Getting started with Simulis® Thermodynamics

Use Case 13: Estimating binary interaction parameters from predictive models

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Introduction

- Some thermodynamic models require binary interaction parameters (BIPs) to correctly predict fluid phase equilibria. Unfortunately these BIPs are not always available in the software database or in the literature. In such case two possibilities:
  1. Regression of the binary interaction parameters from experimental data: Necessity for the user to create its own tools (e.g. in MS-Excel using Simulis® Thermodynamics Add-In)

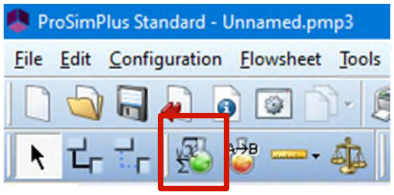
Refer to “Getting Started with Simulis® Thermodynamics, use case 8: Fitting binary interaction parameters from experimental data in Excel”

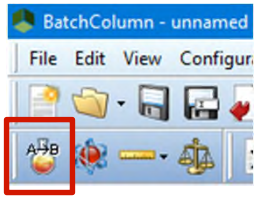
  2. For Dechema-compatible Wilson, NRTL, NRTL ProSim, UNIQUAC and UNIQUAC ProSim models, it’s possible to estimate the BIPs from one of the predictive models if their parameters are available (UNIFAC type group decompositions or COSMO-SAC-dsp files or NRTL-SAC parameters).

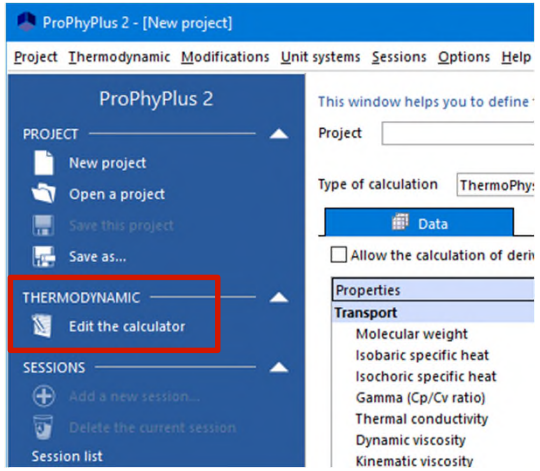
This document presents this second possibility to represent the vapor-liquid equilibria at atmospheric pressure of the quaternary system isopropanol, dichloromethane, tetrahydrofuran, methyl chloride

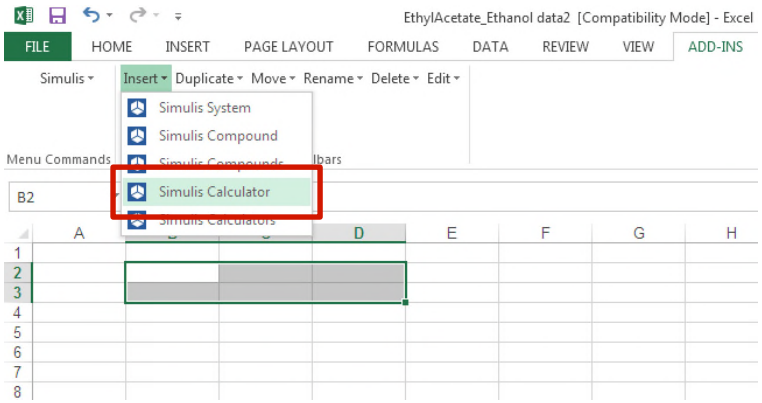
Step 1: Define the thermodynamics

- Depending on your software add, edit or open a calculator





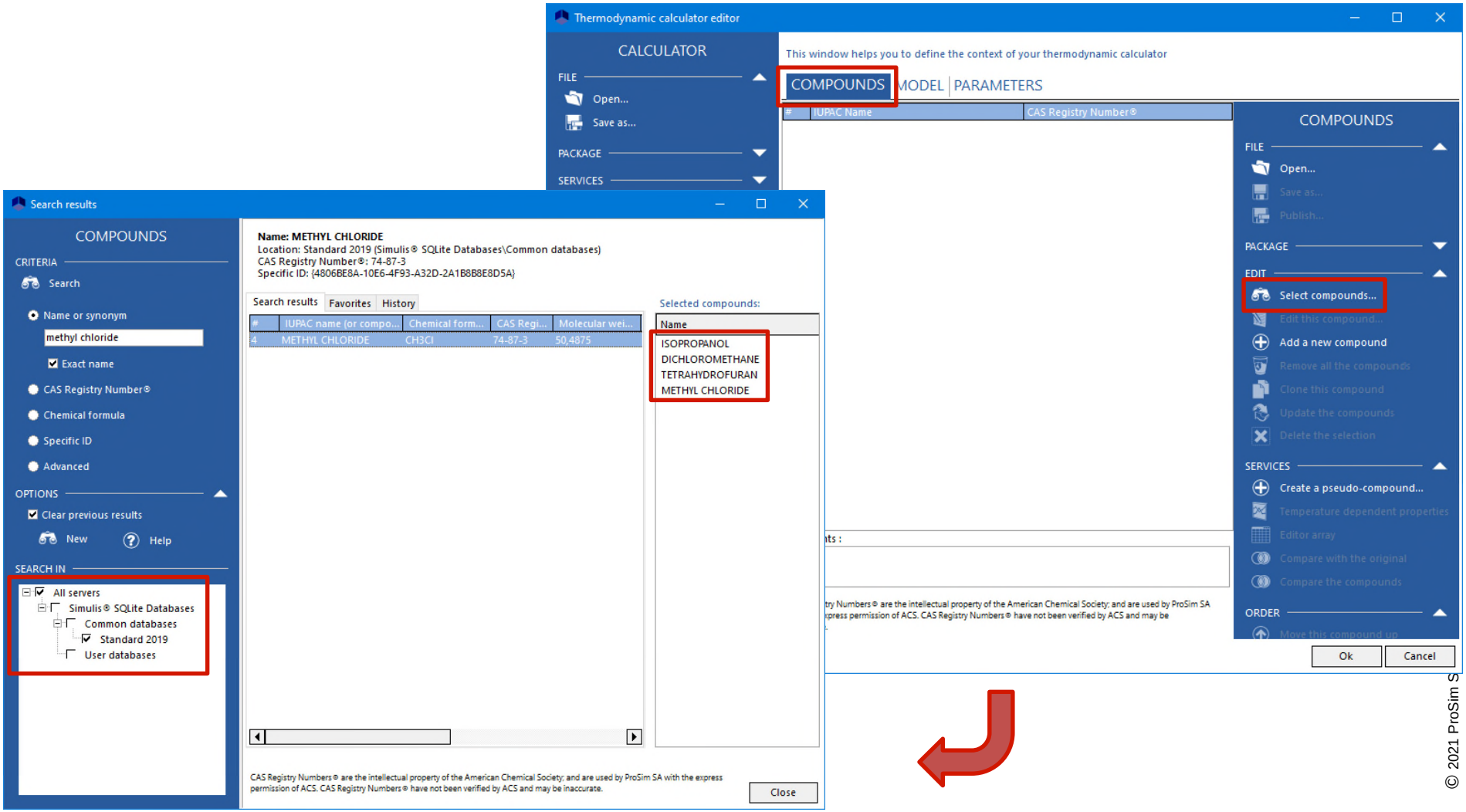




Refer to Getting Started “Use case 1” of your software for details about how to perform the operations of the Step 1 of this document

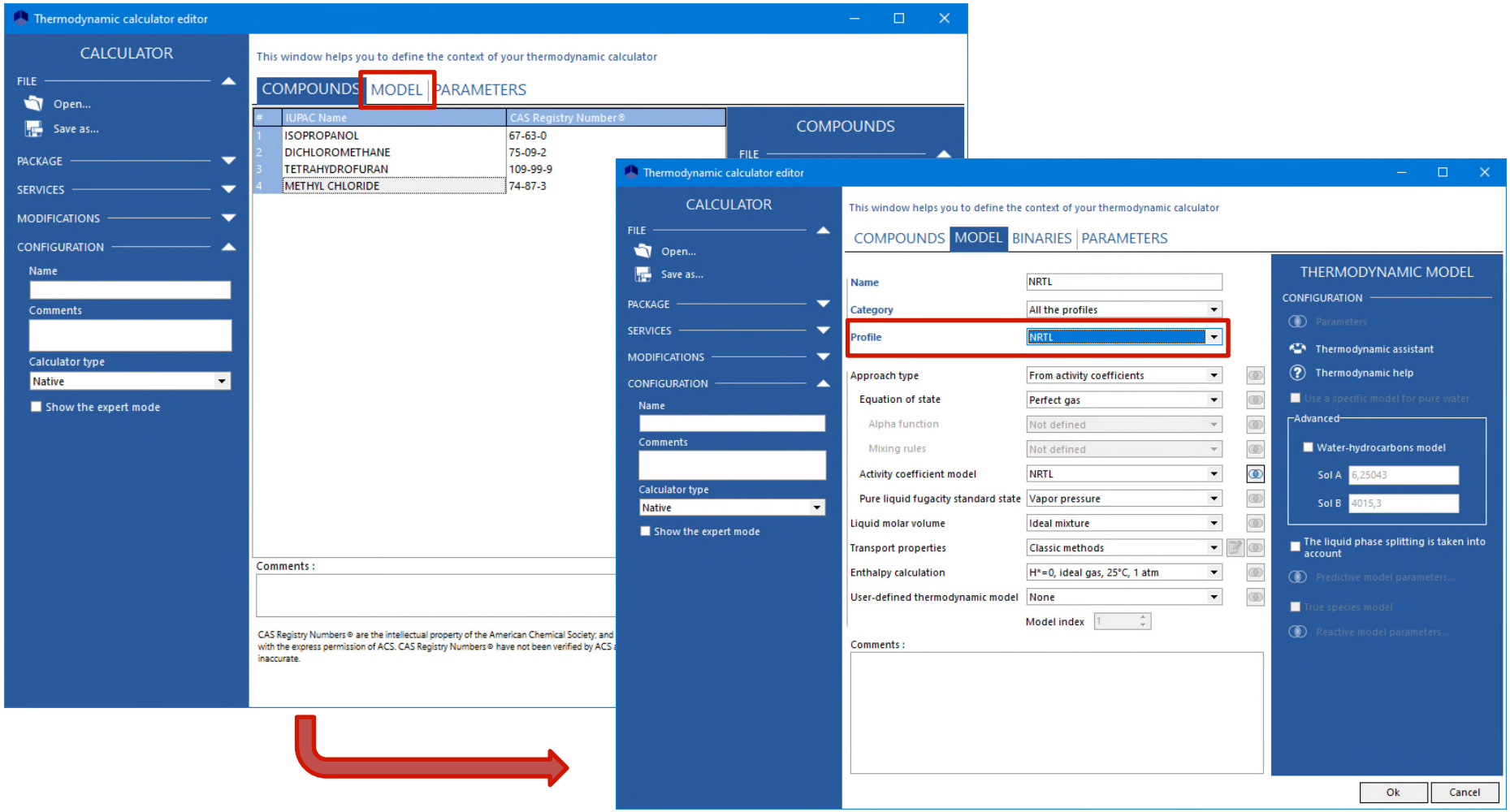
Step 1: Define the thermodynamics

- Select the compounds isopropanol, dichloromethane, tetrahydrofuran and methyl chloride from the latest compounds database



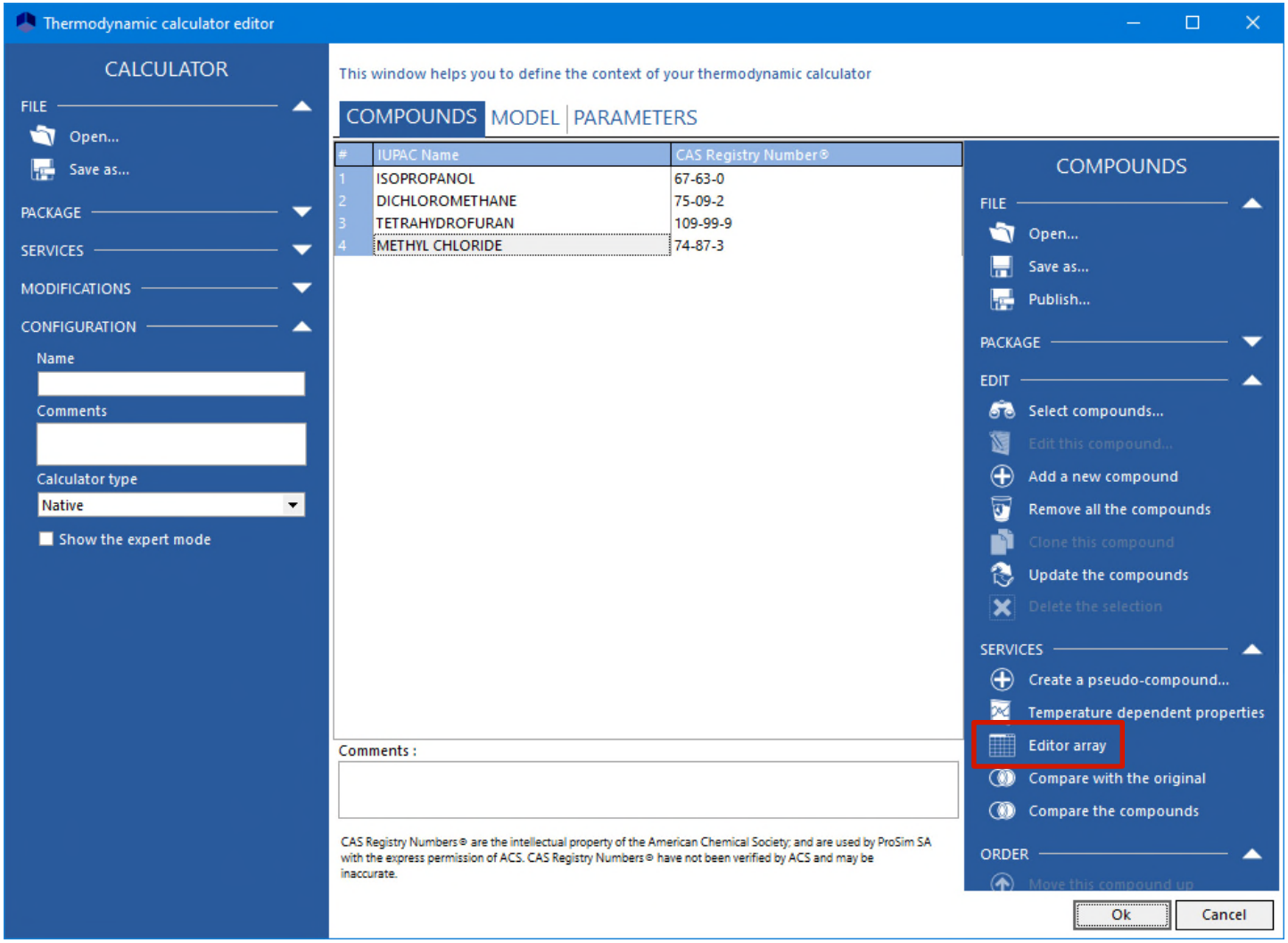
Step 1: Define the thermodynamics

- Select the NRTL thermodynamic profile
  - Note that the “binaries” tab appears only when the selected thermodynamic model requires BIPs and at least 2 compounds are present



Step 2: Choice of the predictive models

- Use the “Editor array” service to analyze which predictive models can be used



Step 2: Choice of the predictive models

- Analyze of the available parameters

Properties	ISOPROPANOL	DICHLOROMETHANE	TETRAHYDROFURAN	METHYL CHLORIDE
Identification				
IUPAC name				
Specific name	ISOPROPANOL	DICHLOROMETHANE	TETRAHYDROFURAN	METHYL CHLORIDE
CAS Registry Number®	67-63-0	75-09-2	109-99-9	74-87-3
Chemical family	Other Aliphatic ...	C1/C2 Aliphatic Chlorides	Epoxydes	C1/C2 Aliphatic Chlorides
Chemical formulae	C3H8O	CH2Cl2	C4H8O	CH3Cl
Smiles	CC(O)C	ClCCl	C1COCC1	C[Cl]
Set identifier				
Intrinsic number (ProSim specific)	134	53	168	57
Synonyms	1-METHYLETHAN...	FREON 30	BUTYLENE OXIDE	ARTIC
Compound comments				
Cosmo file	Known	Known	Known	Known
Group contribution model				
Standard				
UNIFAC modified (Dortmund) 1993 chemical structure	[OH(s)] 1 [CH3] 2 ...	[CH2Cl2] 1	[c-CH2OCH] 1 [c-CH2] 2	<unknown>
UNIFAC original chemical structure	[OH] 1 [CH3] 2 [C...	[CH2CL2] 1	[THF] 1 [CH2] 3	<unknown>
UNIFAC PSRK chemical structure	[OH] 1 [CH3] 2 [C...	[CH2CL2] 1	[THF] 1 [CH2] 3	<unknown>
UNIFAC LLE chemical structure	[P2] 1	[CH2Cl2] 1	[CH2] 3 [FCH2O] 1	<unknown>
UNIFAC modified (Dortmund) chemical structure	[OH (S)] 1 [CH3] 2...	[CH2CL2] 1	[THF] 1 [CY-CH2] 2	<unknown>
UNIFAC modified (Larsen) chemical structure	[CH3] 2 [CH] 1 [O...	[CH2Cl2] 1	[FCH2O] 1 [CH2] 3	<unknown>
PPR 78 chemical structure	<unknown>	<unknown>	<unknown>	<unknown>
UNIFAC VTPR chemical structure	[OH (S)] 1 [CH3] 2...	[CH2CL2] 1	[THF] 1 [CY-CH2] 2	[CH3Cl] 1
UNIFAC UMRPRU chemical structure	[OH] 1 [CH3] 2 [C...	[CH2CL2] 1	[THF] 1 [CH2] 3	<unknown>
NRTL PR chemical structure	<unknown>	<unknown>	<unknown>	<unknown>
GC-PPC-SAFT chemical structure	[OHb](2, 0) 1 [CH...	<unknown>	[-O-](3, 0) 1 [CH2c](1, 0) 4	<unknown>
UNIFAC modified (NIST) chemical structure	[OH (S)] 1 [CH3] 2...	[CH2CL2] 1	[THF] 1 [CY-CH2] 2	<unknown>
User				
Atomic				
Phase change				
Combustion, security, toxicity				
Condensed phase				
Phase thermochemistry				
Interaction, gas phase reaction				
User properties				
PPC-SAFT				
NRTL-SAC				
Number of hydrophobic segments type (X)	0,332	0,459	0,235	<unknown>
Number of hydrophilic segments type (Z)	0,636	0,038	0	<unknown>
Number of polar segments type (Y-)	0	0	0,04	<unknown>
Number of polar segments type (Y+)	0	0,427	0,32	<unknown>

COSMO-SAC-dsp model can be used for all binaries

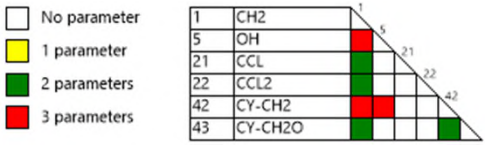
Only UNIFAC VTPR can be used for all binaries.
All the other UNIFACs models can be used for all binaries except the ones with methyl chloride.

NRTL-SAC can be used for all binaries except the ones with methyl chloride

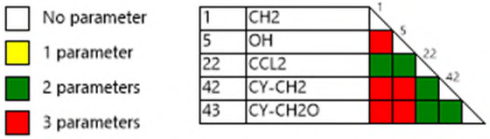
Step 2: Choice of the predictive models

- NTRL-SAC is more particularly adapted for the solubility of organic solids in solvents, which is not the scope in this example. Thus, other models will be selected.

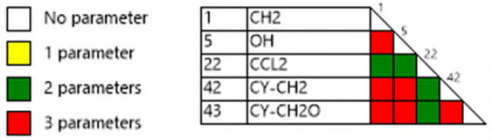
- UNIFAC VTPR will not be used because some interaction between groups are missing:



UNIFAC modified (Dortmund) or UNIFAC modified (NIST) can be used to predict binary sub-systems of the ternary isopropanol – dichloromethane – tetrahydrofuran system because interactions between groups are known:



UNIFAC modified (Dortmund)



UNIFAC modified (NIST)

- However, COSMO-SAC-dsp must be used to predict the binaries involving the methyl chloride.

Step 2: Choice of the predictive models

- It's reported that the behavior of the following binaries is zeotropic
  - Isopropanol – Dichloromethane
  - Isopropanol – Tetrahydrofuran
  - Dichloromethane - Tetrahydrofuran

Gmehling J., Menke J., Krafczyk J., Fischer K., "Azeotropic Data", 2nd edition, Wiley-VCH (2004)

- The UNIFAC modified (Dortmund) model predicts a zeotropic behavior for two of the three binaries: Isopropanol – Dichloromethane and Dichloromethane – Tetrahydrofuran. But it predicts an azeotrope behavior for the Isopropanol – Tetrahydrofuran. Thus, it cannot be used for that binary.

- The UNIFAC modified (NIST) model predicts a zeotropic behavior for the two binaries with isopropanol but an azeotropic behavior for the binary Dichloromethane – Tetrahydrofuran. This, it cannot be used for that binary.

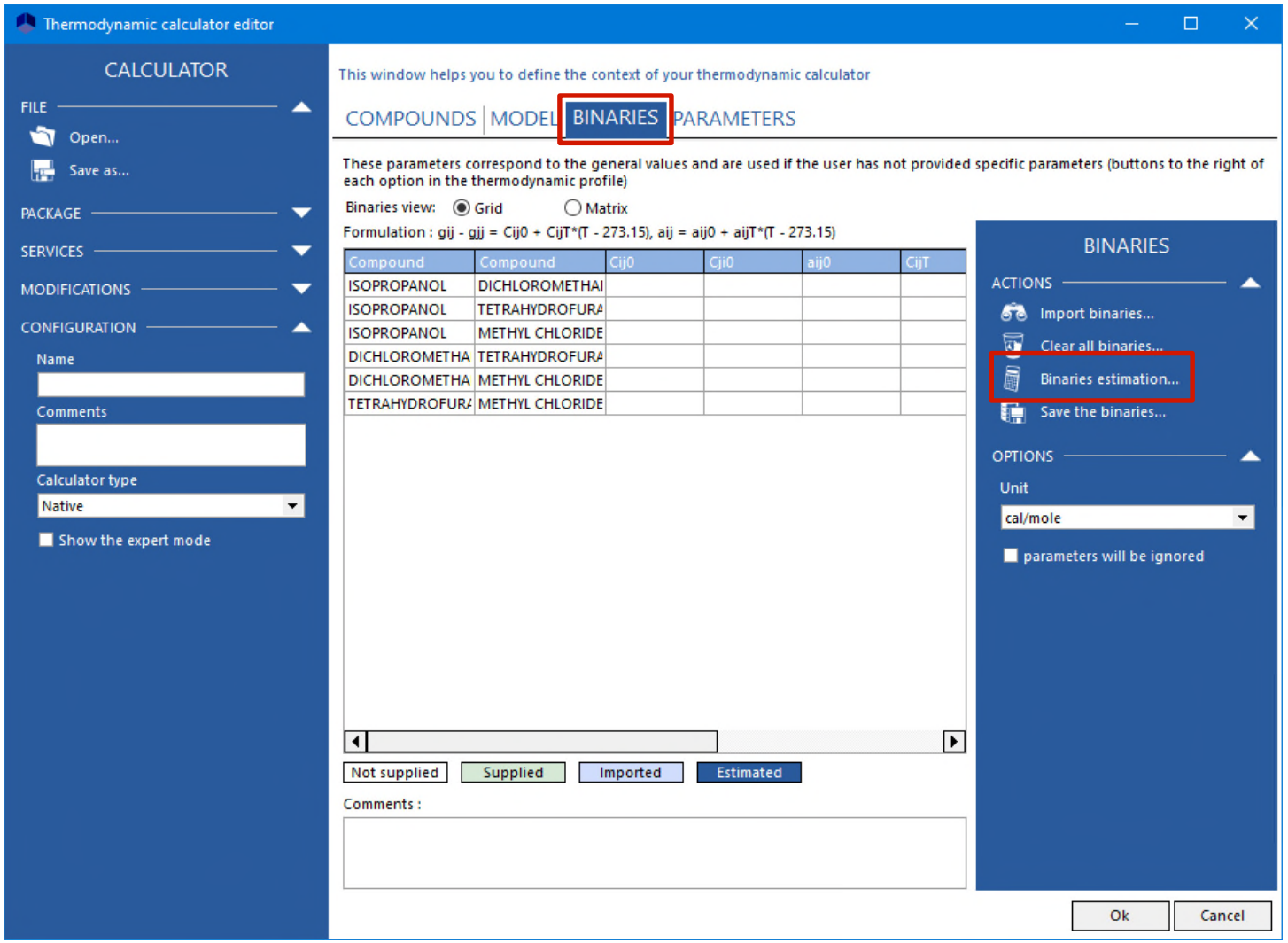
If no experimental data is available, it's interesting to compare the predictions done by the different usable predictive models to verify if they are coherent with each other. Refer to "Getting started with ProPhyPlus®, use case 1: Main features overview » to plot a vapor-liquid equilibrium curve.

Step 2: Choice of the predictive models

- To sum up the models used to predict the BIPs
  - All binaries with methyl chloride: COSMO-SAC-dsp
  - Isopropanol – Dichloromethane: UNIFAC modified (Dortmund)
  - Isopropanol – Tetrahydrofuran: UNIFAC modified (NIST)
  - Dichloromethane – Tetrahydrofuran: UNIFAC modified (Dortmund)

Step 3: Prediction of the BIPs

- Go to “Binaries” tab and click on “Binaries estimation…”



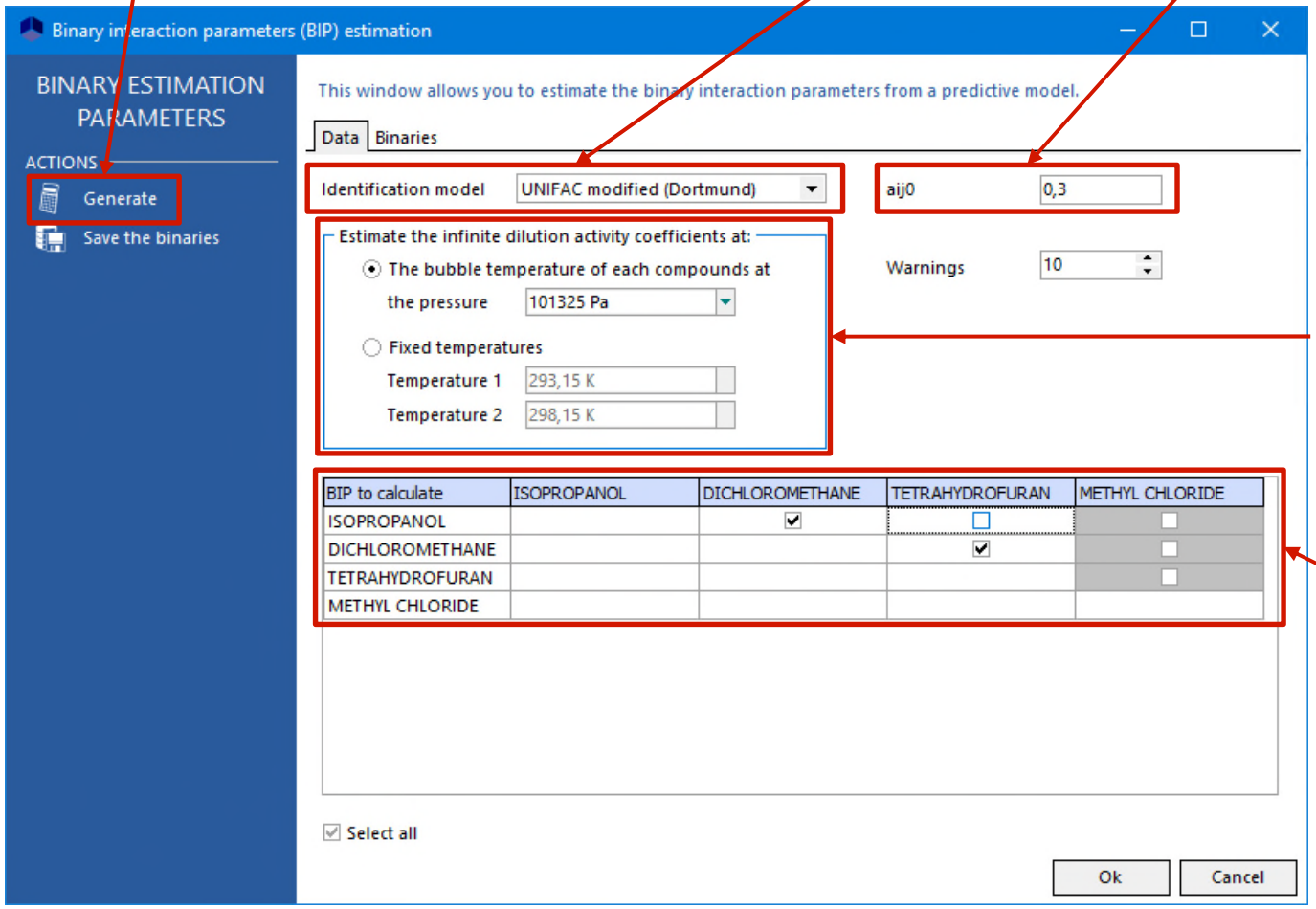
Step 3: Prediction of the BIPs

- Prediction of the 1st set of BIPs

5. Generate

1. Select the predictive model UNIFAC modified (Dortmund)

2. a_{ij}^0 is generally set to 0.3 for vapor-liquid equilibria (current case) and to 0.2 for liquid phase splitting case



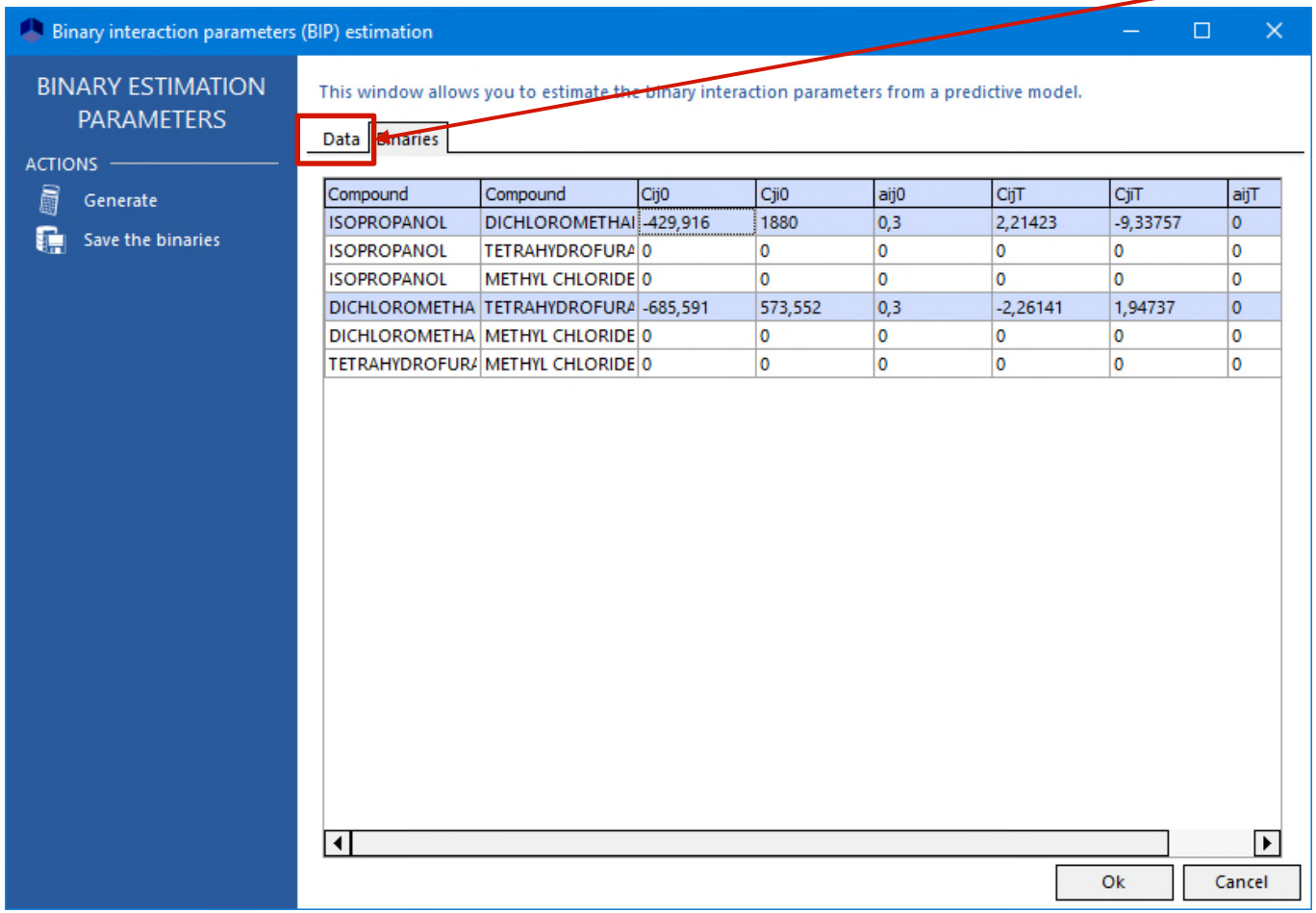
3. If the process is roughly isobaric, specify the corresponding pressure (current case). If the process works at two pressures (or more), specify the working temperatures at these two pressures (or the two extremes)

4. Select the binaries to estimate. In grey, the ones that cannot be estimated using the selected predictive model

Step 3: Prediction of the BIPs

- Prediction of the 1st set of BIPs
  - Visualization of the predicted BIPs

Click to continue and predict the 2nd set of BIPs



Compound	Compound	Cij0	Cji0	aij0	CijT	CjiT	aijT
ISOPROPANOL	DICHLOROMETHAI	-429,916	1880	0,3	2,21423	-9,33757	0
ISOPROPANOL	TETRAHYDROFURA	0	0	0	0	0	0
ISOPROPANOL	METHYL CHLORIDE	0	0	0	0	0	0
DICHLOROMETHA	TETRAHYDROFURA	-685,591	573,552	0,3	-2,26141	1,94737	0
DICHLOROMETHA	METHYL CHLORIDE	0	0	0	0	0	0
TETRAHYDROFURA	METHYL CHLORIDE	0	0	0	0	0	0

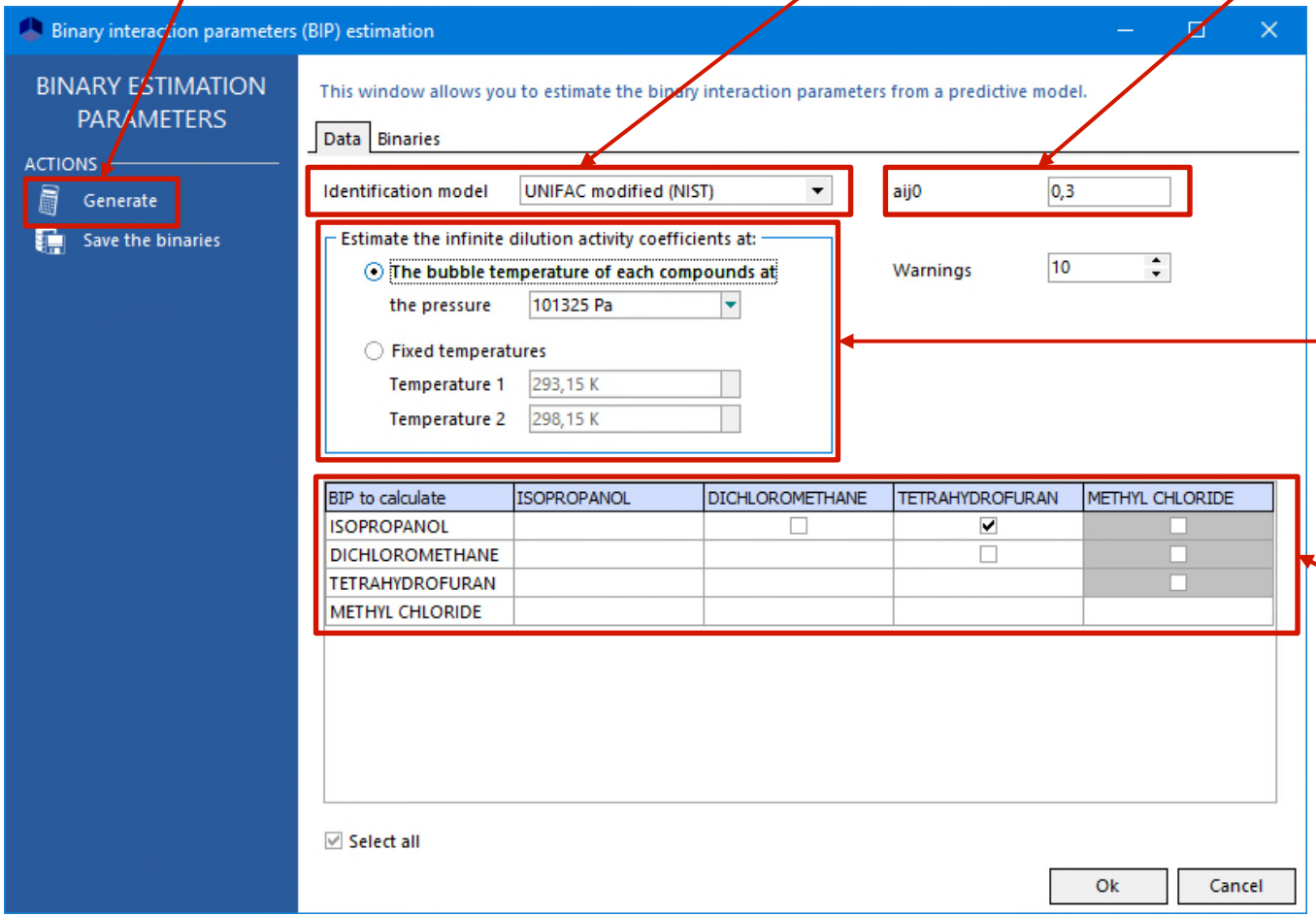
Step 3: Prediction of the BIPs

- Prediction of the 2nd set of BIPs

5. Generate

1. Select the predictive model UNIFAC modified (NIST)

2. a_{ij}^0 set to 0.3



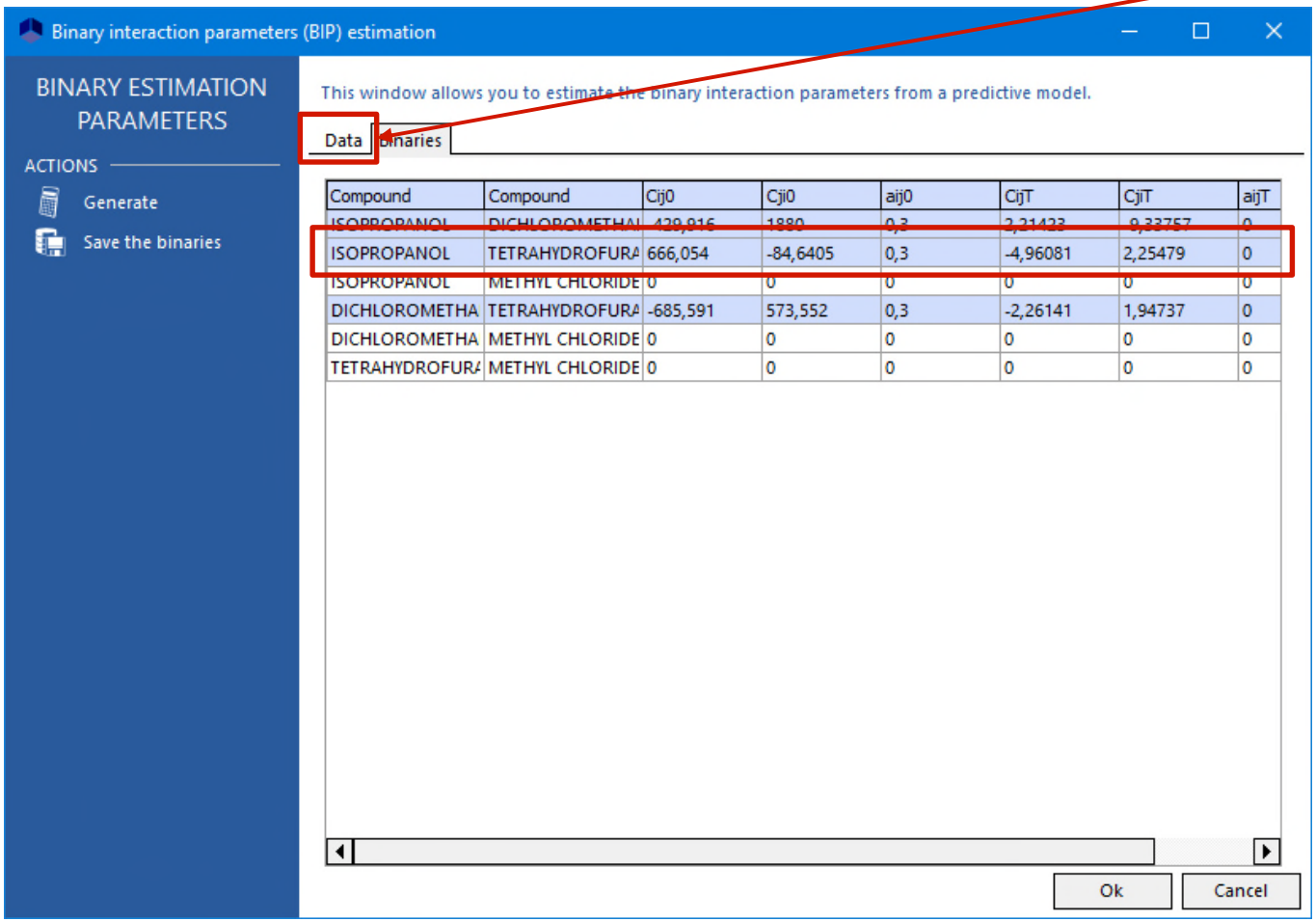
3. Estimation at atmospheric pressure

4. Select the binaries to be estimated

Step 3: Prediction of the BIPs

- Prediction of the 2nd set of BIPs
  - Visualization of the predicted BIPs

Click to continue and predict the 3rd set of BIPs



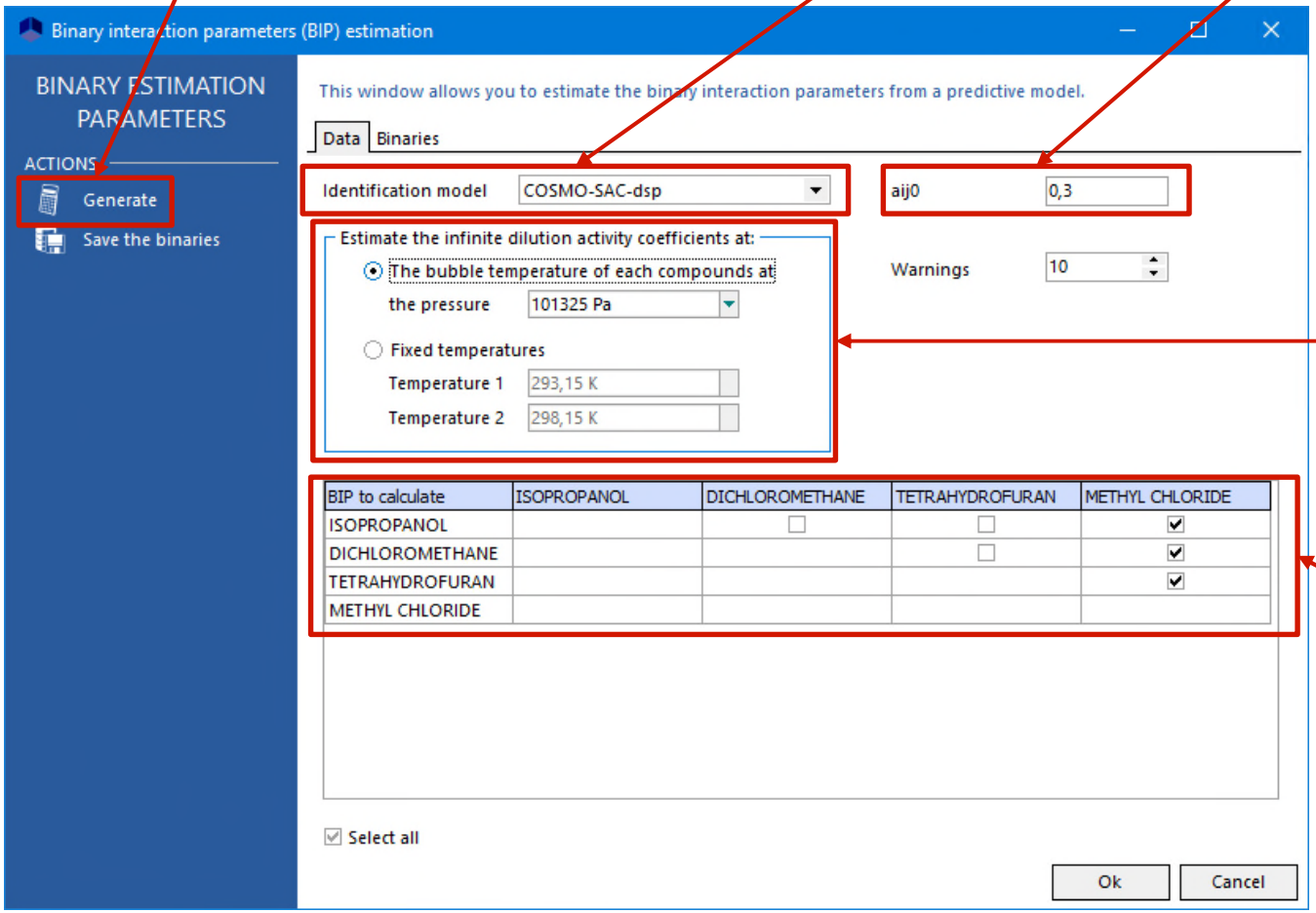
Step 3: Prediction of the BIPs

- Prediction of the 3rd set of BIPs

5. Generate

1. Select the predictive model COSMO-SAP-dsp

2. a_{ij}^0 set to 0.3

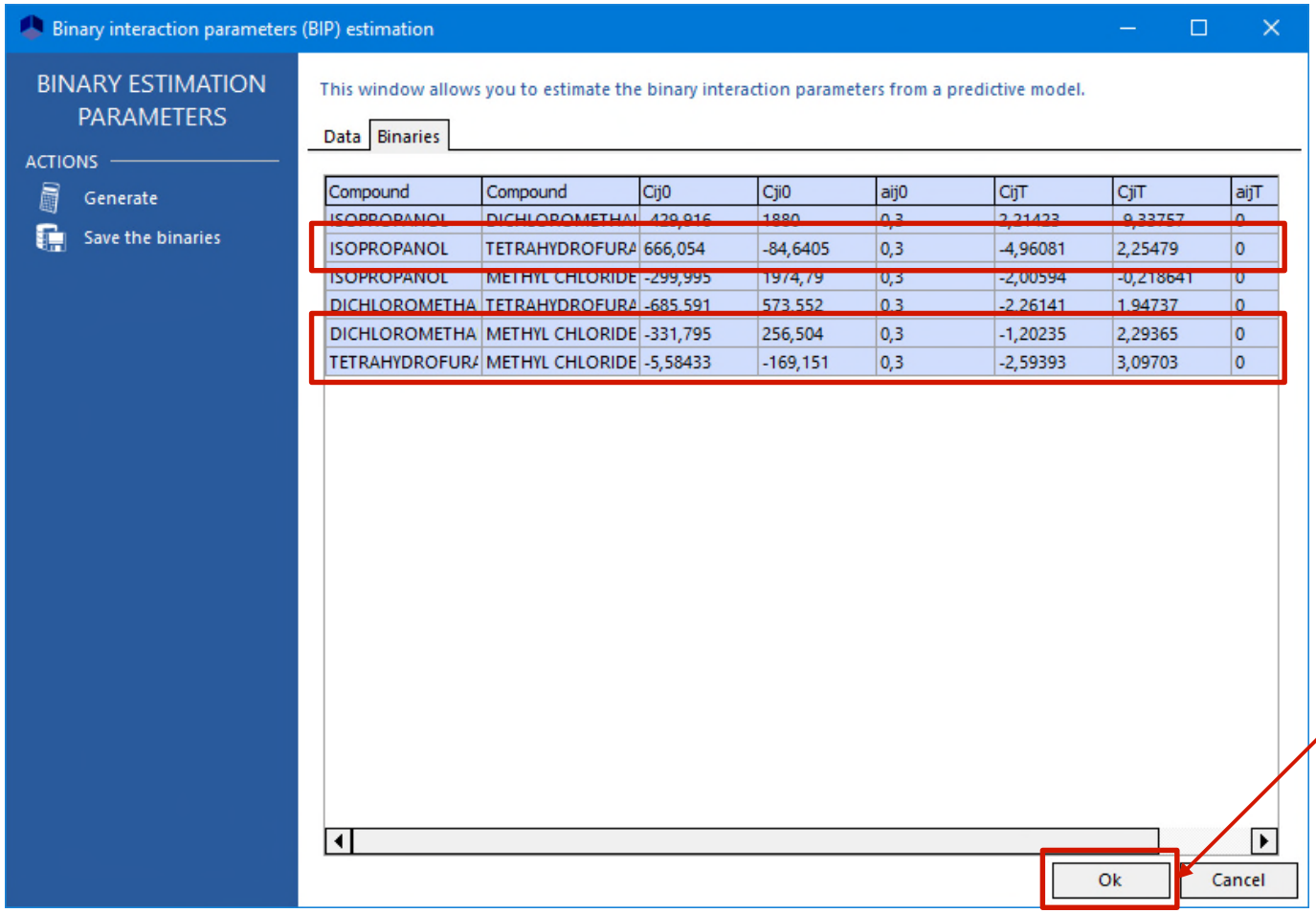


3. Estimation at atmospheric pressure

4. Select the binary to be estimated

Step 3: Prediction of the BIPs

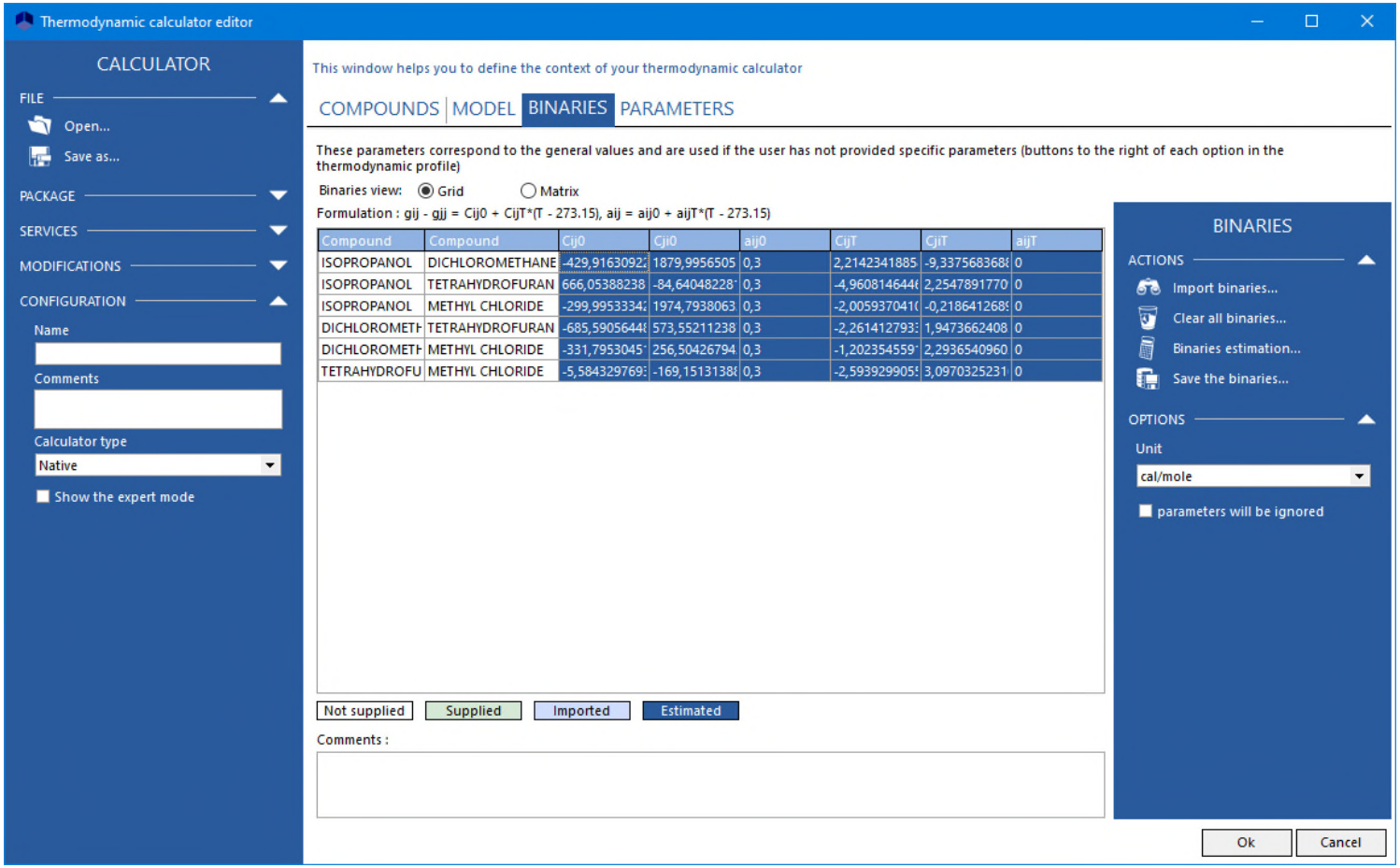
- Prediction of the 3rd set of BIPs
  - Visualization of the predicted BIPs



Click to validate

Step 3: Prediction of the BIPs

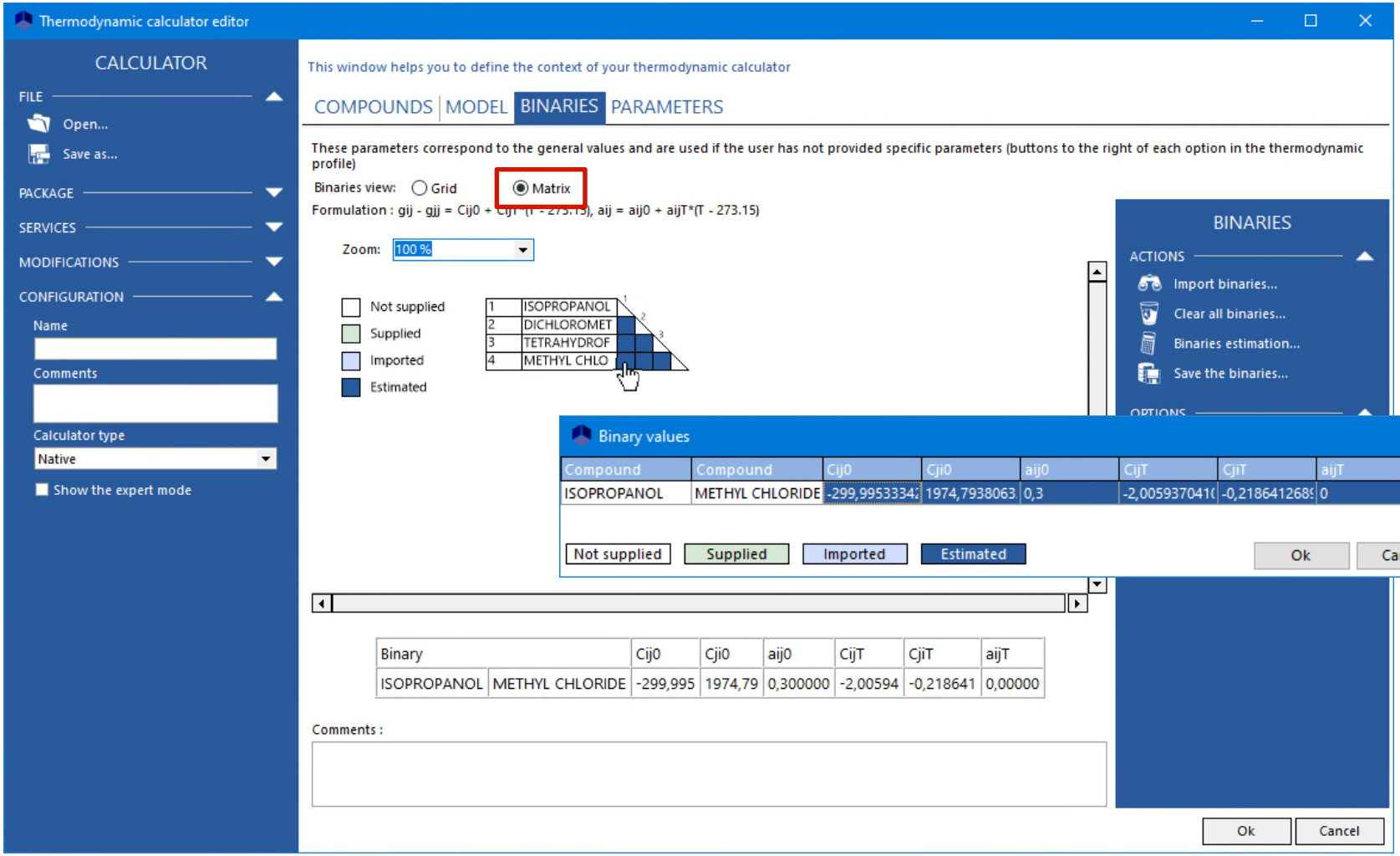
- The model is ready to use



It's interesting to verify that the model with the predicted BIPs gives for each binary the same behavior as the predictive model used for them. Refer to "Getting started with ProPhyPlus®, use case 1: Main features overview » to plot a vapor-liquid equilibrium curve.

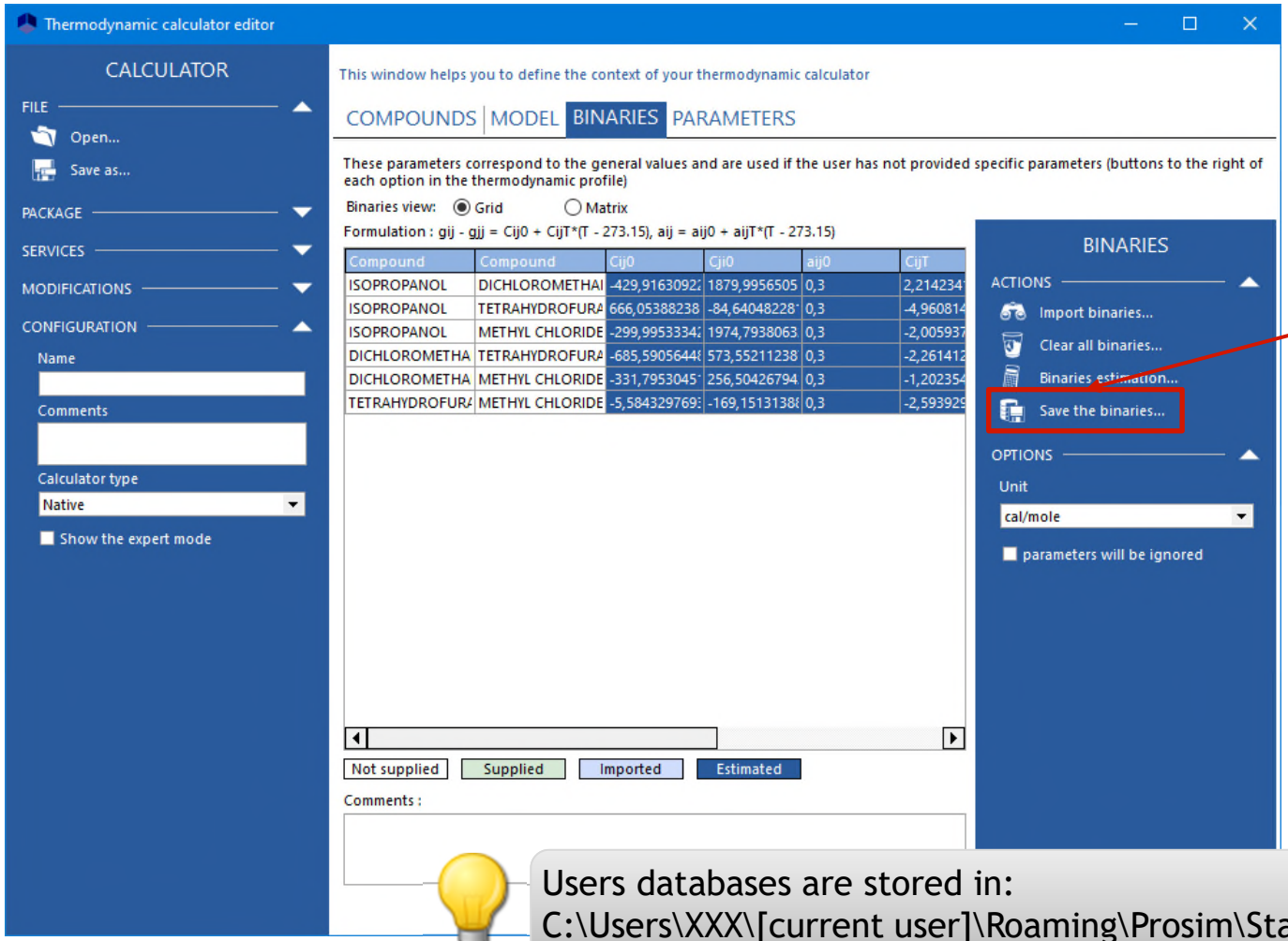
Step 3: Prediction of the BIPs

- It's possible to visualize the BIPs in form of a matrix instead of a grid.
  - Place the mouse on a binary or click on it to see its BIP values



Step 4: Save the binaries

- It’s possible to save the binaries in your own BIPs database to reuse them in another project. Several users databases can be created and managed.

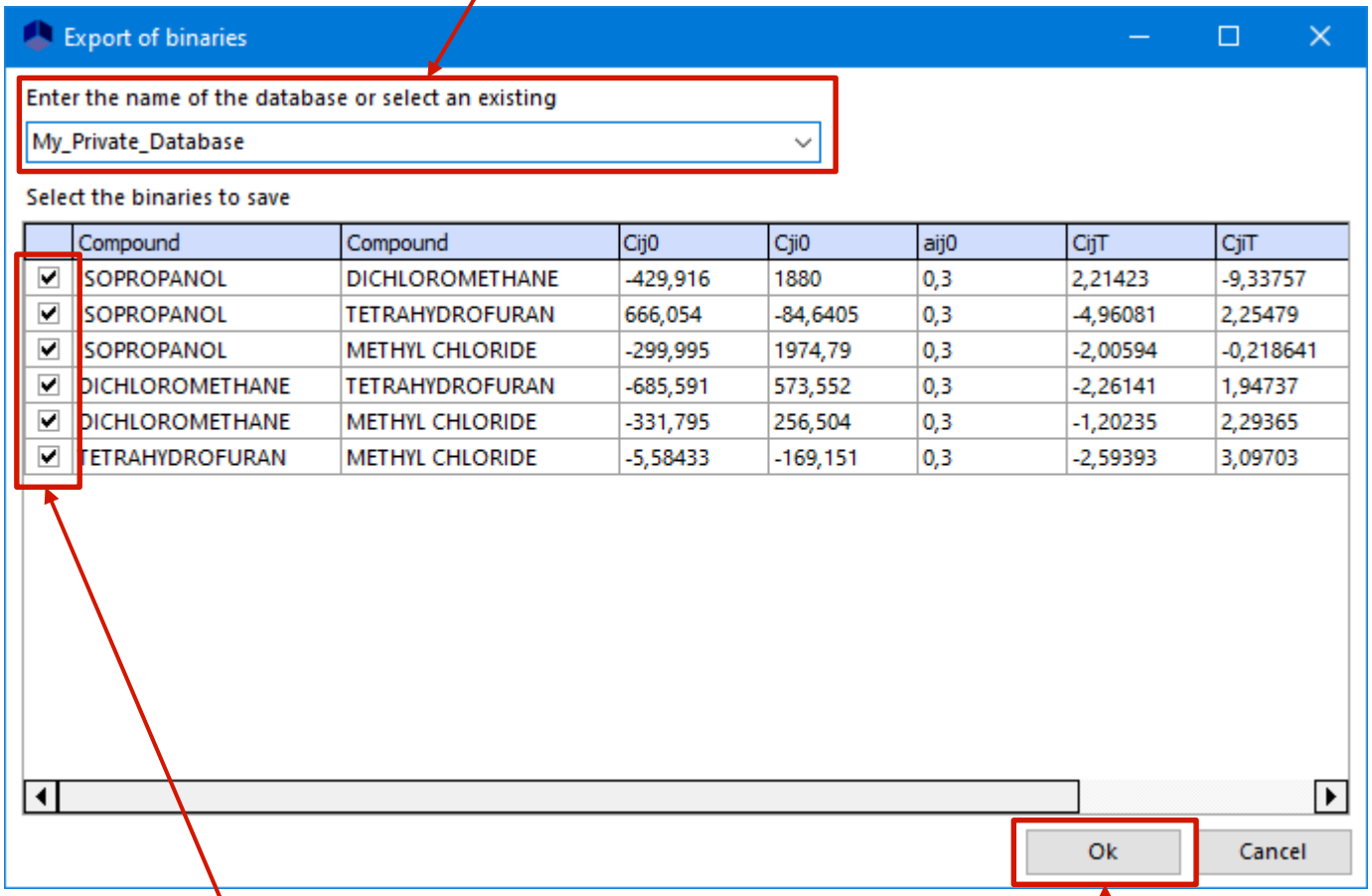


1. “Save the binaries…”

Users databases are stored in:
C:\Users\XXX\[current user]\Roaming\Prosim\Stardust\Binaries\Databases

Step 4: Save the binaries

2. Enter a name to create a new user database or select an existing user database.
In the case of an existing user database you can:
* Add the selected binaries to the user database
* Replace the values of the user database by the ones selected



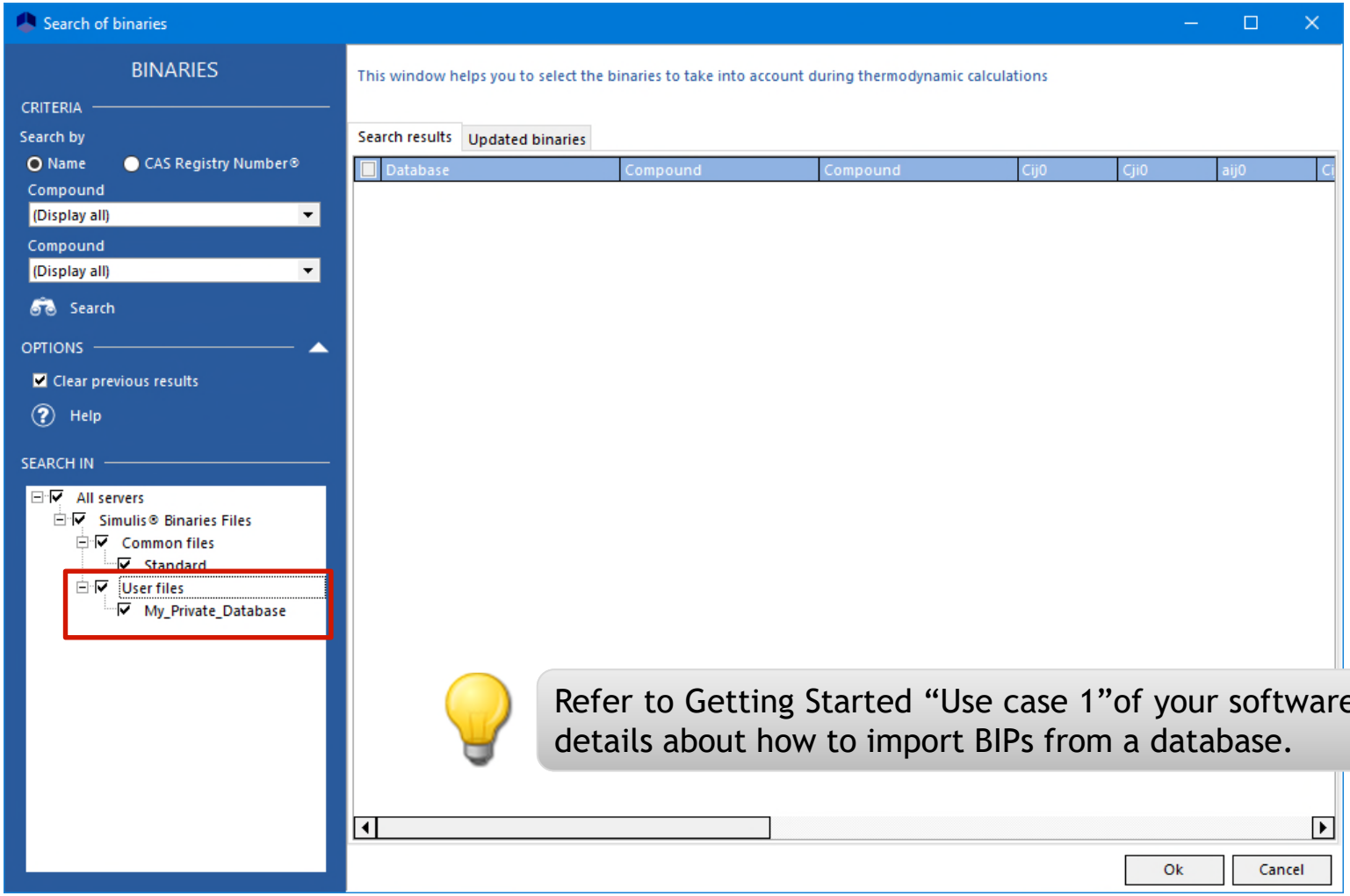
	Compound	Compound	Cij0	Cji0	aij0	CijT	CjiT
☑	SOPROPANOL	DICHLOROMETHANE	-429,916	1880	0,3	2,21423	-9,33757
☑	SOPROPANOL	TETRAHYDROFURAN	666,054	-84,6405	0,3	-4,96081	2,25479
☑	SOPROPANOL	METHYL CHLORIDE	-299,995	1974,79	0,3	-2,00594	-0,218641
☑	DICHLOROMETHANE	TETRAHYDROFURAN	-685,591	573,552	0,3	-2,26141	1,94737
☑	DICHLOROMETHANE	METHYL CHLORIDE	-331,795	256,504	0,3	-1,20235	2,29365
☑	TETRAHYDROFURAN	METHYL CHLORIDE	-5,58433	-169,151	0,3	-2,59393	3,09703

3. Select the binaries to be saved

4. “Ok” to validate

Step 4: Save the binaries

- To perform a search in your private database, select it in the “Search of binaries” window



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