SUPPLEMENTARY MATERIAL TO

**Multicomponent synthesis of the new bispyranpyrazole and their antimicrobial-antioxidant evaluations**

MOHAMAD YUSUF[[1]](#footnote-2)\* and SALONI THAKUR

*Department of Chemistry, Punjabi University, Patiala-147002, Punjab, India.*

*email:* [*yusuf\_sah04@yahoo.co.in*](mailto:yusuf_sah04@yahoo.co.in)

ANALYTICAL AND SPECTRAL DATA FOR SYNTHESISED COMPOUNDS

*Synthesis of 4,4’-[{biphenyl-4,4*’*-diylbbis(methylene)}bis(oxy)bis(4,1-phenylene)-)bis(6-amino-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)(****3a***).Brown solid; Yield: 69%; m.p.: 209-2110C; IR (KBr) cm-1 3323, 3150 (N-H), 2974, 2828 (methylene C-H), 2189 (C≡N), 1638 (C=N) & 1233, 1172 (C-O); 1H-NMR (400 MHz, CDCl3): δ 12.0 (2H, bs, 1-N***H***), 7.41 (4H, d, *J*o=8.1 Hz, H-2’’,6’’), 7.09 (4H, d, *J*o=8.0 Hz, H-3’’,5’’), 6.89 (4H, dt, *J*=8.0, 10.0 Hz, 2’, 6’), 6.57 (4H, *J*o=10.0 Hz, H-3’,5’), 6.04 (4H, bs, N***H2***), 5.35 (4H, s, OC***H2***), 4.50 (2H, s, H-4), 1.80 (6H, s, C***H3***); 13C-NMR (CDCl3): δ 160.56 (C-6), 154.70 (C-3), 131.52 (C-4’), 128.70 (C-7a), 128.32 (C-4’’), 128.16 (C-1’’), 128.03 (C-2’,6’), 127.97 (C-3’’,5’’), 127.83 (C-2’’,6’’), 120.70 (C-1’), 113.21(**C**≡N), 110.51 (C-3’,5’), 97.56 (C-3a), 67.10 (O***C***H2), 57.89 (C-5), 35.59 (C-4), 9.69 (***C***H3); ESI-MS: m/z 737 (M+Na, 10%), 715 (M+1, 15%), 511 (10%), 489 (15%), 475 (5%), 371 (9%), 294 (13%), 243 (19%), 242 (100%), 215 (7%), 121 (4%), 107 (8%); Anal. Calc. For C42H34N8O4: C, 70.58; H, 4.79; N, 15.68; found C, 70.30; H, 4.78; N, 15.62%.

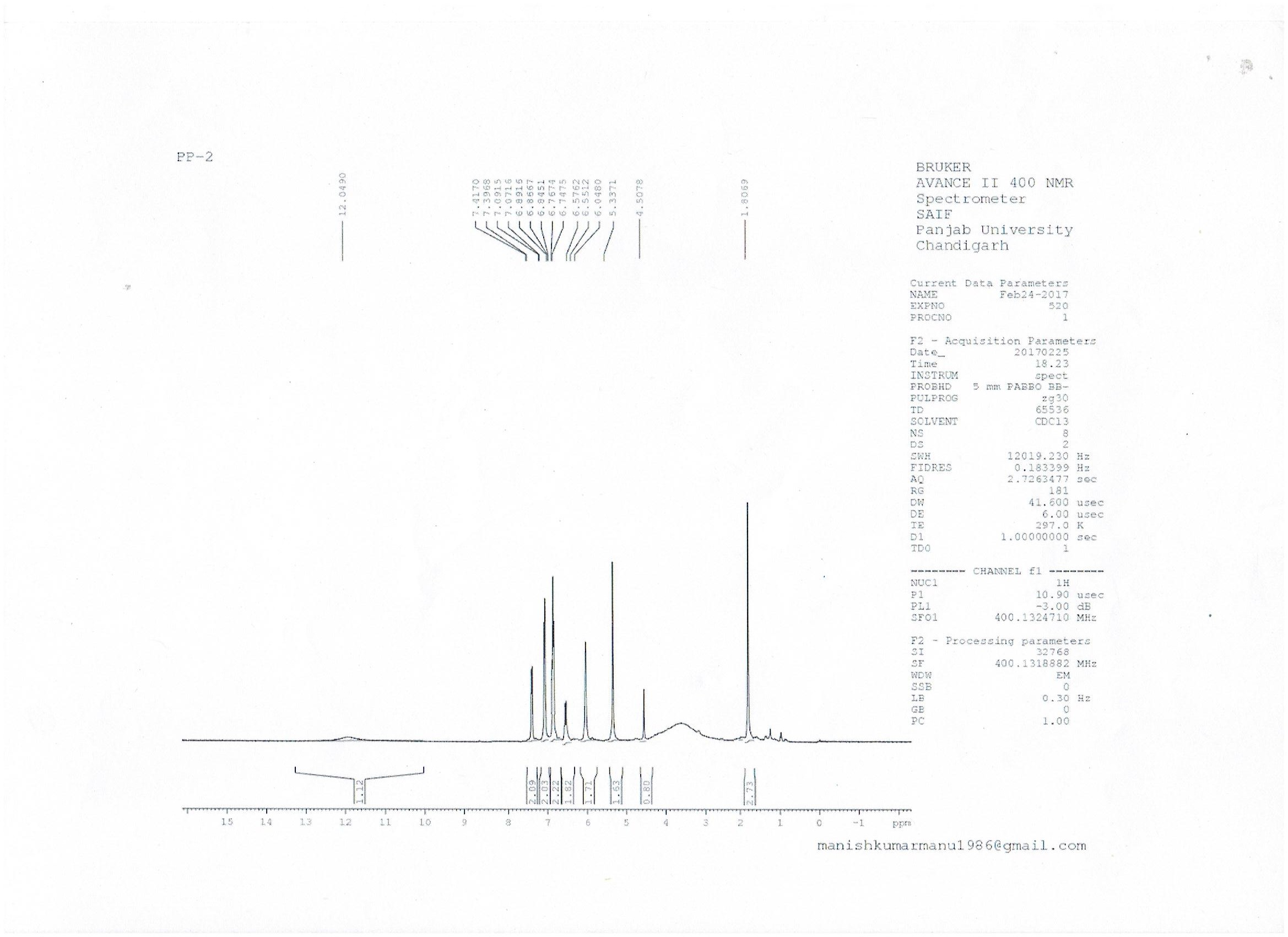
*Synthesis of 4,4’-[{but-2-yne-1,4-diylbis(oxy)} bis(4,1-phenylene)bis(6-amino-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)*(***3b***). Light yellow solid; Yield: 58%; m.p.: 98-1000C; IR (KBr) cm-1 3471, 3263 (N-H), 2971, 2880 (methylene C-H), 2190 (C≡N), 1600 (C=N) & 1220, 1054 (C-O); 1H-NMR (400 MHz, DMSO-*d*6): δ 12.0 (2H, bs, 1-N***H***), 7.09 (4H, d, *J*o=7.2 Hz, H-2’,6’), 6.89 (4H, d, *J*o=7.5 Hz, H-3’,5’), 6.75 (4H, bs, N***H2***), 4.81 (4H, s, OC***H2*** ) 4.53 (2H, s, H-4), 1.79(6H, s, C***H3***); 13C-NMR ( DMSO-*d*6): δ 160.68 (C-6), 155.93 (C-3), 137.15 (C-4’), 135.41(C-7a), 128.40 (C-2’,6’), 124.68 (C-3’, 5’), 120.41(C-1’), 114.48 (**C**≡N), 97.68 (C-3a), 82.38 (C≡C), 57.51 (O***C***H2), 55.44 (C-5), 35.51 (C-4), 9.74 (***C***H3); ESI-MS: m/z 609 (M+Na, 10%), 587 (M+1, 15%), 511 (10%), 489 (15%), 475 (5%), 371 (9%), 294 (13%), 243 (19%), 242 (100%), 215 (7%), 121 (4%), 107 (8%); Anal. Calc. For C32H26N8O4: C, 65.52; H, 4.47; N, 19.10; found C, 65.26; H, 4.46; N, 19.03%.

*Synthesis of 4,4’-[{1,2-phenylenebis (methylene)}bis(oxy)bis(4,1-phenylene)]bis(6-amino-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)*(***3c***)Grey solid; Yield: 67%; m.p.: 158-1600C; IR (KBr) cm-1 3314-3184 (N-H), 2922, 2871 (methylene C-H), 2190 (C≡N), 1599 (C=N) & 1266, 1037 (C-O); 1H-NMR (400 MHz, DMSO-*d*6): δ 11.80 (2H, bs, 1-N***H***), 7.53 (2H, t, *J*=3.2, 5.4 Hz, H-5’’), 7.36 (2H, dd, *J*=2.1, 3.2 Hz, H-6’’), 7.10 (4H, dd, *J*m,o=2.0, 8.3 Hz, H-2’,6’), 6.91 (4H, d, *J*o=7.0 Hz, H-3’,5’), 6.38 (4H, bs, N***H2***), 5.15 (4H, s, OC***H2***), 4.57 (2H, s, H-4), 1.80 (6H, s, C***H3***); 13C-NMR (DMSO-*d*6): δ 160.49 (C-6), 156.98 (C-3), 154.73 (C-4’), 136.37(C-7a), 135.53 (C-1’’), 134.90 (C-2’, 6’),128.34 (C-6’’), 127.84 (C-5’’), 120.68 (C-1’), 118.30 (**C**≡N), 97.45 (C-3a), 67.30 (O***C***H2), 58.25 (C-5), 35.62(C-4), 9.72 (***C***H3); ESI-MS: m/z 661 (M+Na, 10%), 639 (M+1, 15%), 511 (10%), 489 (15%), 475 (5%), 371 (9%), 294 (13%), 243 (19%), 242 (100%), 215 (7%), 121 (4%), 107 (8%); Anal. Calc. For C36H30N8O4: C, 67.70; H, 4.73; N, 17.54; found C, 67.43; H, 4.72; N, 17.47%.

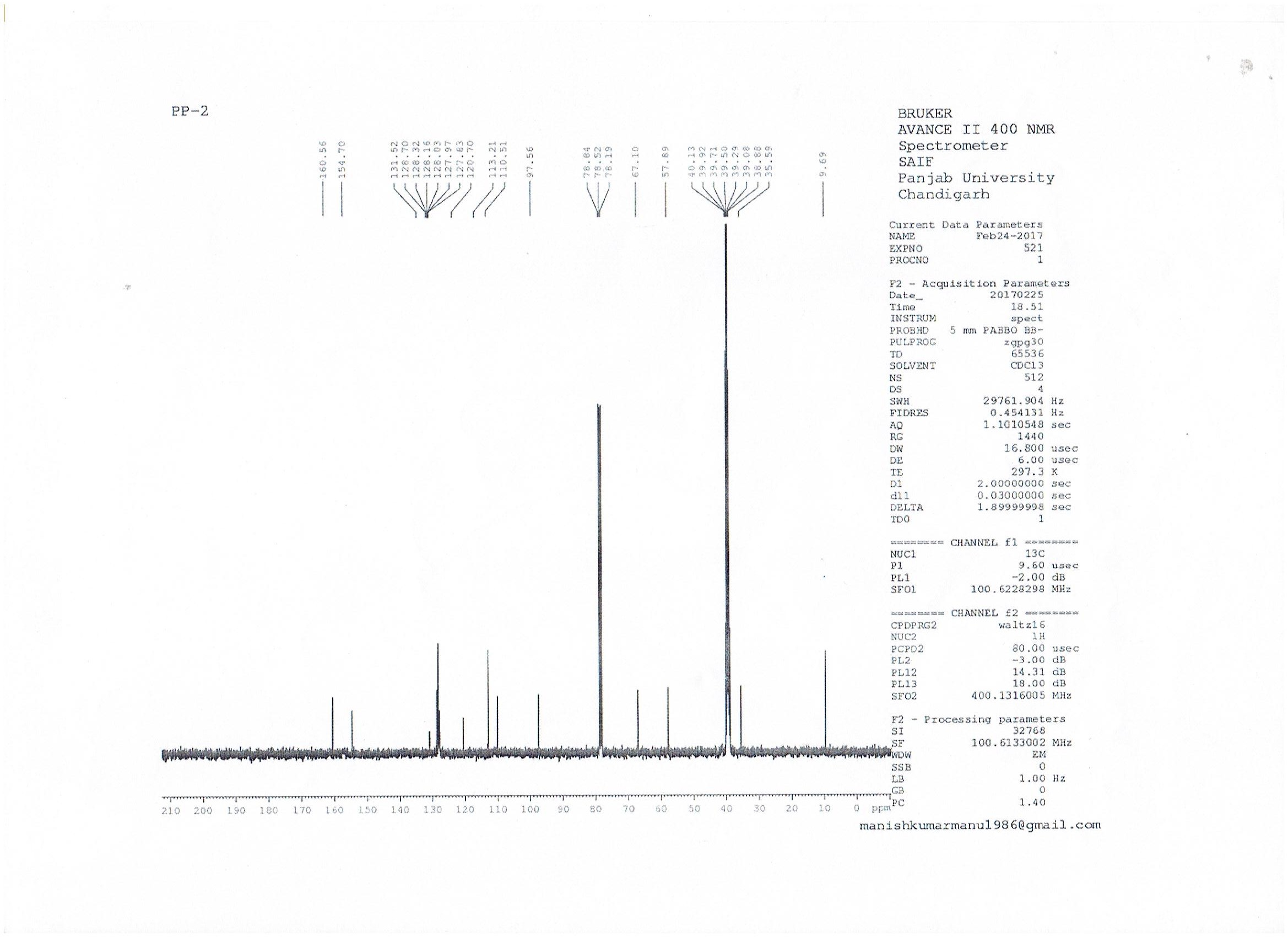
*Synthesis of 4,4’-[{1,4-phenylenebis (methylene)}bis(oxy)bis(4,1-phenylene)]bis(6-amino-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)*(***3d***).Light brown solid; Yield: 64%; m.p.: 178-1800 C; IR (KBr) cm-1 3392, 3156 (N-H), 2956, 2880 (methylene C-H), 2189 (C≡N), 1598 (C=N) & 1256, 1018 (C-O); 1H-NMR (400 MHz,CDCl3): δ 12.0 (2H, bs, 1-N***H***), 7.49 (4H, d, *J*=4.1 Hz, H-2’’, 6’’), 6.86 (4H, dd, *J*o=7.1, *J*m=1.1 Hz, H-2’,6’), 6.78 (4H, d, *J*o=7.0 Hz, H-3’,5’), 6.65 (4H, bs, N***H2***), 5.07 (4H, s, OC***H2***), 4.98 (2H, s, H-4), 1.78 (6H, s, C***H3***); 13C-NMR (CDCl3): δ 160.85 (C-6), 154.76 (C-3), 145.82 (C-4’), 129.30 (C-7a), 127.58 (C-1’’), 121.47 (C-2’, 6’), 120.73 (C-1’), 119.98 (C-2’’, 6’’), 114.11(**C**≡N), 112.69 (C-3’, 5’), 97.21 (C-3a), 68.95 (O***C***H2), 57.41 (C-5), 36.39 (C-4), 9.73 (***C***H3); ESI-MS: m/z 661 (M+Na, 10%), 638 (M, 10%), 489 (15%), 371 (9%), 294 (13%), 243 (19%), 215 (7%); Anal. Calc. For C36H30N8O4: C, 67.70; H, 4.73; N, 17.54; found C, 67.41; H, 4.70; N, 17.45%.

*Synthesis of 4,4’-[{1,3-phenylenebis (methylene)}bis(oxy)bis(4,1-phenylene)]bis(6-amino-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)*(***3e***).Light yellow solid; Yield: 70%; m.p.: 128-1300 C; IR (KBr) cm-1 3392, 3210-3156 (N-H), 2956, 2888 (methylene C-H), 2169 (C≡N), 1592 (C=N) & 1256, 1018 (C-O); 1H-NMR (400 MHz, DMSO-*d*6): δ 11.74 (2H, bs, 1-N***H***), 7.38 (1H, dt, *J*=4.1, 5.4 Hz, H-5’’), 7.09 (2H, dd, *J*=1.6, 6.4 Hz, H-4’’,6’’), 6.92 (1H, d, *J*m=1.8 Hz, H-2’’), 6.83 (4H, dd, *J*= 4.3, 6.8 Hz, H-2’, 6’), 6.67(4H, d, *J*= 2.0, 3.6 Hz, H-3’, 5’), 6.42 (4H, bs, N***H2***), 4.72 (4H, s, OC***H2*** ), 4.51 (2H, s, H-4),), 1.81(6H, s, C***H3***); 13C-NMR (DMSO-*d*6): δ 160.83 (C-6), 154.73 (C-3), 139.73 (C-4’), 129.49 (C-7a), 128.35 (C-5’’), 128.13 (C-4’’, 6’’), 127.02(C-2’, 6’), 126.76 (C-1’’, 3’’), 120.71 (C-1’), 114.59 (C-2’’), 114.29(**C**≡N), 113.76 (C- 3’, 5’), 97.47 (C-3a), 58.16 (C-5), 69.14 (O***C***H2), 35.64(C-4), 9.72 (***C***H3); ESI-MS: m/z 639 (M+1, 15%), 489 (15%), 371 (9%), 243 (19%), 242 (100%), 215 (7%), 107 (8%); Anal. Calc. For C36H30N8O4: C, 67.70; H, 4.73; N, 17.54; found C, 67.44; H, 4.71; N, 17.49%.

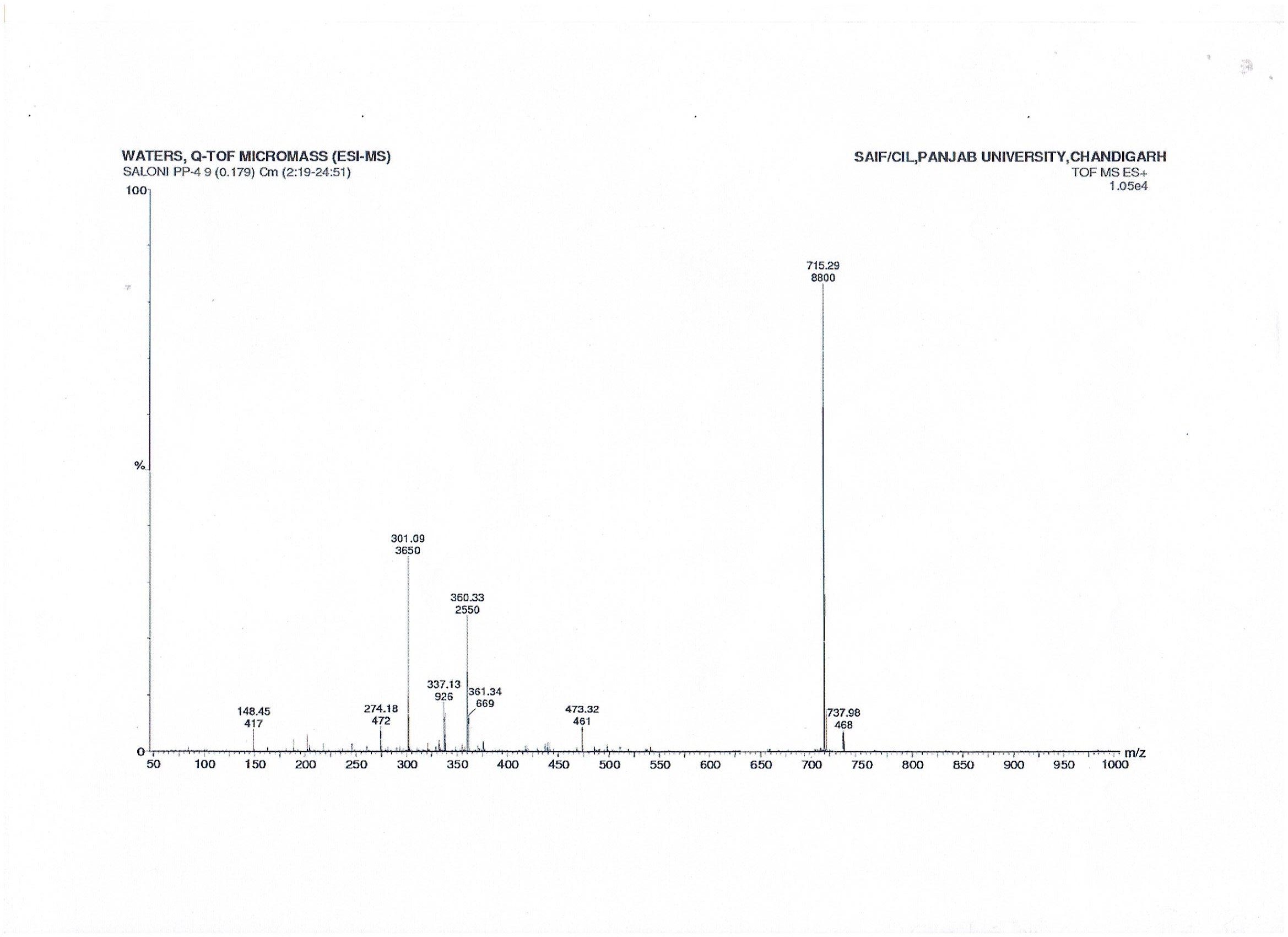
*Synthesis of 4,4’-[{but-2-ene-1,4-diylbis} bis(oxy)bis(4,1-phenylene)]bis(6-amino-3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)*(***3f***)Brown solid; Yield: 67%; m.p.: 235-2370 C; IR (KBr) cm-1 3335-3191 (N-H), 2961, 2925 (methylene C-H), 2189 (C≡N), 1607 (C=N) & 1221, 1015 (C-O); 1H-NMR (400 MHz, DMSO-*d*6): δ 12.00 (2H, bs, 1-N***H***), 7.08 (4H, dt, *J*=2.0, 6.8 Hz, H-2’, 6’), 4.81 (4H, d, *J*o=8.6 Hz, H-3’, 5’),6.76 (4H, bs, N***H2***), 6.12 (2H, t, *J*vic=6.1 Hz, OCH2C***H***=), 4.81 (4H, *Jvic*=6.1 Hz, s, OC***H***2), 4.52 (2H, s, H-4), 1.79(6H, s, C***H3***); 13C-NMR (DMSO-*d*6): δ 160.68 (C-6), 155.94 (C-3), 137.16 (C-4’), 135.42 (C-7a), 128.40 (C-2’, 6’), 126.78 (OCH2***C***H=), 120.79 (C-1’), 117.67 (C≡N), 114.48 (C-3’, 5’), 97.67 (C-3a), 57.50 (O***C***H2), 55.45 (C-5), 35.50(C-4), 9.74 (***C***H3); ESI-MS: m/z 611 (M+Na, 10%), 589 (M+1, 15%), 511 (10%), 489 (15%), 475 (5%), 371 (9%), 294 (13%), 243 (19%), 242 (100%), 215 (7%), 121 (4%), 107 (8%); Anal. Calc. For C32H28N8O4: C, 65.30; H, 4.79; N, 19.04; found C, 65.03; H, 4.77; N, 18.96%.



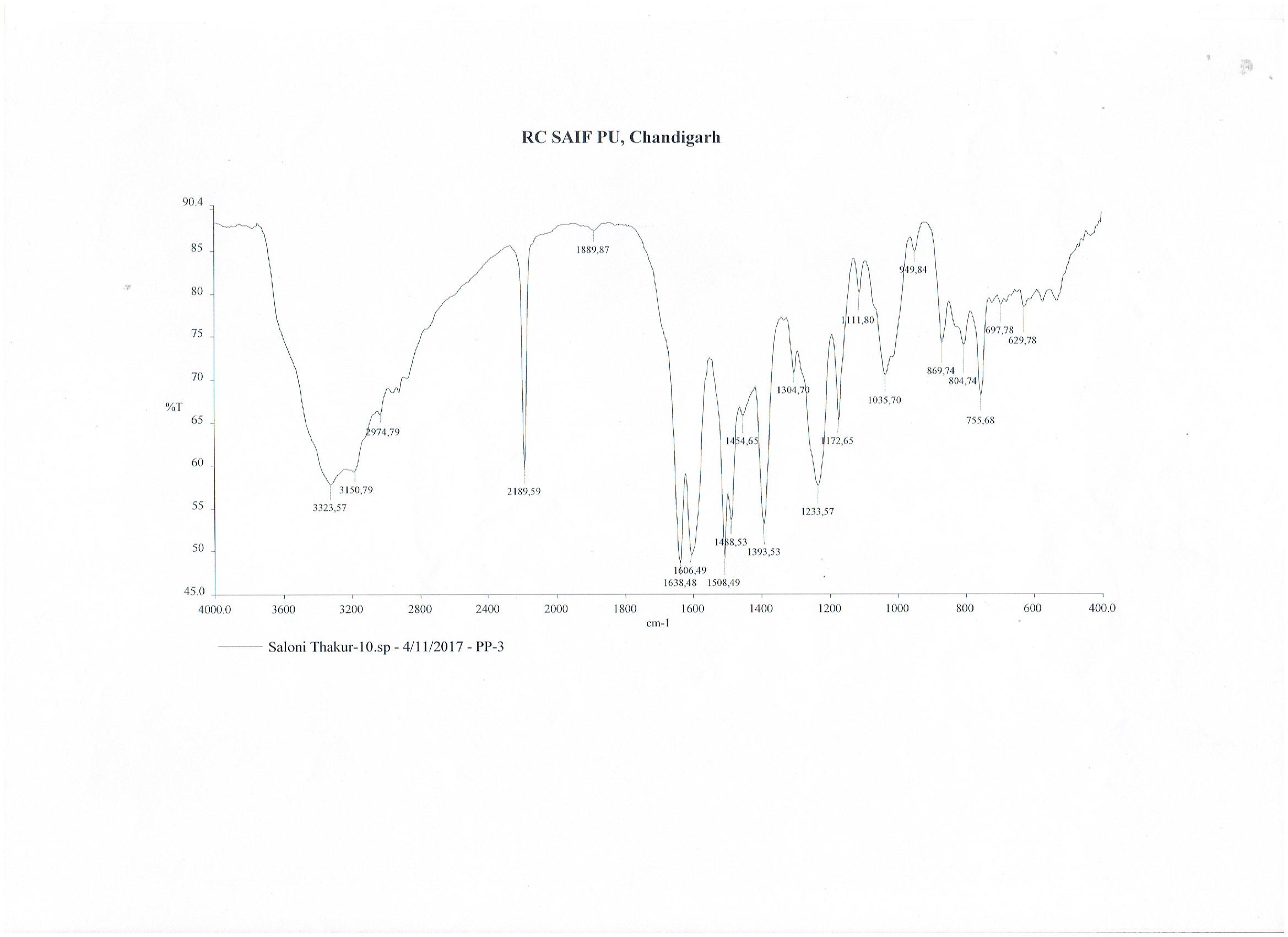
**1H-NMR (3a)**



**13C-NMR (3a)**

****

**ESI-MS(3a)**

****

**IR(3a)**

1. \*Corresponding author. e-mail: yusuf\_sah04@yahoo.co.in [↑](#footnote-ref-2)