

Supplementary material

A highly active and reusable copper(I)-tren catalyst for the “click” 1,3-dipolar cycloaddition of azides and alkynes

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General Remarks: NMR analysis were carried out on spectrometers Bruker DPX-300 (300 MHz for proton, 75 MHz for carbon) and Bruker DPX-200 (200 MHz for proton, 50 MHz for carbon) by using deuterated chloroform as solvent. The chemical shifts (δ) for carbon and proton are given compared to the internal reference (TMS) and are expressed in ppm. The ESI-TOF mass spectra (low and high resolution) were recorded at the CESAMO analytical center (University Bordeaux 1) on a QSTAR Elite spectrometer from Applied Biosystem .

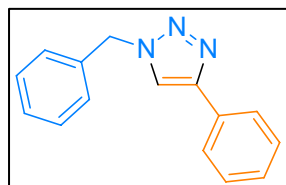
General procedure for the 1-catalyzed “click” reactions: In a 2-mL flask fitted with a stirring bar and a rubber septum, the catalyst **1** (0.01-0.1 mol%), the azide (1 mmol) and the alkyne (1 mmol) are stirred in the desired solvent (1 mL) at 60 °C. After 24 h the flask is placed at –18 °C for 2 h leading to the precipitation of the product which is recovered by filtration, washed two times and dried under vacuum.

In the case of the liquid triazole **7**, purification was achieved by silica gel column chromatography (DCM/MeOH, 100/0 to 95/5).

The dendrimer **9** was prepared as described above except that 1.5 equiv. of the alkyne synthon with respect to the azide group was employed and that the reaction was run under nitrogen atmosphere. After 24 h, cooling the reaction mixture to –18 °C led to the separation of the

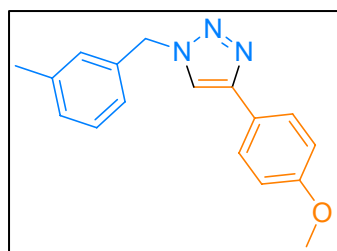
dendrimer as a sticky solid. After removal of the supernatant solution, the residue was washed with cooled octane to afford **9** in 76% yield as a colourless waxy solid.

Characterization of the triazoles:



1-benzyl-4-phenyl-1H-1,2,3-triazole : White powder; RMN ^1H (300 MHz, CDCl_3) : 7.83 (d, $J = 7$ Hz, 2H), 7.69 (s, 1H), 7.37 (m, 8H), 5.58 (s, 2H);

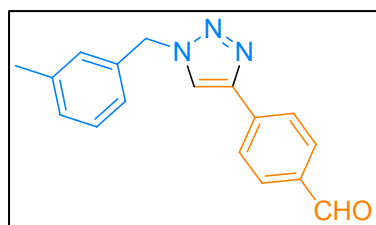
RMN ^{13}C (75 MHz, CDCl_3) : 148.4 (C, triazole), 134.8 (C, C^{Ar}), 131.3 (C, C^{Ar}), 129.3 (CH, C^{Ar}), 128.9 (CH, C^{Ar}), 128.9 (CH, C^{Ar}), 128.2 (CH, C^{Ar}), 125.8 (CH, C^{Ar}), 119.6 (CH, triazole), 54.4 (CH_2); MS (TOF+): m/z (%) = 236.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{15}\text{H}_{14}\text{N}_3$ $[\text{M}+\text{H}]^+ = 236.1187$, found = 236.1190; mp : 132-133°C (Lit. 126-130°C)¹.



4-(4-methoxyphenyl)-1-(3-methylbenzyl)-1H-1,2,3-triazole :

White powder ; RMN ^1H (300 MHz, CDCl_3) : 7.75 (d, $J = 9$ Hz, 2H), 7.59 (s, 1H), 7.28 (m, 4H), 6.96 (d, $J = 9$ Hz, 2H), 5.53 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); RMN ^{13}C (75 MHz, CDCl_3) :

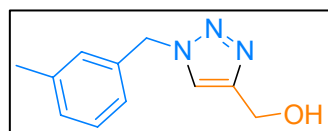
159.6 (C, C^{Ar}), 148.1 (C, triazole), 139.0 (C, C^{Ar}), 134.7 (C, C^{Ar}), 129.5 (CH, C^{Ar}), 129.0 (CH, C^{Ar}), 128.7 (CH, C^{Ar}), 127.0 (CH, C^{Ar}), 125.1 (CH, C^{Ar}), 123.4 (CH, C^{Ar}), 118.6 (C, triazole), 114.2 (CH, C^{Ar}), 55.3 (CH_3), 54.2 (CH_2), 21.3 (CH_3); MS (TOF+): m/z (%) = 280.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{17}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 280.1449$, found = 280.1452; mp : 101-102°C.



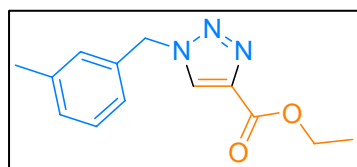
4-(4-benzaldehyde)-1-(3-methylbenzyl)-1H-1,2,3-triazole :

Yellowish powder ; RMN ^1H (300 MHz, CDCl_3) : 10.02 (s, 1H), 7.93 (q, $J = 8$ Hz, 4H), 7.79 (s, 1H), 7.27 (m, 4H), 5.57 (s, 2H), 2.37 (s, 3H); RMN ^{13}C (75 MHz, CDCl_3) :

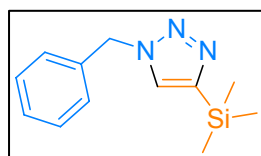
191.6 (C, CHO), 148.3 (C, triazole), 139.2 (C, C^{Ar}), 136.4 (C, C^{Ar}), 135.9 (C, C^{Ar}), 134.2 (C, C^{Ar}), 130.2 (CH, C^{Ar}), 129.7 (CH, C^{Ar}), 129.1 (CH, C^{Ar}), 128.9 (CH, C^{Ar}), 126.0 (CH, C^{Ar}), 125.2 (CH, C^{Ar}), 120.6 (CH, triazole), 54.4 (CH_2), 21.3 (CH_3); MS (TOF+): m/z (%) = 278.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{17}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 278.1293$, found = 278.1295; mp : 93-94°C.



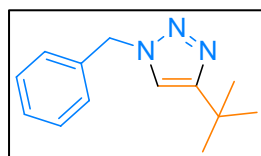
4-methanol-1-(3-methylbenzyl)-1H-1,2,3-triazole : White powder; RMN ^1H (300 MHz, CDCl_3) : 7.46 (s, 1H), 7.14 (m, 4H), 5.44 (s, 2H), 4.73 (d, $J = 5$ Hz, 2H), 3.90 (t, $J = 6$ Hz, 1H), 2.32 (s, 3H); RMN ^{13}C (75 MHz, CDCl_3) : 148.2 (C, triazole), 139.1 (C, C^{Ar}), 134.5 (C, C^{Ar}), 129.6 (CH, C^{Ar}), 129.1 (CH, C^{Ar}), 128.9 (CH, C^{Ar}), 125.3 (CH, C^{Ar}), 121.7 (CH, triazole), 56.5 (CH_2), 54.3 (CH_2), 21.4 (CH_3); MS (TOF+): m/z (%) = 226.1 (100) $[\text{M}+\text{Na}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{11}\text{H}_{13}\text{N}_3\text{ONa}$ $[\text{M}+\text{Na}]^+ = 226.0956$, found = 226.0955; mp : 77-78°C.



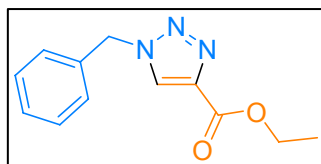
4-ethanoate-1-(3-methylbenzyl)-1H-1,2,3-triazole : White powder; RMN ^1H (300 MHz, CDCl_3) : 7.98 (s, 1H), 7.20 (m, 4H), 5.54 (s, 2H), 4.41 (q, $J = 7$ Hz, 2H), 2.36 (s, 3H), 1.39 (t, $J = 7$ Hz, 3H); RMN ^{13}C (75 MHz, CDCl_3) : 160.7 (C, ester), 140.6 (C, triazole), 139.2 (C, C^{Ar}), 133.6 (C, C^{Ar}), 129.9 (CH, C^{Ar}), 129.1 (CH, C^{Ar}), 128.9 (CH, C^{Ar}), 127.6 (CH, C^{Ar}), 125.3 (CH, triazole), 61.3 (CH_2), 54.5 (CH_2 , bn), 21.3 (CH_3 bn), 14.3 (CH_3) ; MS (TOF+): m/z (%) = 268.1 (100) $[\text{M}+\text{Na}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+ = 268.1061$, found = 268.1062; mp : 74-75°C (Lit. 75-77°C)².



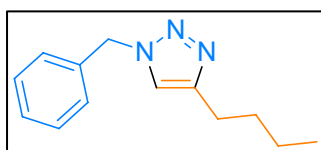
1-benzyl-4-trimethylsilyl-1H-1,2,3-triazole : White powder; RMN ^1H (300 MHz, CDCl_3) : 7.44 (s, 1H), 7.33 (m, 5H), 5.57 (s, 2H), 0.31 (s, 9H); RMN ^{13}C (75 MHz, CDCl_3) : 148.2 (C, triazole), 136.17 (C, C^{Ar}), 131.2 (CH, C^{Ar}), 130.2 (CH, triazole), 129.7 (CH, C^{Ar}), 129.2 (CH, C^{Ar}), 54.5 (CH_2), 0.0 (CH_3) ; MS (TOF+): m/z (%) = 232.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{12}\text{H}_8\text{N}_3\text{Si}$ $[\text{M}+\text{H}]^+ = 232.1270$, found = 232.1267 ; mp : 60-61°C.



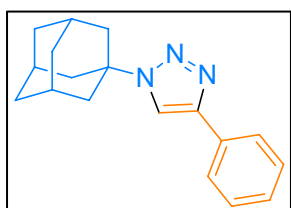
1-benzyl-4-tertbutyl-1H-1,2,3-triazole : White powder ; RMN ^1H (300 MHz, CDCl_3) : 7.37 (m, 5H), 7.17 (s, 1H), 5.50 (s, 2H), 1.34 (s, 9H); RMN ^{13}C (75 MHz, CDCl_3) : 158.1 (C, triazole), 135.1 (C, C^{Ar}), 130.0 (CH, C^{Ar}), 128.8 (CH, C^{Ar}), 128.0 (CH, C^{Ar}), 118.3 (CH, triazole), 53.9 (CH_2), 30.8 (C, CCH_3), 30.3 (CH_3); MS (TOF+): m/z (%) = 216.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{13}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+ = 216.1500$, found = 216.1499; mp : 84-85°C.



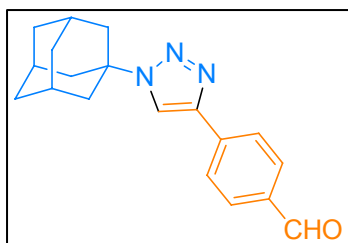
1-benzyl-4-ethanoate-1H-1,2,3-triazole : White powder ; RMN ^1H (300 MHz, CDCl_3) : 7.98 (s, 1H), 7.32 (m, 5H), 5.59 (s, 2H), 4.41 (q, $J = 7$ Hz, 2H), 1.4 (t, $J = 7$ Hz, 3H); RMN ^{13}C (75 MHz, CDCl_3) : 181.6 (C, CO), 160.7 (C, triazole), 140.7 (C, C^{Ar}), 133.8 (CH, C^{Ar}), 129.2 (CH, C^{Ar}), 128.2 (CH, C^{Ar}), 127.3 (CH, triazole), 61.3 (CH_2 , ethyl), 54.5 (CH_2), 14.3 (CH_3 , ethyl) ; MS (TOF+): m/z (%) = 254.1 (100) $[\text{M}+\text{Na}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+ = 254.0905$, found = 254.0901; mp : 88-89°C (Lit. 88-90°C)³.



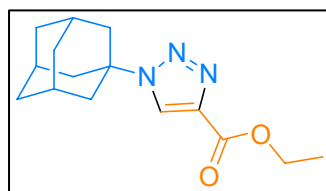
1-benzyl-4-butyl-1H-1,2,3-triazole : White powder ; RMN ^1H (300 MHz, CDCl_3) : 7.35 (m, 5H), 7.19 (s, 1H), 5.50 (s, 2H), 2.70 (t, $J = 7$ Hz, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 0.92 (t, $J = 7$ Hz, 3H); RMN ^{13}C (75 MHz, CDCl_3) : 148.9 (C, triazole), 135.0 (C, C^{Ar}), 129.0 (CH, C^{Ar}), 128.6 (CH, C^{Ar}), 127.9 (CH, C^{Ar}), 120.4 (CH, triazole), 53.9 (CH_2 , Bn), 31.5 (CH_2 , alk), 25.4 (CH_2 , alk), 22.3 (CH_2 , alk), 13.8 (CH_3) ; MS (TOF+): m/z (%) = 216.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{13}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+ = 216.1500$, found = 216.1498; mp : 62-63°C.



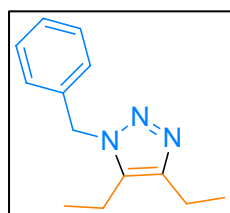
1-adamantane-4-phenyl-1H-1,2,3-triazole : White powder ; RMN ^1H (300 MHz, CDCl_3) : 7.87 (d, 3H), 7.38 (m, 3H), 2.30 (s, 9H), 1.82 (s, 6H); RMN ^{13}C (75 MHz, CDCl_3) : 146.5 (C, triazole), 130.9 (C, C^{Ar}), 128.4 (CH, C^{Ar}), 126.5 (CH, C^{Ar}), 125.3 (CH, C^{Ar}), 115.7 (CH, triazole), 59.3 (C, ad), 42.7 (CH_2 , ad), 35.6 (CH_2 , ad), 29.2 (CH, ad) ; MS (TOF+): m/z (%) = 280.1 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{18}\text{H}_{22}\text{N}_3$ $[\text{M}+\text{H}]^+ = 280.1813$, found = 280.1819; mp : 205-206°C (Lit. 205-206°C)⁴.



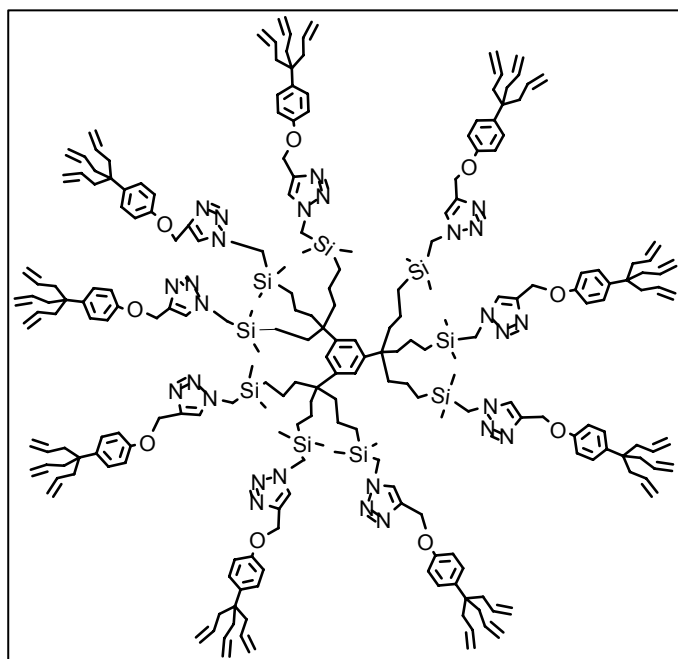
1-adamantane-4-(4-benzaldehyde)-1H-1,2,3-triazole : Yellow powder ; RMN ^1H (300 MHz, CDCl_3) : 10.04 (s, 1H), 7.97 (m, 5H), 2.33 (s, 9H), 1.85 (s, 6H); RMN ^{13}C (75 MHz, CDCl_3) : 191.7 (C, CHO), 145.5 (C, triazole), 136.9 (C, C^{Ar}), 135.6 (C, C^{Ar}), 132.7 (CH, C^{Ar}), 130.4 (CH, C^{Ar}), 129.5 (CH, C^{Ar}), 125.9 (CH, C^{Ar}), 117.3 (CH, triazole), 60.0 (C, ad), 43.0 (CH_2 , ad), 35.8 (CH_2 , ad), 29.5 (CH, ad) ; MS (TOF+): m/z (%) = 308.2 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{19}\text{H}_{22}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 308.1762$, found = 308.1765; mp : 168-169°C.



1-adamantane-4-ethanoate-1H-1,2,3-triazole : White powder ;
RMN ^1H (300 MHz, CDCl_3) : 8.15 (s, 1H), 4.41 (q, $J = 6$ Hz, 2H), 2.27 (s, 9H), 1.81 (s, 6H), 1.41 (t, $J = 6$ Hz, 3H); RMN ^{13}C (75 MHz, CDCl_3) : 161.0 (C, CO), 139.2 (C, triazole), 124.1 (CH, triazole), 60.9 (CH_2 , ethyl), 60.2 (C, ad), 42.8 (CH_2 , ad), 35.8 (CH_2 , ad), 29.7 (CH, ad), 14.2 (CH_3 , ethyl) ; MS (TOF+): m/z (%) = 276.2 (100) $[\text{M}+\text{H}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{15}\text{H}_{22}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+ = 276.1712$, found = 276.1719; mp : 93-94°C (Lit. 98-99°C)⁴.

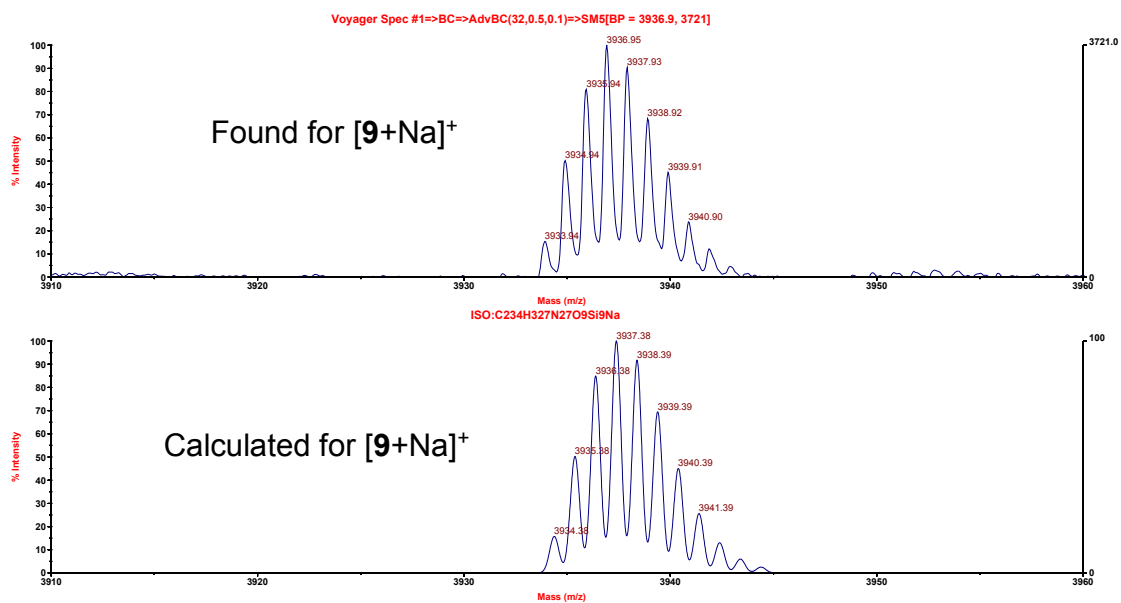


1-benzyl-4,5-diethyl-1H-1,2,3-triazole : Colorless oil ; RMN ^1H (300 MHz, CDCl_3) : 7.29 (m, 5H), 5.46 (s, 2H), 2.68 (q, $J = 7$ Hz, 2H), 2.53 (q, $J = 7$ Hz, 2H), 1.27 (t, $J = 7$ Hz, 3H), 0.94 (t, $J = 7$ Hz, 3H); RMN ^{13}C (75 MHz, CDCl_3) : 147.4 (C, triazole), 135.9 (C, C^{Ar}), 134.2 (C, triazole), 129.2 (CH, C^{Ar}), 128.9 (CH, C^{Ar}), 128.5 (CH, C^{Ar}), 127.4 (CH, C^{Ar}), 52.2 (CH_2 , bn), 18.9 (CH_2 , ethyl), 16.3 (CH_2 , ethyl), 13.7 (CH_3), 12.6 (CH_3); MS (TOF+): m/z (%) = 239 (100) $[\text{M}+\text{Na}]^+$; HRMS (ESI-TOF): calcd for $\text{C}_{13}\text{H}_{18}\text{N}_3$ $[\text{M}+\text{H}]^+ = 216.1500$, found = 216.1501.

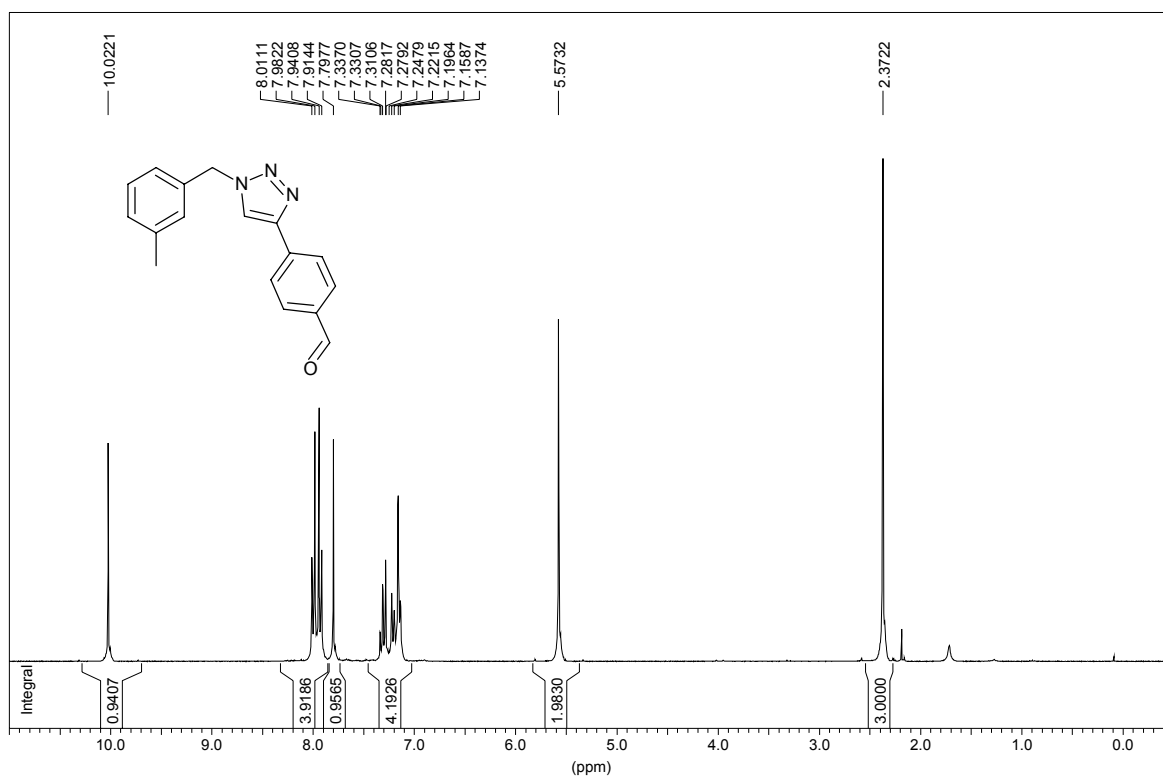
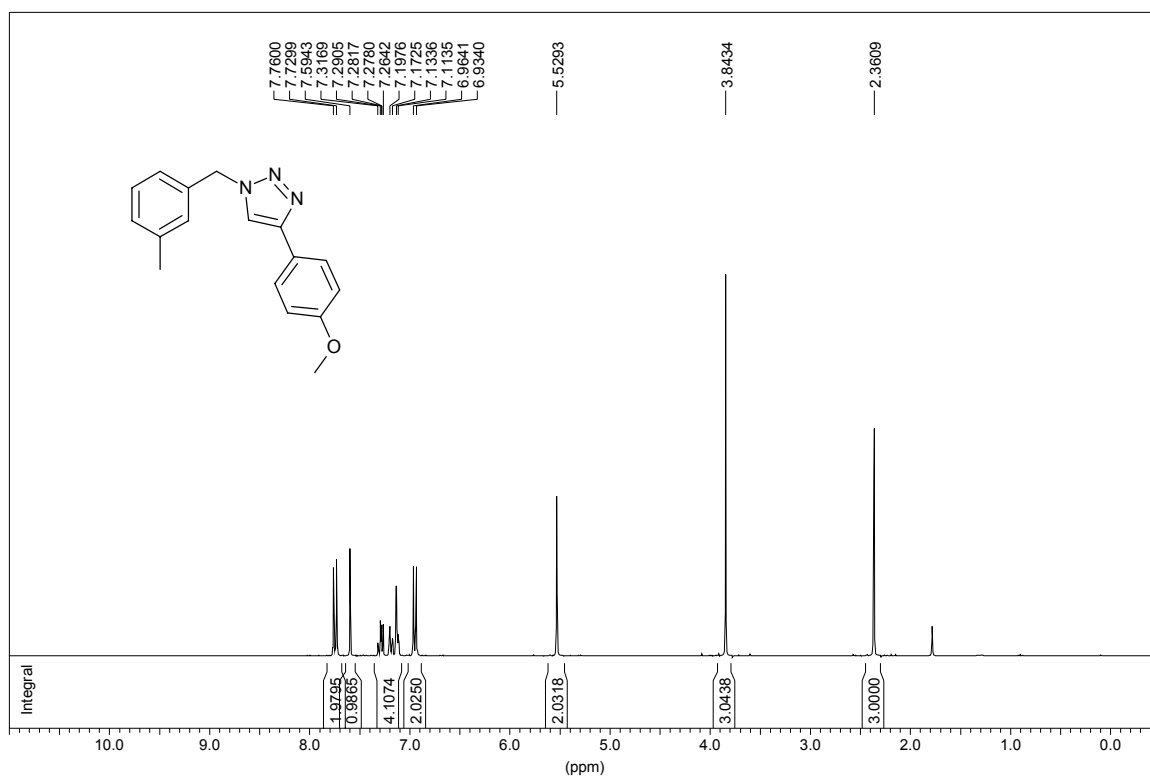


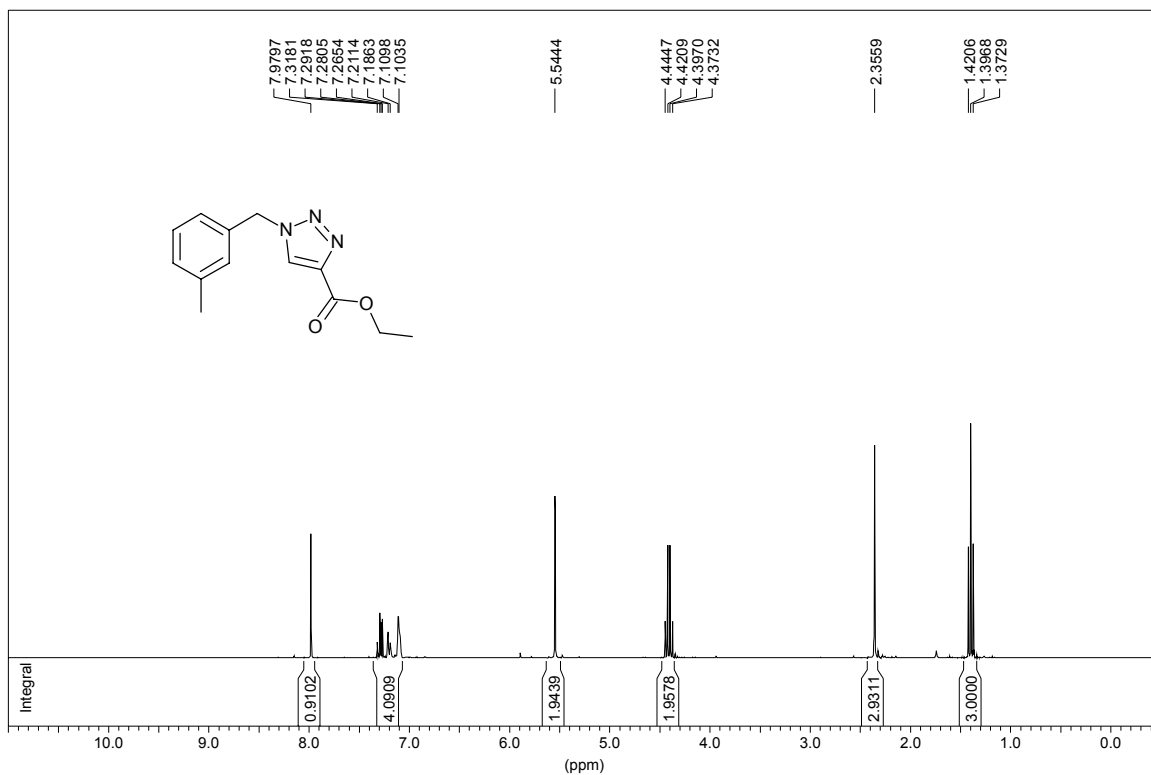
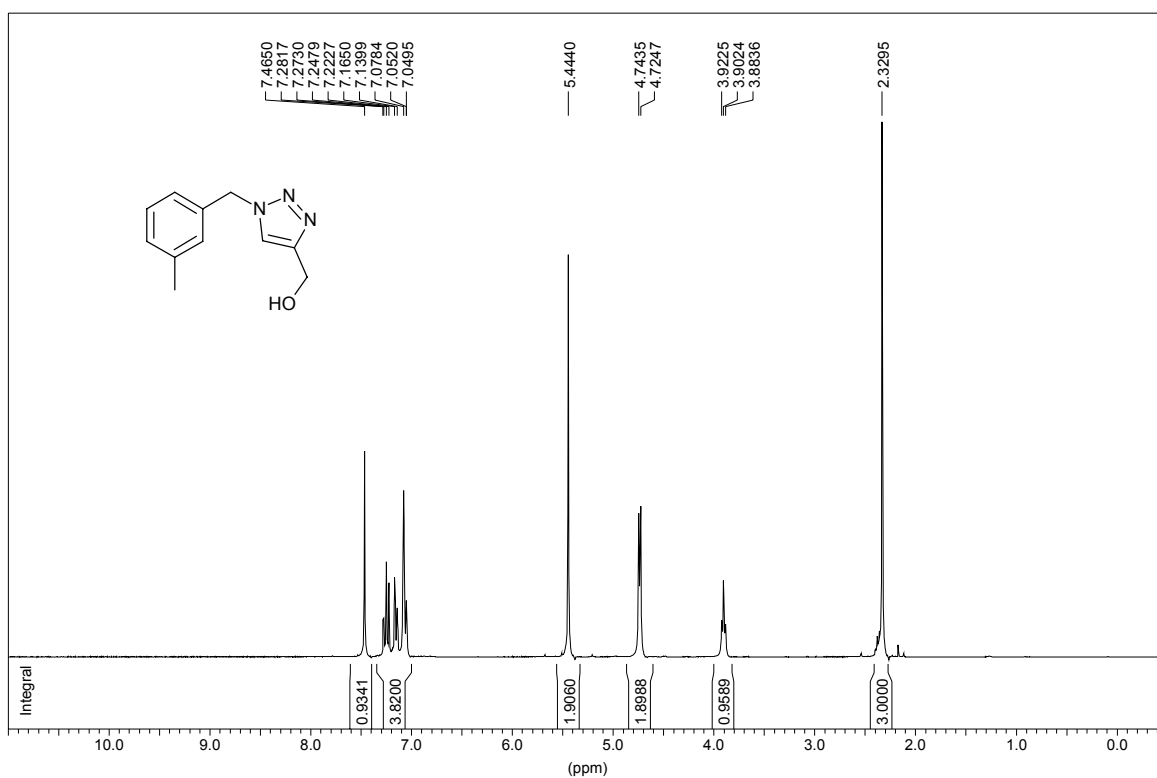
Dendrimer 9 : Colorless oil ; RMN ^1H (300 MHz, CDCl_3) : 7.50 (s, 9H, triazole CH), 7.20 and 6.91 (double d, 36H, $p\text{-C}_6\text{H}_4$), 5.53 (m, 27H, $\text{CH}=\text{CH}_2$), 5.10 (s, 18H, CH_2O), 4.97 (t, 54H, $\text{CH}=\text{CH}_2$), 3.86 (s, 18H, SiCH_2N), 2.40 (d, 54H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.64 (s, 18H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.10 (s, 18H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.64 (s, 18H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 0.049 (s, 54H, $\text{Si}(\text{CH}_3)_2$). RMN ^{13}C (50 MHz, CDCl_3) : 156.1, 143.7, 138.2, 136.8, 134.4, 127.8, 123.6, 117.5, 114.0, 61.9, 43.8, 42.6, 41.8, 40.9, 40.3, 17.5, 14.8, -3.9 ; MS (TOF+) : m/z (%) = 3936.95 (100) $[\text{M}+\text{Na}]^+$.

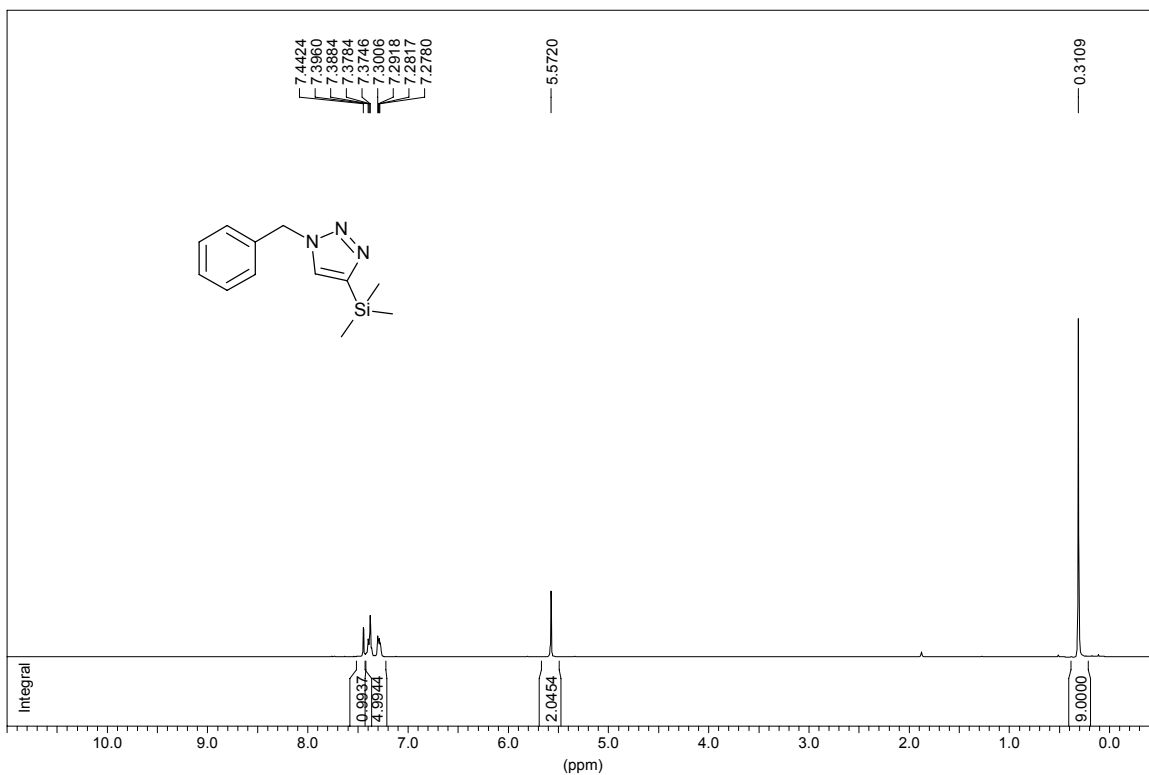
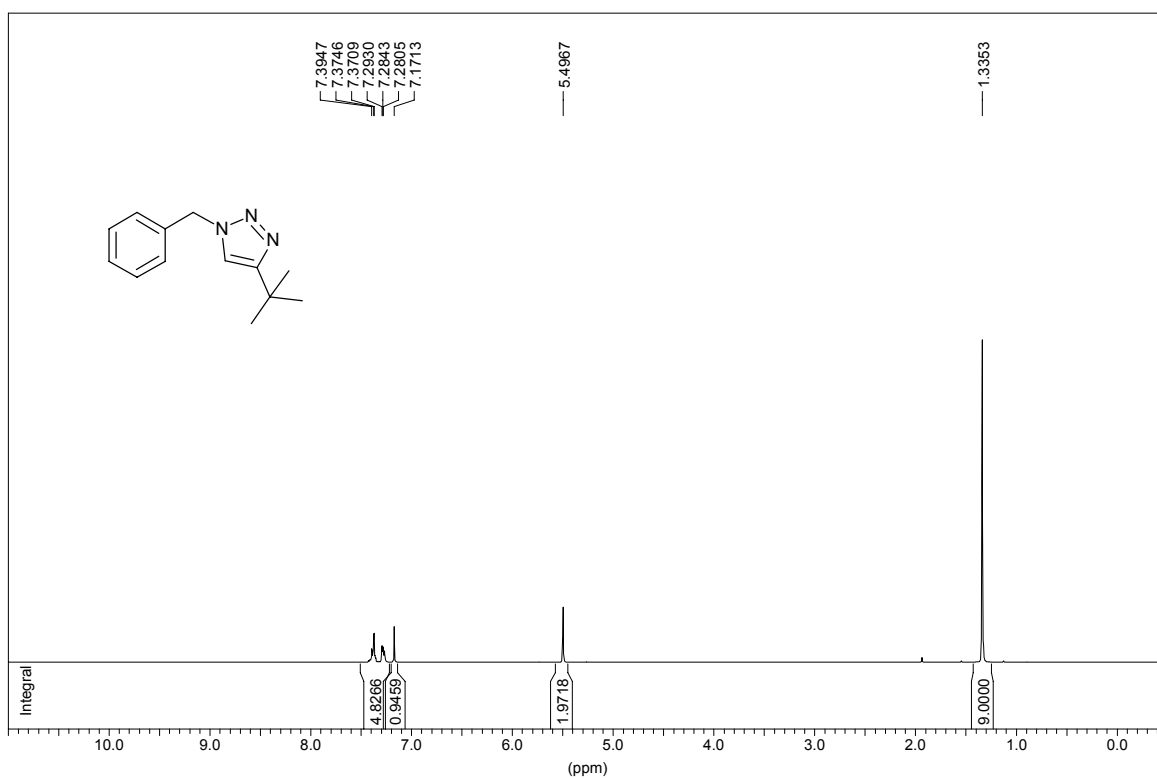
Comparison of the experimental and calculated isotopic patterns for the peak $[9+\text{Na}]^+$ of the mass spectrum of **9 :**

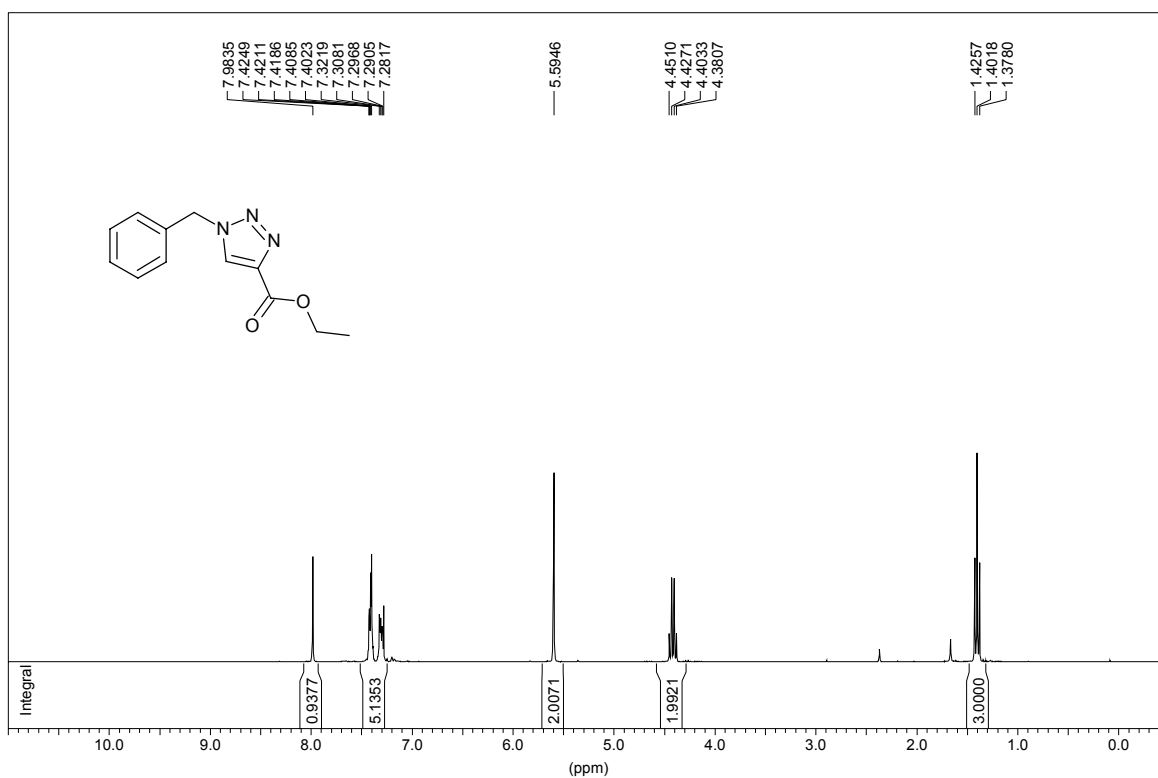
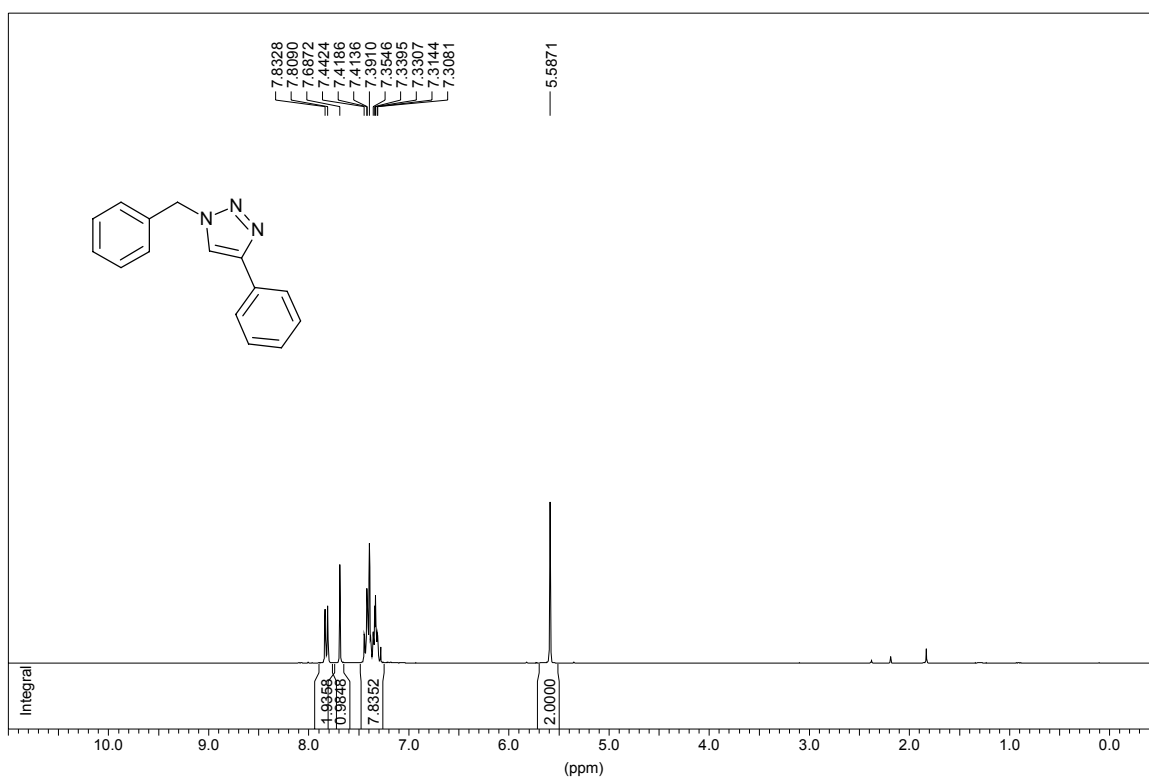


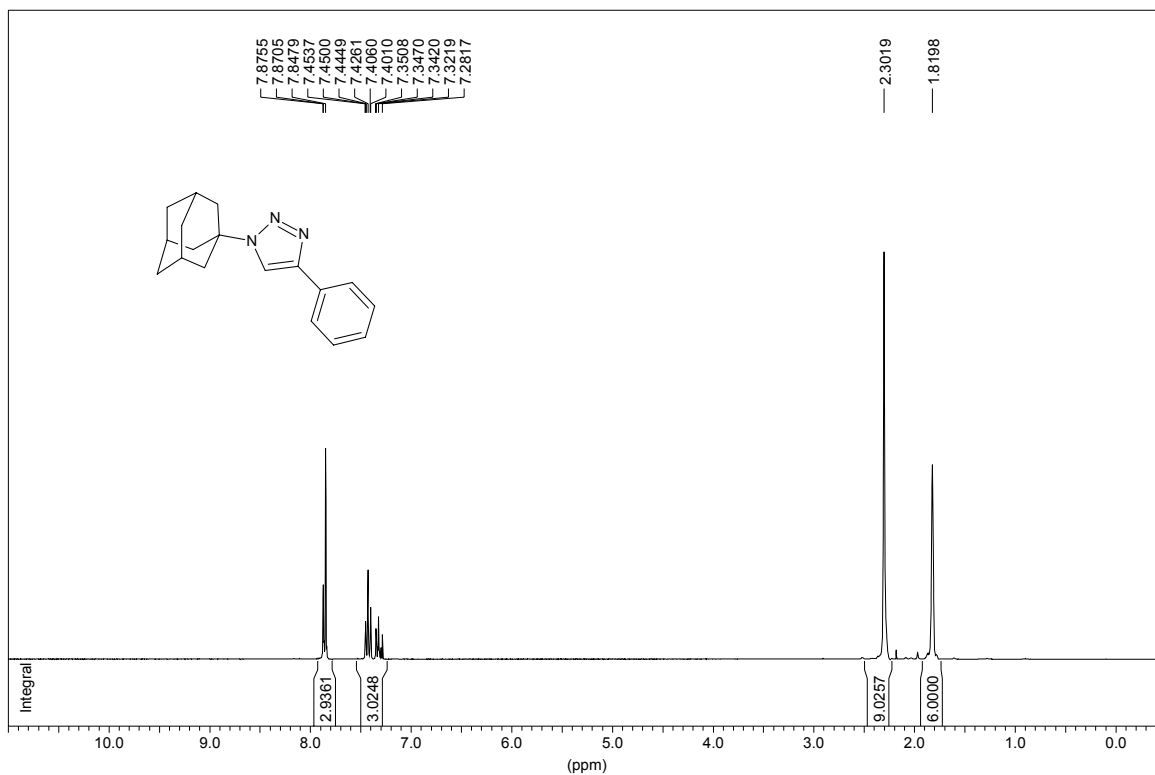
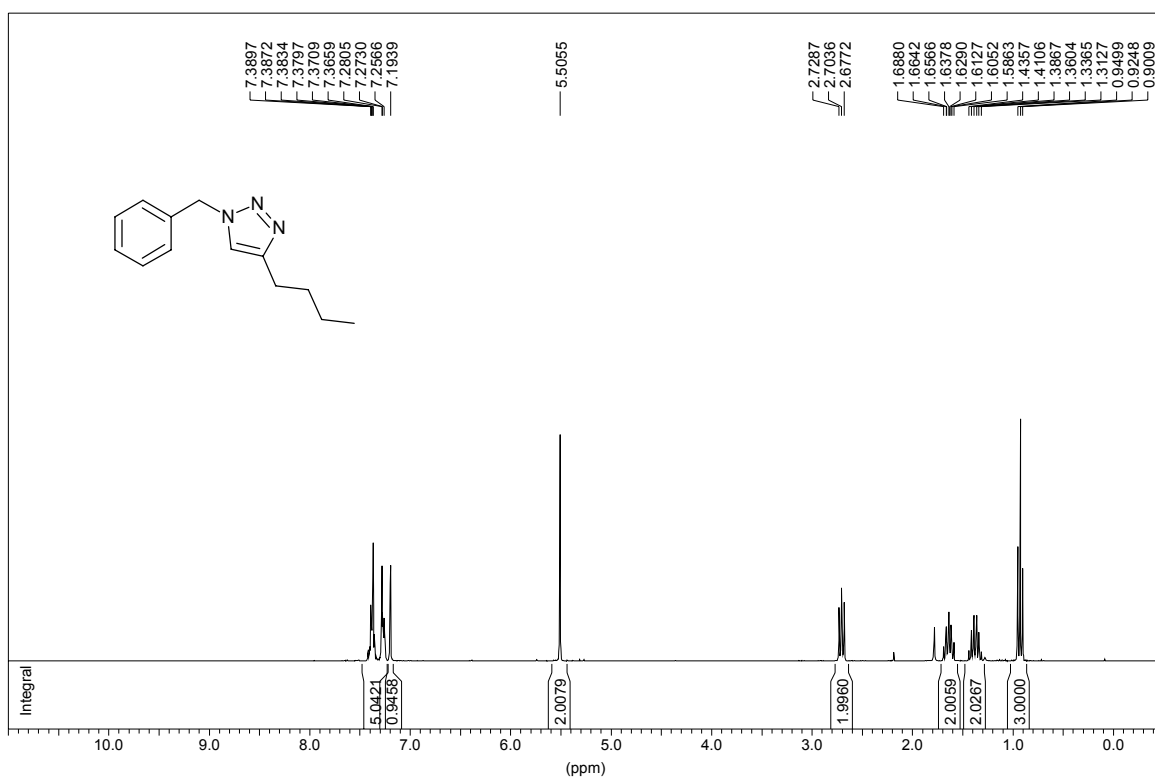
¹H NMR spectra for the « click » triazoles :

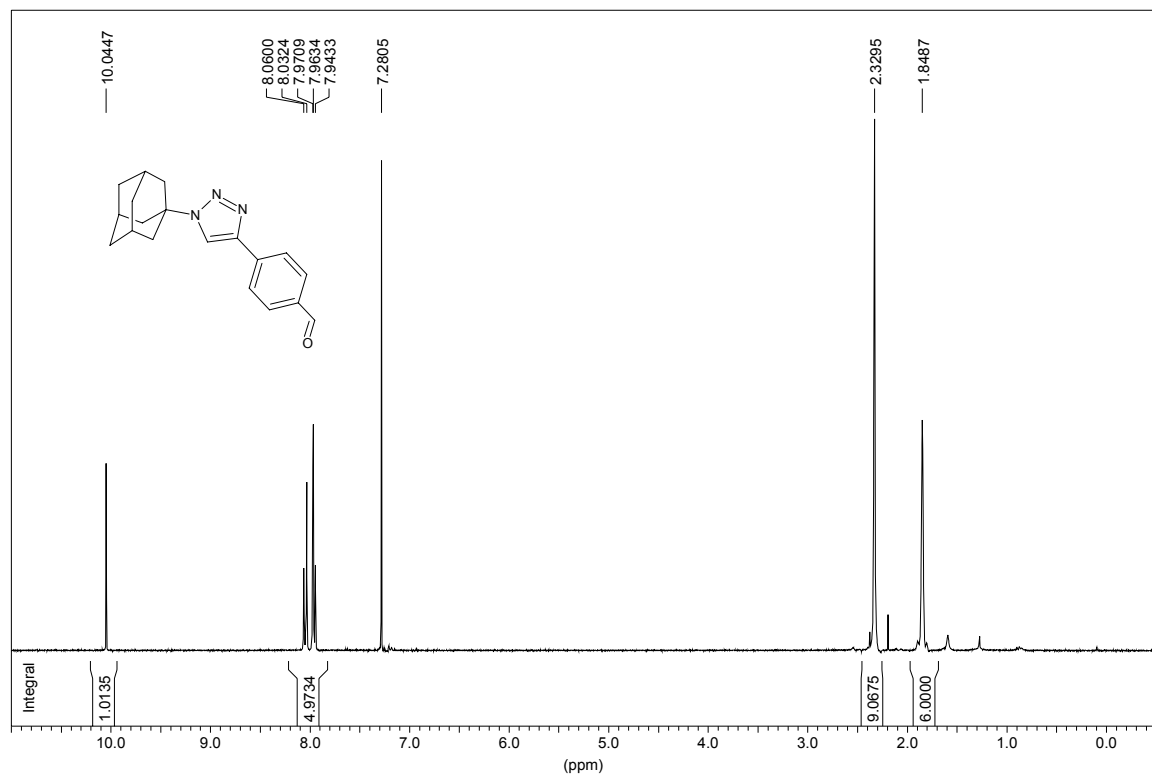
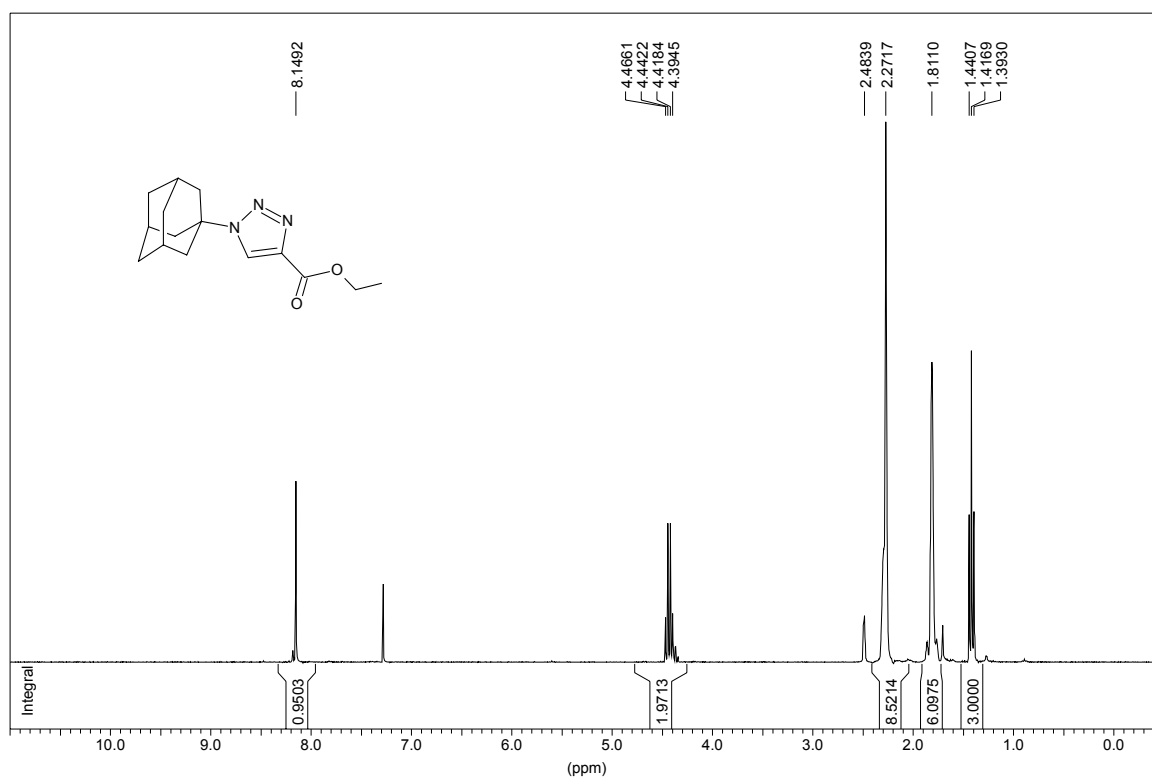


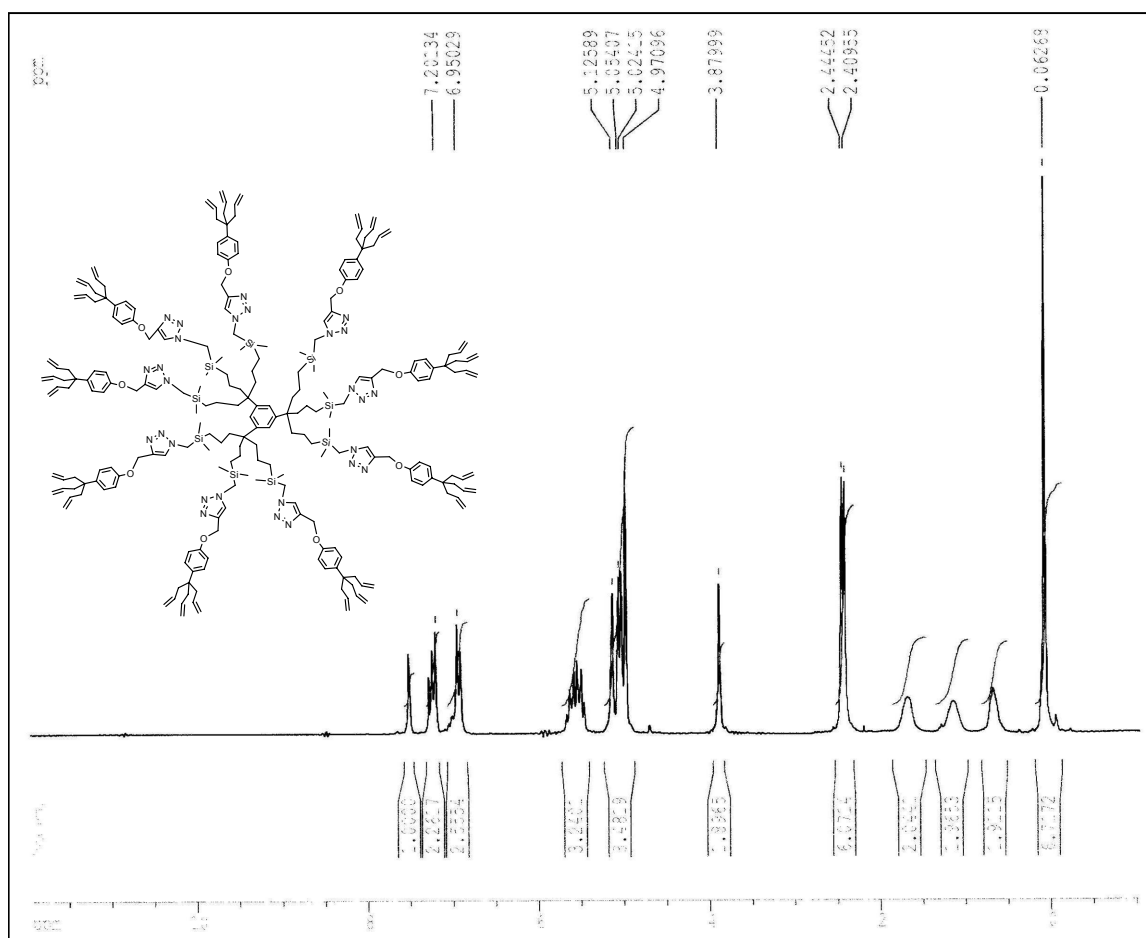
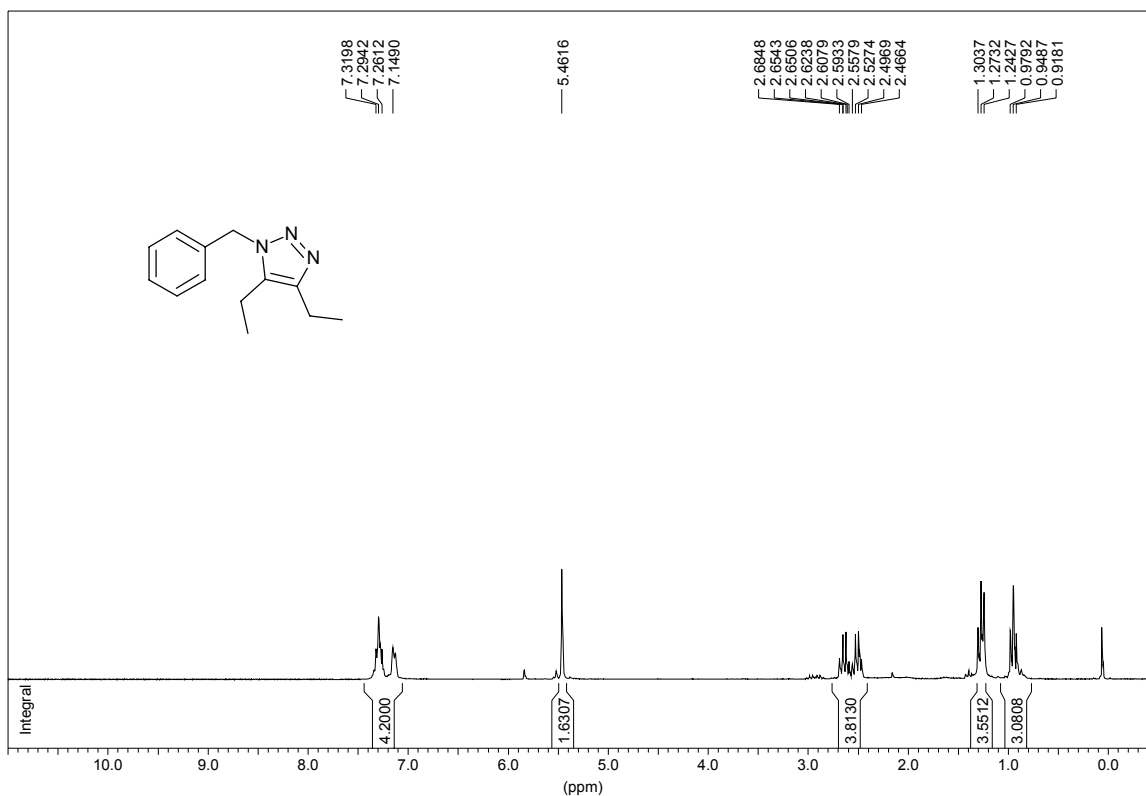












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- 3 W. Holzer, *Tetrahedron*, 1991, **47**, 9783.
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