Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Recyclable Mesalamine-Functionalized on Magnetic Nanoparticles (Mesalamine/GPTMS@SiO_2@Fe_3O_4) for Tandem Knoevenagel–Michael Cyclocondensation: Grinding Technique for the Synthesis of Biologically Active 2-Amino-4*H*-benzo[b]pyran Derivatives

Mahdiyeh Partovi[1], Sobhan Rezayati[1], Ali Ramazani[1,2] *, Yavar Ahmadi[3], Hooman Taherkhani[1]

[1]*Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan 45371-38791, Iran*

[2]*Department of Biotechnology, Research Institute of Modern Biological Techniques (RIMBT), University of Zanjan, Zanjan 45371-38791, Iran*

[3] *Department of Chemistry Education, Farhangian University, P.O. Box 14665-889, Tehran, Iran*

Corresponding author :aliramazani@znu.ac.ir; aliramazani@gmail.com

2-Amino-7, 7-dimethyl-4-(4-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4b)

FT-IR (KBr, cm^{-1}): 3379, 3182, 2958, 2188, 1674, 1589, 1459, 1367, 1215, 1094, 1013, 828, 616, 521. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.33 (d, 2H, J = 7.5 MHz, Ar-H), 7.19 (d, 2H, J = 8.25 MHz, Ar-H), 7.05 (s, 2H, NH_2), 4.65 (s, 1H, C-H), 2.19-2.41 (m, 2H, CH_2), 2.02-2.08 (m, 2H, CH2), 1.01 (s, 3H, Me), 0.95 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 18.9, 27.3, 28.7, 32.1, 33.1, 38.9, 50.3, 56.4, 56.7, 111.8, 119.5, 128.0, 129.1, 131.8, 132.2, 133.4, 141.1, 159.1, 163.7, 196.0.

2-Amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4c)

FT-IR (KBr, cm^{-1}): 3396, 3324, 3212, 2960, 2199, 1679, 1604, 1604, 1371, 1214, 1036, 839, 695. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 6.91-7.84 (m, 6H, Ar-H, NH_2), 4.16 (s, 1H, C-H), 2.10-2.48 (m, 4H, $2CH_2$), 0.92 (s, 3H, Me), 1.00 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 31.0, 31.7, 32.2, 32.9, 35.6, 47.1, 50.4, 56.5, 114.6, 129.2, 129.9, 131.0, 132.5, 133.1, 158.9, 160.7, 196.6.

2-Amino-7, 7-dimethyl-4-(4-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4e)

FT-IR (KBr, cm^{-1}): 3405, 3321, 3185, 2963, 2192, 1682, 1652, 1631, 1594, 1521, 1349, 1215, 1033, 827. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.15-8.25 (m, 6H, Ar-H, NH_2), 4.34 (s, 1H, C-H), 3.03-3.39 (m, 2H, CH_2), 2.06-2.20 (m, 2H, CH_2), 1.13 (s, 3H, Me), 1.01 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 22.9, 24.2, 27.7, 31.8, 45.8, 52.0, 53.1, 114.7, 115.3, 124.3, 128.3, 146.2, 154.5, 159.0.

2-Amino-7, 7-dimethyl-4-(4-methylphenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4f)

FT-IR (KBr, cm^{-1}): 3383, 3316, 3208, 3026, 2963, 2192, 1682, 1654, 1605, 1510, 1410, 1368, 1250, 1214, 1036, 845, 770. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 6.93-8.42 (m, 6H, Ar-H, NH_2), 4.11 (s, 1H, C-H), 2.21 (s, 3H, Me), 2.36-2.46 (m, 4H, $2CH_2$), 1.00 (s, 3H, Me), 0.93 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 14.5, 22.8, 24.2, 27.7, 31.1, 45.9, 52.9, 53.6, 108.2, 115.5, 125.5, 127.1, 140.1, 154.4, 158.6, 191.6.

2-Amino-7, 7-dimethyl-4-(4-fluorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4h)

FT-IR (KBr, cm^{-1}): 3431, 2230, 1635, 1595, 1507, 1416, 1367, 1304, 1244, 1165, 838, 616, 529, 438.^{1}H-NMR (250 MHz, DMSO-d_6): δ 6.98-8.50 (m, 6H, Ar-H, NH_2), 4.17 (s, 1H, C-H), 2.19-2.51 (m, 2H, CH_2), 2.04-2.10 (m, 2H, CH_2), 1.0 (s, 3H, Me), 0.92 (s, 3H, Me). ^{13}C-NMR (62.5

MHz, DMSO-d_6): δ 27.3, 28.2, 28.7, 32.2, 35.3, 47.1, 50.4, 115.2, 115.6, 117.2, 117.5, 129.5, 134.0, 141.3, 160.6, 162.9, 196.1.

2-Amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4m)

FT-IR (KBr, cm^{-1}): 3396, 3323, 3212, 2959, 2190, 1682, 1654, 1604, 1489, 1366, 1250, 1214, 1034, 847, 561. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.13-7.90 (m, 4H, Ar-H), 7.02 (s, 2H, NH_2), 4.32 (s, 1H, CH), 2.09-2.47 (m, 4H, $2CH_2$), 1.00 (s, 3H, Me), 0.98 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 26.6, 28.3, 29.5, 32.5, 35.3, 50.7, 55.2, 59.4, 102.8, 104.3, 110.6, 113.6, 128.8, 140.4, 145.0, 149.7, 157.7, 194.7.

2-Amino-7, 7-dimethyl-4-(2,4-dichlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4o)

FT-IR (KBr, cm^{-1}): 3531, 3364, 3158, 2961, 2191, 1721, 1685, 1609, 1475, 1368, 1216, 1042, 861, 563. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.21-7.41 (m, 3H, Ar-H), 7.07 (s, 2H, NH_2), 5.19 (s, 1H, CH), 2.06-2.51 (m, 4H, $2CH_2$), 0.98 (s, 6H, 2Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 18.9, 27.3, 28.9, 31.9, 32.7, 50.3, 54.0, 56.4, 110.4, 119.4, 128.9, 129.4, 130.6, 134.6, 136.3, 136.7, 159.9, 164.1, 196.1.

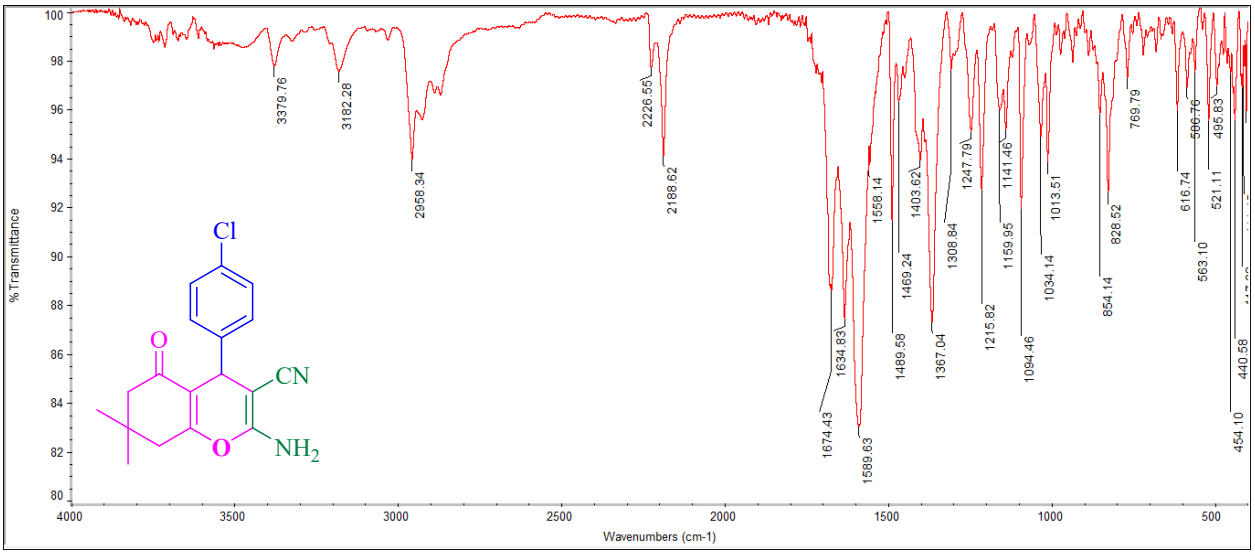

Figure S1. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(4-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4b)

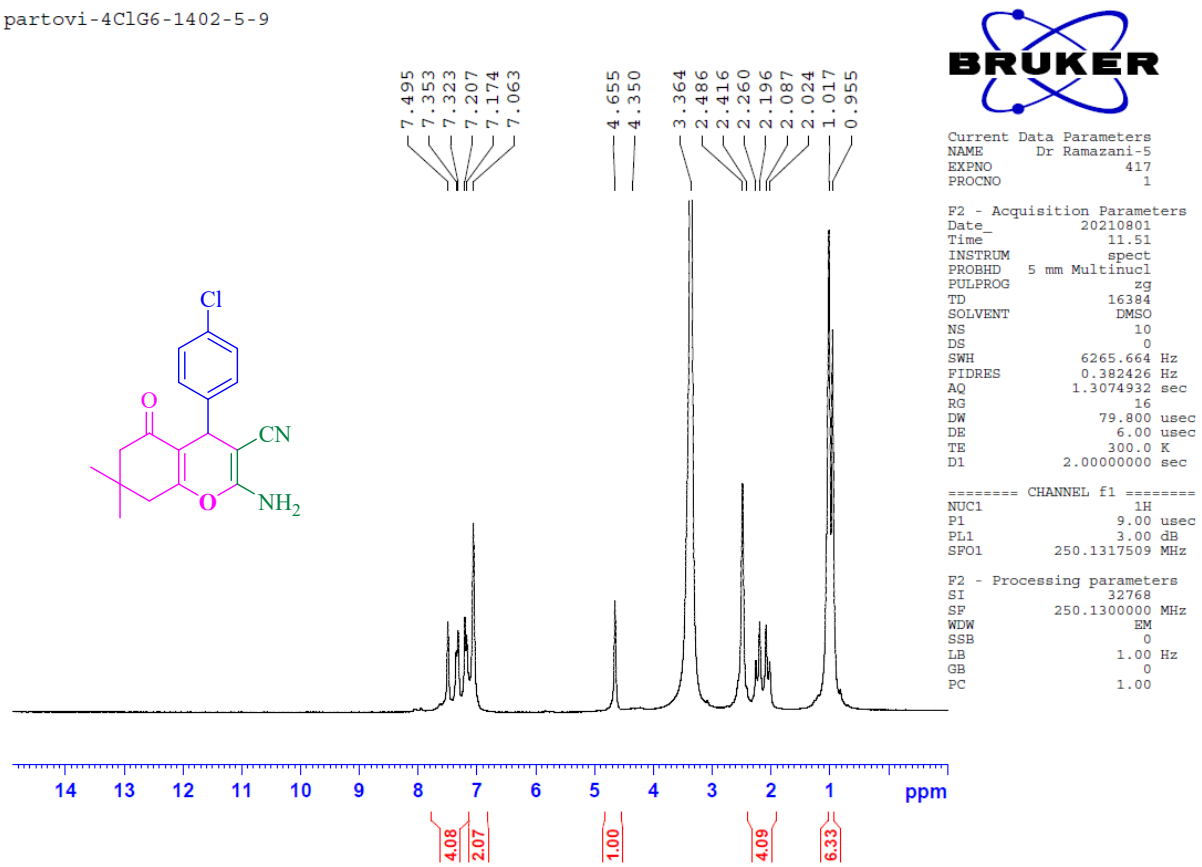

Figure S2. ^{1}H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4b)

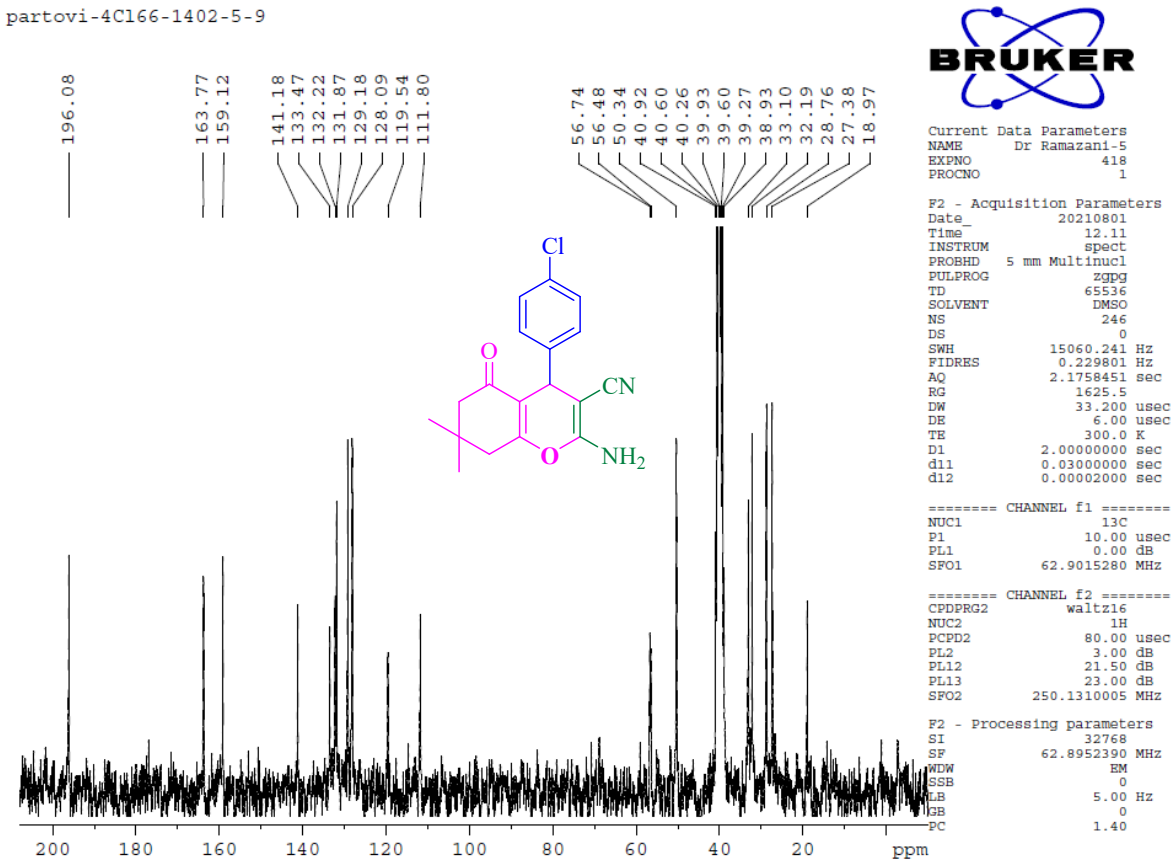

Figure S3. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4b)

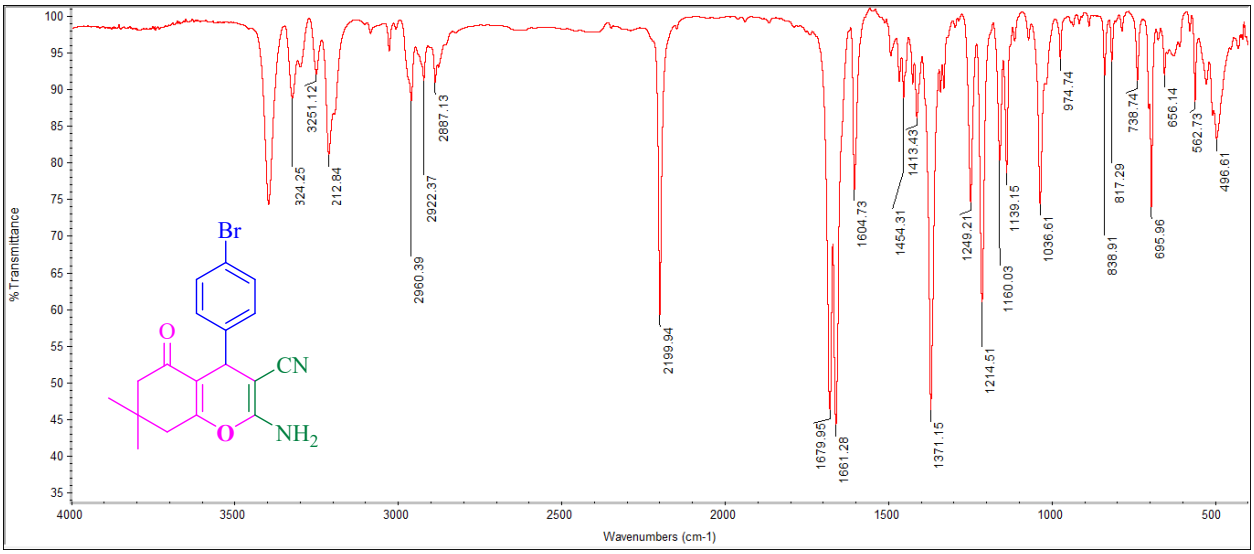

Figure S4. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4c)

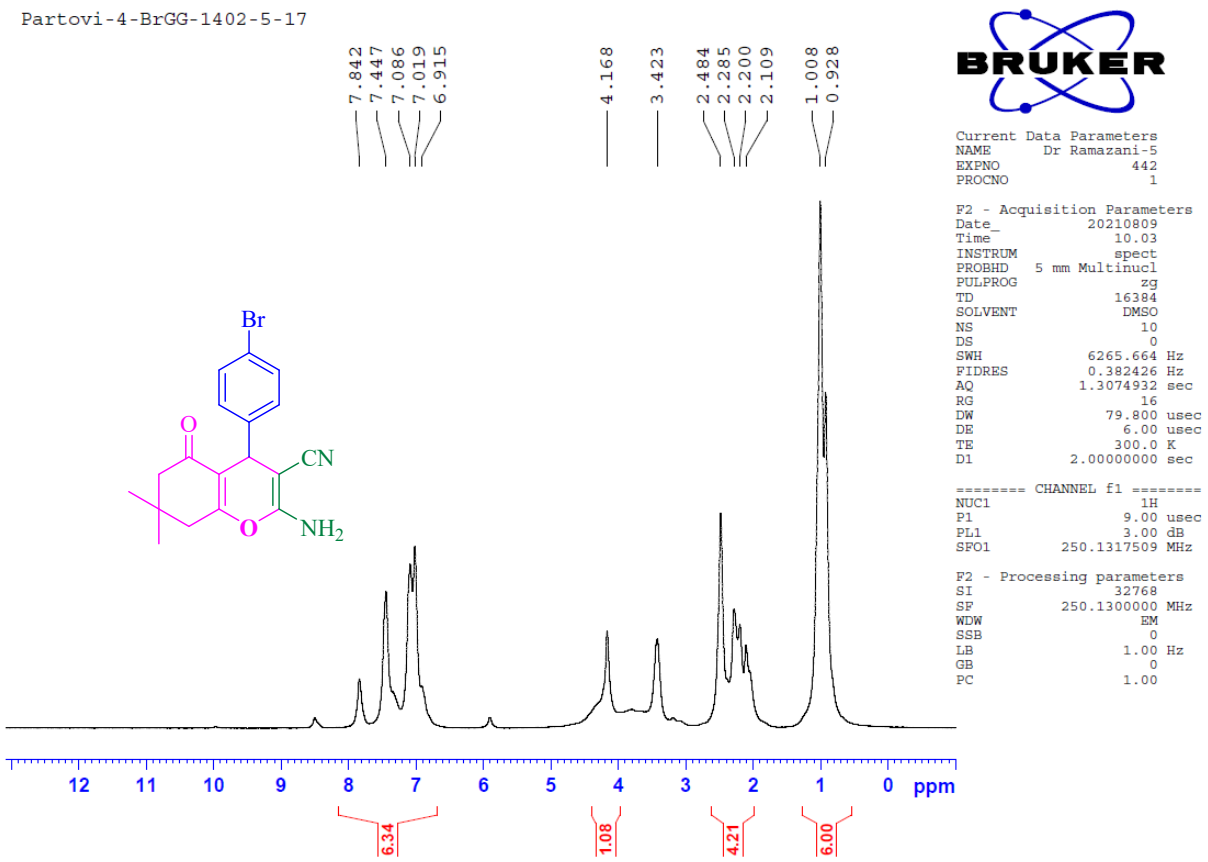

Figure S5. [1]H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4c)

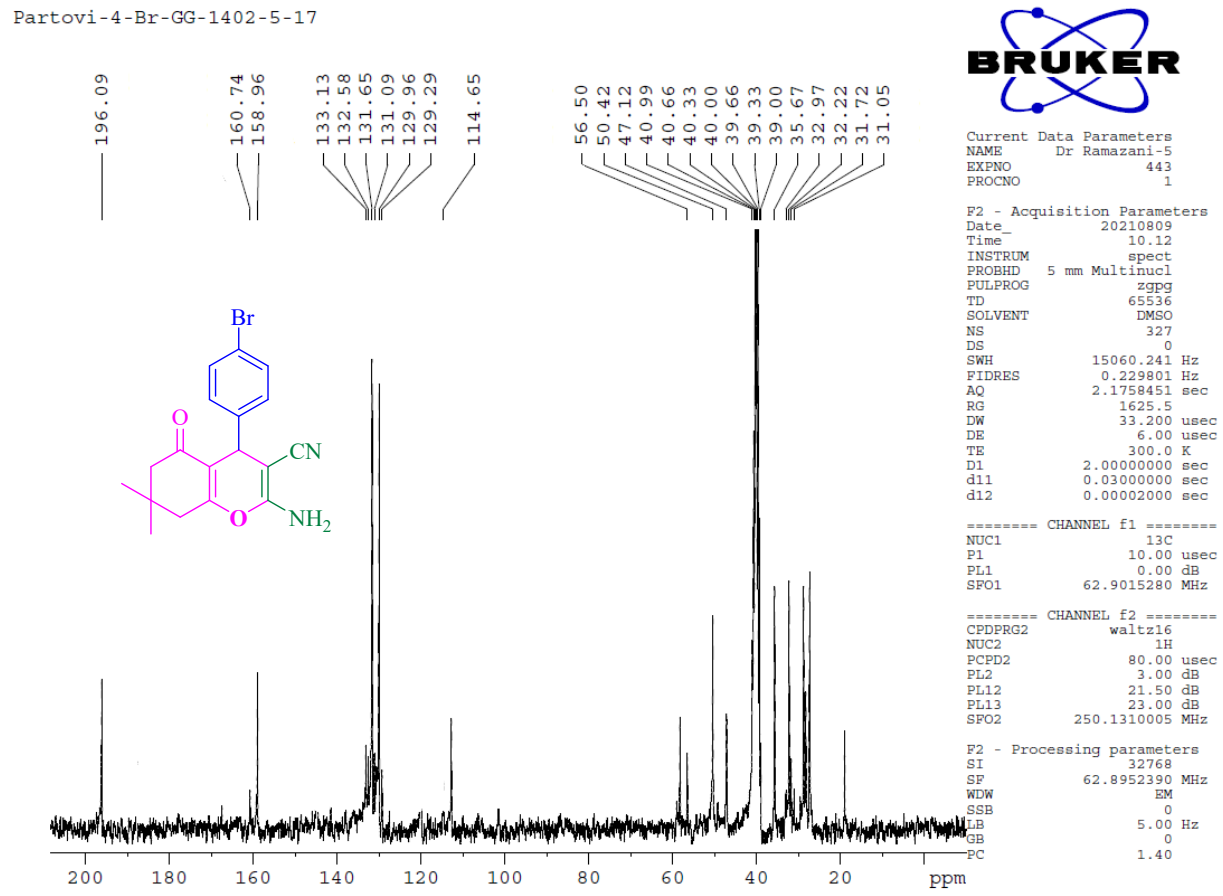

Figure S6. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4c)

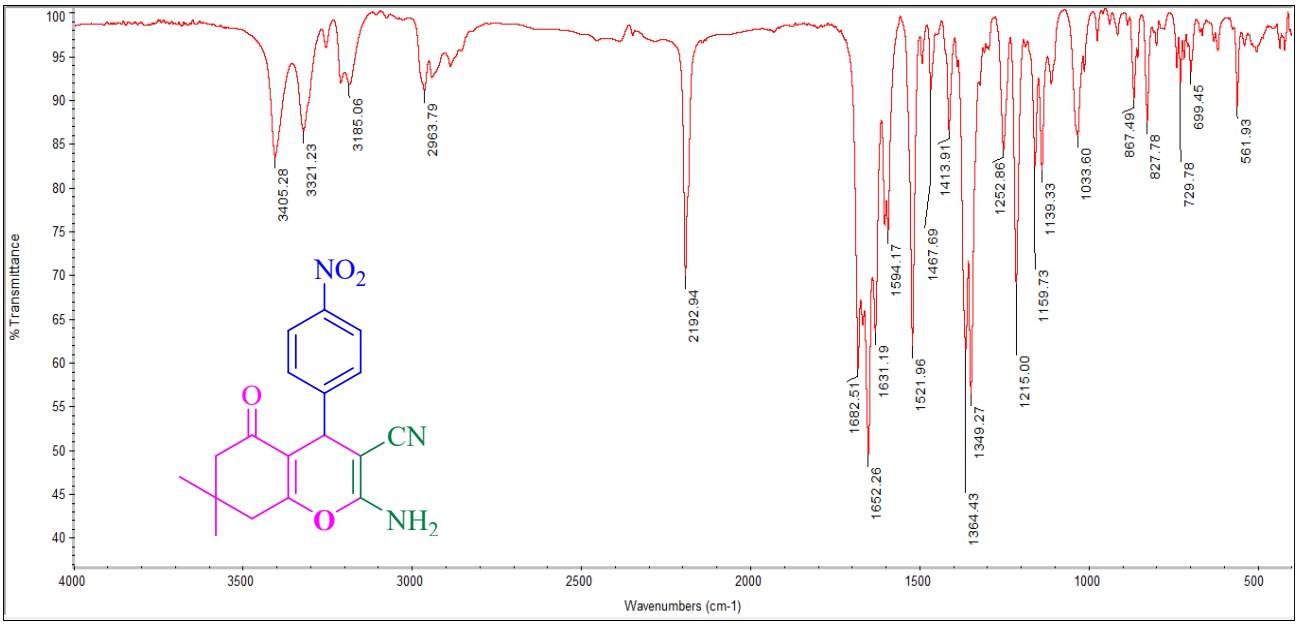

Figure S7. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(4-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4e)

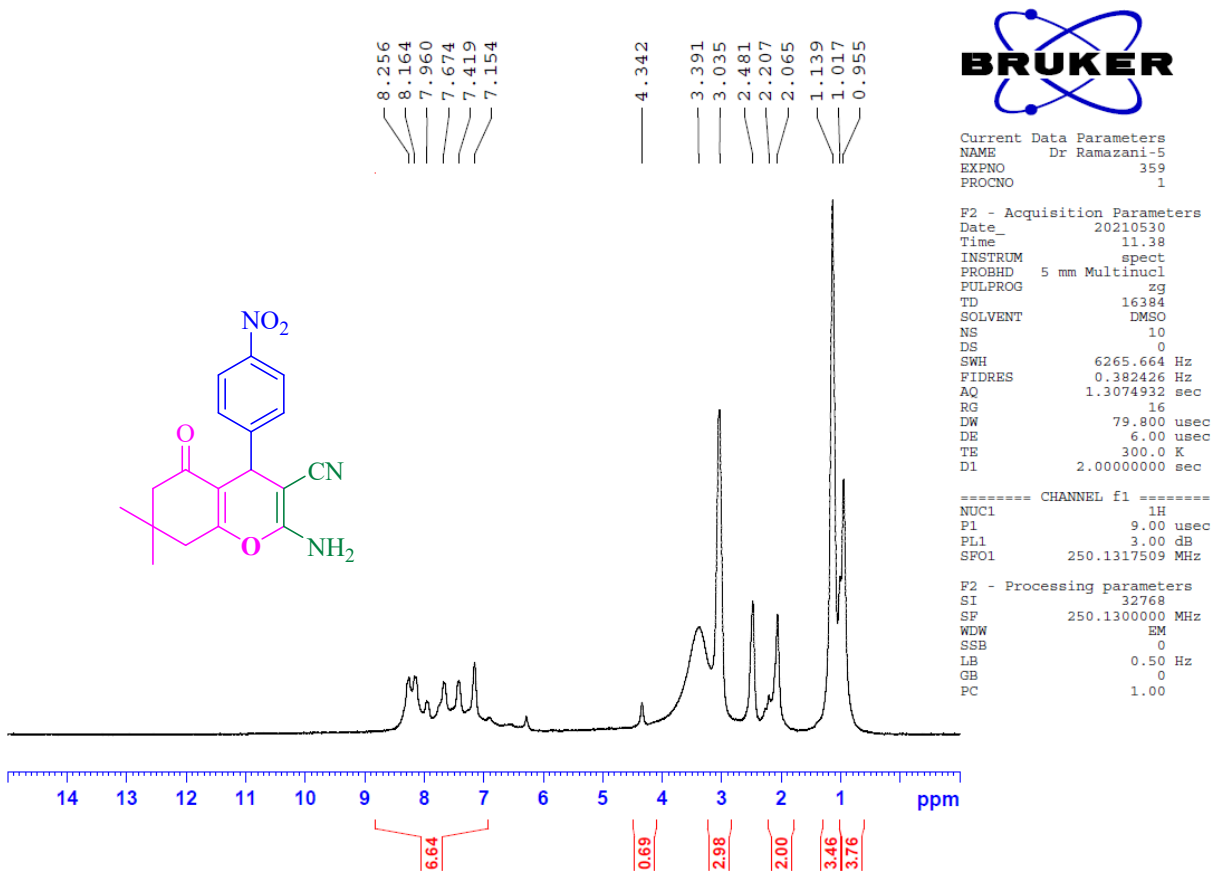

Figure S8. [1]H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4e)

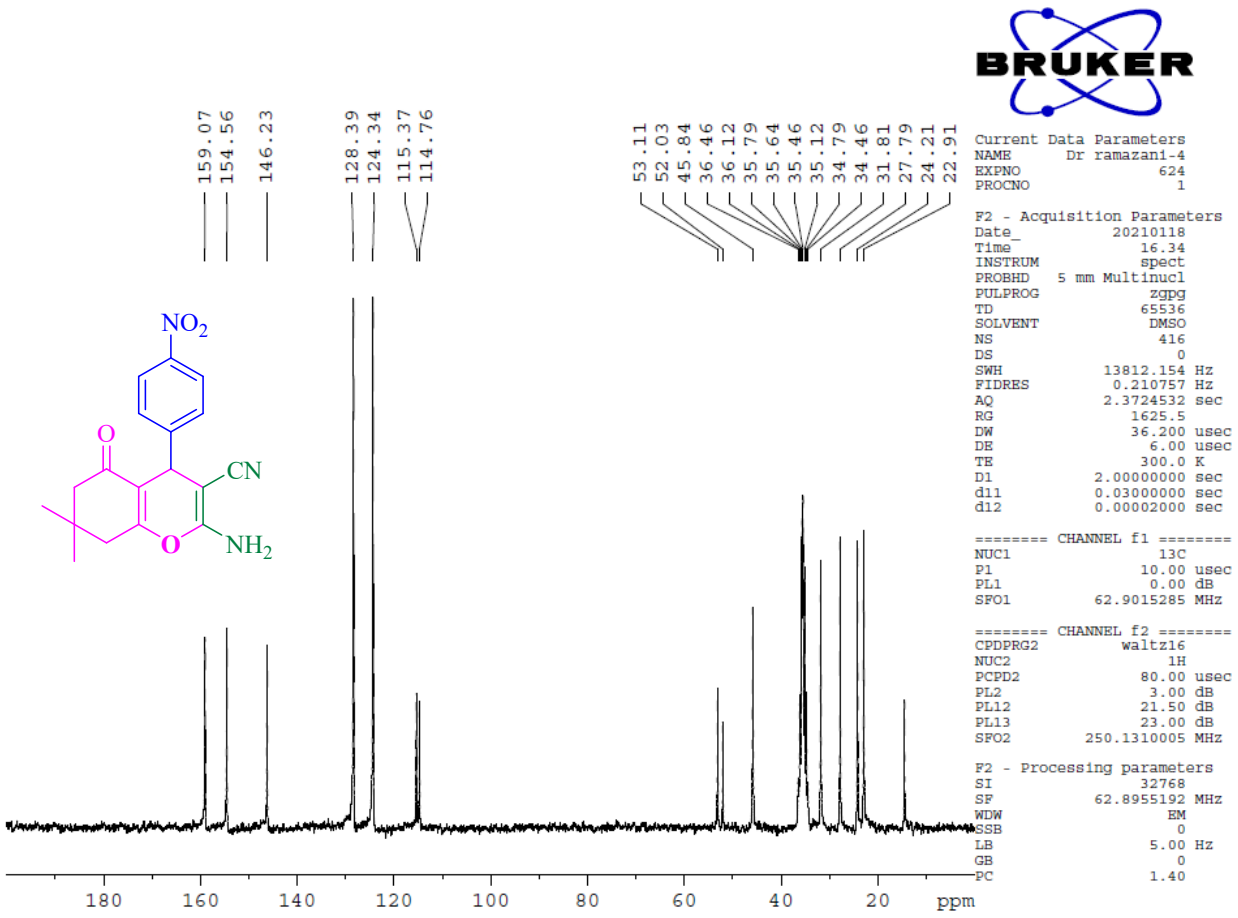

Figure S9. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4e)

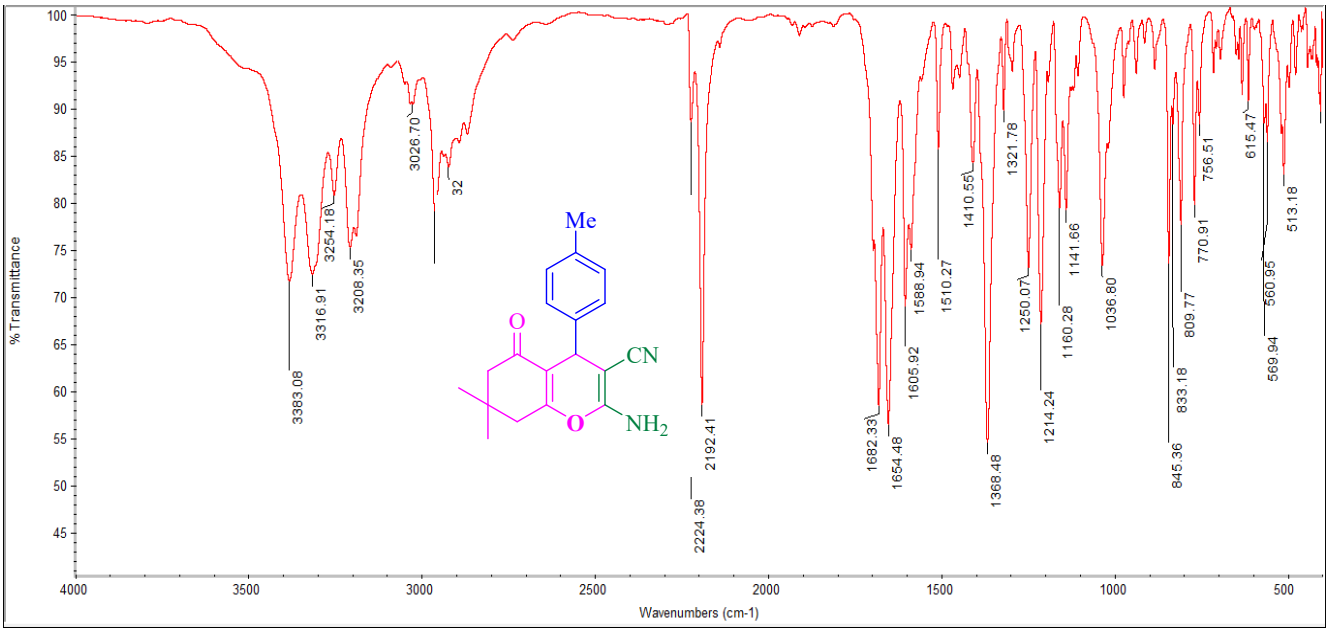

Figure S10. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(4-methylphenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4f)

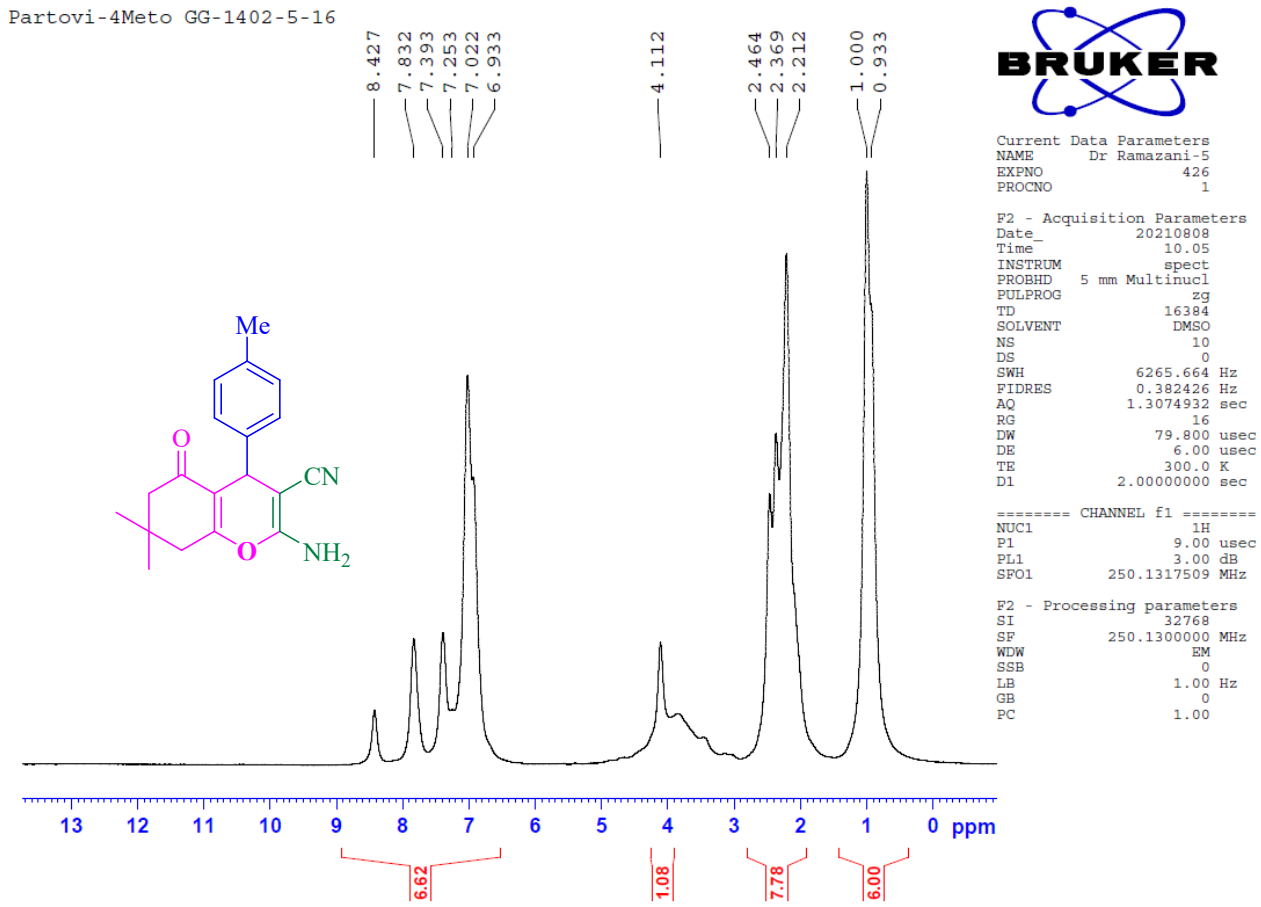

Figure S11. [1]H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-methylphenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4f)

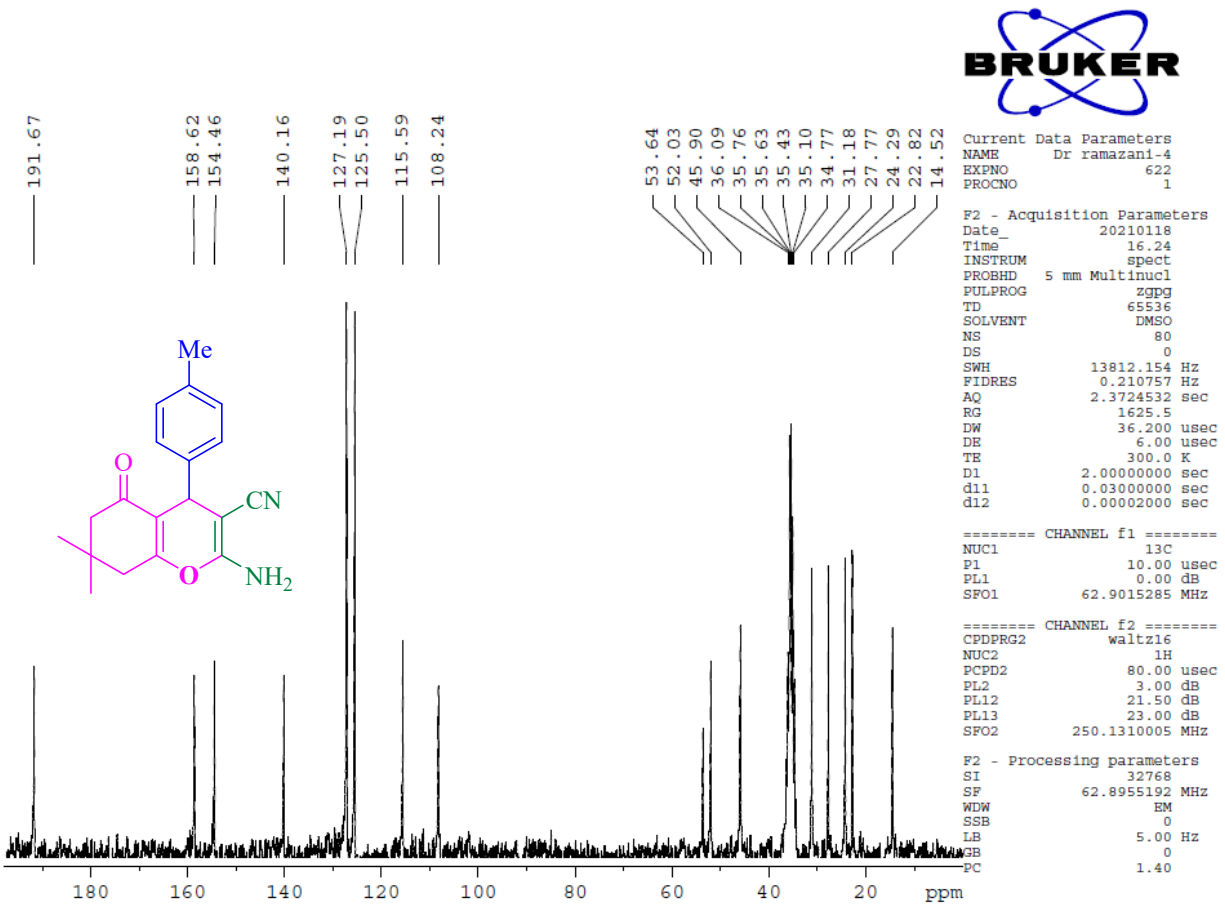

Figure S12. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-methylphenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4f)

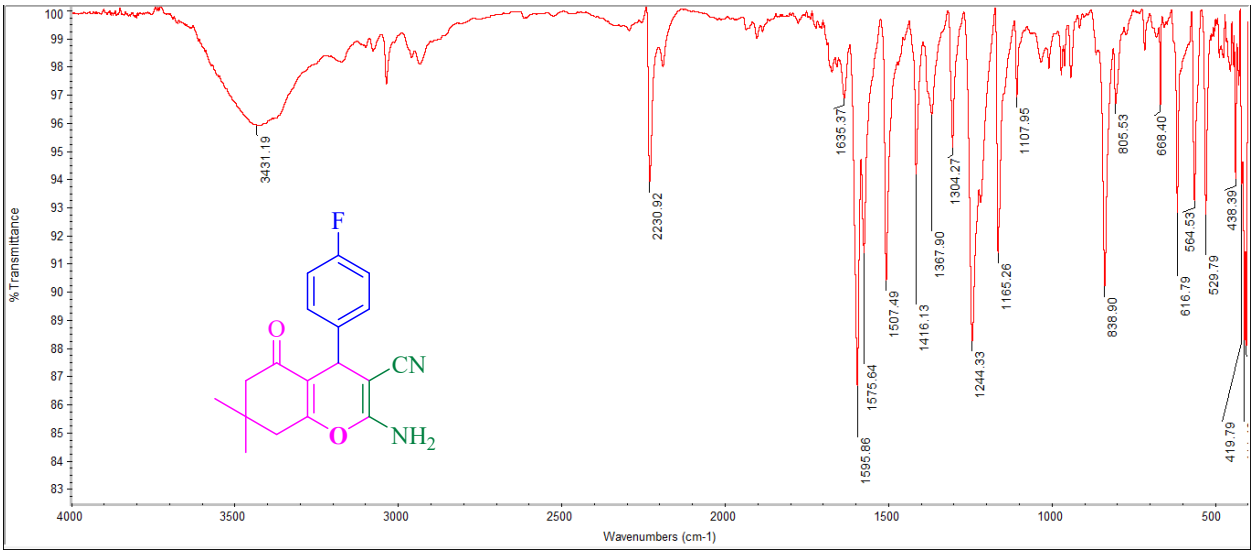

Figure S13. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(4-fluorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4h)

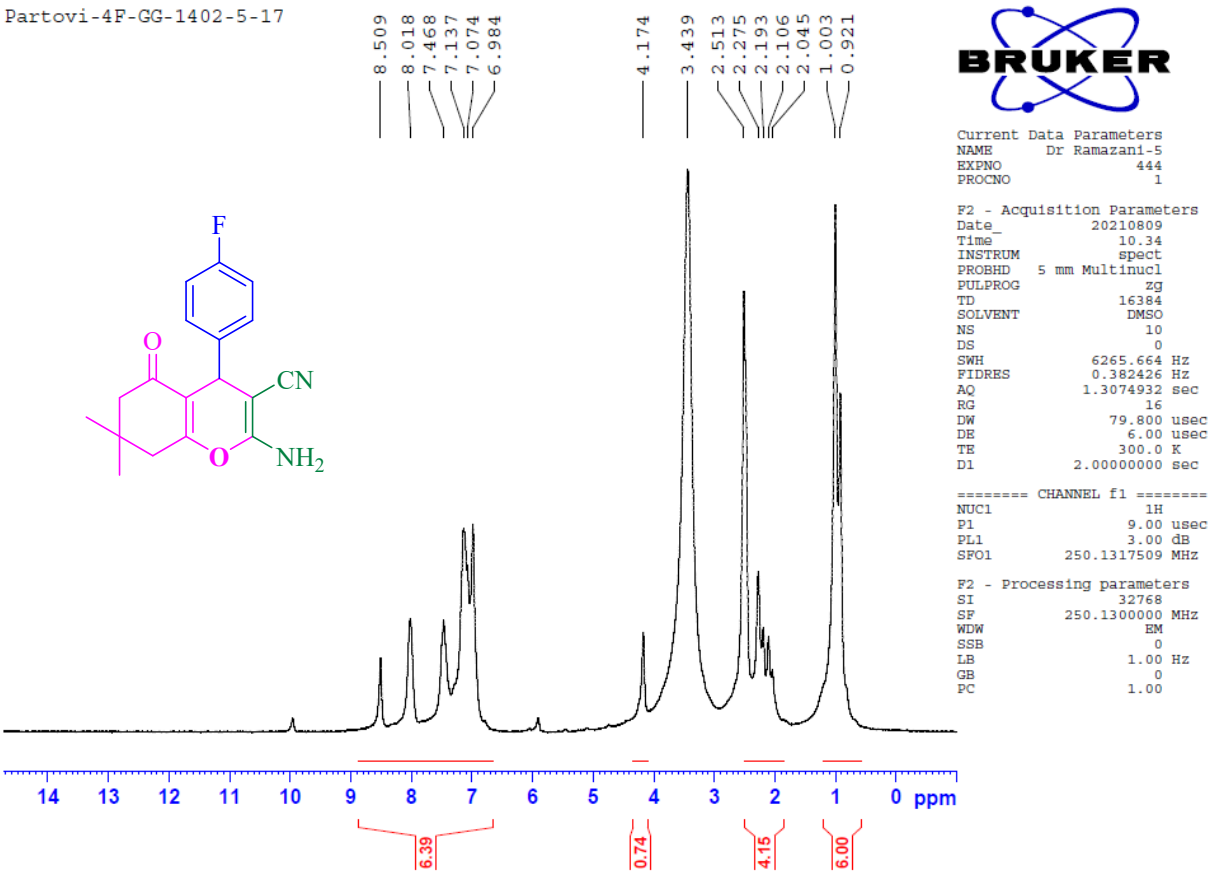

Figure S14. ^{1}H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-fluorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4h)

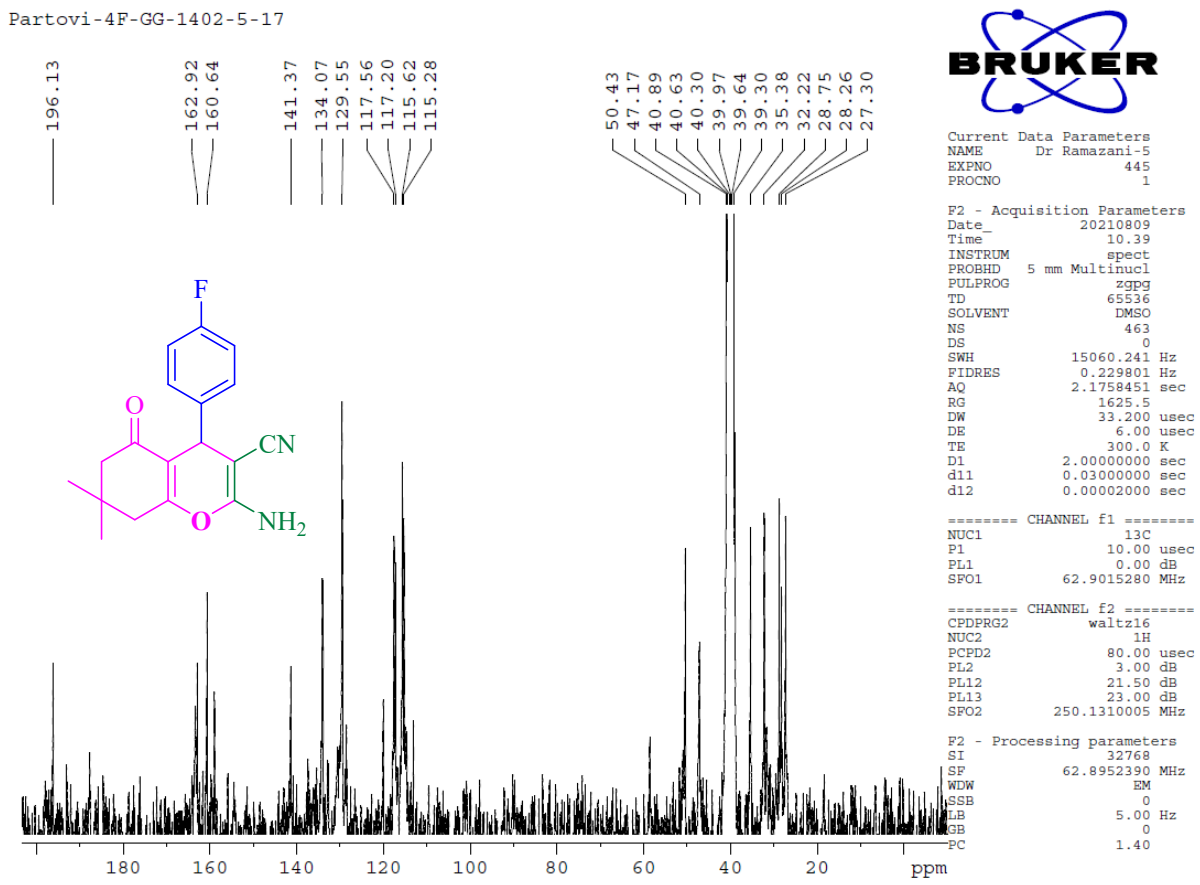

Figure S15. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(4-fluorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4h)

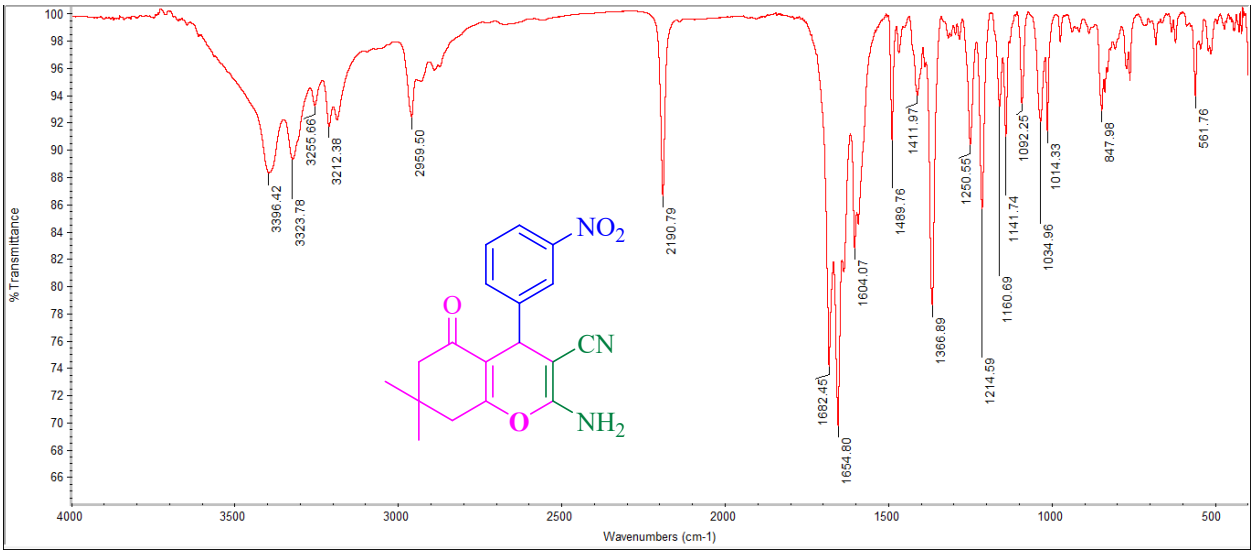

Figure S16. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4m)

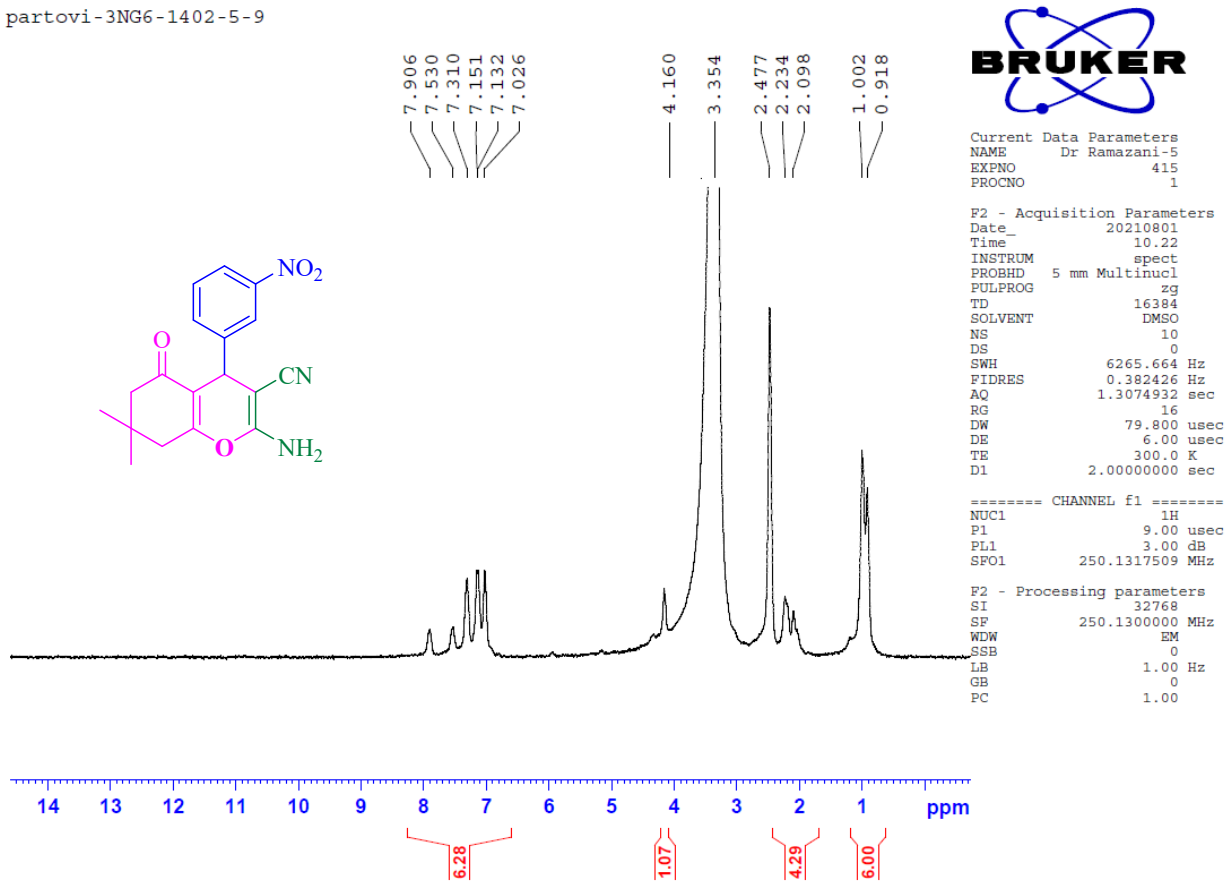

Figure S17. ^{1}H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4m)

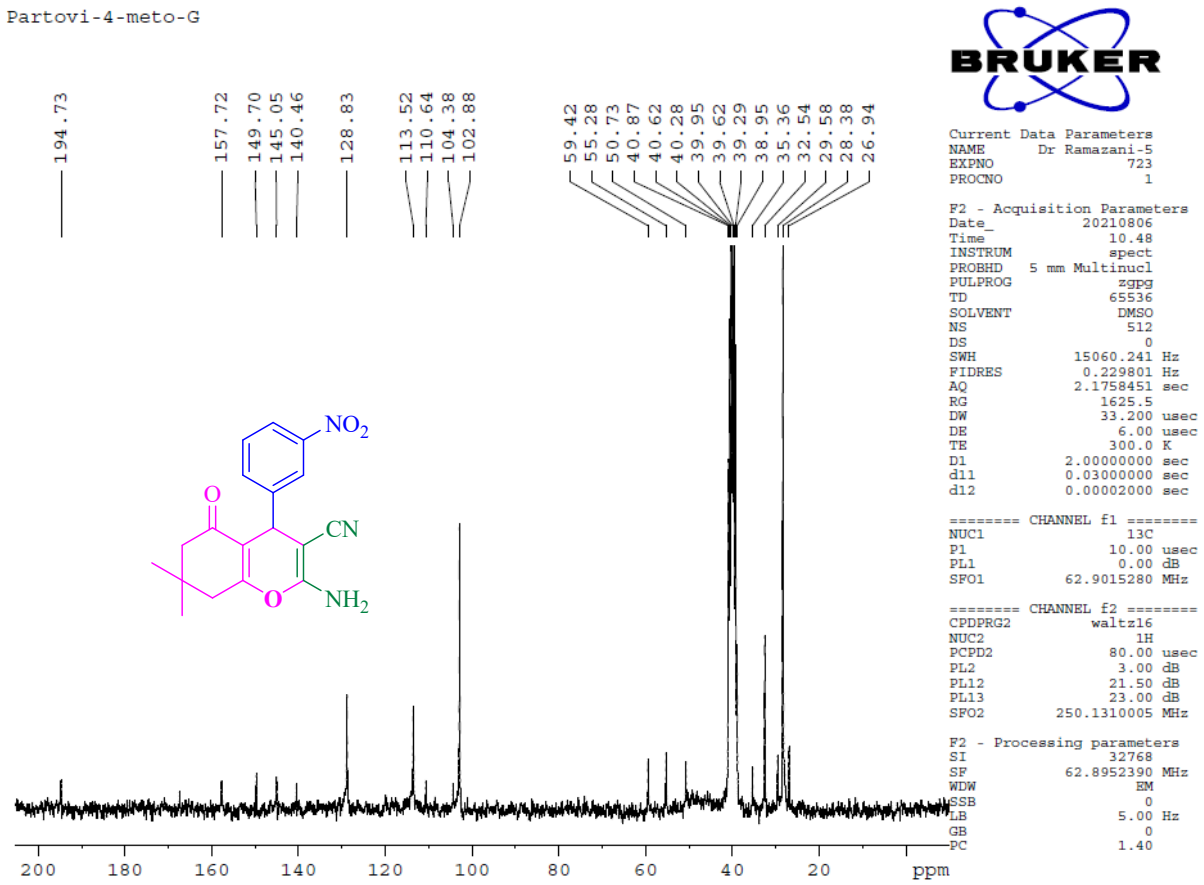

Figure S18. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4m)

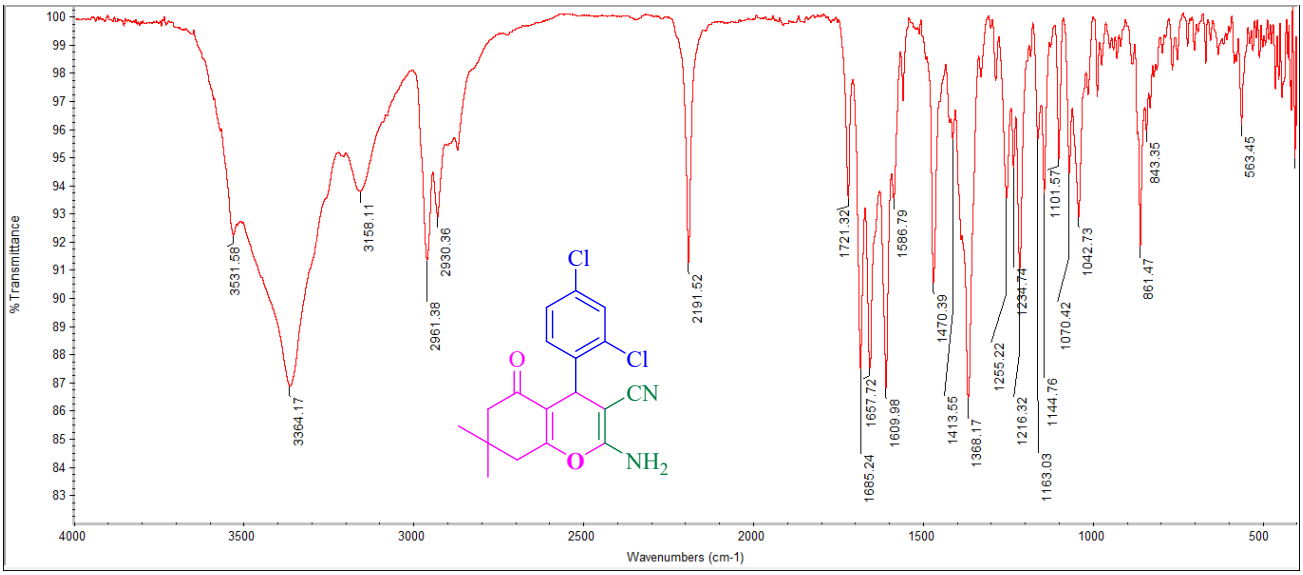

Figure S19. FT-IR spectrum of 2-Amino-7, 7-dimethyl-4-(2,4-dichlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4o)

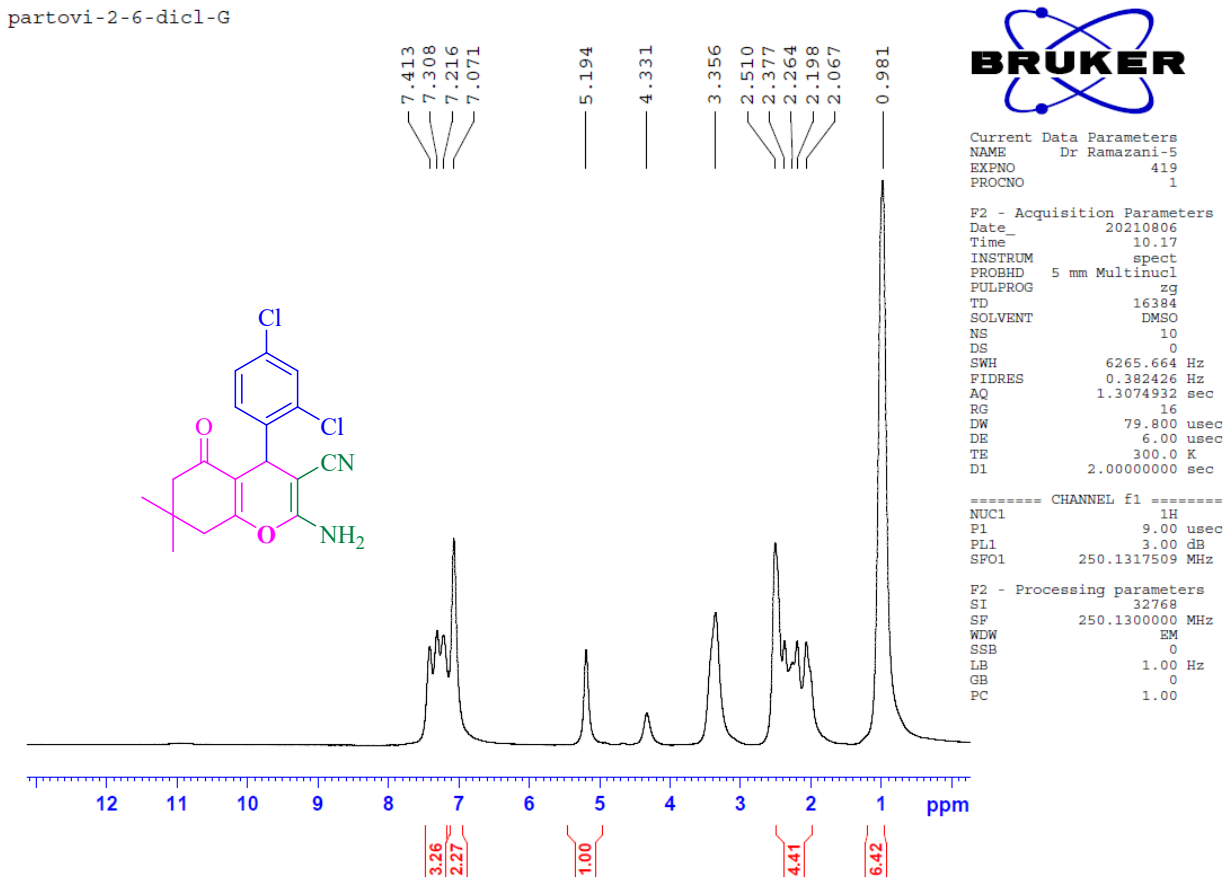

Figure S20. [1]H NMR spectrum of 2-Amino-7, 7-dimethyl-4-(2,4-dichlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4o)

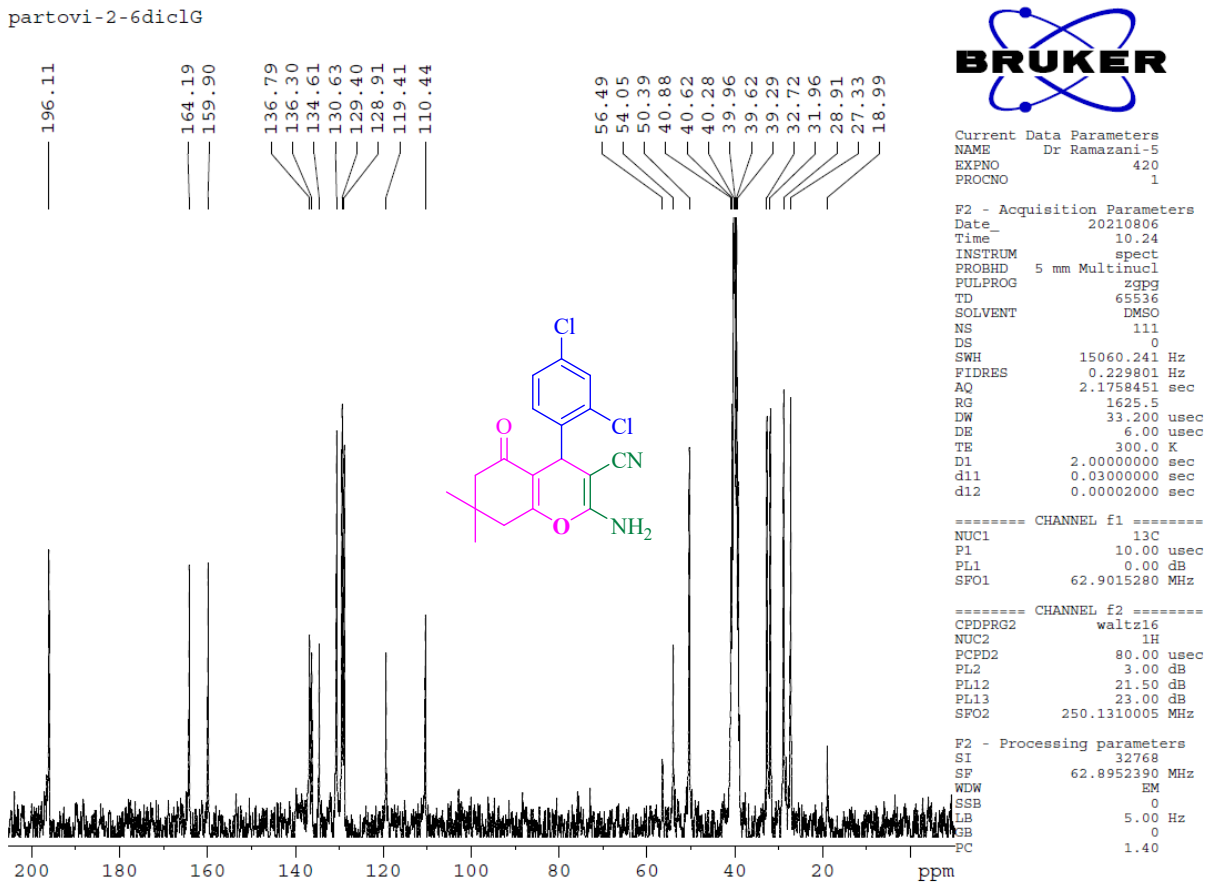

Figure S21. ^{13}C NMR spectrum of 2-Amino-7, 7-dimethyl-4-(2,4-dichlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (4o)