

Supporting information

for

A Straightforward Synthesis of Alkyl 1*H*-Tetrazol-5-yl Thioethers via a One-pot Reaction of Aldehydes and 1*H*-Tetrazole-5-thiols Mediated by *N*-Tosylhydrazones

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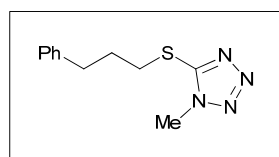
General methods: Unless otherwise noted, all solvents were purified according to the standard procedures. Dioxane, toluene, MeCN, DME and THF were distilled prior to use. 3-Phenylpropanal, propionaldehyde, benzaldehyde and furan-2-carbaldehyde were distilled prior to use. *N*-Tosylhydrazones **7a** was prepared from 3-phenylpropanal according to the known procedure.^[1] Other reagents were reagent grade and were used without purification. The ¹H-NMR spectra were recorded at 400, or 300 MHz (Bruker AV) in CDCl₃, CD₃OD, acetone-d₆ or DMSO-d₆. The ¹³C-NMR spectra were recorded at 150 or 100 MHz in CDCl₃, CD₃OD or DMSO-d₆. Chemical shifts are given in ppm relative to TMS or the appropriate solvent peak. Coupling constants (*J* values) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were measured using an IonSpec Ultima 7.0 TFT-ICR-MS instrument (IonSpec, USA) with a Waters Z-spray source. Column chromatography was performed on silica gel 100-200 mesh or 200-300 mesh.

General procedure for the synthesis of **9a** from *N*-tosylhydrazones **7a** and 1-methyl-1*H*-tetrazole-5-thiol **8a**

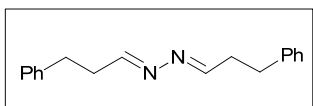
A mixture of **7a** (0.8 mmol, 1.0 equiv), **8a** (1.6 mmol, 2.0 equiv), and base (2.4 mmol, 3.0 equiv) in solvent (4.0 mL) was stirred at 110 °C for 2 h under Ar atmosphere. After the completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature and diluted with CH₂Cl₂ (20 mL). The mixture was filtered through a celite pad to remove the insoluble materials, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using a mixed solvent of EtOAc and petroleum ether as eluent to afford product **9a**.

General synthesis of thioethers **9** from aldehydes **12** and 1*H*-tetrazole-5-thiol **8** through a one-pot procedure

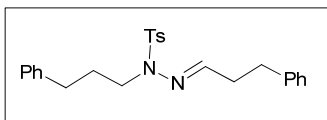
A mixture of aldehyde **12** (1.6 mmol, 2.0 equiv) and TsNHNH₂ (1.6 mmol, 2.0 equiv) in dioxane (5.0 mL) was stirred at rt for 0.5 h under argon atmosphere. Then, LiOH (3.2 mmol, 4.0 equiv), **8** (0.8 mmol, 1.0 equiv), LiI (0.8 mmol, 1.0 equiv), and dioxane (3.0 mL) were recharged *in situ* to the reaction vessel. The resulting mixture was then stirred vigorously at 110 °C for 4 h under Ar atmosphere. After the completion of the reaction as monitored by TLC, the mixture was cooled to room temperature and diluted with CH₂Cl₂ (20 mL). The mixture was filtered through a celite pad to remove the insoluble materials, and the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel by a mixed solvent of EtOAc and petroleum ether as eluent to afford product **9**.



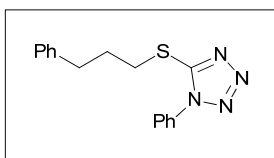
9a: ¹H NMR (300 MHz, DMSO) δ 7.31–7.17 (m, 5H), 3.93 (s, 3H), 3.27 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.07–1.97 (m, 2H). ¹³C NMR (150 MHz, DMSO) δ 153.6, 140.8, 128.3, 128.3, 125.9, 33.7, 33.5, 32.2, 30.6. HRMS (ESI-MS) Found 235.1011 [M+H]⁺, C₁₁H₁₅N₄S requires 235.1017.



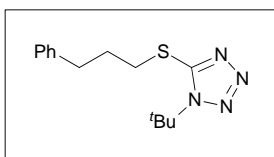
10: ^1H NMR (300 MHz, DMSO) δ 7.78 (t, J = 5.1 Hz, 2H), 7.31–7.16 (m, 10H), 2.83 (t, J = 7.6 Hz, 4H), 2.61–2.54 (m, 4H). ^{13}C NMR (100 MHz, DMSO) δ 163.2, 159.1, 140.9, 128.3, 125.9, 33.5, 31.5. HRMS (ESI-MS) Found 287.1519 $[\text{M}+\text{Na}]^+$, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{Na}$ requires 287.1524.



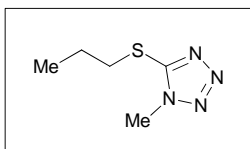
11: ^1H NMR (300 MHz, Acetone) δ 7.64–7.59 (m, 3H), 7.38 (d, J = 8.0 Hz, 2H), 7.30–7.14 (m, 10H), 3.34 (t, J = 7.2 Hz, 2H), 2.85 (dd, J = 15.2, 7.6 Hz, 2H), 2.69–2.56 (m, 4H), 2.42 (s, 3H), 1.75–1.65 (m, 2H). ^{13}C NMR (100 MHz, Acetone) δ 160, 144.7, 142.5, 141.8, 135.4, 130.3, 129.3, 129.3, 129.2, 126.9, 126.8, 49.5, 35.2, 33.4, 32.7, 30.1, 21.5. HRMS (ESI-MS) found 443.1740 $[\text{M}+\text{Na}]^+$, $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}_2\text{S}$ requires 443.1769; found 459.1492 $[\text{M}+\text{K}]^+$, $\text{C}_{25}\text{H}_{28}\text{KN}_2\text{O}_2\text{S}$ requires 459.1509.



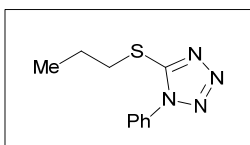
9b: ^1H NMR (300 MHz, DMSO) δ 7.66 (s, 5H), 7.31–7.16 (m, 5H), 3.33 (t, J = 7.1 Hz, 2H), 2.71 (t, J = 7.6 Hz, 2H), 2.10–2.00 (m, 2H). ^{13}C NMR (150 MHz, DMSO) δ 154.3, 140.8, 133.1, 130.5, 129.9, 128.3, 128.3, 125.9, 124.5, 33.8, 32.3, 30.3. HRMS (ESI-MS) Found 297.1165 $[\text{M}+\text{H}]^+$, $\text{C}_{16}\text{H}_{17}\text{N}_4\text{S}$ requires 297.1174.



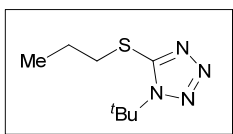
9c: ^1H NMR (300 MHz, DMSO) δ 7.31–7.16 (m, 5H), 3.35 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 7.6 Hz, 2H), 2.09–1.99 (m, 2H), 1.67 (s, 9H). ^{13}C NMR (150 MHz, DMSO) δ 152.1, 140.8, 128.3, 128.2, 125.9, 60.8, 33.9, 32.8, 30.3, 28.0. HRMS (ESI-MS) Found 277.1478 $[\text{M}+\text{H}]^+$, $\text{C}_{14}\text{H}_{21}\text{N}_4\text{S}$ requires 277.1487; found 299.1298 $[\text{M}+\text{Na}]^+$, $\text{C}_{14}\text{H}_{20}\text{N}_4\text{NaS}$ requires 299.1306; found 315.1037 $[\text{M}+\text{K}]^+$, $\text{C}_{14}\text{H}_{20}\text{N}_4\text{KS}$ requires 315.1046.



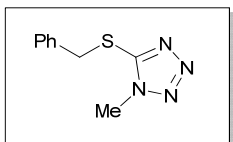
9d: ^1H NMR (300 MHz, CDCl_3) δ 3.92 (s, 3H), 3.34 (t, J = 7.2 Hz, 2H), 2.00–1.72 (m, 2H), 1.07 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.4, 35.3, 33.3, 22.8, 13.1. HRMS (ESI-MS) Found 159.0699 $[\text{M}+\text{H}]^+$, $\text{C}_5\text{H}_{11}\text{N}_4\text{S}$ requires 159.0704.



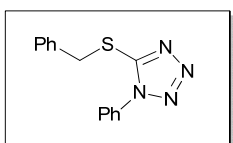
9e (Contaminated by a small amount of inseparable side-product **S1**): ^1H NMR (300 MHz, DMSO) δ 7.66 (s, 5H), 3.31 (t, J = 7.1 Hz, 2H), 1.82–1.70 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, DMSO): δ 154.4, 133.1, 130.5, 129.9, 124.5, 34.6, 22.1, 12.8. HRMS (ESI-MS) Found 221.0851 $[\text{M}+\text{H}]^+$, $\text{C}_{10}\text{H}_{13}\text{N}_4\text{S}$ requires 221.0861.



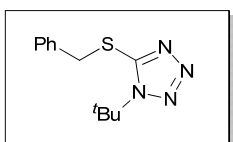
9f: ^1H NMR (300 MHz, DMSO) δ 3.33 (t, J = 6.7 Hz, 2H), 1.79–1.67 (m, 11H), 0.99 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, DMSO) δ 152.2, 60.8, 35.07, 28.0, 22.1, 12.8. HRMS (ESI-MS) Found 201.1167 $[\text{M}+\text{H}]^+$, $\text{C}_8\text{H}_{17}\text{N}_4\text{S}$ requires 201.1174; found 223.0988 $[\text{M}+\text{Na}]^+$, $\text{C}_8\text{H}_{16}\text{N}_4\text{NaS}$ requires 223.0993.



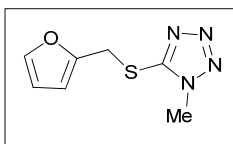
9g: ^1H NMR (300 MHz, DMSO) δ 7.40–7.27 (m, 5H), 4.51 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (150 MHz, DMSO) δ 153.1, 136.5, 128.9, 128.5, 127.7, 36.8, 33.5. HRMS (ESI-MS) Found 229.0513 $[\text{M}+\text{Na}]^+$, $\text{C}_9\text{H}_{10}\text{N}_4\text{NaS}$ requires 229.0524; found 245.0254 $[\text{M}+\text{K}]^+$, $\text{C}_9\text{H}_{10}\text{KN}_4\text{S}$ requires 245.0263.



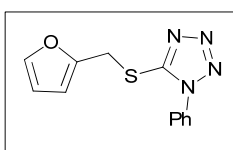
9h: ^1H NMR (300 MHz, DMSO) δ 7.66–7.57 (m, 5H), 7.45–7.28 (m, 3H), 4.60 (s, 2H). ^{13}C NMR (150 MHz, DMSO) δ 153.9, 136.1, 133.0, 130.5, 129.9, 129.1, 128.5, 127.7, 124.4, 36.7. HRMS (ESI-MS) Found 269.0852 $[\text{M}+\text{H}]^+$, $\text{C}_{14}\text{H}_{13}\text{N}_4\text{S}$ requires 269.0861.



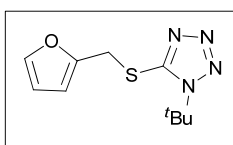
9i: ^1H NMR (300 MHz, DMSO) δ 7.47–7.25 (m, 5H), 4.62 (s, 2H), 1.62 (s, 9H). ^{13}C NMR (150 MHz, DMSO) δ 151.8, 136.2, 129.1, 128.5, 127.7, 60.9, 39.9, 39.8, 39.7, 39.5, 39.4, 39.2, 39.1, 37.3, 28.1. HRMS (ESI-MS) Found 249.1169 $[\text{M}+\text{H}]^+$, $\text{C}_{12}\text{H}_{17}\text{N}_4\text{S}$ requires 249.1174; found 271.0984 $[\text{M}+\text{Na}]^+$, $\text{C}_{12}\text{H}_{16}\text{N}_4\text{NaS}$ requires 271.0993; found 287.0727 $[\text{M}+\text{K}]^+$, $\text{C}_{12}\text{H}_{16}\text{N}_4\text{KS}$ requires 287.0733.



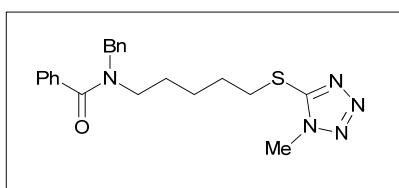
9j: ^1H NMR (300 MHz, CDCl_3) δ 7.36 (t, J = 1.2 Hz, 1H), 6.30 (s, 2H), 4.56 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (150 MHz, DMSO) δ 152.6, 149.3, 143.2, 110.9, 109.2, 33.6, 29.8. HRMS (ESI-MS) Found 219.0308 $[\text{M}+\text{Na}]^+$, $\text{C}_7\text{H}_8\text{N}_4\text{NaOS}$ requires 219.0317; found 235.0044 $[\text{M}+\text{K}]^+$, $\text{C}_7\text{H}_8\text{KN}_4\text{OS}$ requires 235.0056.



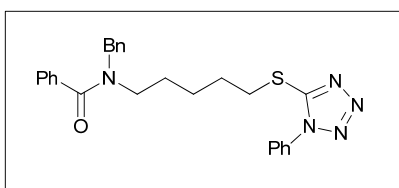
9k: ^1H NMR (300 MHz, CDCl_3) δ 7.54 (s, 5H), 7.36 (d, J = 1.8 Hz, 1H), 6.41 (d, J = 3.2 Hz, 1H), 6.31 (dd, J = 3.1, 1.9 Hz, 1H), 4.68 (s, 2H). ^{13}C NMR (150 MHz, DMSO) δ 153.4, 148.9, 143.2, 133.0, 130.6, 129.9, 124.5, 110.8, 109.4, 29.6. HRMS (ESI-MS) Found 259.0648 $[\text{M}+\text{H}]^+$, $\text{C}_{12}\text{H}_{11}\text{N}_4\text{OS}$ requires 259.0654.



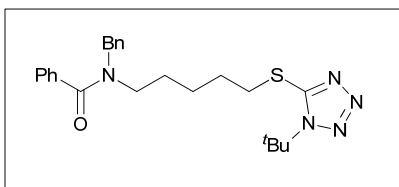
9l: ^1H NMR (300 MHz, CDCl_3) δ 7.36 (dd, J = 1.7, 0.7 Hz, 1H), 6.35 (d, J = 2.8 Hz, 1H), 6.30 (dd, J = 3.1, 1.9 Hz, 1H), 4.66 (s, 2H), 1.69 (s, 9H). ^{13}C NMR (150 MHz, DMSO) δ 151.3, 149.1, 143.1, 110.8, 109.2, 61.1, 30.3, 28.1. HRMS (ESI-MS) Found 261.0775 $[\text{M}+\text{Na}]^+$, $\text{C}_{10}\text{H}_{14}\text{N}_4\text{NaOS}$ requires 261.0786; found 277.0517 $[\text{M}+\text{K}]^+$, $\text{C}_{10}\text{H}_{14}\text{KN}_4\text{OS}$ requires 277.0525.



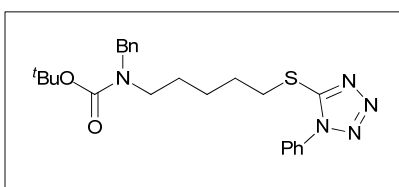
9m (Containing some inseparable side-product **S2**): ^1H NMR (300 MHz, CD_3OD) δ 7.86–6.95 (m, 10H), 4.79 (s, 1H), 4.54 (s, 1H), 3.93 (s, 3H), 3.46 (br, 2H), 3.19 (br, 2H), 1.96–0.73 (m, 6H). ^{13}C NMR (100 MHz, CD_3OD) δ 174.3, 155.8, 145.7, 137.8, 135.5, 130.9, 130.7, 129.9, 129.8, 129.5, 129.1, 128.8, 128.3, 127.7, 54.0, 46.1, 34.1, 30.1, 28.1, 26.5, 21.7. HRMS (ESI-MS) Found 396.1849 $[\text{M}+\text{H}]^+$, $\text{C}_{21}\text{H}_{26}\text{N}_5\text{OS}$ requires 396.1858.



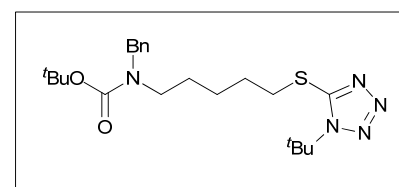
9n: ^1H NMR (300 MHz, CD_3OD) δ 7.62 (s, 5H), 7.42 (s, 5H), 7.38–7.16 (m, 5H), 4.78 (s, 1H), 4.53 (s, 1H), 3.46 (br, 2H), 3.22 (br, 2H), 1.85–1.19 (m, 6H). ^{13}C NMR (100 MHz, CD_3OD) δ 171.5, 153.3, 135.9, 135.3, 135.0, 132.2, 128.8, 128.3, 128.0, 127.1, 127.0, 126.3, 125.9, 125.4, 124.8, 122.6, 51.1, 43.2, 31.1, 27.0, 25.2, 23.7. HRMS (ESI-MS) Found 458.1999 $[\text{M}+\text{H}]^+$, $\text{C}_{26}\text{H}_{28}\text{N}_5\text{OS}$ requires 458.2015.



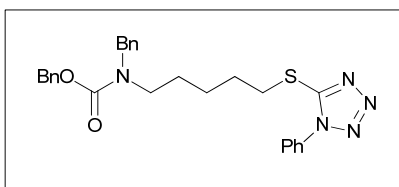
9o: ^1H NMR (300 MHz, CD_3OD) δ 7.42 (s, 5H), 7.38–7.16 (m, 5H), 4.78 (s, 1H), 4.53 (s, 1H), 3.55–3.34 (m, 2H), 3.21 (br, 2H), 1.97–1.31 (m, 15H). ^{13}C NMR (100 MHz, CD_3OD) δ 171.5, 151.5, 135.9, 135.3, 135.0, 128.0, 127.0, 127.0, 126.3, 125.9, 125.4, 124.8, 59.8, 51.2, 43.2, 31.7, 27.0, 26.2, 25.2, 23.8. HRMS (ESI-MS) Found 438.2317 $[\text{M}+\text{H}]^+$, $\text{C}_{24}\text{H}_{32}\text{N}_5\text{OS}$ requires 438.2328.



9p: ^1H NMR (400 MHz, CD_3OD) δ 7.61 (d, $J = 4.0$ Hz, 4H), 7.41–7.11 (m, 6H), 4.42 (s, 2H), 3.34 (d, $J = 7.2$ Hz, 2H), 3.19 (br, 2H), 1.58–1.34 (m, 15H). ^{13}C NMR (100 MHz, CD_3OD) δ 154.8, 153.3, 137.1, 132.2, 128.8, 128.2, 126.8, 125.7, 125.5, 122.6, 78.4, 48.6, 45.0, 31.3, 27.2, 26.0, 25.8, 23.9. HRMS (ESI-MS) Found 476.2078 $[\text{M}+\text{Na}]^+$, $\text{C}_{24}\text{H}_{31}\text{N}_5\text{NaO}_2\text{S}$ requires 476.2096; found 492.1806 $[\text{M}+\text{K}]^+$, $\text{C}_{24}\text{H}_{31}\text{KN}_5\text{O}_2\text{S}$ requires 492.1836.

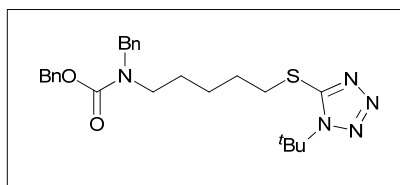


9q: ^1H NMR (400 MHz, CD_3OD) δ 7.35–7.27 (m, 2H), 7.24 (t, $J = 6.3$ Hz, 3H), 4.43 (s, 2H), 3.41–3.32 (m, 2H), 3.20 (br, 2H), 1.90–1.64 (m, 9H), 1.64–1.13 (m, 15H). ^{13}C NMR (100 MHz, CD_3OD) δ 154.8, 151.5, 137.1, 126.8, 125.7, 125.5, 78.4, 59.8, 48.7, 45.0, 32.0, 27.2, 26.3, 26.1, 25.8, 24.0. HRMS (ESI-MS) Found 456.2450 $[\text{M}+\text{Na}]^+$, $\text{C}_{22}\text{H}_{35}\text{N}_5\text{NaO}_2\text{S}$ requires 456.2409.

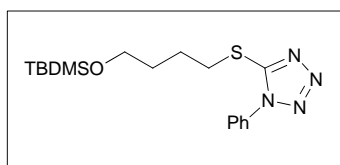


9r: ^1H NMR (400 MHz, CD_3OD) δ 7.67–7.54 (m,

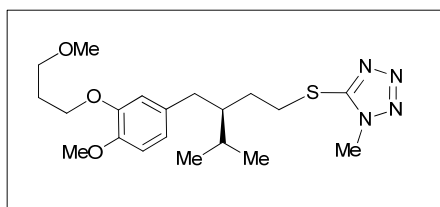
4H), 7.45–7.09 (m, 11H), 5.14 (s, 2H), 4.49 (s, 2H), 3.25 (br, 4H), 1.85–1.25 (m, 6H). ^{13}C NMR (100 MHz, CD_3OD) δ 155.6, 153.4, 136.5, 135.3, 132.2, 128.8, 128.2, 126.8, 126.7, 126.3, 126.2, 125.9, 125.6, 122.6, 65.6, 48.7, 44.6, 31.2, 27.1, 25.6, 23.7. HRMS (ESI-MS) Found 488.2169 $[\text{M}+\text{H}]^+$, $\text{C}_{27}\text{H}_{30}\text{N}_5\text{O}_2\text{S}$ requires 488.2120; found 510.1890 $[\text{M}+\text{Na}]^+$, $\text{C}_{27}\text{H}_{29}\text{N}_5\text{NaO}_2\text{S}$ requires 510.1940; found 526.1705 $[\text{M}+\text{K}]^+$, $\text{C}_{27}\text{H}_{29}\text{KN}_5\text{O}_2\text{S}$ requires 526.1679.



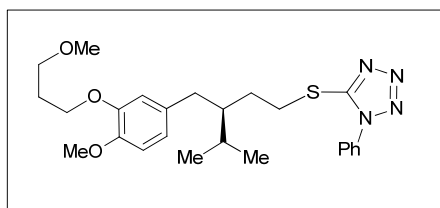
9s: ^1H NMR (400 MHz, CD_3OD) δ 7.45–7.07 (m, 10H), 5.15 (s, 2H), 4.50 (s, 2H), 3.26 (br, 4H), 1.90–1.21 (m, 15H). ^{13}C NMR (100 MHz, CD_3OD) δ 158.4, 154.3, 139.4, 138.2, 129.7, 129.6, 129.2, 129.1, 128.8, 128.5, 68.5, 62.6, 51.6, 47.9, 34.7, 29.9, 29.1, 28.6, 26.7. HRMS (ESI-MS) Found 468.2441 $[\text{M}+\text{H}]^+$, $\text{C}_{25}\text{H}_{34}\text{N}_5\text{O}_2\text{S}$ requires 468.2433; found 490.2268 $[\text{M}+\text{Na}]^+$, $\text{C}_{25}\text{H}_{33}\text{N}_5\text{NaO}_2\text{S}$ requires 490.2253; found 506.2021 $[\text{M}+\text{K}]^+$, $\text{C}_{25}\text{H}_{33}\text{KN}_5\text{O}_2\text{S}$ requires 506.1992.



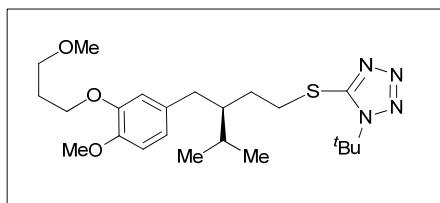
9t: ^1H NMR (300 MHz, CDCl_3) δ 7.67–7.51 (m, 5H), 3.65 (t, $J = 6.1$ Hz, 2H), 3.44 (t, $J = 7.3$ Hz, 2H), 1.96–1.86 (m, 2H), 1.71–1.62 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.5, 134.0, 130.1, 129.9, 124.0, 62.4, 33.4, 31.7, 26.0, 25.9, 18.4, -5.23. HRMS (ESI-MS) Found 365.1846 $[\text{M}+\text{H}]^+$, $\text{C}_{17}\text{H}_{29}\text{N}_4\text{OSSi}$ requires 365.1831; Found 387.1666 $[\text{M}+\text{Na}]^+$, $\text{C}_{17}\text{H}_{28}\text{N}_4\text{NaOSSi}$ requires 387.1651.



9u: ^1H NMR (300 MHz, CDCl_3) δ 6.78–6.63 (m, 3H), 4.10 (t, $J = 6.5$ Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 3.58 (t, $J = 6.2$ Hz, 2H), 3.36 (s, 3H), 3.34–3.01 (m, 2H), 2.63 (dd, $J = 13.7, 5.5$ Hz, 1H), 2.32–2.36 (m, 2H), 2.17–2.03 (m, 2H), 1.90–1.54 (m, 4H), 0.92 (dd, $J = 14.5, 6.8$ Hz, 6H). The data were consistent with those reported previously.²



9v: ^1H NMR (300 MHz, CDCl_3) δ 7.55 (s, 5H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.70–6.66 (m, 2H), 4.08 (t, $J = 6.5$ Hz, 2H), 3.83 (s, 3H), 3.57 (t, $J = 6.2$ Hz, 2H), 3.35 (s, 3H), 3.33–3.21 (m, 2H), 2.63 (dd, $J = 13.8, 5.6$ Hz, 1H), 2.38 (dd, $J = 13.8, 7.9$ Hz, 1H), 2.09 (p, $J = 6.4$ Hz, 2H), 1.93–1.57 (m, 4H), 0.91 (dd, $J = 12.8, 6.8$ Hz, 6H). The data were consistent with those reported previously.²



9w: ^1H NMR (300 MHz, CDCl_3) δ 6.78 (d, $J = 7.9$ Hz, 1H), 6.74–6.65 (m, 2H), 4.10 (t, $J = 6.5$ Hz, 2H), 3.84 (s, 3H), 3.58 (t, $J = 6.2$ Hz, 2H),

3.36 (s, 3H), 3.35–3.26 (m, 2H), 2.62 (dd, $J = 13.8, 5.8$ Hz, 1H), 2.41 (dd, $J = 13.7, 7.7$ Hz, 1H), 2.10 (p, $J = 6.3$ Hz, 2H), 1.85–1.79 (m, 2H), 1.70 (s, 9H), 1.67–1.58 (m, 2H), 0.91 (dd, $J = 12.5, 6.8$ Hz, 6H). The data were consistent with those reported previously.²

References:

- [1] W. J. Miao, Y. Z. Gao, X. Q. Li, Y. X. Gao, G. Tang and Y. F. Zhao, *Adv. Synth. Catal.*, 2012, **354**, 2659.
- [2] L.-L. Li, J.-Y. Ding, L.-X. Gao and F.-S. Han, *Org. Biomol. Chem.*, 2015, **13**, 1133.

Copies of NMR spectra

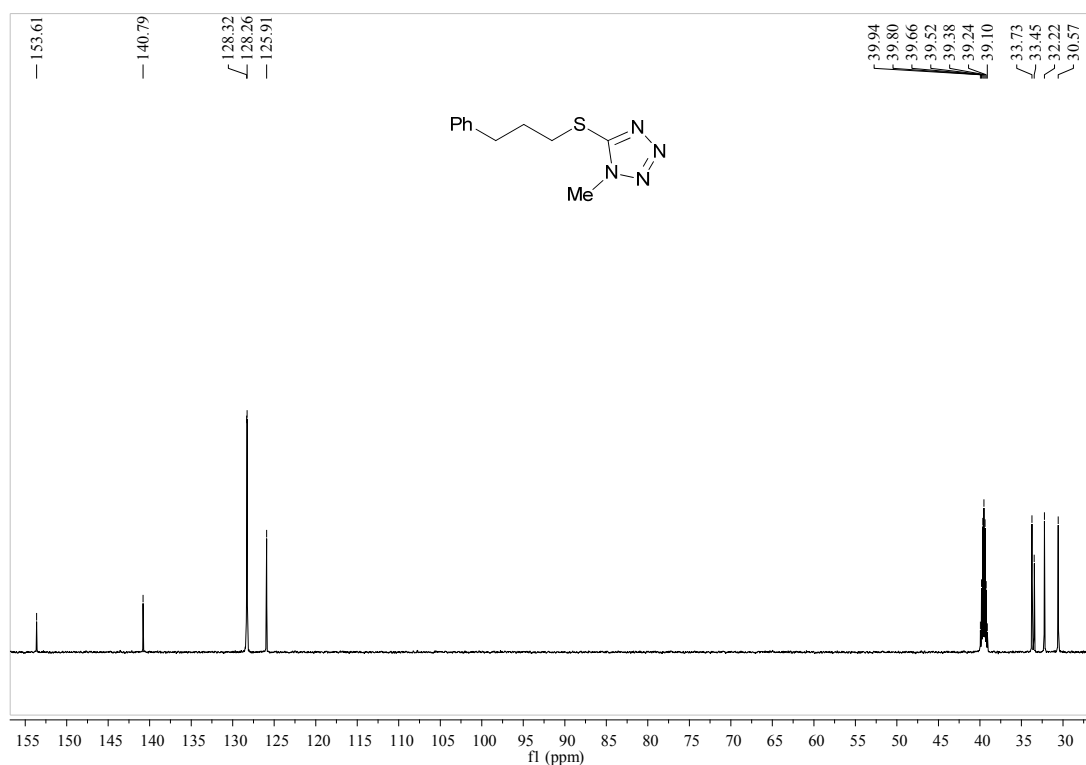
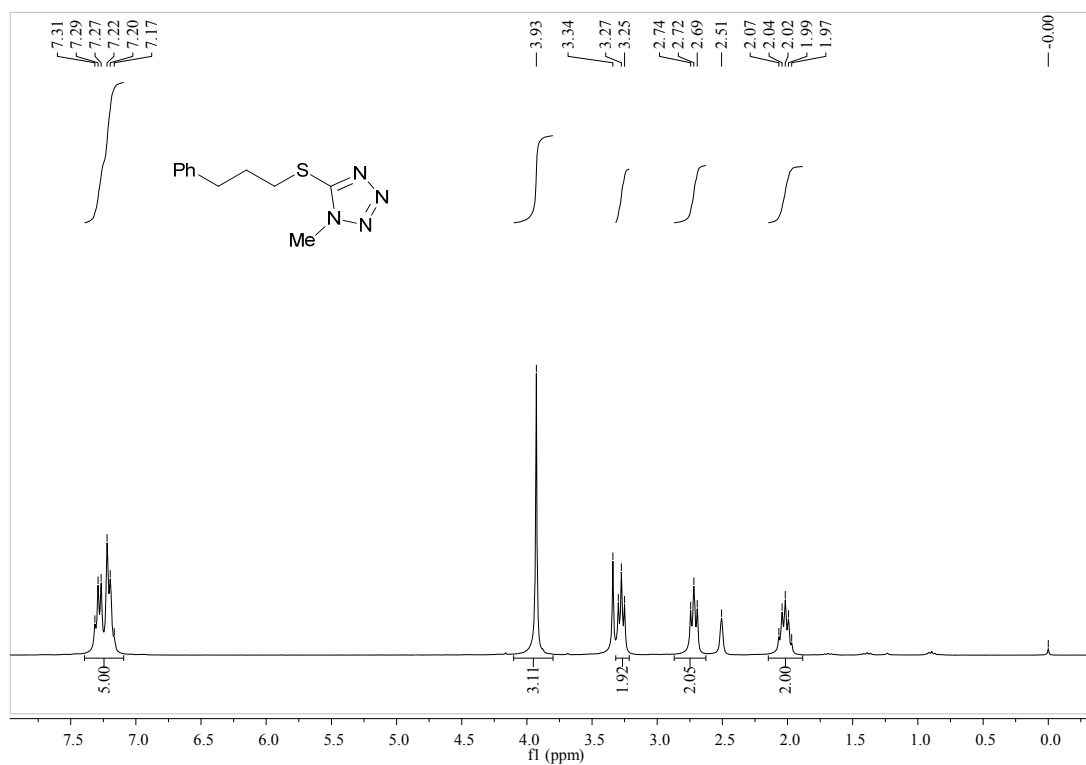


Figure S1. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9a**

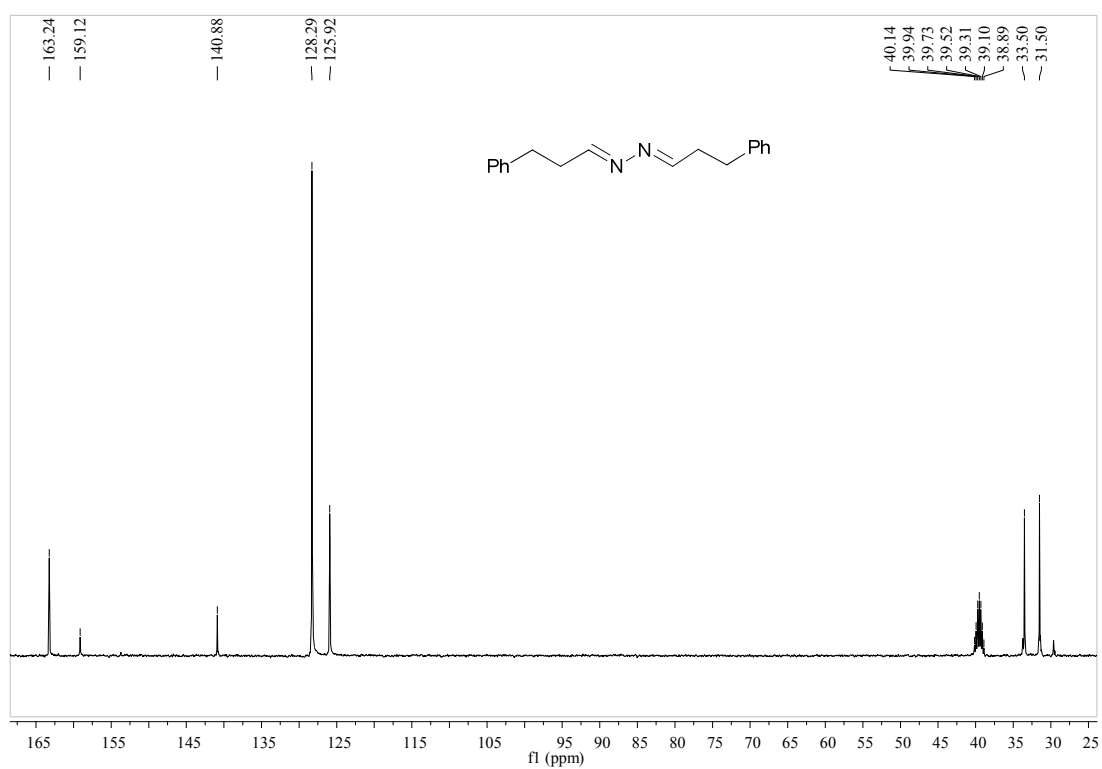
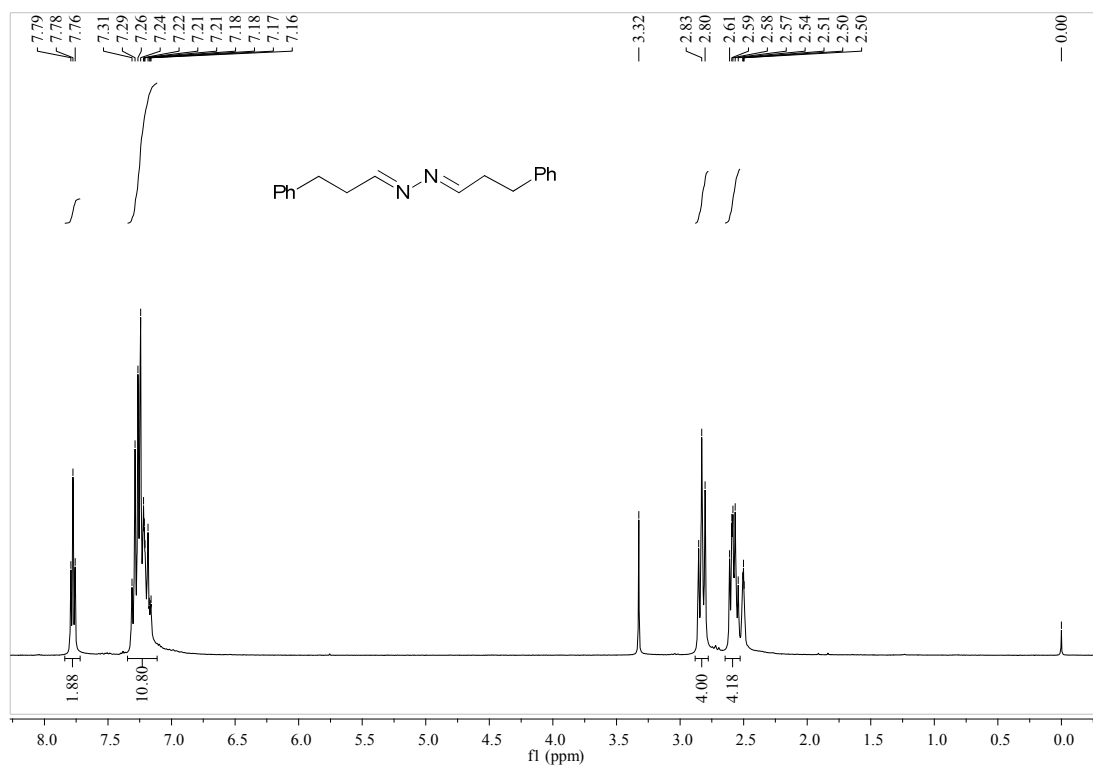


Figure S2. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **10**

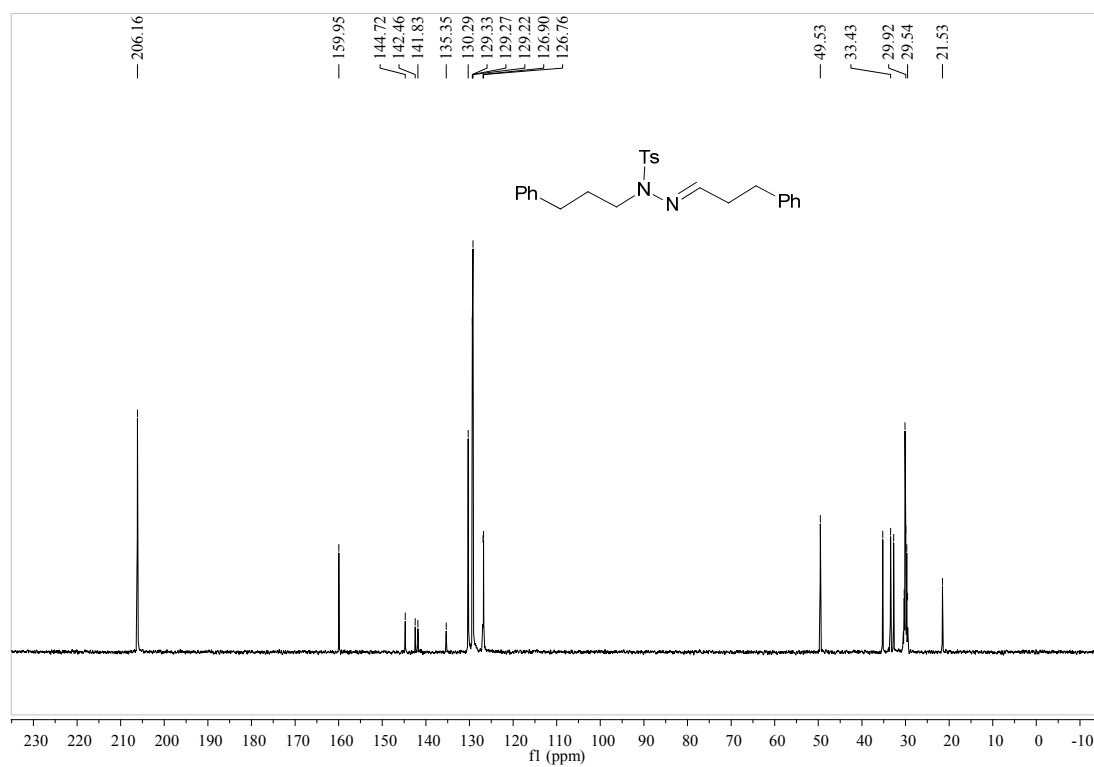
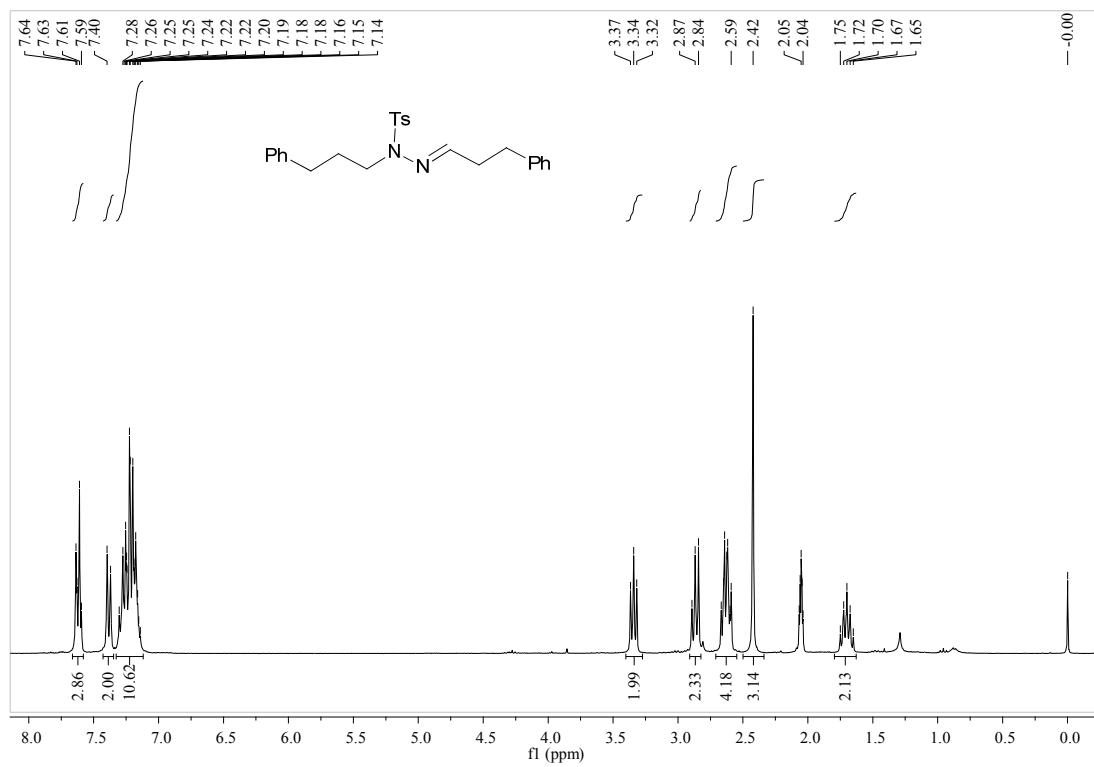


Figure S3. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **11**

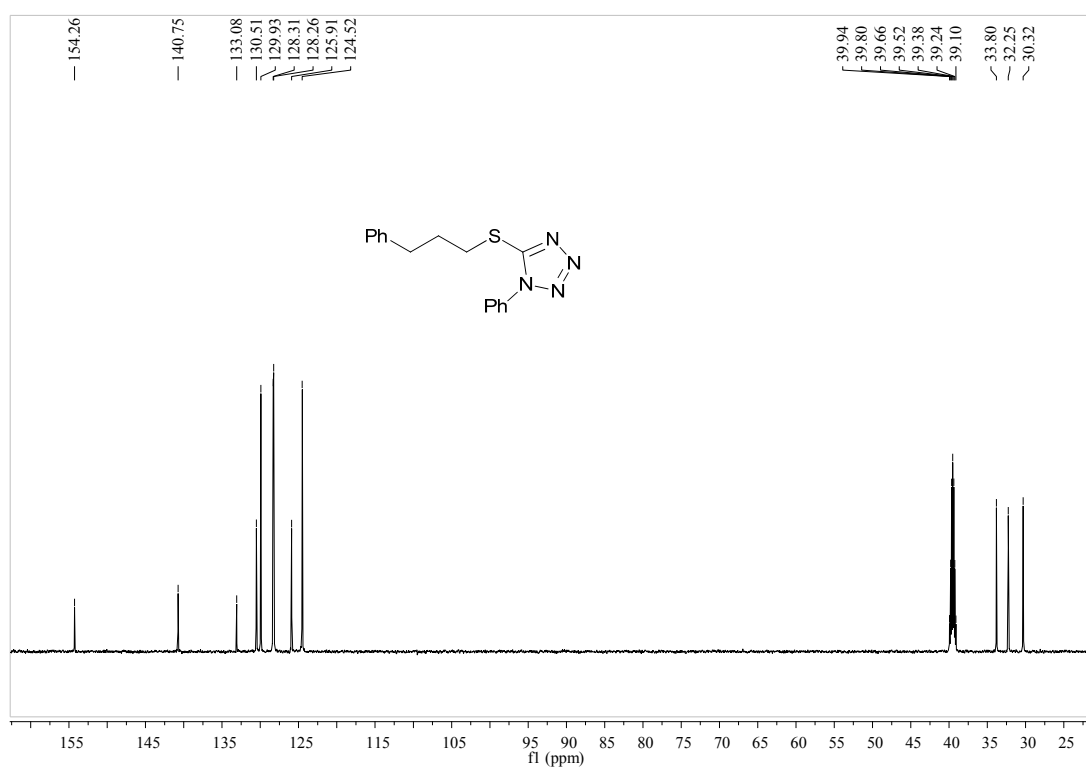
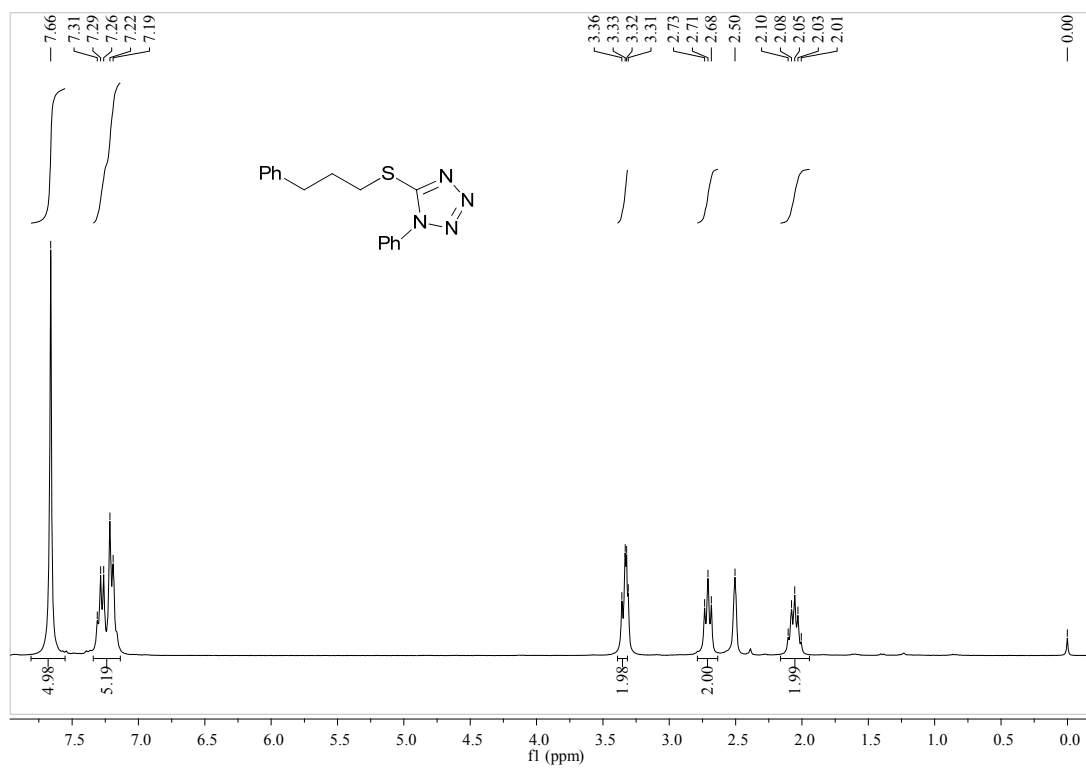


Figure S4. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9b**

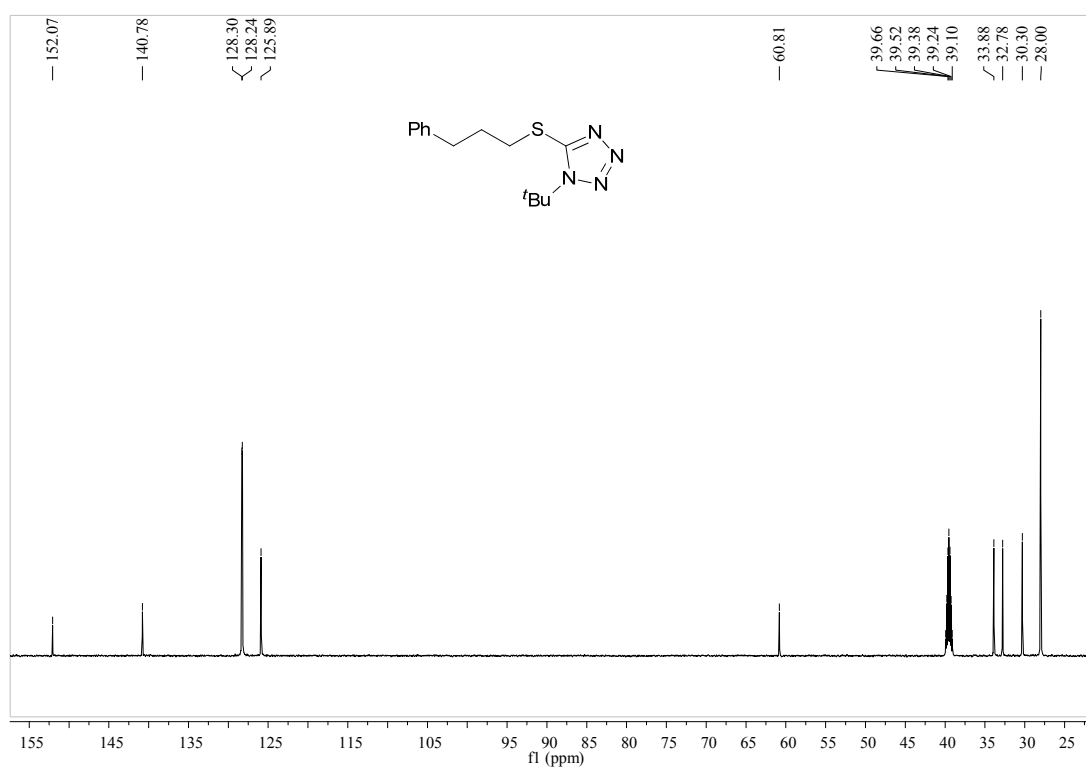
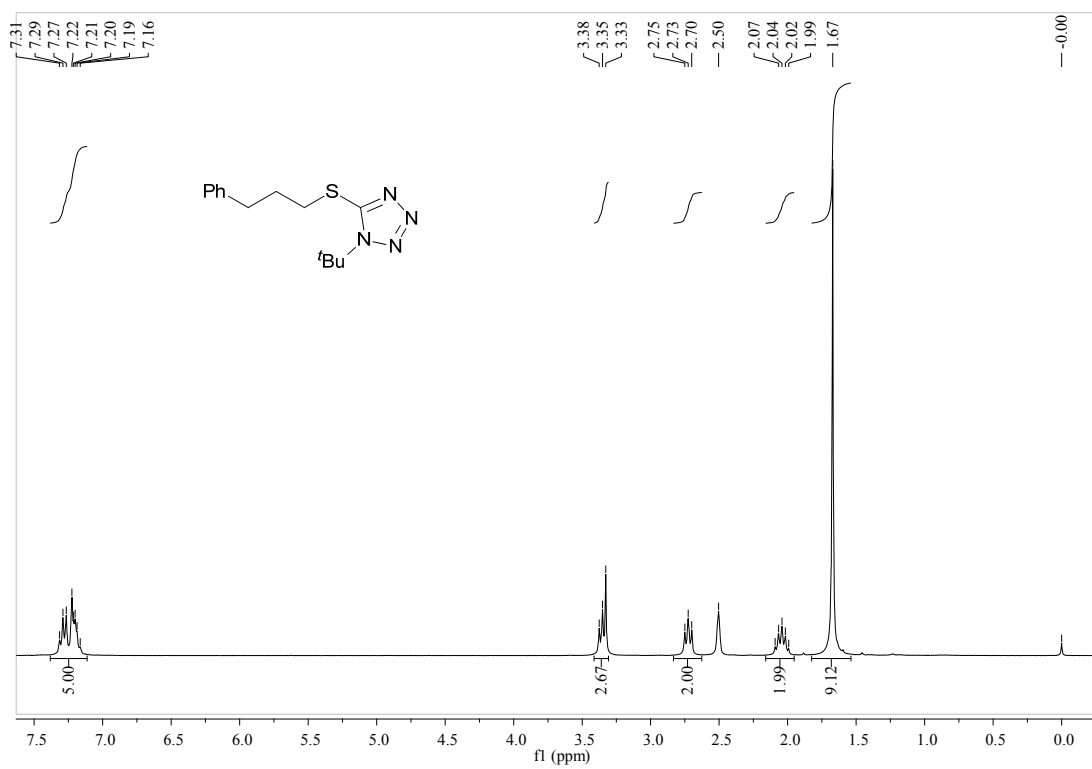


Figure S5. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9c**

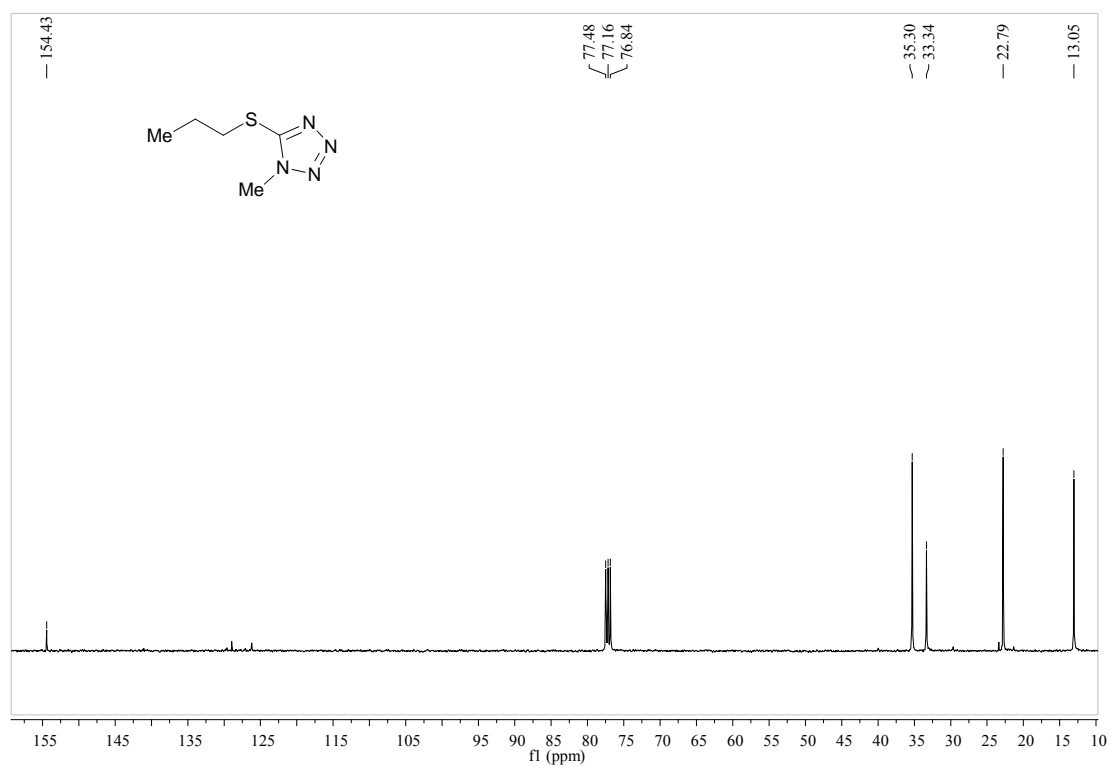
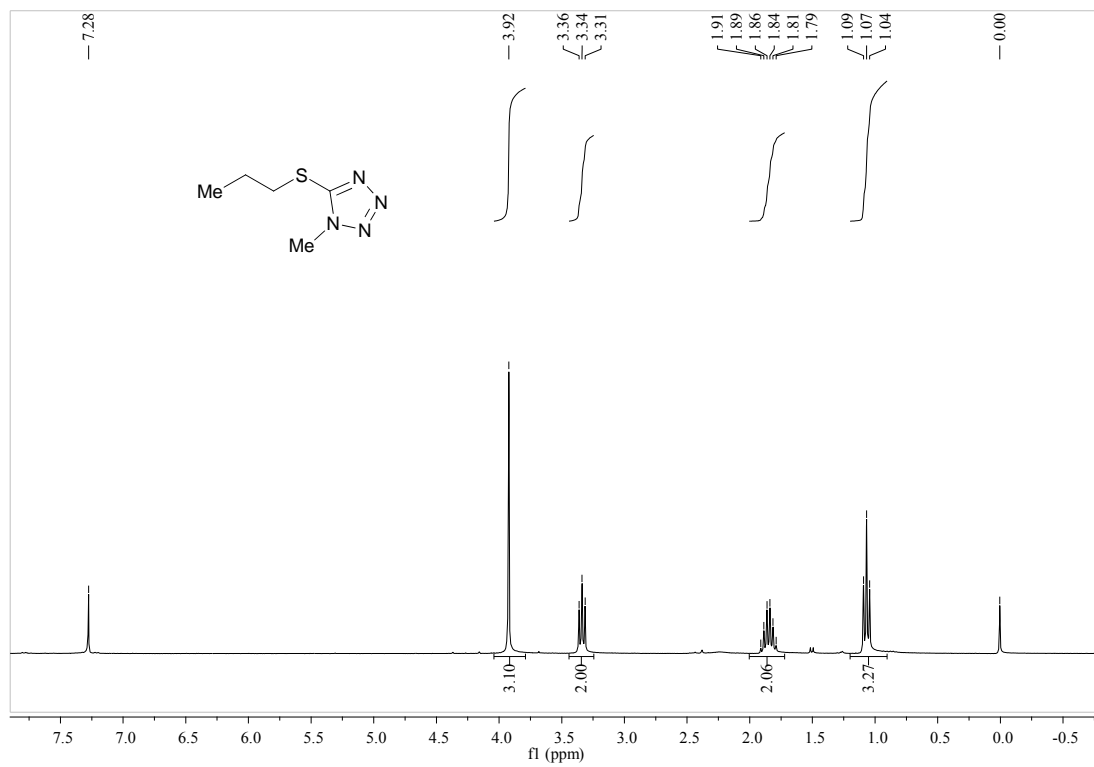


Figure S6. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9d**

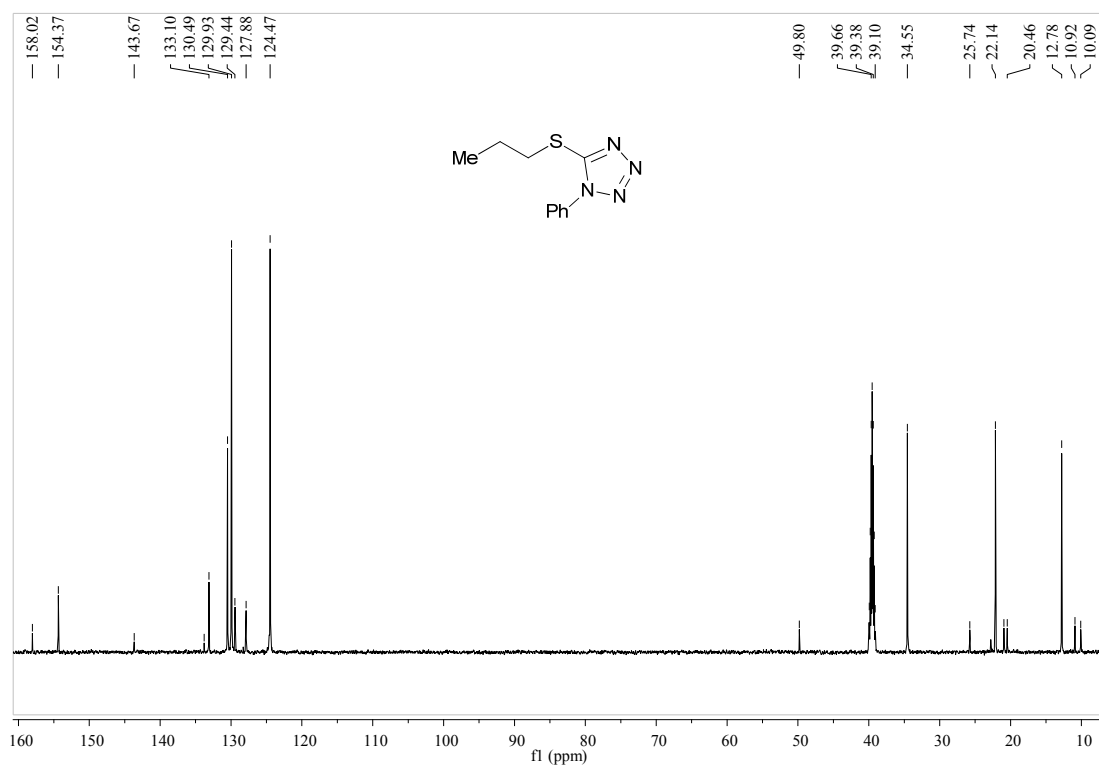
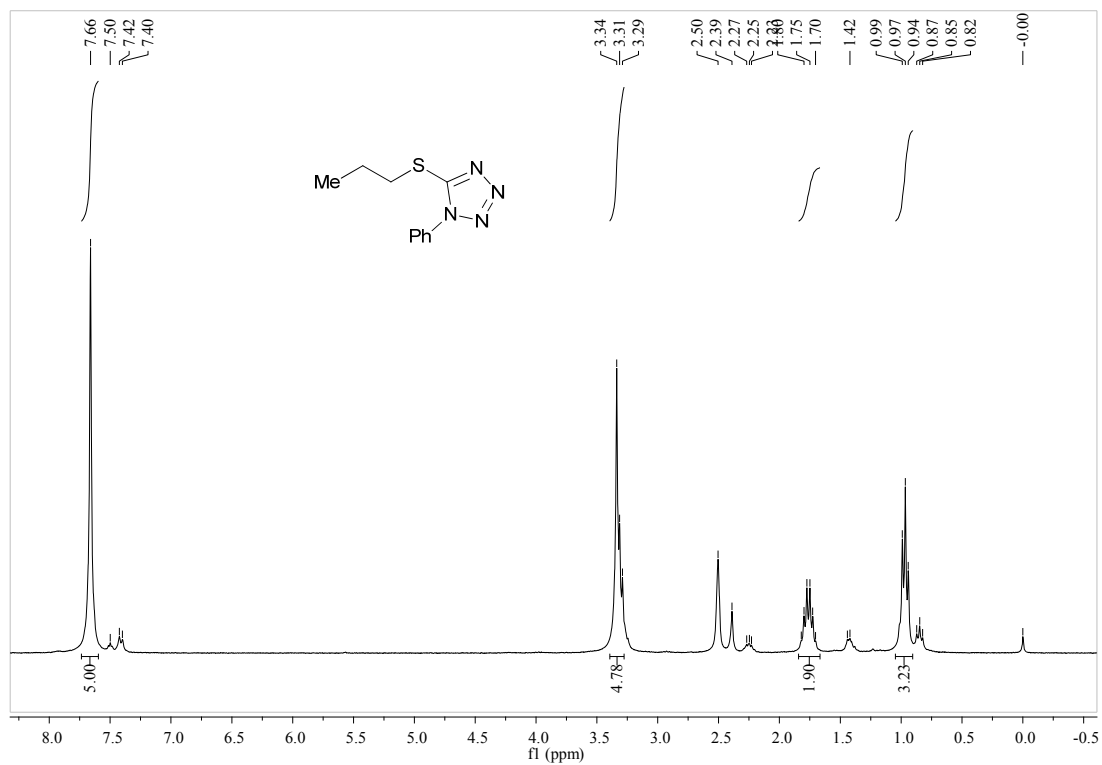


Figure S7. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9e**

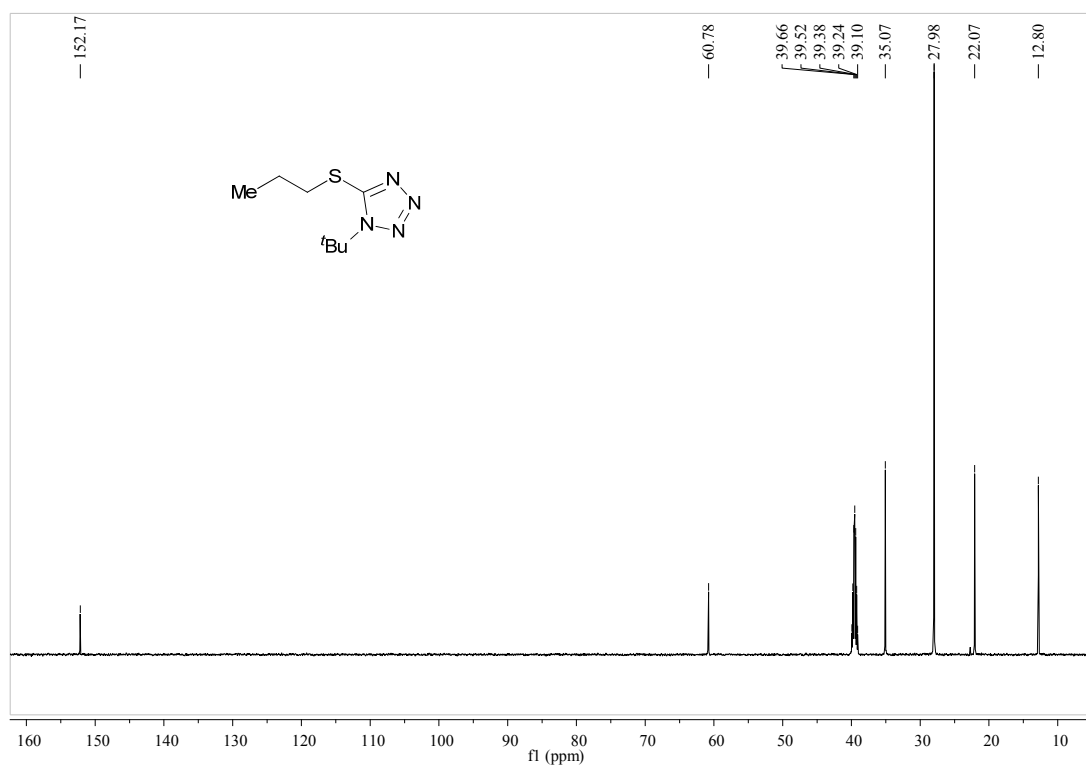
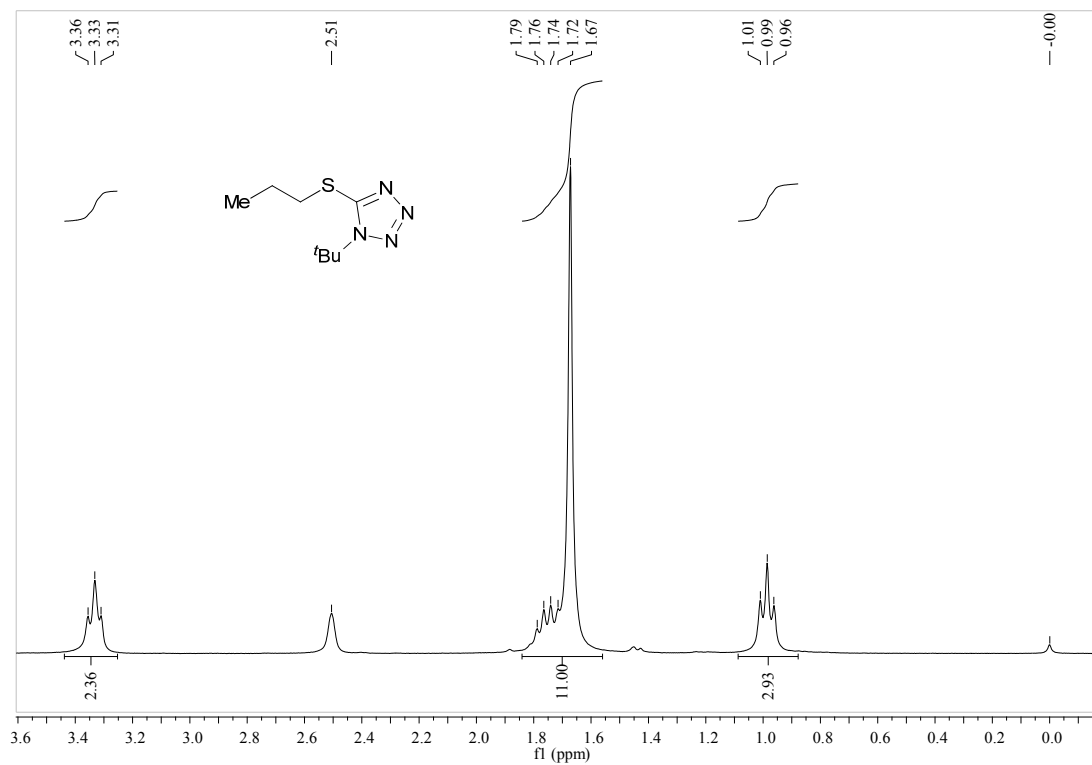


Figure S8. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9f**

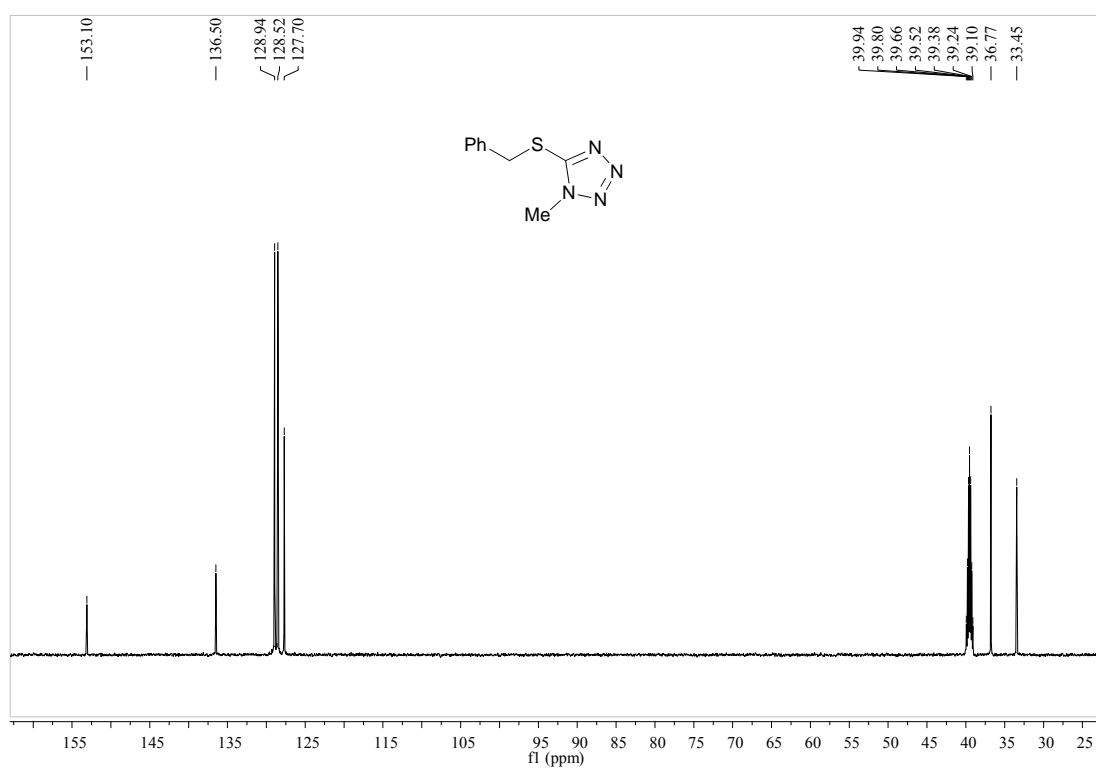
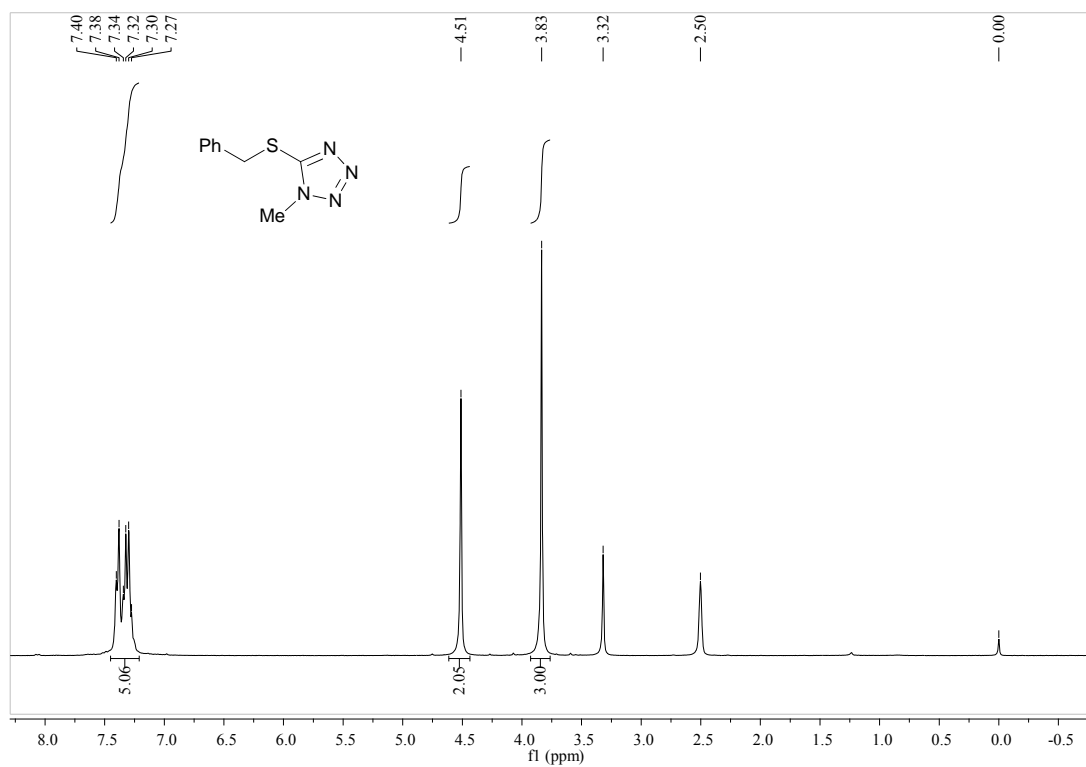


Figure S9. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9g**

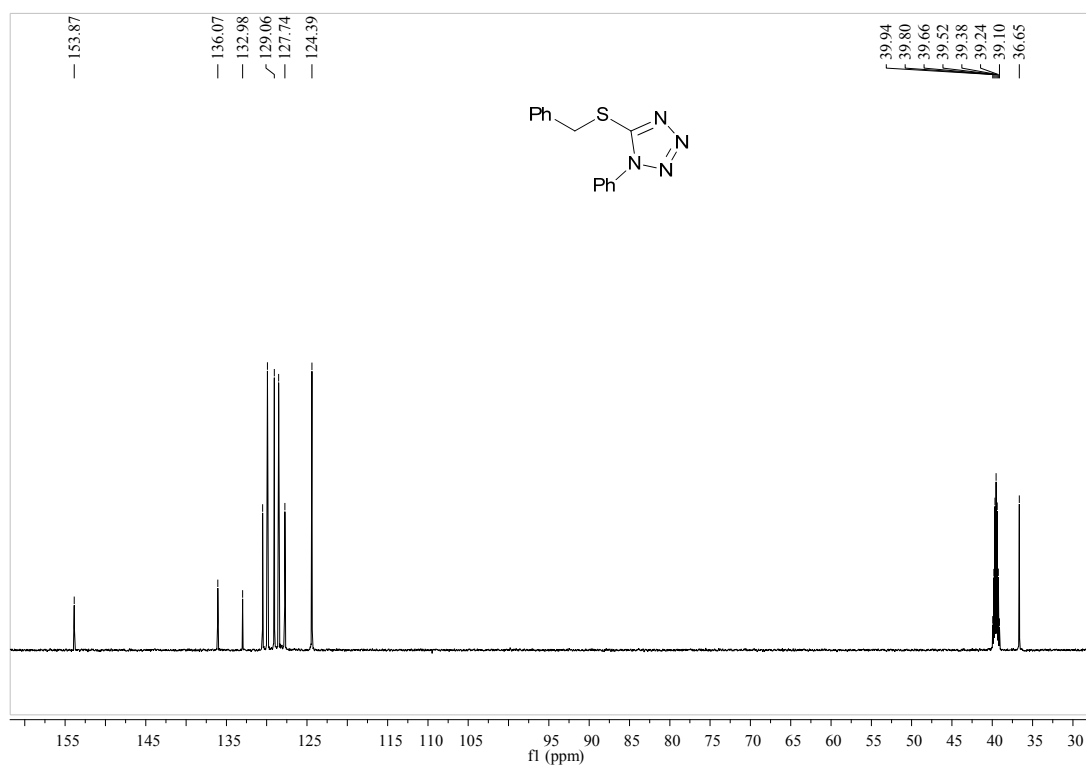
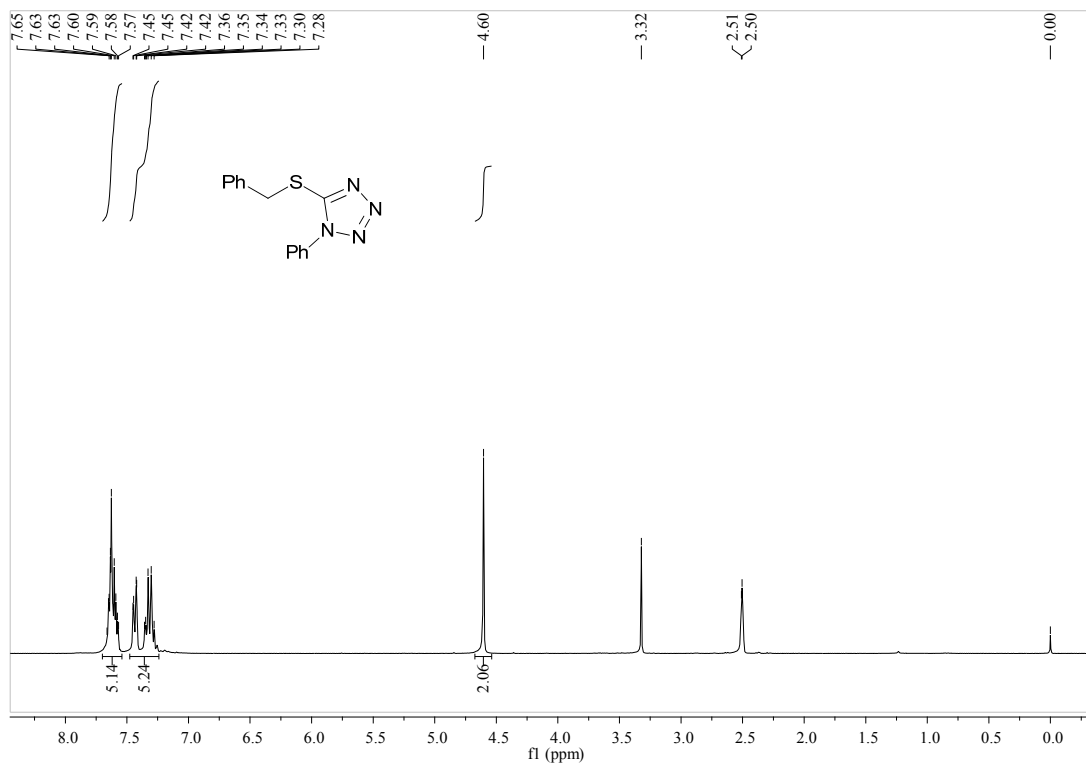


Figure S10. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9h**

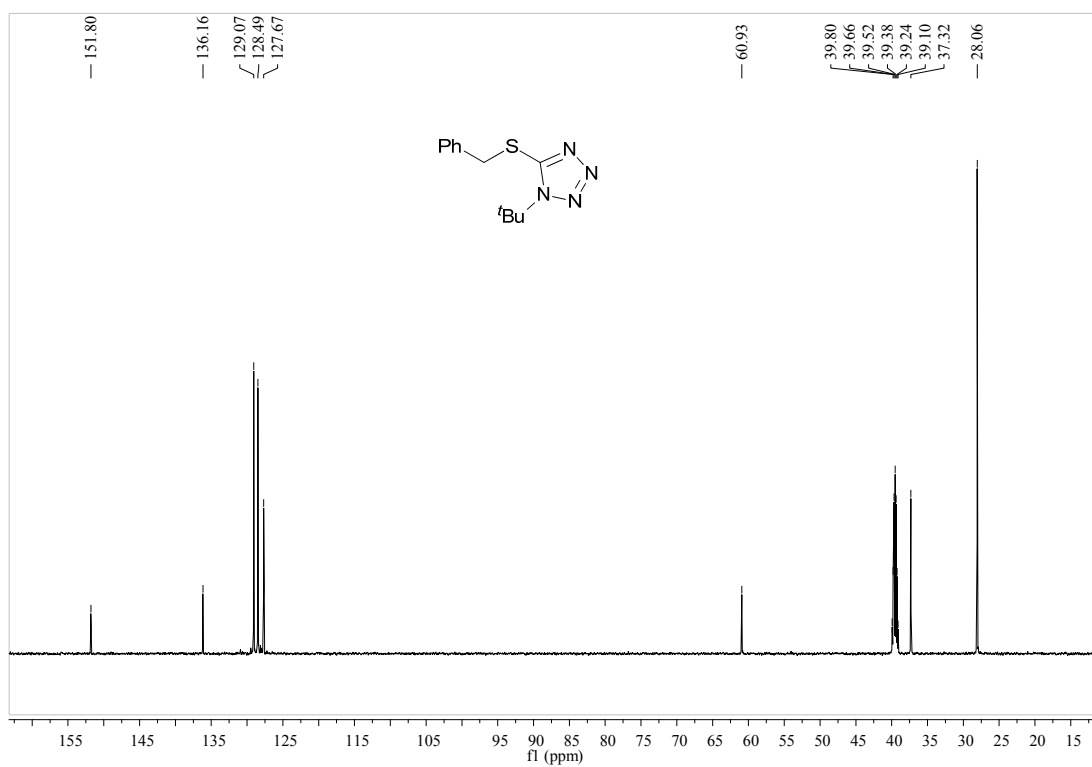
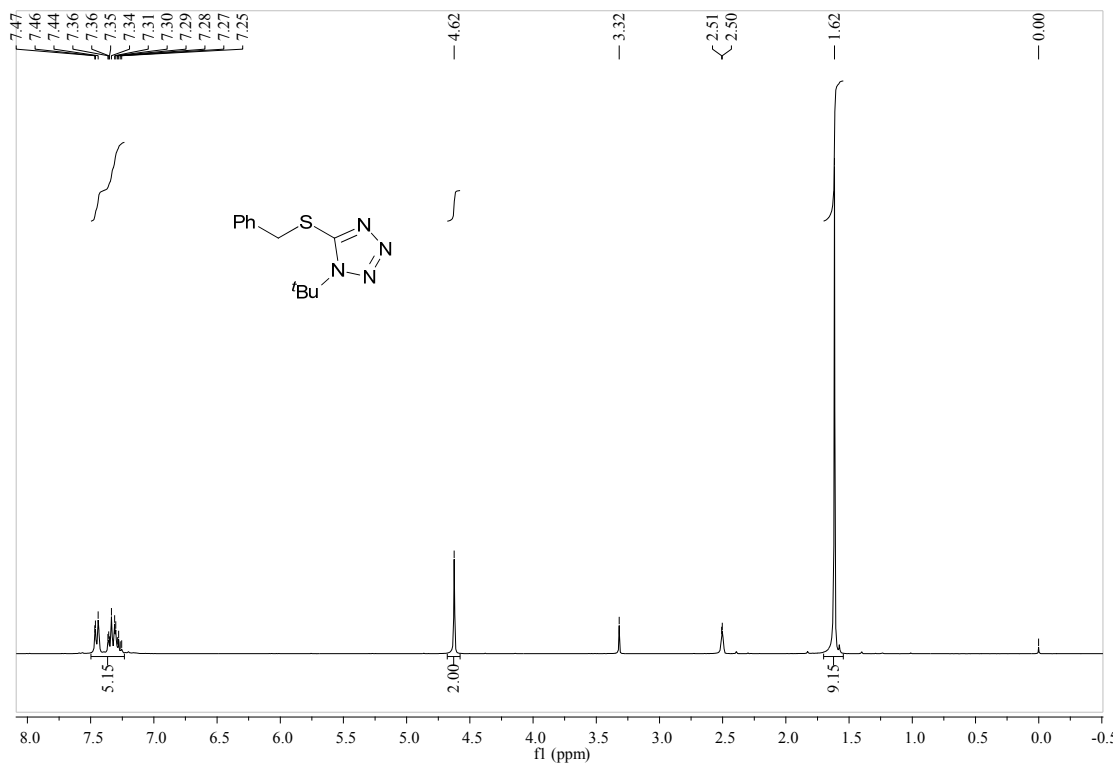


Figure S11. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9i**

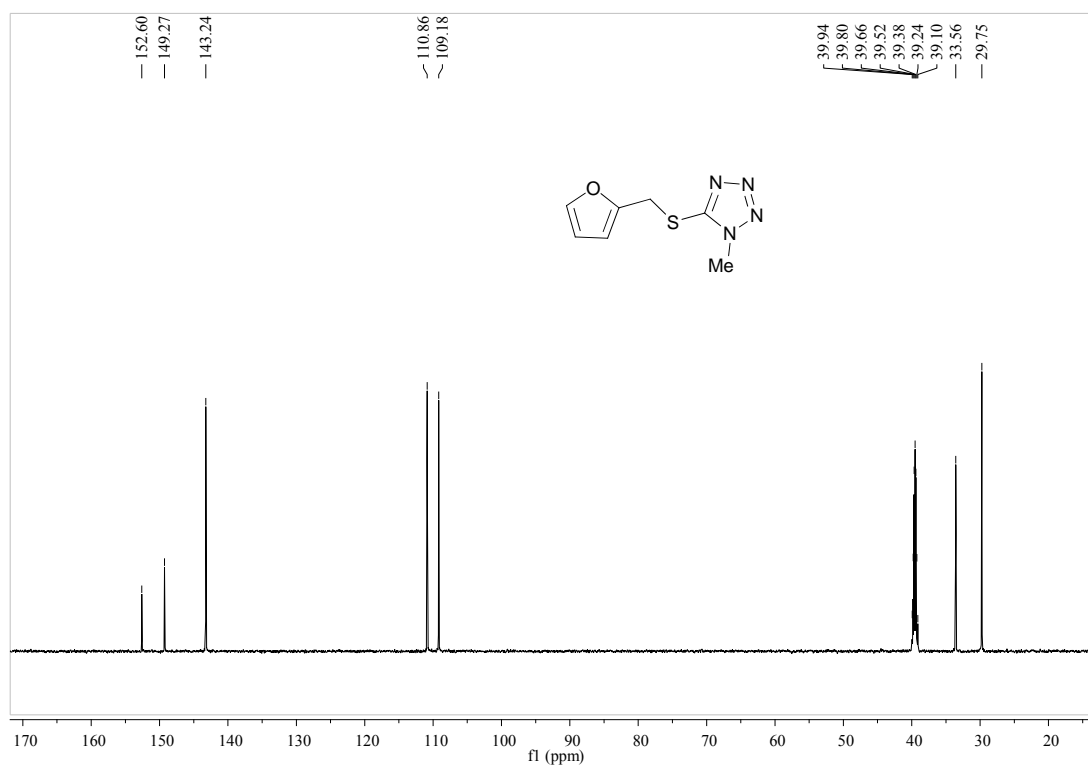
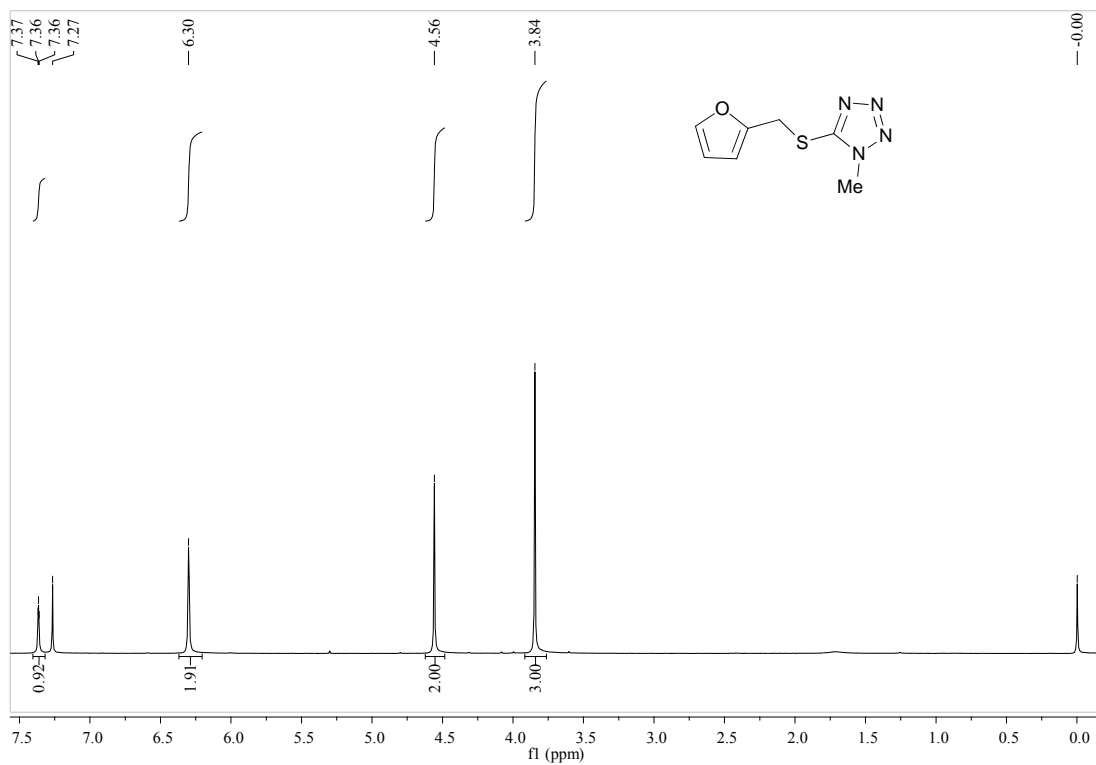


Figure S12. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9j**

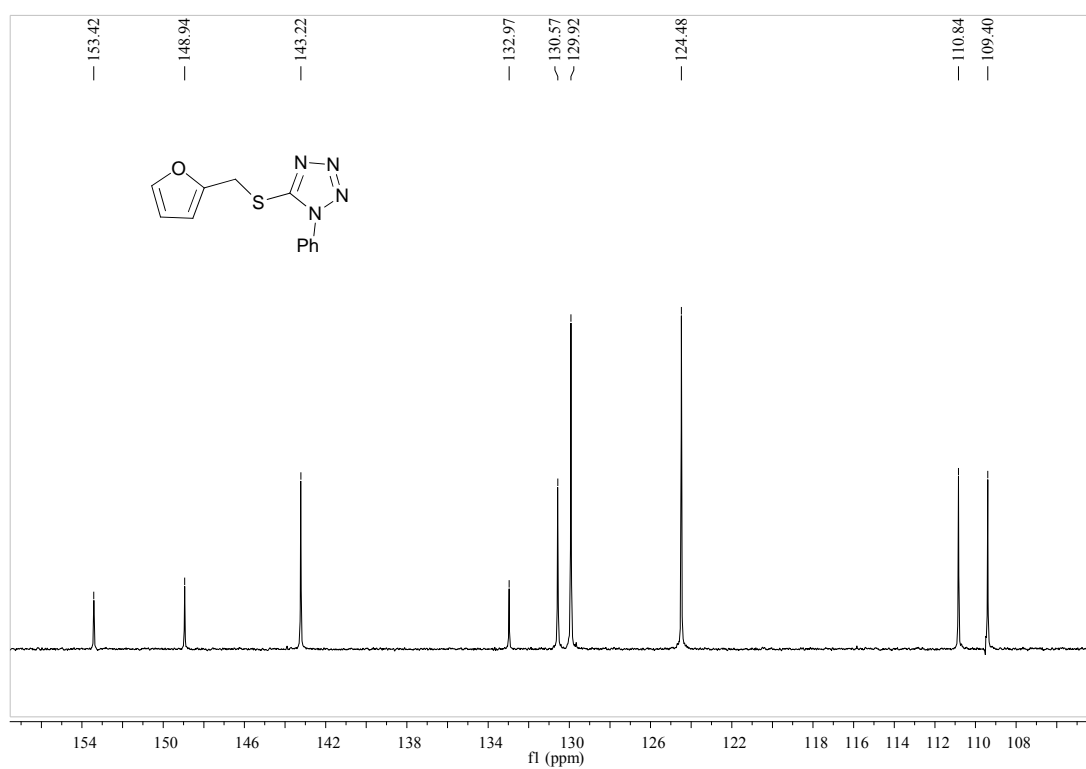
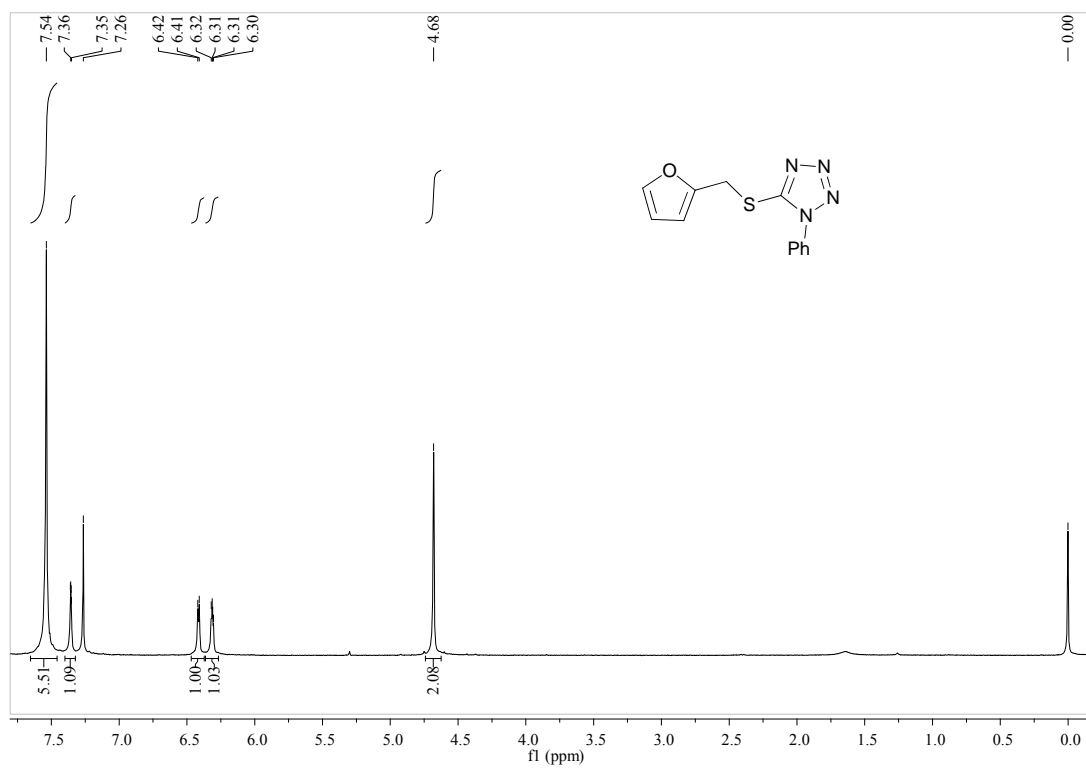


Figure S13. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9k**

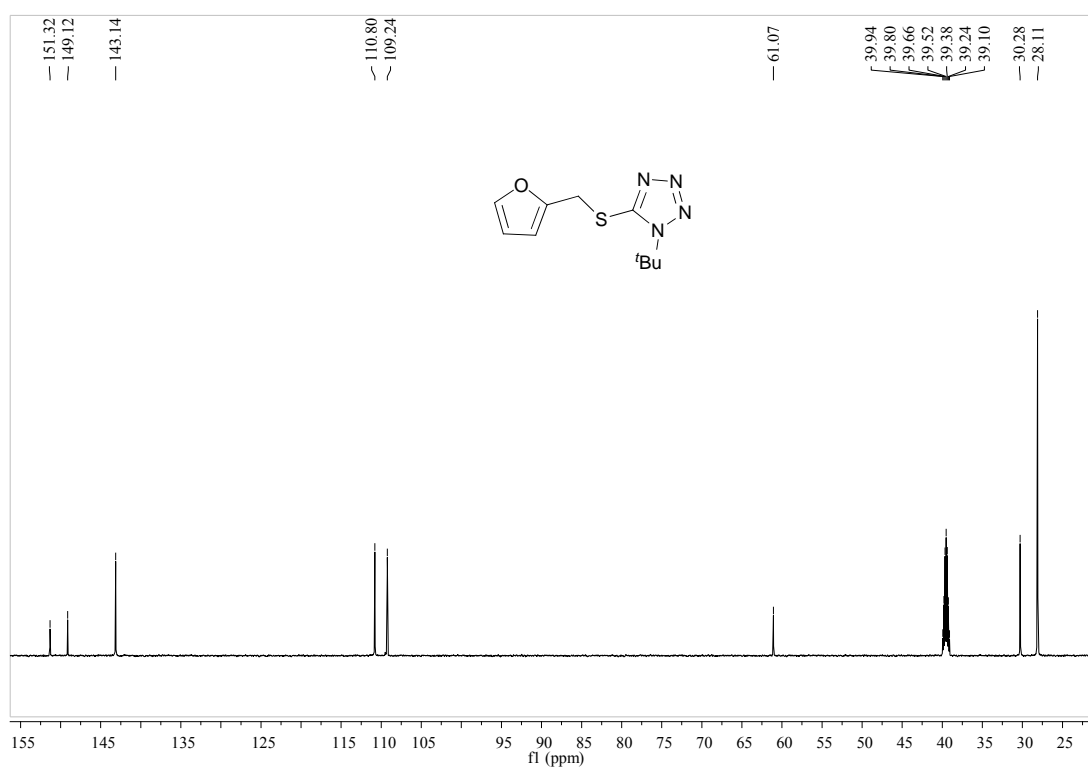
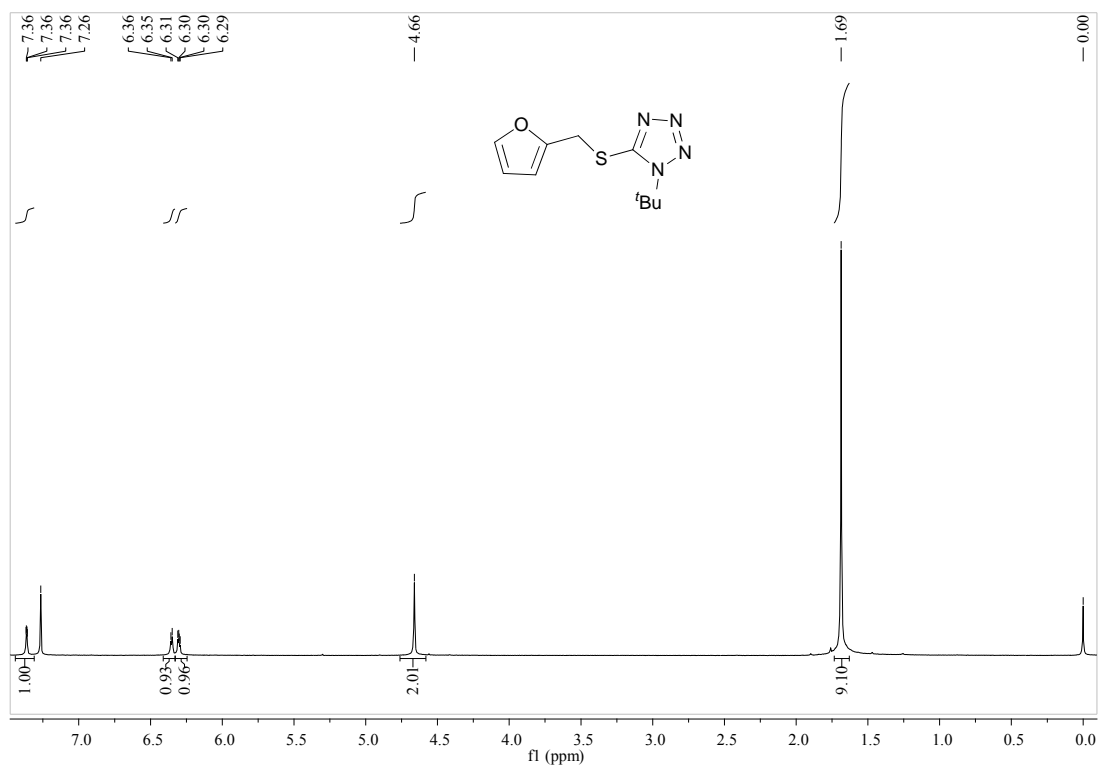


Figure S14. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9l**

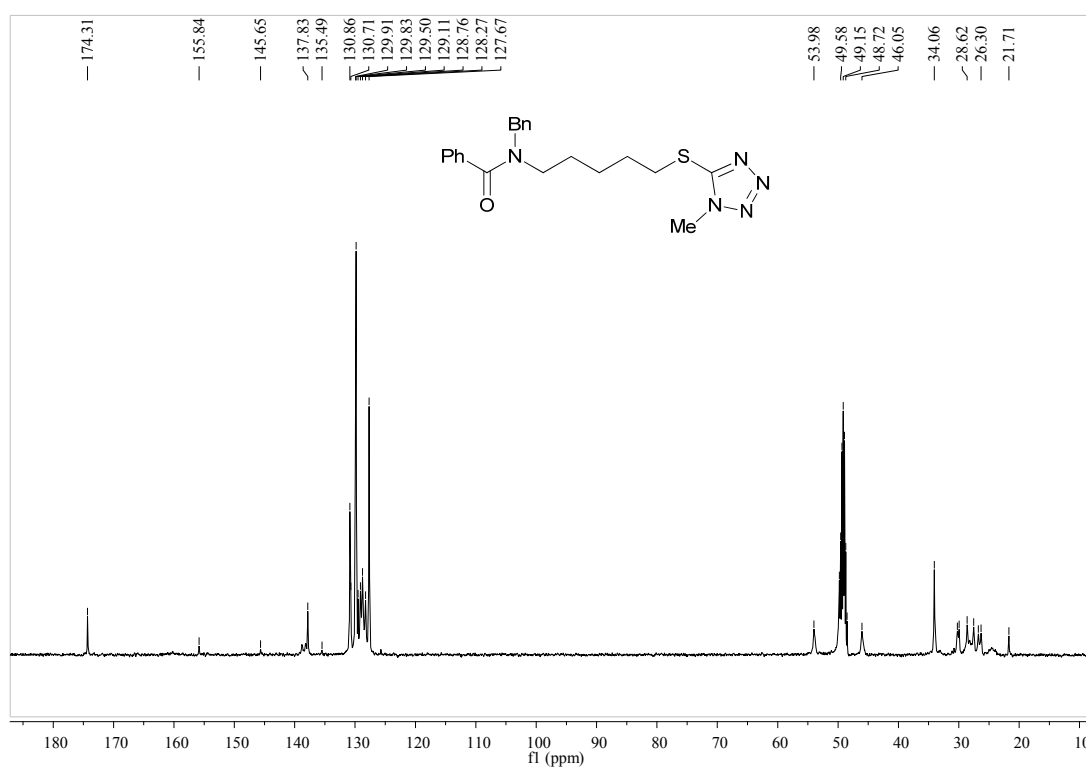
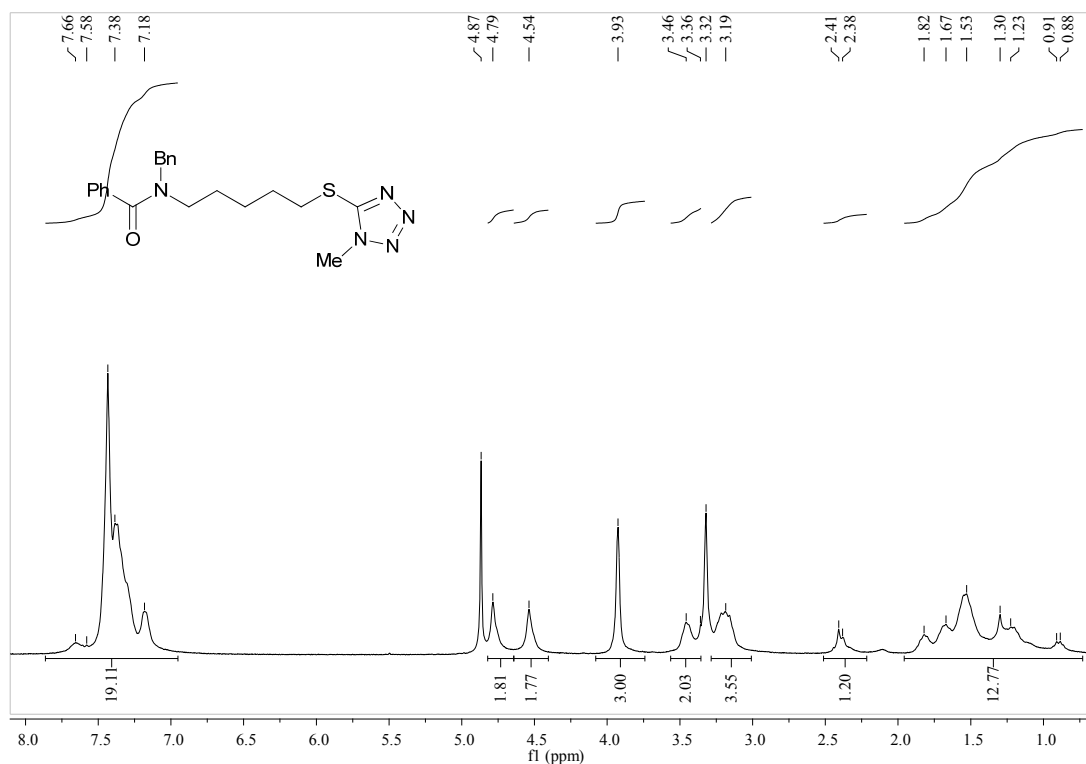


Figure S15. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9m**

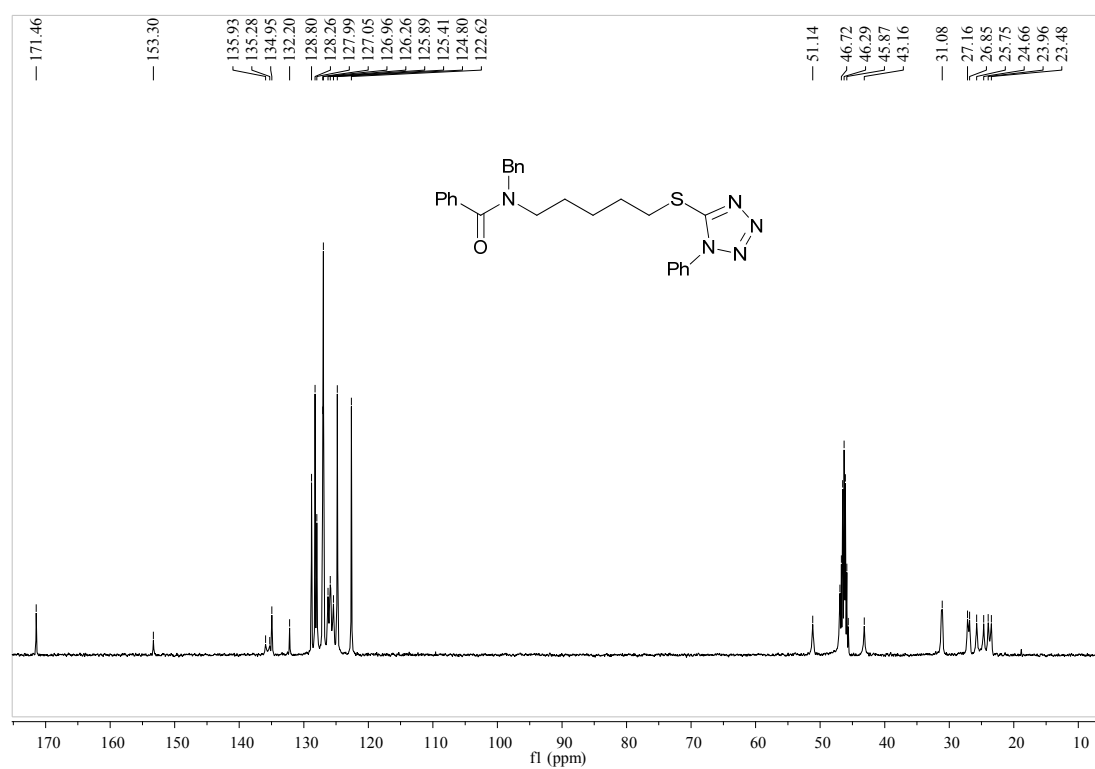
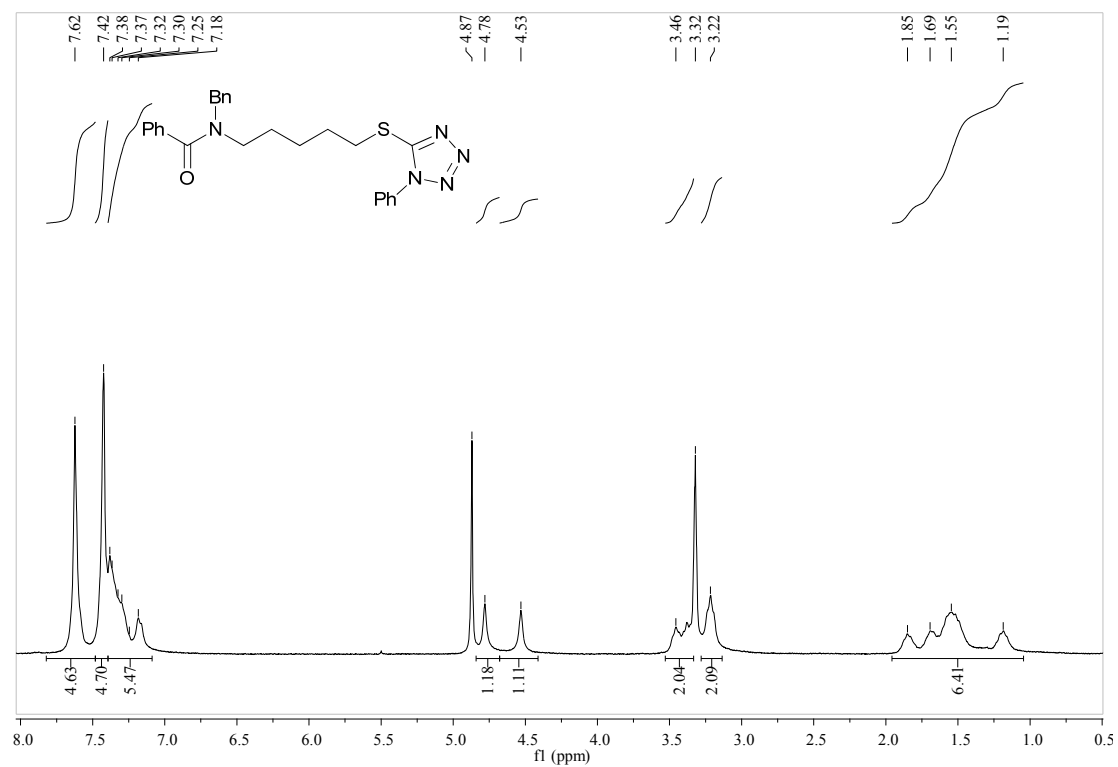


Figure S16. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound 9n

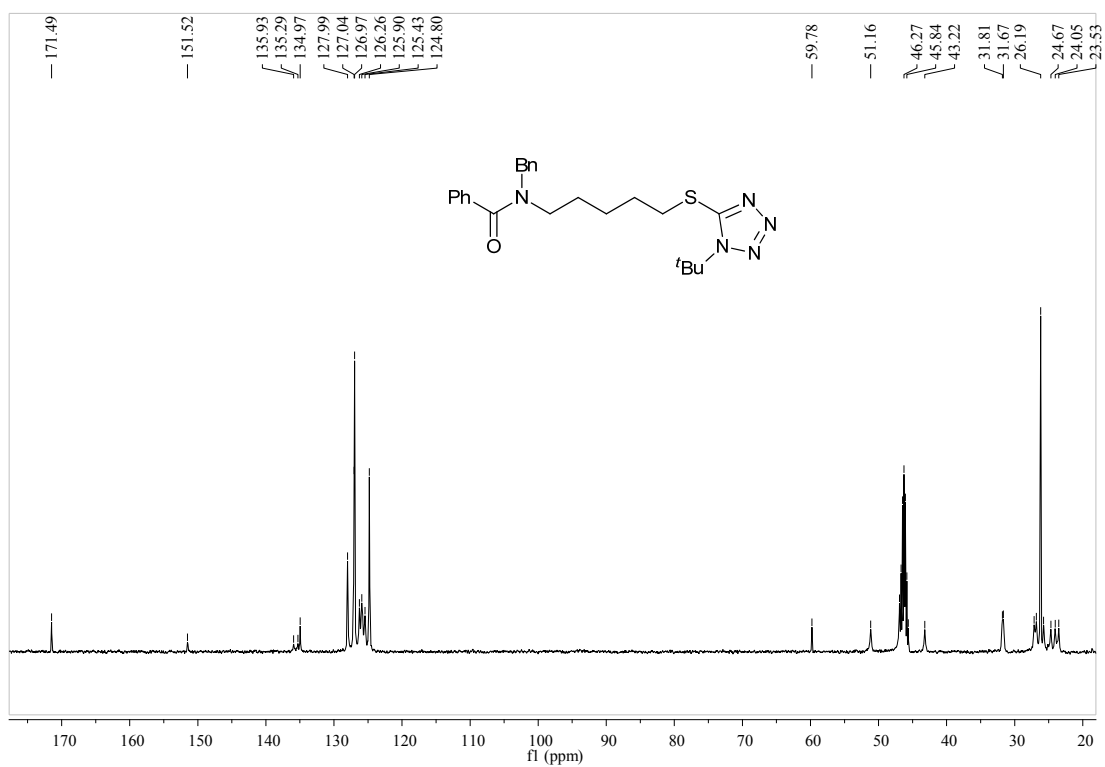
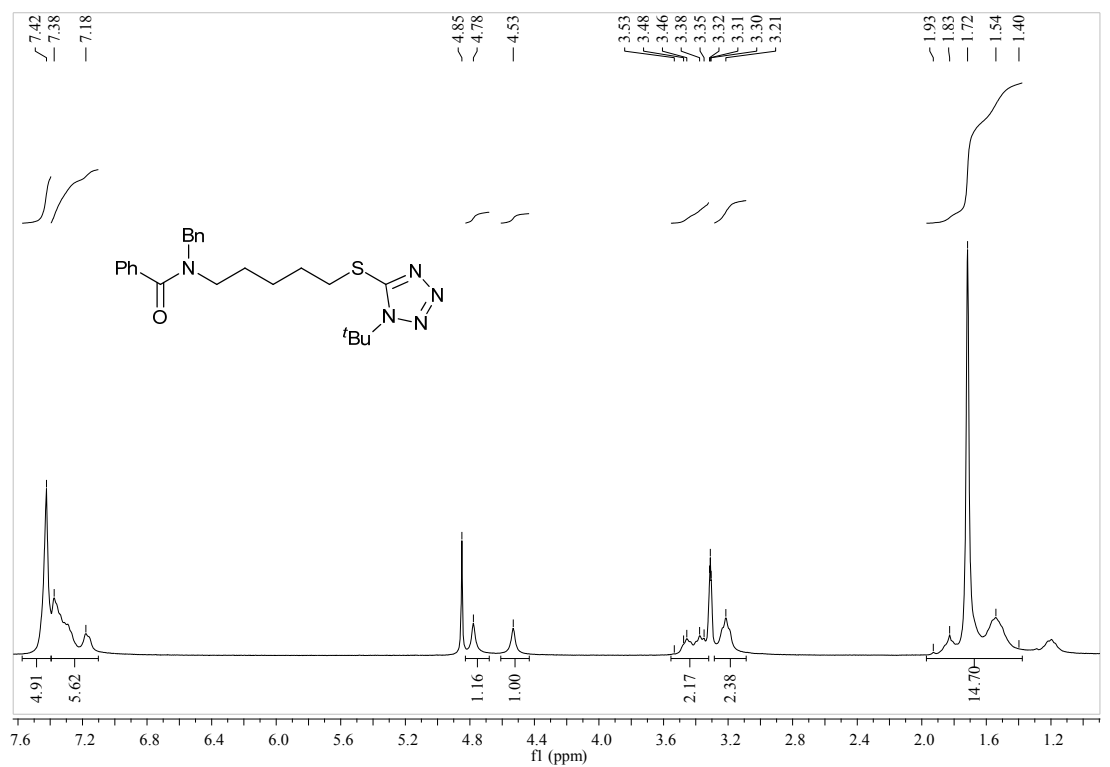


Figure S17. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9o**

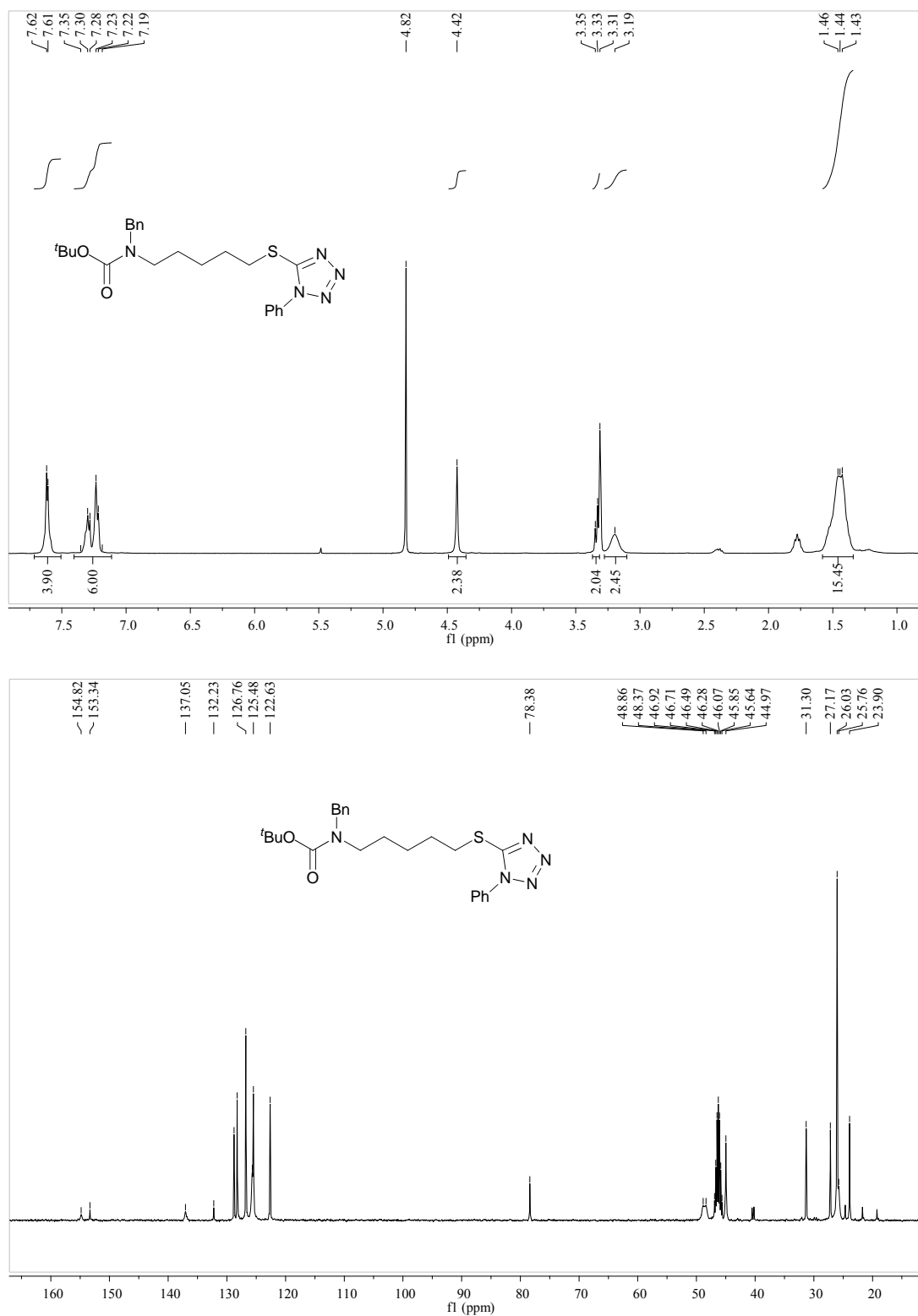


Figure S18. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9p**

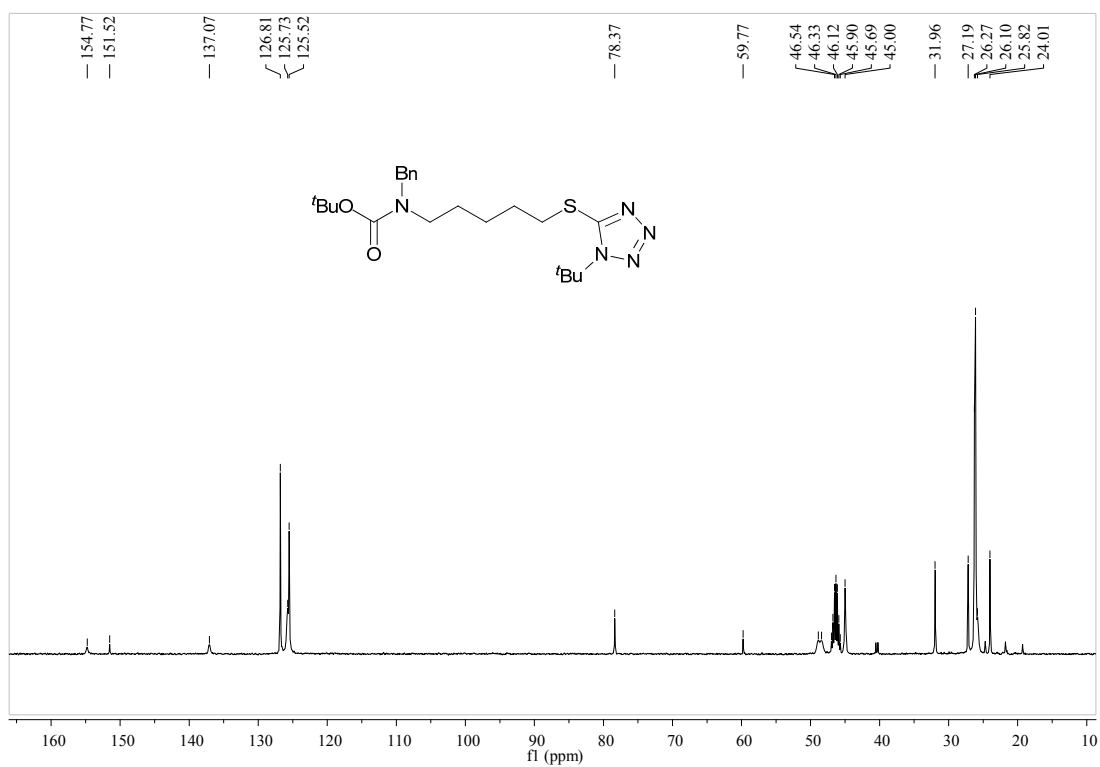
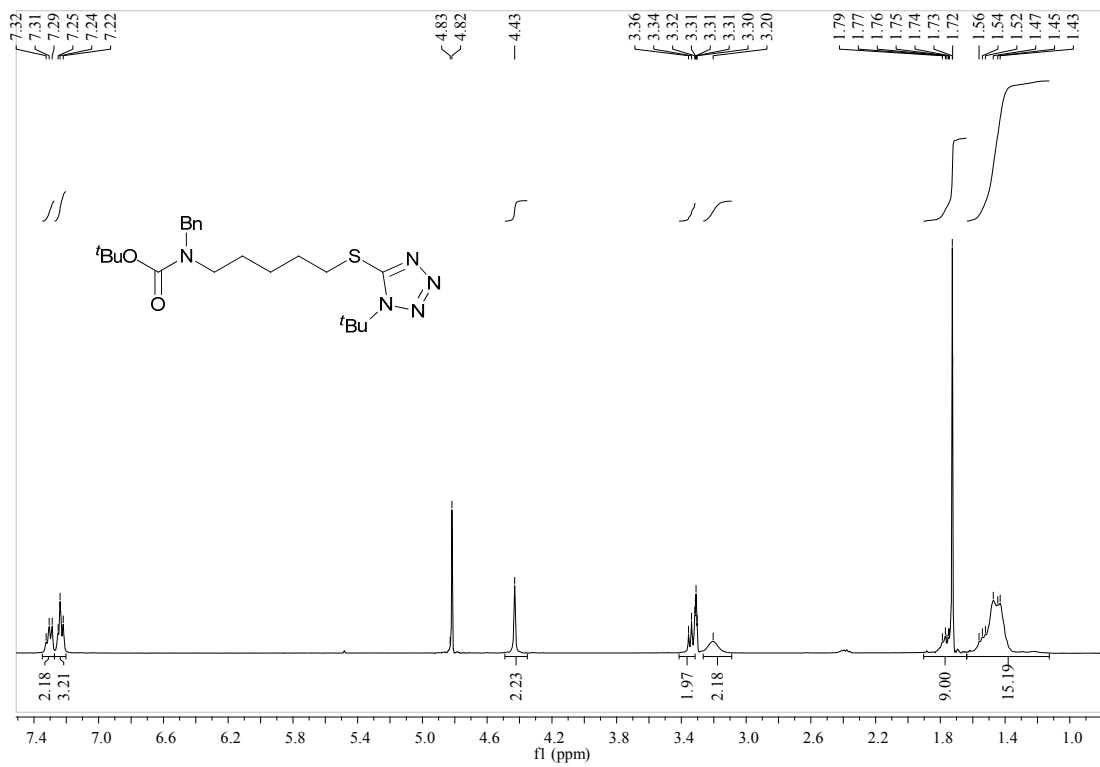


Figure S19. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9q**

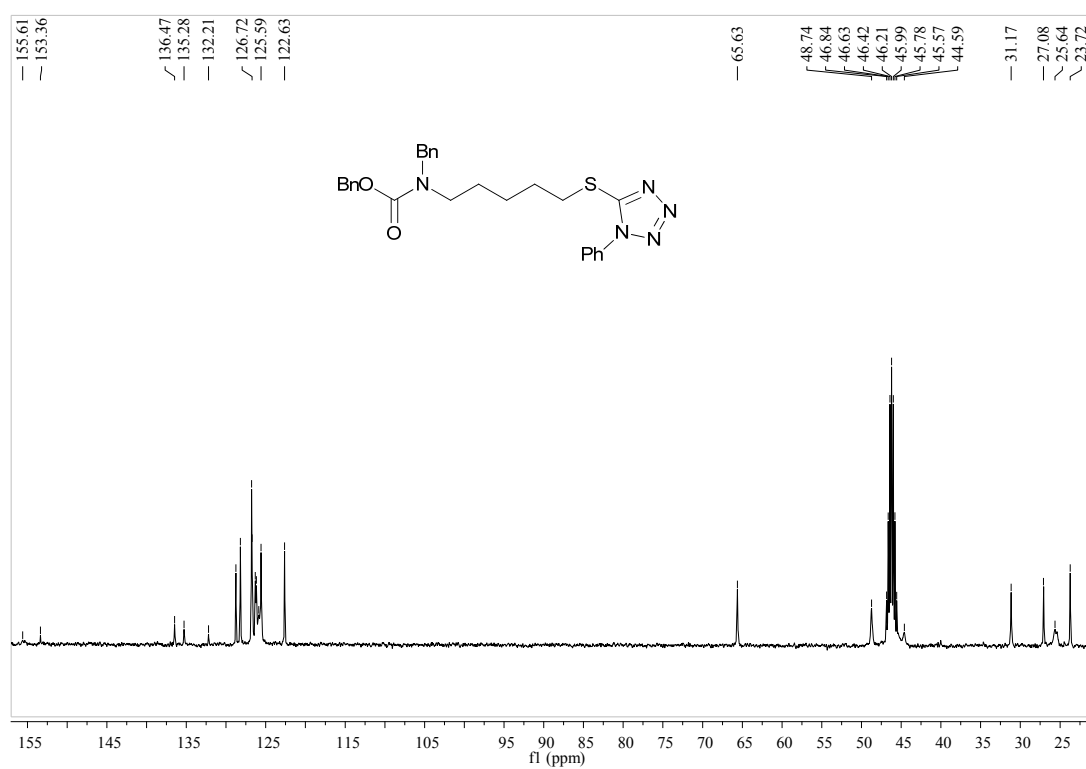
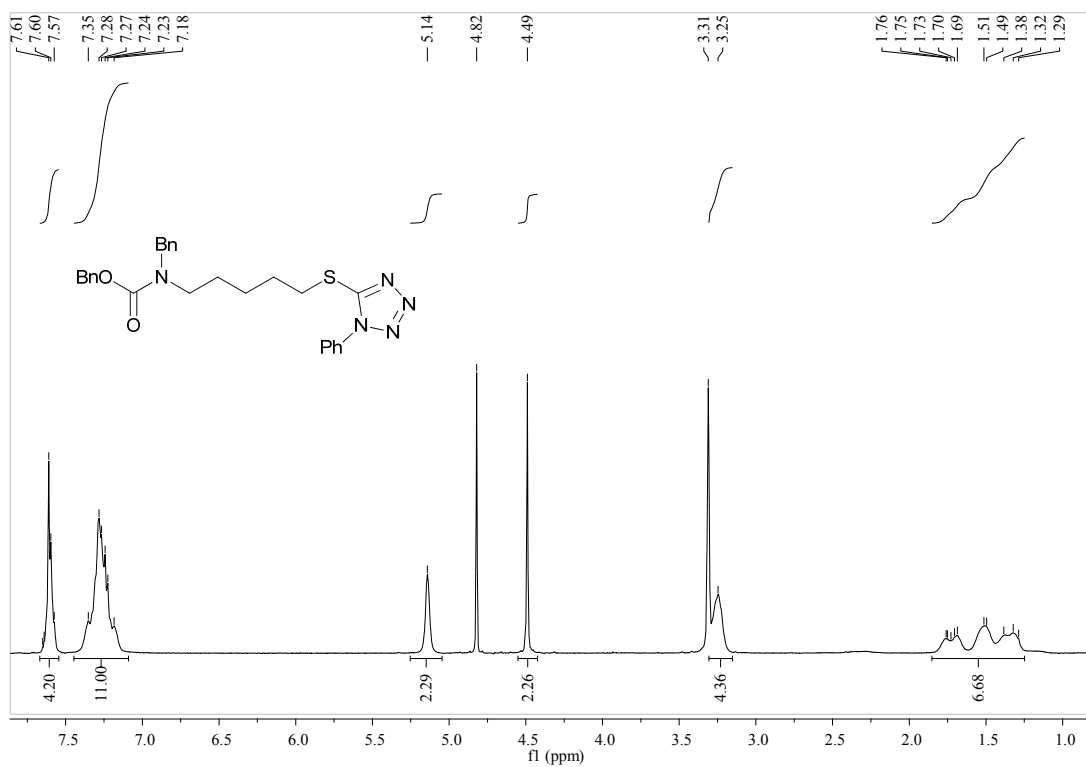


Figure S20. ^1H - (upper) and ^{13}C -NMR (lower) spectra of compound **9r**

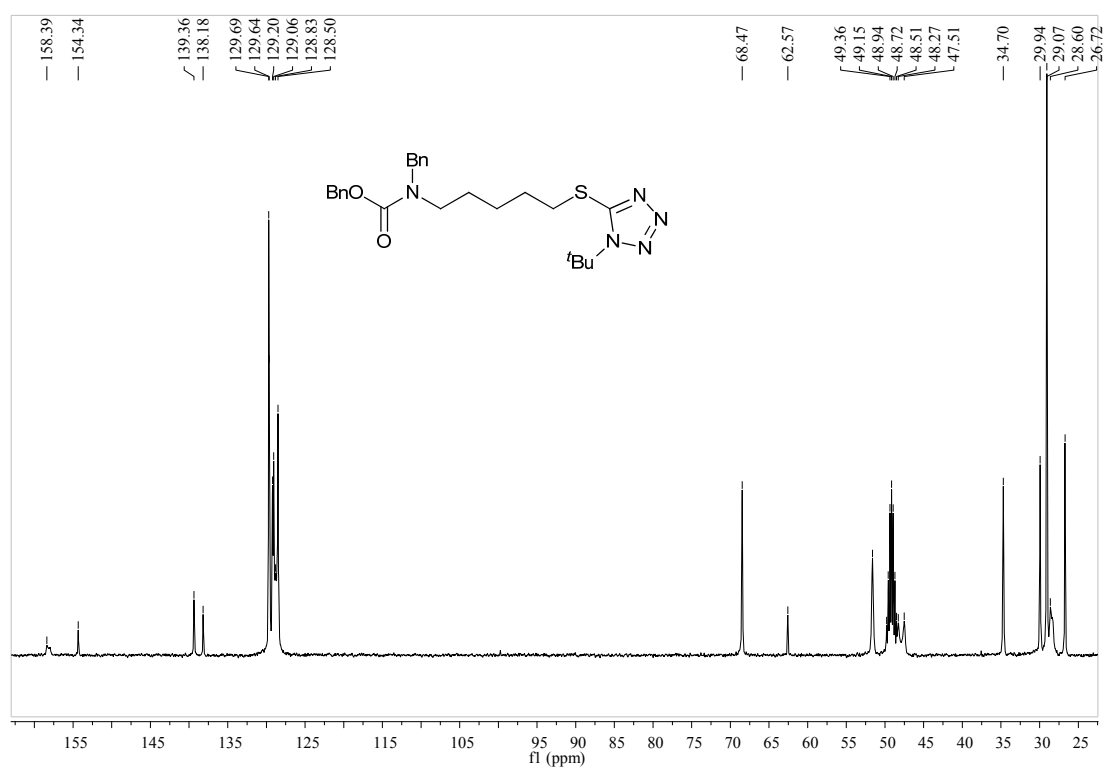
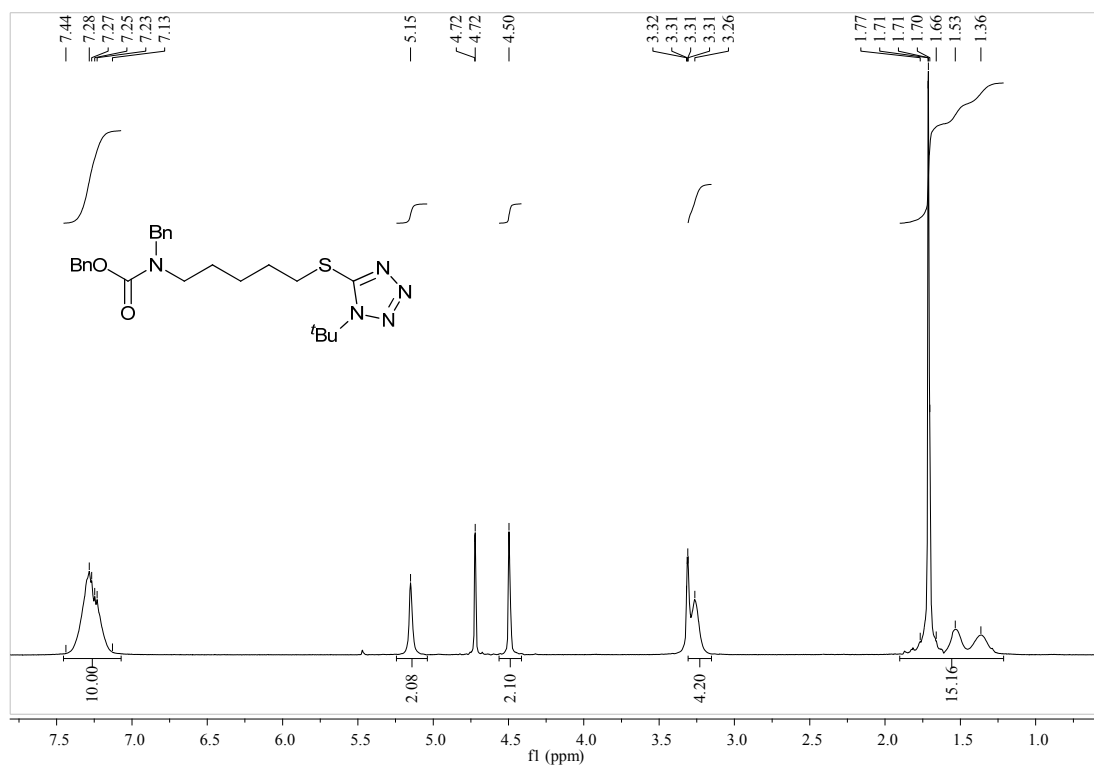


Figure S21. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9s**

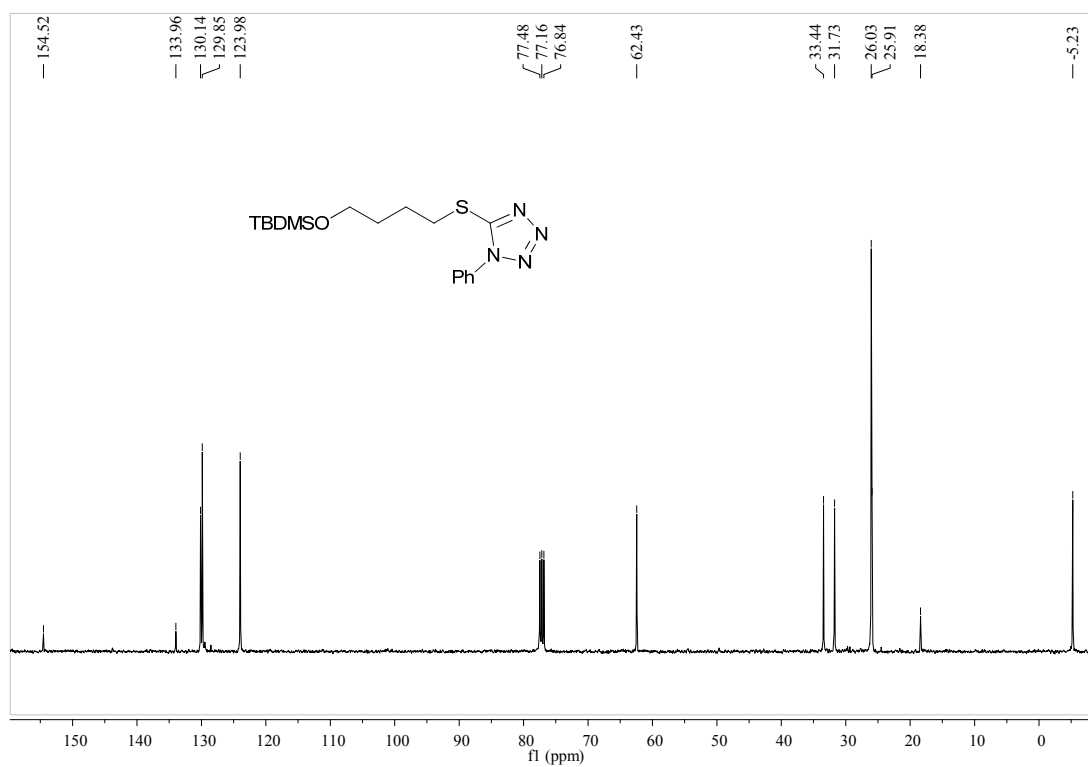
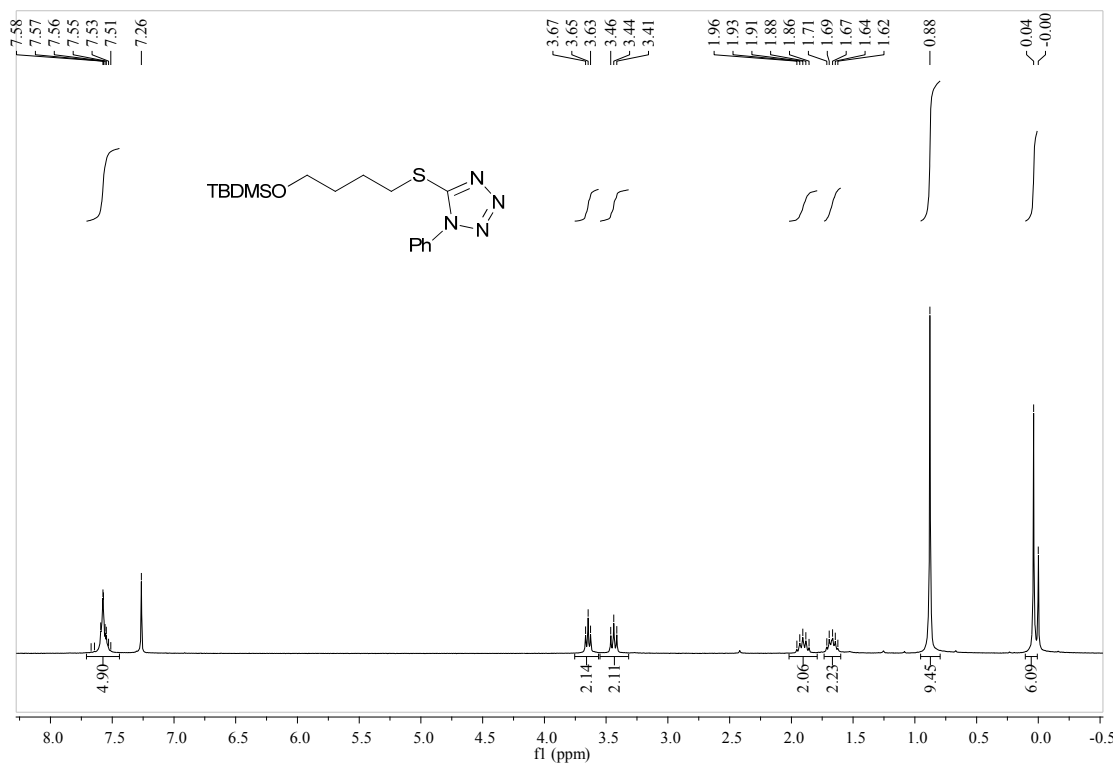


Figure S22. ¹H- (upper) and ¹³C-NMR (lower) spectra of compound **9t**

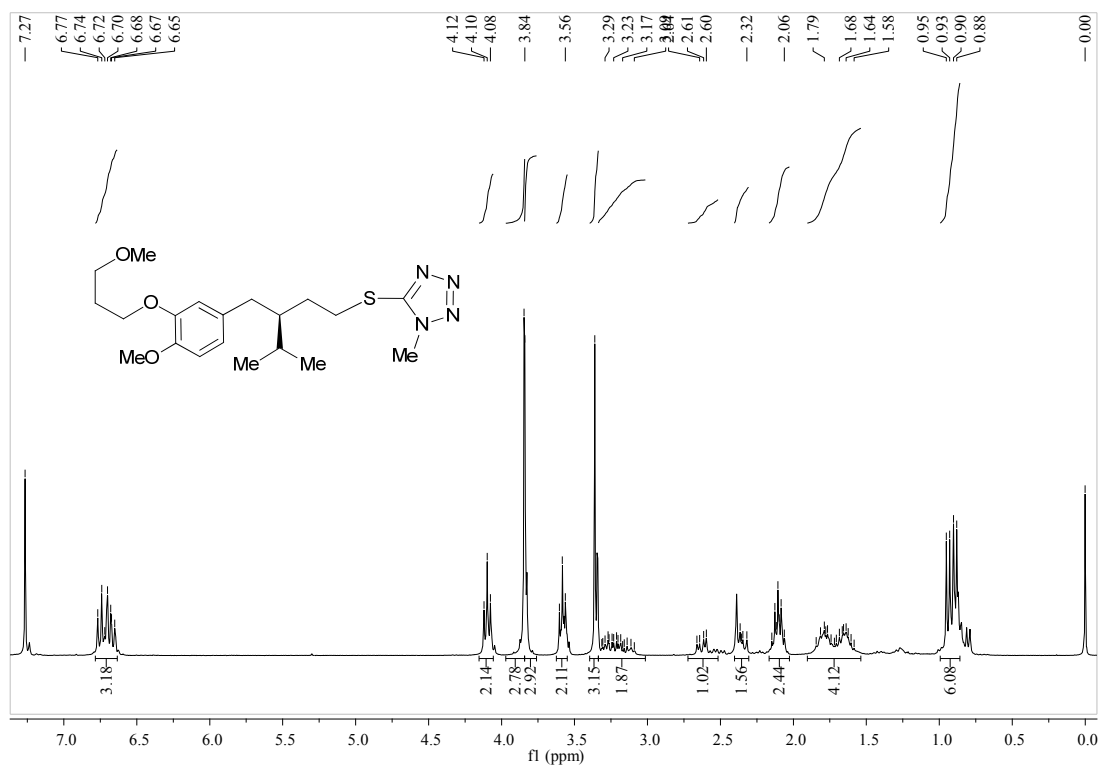


Figure S23. ¹H-NMR spectra of compound **9u**

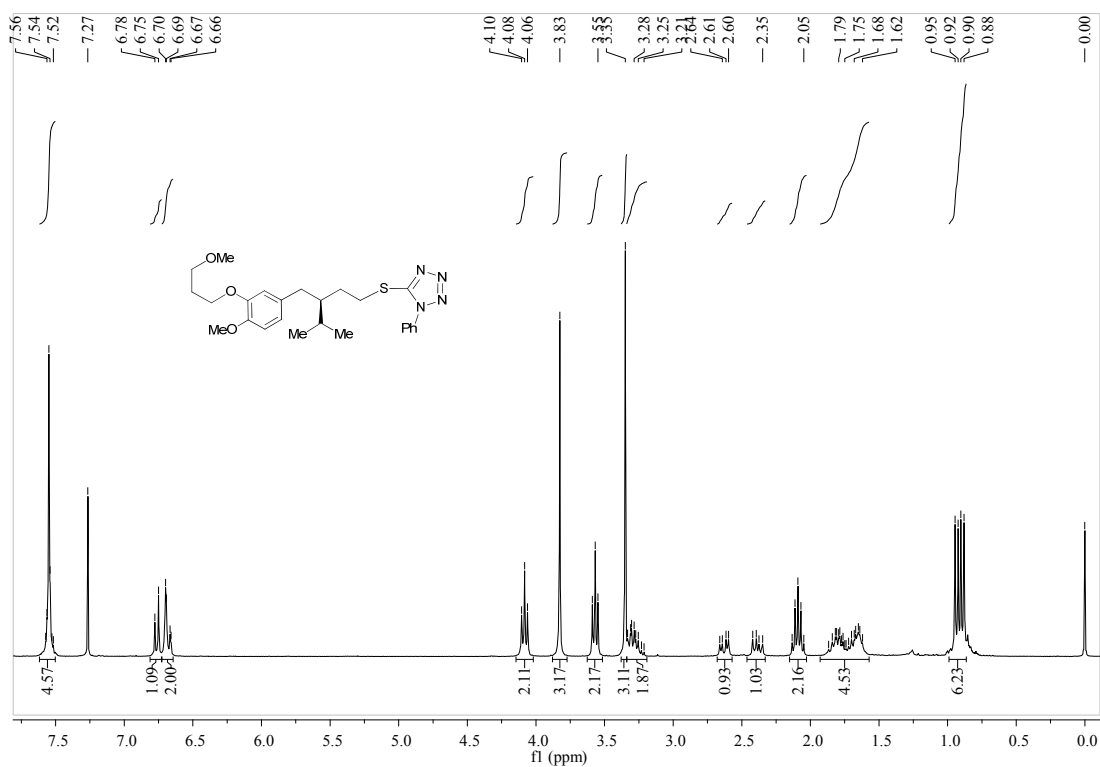


Figure S24. ¹H-NMR spectra of compound **9v**

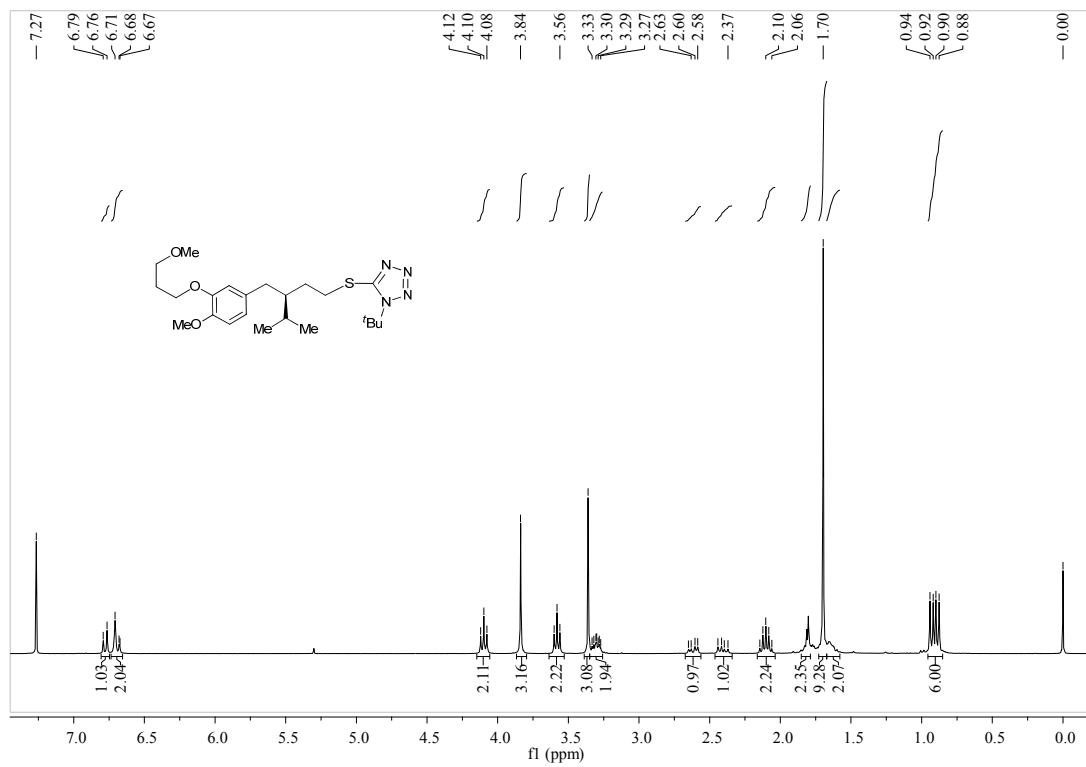


Figure S25. ¹H-NMR spectra of compound **9w**