Electronic Supplementary Information

From *N*-Benzoylpyridinium Imides to Pyrazolo[1,5-*a*]pyridines: A Mechanistic Discussion on a Stoichiometric Cu Protocol

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Part 2. Computational Section

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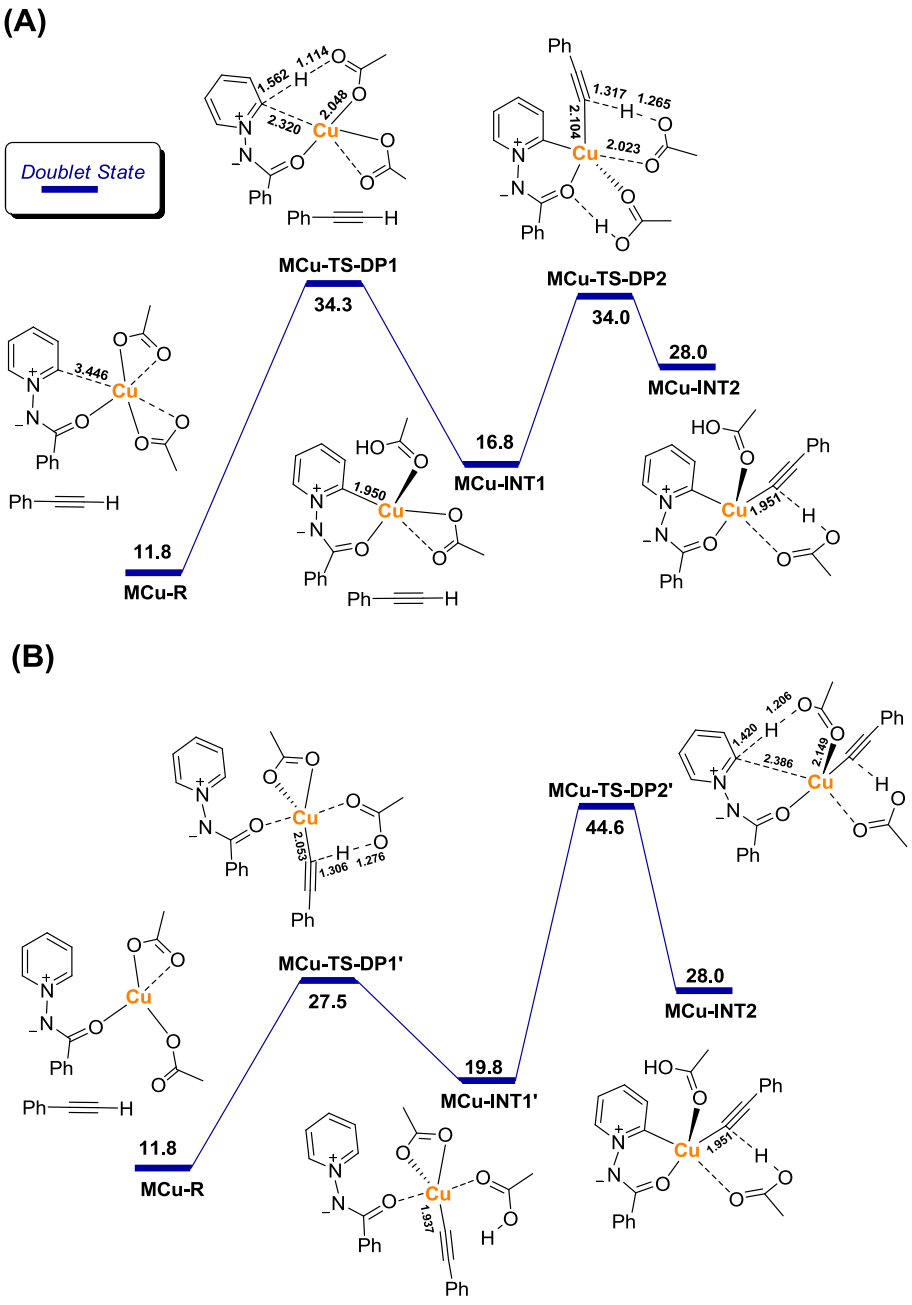
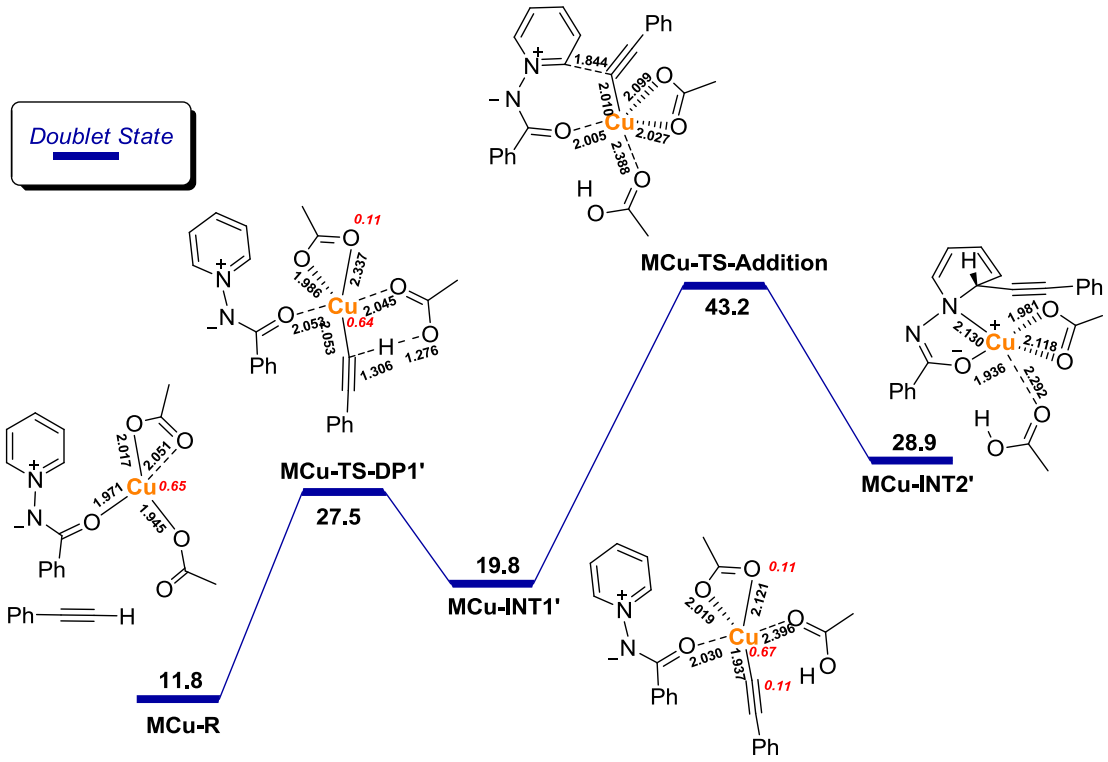
The different sequences of deprotonation



Scheme ESI2-1. (A) The calculated energies for the more favourable sequence of deprotonation (aromatic C–H before alkynyl C–H). **(B)** The calculated energies for the reverse sequence of deprotonation (aromatic C–H after alkynyl C–H). The relative free energies are in kcal/mol; selected bond lengths are in Å.

The calculated addition-rearomatization pathway (cf. Scheme 5 in main text)



Scheme ESI2-2. The calculated energies for the addition step. The relative free energies are in kcal/mol; selected bond lengths are in Å.

Details for locating the Crossing Point

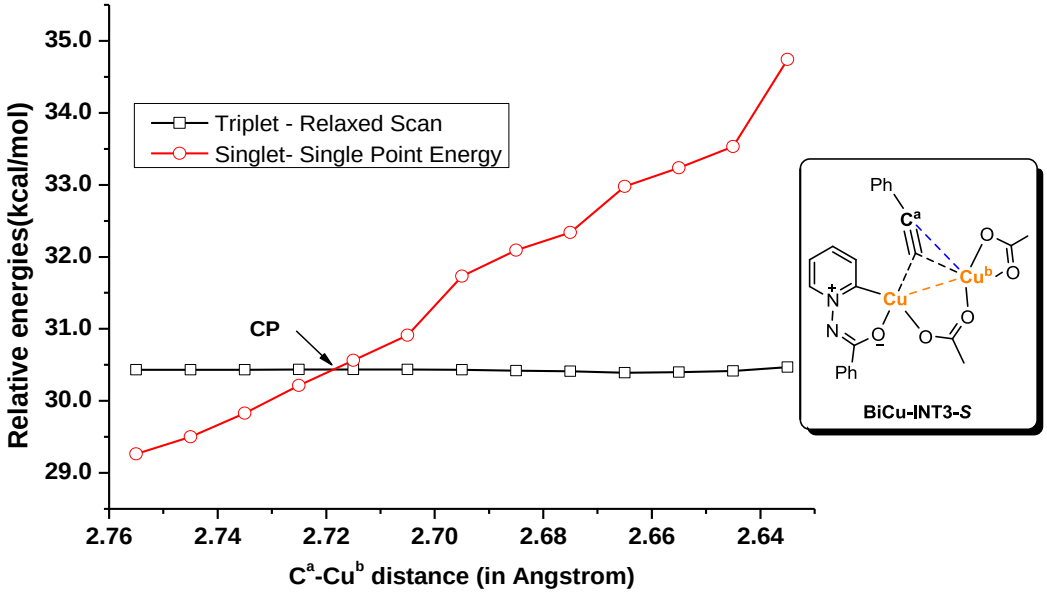


Figure ESI2-1. Triplet and singlet potential energies of **BiCu-INT3-*S*** as a function of the C^a–Cu^b distance.

First, the approach proposed by Yoshizawa *et al* was used to locate the possible crossing point of the singlet and triplet potential energy surface (see ref 39 in the main text). Around **BiCu-Dis-TS1**, the PES is very flat, the IRC calculation failed. The vibration mode of **BiCu-Dis-TS1** is mainly composed of the change in the C^a–Cu^b distance. Therefore, the C^a–Cu^b distance can be considered as the main reaction coordinate. A relaxed potential energy surface scan along C^a–Cu^b distance with **BiCu-INT3-*S*** has been performed, and the single point energies of the triplet state have been calculated. Thus a crossing point (**CP**) was located, and the energy difference between the singlet and triplet states is 0.132 kcal/mol. Using **CP** as the initial structure, the **MECP** was obtained after optimization with the code developed by Harvey *et al*. Both the structure and energies of **CP** and **MECP** are very close. After optimization, the energies of the singlet and triplet states decreased by 0.00542 kcal/mol and 0.124 kcal/mol, respectively. For **MECP**, the energy difference between the singlet and triplet states is 0.0134 kcal/mol.

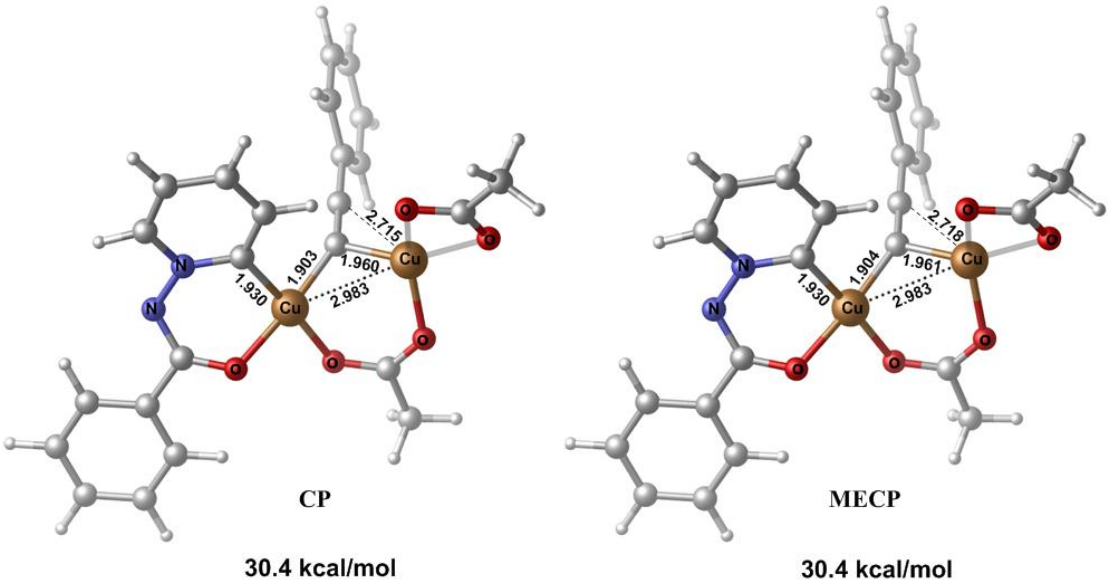


Figure ESI2-2. The structures of crossing point (**CP**)and optimized minimum energy crossing point (**MECP**).

Optimized key structures

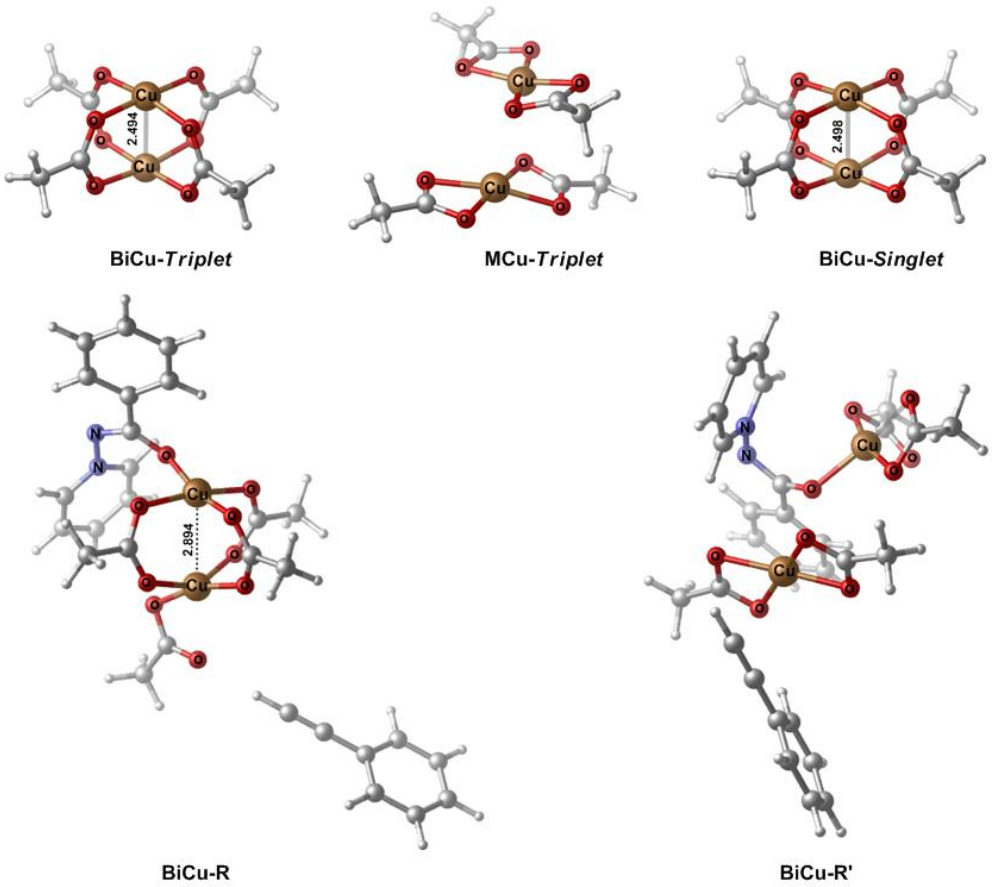


Figure ESI2-3. The optimized key structures in Scheme 8 in the main text.

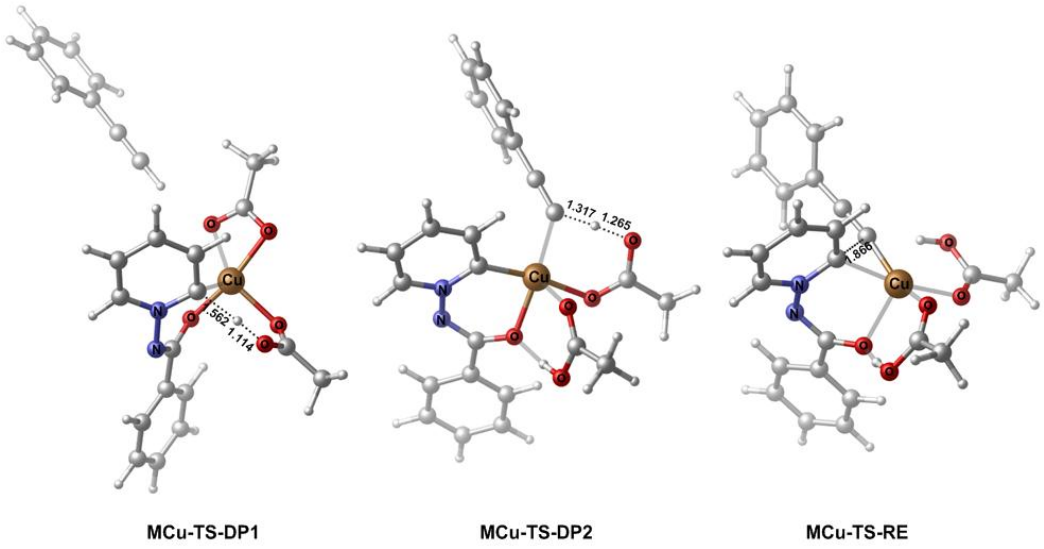


Figure ESI2-4. The optimized key structures in Scheme 10 in the main text.

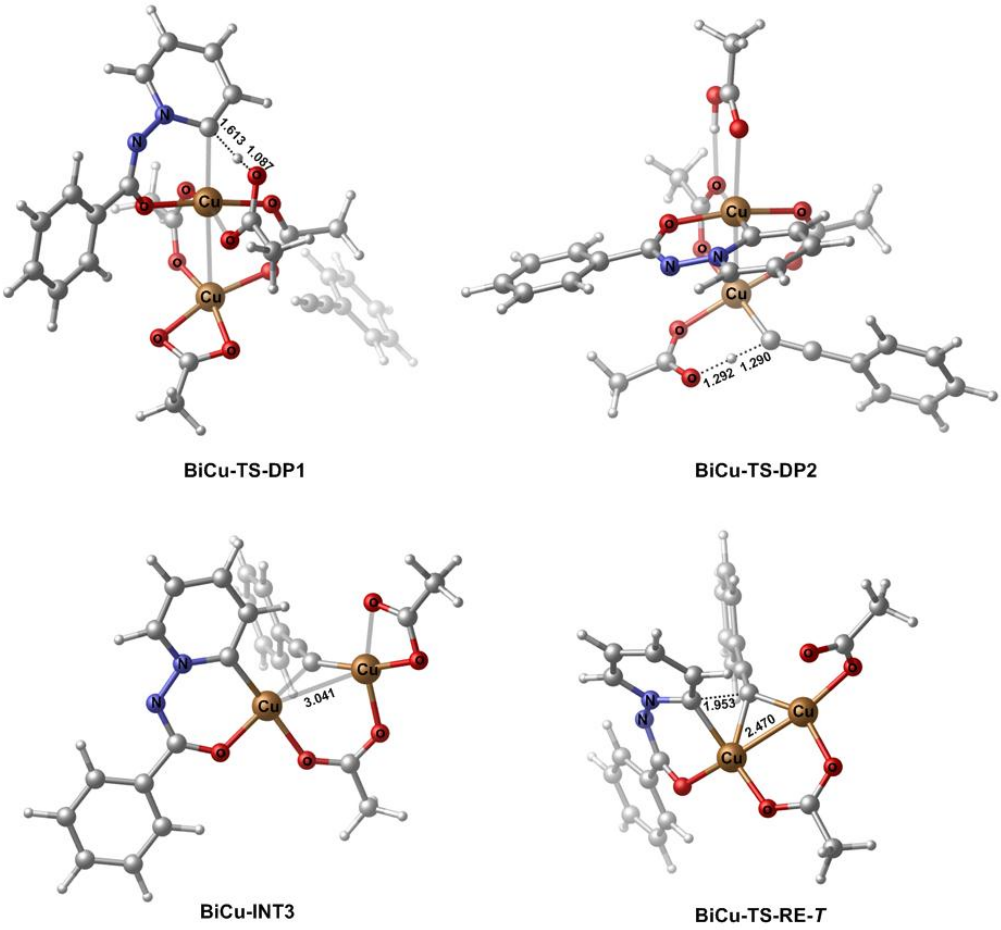


Figure ESI2-5. The optimized key structures in Scheme 11 in the main text.

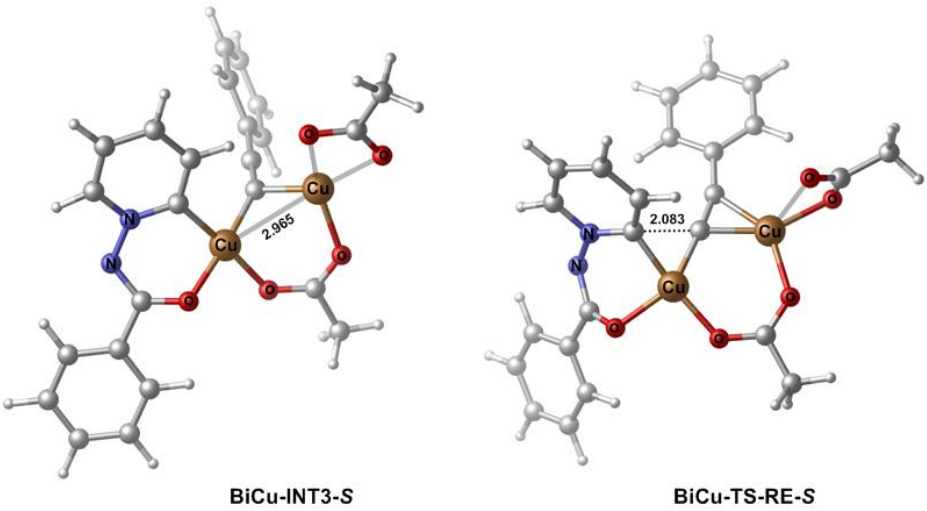
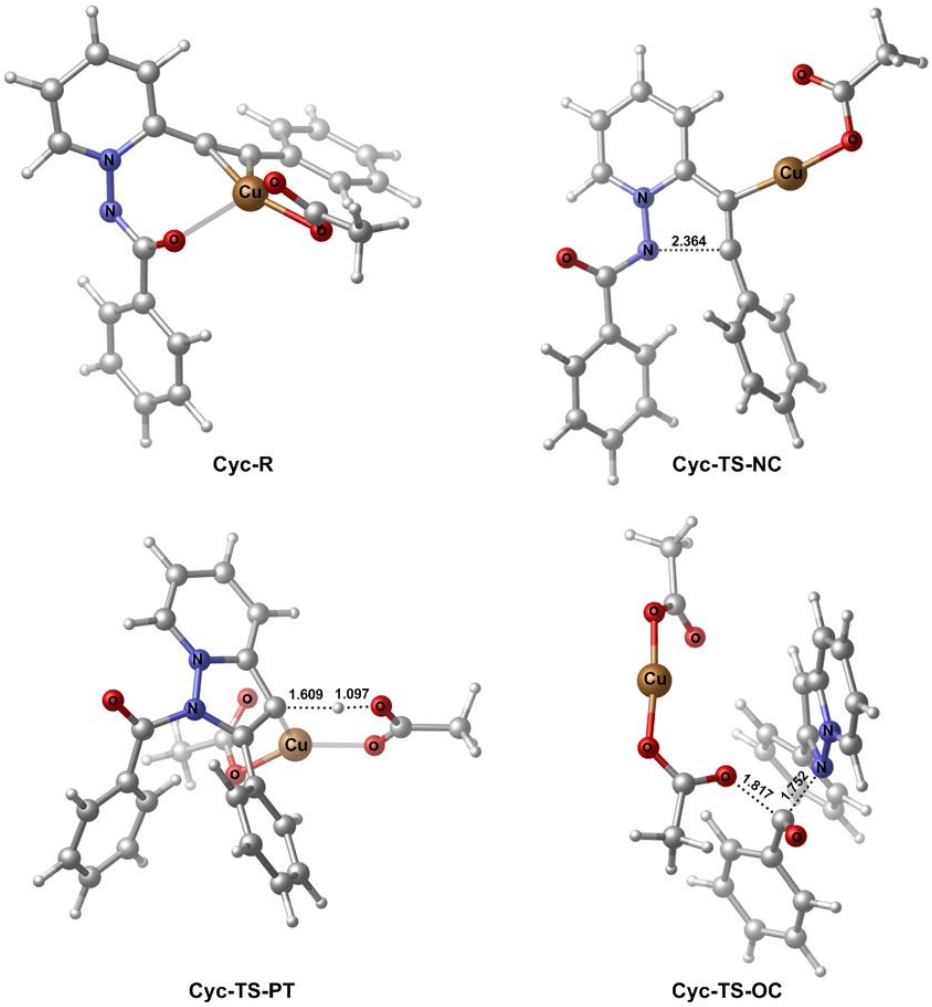


Figure ESI2-6. The optimized key structures in Scheme 12 in the main text.



FigureESI2-7. The optimized key structures in Scheme 13 in the main text.

Calculated total energies and geometrical coordinates

The structures shown in Scheme 8 in the main text

BiCu-Triplet

E(RB+HF-LYP)= -1308.80676762 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1308.648045 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4195.62974702 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,0.0107791517,-0.0097586338,1.2452425074
Cu,0,-0.0019923501,0.0021070624,-1.2483509048
C,0,-1.6515175825,-1.9462986852,0.0705126229
O,0,-1.2602652423,-1.5009256225,1.1970999102
O,0,-1.2838635864,-1.5085042767,-1.064571115
C,0,-2.662541808,-3.0696276375,0.0832832821
H,0,-3.6653699921,-2.6406961828,-0.033776397
H,0,-2.4892306412,-3.7488593097,-0.7550861046
H,0,-2.6277482209,-3.6146799958,1.0287055681
C,0,-1.9391653706,1.6518285902,-0.0550830243
O,0,-1.4987467784,1.2760184477,1.0754873847
O,0,-1.4934993606,1.2719900672,-1.1862090179
C,0,-3.0894728801,2.6322018585,-0.0726405779
H,0,-2.7899092485,3.5355605484,-0.6147114869
H,0,-3.9344706043,2.1927795789,-0.6135363445
H,0,-3.3970906226,2.8952795331,0.9405691143
C,0,1.6598067034,1.9389041522,0.0731433678
O,0,1.2795582343,1.4839093894,1.1991677184
O,0,1.2848686658,1.5077607962,-1.0625089464
C,0,2.6406014556,3.0888287847,0.0791813762
H,0,3.5496035258,2.7943950371,-0.4562448277
H,0,2.2075253532,3.9399352241,-0.4570742028
H,0,2.8933195565,3.3852182932,1.0984219414
C,0,1.9467267546,-1.658339218,-0.090624305
O,0,1.4903773738,-1.2693939341,-1.2130481523
O,0,1.5175638576,-1.2915970987,1.0485771865
C,0,3.0965756374,-2.639067101,-0.104796865
H,0,3.9500212124,-2.2071094066,0.4287358322
H,0,2.8047986923,-3.5494375353,0.4296901443
H,0,3.3885271096,-2.8889071294,-1.1260130874

MonoCu-Triplet

E(RB+HF-LYP)= -1308.78437016 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1308.632783 Hartree (6-31G*/SDD in

dioxane)

E(RB+HF-LYP)= -4195.60654521 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,-0.0129293295,0.0352844018,-0.0278732898
C,0,-0.0009305218,-0.0181251164,2.3529307648
O,0,1.1030844313,-0.009590832,1.6902295304
O,0,-1.0794535409,0.0248150676,1.6814382819
C,0,-0.0001208774,-0.056626154,3.8499537269
H,0,0.2235372019,0.9474016971,4.2305507936
H,0,-0.9758966003,-0.3668709118,4.2287779726
H,0,0.7822711763,-0.7308062956,4.2090515233
C,0,-0.1067522005,-0.2982823118,-2.3397923522
O,0,-1.1664178142,-0.0950285254,-1.6531610158
O,0,0.9987626147,-0.3502786155,-1.7033645098
C,0,-0.15269255,-0.4355097828,-3.830573815
H,0,0.1180947903,0.5279416127,-4.2799675391
H,0,0.5773488741,-1.1775337321,-4.1650762319
H,0,-1.1555031557,-0.7089850294,-4.1653834445
Cu,0,2.1307359762,2.1902913247,1.3868632136
C,0,4.3929298357,1.6889050426,1.6965989501
O,0,3.6813139845,2.1647719269,2.6462249127
O,0,3.8250884261,1.5366860361,0.5629014408
C,0,5.8254618208,1.3034882209,1.903448376
H,0,5.9084348519,0.211045308,1.861050142
H,0,6.4416284584,1.7120293943,1.0965788563
H,0,6.1892153613,1.6553178477,2.8706910736
C,0,-0.0458462234,3.0785881007,1.0063370914
O,0,0.5633338975,2.41555683,0.0859147697
O,0,0.554546514,3.2106652551,2.1191446901
C,0,-1.3888063636,3.6903157893,0.7514451876
H,0,-1.8495818453,4.0213776786,1.6839099666
H,0,-1.2591291325,4.5554722763,0.089674439
H,0,-2.0405337523,2.9775766975,0.2376527919

BiCu-Singlet

E(RB+HF-LYP)= -1308.80784871 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1308.648180 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4195.6308989 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,0.0009471357,0.0043481774,-0.0020295389
Cu,0,-0.0011014619,-0.0053346047,2.4955135295
C,0,2.5510486181,0.0018790001,1.1757446705

O,0,1.9609367956,0.0039884017,0.0485841512
O,0,1.9791364186,-0.005893146,2.3109463303
C,0,4.0627242215,0.0307293128,1.1701821422
H,0,4.4007828488,1.012717292,1.5211736632
H,0,4.4531008617,-0.7184011166,1.8652746962
H,0,4.4553229248,-0.1455825434,0.167410011
C,0,-0.0001441237,2.5504917043,1.3281454796
O,0,0.0013202292,1.9840461882,0.1913097643
O,0,-0.0010026666,1.954786858,2.4534544089
C,0,-0.0009496424,4.0621552927,1.3606729261
H,0,-0.8845997642,4.4138704463,1.9038417708
H,0,0.8797795831,4.4149132388,1.9078720441
H,0,0.0009994739,4.4771440447,0.3517144578
C,0,-2.5510503095,-0.0002757477,1.1708667558
O,0,-1.9592844768,0.0061411307,0.0447292247
O,0,-1.9808720991,-0.0066036127,2.3070414582
C,0,-4.0629678595,-0.0010605912,1.1649154367
H,0,-4.4279901367,-0.8897296503,1.6908177816
H,0,-4.4294955927,0.8746468313,1.7109889432
H,0,-4.4527251998,0.0099829313,0.1459264793
C,0,-0.0002127693,-2.5515147128,1.3070766346
O,0,-0.0006548548,-1.9660820637,2.4364467708
O,0,-0.0003800285,-1.9750898814,0.1739324988
C,0,0.0004276249,-4.0634052378,1.3033980156
H,0,-0.8812880271,-4.4259781727,0.7643009044
H,0,0.8831365042,-4.4251223201,0.7653597116
H,0,0.0000392626,-4.4599982,2.3197871287

BiCu-R

E(RB+HF-LYP)= -2265.19982292 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -2264.773877 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.29268277 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu, 1.615282577265,-1.252447336975,-0.251837066242
Cu, -0.631596798005, 0.268944497490, 0.753320374659
C , -0.248225315490,-0.352506954165,-2.142264008760
O , 0.646232812560,-1.241600889933,-1.960898064610
O , -0.664343918612, 0.463791197774,-1.271306920977
C , -0.878376989149,-0.282414277906,-3.518291065819
H , -1.857755576691,-0.774804179578,-3.478890761359
H , -1.047954547382, 0.759766055894,-3.802983747879
H , -0.262129715965,-0.784776547177,-4.266821990293
C , -0.723238395154,-2.630903468285, 0.636846257745

O , 0.519894919002,-2.741547966607, 0.396790943649
O , -1.369273924979,-1.542997267342, 0.681799519535
C , -1.501242422230,-3.899679585674, 0.906781047968
H , -1.825759028233,-3.903681565877, 1.953688555847
H , -2.403051820769,-3.916069954035, 0.286751223471
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C , 1.646850307499,-0.589206753140, 2.499334804613
O , 2.381520758700,-0.961203949803, 1.523161626400
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C , 2.249398585970,-0.700149455229, 3.885161776508
H , 1.946545663328, 0.150931275893, 4.501207975919
H , 1.862237792186,-1.609727571627, 4.360882389572
H , 3.338312245515,-0.770054136249, 3.840119042679
C , -1.585994131115, 2.466302076274, 1.369282439548
O , -2.433623282592, 1.543908335437, 1.459459356283
O , -0.379317494045, 2.210761359520, 1.003762689209
C , -1.931709546072, 3.900312658388, 1.700314368255
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H , -1.636272797180, 4.559615468141, 0.877163928017
H , -3.001011505285, 4.008810232554, 1.892756199831
C , 3.077910378978, 4.271948596912, 0.431902637098
C , 3.841671909621, 3.119651801444, 0.481773741949
N , 3.924337914800, 2.300520787192,-0.592706319380
C , 3.272934802303, 2.591958970777,-1.744609269951
C , 2.496750809287, 3.735258818837,-1.837023570640
C , 2.389665429348, 4.588946610830,-0.739964608534
N , 4.792470667176, 1.208635640821,-0.486523017206
C , 4.215291937594, 0.033030057952,-0.710241508811
O , 3.000084108603,-0.121261006716,-1.086098912369
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H , 4.408115618402, 2.797843887670, 1.345693827006
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H , 1.783805296086, 5.487048129479,-0.797914015185
C , 5.117375577297,-1.147239269113,-0.552514162382
C , 6.327631705420,-1.053488117412, 0.152121129256
C , 4.752481902267,-2.372299100031,-1.129463955484
C , 7.149284538466,-2.170248625954, 0.285835403375
H , 6.609163797765,-0.105755010563, 0.597823253003
C , 5.578456668504,-3.488114160197,-0.996189692119
H , 3.830024088177,-2.443675244685,-1.697916491971
C , 6.776552334590,-3.390338932918,-0.286072423038
H , 8.080275251359,-2.090944553784, 0.840742090729
H , 5.286651984282,-4.431513915575,-1.449455566260
H , 7.418522520487,-4.260619005793,-0.178377490421

C , -5.384477798201, 0.801691981347, 0.545707697926
C , -6.493921624741, 0.465169462185, 0.192399642176
C , -7.802994654857, 0.062434062236,-0.219484739924
C , -8.743174140682,-0.388339050095, 0.728012174997
C , -8.174377940029, 0.108647708852,-1.577503374820
C ,-10.017336217556,-0.780851107919, 0.324252688850
H , -8.461629240773,-0.426619437602, 1.776032416992
C , -9.450635857776,-0.286024547747,-1.972663484176
H , -7.453207620430, 0.454829400038,-2.311854324287
C ,-10.376104283984,-0.731366747032,-1.025289421465
H ,-10.732763346882,-1.127069534708, 1.065649029740
H , -9.723694519400,-0.245966560894,-3.023952295620
H ,-11.370976937795,-1.038327317176,-1.336902569381
H , -4.401426728177, 1.098917327893, 0.867172351598
H , 3.410299699851, 1.893932142164,-2.557037873656

BiCu-R'

E(RB+HF-LYP)= -2265.17753414 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -2264.757980 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.26743968 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,4.2633302414,-1.4148531701,2.7417296387
C,0,3.8609890072,-0.2315463111,2.1430361083
N,0,2.5955332112,0.21653109,2.3104034095
C,0,1.6915123217,-0.4651024907,3.0497241286
C,0,2.0544480153,-1.6525060806,3.6650460305
C,0,3.3541837013,-2.137223037,3.5157568514
N,0,2.2527150478,1.469854171,1.779657507
C,0,1.6384760159,1.3865875227,0.6084012813
O,0,1.3260215097,0.2927217906,0.0041218059
Cu,0,2.6481794312,-0.7881190834,-1.0375206177
H,0,5.2805353272,-1.7580707864,2.5902983301
H,0,4.486127981,0.3801692633,1.5054311385
H,0,0.7048791406,-0.0204741856,3.109162225
H,0,1.3131670215,-2.1849164927,4.2503534763
H,0,3.6540379329,-3.0639286255,3.9944730063
C,0,1.2713758458,2.6974915251,-0.0100192489
C,0,1.5086798374,3.9134910414,0.6535341881
C,0,0.6804720068,2.710863792,-1.2812346206
C,0,1.1587494304,5.1202515187,0.0519378409
H,0,1.9707544394,3.9018958569,1.6349778651
C,0,0.3353313253,3.922172208,-1.8813735691
H,0,0.497459059,1.7719820337,-1.7908108086

C,0,0.5713550785,5.1271978332,-1.2175913295
H,0,1.3466682613,6.0564728747,0.5711874319
H,0,-0.1184465785,3.9215034251,-2.868496384
H,0,0.3009946267,6.0696940919,-1.6868442547
C,0,2.5505558991,-3.0608943996,-1.7315308729
O,0,1.4999478821,-2.3825974847,-1.4641502307
O,0,3.6819813512,-2.5095140674,-1.5593354145
C,0,2.4340197781,-4.4646188683,-2.2592074119
H,0,2.0137390629,-4.4320717269,-3.2712565643
H,0,3.4106030439,-4.9514729296,-2.2947567827
H,0,1.7491581467,-5.0475878556,-1.6355961582
C,0,4.0424821466,1.0218295983,-2.073339447
O,0,3.1975998212,0.638281702,-2.9030400421
O,0,4.1015128639,0.5079565484,-0.879069989
C,0,5.0484627491,2.1069592691,-2.3895279991
H,0,4.9034702982,2.9529500482,-1.7080741849
H,0,6.0661020131,1.7311995009,-2.2351273467
H,0,4.935971234,2.4476220805,-3.4207014423
Cu,0,-1.5562022208,-0.4294335422,0.6252949633
C,0,-4.3205773992,-1.4734119043,1.9829303249
C,0,-5.0182417688,-1.0159417755,1.1032855032
C,0,-5.8542215325,-0.4895302826,0.0676895198
C,0,-5.4731068703,0.6643547871,-0.6441460424
C,0,-7.0714633834,-1.123884233,-0.2470277495
C,0,-6.296608591,1.1651029321,-1.6501065701
H,0,-4.5343333934,1.1534827099,-0.4030934037
C,0,-7.8873538251,-0.613284557,-1.2537218015
H,0,-7.3654313569,-2.0137108859,0.3016290546
C,0,-7.5029843445,0.5308457535,-1.9577089685
H,0,-5.9928709286,2.0533360993,-2.1973547587
H,0,-8.8243679827,-1.1103959277,-1.4899140965
H,0,-8.1407167243,0.925751609,-2.7440206133
C,0,-1.4735965507,-2.4708885209,-0.49878027
O,0,-1.8532393021,-1.3995780474,-1.0806563851
O,0,-1.1338104941,-2.3800017168,0.7306789018
C,0,-1.4856968354,-3.7826059975,-1.2203165986
H,0,-1.0102770551,-3.6675417395,-2.1971434075
H,0,-0.9738705047,-4.5509119385,-0.6380266117
H,0,-2.5268006972,-4.0867704267,-1.3828834551
C,0,-1.8268081699,1.5855033482,1.8215781059
O,0,-1.3090357054,0.5519886304,2.3743289282
O,0,-2.1749400784,1.4856258757,0.6004369117
C,0,-2.00579034,2.8698609816,2.5739336438
H,0,-1.3185031735,3.6199098905,2.1659019071

H,0,-3.0247243737,3.2429399804,2.430885559
H,0,-1.8027352395,2.7338933778,3.6378448233
H,0,-3.7274082051,-1.8826991135,2.7708850218

The structures shown in Scheme 9 in the main text

$Cu(AcO)_2$

E(RB+HF-LYP)= -654.386177166 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -654.322464 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2097.80042519 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,-0.0008182103,0.0014123349,-0.0000019662
C,0,-0.0000789581,-0.0240805482,2.3389431709
O,0,1.090368333,-0.0304187207,1.6719695364
O,0,-1.0908167925,-0.0351888591,1.6725605765
C,0,0.000337118,0.0381315728,3.8352378474
H,0,0.0013583405,1.0921179326,4.1405766353
H,0,-0.897970602,-0.4332526549,4.2402826217
H,0,0.8982758548,-0.4345589443,4.239643144
C,0,-0.0040391749,0.0265784263,-2.3389475959
O,0,-1.0936885094,0.0327182246,-1.6706909829
O,0,1.0874981171,0.0378691389,-1.6738560873
C,0,-0.0060116591,-0.035079669,-3.8352630516
H,0,0.890022883,0.4399901179,-4.2410808909
H,0,-0.0029952629,-1.088953908,-4.1409767321
H,0,-0.9062199362,0.4341953975,-4.238557632

$Cu(AcO)_2$-HAcO

E(RB+HF-LYP)= -883.489997375 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -883.368928 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2326.98343282 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,-0.0134456537,-0.0152569598,-0.0049593737
C,0,-0.0092473423,-0.0041884821,2.3834592079
O,0,1.0641206583,-0.0040938534,1.7130617109
O,0,-1.1221424981,-0.043326542,1.7303094614
C,0,-0.0130974202,0.0428420592,3.8814824952
H,0,-0.5206698352,0.9549815771,4.216493107
H,0,-0.5803158815,-0.8079780116,4.273627246
H,0,1.0045453368,0.0254743375,4.2748432591
C,0,0.068901764,-0.6542362767,-2.2596519345
O,0,-1.0427867718,-0.6039682625,-1.6351190706
O,0,1.1282166509,-0.3782056062,-1.6003855317
C,0,0.1285771874,-0.9910670861,-3.7192857017
H,0,-0.0002621311,-0.0693469124,-4.3001747077

H,0,1.0979735065,-1.4249769128,-3.9753713306
H,0,-0.6796986811,-1.6765600838,-3.9859567718
C,0,-1.4672080471,2.8324729934,0.2089242318
O,0,-0.5236342451,2.2017932373,-0.2669399631
O,0,-2.2378074587,2.373048071,1.1882897433
H,0,-1.9218725581,1.4669848171,1.4540638856
C,0,-1.8692409525,4.1995938694,-0.2680783821
H,0,-2.8537499656,4.141432855,-0.7468169524
H,0,-1.9589284966,4.8861429439,0.5797856424
H,0,-1.1385813907,4.5776611642,-0.9839209964

CuAcO-HAcO

E(RB+HF-LYP)= -654.981403099 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -654.906943 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2098.40620182 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,0.3088803018,-0.0117925699,-0.054068713
C,0,0.109408848,0.1334533074,2.7679873318
O,0,1.4228679863,0.274561892,2.8588757594
O,0,-0.4809063568,0.0198644546,1.6844975512
C,0,-0.6025015921,0.1200484331,4.0808766635
H,0,-0.3615717456,1.028336036,4.6431868152
H,0,-1.6783973828,0.0506306052,3.921434854
H,0,-0.257756316,-0.7344289363,4.6740487065
C,0,0.2567749907,0.005000195,-2.6018629561
O,0,-0.9501906554,0.0535154943,-2.3286413758
O,0,1.1989649189,-0.0432182102,-1.6981621846
C,0,0.7511485838,-0.0062462257,-4.0376035024
H,0,1.4324304337,0.835108793,-4.2075201429
H,0,1.3184759774,-0.9238235592,-4.231221184
H,0,-0.0873859522,0.0564887064,-4.7340612134
H,0,1.8054139564,0.2689108142,1.951555027

Cu(AcO)$_3$

E(RB+HF-LYP)= -882.813147919 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -882.703011 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2326.30605593 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

Cu,0,-0.0138734309,0.010896556,-0.0071874723
C,0,0.006088595,-0.0154631565,2.5332023617
O,0,0.9211603547,0.0126784447,1.5771896148

O,0,-1.1958894539,-0.062280662,2.2900962726
C,0,0.6000574903,0.012091441,3.9245903766
H,0,1.2682603117,0.8718833807,4.0358119374
H,0,-0.2047057995,0.0668567584,4.6603309899
H,0,1.1933513004,-0.893369395,4.0913450316
C,0,-0.9451621474,1.6512623919,-1.3201660102
O,0,-1.0044066441,0.4047453054,-1.6150088964
O,0,-0.3318530714,1.903716048,-0.222830749
C,0,-1.5082097419,2.7140005005,-2.191648264
H,0,-1.8577228748,3.5537797055,-1.5854120672
H,0,-0.7155493618,3.0758219843,-2.8588822015
H,0,-2.3215459609,2.3136871565,-2.801800265
C,0,1.1793137319,-2.0498841982,-0.8872456781
O,0,0.1068299662,-1.8197680195,-0.1468807783
O,0,1.8871003498,-1.1444038295,-1.3179481457
C,0,1.4269958271,-3.5225014474,-1.132224747
H,0,2.2800320759,-3.6378942111,-1.8036898938
H,0,1.6321039714,-4.0270244342,-0.1819784092
H,0,0.5393193415,-3.989177296,-1.5709801505

The structures shown in Scheme 10 in the main text

MCu-R

E(RB+HF-LYP)= -1610.78400930 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.446072 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.46641652 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.1776507733,0.1429343558,-0.0641404751
C,0,0.0911225531,0.0353269004,1.3135891377
N,0,1.2094025539,0.0471507033,2.0760111263
C,0,2.4382828636,0.1692882477,1.5113205673
C,0,2.5693311849,0.2728952865,0.1367758126
C,0,1.4292008678,0.2589105181,-0.6685570192
N,0,1.0349081781,0.0552819695,3.4594830826
C,0,1.6633160519,-0.9223797995,4.1074946088
O,0,2.3739838842,-1.8539284474,3.5933498632
Cu,0,1.9329517745,-3.1705227026,2.1940112397
H,0,-0.7355467906,0.1273580425,-0.6480309354
H,0,-0.8337092859,-0.0648579114,1.8634182649
H,0,3.2736119606,0.1887357646,2.1967409779
H,0,3.5627155244,0.369839568,-0.2869404433
H,0,1.5152410102,0.3422930344,-1.746980511
C,0,1.5248361271,-0.8773038974,5.5946899835
C,0,0.9163382423,0.2081815668,6.2451213089
C,0,2.0171620914,-1.9480687047,6.3541086377
C,0,0.8032262975,0.2182351732,7.6331904878
H,0,0.5370930365,1.0361455219,5.6559094097
C,0,1.8994223405,-1.9352692023,7.7434253083
H,0,2.4858010651,-2.7834873421,5.8460412114
C,0,1.2938453642,-0.8533728048,8.3856367647
H,0,0.3320440944,1.0621835665,8.1301138585
H,0,2.2801624442,-2.7714080982,8.323651897
H,0,1.2030787297,-0.8440130872,9.4687911661
C,0,3.3999795944,-4.3969023118,0.7914067612
O,0,3.8284390357,-3.7318602685,1.794126423
O,0,2.1557245095,-4.3450177548,0.5273422873
C,0,4.3320922619,-5.2461049031,-0.0258093637
H,0,4.3828607946,-6.244461038,0.4264572341
H,0,3.9607531975,-5.3547979625,-1.0477936015
H,0,5.3403621564,-4.8243604081,-0.0277463415
C,0,-0.3995125444,-3.8733416876,2.9715597155
O,0,0.3972989257,-4.6713101596,3.5036388947
O,0,0.007921795,-2.896752897,2.2211979581

C,0,-1.8985528113,-3.9853106599,3.1624863173
H,0,-2.2787993465,-3.0742569913,3.6382939997
H,0,-2.3906946893,-4.0750411431,2.1878046564
H,0,-2.1530308376,-4.8491483548,3.7799498081
C,0,-0.743157315,-7.0116034112,5.2802814639
C,0,-1.3045899136,-7.8715125169,5.9246472584
H,0,-0.2559650508,-6.2420842008,4.7024813769
C,0,-1.9659594312,-8.8875126279,6.6835863052
C,0,-2.1024462756,-8.7640776886,8.0801871453
C,0,-2.4908922446,-10.0290036708,6.0463968854
C,0,-2.7473114998,-9.7565180598,8.814987275
H,0,-1.6989430288,-7.8862635922,8.5758307069
C,0,-3.1343553501,-11.0165646074,6.7888006348
H,0,-2.3869613051,-10.1290440834,4.9701834375
C,0,-3.2650737805,-10.8848262408,8.1736895236
H,0,-2.8459807713,-9.6492298582,9.8920430828
H,0,-3.5343981124,-11.8924729192,6.2847635836
H,0,-3.767044929,-11.6574845013,8.7499827052

MCu-TS-DP1

E(RB+HF-LYP)= -1610.74415714 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.407957 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.42881073 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.011695749,0.1534197553,0.0016385749
C,0,0.0051149309,0.1473139322,1.3822006944
N,0,1.1810430706,0.0923835271,2.0584273478
C,0,2.4090535149,0.0472245622,1.450317124
C,0,2.3853777818,0.0568201325,0.0457022749
C,0,1.2034015747,0.110232066,-0.6874191124
N,0,1.0440020881,0.2101108466,3.4482051026
C,0,1.6153715712,-0.7253297118,4.1833349543
O,0,2.3126341975,-1.7354699263,3.7886696056
Cu,0,3.6295064937,-1.6853685459,2.3947512998
H,0,-0.9638999929,0.1956602378,-0.5155919843
H,0,-0.8820685122,0.1931144163,2.0009274236
H,0,3.5887933715,0.7200665677,2.2216924095
H,0,3.3407169116,0.0214241012,-0.4704276467
H,0,1.220050481,0.1237028534,-1.7735073065
C,0,1.3769338845,-0.6039026591,5.6568863204
C,0,0.5049465938,0.362693877,6.1827297466
C,0,2.0419879748,-1.4754701309,6.5308751922
C,0,0.3085342586,0.4558585236,7.5585046013

H,0,-0.0119380197,1.0337771292,5.5057654552
C,0,1.8414436956,-1.3805606414,7.9078086653
H,0,2.712108056,-2.2227144193,6.1206621512
C,0,0.9757135937,-0.4151604834,8.4251500206
H,0,-0.3683963874,1.2073509211,7.9563962456
H,0,2.3622199968,-2.0612434182,8.5761252627
H,0,0.8190679627,-0.3416895839,9.4982737279
C,0,5.1236843726,0.5689706812,3.4624940876
O,0,4.3685099399,1.3284017327,2.7334696118
O,0,5.0136915654,-0.6774278687,3.5175935375
C,0,6.1651464511,1.2783110255,4.2847036014
H,0,6.843098215,0.5604324307,4.7490787197
H,0,6.7264921665,1.9776652718,3.6572475838
H,0,5.6656485513,1.8646170822,5.0648944538
C,0,4.2351573172,-3.2303421268,0.6744001104
O,0,3.2040137034,-3.4646663485,1.3825733223
O,0,4.894464102,-2.1624085179,0.9181264479
C,0,4.695072467,-4.1925977385,-0.3830356389
H,0,5.2146920849,-3.6643023111,-1.1863531964
H,0,5.4011504471,-4.8993470416,0.0707551576
H,0,3.8527475823,-4.7630823498,-0.7822798295
C,0,1.1216021873,-5.6320846738,0.1927434293
C,0,0.4763661861,-6.4492717375,-0.4274199671
H,0,1.7021779089,-4.9144550601,0.7420181518
C,0,-0.2835736747,-7.4183969141,-1.1548982582
C,0,-1.2848607686,-7.0131379989,-2.0587031464
C,0,-0.0414485383,-8.7944823736,-0.9763074089
C,0,-2.0220571855,-7.9622726482,-2.7631351328
H,0,-1.475489902,-5.9533315992,-2.1986712622
C,0,-0.7829630062,-9.7366338757,-1.6854371462
H,0,0.728705971,-9.1111176237,-0.2795469597
C,0,-1.7744445102,-9.3251453941,-2.57989754
H,0,-2.7926709338,-7.6372444491,-3.4570440445
H,0,-0.5869683694,-10.795387607,-1.5384657995
H,0,-2.3517491401,-10.0627103718,-3.1308887583

MCu-INT1

E(RB+HF-LYP)= -1610.77427402 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.435034 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.45984257 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.1233796851,0.2313324835,0.0812219276
C,0,-0.0667280661,0.1661251891,1.4535707258

N,0,1.1281248965,0.0849911197,2.1169828785
C,0,2.3261472702,0.0712034425,1.4511380496
C,0,2.2691668818,0.1359626418,0.0508533625
C,0,1.0709934947,0.2160964333,-0.6470560535
N,0,0.9304766543,0.0486233334,3.4934286588
C,0,1.9300450393,-0.1785554655,4.3256036527
O,0,3.1776462532,-0.3708122918,4.0900360212
Cu,0,4.0248058735,-0.0618454775,2.3992288139
H,0,-1.0915240922,0.2932480293,-0.4035126751
H,0,-0.9350019426,0.1743974524,2.0980963966
H,0,5.5667619447,1.7115397727,0.7006220014
H,0,3.2123468483,0.1195684324,-0.48593404
H,0,1.0599170861,0.2655422671,-1.731913468
C,0,1.521941042,-0.2263728159,5.7693041246
C,0,0.1754366521,-0.1597642361,6.1607433115
C,0,2.5145634565,-0.3448661921,6.7529966251
C,0,-0.1677566719,-0.2096508666,7.5099216633
H,0,-0.5919186924,-0.0698224364,5.4004853252
C,0,2.1674445617,-0.3943275587,8.1026332794
H,0,3.5540717003,-0.3972670716,6.4493399012
C,0,0.8264943717,-0.326915277,8.4854615037
H,0,-1.2135714055,-0.1586029972,7.8017667793
H,0,2.9461478939,-0.4857918366,8.855217704
H,0,0.5562300651,-0.3664525084,9.5376044462
C,0,5.0191319868,3.0872537724,1.8947524443
O,0,5.5910298081,2.7076560006,0.7522368002
O,0,4.5431013303,2.3008806981,2.7068642569
C,0,5.0207425476,4.5811312896,2.0787611757
H,0,4.5703721966,4.8424401082,3.0369708857
H,0,6.0468246116,4.9618003302,2.0332154542
H,0,4.4615521159,5.0559557946,1.2647119518
C,0,6.3369131394,-0.4661278694,1.6827207339
O,0,5.9579983968,-0.7395044468,2.8550147732
O,0,5.4704116477,0.0052825734,0.8512742415
C,0,7.7633170092,-0.649624704,1.2437355255
H,0,7.797442412,-1.194974236,0.2953066706
H,0,8.2129856173,0.3355438059,1.0688230243
H,0,8.3460071469,-1.1781760535,2.0007231946
C,0,8.1571357629,-2.0126583687,4.8727706062
C,0,9.1108173128,-2.489729599,5.4485503661
H,0,7.3167063948,-1.5896740273,4.3548031633
C,0,10.2352956209,-3.0527604437,6.1298918536
C,0,10.5950709862,-4.3991355861,5.9249440179
C,0,10.9984216801,-2.2700706851,7.0182101497

C,0,11.6901197166,-4.9436370409,6.5919258098
H,0,10.0082339213,-5.0069504026,5.2428177564
C,0,12.0919696785,-2.822931426,7.6808323757
H,0,10.7237314828,-1.2321361589,7.1801766059
C,0,12.4416521678,-4.1593277991,7.4707588946
H,0,11.9571485698,-5.9839114078,6.4257298842
H,0,12.672992648,-2.2087186735,8.3636807746
H,0,13.2948170002,-4.5875739331,7.9900486329

MCu-TS-DP2

E(RB+HF-LYP)= -1610.74581926 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.407259 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.43166027 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.0713392671,0.2617045443,-0.1249647051
C,0,0.0452771141,0.1994064873,1.2474983732
N,0,1.1998563233,0.1167658618,1.9762193989
C,0,2.4374085727,0.048063764,1.3961340588
C,0,2.4622192233,0.1089115253,-0.0075087341
C,0,1.3110989153,0.2242431566,-0.7740278059
N,0,0.9260299529,0.0458817082,3.3482880616
C,0,1.8318398384,0.4761713745,4.1983544661
O,0,3.0296620215,0.891183609,3.9447722341
Cu,0,4.0973184995,0.011016908,2.4660521788
H,0,-0.8630931812,0.3349154001,-0.6703356773
H,0,-0.859421733,0.2135544163,1.8402224239
H,0,3.431666155,0.0538620542,-0.4893976897
H,0,1.3689483585,0.2739443893,-1.8576221897
C,0,1.4049131409,0.4741757699,5.6335081382
C,0,0.0749322877,0.2261181101,6.0093430318
C,0,2.3608790199,0.7310337128,6.6269010711
C,0,-0.2876139442,0.2347240304,7.3540540856
H,0,-0.664239368,0.0292491935,5.2409446215
C,0,1.9939373378,0.740171814,7.9722952866
H,0,3.3878385525,0.9182703158,6.3330651719
C,0,0.6700279969,0.4924206619,8.3396856056
H,0,-1.3199055888,0.0429488261,7.634981779
H,0,2.7435897571,0.938661,8.7337314968
H,0,0.3840448371,0.5001762994,9.3883614751
C,0,5.0807608082,-1.4380238013,1.2999421701
C,0,4.7175425873,-2.4577302434,0.70455874
C,0,4.2848023851,-3.6216494472,0.0093552693
C,0,4.2258098223,-3.6358885275,-1.4009208224

C,0,3.9065276939,-4.7806512728,0.7206490029
C,0,3.8027772566,-4.7777888726,-2.0749917499
H,0,4.520731761,-2.7474945688,-1.951237568
C,0,3.4793264928,-5.9156945678,0.0377134427
H,0,3.9533397639,-4.773226615,1.8053770044
C,0,3.4272582276,-5.9184987185,-1.3593353389
H,0,3.7643265285,-4.7793517292,-3.1609793253
H,0,3.1879259855,-6.8017379186,0.5951254965
H,0,3.0964932717,-6.8079024964,-1.8889296994
C,0,6.8648104086,-0.0213967564,3.4377063567
O,0,7.2572642383,-0.5296072587,2.333568676
O,0,5.6543629165,0.1723948943,3.7474414093
C,0,7.9278392728,0.3306461826,4.4539487223
H,0,8.8813887578,0.5380384407,3.9625228113
H,0,7.6126797647,1.1866273995,5.0559540445
H,0,8.0682833927,-0.5243324769,5.1272836841
H,0,6.2125440837,-0.9326843015,1.7443632563
H,0,3.7532284144,2.4329943471,3.8146850894
C,0,4.8655235529,3.2378042148,2.4882831376
O,0,4.2115810779,3.3015154257,3.6451683773
O,0,4.8605009271,2.2568341014,1.7523719654
C,0,5.6149910646,4.5079301275,2.1774360669
H,0,6.1190027936,4.4210376365,1.2140812206
H,0,4.9248719421,5.3585117133,2.1607680394
H,0,6.3529804584,4.7044905139,2.9632747854

MCu-INT2

E(RB+HF-LYP)= -1610.75715870 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.415255 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.44455292 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.0192120609,0.1511136784,-0.0025470062
C,0,0.0118038663,0.0939423362,1.370494165
N,0,1.177920066,0.038801061,2.0841448048
C,0,2.4095531054,-0.0000092789,1.4881769548
C,0,2.4144226312,0.0524562324,0.0844890933
C,0,1.2508666612,0.1361283484,-0.6676700601
N,0,0.9201818889,-0.0321932218,3.4578853241
C,0,1.8506786311,0.3311204584,4.3095506303
O,0,3.069735625,0.6889629651,4.0639515782
Cu,0,4.1237716258,-0.0266013342,2.5372802789
H,0,-0.9237280196,0.2013144798,-0.5359411742
H,0,-0.8851393814,0.0897477363,1.9750484654

H,0,3.3808072994,0.0134359436,-0.4056495678
H,0,1.2935600534,0.1790747382,-1.7523034906
C,0,1.4271629809,0.3242910928,5.7455643351
C,0,0.0774978576,0.207235734,6.1145210591
C,0,2.4027087132,0.4415332897,6.7463682358
C,0,-0.2858133401,0.2080130783,7.4590077946
H,0,-0.6757261419,0.1187465838,5.339701657
C,0,2.0352884991,0.4414014908,8.0917468801
H,0,3.4454750555,0.5244910132,6.4599821763
C,0,0.6914563122,0.32552452,8.4519205477
H,0,-1.3335848098,0.120254542,7.7341305169
H,0,2.7998902426,0.5293965999,8.8591086846
H,0,0.4055232798,0.3273333212,9.5005884051
C,0,5.2338131591,-0.9680215272,1.2382987928
C,0,5.8449387157,-1.5660114618,0.3529690499
C,0,6.5641674291,-2.255692859,-0.6754939795
C,0,7.4375512742,-1.5574154578,-1.5343934011
C,0,6.4109314151,-3.6457638791,-0.8533668416
C,0,8.1327309471,-2.2303961297,-2.5365295954
H,0,7.561199507,-0.4862500783,-1.4036972929
C,0,7.1086328838,-4.3114796039,-1.8588097164
H,0,5.7408273863,-4.1913508313,-0.1954979857
C,0,7.9716563111,-3.6084592719,-2.7035103371
H,0,8.8027945273,-1.6772682636,-3.1897031378
H,0,6.9791425253,-5.3835957004,-1.9829160959
H,0,8.5155198316,-4.1310860196,-3.4859643357
C,0,6.8733387025,-0.317909234,4.1048196685
O,0,7.511827291,-0.6675741961,3.0025166127
O,0,5.6545774784,-0.1461952977,4.1714919779
C,0,7.7815205164,-0.1559346109,5.2938442584
H,0,7.2223194247,0.232692102,6.1457848896
H,0,8.2202971771,-1.1256784192,5.5555616847
H,0,8.607285255,0.5191710044,5.0463430954
H,0,6.8429657098,-0.7989339411,2.2678951159
H,0,3.865635229,2.1632780374,4.331516595
C,0,5.0496067644,3.1131787408,3.1843997402
O,0,4.3563315362,3.0327646598,4.3169626402
O,0,5.0710521614,2.2294563386,2.3341603777
C,0,5.8069750164,4.4091432107,3.0552946576
H,0,6.3507001355,4.4333974669,2.1100080118
H,0,5.1124019258,5.2547992634,3.1066039547
H,0,6.509839723,4.5146295692,3.8892887018

MCu-TS-RE

E(RB+HF-LYP)= -1610.71720377 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.375392 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.40620846 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.0261872446,0.0446559839,-0.0365811794
O,0,-0.0088448777,0.0076092983,1.2849614345
O,0,0.9955875798,0.0408041732,-0.7290413842
C,0,-1.408515645,0.0772322109,-0.6255039529
H,0,-1.3551787115,0.2922179332,-1.6934995804
H,0,-1.8879130855,-0.8974485046,-0.4758073997
H,0,-2.0226669705,0.8266734841,-0.1170384793
H,0,0.9475272214,-0.0328014334,1.5877914727
H,0,4.5441198136,-1.1366211399,-1.6599486151
C,0,4.5047657992,0.6718539899,-2.3004877668
O,0,4.947926148,-0.5642386548,-2.3911832822
O,0,3.728203206,1.0668462335,-1.4220341384
C,0,5.0207944073,1.5834986106,-3.3791303522
H,0,4.6873033343,2.6067657003,-3.2024937006
H,0,6.1146247221,1.5451432563,-3.4123923202
H,0,4.6534144619,1.2414370714,-4.3533862048
C,0,7.3291766398,-0.0500656826,2.1529602341
C,0,6.6463960469,-1.2224746048,1.9405619441
N,0,5.3289587378,-1.2240881758,1.5818653794
C,0,4.5934661435,-0.0650030022,1.5117870328
C,0,5.2854198032,1.1457729127,1.735952692
C,0,6.6352187301,1.1693661379,2.0262799347
N,0,4.7761167598,-2.5094766176,1.4650277877
C,0,4.0375715542,-2.7503350113,0.3991682156
O,0,3.7184714949,-1.9296331638,-0.5436139998
Cu,0,2.9649029274,-0.0343996848,0.1950716363
C,0,2.8286591982,-0.1090634623,2.1169815111
C,0,2.852837634,-0.2507340506,3.3667742201
H,0,8.3797642542,-0.086750022,2.4176150435
H,0,7.0868170425,-2.2079500954,2.0253785395
H,0,4.7115599311,2.0658366961,1.6816356483
H,0,7.1522483502,2.1138048859,2.1709870441
C,0,3.5120369929,-4.1512764501,0.3060155956
C,0,3.8322851729,-5.1297403377,1.261097221
C,0,2.6828597571,-4.4941505402,-0.7710582156
C,0,3.3285942825,-6.422655464,1.1387645925
H,0,4.4763039022,-4.8653284492,2.0925077905
C,0,2.1806320218,-5.7899140627,-0.8917937502
H,0,2.4408400954,-3.7348845383,-1.5066595954

C,0,2.5012589174,-6.7573478926,0.0622973166
H,0,3.58236294,-7.1723762274,1.8838154354
H,0,1.5380439466,-6.0432892941,-1.731095846
H,0,2.1099946998,-7.7672410733,-0.031221315
C,0,2.9316494324,-0.4247246061,4.7589541459
C,0,2.9896311727,0.6907999751,5.6359455242
C,0,2.9423930181,-1.7264008459,5.3278382563
C,0,3.054150424,0.5054516098,7.0116214738
H,0,2.9783748366,1.6923594402,5.2157926895
C,0,3.0054711849,-1.8938027121,6.7055219885
H,0,2.9037764366,-2.5871900985,4.667066467
C,0,3.0617822078,-0.7837478402,7.5572198649
H,0,3.0976394181,1.372042899,7.6668310105
H,0,3.0123795178,-2.8980969424,7.1219818904
H,0,3.1098877905,-0.9218395041,8.6338937318

MCu-RE-P

E(RB+HF-LYP)= -1610.77357751 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.429406 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.46089452 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.412471953,-0.0198933584,0.0126308043
O,0,-0.2932896284,0.876897663,0.9880139145
O,0,0.4824766892,-0.8162786142,-0.2730883127
C,0,-1.7360620079,0.029090958,-0.6904324353
H,0,-1.7585729222,-0.7058498023,-1.4954566691
H,0,-2.5415899041,-0.1761343766,0.0233040652
H,0,-1.9051180884,1.0325951676,-1.0952765004
H,0,0.5878767853,0.7398423412,1.4175685742
H,0,4.5158414682,-0.9852703122,-0.9722990137
C,0,4.0665850327,0.7935943897,-1.541203923
O,0,4.8741347528,-0.2447065058,-1.5759152849
O,0,3.0249977004,0.8374116788,-0.8764861918
C,0,4.5341194547,1.9536520762,-2.3793891393
H,0,3.747273478,2.7049871475,-2.4605152519
H,0,5.4157282906,2.4028313952,-1.9065746249
H,0,4.8350691619,1.6109731195,-3.3740206102
C,0,7.8413292862,-0.1733528069,1.2552271344
C,0,7.1198743498,-1.3368360168,1.2056167137
N,0,5.7932256021,-1.3842687896,1.5094890299
C,0,5.1119787829,-0.2360932978,1.971296959
C,0,5.8604238986,0.9819327178,2.0085453222
C,0,7.1852071084,1.0244492182,1.6603364609

N,0,5.21425925,-2.6629722291,1.5971705145
C,0,4.224920601,-2.8944253295,0.7569394328
O,0,3.755650255,-2.0941763013,-0.1443089236
Cu,0,2.3739653617,-0.5977581094,0.6338815554
C,0,3.7840501571,-0.3086826785,2.330819215
C,0,2.5398909944,-0.3038217397,2.6136066361
H,0,8.8912189831,-0.1851211073,0.9871439566
H,0,7.53988726,-2.2943142449,0.9225638518
H,0,5.3350744687,1.8724338948,2.3379038737
H,0,7.733440112,1.9604025909,1.7069496906
C,0,3.5898393948,-4.2464462332,0.8837544091
C,0,3.9512622473,-5.1387310989,1.9061879105
C,0,2.6206907939,-4.6368181228,-0.0513007278
C,0,3.3518589772,-6.3935469641,1.9891995615
H,0,4.6994472715,-4.8356574734,2.6302032162
C,0,2.0219392852,-5.8940936847,0.0342617482
H,0,2.3485715181,-3.9470439169,-0.842832075
C,0,2.3851031101,-6.7757086112,1.05414302
H,0,3.6377427337,-7.0750680801,2.7863653881
H,0,1.2727838284,-6.1853020794,-0.6976496487
H,0,1.9181245017,-7.7551311727,1.1217277056
C,0,1.6702201836,-0.364138935,3.7830360693
C,0,1.9858377043,0.3711974608,4.9438021525
C,0,0.4891710978,-1.129815899,3.7726354783
C,0,1.1454973725,0.3375019769,6.0539050979
H,0,2.8936322535,0.9678758755,4.9616913481
C,0,-0.3382245698,-1.1739425105,4.8933836697
H,0,0.2377540522,-1.7042164945,2.8849788375
C,0,-0.0187594378,-0.4361313485,6.0358808862
H,0,1.4032967487,0.9131756176,6.9394281697
H,0,-1.2385195403,-1.7827228567,4.8720007724
H,0,-0.6713017858,-0.4622527638,6.9043907538

The structures shown in Scheme 11 in the main text

BiCu-TS-DP1

E(RB+HF-LYP)= -2265.15421039 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -2264.728741 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.24956378 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.2998874876,-0.251990163,-0.4404940289
C,0,0.2182715906,0.0971457907,0.8928404454
N,0,1.3294929615,0.1072986697,1.672329973
C,0,2.5842235141,-0.2099964544,1.2218575689
C,0,2.6597407627,-0.5636656214,-0.1357939042
C,0,1.5476784877,-0.5886939385,-0.9723448549
N,0,1.1069732423,0.5863886807,2.9733417173
C,0,1.486625766,-0.2021530192,3.9614838025
O,0,2.0719744145,-1.347730569,3.8839088635
Cu,0,3.5740320377,-1.6927257287,2.7160219234
H,0,-0.6013505466,-0.2532149671,-1.0438467247
H,0,-0.6985949197,0.3874530732,1.3902261341
H,0,3.8004716386,0.603767715,1.9003609074
H,0,3.6375838233,-0.8260167278,-0.5297714295
H,0,1.6432454021,-0.8593945796,-2.0201587515
C,0,1.1425268806,0.2904840839,5.3339328631
C,0,0.3681848223,1.4455253103,5.5269631458
C,0,1.6017220773,-0.4227879461,6.4505720978
C,0,0.0638084875,1.879502249,6.8151100137
H,0,0.0104531915,1.992789034,4.6618076162
C,0,1.2907516883,0.0128124954,7.7388003557
H,0,2.1973762312,-1.3162809608,6.2992003531
C,0,0.5230281939,1.1639798965,7.9250787374
H,0,-0.5366894204,2.7747195251,6.9543384096
H,0,1.6478188186,-0.5493716309,8.597757799
H,0,0.2802744427,1.5017722719,8.9293755365
C,0,5.0535374063,0.7635128016,3.3871293994
O,0,4.5578417727,1.2737682962,2.2993520505
O,0,4.745405629,-0.3652094986,3.8231007004
C,0,6.0275510233,1.6363062321,4.1299127163
H,0,6.5466210434,1.060221551,4.8976027932
H,0,6.7478238875,2.0755141584,3.4330681749
H,0,5.4809843778,2.4606394844,4.6033265068
C,0,5.3877170351,-3.1459459602,6.7759509333
O,0,6.2696328312,-3.0142278185,5.862870329
O,0,4.2661199771,-3.6536873241,6.4390195577

C,0,5.6473054073,-2.686985236,8.1797622766
H,0,4.9807896101,-3.1919146235,8.8825608848
H,0,6.6914233984,-2.8629778944,8.4521330538
H,0,5.4614506745,-1.6071747966,8.2353781921
Cu,0,4.947910932,-3.7725916555,4.5426367618
C,0,2.7919869857,-4.5449646557,2.7730697063
O,0,2.7529759454,-3.4400042242,2.1648662162
O,0,3.5199841091,-4.822362104,3.7815949147
C,0,1.8744728637,-5.6500508873,2.2943326341
H,0,2.4103175414,-6.6030268072,2.2656259142
H,0,1.0504570464,-5.7550471778,3.010227681
H,0,1.4615044798,-5.4175553433,1.3111234766
C,0,6.0622399198,-2.9651778749,1.9282482139
O,0,5.1915457914,-2.0851823171,1.6692196867
O,0,6.0844031776,-3.7206473205,2.9539040242
C,0,7.1996373425,-3.1380651863,0.9458016375
H,0,8.1411203636,-2.865806475,1.4363739585
H,0,7.279737882,-4.1889564169,0.6491373451
H,0,7.0556801944,-2.5123932164,0.0635183269
C,0,7.526953372,-6.6336416557,2.2728507975
C,0,7.9456577369,-7.6414607545,1.7461983932
C,0,8.4396359254,-8.8312275195,1.1249468146
C,0,9.7550658676,-9.2720115405,1.3681170776
C,0,7.6175694346,-9.5778278148,0.2585689913
C,0,10.2317113114,-10.4300262507,0.7580071742
H,0,10.391606489,-8.6996206606,2.0360548068
C,0,8.102881344,-10.7343980145,-0.3473425222
H,0,6.6026745324,-9.2413715151,0.0695310682
C,0,9.4093506755,-11.1641052805,-0.1005763508
H,0,11.2482508295,-10.7607705184,0.9534618061
H,0,7.4593446166,-11.3022448904,-1.0139415434
H,0,9.7846138892,-12.0669896342,-0.5747654113
H,0,7.1559183977,-5.7315523819,2.7172130575

BiCu-INT1

E(RB+HF-LYP)= -2265.18913207 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -2264.757032 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.28388483 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.1269676611,-0.0618676781,0.1141591629
C,0,-0.0820671075,-0.0634053341,1.4875430462
N,0,1.1081300026,-0.0503942357,2.1637206474
C,0,2.3150268607,-0.0204385963,1.5171177204

C,0,2.2687530479,-0.0223484285,0.113830721
C,0,1.077128479,-0.0427459002,-0.5980573417
N,0,0.893019374,-0.034220005,3.5420954241
C,0,1.8860487003,-0.2753152788,4.3783870108
O,0,3.1315630882,-0.4731798332,4.1447569945
Cu,0,4.0407410683,-0.0211620819,2.4786175916
H,0,-1.0904817518,-0.0717003902,-0.3835469837
H,0,-0.9564947604,-0.0756951639,2.1239304098
H,0,6.332048584,-1.3172967465,3.6264758728
H,0,3.2168442542,0.0070347414,-0.4098924891
H,0,1.0785786589,-0.0339515902,-1.683836835
C,0,1.4678792135,-0.326646502,5.8196649495
C,0,0.1210650376,-0.4487703908,6.1950559611
C,0,2.4518909333,-0.2628054082,6.816602027
C,0,-0.2315715184,-0.5045267127,7.5420571334
H,0,-0.6393042696,-0.5056860901,5.4243014726
C,0,2.095812248,-0.3143495398,8.1637683058
H,0,3.4911969337,-0.168262814,6.5226338609
C,0,0.7540078733,-0.4363297608,8.5306698687
H,0,-1.2771626271,-0.6049723631,7.8215564084
H,0,2.8669554669,-0.2580612059,8.9276133232
H,0,0.477033787,-0.4798262542,9.5808681358
C,0,5.7553669608,-2.8197956339,2.6127880568
O,0,6.5772521766,-2.2802795483,3.5049998531
O,0,4.8460509872,-2.2006286589,2.0660996671
C,0,6.0550777825,-4.2689230455,2.336026015
H,0,5.3542286307,-4.6649557746,1.6001013864
H,0,7.0809651131,-4.3729082573,1.9661028805
H,0,5.9833214598,-4.8469534834,3.2639881934
C,0,6.1572148999,1.2629051033,4.3138925802
O,0,5.7632798648,0.2585968309,3.6447307956
O,0,5.615224539,2.4090394408,4.2833460479
C,0,7.3508383006,1.0780836247,5.2243667197
H,0,8.1765621739,0.6234319664,4.6671534668
H,0,7.6725251249,2.0285352055,5.6527653267
H,0,7.081603063,0.3893506558,6.0337652676
C,0,5.4311247318,1.8917731867,0.7103705791
O,0,5.0954704595,0.691748018,0.9056129567
O,0,5.1631937292,2.8777368672,1.474393213
C,0,6.1939643556,2.2237765815,-0.5540164738
H,0,5.5030570187,2.7041193595,-1.2574573345
H,0,6.9954185144,2.9366737641,-0.3409118239
H,0,6.6029276061,1.3213558442,-1.0127254489
Cu,0,4.1307318205,2.8485276103,3.1043137214

C,0,2.3367150948,3.5660033607,-0.9196645497
C,0,2.4329380347,3.6525762671,-2.1250468291
C,0,2.5442544293,3.7617146939,-3.5473641993
C,0,3.2417953976,2.789243298,-4.2903149333
C,0,1.9569233965,4.8470906963,-4.226543901
C,0,3.3481817734,2.9038194676,-5.6745936565
H,0,3.6965109002,1.9497193725,-3.7726701075
C,0,2.0678636747,4.9533865085,-5.6110410835
H,0,1.4193431628,5.5999767094,-3.6580985472
C,0,2.7626307952,3.9842820108,-6.3393158628
H,0,3.8905108042,2.1477579721,-6.2360667008
H,0,1.6114237279,5.7964270249,-6.122790079
H,0,2.8481415304,4.0711286363,-7.4190871549
C,0,1.8833798583,3.4321432944,3.5606534497
O,0,2.3173753795,3.3704927884,2.3584295817
O,0,2.7227225886,3.2116392588,4.4942530068
C,0,0.4436653301,3.7154964539,3.8648083746
H,0,0.3633775977,4.3725107468,4.7352930363
H,0,-0.0578258756,4.1617920677,3.0033822733
H,0,-0.0454989136,2.7660902318,4.1142717255
H,0,2.2364574927,3.5053536518,0.1464990061

BiCu-TS-DP2

E(RB+HF-LYP)= -2265.16164664 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -2264.731259 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.25666712 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.0423456697,-0.166150339,-0.0259934085
C,0,-0.0130905814,-0.177723069,1.3473225791
N,0,1.1665613027,-0.0919233325,2.0388762046
C,0,2.3749425687,0.032380191,1.4071575917
C,0,2.3439982521,0.0498273064,0.0025808523
C,0,1.1659917137,-0.054309182,-0.7240650023
N,0,0.9341784928,-0.1149943519,3.41119903
C,0,1.9327754264,-0.2193300565,4.2657674969
O,0,3.1972400193,-0.2968822858,4.0615114095
Cu,0,4.0966995786,0.0548188042,2.3674905658
H,0,-0.9969987087,-0.2429309315,-0.5349403247
H,0,-0.8913509934,-0.2532104502,1.9737252238
H,0,6.3726097011,-1.5474929228,3.1679407032
H,0,3.2963940336,0.1491211272,-0.5058605758
H,0,1.1789211438,-0.0491576197,-1.8104313944
C,0,1.4969768476,-0.2604209708,5.7035348073

C,0,0.1506526953,-0.4208898209,6.0660744784
C,0,2.464551264,-0.131353705,6.7109982564
C,0,-0.2175319077,-0.4544105512,7.4095680224
H,0,-0.5970194061,-0.5191716024,5.2874572227
C,0,2.0924325091,-0.161431136,8.0555753642
H,0,3.5031728331,-0.0018895517,6.4278798675
C,0,0.7509966391,-0.3242068011,8.4089838842
H,0,-1.2629209706,-0.5833571268,7.6780246961
H,0,2.8514476592,-0.0587202692,8.8268303012
H,0,0.4614590763,-0.3506498736,9.4564337747
C,0,5.626249421,-2.9243381116,2.0926372381
O,0,6.5799071022,-2.4952385969,2.9117147927
O,0,4.6703809715,-2.2361758361,1.7470696674
C,0,5.8449248135,-4.3391377395,1.6245385806
H,0,5.0070032447,-4.6661553676,1.0073880164
H,0,6.7728221197,-4.395152433,1.0439028718
H,0,5.9585685044,-5.0071397863,2.4849508071
C,0,6.3012822626,0.8413896254,4.3044434378
O,0,5.8654655678,0.0181052551,3.4331199378
O,0,5.8548366628,2.0061989495,4.4877161412
C,0,7.4428766522,0.3731953039,5.1827070612
H,0,8.2854102137,0.0588184487,4.5568388296
H,0,7.7682623628,1.1631715276,5.861510627
H,0,7.1224350746,-0.49864609,5.764365648
C,0,5.8358535867,1.8949779355,0.8826067051
O,0,5.1468964728,0.8376330053,0.8235279741
O,0,5.8134953109,2.7579524699,1.8176367824
C,0,6.7686511182,2.2004835143,-0.2738922205
H,0,6.3416822984,3.0189512503,-0.8658836344
H,0,7.7382236579,2.5396316329,0.1028417144
H,0,6.9012079315,1.3269163482,-0.9151766953
Cu,0,4.5370598828,2.9110324316,3.30487493
C,0,3.1088758884,3.7885093438,2.109493699
C,0,3.1215088544,4.3034221512,0.9859565727
C,0,3.142523057,4.8865907744,-0.3093844001
C,0,2.7096196478,4.1493986333,-1.4329461906
C,0,3.5981928357,6.2108239262,-0.4877526346
C,0,2.7347405128,4.7263838178,-2.6989701036
H,0,2.3556627147,3.1327541461,-1.2925562201
C,0,3.6222193529,6.7766388073,-1.7586099476
H,0,3.9291551813,6.7771352031,0.3773073933
C,0,3.1908908531,6.0377774483,-2.8645625526
H,0,2.3992908553,4.1545051402,-3.559689922
H,0,3.9760458318,7.7954988281,-1.8887135526

H,0,3.2095201166,6.4840455916,-3.8551937718
C,0,2.3757779371,3.6876324951,5.1252479031
O,0,1.558841396,3.8471644618,4.1639399069
O,0,3.5949852346,3.3505401284,4.9908809654
C,0,1.8739340321,3.9077642237,6.5328968166
H,0,2.5434776119,4.5964192824,7.0584986699
H,0,0.8573085616,4.304716948,6.526210631
H,0,1.8912439549,2.9546340037,7.0727144624
H,0,2.2632488556,3.7671888011,3.083612088

BiCu-INT2

E(RB+HF-LYP)= -2265.17389360 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -2264.739372 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.27054948 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.6319454885,0.1779817652,-0.4993611669
C,0,0.5150107529,0.1803403692,0.8697682823
N,0,1.6152364843,0.0887806019,1.6803678482
C,0,2.8866028034,0.0064907649,1.1797404098
C,0,3.0059818613,0.0104191889,-0.2197129764
C,0,1.90935651,0.0899012366,-1.0658011628
N,0,1.2460691975,0.1478228881,3.023356609
C,0,2.1104116089,-0.1523340553,3.9723668777
O,0,3.3437047179,-0.496881874,3.8921959398
Cu,0,4.4790550397,-0.2144454411,2.3213141207
H,0,-0.2642741853,0.2466077343,-1.1064441049
H,0,-0.4248246905,0.254228846,1.3996253371
H,0,6.411138747,-2.0626217258,3.4252681731
H,0,4.0094963946,-0.0436514498,-0.6257881036
H,0,2.0377241261,0.0889548372,-2.1443999156
C,0,1.5352494907,-0.0781911105,5.360589085
C,0,0.1676483259,0.1460093407,5.5874102984
C,0,2.3921926844,-0.2293231986,6.460751626
C,0,-0.3288517629,0.2144776399,6.8882418988
H,0,-0.4961573425,0.2626876727,4.7385297971
C,0,1.8926756803,-0.160414347,7.761585587
H,0,3.4484689643,-0.3970293657,6.2828098362
C,0,0.5314092484,0.0608315352,7.9800235913
H,0,-1.3903828423,0.3829950447,7.0507547089
H,0,2.5682249246,-0.2802496568,8.604612148
H,0,0.1413666436,0.111189564,8.9933876927
C,0,5.602460426,-3.3848159844,2.3237913385
O,0,6.4976760811,-3.0448423299,3.2452606108

O,0,4.8317289955,-2.5858726284,1.8005678552
C,0,5.6306304596,-4.8543086531,1.9924999925
H,0,4.9072849522,-5.0782081848,1.2072894208
H,0,6.635191822,-5.1466815902,1.6681907568
H,0,5.3944083262,-5.4392633457,2.8887300286
C,0,6.4855431725,0.3563922382,4.5147085087
O,0,6.0966116467,-0.4311497749,3.5920532625
O,0,6.1154961063,1.5572489251,4.6422051447
C,0,7.4617275239,-0.1950475143,5.5311672123
H,0,8.3576776763,-0.5638323466,5.0194108228
H,0,7.7459708858,0.567424714,6.2581435982
H,0,7.0083406229,-1.0462828207,6.0516083449
C,0,6.5690432515,1.4091978349,1.0534464215
O,0,5.7880764051,0.423008146,0.9206357618
O,0,6.5484954771,2.2689038797,1.9901749819
C,0,7.6180924392,1.6185795262,-0.0220851085
H,0,7.2293636079,2.3415106269,-0.7502558483
H,0,8.5325504451,2.0365822782,0.4068668529
H,0,7.8367092427,0.6832748031,-0.5420798596
Cu,0,5.0777921808,2.5516200616,3.3110174287
C,0,3.9984219317,3.5216023819,2.0397025473
C,0,3.4228667383,4.1842943587,1.1796726069
C,0,2.7720449591,4.9755187306,0.1795848453
C,0,1.4909940442,4.6336732185,-0.2972917848
C,0,3.4094598656,6.1176154743,-0.3462999366
C,0,0.869273917,5.4141236521,-1.2695611356
H,0,0.9954785606,3.7530697637,0.1005286278
C,0,2.7816726138,6.8907160436,-1.3200863127
H,0,4.3964439355,6.3863298973,0.0182398285
C,0,1.5103632852,6.5438691612,-1.7845494316
H,0,-0.1194895193,5.1394318115,-1.6277278304
H,0,3.2860260269,7.7681941054,-1.7163371226
H,0,1.0224760712,7.1502473118,-2.5429443786
C,0,2.8031583464,3.5495315511,5.1310250574
O,0,2.0575650726,3.9447011445,4.1211136364
O,0,3.9510309882,3.0976298999,5.0123715997
C,0,2.1407316729,3.6921438966,6.4702607514
H,0,1.8129475695,4.7273887974,6.6124558414
H,0,1.2502868734,3.055044042,6.5034013566
H,0,2.8289706582,3.4021990642,7.2641495499
H,0,2.5769402375,3.8535259161,3.2686354752

BiCu-INT2'

E(RB+HF-LYP)= -2265.17273999 Hartree (6-31G*/SDD in dioxane)

Sum of electronic and thermal Free Energies= -2264.742940 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -5152.26937487 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.4824032305,0.163194147,-0.3431501564
C,0,0.4898523491,0.120127755,1.0305432846
N,0,1.6597606027,0.0657930613,1.7395137593
C,0,2.8868830574,0.019852678,1.1253370915
C,0,2.8767057211,0.0629050239,-0.2794673488
C,0,1.7050955008,0.1422570064,-1.0211096906
N,0,1.4043937003,0.0189101979,3.1081213062
C,0,2.3656592839,0.3138577259,3.9637556332
O,0,3.5950446475,0.60095819,3.7402721362
Cu,0,4.5747322802,-0.017997586,2.1563162327
C,0,5.745063713,-1.0011507421,0.7128085049
C,0,5.6591363453,-2.2367705699,0.6829580736
H,0,-0.4671524631,0.213008184,-0.8649712904
H,0,-0.4014723357,0.1288334896,1.6428578536
H,0,3.8327715085,0.033707555,-0.7893471336
H,0,1.7391122249,0.1805774408,-2.1061443538
C,0,1.9305335828,0.317955297,5.4005871629
C,0,0.581132607,0.1963391235,5.7675298651
C,0,2.9025163165,0.450960782,6.4026864896
C,0,0.2146238155,0.2044273564,7.1115923662
H,0,-0.1703394772,0.0968084749,4.9926650807
C,0,2.53226938,0.45840929,7.7472016706
H,0,3.9435756326,0.5473459184,6.1141989407
C,0,1.1884743226,0.335029737,8.1058692596
H,0,-0.8334216435,0.1111584518,7.384488032
H,0,3.2946672225,0.5602038542,8.5151692303
H,0,0.8999648416,0.3422320998,9.1539071129
C,0,5.5156040417,-3.6515979143,0.646738026
C,0,4.6927750223,-4.2596111878,-0.3265557459
C,0,6.1952213103,-4.4679180727,1.5769591209
C,0,4.5556088954,-5.6437419208,-0.3633742039
H,0,4.1737536594,-3.6319439378,-1.0443181833
C,0,6.0505470498,-5.8512143555,1.5323801435
H,0,6.8306034125,-4.0016614904,2.3237633492
C,0,5.2324132445,-6.4416272059,0.5642631267
H,0,3.9205309209,-6.1031745975,-1.1158625757
H,0,6.5763790184,-6.471818068,2.2526487298
H,0,5.1226156773,-7.5222936788,0.5324645922
Cu,0,6.7200418558,0.6048928078,0.1154171161
C,0,6.5694351349,2.0375751013,-1.8004570099

O,0,5.9098582074,0.9441819711,-1.7451351767
O,0,7.3022917768,2.3440880209,-0.8065994642
C,0,6.4813720387,2.9179292433,-3.0154090611
H,0,7.0374737465,3.8458686955,-2.8687800448
H,0,6.8887978231,2.3791369474,-3.8779480909
H,0,5.4320384122,3.1447144441,-3.2324918514
C,0,7.3843513123,0.5965948689,2.9232217906
O,0,7.7613678753,0.9000727132,1.7428152733
O,0,6.2191469351,0.2635560844,3.2721939079
C,0,8.4583051905,0.6431612702,3.9920590697
H,0,8.0187760298,0.6369435465,4.9912473655
H,0,9.1048715346,-0.2363617584,3.8824758933
H,0,9.0845782239,1.5305694269,3.8617948054
H,0,7.9281698844,-1.2468198617,-2.3277029648
C,0,7.4448321722,-1.0332729667,-4.1630164134
O,0,7.3780659925,-1.7064677622,-3.0284805043
O,0,8.1985012028,-0.0748733652,-4.3501774956
C,0,6.5020733046,-1.5440395435,-5.2170954416
H,0,5.4763006261,-1.274935912,-4.9384732985
H,0,6.7415324133,-1.1003575275,-6.1843323495
H,0,6.550231316,-2.6354402435,-5.2779858085
C,0,9.7294061368,0.3587440284,-1.3563785025
O,0,8.827759223,-0.459467544,-1.1235837739
O,0,9.9844675192,0.8198825199,-2.5648235137
C,0,10.6398455245,0.875204545,-0.2816466167
H,0,11.3309839898,0.0728479866,0.0047065323
H,0,11.2153026054,1.7376314769,-0.6222469447
H,0,10.0423337568,1.1311965908,0.597175208
H,0,9.31722646,0.449927076,-3.2213418193

BiCu-INT3

E(RB+HF-LYP)= -1806.97035116 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.650356 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.90752291 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.6938342937,0.791246268,4.4692873994
C,0,-1.7815155156,0.6021545467,3.6504013232
N,0,-1.6362713019,0.2531996053,2.334719016
C,0,-0.4033637829,0.0992468869,1.7511639426
C,0,0.7075137449,0.2968932289,2.5888608906
C,0,0.5868682113,0.6300986656,3.9319018924
N,0,-2.8778572038,0.1413856403,1.7140342557
C,0,-2.9832384665,-0.5106345853,0.5708442992

O,0,-2.0674592905,-1.0544399523,-0.143455304
Cu,0,-0.1960130165,-0.4698981462,-0.1261564689
C,0,1.6355343013,0.4907635027,-0.5042266337
C,0,1.5674082161,1.6861352817,-0.8242677425
H,0,-0.8551398204,1.0606931399,5.507355633
H,0,-2.8087524014,0.7087384658,3.9711135796
H,0,1.6938981409,0.1830710944,2.153035546
H,0,1.4700563068,0.7691498444,4.5486505147
C,0,-4.388965056,-0.6347351116,0.0587048005
C,0,-5.4903793481,-0.1636532929,0.7905520775
C,0,-4.6047975263,-1.2426441673,-1.1864865753
C,0,-6.780855987,-0.2990017092,0.2834189018
H,0,-5.3238935706,0.3057417604,1.7533261504
C,0,-5.8980661117,-1.3785419126,-1.6901718327
H,0,-3.7508297088,-1.6050330722,-1.7479928167
C,0,-6.9894076741,-0.9074773806,-0.9576933599
H,0,-7.6267757899,0.0689207478,0.8583432681
H,0,-6.0530216674,-1.8522053389,-2.6560787597
H,0,-7.9974825933,-1.013724813,-1.3501719607
C,0,1.4557524805,3.0648350072,-1.1558494155
C,0,1.73750633,4.0557521228,-0.1899466025
C,0,1.0674655111,3.4619531887,-2.4541095816
C,0,1.6309746788,5.4037633802,-0.5177707058
H,0,2.0383969616,3.7500611069,0.8074111766
C,0,0.9618532095,4.8126141652,-2.7709805441
H,0,0.8525180125,2.7002929374,-3.1974541414
C,0,1.2431116528,5.7847919303,-1.806043148
H,0,1.8497323094,6.1601334032,0.2309016382
H,0,0.661007026,5.1100470362,-3.7716474037
H,0,1.1604902681,6.8385950544,-2.0580104694
Cu,0,2.7627890963,-1.1196921207,-0.39118889
C,0,4.4271503369,-1.8708107424,1.1464578096
O,0,3.8903549556,-0.7174758802,1.274614396
O,0,4.043715115,-2.6040054963,0.1801303649
C,0,5.4971919387,-2.3254424602,2.0979767604
H,0,5.6809530712,-3.3967364838,1.9946753507
H,0,6.4243198701,-1.7823599593,1.8780306178
H,0,5.2129371033,-2.0880865676,3.1275978791
C,0,0.9593795358,-1.8903678766,-2.4889197825
O,0,2.142763001,-1.9801432894,-2.0193096333
O,0,-0.0474946401,-1.4242952981,-1.8892829619
C,0,0.7684479983,-2.3839232482,-3.9084752179
H,0,-0.2723459856,-2.6630189447,-4.0856480084
H,0,1.032237427,-1.571445428,-4.5976832463

H,0,1.4304549061,-3.2278574832,-4.1177110442

BiCu-TS-RE-T

E(RB+HF-LYP)= -1806.91840635 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.598954 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.85851509 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.1685542177,0.7158934237,4.3745721745
C,0,-1.1965549174,0.7398080497,3.4568311176
N,0,-1.0213978259,0.2899835582,2.1826299851
C,0,0.2036384893,-0.1545599784,1.7488692916
C,0,1.2711885312,-0.1586215003,2.662472671
C,0,1.0904776328,0.2459655947,3.9775000531
N,0,-2.1461876968,0.4376134745,1.375749386
C,0,-2.4632534838,-0.5726458271,0.5705695367
O,0,-1.8277295597,-1.6655758459,0.3836738823
Cu,0,0.1691418099,-1.578778607,0.2785040086
C,0,0.8529017935,0.3487134085,-0.0224158541
C,0,0.3840717062,1.4737261066,-0.3722413548
H,0,-0.3548285358,1.0708104953,5.3820052622
H,0,-2.1965712332,1.0944572973,3.6703467319
H,0,2.2523386951,-0.4487885532,2.2971927986
H,0,1.9190250012,0.2198389736,4.6785620427
C,0,-3.7419939901,-0.3760280015,-0.1873117024
C,0,-4.5837543117,0.7231657165,0.0465898965
C,0,-4.1023055309,-1.3203399469,-1.1597067008
C,0,-5.7611595587,0.8728942176,-0.6832213973
H,0,-4.3076347546,1.4517749366,0.8004887785
C,0,-5.2819286777,-1.1679722416,-1.8874043748
H,0,-3.450188181,-2.1693845148,-1.3333368556
C,0,-6.11399677,-0.071478023,-1.6517237145
H,0,-6.4073109913,1.7261613058,-0.4939811744
H,0,-5.5508954767,-1.9057731724,-2.6387270704
H,0,-7.0339547813,0.0468467033,-2.2185137001
C,0,-0.090627946,2.7424077701,-0.7172930072
C,0,0.4914097834,3.9088668378,-0.1506988745
C,0,-1.1506691919,2.8886983068,-1.6526333725
C,0,0.0261183079,5.1654421676,-0.5123226257
H,0,1.305839538,3.8016021313,0.5589415523
C,0,-1.6059831706,4.1536715492,-1.9957963806
H,0,-1.6006180127,2.0011010903,-2.0851544076
C,0,-1.0222720229,5.295338857,-1.4318988104
H,0,0.4802531156,6.0516040985,-0.0777456167

H,0,-2.420079145,4.2549172342,-2.707923163
H,0,-1.3820473952,6.2822555584,-1.7088671282
Cu,0,2.3367717191,-0.798784339,-0.6127070594
C,0,4.6426500257,0.1795733289,-0.1145594463
O,0,4.2406566549,-0.2876118702,0.9681751795
O,0,3.9353667598,0.1366401075,-1.200937781
C,0,6.011373332,0.8187724767,-0.2512014371
H,0,6.6533376073,0.1763343142,-0.8653858361
H,0,5.9334238128,1.7842059002,-0.7618495447
H,0,6.4739286901,0.9527474914,0.7290328688
C,0,1.8783410815,-3.5326553748,-0.933691847
O,0,2.7743635345,-2.6547475217,-1.1209013458
O,0,0.7451147678,-3.3167128735,-0.3879405687
C,0,2.1791224513,-4.9505496888,-1.3586049778
H,0,2.5532876779,-5.5064631877,-0.4897529226
H,0,1.2709966,-5.4483794383,-1.7077388751
H,0,2.946819447,-4.9684060184,-2.1349254435

BiCu-RE-P-T

E(RB+HF-LYP)= -1806.96454724 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.642427 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.90078591 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.0204976716,0.0192270184,0.0148364286
C,0,0.016937694,0.0167664215,1.3928688164
N,0,1.1734681563,0.0072036969,2.1064696047
C,0,2.3952306199,-0.0012903503,1.4824970334
C,0,2.4249047522,0.0156659841,0.0822497683
C,0,1.2486796955,0.0146166569,-0.6539676851
N,0,1.0071072485,-0.1302483984,3.4950100447
C,0,1.3777797217,0.920048584,4.2185021272
O,0,1.9057375532,2.0072931628,3.7936167607
Cu,0,3.7381633019,1.9497099012,2.9509070768
C,0,3.6206417466,0.0589409823,2.3126632443
C,0,4.0884476709,-0.949454646,3.022717334
H,0,-0.9238641788,0.0269010986,-0.5175469846
H,0,-0.8791917112,0.012169672,1.9992224876
H,0,3.3962680219,0.0476682308,-0.4024599907
H,0,1.2879342041,0.0150741912,-1.7388331585
C,0,1.1244423364,0.7750532474,5.6897946276
C,0,0.5317105938,-0.378726741,6.2294374581
C,0,1.4938170214,1.8203476926,6.5479609326
C,0,0.3190292489,-0.4819181962,7.6026518967

H,0,0.2424557809,-1.186225682,5.5657452451
C,0,1.2771242462,1.7147343471,7.9218400432
H,0,1.9457346838,2.7110939073,6.1249808848
C,0,0.6906951132,0.5641397951,8.4526253895
H,0,-0.1388581142,-1.3790799092,8.0110629895
H,0,1.5664072739,2.5317672671,8.577501874
H,0,0.5227068672,0.4814669593,9.5233433608
C,0,4.9440134983,-1.6472960889,3.8696307566
C,0,6.1699118716,-2.2011256232,3.3890882357
C,0,4.5803181676,-1.876673848,5.2315715518
C,0,6.9835472337,-2.9325708902,4.2418997856
H,0,6.4608593699,-2.0238235448,2.3585122752
C,0,5.4180100456,-2.6041542256,6.062946345
H,0,3.6426341427,-1.4768252014,5.6044621877
C,0,6.6197574338,-3.1407859689,5.5791927989
H,0,7.9172920258,-3.3405514197,3.8638675747
H,0,5.132351811,-2.7616039309,7.0996474131
H,0,7.2653514678,-3.7142435606,6.2379867057
Cu,0,5.4363827835,1.0053852465,1.6460781658
C,0,6.4395229104,0.0424508219,-0.5094430088
O,0,5.4054891934,0.659241027,-0.8450088099
O,0,6.8073991426,-0.0572118815,0.7261245016
C,0,7.3384582425,-0.6144864926,-1.5364055812
H,0,8.2870532984,-0.0674285516,-1.5922920441
H,0,7.5736023487,-1.6411035707,-1.2366522341
H,0,6.8674838448,-0.6130233421,-2.5216760303
C,0,5.8680751342,3.6621891596,2.5393697131
O,0,6.417753991,2.693968901,1.9222306715
O,0,4.7159525274,3.625153802,3.0801011842
C,0,6.6287569909,4.964631675,2.6042523937
H,0,6.3788856556,5.55910099,1.7164006352
H,0,6.3415240307,5.5367209804,3.4894361008
H,0,7.7063753277,4.7853915955,2.5980693873

The structures shown in Scheme 12 in the main text

BiCu-INT3-S

E(RB+HF-LYP)= -1806.94893963 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.628353 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.89077197 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.7600295891,2.6191618121,3.6403860939
C,0,-1.8141036284,2.4279241805,2.7778798748
N,0,-1.7397134541,1.5214565266,1.7572937444
C,0,-0.597559537,0.8128287739,1.5104897043
C,0,0.4754577625,0.975110153,2.3941158966
C,0,0.4017572292,1.8631873771,3.4619155365
N,0,-2.936098296,1.4491130761,1.0417257499
C,0,-3.2167782409,0.2933428088,0.4727301554
O,0,-2.4514711681,-0.7432575581,0.3804631633
Cu,0,-0.5924630838,-0.4254916785,0.0284471495
C,0,1.1904132535,0.0713921539,-0.4235307161
C,0,1.8622774332,0.940364476,-0.9916931425
H,0,-0.8590458694,3.3421229961,4.4425511001
H,0,-2.7616010714,2.944728512,2.8457255037
H,0,1.37402437,0.3925720185,2.2321715434
H,0,1.2457760703,1.9745596244,4.1357500262
C,0,-4.58322711,0.1780063056,-0.1164972008
C,0,-5.5655657815,1.1533685333,0.1189016985
C,0,-4.8908498727,-0.932158823,-0.916759045
C,0,-6.8320019389,1.0201079126,-0.4444483164
H,0,-5.3271572825,2.0073224842,0.7429704722
C,0,-6.1612269559,-1.0622053046,-1.4759782376
H,0,-4.1282718411,-1.6819441263,-1.0955385621
C,0,-7.1335701841,-0.0876348693,-1.2423980576
H,0,-7.587053379,1.779051637,-0.2580630499
H,0,-6.3909055967,-1.9245090484,-2.0960026193
H,0,-8.1236428004,-0.1902641035,-1.6788083066
C,0,2.6725147585,1.9284478687,-1.6191291238
C,0,3.3092601778,2.9252615671,-0.8480758016
C,0,2.84383697,1.9356531951,-3.0204394213
C,0,4.0916817995,3.8971990574,-1.4645246053
H,0,3.1820616644,2.920891681,0.2302704332
C,0,3.6258183184,2.9145675287,-3.6267096246
H,0,2.3580474899,1.1692220311,-3.616752721
C,0,4.251923614,3.8965728171,-2.8533734165
H,0,4.5784982496,4.6584216544,-0.8608332074

H,0,3.7499306785,2.9108108808,-4.7062015362
H,0,4.8632317629,4.6574763353,-3.3309041986
Cu,0,2.1441353809,-1.5641690907,0.1205518705
C,0,3.7866451961,-2.0476369442,1.8658047222
O,0,2.9065168726,-1.1565214986,2.095639613
O,0,3.8029795338,-2.6653838399,0.7567397518
C,0,4.840557408,-2.3519371012,2.9061261881
H,0,5.0500019425,-3.4251127939,2.9333066519
H,0,5.771288113,-1.840340951,2.6302919425
H,0,4.532670813,-2.0040568855,3.8951452969
C,0,0.1103987383,-2.6099828893,-1.7055955074
O,0,1.2055981108,-2.82675413,-1.1299736993
O,0,-0.7195810335,-1.6726763353,-1.4403104286
C,0,-0.3191818331,-3.5516281186,-2.8156745427
H,0,-1.1964241343,-4.1193518969,-2.4857277824
H,0,-0.61410806,-2.9757186284,-3.6984347714
H,0,0.4851646775,-4.2432144765,-3.0704323149

BiCu-Dis-TS1

E(RB+HF-LYP)= -1806.94894461 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.625407 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.89104772 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.0083734706,0.0018718639,0.0106063118
C,0,-0.0085322447,0.0071866078,1.3860418102
N,0,1.1603087974,0.0006776398,2.0946897732
C,0,2.3738896405,-0.0752326128,1.4724577522
C,0,2.3951938845,-0.0536805877,0.0735497334
C,0,1.2161744761,-0.0054735987,-0.6628017558
N,0,0.9336967332,0.0680427542,3.4704281277
C,0,1.8669504835,0.6544668644,4.1939100351
O,0,3.0333257869,1.0491612416,3.8017735898
Cu,0,3.9634279375,-0.0826561019,2.5648867584
C,0,4.7564205537,-1.391558969,1.4363049477
C,0,4.7850135191,-2.5970471522,1.1575252141
H,0,-0.955539103,0.0151146322,-0.5172632006
H,0,-0.8996815134,0.0379987464,1.9978851578
H,0,3.3524160999,-0.074412823,-0.4332738727
H,0,1.2536901907,0.0107273432,-1.7477500064
C,0,1.5185255126,0.8966658299,5.6244822246
C,0,0.2062325394,0.7280899127,6.0948323879
C,0,2.5231724111,1.3070080506,6.5131934143
C,0,-0.0910500696,0.960755763,7.43511047

H,0,-0.5695668761,0.4174390956,5.4040402322
C,0,2.2195882146,1.540871191,7.8535858386
H,0,3.5347679361,1.4353407757,6.1444935092
C,0,0.9139551851,1.3680531693,8.3176229826
H,0,-1.1088870055,0.8285243737,7.7919516673
H,0,3.0038809674,1.856596214,8.5361611113
H,0,0.6785362248,1.5512163781,9.3627261978
C,0,4.8187433329,-3.9740379636,0.7968067459
C,0,4.0788696584,-4.4386057526,-0.3122943385
C,0,5.5783790284,-4.8970924369,1.5473727374
C,0,4.1010935278,-5.7870177751,-0.6557328573
H,0,3.4962902806,-3.7300735552,-0.8933061825
C,0,5.5901387325,-6.2441654287,1.1971326588
H,0,6.1508035867,-4.5428045292,2.3992955115
C,0,4.8541193143,-6.6933027389,0.0967379323
H,0,3.5295516374,-6.1334743031,-1.5125392839
H,0,6.1772795631,-6.9465079227,1.7824568401
H,0,4.8683688085,-7.7454510969,-0.1743290946
Cu,0,6.1384970679,-0.3516101759,0.5224029074
C,0,6.4712321501,0.3924365902,-1.7913245981
O,0,5.2731925157,0.3643198716,-1.3718133792
O,0,7.4351476791,0.0460850298,-1.0359862525
C,0,6.7724755865,0.8460791791,-3.2030922087
H,0,7.4317363275,1.7209322112,-3.1758170365
H,0,7.3084343724,0.0542157806,-3.7383022677
H,0,5.8574038244,1.0971791442,-3.7439830038
C,0,6.7024536236,0.2464762666,3.3445802271
O,0,7.1122687838,0.3305227817,2.1615535387
O,0,5.5026140814,0.0017758564,3.7231872614
C,0,7.6945995948,0.4625088243,4.4727576235
H,0,7.7394385465,-0.4381003596,5.0948383638
H,0,8.6868169661,0.6873434605,4.0789498951
H,0,7.3520340244,1.2839058362,5.1104563346

BiCu-Dis-INT1

E(RB+HF-LYP)= -1806.95015142 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.626253 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.89312574 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-1.1129781118,3.8392340705,2.3333805747
C,0,-2.1338087891,3.3182105531,1.5717414692
N,0,-2.0158600434,2.0971764255,0.9702100272
C,0,-0.8595740591,1.3758782187,1.0452841391

C,0,0.176702576,1.8719171337,1.8406614634
C,0,0.0581959471,3.0945834906,2.4935229278
N,0,-3.1840523598,1.7213558032,0.3060437284
C,0,-3.4383708784,0.427080052,0.2776387651
O,0,-2.6525500409,-0.5287110521,0.6584845311
Cu,0,-0.8169159288,-0.3370703575,0.1845681323
C,0,0.9289337247,0.0332730527,-0.3637256027
C,0,1.9740370935,0.5883744611,-0.770127213
H,0,-1.2454012411,4.8084002815,2.801089202
H,0,-3.0878267458,3.8022130756,1.412007847
H,0,1.0880905867,1.2943619695,1.9234819244
H,0,0.8765354633,3.4679979513,3.1010161193
C,0,-4.7804604249,0.035608156,-0.2353741702
C,0,-5.7931969345,0.9893339621,-0.4288058594
C,0,-5.0341366854,-1.313274708,-0.526266147
C,0,-7.0379251605,0.59603841,-0.9127280828
H,0,-5.5960512027,2.0300604262,-0.1972251188
C,0,-6.2834067942,-1.7012083548,-1.0074731785
H,0,-4.2471465873,-2.0440324291,-0.3771981588
C,0,-7.2863721561,-0.7492137381,-1.2019821578
H,0,-7.8178543817,1.3380565278,-1.0602389527
H,0,-6.4727580284,-2.7469859915,-1.2332655915
H,0,-8.2600397928,-1.0536326486,-1.5766871585
C,0,2.9504635434,1.5113212724,-1.2842042792
C,0,4.3146990816,1.1697270648,-1.3406303936
C,0,2.5375136208,2.7808509933,-1.7371547465
C,0,5.2420982373,2.0855136394,-1.8335462631
H,0,4.6272374645,0.1880906059,-0.9959656
C,0,3.4727170611,3.6858663186,-2.231795566
H,0,1.4839120832,3.0433120538,-1.7027810535
C,0,4.8268674815,3.3422911763,-2.2801399868
H,0,6.2935746014,1.8140486945,-1.8722115435
H,0,3.1443494653,4.6609337907,-2.581993175
H,0,5.5541389145,4.0509974807,-2.6671450541
Cu,0,2.2235056816,-1.3660478399,-0.0424797442
C,0,4.3612485497,-1.8669201922,1.2863591152
O,0,3.566428097,-1.3606204194,2.1029865415
O,0,4.0768097856,-2.0415935203,0.0361979338
C,0,5.7461667219,-2.3207573212,1.7210333106
H,0,5.860964567,-3.3953642014,1.5382794906
H,0,6.5137430456,-1.810344079,1.1278392884
H,0,5.9096755711,-2.1150657921,2.781401244
C,0,-0.101681929,-3.0678346714,-0.4159264388
O,0,1.0490370763,-3.0127805252,0.0766802251

O,0,-0.9142715147,-2.0869681072,-0.5979629749
C,0,-0.6538061988,-4.4188426941,-0.8340819993
H,0,-1.0355044762,-4.365433118,-1.8585923602
H,0,0.1177129979,-5.1871049479,-0.7631592689
H,0,-1.4951889776,-4.6825558739,-0.1834031718

BiCu-TS-RE-S

E(RB+HF-LYP)= -1806.94279385 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.620091 Hartree (6-31G*/SDD in dioxane)
E(RB+HF-LYP)= -4693.886151 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.983330879,2.9886960996,3.1925206095
C,0,-1.839053517,2.71830979,2.1471003237
N,0,-1.6726301161,1.6147790571,1.3634871092
C,0,-0.6159460579,0.774921876,1.5552147167
C,0,0.2501743996,1.0040005869,2.6302616018
C,0,0.066787625,2.1033603384,3.4598324672
N,0,-2.673440331,1.4461500653,0.4012422694
C,0,-3.1895291371,0.2195864836,0.3428844975
O,0,-2.7474228237,-0.8414893562,0.9230047636
Cu,0,-0.7878100078,-0.921698498,0.7209503608
C,0,0.6482603349,0.0585490953,0.0624626267
C,0,1.4951406948,0.798660095,-0.5043706367
H,0,-1.1488315577,3.8766182094,3.7920367975
H,0,-2.7004317352,3.3202523755,1.8894697266
H,0,1.088574713,0.3319582251,2.7718494373
H,0,0.7501307335,2.2837880341,4.2833230675
C,0,-4.4167629246,0.0892005843,-0.4945882625
C,0,-5.1328468057,1.2160980521,-0.9294185664
C,0,-4.8627173941,-1.1928428114,-0.8499751857
C,0,-6.2727020344,1.0594001537,-1.7139305019
H,0,-4.7904804781,2.2053515618,-0.6469507092
C,0,-6.0048564651,-1.3441516182,-1.6343066898
H,0,-4.3061242333,-2.0591888638,-0.5097396245
C,0,-6.7111530995,-0.2200134794,-2.0680142731
H,0,-6.8229895495,1.935402731,-2.0464896998
H,0,-6.3416962818,-2.3399010374,-1.9091942037
H,0,-7.6021586315,-0.3395594609,-2.6787510599
C,0,2.1149602437,1.9761733159,-1.0497690168
C,0,3.4503102179,1.954949782,-1.4935963939
C,0,1.373105175,3.1724891353,-1.1390421426
C,0,4.0322146068,3.1146857405,-2.0007600289
H,0,4.0058902018,1.0233169757,-1.4425307419

C,0,1.9644627624,4.3235752862,-1.6508458908
H,0,0.3362918854,3.18436114,-0.8150791446
C,0,3.2952506727,4.298778534,-2.0795791414
H,0,5.063851323,3.0920777985,-2.3408388387
H,0,1.386608226,5.2413867573,-1.719031753
H,0,3.7534471115,5.199337343,-2.4795256124
Cu,0,2.1487611744,-1.1216054288,-0.3413370666
C,0,4.6638261497,-1.3913075402,0.1268564221
O,0,4.1418545531,-1.2015577382,1.2421852816
O,0,3.9983591057,-1.3702350187,-0.9838841333
C,0,6.1523425689,-1.6774178389,-0.001708584
H,0,6.2992525419,-2.7029705248,-0.3610359013
H,0,6.6083079203,-1.0091653117,-0.7406277436
H,0,6.655785458,-1.5614099148,0.960977141
C,0,0.340525215,-3.4560384778,-0.0730681766
O,0,1.515685606,-3.0260336412,-0.1757998096
O,0,-0.7073674653,-2.7662657543,0.1983335675
C,0,0.0924146005,-4.9347738047,-0.2999939335
H,0,-0.5059215199,-5.0599730123,-1.2101241563
H,0,1.0334900321,-5.4761548024,-0.4091705838
H,0,-0.4873160527,-5.3507978483,0.5299840255

BiCu-RE-P-S

E(RB+HF-LYP)= -1807.01966965 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1806.696669 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -4693.95973958 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.0727379213,0.1039063251,0.0359947228
C,0,-0.0375308726,0.1357780941,1.4154731683
N,0,1.1345029303,0.0588230219,2.0935474214
C,0,2.3360264027,-0.0528699977,1.4313730663
C,0,2.3235314219,-0.0884481844,0.0272126794
C,0,1.1287404083,-0.0171251615,-0.6717343902
N,0,1.0584266767,-0.050542859,3.4847399239
C,0,1.2715731323,1.0703974823,4.1652661582
O,0,1.587766944,2.225519479,3.7133282579
Cu,0,2.5772268758,2.9125183674,2.2897707283
C,0,3.5387188457,-0.0941144427,2.189761193
C,0,4.3559169875,-0.3304588866,3.1206388963
H,0,-1.0293940845,0.1697020537,-0.4694356041
H,0,-0.9168941274,0.2077165821,2.0423266187
H,0,3.2763144934,-0.1654896933,-0.4822923558
H,0,1.129187852,-0.0544133087,-1.7562105802

C,0,1.075267215,0.9461481971,5.6439032542
C,0,0.5056734317,-0.2041408767,6.2124546208
C,0,1.4631638305,2.0043895206,6.4774993268
C,0,0.3307614299,-0.2917622867,7.5915673107
H,0,0.199149522,-1.0195751661,5.5664785962
C,0,1.2886005375,1.9121823787,7.857810246
H,0,1.9017420259,2.8925575288,6.036329361
C,0,0.7223378849,0.7654505284,8.417987082
H,0,-0.1142370372,-1.1845216638,8.0228391698
H,0,1.5960406144,2.7364589196,8.495612239
H,0,0.5846923348,0.6953748258,9.4938371745
C,0,4.8538378275,-0.9696838117,4.3088040141
C,0,6.1075782588,-0.637532845,4.854123374
C,0,4.0517634701,-1.9438044552,4.9406994525
C,0,6.5512212918,-1.2785417376,6.008218476
H,0,6.7070446102,0.1260147785,4.3688177286
C,0,4.508771614,-2.5781899821,6.0909743378
H,0,3.0792346526,-2.1847415035,4.5231506824
C,0,5.7584647985,-2.2491259454,6.6256235049
H,0,7.5193710927,-1.0190530346,6.4272779427
H,0,3.8890799754,-3.3287082373,6.5738722201
H,0,6.1114662873,-2.7477407281,7.5243758309
Cu,0,5.1627180693,0.9953846946,1.8916205501
C,0,7.7670681211,0.8385616487,1.8403800058
O,0,7.4222648569,-0.094152302,1.0959230577
O,0,6.9323876244,1.5833817761,2.499012026
C,0,9.2360485815,1.1938674175,2.026088272
H,0,9.4447357077,2.1500770203,1.5306283715
H,0,9.4709029028,1.3237234028,3.0880444016
H,0,9.8803539246,0.4241995627,1.594738258
C,0,4.3471049791,3.2552785789,0.1160650125
O,0,4.9243936728,2.1472890366,0.2669272779
O,0,3.453945484,3.7574467577,0.8836044253
C,0,4.7556344511,4.11215047,-1.0650425086
H,0,5.5277142111,4.8167567712,-0.7308772087
H,0,5.1799147756,3.4972207075,-1.8616181288
H,0,3.9099618814,4.694749176,-1.4393902851

CP

E(RB+HF-LYP)= -1806.94893322 Hartree (6-31G*/SDD in dioxane singlet)
E(RB+HF-LYP)= -1806.94873239 Hartree (6-31G*/SDD in dioxane triplet SP)

C ,-0.763848, 2.645398, 3.608052
C ,-1.816990, 2.453290, 2.744533

N ,-1.744904, 1.538720, 1.731089
C ,-0.605901, 0.822974, 1.492507
C , 0.465937, 0.985168, 2.377445
C , 0.394121, 1.881581, 3.438431
N ,-2.940537, 1.464317, 1.014466
C ,-3.225959, 0.302529, 0.460277
O ,-2.464690,-0.738271, 0.380331
Cu,-0.604323,-0.433702, 0.027768
C , 1.173816, 0.066404,-0.431854
C , 1.859185, 0.923764,-1.002559
H ,-0.860893, 3.374738, 4.404667
H ,-2.762162, 2.975051, 2.806582
H , 1.361530, 0.395820, 2.223071
H , 1.236834, 1.992762, 4.113911
C ,-4.593318, 0.184579,-0.125863
C ,-5.575027, 1.160939, 0.107990
C ,-4.902868,-0.929160,-0.920404
C ,-6.842994, 1.025110,-0.451243
H ,-5.335010, 2.017362, 0.728053
C ,-6.174683,-1.061532,-1.475786
H ,-4.140834,-1.679857,-1.097818
C ,-7.146497,-0.086057,-1.243669
H ,-7.597733, 1.784582,-0.265773
H ,-6.405969,-1.926432,-2.091564
H ,-8.137781,-0.190717,-1.676824
C , 2.676087, 1.905799,-1.631424
C , 3.314067, 2.902753,-0.861710
C , 2.850865, 1.907521,-3.032186
C , 4.101362, 3.870017,-1.479252
H , 3.183943, 2.902226, 0.216291
C , 3.637453, 2.882061,-3.639608
H , 2.363975, 1.140792,-3.627197
C , 4.264838, 3.864355,-2.867717
H , 4.589253, 4.631528,-0.876831
H , 3.764156, 2.874635,-4.718757
H , 4.879815, 4.621737,-3.346131
Cu, 2.168394,-1.530890, 0.115250
C , 3.801939,-2.010195, 1.876111
O , 2.900600,-1.152655, 2.137522
O , 3.843115,-2.581786, 0.741204
C , 4.856558,-2.339509, 2.908938
H , 5.052166,-3.415888, 2.921469
H , 5.793640,-1.838662, 2.635304
H , 4.556379,-2.001540, 3.903602

C , 0.106695,-2.663341,-1.639381
O , 1.200496,-2.859571,-1.055656
O ,-0.724393,-1.716293,-1.408908
C ,-0.322719,-3.641862,-2.717444
H ,-1.212914,-4.183353,-2.378639
H ,-0.597187,-3.096337,-3.625862
H , 0.475100,-4.353440,-2.935016

MECP

E(RB+HF-LYP)= -1806.94893389 Hartree (6-31G*/SDD in dioxane singlet)
E(RB+HF-LYP)= -1806.94891247 Hartree (6-31G*/SDD in dioxane triplet)

C ,-0.764062, 2.645760, 3.608103
C ,-1.817238, 2.453535, 2.744579
N ,-1.745242, 1.538831, 1.731165
C ,-0.606074, 0.823130, 1.492703
C , 0.465747, 0.985558, 2.377497
C , 0.393935, 1.882004, 3.438452
N ,-2.940650, 1.464320, 1.014513
C ,-3.226142, 0.302480, 0.460214
O ,-2.464857,-0.738491, 0.380236
Cu,-0.604013,-0.433414, 0.027607
C , 1.175020, 0.066380,-0.432085
C , 1.858738, 0.925051,-1.003087
H ,-0.861143, 3.375053, 4.404640
H ,-2.762435, 2.975304, 2.806549
H , 1.361343, 0.396358, 2.223000
H , 1.236711, 1.993202, 4.113958
C ,-4.593377, 0.184557,-0.126045
C ,-5.575149, 1.160817, 0.107778
C ,-4.902802,-0.929252,-0.920564
C ,-6.843092, 1.024863,-0.451447
H ,-5.335149, 2.017225, 0.727864
C ,-6.174603,-1.061751,-1.475955
H ,-4.140699,-1.679865,-1.097885
C ,-7.146502,-0.086350,-1.243861
H ,-7.597901, 1.784274,-0.265982
H ,-6.405799,-1.926695,-2.091706
H ,-8.137765,-0.191101,-1.677026
C , 2.675948, 1.906810,-1.631829
C , 3.313951, 2.903407,-0.861858
C , 2.850819, 1.908085,-3.032460
C , 4.101274, 3.870572,-1.479360
H , 3.183731, 2.902701, 0.216144

C , 3.637447, 2.882530,-3.639816
H , 2.363949, 1.141194,-3.627292
C , 4.264706, 3.864867,-2.867850
H , 4.589114, 4.632148,-0.876925
H , 3.764165, 2.875096,-4.718990
H , 4.879605, 4.622288,-3.346254
Cu, 2.167927,-1.532768, 0.116416
C , 3.802179,-2.009882, 1.875952
O , 2.900797,-1.152212, 2.136766
O , 3.843268,-2.582055, 0.741397
C , 4.856757,-2.338917, 2.908940
H , 5.052353,-3.415275, 2.921467
H , 5.793744,-1.838026, 2.635274
H , 4.556443,-2.000931, 3.903529
C , 0.106989,-2.663301,-1.639637
O , 1.201079,-2.859206,-1.055903
O ,-0.724351,-1.716419,-1.409006
C ,-0.322211,-3.641889,-2.717534
H ,-1.212415,-4.183301,-2.378677
H ,-0.596778,-3.096314,-3.625860
H , 0.475593,-4.353456,-2.935158

The structures shown in Scheme 13 in the main text

Cyc-R

E(RB+HF-LYP)= -1381.09530701 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1380.815712 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2824.69744035 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.1026666344,-0.2505339677,-0.0850794044
C,0,0.0298257519,-0.2445732181,1.293652687
N,0,1.1383548435,-0.1303367341,2.0678787632
C,0,2.3834064548,-0.0290409513,1.489055794
C,0,2.4838215105,-0.0213804044,0.0894115365
C,0,1.3512752738,-0.133516526,-0.7029667585
N,0,0.9417234983,-0.2585655452,3.437594156
C,0,1.3212031999,0.8066454562,4.1650311886
O,0,1.8253110746,1.8770475373,3.7251611138
Cu,0,3.9098318816,1.9235933724,3.0945587977
C,0,3.5312108027,0.067285844,2.3188789622
C,0,4.5994622166,0.0190611567,2.9614786911
H,0,-0.812237135,-0.3387223409,-0.6599000719
H,0,-0.8920726962,-0.3315784465,1.8531020912
H,0,3.4720816853,0.0720820104,-0.3456338652
H,0,1.4381814665,-0.131821991,-1.7845128023
C,0,1.0780004884,0.6500793586,5.6381016819
C,0,0.4576235473,-0.4877959066,6.1769693819
C,0,1.4827450273,1.681575551,6.496741426
C,0,0.2508121191,-0.5902674922,7.5513803563
H,0,0.1420504091,-1.2844912521,5.5120292889
C,0,1.2754081485,1.5763002983,7.8717147426
H,0,1.9580242092,2.5591395909,6.0713582342
C,0,0.6589862391,0.4410137777,8.4023556522
H,0,-0.2305266709,-1.4750088109,7.9602822075
H,0,1.5952640774,2.38099024,8.5286262417
H,0,0.4962674447,0.3593522444,9.4740895873
C,0,5.795830445,-0.5360904684,3.5424961264
C,0,6.0674111525,-1.9091565938,3.3761013499
C,0,6.6934691524,0.2686387128,4.2664879725
C,0,7.2183149525,-2.4620729058,3.9290053455
H,0,5.3706016219,-2.5287151681,2.8193817457
C,0,7.8443461052,-0.29669396,4.8123697097
H,0,6.4803476346,1.3266591951,4.38679869
C,0,8.1088563707,-1.6580272598,4.6472114388
H,0,7.421278233,-3.521742421,3.8005631395

H,0,8.5352097991,0.3292396895,5.3701238216
H,0,9.0064842869,-2.0940069276,5.0772827318
C,0,4.7662677166,4.2095016335,3.0542116324
O,0,5.0877173334,3.3318771212,3.935251389
O,0,3.9812521225,3.9286107503,2.1110635815
C,0,5.3457158631,5.6015962681,3.1954438808
H,0,6.4296665192,5.5481705631,3.3423320319
H,0,5.1196401685,6.2112610303,2.3179072214
H,0,4.9213486188,6.0835655081,4.0843464612

Cyc-TS-NC

E(RB+HF-LYP)= -1381.08333553 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1380.803693 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2824.68691247 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.2636230447,0.7189662844,0.099377991
C,0,0.1517003558,0.4704500281,1.4543755149
N,0,1.2350775577,0.5520624254,2.2744089607
C,0,2.4719985797,0.8884347323,1.7560931163
C,0,2.6088447488,1.1316521856,0.3887083262
C,0,1.5038828156,1.0534094684,-0.4495834571
N,0,1.1774976325,0.2261086917,3.607716651
C,0,0.1141298153,0.7754636413,4.2919481665
O,0,-0.6945283604,1.594187771,3.8361847072
C,0,3.5447454117,0.9606662769,2.7147834312
C,0,3.4622950814,0.7165548158,3.9637225563
H,0,-0.6261387083,0.6383733313,-0.5153844617
H,0,-0.7774099159,0.1981413704,1.9293035669
H,0,3.598329329,1.385921633,0.0197738338
H,0,1.6071553406,1.2469393939,-1.512221815
C,0,-0.0028984513,0.2872346057,5.7067024594
C,0,0.6360041881,-0.875389922,6.1608860316
C,0,-0.8276027341,1.0050636104,6.5847914735
C,0,0.4579089045,-1.3062500829,7.4756602853
H,0,1.2579652307,-1.442653855,5.4772530062
C,0,-0.9970687593,0.578853119,7.9003192829
H,0,-1.3295798295,1.8932829487,6.2152990323
C,0,-0.354727545,-0.578913682,8.3486499693
H,0,0.9505785742,-2.2124927065,7.8179888436
H,0,-1.6332439471,1.1452784999,8.5755350439
H,0,-0.4920167428,-0.9160369436,9.3729951706
C,0,3.7751343317,0.4999472827,5.3299589508
C,0,3.5481373207,1.5156035223,6.2840496096

C,0,4.3168839678,-0.7383169466,5.7418225667
C,0,3.8704408805,1.2962410895,7.6184426412
H,0,3.1233956793,2.4614267084,5.963596725
C,0,4.637484714,-0.9435978774,7.0786779183
H,0,4.4855881115,-1.5158174662,5.003387287
C,0,4.4145524199,0.0709134434,8.015797793
H,0,3.6971066224,2.0787679411,8.3509901073
H,0,5.0614228286,-1.8928476404,7.3928669352
H,0,4.6659429821,-0.0943298796,9.0598396616
Cu,0,5.3452191225,1.4804398127,2.3259957078
C,0,7.0167334695,2.1203646811,0.5098764951
O,0,5.9723783598,1.887679535,-0.1298351056
O,0,7.1033047085,2.0280550472,1.7995443649
C,0,8.2947709468,2.527383739,-0.2035945325
H,0,8.69372867,3.4489327236,0.2340096355
H,0,9.0561879275,1.7502839573,-0.06665731
H,0,8.1178919711,2.6729889653,-1.2713293613

Cyc-INT1

E(RB+HF-LYP)= -1381.13094682 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1380.846364 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -2824.72885425 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.1687458096,1.3267651503,0.2922224455
C,0,0.0430987182,1.3448678229,1.6585738403
N,0,1.184899418,1.2498369422,2.4052877054
C,0,2.4601989821,1.1606113627,1.8674966858
C,0,2.5773694942,1.1503907469,0.4621720156
C,0,1.4425875416,1.2268674542,-0.3159476222
N,0,1.3081965719,1.1806671682,3.7807744479
C,0,0.1516435162,0.9721954546,4.6057287559
O,0,-0.87782567,1.5723039154,4.3476154362
C,0,3.4380368682,1.1166475901,2.9050332114
C,0,2.695693742,1.1531345706,4.0694017936
H,0,-0.7314552571,1.410530435,-0.3059525595
H,0,-0.8885920793,1.4542939046,2.1905611173
H,0,3.5782973008,1.0781865648,0.0438135635
H,0,1.5222588793,1.2203725174,-1.3982673182
C,0,0.2568277074,-0.0247749005,5.6969481056
C,0,1.0989667874,-1.1454083108,5.6179297057
C,0,-0.6207862786,0.1147185956,6.785436779
C,0,1.0678795796,-2.1076199164,6.6248391848
H,0,1.7583089993,-1.2787179637,4.7668338171

C,0,-0.6330508625,-0.8402443329,7.7964309534
H,0,-1.2809157191,0.9749507327,6.8266346472
C,0,0.2112135008,-1.952288478,7.7170166311
H,0,1.712969123,-2.9784601588,6.5559276894
H,0,-1.3018221407,-0.7220070719,8.6439851368
H,0,0.1972876335,-2.7004735692,8.5047345212
C,0,3.1772715817,1.3343890819,5.448536436
C,0,2.5689822395,2.2522105462,6.322900777
C,0,4.3175518688,0.6368362755,5.8816231702
C,0,3.0847799681,2.4578277114,7.601293363
H,0,1.7115619758,2.8324558521,5.9925846553
C,0,4.8287496176,0.8455431773,7.1609102086
H,0,4.7966297577,-0.068043494,5.2090611543
C,0,4.2131570611,1.7532832193,8.0261775251
H,0,2.6092015172,3.1774610369,8.2620850656
H,0,5.709524645,0.2964147321,7.4822698043
H,0,4.6142097803,1.915603201,9.0228673888
Cu,0,5.2754674351,1.0798964918,2.4682673882
C,0,7.0877081508,0.9152069918,0.5256841945
O,0,6.1006007233,0.8525565456,-0.2227652231
O,0,7.0464019956,1.012674211,1.8221652651
C,0,8.4987139933,0.8872241693,-0.0512027394
H,0,9.0156120679,1.8258081907,0.1820921303
H,0,9.0807762445,0.0797947713,0.4076677488
H,0,8.4745838363,0.7498312445,-1.1347878379

Cyc-INT1'

E(RB+HF-LYP)= -1610.22177528 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1609.884975 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3053.90272159 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.2154172539,-0.4631161027,-0.1353916922
C,0,-0.2085247765,-0.2391670321,1.2185027096
N,0,1.0039658984,-0.1685156471,1.8461342746
C,0,2.2233646411,-0.2776103818,1.196700135
C,0,2.2053299815,-0.502974514,-0.1952410444
C,0,0.9971761876,-0.6011202518,-0.8513088611
N,0,1.2626009372,-0.0124082612,3.1957724032
C,0,0.2092501281,-0.1980742611,4.159916063
O,0,-0.8785715031,0.3086128743,3.948737355
C,0,3.2962976163,-0.1069765144,2.1226203406
C,0,2.6670252836,0.0745136664,3.3411920991
H,0,-1.172603423,-0.512287862,-0.6420486004

H,0,-1.0888217169,-0.090628649,1.8237969542
H,0,3.1633583031,-0.6022636845,-0.7004077985
H,0,0.9723980962,-0.7756585279,-1.9222600794
C,0,0.4933625423,-1.0619123328,5.328992103
C,0,1.4176522305,-2.1181139884,5.2820198867
C,0,-0.2942856398,-0.8722809547,6.4773395345
C,0,1.5566749642,-2.9655372215,6.378835156
H,0,2.009148997,-2.2924786904,4.3894101127
C,0,-0.1363304142,-1.7104268928,7.575605798
H,0,-1.0195171575,-0.0655337384,6.4946707637
C,0,0.7892433665,-2.7577783403,7.5272439686
H,0,2.2645741613,-3.7878095119,6.3363139329
H,0,-0.7355889184,-1.5522452271,8.4674302545
H,0,0.9087193748,-3.415169086,8.383979063
C,0,3.2585660973,0.4852654737,4.6238200212
C,0,2.6405419069,1.4490611322,5.4407728823
C,0,4.5038199852,-0.0372732538,5.0115225783
C,0,3.2493795919,1.866987967,6.6223629713
H,0,1.7001376985,1.9002454822,5.1360746831
C,0,5.1081297047,0.3847207358,6.1933992767
H,0,4.9919198553,-0.7740913049,4.3808933547
C,0,4.4821482883,1.3339325691,7.0047161462
H,0,2.7646843073,2.6193028263,7.2385648067
H,0,6.0714537667,-0.0280541202,6.4793176647
H,0,4.9568436478,1.6635366228,7.9247713607
Cu,0,5.0790243932,-0.2634639394,1.5121269063
C,0,6.6198400286,-0.9012889441,-0.5674843364
O,0,5.5504012996,-0.9571855429,-1.1936435077
O,0,6.7415694529,-0.5939798889,0.6905778562
C,0,7.9436346435,-1.1983852637,-1.2622607579
H,0,8.5841028325,-0.3087400103,-1.2367313928
H,0,8.4784123121,-1.9927711986,-0.7292481906
H,0,7.7833643217,-1.4984126463,-2.3004183408
C,0,5.1741134862,3.7436087105,2.2025776858
O,0,6.0513932058,3.211419599,2.8503503313
O,0,4.1914585224,3.0570957579,1.5809463058
H,0,4.3436971826,2.0962057483,1.7399224622
C,0,5.0343242776,5.2302702234,1.9839320431
H,0,5.1159030857,5.4591228996,0.9154485093
H,0,4.048265122,5.5719611757,2.3166760768
H,0,5.814727004,5.7596228714,2.5324029955

Cyc-TS-PT

E(RB+HF-LYP)= -1610.20003862 Hartree (6-31G*/SDD in dioxane)

Sum of electronic and thermal Free Energies= -1609.863696 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3053.87907656 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.2274545523,0.3233443291,-0.2346228006
C,0,0.1674710676,0.0887901962,1.115775574
N,0,1.3023521957,0.2921746125,1.8481015912
C,0,2.5051548682,0.7518653675,1.3300321242
C,0,2.5477847376,0.9907180899,-0.0584528084
C,0,1.4276659103,0.7751800446,-0.8312213068
N,0,1.486249089,0.0740170353,3.2011676883
C,0,0.5963304716,-0.8170384885,3.9096549324
O,0,-0.6064228658,-0.6617467988,3.789266728
C,0,3.475160024,0.9026367524,2.366412031
C,0,2.790115033,0.5150554245,3.5111748984
H,0,-0.6683138805,0.1697416635,-0.825307435
H,0,-0.71404289,-0.2281428271,1.6517847015
H,0,3.4828885938,1.3312769567,-0.4869292826
H,0,1.4611857248,0.9556568573,-1.900769649
C,0,1.2132476973,-1.9059629171,4.6986890307
C,0,2.4434526725,-2.4902050664,4.3492642895
C,0,0.460359768,-2.4348879114,5.7621479417
C,0,2.9119658216,-3.5862195623,5.0718266499
H,0,3.0326742886,-2.1261070775,3.5122103473
C,0,0.9466098359,-3.5157408967,6.4886851984
H,0,-0.4961994365,-1.9855979456,6.0089074452
C,0,2.173728223,-4.092471265,6.1436522509
H,0,3.8579945345,-4.0394119082,4.7918529267
H,0,0.3714596091,-3.9118599602,7.3206450748
H,0,2.5508364295,-4.9404649068,6.7090120679
C,0,3.1928672178,0.6600855108,4.9174873161
C,0,2.2704570057,1.0583328504,5.9032805267
C,0,4.5350366819,0.4654388927,5.2866563016
C,0,2.6813273388,1.2482880134,7.2208775438
H,0,1.2363475885,1.2540383188,5.6336034201
C,0,4.9405807071,0.6568288263,6.6054589085
H,0,5.2524579681,0.1464044333,4.5352755128
C,0,4.0163262266,1.0459558142,7.5780156959
H,0,1.9579696317,1.5641091703,7.9676517696
H,0,5.980815389,0.4943098113,6.8741563641
H,0,4.3346337928,1.1936002925,8.6063890901
Cu,0,5.3001725835,-0.1538792955,2.0026210379
C,0,4.9580380375,-2.4951219986,0.926494933
O,0,4.9276444355,-1.7074529724,-0.0379772072

O,0,5.1128331982,-2.1249219887,2.1548995078
C,0,4.8136399383,-3.9967680616,0.7054618449
H,0,5.7144118143,-4.5130949545,1.0578187108
H,0,3.9712283948,-4.3870219132,1.2887526377
H,0,4.6595181854,-4.2246588311,-0.351869189
C,0,6.4740882602,2.4886678522,2.0063892783
O,0,6.763522636,1.2837787858,1.8624065338
O,0,5.2693488696,2.9224109586,2.2425106667
H,0,4.5791259438,2.0718787017,2.299462871
C,0,7.5349868992,3.5560245982,1.9210390617
H,0,7.2555786966,4.3020682634,1.1693832711
H,0,7.6106752617,4.0760053699,2.8829008355
H,0,8.4998295521,3.1149655337,1.6656009991

Cyc-INT2

E(RB+HF-LYP)= -1610.24162680 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1609.902551 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3053.91979045 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.0495165791,-0.2105629851,-0.047893199
C,0,-0.0239667174,-0.2993481036,1.3193191081
N,0,1.1755325962,-0.1194127917,1.9493950347
C,0,2.359853444,0.1160510645,1.2828533409
C,0,2.3298626712,0.2096609216,-0.1200753774
C,0,1.1331118757,0.0486813658,-0.7783526795
N,0,1.446280056,-0.2086862796,3.3038963742
C,0,0.4039793512,-0.5835110056,4.2449968154
O,0,-0.6959447388,-0.0823571838,4.1115556667
C,0,3.3810485915,0.2355327845,2.246935362
C,0,2.8065253095,0.0632286358,3.4834106709
H,0,-0.9992211567,-0.3425739467,-0.5528800612
H,0,-0.8901755338,-0.4713684363,1.9379890716
H,0,3.2617505694,0.3867272093,-0.6439872725
H,0,1.0928298282,0.1125186863,-1.8605720346
C,0,0.7478660345,-1.5943649351,5.2618286288
C,0,1.7540824515,-2.5560452471,5.0668656491
C,0,-0.0470684996,-1.6302368071,6.4227116183
C,0,1.9633391141,-3.5357299034,6.0359675246
H,0,2.3517548554,-2.5770042138,4.1612955034
C,0,0.1830172442,-2.6000010343,7.3908176852
H,0,-0.8310118542,-0.8913035736,6.5526966243
C,0,1.1894556427,-3.5533786158,7.198229637
H,0,2.7316745087,-4.2855687537,5.8744827483

H,0,-0.4206863571,-2.6178036489,8.2934795483
H,0,1.3650550292,-4.314172661,7.9538801662
C,0,3.4425345465,0.2522835164,4.7938933834
C,0,2.7721547292,0.8639522789,5.8674199328
C,0,4.7938494199,-0.1095443845,4.9385573011
C,0,3.4333596069,1.0796207891,7.0741335069
H,0,1.7466338694,1.2032541396,5.7558940415
C,0,5.4450688005,0.1079839654,6.1509337312
H,0,5.331381205,-0.5384876527,4.0971777833
C,0,4.7678069909,0.6944457263,7.2223866127
H,0,2.9077011764,1.5578626955,7.8957612769
H,0,6.4874615948,-0.1795865065,6.25440432
H,0,5.2806578714,0.8626693534,8.1653902398
Cu,0,4.9753851028,-2.9794840536,1.865552747
C,0,2.3227415204,-3.7345892379,1.5821984107
O,0,2.1620693744,-2.9376914593,0.6521288906
O,0,3.3795645055,-3.8252069833,2.3404236313
C,0,1.2339988773,-4.7466071584,1.9348995357
H,0,1.583134923,-5.7568033085,1.6886601557
H,0,1.0210069413,-4.7363051383,3.0094220239
H,0,0.3181591119,-4.5439874439,1.3738848771
C,0,7.1102276005,-1.1686390915,1.5843064989
O,0,6.6922773742,-2.3888854735,1.466578466
O,0,6.4438347287,-0.1929400348,1.9644648043
H,0,4.4343131448,0.4013822591,2.0512747627
C,0,8.5780808569,-0.9906138917,1.2073113594
H,0,8.7500637436,-1.3407764094,0.183163831
H,0,8.8781632191,0.0565392103,1.2904325262
H,0,9.2087653095,-1.6021189774,1.8632854468

Cyc-INT2'

E(RB+HF-LYP)= -1610.24590379 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1609.906787 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3053.92308813 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.0036987573,0.0022799741,-0.0095439245
C,0,-0.0000875626,-0.0004509863,1.3626140162
N,0,1.2095770261,-0.0024792929,1.9972320512
C,0,2.4250294029,-0.0514173925,1.3414222767
C,0,2.4229953231,-0.0624697228,-0.0652502119
C,0,1.2178202276,-0.0253385503,-0.7321985088
N,0,1.4353178505,-0.0467219851,3.3548835556
C,0,0.3512472905,0.2736433646,4.3093704323

O,0,-0.3904241608,1.1843900323,4.0192057537
C,0,3.4295657118,-0.0701869696,2.3299832251
C,0,2.8080087526,-0.0400894627,3.5552762239
H,0,-0.9502938426,0.0071099092,-0.5233809425
H,0,-0.8837858477,-0.0485966004,1.9785066391
H,0,3.3715828118,-0.1066290087,-0.5878071483
H,0,1.1969010987,-0.0316640216,-1.8171835466
C,0,0.3007905289,-0.546624254,5.5262202789
C,0,0.9024497805,-1.8138758294,5.6114965532
C,0,-0.4429507115,-0.039497434,6.6077866901
C,0,0.7572836098,-2.5584058571,6.7807316436
H,0,1.4623961528,-2.2329522408,4.7795271555
C,0,-0.5710025887,-0.7873731671,7.7715869444
H,0,-0.9108389364,0.935576221,6.519733868
C,0,0.0290139049,-2.0490454098,7.8579671768
H,0,1.2123644949,-3.5423928864,6.8430006865
H,0,-1.1389749751,-0.3934415485,8.6095015743
H,0,-0.075734898,-2.636034022,8.76663484
C,0,3.4501982297,0.0849539856,4.8790402851
C,0,3.2388730596,1.2250101796,5.6706487691
C,0,4.3449917881,-0.9089418551,5.3024818264
C,0,3.9194923122,1.3674541985,6.8784092925
H,0,2.5609213034,2.00541324,5.3351408266
C,0,5.0196718736,-0.7564491894,6.5139705458
H,0,4.4555352517,-1.806644854,4.7012962061
C,0,4.811391893,0.3784411626,7.3006630591
H,0,3.7568552609,2.2529679597,7.4863921673
H,0,5.7042943191,-1.5317991674,6.8465516199
H,0,5.3407683997,0.4921804711,8.2428332921
Cu,0,0.3370740649,-4.167975213,2.6448811476
C,0,-1.9484543139,-2.8334561907,3.4042301689
O,0,-1.4299262379,-1.75524445,3.0674468805
O,0,-1.3997212989,-3.9995371,3.3032750981
C,0,-3.3488219171,-2.8563244061,4.0058828729
H,0,-3.983057383,-3.5709165828,3.4699410578
H,0,-3.2945529519,-3.1934542975,5.0480015338
H,0,-3.8028261807,-1.8631780476,3.9747516466
C,0,3.0911931055,-4.0216667455,2.5420540814
O,0,2.0394484182,-4.490954554,1.951278209
O,0,3.0997891711,-3.2867139855,3.5434445437
C,0,4.4050789973,-4.4756350479,1.9121357916
H,0,4.3645526479,-4.3901012365,0.8212172886
H,0,5.2460512069,-3.8950585671,2.2996185081
H,0,4.5723050925,-5.5343983549,2.1454884733

H,0,4.4949165532,-0.0697590657,2.1591279655

Cyc-TS-OC

E(RB+HF-LYP)= -1610.22399943 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1609.883172 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3053.89748986 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.1127385146,0.5132634301,0.20823549
C,0,-0.0488331657,0.6014908293,1.5777927885
N,0,1.0780526613,0.1586455625,2.2052699155
C,0,2.1942858461,-0.2935427184,1.5251287417
C,0,2.1395873324,-0.3717756261,0.1205755277
C,0,0.9854711321,0.0129916474,-0.5283777416
N,0,1.3036987428,0.1878694748,3.5695668383
C,0,-0.0004227986,-0.648034465,4.3887659728
O,0,-1.0728047681,-0.3626228236,3.9116035317
C,0,3.1914863455,-0.5154814407,2.4925951499
C,0,2.6360243967,-0.2000557969,3.7142936671
H,0,-1.0089714703,0.8593854199,-0.293419887
H,0,-0.8272856588,1.0046922162,2.2032685743
H,0,3.0107314598,-0.7280035466,-0.417557737
H,0,0.9266743547,-0.041977655,-1.6107937996
C,0,0.2537683868,-0.7129678893,5.8679705684
C,0,1.0165635053,-1.6979503801,6.5053330745
C,0,-0.4012556594,0.2626833132,6.635351705
C,0,1.1254782974,-1.7001436775,7.8964572568
H,0,1.5223713341,-2.4556692421,5.9211100527
C,0,-0.278282344,0.262506361,8.0234579455
H,0,-1.0111749229,1.0109550426,6.1394092453
C,0,0.4850248884,-0.7207439198,8.6572256116
H,0,1.7182952723,-2.469360285,8.3829981301
H,0,-0.7875173253,1.022929881,8.6092941241
H,0,0.5758593595,-0.7261730381,9.7401398573
C,0,3.3470363335,-0.1354926364,4.9965808187
C,0,3.0982043203,0.9072694465,5.9048536294
C,0,4.3522181143,-1.0778065808,5.2775811269
C,0,3.83466108,0.9987607924,7.0834910035
H,0,2.3369284643,1.6466014643,5.6771622316
C,0,5.0819023413,-0.9785555724,6.4613260713
H,0,4.5424250457,-1.887320189,4.5770947209
C,0,4.826355111,0.0554193742,7.3657470637
H,0,3.6378169678,1.8092704817,7.7799275888
H,0,5.8523210384,-1.713943779,6.6770658606

H,0,5.4000048934,0.1289271346,8.2860214267
Cu,0,2.1186717654,-4.336430793,2.2308009505
C,0,-0.0824772432,-3.28257008,3.5906801886
O,0,0.6315195477,-2.2252118607,3.7438786366
O,0,0.3786208231,-4.2829524821,2.9727741427
C,0,-1.4753493768,-3.3805322415,4.1586621429
H,0,-1.9232188177,-4.3384446438,3.8912229008
H,0,-1.4341960549,-3.2888746176,5.2500476203
H,0,-2.0923340142,-2.5576097201,3.7895295505
C,0,4.828637605,-4.0255168541,1.8476746774
O,0,3.7439522483,-4.5547296283,1.3611421767
O,0,4.9106241265,-3.3519559648,2.8817210501
C,0,6.068199508,-4.3071764285,1.0032188702
H,0,5.9361633054,-3.9045456492,-0.0081400875
H,0,6.9566447877,-3.8629841587,1.4578335462
H,0,6.2135625074,-5.3883482513,0.8986776266
H,0,4.199324522,-0.8545680556,2.3101353986

3a

E(RB+HF-LYP)= -1610.26243086 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1609.924587 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3053.93610958 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,4.6179310981,0.8143581507,1.4740324655
C,0,3.3523186065,1.3186370576,1.605447592
N,0,2.3074681152,0.4520678468,1.7719639292
C,0,2.4672234908,-0.9374612607,1.822841214
C,0,3.7801927794,-1.4565516676,1.68907169
C,0,4.8355680832,-0.5933265981,1.5166119457
N,0,1.0200051869,0.83332043,1.9115299951
C,0,0.7096466561,2.1826244018,-1.2423498153
O,0,1.6798536023,2.8742118928,-1.0613782009
C,0,1.1811601657,-1.4470378833,2.0040989432
C,0,0.3335830736,-0.3213639448,2.0577072845
H,0,5.4480930062,1.5004976848,1.34816208
H,0,3.0894467399,2.3684487529,1.5895414647
H,0,3.9251178403,-2.5313173342,1.7264828091
H,0,5.844633436,-0.9810065166,1.4158963508
C,0,-0.7032274702,2.5723014336,-1.1280135225
C,0,-1.7626071194,1.6684473132,-1.3210269228
C,0,-0.9675328944,3.9178308462,-0.8122613021
C,0,-3.0749371972,2.1228841529,-1.2027322171
H,0,-1.5807997489,0.6234546807,-1.5493586648

C,0,-2.280498632,4.3584925219,-0.7006922347
H,0,-0.1372828691,4.5995071127,-0.6604043236
C,0,-3.3355231373,3.4600741859,-0.8970513706
H,0,-3.8915430346,1.4221419376,-1.3460754507
H,0,-2.4847989062,5.3978906803,-0.4602700922
H,0,-4.3623146614,3.8052029454,-0.8082109409
C,0,-1.1237621896,-0.2893829637,2.2680511329
C,0,-1.7642195757,0.9092136974,2.6256207161
C,0,-1.8984043641,-1.4522711247,2.1246826177
C,0,-3.1403240196,0.9401811777,2.8406742841
H,0,-1.1710825408,1.8111908403,2.7363052925
C,0,-3.2752399975,-1.4179945137,2.3418363535
H,0,-1.4274403516,-2.3811116446,1.8183435353
C,0,-3.9017480089,-0.2232382812,2.7032348818
H,0,-3.6192411574,1.8751966927,3.1200033329
H,0,-3.8598921302,-2.3263575893,2.2228661651
H,0,-4.9749165496,-0.1985851784,2.8740169366
Cu,0,0.4593967129,-2.1305302561,-1.5546345175
C,0,1.9429304043,0.2143102522,-2.0531331372
O,0,0.8265905074,0.8146642261,-1.60742879
O,0,1.9255075695,-1.0190662413,-2.0909931445
C,0,3.1290631589,0.9849978549,-2.5373180197
H,0,3.7910871246,0.2969073808,-3.0648663842
H,0,2.8266655706,1.8038636874,-3.1952382879
H,0,3.6560408657,1.428071567,-1.6873495415
C,0,-2.09282869,-2.7300681665,-1.3837107311
O,0,-0.944013569,-3.2601422533,-1.0674727577
O,0,-2.2359669294,-1.6351823797,-1.9438840272
C,0,-3.298590006,-3.5992500635,-1.0537940029
H,0,-3.1280717849,-4.1981123226,-0.1548810105
H,0,-4.1923361095,-2.9820795658,-0.9333417802
H,0,-3.4748259899,-4.2943652571,-1.8848762699
H,0,0.9143200622,-2.4877801121,2.109683638

The structures shown in Scheme ESI2-1

MCu-TS-DP1'

E(RB+HF-LYP)= -1610.75336803 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.421042 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.43575365 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-1.0026687919,-0.5217936109,-0.1142215492
C,0,-0.7783739294,-0.3714144065,1.2432159167
N,0,0.4371735895,0.006533882,1.7040327756
C,0,1.4630685854,0.2436207103,0.8472359603
C,0,1.2826953061,0.0988896557,-0.5181975507
C,0,0.0372697874,-0.2880361541,-1.0140310825
N,0,0.5424246822,0.2500001426,3.0706509849
C,0,1.5267414456,-0.41335842,3.6787240116
O,0,2.3582199085,-1.2131589209,3.1375894456
Cu,0,2.0012893696,-3.022608418,2.2349701903
H,0,-1.986785649,-0.8279090969,-0.4505129757
H,0,-1.5213714964,-0.5396408253,2.0098950573
H,0,2.3937324496,0.5539839172,1.298847662
H,0,2.1197349286,0.2977906151,-1.1782484831
H,0,-0.1206148382,-0.4008476841,-2.0816699087
C,0,1.6442832441,-0.1354098043,5.145714067
C,0,0.8294438867,0.8105237555,5.7882544825
C,0,2.6006099009,-0.8379955781,5.8920775808
C,0,0.9696709621,1.0448042711,7.1542355799
H,0,0.0898549804,1.3542550588,5.2104488176
C,0,2.7365827886,-0.6026318844,7.2600039161
H,0,3.2289033426,-1.5651780264,5.3896431841
C,0,1.9230700875,0.3386059479,7.8940675315
H,0,0.3344576481,1.7786662665,7.6435896519
H,0,3.4789870436,-1.1549347326,7.8299876406
H,0,2.0298628596,0.5216724701,8.9602601763
C,0,0.2255178306,-3.8912185983,3.7446804849
O,0,1.3192450985,-4.4657663883,3.9418851121
O,0,0.1096876812,-2.977270332,2.838708042
C,0,-1.0086851087,-4.2243537163,4.5546827434
H,0,-1.3339274007,-3.338250744,5.1118393427
H,0,-1.8287628855,-4.5112637952,3.8870025417
H,0,-0.8045637689,-5.0375589631,5.2543664091
C,0,4.0005156694,-3.379366698,1.9368032792
C,0,5.002039749,-3.1877104151,2.6321349168

C,0,6.1512581067,-2.9720689439,3.4422348335
C,0,6.4874852862,-3.8895534188,4.4605885841
C,0,6.9718523754,-1.842578644,3.2372697268
C,0,7.6134791634,-3.6766574829,5.250628597
H,0,5.8549824205,-4.7577180845,4.6178055094
C,0,8.0967202749,-1.6396501876,4.0310053417
H,0,6.7127171763,-1.1371448251,2.4537675996
C,0,8.4196521896,-2.5544128934,5.0378417376
H,0,7.864836896,-4.386633124,6.0337711873
H,0,8.7233009982,-0.7673430175,3.8664449987
H,0,9.2987863948,-2.3926473518,5.6558828671
C,0,2.1177366987,-4.4499346356,-0.3639276797
O,0,3.3831466502,-4.5809302044,-0.2614729485
O,0,1.380207818,-3.8565164961,0.4743935213
C,0,1.4747073595,-5.0452524078,-1.5990270106
H,0,1.7916911526,-6.0866601821,-1.7148014488
H,0,0.3861248603,-4.9916279241,-1.538447402
H,0,1.8191038922,-4.5004825179,-2.4859518282
H,0,3.7308284409,-3.9949783903,0.8172154933

MCu-INT1'

E(RB+HF-LYP)= -1610.77257933 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.432560 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.45573282 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.1174039775,-0.1477304877,-0.0311952958
C,0,0.06489571,-0.1595526668,1.3511418689
N,0,1.1918945345,0.0060636884,2.086599081
C,0,2.3944075477,0.1861322201,1.4833921098
C,0,2.4909843601,0.1985493573,0.1011359059
C,0,1.3443042517,0.0316907875,-0.6733882794
N,0,1.0313257355,0.1101440512,3.4657807791
C,0,1.7818140114,-0.7211088295,4.1908184102
O,0,2.5846243126,-1.615525172,3.7706916282
Cu,0,2.3938251653,-2.9979238145,2.2967667053
H,0,-0.8013995825,-0.2815071737,-0.5912233133
H,0,-0.8383318949,-0.2912418631,1.9307511028
H,0,3.2409012008,0.3150764578,2.1418864914
H,0,3.4678386629,0.3314156042,-0.3493231351
H,0,1.4043766022,0.0413930681,-1.7567306613
C,0,1.6448292506,-0.5356941199,5.6714322555
C,0,0.9447410737,0.5508609888,6.2184436726

C,0,2.2387175044,-1.4719828061,6.5286286263
C,0,0.8419947487,0.6950033575,7.6003536018
H,0,0.4856868667,1.2750244648,5.554222624
C,0,2.1317218211,-1.3265031459,7.9112424636
H,0,2.7754123355,-2.3096181415,6.0973447666
C,0,1.4348864374,-0.243068485,8.4504510457
H,0,0.2998054655,1.5405364569,8.0157047184
H,0,2.5925527553,-2.0594686991,8.5682022629
H,0,1.3532534795,-0.1290363304,9.5283856958
C,0,0.3415447615,-3.9993317097,1.5492925759
O,0,1.3930431138,-4.213546605,0.8755608735
O,0,0.4005734721,-3.1991730737,2.5457344648
C,0,-0.9514897741,-4.6971261666,1.2189126325
H,0,-1.0591675631,-5.5687470683,1.8762010812
H,0,-1.8037850786,-4.0364949783,1.4025207156
H,0,-0.9558643028,-5.0432354432,0.1826600118
C,0,4.1614637602,-2.7868901619,1.532748743
C,0,5.2667912568,-2.6392068749,1.0156831825
C,0,6.5481316147,-2.4737435234,0.3986021699
C,0,7.5663572888,-1.7334244976,1.0336102326
C,0,6.8169973691,-3.0452261514,-0.8622991077
C,0,8.8093210742,-1.5716830925,0.4254882173
H,0,7.3694521686,-1.2929024499,2.0067638776
C,0,8.0618513655,-2.8781833885,-1.4648608482
H,0,6.0392682836,-3.620493193,-1.356031397
C,0,9.0623449404,-2.1415274156,-0.825154528
H,0,9.583850812,-0.9991753121,0.9294295892
H,0,8.252725,-3.3263579855,-2.4366482764
H,0,10.032930971,-2.0136106723,-1.2971927865
C,0,3.9250186113,-5.4019819143,3.9161382665
O,0,5.0573096418,-4.9995753863,3.3467449293
O,0,2.8334279997,-4.8831867794,3.7082302154
C,0,4.1255230677,-6.5724379199,4.8429224619
H,0,4.860026718,-6.3195496321,5.6152182678
H,0,3.1781202655,-6.8474132215,5.3082709593
H,0,4.5235163144,-7.4251551887,4.2818498401
H,0,4.8625440733,-4.2483518439,2.7233823941

MCu-TS-DP2'

E(RB+HF-LYP)= -1610.73032455 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.390237 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.41625115 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.0585568018,0.0136113388,0.0343043872
C,0,-0.0253104443,0.0344018707,1.4139969262
N,0,1.1587685012,0.0161726957,2.0793094134
C,0,2.3761337863,-0.0230797127,1.4498226074
C,0,2.3400856919,-0.0429784092,0.0462148694
C,0,1.1484971581,-0.0203676647,-0.6700051503
N,0,1.0371858604,0.154509331,3.4625607402
C,0,1.68038365,-0.7446250503,4.1881731015
O,0,2.4024164337,-1.7205871401,3.7691620983
H,0,-1.0180403477,0.0286662629,-0.4709576836
H,0,-0.9047608974,0.0758479218,2.0436451134
H,0,3.434819101,0.6403192003,2.1240937957
H,0,3.2909044409,-0.0775236125,-0.4742358631
H,0,1.1528537597,-0.0245608795,-1.7560703035
C,0,1.4809711455,-0.6253168717,5.6667944273
C,0,0.6089889397,0.3266245474,6.2183933079
C,0,2.1832991411,-1.4887482723,6.5191800591
C,0,0.44844031,0.4135531952,7.5993040239
H,0,0.0640374884,0.9914081298,5.5573284809
C,0,2.0184237694,-1.4001527336,7.9011193691
H,0,2.8537925516,-2.2223492194,6.0854373683
C,0,1.152039382,-0.44962423,8.4446705238
H,0,-0.2281763724,1.1540944923,8.017797178
H,0,2.5684277561,-2.0729955093,8.5538851168
H,0,1.0241401603,-0.3812238612,9.5219935541
C,0,5.0376095174,0.8194403068,3.4128762465
O,0,4.2133854837,1.4169292449,2.6182543305
O,0,5.0754824928,-0.4197719039,3.5896504482
C,0,5.9915637161,1.7212674762,4.1630389614
H,0,6.7098138565,1.1322413264,4.7366135218
H,0,6.5211744043,2.3729028163,3.459979717
H,0,5.4251354891,2.3676132525,4.8434466695
Cu,0,3.7842084637,-1.6838765082,2.4259031763
C,0,4.8908785837,-1.8522486981,0.8590448957
C,0,5.6023630936,-1.9314014044,-0.139685118
C,0,6.4289592044,-2.0156635069,-1.3062848045
C,0,7.3055791245,-0.9633283252,-1.6398392503
C,0,6.3821050133,-3.148985353,-2.143044298
C,0,8.1072924337,-1.0453365635,-2.7761172971
H,0,7.3483874335,-0.0880081102,-0.9984562144
C,0,7.1884571138,-3.2241923547,-3.2764214706
H,0,5.7096187277,-3.9641937471,-1.8922350002
C,0,8.0527980764,-2.1742782197,-3.5977392019
H,0,8.7782962498,-0.2259342916,-3.0202699557

H,0,7.1423907522,-4.1053048061,-3.9110608991
H,0,8.6807823359,-2.235881872,-4.4824775403
C,0,5.3571062687,-4.2719878969,3.1611707682
O,0,6.2991166249,-3.9936007059,2.2769907321
O,0,4.307730375,-3.6340875503,3.2756164428
C,0,5.6816278895,-5.4550493667,4.0300872715
H,0,6.597528674,-5.2537612693,4.5969459932
H,0,4.8587161158,-5.6533991397,4.7173349294
H,0,5.8699099003,-6.3350099413,3.405823329
H,0,5.9961200398,-3.2322112016,1.7063642546

The structures shown in Scheme ESI2-2

MCu-TS-Addition

E(RB+HF-LYP)= -1610.74251435 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.397636 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.42338161 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,-0.460534983,-0.6968892395,0.5011416334
C,0,-0.0346195391,-0.3377656783,1.7577389796
N,0,1.2817996257,-0.1313480878,2.0137653791
C,0,2.2844576372,-0.5324281694,1.1221009712
C,0,1.8357930438,-0.6637174855,-0.2553051392
C,0,0.5065456994,-0.7953574584,-0.5382498754
N,0,1.7122748909,0.3800199465,3.2539049774
C,0,1.6943026633,-0.4870719661,4.2437135447
O,0,1.3529097338,-1.7394804894,4.194002164
Cu,0,1.4056934651,-3.0346863251,2.6648969473
H,0,-1.5189405118,-0.8286724578,0.3108595273
H,0,-0.7051373014,-0.1426167936,2.5861603011
H,0,3.1972847263,0.0254773708,1.3041832161
H,0,2.5954249826,-0.7317948448,-1.0265971165
H,0,0.1794522391,-0.9474024857,-1.5630583735
C,0,2.10609047,0.0752133293,5.5690616904
C,0,1.9739859257,1.4483714668,5.8301163595
C,0,2.6471827689,-0.7575862559,6.5581267988
C,0,2.3685190355,1.9733604206,7.0588071765
H,0,1.5583623957,2.0927550244,5.0632406492
C,0,3.0478418595,-0.2281013308,7.7849872554
H,0,2.7655853688,-1.8176886399,6.3669954269
C,0,2.907227643,1.1369248988,8.0402676606
H,0,2.2535802773,3.0366667745,7.2519596823
H,0,3.4706384178,-0.8844636891,8.5409542804
H,0,3.214457987,1.5474320701,8.9986486792
C,0,-0.2495469664,-4.6306511121,1.9899020638
O,0,0.8065259511,-4.4126278001,1.3050086054
O,0,-0.4457227491,-3.9485505853,3.0423193461
C,0,-1.214000745,-5.703691214,1.5608310552
H,0,-0.814206711,-6.6809260849,1.8586811667
H,0,-2.187558625,-5.5653739676,2.0367728245
H,0,-1.3225082396,-5.7084272488,0.4724589573
C,0,2.9203944296,-2.1776281313,1.658342546
C,0,4.046377824,-2.6261805881,1.3750467572
C,0,5.323327553,-3.1167690993,1.0142686

C,0,6.4553196863,-2.8368219347,1.8142269313
C,0,5.4858934922,-3.8937450404,-0.1564645637
C,0,7.7079288806,-3.3163778377,1.4471435957
H,0,6.3310254918,-2.2452174728,2.7160757161
C,0,6.7429559046,-4.3706583959,-0.5112379455
H,0,4.6154819282,-4.1159406134,-0.7660991242
C,0,7.8554306321,-4.0830302475,0.2864606447
H,0,8.5726365681,-3.0954100374,2.0667022224
H,0,6.8585832909,-4.969258585,-1.4105312026
H,0,8.8358065033,-4.4578781618,0.0051298433
C,0,1.7734127741,-4.7667907351,5.3289201762
O,0,1.1666999086,-3.7718427922,5.9695464019
O,0,2.2429598052,-4.6616868478,4.1993958397
C,0,1.8173654818,-6.0379551048,6.1346879249
H,0,2.4245037222,-6.7871070516,5.6247055376
H,0,2.219689978,-5.8423206868,7.1338358365
H,0,0.7975851822,-6.4196808817,6.262345218
H,0,1.1670322029,-2.9617663212,5.3843289818

MCu-INT2'

E(RB+HF-LYP)= -1610.76551667 Hartree (6-31G*/SDD in dioxane)
Sum of electronic and thermal Free Energies= -1610.418424 Hartree (6-31G*/SDD in dioxane)

E(RB+HF-LYP)= -3054.44844559 Hartree (6-311+G**/Aug-cc-PVTZ in dioxane)

C,0,0.1706290263,-0.0508633507,-0.0823154912
C,0,0.0753375557,-0.0458392897,1.2576234111
N,0,1.2456911261,-0.1074449088,2.0933885815
C,0,2.3973316369,0.6405017979,1.4604077631
C,0,2.571795005,0.2001081982,0.015283832
C,0,1.4826613013,-0.0780937427,-0.7156527133
N,0,0.9681304658,0.5399471423,3.3681948772
C,0,1.1555986363,-0.2558758537,4.3835846572
O,0,1.4707744795,-1.5272517686,4.305508552
Cu,0,1.5880291765,-2.1726311802,2.4843730907
H,0,-0.7329119459,-0.0812947965,-0.682107381
H,0,-0.8571939657,-0.07926591,1.8080419422
H,0,2.0882067126,1.7029899182,1.478240839
H,0,3.5760131401,0.2000024684,-0.3942297912
H,0,1.5625262253,-0.3390579338,-1.767059683
C,0,0.9694579063,0.3150837079,5.7481222208
C,0,0.8775381357,1.7025610769,5.9427136037
C,0,0.8829956162,-0.5416210464,6.8545924039
C,0,0.7040441575,2.220047401,7.2239951521

H,0,0.9469676622,2.3613970245,5.0840534762
C,0,0.7078205623,-0.0191765864,8.1360222399
H,0,0.9455687135,-1.6140842452,6.7039073255
C,0,0.6188924567,1.3612259861,8.3241609259
H,0,0.6374442171,3.2954632882,7.3660016579
H,0,0.6393177505,-0.6917889055,8.9868017894
H,0,0.4844354169,1.7675739132,9.3232738663
C,0,0.9929820313,-4.1769976083,1.342585888
O,0,1.3752601536,-3.105318038,0.7501480512
O,0,0.8633052349,-4.15976446,2.6018133214
C,0,0.745514972,-5.4245299512,0.5391625841
H,0,1.7090460229,-5.900600684,0.3192318157
H,0,0.1268121349,-6.1301701683,1.0980223286
H,0,0.2709904187,-5.1771060913,-0.414641493
C,0,3.617561803,0.5033212758,2.2506160415
C,0,4.6618265605,0.4328991359,2.8622270821
C,0,5.8878234977,0.3330979033,3.5902509717
C,0,6.0289159914,0.9612816615,4.8431495847
C,0,6.9706328244,-0.3990469317,3.0637474979
C,0,7.2252427675,0.8569433644,5.5487425076
H,0,5.1943944964,1.5224673468,5.2523473926
C,0,8.164558904,-0.4949628521,3.775829389
H,0,6.8637010382,-0.8840759431,2.0981164661
C,0,8.2951996653,0.1309854206,5.0186308121
H,0,7.322774288,1.3432106711,6.515518939
H,0,8.9952831031,-1.0586189073,3.3596475679
H,0,9.2274052628,0.0532542084,5.5716101986
C,0,4.2360927262,-3.1667530174,3.9298498961
O,0,3.7394751414,-2.7182258028,5.073495059
O,0,3.7014625493,-2.9883763909,2.8353756328
C,0,5.521766392,-3.9295468597,4.1005861647
H,0,5.3584727372,-4.7794866943,4.7723691602
H,0,5.8785523496,-4.2867271433,3.1337482364
H,0,6.2785230204,-3.2867347723,4.5622564205
H,0,2.8885566168,-2.2244280463,4.8897778575