All supporting tables are in a machine-readable Excel Open XML spreadsheet format.

**Table S1. Chemical space explored in the study.**

Columns A-D give the code names, SMILES structural formulas, full names, and IUPAC proper names for all molecules in our chemical space. Column E gives the aggregate state (liquid or solid) at 25 oC, column F gives the chemical class (which can be ambiguous in a multifunctional molecule), and density in kg/m3 (for liquids only), when known. Column H indicates whether the molecule has been measured (1 for measured, 0 otherwise). Column I indicates to which initial K-means cluster the molecule belongs when the chemical space is grouped into eight classes using the Euclidean distances between the molecular descriptor vectors. Columns J-M give the projections of these vectors on the four main principal components (eigenvectors of covariance matrix with the largest eigenvalues) labeled PC1 to PC4. Column N gives the CAS numbers, column O gives their purity, and column P gives the source for molecules we studied. In column O, [1] is for reagents that were dried over molecular sieves, [2] is for HiPerSolv CHROMANORM for HPLC grade chemicals.

**Table S2. Summary of step-1 kinetic data.**

Columns A-F give the code names, SMILES structural formulas, full chemical names, class, molecular weights (g/mol) and densities (kg/m3) for reagents. Column G gives the molarity of MPT-BF4 in MeCN solutions. Column H gives the estimate of second-order reaction rate constants for the corresponding reagents with the time expressed in the units of hours and the concentrations expressed in the units of stock solution (by default, 100 vol% reagent). Column I indicates the relative error in the measurement (the standard deviation in the measured slope of the median reaction rate vs. reagent concentration). Column J indicates stock dilution factors for solid reagents. Column K gives the molarity of stock reagents. Column L converts the data in column H to the units of h-1 M-1 assuming ideality of the reaction mixtures. Column M gives the logarithms of these reaction constants. The last column (N) logs additions to SQL database keeping track of step-1 iterations. After each iteration, machine learning models are used to select reagents for the next iteration. The table does not include long-lived reagents for which rate constants could not be determined in dilute MeCN solutions over the observation period. These chemicals were used in step-2 trials, see Table S3.

**Table S3. Summary of step-2 kinetic data.**

Columns A-E give the code name of the solvent, SMILES structural formulas, full chemical names and chemical classes of the solvent molecules. All solutions initially contained 1 mM MPT-BF4. Column E indicates when the molecule was labeled “slow” in step-1 trials. Column F indicates the stability rank. Rank 0 molecules have projected lifetimes < 100 h. Rank 1-6 molecules, have the projected lifetimes > 1500 h, > 1000 h, > 500 h, > 300 h, > 200 h, and > 100 h, respectively (columns G to L). The solvents are grouped according to these ranks in the descending order of stability in step-2 trials. Column M indicates the diluent (FEC or MeCN) and column N gives the volume (for liquids) or weight (for solids) fractions of the reagent/solvent. Columns O and P give the projected lifetimes in step-2 and step-3 trials, and column Q gives the plate codes. By default, the step-3 trials are for PYR14 TFSI ionic liquid diluent at 50 vol%. Columns T to U indicate trial progress. The molecules suggested by logistic regression (LGR) and random forest (rf) models in Section S3.6 are indicated accordingly. “Linear” in column R refers to the molecules with extrapolated rate constants below that for water, and the asterisk refers to the molecules introduced from step-1 trials. In column S, “pos” refers to LGR predictions of > 100 h molecules. In columns T and U, these predictions were of > 1000 h molecules for LGR, whereas rf refers to the predictions of the rf model that were not threshold categorized (so all the top ranked candidates were tested). The lower part of the table included molecules that were too slow for step-1 but too fast for step-2. There are also molecules that were tested in step-2 (some of them predicted through LGR and rf models) that, actually, reacted rapidly, contrary to the model predictions.

**Table S4. Summary of step-3 kinetic data.**

The table summarizes data from the mixtures of solvent molecules and ionic liquid PYR14 TFSI that served as a co-solvent and electrolyte, typically at 50 vol%. All solutions initially contained 1 mM MPT-BF4. Columns A-D give the name, SMILES structural formulas, full chemical names, and chemical classes of the solvent molecules. Column E gives the composition of the solutions, and column F gives the linearly projected times in hours. Column G specifies the plate code, column H indicates the fit order (single vs double exponential), column I indicates the time frame of the observation, and column J shows the survival rate at the end of the observation period. Columns K to V give the data reduction tuples defined in Section S3.3. The column names correspond to the survival rates , and the rows give the interpolated or extrapolated times and uncertainties in the extrapolated times (where appropriate) corresponding to the attainment of the fraction of the surviving radical cation. The extrapolated values are indicated with the asterisks.