

# Characterizing Nitrogen Sites in Nitrogen-Doped Reduced Graphene Oxide: A Combined Solid-State $^{15}\text{N}$ NMR, XPS and DFT Approach

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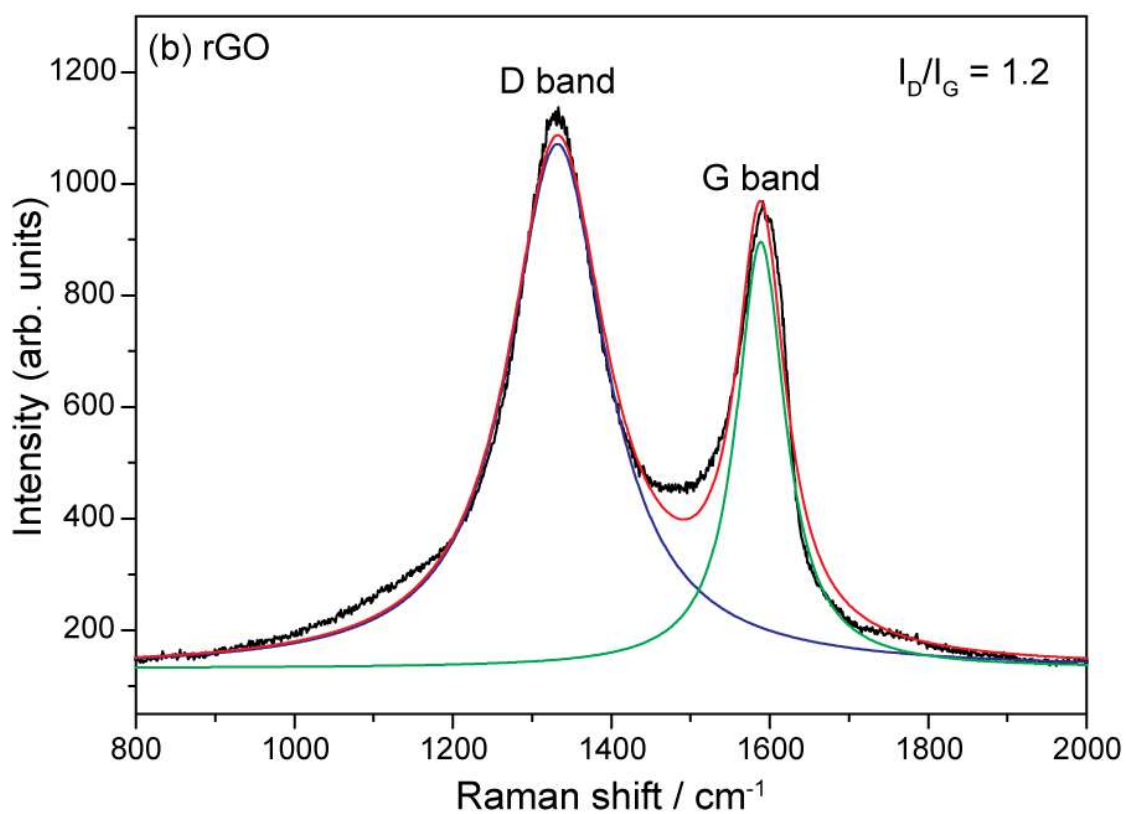
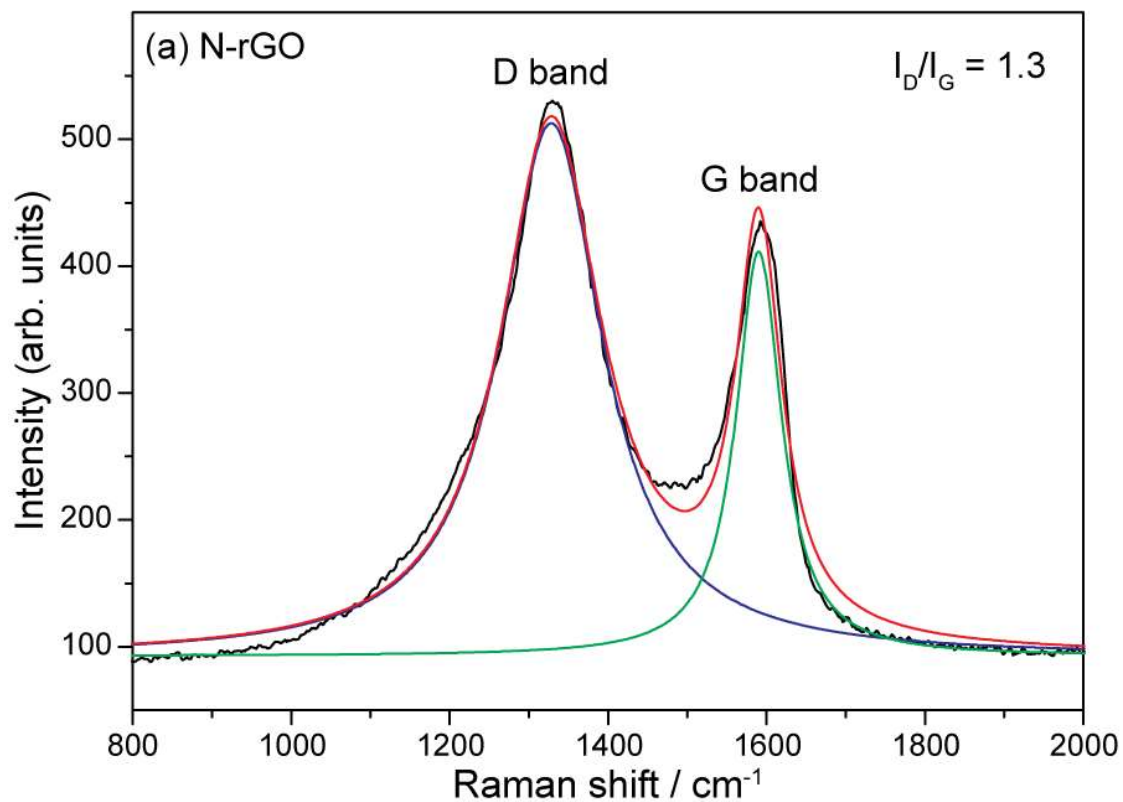
<sup>d</sup>Current Address: Shanghai Key Laboratory of Chemical Assessment and Sustainability, Department of Chemistry, Tongji University, Shanghai, China

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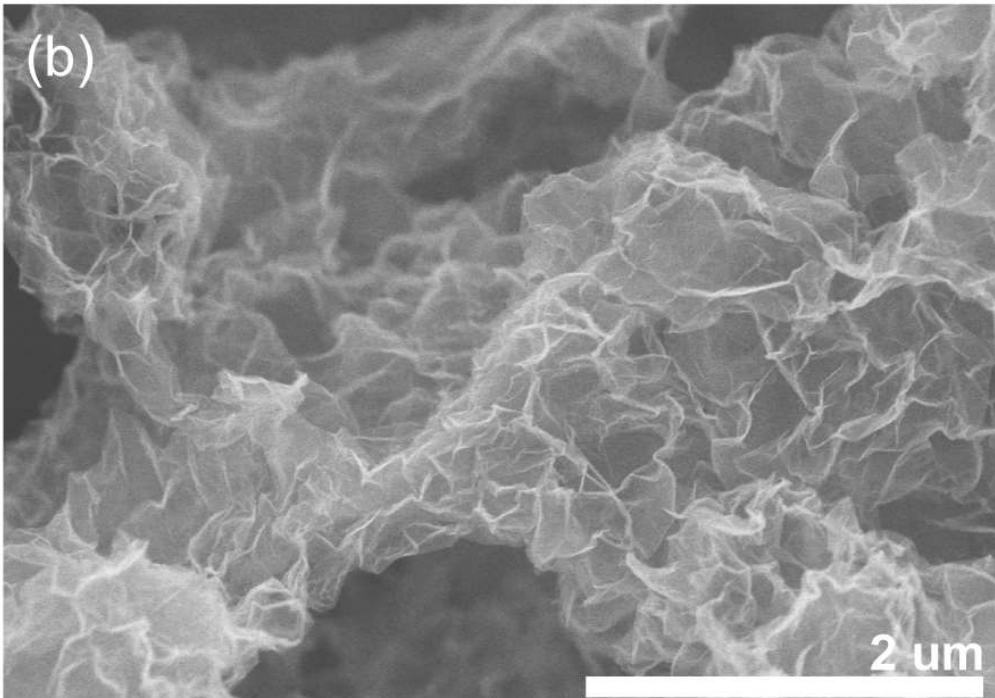
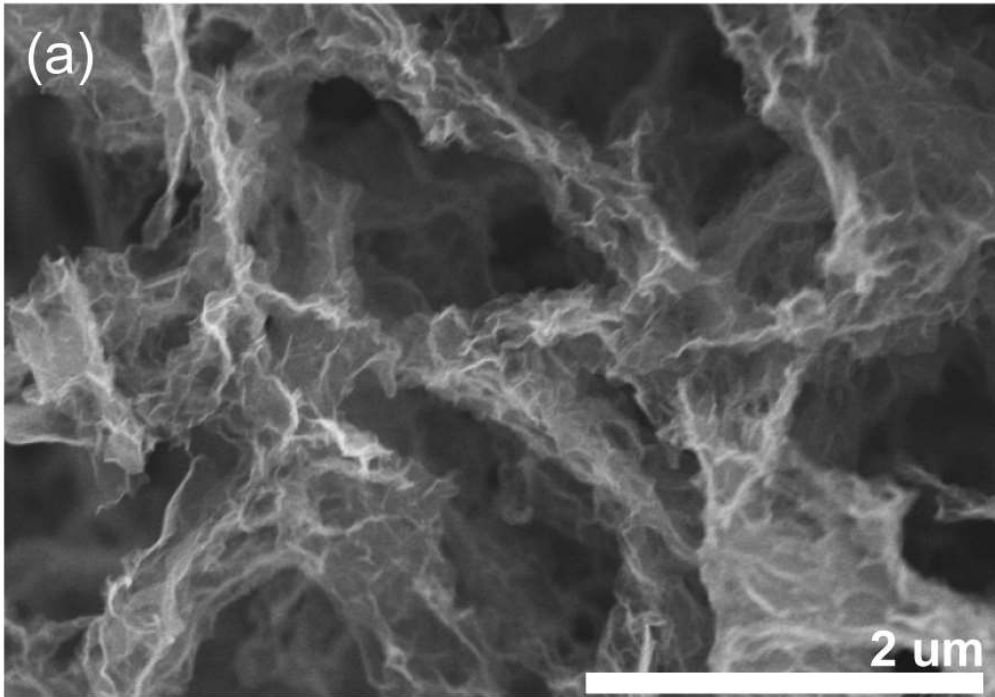
<sup>+</sup> G. K. and J. L. contributed equally to this work.

## Corresponding Author

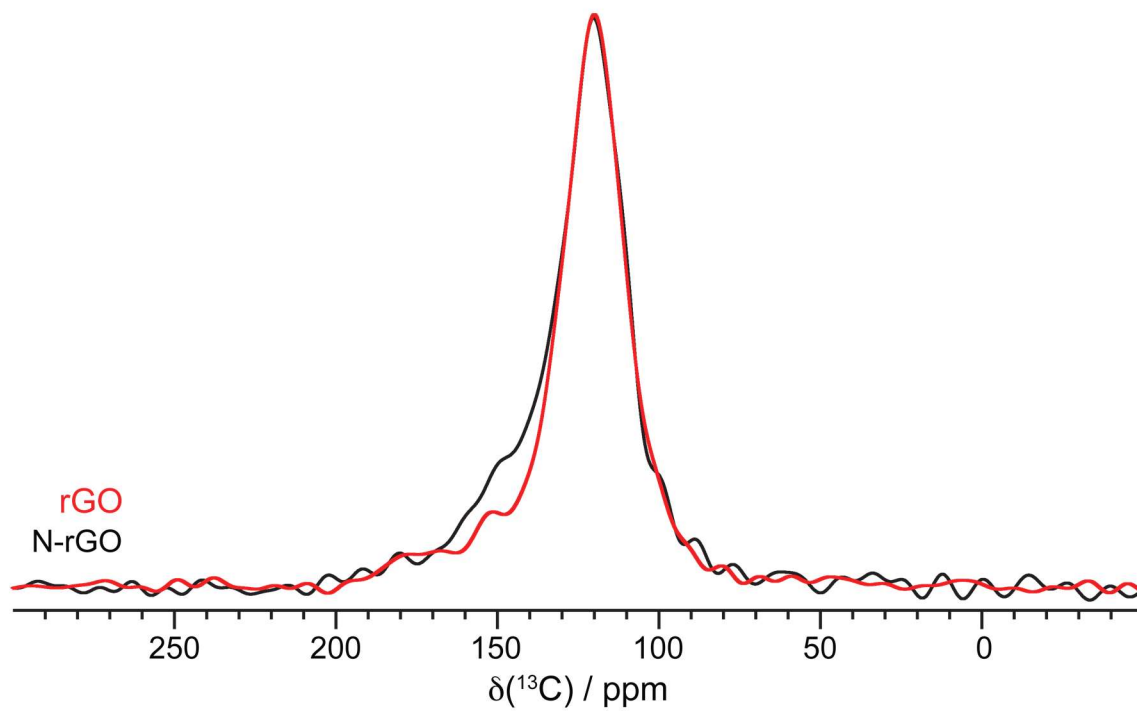
[cpg27@cam.ac.uk](mailto:cpg27@cam.ac.uk)



**Figure S1.** Raman spectra of (a) N-rGO and (b) rGO and a total fit and individual deconvolution are depicted as red, blue, and green solid lines, respectively.

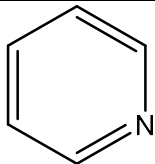
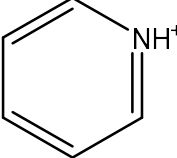
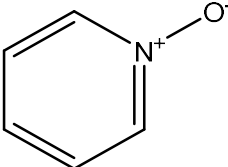
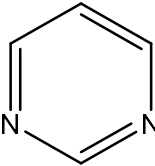
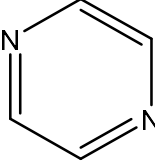
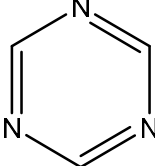
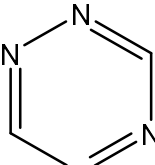
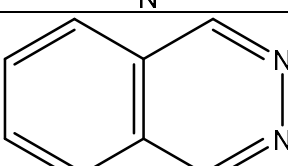
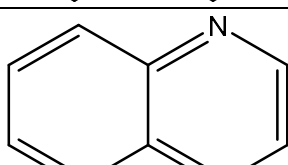
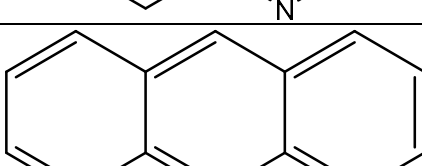


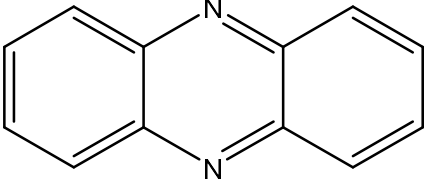
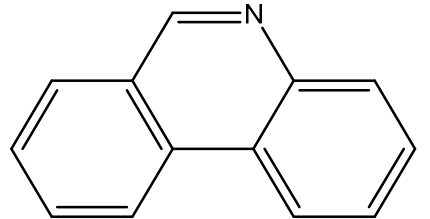
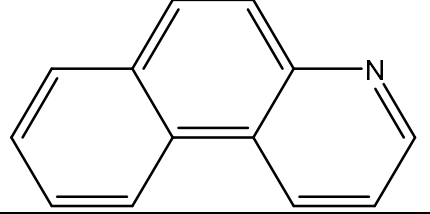
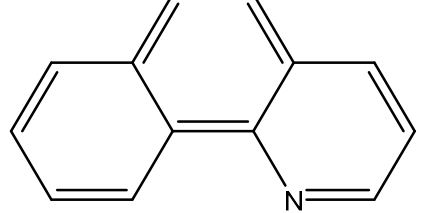
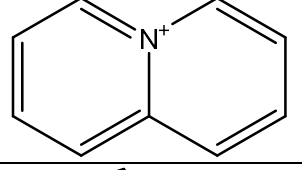
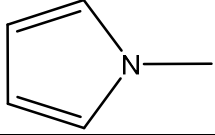
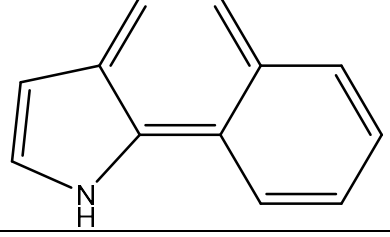
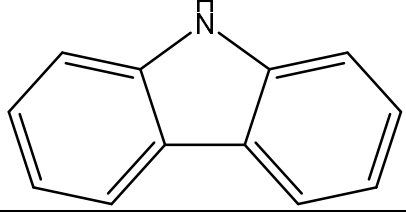
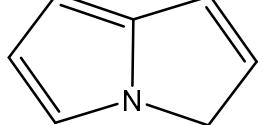
**Figure S2.** SEM images of (a) rGO and (b) N-rGO.

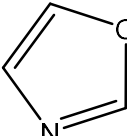
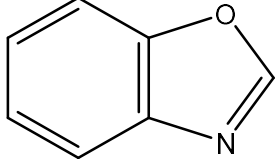
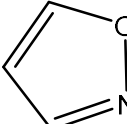
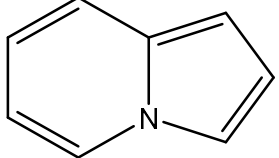
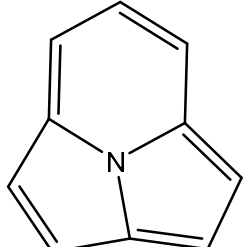
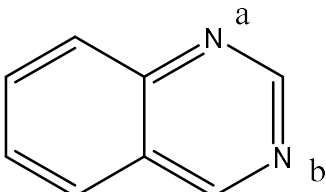
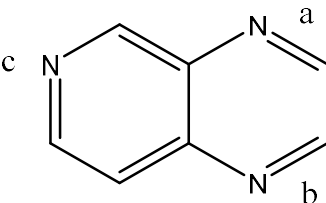
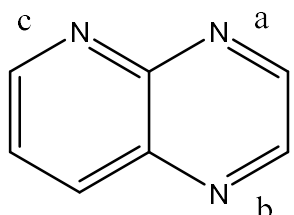
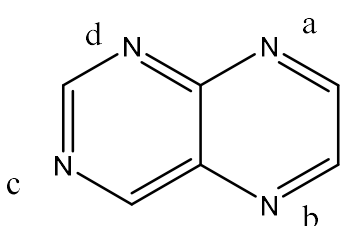


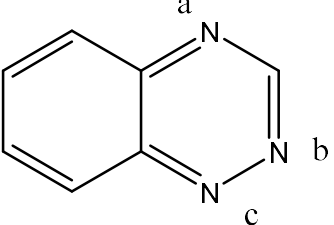
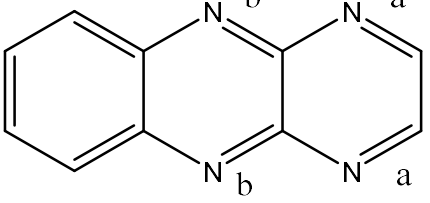
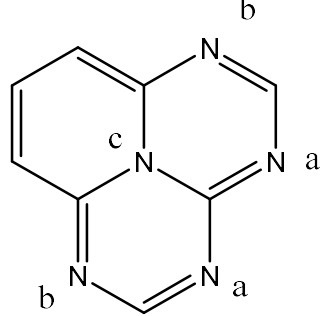
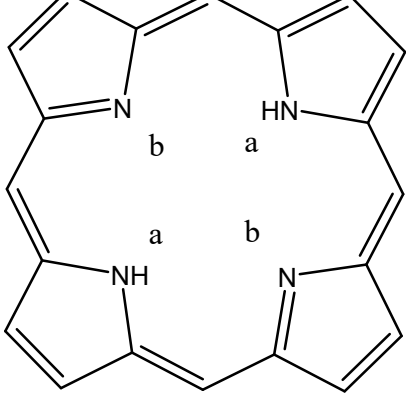
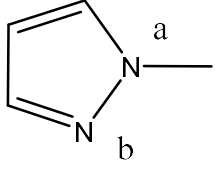
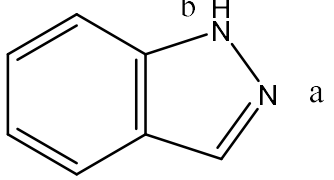
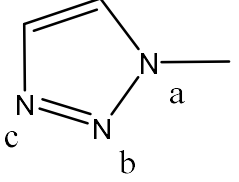
**Figure S3.** Solid-state  $^{13}\text{C}$  CPMG NMR spectra of pristine rGO (red) and N-rGO (black), acquired at 16.4 T with a MAS frequency of 50 kHz.

**Table S1. Library of calculated chemical shielding versus chemical shifts**

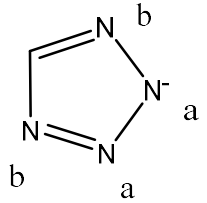
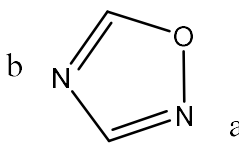
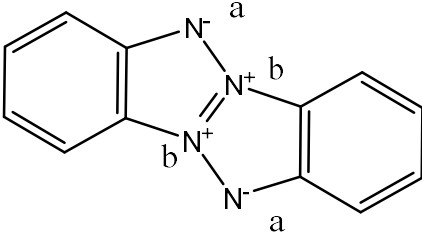
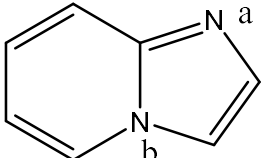
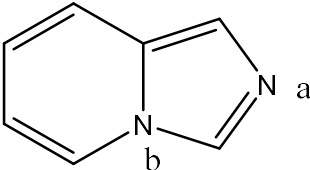
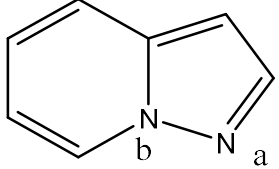
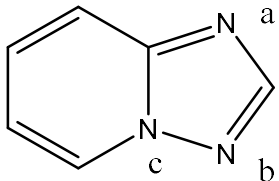
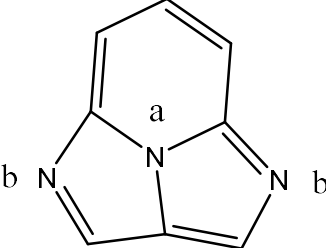
Label	Structure	moiety	$\sigma_{\text{iso}}$ / ppm	$\delta_{\text{iso}}$ / ppm	solvent	reference
1		pyridinic	-62.31	-62.00	neat	1
2		pyridinium	76.46	-167.00	solid	1
3		N-oxide	-50.00	-76.00	DMSO	1
5		pyridinic	-39.01	-83.90	DMSO	1
6		pyridinic	-78.13	-45.34	DMSO	1
7		pyridinic	-24.47	-98.06	DMSO	1
9		N=N	-147.13	4.00	acetone	1
12		N=N	-134.70	-10.30	DMSO	1
14		pyridinic	-74.84	-50.10	DMSO	1
19		pyridinic	-52.77	-74.40	DMSO	1

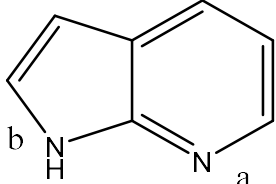
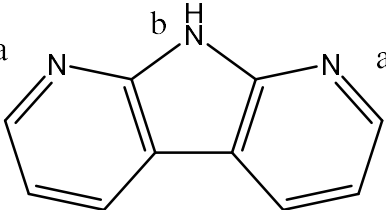
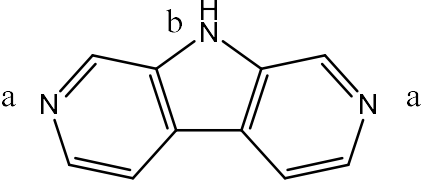
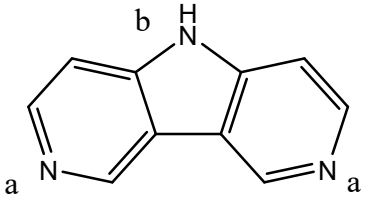
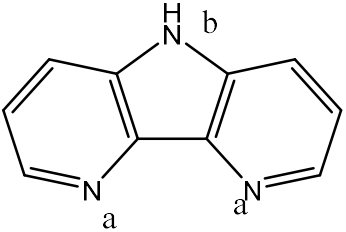
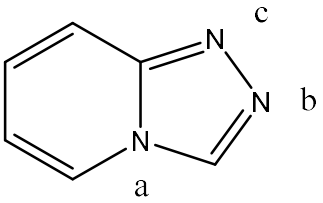
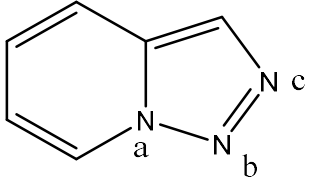
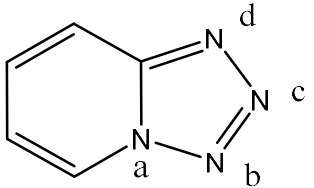
20		pyridinic	-70.75	-53.90	DMSO	1
22		pyridinic	-54.88	-70.80	DMSO	1
23		pyridinic	-58.17	-67.50	DMSO	1
24		pyridinic	-46.77	-76.80	DMSO	1
25		graphitic (tertiary)	50.29	-171.40	DMSO	1
27		pyrrolic	106.39	-230.00	DMSO	1
28		pyrrolic	132.57	-254.10	CDCl <sub>3</sub>	1
29		pyrrolic	147.69	-262.80	DMSO	1
30		graphitic (tertiary)	84.18	-212.40	DMSO	1

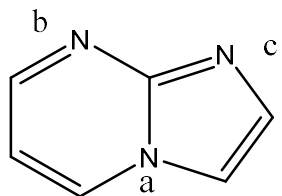
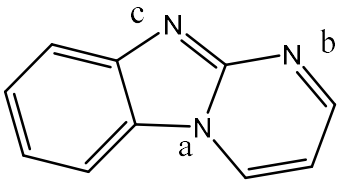
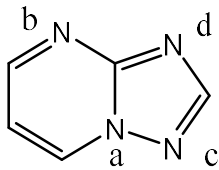
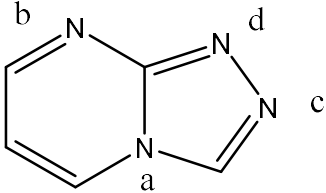
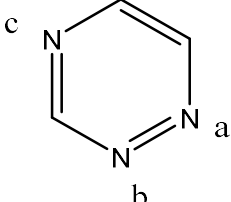
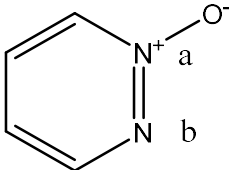
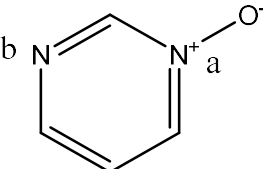
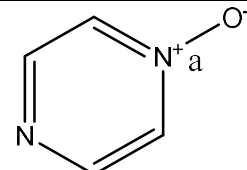
38		pyrrol	-0.89	-123.70	DMSO	1
39		pyrrol	6.69	-131.50	DMSO	1
40		oxazole	-129.89	2.70	DMSO	1
43		graphitic (tertiary)	61.07	-189.04	DMSO	1
49		graphitic (tertiary)	67.53	-192.40	DMSO	1
13a		pyridinic	-26.34	-97.80	DMSO	1
13b		pyridinic	-37.53	-86.50	DMSO	1
15a		pyridinic	-75.67	-51.70	DMSO	1
15b		pyridinic	-73.04	-52.70	DMSO	1
15c		pyridinic	-67.91	-57.70	DMSO	1
16a		pyridinic	-82.86	-49.10	DMSO	1
16b		pyridinic	-81.39	-45.00	DMSO	1
16c		pyridinic	-69.56	-62.20	DMSO	1
17a		pyridinic	-81.66	-52.20	DMSO	1
17b		pyridinic	-80.62	-46.60	DMSO	1
17c		pyridinic	-50.85	-73.80	DMSO	1
17d		pyridinic	-35.80	-92.10	DMSO	1

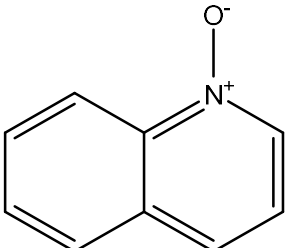
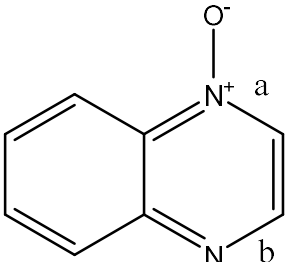
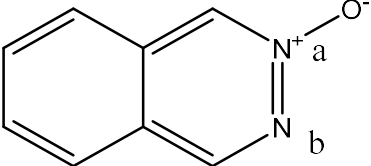
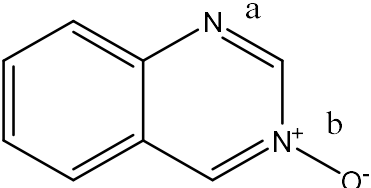
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18b		N=N	-163.66	23.40	DMSO	1
18c		N=N	-214.12	68.20	DMSO	1
21a		pyridinic	-91.22	-43.60	DMSO	1
21b		pyridinic	-85.18	-49.60	DMSO	1
26a		pyridinic	30.21	-160.70	DMSO	1
26b		pyridinic	23.47	-146.10	DMSO	1
26c		graphitic (tertiary)	59.30	-185.10	DMSO	1
31a		pyrrolic	120.52	-234.00	solid	1
31b		pyrrolic	15.77	-126.00	solid	1
33a		pyrrolic	55.05	-180.80	CDCl <sub>3</sub>	1
33b		pyrrolic	-51.09	-76.50	CDCl <sub>3</sub>	1
34a		pyrrolic	-52.00	-65.00	DMSO	1
34b		pyrrolic	85.87	-195.00	DMSO	1
36a		pyrrolic	22.29	-144.00	neat	1
36b		pyrrolic	-113.99	-12.00	neat	1
36c		pyrrolic	-98.56	-30.00	neat	1



37a		N=N (negative)	-134.22	-11.40	solid	1
37b		N=N (negative)	-55.84	-56.40	solid	1
41a		oxazole	-109.82	-20.00	Et <sub>2</sub> O	1
41b		pyrryl	15.11	-140.00	Et <sub>2</sub> O	1
42a		pyrryl	18.77	-159.00	CH <sub>2</sub> Cl <sub>2</sub>	1
42b		N=N (positive)	-3.34	-105.00	CH <sub>2</sub> Cl <sub>2</sub>	1
44a		pyrryl	10.63	-139.19	DMSO	1
44b		graphitic (tertiary)	50.87	-178.04	DMSO	1
45a		pyrryl	-21.88	-107.30	DMSO	1
45b		graphitic (tertiary)	59.17	-185.30	DMSO	1
46a		pyrryl	-27.20	-93.20	DMSO	1
46b		graphitic (tertiary)	17.90	-144.10	DMSO	1
47a		pyrryl	23.75	-139.80	DMSO	1
47b		pyrryl	-17.82	-102.00	DMSO	1
47c		graphitic (tertiary)	12.66	-148.10	DMSO	1
50a		graphitic (tertiary)	46.39	-165.40	DMSO	1
50b		pyrryl	-21.24	-102.10	DMSO	1

51a		pyridinic	-9.32	-123.30	EtOH	1
51b		pyrrolic	127.06	-243.90	EtOH	1
52a		pyridinic	-8.43	-111.20	DMSO	1
52b		pyrrolic	132.72	-251.10	DMSO	1
53a		pyridinic	-61.28	-64.90	DMSO	1
53b		pyrrolic	158.50	-268.30	DMSO	1
54a		pyridinic	-39.46	-88.30	DMSO	1
54b		pyrrolic	145.81	-256.50	DMSO	1
55a		pyridinic	-53.37	-78.60	DMSO	1
55b		pyrrolic	158.52	-271.10	DMSO	1
56a		graphitic (tertiary)	57.05	-183.60	DMSO	1
56b		pyrrolic	-91.43	-49.50	DMSO	1
56c		pyrrolic	-59.56	-80.90	DMSO	1
57a		graphitic (tertiary)	-4.42	-120.60	DMSO	1
57b		N=N	-83.00	-44.20	DMSO	1
57c		N=N	-106.53	-24.90	DMSO	1
58a		graphitic (tertiary)	2.66	-128.30	DMSO	1
58b		N=N	-88.39	-34.40	DMSO	1
58c		N=N	-154.98	18.30	DMSO	1

59a		graphitic (tertiary)	63.98	-190.80	DMSO	1
59b		pyridinic	-32.09	-100.30	DMSO	1
59c		pyrryl	6.89	-141.50	DMSO	1
60a		graphitic (tertiary)	80.59	-206.10	DMSO	1
60b		pyridinic	-30.84	-100.50	DMSO	1
60c		pyrryl	25.87	-158.80	DMSO	1
61a		graphitic (tertiary)	26.90	-153.30	DMSO	1
61b		pyridinic	-28.52	-105.00	DMSO	1
61c		pyrryl	-14.57	-102.10	DMSO	1
61d		pyrryl	19.67	-149.40	DMSO	1
62a		graphitic (tertiary)	71.35	-196.90	DMSO	1
62b		pyridinic	-32.69	-103.50	DMSO	1
62c		pyrryl	-93.91	-49.40	DMSO	1
62d		pyrryl	-63.60	-84.30	DMSO	1
8a		N=N	-189.15	39.80	DMSO	1
8b		N=N	-142.25	1.80	DMSO	1
8c		pyridinic	-36.30	-62.20	DMSO	1
old104a		N-oxide	-76.5745	-55.1	DMSO	2
old104b		pyridinic	-97.0977	-33.6	DMSO	2
old105a		N-oxide	-41.7641	-90	DMSO	2
old105b		pyridinic	-44.5874	-80	DMSO	2
old106a		N-oxide	-61.0246	-75	DMSO	2
old106b		pyridinic	-38.0659	-70.4	DMSO	2

old107		N-oxide	-37.8996	-101.5	DMSO	3
old109a		N-oxide	-50.44	-76.8	DMSO	3
old109b		pyridinic	-38.4959	-80.7	DMSO	3
old110a		N-oxide	-65.1271	-68.9	DMSO	3
old110b		pyridinic	-96.7976	-53.2	DMSO	3
old112a		N-oxide	-31.7997	-89.5	DMSO	3
old112b		pyridinic	-39.331	-89.5	DMSO	3

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