	-0.946007000
C	1.943784000	2.133166000	0.214687000
O	2.218780000	-1.187858000	0.410451000
C	3.393469000	-1.388488000	0.204959000
H	3.858068000	-2.374132000	0.358045000
H	1.453714000	3.083604000	0.476593000
O	3.169950000	2.085810000	0.800515000
C	-0.474319000	-0.354836000	-3.247852000
H	0.495834000	0.090212000	-3.502421000
H	-0.725364000	-1.124169000	-3.990518000
H	-1.237733000	0.430319000	-3.297324000
C	0.502707000	-2.655598000	-1.956633000
H	-0.072477000	-3.250870000	-2.678582000
H	1.476982000	-2.410436000	-2.398129000
H	0.675695000	-3.250888000	-1.053277000
C	-1.880572000	2.618601000	1.269102000
H	-1.031829000	3.196067000	1.656189000
H	-2.672168000	3.311390000	0.952638000
H	-2.271686000	1.994248000	2.081064000
C	-1.170542000	2.861692000	-1.460069000
H	-2.144119000	3.325645000	-1.668244000
H	-0.473078000	3.638568000	-1.124952000
H	-0.763343000	2.420146000	-2.376016000
C	-0.259898000	-2.700163000	1.847236000
H	0.794338000	-2.745329000	2.142394000
H	-0.874291000	-3.169321000	2.627441000
H	-0.382850000	-3.266478000	0.916940000
C	-0.779058000	-0.391563000	3.367004000
H	-1.458521000	-1.008986000	3.970105000
H	0.238527000	-0.482767000	3.767647000
H	-1.079479000	0.659487000	3.443116000
H	1.086614000	1.351714000	1.310282000
H	3.670588000	1.375581000	0.353451000
O	4.211780000	-0.430747000	-0.218963000
H	5.124679000	-0.754019000	-0.322676000

Sum of electronic and thermal Energies=-1894.128995
Sum of electronic and thermal Enthalpies=-1894.128050
Sum of electronic and thermal Free Energies=-1894.211405
Lowest vibration frequencies (/cm^{-1}): -563.5999 30.8361 65.9383

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C	3.9852780	-1.0040230	0.7227420
H	4.9732480	-1.4090520	0.993331
C	4.0884740	0.5146440	0.9419140
H	4.2103740	0.7183570	2.0176120
H	4.9976050	0.8984770	0.4538310
C	3.7660190	-1.3918190	-0.7509040
H	4.4251710	-0.7840110	-1.3907180
H	4.0672330	-2.4392940	-0.9070840
C	2.9832100	-1.6764620	1.6794490
H	2.8528330	-2.7315740	1.3925570
H	3.3958200	-1.6855640	2.7000280
P	2.0243540	-1.1932130	-1.3653250
P	1.3019520	-0.8835920	1.7644410
P	2.6469960	1.5166680	0.3285200
Ru	0.7842850	0.3219900	-0.0318590
O	-1.1148080	-0.7222460	-0.6075200
C	-2.2152330	-0.4523450	-0.0951500
O	0.0275800	1.5806460	-1.8821220
C	-0.8648580	2.4381560	-1.3157060
O	-2.0549000	2.3478140	-1.4634350
H	-0.3317920	3.2145320	-0.7500780
H	-2.2819640	0.0397940	0.8883670
C	1.4304110	-2.9339150	-1.4528620
H	0.4008030	-2.9483750	-1.8319290
H	2.0689110	-3.5260440	-2.1229690
H	1.4376250	-3.4052970	-0.4626720
C	2.2571680	-0.8686940	-3.1617450
H	2.9848800	-1.5660630	-3.5991090
H	1.2936190	-1.0055600	-3.6718970
H	2.5927030	0.1602250	-3.3377330
C	1.3251450	-0.0834570	3.4142490
H	0.3607600	0.4094800	3.5864560
H	1.4956780	-0.8377810	4.1946320
H	2.1183200	0.6702310	3.4833850
C	0.1655000	-2.2821800	2.1038060
H	0.5891560	-2.9431080	2.8720640
H	-0.7857470	-1.8779910	2.4735390
H	-0.0367140	-2.8586470	1.1941290
C	3.3290310	2.3579300	-1.1564680
H	2.5672350	3.0190770	-1.5882600
H	4.2069230	2.9587980	-0.8819330
H	3.6267760	1.6299180	-1.9196690
C	2.5987610	2.9328660	1.4922770
H	3.5990880	3.3675060	1.6246590
H	1.9264270	3.6969800	1.0805850
H	2.2018570	2.6259080	2.4663570
H	-0.0668540	1.3517580	1.0013780
H	-0.4811960	0.9316910	-2.4127810
N	-3.3929570	-0.7251610	-0.6685050
C	-3.4571320	-1.3730840	-1.9752300
H	-4.1501570	-0.8183850	-2.6160230
H	-2.4574350	-1.3697760	-2.4164670
H	-3.7982460	-2.4107590	-1.8838810
C	-4.6075220	-0.2982470	-0.0469870
C	-4.7382870	1.0215870	0.3858020
C	-5.6613450	-1.2005140	0.0990450
C	-5.9214080	1.4269060	0.9991120
H	-3.9270060	1.7301240	0.2179900
C	-6.8457220	-0.7805360	0.6967480

H	-5.5528690	-2.2285990	-0.2433550
C	-6.9759770	0.5299300	1.1546640
H	-6.0230920	2.4556670	1.3400770
H	-7.6666820	-1.4857390	0.8133760
H	-7.9026890	0.8535630	1.6250860

Sum of electronic and thermal Energies= -2144.289791
Sum of electronic and thermal Enthalpies= -2144.288847
Sum of electronic and thermal Free Energies= -2144.388765
Lowest vibration frequencies (/cm^-1): 20.0445 27.7230 38.9869

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C	-3.139796000	-0.455477000	0.497466000
H	-4.214430000	-0.613166000	0.677736000
C	-2.494772000	-0.302670000	1.885305000
H	-2.792338000	0.661202000	2.325974000
H	-2.879573000	-1.080936000	2.561871000
C	-2.646199000	-1.701787000	-0.251738000
H	-2.634387000	-2.567465000	0.428128000
H	-3.349728000	-1.955700000	-1.059188000
C	-3.035656000	0.816292000	-0.359605000
H	-3.399955000	0.605914000	-1.377011000
H	-3.696488000	1.596675000	0.046680000
P	-0.964911000	-1.539251000	-1.017435000
P	-1.332325000	1.544768000	-0.487209000
P	-0.642020000	-0.406818000	1.908188000
Ru	0.336465000	0.062144000	-0.088050000
C	-0.167253000	0.639306000	3.333513000
H	-0.782665000	0.391393000	4.208775000
H	0.887197000	0.453528000	3.569934000
H	-0.285265000	1.702914000	3.098303000
C	-0.343306000	-2.082482000	2.590569000
H	0.733750000	-2.280547000	2.606658000
H	-0.743367000	-2.148121000	3.611107000
H	-0.829799000	-2.850649000	1.978344000
C	-0.324858000	-3.254957000	-0.992301000
H	0.020609000	-3.537586000	0.007961000
H	-1.117108000	-3.944121000	-1.314091000
H	0.519850000	-3.332401000	-1.687068000
C	-1.343238000	-1.340516000	-2.800345000
H	-0.411327000	-1.211044000	-3.362221000
H	-1.864471000	-2.234484000	-3.168263000
H	-1.984150000	-0.468821000	-2.974952000
C	-1.473904000	2.994160000	0.634735000
H	-0.530779000	3.550193000	0.661742000
H	-2.265273000	3.659702000	0.263580000
H	-1.736512000	2.687103000	1.653566000
C	-1.329810000	2.380593000	-2.115643000
H	-2.266924000	2.936886000	-2.252322000
H	-0.485265000	3.079128000	-2.148635000
H	-1.207158000	1.661647000	-2.932425000
O	1.792172000	1.533401000	0.814388000
C	2.219643000	2.625152000	0.496538000
H	3.111800000	3.054843000	0.975337000
O	1.362661000	0.561857000	-1.974053000
C	2.061884000	-0.237396000	-2.662428000
H	2.468947000	0.194097000	-3.601076000

O	2.329830000	-1.431614000	-2.405882000
H	2.149575000	-1.645616000	-0.754657000
O	2.007382000	-1.450286000	0.216635000
C	3.265291000	-1.066886000	0.759392000
H	4.016868000	-1.788339000	0.404434000
H	3.531475000	-0.056316000	0.427288000
O	3.184389000	-1.031063000	2.140220000
H	3.209421000	-1.937321000	2.483186000
O	1.637350000	3.369415000	-0.425694000
H	2.113425000	4.208915000	-0.555311000

Sum of electronic and thermal Energies=-2083.824578
Sum of electronic and thermal Enthalpies=-2083.823634
Sum of electronic and thermal Free Energies=-2083.912759
Lowest vibration frequencies (/cm^{-1}): 57.8729 69.3957 79.4608

HCOOH

O	–1.135763000	–0.263323000	–0.000034000
C	–0.127894000	0.400220000	0.000054000
H	–0.097012000	1.499765000	0.000162000
O	1.111251000	–0.090946000	–0.000085000
H	1.060478000	–1.066930000	0.000474000

Sum of electronic and thermal Energies=–189.642505
Sum of electronic and thermal Enthalpies=–189.641560
Sum of electronic and thermal Free Energies=–189.669764
Lowest vibration frequencies (/ cm^–1): 623.6625 664.1272 1059.4195

CO_2

C	0.000000000	0.000000000	0.000000000
O	0.000000000	0.000000000	1.164574000
O	0.000000000	0.000000000	–1.164574000

Sum of electronic and thermal Energies=–188.493954
Sum of electronic and thermal Enthalpies=–188.493009
Sum of electronic and thermal Free Energies=–188.517264
Lowest vibration frequencies (/ cm^–1): 676.3023 676.3023 1396.6752

H_2

H	0.000000000	0.000000000	0.371102000
H	0.000000000	0.000000000	–0.371102000

Sum of electronic and thermal Energies=–1.154448
Sum of electronic and thermal Enthalpies=–1.153503
Sum of electronic and thermal Free Energies=–1.168294
Vibration frequency (/ cm^–1): 4369.72

$CH_2(OH)_2$

C	0.000101000	0.502317000	0.093614000
H	0.000101000	1.317560000	–0.634576000
H	0.000272000	0.913947000	1.114408000
O	1.172083000	–0.228372000	–0.142432000
H	1.365690000	–0.795988000	0.618179000
O	–1.172318000	–0.228162000	–0.142231000
H	–1.364787000	–0.797147000	0.617616000

Sum of electronic and thermal Energies=–190.795449
Sum of electronic and thermal Enthalpies=–190.794505
Sum of electronic and thermal Free Energies=–190.824805
Lowest vibration frequencies (/ cm^–1): 161.6277 429.4798 542.5784

CH_2O

O	0.677198000	–0.000089000	0.000028000
C	–0.530690000	0.000015000	–0.000113000
H	–1.117372000	–0.941234000	0.000228000
H	–1.116075000	0.941853000	0.000227000

Sum of electronic and thermal Energies=–114.414768
Sum of electronic and thermal Enthalpies=–114.413824
Sum of electronic and thermal Free Energies=–114.439304
Lowest vibration frequencies (/ cm^–1): 1208.3514 1251.1382 1514.2870

CH_3OH

C	0.662773000	–0.020587000	–0.000003000
H	1.085917000	0.988320000	–0.000325000
H	1.022474000	–0.549353000	–0.894679000
H	1.022488000	–0.548748000	0.895032000
O	–0.744824000	0.123567000	–0.000005000
H	–1.148923000	–0.755231000	0.000029000

Sum of electronic and thermal Energies=–115.601040
Sum of electronic and thermal Enthalpies=–115.600096
Sum of electronic and thermal Free Energies=–115.627261
Lowest vibration frequencies (/ cm^–1): 266.3358 1054.8920 1099.6950

H_2O

O	0.000000000	0.000000000	0.117886000
H	0.000000000	0.766487000	-0.471542000
H	0.000000000	-0.766487000	-0.471542000

Sum of electronic and thermal Energies=-76.368863
Sum of electronic and thermal Enthalpies=-76.367918
Sum of electronic and thermal Free Energies=-76.389355
Lowest vibration frequencies (/cm^{-1}): 1654.6132 3789.9705 3912.4768

$HCOO^-$

C	0.000000000	0.000000000	0.326831000
H	0.000000000	0.000000000	1.454803000
O	0.000000000	1.131055000	-0.213487000
O	0.000000000	-1.131055000	-0.213487000

Sum of electronic and thermal Energies=-189.191289
Sum of electronic and thermal Enthalpies=-189.190344
Sum of electronic and thermal Free Energies=-189.217421
Lowest vibration frequencies (/cm^{-1}): 739.5229 1058.2886 1379.6805

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C	3.985278000	-1.004023000	0.722742000

H	4.973248000	-1.409052000	0.993331000
C	4.088474000	0.514644000	0.941914000
H	4.210374000	0.718357000	2.017612000
H	4.997605000	0.898477000	0.453831000
C	3.766019000	-1.391819000	-0.750904000
H	4.425171000	-0.784011000	-1.390718000
H	4.067233000	-2.439294000	-0.907084000
C	2.983210000	-1.676462000	1.679449000
H	2.852833000	-2.731574000	1.392557000
H	3.395820000	-1.685564000	2.700028000
P	2.024354000	-1.193213000	-1.365325000
P	1.301952000	-0.883592000	1.764441000
P	2.646996000	1.516668000	0.328520000
Ru	0.784285000	0.321990000	-0.031859000
O	-1.114808000	-0.722246000	-0.607520000
C	-2.215233000	-0.452345000	-0.095150000
O	0.027580000	1.580646000	-1.882122000
C	-0.864858000	2.438156000	-1.315706000
O	-2.054900000	2.347814000	-1.463435000
H	-0.331792000	3.214532000	-0.750078000
H	-2.281964000	0.039794000	0.888367000
C	1.430411000	-2.933915000	-1.452862000
H	0.400803000	-2.948375000	-1.831929000
H	2.068911000	-3.526044000	-2.122969000
H	1.437625000	-3.405297000	-0.462672000
C	2.257168000	-0.868694000	-3.161745000
H	2.984880000	-1.566063000	-3.599109000
H	1.293619000	-1.005560000	-3.671897000
H	2.592703000	0.160225000	-3.337733000
C	1.325145000	-0.083457000	3.414249000
H	0.360760000	0.409480000	3.586456000
H	1.495678000	-0.837781000	4.194632000
H	2.118320000	0.670231000	3.483385000
C	0.165500000	-2.282180000	2.103806000
H	0.589156000	-2.943108000	2.872064000
H	-0.785747000	-1.877991000	2.473539000
H	-0.036714000	-2.858647000	1.194129000
C	3.329031000	2.357930000	-1.156468000
H	2.567235000	3.019077000	-1.588260000
H	4.206923000	2.958798000	-0.881933000
H	3.626776000	1.629918000	-1.919669000
C	2.598761000	2.932866000	1.492277000
H	3.599088000	3.367506000	1.624659000
H	1.926427000	3.696980000	1.080585000
H	2.201857000	2.625908000	2.466357000
H	-0.066854000	1.351758000	1.001378000
H	-0.481196000	0.931691000	-2.412781000
N	-3.392957000	-0.725161000	-0.668505000
C	-3.457132000	-1.373084000	-1.975230000
H	-4.150157000	-0.818385000	-2.616023000
H	-2.457435000	-1.369776000	-2.416467000
H	-3.798246000	-2.410759000	-1.883881000
C	-4.607522000	-0.298247000	-0.046987000
C	-4.738287000	1.021587000	0.385802000
C	-5.661345000	-1.200514000	0.099045000
C	-5.921408000	1.426906000	0.999112000
H	-3.927006000	1.730124000	0.217990000
C	-6.845722000	-0.780536000	0.696748000
H	-5.552869000	-2.228599000	-0.243355000
C	-6.975977000	0.529930000	1.154664000

H	-6.023092000	2.455667000	1.340077000
H	-7.666682000	-1.485739000	0.813376000
H	-7.902689000	0.853563000	1.625086000

Sum of electronic and thermal Energies=-2144.289791
Sum of electronic and thermal Enthalpies=-2144.288847
Sum of electronic and thermal Free Energies=-2144.388765
Lowest vibration frequencies (/cm^{-1}): 20.0445 27.723 38.9869

PhNMeC(O)H

C	2.230735000	0.998961000	-0.446885000
C	0.850909000	1.182693000	-0.400129000
C	0.021827000	0.157365000	0.062244000
C	0.587206000	-1.048732000	0.487470000
C	1.966172000	-1.224741000	0.431802000
C	2.794925000	-0.205779000	-0.035631000
H	2.864826000	1.805744000	-0.811210000
H	0.423257000	2.126359000	-0.733575000
H	-0.051521000	-1.843344000	0.862325000
H	2.395608000	-2.167435000	0.767800000
H	3.873490000	-0.348594000	-0.073458000
N	-1.385033000	0.367824000	0.134787000
C	-1.871827000	1.693967000	0.494290000
H	-1.746862000	2.413459000	-0.324525000
H	-2.937829000	1.632020000	0.733835000
H	-1.335004000	2.059023000	1.376709000
C	-2.285766000	-0.597045000	-0.210832000
O	-2.028490000	-1.718377000	-0.619278000
H	-3.327906000	-0.245115000	-0.081156000

Sum of electronic and thermal Energies=-439.784465
Sum of electronic and thermal Enthalpies=-439.783521
Sum of electronic and thermal Free Energies=-439.827719
Lowest vibration frequencies (/cm^{-1}): 36.2919 121.0864 168.9433

TS3

C	3.9866190	-0.3697060	-0.4091380
H	5.0679680	-0.5046250	-0.5682080
C	3.7791230	-0.4032580	1.1133560
H	3.9712890	-1.4232150	1.4828850
H	4.5149730	0.2476170	1.6098530
C	3.6350370	0.9800310	-1.0586290
H	4.0725200	1.7999490	-0.4686400
H	4.1083290	1.0350970	-2.0513740
C	3.3111550	-1.5515430	-1.1155560
H	3.4114550	-1.4352620	-2.2052560
H	3.8304890	-2.4863470	-0.8563270
P	1.8223000	1.3411270	-1.2658030
P	1.5103730	-1.8026610	-0.7372440
P	2.0994980	0.1144640	1.7063330
Ru	0.4519120	0.0008840	0.1286000
C	-1.5664430	-0.9539670	0.0066120
O	-0.4467080	1.8057710	1.0516990
C	-1.2224190	2.5820310	0.5031770
O	-1.8540010	2.3589210	-0.6136960
H	-1.4327630	3.5713020	0.9300490
H	-1.4582600	-2.0472320	-0.1094940
C	1.5585620	1.2034120	-3.0765340

H	0.5104370	1.4309840	-3.3099600
H	2.2056760	1.9114760	-3.6105540
H	1.7807940	0.1913520	-3.4369250
C	1.7895650	3.1659030	-1.0730550
H	2.5606910	3.6206360	-1.7098220
H	0.8158110	3.5640410	-1.3797730
H	1.9652650	3.4562920	-0.0313480
C	1.5522550	-3.3531530	0.2445810
H	0.5482180	-3.6652220	0.5503010
H	1.9988620	-4.1567530	-0.3564690
H	2.1590540	-3.2151390	1.1481740
C	0.8364750	-2.4166880	-2.3264660
H	1.4820210	-3.2108320	-2.7240820
H	-0.1691700	-2.8250420	-2.1700000
H	0.7616360	-1.6055320	-3.0582790
C	2.3971970	1.7715320	2.4279460
H	1.4499100	2.1751880	2.8046440
H	3.1178400	1.6906140	3.2525530
H	2.7990310	2.4661330	1.6816950
C	1.8640220	-0.8871150	3.2187010
H	2.7643190	-0.8676940	3.8478860
H	1.0198820	-0.4748850	3.7863330
H	1.6237080	-1.9251690	2.9592480
H	-0.3668150	-0.9623020	1.2047650
O	-1.3695330	-0.2301630	-1.0578920
N	-2.5965380	-0.5532860	0.8988350
C	-3.8852760	-0.3223820	0.3021370
C	-4.7528930	0.5894540	0.9015200
C	-4.3141810	-1.0651380	-0.7990170
C	-6.0378950	0.7637980	0.3928160
H	-4.4090490	1.1569660	1.7667180
C	-5.5921870	-0.8741720	-1.3187650
H	-3.6463570	-1.7990520	-1.2503090
C	-6.4587210	0.0401240	-0.7226690
H	-6.7117020	1.4758790	0.8671520
H	-5.9145330	-1.4517530	-2.1837450
H	-7.4606370	0.1858900	-1.1226350
C	-2.6961050	-1.3891800	2.0918770
H	-2.7927640	-2.4600460	1.8362540
H	-1.8087320	-1.2615970	2.7290390
H	-3.5804050	-1.0954690	2.6661060
H	-1.7213020	1.3977710	-0.8782250

Sum of electronic and thermal Energies= -2144.278737
Sum of electronic and thermal Enthalpies= -2144.277793
Sum of electronic and thermal Free Energies= -2144.375008
Lowest vibration frequencies (/cm^-1)= -398.5408 -100.0809 (rotation of one Me group)
27.7965

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C	-3.523244000	0.027468000	1.108601000
H	-4.540237000	0.026651000	1.530428000
C	-3.421318000	1.297022000	0.250754000
H	-4.044738000	1.188148000	-0.649441000
H	-3.827390000	2.157247000	0.803302000
C	-2.568429000	0.033823000	2.312886000
H	-2.620343000	1.008514000	2.821940000
H	-2.901397000	-0.712952000	3.049367000

C	-3.410734000	-1.252429000	0.273362000
H	-3.411590000	-2.128335000	0.940623000
H	-4.297438000	-1.359711000	-0.370454000
P	-0.786368000	-0.320635000	1.928614000
P	-1.921911000	-1.379013000	-0.834094000
P	-1.697673000	1.731489000	-0.264557000
Ru	-0.202610000	0.025646000	-0.226664000
C	1.420030000	-0.985549000	-2.242824000
O	1.269836000	1.517623000	0.410402000
C	1.889166000	2.324717000	-0.343828000
O	1.828551000	2.402145000	-1.590494000
H	2.551357000	3.037190000	0.191113000
H	2.339477000	-0.904662000	-2.837495000
O	0.647589000	0.187980000	-2.311962000
C	-0.575401000	-2.027155000	2.573881000
H	0.467111000	-2.350443000	2.466261000
H	-0.841347000	-2.056973000	3.639319000
H	-1.212882000	-2.737531000	2.035480000
C	0.124803000	0.640303000	3.190415000
H	-0.324465000	0.477466000	4.179107000
H	1.172035000	0.313745000	3.209404000
H	0.116394000	1.708150000	2.949724000
C	-2.632883000	-1.058993000	-2.500475000
H	-1.840016000	-1.058377000	-3.258542000
H	-3.361708000	-1.842731000	-2.745993000
H	-3.145605000	-0.091398000	-2.538881000
C	-1.757572000	-3.209479000	-0.944901000
H	-2.760128000	-3.647792000	-1.044514000
H	-1.180771000	-3.486911000	-1.835962000
H	-1.272342000	-3.635193000	-0.058944000
C	-1.341357000	3.203977000	0.766846000
H	-0.358963000	3.617201000	0.516733000
H	-2.110312000	3.963891000	0.573260000
H	-1.354896000	2.960659000	1.835093000
C	-1.859516000	2.510427000	-1.911903000
H	-2.675903000	3.245252000	-1.905239000
H	-0.916486000	3.022101000	-2.142872000
H	-2.044887000	1.765359000	-2.692633000
H	0.813809000	-1.790083000	-2.672672000
H	1.192699000	1.028651000	-2.199190000
N	1.669161000	-1.331479000	-0.826619000
C	1.690088000	-2.802566000	-0.667910000
H	0.780583000	-3.229279000	-1.093810000
H	2.566940000	-3.233457000	-1.175105000
H	1.732574000	-3.071814000	0.389736000
C	2.875438000	-0.771668000	-0.232973000
C	3.060030000	-0.950104000	1.142031000
C	3.839936000	-0.074473000	-0.955141000
C	4.181125000	-0.444159000	1.782296000
H	2.297793000	-1.467648000	1.724019000
C	4.965636000	0.439810000	-0.307379000
H	3.734443000	0.115063000	-2.019837000
C	5.145523000	0.258490000	1.057805000
H	4.296373000	-0.588646000	2.855540000
H	5.702752000	0.991065000	-0.888890000
H	6.023767000	0.663120000	1.557336000

Sum of electronic and thermal Energies=-2144.319057
Sum of electronic and thermal Enthalpies=-2144.318113
Sum of electronic and thermal Free Energies=-2144.412223

Lowest vibration frequencies (/cm^{-1}): 42.8393 51.6361 56.2934

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C	2.238029000	-2.351019000	-1.736805000
H	2.669872000	-3.154557000	-2.353316000
C	1.312303000	-1.555940000	-2.670653000
H	1.916862000	-1.002843000	-3.405740000
H	0.686910000	-2.251170000	-3.251027000
C	1.474493000	-3.050267000	-0.603966000
H	0.573272000	-3.538055000	-1.006071000
H	2.093467000	-3.853655000	-0.176799000
C	3.428621000	-1.530605000	-1.216777000
H	3.970188000	-2.112075000	-0.454662000
H	4.146809000	-1.352255000	-2.031415000
P	0.962544000	-1.943434000	0.792529000
P	2.994662000	0.120730000	-0.489689000
P	0.174952000	-0.351632000	-1.828403000
Ru	0.857169000	0.255657000	0.256362000
C	0.003159000	0.987451000	-3.071767000
H	-0.166924000	0.555813000	-4.067520000
H	-0.856375000	1.616644000	-2.810144000
H	0.894299000	1.624408000	-3.102095000
C	-1.467234000	-1.152141000	-1.983554000
H	-2.226755000	-0.519651000	-1.506135000
H	-1.715733000	-1.286302000	-3.045110000
H	-1.482639000	-2.135116000	-1.498895000
C	-0.585242000	-2.709414000	1.403386000
H	-1.424978000	-2.515305000	0.727244000
H	-0.437618000	-3.793397000	1.503499000
H	-0.828546000	-2.289096000	2.387493000
C	2.111314000	-2.415561000	2.141169000
H	1.841712000	-1.875842000	3.056080000
H	2.025195000	-3.494477000	2.327805000
H	3.153076000	-2.188003000	1.889540000
C	3.516107000	1.257648000	-1.837066000
H	3.311797000	2.298200000	-1.562639000
H	4.594804000	1.141120000	-2.009334000
H	2.992913000	1.028333000	-2.772825000
C	4.318018000	0.413953000	0.738259000
H	5.295588000	0.182014000	0.294545000
H	4.292230000	1.467662000	1.038574000
H	4.165988000	-0.195496000	1.635220000
O	0.508607000	2.463280000	-0.124932000
C	1.149618000	3.469363000	0.110895000
H	0.692119000	4.468318000	0.058214000
O	2.429428000	3.429606000	0.424408000
O	1.537249000	0.949127000	2.230818000
C	0.966109000	0.717423000	3.336255000
H	1.487851000	1.136183000	4.222449000
O	-0.091197000	0.078656000	3.528684000
H	-0.945771000	0.134247000	2.092647000
O	-1.219680000	0.298682000	1.146352000
C	-2.123669000	1.409460000	1.134257000
H	-2.703520000	1.362741000	2.069761000
H	-1.557967000	2.347714000	1.119681000
H	2.783108000	4.321475000	0.590652000
N	-2.976855000	1.367613000	-0.003765000
C	-4.088664000	0.522938000	-0.005403000
C	-4.218559000	-0.508729000	0.944950000

C	-5.102131000	0.662308000	-0.970657000
C	-5.330731000	-1.342622000	0.937630000
H	-3.437278000	-0.677092000	1.682743000
C	-6.204340000	-0.189275000	-0.971286000
H	-5.045204000	1.446946000	-1.721828000
C	-6.334574000	-1.195839000	-0.018811000
H	-5.405037000	-2.127206000	1.690096000
H	-6.974574000	-0.051329000	-1.729570000
H	-7.200345000	-1.855470000	-0.021829000
C	-2.871913000	2.412190000	-1.002086000
H	-1.900052000	2.905285000	-0.899164000
H	-2.932135000	1.991460000	-2.017422000
H	-3.665977000	3.169930000	-0.903285000

Sum of electronic and thermal Energies=-2333.971920
Sum of electronic and thermal Enthalpies=-2333.970975
Sum of electronic and thermal Free Energies=-2334.073296
Lowest vibration frequencies (/cm^{-1}): 30.2699 35.3551 66.3578

$HOCH_2NMePh$

C	-2.362372000	0.997617000	0.269854000
C	-1.000892000	1.228700000	0.092509000
C	-0.121624000	0.175621000	-0.223383000
C	-0.672658000	-1.117440000	-0.330364000
C	-2.034220000	-1.333804000	-0.148660000
C	-2.897440000	-0.281879000	0.151671000
H	-3.009272000	1.840701000	0.510910000
H	-0.628952000	2.244213000	0.199737000
H	-0.046601000	-1.975972000	-0.564460000
H	-2.420795000	-2.348309000	-0.241213000
H	-3.961654000	-0.457817000	0.296984000
N	1.239804000	0.419179000	-0.439997000
C	1.781226000	1.704200000	-0.032471000
H	1.608332000	1.913766000	1.035791000
H	2.860942000	1.702650000	-0.209440000
H	1.347860000	2.520852000	-0.623284000
C	2.164622000	-0.676963000	-0.414446000
O	2.480017000	-1.147412000	0.885993000
H	3.115610000	-0.338715000	-0.836492000
H	1.790966000	-1.493460000	-1.044968000
H	1.684947000	-1.539184000	1.280206000

Sum of electronic and thermal Energies=-440.939253
Sum of electronic and thermal Enthalpies=-440.938308
Sum of electronic and thermal Free Energies=-440.983773
Lowest vibration frequencies (/cm^{-1}): 31.6515 100.9112 136.8103

$H_2CNMePh^+$

N	-1.622673000	-0.092856000	-0.069054000
C	-2.234894000	-1.041329000	-0.676284000
H	-1.664429000	-1.781820000	-1.233139000
H	-3.319979000	-1.096389000	-0.636188000
C	-2.357987000	0.957680000	0.657650000
H	-1.944797000	1.030410000	1.666687000
H	-2.229518000	1.910559000	0.137669000
H	-3.417370000	0.698859000	0.690439000
C	-0.177310000	-0.035737000	-0.035910000
C	0.467157000	1.165061000	-0.322304000

C	0.529107000	-1.189322000	0.296022000
C	1.857081000	1.195361000	-0.297884000
H	-0.093840000	2.057909000	-0.588752000
C	1.918789000	-1.139996000	0.320945000
H	0.001009000	-2.102856000	0.565302000
C	2.581671000	0.048144000	0.021795000
H	2.375061000	2.122096000	-0.534332000
H	2.482252000	-2.031323000	0.587369000
H	3.668645000	0.083376000	0.044141000

Sum of electronic and thermal Energies=-364.965689
Sum of electronic and thermal Enthalpies=-364.964745
Sum of electronic and thermal Free Energies=-365.006806
Lowest vibration frequencies (/cm^{-1}): 49.2961 141.5426 157.3621

$PhNMe_2$

C	-1.9373720	-1.1964660	0.0133430
C	-0.5472730	-1.2060310	-0.0251120
C	0.1859820	0.0000020	-0.0577660
C	-0.5472800	1.2060400	-0.0250440
C	-1.9373750	1.1964660	0.0134060
C	-2.6522390	-0.0000050	0.0304060
H	-2.4674980	-2.1486620	0.0346900
H	-0.0327300	-2.1637590	-0.0312920
H	-0.0327440	2.1637710	-0.0311510
H	-2.4675130	2.1486540	0.0348140
H	-3.7402210	0.0000000	0.0625970
N	1.5674100	-0.0000040	-0.1277510
C	2.2860520	1.2430050	0.0493280
H	2.1001380	1.7039860	1.0349680
H	3.3590880	1.0527780	-0.0415280
H	2.0156130	1.9738170	-0.7254130
C	2.2860370	-1.2430050	0.0494470
H	2.0157790	-1.9738310	-0.7253470
H	3.3590920	-1.0527680	-0.0411810
H	2.0999390	-1.7039880	1.0350500

Sum of electronic and thermal Energies= -365.749444
Sum of electronic and thermal Enthalpies= -365.748500
Sum of electronic and thermal Free Energies= -365.791751
Lowest vibration frequencies (/cm^-1):59.6199 94.1690 161.2880

(HCOO)(H_2CNMePh)

C	1.944089000	-1.499869000	-0.022770000
H	1.189532000	-1.778340000	0.740023000
O	2.394711000	-2.274638000	-0.828681000
O	2.327004000	-0.224832000	0.035652000
C	1.644567000	0.647702000	0.987722000
H	2.421597000	1.343741000	1.314363000
H	1.315407000	0.039242000	1.837070000
N	0.565319000	1.349637000	0.397542000
C	-0.633786000	0.620081000	0.188354000
C	-1.231288000	0.526145000	-1.073182000
C	-1.255260000	-0.010072000	1.277314000
C	-2.418215000	-0.187836000	-1.239640000
H	-0.771111000	1.003802000	-1.935766000
C	-2.429131000	-0.731220000	1.100608000

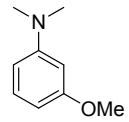
H	-0.827632000	0.087565000	2.275126000
C	-3.020579000	-0.825735000	-0.160441000
H	-2.865680000	-0.250197000	-2.230734000
H	-2.896280000	-1.209895000	1.960303000
H	-3.945032000	-1.384399000	-0.294972000
C	0.968595000	2.296933000	-0.630802000
H	1.792346000	2.905718000	-0.240715000
H	1.310803000	1.811889000	-1.559085000
H	0.131155000	2.962399000	-0.867148000

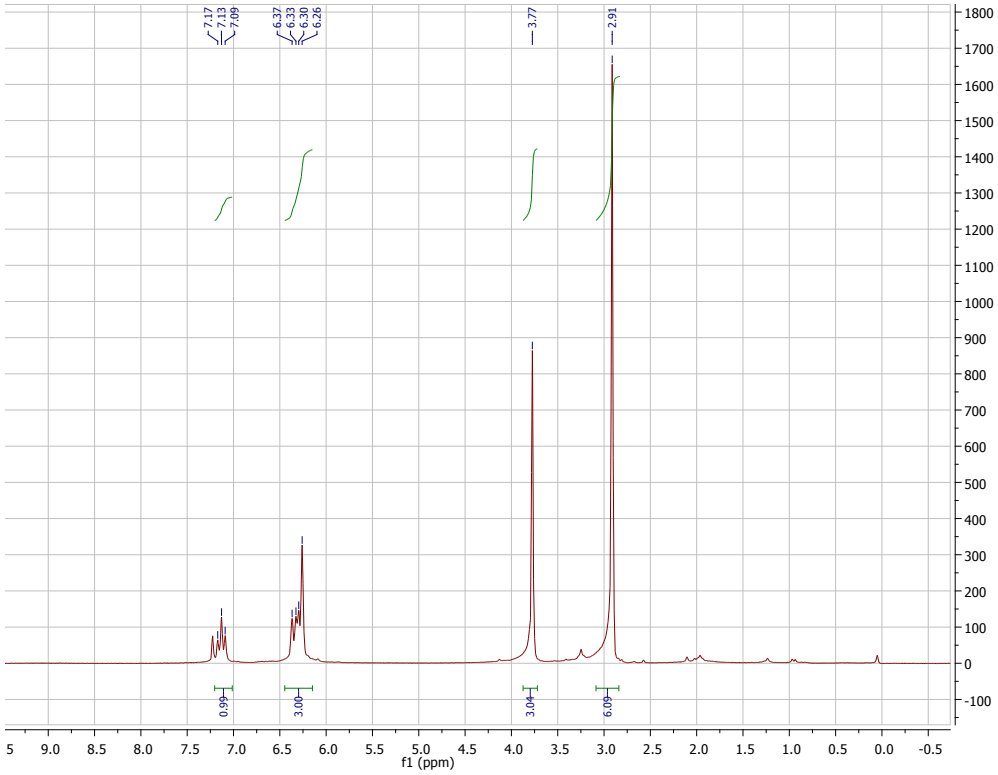
Sum of electronic and thermal Energies= -554.214256
Sum of electronic and thermal Enthalpies= -554.213312
Sum of electronic and thermal Free Energies= -554.264048

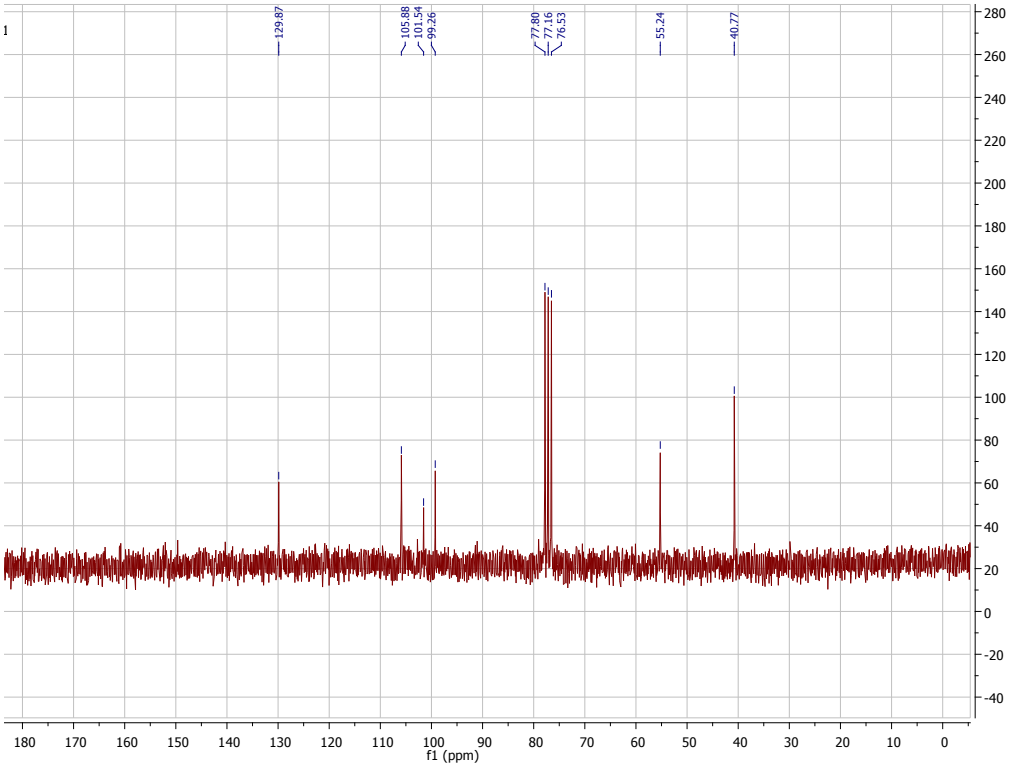
Lowest vibration frequencies (/cm^-1):29.78 49.16 70.85

Spectral Data

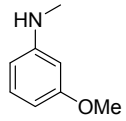
- N,N-Dimethyl-m-anisidine (3h): ^{1}H NMR (200 Hz, $CDCl_3$) δ = 2.91 (s, 6H), 3.77 (s, 3H), 6.29-6.37 (m, 3H), 7.13 (t, J = 8.0 Hz, 1H) ^{13}C NMR (50 Hz, $CDCl_3$) δ = 40.77, 55.24, 99.26, 101.51, 106.88, 129.67.

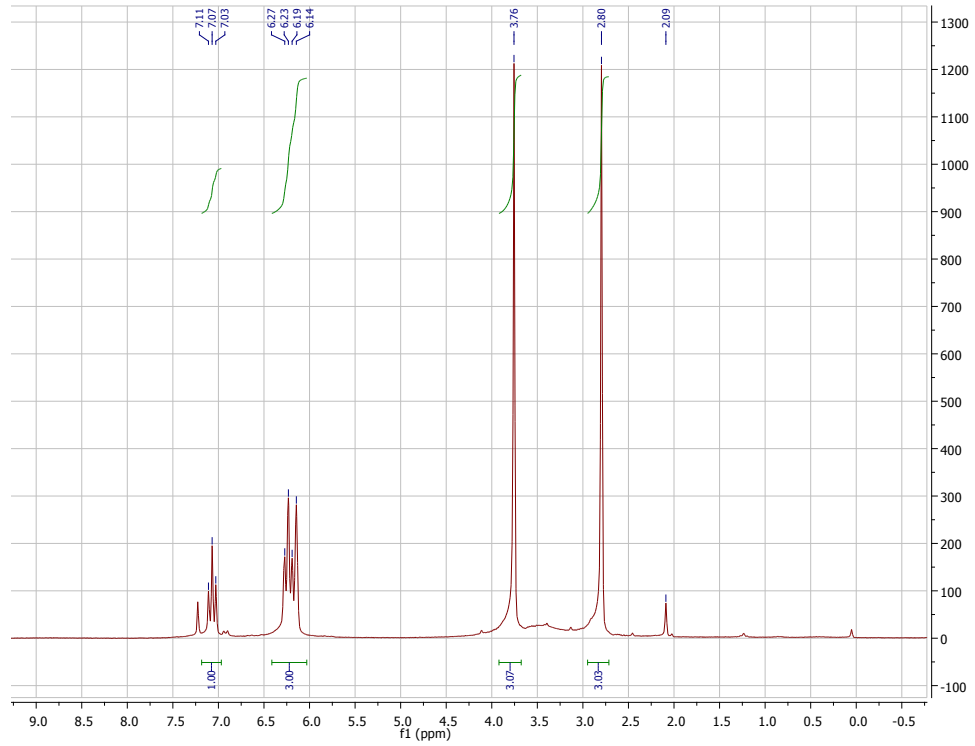


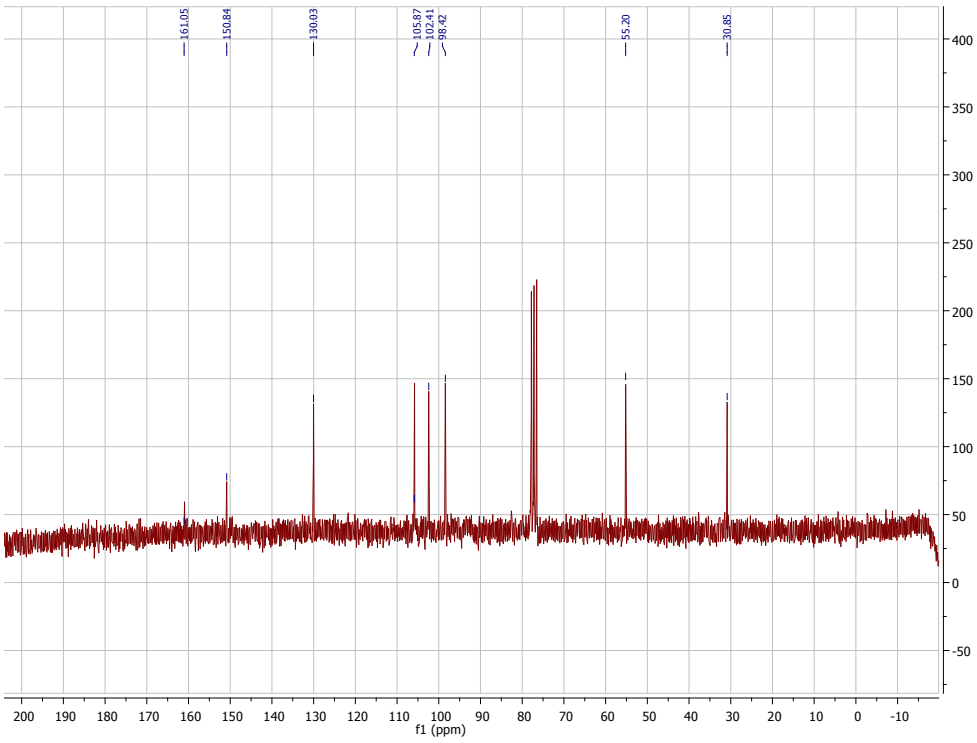




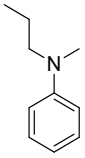
- **N-methyl-o-anisidine (2h):** ^{1}H NMR (200 Hz, $CDCl_3$) δ = 2.80 (s, 3H), 3.76 (s, 3H), 6.14-6.27 (m, 3H), 7.07 (t, J = 8.0 Hz, 1H) ^{13}C NMR (50 Hz, $CDCl_3$) δ = 30.85, 55.20, 98.42, 102.41, 107.83, 130.03.

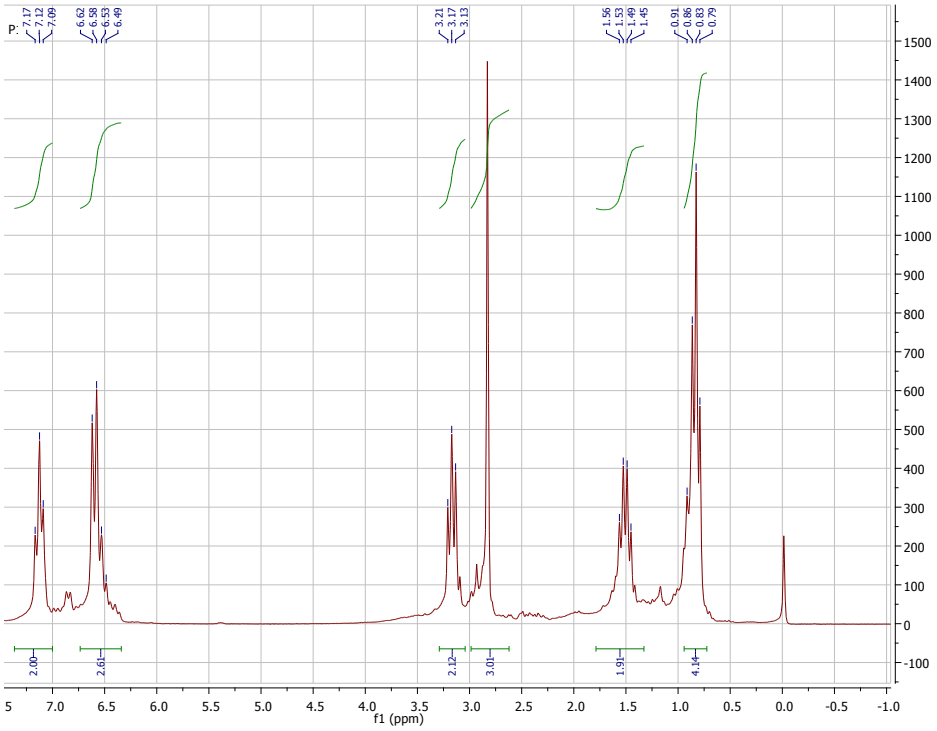


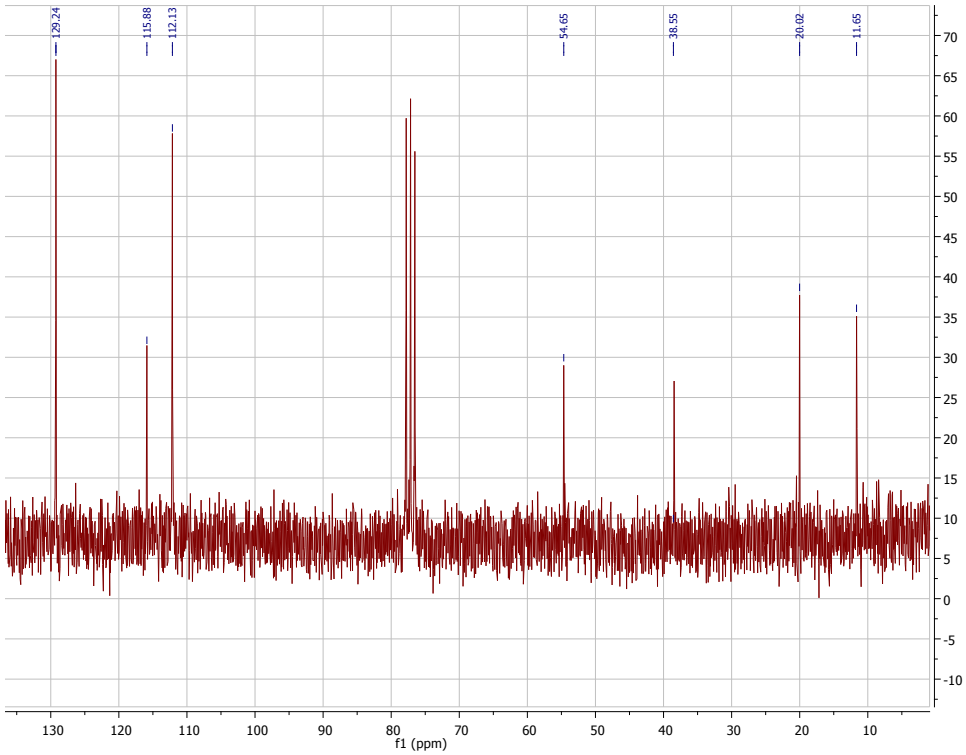




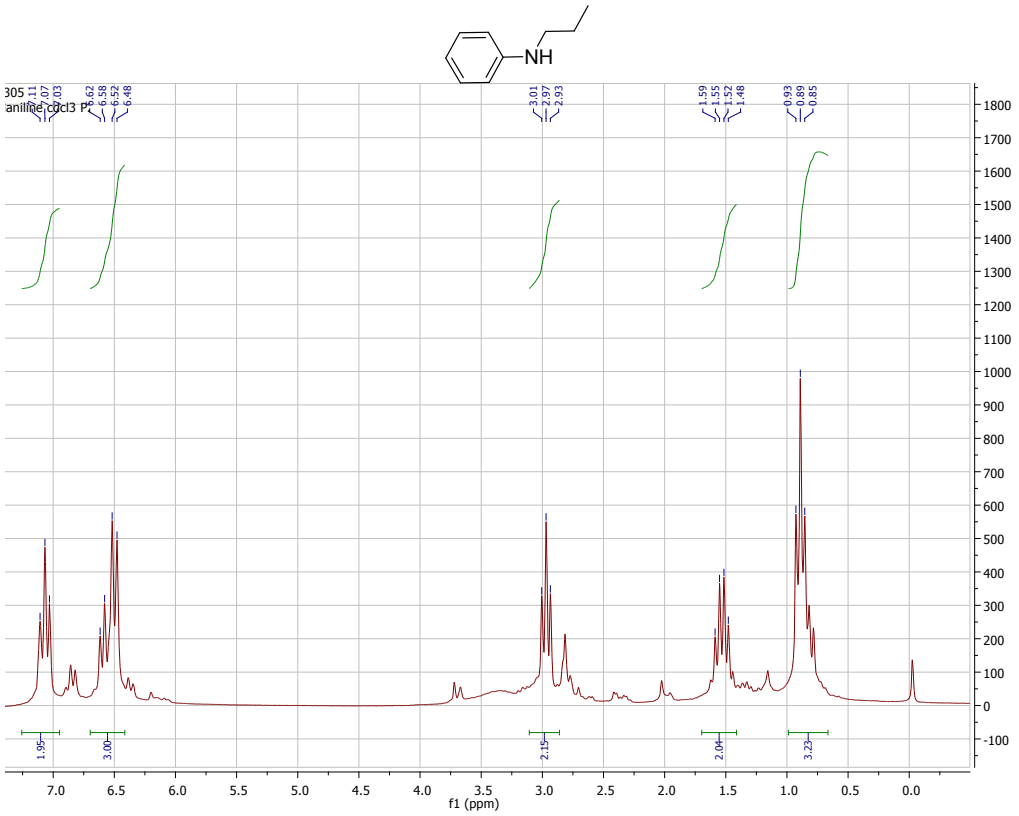
-N-methyl-N-propylaniline (3x): ^{1}H NMR (200 Hz, $CDCl_3$) δ = 0.79-0.91 (m, 3H), 1.51 (q, J = 8.0 Hz, 2H), 2.72 (s, 3H), 3.17 (t, J = 8.0 Hz, 2H), 6.49-6.62 (m, 3H), 7.12 (t, J = 8.0 Hz, 1H) ^{13}C NMR (50 Hz, $CDCl_3$) δ = 11.65, 20.02, 38.55, 54.65, 112.13, 115.88, 129.24.

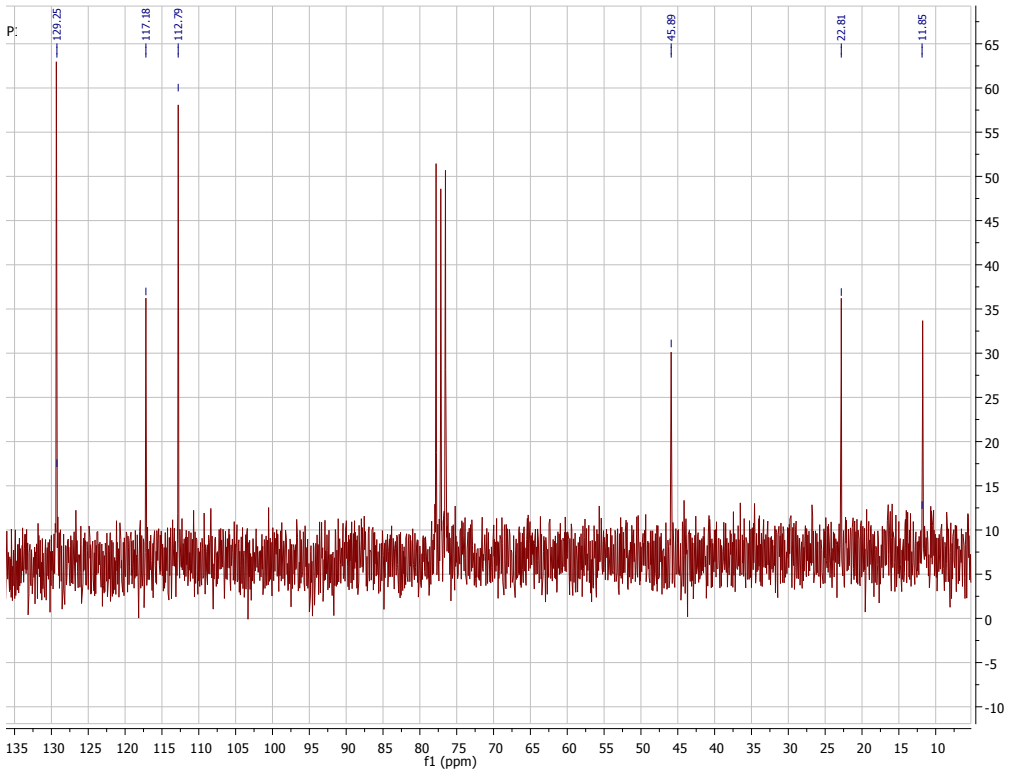




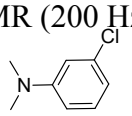


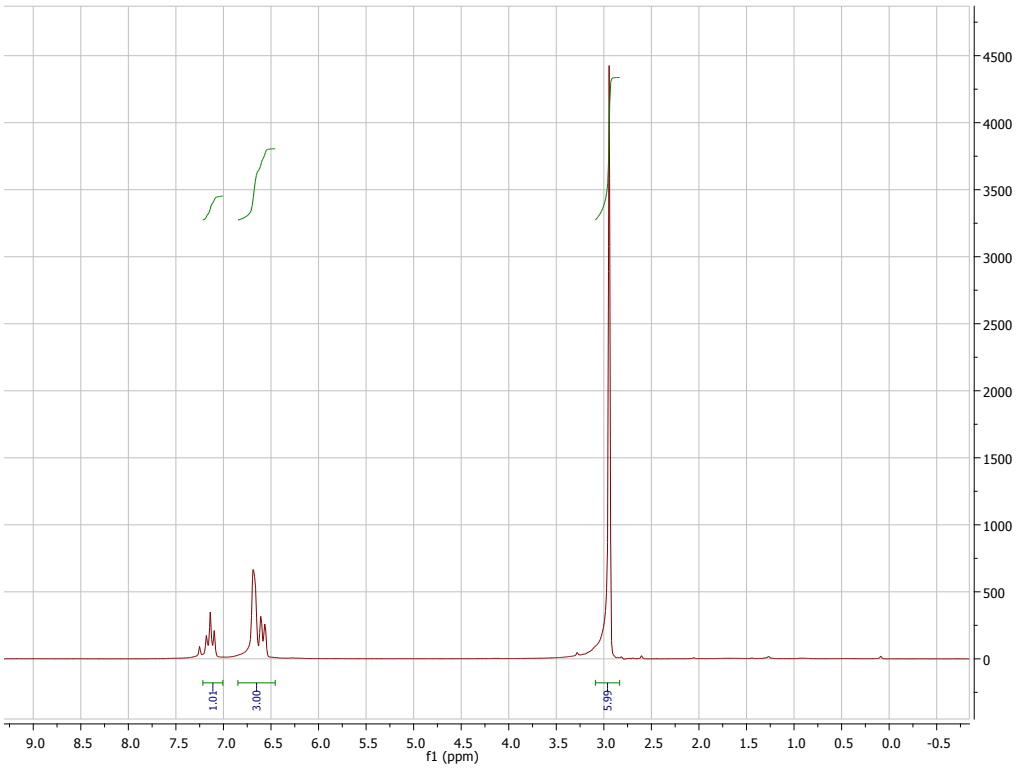
- **N-propylaniline (2x)** : ^{1}H NMR (200 Hz, $CDCl_3$) δ = 0.85-0.93 (m, 3H), 1.52 (q, J = 8.0 Hz, 2H), 2.97 (t, J = 8.0 Hz, 2H), 6.48-6.62 (m, 3H), 7.07 (t, J = 8.0 Hz, 1H) ^{13}C NMR (50 Hz, $CDCl_3$) δ = 11.85, 22.81, 45.89, 112.79, 117.18, 129.25.



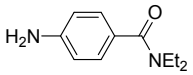


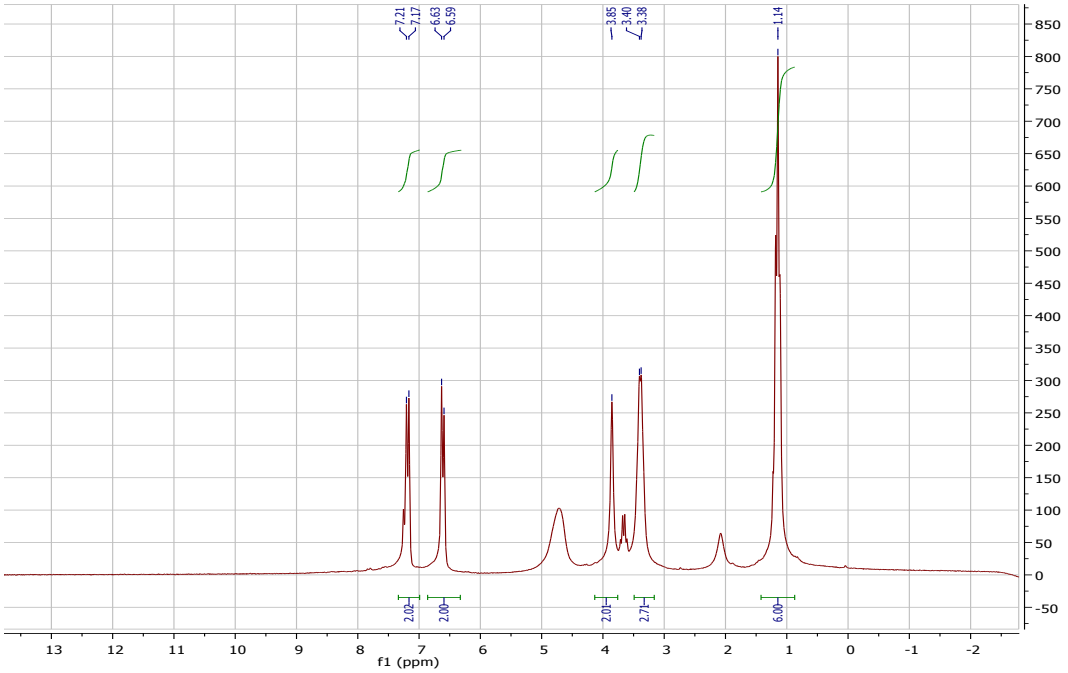
- **N,N-dimethyl-3-chlororaniline (3p) :** ^{1}H NMR (200 Hz, $CDCl_3$) δ = 2.92 (s, 6H), 6.56 (m, 3H), 7.20 (t, J = 8.0 Hz, 1H).





- 4-**Amino-*N*,*N*-diethylbenzamide** : ^{1}H NMR (200 Hz, $CDCl_3$) δ = 1.14 (m, 6H), 3.38 (bs, 2H), 3.85 (bs, 2H), 6.61 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H)





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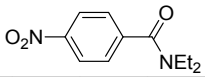
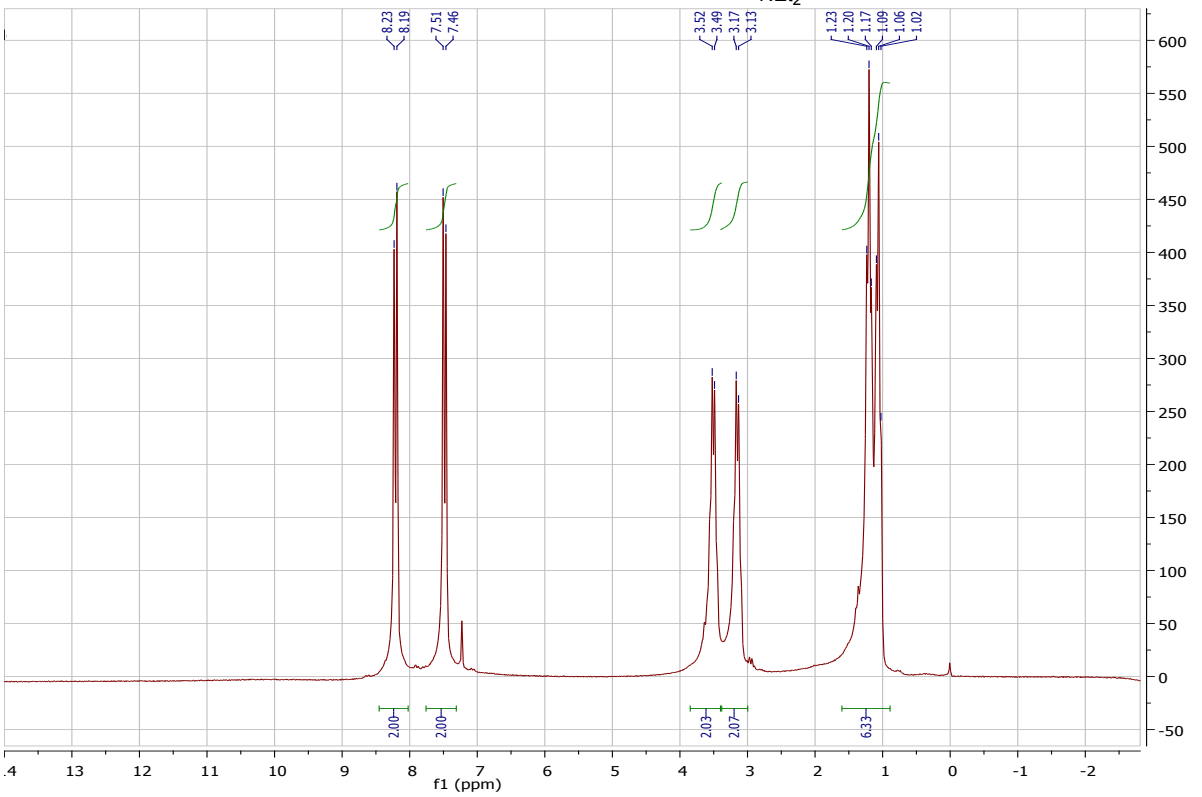
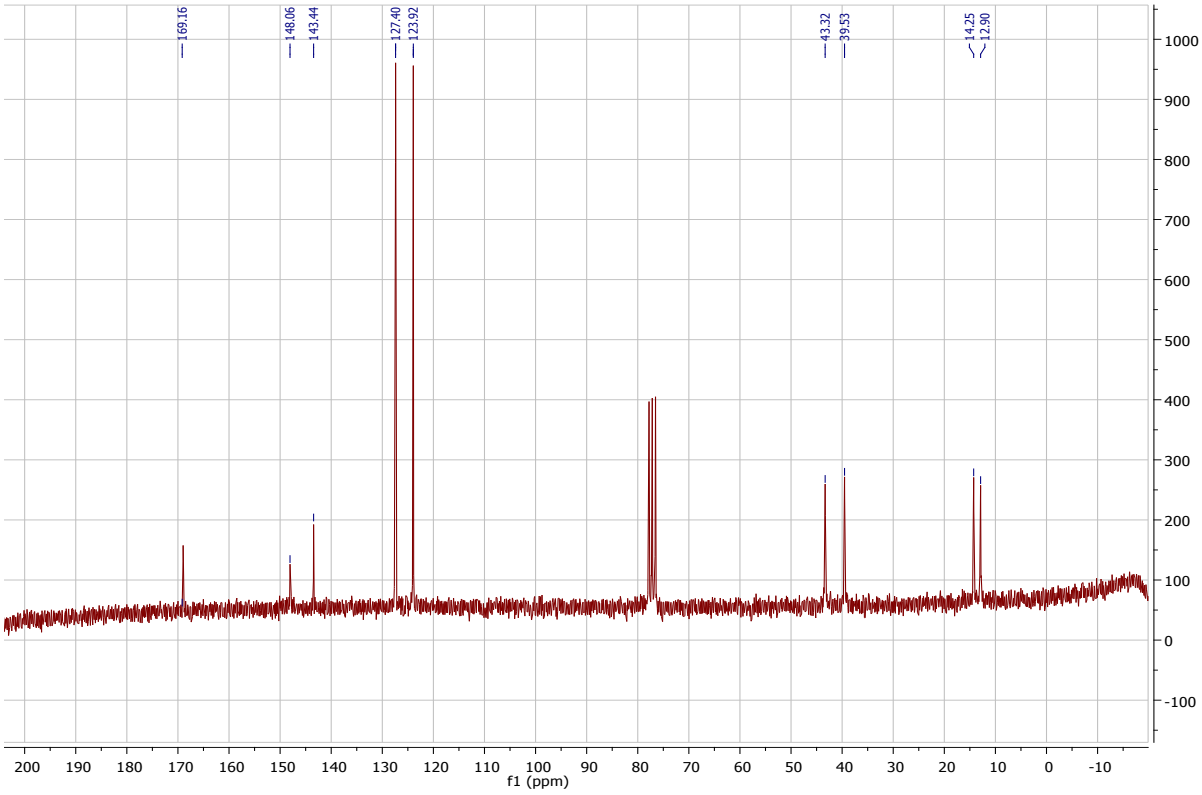
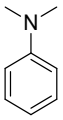
- 4-nitro-N,N-diethylbenzamide (1y): ^{1}H NMR (200 Hz, $CDCl_3$) δ = 8.21 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 3.51 (d, J = 6.8 Hz, 2H), 3.15 (d, J = 6.9 Hz, 2H), 1.13 (dt, J = 28.7, 6.7 Hz, 6H ^{13}C NMR (50 Hz, $CDCl_3$) δ = 12.90,14.25, 39.53, 43.32, 123.92, 127.40, 143.44, 148.06, 169.16.

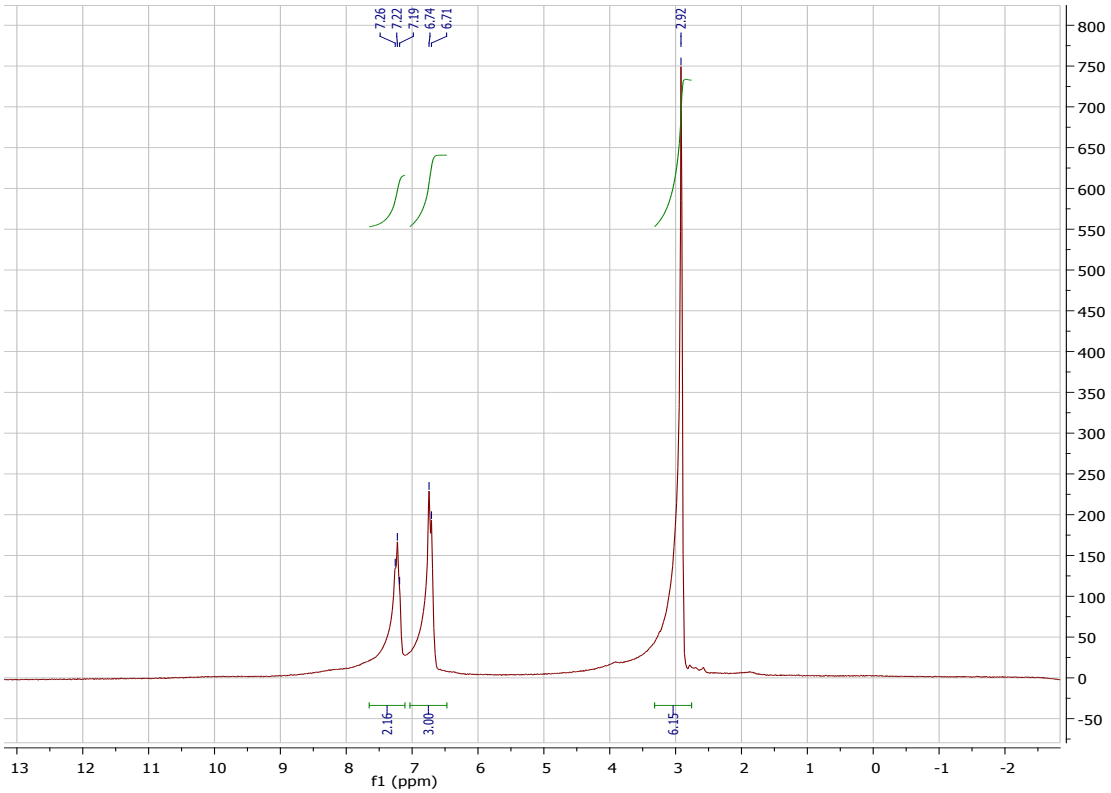


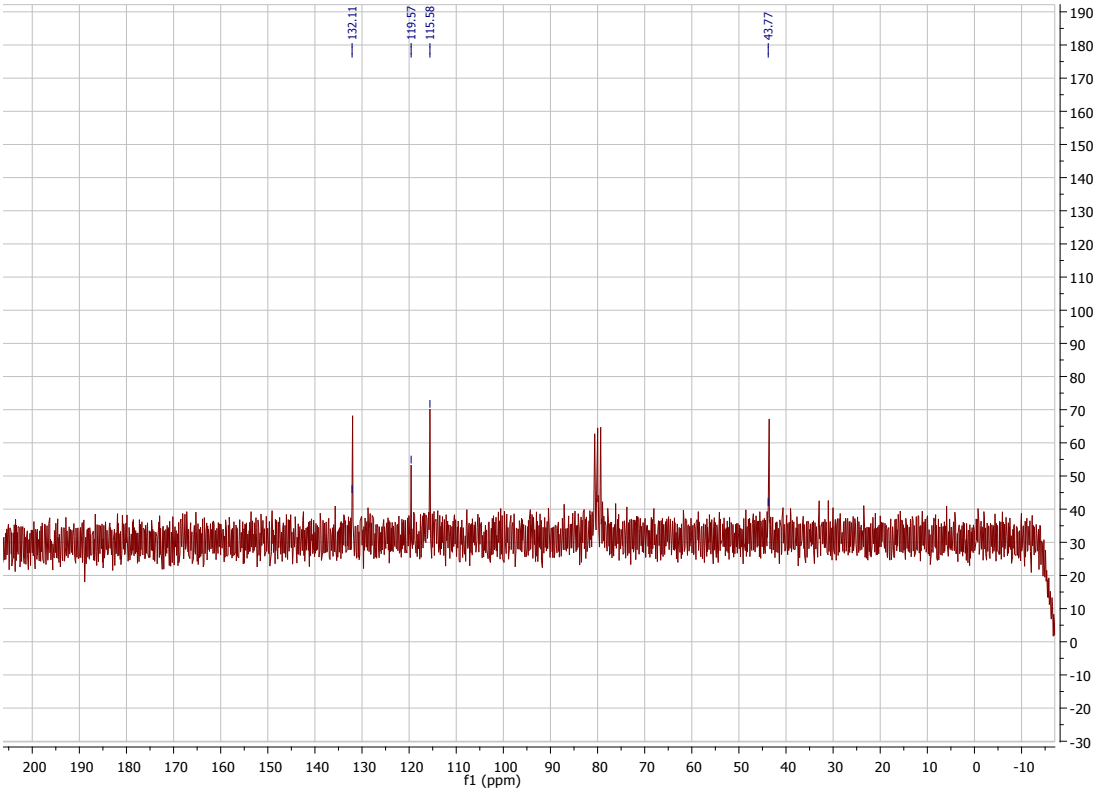




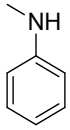
- N,N-dimethylaniline (3a): ^{1}H NMR (200 Hz, $CDCl_3$) δ = 2.92 (s, 6H), 6.72 (m, 3H), 7.22 (m, 2H) ^{13}C NMR (50 Hz, $CDCl_3$) δ = 43.77, 115.58, 119.57, 132.11.

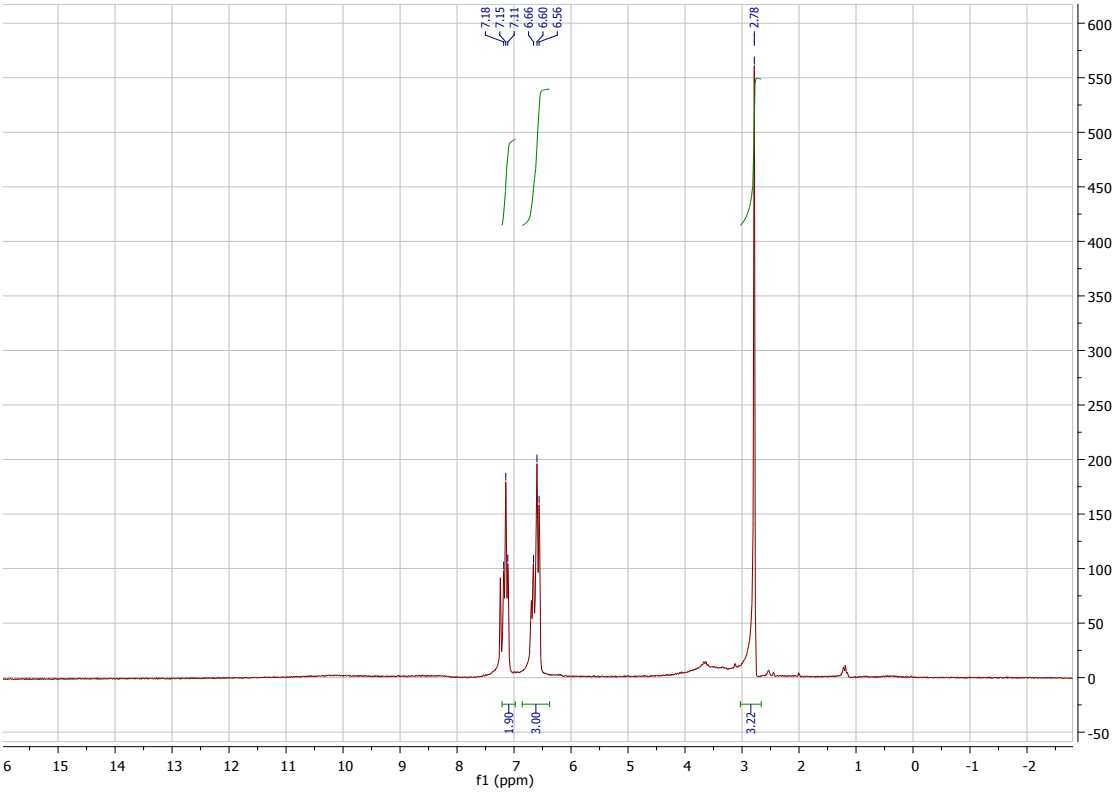


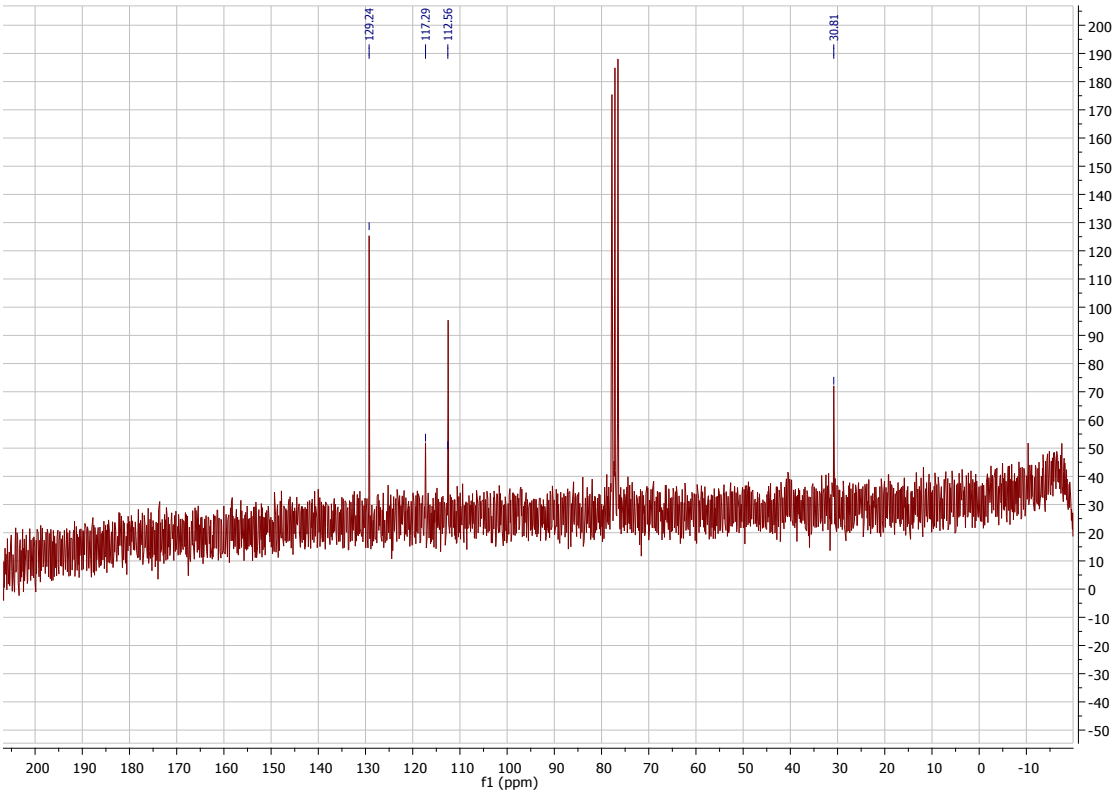




-N-methylaniline (2a): ^{1}H NMR (200 Hz, $CDCl_3$) δ = 2.78 (s, 3H), 6.60 (m, 3H), 7.15 (t, J= 8.0 Hz, 2H) ^{13}C NMR (50 Hz, $CDCl_3$) δ = 30.81, 112.56, 117.29, 129.24.







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