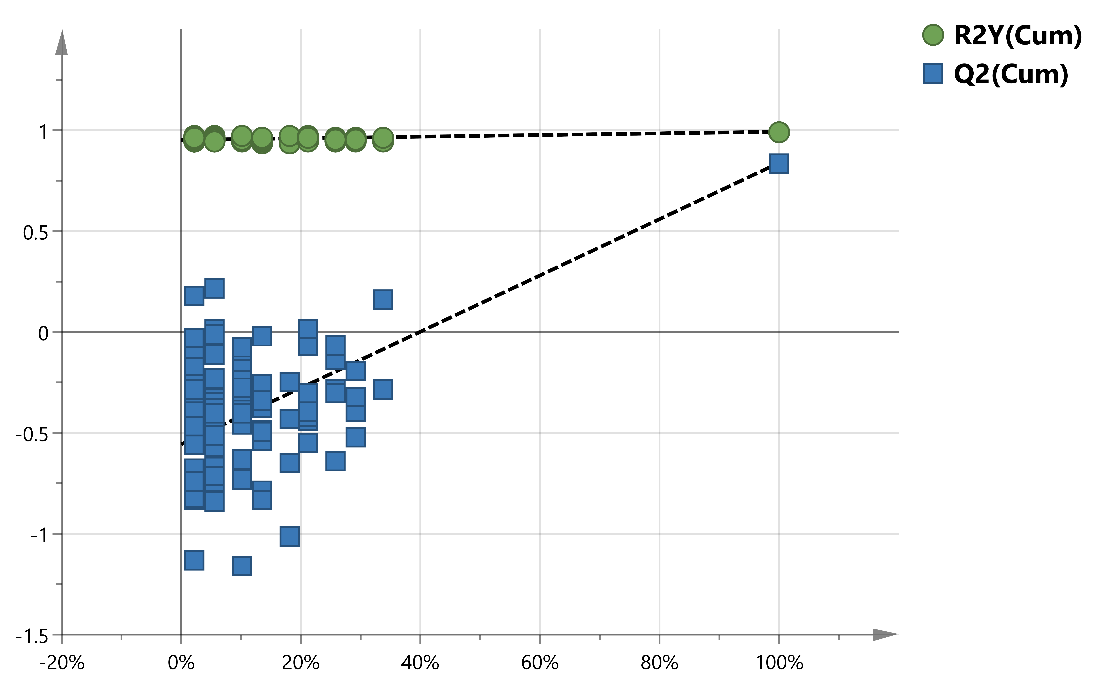
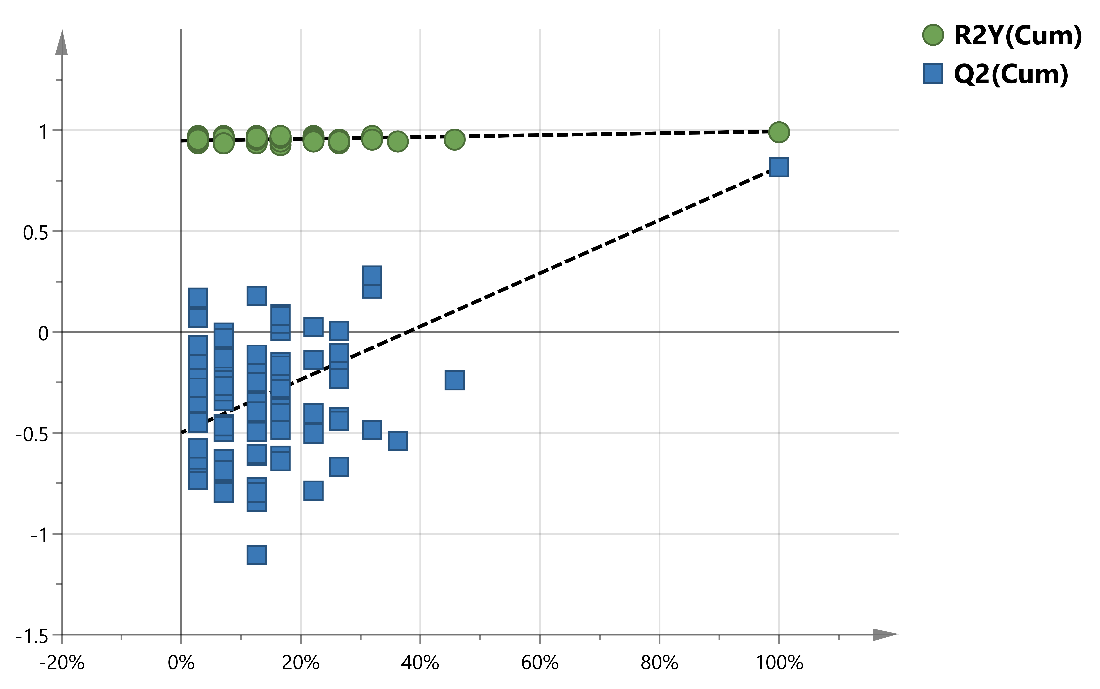
**Figures S.2 & S.3**

**Figure S.2A**



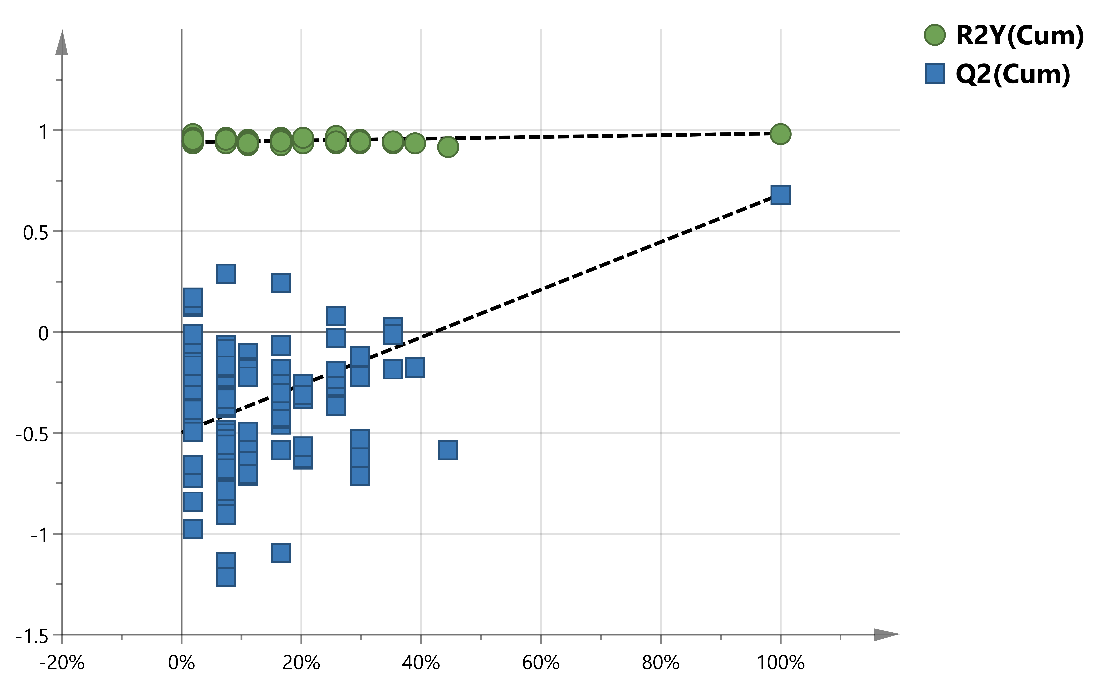
Positive ion mode; Controls vs PPMS. A permutation test performed with 100 random permutations on the generated OPLS-DA model showed no overfitting of the model (Q2 = (0.0, -0.557)).

**Figure S.2B**

****

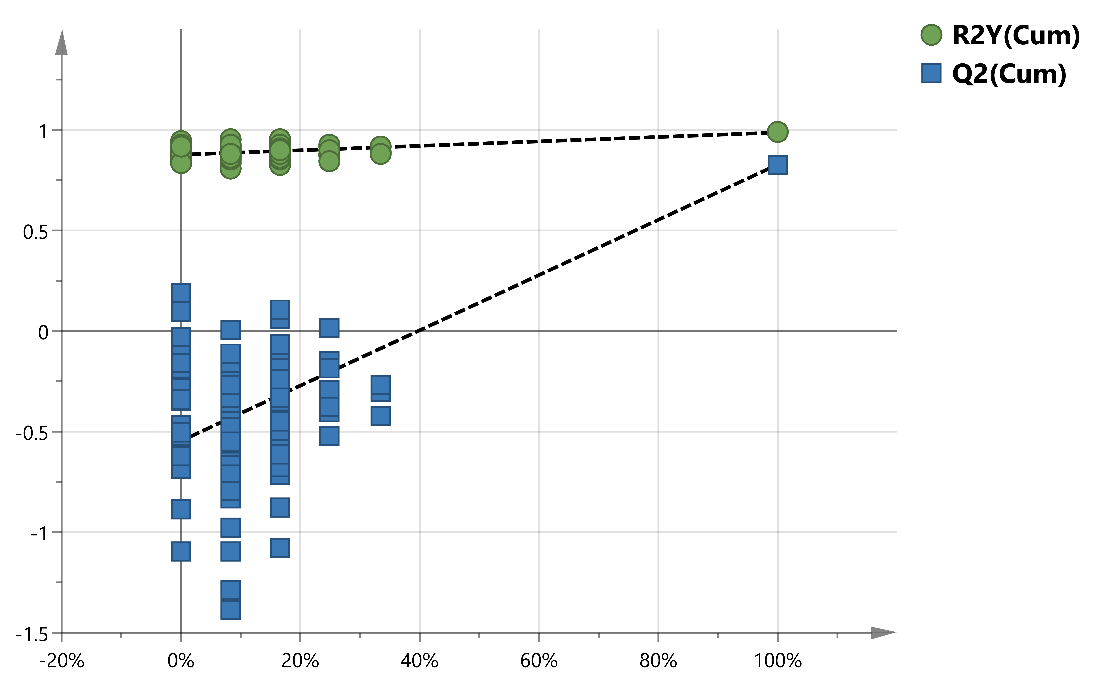
Positive ion mode; Controls vs SPMS. A permutation test performed with 100 random permutations on the generated OPLS-DA model showed no overfitting of the model (Q2 = (0.0, -0.517)).

**Figure S.2C**

****

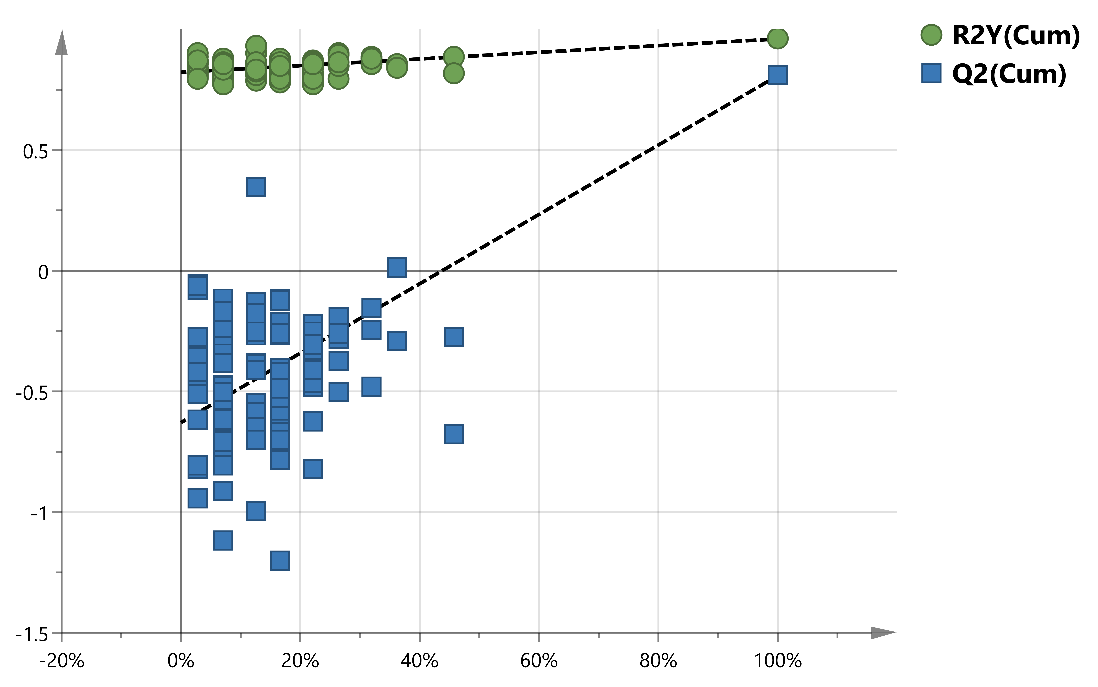
Positive ion mode; PPMS vs SPMS. A permutation test performed with 100 random permutations on the generated OPLS-DA model showed no overfitting of the model (Q2 = (0.0, -0.512)).

**Figure S.3A**

****

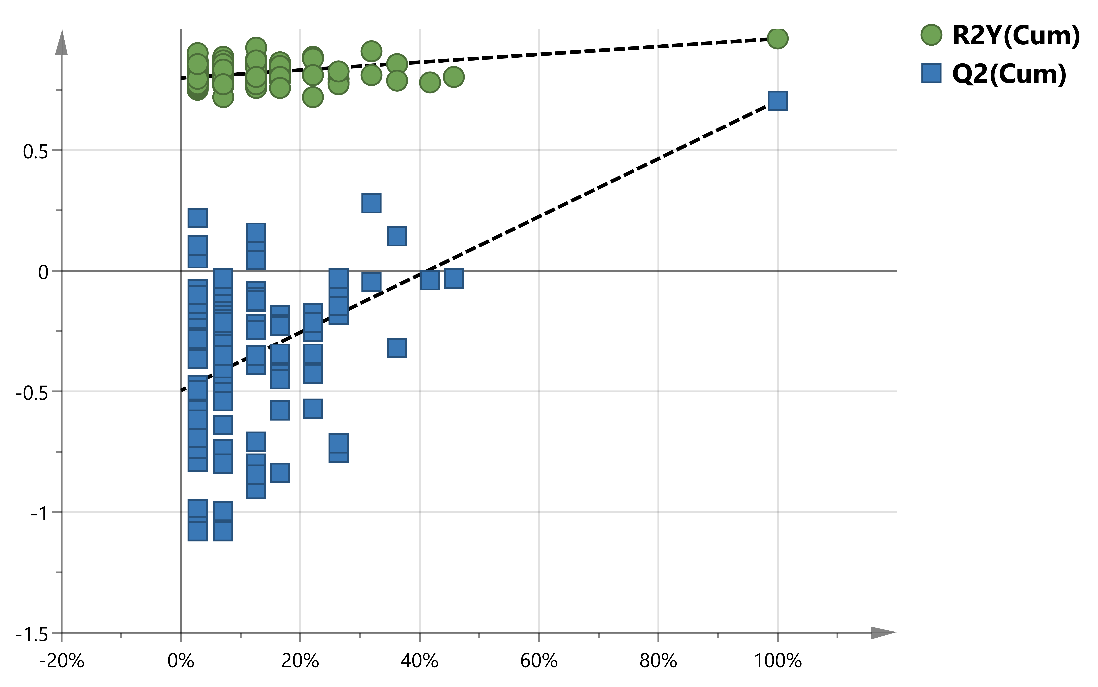
Negative ion mode; Controls-PPMS. A permutation test performed with 100 random permutations on the generated OPLS-DA model showed no overfitting of the model (Q2 = (0.0, -0.546)).

**Figure S.3B**

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Negative ion mode; Controls-SPMS. A permutation test performed with 100 random permutations on the generated OPLS-DA model showed no overfitting of the model (Q2 = (0.0, -0.557)).

**Figure S.3C**



Negative ion mode; PPMS-SPMS. A permutation test performed with 100 random permutations on the generated OPLS-DA model showed no overfitting of the model (Q2 = (0.0, -0.512)).