Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Copper (I)-carbenes as key intermediates in the [3+2]-cyclization of pyridine derivatives with alkenyldiazoacetates: A computational study

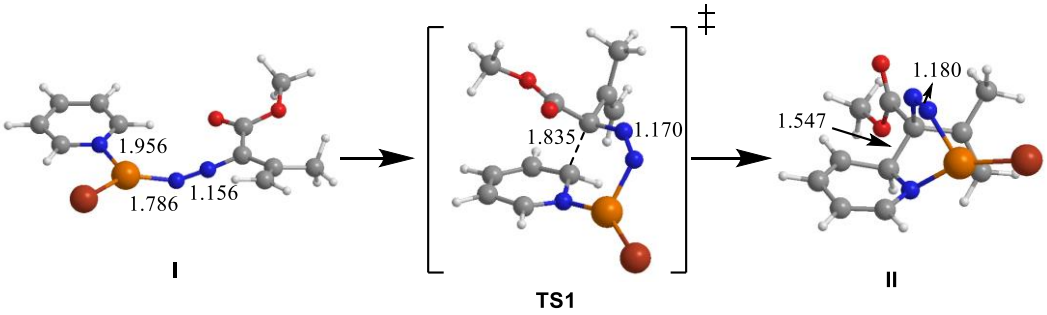
ELECTRONIC SUPPLEMENTARY INFORMATION

CONTENTS [#]

[#] *Through all this document, G (in hartrees) corresponds to the sum of electronic and thermal Gibbs free-energies and* ν_i *is the imaginary harmonic frequency of transition states.*

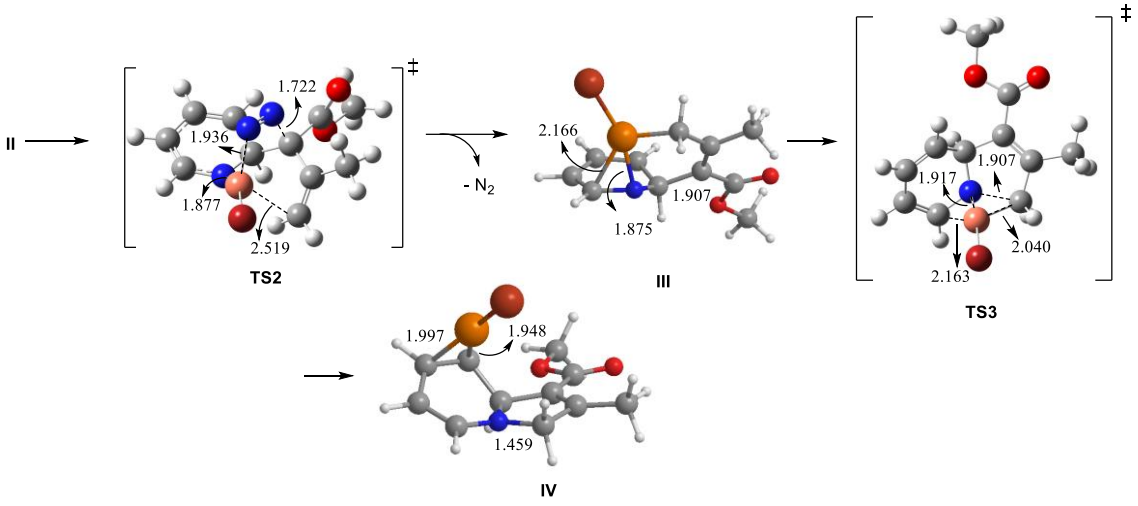
I.- Stationary points of the potential-energy surface corresponding to the direct addition reaction of diazocompound 2a to CuBr-activated pyridine derivatives 1b-c.

The potential-energy surface corresponding to the direct addition reaction of diazocompound **2a** to the complex formed by pyridine **1a** and CuBr and the was studied and several stationary points were located (see Scheme S1).



Scheme S1. Stationary points corresponding to the first step of the reaction of **1a** with **2a** in presence of CuBr. Lengths are in Å.

Pyridine derivative **1a**, CuBr and **2a** form a complex **I**, which undergoes an intramolecular *ortho*-addition of the nucleophilic carbon atom of diazocompound moiety to the electrophilic carbon atom adjacent to the nitrogen of pyridine ring, *via* transition structure **TS1**, leading to bicyclic intermediate **II**. The imaginary normal mode corresponding to **TS1** is associated to the process of bond forming between the diazo carbon atom of **2a** to the C-2 of the pyridine ring. Intermediate **II** is predicted to undergo extrusion of the dinitrogen molecule through the transition structure **TS2**, leading to the metallacycle intermediate **III** (Scheme S2).

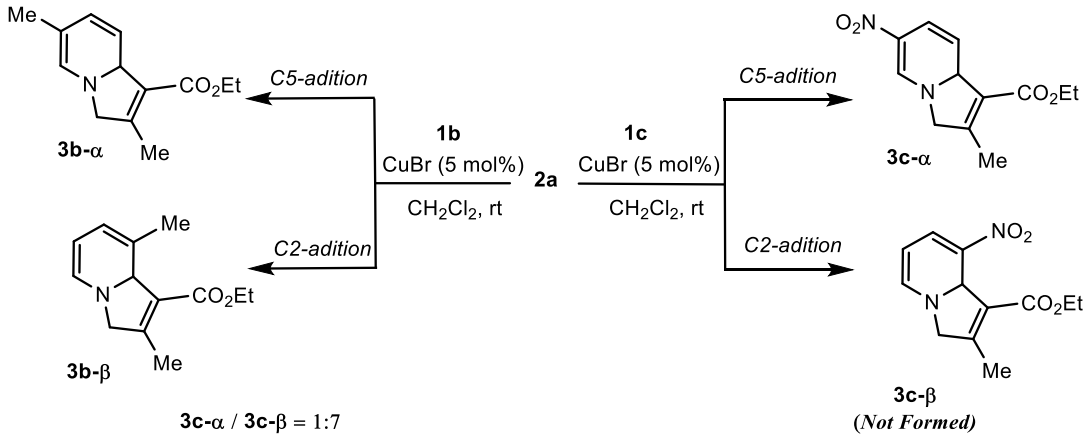


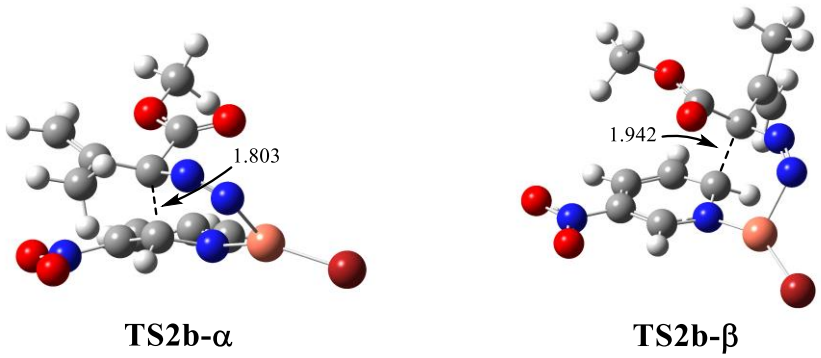
Scheme S2. Stationary points corresponding to the extrusion of dinitrogen and reductive elimination to form the η^2-CuBr coordinated to the indolizine structure, **IV**. Lengths are in Å.

The imaginary normal mode corresponding to **TS1** is associated to the bond forming between the diazo carbon atom of **2a** to the C-2 of the pyridine ring.

Finally, reductive elimination of CuBr from metallacycle **III**, with a simultaneous formation of the carbon-carbon bond, *via* the transition structure **TS3**, leads to the indolizine derivative **IV**, in which the CuBr moiety is η^2-coordinated to the pyridine ring.

According to the experimental evidence, the reaction of diazocompound **2a** with 3-substituted pyridines, as **1b** and **1c**, is regioselective. In the case of the reaction of 3-nitropyridine (**1c**), only the regioisomer corresponding to the addition to the C3 position of pyridine ring, **3b-α**, is formed; in the case of the reaction of **1b**, a 1:7 mixture of regioisomers was obtained (see Scheme S3). In the case of the reaction of 3-nitropyridine **1b**, two transition structures for the direct addition step, **TS2b-α** and **TS2b-β**, were found,





TS2b-α **TS2b-β**

Scheme S3: Reaction of **2a** with **1b** and **1c**. The Transition Structures corresponding to the addition to the position 2 and 5 of **1b**, **TS2b-α** and **TS2b-β**, respectively, are shown.

The difference in the Gibbs free energy of activation is predicted to be very samall: $\Delta\Delta G^{\#}$ (**TS2b-α** - **TS2b-β**) = 0.23 kcal mol^{-1}. This result is in clear disagreement with the

complete regioselectivity observed in this reaction. On the other hand, in the case of the reaction of 3-methylpyridine, only the transition structure corresponding to the addition to the C5 position of pyridine ring was located, after an extensive search.

According to these results, the mechanism of the direcct addition of diazocompunds to the CuBr-activated pyridine was ruled out.

Stationary points located at Becke3LYP/6-31G(d) level of theory.

CuBr	***N_2***
Cu -1.1171410201, 0.1921897991, -0.1653679279 Br 0.925631131, -0.1592429764, 0.1370191402 G = -4212.005922	N, 0, 0.0 ,0.0 ,-0.5527503374 N, 0, 0.0, 0.0, 0.5527503374 G = -109.536980
1a	***1b***
N,0,-1.1958133585,0.728334289,0.242386975 C,0,-0.4483100011,0.2570107047,1.2485173343 C,0,0.7335381231,-0.4636167059,1.0661560391 C,0,1.1660842366,-0.7101946274,-0.2363792647 C,0,0.3992329534,-0.2263436122,-1.2957608349 C,0,-0.7668572522,0.4830812823,-1.002181534 H,0,-0.8140577958,0.4669378726,2.2526855908 H,0,1.2961645242,-0.8196547008,1.924310764 H,0,2.080752103,-1.2672562125,-0.4218007743 H,0,0.6942315592,-0.3925697807,-2.3278033836 H,0,-1.3885252396,0.8745805491,-1.8062114619 G = -248.223338	C,0,0.7575361617,-0.477551385,-0.0001441555 C,0,0.7435621838,0.9228897106,0.0009050408 C,0,-0.4872053728,-1.1185100383,-0.0010326266 C,0,-1.651991466,-0.355858954,-0.0008044594 C,0,-1.5377273732,1.0357710976,0.0003041155 N,0,-0.3632804954,1.6753495588,0.0011447845 H,0,-0.5408349258,-2.2054148238,-0.0019006965 H,0,-2.6308713779,-0.8269118617,-0.0014822484 C,0,2.0537430958,-1.2498762818,-0.0002318052 H,0,1.6876418979,1.4684553995,0.0015919758 H,0,-2.4272930848,1.6638988283,0.0005154102 H,0,2.1352893188,-1.8963820156,-0.8826872357 H,0,2.1353626256,-1.8963698829,0.8822324913 H,0,2.9161656388,-0.5759074504,-0.0002598459 G = -287.517391
1c	***2a***
N,0,-0.0043398519,-0.0015655737,0. C,0,0.0051216776,1.3383243477,0. C,0,1.1695674633,2.1115337394,0. C,0,2.3997399567,1.4618610787,0. C,0,2.3842947646,0.0701837634,0. C,0,1.1755348827,-0.6275891275,0. N,0,3.6535928244,-0.6711182088,0. O,0,4.6939415343,-0.0145648305,0. O,0,3.5944820865,-1.8991189935,0. H,0,-0.9711069111,1.8194594907,0. H,0,1.1108689121,3.1951327581,0. H,0,3.343574111,1.993996511,0. H,0,1.1725905495,-1.7129029551,0. G = -452.722900	C,0,2.2085985366,1.7170801886,0.153671731 C,0,0.5702046274,-0.1051565382,-0.0894811695 C,0,-0.7310442732,-0.767705965,0.0989842313 C,0,-0.1142407007,2.3373741251,-0.4770216767 N,0,2.391538415,-1.7288302786,-0.3699471128 N,0,1.5427841097,-0.9866071657,-0.236454577 C,0,0.948678487,1.3284738277,-0.1040482335 O,0,-0.8909604338,-1.974295523,0.0523786562 O,0,-1.7292759732,0.112756022,0.337581657 C,0,-3.0249154831,-0.4821240579,0.521602927 H,0,2.491458358,2.7615902556,0.0754702968 H,0,2.9939073781,1.0247870925,0.4439547378 H,0,-3.0210846813,-1.149038658,1.3874780055 H,0,-3.3166687887,-1.0516450591,-0.3644294453 H,0,-3.7055362536,0.354230603,0.6834433654 H,0,0.3418347931,3.323553958,-0.6005976321 H,0,-0.8903427482,2.4049067161,0.2900476045 H,0,-0.6156216374,2.0643437277,-1.4124844671 G = -493.237917

I	***II***
N,0,-0.6029721487,-2.027297389,-0.7610963225 C,0,1.8713776718,3.8270560476,1.1216108664 C,0,-1.507615139,-1.9675429334,0.2387628907 C,0,-2.3447562857,-3.0351583041,0.5465006357 C,0,-2.2525143718,-4.2065184085,-0.2041080202 C,0,-1.3185172614,-4.2683368794,-1.2377152415 C,0,-0.5134561554,-3.1622764651,-1.484136211 H,0,-1.5508047459,-1.0395590406,0.8014798286 H,0,-3.0540458155,-2.9386002016,1.3619099897 H,0,-2.8950134174,-5.0552458435,0.0130943358 H,0,-1.207899243,-5.1586048407,-1.8481764902 H,0,0.2410310933,-3.1529223532,-2.2655457097 C,0,-0.1112491092,2.4476785938,1.5430442713 Cu,0,0.5565521311,-0.5266405283,-1.2400909639 Br,0,2.109334889,-1.1159880309,-2.7907278289 C,0,-1.0915052741,1.820704345,2.4499662713 C,0,0.0620782085,4.8347353047,2.5016246234 N,0,0.1465371613,1.0137238505,-0.4403676405 N,0,0.091496883,1.7262800821,0.4684304798 C,0,0.6726522572,3.6985220709,1.7125348735 O,0,-1.682015501,0.7772492492,2.2089293016 O,0,-1.2673597441,2.5184230489,3.5907727585 C,0,-2.2147481771,1.9554647651,4.5136914271 H,0,2.4198133439,4.7621459259,1.1753120099 H,0,2.3403014173,3.0201003346,0.565325173 H,0,-1.8927330411,0.9614765127,4.8343700529 H,0,-3.202693401,1.8799736058,4.0522996091 H,0,-2.2366583213,2.6433403654,5.3591836595 H,0,0.6705423931,5.7357348068,2.3831969774 H,0,-0.0031000014,4.5972472925,3.5669664987 H,0,-0.9563826687,5.0567768274,2.1616556096 G = -4953.566325	N,0,0.7840073797,-1.2912566646,-0.4671677427 C,0,-0.550704969,0.9887705221,-1.9121721895 C,0,-0.655435594,-1.5008960628,-0.2922851919 C,0,-1.0247391624,-2.6762896803,0.5725614335 C,0,-0.1139843466,-3.6271989097,0.8743565562 C,0,1.2507550472,-3.4856504057,0.4538905988 C,0,1.6309996724,-2.3109998545,-0.1340934638 H,0,-1.1043601367,-1.6334602214,-1.2932065766 H,0,-2.0514112675,-2.7637471883,0.9139757781 H,0,-0.4074753856,-4.4950771054,1.4591287441 H,0,1.9768848266,-4.2708839361,0.6295966855 H,0,2.6726008022,-2.1310548523,-0.3918534553 C,0,-1.3508570842,-0.1666771065,0.1688779068 Cu,0,1.4721484018,0.3952968261,-0.0629612903 Br,0,2.7786338278,2.1846504509,-0.345934979 C,0,-2.8398084749,-0.3750089509,0.4809143367 C,0,-1.7566393434,2.3452081012,-0.2033005712 N,0,0.513726426,0.3243082293,1.5702659223 N,0,-0.6553855584,0.1723321517,1.5293998906 C,0,-1.1930876584,1.0478910377,-0.7368286991 O,0,-3.3936362569,-0.0568815665,1.5040379891 O,0,-3.4516358738,-0.9348363766,-0.5803774971 C,0,-4.8694031899,-1.1568452599,-0.4310440031 H,0,-0.4375117227,1.8864413703,-2.5130268865 H,0,-0.1479884104,0.0745804739,-2.330883005 H,0,-5.3818402278,-0.2117183467,-0.2376308167 H,0,-5.0612002719,-1.8455962801,0.3953430725 H,0,-5.1947360493,-1.5880044598,-1.3772169485 H,0,-1.5883670786,3.1538408308,-0.9184318343 H,0,-1.282794339,2.6274555033,0.7442233897 H,0,-2.8331184315,2.2730874186,-0.0084471694 G = -4953.497209
III	***IV***
N,0,0.7273856111,-1.1998680986,-0.5692584333 C,0,0.7440988713,1.4119675136,-0.7480762272 C,0,-0.7371681303,-1.1956758178,-0.6390989991 C,0,-1.4163756856,-1.3531007622,0.7064621599 C,0,-0.7762936575,-1.9709294668,1.7256348223 C,0,0.5880808059,-2.397154607,1.545296345 C,0,1.2811610466,-1.9949873899,0.4248128498 H,0,-1.0115947125,-2.0776056224,-1.2419553923 H,0,-2.4383664614,-1.0028145337,0.8122585146 H,0,-1.2611117682,-2.1248634986,2.6852454481 H,0,1.0816118687,-3.0011132635,2.300214363 H,0,2.3281113939,-2.259629923,0.2902396219 C,0,-1.2441904277,0.019019496,-1.413686578 Cu,0,1.2913572179,0.1645610777,0.5870613914 Br,0,2.4129332155,1.29703738,2.1622289555 C,0,-2.5478825087,-0.125867056,-2.1073767302 C,0,-1.0500946971,2.4261108665,-2.1718311727 C,0,-0.5627406274,1.1914380594,-1.4315539514 O,0,-3.0919678612,0.6984631957,-2.8189795773 O,0,-3.1215427009,-1.33516544,-1.8457794664 C,0,-4.3902184437,-1.5599116547,-2.4787441493 H,0,0.7651279098,2.389816457,-0.2587537389 H,0,1.5759320602,1.3642675284,-1.462246578 H,0,-4.2917239614,-1.5070425284,-3.5661138902 H,0,-5.1207322385,-0.8142528508,-2.1538782572 H,0,-4.6972352063,-2.5594802222,-2.1690879679 H,0,-0.3553834495,3.2588023491,-2.0321653466 H,0,-2.0445622611,2.7305657376,-1.8326256298 H,0,-1.145969091,2.2220103764,-3.24207377 G = -4843.961726	N,0,0.4258272478,-1.7900746811,-0.1198619781 C,0,-0.9805515577,-2.0073592765,-0.4428159347 C,0,0.6162064756,-0.9777494454,1.1016004099 C,0,1.4952240326,0.2122086992,0.7512465062 C,0,2.5673433158,-0.0505047906,-0.1150386001 C,0,2.6226551551,-1.2933279829,-0.8684075253 C,0,1.4812414481,-2.042823109,-0.9448521321 H,0,1.1315767988,-1.5808580646,1.8720660796 H,0,1.5452217803,1.0343514145,1.4579910008 H,0,3.4245194101,0.6194563604,-0.1382784989 H,0,3.4789602883,-1.5275539315,-1.4883025787 H,0,1.3532787219,-2.846821134,-1.6653707552 C,0,-0.8201618256,-0.7074442759,1.5105096174 Cu,0,1.0000949626,0.7587466827,-1.0519745151 Br,0,-0.4009887798,1.2300398855,-2.691819971 C,0,-1.1659471704,0.0406843189,2.7363167539 C,0,-3.1964437393,-1.2602953881,0.6855769065 C,0,-1.7026919519,-1.2760744123,0.6625985776 O,0,-2.2838317316,0.3049007878,3.1356394017 O,0,-0.0431808419,0.406632209,3.408668053 C,0,-0.2686118455,1.1305463583,4.6297830007 H,0,-1.2367582061,-1.5877447233,-1.4267449403 H,0,-1.2438997615,-3.0778213078,-0.4498671433 H,0,-0.8524264829,0.5274973382,5.3299475023 H,0,-0.8056421742,2.061284637,4.4296751392 H,0,0.7229809263,1.336688643,5.0334216436 H,0,-3.590717196,-2.2839062743,0.6342237115 H,0,-3.5727952738,-0.7320017428,-0.2007719811 H,0,-3.5767096214,-0.7665263854,1.5784394727 G = -4844.070045

TS1

N,0,-0.5092873667,-0.8202210519,-0.7946339309
C,0,-1.8173157,3.3901822543,-0.7883028462
C,0,-1.2633806888,0.3745780387,-0.8434973465
C,0,-2.7206621176,0.2125456733,-0.7223736726
C,0,-3.2471065527,-0.9476768717,-0.2416493439
C,0,-2.3936167826,-2.0396376273,0.0853061107
C,0,-1.0578633415,-1.9195010053,-0.2118134981
H,0,-0.9288897124,0.9973584634,-1.6770398652
H,0,-3.3545611665,1.0594471607,-0.9565309276
H,0,-4.3241200717,-1.05095955,-0.1362238459
H,0,-2.7892495938,-2.9805917444,0.4498730221
H,0,-0.3863140126,-2.7672606118,-0.1038473123
C,0,-0.7278747945,1.5180148656,0.488300286
Cu,0,1.3550219001,-0.7924325588,-0.8303478328
Br,0,3.2135982018,-1.86070912,-1.4301983672
C,0,-1.0748379395,0.8251127482,1.8068414917
C,0,-0.9472475514,3.8791018757,1.4869203199
N,0,1.5685014551,0.855698354,0.0335296143
N,0,0.7187463087,1.551203529,0.437116371
C,0,-1.232431424,2.9493892129,0.3294447771
O,0,-0.347820658,0.033764003,2.3652774247
O,0,-2.3117403066,1.1503356966,2.2108322379
C,0,-2.7924259149,0.4194374545,3.3580535033
H,0,-2.1279676435,4.4281115091,-0.8682800435
H,0,-2.0167374574,2.7711733751,-1.6545479387
H,0,-2.1368303962,0.5856106968,4.2158294941
H,0,-2.8290530551,-0.648312025,3.1297969934
H,0,-3.7910769597,0.8107316235,3.5503817768
H,0,-1.2670397618,4.8992104493,1.25558231
H,0,0.1261958346,3.8982452426,1.7128936546
H,0,-1.4665863898,3.5537556889,2.3948023164

ν_i =-308.5 cm^{-1}
G = -4953.492652

TS2

N,0,0.3205296844,-1.2237899683,-0.968349664
C,0,0.7942163739,1.6370658029,-1.0809654389
C,0,-1.0396421597,-0.6972616261,-1.1356351385
C,0,-2.1352050754,-1.7249475277,-1.0440832725
C,0,-1.855866559,-3.0461972947,-1.0961119664
C,0,-0.4968648922,-3.5001226398,-1.1469268624
C,0,0.5040864382,-2.5741795008,-1.0261478479
H,0,-1.088592038,-0.219012149,-2.1336834988
H,0,-3.160133207,-1.3754353062,-0.9842205093
H,0,-2.6637509698,-3.7730084119,-1.0769984797
H,0,-0.2594713002,-4.5524239292,-1.2522295281
H,0,1.5458200056,-2.8860270969,-0.991204646
C,0,-1.26972485,0.5391397022,-0.215600801
Cu,0,1.4090347875,-0.3758178257,0.3034391627
Br,0,3.3217457989,0.3584232007,1.2103504981
C,0,-2.6961620943,1.0755772257,-0.2023097638
C,0,-0.4552226465,2.764013652,0.7581021679
N,0,-0.033547902,-0.6684924043,1.5613142506
N,0,-1.0702064806,-0.1870227061,1.3327498206
C,0,-0.2786627463,1.6568567928,-0.2581750764
O,0,-3.2962397236,1.4258220641,0.7846913176
O,0,-3.1795639092,1.1593119561,-1.4592934326
C,0,-4.5111509778,1.7044423817,-1.5722431022
H,0,1.5225958993,2.4406995866,-1.0331777692
H,0,0.914219768,0.9268644643,-1.8895193712
H,0,-4.5385450643,2.7206780173,-1.172267827
H,0,-5.2239143615,1.0835406653,-1.0242993012
H,0,-4.7340627963,1.7015749759,-2.6387325766
H,0,0.4012674178,3.4414168125,0.727936676
H,0,-0.5440985144,2.3671154609,1.7754601775
H,0,-1.364249555,3.3456634128,0.568332186

ν_i = -223.1 cm^{-1}
G = -4953.496124

TS3

N,0,0.3795417712,-1.2854694078,-0.6012492181
C,0,1.0982983381,0.248811409,-1.4208270796
C,0,-1.068400879,-1.0346160465,-0.5105508967
C,0,-1.4969342079,-0.921964371,0.9359533432
C,0,-0.9267356639,-1.7832622973,1.8112570564
C,0,0.1979993598,-2.6005488588,1.4072591056
C,0,0.916221074,-2.218796469,0.3044645211
H,0,-1.5490437995,-1.9231491237,-0.9544803826
H,0,-2.2727816214,-0.2215340414,1.2254754985
H,0,-1.2493075338,-1.8181184571,2.8487447109
H,0,0.5475106598,-3.4175893286,2.0289789558
H,0,1.8414370313,-2.6999575066,-0.0016492503
C,0,-1.3244568799,0.150745337,-1.4201308362
Cu,0,1.3429900797,-0.1151202141,0.5715147271
Br,0,2.6114149373,1.0257164439,1.999137406
C,0,-2.717136706,0.5259785507,-1.7698577776
C,0,-0.1493800184,1.9338224741,-2.8386082591
C,0,-0.2202610171,0.7625166878,-1.8988371946
O,0,-3.0719133253,1.4529707022,-2.4729388139
O,0,-3.5985857665,-0.3254785947,-1.1887218375
C,0,-4.9844492135,-0.0588005932,-1.4617534439
H,0,1.7340040208,1.0823051664,-1.0680658394
H,0,1.6694492204,-0.3050768414,-2.1654158136
H,0,-5.1836234293,-0.1323167408,-2.533990884
H,0,-5.256689216,0.9422618228,-1.1178338684
H,0,-5.5398673976,-0.8199564754,-0.9136105968
H,0,0.4881581521,1.6890408413,-3.6983438004
H,0,0.3201090754,2.7890616548,-2.3339629484
H,0,-1.1369750609,2.2284737575,-3.1877635707

ν_i = -414.6 cm^{-1}
G = -4843.999171

TS2b-α	***TS2b-β***
N,0,0.3271910147,0.7308279554,0.7493938604	N,0,-0.3644320843,-0.4115477294,-0.7905323851
C,0,-3.2671744169,-0.8899808992,-2.0237895304	C,0,-0.3022032881,4.0215571723,-0.8990770637
C,0,-0.6849988595,0.8919849891,-0.2370001648	C,0,-0.7544275624,0.9324651452,-0.9080900652
C,0,-1.9560479182,1.4088375367,0.2950834473	C,0,-2.1669185138,1.2330937663,-0.7008452999
C,0,-2.2795555306,1.2790173127,1.6210490398	C,0,-2.9924370951,0.315197249,-0.1302508943
C,0,-1.3236460033,0.750504166,2.5107514588	C,0,-2.4658270216,-0.9632080284,0.1979356443
C,0,-0.0420471114,0.5318775792,2.0296004296	C,0,-1.1692987087,-1.2798730592,-0.1514453711
H,0,-0.3202845833,1.4590026687,-1.092487046	H,0,-0.274834956,1.4110229745,-1.761655458
N,0,-2.8258994217,2.1390194833,-0.5918677185	H,0,-2.5303264372,2.2198333197,-0.9609521309
H,0,-3.2391836639,1.6471621178,1.9660610529	H,0,-4.0409028488,0.5173371009,0.0530440425
H,0,-1.5299555617,0.6622831895,3.5705660006	N,0,-3.3003090084,-1.9585438249,0.826935073
H,0,0.7655778433,0.2857806091,2.7144663771	H,0,-0.7945886892,-2.283908086,0.0143062105
C,0,-0.9590847385,-0.6994367107,-1.0388111609	C,0,0.2447714446,1.9550658633,0.4066783091
Cu,0,2.0204330461,0.1008688888,0.2602187103	Cu,0,1.4286094258,-0.9290890303,-0.9912615378
Br,0,4.1887788384,0.0402494563,0.717449814	Br,0,2.9092084086,-2.3814177493,-1.76769765
C,0,-1.1239227241,-1.7455829903,0.0780500342	C,0,-0.2499448013,1.3950921202,1.7327358774
C,0,-1.4185002718,-0.0752617474,-3.470002191	C,0,0.7936514424,4.2939478885,1.3189405635
N,0,1.4615304851,-0.7956069543,-1.2904524996	N,0,2.1852215043,0.5910780204,-0.1642855429
N,0,0.3604432355,-0.9981355957,-1.6088030597	N,0,1.5834246122,1.5006466324,0.2427372827
C,0,-1.9673401893,-0.5998009839,-2.1610262235	C,0,0.1880125934,3.4623332603,0.2111327449
O,0,-0.1917202543,-2.3689533499,0.5381601188	O,0,0.1928670959,0.3891199065,2.2436679011
O,0,-2.3768335729,-1.8193217189,0.5323486265	O,0,-1.2881956709,2.1059044455,2.1903627557
C,0,-2.5746558139,-2.6983424781,1.6627317226	C,0,-1.9469997063,1.5633035777,3.3580184019
H,0,-3.9386727194,-0.7291041705,-2.8619418627	H,0,-0.3023347109,5.1018660543,-1.0129291768
H,0,-3.7042196863,-1.2661752346,-1.1105045466	H,0,-0.7187231396,3.4610054314,-1.7276016854
H,0,-2.233725816,-3.706713821,1.4213392509	H,0,-1.2250468146,1.4105127651,4.1624973938
H,0,-2.0219708605,-2.3175724144,2.5243769813	H,0,-2.424703453,0.6131899472,3.1078297902
H,0,-3.647456414,-2.6814409988,1.8509799568	H,0,-2.6926106382,2.307074937,3.636285324
H,0,-2.2302179445,0.0667246183,-4.1870817553	H,0,0.769231467,5.3576511976,1.0660903068
H,0,-0.9207518017,0.8925344083,-3.3422445321	H,0,1.8386355307,4.0071091349,1.4928297562
H,0,-0.6914512373,-0.7714342873,-3.9062314986	H,0,0.2542918939,4.1504865447,2.2611887196
O,0,-3.9339442698,2.4887212839,-0.1743059188	O,0,-4.4268942133,-1.6016908915,1.1927937971
O,0,-2.3935670238,2.4082282477,-1.7227152909	O,0,-2.8412350513,-3.0939909155,0.9815119434
ν_i =-224.3246 cm^{-1}	ν_i = -359.0419 cm^{-1}
G =-5157.999322	G = -5157.998956

II.- Cartesian coordinates and Gibbs free energies of the stationary points located on the potential-energy surface for formation of copper(I) carbene intermediate VII via N_2-extrusion from complex Va.

Stationary points located at Becke3LYP/6-31G(d) level of theory.

Va	***TS4***
C,0,1.2938922796,-0.8026148624,-1.4258392517 C,0,1.472795082,1.7366526506,-1.6381821501 C,0,-0.8069109074,0.5706106664,-1.6106584536 Cu,0,0.760560491,-0.2637239308,0.3829323752 Br,0,1.4533410302,-1.4049748652,2.17990455 C,0,-1.5920781205,0.8442895036,-0.4245443427 N,0,-1.8241691696,0.6239559113,-3.8395824362 N,0,-1.368313807,0.6162750021,-2.7981343835 C,0,0.68208937,0.4541905369,-1.4542312134 H,0,2.5276322528,1.5932895776,-1.3837253244 H,0,1.0752738516,2.5453104257,-1.014301656 H,0,1.4231209305,2.0733810731,-2.6830597104 H,0,2.3714127324,-0.886783445,-1.5438885047 H,0,0.728388447,-1.7026900508,-1.6579661423 O,0,-1.0537481267,0.7820922945,0.6917232496 O,0,-2.8764793063,1.1379226666,-0.6147421424 C,0,-3.6624211502,1.3530329685,0.579829374 H,0,-4.6737038081,1.5428385978,0.222312584 H,0,-3.2778349357,2.2122981886,1.1332651187 H,0,-3.6324787869,0.4657650424,1.2155906115 G = -4705.338952	C,0,1.5363035509,-0.2994767424,1.4256475387 C,0,1.1072299624,2.2240114473,1.3104771494 C,0,-0.7560536019,0.4229101484,1.2477394394 Cu,0,0.6498154783,-0.2901337596,-0.3445588029 Br,0,1.626135133,-1.7369948295,-1.7545687643 C,0,-1.5466271308,0.8818035888,0.1477053576 N,0,-2.000342617,0.4658619655,3.7406238843 N,0,-1.6723676388,0.8044011889,2.72863448 C,0,0.6401681963,0.783960931,1.358982006 H,0,2.1886856217,2.2953256034,1.1590755402 H,0,0.8686605979,2.7172542148,2.2626951517 H,0,0.6044300542,2.7861215741,0.5160364225 H,0,2.6089711326,-0.1230605016,1.4356197407 H,0,1.2113324788,-1.2581860648,1.8218771802 O,0,-1.0381019402,0.7166910548,-0.9934442286 O,0,-2.7898635155,1.3143167438,0.3266575623 C,0,-3.5769255996,1.4923063416,-0.8720967953 H,0,-4.5500592765,1.8360461667,-0.5228470184 H,0,-3.6689919569,0.5452528476,-1.4084131977 H,0,-3.1142840033,2.2369454594,-1.5231751808 ν_i = -495.7 cm^{-1} G = -4705.304876
TS5	***VI***
C,0,2.0088394137,-0.0993218519,1.241998022 C,0,2.0365305264,2.4426585622,1.1927933168 C,0,-0.0376230742,0.9073734082,0.8552544 Cu,0,-0.0446342114,-0.7438255457,0.0800627102 Br,0,0.146878975,-2.6525824834,-1.016554339 C,0,-0.8935367454,2.0659115155,0.5776448945 C,0,1.3274875386,1.1098360874,1.1660978796 H,0,3.0756839362,2.3430039982,1.5177616017 H,0,1.516100368,3.1152902903,1.8812635857 H,0,2.0254357197,2.9195176849,0.2052705674 H,0,3.0847090693,-0.1694780061,1.086860986 H,0,1.522384225,-1.0048389851,1.5873629365 O,0,-1.1598941073,2.9029268736,1.4218196357 O,0,-1.3960947052,2.0536440587,-0.6707979289 C,0,-2.2904523211,3.1360111486,-0.9955488577 H,0,-2.5662598746,2.9801045892,-2.0379571538 H,0,-1.7903592249,4.0994336553,-0.86757263 H,0,-3.1736277393,3.1009138381,-0.3530182109 ν_i = -286.6 cm^{-1} G = -4595.801857	C,0,1.7549279841,0.0763504285,1.3540424431 C,0,1.5705697457,2.5865790676,2.3761702838 C,0,0.1755025338,1.1693214446,0.6729300323 Cu,0,0.4610280262,-0.5818748817,0.0770651448 Br,0,0.1402693051,-2.4740298446,-1.0394023873 C,0,-0.9704734723,1.9536390626,0.1753203414 C,0,1.1522903934,1.4377524041,1.5309029396 H,0,2.5886751237,2.9024053659,2.1122036433 H,0,1.5962354144,2.2914746456,3.4336282335 H,0,0.8890759514,3.4309980593,2.2547676216 H,0,2.7187637147,0.0299969778,0.8376964239 H,0,1.6885616817,-0.6041718531,2.2085763581 O,0,-1.2273688355,3.0915024079,0.509955771 O,0,-1.6962417575,1.2326116985,-0.7046841705 C,0,-2.8470380413,1.8923771688,-1.2637468955 H,0,-3.2965445619,1.1650703295,-1.938789972 H,0,-2.5427589533,2.7900439633,-1.8079845612 H,0,-3.5470369254,2.1705683353,-0.4717910624 G = -4595.824850

***VI* + N_2**	***VII***
C,0,1.7798843588,-0.5471132427,0.9213305175 C,0,1.5525967454,2.0117438954,1.258172 C,0,-0.3375871892,0.2350972674,1.0209498512 Cu,0,0.3785570248,-0.7421680271,-0.4665767387 Br,0,1.3172112167,-1.9397843539,-2.1185972884 C,0,-1.3326607847,0.8937150149,0.2347147964 N,0,-2.2052251532,1.896868754,4.399140886 N,0,-1.2224836732,1.95637293,3.8967986417 C,0,0.9817704391,0.6217957496,1.1776662436 H,0,2.3144306211,2.1688586147,0.485121363 H,0,2.0441389497,2.1529007731,2.228855551 H,0,0.7749612751,2.7727979746,1.1537770363 H,0,2.8050102079,-0.4430141952,0.5697976135 H,0,1.5689271787,-1.4589540864,1.473677226 O,0,-1.3432453665,0.4852929458,-0.9561181936 O,0,-2.2049717227,1.7574657637,0.7278896412 C,0,-3.2556542211,2.1872919153,-0.1711111791 H,0,-3.9034426555,2.8220813166,0.4323065603 H,0,-3.8023265563,1.3218368013,-0.551309717 H,0,-2.8326429161,2.7488729083,-1.0066767686 G = -4705.345226	C,0,0.3420334238,-2.6222855665,-1.0258278691 C,0,0.5962605586,-0.2603445707,-0.867232331 C,0,1.2936949099,0.9526162355,-1.3379358468 C,0,1.9374337776,-1.5671157365,-2.6516697868 Br,0,-2.019416674,-0.1266585912,2.1128990467 Cu,0,-0.6425627921,-0.0875588596,0.4119758012 C,0,0.9393093548,-1.5038609663,-1.5174547015 O,0,0.9798121326,1.4847420941,-2.3874559476 O,0,2.2205815174,1.4105545065,-0.4859253435 C,0,2.8651994124,2.6443399101,-0.8692673983 H,0,0.5740236976,-3.6177233295,-1.3960718272 H,0,-0.3820176265,-2.5394212085,-0.2203773818 H,0,2.128831468,3.4484408482,-0.939003175 H,0,3.3684814037,2.5299926052,-1.8323619933 H,0,3.5858950081,2.849371269,-0.0785148308 H,0,2.0603956959,-2.5895721635,-3.0186614697 H,0,2.918750124,-1.1989253873,-2.3280064468 H,0,1.612806967,-0.9323736518,-3.4823898149 G = -4595.815235

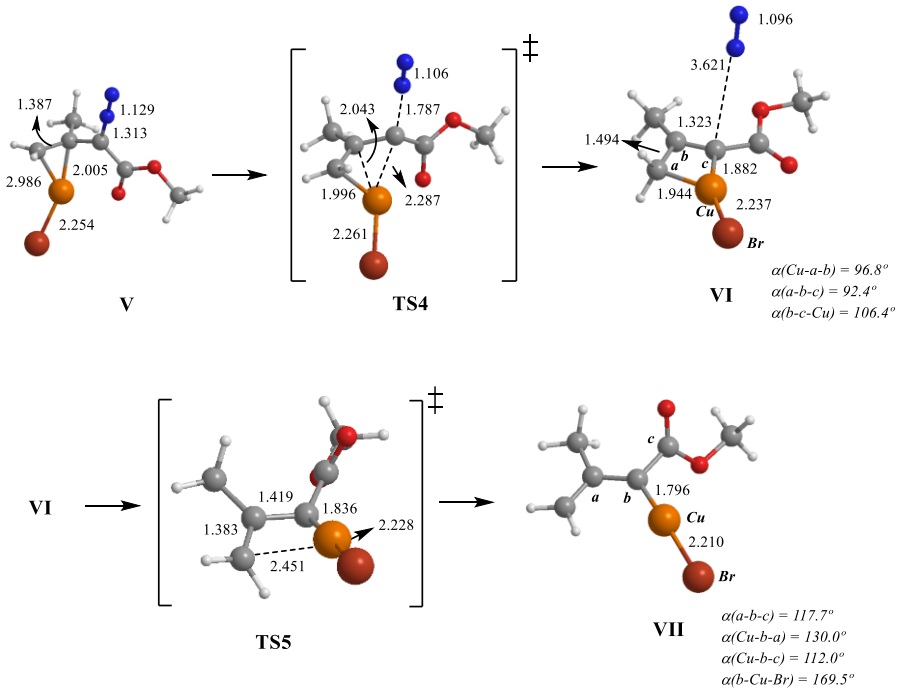
III.- Potential-energy Surface for Formation of Copper(I) carbene Intermediate VII via N_2-extrusion from Complex Va at Becke3LYP/6-311+G(d) and MP2/6-311+G(d) Levels of theory.

The formation of copper(I) carbene intermediate **VII**, was also studied at Becke3LYP/6-311+G(d) and MP2/6-311+G(d) levels of theory [using the 6-31G(d) basis set for Cu and Br]. In both cases, the potential-energy surface is very close to that obtained at the Becke3/6-31G(d) level of theory.

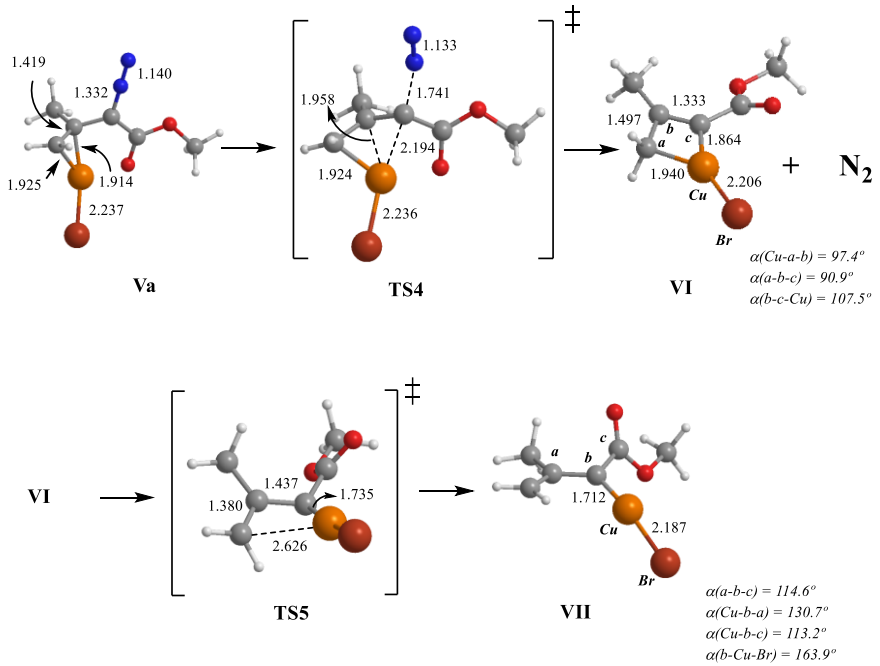
The values of the activation and reaction free energies are collected in Table S3.

Table S3. Values of ΔG in the Formation of VII at different levels of theory (the values at the Becke3LYP/6-31G(d) are also given for comparison).

Level of Theory: B3LYP/6-311+G [6-31G* in Cu and Br]*						
Stationary Point	**Va**	**TS4**	**VI + N_2**	**VI**	**TS5**	**VII**
ΔG	0.0	+22.3	-8.4	0.0	+11.8	+2.0
Level of Theory: MP2/6-311+G [6-31G* in Cu and Br]*						
Stationary Point	**Va**	**TS4**	**VI + N_2**	**VI**	**TS5**	**VII**
ΔG	0.0	+19.4	-19.4	0.0	+26.6	+20.1
*Level of Theory: B3LYP/6-31G**						
Stationary Point	**Va**	**TS4**	**VI + N_2**	**VI**	**TS5**	**VII**
ΔG	0.0	+21.4	-3.9	0.0	+14.4	+6.0



Scheme S4. Selected geometrical parameters of the stationary points located for the formation of **VII** at the B3LYP/6-311+G* [6-31G* on Cu and Br] level of theory.



Scheme S5. Selected geometrical parameters of the stationary points located for the formation of **VII** at the MP2/6-311+G* [6-31G* on Cu and Br] level of theory.

Stationary points located at Becke3LYP/6-311+G(d) [6-31G on Cu and Br] level of theory.*

V-a	***TS4***
C,0,1.2521616945,-0.5544441212,-1.595116736 C,0,1.2800369257,1.9873220016,-1.5093643948 C,0,-0.9184383475,0.6830075151,-1.5261189002 Cu,0,0.8327434414,-0.2664275034,0.3246751798 Br,0,1.6411252128,-1.4982814659,2.0308190587 C,0,-1.6786984282,0.8112745956,-0.3015004029 N,0,-2.0365630465,0.7348246227,-3.695981631 N,0,-1.528088422,0.7234651581,-2.6878435416 C,0,0.5773166284,0.6475723455,-1.441658901 H,0,2.3540314333,1.8881565704,-1.3384194606 H,0,0.8822511977,2.6946926707,-0.7766625864 H,0,1.1432938472,2.4382681492,-2.4995961727 H,0,2.3247158161,-0.5561532935,-1.7580063628 H,0,0.721847995,-1.4615903722,-1.8672043881 O,0,-1.1008010472,0.7392240347,0.7822475287 O,0,-2.9915283908,0.990132048,-0.4381867917 C,0,-3.757304384,1.0678435573,0.7857623063 H,0,-4.789780385,1.1785653679,0.4659298966 H,0,-3.4388417553,1.9283732811,1.3727713219 H,0,-3.6257091506,0.1576040408,1.3692129689 G = -4705.169888	C,0,1.5223050862,-0.6012683514,1.3401358466 C,0,1.5220757318,1.9515470803,1.3132010243 C,0,-0.6170533861,0.4991785034,1.3176855965 Cu,0,0.5808761542,-0.4038442223,-0.4083185906 Br,0,1.2485244617,-1.9274191336,-1.9397345521 C,0,-1.3853370005,1.1357247792,0.2942024569 N,0,-1.7386173433,0.684753645,3.870928555 N,0,-1.3583091954,0.9740635721,2.8730571474 C,0,0.8238524478,0.6111137948,1.3482398573 H,0,2.5848579288,1.8548392461,1.0817344226 H,0,1.4420141758,2.4289173342,2.2971805815 H,0,1.0689352615,2.6323082561,0.5887653915 H,0,2.6050723403,-0.6004150413,1.2777818369 H,0,1.0555279597,-1.5037148776,1.7197477502 O,0,-0.9788893692,0.9666229757,-0.8765834072 O,0,-2.528729976,1.749361286,0.5782119128 C,0,-3.348428747,2.1281761173,-0.5505352781 H,0,-4.2262559374,2.5986970336,-0.1157176495 H,0,-3.6268244288,1.2461064341,-1.1260923114 H,0,-2.8121361905,2.8279875841,-1.1899565546 ν_i = -496.3014 cm^{-1} G = -4705.134521

VI + N_2	***VI***
C,0,2.0863602254,-0.005791327,-0.5721775167 C,0,2.0584584192,2.613744088,-1.2139656551 C,0,0.2418393846,0.8575572399,-0.5345249282 Cu,0,0.4453925175,-0.9866964857,-0.218300537 Br,0,-0.0081725674,-3.122816955,0.2646733147 C,0,-1.1445158721,1.3236412223,-0.6839226883 N,0,-0.1691909541,2.9953652709,3.636902457 N,0,-0.1275335321,2.3864461713,2.7270927322 C,0,1.4528916129,1.3313536685,-0.780161517 H,0,2.5626491416,2.4857106556,-2.1787798745 H,0,2.8234729635,2.9398483259,-0.5004048495 H,0,1.3076733518,3.3982776746,-1.3097916198 H,0,2.5439719615,-0.4644600104,-1.4507718454 H,0,2.638646264,-0.1583320306,0.3566909094 O,0,-2.092945839,0.5804409684,-0.7930628943 O,0,-1.2320938572,2.6709411693,-0.6952682743 C,0,-2.5610678792,3.2084678605,-0.8523688632 H,0,-2.9760726372,2.9174223767,-1.8175529113 H,0,-2.4438984537,4.2882210573,-0.7941014726 H,0,-3.213192111,2.8485297479,-0.0567287434 G =-4705.183256	C,0,2.0473620262,0.3130020493,0.2030614243 C,0,2.0466842334,3.0039848957,0.1024124454 C,0,0.186321475,1.166201189,0.1645609963 Cu,0,0.3942060389,-0.6985853127,0.0439292426 Br,0,0.0195313899,-2.8968088095,-0.1121692976 C,0,-1.1665634064,1.6865976108,-0.0779434801 C,0,1.413713796,1.6649413121,0.1882323147 H,0,2.7115804122,3.0543281474,-0.7673691497 H,0,2.6705390017,3.1914872255,0.9834968197 H,0,1.3018741278,3.7958699122,0.026180749 H,0,2.6578719125,0.0505430535,-0.6632098643 H,0,2.4373981705,-0.0455572967,1.1565986683 O,0,-2.0631955727,1.0249523435,-0.5499981904 O,0,-1.2882733843,2.9809270885,0.2837858509 C,0,-2.5908057281,3.5651480179,0.0773625664 H,0,-2.8440730317,3.5636005505,-0.9829133364 H,0,-2.511926691,4.5824839135,0.452836241 H,0,-3.3473603981,3.0082409897,0.6299383682 G = -4595.619349
TS5	***VII***
C,0,2.0747571274,-0.282884862,0.880032318 C,0,2.0852109417,2.2447618726,0.8530107371 C,0,-0.0282742459,0.7412018067,0.8583198686 Cu,0,-0.075517241,-0.7620738227,-0.1944992015 Br,0,0.0962844911,-2.5136743383,-1.5611214062 C,0,-0.9150118828,1.8968956094,0.7588707849 C,0,1.3793484594,0.9121813346,0.9067737748 H,0,3.1691099461,2.1314029403,0.7980329634 H,0,1.8548158771,2.8174852932,1.7559154792 H,0,1.7550219145,2.8403471432,-0.0019397998 H,0,3.135885959,-0.3206416497,0.6454856983 H,0,1.6531232947,-1.1980663254,1.2746128669 O,0,-1.3874375539,2.2429994021,-0.3051566543 O,0,-1.1706814691,2.488200865,1.9361355849 C,0,-2.1296239137,3.5668694189,1.9103776668 H,0,-2.2506090103,3.8677591244,2.9478074081 H,0,-3.0768864321,3.2209854926,1.4971152228 H,0,-1.7539054822,4.3957174621,1.3105538776 ν_i = -257.1833 cm^{-1} G = -4595.600492	C,0,1.0306888493,-2.8432269936,-0.4401194199 C,0,1.0248255493,-0.4585218931,-0.3941095473 C,0,1.8002650664,0.7989275251,-0.3910803053 C,0,3.2676677095,-1.7353802286,-0.468876503 Br,0,-2.8169715417,0.1554008911,0.4879265696 Cu,0,-0.7335696673,-0.1662700749,-0.1755161715 C,0,1.7569189949,-1.6958847752,-0.4421629166 O,0,2.4507978821,1.1772819267,-1.3407773507 O,0,1.6228751902,1.4879344141,0.7466619166 C,0,2.3404066847,2.7343574437,0.8607276361 H,0,1.5012252173,-3.8216944888,-0.4309428547 H,0,-0.053160405,-2.8161265758,-0.4331335479 H,0,2.0030314973,3.4349062963,0.097395836 H,0,3.4123795477,2.5679973944,0.7541800467 H,0,2.1061059683,3.1079412372,1.8537110137 H,0,3.6394514386,-2.7610062268,-0.4828704596 H,0,3.6902556094,-1.2367217038,0.4086415836 H,0,3.6542137326,-1.2158521449,-1.3477927699 G = -4595.616189

Stationary points located at MP2/6-311+G(d) [6-31G on Cu and Br] level of theory.*

V-a

C,0,1.4275366221,-0.5837286261,-1.4658694677
C,0,1.3172279519,1.9839692657,-1.5556520233
C,0,-0.8026373917,0.5689114317,-1.5281999384
Cu,0,0.8224407418,-0.1960608035,0.3203994876
Br,0,1.4100184051,-1.4825559098,2.0530904344
C,0,-1.5742219318,0.78308441,-0.3342724395
N,0,-1.9119775506,0.6248957759,-3.7367756329
N,0,-1.4072397867,0.6236980473,-2.7141299373
C,0,0.6803158235,0.6205901662,-1.4046468551
H,0,2.3861082862,1.9498267802,-1.3267040135
H,0,0.8476207754,2.7212588195,-0.8971346295
H,0,1.2083750891,2.3438866212,-2.5863156302
H,0,2.5030800316,-0.5231037005,-1.6137945887
H,0,0.9429354481,-1.5073854137,-1.7759593927
O,0,-0.990267,0.7810954039,0.7634802591
O,0,-2.8852772492,0.9497084842,-0.4812909019
C,0,-3.6206644231,1.0750772569,0.7586655323
H,0,-4.6597531202,1.1711283527,0.4562999608
H,0,-3.2872184895,1.9584052943,1.3014659283
H,0,-3.4690382616,0.1871920986,1.3710673072

G = -4700.802797

TS4

C,0,1.5878115475,-0.7036801051,1.2430179803
C,0,1.5911215274,1.8820306319,1.3419272344
C,0,-0.5389827709,0.4370016435,1.3478330843
Cu,0,0.5778752223,-0.3690047847,-0.3596238402
Br,0,1.0821623784,-1.8200539009,-1.984915374
C,0,-1.3017710073,1.0911892756,0.3298278242
N,0,-1.6738800438,0.6646357707,3.8789562782
N,0,-1.2687154498,0.9223024532,2.8522964549
C,0,0.8931560956,0.544017491,1.343643367
H,0,2.6423291747,1.7929059055,1.055211495
H,0,1.5540449645,2.3066585525,2.3527794451
H,0,1.1006840535,2.5917219499,0.6693373115
H,0,2.6721557509,-0.6900090586,1.160577898
H,0,1.1370597386,-1.5913787831,1.6820113817
O,0,-0.8698702322,0.9487266402,-0.8478706374
O,0,-2.4628396625,1.6733585395,0.6032768473
C,0,-3.2527412505,2.0163252651,-0.5578666561
H,0,-4.1438917454,2.4918435895,-0.1570991715
H,0,-3.507526387,1.1142702111,-1.1134800065
H,0,-2.7006374807,2.7004587062,-1.2005247111

ν_i = -621.1028 cm^{-1}
G = -4700.771859

VI

C	0.089356552736	2.173018310555	-0.001997792927
C	2.786051629698	2.429135861879	0.107302919831
C	1.095392289554	0.421793113245	-0.049621583290
Cu	-0.768125955883	0.433287118632	-0.009321490128
Br	-2.758294220922	-0.517577071721	-0.044600907997
C	1.727771467916	-0.902061765270	0.130467605380
C	1.506136864006	1.689549357394	-0.007271879121
H	2.783434901985	3.049045085639	1.010503484555
H	2.913196816628	3.104526049530	-0.745484341157
H	3.633344407771	1.742525598920	0.144507986030
H	-0.238217050043	2.672976831208	0.914471896803
H	-0.288144383088	2.604299781020	-0.934283808001
O	1.186798850174	-1.845885974679	0.668283804469
O	2.977273188888	-0.909904979295	-0.374802245931
C	3.661023210042	-2.172765938909	-0.229093343568
H	3.765421299752	-2.426674938072	0.825763710965
H	4.633373522207	-2.022203469106	-0.691164357210
H	3.106572541470	-2.960309870787	-0.739527604524

G = -4591.518650

N_2

N,0,0.,0.,0.0348364593
N,0,0.,0.,1.1551635407

G = -109.315076

TS5

C,0,2.2289020461,-0.2865285127,0.989507791
C,0,2.052827603,2.2318724002,0.9675542191
C,0,0.041173094,0.5914451882,0.879420957
Cu,0,-0.08358361,-0.7999459554,-0.1436880219
Br,0,-0.0360681533,-2.3332241377,-1.7260186156
C,0,-0.8663832088,1.7443503417,0.8108307911
C,0,1.4500916374,0.8523758395,0.9933177099
H,0,3.1435867629,2.1945922202,0.9465116945
H,0,1.7415088659,2.776278964,1.8626885268
H,0,1.703003716,2.7979919708,0.0997053748
H,0,3.307939625,-0.2408853454,0.8539235173
H,0,1.819291409,-1.2446915252,1.2911684234
O,0,-1.4713130333,2.0239466647,-0.2116361217
O,0,-0.9586036461,2.42326472,1.9670792827
C,0,-1.926217699,3.4913177106,1.9560703441
H,0,-1.9295357638,3.8839869296,2.9697168459
H,0,-2.9100639751,3.1059141306,1.6875832105
H,0,-1.6324479845,4.2614012997,1.2425504288

ν_i = -240.3269 cm^{-1}
G = -4591.476209

VII

C,0,1.2918830747,-2.8672991571,-0.0053232001
C,0,1.0263832187,-0.4960740516,-0.2432853196
C,0,1.7763693971,0.7847489252,-0.3565557004
C,0,3.2003943216,-1.4521782249,0.777907834
Br,0,-2.7642221195,0.1127645191,0.1672665738
Cu,0,-0.6720508244,-0.2927442448,-0.3219009885
C,0,1.8232641537,-1.6267444124,0.1869449598
O,0,2.7505302302,0.9695206522,-1.0611203063
O,0,1.1774082018,1.7297064471,0.396639823
C,0,1.8698686459,2.9913863264,0.4428011337
H,0,1.8393707441,-3.7704424718,0.2536707449
H,0,0.3086286709,-2.9831420579,-0.4508692553
H,0,1.8997726697,3.4409177553,-0.5494057506
H,0,2.8868248805,2.851600871,0.8103692623
H,0,1.2924750035,3.6062353313,1.1278355447
H,0,3.5911401723,-2.400782678,1.1507786428
H,0,3.1771765347,-0.7426949301,1.6102464904
H,0,3.8893750873,-1.0557201173,0.0290785272

G = -4591.486628

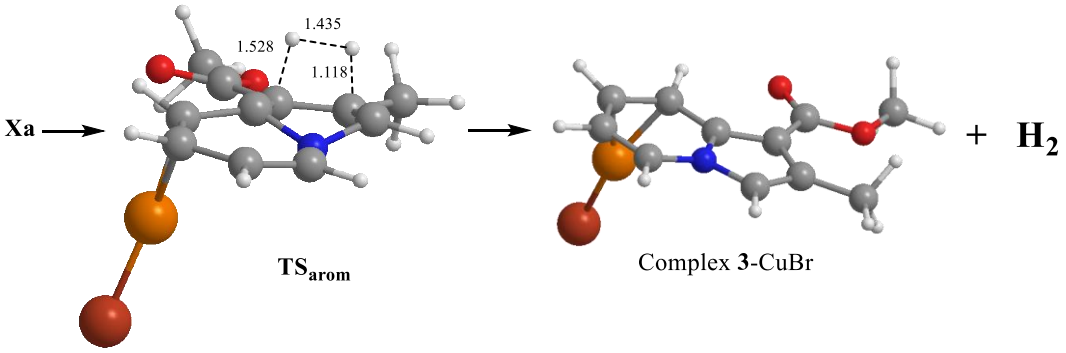
IV.- Cartesian coordinates and Gibbs free energies of the stationary points for conjugate addition of pyridine (1a) to carbene intermediate VII, intramolecular cyclization, reductive elimination, and aromatization steps.

Stationary points located at Becke3LYP/6-31G(d) level of theory.

TS6	***VIIIa***
C,0,1.920108261,-0.5113292512,0.8090193742 N,0,1.9118238984,1.7146362005,0.8118031431 C,0,-0.3891817313,-1.0464434136,0.8150677895 C,0,-1.6296794069,-1.2679196983,1.582162206 C,0,0.7302872435,2.2658995648,1.0957400253 C,0,0.9070354205,-1.1218042273,3.04154254 Br,0,-0.322445553,-0.6721679604,-3.1604866863 Cu,0,-0.4937256905,-0.8483673962,-0.9772274918 C,0,0.529940084,3.6452866567,1.0474901637 C,0,0.8085905119,-0.9173355231,1.5417462929 C,0,1.5999017783,4.4633870281,0.6870754092 O,0,-2.2027208318,-0.3602415659,2.1637946434 O,0,-2.0874959078,-2.5321372422,1.5209055027 C,0,-3.3446810485,-2.7678081687,2.1810367204 H,0,2.919372146,-0.5016241266,1.2335846744 C,0,2.8312446869,3.8778697908,0.3879123642 H,0,1.8369122757,-0.4846504175,-0.2720123644 C,0,2.9426139189,2.4913511769,0.4620003518 H,0,-4.1310444628,-2.1548272581,1.7331552289 H,0,-0.0703883578,1.5781524998,1.3643659607 H,0,-3.2715496343,-2.533228386,3.2462901757 H,0,-3.554491919,-3.8273412023,2.0345307635 H,0,0.2292907727,-0.4491434197,3.5789968438 H,0,-0.4449914395,4.0590149071,1.2833730473 H,0,1.9235053775,-0.9454618716,3.4066474446 H,0,0.6266154998,-2.1464476395,3.3144817993 H,0,1.4767852679,5.5414031503,0.6360872189 H,0,3.6882643766,4.4779866558,0.0992968532 H,0,3.877247798,1.9843536609,0.232851041 ν_i = -89.4863 cm^{-1} G = -4844.025660	C,0,1.8289305878,-0.2300764683,0.8349512745 N,0,1.8279124676,1.2867691897,0.8334535474 C,0,-0.4700458511,-1.0605169729,0.8309925516 C,0,-1.6922487561,-1.517104137,1.5283895292 C,0,0.9436176623,1.8963093604,0.0135199004 C,0,0.7987248152,-0.9001486019,3.0704984589 Br,0,-0.1521222938,-0.0394018475,-3.0636376077 Cu,0,-0.5291797399,-0.742906028,-0.9986997742 C,0,0.8468601423,3.2771553604,-0.010537375 C,0,0.6276651742,-0.7776355364,1.573123821 C,0,1.6601762813,4.0346422866,0.8320938404 O,0,-2.3167099155,-0.8980457792,2.3751257922 O,0,-2.1098045068,-2.724076214,1.0605947196 C,0,-3.3227483716,-3.2175581969,1.6415304337 H,0,2.7921472821,-0.5258330611,1.261573843 C,0,2.5598825142,3.3824569461,1.6794918484 H,0,1.7820062996,-0.5068643694,-0.2195416063 C,0,2.6279115259,1.9990336992,1.6551186236 H,0,-4.1522571796,-2.5316005823,1.446819047 H,0,0.3337793189,1.2125725226,-0.5761912303 H,0,-3.2174045334,-3.3406937643,2.7237391716 H,0,-3.505592775,-4.1815980291,1.1647913175 H,0,-0.1267399418,-1.2177108309,3.5533466369 H,0,0.1378501319,3.7368059994,-0.6897014367 H,0,1.0801321097,0.0626511744,3.5264098097 H,0,1.5944030317,-1.6144243865,3.3294646549 H,0,1.5970198541,5.1183821001,0.8309250895 H,0,3.2091828287,3.9340163027,2.3499599108 H,0,3.3103400719,1.4278815792,2.273038146 G = -4844.043749
TS7	***IXa***
C,0,2.0279709044,-0.5593466444,0.8319114421 N,0,2.0302816992,0.9448107774,0.8412939616 C,0,-0.3762681693,-1.017017089,0.8320497244 C,0,1.4519974422,1.5888151742,-0.1994937308 C,0,-1.6352357325,-1.404964054,1.505231242 C,0,0.9888173252,-1.554301003,2.9487533893 C,0,1.2670080253,2.9659687421,-0.1580788672 C,0,1.6792018793,3.6802685052,0.9599672443 Br,0,-0.3848138047,0.1929542478,-3.0557840341 Cu,0,-0.5122268235,-0.4392039595,-0.9259155275 C,0,2.2760237576,2.9925788549,2.027249359 C,0,0.7778347285,-1.0783953203,1.5289794597 C,0,2.4331986127,1.6237720639,1.9425765052 H,0,1.1475751475,0.9791358046,-1.0420582898 O,0,-2.0722374784,-0.9502873209,2.5499257398 O,0,-2.3245190654,-2.3236058817,0.7743442306 H,0,0.7997747696,3.4460260875,-1.0106653624 C,0,-3.5839964162,-2.7248251748,1.3272760575 H,0,1.5487246586,4.7567874736,1.0072827536 H,0,2.9595245229,-0.8761758689,1.3090658308 H,0,2.616240166,3.511452128,2.9161056957 H,0,2.876041322,1.0294511269,2.7320907135 H,0,-4.25585328,-1.8668238293,1.4215236668 H,0,-3.4511213067,-3.1757885579,2.3153222068 H,0,-3.9928944006,-3.4545202715,0.6271882593 H,0,1.7164457942,-2.3778525252,2.9920917992 H,0,0.0532056821,-1.887325994,3.3997232645 H,0,1.382722923,-0.7536048958,3.5948051376 H,0,2.045441359,-0.8450986786,-0.2202326338 ν_i = -55.7638 cm^{-1} G = -4844.040627	C,0,2.3764928787,-1.4270411811,0.6772988558 N,0,2.3714414823,0.0287978823,0.6783670966 C,0,-0.107258133,-1.29922709,0.66620203 C,0,1.7120972967,0.6552040845,-0.3789125699 C,0,-1.4616575945,-1.817555984,0.962771976 C,0,1.0635213441,-3.3953506615,1.5646820475 C,0,1.706214523,2.0929533454,-0.346647205 C,0,2.0173618286,2.7683563436,0.8022904271 Br,0,-1.1545366527,1.5532178777,-2.0587223945 Cu,0,-0.2779131553,0.2464249662,-0.4235466567 C,0,2.4081670734,2.0412982918,1.9600428714 C,0,0.9869608871,-2.0093131649,0.9718016029 C,0,2.5713799545,0.6876541367,1.8596232858 H,0,1.8905154326,0.1685907154,-1.3377789495 O,0,-1.83268538,-2.5362071051,1.8711675916 O,0,-2.3270516389,-1.3023473413,0.0390465581 H,0,1.3748942501,2.6084218058,-1.238682068 C,0,-3.7077984365,-1.664970831,0.1832901211 H,0,1.9723232061,3.8525897494,0.8294520863 H,0,3.0995304366,-1.765420859,1.4263374701 H,0,2.6177711827,2.5383737453,2.8998049082 H,0,2.903052366,0.0727662513,2.6883436719 H,0,-4.0860993709,-1.349395482,1.1594690749 H,0,-3.8312224878,-2.7473280738,0.0866332315 H,0,-4.2304849679,-1.1450967082,-0.6193900632 H,0,1.7158701394,-4.0400639164,0.9579190244 H,0,0.0795691999,-3.8549368324,1.6487271294 H,0,1.5048553015,-3.3608778003,2.5712459472 H,0,2.7426057029,-1.771765678,-0.298888143 G = -4844.060347

TS8	*Xa*
C,0,2.5661195269,-1.5686010831,-0.6853786973 N,0,2.5608976711,-0.1078738284,-0.6819364535 C,0,0.1851795778,-1.0949737383,-0.6779043486 C,0,1.3763787803,0.3674548626,-1.329790142 C,0,-1.2315293943,-1.3542593709,-1.0315835433 C,0,0.9305513826,-3.5424926286,-0.5655244228 C,0,1.0561854693,1.7854767077,-1.1315159804 C,0,1.4388756382,2.3839398628,0.0505334386 Br,0,-1.5118835282,0.7976201897,1.941365767 Cu,0,-0.0610828661,0.7205913801,0.2060846878 C,0,2.4334461085,1.7294157174,0.879433755 C,0,1.1214575511,-2.054260174,-0.5896496404 C,0,2.941905316,0.5350413916,0.4934473862 H,0,1.2924343053,0.042874111,-2.3630446502 O,0,-1.8757984782,-2.3667594432,-0.8570198921 O,0,-1.7472619383,-0.2405425585,-1.6277076008 H,0,0.4333203189,2.2881491343,-1.8641458036 C,0,-3.1563960196,-0.291080875,-1.9177638975 H,0,1.1496297957,3.4059673187,0.2699577022 H,0,3.2092515981,-1.947216543,0.1160787251 H,0,2.7852273761,2.2005975191,1.7887313554 H,0,3.7220479167,0.0316878453,1.0539466764 H,0,-3.7218119606,-0.3949900862,-0.9887682006 H,0,-3.3811976775,-1.1307342135,-2.5798322689 H,0,-3.3874559319,0.6571684676,-2.4032114215 H,0,1.575728843,-4.032077368,-1.308515501 H,0,-0.1097336975,-3.8155255326,-0.7416198852 H,0,1.2233299043,-3.9390244052,0.4168001998 H,0,2.9817118285,-1.9411641306,-1.6350830489 ν_i = -229.0861 cm^{-1} G = -4844.030829	C,0,2.6072137643,-2.1479488816,-1.1624602653 N,0,2.6052557618,-0.6803713976,-1.1602394431 C,0,0.3762350612,-1.4598448305,-1.1769498205 C,0,1.2648075484,-0.2851273481,-1.6585526221 C,0,-1.0964444363,-1.4578074342,-1.0756792583 C,0,0.7830990042,-3.9294164293,-0.5489765833 C,0,0.8777818076,1.133767079,-1.2851075047 C,0,1.5157387598,1.7856106078,-0.2246424907 Br,0,-1.4813351251,1.5330177686,2.1350004745 Cu,0,-0.2864545791,1.1246895861,0.275945984 C,0,2.6151982649,1.118890956,0.4667524358 C,0,1.1522015272,-2.5366417241,-0.9421374354 C,0,3.0810688091,-0.0546718911,-0.0107098082 H,0,1.2944496592,-0.3458564778,-2.7579445499 O,0,-1.8299558189,-2.4170916554,-1.1691150691 O,0,-1.5908043344,-0.1975153631,-0.8235411179 H,0,0.3869974456,1.7175657191,-2.0607398687 C,0,-3.0318027666,-0.1089019389,-0.6646668965 H,0,1.4650095871,2.871031143,-0.1620032711 H,0,3.2807769091,-2.5464223825,-0.3965791099 H,0,3.0790097127,1.577863063,1.3312019418 H,0,3.9269451321,-0.5581454304,0.4493085569 H,0,-3.3367509186,-0.6575093576,0.2266730575 H,0,-3.5173826194,-0.5187696991,-1.5512346214 H,0,-3.2373285257,0.9524472078,-0.543498455 H,0,1.1110149249,-4.6364056952,-1.3239178363 H,0,-0.2923820258,-4.044306709,-0.4166942732 H,0,1.3012876681,-4.2167150035,0.375376431 H,0,2.9509720527,-2.5343893352,-2.135691052 G = -4844.065713

In the case of the reaction of pyridine **1a**, the transition state $\mathbf{TS_{arom}}$ corresponding to the aromatization of intermediate **Xa** to give the complex between CuBr and indolizine **2** and dihydrogen, was also located, at the Becke3LYP/6-31G(d) level of theory (see Scheme S4). In this transition structure, the dihydrogen molecule is almost fully formed. The values of the activation and reaction free-energies are predicted to be, $\Delta G^{\#}$=39.8 kcal mol^{-1} and ΔG_{rxn}=63.4 kcal mol^{-1}**.**



Scheme S5. Selected geometrical parameters of the stationary points located for the deshidrogenation of **Xa**.

TS_{arom}	**Complex 3-CuBr**
N,0,-0.0379869031,0.402312984,2.0884377889 C,0,0.0717324663,-0.5798767309,1.0601812723 C,0,1.3740612567,-1.2216211346,0.903510081 C,0,2.263491106,-1.1659620575,1.9968800048 C,0,1.8969670039,-0.4275931682,3.1890215551 C,0,0.7581609666,0.3119925246,3.2110129731 C,0,-0.8831296283,-0.1483062301,0.0404932303 H,0,1.4443508367,-2.0050308918,0.1562220326 H,0,3.0588618153,-1.9042062361,2.0763554574 H,0,2.5474211472,-0.4372010091,4.0558418345 H,0,0.4434972796,0.9005454598,4.0660621217 C,0,-1.8190438962,0.6399867369,0.673135982 C,0,-1.4268462786,0.6550212789,2.0730685665 O,0,-0.064370106,-1.5022776965,-1.7367690613 C,0,-0.8543776735,-0.6665322569,-1.3320874414 C,0,-3.1022131051,1.2181371874,0.1597014507 H,0,-3.7164313779,0.4619848126,-0.3390785405 H,0,-3.6827395535,1.6634177732,0.9734386641 H,0,-2.9016333178,1.9983705915,-0.5827599922 Cu,0,2.8004689012,0.0533043738,0.5416740136 H,0,-1.8475680552,1.3283326525,2.81364755 H,0,-1.678530495,-0.7413190192,2.2864787052 O,0,-1.800778446,-0.1024869226,-2.1180386987 H,0,-0.9504687714,-1.4386970425,1.8037697149 C,0,-1.8005359435,-0.5447603072,-3.4863196876 H,0,-0.8411066734,-0.3222959,-3.9599770778 H,0,-1.9842817395,-1.6208053704,-3.5424787861 H,0,-2.6058339433,0.0088148376,-3.9699506632 Br,0,4.1592006119,1.4177649987,-0.5082110571 vi = -1776.1 cm-1 G = -4844.002225	N,0,-0.8101153853,-1.4294853169,-1.4993637444 C,0,-0.6972299704,-0.0975276524,-1.082332097 C,0,0.5648750359,0.562542309,-1.2236113263 C,0,1.6494200434,-0.1468175263,-1.7988016256 C,0,1.443912336,-1.5035237253,-2.2474677565 C,0,0.2403890914,-2.1118236748,-2.0790401661 C,0,-1.9500404256,0.2897519851,-0.5920424589 H,0,0.5606953885,1.6446323723,-1.1431912011 H,0,2.4966073217,0.40512169,-2.1994573966 H,0,2.2548195566,-2.0525050529,-2.712529313 H,0,0.0282629976,-3.1275356772,-2.3912194659 C,0,-2.8320839822,-0.8343539125,-0.7150983964 C,0,-2.1016692842,-1.8621375173,-1.2718697647 O,0,-1.3692988802,2.5289663624,-0.0288901134 C,0,-2.1977491088,1.6318662839,-0.0667147261 C,0,-4.2771229322,-0.9282202196,-0.3259136032 H,0,-4.8827530441,-0.189056492,-0.8604208095 H,0,-4.6718918864,-1.9247936464,-0.5477679517 H,0,-4.4136986537,-0.7314025187,0.7423254908 Cu,0,1.8198597709,-0.0817731031,0.1542521827 H,0,-2.3959285909,-2.8701414331,-1.527383107 O,0,-3.4661574417,1.7906168389,0.3861189788 C,0,-3.7625839113,3.0878495361,0.9260429896 H,0,-3.1114845759,3.3089056073,1.7758133706 H,0,-3.6277543279,3.8621257116,0.1660793455 H,0,-4.8048145721,3.0392398535,1.2434172549 Br,0,2.7904503986,-0.3448306895,2.0994236959 G = -4842.926545
Dihydrogen H,0,0.,0.,-0.3712061013 H,0,0.,0.,0.3712061013 G = -1.176811	

V.- Cartesian coordinates and Gibbs free energies of the stationary points for conjugate addition of 3-methylpyridine (1b) to carbene intermediate VII, intramolecular cyclization and reductive elimination steps.

Stationary points located at Becke3LYP/6-31G(d) level of theory for the ortho reaction path:

TS6_b	***VIIIb***
C,0,-0.5077129613,-0.6572014269,1.8867873611 N,0,-2.30995573,-0.6696050976,0.4845931287 C,0,1.3136586791,-0.8559275009,0.3827540409 C,0,2.20428079,-1.7262839693,-0.4081918058 C,0,-2.0283285858,-1.061624229,-0.7575365311 C,0,0.4760774532,-2.9645060908,1.6068304307 Br,0,1.2381347804,3.1098551812,-0.0704249725 Cu,0,1.3216613201,0.9181873731,0.0545841109 C,0,-2.9937708898,-1.0437449125,-1.7647621609 C,0,0.4460403717,-1.4789694423,1.3031280369 C,0,-4.2759110684,-0.6001276,-1.4543151519 O,0,1.8035124149,-2.3559711594,-1.3740216325 O,0,3.4867823861,-1.702784005,-0.001060299 C,0,4.4049419901,-2.4689034548,-0.8025355759 H,0,-1.1559243017,-0.9994069657,2.6873587107 C,0,-4.5785166452,-0.181477032,-0.150965076 H,0,-0.4385359365,0.41210321,1.7209102585 C,0,-3.5406487055,-0.2407297705,0.7833633424 H,0,4.4231290686,-2.0903450241,-1.8277387981 H,0,-1.0076589277,-1.392292691,-0.9441846863 H,0,4.1184509722,-3.5238071992,-0.8156440195 H,0,5.3785038803,-2.3409164896,-0.3294180831 H,0,0.3350623652,-3.5572658603,0.6962581692 H,0,-2.7375997411,-1.3677493159,-2.7683329006 H,0,-0.3037027101,-3.2450899612,2.3213655844 H,0,1.4432996637,-3.2556917034,2.0344252882 H,0,-5.0454064069,-0.573381741,-2.222386507 C,0,-5.9503677077,0.3143733467,0.2317759264 H,0,-3.7052830475,0.0734337952,1.8127986863 H,0,-6.7155641965,-0.4483980997,0.0450036892 H,0,-6.2269116125,1.2019071808,-0.3495494866 H,0,-5.9958792849,0.5825451984,1.2915754468 ν_i = -60.8302 cm^{-1} G = -4883.319951	C,0,1.4063413474,0.3287124544,1.6017199755 N,0,1.1912543031,1.7288824954,1.0539313181 C,0,-0.5249294741,-1.0918426271,1.0918570226 C,0,1.554181959,2.8326078873,1.7400654116 C,0,-1.8303601977,-1.6889442905,1.4528492172 C,0,-0.3410038656,-0.0096667037,3.4235576108 C,0,1.3285424018,4.0868598762,1.1976260234 C,0,0.7439994203,4.1927041559,-0.0665085121 Br,0,0.8834644351,-0.8581405175,-2.6934355063 Cu,0,0.0465661726,-1.2412287602,-0.6698504115 C,0,0.3710295266,3.0421545306,-0.7716118401 C,0,0.1082284887,-0.3278101231,2.0144459152 C,0,0.6061656109,1.8172011956,-0.1567906296 H,0,2.0245211667,2.6724873557,2.7025648066 O,0,-2.8458084541,-1.0848401118,1.7593811354 O,0,-1.8035361723,-3.044583175,1.3373942545 H,0,1.6215770336,4.9680815353,1.7573555546 C,0,-3.0437999642,-3.7050417633,1.6157465474 H,0,0.5823574496,5.1727269209,-0.5072924428 H,0,2.1252249322,0.4398255888,2.4190805865 C,0,-0.2574912256,3.06580474,-2.1401864368 H,0,0.3384989278,0.8570337053,-0.5929161602 H,0,-3.821257384,-3.379043346,0.9186402514 H,0,-3.3790691184,-3.4956763478,2.6361007687 H,0,-2.8436626291,-4.770313246,1.4917447823 H,0,0.3727470704,-0.3868415448,4.1710705248 H,0,-1.3244353197,-0.4320059122,3.635338035 H,0,-0.4192060541,1.0771612591,3.58450076 H,0,0.0711610909,3.9393215721,-2.7114430741 H,0,-1.3509454567,3.1086632961,-2.0605116054 H,0,-0.0018206696,2.1557639511,-2.6928126111 H,0,1.8631874487,-0.2198597973,0.7761402999 G = -4883.340824

TS7_b-ortho	***IXb-ortho***
C,0,2.0790688906,-0.7406119963,0.8324469986 N,0,2.0476275619,0.761928645,0.8861218597 C,0,-0.3162773615,-1.2525238977,0.8670064829 C,0,2.4618245687,1.4138501302,1.9969531116 C,0,-1.5479361121,-1.7003428947,1.5542337365 C,0,1.1126984095,-1.8562622685,2.9215150361 C,0,2.2809658462,2.7780691786,2.1105349614 C,0,1.6569752683,3.4759081064,1.0701364089 Br,0,-0.6194711498,0.204369954,-2.9309697561 Cu,0,-0.5463500621,-0.5882115016,-0.8495126405 C,0,1.2284688472,2.801782702,-0.0755595167 C,0,0.85607804,-1.3174674042,1.5318522547 C,0,1.4405288706,1.4224189188,-0.1267228062 H,0,2.9263808215,0.807552226,2.7642821693 O,0,-1.9677510234,-1.3074722359,2.6304944216 O,0,-2.2370938752,-2.5986789206,0.7968883197 H,0,2.6250324255,3.2871108782,3.0037966509 C,0,-3.4729197027,-3.0536133102,1.3609797691 H,0,1.5109634442,4.5496935784,1.1505761228 H,0,3.0254772324,-1.0473632472,1.2866392311 C,0,0.5703078587,3.5016128703,-1.23685039 H,0,1.1252363433,0.8183178324,-0.9684517779 H,0,-4.1591657524,-2.2159511005,1.5154790049 H,0,-3.3050338036,-3.550277192,2.3214216373 H,0,-3.885765635,-3.7561573026,0.6358188256 H,0,1.8603980946,-2.662717134,2.9071587283 H,0,0.1969214101,-2.2341533185,3.3776575464 H,0,1.5037527113,-1.0777657886,3.5955060773 H,0,1.3031316993,4.1046959411,-1.7871964512 H,0,-0.216430223,4.1779104349,-0.8857488411 H,0,0.129286102,2.7799548248,-1.9308274313 H,0,2.0921228894,-0.9968775485,-0.2273746852 ν_i = -38.2624 cm^{-1} G = -4883.337616	C,0,0.7483282366,0.2019629559,2.8608565782 N,0,1.3036619282,1.0156452953,1.7912200473 C,0,-0.3798722604,-1.156057576,1.0927588314 C,0,2.6327396911,0.9727477659,1.5076905239 C,0,-1.1494048779,-2.3444309769,0.6465205161 C,0,-0.2380828075,-2.0149455398,3.5001072178 C,0,3.150589809,1.6982576414,0.4657386414 C,0,2.2851799181,2.5347373902,-0.2788208417 Br,0,-0.3559259796,0.3871859111,-2.5997619831 Cu,0,-0.1735424383,0.0332980177,-0.3698085291 C,0,0.9241008973,2.5117514155,-0.0677032461 C,0,0.0086839154,-1.0456392616,2.3681920234 C,0,0.3975090333,1.541602672,0.8663573462 H,0,3.2432332481,0.3810516819,2.1797790833 O,0,-0.965803043,-3.5112539318,0.9412785709 O,0,-2.1219950177,-1.9542580656,-0.2218659984 H,0,4.2175625251,1.6805693885,0.2784308786 C,0,-2.9036801785,-3.0087806957,-0.8011309928 H,0,2.7030452468,3.2204750167,-1.0103625428 H,0,0.0611448442,0.8275195122,3.4487832238 C,0,-0.0135927333,3.4251903415,-0.8051669404 H,0,-0.5694866691,1.7681092346,1.3129528116 H,0,-3.4638540898,-3.5430461285,-0.028182668 H,0,-2.2584242033,-3.7173093024,-1.326957768 H,0,-3.5822595437,-2.5182138794,-1.4989716443 H,0,0.7109036319,-2.4397055094,3.8570754308 H,0,-0.8736383535,-2.8438877116,3.1909236006 H,0,-0.6980906128,-1.5042118261,4.3588898629 H,0,-0.4446674522,2.9007721532,-1.6676774682 H,0,0.5167927381,4.309196751,-1.1711320101 H,0,-0.8382509491,3.7576117252,-0.1640166718 H,0,1.5678887623,-0.0798783888,3.5303437789 G = -4883.353763
TS8_b-ortho	***Xb-ortho***
C,0,3.051566847,0.2751457977,-0.4946300461 N,0,2.3156553046,1.2753514524,0.2755085576 C,0,0.9464391318,-0.8633093133,-0.0964872818 C,0,1.8244573441,2.38408554,-0.412314819 C,0,0.0741390562,-2.0015241054,0.264171478 C,0,2.7187899386,-2.0615746431,-1.5046524448 C,0,0.6817433316,3.0135605008,-0.0522587254 C,0,-0.0777879539,2.5344955414,1.0888372124 Br,0,-2.3735794294,0.336919689,-1.070717739 Cu,0,-0.4771801405,0.5547664873,0.1404469379 C,0,0.3708160119,1.439930567,1.8021514662 C,0,2.1238033661,-0.9166737592,-0.73607373 C,0,1.4096648566,0.6161258101,1.1593105907 H,0,2.4531433254,2.7371505192,-1.222039504 O,0,-0.3547694791,-2.1536092793,1.3980755057 O,0,-0.2113262996,-2.8272341137,-0.7570712152 H,0,0.3496399596,3.8888424923,-0.5968376928 C,0,-1.1808322759,-3.8544380585,-0.4674968898 H,0,-0.8890012156,3.1419483972,1.4773140246 H,0,3.9164665944,-0.0825061601,0.0861769912 C,0,-0.178565489,0.9997429156,3.1342896757 H,0,1.9030397651,-0.065078118,1.84722188 H,0,-2.1245102082,-3.3970535532,-0.1623013799 H,0,-0.8187940257,-4.5134016915,0.3256614361 H,0,-1.304317831,-4.403301486,-1.4011048118 H,0,2.8920499802,-1.7669724323,-2.5488438103 H,0,2.0650393584,-2.9339241753,-1.5077448826 H,0,3.697432083,-2.3449313921,-1.0911109792 H,0,-0.3401337428,-0.083240112,3.1583060357 H,0,-1.127892574,1.4978059386,3.3513249396 H,0,0.5302715745,1.2502213611,3.9355108075 H,0,3.4448451665,0.7199093836,-1.415046532 ν_i = -217.1828 cm^{-1} G = -4883.325494	C,0,2.8108164886,-1.9243633992,0.8164027488 N,0,2.7183344198,-0.460165269,0.8051648214 C,0,0.555338947,-1.3866276121,1.0340096482 C,0,2.9878415577,0.1615112077,-0.4216478446 C,0,-0.909977528,-1.3322110781,0.9985671235 C,0,1.0696376481,-3.8188450862,0.3125481823 C,0,2.3671731426,1.2756527404,-0.8527748785 C,0,1.3270332023,1.8963919087,-0.0308177433 Br,0,-1.642776854,1.3861413982,-2.2126758709 Cu,0,-0.4683639316,1.1054991307,-0.3005455589 C,0,0.8715425723,1.2407608484,1.1224573051 C,0,1.3687936856,-2.4124984504,0.7175002099 C,0,1.4115076332,-0.1531371132,1.4300812168 H,0,3.8000555005,-0.2940193073,-0.9811053228 O,0,-1.5375793266,-0.2947540039,0.7574193757 O,0,-1.5381314023,-2.4825749498,1.2485993273 H,0,2.6617454279,1.7331015547,-1.7896410896 C,0,-2.9799876255,-2.4561313925,1.1212028834 H,0,1.21949486,2.9780917973,-0.0960556 H,0,3.2560904081,-2.2762219374,1.761206085 C,0,0.3109245014,2.0050392872,2.3021149504 H,0,1.5529460394,-0.2157748588,2.5214498339 H,0,-3.2646717809,-2.0936076079,0.1314569167 H,0,-3.4111747422,-1.8044933399,1.8842935862 H,0,-3.2957931063,-3.4880744805,1.2703437667 H,0,1.5241661691,-4.0384473896,-0.6623685373 H,0,-0.0002317276,-4.019356826,0.261302019 H,0,1.5167789368,-4.5204258183,1.0304655451 H,0,-0.5185115341,1.4712310818,2.7812243428 H,0,-0.0593457759,2.9898084931,1.9987542253 H,0,1.0881292788,2.1612042261,3.0647211002 H,0,3.4435454961,-2.2909019667,0.0012636308 G = -4883.362637

Stationary points located at Becke3LYP/6-31G(d) level of theory for the para reaction path:

TS7_b-para	***IXb-para***
C,0,1.9037625696,-0.7496290157,0.6601067023 N,0,1.9080295545,0.7538053022,0.6892284081 C,0,-0.5024960705,-1.2001970142,0.6543338199 C,0,1.3373632698,1.4115101359,-0.3429875157 C,0,-1.7607482711,-1.600681324,1.3207136059 C,0,0.8641026362,-1.7902810743,2.7552835125 C,0,1.1623048594,2.7895039036,-0.2736968682 C,0,1.5720843111,3.4770739646,0.8584881342 Br,0,-0.5359447232,0.0738170984,-3.213068805 Cu,0,-0.6441415137,-0.5880187994,-1.0914930381 C,0,2.1627871847,2.7844182871,1.9349692634 C,0,0.6525613293,-1.2792441388,1.3476624509 C,0,2.3069806588,1.4137951651,1.8049478238 H,0,1.0319296289,0.8177389919,-1.1961212752 O,0,-2.1998417185,-1.163971181,2.3723453076 O,0,-2.4479800792,-2.5092523241,0.5747462914 H,0,0.7030458959,3.2926895296,-1.1172574577 C,0,-3.7070855385,-2.9214504396,1.1196645383 H,0,1.4447649937,4.5545398149,0.919557603 H,0,2.8343623356,-1.0740953099,1.1340299814 C,0,2.6196560541,3.497276933,3.1819161924 H,0,2.7419451343,0.7994711035,2.584204598 H,0,-4.3813727744,-2.0666474399,1.2254783224 H,0,-3.5750322364,-3.38677153,2.1011835387 H,0,-4.1132842095,-3.6416325689,0.4081674314 H,0,1.582186845,-2.6231044603,2.7764393861 H,0,-0.0733397891,-2.1234694652,3.2024299442 H,0,1.2703712533,-1.0095248647,3.4176617548 H,0,1.7749470257,3.9821662016,3.684514574 H,0,3.3510452332,4.2778534929,2.9430711536 H,0,3.081700361,2.8073460914,3.8934500188 H,0,1.9236290549,-1.0210342194,-0.3958449002 ν_i = -48.8947 cm^{-1} G = -4883.335297	C,0,2.2738170392,-1.6066734489,0.0010873425 N,0,2.2502274831,-0.2239481499,0.4556477108 C,0,-0.212254563,-1.5196134571,0.0339790311 C,0,1.5810512219,0.6890958561,-0.3516877931 C,0,-1.5570159703,-2.1262974591,0.1527992634 C,0,0.9928874932,-3.772378442,0.2423778579 C,0,1.5537351866,2.0402266127,0.1371194163 C,0,1.8593736373,2.3188744965,1.4397990744 Br,0,-1.3048394522,2.0353038128,-1.6550758438 Cu,0,-0.4077111785,0.2860540627,-0.5210339235 C,0,2.2634969938,1.2775791655,2.3300439679 C,0,0.8937429111,-2.2725856228,0.1046263049 C,0,2.4421743001,0.0321930951,1.7875441329 H,0,1.7605532429,0.5325049644,-1.4151472017 O,0,-1.9168893021,-3.0887092755,0.8040627025 O,0,-2.4307327011,-1.3756913459,-0.5831687276 H,0,1.2125712355,2.8095642872,-0.5432963741 C,0,-3.8038311461,-1.7906016392,-0.563763764 H,0,1.7984205742,3.3402946083,1.8057035816 H,0,3.0077452274,-2.1511758928,0.6037276881 C,0,2.5253077771,1.5484954579,3.7878611385 H,0,2.7833509674,-0.8111823042,2.3777176081 H,0,-4.1897660342,-1.789418631,0.4593391169 H,0,-3.9061714489,-2.796362166,-0.9811920352 H,0,-4.3359966712,-1.0638542323,-1.1773696102 H,0,1.6423582694,-4.1912956986,-0.5400379851 H,0,0.0145538586,-4.2487093206,0.1926377638 H,0,1.4490023538,-4.0419695116,1.2059589188 H,0,1.6169877451,1.8976991872,4.2937566354 H,0,3.2860972413,2.3287593828,3.9156667755 H,0,2.8728867169,0.6510590363,4.3085744901 H,0,2.6348860862,-1.6241606419,-1.0358026706 G =-4883.354074
TS8_b-para	***Xb-para***
C,0,2.2950556521,-2.0118794372,0.293012942 N,0,2.5022140807,-0.573331988,0.1437004072 C,0,0.1522225758,-1.3141049613,-0.6086493516 C,0,1.713059784,-0.0958732218,-0.9419013081 C,0,-1.0857040684,-1.4797343807,-1.406082055 C,0,0.4490662672,-3.7767662232,0.0305215165 C,0,1.5369162008,1.3541540335,-1.0229090085 C,0,1.5183176511,2.0738348511,0.1550060977 Br,0,-2.0139355576,1.1101324376,1.0867914175 Cu,0,-0.1154761346,0.6400434121,-0.0597792795 C,0,2.0250609764,1.4663458063,1.3819059597 C,0,0.8508580327,-2.3357035351,-0.0869333989 C,0,2.48182238,0.1915048515,1.3170341445 H,0,1.9487047057,-0.5696778463,-1.890208797 O,0,-1.8864305356,-2.3902371667,-1.3744457835 O,0,-1.2155225788,-0.4086729422,-2.2434686722 H,0,1.302250288,1.8025041075,-1.9827307977 C,0,-2.4391408878,-0.3596430476,-2.9997254191 H,0,1.3147781482,3.1399433923,0.1437855161 H,0,2.5611966666,-2.3304530298,1.3062810997 C,0,2.0328822552,2.2613543288,2.6582132198 H,0,2.9196212718,-0.2990457003,2.1800203085 H,0,-3.2898844655,-0.2640935225,-2.3208833014 H,0,-2.5521218697,-1.2626152245,-3.604400438 H,0,-2.3543092621,0.5228694759,-3.6339954422 H,0,1.2358558475,-4.4359145642,-0.3624118379 H,0,-0.4909394876,-3.9736743076,-0.484699368 H,0,0.316617114,-4.0401514296,1.0893252956 H,0,1.0099226188,2.530806636,2.9485688277 H,0,2.6009398579,3.1941347523,2.5467986658 H,0,2.4774107951,1.692181554,3.4803778861 H,0,2.954135626,-2.5590381579,-0.3994753642 ν_i = -227.7751 cm^{-1} G = -4883.325273	C,0,2.7086760741,-2.0809173623,-0.9460108401 N,0,2.6281069827,-0.6146779834,-0.9472474831 C,0,0.4601656115,-1.5197062048,-1.2230415685 C,0,1.337342435,-0.2988405886,-1.602737942 C,0,-1.0112276418,-1.6001945311,-1.2980906847 C,0,0.9269061573,-3.9642181358,-0.5409430662 C,0,0.8380118425,1.0959729745,-1.2836754463 C,0,1.2948165023,1.7637581599,-0.1438266033 Br,0,-1.9263466775,1.3451552805,1.8350539107 Cu,0,-0.5158958213,1.0136737986,0.1159638067 C,0,2.3140588305,1.1494824319,0.7131918274 C,0,1.2619581624,-2.5523758392,-0.8940204901 C,0,2.8978619771,0.0129961951,0.2742892178 H,0,1.499359428,-0.3569590472,-2.6905118968 O,0,-1.6759055027,-2.5980036145,-1.4695809347 O,0,-1.6026091166,-0.3676782515,-1.1188230546 H,0,0.4306289319,1.6667221138,-2.1152672976 C,0,-3.0547450585,-0.3599056061,-1.1368800544 H,0,1.1891943449,2.846742394,-0.0875878363 H,0,3.3121119231,-2.4470142946,-0.1089124922 C,0,2.7054606519,1.8185901688,2.0025626978 H,0,3.6988552451,-0.4560195089,0.8402307636 H,0,-3.4357399485,-0.9275074669,-0.2876663925 H,0,-3.4052383838,-0.7931202556,-2.0745982385 H,0,-3.3323105871,0.6881016727,-1.0462224393 H,0,1.3825450579,-4.6500887053,-1.2688815571 H,0,-0.1486051248,-4.1392314467,-0.5352443098 H,0,1.3485189127,-4.2241179551,0.4389655874 H,0,1.8513796233,1.884026455,2.6884697938 H,0,3.0611412719,2.8447079209,1.8337213864 H,0,3.5051098357,1.2692111087,2.5103644399 H,0,3.1818168086,-2.4420771242,-1.8736347674 G = -4883.358768

VI.- Cartesian coordinates and Gibbs free energies of the stationary points for conjugate addition of 3-nitropyridine (1c) to carbene intermediate VII, intramolecular cyclization and reductive elimination steps.

Stationary points located at Becke3LYP/6-31G(d) level of theory for the ortho reaction path:

TS6_c	***VIIIc***
C,0,1.4754453835,-1.2984834443,0.1506694613 N,0,1.6986624492,0.7554181606,0.1353627077 C,0,-0.8188996487,-1.7205297711,0.6498591591 C,0,-1.8553734473,-2.0876026258,1.6383405659 C,0,0.6124506061,1.3838799734,-0.3294339417 C,0,0.9166645974,-1.9620372612,2.525821517 Br,0,-1.8114704909,-0.2316556306,-2.9446074189 Cu,0,-1.3905198382,-1.1149196698,-0.9697522545 C,0,0.5299335037,2.7733523263,-0.3764975876 C,0,0.5025698103,-1.6773533237,1.0945425856 C,0,1.6049135181,3.5251068602,0.0898658111 O,0,-2.4021062771,-1.267413449,2.3541202609 O,0,-2.165437411,-3.3998816914,1.6189784146 C,0,-3.242216316,-3.7906401759,2.4912192166 H,0,2.5325634881,-1.4635500961,0.3434923643 C,0,2.716385457,2.8388983508,0.5744597313 H,0,1.181098295,-1.2599046285,-0.8929490016 C,0,2.7465441321,1.447721983,0.5834899301 H,0,-4.1597163051,-3.2591681017,2.2257253316 H,0,-0.1909293599,0.7295338921,-0.6636225841 H,0,-2.9930566878,-3.5741539228,3.5333282628 H,0,-3.3630270095,-4.8633889585,2.3399799287 H,0,0.5716140574,-1.1707160224,3.2026449879 H,0,-0.3615765981,3.2456790425,-0.7735987756 H,0,2.003954335,-2.0435136297,2.6275719019 H,0,0.4770258955,-2.9013666454,2.8792596303 H,0,1.6015529775,4.608799076,0.0872231411 N,0,3.8796844473,3.5834877059,1.0839680961 H,0,3.6108942107,0.9047156917,0.9499550758 O,0,4.8289700107,2.9235436017,1.5005607373 O,0,3.8182250948,4.8089307114,1.0558068949 ν_i = -160.9056 cm^{-1} G = -5048.522746	C,0,1.3565251569,-0.8664391182,0.4784724914 N,0,1.4532555882,0.6491354213,0.509404511 C,0,-1.000537123,-1.5109865486,0.4518964355 C,0,-2.2623104922,-1.8820491727,1.1319336103 C,0,0.6252854617,1.3340038792,-0.3176942032 C,0,0.2672609115,-1.4950157646,2.6977912309 Br,0,-0.5301441289,-0.4187908922,-3.3981022319 Cu,0,-1.0280618275,-1.160961287,-1.3721114618 C,0,0.5983052343,2.7192779619,-0.2997351715 C,0,0.1124699821,-1.3331337514,1.2032495705 C,0,1.4199365178,3.4140113301,0.5850004358 O,0,-2.8322372143,-1.2355492285,1.9955742657 O,0,-2.7788052599,-3.0308732948,0.6237318925 C,0,-4.0326051229,-3.4400261539,1.18654465 H,0,2.2945942933,-1.2316969156,0.9060349154 C,0,2.2483503034,2.6693712078,1.4228762981 H,0,1.2984465139,-1.1161671025,-0.5817007987 C,0,2.2639289226,1.2852484902,1.374041989 H,0,-4.8006391714,-2.6817997459,1.0092983444 H,0,-0.0080846217,0.7029492238,-0.9407485738 H,0,-3.9423740244,-3.6031891391,2.2645126334 H,0,-4.2910865651,-4.3708168013,0.6801968076 H,0,0.6275768819,-0.5673595451,3.1712286969 H,0,-0.0646039381,3.2364913265,-0.9837360061 H,0,0.9989304863,-2.2775460791,2.9460155788 H,0,-0.6838693037,-1.7402977534,3.1724552924 H,0,1.4357065309,4.496240607,0.6381795577 N,0,3.1436984037,3.3449259092,2.3769633492 H,0,2.9119816566,0.691182306,2.0045920333 O,0,3.8518896223,2.6288505033,3.0801422724 O,0,3.1133931416,4.5705176073,2.3940069423 G = -5048.533465

TS7_c-ortho	***IXc-ortho***
C,0,0.0284701034,-1.0723491892,-2.0125620692 N,0,1.3011704642,-1.2632274731,-1.2328439591 C,0,-1.517600395,-0.8058422404,-0.1502940741 C,0,1.7078643321,-0.2660930687,-0.4038014185 C,0,-2.5400650756,-1.2817592151,0.8050314303 C,0,-1.6386955086,-2.9714732419,-1.5427201431 C,0,2.7366837733,-0.5389712942,0.4970476741 C,0,3.3385548635,-1.7838423536,0.5686557892 Br,0,-0.285242627,2.9763462668,-0.6922240839 Cu,0,-0.8805517038,0.9366631382,-0.0431650587 C,0,2.8985923112,-2.7792664879,-0.3115678449 C,0,-1.1260654721,-1.6010034843,-1.167274006 C,0,1.87681413,-2.4889713342,-1.1934893071 H,0,1.2587062318,0.7146860323,-0.5190707927 O,0,-2.5405469129,-2.3503164476,1.3938592412 O,0,-3.491874226,-0.3355919094,1.0173134317 N,0,3.2012572946,0.536218665,1.3908423082 C,0,-4.5096756168,-0.6865321449,1.9643812644 H,0,4.1345084273,-1.9519027604,1.2841346514 H,0,0.1611937179,-1.5935311976,-2.9642009428 H,0,3.3425155942,-3.7675594619,-0.3117965961 H,0,1.479406615,-3.217173197,-1.889339204 H,0,-4.0720638089,-0.8699775801,2.9497991863 H,0,-5.0461643392,-1.5846708282,1.6446808146 H,0,-5.1845061185,0.1693440587,1.9991976412 H,0,-1.994360398,-2.9941952752,-2.5825907867 H,0,-2.4501639457,-3.2820939837,-0.8835471744 H,0,-0.8545894739,-3.7410656727,-1.4608321069 H,0,-0.0555359546,0.0005733667,-2.1889226916 O,0,4.1268360394,0.263490927,2.1536153807 O,0,2.6248708273,1.6134051971,1.3071726246 ν_i = -44.1306 cm^{-1} G = -5048.525664	C,0,2.3211817583,-1.9680207799,0.2103089431 N,0,2.324147936,-0.5115660787,0.2081572541 C,0,-0.1805830608,-1.8458160451,0.2127711511 C,0,1.4138927483,0.0956996416,-0.6821102581 C,0,-1.5431196629,-2.4417058353,0.1739335136 C,0,1.0145005652,-4.0854815625,0.5148859485 C,0,1.5647412358,1.5330653525,-0.7751238773 C,0,2.2472517462,2.2621823292,0.1628754849 Br,0,-1.546229054,1.8194312155,0.8737600303 Cu,0,-0.3882691559,0.0347419928,0.1062756229 C,0,2.8868211045,1.578165478,1.2182982678 C,0,0.9255065682,-2.5896151871,0.3284450818 C,0,2.9173993966,0.2015684301,1.1936182809 H,0,1.3005043763,-0.4301340337,-1.6243180614 O,0,-1.9332844078,-3.4903305736,0.6482524979 O,0,-2.3613101553,-1.5825247197,-0.4899785316 N,0,0.9349829417,2.1880279525,-1.9025157377 C,0,-3.7470757248,-1.9553312144,-0.5758649022 H,0,2.280770791,3.3415895254,0.0755268525 H,0,2.9680107454,-2.3122332779,1.0243139224 H,0,3.3983692374,2.1127037531,2.0084106449 H,0,3.4576039958,-0.3778891424,1.9342048267 H,0,-4.1617961522,-2.1015278543,0.4244681002 H,0,-3.8576115062,-2.8783458676,-1.151318446 H,0,-4.238491601,-1.1236494595,-1.0794848328 H,0,1.7218359058,-4.5248862448,-0.2026632133 H,0,0.0406540419,-4.560449401,0.4072725672 H,0,1.3934539517,-4.3211893189,1.5193621881 H,0,2.7769022166,-2.3170225475,-0.7279444342 O,0,1.0947451277,3.3998237279,-2.0377786413 O,0,0.2699244623,1.4682724123,-2.6583879072 G =-5048.557822
TS8_c-ortho	***Xc-ortho***
C,0,2.5969328798,-2.060093705,0.9393386432 N,0,2.3085278168,-0.6402079543,0.8963684416 C,0,0.1707577896,-2.2686416662,0.4919727236 C,0,2.8391991126,0.14045474,-0.1143638772 C,0,-1.0853541454,-1.707380451,0.6341415394 C,0,1.6777403549,-4.1303512038,-0.2907668804 C,0,2.268599066,1.3109894443,-0.5003107128 C,0,1.0122068249,1.7299533044,0.0634452669 Br,0,-0.7064599676,1.5569341078,-2.7474659464 Cu,0,-0.4544662485,0.6738795151,-0.6909161921 C,0,0.4667759431,0.8964695125,1.089039435 C,0,1.3580927773,-2.8001718394,0.359800809 C,0,1.0960338609,-0.3343688943,1.4663410241 H,0,3.7597123228,-0.2329254336,-0.5466323189 O,0,-1.5688380184,-0.7801865536,-0.0861121706 O,0,-1.8102857545,-2.2113980557,1.6555733608 H,0,2.7372468096,1.9107990418,-1.2704688131 C,0,-3.0347158718,-1.5250917315,1.9753833196 H,0,0.7204629843,2.7730076312,0.0254477044 H,0,2.7634069599,-2.3800413168,1.9752006417 N,0,-0.4793226009,1.4736099051,2.040748779 H,0,0.8776769238,-0.7674456722,2.4322056307 H,0,-3.69919099,-1.4929561078,1.1092104831 H,0,-2.8239715683,-0.5093663954,2.3205453348 H,0,-3.4815501187,-2.1107510843,2.7795842874 H,0,2.3309312732,-3.9930621922,-1.1630528896 H,0,0.7689387936,-4.6401143502,-0.615109693 H,0,2.210660128,-4.7882085764,0.4096833418 O,0,-0.8028100769,0.7800261574,3.010234648 O,0,-0.9138015374,2.6019055715,1.8113427564 H,0,3.5051315899,-2.2713309282,0.3690069401 ν_i = -226.2486 cm^{-1} G = -5048.519664	C,0,-2.7543531347,-1.704381687,-1.3468737917 N,0,-1.5704730468,-2.1929236951,-0.6277566658 C,0,-1.8900852885,0.0852672823,-0.1281677053 C,0,-0.4848440359,-2.6319144624,-1.3656849531 C,0,-1.4114160092,1.3945509757,0.3398673259 C,0,-3.5503109488,0.7168434746,-1.9959629796 C,0,0.806693734,-2.5031065435,-0.9771717868 C,0,1.131106427,-1.8204481496,0.2613145427 Br,0,2.8502968259,0.9556221464,-1.1115625852 Cu,0,1.1253059575,0.1606272706,0.0878511174 C,0,0.0781287093,-1.2245318264,0.9831437804 C,0,-2.7323909251,-0.1917875905,-1.1371563687 C,0,-1.3442801226,-1.229160526,0.4715130877 H,0,-0.7495623135,-3.1631345336,-2.2753921224 O,0,-0.2152735078,1.6186037075,0.5654828062 O,0,-2.3417114148,2.3274300829,0.4929463817 H,0,1.5996385734,-2.9230571937,-1.5824818084 C,0,-1.8769355358,3.6309106294,0.9261442071 H,0,2.0405818131,-2.0811699572,0.793020066 H,0,-3.6737137442,-2.1309429495,-0.9163042436 N,0,0.2051331852,-1.0389892599,2.4202441414 H,0,-1.9992052435,-1.4927897742,1.3110292643 H,0,-1.1498967892,4.026581374,0.2141456348 H,0,-1.4176448631,3.5496406878,1.9131034336 H,0,-2.7716068297,4.2507669196,0.9619206222 H,0,-3.2717460339,0.6054850438,-3.0518804866 H,0,-3.4405653352,1.7635492994,-1.7085601763 H,0,-4.6137480261,0.4526714877,-1.9208516511 O,0,-0.7811211016,-0.5731347159,3.0102787127 O,0,1.2759691585,-1.3083238875,2.9674831361 H,0,-2.720196144,-1.9892266456,-2.4034732268 G = -5048.578385

Stationary points located at Becke3LYP/6-31G(d) level of theory for the para reaction path:

TS7_c-para	***IXc-para***
C,0,1.5737125817,-0.9138030284,0.4279566067 N,0,1.5917611829,0.5963809238,0.4589746829 C,0,-0.8024725676,-1.4606454881,0.4194312896 C,0,0.9647541047,1.2645131042,-0.5450081862 C,0,-2.0680401911,-1.8532191147,1.0802947888 C,0,0.5291527919,-1.7698109623,2.6042270005 C,0,0.8054028726,2.6435735745,-0.4807445499 C,0,1.2993493326,3.3498093655,0.6087668318 Br,0,-0.5417747313,-0.4472881049,-3.5017210772 Cu,0,-0.8708115452,-1.0044754809,-1.3775740607 C,0,1.9471984193,2.6232159132,1.6126875206 C,0,0.3352334307,-1.4227953475,1.1464779011 C,0,2.0854686669,1.2509811548,1.5287477783 H,0,0.5806089934,0.6556830945,-1.3586570651 O,0,-2.5397645365,-1.3641413096,2.0929921553 O,0,-2.7120775587,-2.8173059129,0.3712395924 H,0,0.3004681469,3.1436804702,-1.2993915754 C,0,-3.9749230221,-3.2347244888,0.9079251853 H,0,1.2102073495,4.4258873925,0.6967518281 H,0,2.5171392498,-1.2408633517,0.8735264914 N,0,2.5148536671,3.3102679517,2.7814286806 H,0,2.5841052129,0.6744821097,2.2960812205 H,0,-4.6721995591,-2.3933141361,0.9510658628 H,0,-3.8539836586,-3.6434392886,1.9153737094 H,0,-4.3433468955,-4.0021462823,0.2263114707 H,0,1.2960354439,-2.546974415,2.7328088017 H,0,-0.4017994438,-2.1130211014,3.0569195715 H,0,0.8603651744,-0.8993791751,3.1926273372 H,0,1.5494878311,-1.1767069724,-0.6295213934 O,0,3.095504278,2.6160285899,3.6131542163 O,0,2.3654928286,4.5269028887,2.8361881184 ν_i = -27.6436 cm^{-1} G = -5048.530753	C,0,1.0018432858,-1.7819853422,-1.8060681054 N,0,0.7060561762,-0.3574968955,-1.9023402895 C,0,-0.0889143812,-1.6994344394,0.4145045293 C,0,-0.3186516465,0.0419415468,-2.6892536362 C,0,-0.8304543736,-2.2333398741,1.5803728068 C,0,0.013886269,-3.9169289471,-0.8611831799 C,0,-0.7340080836,1.3474922443,-2.6904304441 C,0,-0.0757837322,2.3102549894,-1.8735701347 Br,0,1.3341899747,1.6321963513,2.314845581 Cu,0,0.468843199,0.0368652119,0.9466612536 C,0,0.8854842492,1.8760434061,-1.011962154 C,0,0.251433191,-2.4438924666,-0.6440318756 C,0,1.1988801704,0.468463616,-0.8681991648 H,0,-0.7729074575,-0.6926421955,-3.3415362795 O,0,-1.4378557989,-3.2703673864,1.7382465466 O,0,-0.7470033197,-1.2703510996,2.5537779748 N,0,-1.7926417645,1.7378764951,-3.6009374258 C,0,-1.3826759438,-1.5437460313,3.8151207138 H,0,-0.3403154257,3.3560779689,-1.9664497543 H,0,2.0859376078,-1.9042562123,-1.6824798585 H,0,1.4054749946,2.5625053452,-0.3567699844 H,0,2.2284565812,0.2201072556,-0.6079125176 H,0,-0.9563840991,-2.4442923104,4.2641284598 H,0,-2.4570939558,-1.6836316517,3.6717689226 H,0,-1.1835325443,-0.6705149839,4.4351193042 H,0,-0.6843325426,-4.0727565091,-1.6959114276 H,0,-0.4029086471,-4.3907478183,0.0264215603 H,0,0.9513331202,-4.4198528312,-1.1380008391 H,0,0.7313876922,-2.2509540175,-2.756647357 O,0,-2.1156773751,2.9267656568,-3.608673884 O,0,-2.3017575211,0.8618434679,-4.307519893 G = -5048.560054
TS8_c-para	***Xc-para***
C,0,0.4084622717,2.8327604111,-0.3991264586 N,0,1.123503184,1.8032173023,0.34952821 C,0,-1.2891807331,1.1564971814,-0.0011676326 C,0,0.2276871611,0.9846573884,1.1474617805 C,0,-2.6660896795,0.6852890827,0.3108639897 C,0,-1.9516373266,3.2559463525,-1.3083764225 C,0,0.8712729777,-0.2601204331,1.6817237558 C,0,2.155803345,-0.5941733114,1.3733755485 Br,0,-0.8516797179,-2.3254711127,-1.2869536327 Cu,0,-0.3881858076,-0.5855142658,0.0272246195 C,0,2.9141703683,0.2458015042,0.4926487374 C,0,-1.0111559493,2.3325769487,-0.5947186263 C,0,2.3647814554,1.3983384562,0.0014351904 H,0,-0.2538464994,1.5363770327,1.9569728598 O,0,-3.6940927664,0.9836134417,-0.2562550125 O,0,-2.6142966259,-0.1598814973,1.3758326189 H,0,0.3458762893,-0.7773446167,2.4789717768 C,0,-3.8655754384,-0.7787154788,1.7402892408 H,0,2.6391412567,-1.4582134013,1.8130465112 H,0,0.9322799887,3.0488115368,-1.3372769481 N,0,4.2667334117,-0.0900602029,0.1312665539 H,0,2.9252596865,2.0355736482,-0.6719603934 H,0,-4.2304087811,-1.3924406136,0.9137885851 H,0,-4.6077356615,-0.0162704882,1.9872040748 H,0,-3.6397892199,-1.3969319081,2.6085517071 H,0,-1.8427167962,4.2842351913,-0.937208303 H,0,-2.9864321114,2.9317964704,-1.2030686203 H,0,-1.7095920953,3.2782998538,-2.3800493665 O,0,4.8844130863,0.6866118197,-0.6082447336 O,0,4.7299391129,-1.137848049,0.5908090294 H,0,0.3635531549,3.7722959191,0.1757381111 ν_i = -224.2095 cm^{-1} G = -5048.535006	C,0,2.2254688803,-2.4626422987,-0.9249516477 N,0,2.2163198417,-0.9976482508,-1.0087816452 C,0,0.0287357278,-1.7592243778,-1.3248566682 C,0,0.976548484,-0.6100095917,-1.727546084 C,0,-1.4476040448,-1.7209423769,-1.4009771241 C,0,0.3024304831,-4.1909383182,-0.5124972903 C,0,0.5556989975,0.8236269023,-1.4747664874 C,0,1.1390163926,1.5816420526,-0.4546933583 Br,0,-2.0387129784,1.1914936551,1.7645860884 Cu,0,-0.6770898648,0.9124724698,0.0159103764 C,0,2.2562655051,1.0099525977,0.2812209347 C,0,0.7477545811,-2.8258978027,-0.9226760715 C,0,2.7160664272,-0.2416414503,-0.0008651249 H,0,1.1762565619,-0.716751918,-2.8062730173 O,0,-2.182970219,-2.6688819345,-1.5615620889 O,0,-1.9248894974,-0.4478310438,-1.2237704163 H,0,0.0791789919,1.3318661152,-2.3098821037 C,0,-3.3721821247,-0.3137409741,-1.2268387173 H,0,1.0685017832,2.6646075775,-0.4680301088 H,0,2.7553353856,-2.8027464074,-0.0299138379 N,0,2.8968828551,1.7652878066,1.3207853531 H,0,3.5344571317,-0.6623951318,0.5726226207 H,0,-3.7913844258,-0.8419074504,-0.3704554132 H,0,-3.7684093132,-0.7194578126,-2.1586545037 H,0,-3.5569278673,0.7548023398,-1.1400138048 H,0,0.735582353,-4.9445998776,-1.1845749127 H,0,-0.7823668549,-4.2883284727,-0.5448396511 H,0,0.6634844574,-4.4252442246,0.4972886399 O,0,3.8709277488,1.2662698072,1.900943051 O,0,2.4354369053,2.8846337578,1.5687354828 H,0,2.7271978851,-2.9019320468,-1.8012962676 G = -5048.572842

VII.- Cartesian coordinates and Gibbs free energies of the stationary points for conjugate addition of 3-methoxycarbonylpyridine (1d) and 3-fluoropyridine (1e) to carbene intermediate VII, intramolecular cyclization and reductive elimination steps.

*Stationary points located at Becke3LYP/6-31G(d) level of theory for the reductive elimination step on the reaction of **1d** and **1e**:*

TS8_d-ortho	***TS8_d-para***
C,0,3.3223056964,0.1961911533,-0.2737512518	C,0,2.0286977751,-1.9119185644,-1.0731617348
N,0,2.3314270742,1.2530942104,-0.0942996756	N,0,1.9946449664,-0.4529404248,-1.0110966553
C,0,1.2413809122,-1.0451539859,-0.4283394616	C,0,-0.3510505532,-1.4549168447,-1.1932430722
C,0,1.1333248671,0.9144163832,-0.8033099092	C,0,0.8349726605,0.0453400213,-1.7032653224
C,0,0.3597581654,-2.1374195423,-0.9146748563	C,0,-1.7434691103,-1.7018136823,-1.6427989403
C,0,3.4427948854,-2.3515139244,-0.5362784843	C,0,0.4092430174,-3.9002516835,-1.1450839601
C,0,-0.0394674421,1.7567374452,-0.5062063198	C,0,0.5289490457,1.4673256622,-1.4740371243
C,0,-0.1477716877,2.2813395849,0.7718653781	C,0,0.9272707748,2.0527540782,-0.2984843148
Br,0,-1.3249528123,-0.9487615145,2.2775998464	Br,0,-2.0798120096,0.2508895043,1.4809260156
Cu,0,-0.1841972926,0.0020822283,0.5690229863	Cu,0,-0.6466204428,0.3117084375,-0.2584138952
C,0,1.0136911909,2.3113576856,1.622055699	C,0,1.9218020415,1.3934374225,0.5293042254
C,0,2.5806811618,-1.1345708533,-0.3690988308	C,0,0.5876894397,-2.4113551452,-1.0934909296
C,0,2.1913751287,1.8109890085,1.1625889475	C,0,2.4006620034,0.1762838973,0.1397313516
H,0,1.2771843962,0.7738567037,-1.86914896	H,0,0.8148661926,-0.2309029034,-2.7541049947
O,0,0.5911638339,-3.3274558112,-0.9534825249	O,0,-2.3765330529,-2.7341739074,-1.5879794217
O,0,-0.8128546367,-1.592482356,-1.3404397282	O,0,-2.245166765,-0.5492342293,-2.1717217085
C,0,-1.0411206645,1.9422698171,-1.5853300104	H,0,-0.0816840734,1.9911685068,-2.2024932678
C,0,-1.8303671804,-2.5243704132,-1.7495495613	C,0,-3.6321098713,-0.5955472662,-2.5579198707
H,0,-1.0451027412,2.8145060269,1.0628601149	H,0,0.6616709288,3.0741445259,-0.0511658918
H,0,4.0611691813,0.2279706066,0.5337218172	H,0,2.619964782,-2.3116783826,-0.2428737441
H,0,0.9589753305,2.7537612084,2.6085005139	C,0,2.411437926,2.0909430743,1.7331264526
H,0,3.1046946181,1.8651920299,1.745274739	H,0,3.1665076504,-0.3363186482,0.7090716835
H,0,-2.1634774347,-3.1085244822,-0.8882323346	H,0,-4.2551973252,-0.7900460521,-1.6820456093
H,0,-1.4454167324,-3.1925799019,-2.5229372658	H,0,-3.7941248272,-1.3772803837,-3.3037973105
H,0,-2.6441789382,-1.9117000047,-2.1363703074	H,0,-3.8505631429,0.3879712502,-2.9736223114
H,0,4.2388792212,-2.1661201575,-1.2709082823	H,0,1.1053723115,-4.352505143,-1.8652429103
H,0,2.8561596476,-3.218452606,-0.8385387354	H,0,-0.6146963833,-4.1710847352,-1.4011652054
H,0,3.9397182686,-2.5902337878,0.4144810116	H,0,0.6408243903,-4.3373705591,-0.1637006765
H,0,3.8664204673,0.348027883,-1.2187384394	H,0,2.5130007535,-2.2399941457,-2.0064224023
O,0,-0.8835377545,1.5545801697,-2.727322406	O,0,2.0417764816,3.1986738275,2.071448026
O,0,-2.1317360736,2.610623907,-1.1586388847	O,0,3.3239160356,1.3640318809,2.4238867527
C,0,-3.1453291488,2.8348509185,-2.1529779123	C,0,3.8192638356,1.9867968422,3.6198982237
H,0,-3.5132296154,1.8829177555,-2.5440374186	H,0,3.0001160596,2.1824106918,4.3164415053
H,0,-2.7466287073,3.4310051349,-2.9779122669	H,0,4.319282743,2.9299022447,3.3838861372
H,0,-3.9419048248,3.372115567,-1.6384698943	H,0,4.5254628479,1.2746419245,4.0479849057
ν_i = -213.3 cm^{-1}	ν_i =-224.6 cm^{-1}
G = -5071.875706	G =-5071.877534

TS8_e-ortho	***TS8_e-para***
C,0,2.545749422,-1.6880078415,-0.5856824945	C,0,2.4304946775,-1.6835519846,-0.767684769
N,0,2.5474439776,-0.2260299628,-0.5885516981	N,0,2.4455250337,-0.2208574604,-0.7841985551
C,0,0.1633147002,-1.2114170289,-0.5809466755	C,0,0.0488357853,-1.2009377715,-0.7766541856
C,0,1.3568327344,0.2396550368,-1.2318812315	C,0,1.2760381299,0.2551088643,-1.4458658012
C,0,-1.2539199943,-1.4660616238,-0.9453924418	C,0,-1.3677948709,-1.4532252258,-1.1330972433
C,0,0.9060057688,-3.6579153073,-0.4653704783	C,0,0.7861794644,-3.6474648531,-0.6286887904
C,0,1.0734530079,1.6625051548,-1.0315779094	C,0,0.9318018115,1.6638823777,-1.2511690522
C,0,1.4286054631,2.2884132596,0.1315418005	C,0,1.2624562268,2.262127807,-0.0493040674
Br,0,-1.533409965,0.7217499375,2.0297134208	Br,0,-1.6044693788,0.6706080361,1.8629182339
Cu,0,-0.0602001622,0.5829955093,0.320066472	Cu,0,-0.1917176206,0.6302833398,0.0958319769
C,0,2.4029598991,1.6112521625,0.9750553369	C,0,2.2513870481,1.5988798817,0.770932587
C,0,1.100622071,-2.1702862552,-0.4924278381	C,0,0.9820472848,-2.1601050627,-0.672898279
C,0,2.9112213064,0.4156279352,0.6000699844	C,0,2.7939586759,0.415896084,0.4166915409
H,0,1.2654989958,-0.0545750415,-2.2739243513	H,0,1.1955524828,-0.081895293,-2.4744992446
O,0,-1.8883608447,-2.4891026224,-0.796519955	O,0,-2.0129334234,-2.4689826764,-0.985118491
O,0,-1.7708922561,-0.3431184813,-1.5114019373	O,0,-1.8832511,-0.3225995053,-1.699917334
F,0,0.3404417327,2.2690405932,-1.9843238113	H,0,0.3217483625,2.1638155401,-1.9958887602
C,0,-3.1771145118,-0.3882545526,-1.8171554453	C,0,-3.293607728,-0.3607301653,-1.9878652971
H,0,1.1540953093,3.3210374559,0.3116649661	H,0,0.9867865396,3.2834696508,0.1857028373
H,0,3.1846070607,-2.0654731988,0.2193704551	H,0,3.0672375335,-2.0594945021,0.0396780405
H,0,2.7348114625,2.0796537475,1.8928474402	F,0,2.6461435671,2.2189545893,1.8973844891
H,0,3.6780132324,-0.0914035578,1.1740161203	H,0,3.5726081744,-0.0512157286,1.0063755837
H,0,-3.7515369859,-0.512819761,-0.896257682	H,0,-3.8572793328,-0.4606737354,-1.0573240691
H,0,-3.3930254303,-1.2138092247,-2.4994871203	H,0,-3.5260983784,-1.1976505631,-2.6504002505
H,0,-3.4022457507,0.5704466236,-2.2836549382	H,0,-3.5177510388,0.5901869534,-2.4712874432
H,0,1.5575122972,-4.1506746962,-1.2003658487	H,0,1.4423248985,-4.1508028759,-1.3523933581
H,0,-0.1331311092,-3.9287957813,-0.6503043734	H,0,-0.2519939292,-3.919671044,-0.8179666479
H,0,1.1890619154,-4.0507519533,0.5212518566	H,0,1.0610546197,-4.0278204009,0.3650697362
H,0,2.9630546502,-2.0654046029,-1.5322982565	H,0,2.8467791403,-2.0689574558,-1.7114957139
ν_i = - 218.2 cm^{-1}	ν_i = - 223.1 cm^{-1}
G = -4943.268232	G = -4943.266029