

Supplementary Information for

A Rapid and Novel Method for the Synthesis of 5-Substituted 1*H*-tetrazole Catalyzed by Exceptional Reusable Monodisperse Pt NPs@AC under the Microwave Irradiation

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Materials and Instrumentation

PtCl₄ (99 % Alfa Aesar), tetrahydrofuran (THF) (99.5 %, Merck) and ethanol (99.9 %) were purchased from Merck, propylamine (Sigma Aldrich) were used as received from suppliers. THF was distilled over sodium under argon atmosphere and stored under inert atmosphere. De-ionized water was filtered by Millipore water purification system (18 MΩ) analytical grade. Activated Carbon (AC) was acquired from Cabot Europa Ltd. All glassware and Teflon-coated magnetic stir bars were cleaned with aqua regia, followed by washing with distilled water before drying in an oven.

The chemicals used in the synthesis of tetrazole derivatives were obtained from Merck and Aldrich Chemical Company. All chemicals and solvents used for the synthesis were of spectroscopic reagent grade.

Transmission electron microscopy (TEM) images were obtained on a JEOL 200 kV TEM instrument. Sample preparation for TEM analysis involves placement of a drop of 0.5 mg/mL ethanol solution of the prepared catalyst on a carbon covered 400-mesh copper grid; the solvent is then allowed to evaporate. Excess solution was removed with an adsorbent paper and the sample was dried under vacuum at room temperature before analysis. More than 300 particles were calculated to get the integrated information about the overall distribution of Pt-based catalyst sample.

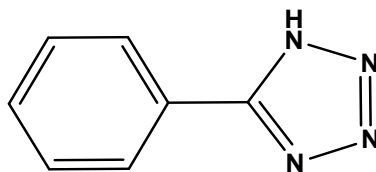
Thermo Scientific spectrometer was used for X-ray Photoelectron Spectroscopy (XPS) measurements and the X-ray source was K α lines of Mg (1253.6 eV, 10 mA). Samples were prepared by depositing the catalyst on Cu double-sided tape (3M Inc.). C 1s line at 284.6 eV was chosen as a reference point and all XPS peaks were fitted using a Gaussian function and the C 1s line at 284.6 eV was used as the reference line.

A Panalytical Empirian diffractometer with Ultima+theta-theta high resolution goniometer, having an X-ray generator (Cu K α radiation, $k = 1.54056 \text{ \AA}$) and operating condition of 45 kV and 40 mA, were employed in XRD analysis.

An MFP-3D (Asylum Research) was used to carry out tapping-mode atomic force microscopy (AFM) imaging. Samples were directly deposited on a 75 mm 25 mm glass slide (VWR International) and imaged using rectangular silicon tips (Olympus AC240TS) with a nominal spring constant of 2 N m⁻¹. Both topographic and height images were recorded during AFM analysis. Height analysis was performed using Igor Pro software.

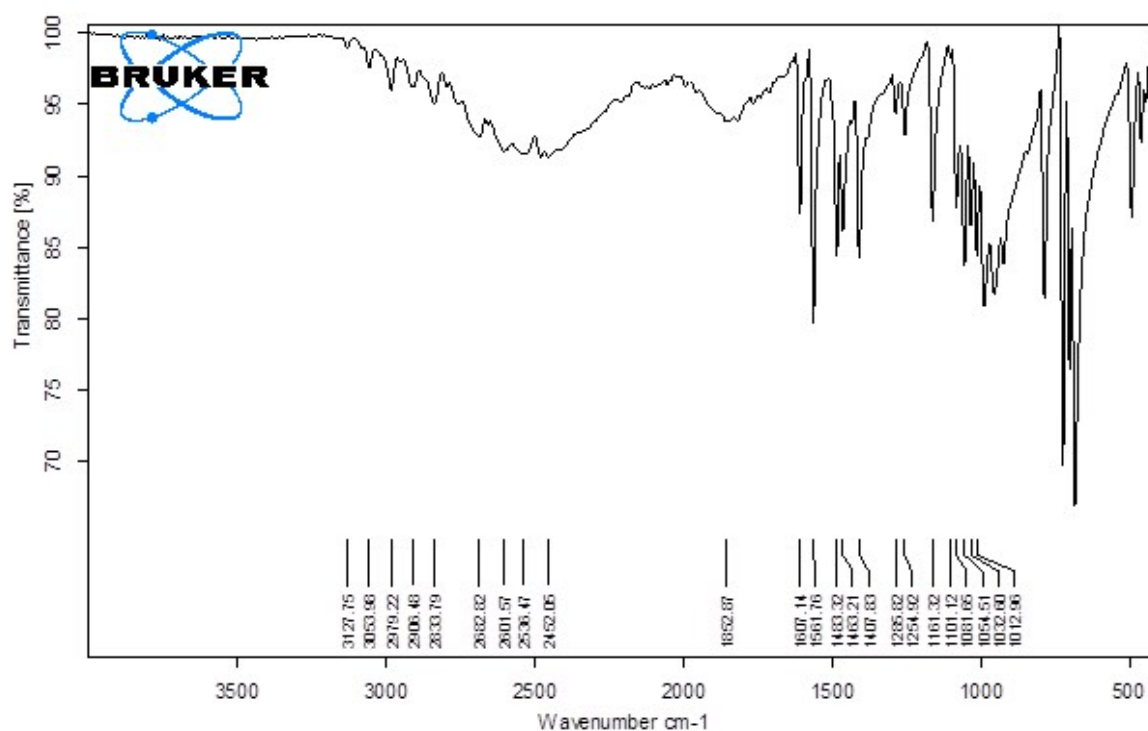
Reactions of tetrazoles were performed in CEM Discover and Explorer SP microwave irradiation apparatus. Melting points were measured on a Bibby Scientific Stuart Digital, Advanced, and SMP30. Fourier Transform Infrared (FT-IR) spectra were recorded on a Bruker Optics, ALPHA FT-IR spectrometer. The ¹H NMR and ¹³C NMR spectra were obtained in DMSO-*d*₆ with Bruker DPX-300 as solvents with trimethylsilane as the internal reference. The mass analyses were performed on a Agilent Technologies 6530 Accurate-Mass Q-TOF LC/HRMS at the advanced technology research centre of Dumlupınar University (ILTEM).

Characterization of 5-substituted 1*H*-tetrazoles



5-Phenyl 1*H*-tetrazole: As a white powder, M.p.: 215-217 °C (lit. 215-216 °C)¹, FT-IR (cm⁻¹): 3053, 2979, 2906, 2833, 2682, 2601, 1607, 1561, 1285, 1254 ¹H NMR (300 MHz, DMSO-*d*₆): δ = 7.60-7.65 (m, 3H, Ar-H), 8.03-8.07 (m, 2H, Ar-H), 16.85 (br, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 124.60, 127.40, 129.79, 131.62, 155.77 ppm, HRMS (QTOF-ESI): *m/z* [M-H]⁻ calcd. for C₇H₅N₄: 145.0514; found [M-H]⁻: 145.0517

a)



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Instrument type and / or accessory

The figure displays two NMR spectra for compound 1. The top spectrum is the ^1H NMR spectrum, recorded in CDCl_3 , showing peaks in the aromatic region (7.6–8.1 ppm) and aliphatic region (2.3–2.9 ppm). The bottom spectrum is the ^{13}C NMR spectrum, recorded in CDCl_3 , showing peaks from 15.5 to 242.0 ppm. Integration values are provided for the ^1H NMR peaks.

^1H NMR Data:

Chemical Shift (ppm)	Integration
8.15, 8.12, 8.09, 8.06, 8.03	0.49
7.65, 7.62, 7.59, 7.56, 7.53	1.00
2.85, 2.82, 2.79, 2.76, 2.73	1.49

^{13}C NMR Data:

Chemical Shift (ppm)
241.9, 241.5, 241.1, 240.7, 240.3
229.5, 229.1, 228.7, 228.3, 228.1
15.5, 15.2, 14.9, 14.6, 14.3

155.77
131.62
129.79
127.40
124.60
40.75
40.47
40.19
39.91
39.63
39.35
39.08

200 180 160 140 120 100 80 60 40 20 0 ppm

d)

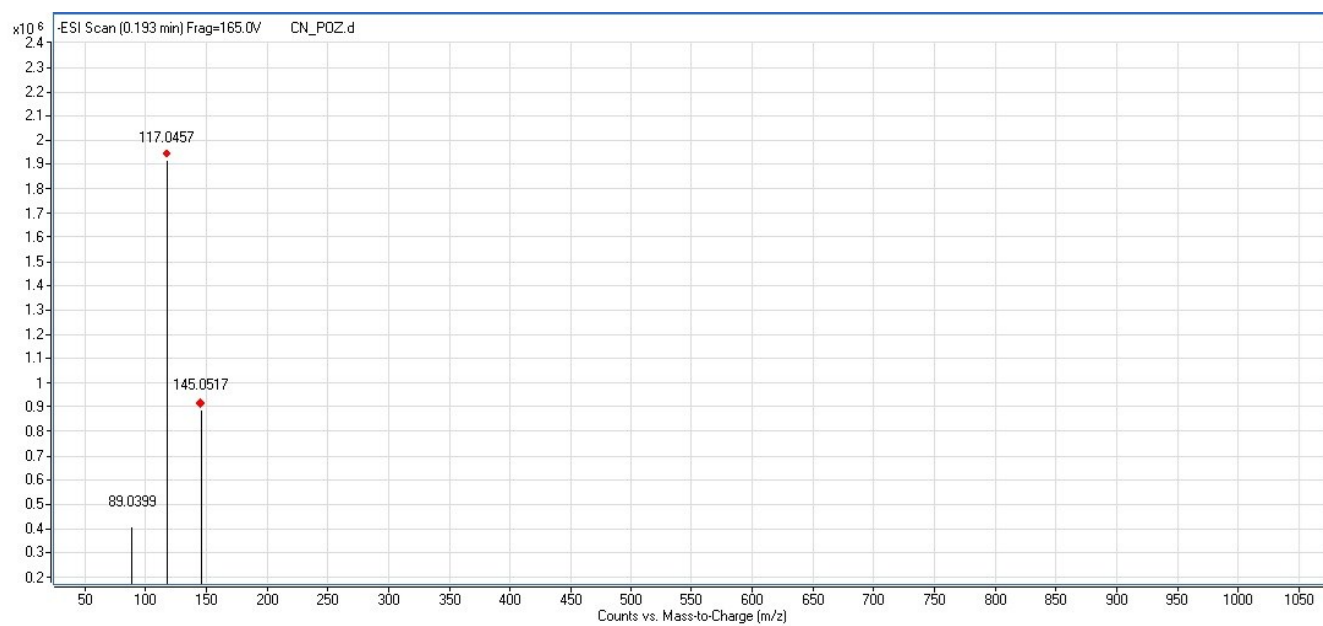
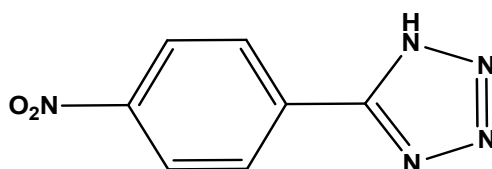
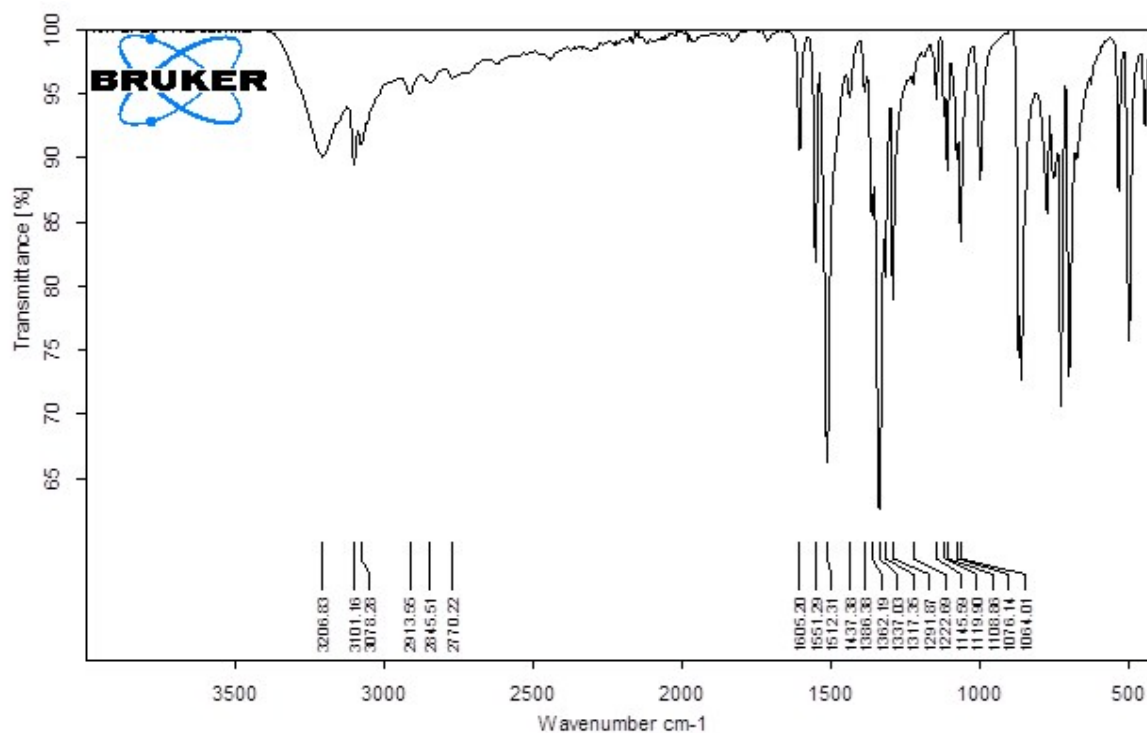


Fig. S1. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of 5-Phenyl 1*H*-tetrazole



5-(4-Nitrophenyl) 1H-tetrazole: As a grey powder, M.p.: 217-219 °C (lit. 219-221 °C)¹, FT-IR (cm⁻¹): 3078, 2913, 2845, 2770, 1605, 1551, 1291, 1222, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.31 (d, *J*= 9.01 Hz, 2H, Ar-H), 8.46 (d, *J*= 9.00 Hz, 2H, Ar-H), 17.15 (br, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 125.03, 128.63, 131.10, 149.16, 155.92 ppm, HRMS (QTOF-ESI): *m/z* [M-H]⁻ calcd. for C₇H₄N₅O₂: 190.0365; found [M-H]⁻: 190.0367

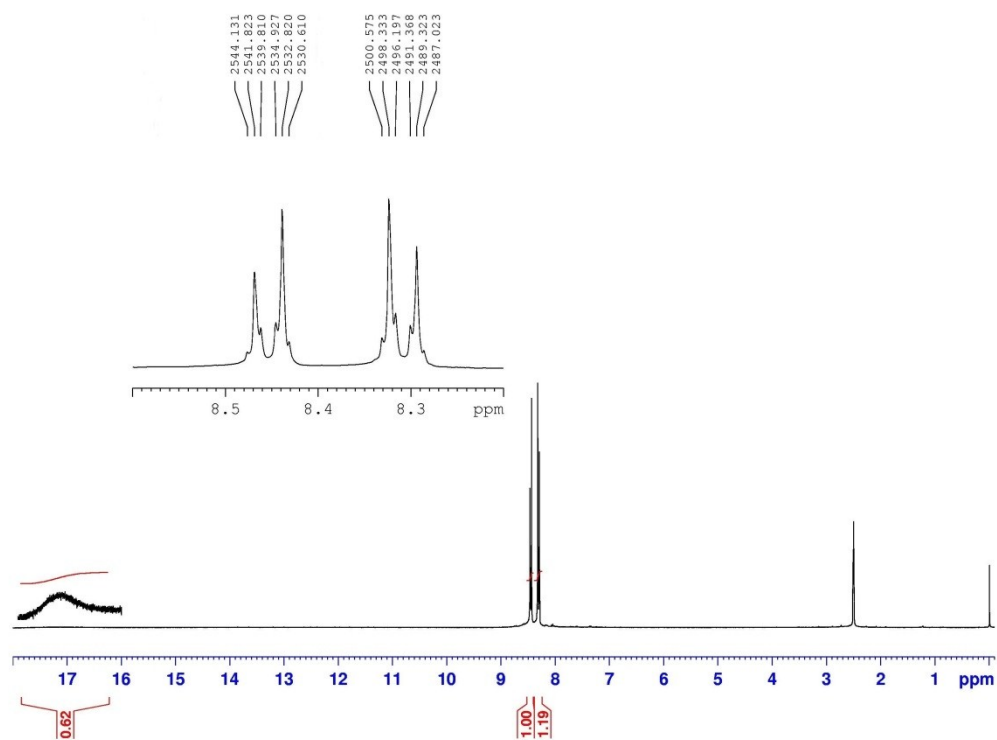
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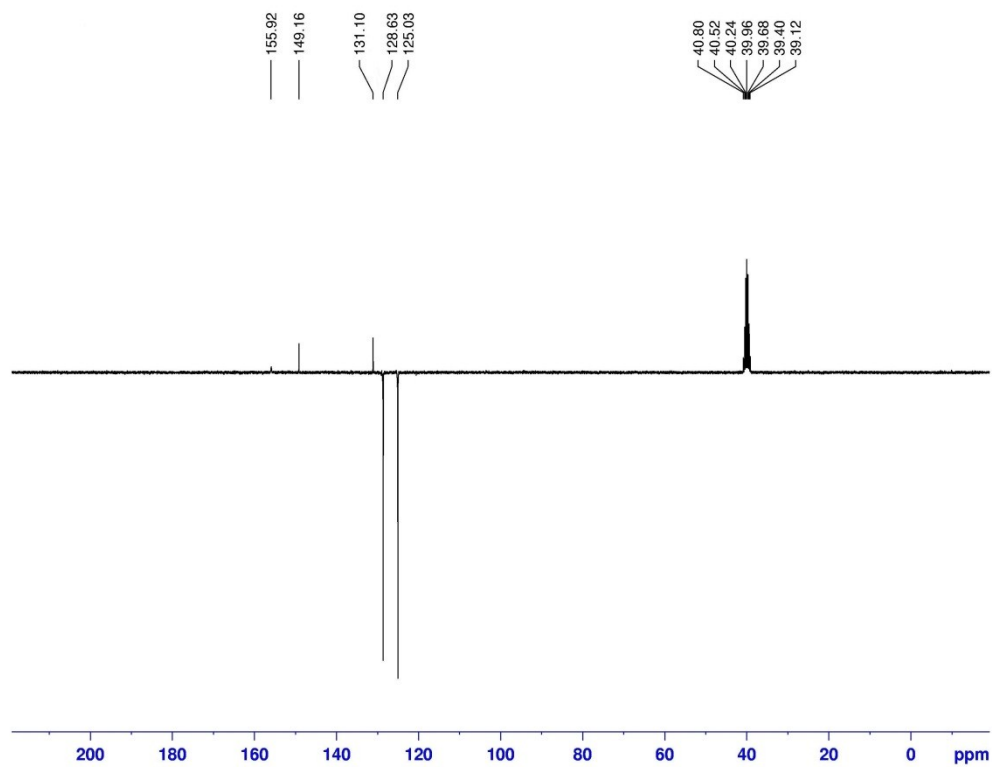
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Instrument type and / or accessory

b)



c)



d)

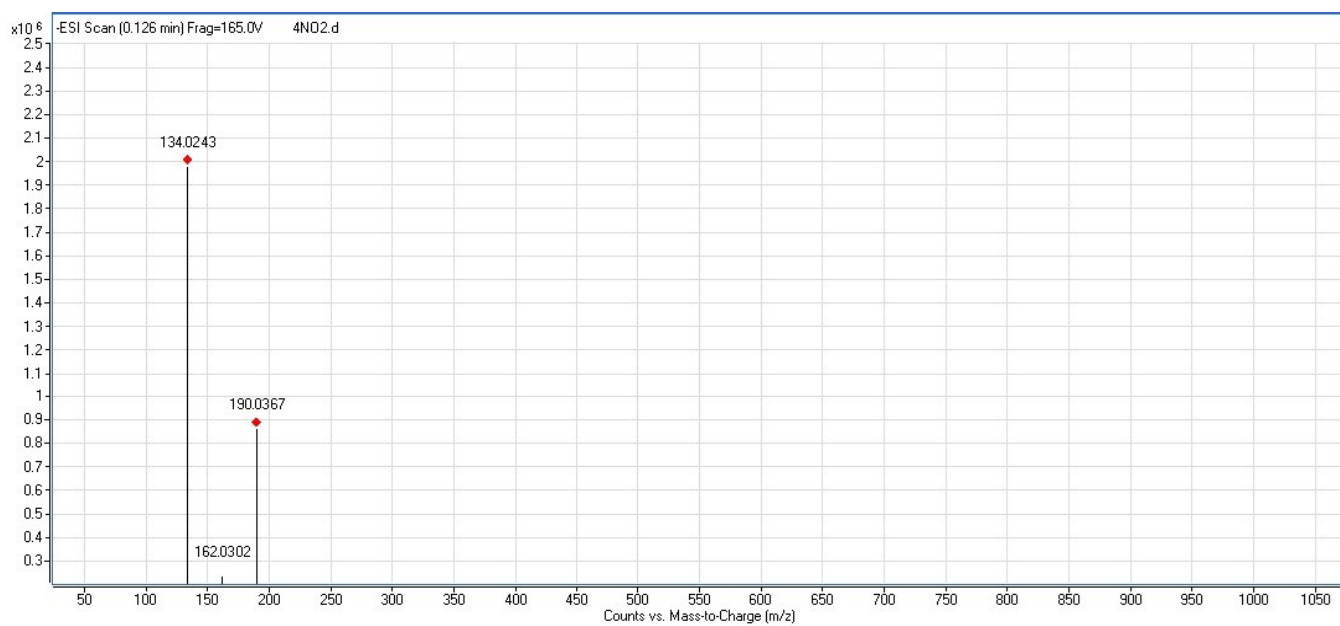
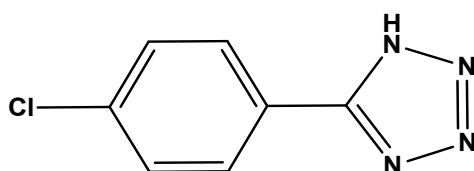
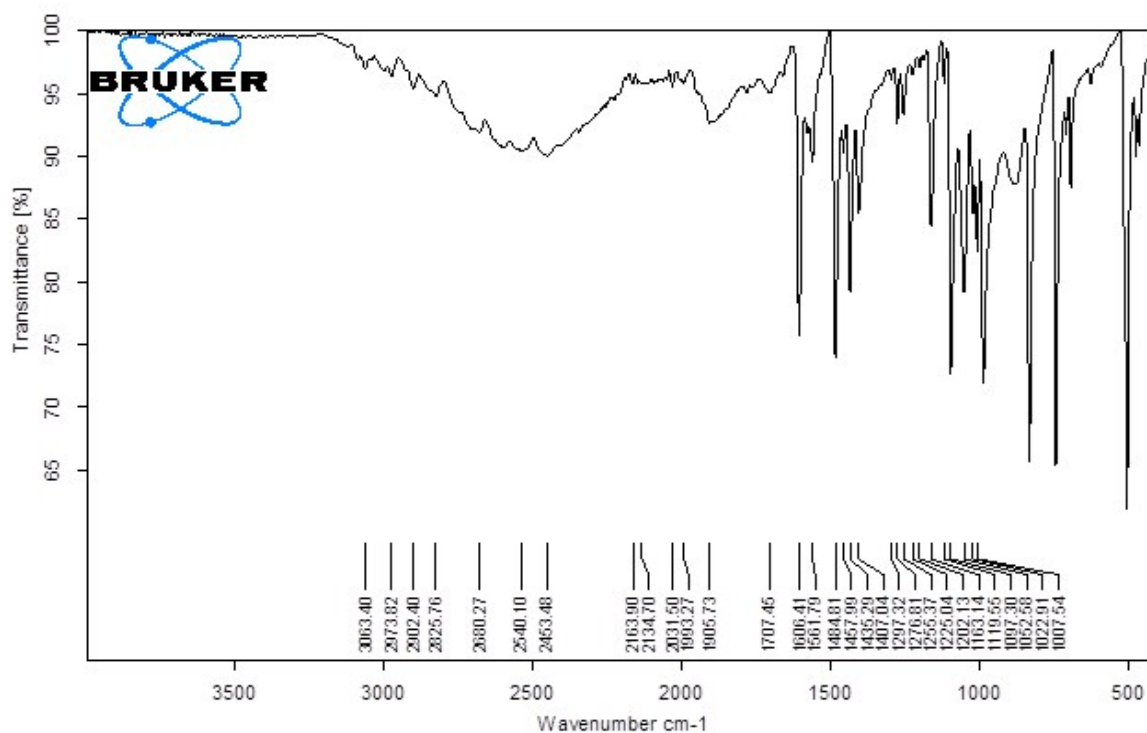


Fig. S2. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of 5-(4-Nitrophenyl) 1H-tetrazole



5-(4-Chlorophenyl) 1H-tetrazole: As a white powder, M.p.: 248-249 °C (lit. 250-252 °C)², FT-IR (cm⁻¹): 3063, 2973, 2902, 2680, 2540, 1606, 1561, 1276, 1255, 1097, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 7.70 (d, *J* = 8.56 Hz, 2H, Ar-H), 8.06 (d, *J* = 8.57 Hz, 2H, Ar-H), 16.95 (br, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 123.67, 129.18, 130.03, 136.37, 155.92 ppm, HRMS (QTOF-ESI): *m/z* [M-H]⁻ calcd. for C₇H₄ClN₄: 179.0124; found [M-H]⁻: 179.0123

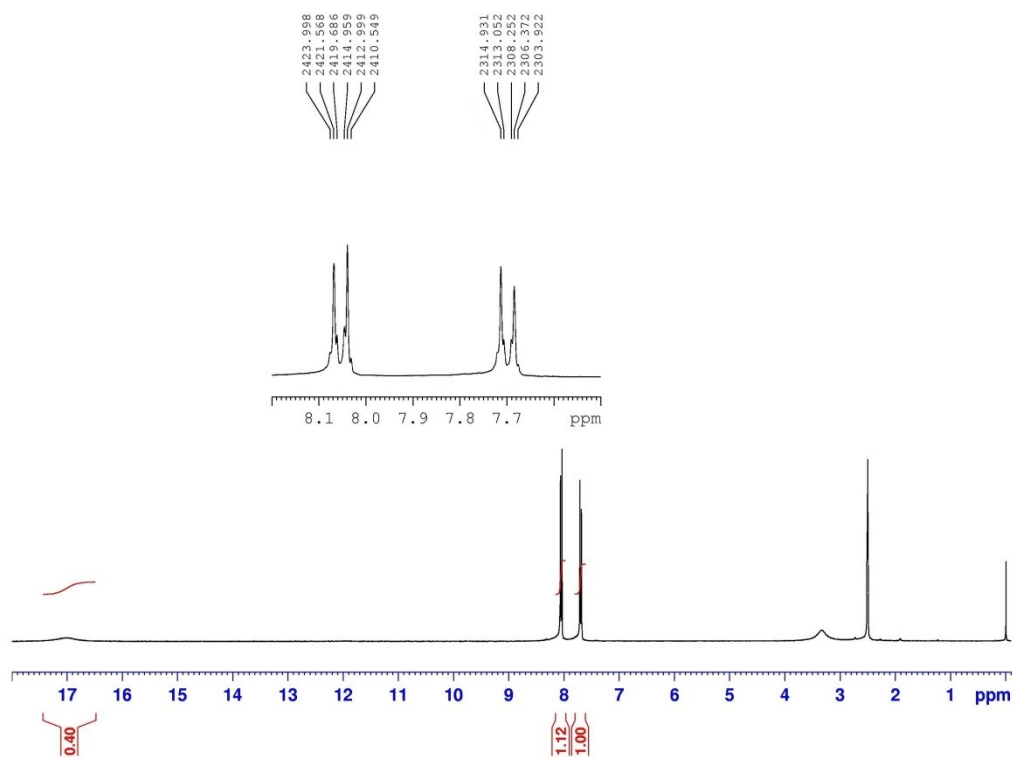
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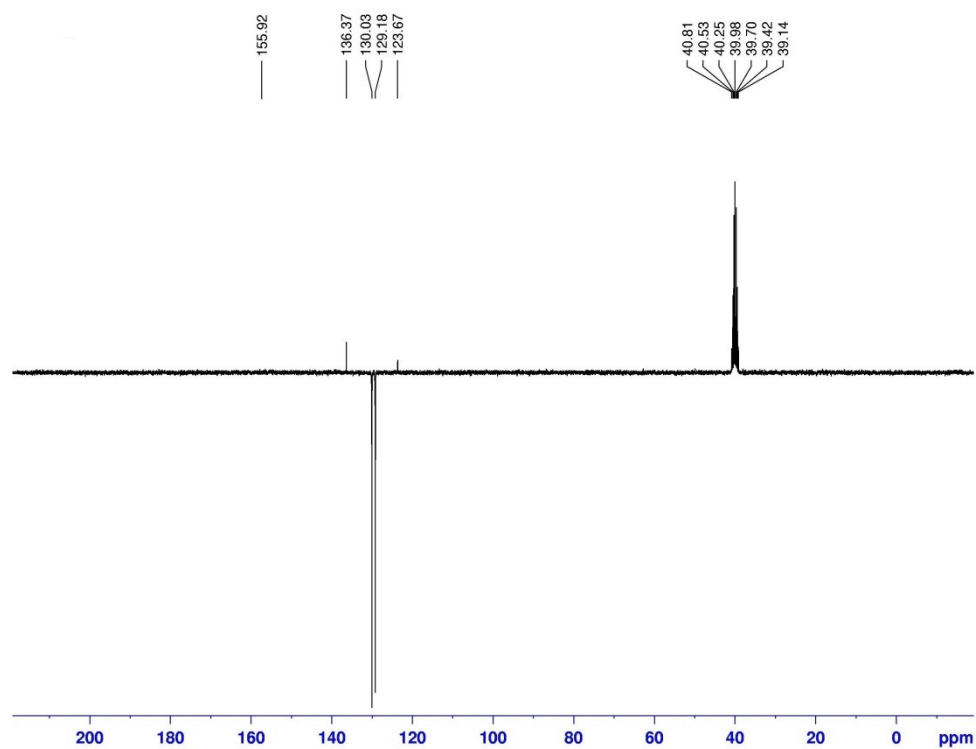
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Instrument type and / or accessory

b)



c)



d)

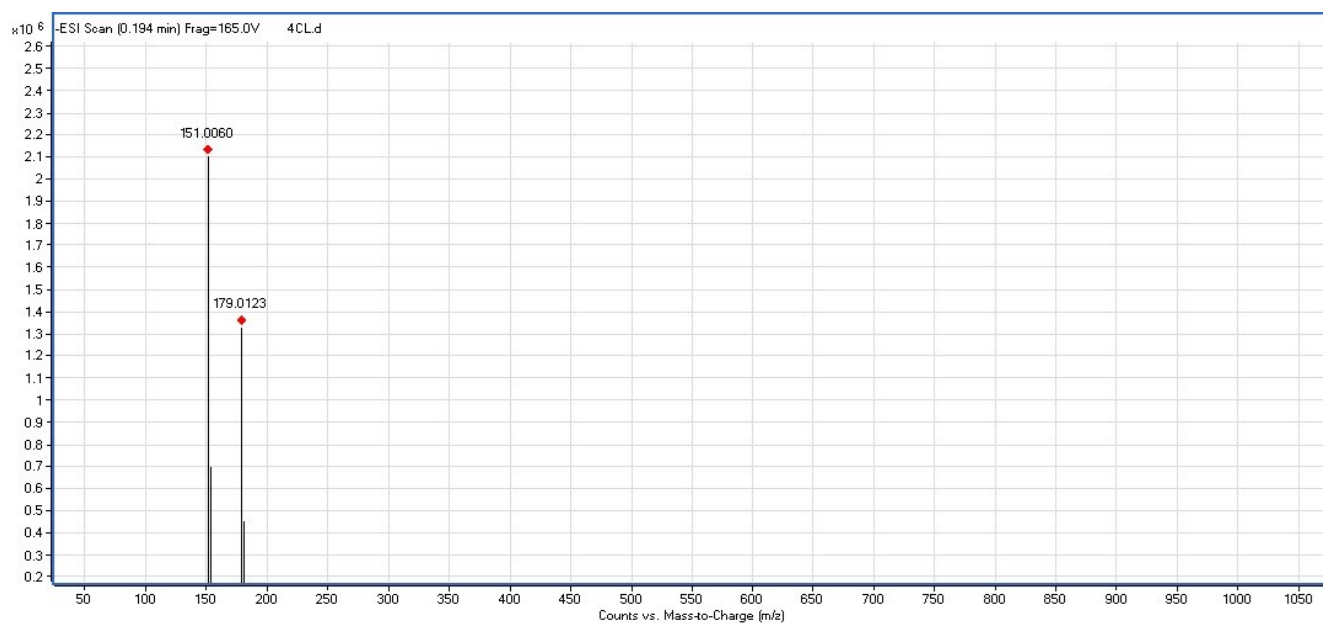
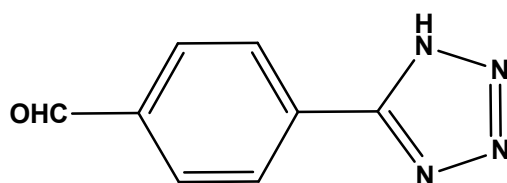
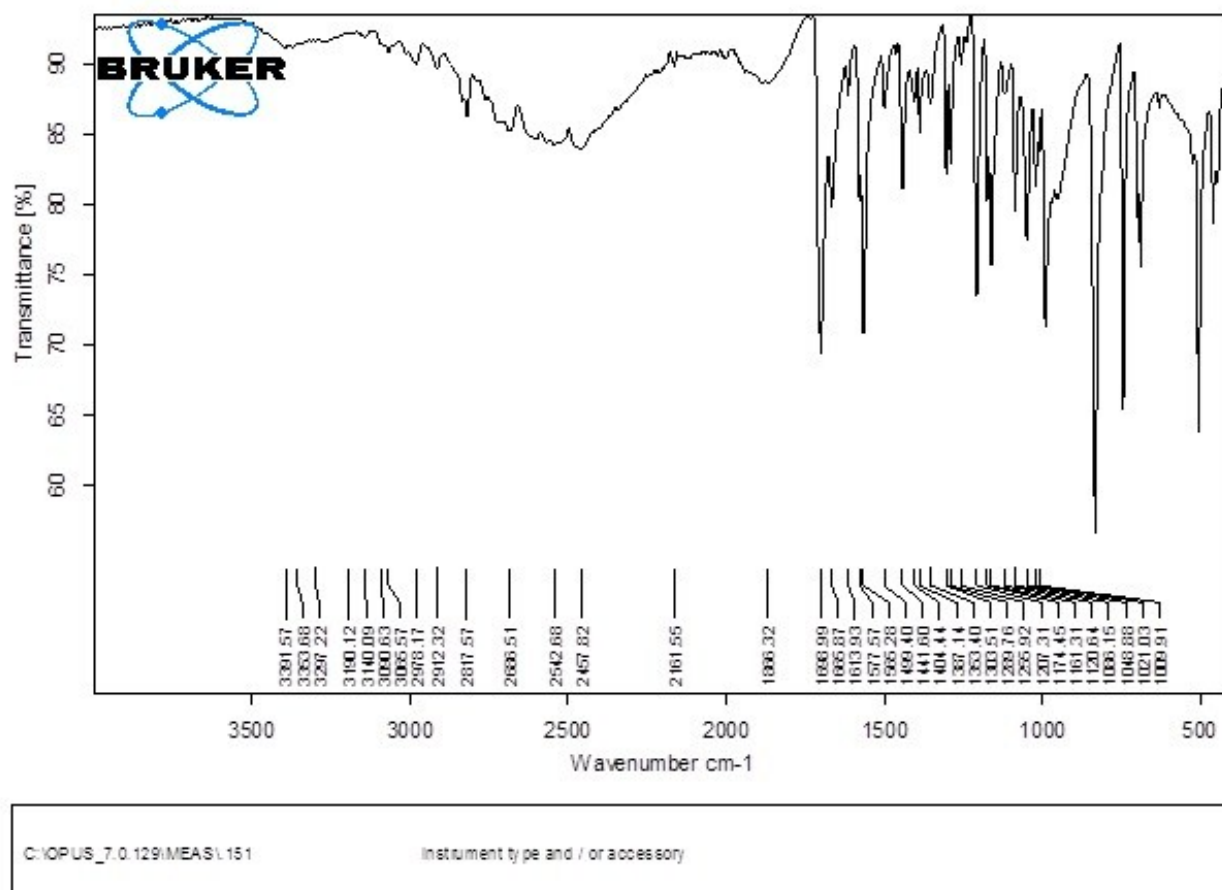


Fig. S3. a) FT-IR, b) ¹H NMR, c) ¹³C NMR (APT), d) Q-TOF LC/HRMS of 5-(4-Chlorophenyl) 1H-tetrazole

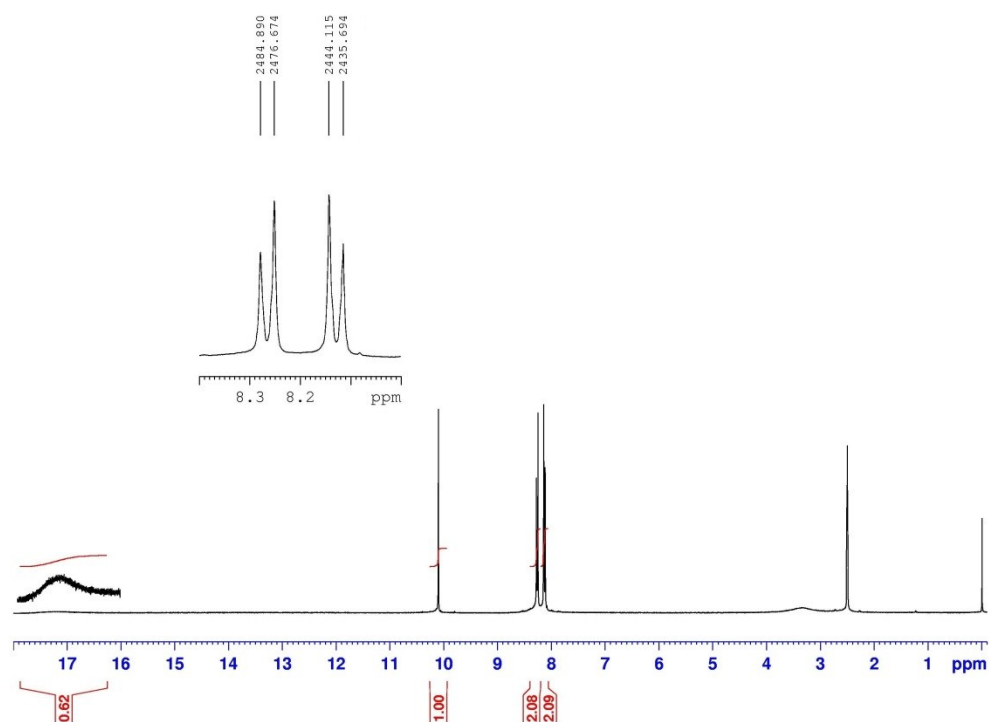


4-(1H-tetrazol-5-yl)benzaldehyde: As a white powder, M.p.: 183-185 °C (lit. 183-185 °C)³, FT-IR (cm⁻¹): 3065, 2978, 2912, 2817, 2686, 2542, 1698, 1565, 1557, 1289, 1255, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.13 (d, *J* = 8.42 Hz, 2H, Ar-H), 8.27 (d, *J* = 8.22 Hz, 2H, Ar-H), 10.10 (s, 1H, -CHO), 17.15 (br, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 128.07, 130.00, 130.82, 138.07, 155.77, 193.13 ppm, HRMS (QTOF-ESI): *m/z* [M-H]⁻ calcd. for C₈H₆N₄O: 173.0463; found [M-H]⁻: 173.0465

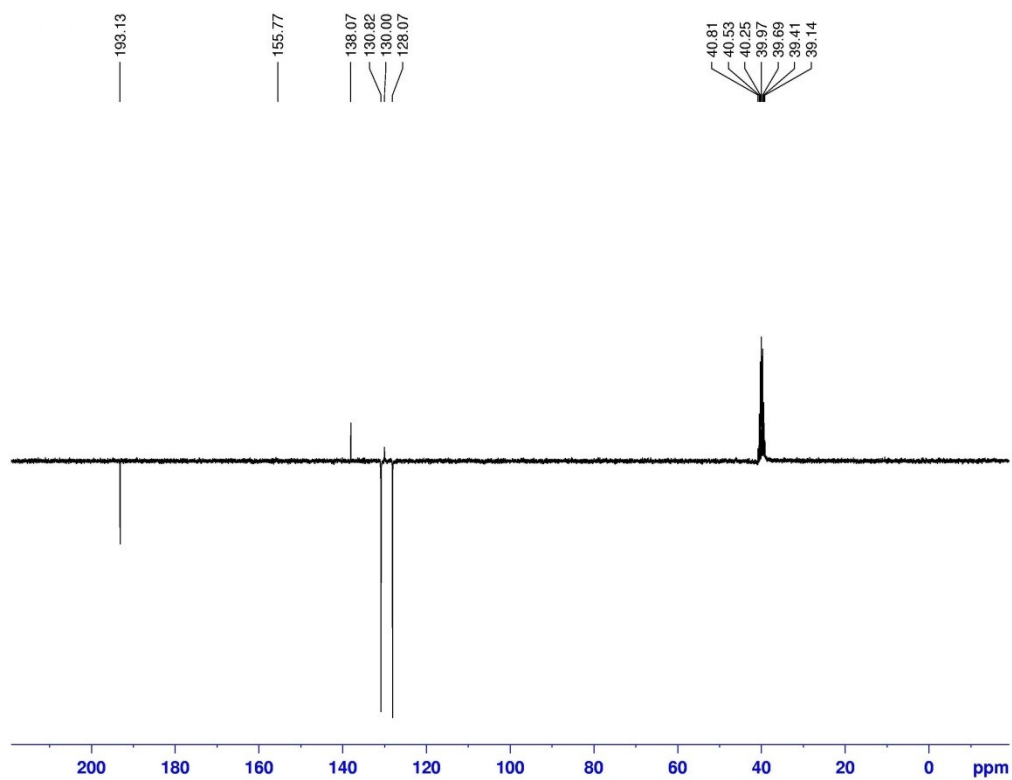
a)



b)



c)



d)

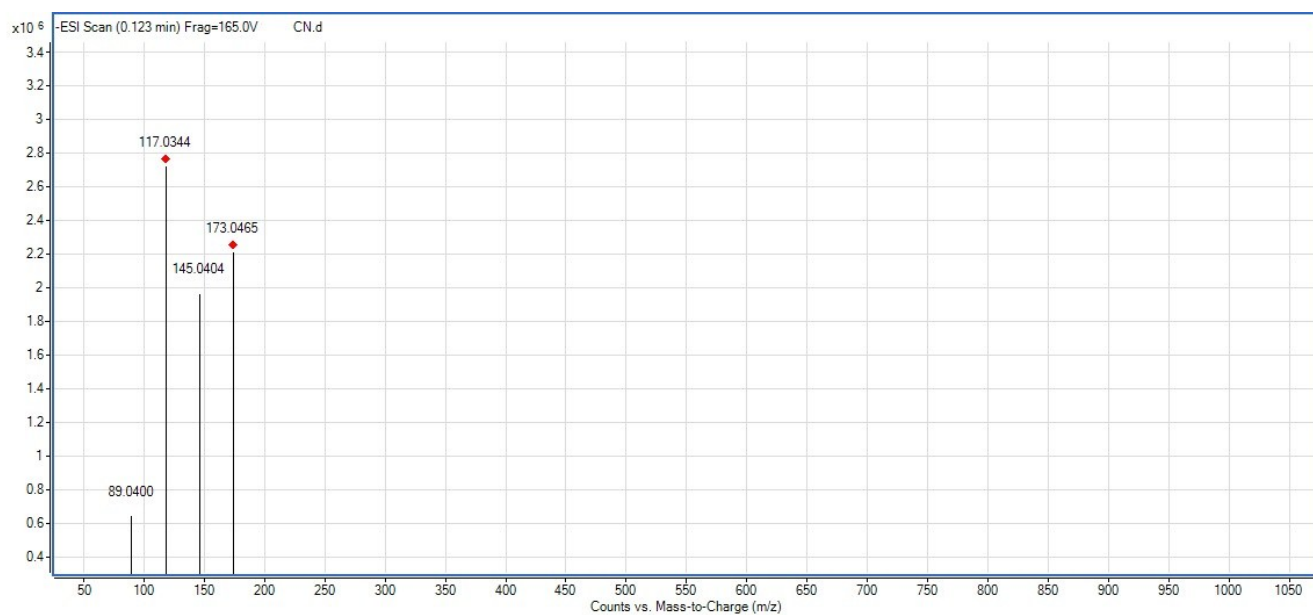
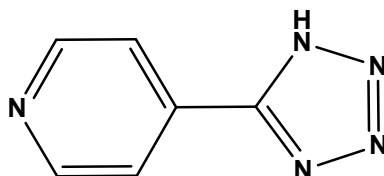
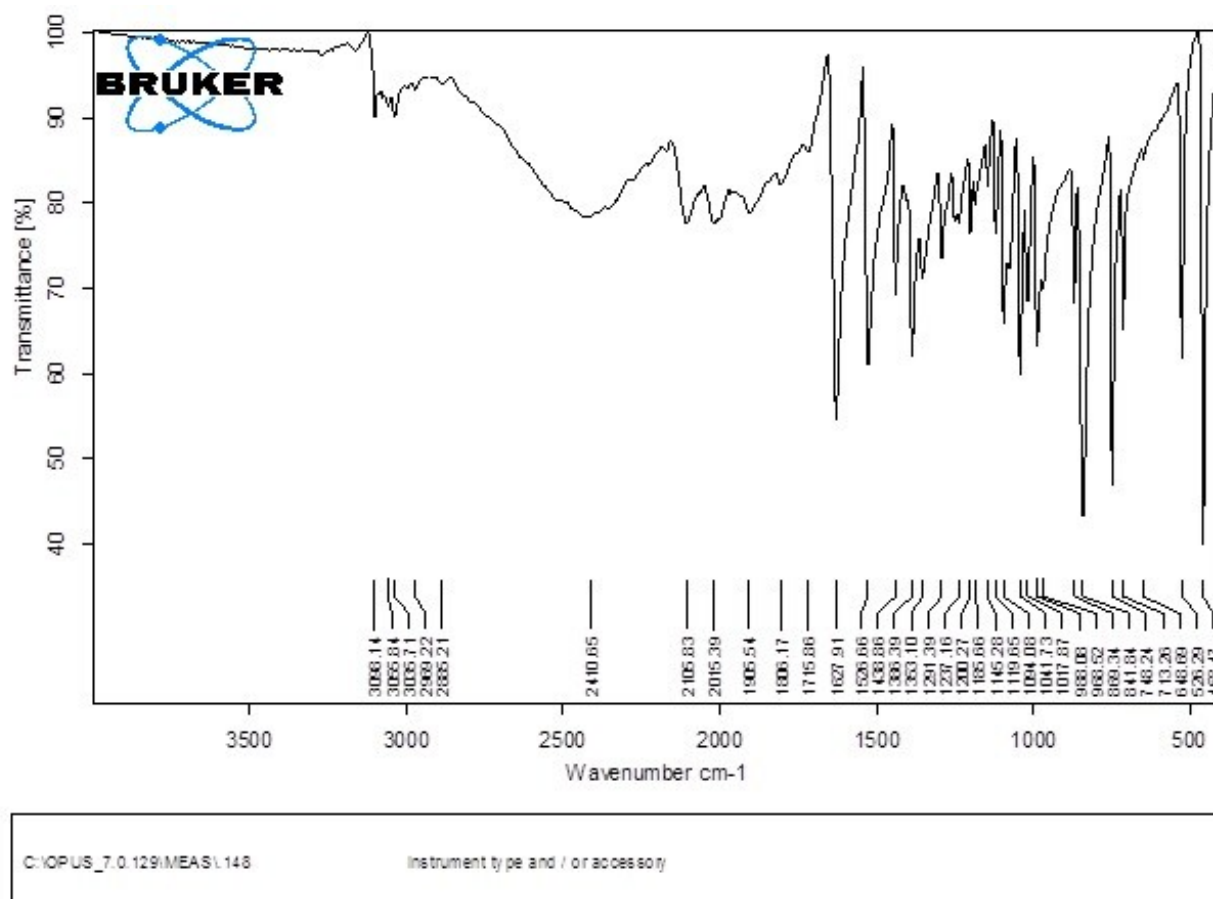


Fig. S4. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of 4-(1*H*-tetrazol-5-yl)benzaldehyde

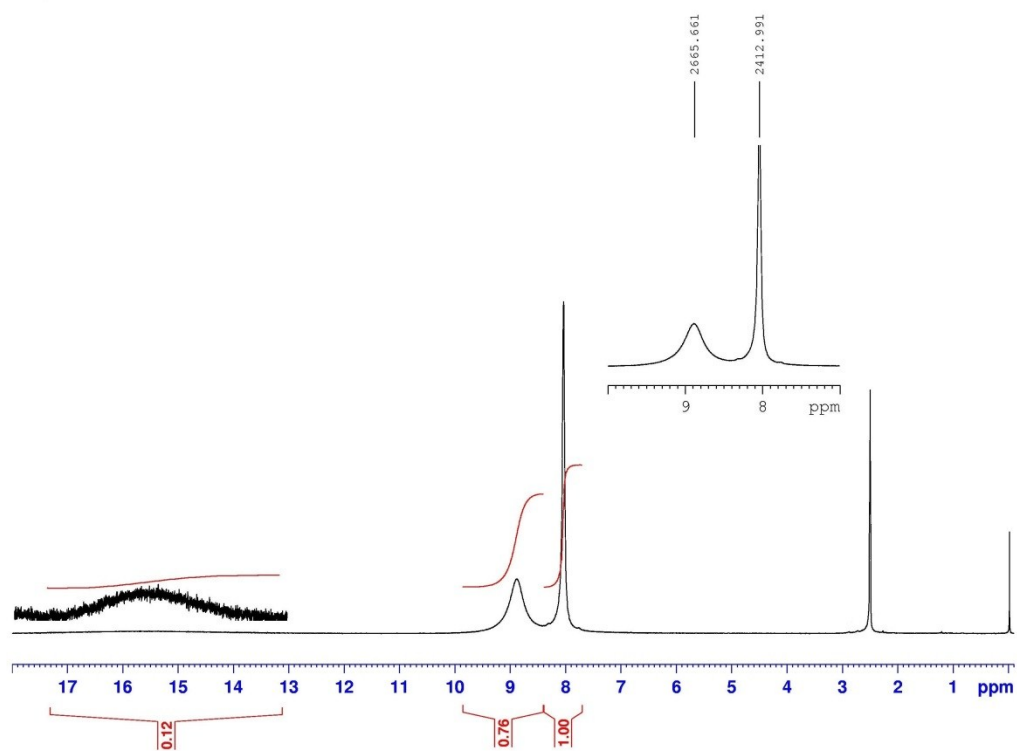


4-(1H-tetrazol-5-yl)pyridine: As a white powder, M.p.: 254 °C (lit. 254-255 °C)¹, FT-IR (cm⁻¹): 3055, 2969, 2885, 2410, 1627, 1526, 1291, 1237, 1041, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 8.05 (s, 2H, Ar-H), 8.90 (s, 2H, Ar-H), 15.60 (br, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 121.60, 133.91, 150.51, 155.64 ppm, HRMS (QTOF-ESI): m/z [M-H]⁻ calcd. for C₆H₅N₅: 146.0467; found [M-H]⁻: 146.0468

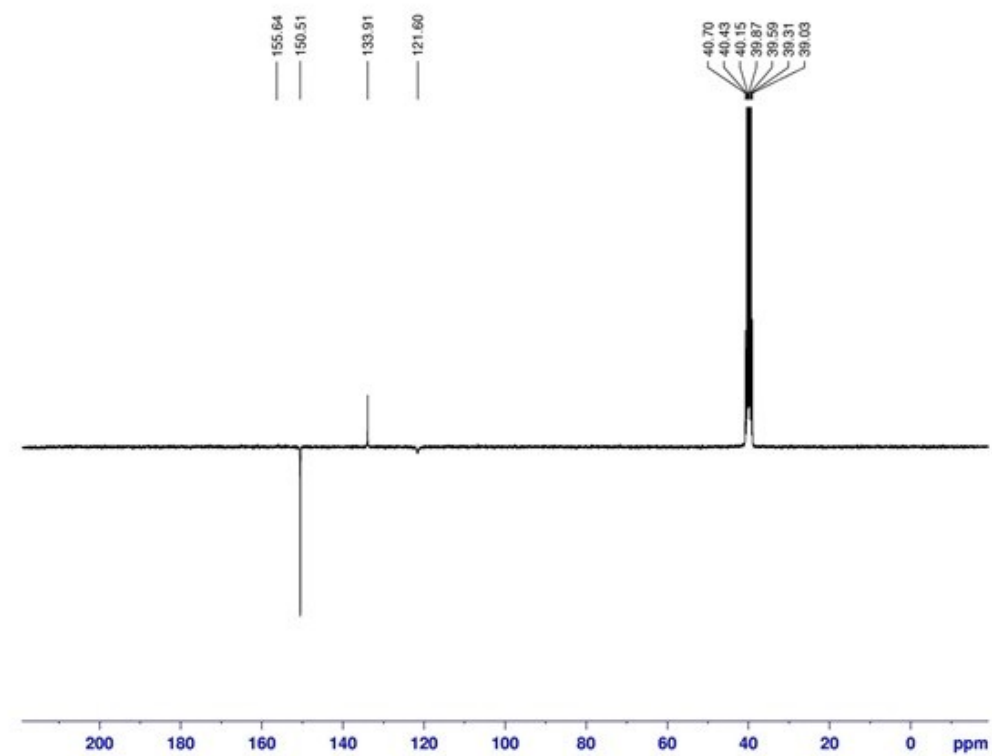
a)



b)



c)



d)

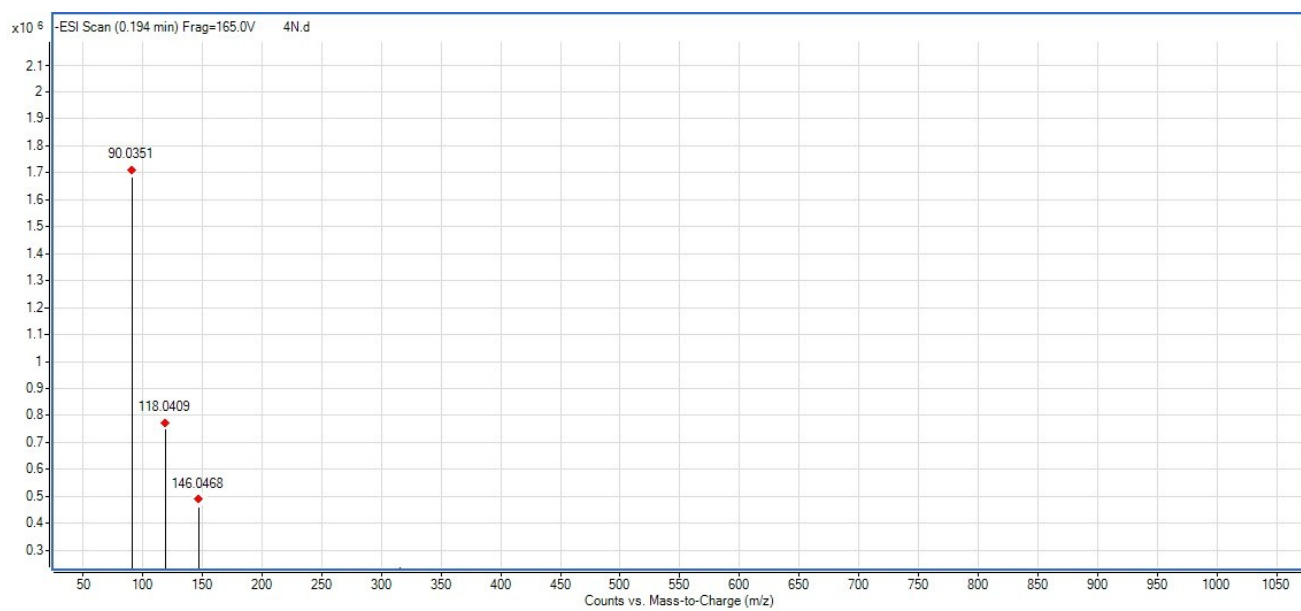
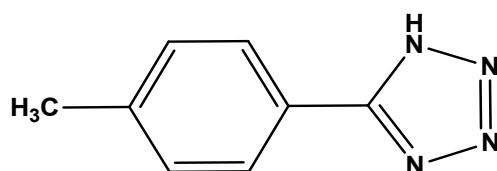
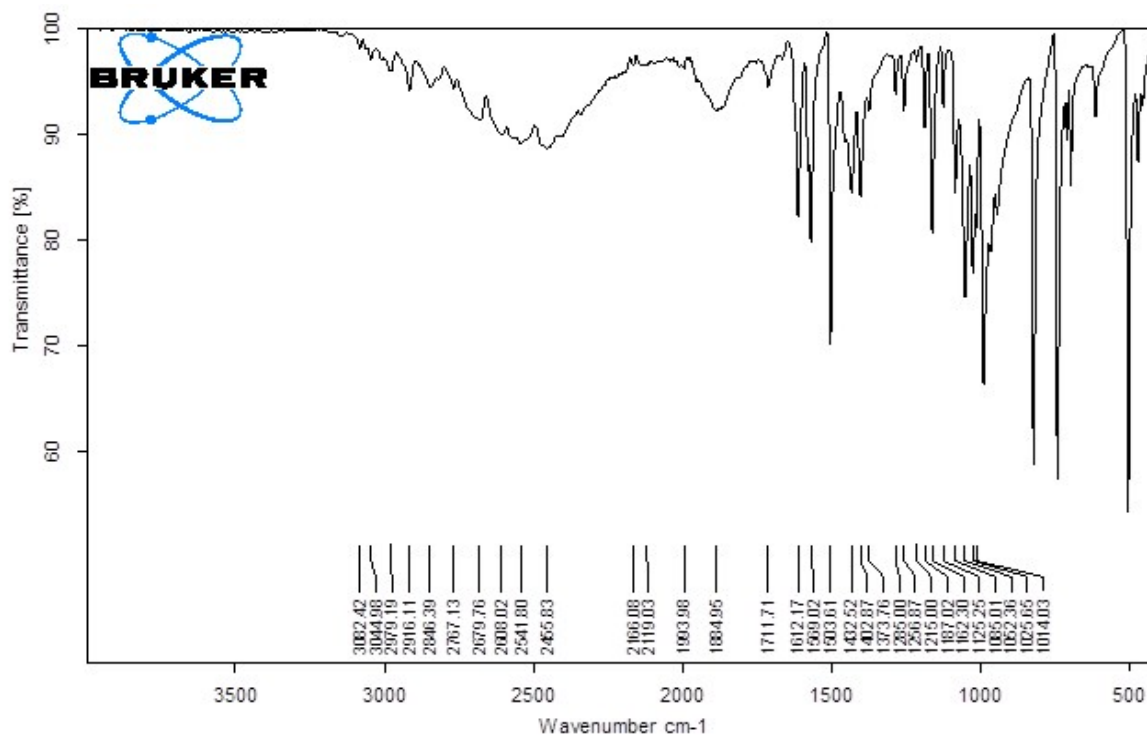


Fig. S5. a) FT-IR, b) ¹H NMR, c) ¹³C NMR (APT), d) Q-TOF LC/HRMS of 4-(1*H*-tetrazol-5-yl)pyridine



5-(p-tolyl) 1H-tetrazole: As a white powder, M.p.: 249-250 °C (lit. 248-249 °C)⁴, FT-IR (cm⁻¹): 3044, 2979, 2916, 2846, 2767, 2679, 2608, 1612, 1569, 1285, 1256, 1162, 1085, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 2.40 (s, 3H, -CH₃), 7.42 (d, *J* = 8.09 Hz, 2H, Ar-H), 7.93 (d, *J* = 8.17 Hz, 2H, Ar-H), 16.75 (br, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 21.47, 121.71, 127.34, 130.40, 141.69, 155.53 ppm, HRMS (QTOF-ESI): *m/z* [M-H]⁻ calcd. for C₈H₇N₄: 159.0671; found [M-H]⁻: 159.0674

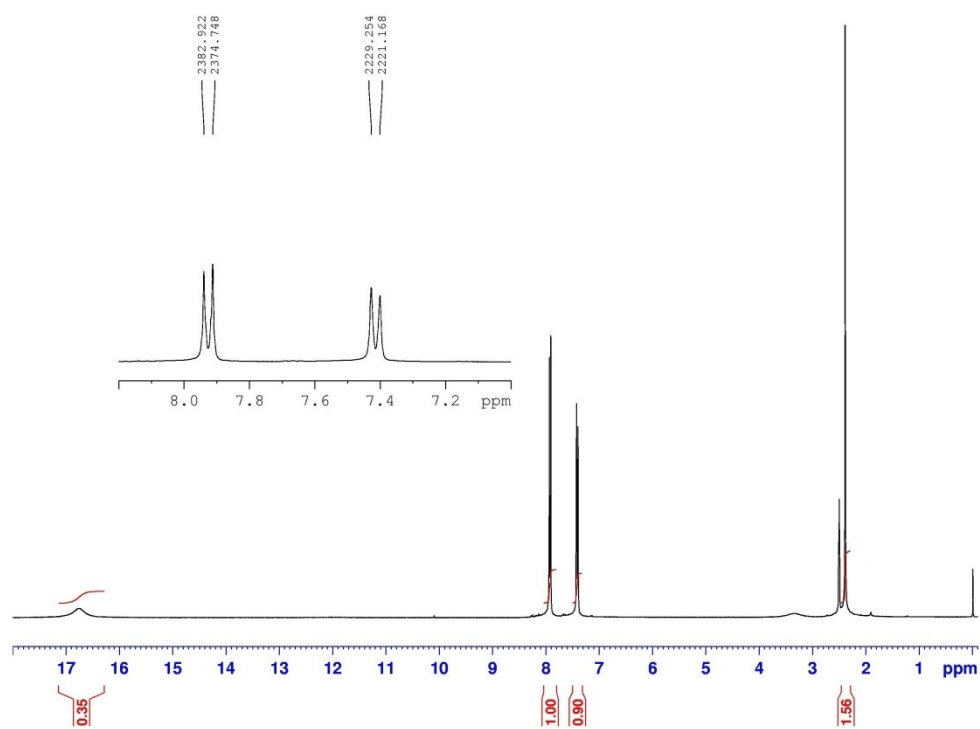
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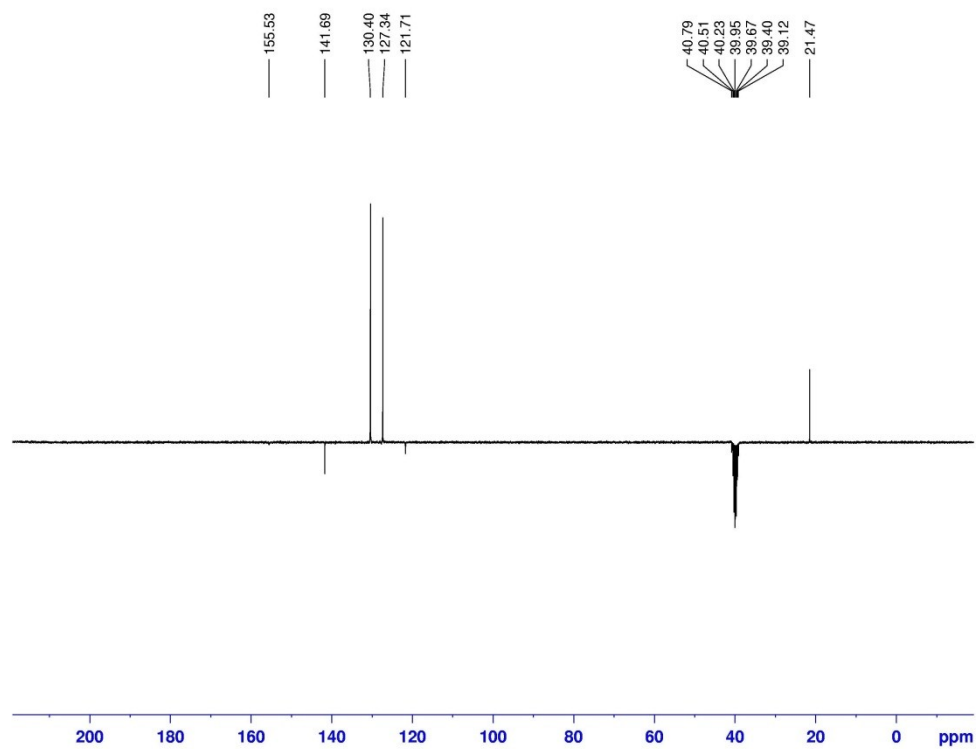
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Instrument type and / or accessory

b)



c)



d)

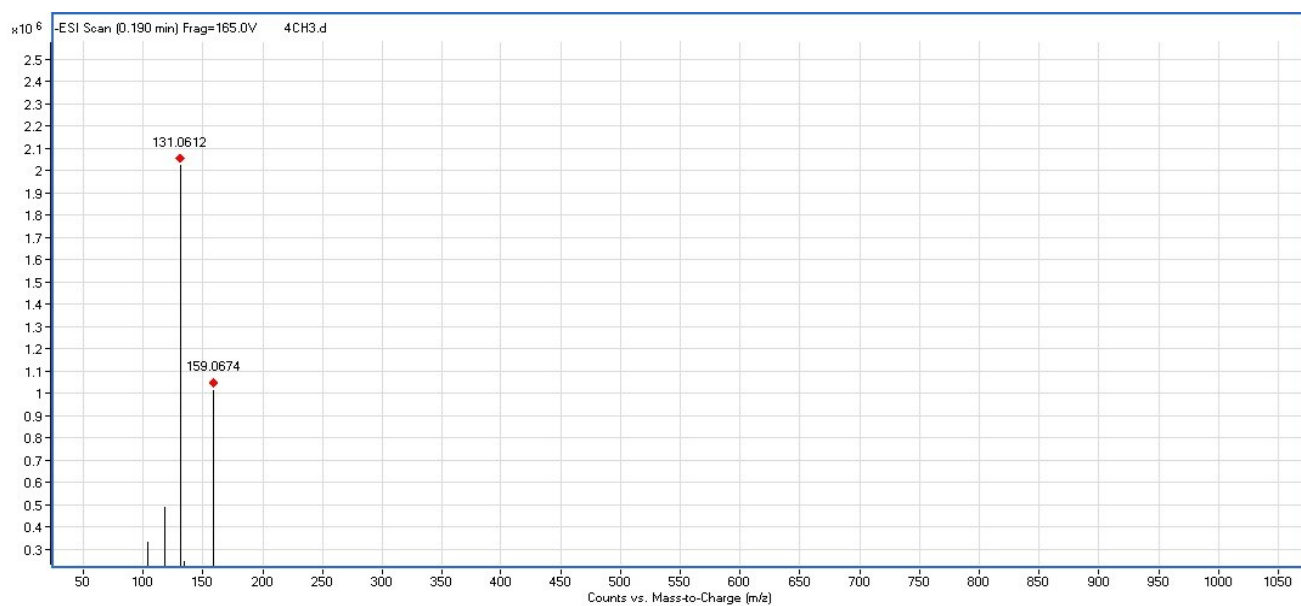
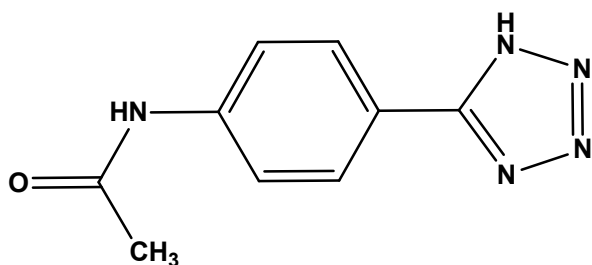
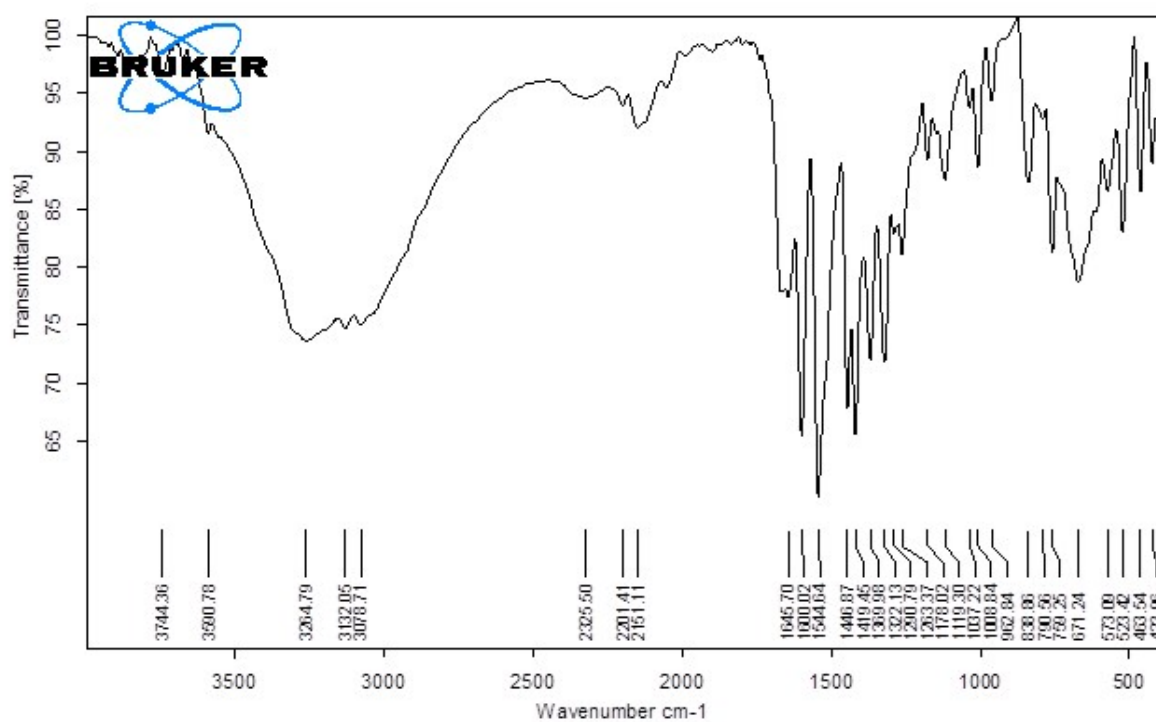


Fig. S6. a) FT-IR, **b)** ¹H NMR, **c)** ¹³C NMR (APT), **d)** Q-TOF LC/HRMS of **5-(p-tolyl) 1H-tetrazole**



N-(4-(1H-tetrazol-5-yl)phenyl)acetamide: As a white powder, M.p.: 288-289 °C (lit. 287 °C)⁵, FT-IR (cm⁻¹): 3264, 3132, 3078, 2325, 2201, 2151, 1600, 1544, 1322, 1290, 1263, ¹H NMR (300 MHz, DMSO-*d*₆): δ = 2.07 (s, 3H, -CH₃), 7.58 (d, *J* = 8.21 Hz, 2H, Ar-H), 7.88 (d, *J* = 8.26 Hz, 2H, Ar-H), 9.95 (s, 1H, -NH) ppm, ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 24.47, 119.40, 126.59, 127.91, 138.74, 155.92, 168.73 ppm, HRMS (QTOF-ESI): *m/z* [M-H]⁻ calcd. for C₉H₈N₅O: 202.0729; found [M-H]⁻: 202.0732

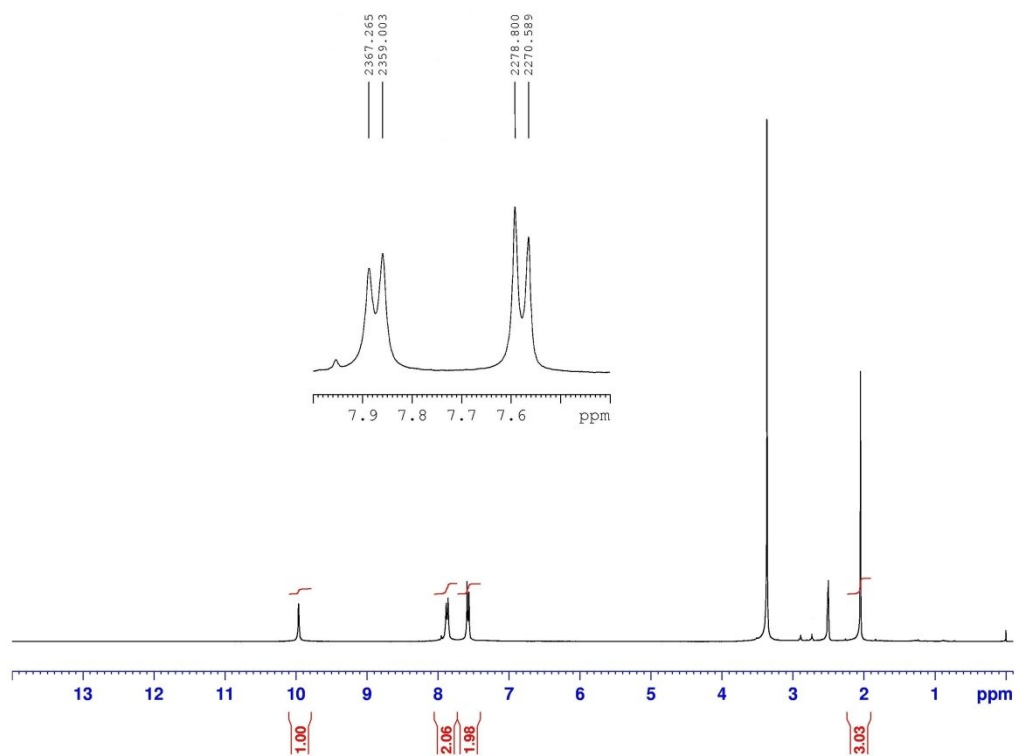
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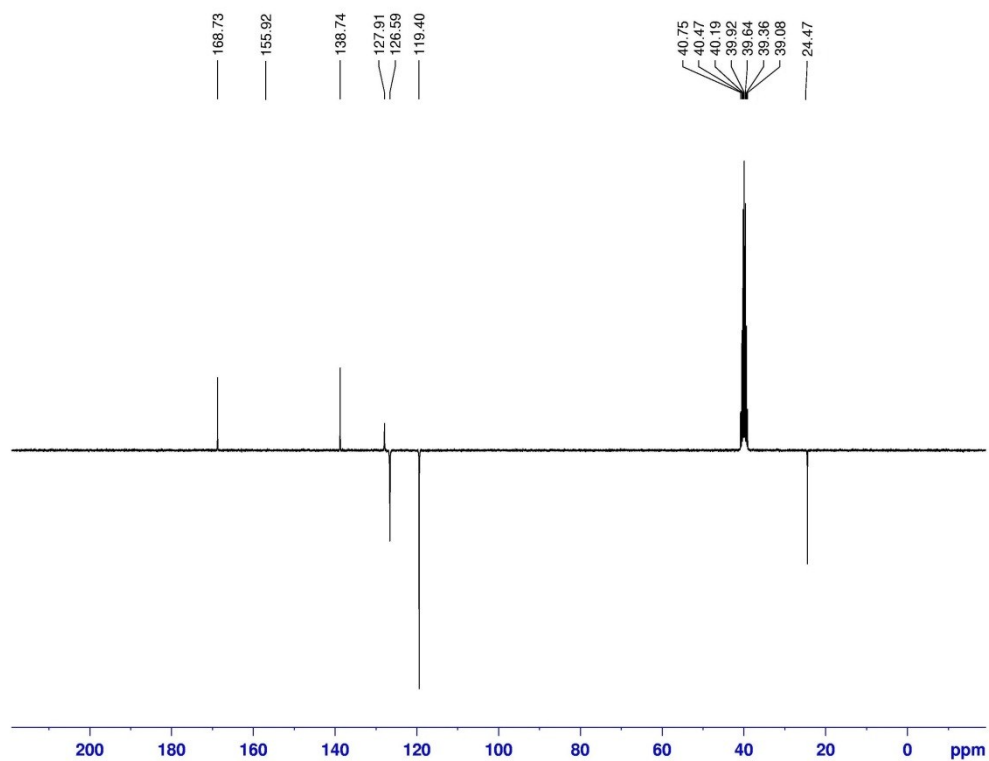
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Instrument type and / or accessory

b)



c)



d)

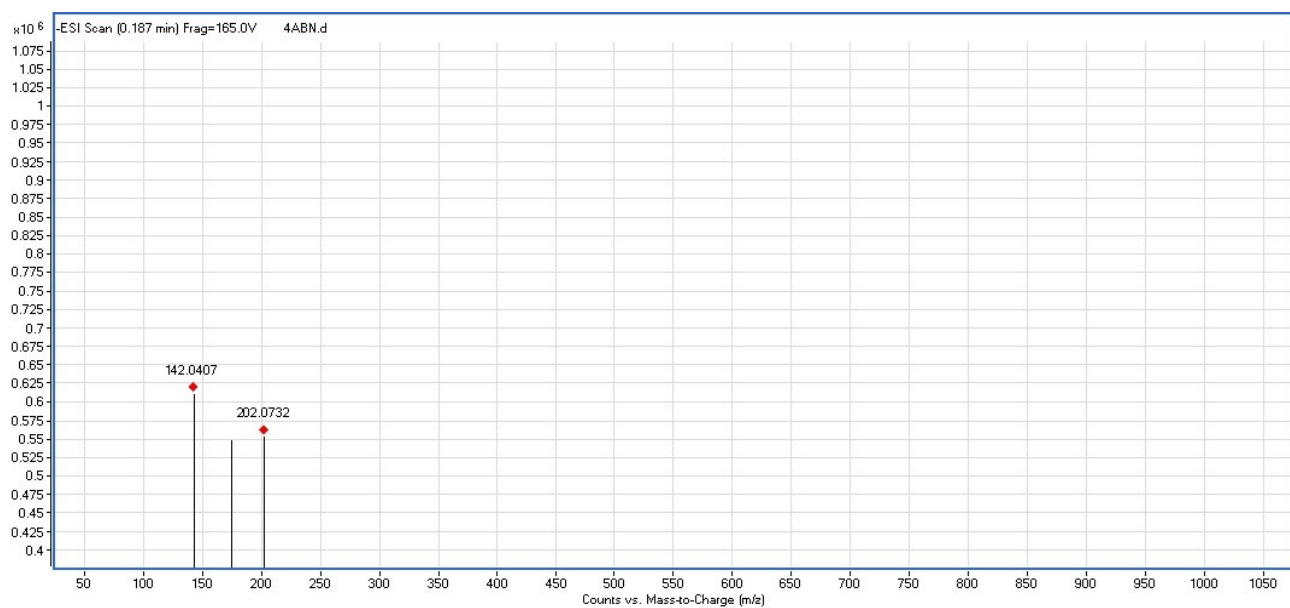


Fig. S7. a) FT-IR, b) ^1H NMR, c) ^{13}C NMR (APT), d) Q-TOF LC/HRMS of N-(4-(1*H*-tetrazol-5-yl)phenyl)acetamide

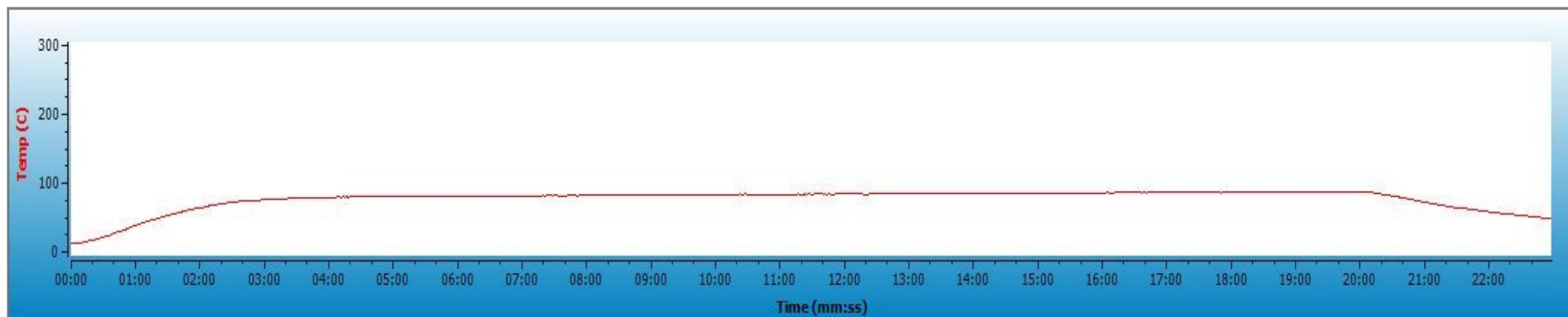
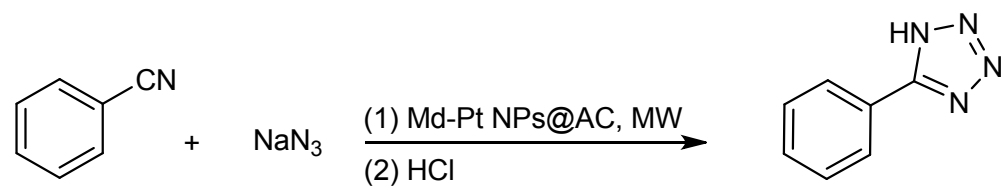


Fig. S8. Temperature-time diagram of **5-Phenyl 1H-tetrazole**.

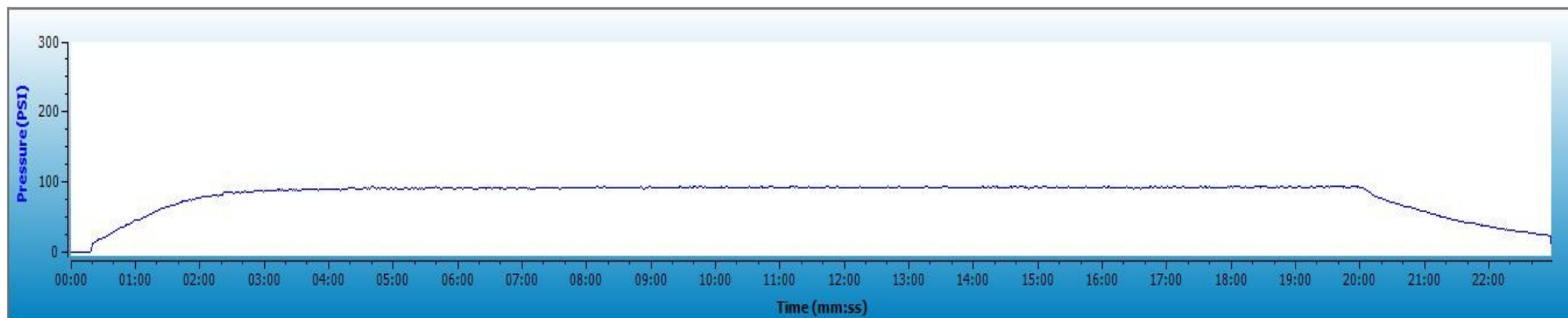


Fig. S9. Pressure-time diagram of **5-Phenyl 1*H*-tetrazole**.

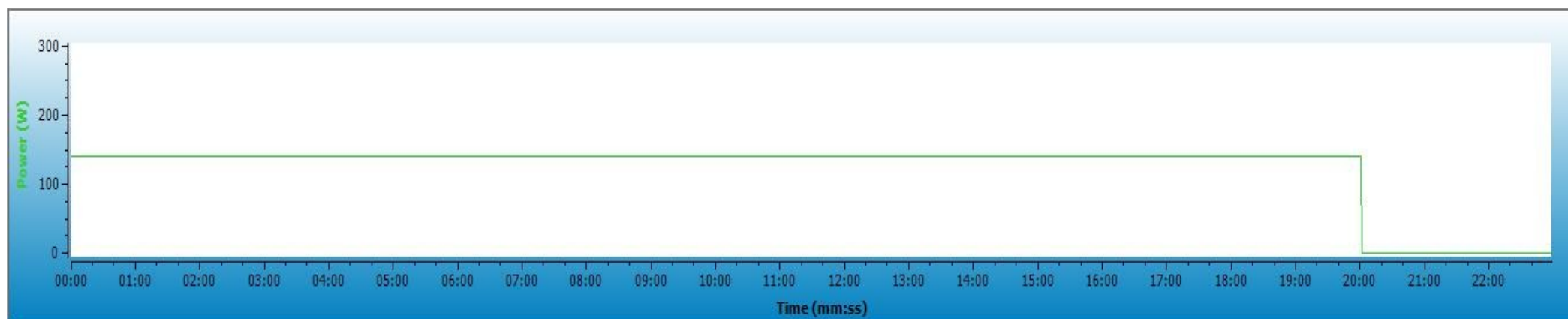


Fig. S10. Power-time diagram of **5-Phenyl 1*H*-tetrazole**.

References

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2. Sreedhar, B.; Suresh Kumar, A.; Yada, D. *Tetrahedron Lett.* **2011**, *52*, 3565–3569.
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