**Electronic Supplementary Information for**

# DFT study to design Super- and Hyperacids with 1-(cyclopenta-2,4-dien-1-yl)-4-nitrobenzene and 3-(cyclopenta-2,4-dien-1-ylmethylene)-6-methylenecyclohexa-1,4-diene molecules

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## Theoretical Methods

The gas phase acidity is measured by the calculating the enthalpy change ($\Delta H_{acid}$) for the proton dissociation reaction given below

$$AH(g) \rightarrow A^-(g) + H^+(g) \quad (1)$$

Where ΔH acid can be calculated by the equation **2**

$$\Delta H_{acid} = \Delta E_{acid} + \Delta(pV) \quad (2)$$

$\Delta E_{acid}$ is the change of total molecular energy of the species involved in the equation **1** and the electronic energy involves the electronic energy, the repulsion of nuclei, the zero point vibrational energy (ZPVE) and the finite room temperature correction at 298.15 K.

The DFT-B3LYP method gives the satisfactory result for calculating the acidity which is comparable to experimental result [1, 2]. The series of papers published that reported the DFT methods are useful for calculating the electron affinity of molecules [3-7]. Hence we have optimized the compounds in B3LYP/6-31G(d) and further the single point energy calculated in

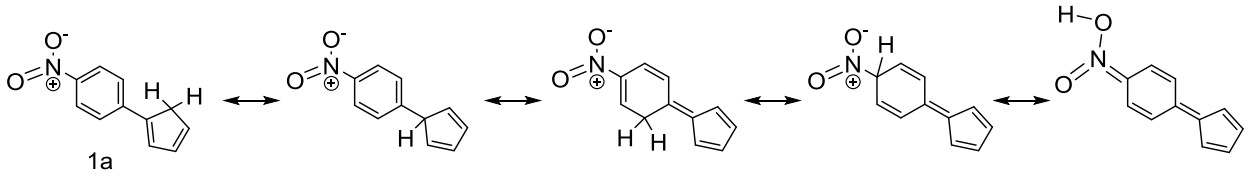
B3LYP/6-311+G(2d,P) method. We have calculated the acidities of the compounds in solvent medium. The PCM solvent model is important for determining the acidity [8, 9].We have calculated the acidity of compounds **4a** in DMSO solvent which based on previously reported the proton transfer reaction between solvated acids and dimethyl sulfoxide molecule [10].

$AH + DMSO \rightarrow A^- + DMSOH^+ + \Delta_rH_{DMSO}$

Where $A^-$ is the conjugate base and $\Delta_rH_{DMSO}$ is enthalpy change in above equation. All calculations are performed at IPCM/B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory by using the thermal correction at B3LYP/6-31G(d) level of theory. We have calculated the pKa values for compound **4a** by using equation **3** which is previous reported to calculate the pKa for neutral organic acid [10].

$pKa(exp) = 0.661.\ \Delta_rH_{DMSO} - 7.7$ (3)

All calculations were performed with the GAUSSIAN09 program package [11].




**Scheme S1** The process of tautomarization of hydrogen from $sp^3$ carbon atom of **1a** on the nitro group, forming –N(O)OH.

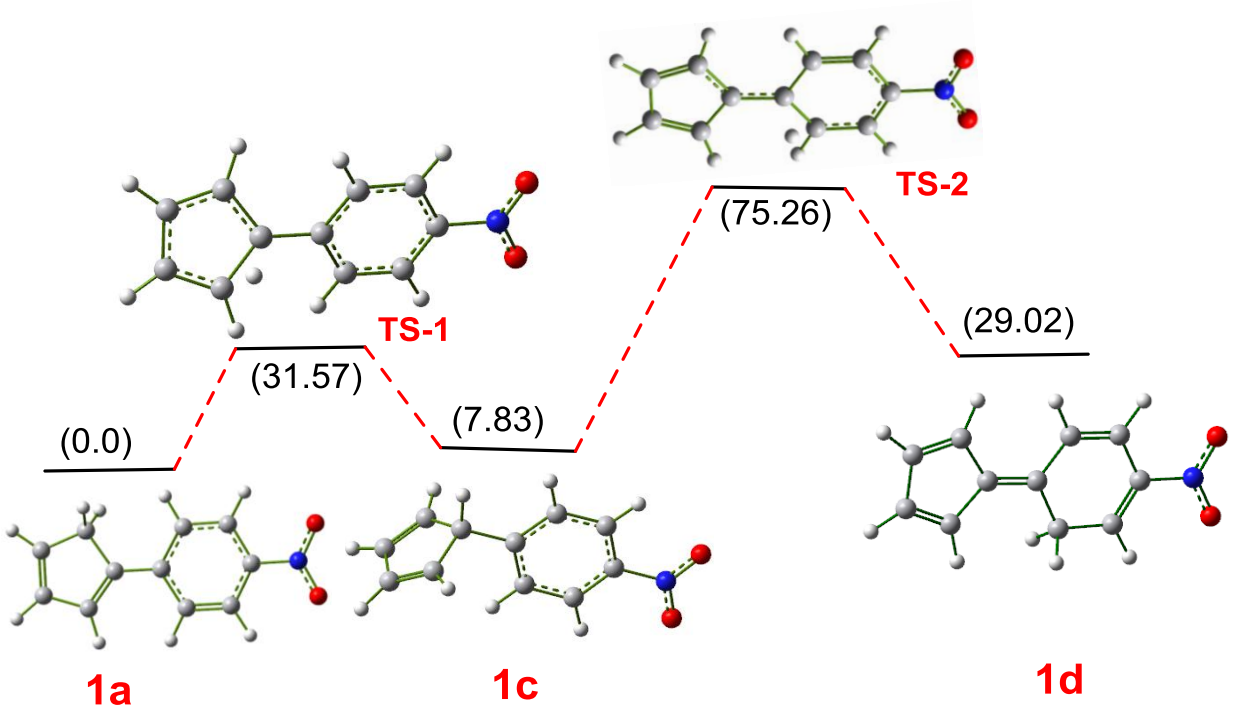



**Figure S1** The potential energy diagram for the transfer of proton from $sp^3$ carbon center of **1a** to $sp^2$ carbon center of **1c** and from **1c** to **1d** at B3LYP/6-311+G(2d, p)//B3LYP/6-31G(d) method. (The energies are given in kcal/mol)

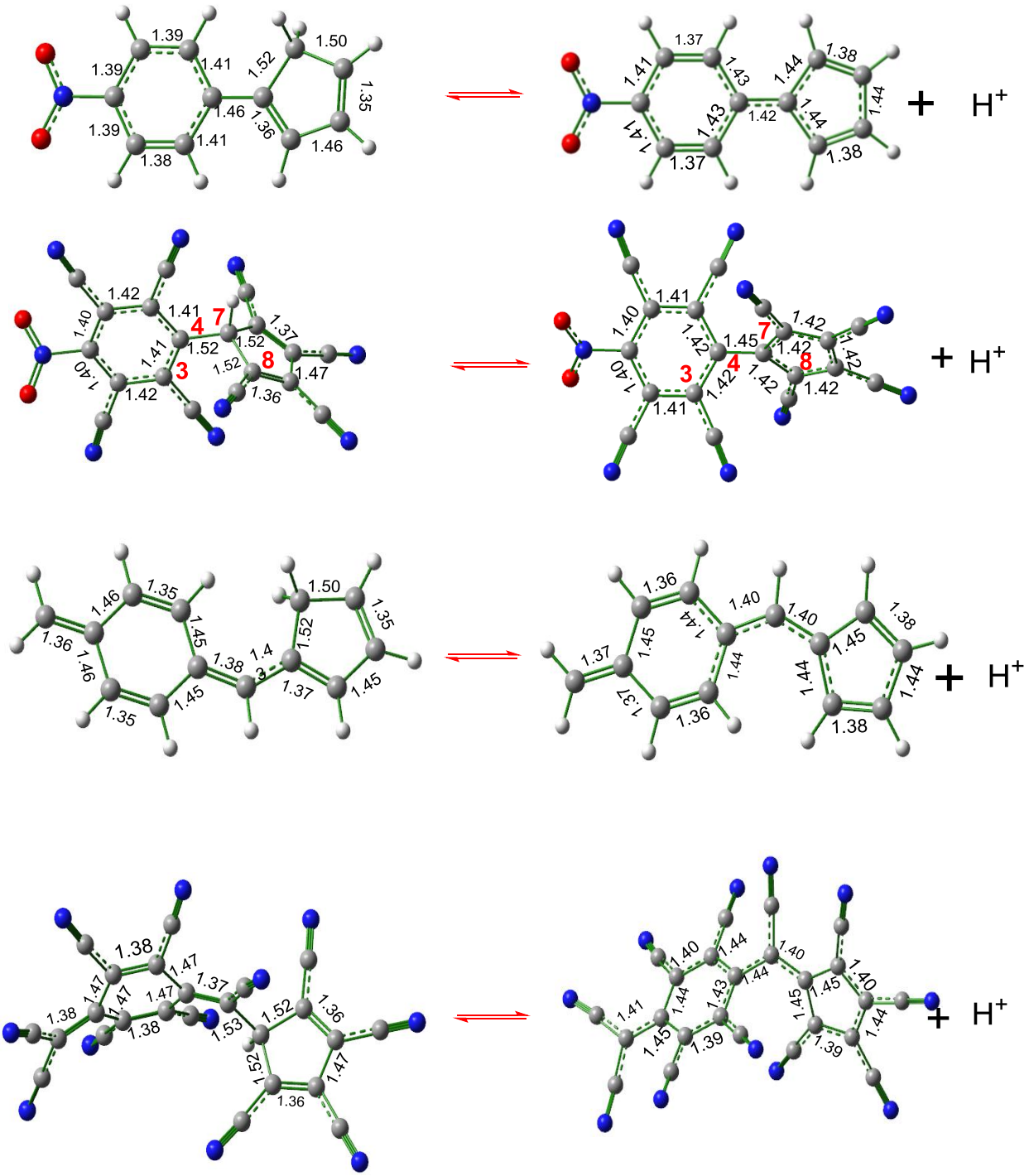
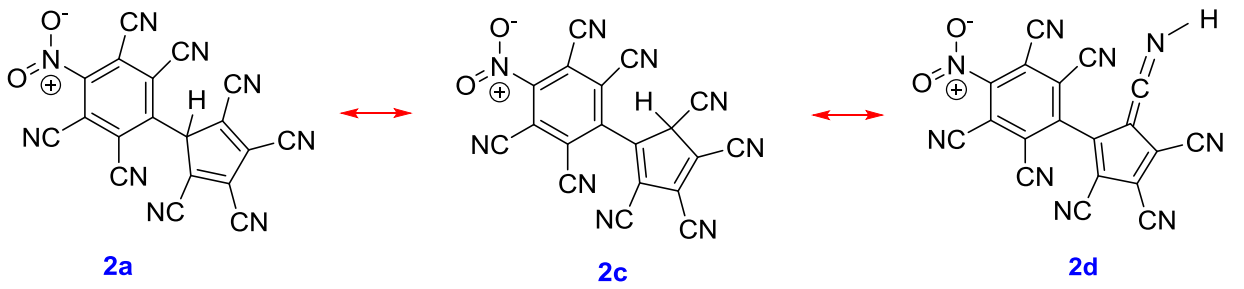


**Figure S2** The geometrical parameters for **1a, 2a, 3a** and **4a** molecules and their conjugate bases. (The red color numbers indicate the dihedral angle (-$C_3$-$C_4$-$C_7$-$C_8$)




**Scheme S2** The process of tautomarization of hydrogen from $sp^3$ carbon atom of **2a**, forming ketene imine (**2d**).

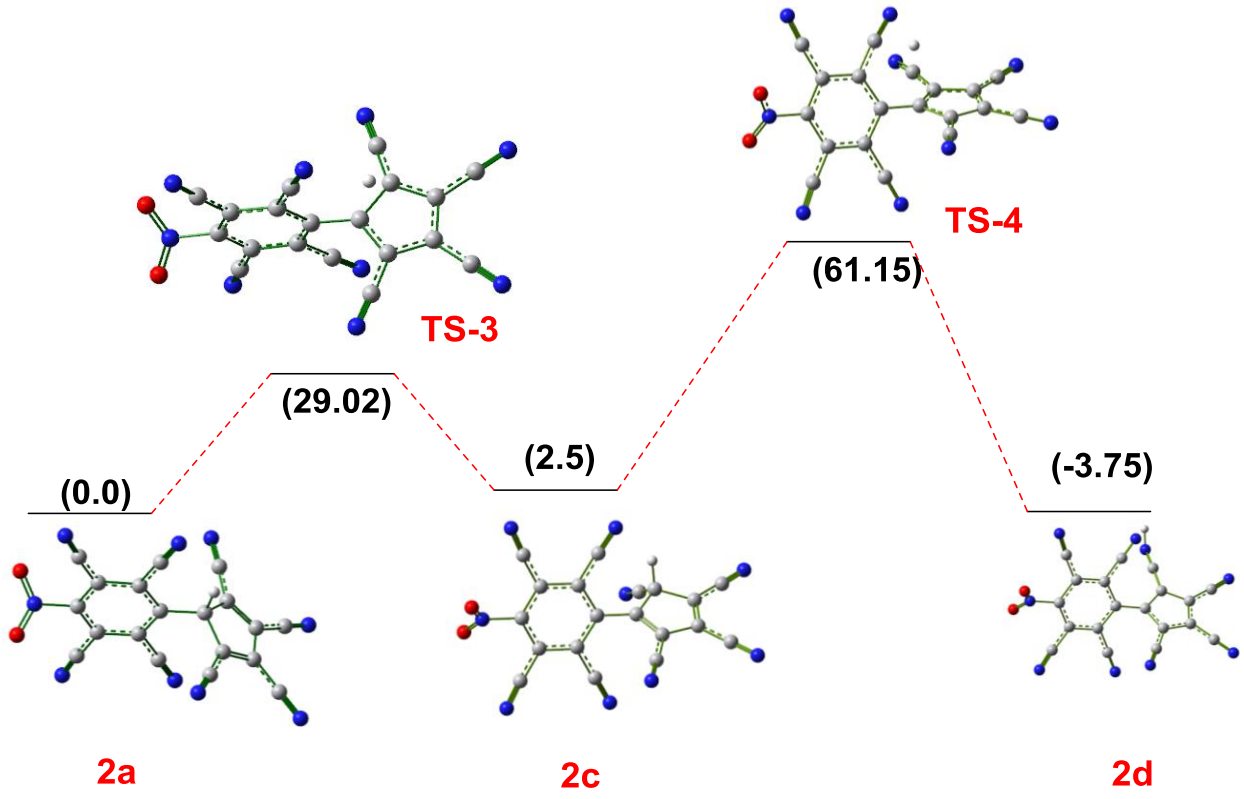



**Figure S3** The potential energy diagram for the transfer of proton from **2a** to **2d** at B3LYP/6-311+G(2d, p)//B3LYP/6-31G(d) method. (The energies are given in kcal/mol).

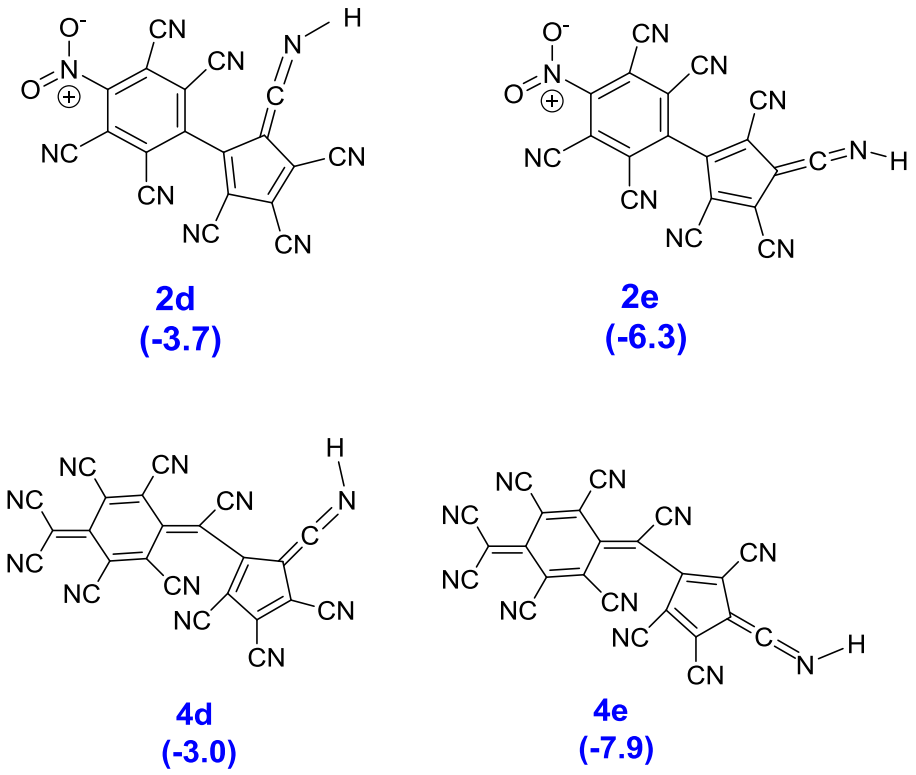



**Figure S4** Structure of ketene imine tautomers of octacyano substituted 1-(cyclopenta-2,4-dien-1-yl)-4-nitrobenzene and cyano group substituted 3-(cyclopenta-2,4-dien-1-ylmethylene)-6-methylenecyclohexa-1,4-diene and their relative energies with respect to tautomers (**2a** and **4a** respectively) obtained with B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) in gas phase (in kcal/mol)

**Table S1** The $\Delta H_{acid}$ values calculated at B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level of theory at gas phase for the compounds **2d**, **2e**, **4d**, and **4e**.

| Molecules | Energy | $H_{corrected}$ | $\Delta H_{acid}$ |
|---|---|---|---|
| **2d** | -1367.89780 | 0.18942 | 256.5 |
| **2e** | -1367.90185 | 0.18950 | 258.9 |
| **$2^-$** | -1367.48015 | 0.17809 | - |
| **4d** | -1517.49048 | 0.22001 | 238.8 |
| **4e** | -1517.49048 | 0.21020 | 246.63 |
| **$4^-$** | 1517.09638 | 0.2088 | - |

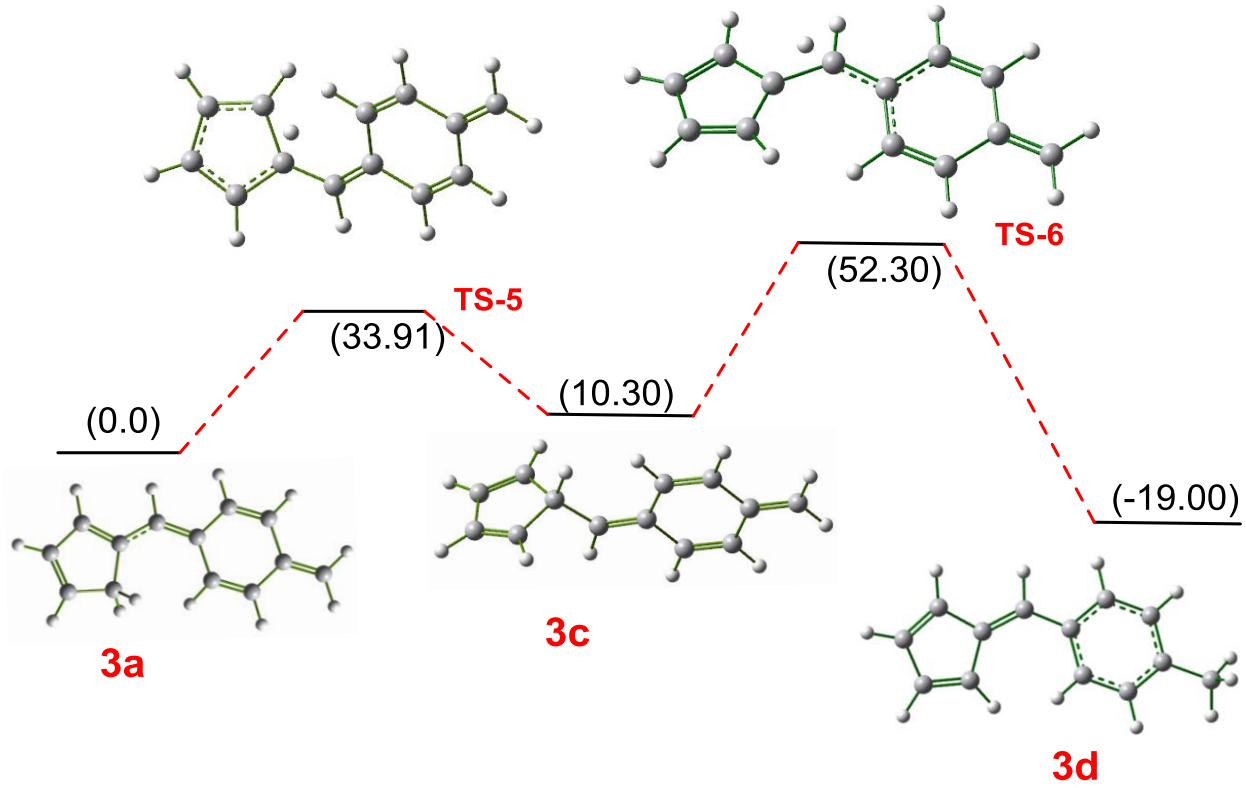


**Figure S5** The potential energy diagram for the transfer of proton from $sp^3$ carbon center of **3a** to $sp^2$ carbon center of **3c** and **3c** to **3d** with B3LYP/6-311+G(2d, p)//B3LYP/6-31G(d) level of theory. (The energies are given in kcal/mol).

**References**


1. A. D. Becke, Phys. Rev., 1988, **A38**, 3098-3100.
2. C. Lee, W. Yang, R. G. Parr, Phys. Rev., 1988, **37**, 785-789.
3. R. A. King, J. M. Galbraith, H. F. Schaefer III, J. Chem. Phys., 1996, **100**, 6061-6068.
4. J. M. Galbraith, H. F. J. Schaefer III, Chem. Phys., 1996, **105**, 862-864.
5. Q. -Sh. Li, W. -G. Xu, Y. Xie, H. F. J. Schaefer III, J. Phys. Chem. A, 1999, **103**, 7496-7505.
6. J. C. Rienstra-Kiracofe, G. S. Tschumper, H. F. Schaefer III, N. Sreela, G. B. Ellison, Chem. Rev., 2002, **102**, 231-282.
7. Y. Xie, H. F. Schaefer III, F. A. Cotton, Chem. Commum., 2003, 102-103.
8. S. Miertuš, E. Scrocco, J. Tomasi, Chem phys., 1981, **55**, 117-129.
9. S. Miertuš, J. Tomasi, Chem phys., 1982, **65**, 239-245.
10. R. Vianello, Z. B. Maksić, Eur. J. Org. Chem., 2004, 5003-5010.
11. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. Gaussian 09, Revision B01, Gaussian, Inc, Wallingford CT 2010.


**Table S2**. B3LYP/6-31G(d) optimized Cartesian coordinate of compounds **1a, 2a, 3a,** and **4a** (The electronic energies (E) are given in atomic unit).

| **1a** | | | | **$1^-$** | | | |
|---|---|---|---|---|---|---|---|
| **E =** | **-629.87011** | | | **E = -629.40585** | | | |
| C | 0.69107800 | 0.05654000 | -0.00000700 | C | -0.76203500 | 0.00000000 | -0.00001700 |
| C | -0.01771600 | -1.16414500 | -0.00009400 | C | 0.00541100 | 1.21146500 | -0.00005000 |
| C | -1.40597400 | -1.19894700 | -0.00008000 | C | 1.38131600 | 1.21646400 | -0.00006100 |

| | | | |
|---|---|---|---|
| C | -2.11144100 | 0.00310400 | 0.00002200 |
| C | -1.44944800 | 1.23291200 | 0.00011900 |
| C | -0.06372400 | 1.25151600 | 0.00010900 |
| H | 0.52736200 | -2.10250200 | -0.00018300 |
| H | -1.94973400 | -2.13564300 | -0.00015100 |
| H | -2.02838100 | 2.14826600 | 0.00021000 |
| H | 0.44530300 | 2.20975000 | 0.00021700 |
| C | 2.15114400 | 0.07234000 | -0.00003200 |
| C | 2.98463600 | 1.15161200 | -0.00024300 |
| C | 3.01674700 | -1.17324400 | 0.00016300 |
| H | 2.68299100 | 2.19345200 | -0.00045200 |
| C | 4.37559400 | 0.71601700 | -0.00015900 |
| H | 2.82739800 | -1.80706500 | -0.87878700 |
| C | 4.41988700 | -0.63388300 | 0.00007800 |
| H | 5.30580800 | -1.25797200 | 0.00018500 |
| N | -3.57449900 | -0.02379600 | 0.00003700 |
| O | -4.16895200 | 1.05620200 | 0.00011000 |
| O | -4.12941500 | -1.12465800 | -0.00005700 |
| H | 5.22560600 | 1.38981200 | -0.00028300 |
| H | 2.82737900 | -1.80680800 | 0.87929300 |

**2a**

**E = -1367.89176**

| | | | |
|---|---|---|---|
| C | -0.18716600 | 0.43327400 | 0.02479200 |
| C | -1.24285000 | 1.36429700 | 0.07208200 |
| C | -2.59625700 | 0.94499600 | 0.03634100 |
| C | -2.87446300 | -0.42421200 | -0.01726900 |
| C | -1.85078100 | -1.37824900 | -0.05089800 |
| C | -0.50461400 | -0.93703100 | -0.04441700 |
| C | 1.25451500 | 0.92437600 | 0.04900700 |
| C | 2.11739800 | 0.59363300 | -1.15733300 |
| C | 2.12281100 | 0.46255500 | 1.20728700 |
| C | 3.33451900 | 0.13870500 | -0.73583200 |
| C | 3.33780300 | 0.05705500 | 0.73265200 |
| N | -4.28448900 | -0.87525000 | -0.03866500 |
| O | -4.56516000 | -1.81302100 | 0.69509200 |
| O | -5.03692700 | -0.26738700 | -0.78773300 |
| C | 0.53740500 | -1.91697600 | -0.10630200 |
| C | -2.11804700 | -2.78191000 | -0.13164300 |
| C | -3.62850800 | 1.93434200 | 0.09524800 |
| C | -0.95637700 | 2.76591000 | 0.15454600 |
| C | 1.68909600 | 0.80925500 | -2.48792100 |
| C | 4.44200800 | -0.20199800 | -1.55957400 |
| C | 4.44877200 | -0.37284700 | 1.50860200 |
| N | -2.25947300 | -3.93141800 | -0.22486100 |
| N | 1.39506400 | -2.69970100 | -0.15648100 |
| N | -4.40985700 | 2.79091300 | 0.17220700 |
| N | -0.68227600 | 3.89394700 | 0.22119700 |
| N | 1.28425000 | 0.99119900 | -3.56446300 |
| N | 5.35527300 | -0.47698900 | -2.22416300 |
| N | 5.36482500 | -0.71998300 | 2.13444900 |
| H | 1.22501400 | 2.02453000 | 0.10979300 |
| C | 1.70011300 | 0.52958100 | 2.55534700 |
| C | 2.09560000 | 0.00000000 | -0.00003000 |
| C | 1.38131600 | -1.21646400 | 0.00001700 |
| C | 0.00541100 | -1.21146500 | 0.00003100 |
| H | -0.52127400 | 2.16076200 | -0.00008800 |
| H | 1.94061700 | 2.14514400 | -0.00010200 |
| H | 1.94061700 | -2.14514400 | 0.00005300 |
| H | -0.52127500 | -2.16076200 | 0.00010500 |
| C | -2.18402800 | 0.00000000 | 0.00003400 |
| C | -3.05032600 | -1.15370500 | 0.00009200 |
| C | -3.05032600 | 1.15370400 | 0.00029200 |
| H | -2.72527100 | -2.18896700 | 0.00003900 |
| C | -4.36320200 | -0.71886500 | -0.00022700 |
| H | -2.72527000 | 2.18896700 | 0.00053200 |
| C | -4.36320200 | 0.71886600 | 0.00012700 |
| H | -5.24711700 | -1.35142000 | -0.00049100 |
| H | -5.24711700 | 1.35142100 | 0.00018800 |
| N | 3.51473800 | 0.00000000 | -0.00004100 |
| O | 4.12045800 | -1.09542400 | -0.00004400 |
| O | 4.12045800 | 1.09542300 | -0.00010600 |

**$2^-$**

**E = -1367.48015**

| | | | |
|---|---|---|---|
| C | -0.13386000 | -0.00033900 | -0.00029500 |
| C | -0.87066800 | 1.13376800 | -0.42979000 |
| C | -2.28447500 | 1.15156900 | -0.40595500 |
| C | -2.97345600 | -0.00004900 | -0.00029400 |
| C | -2.28467900 | -1.15180600 | 0.40532500 |
| C | -0.87087900 | -1.13426700 | 0.42921400 |
| C | 1.32535200 | -0.00027700 | -0.00005700 |
| C | 2.16499700 | -0.92864500 | -0.67444200 |
| C | 2.16458700 | 0.92830800 | 0.67455300 |
| C | 3.51254400 | -0.56890900 | -0.42434000 |
| C | 3.51229600 | 0.56899700 | 0.42471100 |
| N | -4.44433700 | 0.00019200 | -0.00010700 |
| O | -5.00170700 | -1.02479800 | -0.38130600 |
| O | -5.00125700 | 1.02537000 | 0.38123300 |
| C | -0.19080300 | -2.26664800 | 0.98454300 |
| C | -2.97059100 | -2.31759800 | 0.87999100 |
| C | -2.97018800 | 2.31768700 | -0.88011400 |
| C | -0.19034100 | 2.26630800 | -0.98450700 |
| C | 1.72218800 | 1.96057700 | 1.53958600 |
| C | 1.72312300 | -1.96086500 | -1.53979800 |
| C | 4.65833400 | -1.21846800 | -0.94835200 |
| C | 4.65777900 | 1.21889100 | 0.94897500 |
| N | -3.46303500 | -3.28062800 | 1.30467800 |
| N | 0.31611900 | -3.18660300 | 1.48240500 |
| N | -3.46266900 | 3.28093400 | -1.30426500 |
| N | 0.31711900 | 3.18626900 | -1.48181000 |
| N | 1.32773600 | -2.79395300 | -2.25292900 |
| N | 5.60003400 | -1.75210400 | -1.37965900 |
| N | 5.59921700 | 1.75296200 | 1.38031400 |
| N | 1.32640900 | 2.79379100 | 2.25235300 |

**$3^-$**

| | | | |
|---|---|---|---|
| N | 1.29945700 | 0.59159800 | 3.64692900 |

**3a**

**E = -502.68525**

| | | | |
|---|---|---|---|
| C | -2.23153900 | -1.24969900 | -0.00001200 |
| C | -0.93530200 | -0.85648300 | -0.00032000 |
| C | -0.55765200 | 0.54746200 | -0.00036500 |
| C | -1.66227000 | 1.49450200 | 0.00018200 |
| C | -2.95840700 | 1.10710200 | 0.00044300 |
| C | -3.33661900 | -0.29993700 | 0.00011200 |
| C | 0.73189700 | 1.03559000 | -0.00031300 |
| C | 2.00395200 | 0.37697700 | -0.00029200 |
| C | 2.31863100 | -1.11023400 | 0.00015900 |
| C | 3.20510800 | 1.04317400 | -0.00012500 |
| C | 3.82314000 | -1.16000900 | 0.00032100 |
| C | 4.31000300 | 0.10214900 | 0.00020900 |
| C | -4.63213500 | -0.70493500 | -0.00005500 |
| H | -4.89802300 | -1.75796300 | -0.00029400 |
| H | -5.45027100 | 0.00933200 | 0.00006700 |
| H | -2.47672600 | -2.30942700 | -0.00005100 |
| H | -0.16020200 | -1.61267600 | -0.00060100 |
| H | -3.75325800 | 1.84917500 | 0.00075300 |
| H | -1.41472800 | 2.55393100 | 0.00027700 |
| H | 0.81448200 | 2.12296700 | -0.00031300 |
| H | 3.31461100 | 2.12326500 | -0.00030100 |
| H | 5.35713600 | 0.38627400 | 0.00014600 |
| H | 4.39515500 | -2.08059500 | 0.00043300 |
| H | 1.89928000 | -1.61899000 | 0.87989500 |
| H | 1.89971900 | -1.61924600 | -0.87967100 |

**4a**

**E = -1517.48571**

| | | | |
|---|---|---|---|
| C | -2.32111000 | -0.95411000 | -0.96204600 |
| C | -0.99824500 | -0.62501800 | -1.14983100 |
| C | -0.41327000 | 0.54798600 | -0.47584500 |
| C | -1.41147300 | 1.59454300 | -0.17777300 |
| C | -2.73314100 | 1.26668600 | 0.01414600 |
| C | -3.17555000 | -0.12826100 | -0.10083600 |
| C | 0.90660500 | 0.66767800 | -0.11053900 |
| C | 1.99448000 | -0.39097800 | -0.28385600 |
| C | 2.49110100 | -0.94986300 | 1.04113100 |
| C | 3.27380900 | 0.13158700 | -0.91531900 |
| C | 3.84672300 | -0.81047800 | 1.11943900 |
| C | 4.33373500 | -0.13864300 | -0.09753100 |
| C | -4.29122000 | -0.62222900 | 0.54423100 |
| C | -4.69904900 | -1.99248500 | 0.48834300 |
| N | -5.07748100 | -3.09222800 | 0.52592500 |
| C | -5.09276800 | 0.14832000 | 1.44449600 |
| N | -5.77287400 | 0.68868900 | 2.21879800 |
| C | -3.68185800 | 2.31170800 | 0.24073300 |
| N | -4.43552800 | 3.18776500 | 0.36997400 |
| C | -2.86423500 | -2.06180100 | -1.68459600 |
| N | -3.27644900 | -2.93615200 | -2.33113700 |
| C | -1.03403700 | 2.97237700 | -0.16437200 |

**E = -502.21502**

| | | | |
|---|---|---|---|
| C | 2.27826600 | -1.23647800 | -0.10138800 |
| C | 0.96185500 | -0.88110900 | -0.11031600 |
| C | 0.52898000 | 0.48997100 | -0.02020300 |
| C | 1.59451800 | 1.45583600 | 0.05312800 |
| C | 2.91519100 | 1.11668000 | 0.07061100 |
| C | 3.35934800 | -0.26686300 | 0.00383800 |
| C | -0.80403300 | 0.93346900 | -0.01005200 |
| C | -2.05117000 | 0.28564800 | 0.00927500 |
| C | -2.42130400 | -1.10718300 | 0.12467100 |
| C | -3.29592100 | 1.01907400 | -0.08936000 |
| C | -3.80104700 | -1.19683700 | 0.09172100 |
| C | -4.34832300 | 0.12702400 | -0.04867100 |
| C | 4.67873100 | -0.62966700 | 0.02413300 |
| H | 4.98176000 | -1.67226500 | -0.03190500 |
| H | 5.47057500 | 0.11215600 | 0.09479400 |
| H | 2.55156300 | -2.28819700 | -0.18509800 |
| H | 0.21022600 | -1.65589600 | -0.21943500 |
| H | 3.67647200 | 1.89380400 | 0.13393800 |
| H | 1.31603000 | 2.50927300 | 0.10816600 |
| H | -0.89141500 | 2.02436000 | -0.01890000 |
| H | -3.35800200 | 2.09887100 | -0.19885700 |
| H | -5.40579800 | 0.37123500 | -0.10822500 |
| H | -4.38114800 | -2.11300500 | 0.17322700 |
| H | -1.74080500 | -1.93773700 | 0.26796100 |

**$4^-$**

**E = -1517.09638**

| | | | |
|---|---|---|---|
| C | -2.70600000 | 1.06532600 | -0.33733800 |
| C | -1.39080100 | 1.52874100 | -0.26496700 |
| C | -0.32608200 | 0.73252900 | 0.26131800 |
| C | -0.69321500 | -0.55436000 | 0.76769400 |
| C | -2.01151900 | -1.01255500 | 0.75176800 |
| C | -3.08972500 | -0.23818200 | 0.16745600 |
| C | 1.03319200 | 1.21679000 | 0.34704600 |
| C | 2.16316800 | 0.44844600 | 0.02096000 |
| C | 3.52871100 | 0.64244800 | 0.46850300 |
| C | 2.19414100 | -0.66138600 | -0.91583700 |
| C | 4.33324000 | -0.31322700 | -0.14998800 |
| C | 3.50741800 | -1.11151800 | -1.02414400 |
| C | -4.41271900 | -0.71429700 | 0.10805900 |
| C | -5.55645200 | 0.11511300 | -0.07937000 |
| N | -6.55594500 | 0.71110500 | -0.15719700 |
| C | -4.77115400 | -2.08832600 | 0.22928400 |
| N | -5.15869400 | -3.18809400 | 0.25004400 |
| C | -2.27618000 | -2.21639100 | 1.47974400 |
| N | -2.42255600 | -3.16813600 | 2.13244100 |
| C | -3.62945000 | 1.89167000 | -1.05423800 |
| N | -4.30292800 | 2.60366700 | -1.68081800 |
| C | 0.27897200 | -1.34406800 | 1.47140500 |
| N | 1.04973800 | -1.97999900 | 2.06521200 |
| C | -1.08569500 | 2.78406100 | -0.89073300 |
| N | -0.83970800 | 3.78583800 | -1.42639900 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N | -0.77134900 | 4.10461400 | -0.20794000 | C | 1.21802800 | 2.54817600 | 0.83759700 |
| C | -0.22813900 | -1.40337700 | -2.06865800 | N | 1.34161800 | 3.62055300 | 1.27507200 |
| N | 0.40010000 | -2.02235600 | -2.82813900 | C | 1.11768900 | -1.12610300 | -1.71206600 |
| C | 1.38094300 | 1.79352300 | 0.63311800 | N | 0.23817200 | -1.50591700 | -2.37491900 |
| N | 1.87810200 | 2.62597400 | 1.27754200 | C | 3.97814900 | -2.14233600 | -1.87601900 |
| C | 3.30001700 | 0.76594200 | -2.17935900 | N | 4.37533600 | -2.98561900 | -2.57359100 |
| N | 3.27416300 | 1.28863900 | -3.21938400 | C | 5.72833800 | -0.48578000 | 0.03556900 |
| C | 5.70115800 | 0.15141100 | -0.35671700 | N | 6.87456000 | -0.63243200 | 0.17720100 |
| N | 6.82314800 | 0.38024500 | -0.55723900 | C | 3.99975200 | 1.56022400 | 1.44184000 |
| C | 4.68365100 | -1.24987700 | 2.18152300 | N | 4.43028800 | 2.28903700 | 2.24134300 |
| N | 5.37678700 | -1.60779800 | 3.04343600 | | | | |
| C | 1.61833900 | -1.53725000 | 1.98631400 | | | | |
| N | 0.84506000 | -2.00290400 | 2.72198800 | | | | |
| H | 1.63546400 | -1.22576900 | -0.89394400 | | | | |