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Supporting Information

Novel route for the synthesis of 5-substituted 1-*H* tetrazoles in presence of polymer-supported palladium nanoparticles

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Content

Material

All chemicals were commercial products. Poly (4-vinylpyridine) cross-linked with 2 % divinyl benzene (DVB), [P_4-VP] 2 % DVB, was purchased from Fluka company (Busch, Switzerland) and [P_4-VP]-PdNPs was prepared in our laboratory. The reactions were monitored by thin layer chromatography (TLC) using silica gel Poly Gram SIL G/UV 254 plates and all yields refer to the isolated products. The FT-IR spectra were obtained with a Bruker Equinox (model 55, Germany), and the NMR spectra were recorded on a Bruker (DRX-500 AVANCE) 500 MHz spectrometer at 500 MHz for ^1H and at 125 MHz for ^{13}C NMR in $CDCl_3$ (using tetramethylsilane as internal reference). Capacity measurements were carried out with an Analytik Jena nova 300 (model 330, Germany) atomic absorption spectrometer utilizing an air-acetylene flame atomizer. The UV-visible absorption spectra were recorded on an avantes photodiode array spectrophotometer model AvaSpec-2048 equipped with a source model of AvaLight-DH-S-BAL. TEM images were recorded using ZEISS 10A conventional TEM model Carl Zeiss-EM10C-100 KV (Germany). FESEM image were recorded using FESEM MIRA 3-XMU with a high-energy beam of electrons from Razi Metallurgical Research Center. EDX analysis was performed using ZEISS (model SIGMA VP-500, Germany) with Oxford Instrument detector (England). XRD pattern was recorded on a PANalytical (model X'Pert PRO) X-ray diffractometer. The uncorrected melting points of compounds were taken by a Buchi melting point B-540 B.V. CHI apparatus.

Preparation of [P_4-VP]-PdNPs

The [P_4-VP]-PdNPs was prepared by the following procedure: In the first step, aqueous solution of H_2PdCl_4 was prepared by mixing 106.4 mg of $PdCl_2$ (0.6 mmol), 6.0 mL of 0.2 M HCl, and 294 mL of distilled water. In the second step, a mixture of 15 mL solution of H_2PdCl_4 (prepared in the first step), 21 mL of methanol and 0.2668 g of [P_4-VP] 2 % DVB was refluxed in a 100 mL flask for 1 h. In the final step, 15 ml of 0.015 M solution of sodium borohydride in methanol

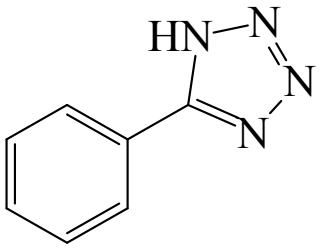
was added into the above mixture dropwise immediately. The abrupt color change from pale green to dark brown indicates that Pd^{2+} reduced to Pd (0) nanoclusters that stabilized by [P_4-VP] 2% DVB and consequently, the [P_4-VP]-PdNPs was formed. Methanol was removed from the solution by evaporation in a rotary evaporator (Heidolph Laborata-4000) and [P_4-VP]-PdNPs was washed with excess acetone to remove the excess residuals.

General procedure for synthesis of 5-substituted 1-H tetrazoles

A mixture of halobenzene (1 mmol), K_2CO_3 (3 mmol), $K_4[Fe(CN)_6]$ (300 mg), NaN_3 (3 mmol), DMF (2mL) and [P_4-VP]-PdNPs (20mg) was taken in 5 mL round bottomed flask and heated at 120 °C. After completion of reaction (monitored by TLC), the catalyst was separated from reaction mixture by an external magnet. The solvent was removed under reduced pressure and residue was dissolved in water (5mL) and acidified with HCl, then a white solid was obtained.

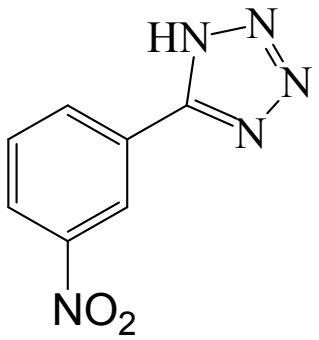
Physical characterization data for synthesized compounds

5-phenyl-1*H*-tetrazole (2a):



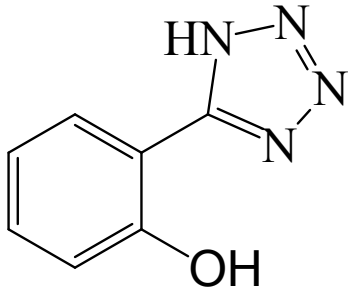
FT-IR (KBr); ν_{max} (cm^{-1}) = 3467, 3083, 3046, 2981, 2918, 2848, 2768, 2698, 2612, 2577, 2475, 1890, 1614, 1570, 1505, 1434, 1404, 1285, 1258, 1187, 1164, 1125, 1086, 1054, 1027, 991, 823, 744, 711, 698, 615, 506, 486, 475, 457, 440, 420.^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.61 (d, 3H, J = 7 Hz, ArH), 8.10 (m, 2H, J = 7 Hz, ArH) ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 124.9, 127.8, 130.3, 132.1, 156.1

5-(3-Nitrophenyl)-1*H*-tetrazole (2c):



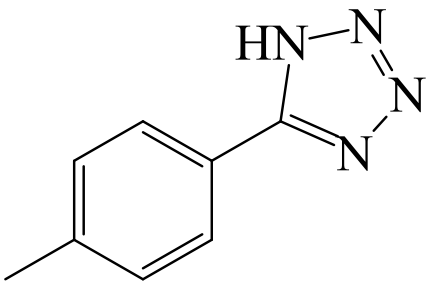
FT-IR (KBr); v_{max} (cm^{-1}) =3101, 3079, 2998, 2909, 2862, 2695, 2608, 2483, 1988, 1931, 1796, 1754, 1627, 1588, 1531, 1479, 1409, 1348, 1307, 1278, 1251,1176, 1163, 1090, 1059, 1033, 992, 916, 870, 817, 765, 738, 726, 709, 677, 655, 551, 523, 445, 424 ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.79 (t, 1H, J = 8 Hz, ArH), 8.42 (d, 1H, J = 8 Hz, ArH), 8.59 (d, 1H, J = 8 Hz, ArH), 8.10 (s, 1H, ArH) ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 122.2, 126.3, 126.9, 131.9, 133.8, 149.0, 157.7

2-(1*H*-tetrazol-5-yl) phenol (2f):



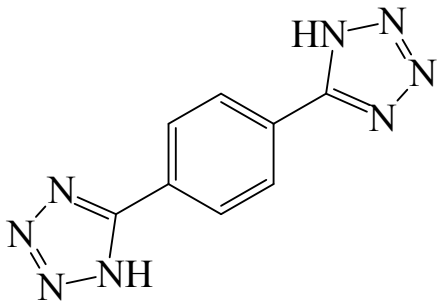
FT-IR (KBr); v_{max} (cm^{-1}) =3096, 1597, 1526, 1472, 1449, 1375, 1344, 1287, 1255, 1233, 1205, 1160, 1143, 1096, 1059, 987, 911, 829, 762, 743, 716, 695, 668, 526, 466. ^{1}H-NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.13 (t, 1H, J = 7.5 Hz, ArH), 7.2 (d, 1H, J = 7.5 Hz, ArH), 7.33 (d, 1H, J = 7.5 Hz, ArH), 7.51 (t, 1H, J = 7.5 Hz, ArH), 7.92 (s, 1H, OH) ^{13}C-NMR (125 MHz, DMSO-d_6): δ (ppm) = 111.4, 117.2, 120.6, 129.9, 133.5, 152.7, 156.2

5-(*P*-tolyl)-1H-tetrazole (2g):



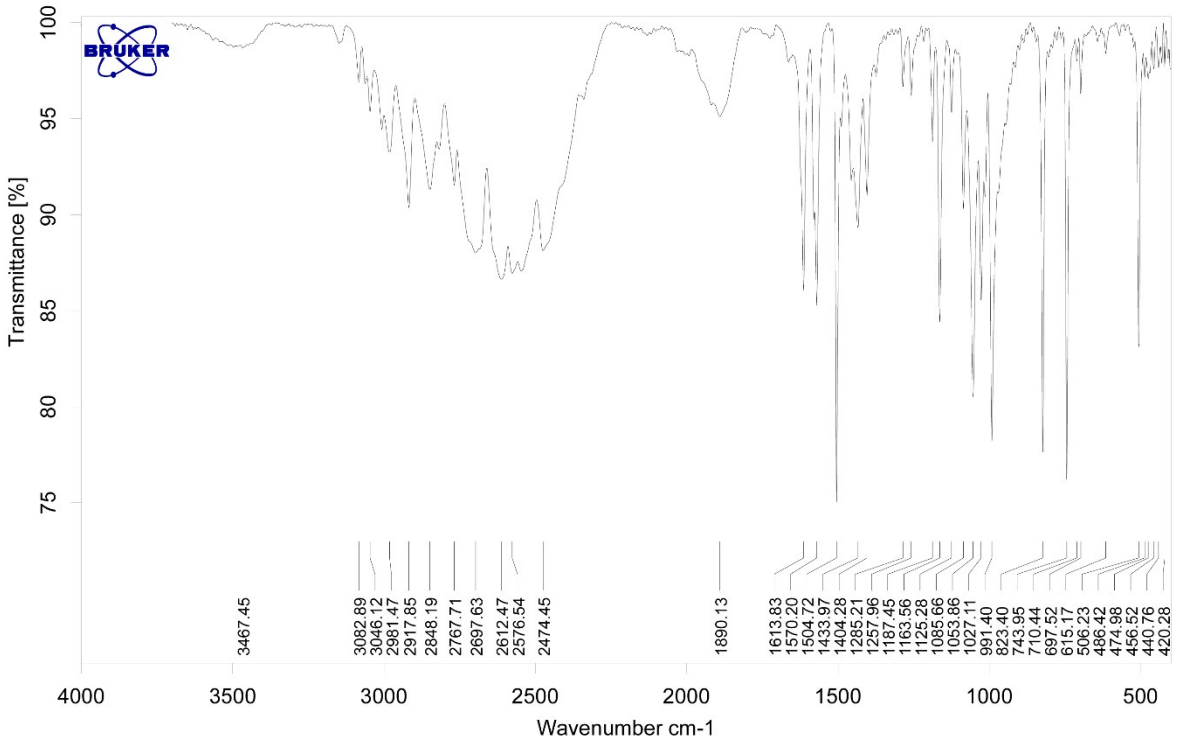
FT-IR (KBr); ν_{max} (cm^{-1}) = 3467, 3082, 2848, 1613 1433 1504, 1187, 1053, 823, 743

1,4-bis(1H-tetrazol-5-yl)benzene (2d):

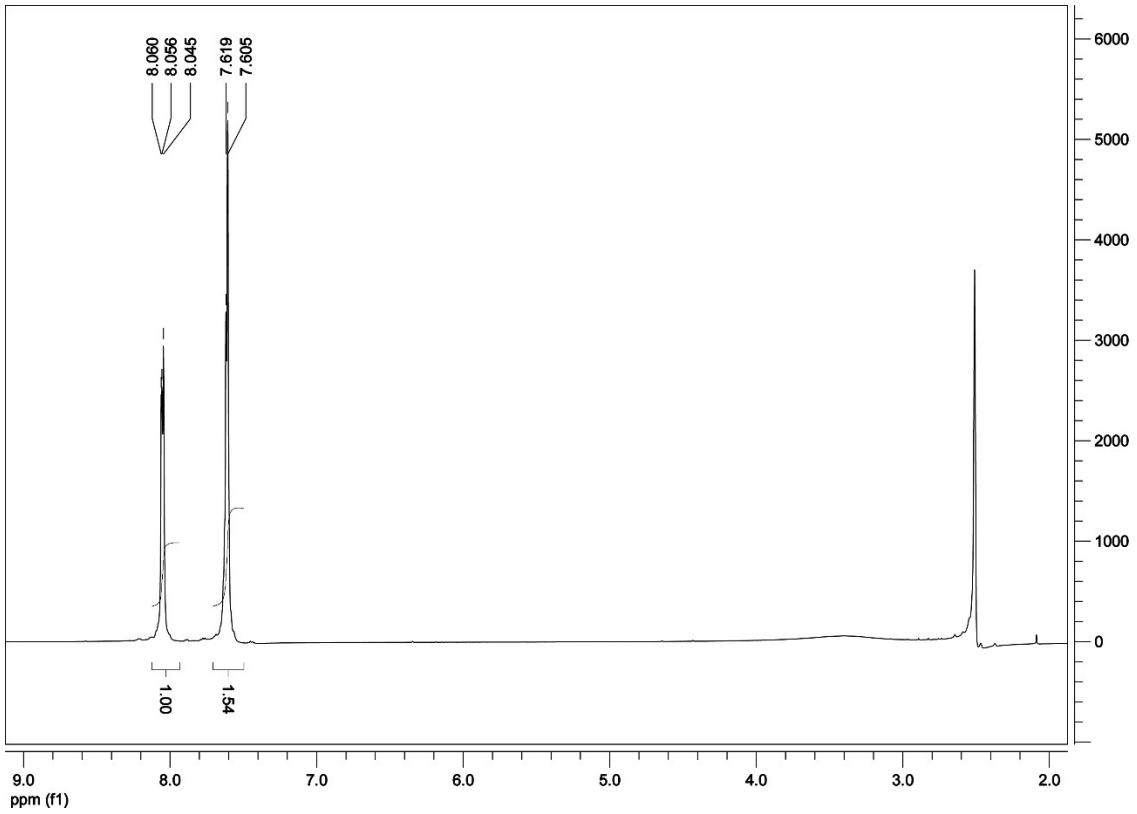


FT-IR (KBr); ν_{max} (cm^{-1}) = 3377, 3034, 1620, 1483, 1682, 1176, 1042, 864, 759

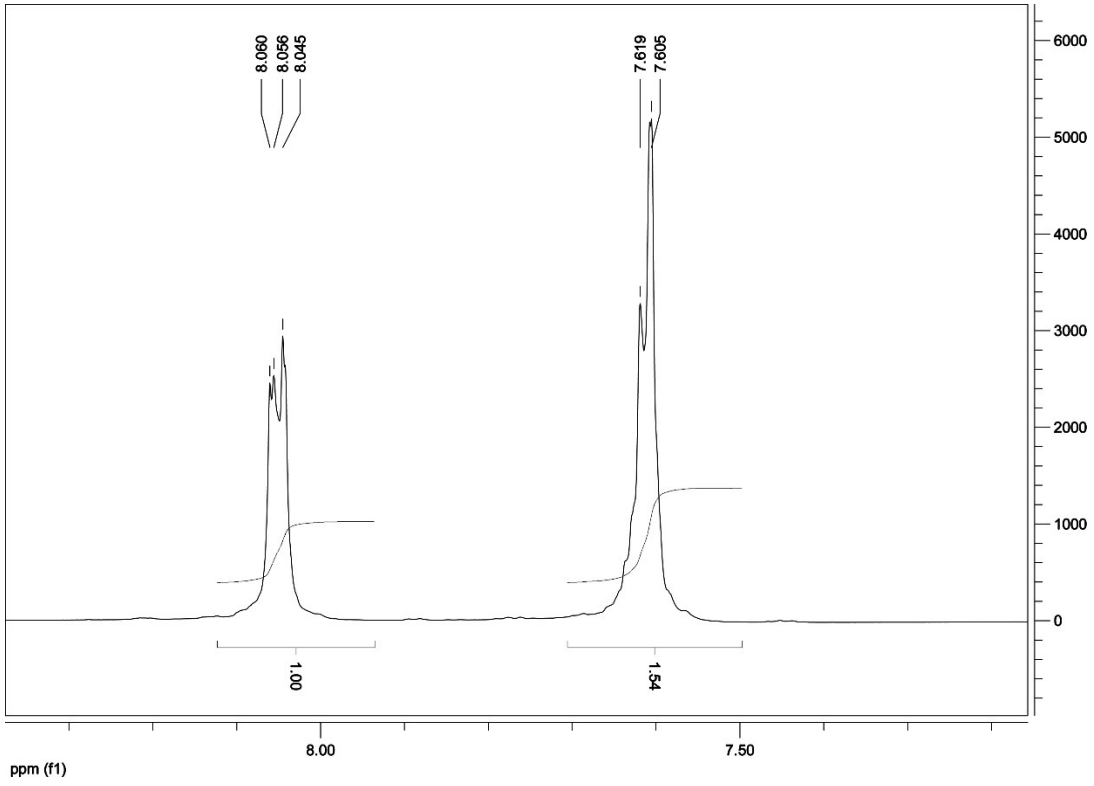
FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra of compounds (2a-2g)



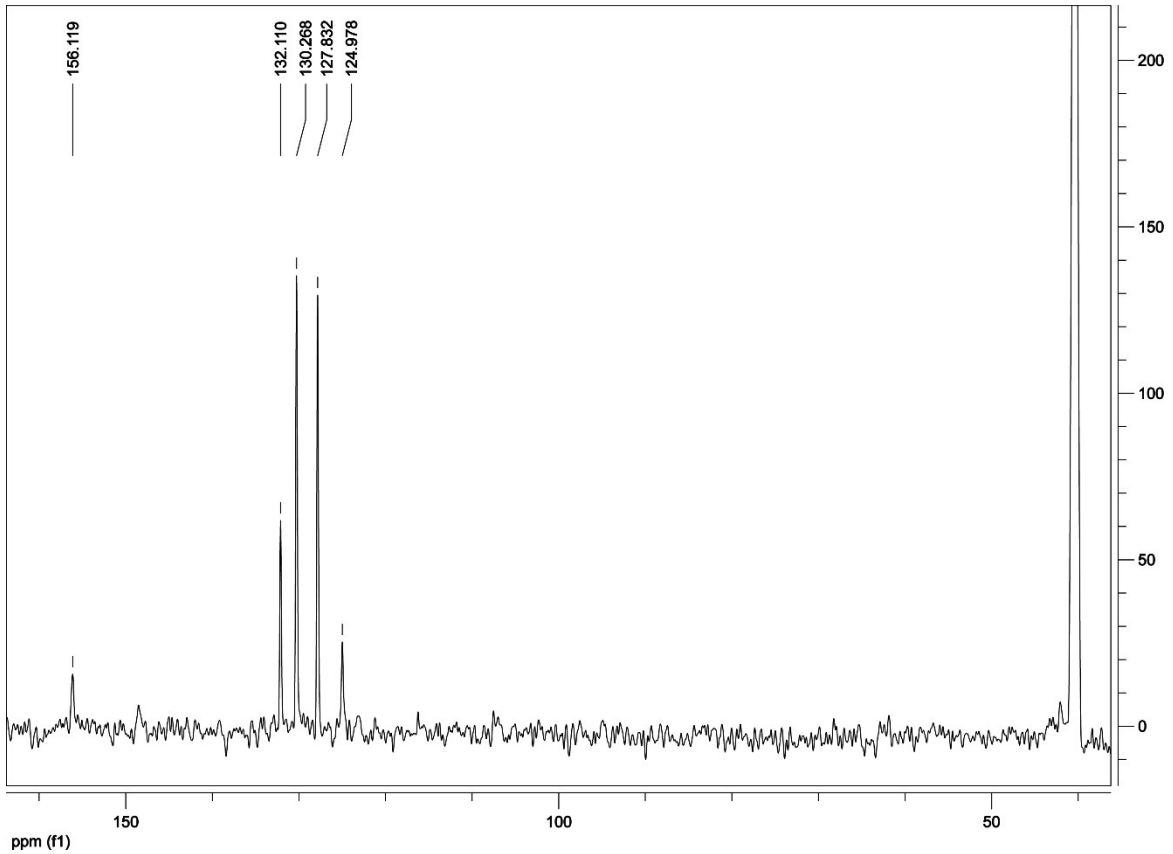
FT-IR of Compound 2a



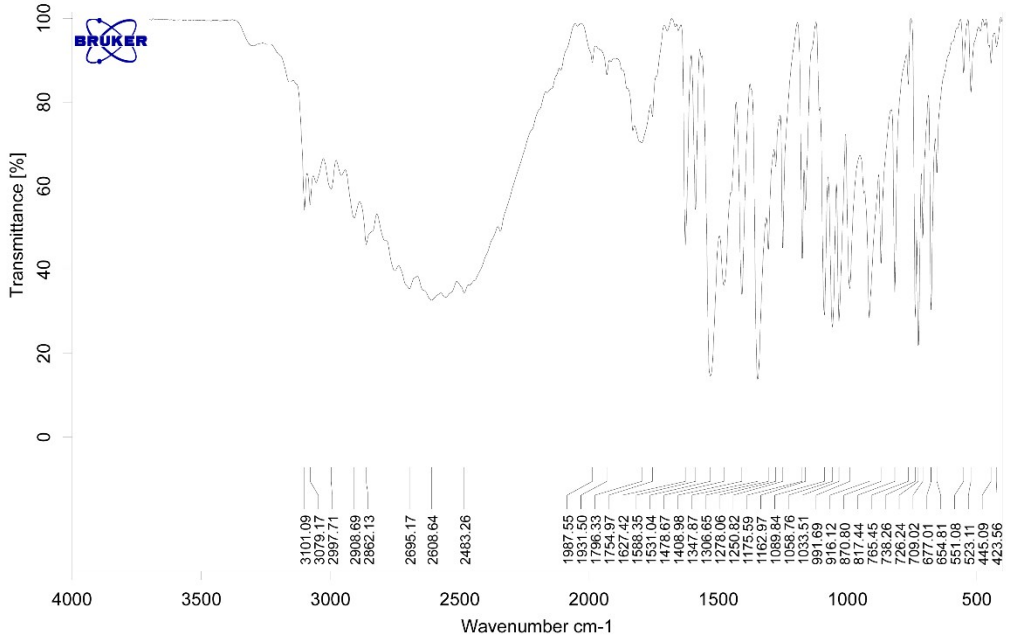
^{1}H-NMR of Compound 2a



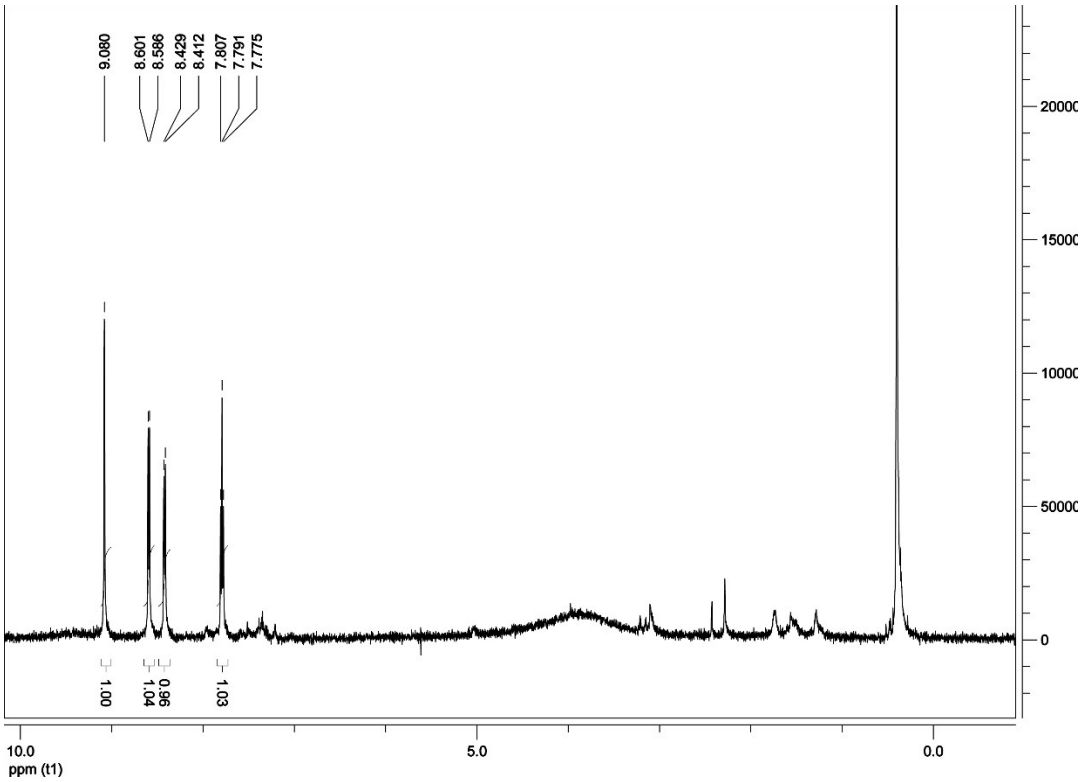
Expanded ^{1}H-NMR of Compound 2a



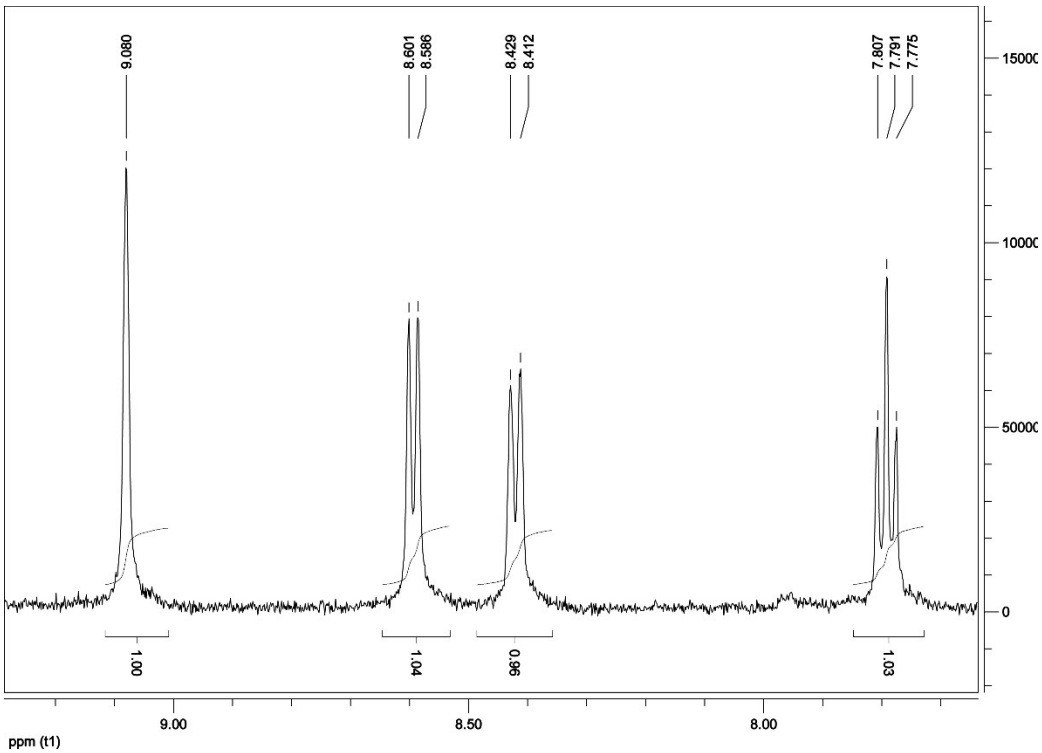
^{13}C-NMR of Compound 2a



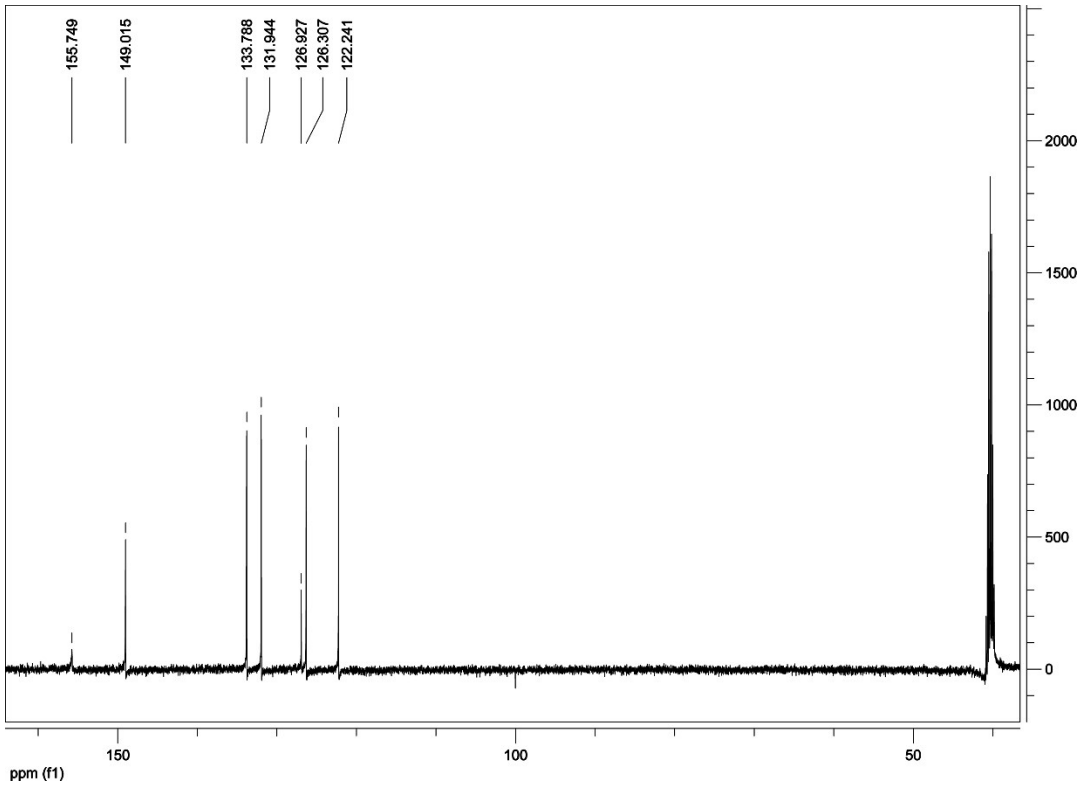
FT-IR of Compound 2c



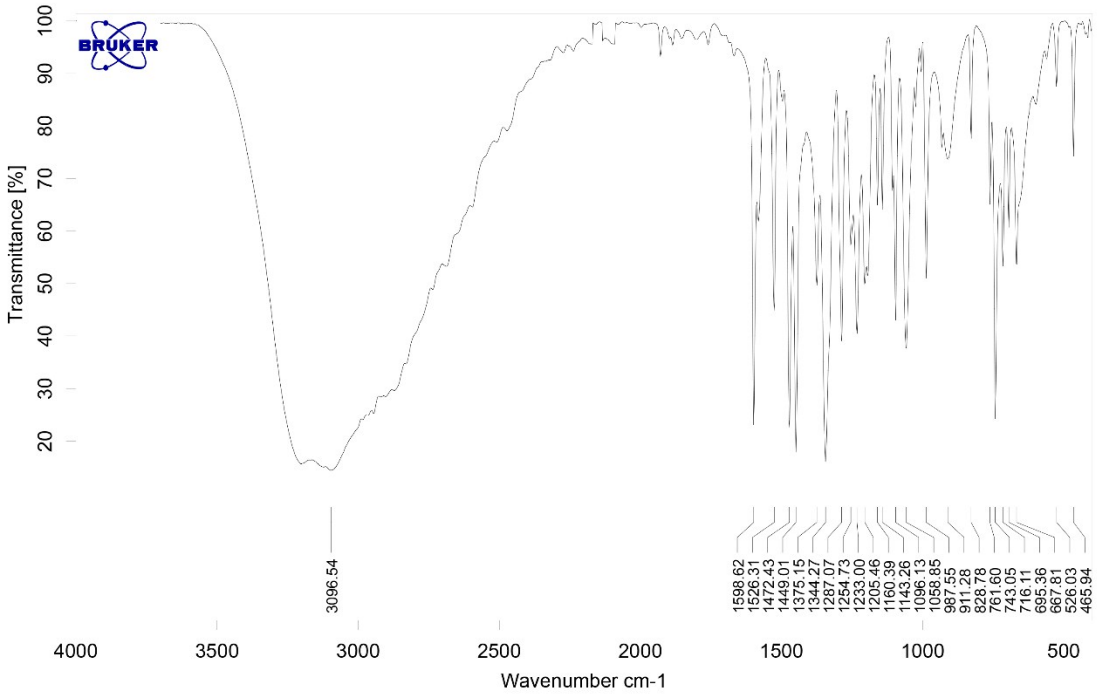
^{1}H-NMR of Compound 2c



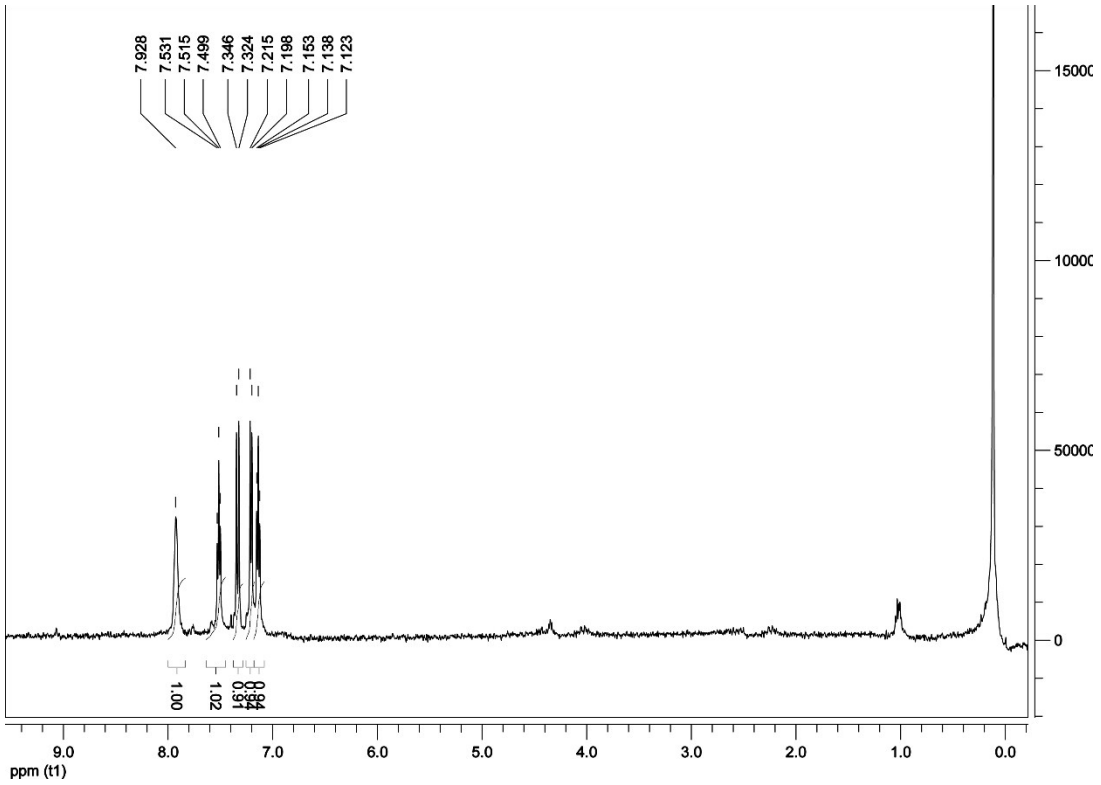
Expanded ^{1}H-NMR of Compound 2c



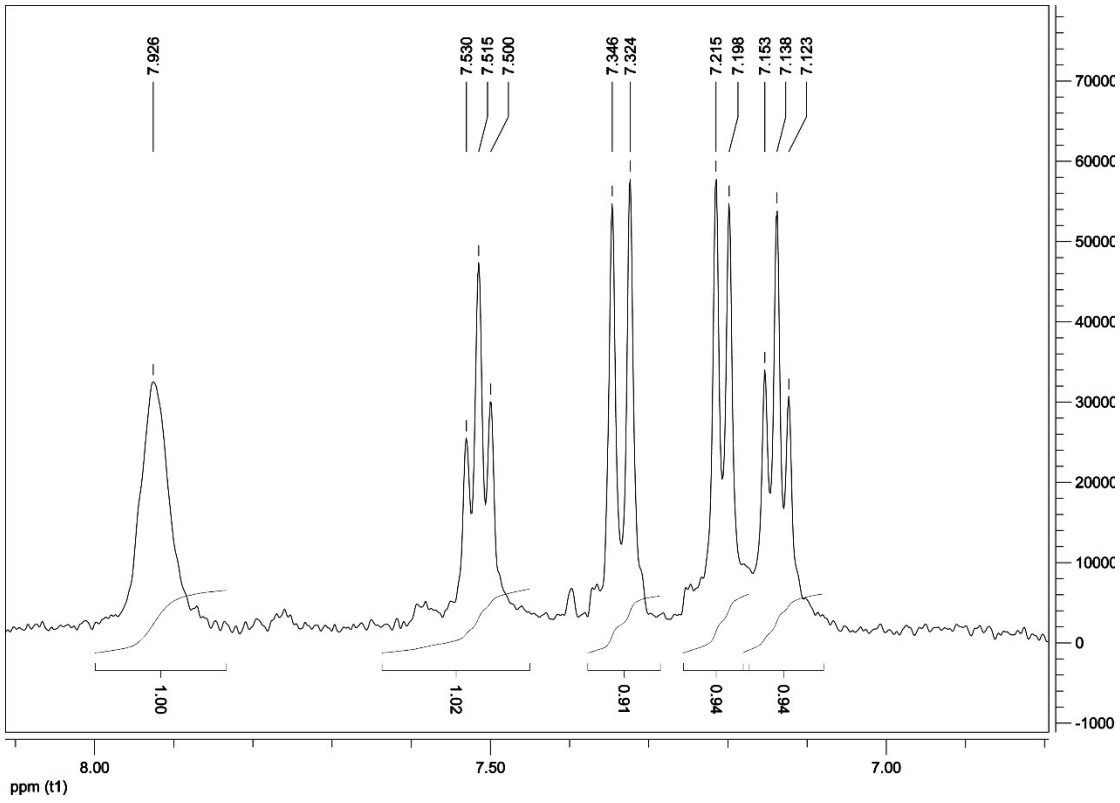
^{13}C-NMR of Compound 2c



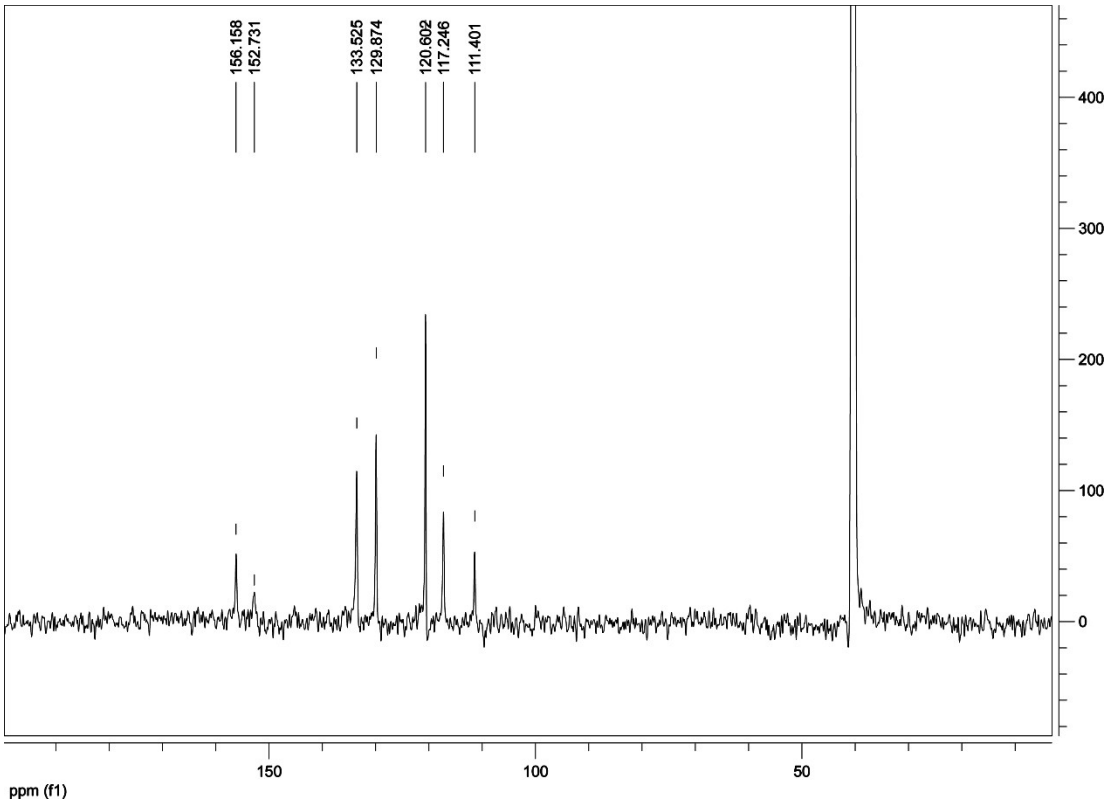
FT-IR of Compound 2f



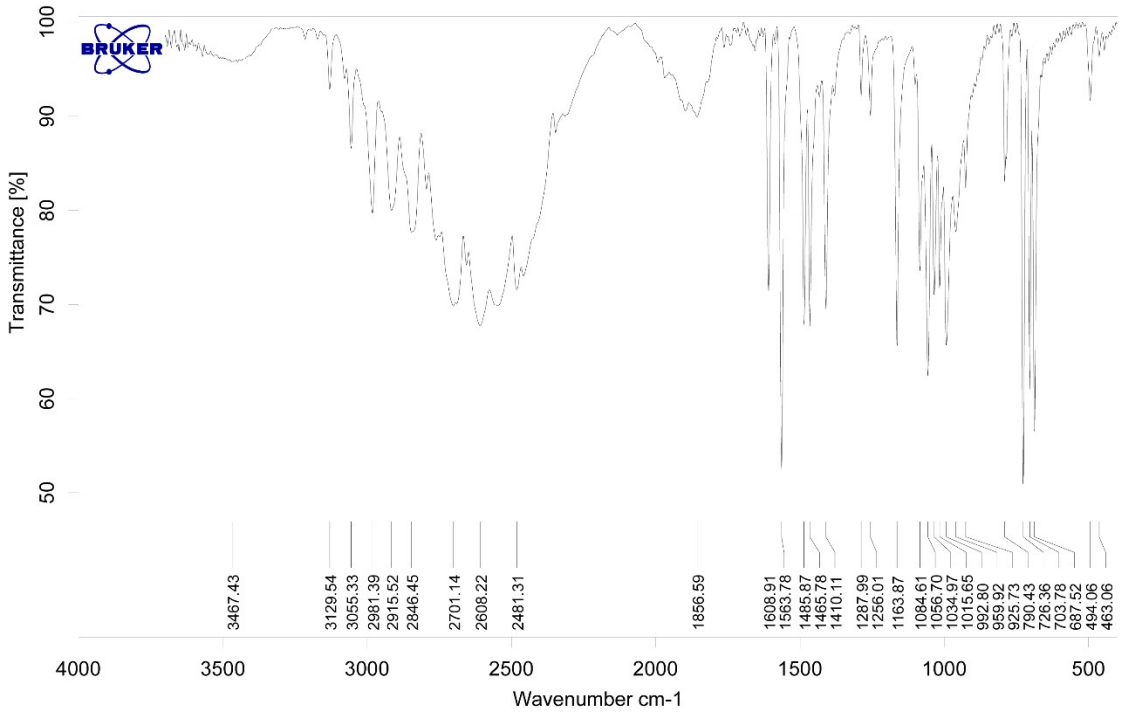
^{1}H-NMR of Compound 2f



Expanded ^{1}H-NMR of Compound 2f



^{13}C-NMR of Compound 2f



FT-IR of Compound 2g