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# Solvent and structural effects in tautomeric 2(6)-hydroxy-4-methyl-6(2)-oxo-1-(substituted phenyl)-1,2(1,6)-dihydro pyridine-3-carbonitriles: UV, NMR and quantum chemical study

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*FTIR and NMR characterization methods*

FTIR spectra were recorded in transmission mode on BOMEM (Hartmann & Braun) instrument, MB series in the form of KBr pellets. The purity of the obtained compounds was confirmed by elemental analysis.

$^1$H and $^{13}$C NMR characterizations were performed on a Varian Gemini 2000 (200/50 MHz) instrument at 25 °C. Chemical shifts ($\delta$) were reported in part per million (ppm) relative to tetramethylsilane ($\delta_H=0$ ppm) in $^1$H NMR, and to dimethyl sulfoxide ($\delta_C=39.5$ ppm) in $^{13}$C NMR, using the residual solvent peak as a reference standard. 2D Nuclear Overhauser effect spectroscopy (NOESY), Heteronuclear Multiple Bond Correlation (HMBC) and Heteronuclear single quantum coherence spectroscopy (HSQC) spectra were recorded on a Bruker Avance 500 spectrometer (500/125 MHz) equipped with inverse detection triple resonance 5 mm probe (TXI). Standard pulse sequences were used for 2D spectra.

**Table S1.** Solvent parameters[1,2] used in Kamlet–Taft equation.

| Solvent | $\pi^*$ | $\alpha$ | $\beta$ |
|---|---|---|---|
| Ethanol | 0.54 | 0.83 | 0.77 |
| Methanol | 0.6 | 0.93 | 0.62 |
| 2-Propanol | 0.48 | 0.76 | 0.95 |
| 1-Propanol | 0.52 | 0.78 | 0.83 |
| 1-Butanol | 0.47 | 0.79 | 0.88 |
| 2-Butanol | 0.4 | 0.69 | 0.8 |
| DMSO | 1 | 0 | 0.76 |
| THF | 0.58 | 0 | 0.55 |
| AcN | 0.75 | 0.19 | 0.31 |
| Anisol | 0.73 | 0 | 0.32 |
| DMAc | 0.88 | 0 | 0.76 |
| DMF | 0.88 | 0 | 0.69 |
| EtAc | 0.55 | 0 | 0.45 |
| Chl | 0.58 | 0.44 | 0 |
| Dioxane | 0.55 | 0 | 0.37 |
| DEE | 0.27 | 0 | 0.47 |

**Table S2.** Solvent parameters[3] used in Catalán equation.

| Solvent* | SP | SdP | SA | SB |
|---|---|---|---|---|
| Ethanol | 0.633 | 0.783 | 0.4 | 0.658 |
| Methanol | 0.608 | 0.904 | 0.605 | 0.545 |
| 2-Propanol | 0.633 | 0.808 | 0.283 | 0.83 |
| 1-Propanol | 0.658 | 0.748 | 0.367 | 0.782 |
| 1-Butanol | 0.674 | 0.655 | 0.341 | 0.809 |
| 2-Butanol | 0.656 | 0.706 | 0.221 | 0.888 |
| DMSO | 0.83 | 1 | 0.072 | 0.647 |
| THF | 0.714 | 0.634 | 0 | 0.591 |
| AcN | 0.645 | 0.974 | 0.044 | 0.286 |
| Anisol | 0.82 | 0.543 | 0.084 | 0.299 |
| DMAc | 0.763 | 0.987 | 0.028 | 0.65 |
| DMF | 0.759 | 0.977 | 0.031 | 0.613 |
| EtAc | 0.656 | 0.603 | 0 | 0.542 |
| Chl | 0.783 | 0.614 | 0.047 | 0.071 |
| Dioxane | 0.737 | 0.312 | 0 | 0.444 |
| DEE | 0.617 | 0.385 | 0 | 0.562 |

**Table S3.** Substituent constants $\sigma$, $\sigma_I$, $\sigma_R^0$ and $\sigma_R$.[4]

| Comp. | $\sigma$ | $\sigma_I$ | $\sigma_R^0$ | $\sigma_R$ | Comp. | $\sigma$ | $\sigma_I$ | $\sigma_R^0$ | $\sigma_R$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 0 | 0 | 0 | 0 | **9** | 0.23 | 0.44 | -0.25 | -0.19 |
| **2** | -0.17 | -0.04 | -0.14 | -0.10 | **10** | 0.06 | 0.52 | -0.48 | -0.37 |
| **3** | -0.27 | 0.27 | -0.43 | -0.66 | **11** | 0.43 | 0.40 | 0.15 | 0.15 |
| **4** | 0.78 | 0.64 | 0.15 | 0.15 | **12** | 0.37 | 0.47 | -0.25 | -0.21 |
| **5** | 0.5 | 0.30 | 0.20 | 0.06 | **13** | 0.39 | 0.44 | -0.25 | -0.19 |
| **6** | -0.37 | 0.29 | -0.43 | -0.64 | **14** | 0.12 | 0.27 | -0.43 | -0.66 |
| **7** | 0.18 | 0.39 | -0.16 | -0.18 | **15** | -0.07 | -0.04 | -0.14 | - |
| **8** | 0.23 | 0.47 | -0.25 | -0.21 | **16** | 0.38 | 0.30 | 0.20 | 0.06 |

**Table S4.** Experimental and calculated ^{1}H and ^{13}C NMR chemical shifts for **2-PY** tautomer.[5]

| No. | Substituent | $q_{C5}$ | C4 | | C3 | | C2 | | C6 | | C5 | | H5 | | C4' | | 4-CH3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp |
| 1 | H | -0.602 | 158.9 | 159.1 | 93.3 | 88.2 | 154.6 | 160.7 | 154.4 | 161.0 | 89.4 | 92.6 | 5.89 | 5.69 | 124.5 | 128.2 | 19.2 | 20.8 |
| 2 | 4-CH3 | -0.601 | 158.9 | 159.4 | 93.1 | 88.6 | 154.8 | 161.1 | 154.6 | 162.5 | 89.5 | 92.7 | 5.88 | 5.69 | 137.3 | 138.0 | 19.3 | 20.9 |
| 3 | 4-OCH3 | -0.588 | 158.8 | 159.3 | 93.2 | 89.0 | 154.9 | 161.2 | 154.7 | 162.7 | 89.6 | 92.6 | 5.89 | 5.69 | 155.1 | 159.4 | 19.2 | 21.0 |
| 4 | 4-NO2 | -0.581 | 160.0 | 159.0 | 93.9 | 88.1 | 154.0 | 160.9 | 153.4 | 161.3 | 90.1 | 95.9 | 5.97 | 5.69 | 147.4 | 141.0 | 19.3 | 20.9 |
| 5 | 4-COCH3 | -0.579 | 159.4 | 158.9 | 93.7 | 87.3 | 154.2 | 160.7 | 153.7 | 161.0 | 89.9 | 93.2 | 5.94 | 5.66 | 132.5 | 136.5 | 19.3 | 20.8 |
| 6 | 4-OH | -0.602 | 158.7 | 159.5 | 93.2 | 89.1 | 154.9 | 161.3 | 154.7 | 161.4 | 89.5 | 92.5 | 5.87 | 5.69 | 152.5 | 157.6 | 19.1 | 21.0 |
| 7 | 4-I* | - | - | 159.2 | - | 88.0 | - | 160.6 | - | 160.8 | - | 92.8 | - | 5.66 | - | 159.2 | - | 20.8 |
| 8 | 4-Cl | -0.598 | 159.4 | 159.5 | 93.5 | 88.2 | 154.5 | 161.0 | 154.0 | 161.2 | 89.7 | 93.1 | 5.91 | 5.66 | 131.7 | 133.2 | 19.2 | 21.0 |
| 9 | 4-Br | -0.600 | 159.3 | 159.4 | 93.4 | 88.0 | 154.4 | 160.9 | 154.0 | 162.4 | 89.7 | 93.1 | 5.92 | 5.66 | 124.9 | 122.4 | 19.3 | 21.0 |
| 10 | 4-F | -0.615 | 159.2 | 159.1 | 93.4 | 87.8 | 154.7 | 160.6 | 154.3 | 161.1 | 89.6 | 92.8 | 5.90 | 5.67 | 159.0 | 162.8 | 19.2 | 20.8 |
| 11 | 3-CF3 | -0.600 | 159.4 | - | 93.4 | - | 154.3 | - | 153.8 | - | 89.8 | - | 5.94 | - | 132.9 | - | 19.3 | - |
| 12 | 3-Cl | -0.602 | 159.3 | 159.4 | 93.4 | 88.6 | 154.4 | 161.3 | 153.9 | 162.4 | 89.6 | 93.2 | 5.91 | 5.67 | 124.8 | 128.7 | 19.3 | 21.0 |
| 13 | 3-Br | -0.601 | 159.3 | 159.2 | 93.4 | 87.6 | 154.4 | 161.1 | 153.9 | 152.5 | 89.6 | 93.3 | 5.90 | 5.65 | 127.4 | 128.3 | 19.2 | 21.0 |
| 14 | 3-OCH3 | -0.613 | 158.9 | 159.5 | 93.3 | 88.9 | 154.6 | 160.8 | 154.4 | 162.1 | 89.6 | 92.3 | 5.89 | 5.70 | 115.8 | 114.2 | 19.1 | 20.8 |
| 15 | 3-CH3 | -0.621 | 158.9 | 159.2 | 93.1 | 88.5 | 154.6 | 160.7 | 154.4 | 162.2 | 89.6 | 92.5 | 5.89 | 5.69 | 124.9 | 125.4 | 19.2 | 20.7 |
| 16 | 3-COCH3 | -0.586 | 159.2 | 159.6 | 93.3 | 88.2 | 154.4 | 161.1 | 153.9 | 162.6 | 89.9 | 93.2 | 5.95 | 5.70 | 126.3 | 128.8 | 19.2 | 21.1 |

*basis set for I substituent is not available

**Table S5.** Experimental and calculated ^{1}H and ^{13}C NMR chemical shifts for **6-PY** tautomer. [5]

| No. | Substituent | $q_{C5}$ | C3 | | C2 | | C4 | | C5 | | C6 | | H5 | | C4' | | 4-CH3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp | calc | exp |
| 1 | H | -0.562 | 76.3 | 83.4 | 159.0 | 171.6 | 148.4 | 152.8 | 107.3 | 98.8 | 153.4 | 162.2 | 6.10 | 6.09 | 132.5 | 128.8 | 19.5 | 21.7 |
| 2 | 4-CH3 | -0.534 | 76.2 | 83.6 | 159.1 | 171.9 | 148.3 | 153.3 | 108.3 | 99.0 | 153.6 | 161.2 | 6.09 | 6.08 | 137.6 | 138.6 | 19.4 | 21.9 |
| 3 | 4-OCH3 | -0.559 | 76.3 | 83.6 | 159.3 | 171.9 | 148.2 | 153.6 | 108.4 | 99.0 | 153.6 | 161.5 | 6.09 | 6.07 | 155.2 | 159.5 | 19.4 | 22.0 |
| 4 | 4-NO2 | -0.564 | 76.3 | 83.4 | 158.3 | 172.1 | 149.3 | 152.1 | 107.5 | 99.4 | 152.5 | 162.0 | 6.18 | 6.13 | 147.5 | 143.2 | 19.5 | 21.5 |
| 5 | 4-COCH3 | -0.525 | 76.9 | 83.4 | 158.6 | 171.9 | 148.8 | 152.3 | 107.4 | 99.1 | 152.9 | 162.0 | 6.15 | 6.13 | 133.1 | 137.0 | 19.4 | 21.6 |
| 6 | 4-OH | -0.529 | 76.3 | - | 159.3 | - | 148.1 | - | 107.2 | - | 153.6 | - | 6.08 | - | 152.6 | - | 19.4 | - |
| 7 | 4-I* | - | - | 83.4 | - | 171.8 | - | 152.5 | - | 99.0 | - | 162.1 | - | 6.08 | - | 95.4 | - | 21.7 |
| 8 | 4-Cl | -0.561 | 76.7 | 83.5 | 158.8 | 172.1 | 148.7 | 152.9 | 107.3 | 99.3 | 153.1 | 162.5 | 6.12 | 6.10 | 131.4 | 133.8 | 19.4 | 21.9 |
| 9 | 4-Br | -0.552 | 76.7 | 83.6 | 158.8 | 172.1 | 148.7 | 152.9 | 107.3 | 99.3 | 153.1 | 161.2 | 6.12 | 6.09 | 124.7 | 121.7 | 19.4 | 21.9 |
| 10 | 4-F | -0.553 | 76.6 | 83.4 | 159.0 | 171.7 | 148.6 | 152.9 | 107.3 | 99.0 | 153.3 | 160.8 | 6.11 | 6.09 | 159.2 | 162.3 | 19.4 | 21.7 |
| 11 | 3-CF3 | -0.546 | 76.9 | 83.6 | 158.7 | 172.3 | 148.8 | 152.7 | 107.3 | 99.5 | 152.9 | 162.5 | 6.16 | 6.18 | 123.4 | 126.1 | 19.5 | 21.9 |
| 12 | 3-Cl | -0.555 | 76.7 | 83.6 | 158.7 | 172.1 | 148.8 | 152.8 | 107.4 | 99.3 | 153.0 | 161.0 | 6.12 | 6.10 | 125.0 | 129.0 | 19.5 | 21.8 |
| 13 | 3-Br | -0.552 | 76.6 | 83.5 | 158.7 | 172.1 | 148.7 | 152.8 | 107.3 | 98.3 | 153.0 | 161.3 | 6.13 | 6.10 | 127.8 | 128.6 | 19.5 | 21.8 |
| 14 | 3-OCH3 | -0.549 | 76.2 | 83.4 | 159.1 | 171.7 | 148.4 | 152.9 | 107.4 | 98.8 | 153.3 | 160.6 | 6.10 | 6.08 | 113.8 | 114.7 | 19.4 | 21.5 |
| 15 | 3-CH3 | -0.574 | 76.2 | 83.4 | 159.1 | 171.6 | 148.2 | 152.8 | 107.5 | 98.8 | 153.5 | 160.9 | 6.09 | 6.08 | 125.4 | 125.3 | 19.5 | 21.7 |
| 16 | 3-COCH3 | -0.545 | 76.9 | 83.7 | 158.7 | 172.2 | 148.7 | 153.0 | 107.3 | 99.4 | 153.0 | 161.4 | 6.16 | 6.13 | 126.6 | 128.6 | 19.5 | 22.0 |

*basis set for I substituent is not available

**Table S6.** Results of TD-DFT calculations for transitions from ground to first vertical excited state for **2-PY** tautomers in DMSO.

| Compound No. | Energy (eV) | Oscillator strenght | Excitation | CI expansion coefficient[*] | % of single particle excitation contribution |
|---|---|---|---|---|---|
| 1 | 4.0907 | 0.2780 | HOMO → LUMO | 0.69596 | 96.9 |
| 2 | 4.1091 | 0.2873 | HOMO → LUMO | 0.69649 | 97.0 |
| 3 | 4.0230 | 0.2269 | HOMO → LUMO | 0.67684 | 91.6 |
| | | | HOMO-1 → LUMO | 0.17801 | 6.3 |
| 4 | 2.9894 | 0.0221 | HOMO → LUMO | 0.70513 | 99.4 |
| 5 | 3.6954 | 0.0863 | HOMO → LUMO | 0.69977 | 97.9 |
| 6 | 4.0177 | 0.2444 | HOMO → LUMO | 0.68143 | 92.9 |
| | | | HOMO-1 → LUMO | -0.15775 | 5.0 |
| 8 | 4.0454 | 0.2740 | HOMO → LUMO | 0.69464 | 96.5 |
| 9 | 4.0407 | 0.2777 | HOMO → LUMO | 0.69443 | 96.4 |
| 10 | 4.0738 | 0.2740 | HOMO → LUMO | 0.69534 | 96.7 |
| 11 | 4.0079 | 0.2424 | HOMO → LUMO | 0.69425 | 96.4 |
| 12 | 4.0427 | 0.2651 | HOMO → LUMO | 0.69511 | 96.6 |
| 13 | 4.0390 | 0.2659 | HOMO → LUMO | 0.69513 | 96.6 |
| 14 | 4.0590 | 0.2696 | HOMO → LUMO | 0.69113 | 95.5 |
| 15 | 4.0751 | 0.2754 | HOMO → LUMO | 0.69555 | 96.8 |
| 16 | 3.7908 | 0.0205 | HOMO → LUMO | 0.64289 | 82.7 |
| | | | HOMO-1 → LUMO | -0.26502 | 14.0 |

**Table S7.** Results of TD-DFT calculations for transitions from ground to first vertical excited state for **6-PY** tautomers in DMSO.

| Compound No. | Energy (eV) | Oscillator strenght | Excitation | CI expansion coefficient[*] | % of single particle excitation contribution |
|---|---|---|---|---|---|
| **1** | 4.4239 | 0.1229 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.67186<br>-0.17651 | 90.3<br>6.2 |
| **2** | 4.4269 | 0.1287 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.66974<br>-0.18141 | 89.7<br>6.6 |
| **3** | 4.4188 | 0.1278 | HOMO → LUMO<br>HOMO – LUMO+1 | 0.67150<br>-0.17619 | 90.2<br>6.2 |
| **4** | 3.0269 | 0.0170 | HOMO → LUMO | 0.70527 | 99.5 |
| **5** | 3.7557 | 0.0258 | HOMO → LUMO<br>HOMO-1 → LUMO | 0.63653<br>0.29106 | 81.0<br>16.9 |
| **6** | 4.3774 | 0.1200 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.66228<br>-0.18439 | 87.7<br>6.8 |
| **8** | 4.3190 | 0.1057 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.68301<br>-0.13746 | 93.3<br>3.8 |
| **9** | 4.3157 | 0.1059 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.68212<br>-0.14394 | 93.1<br>4.1 |
| **10** | 4.4034 | 0.1204 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.67457<br>-0.16552 | 91.0<br>5.5 |
| **11** | 4.2521 | 0.0733 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.68942<br>-0.11035 | 95.1<br>2.4 |
| **12** | 4.3352 | 0.0994 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.68132<br>-0.14575 | 92.8<br>4.2 |
| **13** | 4.3401 | 0.1002 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.68085<br>-0.14717 | 92.7<br>4.3 |
| **14** | 4.4493 | 0.1152 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.66897<br>-0.17690 | 89.5<br>6.3 |
| **15** | 4.4518 | 0.1294 | HOMO → LUMO<br>HOMO → LUMO+1 | 0.66826<br>-0.18921 | 89.3<br>7.2 |
| **16** | 3.8159 | 0.0015 | HOMO → LUMO<br>HOMO-1 → LUMO | 0.46736<br>0.50970 | 43.7<br>52.0 |

**Table S8.** Absorption frequencies of **6-PY** tautomer in selected solvents.

| Solvent/ Comp. | $\nu_{max}\times10^{-3}$ (cm$^{-1}$) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
| Ethanol | 32.95 | 32.46 | 32.43 | 32.31 | 31.87 | 31.51 | 31.94 | 31.56 | 32.99 | 32.51 | 29.45 | 32.43 | 31.56 | 32.78 | 36.15 | 31.21 |
| Methanol | 33.5 | 32.41 | 32.78 | 32.75 | 31.55 | 31.94 | 31.96 | 31.32 | 32.66 | 32.94 | 28.10 | 32.26 | 31.89 | 32.95 | 37.51 | 31.33 |
| 2-Propanol | 32.97 | 31.97 | 32.45 | 32.68 | 31.71 | 31.12 | 32.14 | 31.67 | 32.51 | 32.46 | 30.06 | 32.43 | 31.25 | 32.95 | 35.54 | 31.05 |
| 1-Propanol | 33.00 | 32.24 | 32.53 | 32.61 | 31.79 | 31.46 | 32.10 | 31.86 | 32.96 | 32.43 | 29.68 | 32.09 | 31.43 | 32.60 | 35.96 | 31.11 |
| 1-Butanol | 32.86 | 32.21 | 32.50 | 31.46 | 32.05 | 31.56 | 32.01 | 31.77 | 32.65 | 32.35 | 29.89 | 32.09 | 31.54 | 32.60 | 35.87 | 31.16 |
| 2-Butanol | 32.71 | 31.67 | 32.35 | 32.65 | 31.63 | 31.13 | 31.98 | 31.56 | 32.63 | 32.21 | 30.45 | 32.09 | 31.23 | 32.71 | 35.12 | 31.01 |
| DMSO | 32.22 | 31.45 | 31.51 | 30.56 | 31.00 | -* | 31.31 | 31.41 | 32.41 | 31.72 | 30.21 | 31.84 | 31.14 | 32.70 | 34.12 | 31.00 |
| THF | 31.84 | 31.41 | 31.59 | 31.66 | 33.38 | 30.86 | 31.21 | 32.42 | 31.66 | 31.54 | 31.89 | 31.57 | 31.11 | 31.97 | 33.84 | 31.21 |
| AcN | 32.00 | 31.75 | 31.62 | 31.47 | 31.58 | 30.56 | 31.13 | 31.67 | 31.84 | 31.74 | 31.45 | 31.94 | 31.45 | 32.17 | 33.98 | 31.51 |
| Anisol | 31.52 | 31.84 | 31.34 | 31.40 | 31.79 | 31.54 | 31.21 | 31.95 | 31.46 | 31.19 | 30.67 | 31.73 | 31.52 | 31.60 | 34.24 | 31.26 |
| DMAc | 32.20 | 31.34 | 31.65 | 31.63 | 31.73 | - | 31.82 | 31.79 | 31.95 | 31.73 | 30.70 | 32.96 | 31.03 | 32.47 | 33.94 | 31.00 |
| DMF | 32.11 | 31.35 | 31.66 | 30.50 | 32.06 | - | 31.11 | 31.48 | 31.68 | 31.72 | 30.74 | 30.63 | 31.11 | 32.29 | 33.82 | 31.10 |
| EtAc | 31.82 | 31.33 | 31.74 | 31.84 | 32.86 | 30.56 | 31.24 | 32.31 | 31.74 | 31.54 | 31.99 | 31.65 | 31.15 | 31.97 | 33.78 | 31.23 |
| Chl | 31.30 | 32.10 | 31.12 | 32.12 | 31.45 | 31.26 | 31.65 | 31.31 | 32.65 | 31.10 | 30.93 | 31.95 | 31.45 | 32.07 | 33.98 | 31.45 |
| Dioxane | 31.39 | 31.45 | 31.46 | 31.52 | 32.67 | 30.86 | 31.25 | 32.11 | 31.45 | 31.19 | 31.94 | 31.15 | 31.21 | 31.90 | 33.79 | 31.40 |
| DEE | 31.74 | 31.33 | 31.88 | 31.21 | 32.00 | 30.42 | 31.03 | 32.03 | 31.21 | 31.33 | 32.45 | 30.75 | 31.11 | 31.50 | 33.64 | 31.42 |

* tautomer **2-PY** predominates

**Table S9.** Results of the correlation analysis for **6-PY** tautomer according to Kamlet–Taft equation.

| Comp. | $\nu_0\times10^{-3}$ $(cm^{-1})$ | $s\times10^{-3}$ $(cm^{-1})$ | $b\times10^{-3}$ $(cm^{-1})$ | $a\times10^{-3}$ $(cm^{-1})$ | $R^{a}$ | $Sd^{b}$ | $F^{c}$ | Solvent excluded from correlation |
|---|---|---|---|---|---|---|---|---|
| **1** | 30.81 ±0.25 | 0.51 ±0.34 | 1.24 ±0.26 | 1.15 ±0.19 | 0.95 | 0.22 | 39.43 | - |
| **2** | 31.40 ±0.18 | 0.47 ±0.24 | −0.54 ±0.18 | 1.21 ±0.13 | 0.94 | 0.16 | 30.95 | - |
| **3** | 31.45 ±0.21 | −0.56 ±0.29 | 0.95 ±0.21 | 0.70 ±0.16 | 0.94 | 0.19 | 33.12 | - |
| **4** | 32.32 ±0.36 | −1.35 ±0.49 | 0.41 ±0.27 | 1.58 ±0.27 | 0.93 | 0.31 | 22.39 | DMAc, 1-Butanol |
| **5** | 34.87 ±0.46 | −4.39 ±0.66 | 1.03 ±0.37 | −1.81 ±0.30 | 0.92 | 0.29 | 16.62 | DEE, 2-Butanol, 2-Propanol |
| **6** | 29.71 ±0.38 | 2.19 ±0.58 | $-^{d}$ | 0.93 ±0.20 | 0.92 | 0.20 | 15.56 | AcN |
| **7** | 30.98 ±0.15 | - | 0.51 ±0.20 | 0.84 ±0.12 | 0.97 | 0.11 | 61.40 | DMAc, Chl |
| **8** | 32.26 ±0.24 | −2.21 ±0.33 | 0.54 ±0.18 | −1.11 ±0.15 | 0.92 | 0.15 | 19.58 | 2-Butanol, DEE |
| **9** | 30.72 ±0.25 | 0.85 ±0.32 | 0.74 ±0.35 | 1.24 ±0.20 | 0.95 | 0.20 | 35.09 | Chl |
| **10** | 30.70 ±0.23 | 0.44 ±0.31 | 0.89 ±0.23 | 1.05 ±0.17 | 0.95 | 0.20 | 33.71 | - |
| **11** | 33.86 ±0.48 | −3.32 ±0.65 | - | -2.91 ±0.36 | 0.94 | 0.42 | 31.66 | - |
| **12** | 30.62 ±0.26 | 1.35 ±0.36 | - | 1.12 ±0.18 | 0.92 | 0.21 | 18.18 | DMF, DMAc |
| **13** | 31.35 ±0.11 | 0.47 ±0.14 | −0.95 ±0.15 | 0.83 ±0.09 | 0.94 | 0.09 | 29.95 | Chl |
| **14** | 30.93 ±0.18 | 1.10 ±0.25 | 0.69 ±0.19 | 0.92 ±0.14 | 0.95 | 0.16 | 36.26 | - |
| **15** | 32.99 ±0.54 | 0.83 ±0.43 | - | 2.80 ±0.41 | 0.93 | 0.48 | 25.48 | - |
| **16** | 31.75 ±0.09 | - | −0.81 ±0.13 | 0.17 ±0.08 | 0.90 | 0.08 | 16.36 | Chl |

[a] Correlation coefficient; [b] Standard deviation; [c] Fisher test of significance; [d] Negligible values with high standard errors

**Table S10.** Results of the correlation analysis for **6-PY** tautomer according to Catalán equation.

| Comp. | $v_0\times10^{-3}$ $(cm^{-1})$ | $c\times10^{-3}$ $(cm^{-1})$ | $d\times10^{-3}$ $(cm^{-1})$ | $b\times10^{-3}$ $(cm^{-1})$ | $a\times10^{-3}$ $(cm^{-1})$ | $R$[a] | $Sd$[b] | $F$[c] | Solvent excluded from correlation |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 31.63 ±0.09 | −1.28 ±0.12 | 0.83 ±0.04 | 0.99 ±0.04 | 2.19 ±0.05 | 0.99 | 0.03 | 2036.37 | - |
| **2** | 31.63 ±0.59 | -[d] | - | −0.68 ±0.24 | 2.35 ±0.31 | 0.93 | 0.18 | 17.74 | - |
| **3** | 32.74 ±0.14 | −2.20 ±0.19 | - | 0.84 ±0.06 | 1.54 ±0.08 | 0.99 | 0.04 | 523.75 | - |
| **4** | 35.43 ±1.38 | −5.06 ±1.78 | −1.17 ±0.51 | 0.95 ±0.61 | 1.59 ±0.71 | 0.93 | 0.35 | 11.78 | 1-Butanol, Chl, DEE |
| **5** | 35.74 ±1.06 | −3.97 ±1.34 | −1.72 ±0.40 | 1.13 ±0.47 | −2.51 ±0.74 | 0.90 | 0.27 | 7.84 | DEE, 2-Butanol, THF, Methanol |
| **6** | 27.66 ±0.27 | 4.50 ±0.31 | - | - | 2.67 ±0.10 | 0.99 | 0.05 | 258.84 | - |
| **7** | 30.43 ±0.68 | -[d] | - | 1.14 ±0.34 | 1.39 ±0.37 | 0.92 | 0.20 | 13.00 | Chl |
| **8** | 34.26 ±0.77 | −2.97 ±1.05 | −0.83 ±0.28 | 0.85 ±0.28 | −1.63 ±0.38 | 0.90 | 0.19 | 8.87 | 2-Butanol, DEE, Anisol |
| **9** | 30.24 ±0.85 | - | 0.60 ±0.30 | 1.23 ±0.42 | 2.03 ± 0.46 | 0.93 | 0.25 | 16.38 | Chl |
| **10** | 31.75 ±0.16 | −1.55 ±0.21 | 0.72 ±0.06 | 0.65 ±0.06 | 1.87 ± 0.08 | 0.99 | 0.05 | 502.35 | - |
| **11** | 36.27 ±0.37 | −5.38 ±0.49 | -1.26 ±0.15 | - | -6.21 ± 0.20 | 0.99 | 0.11 | 375.14 | - |
| **12** | 30.64 ±0.88 | - | 1.15 ±0.38 | - | 2.27 ± 0.62 | 0.91 | 0.24 | 9.30 | DMAc, DMF, Methanol |
| **13** | 31.52 ±0.23 | - | - | −0.67 ±0.09 | 1.33 ± 0.12 | 0.97 | 0.07 | 40.14 | - |
| **14** | 30.53 ±0.70 | - | 1.04 ±0.29 | 0.69 ±0.28 | 1.27 ± 0.38 | 0.93 | 0.21 | 15.94 | DMF |
| **15** | 33.77 ±0.22 | - | - | - | 6.19 ± 0.12 | 0.99 | 0.07 | 1119.12 | - |
| **16** | 32.62 ±0.18 | −1.23 ±0.24 | - | −0.72 ±0.07 | - | 0.96 | 0.05 | 32.34 | - |

[a] Correlation coefficient; [b] Standard deviation; [c] Fisher test of significance; [d] Negligible values with high standard errors

**Table S11.** Percentage contribution of solvatochromic parameters calculated from correlation results given in Table 3 for **2-PY** tautomer according to Kamlet–Taft equation.

| Compound | $P_s$ (%) | $P_b$ (%) | $P_a$ (%) |
|---|---|---|---|
| 1 | 56.13 | 29.76 | 14.11 |
| 2 | 42.37 | 34.32 | 23.31 |
| 3 | 57.37 | 33.66 | 8.97 |
| 4 | 28.41 | 64.85 | 6.74 |
| 5 | 50.87 | 35.76 | 13.37 |
| 6 | 37.93 | 29.89 | 32.18 |
| 7 | 16.14 | 49.33 | 34.53 |
| 8 | 38.00 | 40.80 | 21.20 |
| 9 | 33.72 | 42.07 | 24.21 |
| 10 | 63.48 | 36.52 | - |
| 11 | 43.40 | 25.51 | 31.09 |
| 12 | 44.26 | 18.04 | 37.70 |
| 13 | 25.36 | 31.52 | 43.12 |
| 14 | 26.15 | 53.59 | 20.26 |
| 15 | 25.40 | - | 74.60 |
| 16 | 66.14 | 27.13 | 6.73 |

**Table S12.** Percentage contribution of solvatochromic parameters calculated from correlation results given in Table S3 for **6-PY** tautomer according to Kamlet–Taft equation.

| Compound | $P_s$ (%) | $P_b$ (%) | $P_a$ (%) |
|---|---|---|---|
| 1 | 17.59 | 42.76 | 39.65 |
| 2 | 21.17 | 24.33 | 54.50 |
| 3 | 25.34 | 42.99 | 31.67 |
| 4 | 40.42 | 12.28 | 47.30 |
| 5 | 60.72 | 14.25 | 25.03 |
| 6 | 70.19 | - | 29.81 |
| 7 | - | 37.78 | 62.22 |
| 8 | 57.25 | 13.99 | 28.76 |
| 9 | 30.03 | 26.15 | 43.82 |
| 10 | 18.49 | 37.39 | 44.12 |
| 11 | 53.29 | - | 46.71 |
| 12 | 54.66 | - | 45.34 |
| 13 | 20.89 | 42.22 | 36.89 |
| 14 | 40.59 | 25.46 | 33.95 |
| 15 | 22.86 | - | 77.14 |
| 16 | - | 82.65 | 17.35 |

**Table S13.** Results of the correlations of log $K_T$ with Kamlet–Taft solvent parameters.

| Comp. | c | s | b | a | $R^a$ | $Sd^b$ | $F^c$ | Solvent excluded from correlation |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.56 ±0.18 | -0.25 ±0.26 | -0.83 ±0.14 | -0.03 ±0.22 | 0.918 | 0.15 | 12.52 | 1- and 2-Propanol,1- and 2-Butanol, DMAc |
| 2 | 1.25 ±0.20 | -1.78 ±0.27 | -0.79 ±0.14 | 0.44 ±0.14 | 0.917 | 0.12 | 15.87 | DEE, EtAc, Ethanol |
| 3 | 1.49 ±0.29 | -2.37 ±0.40 | -1.06 ±0.19 | 0.75 ±0.21 | 0.905 | 0.18 | 13.73 | DEE, 2-Butanol, Ethanol |
| 4 | 0.82 ±0.27 | 0.31 ±0.37 | -0.55 ±0.20 | -1.25 ±0.30 | 0.900 | 0.23 | 12.80 | 2-Propanol, Anisol, 1-Butanol |
| 5 | -0.73 ±0.15 | 0.62 ±0.20 | 0.66 ±0.10 | 0.39 ±0.14 | 0.950 | 0.11 | 27.59 | 1-Propanol, DMSO, EtAc |
| 6 | -0.52 ±0.12 | 1.33 ±0.18 | 0.22 ±0.04 | -0.30 ±0.06 | 0.978 | 0.04 | 52.24 | Anisol, DEE |
| 7 | 0.71 ±0.16 | -0.81 ±0.22 | 0.08 ±0.11 | -0.34 ±0.13 | 0.896 | 0.10 | 10.88 | DMAc, AcN, Anisol, DEE |
| 8 | 0.63 ±0.22 | −1.09 ±0.30 | -0.04 ±0.14 | 0.06 ±0.17 | 0.851 | 0.13 | 6.11 | 1-Propanol, 2-Butanol, DMAc, Anisol, DEE |
| 9 | 0.34 ±0.14 | -0.14 ±0.18 | -0.29 ±0.11 | -0.46 ±0.21 | 0.887 | 0.11 | 9.79 | 2-Propanol, 1-Butanol, DMF, Chl |
| 10 | 1.74 ±0.28 | -2.51 ±0.37 | -0.73 ±0.16 | 0.54 ±0.17 | 0.926 | 0.14 | 17.99 | DMSO, EtAc, DEE |
| 11 | -0.39 ±0.31 | 2.84 ±0.43 | -0.10 ±0.21 | 0.31 ±0.29 | 0.912 | 0.25 | 18.09 | DMSO |
| 12 | 0.59 ±0.11 | -0.71 ±0.15 | -0. 57 ±0.08 | 0.33 ±0.08 | 0.928 | 0.07 | 16.59 | Methanol, Anisol, DMAc, DEE |
| 13 | 0.02 ±0.11 | -0.31 ±0.15 | 0.18 ±0.08 | 0.27 ±0.10 | 0.909 | 0.09 | 11.04 | 1-Propanol, 2-Butanol, THF, EtAc, Dioxane |
| 14 | -0.12 ±0.11 | -0.49 ±0.16 | -0.24 ±0.09 | 0.75 ±0.11 | 0.934 | 0.09 | 18.26 | Methanol, Anisol, DMSO |
| 15 | 0.26 ±0.10 | 0.32 ±0.14 | -0.36 ±0.07 | -0.23 ±0.10 | 0.936 | 0.08 | 18.90 | 1-Butanol, 2-Butanol, DMF |
| 16 | -0.67 ±0.25 | 1.20 ±0.34 | -0.24 ±0.13 | 0.32 ±0.16 | 0.891 | 0.12 | 9.02 | Ethanol, Anisol, DMSO, DMAc, DEE |

[a] Correlation coefficient; [b] Standard deviation; [c] Fisher test of significance; [d] Negligible values with high standard errors

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**Table S14.** Results of the correlations of log $K_T$ with Catalán solvent parameters.

| Comp. | *h* | *c* | *d* | *a* | *b* | $R^a$ | $Sd^b$ | $F^c$ | Solvent excluded from correlation |
|---|---|---|---|---|---|---|---|---|---|
| **1** | -0.15 ±0.58 | 0.76 ±0.76 | -0.40 ±0.25 | -1.13 ±0.33 | 0.47 ±0.31 | 0.913 | 0.17 | 7.52 | 1- and 2-Butanol, 1-and 2-Propanol, DMAc |
| **2** | 1.55 ±0.71 | -1.39 ±0.88 | -0.86 ±0.23 | -0.75 ±0.35 | 0.53 ±0.22 | 0.859 | 0.16 | 5.63 | DEE, EtAc, Ethanol |
| **3** | 1.24 ±0.75 | -1.00 ±0.95 | -1.21 ±0.27 | -1.15 ±0.38 | 1.08 ±0.28 | 0.905 | 0.19 | 9.10 | DEE, 2-Butanol, Ethanol |
| **4** | 1.56 ±0.85 | -0.85 ±1.22 | 0.12 ±0.34 | -1.48 ±0.46 | -1.28 ±0.35 | 0.911 | 0.23 | 9.82 | 2-Propanol, Anisol, 1-Butanol |
| **5** | -1.25 ±0.49 | 0.94 ±0.62 | 0.40 ±0.16 | 1.32 ±0.22 | 0.34 ±0.16 | 0.954 | 0.11 | 20.47 | 1-Propanol, DMSO, EtAc |
| **6** | 0.04 ±0.61 | 0.21 ±0.71 | 0.39 ±0.17 | 0.13 ±0.12 | -0.59 ±0.11 | 0.962 | 0.06 | 18.40 | Anisol, DEE |
| **7** | 1.85 ±0.82 | -1.80 ±1.14 | -0.42 ±0.30 | -0.03 ±0.38 | -0.39 ±0.25 | 0.798 | 0.15 | 3.07 | DMAc, AcN, Anisol, DEE |
| **8** | 1.37 ±0.66 | -1.42 ±0.88 | –0.63 ±0.25 | 0.09 ±0.33 | 0.07 ±0.25 | 0.817 | 0.16 | 3.00 | 1-Propanol, 2-Butanol, DMAc, Anisol, DEE |
| **9** | 0.24 ±0.45 | 0.34 ±0.61 | -0.33 ±0.19 | -0.31 ±0.25 | -0.51 ± 0.24 | 0.852 | 0.13 | 4.64 | 2-Propanol, 1-Butanol, DMF, Chl |
| **10** | 2.89 ±0.87 | -2.84 ±1.04 | -1.27 ±0.24 | -0.87 ±0.33 | 0.74 ± 0.21 | 0.924 | 0.15 | 11.69 | DMSO, EtAc, DEE |
| **11** | -3.15 ±1.08 | 4.74 ±1.38 | 1.86 ±0.38 | -0.35 ±0.48 | 0.05 ± 0.38 | 0.901 | 0.27 | 10.73 | DMSO |
| **12** | 0.41 ±0.39 | -0.27 ±0.52 | -0.33 ±0.15 | -0.93 ±0.25 | 0.51 ± 0.15 | 0.874 | 0.09 | 5.64 | Methanol, Anisol, DMAc, DEE |
| **13** | 0.23 ±0.32 | -0.35 ±0.42 | -0.25 ±0.14 | 0.46 ±0.18 | 0.30 ± 0.14 | 0.916 | 0.09 | 7.78 | 1-Propanol, 2-Butanol, THF, EtAc, Dioxane |
| **14** | -0.64 ±0.33 | 0.39 ±0.46 | -0.11 ±0.29 | -0.08 ±0.19 | 0.93 ± 0.12 | 0.958 | 0.07 | 19.74 | Methanol, Anisol, DMSO |
| **15** | -0.35 ±0.37 | 1.02 ±0.48 | 0.03 ±0.16 | -0.56 ±0.21 | -0.14 ± 0.17 | 0.901 | 0.011 | 7.57 | 1-Butanol, 2-Butanol, DMF |
| **16** | -2.35 ±1.25 | 2.72 ±1.57 | 0.68 ±0.35 | -0.28 ±0.42 | 0.27 ±0.29 | 0.741 | 0.20 | 1.83 | Ethanol, Anisol, DMSO, DMAc, DEE |

[a] Correlation coefficient; [b] Standard deviation; [c] Fisher test of significance;

**Table S15.** Results of the correlations of log $K_T$ with $\sigma_p$ substituent parameters.

| | h | ρ x 10⁻³ | R | Sd | F | h | ρ x 10⁻³ | R | Sd | F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **1, 2, 3, 10, 11, 14, 15** | | | | | **5, 8, 9, 12, 13, 16** | | | |
| Methanol | -0.04 ± 0.12 | 2.90 ± 0.58 | 0.912 | 0.32 | 24.86 | -0.74 ± 0.12 | 2.56 ± 0.33 | 0.968 | 0.08 | 59.17 |
| | | **1, 2, 3, 7, 10, 11, 15** | | | | | **5, 8, 9, 12, 13, 16** | | | |
| Ethanol | 0.04 ± 0.12 | 2.68 ± 0.54 | 0.911 | 0.31 | 24.54 | -0.97 ± 0.20 | 2.77 ± 0.54 | 0.930 | 0.13 | 25.83 |
| | | **1, 2, 3, 6, 10, 11** | | | | | **8, 9, 12, 13, 16** | | | |
| 1-Propanol | 0.41 ± 0.06 | 1.15 ±0.23 | 0.929 | 0.15 | 25.31 | -0.76 ± 0.405 | 2.16 ± 0.16 | 0.992 | 0.03 | 184.48 |
| | | **1, 2, 3, 6, 10, 11** | | | | | **4, 5, 7, 8, 9, 12, 13, 14, 15** | | | |
| 2-Propanol | 0.60 ± 0.06 | 1.48 ± 0.21 | 0.963 | 0.13 | 50.51 | 0.01 ± 0.04 | 0.64 ± 0.10 | 0.921 | 0.07 | 38.86 |
| | | **1, 2, 3, 6, 10, 11, 15** | | | | | **4, 5, 8, 9, 12, 13** | | | |
| 1-Butanol | 0.37 ± 0.05 | 1.15 ± 0.20 | 0.934 | 0.13 | 34.35 | -0.17 ± 0.209 | 1.04 ± 0.520 | 0.933 | 0.09 | 26.91 |
| | | **2, 3, 6, 10, 11, 15** | | | | | **1, 5, 8, 9, 12, 13, 16** | | | |
| 2-Butanol | 0.33 ± 0.07 | 1.50 ± 0.26 | 0.945 | 0.17 | 33.28 | -0.75 ± 0.08 | 1.90 ± 0.23 | 0.965 | 0.09 | 67.39 |
| | | **1, 2, 3, 10, 11, 15** | | | | | **7, 8, 9, 12, 13, 14, 16** | | | |
| DMSO | 0.29 ± 0.13 | 2.99 ± 0.57 | 0.935 | 0.31 | 27.75 | -0.77 ± 0.10 | 2.25 ± 0.33 | 0.949 | 0.09 | 45.06 |
| | | **2, 3, 11, 15** | | | | | **1, 5, 8, 9, 10, 12, 16** | | | |
| DMAc | 0.87 ± 0.16 | 3.58 ± 0.61 | 0.972 | 0.233 | 34.38 | -0.22 ± 0.03 | 0.59 ± 0.09 | 0.937 | 0.04 | 36.14 |
| | | **1, 2, 3, 11, 15** | | | | | **5, 8, 9, 12, 13** | | | |
| DMF | 0.63 ± 0.12 | 4.31 ± 0.50 | 0.980 | 0.27 | 74.53 | -0.68 ± 0.17 | 1.49 ± 0.48 | 0.874 | 0.11 | 9.75 |
| | | **1, 2, 6, 10, 11, 15** | | | | | **7, 8, 9, 12, 14, 16** | | | |
| THF | 0.63 ± 0.05 | 1.28 ± 0.21 | 0.940 | 0.13 | 37.93 | -0.12 ± 0.06 | 1.01 ± 0.21 | 0.925 | 0.05 | 23.80 |
| | | **1, 2, 3, 6, 11, 15** | | | | | **4, 5, 7, 8, 9, 10, 12, 13, 14, 16** | | | |
| EtAc | 0.41 ± 0.08 | 1.29 ± 0.130 | 0.905 | 0.19 | 18.03 | -0.12 ± 0.07 | 0.90 ± 0.18 | 0.872 | 0.11 | 25.62 |
| | | **1, 2, 3, 6, 10, 11, 15** | | | | | **4, 7, 8, 9, 12, 13, 14, 16** | | | |
| DEE | 0.37 ± 0.03 | 0.83 ± 0.13 | 0.946 | 0.08 | 42.62 | -0.04 ± 0.02 | 0.44 ± 0.05 | 0.966 | 0.03 | 83.03 |
| | | **1, 2, 3, 6, 10, 11, 15** | | | | | **4, 7, 8, 9, 12, 13, 14, 16** | | | |
| Dioxane | 0.61 ± 0.05 | 1.14 ± 0.22 | 0.918 | 0.14 | 26.64 | -0.02 ± 0.04 | 0.55 ± 0.09 | 0.926 | 0.05 | 35.86 |
| | | **1, 2, 3, 11, 15** | | | | | **4, 5, 8, 9, 12, 13, 14, 16** | | | |
| ChL | 0.32 ± 0.09 | 2.62 ± 0.037 | 0.971 | 0.20 | 48.97 | -0.57 ± 0.10 | 1.53 ± 0.23 | 0.938 | 0.12 | 44.08 |
| | | **1, 2, 3, 7, 10, 11, 15** | | | | | **4, 5, 8, 9, 12, 13, 14, 16** | | | |
| AcN | 0.20 ± 0. 10 | 2.20 ± 0.47 | 0.902 | 0.27 | 21.99 | -0.57 ± 0.11 | 1.52 ± 0.26 | 0.920 | 0.14 | 32.89 |
| | | **1, 2, 3, 6, 11, 15** | | | | | **4, 5, 12, 13, 16** | | | |
| Anisol | 0.63 ± 0.08 | 2.11 ± 0.30 | 0.962 | 0.19 | 49.84 | -0.25 ± 0.05 | 0.54 ± 0.11 | 0.944 | 0.04 | 24.75 |

**Table S16.** Regression fits according to eq. (3) for the **6-PY** form.

| | $v_0$ x $10^{-3}$ (cm$^{-1}$) | $\rho$ x $10^{-3}$ (cm$^{-1}$) | $R$ | $Sd$ | $F$ | $v_0$ x $10^{-3}$ (cm$^{-1}$) | $\rho$ x $10^{-3}$ (cm$^{-1}$) | $R$ | $Sd$ | $F$ | $v_0$ x $10^{-3}$ (cm$^{-1}$) | $\rho$ x $10^{-3}$ (cm$^{-1}$) | $R$ | $Sd$ | $F$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **1, 5, 9, 10, 12, 13, 14, 16** | | | | | **7, 8, 11** | | | | | **3, 2, 6** | | | | |
| Methanol | 33.38 ± 0.19 | -3.90 ± 0.62 | 0.93 | 0.30 | 39.32 | 34.84 ± 0.16 | -15.63 ± 0.54 | 0.99 | 0.10 | 824.27 | 32.90 ± 0.45 | 2.35 ± 1.59 | 0.83 | 0.22 | 2.19 |
| | **1, 7, 8, 10, 11, 13, 16** | | | | | **5, 9, 12, 14** | | | | | **3, 6, 15** | | | | |
| Ethanol | 32.95 ± 0.43 | -5.68 ± 0.52 | 0.86 | 0.63 | 13.94 | 33.32 ± 0.32 | -2.63 ± 0.96 | 0.89 | 0.27 | 7.52 | 36.62 ± 0.75 | 13.37 ± 2.80 | 0.98 | 0.60 | 22.87 |
| 1-Propanol | 33.14 ± 0.36 | -5.68 ±1.25 | 0.90 | 0.52 | 20.50 | 33.17 ± 0.40 | -2.66 ± 1.20 | 0.84 | 0.34 | 4.91 | 33.77 ± 0.36 | 5.44 ± 1.34 | 0.97 | 0.29 | 16.59 |
| 2-Propanol | 32.96 ± 0.23 | -5.48 ± 0.81 | 0.95 | 0.34 | 45.28 | 33.30 ± 0.23 | -2.95 ± 0.67 | 0.95 | 0.19 | 19.18 | 36.56 ± 0.06 | 14.78 ± 0.23 | 0.99 | 0.05 | 3952.69 |
| 1-Butanol | 32.85 ± 0.33 | -5.00 ± 1.16 | 0.89 | 0.48 | 18.51 | 32.88 ± 0.20 | -1.76 ± 0.59 | 0.90 | 0.17 | 8.88 | 36.77 ± 0.64 | 14.83 ± 2.40 | 0.99 | 0.52 | 38.17 |
| 2-Butanol | 32.64 ± 0.15 | -4.39 ± 0.53 | 0.97 | 0.21 | 69.53 | 33.17 ± 0.15 | -2.98 ± 0.46 | 0.98 | 0.13 | 42.26 | 35.89 ± 0.94 | 13.98 ± 3.53 | 0.97 | 0.76 | 15.72 |
| DMSO | 32.08 ± 0.20 | -3.32 ± 0.71 | 0.90 | 0.30 | 21.65 | 33.34 ± 0.19 | -4.45 ± 0.58 | 0.98 | 0.16 | 59.68 | | | | | |
| | **1, 7, 8, 10, 11, 13, 16,** | | | | | **9, 12, 14** | | | | | | | | | |
| DMAc | 31.19 ± 0.15 | -3.05 ± 0.52 | 0.93 | 0.22 | 34.28 | 31.93 ± 0.88 | 2.19 ± 3.38 | 0.54 | 0.60 | 0.42 | | | | | |
| DMF | 31.93 ± 0.15 | -2.46 ± 0.53 | 0.90 | 0.22 | 21.70 | 33.14 ± 0.14 | -6.68 ± 0.55 | 0.99 | 0.10 | 145.61 | | | | | |
| | **1, 2, 5, 6, 8, 14** | | | | | **9, 10, 11** | | | | | **13, 7, 16** | | | | |
| THF | 31.77 ± 0.09 | 2.80 ± 0.33 | 0.97 | 0.23 | 71.75 | 31.47 ± 0.04 | 0.95 ± 0.13 | 0.99 | 0.03 | 56.10 | 31.26 ± 0.13 | -0.26 ± 0.41 | 0.54 | 0.07 | 0.40 |
| EtAc | 31.68 ± 0.05 | 2.58 ± 0.19 | 0.99 | 0.13 | 181.23 | 31.46 ± 0.01 | 1.22 ± 0.02 | 0.99 | 0.01 | 3346.68 | 31.29 ± 0.11 | -0.26 ± 0.33 | 0.62 | 0.05 | 0.62 |
| | **1, 2, 8, 11** | | | | | **5, 7, 9,** | | | | | **6, 10, 14** | | | | |
| DEE | 31.67 ± 0.04 | 1.79 ± 0.15 | 0.99 | 0.07 | 147.73 | 30.50 ± 0.03 | 3.00 ± 0.09 | 0.99 | 0.02 | 1142.25 | 31.22 ± 0.02 | 2.17 ± 0.07 | 0.99 | 0.03 | 843.64 |
| | **1, 2, 5, 6, 8, 14** | | | | | **7, 9, 11** | | | | | **4, 12, 13** | | | | |
| Dioxane | 31.62 ± 0.06 | 2.03 ± 0.21 | 0.98 | 0.15 | 88.78 | 30.80 ± 008 | 2.67 ± 0.26 | 0.99 | 0.05 | 109.16 | 30.85 ± 0.05 | 0.85 ± 0.09 | 0.99 | 0.03 | 84.47 |
| | **6, 3, 9, 14** | | | | | **1, 7, 12** | | | | | **4, 8, 10, 13, 16** | | | | |
| ChL | 32.01 ± 0.09 | 2.10 ± 0.35 | 0.97 | 0.18 | 30.18 | 31.31 ± 0.02 | 1.75 ± 0.10 | 0.99 | 0.03 | 277.25 | 30.96 ± 0.05 | 1.42 ± 0.12 | 0.99 | 0.06 | 134.35 |
| | **1, 2, 14** | | | | | **7, 11, 13, 16** | | | | | **9, 10, 12** | | | | |
| AcN | 32.00 ± 0.01 | 1.45 ± 0.01 | 0.99 | 0.01 | 9397.8 | 30.88 ± 0.12 | 1.46 ± 0.35 | 0.95 | 0.07 | 17.47 | 31.70 ± 0.01 | 0.64 ± 0.04 | 0.99 | 0.01 | 320.33 |
| | **1, 5, 12, 16** | | | | | **4, 7, 10, 16** | | | | | **2, 6, 15** | | | | |
| Anisol | 31.53 ± 0.01 | 0.54 ± 0.02 | 0.99 | 0.01 | 525.07 | 31.16 ± 0.01 | 0.30 ± 0.02 | 0.99 | 0.01 | 135.73 | 34.15 ± 1.33 | 7.93 ± 5.57 | 0.82 | 1.2 | 2.03 |

**Table S17.** Elements of geometry of the **2-PY** tautomer obtained by the use of B3LYP/6-11++G(d,p) method.

| No. | Sub. | Torsion angle | Charge | Bond length | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\theta$ | $q_{C5}$ | N1-C2 | N1-C6 | N1-C1' | C6-O | C2-O |
| 1 | H | 79.65 | -0.602 | 1.441 | 1.363 | 1.449 | 1.347 | 1.218 |
| 2 | 4-CH$_3$ | 80.18 | -0.601 | 1.441 | 1.363 | 1.448 | 1.347 | 1.219 |
| 3 | 4-OCH$_3$ | 76.25 | -0.588 | 1.442 | 1.363 | 1.447 | 1.347 | 1.219 |
| 4 | 4-NO$_2$ | 66.55 | -0.581 | 1.444 | 1.367 | 1.443 | 1.346 | 1.218 |
| 5 | 4-COCH$_3$ | 68.93 | -0.579 | 1.443 | 1.365 | 1.446 | 1.346 | 1.219 |
| 6 | 4-OH | 73.35 | -0.602 | 1.442 | 1.364 | 1.446 | 1.347 | 1.219 |
| 7 | 4-I$^*$ | - | - | - | - | - | | |
| 8 | 4-Cl | 73.05 | -0.598 | 1.442 | 1.365 | 1.446 | 1.347 | 1.218 |
| 9 | 4-Br | 73.05 | -0.600 | 1.442 | 1.365 | 1.446 | 1.346 | 1.218 |
| 10 | 4-F | 75.69 | -0.615 | 1.442 | 1.364 | 1.446 | 1.347 | 1.217 |
| 11 | 3-CF$_3$ | 68.54 | -0.600 | 1.443 | 1.363 | 1.445 | 1.346 | 1.219 |
| 12 | 3-Cl | 73.57 | -0.602 | 1.442 | 1.365 | 1.446 | 1.346 | 1.218 |
| 13 | 3-Br | 72.50 | -0.601 | 1.442 | 1.365 | 1.446 | 1.346 | 1.218 |
| 14 | 3-OCH$_3$ | 74.09 | -0.613 | 1.441 | 1.363 | 1.449 | 1.346 | 1.219 |
| 15 | 3-CH$_3$ | 77.42 | -0.621 | 1.441 | 1.363 | 1.449 | 1.347 | 1.219 |
| 16 | 3-COCH$_3$ | 66.19 | -0.586 | 1.443 | 1.366 | 1.446 | 1.346 | 1.219 |

**Table S18.** Elements of geometry of the **6-PY** tautomer obtained by the use of B3LYP/6-311++G(d,p) method.

| No. | Sub. | Torsional angle | Charge | Bond length | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $\theta$ | $q_{C5}$ | N1-C2 | N1-C6 | N1-C1' | C6-O | C2-O |
| 1 | H | 78.19 | -0.562 | 1.356 | 1.452 | 1.448 | 1.219 | 1.338 |
| 2 | 4-CH$_3$ | 77.85 | -0.534 | 1.356 | 1.452 | 1.448 | 1.220 | 1.338 |
| 3 | 4-OCH$_3$ | 74.04 | -0.559 | 1.356 | 1.453 | 1.446 | 1.220 | 1.338 |
| 4 | 4-NO$_2$ | 66.07 | -0.564 | 1.360 | 1.457 | 1.443 | 1.219 | 1.338 |
| 5 | 4-COCH$_3$ | 68.58 | -0.525 | 1.358 | 1.455 | 1.446 | 1.219 | 1.338 |
| 6 | 4-OH | 73.44 | -0.529 | 1.357 | 1.453 | 1.446 | 1.220 | 1.338 |
| 7 | 4-I$^*$ | - | - | - | - | - | | |
| 8 | 4-Cl | 71.82 | -0.561 | 1.358 | 1.454 | 1.446 | 1.219 | 1.338 |
| 9 | 4-Br | 71.46 | -0.552 | 1.358 | 1.455 | 1.446 | 1.219 | 1.338 |
| 10 | 4-F | 67.22 | -0.553 | 1.357 | 1.454 | 1.446 | 1.219 | 1.338 |
| 11 | 3-CF$_3$ | 69.63 | -0.546 | 1.358 | 1.455 | 1.445 | 1.219 | 1.338 |
| 12 | 3-Cl | 73.16 | -0.555 | 1.358 | 1.454 | 1.446 | 1.219 | 1.338 |
| 13 | 3-Br | 73.86 | -0.552 | 1.358 | 1.454 | 1.446 | 1.219 | 1.338 |
| 14 | 3-OCH$_3$ | 82.77 | -0.549 | 1.356 | 1.452 | 1.450 | 1.220 | 1.338 |
| 15 | 3-CH$_3$ | 80.91 | -0.574 | 1.356 | 1.452 | 1.449 | 1.219 | 1.338 |
| 16 | 3-COCH$_3$ | 67.22 | -0.545 | 1.358 | 1.454 | 1.446 | 1.220 | 1.338 |

$^*$basis set for I substituent is not available; $^a$ torsional angle C2-N1-C1'-C2'; $^b$ torsional angle C6-N1-C1'-C6'

**Table S19.** Correlation results of the SCS values with the Hammett substituent constants $\sigma_p/\sigma_m$ and $\sigma_p^+/\sigma_m^+$ for **6-PY** tautomer according to eq. (3).

| Atom | | $\rho$ | h | R | F | sd | n | |
|---|---|---|---|---|---|---|---|---|
| | $\sigma$ | 11.73±1.88 | −2.13±0.64 | 0.866 | 39 | 1.94 | 15 | all |
| | $\sigma^+$ | 8.59±1.28 | −0.94±0.51 | 0.880 | 45 | 1.85 | 15 | all |
| | $\sigma$ | 8.68±1.09 | −1.88±0.50 | 0.911 | 63 | 1.61 | 15 | all |
| | $\sigma$ | 14.04±2.08 | −2.48±0.73 | 0.931 | 46 | 1.90 | 9 | 4-substituted[a] |
| | $\sigma^+$ | 10.23±1.42 | −0.68±0.60 | 0.939 | 52 | 1.79 | 9 | 4-substituted |
| $C_{1'}$ | $\sigma$ | 9.36±1.15 | −2.53±0.62 | 0.951 | 67 | 1.61 | 9 | 4-substituted |
| | $\sigma$ | 16.58±1.20 | −3.82±0.47 | 0.987 | 191 | 0.97 | 7 | 4-sub. (H i Me excluded) |
| | $\sigma$ | 10.50±0.66 | -3.57±0.40 | 0.990 | 257 | 0.84 | 7 | 4-sub. (H i Me excluded) |
| | $\sigma$ | 2.57±1.02 | 0.24±0.31 | 0.747 | 6 | 0.52 | 7 | 3-substituted[b] |
| | $\sigma^+$ | 2.05±0.97 | 0.55±0.52 | 0.687 | 4 | 0.57 | 7 | 3-substituted |
| | $\sigma^+$ | 1.72±0.23 | -0.01±0.07 | 0.985 | 58 | 0.11 | 4 | H, 3-Me, 3-COMe, 3-CF$_3$ |
| | $\sigma^+$ | 1.55±0.21 | 1.02±0.07 | 0.991 | 57 | 0.06 | 3 | 3-OMe, 3-Br, 3-Cl |
| | $\sigma$ | 1.39±0.15 | 0.02±0.04 | 0.973 | 96 | 0.08 | 7 | H, 3-CF$_3$, 3-Cl, 3-Br, 3-OMe, 3-Me, 3-COMe |
| $C_2$ | $\sigma^+$ | 1.22±0.09 | 0.05±0.03 | 0.986 | 171 | 0.06 | 7 | H, 3-CF$_3$, 3-Cl, 3-Br, 3-OMe, 3-Me, 3-COMe |
| | $\sigma$ | 2.05±0.45 | -0.03±0.08 | 0.934 | 20 | 0.09 | 5 | H, F, Cl, Br, I |
| | $\sigma$ | -1.19±0.15 | 0.25±0.05 | 0.911 | 64 | 0.20 | 15 | all $\sigma^+$(Me, OMe), $\sigma$(NO$_2$, I) |
| $C_4$ | $\sigma$ | -1.33±0.21 | 0.24±0.07 | 0.922 | 40 | 0.19 | 9 | 4-substituted |
| | $\sigma^+$ | -0.78±0.14 | 0.14±0.06 | 0.840 | 31 | 0.20 | 15 | all |
| $C_5$ | $\sigma$ | 1.44±0.26 | -0.01±0.08 | 0.941 | 31 | 0.12 | 6 | 3-substituted |
| $C_6$ | $\sigma$ | (0.51±0.09) $\sigma^2$ | (-0.65±0.01) $\sigma$ | 1.000 | 11078 | 0.00 | 4 | H, I, COMe, NO$_2$, |
| | $\sigma$ | (6.32±1.12) $\sigma^2$ | (-1.18±0.28) $\sigma$ | 0.930 | 16 | 0.14 | 8 | Me, OMe, F, 3-Cl, 3-Br, 3-OMe, 3-Me, 3-COMe |

[a] all 4-substituted compounds; [b] all 3-substituted compounds

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**Table S20.** Correlation results for **6-PY** tautomer obtained according to eq. (4).

| Atom | | $\rho_I$ | $\rho_R$ | h | R | $\lambda^a$ | F | sd | n | Compounds included |
|---|---|---|---|---|---|---|---|---|---|---|
| C$_{1'}$ | $\sigma$ | 8.28±2,61 | 13.23±2,39 | −0.77±1.03 | 0.870 | 1.60 | 19 | 2.00 | 15 | all |
| | $\sigma$ | 7.93±2.34 | 12.96±2.34 | 0.32±1.00 | 0.963 | 1.58 | 39 | 1.51 | 9 | 4-substituted[b] |
| | $\sigma$ | 6.00±6.61 | 18.44±3.15 | 1.32±3.28 | 0.963 | 3.07 | 26 | 1.82 | 7 | 4- (H i Me excluded) |
| | $\sigma$ | 3.68±0.93 | 1.34±0.87 | -0.19±0.33 | 0.917 | 0.36 | 8 | 0.35 | 6 | 3-substituted[c] |
| C$_2$ | $\sigma$ | 1.09±0.48 | -0.14±0.41 | 0.02±0.15 | 0.855 | 0.13 | 5 | 0.19 | 7 | H, 3-CF$_3$, 3-Cl, 3-Br, 3-OMe, 3-Me, 3-COMe |
| | $\sigma$ | 2.31±0.68 | 2.95±1.09 | -0.02±0.12 | 0.927 | 1.28 | 6 | 0.12 | 5 | H, F, Cl, Br, I |
| C$_4$ | $\sigma$ | -0.85±0.27 | -1.20±0.24 | 0.15±0.11 | 0.851 | 1.41 | 16 | 0.20 | 15 | all |
| | $\sigma$ | -0.96±0.29 | -1.56±0.27 | 0.07±0.12 | 0.938 | 1.63 | 22 | 0.19 | 9 | 4-substituted |
| C$_5$ | $\sigma$ | 0.93±0.61 | -0.59±0.58 | -0.03±0.22 | 0.810 | 0.63 | 3 | 0.23 | 6 | 3-substituted |

[a] $\lambda = \rho_R/\rho_I$; [b] all 4-substituted compounds; [c] all 3-substituted compounds

**Table S21.** Calculated energies of the HOMO and LUMO orbitals and energy gap for compounds **1 - 16** in gas phase.

| Compound | Tautomer | Gas phase | | |
|---|---|---|---|---|
| | | Orbitals energy (eV) | | |
| | | $E_{HOMO}$ | $E_{LUMO}$ | $E_{gap}$ |
| 1 | 2-PY | -6.02 | -1.49 | 4.53 |
| | 6-PY | -6.12 | -1.18 | 4.94 |
| 2 | 2-PY | -5.98 | -1.45 | 4.53 |
| | 6-PY | -6.07 | -1.13 | 4.94 |
| 3 | 2-PY | -5.94 | -1.44 | 4.50 |
| | 6-PY | -6.03 | -1.1 | 4.92 |
| 4 | 2-PY | -6.40 | -2.70 | 3.70 |
| | 6-PY | -6.49 | -2.72 | 3.77 |
| 5 | 2-PY | -6.18 | -1.93 | 4.25 |
| | 6-PY | -6.27 | -1.90 | 4.37 |
| 6 | 2-PY | -5.98 | -1.47 | 4.51 |
| | 6-PY | -6.07 | -1.15 | 4.92 |
| 8 | 2-PY | -6.17 | -1.67 | 4.50 |
| | 6-PY | -6.26 | -1.38 | 4.88 |
| 9 | 2-PY | -6.16 | -1.67 | 4.49 |
| | 6-PY | -6.25 | -1.38 | 4.87 |
| 10 | 2-PY | -6.11 | -1.59 | 4.52 |
| | 6-PY | -6.21 | -1.28 | 4.93 |
| 11 | 2-PY | -6.22 | -1.74 | 4.48 |
| | 6-PY | -6.31 | -1.47 | 4.84 |
| 12 | 2-PY | -6.17 | -1.67 | 4.50 |
| | 6-PY | -6.26 | -1.38 | 4.88 |
| 13 | 2-PY | -6.16 | -1.67 | 4.49 |
| | 6-PY | -6.25 | -1.37 | 4.88 |
| 14 | 2-PY | -6.01 | -1.50 | 4.51 |
| | 6-PY | -6.10 | -1.14 | 4.96 |
| 15 | 2-PY | -5.99 | -1.47 | 4.52 |
| | 6-PY | -6.08 | -1.12 | 4.96 |
| 16 | 2-PY | -6.11 | -1.81 | 4.30 |
| | 6-PY | -6.20 | -1.80 | 4.40 |

**Table S22.** Calculated energies of the HOMO and LUMO orbitals and energy gap for compounds **1 - 16** in DMSO, EtOH and THF.

| Comp. | Tautomer | DMSO | | | Ethanol | | | THF | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Orbitals energy (eV) | | | | | | | | |
| | | $E_{HOMO}$ | $E_{LUMO}$ | $E_{gap}$ | $E_{HOMO}$ | $E_{LUMO}$ | $E_{gap}$ | $E_{HOMO}$ | $E_{LUMO}$ | $E_{gap}$ |
| **1** | **2-PY** | -6.07 | -1.46 | 4.62 | -6.07 | -1.46 | 4.61 | -6.07 | -1.47 | 4.60 |
| | **6-PY** | -6.15 | -1.13 | 5.02 | -6.15 | -1.13 | 5.02 | -6.15 | -1.14 | 5.01 |
| **2** | **2-PY** | -6.06 | -1.45 | 4.61 | -6.06 | -1.45 | 4.61 | -6.05 | -1.46 | 4.60 |
| | **6-PY** | -6.14 | -1.12 | 5.02 | -6.13 | -1.12 | 5.02 | -6.13 | -1.12 | 5.01 |
| **3** | **2-PY** | -6.03 | -1.45 | 4.58 | -6.03 | -1.45 | 4.58 | -6.02 | -1.46 | 4.57 |
| | **6-PY** | -6.09 | -1.12 | 4.97 | -6.09 | -1.11 | 4.97 | -6.09 | -1.12 | 4.96 |
| **4** | **2-PY** | -6.18 | -2.71 | 3.47 | -6.18 | -2.71 | 3.48 | -6.23 | -2.70 | 3.52 |
| | **6-PY** | -6.26 | -2.73 | 3.53 | -6.26 | -2.72 | 3.53 | -6.30 | -2.72 | 3.58 |
| **5** | **2-PY** | -6.12 | -1.86 | 4.26 | -6.13 | -1.86 | 4.27 | -6.15 | -1.87 | 4.28 |
| | **6-PY** | -6.20 | -1.85 | 4.35 | -6.20 | -1.85 | 4.35 | -6.23 | -1.85 | 4.37 |
| **6** | **2-PY** | -6.01 | -1.45 | 4.57 | -6.01 | -1.44 | 4.57 | -6.01 | -1.45 | 4.56 |
| | **6-PY** | -6.08 | -1.11 | 4.96 | -6.07 | -1.11 | 4.96 | -6.08 | -1.12 | 4.96 |
| **8** | **2-PY** | -6.12 | -1.53 | 4.59 | -6.11 | -1.53 | 4.58 | -6.13 | -1.56 | 4.57 |
| | **6-PY** | -6.19 | -1.23 | 4.96 | -6.19 | -1.23 | 4.96 | -6.21 | -1.26 | 4.95 |
| **9** | **2-PY** | -6.11 | -1.53 | 4.58 | -6.11 | -1.53 | 4.58 | -6.13 | -1.56 | 4.57 |
| | **6-PY** | -6.19 | -1.24 | 4.95 | -6.19 | -1.24 | 4.95 | -6.21 | -1.26 | 4.95 |
| **10** | **2-PY** | -6.09 | -1.49 | 4.60 | -6.09 | -1.49 | 4.60 | -6.10 | -1.51 | 4.59 |
| | **6-PY** | -6.17 | -1.16 | 5.00 | -6.17 | -1.16 | 5.00 | -6.18 | -1.19 | 5.00 |
| **11** | **2-PY** | -6.13 | -1.56 | 4.56 | -6.13 | -1.57 | 4.56 | -6.15 | -1.60 | 4.55 |
| | **6-PY** | -6.20 | -1.28 | 4.92 | -6.20 | -1.28 | 4.92 | -6.23 | -1.31 | 4.92 |
| **12** | **2-PY** | -6.12 | -1.54 | 4.58 | -6.12 | -1.54 | 4.58 | -6.14 | -1.57 | 4.57 |
| | **6-PY** | -6.20 | -1.23 | 4.97 | -6.20 | -1.23 | 4.96 | -6.22 | -1.26 | 4.96 |
| **13** | **2-PY** | -6.12 | -1.54 | 4.58 | -6.12 | -1.54 | 4.58 | -6.13 | -1.57 | 4.57 |
| | **6-PY** | -6.20 | -1.23 | 4.97 | -6.20 | -1.23 | 4.97 | -6.21 | -1.25 | 4.96 |
| **14** | **2-PY** | -6.07 | -1.47 | 4.59 | -6.07 | -1.48 | 4.59 | -6.07 | -1.49 | 4.58 |
| | **6-PY** | -6.14 | -1.12 | 5.03 | -6.14 | -1.12 | 5.03 | -6.15 | -1.13 | 5.02 |
| **15** | **2-PY** | -6.06 | -1.45 | 4.60 | -6.06 | -1.46 | 4.60 | -6.05 | -1.46 | 4.59 |
| | **6-PY** | -6.14 | -1.11 | 5.03 | -6.14 | -1.11 | 5.03 | -6.14 | -1.11 | 5.02 |
| **16** | **2-PY** | -6.11 | -1.74 | 4.37 | -6.11 | -1.74 | 4.37 | -6.12 | -1.75 | 4.37 |
| | **6-PY** | -6.19 | -1.75 | 4.43 | -6.18 | -1.75 | 4.43 | -6.20 | -1.75 | 4.44 |

**Table S23.** Difference in atomic charges ($\Delta_{Charge}$) between excited and ground state of appropriate atom in **2-PY** form of *para* substituted compounds.

| Atom number[*]/Compound | $\Delta_{Charge}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | **8** | **9** | **10** |
| 1 | 0.3529 | 0.3623 | 0.3512 | 0.0214 | 0.0093 | 0.345 | 0.3296 | 0.33 | 0.3497 |
| 2 | -0.1151 | -0.1122 | -0.0435 | -0.2623 | -0.0068 | -0.0626 | -0.1207 | -0.1168 | -0.1121 |
| 3 | 0.0391 | 0.0435 | 0.0263 | 0.0099 | 0.0092 | 0.0283 | 0.0421 | 0.0384 | 0.0402 |
| 4 | -0.0213 | -0.0241 | -1E-04 | -0.0616 | -0.0081 | -0.0099 | -0.0261 | -0.0264 | -0.0183 |
| 5 | 0.2102 | 0.2128 | 0.242 | -0.0599 | 0.0112 | 0.2127 | 0.194 | 0.1934 | 0.214 |
| 6 | -0.2941 | -0.3023 | -0.2301 | -0.2617 | -0.0116 | -0.2261 | -0.291 | -0.2907 | -0.2976 |
| 7 | -0.0208 | -0.0183 | -0.0186 | -0.0004 | -0.0004 | -0.0233 | -0.0161 | -0.024 | -0.0188 |
| 8 | 0.0261 | 0.0243 | 0.0186 | -0.0002 | 0.0005 | 0.022 | 0.0212 | 0.0179 | 0.022 |
| 9 | 0.0218 | 0.0197 | 0.0269 | -1E-04 | 0.0006 | 0.0287 | 0.0209 | 0.0283 | 0.0212 |
| 10 | 1E-04 | 0.0003 | 0.001 | 0.0001 | 0 | 0.001 | -1E-04 | 0.0006 | 0.0002 |
| 11 | 0.0475 | 0.0449 | 0.0397 | 0.0184 | 0.0009 | 0.0407 | 0.0374 | 0.0431 | 0.0423 |
| 12 | -0.0409 | -0.0342 | -0.0036 | -0.12 | -0.0026 | -0.0144 | -0.039 | -0.0474 | -0.0391 |
| 13 | -0.2202 | -0.2219 | -0.1703 | -0.1917 | -0.0069 | -0.1855 | -0.2122 | -0.2108 | -0.216 |
| 14 | -0.0081 | -0.0051 | 0.0032 | -0.031 | 0.0003 | 0.0025 | -0.0065 | -0.0052 | -0.01 |
| 15 | 0.0004 | 0.0004 | -0.0008 | 0.0008 | 0.0003 | 0.0005 | 0.0005 | 0.0002 | 0.0003 |
| 16 | 0.002 | 0.0043 | 0.002 | 0.0037 | 0.0004 | 0.0021 | 0.0035 | 0.0077 | 0.0021 |
| 17 | 0.0022 | -0.0039 | -0.0854 | 0.1569 | 0.1307 | -0.0616 | 0.0176 | 0.0169 | -0.0022 |
| 18 | 0.0032 | 0.0025 | 0.0048 | 0.0048 | -0.0029 | 0.0002 | 0.0059 | 0.028 | 0.0037 |
| 19 | 0 | -0.0004 | 0.0003 | -0.0003 | -0.001 | 0.0006 | -0.0004 | -0.0002 | 0 |
| 20 | 0.0069 | 0.0053 | -0.0092 | 0.0074 | 0.0018 | -0.0025 | 0.0183 | 0.0193 | 0.0132 |
| 21 | 0.0005 | 0 | 0.0006 | 1E-04 | -0.0024 | 0.0003 | 1E-04 | 0.0003 | -1E-04 |
| 22 | 0.0014 | 0.0013 | -0.0448 | 0.0864 | 0.0837 | -0.0301 | 0.003 | -0.0192 | -0.0005 |
| 23 | 0.0002 | -1E-04 | 0.0009 | -0.0008 | -0.0023 | 0.0007 | -0.0004 | -0.0002 | 0.0008 |
| 24 | 0.0003 | 0.0005 | -0.015 | 0.0814 | 0.0865 | -0.0101 | -0.0011 | -0.0008 | 1E-04 |
| 25 | 1E-04 | 0 | -0.0005 | -0.0008 | 0.0002 | 0.0006 | -1E-04 | -0.0002 | 0 |
| 26 | 0.0053 | 0.0002 | -0.0437 | 0.0649 | -0.0551 | -0.0339 | 0.0209 | 0.0223 | 0.0055 |
| 27 | 0.0001 | 0 | -0.046 | 0.216 | 0.4388 | -0.0269 | -0.0015 | -0.0048 | -0.0007 |
| 28 | | 0 | 0.0017 | 0.1594 | -0.554 | 0.0005 | | | |
| 29 | | 0 | 0 | 0.1594 | -0.1911 | | | | |
| 30 | | 1E-04 | -0.0036 | | 0.0019 | | | | |
| 31 | | | -0.0039 | | 0.0577 | | | | |
| 32 | | | | | 0.0111 | | | | |

**Table S24.** Difference in atomic charges (Δ_Charge) between excited and ground state of appropriate atom in **2-PY** form of *meta*-substituted compounds.

| Atom number* /Compound | Δ_Charge | | | | | |
|---|---|---|---|---|---|---|
| | **11** | **12** | **13** | **14** | **15** | **16** |
| 1 | 0.2966 | 0.3253 | 0.32 | 0.3448 | 0.3464 | 0.0253 |
| 2 | -0.1445 | -0.1234 | -0.121 | -0.1164 | -0.1148 | -0.1271 |
| 3 | 0.0434 | 0.0411 | 0.0388 | 0.0393 | 0.0384 | 0.0024 |
| 4 | -0.0344 | -0.0278 | -0.0258 | -0.0214 | -0.0242 | -0.0334 |
| 5 | 0.1668 | 0.1905 | 0.1934 | 0.2027 | 0.2147 | -0.0148 |
| 6 | -0.285 | -0.2879 | -0.2862 | -0.2925 | -0.2964 | -0.1413 |
| 7 | -0.0157 | -0.0176 | -0.0261 | -0.0163 | -0.0213 | -0.0019 |
| 8 | 0.022 | 0.0242 | 0.0324 | 0.0243 | 0.0183 | 0.0014 |
| 9 | 0.0163 | 0.0192 | 0.0179 | 0.0189 | 0.0286 | 0.0012 |
| 10 | 0.0002 | 0.0003 | -0.0002 | 0.0003 | 0.0013 | 1E-04 |
| 11 | 0.0413 | 0.0411 | 0.043 | 0.0429 | 0.0458 | 0.0117 |
| 12 | -0.0597 | -0.0469 | -0.049 | -0.0386 | -0.038 | -0.0552 |
| 13 | -0.2117 | -0.211 | -0.2097 | -0.2162 | -0.2202 | -0.1068 |
| 14 | -0.0089 | -0.0073 | -0.0068 | -0.0053 | -0.0056 | -0.0117 |
| 15 | 0.0007 | 0.0002 | 0.0004 | 0.0004 | 0.0007 | 0.0008 |
| 16 | 0.0017 | 0.0037 | 0.0056 | 0.0037 | 0.0049 | 0.0025 |
| 17 | 0.0425 | 0.0225 | 0.0211 | -0.0184 | 0.0009 | 0.0111 |
| 18 | 0.0484 | 0.0144 | 0.0142 | 0.0249 | 0.0036 | 0.1742 |
| 19 | 0.001 | -0.0003 | 1E-04 | 0 | 0 | 0.0006 |
| 20 | 0.002 | 0.0108 | 0.01 | 0.0117 | 0.0089 | 0.0607 |
| 21 | 1E-04 | 1E-04 | -1E-04 | -0.0004 | 0 | -0.0002 |
| 22 | -0.0018 | 0.0008 | 0.0018 | 0.0021 | 0.001 | -0.0015 |
| 23 | -0.0004 | -1E-04 | -0.0002 | 1E-04 | -0.0002 | -0.003 |
| 24 | 0.0181 | 0.0032 | 0.0031 | -0.0004 | -0.0008 | 0.0336 |
| 25 | 0.003 | -0.0007 | -0.001 | -0.0005 | 0 | 0.3305 |
| 26 | 0.0008 | 0.0256 | 0.0232 | 1E-04 | 1E-04 | -0.2165 |
| 27 | 0.001 | -1E-04 | 0.001 | 0.0001 | 0.0001 | -0.0811 |
| 28 | 0.0004 | | | 0.0002 | 0 | 0 |
| 29 | 0.0565 | | | 0 | 0.0077 | 0.0128 |
| 30 | -0.0009 | | | 0.0101 | 0 | 0.0149 |
| 31 | | | | -0.0003 | | 0.1097 |
| 32 | | | | | | 0.0008 |

**Table S25.** Difference in atomic charges ($\Delta_{Charge}$) between excited and ground state of appropriate atom in **6-PY** form of *para* substituted compounds.

| Atom number[*] /Compound | $\Delta_{Charge}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | **8** | **9** | **10** |
| 1 | -0.2946 | 0.2691 | 0.2657 | 0.0125 | 0.0036 | -0.2512 | 0.2213 | 0.2139 | 0.2616 |
| 2 | 0.2142 | -0.0751 | -0.076 | -0.2591 | -0.0001 | 0.249 | -0.1212 | -0.1144 | -0.0868 |
| 3 | 0.2565 | 0.0867 | 0.0851 | 0.0058 | 0.0097 | 0.2699 | 0.0855 | 0.0701 | 0.0797 |
| 4 | 0.0011 | -0.0097 | -0.0099 | -0.0619 | -0.0094 | 0.0145 | -0.0617 | -0.023 | 0.0006 |
| 5 | -0.0844 | 0.2205 | 0.2254 | -0.0141 | 0.0106 | -0.0263 | 0.2134 | 0.1896 | 0.2129 |
| 6 | 0.0802 | -0.289 | -0.2909 | -0.3059 | -0.0004 | 0.0746 | -0.2794 | -0.2852 | -0.2908 |
| 7 | 0.0248 | -0.0111 | -0.0215 | 0.0005 | -0.0003 | -0.0514 | -0.012 | -0.0134 | -0.0167 |
| 8 | 0.0062 | 0.0162 | 0.0181 | -0.0011 | 0.0003 | -0.0004 | 0.015 | 0.0149 | 0.0179 |
| 9 | 0.033 | -0.0003 | 0 | 1E-04 | 0 | 0.015 | 0.0002 | 1E-04 | 1E-04 |
| 10 | 0.0112 | 0.0154 | 0.0236 | -0.0013 | 0.0002 | -0.0216 | 0.0124 | 0.0158 | 0.0174 |
| 11 | -0.0011 | 0.0231 | 0.0232 | 0.0189 | 0.0007 | -0.0076 | 0.0249 | 0.0248 | 0.0283 |
| 12 | 0.0299 | -0.1181 | -0.1173 | -0.1168 | 1E-04 | -0.0241 | -0.1169 | -0.1145 | -0.1236 |
| 13 | -0.1908 | -0.0079 | -0.0088 | -0.0296 | 0.0008 | -0.1641 | -0.0119 | -0.0113 | -0.008 |
| 14 | -0.0104 | 0.001 | 0.0004 | 0.0009 | 0.0002 | 0.0021 | 0.0007 | -1E-04 | 0.0004 |
| 15 | 0.0246 | -0.1868 | -0.186 | -0.1924 | -0.0003 | 0.019 | -0.1922 | -0.1886 | -0.188 |
| 16 | -0.1211 | 0.0033 | 0.0028 | 0.0051 | 0.0011 | -0.0996 | 0.0042 | 0.0031 | 0.0036 |
| 17 | -0.0115 | 0.0092 | 0.0375 | 0.1581 | 0.1342 | -0.0145 | 0.0585 | 0.0614 | 0.0147 |
| 18 | 0.0031 | 0.0205 | 0.0273 | 0.005 | -0.0079 | 0.0027 | 0.0532 | 0.0218 | 0.0396 |
| 19 | 1E-04 | 0.0003 | 0.0003 | 0 | -0.0014 | 0.0003 | -0.0018 | 0.0008 | 0.0002 |
| 20 | -0.003 | 0.0091 | -0.0261 | 0.0057 | 0.0025 | 0.0011 | 0.0158 | 0.0151 | 0.0013 |
| 21 | 0.0004 | -0.0003 | -0.0002 | 0.0001 | -0.0027 | 0.0004 | 0 | 1E-04 | -1E-04 |
| 22 | 0 | 0.0007 | 0.0003 | 0.0822 | 0.0873 | 0.0002 | -0.0006 | 0.0292 | -0.0019 |
| 23 | 0.0003 | 0 | 0 | 0.0002 | -0.0031 | -0.0249 | -1E-04 | -0.0002 | 0 |
| 24 | 0.0007 | 0.0037 | 0.0092 | 0.0842 | 0.0852 | 1E-04 | 0.022 | 0.0205 | 0.0123 |
| 25 | 0.0152 | 0.0002 | -0.0007 | 1E-04 | 0 | 0.018 | 0.0003 | 0 | 0.0003 |
| 26 | 1E-04 | 0.0187 | 0.0173 | 0.0646 | -0.0501 | 1E-04 | 0.068 | 0.0691 | 0.0249 |
| 27 | 0.0151 | -0.0023 | -0.0001 | 0.2164 | 0.4395 | 0.0179 | 0.0021 | 0.0004 | 1E-04 |
| 28 | | 0 | 0.0012 | 0.1597 | -0.5768 | 0.0009 | | | |
| 29 | | 0.002 | 0.0004 | 0.1618 | -0.151 | | | | |
| 30 | | 0.0013 | 0 | | 0.0012 | | | | |
| 31 | | | 1E-04 | | 0.015 | | | | |
| 32 | | | | | 0.0112 | | | | |

**Table S26.** Difference in atomic charges ($\Delta_{Charge}$) between excited and ground state of appropriate atom in **6-PY** form of *meta*-substituted compounds.

| Atom number* | $\Delta_{Charge}$ | | | | | |
|---|---|---|---|---|---|---|
| | **11** | **12** | **13** | **14** | **15** | **16** |
| 1 | 0.1654 | 0.2152 | 0.2168 | 0.2795 | 0.2763 | 0.0022 |
| 2 | -0.1552 | -0.1181 | -0.1171 | -0.0573 | -0.0783 | -0.0169 |
| 3 | 0.0715 | 0.0759 | 0.0724 | 0.0831 | 0.0803 | 0.0004 |
| 4 | -0.0402 | -0.018 | -0.062 | 0.0137 | 0.0022 | -0.0093 |
| 5 | 0.1252 | 0.1752 | 0.2194 | 0.2227 | 0.2277 | -0.0003 |
| 6 | -0.284 | -0.2845 | -0.2844 | -0.2759 | -0.2967 | -0.0213 |
| 7 | -0.0103 | -0.0099 | -0.0126 | -0.0384 | -0.0144 | -0.0002 |
| 8 | 0.0103 | 0.0149 | 0.0136 | 0.0176 | 0.0177 | 0 |
| 9 | 0 | -1E-04 | -0.0002 | 0.0003 | 0.0003 | 0 |
| 10 | 0.0097 | 0.0112 | 0.0144 | 0.0417 | 0.0168 | 0.0004 |
| 11 | 0.026 | 0.0215 | 0.026 | 0.0193 | 0.0235 | 0.0009 |
| 12 | -0.1167 | -0.1175 | -0.1164 | -0.1094 | -0.1192 | -0.0078 |
| 13 | -0.0141 | -0.0136 | -0.0137 | -0.0133 | -0.0136 | -0.0003 |
| 14 | 0.0011 | 0.0014 | 0.0014 | 0.0008 | 0.0006 | 0.0003 |
| 15 | -0.1992 | -0.1918 | -0.1871 | -0.1754 | -0.1897 | -0.0156 |
| 16 | 0.0045 | 0.0037 | 0.0039 | 0.0028 | 0.0045 | 0.0002 |
| 17 | 0.102 | 0.07 | 0.0672 | 0.0093 | 0.013 | 0.0014 |
| 18 | 0.118 | 0.0401 | 0.0442 | -0.0132 | 0.0196 | 0.1436 |
| 19 | 0.0005 | 0.0049 | -1E-04 | 0.0007 | -0.0003 | -1E-04 |
| 20 | -0.0064 | 0.0226 | 0.0171 | 0.0045 | 0.0045 | 0.0758 |
| 21 | 0 | -0.0003 | 0.0004 | 0.0004 | -0.0002 | 0.0004 |
| 22 | -0.0098 | 0.0017 | 0.0006 | 0.0065 | -0.0017 | -0.0105 |
| 23 | -0.0006 | -1E-04 | -0.0003 | 1E-04 | 0.0002 | -0.0031 |
| 24 | 0.0608 | 0.0182 | 0.0193 | -0.0163 | 0.0072 | -0.0022 |
| 25 | 0.0073 | 0.0014 | 0.0019 | -0.0152 | -0.0001 | 0.4659 |
| 26 | 0.001 | 0.0744 | 0.0741 | 0.0006 | 0 | -0.523 |
| 27 | 0.0029 | 0.0017 | 0.0009 | 1E-04 | 0 | -0.1592 |
| 28 | 0.0007 | | | -0.0012 | 0.0022 | 0.0003 |
| 29 | 0.1295 | | | -0.0012 | 0.017 | 0.0133 |
| 30 | 0 | | | 0.0138 | 0.0006 | 0.0133 |
| 31 | | | | -0.0003 | | 0.0518 |
| 32 | | | | | | -0.0004 |

**Table S27.** Difference in charges of $R_1$ and $R_2$ rings between excited and ground state in both **2-PY** and **6-PY** forms.

| Compound | $\Delta_{Charge}$ | | | |
|---|---|---|---|---|
| | **2-PY** | | **6-PY** | |
| | $R_1$ | $R_2$ | $R_1$ | $R_2$ |
| 1 | -0.0204 | 0.0202 | -0.0207 | 0.0205 |
| 2 | -0.0056 | 0.0055 | -0.0627 | 0.0631 |
| 3 | 0.2439 | -0.2438 | -0.0661 | 0.0665 |
| 4 | -0.9346 | 0.9348 | -0.9384 | 0.9381 |
| 5 | -0.0037 | 0.0036 | 0.0168 | -0.0169 |
| 6 | 0.1617 | -0.1622 | -0.0022 | 0.0023 |
| 8 | -0.0625 | 0.0623 | -0.2177 | 0.2174 |
| 9 | -0.0617 | 0.0614 | -0.2182 | 0.2182 |
| 10 | -0.0199 | 0.0198 | -0.0914 | 0.0914 |
| 11 | -0.1709 | 0.1707 | -0.406 | 0.4059 |
| 12 | -0.0763 | 0.0762 | -0.2345 | 0.2346 |
| 13 | -0.0733 | 0.0732 | -0.2256 | 0.2253 |
| 14 | -0.0294 | 0.0293 | 0.0118 | -0.0114 |
| 15 | -0.0214 | 0.0213 | -0.062 | 0.062 |
| 16 | -0.4468 | 0.4466 | -0.0673 | 0.0673 |
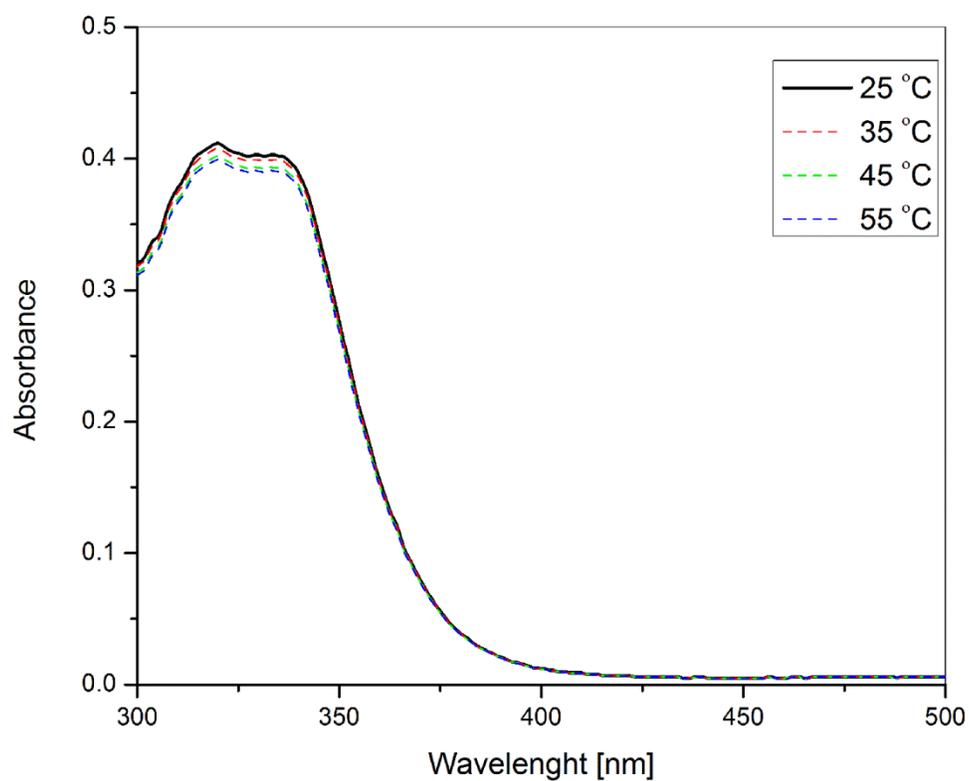
**Fig. S1.** Temperature-dependent UV spectra of compound **3** in DMF.
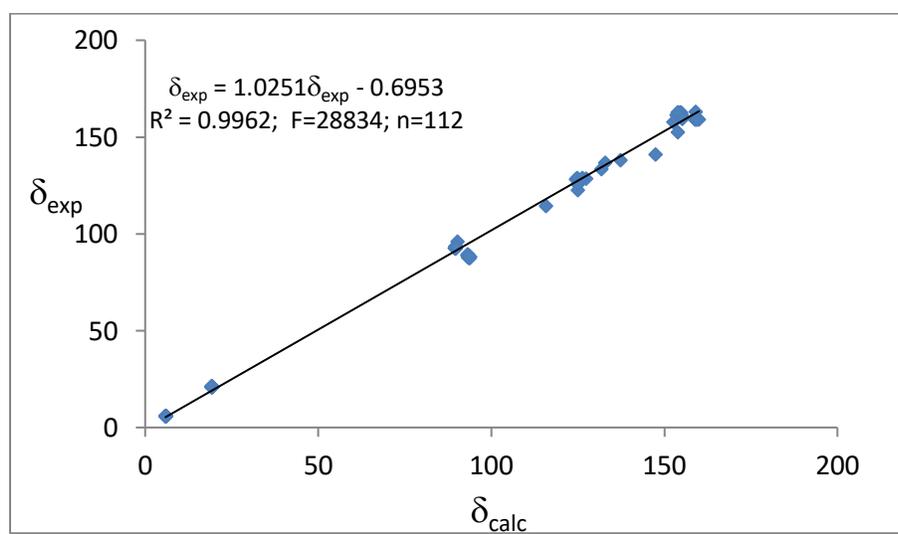


**Fig. S2.** Plot of $\delta_{exp}$ vs $\delta_{calc}$ NMR values
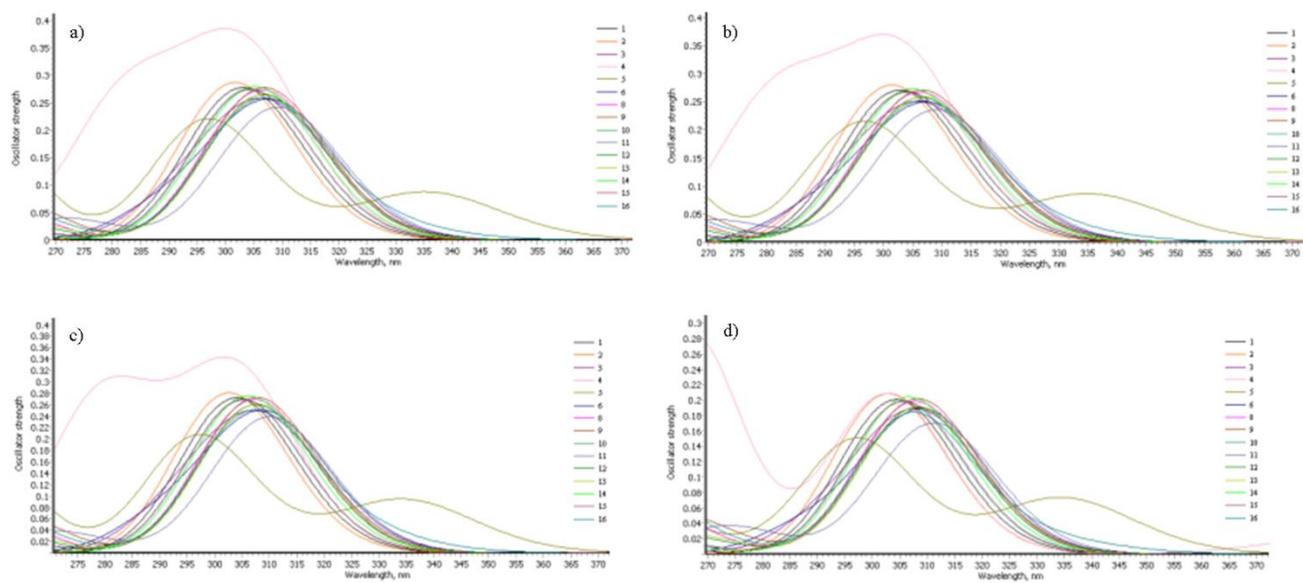
**Fig. S3.** TD-DFT calculated UV-Vis spectra of **2-PY** form in a) DMSO, b) ethanol, c) THF and d) gas phase.
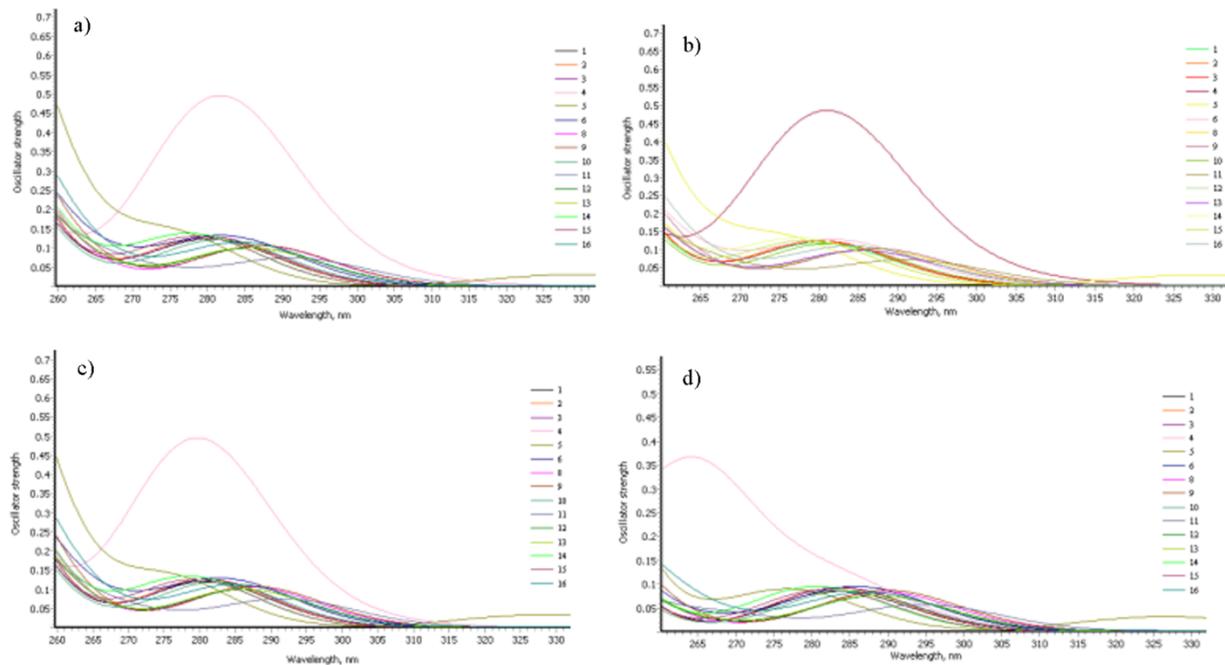
**Fig. S4.** TD-DFT calculated UV-Vis spectra of **6-PY** form in a) DMSO, b) ethanol, c) THF and d) gas phase.
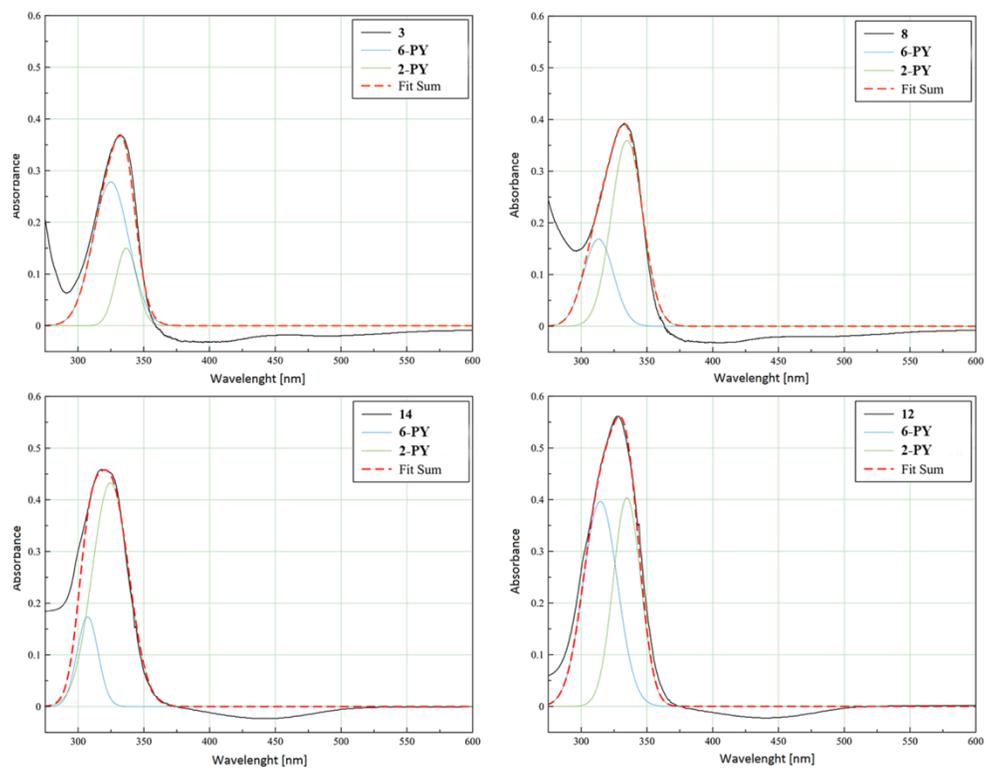
**Fig. S5.** Resolved overlapping bands of compounds **3**, **8**, **14** and **12** in DMSO.
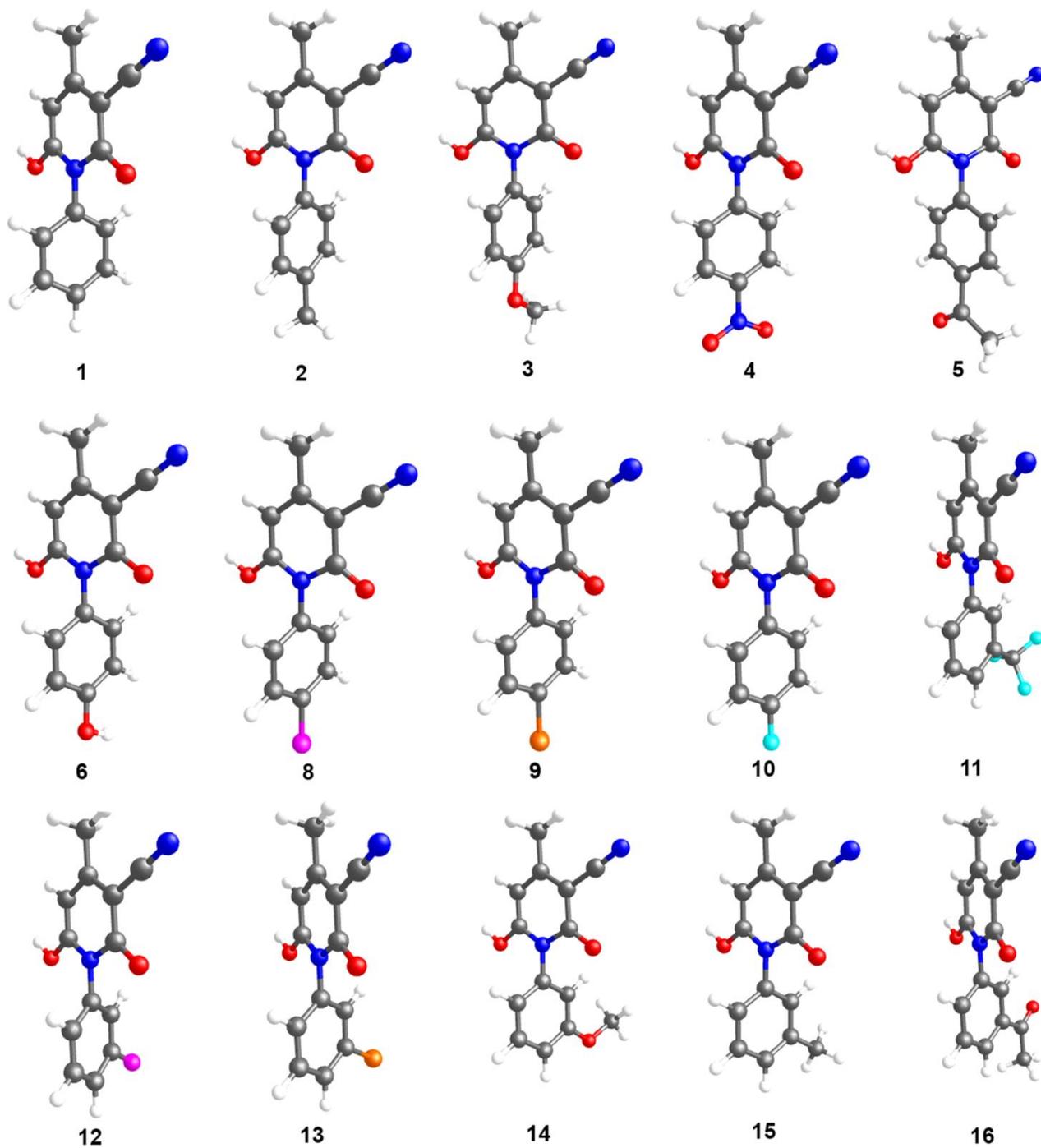
**Fig. S6.** Optimal geometries of compounds **1** - **16** in **2-PY** forms.
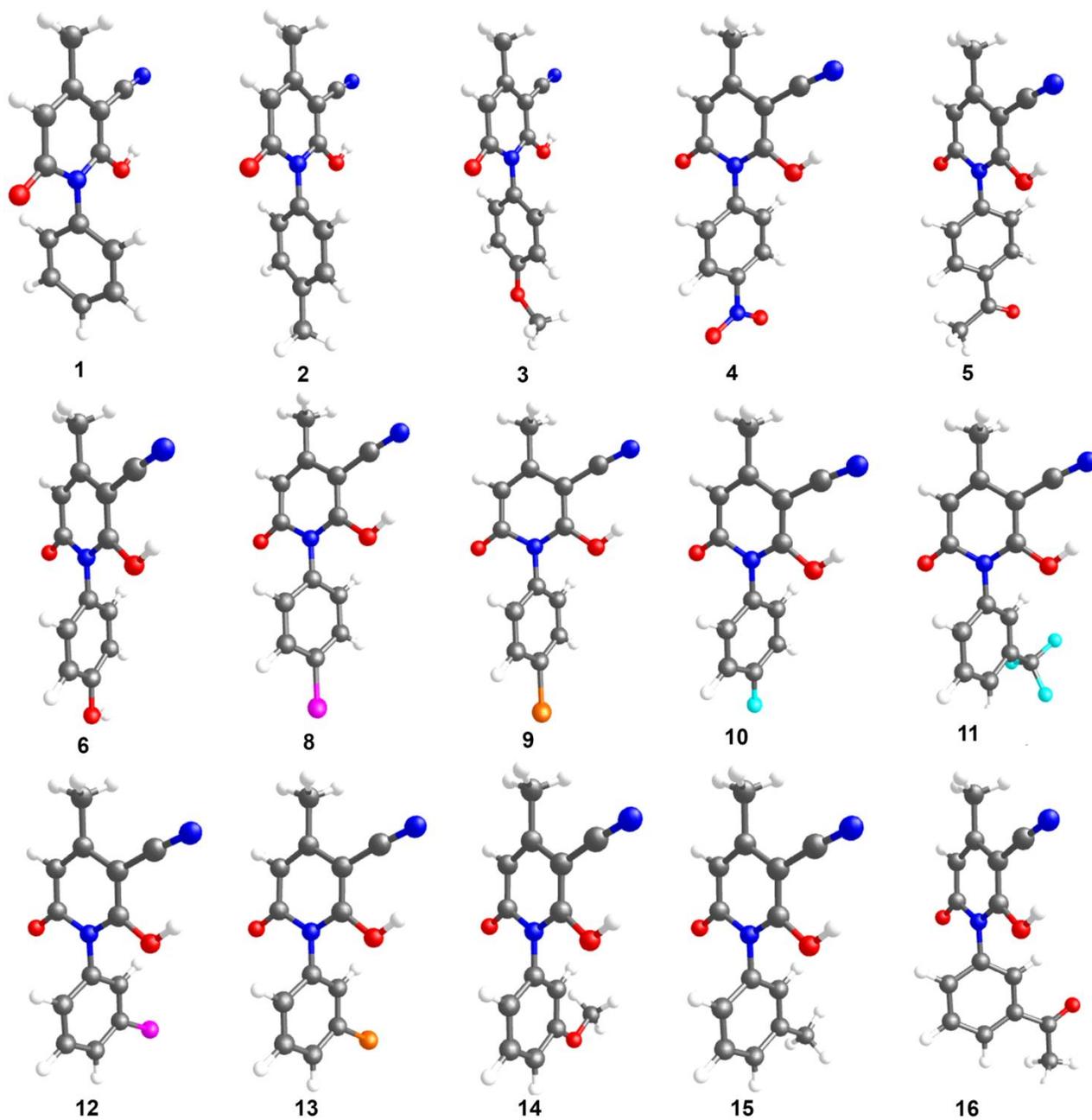
**Fig. S7.** Optimal geometries of compounds **1** - **16** in **6-PY** form.
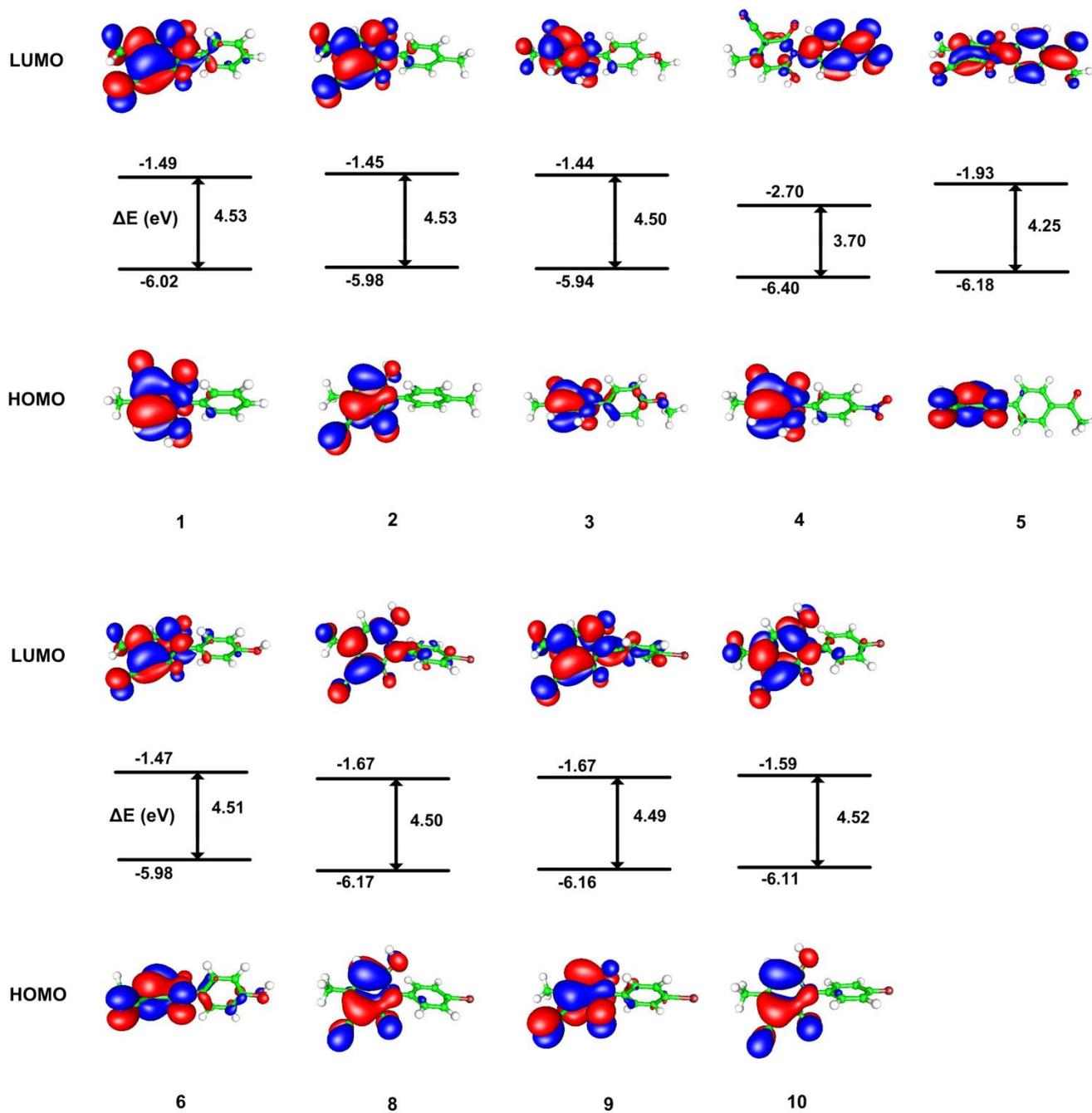
**Fig. S8.** The molecular orbitals and energy gaps between HOMO and LUMO orbitals of compounds **1** - **10** in the 2-**PY** form in a gas phase.
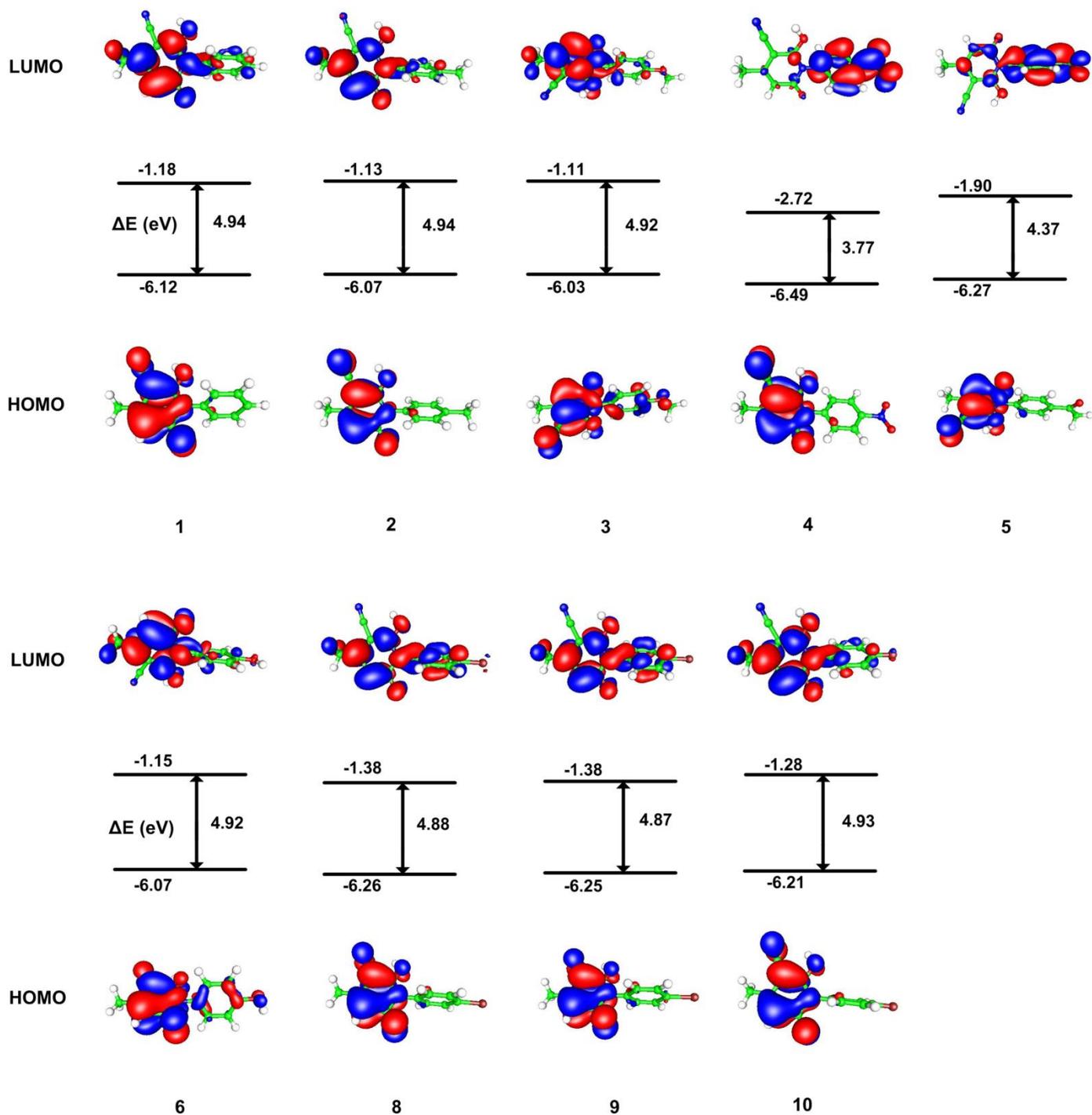
**Fig. S9.** The molecular orbitals and energy gaps between HOMO and LUMO orbitals of compounds **1** - **10** in the **6-PY** form in a gas phase.
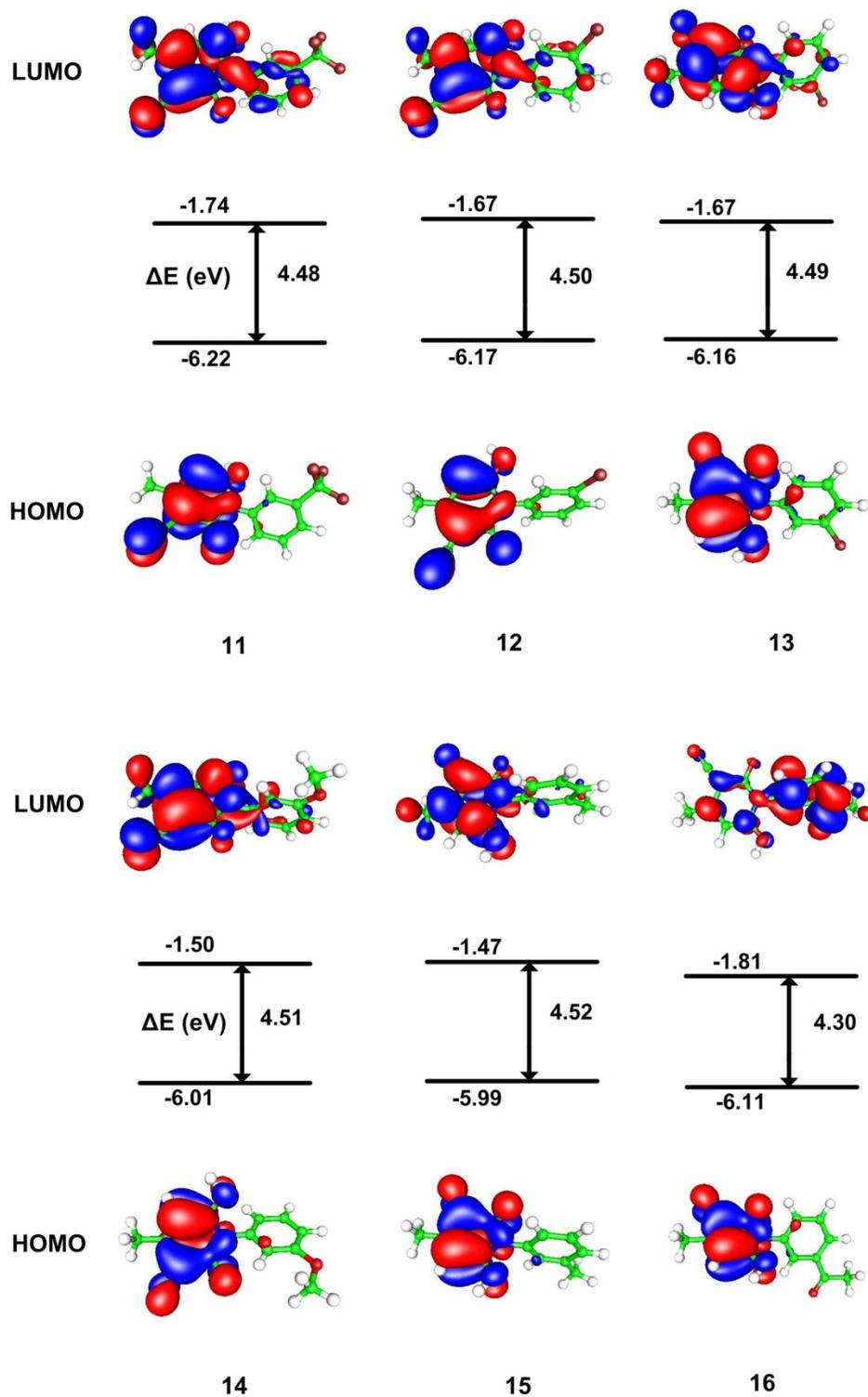
**Fig. S10.** The molecular orbitals and energy gaps between HOMO and LUMO orbitals of compounds **11** - **16** in the **2-PY** form in a gas phase.
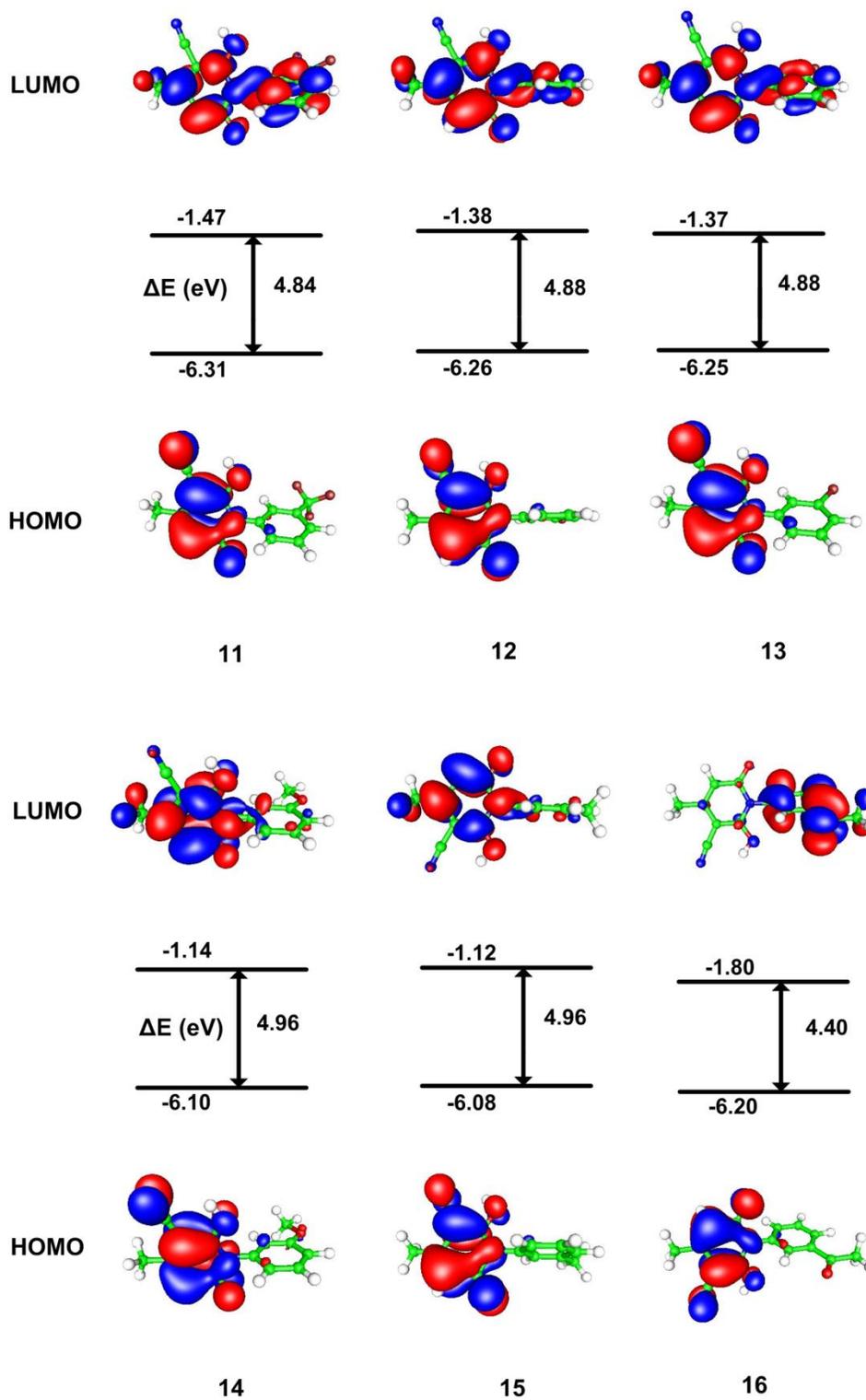
**Fig. S11.** The molecular orbitals and energy gaps between HOMO and LUMO orbitals of compounds **11** - **16** in the **6-PY** form in a gas phase.
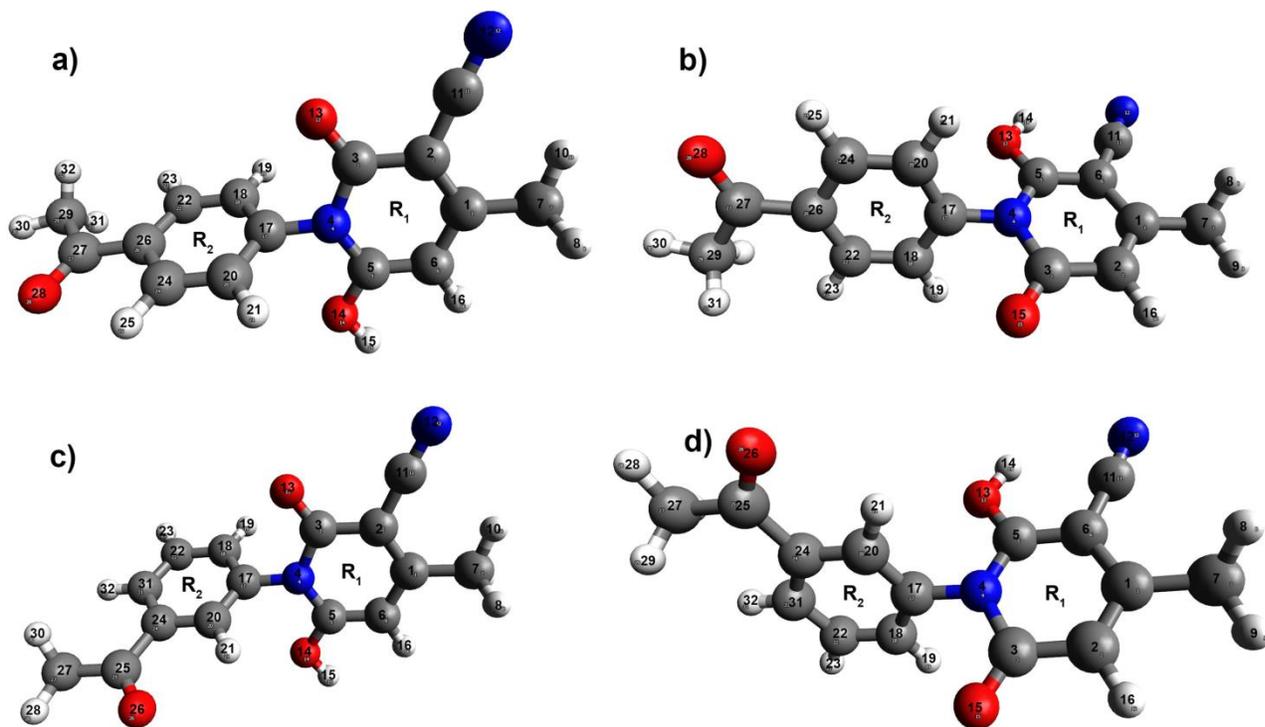
**Fig. S12.** Numbering of the atoms used in Bader's analysis for all investigated compounds (examples given for **5** (**2-PY**), **5** (**6-PY**), **16** (**2-PY**) and **16** (**6-PY**) compounds).
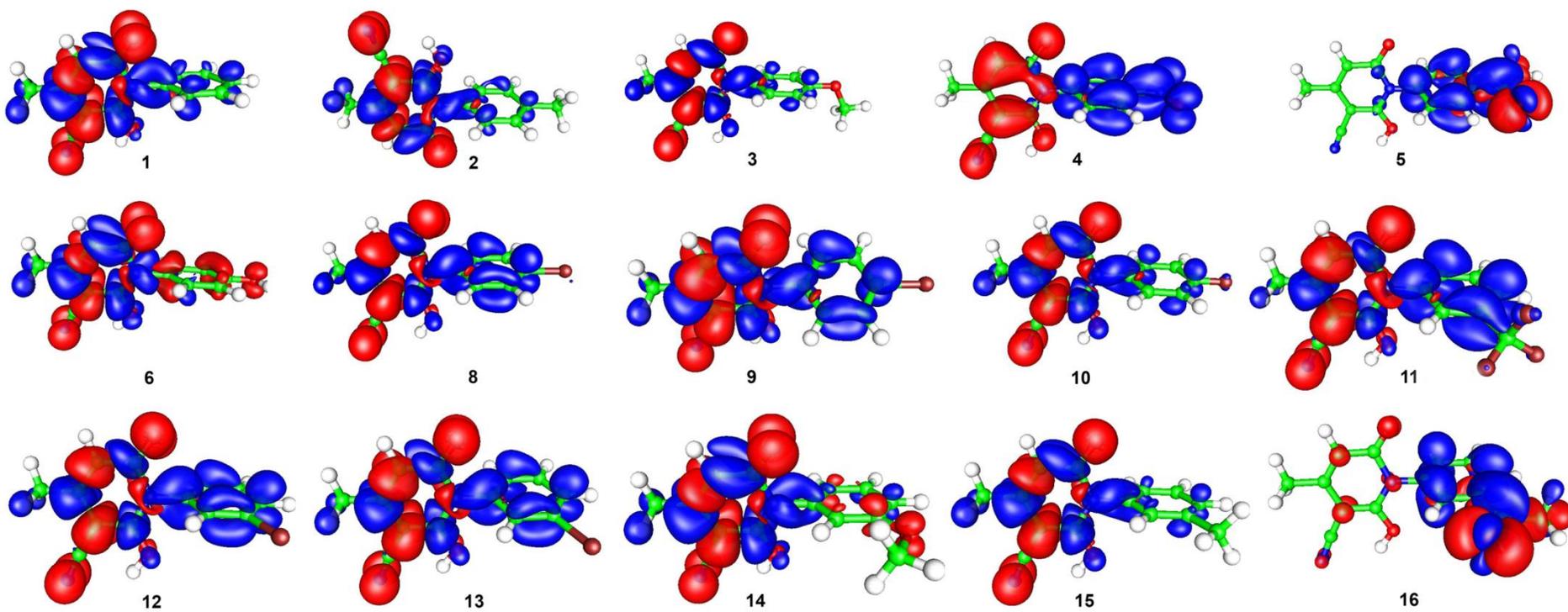
**Fig. S13.** ICT processes from ground state (red) to excited state (blue) for compounds **1** - **16** in **6-PY** form.

The obtained ground state-DFT results (Tables S21 and S22; Figs. S8 - S11), TD-DFT results (Tables S6 and S7) and plots of electron density differences between ground and excited state (Figs. 4 and S13) indicated that the ICT process is highly feaseable for the *nitro*-substitued compounds in both **2-PY** and **6-PY** forms; while in the electron-donor substituted compounds ICT is significantly weaker. Molecular orbitals given in Figs. 4 and S13, clearly show the ICT process during the electronic transition in electron-acceptor substituted compounds. Electron density shifts from pyridone ring to the substituted phenyl ring were observed. On the other hand, both HOMO and LUMO orbitals in electron-donor substituted compounds were associated with the part of molecule without significant ICT. The mechanism of the electronic excitations, and changes in the overall charge distribution in both ground and excited states of the investigated molecules may be related to electron-deficiency of both pyridone and substituted phenyl rings in electron-acceptor substituted compounds and thus higher $\pi$-electron mobility was a consequence. In compounds with electron-acceptor substituents, a lower torsional angle around the $C_{1'}$-$N_1$ bond is evident (Tables S17 and S18). Because of this, larger $\pi,\pi$-delocalization from the $\pi$-electronic system of pyridone moieties occurs, and allows larger charge transfer (Figs. S14 and S15; resonance structures (r.s.) f and n, respectively). The polarizable excited states of electron-acceptor substituted compounds can be, under appropriate preferable solvent-solute interactions, better stabilized with respect to the ground state. Electron-donating substituents increase electron-density at substituted phenyl ring which acts as a $\pi$-donor both in 2-**PY** form (Fig. S14; r.s. b and c), and in **6-PY** form (Fig S15; r.s. n). Electron-donating substituents support resonance interaction in the pyridone unit, *i.e.* extended $\pi$ - electronic system of the pyridone ring. Extended $\pi,\pi$-delocalization in pyridone ring (Fig. S14; r.s. b and Fig. S15; r.s. j) contributes to higher HBD solvent ability (Tables S9) in compounds with electron-donating substitutents. The substituent-dependent properties of both **2-PY** and **6-PY** forms can be described by two structures: first strucutre is quinoid, polarized, and formally aromatic (Figs. S14 and S15; r.s. b and c; and j and k, respectively); the second one is polarized and partially aromatic with respect to localized $\pi$- units (Figs. S14 and S15; r.s. f and g; n and o).

Absorption maxima shifts of both **2-PY** and **6-PY** forms are mostly influenced by non-specific solvent effect (Tables 2 and S9), or expressed by Eq. (2) - the largest contribution of solvent polarizability and lesser dipolarity effect (Tables 3 and S10). An appropriate extent of resonance interaction is operative within overall $\pi$-resonance system (Figs. S14 and S15), what give rise for larger contribution of solvent effects, *i.e.* polarizability and dipolarity, to the stabilization of excited state in **2-PY** and most compounds in **6-PY** forms in ground state (Tables 3 and S10). In the case of electron-acceptor substituted compounds a high contribution of resonance structure n) in overall resonance hybrid (Figs. S14 and S15; r.s. f and n) could contribute to largest red shifts of compound **4**. This is consistent with the strong electron–accepting properties of the $NO_2$ group and thus a larger contribution of non-specific interactions (Table 3). Somewhat lower values of coefficient *c* and *d* was obtained for compound **4** in **6-PY** form.

It was shown that transmission of the substituent effect by $\pi$-polarization mechanism, through differently polarized $\pi$-units is not necessarily transmitted in a direct line through the molecular framework but also could be electrostatically interact through the space with electron density at the pyridone ring.[6] Therefore, the contribution of through space field effect was found to be significant, causing perturbation of $\pi,\pi$-electron density of the pyridone ring (Figs. S14 and S15; r.s. c, g, k and o). All *meta*-substituent showed moderate influences on absorption maxima shifts due to lower extent of direct $\pi$-electron delocalization, where higher contribution of $\pi$-resonance induced field effect is operative (Figs. S14 and S15; r.s. d, h, l and p). Also, transmission of the electronic effect of *meta*-substituents was achieved by adjustment of the orientation of the induced dipole at substituted phenyl ring achieving, through the space, electrostatic stabilization/destabilization of surrounding/neighboring charges (Figs. S14 and S15; r. s. d, h, l and p).
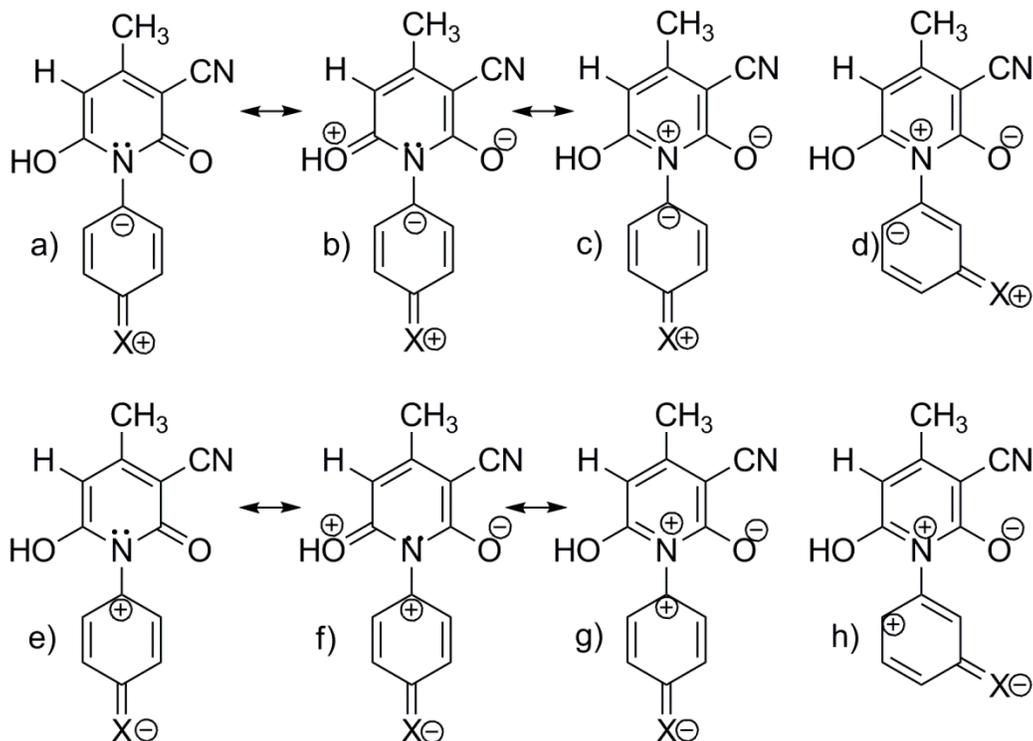


**Fig.** S14. Resonance structures of **2-PY** form for electron-donor a) - d) and electron-acceptor substituted compounds e) - h).
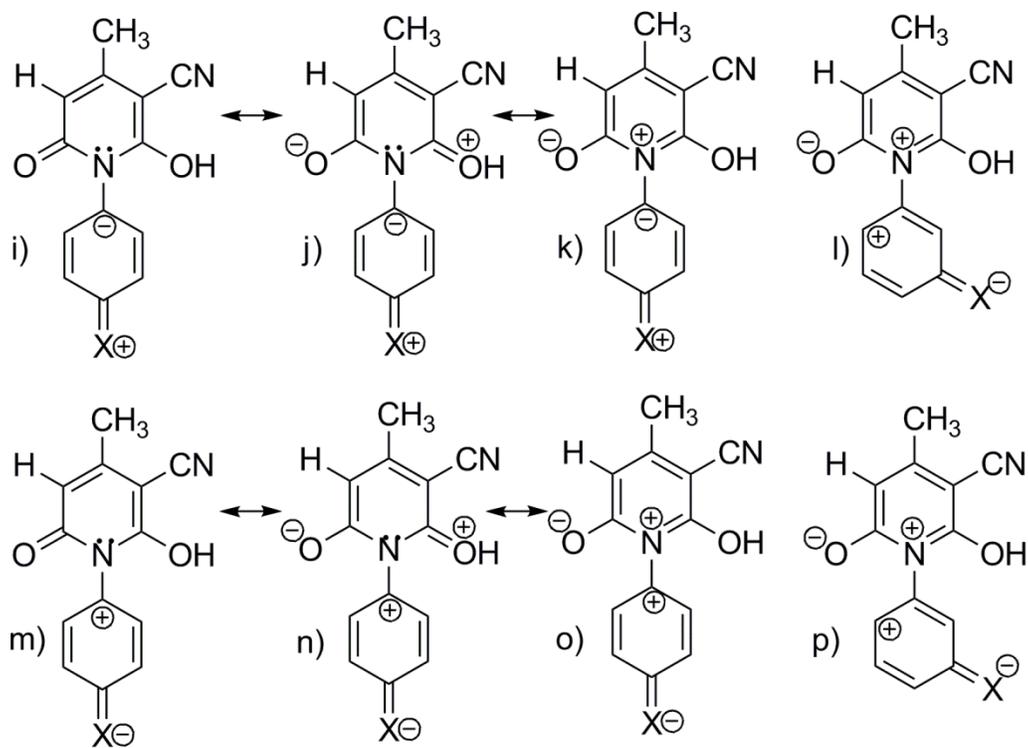
**Fig.** S15.Resonance structures of **6-PY** form for electron-donor i) - l) and electron-acceptor substituted compounds m) - p).

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