

Selective hydrogenation of amides and imides over heterogeneous Pt-based catalysts

Ruiyang Qu, Shuxin Mao, Jana Weiß, Vita A. Kondratenko, Evgenii V. Kondratenko, Stephan Bartling, Haifeng Qi, Annette-Enrica Surkus, Kathrin Junge*, and Matthias Beller*

Leibniz-Institut für Katalyse e.V., Albert-Einstein Straße 29a, 18059 Rostock, Germany

*Correspondence to: Kathrin.Junge@catalysis.de; Matthias.Beller@catalysis.de

Contents

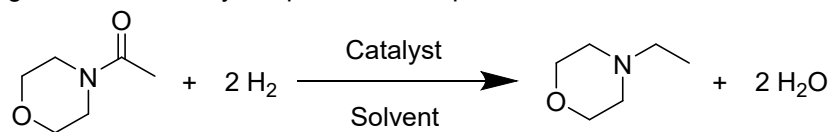
1. General remarks
2. Solvent screening
3. Time on line plot
4. Catalyst recycling
5. Analysis of catalysts before and after reaction
6. Other substrates
7. Comparison of results in the literatures
8. Characterization data for products
9. ^1H NMR and ^{13}C NMR spectra for products
10. References

1. General remarks

Unless otherwise stated, reactions were performed in autoclaves. Solvents were used directly without further purification. Gas chromatography was performed on a HP 6890 with a HP5 column (Agilent). NMR spectra were recorded on Bruker AV 300 spectrometers. All chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in Hz. All chemical shifts are reported relative to CDCl_3 peaks (δ (ppm) = 7.26 for ^1H NMR and δ (ppm) = 77.16 for ^{13}C NMR, respectively).

2. Solvent screening

Table S1. Hydrogenation of 4-acetylmorpholine in the presence of different solvents.



Entry	Solvent	Selectivity / %	Yield / %
1	EtOH (>99.9% HPLC grade)	99	80
2	EtOH (96% HPLC grade)	94	15
3	EtOH (>99.9% HPLC grade, 1.92 mL) + H ₂ O (0.08 mL)	92	22
4	MeOH	0	0
5	<i>i</i> -PrOH	63	41
6	2-MeTHF	27	3
7	DME	71	39
8	1,4-Dioxane	96	43
9	Cyclohexane	60	25
10	Toluene	72	31

Reaction conditions: 4-acetylmorpholine (0.5 mmol), Pt-MoO_x/TiO₂ catalyst (2 mol% Pt), solvent (2 mL), reaction temperature (120 °C), H₂ pressure (50 bar), reaction time (16 h). Yield was determined by GC-FID using *n*-hexadecane as an internal standard.

3. Time on line plot

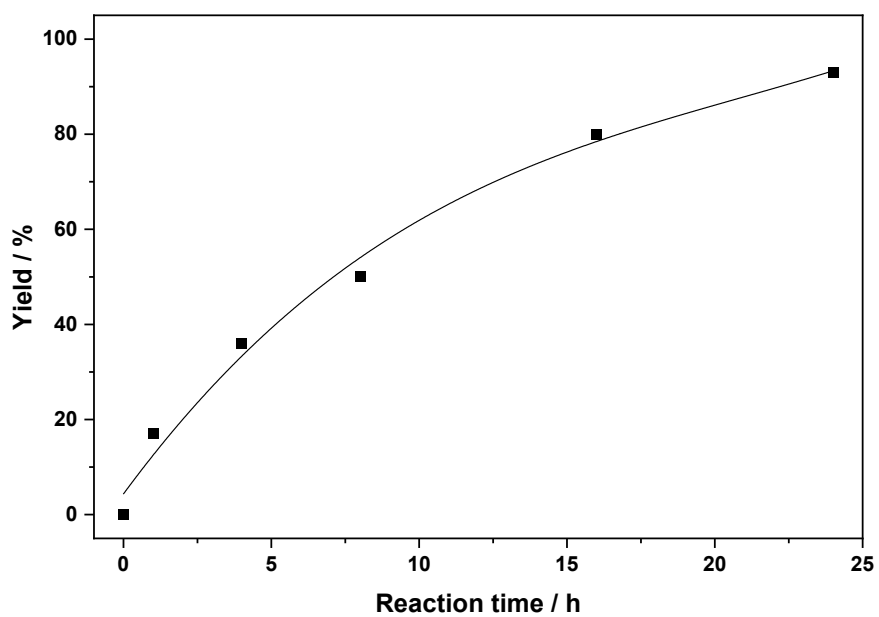


Figure. S1 Time on line plot. Reaction conditions: 4-acetylmorpholine (0.5 mmol), Pt-MoO_x/TiO₂ catalyst (2 mol% Pt), ethanol (2 mL), reaction temperature (120 °C), H₂ pressure (50 bar). Yield was determined by GC-FID using *n*-hexadecane as an internal standard.

4. Catalyst recycling

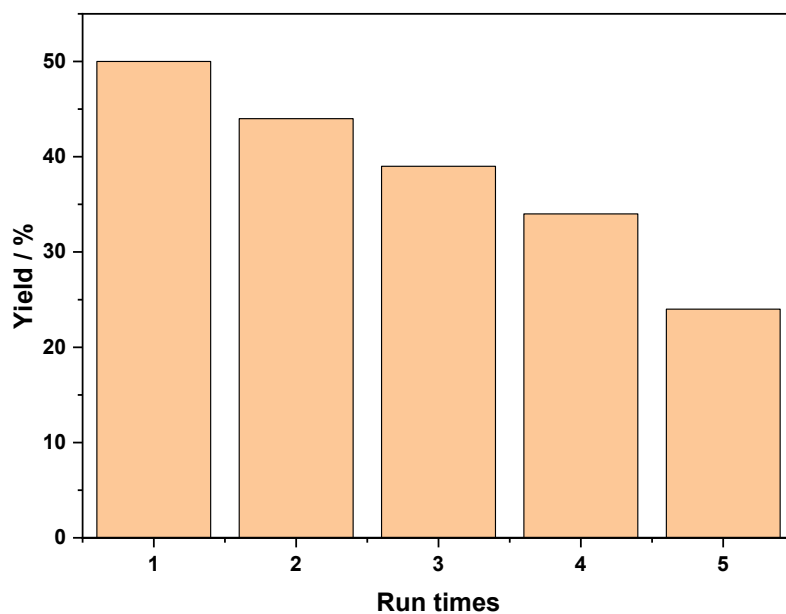


Figure. S2 Catalyst recycling. Reaction conditions: 4-acetylmorpholine (0.5 mmol), Pt-MoO_x/TiO₂ catalyst (2 mol% Pt), ethanol (2 mL), reaction temperature (120 °C), H₂ pressure (50 bar), reaction time (8 h). Yield was determined by GC-FID using *n*-hexadecane as an internal standard.

5. Analysis of catalysts before and after reaction

ICP-OES was performed on Pt-MoO_x/TiO₂ catalysts before and after reaction to explore the possible leaching during the reaction. Each sample was tested twice to reduce the error. As shown in Table S2, slight Pt leaching is observed while Mo leaching is negligible. Hence the slight decrease of activity during the cycles might be mainly due to Pt leaching.

Table S2. ICP-OES analysis of Pt-MoO_x/TiO₂ catalysts before and after reaction.

Samples	Pt loading (wt%)			Mo loading (wt%)		
	1 st	2 nd	average	1 st	2 nd	average
Pt-MoO _x /TiO ₂ before reaction	4.74	4.74	4.74	2.49	2.49	2.49
Pt-MoO _x /TiO ₂ after reaction	4.57	4.65	4.61	2.47	2.51	2.49

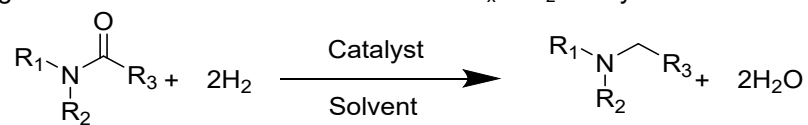
XPS measurements were performed for the catalyst after reaction as well. The results were summarized in Table S3. After reaction, the ratio of Pt⁰ and Mo⁵⁺ species increased, which is mostly likely due to the reducing atmosphere during the reaction, leading to the *in situ* reduction of Pt and Mo. As stated in the manuscript, the increasing amount of Mo⁵⁺ during the reaction would favor the adsorption and activation of C=O bond in amide. Hence this could also be one of the reasons why the developed Pt-MoO_x/TiO₂ catalyst works at a relatively mild reaction condition.

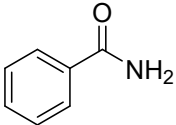
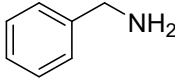
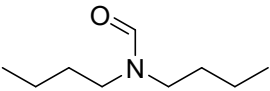
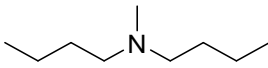
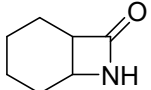
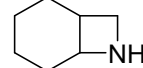
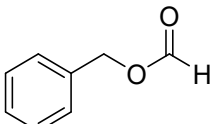
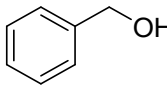
Table S3. Summary of XPS analysis of Pt-MoO_x/TiO₂ catalysts before and after reaction.

Samples	Pt		Mo	
	Pt ⁰ /Pt _{total}	Pt ²⁺ /Pt _{total}	Mo ⁵⁺ /Mo _{total}	Mo ⁶⁺ /Mo _{total}
Pt-MoO _x /TiO ₂ before reaction	68%	32%	27%	73%
Pt-MoO _x /TiO ₂ after reaction	92%	8%	40%	60%

6. Other substrates

Table S4. Hydrogenation of other substrates over Pt-MoO_x/TiO₂ catalyst.



Entry	Substrate	Product	Temperature / °C	Time / h	Selectivity / %	Yield / %
1			120	24	0	0
2			120	24	92	12
3			120	24	0	0
4			120	24	88	87

Reaction conditions: Substrate: 0.5 mmol, [Pt] catalyst (2 mol%), H₂ (50 bar), EtOH (2 mL). Yield was determined by GC-FID using *n*-hexadecane as an internal standard.

7. Comparison of results in the literatures

Table S5. Development of heterogeneous catalysts for amide hydrogenation in recent 15 years.

No.	Scission	Catalysts	Solvents	Temperature / °C	Pressure / bar H ₂	Time / h	Conversion / %	Yield / %	TON	Additives	Refs
1	C-O	Pt-MoO _x /TiO ₂	Ethanol	120	50	24	93	92	47	-	This work
2	C-O	Unsupported Rh/Re	DME	160	100	16	98	88	20	-	S1
3	C-O	Unsupported Ru/Re	DME	160	100	16	95	86	19	-	S1
4	C-O	Unsupported Rh/Mo	DME	160	100	16	94	89	94	-	S2
5	C-O	Rh/Mo/SiO ₂	DME	160	100	16	90	81	150	-	S2
6	C-O	Rh-MoO _x /SiO ₂	DME	140	80	8	>99	63	51	CeO ₂	S3
7	C-O	Unsupported Ru/Mo	DME	160	50	16	99	83	20	-	S4
8	C-O	Re/TiO ₂	<i>n</i> -octane	180	50	24		86	43	-	S5
9	C-O	PtRe/graphite	DME	160	70	20	>99	>99	200	-	S6
10	C-O	PdRe/ graphite	DME	160	70	20	>99	>99	59	-	S6
11	C-O	PdRe/ graphite	DME	140	30	20	>99	>99	168	4Å MS	S6
12	C-O	PtRe/TiO ₂	Hexane	120	20	16	100	100	62	-	S7, S8
13	C-O	Pt/Nb ₂ O ₅	No solvent	180	50	24	100	99	200	-	S9
14	C-O	PtV/HAP	DME	70	30	8	100	99	17	4Å MS	S10
15	C-O	RuWO _x /MgAl ₂ O ₄	CPME	200	50	6	>99	83	200	6 bar NH ₃	S11
16	C-O	Ir/MoO ₃ -KIT-6	DME	130	30	4	85	84	17	-	S12
17	C-O	Ni/LaAlSiO	DME	180	40	-	99	97	-	-	S13
18	C-N	Pd/In ₂ O ₃	Toluene	160	60	15	>99	92	13	-	S14
19	C-N	Ru/CeO ₂	H ₂ O	60	80	48		93	7	-	S15
20	C-N	Ag/γ-Al ₂ O ₃	1,4-dioxane	150	50	48	99	96	40	<i>t</i> -BuOK	S16

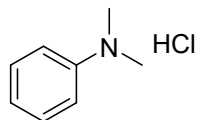
DME: 1,2-dimethoxyethane

CPME: cyclopentyl methyl ether

8. Characterization data for products

Table 2, entry 9

N,N-dimethylaniline hydrochloride

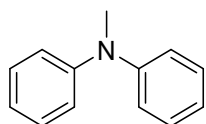


^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.76 (d, $J = 8.2$ Hz, 2H), 7.43 (d, $J = 7.6$ Hz, 3H), 3.15 (s, 6H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 142.85, 130.48, 130.15, 120.78, 46.69.

Table 2, entry 10

N-methyl-*N*-phenylaniline

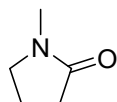


^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.36 – 7.26 (m, 4H), 7.10 – 7.03 (m, 4H), 7.03 – 6.95 (m, 2H), 3.35 (s, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 149.1, 129.3, 121.5, 120.6, 77.6, 77.2, 76.7, 40.4.

Table 2, entry 13

1-methylpyrrolidin-2-one

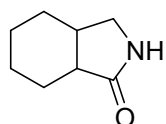


^1H NMR (300 MHz, CDCl_3) δ (ppm) 3.42 – 3.34 (m, 2H), 2.84 (s, 3H), 2.38 (t, $J = 8.1$ Hz, 2H), 2.08 – 1.97 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 175.42, 49.63, 30.82, 29.75, 17.78.

Table 2, entry 15

octahydro-1*H*-isoindol-1-one



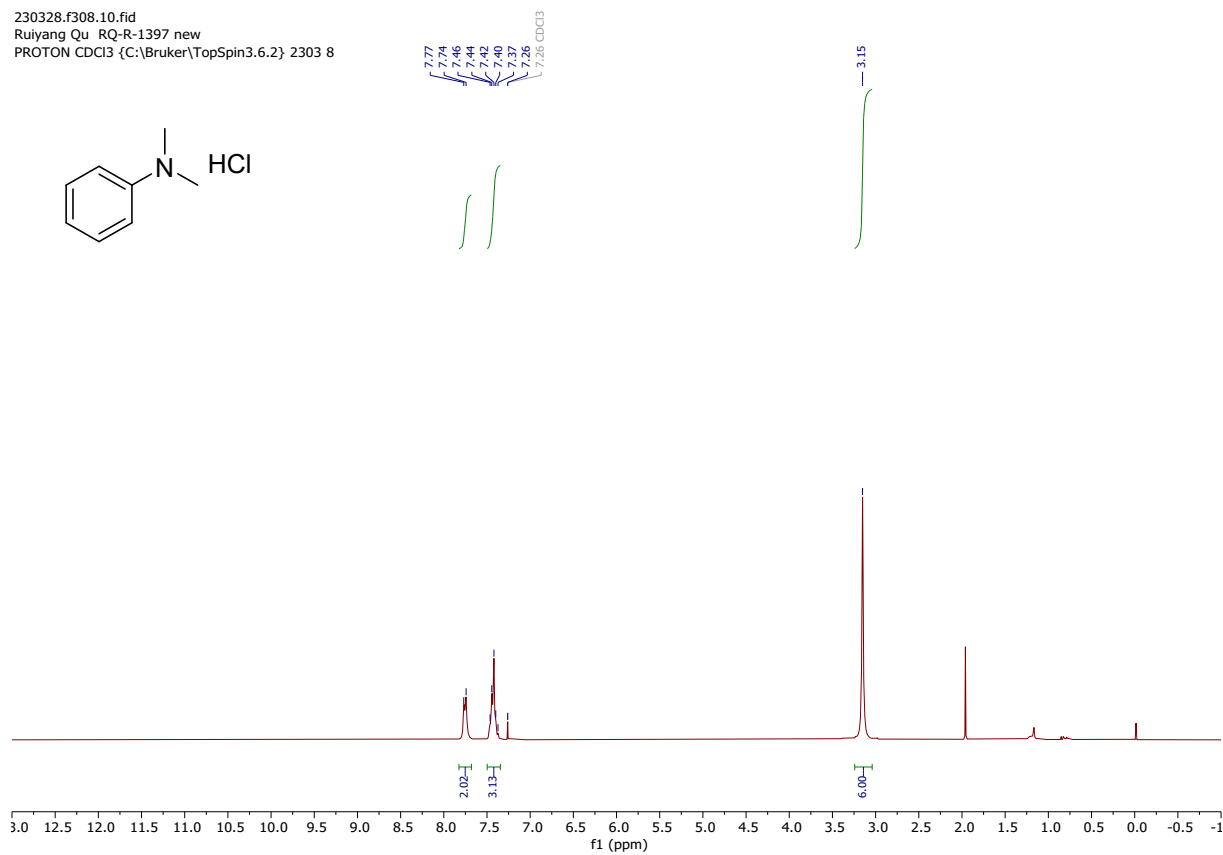
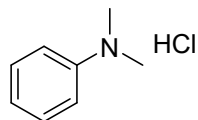
^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.04 (s, 1H), 3.33 (dd, $J = 9.7, 6.0$ Hz, 1H), 2.90 (dt, $J = 9.4, 1.9$ Hz, 1H), 2.44 – 2.26 (m, 2H), 2.01 – 1.89 (m, 1H), 1.66 (dtdd, $J = 11.3, 6.2, 2.9, 1.2$ Hz, 1H), 1.59 – 1.37 (m, 3H), 1.32 – 1.13 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 180.15, 46.51, 41.15, 34.86, 27.82, 23.74, 23.17, 23.01.

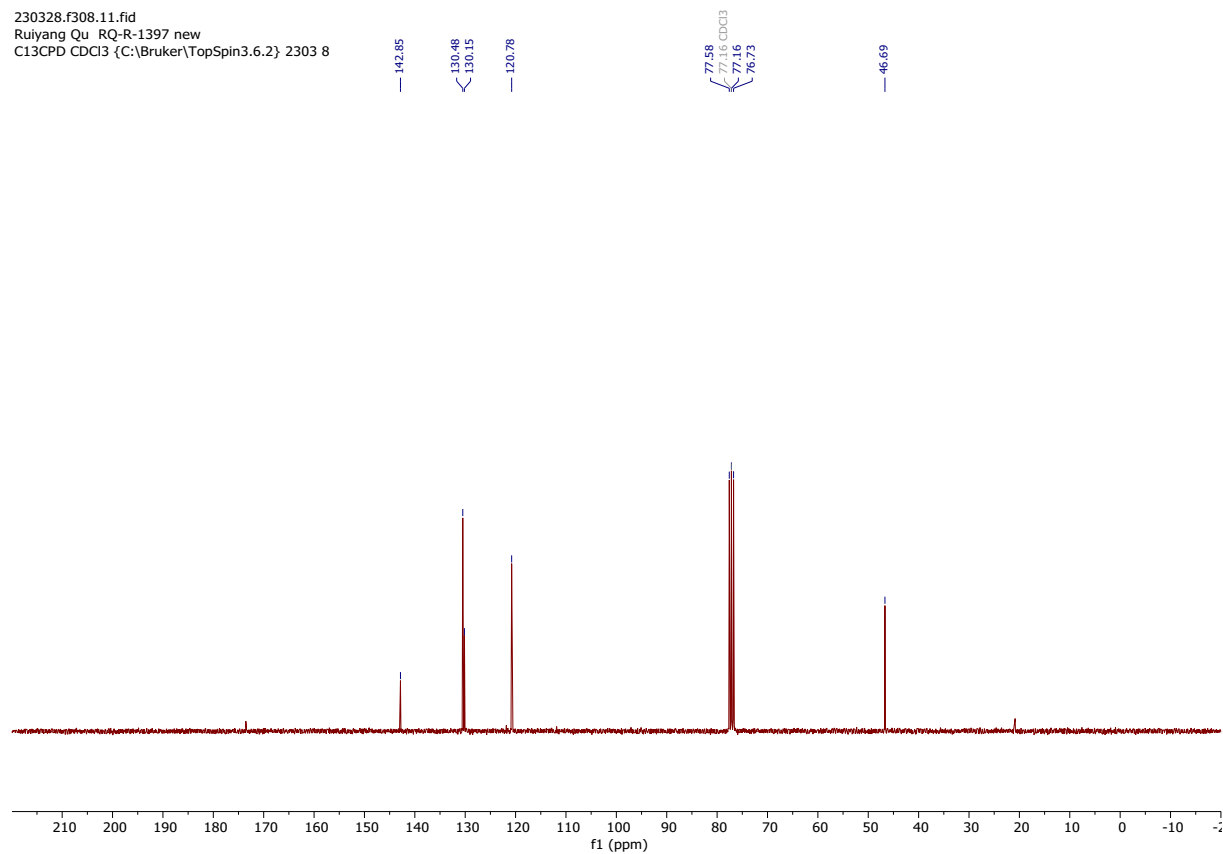
9. ^1H NMR and ^{13}C NMR spectra for products

Original spectra for *N,N*-dimethylaniline hydrochloride:

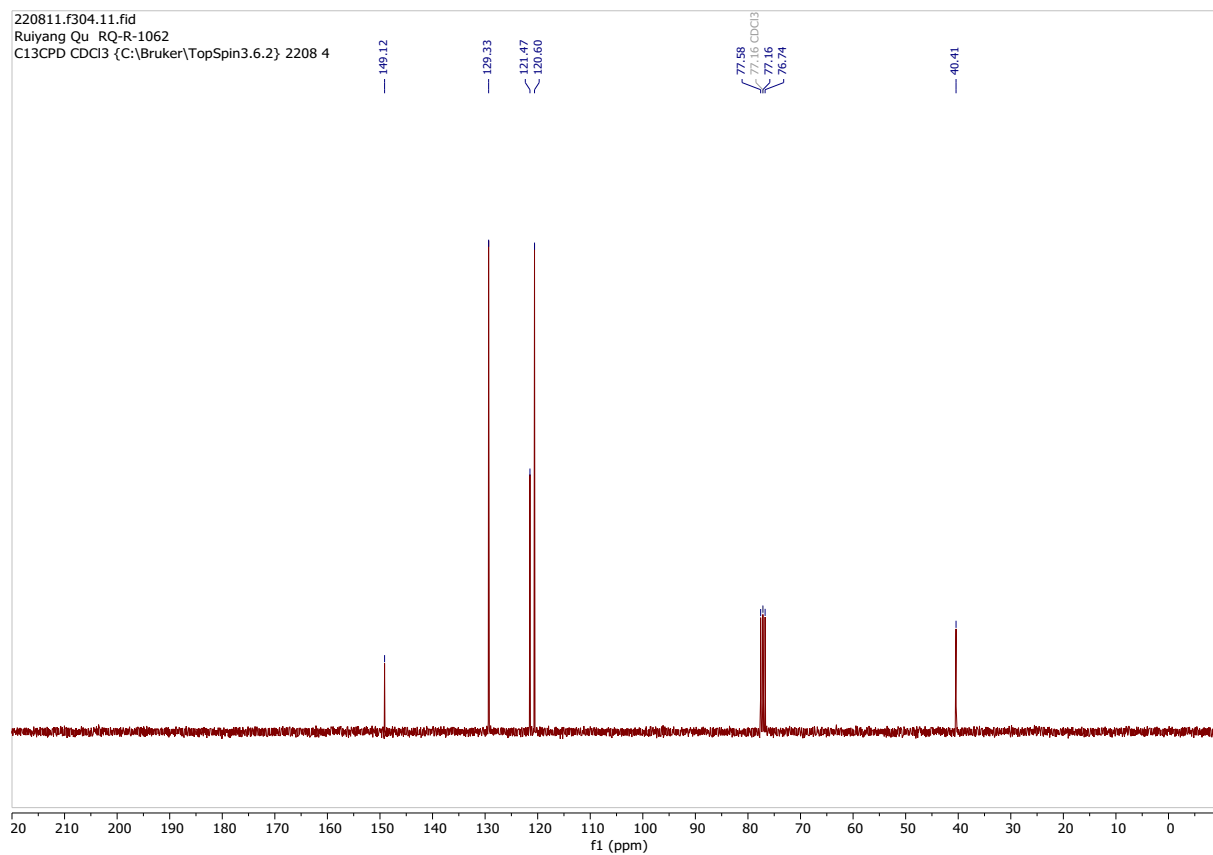
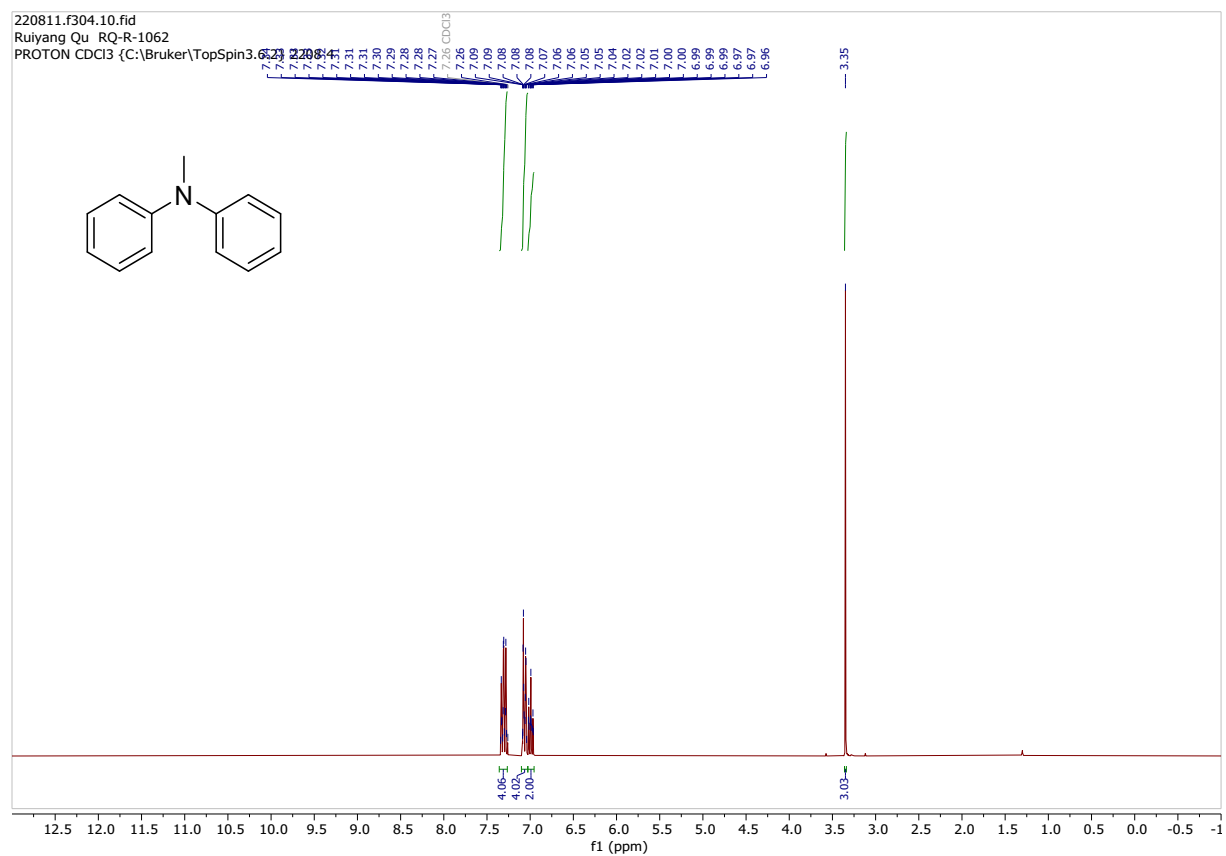
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Ruiyang Qu RQ-R-1397 new
PROTON CDCl₃ {C:\Bruker\TopSpin3.6.2} 2303 8



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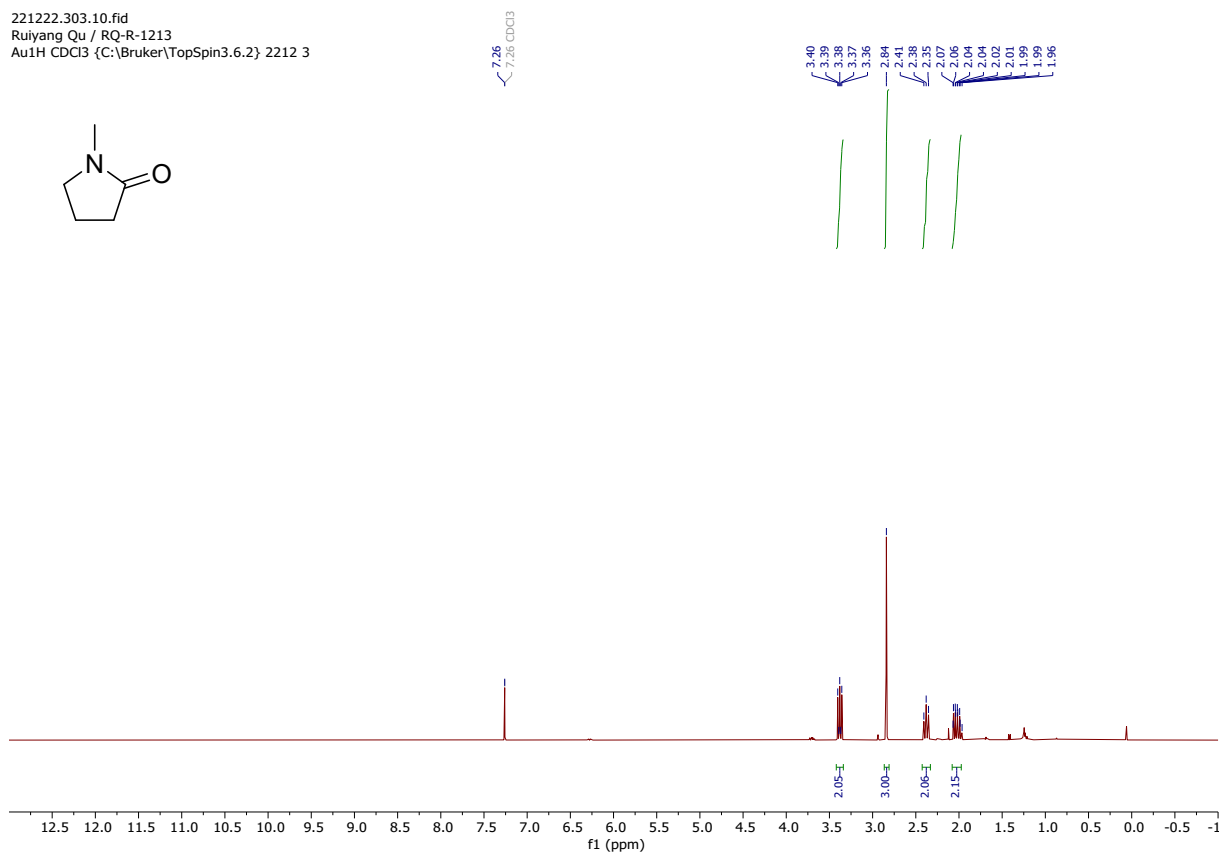
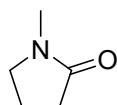


Original spectra for *N*-methyl-*N*-phenylaniline:

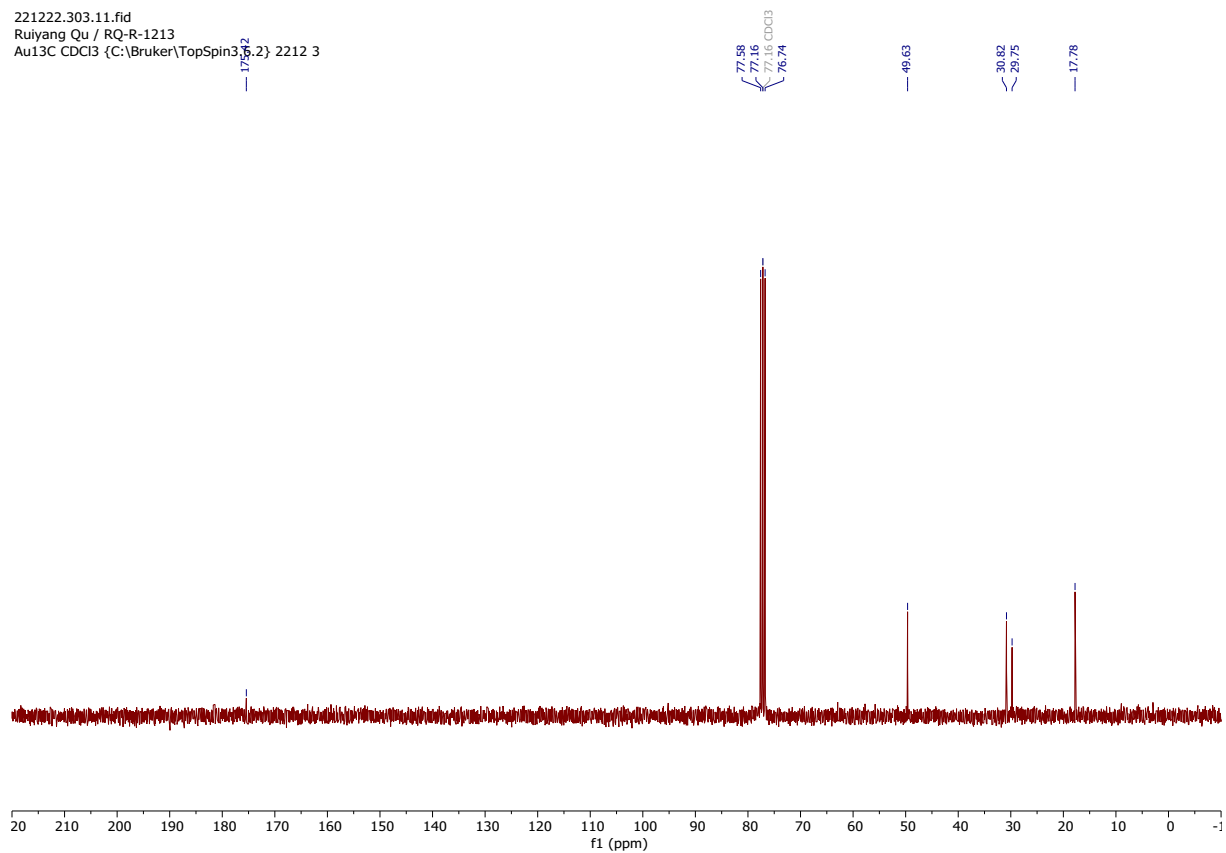


Original spectra for 1-methylpyrrolidin-2-one:

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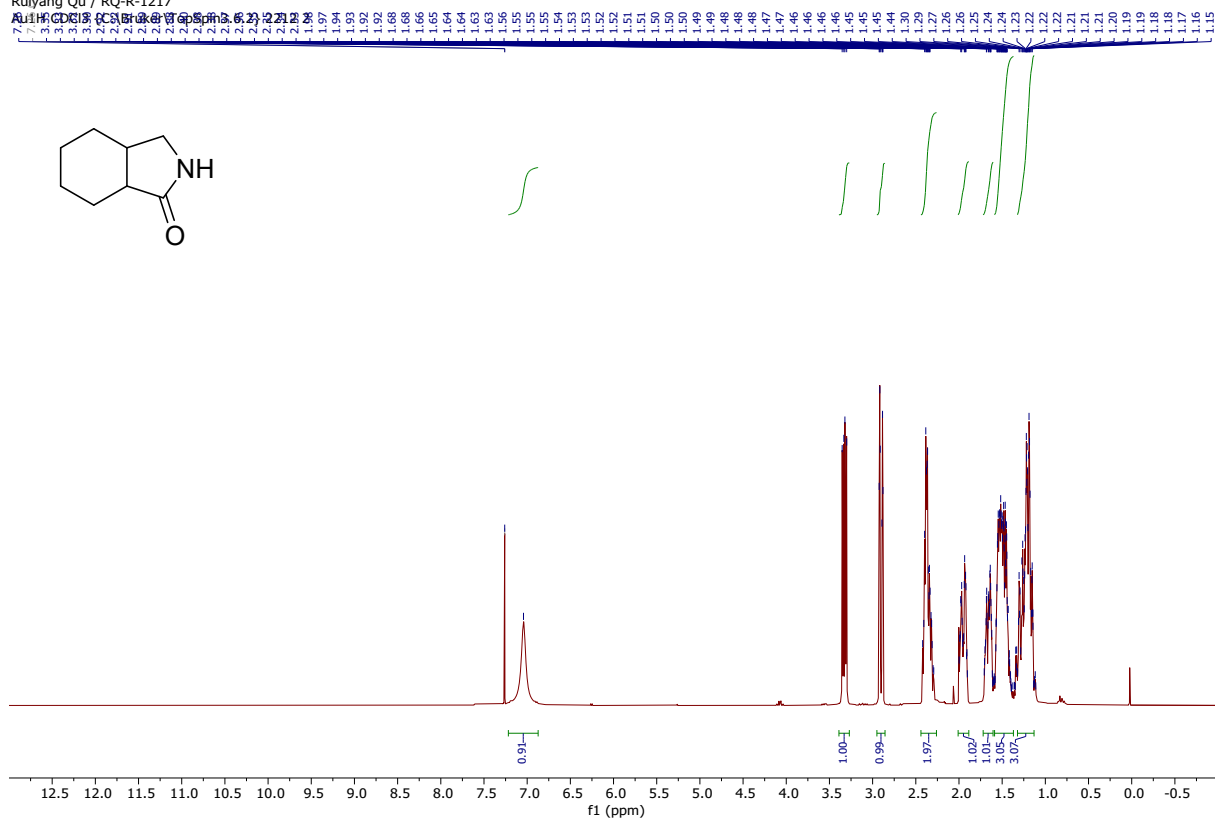
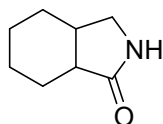


221222.303.11.fid
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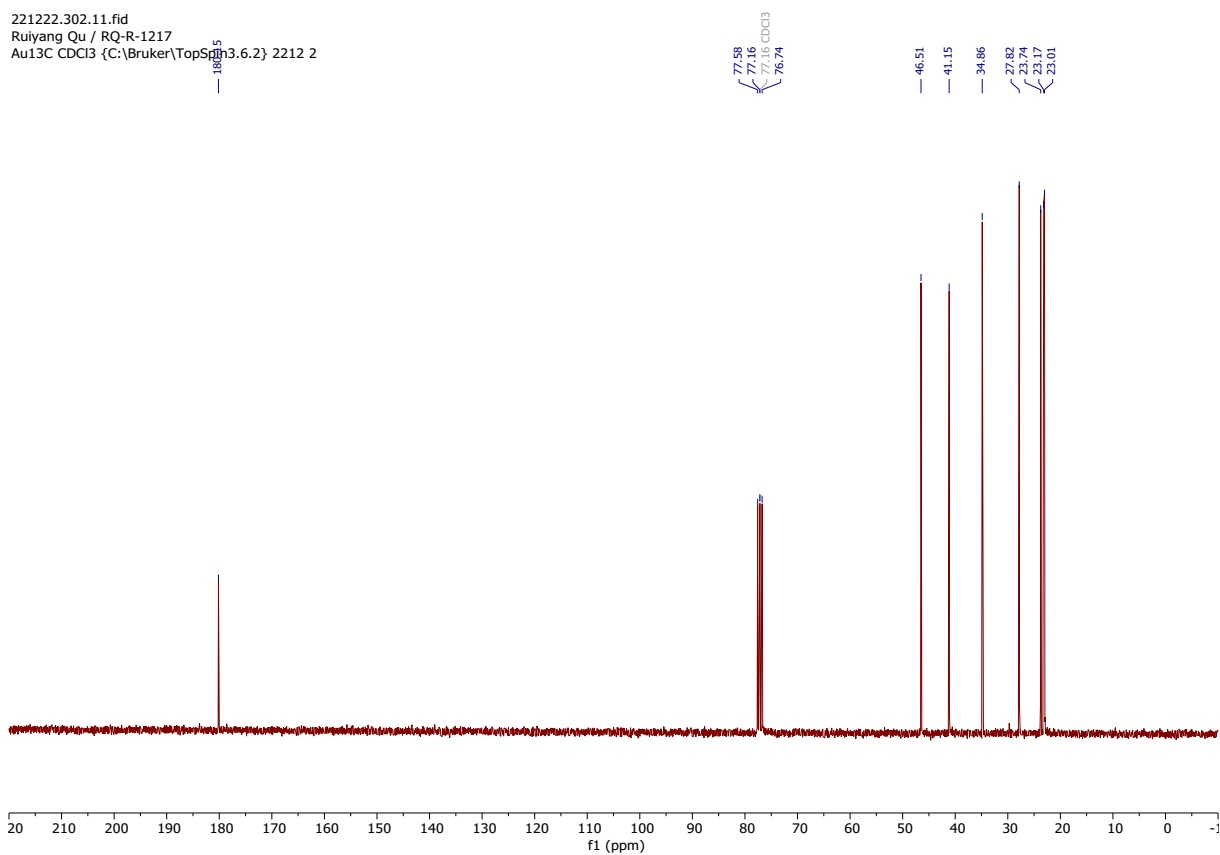


Original spectra for octahydro-1H-isindol-1-one:

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Au13C CDCl3 {C:\Bruker\TopSpin3.6.2\221222.302.10}



221222.302.11.fid
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