

## Supporting Information for

# Harvesting the Fragment-Based Nature of Bifunctional Organocatalysts to Enhance Their Activity

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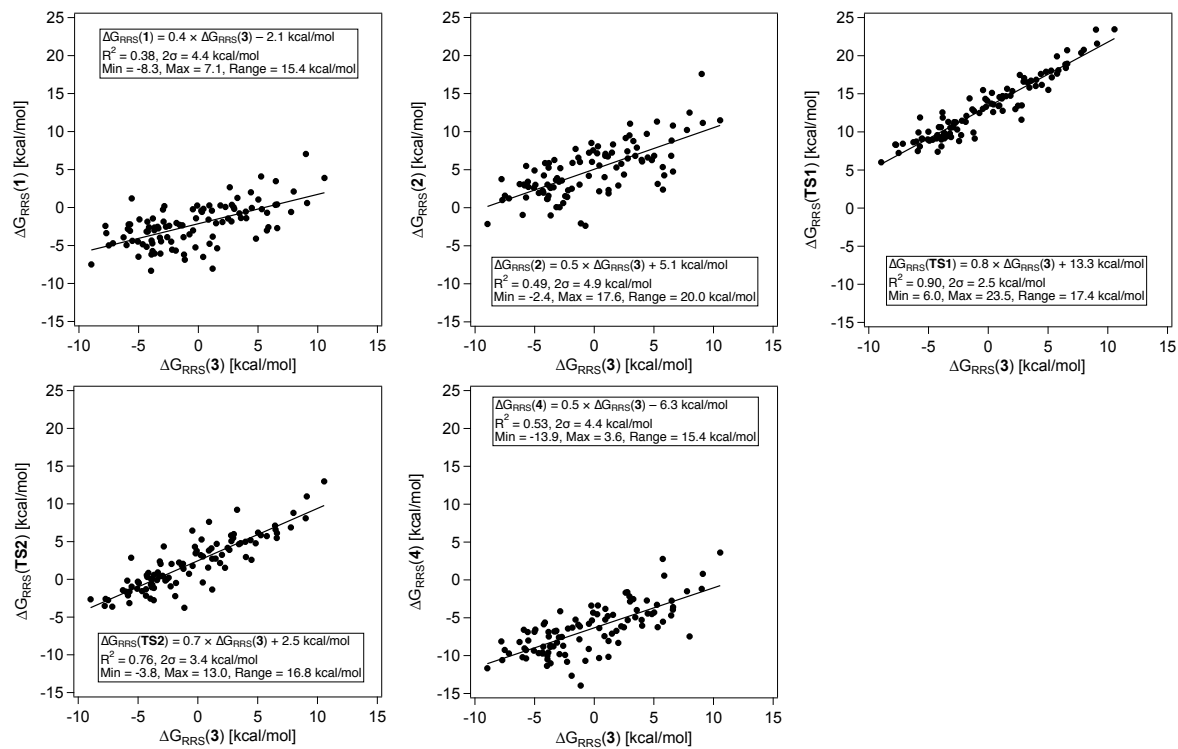
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# 1. Computational Details

## 1.1 Linear Free Energy Scaling Relationships



**Figure S1.** Linear free energy scaling relationships of catalytic cycle intermediates (1–4) and transition states TS1–2 for class 0 organocatalysts. X-axis is the chosen descriptor variable,  $\Delta G_{RRS}(3)$ .

## 1.2 Construction of TOF Volcano Plot

The TOF volcano plot was constructed based on the LFESRs shown in Figure S1. Detailed instructions are provided in ref. 1. The open source toolkit volcanic<sup>2</sup> was used to automatically generate the 1D (TOF volcano) and 2D (activity map) plots. The input files for volcanic containing the relative Gibbs Free energies of the class 0 organocatalysts to generate the Figure 2c plot and of the class 1–2 organocatalysts for the Figure 3 activity map are provided in Table S1 and Table S2, respectively. Based on the mean R<sup>2</sup> of 0.57, mean MAE of 1.05 kcal/mol and MAPE of 0.77, volcanic indicates  $\Delta G_{RRS}(3)$  to be the best descriptor for a 1D volcano plot.

**Table S1.** Relative Gibbs free energies (kcal/mol) of class 0 organocatalysts. This is the format of the input file for volcanic.

Catalyst	Cat	Int1	Int2	TS1	Int3	TS2	Int4	Product
Cat0	0	-2.2	2.9	9.9	-5.8	-2.1	-9.0	-8.8
Cat1	0	-2.4	3.8	8.3	-7.8	-3.5	-8.1	-8.8
Cat2	0	-4.5	2.6	9.0	-5.1	-1.2	-9.3	-8.8
Cat3	0	-3.9	3.1	8.6	-6.3	-1.4	-8.2	-8.8
Cat4	0	-5.2	2.2	9.3	-4.3	-2.2	-9.6	-8.8
Cat5	0	-5.0	1.6	7.2	-7.5	-2.7	-9.2	-8.8
Cat6	0	-4.5	1.4	9.6	-2.3	-0.9	-10.8	-8.8
Cat7	0	-4.3	1.1	8.1	-3.9	-0.7	-10.5	-8.8
Cat8	0	-2.8	3.1	7.5	-5.9	-0.2	-6.6	-8.8
Cat9	0	-2.2	5.5	11.9	-5.7	-1.6	-10.4	-8.8
Cat10	0	-5.5	2.3	11.5	-2.2	2.0	-6.4	-8.8
Cat11	0	-3.1	1.4	8.1	-5.7	-3.1	-9.3	-8.8
Cat12	0	-2.5	2.7	9.4	-3.4	-0.1	-8.8	-8.8
Cat13	0	-1.6	3.0	8.9	-4.9	-0.5	-6.6	-8.8
Cat14	0	-3.0	2.7	9.8	-3.7	-2.8	-8.8	-8.8
Cat15	0	-6.2	3.0	9.0	-3.9	0.1	-10.0	-8.8
Cat16	0	-3.2	2.1	9.1	-4.3	-1.3	-9.7	-8.8
Cat17	0	-3.9	0.6	10.3	-2.6	0.0	-8.7	-8.8
Cat18	0	-1.8	0.1	10.9	-2.9	0.4	-9.8	-8.8
Cat19	0	-7.5	-2.1	6.0	-9.0	-2.6	-11.7	-8.8
Cat20	0	-1.9	2.0	9.6	-4.3	0.6	-8.8	-8.8
Cat21	0	-4.7	1.2	8.5	-7.2	-3.6	-9.7	-8.8
Cat22	0	-3.4	1.0	8.3	-7.7	-2.6	-10.6	-8.8
Cat23	0	-1.4	6.0	13.3	-0.2	3.4	-5.3	-8.8
Cat24	0	2.7	9.2	17.5	2.6	3.9	-1.7	-8.8
Cat25	0	0.3	6.8	13.5	0.9	3.8	-5.2	-8.8
Cat26	0	-2.3	7.7	14.4	-1.6	2.2	-5.2	-8.8
Cat27	0	0.3	5.3	14.7	1.9	2.2	-6.7	-8.8
Cat28	0	-0.6	8.1	15.1	0.3	5.3	-3.4	-8.8
Cat29	0	-2.0	5.9	12.1	-1.8	-0.5	-6.3	-8.8
Cat30	0	-2.7	6.3	11.3	-3.4	0.9	-6.8	-8.8
Cat31	0	-4.4	2.7	9.1	-5.5	-1.0	-8.0	-8.8
Cat32	0	0.3	7.5	14.1	-0.1	3.8	-4.3	-8.8
Cat33	0	-0.8	6.8	15.8	3.4	4.7	-4.9	-8.8
Cat34	0	-2.6	5.9	10.6	-4.1	0.9	-5.6	-8.8
Cat35	0	-6.2	6.0	12.8	-1.2	1.4	-6.2	-8.8
Cat36	0	-2.5	3.6	11.3	-2.7	-0.2	-7.5	-8.8
Cat37	0	3.5	8.8	18.4	6.5	6.6	-2.7	-8.8
Cat38	0	-0.2	3.1	17.2	5.3	17.6	-6.2	-8.8
Cat39	0	0.6	11.2	21.6	9.1	11.0	0.8	-8.8
Cat40	0	-6.5	2.2	12.6	0.4	-0.4	-10.3	-8.8
Cat41	0	4.1	11.3	18.0	5.3	5.8	-3.3	-8.8
Cat42	0	-4.9	-0.9	8.7	-6.0	-1.6	-10.2	-8.8
Cat43	0	-2.3	6.6	13.0	-1.3	1.8	-5.9	-8.8
Cat44	0	-3.9	3.0	9.9	-1.2	2.1	-7.8	-8.8
Cat45	0	-0.2	11.0	17.1	3.0	6.0	-2.9	-8.8
Cat46	0	3.9	11.5	23.5	10.6	13.0	3.6	-8.8
Cat47	0	-0.4	7.2	13.7	0.2	3.2	-4.5	-8.8
Cat48	0	-4.7	1.6	9.4	-3.9	-1.0	-9.6	-8.8
Cat49	0	-2.1	7.2	14.7	1.5	2.7	-7.1	-8.8
Cat50	0	2.0	9.7	17.6	4.4	5.2	-2.7	-8.8
Cat51	0	-3.0	5.4	19.9	5.7	15.3	2.8	-8.8
Cat52	0	-0.7	2.4	17.6	5.8	5.7	-5.5	-8.8
Cat53	0	-6.1	0.1	10.6	-3.2	2.4	-6.7	-8.8
Cat54	0	-0.2	5.6	13.6	0.4	3.0	-6.4	-8.8
Cat55	0	-0.1	6.6	16.2	4.5	2.6	-4.4	-8.8
Cat56	0	-0.5	6.3	16.0	4.0	5.0	-5.3	-8.8

Cat57	0	-0.4	6.7	14.4	1.1	4.1	-4.8	-8.8
Cat58	0	0.2	5.2	11.3	-2.9	4.4	-4.1	-8.8
Cat59	0	-4.0	3.7	9.8	-3.2	0.4	-6.8	-8.8
Cat60	0	-0.2	4.2	13.0	-0.5	6.5	-9.1	-8.8
Cat61	0	-1.4	5.9	11.9	-3.8	-0.7	-7.5	-8.8
Cat62	0	1.3	8.8	16.5	3.3	9.2	-2.5	-8.8
Cat63	0	-1.6	4.0	13.4	0.9	1.6	-7.4	-8.8
Cat64	0	-0.3	3.4	10.6	-3.0	0.5	-7.6	-8.8
Cat65	0	-5.7	2.5	11.3	-1.9	-2.2	-12.7	-8.8
Cat66	0	-4.8	1.9	9.0	-4.7	-1.6	-9.7	-8.8
Cat67	0	-1.4	7.9	16.7	3.6	4.8	-4.0	-8.8
Cat68	0	0.4	10.8	20.7	6.6	5.5	-3.9	-8.8
Cat69	0	-8.3	1.2	10.6	-4.0	-2.6	-11.4	-8.8
Cat70	0	-5.7	5.3	12.6	-3.8	0.0	-6.9	-8.8
Cat71	0	-2.6	2.6	9.9	-3.7	-1.1	-8.7	-8.8
Cat72	0	-8.0	2.3	14.7	1.2	-1.3	-10.1	-8.8
Cat73	0	-2.7	4.8	18.9	6.6	6.1	-3.6	-8.8
Cat74	0	-4.1	6.3	17.9	4.8	4.8	-4.5	-8.8
Cat75	0	-0.6	10.2	20.4	7.8	6.9	-1.5	-8.8
Cat76	0	-4.8	7.1	14.6	0.9	7.6	-3.8	-8.8
Cat77	0	-3.0	7.2	15.5	-0.4	1.8	-5.8	-8.8
Cat78	0	-1.4	6.1	16.8	4.0	3.0	-6.0	-8.8
Cat79	0	0.1	9.5	16.6	2.9	5.5	-2.2	-8.8
Cat80	0	-6.1	-1.0	9.2	-3.7	0.6	-11.0	-8.8
Cat81	0	1.2	3.4	9.1	-5.6	2.9	-6.9	-8.8
Cat82	0	-1.9	2.9	15.4	2.0	3.3	-8.3	-8.8
Cat83	0	0.4	6.8	18.9	6.4	7.1	-4.7	-8.8
Cat84	0	-3.8	1.9	12.8	1.2	2.7	-8.1	-8.8
Cat85	0	-2.6	4.3	18.1	5.9	16.5	0.6	-8.8
Cat86	0	-3.5	-2.4	12.5	-0.7	0.7	-10.7	-8.8
Cat87	0	0.4	6.5	13.5	2.8	5.1	-5.3	-8.8
Cat88	0	-6.9	-2.1	9.1	-1.1	-3.8	-13.9	-8.8
Cat89	0	-2.4	1.5	8.8	-2.4	0.2	-9.9	-8.8
Cat90	0	-1.4	4.4	13.4	2.5	4.2	-6.3	-8.8
Cat91	0	1.1	6.8	15.5	5.0	6.2	-4.3	-8.8
Cat92	0	-3.2	4.3	7.4	-4.2	0.3	-5.9	-8.8
Cat93	0	-4.4	3.9	9.3	-3.1	2.1	-8.3	-8.8
Cat94	0	0.1	5.8	13.0	2.3	1.5	-6.1	-8.8
Cat95	0	-1.8	7.4	11.6	2.8	5.8	-1.6	-8.8
Cat96	0	-5.2	8.5	14.3	-0.2	4.3	-3.4	-8.8
Cat97	0	-5.4	8.3	15.7	1.6	4.7	-4.6	-8.8
Cat98	0	2.1	12.5	20.8	8.0	8.8	-7.5	-8.8
Cat99	0	7.1	17.6	23.4	9.0	8.1	-1.2	-8.8
Cat100	0	-6.5	4.9	10.0	-5.0	-0.3	-6.9	-8.8

**Table S2.** Relative Gibbs free energies (kcal/mol) of class 1–2 organocatalysts.

Catalyst	Cat	Int1	Int2	TS1	Int3	TS2	Int4	Product
Cat101	0	-1.4	3.6	6.3	-6.0	0.4	-6.3	-8.8
Cat102	0	-4.2	1.1	7.2	-6.2	-1.0	-7.9	-8.8
Cat103	0	-3.7	1.7	5.9	-6.9	-2.3	-8.1	-8.8
Cat104	0	-5.8	2.6	9.9	-4.9	1.0	-5.7	-8.8
Cat105	0	-4.2	2.6	6.7	-4.9	0.8	-6.7	-8.8
Cat106	0	-4.4	2.4	5.5	-6.2	0.1	-6.9	-8.8
Cat107	0	-4.1	2.6	5.8	-6.0	-0.4	-5.5	-8.8
Cat108	0	-2.5	3.1	5.4	-6.9	-0.6	-8.5	-8.8
Cat109	0	-3.7	1.9	5.6	-7.0	0.3	-8.6	-8.8
Cat110	0	-7.2	-0.3	2.7	-9.5	-5.3	-10.4	-8.8
Cat111	0	-6.6	0.8	3.6	-8.6	-3.5	-11.6	-8.8
Cat112	0	-1.7	4.5	7.7	-4.2	1.5	-6.3	-8.8
Cat113	0	-3.5	1.9	6.0	-6.4	-2.8	-9.9	-8.8
Cat114	0	-3.2	4.9	6.3	-5.8	-0.4	-6.7	-8.8
Cat115	0	-3.9	3.5	5.8	-5.8	-1.2	-7.5	-8.8
Cat116	0	-4.2	3.3	5.5	-6.5	-1.0	-7.4	-8.8
Cat117	0	-5.2	2.8	5.7	-6.0	-0.5	-7.8	-8.8
Cat118	0	-4.7	3.6	7.4	-3.8	1.8	-7.0	-8.8
Cat119	0	-4.6	3.3	7.9	-5.4	0.8	-6.9	-8.8
Cat120	0	-3.0	3.4	6.2	-7.0	1.3	-7.6	-8.8
Cat121	0	-4.4	3.0	6.9	-6.6	0.2	-7.3	-8.8
Cat122	0	-3.1	3.8	8.0	-6.1	-0.2	-7.8	-8.8
Cat123	0	-0.5	3.0	8.2	-6.2	-0.5	-7.8	-8.8
Cat124	0	-3.1	2.2	8.0	-5.9	-1.5	-8.9	-8.8
Cat125	0	-2.4	2.6	7.4	-7.0	-1.2	-8.4	-8.8

Cat126	0	-3.1	2.2	9.4	-4.1	-0.9	-9.4	-8.8
Cat127	0	-2.6	2.8	5.6	-7.7	0.4	-8.7	-8.8
Cat128	0	-2.2	2.6	6.4	-6.9	-0.8	-8.8	-8.8
Cat129	0	-5.7	2.6	5.8	-7.7	-2.3	-10.1	-8.8
Cat130	0	-3.2	3.2	6.2	-5.8	-1.5	-8.2	-8.8
Cat131	0	-2.5	2.5	7.8	-7.0	-0.5	-7.8	-8.8
Cat132	0	-8.3	0.3	4.3	-7.4	-5.0	-12.8	-8.8
Cat133	0	-2.6	1.9	6.6	-7.9	-1.7	-8.4	-8.8
Cat134	0	-4.3	1.0	6.3	-8.4	-2.3	-10.0	-8.8
Cat135	0	-1.3	2.6	6.4	-7.8	-1.3	-7.9	-8.8
Cat136	0	-4.2	2.0	8.3	-5.7	-1.4	-9.1	-8.8
Cat137	0	-2.3	3.4	5.8	-6.5	-0.2	-7.0	-8.8
Cat138	0	-1.8	4.0	5.5	-6.8	-0.4	-8.5	-8.8
Cat139	0	-8.2	-0.5	5.3	-8.7	-5.7	-13.0	-8.8
Cat140	0	-2.4	3.4	4.7	-7.5	-2.5	-9.1	-8.8
Cat141	0	-2.4	1.3	5.5	-9.2	-2.8	-9.2	-8.8
Cat142	0	-2.4	1.2	5.1	-8.8	-2.7	-9.1	-8.8
Cat143	0	-2.4		5.5	-9.2	-2.1	-8.5	-8.8
Cat144	0	-2.5	1.4	5.6	-9.4	-2.5	-8.8	-8.8
Cat145	0	-2.2	1.6	5.0	-9.7	-2.9	-9.3	-8.8

### 1.3 Multivariate Linear Regression Analysis

The organocatalyst's fragments NCBG, CBG, and BB were optimized following the same methods as in section 1.1, with the only difference that NCBGs were optimized and their single-point energies computed in a dimethyl sulfoxide (DMSO) continuum solvent (with the PCM method), in analogy with typical experimental acidity measurements.<sup>3</sup> NBO charges were calculated using NBO 3.1 in Gaussian16 at the PCM/ $\omega$ B97X-D/Def2-TZVP level.<sup>4</sup>

Conceptual DFT descriptors<sup>5-7</sup> were calculated as follows:

$$\text{Vertical ionization energy } I = E(N-1) - E(N)$$

$$\text{Vertical electron affinity } A = E(N) - E(N+1)$$

where  $E(N)$  stands for the PCM/ $\omega$ B97X-D/Def2-TZVP single-point energy of the  $N$ -electron species,  $E(N-1)$  and  $E(N+1)$  refer to the PCM/ $\omega$ B97X-D/Def2-TZVP energies of the species with  $N-1$  or  $N+1$  electrons, fixed to the optimized  $N$ -electron geometry.

$$\text{Hardness } \eta = (I - A)/2$$

$$\text{Softness } S = 1/\eta$$

$$\text{Electronegativity } \chi = (I + A)/2$$

$$\text{Global electrophilicity index } \omega = \chi^2 / 2\eta$$

$$\text{Global nucleophilicity index} = 1/\omega$$

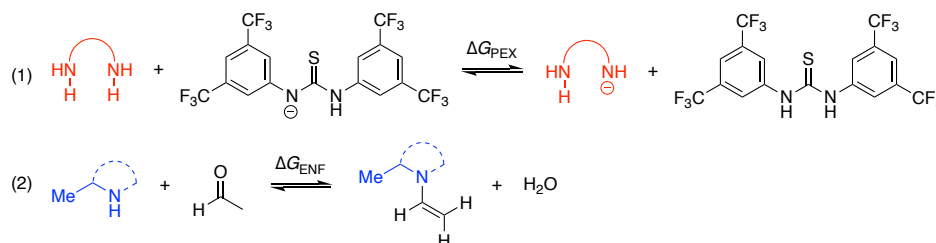
$$\text{Relative nucleophilicity } N = \varepsilon_{\text{HOMO}} - \varepsilon_{\text{HOMO}(\text{TCNE})}; \text{ TCNE} = \text{tetracyanoethylene}$$

$$\text{Fukui function } f_k^- = \text{NBO}(N)_{[N]} - \text{NBO}(N)_{[N-1]}$$

$$\text{Local nucleophilicity } N_k = \text{relative nucleophilicity } N \times f_k^-$$

where  $\text{NBO}(N)_{[N]}$  is the NBO charge of the CBG nitrogen atom of the  $N$ -electron species, while  $\text{NBO}(N)_{[N-1]}$  is the NBO charge of the CBG nitrogen atom of the  $N-1$ -electron species (fixed to the optimized  $N$ -electron geometry).

The NCBG descriptor  $\Delta G_{\text{PEX}}$  (Gibbs free energy change for proton exchange) and the CBG descriptor  $\Delta G_{\text{ENF}}$  (Gibbs free energy change for enamine formation) were calculated according to equations (1) and (2) in Figure S2.



**Figure S2.** Equilibria for proton exchange (1) and enamine formation (2).

Multidimensional Sterimol descriptors were calculated using the toolkit wSterimol by Paton and co-workers interfaced with Gaussian16.<sup>8</sup> Geometry optimizations were performed at the B97-D/Def2-SVP level and CPK atomic radii were used. The “primary bond” was defined as the  $\text{H}_2\text{N}-\text{X}$  bond in the BB fragment.

**Table S3.** NCBG descriptors for MLR analysis.

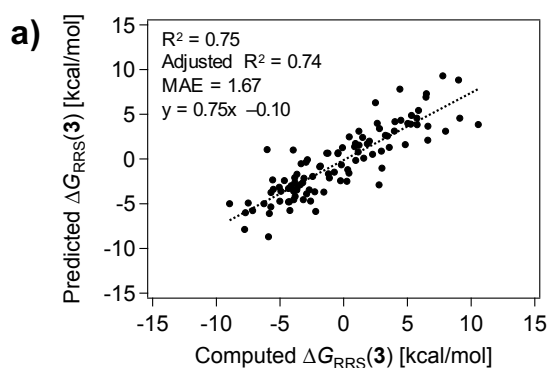
NCBG	HOMO (eV)	LUMO (eV)	I (eV)	A (eV)	$\eta$ (eV)	$S$ (1/eV)	$\chi$ (eV)	$\omega$ (eV)	$1/\omega$ (1/eV)	$\Delta G_{\text{PEX}}$ (kcal/mol)
0	-7.879	0.876	5.984	1.096	2.444	0.409	3.540	2.563	0.390	13.626
I	-7.734	-0.374	5.850	2.343	1.753	0.570	4.097	4.785	0.209	0.137
II	-9.754	2.949	7.891	-0.120	4.005	0.250	3.886	1.885	0.531	25.039
III	-8.340	1.649	6.219	0.505	2.857	0.350	3.362	1.978	0.505	15.712
IV	-8.816	2.855	6.715	-0.317	3.516	0.284	3.199	1.455	0.687	28.181
V	-8.934	1.712	6.947	0.042	3.452	0.290	3.495	1.769	0.565	14.297
VI	-7.939	2.587	6.060	-0.131	3.096	0.323	2.965	1.420	0.704	22.331
VII	-7.640	1.975	5.683	-0.124	2.903	0.344	2.780	1.331	0.751	16.461
VIII	-7.996	-0.960	6.104	2.885	1.609	0.621	4.494	6.277	0.159	4.090
IX	-10.356	2.540	8.468	-0.144	4.306	0.232	4.162	2.011	0.497	10.700

**Table S4.** CBG descriptors for MLR analysis.

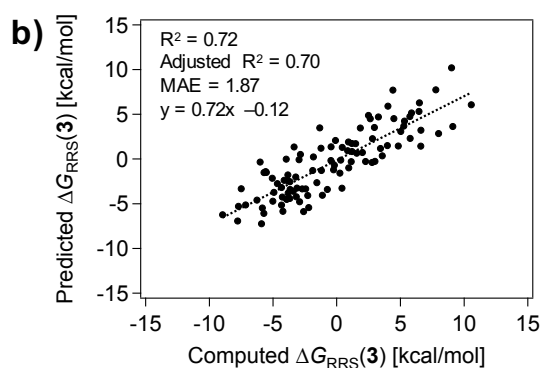
CBG	HOMO (eV)	LUMO (eV)	NBO(N) <sub>[N]</sub>	$N$ (eV)	NBO(N) <sub>[N-1]</sub>	$f_k^-$	$N_k$ (eV)	$\Delta G_{\text{ENF}}$ (kcal/mol)
0	-8.594	2.860	-0.633	2.341	-0.047	-0.586	-1.372	1.631
I	-8.837	2.971	-0.626	2.099	-0.044	-0.582	-1.221	2.590
II	-8.615	2.825	-0.632	2.320	-0.057	-0.575	-1.334	1.861
III	-8.515	2.762	-0.638	2.420	-0.065	-0.574	-1.388	1.723
IV	-8.237	2.195	-0.616	2.698	-0.574	-0.043	-0.115	4.918
V	-8.216	2.198	-0.637	2.719	-0.599	-0.038	-0.103	8.828
VI	-8.753	2.427	-0.627	2.182	-0.555	-0.073	-0.159	6.977
VII	-8.209	2.867	-0.636	2.726	-0.096	-0.540	-1.471	3.753
VIII	-7.412	1.461	-0.601	3.524	-0.346	-0.254	-0.896	7.715
IX	-8.873	2.770	-0.849	2.062	-0.259	-0.590	-1.217	5.611
X	-9.002	3.018	-0.840	1.933	-0.189	-0.651	-1.257	5.993
XI	-8.624	1.350	-0.837	2.311	-0.352	-0.484	-1.120	6.070
XII	-8.345	1.378	-0.628	2.590	-0.089	-0.539	-1.396	3.943
XIII	-8.570	1.252	-0.830	2.365	-0.768	-0.062	-0.147	6.576

**Table S5.** BB descriptors for MLR analysis.

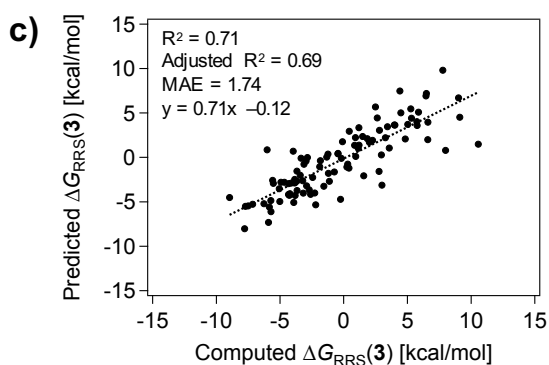
BB	HOMO (eV)	LUMO (eV)	wL	wB1	wB5	$v_{(N-H)}$ sym	$i_{(N-H)}$ sym	NBO(N) <sub>[N]</sub>
0	-8.210	0.395	7.410	2.330	5.050	3516.840	103.339	-0.781
I	-8.281	1.210	7.330	1.720	3.780	3501.754	91.585	-0.788
II	-7.274	1.347	8.840	1.780	3.610	3481.378	29.563	-0.807
III	-9.009	3.112	3.350	1.630	3.650	3402.236	1.236	-0.843
IV	-10.799	3.264	3.710	1.990	3.660	3469.720	36.043	-0.873
V	-9.770	2.954	4.400	1.550	3.670	3261.988	13.238	-0.529
VI	-8.682	1.304	5.350	1.610	6.040	3390.607	0.384	-0.826
VII	-7.322	0.439	6.750	1.820	5.700	3495.900	41.141	-0.798
VIII	-7.938	0.253	8.440	2.700	6.040	3406.069	0.186	-0.831
IX	-8.790	2.264	6.010	3.140	5.160	3423.121	4.687	-0.837
X	-7.816	-0.096	9.260	3.600	7.880	3419.073	0.478	-0.828
XI	-9.138	0.212	6.730	1.590	7.170	3398.650	0.167	-0.820
XII	-7.997	1.164	8.090	1.880	3.610	3513.228	95.099	-0.784
XIII	-8.587	0.668	8.130	2.200	3.810	3523.675	175.890	-0.770



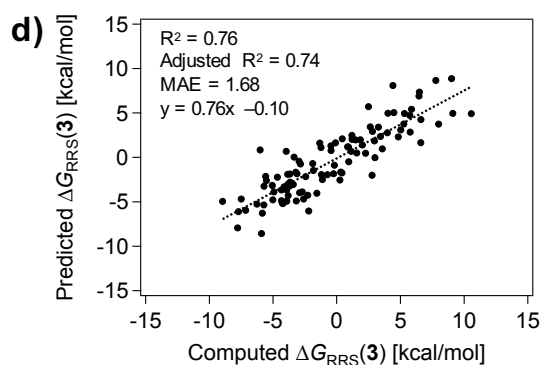
$$\Delta G_{\text{RRS}}(\mathbf{3}) = 4.18 \epsilon_{\text{LUMO,NCBG}} - 3.34 w_{\text{L}_{\text{BB}}} - 1.77 i_{(\text{N-H}),\text{BB}} + 10.46 \Delta G_{\text{ENF,CBG}} + 1.81 N_{\text{k,CBG}} - 3.13$$



$$\Delta G_{\text{RRS}}(\mathbf{3}) = -4.11 w_{\text{L}_{\text{BB}}} + 11.74 \Delta G_{\text{ENF,CBG}} + 9.15 \eta_{\text{,NCBG}} - 1.81 \epsilon_{\text{LUMO,CBG}} - 0.95 \text{NBO}(\text{N})_{[\text{M}],\text{BB}} - 8.66$$



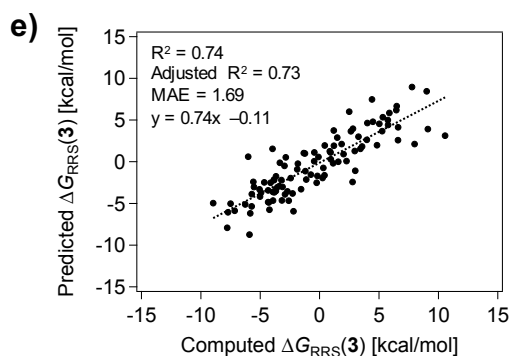
$$\Delta G_{\text{RRS}}(\mathbf{3}) = 5.10 \Delta G_{\text{PEX,NCBG}} - 3.94 w_{\text{L}_{\text{BB}}} - 1.87 i_{(\text{N-H}),\text{BB}} + 10.26 \Delta G_{\text{ENF,CBG}} + 1.93 N_{\text{k,CBG}} - 3.12$$



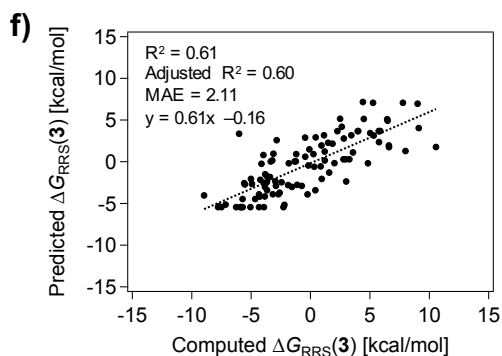
$$\Delta G_{\text{RRS}}(\mathbf{3}) = 2.53 \epsilon_{\text{LUMO,NCBG}} - 3.03 w_{\text{L}_{\text{BB}}} - 2.00 i_{(\text{N-H}),\text{BB}} + 9.74 \Delta G_{\text{ENF,CBG}} + 1.47 N_{\text{k,CBG}} + 3.72 \eta_{\text{,NCBG}} - 2.32 \epsilon_{\text{LUMO,CBG}} + 1.13 \text{NBO}(\text{N})_{[\text{M}],\text{BB}} - 1.92$$

**Figure S3.** Representative MLR models involving  $\Delta G_{\text{RRS}}(\mathbf{3})$  and the fragment parameters. Model *a* is reported in Figure 2d.

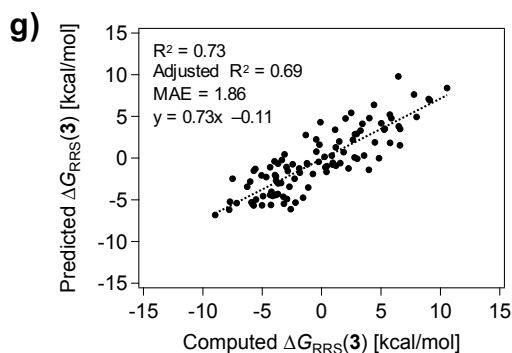




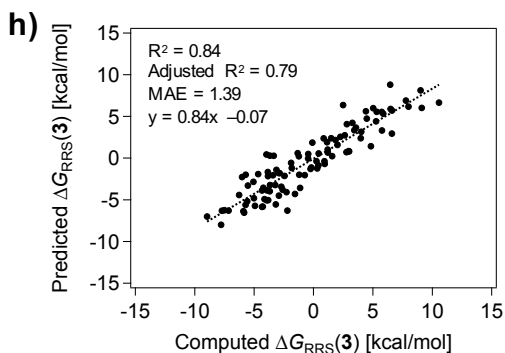
$$\Delta G_{RRS}(3) = 4.09 \epsilon_{LUMO,NCBG} - 3.20 w_{L_{BB}} - 1.87 i_{(N-H),BB} + 12.06 \Delta G_{ENF,CBG} - 5.20$$



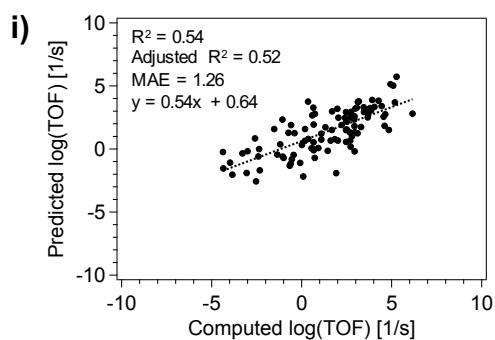
$$\Delta G_{RRS}(3) = -3.49 w_{L_{BB}} - 2.11 i_{(N-H),BB} + 10.43 \Delta G_{ENF,CBG} + 1.30 N_{k,CBG} - 1.24$$



$$\Delta G_{RRS}(3) = -38.73 \epsilon_{HOMO,NCBG} + 79.98 l_{,NCBG} - 58.35 \eta_{,NCBG} - 39.78 X_{,NCBG} + 13.86 1/\omega_{NCBG} + 43.66 \epsilon_{HOMO,CBG} - 24.45 NBO(N)_{[M],CBG} + 6.32 NBO(N)_{[N-1],CBG} + 11.92 N_{k,CBG} + 7.97 \epsilon_{HOMO,BB} - 6.72 w_{L_{BB}} - 0.80 w_{B5_{BB}} + 12.70$$



$$\Delta G_{RRS}(3) = -75.92 \epsilon_{HOMO,NCBG} + 12.06 \epsilon_{LUMO,NCBG} - 1.95 l_{,NCBG} + 170.08 A_{,NCBG} + 10.06 \eta_{,NCBG} - 51.35 S_{,NCBG} + 62.85 X_{,NCBG} - 95.39 \omega_{NCBG} + 119.38 1/\omega_{NCBG} - 1.79 \Delta G_{PEX,NCBG} - 160.56 \epsilon_{HOMO,CBG} - 1.89 \epsilon_{LUMO,CBG} - 29.64 NBO(N)_{[M],CBG} + 70.54 N_{,CBG} + 21.17 NBO(N)_{[N-1],CBG} + 14.34 f_{k^{-},CBG} + 4.98 N_{k,CBG} + 8.28 \Delta G_{ENF,CBG} + 8.11 \epsilon_{HOMO,BB} - 9.87 \epsilon_{LUMO,BB} - 12.88 w_{L_{BB}} + 7.12 w_{B1_{BB}} - 19.77 w_{B5_{BB}} - 89.95 v_{(N-H),BB} - 1.92 i_{(N-H),BB} - 9.78 NBO(N)_{[M],BB} - 268.91$$



$$\log(\text{TOF}) = -2.95 \epsilon_{LUMO,NCBG} - 1.57 w_{L_{BB}} + 1.25 i_{(N-H),BB} - 4.91 \Delta G_{ENF,CBG} + 0.51 N_{k,CBG} + 6.15$$

**Figure S4.** Representative MLR models involving  $\Delta G_{RRS}(3)$  and the fragment parameters (continued). In model *i* the turnover frequency is parametrized.

**Table S6.** Training set.

Catalyst	$\Delta G_{RRS}(3)$	$\Delta G_{RRS}(3)$
	computed [kcal/mol]	predicted [kcal/mol]
Cat2	-5.1	-3.3
Cat3	-6.3	-5.0
Cat5	-7.5	-4.9
Cat6	-2.3	-3.7
Cat8	-5.9	-8.5
Cat10	-2.2	-5.8
Cat13	-4.9	-3.8
Cat14	-3.7	-3.7
Cat15	-3.9	-3.8
Cat16	-4.3	-4.9
Cat17	-2.6	-4.9
Cat21	-7.2	-5.7
Cat23	-0.2	-1.1
Cat25	0.9	1.2
Cat26	-1.6	-3.6
Cat27	1.9	1.5
Cat28	0.3	-1.2
Cat29	-1.8	-0.8
Cat30	-3.4	-0.6
Cat32	-0.1	0.8
Cat33	3.4	1.7
Cat34	-4.1	-3.1
Cat36	-2.7	-3.5
Cat37	6.5	6.3
Cat41	5.3	3.2
Cat42	-6.0	0.5
Cat43	-1.3	0.5
Cat49	1.5	2.0
Cat51	5.7	4.1
Cat53	-3.2	-4.6
Cat54	0.4	1.8
Cat55	4.5	3.8
Cat58	-2.9	-0.3
Cat59	-3.2	-2.8
Cat62	3.3	2.3
Cat63	0.9	0.8
Cat65	-1.9	-1.3
Cat66	-4.7	-2.7
Cat67	3.6	1.0
Cat71	-3.7	-2.1
Cat72	1.2	2.7
Cat73	6.6	3.2
Cat75	7.8	8.3
Cat78	4.0	3.7
Cat82	2.0	1.3
Cat83	6.5	5.9
Cat87	2.8	3.0
Cat89	-2.4	-2.3
Cat93	-3.1	-2.7
Cat94	2.3	-0.1
Cat100	-5.0	-4.7

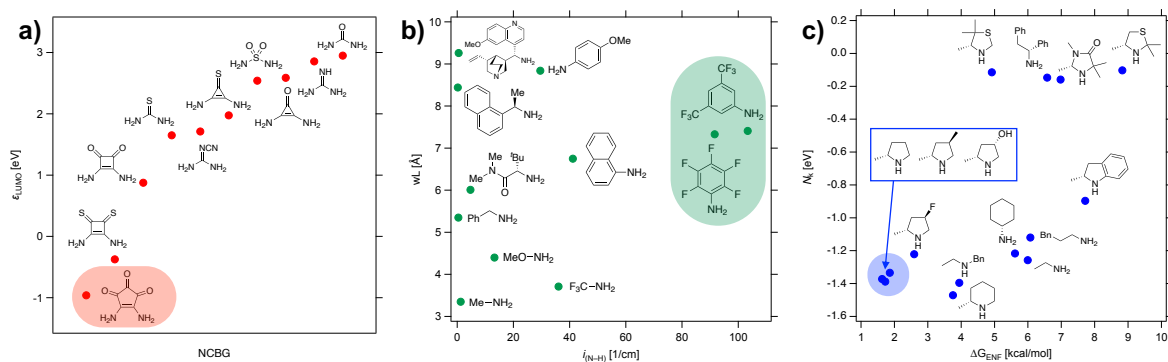
**Table S7.** Validation set.

Catalyst	$\Delta G_{RRS}(3)$	$\Delta G_{RRS}(3)$
	computed [kcal/mol]	predicted [kcal/mol]
Cat0	-5.8	-6.0
Cat1	-7.8	-7.7
Cat4	-4.3	-3.4
Cat7	-3.9	-4.6
Cat9	-5.7	-3.8
Cat11	-5.7	-5.4
Cat12	-3.4	-3.2
Cat18	-2.9	-4.1
Cat19	-9.0	-5.1
Cat20	-4.3	-4.8
Cat22	-7.7	-5.9
Cat24	2.6	3.4
Cat31	-5.5	-3.3
Cat35	-1.2	-1.8
Cat38	5.3	4.4
Cat39	9.1	3.7
Cat40	0.4	-1.9
Cat44	-1.2	0.3
Cat45	3.0	-1.4
Cat46	10.6	3.2
Cat47	0.2	-2.6
Cat48	-3.9	-2.4
Cat50	4.4	6.9
Cat52	5.8	3.4
Cat56	4.0	2.4
Cat57	1.1	0.0
Cat60	-0.5	0.0
Cat61	-3.8	-4.2
Cat64	-3.0	-0.8
Cat68	6.6	1.7
Cat69	-4.0	0.7
Cat70	-3.8	-2.6
Cat74	4.8	1.2
Cat76	0.9	-0.4
Cat77	-0.4	0.3
Cat79	2.9	0.7
Cat80	-3.7	-3.4
Cat81	-5.6	-2.6
Cat84	1.2	1.1
Cat85	5.9	4.9
Cat86	-0.7	-1.8
Cat88	-1.1	-2.4
Cat90	2.5	5.5
Cat91	5.0	3.5
Cat92	-4.2	-5.9
Cat95	2.8	-2.9
Cat96	-0.3	-2.7
Cat97	1.6	-0.4
Cat98	8.0	2.2
Cat99	9.0	7.9

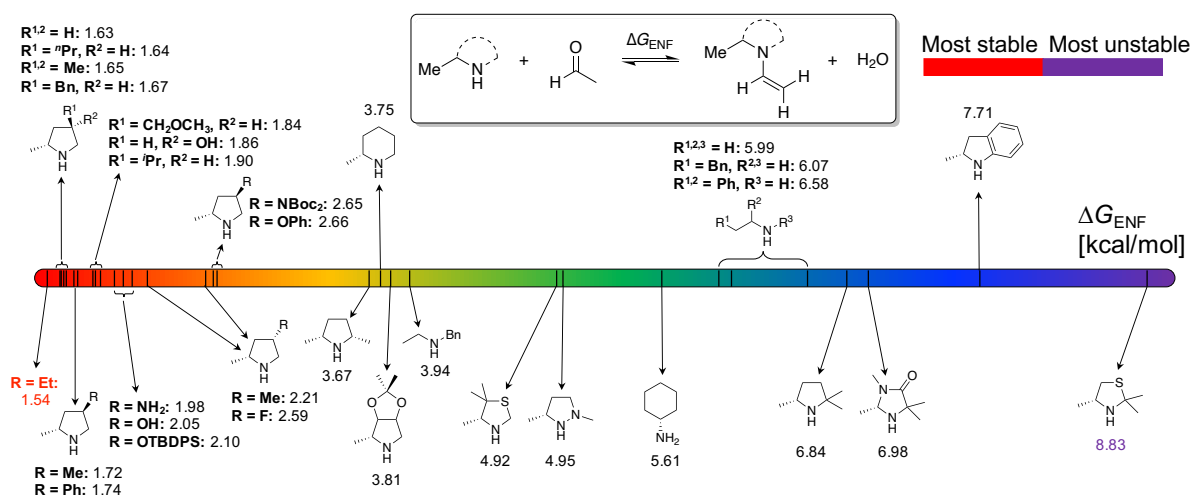
**Table S8.** NCBG–BB–CBG combinations for class 0 organocatalysts.

Catalyst	NCBG	BB	CBG
Cat0	0	0	0
Cat1	I	0	0
Cat2	II	0	0
Cat3	III	0	0
Cat4	IV	0	0
Cat5	V	0	0
Cat6	VI	0	0
Cat7	VII	0	0
Cat8	VIII	0	0
Cat9	IX	0	0
Cat10	0	I	0
Cat11	0	II	0
Cat12	0	III	0
Cat13	0	IV	0
Cat14	0	V	0
Cat15	0	VI	0
Cat16	0	VII	0
Cat17	0	VIII	0
Cat18	0	IX	0
Cat19	0	X	0
Cat20	0	0	I
Cat21	0	0	II
Cat22	0	0	III
Cat23	0	0	IV
Cat24	0	0	V
Cat25	0	0	VI
Cat26	0	0	VII
Cat27	0	0	VIII
Cat28	0	0	IX
Cat29	0	0	X
Cat30	0	0	XI
Cat31	0	0	XII
Cat32	0	0	XIII
Cat33	0	III	IV
Cat34	I	IV	VII
Cat35	I	VII	IX
Cat36	III	I	I
Cat37	II	V	VI
Cat38	VI	II	VIII
Cat39	III	IX	XIII
Cat40	IV	VIII	II
Cat41	VIII	VI	V
Cat42	I	X	VI
Cat43	V	0	XI
Cat44	VII	IV	XII
Cat45	IX	V	III
Cat46	IX	I	XIII
Cat47	VIII	VII	IX
Cat48	II	II	II
Cat49	III	VI	IX
Cat50	V	V	V
Cat51	VII	VII	VIII
Cat52	VI	IX	X
Cat53	0	I	I
Cat54	0	II	VI
Cat55	0	V	VIII
Cat56	0	VIII	VI
Cat57	I	III	IV
Cat58	I	IV	X
Cat59	I	VI	XII
Cat60	I	X	XIII
Cat61	I	VII	VII
Cat62	II	I	XI
Cat63	II	III	I
Cat64	II	IV	II
Cat65	II	IX	III
Cat66	II	II	0
Cat67	III	VIII	IX
Cat68	III	IX	IX
Cat69	III	X	IX
Cat70	III	0	VII
Cat71	III	III	III

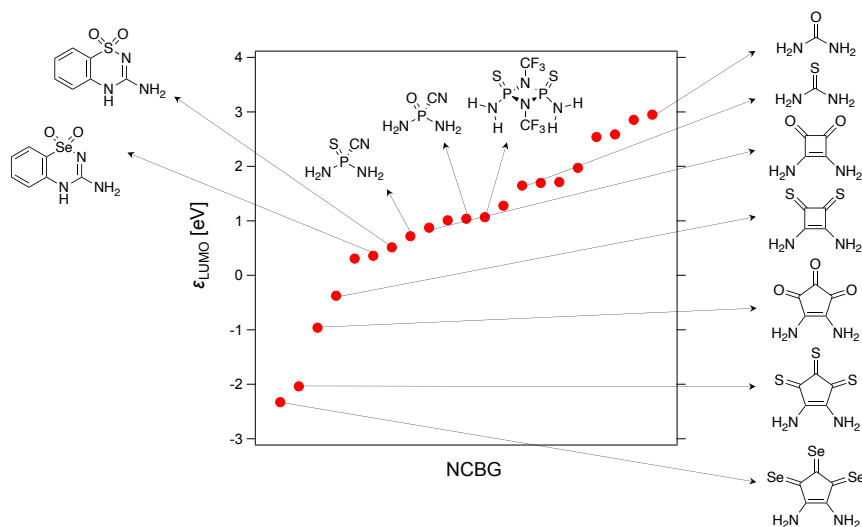
Cat72	IV	X	X
Cat73	IV	VIII	XI
Cat74	IV	IX	XII
Cat75	IV	VI	V
Cat76	IV	II	VII
Cat77	V	III	VII
Cat78	V	VII	VIII
Cat79	V	I	XI
Cat80	V	VIII	II
Cat81	V	IV	III
Cat82	VI	I	IV
Cat83	VI	III	XIII
Cat84	VI	VI	XII
Cat85	VI	VII	VIII
Cat86	VI	IX	0
Cat87	VII	V	X
Cat88	VII	X	I
Cat89	VII	VI	III
Cat90	VII	II	V
Cat91	VII	III	X
Cat92	VIII	V	II
Cat93	VIII	X	IV
Cat94	VIII	VIII	VI
Cat95	VIII	I	XI
Cat96	IX	VII	0
Cat97	IX	VI	I
Cat98	IX	VIII	IV
Cat99	IX	IV	V
Cat100	I	II	VII



**Figure S5.** a) Comparison of NCBG fragments according to their  $\epsilon_{LUMO}$ . b) BBs analyzed according to their  $i_{(N-H)}$  (x-axis) and  $wL$  (y-axis) descriptor values. c) CBGs analyzed according to their  $\Delta G_{ENF}$  (x-axis) and  $N_k$  (y-axis) values. The fragments giving the lowest  $\Delta G_{RRS}$ (3) values, according to the MLR analysis, are highlighted.



**Figure S6.**  $\Delta G_{ENF}$  values (kcal/mol) of all CBG fragments considered.



**Figure S7.**  $\epsilon_{LUMO}$  values (eV) of all NCBG fragments considered.

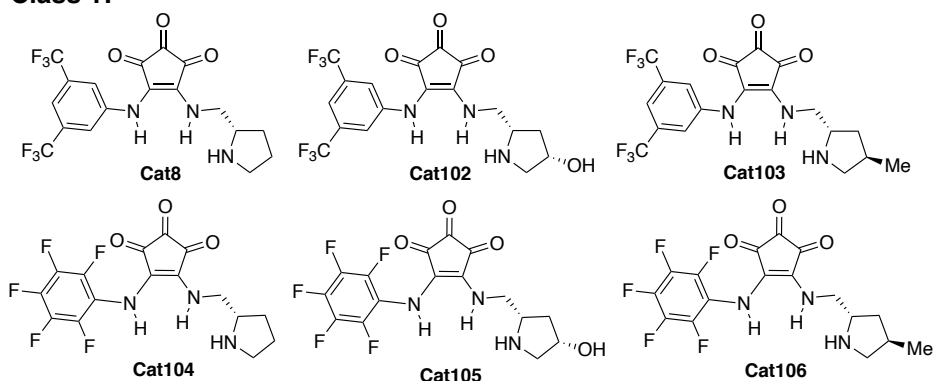
## 2. Structure of Class 0–2 Organocatalysts

Table S9. SMILES strings of class 0–2 organocatalysts.

Catalyst	Class	SMILES
Cat0	0	O=C1C(NC2=CC(C(F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCCC3)C1=O
Cat1	0	S=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCCC3)C1=O
Cat2	0	O=C(NC[C@H]1NCCC1)NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2
Cat3	0	S=C(NC[C@H]1NCCC1)NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2
Cat4	0	N=C(NC[C@H]1NCCC1)NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2
Cat5	0	N#CN=C(NC[C@H]1NCCC1)NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2
Cat6	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C1NC[C@H]3NCCC3
Cat7	0	S=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C1NC[C@H]3NCCC3
Cat8	0	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCCC2)C3=O)C3=O
Cat9	0	O=S(NC1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=NC[C@H]2NCCC2)O
Cat10	0	O=C1C(NC[C@H]2NCCC2)=C(NC3=CC(C(F)F)F)=C(F)C(F)=C3)F)C1=O
Cat11	0	O=C1C(NC2=CC=C(OC)C=C2)=C(NC[C@H]3NCCC3)C1=O
Cat12	0	O=C1C(NC)=C(NC[C@H]2NCCC2)C1=O
Cat13	0	O=C1C(NC(F)F)=C(NC[C@H]2NCCC2)C1=O
Cat14	0	O=C1C(NOC)=C(NC[C@H]2NCCC2)C1=O
Cat15	0	O=C1C(NC2=CC=CC=C2)=C(NC[C@H]3NCCC3)C1=O
Cat16	0	O=C1C(NC2=CC=CC3=C2C=CC=C3)=C(NC[C@H]4NCCC4)C1=O
Cat17	0	O=C1C(NC[C@H]1)C2=C(C=CC=C3)C3=CC=C2)=C(NC[C@H]4NCCC4)C1=O
Cat18	0	O=C1C(NC[C@H]1(C)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat19	0	O=C1C(NC[C@H]1(C)C2=CC=NC3=C2C=C(OC)C=C3)[C@H]4[C@H]1(C)C5)[C@H]1(C)C=C)C[N@]5C4)=C(NC[C@H]6NCCC6)C1=O
Cat20	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC3)C1=O
Cat21	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat22	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat23	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat24	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat25	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat26	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCCC3)C1=O
Cat27	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat28	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]3NCCC3)C1=O
Cat29	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NCCN)C1=O
Cat30	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]1)C3=CC=CC=C3)C1=O
Cat31	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NCCNCC3=CC=CC=C3)C1=O
Cat32	0	O=C1C(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=C(NC[C@H]1)C3=CC=CC=C3)[C@H]1(C)C4=CC=CC=C4)N)C1=O
Cat33	0	O=C1C(NC)=C(NC[C@H]2NCCC2)C1=O
Cat34	0	S=C1C(NC(F)F)=C(NC[C@H]2NCCC2)C1=S
Cat35	0	S=C1C(NC2=CC=CC3=C2C=CC=C3)=C(NC[C@H]4C@H]1(N)CCCC4)C1=S
Cat36	0	S=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat37	0	O=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat38	0	O=C1C(NC2=CC=C(OC)C=C2)=C1NC[C@H]3NCC(C)C)C1=O
Cat39	0	S=C(NC[C@H]1(C)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat40	0	N=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat41	0	O=C(C(N[H])C1=CC=CC=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat42	0	S=C1C(NC[C@H]1(C)C2=CC=NC3=C2C=C(OC)C=C3)[C@H]4[C@H]1(C)C5)[C@H]1(C)C=C)C[N@]5C4)=C(NC[C@H]6NCC(C)C)C1=O
Cat43	0	NC[C@H]1(C)C1=CC=CC=C1)NC(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)=NC#N
Cat44	0	S=C1C(NC(F)F)=C1NCCNCC2=CC=CC=C2
Cat45	0	O=S(NOC)N(C)C[C@H]1NCC1)C1=O
Cat46	0	O=S(NC1=C(F)F)=C1F)C(F)=C1F)N(C)C[C@H]1(C)C2=CC=CC=C2)N)C3=CC=CC=C3)O)C4=O
Cat47	0	O=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat48	0	O=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat49	0	S=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat50	0	N#CN=C(NC1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat51	0	S=C1C(NC2=CC=CC3=C2C=CC=C3)=C1NC[C@H]4NCC(C)C)C1=O
Cat52	0	O=C1C(NC[C@H]1(C)C(C)C(N)C)O)=C1NCCN
Cat53	0	O=C1C(NC[C@H]2NCC(C)C)C2)=C(NC3=C(F)F)=C(F)C(F)=C3)C1=O
Cat54	0	O=C1C(NC2=CC=C(OC)C=C2)=C(NC[C@H]3NCC(C)C)C1=O
Cat55	0	O=C1C(NC[C@H]2NCC(C)C)C2)=C(NOC)C1=O
Cat56	0	O=C1C(NC[C@H]1(C)C(C)C(N)C)O)=C(NC[C@H]2NCC(C)C)C1=O
Cat57	0	S=C1C(NC)=C(NC[C@H]2NCCC2)C1=S
Cat58	0	S=C1C(NC(F)F)=C(NCCN)C1=S
Cat59	0	S=C1C(NC2=CC=CC=C2)=C(NCCNCC3=CC=CC=C3)C1=S
Cat60	0	S=C1C(NC[C@H]1(C)C2=CC=NC3=C2C=C(OC)C=C3)[C@H]4[C@H]1(C)C5)[C@H]1(C)C=C)C[N@]5C4)=C(NC[C@H]6NCC(C)C)C1=O
Cat61	0	S=C1C(NC2=CC=CC3=C2C=CC=C3)=C(NC[C@H]4NCCC4)C1=S
Cat62	0	O=C(NC[C@H]1(C)C1=CC=CC=C1)NC(NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2)F
Cat63	0	O=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat64	0	O=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat65	0	O=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat66	0	O=C(NC[C@H]1NCCC1)NC2=CC=C(OC)C=C2
Cat67	0	S=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat68	0	S=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat69	0	S=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat70	0	S=C(NC[C@H]1NCC1)NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2
Cat71	0	S=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat72	0	N=C(NCCN)N(C)C[C@H]1(C)C2=CC=C(OC)C=C2)[C@H]3[C@H]1(C)C4)[C@H]1(C)C=C)C[N@]4C3
Cat73	0	N=C(NC[C@H]1(C)C1=CC=CC=C1)NC(NC[C@H]1(C)C2=C(C=CC=C3)C3=CC=C2)
Cat74	0	N=C(NCCNCC1=CC=CC=C1)NC(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat75	0	N=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat76	0	N=C(NC[C@H]1NCCC1)NC2=CC=C(OC)C=C2
Cat77	0	N#CN=C(NC[C@H]1NCCC1)NC
Cat78	0	N#CN=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C2C1)NC3=CC=CC4=C3C=CC=C4
Cat79	0	FC1=C(F)C(F)=C(F)C(NC[N]C@H]1(C)C2=CC=CC=C2)CN=N)C1=O
Cat80	0	O[C@H]1(C)C1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat81	0	N#CN=C(NC[C@H]1NCC1)C(C)C(N)C)O)=C(NC[C@H]2NCCC2)C1=O
Cat82	0	O=C1C(NC2=C(F)F)=C(F)C(F)=C2F)=C1NC[C@H]3NCC3)C1=O
Cat83	0	O=C1C(NC)=C1N[C@H]1(C)C2=CC=CC=C2)[C@H]1(C)C3=CC=CC=C3)N
Cat84	0	O=C1C(NC2=CC=CC=C2)=C1NCCNCC3=CC=CC=C3
Cat85	0	O=C1C(NC2=CC=CC3=C2C=CC=C3)=C1NC[C@H]4NCC(C)C)C1=O
Cat86	0	O=C1C(NC[C@H]1(C)C(C)C(N)C)O)=C1NC[C@H]2NCCC2
Cat87	0	S=C1C(NOC)=C1NCCN
Cat88	0	S=C1C(NC[C@H]1(C)C2=CC=NC3=C2C=C(OC)C=C3)[C@H]4[C@H]1(C)C5)[C@H]1(C)C=C)C[N@]5C4)=C(NC[C@H]6NCC(C)C)C1=O
Cat89	0	S=C1C(NCC2=CC=CC=C2)=C1NC[C@H]3NCC(C)C)C1=O
Cat90	0	S=C1C(NC2=CC=C(OC)C=C2)=C1NC[C@H]3NCC(C)C)C1=O
Cat91	0	S=C1C(NC)=C1NCCN
Cat92	0	O=C(C(N[H])C1=CC=CC=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat93	0	O=C(C(N[H])C1=CC=CC=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat94	0	O=C(C(N[H])C1=CC=CC=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat95	0	O=C(C(N[H])C1=CC=CC=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat96	0	O=S(NC1=CC=CC=C1)NC(C)C(N)C)O)=C(NC[C@H]3NCCC3)C1=O
Cat97	0	O=S(NCC1=CC=CC=C1)NC(C)C(N)C)O)=C(NC[C@H]3NCCC3)C1=O
Cat98	0	O=S(NC[C@H]1(C)C1=CC=CC=C1)NC(C)C(N)C)O)=C(NC[C@H]3NCCC3)C1=O
Cat99	0	O=S(NC(F)F)N(C)C[C@H]1NCC1)C1=O
Cat100	0	S=C1C(NC2=CC=C(OC)C=C2)=C(NC[C@H]3NCCC3)C1=O
Cat101	1	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat102	1	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat103	1	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat104	1	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat105	1	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat106	1	O=C(C(N[H])C1=CC(C(F)F)F)=CC(C(F)F)F)=C1)=C(N[H])C[C@H]2NCC(C)C)C3=O)C3=O
Cat122	2	O=P([N]C[C@H]1NCCC1)C(N)NC2=CC(C(F)F)F)=CC(C(F)F)F)=C2
Cat123	2	F[B-]1(F)C(C=CC=C2)=C2NC(NC[C@H]3NCCC3)=O+1
Cat124	2	O=C1C(C=CC=C2)=C2NC(NC[C@H]3NCCC3)=N1
Cat125	2	O=S1(C)C=CC=C2)=C2NC(NC[C@H]3NCCC3)=N1=O
Cat126	2	FC1=C(C(F)F)F)=C2=C1NC(NC[C@H]3NCCC3)=N2)F)F

Cat131	2	S=[P@](NC[C@H]1NCCC1)(C#N)NC2=CC(C(F)F)F=CC(C(F)F)F=C2
Cat132	2	S=[P@@](N1C(C)C(C)N(C2=CC(C(F)F)F)=CC(C(F)F)F=C2)[H]N(C)C(C)C[P@@]1(N([H])C[C@H]3NCCC3)=S
Cat133	2	F[B-]1(F)C(C)C(F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NCCC3)=[O+]
Cat134	2	O=C1C(C(F)F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NCCC3)=N1
Cat135	2	O=S1C(C)C(F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NCCC3)=N1=O
Cat136	2	FC1=CC(C(F)F)F=CC(N2)=C1N=C2NC[C@H]3NCCC3(F)F
Cat139	2	S=[P@@](N1C(F)F)N(C2=CC(C(F)F)F)=CC(C(F)F)F=C2)[H]N(C(F)F)F[P@@]1(N([H])C[C@H]3NCCC3)=S
Cat141	2	O=S1C(C)C(F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NC[C@H](C)C3)=N1=O
Cat142	2	O=S1C(C)C(F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NC[C@H](CC)C3)=N1=O
Cat101	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NCC2)C3=S)C3=S
Cat107	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](O)C2)C3=S)C3=S
Cat108	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](C)C2)C3=S)C3=S
Cat109	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC(C)C2)C3=S)C3=S
Cat110	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NCC2)C3=S)C3=S
Cat111	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](O)C2)C3=S)C3=S
Cat112	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](C)C2)C3=S)C3=S
Cat113	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC(C)C2)C3=S)C3=S
Cat114	2	S=C(CN([H])C1=CC=C(C(F)F)F=C1)=C(N([H])C[C@H]2NCC2)C3=S)C3=S
Cat115	2	S=C(CN([H])C1=CC=C(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](O)C2)C3=S)C3=S
Cat116	2	S=C(CN([H])C1=CC=C(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](C)C2)C3=S)C3=S
Cat117	2	S=C(CN([H])C1=CC=C(C(F)F)F=C1)=C(N([H])C[C@H]2NCC(C)C2)C3=S)C3=S
Cat118	2	S=C(CN([H])C1=C(F)F)F=C(C(F)F)F)F=C1F)=C(N([H])C[C@H]2NCC2)C3=S)C3=S
Cat119	2	S=C(CN([H])C1=C(F)F)F=C(C(F)F)F)F=C1F)=C(N([H])C[C@H]2NC[C@H](O)C2)C3=S)C3=S
Cat120	2	S=C(CN([H])C1=C(F)F)F=C(C(F)F)F)F=C1F)=C(N([H])C[C@H]2NC[C@H](C)C2)C3=S)C3=S
Cat121	2	S=C(CN([H])C1=C(F)F)F=C(C(F)F)F)F=C1F)=C(N([H])C[C@H]2NCC(C)C2)C3=S)C3=S
Cat127	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](CC)C2)C3=S)C3=S
Cat128	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](CC)C2)C3=S)C3=S
Cat129	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](CC)C2)C3=S)C3=S
Cat130	2	S=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](CC)C2)C3=S)C3=S
Cat137	2	[Se]=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NCC2)C3=[Se])C3=[Se]
Cat138	2	[Se]=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](C)C2)C3=[Se])C3=[Se]
Cat140	2	[Se]=C(CN([H])C1=CC(C(F)F)F=CC(C(F)F)F=C1)=C(N([H])C[C@H]2NC[C@H](CC)C2)C3=[Se])C3=[Se]
Cat143	2	O=[Se]1(C)C(C(F)F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NCCC3)=N1=O
Cat144	2	O=[Se]1(C)C(C(F)F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NC[C@H](C)C3)=N1=O
Cat145	2	O=[Se]1(C)C(C(F)F)F=CC(C(F)F)F=C2=C2NC(NC[C@H]3NC[C@H](CC)C3)=N1=O

### Class 1:



### Class 2:

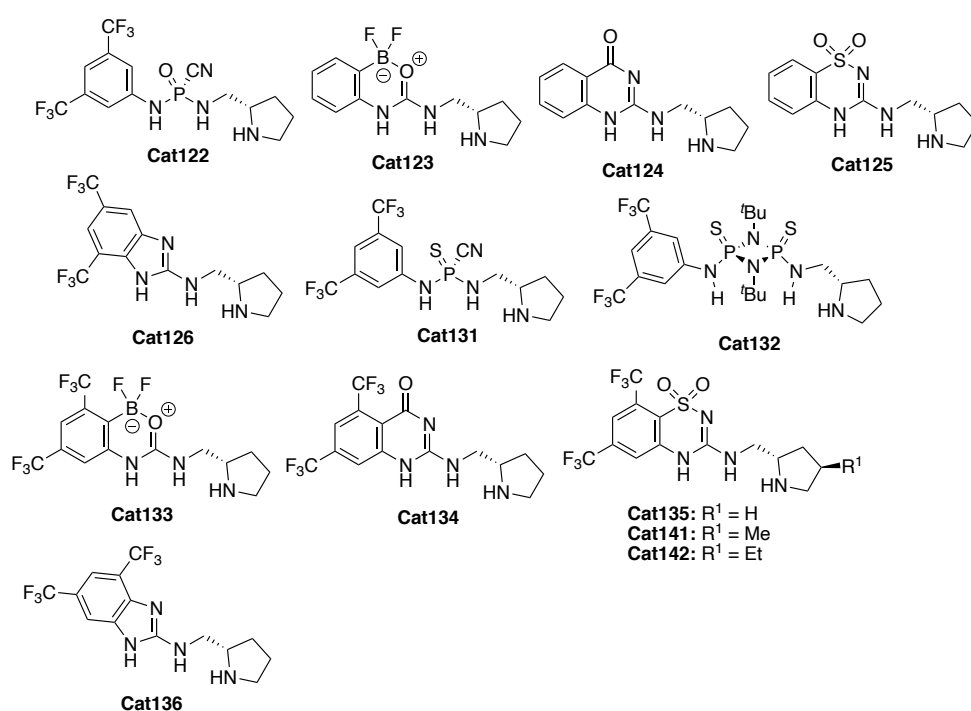
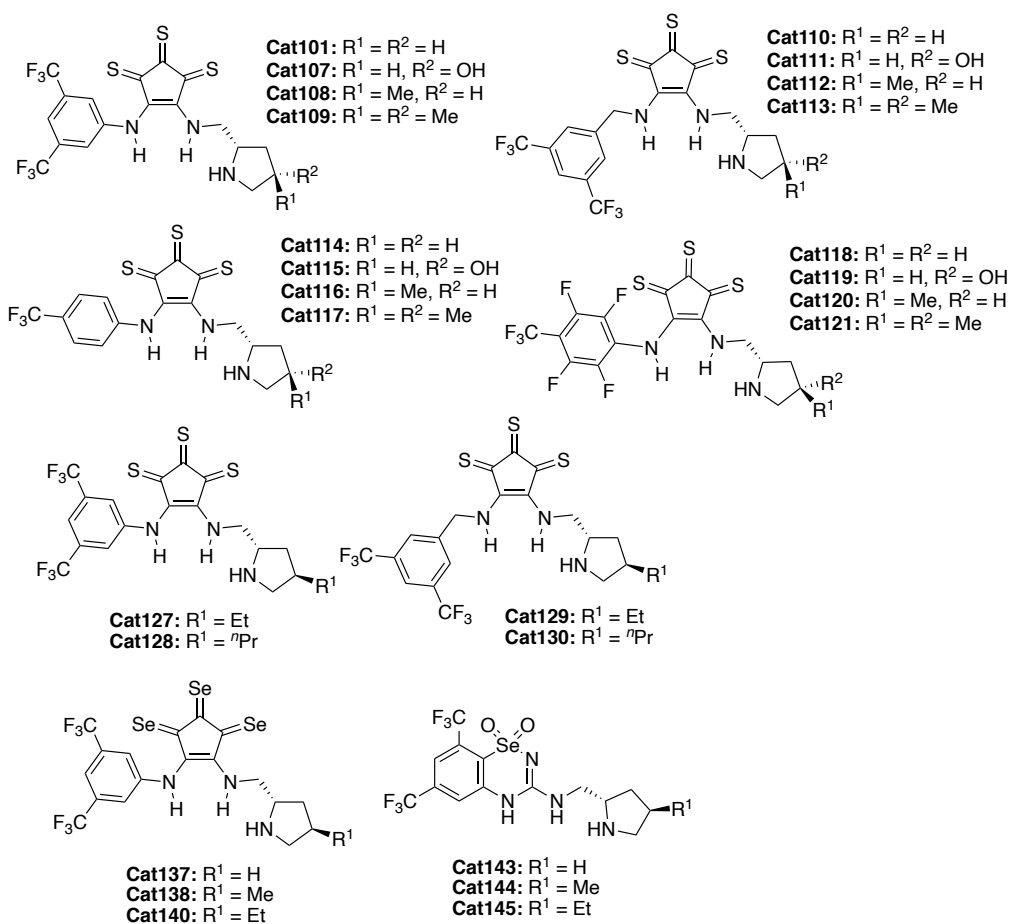


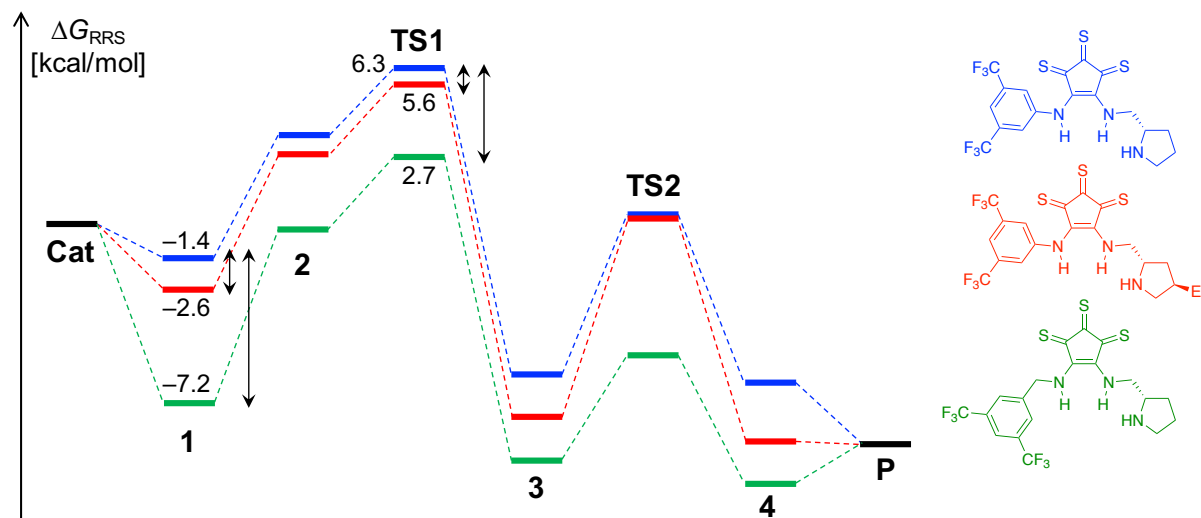
Figure S8. Structure of class 1–2 organocatalysts.



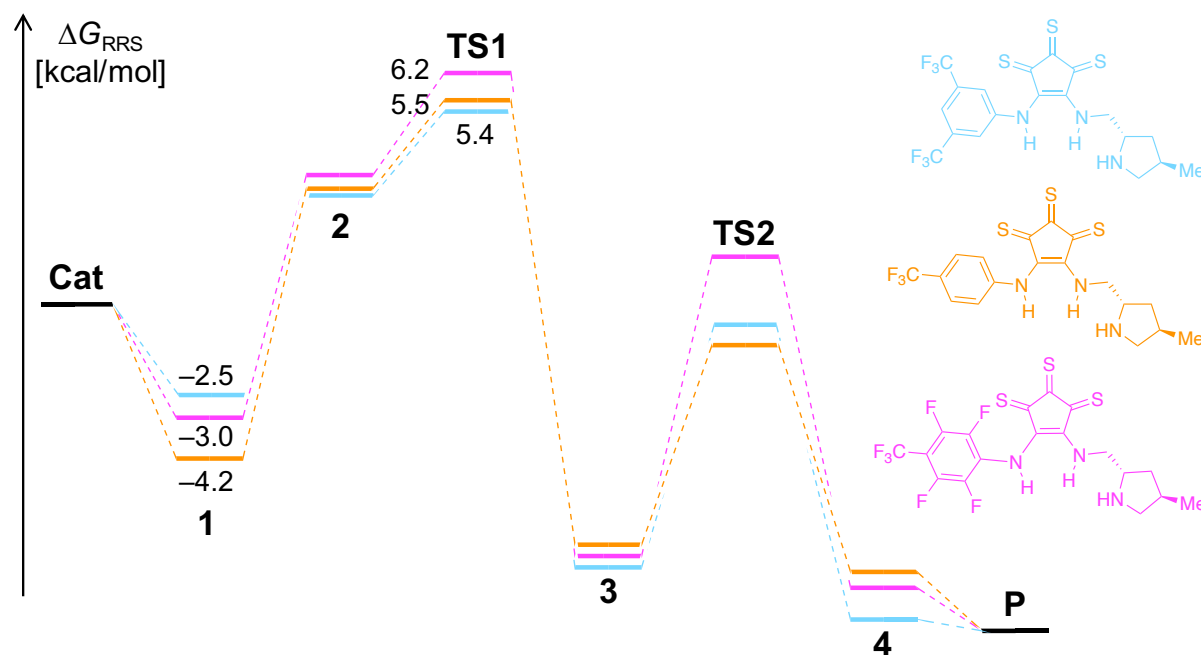


**Figure S9.** Structure of class 2 organocatalysts (continued).

### 3. Comparison of Potential Energy Surfaces



**Figure S10.** Comparison of PES of organocatalysts **Cat101** (blue), **Cat127** (red), and **Cat110** (green), showing the adverse effect of fragments that over-stabilized intermediate **1**. Although better molecular building blocks help stabilize **TS1** (TDTS), if **1** (TDI) is more significantly stabilized, the energy span increases *i.e.*, the catalyst becomes less active.



**Figure S11.** Comparison of PES of organocatalysts **Cat108** (light blue), **Cat116** (orange), and **Cat120** (pink).

## 4. Enantioselectivity Prediction of Selected Class 0 Organocatalysts

Despite this work being focused on activity-based screening, the enantioselectivity of 32 organocatalysts from class 0 was estimated. These catalysts are variations of Jørgensen's original pyrrolidine/squaramide catalyst (*i.e.*, one NCBG/BB/CBG unit is kept constant, and the other two are systematically varied). Based on the low-energy pathway leading to the (*S,S*)-product (the enantiomer of the product considered in the present study) identified by Wheeler and co-workers,<sup>9</sup> **TS1-(*S*)** of catalysts **0–32** was located and optimized using AARON.<sup>10</sup> Table S10 reports the relative quasi-harmonic Gibbs free energies of **TS1-(*R*)**/**TS1-(*S*)**, along with the predicted % (*R,R*)-product. In all cases, **TS1-(*R*)** lies significantly higher in energy than **TS1-(*S*)**. The free energy differences are consistent with the experimentally reported high enantioselectivity (in the case of **Cat0**).<sup>11</sup> However, as noted by Wheeler *et al.*,<sup>9</sup> the computed enantioselectivity is overestimated compared to the experimental one (**Cat0** = *er* 99.0 : 1.0). Indeed, significantly high  $\Delta\Delta G^\ddagger$  ( $\gg 2$  kcal/mol) values were obtained.

**Table S10.** Relative Gibbs free energies of **TS1** leading to the (*R,R*)- or to the (*S,S*)-product for selected class 0 organocatalysts. % (*R,R*)-product =  $100 \times \exp(\Delta\Delta G^\ddagger/RT) / [1 + \exp(\Delta\Delta G^\ddagger/RT)]$ .

	<b>TS1-(<i>R</i>)</b>	<b>TS1-(<i>S</i>)</b>	$\Delta\Delta G^\ddagger$	% ( <i>R,R</i> )-product
<b>Cat0</b>	9.9	12.9	3.0	99.3
<b>Cat1</b>	8.3	11.8	3.5	99.7
<b>Cat2</b>	9.0	16.8	7.8	100.0
<b>Cat3</b>	8.6	15.7	7.0	100.0
<b>Cat4</b>	9.3	16.7	7.4	100.0
<b>Cat5</b>	7.2	14.6	7.3	100.0
<b>Cat6</b>	9.6	17.4	7.9	100.0
<b>Cat7</b>	8.1	18.7	10.6	100.0
<b>Cat8</b>	7.5	13.4	5.9	100.0
<b>Cat9</b>	11.9	19.4	7.5	100.0
<b>Cat10</b>	11.5	14.8	3.4	99.7
<b>Cat11</b>	8.1	12.7	4.6	100.0
<b>Cat12</b>	9.4	14.9	5.5	100.0
<b>Cat13</b>	8.9	13.8	5.0	100.0
<b>Cat14</b>	9.8	15.8	6.0	100.0
<b>Cat15</b>	9.0	12.4	3.4	99.7
<b>Cat16</b>	9.1	14.6	5.4	100.0
<b>Cat17</b>	10.3	14.0	3.7	99.8
<b>Cat18</b>	10.9	16.3	5.3	100.0
<b>Cat19</b>	6.0	13.8	7.8	100.0
<b>Cat20</b>	9.6	13.8	4.2	99.9
<b>Cat21</b>	8.5	11.9	3.4	99.7
<b>Cat22</b>	8.3	11.4	3.1	99.5
<b>Cat23</b>	13.3	17.1	3.8	99.8
<b>Cat24</b>	17.5	24.0	6.5	100.0
<b>Cat25</b>	13.5	20.2	6.7	100.0
<b>Cat26</b>	14.4	22.5	8.1	100.0
<b>Cat28</b>	15.1	20.1	5.0	100.0
<b>Cat29</b>	12.1	16.6	4.5	100.0
<b>Cat30</b>	11.3	17.3	6.0	100.0
<b>Cat31</b>	9.1	14.1	5.0	100.0
<b>Cat32</b>	14.1	19.1	5.0	100.0

## 5. Computed Electronic Energies and Gibbs Free Energies

**Table S11.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of substrates and (*R,R*)-product at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Compound	E_SPC	qh-H_SPC	qh-G(T)_SPC
Anthracene	-692.159666	-691.920762	-691.973502
Nitrostyrene	-514.174552	-514.031911	-514.076676
Product	-1206.377928	-1205.993396	-1206.064176
Water	-76.443735	-76.419150	-76.440608

**Table S12.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of Cat at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E_SPC	qh-H_SPC	qh-G(T)_SPC
Cat0	-1570.763709	-1570.436923	-1570.518470
Cat1	-2216.679976	-2216.356620	-2216.438905
Cat2	-1381.271652	-1380.967397	-1381.041716
Cat3	-1704.219410	-1703.917509	-1703.992466
Cat4	-1361.368237	-1361.051689	-1361.125871
Cat5	-1453.610917	-1453.294355	-1453.372371
Cat6	-1457.387483	-1457.072073	-1457.150195
Cat7	-1780.359814	-1780.045934	-1780.124735
Cat8	-1684.103690	-1683.765582	-1683.849383
Cat9	-1816.548646	-1816.243792	-1816.321099
Cat10	-1392.789191	-1392.513122	-1392.587144
Cat11	-1011.088978	-1010.742837	-1010.812553
Cat12	-704.818906	-704.560424	-704.618269
Cat13	-1002.607899	-1002.371353	-1002.433914
Cat14	-779.979233	-779.717183	-779.777691
Cat15	-935.870595	-935.529109	-935.596245
Cat16	-1050.189926	-1049.829511	-1049.898934
Cat17	-1128.826162	-1128.408087	-1128.484013
Cat18	-1109.429986	-1108.972051	-1109.052656
Cat19	-1625.611332	-1624.989874	-1625.085543
Cat20	-1670.022868	-1669.702645	-1669.785271
Cat21	-1645.993309	-1645.660721	-1645.743710
Cat22	-1610.081204	-1609.725617	-1609.808888
Cat23	-2008.285011	-2007.927301	-2008.014002
Cat24	-2008.288601	-2007.931349	-2008.018386
Cat25	-1778.806199	-1778.422662	-1778.513809
Cat26	-1610.085300	-1609.729163	-1609.812605
Cat27	-1723.190638	-1722.839042	-1722.924400
Cat28	-1610.099959	-1609.743598	-1609.825907
Cat29	-1454.028366	-1453.765375	-1453.841272
Cat30	-1724.396495	-1724.021868	-1724.109708
Cat31	-1724.383786	-1724.010384	-1724.097070
Cat32	-1916.126510	-1915.698265	-1915.793111
Cat33	-1142.340585	-1142.051031	-1142.115300
Cat34	-1687.841391	-1687.578897	-1687.644426
Cat35	-1735.442482	-1735.055568	-1735.128110
Cat36	-1625.503019	-1625.258874	-1625.328572
Cat37	-798.531051	-798.234763	-798.297863
Cat38	-1050.140141	-1049.780710	-1049.851414
Cat39	-1588.247948	-1587.713015	-1587.801717
Cat40	-994.657221	-994.244103	-994.314311
Cat41	-1486.741258	-1486.357331	-1486.431353
Cat42	-2479.575704	-2478.899789	-2479.004155
Cat43	-1607.239957	-1606.875539	-1606.960661
Cat44	-1365.821683	-1365.551280	-1365.619221
Cat45	-1065.089330	-1064.820638	-1064.879346
Cat46	-1983.947913	-1983.591898	-1983.674596
Cat47	-1202.864816	-1202.462969	-1202.536332
Cat48	-896.824632	-896.495776	-896.560784
Cat49	-1108.662115	-1108.315676	-1108.377899
Cat50	-1100.353839	-1100.070432	-1100.132198
Cat51	-1412.211213	-1411.839010	-1411.910893
Cat52	-879.312183	-878.929914	-879.002242

Cat53	-1492.042927	-1491.774141	-1491.850060
Cat54	-1219.131620	-1218.728773	-1218.808116
Cat55	-932.406325	-932.119175	-932.183841
Cat56	-1336.869615	-1336.394616	-1336.479455
Cat57	-1788.262711	-1787.976236	-1788.041542
Cat58	-1531.787176	-1531.618641	-1531.676139
Cat59	-1735.412364	-1735.027087	-1735.103854
Cat60	-2616.892440	-2616.173111	-2616.284026
Cat61	-1735.428833	-1735.042392	-1735.115045
Cat62	-1356.934536	-1356.633207	-1356.706944
Cat63	-614.580806	-614.352912	-614.405742
Cat64	-888.347877	-888.128557	-888.186365
Cat65	-959.248828	-958.784615	-958.859954
Cat66	-821.593979	-821.270713	-821.333541
Cat67	-1301.622940	-1301.199490	-1301.269279
Cat68	-1282.221477	-1281.758162	-1281.833403
Cat69	-1798.403346	-1797.775472	-1797.864010
Cat70	-1743.538471	-1743.206804	-1743.282473
Cat71	-877.597075	-877.335377	-877.390183
Cat72	-1299.479161	-1298.931272	-1299.014027
Cat73	-1073.061907	-1072.606281	-1072.681184
Cat74	-1053.653373	-1053.157339	-1053.235939
Cat75	-1163.995081	-1163.633570	-1163.699943
Cat76	-841.009805	-840.644894	-840.709391
Cat77	-626.990789	-626.713278	-626.769495
Cat78	-1085.468717	-1085.093641	-1085.164104
Cat79	-1429.272655	-1428.958835	-1429.036292
Cat80	-1086.906792	-1086.493169	-1086.567313
Cat81	-924.775889	-924.521574	-924.584115
Cat82	-1716.930970	-1716.635286	-1716.712555
Cat83	-936.805304	-936.457528	-936.527138
Cat84	-976.109773	-975.732916	-975.804571
Cat85	-1089.238430	-1088.864614	-1088.935721
Cat86	-996.045052	-995.598757	-995.676037
Cat87	-872.837870	-872.652768	-872.705819
Cat88	-1934.458042	-1933.857217	-1933.952377
Cat89	-1184.781610	-1184.425089	-1184.493179
Cat90	-1658.208733	-1657.845726	-1657.916724
Cat91	-797.678930	-797.498097	-797.549609
Cat92	-968.551760	-968.272516	-968.337883
Cat93	-2176.476692	-2175.811660	-2175.913755
Cat94	-1450.213579	-1449.726862	-1449.813339
Cat95	-1659.764313	-1659.429143	-1659.512365
Cat96	-1295.979979	-1295.641671	-1295.706940
Cat97	-1280.911246	-1280.598741	-1280.662444
Cat98	-1812.137513	-1811.709963	-1811.785861
Cat99	-1685.920181	-1685.674767	-1685.738314
Cat100	-1696.325969	-1695.953802	-1696.026396
Cat101	-2652.977398	-2652.645124	-2652.731420
Cat102	-1759.333242	-1758.989543	-1759.075480
Cat103	-1723.421192	-1723.054551	-1723.141002
Cat104	-1506.132041	-1505.844482	-1505.921569
Cat105	-1581.361529	-1581.068454	-1581.147943
Cat106	-1545.449530	-1545.133319	-1545.212814
Cat107	-2728.207828	-2727.869950	-2727.957847
Cat108	-2692.295051	-2691.934454	-2692.023538
Cat109	-2731.613709	-2731.225127	-2731.314091
Cat110	-2692.293990	-2691.930975	-2692.016881
Cat111	-2767.524113	-2767.156292	-2767.245073
Cat112	-2731.620568	-2731.230051	-2731.318476
Cat113	-2770.933214	-2770.513421	-2770.604131
Cat114	-2315.874782	-2315.549736	-2315.627501
Cat115	-2391.105785	-2390.775782	-2390.853923
Cat116	-2355.192972	-2354.839448	-2354.919744
Cat117	-2394.509083	-2394.126876	-2394.210150
Cat118	-2712.857677	-2712.561807	-2712.646538
Cat119	-2788.088863	-2787.787385	-2787.874131
Cat120	-2752.175920	-2751.851681	-2751.939067
Cat121	-2791.492047	-2791.139029	-2791.229525
Cat122	-1777.409251	-1777.099598	-1777.180640
Cat123	-931.201621	-930.909386	-930.971216
Cat124	-799.329121	-799.037810	-799.097051
Cat125	-1234.623689	-1234.331207	-1234.393005
Cat126	-1360.179826	-1359.885668	-1359.957591
Cat127	-2731.611207	-2731.222039	-2731.313727

Cat128	-2770.927487	-2770.509869	-2770.604724
Cat129	-2770.932731	-2770.514428	-2770.603859
Cat130	-2810.252636	-2809.805194	-2809.897626
Cat131	-2100.362624	-2100.053932	-2100.134438
Cat132	-3172.431489	-3171.866431	-3171.973913
Cat133	-1605.407923	-1605.101073	-1605.178343
Cat134	-1473.524617	-1473.218973	-1473.293868
Cat135	-1908.818193	-1908.511693	-1908.589837
Cat136	-1360.180959	-1359.886629	-1359.957836
Cat137	-8663.207851	-8662.877600	-8662.966871
Cat138	-8702.525774	-8702.167251	-8702.259844
Cat139	-3532.085727	-3531.735074	-3531.835419
Cat140	-8741.841749	-8741.454455	-8741.549401
Cat141	-1948.136531	-1947.801127	-1947.881148
Cat142	-1987.452630	-1987.088599	-1987.171901
Cat143	-3912.148414	-3911.844127	-3911.924131
Cat144	-3951.466714	-3951.134136	-3951.216862
Cat145	-3990.782812	-3990.421542	-3990.507092

**Table S13.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of intermediate **1** at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E_SPC	qh-H_SPC	qh-G(T)_SPC
Cat0	-2186.494995	-2185.953655	-2186.054889
Cat1	-2832.411032	-2831.873094	-2831.975640
Cat2	-1997.005937	-1996.487284	-1996.581742
Cat3	-2319.953668	-2319.437071	-2319.531612
Cat4	-1977.102911	-1976.572217	-1976.666991
Cat5	-2069.346496	-2068.815431	-2068.913202
Cat6	-2073.120503	-2072.590990	-2072.690243
Cat7	-2396.093533	-2395.565572	-2395.664555
Cat8	-2299.836343	-2299.283420	-2299.386758
Cat9	-2432.278989	-2431.760358	-2431.857517
Cat10	-2008.524242	-2008.033784	-2008.128876
Cat11	-1626.818002	-1626.257956	-1626.350166
Cat12	-1320.546279	-1320.073977	-1320.155200
Cat13	-1618.334202	-1617.883980	-1617.969297
Cat14	-1395.706779	-1395.230909	-1395.315335
Cat15	-1551.603954	-1551.049226	-1551.138993
Cat16	-1665.919251	-1665.344821	-1665.436854
Cat17	-1744.558655	-1743.926452	-1744.023102
Cat18	-1725.159894	-1724.487171	-1724.588493
Cat19	-2241.347888	-2240.512642	-2240.630364
Cat20	-2285.752501	-2285.218291	-2285.321128
Cat21	-2261.728337	-2261.181369	-2261.284098
Cat22	-2225.813446	-2225.243532	-2225.347146
Cat23	-2624.013993	-2623.442153	-2623.549135
Cat24	-2624.012089	-2623.440212	-2623.547020
Cat25	-2394.532040	-2393.934774	-2394.046249
Cat26	-2225.818441	-2225.247075	-2225.349142
Cat27	-2338.918167	-2338.351560	-2338.456848
Cat28	-2225.828552	-2225.257671	-2225.359713
Cat29	-2069.758367	-2069.281107	-2069.377411
Cat30	-2340.127581	-2339.538539	-2339.646946
Cat31	-2340.121413	-2339.531124	-2339.636940
Cat32	-2531.852203	-2531.209897	-2531.325573
Cat33	-1758.065327	-1757.562573	-1757.649418
Cat34	-2303.569939	-2303.093433	-2303.181459
Cat35	-2351.177344	-2350.576646	-2350.670870
Cat36	-2241.233448	-2240.774694	-2240.865478
Cat37	-1414.247934	-1413.738549	-1413.825215
Cat38	-1665.864603	-1665.291411	-1665.384650
Cat39	-2203.971926	-2203.223110	-2203.333666
Cat40	-1610.391968	-1609.765335	-1609.857557
Cat41	-2102.458679	-2101.860387	-2101.957717
Cat42	-3095.304485	-3094.416456	-3094.544909
Cat43	-2222.970870	-2222.392375	-2222.497285
Cat44	-1981.552683	-1981.068628	-1981.158328
Cat45	-1680.810217	-1680.328327	-1680.412503
Cat46	-2599.663154	-2599.094191	-2599.201269
Cat47	-1818.589477	-1817.973754	-1818.069887
Cat48	-1512.556434	-1512.013682	-1512.101191
Cat49	-1724.388962	-1723.828739	-1723.914064

Cat50	-1716.072078	-1715.575750	-1715.661899
Cat51	-2027.940708	-2027.354584	-2027.448584
Cat52	-1495.037431	-1494.441204	-1494.536235
Cat53	-2107.779279	-2107.295861	-2107.392601
Cat54	-1834.856024	-1834.239574	-1834.341273
Cat55	-1548.129288	-1547.628858	-1547.716827
Cat56	-1952.594061	-1951.905730	-1952.013215
Cat57	-2403.986602	-2403.486870	-2403.575076
Cat58	-2147.510320	-2147.127256	-2147.208735
Cat59	-2351.144229	-2350.545002	-2350.643057
Cat60	-3232.620040	-3231.686149	-3231.817279
Cat61	-2351.157729	-2350.556220	-2350.650236
Cat62	-1972.659314	-1972.143353	-1972.237815
Cat63	-1230.307297	-1229.864841	-1229.941157
Cat64	-1504.073358	-1503.639898	-1503.719684
Cat65	-1574.982639	-1574.304401	-1574.401865
Cat66	-1437.325949	-1436.788623	-1436.874139
Cat67	-1917.349842	-1916.712353	-1916.804363
Cat68	-1897.945049	-1897.267851	-1897.365651
Cat69	-2414.139693	-2413.298580	-2413.410169
Cat70	-2359.275350	-2358.728840	-2358.824506
Cat71	-1493.324080	-1492.848770	-1492.927265
Cat72	-1915.215303	-1914.454272	-1914.559734
Cat73	-1688.790926	-1688.121688	-1688.218392
Cat74	-1669.383387	-1668.674209	-1668.775354
Cat75	-1779.720493	-1779.145261	-1779.233752
Cat76	-1456.743036	-1456.163443	-1456.249888
Cat77	-1242.719906	-1242.227820	-1242.307177
Cat78	-1701.194860	-1700.606069	-1700.699224
Cat79	-2044.997871	-2044.470128	-2044.569072
Cat80	-1702.642052	-1702.014564	-1702.109852
Cat81	-1540.500634	-1540.032656	-1540.115087
Cat82	-2332.659853	-2332.150615	-2332.248474
Cat83	-1552.528912	-1551.967152	-1552.059464
Cat84	-1591.839296	-1591.249038	-1591.343568
Cat85	-1704.967156	-1704.379540	-1704.472729
Cat86	-1611.775924	-1611.115497	-1611.214543
Cat87	-1488.559766	-1488.161032	-1488.238150
Cat88	-2550.196320	-2549.380357	-2549.496220
Cat89	-1800.508758	-1799.938483	-1800.029904
Cat90	-2273.933595	-2273.356344	-2273.451905
Cat91	-1413.402332	-1413.007036	-1413.080815
Cat92	-1584.280579	-1583.787539	-1583.875814
Cat93	-2792.205126	-2791.327712	-2791.453740
Cat94	-2065.936859	-2065.236539	-2065.346106
Cat95	-2275.493312	-2274.943421	-2275.048157
Cat96	-1911.713128	-1911.160710	-1911.248185
Cat97	-1896.640965	-1896.115655	-1896.203880
Cat98	-2427.858671	-2427.218658	-2427.315384
Cat99	-2301.630837	-2301.172290	-2301.259963
Cat100	-2312.061652	-2311.475224	-2311.569607
Cat101	-3268.708183	-3268.160947	-3268.266492
Cat102	-2375.067023	-2374.509311	-2374.615022
Cat103	-2339.154526	-2338.573516	-2338.679771
Cat104	-2121.866550	-2121.364849	-2121.463664
Cat105	-2197.095535	-2196.587962	-2196.687588
Cat106	-2161.183137	-2160.652510	-2160.752759
Cat107	-3343.941377	-3343.389476	-3343.497245
Cat108	-3308.026712	-3307.451611	-3307.560423
Cat109	-3347.344977	-3346.741992	-3346.852924
Cat110	-3308.028454	-3307.452024	-3307.561206
Cat111	-3383.259208	-3382.677204	-3382.788464
Cat112	-3347.346146	-3346.741549	-3346.854058
Cat113	-3386.663047	-3386.030298	-3386.142672
Cat114	-2931.606583	-2931.066652	-2931.165484
Cat115	-3006.837290	-3006.292174	-3006.392955
Cat116	-2970.924847	-2970.357027	-2970.459256
Cat117	-3010.242235	-3009.646670	-3009.751259
Cat118	-3328.592300	-3328.081401	-3328.186886
Cat119	-3403.823285	-3403.307148	-3403.414292
Cat120	-3367.908135	-3367.368873	-3367.476752
Cat121	-3407.226548	-3406.659243	-3406.769381
Cat122	-2393.141605	-2392.617538	-2392.718400
Cat123	-1546.926135	-1546.419813	-1546.504940
Cat124	-1415.060028	-1414.554214	-1414.634874

Cat125	-1850.353601	-1849.846499	-1849.929784
Cat126	-1975.911213	-1975.402621	-1975.495477
Cat127	-3347.343021	-3346.739303	-3346.850712
Cat128	-3386.659356	-3386.026912	-3386.141108
Cat129	-3386.663289	-3386.030209	-3386.145812
Cat130	-3425.979690	-3425.317895	-3425.435576
Cat131	-2716.091955	-2715.569440	-2715.671272
Cat132	-3788.171942	-3787.392780	-3787.520098
Cat133	-2221.139482	-2220.617723	-2220.715382
Cat134	-2089.259527	-2088.739054	-2088.833559
Cat135	-2524.549300	-2524.027338	-2524.124772
Cat136	-1975.913779	-1975.405383	-1975.497398
Cat137	-9278.939248	-9278.394089	-9278.503367
Cat138	-9318.257263	-9317.683871	-9317.795613
Cat139	-4147.826033	-4147.260271	-4147.381425
Cat140	-9357.573968	-9356.972041	-9357.086116
Cat141	-2563.867560	-2563.317497	-2563.417879
Cat142	-2603.184012	-2602.605417	-2602.708691
Cat143	-4527.879980	-4527.361037	-4527.460891
Cat144	-4567.198273	-4566.651082	-4566.753793
Cat145	-4606.514788	-4605.938610	-4606.043552

**Table S14.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of intermediate **2** at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E SPC	qh-H SPC	qh-G(T) SPC
Cat0	-2700.686621	-2700.001846	-2700.123360
Cat1	-3346.600963	-3345.919629	-3346.042483
Cat2	-2511.194349	-2510.531984	-2510.647137
Cat3	-2834.140209	-2833.480391	-2833.597080
Cat4	-2491.291103	-2490.616633	-2490.731871
Cat5	-2583.534069	-2582.859895	-2582.979409
Cat6	-2587.309883	-2586.637290	-2586.757498
Cat7	-2910.282567	-2909.611444	-2909.732473
Cat8	-2814.025420	-2813.329297	-2813.454087
Cat9	-2946.468099	-2945.805150	-2945.921918
Cat10	-2522.711351	-2522.077205	-2522.193056
Cat11	-2141.011156	-2140.307697	-2140.419963
Cat12	-1834.737463	-1834.121701	-1834.223560
Cat13	-2132.527217	-2131.933548	-2132.038674
Cat14	-1909.897766	-1909.278538	-1909.382889
Cat15	-2065.790801	-2065.092628	-2065.200969
Cat16	-2180.110102	-2179.392361	-2179.505086
Cat17	-2258.750734	-2257.975215	-2258.092605
Cat18	-2239.356732	-2238.540434	-2238.662127
Cat19	-2755.540587	-2754.561370	-2754.698513
Cat20	-2799.944539	-2799.267438	-2799.391690
Cat21	-2775.917118	-2775.227323	-2775.351313
Cat22	-2740.004723	-2739.292045	-2739.416849
Cat23	-3138.201320	-3137.486536	-3137.613969
Cat24	-3138.200564	-3137.485762	-3137.613352
Cat25	-2908.721712	-2907.980863	-2908.112501
Cat26	-2740.000753	-2739.286679	-2739.409864
Cat27	-2853.108562	-2852.399196	-2852.525540
Cat28	-2740.013222	-2739.299255	-2739.422605
Cat29	-2583.944748	-2583.324473	-2583.441447
Cat30	-2854.315249	-2853.581729	-2853.709267
Cat31	-2854.305247	-2853.573746	-2853.702284
Cat32	-3046.041502	-3045.255454	-3045.390660
Cat33	-2272.252318	-2271.606230	-2271.714019
Cat34	-2817.755664	-2817.136217	-2817.244648
Cat35	-2865.356398	-2864.612531	-2864.728103
Cat36	-2755.422211	-2754.820269	-2754.932436
Cat37	-1928.439356	-1927.785999	-1927.893352
Cat38	-2180.059094	-2179.342123	-2179.455992
Cat39	-2718.153316	-2717.261869	-2717.393515
Cat40	-2124.577283	-2123.806679	-2123.920443
Cat41	-2616.645020	-2615.904204	-2616.022884
Cat42	-3609.498068	-3608.466464	-3608.615222
Cat43	-2737.154208	-2736.432994	-2736.559754
Cat44	-2495.739661	-2495.112237	-2495.223953
Cat45	-2194.994631	-2194.368660	-2194.471316
Cat46	-3113.852169	-3113.139550	-3113.265860



Cat47	-2332.776856	-2332.017841	-2332.134491
Cat48	-2026.746017	-2026.059687	-2026.167847
Cat49	-2238.573353	-2237.869761	-2237.975916
Cat50	-2230.259289	-2229.619690	-2229.726291
Cat51	-2542.127802	-2541.397365	-2541.511932
Cat52	-2009.233101	-2008.493230	-2008.608004
Cat53	-2621.969072	-2621.342021	-2621.459512
Cat54	-2349.046175	-2348.286403	-2348.408841
Cat55	-2062.318906	-2061.674539	-2061.782882
Cat56	-2466.783030	-2465.950930	-2466.079002
Cat57	-2918.174466	-2917.531476	-2917.640383
Cat58	-2661.701240	-2661.175323	-2661.277407
Cat59	-2865.330276	-2864.587947	-2864.707595
Cat60	-3746.812348	-3745.735215	-3745.886903
Cat61	-2865.343039	-2864.599402	-2864.715265
Cat62	-2486.844153	-2486.185752	-2486.302540
Cat63	-1744.497455	-1743.911592	-1744.008894
Cat64	-2018.266942	-2017.690062	-2017.790485
Cat65	-2089.169171	-2088.347287	-2088.465537
Cat66	-1951.515228	-1950.834182	-1950.940024
Cat67	-2431.532715	-2430.752306	-2430.866246
Cat68	-2412.129437	-2411.308214	-2411.425756
Cat69	-2928.322079	-2927.338298	-2927.471746
Cat70	-2873.454773	-2872.765470	-2872.883643
Cat71	-2007.515716	-2006.896686	-2006.995604
Cat72	-2429.398179	-2428.493709	-2428.619873
Cat73	-2202.978098	-2202.165332	-2202.283177
Cat74	-2183.563924	-2182.711321	-2182.835529
Cat75	-2293.901109	-2293.182868	-2293.293222
Cat76	-1970.921907	-1970.199529	-1970.307659
Cat77	-1756.901862	-1756.266995	-1756.367540
Cat78	-2215.382275	-2214.649976	-2214.763974
Cat79	-2559.180861	-2558.510217	-2558.630710
Cat80	-2216.832761	-2216.062260	-2216.178488
Cat81	-2054.695159	-2054.083461	-2054.188239
Cat82	-2846.850763	-2846.197991	-2846.317459
Cat83	-2066.715922	-2066.011566	-2066.125829
Cat84	-2106.028095	-2105.294516	-2105.411130
Cat85	-2219.156813	-2218.424883	-2218.538507
Cat86	-2125.974046	-2125.170095	-2125.289379
Cat87	-2002.749839	-2002.207586	-2002.305062
Cat88	-3064.387458	-3063.428336	-3063.565231
Cat89	-2314.701901	-2313.988277	-2314.100295
Cat90	-2788.123766	-2787.403190	-2787.519339
Cat91	-1927.589964	-1927.051954	-1927.148303
Cat92	-2098.468766	-2097.832409	-2097.940680
Cat93	-3306.394352	-3305.372579	-3305.517126
Cat94	-2580.127354	-2579.283501	-2579.413703
Cat95	-2789.676975	-2788.984130	-2789.110111
Cat96	-2425.890432	-2425.194563	-2425.302939
Cat97	-2410.820016	-2410.150762	-2410.258743
Cat98	-2942.039701	-2941.255809	-2941.375509
Cat99	-2815.814868	-2815.212956	-2815.319863
Cat100	-2826.241964	-2825.512585	-2825.628158
Cat101	-3782.899287	-3782.208725	-3782.335248
Cat102	-2889.257407	-2888.556057	-2888.683231
Cat103	-2853.344508	-2852.620078	-2852.747846
Cat104	-2636.053699	-2635.408399	-2635.526958
Cat105	-2711.283458	-2710.632841	-2710.753369
Cat106	-2675.370985	-2674.697341	-2674.818527
Cat107	-3858.130840	-3857.435029	-3857.563206
Cat108	-3822.218132	-3821.499279	-3821.628213
Cat109	-3861.535832	-3860.788679	-3860.920585
Cat110	-3822.216812	-3821.497224	-3821.626876
Cat111	-3897.448025	-3896.723662	-3896.853384
Cat112	-3861.535492	-3860.787755	-3860.920907
Cat113	-3900.853424	-3900.077721	-3900.210600
Cat114	-3445.793828	-3445.110613	-3445.229331
Cat115	-3521.025150	-3520.336930	-3520.457895
Cat116	-3485.112777	-3484.401581	-3484.524013
Cat117	-3524.430844	-3523.690964	-3523.815285
Cat118	-3842.777607	-3842.124060	-3842.250304
Cat119	-3918.009078	-3917.350198	-3917.478399
Cat120	-3882.096291	-3881.414276	-3881.543150
Cat121	-3921.414075	-3920.703386	-3920.834359

Cat122	-2907.329454	-2906.661954	-2906.784165
Cat123	-2061.122118	-2060.471908	-2060.575956
Cat124	-1929.251112	-1928.601997	-1928.703104
Cat125	-2364.544861	-2363.894461	-2363.998376
Cat126	-2490.100937	-2489.449727	-2489.563646
Cat127	-3861.534397	-3860.786992	-3860.918792
Cat128	-3900.850873	-3900.075149	-3900.210224
Cat129	-3900.851860	-3900.076100	-3900.209265
Cat130	-3940.167929	-3939.363137	-3939.502117
Cat131	-3230.282440	-3229.616730	-3229.740053
Cat132	-4302.357638	-4301.435093	-4301.583053
Cat133	-2735.330100	-2734.665643	-2734.784919
Cat134	-2603.448930	-2602.785615	-2602.901879
Cat135	-3038.741116	-3038.076309	-3038.195311
Cat136	-2490.102867	-2489.451165	-2489.564185
Cat137	-9793.129812	-9792.441319	-9792.571021
Cat138	-9832.448626	-9831.732536	-9831.863117
Cat139	-4662.012326	-4661.303394	-4661.445772
Cat140	-9871.764998	-9871.020295	-9871.153631
Cat141	-3078.059899	-3077.366843	-3077.488599
Cat142	-3117.376080	-3116.654585	-3116.779560
Cat144	-5081.390158	-5080.699904	-5080.824132
Cat145	-5120.706339	-5119.987393	-5120.114129

**Table S15.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of TS1 at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E SPC	qh-H SPC	qh-G(T) SPC
Cat0	-2700.679897	-2699.995754	-2700.112220
Cat1	-3346.596334	-3345.915218	-3346.035178
Cat2	-2511.186741	-2510.524549	-2510.636918
Cat3	-2834.135035	-2833.475245	-2833.588267
Cat4	-2491.282327	-2490.607983	-2490.720614
Cat5	-2583.528148	-2582.854080	-2582.970394
Cat6	-2587.300557	-2586.627829	-2586.744510
Cat7	-2910.276360	-2909.605718	-2909.721387
Cat8	-2814.023597	-2813.327890	-2813.447027
Cat9	-2946.458392	-2945.796278	-2945.911717
Cat10	-2522.699141	-2522.065265	-2522.178444
Cat11	-2141.003778	-2140.300169	-2140.409223
Cat12	-1834.729749	-1834.113991	-1834.212784
Cat13	-2132.521306	-2131.927587	-2132.029362
Cat14	-1909.890202	-1909.270810	-1909.371614
Cat15	-2065.783060	-2065.084356	-2065.191465
Cat16	-2180.102192	-2179.384392	-2179.493938
Cat17	-2258.737788	-2257.961924	-2258.077147
Cat18	-2239.342318	-2238.526123	-2238.644823
Cat19	-2755.530083	-2754.551199	-2754.685515
Cat20	-2799.936556	-2799.259049	-2799.379583
Cat21	-2775.909767	-2775.219632	-2775.339809
Cat22	-2739.998298	-2739.285936	-2739.405232
Cat23	-3138.193034	-3137.478058	-3137.602375
Cat24	-3138.190848	-3137.476086	-3137.600110
Cat25	-2908.713486	-2907.972877	-2908.101921
Cat26	-2739.993332	-2739.279189	-2739.399229
Cat27	-2853.096700	-2852.387386	-2852.510468
Cat28	-2740.005934	-2739.291531	-2739.411381
Cat29	-2583.938635	-2583.317870	-2583.431566
Cat30	-2854.307456	-2853.575323	-2853.701243
Cat31	-2854.297336	-2853.565780	-2853.692113
Cat32	-3046.033055	-3045.247382	-3045.380219
Cat33	-2272.241301	-2271.595234	-2271.699673
Cat34	-2817.750961	-2817.131585	-2817.237048
Cat35	-2865.349374	-2864.605346	-2864.717352
Cat36	-2755.413235	-2754.811344	-2754.920204
Cat37	-1928.426868	-1927.773809	-1927.878119
Cat38	-2180.038775	-2179.322141	-2179.433638
Cat39	-2718.141196	-2717.249186	-2717.376884
Cat40	-2124.564302	-2123.793540	-2123.903773
Cat41	-2616.638058	-2615.898294	-2616.012186
Cat42	-3609.485981	-3608.454506	-3608.599793
Cat43	-2737.147349	-2736.425689	-2736.549588
Cat44	-2495.732662	-2495.105138	-2495.212984

Cat45	-2194.987925	-2194.362182	-2194.461720
Cat46	-3113.836027	-3113.123423	-3113.246785
Cat47	-2332.769667	-2332.010809	-2332.124045
Cat48	-2026.736937	-2026.050579	-2026.155360
Cat49	-2238.565047	-2237.862316	-2237.964058
Cat50	-2230.249624	-2229.610261	-2229.713710
Cat51	-2542.108710	-2541.379075	-2541.488733
Cat52	-2009.211792	-2008.471886	-2008.583705
Cat53	-2621.955013	-2621.328118	-2621.442814
Cat54	-2349.036529	-2348.276876	-2348.395994
Cat55	-2062.305596	-2061.661646	-2061.767645
Cat56	-2466.769970	-2465.938260	-2466.063474
Cat57	-2918.165271	-2917.522392	-2917.628184
Cat58	-2661.694797	-2661.168866	-2661.267723
Cat59	-2865.322770	-2864.580550	-2864.697816
Cat60	-3746.801733	-3745.724644	-3745.872826
Cat61	-2865.336416	-2864.592728	-2864.705696
Cat62	-2486.835281	-2486.176727	-2486.290212
Cat63	-1744.486155	-1743.900099	-1743.993956
Cat64	-2018.258728	-2017.681901	-2017.779019
Cat65	-2089.158862	-2088.337659	-2088.451470
Cat66	-1951.507101	-1950.826044	-1950.928811
Cat67	-2431.522321	-2430.741614	-2430.852187
Cat68	-2412.117027	-2411.296785	-2411.409958
Cat69	-2928.310982	-2927.326880	-2927.456673
Cat70	-2873.447742	-2872.759053	-2872.872024
Cat71	-2007.507920	-2006.888606	-2006.984050
Cat72	-2429.382224	-2428.478875	-2428.600169
Cat73	-2202.959925	-2202.146736	-2202.260557
Cat74	-2183.551344	-2182.699068	-2182.816998
Cat75	-2293.889423	-2293.170607	-2293.277049
Cat76	-1970.913508	-1970.190901	-1970.295750
Cat77	-1756.892668	-1756.258312	-1756.354390
Cat78	-2215.367548	-2214.635606	-2214.746831
Cat79	-2559.172376	-2558.501866	-2558.619424
Cat80	-2216.819167	-2216.048807	-2216.162293
Cat81	-2054.688903	-2054.077434	-2054.179194
Cat82	-2846.833125	-2846.180715	-2846.297650
Cat83	-2066.701246	-2065.997533	-2066.106646
Cat84	-2106.014821	-2105.281156	-2105.393793
Cat85	-2219.137125	-2218.405649	-2218.516469
Cat86	-2125.953552	-2125.150263	-2125.265709
Cat87	-2002.741437	-2002.199341	-2002.293905
Cat88	-3064.371776	-3063.412743	-3063.547385
Cat89	-2314.693421	-2313.979888	-2314.088726
Cat90	-2788.111736	-2787.391253	-2787.504882
Cat91	-1927.580302	-1927.041999	-1927.134447
Cat92	-2098.466474	-2097.830361	-2097.935675
Cat93	-3306.387945	-3305.366856	-3305.508456
Cat94	-2580.118354	-2579.275024	-2579.402210
Cat95	-2789.673537	-2788.980905	-2789.103444
Cat96	-2425.884243	-2425.188456	-2425.293672
Cat97	-2410.811542	-2410.142356	-2410.247050
Cat98	-2942.029583	-2941.245942	-2941.362330
Cat99	-2815.808861	-2815.207221	-2815.310551
Cat100	-2826.236861	-2825.507460	-2825.619995
Cat101	-3782.897814	-3782.207572	-3782.331004
Cat102	-2889.253789	-2888.552679	-2888.673620
Cat103	-2853.342367	-2852.618672	-2852.741186
Cat104	-2636.045518	-2635.401127	-2635.515355
Cat105	-2711.280126	-2710.629641	-2710.746828
Cat106	-2675.368613	-2674.695340	-2674.813678
Cat107	-3858.128236	-3857.432596	-3857.558137
Cat108	-3822.216615	-3821.498176	-3821.624496
Cat109	-3861.532923	-3860.786013	-3860.914771
Cat110	-3822.215156	-3821.495596	-3821.622157
Cat111	-3897.445539	-3896.720537	-3896.848962
Cat112	-3861.533970	-3860.786274	-3860.915737
Cat113	-3900.850227	-3900.074525	-3900.204155
Cat114	-3445.793754	-3445.111118	-3445.227107
Cat115	-3521.024207	-3520.336240	-3520.454193
Cat116	-3485.112568	-3484.401692	-3484.520529
Cat117	-3524.428921	-3523.689492	-3523.810698
Cat118	-3842.775974	-3842.123066	-3842.244317
Cat119	-3918.006462	-3917.348123	-3917.471065

Cat120	-3882.095295	-3881.414396	-3881.538749
Cat121	-3921.411333	-3920.701903	-3920.828032
Cat122	-2907.325011	-2906.657734	-2906.777476
Cat123	-2061.116812	-2060.466758	-2060.567783
Cat124	-1929.244858	-1928.595828	-1928.693869
Cat125	-2364.540306	-2363.890012	-2363.990774
Cat126	-2490.093125	-2489.441699	-2489.552146
Cat127	-3861.532903	-3860.786565	-3860.914427
Cat128	-3900.849149	-3900.074226	-3900.204091
Cat129	-3900.850247	-3900.074307	-3900.204255
Cat130	-3940.166492	-3939.361738	-3939.497332
Cat131	-3230.277158	-3229.611402	-3229.731559
Cat132	-4302.355796	-4301.432776	-4301.576600
Cat133	-2735.326463	-2734.661762	-2734.777430
Cat134	-2603.443491	-2602.780199	-2602.893398
Cat135	-3038.737968	-3038.073187	-3038.189194
Cat136	-2490.095936	-2489.444140	-2489.554165
Cat137	-9793.129360	-9792.441133	-9792.567227
Cat138	-9832.448174	-9831.731708	-9831.860658
Cat139	-4662.005731	-4661.297045	-4661.436595
Cat140	-9871.764536	-9871.019523	-9871.151529
Cat141	-3078.056567	-3077.363356	-3077.481981
Cat142	-3117.372981	-3116.651556	-3116.773318
Cat143	-5042.068970	-5041.406739	-5041.524970
Cat144	-5081.387623	-5080.697068	-5080.817443
Cat145	-5120.703973	-5119.985119	-5120.108771

**Table S16.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of intermediate **3** at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E_SPC	qh-H_SPC	qh-G(T)_SPC
Cat0	-2700.706224	-2700.019521	-2700.137357
Cat1	-3346.624609	-3345.941520	-3346.060887
Cat2	-2511.211146	-2510.547111	-2510.659364
Cat3	-2834.160483	-2833.498946	-2833.612024
Cat4	-2491.306536	-2490.630162	-2490.742355
Cat5	-2583.553714	-2582.877777	-2582.993901
Cat6	-2587.323903	-2586.648102	-2586.763393
Cat7	-2910.297142	-2909.624207	-2909.740556
Cat8	-2814.044845	-2813.347060	-2813.468366
Cat9	-2946.484221	-2945.820562	-2945.935390
Cat10	-2522.723152	-2522.087562	-2522.200228
Cat11	-2141.027685	-2140.322391	-2140.431250
Cat12	-1834.752323	-1834.134797	-1834.233288
Cat13	-2132.545023	-2131.949687	-2132.051355
Cat14	-1909.913174	-1909.292179	-1909.393141
Cat15	-2065.805373	-2065.104906	-2065.212084
Cat16	-2180.125646	-2179.406093	-2179.515422
Cat17	-2258.760517	-2257.983009	-2258.097738
Cat18	-2239.366581	-2238.548546	-2238.666872
Cat19	-2755.555641	-2754.575093	-2754.709401
Cat20	-2799.961033	-2799.281816	-2799.401649
Cat21	-2775.936613	-2775.244805	-2775.364685
Cat22	-2740.024402	-2739.309744	-2739.430755
Cat23	-3138.217541	-3137.500528	-3137.623882
Cat24	-3138.217073	-3137.500355	-3137.623762
Cat25	-2908.736692	-2907.994016	-2908.121916
Cat26	-2740.021211	-2739.305059	-2739.424678
Cat27	-2853.120424	-2852.409063	-2852.531020
Cat28	-2740.032192	-2739.315889	-2739.434991
Cat29	-2583.963435	-2583.340713	-2583.453765
Cat30	-2854.333127	-2853.599291	-2853.724619
Cat31	-2854.323753	-2853.590179	-2853.715459
Cat32	-3046.058714	-3045.270850	-3045.402838
Cat33	-2272.263027	-2271.615177	-2271.719398
Cat34	-2817.776708	-2817.155592	-2817.260588
Cat35	-2865.373537	-2864.627741	-2864.739601
Cat36	-2755.437179	-2754.833748	-2754.942474
Cat37	-1928.448112	-1927.793146	-1927.897098
Cat38	-2180.059843	-2179.341441	-2179.452517
Cat39	-2718.163648	-2717.269643	-2717.396783
Cat40	-2124.586276	-2123.813500	-2123.923236
Cat41	-2616.659488	-2615.917103	-2616.032546

Cat42	-3609.511159	-3608.477989	-3608.623314
Cat43	-2737.172151	-2736.448798	-2736.572361
Cat44	-2495.752403	-2495.123053	-2495.230774
Cat45	-2195.012614	-2194.385012	-2194.484136
Cat46	-3113.858301	-3113.144244	-3113.267342
Cat47	-2332.793156	-2332.032471	-2332.145516
Cat48	-2026.760028	-2026.071921	-2026.176493
Cat49	-2238.588379	-2237.882660	-2237.985112
Cat50	-2230.273125	-2229.631819	-2229.734753
Cat51	-2542.132114	-2541.400141	-2541.511315
Cat52	-2009.232794	-2008.491015	-2008.602641
Cat53	-2621.978532	-2621.350132	-2621.464700
Cat54	-2349.058919	-2348.297760	-2348.417010
Cat55	-2062.326814	-2061.681104	-2061.786277
Cat56	-2466.791022	-2465.957691	-2466.082701
Cat57	-2918.188617	-2917.543947	-2917.649307
Cat58	-2661.719683	-2661.191930	-2661.290257
Cat59	-2865.346677	-2864.602528	-2864.718561
Cat60	-3746.824958	-3745.746124	-3745.894334
Cat61	-2865.363258	-2864.617922	-2864.730696
Cat62	-2486.858553	-2486.198149	-2486.311301
Cat63	-1744.508018	-1743.920195	-1744.013952
Cat64	-2018.282145	-2017.703693	-2017.800658
Cat65	-2089.182278	-2088.358165	-2088.472544
Cat66	-1951.530562	-1950.847787	-1950.950540
Cat67	-2431.545734	-2430.763212	-2430.873165
Cat68	-2412.142001	-2411.318885	-2411.432467
Cat69	-2928.335389	-2927.349854	-2927.479901
Cat70	-2873.474609	-2872.783417	-2872.898161
Cat71	-2007.531660	-2006.910488	-2007.005614
Cat72	-2429.405144	-2428.498691	-2428.621699
Cat73	-2202.981666	-2202.166721	-2202.280232
Cat74	-2183.574120	-2182.719056	-2182.837816
Cat75	-2293.911605	-2293.191014	-2293.297131
Cat76	-1970.938073	-1970.213306	-1970.317476
Cat77	-1756.918978	-1756.282440	-1756.379776
Cat78	-2215.390177	-2214.656385	-2214.767285
Cat79	-2559.196375	-2558.524076	-2558.641163
Cat80	-2216.842395	-2216.070051	-2216.182727
Cat81	-2054.713924	-2054.100959	-2054.202580
Cat82	-2846.857314	-2846.202912	-2846.318920
Cat83	-2066.722411	-2066.016194	-2066.126430
Cat84	-2106.034879	-2105.299352	-2105.412236
Cat85	-2219.158817	-2218.425450	-2218.535945
Cat86	-2125.975974	-2125.170149	-2125.286795
Cat87	-2002.760397	-2002.216482	-2002.310925
Cat88	-3064.391101	-3063.430042	-3063.563757
Cat89	-2314.713061	-2313.997775	-2314.106648
Cat90	-2788.131399	-2787.409091	-2787.522335
Cat91	-1927.599123	-1927.058968	-1927.151174
Cat92	-2098.486675	-2097.848798	-2097.954202
Cat93	-3306.409356	-3305.386681	-3305.528300
Cat94	-2580.137751	-2579.292401	-2579.419302
Cat95	-2789.690535	-2788.995528	-2789.117518
Cat96	-2425.909670	-2425.212036	-2425.316908
Cat97	-2410.835690	-2410.164834	-2410.269511
Cat98	-2942.052593	-2941.266987	-2941.382705
Cat99	-2815.833363	-2815.230126	-2815.333534
Cat100	-2826.262359	-2825.531301	-2825.643963
Cat101	-3782.919086	-3782.227241	-3782.350548
Cat102	-2889.274843	-2888.571751	-2888.694960
Cat103	-2853.363639	-2852.637508	-2852.761630
Cat104	-2636.070465	-2635.423681	-2635.539005
Cat105	-2711.300448	-2710.648278	-2710.765340
Cat106	-2675.389239	-2674.714223	-2674.832311
Cat107	-3858.149210	-3857.451949	-3857.577024
Cat108	-3822.237896	-3821.517855	-3821.644166
Cat109	-3861.554009	-3860.805429	-3860.934798
Cat110	-3822.235378	-3821.514378	-3821.641558
Cat111	-3897.465573	-3896.739112	-3896.868407
Cat112	-3861.554230	-3860.804955	-3860.934764
Cat113	-3900.870311	-3900.092374	-3900.223933
Cat114	-3445.814613	-3445.130225	-3445.246258
Cat115	-3521.044706	-3520.354922	-3520.472751
Cat116	-3485.133410	-3484.420786	-3484.539604

Cat117	-3524.449580	-3523.708256	-3523.829259
Cat118	-3842.795661	-3842.139802	-3842.262239
Cat119	-3918.028079	-3917.367538	-3917.492346
Cat120	-3882.116731	-3881.433689	-3881.559868
Cat121	-3921.432758	-3920.721209	-3920.849644
Cat122	-2907.350684	-2906.681459	-2906.799880
Cat123	-2061.141506	-2060.489805	-2060.590631
Cat124	-1929.269054	-1928.618227	-1928.716045
Cat125	-2364.565186	-2363.913106	-2364.013713
Cat126	-2490.116937	-2489.463610	-2489.573674
Cat127	-3861.554281	-3860.805818	-3860.935624
Cat128	-3900.870572	-3900.093403	-3900.225279
Cat129	-3900.870687	-3900.092968	-3900.225628
Cat130	-3940.186837	-3939.380623	-3939.516396
Cat131	-3230.302475	-3229.635134	-3229.755169
Cat132	-4302.376162	-4301.451363	-4301.595257
Cat133	-2735.351653	-2734.685310	-2734.800574
Cat134	-2603.468383	-2602.803504	-2602.916802
Cat135	-3038.763372	-3038.096698	-3038.211805
Cat136	-2490.120001	-2489.466693	-2489.576557
Cat137	-9793.150715	-9792.460812	-9792.586846
Cat138	-9832.469528	-9831.751384	-9831.880276
Cat139	-4662.031592	-4661.320778	-4661.458804
Cat140	-9871.785853	-9871.039143	-9871.171001
Cat141	-3078.082046	-3077.387078	-3077.505349
Cat142	-3117.398515	-3116.674948	-3116.795540
Cat143	-5042.094978	-5041.431034	-5041.548307
Cat144	-5081.413649	-5080.721377	-5080.841447
Cat145	-5120.730083	-5120.009243	-5120.132099

**Table S17.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of TS2 at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E SPC	qh-H SPC	qh-G(T) SPC
Cat0	-2700.701943	-2700.016156	-2700.131419
Cat1	-3346.618420	-3345.935390	-3346.054069
Cat2	-2511.206456	-2510.542630	-2510.653266
Cat3	-2834.154386	-2833.492809	-2833.604337
Cat4	-2491.303942	-2490.628075	-2490.738886
Cat5	-2583.547971	-2582.872054	-2582.986317
Cat6	-2587.319872	-2586.645572	-2586.761242
Cat7	-2910.292301	-2909.619345	-2909.735412
Cat8	-2814.038259	-2813.340021	-2813.459214
Cat9	-2946.482119	-2945.818473	-2945.933259
Cat10	-2522.717645	-2522.082088	-2522.193450
Cat11	-2141.024438	-2140.319284	-2140.427119
Cat12	-1834.748181	-1834.130878	-1834.227988
Cat13	-2132.539396	-2131.943912	-2132.044229
Cat14	-1909.912728	-1909.291978	-1909.391655
Cat15	-2065.800590	-2065.100199	-2065.205665
Cat16	-2180.121833	-2179.402597	-2179.510584
Cat17	-2258.757038	-2257.979798	-2258.093610
Cat18	-2239.362099	-2238.544369	-2238.661602
Cat19	-2755.545824	-2754.565704	-2754.699317
Cat20	-2799.955179	-2799.275696	-2799.393945
Cat21	-2775.930897	-2775.239210	-2775.359049
Cat22	-2740.017391	-2739.302537	-2739.422586
Cat23	-3138.212927	-3137.495896	-3137.618078
Cat24	-3138.216132	-3137.499480	-3137.621731
Cat25	-2908.733029	-2907.990332	-2908.117300
Cat26	-2740.013569	-2739.298301	-2739.418613
Cat27	-2853.122388	-2852.411470	-2852.530508
Cat28	-2740.021997	-2739.306891	-2739.427067
Cat29	-2583.961217	-2583.339054	-2583.451605
Cat30	-2854.328135	-2853.594189	-2853.717798
Cat31	-2854.318406	-2853.584484	-2853.708176
Cat32	-3046.054140	-3045.266257	-3045.396665
Cat33	-2272.262160	-2271.614574	-2271.717429
Cat34	-2817.770321	-2817.149046	-2817.252627
Cat35	-2865.370233	-2864.624697	-2864.735438
Cat36	-2755.434374	-2754.830955	-2754.938391
Cat37	-1928.448794	-1927.794167	-1927.896938
Cat38	-2180.042010	-2179.324456	-2179.432876

Cat39	-2718.162039	-2717.269373	-2717.393781
Cat40	-2124.588780	-2123.817529	-2123.924535
Cat41	-2616.660937	-2615.918318	-2616.031602
Cat42	-3609.505741	-3608.472374	-3608.616316
Cat43	-2737.169196	-2736.445843	-2736.567316
Cat44	-2495.749182	-2495.119542	-2495.225505
Cat45	-2195.008208	-2194.380920	-2194.479359
Cat46	-3113.853426	-3113.140145	-3113.263475
Cat47	-2332.789827	-2332.029119	-2332.140791
Cat48	-2026.757163	-2026.069036	-2026.172004
Cat49	-2238.586806	-2237.881718	-2237.983090
Cat50	-2230.271432	-2229.630732	-2229.733490
Cat51	-2542.116809	-2541.385677	-2541.496153
Cat52	-2009.234020	-2008.492621	-2008.602680
Cat53	-2621.971831	-2621.344151	-2621.455842
Cat54	-2349.055952	-2348.294850	-2348.412847
Cat55	-2062.330479	-2061.684701	-2061.789279
Cat56	-2466.790859	-2465.957557	-2466.081080
Cat57	-2918.185271	-2917.540680	-2917.644575
Cat58	-2661.709563	-2661.182503	-2661.278772
Cat59	-2865.343042	-2864.598592	-2864.712820
Cat60	-3746.816226	-3745.738451	-3745.883307
Cat61	-2865.359562	-2864.614243	-2864.725734
Cat62	-2486.850761	-2486.191396	-2486.301829
Cat63	-1744.507513	-1743.920253	-1744.012831
Cat64	-2018.277717	-2017.699370	-2017.795185
Cat65	-2089.180395	-2088.358099	-2088.473061
Cat66	-1951.526864	-1950.844223	-1950.945595
Cat67	-2431.544489	-2430.762224	-2430.871204
Cat68	-2412.141920	-2411.320091	-2411.434236
Cat69	-2928.336199	-2927.350226	-2927.477648
Cat70	-2873.469593	-2872.778646	-2872.892031
Cat71	-2007.528259	-2006.907511	-2007.001551
Cat72	-2429.411018	-2428.504940	-2428.625733
Cat73	-2202.984087	-2202.170318	-2202.280977
Cat74	-2183.576405	-2182.722288	-2182.837894
Cat75	-2293.913499	-2293.193356	-2293.298555
Cat76	-1970.928535	-1970.204733	-1970.306818
Cat77	-1756.916741	-1756.280224	-1756.376223
Cat78	-2215.393044	-2214.659448	-2214.768967
Cat79	-2559.193345	-2558.521206	-2558.637118
Cat80	-2216.836925	-2216.065332	-2216.175943
Cat81	-2054.701937	-2054.089584	-2054.189112
Cat82	-2846.855947	-2846.201857	-2846.316941
Cat83	-2066.722339	-2066.016291	-2066.125361
Cat84	-2106.034442	-2105.298789	-2105.409787
Cat85	-2219.143488	-2218.410109	-2218.518966
Cat86	-2125.975305	-2125.170585	-2125.284429
Cat87	-2002.758100	-2002.214480	-2002.307305
Cat88	-3064.396242	-3063.435556	-3063.567950
Cat89	-2314.710343	-2313.995186	-2314.102395
Cat90	-2788.130307	-2787.408087	-2787.519644
Cat91	-1927.598057	-1927.058126	-1927.149308
Cat92	-2098.481279	-2097.843348	-2097.946941
Cat93	-3306.403413	-3305.379958	-3305.520051
Cat94	-2580.140888	-2579.295494	-2579.420466
Cat95	-2789.687363	-2788.992289	-2789.112658
Cat96	-2425.903513	-2425.206113	-2425.309632
Cat97	-2410.831829	-2410.161096	-2410.264528
Cat98	-2942.051549	-2941.266400	-2941.381388
Cat99	-2815.836242	-2815.232594	-2815.334981
Cat100	-2826.256816	-2825.525642	-2825.636438
Cat101	-3782.911478	-3782.219013	-3782.340379
Cat102	-2889.269082	-2888.565615	-2888.686701
Cat103	-2853.358890	-2852.633360	-2852.754248
Cat104	-2636.062898	-2635.415881	-2635.529525
Cat105	-2711.293729	-2710.641079	-2710.756289
Cat106	-2675.381684	-2674.706076	-2674.822191
Cat107	-3858.142376	-3857.444649	-3857.568126
Cat108	-3822.230168	-3821.509609	-3821.634092
Cat109	-3861.546811	-3860.798363	-3860.923242
Cat110	-3822.230299	-3821.509331	-3821.634866
Cat111	-3897.461247	-3896.735477	-3896.860281
Cat112	-3861.548918	-3860.800123	-3860.925711
Cat113	-3900.865466	-3900.087751	-3900.218225

Cat114	-3445.807494	-3445.123011	-3445.237757
Cat115	-3521.038513	-3520.348733	-3520.465350
Cat116	-3485.126285	-3484.413453	-3484.530936
Cat117	-3524.442565	-3523.702077	-3523.820580
Cat118	-3842.789497	-3842.134084	-3842.253209
Cat119	-3918.020560	-3917.359482	-3917.482495
Cat120	-3882.108116	-3881.424553	-3881.546512
Cat121	-3921.424869	-3920.712439	-3920.838759
Cat122	-2907.342688	-2906.673522	-2906.790603
Cat123	-2061.134129	-2060.482316	-2060.581660
Cat124	-1929.262728	-1928.612262	-1928.709014
Cat125	-2364.557421	-2363.905346	-2364.004474
Cat126	-2490.112877	-2489.459761	-2489.568523
Cat127	-3861.546667	-3860.797890	-3860.922733
Cat128	-3900.862858	-3900.085355	-3900.215535
Cat129	-3900.865371	-3900.088201	-3900.217141
Cat130	-3940.181572	-3939.375322	-3939.509531
Cat131	-3230.293693	-3229.626546	-3229.744762
Cat132	-4302.373179	-4301.448689	-4301.591390
Cat133	-2735.343177	-2734.676798	-2734.790691
Cat134	-2603.461239	-2602.796048	-2602.907081
Cat135	-3038.754494	-3038.087794	-3038.201492
Cat136	-2490.114619	-2489.461326	-2489.569636
Cat137	-9793.142535	-9792.452088	-9792.576689
Cat138	-9832.461749	-9831.744060	-9831.870106
Cat139	-4662.027902	-4661.317234	-4661.454128
Cat140	-9871.778068	-9871.031518	-9871.162890
Cat141	-3078.073157	-3077.378329	-3077.495173
Cat142	-3117.389529	-3116.666232	-3116.785721
Cat143	-5042.085483	-5041.421301	-5041.537007
Cat144	-5081.404134	-5080.711859	-5080.830489
Cat145	-5120.720489	-5119.999756	-5120.121284

**Table S18.** Single-point electronic energies, quasi-harmonic enthalpies, and Gibbs free energies (298 K) of intermediate **4** at the PCM/ $\omega$ B97X-D/Def2-TZVP//B97-D/Def2-SVP/PCM level, in Hartree.

Catalyst	E_SPC	qh-H_SPC	qh-G(T)_SPC
Cat0	-2700.711442	-2700.023859	-2700.142439
Cat1	-3346.626080	-3345.941974	-3346.061417
Cat2	-2511.219267	-2510.554540	-2510.666164
Cat3	-2834.164903	-2833.502505	-2833.615097
Cat4	-2491.316056	-2490.639070	-2490.750709
Cat5	-2583.558326	-2582.881369	-2582.996668
Cat6	-2587.336274	-2586.660779	-2586.776996
Cat7	-2910.308772	-2909.634484	-2909.751020
Cat8	-2814.048092	-2813.348966	-2813.469437
Cat9	-2946.495526	-2945.831124	-2945.947178
Cat10	-2522.730416	-2522.093941	-2522.206948
Cat11	-2141.033931	-2140.327819	-2140.436883
Cat12	-1834.761359	-1834.143202	-1834.241818
Cat13	-2132.549628	-2131.952850	-2132.053927
Cat14	-1909.922996	-1909.301127	-1909.401338
Cat15	-2065.815689	-2065.114534	-2065.221775
Cat16	-2180.135475	-2179.415134	-2179.523995
Cat17	-2258.771416	-2257.993033	-2258.107434
Cat18	-2239.378768	-2238.559817	-2238.677841
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Cat20	-2799.969282	-2799.289061	-2799.408893
Cat21	-2775.940841	-2775.248152	-2775.368745
Cat22	-2740.029497	-2739.313951	-2739.435324
Cat23	-3138.227183	-3137.508989	-3137.632080
Cat24	-3138.228360	-3137.507817	-3137.630641
Cat25	-2908.747698	-2908.003787	-2908.131733
Cat26	-2740.027851	-2739.310861	-2739.430524
Cat27	-2853.134818	-2852.422235	-2852.544694
Cat28	-2740.039033	-2739.321639	-2739.440848
Cat29	-2583.970596	-2583.347372	-2583.460863
Cat30	-2854.340661	-2853.605543	-2853.730119
Cat31	-2854.329960	-2853.594851	-2853.719384
Cat32	-3046.066714	-3045.277939	-3045.409576
Cat33	-2272.277293	-2271.628665	-2271.732730
Cat34	-2817.780655	-2817.158358	-2817.262949
Cat35	-2865.382270	-2864.635682	-2864.747484



Cat36	-2755.446346	-2754.841833	-2754.950143
Cat37	-1928.464008	-1927.808178	-1927.911798
Cat38	-2180.080657	-2179.360825	-2179.470915
Cat39	-2718.177872	-2717.283209	-2717.409999
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Cat41	-2616.675136	-2615.931589	-2616.046164
Cat42	-3609.519713	-3608.485177	-3608.629986
Cat43	-2737.180883	-2736.456746	-2736.579647
Cat44	-2495.764958	-2495.134195	-2495.241286
Cat45	-2195.021794	-2194.393669	-2194.493462
Cat46	-3113.869967	-3113.155071	-3113.278407
Cat47	-2332.802334	-2332.040445	-2332.153116
Cat48	-2026.770662	-2026.081699	-2026.185635
Cat49	-2238.601932	-2237.896141	-2237.998767
Cat50	-2230.284994	-2229.642855	-2229.746102
Cat51	-2542.138073	-2541.405313	-2541.516047
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Cat54	-2349.071214	-2348.308800	-2348.427825
Cat55	-2062.342592	-2061.695411	-2061.800475
Cat56	-2466.807140	-2465.972681	-2466.097432
Cat57	-2918.199249	-2917.553588	-2917.658738
Cat58	-2661.723448	-2661.194343	-2661.292292
Cat59	-2865.354307	-2864.608890	-2864.724221
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Cat61	-2865.371116	-2864.624589	-2864.736532
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Cat65	-2089.196177	-2088.373075	-2088.489690
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Cat67	-2431.558126	-2430.775101	-2430.885184
Cat68	-2412.156977	-2411.334034	-2411.449220
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Cat70	-2873.480695	-2872.788741	-2872.902992
Cat71	-2007.539910	-2006.918305	-2007.013563
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Cat73	-2202.998120	-2202.182628	-2202.296465
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Cat75	-2293.927146	-2293.205884	-2293.311898
Cat76	-1970.946440	-1970.220995	-1970.325048
Cat77	-1756.928875	-1756.291212	-1756.388303
Cat78	-2215.407580	-2214.672867	-2214.783297
Cat79	-2559.205623	-2558.532346	-2558.649305
Cat80	-2216.854559	-2216.081508	-2216.194414
Cat81	-2054.717543	-2054.103243	-2054.204644
Cat82	-2846.873810	-2846.218637	-2846.335378
Cat83	-2066.740646	-2066.033517	-2066.144188
Cat84	-2106.051767	-2105.314987	-2105.426989
Cat85	-2219.168233	-2218.433843	-2218.544386
Cat86	-2125.993657	-2125.186955	-2125.302626
Cat87	-2002.774706	-2002.229971	-2002.323837
Cat88	-3064.413364	-3063.451299	-3063.584169
Cat89	-2314.727010	-2314.010598	-2314.118536
Cat90	-2788.148285	-2787.424429	-2787.536257
Cat91	-1927.615468	-1927.074206	-1927.166014
Cat92	-2098.491310	-2097.852109	-2097.956797
Cat93	-3306.420094	-3305.395540	-3305.536520
Cat94	-2580.154117	-2579.307258	-2579.432654
Cat95	-2789.698317	-2789.002501	-2789.124502
Cat96	-2425.915258	-2425.217099	-2425.321905
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Cat98	-2942.078035	-2941.291776	-2941.407311
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Cat103	-2853.367056	-2852.639928	-2852.763558
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Cat106	-2675.392265	-2674.715722	-2674.833446
Cat107	-3858.153809	-3857.454220	-3857.576234
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Cat114	-3445.817242	-3445.131829	-3445.247677
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Cat116	-3485.136035	-3484.422297	-3484.541089
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Cat122	-2907.354037	-2906.684134	-2906.802591
Cat123	-2061.145384	-2060.492704	-2060.593218
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Cat126	-2490.126196	-2489.472125	-2489.582169
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