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Electronic Supplementary Information For:

Effective Hydrogenation of CO_2 to Formate Catalyzed by Ionic Liquids Modified Acetate-Cu

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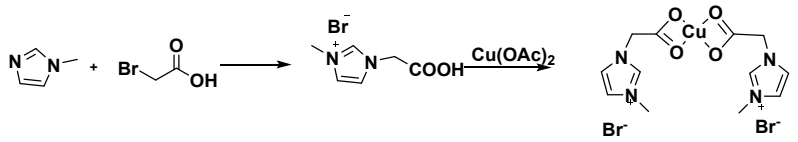
Index:

1. Synthesis and characterization of ligands and catalysts

[Cu-Imace-C1][Br]

8.2 g N-methylimidazole was reacted with 13.9g 2-bromoacetic acid in 30 mL acetonitrile under reflux for 48 h. The reaction mixture was evaporated under reduced pressure at 60 ℃, and a white powder was obtained. Water was used to recrystallize the powder, and pure [Imace-C1][Br] was obtained. In the next step, 4.42 g [Imace-C1][Br] was reacted with 1.99 g $Cu(OAc)_2 \cdot H_2O$ in 50 mL water at 100 ℃. The generated acetic acid was removed using water vapor. New amount of water (50 ml) was continuously added into the reaction system until the reaction was completed.

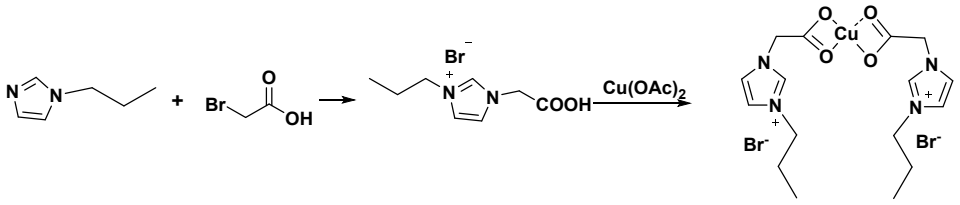


Scheme 1. Synthesis of [Cu-Imace-C1][Br]

[Imace-C1][Br]: ^{1}H NMR (400 MHz, DMSO). δ 9.25 (s, 1H, N-CH-N), 7.80 (d, J = 8.6 Hz, 2H, N-CH), 5.23 (s, 2H, -CH_2-), 3.92 (s, 3H, -CH_3). ^{13}C NMR (d_6-DMSO, 100MHz): δ 168.66 (-COOH), 137.99 (N-CH-N), 124.13 (N-CH), 123.63 (N-CH), 50.14 (-CH_2-), 36.43 (-CH_3).
[Cu-Imace-C1][Br]: IR (v/cm-1) 3521 3469 1640 1381 1289 1105 1189 821 707 492. MS (m/z): [Cu-Imace-H-C1] $^{+}$. Calc. 344.05, found, 343.58.

[Cu-Imace-C3][Br]

11.0 g N-propyl imidazole was reacted with 13.9g 2-bromoacetic acid in 30 mL acetonitrile under reflux for 48 h. The reaction mixture was evaporated under reduced pressure at 60 ℃, and a white powder was obtained. Water was used to recrystallize the powder, and pure [Imace-C3][Br] was obtained. In the next step, 4.98 g [Imace-C3][Br] was reacted with 1.99 g $Cu(OAc)_2$•H_2O in 50 mL water at 100 ℃. The generated acetic acid was removed using water vapor. New amount of water (50 ml) was continuously added into the reaction system until the reaction was completed.

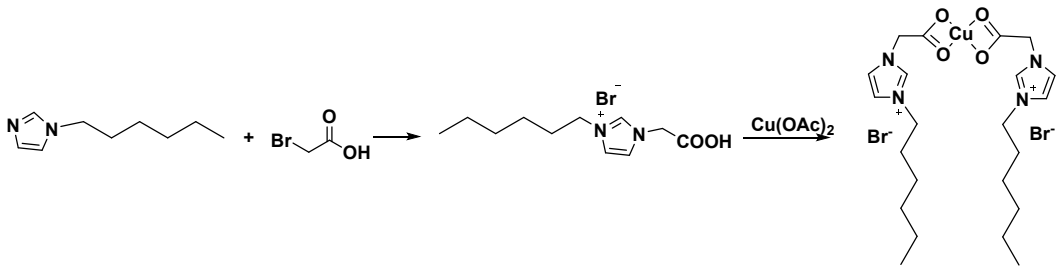


Scheme 2. Synthesis of [Cu-Imace-C3][Br]

[Imace-C3][Br]: ^{1}H NMR (400 MHz, DMSO) δ 9.35 (s, 1H, N-CH-N), 7.89 (d, 2H, *J* = 24.1, N-CH), 5.23 (s, 2H, -CH_2-COOH), 4.23 (t, *J* = 7.0 Hz, 2H, N-CH_2), 1.92 – 1.61 (m, 2H, C-CH_2-C), 0.83 (t, *J* = 7.3 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, d6-DMSO) δ 168.61 (-COOH), 137.61 (N-CH-N), 124.32 (N-CH), 122.43 (N-CH), 50.80 (N-CH_2), 50.19 (N-CH_2), 23.32 (-CH_2-), 10.79 (-CH_3).
[Cu-Imace-C3][Br]: IR (v/cm-1) 3510 3392 1622 1354 1105 1192 805 692 479. MS (m/z): [Cu-Imace-H-C3] $^{+}$. Calc. 400.12, found, 400.50.

[Cu-Imace-C6][Br]

15.2 g N-hexyl imidazole was reacted with 13.9g 2-bromoacetic acid in 30 mL acetonitrile under reflux for 48 h. The reaction mixture was evaporated under reduced pressure at 60 ℃, and a white powder was obtained. Water was used to recrystallize the powder, and pure [Imace-C6][Br] was obtained. In the next step, 5.82 g [Imace-C6][Br] was reacted with 1.99 g $Cu(OAc)_2 \cdot H_2O$ in 50 mL water at 100 ℃. The generated acetic acid was removed using water vapor. New amount of water (50 ml) was continuously added into the reaction system until the reaction was completed.



Scheme 3. Synthesis of [Cu-Imace-C6][Br]

[Imace-C6][Br]
^{1}H NMR (400 MHz, DMSO) δ 9.26 (s, 1H, N-CH-N), 7.82 (d, J = 26.7, 2H, N-CH), 5.18 (s, 2H, N-CH_2), 4.25 (t, J = 7.1 Hz, 2H, N-CH_2), 1.80 (m, 2H, CH_2), 1.25 (m, 6H, -CH_2-CH_2-CH_2-), 0.86 (t, J = 6.9 Hz, 3H, -CH_3). ^{13}C NMR (101 MHz, DMSO) δ 168.66 (-COOH), 137.60 (N-CH-N), 124.37 (N-CH), 122.43 (N-CH), 50.21 (N-CH_2), 49.36 (N-CH_2), 30.96 (-CH_2-), 29.79 -CH_2-), 25.52 (-CH_2-), 22.35 (-CH_2-), 14.29 (-CH_3).
[Cu-Imace-C6][Br]: IR (v/cm^{-1}) 3418 3005 2500 1608 1324 1202 1084 804 681 602 493. MS (m/z) [Cu-Imace-H-C6] $^+$. Calc. 484.21, found, 484.11.

Synthesis of catalysts with different anions was performed using the same method reported reported by our group.[S1]

2. Original NMR spectrums

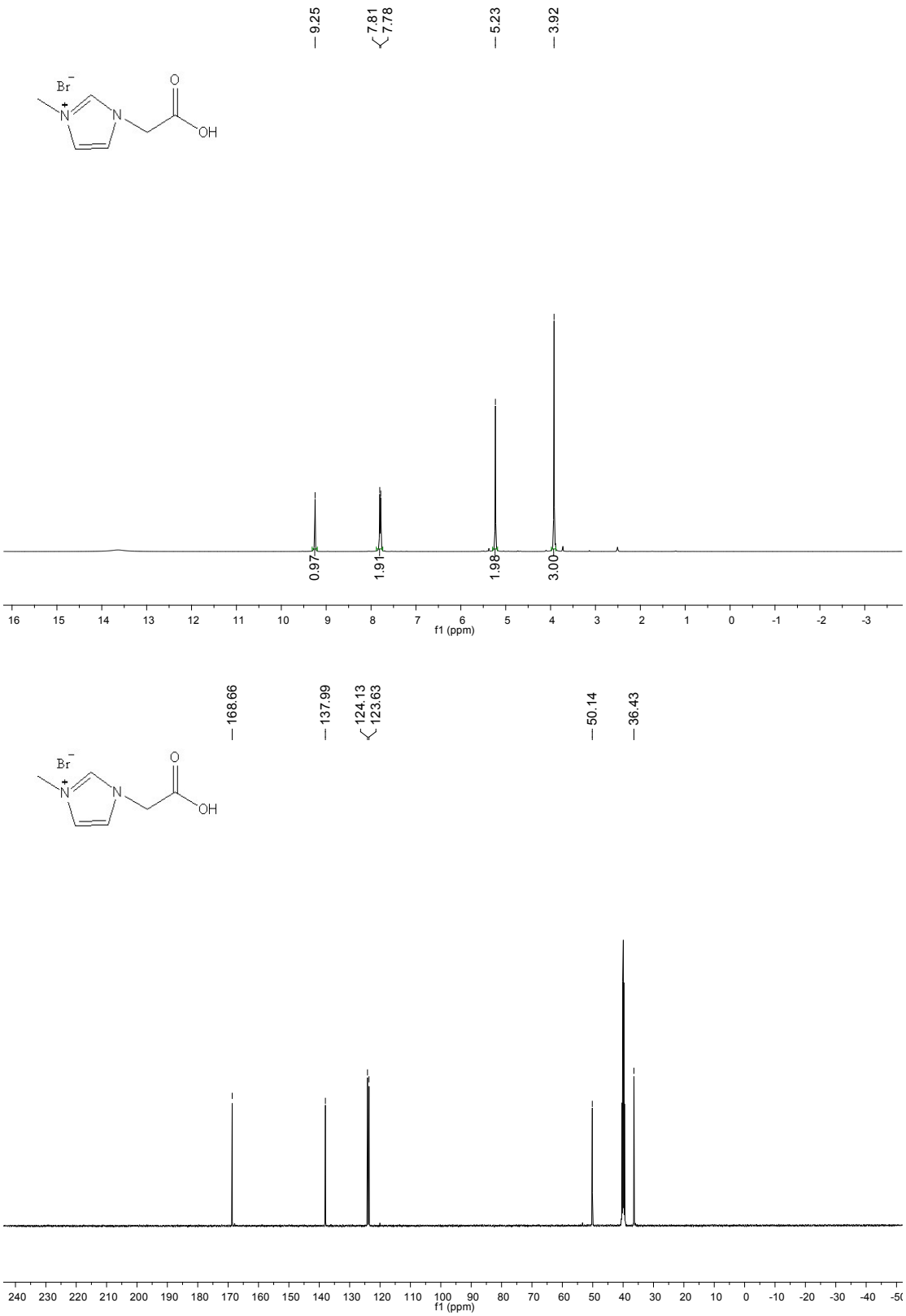


Fig. S1. NMR of [Imace-C1][Br]

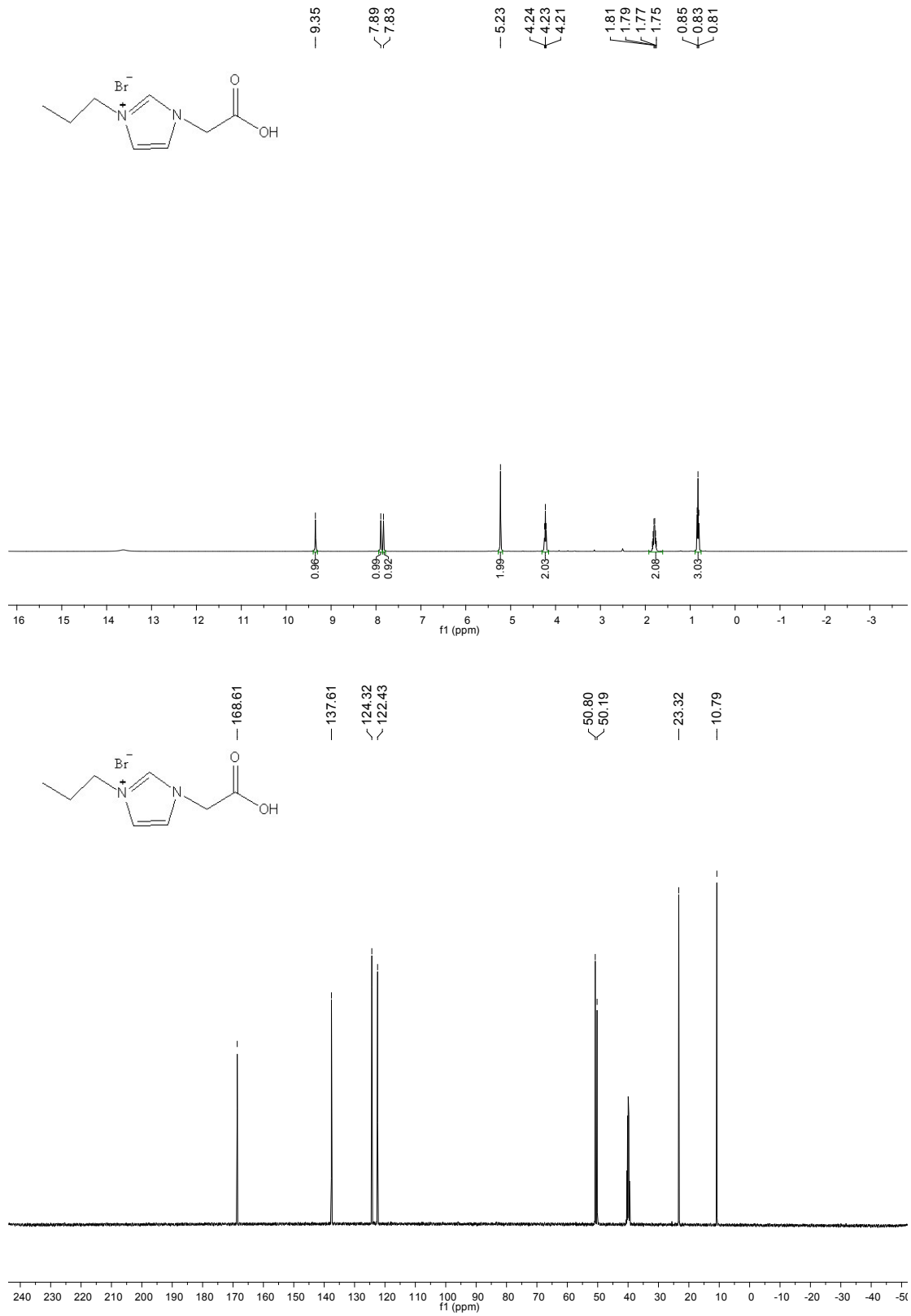


Fig. S2. NMR of [Imace-C3][Br]

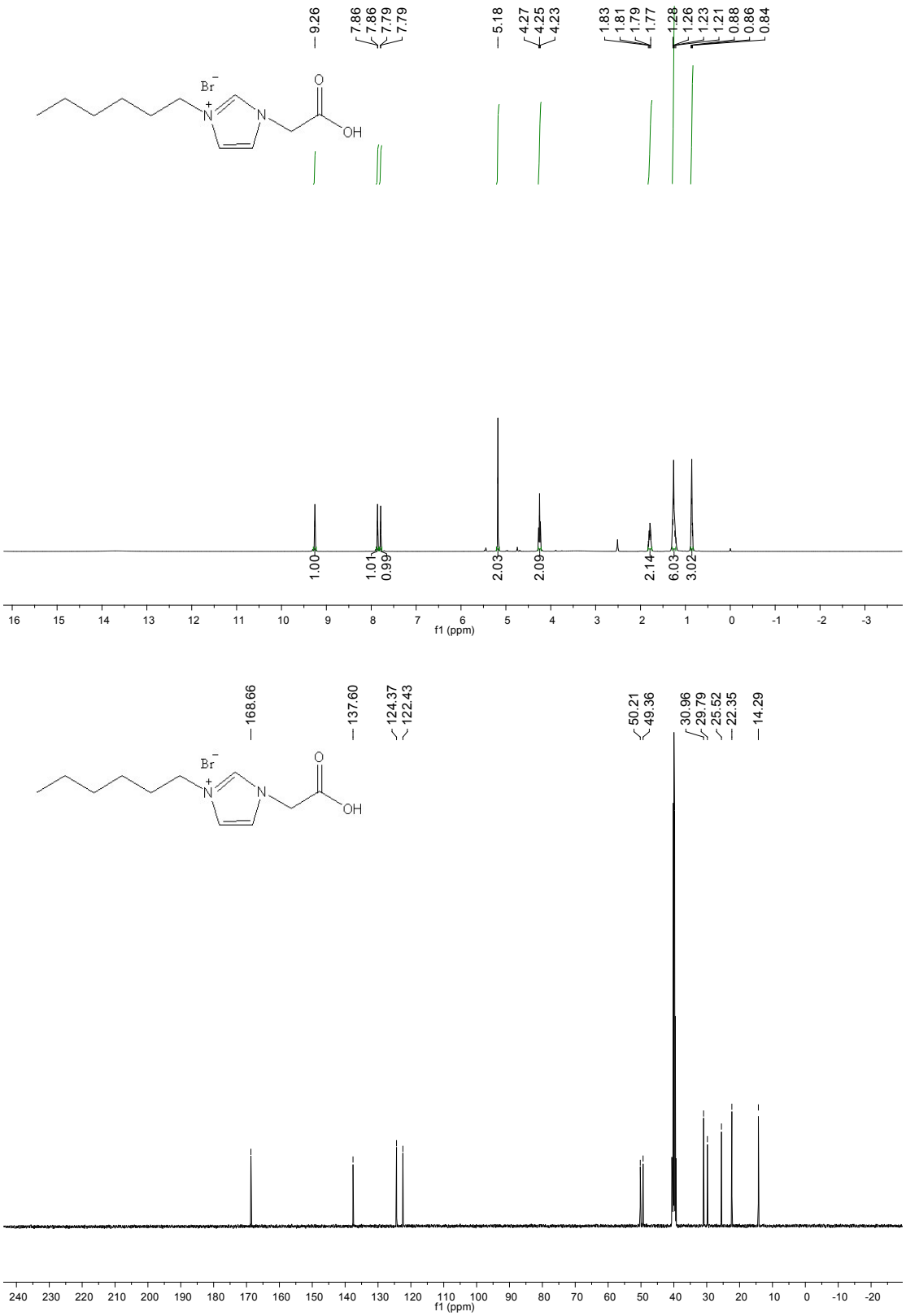


Fig. S3. NMR of [Imace-C6][Br]

3. Original EPR spectrums of catalysts

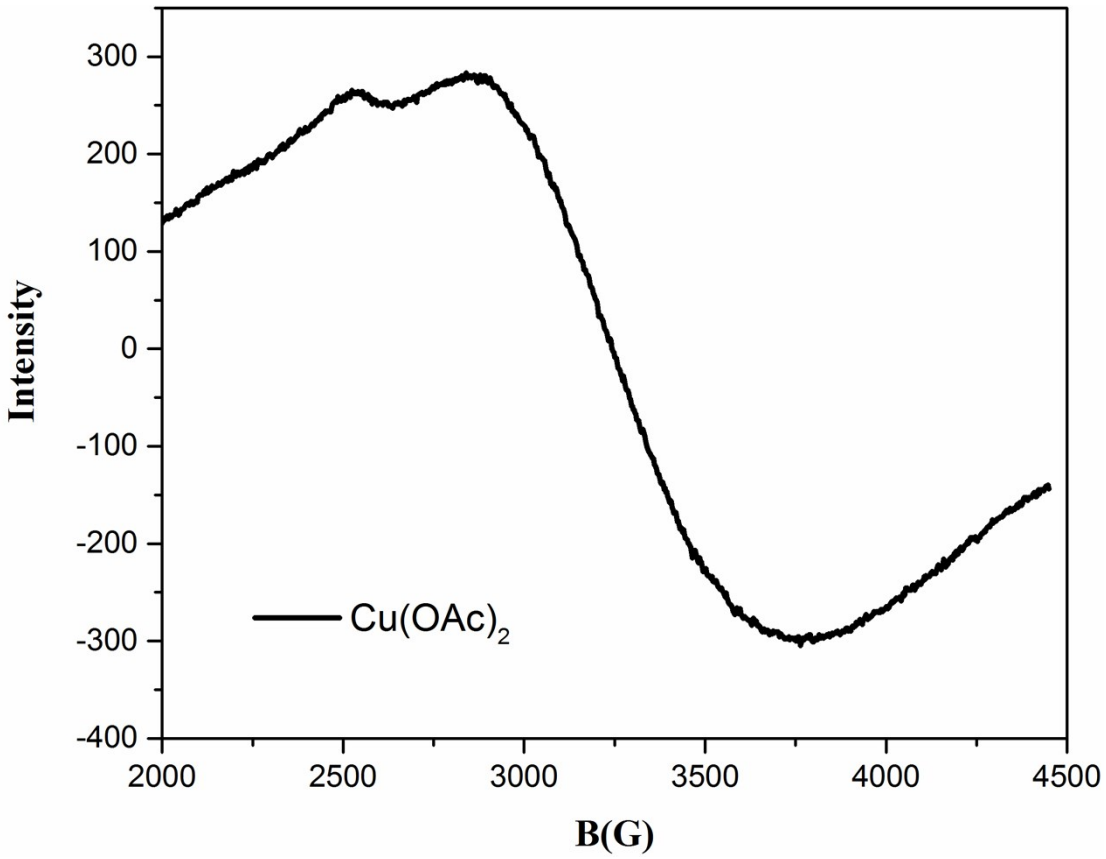


Fig. S4. EPR of copper acetate

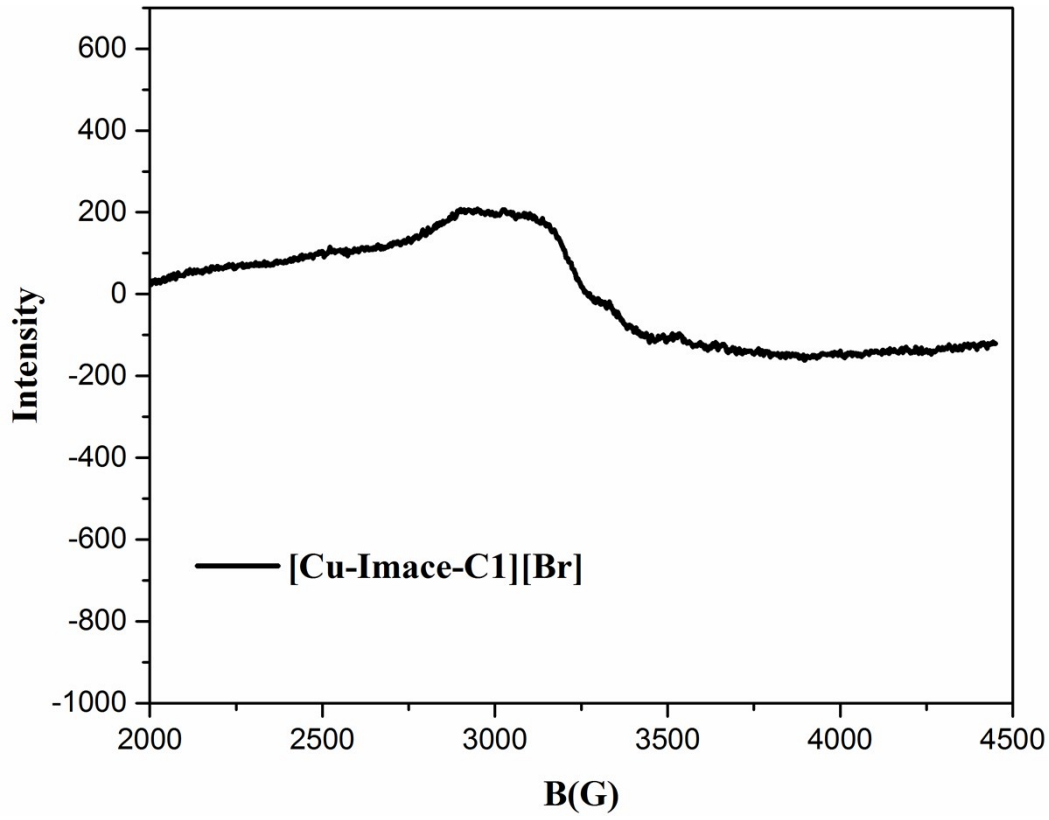


Fig. S5. EPR of [Cu-Imace-C1][Br]

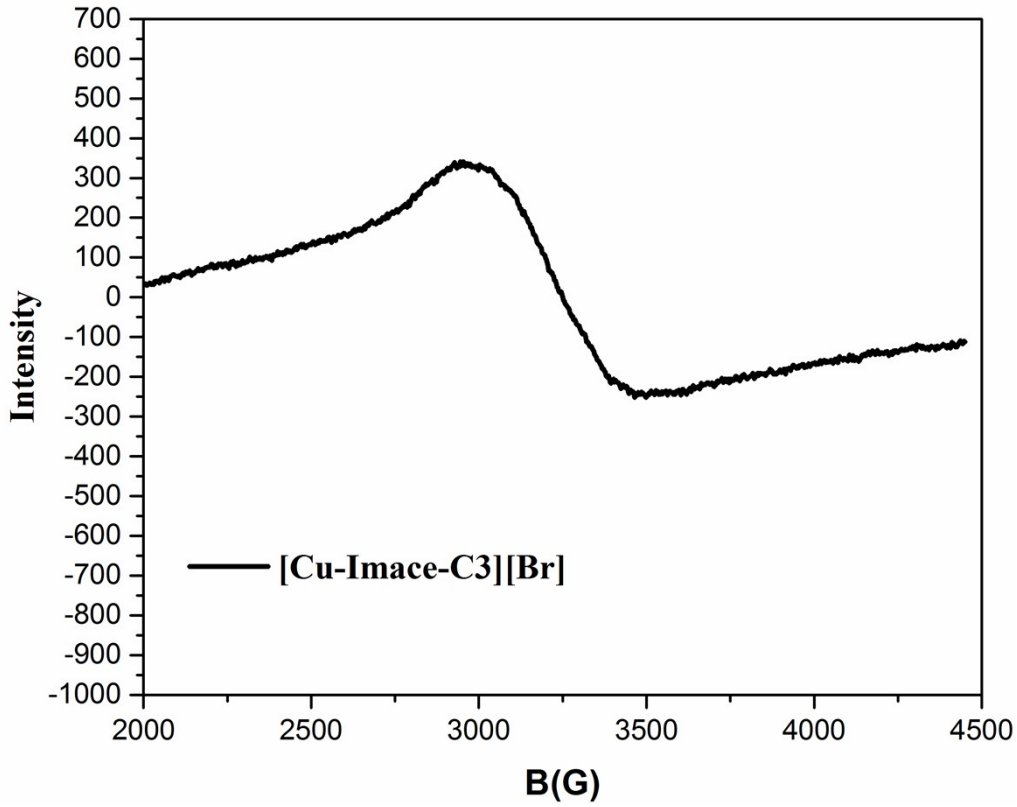


Fig. S6. EPR of [Cu-Imace-C3][Br]

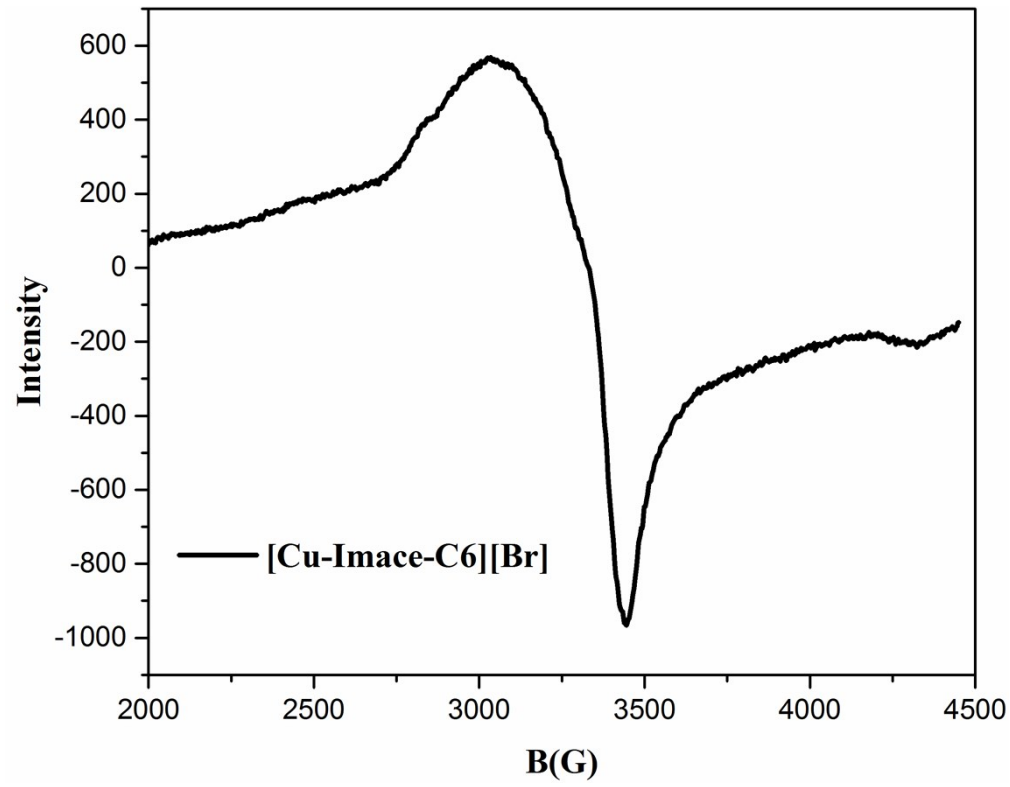


Fig. S7. EPR of [Cu-Imace-C6][Br]

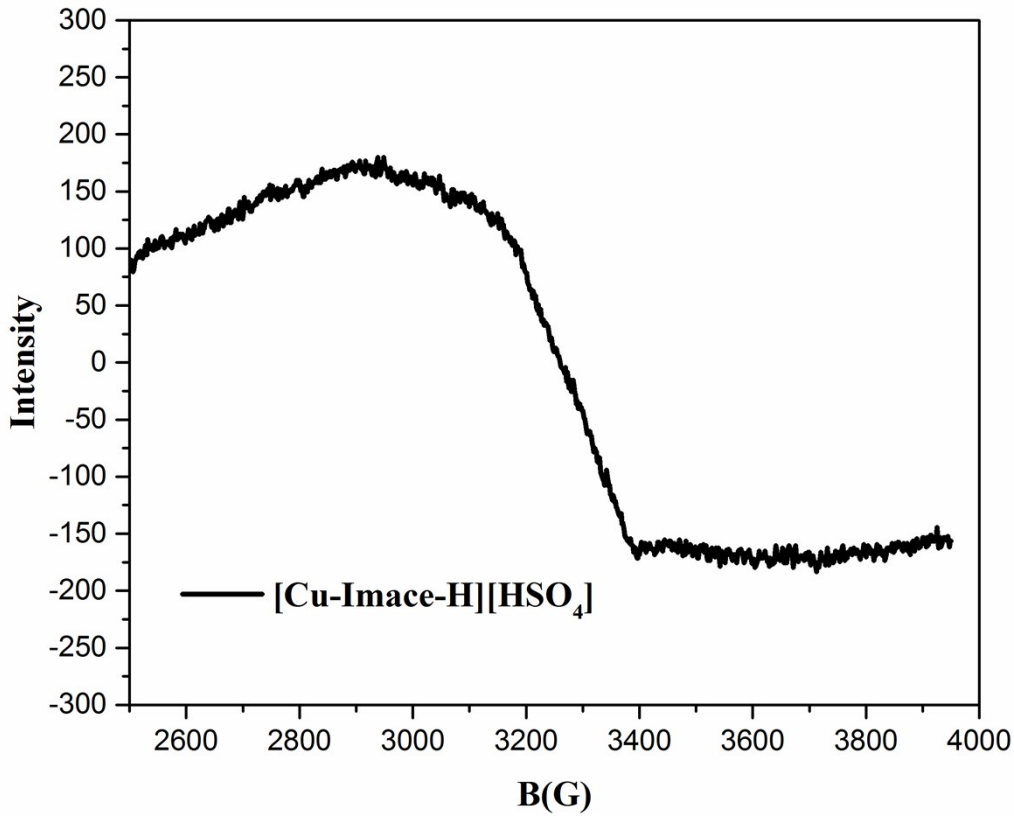


Fig. S8. EPR of [Cu-Imace-H][HSO_4]

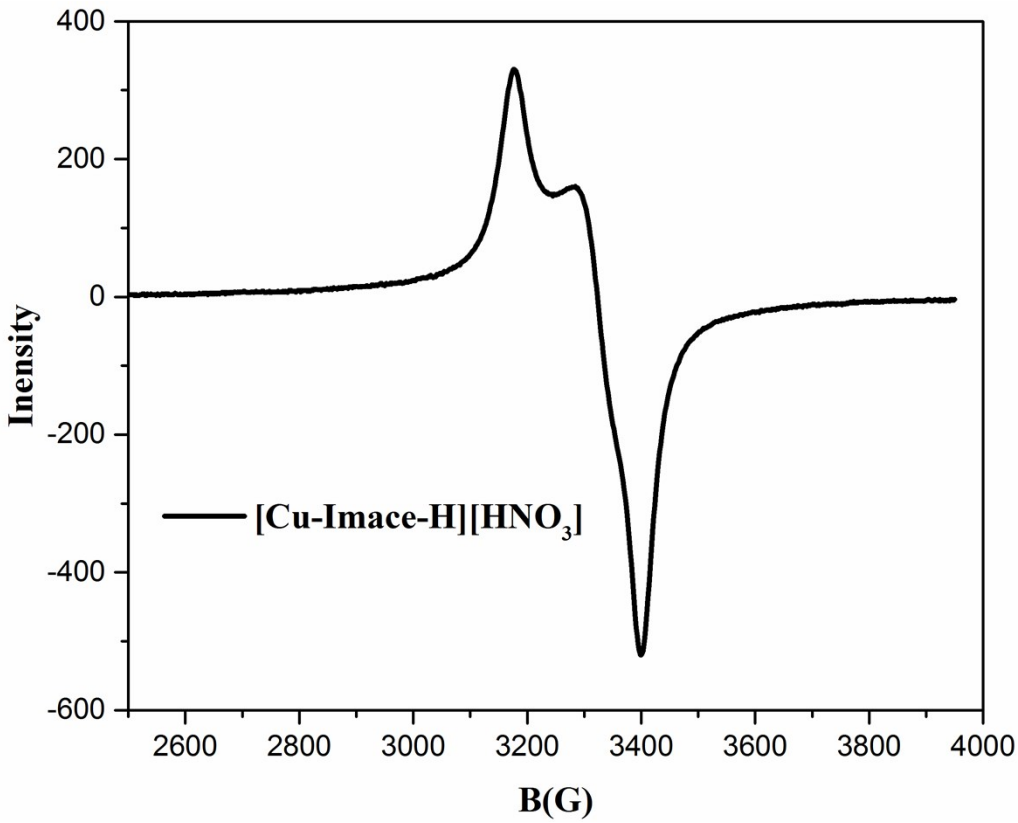


Fig. S9. EPR of [Cu-Imace-H][HNO_3]

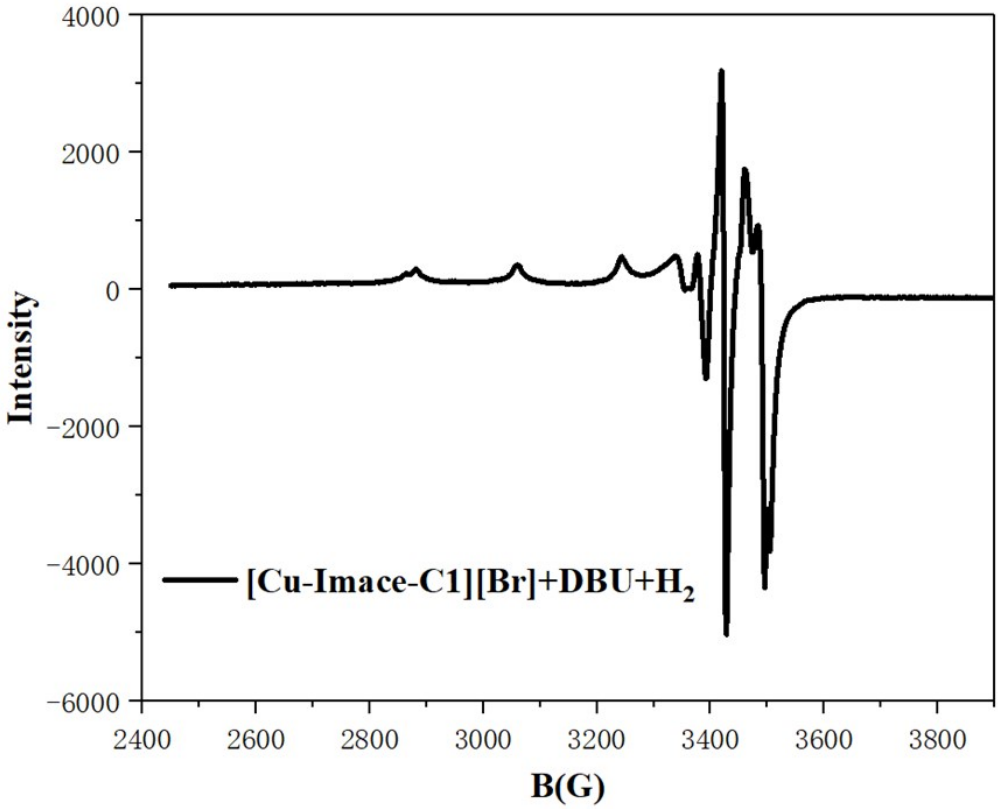


Fig. S10. EPR of [Cu-Imace-C1][Br] with DBU and H_2

4. ESI-MS of the recycled catalyst

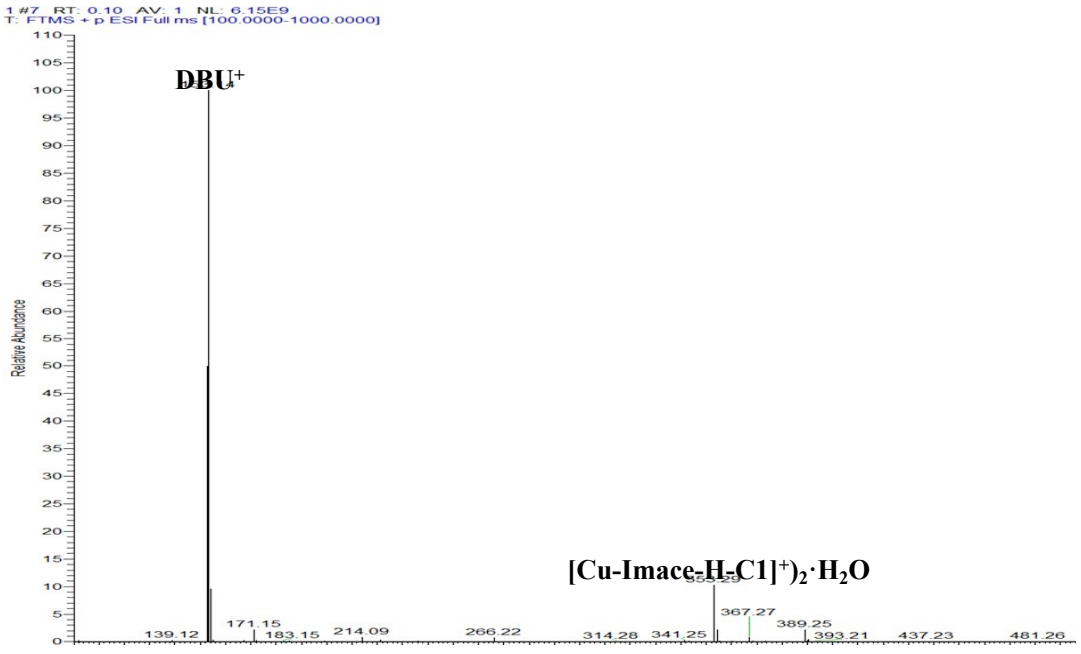


Fig. S11. ESI-MS of the recycled catalyst

5. Theoretical calculation details

All the structures were fully optimized with M06-2X method. [S2-S4] LANL2DZ basis set was used for Cu and Br. 6-311+G* basis set was used for other atoms. Both the high and low spin states were taken into consideration (high spin state: spin density=3; low spin state: spin density=1). Hence, the calculation method was abbreviated as UM06-2X/6-311+G*/LANL2DZ. Energy, frequency, charge and spin density were calculated using the same theoretic method. All calculations were performed with the Gaussian 09 suite of programs. [S5]

6. Cartesians coordinates of the optimized structures

$Cu(OAc)_2$

6	0	-3.827785	0.000741	0.026622
6	0	-2.333621	-0.001235	-0.006517
8	0	-1.676557	1.082627	-0.008823
8	0	-1.676404	-1.084627	-0.007977
1	0	-4.216172	-0.923340	-0.395989
1	0	-4.213309	0.869940	-0.502708
1	0	-4.146106	0.067307	1.069637
6	0	3.827745	0.000612	0.027177
6	0	2.333626	0.000702	-0.007171
8	0	1.676849	-1.083207	-0.009499
8	0	1.676131	1.084050	-0.008753
29	0	0.000009	-0.000291	-0.010569
1	0	4.215456	0.907154	-0.432660
1	0	4.215319	-0.889163	-0.464681
1	0	4.144615	-0.019131	1.072654

[Cu-Imace-C1][Br]

6	0	-2.600962	-0.216308	1.374510
6	0	-1.155262	-0.155190	0.924987
8	0	-0.353371	-1.006584	1.385847
8	0	-0.758935	0.731052	0.130571
7	0	-3.410258	0.821697	0.759967
6	0	-4.472741	0.587175	-0.012069
6	0	-3.219283	2.185069	0.870413
6	0	-6.166347	1.916443	-1.226036
6	0	-4.206555	2.771610	0.150469
7	0	-4.974875	1.758150	-0.388050

1	0	-3.024757	-1.187271	1.113429
1	0	-2.634602	-0.122780	2.461654
1	0	-4.938249	-0.381236	-0.245767
1	0	-2.390272	2.603142	1.415165
1	0	-6.850913	2.606083	-0.734787
1	0	-6.636348	0.935233	-1.325544
1	0	-5.871944	2.305744	-2.199888
1	0	-4.426363	3.809672	-0.032998
29	0	1.132360	-0.109934	0.335881
6	0	4.097213	2.401482	-0.683709
6	0	2.764871	1.927369	-0.073462
8	0	2.411591	2.325363	1.018157
8	0	2.187680	1.046856	-0.807277
7	0	4.979333	1.229794	-0.761835
6	0	4.739517	0.142571	-1.492766
6	0	6.063529	0.978798	0.050458
6	0	6.491274	-0.277264	-0.233524
6	0	5.636772	-2.151612	-1.689862
7	0	5.663020	-0.771311	-1.215949
35	0	3.040313	-1.583583	0.795708
1	0	3.951173	2.802463	-1.686390
1	0	4.578140	3.141056	-0.049016
1	0	3.901182	0.019401	-2.157691
1	0	6.425246	1.708740	0.754275
1	0	7.295732	-0.861773	0.178932
1	0	6.656393	-2.484780	-1.873012
1	0	5.068034	-2.193663	-2.616032
1	0	5.148641	-2.769063	-0.936053
35	0	-6.772255	-1.657719	-0.571153

[Cu-Imace-C3][Br]

6	0	2.417121	-0.789159	-1.564592
6	0	1.039061	-0.546287	-0.983427
8	0	0.149904	-1.409629	-1.195532
8	0	0.776694	0.493952	-0.334247
7	0	3.345017	0.289925	-1.270299
6	0	4.546184	0.116113	-0.711709
6	0	3.158105	1.632103	-1.535770
6	0	6.454547	1.524548	0.001354
6	0	4.284855	2.265120	-1.123141
7	0	5.134978	1.303067	-0.619228
6	0	6.357016	1.559736	1.520668
6	0	7.753308	1.603304	2.129667
1	0	2.822044	-1.716251	-1.156801

1	0	2.317971	-0.917111	-2.644447
1	0	5.017823	-0.817633	-0.379187
1	0	2.240379	2.009536	-1.952497
1	0	6.840575	2.460517	-0.408404
1	0	7.093397	0.694949	-0.306085
1	0	4.553830	3.307831	-1.136495
1	0	5.753995	2.418407	1.836301
1	0	5.855381	0.646135	1.849609
1	0	8.319473	2.474930	1.787656
1	0	8.298917	0.697747	1.855567
1	0	7.699078	1.645750	3.218374
29	0	-1.174485	-0.214956	-0.228848
6	0	-3.524297	3.033238	0.464770
6	0	-2.414912	2.136798	-0.114709
8	0	-2.056906	2.264406	-1.269055
8	0	-2.037157	1.239251	0.720951
7	0	-4.739481	2.206695	0.561195
6	0	-4.804838	1.004196	1.135805
6	0	-5.947315	2.464874	-0.051412
6	0	-6.746714	1.391524	0.175880
6	0	-6.419752	-0.869940	1.294891
7	0	-6.013184	0.494389	0.921882
6	0	-6.855001	-1.675745	0.076460
6	0	-7.015259	-3.146728	0.445869
35	0	-3.192401	-1.612744	-0.224608
1	0	-3.260534	3.398304	1.456807
1	0	-3.743979	3.862177	-0.203047
1	0	-3.985596	0.513831	1.635371
1	0	-6.123503	3.377593	-0.594397
1	0	-7.758337	1.188147	-0.130486
1	0	-7.214602	-0.797544	2.040985
1	0	-5.546452	-1.330808	1.758568
1	0	-7.796460	-1.279033	-0.316807
1	0	-6.095455	-1.564884	-0.700768
1	0	-7.744459	-3.285081	1.248571
1	0	-6.060531	-3.564603	0.772852
1	0	-7.352407	-3.725280	-0.414451
35	0	6.834837	-1.942926	0.511019

[Cu-Imace-C6][Br]

6	0	-2.017571	-0.948204	2.257756
6	0	-0.769727	-0.411015	1.587087
8	0	0.257964	-1.135103	1.596348
8	0	-0.746029	0.725242	1.057312

7	0	-3.151500	-0.046792	2.138400
6	0	-4.344731	-0.405188	1.656515
6	0	-3.192367	1.283686	2.505862
6	0	-6.527779	0.660927	1.189335
6	0	-4.448423	1.718947	2.233020
7	0	-5.147814	0.651043	1.711140
6	0	-6.546150	0.865484	-0.319141
6	0	-7.943970	0.623541	-0.878932
6	0	-7.965786	0.677546	-2.402995
6	0	-9.352407	0.419657	-2.985466
6	0	-9.361018	0.459137	-4.510735
1	0	-2.284626	-1.902526	1.802047
1	0	-1.791914	-1.133439	3.309907
1	0	-4.654122	-1.378010	1.253638
1	0	-2.326549	1.796492	2.886921
1	0	-7.062769	1.447530	1.725498
1	0	-6.962423	-0.310109	1.431253
1	0	-4.902652	2.687498	2.357174
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1	0	-8.652508	1.355199	-0.468840
1	0	-8.272151	-0.369861	-0.555030
1	0	-7.600101	1.653392	-2.749001
1	0	-7.266295	-0.073538	-2.787661
1	0	-10.057327	1.161551	-2.592381
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1	0	-9.031053	1.434153	-4.880548
29	0	1.252280	0.331665	0.614654
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6	0	2.189598	2.836874	0.556203
8	0	2.037364	2.828369	1.761008
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7	0	4.295195	3.270043	-0.583410
6	0	4.358029	2.130495	-1.274913
6	0	5.579763	3.662208	-0.271072
6	0	6.419315	2.733904	-0.796505
6	0	6.090589	0.516974	-2.002160
7	0	5.633566	1.789354	-1.420712
6	0	6.868907	-0.309342	-0.985806
6	0	7.064933	-1.738689	-1.483528
6	0	7.858290	-2.590359	-0.496880
6	0	8.047469	-4.027884	-0.973937

6	0	8.840749	-4.871275	0.019502
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1	0	3.338517	4.684702	0.598186
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1	0	5.778061	4.554530	0.297691
1	0	7.492874	2.658743	-0.772046
1	0	6.684736	0.741681	-2.890726
1	0	5.189724	-0.015333	-2.310257
1	0	7.841427	0.155911	-0.788591
1	0	6.309205	-0.321713	-0.046725
1	0	7.573468	-1.732667	-2.455962
1	0	6.080155	-2.192498	-1.643345
1	0	8.840585	-2.133384	-0.322531
1	0	7.341735	-2.592958	0.470137
1	0	8.556841	-4.023687	-1.944268
1	0	7.065707	-4.482593	-1.143444
1	0	8.972205	-5.894214	-0.338198
1	0	9.834366	-4.447450	0.188818
1	0	8.332385	-4.919674	0.985810
35	0	3.401414	-0.766618	0.156495
35	0	-6.179832	-2.700252	0.099906

[Cu-Imace-H][Br]

6	0	-2.298147	-1.163525	1.461680
6	0	-0.918375	-0.854350	0.913059
8	0	-0.026845	-1.731987	1.037023
8	0	-0.662328	0.250463	0.380882
7	0	-3.275679	-0.141303	1.137391
6	0	-4.409152	-0.335499	0.450442
6	0	-3.204835	1.194328	1.484649
6	0	-4.327322	1.782744	0.990930
7	0	-5.050910	0.808750	0.354454
1	0	-2.634915	-2.118774	1.059566
1	0	-2.216990	-1.273041	2.545485
1	0	-4.770903	-1.268082	0.042949
1	0	-2.354637	1.596442	2.008177
1	0	-4.661202	2.804926	1.032803
1	0	-6.013379	0.803190	-0.166636
29	0	1.293710	-0.434868	0.193888
6	0	3.960897	2.559049	-0.115511
6	0	2.735189	1.768788	0.381933
8	0	2.458991	1.740701	1.563993
8	0	2.165604	1.123026	-0.568883
7	0	4.930084	1.570912	-0.613804

6	0	4.709728	0.736353	-1.623338
6	0	6.109831	1.213537	0.009669
6	0	6.617263	0.154428	-0.667592
7	0	5.739757	-0.102654	-1.695874
35	0	3.309641	-1.810047	-0.027904
1	0	3.693723	3.233127	-0.928631
1	0	4.431641	3.109522	0.694492
1	0	3.820608	0.721696	-2.230502
1	0	6.470360	1.738186	0.877608
1	0	7.505852	-0.429699	-0.506082
1	0	5.751034	-0.919017	-2.290178
35	0	-7.546080	-0.010810	-1.145143

[Cu-Imace-H][Cl]

6	0	2.739480	-1.543124	-1.051676
6	0	1.336794	-1.161830	-0.618243
8	0	0.452576	-2.055223	-0.627351
8	0	1.055114	0.013718	-0.285850
7	0	3.713168	-0.497094	-0.807279
6	0	4.776038	-0.588981	0.009398
6	0	3.710365	0.768246	-1.358178
6	0	4.799283	1.409169	-0.851485
7	0	5.441378	0.543794	-0.005482
1	0	3.040299	-2.443500	-0.516572
1	0	2.712577	-1.788460	-2.115841
1	0	5.049319	-1.460804	0.583276
1	0	2.924739	1.093984	-2.018072
1	0	5.164205	2.408457	-1.017185
1	0	6.413125	0.688791	0.622179
29	0	-0.891494	-0.640436	-0.035302
6	0	-3.611311	2.309795	-0.173704
6	0	-2.354629	1.498131	-0.543389
8	0	-2.075451	1.297085	-1.708271
8	0	-1.777136	1.011761	0.493226
7	0	-4.594457	1.334058	0.327258
6	0	-4.395784	0.524463	1.361382
6	0	-5.764178	0.964566	-0.309586
6	0	-6.286087	-0.077677	0.382330
7	0	-5.426040	-0.314340	1.431270
1	0	-3.404504	3.038693	0.608665
1	0	-4.041527	2.795001	-1.045657
1	0	-3.517615	0.523272	1.984554
1	0	-6.108954	1.471198	-1.194377
1	0	-7.175105	-0.661067	0.220261

1	0	-5.445691	-1.115804	2.045468
17	0	-2.768554	-1.881983	0.309652
17	0	7.789934	0.693905	1.583969

[Cu-Imace-H][BF_4]

6	0	2.087101	0.328642	1.859195
6	0	0.725604	0.196079	1.208966
8	0	-0.212129	0.914526	1.643401
8	0	0.521194	-0.617453	0.276402
7	0	3.088033	-0.512817	1.229238
6	0	4.218021	-0.078528	0.661488
6	0	3.033684	-1.889316	1.113586
6	0	4.165876	-2.267246	0.467613
7	0	4.879100	-1.124542	0.199718
1	0	2.406013	1.369398	1.800340
1	0	1.991806	0.071939	2.916298
1	0	4.562026	0.941076	0.588085
1	0	2.189145	-2.455343	1.466419
1	0	4.517218	-3.239796	0.170214
1	0	5.806501	-1.057361	-0.276840
29	0	-1.420501	0.072421	0.291270
6	0	-4.238473	-2.465397	-1.015351
6	0	-2.979421	-1.938488	-0.307928
8	0	-2.671153	-2.332864	0.799584
8	0	-2.414875	-0.987586	-0.963656
7	0	-5.248244	-1.399754	-0.884267
6	0	-5.048148	-0.128716	-1.225163
6	0	-6.456273	-1.497006	-0.220372
6	0	-6.988821	-0.249201	-0.173882
7	0	-6.092141	0.577575	-0.809952
1	0	-4.054590	-2.658674	-2.071208
1	0	-4.626177	-3.352500	-0.521932
1	0	-4.169215	0.260831	-1.710124
1	0	-6.817617	-2.435323	0.164206
1	0	-7.905555	0.113455	0.257042
1	0	-6.096215	1.590263	-0.855590
5	0	7.565327	0.502611	-0.935565
9	0	6.416366	1.119555	-0.344431
9	0	8.666581	0.691025	-0.137500
9	0	7.231145	-0.916778	-0.952245
9	0	7.731188	0.937922	-2.226040
5	0	-3.033979	2.304749	0.019797
9	0	-4.166298	2.430922	-0.790294
9	0	-2.870322	3.337207	0.872228

9	0	-3.175837	1.038587	0.774616
9	0	-1.894151	2.034214	-0.773318

[Cu-Imace-H][NO_3]

6	0	-2.423719	1.661915	-0.812006
6	0	-1.089241	1.145089	-0.316496
8	0	-0.232250	1.978825	0.073261
8	0	-0.815653	-0.082980	-0.320185
7	0	-3.389369	0.617641	-1.064018
6	0	-4.541449	0.419961	-0.383918
6	0	-3.304353	-0.366705	-2.023201
6	0	-4.430263	-1.121766	-1.880523
7	0	-5.192962	-0.618596	-0.853898
1	0	-2.825843	2.353407	-0.071312
1	0	-2.238282	2.236922	-1.722875
1	0	-4.873409	1.048377	0.428332
1	0	-2.453151	-0.446948	-2.678172
1	0	-4.736261	-1.989740	-2.441569
1	0	-6.571349	-1.064683	-0.262763
29	0	1.039881	0.414062	0.340971
6	0	3.792109	-2.538708	0.334306
6	0	2.663958	-1.552334	-0.039988
8	0	2.748230	-0.961544	-1.109756
8	0	1.801105	-1.338484	0.866247
7	0	5.029658	-1.740110	0.328747
6	0	5.077809	-0.503455	0.812876
6	0	6.206090	-2.002570	-0.342019
6	0	6.979084	-0.889970	-0.244197
7	0	6.249236	0.024723	0.481995
1	0	3.641304	-2.980409	1.316992
1	0	3.896463	-3.312638	-0.424014
1	0	4.269742	0.011660	1.320537
1	0	6.381226	-2.943691	-0.834380
1	0	7.958961	-0.672820	-0.631389
1	0	6.450168	1.006169	0.633776
7	0	-7.829425	-0.488426	1.076921
8	0	-7.042596	0.408014	1.315884
8	0	-8.882519	-0.676395	1.612049
8	0	-7.493385	-1.359098	0.120724
7	0	3.320823	1.997511	0.114803
8	0	2.723856	2.342914	-0.877049
8	0	2.713289	1.234986	0.981306
8	0	4.485924	2.289843	0.369749

[Cu-Imace-H][HSO_4]

6	0	-4.361432	1.011818	1.202388
6	0	-3.039310	0.241754	1.149236
8	0	-3.173670	-1.014889	1.270951
8	0	-1.978515	0.825026	0.938250
7	0	-4.144672	2.405306	0.816475
6	0	-3.494694	2.764041	-0.283958
6	0	-4.426212	3.529934	1.564176
6	0	-3.946524	4.598494	0.882131
7	0	-3.376190	4.091442	-0.268359
1	0	-5.053970	0.540865	0.505883
1	0	-4.782863	0.992292	2.206610
1	0	-3.142713	2.071160	-1.036987
1	0	-4.938151	3.468695	2.509203
1	0	-3.957454	5.650212	1.107662
1	0	-2.910002	4.626232	-0.985872
29	0	-1.439001	-1.583531	0.553076
6	0	2.055693	-2.148874	2.101176
6	0	0.678647	-2.009862	1.477394
8	0	-0.314487	-1.899223	2.237372
8	0	0.540056	-1.995040	0.230337
7	0	3.111637	-2.053295	1.112575
6	0	3.761205	-0.928912	0.788690
6	0	3.509634	-3.054606	0.249985
6	0	4.430442	-2.503862	-0.582962
7	0	4.567274	-1.185467	-0.225866
1	0	2.185969	-1.365257	2.847236
1	0	2.121265	-3.108633	2.616230
1	0	3.667506	0.042634	1.252708
1	0	3.093450	-4.046193	0.302517
1	0	4.992933	-2.936612	-1.391932
1	0	5.206153	-0.436824	-0.672378
8	0	-3.137094	-1.369133	-3.430734
16	0	-3.388535	-1.197952	-1.847073
8	0	-2.049739	-1.622391	-1.289934
8	0	-4.480564	-2.077123	-1.541036
8	0	-3.610754	0.232919	-1.606920
1	0	-2.297789	-0.961740	-3.684249
8	0	4.740073	2.811209	-1.520844
16	0	5.686470	1.995862	-0.466065
8	0	6.032660	0.729746	-1.179348
8	0	4.773453	1.730943	0.642992
8	0	6.829748	2.846543	-0.219561
1	0	5.299368	3.224852	-2.191155

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