SUPPLIMENTARY INFORMATION

on

Tribological studies of some SAPS-free Schiff bases derived from 4-aminoantipyrine and aromatic aldehydes and their synergistic interaction with borate ester

Vinay Jaiswal[¥], Kalyani, Rashmi B. Rastogi[¥]* and Rajesh Kumar[†]

[¥]Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi-221005, India

[†]Department of Mechanical Engineering, Indian Institute of Technology (Banaras Hindu University), Varanasi-221005, India

Corresponding Author: Prof. Rashmi Bala Rastogi

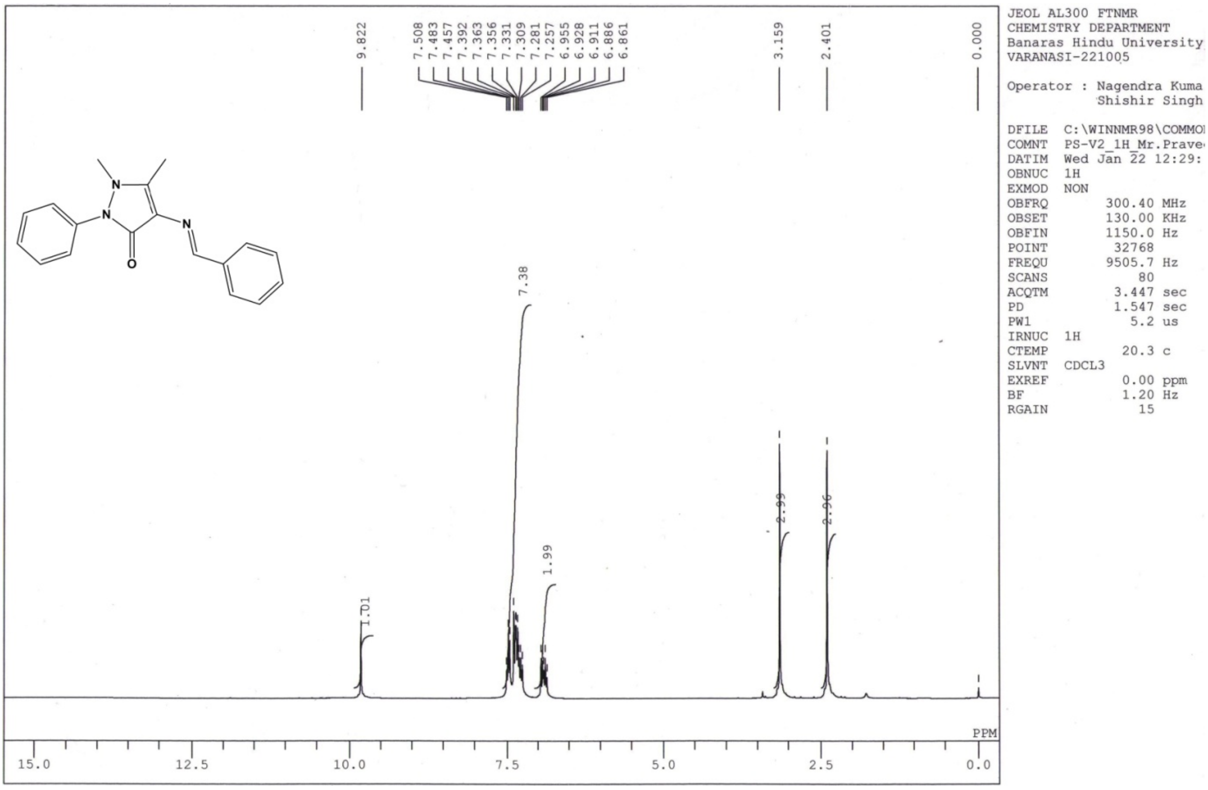
E-mail: rashmi.apc@iitbhu.ac.in

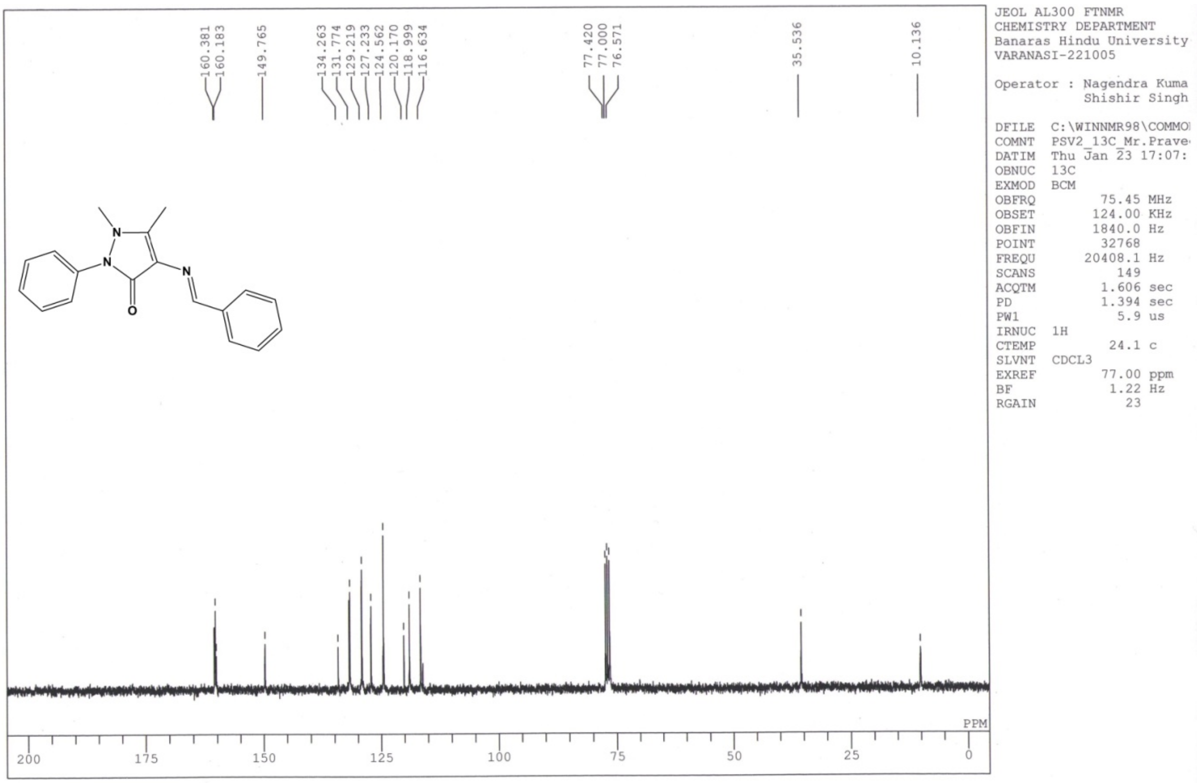
Fax No.: +91 542 2368428

S1. The ^{1}H NMR and ^{13}C NMR spectra of Schiff base additives

(E)-4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one **(AAPB)**

Yield (85%), yellow color solid, mp (178.3^0C). IRν (KBr):1654 (>C=O), 1591 (>C=N) cm^{-1}, ^{1}H NMR (300 MHz, 25^0 C, $Si(CH_3)_4$, $CDCl_3$): δ 2.40 (s, 3H, $=C-CH_3$), 3.16 (s, 3H, $-NCH_3$), 6.86-6.96 (m, 2H, ArH), 7.26-7.51 (m, 8H, ArH), 9.82 (s, 1H, -N=CH). ^{13}C NMR (75 MHz, 25^0 C, $Si(CH_3)_4$, $CDCl_3$): δ 10.1, 35.5, 116.6, 118.9, 120.2, 124.6, 127.2, 129.2, 131.8, 134.3, 149.8, 160.2, 160.4.

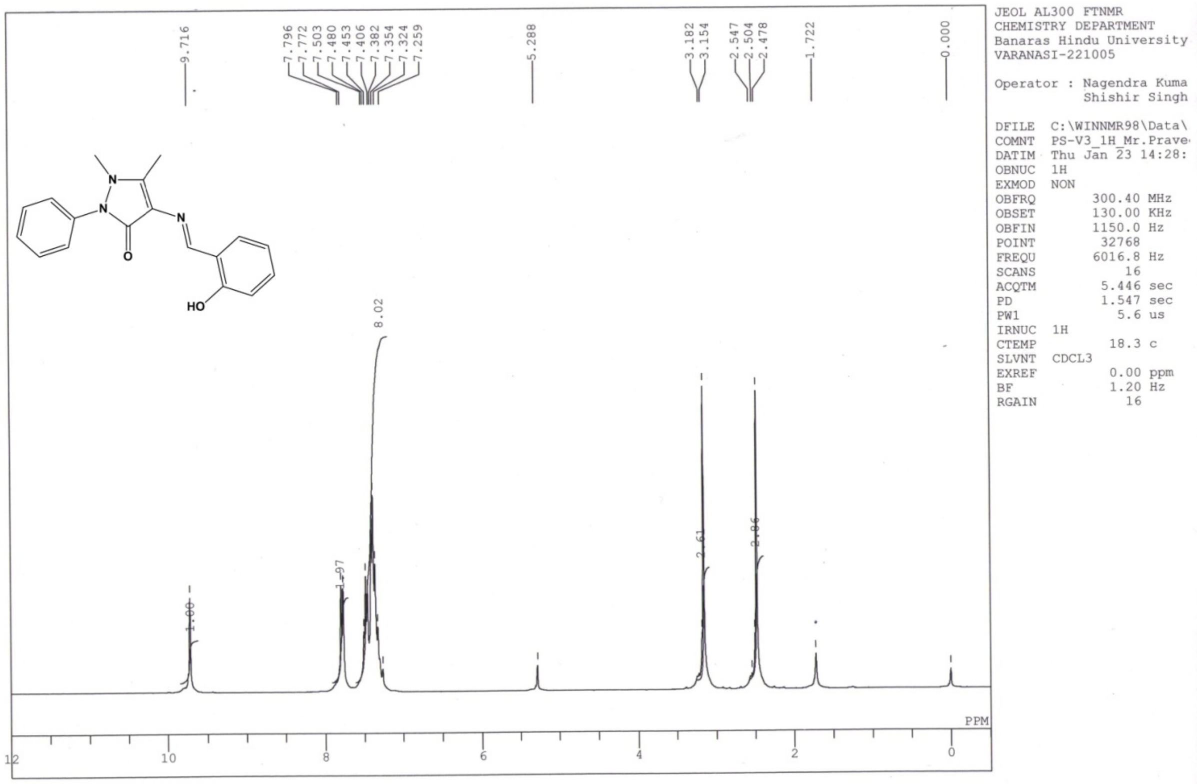


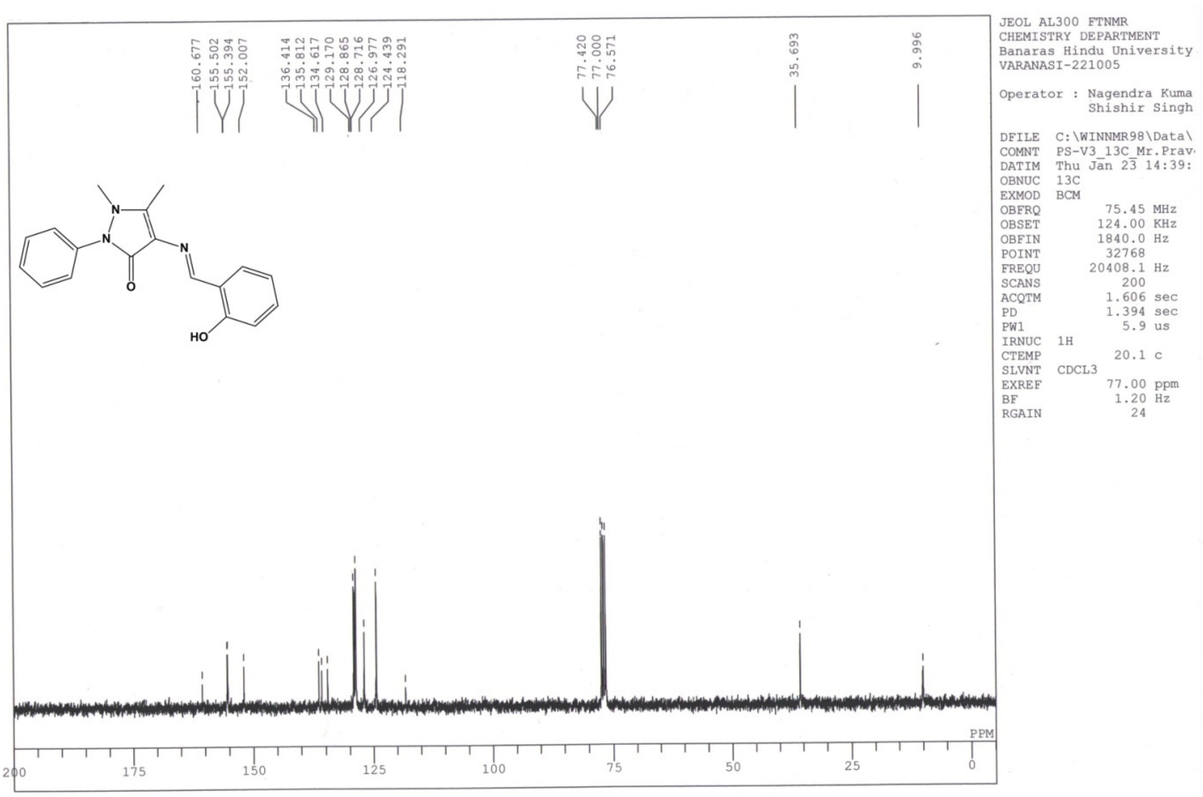


S1.a. ^{1}H NMR and ^{13}C NMR spectra of AAPB Schiff base additive

(E)-4-((2-hydroxybenzylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one

(AAPS) Yield (89%), yellow color solid, mp (185.5^{0}C). IRν (KBr):1650 (>C=O), 1593 (>C=N) cm^{-1}, ^{1}H NMR (300 MHz, 25^{0} C, $Si(CH_3)_4$, $CDCl_3$): δ 2.50 (s, 3H, =C-CH_3), 3.18 (s, 3H, -NCH_3), 5.29 (s, 1H, -OH), 7.26-7.50 (m, 8H, ArH), 9.72 (s, 1H, -N=CH). ^{13}C NMR (75 MHz, 25^{0} C, $Si(CH_3)_4$, $CDCl_3$): δ 9.9, 35.7, 118.3, 124.4, 126.9, 128.7, 128.8, 129.2, 134.6, 135.8, 136.4, 152.0, 155.4, 155.5, 160.7.

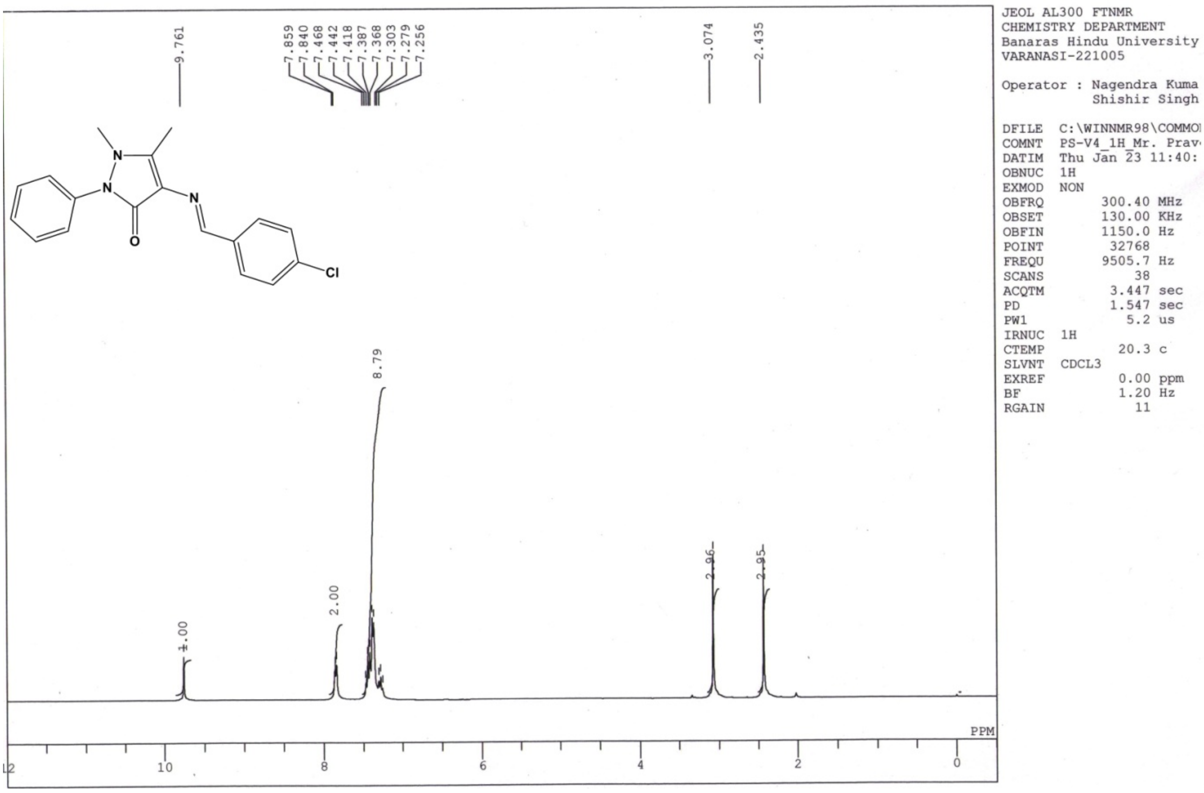


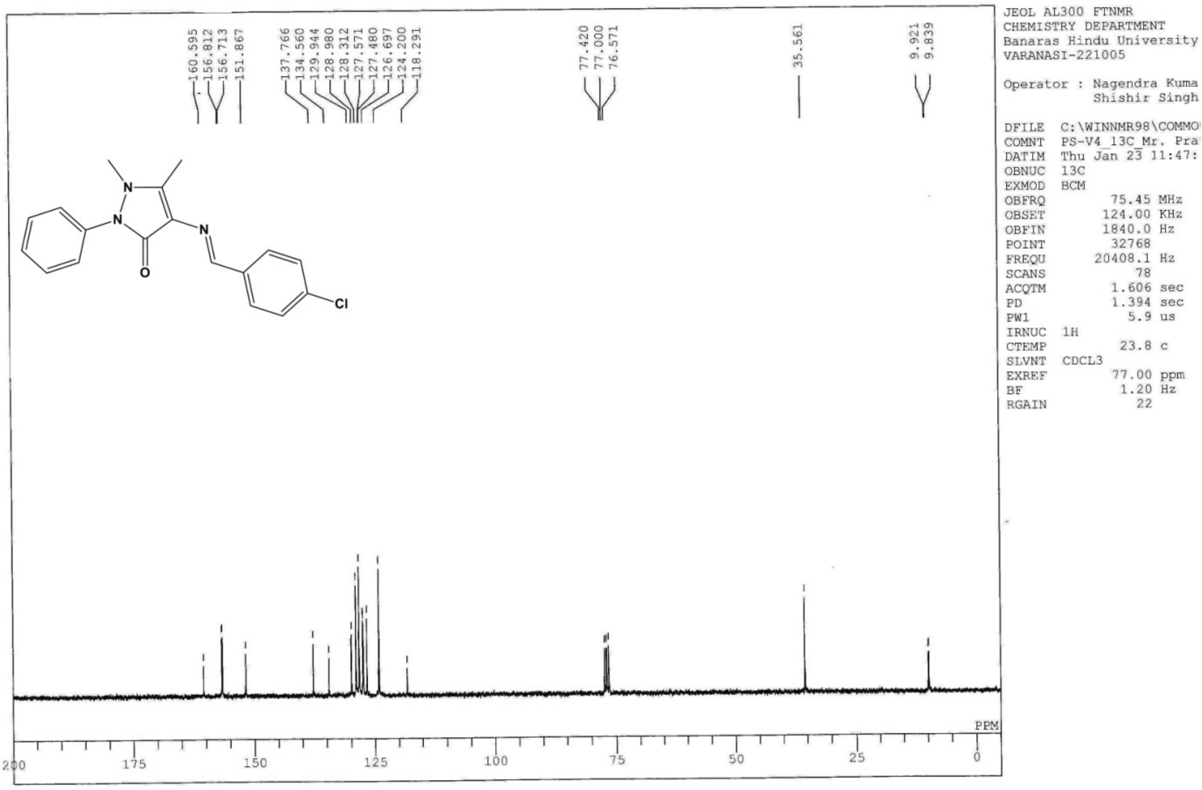


S1.b. ^{1}H NMR and ^{13}C NMR spectra of AAPS Schiff base additive

(E)-4-((4-chlorobenzylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one **(AAPC)**

Yield (90%), yellow color solid, mp (252.4^{0}C). IRν (KBr): 1649 (>C=O), 1594 (>C=N) cm^{-1}. ^{1}H NMR (300 MHz, 25^0 C, $Si(CH_3)_4$, $CDCl_3$): δ 2.44 (s, 3H, =C-CH_3), 3.07 (s, 3H, -NCH_3), 7.26-7.47 (m, 8H, ArH), 7.84-7.86 (d, 2H, ArH), 9.76 (s, 1H, -N=CH). ^{13}C NMR (75 MHz, 25^0 C, $Si(CH_3)_4$, $CDCl_3$): δ 9.8, 9.9, 35.6, 118.3, 124.2, 126.7, 127.5, 127.6, 128.3, 129.0, 129.9, 134.6, 137.8, 151.9, 156.7, 156.8, 160.6.

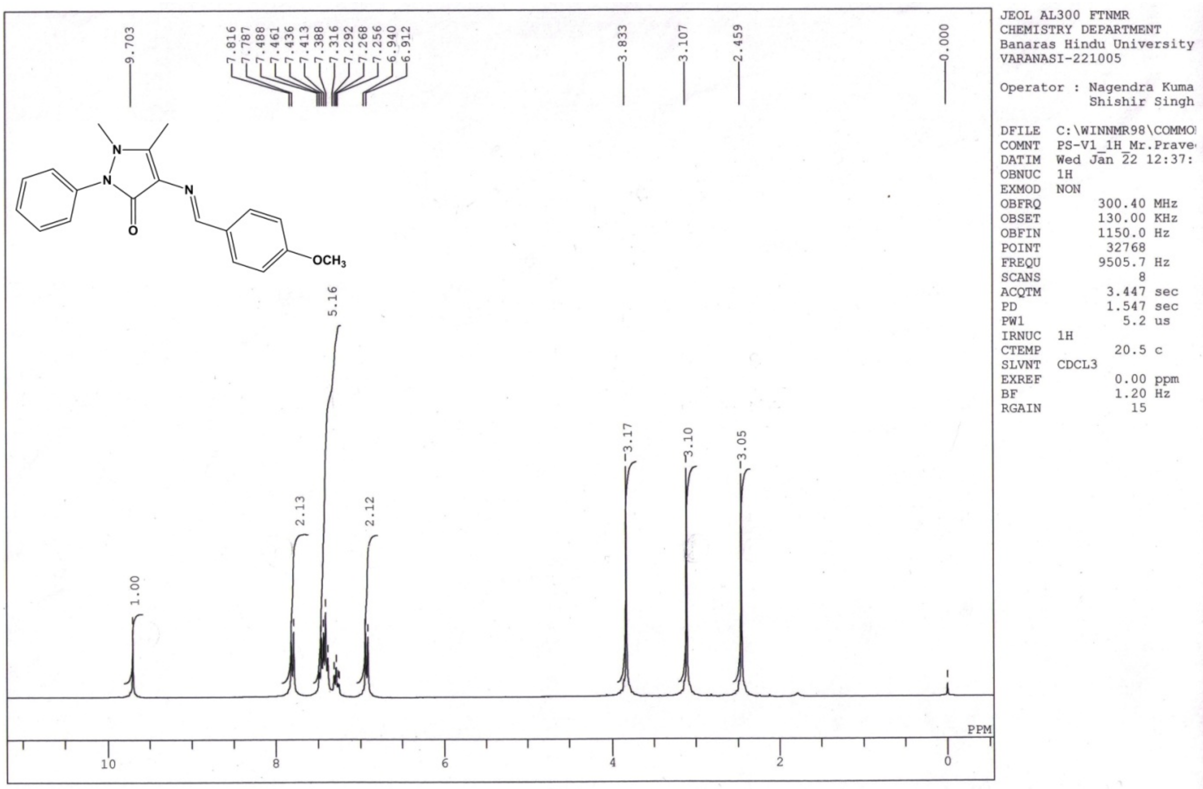


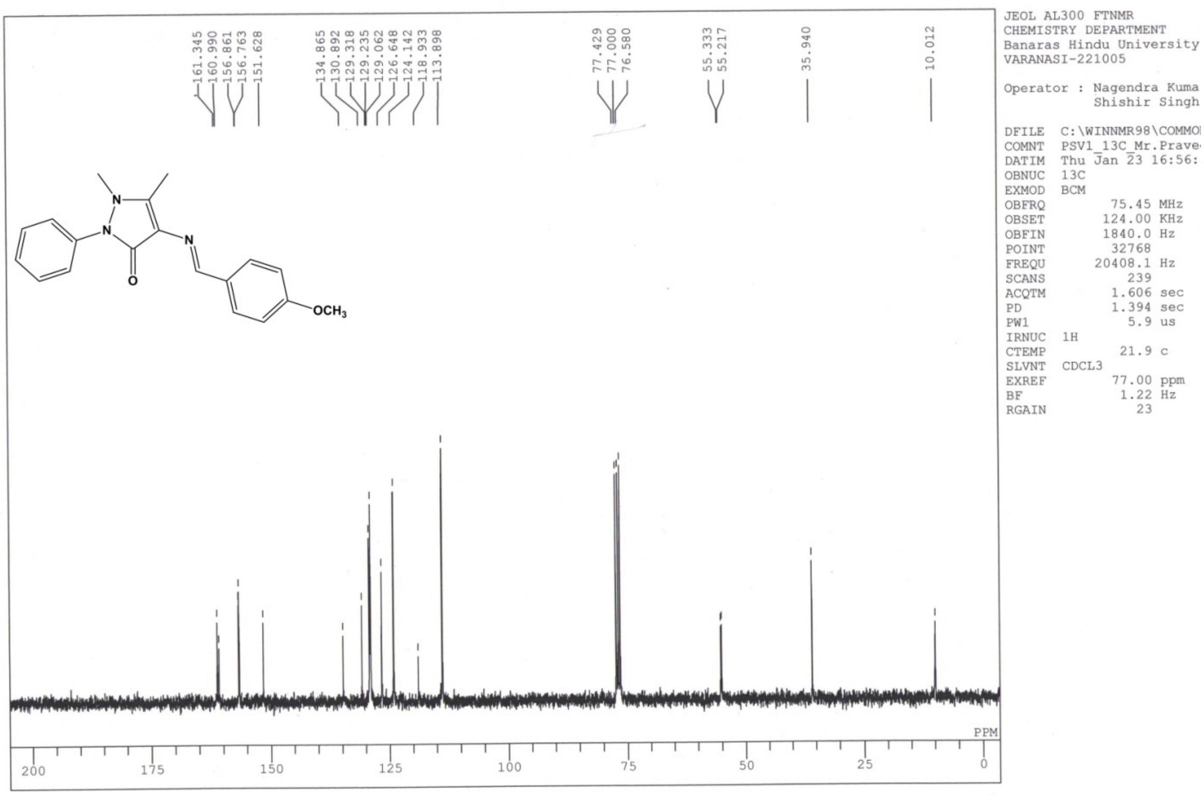


S1.c. ^{1}H NMR and ^{13}C NMR spectra of AAPC Schiff base additive

(E)-4-((4-methoxybenzylidene)amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one

***(*AAPM)** Yield (91%), yellow color solid, mp (168.0^{0}C). IRν (KBr):1646 (>C=O), 1593 (>C=N) cm^{-1}, ^{1}H NMR (300 MHz, 25^{0} C, $Si(CH_3)_4$, $CDCl_3$): δ 2.46 (s, 3H, =C-CH_3), 3.11 (s, 3H, -NCH_3), 3.83 (s, 3H, -OCH_3), 6.91-6.94 (d, 2H, ArH), 7.26-7.49 (m, 5H, ArH), 7.79-7.82 (d, 2H, ArH), 9.70 (s, 1H, -N=CH). ^{13}C NMR (75 MHz, 25^{0} C, $Si(CH_3)_4$, $CDCl_3$): δ 10.0, 35.9, 55.2, 55.3, 113.9, 118.9, 124.1, 126.7, 129.0, 129.2, 129.3, 130.9, 134.9, 151.6, 156.7, 156.9, 161.0, 161.3.





S1.d. ^{1}H NMR and ^{13}C NMR spectra of AAPM Schiff base additive

S2. Experimental details

The wear scar diameter of each of the three horizontal balls was measured in two mutually perpendicular directions, one in the sliding direction (d_s) and the other perpendicular (d_p) to it using an optical microscope. Geometric mean of the two perpendicular diameters on the same ball was taken as given by the equation 1.

For each experiment arithmetic mean of the above diameter of each ball (d_1,d_2 and d_3) was taken as given by equation 2. The three stationary balls were not disturbed while taking the readings and the wear scar diameter was taken by tilting eye piece of the microscope at an angle of 70.5^0 making it perpendicular to the surface of the scar.

S2.1 Tribological Parameters

S2.1.1 Mean wear scar diameter (MWD)

$$d_1 = \sqrt{(d_s d_p)} \quad (1)$$

$$d = \frac{d_1 + d_2 + d_3}{3} \quad (2)$$

S2.1.2 Mean wear volume (MWV)

Wear volume, $$\mathrm{V} = \frac{\Pi\, \mathrm{d}_0^4}{64\,\mathrm{r}}\{(\frac{d}{d_0})^4 - (\frac{d}{d_0})\} \quad (3)$$

Hertzian diameter, $$\mathrm{d}_0 = 2(\frac{3\,\mathrm{Pr}}{4E})^{\frac{1}{3}}$$

Where, $$\frac{1}{r} = \frac{1}{r_1} + \frac{1}{r_2}$$

$$\frac{1}{E^*} = \frac{1-v_1^2}{E_1} + \frac{1-v_2^2}{E_2}$$

Where, E^* = Resultant modulus of elasticity

v = Poissons ratio

r = Radius of steel ball

$E_1 = E_2 = 206$ GPa

$v_1 = v_2 = 0.3$

P = Actual load in Newton on each of the three horizontal balls that is 0.408 times of applied load.

S2.1.3 Friction coefficient (μ)

The coefficient of friction for different antiwear additives is calculated from the pattern observed on the friction paper with the help of equation 4.

$$\mu = \frac{0.222F}{r} \cdot \frac{L}{P} \qquad 4$$

L/P = 0.628

r = 0.367 mm

$$F = \frac{springcons\tan t}{6} \times Y$$

Where, F = Friction force in kgf exerted on the indicator spring.

L = Length in mm of the torque-lever arm.

r = Distance of contact surface of balls from the axis of rotation (0.367 mm).

Y = Displacement after 2.5 s from the baseline.

Value of spring constant upto 80 kgf is 0.226 kgf/cm.

S2.1.4 Wear rate

Overall, running-in and steady-state wear rate have been calculated on the basis of observed mean wear volume data at different time intervals. Mean wear volumes at different times (15, 30, 45, 60, 75 and 90 min.) for each experiment were plotted with time and a linear regression model was fitted on the points including origin to find out overall wear rate.

$$\frac{V}{l} = K\frac{P}{H}$$

V = mean wear volume

l = sliding distance (2πr.N)

K = wear coefficient

H = hardness of steel ball (59-61 HRC)

P = applied load (0.408x392N)

S2.2 AFM Roughness Parameters

S2.2.1 Line Roughness:

Roughness Average, $R_a = \frac{1}{N}\sum_{l=0}^{N-1}|z(x_l)|$

Root Mean Square, $R_q = \sqrt{\frac{1}{N}\sum_{l=o}^{N-1} z(x_l))^2}$

Peak-Valley Height, $R_y = A_p - A_v$

S2.2.2 Area Roughness:

Roughness Average, $S_a = \frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}|z(x_k, y_l)|$

Root Mean Square, $S_q = \sqrt{\frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}(z(x_k, y_l))^2}$

Peak-Valley Height, $S_y = S_p - S_v$

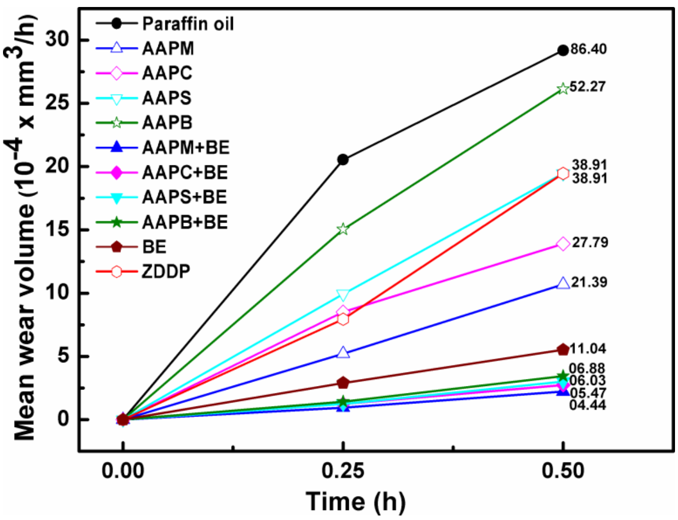


Figure S1. Determination of running-in wear rate by varying mean wear volume with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load

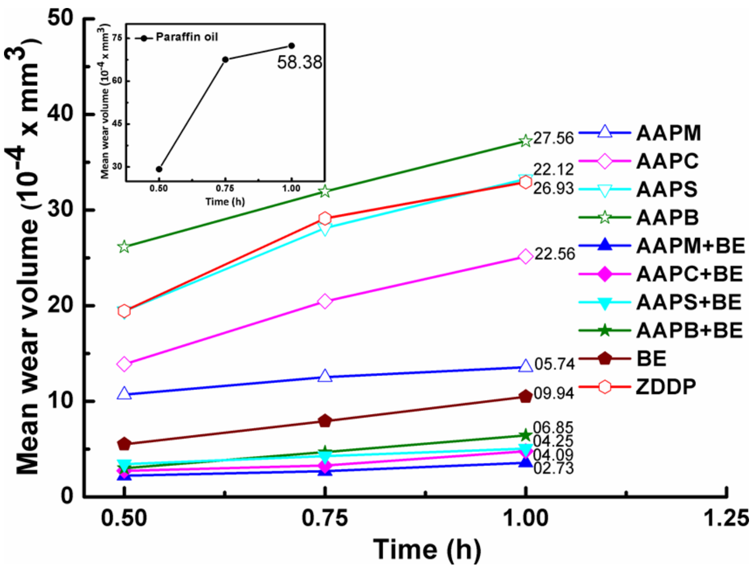
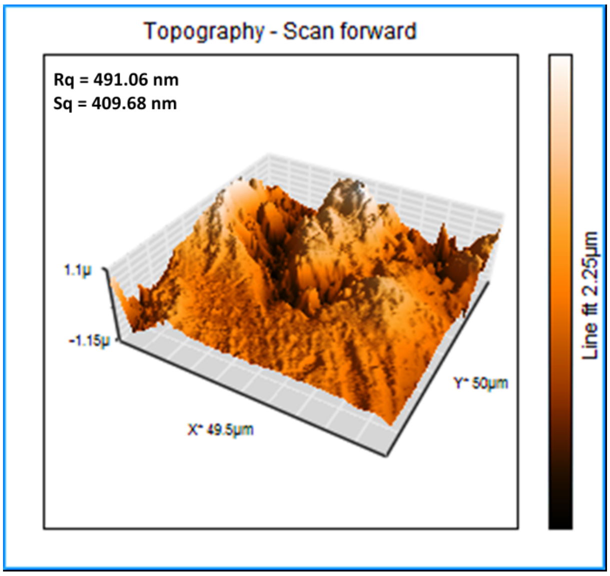


Figure S2. Determination of steady-state wear rate by varying mean wear volume with time in paraffin oil containing (1% w/v) zinc dibutyldithiophosphate (ZDDP), borate ester, Schiff bases and synergistic formulations at 392N applied load

Figure S3a, S3b.



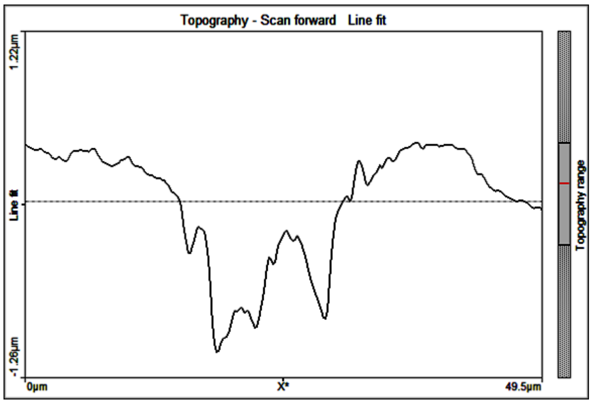
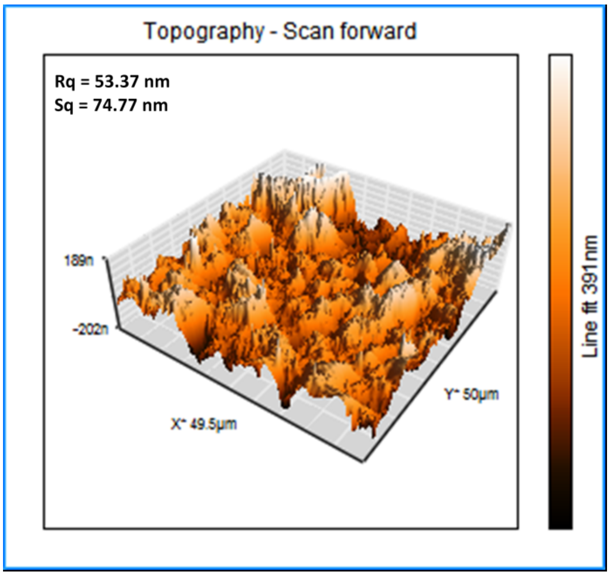


Figure S3c, S3d.



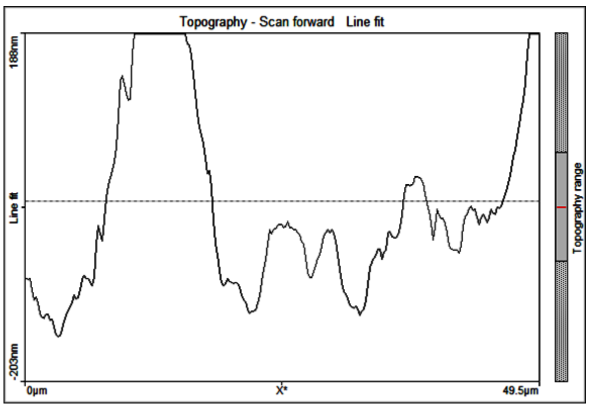
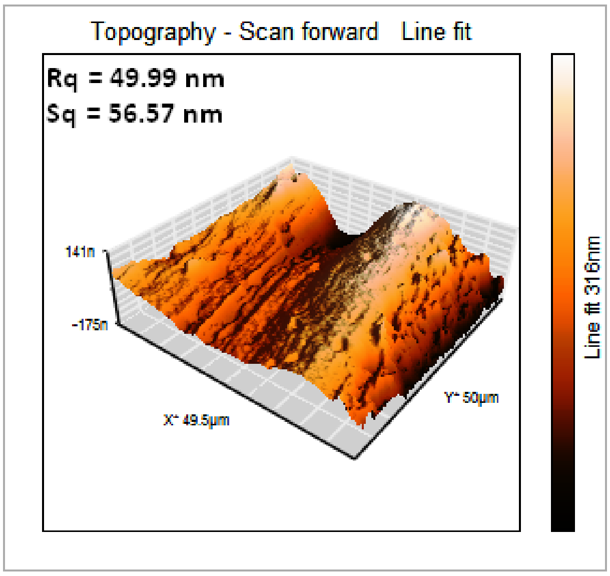


Figure S3e, S3f.



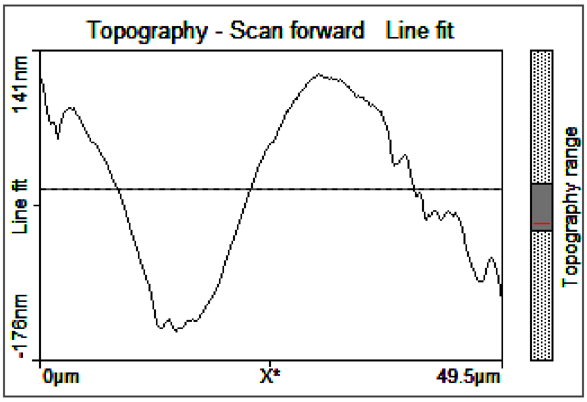
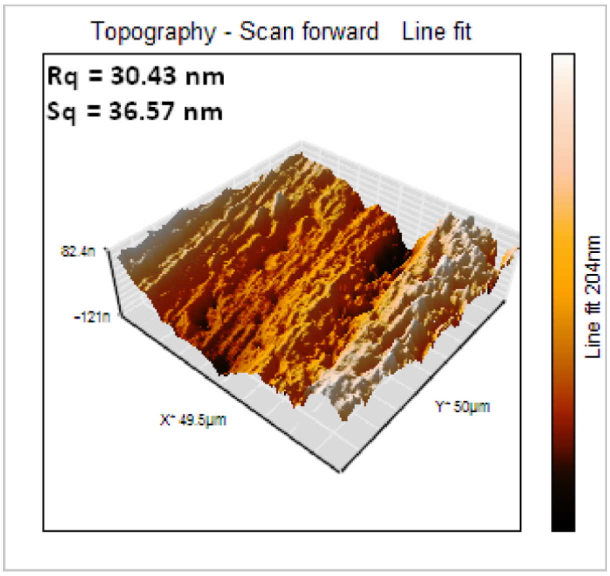


Figure S3g, S3h.



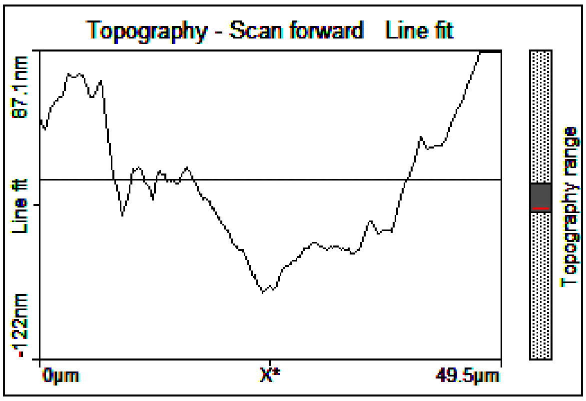


Figure S3i, S3j.

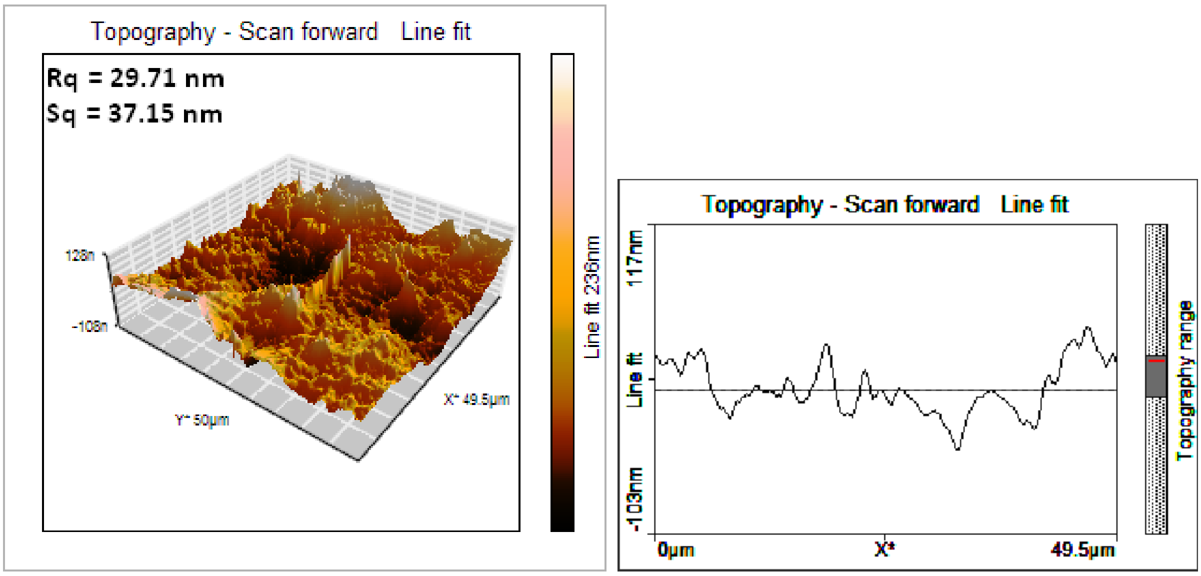


Figure S3k, S3l.

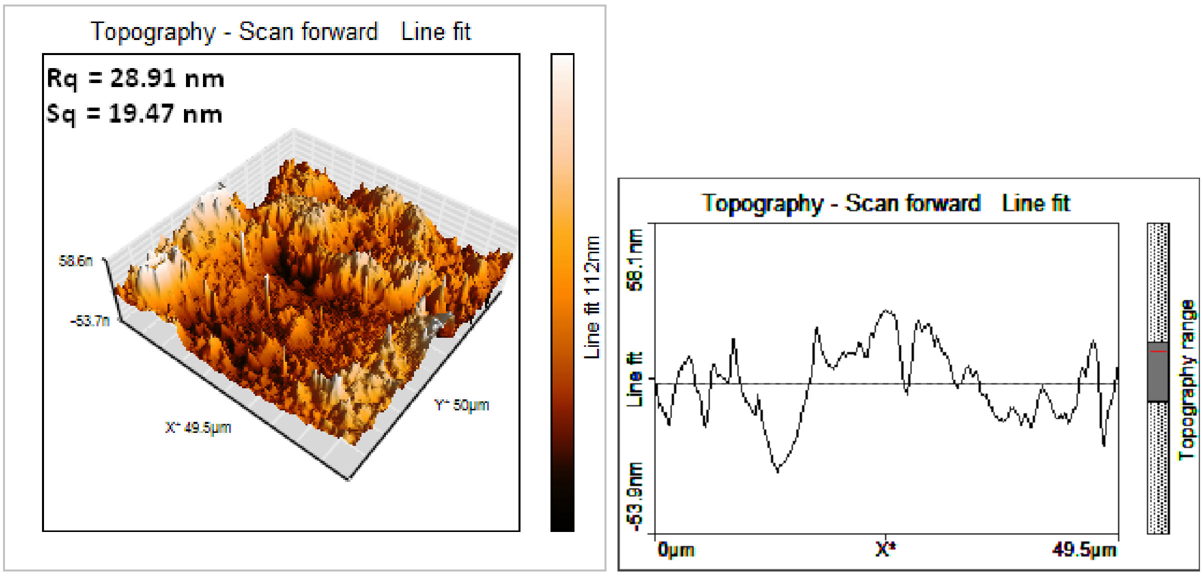
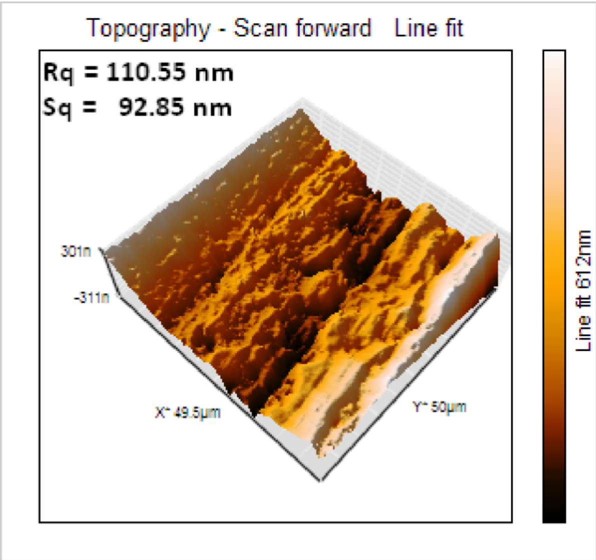


Figure S3. 3*D*-AFM images and corresponding line profile of the worn steel surface with and without additives (1% w/v) in paraffin oil for 90 min test duration at 392N applied load: (a,b) Paraffin oil, (c,d) Zinc dibutyldithiophosphate, (e,f) AAPB+BE, (g,h) AAPS+BE, (i,j) AAPC+BE and (k,l) AAPM+BE

Figure S4a, S4b.



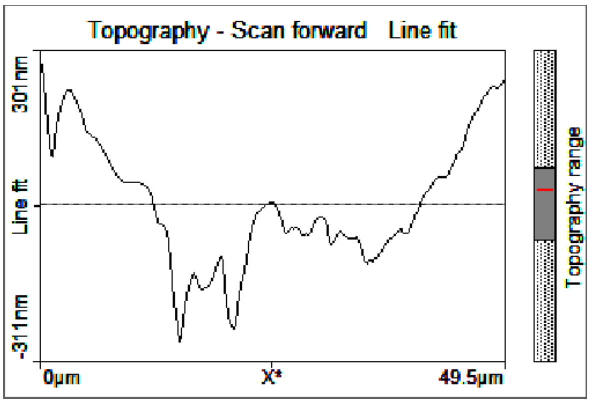
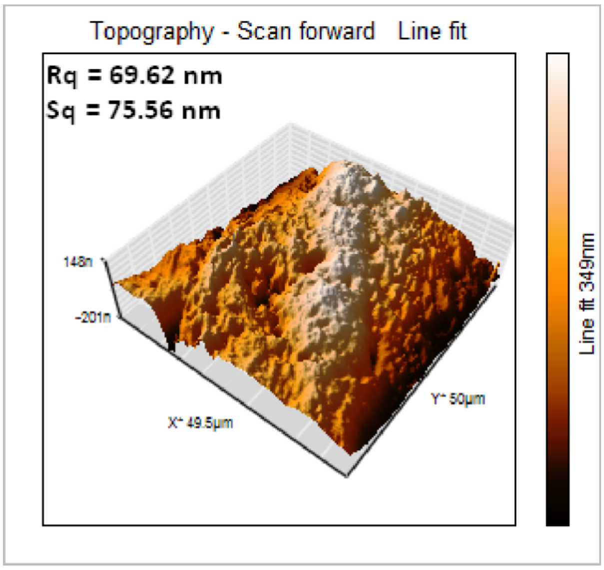


Figure S4c, S4d.



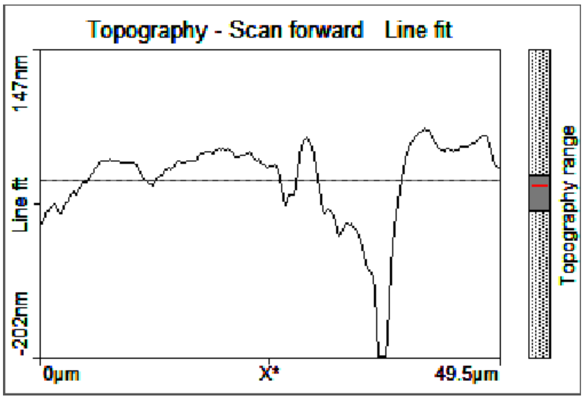


Figure S4e, S4f.

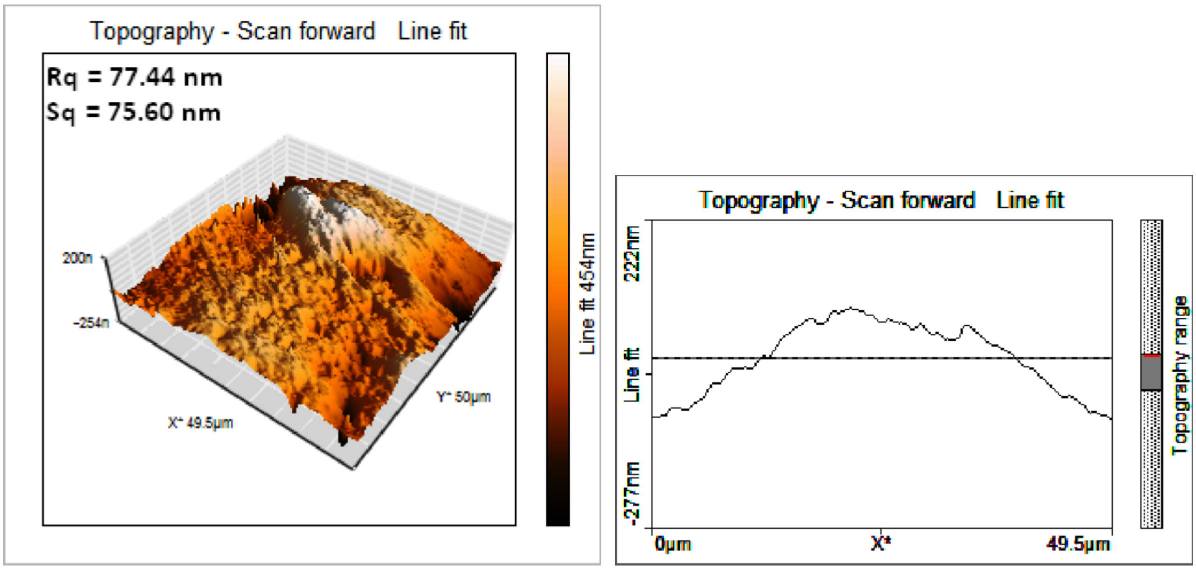


Figure S4g, S4h.

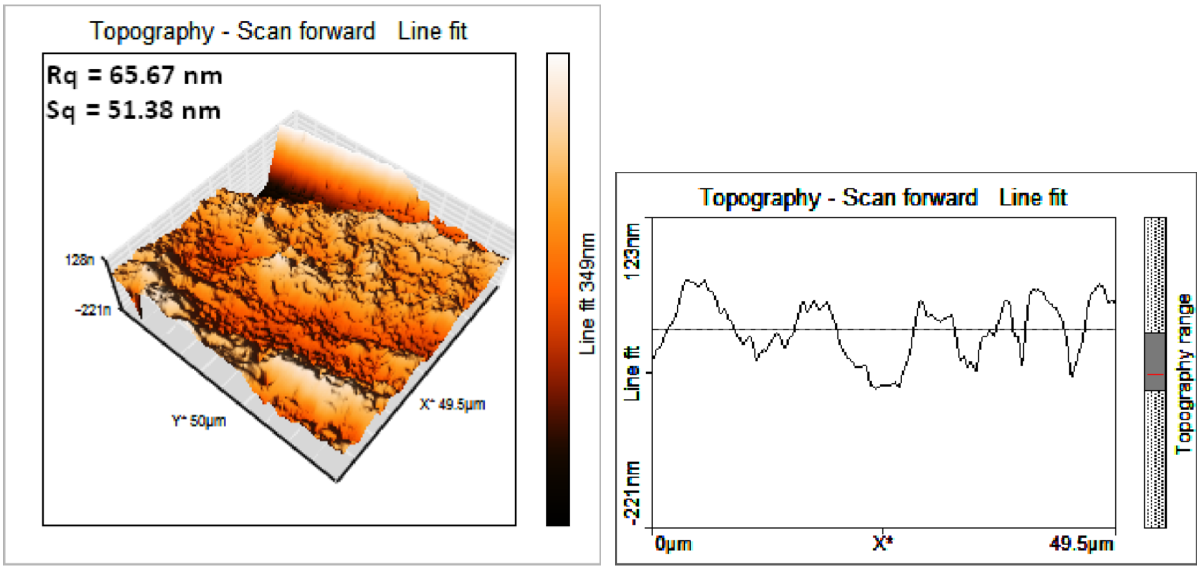


Figure S4. 3*D*-AFM images and corresponding line profile of the worn steel surface lubricated with different additives in paraffin oil for 30 min test duration at 588N applied load: (a,b) ZDDP, (c,d) borate ester, (e,f) AAPM and (g,h) AAPM+BE

Figure S5a.

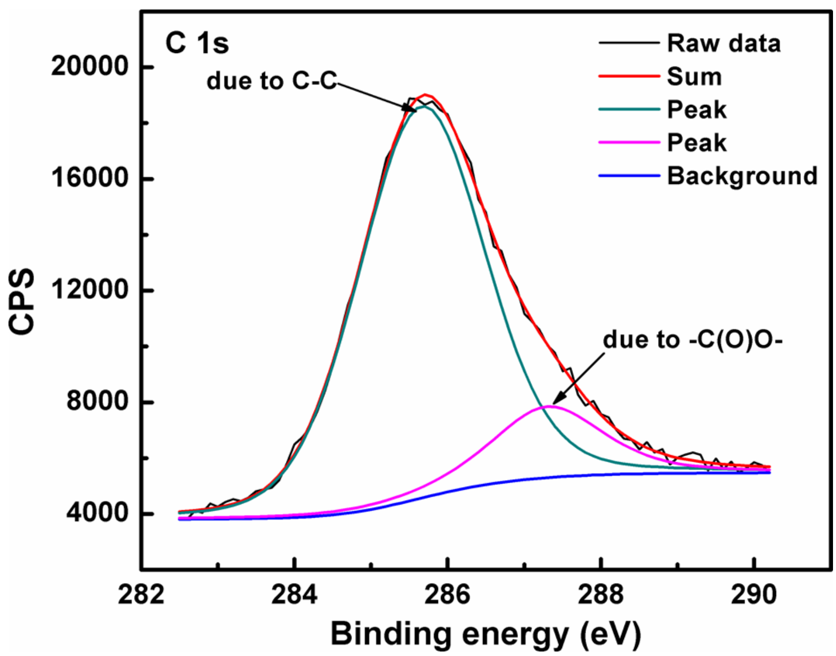


Figure S5b.

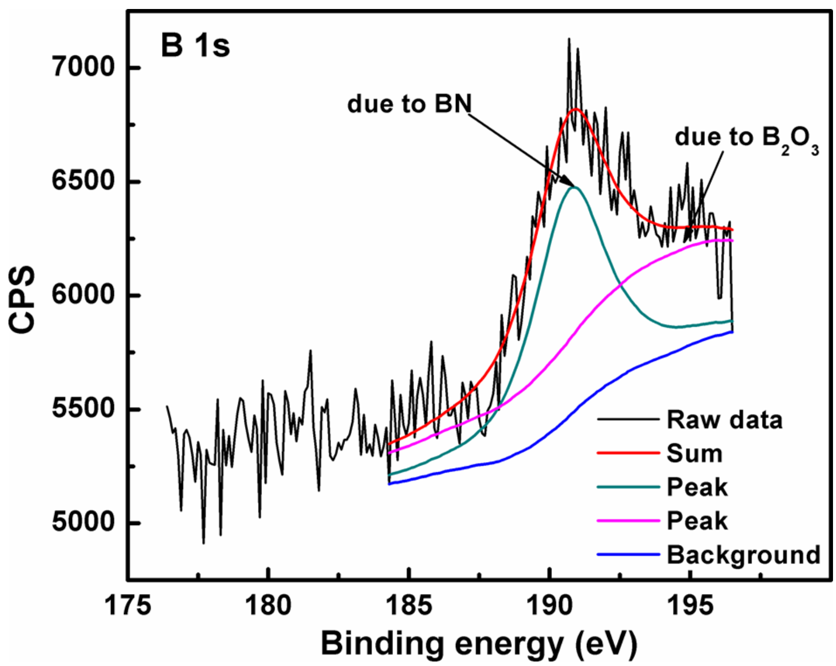


Figure S5c.

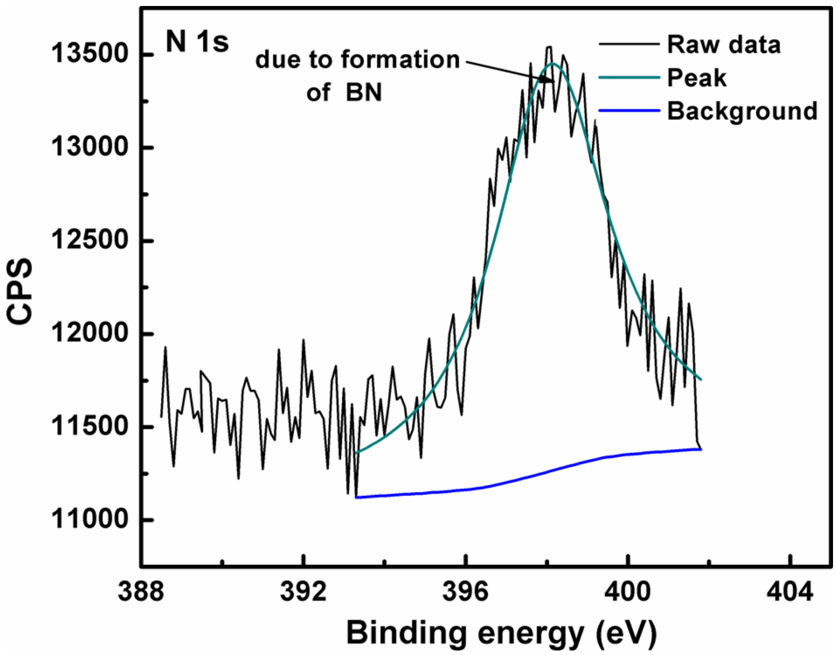


Figure S5d.

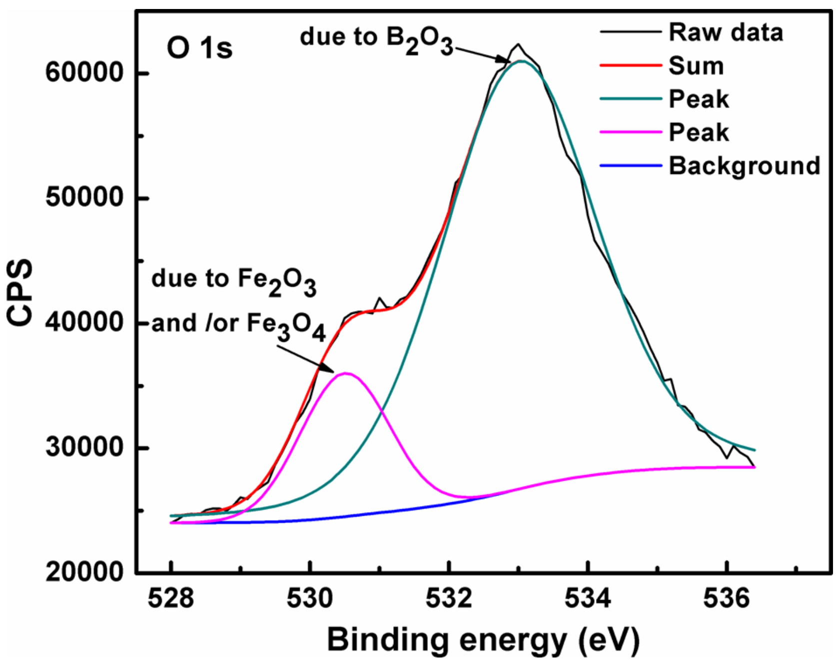


Figure S5e.

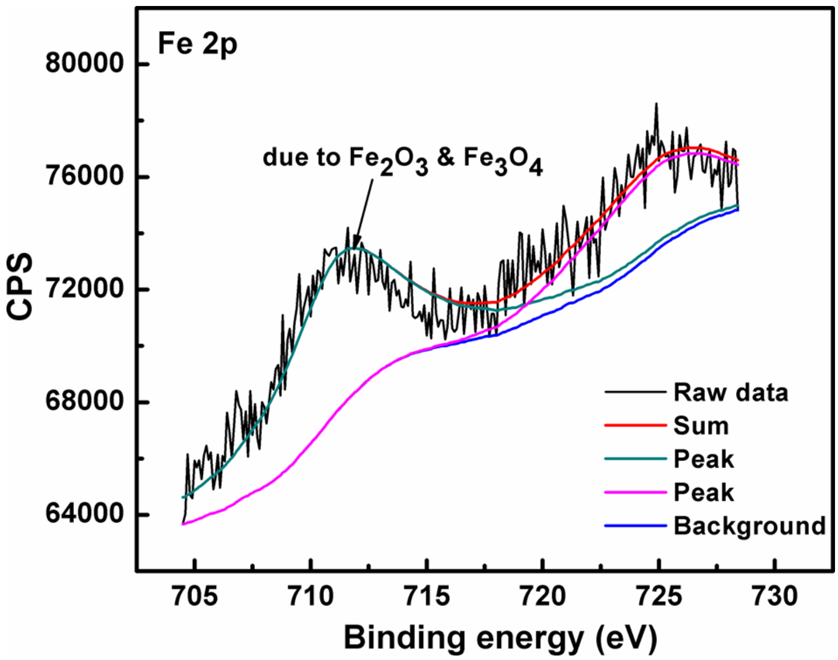


Figure S5. XPS spectra of tribochemical film formed on worn steel surface lubricated with AAPM+BE (1% w/v) at 392N applied load for 90 min test duration in liquid paraffin. **(a).** C 1s, **(b).** B 1s, **(c).** N 1s, **(d).** O 1s and **(e).** Fe 2p