

SUPPORTING INFORMATION

Catalyst and Solvent Free Microwave Assisted Synthesis of Substituted 1,2,3-Triazoles

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General Remarks:

^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Varian 600, 500, and 400 MHz NMR spectrometers. ^1H NMR and ^{13}C chemical shifts were determined relative to the signal of a residual protonated solvent. ^{19}F NMR chemical shifts were determined relative to CFCl_3 as an internal standard (0.0 ppm). IR data was recorded on a JASCO FT/IR-4600 infrared spectrometer. HRMS (EI and ESI) analysis was performed at the School of Chemical Sciences Mass Spectrometry Laboratory, University of Illinois, Urbana-Champaign. Flash chromatographic purification of compounds was performed using a Biotage, Isolera One, accelerated chromatographic isolation (ACI) automated flash column chromatogram. All reactions mixtures were prepared under argon or nitrogen atmosphere (Ar/N_2 glovebox). Unless otherwise mentioned, all reagents were purchased in the highest purity from commercial sources and used without further purification.

Microwave Irradiation Experiment:

All microwave irradiation reactions were carried out in a Biotage® Initiator+ microwave reactor, operating with continuous irradiation power from 0 to 400 W and heating up to 300 °C with a cut-off of 30 bar pressure. The microwave reactor was used in the standard configuration as delivered. All reactions were carried out in a Biotage® microwave vial and sealed with an aluminum/Teflon® crimp top, which enables to bear maximum internal pressure of 30 bar. The built-in IR sensor of the instrument measures the temperature at all time. After the irradiation period, the reaction vial was cooled down to the ambient temperature by the built-in gas jet cooling before the safety cap was removed.

General Procedure:

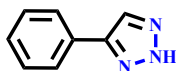
Acetylene derivative (1.0 equivalent) and trimethylsilyl azide (1.5 equivalent) were transferred to a 0.5-2 mL Biotage microwave vial equipped with a magnetic stir-bar under inert condition. The vial was tightly sealed with aluminum/Teflon® crimp top and was exposed to microwave irradiation at a constant temperature of 200 °C for the time indicated in table 2. After completion of the reaction (until no change in pressure was observed), the reaction mixture was cooled to ambient temperature. Subsequently, the reaction mixture was transferred to a beaker using diethyl ether and was exposed to air for 30 minutes. The reaction mixture was dissolved in minimum amount of hot dichloromethane and pure products were obtained by recrystallization in hexanes. Product **2**, **9**, and **12** were purified by flash silica column chromatography (25% ethyl acetate in hexanes).

CAUTION: In presence of moisture, TMSN_3 hydrolyzes to highly toxic hydrazoic acid (HN_3) and therefore all the chemicals MUST be stored free of moisture. The outlined procedures are designed for neat reactions, one must avoid using protic solvents with TMSN_3 as it readily generates HN_3 .

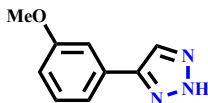
DFT Study:

Gaussian 09 program (Frisch, M. J.; et al. *Gaussian 09*, Revision A.02, 2009) was employed for geometry optimizations and frequency calculations. The geometries were optimized at the B3LYP/6-311+G** level. Vibrational frequencies at the B3LYP/6-311+G** level were used to characterize stationary points as minima (NIMAG (number of imaginary frequency) = 0) or transition state (NIMAG = 1) and to evaluate zero point vibrational energies (ZPE), which were scaled by a factor of 0.96. Relative energies were calculated at the B3LYP/6-311++G(3df,3pd)//B3LYP/6-311+G** + ZPE level.

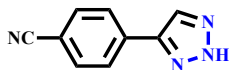
Characterization Data of All Products:



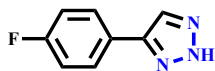
4-Phenyl-2H-1,2,3-triazole (1)¹ was obtained from phenylacetylene (5 mmol) and trimethylsilyl azide and purified by recrystallization as a white solid in 99% yield (717 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 8.33 (bs, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 145.9, 130.5, 128.9, 128.1, 125.5. **HRMS (ESI)** calculated for C₈H₈N₃: [M+H]⁺ 146.0718, found: 146.0720. **FT/IR** (ν_{max} (neat) cm⁻¹) 3154, 3121, 2948, 2822, 1661, 1456, 971, 874.765. **R_f** (1:1-hexanes:ethylacetate): 0.36. This reaction was also carried out with 12 mmol of phenylacetylene and the final product was obtained in 98% yield.



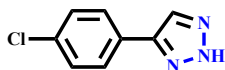
4-(3-Methoxyphenyl)-2H-1,2,3-triazole (2)² was obtained from (3-methoxyphenyl)acetylene (4 mmol) and trimethylsilyl azide and purified by flash column chromatography as a very viscous oil in 90% yield (630 mg). **¹H NMR** (500 MHz, Chloroform-*d*) δ 12.24 (s, 1H), 7.98 (s, 1H), 7.49 – 7.28 (m, 3H), 6.94 (dt, *J* = 7.7, 2.0 Hz, 1H), 3.88 (s, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 160.2, 147.5, 131.2, 130.2 (contains two C signals), 118.7, 114.8, 111.5, 55.5. **HRMS (ESI)** calculated for C₉H₁₀N₃O: [M+H]⁺ 176.0824, found: 176.0820. **FT/IR** (ν_{max} (neat) cm⁻¹) 3142, 3100, 3014, 2925, 2823, 2661, 1609, 1593, 1559, 1486, 1320, 1230, 1320, 1230, 1144, 1075, 1037, 827, 788. **R_f** (1:1-hexanes:ethylacetate): 0.29.



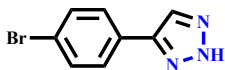
4-(2H-1,2,3-Triazol-4-yl)benzonitrile (3)¹ was obtained from 4-ethynylbenzonitrile (3 mmol) and trimethylsilyl azide and purified by recrystallization as yellow solid in 78% yield (397 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 8.56 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 144.3, 135.1, 133.0, 126.1, 118.8, 110.3. **HRMS (ESI)** calculated for C₉H₇N₄: [M+H]⁺ 171.0671, found: 171.0674. **FT/IR** (ν_{max} (neat) cm⁻¹) 3130, 3007, 2962, 2864, 2231, 1614, 1523, 1472, 1425, 1359, 1299, 1226, 1181, 1081, 999, 971, 841. **R_f** (1:1-hexanes:ethylacetate): 0.23.



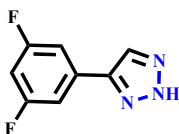
4-(4-Fluorophenyl)-2H-1,2,3-triazole (4)¹ was obtained from (4-fluorophenyl)acetylene (4 mmol) and trimethylsilyl azide and purified by recrystallization as a white crystalline solid in 55% yield (356 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 8.31 (s, 1H), 7.90 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.29 (t, *J* = 8.6 Hz, 2H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 161.9 (d, *J* = 244.7 Hz), 145.1, 130.5, 127.6 (d, *J* = 7.3 Hz), 127.2, 115.8 (d, *J* = 21.6 Hz). **¹⁹F NMR** (470 MHz, Chloroform-*d*) δ -113.1. **HRMS (ESI)** calculated for C₈H₇N₃F: [M+H]⁺ 164.0624, found: 164.0627. **FT/IR** (ν_{max} (neat) cm⁻¹) 3148, 3119, 3044, 2973, 2858, 2775, 1910, 1610, 1534, 1465, 1228, 1160, 1134, 1096, 1003, 972, 839. **R_f** (1:1-hexanes:ethylacetate):0.34.



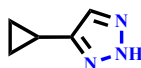
4-(4-Chlorophenyl)-2H-1,2,3-triazole (5)¹ was obtained from (4-chlorophenyl)acetylene (4 mmol) and trimethylsilyl azide and purified by recrystallization as a white crystalline solid in 87% yield (625 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 8.39 (s, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 145.2, 132.9, 129.9, 129.4, 127.7. **HRMS (ESI)** calculated for C₈H₇N₃Cl: [M+H]⁺ 180.0329, found: 180.0329. **FT/IR** (ν_{max} (neat) cm⁻¹) 3157, 3128, 2984, 2958, 2842, 2740, 1918, 1677, 1606, 1524, 1460, 1417, 1297, 1225, 1133, 1100, 1073, 970, 834. **R_f** (1:1-hexanes:ethylacetate):0.30.



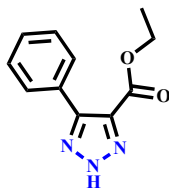
4-(4-Bromophenyl)-2H-1,2,3-triazole (6)¹ was obtained from (4-bromophenyl)acetylene (4 mmol) and trimethylsilyl azide and purified by recrystallization as a white crystalline solid in 88% yield (785 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 8.39 (s, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 2H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 144.8, 131.9, 129.8, 127.5, 121.1. **HRMS (ESI)** calculated for C₈H₇N₃Br: [M+H]⁺ 223.9823, found: 223.9817. **FT/IR** (ν_{max} (neat) cm⁻¹) 3154, 3124, 2988, 2950, 2838, 1922, 1602, 1458, 1411, 1336, 1133, 1070, 1003, 970, 875, 831. **R_f** (1:1-hexanes:ethylacetate): 0.33.



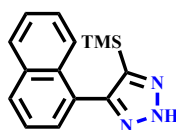
4-(3,5-Difluorophenyl)-2H-1,2,3-triazole (7) was obtained from (3,5-difluorophenyl)acetylene (3.5 mmol) and trimethylsilyl azide and purified by recrystallization as a white solid (m.p. 157-160 °C) in 82% yield (518 mg). **¹H NMR** (400 MHz, Chloroform-*d*) δ 11.89 (s, 1H), 7.97 (s, 1H), 7.36 (dt, *J* = 6.5, 2.3 Hz, 2H), 6.83 (tt, *J* = 8.9, 2.3 Hz, 1H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 163.6 (dd, *J* = 248.6, 13.0 Hz), 146.1, 133.2 (t, *J* = 10.4 Hz), 131.2, 109.2 (dd, *J* = 19.6, 6.5 Hz), 104.15 (t, *J* = 25.4 Hz). **¹⁹F NMR** (470 MHz, Chloroform-*d*) δ -109.4 (pt, *J* = 7.0 Hz). **HRMS (ESI)** calculated for C₈H₆N₃F₂: [M+H]⁺ 182.0530, found: 182.0535. **FT/IR** (ν_{max} (neat) cm⁻¹) 3153, 3103, 3077, 1629, 1590, 1459, 1437, 1249, 1234, 1119, 1076, 987, 840, 808. **R_f** (1:1-hexanes:ethylacetate): 0.42.



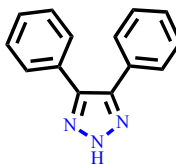
4-Cyclopropyl-2H-1,2,3-triazole (8)³ was obtained from cyclopropylacetylene (5 mmol) and trimethylsilyl azide and purified by recrystallization as a white solid in 81% yield (441 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.52 (s, 1H), 1.95 (tt, *J* = 8.4, 5.0 Hz, 1H), 0.95 – 0.87 (m, 2H), 0.73 – 0.66 (m, 2H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 148.8, 130.1, 7.9, 6.2. **HRMS (ESI)** calculated for C₅H₈N₃: [M+H]⁺ 110.0718, found: 110.0714. **FT/IR** (ν_{max} (neat) cm⁻¹) 3150, 3118, 3086, 2985, 2925, 2876, 2844, 2784, 1518, 1455, 1420, 1348, 1302, 1230, 1123, 1053, 1030, 993, 866. **R_f** (1:1-hexanes:ethylacetate): 0.24.



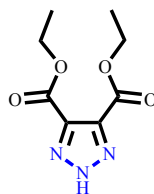
Ethyl 5-phenyl-2H-1,2,3-triazole-4-carboxylate (9)⁴ was obtained from ethyl 3-phenylpropioate (3 mmol) and trimethylsilyl azide and purified by flash column chromatography as a yellow liquid that solidifies when given sufficient time in 92% yield (597 mg). **¹H NMR** (500 MHz, Chloroform-*d*) δ 13.90 (s, 1H), 7.99 – 7.69 (m, 2H), 7.59 – 7.32 (m, 3H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 161.1, 146.8, 134.6, 129.8, 129.4, 128.5, 61.9, 14.2. **HRMS (ESI)** calculated for C₁₁H₁₂N₃O₂: [M+H]⁺ 218.0930, found: 218.0930. **FT/IR** (ν_{max} (neat) cm⁻¹) 3169, 3113, 3078, 3027, 3005, 2978, 2937, 2836, 1718, 1582, 1480, 1442, 1388, 1376, 1320, 1307, 1243, 1222, 1173, 1148, 1087, 922, 839. **R_f** (1:1-hexanes:ethylacetate): 0.22.



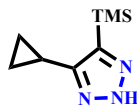
4-(Naphthalen-1-yl)-5-(trimethylsilyl)-2H-1,2,3-triazole (10) was obtained from trimethyl(naphthalen-1-ylethynyl)silane (3 mmol) and trimethylsilyl azide and purified by recrystallization as an off-white solid (m.p. 150-153 °C) in 62% yield (496 mg). **¹H NMR** (399 MHz, Chloroform-*d*) δ 13.66 (s, 1H), 7.97 – 7.83 (m, 2H), 7.67 (d, $J = 8.2$ Hz, 1H), 7.57 – 7.37 (m, 4H), 0.03 (s, 9H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 151.6, 135.4, 133.6, 133.2, 129.9, 129.2, 128.7, 128.2, 126.4, 126.3, 126.1, 124.9, -1.1. **HRMS (ESI)** calculated for C₁₅H₁₈N₃Si: [M+H]⁺ 268.1270, found: 268.1272. **FT/IR** (ν_{max} (neat) cm⁻¹) 3116, 3056, 2945, 2897, 2812, 2781, 1593, 1537, 1385, 1304, 1250, 1180, 961, 834. **R_f** (1:1-hexanes:ethylacetate): 0.30.



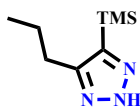
4,5-Diphenyl-2H-1,2,3-triazole (11)¹ was obtained from diphenylacetylene (5 mmol) and trimethylsilyl azide and purified by recrystallization as a white solid in 84% yield (927 mg). **¹H NMR** (500 MHz, DMSO-*d*₆) δ 7.50 (d, $J = 7.0$ Hz, 4H), 7.47 – 7.32 (m, 6H). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 143.0, 131.2, 128.7, 128.2, 127.9. **HRMS (ESI)** calculated for C₁₄H₁₂N₃: [M+H]⁺ 222.1031, found: 222.1030. **FT/IR** (ν_{max} (neat) cm⁻¹) 3088, 3064, 3019, 2987, 2921, 2884, 2834, 2808, 2748, 1604, 1584, 1516, 1490, 1441, 1382, 1227, 1210, 1121, 998, 910, 855. **R_f** (1:1-hexanes:ethylacetate): 0.38.



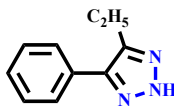
Diethyl 2H-1,2,3-triazole-4,5-dicarboxylate (12)⁵ was obtained from dimethyl acetylenedicarboxylate (1 mmol) and trimethylsilyl azide purified by flash column chromatography as a pale yellow oil in 97% yield (206 mg). **¹H NMR** (400 MHz, Chloroform-*d*) δ 4.46 (q, $J = 7.4$ Hz, 4H), 1.40 (t, $J = 7.4$ Hz, 6H). **¹³C NMR** (100 MHz, Chloroform-*d*) δ 160.2, 138.8, 62.6, 14.2. **HRMS (ESI)** calculated for C₈H₁₂N₃O₄: [M+H]⁺ 214.0828, found: 214.0834. **FT/IR** (ν_{max} (neat) cm⁻¹) 3186, 2985, 2938, 2906, 2872, 1731, 1574, 1500, 1472, 1428, 1300, 1222, 1084, 1013, 988, 856, 831. **R_f** (1:1-hexanes:ethylacetate): 0.22.



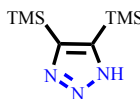
4-Cyclopropyl-5-(trimethylsilyl)-2H-1,2,3-triazole (13)⁶ was obtained from (cyclopropylethynyl)-trimethylsilane (3 mmol) and trimethylsilyl azide and purified by recrystallization as off-white solid in 33% yield (180 mg). ¹H NMR (400 MHz, Chloroform-*d*) δ 1.89 (tt, *J* = 8.2, 5.1 Hz, 1H), 1.05 – 0.91 (m, 4H), 0.39 (s, 9H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 154.3, 134.9, 7.9, 7.2, -1.0. HRMS (ESI) calculated for C₈H₁₆N₃Si: [M+H]⁺ 182.1113, found: 182.1116. FT/IR (ν_{max} (neat) cm⁻¹) 3100, 3053, 3002, 2960, 2906, 2781, 2649, 1543, 1348, 1327, 1258, 1176, 1132, 1052, 1013, 999, 891, 835. R_f (1:1-hexanes:ethylacetate): 0.34.



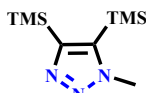
4-Propyl-5-(trimethylsilyl)-2H-1,2,3-triazole (14) was obtained from 1-trimethylsilyl-1-pentyne (3 mmol) and trimethylsilyl azide and purified by recrystallization as a white solid (m.p. 107-109°C) in 57% yield (312 mg). ¹H NMR (400 MHz, Chloroform-*d*) δ 12.78 (s, 1H), 2.77 – 2.69 (m, 2H), 1.72 (h, *J* = 7.4 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.35 (s, 9H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 153.0, 131.0, 28.2, 23.9, 14.0, -0.8. HRMS (ESI) calculated for C₈H₁₈N₃Si: [M+H]⁺ 184.1270, found: 184.1276. FT/IR (ν_{max} (neat) cm⁻¹) 3129, 3053, 2958, 2931, 2871, 1463, 1359, 1250, 1219, 1176, 1123, 1011, 839. R_f (1:1-hexanes:ethylacetate): 0.35.



4-Ethyl-5-phenyl-2H-1,2,3-triazole (15)¹ was obtained from 1-phenyl-1-butyne (4 mmol) and trimethylsilyl azide and purified by recrystallization as a white crystalline solid in 92% yield (640 mg). ¹H NMR (399 MHz, Chloroform-*d*) δ 11.95 (s, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 2.94 (q, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 144.1, 130.9, 128.9, 128.3, 127.6, 19.0, 13.4. HRMS (ESI) calculated for C₁₀H₁₂N₃: [M+H]⁺ 174.1026, found: 174.1031. FT/IR (ν_{max} (neat) cm⁻¹) 3078, 3006, 2975, 2935, 2880, 2639, 2574, 2515, 1818, 1598, 1475, 1448, 1247, 1217, 1076, 1046, 1023, 1217, 1009, 993, 923. R_f (1:1-hexanes:ethylacetate): 0.34.



4,5-Bis(trimethylsilyl)-1H-1,2,3-triazole (16)⁷ was obtained from 1,2-bis(trimethylsilyl)ethyne (3 mmol) and trimethylsilyl azide and purified by recrystallization as a white crystals in 61% yield (392 mg). ¹H NMR (600 MHz, Chloroform-*d*) δ 0.38 (pd, *J* = 3.9 Hz, 18H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 150.6, 139.7, -0.02. HRMS (ESI) calculated for C₈H₂₀N₃Si₂: [M+H]⁺ 214.1196, found: 214.1200. FT/IR (ν_{max} (neat) cm⁻¹) 3110, 2953, 2867, 1412, 1251, 1213, 1143, 1104, 1071, 1014, 826. R_f (1:1-hexanes:ethylacetate): 0.41.



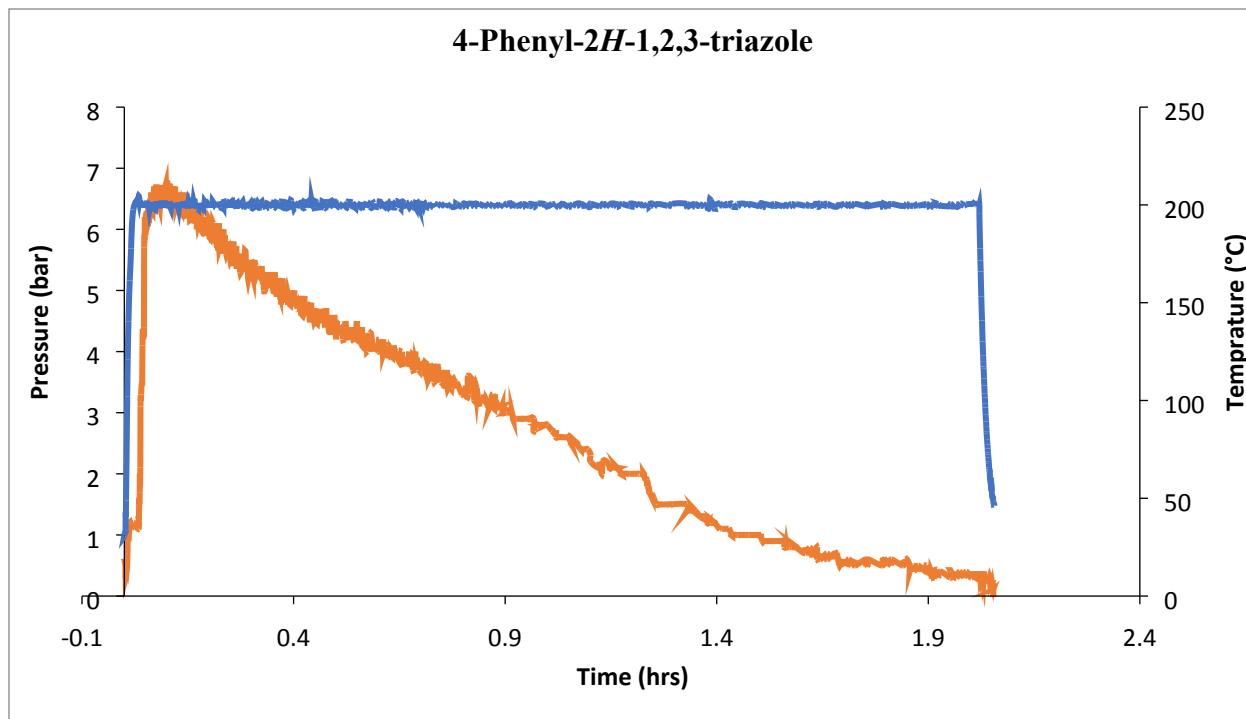
1-Methyl-4,5-bis(trimethylsilyl)-1H-1,2,3-triazole (17)⁷ was obtained from overnight stirring of **16** (0.25 mmol), methyl iodide (0.375 mmol), and potassium carbonate (0.5 mmol) in 2 mL DMF after silica column purification in 82% yield (46.6 mg). ¹H NMR (500 MHz, Chloroform-*d*) δ 4.15 (s, 3H), 0.42 (s, 9H), 0.39 (s, 9H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 153.8, 140.2, 37.9, 0.8, 0.7. R_f (1:1-hexanes:ethylacetate): 0.42.

= 698 (s), 768

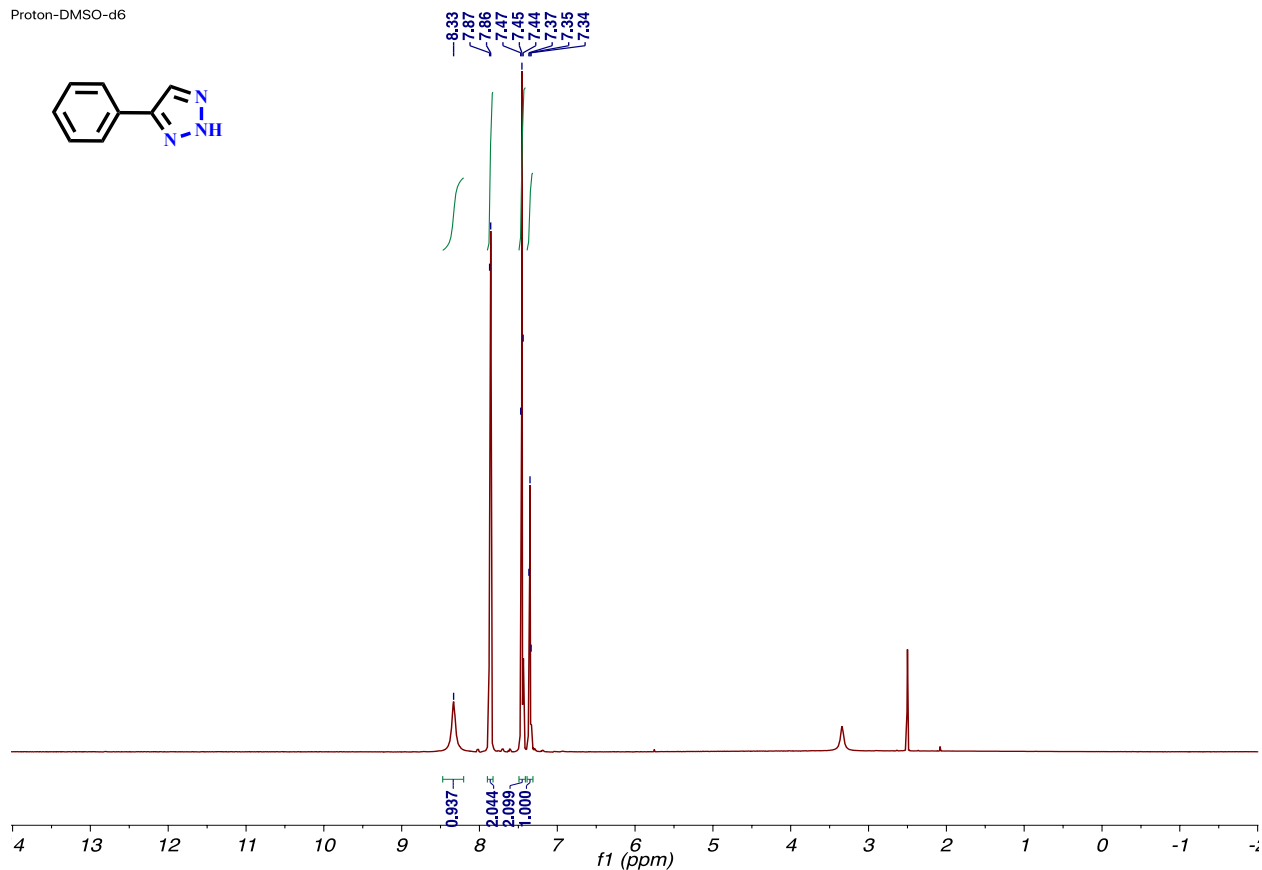
Reference:

- 1 X.-J. Quan, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Org. Lett.*, 2014, **16**, 5728–5731.
- 2 X. Wang, C. Kuang and Q. Yang, *Eur. J. Org. Chem.*, **2012**, 424–428.
- 3 J. Wen, L.-L. Zhu, Q.-W. Bi, Z.-Q. Shen, X.-X. Li, X. Li, Z. Wang and Z. Chen, *Chem. Eur. J.*, 2014, **20**, 974–978.
- 4 R. Hui, M. Zhao, M. Chen, Z. Ren and Z. Guan, *Chin. J. Chem.*, 2017, **35**, 1808–1812.
- 5 T. Hitomi and S. Kozima, *J. Organomet. Chem.*, 1977, **127**, 273–280.
- 6 L. Hu, C. Mück-Lichtenfeld, T. Wang, G. He, M. Gao and J. Zhao, *Chem. Eur. J.*, 2016, **22**, 911–915.
- 7 X. Wang, L. Zhang, D. Krishnamurthy, C. H. Senanayake and P. Wipf, *Org. Lett.*, 2010, **12**, 4632–4635.

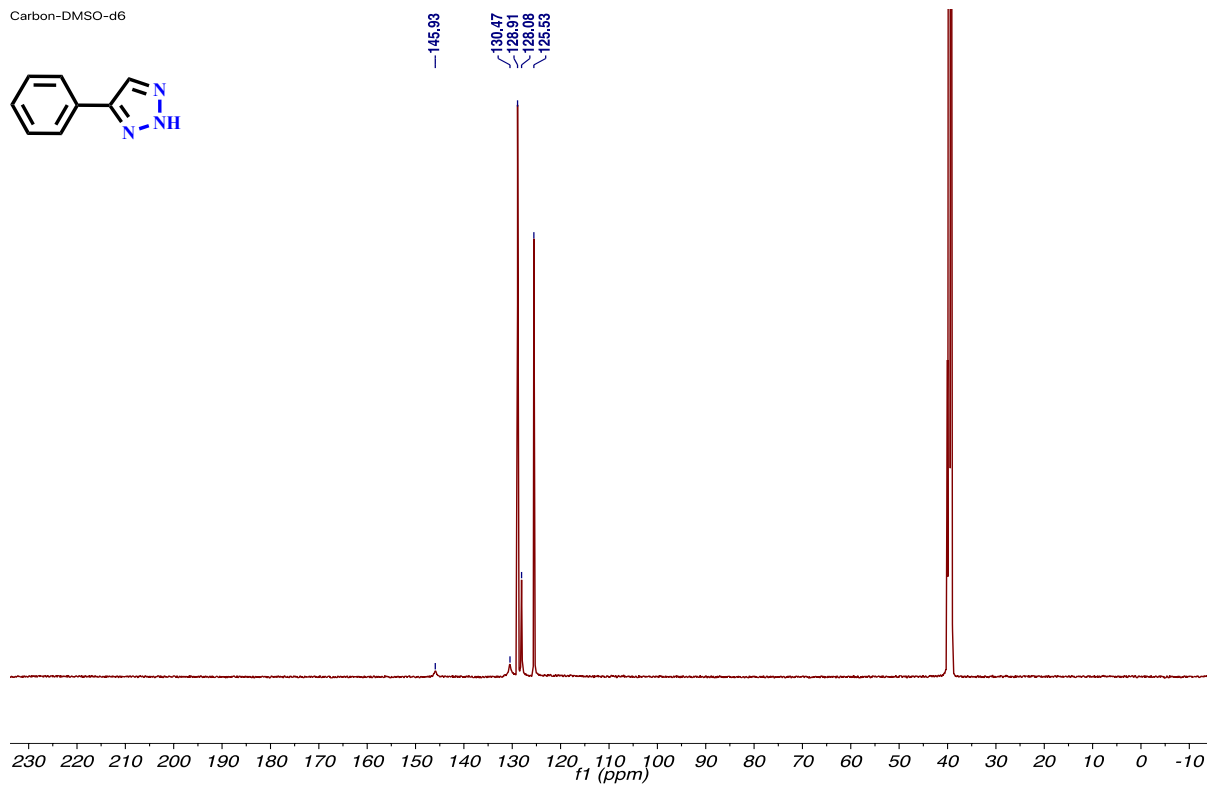
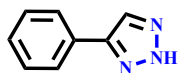
Microwave data and NMR spectra of 4-Phenyl-2H-1,2,3-triazole (1)



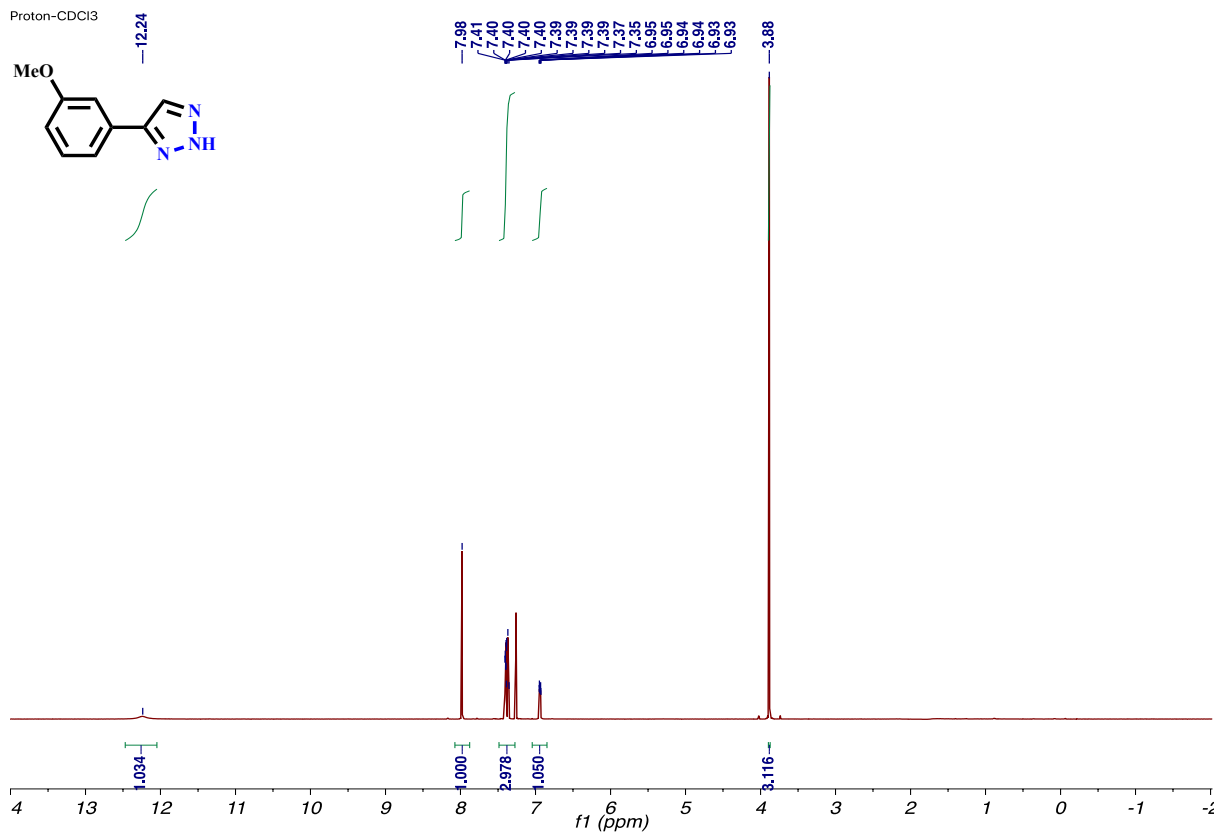
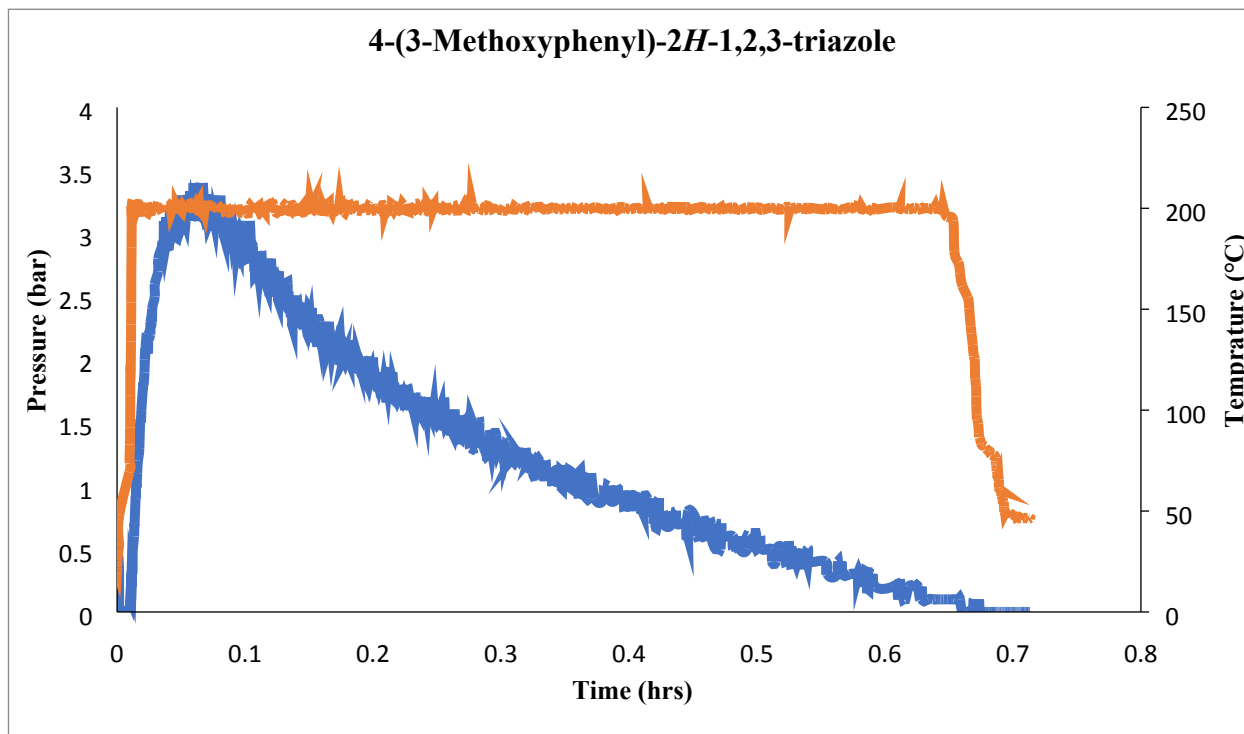
Proton-DMSO-d6

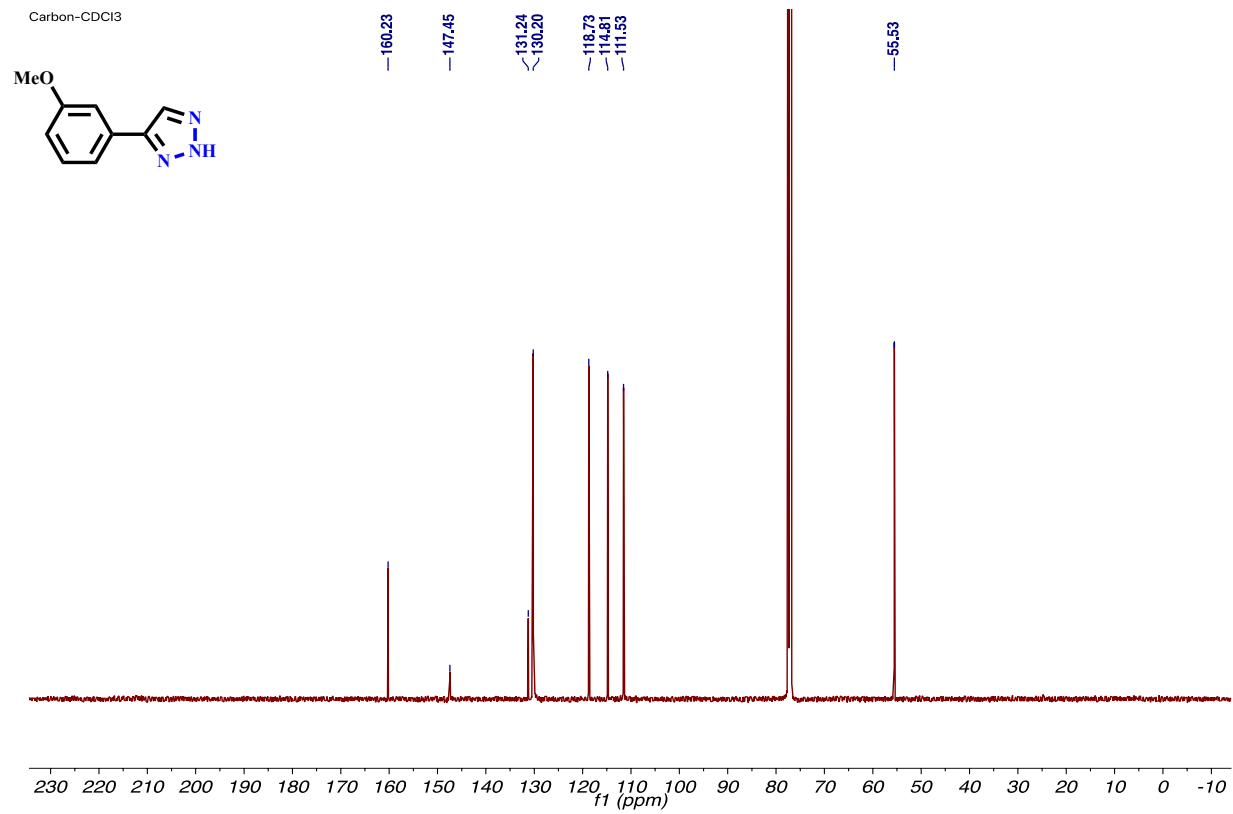


Carbon-DMSO-d6

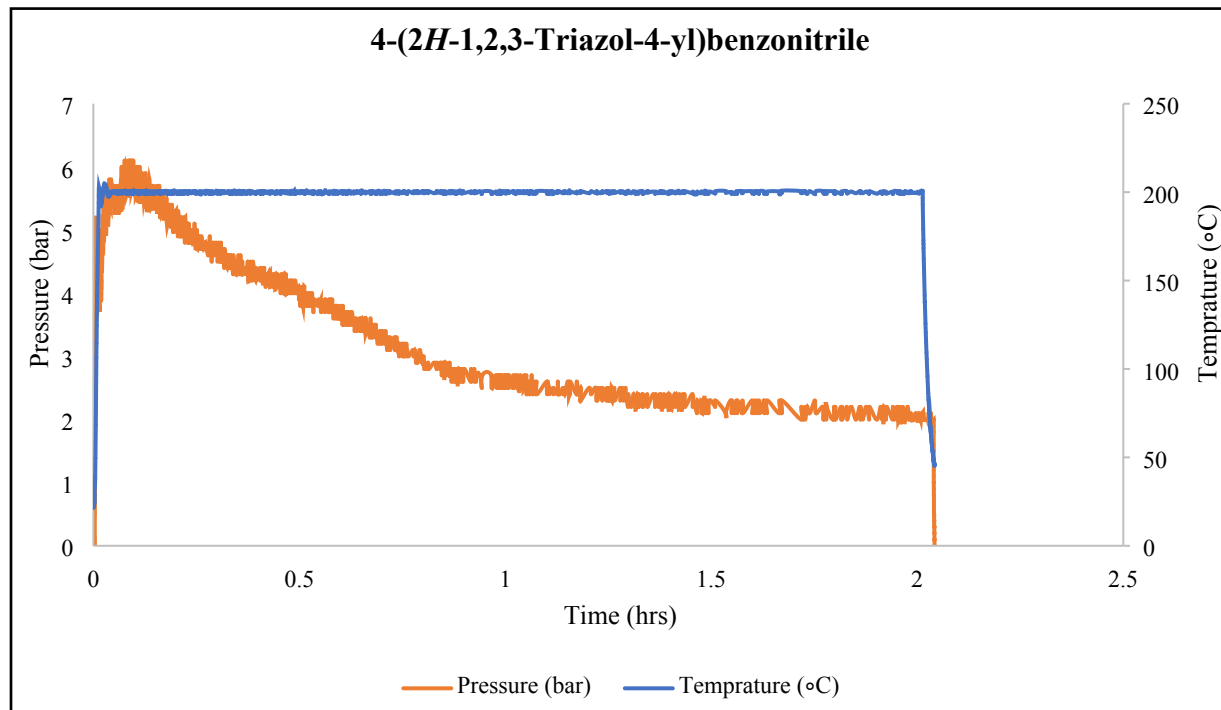


Microwave data and NMR spectra of 4-(3-Methoxyphenyl)-2H-1,2,3-triazole (2)

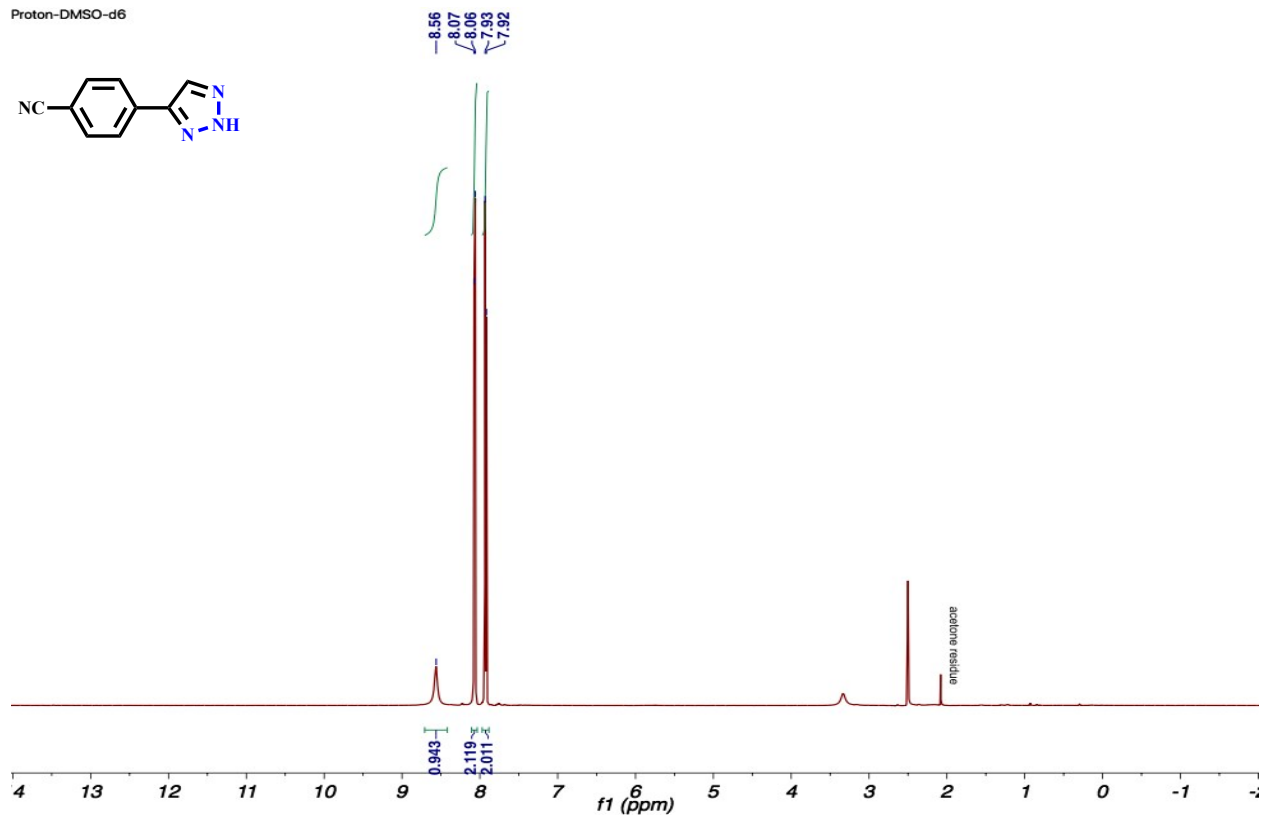
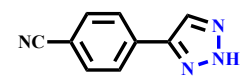




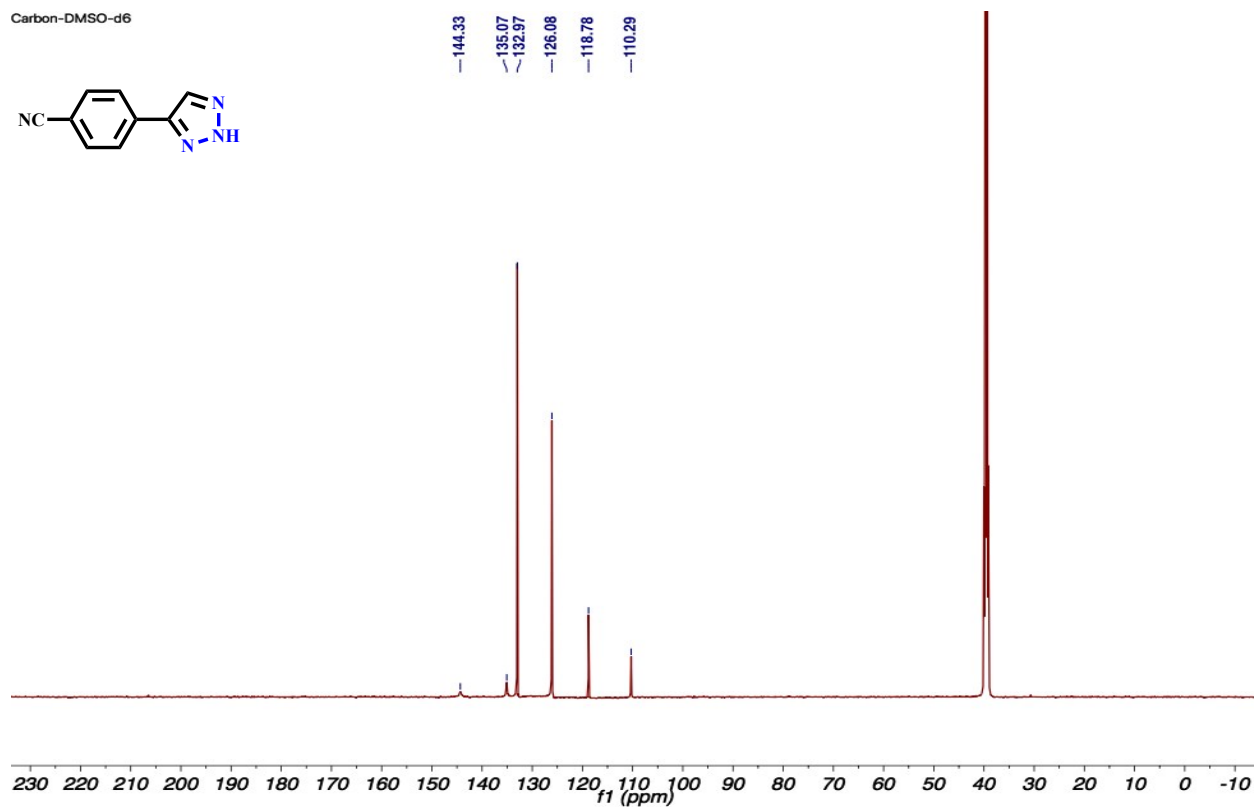
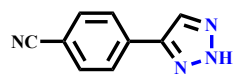
Microwave data and NMR spectra of 4-(2H-1,2,3-Triazol-4-yl)benzonitrile (3)



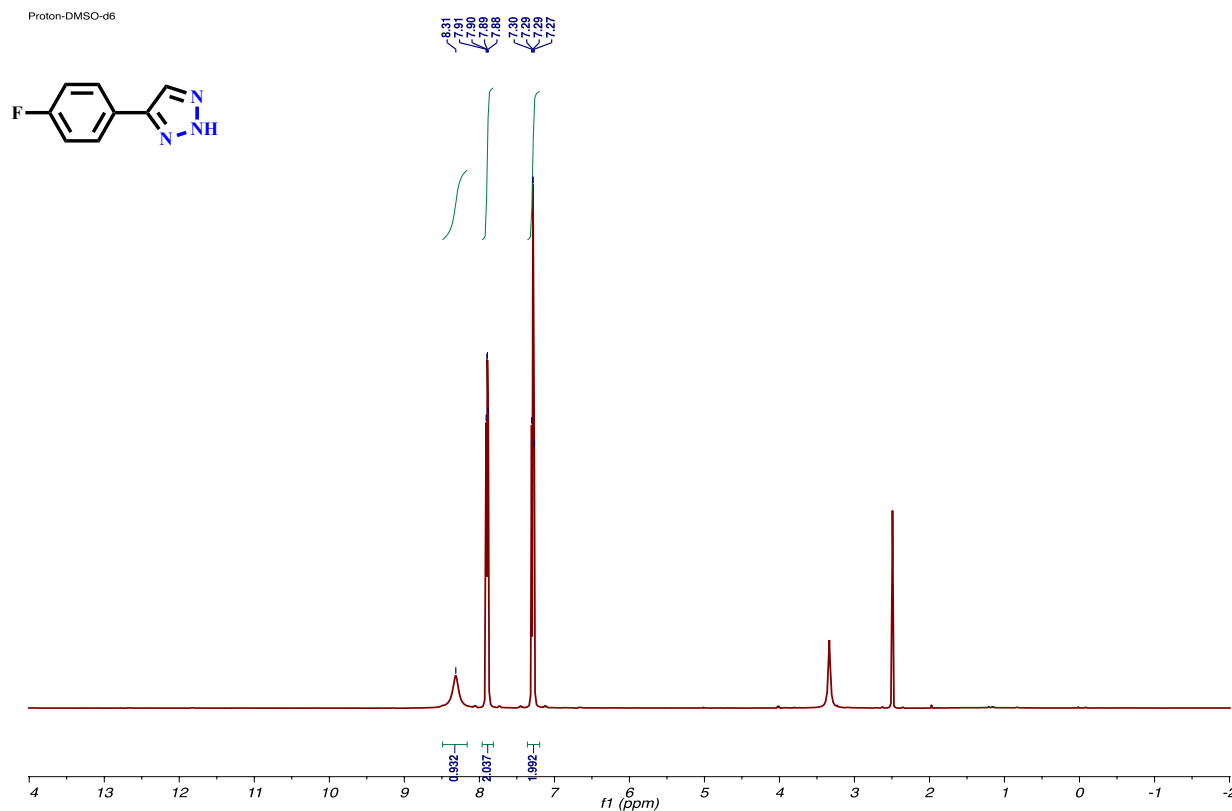
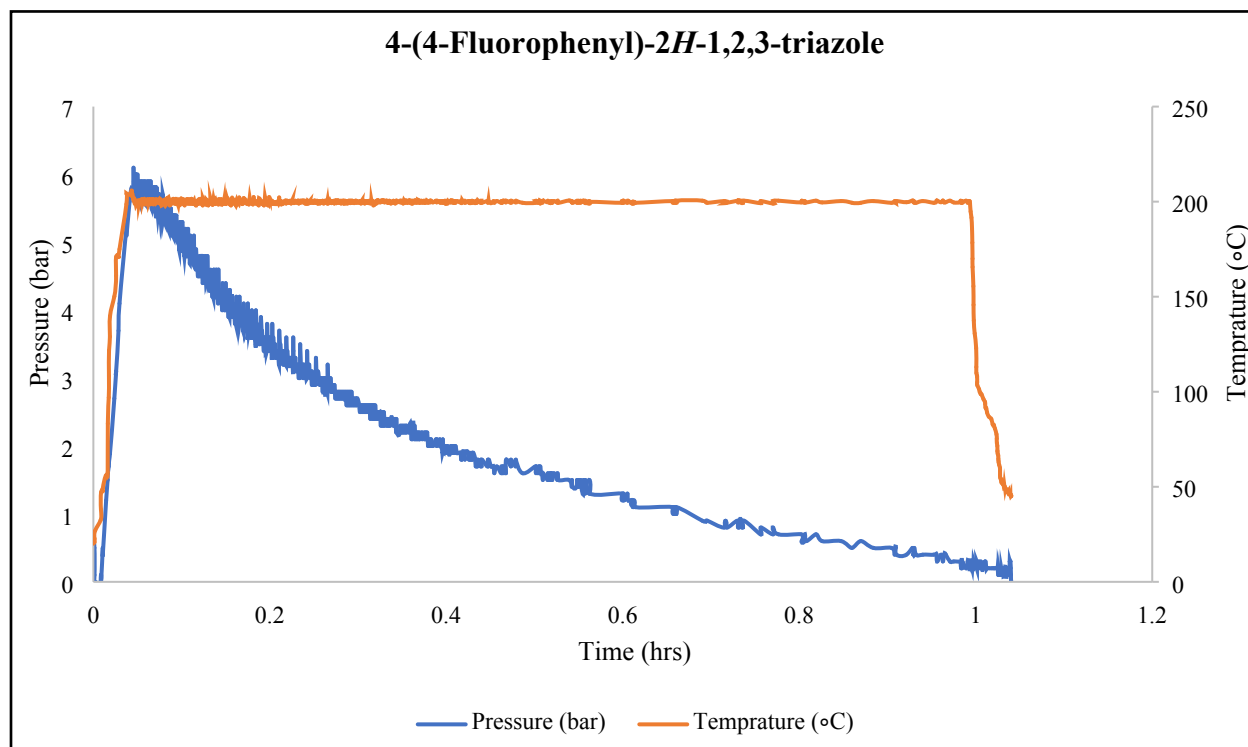
Proton-DMSO-d6



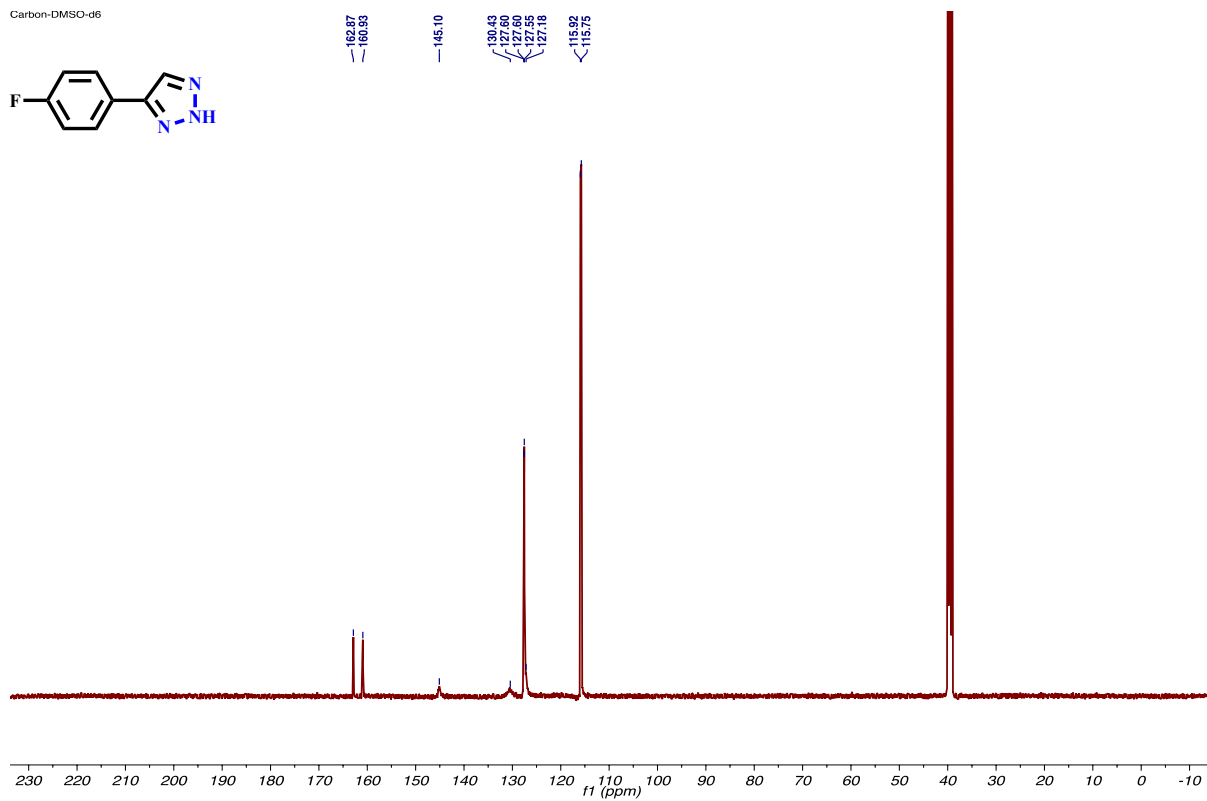
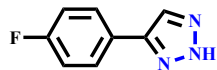
Carbon-DMSO-d6



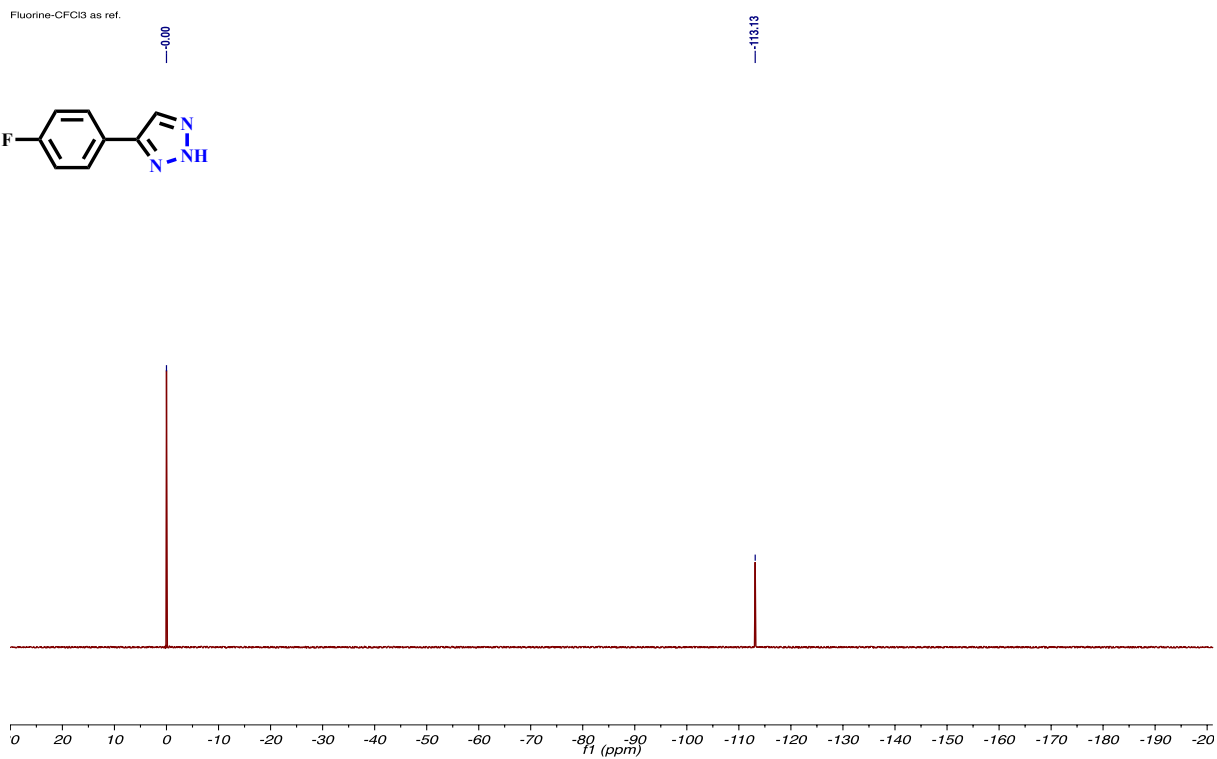
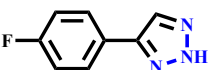
Microwave data and NMR spectra of 4-(4-Fluorophenyl)-2H-1,2,3-triazole (4)



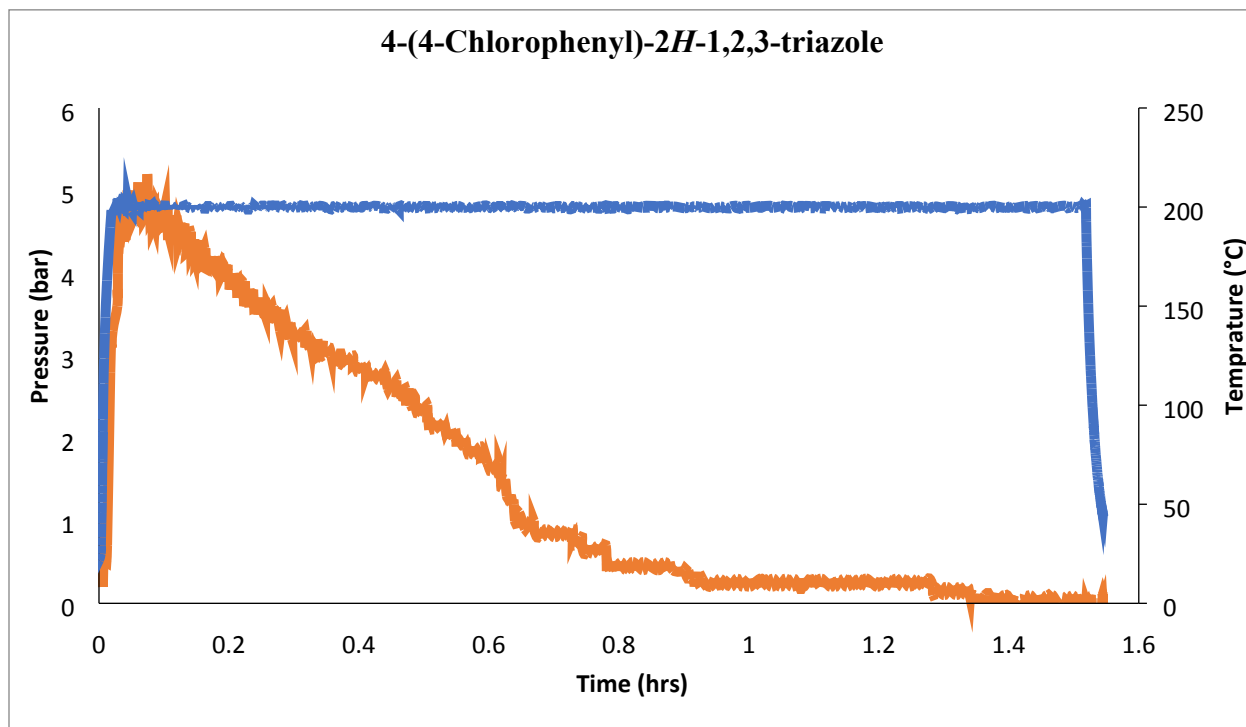
Carbon-DMSO-d6



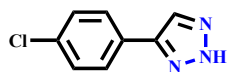
Fluorine-CFCIS as ref.



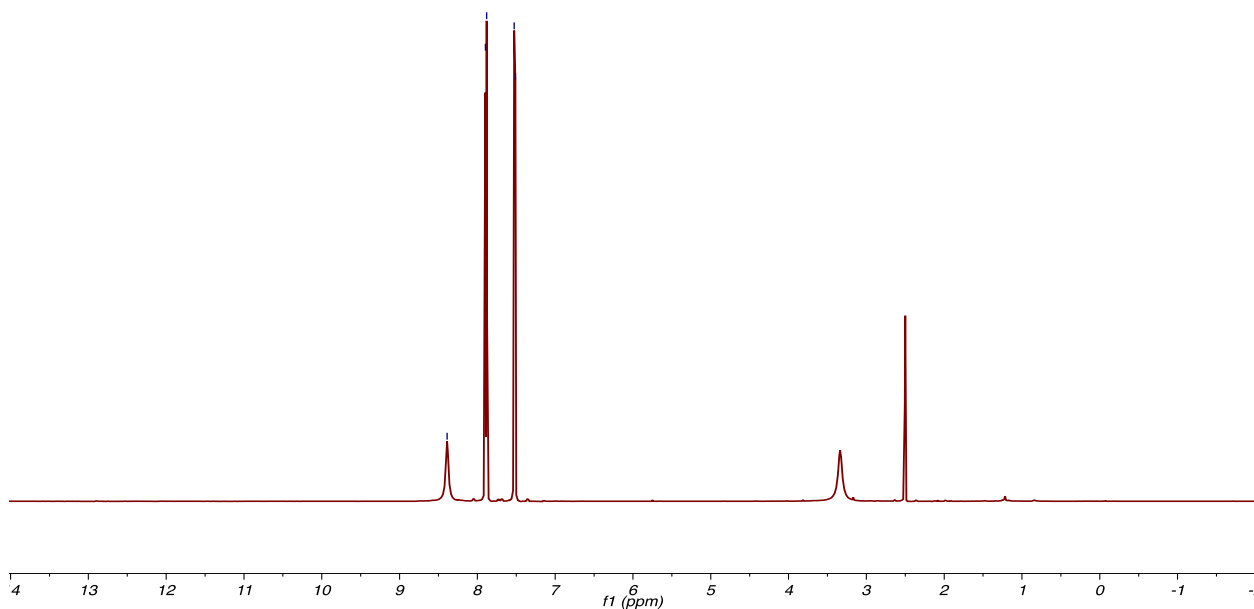
Microwave data and NMR spectra of 4-(4-Chlorophenyl)-2H-1,2,3-triazole (5)



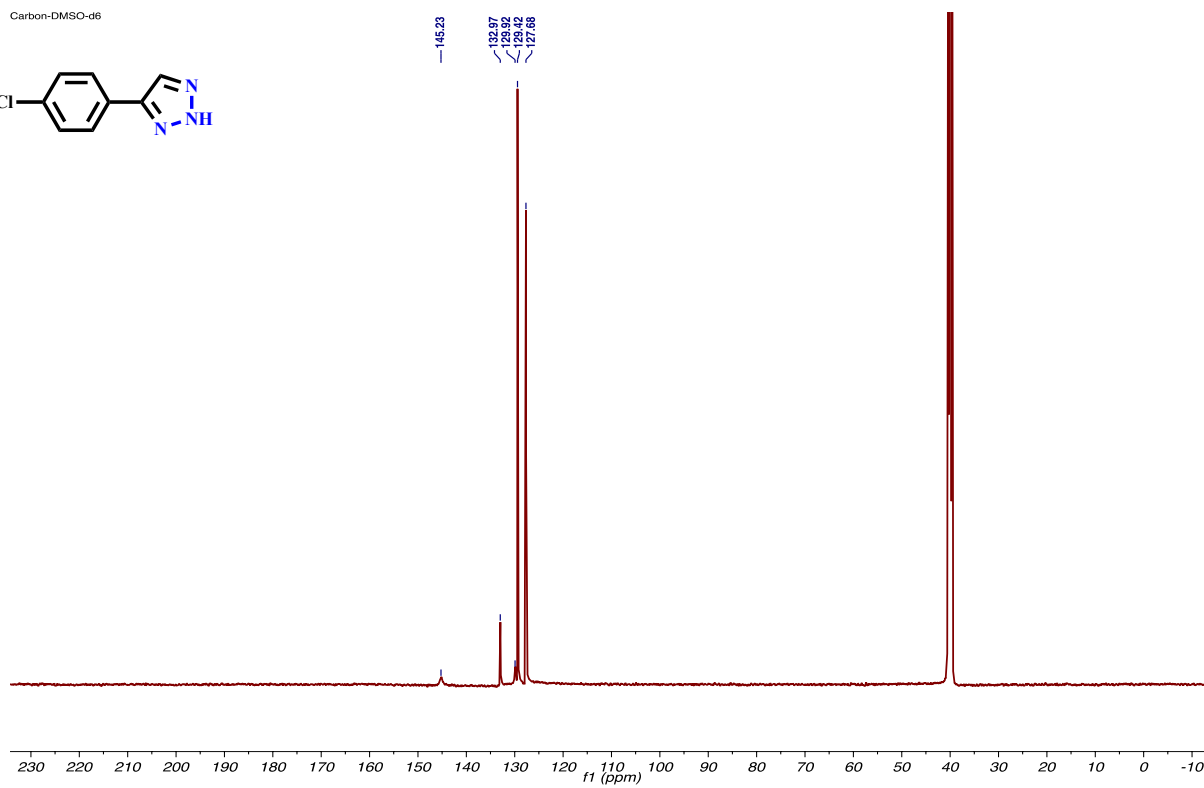
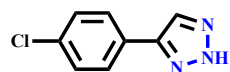
Proton-DMSO-d6



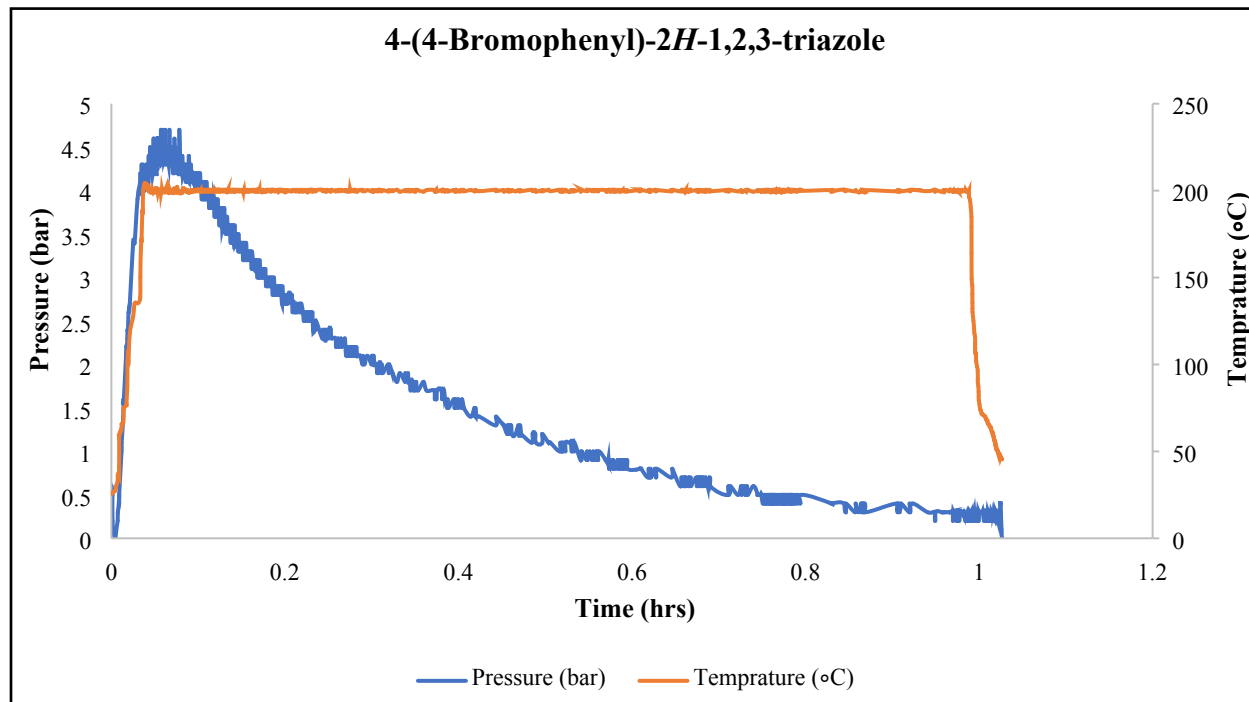
8.39
7.90
7.53



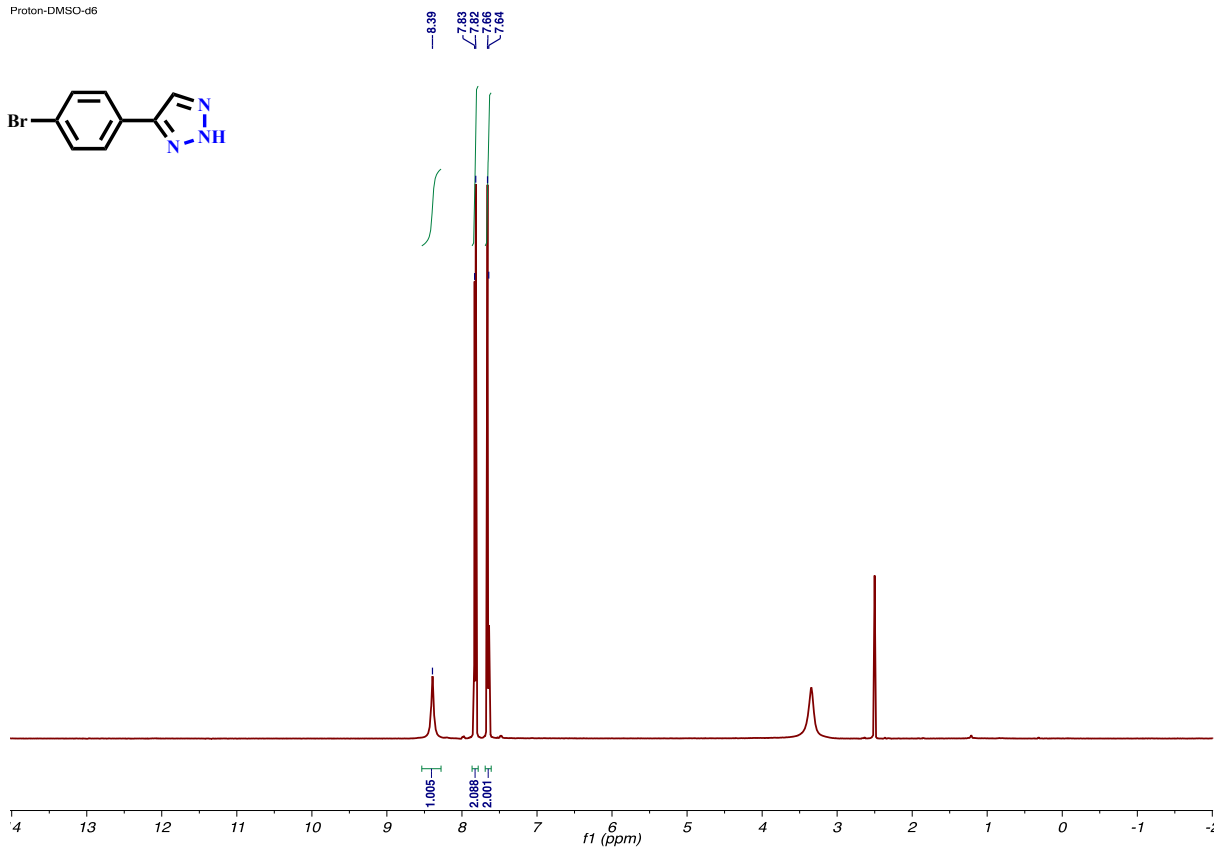
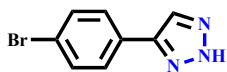
Carbon-DMSO-d6



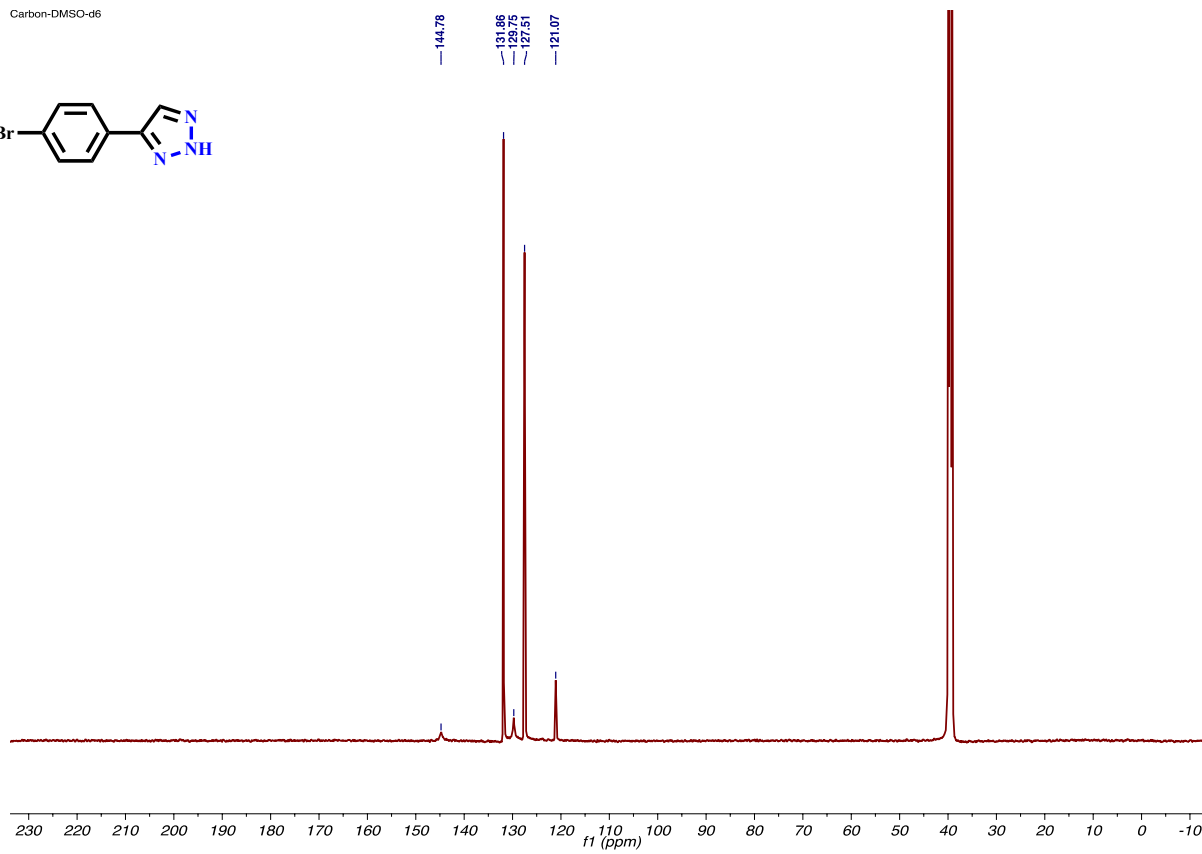
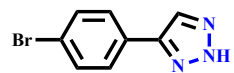
Microwave data and NMR spectra of 4-(4-Bromophenyl)-2H-1,2,3-triazole (6)



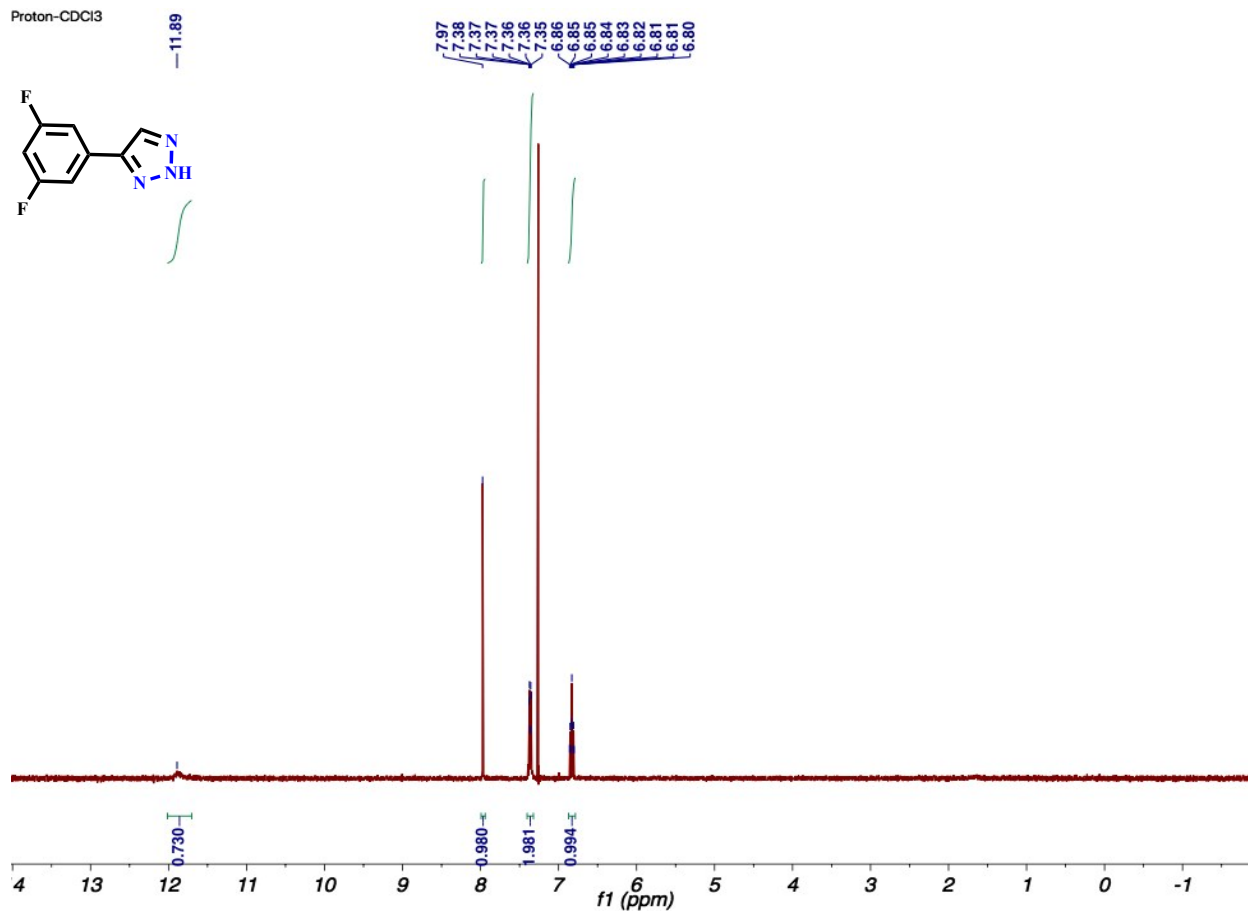
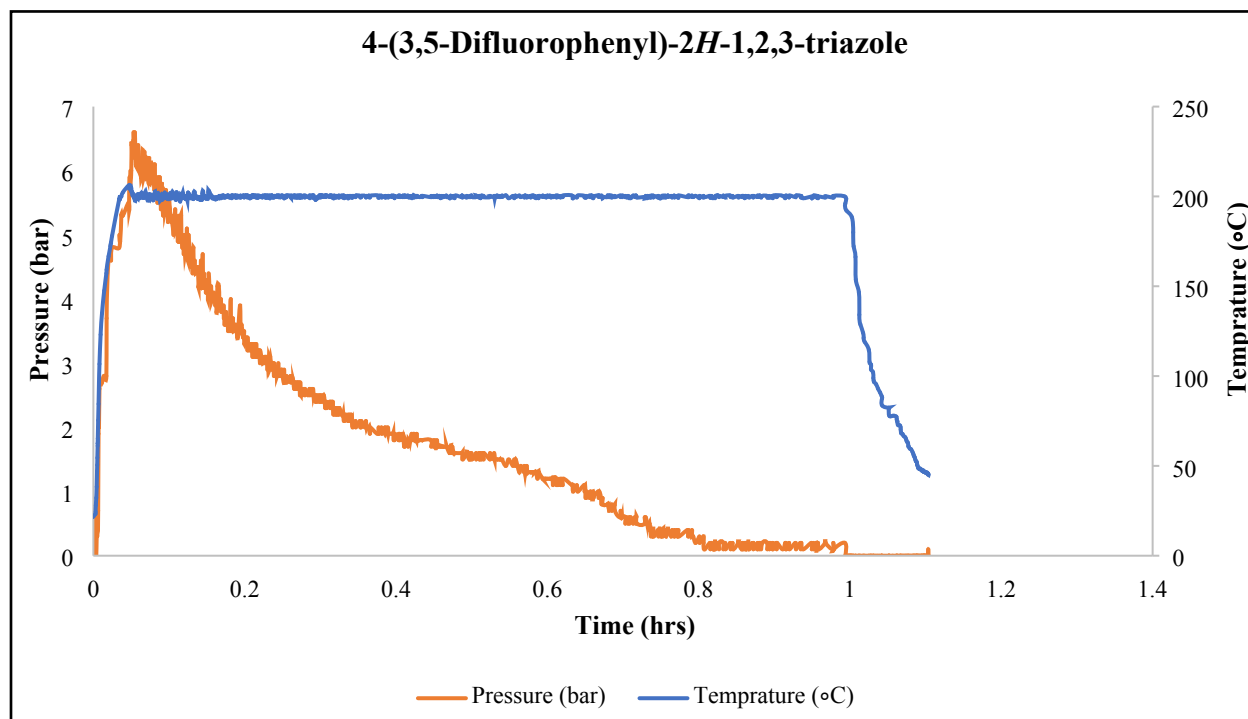
Proton-DMSO-d6



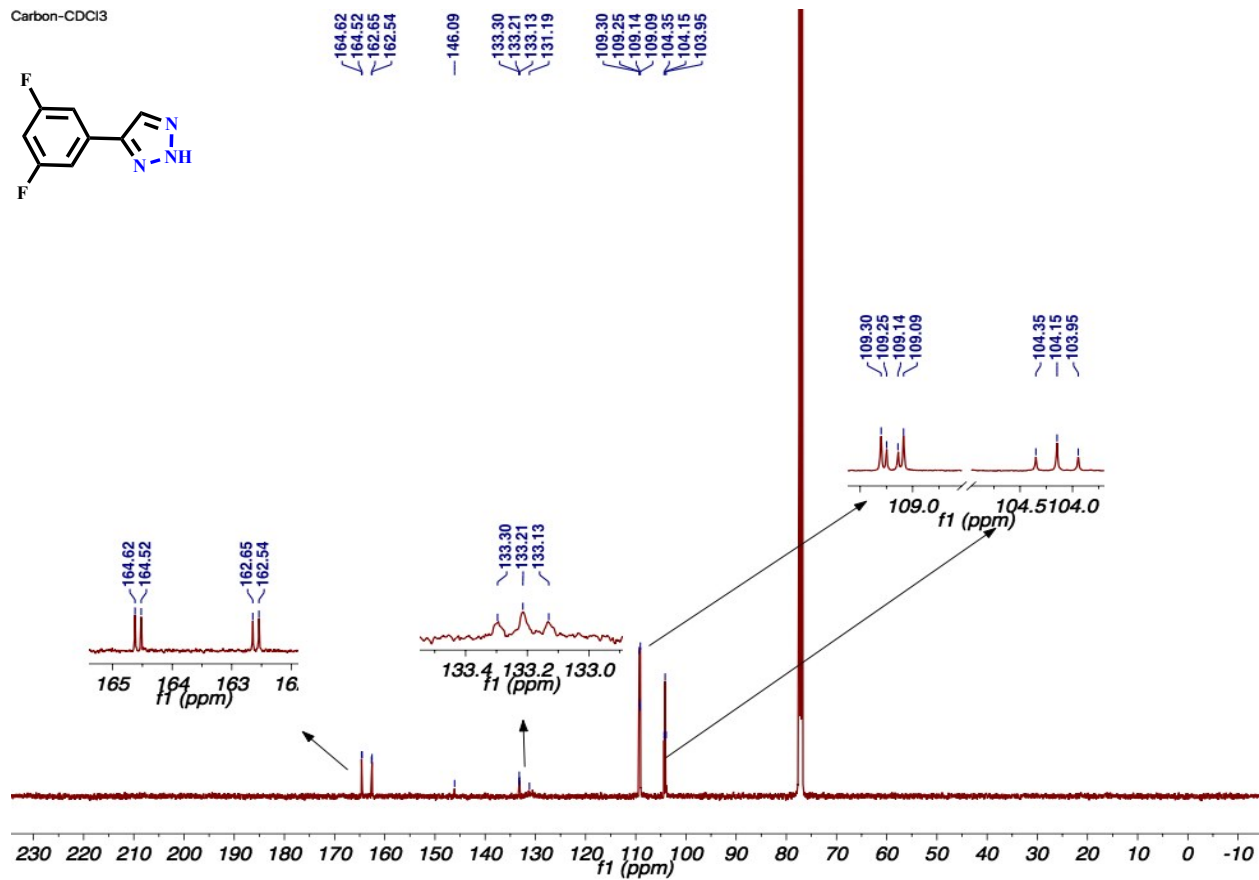
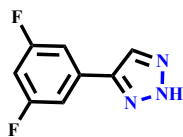
Carbon-DMSO-d6



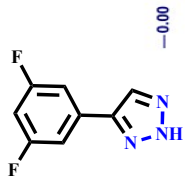
Microwave data and NMR spectra of 4-(3,5-Difluorophenyl)-2H-1,2,3-triazole (7)



Carbon-CDCl₃

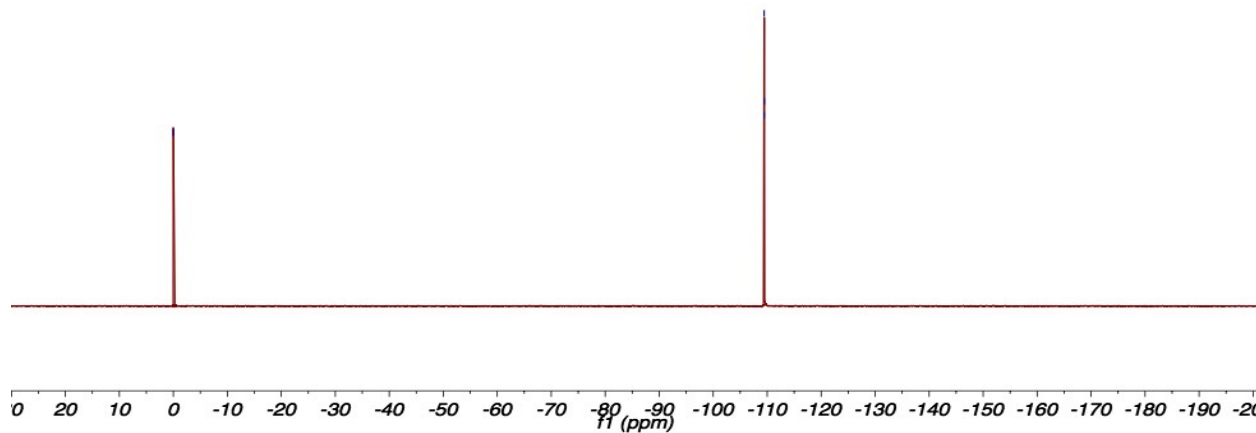


Fluorine-CFCl₃

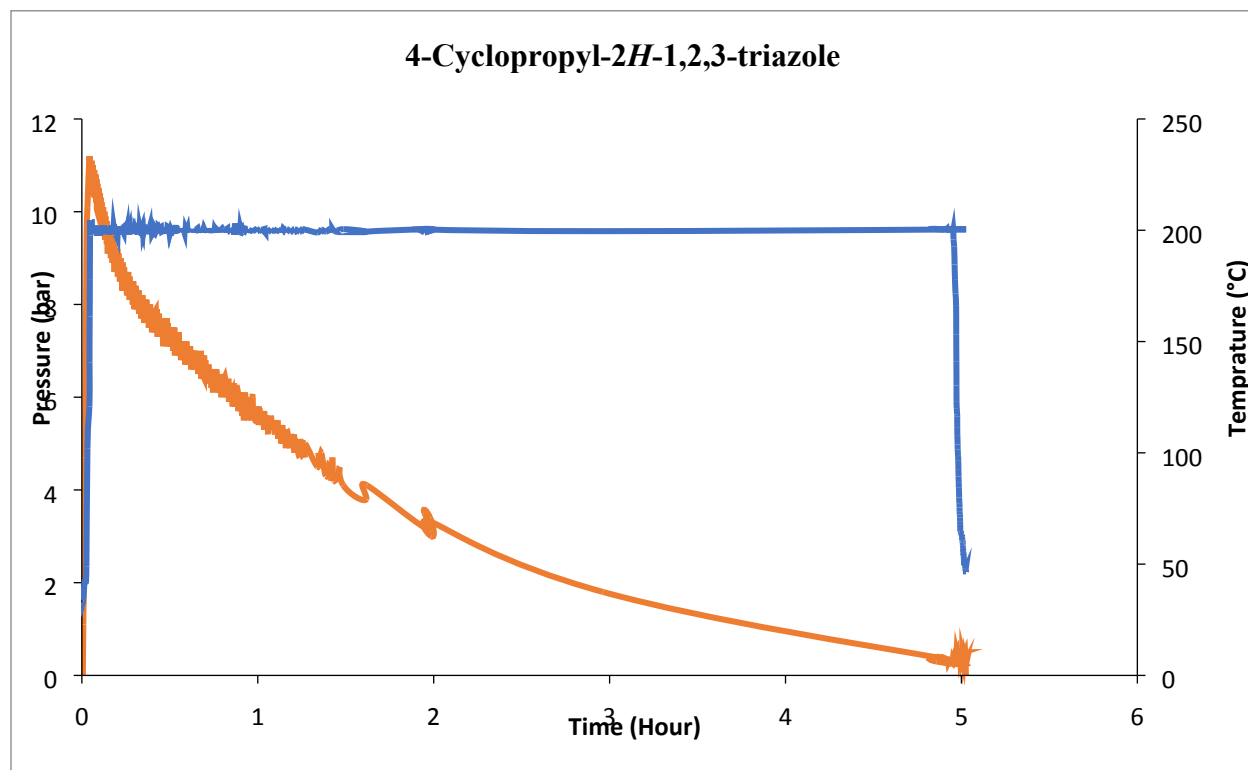


-0.00

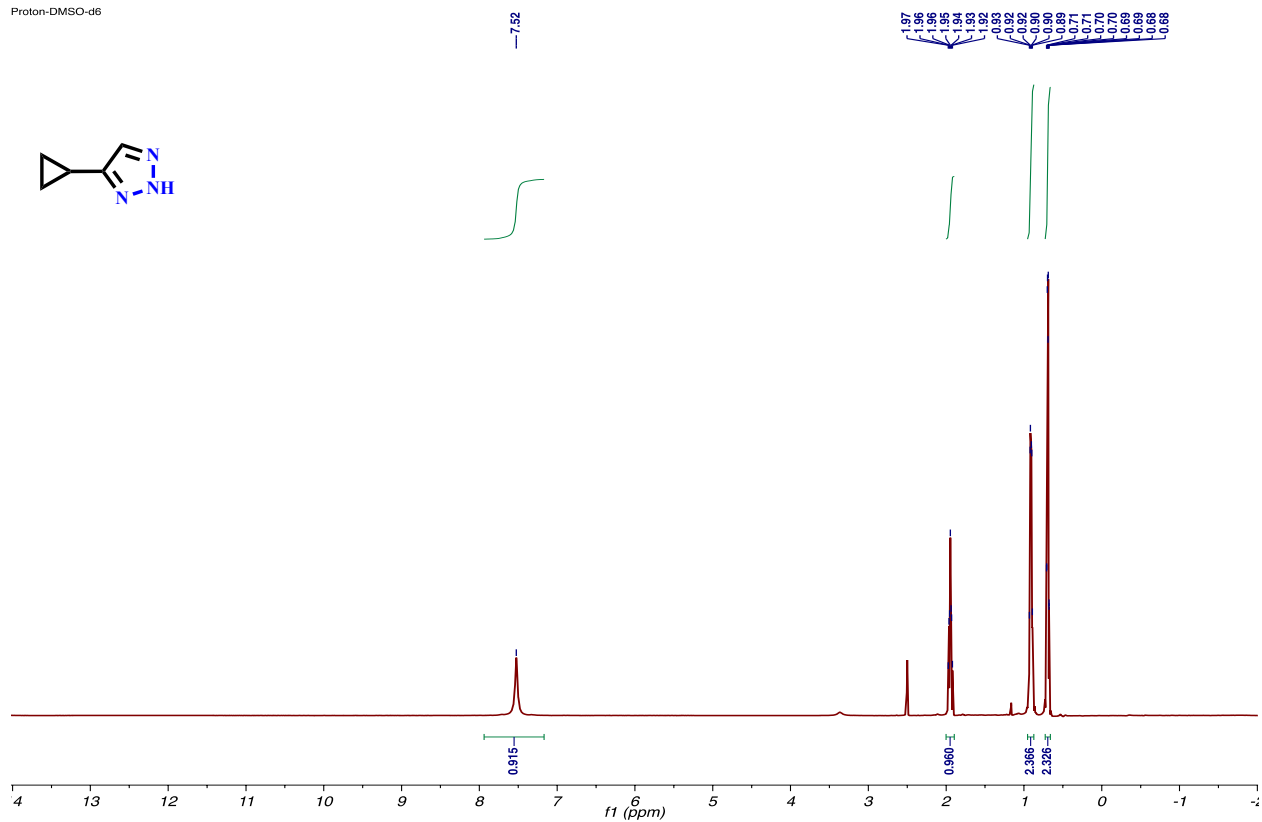
109.43
109.44
109.46



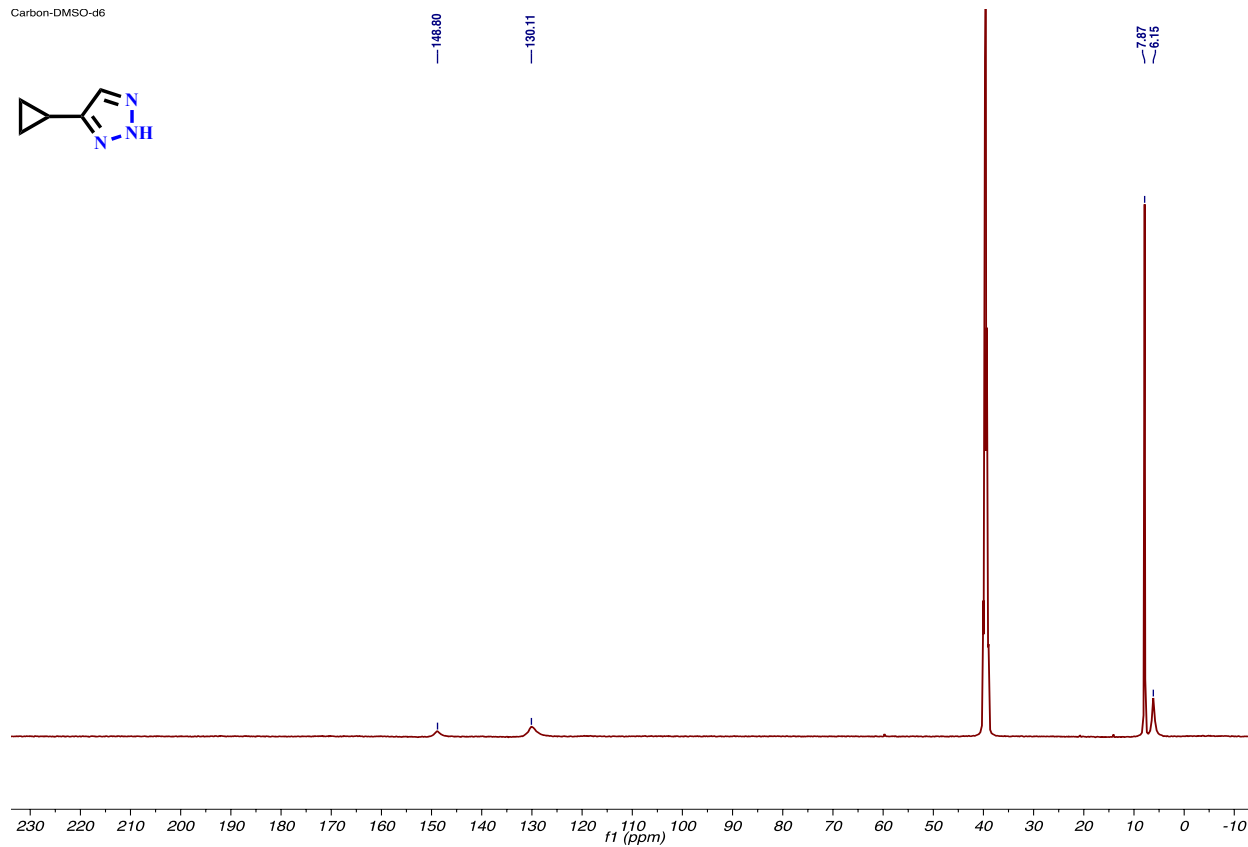
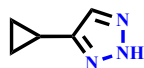
Microwave data and NMR spectra of 4-Cyclopropyl-2H-1,2,3-triazole (8)



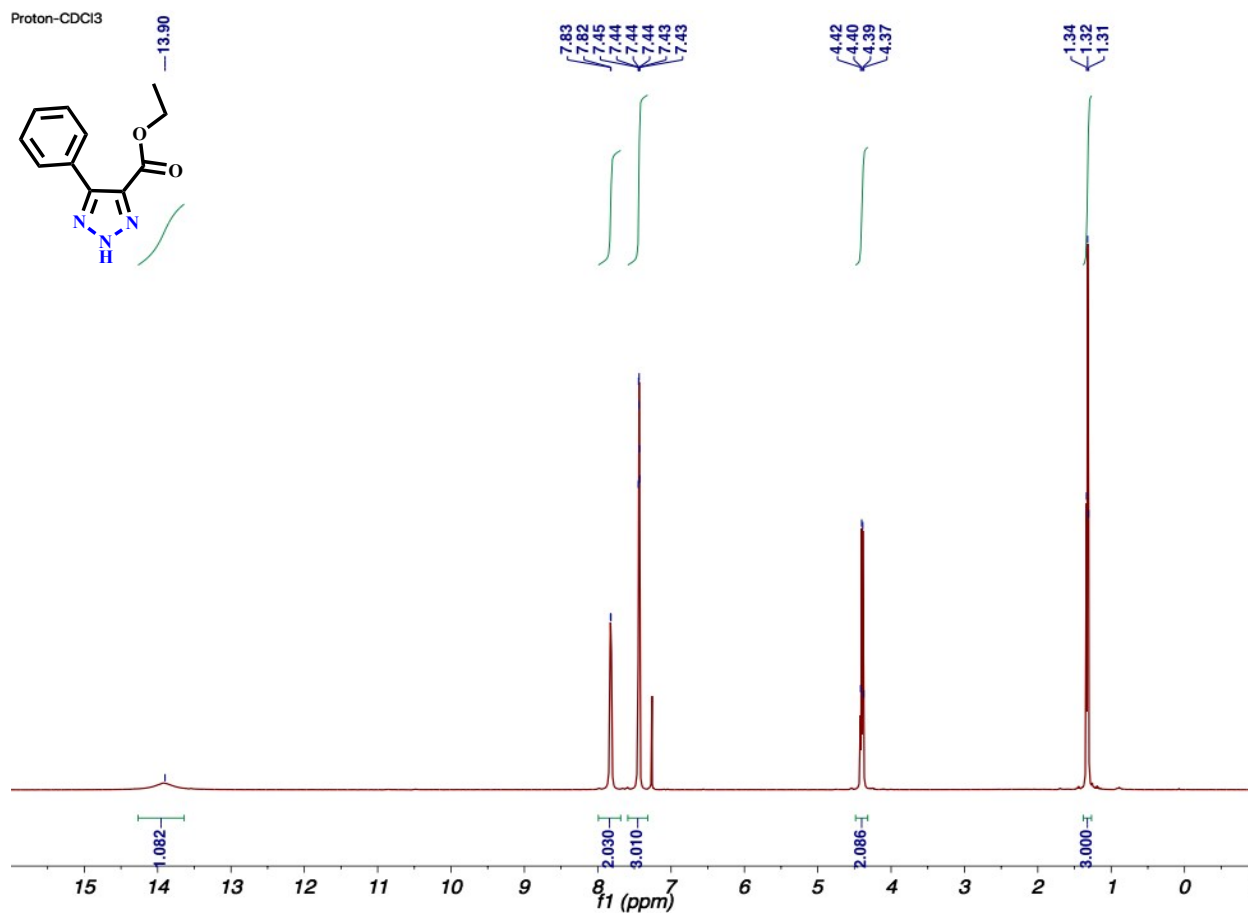
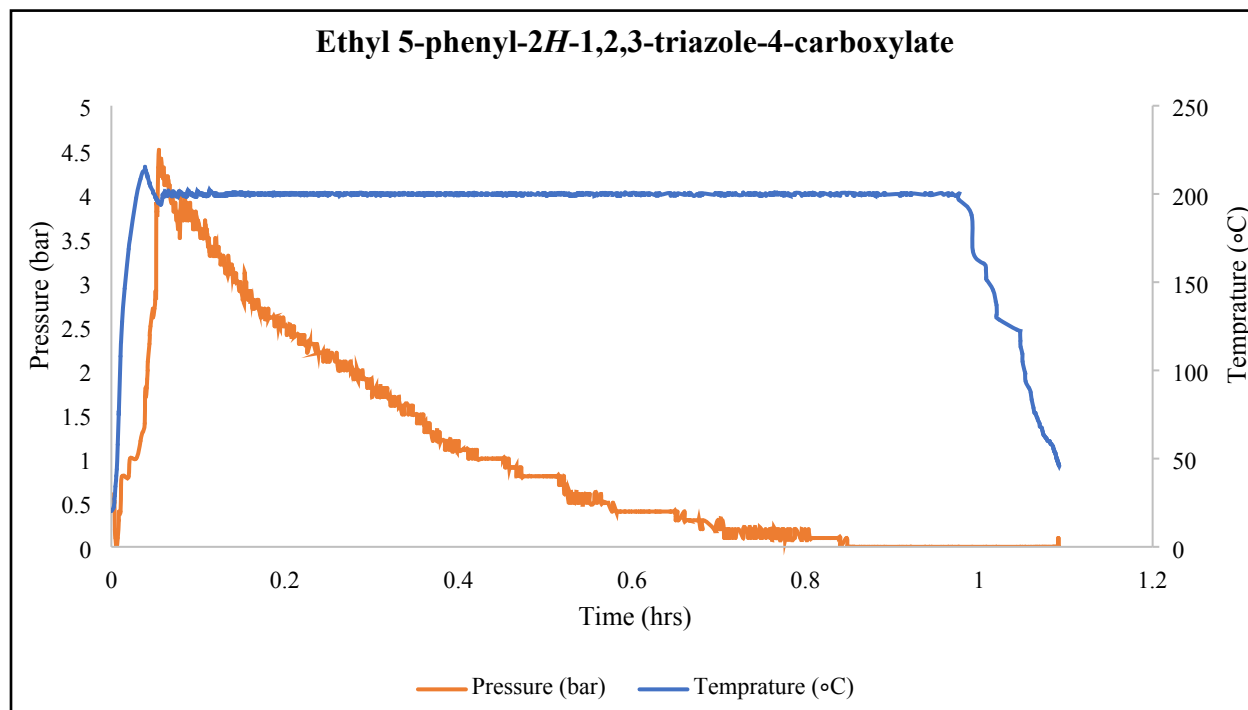
Proton-DMSO-d6



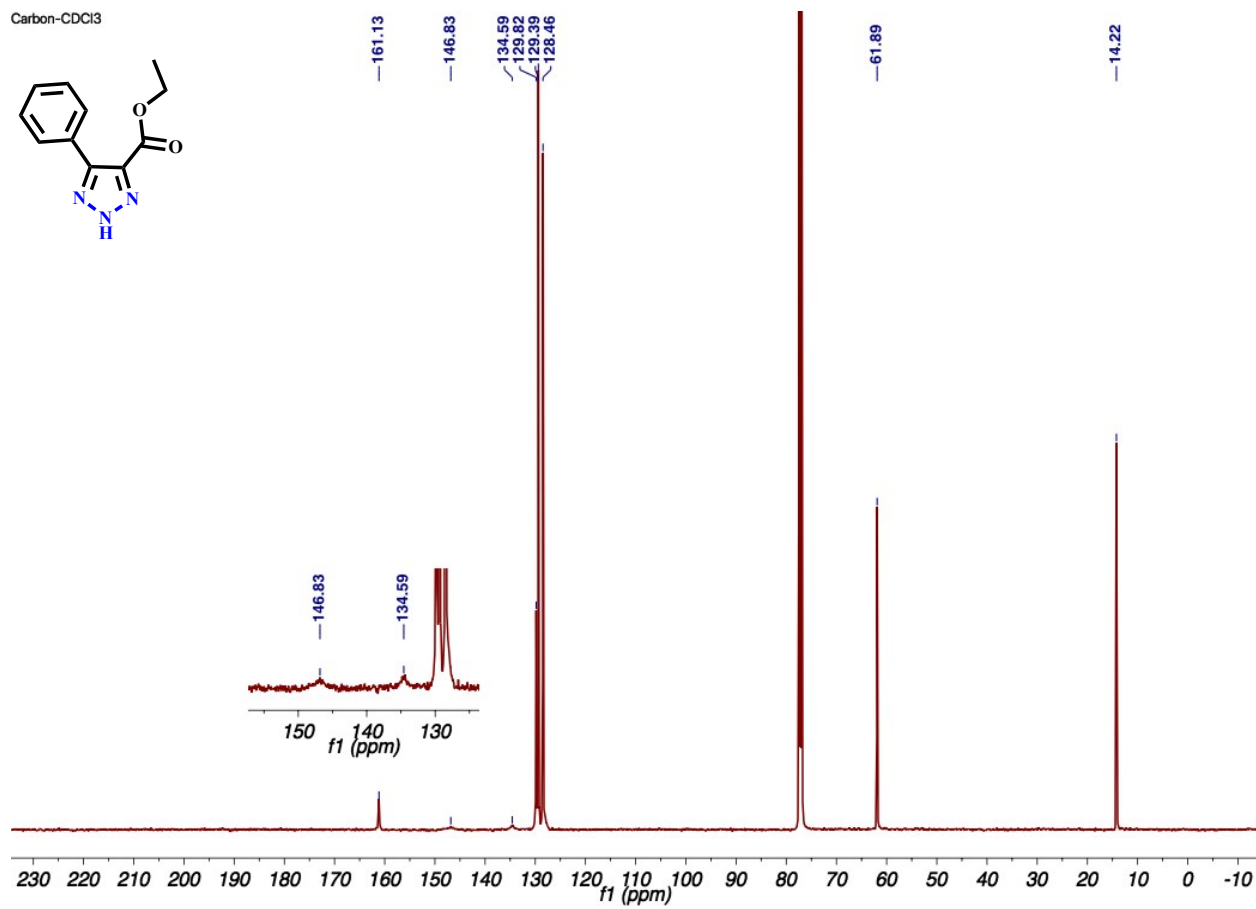
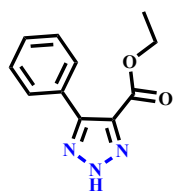
Carbon-DMSO-d6



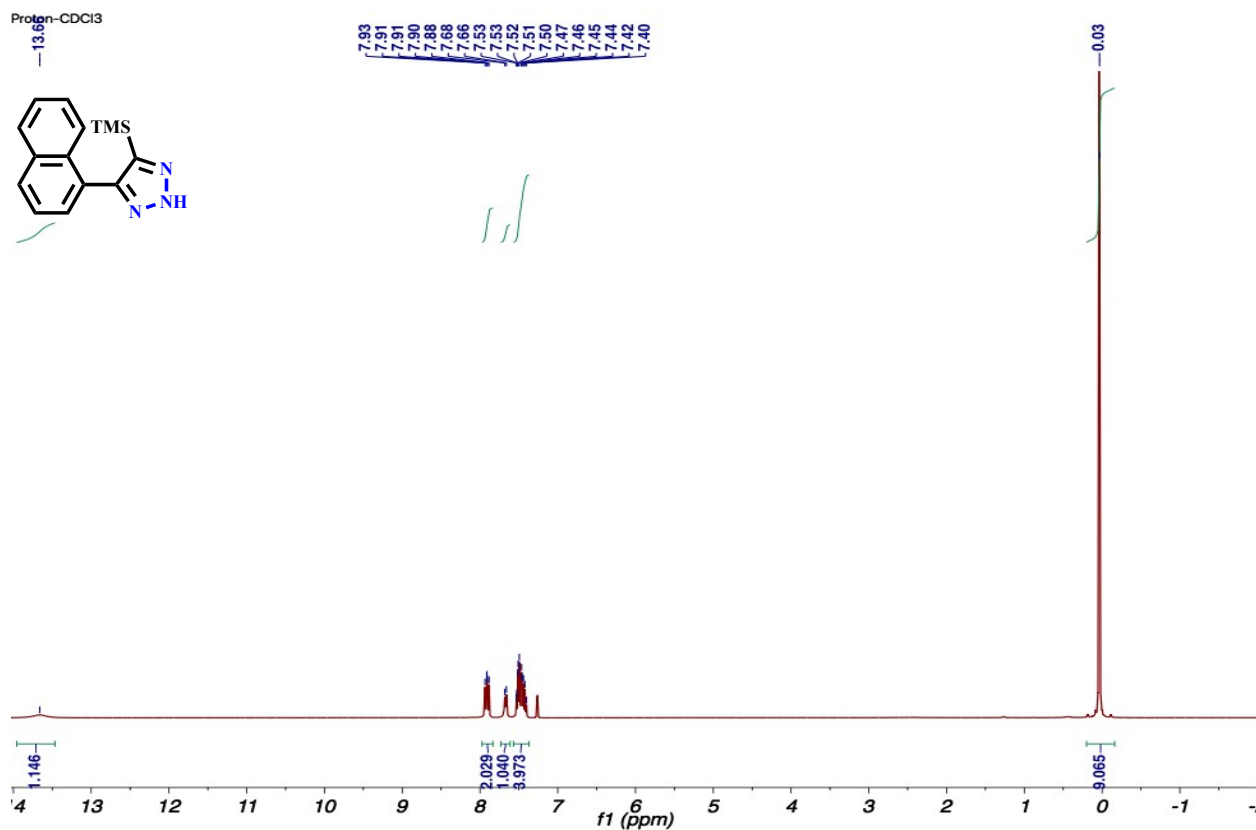
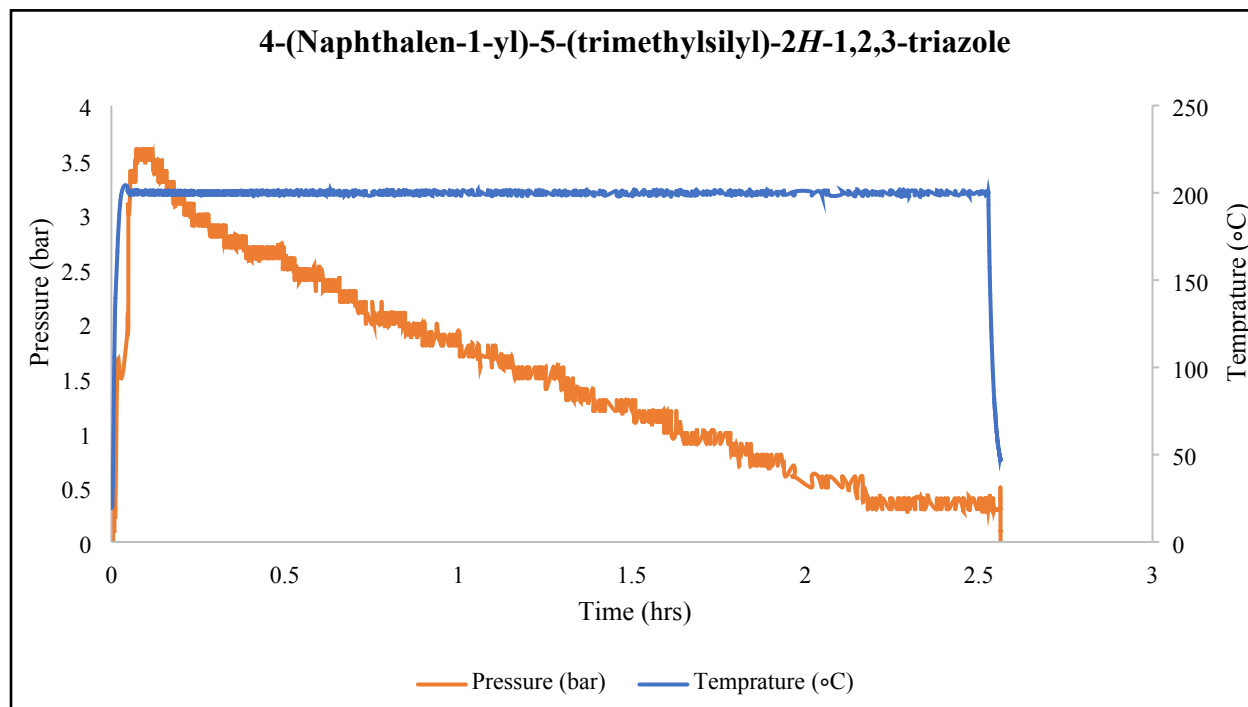
Microwave data and NMR spectra of Ethyl 5-phenyl-2H-1,2,3-triazole-4-carboxylate (9)



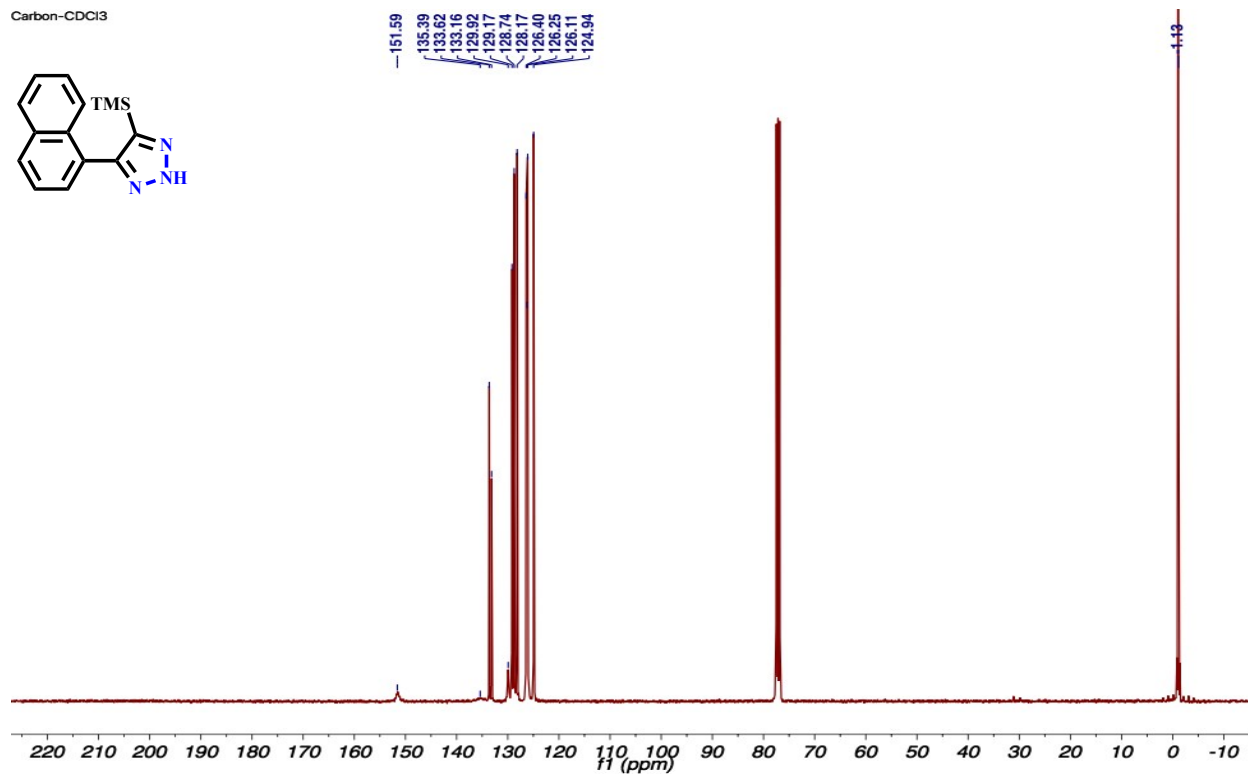
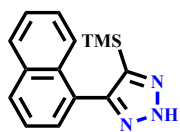
Carbon-CDCl₃



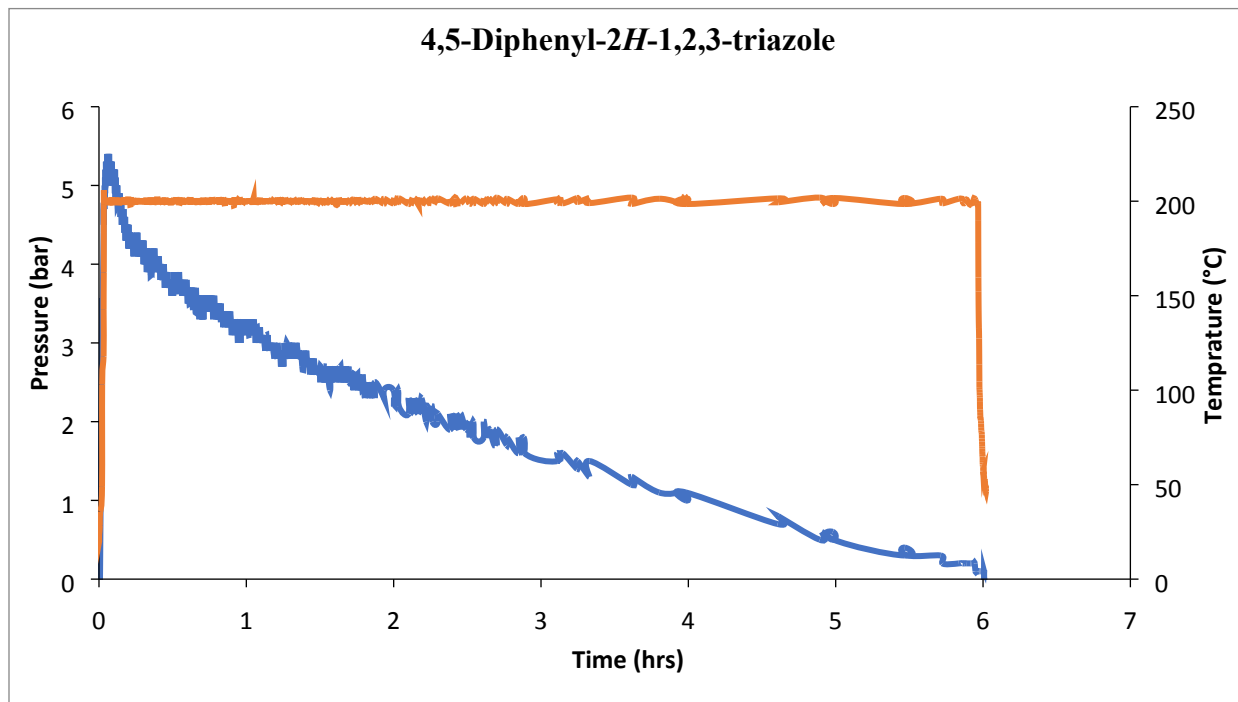
Microwave data and NMR spectra of 4-(Naphthalen-1-yl)-5-(trimethylsilyl)-2H-1,2,3-triazole (10)



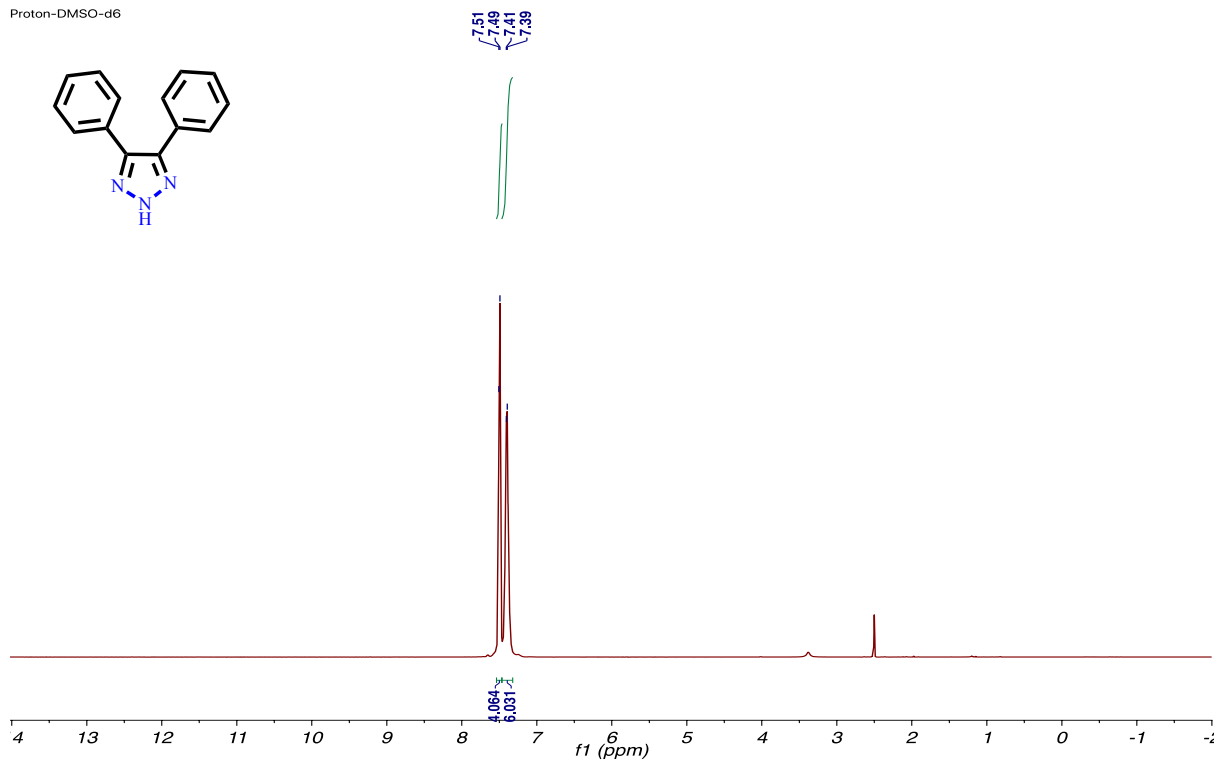
Carbon-CDCl₃



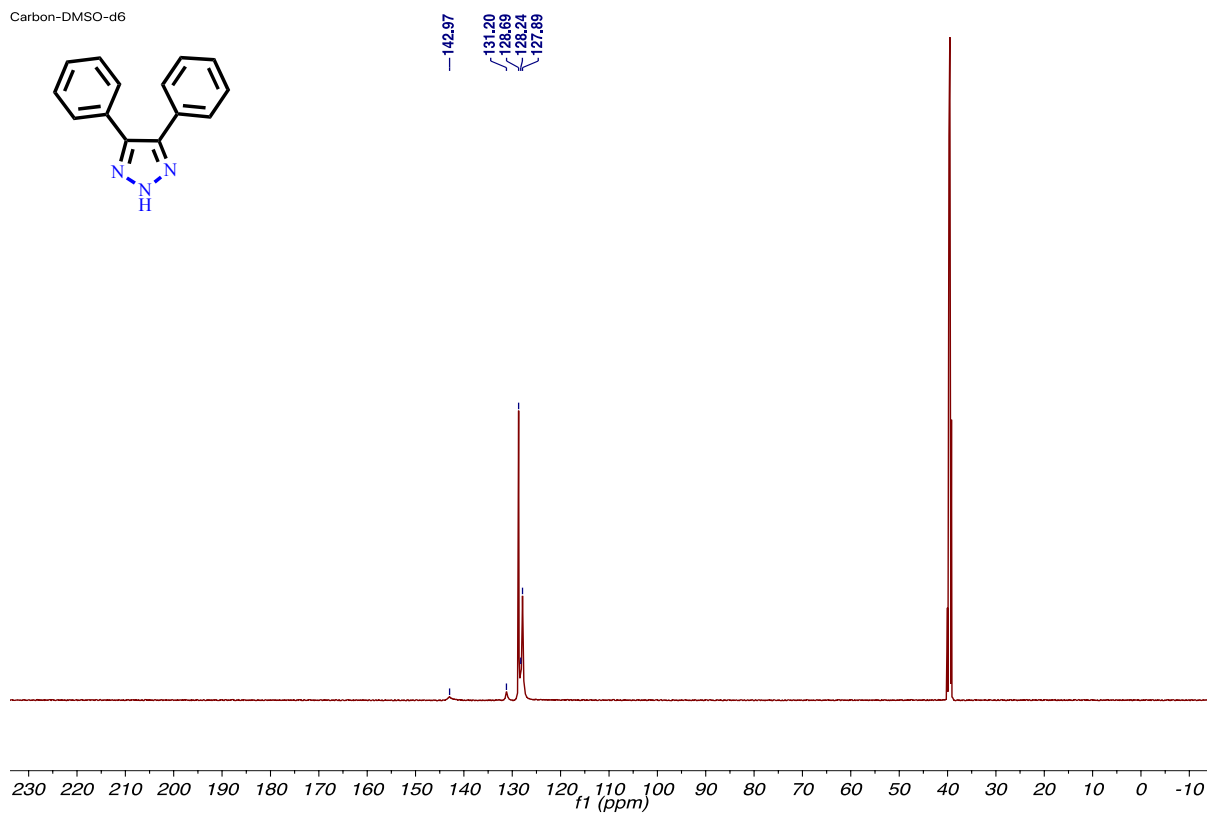
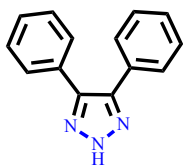
Microwave data and NMR spectra of 4,5-Diphenyl-2H-1,2,3-triazole (11)



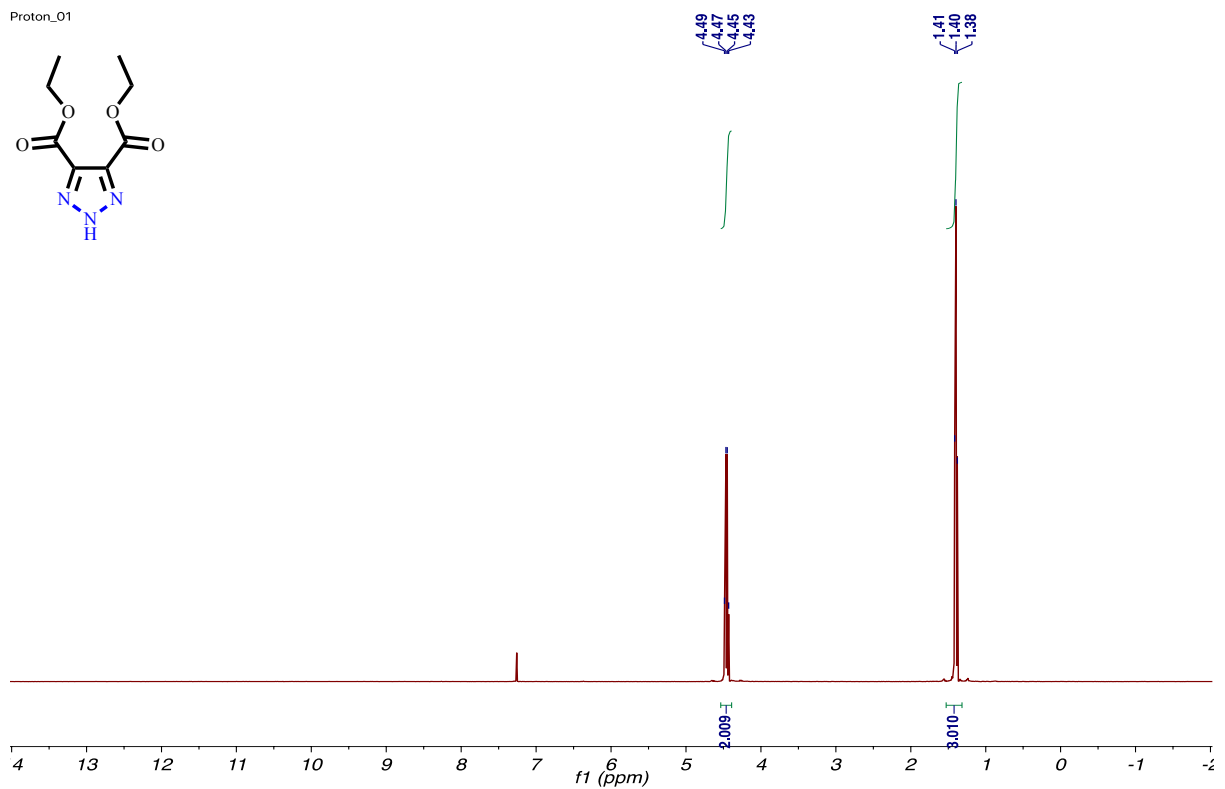
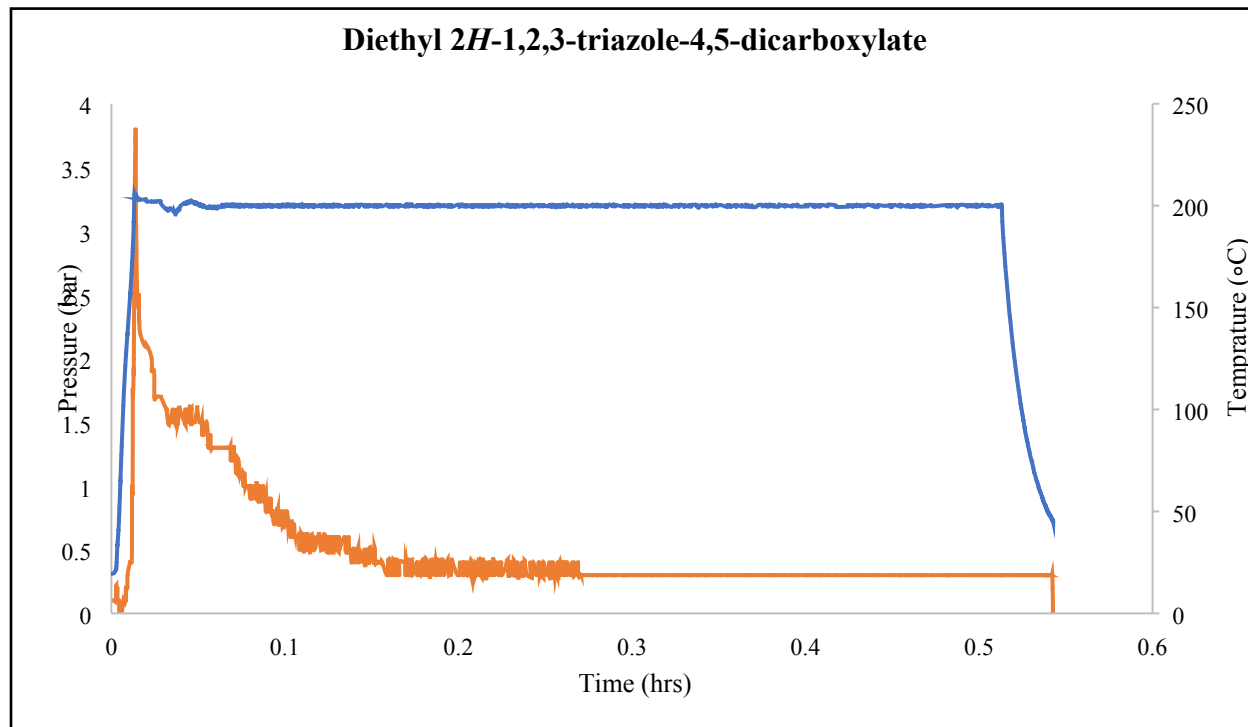
Proton-DMSO-d6



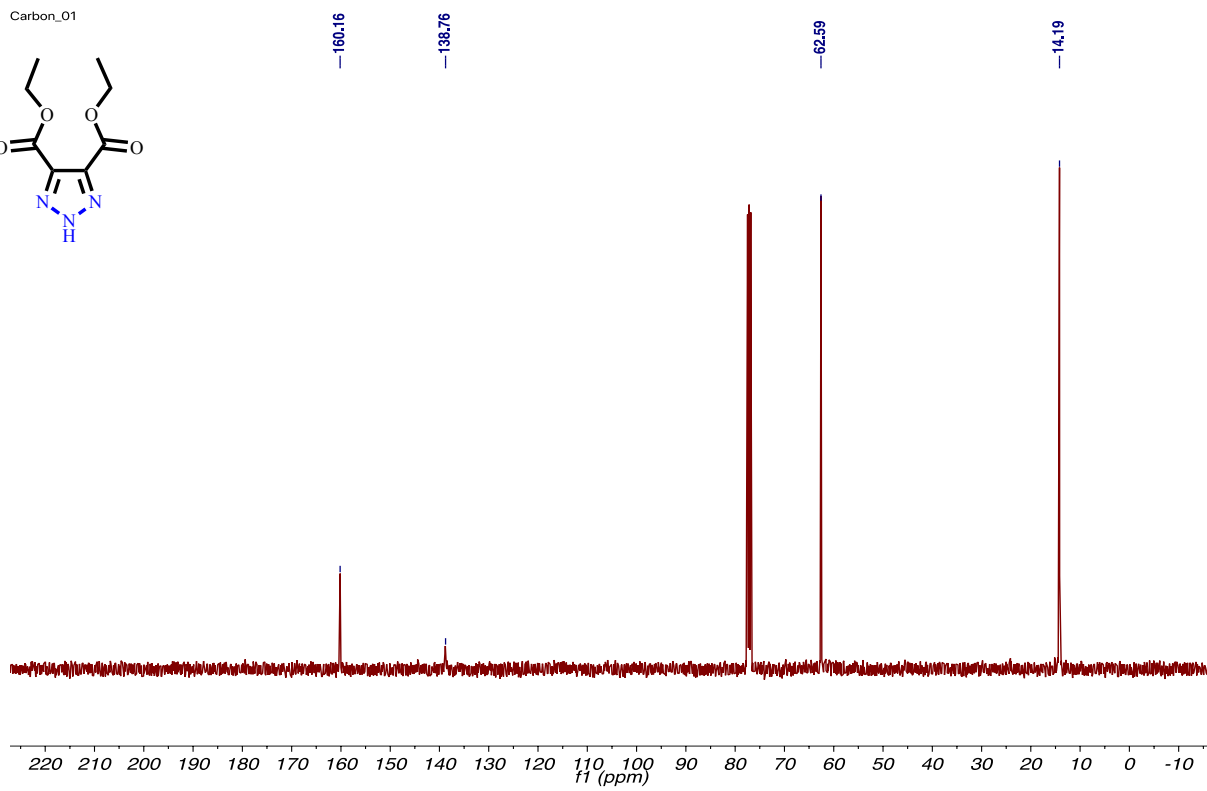
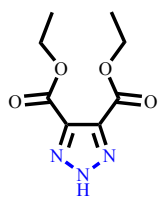
Carbon-DMSO-d6



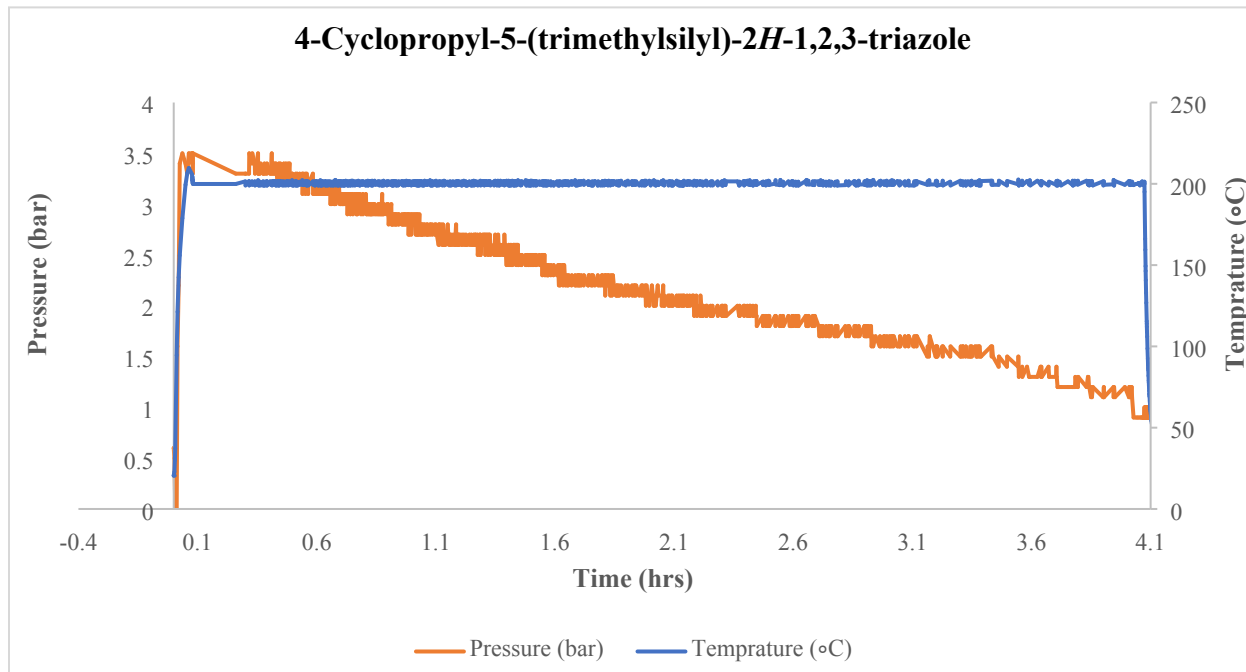
Microwave data and NMR spectra of Diethyl 2*H*-1,2,3-triazole-4,5-dicarboxylate (12)



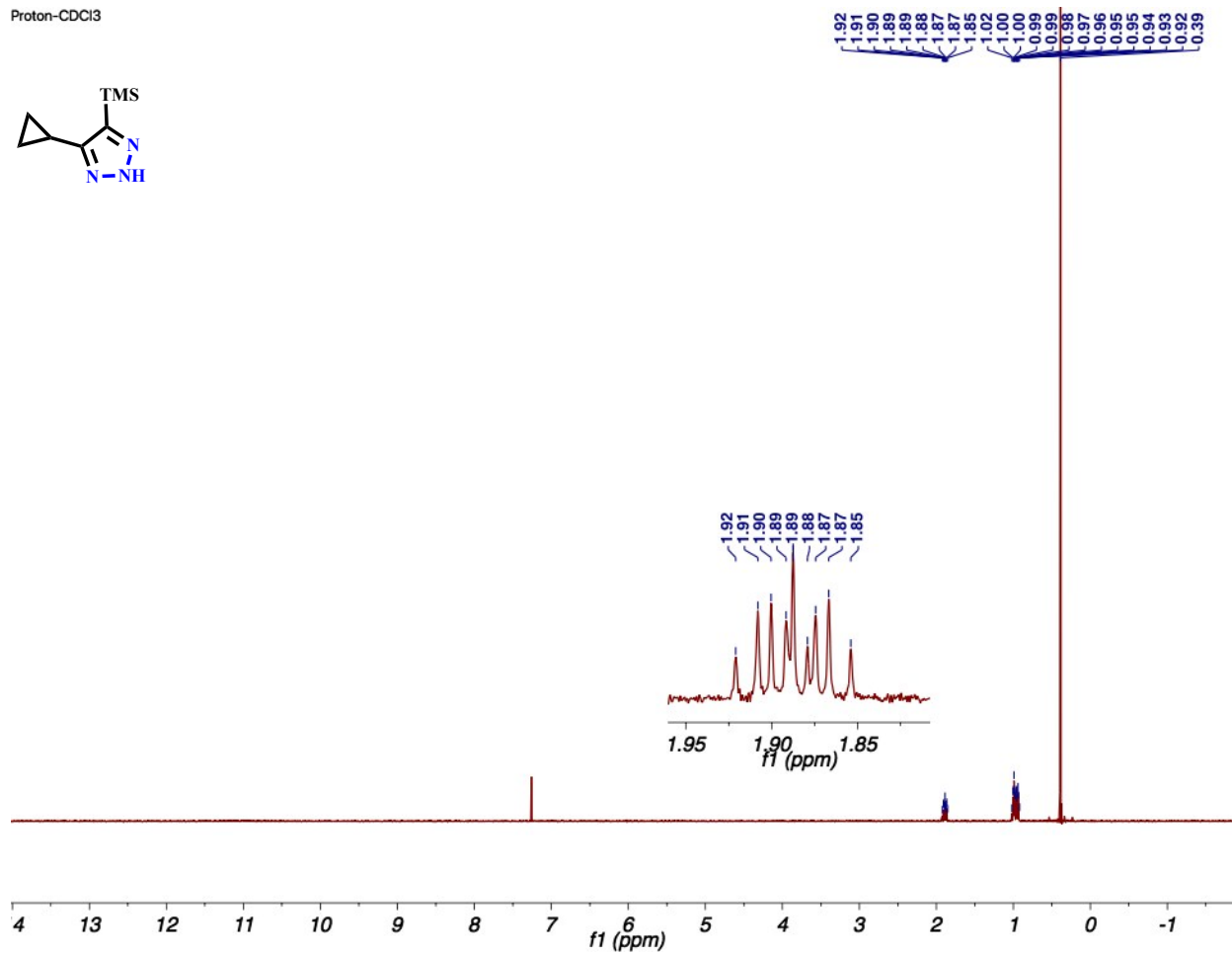
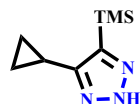
Carbon_01



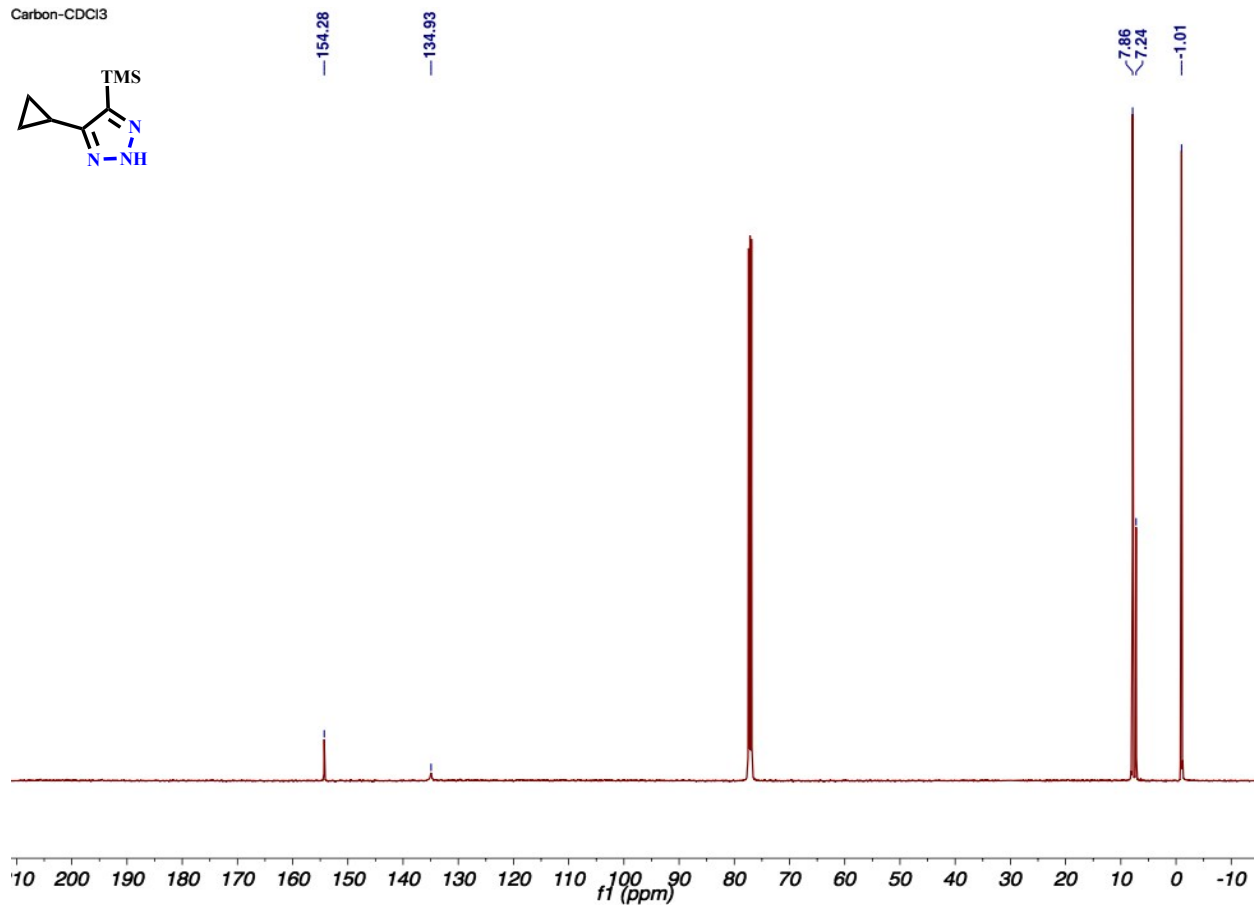
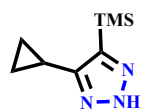
Microwave data and NMR spectra of 4-Cyclopropyl-5-(trimethylsilyl)-2H-1,2,3-triazole (13)



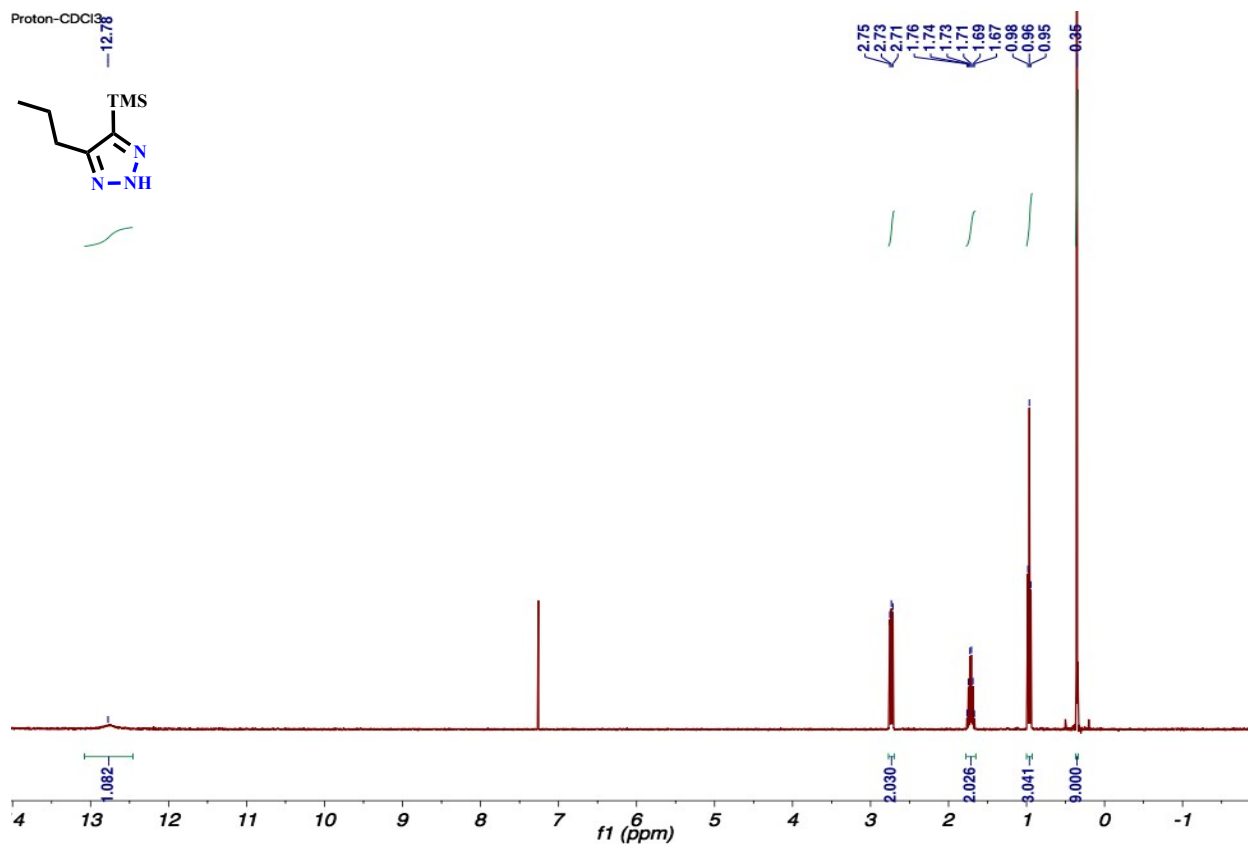
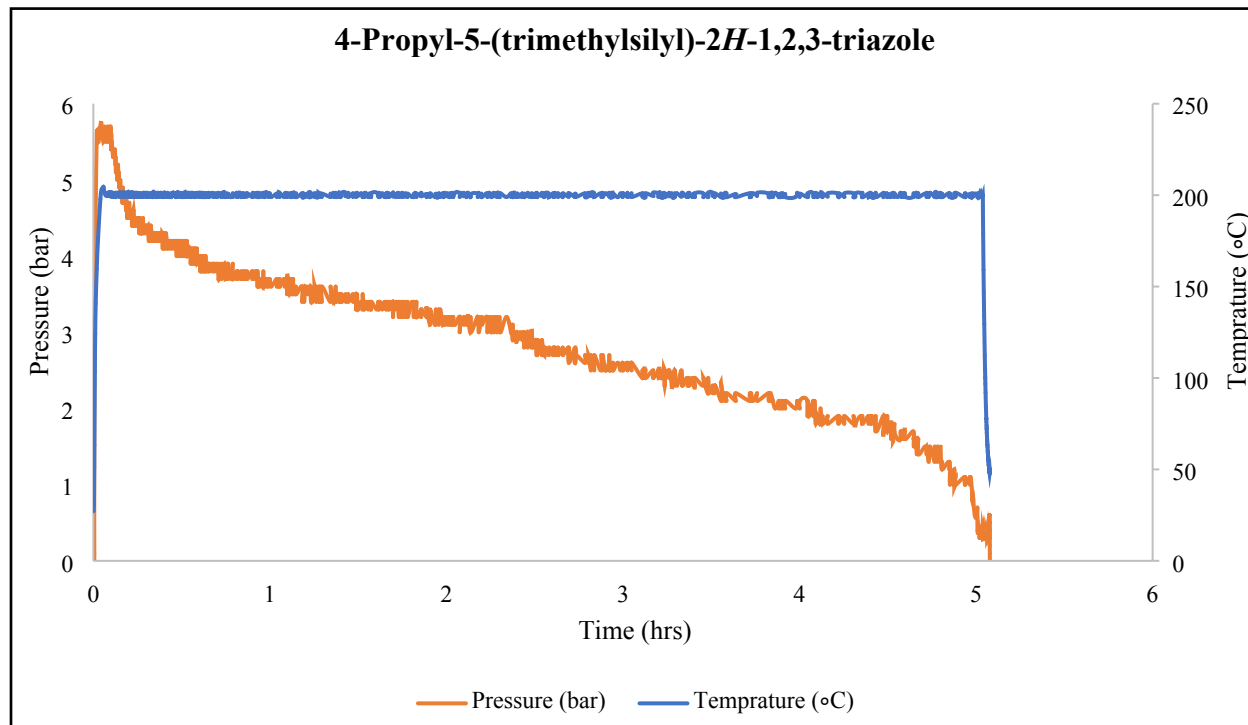
Proton-CDCl₃



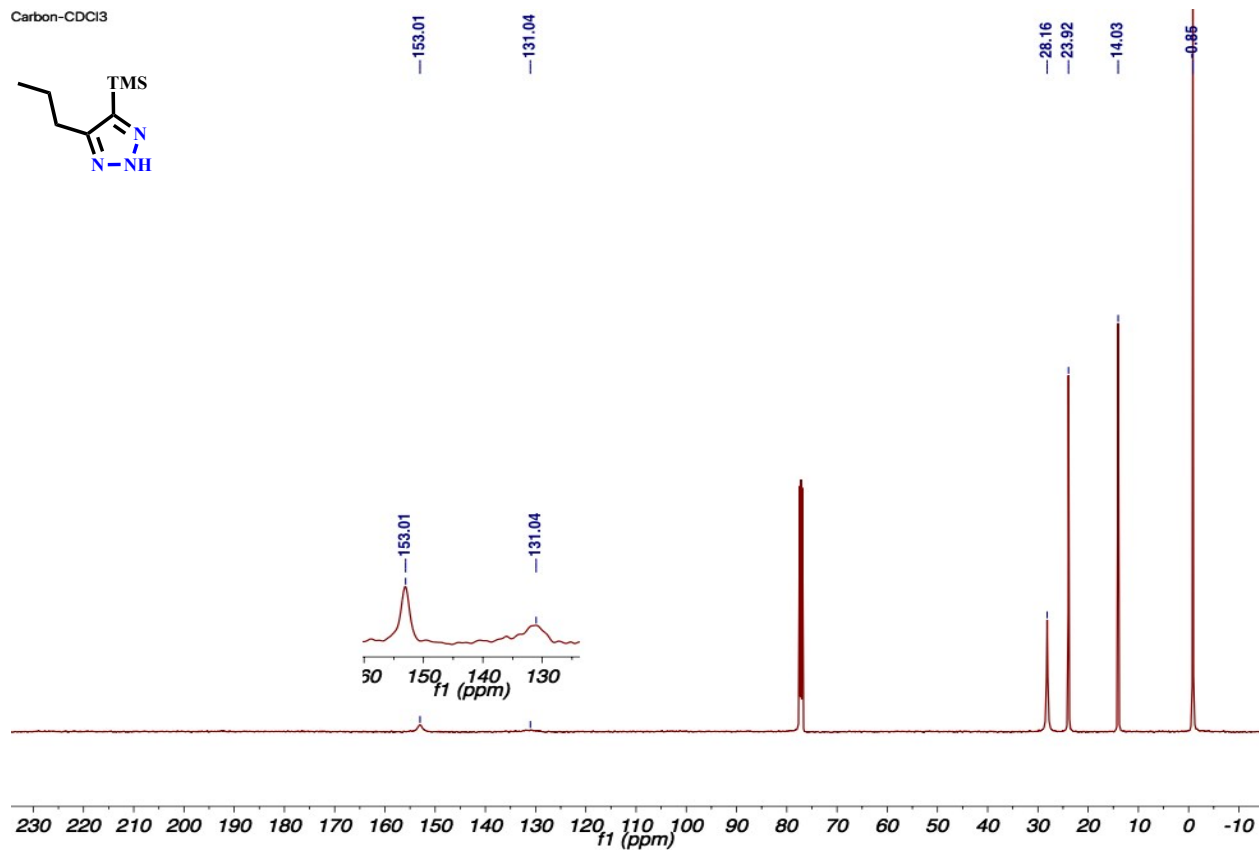
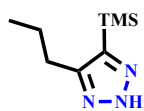
Carbon-CDCl₃



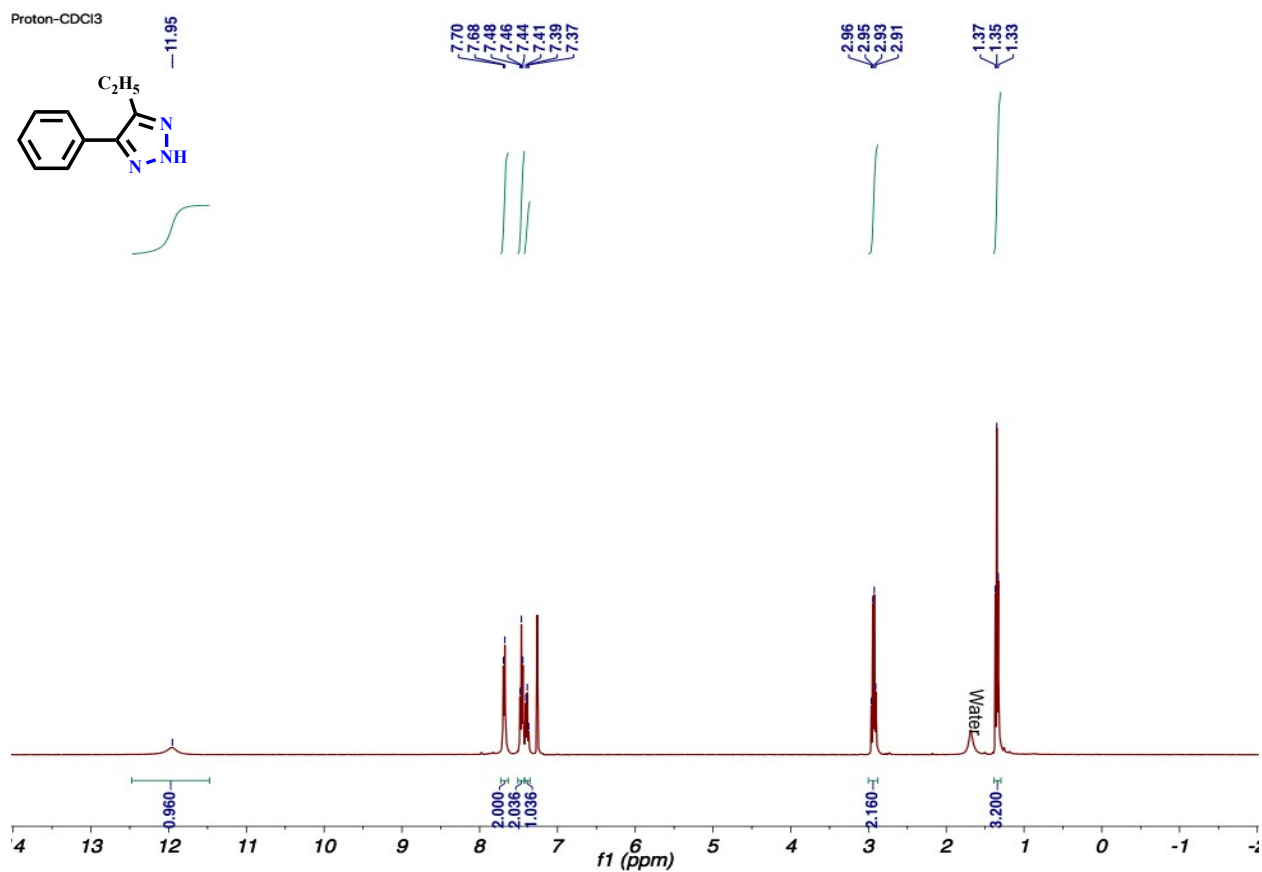
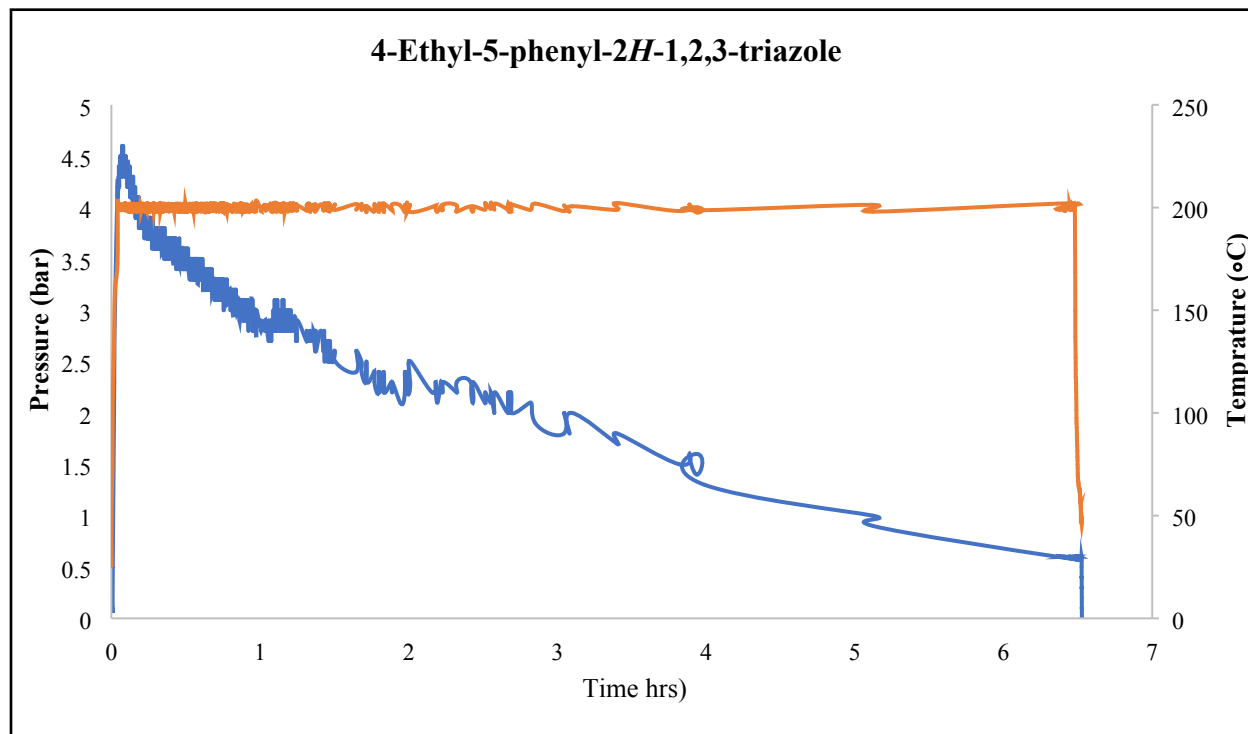
Microwave data and NMR spectra of 4-Propyl-5-(trimethylsilyl)-2H-1,2,3-triazole (14)



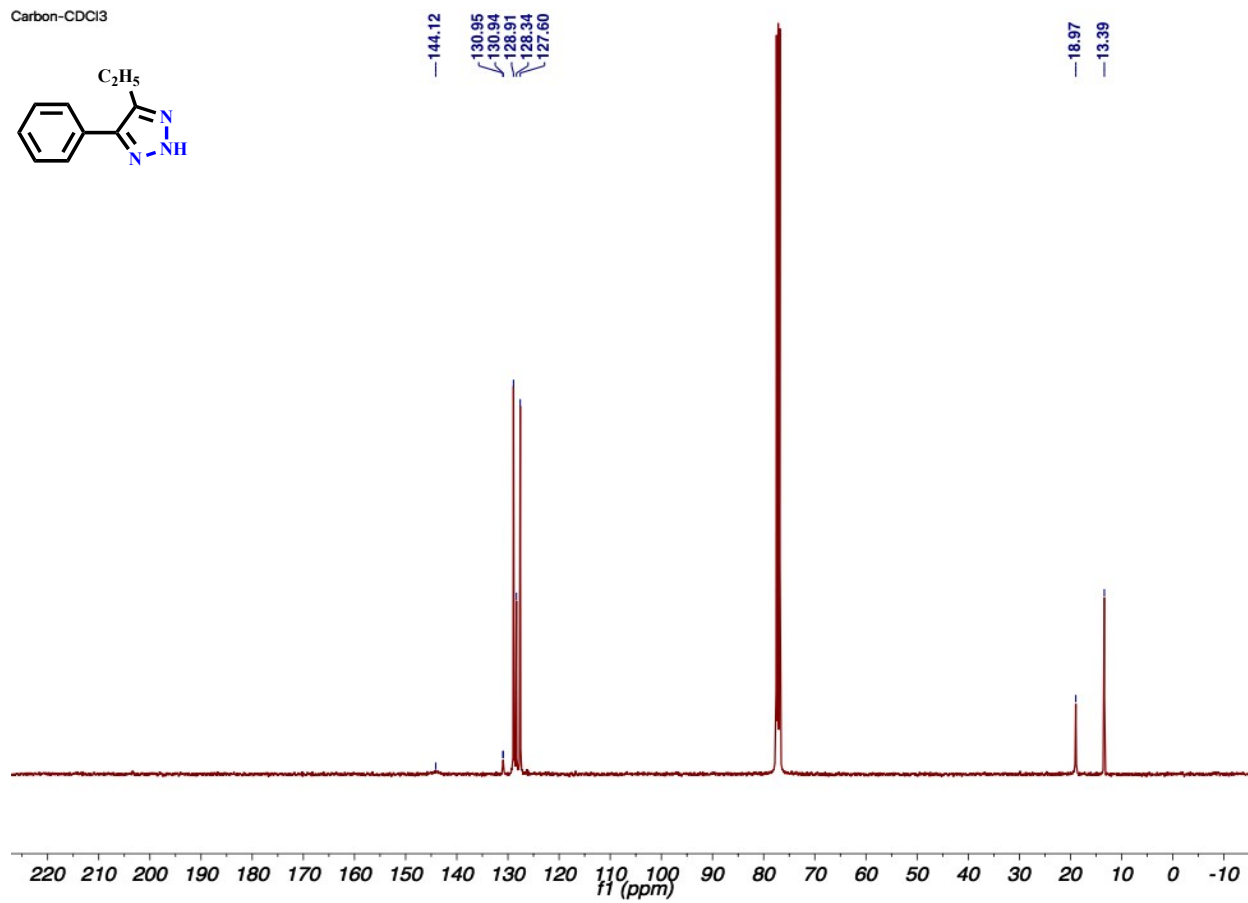
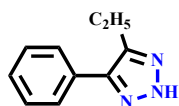
Carbon-CDCl3



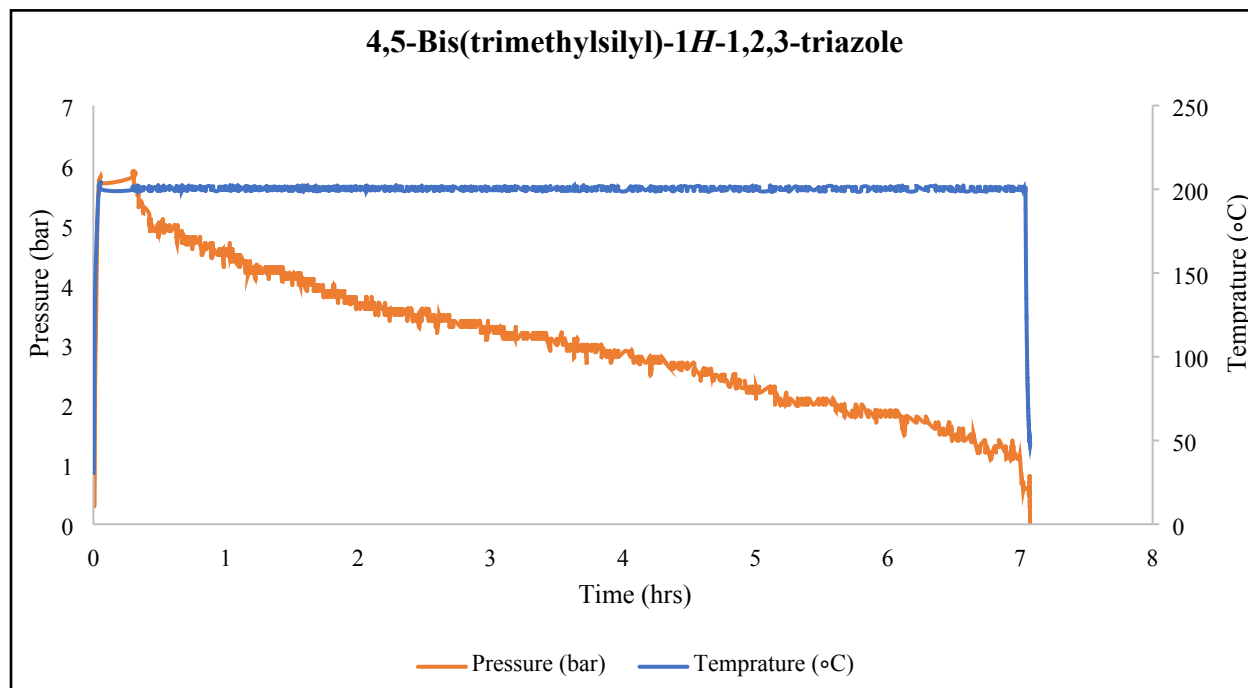
Microwave data and NMR spectra of 4-Ethyl-5-phenyl-2H-1,2,3-triazole (15)



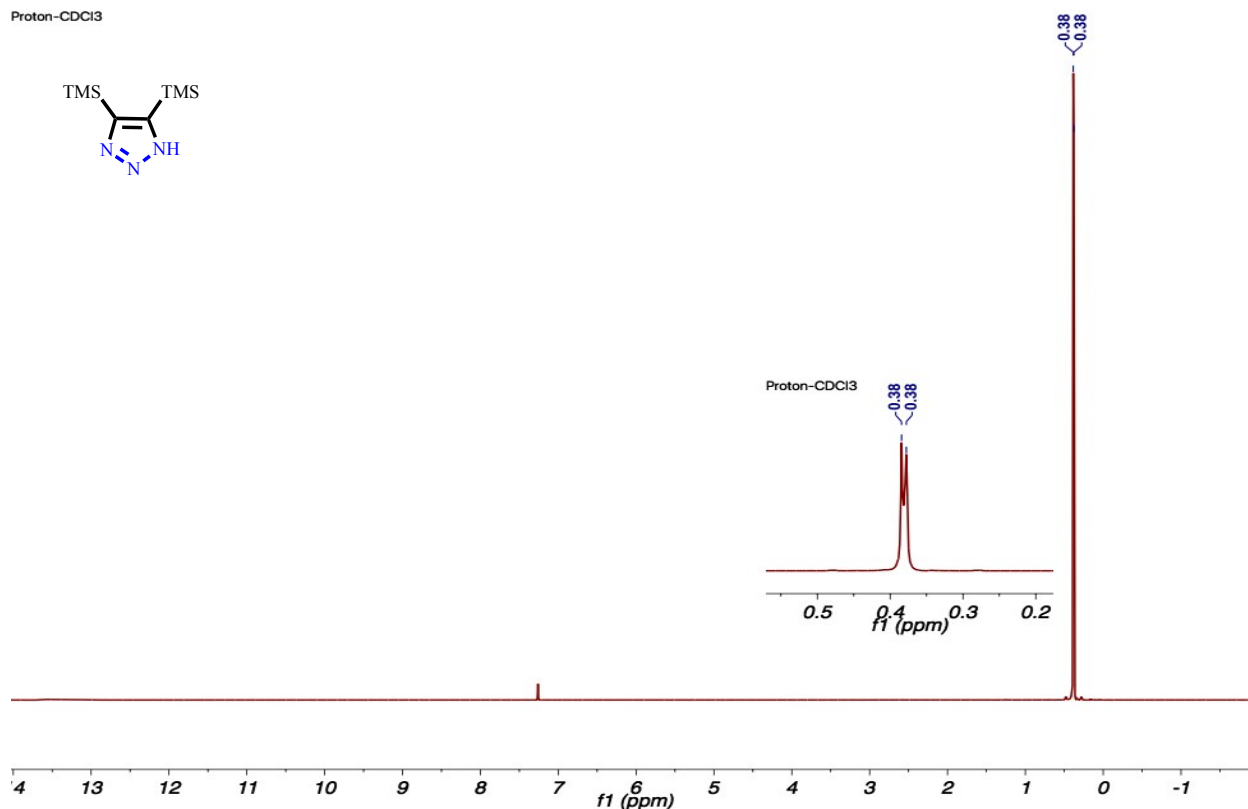
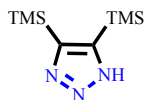
Carbon-CDCl₃



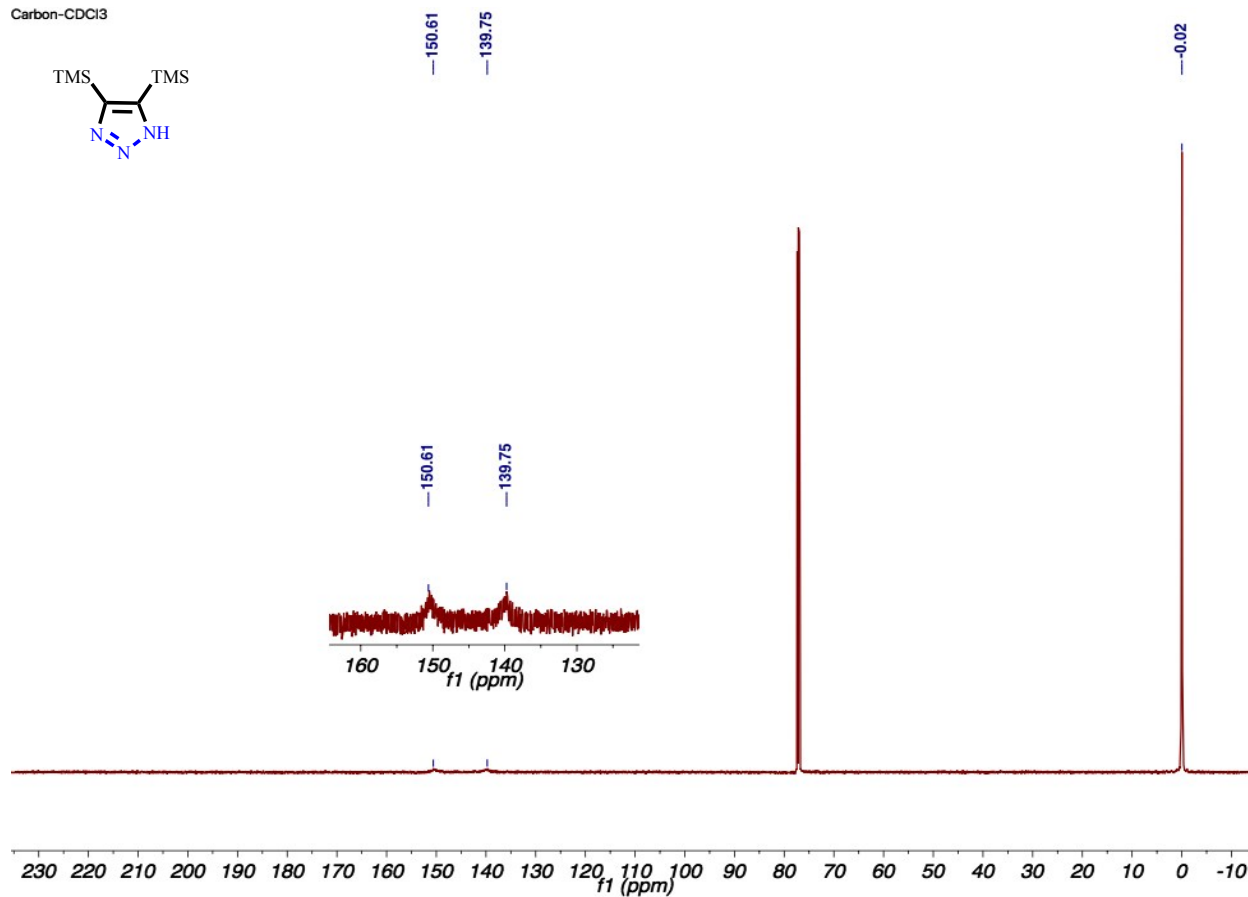
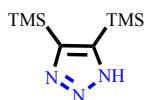
Microwave data, NMR spectra, and Variant Temperature Study of 4,5-Bis(trimethylsilyl)-1H-1,2,3-triazole (16)



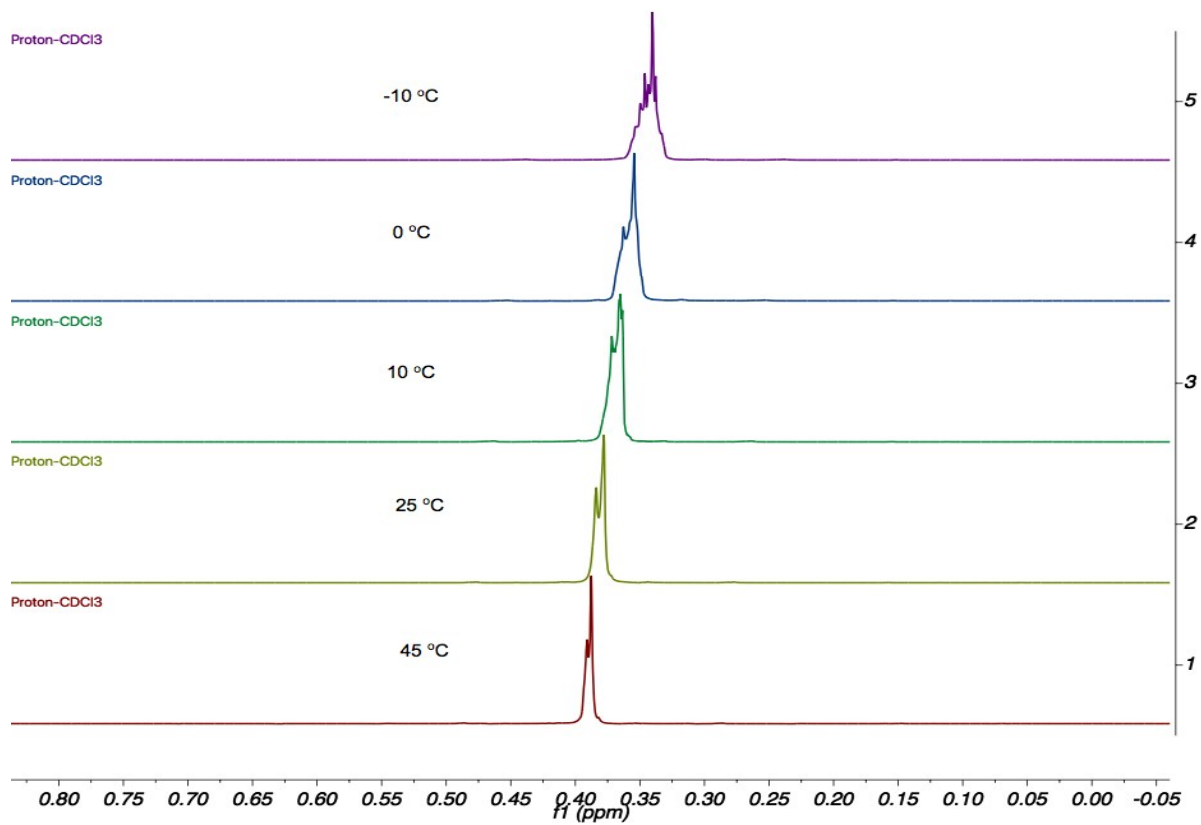
Proton-CDCI3



Carbon-CDCl₃



Proton-CDCl₃



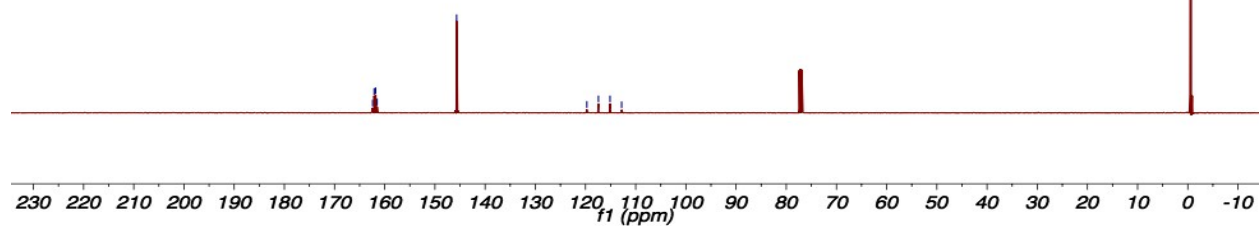
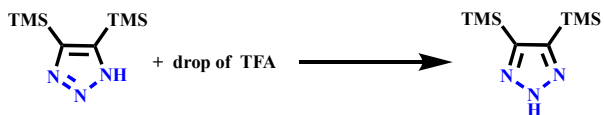
Carbon-CDCl₃+a drop of TFA

162.41
162.11
161.82
161.52

145.68

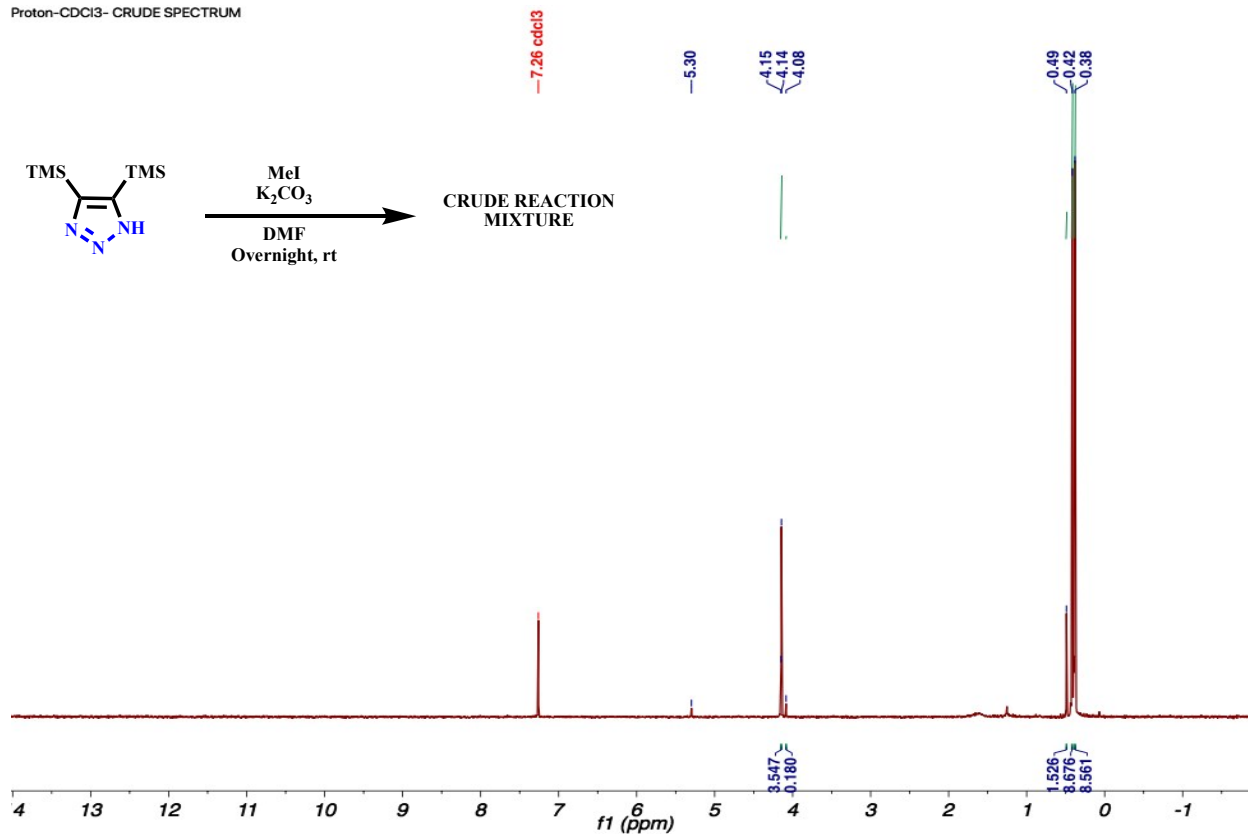
119.73
117.42
115.11
112.80

-0.65

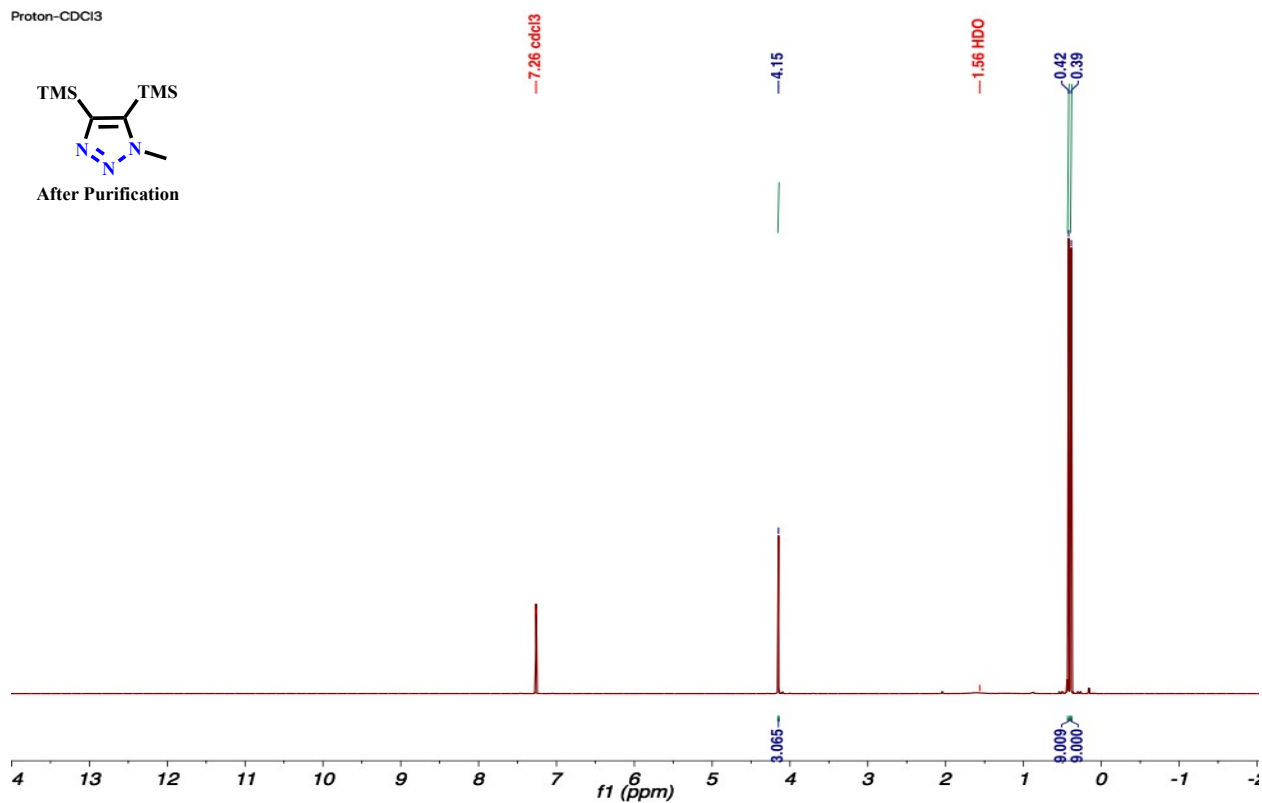


NMR spectra of 1-methyl-4,5-bis(trimethylsilyl)-1H-1,2,3-triazole (17)

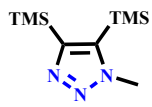
Proton-CDCl₃- CRUDE SPECTRUM



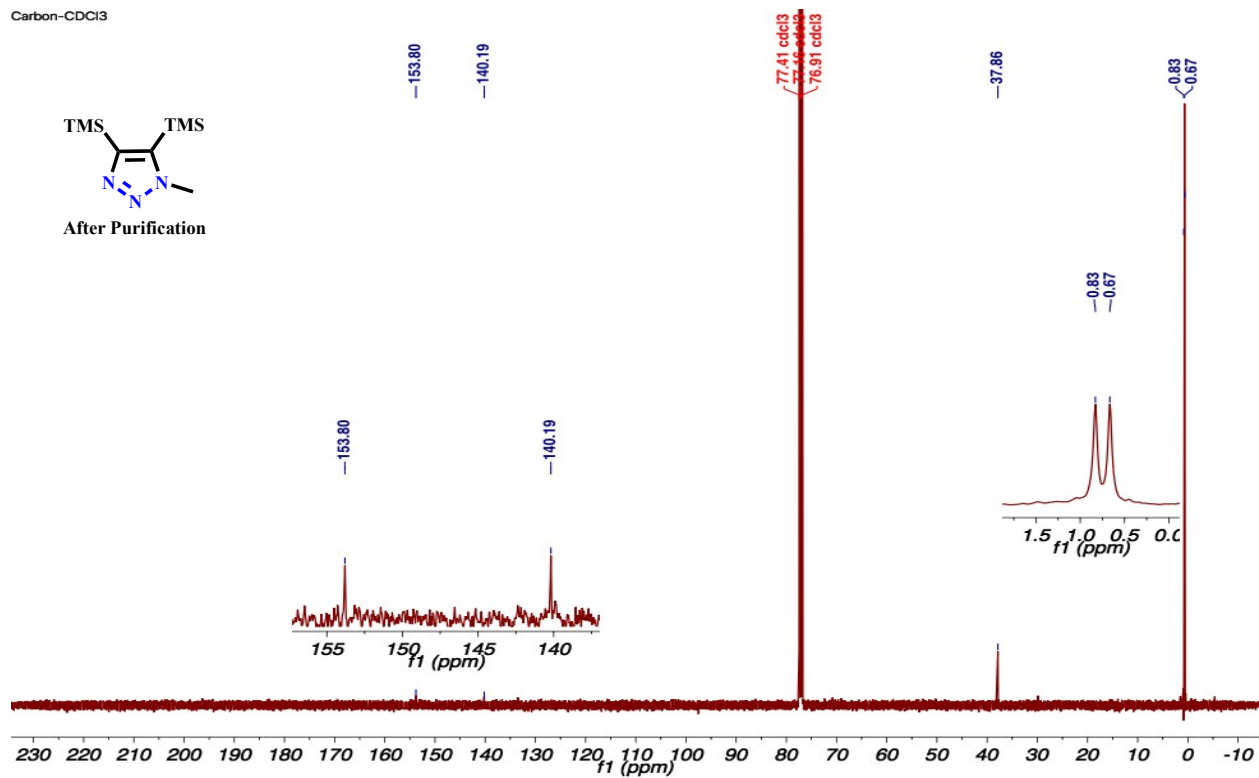
Proton-CDCl₃



Carbon-CDCl3



After Purification



X-ray Structure Determination for 16:

A prism-like specimen of $C_8H_{19}N_3Si_2$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX DUO system equipped with a TRIUMPH curved-crystal monochromator and a MoK α fine-focus tube ($\lambda = 0.71073 \text{ \AA}$).

A total of 2520 frames were collected. The total exposure time was 7.00 hours. The frames were integrated with the Bruker SAINT software package using a SAINT V8.34A (Bruker AXS, 2013) algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24848 reflections to a maximum θ angle of 27.48° (0.77 \AA resolution), of which 2950 were independent (average redundancy 8.423, completeness = 99.7%, $R_{\text{int}} = 4.44\%$, $R_{\text{sig}} = 2.30\%$) and 2747 (93.12%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 6.7038(11) \text{ \AA}$, $b = 9.1027(15) \text{ \AA}$, $c = 21.146(3) \text{ \AA}$, $\beta = 91.335(2)^\circ$, volume = $1290.0(4) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 9881 reflections above $20 \sigma(I)$ with $4.872^\circ < 2\theta < 61.00^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.824.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with $Z = 4$ for the formula unit, $C_8H_{19}N_3Si_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 127 variables converged at $R_1 = 6.55\%$, for the observed data and $wR_2 = 16.65\%$ for all data. The goodness-of-fit was 1.046. The largest peak in the final difference electron density synthesis was $1.013 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.440 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.098 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.099 g/cm^3 and $F(000)$, 464 e^- .

Table S1. Sample and crystal data for compound 16

Chemical formula	$C_8H_{19}N_3Si_2$	
Formula weight	213.44 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 \AA	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	$a = 6.7038(11) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 9.1027(15) \text{ \AA}$	$\beta = 91.335(2)^\circ$
	$c = 21.146(3) \text{ \AA}$	$\gamma = 90^\circ$
Volume	$1290.0(4) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.099 g/cm^3	
Absorption coefficient	0.243 mm^{-1}	
F(000)	464	

Table S2. Data collection and structure refinement for compound 16

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoK α
Theta range for data collection	1.93 to 27.48 $^\circ$
Index ranges	-8 \leq h \leq 8, -11 \leq k \leq 11, -27 \leq l \leq 27
Reflections collected	24848
Independent reflections	2950 [R(int) = 0.0444]
Coverage of independent reflections	99.7%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F 2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2950 / 0 / 127
Goodness-of-fit on F 2	1.046
Final R indices	2747 data; I $>$ 2 σ (I) R1 = 0.0655, wR2 = 0.1652 all data R1 = 0.0685, wR2 = 0.1665
Weighting scheme	w=1/[$\sigma^2(F_o^2)+(0.0196P)^2+8.9477P$] where P=(F $_o^2$ +2F $_c^2$)/3
Largest diff. peak and hole	1.013 and -0.440 e \AA^{-3}
R.M.S. deviation from mean	0.098 e \AA^{-3}

Table S3. Bond lengths (\AA) for compound 16

C1-N3	1.363(4)	C5-H5C	0.98	C1-C2	1.398(5)	C6-Si2	1.869(4)
C1-Si1	1.897(3)	C6-H6A	0.98	C2-N1	1.385(4)	C6-H6B	0.98
C2-Si2	1.880(3)	C6-H6C	0.98	C3-Si1	1.864(4)	C7-Si2	1.864(4)
C3-H3A	0.98	C7-H7A	0.98	C3-H3B	0.98	C7-H7B	0.98
C3-H3C	0.98	C7-H7C	0.98	C4-Si1	1.870(4)	C8-Si2	1.873(4)
C4-H4A	0.98	C8-H8A	0.98	C4-H4B	0.98	C8-H8B	0.98
C4-H4C	0.98	C8-H8C	0.98	C5-Si1	1.870(4)	N1-N2	1.321(4)
C5-H5A	0.98	N2-N3	1.339(4)	C5-H5B	0.98	N3-H1	0.86(5)

Table S4. Bond angles ($^\circ$) for compound 16

N3-C1-C2	103.7(3)	N3-C1-Si1	121.5(3)
C2-C1-Si1	134.7(3)	N1-C2-C1	107.5(3)
N1-C2-Si2	119.5(2)	C1-C2-Si2	132.9(3)
Si1-C3-H3A	109.5	Si1-C3-H3B	109.5
H3A-C3-H3B	109.5	Si1-C3-H3C	109.5
H3A-C3-H3C	109.5	H3B-C3-H3C	109.5

Si1-C4-H4A	109.5	Si1-C4-H4B	109.5
H4A-C4-H4B	109.5	Si1-C4-H4C	109.5
H4A-C4-H4C	109.5	H4B-C4-H4C	109.5
Si1-C5-H5A	109.5	Si1-C5-H5B	109.5
H5A-C5-H5B	109.5	Si1-C5-H5C	109.5
H5A-C5-H5C	109.5	H5B-C5-H5C	109.5
Si2-C6-H6A	109.5	Si2-C6-H6B	109.5
H6A-C6-H6B	109.5	Si2-C6-H6C	109.5
H6A-C6-H6C	109.5	H6B-C6-H6C	109.5
Si2-C7-H7A	109.5	Si2-C7-H7B	109.5
H7A-C7-H7B	109.5	Si2-C7-H7C	109.5
H7A-C7-H7C	109.5	H7B-C7-H7C	109.5
Si2-C8-H8A	109.5	Si2-C8-H8B	109.5
H8A-C8-H8B	109.5	Si2-C8-H8C	109.5
H8A-C8-H8C	109.5	H8B-C8-H8C	109.5
N2-N1-C2	109.4(3)	N1-N2-N3	106.9(3)
N2-N3-C1	112.5(3)	N2-N3-H1	118.(3)
C1-N3-H1	128.(3)	C3-Si1-C5	111.13(18)
C3-Si1-C4	108.15(17)	C5-Si1-C4	112.09(17)
C3-Si1-C1	107.82(16)	C5-Si1-C1	107.18(16)
C4-Si1-C1	110.39(16)	C7-Si2-C6	109.66(19)
C7-Si2-C8	108.01(18)	C6-Si2-C8	111.16(19)
C7-Si2-C2	108.62(16)	C6-Si2-C2	109.96(16)
C8-Si2-C2	109.37(17)		
