Supporting Information

Catalytic formation of N3-Substituted Quinazoline-2,4(1H,3H)-diones by Pd(II)EN@GO composite and its mechanistic investigation through DFT calculations

Surajit Biswas[a], Resmin Khatun[a,#], Malay Dolai[b,#], Imdadul Haque Biswas[a], Najirul Haque[a], Manideepa Sengupta[a,c], Md Sarikul Islam[a], Sk Manirul Islam*[a]

[a]*Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India.*

[b]*Department of Chemistry, Prabhat Kumar College, Purba Medinipur 721401, India.*

[c]*Refinery Technology Division, CSIR-Indian Institute of Petroleum, Dehradun, 248005, Uttarakhand, India.*

 # Authors contributed equally.

Materials and reagents: All solvents and reagents are commercially available and purchased from Merck (India). Graphite flakes was procured from Sigma-Aldrich. All solvents of reagent grade were dried using standard methods prior to use.

Physical measurements: Fourier-transform infrared spectroscopy of samples has been done through a Perkin-Elmer FTIR 783 spectrophotometer using potassium bromide pellets. The crystallinity nature of the materials were studied through powder X-Ray diffraction patterns on a Bruker D8 Advance X-ray diffractometer using Cu-K_α radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 40 mA. Raman spectra of both GO and catalyst was measured on STR500 Raman Spectrometer (Cornes Technology Make) by 514 nm excitation wavelength having 50 mW power. The particle size and structural morphology of the catalyst was investigated through FE-SEM and HRTEM images were carried out through JEOL JEM 6700 and JEOL 1400 Plus, respectively. N_2 adsorption desorption study was carried out through Quantachrome (Model- NOVA 1000e). NMR spectra were done on a Bruker AMX-400 NMR spectrophotometer using tetramethylsilane as internal standard. Optima 2100DV (Perkin Elmer) inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used for measurement of palladium amount present in the composite materials.

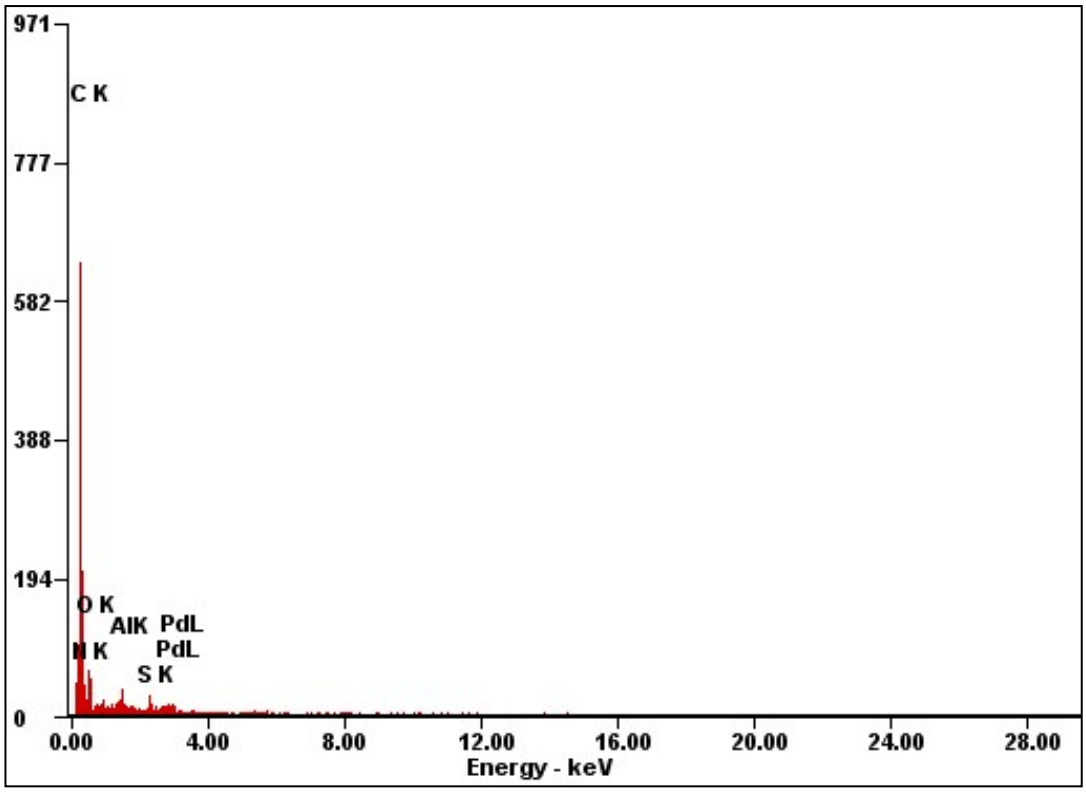
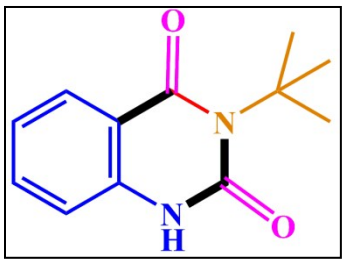


Figure S1: EDX of Pd(II)EN@GO composite from FE-SEM.

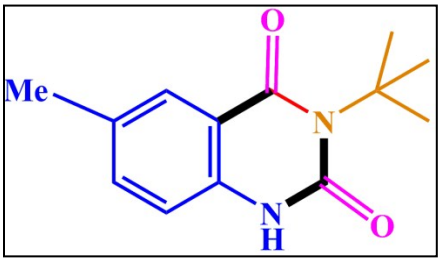
Characterization of products obtanined from catalytic reaction[1]



3-*tert*-butylquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3466, 3058, 2972, 2924, 2852, 1718, 1673,1591, 1437, 1189, 1120, 752, 720, 695, 540.

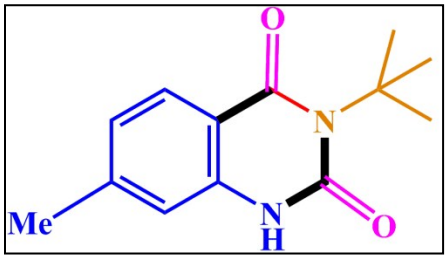
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.93 (d, J =7.6 Hz, 1H), 7.44-7.48 (m, 1H), 7.06 (t, J =7.6 Hz, 1H), 6.89 (d, J =8 Hz, 1H), 1.72 (s, 9H) ppm.



3-*tert*-butyl-6-methylquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3470, 3351, 3200, 2926, 1717, 1645, 1533, 1432, 1290, 1160, 816, 783, 654, 544.

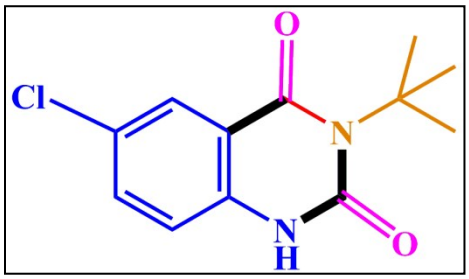
^{1}H NMR (400 MHz, $CDCl_3$) 9.64 (s, 1H), 7.83 (s, 1H), 7.35 (d, J =2 Hz, 1H), 6.86 (d, J =8 Hz, 1H), 2.37 (s, 3H), 1.78 (s, 9H) ppm.



3-*tert*-butyl-7-methylquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3420, 3341, 3204, 2931, 1712, 1643, 1535, 1439, 1285, 1157, 812, 733, 644, 524.

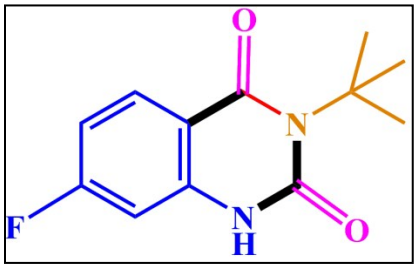
^{1}H NMR (400 MHz, $CDCl_3$) 8.80 (s, 1H), 7.87 (s, 1H), 7.42 (d, J =8 Hz, 1H), 6.50 (d, J =8.4 Hz, 1H), 2.22 (s, 3H), 1.18 (s, 9H) ppm.



3-*tert*-butyl-6-chloroquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3450, 3350, 195, 3073, 2995, 2854, 1719, 1644, 1542, 1467, 1366, 1288, 1232, 819, 771, 718, 647, 517.

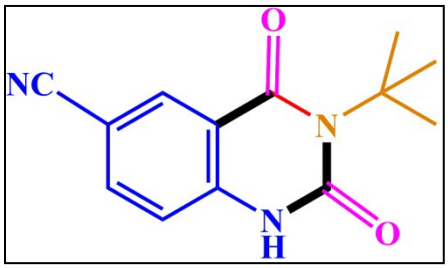
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.91 (d, J =2.4 Hz, 1H), 7.39 (dd, J =8.8, 2.4 Hz, 1H), 6.84 (d, J =8.4 Hz, 1H), 1.69 (s, 9H) ppm.



3-*tert*-butyl-7-fluoroquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3355, 3205, 3126, 3069, 2924, 2853, 1719, 1654, 1619, 1482, 1380, 1292, 1248, 1169, 1125, 860, 772, 662, 490.

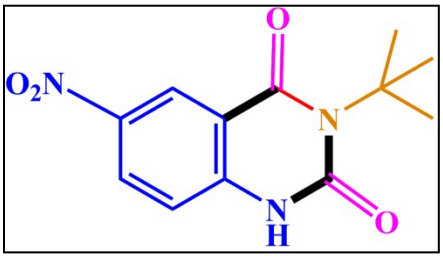
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.95-7.98 (m, 1H), 6.78-6.82 (m, 1H), 6.58 (dd, J =9.0, 2.0 Hz, 1H), 1.72 (s, 9H) ppm.



3-*tert*-butyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline-6-carbonitrile

White solid, **IR** (KBr, ν, cm^{-1}): 3343, 3212, 3129, 3057, 2931, 2848, 1713, 1643, 1623, 1486, 1382, 1288, 1248, 1174, 1127, 855, 770, 666, 485.

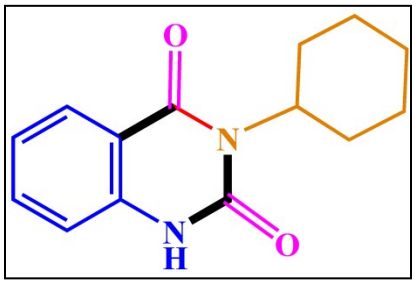
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.55-7.59 (m, 1H), 7.49 (d, J =7.2 Hz, 1H), 6.99 (d, J =8.0 Hz, 1H), 1.70 (s, 9H) ppm.



3-*tert*-butyl-6-nitroquinazoline-2,4(1H,3H)-dione

Pale yellow solid, **IR** (KBr, ν, cm^{-1}): 3335, 3215, 3106, 3078, 2926, 2867, 1709, 1644, 1623, 1485, 1376, 1276, 1238, 1139, 1118, 865, 778, 668, 480.

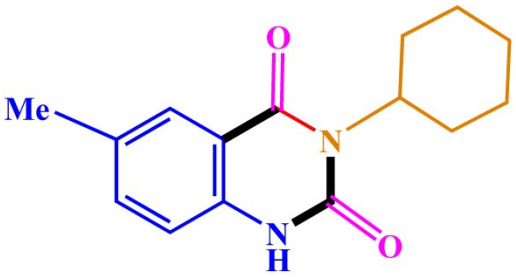
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.401 (s, 1H), 8.25-8.27 (m, 1H), 8.03 (d, , J =7.6 Hz, 1H), 7.54 (t, J =8.0, 1H), 1.403 (s, 9H) ppm.



3-cyclohexylquinazoline-2,4(1H,3H)-dione

Light yellow solid, **IR** (KBr, ν, cm^{-1}): 3433, 3313, 3245, 3092, 2925, 2854, 1715, 1618, 1454, 1229, 1165, 1082, 758, 708.

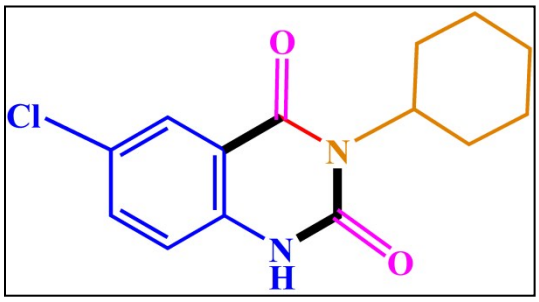
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (dd, J = 8.6, 1.6 Hz, 1H), 7.29-7.33 (m, 1H), 6.64 -6.68 (m, 2H), 6.28 (s, 1H), 3.83-3.91 (m, 1H), 1.22-2.01 (m, 10H) ppm.



3-Cyclohexyl-6-methyl-1H-quinazoline-2,4-dione

Yellow solid, **IR** (KBr, ν, cm^{-1}): 3445, 3340, 3284, 2924, 2853, 1709, 1627, 1584, 1517, 1483, 1298, 1244, 1171, 823, 764, 678, 644.

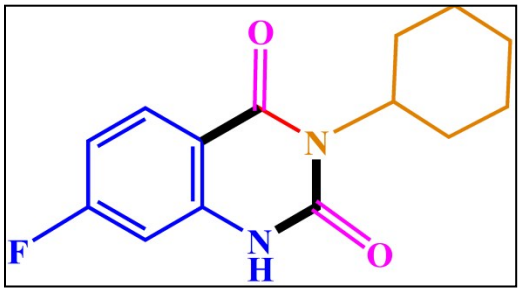
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.13 (dd, J = 8.4, 2.0 Hz, 1H), 6.68 (s, 1H), 6.58 (d, J = 8.4 Hz, 1H), 3.79-3.91 (m, 1H), 2.38 (s, 3H), 1.23-2.32 (m, 10H) ppm.



6-chloro-3-cyclohexylquinazoline-2,4(1H,3H)-dione

Yellow solid, **IR** (KBr, ν, cm^{-1}): 3445, 3333, 3277, 2923, 2851, 1705, 1631, 1580, 1524, 1471, 1295, 1235, 1200, 887, 821, 728, 630.

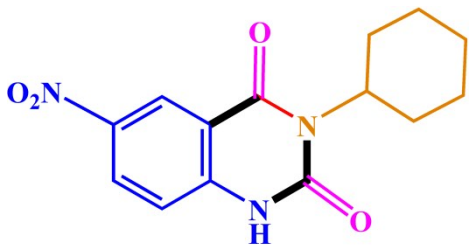
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 2.4 Hz, 1H), 7.24 (dd, J = 9.4, 2.4 Hz, 1H), 6.80 (s, 1H), 6.60 (d, J = 9.2 Hz, 1H), 3.83-3.88 (m, 1H), 1.21-2.04 (m, 10H) ppm.



3-cyclohexyl-7-fluoroquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3423, 3305, 3246, 3095, 2936, 2858, 1708, 1621, 1556, 1446, 1227, 1135, 1076, 855, 779, 703.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (m, 1H), 6.80 (s, 1H), 6.29-6.41 (m, 2H), 3.80-3.88 (m, 1H), 1.22-2.00 (m, 10H) ppm.



3-cyclohexyl-6-nitroquinazoline-2,4(1H,3H)-dione

White solid, **IR** (KBr, ν, cm^{-1}): 3453, 3315, 3245, 3078, 2938, 2864, 1712, 1611, 1542, 1444, 1232, 1139, 1090, 865, 790, 706.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.74 (m, 2H), 7.64-7.71 (m, 1H), 6.51 (s, 1H), 1.17-2.05 (m, 10H) ppm.

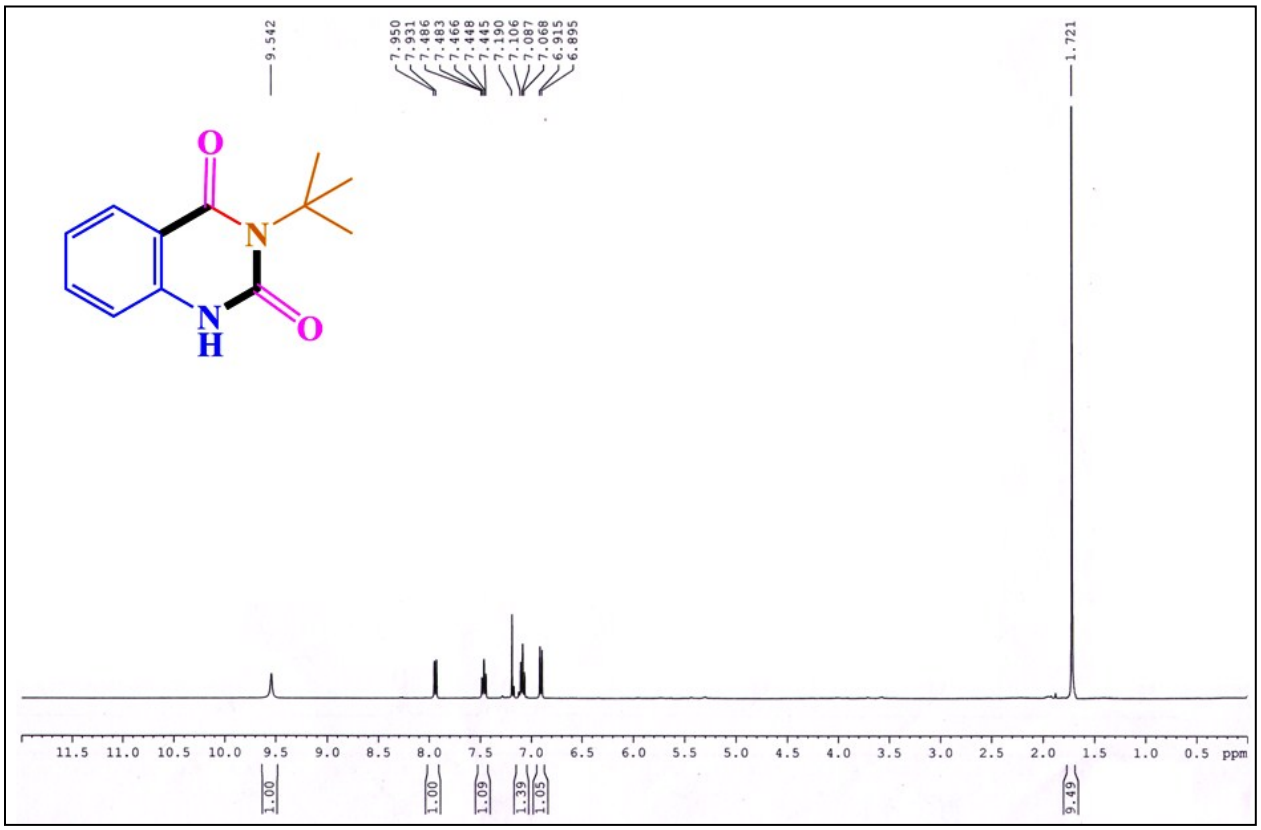


Figure S2: ^{1}H NMR of 3-*tert*-butylquinazoline-2,4(1H,3H)-dione.

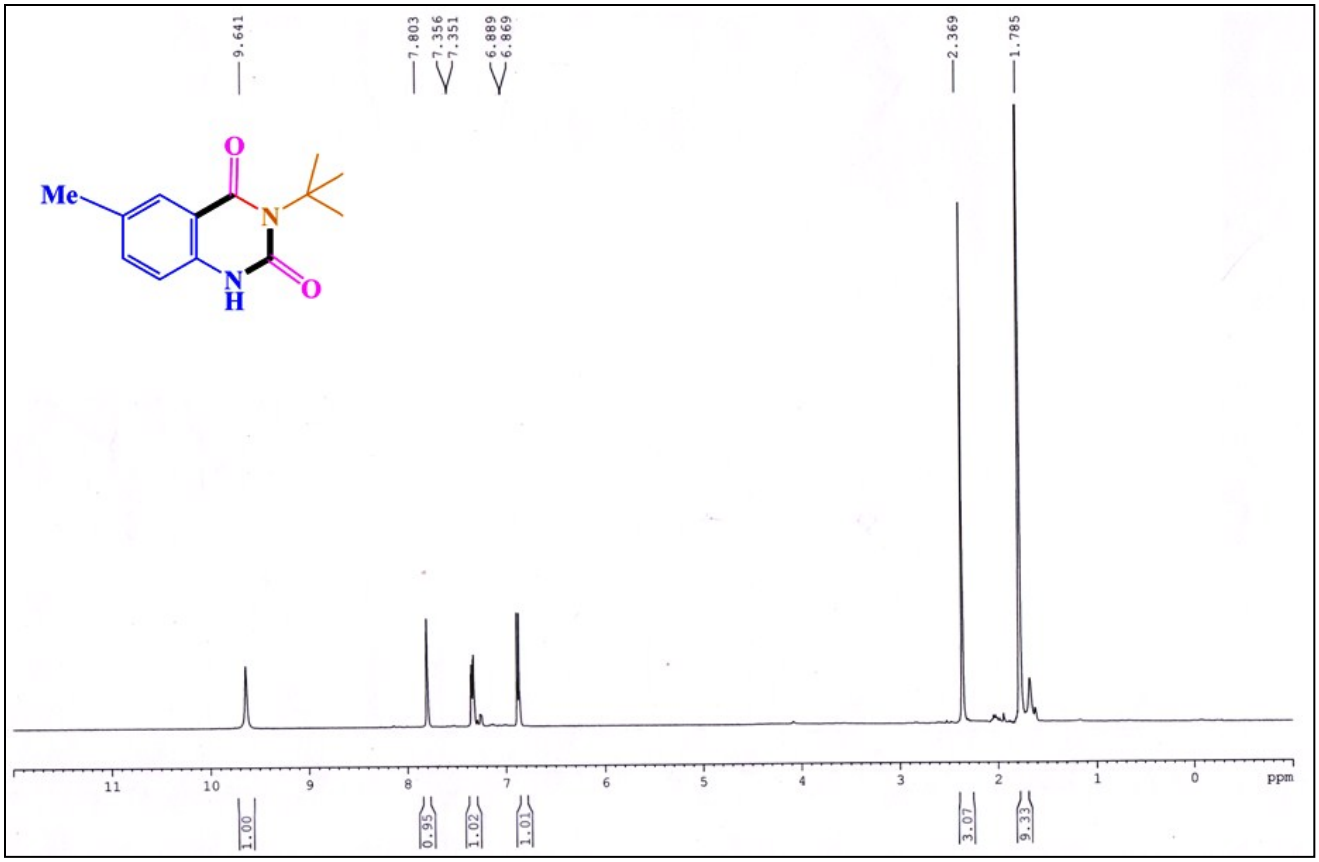


Figure S3: ^{1}H NMR of 3-*tert*-butyl-6-methylquinazoline-2,4(1H,3H)-dione.

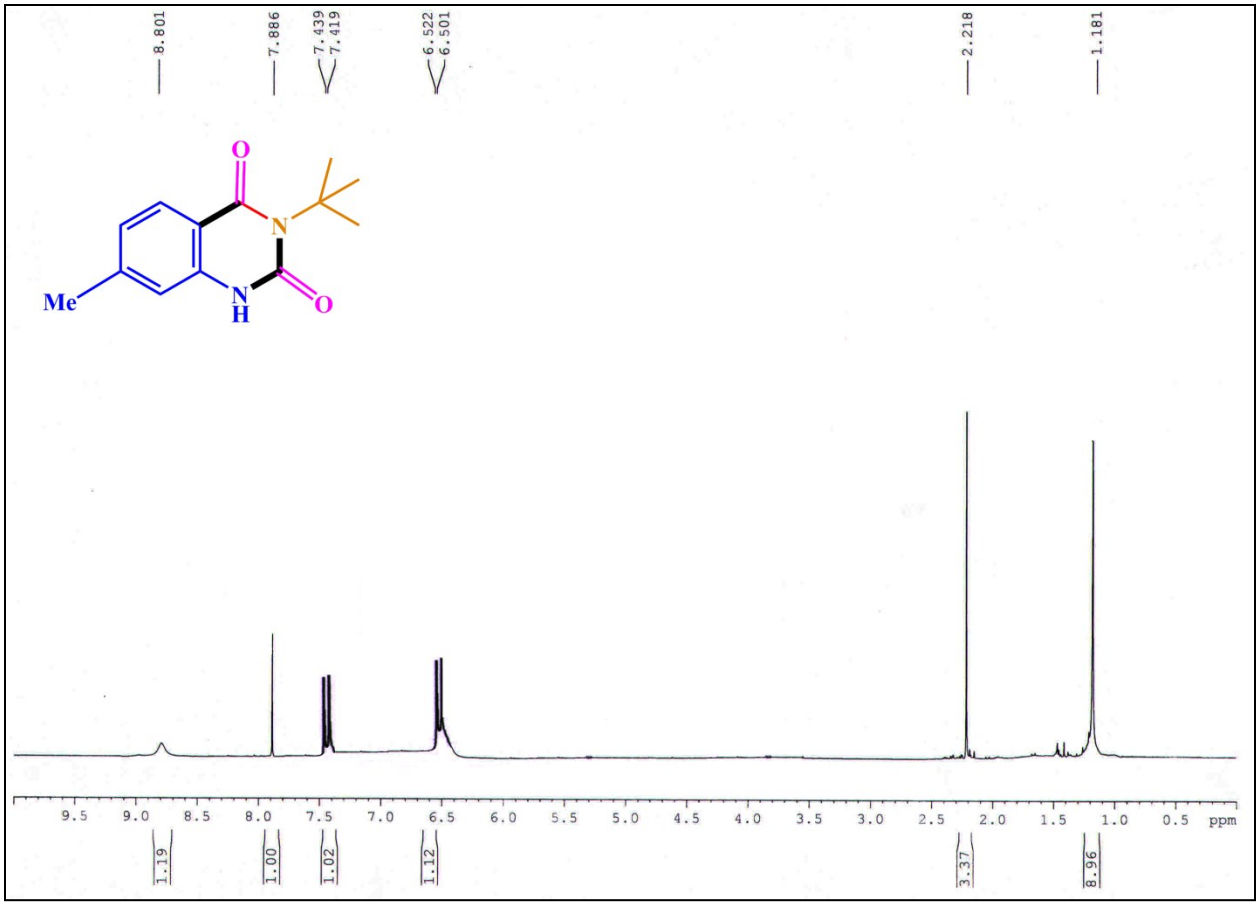


Figure S4: ^{1}H NMR of 3-*tert*-butyl-7-methylquinazoline-2,4(1H,3H)-dione.

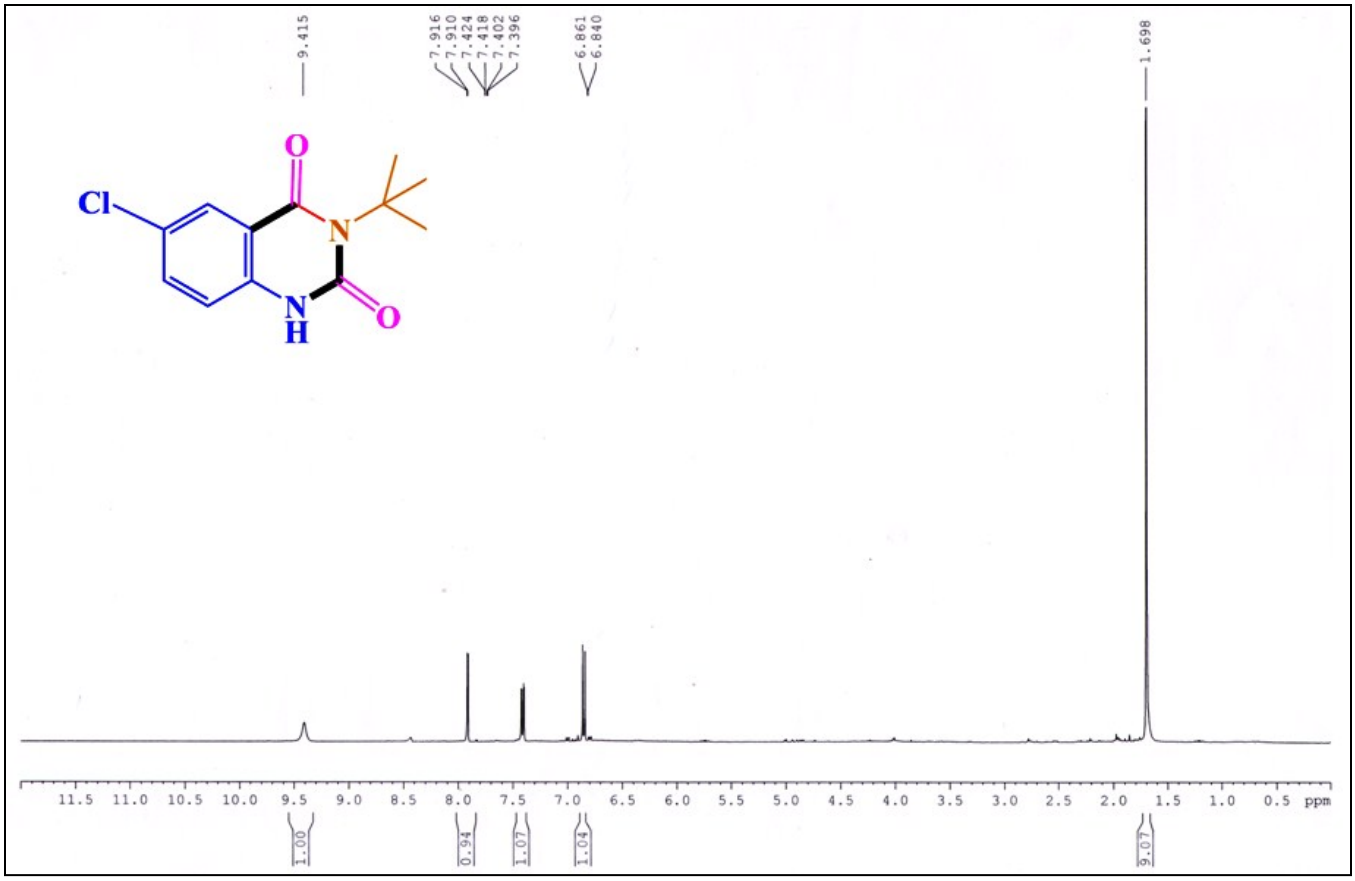


Figure S5: ^{1}H NMR of 3-*tert*-butyl-6-chloroquinazoline-2,4(1H,3H)-dione.

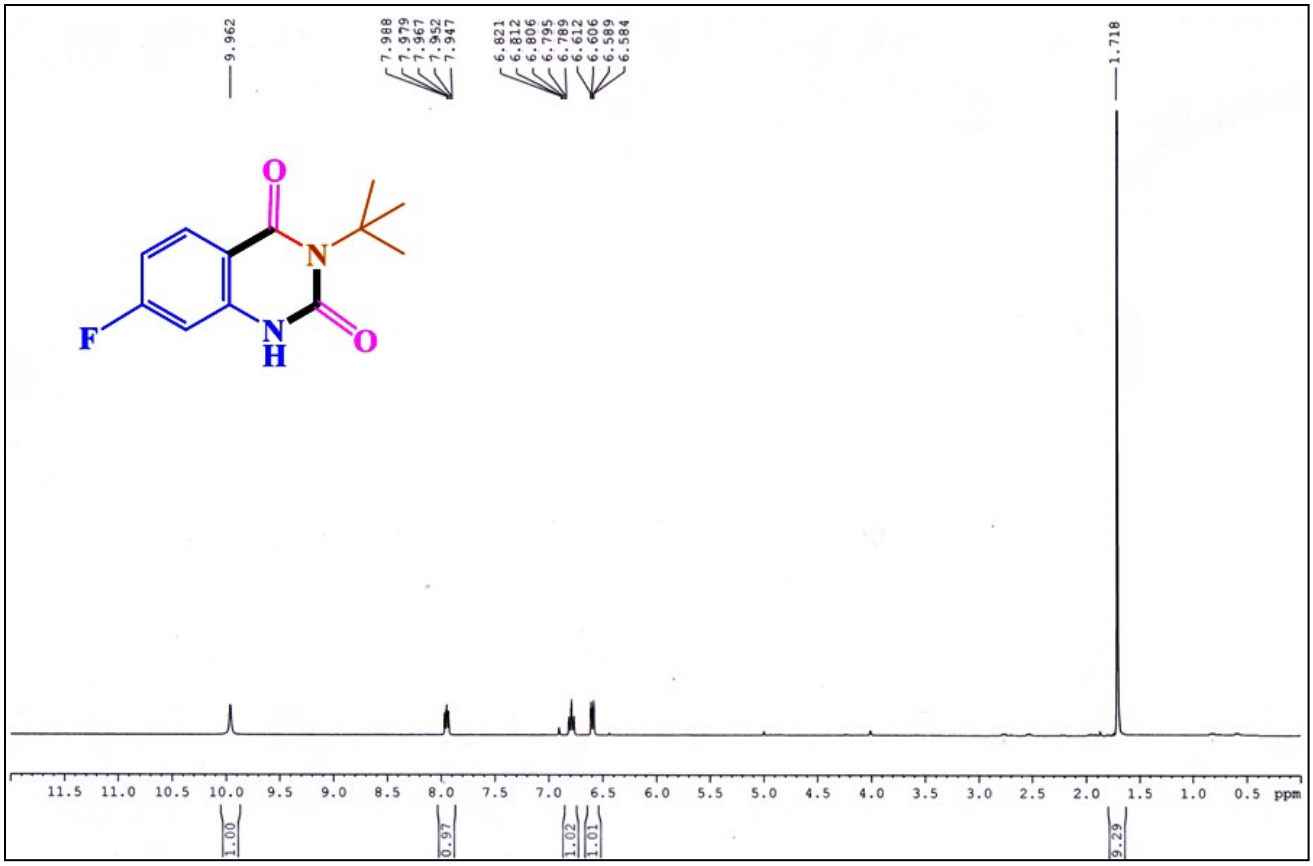


Figure S6: ^{1}H NMR of 3-*tert*-butyl-7-fluoroquinazoline-2,4(1H,3H)-dione.

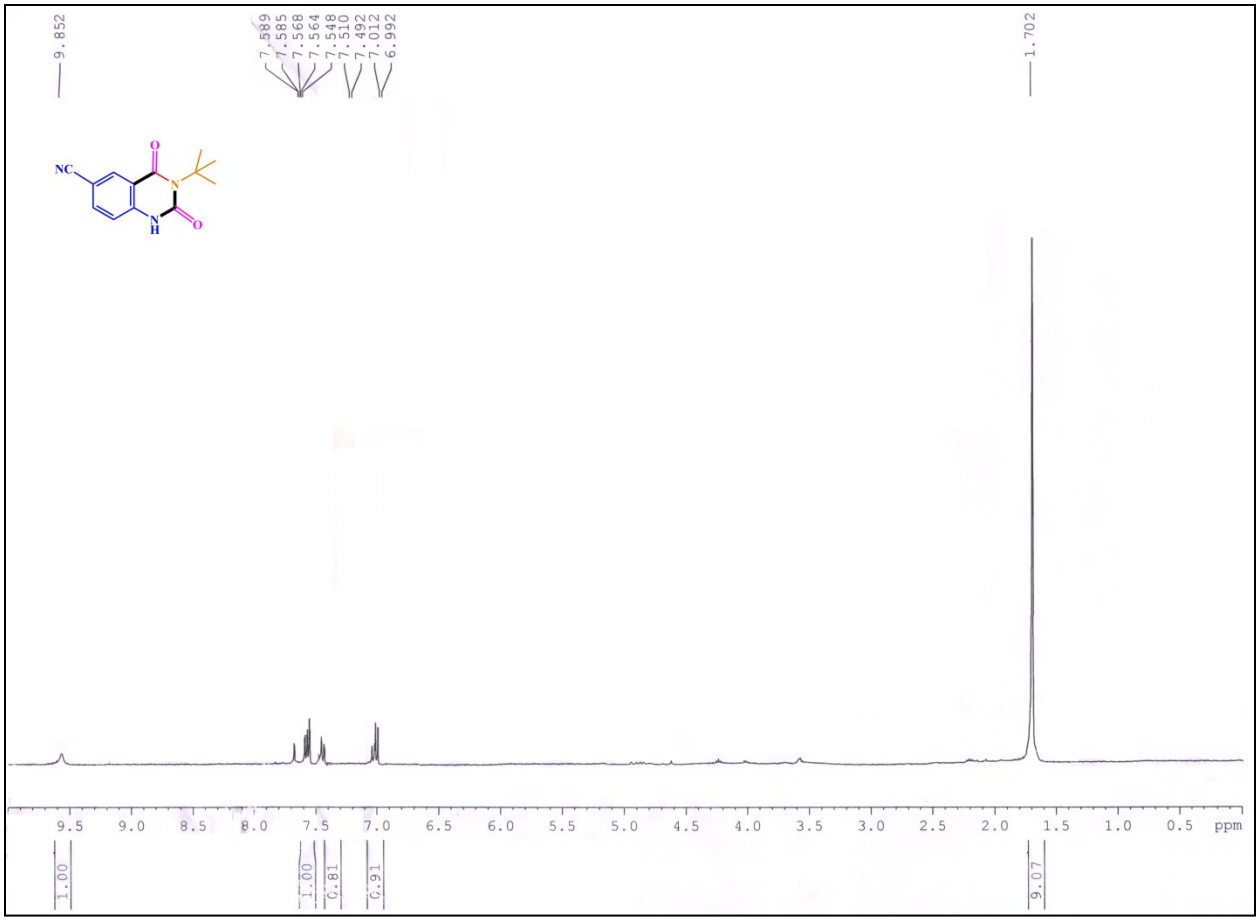


Figure S7: ^{1}H NMR of 3-tert-butyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline-6-carbonitrile.

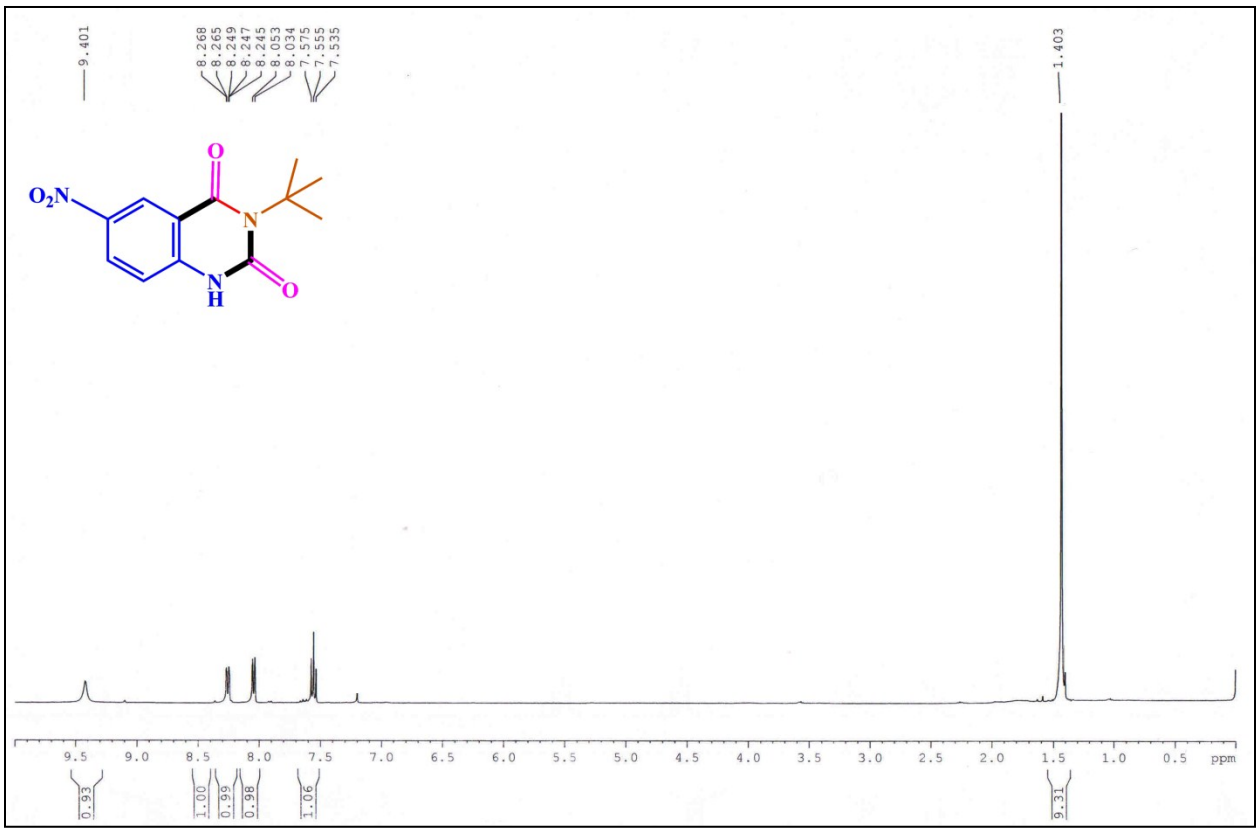


Figure S8: ^{1}H NMR of 3-*tert*-butyl-6-nitroquinazoline-2,4(1H,3H)-dione.

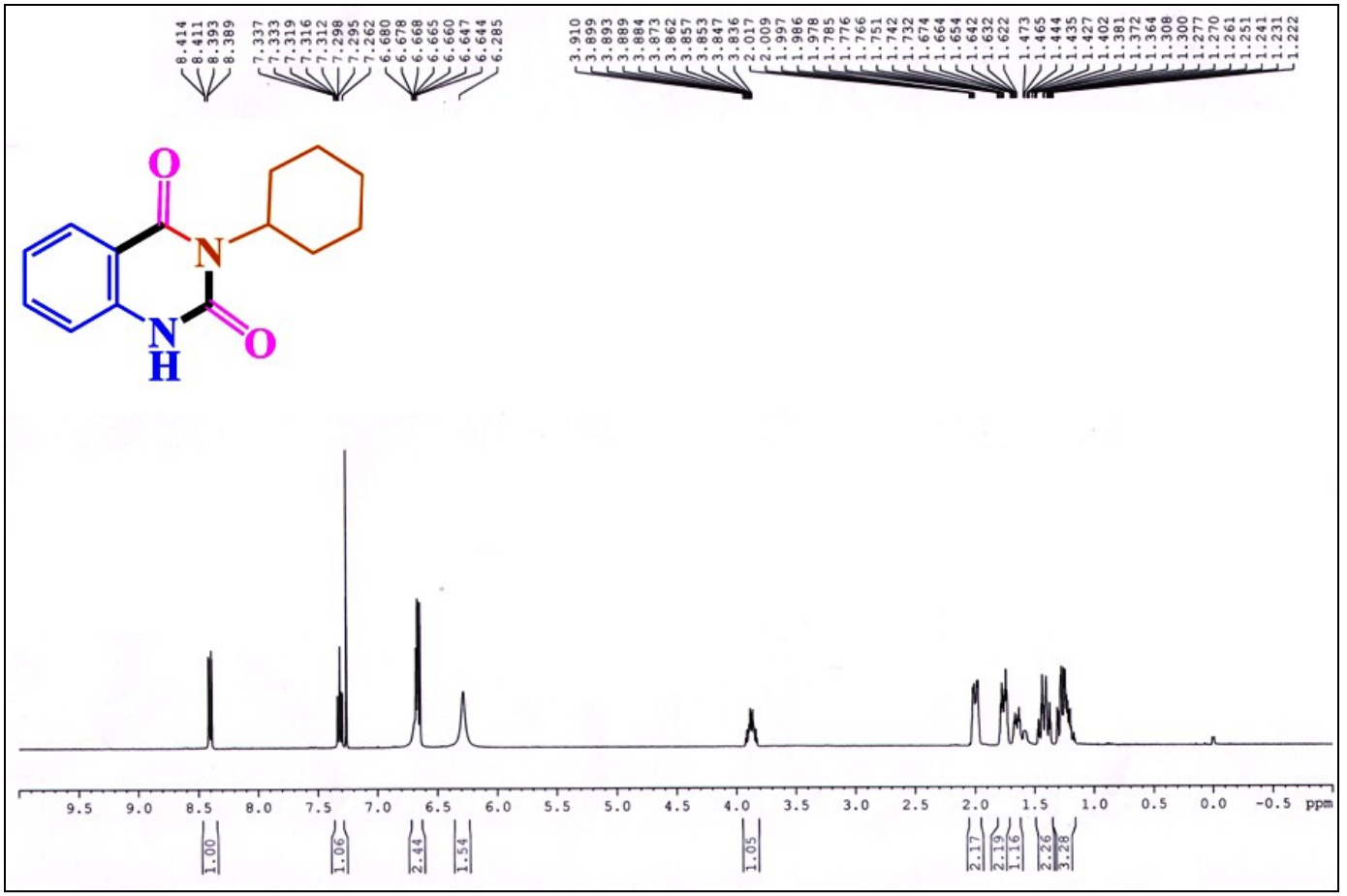


Figure S9: ^{1}H NMR of 3-cyclohexylquinazoline-2,4(1H,3H)-dione.

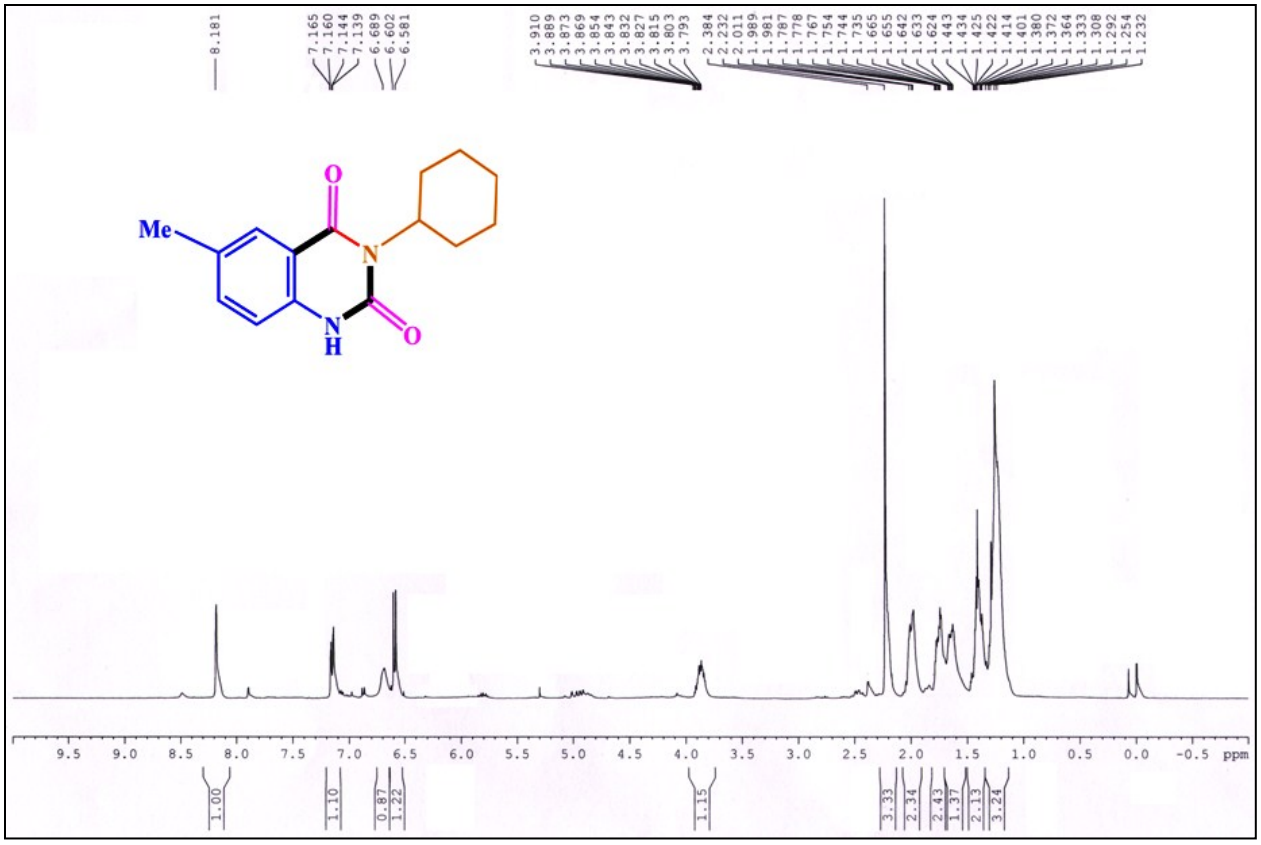


Figure S10: ^{1}H NMR of of 6-methyl-3-cyclohexylquinazoline-2,4(1H,3H)-dione.

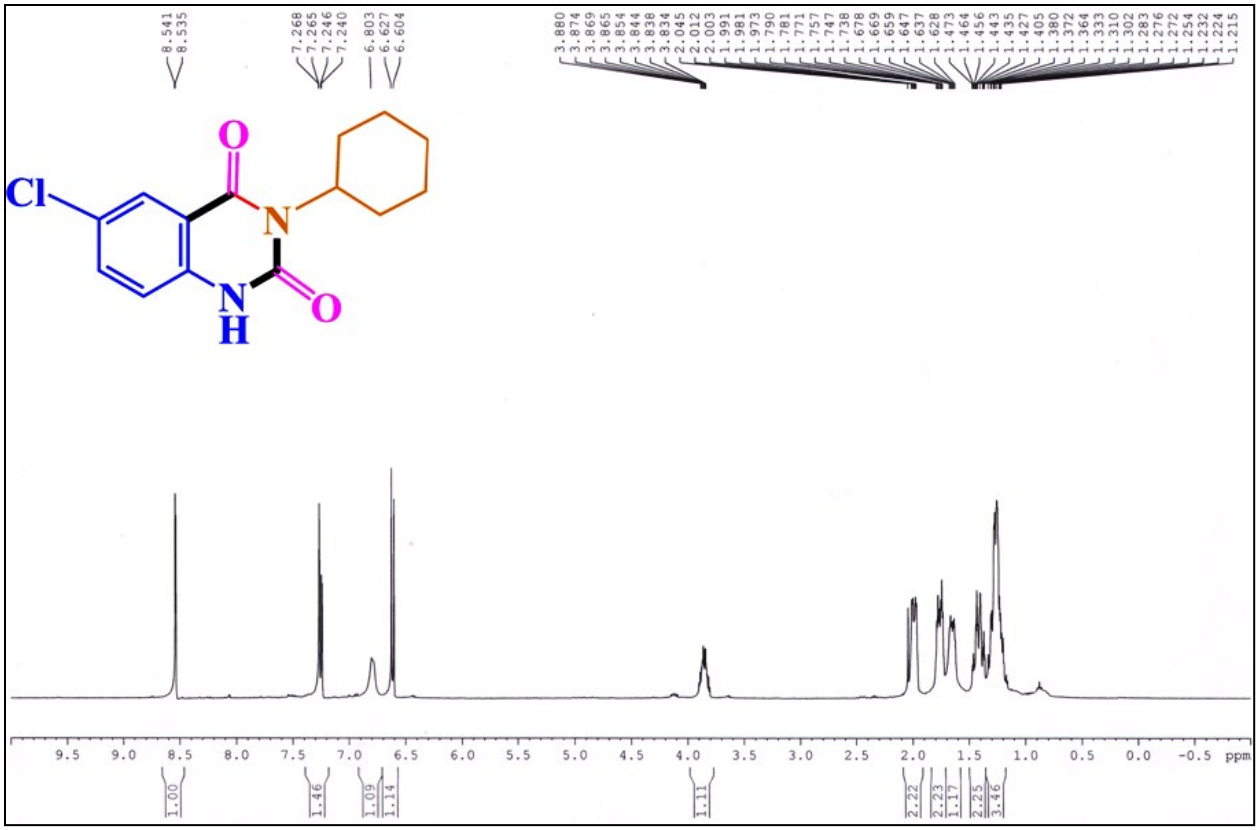


Figure S11: ^{1}H NMR of 6-chloro-3-cyclohexylquinazoline-2,4(1H,3H)-dione.

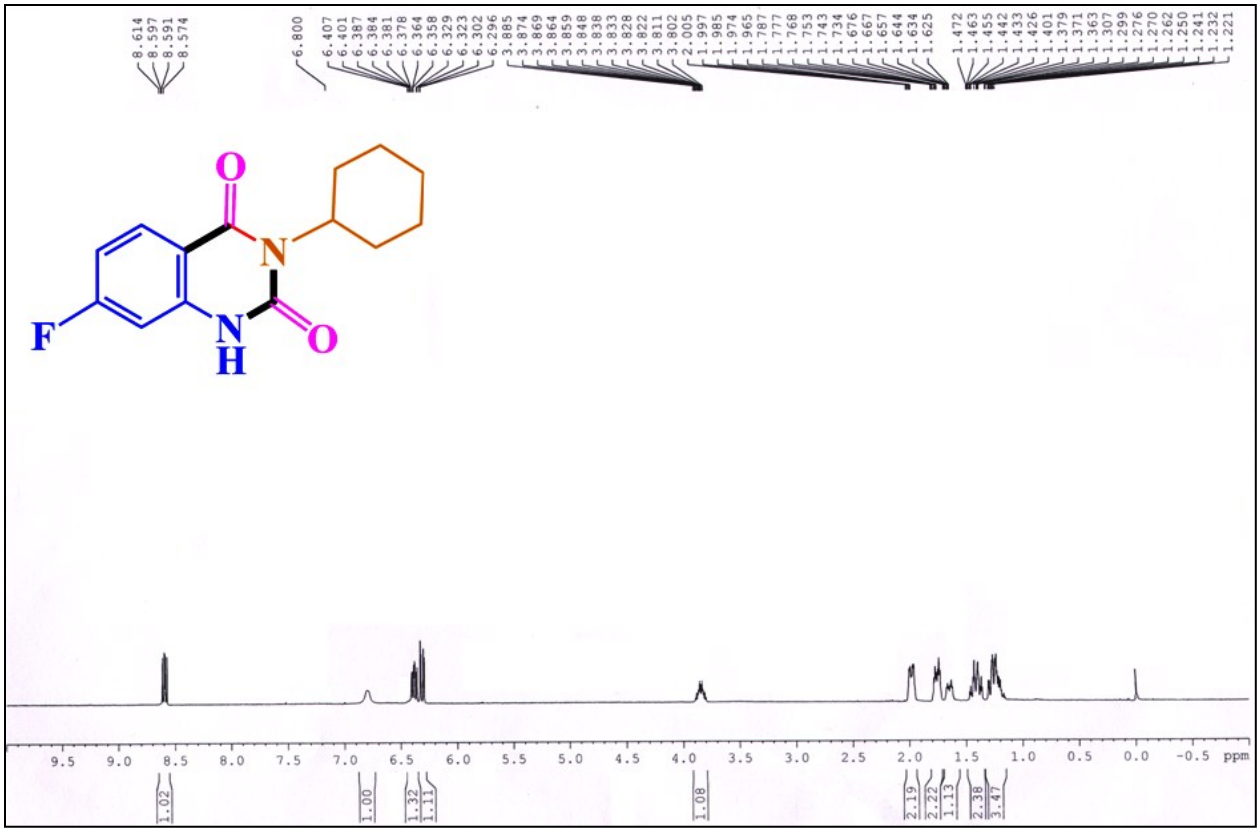


Figure S12: ^{1}H NMR of 3-cyclohexyl-7-fluoroquinazoline-2,4(1H,3H)-dione.

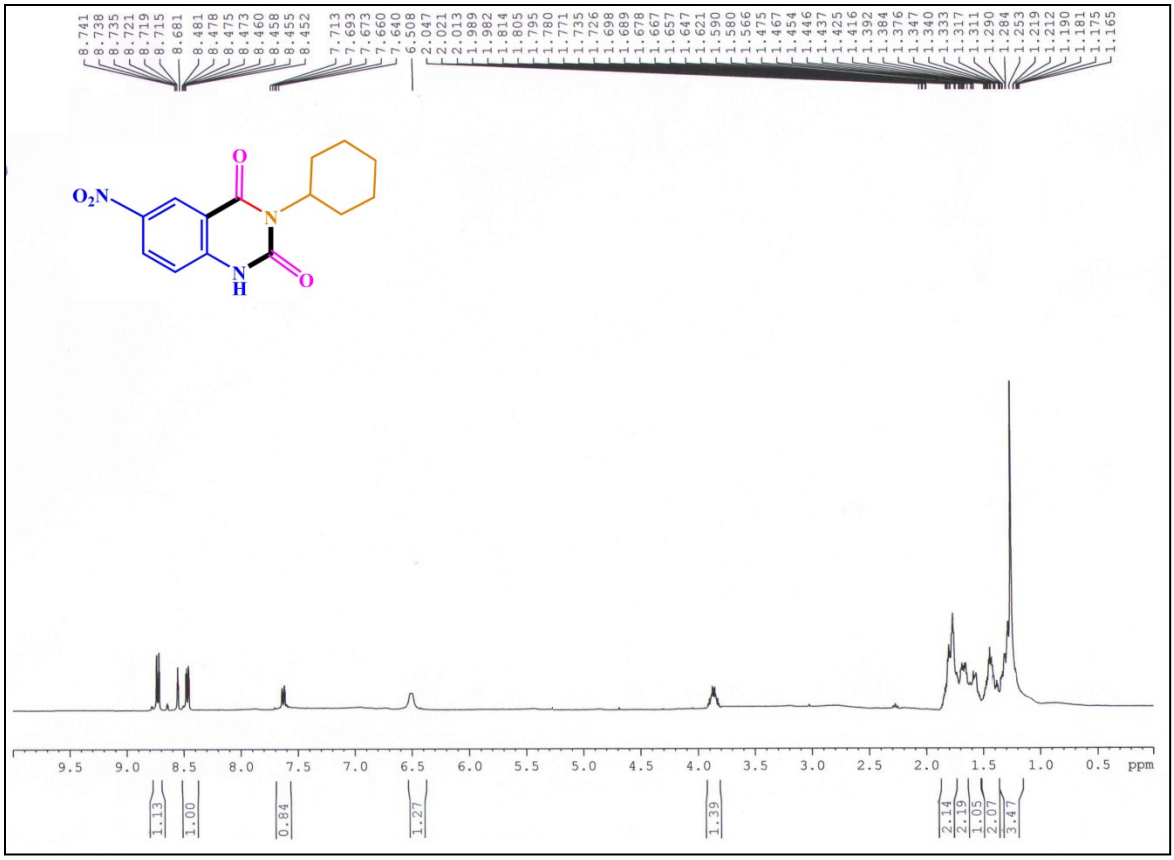


Figure S13: ^{1}H NMR of 3-cyclohexyl-6-nitroquinazoline-2,4(1H,3H)-dione.

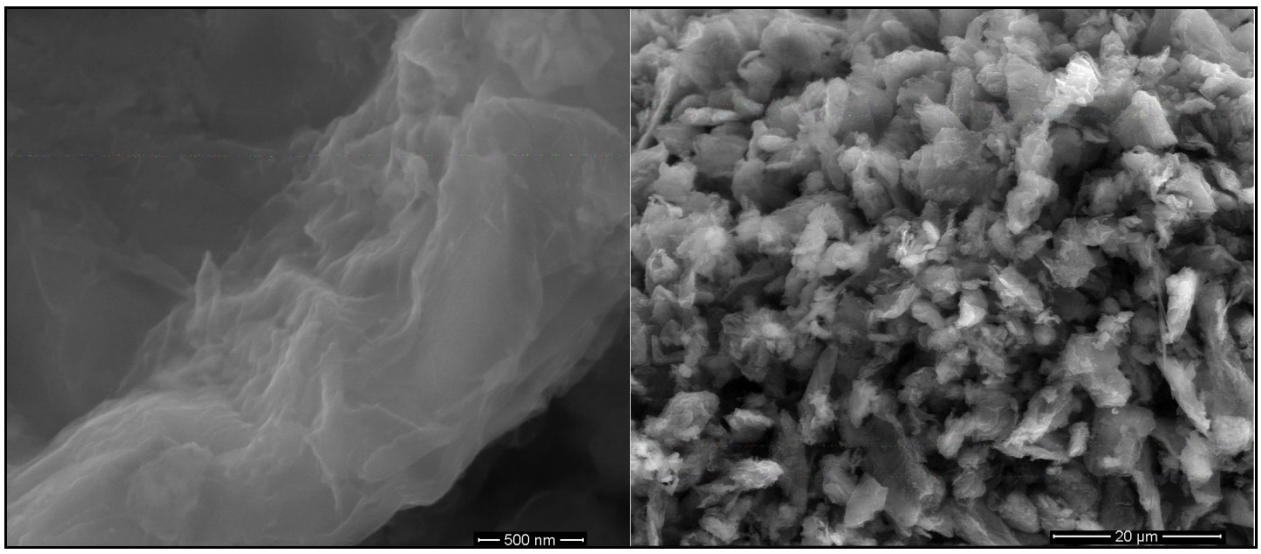


Figure S14: SEM images of reused catalyst.

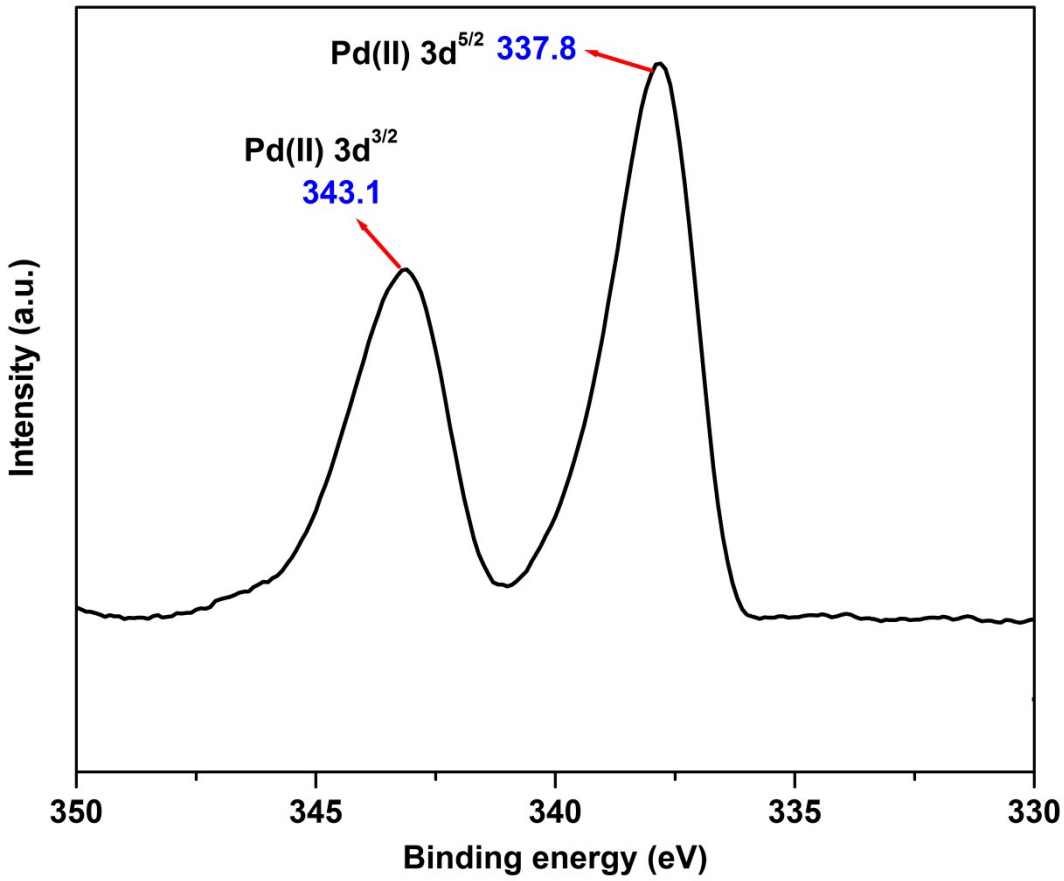


Figure S15: X-ray photoelectron spectra of Pd 3d level of recovered Pd(II)EN@GO catalyst.

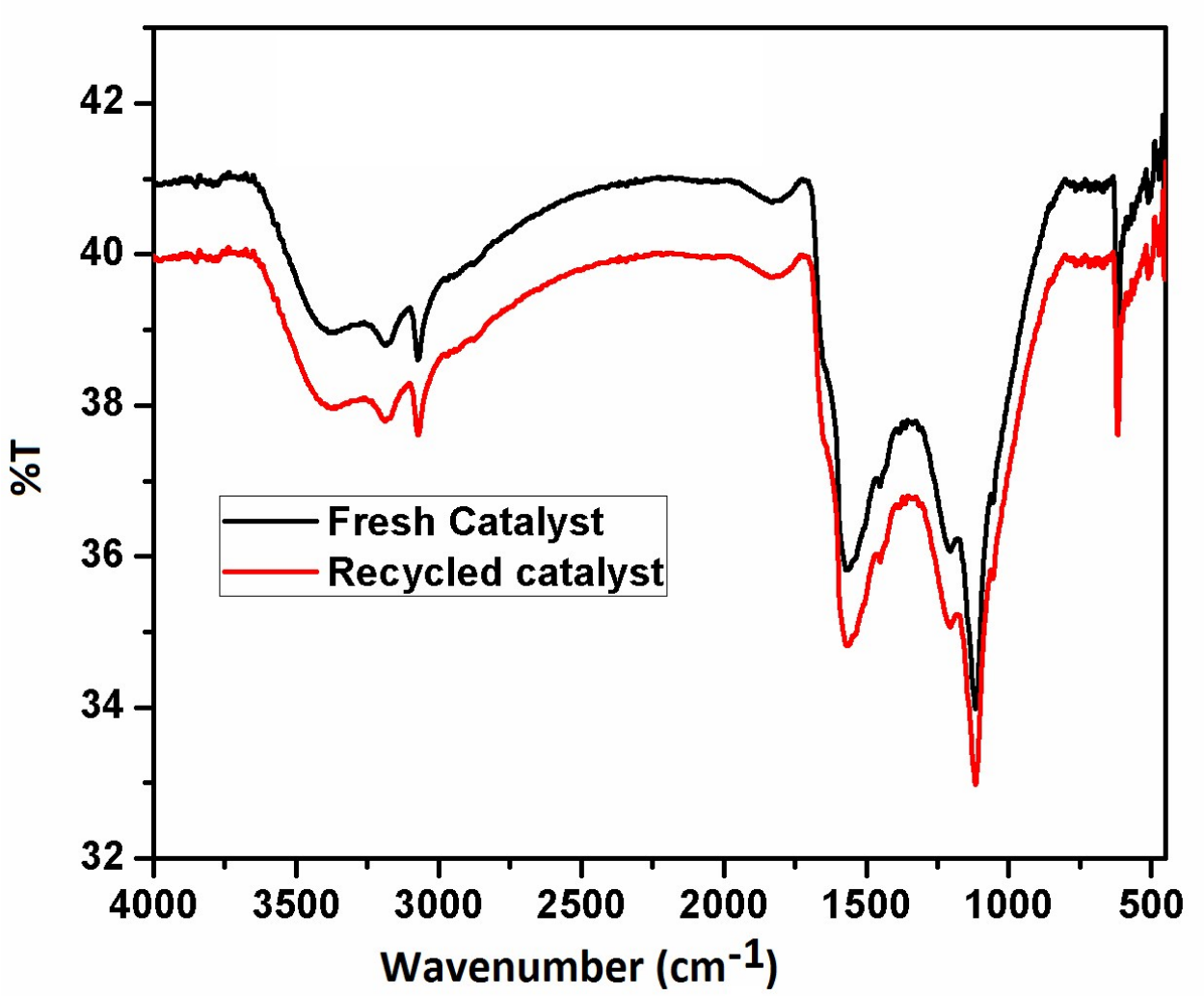


Figure S16: IR spectra of fresh and recycled catalyst.

1 (a) W.-Z. Zhang, H. Li, Y. Zeng, X. Tao and X. Lua, *Chin. J. Chem*., 2018, **36**, 112-118; (b) P. Mampuys, H. Neumann, S. Sergeyev, R. V. A. Orru, H. Jiao, A. Spannenberg, B. U. W. Maes and M. Beller, *ACS Catal*., 2017, **7**, 5549-5556; (c) P. Xu, F. Wang, T.-Q. Wei, L. Yin, S.-Y.Wang and S.-J. Ji, Org. Lett. 2017, **19**, 4484-4487.