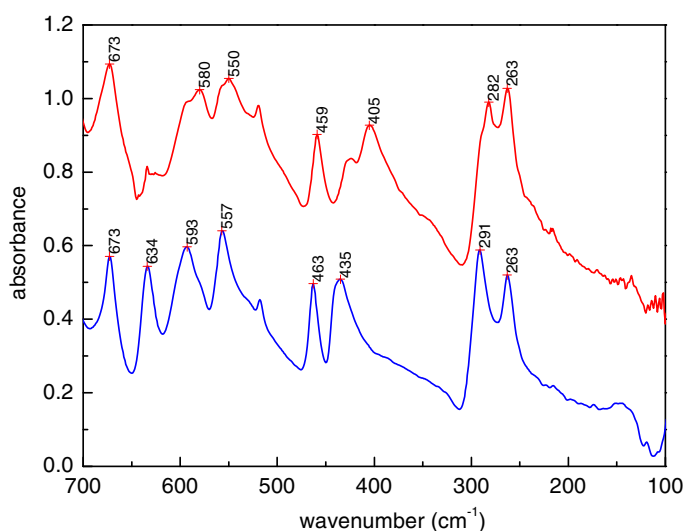


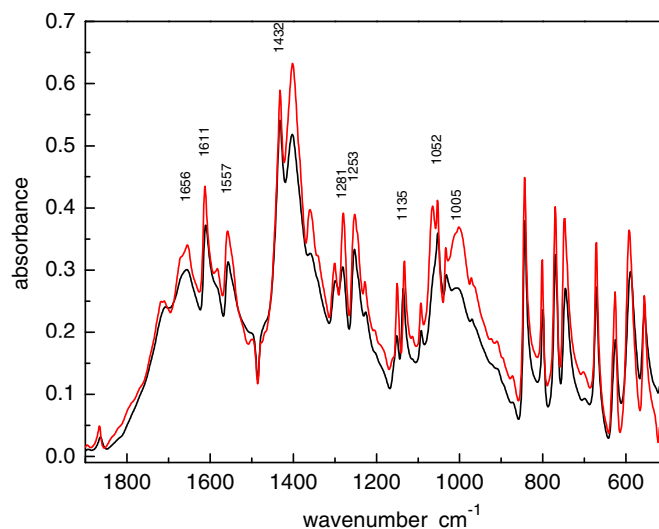
## Supporting information

S1. (a) Gas phase *Gaussian 03* B3LYP/6-31+G(d,p) harmonic frequency output for PANO-h and PANO-d (included in two separate files); (b) periodic CPMD BLYP/PW harmonic frequency output (written in the *Gaussian* format) for PANO-h and PANO-d (included in two separate files). Note that in (b) all the IR intensities are set to zero because CPMD does not support the calculation of intensities.

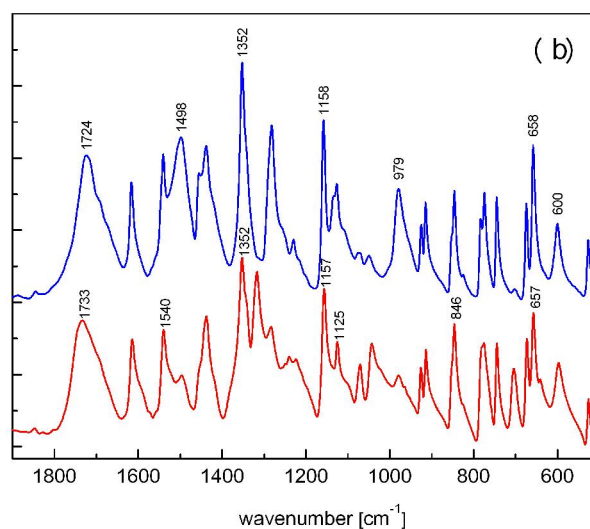
S2a. Far IR spectra (polyethylene pellets) of crystalline picolinic N-oxide in protic (blue line) and deuterated (red line) form.



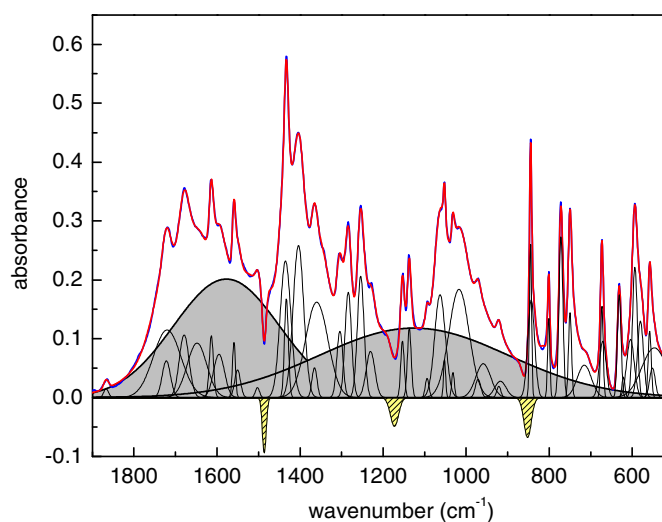
S2b. Infrared spectra of C=<sup>18</sup>O isotopomer of solid-state picolinic acid N-oxide in KBr pellets (black: 300 K; red: 120 K).



S2c. Infrared spectra of 4-nitropicolinic acid *N*-oxide in KBr pellets (see Fig. 1) (blue: normal; red: deuterated).



S2d. A band decomposition of the IR spectrum of crystalline picolinic acid *N*-oxide. The bands with negative intensities simulate the appearance of Evans transmissions in the recorded spectrum. The calculated spectrum is represented by red line, while the recorded and band components with blue and black lines, respectively. The band shape of the band components were approximated by the mixture of Gaussian and Lorentzian functions.



S3. Complete reference 41:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.03*, Gaussian, Inc., Pittsburgh PA, 2003.