

Supporting Information

**Copper-catalyzed one-pot
hydroboration/azidation/cycloaddition
reaction of alkynes**

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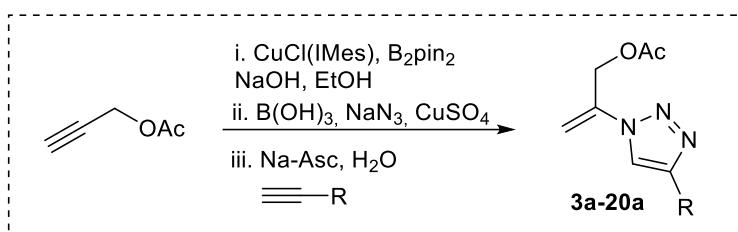
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1. General Information

All reagents were used as received from commercial suppliers unless otherwise stated. Cu(Cl)(IMes) was prepared according to procedures described in the literature.¹ Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with silica gel F254 with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using vanillin solution. Flash column chromatography was performed using silica gel 60 (230-400 mesh). Neat infra-red spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers (= 1/l) are reported in cm⁻¹. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AV-400 spectrometer at 298K. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of CDCl₃, defined at δ = 7.27 ppm (¹H NMR) and δ = 77.0 (¹³C NMR). Coupling constants are quoted in Hz (J). ¹H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qui) and sextet (sex). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m).

2. General Procedure for the synthesis of α -vinyltriazoles

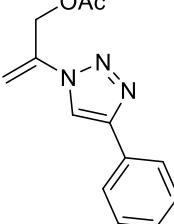


Step 1: To an open flask were added terminal alkyne (0.50 mmol), EtOH (1.0 mL), B₂pin₂ (0.55 mmol, 1.1 equiv., 140 mg), NaOH 1.0 M solution (5 mol%, 25 μ L) and CuCl(IMes) (0.04 mmol, 8 mol%, 17 mg). The reaction was kept stirring for 48 hours at 30° C. After this time, the solvent was completely removed by evaporation under reduced pressure at 35° C (Caution: do not remove EtOH at temperatures above 40° C because it can lead to a proto-deborylation reaction). **Step 2:** After complete removal of EtOH, B(OH)₃ (0.55 mmol, 1.1 equiv., 34 mg), NaN₃ (0.75 mmol, 1.5 equiv., 48.8 mg), EtOH (1.0 mL) and CuSO₄·5H₂O (0.025 mmol, 5 mol%, 6.7 mg) were added. The reaction was kept stirring

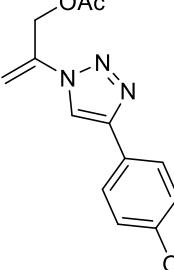
¹ C. A. Citadelle, E. L. Nouy, F. Bisaro, A. M. Z. Slawin, C. S. J. Cazin, *Dalton Trans.* **2010**, 39, 4489.

for 20h at 45°C. **Step 3:** The triazole formation step is performed by the addition of H₂O (0.5 mL), terminal alkyne (0.60 mmol, 1.2 equiv.) and sodium ascorbate (0.015 mmol, 3 mg). The reaction was kept stirring for 20h at 45°C. The solvent was removed under reduced pressure. The product was purified by column chromatography using a mixture of hexane and ethyl acetate as the eluent.

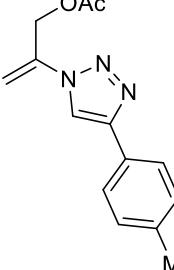
2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)allyl acetate (3a)

 White solid. **Yield:** 51.1 mg, 42%. **¹H NMR** (400 MHz, CDCl₃) δ 8.03 (s, 1H), 7.89 – 7.85 (m, 2H), 7.47 – 7.42 (m, 2H), 7.39 – 7.34 (m, 1H), 5.77 (d, *J* = 1.8 Hz, 1H), 5.37 (dt, *J* = 1.8, 1.0 Hz, 1H), 5.21 (d, *J* = 1.0 Hz, 2H), 2.12 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 147.9, 138.0, 129.9, 128.9, 128.5, 125.8, 117.2, 107.7, 62.3, 20.8. **IR** (vmax, cm⁻¹): 2911, 1738, 1229, 923, 773, 692. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₃H₁₃N₃O₂Na) requires m/z 266.0905, found: m/z 266.0903.

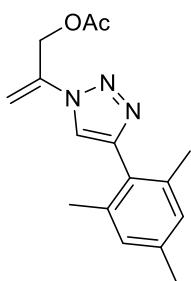
2-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (4a)

 White solid. **Yield:** 56 mg, 41%. **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 5.74 (d, *J* = 1.7 Hz, 1H), 5.35-5.33 (m, 1H), 5.21 (d, *J* = 0.7 Hz, 2H), 3.85 (s, 3H), 2.12 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 159.8, 147.8, 138.1, 127.2, 122.6, 116.4, 114.3, 107.3, 62.3, 55.3, 20.8. **IR** (vmax, cm⁻¹): 3143, 1736, 1447, 1231, 1022. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₄H₁₅N₃O₃Na) requires m/z 296.1011, found: m/z 296.1008.

2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (5a)

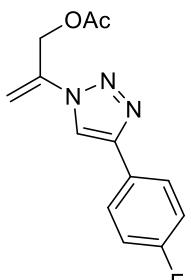
 White solid. **Yield:** 42.5 mg, 33%. **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 5.75 (d, *J* = 1.7 Hz, 1H), 5.34 (dt, *J* = 1.7, 1.0 Hz, 1H), 5.20 (d, *J* = 1.0 Hz, 2H), 2.39 (s, 3H), 2.11 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 148.0, 138.4, 138.1, 129.5, 127.1, 125.7, 116.8, 107.4, 62.3, 21.3, 20.8. **IR** (vmax, cm⁻¹): 3143, 1736, 1231, 877, 812. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₄H₁₅N₃O₂Na) requires m/z 280.1062, found: m/z 280.1059.

2-(4-mesityl-1*H*-1,2,3-triazol-1-yl)allyl acetate (6a)



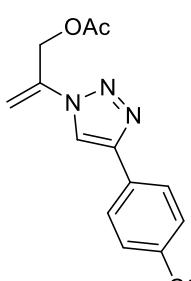
White solid. **Yield:** 34.2 mg, 24%. **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (s, 1H), 6.95 (s, 2H), 5.78 (d, J = 1.7 Hz, 1H), 5.35 (dt, J = 1.7, 1.0 Hz, 1H), 5.23 (d, J = 1.0 Hz, 2H), 2.32 (s, 3H), 2.13 (s, 6H), 2.12 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 145.8, 138.4, 138.0, 137.7, 128.4, 126.4, 120.3, 107.1, 62.3, 29.7, 21.1, 20.9. **IR** (vmax, cm⁻¹): 3155, 2958, 2918, 1745, 1689, 1487, 1431, 1215, 1013. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₆H₁₉N₃O₂Na) requires m/z 308.1375, found: m/z 308.1370.

2-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (7a)



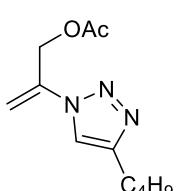
White solid. **Yield:** 40.5 mg, 31%. **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.87 – 7.81 (m, 2H), 7.17 – 7.09 (m, 2H), 5.77 (d, J = 1.7 Hz, 1H), 5.37 (dt, J = 1.7, 1.0 Hz, 1H), 5.21 (d, J = 1.0 Hz, 2H), 2.12 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 162.9 (d, J = 247.9 Hz), 147.0, 138.0, 127.6 (d, J = 8.2 Hz), 126.2 (d, J = 3.1 Hz), 117.0, 115.9 (d, J = 21.8 Hz), 107.8, 62.3, 20.8. **¹⁹F NMR** (376 MHz, CDCl₃): δ -112.9. **IR** (vmax, cm⁻¹): 3126, 1721, 1231, 1029, 789. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₃H₁₂FN₃O₂Na) requires m/z 284.0811, found: m/z 284.0810.

Methyl 4-(1-(3-acetoxyprop-1-en-2-yl)-1*H*-1,2,3-triazol-4-yl)benzoate (8a)



White solid. **Yield:** 78.3 mg, 52%. **¹H NMR** (400 MHz, CDCl₃) δ 8.15 – 8.10 (m, 3H), 7.97 – 7.93 (m, 2H), 5.81 (d, J = 1.8 Hz, 1H), 5.41 (dt, J = 1.8, 1.0 Hz, 1H), 5.22 (d, J = 1.0 Hz, 2H), 3.95 (s, 3H), 2.13 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 166.7, 146.9, 137.9, 134.2, 130.2, 129.9, 125.6, 118.2, 108.3, 62.2, 52.2, 20.8. **IR** (vmax, cm⁻¹): 3143, 2942, 1736, 1705, 1231, 773. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₅H₁₅N₃O₄Na) requires m/z 324.0960, found: m/z 324.0958.

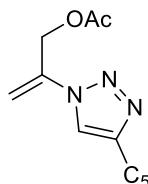
2-(4-butyl-1*H*-1,2,3-triazol-1-yl)allyl acetate (9a)



Yellow oil. **Yield:** 44.6 mg, 40%. **¹H NMR** (400 MHz, CDCl₃) δ 7.54 (s, 1H), 5.65 (d, J = 1.4 Hz, 1H), 5.27 (s, 1H), 5.16 (s, 2H), 2.75 (t, J = 7.8 Hz, 2H), 2.11 (s, 3H), 1.68 (qui, J = 7.6 Hz, 2H), 1.40 (sex, J = 7.5 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 148.7, 138.1, 118.4, 106.7, 62.3, 31.4, 25.2, 22.3, 20.8, 13.8. **IR** (vmax, cm⁻¹): 3143, 2918, 1745,

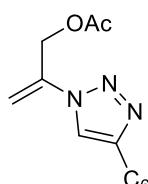
1206, 1029. **HRMS** (ESI+): exact mass calculated for [M+H]⁺ ($C_{11}H_{18}N_3O_2$) requires m/z 224.1399, found: m/z 224.1392.

2-(4-pentyl-1*H*-1,2,3-triazol-1-yl)allyl acetate (10a)



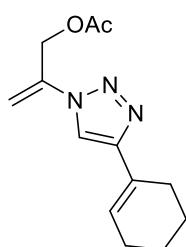
Yellow oil. **Yield:** 55.8 mg, 47%. **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (s, 1H), 5.65 (d, *J* = 1.6 Hz, 1H), 5.29–5.26 (m, 1H), 5.16 (d, *J* = 0.8 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.11 (s, 3H), 1.70 (qui, *J* = 7.8 Hz, 2H), 1.39 – 1.34 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 148.7, 138.1, 118.4, 106.6, 62.3, 31.4, 28.9, 25.5, 22.4, 20.8, 13.9. **IR** (vmax, cm⁻¹): 3143, 2926, 2854, 1736, 1231, 1029. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ ($C_{12}H_{19}N_3O_2Na$) requires m/z 260.1375, found: m/z 260.1372.

2-(4-hexyl-1*H*-1,2,3-triazol-1-yl)allyl acetate (11a)



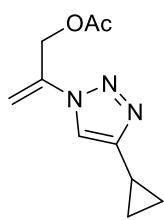
White solid. **Yield:** 54 mg, 43%. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 (s, 1H), 5.66 (d, *J* = 1.5 Hz, 1H), 5.28–5.26 (m, 1H), 5.17 (d, *J* = 0.8 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 2.12 (s, 3H), 1.69 (qui, *J* = 7.8 Hz, 2H), 1.43 – 1.26 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 148.7, 138.1, 118.4, 106.6, 62.3, 31.5, 29.2, 28.8, 25.5, 22.5, 20.8, 14.0. **IR** (vmax, cm⁻¹): 2910, 2845, 1721, 1238, 1038. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ ($C_{13}H_{21}N_3O_2Na$) requires m/z 274.1531, found: m/z 274.1530.

2-(4-(cyclohex-1-en-1-yl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (12a)



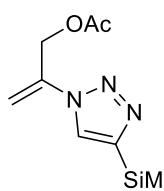
White solid. **Yield:** 42 mg, 34%. **¹H NMR** (400 MHz, CDCl₃) δ 7.63 (s, 1H), 6.62–6.58 (m, 1H), 5.66 (d, *J* = 1.6 Hz, 1H), 5.28 (dd, *J* = 1.6, 1.0 Hz, 1H), 5.17 (d, *J* = 1.0 Hz, 2H), 2.42 – 2.37 (m, 2H), 2.26 – 2.19 (m, 2H), 2.10 (s, 3H), 1.82 – 1.76 (m, 2H), 1.73 – 1.63 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 149.5, 138.0, 126.6, 126.1, 115.8, 106.8, 62.3, 26.3, 25.3, 22.4, 22.1, 20.8. **IR** (vmax, cm⁻¹): 3119, 2926, 1736, 1431, 1215, 1013. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ ($C_{13}H_{17}N_3O_2Na$) requires m/z 270.1218, found: m/z 270.1223.

2-(4-cyclopropyl-1*H*-1,2,3-triazol-1-yl)allyl acetate (13a)



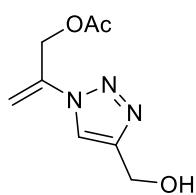
Yellow oil. **Yield:** 42.5 mg, 41%. **¹H NMR** (400 MHz, CDCl₃) δ 7.52 (s, 1H), 5.62 (d, J = 1.6 Hz, 1H), 5.27-5.25 (m, 1H), 5.14 (d, J = 0.9 Hz, 2H), 2.11 (s, 3H), 2.02-1.93 (m, 1H), 1.01-0.96 (m, 2H), 0.93-0.85 (m, 2H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 150.4, 138.0, 117.5, 106.7, 62.2, 20.7, 7.8, 6.5. **IR** (vmax, cm⁻¹): 2999, 1729, 1222, 1029. **HRMS** (ESI+): exact mass calculated for [M+H]⁺ (C₁₀H₁₄N₃O₂) requires m/z 208.1086, found: m/z 208.1085.

2-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (14a)



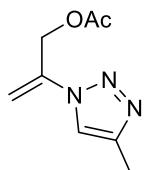
White solid. **Yield:** 28.7 mg, 24%. **¹H NMR** (400 MHz, CDCl₃) δ 7.77 (s, 1H), 5.69 (d, J = 1.5 Hz, 1H), 5.31-5.29 (m, 1H), 5.17 (d, J = 0.8 Hz, 2H), 2.12 (s, 3H), 0.35 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.2, 146.8, 138.0, 126.7, 107.1, 62.5, 20.8, -1.2. **IR** (vmax, cm⁻¹): 3126, 2950, 1736, 1238, 845. **HRMS** (ESI+): exact mass calculated for [M+H]⁺ (C₁₀H₁₈N₃O₂Si) requires m/z 240.1168, found: m/z 240.1164.

2-(4-(hydroxymethyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (15a)



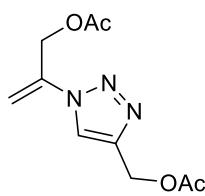
Yellow oil. **Yield:** 21.7 mg, 22%. **¹H NMR** (400 MHz, CDCl₃) δ 7.83 (s, 1H), 5.71 (d, J = 1.8 Hz, 1H), 5.33 (dt, J = 1.8, 1.0 Hz, 1H), 5.13 (d, J = 1.0 Hz, 2H), 4.81 (s, 2H), 3.13 (bs, 1H), 2.09 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 147.9, 138.0, 119.7, 108.1, 62.3, 56.3, 20.7. **IR** (vmax, cm⁻¹): 3368, 3143, 2942, 1745, 1455, 1367, 1215, 1022. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₈H₁₂N₃O₃Na) requires m/z 221.0776, found: m/z 221.0775.

2-(4-(((tert-butyldiphenylsilyl)oxy)methyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (16a)



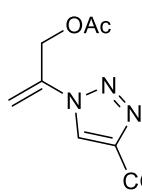
White solid. **Yield:** 89.3 mg, 41%. **¹H NMR** (400 MHz, CDCl₃) δ 7.71 – 7.67 (m, 4H), 7.60 (s, 1H), 7.47 – 7.36 (m, 6H), 5.66 (d, J = 1.6 Hz, 1H), 5.31-5.29 (m, 1H), 5.14 (s, 2H), 4.91 (s, 2H), 2.10 (s, 3H), 1.08 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 148.4, 138.0, 135.5, 133.0, 129.9, 127.8, 119.5, 107.3, 62.3, 58.4, 26.8, 20.7, 19.2. **IR** (vmax, cm⁻¹): 2926, 2861, 1745, 1215, 1110, 1029. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₂₄H₂₉N₃O₃SiNa) requires m/z 458.1876, found: m/z 458.1871.

2-(4-(acetoxymethyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (17a)



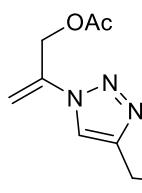
White solid. **Yield:** 40 mg, 33%. **¹H NMR** (400 MHz, CDCl₃) δ 7.89 (s, 1H), 5.73 (d, J = 1.7 Hz, 1H), 5.37–5.35 (m, 1H), 5.25 (s, 2H), 5.16 (d, J = 0.6 Hz, 2H), 2.11 (s, 3H), 2.10 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.9, 170.1, 143.1, 137.9, 121.7, 108.1, 62.2, 57.4, 20.8, 20.7. **IR** (vmax, cm⁻¹): 3143, 2926, 1729, 1222, 1022. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₀H₁₃N₃O₄Na) requires m/z 262.0804, found: m/z 262.0813.

Ethyl 1-(3-acetoxyprop-1-en-2-yl)-1*H*-1,2,3-triazole-4-carboxylate (18a)



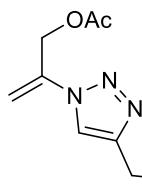
Yellow oil. **Yield:** 31.1 mg, 26%. **¹H NMR** (400 MHz, CDCl₃) δ 8.36 (s, 1H), 5.88 (d, J = 1.8 Hz, 1H), 5.47 (bs, 1H), 5.15 (s, 2H), 4.45 (q, J = 7.1 Hz, 2H), 2.11 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.0, 160.4, 140.4, 137.6, 125.4, 110.1, 62.2, 61.5, 20.7, 14.3. **IR** (vmax, cm⁻¹): 2973, 1738, 1221, 1020. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₀H₁₃N₃O₄Na) requires m/z 262.0804, found: m/z 262.0798.

2-(4-(((tert-butoxycarbonyl)amino)methyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (19a)

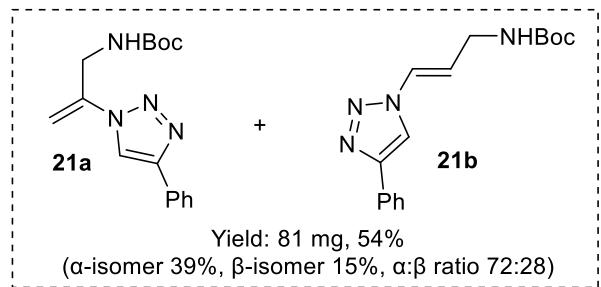


White solid. **Yield:** 88.9 mg, 60%. **¹H NMR** (400 MHz, CDCl₃) δ 7.80 (s, 1H), 5.70 (d, J = 1.7 Hz, 1H), 5.34–5.31 (m, 1H), 5.20 – 5.13 (m, 3H), 4.43 (d, J = 6.1 Hz, 2H), 2.11 (s, 3H), 1.45 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 155.8, 145.7, 137.9, 119.9, 107.7, 79.8, 62.2, 35.9, 28.3, 20.7. **IR** (vmax, cm⁻¹): 3352, 2923, 1752, 1705, 1503, 1222, 1158. **HRMS** (ESI+): exact mass calculated for [M+Na]⁺ (C₁₃H₂₀N₄O₄Na) requires m/z 319.1382, found: m/z 319.1380.

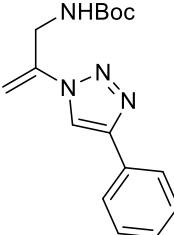
2-(4-((benzyl(methyl)amino)methyl)-1*H*-1,2,3-triazol-1-yl)allyl acetate (20a)



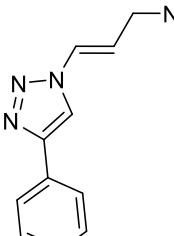
White solid. **Yield:** 69.1 mg, 46%. **¹H NMR** (400 MHz, CDCl₃) δ 7.75 (s, 1H), 7.37 – 7.24 (m, 5H), 5.70 (d, J = 1.6 Hz, 1H), 5.33–5.31 (m, 1H), 5.16 (d, J = 0.7 Hz, 2H), 3.75 (s, 2H), 3.59 (s, 2H), 2.28 (s, 3H), 2.10 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 170.1, 145.7, 138.4, 138.0, 129.0, 128.3, 127.1, 120.4, 107.3, 62.3, 61.5, 51.8, 42.2, 20.7. **IR** (vmax, cm⁻¹): 2937, 1736, 1213, 1030. **HRMS** (ESI+): exact mass calculated for [M+H]⁺ (C₁₆H₂₁N₄O₂) requires m/z 301.1665, found: m/z 301.1663.

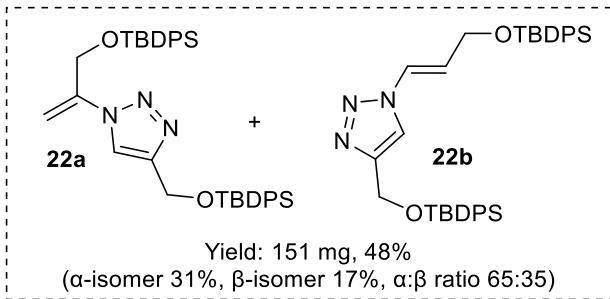


tert-butyl (2-(4-phenyl-1H-1,2,3-triazol-1-yl)allyl)carbamate (21a)

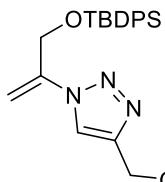
 White solid. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.88 – 7.83 (m, 2H), 7.47 – 7.41 (m, 2H), 7.39 – 7.33 (m, 1H), 5.54 (s, 1H), 5.25 (s, 2H), 4.43 (d, $J = 6.5$ Hz, 2H), 1.43 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 155.7, 147.9, 140.2, 130.0, 128.9, 128.5, 125.8, 117.3, 105.0, 80.1, 42.3, 28.3. **IR** (vmax, cm^{-1}): 3352, 2950, 1680, 1512, 1022. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2\text{Na}$) requires m/z 323.1484, found: m/z 323.1491.

tert-butyl (E)-(3-(4-phenyl-1H-1,2,3-triazol-1-yl)prop-1-enyl)carbamate (21b)

 White solid. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.85 (d, $J = 7.2$ Hz, 2H), 7.48-7.41 (m, 2H), 7.39-7.33 (m, 1H), 7.30 (d, $J = 14.4$ Hz, 1H), 6.30 (dt, $J = 14.4, 6.1$ Hz, 1H), 4.83 (s, 1H), 4.02-3.93 (m, 2H), 1.48 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 155.7, 147.9, 130.0, 128.9, 128.5, 125.8, 125.6, 119.1, 116.6, 80.0, 39.6, 28.2. **IR** (vmax, cm^{-1}): 3352, 3135, 2958, 2918, 1689, 1512, 1247, 1022. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{20}\text{N}_4\text{O}_2\text{Na}$) requires m/z 323.1484, found: m/z 323.1487.

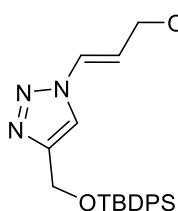


4-(((tert-butyldiphenylsilyl)oxy)methyl)-1-(3-((tert-butyldiphenylsilyl)oxy)prop-1-en-2-yl)-1H-1,2,3-triazole (22a)



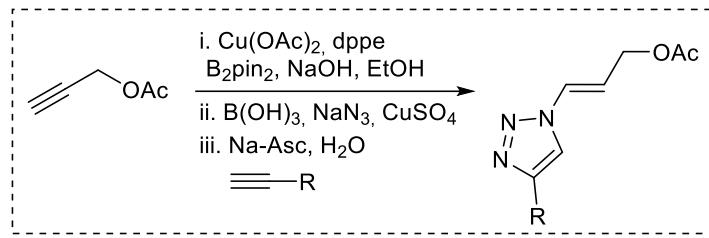
White solid. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.70 – 7.63 (m, 9H), 7.45 – 7.34 (m, 12H), 5.58 (d, $J = 0.9$ Hz, 1H), 5.33 – 5.30 (m, 1H), 4.88 (d, $J = 0.5$ Hz, 2H), 4.68 (s, 2H), 1.08 (s, 9H), 1.07 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 147.9, 141.9, 135.6, 135.5, 133.1, 132.6, 130.0, 129.8, 127.9, 127.8, 119.7, 104.1, 62.7, 58.5, 26.8, 26.7, 19.2, 19.1. **IR** (vmax, cm^{-1}): 2934, 2854, 1110, 700. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{38}\text{H}_{45}\text{N}_3\text{O}_2\text{Si}_2\text{Na}$) requires m/z 654.2948, found: m/z 654.2941.

(E)-4-(((tert-butyldiphenylsilyl)oxy)methyl)-1-(3-((tert-butyldiphenylsilyl)oxy)prop-1-en-1-yl)-1H-1,2,3-triazole (22b)



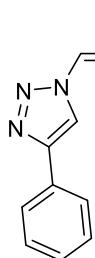
White solid. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.72 – 7.67 (m, 8H), 7.49 (s, 1H), 7.48 – 7.32 (m, 13H), 6.26 (dt, $J = 14.2, 4.4$ Hz, 1H), 4.90 (s, 2H), 4.40 (dd, $J = 4.4, 2.1$ Hz, 2H), 1.11 (s, 9H), 1.09 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 148.4, 135.6, 135.5, 133.1, 133.0, 129.9, 129.8, 127.9, 127.8, 124.2, 121.1, 119.1, 61.4, 58.5, 26.81, 26.80, 19.24, 19.20. **IR** (vmax, cm^{-1}): 3143, 3063, 2926, 1673, 1586, 1423, 1102. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{38}\text{H}_{45}\text{N}_3\text{O}_2\text{Si}_2\text{Na}$) requires m/z 654.2948, found: m/z 654.2947.

2. General Procedure for the synthesis of β -vinyltriazoles

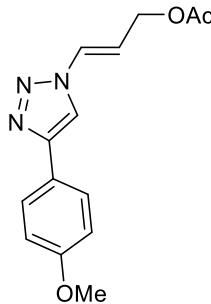


Step 1: To an open flask were added terminal alkyne (0.50 mmol), EtOH (2.0 mL), B₂pin₂ (0.55 mmol, 1.1 equiv., 140 mg), NaOH 1.0 M solution (0.15 mol%, 25 µL), Cu(OAc)₂ (0.04 mmol, 8 mol%, 8.0 mg) and dppe (10 mol%, 0.05 mmol, 19.9 mg). The reaction was kept stirring for 48 hours at 30° C. After this period, the solvent was completely removed by evaporation under reduced pressure at 35° C (Caution: do not remove EtOH at temperatures above 40° C because it can lead to a proto-deborylation reactions). **Step 2:** After complete removal of EtOH, B(OH)₃ (0.55 mmol, 1.1 equiv., 34 mg), NaN₃ (0.75 mmol, 1.5 equiv., 48.8 mg), EtOH (2.0 mL) and CuSO₄.5H₂O (0.025 mmol, 5 mol%, 6.7 mg) were added. The reaction was kept stirring for 20h at 45°C. **Step 3:** The triazole formation step is performed by the addition of H₂O (0.5 mL), terminal alkyne (0.60 mmol, 1.2 equiv.) and sodium ascorbate (0.015 mmol, 3 mg). The reaction was kept stirring for 20h at 45°C. The solvent was removed under reduced pressure. The product was purified by column chromatography using a mixture of hexane and ethyl acetate as the eluent.

(E)-3-(4-phenyl-1H-1,2,3-triazol-1-yl)allyl acetate (3b)

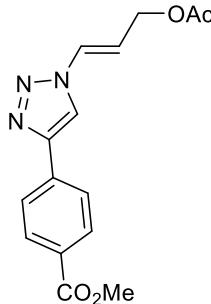


(E)-3-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)allyl acetate (4b)



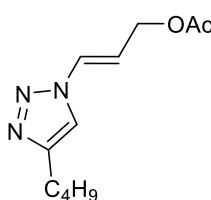
White solid. **Yield:** 59 mg, 48% (α -isomer 13%, β -isomer 35%, $\alpha:\beta$ ratio 27:73). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.78 (d, $J = 8.9$ Hz, 2H), 7.43 (dt, $J = 14.4, 1.3$ Hz, 1H), 6.98 (d, $J = 8.9$ Hz, 2H), 6.35 (dt, $J = 14.4, 6.4$ Hz, 1H), 4.78 (dd, $J = 6.4, 1.3$ Hz, 2H), 3.86 (s, 3H), 2.13 (s, 3H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.6, 159.9, 148.0, 127.7, 127.2, 122.5, 115.7, 115.2, 114.3, 61.6, 55.3, 20.8. **IR** (vmax, cm^{-1}): 3126, 2926, 2854, 1752, 1705, 1455, 1263, 1086, 1029, 780. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_3\text{Na}$) requires m/z 296.1011, found: m/z 296.1015.

methyl (E)-4-(1-(3-acetoxyprop-1-en-1-yl)-1H-1,2,3-triazol-4-yl)benzoate (8b)



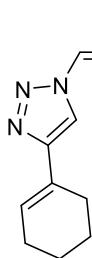
White solid. **Yield:** 77 mg, 48% (α -isomer 14%, β -isomer 34%, $\alpha:\beta$ ratio 29:71). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.14-8.10 (m, 2H), 8.07 (s, 1H), 7.97-7.91 (m, 2H), 7.44 (dt, $J = 14.4, 1.4$ Hz, 1H), 6.43 (dt, $J = 14.4, 6.3$ Hz, 1H), 4.80 (dd, $J = 6.3, 1.4$ Hz, 2H), 3.94 (s, 3H), 2.14 (s, 3H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.5, 166.7, 147.1, 134.1, 130.3, 127.3, 125.6, 117.6, 116.2, 108.3, 61.4, 52.2, 20.8. **IR** (vmax, cm^{-1}): 3126, 2950, 2845, 1736, 1712, 1496, 1263, 1093, 1022. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_4\text{Na}$) requires m/z 324.0960, found: m/z 324.0955.

(E)-3-(4-butyl-1H-1,2,3-triazol-1-yl)allyl acetate (9b)



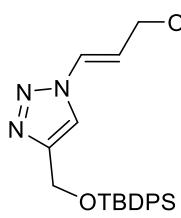
Colorless oil. **Yield:** 62 mg, 56% (α -isomer 14%, β -isomer 42%, $\alpha:\beta$ ratio 25:75). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.51 (s, 1H), 7.36 (dt, $J = 14.4, 1.4$ Hz, 1H), 6.27 (dt, $J = 14.4, 6.5$ Hz, 1H), 4.75 (dd, $J = 6.5, 1.4$ Hz, 2H), 2.74 (t, $J = 7.5$ Hz, 2H), 2.12 (s, 3H), 1.67 (qui, $J = 7.5$ Hz, 2H), 1.39 (sex, $J = 7.5$ Hz, 2H), 0.94 (t, $J = 7.5$ Hz, 3H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.6, 148.9, 127.8, 117.9, 114.6, 61.6, 31.3, 25.1, 22.2, 20.8, 13.7. **IR** (vmax, cm^{-1}): 3143, 3087, 2950, 2918, 1745, 1455, 1215, 1029, 941.

(E)-3-(4-(cyclohex-1-en-1-yl)-1H-1,2,3-triazol-1-yl)allyl acetate (12b)



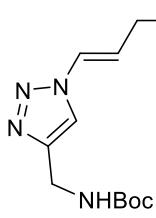
White solid. **Yield:** 76 mg, 62% (α -isomer 18%, β -isomer 44%, $\alpha:\beta$ ratio 29:71). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.37 (d, $J = 14.4$ Hz, 1H), 6.64-6.58 (m, 1H), 6.26 (dt, $J = 14.4, 6.5$ Hz, 1H), 4.75 (dd, $J = 6.5, 1.1$ Hz, 2H), 2.41-2.34 (m, 2H), 2.26-2.18 (m, 2H), 2.12 (s, 3H), 1.82-1.74 (m, 2H), 1.73-1.64 (m, 2H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.6, 149.8, 127.8, 126.6, 126.3, 115.2, 114.6, 61.7, 26.3, 25.3, 22.4, 22.1, 20.8. **IR** (ν_{max} , cm^{-1}): 3143, 2918, 1745, 1455, 1263, 1077, 1022, 805. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_2\text{Na}$) requires m/z 270.1218, found: m/z 270.1225.

(E)-3-((tert-butyldiphenylsilyl)oxy) methyl-1H-1,2,3-triazol-1-ylallyl acetate (16b)



White solid. **Yield:** 77 mg, 36% (α -isomer 9%, β -isomer 27%, $\alpha:\beta$ ratio 25:75). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.68 (d, $J = 7.0$ Hz, 4H), 7.57 (s, 1H), 7.48-7.33 (m, 7H), 6.29 (dt, $J = 14.4, 6.4$ Hz, 1H), 4.89 (s, 2H), 4.76 (dd, $J = 6.4, 0.9$ Hz, 2H), 2.13 (s, 3H), 1.08 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.6, 148.8, 135.5, 133.0, 129.9, 127.8, 127.6, 119.0, 115.3, 119.0, 115.3, 61.6, 58.5, 26.8, 20.8, 19.2. **IR** (ν_{max} , cm^{-1}): 3071, 2918, 2854, 1745, 1423, 1222, 1110, 1029, 692. **HRMS** (ESI+): exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{24}\text{H}_{29}\text{N}_3\text{O}_3\text{SiNa}$) requires m/z 458.1276, found: m/z 458.1282.

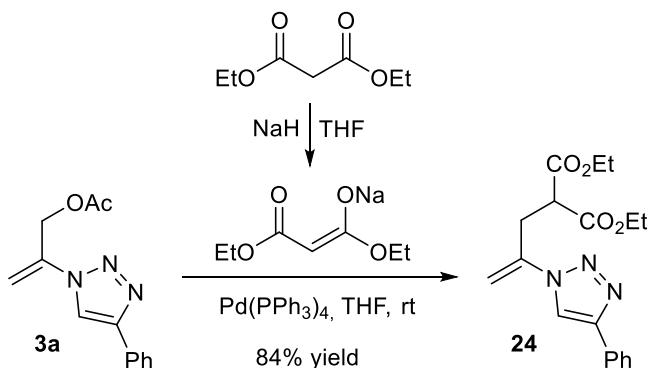
(E)-3-((tert-butoxycarbonyl)amino)methyl-1H-1,2,3-triazol-1-ylallyl acetate (19b)



White solid. **Yield:** 82 mg, 55% (α -isomer 17%, β -isomer 38%, $\alpha:\beta$ ratio 31:69). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.78 (s, 1H), 7.35 (dt, $J = 14.4, 1.3$ Hz, 1H), 6.33 (dt, $J = 14.4, 6.4$ Hz, 1H), 5.29 (bs, 1H), 4.76 (dd, $J = 6.4, 1.3$ Hz, 2H), 4.41 (d, $J = 6.1$ Hz, 2H), 2.12 (s, 3H), 1.44 (s, 9H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 170.5, 155.8, 146.0, 127.4, 119.5, 115.8, 79.9, 61.5, 35.9, 28.3, 20.8. **IR** (ν_{max} , cm^{-1}): 3352, 3143, 3087, 2974, 1736, 1705, 1455, 1022, 941.

4. Allylic Substitution Reaction

- Synthesis of compound 24



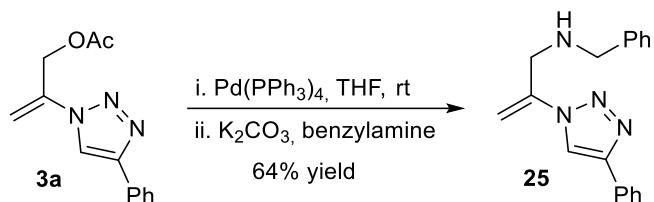
An oven-dried reaction flask equipped with a stir bar was charged with $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 10 mol%) acetate **3a** (46 mg, 0.19 mmol) and dry tetrahydrofuran (1 mL) under an argon atmosphere. The mixture was stirred for 10 minutes at room temperature and a solution of sodium dimethylmalonate (prepared by reaction between diethyl malonate (0.4 mmol) and sodium hydride (60% in mineral oil, 12 mg, 0.3 mmol) in dry tetrahydrofuran (1 mL) under an argon atmosphere) was added. The reaction mixture was then stirred for 20h at room temperature. After this time, saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ was added and the aqueous solution was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried with MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by flash chromatography eluting with hexane/ethyl acetate.

diethyl 2-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)allyl)malonate (24)

diethyl 2-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)allyl)malonate (24)

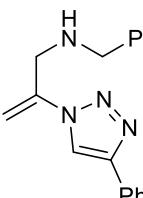
White solid. **Yield:** 55 mg, 84%. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.02 (s, 1H), 7.86 (d, $J = 7.1$ Hz, 2H), 7.48-7.41 (m, 2H), 7.39-7.33 (m, 1H), 5.48 (d, $J = 1.7$ Hz, 1H), 5.11 (s, 1H), 4.20 (q, $J = 7.1$ Hz, 4H), 3.82 (t, $J = 7.7$ Hz, 1H), 3.43 (d, $J = 7.7$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 6H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 168.2, 147.8, 140.0, 130.0, 128.9, 128.5, 125.8, 117.2, 106.2, 61.7, 50.0, 32.1, 14.0. **IR (vmax, cm⁻¹)**: 2958, 1736, 1664, 1423, 1367, 1238, 1150, 1022.

- Synthesis of compound 25

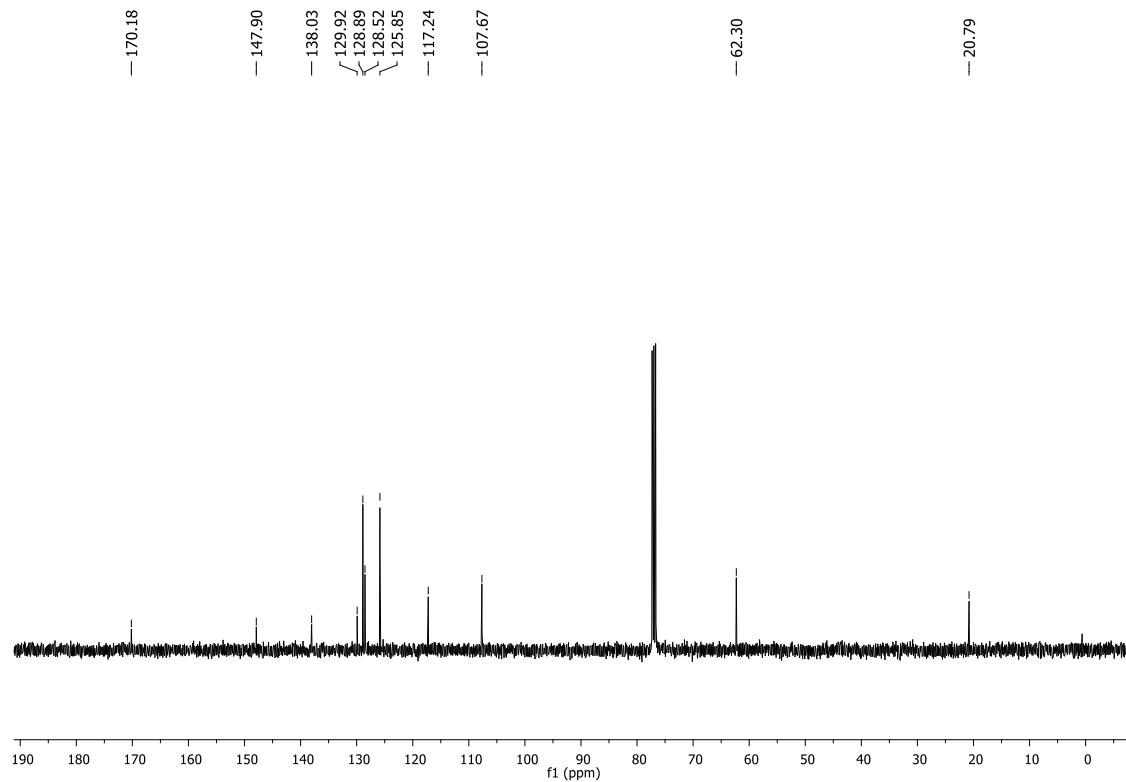
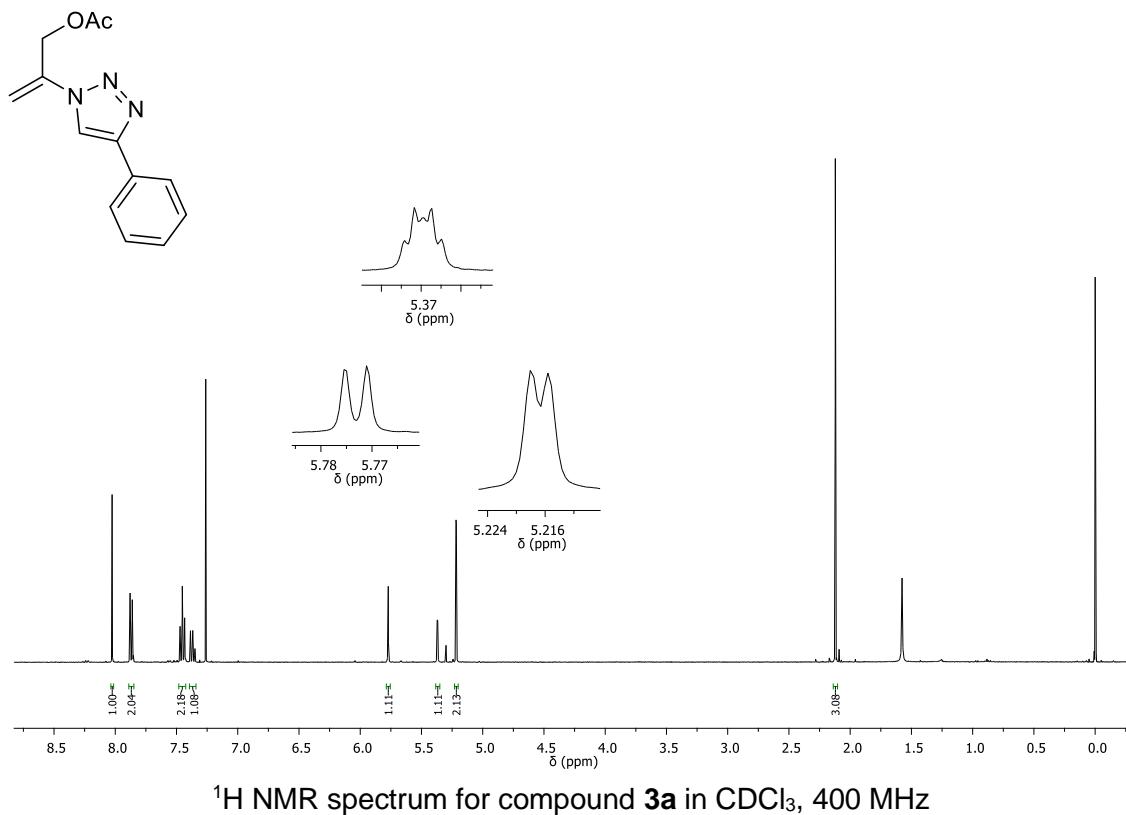


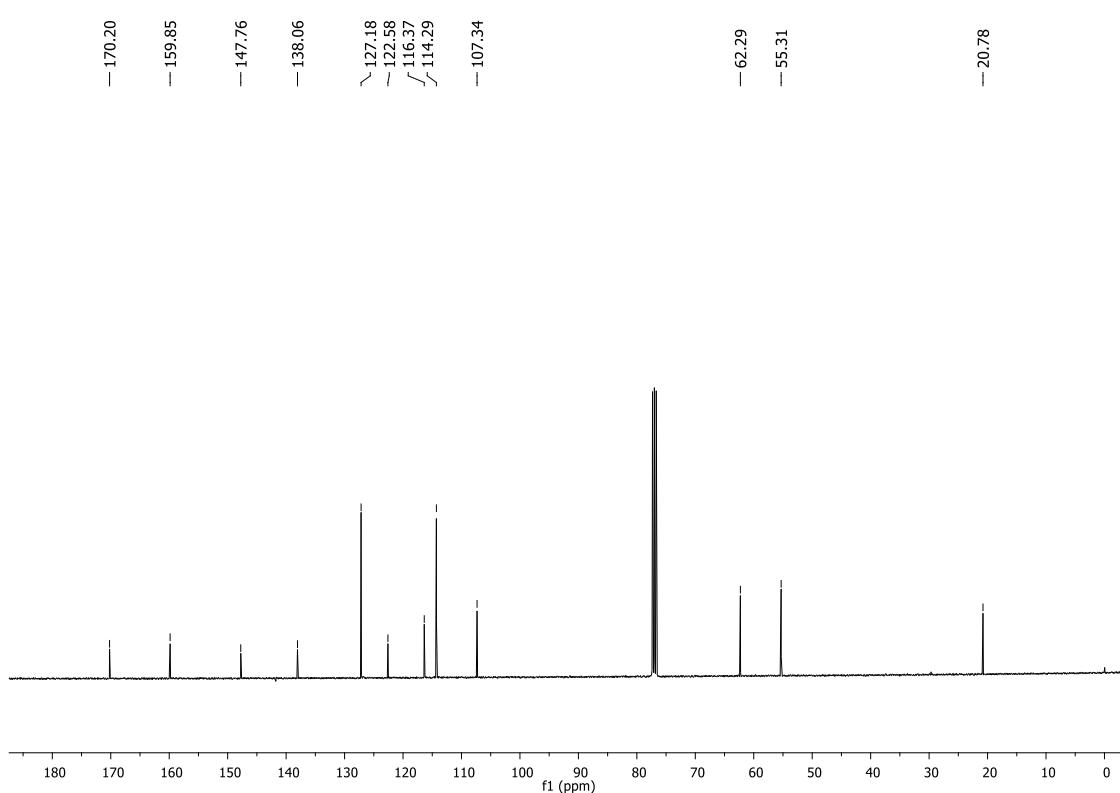
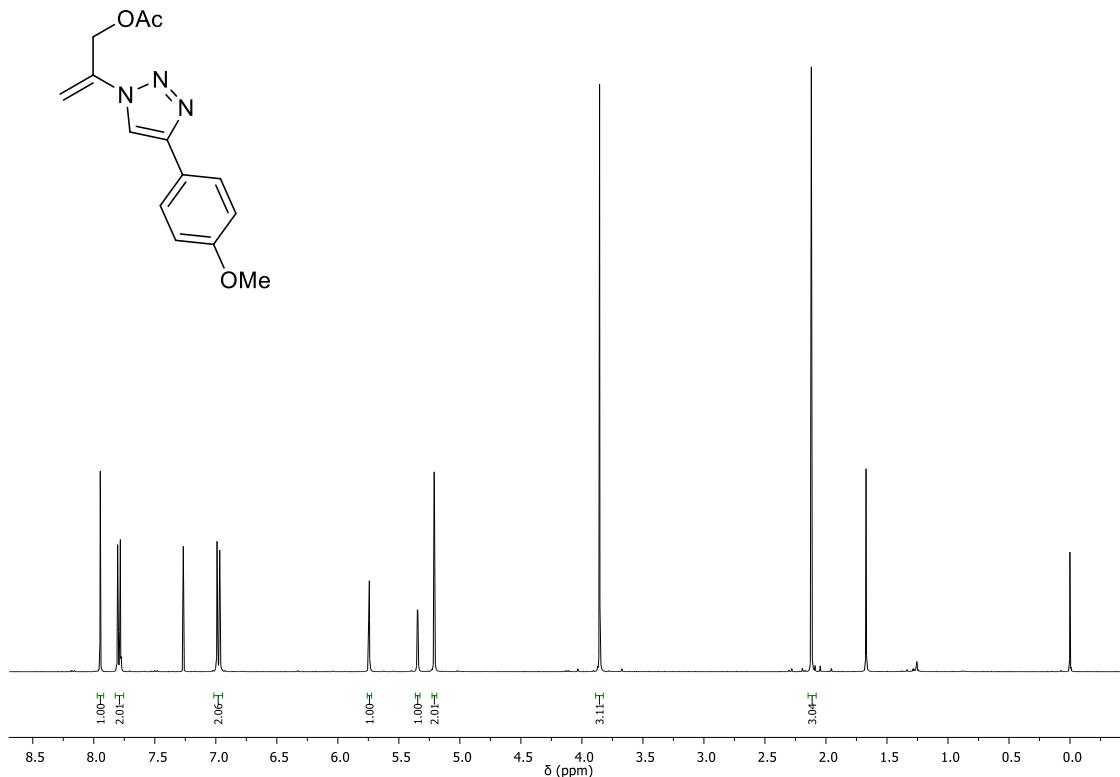
An oven-dried reaction flask equipped with a stir bar was charged with $\text{Pd}(\text{PPh}_3)_4$ (23 mg, 10 mol%) acetate **3a** (46 mg, 0.19 mmol) and dry tetrahydrofuran (1 mL) under an argon atmosphere. The mixture was stirred for 10 minutes at room temperature and potassium carbonate (26 mg, 0.19 mmol) and benzylamine (23 μL , 0.21 mmol) were added. The reaction mixture was then stirred for 20h at room temperature. After this time, saturated $\text{NH}_4\text{Cl}_{(\text{aq})}$ was added and the aqueous solution was extracted with ethyl acetate (3×5 mL). The combined organic layers were dried with MgSO_4 , filtered and the solvent was evaporated. The crude product was purified by flash chromatography eluting with hexane/ethyl acetate.

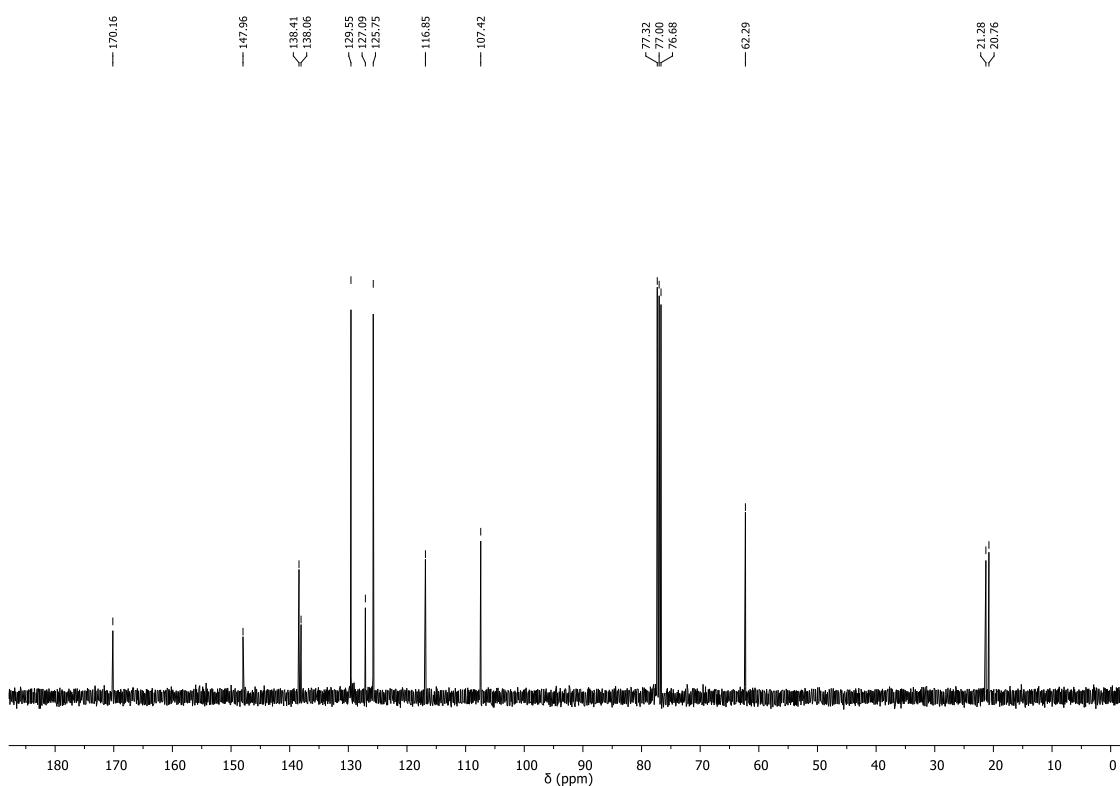
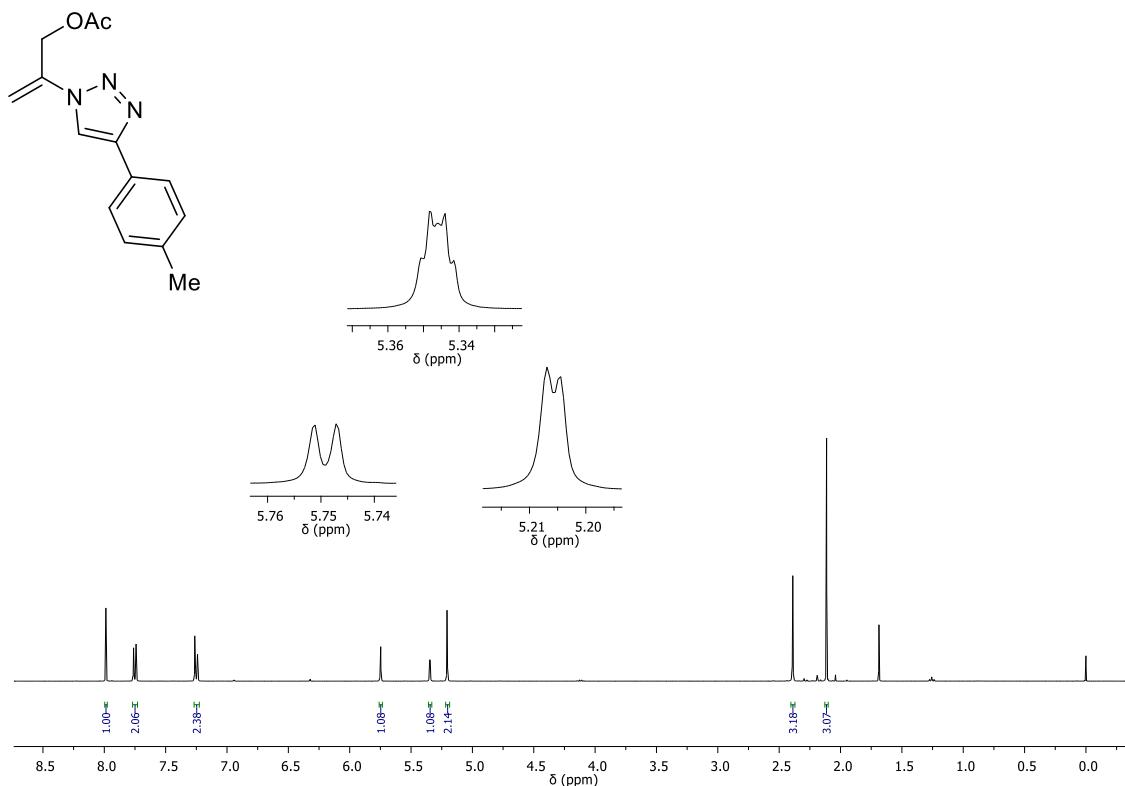
N-benzyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)prop-2-en-1-amine (25)

 White solid. **Yield:** 35 mg, 64%. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.11 (s, 1H), 7.88-7.83 (m, 2H), 7.47-7.41 (m, 2H), 7.38-7.31 (m, 5H), 7.29-7.23 (m, 1H), 5.64 (d, $J = 1.2$ Hz, 1H), 5.21-5.18 (m, 1H), 3.89 (d, $J = 0.5$ Hz, 2H), 3.85 (s, 2H), 2.20 (bs, 1H). **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 147.5, 141.0, 139.5, 130.1, 128.8, 128.5, 128.3, 128.2, 127.2, 125.8, 117.6, 105.8, 52.5, 50.3. **IR** (ν_{max} , cm^{-1}): 3349, 3131, 3060, 3027, 2925, 2843, 1652, 1453, 1234, 1016.

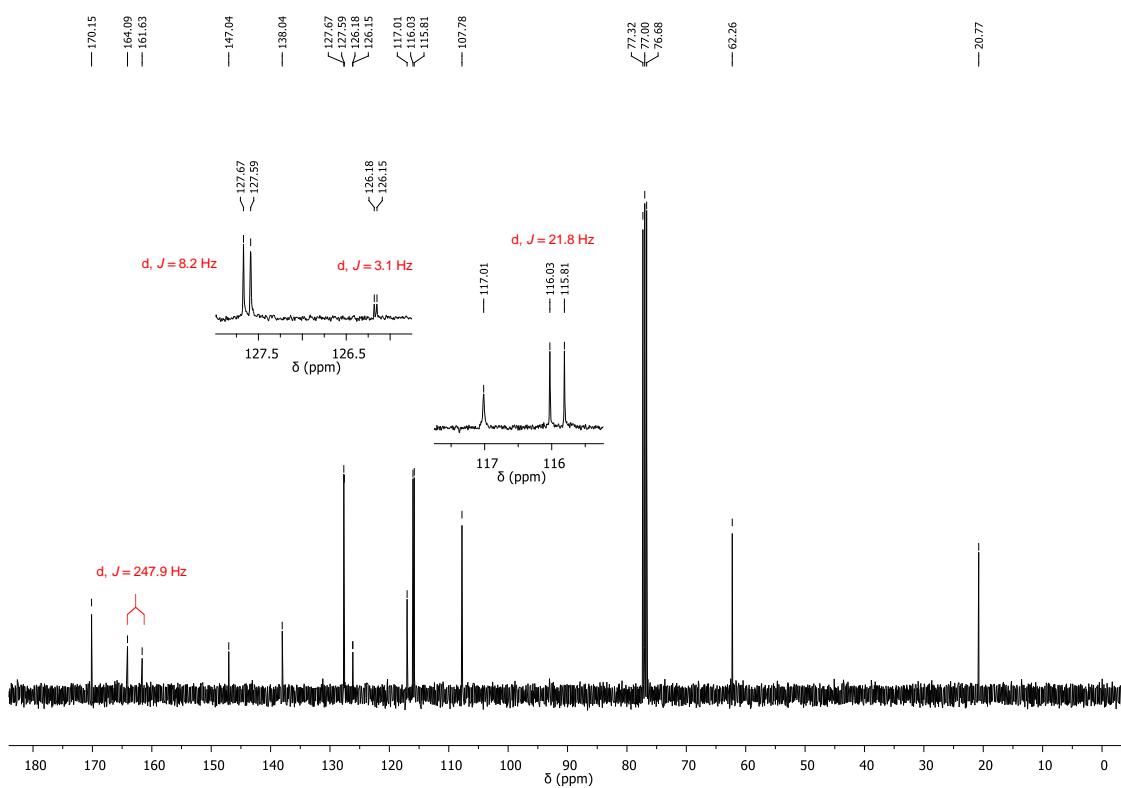
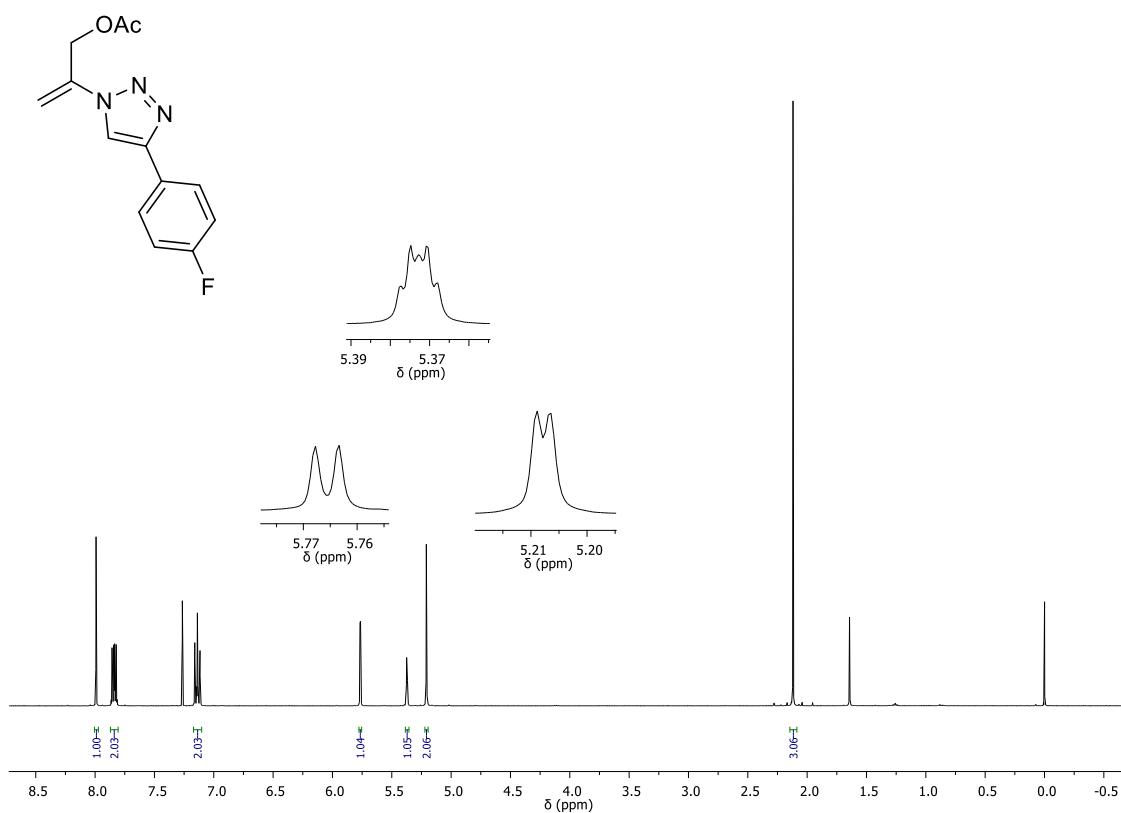
4. NMR SPECTRA

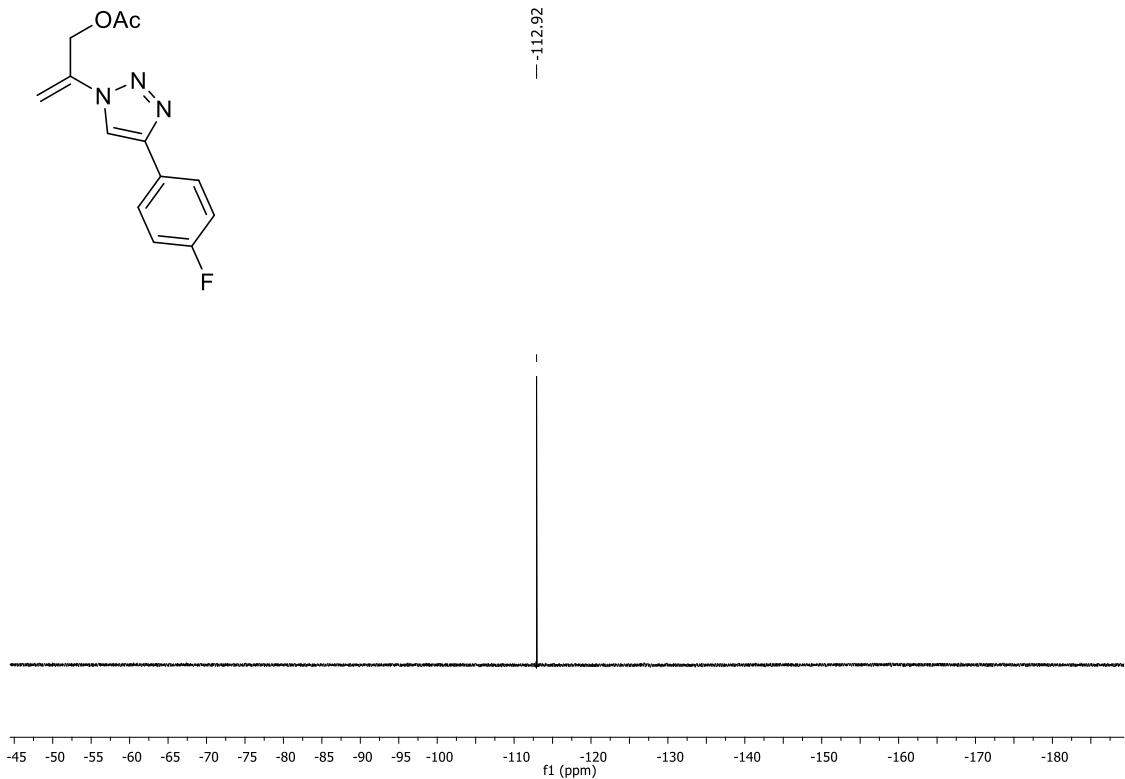
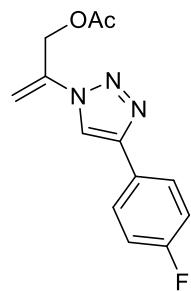




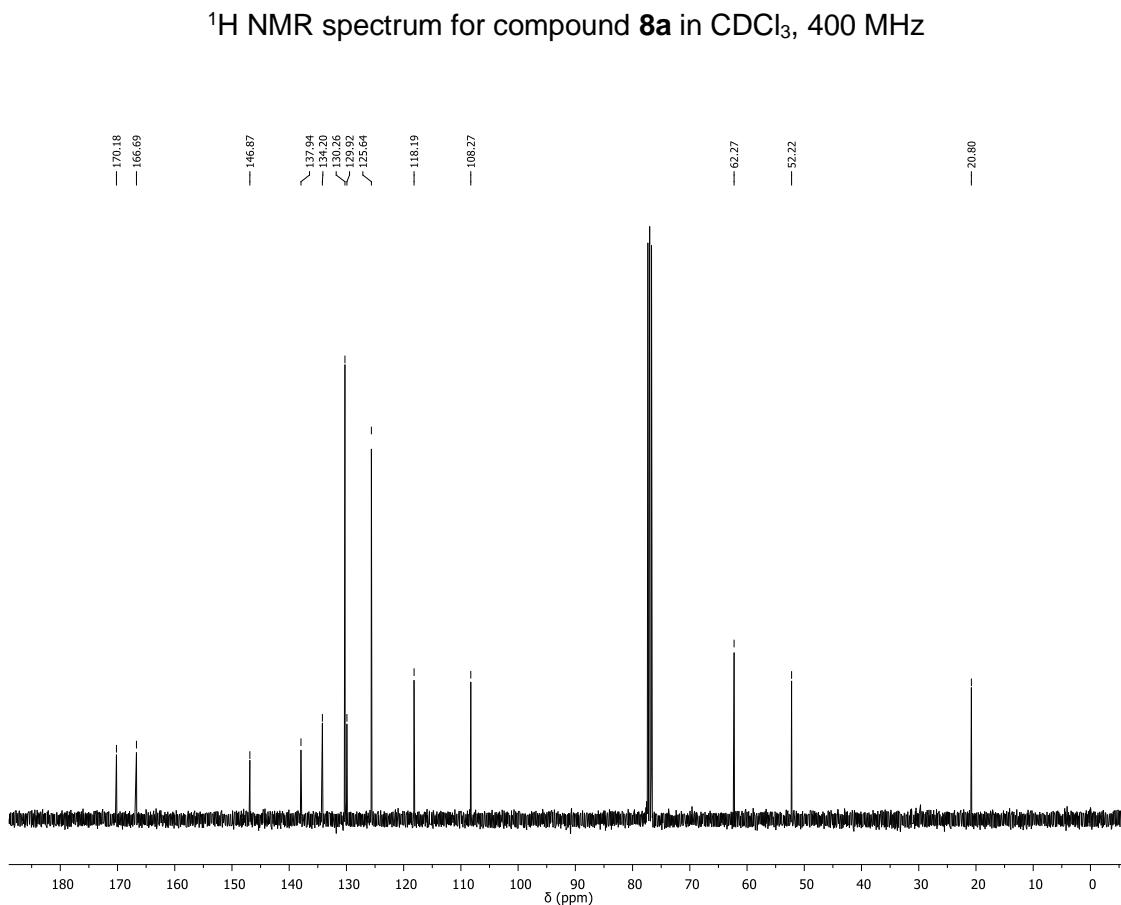
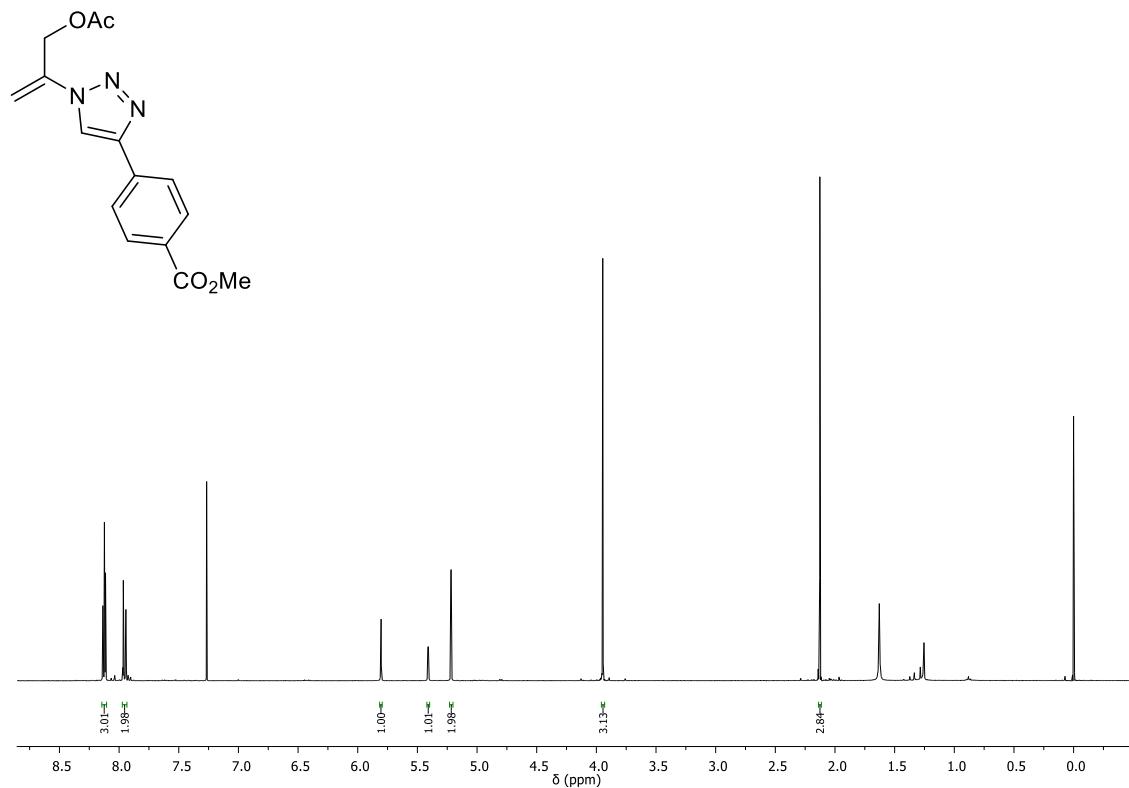


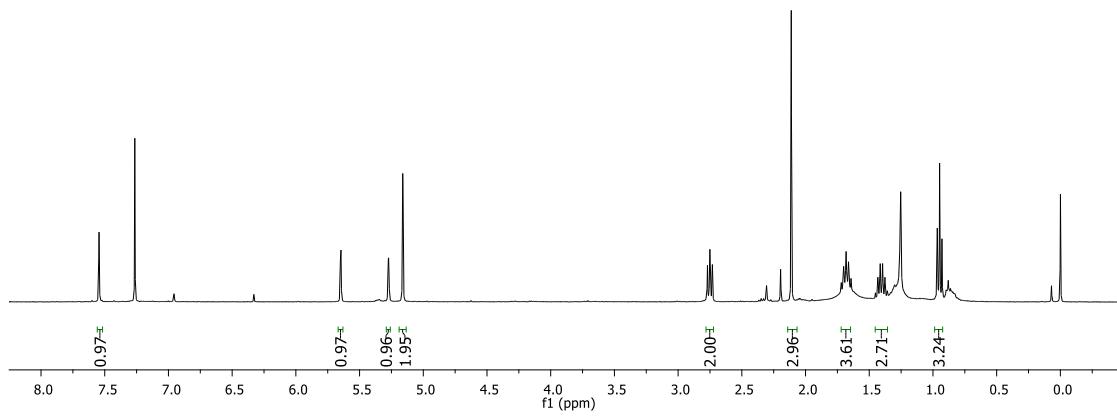
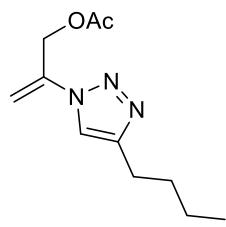
¹³C NMR spectrum for compound **5a** in CDCl_3 , 100 MHz



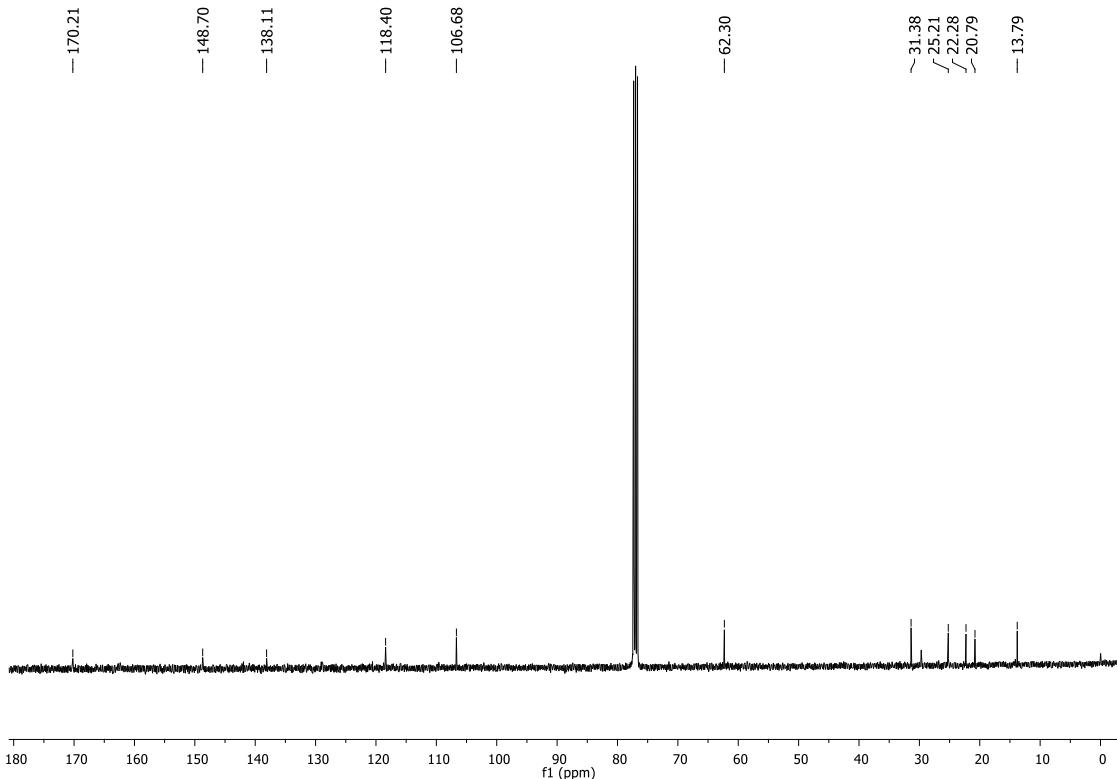


¹⁹F NMR spectrum for compound **7a** in CDCl₃, 376 MHz

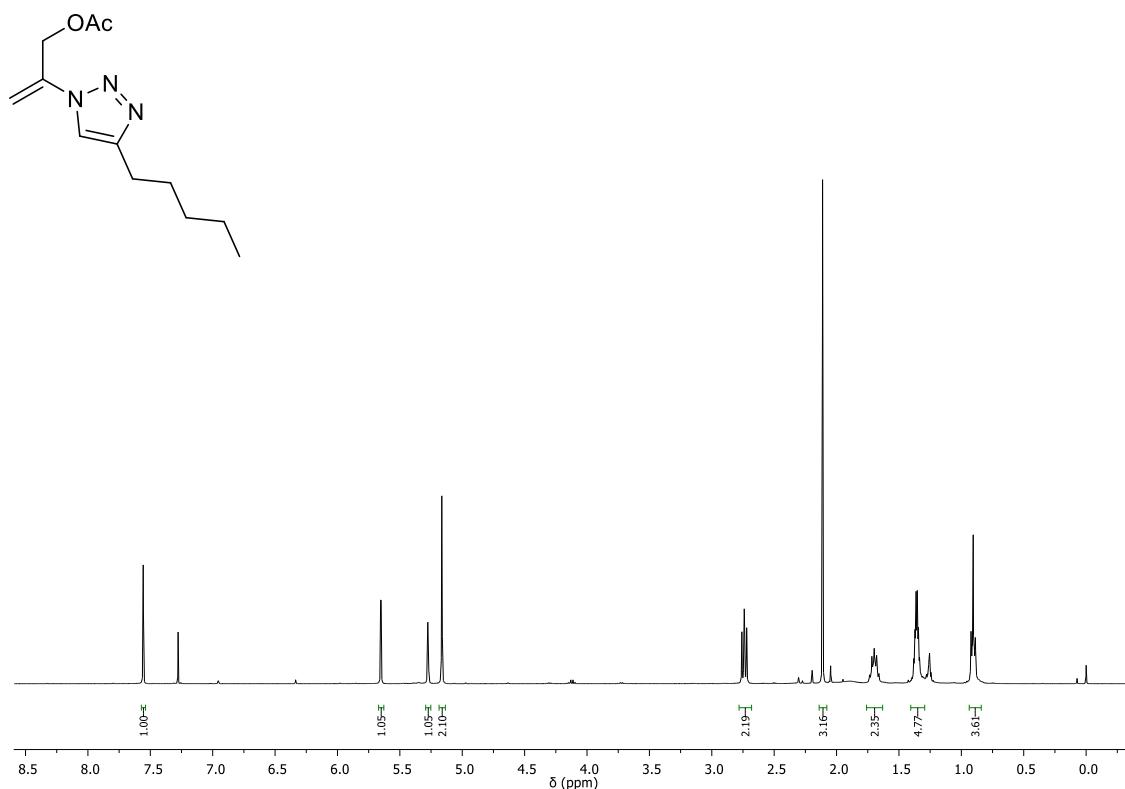




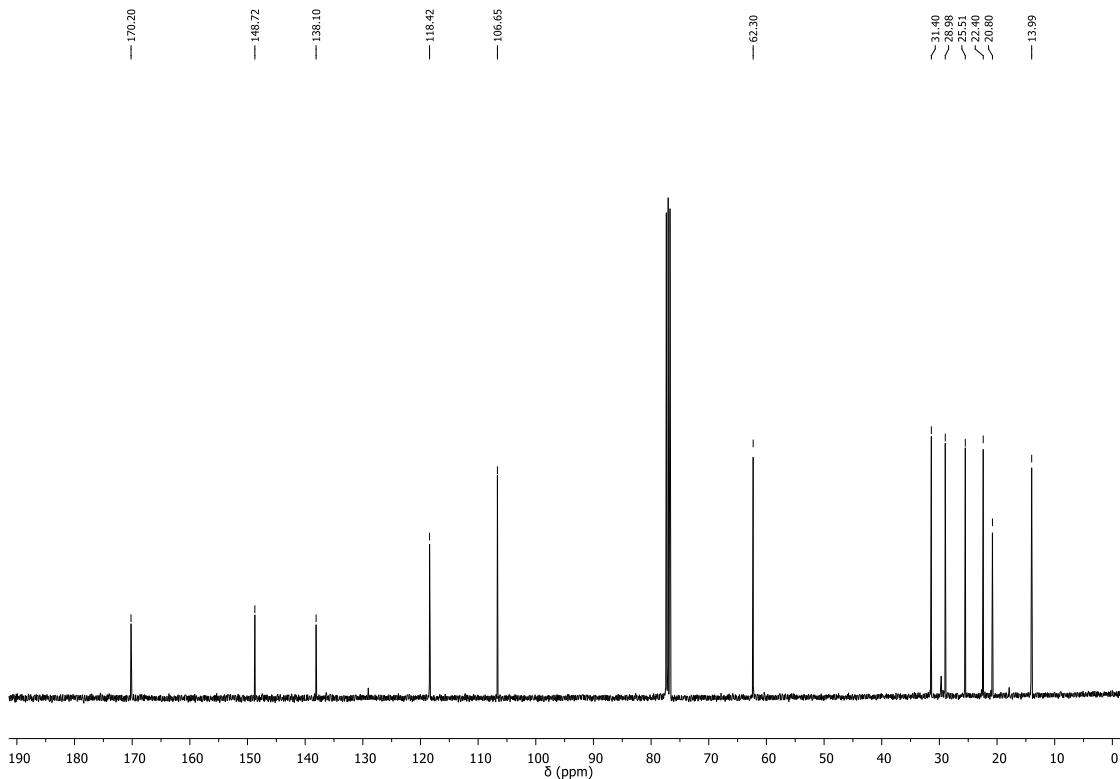
¹H NMR spectrum for compound **9a** in CDCl₃, 400 MHz



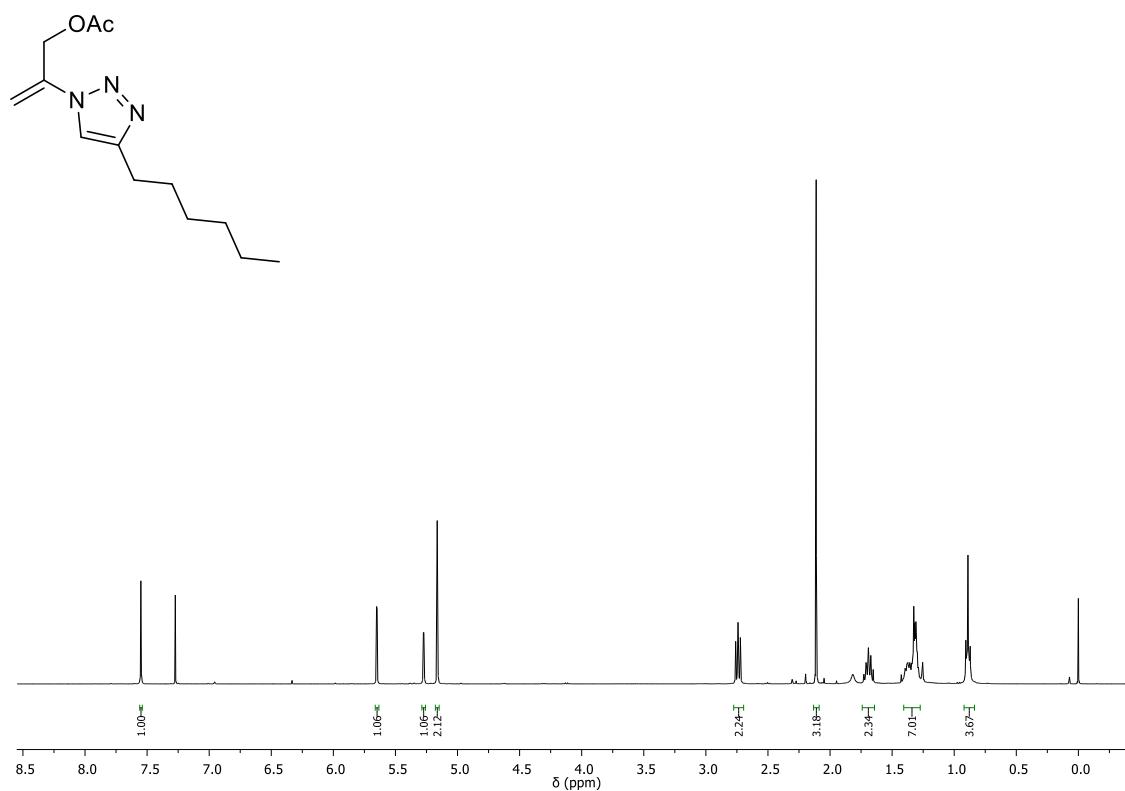
¹³C NMR spectrum for compound **9a** in CDCl₃, 100 MHz



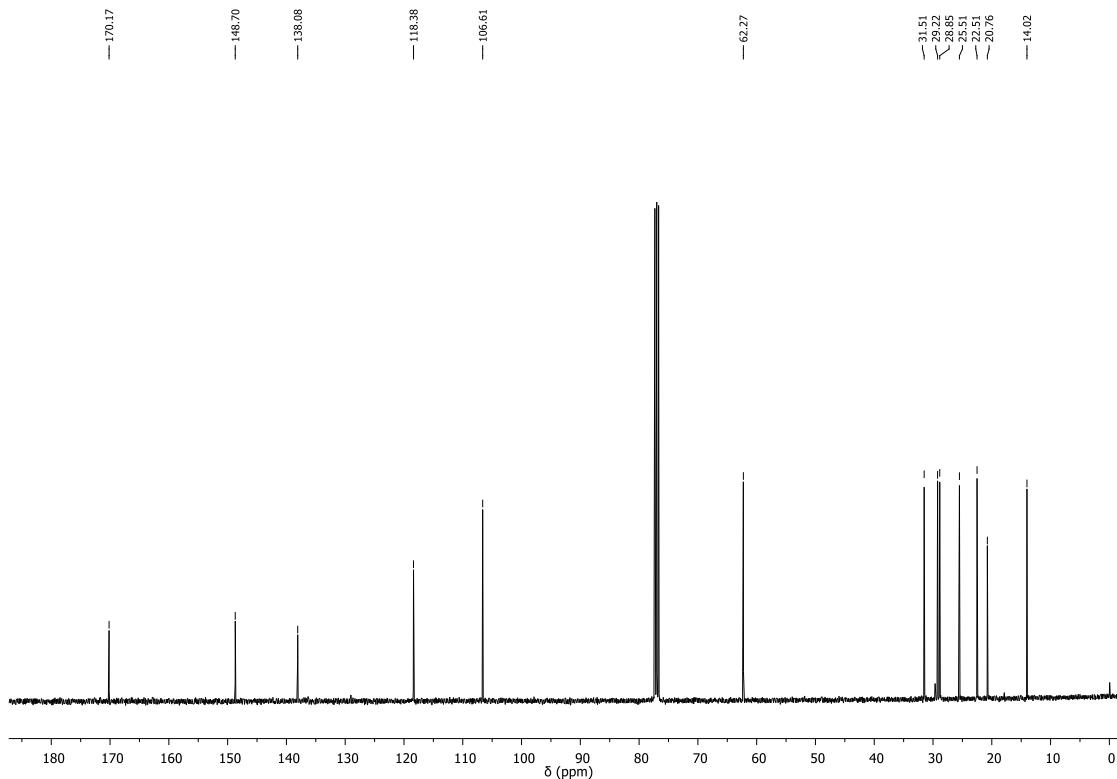
¹H NMR spectrum for compound **10a** in CDCl₃, 400 MHz



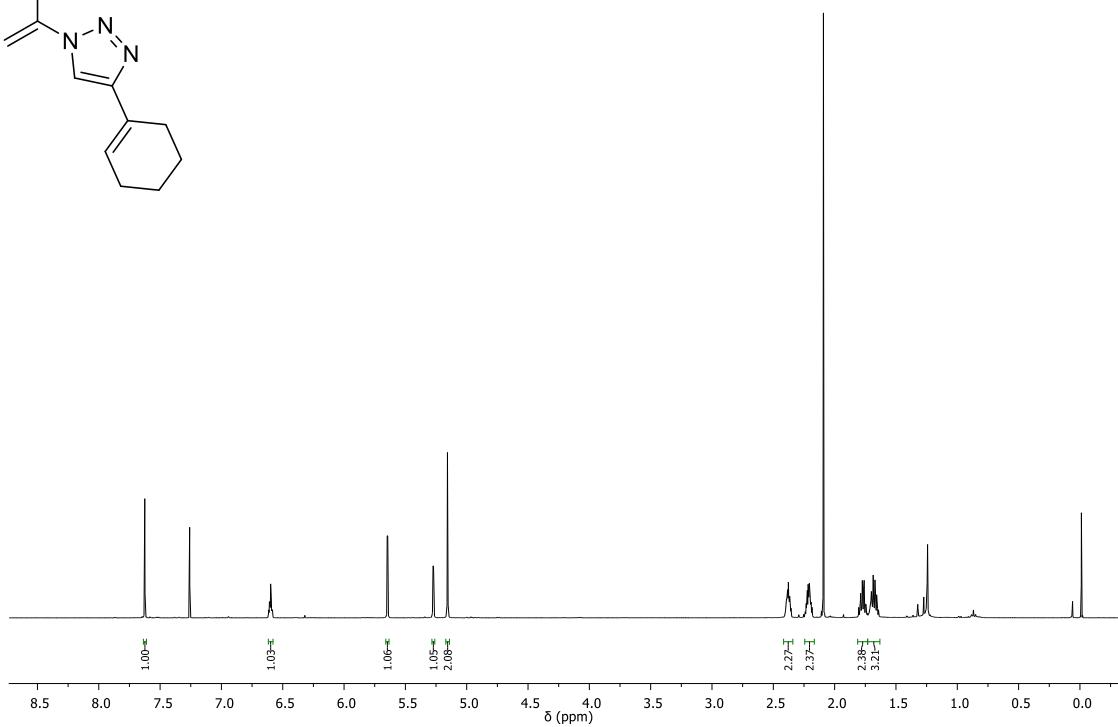
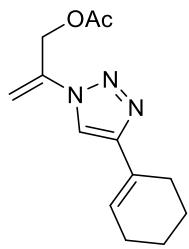
¹³C NMR spectrum for compound **10a** in CDCl₃, 100 MHz



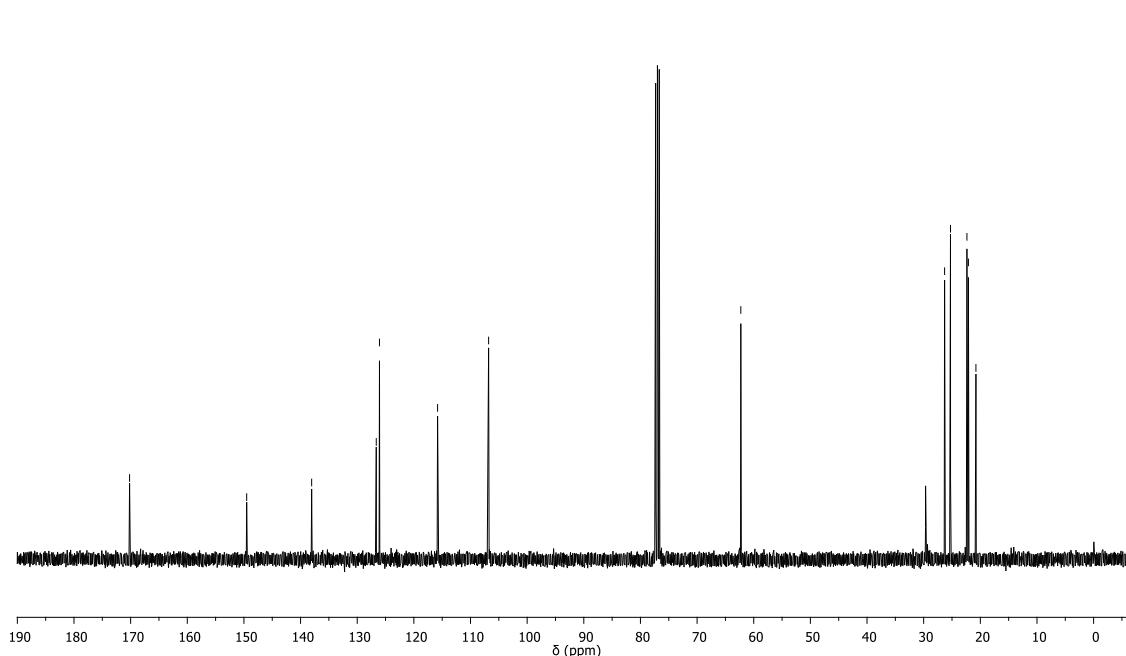
¹H NMR spectrum for compound **11a** in CDCl₃, 400 MHz



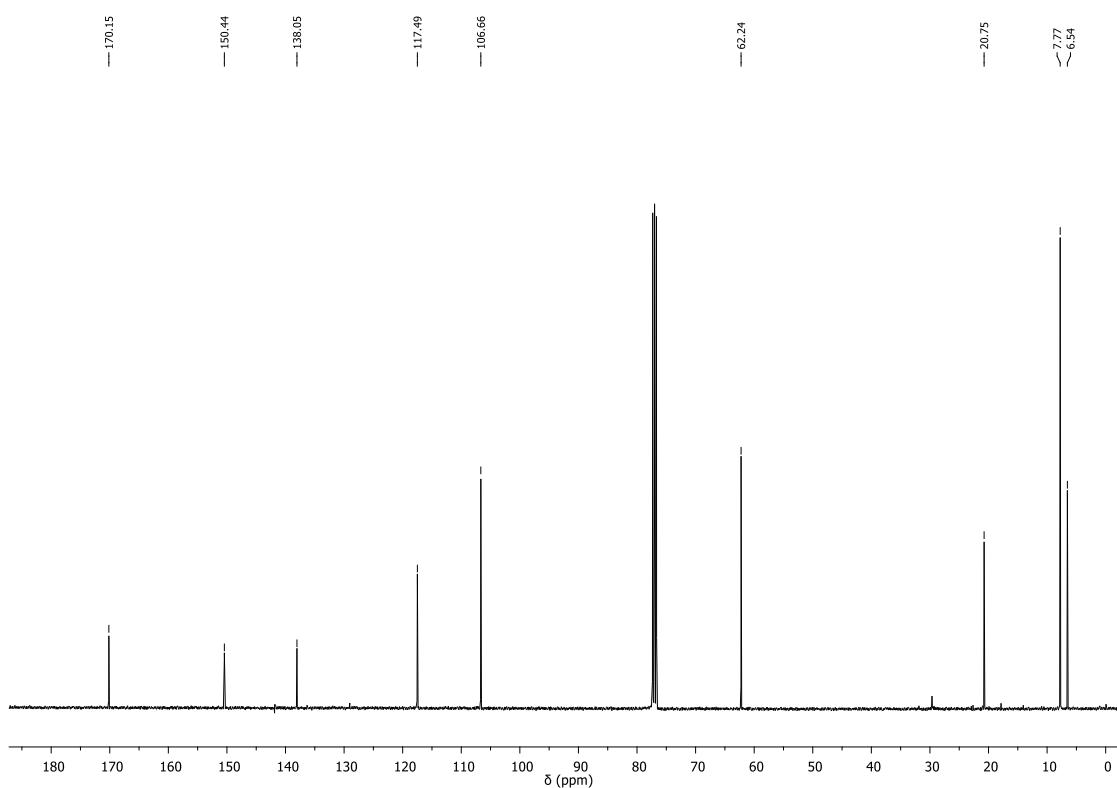
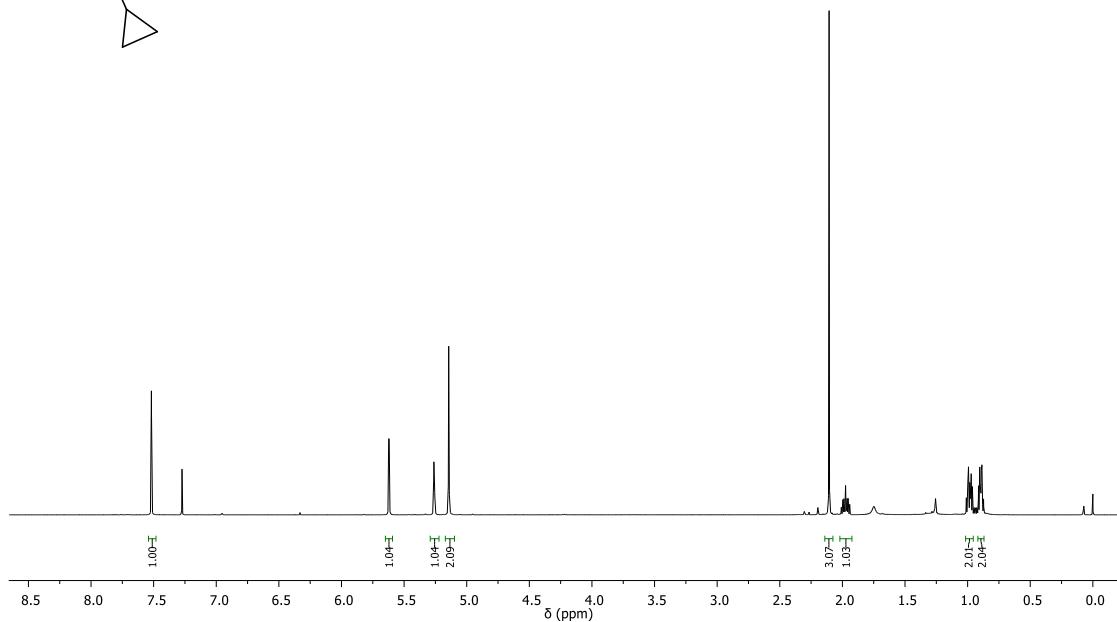
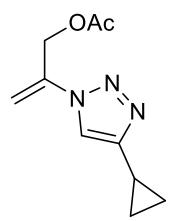
¹³C NMR spectrum for compound **11a** in CDCl₃, 100 MHz

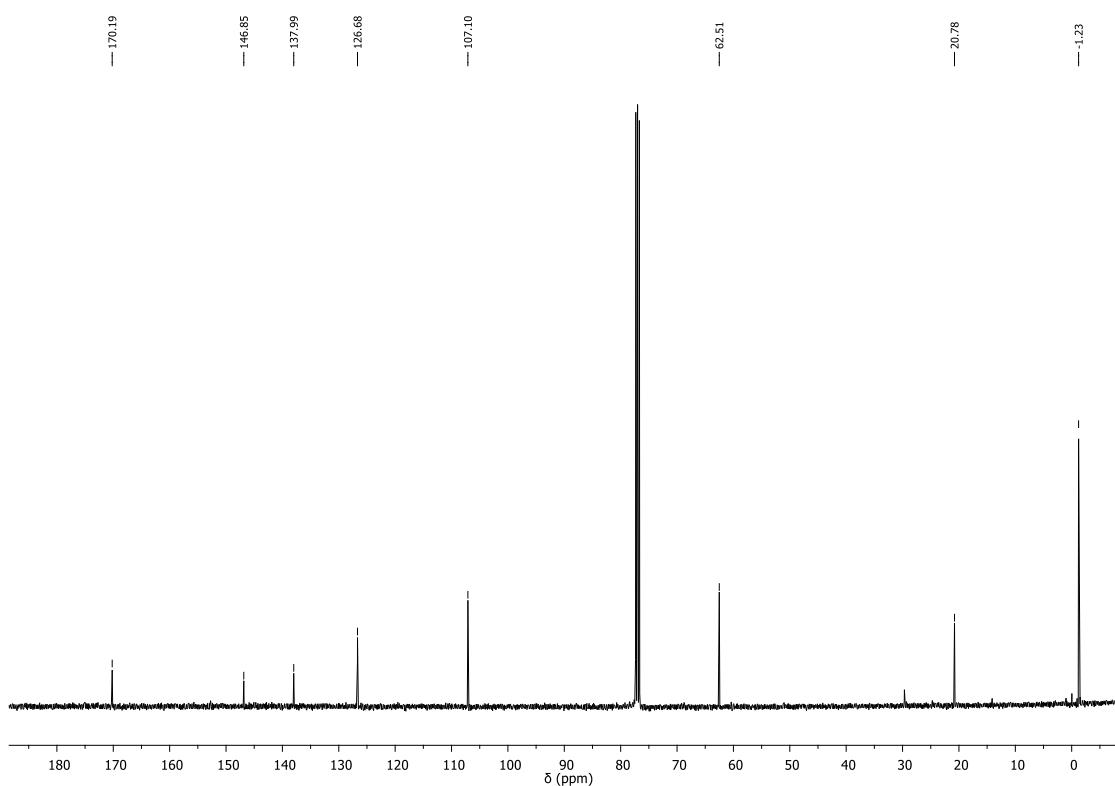
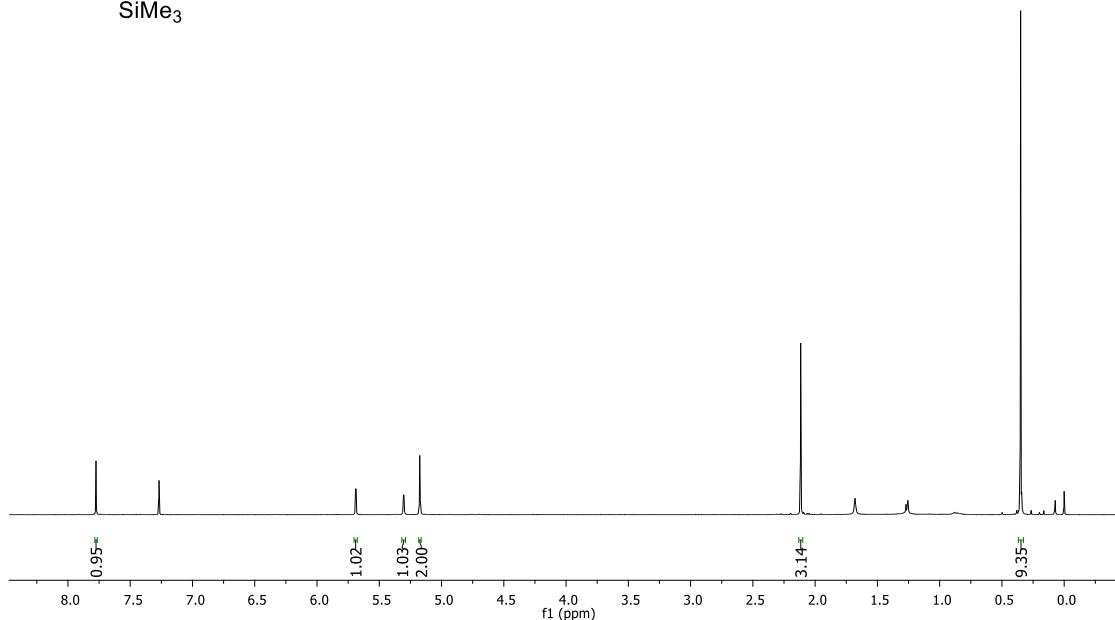
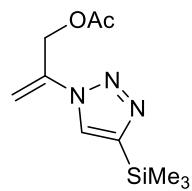


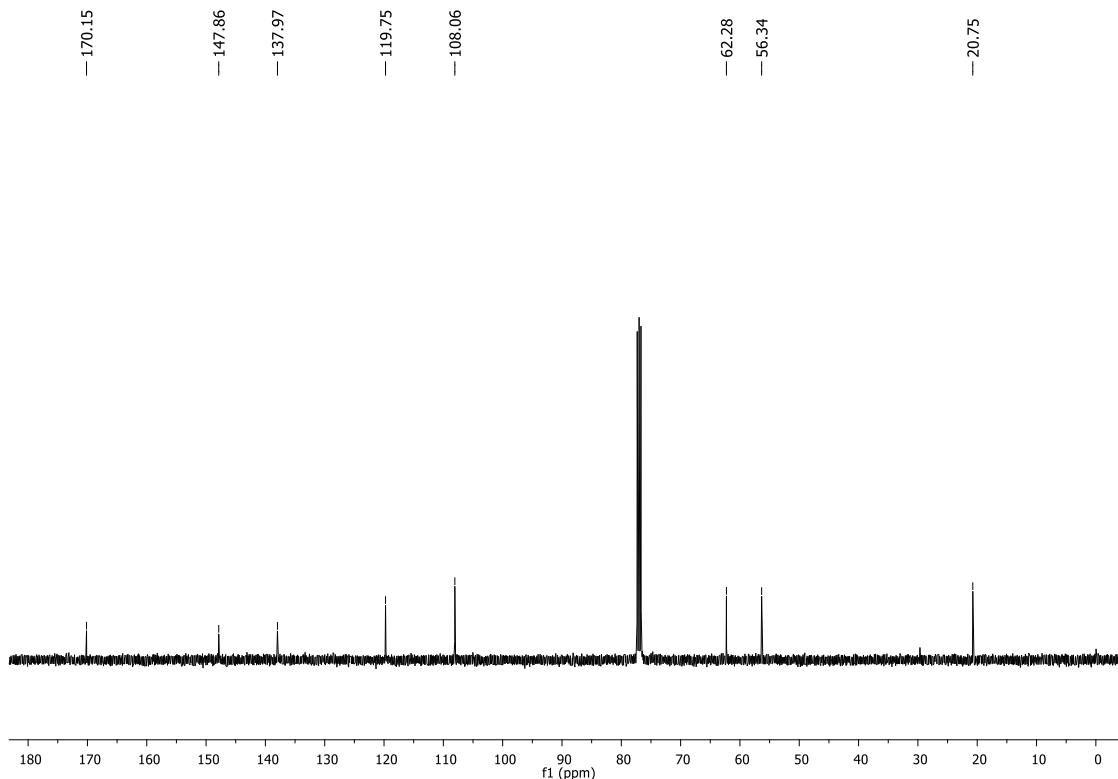
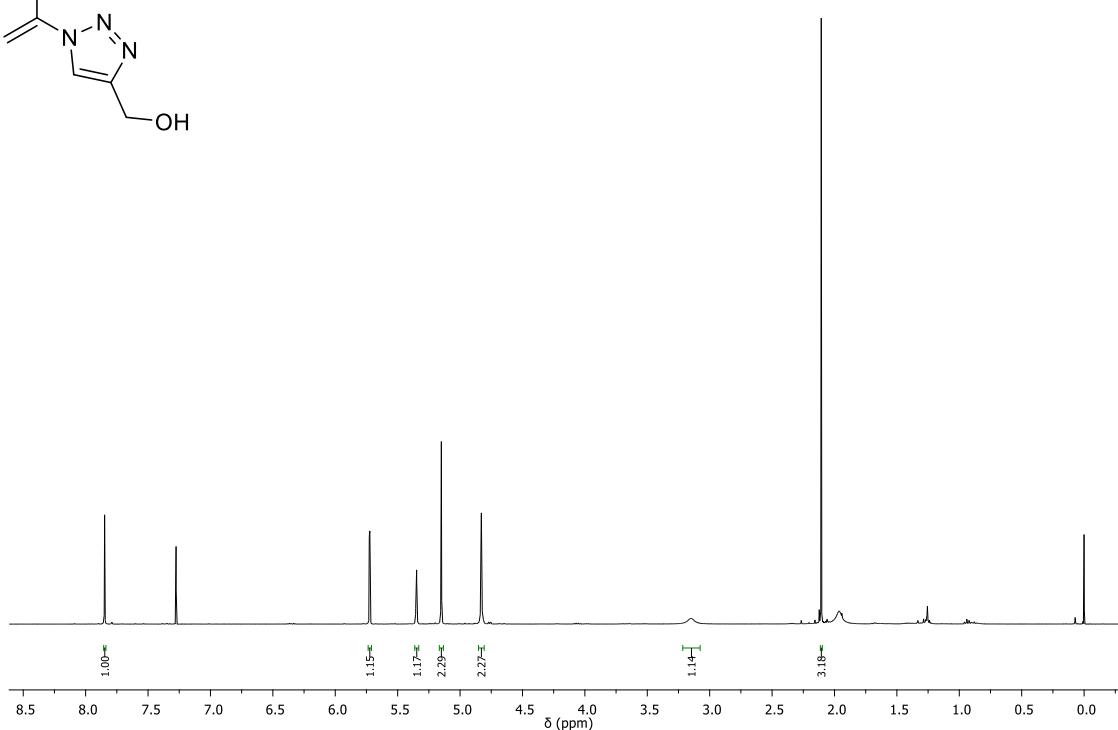
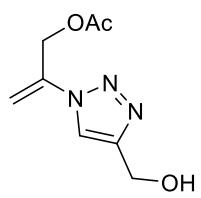
— 170.19
— 149.51
— 138.04
— 126.64
— 126.07
— 115.81
— 106.80
— 62.28
— 26.31
— 25.26
— 22.36
— 22.10
— 20.78

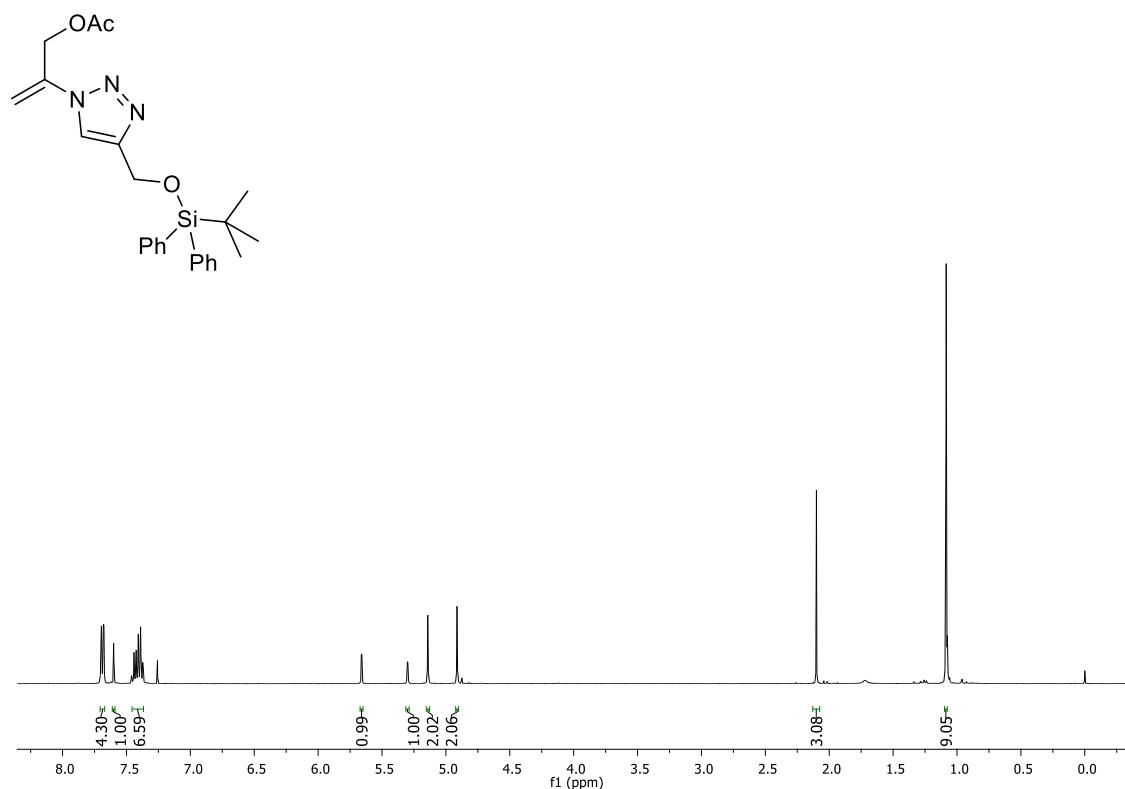


¹³C NMR spectrum for compound **12a** in CDCl_3 , 100 MHz

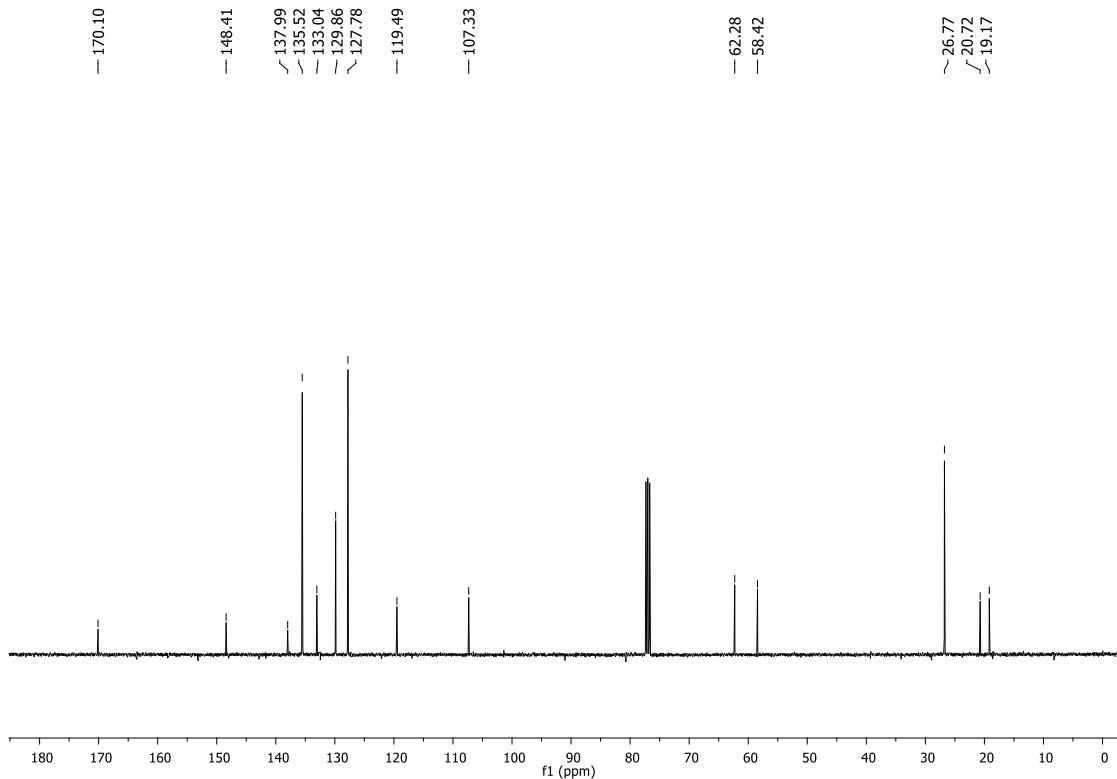




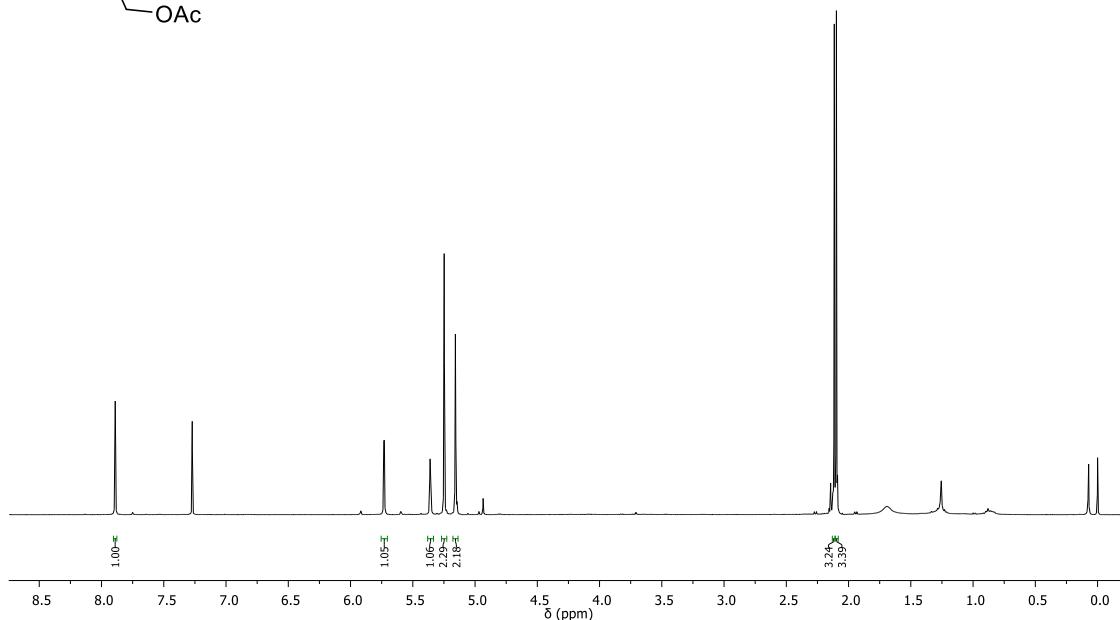
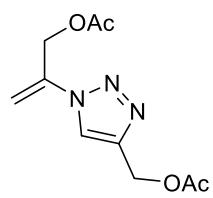




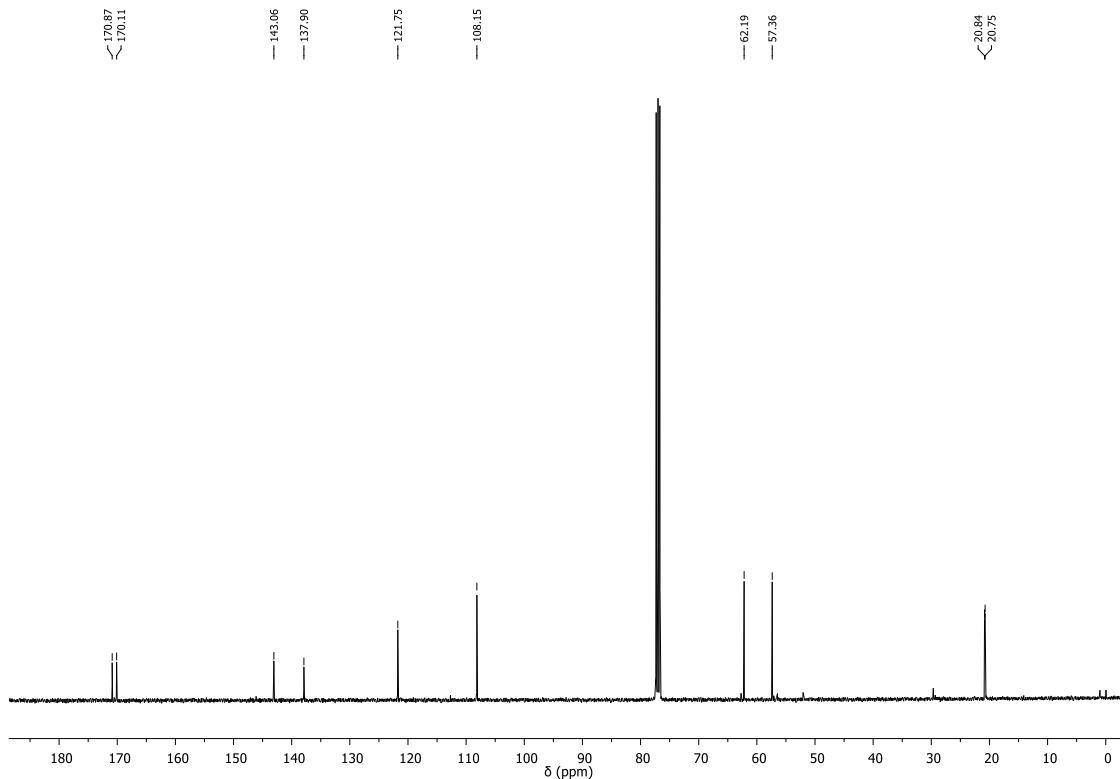
¹H NMR spectrum for compound **16a** in CDCl₃, 400 MHz



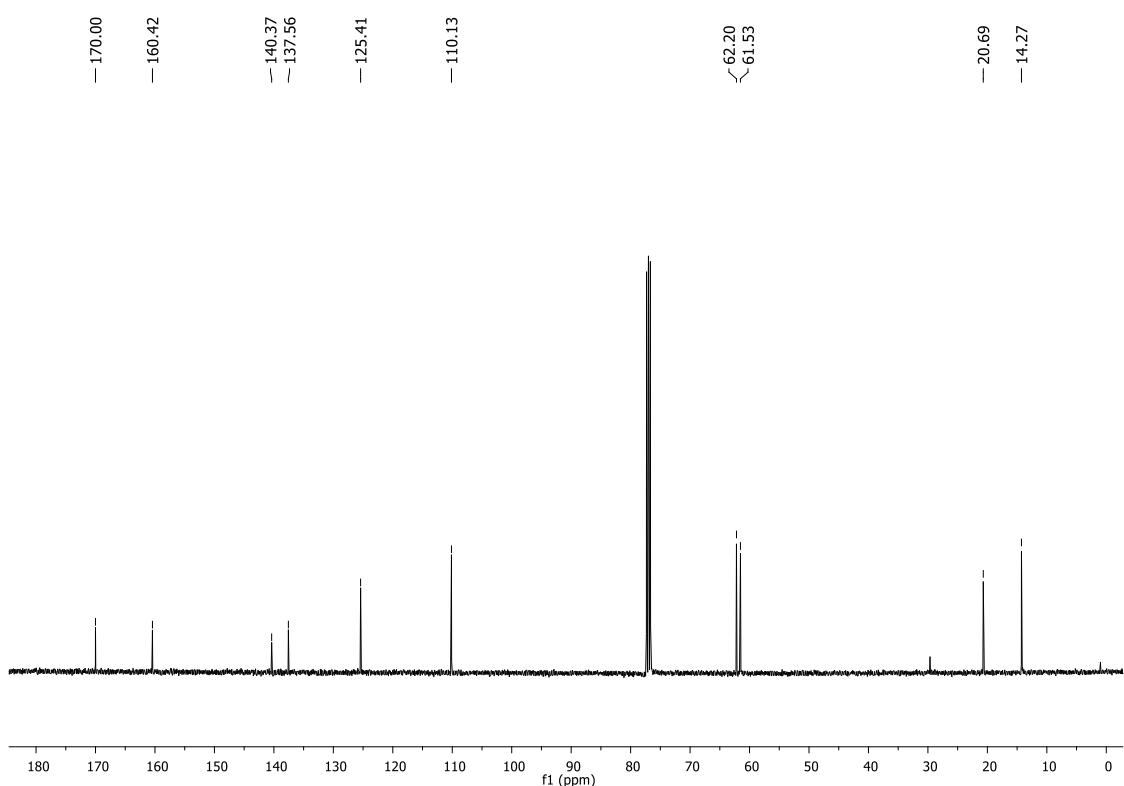
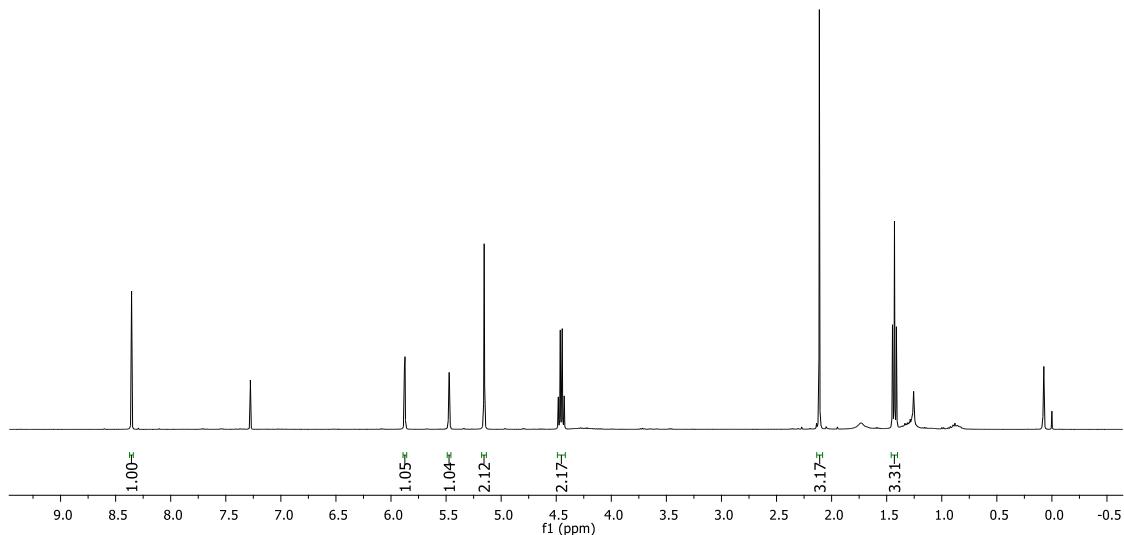
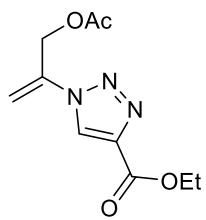
¹³C NMR spectrum for compound **16a** in CDCl₃, 100 MHz

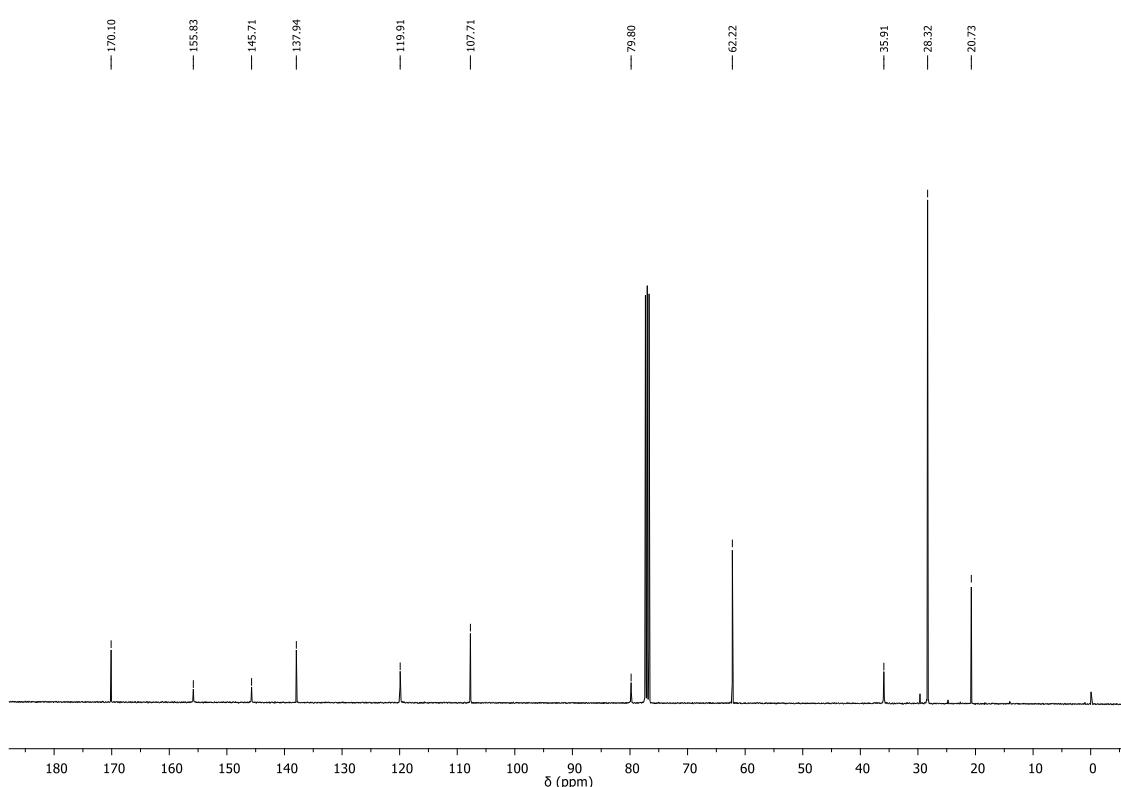
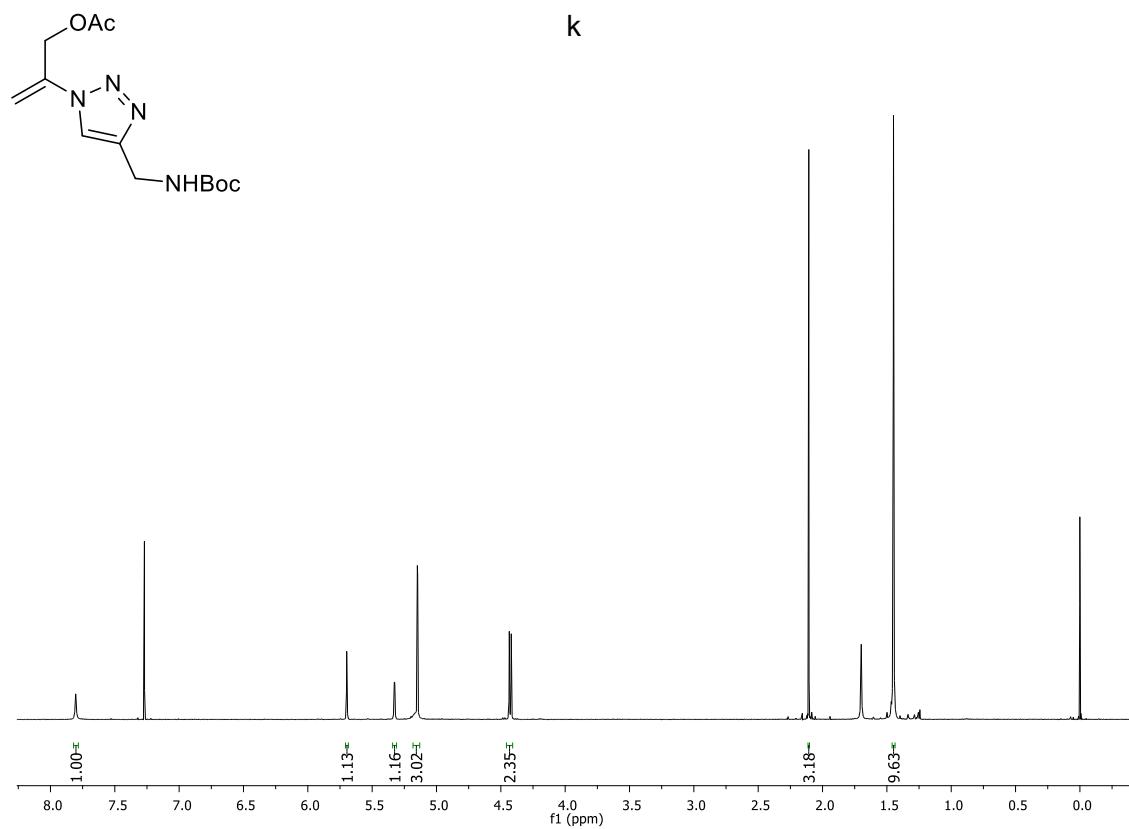


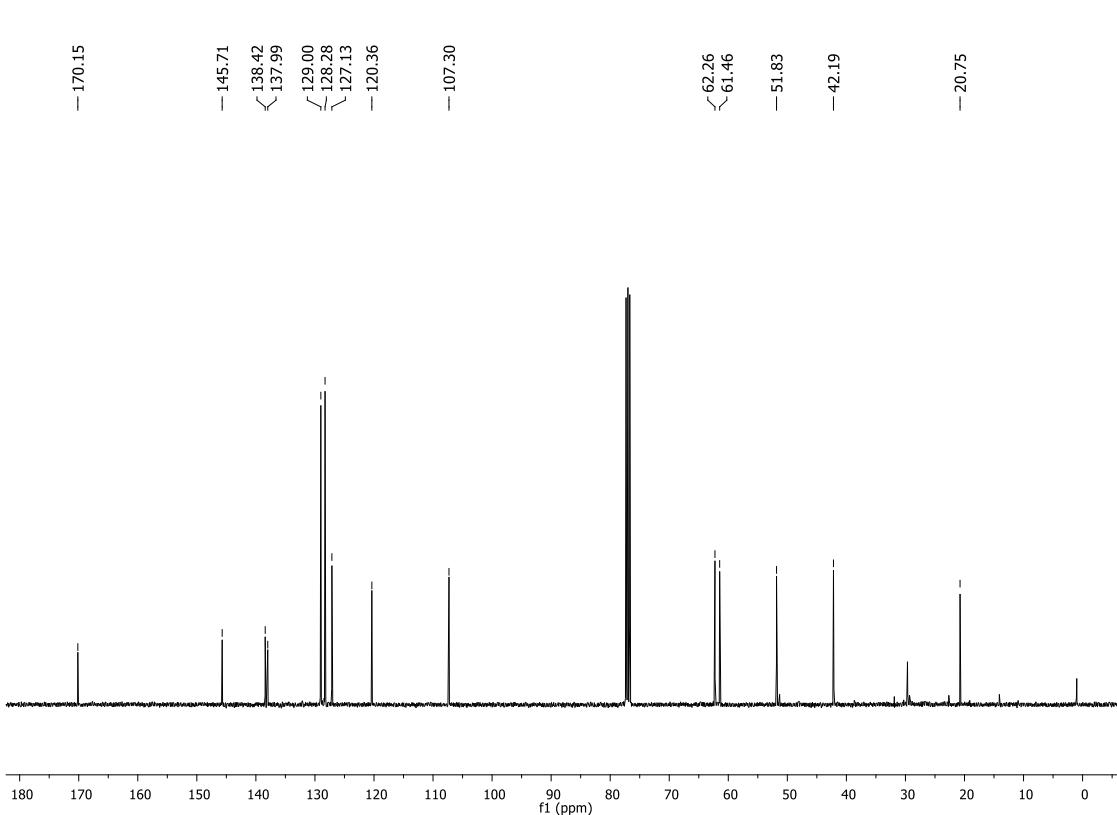
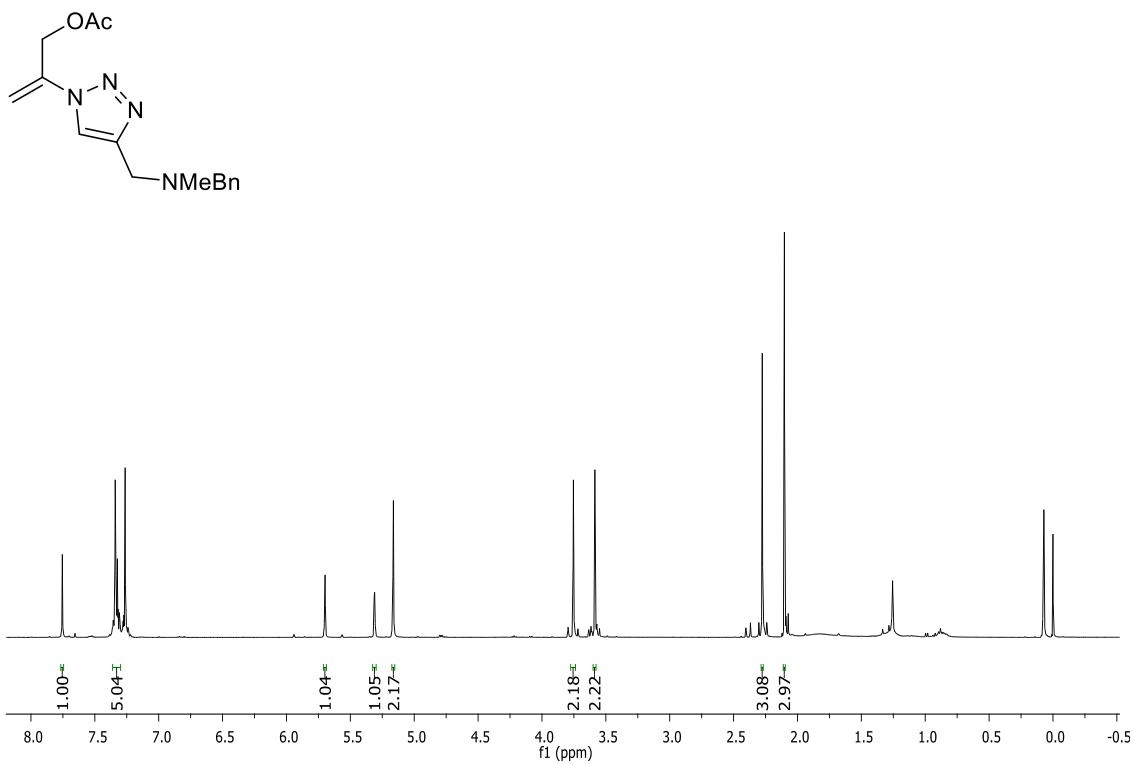
¹H NMR spectrum for compound 17a in CDCl₃, 400 MHz

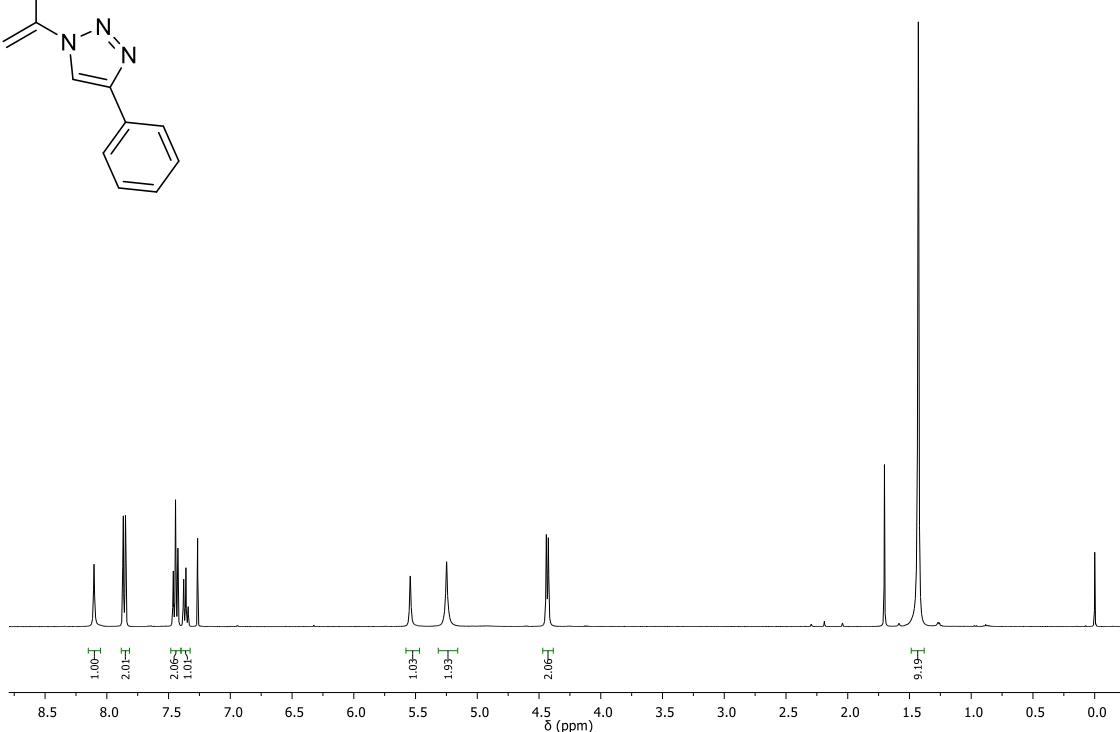
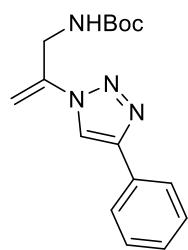


¹³C NMR spectrum for compound 17a in CDCl₃, 100 MHz

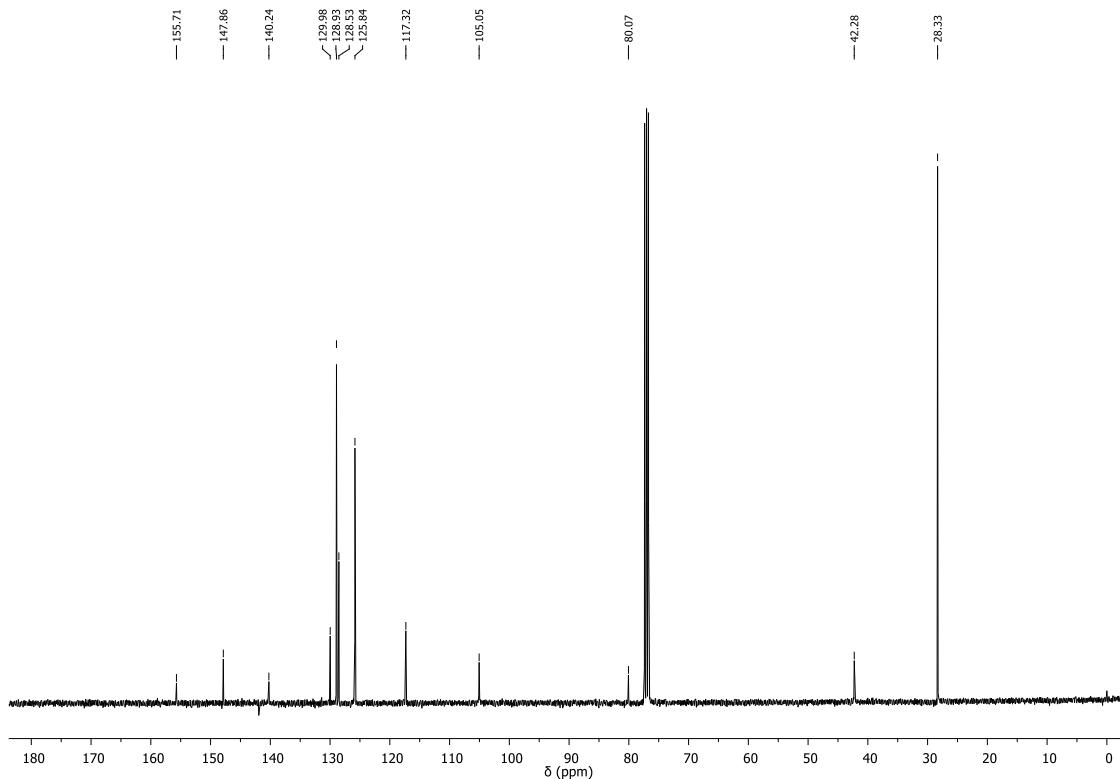




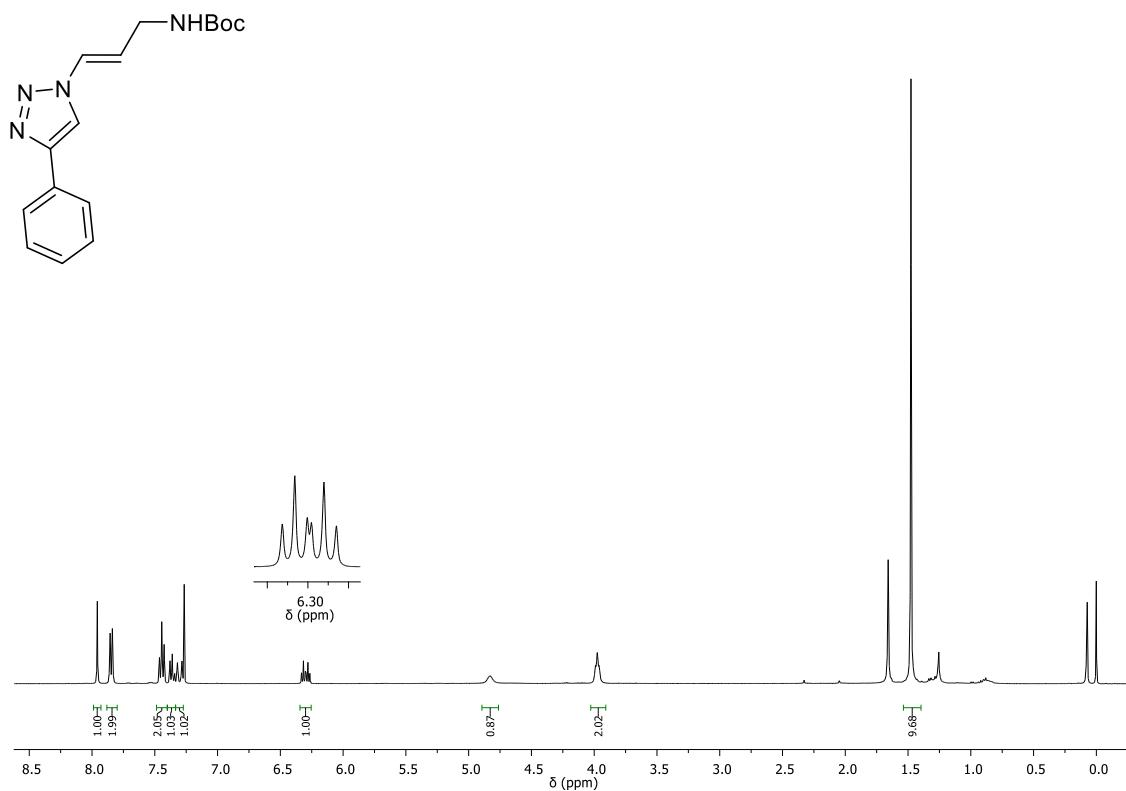




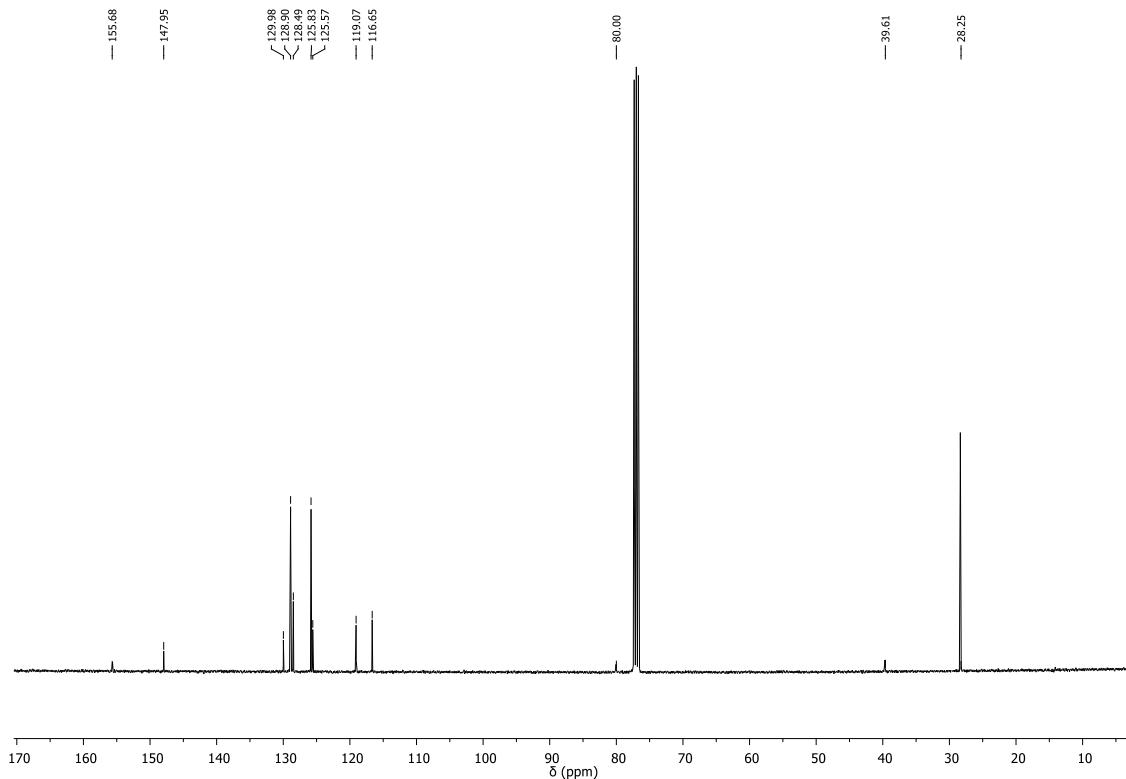
^1H NMR spectrum for compound **21a** in CDCl_3 , 400 MHz



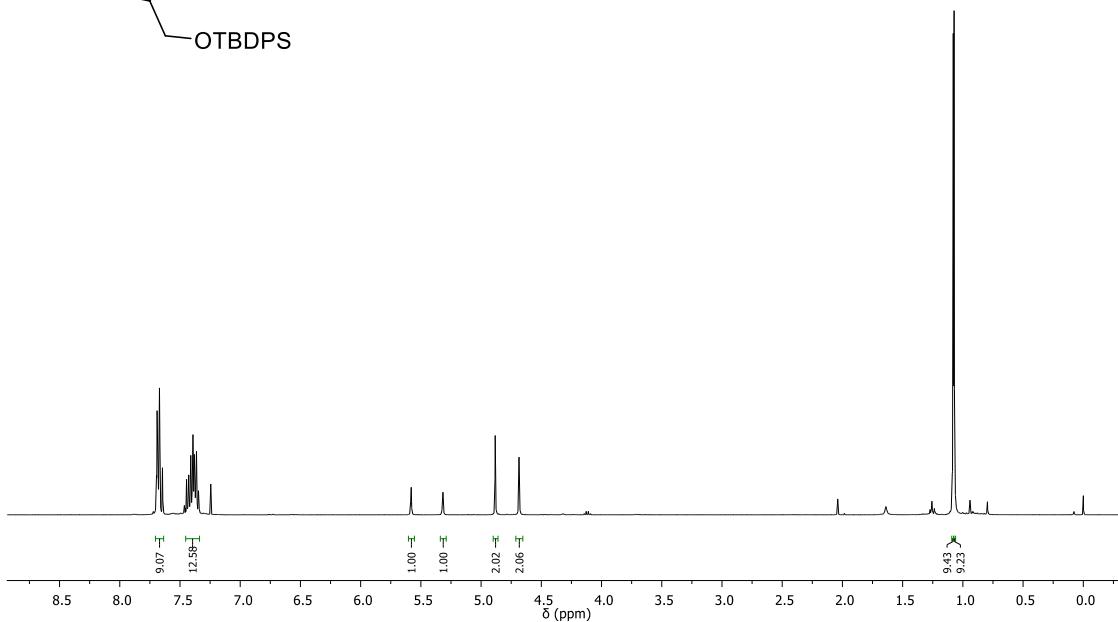
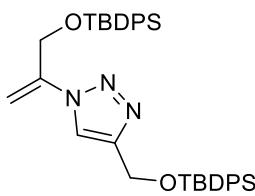
^{13}C NMR spectrum for compound **21a** in CDCl_3 , 100 MHz



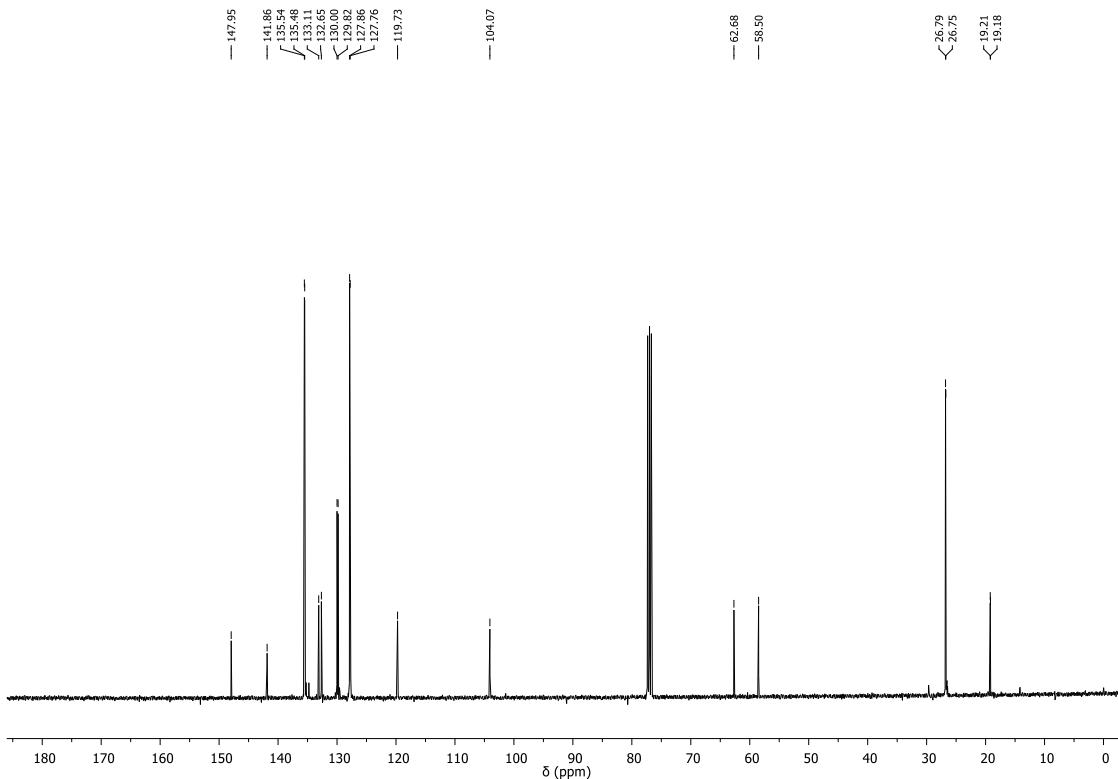
¹H NMR spectrum for compound **21b** in CDCl₃, 400 MHz



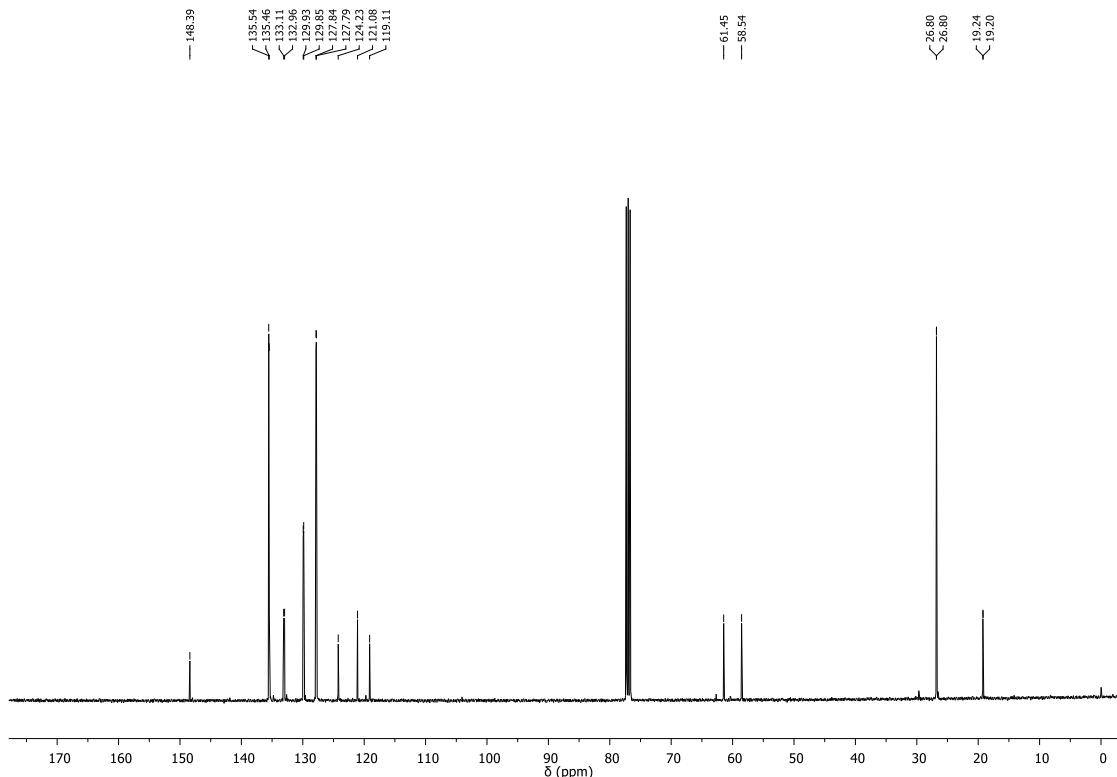
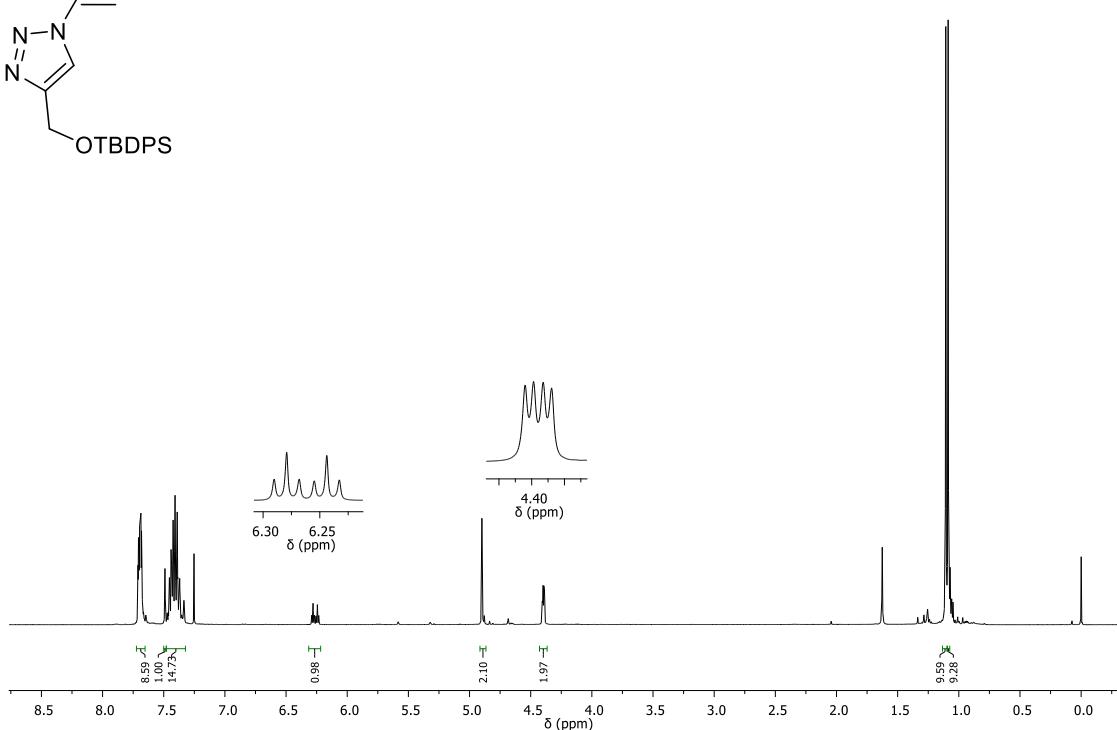
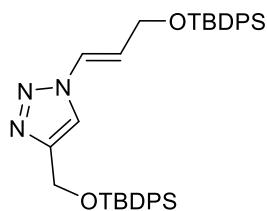
¹³C NMR spectrum for compound **21b** in CDCl₃, 100 MHz

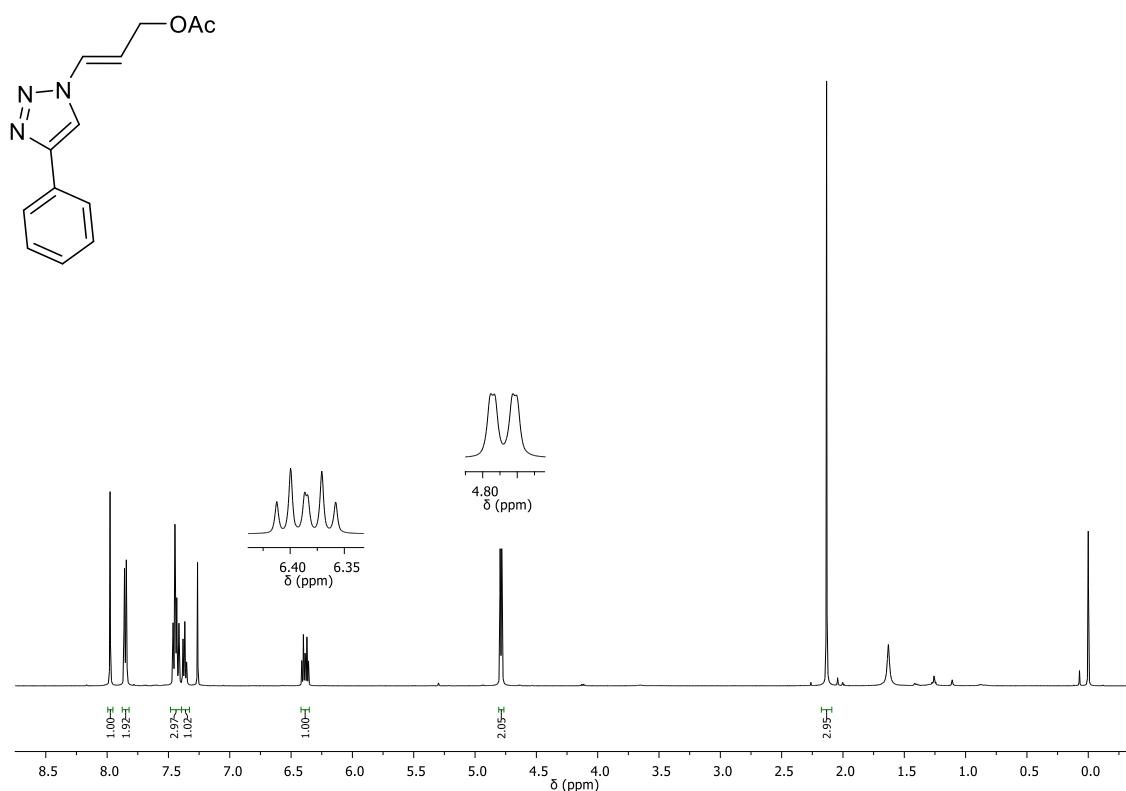


¹H NMR spectrum for compound **22a** in CDCl₃, 400 MHz

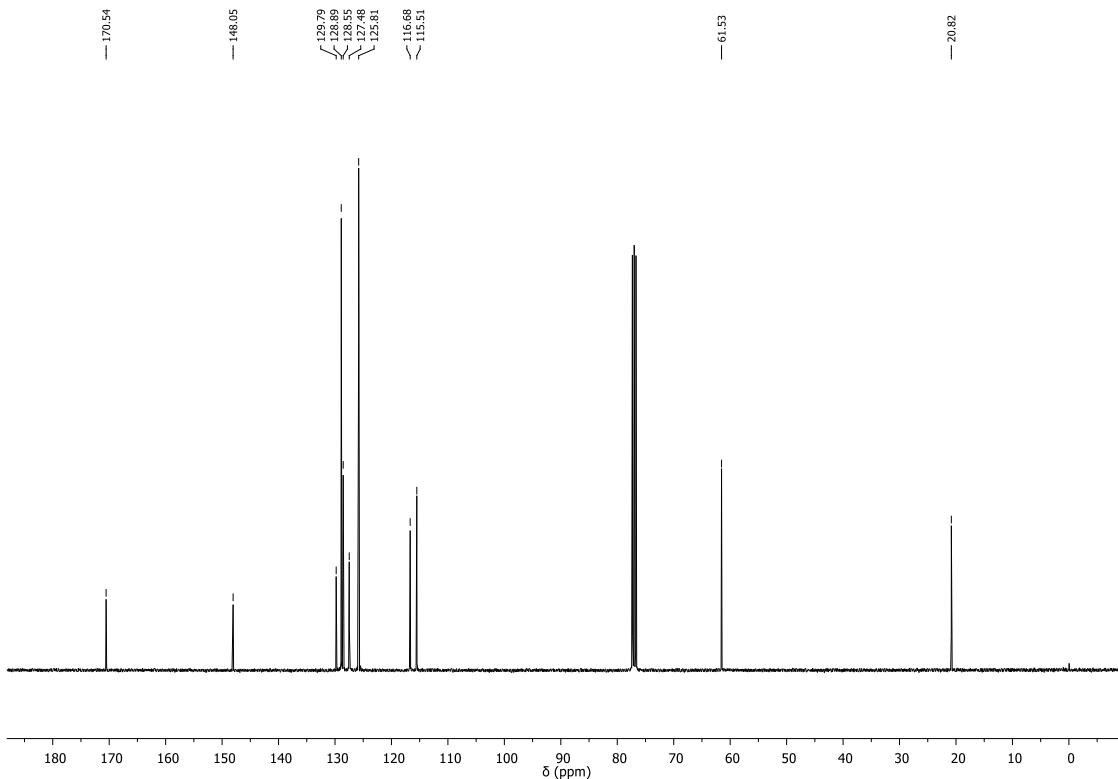


¹³C NMR spectrum for compound **22a** in CDCl₃, 100 MHz

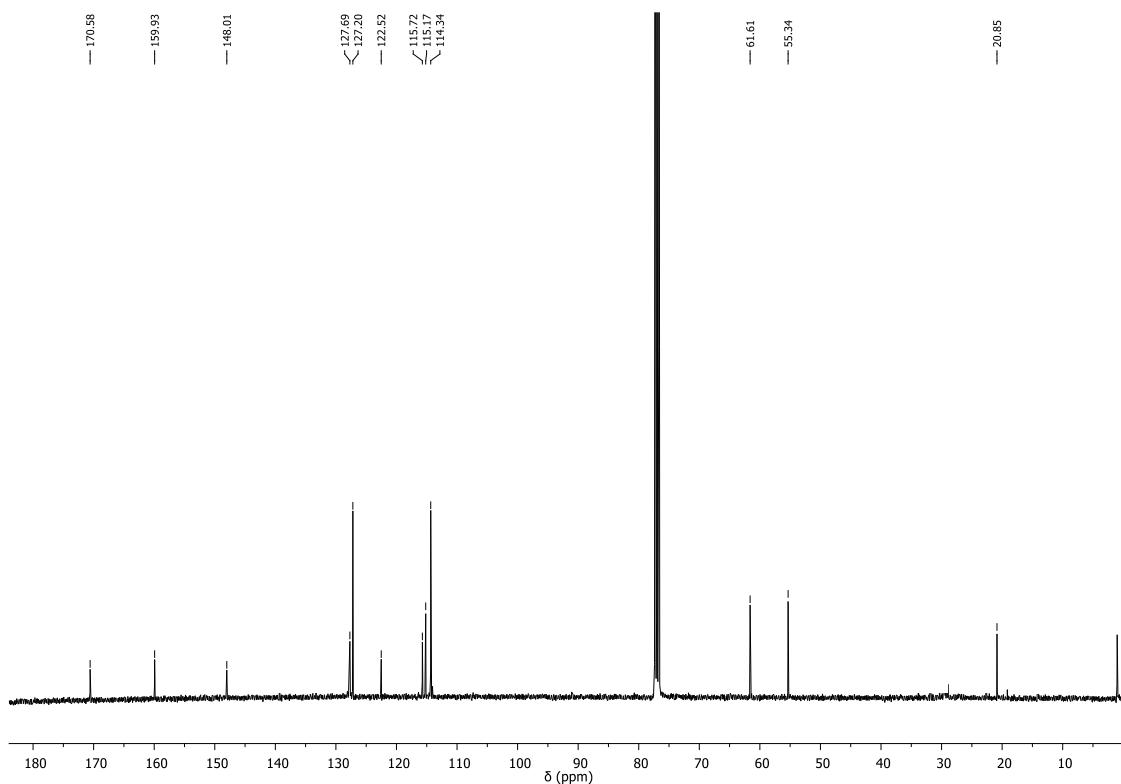
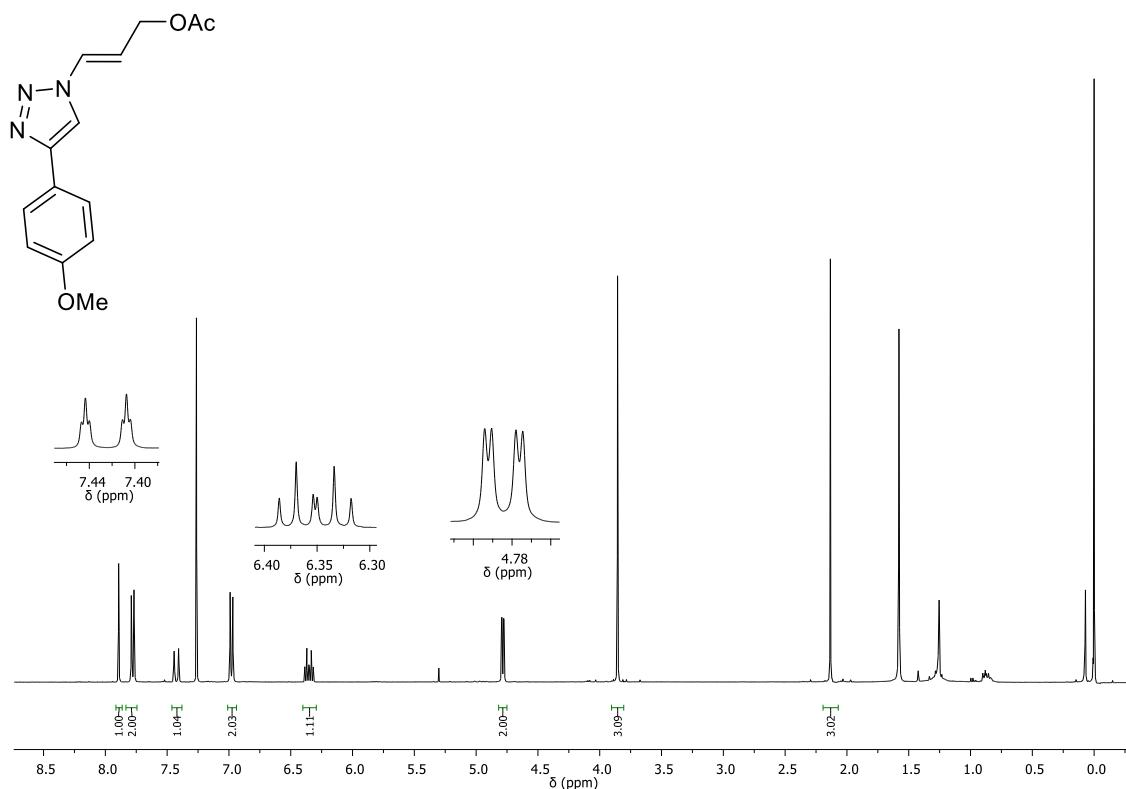


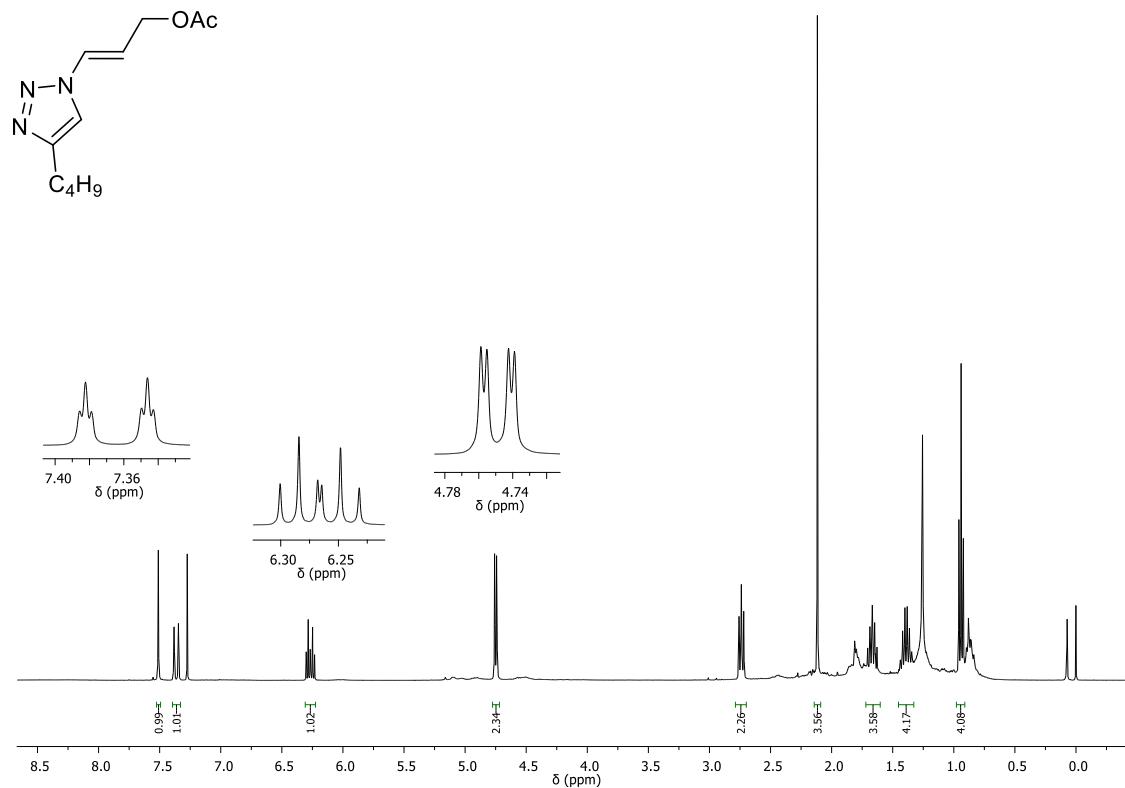


¹H NMR spectrum for compound **3b** in CDCl₃, 400 MHz

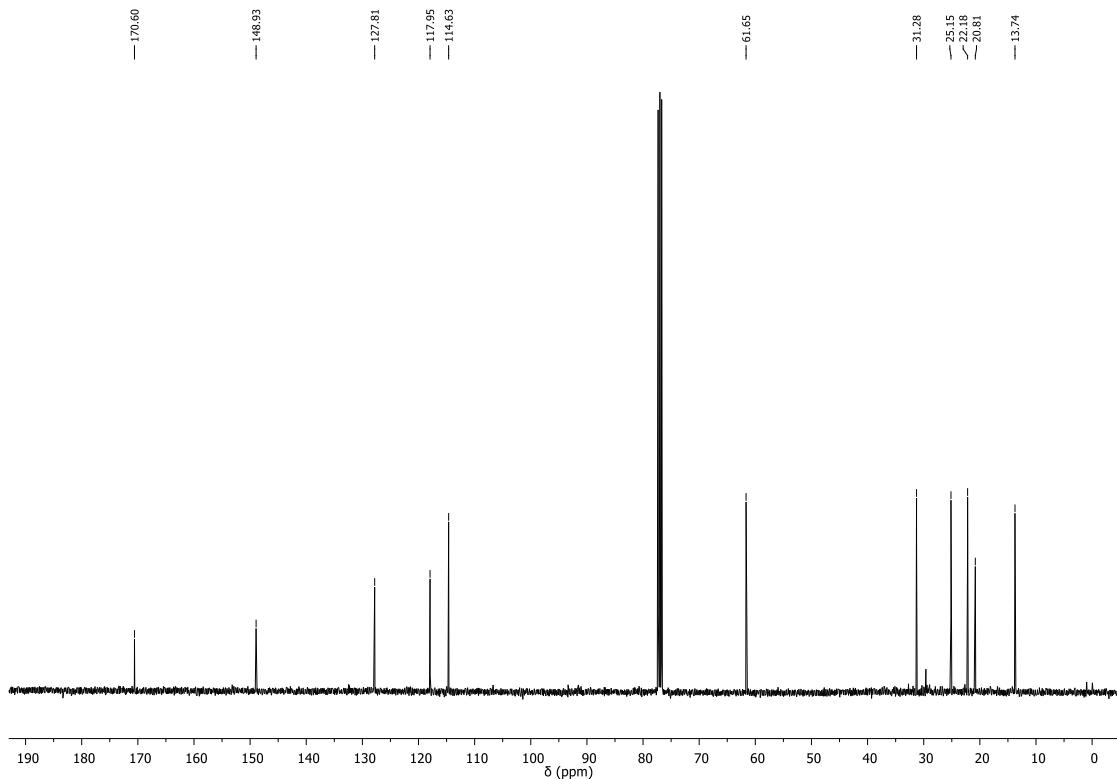


¹³C NMR spectrum for compound **3b** in CDCl₃, 100 MHz

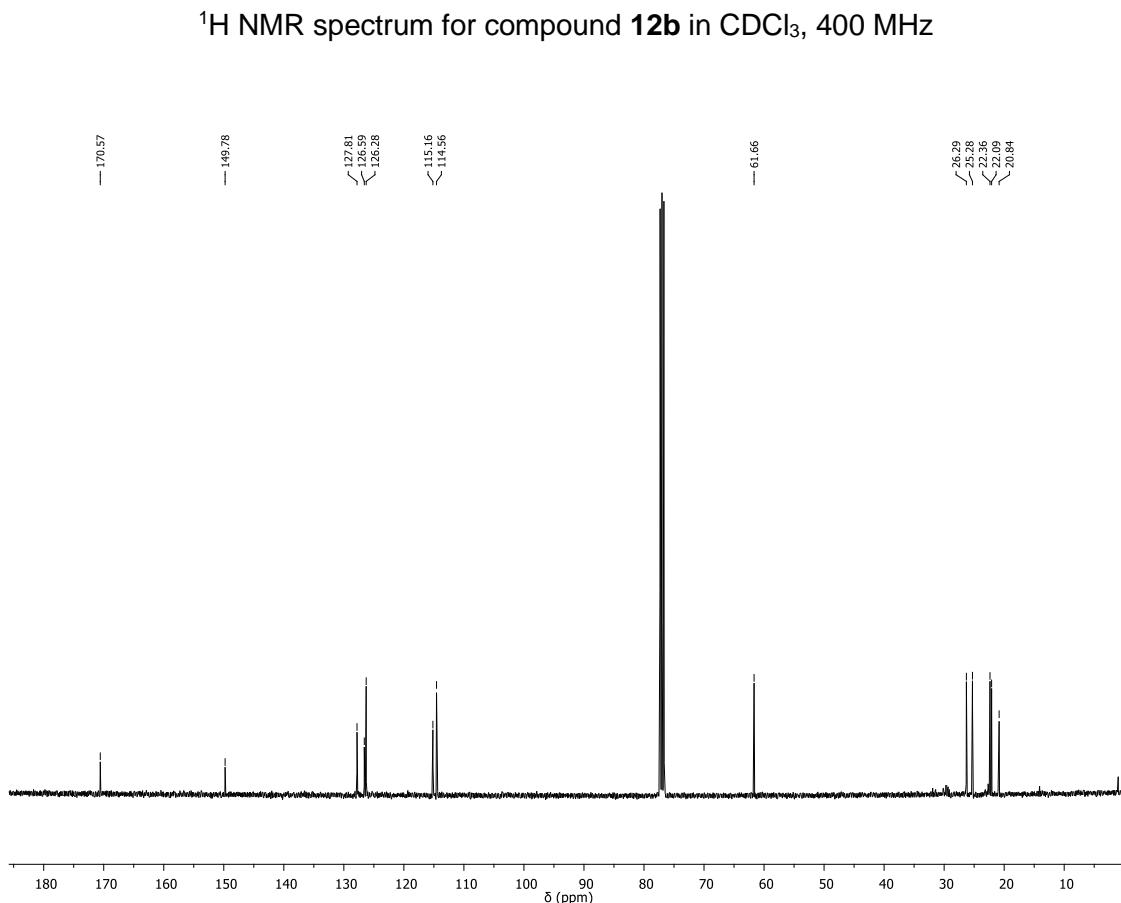
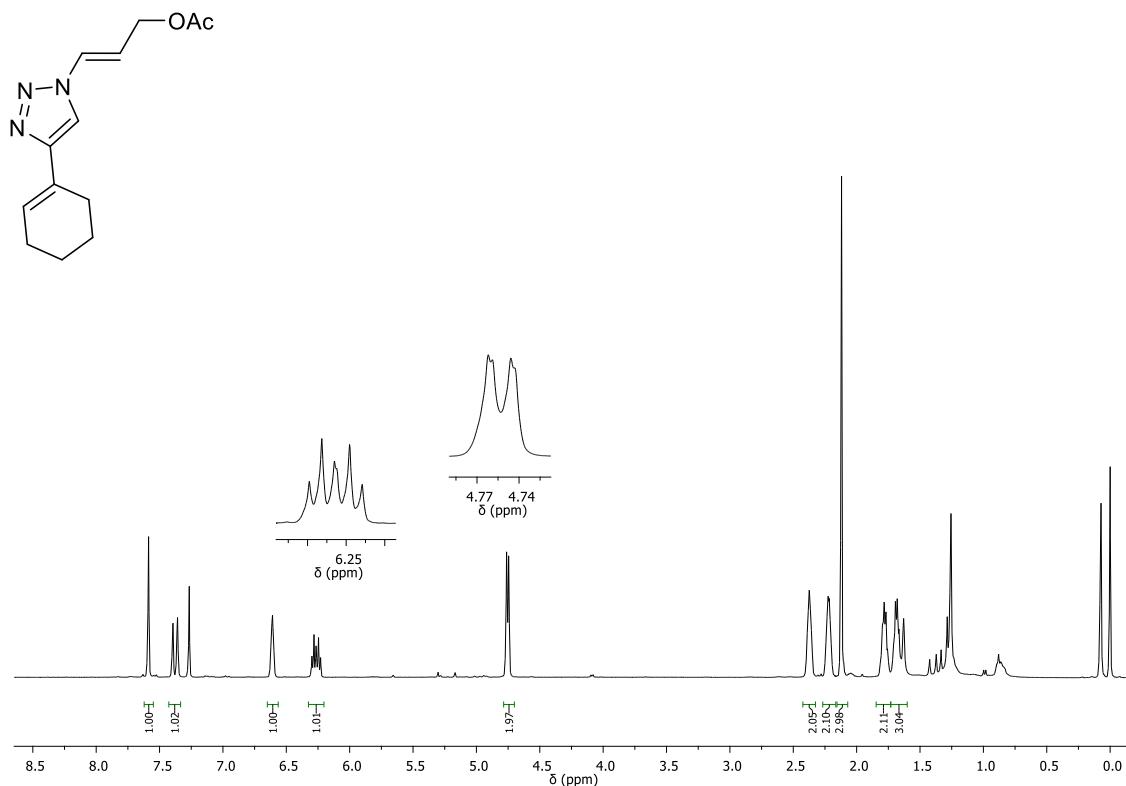


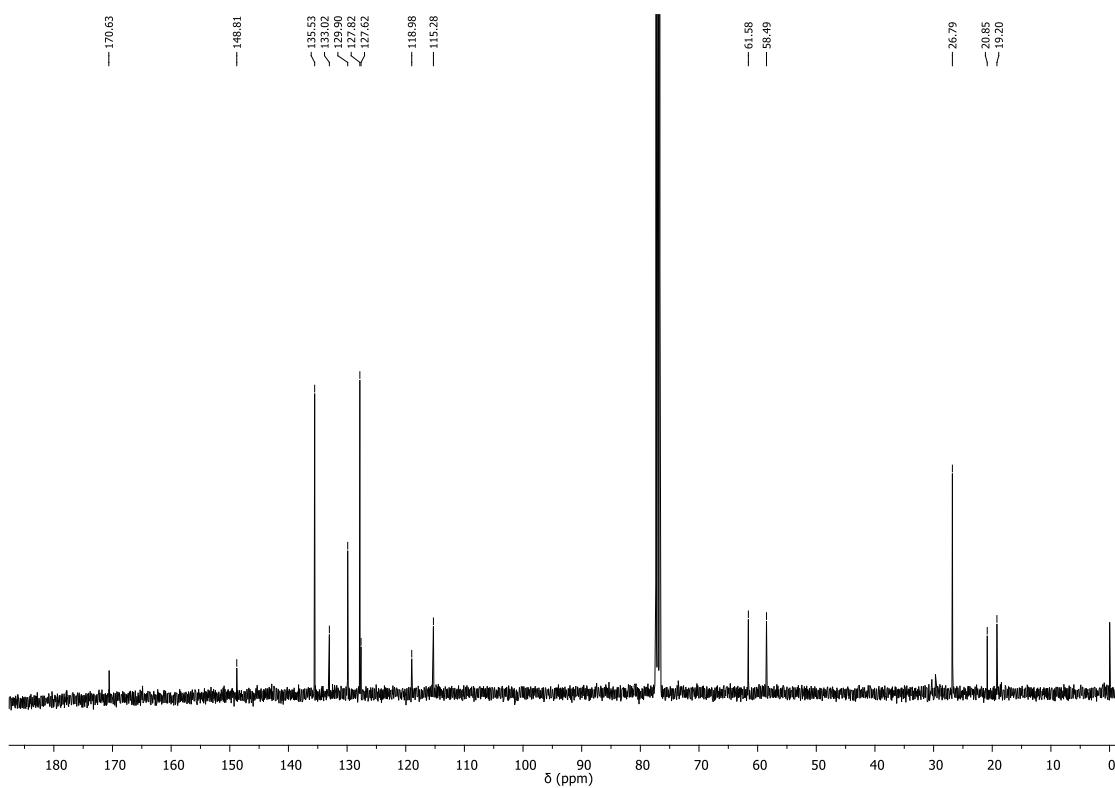
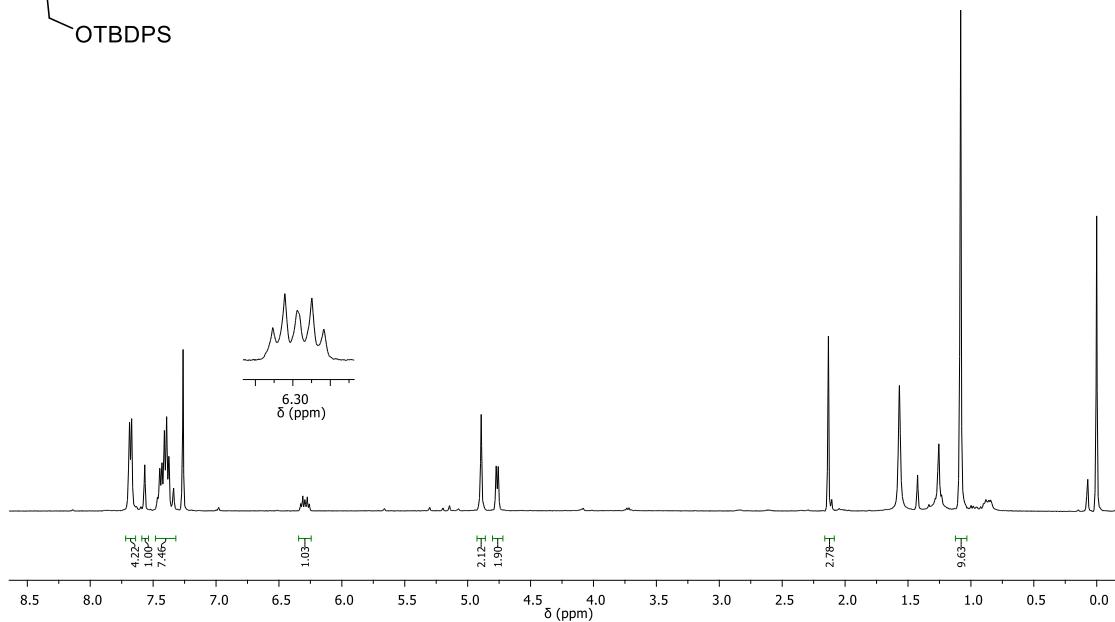
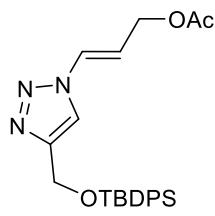


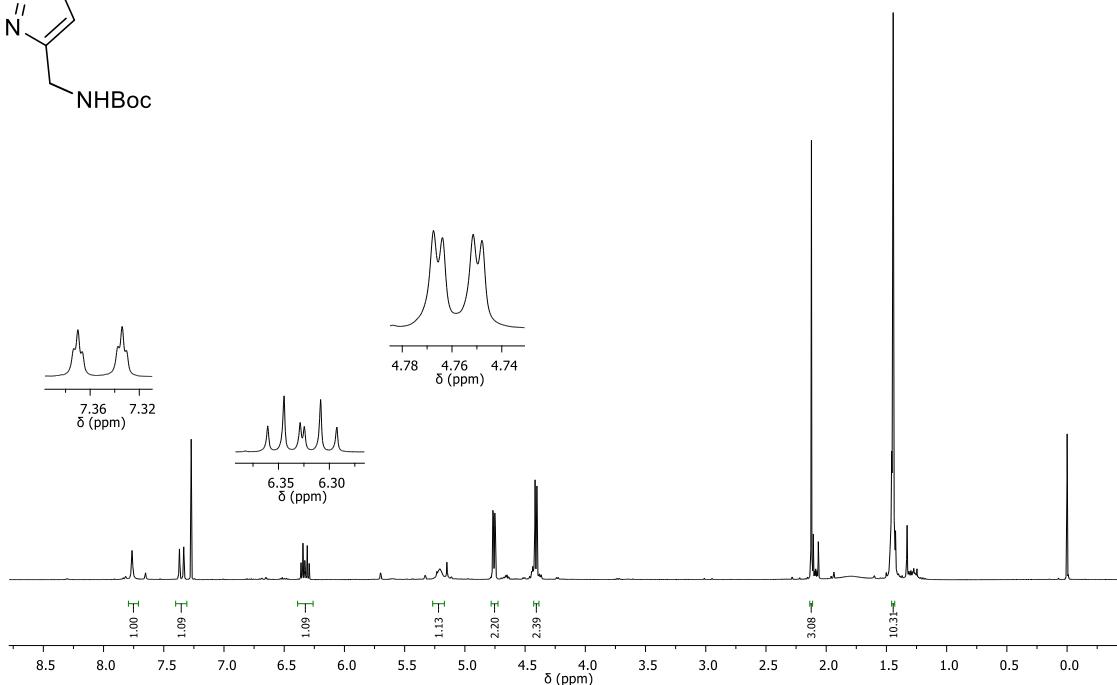
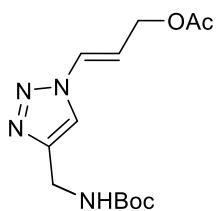
¹H NMR spectrum for compound **9b** in CDCl₃, 400 MHz



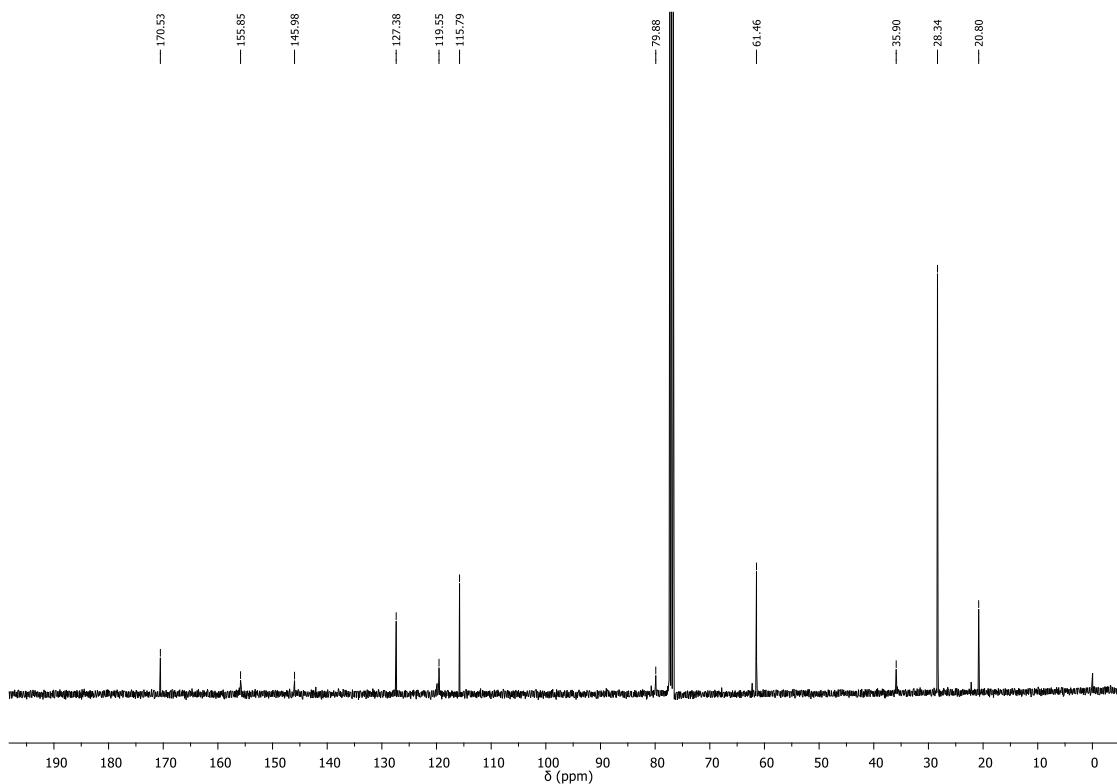
¹³C NMR spectrum for compound **12b** in CDCl₃, 100 MHz



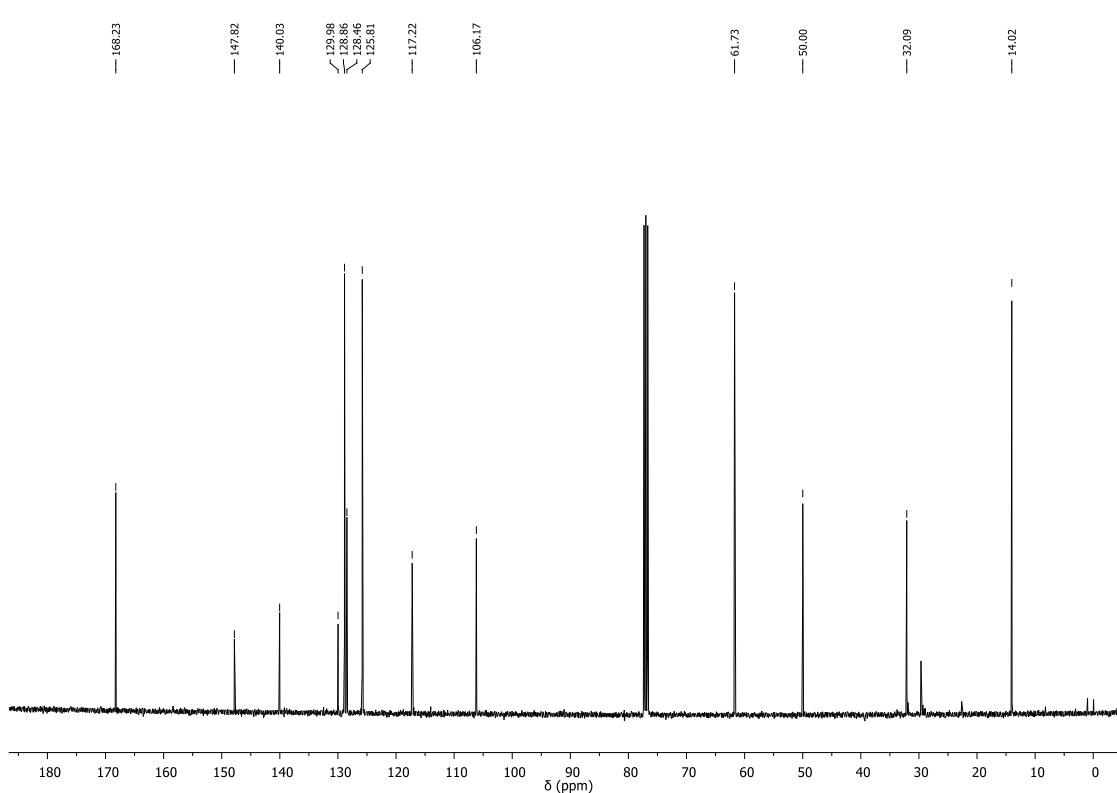
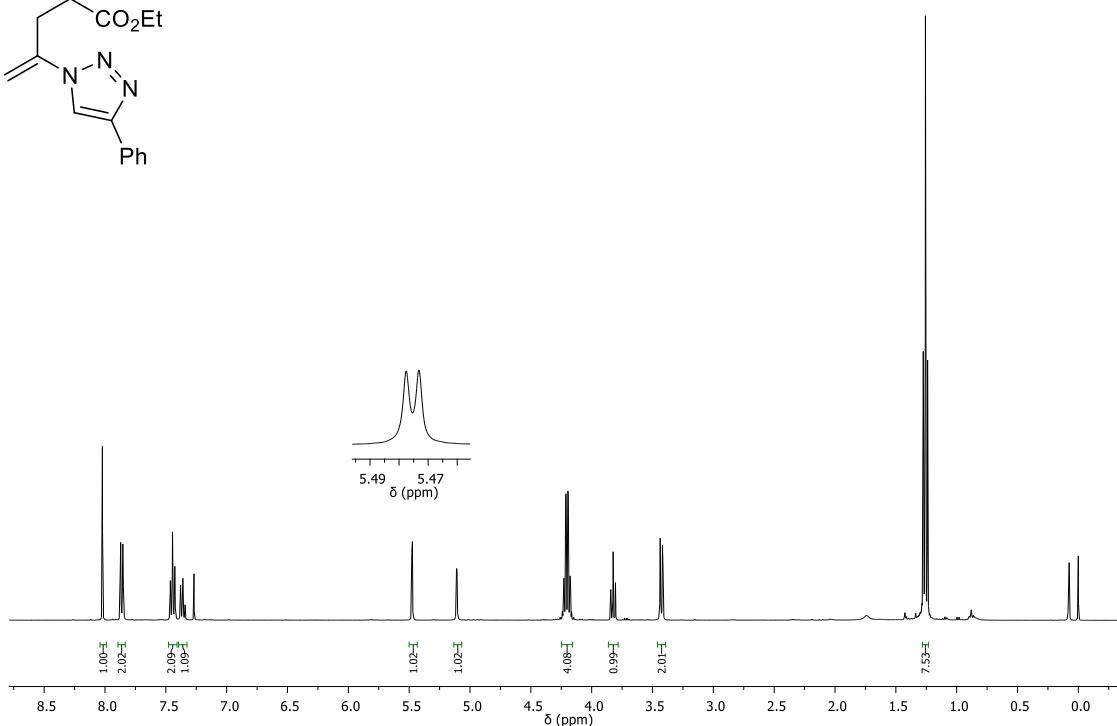
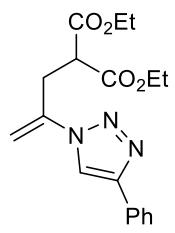


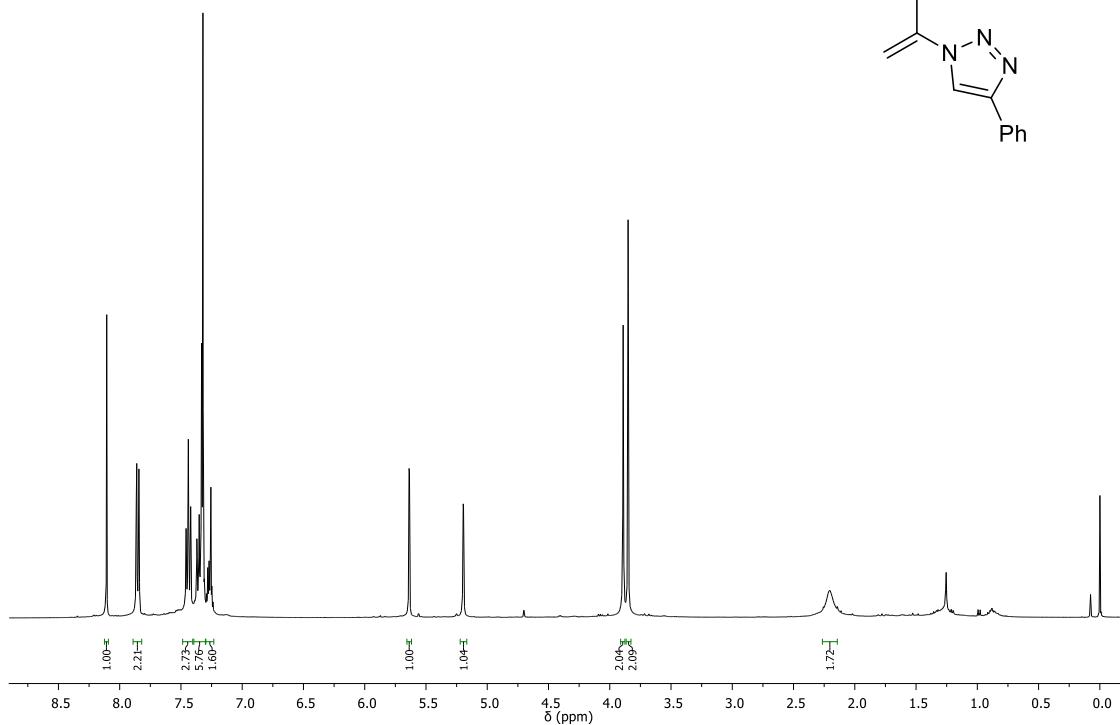
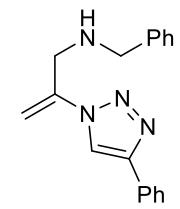


¹H NMR spectrum for compound **19b** in CDCl₃, 400 MHz
(small amount of minor α-isomer)

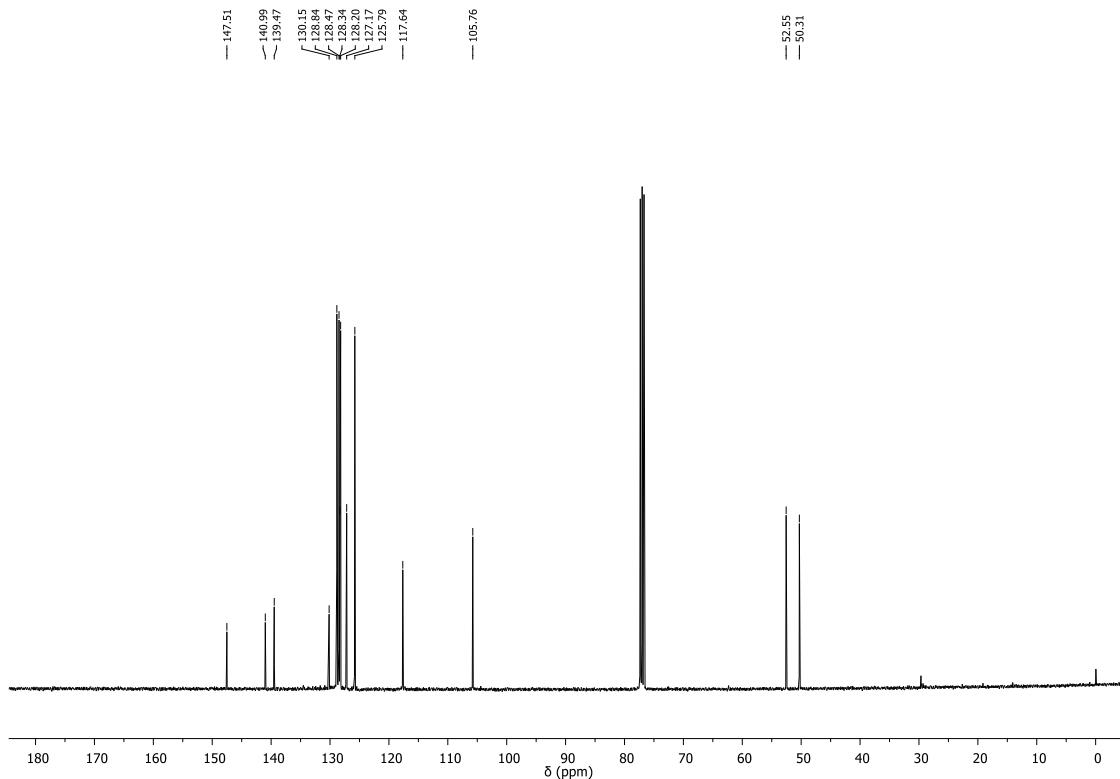


¹³C NMR spectrum for compound **19b** in CDCl₃, 100 MHz





¹H NMR spectrum for compound **25** in CDCl_3 , 400 MHz



¹³C NMR spectrum for compound **25** in CDCl_3 , 100 MHz