Electronic Supplementary Material (ESI) for Green Chemistry

Supporting information for

On the usefulness of Life Cycle Assessment in early chemical methodology development: the case of organophosphorus catalyzed Appel and Wittig reactions

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Table of Contents

Results

Appel reactions

Table 1 Cumulative Energy Demand (CED) of the classic and catalytic Appel reactions, before and after correction for the solvent treatment as predicted by Capello's ecosolvent tool.[1]

CED (MJ-eq)	*No solvent treatment*				*Corrected for solvent treatment*			
		Catalytic Appel reactions				*Catalytic Appel reactions*		
Category	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**
MeCN	537	603	605	604	121	137	139	138
PPh_3	152				93			
CCl_3	7				11			
DECM		182	182	181		134	134	133
Silane		10	126	115		11	66	66
Rest	8	10	13	11	8	10	13	11
Total	*704*	*805*	*926*	*911*	*233*	*292*	*352*	*348*

Table 2. Greenhouse gas emissions (GHG) of the classic and catalytic Appel reactions, before and after correction for the solvent treatment as predicted by Capello's ecosolvent tool.[1]

GHG emissions (CO_2-eq)	*No solvent treatment*				*Corrected for solvent treatment*			
		Catalytic Appel reactions				*Catalytic Appel reactions*		
Category	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**
MeCN	18.8	21.1	21.2	21.2	12.4	14.0	14.1	14.1
PPh_3	4.8				5.8			
CCl_3	0.3				0.3			
DECM	0.0	6.0	6.0	6.0		6.4	6.4	6.4
Silane	0.0	0.4	4.3	3.8		0.5	4.7	4.2
Rest	0.9	1.0	1.0	1.0	0.9	1.0	1.0	1.0
Total	*24.8*	*28.6*	*32.5*	*32.0*	*19.4*	*21.9*	*26.2*	*25.6*

Wittig reactions

Table 3. Cumulative Energy Demand (CED) of the classic and catalytic Wittig reactions, before and after correction for the solvent treatment as predicted by Capello's ecosolvent tool.[1]

CED (MJ-eq)	*No solvent treatment*				*Corrected for solvent treatment*			
		Catalytic Wittig reactions				*Catalytic Wittig reactions*		
Category	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**
Toluene	19	23	23	23	5	5	5	5
EPPA	271				117			
ECA		42	42	42		20	20	20
Na_2CO_3		4	4	4		4	4	4
Silane		10	126	115		10	66	66
Rest	8	9	8	12	8	9	8	12
Total	*298*	*89*	*203*	*196*	*130*	*50*	*104*	*107*

Table 4. Greenhouse gas emissions (GHG) of the classic and catalytic Wittig reactions, before and after correction for the solvent treatment as predicted by Capello's ecosolvent tool.[1]

GHG emissions (CO_2-eq)	*No solvent treatment*				*Corrected for solvent treatment*			
		Catalytic Wittig reactions				*Catalytic Wittig reactions*		
Category	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**	**Classic**	**PMHS**	**$PhSiH_3$**	**Ph_2SiH_2**
Toluene	0.5	0.5	0.5	0.5	0.7	0.8	0.8	0.8
EPPA	7.9				10.4			
ECA		1.2	1.2	1.2		1.6	1.6	1.6
Na_2CO_3		0.2	0.2	0.2		0.2	0.2	0.2
Silane		0.4	4.3	3.8		0.4	4.7	4.2
Rest	0.8	1.0	0.6	1.0	0.8	1.0	0.6	1.0
Total	*9.1*	*3.4*	*6.8*	*6.7*	*11.9*	*4.1*	*8.0*	*7.7*

Table 5 Original and alternative impacts by variation of the diethyl chloromalonate (DECM) process. For the alternative processes, stoichiometric amounts of ethanol and chlorine were used instead of the large excess used in the original process.

	CED (MJ-eq)				**GHG emissions (kg CO_2 eq)**			
	DECM		*Total impact*		*DECM*		*Total impact*	
	org.	*alt.*	*org.*	***alt.***	*org.*	*alt.*	*org.*	***alt.***
Classic Appel	-	-	233	**233**	-	-	19.4	**19.4**
Catalytic Appel:								
PMHS	182	69	292	**226**	6.0	2.1	26.8	**17.5**
$PhSiH_3$	182	69	352	**287**	6.0	2.1	32.5	**22.0**
Ph_2SiH_2	181	69	348	**284**	6.0	2.1	32.0	**21.4**

Table 6. Sensitivity analysis for the greenhouse gas emissions (in CO_2-eq/functional unit) of the Appel reaction in maximum and minimum deviations from the original total values.

Entry		**Classic Appel**	**PMHS**	**Ph_2SiH_2**	**$PhSiH_3$**
1	1 M concentration	-58%			
	Sensitivity predicted by ecosolvent:				
2	MeCN	+/-29%	+/-27%	+/-21%	+/-22%
3	Et_2O (silane)			+/-3%	+/-3%
4	PhMe	+/-4%			
5	EtOH		+/-3%	+/-3%	+/-3%
6	DEBM process efficiency		+/-35%	+/-32%	+/-33%

Table 7. Sensitivity analysis for the greenhouse gas emissions (in CO_2-eq/functional unit) of the Wittig reaction in maximum and minimum deviations from the original total values as provided by the ecosolvent tool.

Entry		**Classic Wittig**	**PMHS**	**Ph_2SiH_2**	**$PhSiH_3$**
1	PhMe in reaction	+/-6%	+/-12%	+/-6%	+/-6%
2	PhMe (ethylchloroacetate)	+/-6%	+/-15%	+/-7%	+/-7%
3	PhMe (ylide)	+/-16%			
4	Et_2O (silane)			+/-16%	+/-9%

Data input

Specified assumptions per reagent/process based on technical data:

	Amount	Yield	Ref.	Comments
lithium aluminum hydride (LAH)	A	97%	[2], [3], [4]	
lithium hydride (LiH)	A	98%	[2], [3]	2 MJ/kg additional heat based on mol. capacity of Li
aluminum trichloride ($AlCl_3$)	A	100%	[3]	
phenylsilane (($PhSiH_3$)	B	86%	[2], [5]	Barry process with $SiCl_4$ and benzene
trichlorophenylsilane ($PhSiCl_3$)	A	95%	[2], [6]	
diphenylsilane (Ph_2SiH_2)	A	78%	[2], [5]	Barry process with $SiCl_4$ and benzene
dichlorodiphenylsilane (Ph_2SiCl_2)	A	95%	[2], [6]	Silicon product from Ecoinvent used. Average of 2000 product from that plant. Mass based on 3 H'equiv.
poly(methylhydrosiloxane) (PMHS)				20 equiv. chlorine used. No reuse applied.
diethyl chloromalonate (DECM)	B	98%	[7]	Carbonylation process
diethyl malonate	B	81%	[3], [8]	Standard esterification
ethyl chloroacetate	A	95%	Expert judgment	
ethyl(triphenylphosphoranylidene)-acetate (ylide, EPPA)	A	95%	Expert judgment	in PhMe/NaOH sol.
triphenylphosphine (PPh_3)	A	95%	[3]	Li replaces Na

A – Stoichiometry from reaction equation
B – Stoichiometry calculated based on technical literature
C – Based on guidelines as suggested by Hischier *et al.*: 4.0^{-10} parts of chemical plant, 2 MJ heat/kg, 0.333 kWh/kg, 0.2% raw materials emitted into the air

Specified process data

$AlCl_3$ (Yield: 100%)	Amount
Product output	
$AlCl_3$	1 kg
Input	
Input from technosphere	
Al	0.201 kg
Cl_2	0.7951 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Cl_2	$1.585E^{-4}$ kg
Al	$4.02E^{-5}$ kg

Cat. Appel reaction – Ph_2SiH_2 (Yield: 80%)	Amount
Product output	
Alkyl chloride	1 mol
Input	
Input from technosphere	
DECM	0.2897 kg
Ph_2SiH_2	0.2534 kg
MeCN (0.1 M)	9.825 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
MeCN	$1.96E^{-2}$ kg
Silicates, unspecified	$4E^{-4}$ kg
Organic substances	$5.8E^{-4}$ kg
Waste	
Hazardous waste, 25% water, incinerated (0.225 kg malonate, 0.25 kg silane)	0.478 kg

Cat. Appel reaction – $PhSiH_3$ (Yield: 80%)	Amount
Product output	
Alkyl chloride	1 mol
Input	
Input from technosphere	
DECM	0.2897 kg
$PhSiH_3$	0.1488 kg
MeCN (0.1 M)	9.825 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
MeCN	$1.96E^{-2}$ kg
Silicates, unspecified	$4E^{-4}$ kg
Organic substances	$5.8E^{-4}$ kg
Waste	
Hazardous waste, 25% water, incinerated (0.225 kg malonate, 0.148 kg silane)	0.373 kg

Cat. Appel reaction – PMHS (Yield: 80%)	Amount
Product output	
Alkyl chloride	1 mol
Input	
Input from technosphere	
DECM	0.2897 kg
silicon product (PMHS)	0.1653 kg
MeCN (0.1 M)	9.825 kg
chemical plant	$4.0E^{-10}$ part

Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
MeCN	$1.96E^{-2}$ kg
Silicates, unspecified	$4E^{-4}$ kg
Organic substances	$5.8E^{-4}$ kg
Waste	
Hazardous waste, 25% water, incinerated (0.225 kg malonate, 0.165 kg silane)	0.39 kg

Classic Appel reaction (Yield: 90%)	Amount
Product output	
Alkyl chloride	1 mol
Input	
Input from technosphere	
PPh_3	0.3497 kg
CCl_4	0.2051 kg
MeCN (0.1 M)	8.7333 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
phosphorus compounds, unspecified	$9E^{-4}$ kg
acetonitrile	$6.1E^{-4}$ kg
Waste	
Hazardous waste, 25% water, incinerated (0.021 kg CCl_4, 0.35 kg PPh_3)	0.39 kg

Cat. Wittig reaction – Ph_2SiH_2 (Yield: 80%)	Amount
Product output	
Olefin	1 mol
Input	
Input from technosphere	
Ethyl chloroacetate	0.184 kg
Na_2CO_3 from $AlCl_3$ production	0.20 kg
Ph_2SiH_2	0.253 kg
Toluene	0.36 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Toluene	$7.2E^{-4}$ kg
Silicates, unspecified	$3E^{-4}$ kg
Organic substances	$1E^{-3}$ kg

Waste	
Hazardous waste, 25% water, incinerated (0.113 kg carbonate, 0.253 kg silane)	0.365 kg

Cat. Wittig reaction – $PhSiH_3$ (Yield: 80%)	Amount
Product output	
Olefin	1 mol
Input	
Input from technosphere	
Ethyl chloroacetate	0.184 kg
Na_2CO_3 from $AlCl_3$ production	0.20 kg
$PhSiH_3$	0.149 kg
Toluene	0.36 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Toluene	$7.2E^{-4}$ kg
Silicates, unspecified	$3E^{-4}$ kg
Organic substances	$1E^{-3}$ kg
Waste	
Hazardous waste, 25% water, incinerated (0.113 kg carbonate, 0.148 kg silane)	0.260 kg

Cat. Wittig reaction – PMHS (Yield: 80%)	Amount
Product output	
Olefin	1 mol
Input	
Input from technosphere	
Ethyl chloroacetate	0.184 kg
Na_2CO_3 from $AlCl_3$ production	0.20 kg
silicon product (PMHS)	0.1653 kg
Toluene	0.36 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Toluene	$7.2E^{-4}$ kg
Silicates, unspecified	$3E^{-4}$ kg
Organic substances	$1E^{-3}$ kg
Waste	
Hazardous waste, 25% water, incinerated (0.112 kg carbonate, 0.330 kg silane)	0.443 kg

Classic Wittig reaction (Yield: 95%)	Amount
Product output	
Alkyl chloride	1 mol

Input	
Input from technosphere	
EPPA (ylide)	0.440 kg
Toluene	0.305 kg
chemical plant	4.0E^{-10} part
Energy input	
heat, natural gas, at industrial furnace	0.6 MJ
electricity, medium voltage	0.1 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
phosphorus compounds, unspecified	6E^{-4} kg
toluene	1.6E^{-2} kg
Waste	
Hazardous waste, 25% water, incinerated (0.02112 kg EPPA, 0.296 kg PPh_3)	0.318 kg

Ph_2SiCl_2 (Yield: 95%)	Amount
Product output	
Ph_2SiCl_2	1 kg
Input	
Input from technosphere	
$SiCl_4$	0.71 kg
benzene	0.7661 kg
chemical plant	4.0E^{-10} part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
silicates	1.4E^{-4} kg
benzene	3.1E^{-4} kg
Waste	
Hazardous waste, 25% water, incinerated	0.111 kg

$PhSiCl_3$ (Yield: 95%)	Amount
Product output	
$PhSiCl_3$	1 kg
Input	
Input from technosphere	
$SiCl_4$	0.845 kg
benzene	0.458 kg
chemical plant	4.0E^{-10} part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
silicates	1.4E^{-4} kg
benzene	3.1E^{-4} kg

Waste	
Hazardous waste, 25% water, incinerated	$6.5E^{-2}$ kg

diethyl chloromalonate (Yield: 98%)	Amount
Product output	
DECM	1 kg
Input	
Input from technosphere	
diethyl malonate	0.8398 kg
Cl_2	7.516 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Cl_2	$1.5E^{-4}$ kg
organic substance	$1.7E^{-4}$ kg
Waste	
Hazardous waste, 25% water, incinerated	$1.5E^{-2}$ kg

diethyl malonate (Yield: 98%)	Amount
Product output	
diethyl malonate	1 kg
Input	
Input from technosphere	
ethyl chloroacetate	0.95 kg
EtOH, from ethylene	6 kg
NaOH, 50% in H_2O	0.5 kg
CO	0.28 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
CO	5.6^{-4} kg
ethyl acetate	$1.9E^{-3}$ kg
EtOH	0.001 kg
Emission to water	
NaOH	0.50 kg

Ph_2SiH_2 (Yield: 95%)	Amount
Product output	
Ph_2SiH_2	1 kg
Input	
Input from technosphere	
LAH	0.132 kg
Ph_2SiCl_2	1.472 kg
Et_2O	3.87 kg

chemical plant	4.0E^{-10} part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
silicates	2.9E^{-3} kg
aluminum	2E^{-4} kg
Et_2O	6E^{-4} kg
Emission to water	
Li-ion	9.6E^{-2} kg
Aluminum oxide	0.1773 kg
silicon	0.04 kg

ethyl chloroacetate (Yield: 98%)	Amount
Product output	
ethyl chloroacetate	1 kg
Input	
Input from technosphere	
chloroacetic acid	0.812 kg
EtOH, from ethylene	0.40 kg
H_2SO_4	8E^{-3} kg
toluene	2.5 kg
chemical plant	4.0E^{-10} part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
chloroacetic acid	1.6^{-3} kg
ethanol	8E^{-4} kg
toluene	5E^{-3} kg
H_2SO_4	1.7E^{-5} kg
Emission to water	
chloroacetic acid	3.90^{-3} kg
ethanol	1.9E^{-2} kg
H_2SO_4	8E^{-3} kg

EPPA – ylide (Yield: 98%)	Amount
Product output	
EPPA (ylide)	1 kg
Input	
Input from technosphere	
PPh_3	0.793 kg
ethyl chloroacetate	0.370 kg
toluene	2.754 kg
NaOH, 50% in H_2O	0.24 kg
water, deinised	3.18 kg
chemical plant	4.0E^{-10} part
Energy input	
heat, natural gas, at industrial furnace	2 MJ

electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
phosphorus compounds	1.6^{-3} kg
ethyl acetate	$7E^{-4}$ kg
toluene	$8.5E^{-3}$ kg
Emission to water	
phosphate	1.44^{-2} kg

$LiAlH_4$ – LAH (Yield: 97%)	Amount
Product output	
LAH	1 kg
Input	
Input from technosphere	
$AlCl_3$	3.81 kg
LiH	0.91 kg
Et_2O	8.6 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Li	$1.8E^{-5}$ kg
Al	$7.6E^{-4}$ kg
Et_2O	$1.7E^{-3}$ kg
Emission to water	
aluminum oxide	0.112 kg
Li-ion	0.727 kg

LiH (Yield: 98%)	Amount
Product output	
LiH	1 kg
Input	
Input from technosphere	
Li	0.891 kg
H_2	0.26 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Li	$1.8E^{-5}$ kg
H_2	$5.2E^{-5}$ kg
Emission to water	
aluminum oxide	0.112 kg
Li-ion	0.727 kg

LiH (Yield: 98%)	Amount

Product output	
LiH	1 kg
Input	
Input from technosphere	
Li	0.891 kg
H_2	0.26 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
Li	$1.8E^{-5}$ kg
H_2	$5.2E^{-5}$ kg
Emission to water	
aluminum oxide	0.112 kg
Li-ion	0.727 kg

$PhSiH_3$ (Yield: 95%)	Amount
Product output	
$PhSiH_3$	1 kg
Input	
Input from technosphere	
LAH	0.306 kg
$PhSiCl_3$	1.472 kg
Et_2O	7.66 kg
chemical plant	$4.0E^{-10}$ part
Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
silicates	$4.6E^{-3}$ kg
aluminum	$6E^{-4}$ kg
Et_2O	$1.5E^{-2}$ kg
Emission to water	
Li-ion	0.22 kg
Aluminum oxide	0.411 kg
silicon	0.04 kg

PPh_3 (Yield: 95%)	Amount
Product output	
PPh_3	1 kg
Input	
Input from technosphere	
PCl_3	0.551 kg
PhCl[9]	1.355 kg
Li	0.166 kg
toluene	3.5 kg
chemical plant	$4.0E^{-10}$ part

Energy input	
heat, natural gas, at industrial furnace	2 MJ
electricity, medium voltage	0.333 kWh
Emissions and waste	
Emissions to air (0.2 wt% raw materials)	
PCl_3	1.1E^{-3} kg
PhCl	2.7E^{-3} kg
Toluene	7.0E^{-3} kg
Emission to water	
phosphate	0.0191 kg
Li-ion	0.166

Calculations to determine maximum allow impact values of aldehyde in catalytic Wittig reactions.

$$I_{cat.} = \textit{impact of aldehyde in catalytic reaction}$$
$$m_{cat.} = \textit{moles of aldehyde required per functional unit in catalytic reaction}$$
$$I_{clas.} = \textit{impact of aldehyde in classic reactions}$$
$$m_{clas.} = \textit{moles of aldehyde required per functional unit in classic reaction}$$
$$\Delta_{max} = \textit{max. allowed difference between } I_{cat.} \textit{ and } I_{clas.} \textit{ in order to for the catalytic reaction to remain benificial} = \textit{difference between impacts shown in Tables } 3 \textit{ and } 4$$
$$\frac{I_{cat.}}{m_{cat.}} = \frac{I_{clas.}}{m_{clas.}}, \textit{thus } I_{clas.} = I_{cat.}\frac{m_{clas.}}{m_{cat.}}$$
$$\Delta_{max} = I_{cat.} - I_{clas.} = I_{cat.} - I_{cat.}\frac{m_{clas.}}{m_{cat.}} = I_{cat.}\left(1 - \frac{m_{clas.}}{m_{cat.}}\right), \textit{thus } I_{cat.} = \frac{\Delta_{max}}{\left(1 - \frac{m_{clas.}}{m_{cat.}}\right)}$$
$$m_{cat.} = 1.3;\ m_{clas.} = 1.1, \textit{thus } I_{cat.} \approx \frac{\Delta_{max}}{0.154}$$

The Δ_{max} can be obtained from Table 3 and 4 in this supporting information and with this the maximum allowed impact of the aldehyde (per functional unit, *i.e.* 1.3 mol aldehyde) in order to remain a beneficial catalytic reaction is determined.

Entry		CED (MJ-eq/mol olefin)		GHG emission (CO_2-eq/mol olefin)	
		Δ_{max}	$I_{cat.}$	Δ_{max}	$I_{cat.}$
1	PMHS	80	519	7.8	51
2	Ph_2SiH_2	23	149	3.9	25
3	$PhSiH_3$	27	175	4.2	27

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