

## Supplementary Data

### **A Schiff base complex of lanthanum on modified MCM-41 as a reusable nanocatalyst in the homoselective synthesis of 5-substituted 1H-tetrazole derivatives**

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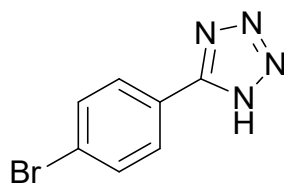
#### **Abstract:**

In this work mesoporous MCM-41 was modified by a new Schiff-base from condensation of triethylenetetramine and 5-bromosalicylaldehyde. Then it was used for stabilization of lanthanum metal (La-Schiff base@MCM-41) as a homoselective, reusable, efficient and biocompatible in the synthesis of 5-substituted 1H-tetrazole derivatives which synthesized tetrazoles were characterized by <sup>1</sup>H NMR and FT-IR spectroscopy and physical properties. La-Schiff base@MCM-41 was characterized by various techniques such as ICP, CHN, XRD, TGA, BET, FT-IR, SEM, EDS and WDX. This catalyst has good stability and heterogeneity nature which can easily recovered and reused for several times without significant loss in catalytic activity. This present strategy has important advantages such as utilize PEG as green solvent, short reaction time, excellent yield, easy recycling of the catalyst and pure separation of the products. The recovered La-Schiff base@MCM-41 catalyst was characterized by FT-IR, SEM and AAS techniques.

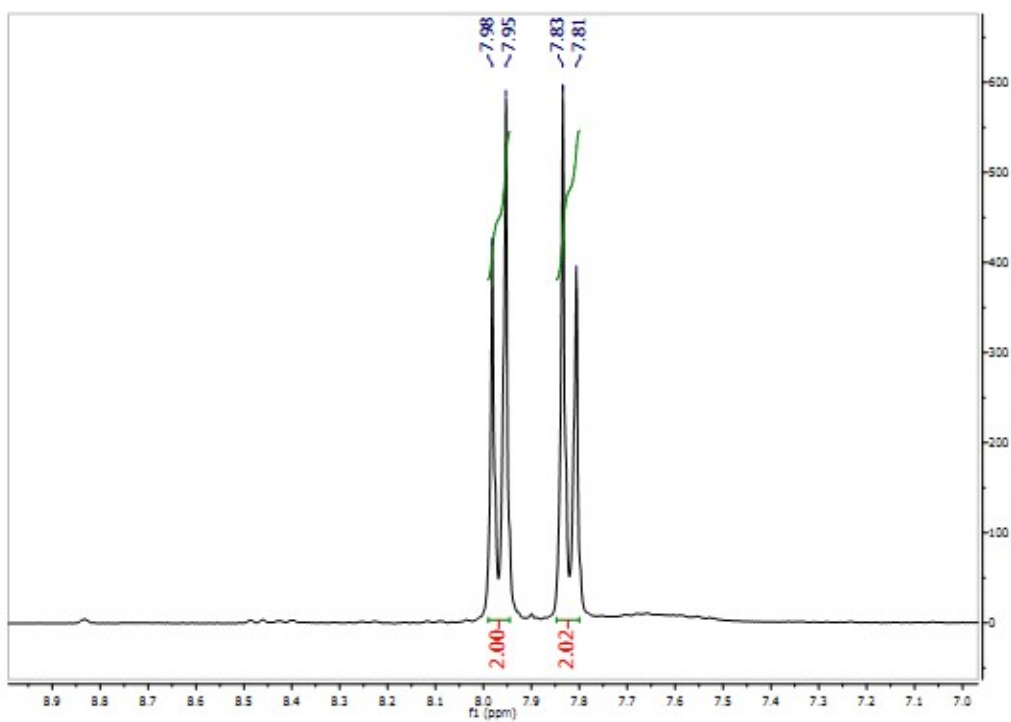
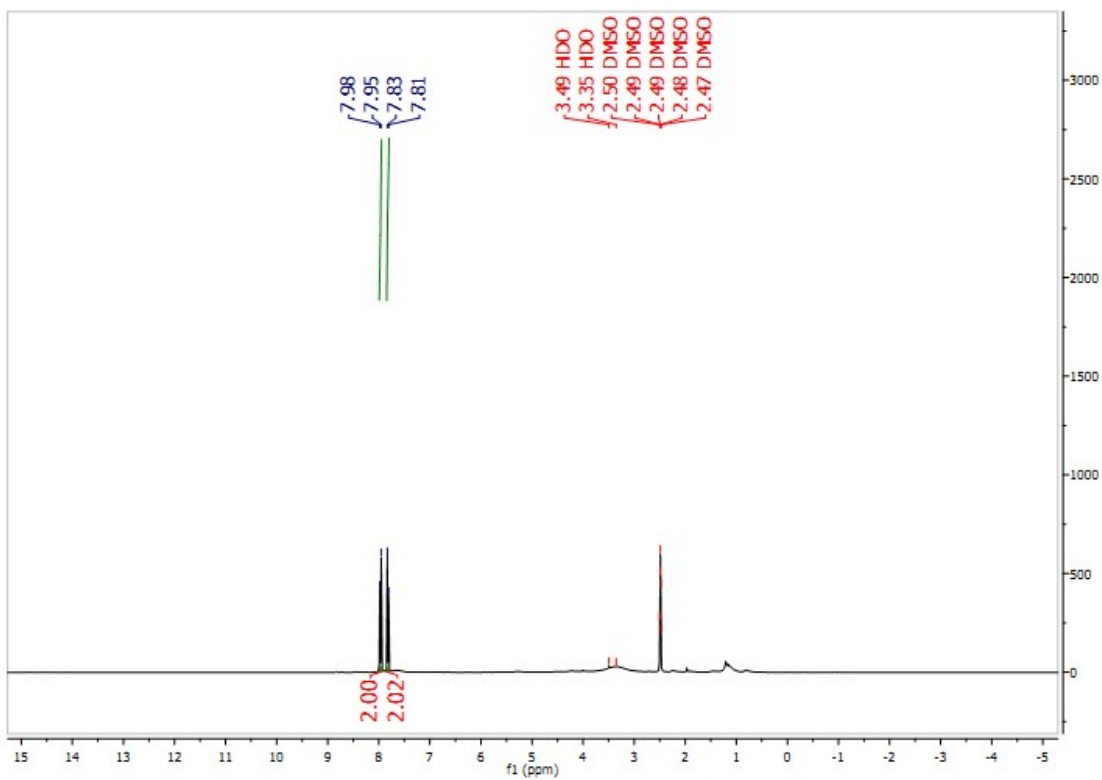
**Keywords:** Mesoporous MCM-41; Heterogeneous catalyst; Schiff-base complex, Lanthanum, 5-substituted 1H-tetrazole.

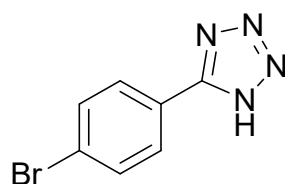
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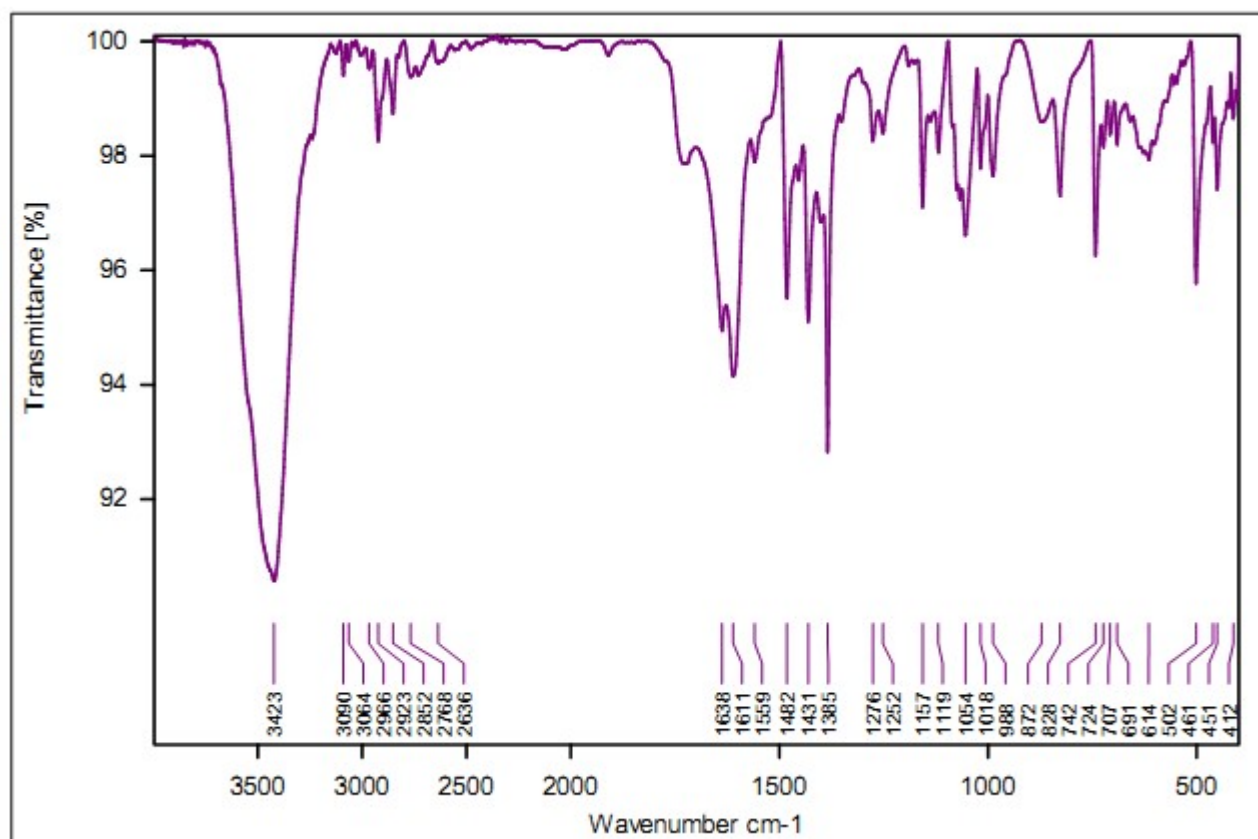


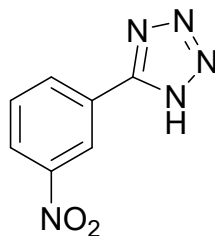
**5-(4-bromophenyl)-1H-tetrazole:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 7.98\text{-}7.95$  (d,  $J = 12$  Hz, 2H),  $7.83\text{-}7.81$  (d,  $J = 12$  Hz, 2H) ppm.



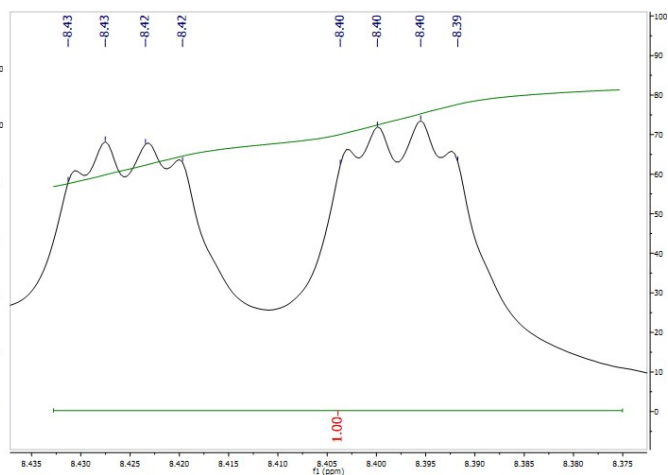
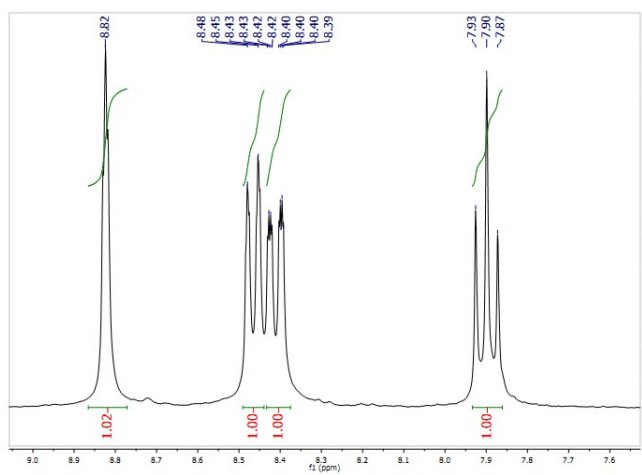
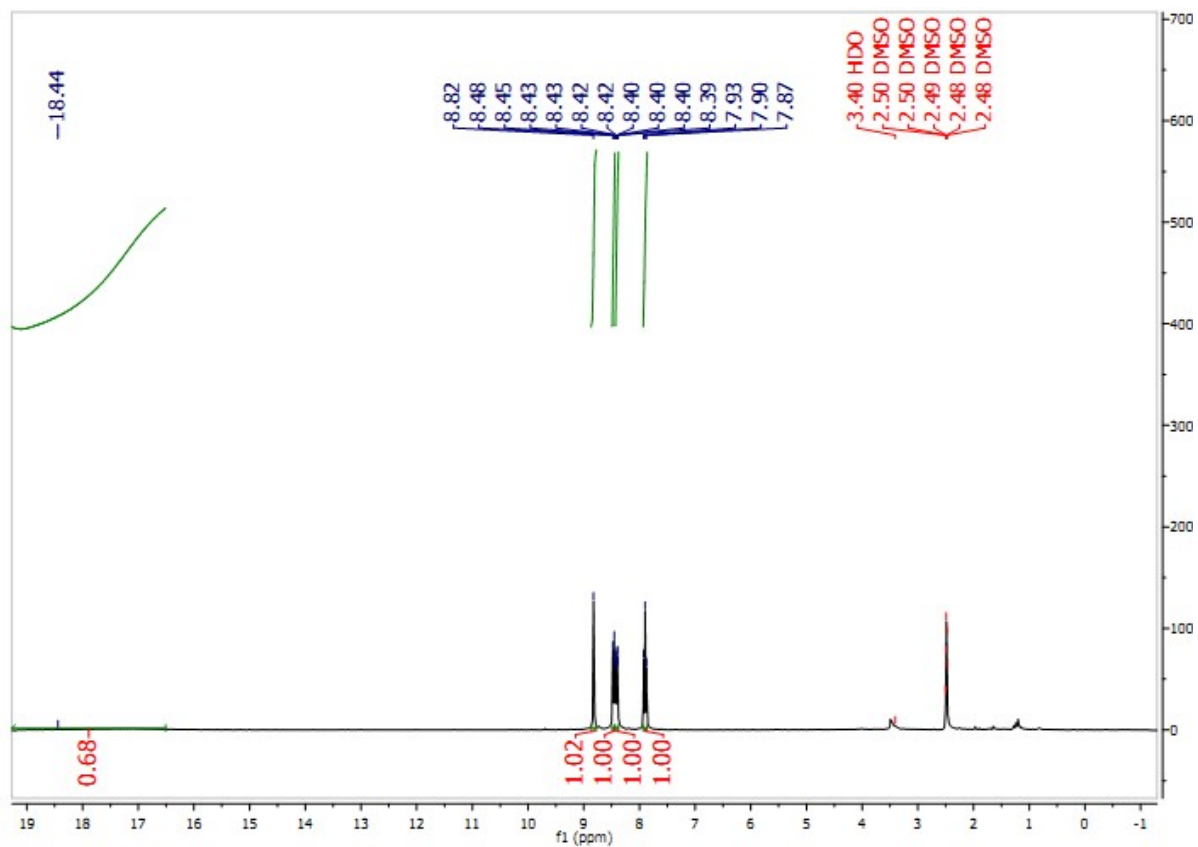


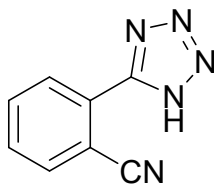
**5-(4-bromophenyl)-1H-tetrazole:** IR (KBr)  $\text{cm}^{-1}$ : 3423, 3090, 3064, 2966, 2852, 2768, 1638, 1611, 1559, 1482, 1431, 1385, 1276, 1252, 1157, 1119, 1054, 1018, 988, 872, 828, 742, 614, 451.



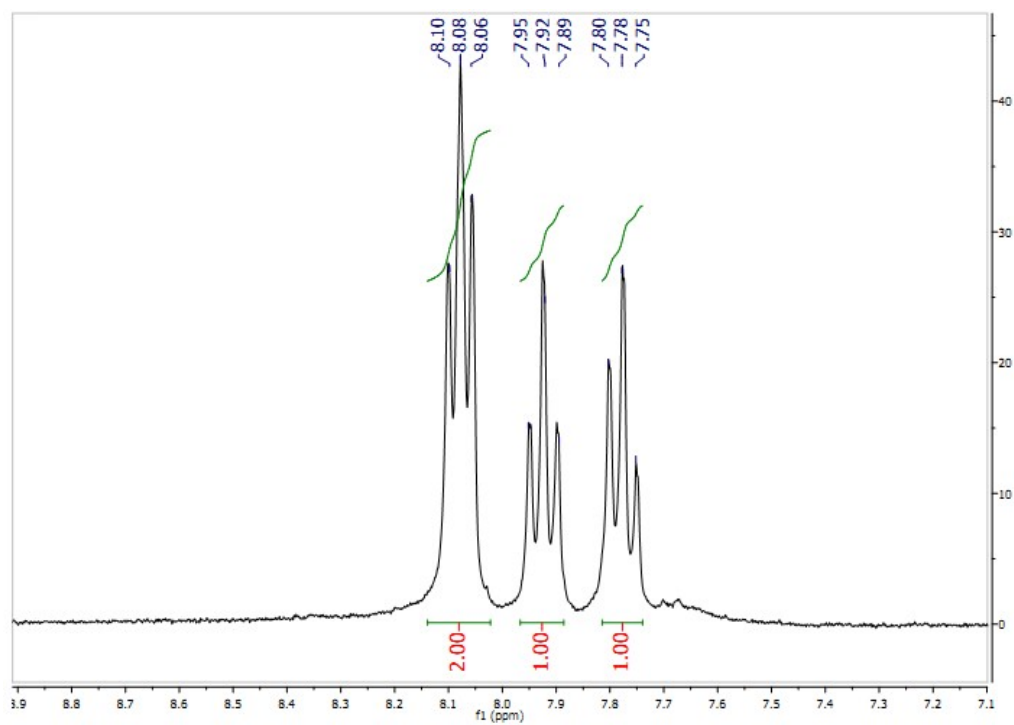
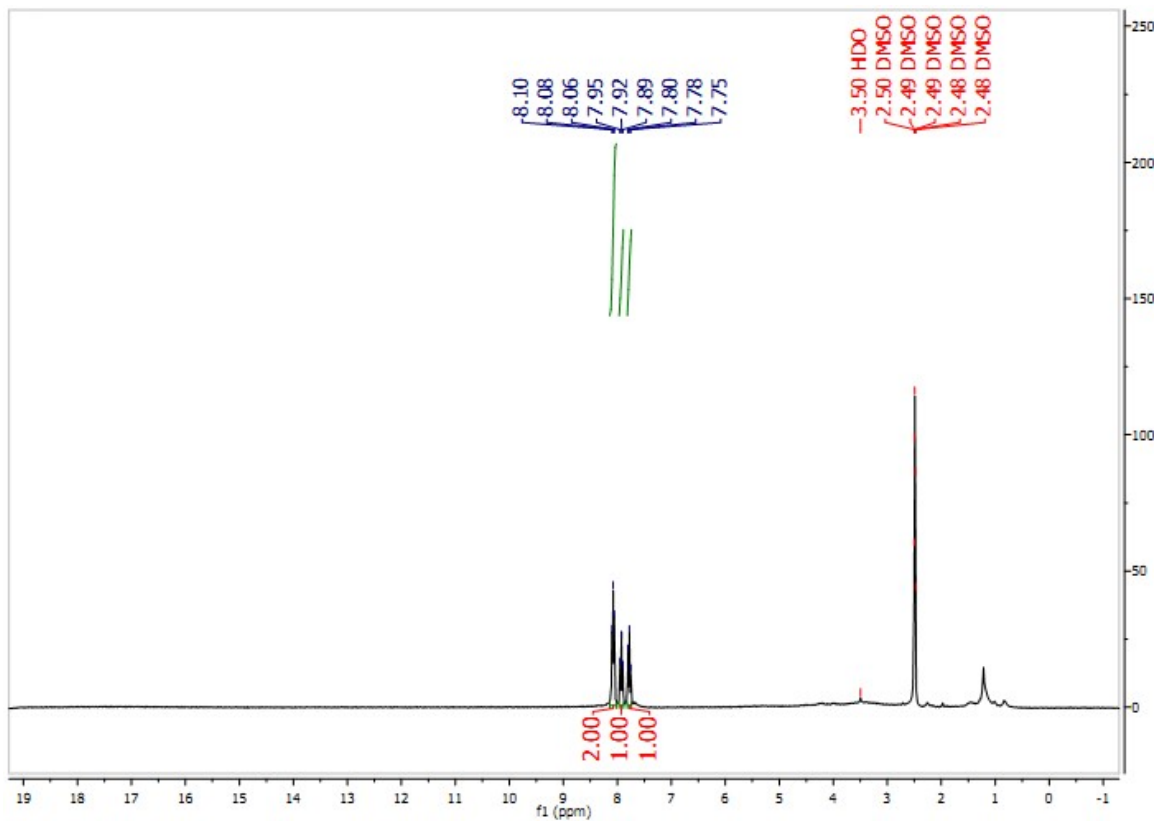


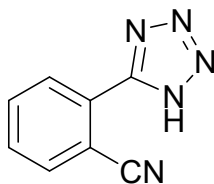
**5-(3-nitrophenyl)-1H-tetrazole:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 18.44$  (br, 1H), 8.82 (s, 1H), 8.48-8.45 (d,  $J = 12$  Hz, 1H), 8.43-8.39 (d of q,  $J(\text{d}) = 12$  Hz,  $J(\text{q}) = 2$  Hz, 1H), 7.93-7.87 (t,  $J = 12$  Hz, 1H) ppm.



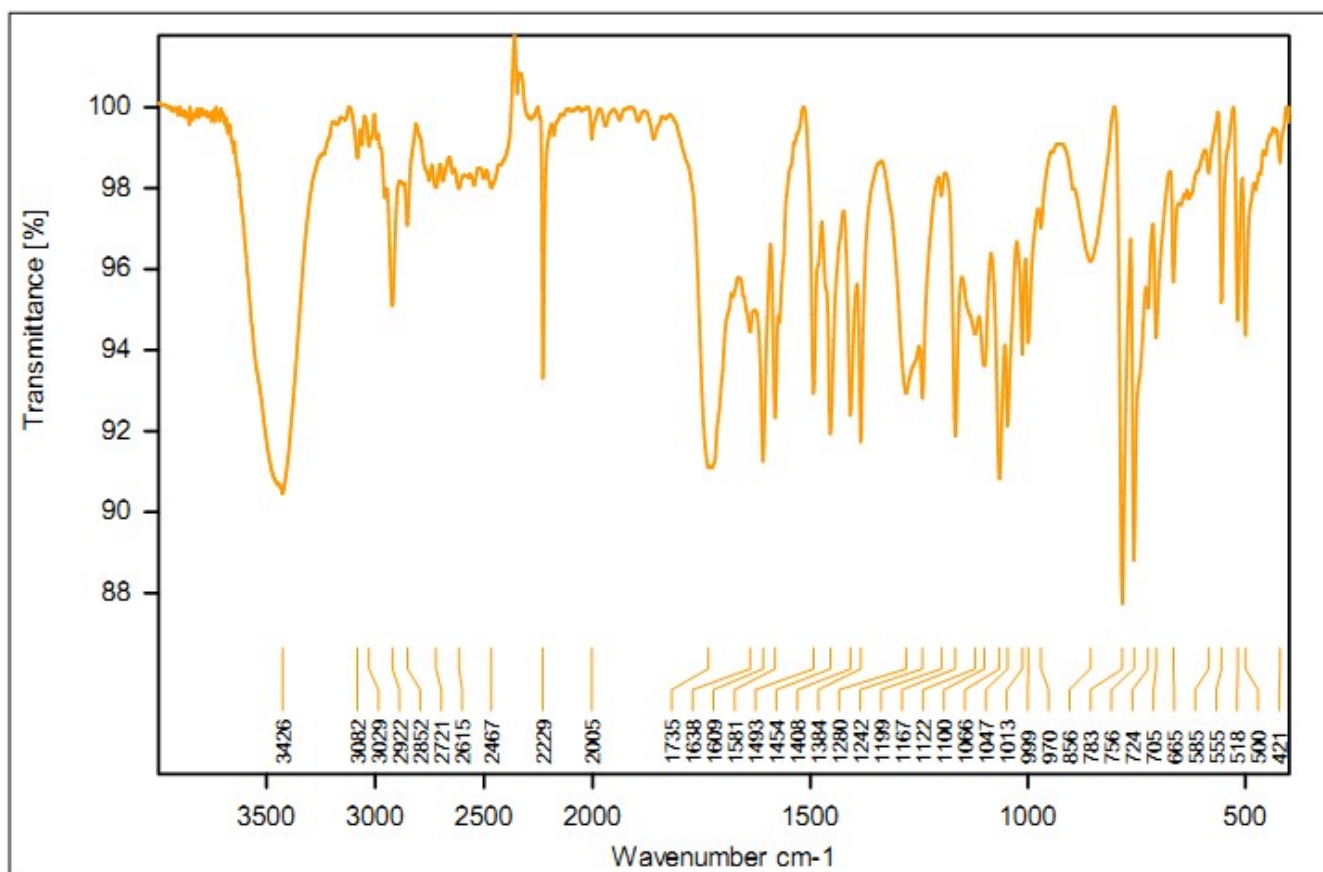


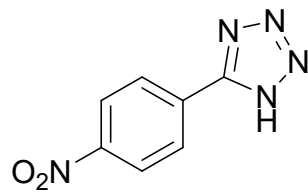
**2-(1H-tetrazol-5-yl)benzonitrile:**  $^1\text{H NMR}$  (400 MHz, DMSO):  $\delta_{\text{H}} = 8.10\text{-}8.06$  (t,  $J = 8$  Hz, 2H),  $7.95\text{-}7.89$  (t,  $J = 12$  Hz, 1H),  $7.80\text{-}7.75$  (t,  $J = 12$  Hz, 1H) ppm.



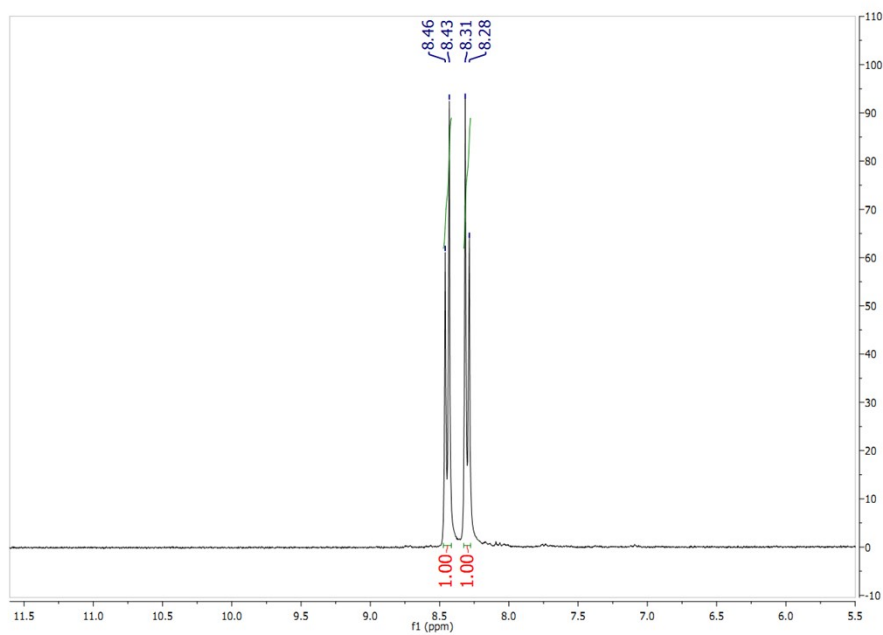
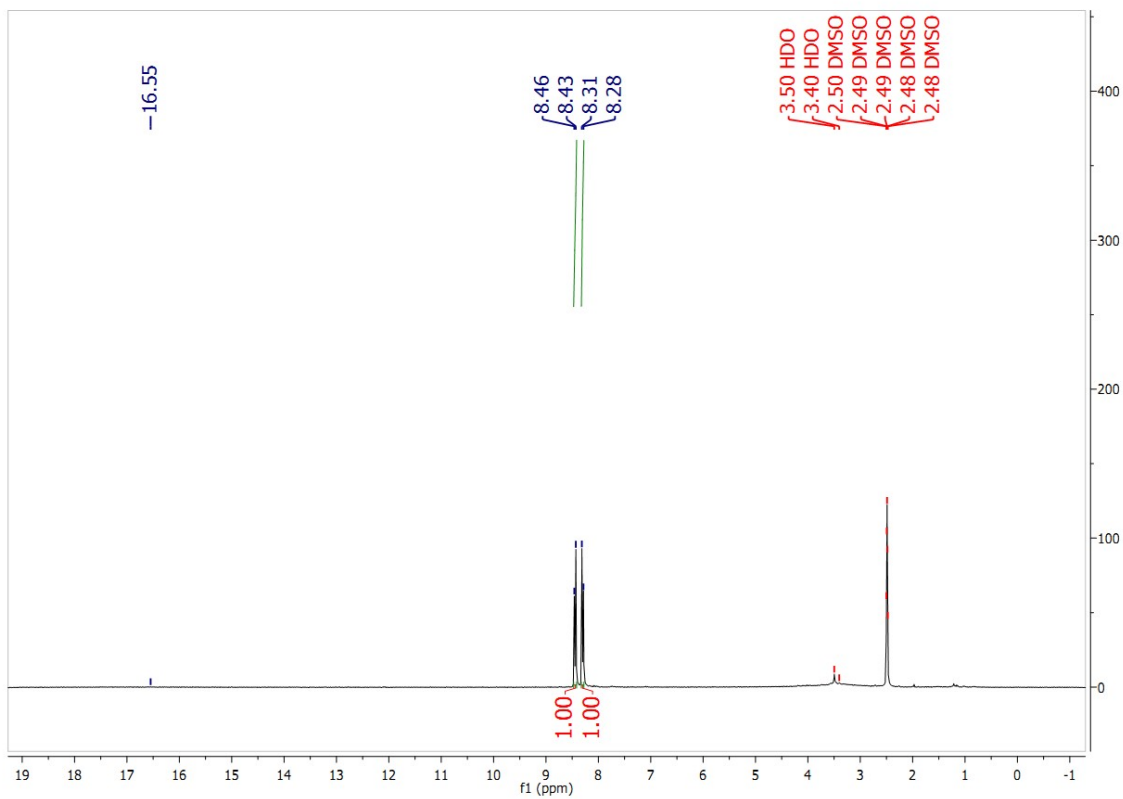


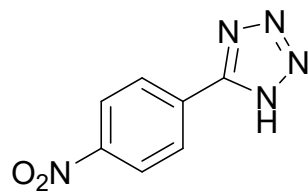
**2-(1H-tetrazol-5-yl)benzonitrile:** IR (KBr)  $\text{cm}^{-1}$ : 3426, 3082, 3029, 2922, 2582, 2721, 2615, 2229, 2005, 1735, 1638, 1609, 1581, 1493, 1454, 1408, 1384, 1280, 1242, 1199, 1167, 1122, 1100, 1066, 1047, 1113, 999, 970, 856, 783, 756, 724, 705, 665, 585, 555, 518, 500.



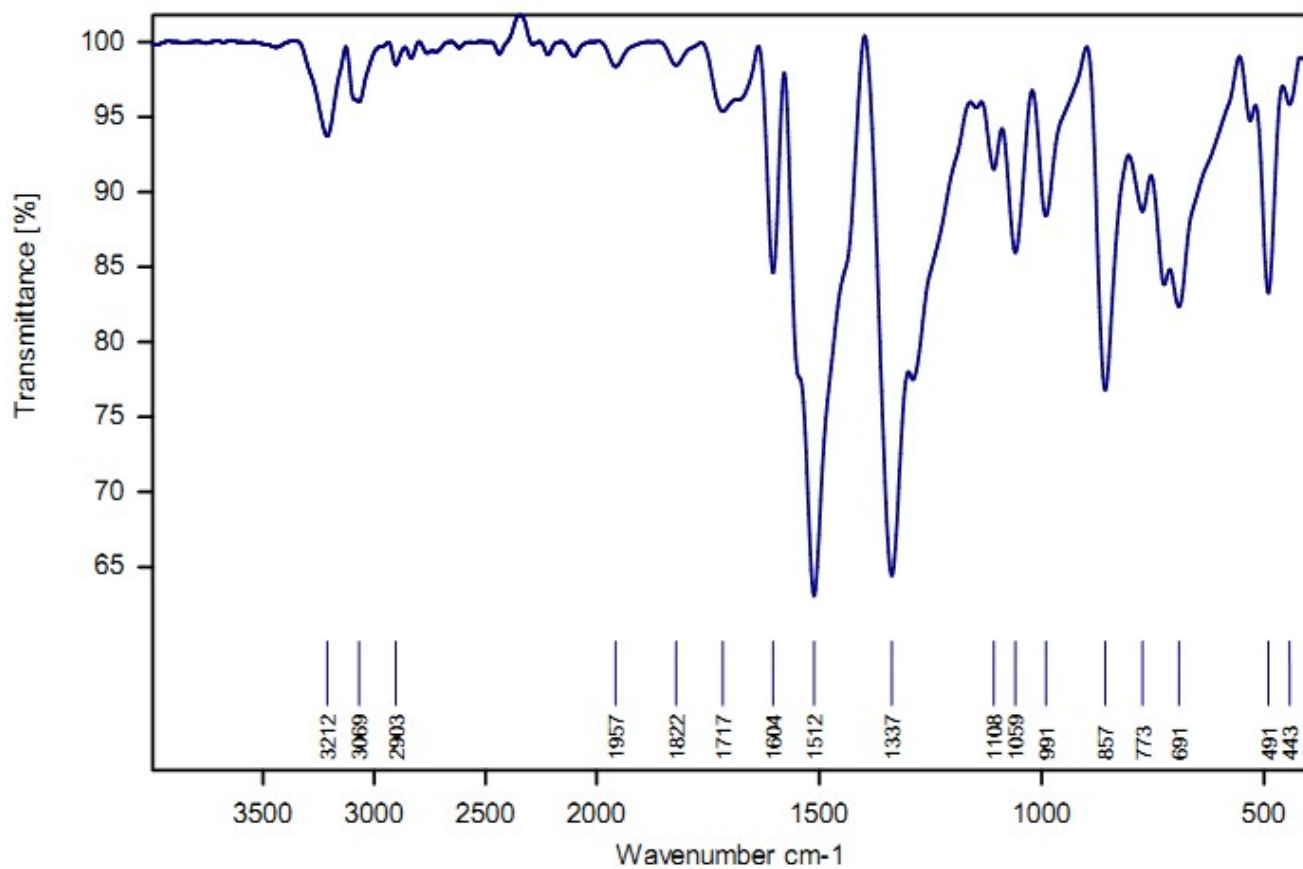


**5-(4-nitrophenyl)-1H-tetrazole:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 16.55$  (br, 1H), 8.46-8.43 (d,  $J = 12$  Hz, 2H), 8.31-8.28 (d,  $J = 12$  Hz, 2H) ppm.

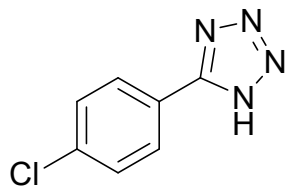




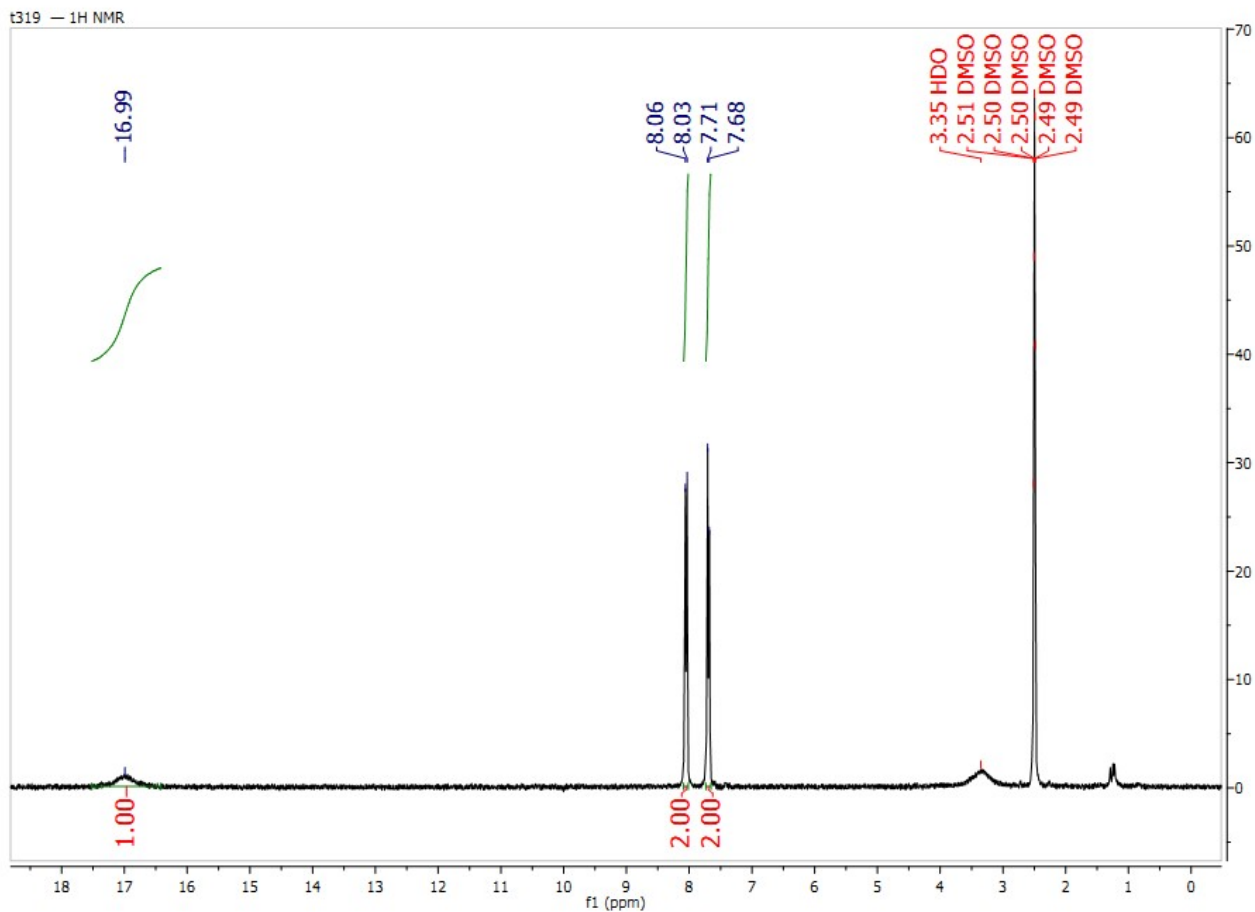
**5-(4-nitrophenyl)-1H-tetrazole:** IR (KBr)  $\text{cm}^{-1}$ : 3212, 3069, 2903, 1957, 1822, 1717, 1604, 1512, 1337, 1108, 1059, 991, 857, 773, 691, 491, 443.

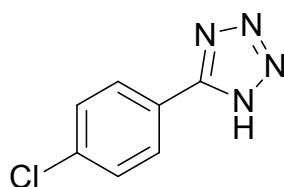




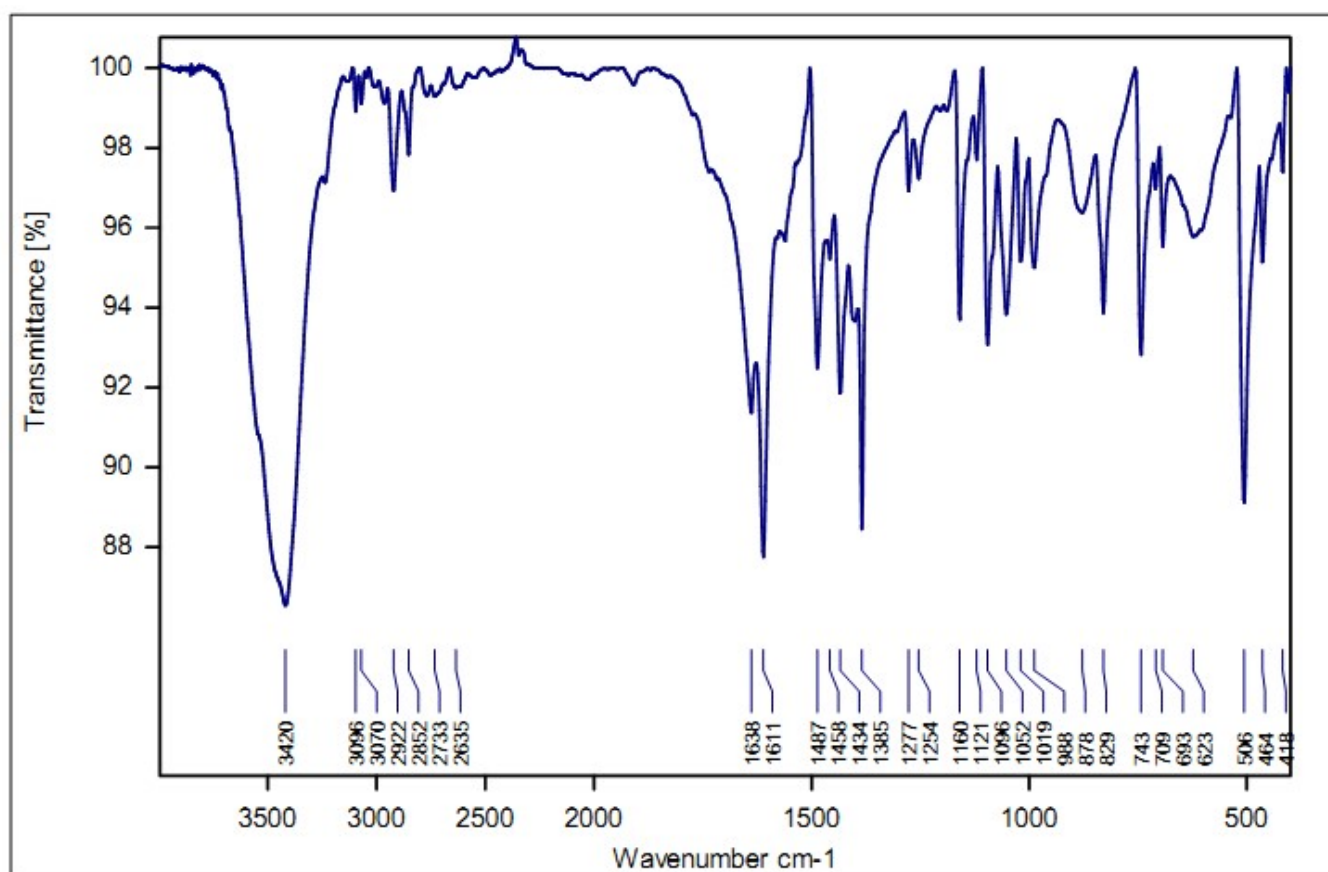


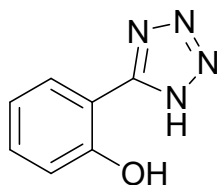
**5-(4-chlorophenyl)-1H-tetrazole:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 16.99$  (br, 1H), 8.06-8.03 (d,  $J = 12$  Hz, 2H), 7.71-7.68 (d,  $J = 12$  Hz, 2H) ppm.



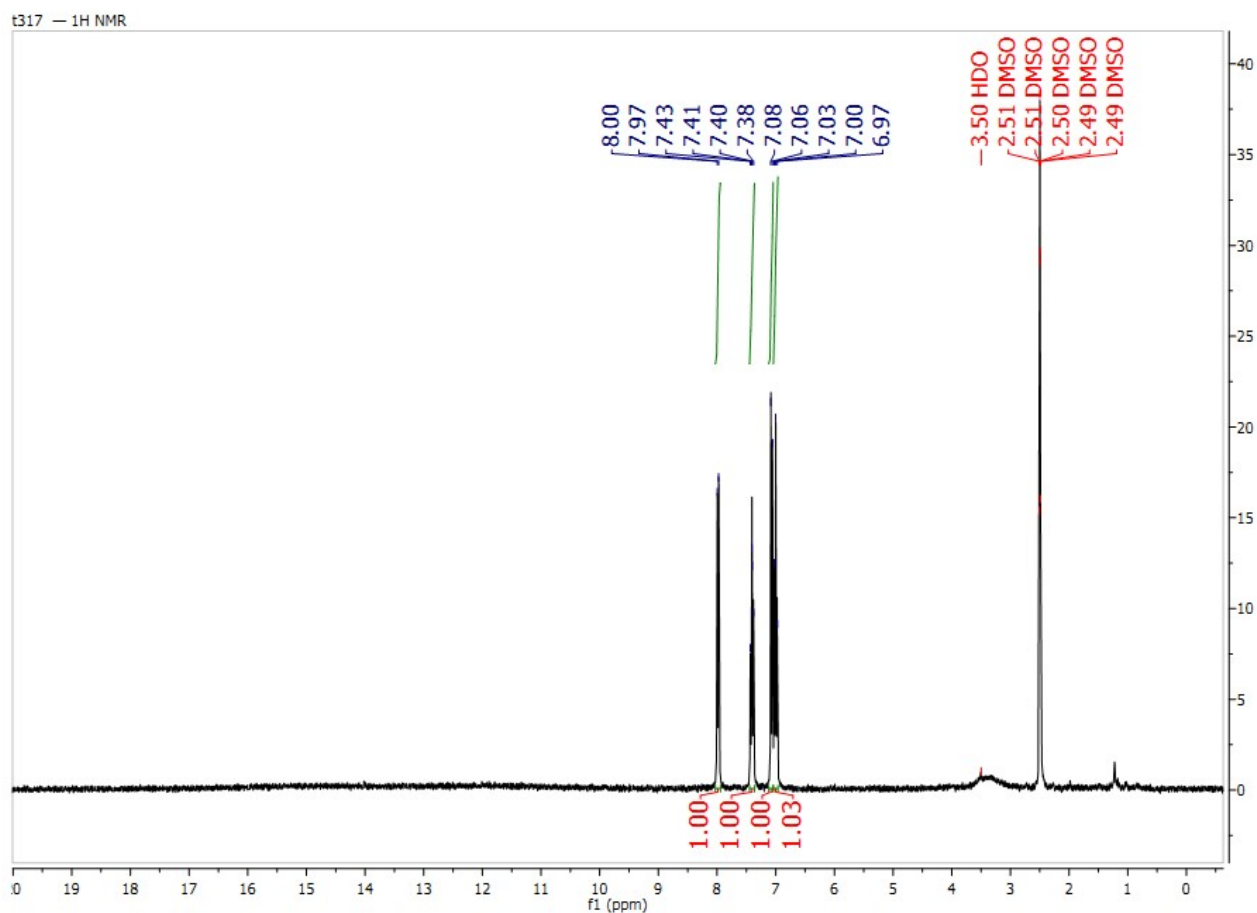


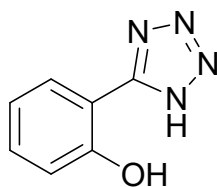
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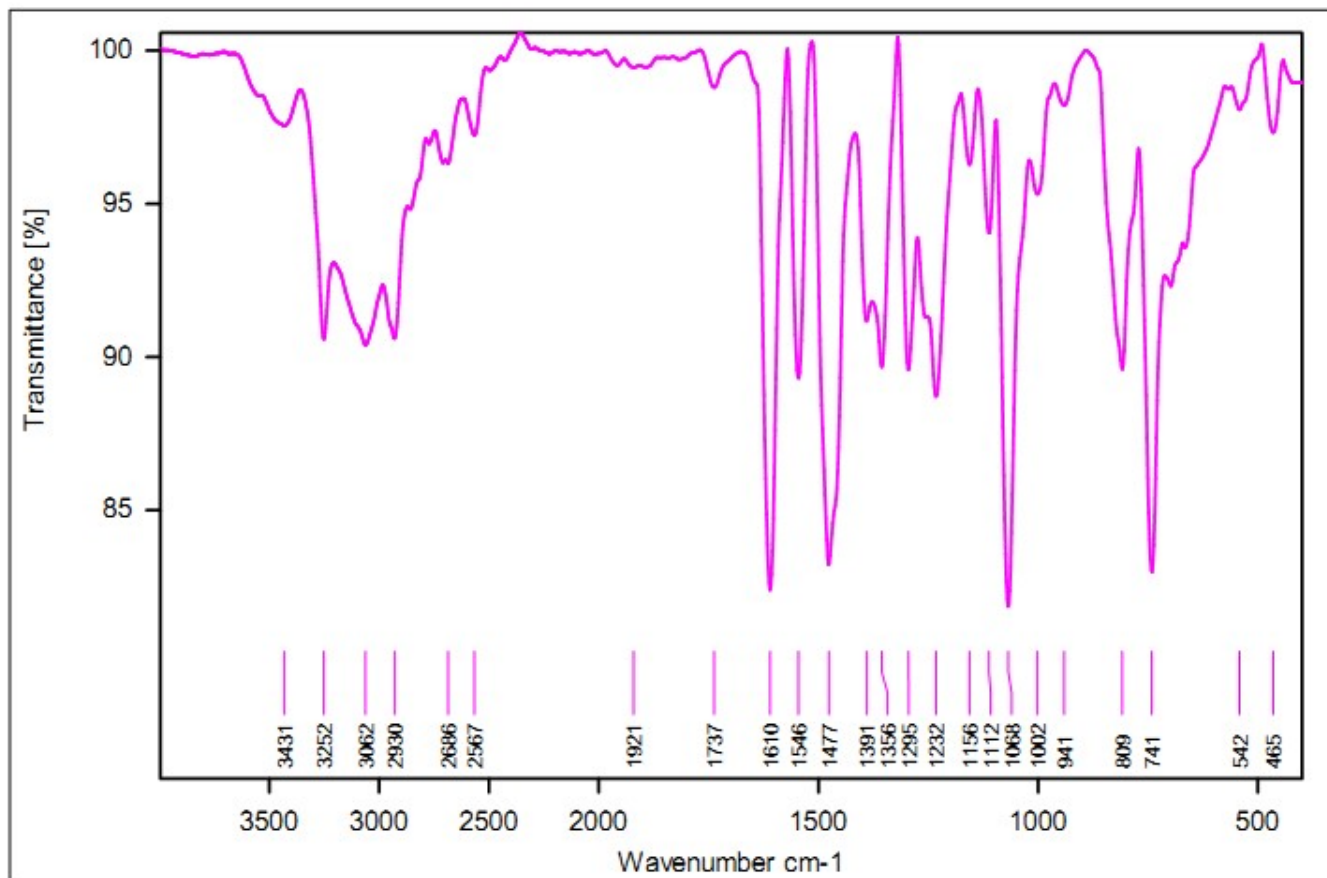


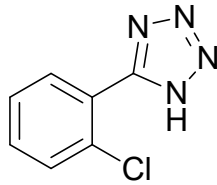
**2-(1H-tetrazol-5-yl)phenol:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 8.00-7.98$  (d,  $J = 12$  Hz, 1H), 7.43-7.38 (t,  $J = 8$  Hz, 1H), 7.08-7.06 (d,  $J = 8$  Hz, 1H), 7.03-6.97 (t,  $J = 12$  Hz, 1H) ppm.



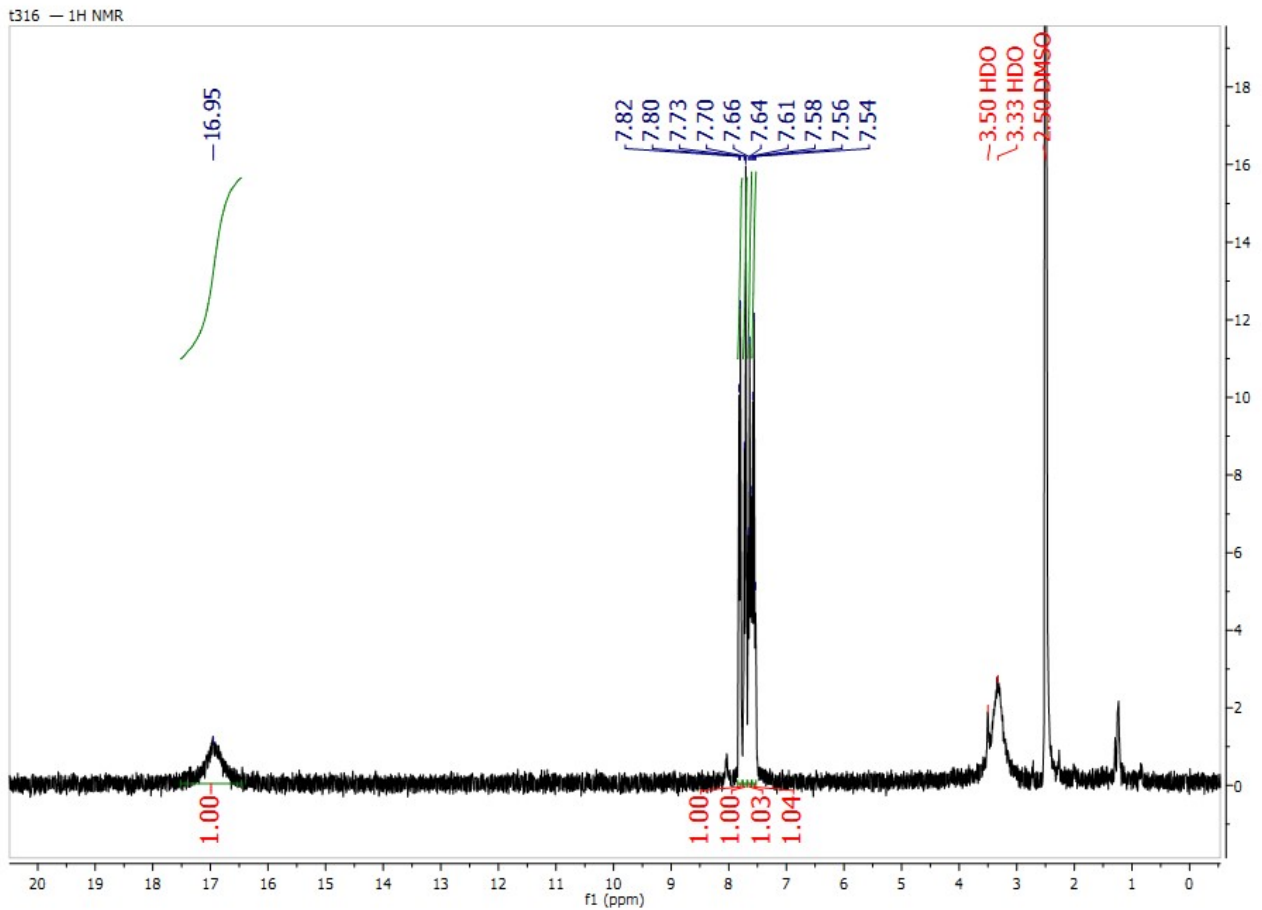


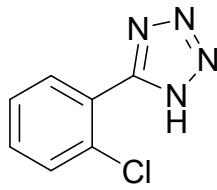
**2-(1H-tetrazol-5-yl)phenol:** IR (KBr)  $\text{cm}^{-1}$ : 3431, 3252, 3062, 2930, 2686, 2567, 1737, 1610, 1546, 1477, 1391, 1356, 1295, 1232, 1156, 1112, 1086, 1002, 941, 809, 741, 542.



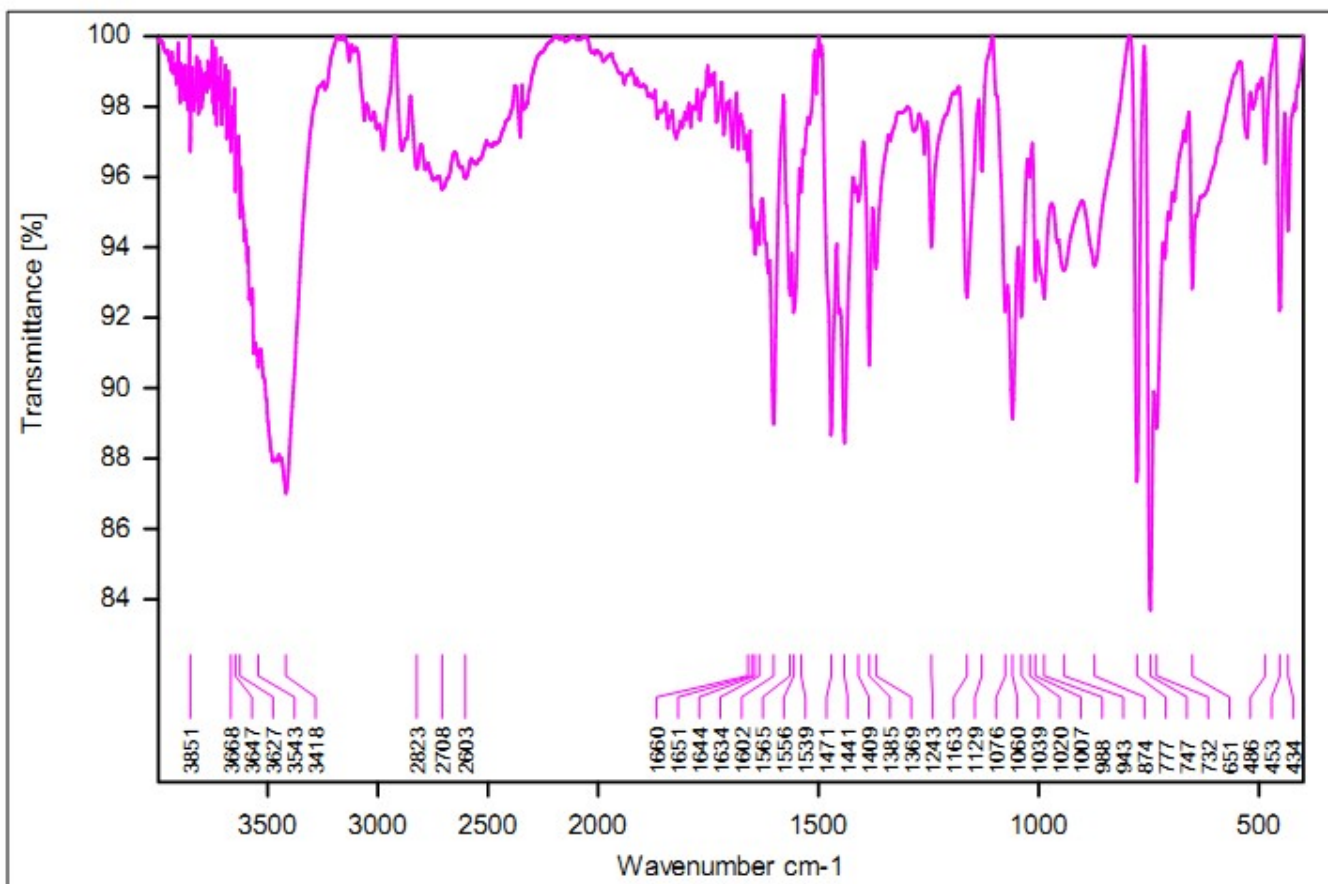


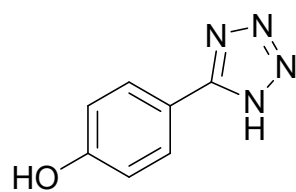
**5-(2-chlorophenyl)-1H-tetrazole:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 16.95$  (br, 1H), 7.82-7.80 (d,  $J = 8$  Hz, 1H), 7.73-7.70 (d,  $J = 12$  Hz, 1H), 7.66-7.61 (t,  $J = 8$  Hz, 1H), 7.58-7.54 (t,  $J = 8$  Hz, 1H) ppm.





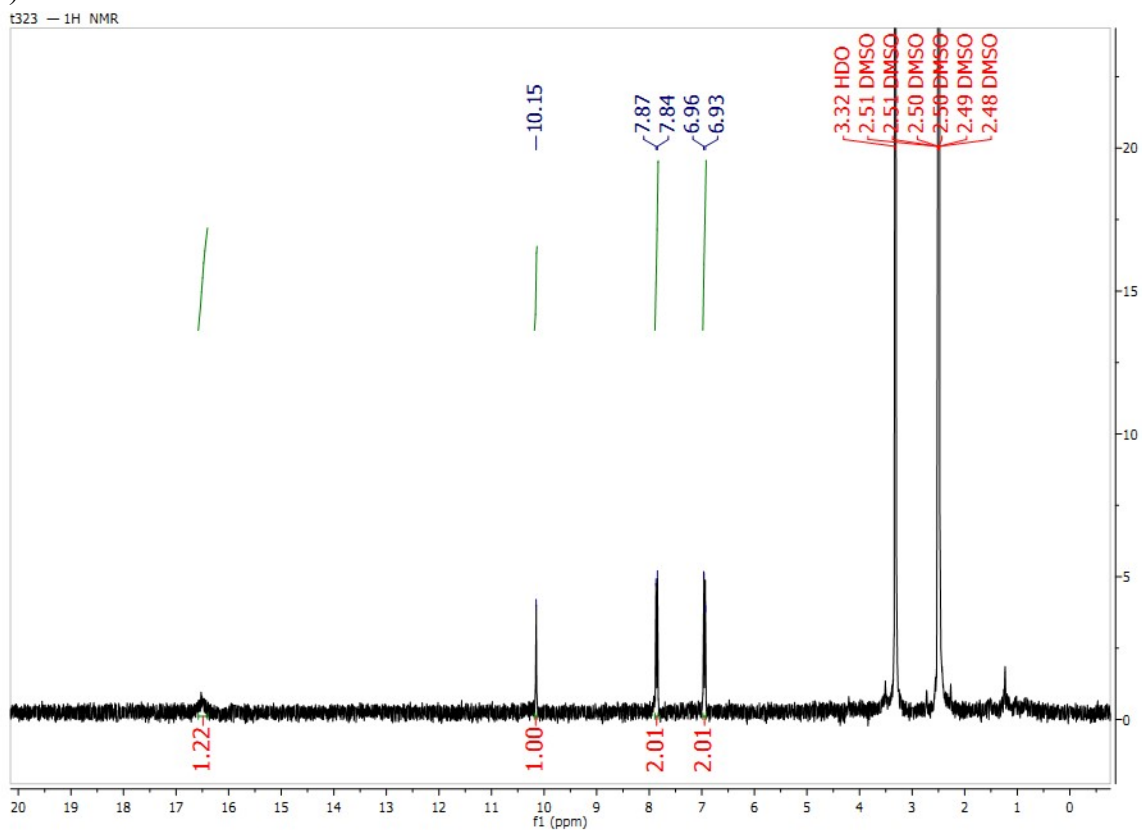
**5-(2-chlorophenyl)-1H-tetrazole:** IR (KBr)  $\text{cm}^{-1}$ : 3418, 2823, 2708, 1660, 1651, 1634, 1602, 1565, 1556, 1539, 1471, 1441, 1409, 1385, 1369, 1243, 1163, 1129, 1076, 1060, 1039, 1020, 1007, 988, 943, 874, 777, 747, 732, 651, 486, 453, 434.

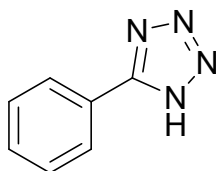
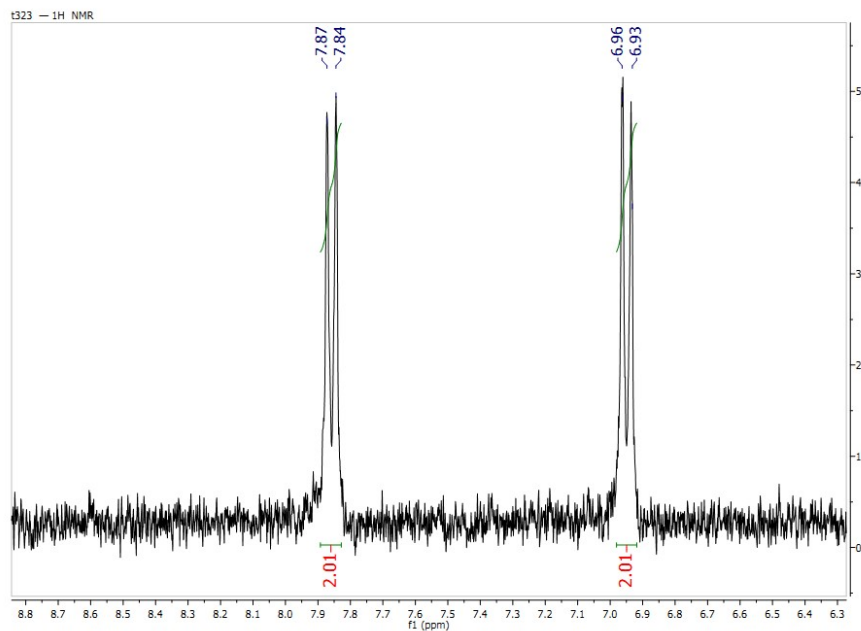




**4-(1H-tetrazol-5-yl)phenol:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 16.51$  (br, 1H), 10.15 (br, 1H), 7.87-7.84 (d,  $J = 12$  Hz, 2H), 6.96-6.93 (d,  $J = 12$  Hz, 1H) ppm.

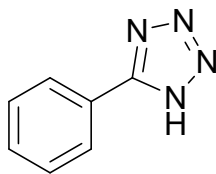
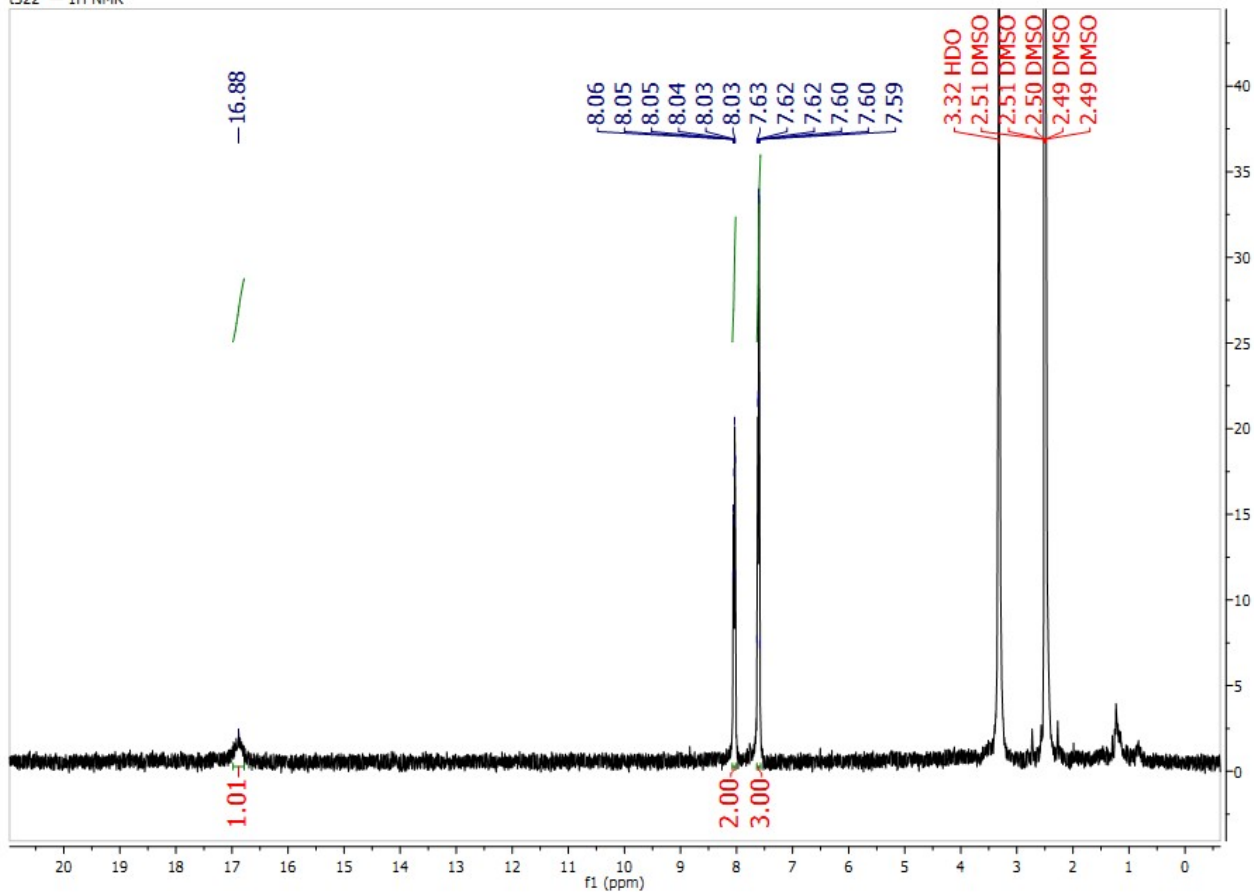
IR (KBr)  $\text{cm}^{-1}$ :





**5-phenyl-1H-tetrazole:**  $^1\text{H}$  NMR (400 MHz, DMSO):  $\delta_{\text{H}} = 16.88$  (br, 1H), 8.06-8.03 (m, 2H), 7.63-7.59 (m, 3H) ppm.





**5-phenyl-1H-tetrazole:** IR (KBr)  $\text{cm}^{-1}$ : 3423, 3055, 2985, 2901, 2832, 1813, 1638, 1611, 1562, 1486, 1466, 1411, 1384, 1288, 1256, 1163, 18084, 1057, 1034, 1015, 991, 959, 925, 784, 726, 703, 687, 619, 493, 462.

