Cu_2O nanoparticle-catalyzed synthesis of diaryl tetrazolones and investigation of their solid-state properties.

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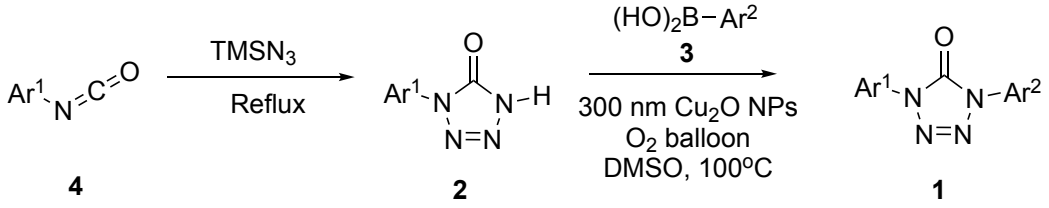
General Procedures

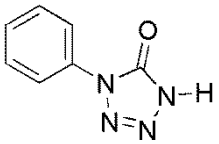
Thin layer chromatography was carried out on 250 μm silica gel plates and UV-light was used as a visualizing agent. Standard column chromatography was performed using 32 – 63 μm silica gel. All IR data was collected using a Perkin Elmer Frontier FTIR spectrometer and recorded by the attenuated total reflectance (ATR) technique. The IR frequencies are listed in cm^{-1}. Size and morphological characterization of the Cu_2O nanoparticles were carried out on a JEOL JEM-14000 transmission electron microscope. ^{1}H and ^{13}CNMR spectra for structural characterization were recorded on 400 MHz JEOL NMR spectrometer and the peaks were referenced to the solvent. Chemical shifts and coupling constants are reported in parts per million and Hertz, respectively. Low resolution mass spectra (LRMS) were obtained on a mass spectrometer equipped with an electrospray ion source operated in the positive or negative ion mode and connected to a linear ion trap mass analyzer. All isocyanates **4** and boronic acids **3** were commercially obtained. **3** were purified via recrystallization in water (except the 3-pyridyl boronic acid which was purified by washing in hot acetonitrile). The C-N coupling reactions were carried out under an atmosphere of oxygen using a balloon.



Scheme 1. *General scheme for the synthesis of 1,4-diaryl tetrazolones **1**.*

Syntheses of aryl tetrazolones 2

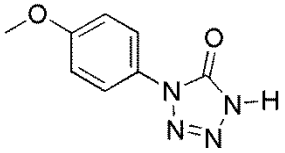
1-Phenyl-1,4-dihydro-5*H*-tetrazol-5-one (2a)[1]



Phenyl isocyanate (0.552 g, 4.63 mmol) and trimethylsilyl azide ($TMSN_3$) (1.24 mL, 9.25 mmol) were combined in a 10 mL round bottom flask. The mixture was stirred and heated to 100 °C for 24 hours, or until TLC indicated the completion of the reaction. The product was precipitated with ethanol (EtOH) and the resulting mixture concentrated *via* roto-evaporation. The crude solid was

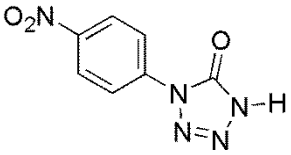
recrystallized in EtOH and dried under vacuum. Recrystallization in ethanol yielded **2a** as a pale yellow solid (660 mg, 88%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 14.75 (br s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 150.3, 134.2, 129.5, 127.6, 119.6.

1-(4-Methoxyphenyl)-1,4-dihydro-5*H*-tetrazol-5-one (2b)[1]



4-Methoxyphenyl isocyanate (1.16 g, 7.81 mmol) and $TMSN_3$ (1.57 mL, 11.7 mmol) were combined in a 10 mL round bottom flask. The mixture was stirred and heated to 100 °C for 24 hours, or until TLC indicated the completion of the reaction. The product was precipitated with ethanol (EtOH) and the resulting mixture concentrated *via* roto-evaporation. Recrystallization in ethanol yielded **2b** as a pale yellow solid (925 mg, 62%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 14.65 (br s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.11 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 158.6, 150.4, 127.1, 122.1, 114.6, 55.5. Anal. Calcd. for $C_8H_8N_4O_2$: C, 50.00; H, 4.20; N, 29.15 Found: C, 50.20; H, 4.22; N, 29.20.

1-(4-Nitrophenyl)-1,4-dihydro-5*H*-tetrazol-5-one (2c)[1]

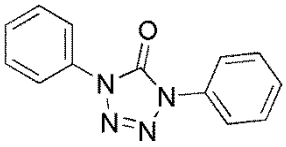


4-Nitrophenyl isocyanate (0.793 g, 4.83 mmol) and $TMSN_3$ (0.97 mL, 7.25 mmol) were combined in a 10 mL round bottom flask. The mixture was stirred and heated to 100 °C for 24 hours, or until TLC indicated the completion of the reaction. The product was precipitated with ethanol (EtOH) and the resulting mixture concentrated *via* roto-evaporation. Recrystallization in ethanol yielded **2c** as a yellow solid (590 mg, 59%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 14.99 (br s, 1H), 8.44 (d, J = 9.3 Hz, 2H), 8.21 (d, J = 9.3 Hz, 2H.); ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 150.1, 145.5, 139.3, 125.3, 119.0.

Synthesis of 1,4-diaryl tetrazolones 1

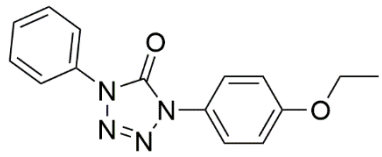
Aryl tetrazolone **2** (1 mmol) and aryl boronic acid **3** (2 mmol) were combined in a two necked round bottom flask with the side neck sealed with a rubber septum. In a separate flask, Cu_2O nanoparticles (300 nm, 5 mol%) were suspended in DMSO (8 mL) and sonicated for 2 min. The resulting suspension was added to the reaction flask and the mixture was stirred and heated to 100 °C in the presence of O_2. (O_2 balloon was attached to the reaction flask through the side arm of the two necked flask). The reaction was monitored using TLC (Hexanes: EtOAc). Upon completion, the reaction mixture was cooled to room temperature while stirring. Subsequently, EtOAc (50 mL) was added and the mixture was transferred to a separatory funnel. The organic layer was washed with 1 M HCl (thrice, 10 mL) and brine (thrice, 10 mL), and then separated, dried over Na_2SO_4, and concentrated under reduced pressure to obtain crude 1,4-diaryl tetrazolone **1**. The product was purified using silica gel chromatography.

1,4-Diphenyl-1,4-dihydro-5*H*-tetrazol-5-one (1aa)



Compound **1aa** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and phenylboronic acid **3a** (150 mg, 1.23 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexane:dichloromethane, 7:3) gave **1aa** as a white solid (123 mg, 83%). FTIR (neat, cm^{-1}): 3062, 3054, 1725, 1593, 1501, 1485, 1465, 1416, 1382, 1362, 1295, 1190,1151,1115, 1067, 962, 747, 685. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91 (d, J = 8.2 Hz, 4H), 7.62 (t, J = 8.2 Hz, 4H), 7.49 (t, J = 7.8 Hz , 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 147.2, 134.0, 129.6, 128.2, 120.3.

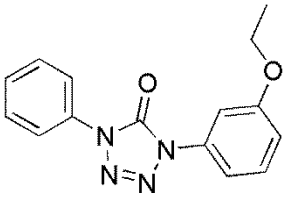
1-(4-Ethoxyphenyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1ab)



Compound **1ab** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and (4-ethoxyphenyl)boronic acid **3b** (204 mg, 1.23 mmol) following the general

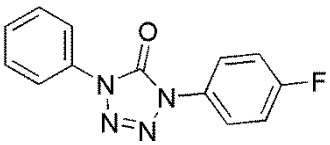
procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, 6:4) gave **1ab** as a white solid (103 mg, 60%). IR (cm^{-1}): 3055, 2976, 2937, 2896, 1727, 1512, 1505, 1494, 1479, 1390, 1380, 1361, 1299, 1245, 1190, 1179, 1152, 1116, 1096, 1071, 1038, 963, 926, 908, 835, 825, 808, 756, 733, 721, 689, 661; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.90 (m, 2H), 7.75 (d, J = 9.1 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 9.1 Hz, 2H), 4.10 (q, J = 6.9 Hz, 2H), 1.36 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 159.1, 147.1, 135.0, 134.0, 130.6, 129.6, 128.2, 120.3, 114.1, 112.0, 106.2, 63.5, 14.5. Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.82; H, 5.00; N, 19.85 Found: C, 63.99; H, 5.02; N, 19.94.

1-(3-Ethoxyphenyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1ac)



Compound **1ac** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and (3-ethoxyphenyl)boronic acid **3c** (204 mg, 1.23 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, 1:1) gave **1ac** as a white solid (151 mg, 87%). FTIR (cm^{-1}): 3069, 2975, 2936, 2896, 1727, 1606, 1588, 1493, 1466, 1382, 1300, 1234, 1182, 1142, 1108, 1044, 939, 852, 840, 777, 733, 721, 683, 664. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.90 (d, J = 8.2 Hz, 2H), 7.62 (m, 2H), 7.53 – 7.46 (m, 4H), 7.05 (d, J = 8.1 Hz 1H), 4.10 (q, J = 6.9 Hz, 2H), 1.36 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$*): δ* 159.1, 147.1, 135.1, 134.0, 130.6, 129.6, 128.2, 120.3, 114.1, 112.0, 106.3, 63.5, 14.6. Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.82; H, 5.00; N, 19.85 Found: C, 63.90; H, 5.10; N, 19.98.

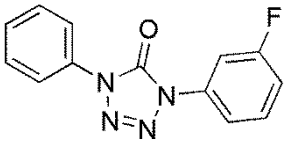
1-(4-Fluorophenyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1ad)



Compound **1ad** was prepared from **2a** (100 mg, 0.617 mmol) and (4-fluorophenyl)boronic acid **3d** (173 mg, 1.23 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, (65:35) gave **1ad** as a white solid (128 mg, 81%). FTIR (neat, cm^{-1}): 3092, 3067, 3059, 3048, 1730, 1597, 1489, 1462, 1394, 1363, 1220, 1190, 1153, 1117,

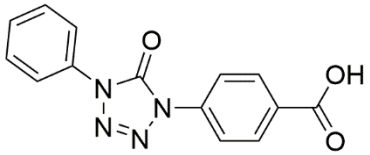
1091, 1068, 963, 835, 753, 723, 689. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.95 – 7.89 (m, 4H), 7.62 (t, J = 7.7 Hz, 2H), 7.51 – 7.46 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.2, (d, $J_{C\text{-}F}$ = 245 Hz), 147.3, 134.0, 130.3 (d, $J_{C\text{-}F}$ = 3 Hz), 129.6, 128.2, 123.1 (d, $J_{C\text{-}F}$ = 9 Hz), 120.2, 116.5 (d, $J_{C\text{-}F}$ = 23 Hz). Anal. Calcd. for $C_{13}H_9FN_4O$: C, 60.94; H, 3.54; N, 21.87 Found: C, 61.12; H, 3.67; N, 22.12.

1-(3-Fluorophenyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1ae)



Compound **1ae** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and (3-fluorophenyl)boronic acid **3e** (173 mg, 1.23 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, 65:35) gave **1ae** as a white solid (120 mg, 76%). FTIR (neat, cm^{-1}): 3105, 3081, 3047, 3038, 1732, 1595, 1493, 1464, 1415, 1383, 1217, 1185, 1142, 1110, 1070, 964, 883, 866, 781, 751, 723, 677 ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.89 (d, J = 8.1 Hz, 2H), 7.81 – 7.77 (m, 2H), 7.71 – 7.65 (m, 1H), 7.63 (t, J = 8.1 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.36 (dt, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6)*:* 162.1, (d, $J_{C\text{-}F}$ = 244 Hz), 147.0, 135.4 (d, $J_{C\text{-}F}$ = 11 Hz), 133.9, 131.6 (d, $J_{C\text{-}F}$ = 8 Hz), 129.6, 128.3, 120.3, 115.7 (d, $J_{C\text{-}F}$ = 3 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21 Hz), 107.0 (d, $J_{C\text{-}F}$ = 25 Hz). Anal. Calcd. for $C_{13}H_9FN_4O$: C, 60.94; H, 3.54; N, 21.87 Found: C, 61.14; H, 3.58; N, 21.91.

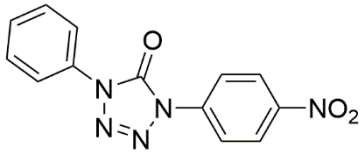
1-(4-Carboxyphenyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1ah)



Compound **1ah** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and (4-carboxyphenyl)boronic acid **3h** (205 mg, 1.23 mmol) according to the general procedure with the following work-up: Upon completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature and diluted with 30 mL of EtOAc. The organic layer was washed thrice with 1% $NaHCO_3$ solution. The aqueous layer was separated. At this time, green precipitate was observed in the aqueous layer which was removed via vacuum filtration. The

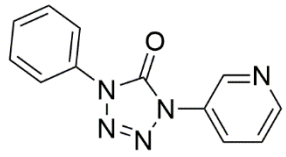
clear filtrate was neutralized with 1M HCl and placed on ice which resulted into the formation of a white precipitate which was filtered, washed with EtOAc and distilled water to obtain **1ah** as a white solid (83 mg, 48%). IR (cm^{-1}): 3400 – 2300 (broad), 3112, 3068, 2984, 2833, 2680, 2558, 1720, 1674, 1608, 1600, 1586, 1515, 1500, 1464, 1433, 1386, 1359, 1321, 1293, 1189, 1183, 1155, 1127, 1108, 1093, 1071, 1015, 962, 934, 906, 860, 824, 780, 768, 741, 724, 682, 664; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 13.22 (bs, 1H), 8.17 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.90 (d, J = 8.1 Hz, 2H), 7.63 (t, J = 7.7 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 166.5, 147.1, 137.5, 133.9, 130.9, 129.8, 129.6, 128.4, 120.5, 119.1. LRMS(ESI): m/z 281 (M-H$^+$), 237, 209, 162, 134, 92. Anal. Calcd. for $C_{14}H_{10}N_4O_3$: C, 59.57; H, 3.57; N, 19.85 Found: C, 59.30; H, 3.43; N, 19.56.

1-(4-Nitrophenyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1ai)



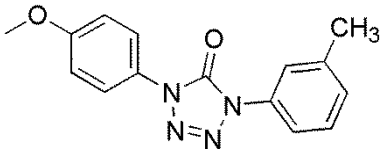
Compound **1ai** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and (4-nitrophenyl)boronic acid **3i** (206 mg, 1.23 mmol) following the general procedure. During the work-up, the product precipitated in the organic layer upon the addition of HCl. The two layers were separated, the solid was removed from the organic layer by filtration. NMR spectrum of the isolated solid indicated pure **1ai**. The filtrate (organic layer) was concentrated *via* rotary evaporation and the crude was subjected to two consecutive recrystallizations in ethyl acetate to obtain **1ai** as a beige solid. Combined yield (80 mg, 46%). IR (cm^{-1}): 3122, 3093, 3065, 1726, 1613, 1595, 1523, 1490, 1467, 1432, 1387, 1367, 1337, 1327, 1310, 1296, 1185, 1150, 1124, 1109, 1096, 1072, 1022, 1009, 960, 918, 851, 782, 761, 754, 745, 720, 688, 682, 662; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.49 (d, J = 9.3 Hz, 2H), 8.26 (d, J = 9.3 Hz, 2H), 7.89 (m, 2H), 7.64 (t, J = 7.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 147.1, 145.9, 139.1, 133.8, 129.7, 128.5, 125.4, 120.6, 119.7. Anal. Calcd. for $C_{13}H_9N_5O_3$: C, 55.13; H, 3.20; N, 24.73 Found: C, 54.97; H, 3.12; N, 24.52.

1-(3-Pyridyl)-4-phenyl-1,4-dihydro-5*H*-tetrazol-5-one (1aj)



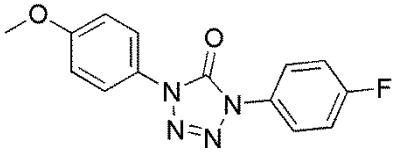
Compound **1aj** was prepared from 1-phenyl-1,4-dihydro-5*H*-tetrazol-5-one **2a** (100 mg, 0.617 mmol) and pyridin-3-ylboronic acid **3j** (152 mg, 1.23 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:ethyl acetate, 75:25) gave **1aj** as a white solid (75 mg, 51%). IR (cm $^{-1}$): 3084, 3069, 3050, 1731, 1694, 1598, 1579, 1504, 1482, 1465, 1444, 1410, 1391, 1362, 1332, 1317, 1295, 1244, 1199, 1182, 1160, 1131, 1110, 1092, 1071, 1026, 1012, 963, 906, 802, 748, 723, 702, 686, 660; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 9.11 (d, J = 2.5 Hz, 1H), 8.70 (dd, J_1 = 4.8 Hz, J_2 = 1.4 Hz, 1H), 8.31 (d, J = 8.3 Hz 1H), 7.90 (d, J = 7.9 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.63 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.2, 147.3, 141.5, 133.9, 130.9, 129.7, 128.4, 128.1, 124.4, 120.3. LRMS(ESI): m/z 240 (M+H$^+$); Anal. Calcd. for $C_{12}H_9N_5O$: C, 60.25; H, 3.79; N, 29.27 Found: C, 60.34; H, 3.81; N, 29.12.

1-(4-Methoxyphenyl)-4-(3-tolyl)-1,4-dihydro-5*H*-tetrazol-5-one (1bk)



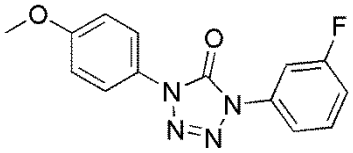
Compound **1bk** was prepared from 1-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazol-5-one **2b** (100 mg, 0.520 mmol) and *m*-tolylboronic acid **3k** (142 mg, 1.04 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, 1:1) gave **1bk** as a white solid (119 mg, 80%). FTIR (neat, cm^{-1}): 3089, 3075, 3046, 2998, 2962, 2925, 2831, 1707, 1608, 1593, 1517, 1499, 1439, 1403, 1361, 1302, 1254, 1181, 1145, 1088, 1030, 971, 859, 823, 775, 726, 690. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.76 (d, J = 9.1 Hz, 2H), 7.73 – 7.68 (m, 2H), 7.49 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 9.1 Hz, 2H), 3.83 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 159.0, 147.4, 139.2, 134.1, 129.4, 128.8, 126.8, 122.9, 120.5, 117.3, 114.7, 55.6, 21.0. Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.82; H, 5.00; N, 19.85 Found: C, 63.73; H, 5.19; N, 19.73.

1-(4-Fluorophenyl)-4-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazol-5-one (1bd)



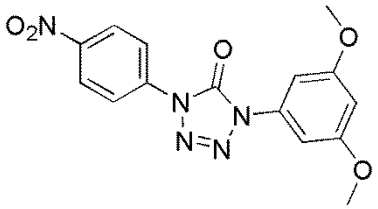
Compound **1bd** was prepared from 1-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazol-5-one **2b** (100 mg, 0.520 mmol) and (4-fluorophenyl)boronic acid **3d** (146 mg, 1.04 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, 1:1) gave **1bd** as a white solid (118 mg, 79%). IR (cm^{-1}): 3126, 3094, 2943, 2845, 1718, 1609, 1508, 1445, 1432, 1388, 1361, 1303, 1256, 1231, 1186, 1154, 1094, 1030, 970, 828, 726, 720, 698, 667. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.95 – 7.90 (m, 2H), 7.76 (d, J = 9.0 Hz, 2H), 7.47(t, J = 8.8 Hz, 2H), 7.16 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 161.2, (d, $J_{C\text{-}F}$ = 245 Hz), 159.0, 147.4, 130.5 (d, $J_{C\text{-}F}$ = 3 Hz), 126.8, 122.91 (d, $J_{C\text{-}F}$ ~ 9 Hz, overlapped by signal from the methoxy substituted phenyl ring), 122.86, 116.5 (d, $J_{C\text{-}F}$ = 23 Hz), 114.7, 55.5. Anal. Calcd. for $C_{14}H_{11}FN_4O_2$: C, 58.74; H, 3.87; N, 19.57 Found: C, 58.87; H, 3.88; N, 19.72.

1-(3-Fluorophenyl)-4-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazol-5-one (1be)



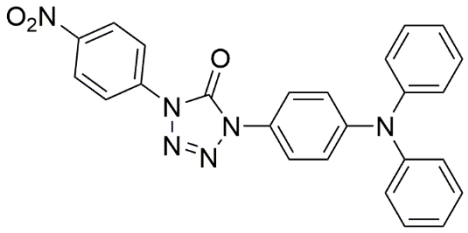
Compound **1be** was prepared from 1-(4-methoxyphenyl)-1,4-dihydro-5*H*-tetrazol-5-one **2b** (100 mg, 0.520 mmol) and (3-fluorophenyl)boronic acid **3e** (146 mg, 1.04 mmol) following the general procedure. Purification by column chromatography (SiO_2, hexanes:dichloromethane, 1:1) gave **1be** as a white solid (119 mg, 80%). FTIR (neat, cm^{-1}): 3117, 3083, 2941, 2845, 1718, 1602, 1517, 1492, 1465, 1442, 1385, 1307, 1254, 1222, 1186, 1164, 1142, 1101, 1031, 969, 873, 823, 775, 724, 676. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.81 – 7.77 (m, 2H), 7.75 (d, J = 9.0 Hz, 2H), 7.71 – 7.65 (m, 1H), 7.35 (td, J_1= 8.6 Hz, J_2 = 2.5 Hz), 7.17 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ162.1, (d, $J_{C\text{-}F}$ = 245 Hz), 159.1, 147.2, 135.5 (d, $J_{C\text{-}F}$ = 11 Hz), 131.6 (d, $J_{C\text{-}F}$ = 9 Hz), 126.6, 123.0, 115.6 (d, $J_{C\text{-}F}$ = 3 Hz), 114.8 (d, $J_{C\text{-}F}$ ~ 21 Hz, overlapped by signal from the methoxy substituted phenyl ring), 114.7, 107.0 (d, $J_{C\text{-}F}$ = 27 Hz), 55.6. Anal. Calcd. for $C_{14}H_{11}FN_4O_2$: C, 58.74; H, 3.87; N, 19.57 Found: C, 58.55; H, 3.82; N, 19.64.

1-(3,5-Dimethoxyphenyl)-4-(4-nitrophenyl)-1,4-dihydro-5*H*-tetrazol-5-one (1cl)



Compound **1cl** was prepared from 1-(4-nitrophenyl)-1,4-dihydro-5*H*-tetrazol-5-one **2c** (100 mg, 0.483 mmol) and (3,5-dimethoxyphenyl)boronic acid **3l** (176 mg, 0.966 mmol) following the general procedure. Purification by recrystallization in water and acetonitrile gave **1cl** as a white (126 mg, 77%). IR (cm^{-1}): 3160, 3119, 3113, 3094, 2973, 2944, 2871, 1739, 1593, 1528, 1482, 1426, 1367, 1338, 1272, 1207, 1136, 1158, 1090, 1060, 1031, 972, 922, 856, 835, 824, 749, 722. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.49 (d, J = 9.2 Hz, 2H), 8.24 (d, J = 9.2 Hz, 2H), 7.09 (d, J = 2.2 Hz, 2H), 6.65 (t, J = 2.2 Hz, 1H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 161.0, 146.9, 145.9, 139.0, 135.3, 125.4, 119.7, 99.8, 98.5, 55.7. Anal. Calcd. for $C_{15}H_{13}N_5O_5$: C, 52:48; H, 3.82; N, 20.40 Found: C, 52.31; H, 3.78; N, 20.56.

1-(4-(diphenylamino)-phenyl)-4-(4-nitrophenyl)-1,4-dihydro-5*H*-tetrazol-5-one (1cm)



Compound **1cm** was prepared from 1-(4-nitrophenyl)-1,4-dihydro-5*H*-tetrazol-5-one **2c** (100 mg, 0.483 mmol) and (4-(diphenylamino)phenyl)boronic acid **3m** (279 mg, 0.966 mmol) according to the general procedure with the following changes. During work-up, upon the addition of HCl, **1cm** precipitated into the organic layer. The crystals were collected using vacuum filtration and washed with ethyl acetate, yielding **1cm** as an orange solid (167 mg, 77%). IR (cm^{-1}): 3117, 3089, 3067, 3039, 1725, 1585, 1522, 1484, 1433, 1355, 1328, 1265, 1181, 1146, 1113, 1089, 1028, 960, 920, 855, 840, 830, 765, 748, 720, 710, 694, 682 ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.49 (J = 9.2 Hz, 2H), 8.26 (d, J = 9.2 Hz, 2H), 7.72 (d, J = 8.9 Hz, 2H), 7.36 (t, J = 7.8 Hz, 4H), 7.12 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 148.3, 147.17, 147.11, 146.4, 139.4, 129.6,127.2, 125.3, 125.1, 123.9, 123.0, 121.6, 119.0. Anal. Calcd. for $C_{25}H_{18}N_6O_3$: C, 66.66; H, 4.03; N, 18.66 Found: C, 66.82; H, 3.91; N, 18.66.

Synthesis of Cu_2O nanoparticles[2, 3]

Procedure A. Two low-temperature hydrothermal approaches were followed to prepare Cu_2O nanocubes with various sizes. For the synthesis of 100 nm Cu_2O nanocubes, a 500 mL round-bottomed flask containing 200 ml of DI water was placed in an oil bath at 60˚C for 15 min. To this, 25 mL of 0.1 M copper (II) acetate was added, and the solution was contentiously stirred. Then, 25 mL of 0.1 M NaOH was added dropwise, and the solution was let to heat to 60˚C for 10 min. Subsequently, 25 mL of 0.1 M hydrazine hydrate solution was added dropwise; hence the color of the solution turned to mustard yellow. The reaction was then allowed to proceed for 15 min at 60˚C with continuous stirring. The generated material was collected and washed multiple times using centrifugation at 10000 rpm for 10 min. The orange-yellow precipitate was then dried in a vacuum oven at 60˚C overnight.

Procedure B. The previous procedure was modified to prepare the 300 nm Cu_2O nanocubes. Briefly, 25 mL of 0.1 M copper acetate was mixed with 25 ml of 0.1 M NaOH in a 250 mL round bottom flask with continuous stirring at room temperature. After 10 min, the flask was placed in an oil bath at 60˚C for 20 min before adding 25 mL of 0.1 M hydrazine hydrate dropwise. The solution was stirred at 60˚C for 15 min then left quiescent for 10 min. Stirring was turned off, and the content was let to continue to heat for an additional 5 to 10 minutes. The content was cooled, filtered, washed, and dried overnight. The orange precipitate was collected, washed, and dried using the procedure above.

Procedure C. The 800-nm Cu_2O nanocubes were prepared according to a previously reported procedure with some modifications. Briefly, 876.4 mg of $CuSO_4 \cdot 5\ H_2O$ was dissolved in a 100 mL of DI water in a 250-mL round bottom flask. Then, 2 g of PVP was added to the solution, and the mixture was vigorously stirred for one h. Subsequently, 50 mL of 0.14 M Na_2CO_3 and 0.24 M sodium citrate solution was added dropwise. After 20 min, 1.26 g of anhydrous glucose was added to the solution. The flask was then transferred to a hot water bath maintained at 80˚C with continuous shaking for three h. After cooling to room temperature, the afforded brick-red precipitate was collected by vacuum filtration and dried overnight at 60˚C.

Figure S1 (A) shows TEM and SEM images of Cu_2O nanostructures afforded by procedure A. The analysis of these images indicate that procedure A resulted in the formation of 100 nm well defined Cu_2O nanocubes. Increasing the concentration of the reagents in procedure B led to the formation of 300 nm Cu_2O nanocubes as demonstrated by TEM and SEM images in Figure S1 (B). On the other hand, procedure C was followed to prepare 800 nm Cu_2O nanocubes as presented in Figure S1(C).

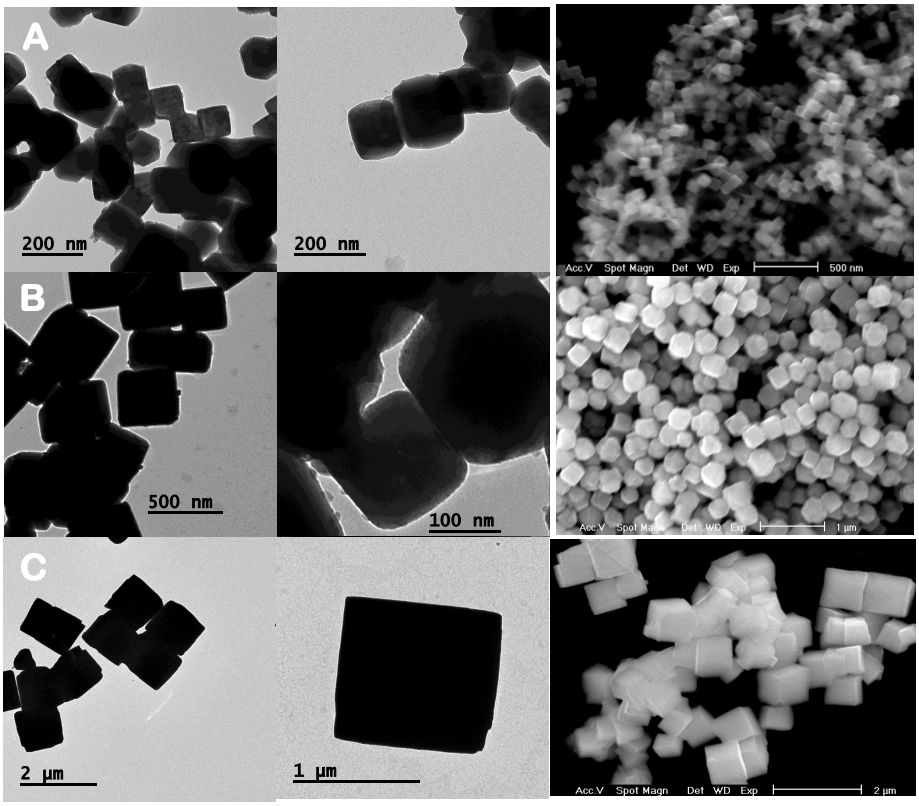


Figure S1. *Electron microscopy analysis of (A) 100 nm Cu_2O cubes, (B) 300 Cu_2O cubes nm, and (C) 800 nm Cu_2O cubes. The left and central panels display low and high magnification TEM images, and the right panel shows SEM images of Cu_2O cubes.*

Computational Methods

All calculations were performed using the Gaussian 09 package of programs.[4] Optimized geometries of all stationary points on the potential energy surface were obtained using the Denisty Functional Theory (M062X) with the employment of 6-311G* basis set. Optimizations were followed with vibrational analysis to ensure an imaginary frequency of zero for the ground states. The molecular electrostatic potentials were visualized using GaussView.[5] Hirshfeld Surface analyses were performed using Crystal Explorer (version 3.1) following established protocols with default values adopted for the underpinning calculations. Detailed descriptions of the technique and analysis are reported elsewhere.[6-8]

Electrostatic Potential Calculations

Similar to **1aa**, **1ac**, **1ad**, **1bk**, **1be and 1cl,** the MESP analyses of **1ab**, **1ae**, **1af**, **1ag**, **1ah**, **1ai**, **1aj**, **1bd** and **1cm** show that the greatest degree of negative charge (red region) is concentrated at the carbonyl oxygen and to a lesser extent near the N=N unit of the tetrazolone ring in these molecules, while positive charge (blue region) is concentrated at the centroid of the tetrazolone (Figure S2).

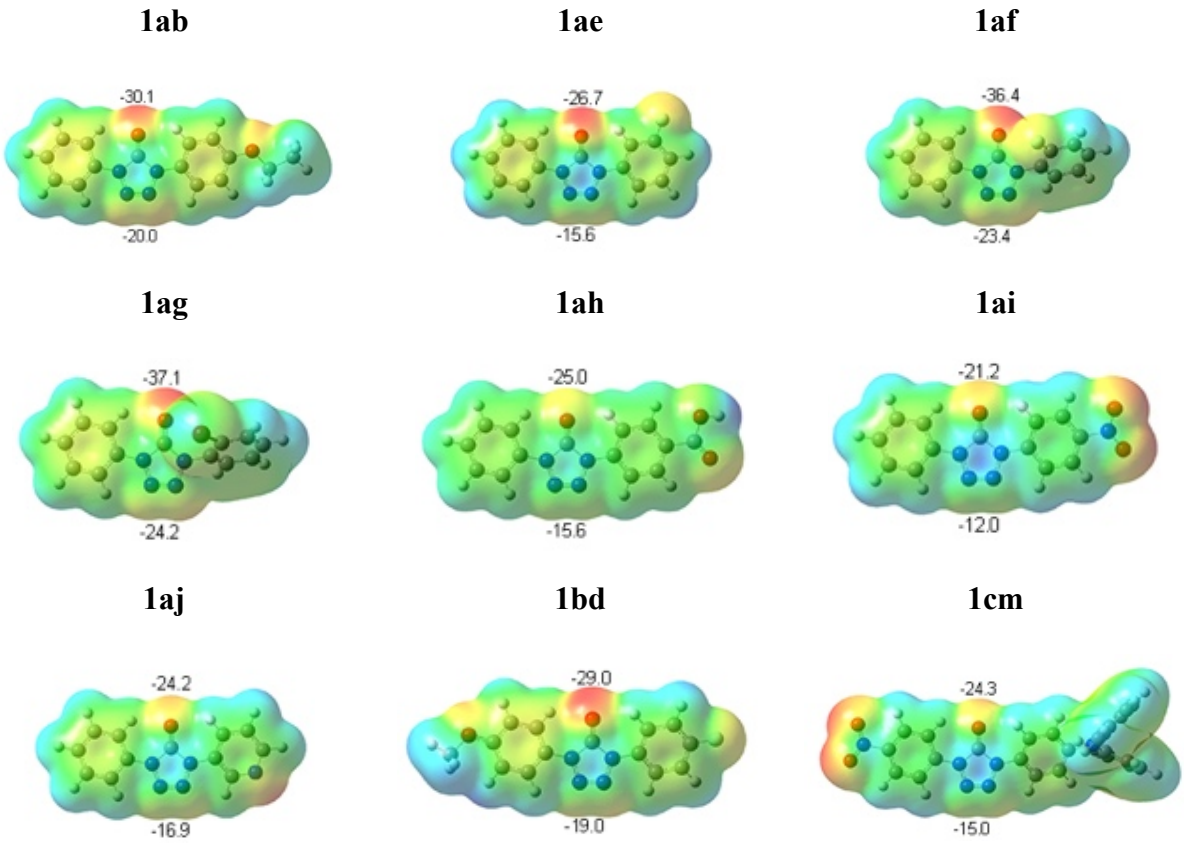


Figure S2. *Molecular electrostatic potentials at 0.001 a.u. iso-surface of electron density for* ***1ab***, ***1ae***, ***1af***, ***1ag***, ***1ah***, ***1ai***, ***1aj***, ***1bd*** *and* ***1cm****, calculated at M062X/6-311G*. The MESP values of the surface minima (Vs, min) at selected points are in kcal/mol.*

Single Crystal X-ray Crystallography

Single crystals of **1aa** suitable for X-ray diffraction were obtained by slow evaporation in dichloromethane. Crystals of **1ac**, **1ac**, **1be$_{MeCN}$** and **1cl** were obtained from acetonitrile; whereas, **1ad** and **1be$_{MeOH}$** were obtained from methanol. For X-ray examination and data collection, all crystals were mounted in a loop with Paratone-N oil and transferred to the goniostat bathed in a cold nitrogen stream.

Intensity data for **1aa**, **1ac**, **1bk**, **1be$_{MeCN}$** and **1cl** were collected at 150K on a Bruker PHOTON-II detector at Beamline 12.2.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ=0.7288Å. For data collection frames were measured in shutterless mode. Intensity data for **1ad** and **1be$_{MeOH}$** were collected at 150K on a Bruker D8 Venture Dual-wavelength Photon-II diffractometer using Cu Kα radiation, λ=1.54178Å or Mo Kα radiation, λ=0.71073Å, respectively. All data frames were measured in shutterless mode. The data frames were collected using the program APEX3[9] and processed using the program SAINT.[10] The data were corrected for decay, Lorentz and polarization effects as well as absorption and beam corrections based on the multi-scan technique as implemented in SADABS.[11]

All structures were solved by a combination of direct methods and the difference Fourier technique as implemented in the SHELX suite of programs,[12, 13] and refined by full-matrix least squares on F^2. Non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were calculated and treated with a riding model. The H-atom isotropic displacement parameters were defined as $a*U_{eq}$ (a=1.5 for methyl and 1.2 for all others) of the adjacent atom. F1 and H5 in **1ad** are disordered (occupancy is 50% at each site) due to crystallographic mirror symmetry. Atoms F1 and H6 in **1be$_{MeOH}$** are disordered with nearly equivalent occupancy (51:49%) at the C4 and C6 sites. Similarly, F1 in **1be$_{MeCN}$** is positionally-disordered (major occupancy 85% at the C6 site). Molecular structures and figures depicting the orientation of the rings in the complexes are given in Figures S3-S9. The refinement for all complexes in this study converged with crystallographic agreement factors as summarized in Tables S1-S7.

Compound 1aa

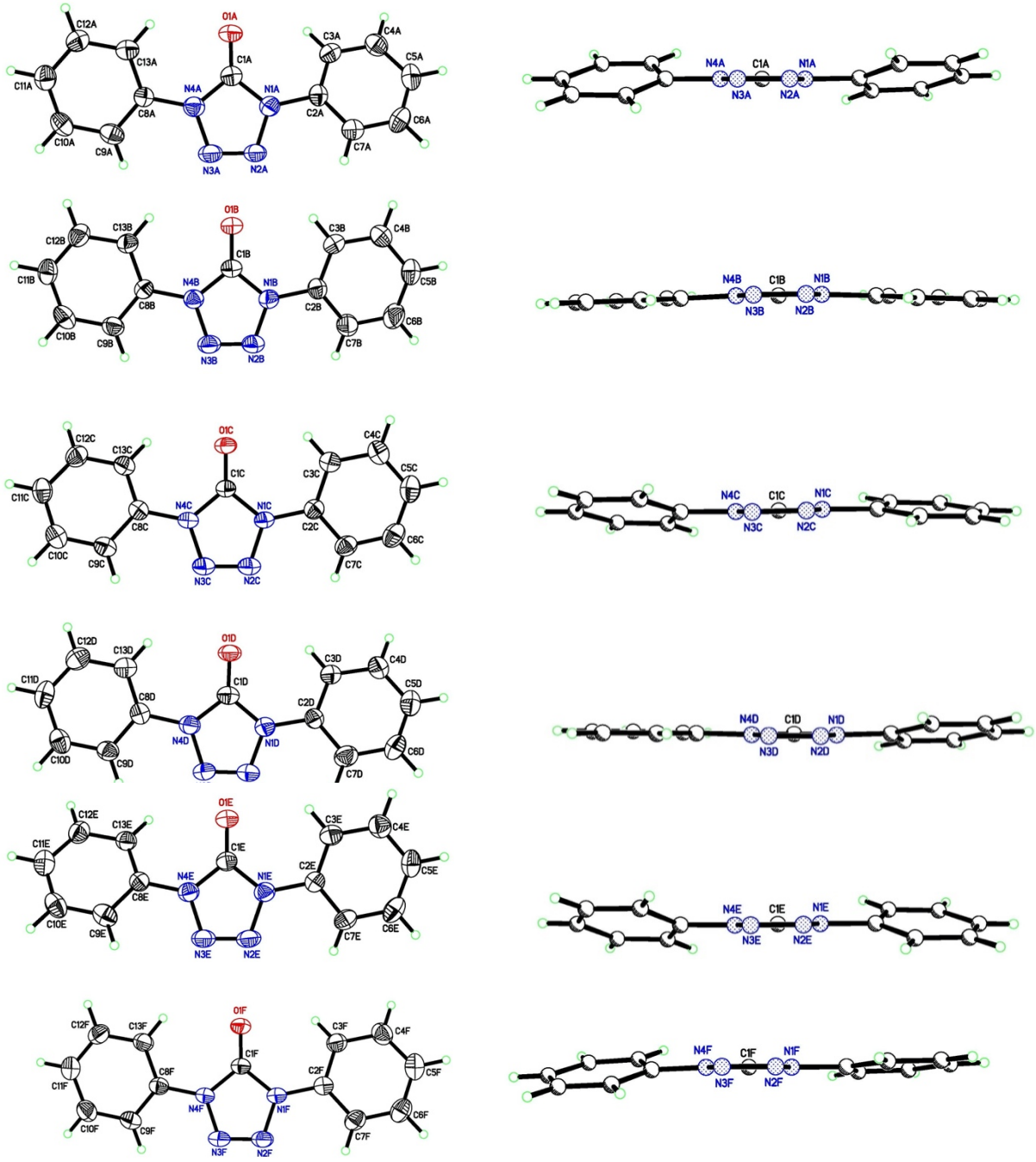


Figure S3. *ORTEP diagrams of* ***1aa*** *drawn at 50% probability ellipsoids (left) and ball-n-stick (right) showing ring orientation for each of the 6 independent molecules in the asymmetric unit.*

Compound 1ac

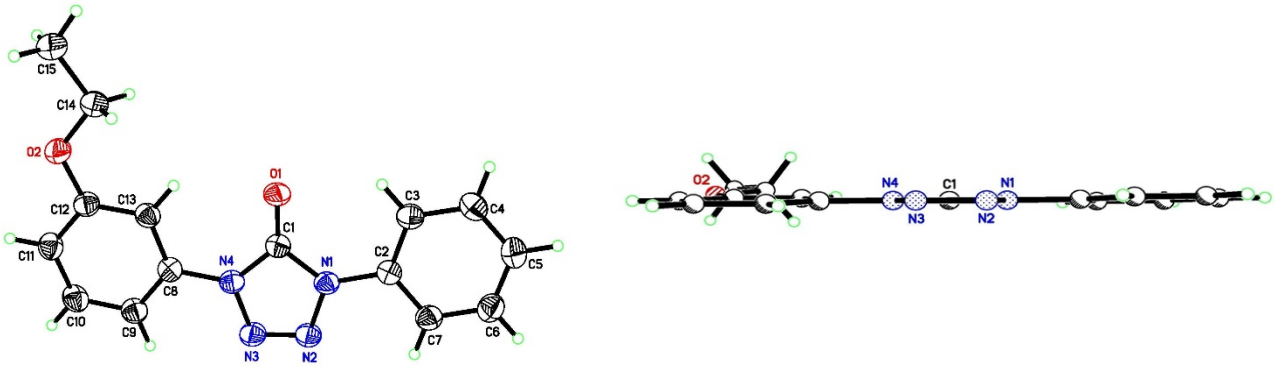


Figure S4. *ORTEP diagram of* ***1ac*** *(left) drawn at 50% probability ellipsoids and ball-n-stick (right) showing ring orientation.*

Compound 1ad

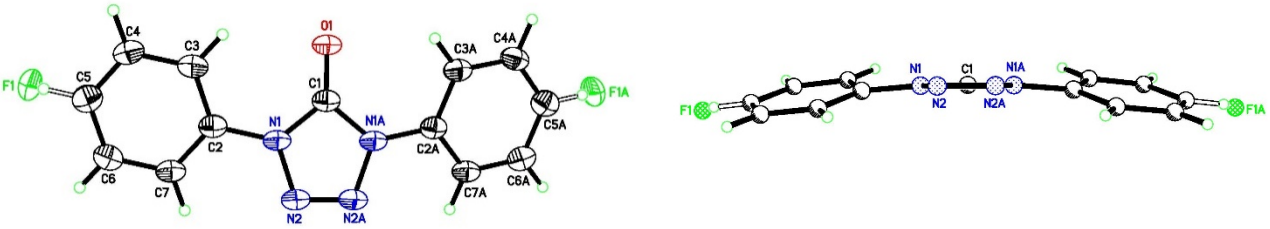


Figure S5. *ORTEP diagram of* ***1ad*** *(left) drawn at 50% probability ellipsoids and ball-n-stick (right) showing ring orientation.*

Compound 1bk

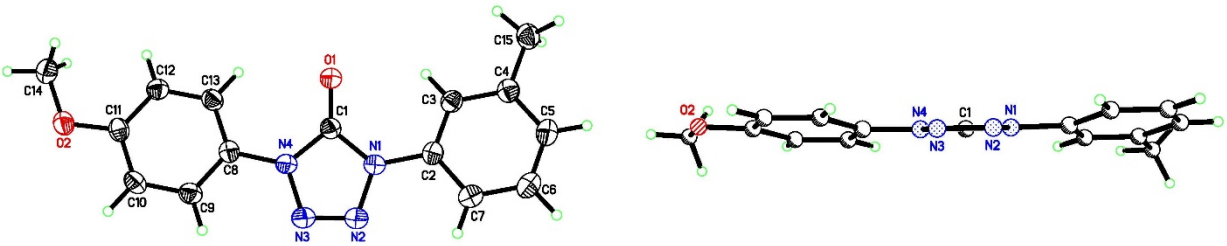


Figure S6. *ORTEP diagram of* ***1bk*** *(left) drawn at 50% probability ellipsoids and ball-n-stick (right) showing ring orientation.*

Compound 1be$_{MeOH}$

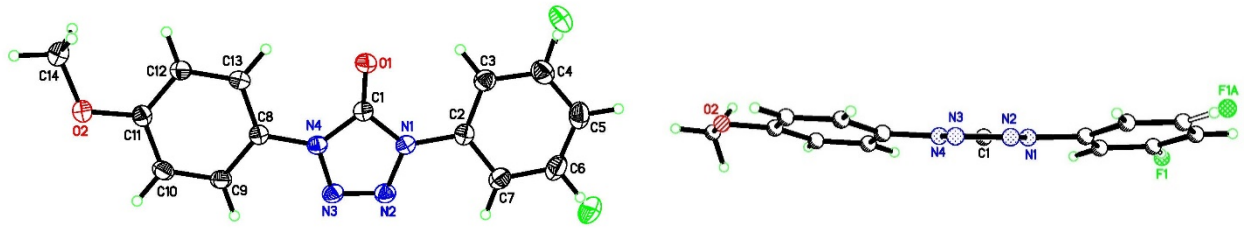


***Figure S7**. ORTEP diagram of **1be$_{MeOH}$** (left) drawn at 50% probability ellipsoids and ball-n-stick (right) showing ring orientation.*

Compound 1be$_{MeCN}$

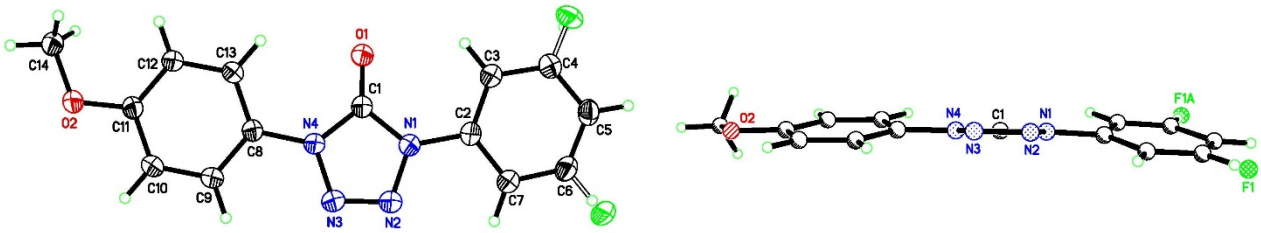


***Figure S8**. ORTEP diagram of **1be$_{MeCN}$** (left) drawn at 50% probability ellipsoids and ball-n-stick (right) showing ring orientation.*

Compound 1cl

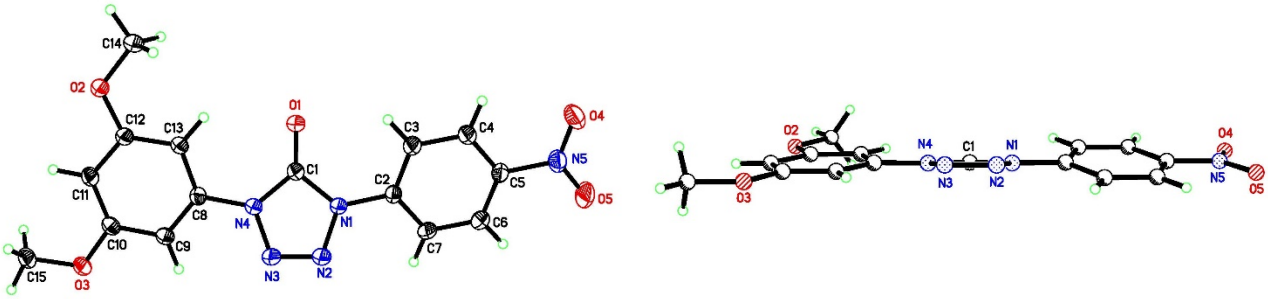
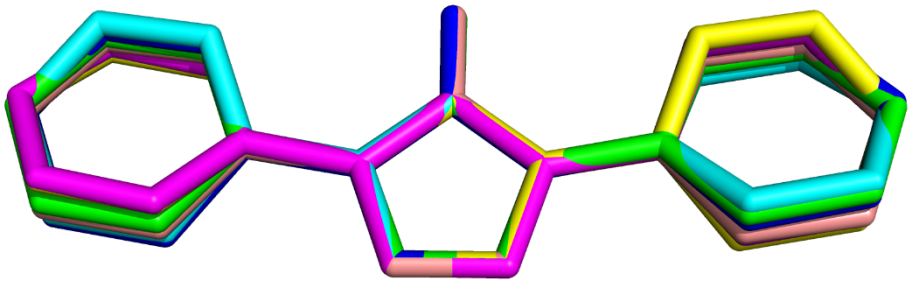
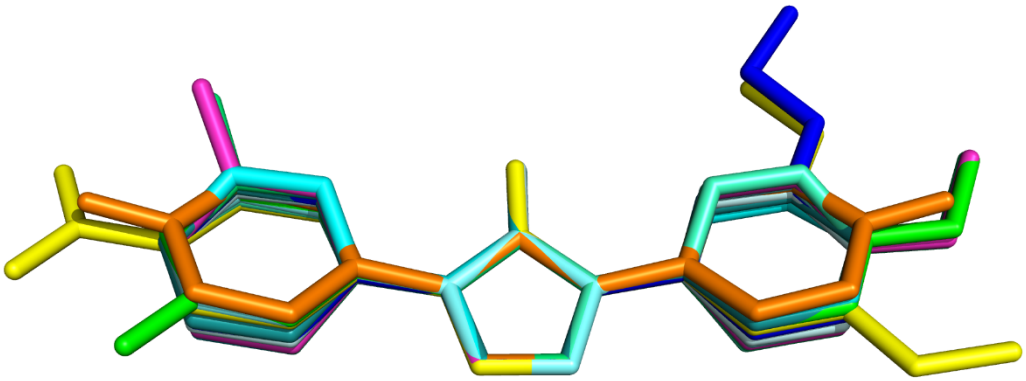


***Figure S9**. ORTEP diagram of **1cl** (left) drawn at 50% probability ellipsoids and ball-n-stick (right) showing ring orientation.*



1aa consists of 6 independent molecules that are overlayed.
Color Codes: Molecule 1: cyan; Molecule 2: pink; Molecule 3: magenta; Molecule 4: green; Molecule 5: yellow; Molecule 6: blue



All 12 molecules (6 independent molecules from **1aa** plus the remaining 6 complexes):
Color Codes: **1aa**: all 6 shown in cyan; **1ac**: blue; **1ad**: orange; **1be**$_{\mathbf{MeOH}}$: green; **1be**$_{\mathbf{MeCN}}$: teal; **1bk**: magenta; **1cl**: yellow

Figure S10. *Overlayed single crystal structures of all molecules.*

Table S1. Crystal data and structure refinement for 1aa

CSD deposition number	CCDC-2052219	
Empirical formula	$C_{13}H_{10}N_4O$	
Formula weight	238.25	
Temperature	150(2) K	
Wavelength	0.7288 Å	
Crystal system	Tetragonal	
Space group	$P4_1$	
Unit cell dimensions	a = 17.1647(6) Å	α = 90°
	b = 17.1647(6) Å	β = 90°
	c = 23.1194(11) Å	γ = 90°
Volume	6811.6(6) $Å^3$	
Z	24	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	2976	
Crystal size	0.152 x 0.036 x 0.014 mm^3	
θ range for data collection	1.216 to 27.901°	
Index ranges	$-22 \leq h \leq 22$, $-21 \leq k \leq 21$, $-29 \leq l \leq 29$	
Reflections collected	212893	
Independent reflections	15040 [R_{int} = 0.0666]	
Completeness to θ = 25.930°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.689	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15040 / 1 / 974	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2σ(I)]	R1 = 0.0545, wR2 = 0.1257	
R indices (all data)	R1 = 0.0692, wR2 = 0.1386	
Absolute structure parameter	0.1(2)	
Extinction coefficient	0.0048(4)	
Largest diff. peak and hole	0.455 and -0.582 $eÅ^{-3}$	

Table S2. Crystal data and structure refinement for 1ac

CSD deposition number	CCDC-2052220	
Empirical formula	$C_{15}H_{14}N_4O$	
Formula weight	282.30	
Temperature	150(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.1904(17) Å	α = 90°
	b = 4.7324(4) Å	β = 109.172(5)°
	c = 27.120(2) Å	γ = 90°
Volume	2690.0(4) $Å^3$	
Z	8	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	1184	
Crystal size	0.223 x 0.014 x 0.009 mm^3	
θ range for data collection	1.993 to 29.111°	
Index ranges	$-29 \le h \le 29$, $-6 \le k \le 6$, $-36 \le l \le 36$	
Reflections collected	36069	
Independent reflections	3353 [R_{int} = 0.0623]	
Completeness to θ = 25.930°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.628	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3353 / 0 / 192	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2σ(I)]	R1 = 0.0381, wR2 = 0.0891	
R indices (all data)	R1 = 0.0506, wR2 = 0.0971	
Extinction coefficient	0.0069(6)	
Largest diff. peak and hole	0.285 and -0.211 $eÅ^{-3}$	

Table S3. Crystal data and structure refinement for 1ad.

CSD deposition number	CCDC-2052221	
Empirical formula	$C_{13}H_9N_4OF$	
Formula weight	256.24	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pnma	
Unit cell dimensions	a = 7.4264(4) Å	α = 90°
	b = 26.8268(16) Å	β = 90°
	c = 5.6645(3) Å	γ = 90°
Volume	1128.52(11) $Å^3$	
Z	4	
Density (calculated)	1.508 Mg/m^3	
Absorption coefficient	0.946 mm^{-1}	
F(000)	528	
Crystal size	0.208 x 0.139 x 0.052 mm^3	
θ range for data collection	6.600 to 72.615°	
Index ranges	$-9 \leq h \leq 8$, $-33 \leq k \leq 33$, $-6 \leq l \leq 7$	
Reflections collected	30973	
Independent reflections	1144 [R_{int} = 0.0485]	
Completeness to θ = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.864 and 0.763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1144 / 0 / 94	
Goodness-of-fit on F^2	1.109	
Final R indices [I>2σ(I)]	R1 = 0.0325, wR2 = 0.0771	
R indices (all data)	R1 = 0.0351, wR2 = 0.0799	
Largest diff. peak and hole	0.170 and -0.180 $eÅ^{-3}$	

Table S4. Crystal data and structure refinement for 1bk.

CSD deposition number	CCDC-2052222	
Empirical formula	$C_{15}H_{14}N_4O_2$	
Formula weight	282.30	
Temperature	150(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.5655(10) Å	α = 90°
	b = 3.9863(4) Å	β = 100.713(2)°
	c = 28.977(3) Å	γ = 90°
Volume	1312.7(2) $Å^3$	
Z	4	
Density (calculated)	1.428 Mg/m^3	
Absorption coefficient	0.103 mm^{-1}	
F(000)	592	
Crystal size	0.103 x 0.031 x 0.011 mm^3	
θ range for data collection	2.128 to 29.129°	
Index ranges	$-15 \leq h \leq 15$, $-5 \leq k \leq 5$, $-38 \leq l \leq 38$	
Reflections collected	19690	
Independent reflections	3265 [R_{int} = 0.0591]	
Completeness to θ = 25.930°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3265 / 0 / 193	
Goodness-of-fit on F^2	1.029	
Final R indices [$I>2\sigma(I)$]	R1 = 0.0477, wR2 = 0.1119	
R indices (all data)	R1 = 0.0757, wR2 = 0.1285	
Extinction coefficient	0.0091(16)	
Largest diff. peak and hole	0.322 and -0.324 $eÅ^{-3}$	

Table S5. Crystal data and structure refinement for 1be$_{MeOH}$.

CSD deposition number	CCDC-2052223	
Empirical formula	$C_{14}H_{11}N_4O_2F$	
Formula weight	286.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 28.9051(18) Å	α = 90°
	b = 3.9102(2) Å	β = 108.226(3)°
	c = 11.6155(7) Å	γ = 90°
Volume	1246.98(13) Å^3	
Z	4	
Density (calculated)	1.525 Mg/m^3	
Absorption coefficient	0.116 mm^{-1}	
F(000)	592	
Crystal size	0.171 x 0.155 x 0.093 mm^3	
θ range for data collection	2.706 to 28.346°	
Index ranges	$-38 \leq h \leq 38$, $-5 \leq k \leq 5$, $-15 \leq l \leq 15$	
Reflections collected	19984	
Independent reflections	3123 [R_{int} = 0.0270]	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.864 and 0.763	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3123 / 1 / 201	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2σ(I)]	R1 = 0.0286, wR2 = 0.0739	
R indices (all data)	R1 = 0.0301, wR2 = 0.0755	
Largest diff. peak and hole	0.190 and -0.175 eÅ^{-3}	

Table S6. Crystal data and structure refinement for 1be$_{MeCN}$.

CSD deposition number	CCDC-2052224	
Empirical formula	$C_{14}H_{11}N_4O_2F$	
Formula weight	286.27	
Temperature	150(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3.84250(10) Å	α = 90°
	b = 21.4042(8) Å	β = 96.8753(12)°
	c = 15.2608(6) Å	γ = 90°
Volume	1246.11(8) Å^3	
Z	4	
Density (calculated)	1.526 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	592	
Crystal size	0.086 x 0.024 x 0.016 mm^3	
θ range for data collection	2.389 to 31.481°	
Index ranges	$-5 \leq h \leq 5$, $-30 \leq k \leq 30$, $-21 \leq l \leq 21$	
Reflections collected	38703	
Independent reflections	3840 [R_{int} = 0.0358]	
Completeness to θ = 25.930°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.681	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3840 / 1 / 201	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2σ(I)]	R1 = 0.0387, wR2 = 0.1024	
R indices (all data)	R1 = 0.0457, wR2 = 0.1082	
Largest diff. peak and hole	0.278 and -0.213 eÅ^{-3}	

Table S7. Crystal data and structure refinement for 1cl.

CSD deposition number	CCDC-2052225	
Empirical formula	C15 H13 N5 O5	
Formula weight	343.30	
Temperature	150(2) K	
Wavelength	0.7288 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 3.8994(2) Å	α = 90°
	b = 21.1784(11) Å	β = 102.3008(17)°
	c = 8.9913(5) Å	γ = 90°
Volume	725.48(7) $Å^3$	
Z	2	
Density (calculated)	1.572 Mg/m^3	
Absorption coefficient	0.127 mm^{-1}	
F(000)	356	
Crystal size	0.074 x 0.041 x 0.036 mm^3	
θ range for data collection	2.377 to 31.399°	
Index ranges	$-5 \leq h \leq 5$, $-30 \leq k \leq 30$, $-12 \leq l \leq 12$	
Reflections collected	21425	
Independent reflections	4367 [R_{int} = 0.0394]	
Completeness to θ = 25.930°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.711	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4367 / 1 / 229	
Goodness-of-fit on F^2	1.073	
Final R indices [I>2σ(I)]	R1 = 0.0410, wR2 = 0.0888	
R indices (all data)	R1 = 0.0437, wR2 = 0.0913	
Extinction coefficient	0.055(12)	
Largest diff. peak and hole	0.398 and -0.415 $eÅ^{-3}$	

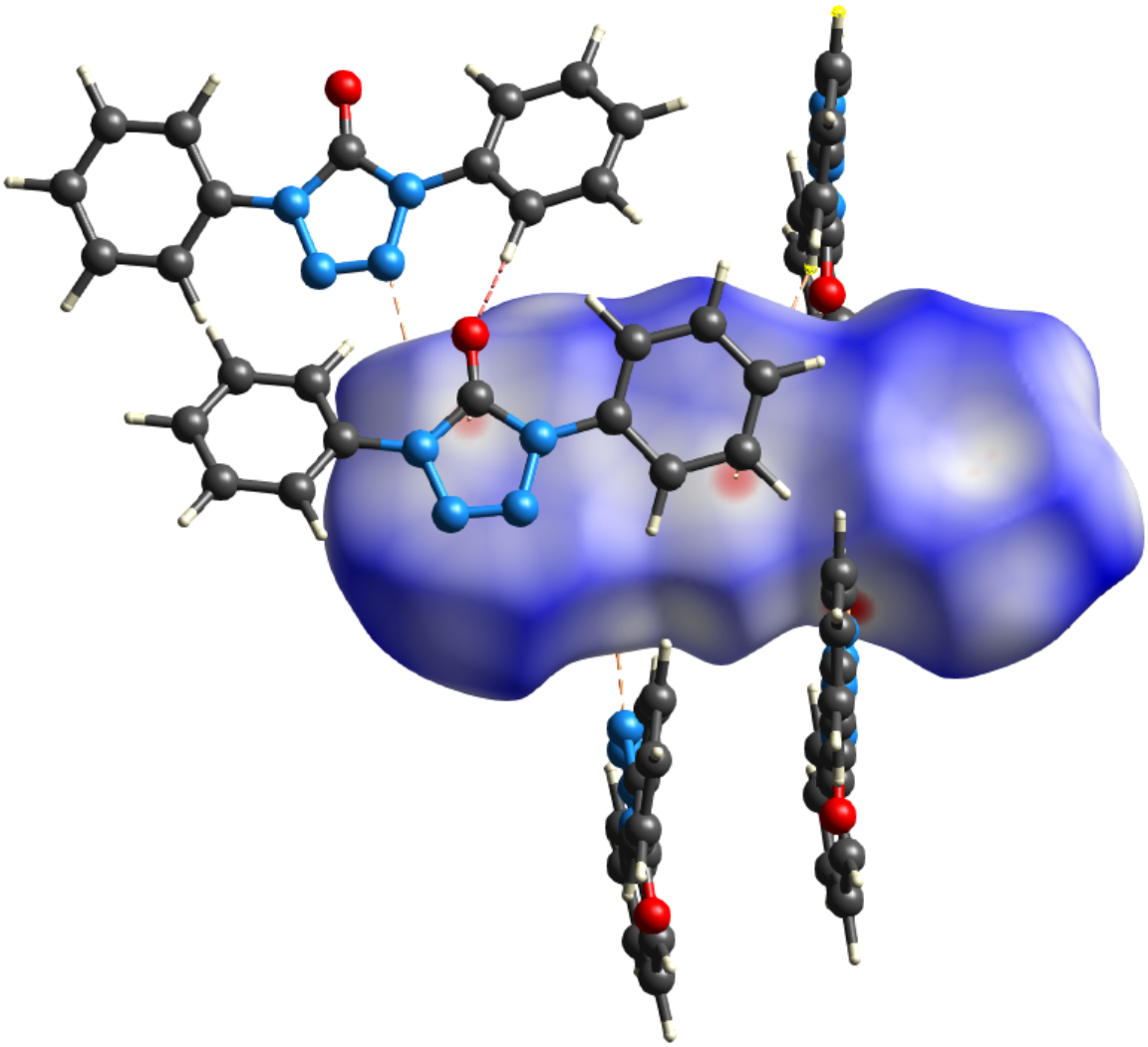


Figure S11A. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1618 to 1.2496 a.u. for* ***1aa*** *molecule 1 showing intermolecular interactions.*

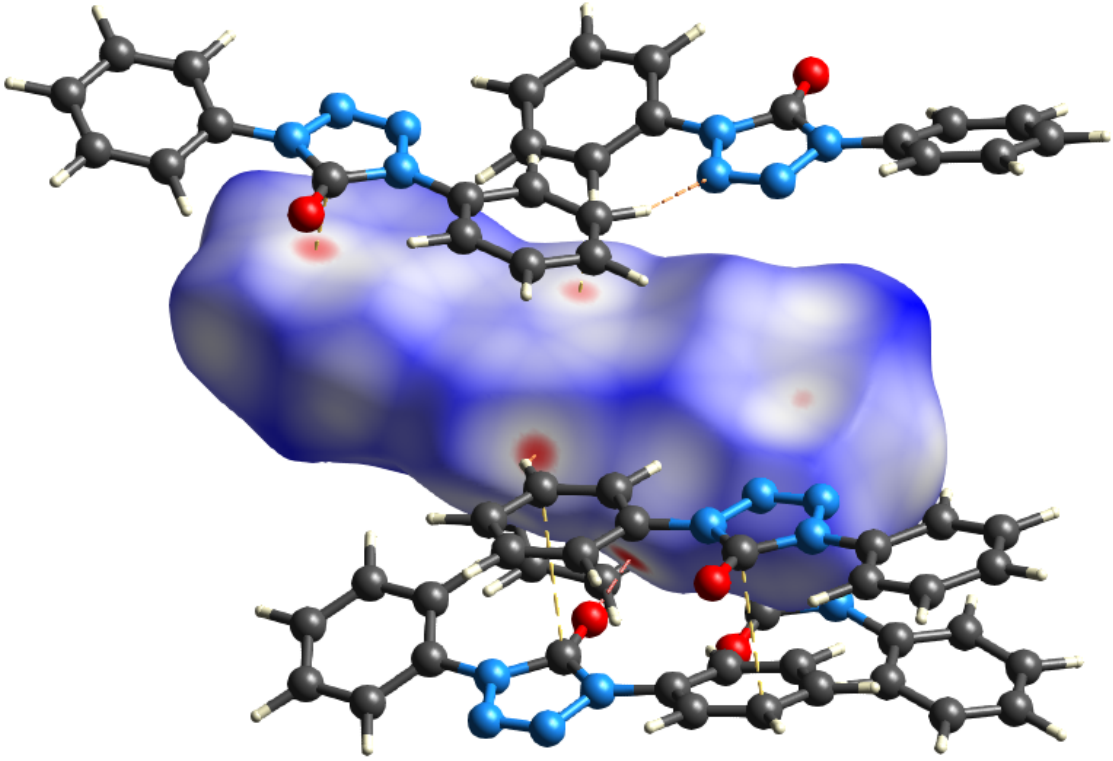


Figure S11B. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1618 to 1.2496 a.u. for* ***1aa*** *molecule 2 showing intermolecular interactions.*

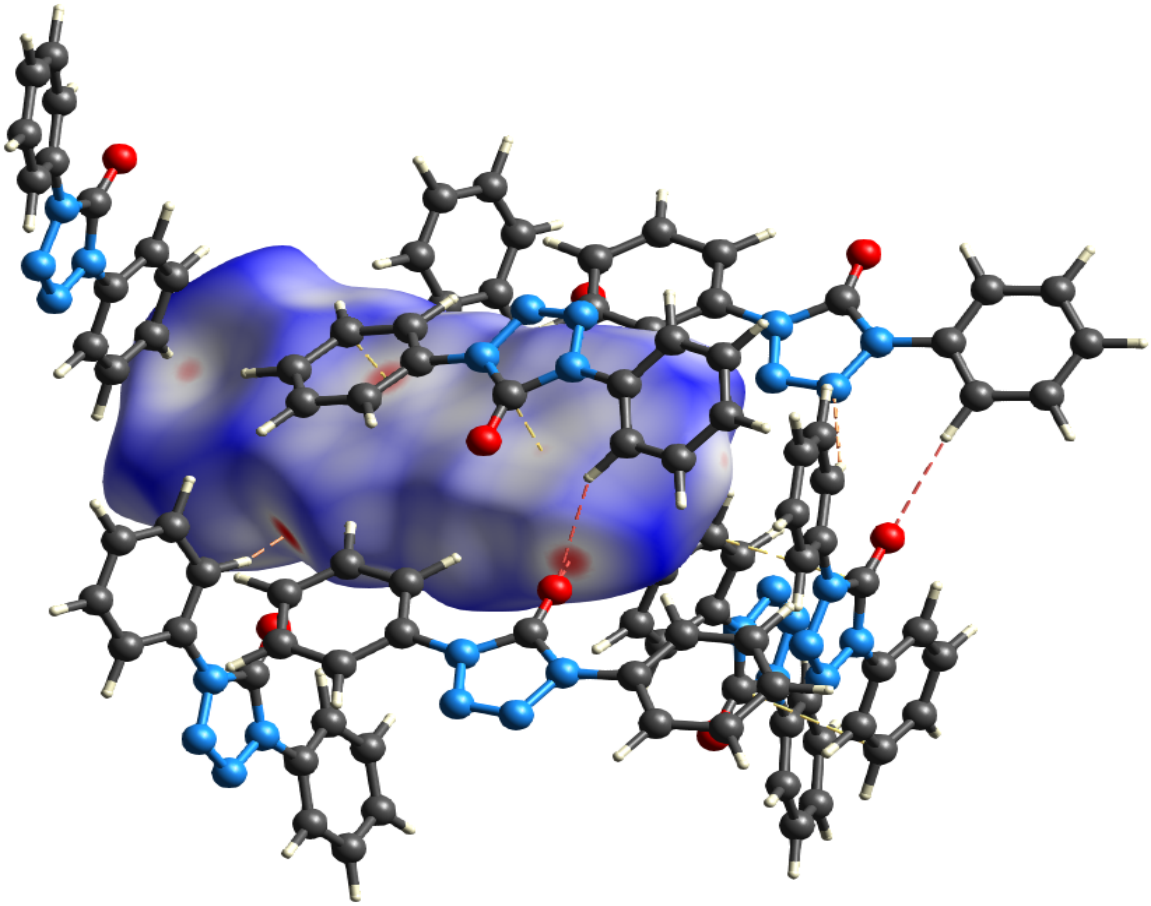


***Figure S11C**. Hirshfeld surfaces mapped over d_{norm} within the range -0.1618 to 1.2496 a.u. for **1aa** molecule 3 showing intermolecular interactions.*

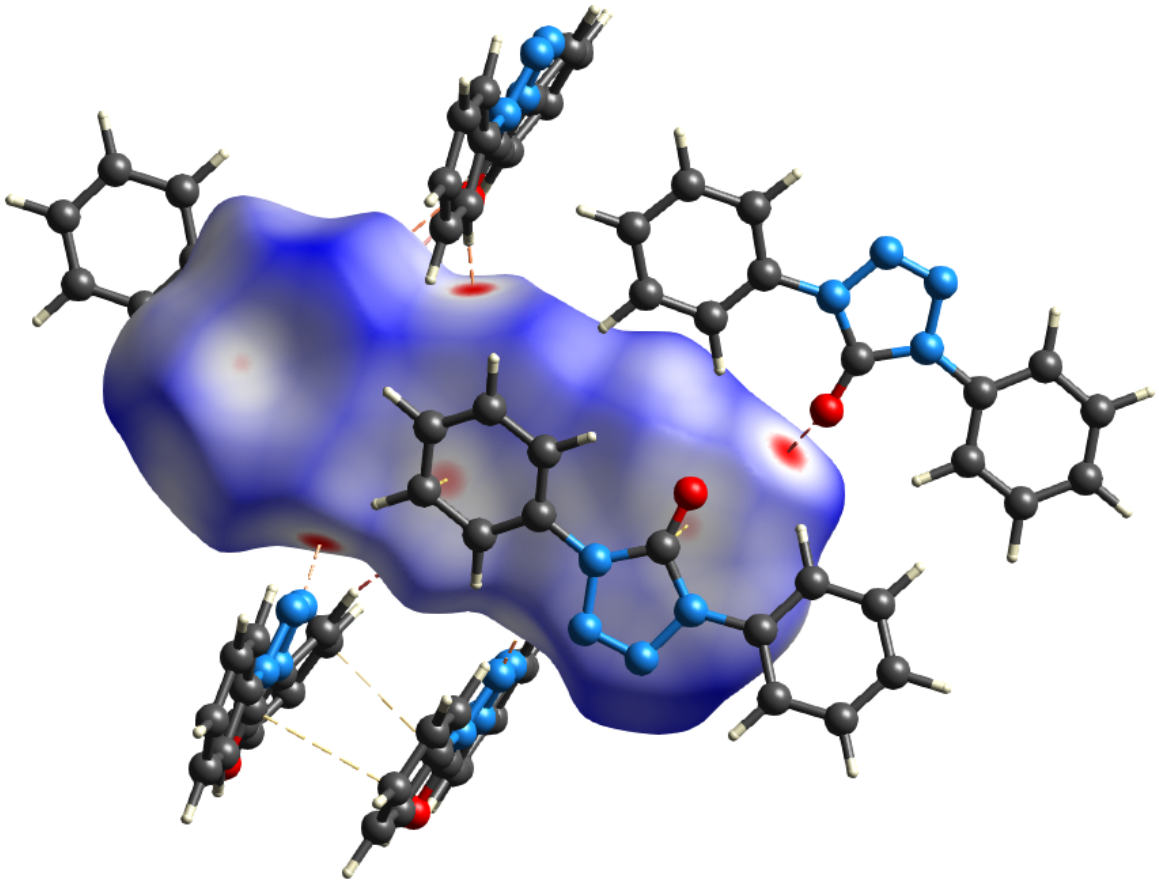


***Figure S11D**. Hirshfeld surfaces mapped over d_{norm} within the range -0.1618 to 1.2496 a.u. for **1aa** molecule 4 showing intermolecular interactions.*

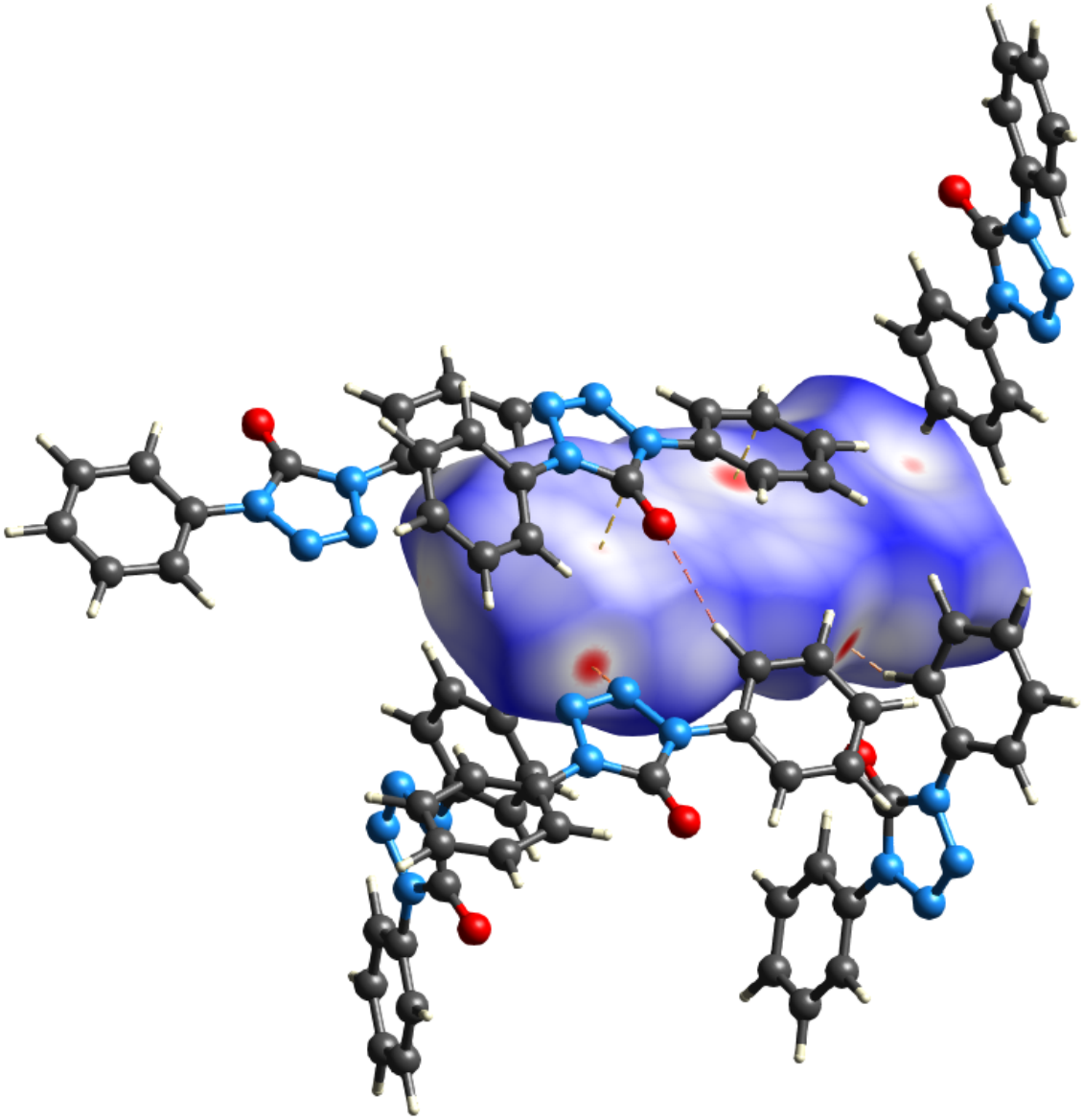


Figure S11E. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1618 to 1.2496 a.u. for* ***1aa*** *molecule 5 showing intermolecular interactions.*

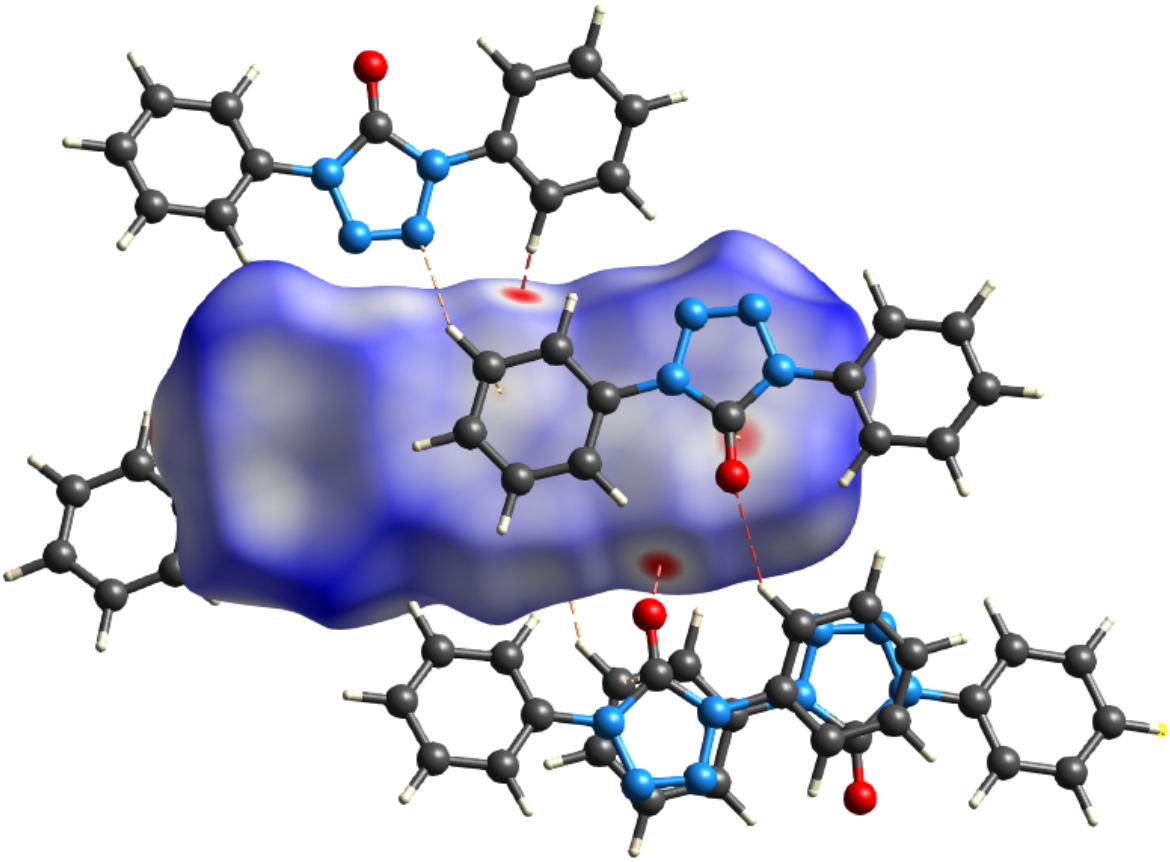


Figure S11F. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1618 to 1.2496 a.u. for* ***1aa*** *molecule 6 showing intermolecular interactions.*

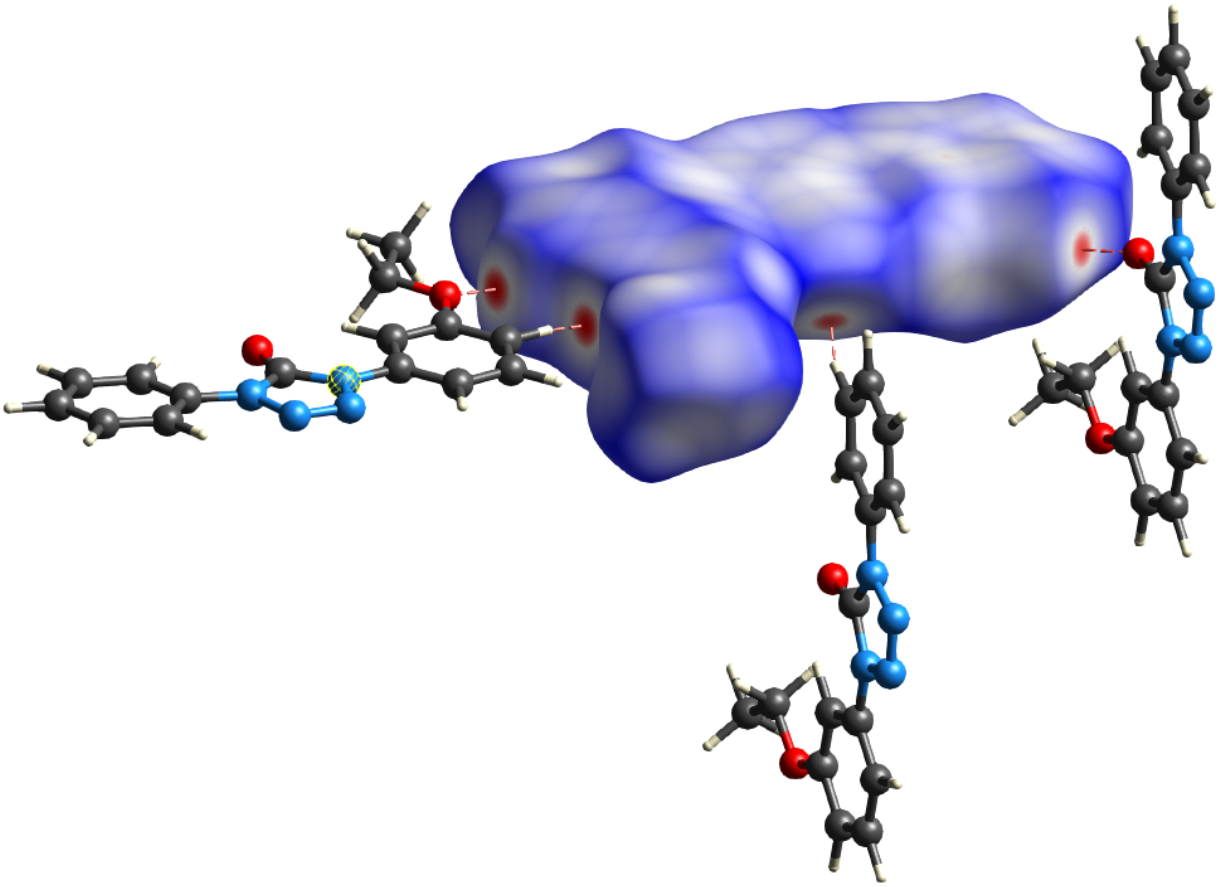


Figure S12. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1651 to1.1310 a.u. for* ***1ac*** *showing intermolecular interactions.*

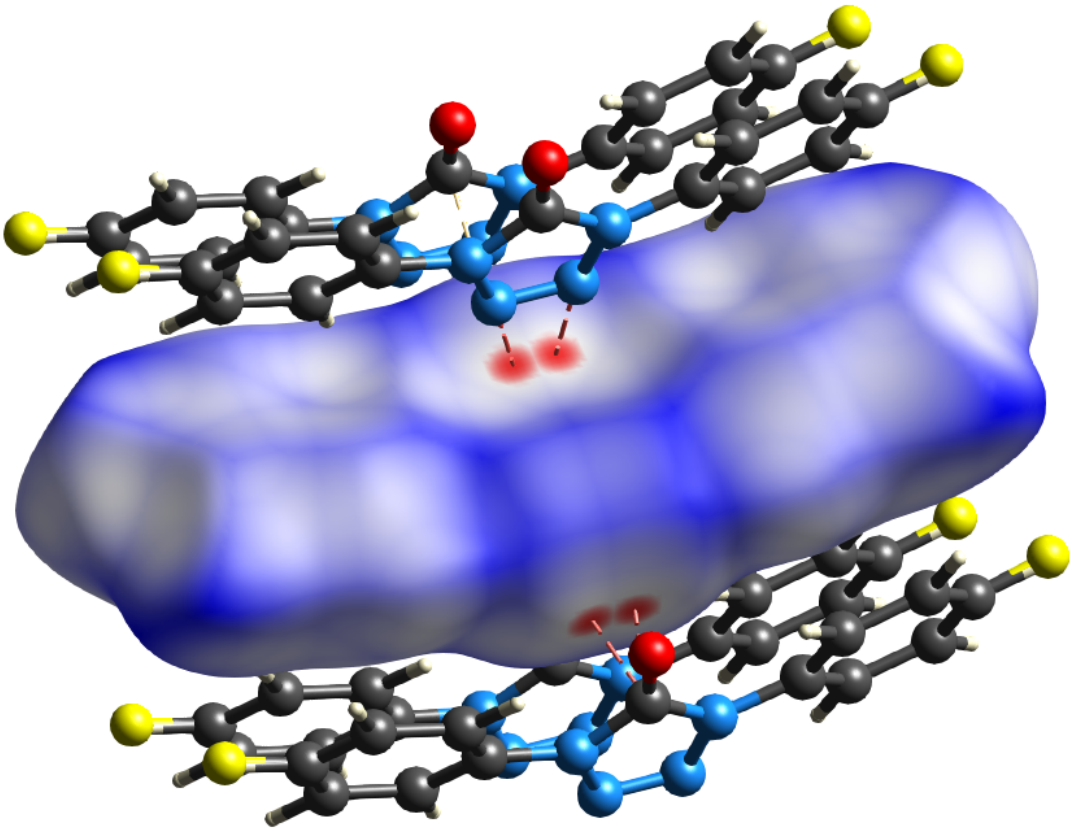


Figure S13. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.0786 to 1.1364 a.u. for* ***1ad*** *showing intermolecular interactions.*

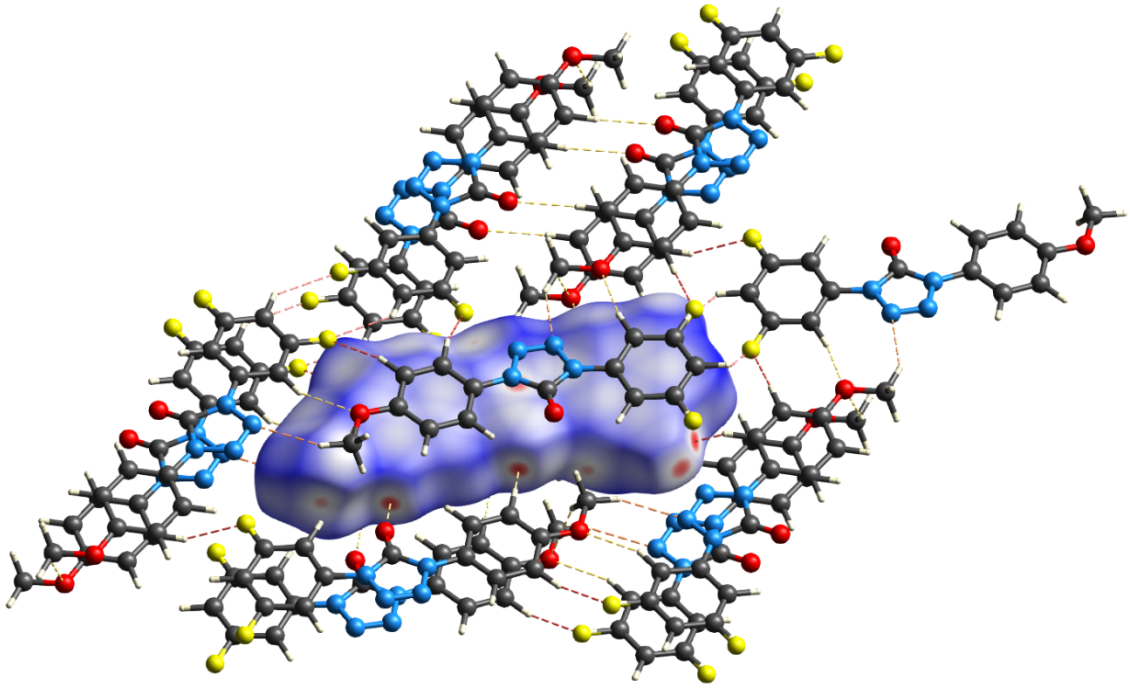


Figure S14. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1469 to 1.0636 a.u. for* ***1be***$_{MeCN}$ *showing intermolecular interactions.*

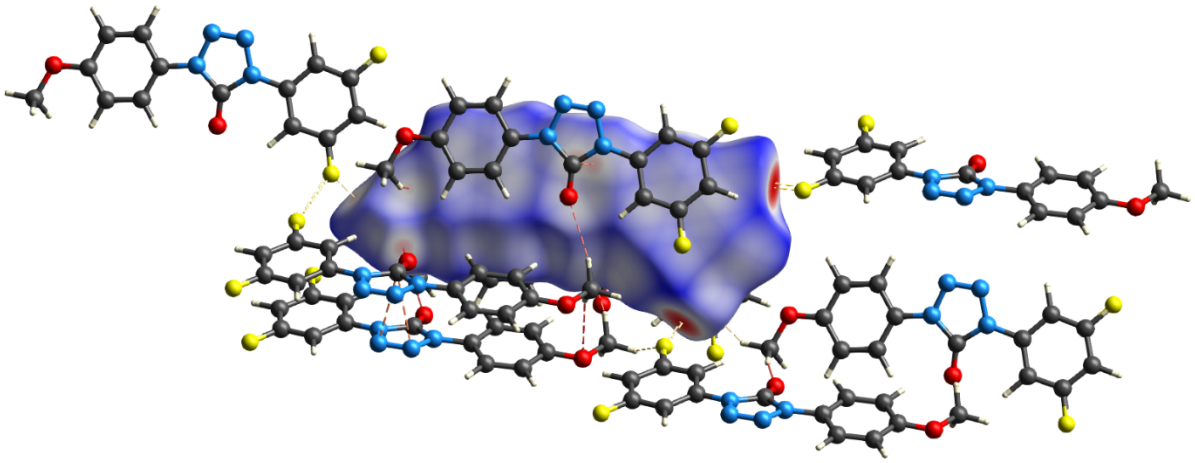


Figure S15. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.4880 to 1.0802 a.u. for* ***1be***$_{MeOH}$ *showing intermolecular interactions.*

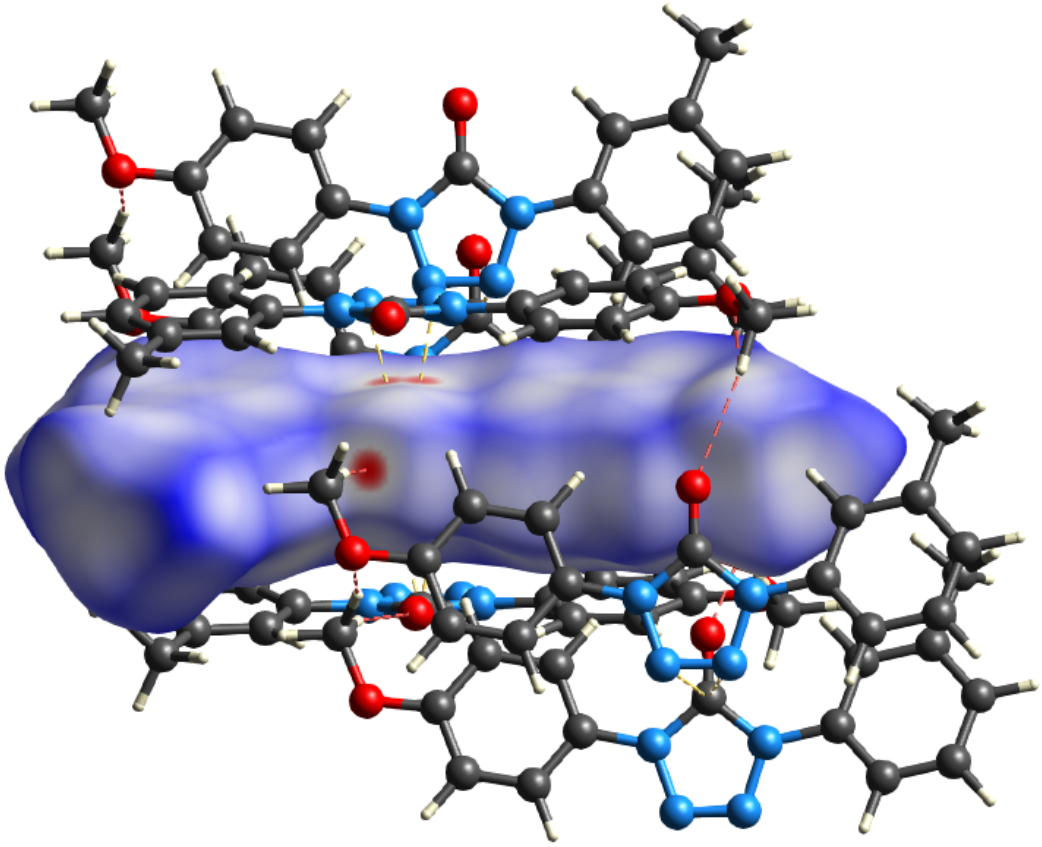


Figure S16. *Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1291 to 1.1881 a.u. for* ***1bk*** *showing intermolecular interactions.*

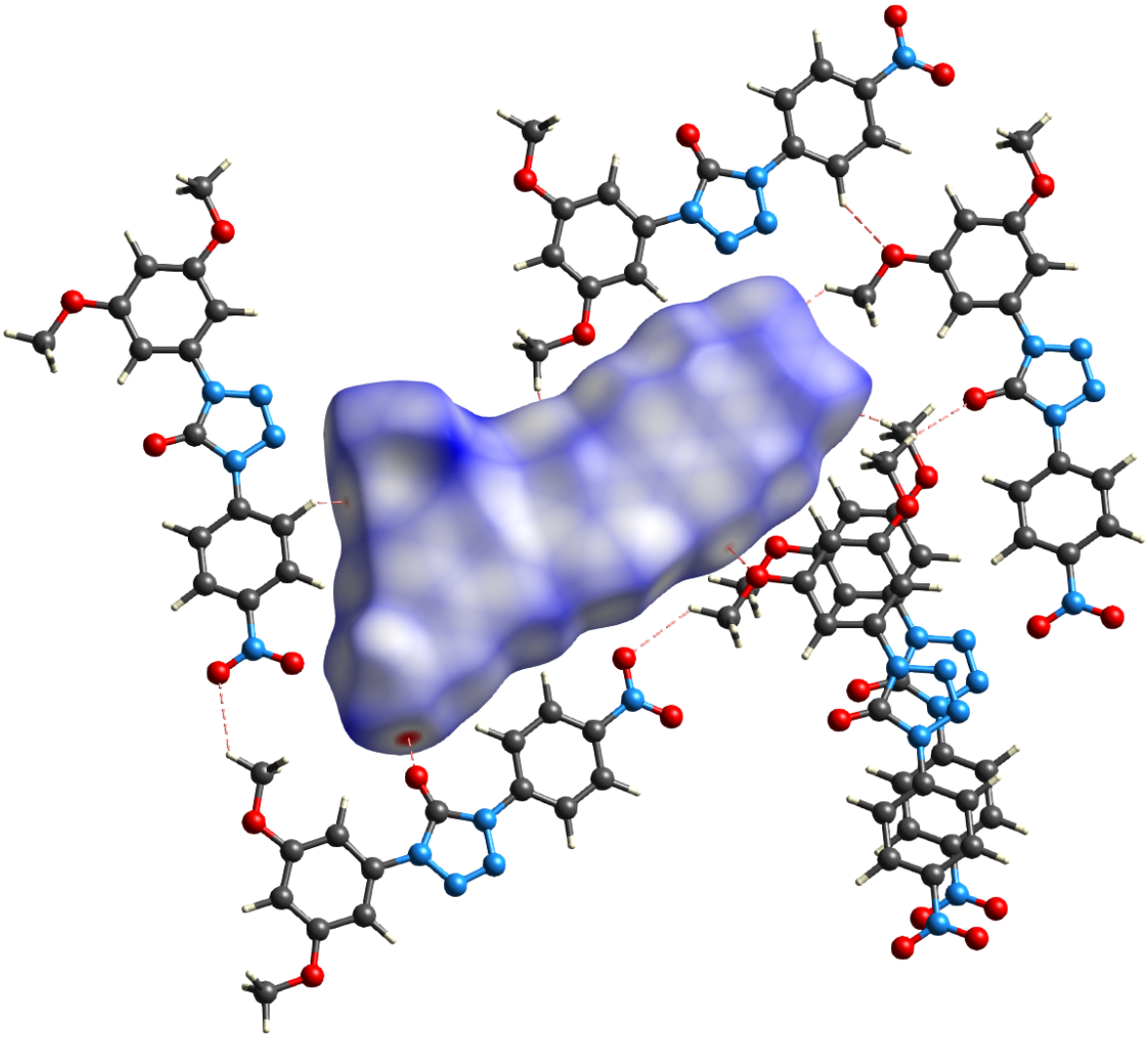


Figure S17*. Hirshfeld surfaces mapped over* d_{norm} *within the range -0.1311 to 1.3046 a.u. for* ***1cl*** *showing intermolecular interactions.*

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TR020720- Phenyl Tetrazolone DRY

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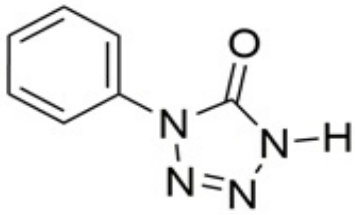
Nucleus	^{1}H



2a

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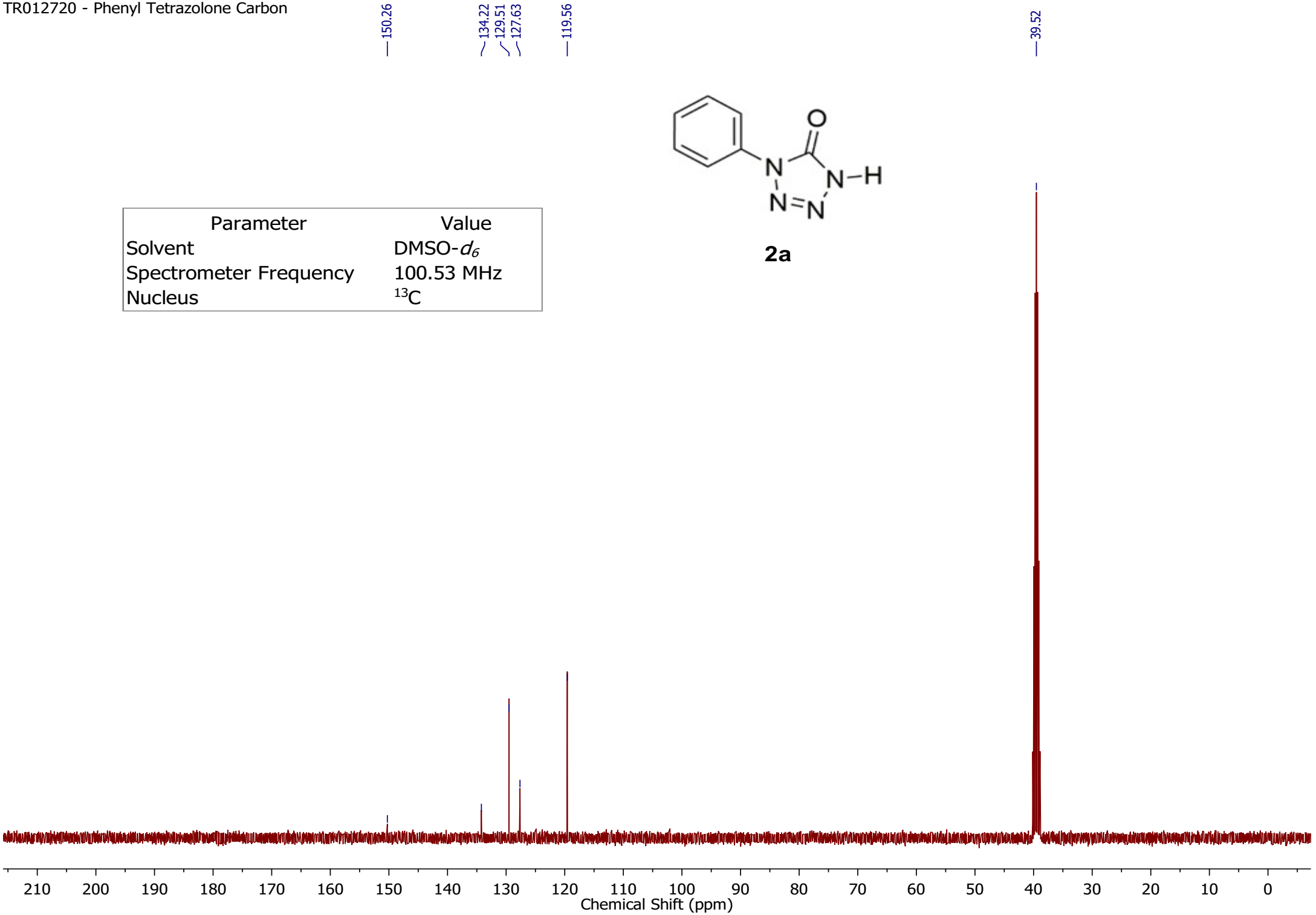

4MeO Tetrazolone_

Parameter	Value
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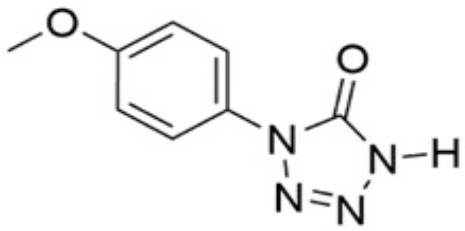
Nucleus	^{1}H



2b

TR050719 - 4MeO Tetrazolone Carbon

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150.37
127.06
122.06
114.58
55.49
39.52

Parameter	Value
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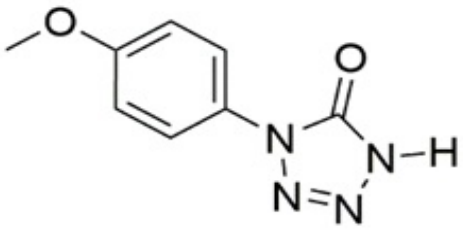
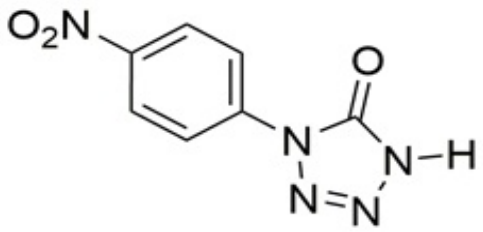


2b

4NO2 Tetrazolone

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



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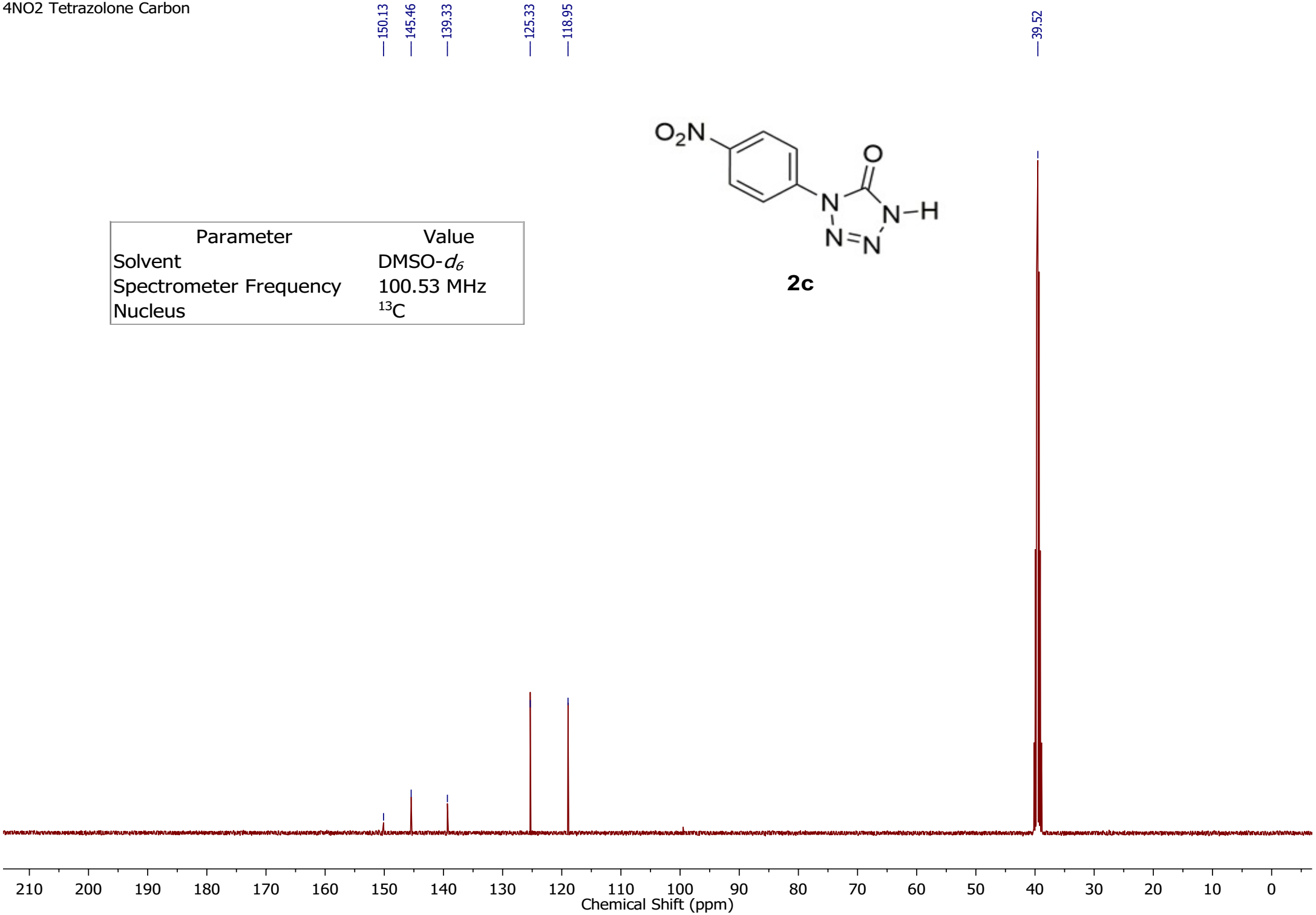

TR012620

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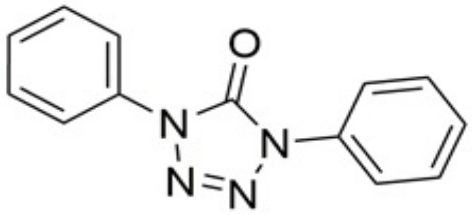

1aa

Phenyl DT_Carbon

147.22
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129.59
128.21
120.27
39.52

Parameter	Value
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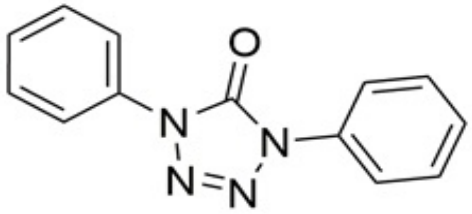
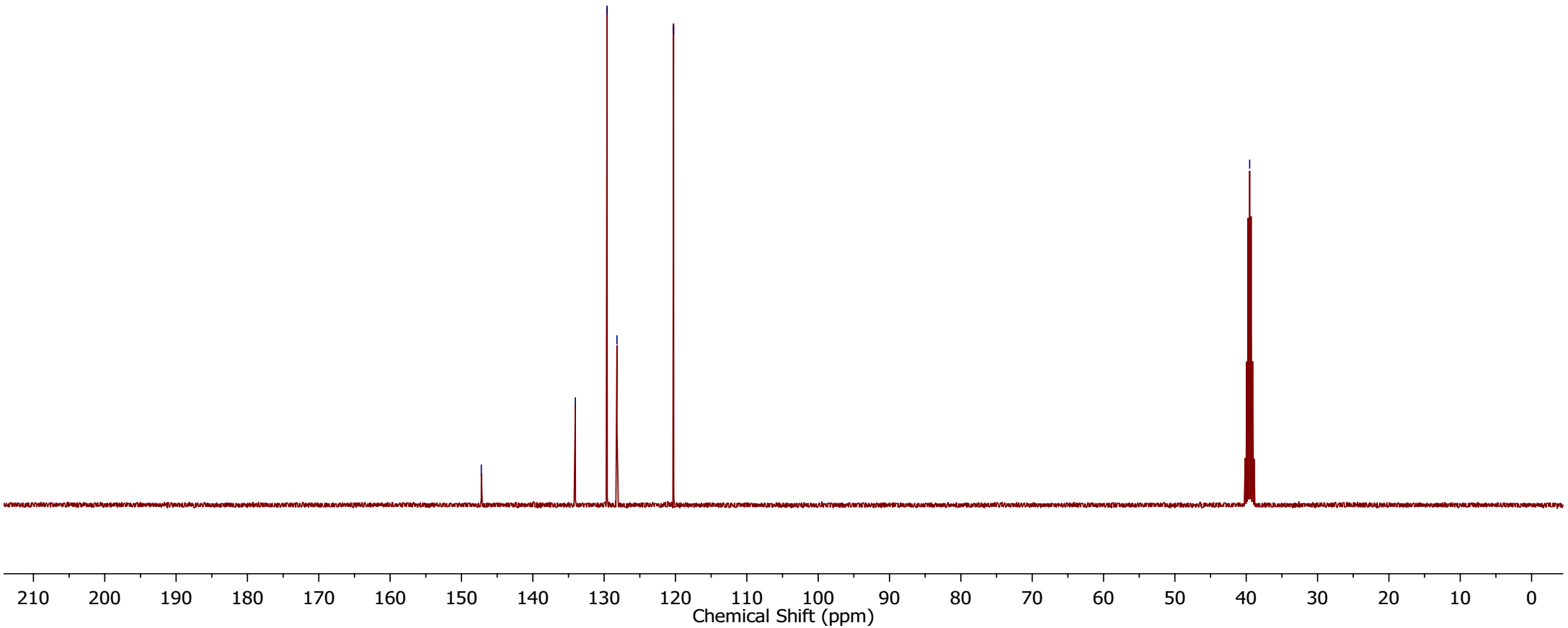


1aa



TR062920_4EtO___DT

Parameter	Value
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Spectrometer Frequency	399.78 MHz
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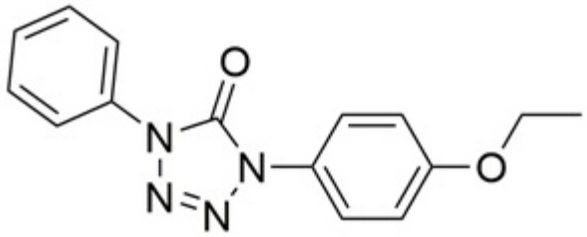

1ab

Chemical Shift (ppm)

TR062920_4EtO DT_Carbon

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129.58
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126.64
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120.12
115.06
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39.94
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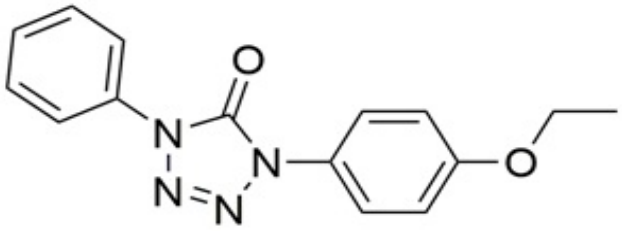
39.52
39.31
39.10
38.89
14.58



1ab

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	100.53 MHz
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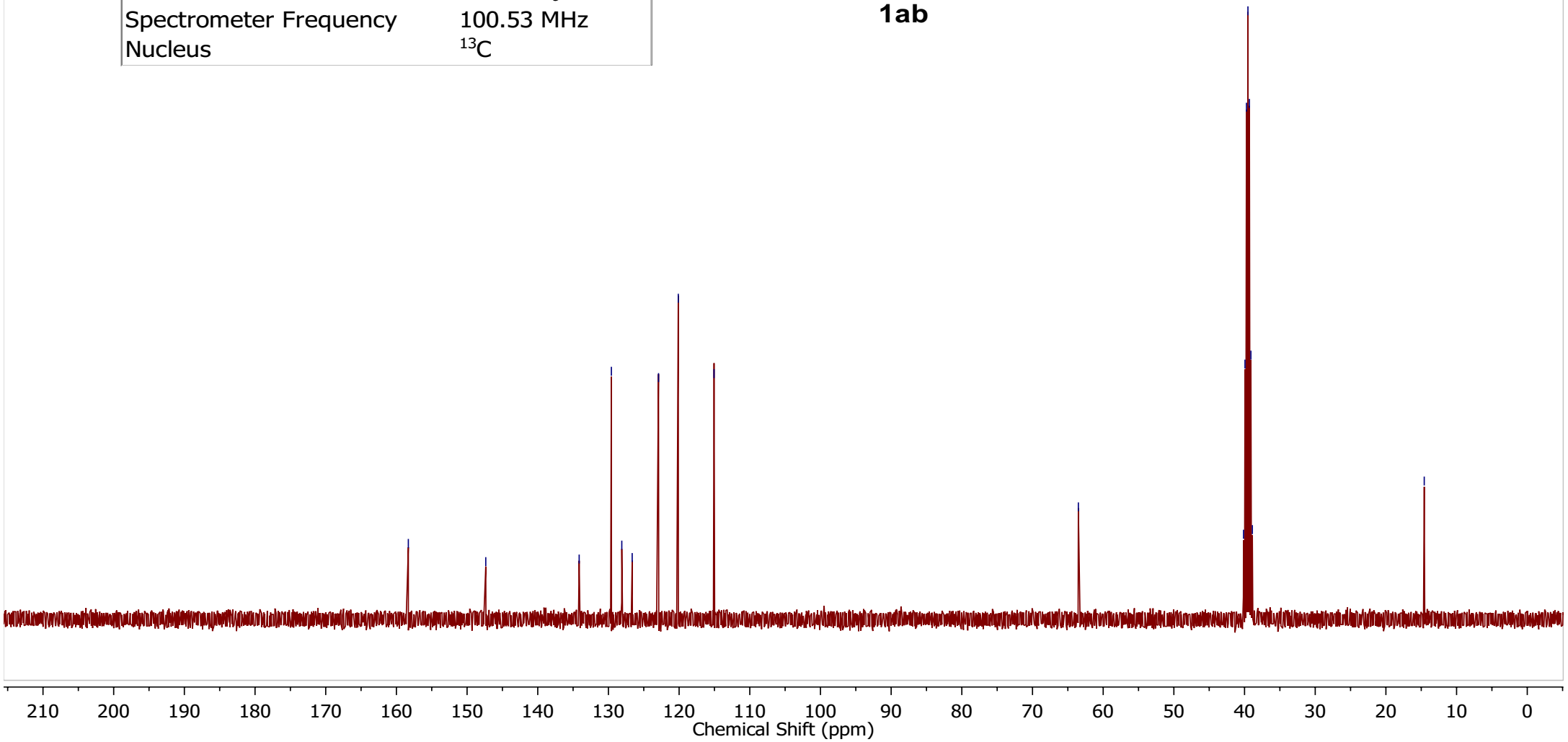

TR021520 - 3EtO DT

Parameter	Value
Solvent	DMSO-d_6
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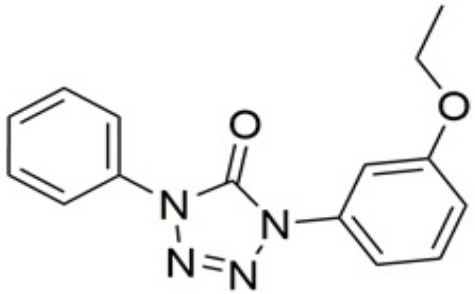
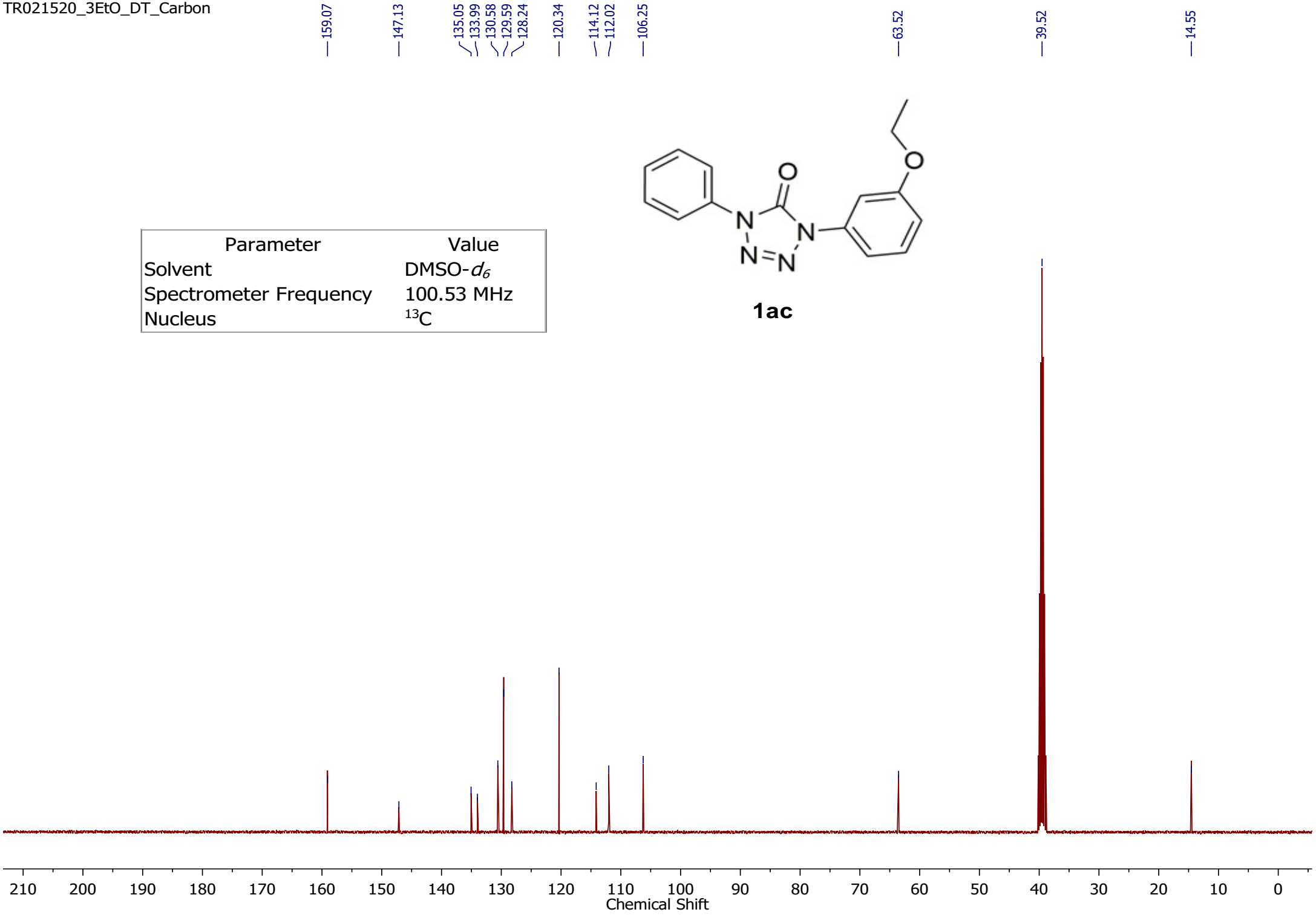


1ac

Chemical Shift (ppm)

TR021520_3EtO_DT_Carbon



TR020620 - 4F Diaryl Tetrazolone

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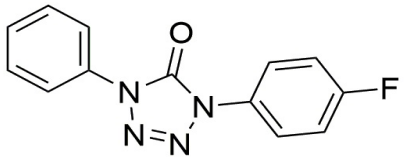

1ad

TR020620 - 4F Diaryl Tetrazolone Carbon

Parameter	Value
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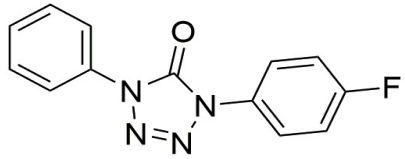

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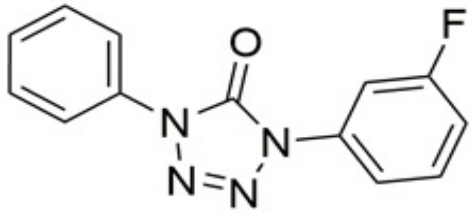
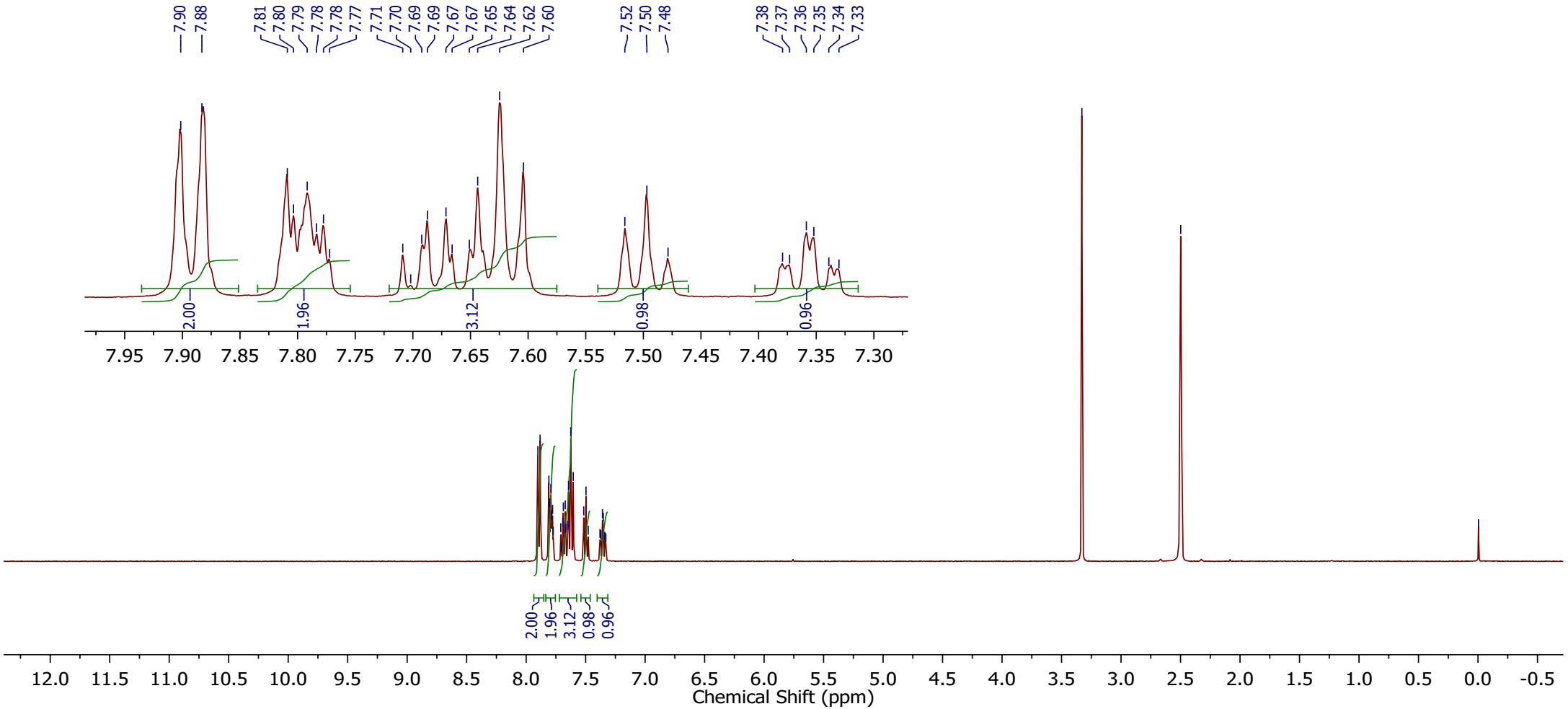
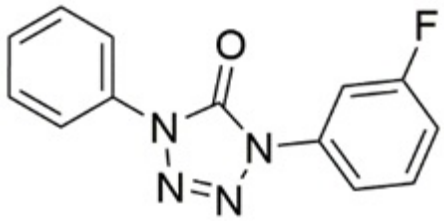


1ae

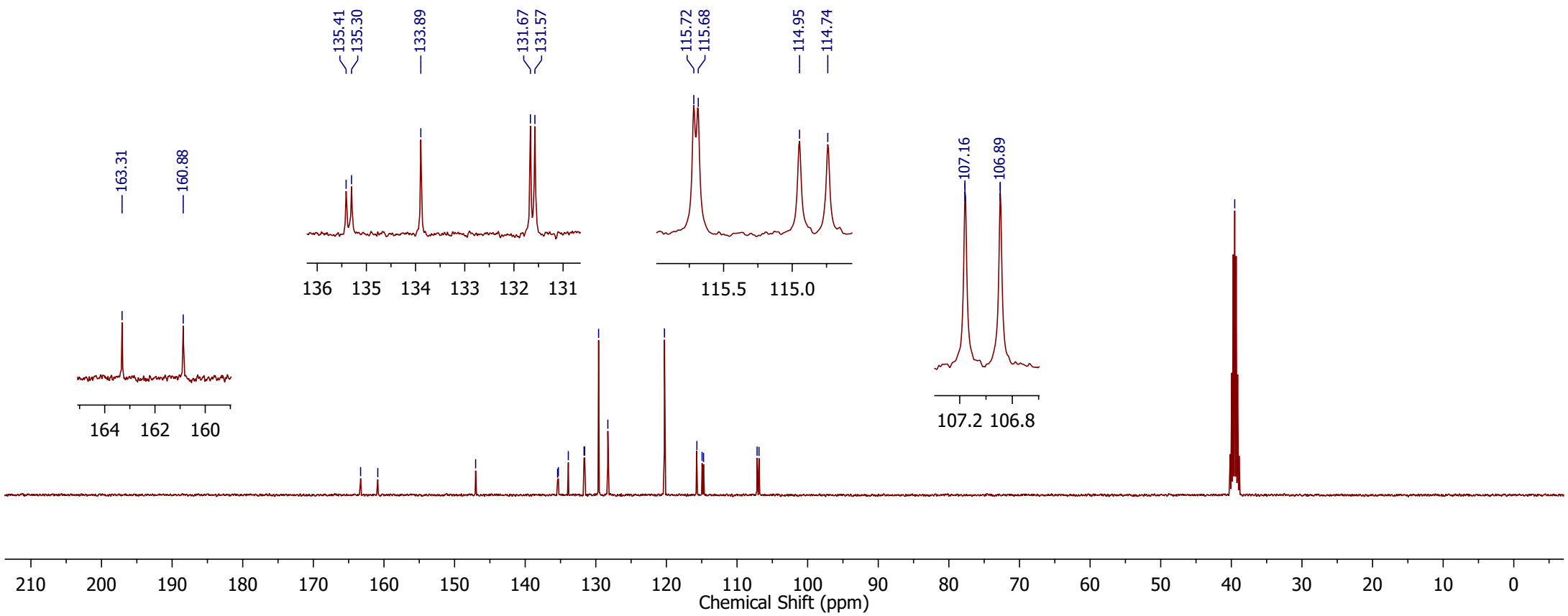


3F_DT_Carbon

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	100.53 MHz
Nucleus	^{13}C

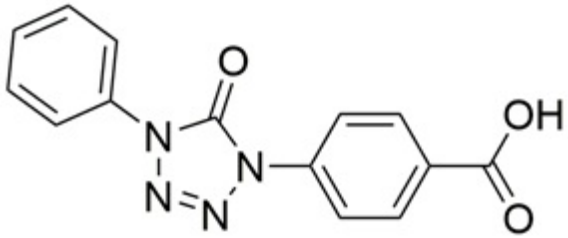


1ae

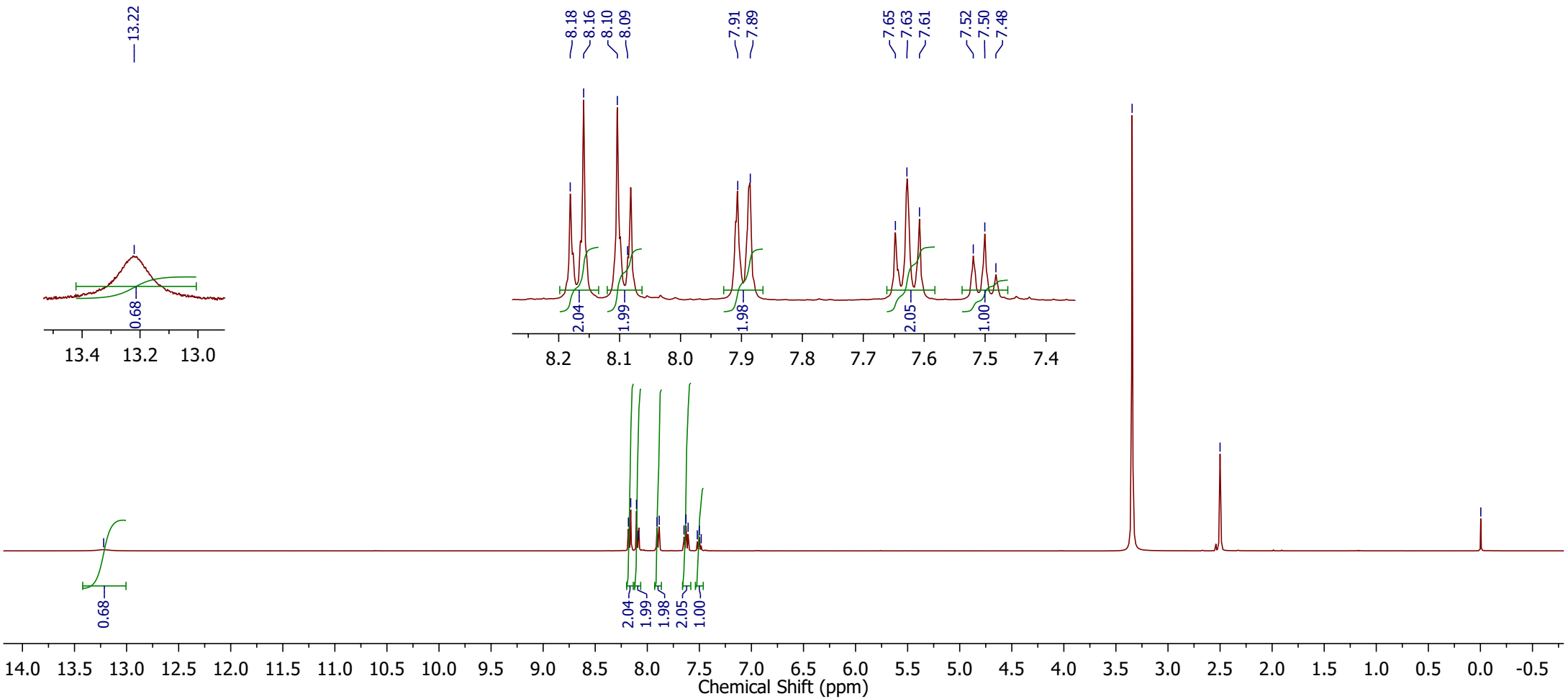


TR060920_4COOH_Precipitate

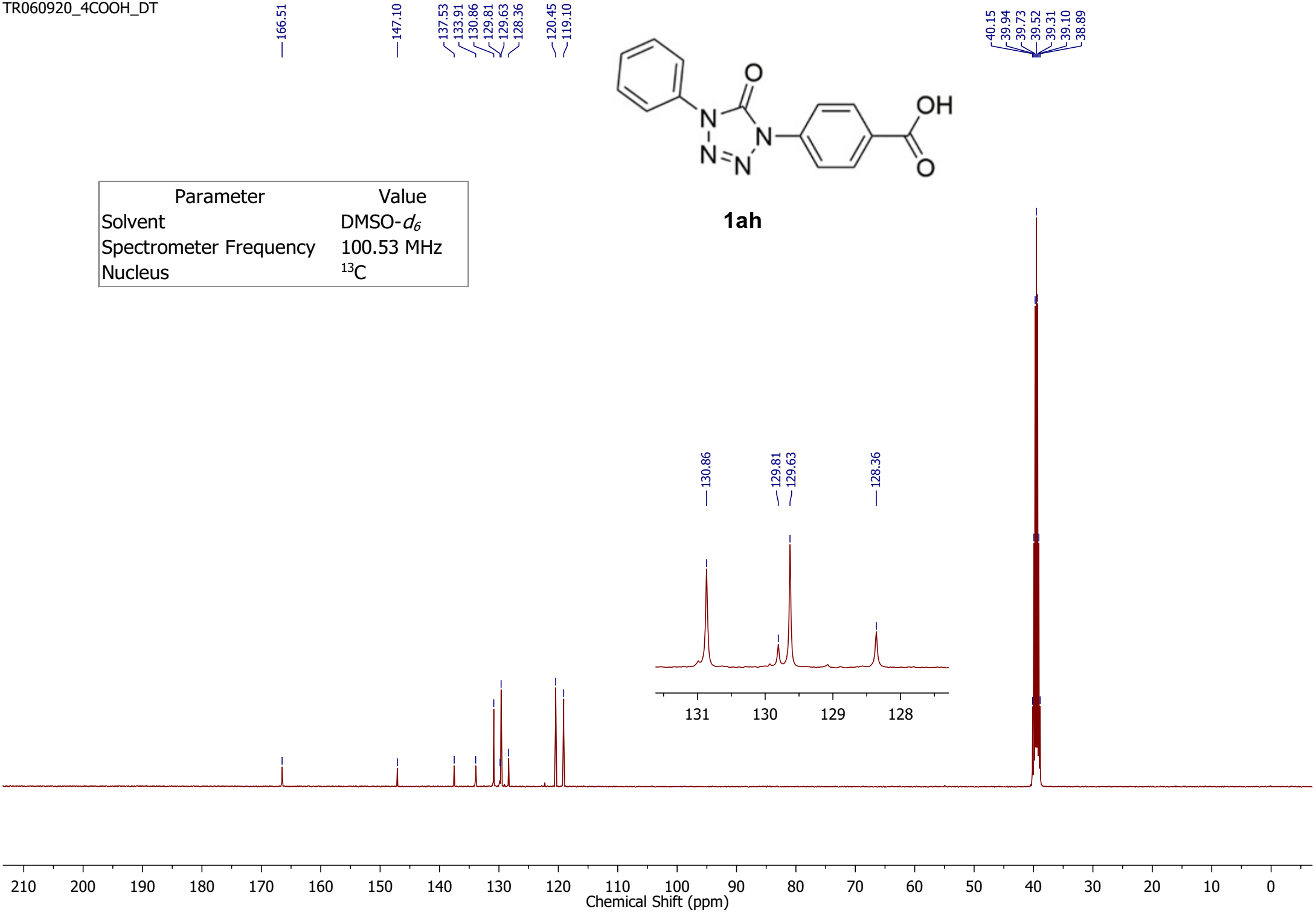
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



1ah

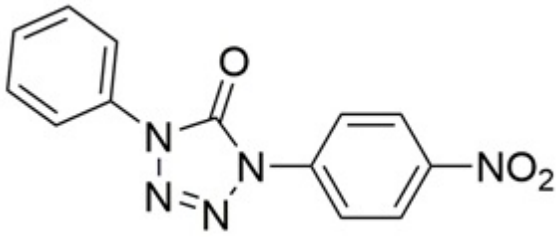


TR060920_4COOH_DT

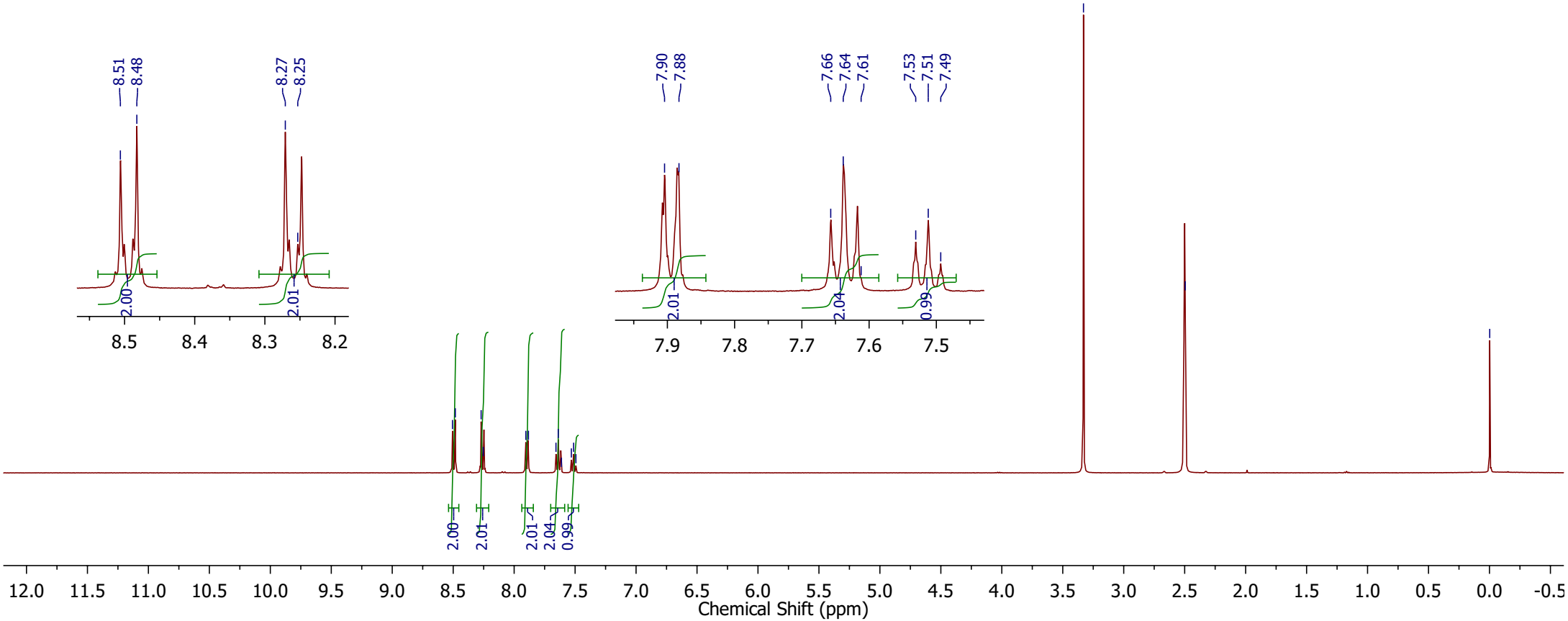


TR062220_4NO2_DT____

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



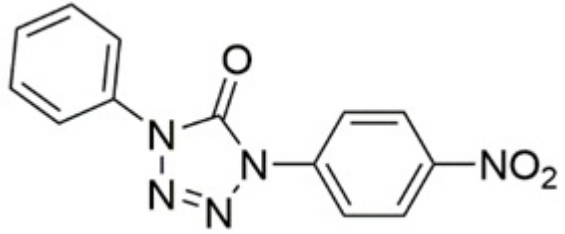
1ai



TR062220_4NO2_DT

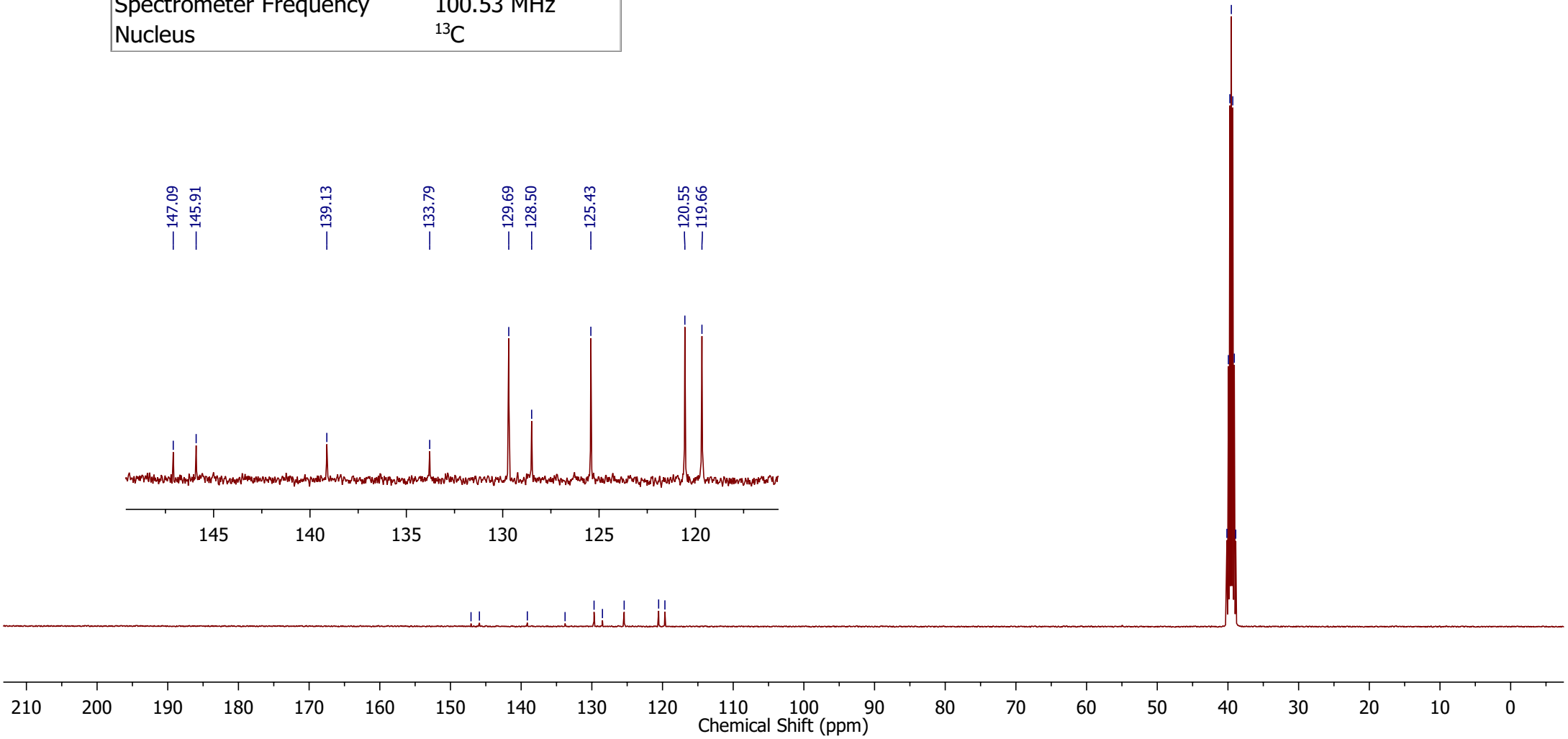
147.09
145.91
139.13
133.79
129.69
128.50
125.43
120.55
119.66

40.15
39.94
39.73
39.52
39.31
39.10
38.90



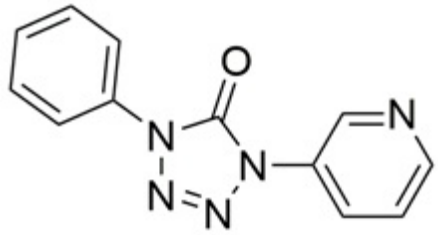
1ai

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	100.53 MHz
Nucleus	^{13}C

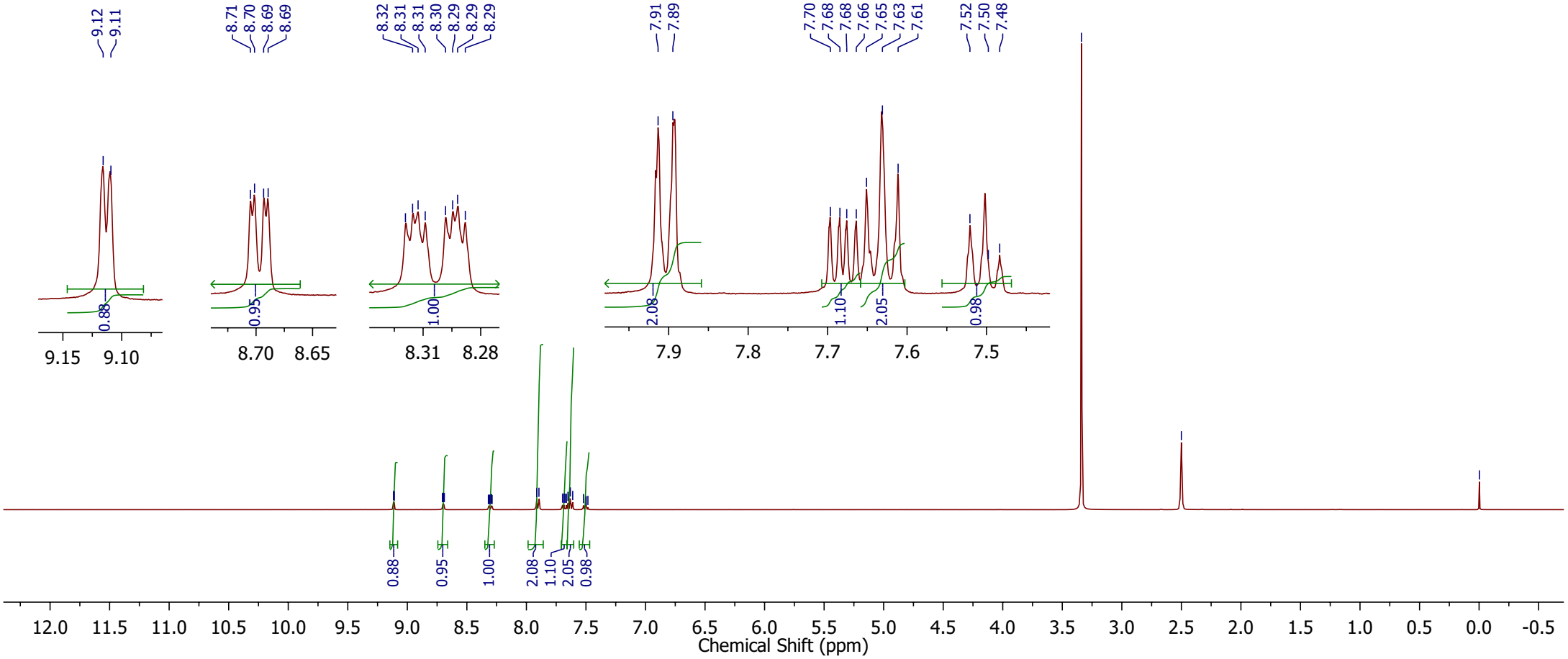


TR070420_3pyr_DT___

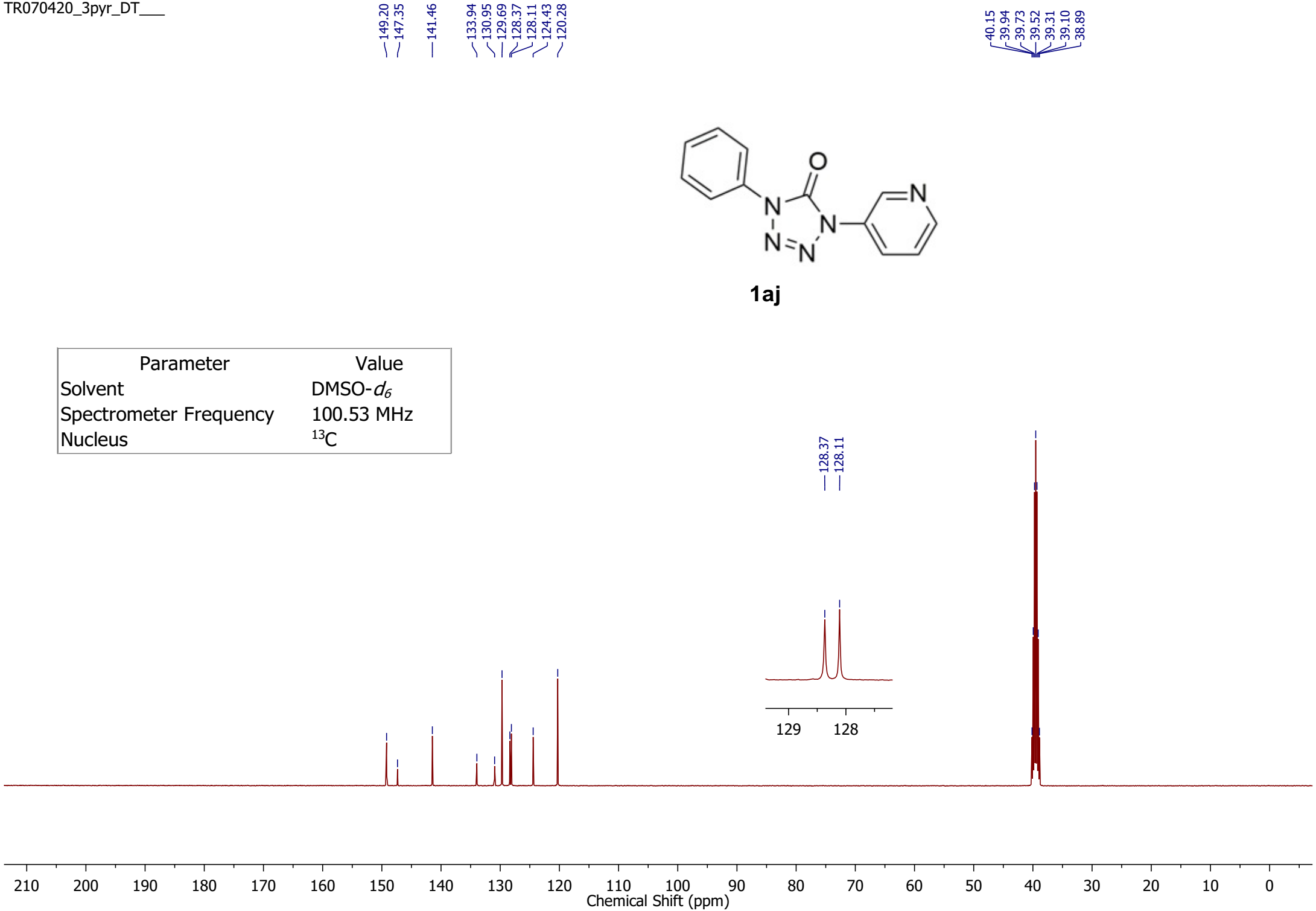
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



1aj

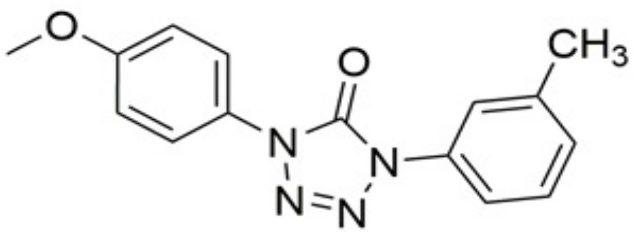


TR070420_3pyr_DT___



TR021020 - 2nd crop

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H

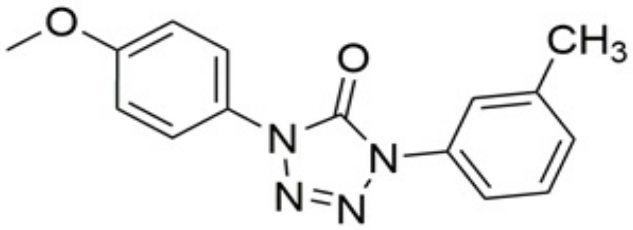


1bk

TR021020_4MeO_3Me_DT_Carbon

159.03
147.35
139.23
134.09
129.41
128.77
126.79
122.94
120.52
117.30
114.67
55.55
39.52
21.04

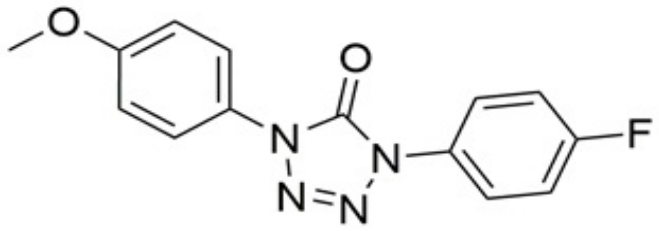
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	100.53 MHz
Nucleus	^{13}C



1bk

TR030220_4MeO_4F_DT

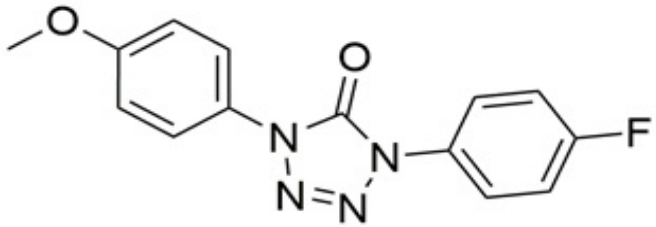
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



1bd

4MeO_4F_DT_Carbon

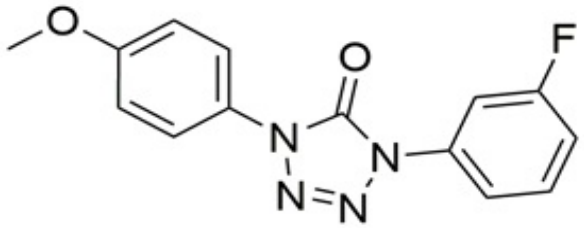
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	100.53 MHz
Nucleus	^{13}C



1bd

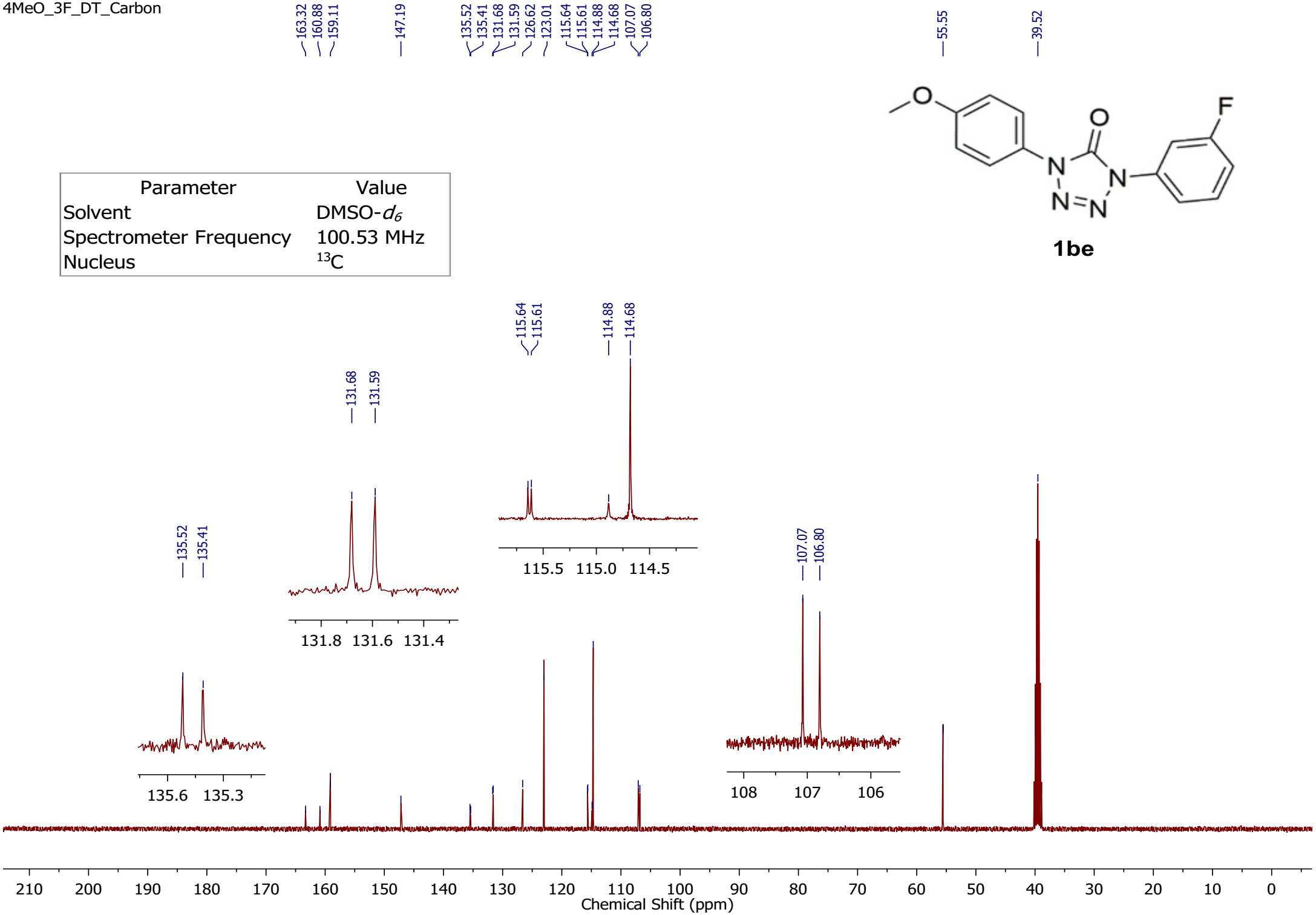
4MeO_3F_DT

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



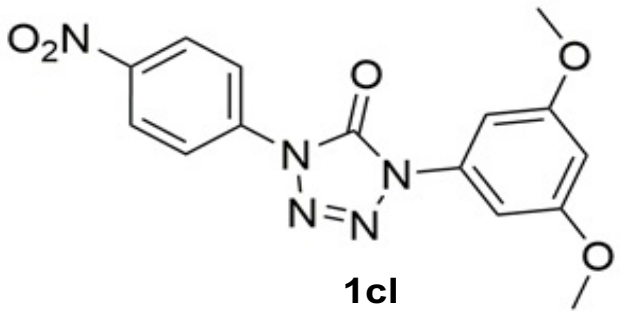
1be

4MeO_3F_DT_Carbon



TR021720 - 4NO2_3,5MeO DT

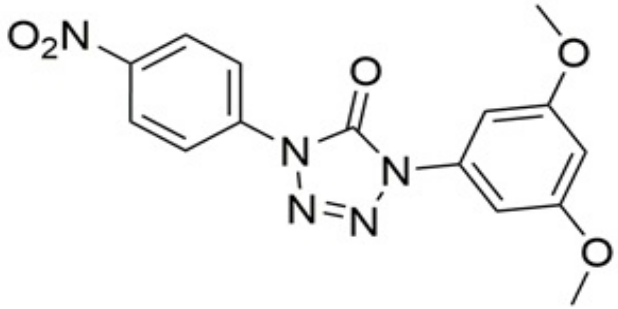
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H



1cl

TR021720_4NO2_3,5MeO DT Carbon

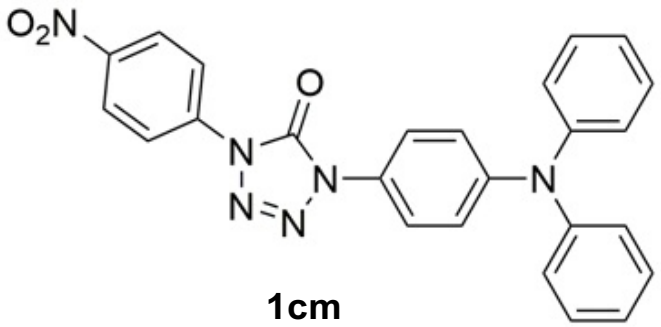
Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	100.53 MHz
Nucleus	^{13}C



1cl

TR070420_4-(diphenamino)_DT

Parameter	Value
Solvent	DMSO-d_6
Spectrometer Frequency	399.78 MHz
Nucleus	^{1}H

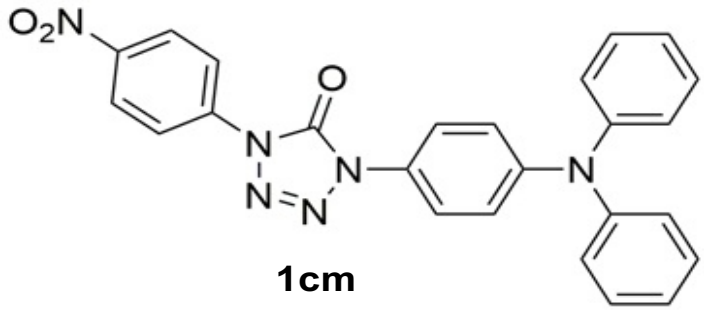


1cm

4NO2_4-(diphenamine)_DT_Carbon_CDCL3

148.42 147.19 146.44 139.49 129.68 127.32 125.37 125.17 124.00 123.03 121.65 119.06 77.48 77.16 76.84

Parameter	Value
Solvent	CHLOROFORM-d
Spectrometer Frequency	100.53 MHz
Nucleus	^{13}Carbon



1cm