Electronic Supplementary Information for Dalton Transactions

Supporting Information

Reversible Substrate Binding at Copper Center in Neutral Copper(I) Carbene Complex Derived from Bis(3-*tert*-butylimidazole-2-ylidene)methane

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Contents:

Calculation results for compounds 3#a-b, **6**-**7 and 3#·Et_3N**.

Calculation results for BP86/SV(P)-optimized structures in a gas phase are presented below. Computed atomic Cartesian coordinates (x, y, z) are given in 1 Å scale; the energy and zero-point corrected energies are given in atomic units; NIMAG is the number of imaginary vibrations.

Results for 3#a

Cu	-0.3725337	-0.0869029	-3.0775495
Cu	-0.3847228	0.0860869	3.0710489
Br	-0.6954422	-1.8806297	-4.3950209
Br	-0.6998855	1.8720869	4.4003818
C	-0.1058778	1.2380531	-1.7636721
N	-0.5540317	1.1233548	-0.4679770
C	-0.1231928	2.1842978	0.3232745
H	-0.3629311	2.2683927	1.3945143
C	0.6104454	2.9934313	-0.5052874
H	1.1164565	3.9353568	-0.2789671
N	0.6122761	2.4041735	-1.7709463
C	-1.3538638	-0.0087334	-0.0141787
H	-1.9633857	-0.3471210	-0.8759226
H	-2.0024160	0.3255307	0.8200861
C	-0.1175842	-1.2410516	1.7590758
N	-0.5642002	-1.1382995	0.4621503
C	-0.1409809	-2.2113743	-0.3166468
H	-0.3789079	-2.3039911	-1.3874561
C	0.5888920	-3.0148490	0.5203351
H	1.0813370	-3.9668246	0.3068630
N	0.5925119	-2.4121636	1.7797126
C	2.3090386	1.9100923	-3.5033612
C	1.2801291	2.9473612	-3.0079855
H	3.0767570	1.7040281	-2.7262049
H	1.8029984	0.9521582	-3.7613522
H	2.8200650	2.2891570	-4.4147463
C	0.1963427	3.1843377	-4.0803913
C	1.9898181	4.2704209	-2.6748076
H	-0.5648517	3.9133327	-3.7266817
H	0.6612971	3.5808954	-5.0085115
H	-0.3177073	2.2290152	-4.3288079
H	2.4768024	4.6537605	-3.5961428
H	1.2781060	5.0505450	-2.3274352
H	2.7856305	4.1370569	-1.9099174
C	2.4071841	-1.9187356	3.3826043
C	1.2976384	-2.9241548	3.0095455
H	3.1336833	-1.7933802	2.5500537
H	1.9645646	-0.9246391	3.6170474
H	2.9575660	-2.2740376	4.2807155
C	0.2707027	-3.0387301	4.1541077
C	1.9108144	-4.3037187	2.7163960
H	-0.5525806	-3.7365691	3.8877187
H	0.7693878	-3.4139779	5.0735825
H	-0.1722600	-2.0426680	4.3810498
H	2.4060825	-4.6757438	3.6379644
H	1.1388732	-5.0498922	2.4281455
H	2.6855004	-4.2571647	1.9201539

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functional BP86

geometry optimisation SV(P)

Energy -9234.0381972320

NIMAG 0

Zero-point correction 0.3696542

single point TZVP

Energy -9236.0353750520

Results for 3#a

Cu	-0.365223	-0.091467	-3.102781
Cu	-0.368158	0.091761	3.099726
Br	-0.701464	-1.920017	-4.391857
Br	-0.702646	1.918151	4.391891
C	-0.083123	1.256209	-1.762652
N	-0.513490	1.126550	-0.473097
C	-0.101829	2.196589	0.310359
H	-0.336309	2.284562	1.373141
C	0.601949	3.014907	-0.517076
H	1.082242	3.961937	-0.295362
N	0.605651	2.427236	-1.780386
C	-1.303121	-0.002901	-0.003242
H	-1.928805	-0.344493	-0.839730
H	-1.935224	0.337822	0.828785
C	-0.085949	-1.257908	1.761527
N	-0.515633	-1.131920	0.471416
C	-0.102768	-2.203764	-0.309039
H	-0.337022	-2.294691	-1.371637
C	0.600632	-3.019671	0.521087
H	1.081779	-3.966933	0.302267
N	0.602574	-2.429007	1.783002
C	2.323862	1.996683	-3.508322
C	1.256376	2.989878	-3.014340
H	3.083523	1.810578	-2.728491
H	1.868033	1.030852	-3.787479
H	2.831511	2.405197	-4.399631
C	0.173809	3.202088	-4.088720
C	1.920398	4.334141	-2.681014
H	-0.610795	3.890785	-3.728336
H	0.627011	3.634381	-4.997687
H	-0.302100	2.245446	-4.365271
H	2.391365	4.731809	-3.595493
H	1.187942	5.083716	-2.334061
H	2.713595	4.227924	-1.920305
C	2.342255	-1.996163	3.487586

C	1.259284	-2.984208	3.017138
H	3.097552	-1.830212	2.698897
H	1.898401	-1.021686	3.755659
H	2.852674	-2.397020	4.380798
C	0.186538	-3.171676	4.105773
C	1.904414	-4.340073	2.693687
H	-0.610601	-3.854272	3.761826
H	0.645227	-3.600040	5.013833
H	-0.274118	-2.206360	4.377982
H	2.375395	-4.734536	3.609527
H	1.159928	-5.082869	2.357947
H	2.694775	-4.251664	1.927774

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functional B3LYP

geometry optimisation SV(P)

Energy -9231.9772522280

NIMAG 0

Zero-point correction 0.3803564

single point TZVP

Energy -9233.9763055270

Results for 3#b

Cu	-0.1439532	-0.7778098	-1.2065986
Cu	-0.1820031	-0.7805169	1.2246446
Br	1.7529294	-1.7976377	0.0289725
Br	-1.9464360	-2.1049440	-0.0062801
C	-0.4460229	0.9719744	-1.9048872
N	-1.2079679	1.9181352	-1.2451378
C	-1.1797822	3.1448657	-1.9031571
H	-1.7362417	4.0222286	-1.5542737
C	-0.3849686	2.9730835	-3.0052644
H	-0.1231564	3.6872007	-3.7906535
N	0.0515674	1.6478028	-2.9914260
C	1.0380333	1.0389339	-3.9529422
C	1.1900781	1.9517288	-5.1827013
H	0.2180416	2.1210730	-5.6966854
H	1.8732734	1.4629410	-5.9090262
H	1.6391640	2.9359114	-4.9252509
C	0.5163993	-0.3414866	-4.3982749
H	-0.4890525	-0.2640609	-4.8661371
H	0.4454840	-1.0325362	-3.5277893
H	1.2197689	-0.7869454	-5.1346690
C	2.3888693	0.8950844	-3.2198509
H	2.2757409	0.2448902	-2.3238864
H	2.7686591	1.8876805	-2.8911253
H	3.1441533	0.4368307	-3.8949994
C	-1.9442184	1.6434840	-0.0135590
H	-2.2023924	0.5606238	-0.0061140
H	-2.8664716	2.2588345	-0.0164284
C	-0.4645684	0.9833702	1.8960939
N	-1.2042938	1.9309363	1.2127514
C	-1.1510930	3.1713058	1.8430670
H	-1.6859007	4.0536420	1.4734231
C	-0.3631671	3.0071559	2.9512491
H	-0.0871189	3.7322184	3.7216757
N	0.0429941	1.6722674	2.9699140
C	1.0214696	1.0689751	3.9424510
C	0.5092197	-0.3173738	4.3798700
H	0.4635965	-1.0124327	3.5106044
H	-0.5048932	-0.2530730	4.8305105
H	1.2064580	-0.7517786	5.1285809
C	2.3826134	0.9377080	3.2260766
H	2.2864783	0.2855868	2.3295553
H	3.1340540	0.4873150	3.9107708
H	2.7573590	1.9334501	2.9011607
C	1.1480356	1.9808468	5.1763761
H	1.6020293	2.9654980	4.9294094
H	1.8170755	1.4929521	5.9163294
H	0.1650699	2.1499037	5.6689880

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functional BP86

geometry optimisation SV(P)

Energy -9234.0351406450

NIMAG 0

Zero-point correction 0.3686085

single point TZVP

Energy -9236.0239496270

Results for 3#b

Cu	-0.187504	-0.828333	-1.250977
Cu	-0.107831	-0.821733	1.218263
Br	1.816658	-1.779899	-0.051380
Br	-1.964381	-2.134451	0.007025
C	-0.472978	0.997642	-1.893450
N	-1.220463	1.910338	-1.194902
C	-1.182773	3.160358	-1.797863

H	-1.724000	4.021881	-1.411508
C	-0.396170	3.032281	-2.898378
H	-0.129979	3.772753	-3.645358
N	0.029373	1.707191	-2.942843
C	0.998430	1.138400	-3.939901
C	1.142362	2.104819	-5.126570
H	0.173015	2.300459	-5.619487
H	1.812191	1.651090	-5.876214
H	1.593439	3.068261	-4.831353
C	0.466680	-0.210840	-4.452867
H	-0.540252	-0.103597	-4.893445
H	0.412057	-0.954275	-3.639473
H	1.147519	-0.606887	-5.226514
C	2.359415	0.956752	-3.241162
H	2.275239	0.264402	-2.385593
H	2.739521	1.925346	-2.868832
H	3.097139	0.545143	-3.952601
C	-1.959903	1.604414	0.024115
H	-2.221096	0.534253	0.009992
H	-2.876280	2.213524	0.026840
C	-0.450052	0.972374	1.915473
N	-1.232638	1.884205	1.256688
C	-1.238634	3.109305	1.910449
H	-1.813106	3.964857	1.560687
C	-0.443849	2.965123	3.002914
H	-0.200738	3.684087	3.778232
N	0.029386	1.655113	2.992093
C	1.026602	1.081253	3.959327
C	0.537175	-0.298057	4.433969
H	0.487099	-1.013320	3.595394
H	-0.464546	-0.230002	4.893954
H	1.241343	-0.703301	5.181475
C	2.382306	0.958311	3.237875
H	2.302546	0.290489	2.362784
H	3.141247	0.543890	3.924881
H	2.732708	1.947182	2.890533
C	1.158612	2.013343	5.174296
H	1.581379	2.997052	4.904365
H	1.846876	1.553249	5.902960
H	0.189124	2.168193	5.680992

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functional B3LYP

geometry optimisation SV(P)

Energy -9231.9687790290

NIMAG 0

Zero-point correction 0.3788347

single point TZVP

Energy -9233.9598379370

Results for 6

Cu	0.1566914	-0.2087183	-1.3744347
Cu	0.1906301	0.4079049	1.2623328
Br	2.2622413	-0.1566897	-0.0172095
Br	-0.8373383	-1.4900608	2.3213457
C	-0.7465658	1.2978614	-2.1401508
N	-1.8299754	1.9594382	-1.5973838
C	-2.2570534	3.0062416	-2.4094690
H	-3.1088435	3.6483751	-2.1583048
C	-1.4308313	3.0072202	-3.5006157
H	-1.4401699	3.6585103	-4.3782895
N	-0.5188902	1.9657828	-3.3245887
C	0.6199412	1.6369864	-4.2536308
C	0.5190095	2.4985735	-5.5257363
H	-0.4332880	2.3269525	-6.0743370
H	1.3513281	2.2206288	-6.2058142
H	0.6215710	3.5839448	-5.3072912
C	0.5312482	0.1471319	-4.6389952
H	-0.4282290	-0.0742940	-5.1566624
H	0.5986777	-0.4977611	-3.7346422
H	1.3694435	-0.1176165	-5.3190372
C	1.9434600	1.9391647	-3.5201278
H	2.0268353	1.3375309	-2.5877526
H	2.0042029	3.0155185	-3.2456620
H	2.8071563	1.6959643	-4.1768527
C	-2.3600363	1.6742791	-0.2693194
H	-2.1178842	0.6187696	-0.0221938
H	-3.4592138	1.8260706	-0.2789876
C	-0.6188797	2.1478474	1.4304920
N	-1.7736895	2.5084295	0.7660092
C	-2.2328004	3.7631412	1.1615921
H	-3.1450214	4.2231016	0.7642879
C	-1.3489012	4.2077712	2.1085181
H	-1.3591964	5.1373170	2.6841311
N	-0.3755061	3.2187887	2.2590188
C	0.8144356	3.2821367	3.1779312
C	0.7636304	2.0712362	4.1307475
H	0.7459930	1.1142237	3.5620288
H	-0.1483952	2.1007982	4.7663685
H	1.6575345	2.0720103	4.7919348
C	2.0906660	3.2504691	2.3119589
H	2.1253877	2.3263666	1.6932562
H	2.9919822	3.2739520	2.9626778
H	2.1269145	4.1294345	1.6303533
C	0.7715977	4.5840708	3.9969381

H	0.8310946	5.4886851	3.3524155
H	1.6509684	4.6043464	4.6753827
H	-0.1391774	4.6500146	4.6320652
C	0.2733107	-2.9935026	-0.4992404
H	1.0186923	-2.6899936	0.2425908
N	-0.1761579	-2.1915208	-1.4677052
C	-1.1276933	-2.9161833	-2.1601139
H	-1.6654231	-2.4919749	-3.0173555
C	-1.2421876	-4.1723768	-1.5976797
H	-1.8781353	-5.0251751	-1.8577427
N	-0.3390959	-4.2092023	-0.5397132
C	-0.2065404	-5.3155224	0.4590090
C	0.9543298	-4.9964304	1.4185459
H	1.9187641	-4.8919619	0.8749452
H	1.0604543	-5.8315253	2.1437629
H	0.7550051	-4.0642441	1.9923045
C	0.0754574	-6.6306119	-0.2964581
H	1.0079234	-6.5512853	-0.8969799
H	-0.7568447	-6.9052953	-0.9805817
H	0.1994720	-7.4619943	0.4309580
C	-1.5269337	-5.3961219	1.2563779
H	-2.3868426	-5.6387793	0.5944325
H	-1.7254534	-4.4228506	1.7569717
H	-1.4543022	-6.1898058	2.0322990

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functional BP86

geometry optimisation SV(P)

Energy -9617.2490806660

NIMAG 0

Zero-point correction 0.5480878

single point TZVP

Energy -9619.6618107170

Results for 6

Cu	0.1779437	-0.3276792	-1.3973137
Cu	0.2336856	0.4709898	1.3111546
Br	2.2895309	-0.1393160	-0.0047713
Br	-1.0190369	-1.3390897	2.3312500
C	-0.7342233	1.1927410	-2.2280984
N	-1.7614951	1.9100528	-1.6763936
C	-2.1910753	2.9213199	-2.5244732
H	-3.0038367	3.5997211	-2.2734122
C	-1.4189737	2.8398021	-3.6386582
H	-1.4469575	3.4418840	-4.5405732
N	-0.5351038	1.7814600	-3.4462002
C	0.5390441	1.3632905	-4.4106640
C	0.4111033	2.1705211	-5.7127437
H	-0.5665993	2.0177455	-6.2039358
H	1.1912923	1.8312170	-6.4145174
H	0.5657656	3.2513217	-5.5494564
C	0.3722403	-0.1327578	-4.7303773
H	-0.6264612	-0.3353869	-5.1576834
H	0.4929146	-0.7513011	-3.8256025
H	1.1358469	-0.4444660	-5.4643327
C	1.9100772	1.6414309	-3.7670374
H	2.0298295	1.0880339	-2.8200161
H	2.0275302	2.7188928	-3.5512596
H	2.7180821	1.3366020	-4.4556990
C	-2.2699160	1.7089213	-0.3272748
H	-2.0508253	0.6764527	-0.0175510
H	-3.3599114	1.8683282	-0.3341795
C	-0.5564271	2.2813912	1.3692350
N	-1.6740828	2.6036477	0.6467887
C	-2.1261980	3.8838124	0.9429409
H	-3.0098667	4.3249484	0.4855203
C	-1.2728251	4.3782259	1.8778162
H	-1.2836710	5.3408173	2.3786971
N	-0.3214272	3.3911878	2.1255920
C	0.8145294	3.4922413	3.1027561
C	0.6480280	2.3881188	4.1631809
H	0.6362221	1.3861061	3.7014286
H	-0.3004334	2.5149666	4.7149924
H	1.4822323	2.4322100	4.8856921
C	2.1374691	3.3271614	2.3335591
H	2.1773319	2.3570994	1.8101146
H	2.9886985	3.3817047	3.0353960
H	2.2558702	4.1283278	1.5814469
C	0.7898657	4.8658254	3.7909083
H	0.9154167	5.6945149	3.0713854
H	1.6310269	4.9181003	4.5028113
H	-0.1388638	5.0271306	4.3664553
C	0.3049784	-3.0655233	-0.3718547
H	1.0531757	-2.7167363	0.3337158
N	-0.1531018	-2.3349874	-1.3777573
C	-1.1067217	-3.1026179	-2.0064650
H	-1.6530253	-2.7422295	-2.8778695
C	-1.2105322	-4.3114164	-1.3654619
H	-1.8459437	-5.1725144	-1.5579316
N	-0.2993193	-4.2764987	-0.3209990
C	-0.1417124	-5.3181684	0.7350895
C	1.0143014	-4.9282312	1.6693518
H	1.9677019	-4.8340595	1.1198739
H	1.1394480	-5.7183280	2.4298478

H	0.8046103	-3.9798602	2.1937610
C	0.1638483	-6.6651512	0.0544742
H	1.0892691	-6.6027937	-0.5452800
H	-0.6573512	-6.9858421	-0.6104679
H	0.2996321	-7.4497021	0.8195956
C	-1.4529063	-5.3873527	1.5426485
H	-2.3037187	-5.6850445	0.9040410
H	-1.6753394	-4.4020121	1.9885620
H	-1.3569440	-6.1324679	2.3527097

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functional B3LYP

geometry optimisation SV(P)

Energy -9614.9137679930

NIMAG 0

Zero-point correction 0.5634515

single point TZVP

Energy -9617.3341102280

Results for 7

Cu	0.0759457	1.3236470	-0.0462566
Cu	0.2161141	-1.2521274	-0.7963411
Br	2.2176980	0.2002737	-0.8072268
Br	-1.2732980	-0.9399260	-2.6968549
C	-0.6252485	1.1136762	1.7312618
N	-1.6194533	0.2210624	2.0964409
C	-1.9132925	0.2964416	3.4538512
H	-2.6694469	-0.3333275	3.9363033
C	-1.0915096	1.2568290	3.9721798
H	-1.0151395	1.6332063	4.9965308
N	-0.3056230	1.7357444	2.9215016
C	0.6819103	2.8516434	3.1122423
C	1.6434906	2.9229532	1.9187854
H	2.2110673	1.9792573	1.7807887
H	2.3626712	3.7548566	2.0825080
H	1.0948354	3.1246374	0.9715789
C	-0.1087565	4.1719842	3.2428897
H	-0.6902887	4.3690238	2.3158248
H	0.5857338	5.0235801	3.4085258
H	-0.8201451	4.1385246	4.0979557
C	1.5018962	2.5767781	4.3928459
H	0.8867577	2.6230537	5.3173657
H	2.2982898	3.3452423	4.4921625
H	1.9906619	1.5797830	4.3414459
C	-2.1924428	-0.7759410	1.1997819
H	-2.0465720	-0.4331942	0.1514445
H	-3.2750002	-0.8778791	1.4214634
C	-0.4520315	-2.4290745	0.5756992
N	-1.5655792	-2.0825237	1.3192084
C	-1.9711891	-3.1122364	2.1647670
H	-2.8437173	-3.0402014	2.8245134
C	-1.0979457	-4.1427785	1.9505347
H	-1.0731437	-5.1413250	2.3994268
N	-0.1813921	-3.7124794	0.9856763
C	0.9113280	-4.5969427	0.4613598
C	0.2573633	-5.8354698	-0.1920561
H	-0.3366217	-6.4293451	0.5371008
H	1.0429372	-6.5023489	-0.6087621
H	-0.4147548	-5.5285679	-1.0224167
C	1.8133174	-5.0097035	1.6454802
H	2.2632041	-4.1128306	2.1239138
H	2.6379475	-5.6609368	1.2824709
H	1.2543088	-5.5777310	2.4213335
C	1.7508381	-3.8497159	-0.5859693
H	2.2346943	-2.9454220	-0.1618464
H	1.1310794	-3.5287799	-1.4522692
H	2.5441650	-4.5332347	-0.9610726
N	-0.4551432	2.1749619	-1.8683241
H	-0.6136331	1.2476403	-2.3356648
C	0.5853680	2.9138007	-2.6218167
H	0.2679494	3.0207022	-3.6904152
H	1.5123423	2.3030776	-2.5985520
C	0.8164313	4.3042500	-2.0192311
H	1.5714605	4.8507871	-2.6275531
H	1.2527675	4.1851358	-1.0005129
C	-0.4959255	5.1047062	-1.9309101
H	-0.3318140	6.0731566	-1.4057643
H	-0.8388636	5.3592515	-2.9618009
C	-1.5934579	4.2843150	-1.2288521
H	-1.3298090	4.1378438	-0.1543860
H	-2.5682087	4.8213559	-1.2580052
C	-1.7439383	2.9058950	-1.8797099
H	-2.4971627	2.2851707	-1.3502234
H	-2.1004850	3.0292886	-2.9344820

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functional BP86

geometry optimisation SV(P)

Energy -9485.7620511120

NIMAG 0

Zero-point correction 0.5244703

single point TZVP

Energy -9488.0379601010

Results for 7

Cu	0.0768741	1.3738818	-0.0379437
Cu	0.2566556	-1.2662387	-0.8820240
Br	2.2570715	0.2125083	-0.7222341
Br	-1.3175388	-0.8854856	-2.7300135
C	-0.6681199	1.0963875	1.7594911
N	-1.6280975	0.1651588	2.0706352
C	-1.9410764	0.1827993	3.4222554
H	-2.6846081	-0.4762431	3.8658560
C	-1.1638687	1.1424993	3.9815217
H	-1.1135537	1.4829018	5.0120489
N	-0.3876967	1.6872988	2.9606825
C	0.6004098	2.7806449	3.2362784
C	1.4069479	3.1246545	1.9803455
H	1.9621523	2.2548130	1.5925573
H	2.1325916	3.9165935	2.2352368
H	0.7572506	3.5073245	1.1766260
C	-0.1758144	4.0263275	3.7078579
H	-0.8784129	4.3631261	2.9251594
H	0.5275512	4.8504265	3.9192928
H	-0.7533191	3.8323816	4.6292879
C	1.5728920	2.2924988	4.3296137
H	1.0617441	2.0745775	5.2835984
H	2.3281535	3.0720371	4.5287125
H	2.0990965	1.3795066	4.0003085
C	-2.1770871	-0.8093720	1.1379188
H	-2.0311006	-0.4452705	0.1092773
H	-3.2545322	-0.9194773	1.3387365
C	-0.4501135	-2.4768924	0.5137552
N	-1.5537094	-2.1165135	1.2438282
C	-1.9707330	-3.1395035	2.0864763
H	-2.8379656	-3.0576082	2.7392286
C	-1.1118050	-4.1703299	1.8808714
H	-1.0965460	-5.1609974	2.3280813
N	-0.1912760	-3.7510469	0.9203812
C	0.9070897	-4.6397436	0.4238112
C	0.2695534	-5.8973288	-0.1998622
H	-0.3424282	-6.4597025	0.5272552
H	1.0605033	-6.5757628	-0.5645320
H	-0.3728328	-5.6229949	-1.0547145
C	1.8018902	-5.0159086	1.6214274
H	2.2126437	-4.1087399	2.0982843
H	2.6467796	-5.6380850	1.2780438
H	1.2518816	-5.5927982	2.3863486
C	1.7495348	-3.9201397	-0.6364164
H	2.2444072	-3.0233158	-0.2308939
H	1.1357608	-3.6129866	-1.5004477
H	2.5279673	-4.6149743	-0.9989476
N	-0.4414646	2.2583902	-1.8719609
H	-0.6237256	1.3491314	-2.3320797
C	0.6240451	2.9543131	-2.6227712
H	0.3194155	3.0651459	-3.6860052
H	1.5248061	2.3214986	-2.5926789
C	0.9001194	4.3365284	-2.0269351
H	1.6669184	4.8521088	-2.6333627
H	1.3294897	4.2090299	-1.0151010
C	-0.3827637	5.1793008	-1.9476600
H	-0.1900924	6.1373763	-1.4296133
H	-0.7093577	5.4377945	-2.9743741
C	-1.5105216	4.4033249	-1.2486122
H	-1.2660086	4.2670770	-0.1768975
H	-2.4594358	4.9688465	-1.2943108
C	-1.7016339	3.0268567	-1.8877666
H	-2.4707434	2.4412865	-1.3578369
H	-2.0527736	3.1555929	-2.9349241

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functional B3LYP

geometry optimisation SV(P)

Energy -9483.5127469420

NIMAG 0

Zero-point correction 0.5394402

single point TZVP

Energy -9485.7951373930

Results for piperidine (chair conformation)

C	-1.4807093	-0.2257821	0.0004164
C	-0.7303895	0.2250802	1.2668458
C	0.7373229	-0.2262404	1.2167510
N	1.3708566	0.2800753	-0.0005783
C	0.7362284	-0.2267126	-1.2173205
C	-0.7312502	0.2255042	-1.2662062
H	1.2921301	0.1693583	2.0966510
H	-0.7571589	1.3365845	1.3412467
H	-1.2199249	-0.1815445	2.1806477
H	-1.5600074	-1.3395906	0.0004212
H	-2.5231176	0.1654962	0.0009807
H	2.3747683	0.0561598	-0.0009410

H	1.2910260	0.1681368	-2.0975955
H	0.7664416	-1.3530766	-1.2875494
H	-0.7572190	1.3371293	-1.3390533
H	-1.2218816	-0.1793033	-2.1802391
H	0.7680444	-1.3525781	1.2876700

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functional BP86

geometry optimisation SV(P)

Energy -251.7050364923

NIMAG 0

Zero-point correction 0.1543393

single point TZVP

Energy -251.9954710735

Results for piperidine (chair conformation)

C	-1.477743	-0.223748	-0.011238
C	-0.738957	0.222784	1.260015
C	0.726807	-0.224049	1.221824
N	1.366191	0.276235	0.010278
C	0.745411	-0.224425	-1.210733
C	-0.719371	0.223019	-1.270849
H	1.270722	0.172596	2.098042
H	-0.769452	1.326104	1.336997
H	-1.233421	-0.185054	2.161149
H	-1.563325	-1.329124	-0.012540
H	-2.510176	0.171481	-0.019249
H	2.364636	0.069562	0.018229
H	1.302400	0.172443	-2.078493
H	0.782635	-1.340999	-1.282128
H	-0.746386	1.326455	-1.348183
H	-1.200193	-0.183348	-2.179998
H	0.761574	-1.340616	1.294195

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functional B3LYP

geometry optimisation SV(P)

Energy -251.5222914308

NIMAG 0

Zero-point correction 0.1586106

single point TZVP

Energy -251.8172519694

Results for *N-tert*-butylimidazole

C	-0.0074902	-1.0745577	-1.1049789
H	-0.0115134	-2.1139024	-0.7543542
N	0.0035772	-0.7060638	-2.3771436
C	0.0018401	0.6695467	-2.3513207
H	0.0060703	1.2639322	-3.2764436
C	-0.0113912	1.1334400	-1.0447137
H	-0.0065903	2.1477627	-0.6296976
N	-0.0181869	0.0011133	-0.2393907
C	0.0026309	-0.0022035	1.2486763
C	-0.1343112	-1.4458205	1.7678538
H	-1.0757451	-1.9190683	1.4141979
H	-0.1565490	-1.4328900	2.8785234
H	0.7227479	-2.0819705	1.4576359
C	-1.1843320	0.8382728	1.7686096
H	-2.1490336	0.4240189	1.4036103
H	-1.1162296	1.8960799	1.4360713
H	-1.1983888	0.8334770	2.8803308
C	1.3438880	0.5972856	1.7289690
H	1.4663721	1.6461008	1.3818857
H	2.2000429	0.0050628	1.3392339
H	1.3927290	0.5958066	2.8398316

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functional BP86

geometry optimisation SV(P)

Energy -383.1865243518

NIMAG 0

Zero-point correction 0.1779110

single point TZVP

Energy -383.6135932059

Results for *N-tert*-butylimidazole

C	-0.011453	-1.069384	-1.101241
H	-0.017378	-2.101090	-0.753223
N	0.003802	-0.704299	-2.363992
C	0.003761	0.665532	-2.343981

H	0.011915	1.254326	-3.263247
C	-0.013271	1.126909	-1.045969
H	-0.012948	2.135805	-0.639098
N	-0.026512	0.001121	-0.241197
C	0.002887	-0.001733	1.243834
C	-0.155444	-1.438767	1.765759
H	-1.101415	-1.892155	1.422173
H	-0.167430	-1.423929	2.869246
H	0.681230	-2.086245	1.451006
C	-1.162753	0.858286	1.770070
H	-2.130644	0.463391	1.414603
H	-1.079350	1.907587	1.439309
H	-1.168592	0.853999	2.874520
C	1.353793	0.573048	1.715249
H	1.490626	1.612409	1.369189
H	2.190944	-0.029988	1.321778
H	1.409841	0.570373	2.818612

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functional B3LYP

geometry optimisation SV(P)

Energy -382.9167210302

NIMAG 0

Zero-point correction 0.1829166

single point TZVP

Energy -383.3498709333

Results for the adduct 3#·Et_3N

Cu	-0.032757	1.464652	-0.074754
Cu	0.203747	-1.274289	-0.543192
Br	2.063988	0.429380	-0.802060
Br	-0.372670	-2.198206	-2.678102
C	-0.640541	1.466431	1.755198
N	-1.676565	0.689029	2.234837
C	-1.849087	0.840270	3.606974
H	-2.623986	0.312594	4.174178
C	-0.905398	1.743346	4.011956
H	-0.715949	2.149372	5.008939
N	-0.179491	2.120148	2.880225
C	1.076313	2.949711	2.929835
C	1.126704	3.881049	1.707346
H	1.150057	3.288680	0.765994
H	2.052991	4.493677	1.747210
H	0.249627	4.563356	1.680149
C	1.079608	3.803660	4.212714
H	0.164635	4.431137	4.293962
H	1.956671	4.484610	4.186030
H	1.178120	3.188523	5.133138
C	2.282179	1.986064	2.923008
H	2.232661	1.287681	3.787879
H	3.231172	2.561316	2.995422
H	2.303346	1.390465	1.983078
C	-2.330129	-0.334656	1.429196
H	-2.177997	-0.058260	0.366018
H	-3.412465	-0.364446	1.672274
C	-0.604883	-2.074619	1.011335
N	-1.762245	-1.652025	1.639376
C	-2.228976	-2.586278	2.563121
H	-3.138618	-2.440506	3.157169
C	-1.349856	-3.632847	2.515950
H	-1.360511	-4.575395	3.070102
N	-0.364901	-3.305905	1.581949
C	0.707488	-4.262076	1.132108
C	0.153019	-5.076658	-0.055812
H	-0.751960	-5.652219	0.242716
H	0.920551	-5.799478	-0.409932
H	-0.109953	-4.399410	-0.900739
C	1.077867	-5.191620	2.306956
H	1.380294	-4.612750	3.207878
H	1.937626	-5.826154	2.005050
H	0.252197	-5.882459	2.583165
C	1.959683	-3.475110	0.704359
H	2.314249	-2.799069	1.511409
H	1.768265	-2.865078	-0.207185
H	2.770624	-4.194544	0.459035
N	-0.718600	2.459420	-1.906122
C	0.328286	3.487159	-2.178504
H	1.273892	2.925189	-2.333720
H	0.465129	4.065706	-1.238695
C	0.108363	4.489114	-3.324985
H	0.959707	5.205852	-3.335942
H	-0.821354	5.085899	-3.197599
C	-2.189395	4.046936	-0.571386
H	-1.812034	3.616822	0.381937
H	-3.256401	4.329167	-0.433588
C	-2.075029	3.028572	-1.706082
H	-2.747435	2.165971	-1.500575
H	-2.448654	3.495318	-2.650079
H	0.070574	4.004406	-4.321404
H	-1.627301	4.983403	-0.780880
C	-0.746314	1.335213	-2.898030
C	-1.331552	1.560533	-4.300064
H	-1.309606	0.503418	-2.422003
H	0.292405	0.955585	-2.977695

H	-1.356934	0.567285	-4.798987
H	-2.373587	1.949576	-4.284319
H	-0.718364	2.234189	-4.935112

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functional BP86

geometry optimisation SV(P)

Energy -9526.2066953030

NIMAG 0

Zero-point correction 0.5696300

single point TZVP

Energy -9528.5365420730

Results for the adduct 3#·Et_3N

Cu	-0.049022	1.377970	0.146936
Cu	0.482726	-1.094332	-0.750637
Br	2.354112	0.413855	-0.299576
Br	-1.034727	-0.368550	-2.601299
C	-0.818253	0.603967	1.827200
N	-1.804717	-0.349184	1.883630
C	-2.094262	-0.715946	3.189077
H	-2.847974	-1.459640	3.439709
C	-1.277885	0.020238	3.981158
H	-1.203143	0.042548	5.063141
N	-0.505539	0.823191	3.144293
C	0.659787	1.618092	3.664283
C	0.901984	2.849135	2.786683
H	1.168690	2.562722	1.757037
H	1.745108	3.427398	3.203337
H	0.011610	3.500288	2.761603
C	0.355133	2.094909	5.097636
H	-0.602012	2.644256	5.147135
H	1.156913	2.779112	5.422499
H	0.327747	1.267436	5.827057
C	1.898234	0.701118	3.657974
H	1.727698	-0.191738	4.287145
H	2.772162	1.242759	4.062486
H	2.137087	0.373761	2.630710
C	-2.345638	-1.062449	0.737258
H	-2.143011	-0.486362	-0.180489
H	-3.431966	-1.185095	0.866698
C	-0.497605	-2.583223	0.096502
N	-1.755659	-2.385700	0.593572
C	-2.368188	-3.586074	0.928269
H	-3.378496	-3.645730	1.329398
C	-1.471737	-4.564525	0.631394
H	-1.567068	-5.640672	0.733584
N	-0.333200	-3.934997	0.132778
C	0.909721	-4.617335	-0.359966
C	1.034145	-4.367870	-1.874384
H	0.169942	-4.793256	-2.415241
H	1.955721	-4.837200	-2.262072
H	1.070141	-3.287433	-2.093989
C	0.815412	-6.127468	-0.093355
H	0.707432	-6.352668	0.982793
H	1.746466	-6.605747	-0.441377
H	-0.019637	-6.596620	-0.642790
C	2.120353	-4.038232	0.394219
H	2.026047	-4.217203	1.480711
H	2.207736	-2.951247	0.229579
H	3.047949	-4.521265	0.039983
N	-0.305451	3.168347	-1.155366
C	0.019928	4.340572	-0.303374
H	1.097424	4.275349	-0.075151
H	-0.508188	4.204717	0.654273
C	-0.307406	5.753642	-0.813984
H	-0.049774	6.480027	-0.020917
H	-1.381330	5.882258	-1.035233
C	-2.769364	3.190812	-0.555561
H	-2.628341	2.351866	0.148528
H	-3.767808	3.088909	-1.018149
C	-1.705202	3.171270	-1.650800
H	-1.820395	2.253750	-2.249787
H	-1.876413	4.030803	-2.329201
H	0.259282	6.033601	-1.715348
H	-2.772182	4.129096	0.028192
C	0.662312	2.936411	-2.270840
C	0.720209	3.933290	-3.437326
H	0.417734	1.940243	-2.672416
H	1.659551	2.844867	-1.812111
H	1.366805	3.498798	-4.221324
H	-0.266888	4.113181	-3.898292
H	1.157036	4.908916	-3.163293

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functional B3LYP

geometry optimisation SV(P)

Energy -9523.9308032480

NIMAG 0

Zero-point correction 0.5863450

single point TZVP

Energy -9526.2648876230

Results for triethylamine E_3N

N	-0.097637	-0.000396	-0.280311
C	0.334653	1.248206	0.350743
C	1.726509	1.740331	-0.078167
H	0.302241	1.172956	1.472508
H	-0.402070	2.036657	0.078623
H	1.934656	2.740928	0.365015
H	2.536406	1.056013	0.251116
H	1.783705	1.825960	-1.185270
C	0.350410	-1.232927	0.372248
C	1.727603	-1.742133	-0.084501
H	-0.395647	-2.027005	0.145758
H	0.351146	-1.124665	1.491369
H	1.944279	-2.733064	0.376308
H	1.752165	-1.854798	-1.190366
H	2.549330	-1.053838	0.204628
C	-1.494271	-0.012376	-0.720770
C	-2.572509	-0.000764	0.382081
H	-1.639597	-0.909372	-1.365617
H	-1.647316	0.864840	-1.390699
H	-3.592460	-0.011721	-0.064940
H	-2.487653	-0.889659	1.046350
H	-2.495097	0.908249	1.019382

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functional BP86

geometry optimisation SV(P)

Energy -292.1687560833

NIMAG 0

Zero-point correction 0.1989311

single point TZVP

Energy -292.5107964360

Results for triethylamine E_3N

N	-0.094618	-0.000513	-0.248170
C	0.344894	1.242690	0.378249
C	1.708973	1.757365	-0.100427
H	0.360937	1.149301	1.489009
H	-0.405340	2.021635	0.153032
H	1.927162	2.743602	0.351668
H	2.531932	1.076495	0.174572
H	1.714948	1.866711	-1.199643
C	0.352314	-1.237020	0.386537
C	1.711060	-1.756349	-0.102284
H	-0.400085	-2.018767	0.178787
H	0.380959	-1.131212	1.495809
H	1.933828	-2.738983	0.355439
H	1.705292	-1.874764	-1.200565
H	2.536831	-1.073449	0.158600
C	-1.474940	-0.006114	-0.721998
C	-2.572380	-0.000198	0.356651
H	-1.609058	-0.891903	-1.370610
H	-1.612329	0.869925	-1.383180
H	-3.576004	-0.006358	-0.108493
H	-2.501589	-0.887681	1.012202
H	-2.505857	0.898105	0.997680

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functional B3LYP

geometry optimisation SV(P)

Energy -291.9543667610

NIMAG 0

Zero-point correction 0.2043762

single point TZVP

Energy -292.3020723678

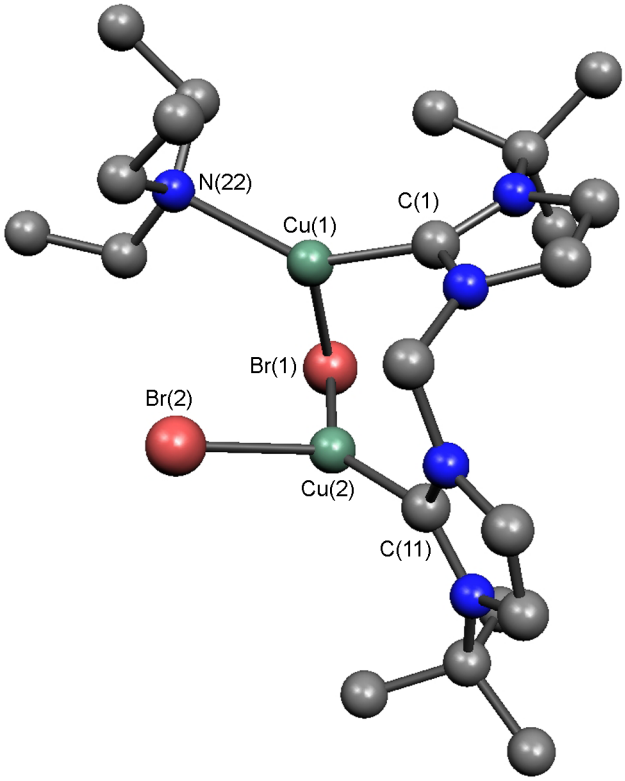

Figure S1. B3LYP/SV(P)-optimised structure of **3#·Et$_3$N** in a gas phase. Hydrogen atoms are omitted.

Table S1. Comparison of geometrical parameters of B3LYP/SV(P) or BP86/SV(P) gas-phase equilibrium structures of **6-7** and **3#·Et$_3$N**.

Distance (Å) or Angle (º)	B3LYP/SV(P)			BP86/SV(P)		
	6	**7**	**3#·Et$_3$N**	**6**	**7**	**3#·Et$_3$N**
Cu(1)-Cu(2)	2.824	2.778	2.683	2.708	2.686	2.789
Cu(1)-C(1)	1.958	1.965	2.004	1.916	1.922	1.928
Cu(2)-C(11)	1.976	1.978	1.974	1.926	1.927	1.926
Cu(1)-N(22)	2.035	2.101	2.229	2.013	2.080	2.194
Cu(1)-Br(1)	2.536	2.563	2.628	2.506	2.535	2.449
Cu(2)-Br(1)	2.516	2.493	2.445	2.50	2.473	2.536
Cu(2)-Br(2)	2.426	2.457	2.501	2.404	2.435	2.397
C(1)-Cu(1)-N(22)	134.0	139.8	139.1	132.7	139.6	133.9
Cu(2)-Br(1)-Cu(1)	68.0	66.6	63.8	65.5	64.9	68.0
C(11)-Cu(2)-Br(2)	117.7	113.4	103.6	119.7	115.0	117.2

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