Supplementary Data

Palladium fabricated on boehmite as an organic-inorganic hybrid nanocatalyst for the C-C cross coupling and homoselective cycloaddition reactions

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Abstract:

Herein, boehmite nanoparticles were prepared using aqueous solution of NaOH and $Al(NO_3)_3.9H_2O$ at room temperature. After modification of boehmite nanoparticles (BNPs) surface by 3-choloropropyltrimtoxysilane (CPTMS), adenine was anchored on its surface. Finally, a complex of palladium was fabricated on the BNPs surface (Pd-adenine@boehmite). The obtained nanoparticles were identified by TGA, FT-IR, BET, EDS, WDX, SEM, XRD and AAS techniques. In continuation, the catalytic application of Pd-adenine@boehmite was employed as efficient, reusable and organic-inorganic hybrid catalyst in the C-C cross coupling reactions without phosphine ligand or inert atmosphere. Moreover, the homoselective synthesis of tetrazoles was studied in the presence of Pd-adenine@boehmite as a heterogeneous and practical nanocatalyst which can be recovered and reused in the described organic reactions. Besides, organic products which were isolated in suitable TOF and TON numbers in the presence of Pd-adenine@boehmite as catalyst revealed the practically of this catalyst. Heterogeneous nature of this catalyst was confirmed by TEM, EDS, WDX, AAS, and FT-IR techniques and, then, compared to the fresh catalyst.

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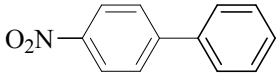
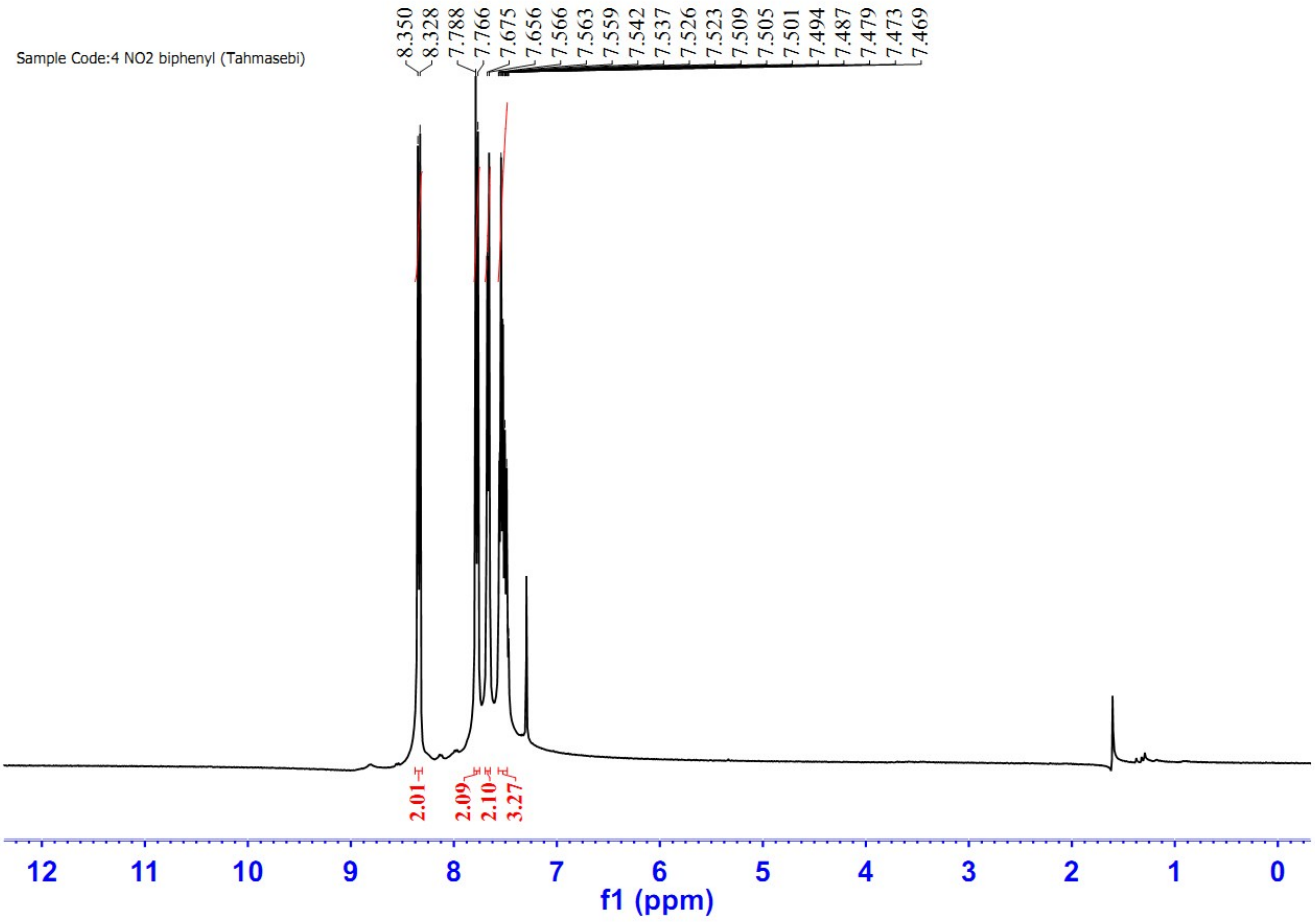
^{1}H NMR spectral data

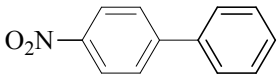


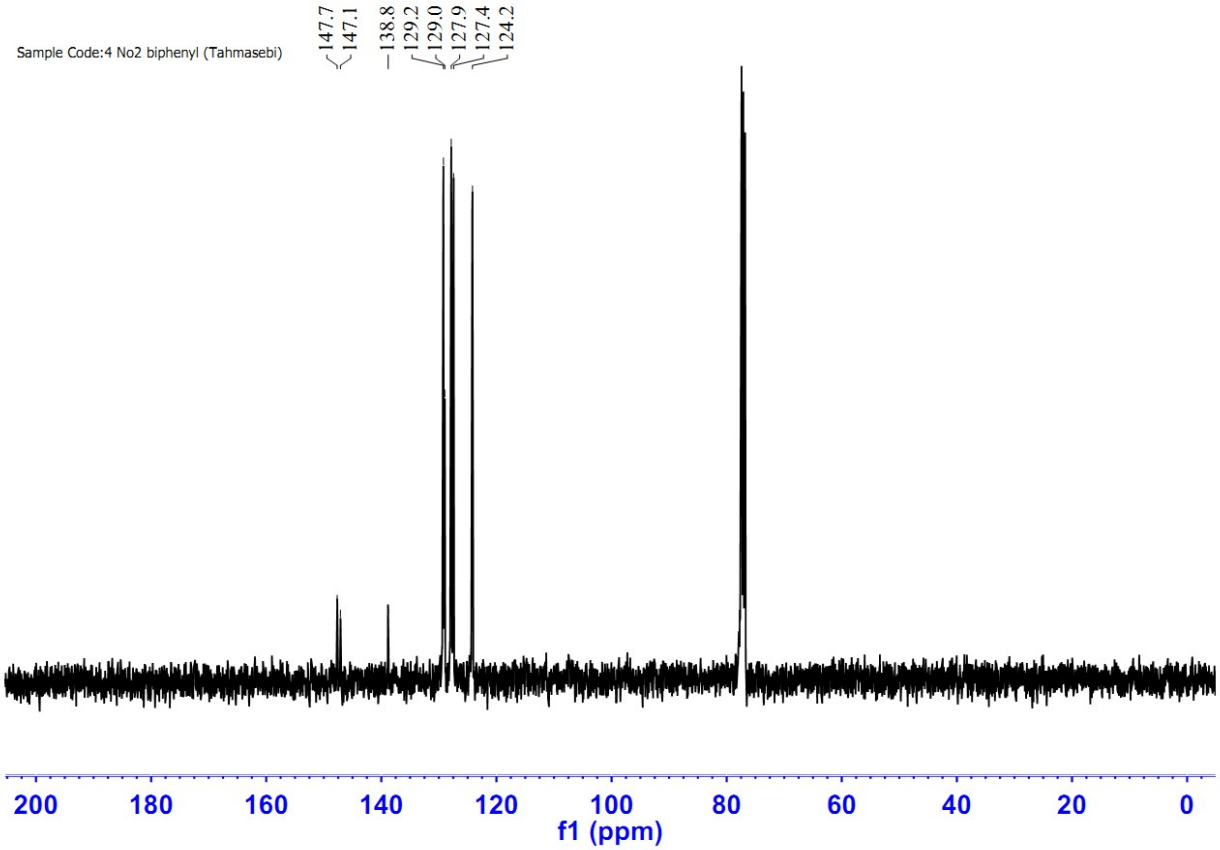
4-nitro-1,1'-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): δ_H= 8.35-8.33 (d, *J*= 8Hz, 2H), 7.79-7.77 (d, *J*= 8 Hz, 2H), 7.67-7.65 (d, *J*= 8Hz, 2H), 7.57-7.47 (m, 3H) ppm.

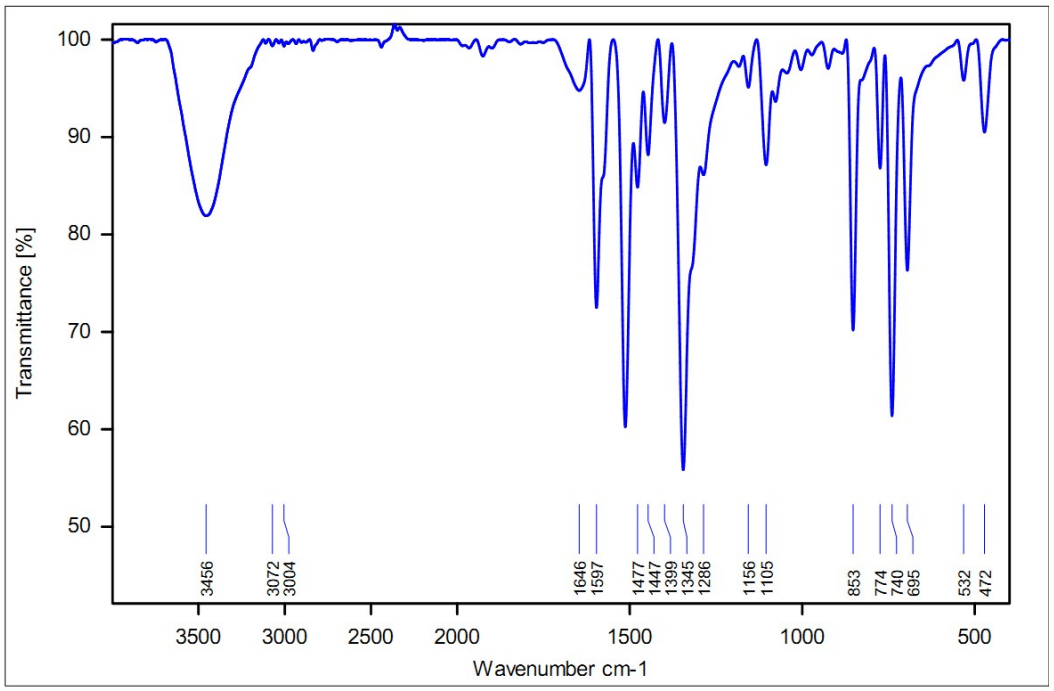
^{13}C NMR (100 MHz, $CDCl_3$): δ= 147.7, 147.1, 138.8, 129.2, 129.0, 127.9, 127.4, 124.2 ppm.

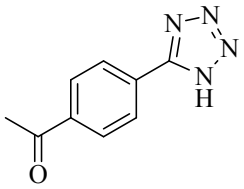
IR (KBr) cm^{-1}: 3072, 3004, 1646, 1597, 1477, 1447, 1399, 1345, 1286, 1156, 1105, 835, 774, 740, 695, 532, 472.




O_2N


Sample Code:4 No2 biphenyl (Tahmasebi)
147.7
147.1
138.8
129.2
129.0
127.9
127.4
124.2
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

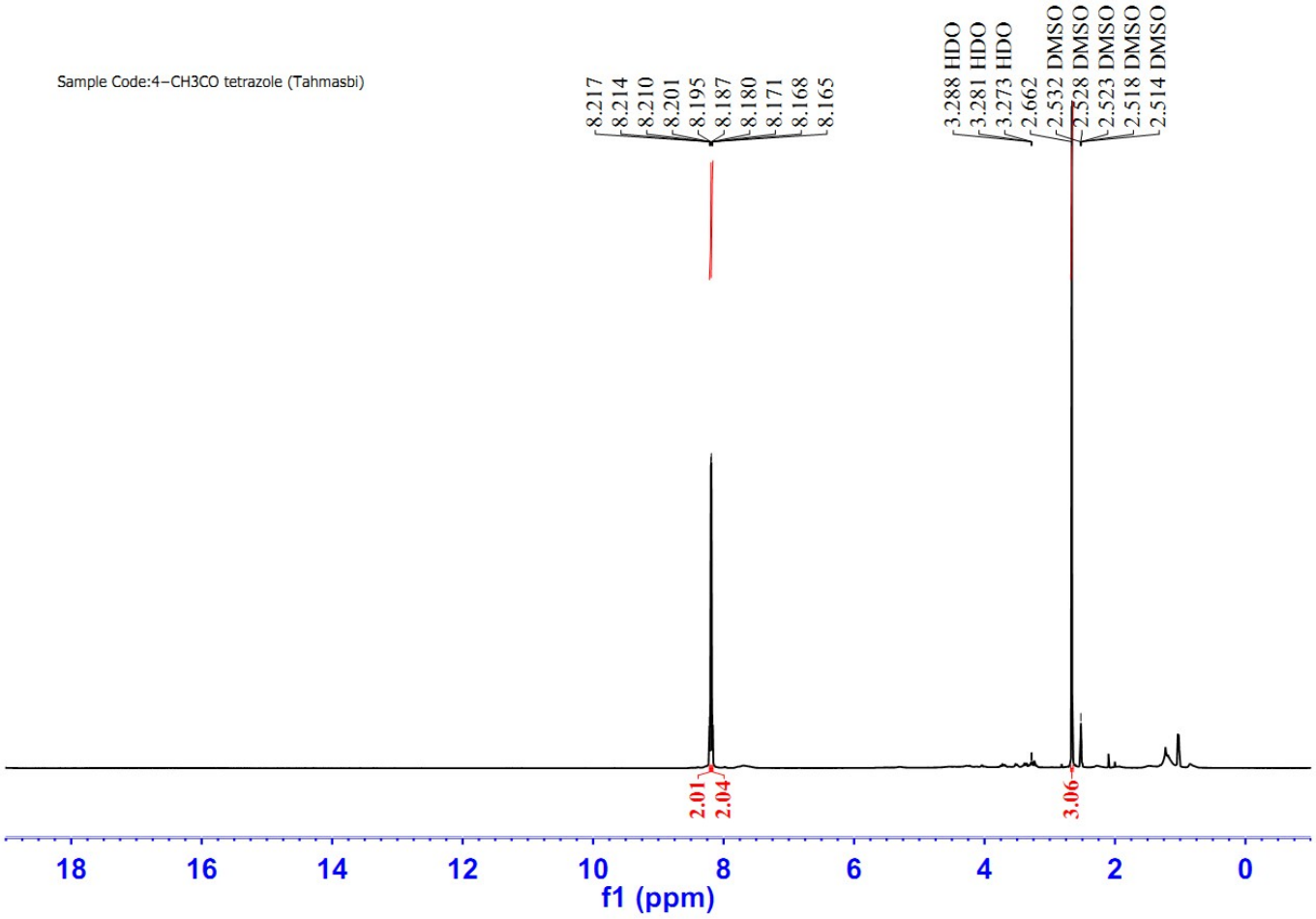

Transmittance [%]
100
90
80
70
60
50
3456
3072
3004
1646
1597
1477
1447
1399
1345
1286
1156
1105
853
774
740
695
532
472
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

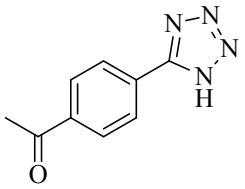


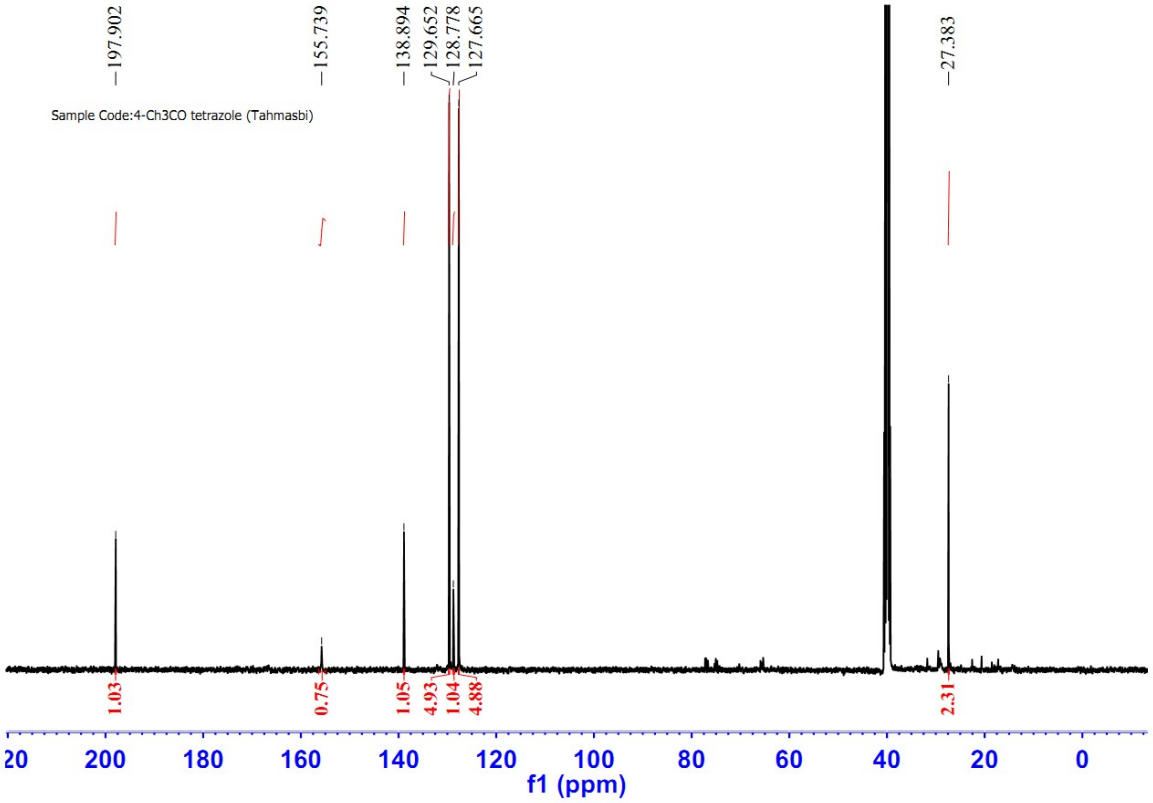
1-(4-(1H-tetrazol-5-yl)phenyl)ethanone: ^{1}H NMR (400 MHz, DMSO): δ_H= 8.21-8.19 (m, 2H), 8.18-8.16 (m, 2H), 2.66 (s, 3H) ppm.

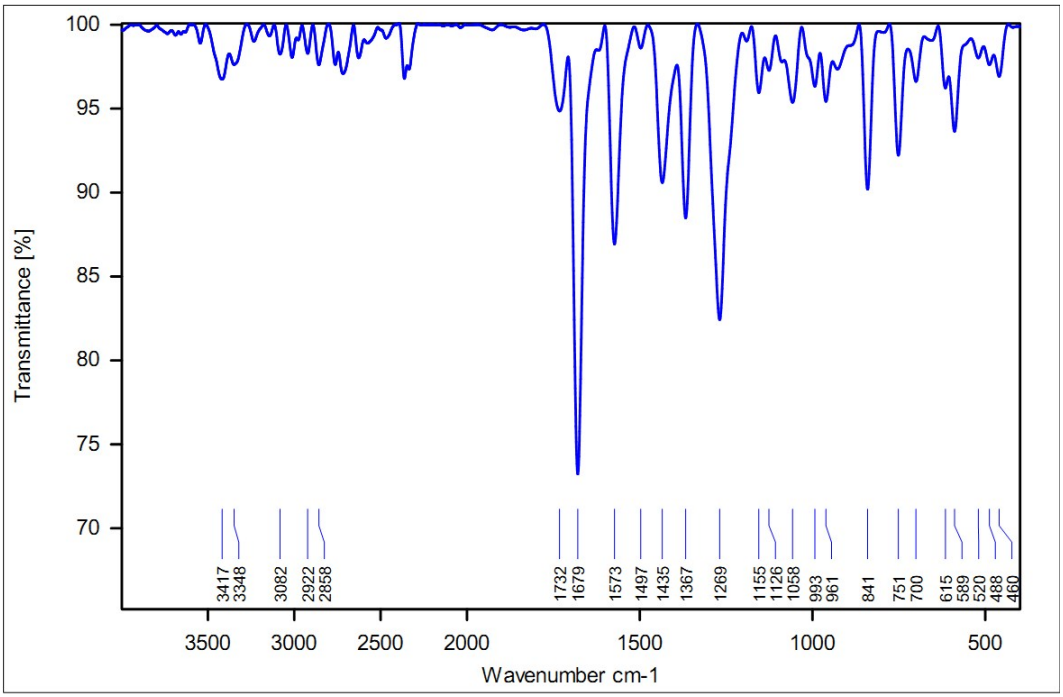
^{13}C NMR (100 MHz, $CDCl_3$): δ= 197.9, 155.7, 138.9, 129.6, 128.8, 127.6, 27.4 ppm.

IR (KBr) cm^{-1}: 3417, 3348, 3082, 2922, 2858, 1732, 1679, 1573, 1497, 1435, 1367, 1269, 1155, 1126, 1058, 993, 961, 841, 751, 700, 615, 589, 520, 488, 460.






197.902
155.739
138.894
129.652
128.778
127.665
27.383
Sample Code:4-Ch3CO tetrazole (Tahmasbi)
1.03
0.75
1.05
4.93
1.04
4.88
2.31
f1 (ppm)


Transmittance [%]
Wavenumber cm-1
3417
3348
3082
2922
2858
1732
1679
1573
1497
1435
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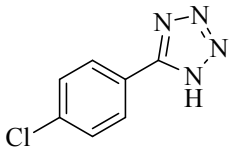
1269
1155
1126
1058
993
961
841
751
700
615
589
520
488
460

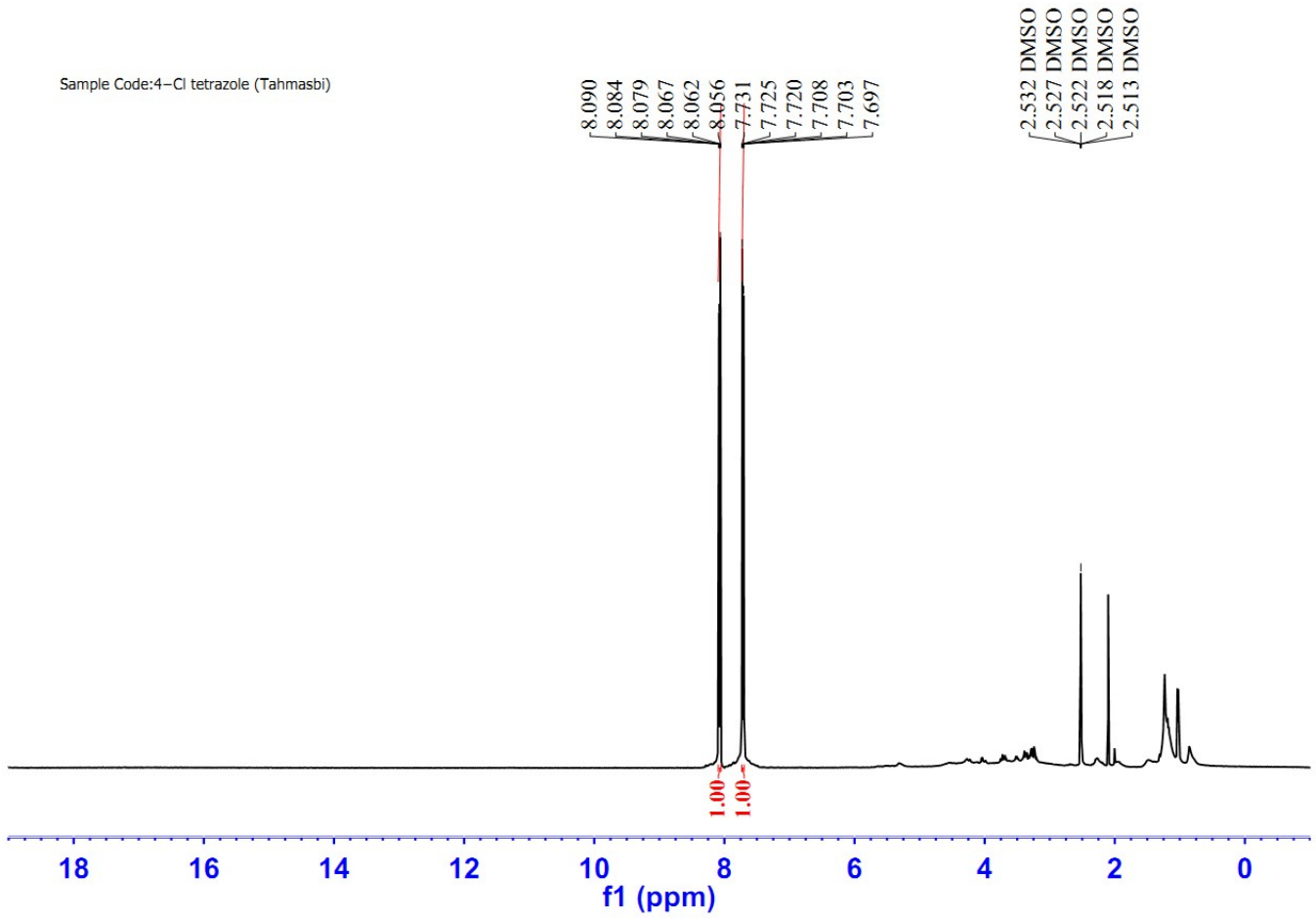


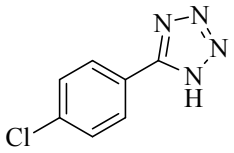
5-(4-chlorophenyl)-1H-tetrazole

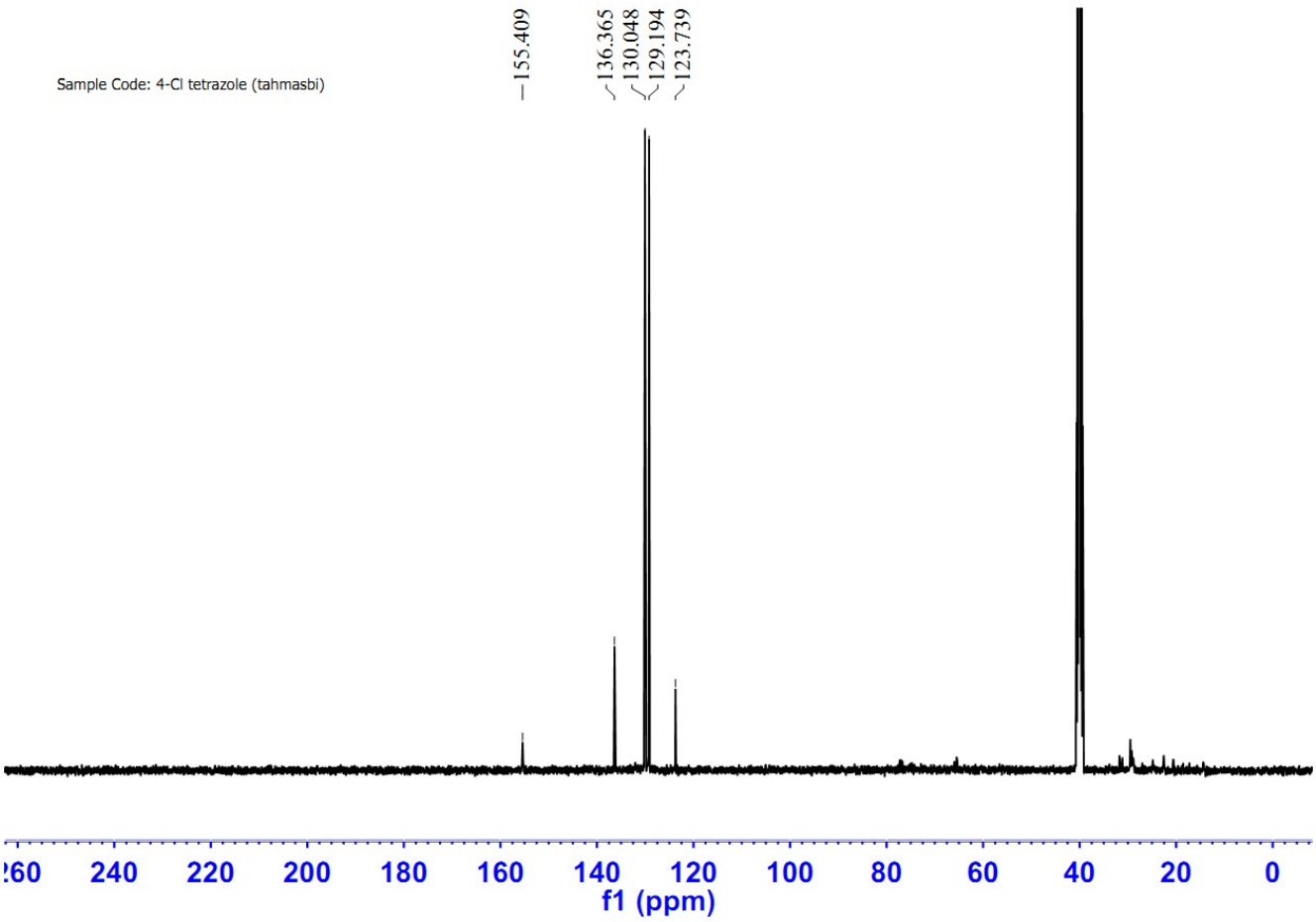
^{1}H NMR (400 MHz, DMSO): δ_H= 8.09-8.05 (m, 2H), 7.73-7.70 (m, 2H) ppm.

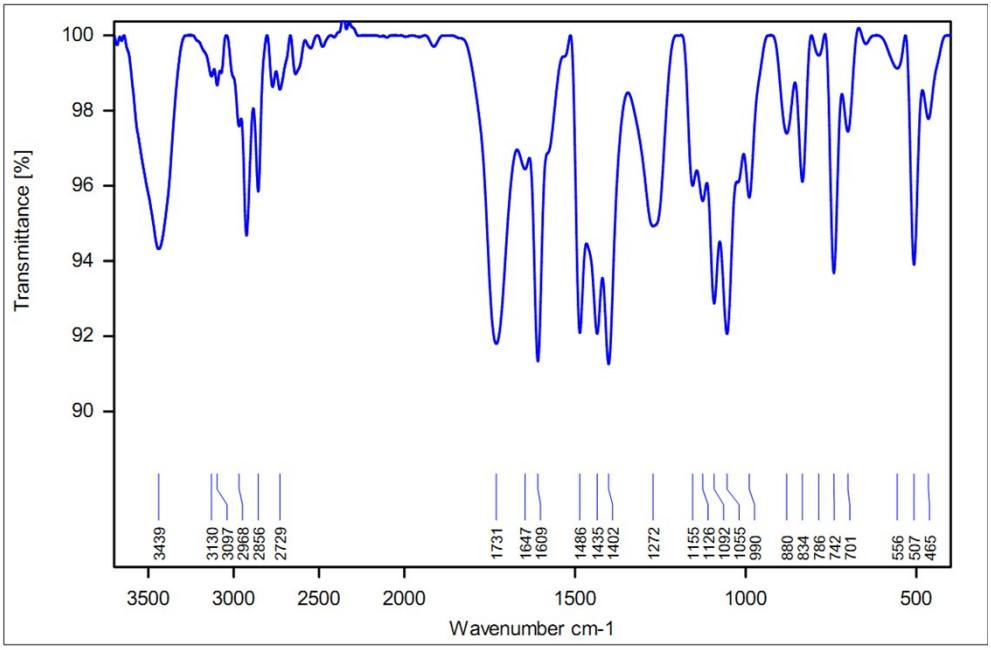
^{13}C NMR (100 MHz, $CDCl_3$): δ= 155.4, 136.4, 130.1, 129.2, 123.7 ppm.

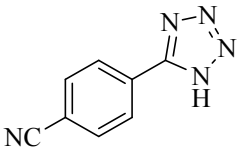
IR (KBr) cm^{-1}: 3439, 3130, 3097, 2968, 2856, 2129, 1731, 1647, 1609, 1486, 1435, 1402, 1272, 1155, 1126, 1092, 1055, 990, 880, 834, 786, 742, 701, 556, 507, 465.




N
N
N
H
Cl


Sample Code: 4-Cl tetrazole (tahmasbi)
155.409
136.365
130.048
129.194
123.739
260
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


Transmittance [%]
100
98
96
94
92
90
3439
3130
3097
2968
2856
2729
1731
1647
1609
1486
1435
1402
1272
1155
1126
1092
1055
990
880
834
786
742
701
556
507
465
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

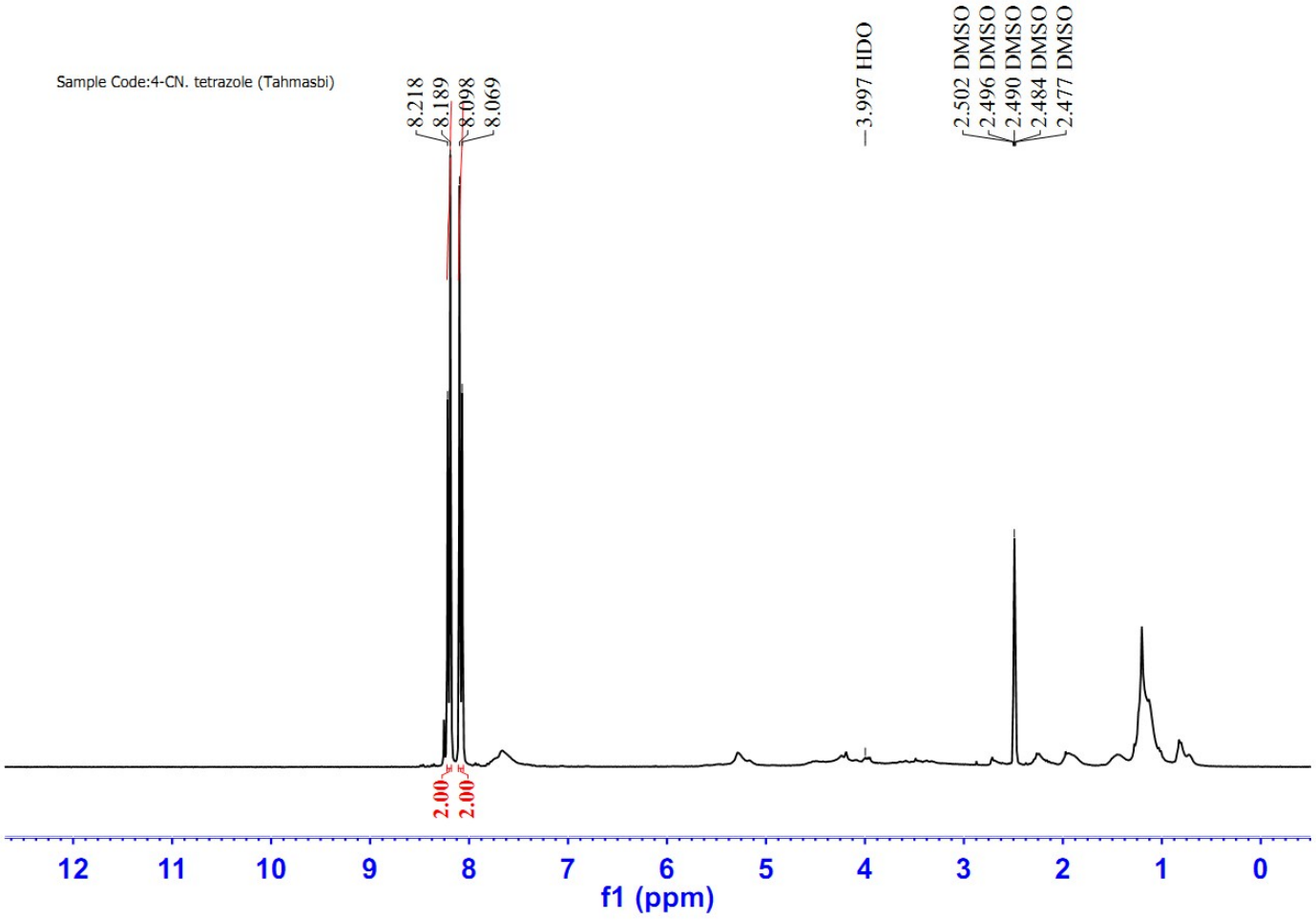


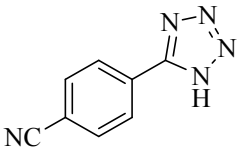
4-(1H-tetrazol-5-yl)benzonitrile

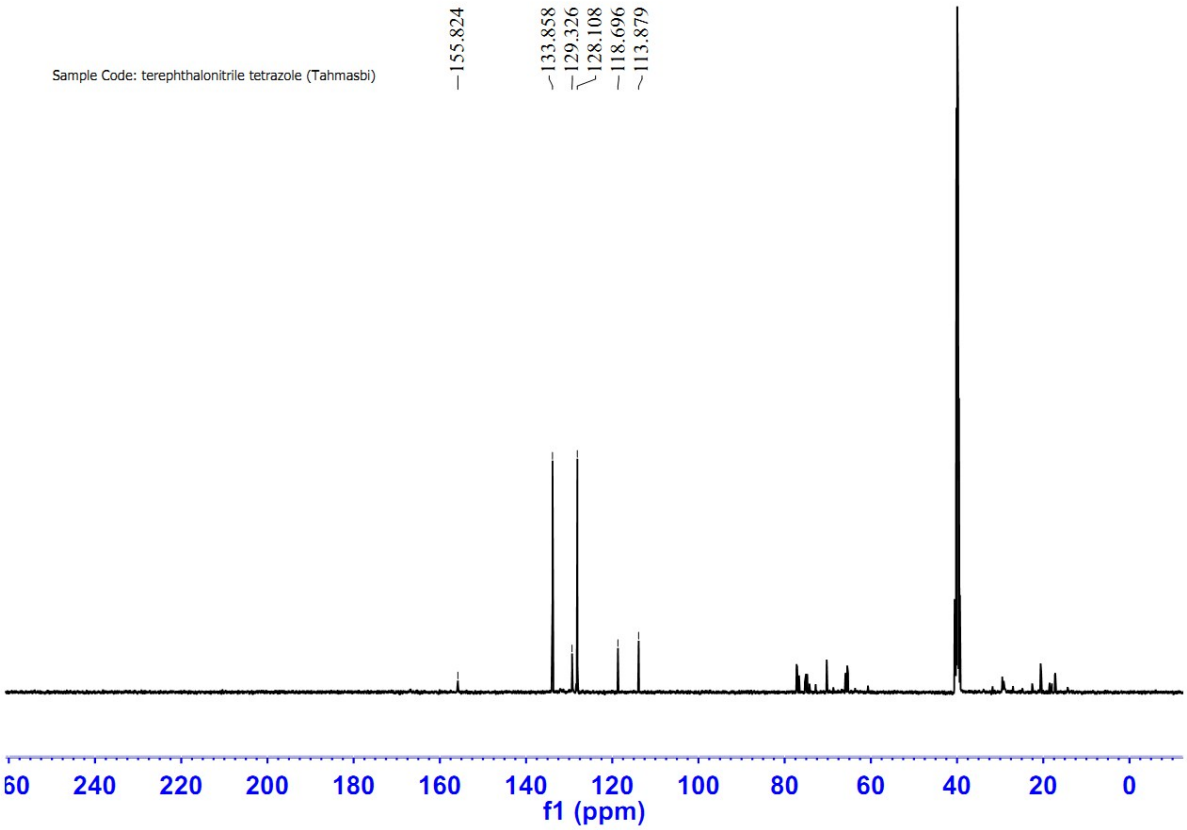
^{1}H NMR (400 MHz, DMSO): δ_H= 8.22-8.19 (d, *J*= 12 Hz, 2H), 8.10-8.07 (d, *J*= 12 Hz, 2H) ppm.

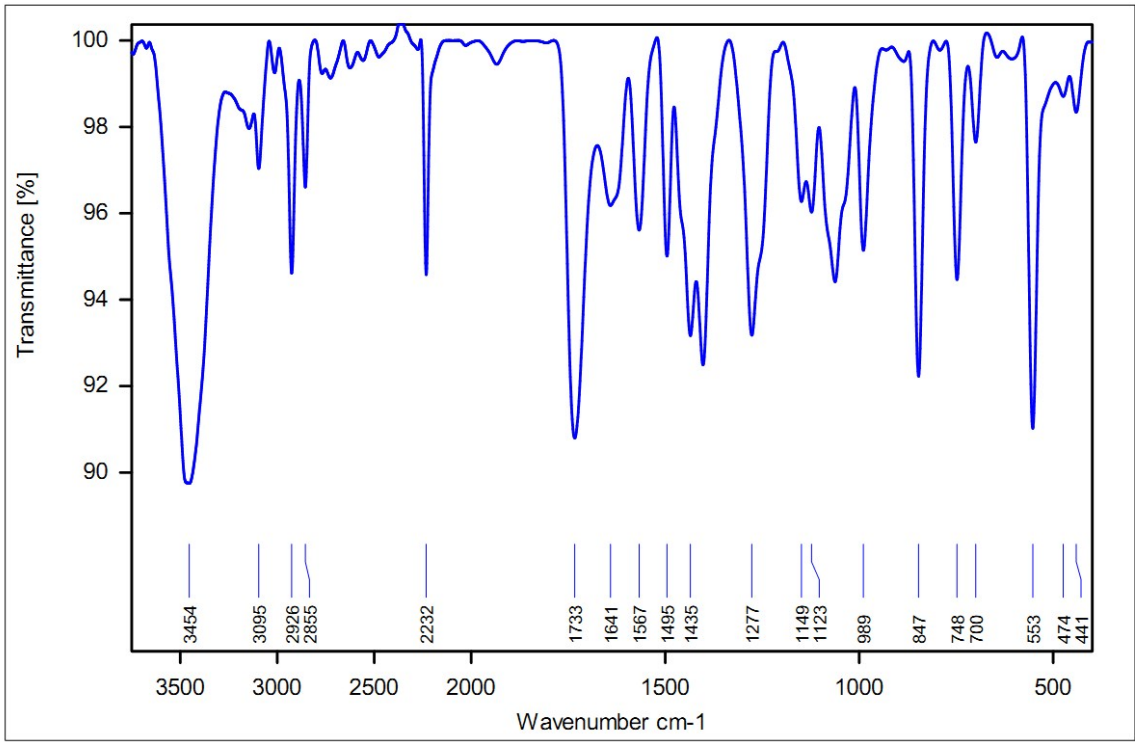
^{13}C NMR (100 MHz, $CDCl_3$): δ= 155.8, 133.8, 129.3, 128.1, 118.7, 113.9 ppm.

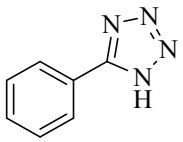
IR (KBr) cm^{-1}: 3454, 3095, 2926, 2855, 2232, 1733, 1641, 1567, 1495, 1435, 1277, 1149, 1123, 989, 847, 748, 700, 553, 474, 441.




N
N
N
N
H
NC


Sample Code: terephthalonitrile tetrazole (Tahmasbi)
155.824
133.858
129.326
128.108
118.696
113.879
60 240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


Transmittance [%]
100
98
96
94
92
90
3454
3095
2926
2855
2232
1733
1641
1567
1495
1435
1277
1149
1123
989
847
748
700
553
474
441
3500 3000 2500 2000 1500 1000 500
Wavenumber cm-1

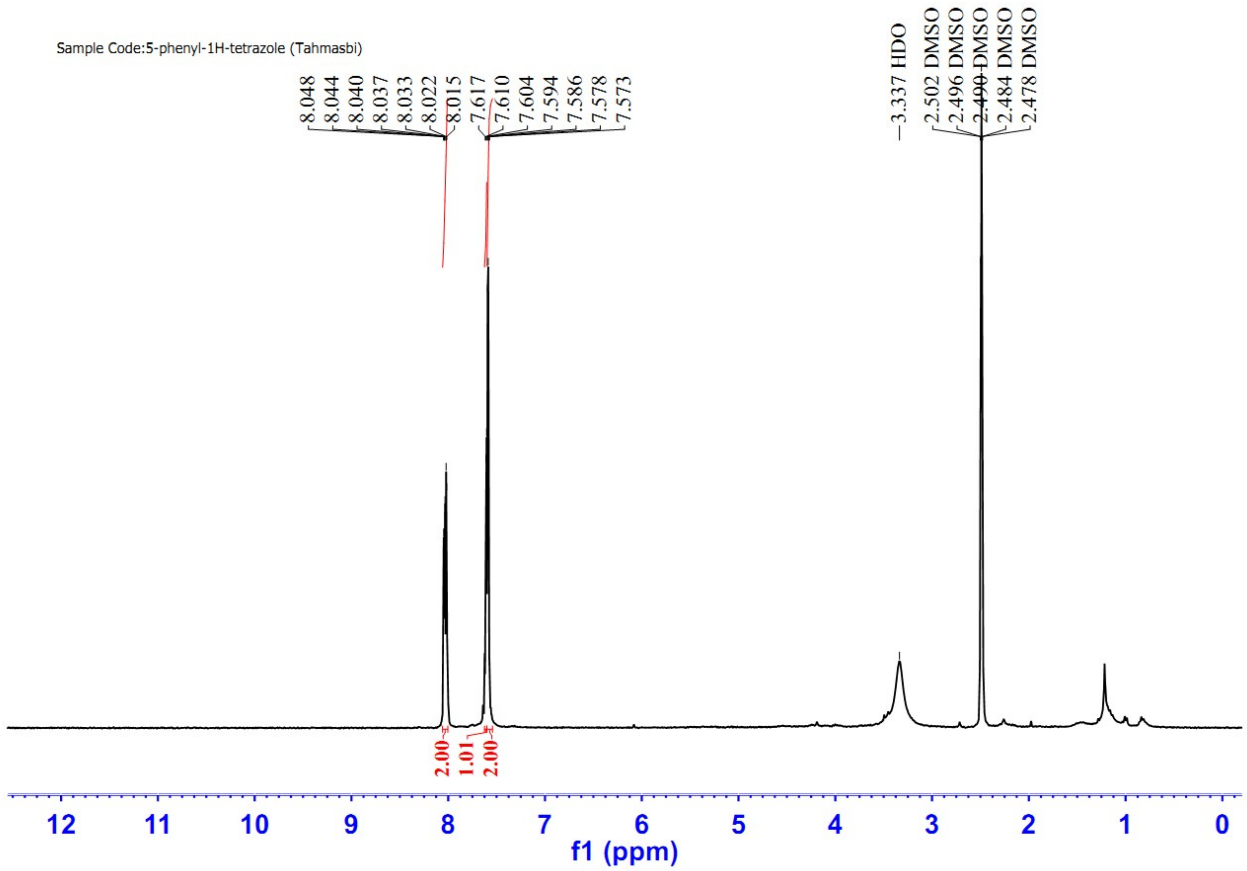


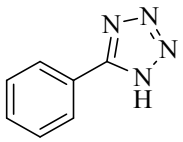
5-phenyl-1H-tetrazole

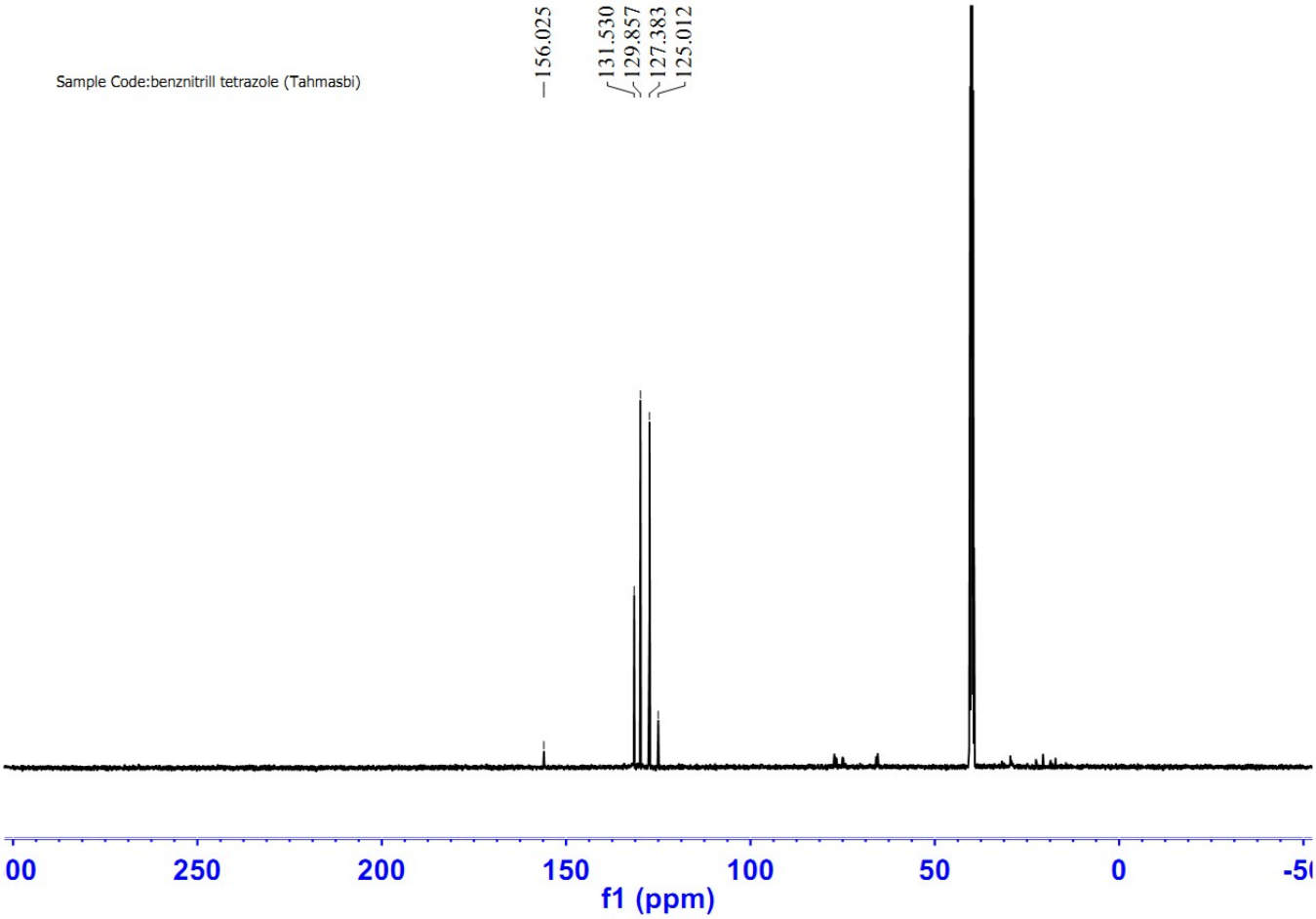
^{1}H NMR (400 MHz, DMSO): δ_H= 8.05-8.01 (m, 2H), 7.62-7.60 (m, 1H), 7.59-7.57 (m, 2H) ppm.

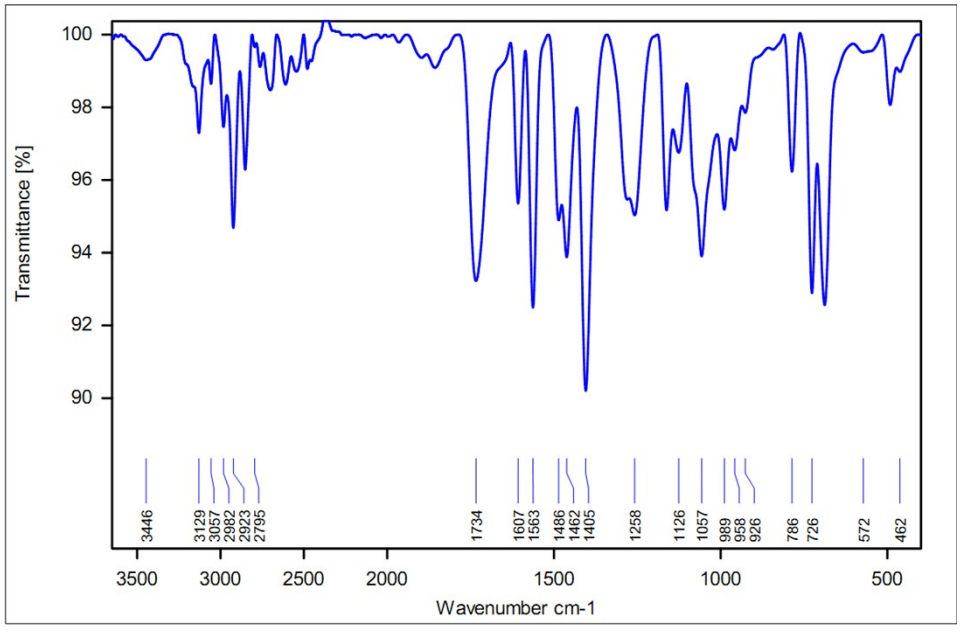
^{13}C NMR (100 MHz, $CDCl_3$): δ= 156.0, 131.5, 129.8, 127.4, 125.0 ppm.

IR (KBr) cm^{-1}: 3446, 3129, 3057, 2982, 2923, 2795, 1734, 1607, 1563, 1486, 1462, 1405, 1258, 1126, 1057, 989, 958, 926, 786, 726, 572, 462.






Sample Code:benznitrill tetrazole (Tahmasbi)
156.025
131.530
129.857
127.383
125.012
00
250
200
150
100
50
0
f1 (ppm)


Transmittance [%]
100
98
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94
92
90
3446
3129
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2795
1734
1607
1563
1486
1462
1405
1258
1126
1057
989
958
926
786
726
572
462
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1