† Electronic Supplementary Information (ESI)

New Insights into Phenazine-based Organic Redox Flow Batteries by using High-Throughput DFT Modeling

A) Details about the DME solvent in the SMD solvation model with the GAUSSIAN 16 software

The DME solvent can be defined within the SMD solvation model in the GAUSSIAN 16 software with the following input file:

```
#p M062X/6-31+G(d,p)/auto integral=(grid=ultrafine)
scf=(intrep,xqc,maxconventionalcycles=350,tight) Guess=Read Geom=Check
SCRF=(SMD,Solvent=Generic,read)

[Title]

0 1

stoichiometry=C4O2H10
solventname=DimethoxyEthane
eps=7.55
epsinf=1.896129
hbondacidity=0.00
hbondbasicity=0.68
SurfaceTensionAtInterface=35.4216652
CarbonAromaticity=0.0
ElectronegativeHalogenicity=0.0
```

The required solvent descriptors (refractive index; Abraham's hydrogen bond acidity and basicity parameters; macroscopic surface tension; dielectric constant at 298.15K have been obtained from [1, 2, 3]:

B) Experimental Results

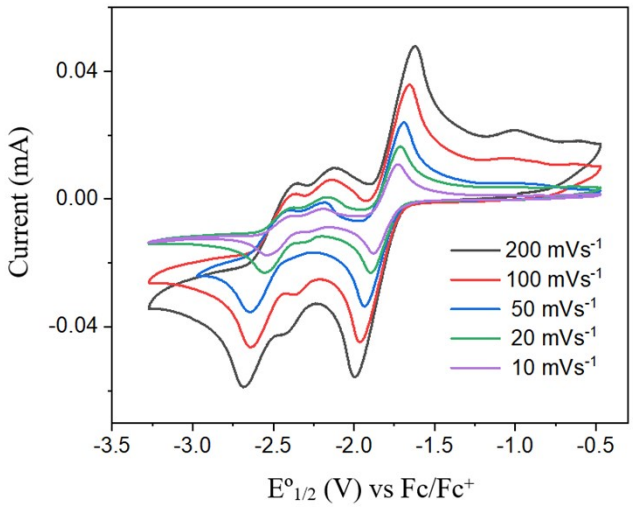

Figure S1. Cyclic voltammetry at different scan rates of 5 mM phenazine in 1,2-dimethoxyethane with 0.5 M of $TBAPF_6$ as supporting salt.

Figure S1 shows a fully reversible first peak at potential $E^{o}_{1/2}$ = -1.74 V vs Fc/Fc^{+} corresponding to the reduction of phenazine to generate the radical anion in aprotic media (Scheme 1). However, the second reduction peak corresponding to the formation of the dianion is not reversible and the reduction potential cannot be estimated accurately. Actually, the well-known irreversible character of this second reaction limits the specific capacity of phenazine-based anolytes in redox flow batteries (RFB) since only one electron per molecule is involved in the energy storage. Therefore, only the first reduction reaction will be investigated and all calculations for the functionalized compounds will refer to this reaction.

C) Computational Results

1. Intermolecular Hydrogen-bonding

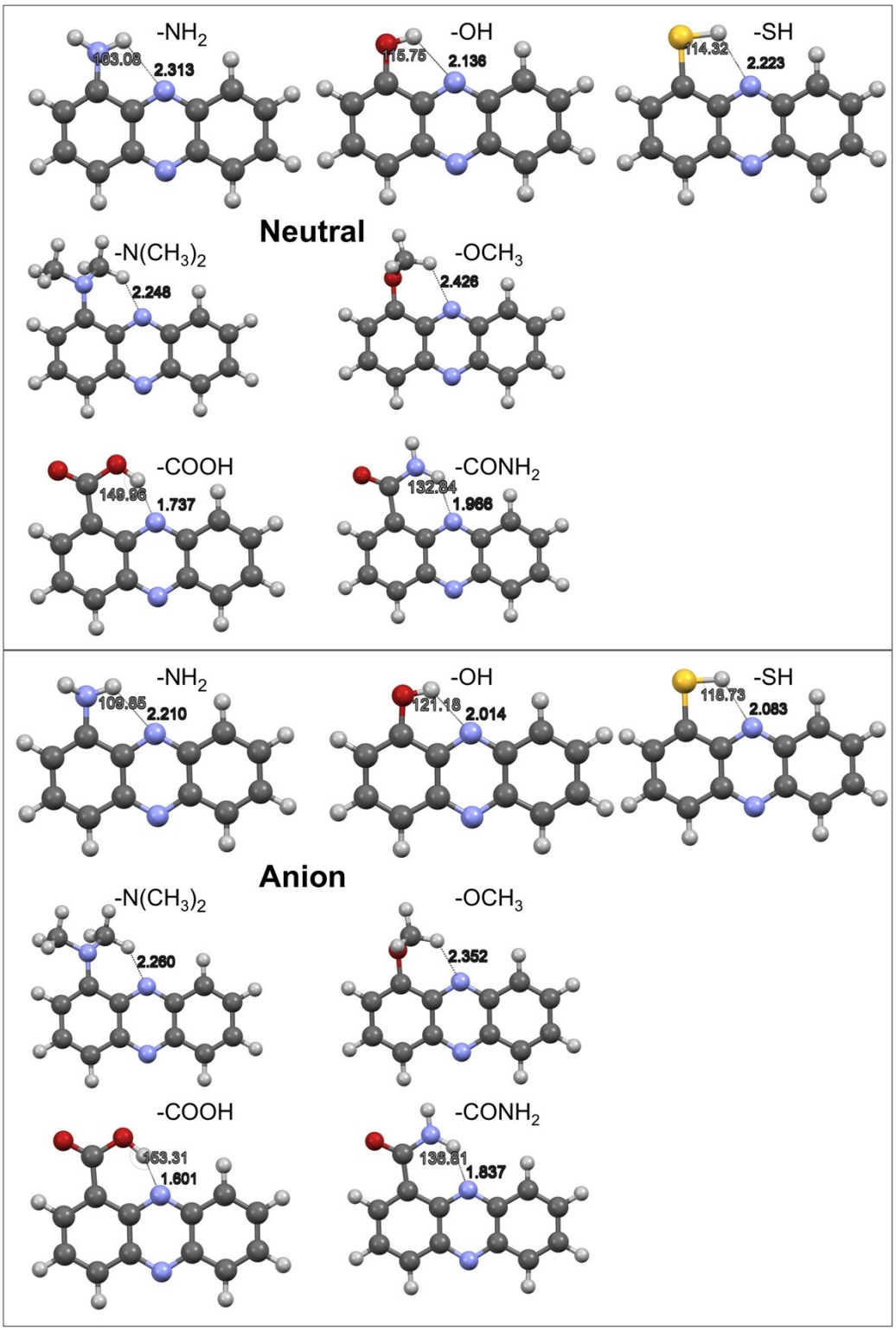

Figure S2. Bond angles and distances between the proton from the FG and the nitrogen from the oxidized (neutral) and reduced (mono-anion) phenazine for the $–NH_2$, –OH, –SH, $–N(CH_3)_2$, $–OCH_3$, –COOH and $–CONH_2$ FGs at the position 1**.**

In Figure S2, we present the main geometrical features (bond distances and angles) between the proton from the $–NH_2$, –OH, –SH, $–N(CH_3)_2$, $–OCH_3$, –COOH and $–CONH_2$ FGs and the nitrogen atom of the Phenazine in the oxidized (neutral) and reduced (mono-anion) form. Based on these values, we can consider the formation of weak H-bonds between the proton from the FGs and the nitrogen atom of the phenazine. The H-bonds become stronger in the reduced (anionic) state, as corroborated by the shorter distances.

2. Reorganization Energies

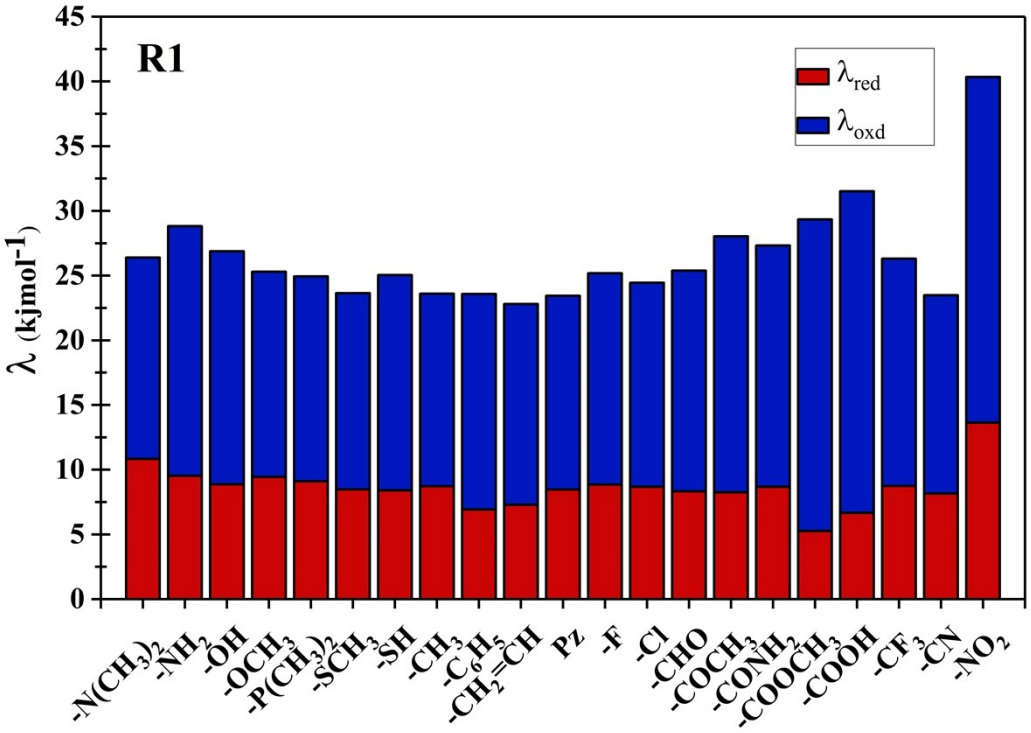

Figure S3. Reorganization energies of the functionalized phenazines on R1 position.

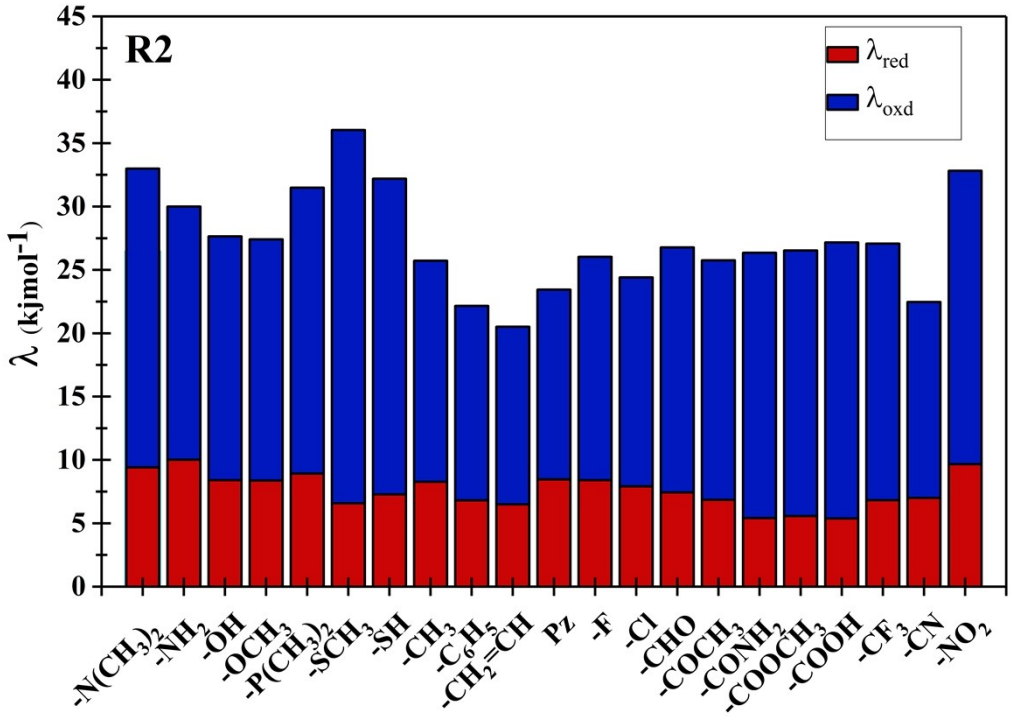

Figure S4. Reorganization energies of the functionalized phenazines on R2 position.

3. Root-mean-square deviation (RMSD) between the optimized coordinates of the neutral and reduced state of the phenazine species

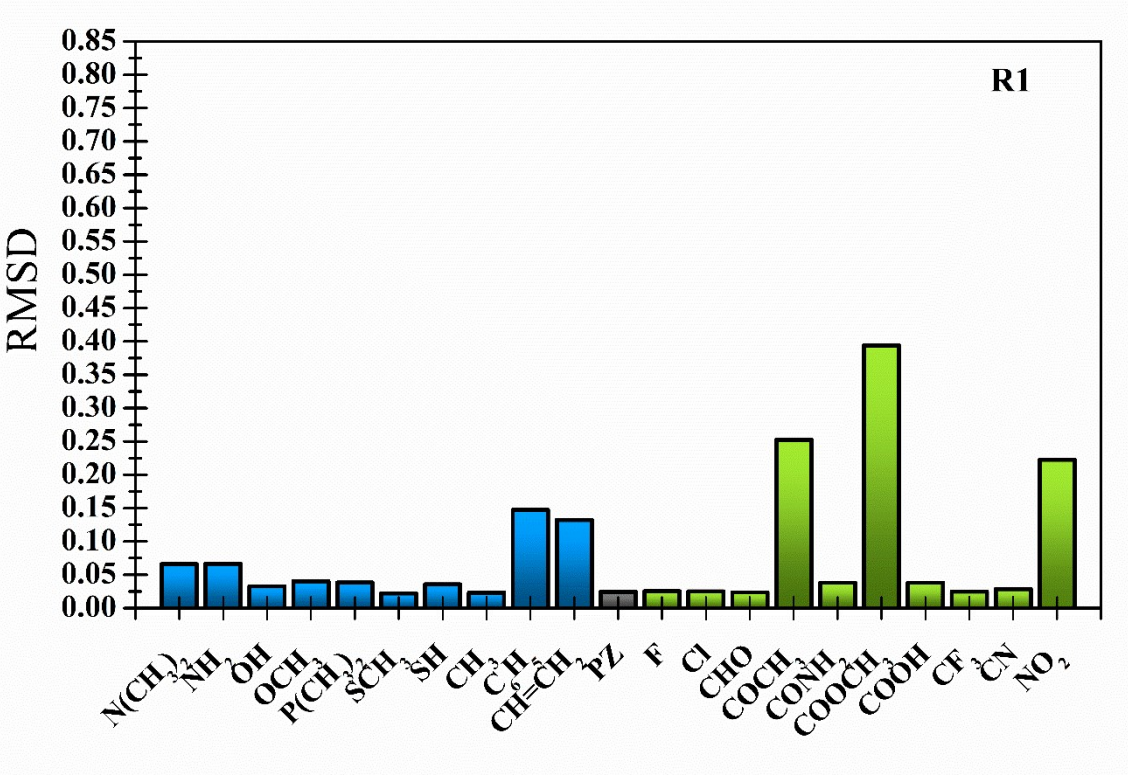

Figure S5. RMSD values of the phenazines functionalized on R1 position.

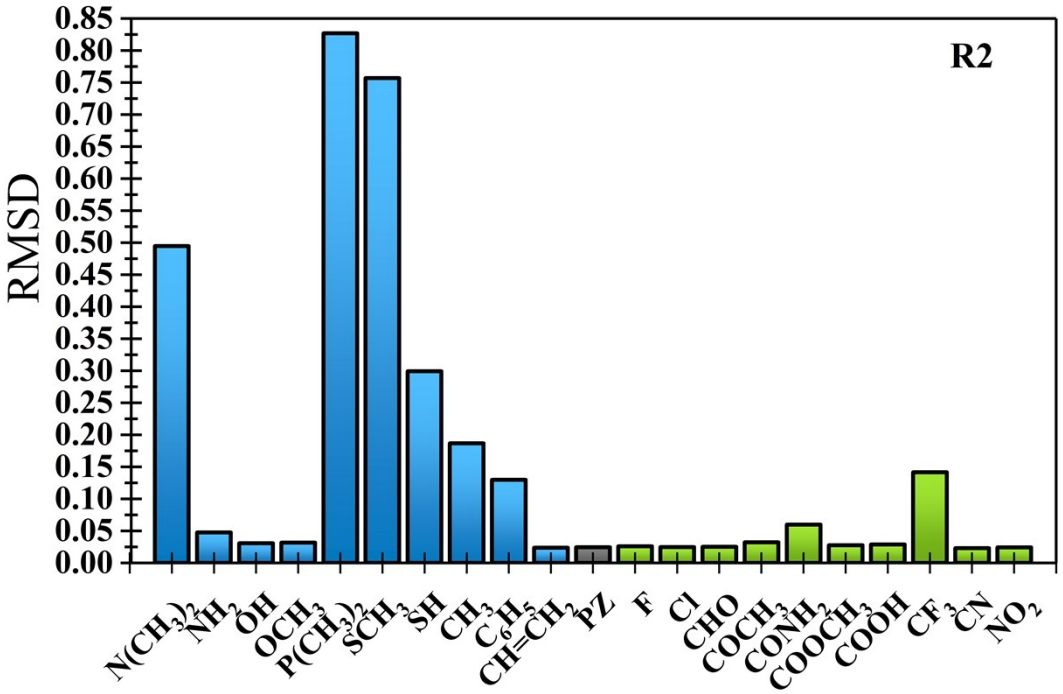

Figure S6. RMSD values of the phenazines functionalized on R2 position.

Table S1. **RMSD values of the phenazines functionalized with the best candidates and the main anolytes used in non-aqueous RFB**.

Compound	RMSD
Pz-$(CN)_4$	0.0199
Pz-$(CN)_3$	0.0255
Pz-$(CN)_2$	0.0621
Pz-CN	0.0285
Phenazine	0.0245
Pz-NH_2	0.0476
Pz-$(NH2)_2$	0.0362
Pz-$(NH2)_3$	0.0500
Pz-$(NH2)_4$	0.0405
MePht	0.0277
Fl	0.0182
DMAQ	0.3208

Table S2: Calculated Redox Potentials of all phenazine derivatives.

	Functional Group (FG)	**FG POSITION**	**E1 (V) vs Fc/Fc+**
Phenazine	-	-	-1.74
1	$N(CH_3)_2$	1	-1.85
2	$N(CH_3)_2$	2	-1.98
3	NH_2	1	-1.85
4	NH_2	2	-1.92
5	OH	1	-1.69
6	OH	2	-1.81
7	OCH_3	1	-1.75
8	OCH_3	2	-1.86
9	$P(CH_3)_2$	1	-1.74
10	$P(CH_3)_2$	2	-1.75
11	$S(CH_3)_2$	1	-1.74
12	$S(CH_3)_2$	2	-1.77
13	SH	1	-1.66
14	SH	2	-1.72
15	CH_2=CH	1	-1.73
16	CH_2=CH	2	-1.72
17	C_6H_5	1	-1.76
18	C_6H_5	2	-1.73
19	CH_3	1	-1.79
20	CH_3	2	-1.79
21	F	1	-1.63
22	F	2	-1.68
23	Cl	1	-1.61
24	Cl	2	-1.63
26	CHO	1	-1.50
27	CHO	2	-1.51
28	$COCH_3$	1	-1.58
29	$COCH_3$	2	-1.55
30	$CONH_2$	1	-1.52
31	$CONH_2$	2	-1.63
32	$COOCH_3$	1	-1.62
33	$COOCH_3$	2	-1.57
34	COOH	1	-1.30
35	COOH	2	-1.53
36	CF_3	1	-1.53
37	CF_3	2	-1.55
38	CN	1	-1.42
39	CN	2	-1.43
40	NO_2	1	-1.35
41	NO_2	2	-1.29
42	CN	1 2	-1.04
43	CN	1 3	-1.10
44	CN	1 4	-1.06
45	CN	1 6	-1.14
46	CN	1 7	-1.15

47	CN	1 8	-1.14
48	CN	1 9	-1.15
49	CN	2 3	-1.18
50	CN	2 7	-1.04
51	CN	2 8	-1.15
52	CN	1 2 3	-0.79
53	CN	1 2 4	-0.68
54	CN	1 2 6	-0.81
55	CN	1 2 7	-0.80
56	CN	1 2 8	-0.80
57	CN	1 2 9	-0.81
58	CN	1 3 6	-0.85
59	CN	1 3 7	-0.86
60	CN	1 3 8	-0.83
61	CN	1 3 9	-0.86
62	CN	1 4 6	-0.82
63	CN	1 4 7	-0.81
64	CN	2 3 6	-0.89
65	CN	2 3 7	-0.89
66	CN	1 2 3 4	-0.37
67	CN	1 2 3 6	-0.56
68	CN	1 2 3 7	-0.55
69	CN	1 2 3 8	-0.54
70	CN	1 2 3 9	-0.57
71	CN	1 2 4 6	-0.48
72	CN	1 2 4 7	-0.45
73	CN	1 2 4 8	-0.46
74	CN	1 2 4 9	-0.47
75	CN	1 2 6 7	-0.52
76	CN	1 2 6 8	-0.69
77	CN	1 2 7 8	-0.58
78	CN	1 2 8 9	-0.52
79	CN	1 3 6 7	-0.55
80	CN	1 3 6 8	-0.57
81	CN	1 3 6 9	-0.56
82	CN	1 3 7 9	-0.59
83	CN	1 4 6 9	-0.56
84	CN	1 4 7 8	-0.58
85	CN	2 3 7 8	-0.64
86	CN	1 2 3 4 6 9	0.02
87	CN	1 2 3 6 7 8	-0.11
88	CN	1 2 3 7 8 9	-0.06
89	CN	2 3 6 7 8 9	-0.06
90	CN	1 2 3 4 6 7 8 9	0.51
91	NH_2	1 2	-1.93
92	NH_2	1 3	-2.03
93	NH_2	1 4	-1.89
94	NH_2	1 6	-1.96

95	NH_2	1 7	-2.02
96	NH_2	1 8	-2.02
97	NH_2	1 9	-1.95
98	NH_2	2 3	-2.04
99	NH_2	2 7	-2.05
100	NH_2	2 8	-2.09
101	NH_2	1 2 3	-2.04
102	NH_2	1 2 4	-2.01
103	NH_2	1 2 6	-2.04
104	NH_2	1 2 7	-2.09
105	NH_2	1 2 8	-2.09
106	NH_2	1 2 9	-2.02
107	NH_2	1 3 6	-2.13
108	NH_2	1 3 7	-2.19
109	NH_2	1 3 8	-2.15
110	NH_2	1 3 9	-1.94
111	NH_2	1 4 6	-1.99
112	NH_2	1 4 7	-2.05
113	NH_2	2 3 6	-2.12
114	NH_2	2 3 7	-2.20
115	NH_2	1 2 3 4	-2.10
116	NH_2	1 2 3 6	-2.18
117	NH_2	1 2 3 7	-2.23
118	NH_2	1 2 3 8	-2.22
119	NH_2	1 2 3 9	-2.11
120	NH_2	1 2 4 6	-2.12
121	NH_2	1 2 4 7	-2.19
122	NH_2	1 2 4 8	-2.18
123	NH_2	1 2 4 9	-2.10
124	NH_2	1 2 6 7	-2.11
125	NH_2	1 2 6 9	-2.07
126	NH_2	1 2 7 8	-2.22
127	NH_2	1 2 8 9	-2.11
128	NH_2	1 3 6 7	-2.21
129	NH_2	1 3 6 8	-2.25
130	NH_2	1 3 6 9	-2.34
131	NH_2	1 3 7 9	-2.29
132	NH_2	1 4 6 9	-2.02
133	NH_2	1 4 7 8	-2.27
134	NH_2	2 3 7 8	-2.32
135	NH_2	1 2 3 6 7 8	-2.38
136	NH_2	1 2 3 7 8 9	-2.36
137	NH_2	2 3 6 7 8 9	-2.35
138	NH_2	1 2 3 4 6 9	-2.21
139	NH_2	1 2 3 4 6 7 8 9	-2.39
140	OH	1 2	-1.84
141	OH	1 7	-1.87
142	OH	1 8	-1.86

143	OH	1 9	-1.74
144	OH	2 3	-1.93
145	OH	27	-1.89
146	OH	28	-1.88
147	OH	1 2 7	-1.80
148	OH	1 2 8	-1.82
149	OH	1 3 7	-1.84
150	OH	1 3 8	-1.82
151	OH	2 3 6	-1.85
152	OH	2 3 7	-1.93
153	OH	1 2 3 4	-1.78
154	OH	1 2 3 6	-1.76
155	OH	1 2 3 7	-1.87
156	OH	1 2 3 8	-1.87
157	OH	1 2 3 9	-1.76
158	OH	1 2 4 8	-1.76
159	OH	1 2 7 8	-1.73
160	OH	1 3 6 7	-1.77
161	OH	1 3 6 8	-1.76
162	OH	1 3 7 9	-1.78
163	OH	1 4 7 8	-1.55
164	OH	2 3 7 8	-1.99
165	OH	1 2 3 6 7 8	-1.90
166	OH	1 2 3 4 6 7 8 9	-1.80
167	NO_2	1 2	-0.91
168	NO_2	1 3	-0.96
169	NO_2	1 4	-0.92
170	NO_2	1 6	-1.11
171	NO_2	1 8	-1.03
172	NO_2	1 9	-1.14
173	NO_2	2 3	-1.10
174	NO_2	2 7	-0.94
175	NO_2	1 2 3	-0.74
176	NO_2	1 2 4	-0.56
177	NO_2	146	-0.75
178	NO_2	1 4 7	-0.70
179	NO_2	2 3 7	-0.74
180	NO_2	1 2 3 4	-0.31
181	NO_2	1 2 4 6	-0.36
182	NO_2	1 2 4 7	-0.29
183	NO_2	1 2 4 8	-0.30
184	NO_2	1 2 4 9	-0.34
185	NO_2	1 2 6 7	-0.35
186	NO_2	1 4 6 9	-0.52
187	NO_2	2 3 7 8	-0.52
188	NO_2	1 2 3 4 6 9	0.16
189	NO_2	1 2 3 4 6 7 8 9	0.80

Cartesian coordinates for all structures can be downloaded from a public repository: https://osf.io/y8hvd/?view_only=0debc99e089f4edb864d74553eb2559d

References:

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2 Christian Wohlfarth, *Surface tension of pure liquids and binary liquid mixtures*, Springer-Verlag Berlin Heidelberg, 2008.

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