Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Copper(II) Complex Containing Pyridine-2-Carbaldehyde and its Direct Binding onto Ethylenediamine Functionalized with Fe_3O_4@SiO_2 Nanoparticles for the Catalytic Applications

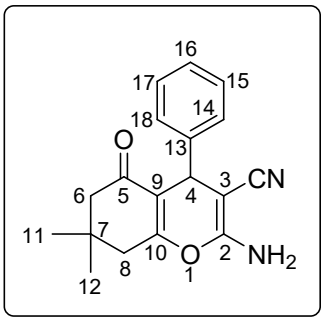
Masoud Karimi[a], Ali Ramazani*[a,b], Sami Sajjadifar[c], Sobhan Rezayati[a]

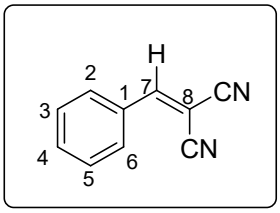
[a]*Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan 45371-38791, Iran*

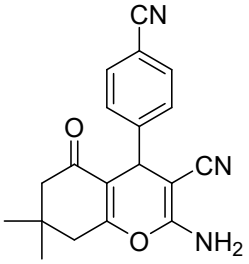
[b]*Department of Biotechnology, Research Institute of Modern Biological Techniques (RIMBT), University of Zanjan, Zanjan 45371-38791, Iran*

[c]*Department of Chemistry, Payame Noor University, PO BOX 19395-4697, Iran, Tehran*

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


16
17
15
18
14
O
13
3
CN
6
5
9
4
11
7
10
O
2
NH2
8
1
12

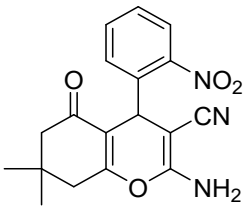

H
2
1
7
8
CN
3
CN
4
6
5



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

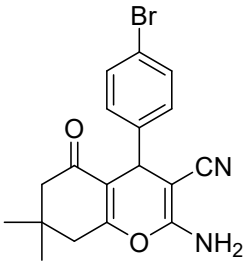
FT-IR (KBr, cm^{-1}): 3354, 3062, 2962, 2227, 2190, 1693, 1503, 1470, 1039, 59, 74. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.72 (d, 2H, J = 7, Ar-H), 7.33 (d, 2H, J = 7.25, Ar-H), 7.10 (s, 2H, NH_2), 4.26 (s, 1H, C-H), 2.19-2.25 (m, 2H, CH_2), 2.04-2.10 (m, 2H, CH_2), 0.99 (s, 3H, Me), 0.91 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 27.3 (C11 & C12), 28.6 (C7), 32.2 (C8), 36.2 (C4), 50.2 (C6), 56.4 (C3), 109.8 (C16), 112.1 (C9), 119.1 (CN), 119.8 (CN), 128.7 (C18 & C14), 132.8 (C15 & C17), 150.6 (C13), 159.5 (C10), 163.5 (C2), 196.1 (C5).

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



FT-IR (KBr, cm^{-1}): 3333, 3185, 2957, 2193, 1694, 1580, 1526, 1469, 1327, 1255, 1041, 869, 736. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.76 (d, 1H, J = 7, Ar-H), 7.59 (d, 1H, J = 7.25, Ar-H), 7.29-7.39 (m, 2H, Ar-H), 7.16 (s, 2H, NH_2), 4.88 (s, 1H, C-H), 2.12-2.18 (m, 2H, CH_2), 1.92-1.99 (m, 2H, CH_2), 0.96 (s, 3H, Me), 0.82 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 27.0 (C11 & C12), 28.6 (C7), 30.3 (C8), 32.2 (C4), 49.9 (C6), 56.7 (C3), 112.7 (C9), 119.4 (CN), 124.1 (C15), 128.2 (C16), 130.6 (C18), 133.6 (C17), 133.7 (C13), 139.3 (C14), 149.4 (C10), 159.5 (C2), 196.2 (C5).

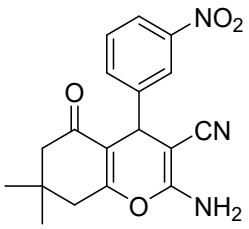
2-Amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran



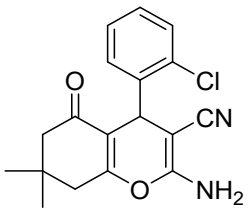
FT-IR (KBr, cm^{-1}): 3364, 3153, 2965, 2191, 166, 1607, 1473, 1365, 1255, 1042, 632. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.45 (d, 2H, J = 7.25, Ar-H), 7.07 (d, 2H, J = 8.5, Ar-H), 7.04 (s, 2H, NH_2), 4.14 (s, 1H, C-H), 2.18-2.25 (m, 2H, CH_2), 2.03-2.09 (m, 2H, CH_2), 1.0 (s, 3H, Me), 0.91 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 27.2 (C11 & C12), 28.7 (C7), 32.2 (C8), 35.6 (C4), 50.3 (C6), 58.0 (C3), 112.7 (C9), 119.9 (CN), 129.9 (C15 & C17), 131.6 (C14 & C18), 144.6 (C13), 158.9 (C10), 163.0 (C2), 196.0 (C5).

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

FT-IR (KBr, cm^{-1}): 3430, 3335, 3100, 2956, 2186, 1685, 1599, 1529, 1417, 1347, 1427, 1252, 1037, 714. ^{1}H-NMR (250 MHz, DMSO-d_6):



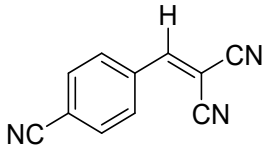
δ 7.61-8.03 (m, 4H, Ar-H), 7.16 (s, 2H, NH_2), 4.38 (s, 1H, CH), 2.04-2.51 (m, 4H, $2CH_2$), 1.0 (s, 3H, Me), 0.91 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 27.1 (C11 & C12), 28.7 (C7), 32.2 (C8), 35.8 (C4), 50.2 (C6), 57.5 (C3), 112.2 (C9), 119.8 (CN), 122.2 (C16), 130.4 (17), 134.6 (C18), 147.4 (C13), 148.2 (15), 159.0 (C10), 163.6 (C2), 196.2 (C5).



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

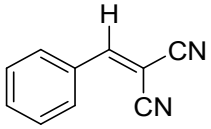
FT-IR (KBr, cm^{-1}): 3396, 3330, 3198, 2959, 2199, 1682, 1603, 1468, 1368, 1214, 1037, 750. ^{1}H-NMR (250 MHz, DMSO-d_6): δ 7.14-7.31 (m, 4H, Ar-H), 7.01 (s, 2H, NH_2), 4.65 (s, 1H, CH), 2.0-2.29 (m, 4H, $2CH_2$), 1.0 (s, 3H, Me), 0.94 (s, 3H, Me). ^{13}C-NMR (62.5 MHz, DMSO-d_6): δ 27.3 (C11 & C12), 28.8 (C7), 32.1 (C8), 32.2 (C4), 50.3 (C6), 57.2 (C3), 112.2 (C9), 119.6 (CN), 127.8 (C18), 128.6 (C17), 129.8 (C16), 130.3 (C14), 132.5 (C13), 141.9 (C10), 159.1 (C2), 163.5 (C5).

2-(4-Cyanobenzylidene)malononitrile



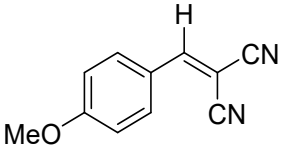
FT-IR (KBr, cm^{-1}): 3044, 2307, 2230, 1652, 1414, 1211, 960, 785, 619. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.99 (d, 2H, J = 7, Ar-H), 7.82 (d, 3H, J = 3.5, Ar-H, C-H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 111.7 (C4), 112.7 (2CN), 117.3 (CN), 130.7 (C2 & C6), 133.1 (C3 & C5), 134.2 (C1), 157.4 (C7).

2-Benzylidenemalononitrile



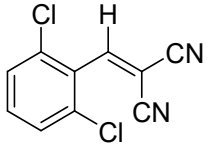
FT-IR (KBr, cm^{-1}): 3012, 2223, 1592, 1449, 1217, 957, 775. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.23-7.54 (m, 3H, Ar-H), 7.76 (s, 1H, C-H), 7.88 (m, 2H, Ar-H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 82.8 (C8), 112.5 (CN), 113.6 (CN), 129.6 (C4, C3 & C5), 130.7 (C2 & C6), 134.6 (C1), 159.9 (C7).

2-(4-Methoxybenzylidene)malononitrile



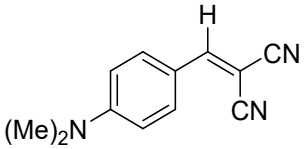
FT-IR (KBr, cm^{-1}): 2223, 1605, 1445, 1278, 1185, 833, 578. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.63 (d, 2H, J = 8.25, Ar-H), 7.69 (s, 1H), 6.99 (d, 2H, J = 8.25, Ar-H), 3.89 (s, 3H, OMe). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 55.8 (OMe), 78.3 (C8), 113.4 (CN), 114.4 (CN), 115.1 (C3 & C5), 124 (C1), 133.4 (C2 & C6), 158.9 (C4), 164.8 (C7).

2-(2,6-Dichlorobenzylidene)malononitrile



FT-IR (KBr, cm^{-1}): 3026, 2236, 1610, 1432, 1197, 1098, 892, 615, 520. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.94 (s, 1H, C-H), 7.37-7.42 (m, 3H, Ar-H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 94.2 (C8), 110.6 (CN), 111.8 (CN), 128.8 (C4), 129.7 (C3 & C5), 132.8 (C2 & C6), 133.6 (C1), 156.6 (C7).

2-(4-(Dimethylamino)benzylidene)malononitrile



FT-IR (KBr, cm^{-1}): 2210, 1614, 1521, 1198, 816, 727, 600, 518. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.75 (d, 2H, J = 7, Ar-H), 7.38 (s, 1H, C-H), 6.66 (d, 2H, J = 7.25, Ar-H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ (ppm): 40 (NMe_2), 71.54 (C7), 111.6 (C3 & C5), 114.9 (CN), 116 (CN), 119.2 (C1), 133.8 (C2 & C6), 154.2 (C4) 158 (C7).

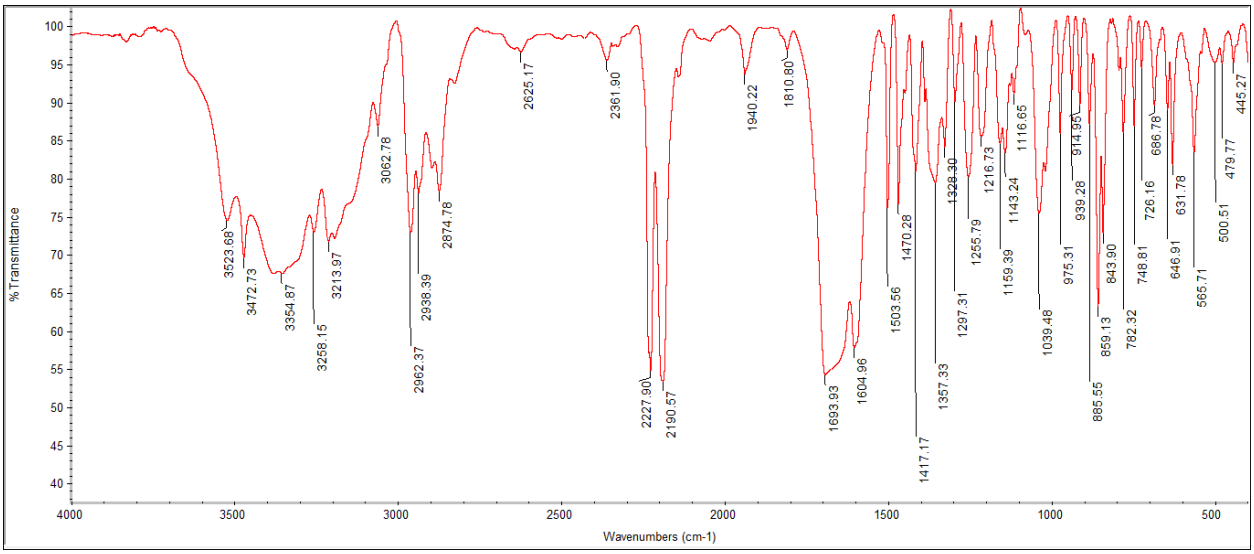


Figure S1: FT-IR spectrum of 2-amino-7,7-dimethyl-4-(4-cyanophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

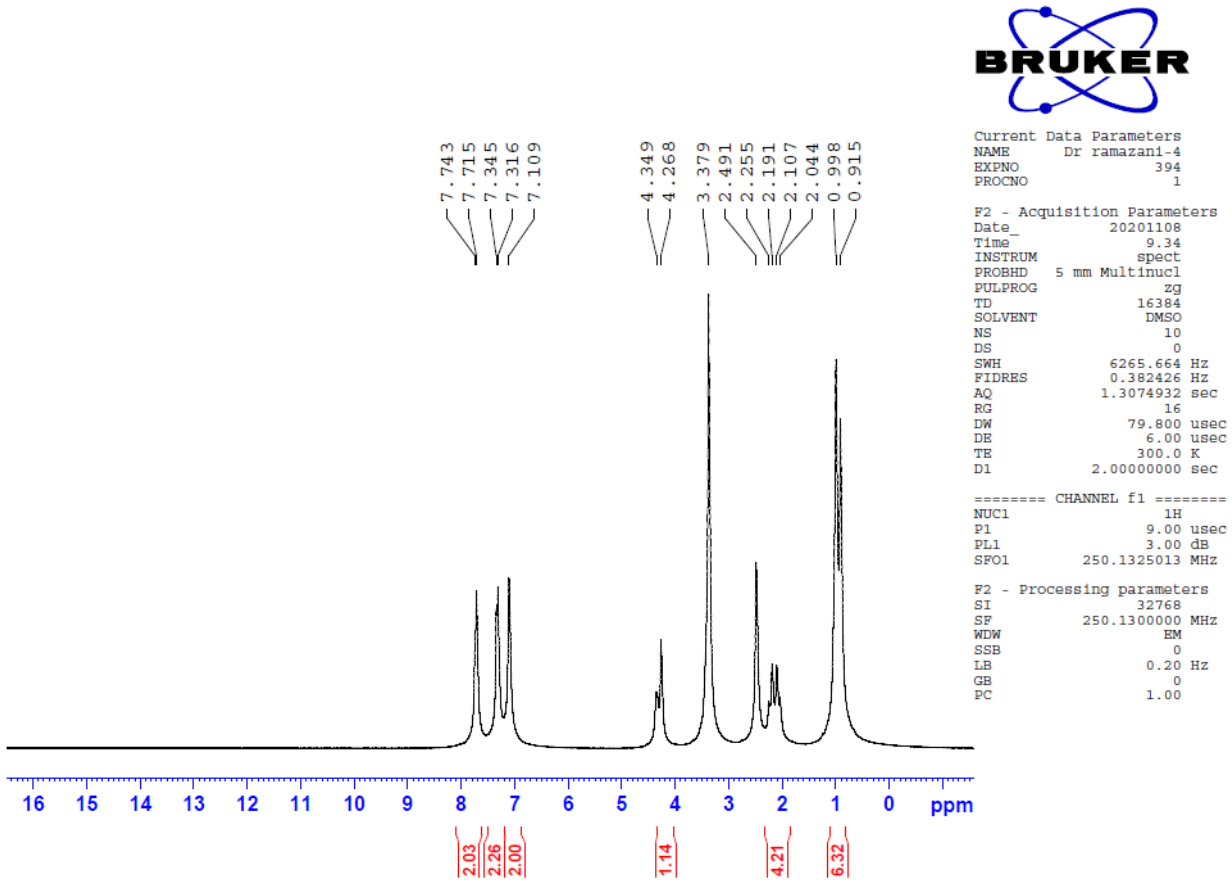


Figure S2: [1]H-NMR spectrum of 2-amino-7,7-dimethyl-4-(4-cyanophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

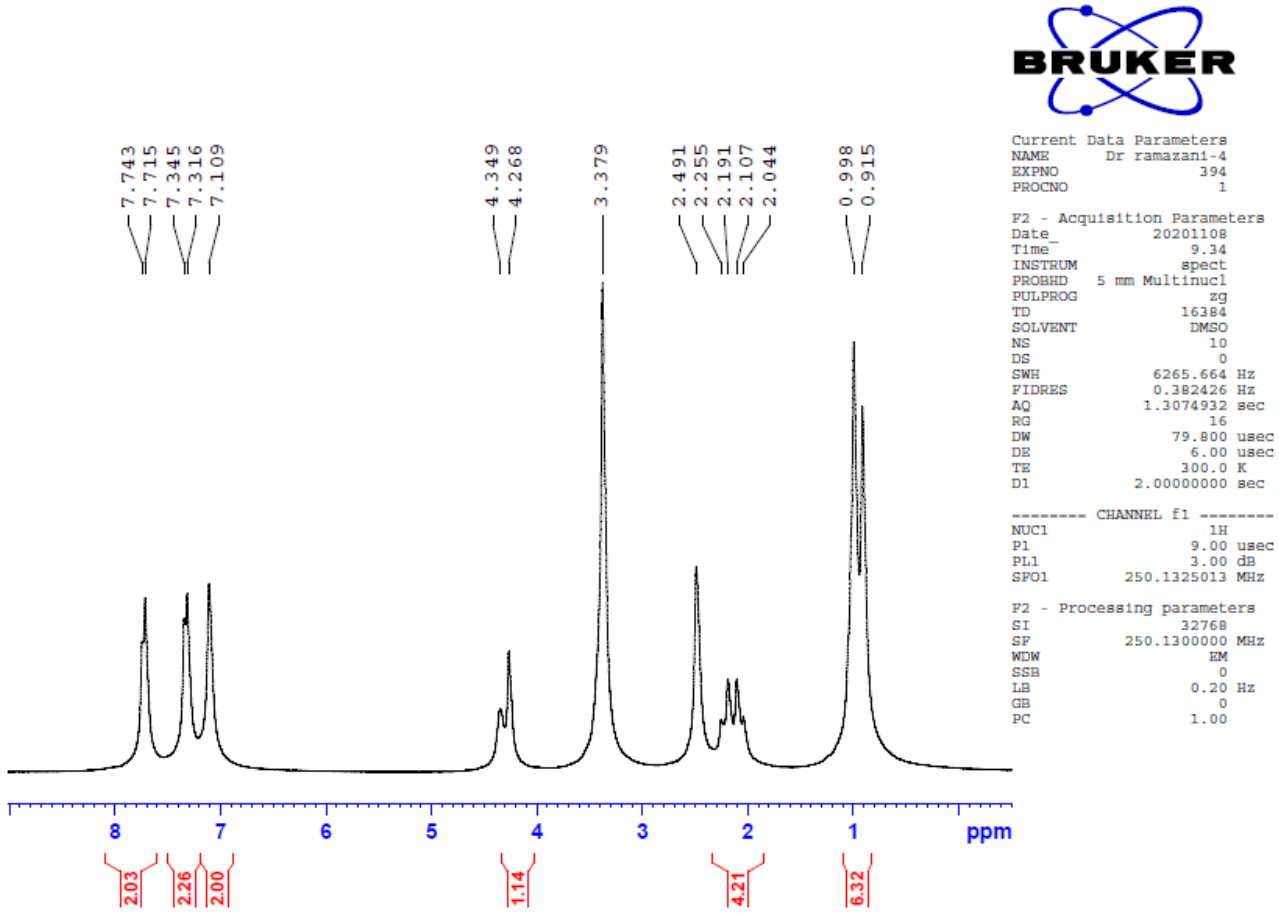


Figure S3: The expanded ^{1}H-NMR spectrum of 2-amino-7,7-dimethyl-4-(4-cyanophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

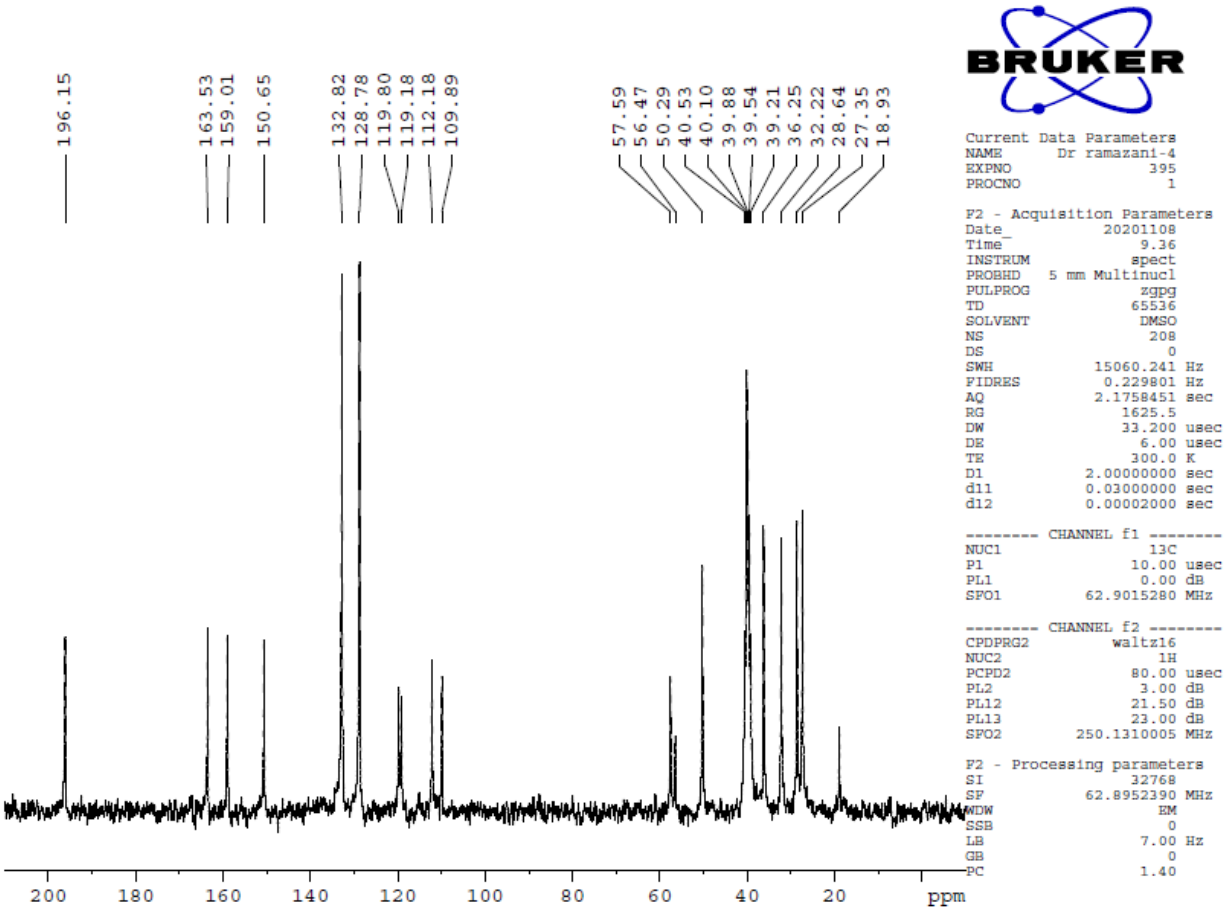


Figure S4: ^{13}C-NMR spectrum of 2-amino-7,7-dimethyl-4-(4-cyanophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran (solvent in purity due to in presence of EtOH, δ = 18.9 and 57.7)

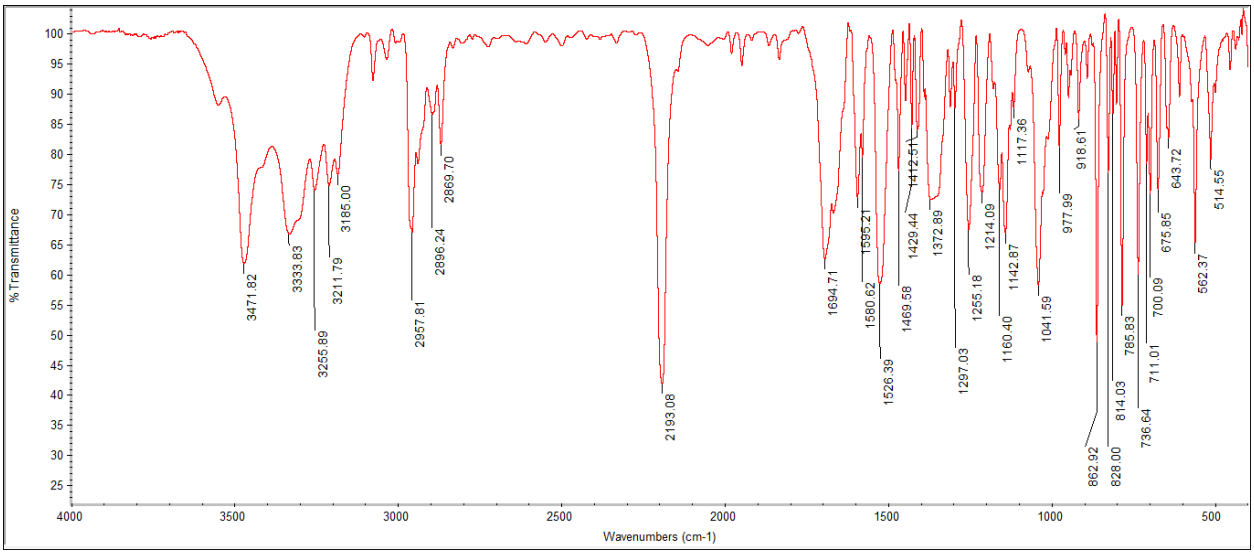


Figure S5: FT-IR spectrum of 2-amino-7, 7-dimethyl-4-(2-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

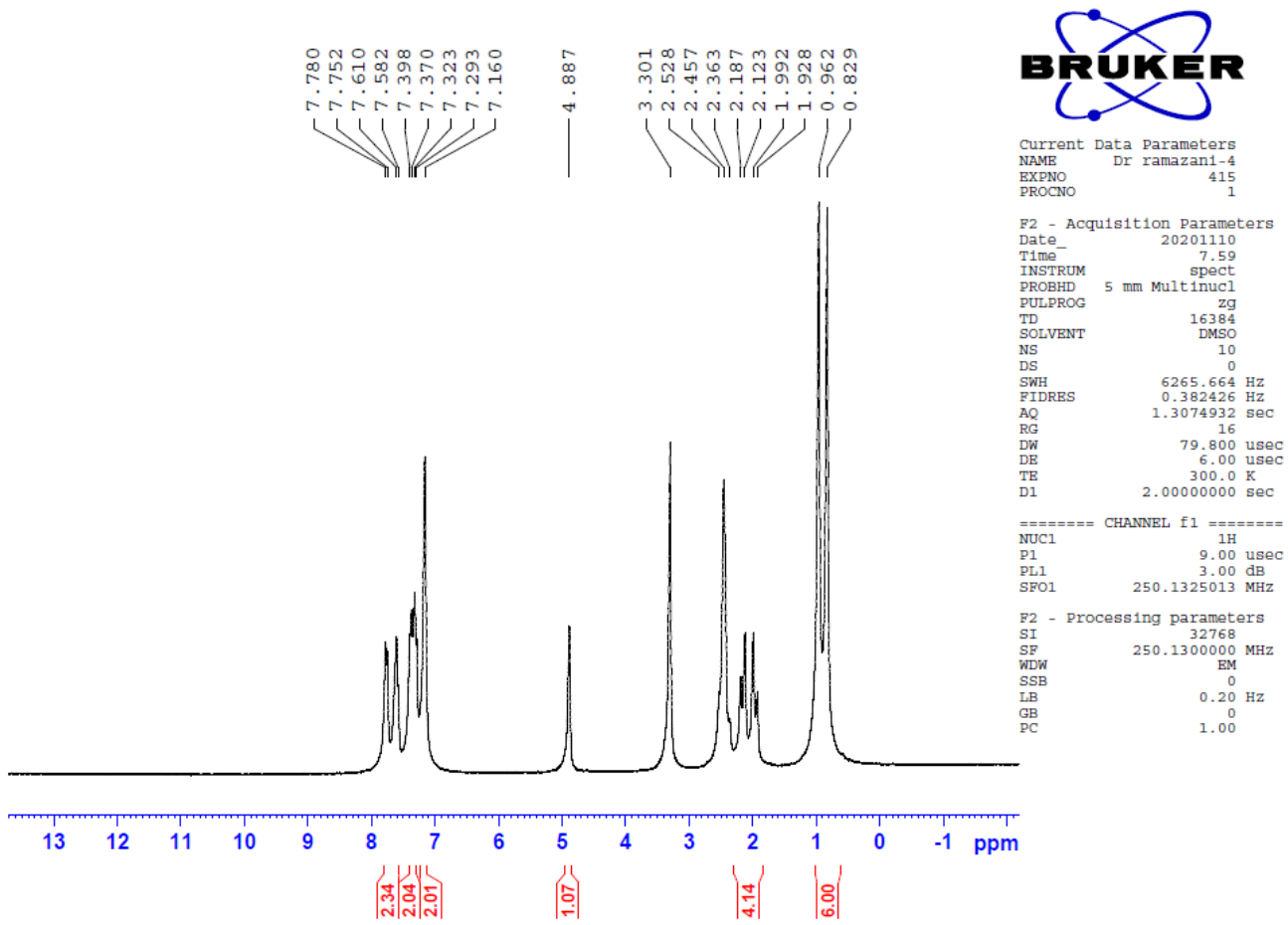


Figure S6: [1]H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(2-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

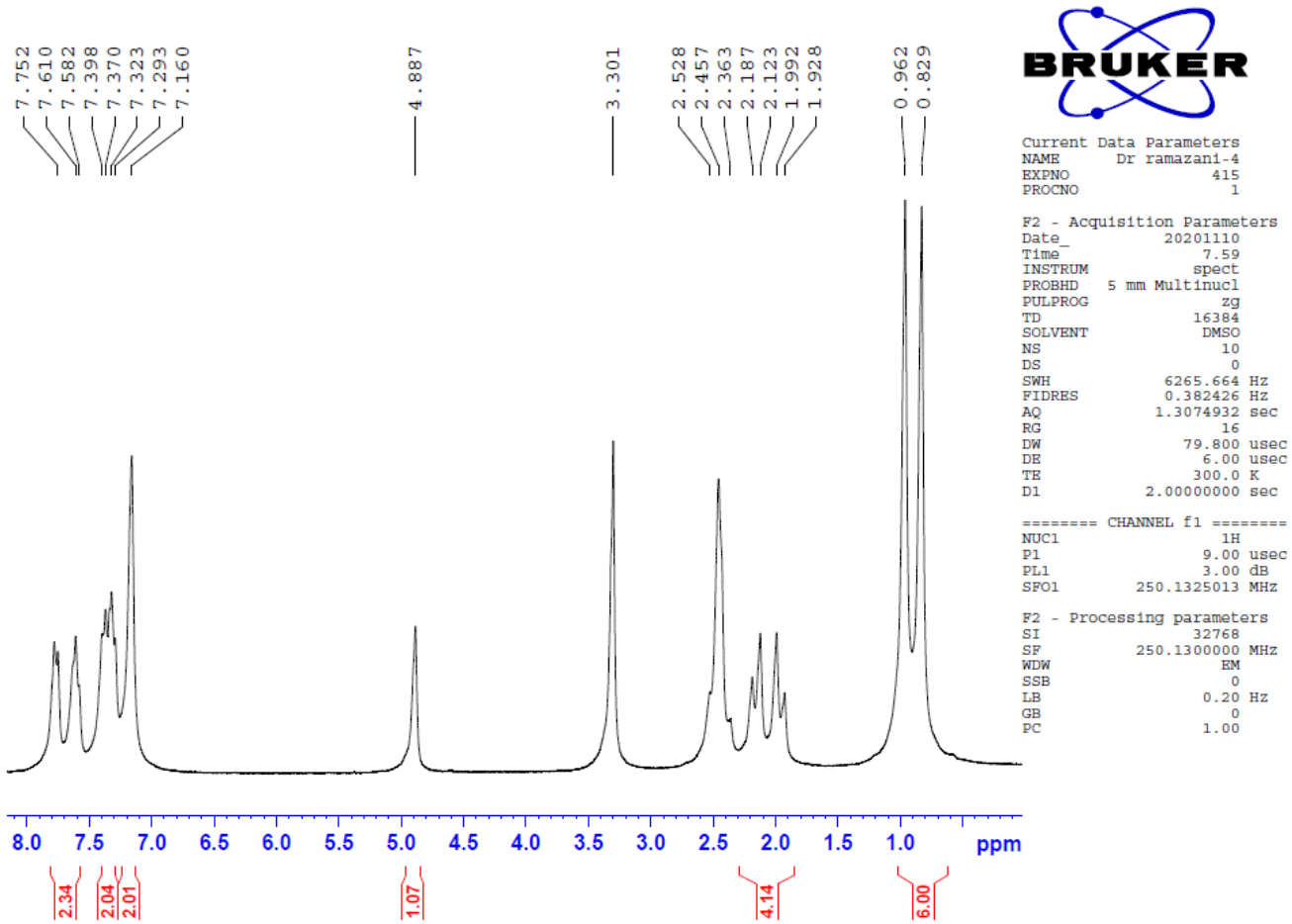


Figure S7: The expanded ^{1}H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(2-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

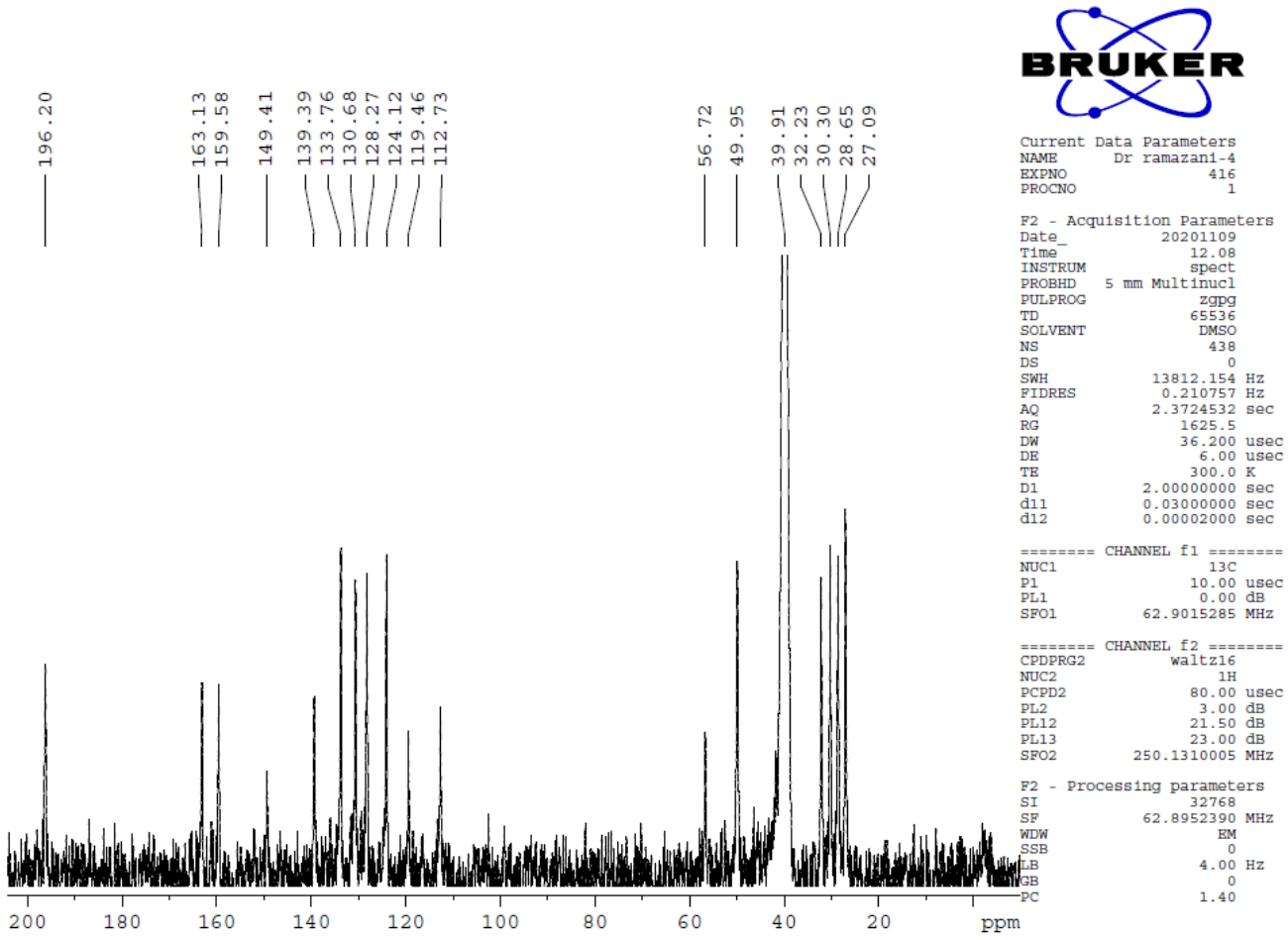


Figure S8: ^{13}C-NMR spectrum of 2-amino-7, 7-dimethyl-4-(2-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

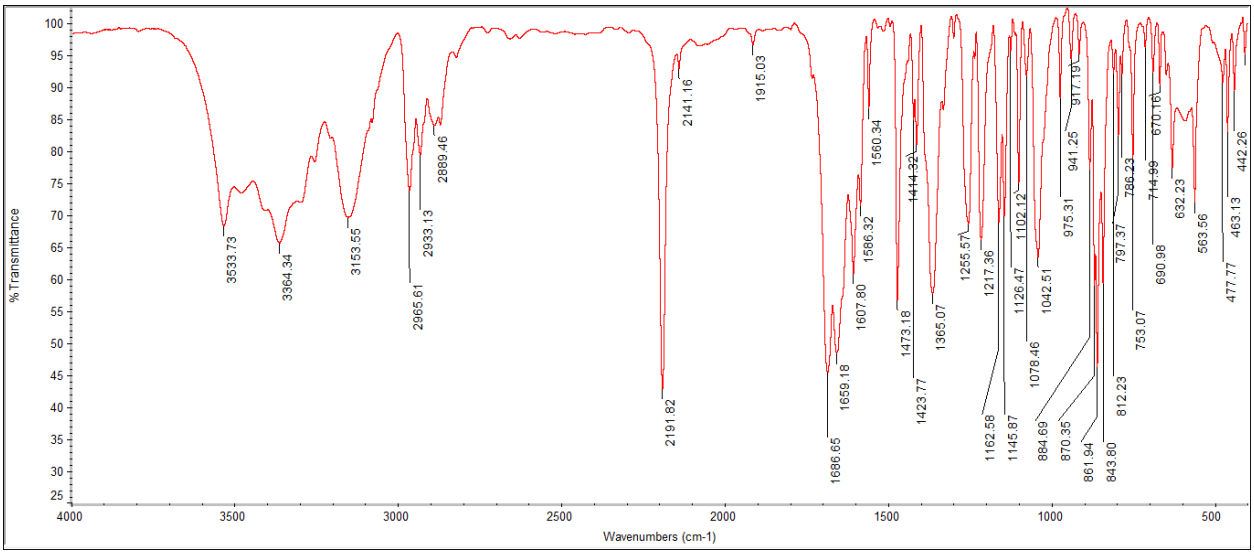


Figure S9: FT-IR spectrum of 2-amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

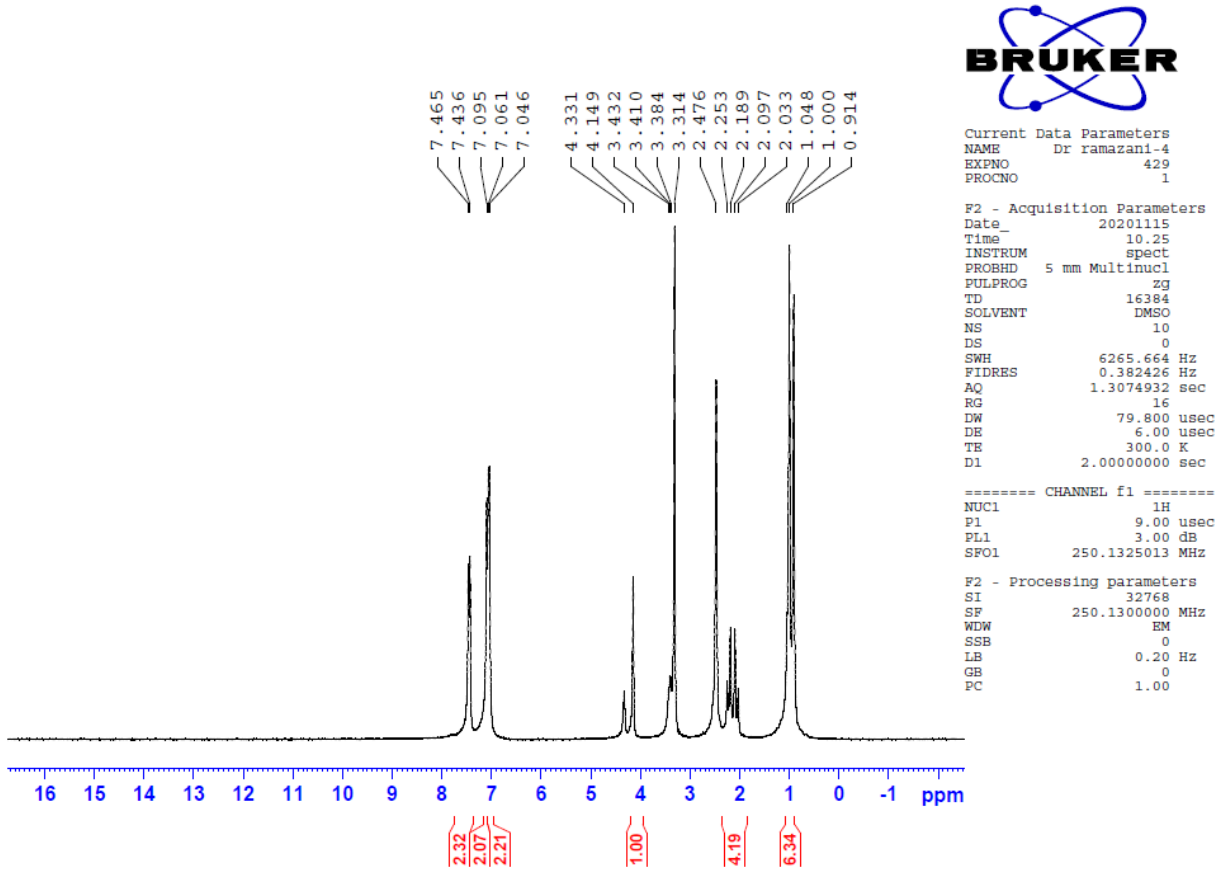


Figure S10: [1]H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

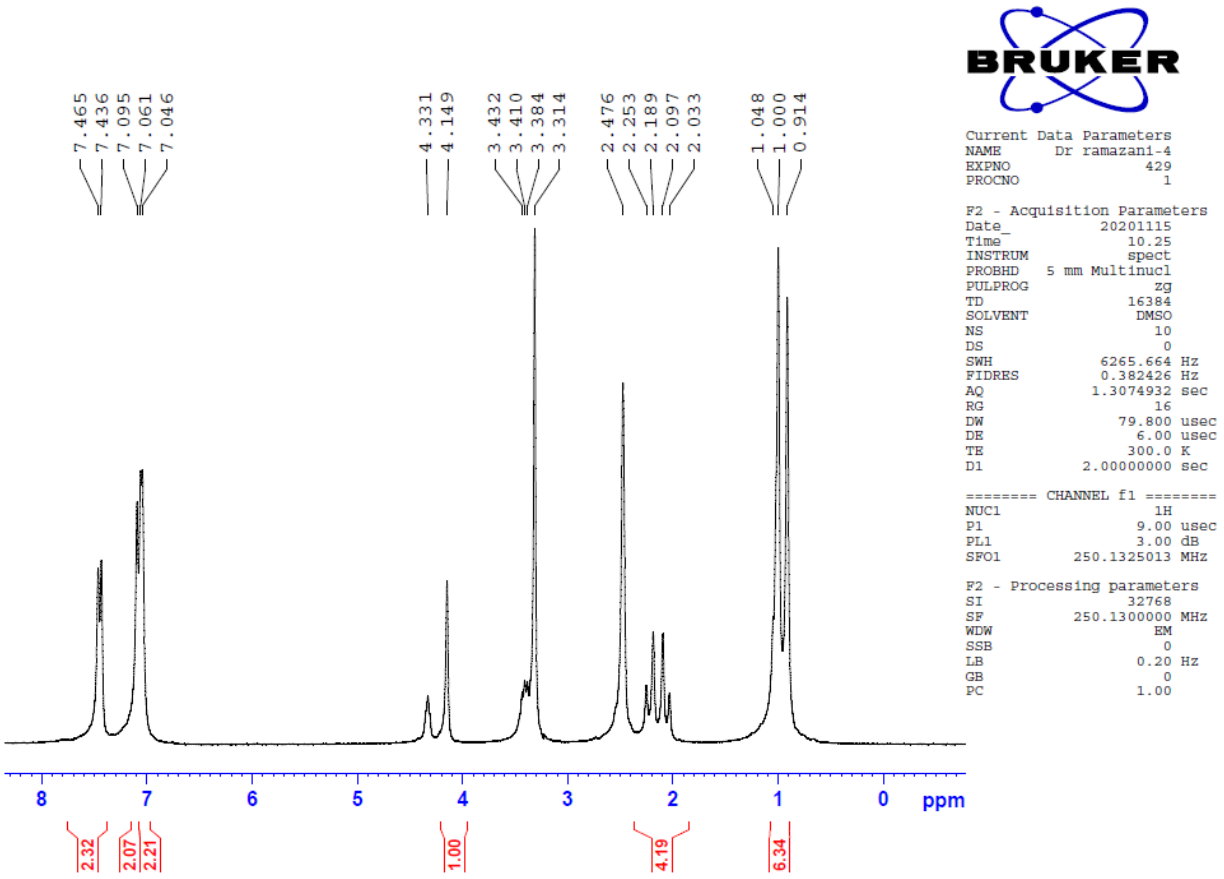


Figure S11: The expanded ^{1}H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

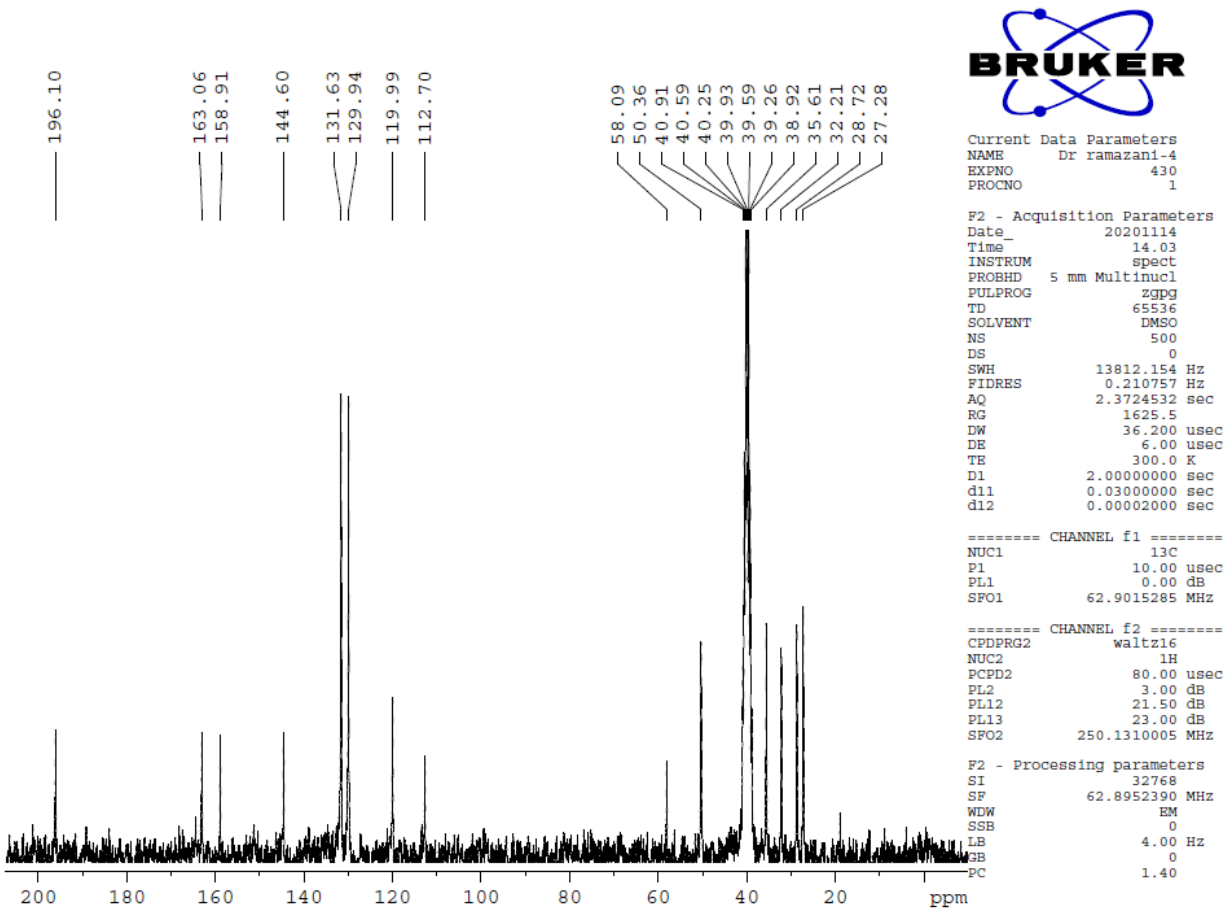


Figure S12: ^{13}C-NMR spectrum of 2-amino-7, 7-dimethyl-4-(4-bromophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

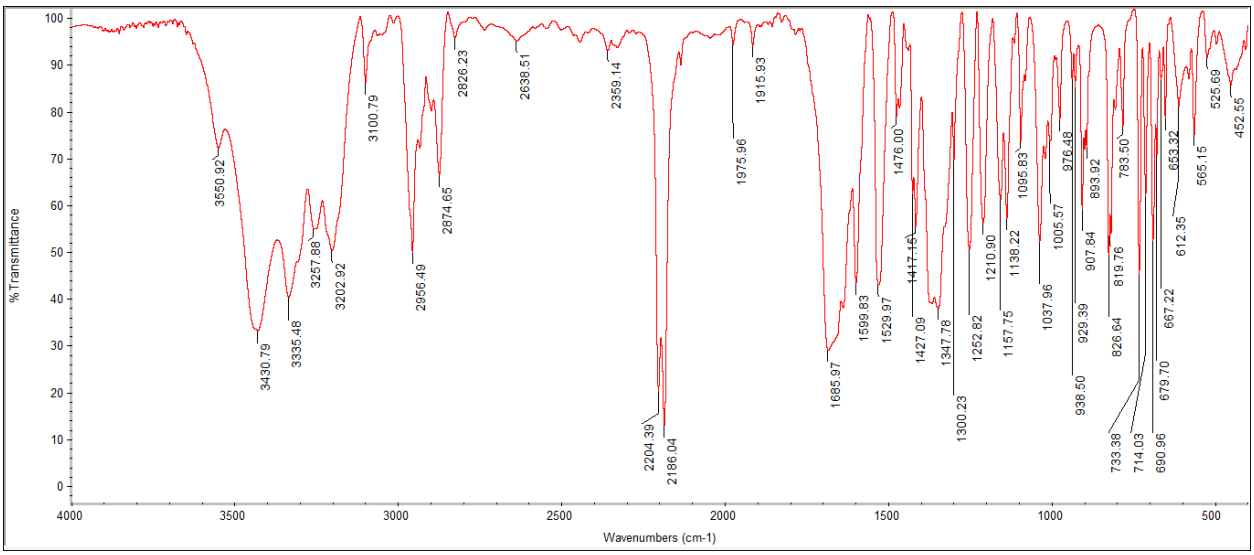


Figure S13: FT-IR spectrum of 2-amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

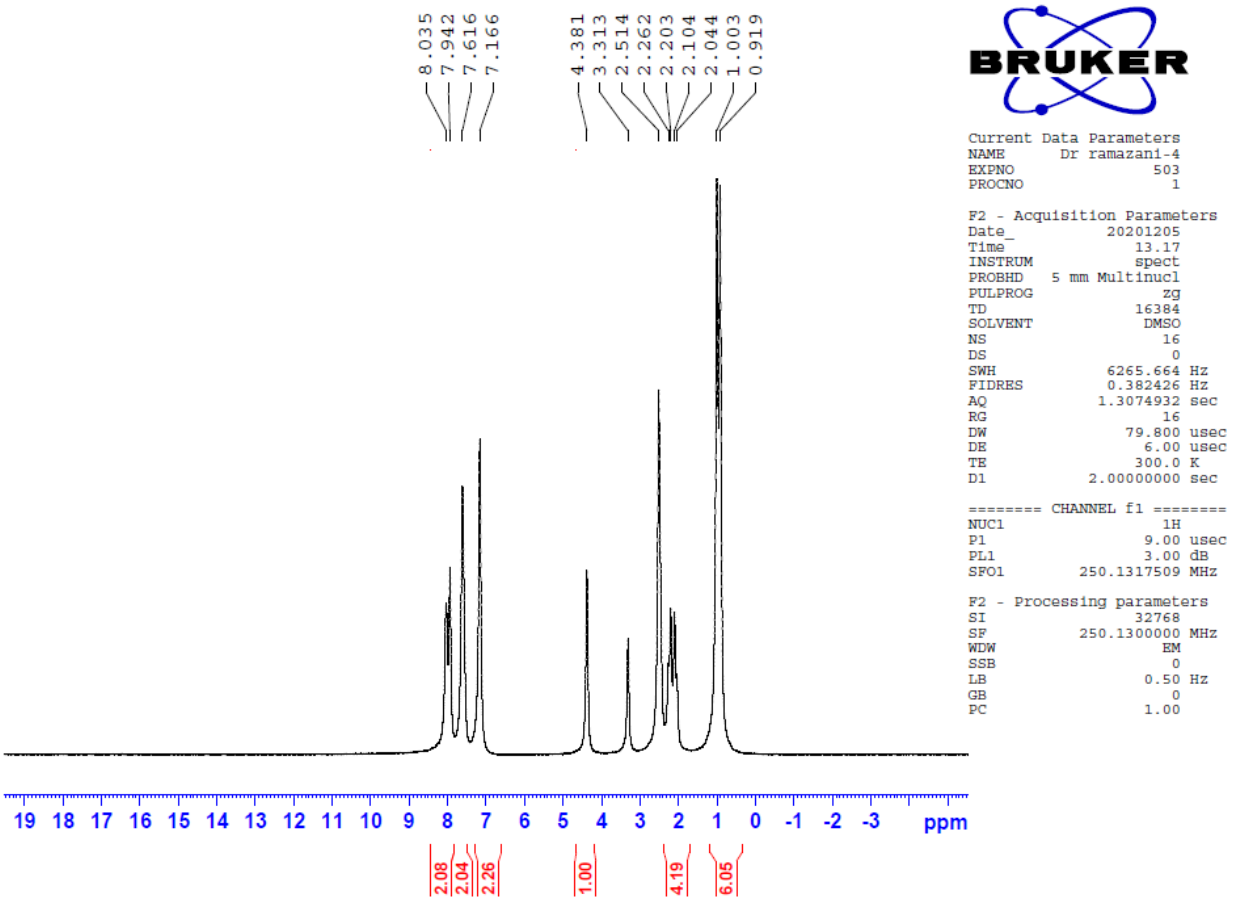


Figure S14: [1]H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

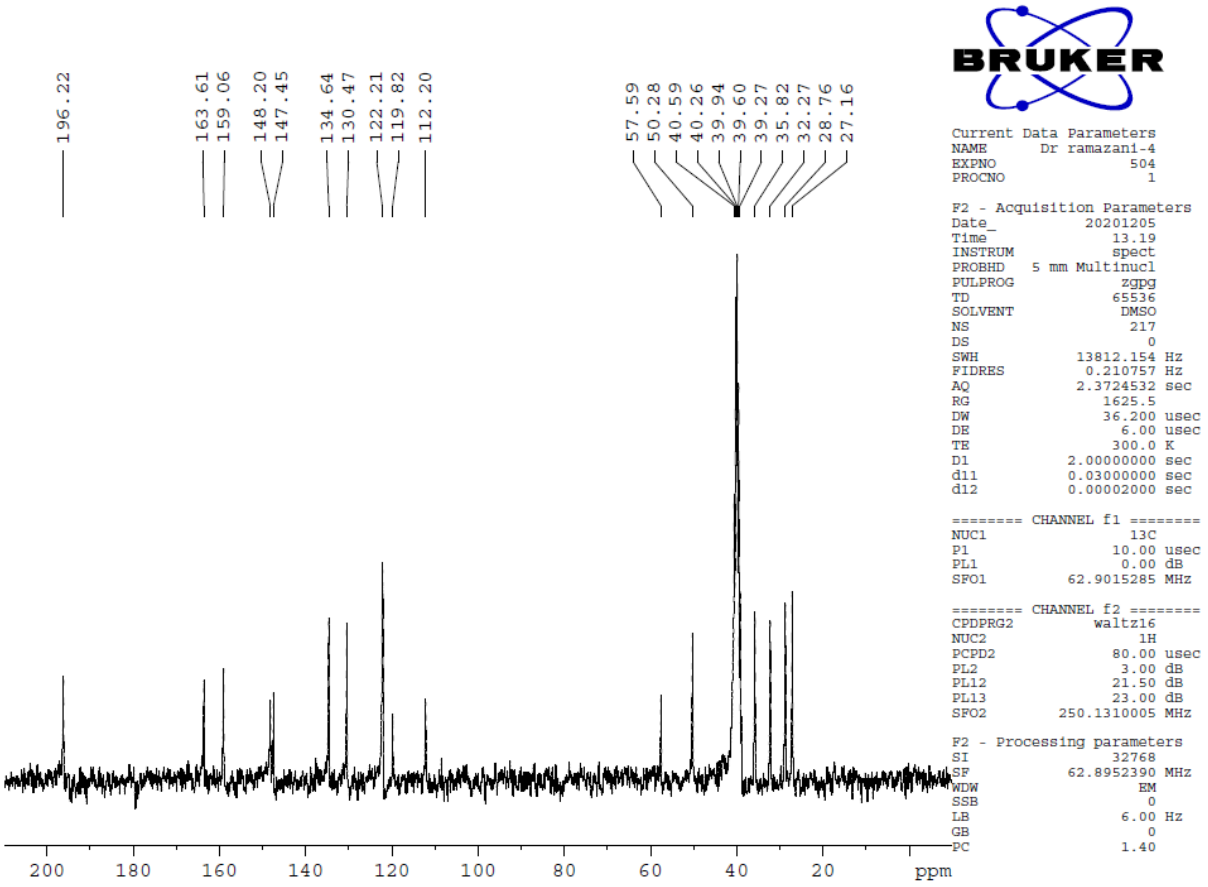


Figure S15: ^{13}C-NMR spectrum of 2-amino-7, 7-dimethyl-4-(3-nitrophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

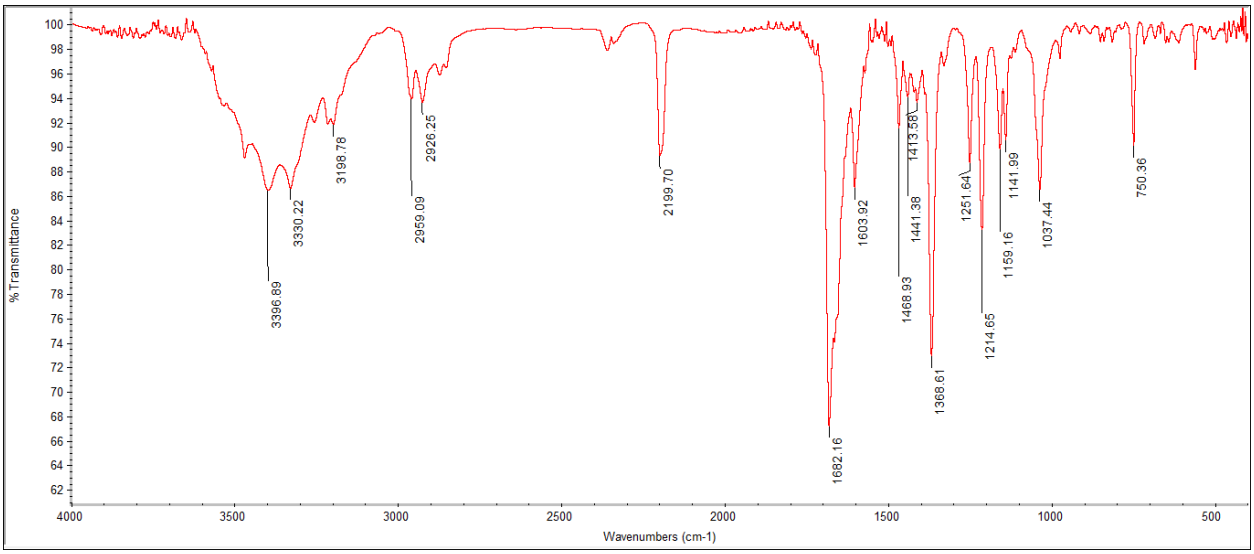


Figure S16: FT-IR spectrum of 2-amino-7, 7-dimethyl-4-(2-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

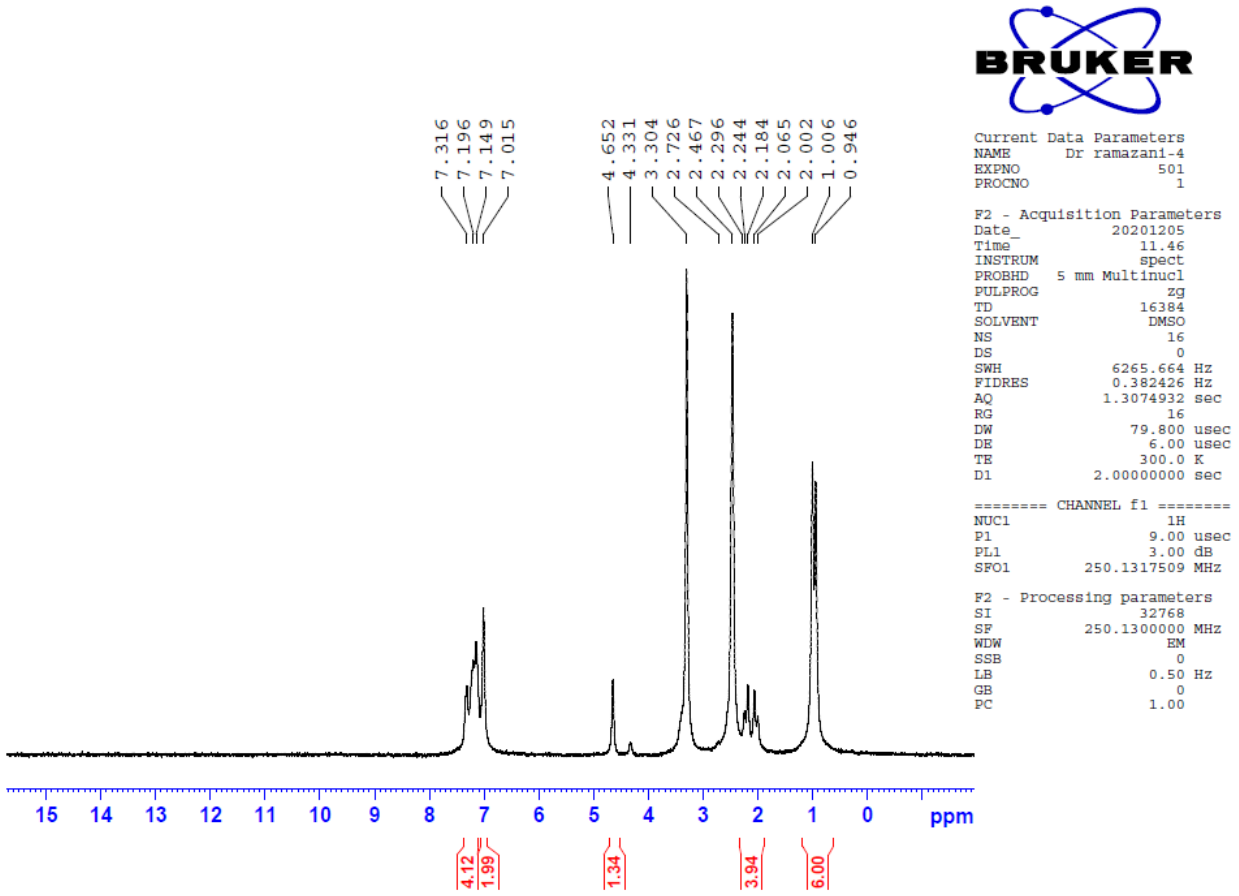


Figure S17: [1]H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(2-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

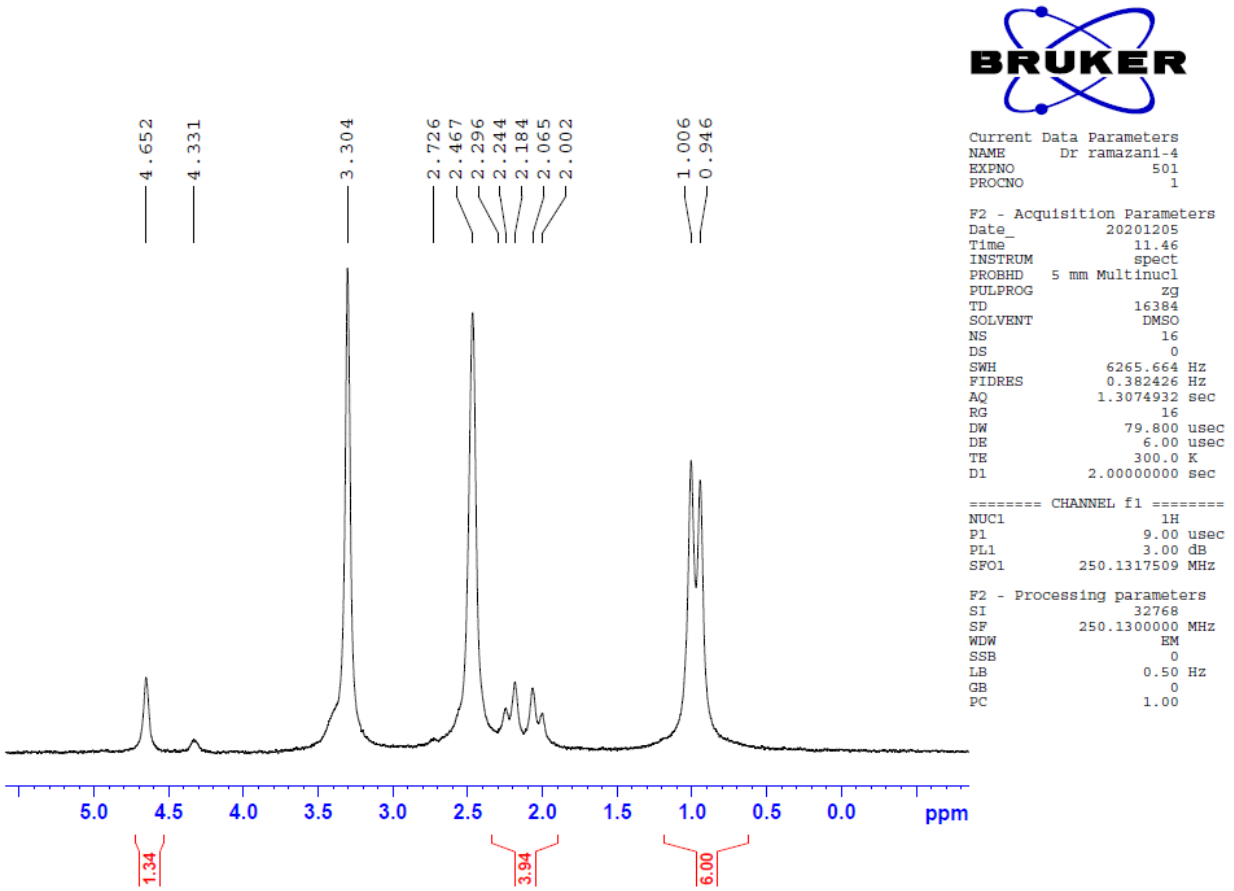


Figure S18: The expanded ^{1}H-NMR spectrum of 2-amino-7, 7-dimethyl-4-(2-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

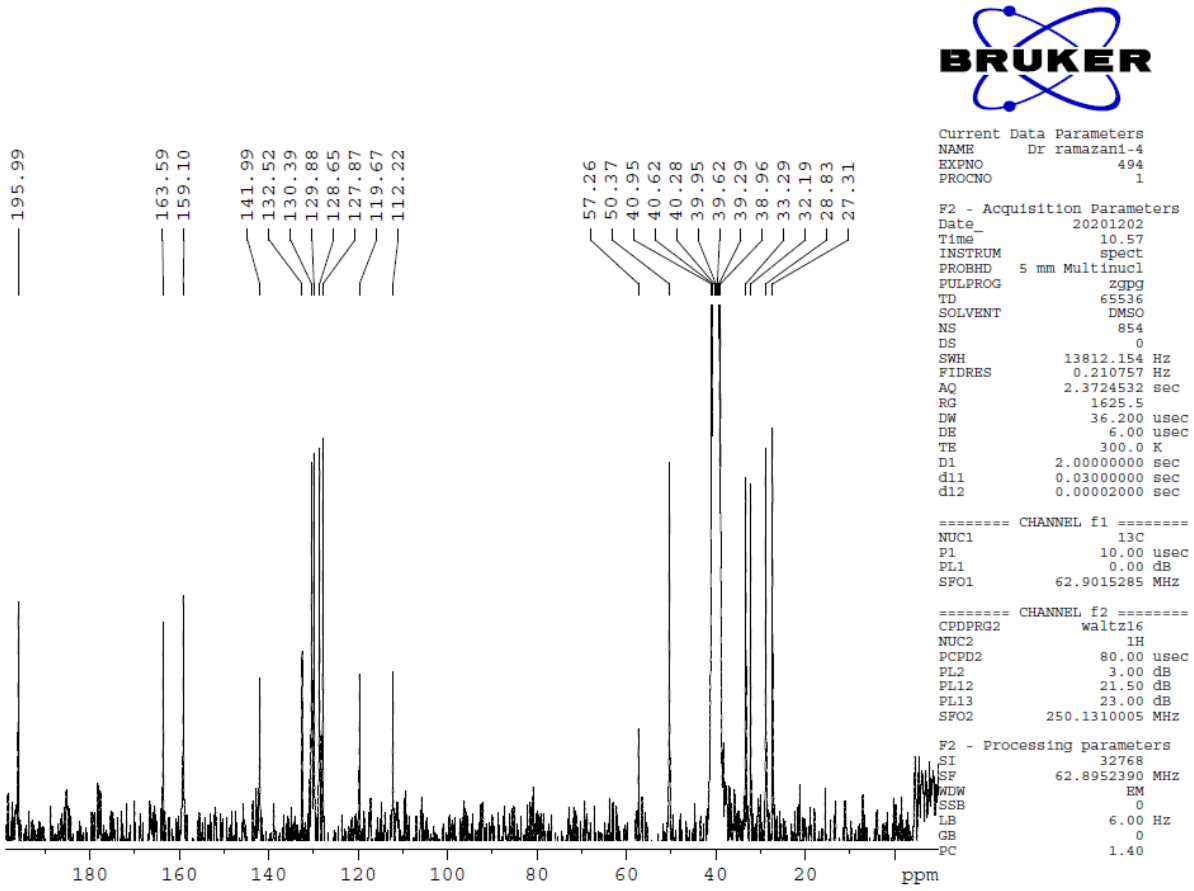


Figure S19: ^{13}C-NMR spectrum of 2-amino-7, 7-dimethyl-4-(2-chlorophenyl)-5-oxo-5, 6, 7, 8-tetrahydrobenzo[b]pyran

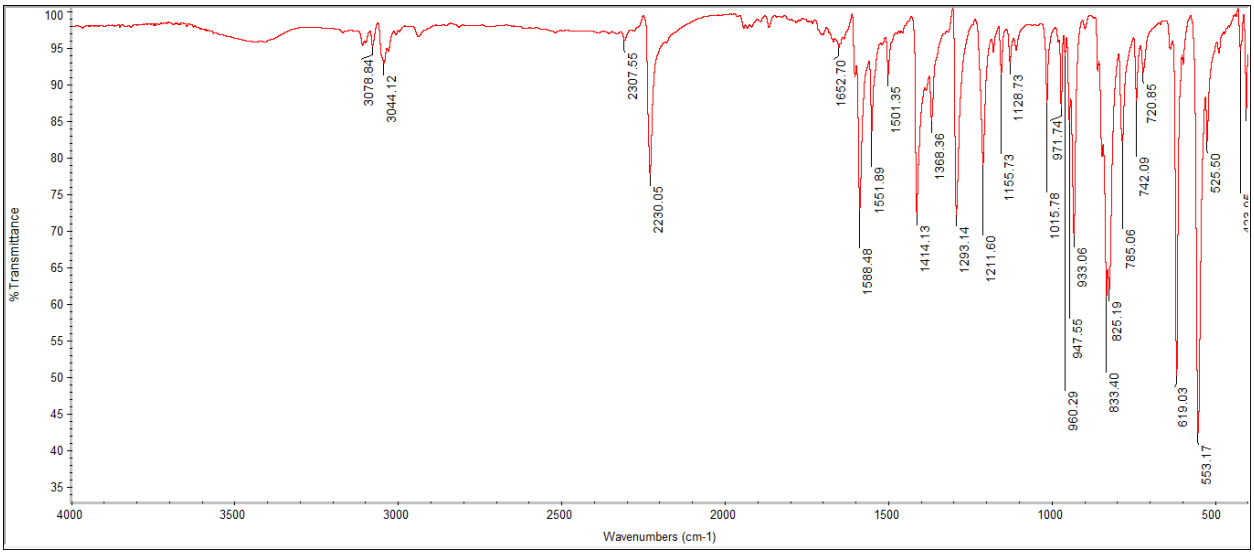


Figure S20: FT-IR spectrum of 2-(4-cyanobenzylidene)malononitrile

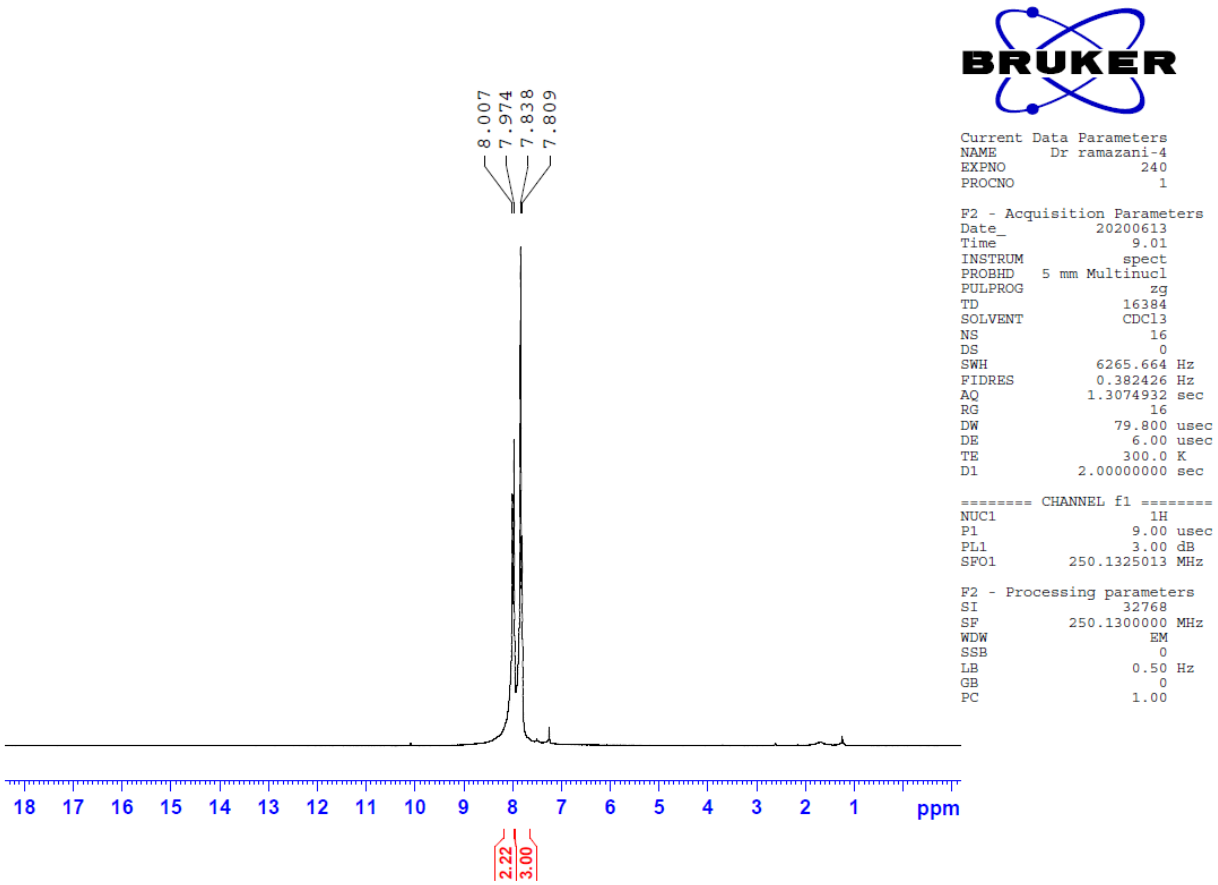


Figure S21: ^{1}H-NMR spectrum of 2-(4-cyanobenzylidene)malononitrile

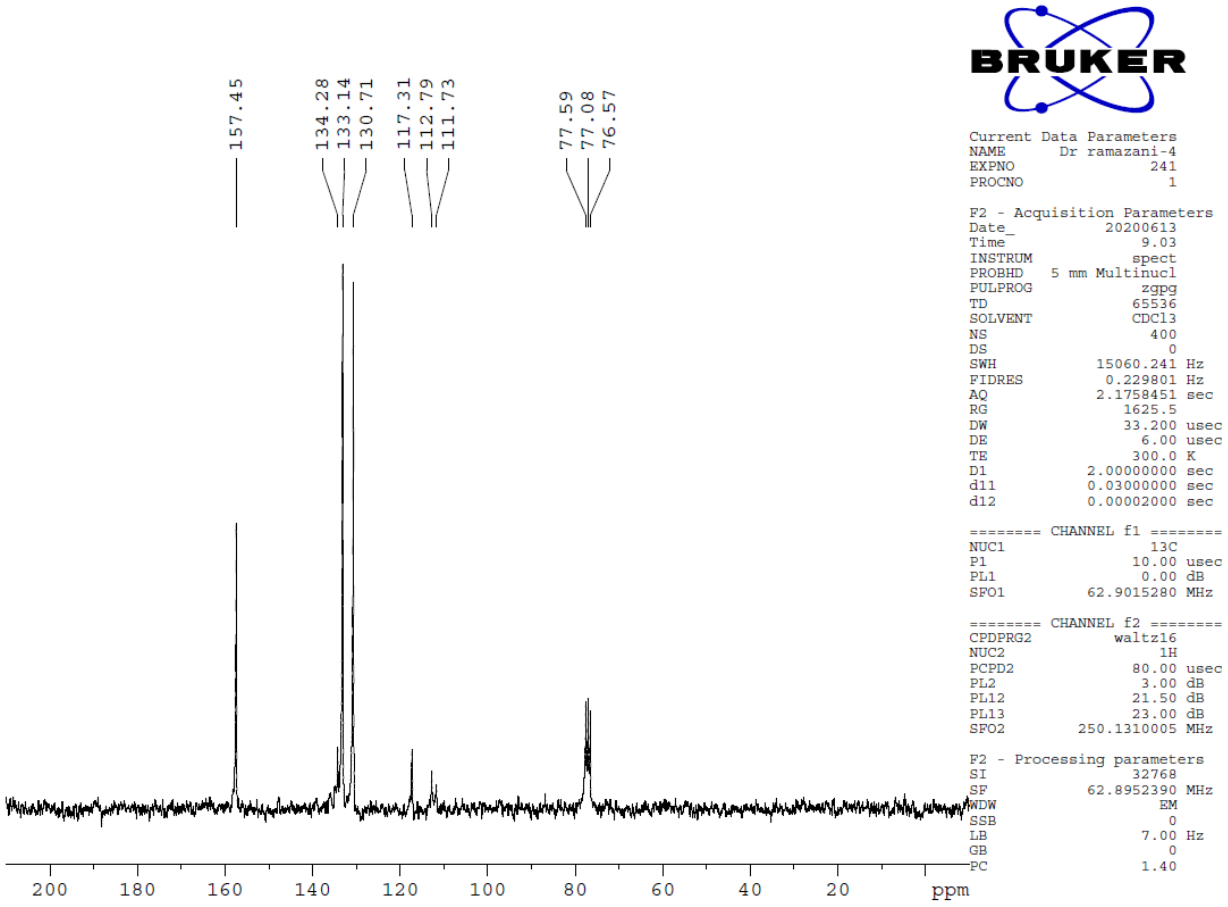


Figure S22: ^{13}C-NMR spectrum of 2-(4-cyanobenzylidene)malononitrile

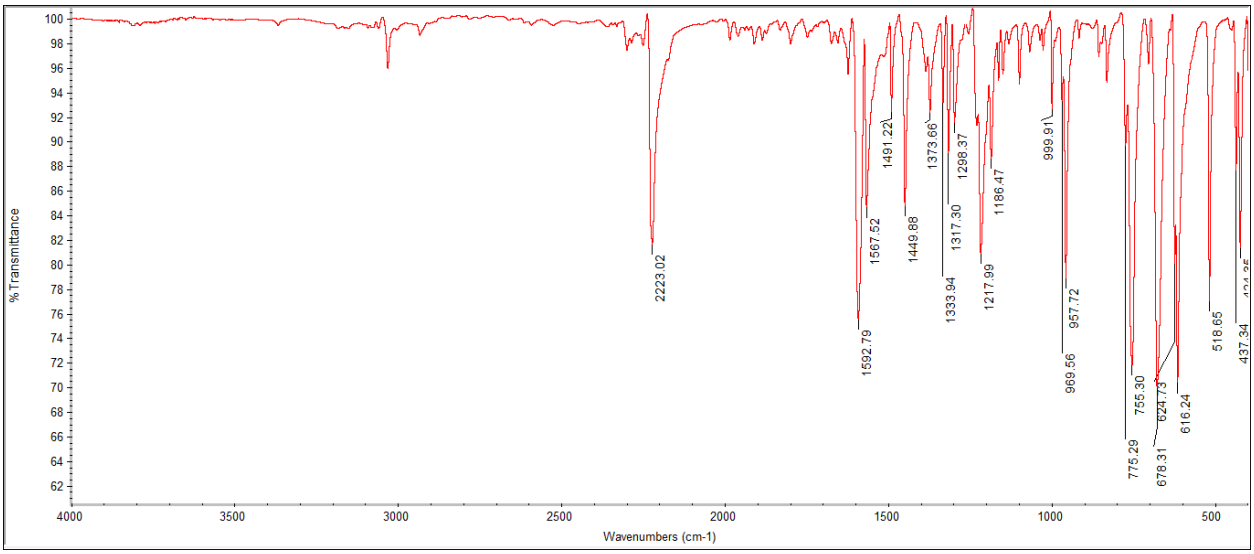


Figure 23: FT-IR spectrum of 2-benzylidenemalononitrile

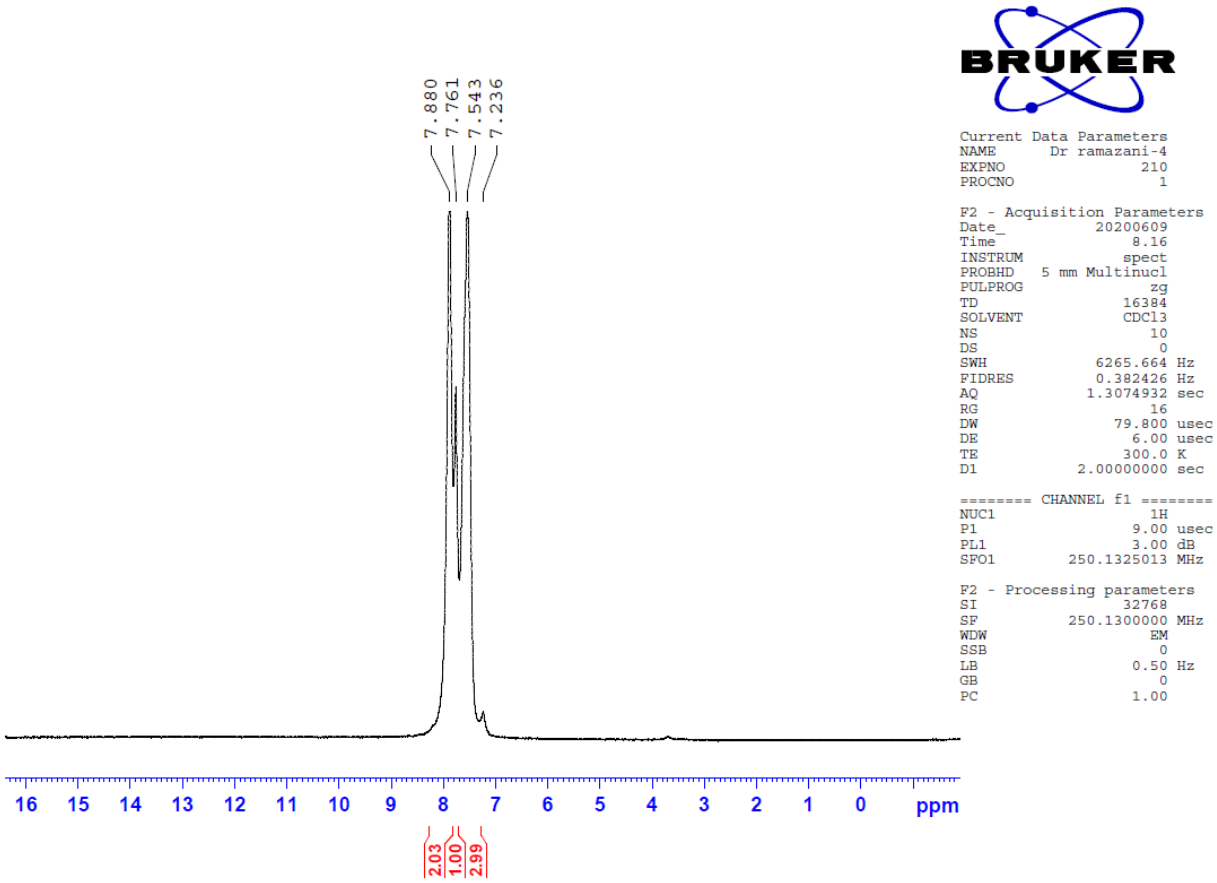


Figure 24: ^{1}H-NMR spectrum of 2-benzylidenemalononitrile

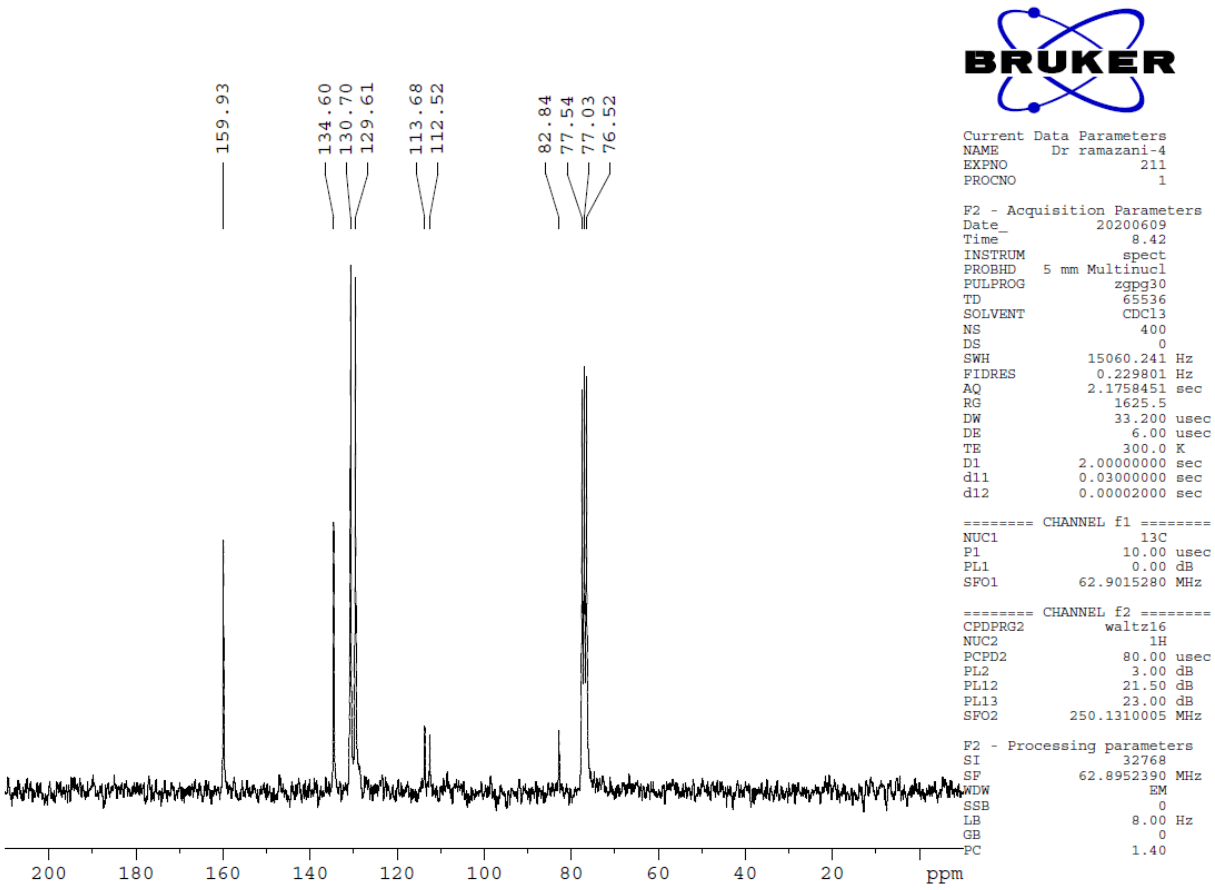


Figure 25: ^{13}C-NMR spectrum of 2-benzylidenemalononitrile

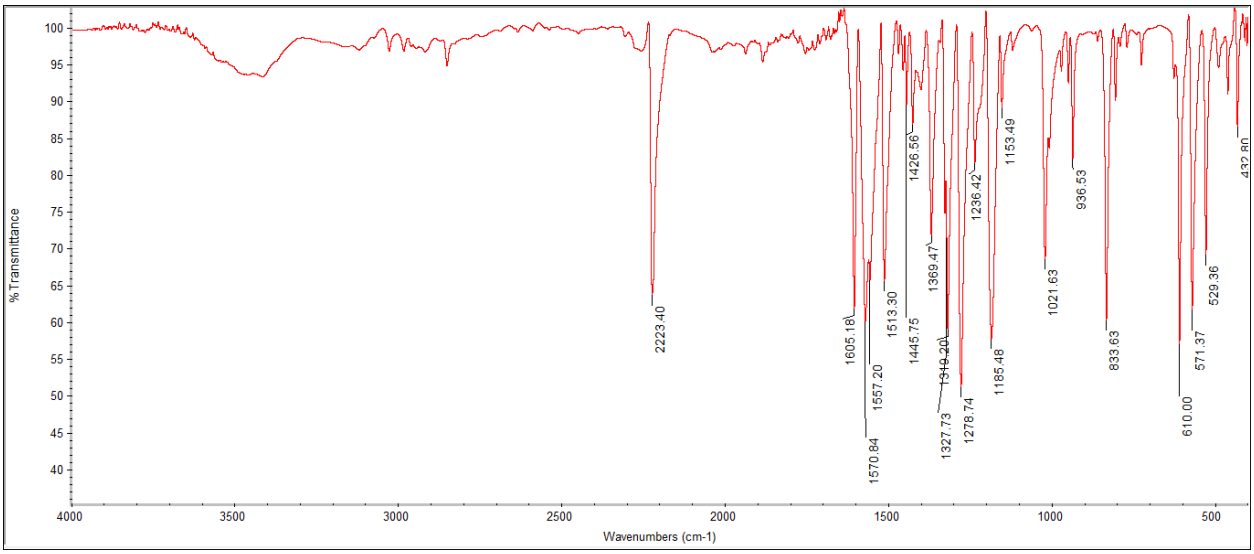


Figure 26: FT-IR spectrum of 2-(4-methoxybenzylidene)malononitrile

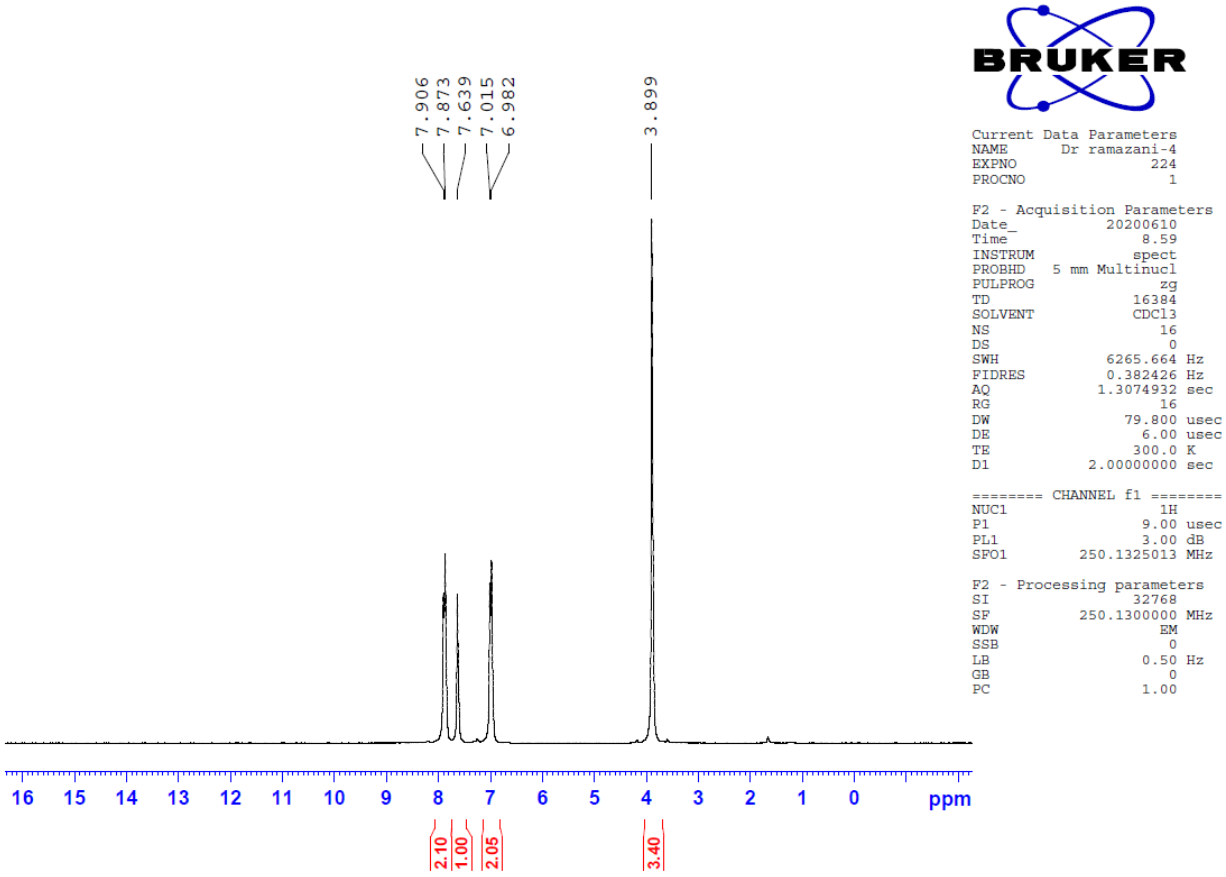


Figure 27: ^{1}H-NMR spectrum of 2-(4-methoxybenzylidene)malononitrile

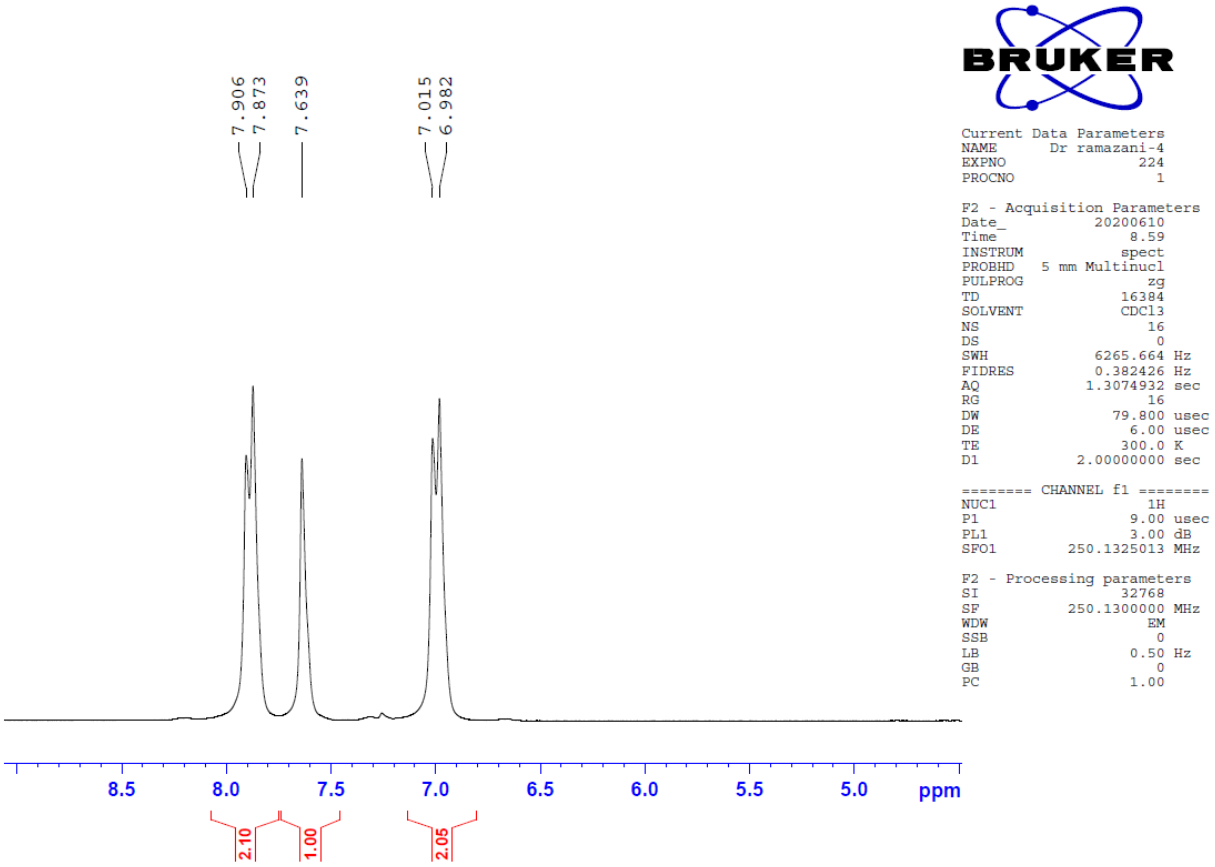


Figure 28: The expanded ^{1}H-NMR spectrum of 2-(4-methoxybenzylidene)malononitrile

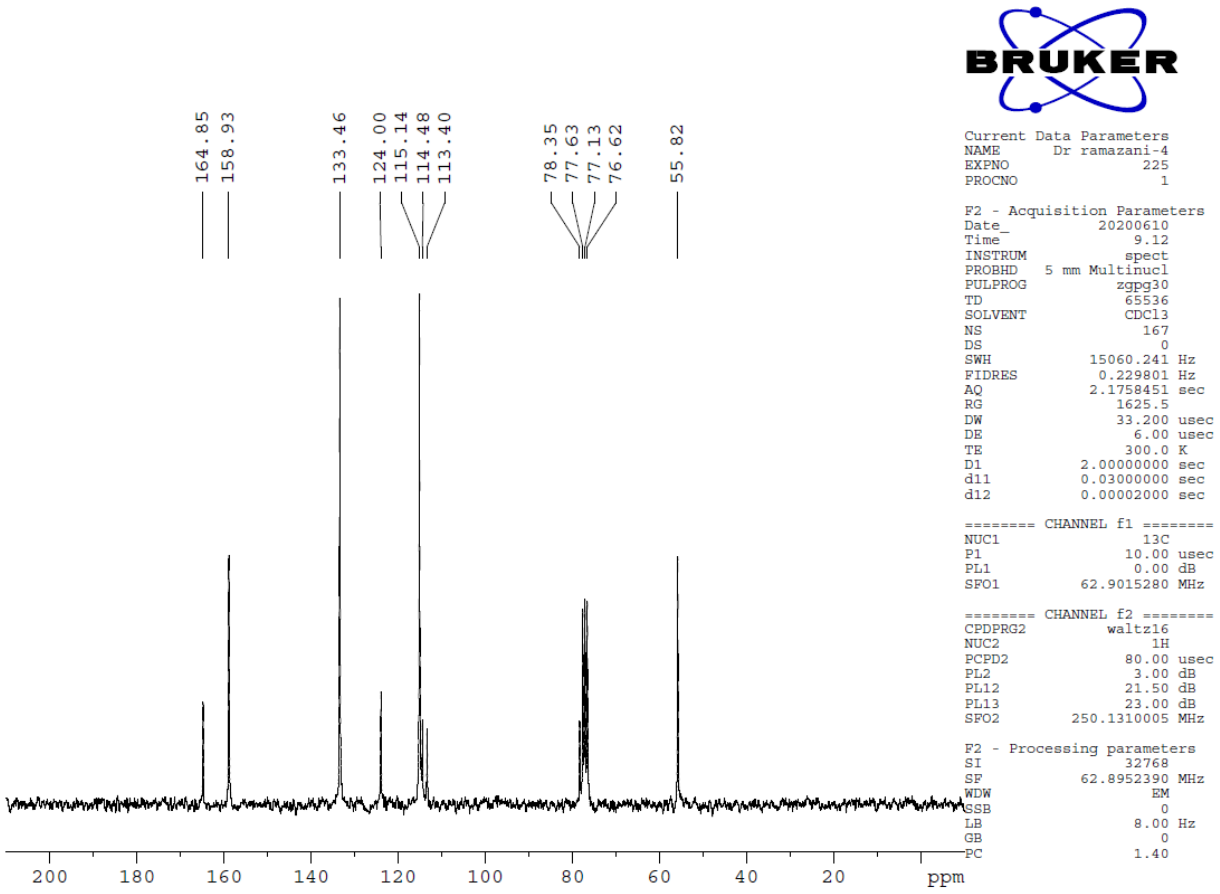


Figure 29: ^{13}C-NMR spectrum of 2-(4-methoxybenzylidene)malononitrile

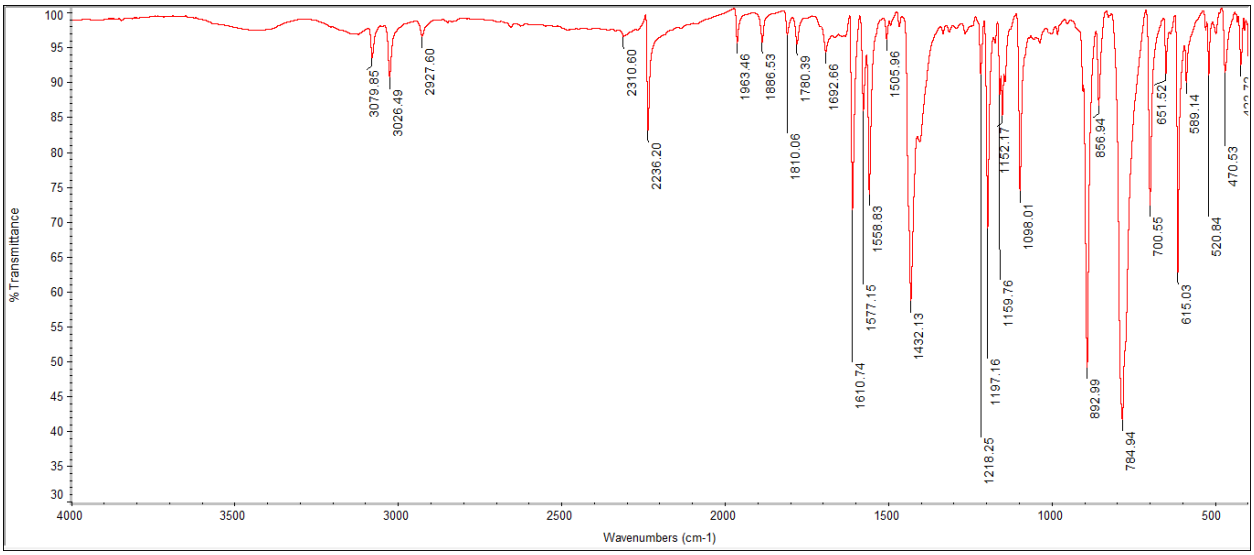


Figure 30: FT-IR spectrum of 2-(2,6-dichlorobenzylidene)malononitrile

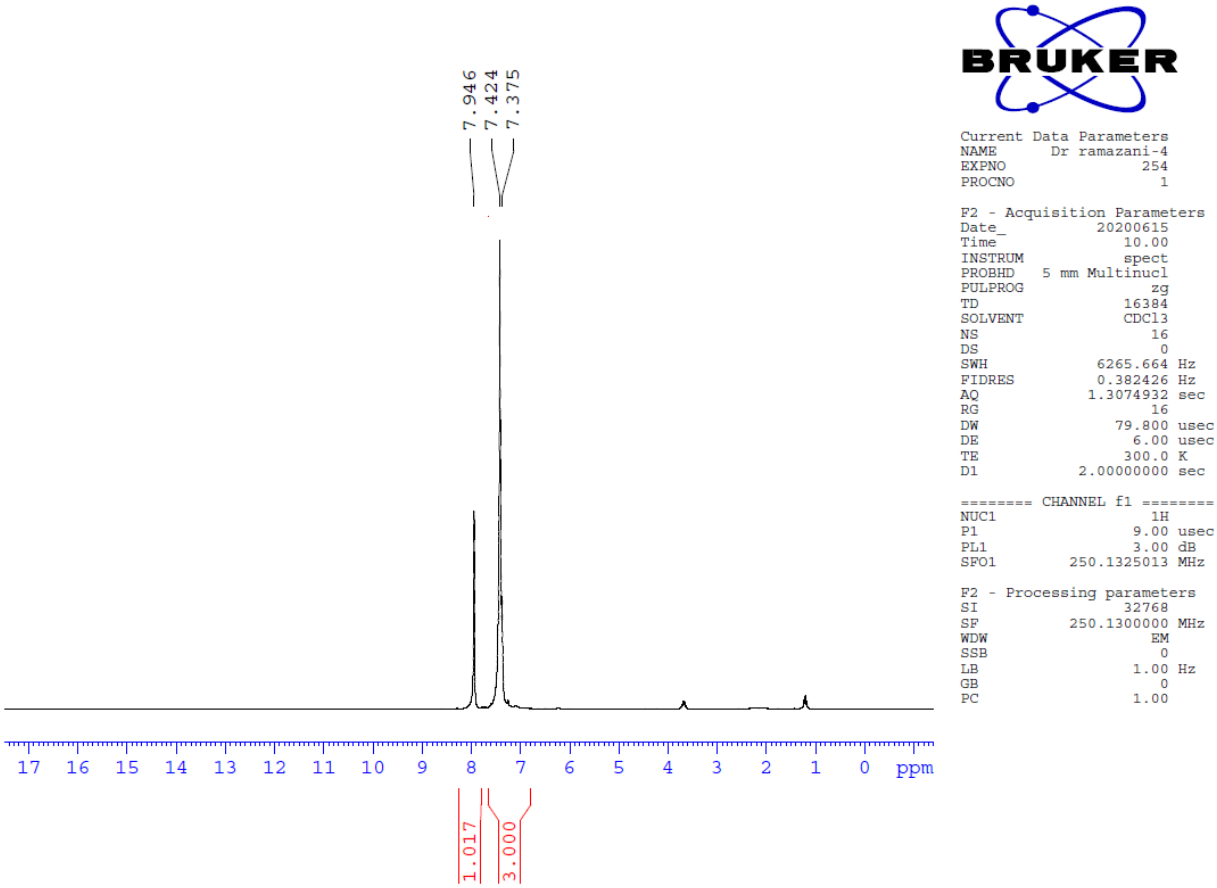


Figure 31: ^{1}H-NMR spectrum of 2-(2,6-dichlorobenzylidene)malononitrile

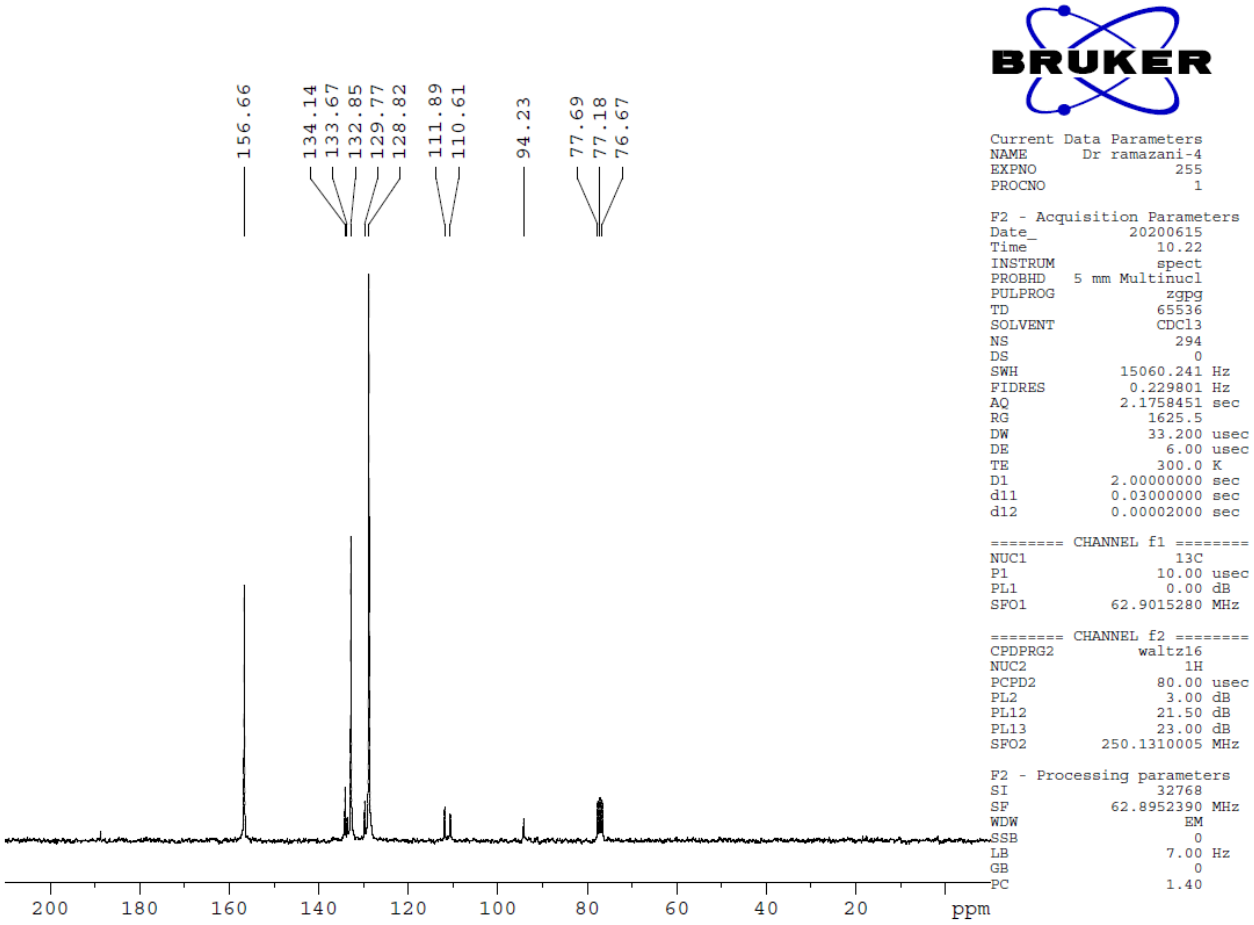


Figure 32: ^{13}C-NMR spectrum of 2-(2,6-dichlorobenzylidene)malononitrile

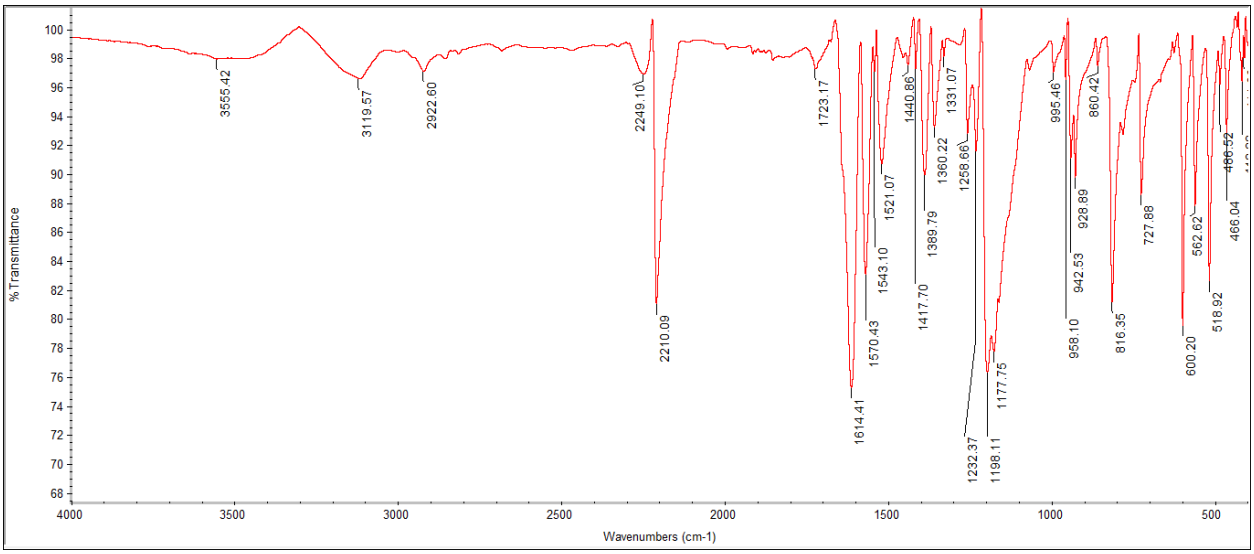


Figure 33: FT-IR spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile

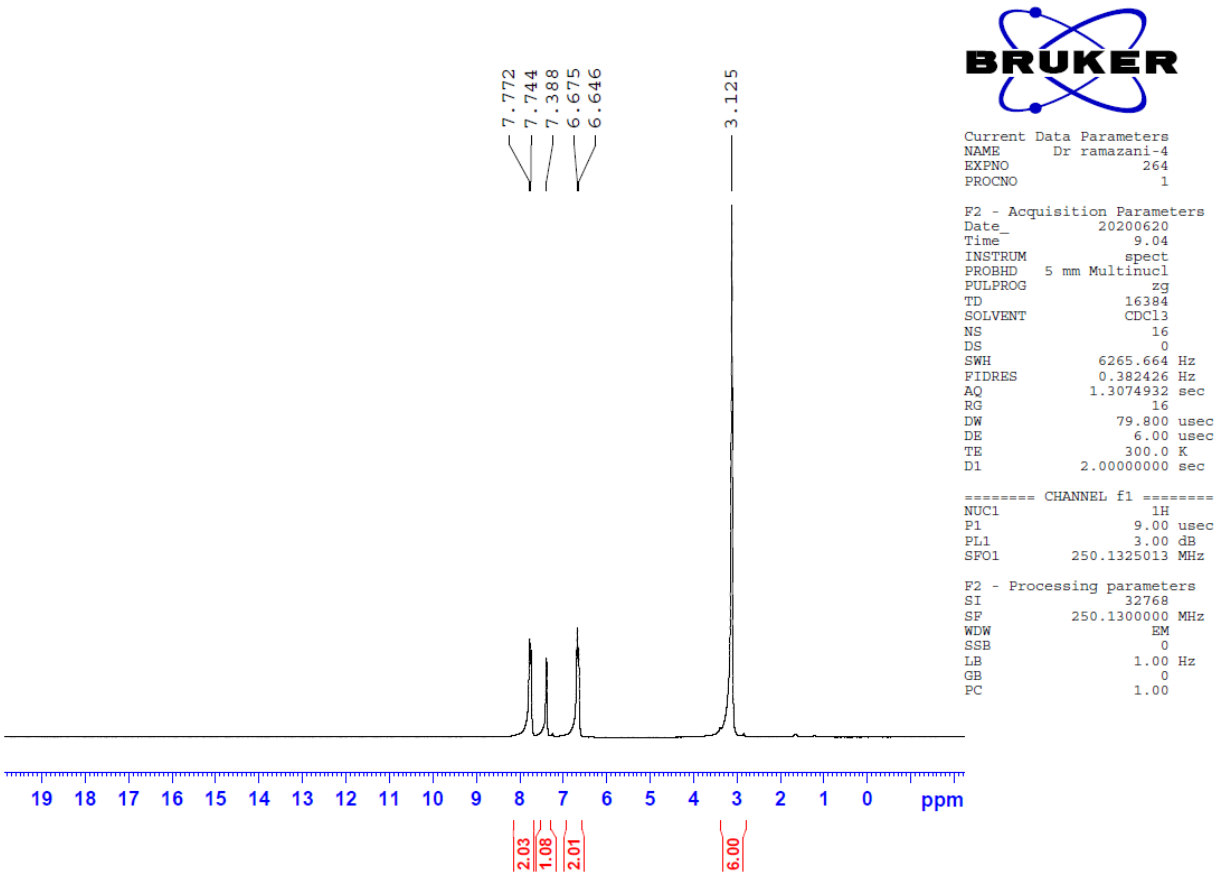


Figure 34: ^{1}H-NMR spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile

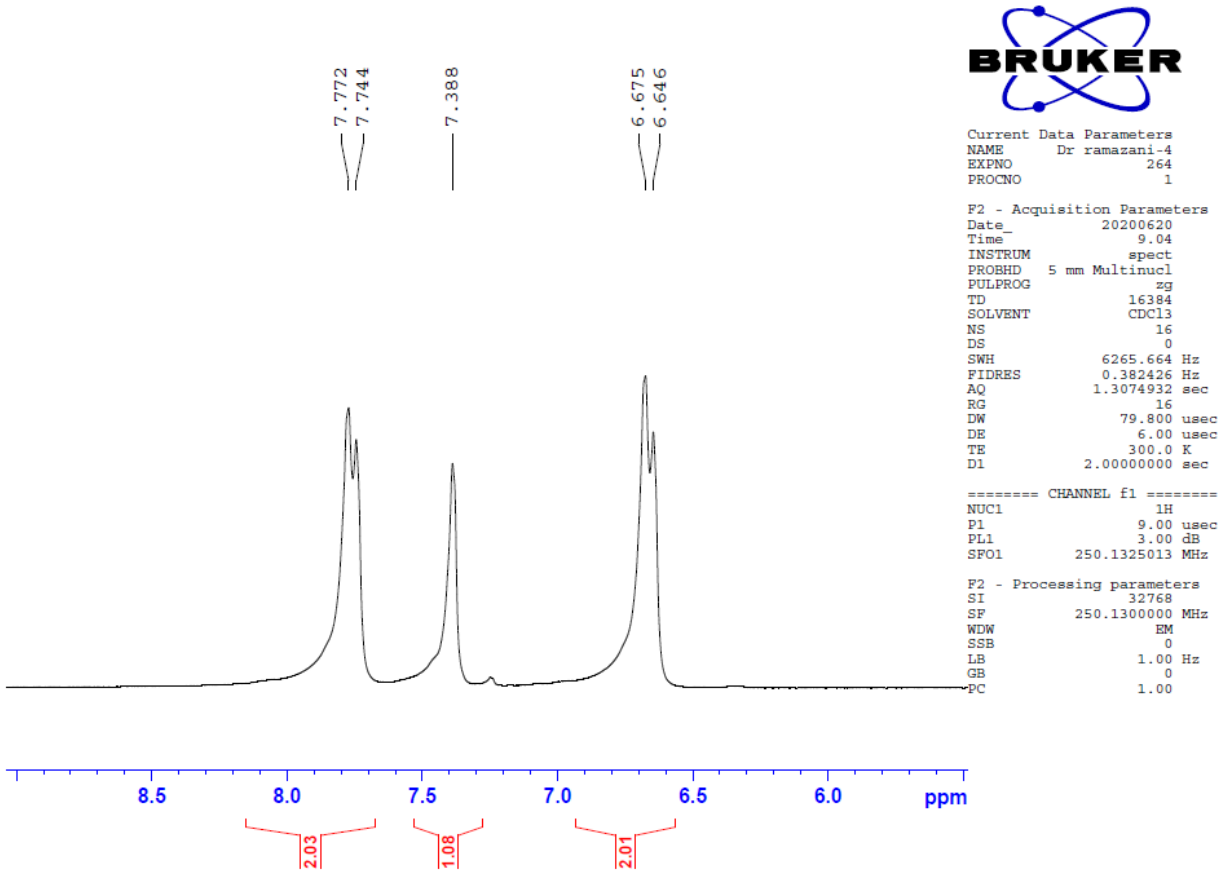


Figure 35: The expanded ^{1}H-NMR spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile

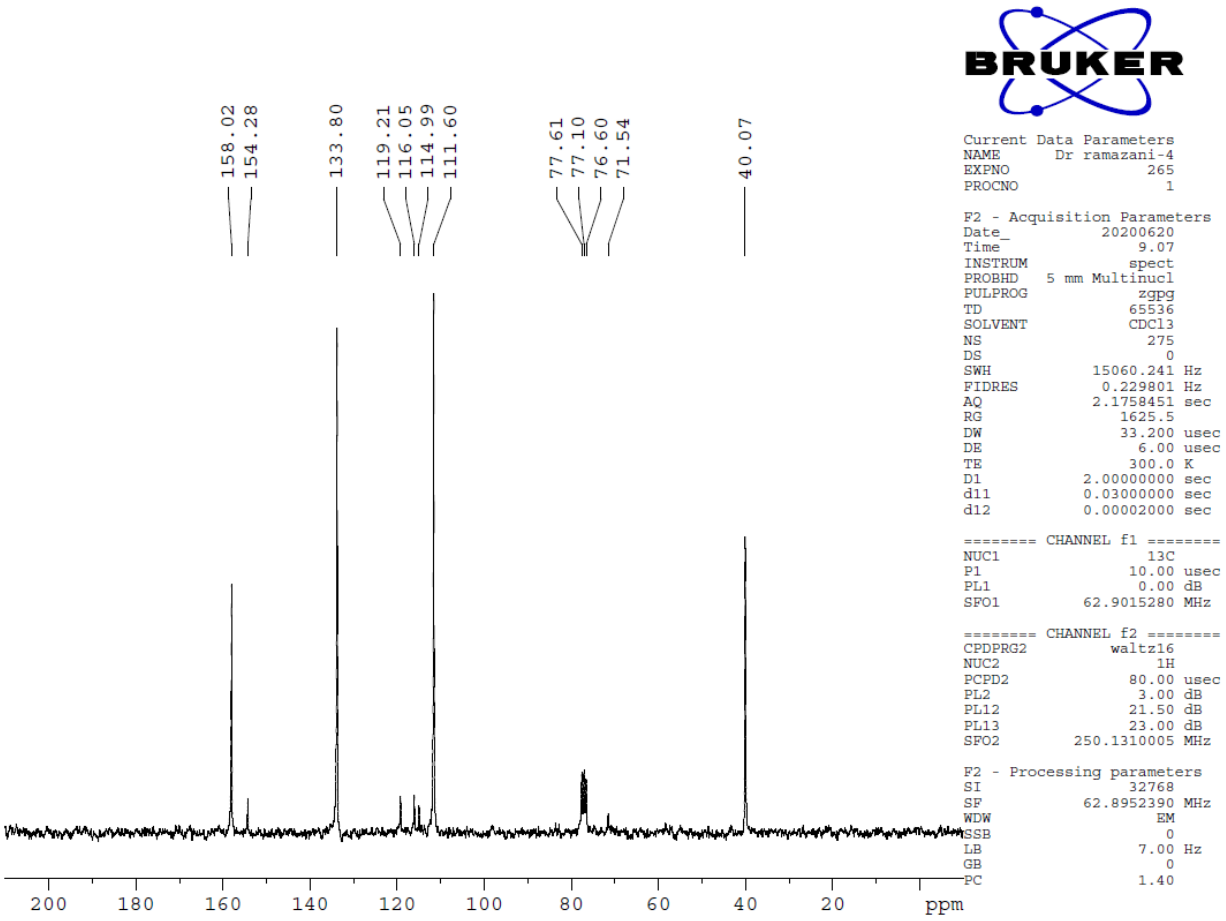


Figure 36: ^{13}C-NMR spectrum of 2-(4-(dimethylamino)benzylidene)malononitrile