Supplement Materials

Figures

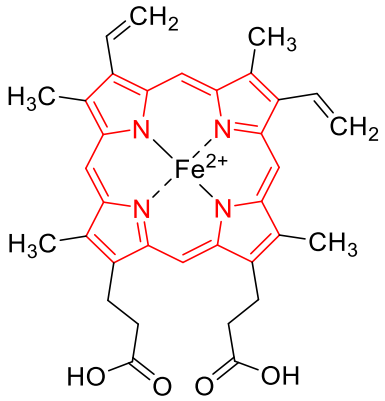


Figure S1. Structural formula of heme b. Tetrapyrrole is indicated in red

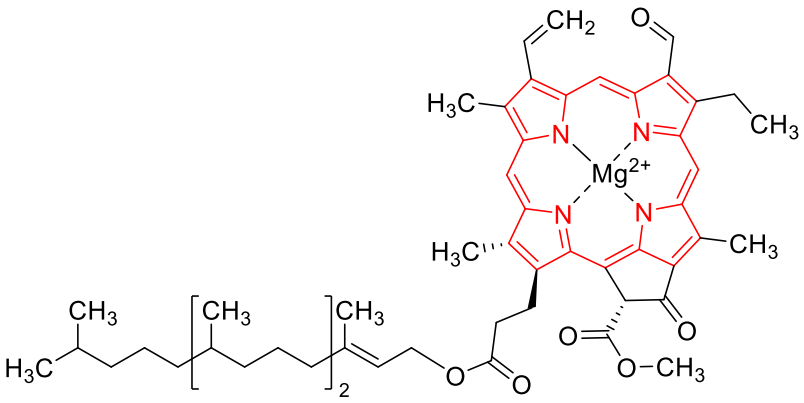


Figure S2. Structural formula of chlorophyll b. Tetrapyrrole is indicated in red

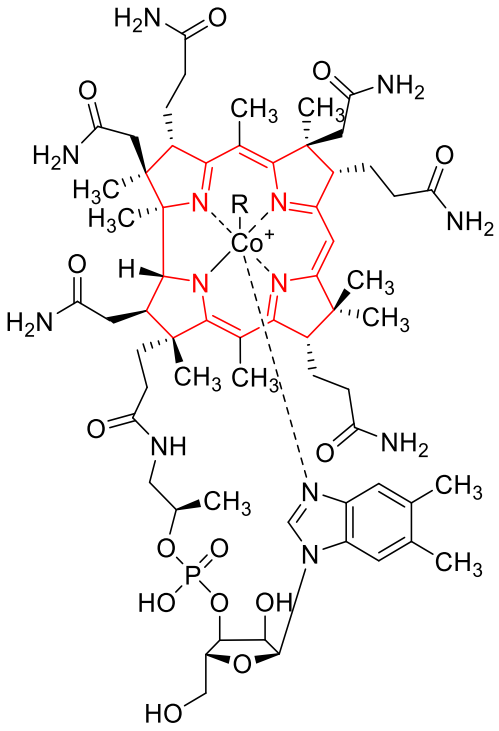


Figure S3. Structural formula of cobalamin (vitamin B12). Tetrapyrrole is indicated in red

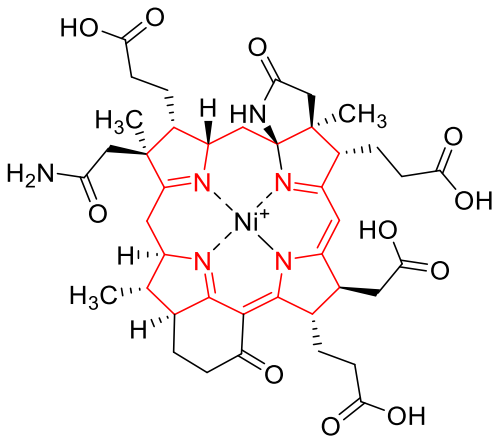


Figure S4. Structural formula of coenzyme F430. Tetrapyrrole is indicated in red

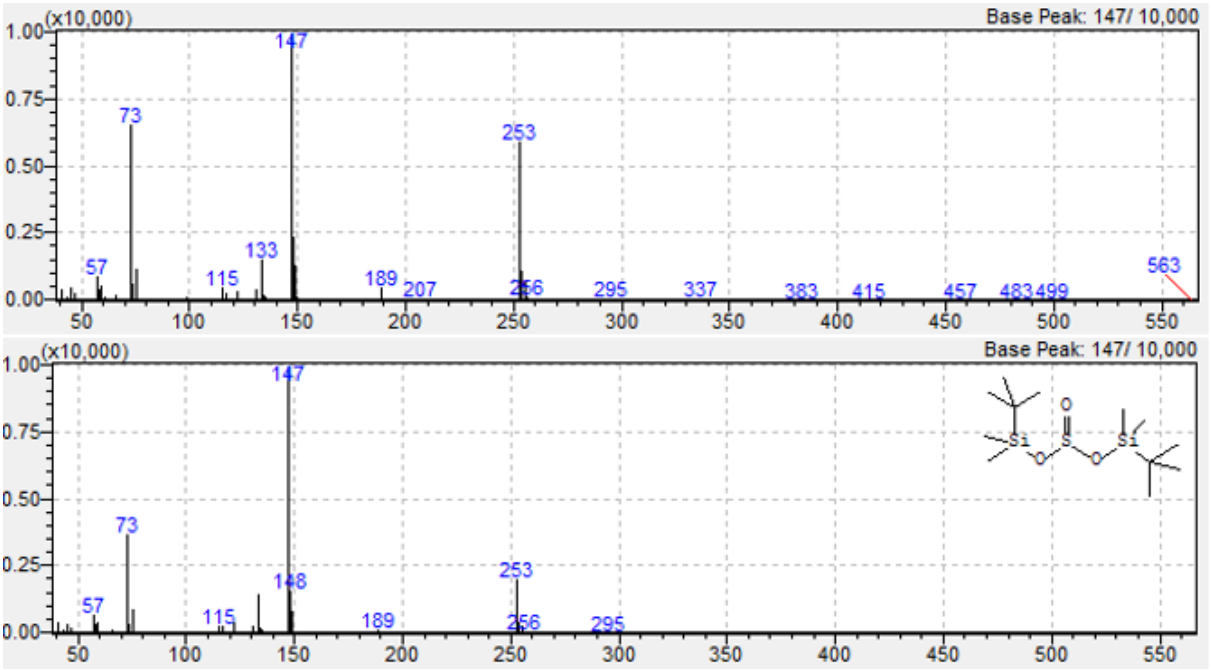


Figure S5. Mass-spectra of Bis(tert-butyldimethylsilyl)-sulfite. First spectrum is of a typical run, second spectrum is from NIST.

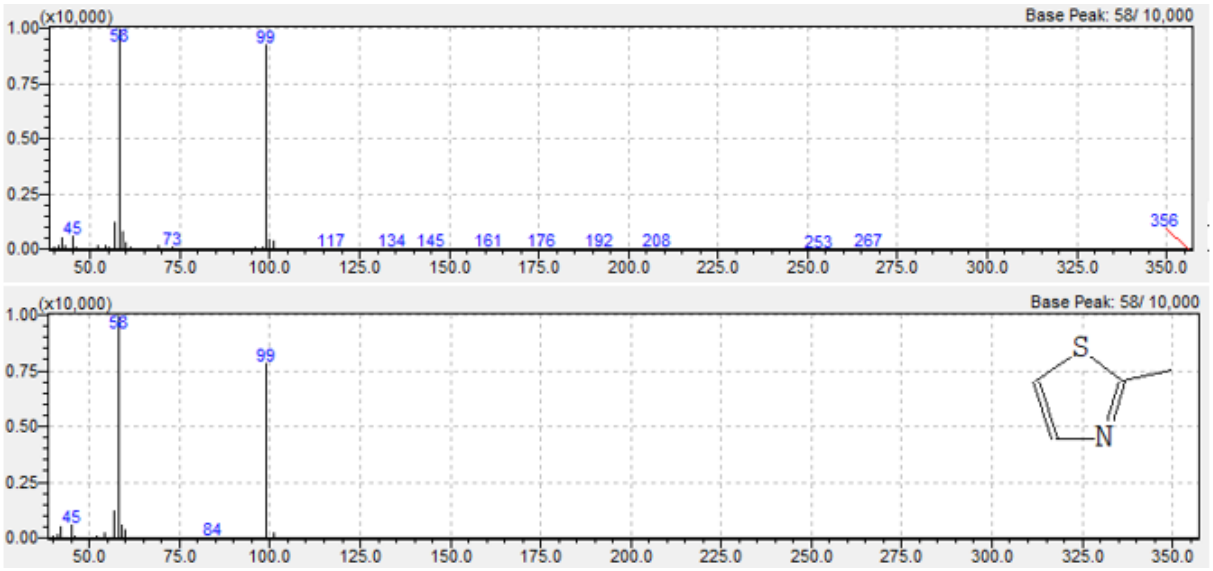


Figure S6. Mass-spectra of 2-methylthiazol. First spectrum is of a typical run, second spectrum is from NIST.

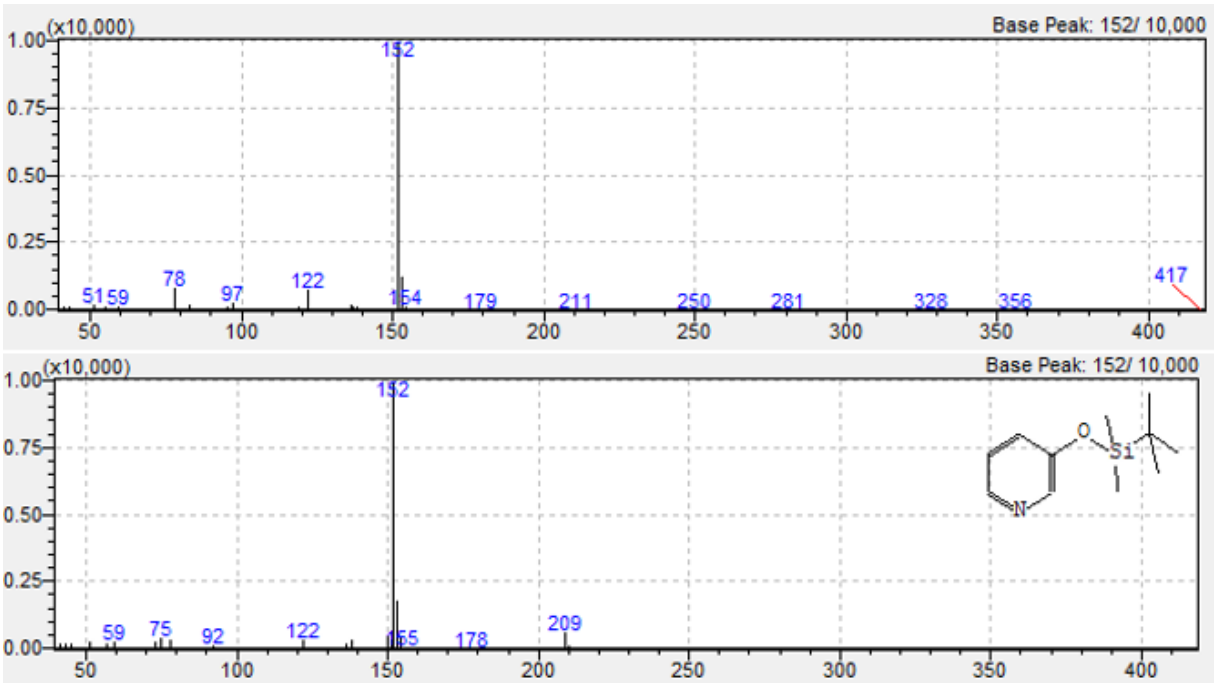
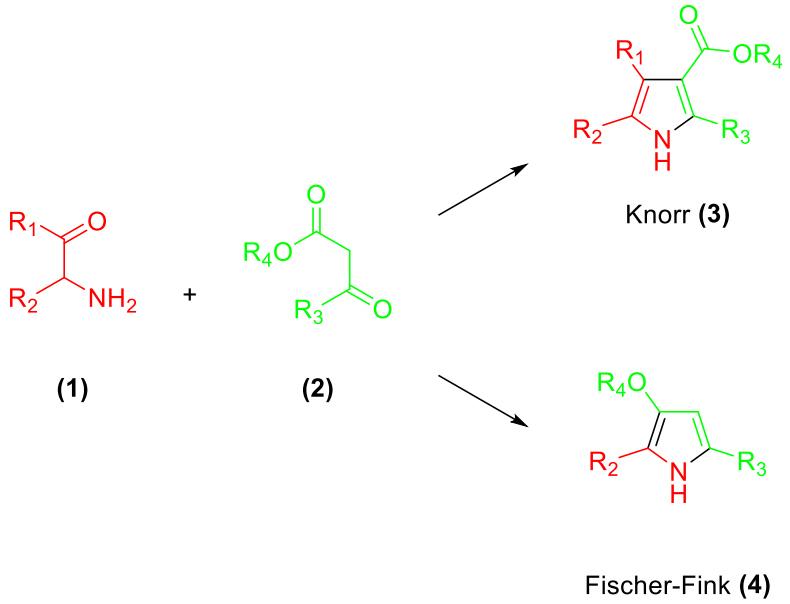
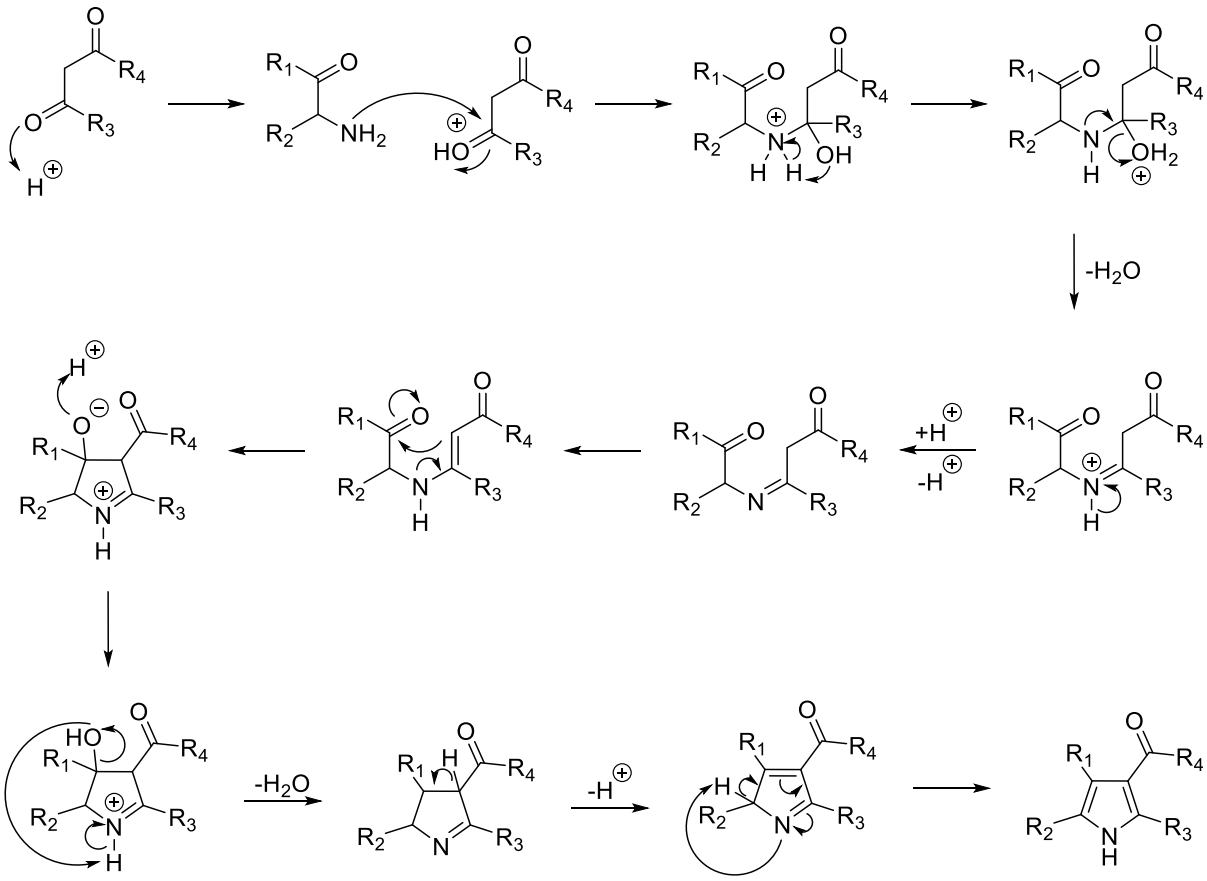


Figure S7. Mass-spectra of 3-tert-Butyldimethylsilyloxypyridine. First spectrum is of a typical run, second spectrum is from NIST.

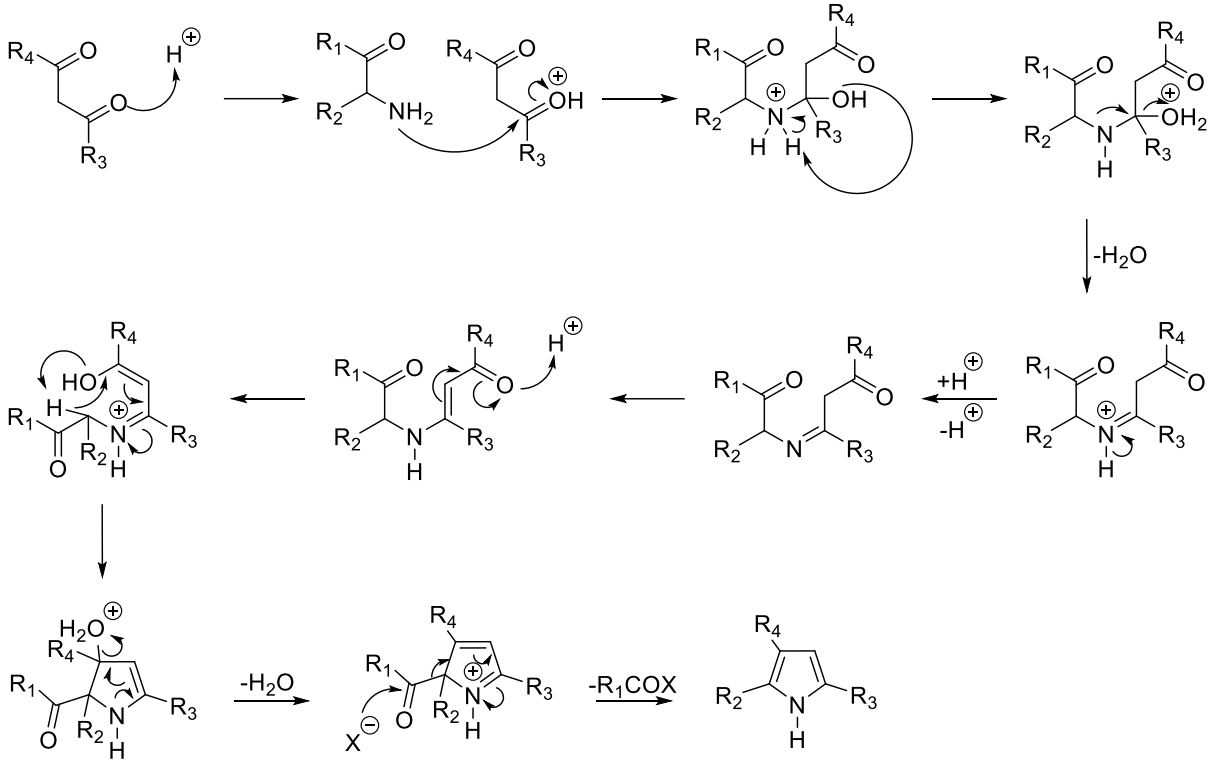
Schemes



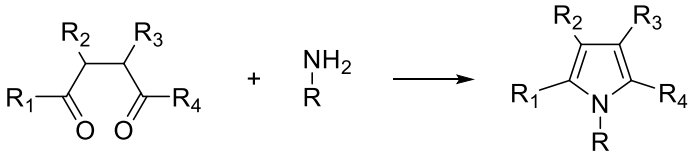
Scheme S1. Knorr-pyrrole synthesis. *Knorr*-product (4) as well as *Fischer-Fink*-product (5) can be observed in this reaction



Scheme S2. Mechanism of the *Knorr*-pyrrole-synthesis

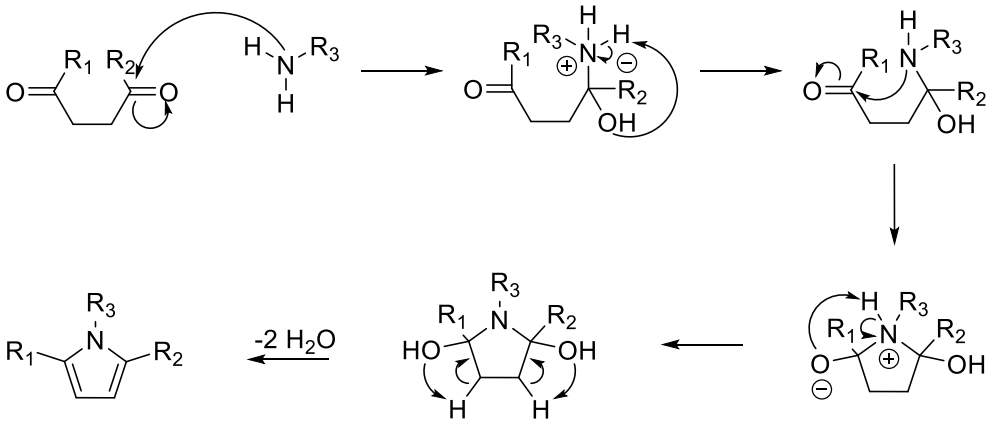


Scheme S3. Mechanism of the *Fischer-Fink*-pyrrole-synthesis

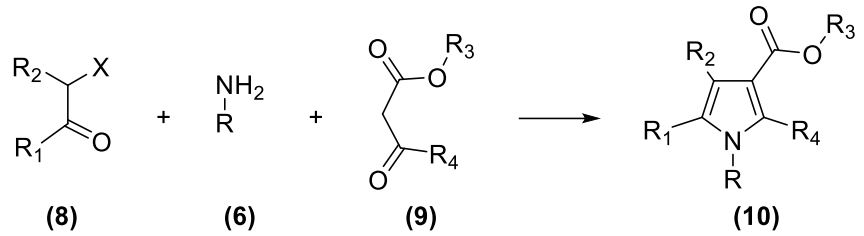


(5) **(6)** **(7)**

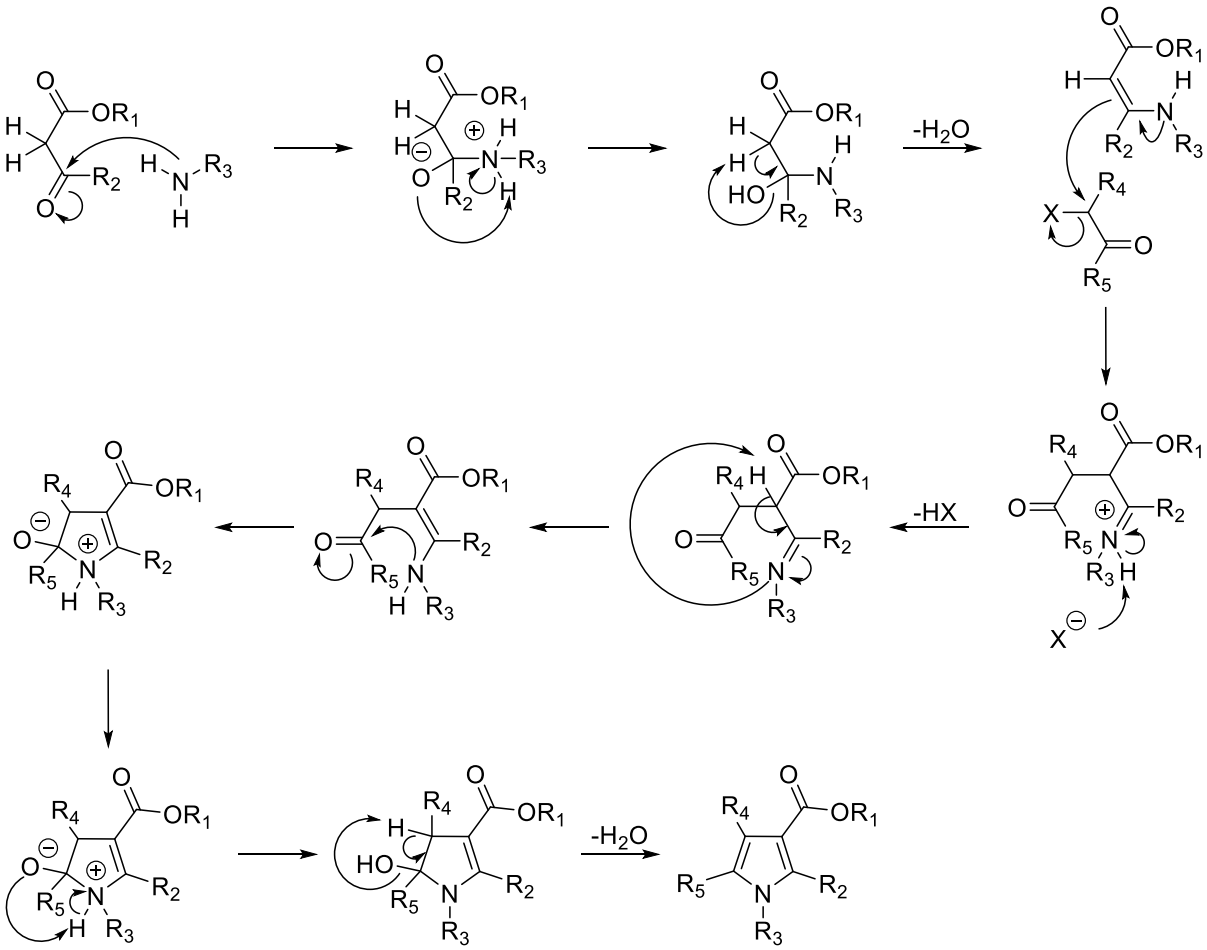
Scheme S4. *Paal-Knorr*-reaction.



Scheme S5. Mechanism of the *Paal-Knorr*-pyrrole-synthesis



Scheme S6. Pyrrole synthesis according to *Hantzsch*.



Scheme S7. Mechanism of the *Hantzsch'sche*-pyrrole-synthesis

Tables

If not stated otherwise, all runs were performed with 1.00 mmol $NiSO_4$, 1.00 mmol Na_2S, 1 mL NaOH, 60 mL CO and 60 mL acetylene for one day at 105 °C. A total reaction volume of 5 mL was achieved by adding argon-saturated water. Yields are given at mol% conversion based on NH_4Cl. pH was measured at the end of the reaction time.

Table S1. Formation of pyrrole depending on pH. Different values were achieved by adding different amounts of 1 M NaOH (run 5, 7, 8, 10, 11, 12, 14), $Ca(OH)_2$ (run 6, 9, 10), 1 M H_2SO_4 (run 1-3) or none of them (run 4). Other parameters as stated above. The defined standard run is run 8 in this table (1 mL NaOH (1M)).

Run	pH	NaOH (1 M)	$Ca(OH)_2$	H_2SO_4 (1 M)	pyrrole	yield
		[mmol]	[mmol]	[mmol]	[µM]	[%]
1	1.8	-	-	1	<0.1	<0.01
2	2.4	-	-	0.5	<0.1	<0.01
3	3.8	-	-	0.1	<0.1	<0.01
4	6.8	-	-	-	0.71	0.071
5	7.1	0.1	-	-	0.65	0.065
6	7.6	-	0.3	-	1.25	0.546
7	7.8	0.5	-	-	2.53	0.253
8	9.1	1.0	-	-	11.38	1.138
9	9.4	-	1.3	-	1.70	0.17
10	9.6	1.5	-	-	1.70	0.17
11	10.3	2.0	-	-	0.75	0.075
12	10.9	3.0	-	-	0.40	0.04
13	10.9	-	2.6	-	0.18	0.018
14	11.3	4.0	-	-	0.16	0.016

Table S2. Formation of pyrrole depending on reaction time. Other parameters as stated above. The defined standard run is run 19 in this table (1 d).

Run	t_{reac}	pH	pyrrole	yield
	[h]		[µM]	[%]
15	0.00	8.7	<0. 1	<0.01
16	0.08	8.8	<0. 1	<0.01
17	0.17	8.8	<0. 1	<0.01
18	0.50	8.7	<0. 1	<0.01
19	1.00	8.8	0.82	0.08
20	2.00	8.9	1.58	0.16
21	4.00	8.7	2.20	0.22
22	8.00	8.5	3.40	0.34

23	24.0	9.1	11.377	1.138
24	48.0	8.2	3.66	0.37
25	72.0	8.6	2.85	0.29
26	96.0	8.5	1.88	0.19
27	120	8.2	1.52	0.15
28	144	8.4	1.00	0.10
29	168	8.3	0.92	0.09

Table S3. Formation of pyrrole depending on concentration of catalyst. Different concentrations of NiS were achieved by adding different amounts of Na_2S to a constant amount of $NiSO_4$ (1 mmol). NiS, the actual catalyst is formed *in situ*. Other parameters as stated above. The defined standard run is run 34 in this table (1.00 mmol Na_2S).

Run	Na2S	pH	pyrrole	yield
	[mmol]		[µM]	[%]
30	0.00	6.9	<0.1	<0.01
31	0.25	7.2	<0.1	<0.01
32	0.50	7.5	0.76	0.08
33	0.75	7.9	0.62	0.06
34	1.00	9.1	11.377	1.138
35	1.25	9.0	4.78	0.48
36	1.50	9.4	2.63	0.26
37	1.75	9.8	0.57	0.06
38	2.00	11.1	0.32	0.03