

Supplementary Information

Iron(III) Chloride Catalyzed Glycosylation of Peracetylated Sugars with Allyl/Alkynyl Alcohols

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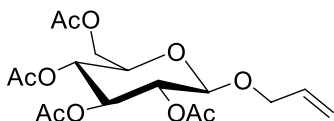
General Information

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz on a Bruker ARX-400 NMR spectrometer (Germany) with tetramethylsilane as internal standard. Column chromatography was performed using Merck (Germany) silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck silica gel GF254, 0.25 mm thickness. For visualization, TLC plates were placed under acidic vanillin. All solvents were used in dry conditions. ¹H and ¹³C NMR spectral data of the compounds are identical to previous works.¹⁻⁵

General procedure for the synthesis of allyl/alkynyl glycoside (3a-h)

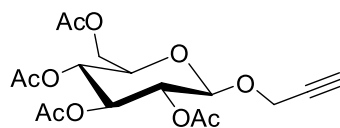
To a suspension of the respective sugar (1 mmol) and FeCl₃ (0.1 mmol) in dry dichloromethane (1 mL), the allyl/alkynyl alcohol (1.2 mmol) was added slowly. The reaction mixture was allowed to stir for 8 h at room temperature under inert atmosphere. After completion of the reaction (monitored by TLC), 10 mL dichloromethane were added and washed with water, brine and dried over NaSO₄ and evaporated to leave the crude product. Purification by column chromatography over silica gel (hexane/ethyl acetate 1:1) furnished the pure corresponding products.

Compound characterization data

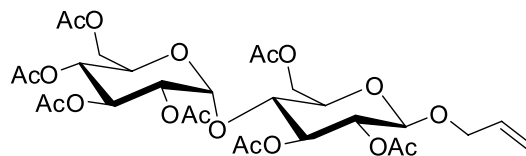


Compound **3a**:¹ 64% of yield; ¹H NMR (400 MHz, CDCl₃) δ 2.01, 2.02, 2.05, 2.09 (12H, 4 × s), 3.69 (1H,

dd, *J* 9.9, 4.8), 4.13 (1H, dd, *J* 13.1, 6.1), 4.16 (1H, dd, *J* 13.1, 6.1), 4.26 (1H, dd, *J* 13.1, 4.8), 4.56 (1H, d, *J* 7.9), 5.0 (1H, dd, *J* 10.0, 7.9), 5.09 (1H, t, *J* 10.8), 5.19-5.26 (2H, m), 5.80-5.90 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.6 (br, 2 × Ac), 20.7; 20.8; 61.7; 68.4; 70.0; 71.3; 71.8; 72.8; 99.5; 117.6; 133.3; 169.3; 169.4; 170.2; 170.6.

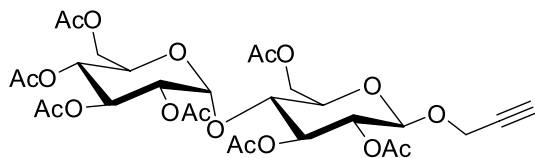


Compound **3b**:² 53% of yield; ¹H NMR (400 MHz, CDCl₃) δ 2.01, 2.03, 2.06, 2.09 (12H, 4 × s), 2.50 (1H, t, *J* 3.2), 3.72-3.76 (1H, m), 4.15 (1H, dd, *J* 12.3, 2.28), 4.28 (1H, dd, *J* 12.1, 4.78), 4.36 (2H, d, *J* 2.3), 4.79 (1H, d, *J* 7.9), 5.01 (1H, t, *J* 9.7), 5.10 (1H, t, *J* 10.5), 5.25 (1H, t, *J* 10.0); ¹³C NMR (100 MHz, CDCl₃) δ 20.6 (br, 2 × Ac), 20.7; 20.7; 55.9; 61.7; 68.2; 70.9; 71.9; 72.5; 75.5; 76.7; 77.1; 77.4; 78.1; 98.1; 169.4 (br, 2 × Ac), 170.2; 170.6.

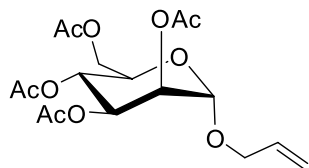


Compound **3c**:³ 48% yield; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 2.13 (s, 3H), 2.14 (s, 3H), 2.15 (s, 3H), 3.70 (1H, d, *J* 9.9), 3.85 (2H, m), 3.98 (1H, m), 4.03 (3H, m), 4.09 (1H, m), 4.15 (1H, m), 4.40 (1H, dd, *J* 12.3, 5.7 Hz), 4.42 (1H, d, *J* 8.1 Hz), 4.46 (1H, d, *J* 7.9 Hz), 4.90 (1H, dd, *J* 7.6, 3.6 Hz), 5.07 (1H, dd, *J* 10.0, 3.3 Hz), 5.31 (4H, m), 5.88 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.6 (br, 3 × Ac), 20.6; 20.7; 20.8; 20.9; 61.4; 61.5; 62.8; 67.7; 68.8; 69.4; 70.0; 71.3; 72.1; 72.7; 72.9; 75.5; 94.6; 95.5; 118.8; 133.1; 133.5; 169.4 (br, 3 × Ac), 169.9; 170.3; 170.5; 170.6.

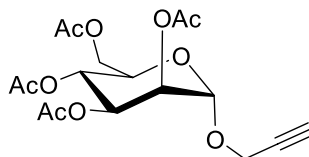
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Compound 3d:⁴ 58% of yield; ¹H NMR (400 MHz, CDCl₃) δ 2.00; 2.01, 2.03, 2.04, 2.05, 2.10, 2.15 (21H, 7 × s), 2.47 (1H, t, *J* 2.8), 3.72 (1H, m), 3.96 (1H, m), 4.05 (2H, m), 4.25 (2H, m), 4.35 (2H, d, *J* 2.5), 4.81 (1H, t, *J* 9.7), 4.85 (1H, dd, *J* 10.4, 4.01), 5.05 (1H, t, *J* 5.1) 5.28 (1H, t, *J* 9.1), 5.36 (1H, t, *J* 9.7), 5.41 (1H, d, *J* 3.9); ¹³C NMR (100 MHz, CDCl₃) δ 20.5; 20.6; 20.7 (br, 3 × Ac), 20.8; 20.9; 55.9; 61.5; 62.6; 68.0; 68.5; 69.3; 70.0; 71.1; 72.3; 72.6; 75.3; 75.5; 78.1; 95.5; 97.6; 169.4; 169.7; 169.9; 170.4; 170.5 (br, 2 × Ac).

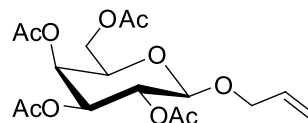


Compound 3e:¹ 51% of yield; ¹H NMR (400 MHz, CDCl₃) δ 2.00, 2.04, 2.11, 2.16 (12H, 4 × s), 3.99-4.05 (2H, m), 4.11 (1H, dd, *J* 12.1, 2.3), 4.20 (1H, m), 4.29 (1H, dd, *J* 12.2, 5.40), 4.87 (1H, d, *J* 1.67), 5.2-5.39 (m, 5 H), 5.85-5.94 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.7 (br, 2 × Ac), 20.8; 20.9; 62.5; 66.2; 68.5; 68.7; 69.1; 69.7; 96.6; 118.4; 132.9; 169.7; 169.9; 170.0; 170.6.

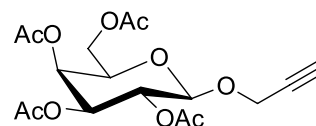


Compound 3f:⁵ 53% of yield; ¹H NMR (400 MHz, CDCl₃) δ 1.99, 2.04, 2.11, 2.17 (12H, 4 × s), 2.48 (1H, t, *J* 2.9), 4.01-4.05 (1H, m), 4.12 (1H, dd, *J* 12.2, 2.5), 4.28 (2H, d, *J* 2.2), 5.03 (1H, d, *J* 1.7), 5.28 (1H, t, *J* 3.2), 5.33 (1H, t, *J* 3.5); ¹³C NMR (100 MHz, CDCl₃) δ 20.6;

20.7; 20.8; 20.9; 55.0; 62.3; 66.1; 69.0; 69.5; 75.6; 78.0; 96.2; 169.7; 169.8; 169.9; 170.0.



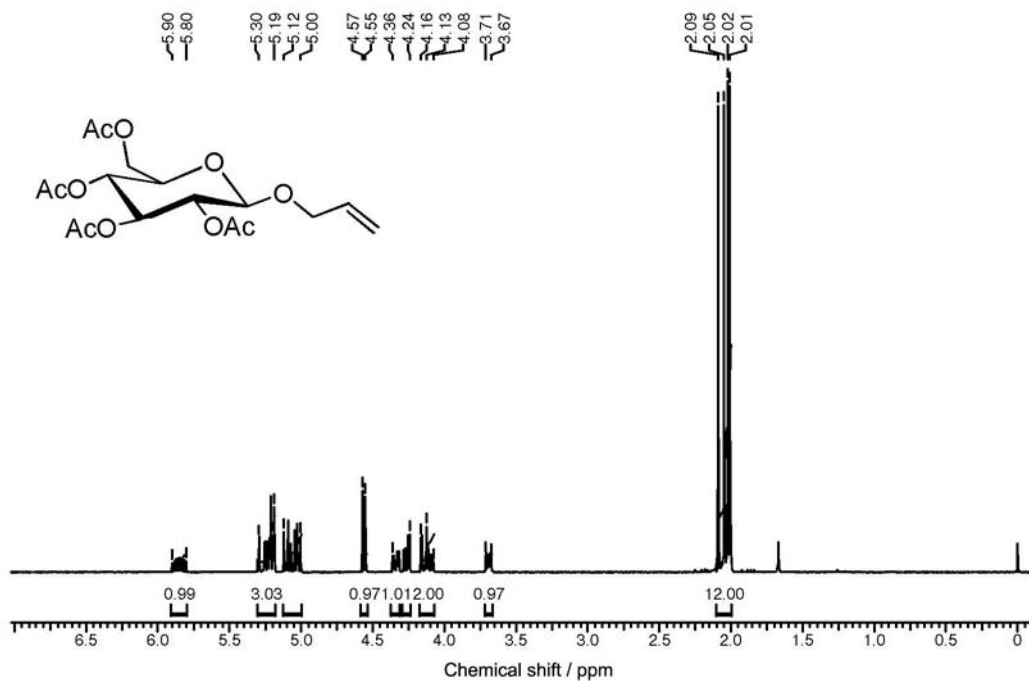
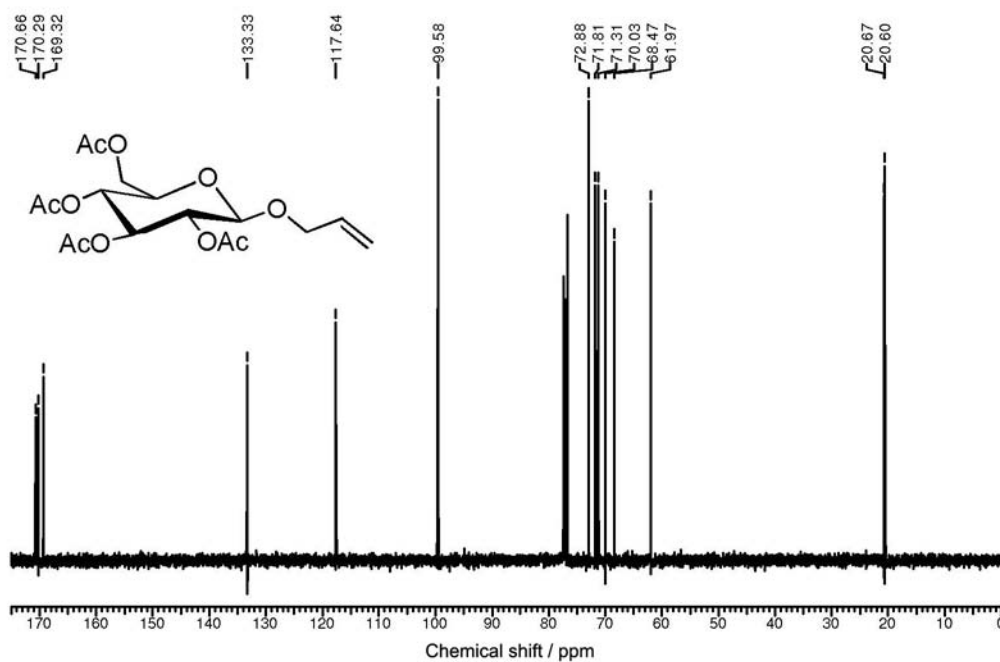
Compound 3g:¹ 64% of yield; ¹H NMR (400 MHz, CDCl₃) δ 1.99; 2.05; 2.06; 2.15 (12H, 4 × s), 4.17 (2H, dd, *J* 12.6, 6.7), 4.35 (1H, m), 4.52 (1H, d, *J* 7.9), 5.05 (1H, dd, *J* 10.6, 3.54), 5.85 (1H, m); ¹³C NMR (100 MHz, CDCl₃) δ 20.6; 20.7 (br, 2 × Ac), 20.8; 61.3; 67.1; 68.9; 70.0; 70.6; 70.9; 100.0; 117.6; 133.3; 169.4; 170.2; 170.3; 170.4.



Compound 3h:⁵ 39% of yield; ¹H NMR (400 MHz, CDCl₃) δ 1.99, 2.05, 2.09, 2.15 (12H, 4 × s), 2.45 (1H, t, *J* 2.8), 4.12 (3H, t, *J* 7.8), 4.26 (2H, d, *J* 2.2), 5.17 (1H, dd, *J* 11.3, 3.9), 5.32 (1H, d, *J* 3.7), 5.37. (1H; dd, *J* 11.1, 3.3), 5.47 (1H, dd, *J* 3.2, 1.2); ¹³C NMR (100 MHz, CDCl₃) δ 20.6 (br, 2 × Ac), 20.7 (br, 2 × Ac), 20.8; 55.3; 61.5; 66.8; 67.4; 67.7; 67.9; 75.2; 77.2; 94.4; 169.8; 170.2; 170.2; 170.4 (br, 2 × Ac).

References

1. Lin, Y. A.; Chalker, J. M.; Davis, B. J.; *J. Am. Chem. Soc.* **2010**, *132*, 16805.
2. Hoheisel, T. H.; Frauenrath, H.; *Org. Lett.* **2008**, *10*, 4525.
3. Kopitzki, S.; Jensen, K. J.; Thien, J.; *Chem. Eur. J.* **2010**, *16*, 7017.
4. Otsuka, A.; Sakurai, K.; Hasegawa, T.; *Chem. Commun.* **2009**, *36*, 5442.
5. Cecioni, S.; Oerthel, V.; Iehl, J.; Holler, M.; Goyard, D.; Praly, J. R.; Imbert, A.; Nieregarten, J. F.; Vidal, S.; *Chem. Eur. J.* **2011**, *17*, 3252.

Reproduced ^1H and ^{13}C NMR spectraFigure S1. ^1H NMR (400 MHz, CDCl_3) spectrum of **3a**.Figure S2. ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3a**.

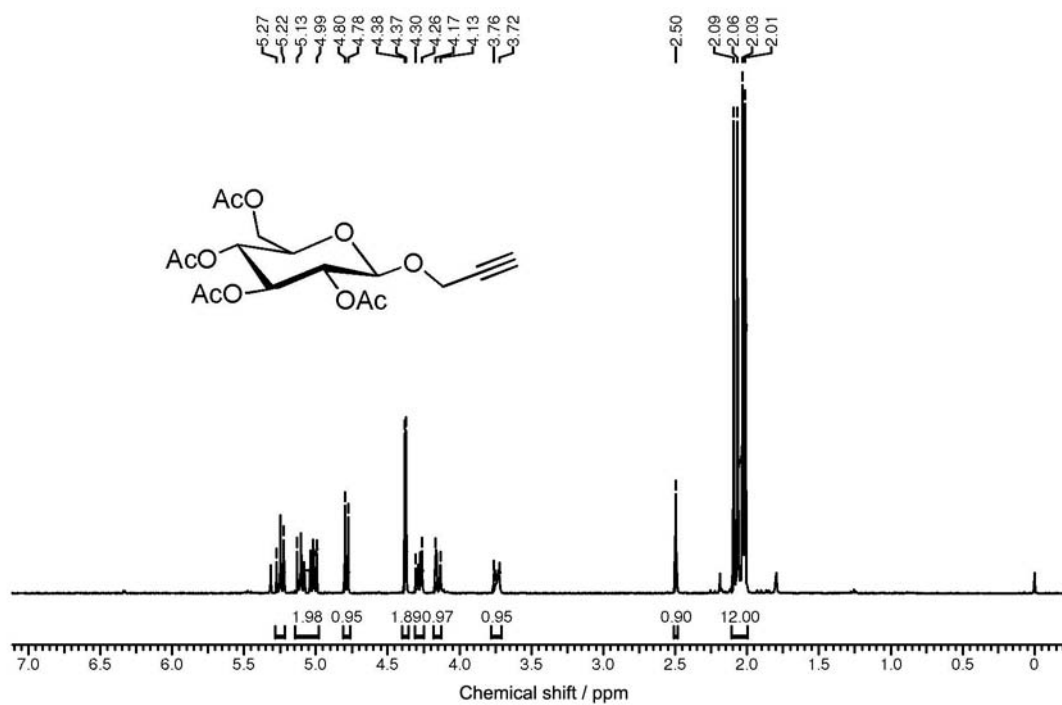


Figure S3. ¹H NMR (400 MHz, CDCl₃) spectrum of **3b**.

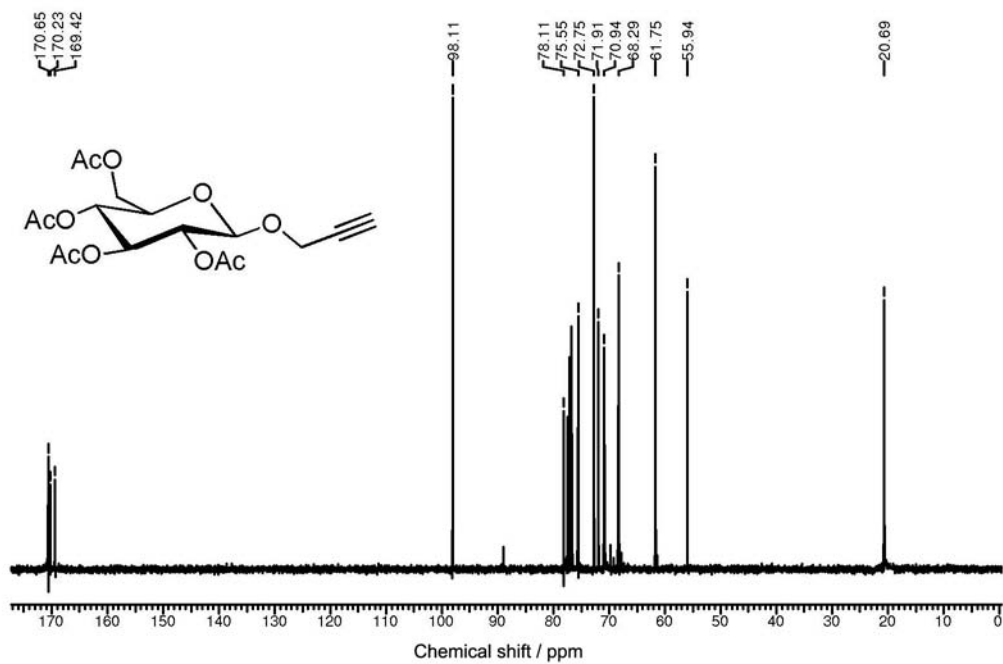


Figure S4. ¹³C NMR (100 MHz, CDCl₃) spectrum of **3b**.

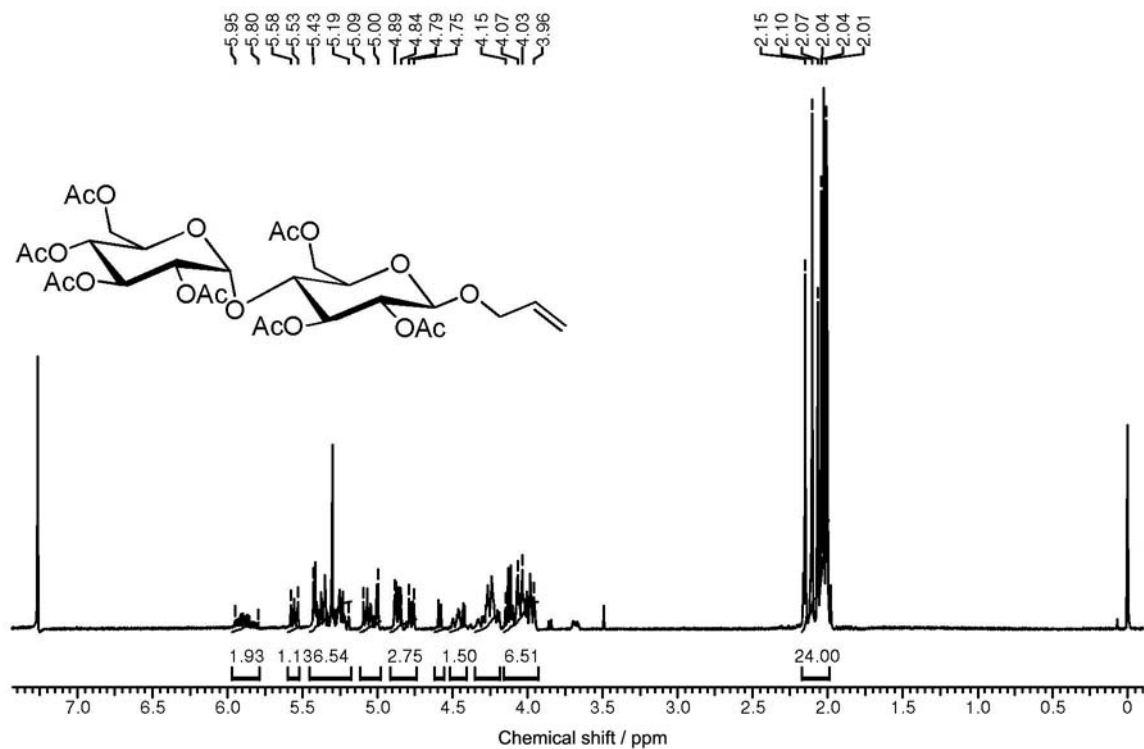


Figure S5. ^1H NMR (400 MHz, CDCl_3) spectrum of **3c**.

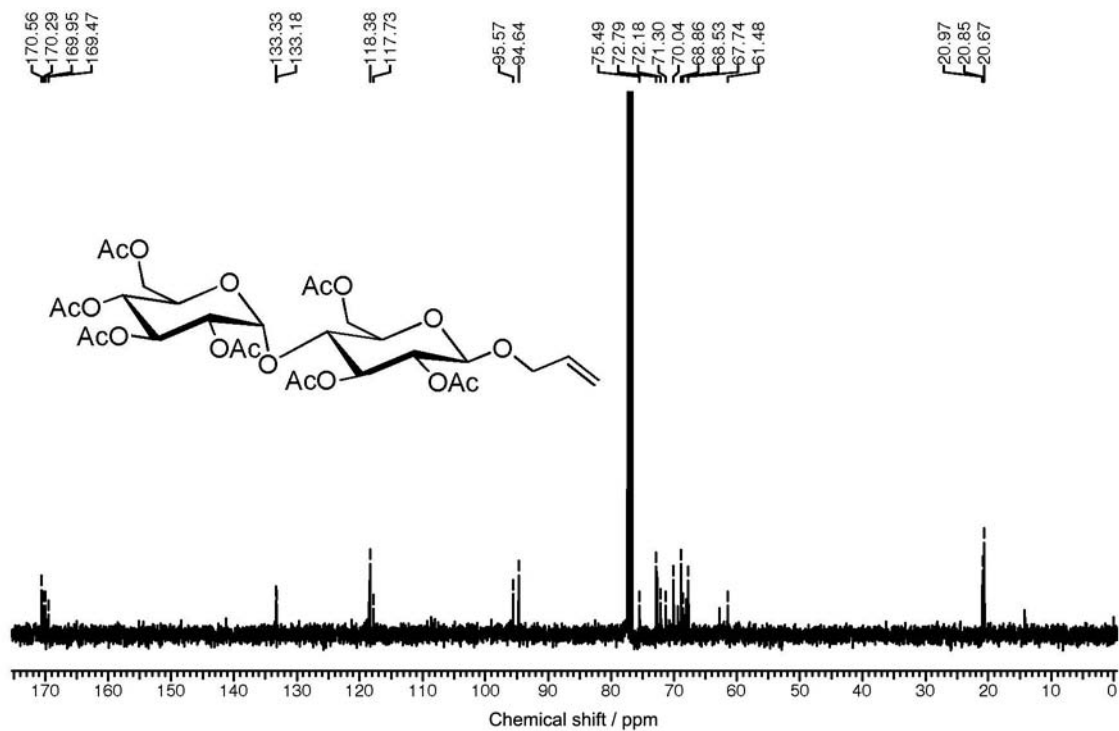


Figure S6. ^{13}C NMR (100 MHz, CDCl_3) spectrum of **3c**.

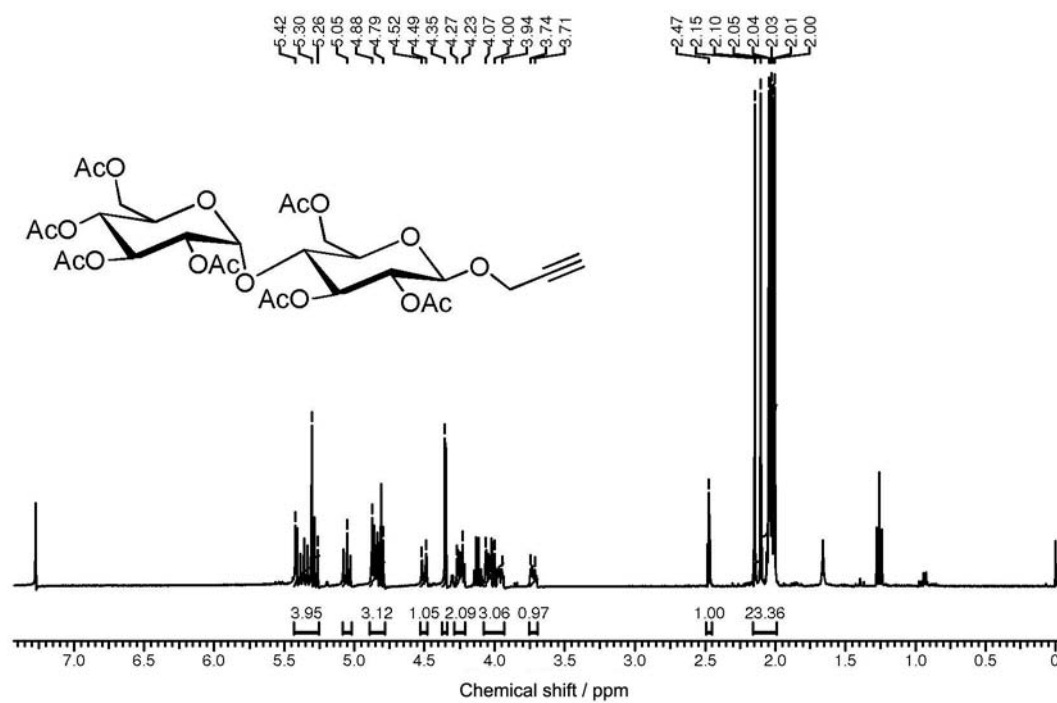


Figure S7. ¹H NMR (400 MHz, CDCl₃) spectrum of 3d.

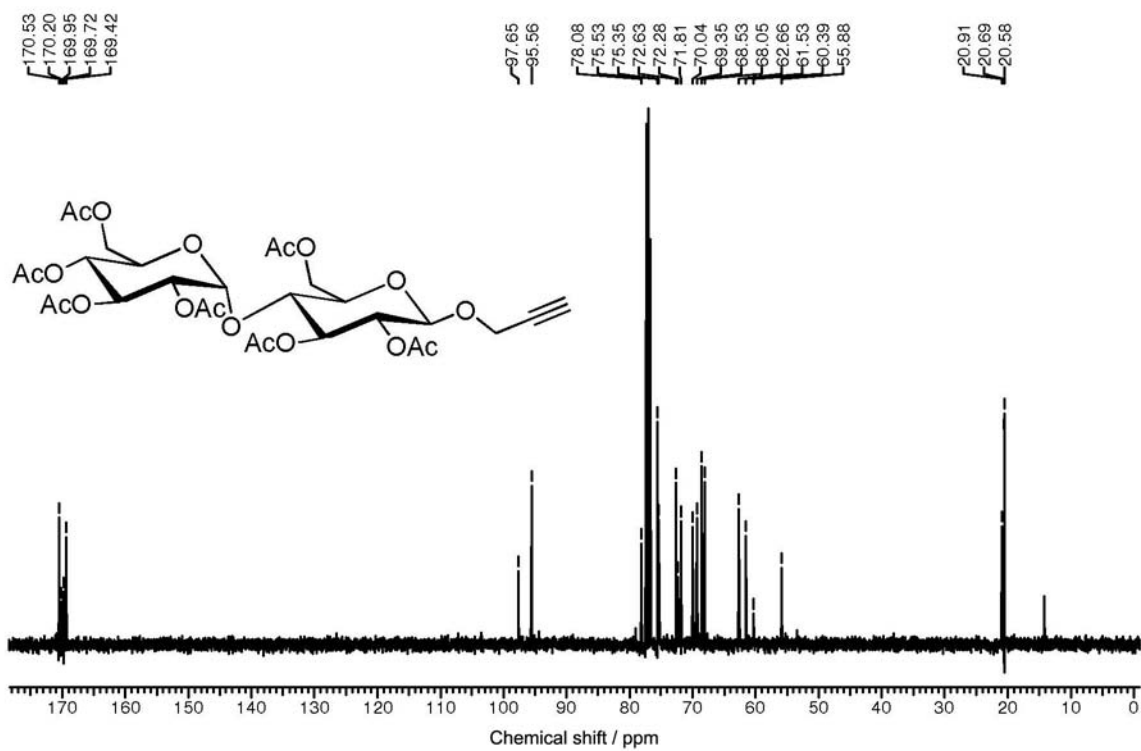


Figure S8. ¹³C NMR (100 MHz, CDCl₃) spectrum of 3d.

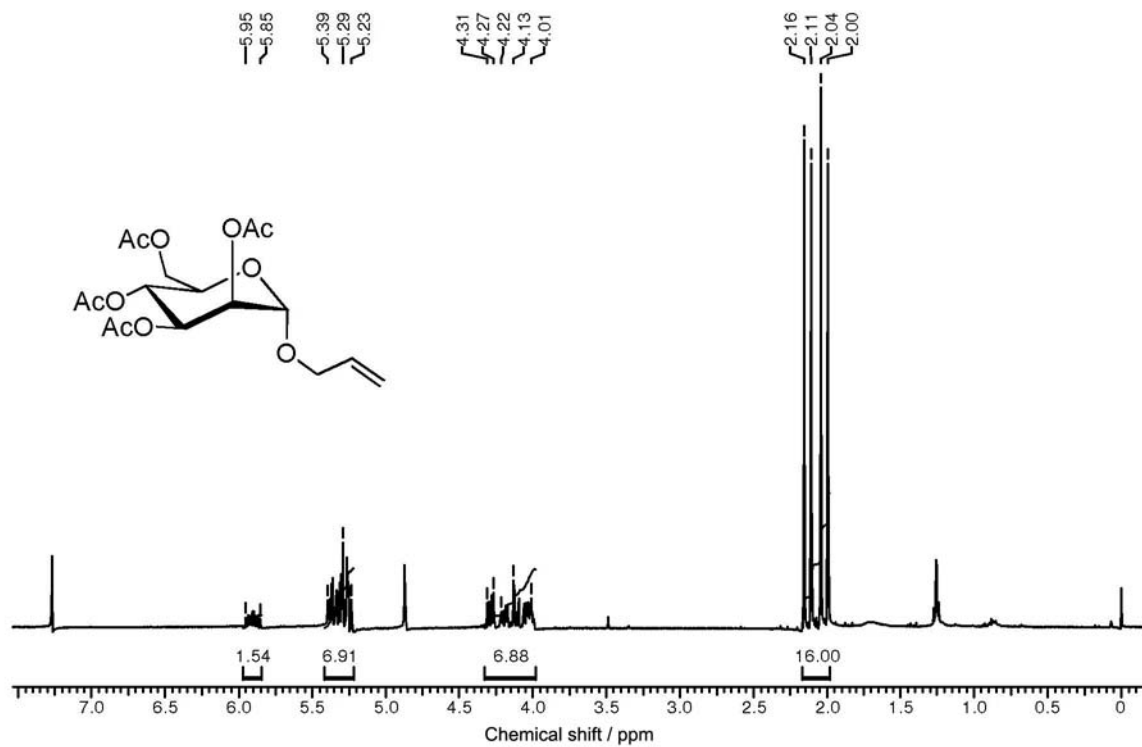


Figure S9. ¹H NMR (400 MHz, CDCl₃) spectrum of 3e.

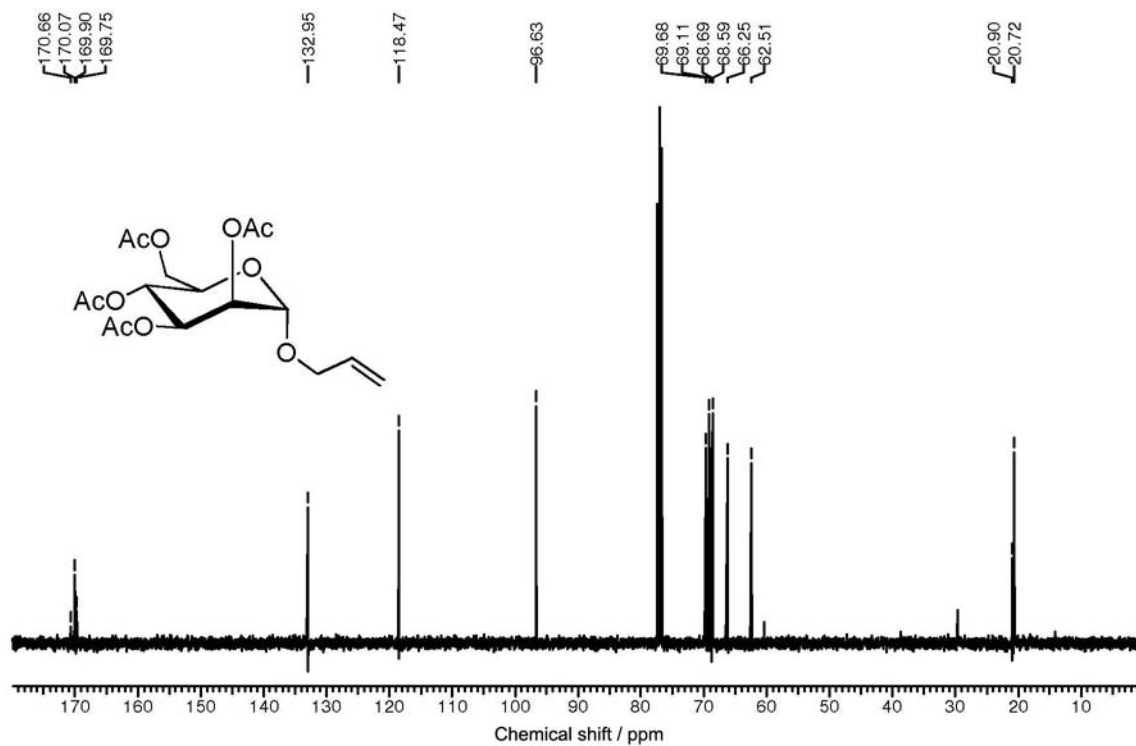
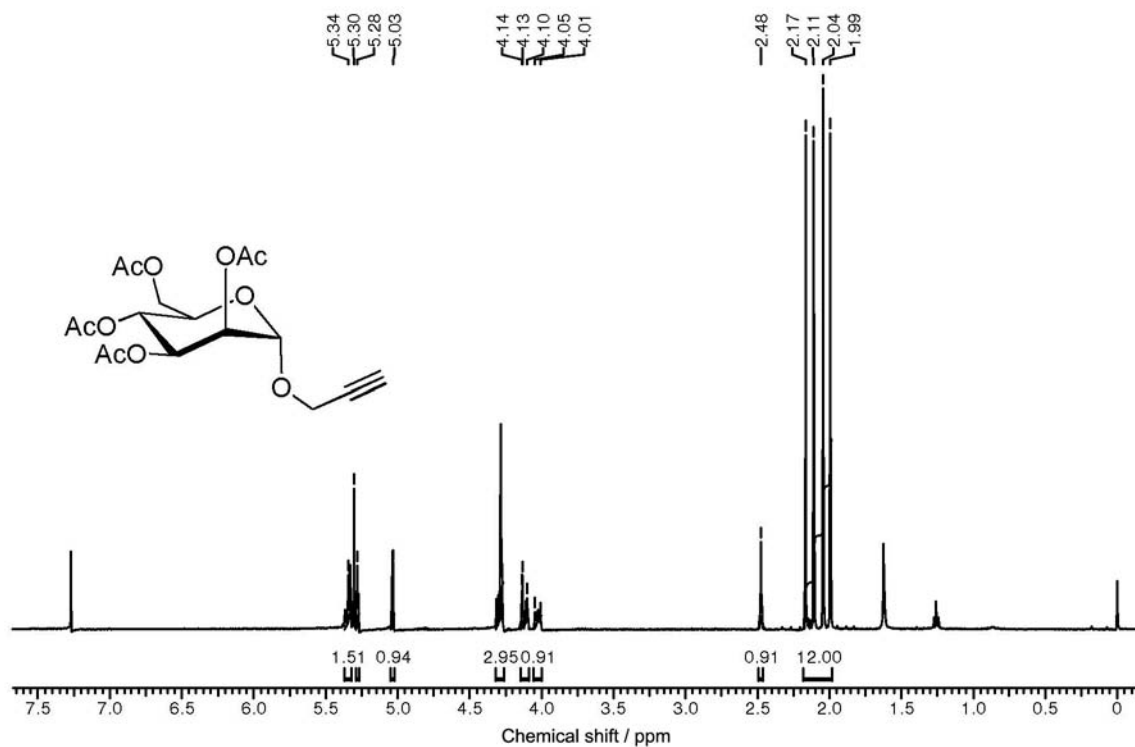
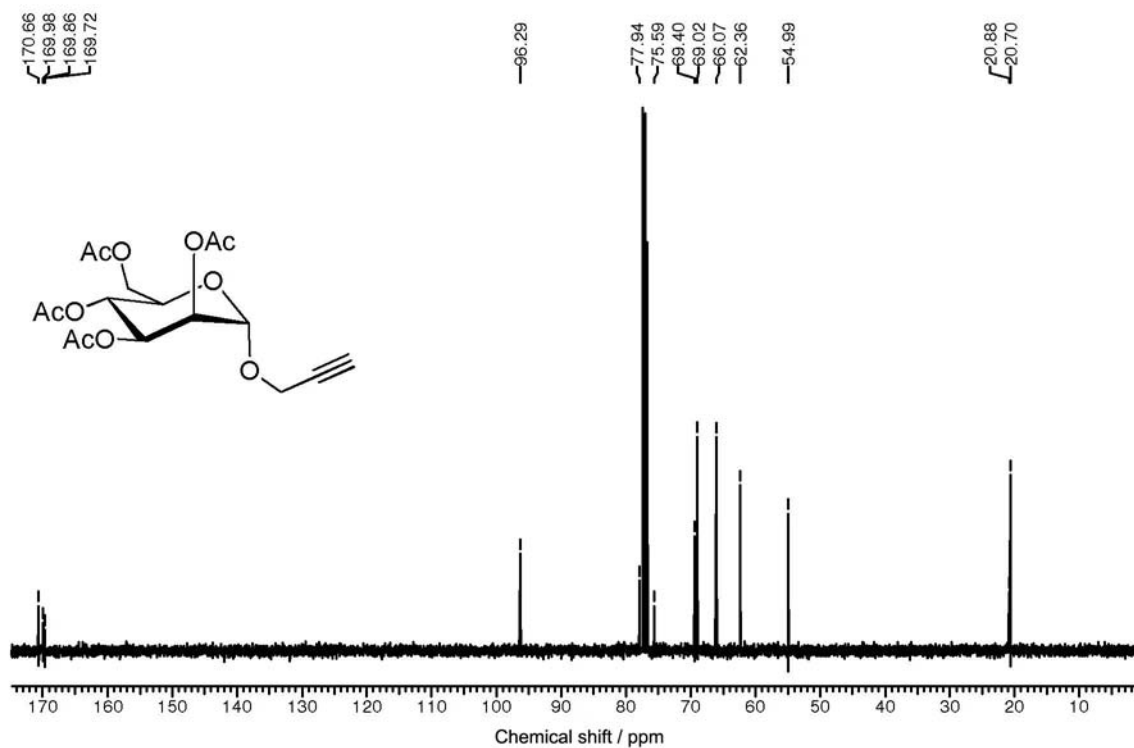


Figure S10. ¹³C NMR (100 MHz, CDCl₃) spectrum of 3e.

Figure S11. ¹H NMR (400 MHz, CDCl₃) spectrum of 3f.Figure S12. ¹³C NMR (100 MHz, CDCl₃) spectrum of 3f.

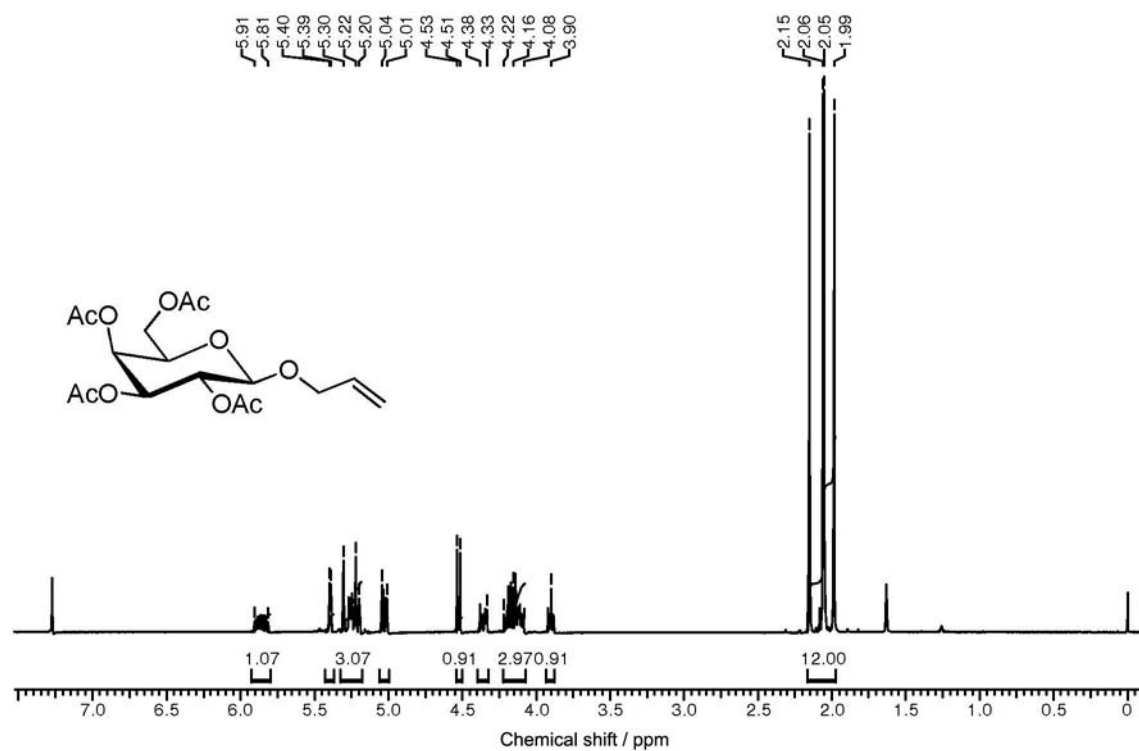


Figure S13. ¹H NMR (400 MHz, CDCl₃) spectrum of **3g**.

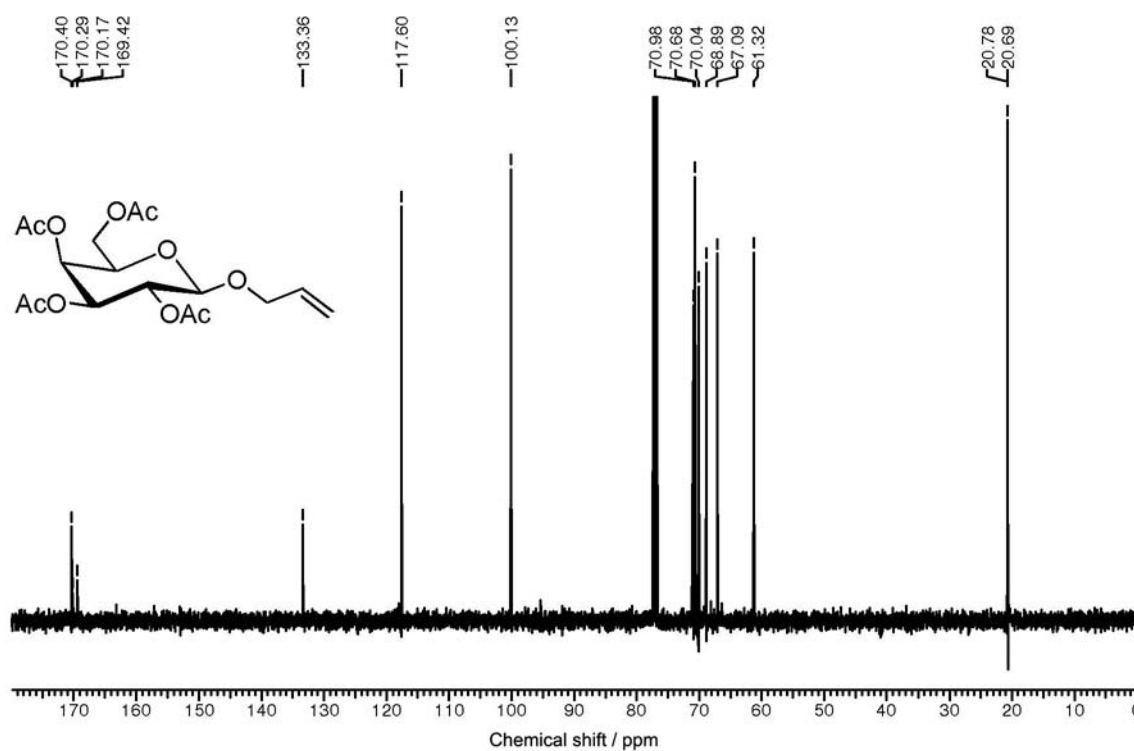


Figure S14. ¹³C NMR (100 MHz, CDCl₃) spectrum of **3g**.

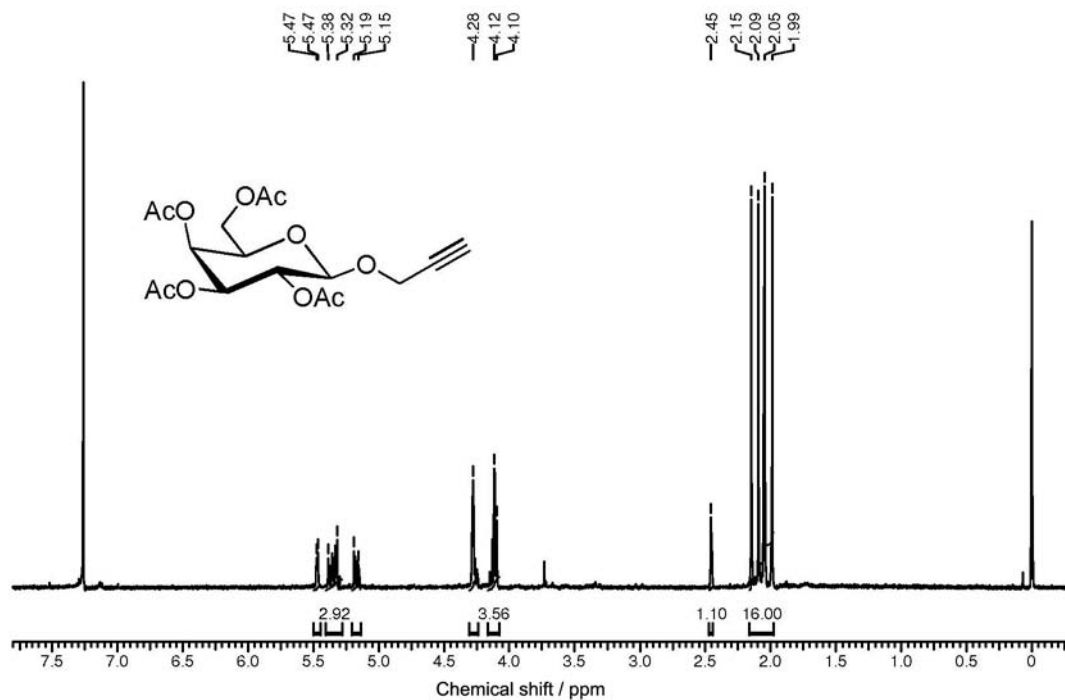


Figure S15. ¹H NMR (400 MHz, CDCl₃) spectrum of 3h.

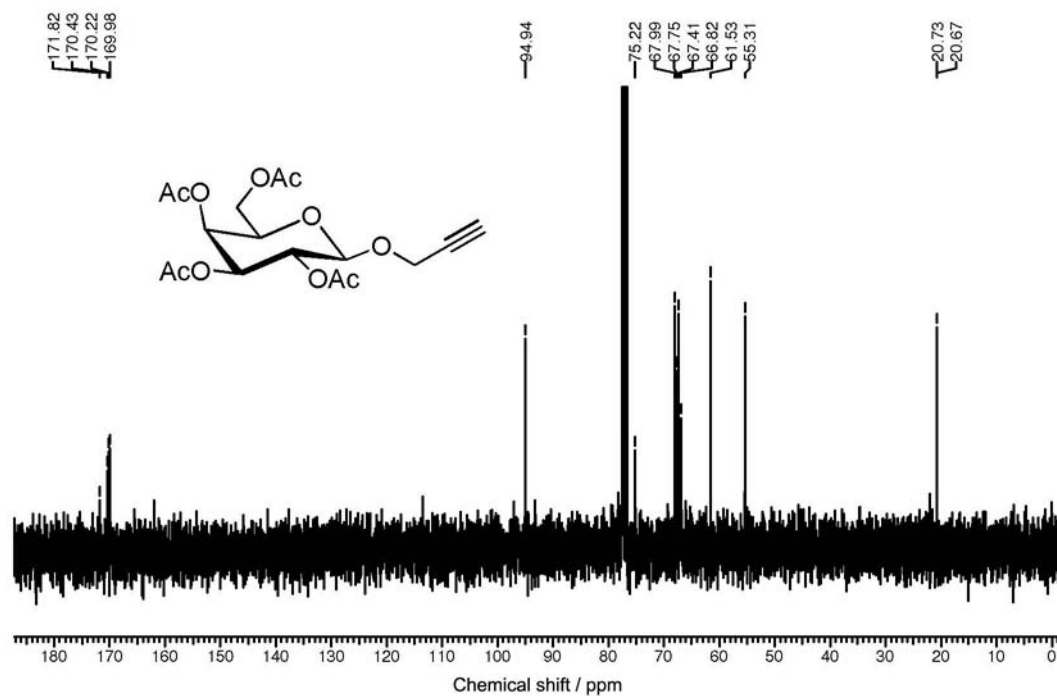


Figure S16. ¹³C NMR (100 MHz, CDCl₃) spectrum of 3h.