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Supplementary Material

Full Cleavage of C≡C Bond in Electron-Deficient Acetylenes Via Reaction with Ethylenediamine

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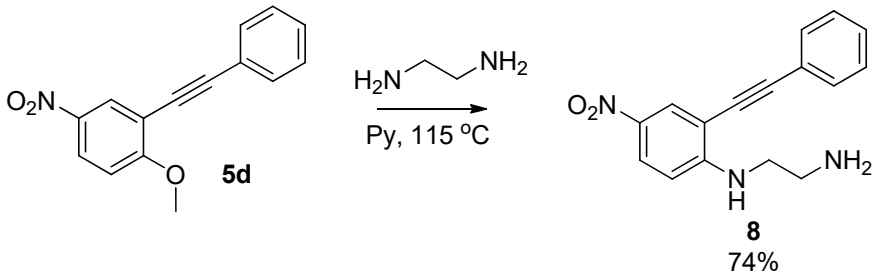
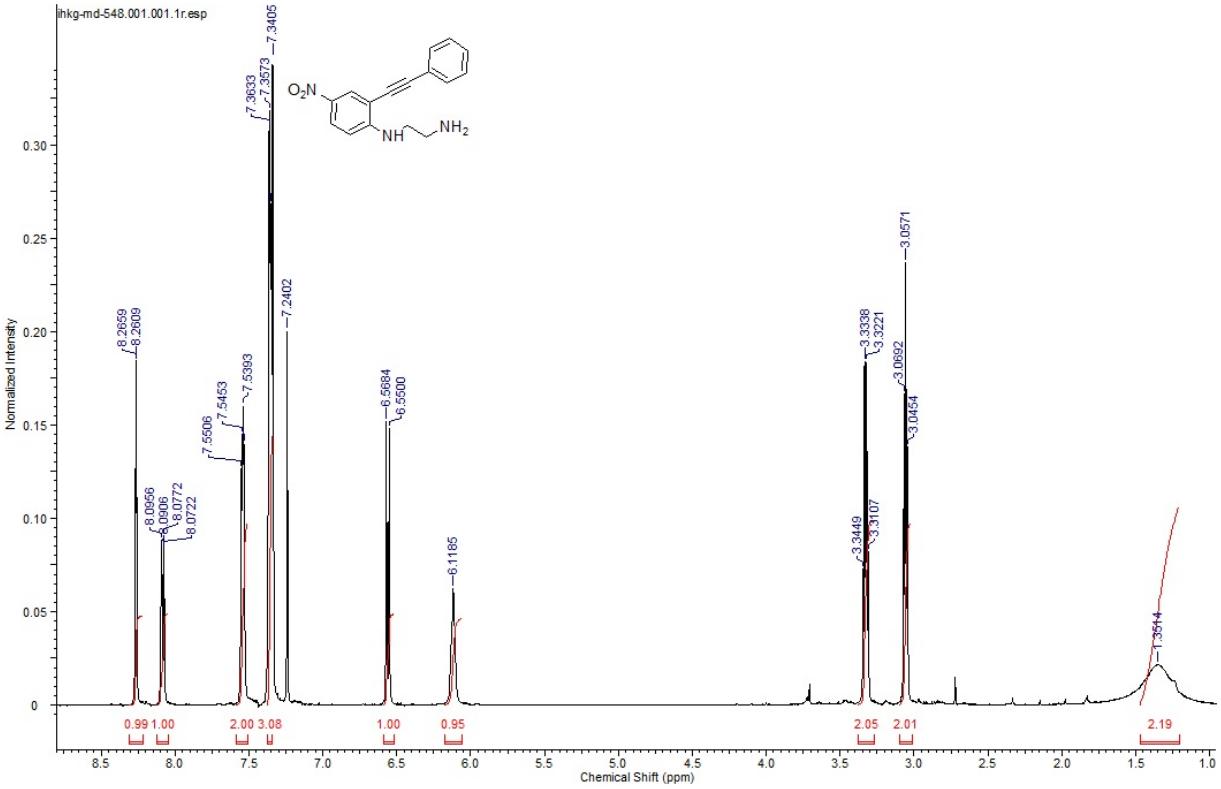
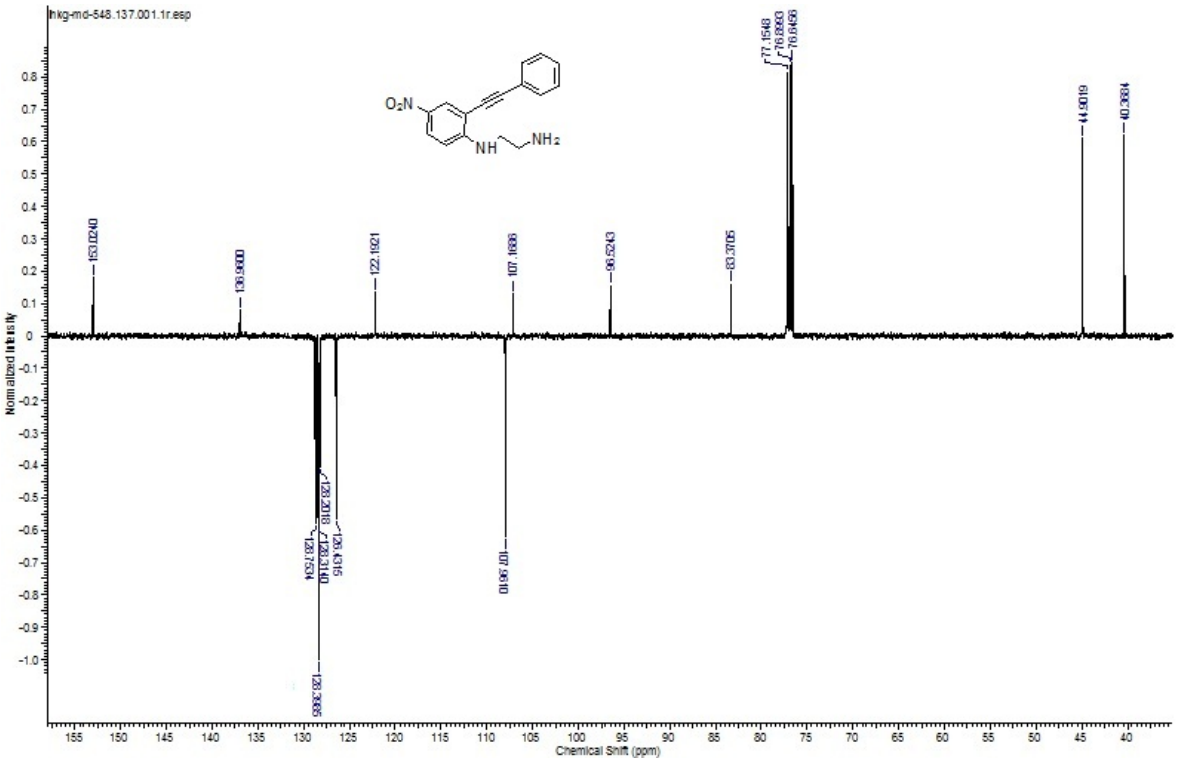
Reaction of 1-methoxy-4-nitro-2-(phenylethynyl)benzene (5d) with ethylene diamine.

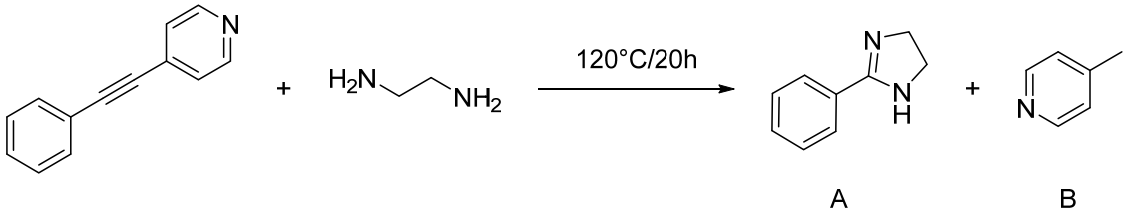


A mixture of alkyne **5d** (1.6 mmol), ethylenediamine (5 ml, 75.0 mmol) in pyridine was refluxed for 8 h to give *N*[1]-(4-nitro-2-(phenylethynyl)phenyl)ethane-1,2-diamine (**8**). ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.35 (br.s, 2H, NH$_2$), 3.05-3.07 (m, 2H, CH$_2$), 3.31-3.34 (m, 2H, CH$_2$), 6.12 (br.s, 1H, NH), 6.56 (d, 1H, *J* 7.36 Hz, CHAr), 7.35-7.36 (m, 3H, CHAr), 7.53-7.55 (m, 2H, CH$_{Ar}$), 8.07-8.10 (m, 1H, CH$_{Ar}$), 8.26 (d, 1H, *J* 2 Hz, CH$_{Ar}$). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 40.37 (CH$_2$), 44.90 (CH$_2$), 83.37 (CH), 96.52 (CH), 107.17, 107.96, 122.19, 126.43, 128.20, 128.31, 128.75, 136.96, 153.02. IR (film, cm^{-1}) 3387 (NH$_2$), 3321 (NH), 2201 (C≡C). HRMS (*m/z*): calcd for C$_{16}$H$_{15}$O$_2$N$_3$ [M]$^+$ 281.1159, found, 281.1158.

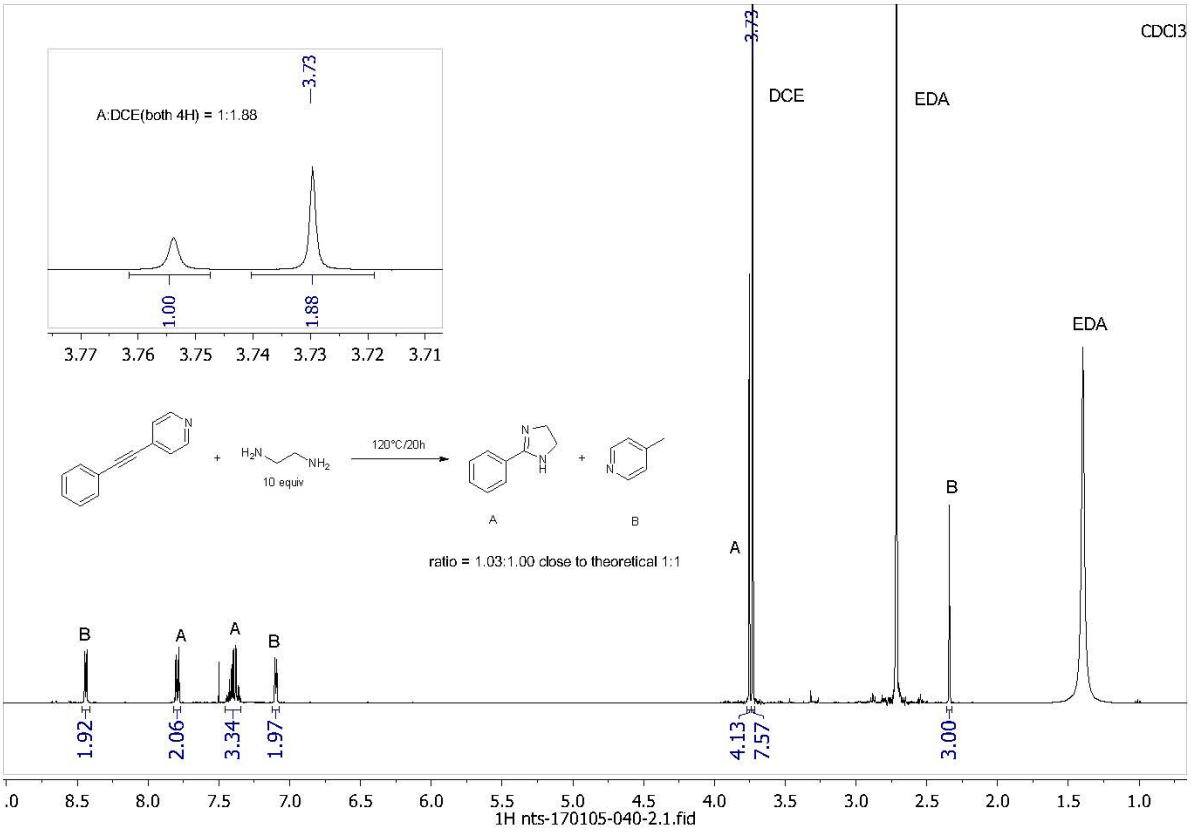




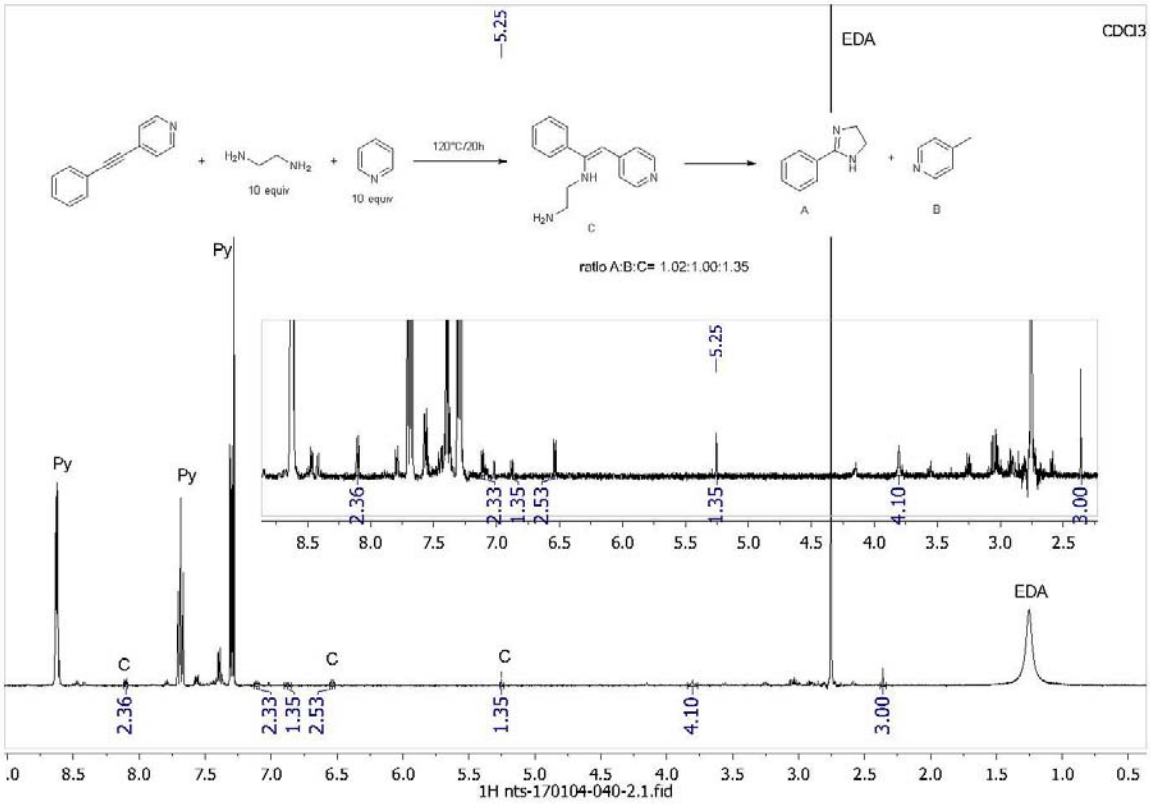
Reaction of 4-(phenylethynyl)pyridine (7a) with ethylene diamine.



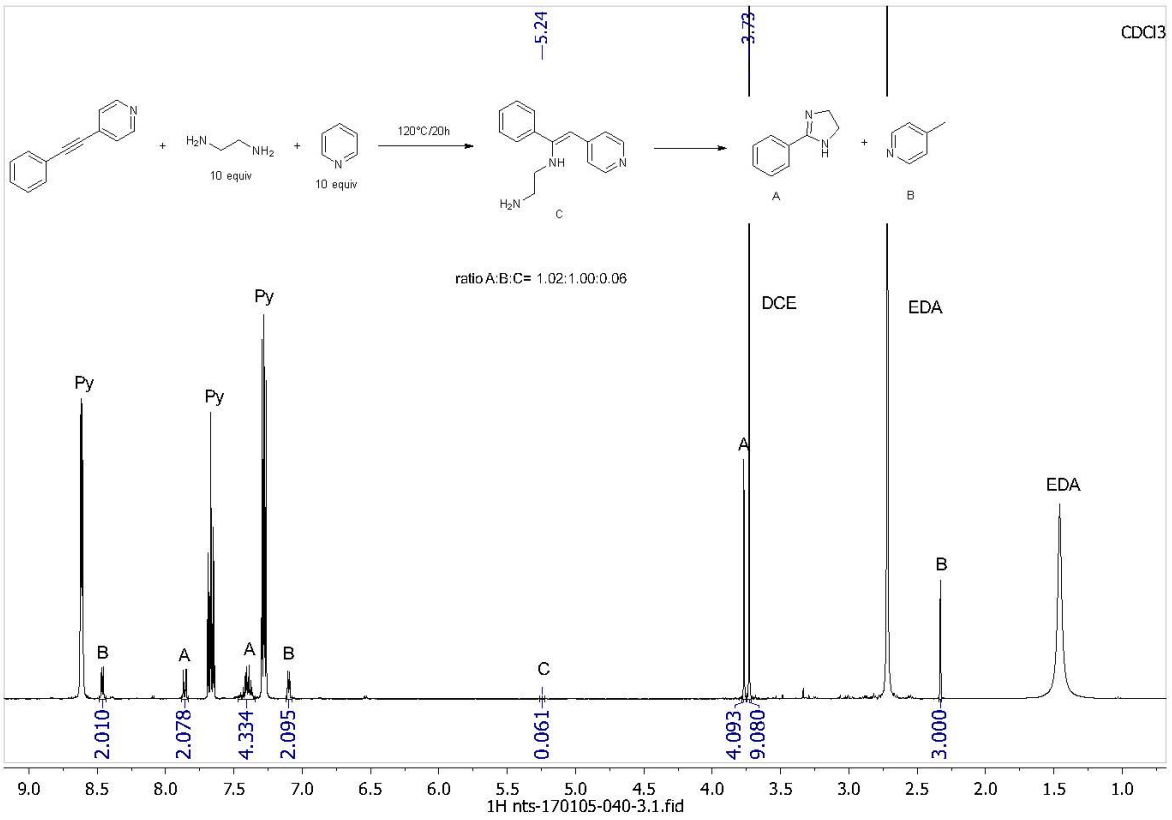
Condition#1: 18.1 mg of 4-(phenylethynyl)pyridine **7a** (0.101 mmol) were placed into 1/2dr vial followed by 60 mg of ethylenediamine (EDA) (1 mmol). Vial was tightly closed and heated to 120°C for 20h by oil bath. Reaction mixture was cooled to room temperature and content was dissolved in 0.5 mL of $CDCl_3$. Resulting solution was transferred into NMR tube with 14.3 mg of dichloroethane (DCE, 0.145 mmol) as a reference compound. ^1H NMR spectrum showed complete conversion of starting material, presence of the unreacted ethylenediamine and two new products. DCE chemical shift 3.73 ppm was chosen as a reference. Products A and B were assigned as fragmentation compounds and its ratio was established by comparing integrals of the $(CH_2)_2$ group for A and CH_3 for B. A:B = 1.03:1.00 which is close to the expected 1:1 distribution. Yield was calculated by comparing integrals of the DCE protons and $(CH_2)_2$ group for A. Yield: 76% which is in agreement with GC results.



Condition#2 is similar to Condition#1 except the addition of the 80 mg of extra solvent: pyridine (1 mmol). Scale 18.2 mg of 4-substituted Pyridine (0.102 mmol). One ^{1}H NMR experiment was performed after 6h of heating. ^{1}H NMR showed complete conversion of 4-substituted Pyridine to products A, B, and one more compound which we assigned as intermediate, enamine C.



Reaction mixture was heated for another 14h (20 h total). Reaction mixture was dissolved in 0.5 mL of $CDCl_3$. Resulting solution was transferred into NMR tube with 15.9 mg of dichloroethane (DCE, 0.161 mmol) as a reference compound. Traces (~6 mol%) of the peak of C were still observed after 20h. Results were established using same principles. Ratio A:B:C = 1.02:1.00:0.06. Yield of fragmented products: 70%.



Computational Data

Coordinates for optimized starting material geometries at the B3LYP/6-31+G(d,p) level

Ph_Ph
1,2-diphenylethyne
HF= -539.4622434

C	-0.60893900	-0.00041300	0.00026300
C	0.60893900	0.00049000	0.00013600
C	-2.03543200	-0.00021800	0.00018900
C	-2.75368000	-1.21436600	-0.00038300
C	-4.14738400	-1.20932300	-0.00062500
C	-4.84966800	0.00022000	-0.00029400
C	-4.14700200	1.20954700	0.00031900
C	-2.75329900	1.21416800	0.00056500
H	-2.20746300	-2.15217700	-0.00066500
H	-4.68724200	-2.15184200	-0.00110400
H	-5.93565000	0.00039100	-0.00051400
H	-4.68657100	2.15223300	0.00058000
H	-2.20678200	2.15180300	0.00101900

C	4.84966800	-0.00028500	-0.00019300
C	4.14695500	-1.20958400	0.00039000
C	2.75325300	-1.21414900	0.00057100
C	2.03543200	0.00026500	0.00016500
C	2.75372600	1.21438600	-0.00037200
C	4.14743200	1.20928600	-0.00055200
H	5.93565000	-0.00050200	-0.00037900
H	4.68648600	-2.15229200	0.00068000
H	2.20669700	-2.15176000	0.00099200
H	2.20754800	2.15222000	-0.00068400
H	4.68732800	2.15178300	-0.00100000

PhpNO2_Ph
1-nitro-4-(phenylethynyl)benzene (**5a**)
HF= -555.4980593

C	0.66362900	0.00051700	0.00058900
C	1.88178100	0.00046400	0.00043600
C	-0.75859800	0.00038500	0.00056100
C	-2.86540700	-1.22037200	-0.00026900
C	-2.86576000	1.22051800	0.00080800
C	-1.47651000	1.21737100	0.00100500
H	-3.42768700	-2.14592300	-0.00077800
H	-3.42831000	2.14590300	0.00112700
H	-0.93189100	2.15517500	0.00148600
C	6.11679300	-0.00045700	-0.00075700
C	5.41569800	-1.21079400	-0.00005800
C	4.02241700	-1.21570500	0.00037200
C	3.30716200	0.00020500	0.00011000
C	4.02298400	1.21577600	-0.00056300
C	5.41626600	1.21020800	-0.00100300
H	7.20269200	-0.00071100	-0.00111200
H	5.95604100	-2.15275400	0.00014700
H	3.47540900	-2.15295200	0.00090500
H	3.47642900	2.15328700	-0.00076600
H	5.95706100	2.15191000	-0.00155300
C	-1.47616600	-1.21681100	-0.00002200
H	-0.93126300	-2.15445100	-0.00032200
C	-3.54429500	-0.00002400	0.00013000
N	-5.01310200	-0.00025300	-0.00020400
O	-5.58837900	-1.09119200	-0.00129700
O	-5.58871200	1.09051700	0.00058100

PhmNO2_Ph
1-nitro-3-(phenylethynyl)benzene (**5c**)
HF= -744.0066337

C	0.44767800	0.47055300	0.00002500
C	1.64611300	0.25669200	0.00001500
C	-0.95517800	0.72128900	0.00006400
C	-2.82565500	2.28749400	0.00024200
C	-3.23262500	-0.07105800	0.00002200
C	-1.86964300	-0.34884400	0.00001000
H	-3.19056300	3.30958200	0.00035900
H	-4.80634900	1.39395200	0.00019500
H	-1.52623900	-1.37518100	-0.00003200
C	5.81182600	-0.51544400	-0.00002700
C	4.90119300	-1.57699300	0.00019500
C	3.53025900	-1.32735900	0.00019400
C	3.04887600	-0.00166500	-0.00003000
C	3.97455200	1.06234900	-0.00027300
C	5.34369200	0.80249400	-0.00027400
H	6.87945200	-0.71388700	-0.00001200
H	5.25988800	-2.60201800	0.00037700
H	2.82142300	-2.14906400	0.00037000
H	3.60876200	2.08410900	-0.00045700
H	6.04714100	1.62989000	-0.00045600
C	-1.45316600	2.04252500	0.00016200
H	-0.75063900	2.86926600	0.00018500
C	-3.73626500	1.23005900	0.00015500
N	-4.18327000	-1.20124900	-0.00010200
O	-3.71995200	-2.34221100	0.00021000
O	-5.38629000	-0.93659700	-0.00054600

PhpNO2_PhpNO2
1,2-bis(4-nitrophenyl)ethyne (**5f**)
HF= -948.5152251

C	-0.60884000	0.00043500	-0.00109000
C	0.60884000	0.00039100	-0.00107000
C	-2.03213500	0.00029900	-0.00082800
C	-4.13642900	-1.22093700	0.00086700
C	-4.13673900	1.22098800	-0.00107900
C	-2.74703100	1.21805100	-0.00157500
H	-4.69948600	-2.14598300	0.00182900
H	-4.70003500	2.14588900	-0.00161700
H	-2.20225800	2.15571700	-0.00251600

C	4.81297000	-0.00006300	0.00019400
C	4.13672800	1.22097900	0.00088300
C	2.74702000	1.21802600	0.00036400
C	2.03213500	0.00026600	-0.00080900
C	2.74673500	-1.21766300	-0.00156300
C	4.13644000	-1.22094600	-0.00107600
H	4.70001500	2.14588600	0.00184600
H	2.20223800	2.15568600	0.00092400
H	2.20172700	-2.15519200	-0.00250300
H	4.69950600	-2.14598600	-0.00162200
C	-2.74672400	-1.21763800	0.00034100
H	-2.20170700	-2.15516100	0.00089300
C	-4.81297100	-0.00006100	0.00018600
N	-6.28509200	-0.00025400	0.00086000
O	-6.85778200	-1.09131700	0.00193200
O	-6.85806600	1.09066200	-0.00009800
N	6.28509200	-0.00023800	0.00085700
O	6.85779300	-1.09129800	-0.00018100
O	6.85805600	1.09068100	0.00188300

PhpNO2_PHpOMe
1-methoxy-4-((4-nitrophenyl)ethynyl)benzene (**5e**)
HF= -858.5384257

C	0.30704300	0.05902600	0.00188500
C	-0.91161700	0.09046400	0.00482300
C	1.72732100	0.02304100	0.00076400
C	3.86536400	1.19029900	-0.00116400
C	3.80435200	-1.24945500	-0.00001400
C	2.41603400	-1.21158800	0.00077000
H	4.45028200	2.10175500	-0.00193700
H	4.34324000	-2.18882400	0.00011400
H	1.84833200	-2.13562900	0.00148600
C	-5.15109700	0.21387900	-0.00054200
C	-4.48549000	-1.02091400	0.00106100
C	-3.09153400	-1.05376400	0.00303400
C	-2.33344900	0.13178100	0.00329600
C	-3.02306100	1.36688500	0.00213500
C	-4.40780400	1.40730600	0.00023600
H	-5.03649700	-1.95353300	0.00077200
H	-2.57969400	-2.01073000	0.00424200
H	-2.45532900	2.29166600	0.00261700
H	-4.94172800	2.35177600	-0.00081300
C	2.47690100	1.22170400	-0.00041200

H	1.95608600	2.17296100	-0.00067800
C	4.51466100	-0.04659100	-0.00083800
N	5.98108400	-0.08331700	-0.00134500
O	6.58477900	0.99286500	-0.00123200
O	6.53026100	-1.18834900	-0.00162400
O	-6.50410000	0.36098700	-0.00302000
C	-7.32271700	-0.80550900	-0.00427900
H	-8.35126300	-0.44404300	-0.00615700
H	-7.14738200	-1.41294600	-0.90041900
H	-7.15058400	-1.41263900	0.89265900

4-Py_Ph
4-(phenylethynyl)pyridine (**7a**)
HF= -555.4980593

C	0.61324400	0.00004600	-0.00010700
C	-0.60429800	-0.00014200	-0.00000500
C	2.03776500	0.00003100	-0.00005700
C	4.16336600	-1.14264500	0.00040200
C	4.16341100	1.14262400	-0.00037800
C	2.77117300	1.20218000	-0.00044400
H	4.74626300	-2.06125000	0.00073400
H	4.74634200	2.06120700	-0.00066800
H	2.25883400	2.15831400	-0.00078900
C	-4.84145800	0.00008400	0.00003600
C	-4.14030600	-1.21014600	-0.00035600
C	-2.74678900	-1.21520600	-0.00036600
C	-2.03064000	-0.00007100	0.00001200
C	-2.74665400	1.21514900	0.00041100
C	-4.14017000	1.21023900	0.00042000
H	-5.92740700	0.00014400	0.00004100
H	-4.68071500	-2.15216600	-0.00065400
H	-2.19989300	-2.15255900	-0.00067000
H	-2.19965200	2.15244000	0.00070600
H	-4.68047900	2.15231600	0.00072600
C	2.77112900	-1.20214700	0.00037200
H	2.25875000	-2.15825900	0.00067800
N	4.86561600	-0.00002300	0.00003800

2-Py_Ph
2-(phenylethynyl)pyridine (**7b**)
HF= -555.4963819

C	0.62562900	-0.00458900	0.01023100
C	-0.59098800	0.01312800	0.01107400
C	2.05577700	-0.00707900	0.00460300
C	4.01194700	-1.21613600	-0.00466000
C	4.80145200	-0.06183900	-0.00759400
C	4.15737600	1.17665600	-0.00401000
C	2.76607600	1.21024400	0.00224800
H	4.47774400	-2.19966800	-0.00723200
H	5.88410100	-0.13746100	-0.01245000
H	4.72819800	2.10073500	-0.00601400
H	2.22350300	2.14947700	0.00523700
C	-4.82820900	-0.01280500	-0.00784700
C	-4.13594400	1.20251400	-0.00521100
C	-2.74234000	1.21762600	0.00147200
C	-2.01711900	0.00813600	0.00532400
C	-2.72400200	-1.21255200	0.00292400
C	-4.11753500	-1.21758400	-0.00377300
H	-5.91418200	-0.02095500	-0.01303100
H	-4.68332300	2.14061500	-0.00833500
H	-2.20264400	2.15925500	0.00351900
H	-2.16831900	-2.14461100	0.00608500
H	-4.65069400	-2.16381500	-0.00576100
N	2.67612900	-1.20827100	0.00132800

Anth_Ph
2-(phenylethynyl)anthracene-9,10-dione (**1b**)
HF= -996.0454641

C	2.38471300	0.39939400	0.00019900
C	3.58261000	0.17892200	0.00006300
C	0.98612800	0.66363900	0.00023900
C	0.50559300	1.99430700	0.00026400
C	-0.85830800	2.25162600	0.00023500
C	-1.31512500	-0.13326700	0.00019100
C	0.05652100	-0.39269100	0.00023100
H	1.21746200	2.81319300	0.00029400
H	-1.23473300	3.26903300	0.00024300
H	0.39356500	-1.42312100	0.00023200
C	7.74343000	-0.61562300	-0.00024000
C	7.28238600	0.70490000	-0.00053900
C	5.91473800	0.97192200	-0.00043800
C	4.98313000	-0.08730500	-0.00003400
C	5.45772900	-1.41572800	0.00026000
C	6.82726100	-1.67252600	0.00015900

H	8.81003100	-0.81968500	-0.00032200
H	7.99027200	1.52850900	-0.00085300
H	5.55394000	1.99543500	-0.00067600
H	4.74421600	-2.23335500	0.00056700
H	7.18077300	-2.69936900	0.00039100
C	-1.78323300	1.19741300	0.00017800
C	-3.23950700	1.50638300	0.00006400
C	-2.26662100	-1.28604800	0.00015400
C	-3.72636000	-0.97625300	-0.00002500
C	-4.19043600	0.35546100	-0.00006900
C	-5.56799900	0.61049000	-0.00024900
C	-4.64672200	-2.03284100	-0.00016100
C	-6.47619500	-0.44652800	-0.00039500
H	-5.90217400	1.64254900	-0.00027400
C	-6.01516700	-1.76953900	-0.00035200
H	-4.26726100	-3.04913400	-0.00012400
H	-7.54296100	-0.24307500	-0.00054600
H	-6.72424000	-2.59207700	-0.00047100
O	-1.86115300	-2.44451200	0.00029700
O	-3.64513300	2.66631700	0.00009500