Supporting Information

Au(I) π-Bis(*tert*-butyldimethylsilyl)acetylene Triphenylphosphine Complex: An Effective Catalyst for Au(I)-Catalyzed Reactions

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General experimental procedures. Unless otherwise noted, all reagents were obtained commercially and used without further purification. Solvents were purchased from local suppliers and treated in standard process if necessary. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with Brucker AMX 400, MERCURY 300, Aglient 500/54 or Aglient 400-MR spectrometers. ^{31}P NMR chemical shifts were reported relative to external aqueous 85% H_3PO_4 (δ 0.00 ppm). MALDI-HRMS were recorded with IonSpec 4.7T. ESI^+-HRMS spectra were recorded with Bruker APEXIII 7.0 TESLA FTMS. EI^+-MS were recorded with Agilent Technologies 5973N, EI^+-HRMS were recorded with Waters Micromass GCT Premier, and the electron energy was 70eV. IR spectra were collected with Nicolet iN10 MX spectrometer. Raman spectra were recorded with Thermo Scientific DXR Raman microscope. Single crystal X-ray data were collected on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å) at 133 K. All optical rotations were measured at room temperature using the sodium D line. Preparation of the known substrates adopted literature methods.

Table S1. Characterization data for the new compounds and references for the known compounds.

1	X-ray diffraction analysis of complex **1** (CCDC 1043329): $C_{32}H_{45}AuF_6PSbSi_2$, *Mr* =949.55 g.mol^{-1}, colorless block, crystal size 0.22 × 0.18 × 0.09 mm. Momoclinic, space group P2(1)/n, a = 15.3104(16) Å, b = 12.4711(14) Å, c = 19.992(2) Å, α = 90°, β = 103.698(2)°, γ = 90°, V = 3708.7(7) Å^3, T = 140 K, Z = 4, D_{cal} = 1.701 g·cm^{-3}, λ = 0.71073 Å, μ(Mo-Kα) = 4.838 mm^{-1}. Empirical absorption correction (T_{min}= 0.416, T_{max} = 0.670), Bruker APEX-II CCD diffractometer, 0.994 <θ< 30.560°, 35824 measured reflections, 11309 independent reflections, 8803 reflections with I > 2σ(I). Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.0342 [I > 2σ(I)], wR_2 = 0.0995, 398 parameters, H atoms riding, S = 1.040.
5	R. West, L. C. Quass, *J. Organomet. Chem.*, 1969, **18**, 55-67.
7 & **8**	Y. Tang, J. Li, Y. Zhu, Y. Li, B. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 18396-18405.
9	**9α**: $[\alpha]_D^{27}$ = 56.5 (*c* 0.76, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05–8.01 (m, 3H), 7.98–7.92 (m, 4H), 7.56–7.47 (m, 5H), 7.43–7.33 (m, 7H), 6.67 (d, *J* = 2.8 Hz, 1H), 5.94–5.87 (m, 1H), 5.76 (t, *J* = 9.9 Hz, 1H), 4.67–4.60 (m, 2H), 4.49 (dd, *J* = 12.5, 4.6

	Hz, 1H), 2.75 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.31 (ddd, *J* = 13.8, 11.6, 3.7 Hz, 1H), 1.62 (ddd, *J* = 7.0, 6.0, 4.1 Hz, 1H), 0.94–0.83 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.14, 165.71, 165.39, 164.36, 134.68, 133.35, 133.23, 132.99, 132.13, 130.73, 130.68, 129.74, 129.68, 129.36, 129.11, 128.39, 128.32, 127.21, 124.99, 99.88, 91.90, 77.25, 77.00, 76.75, 74.73, 70.94, 69.78, 69.64, 62.91, 34.50, 9.05, 0.75. HRMS-MALDI: calcd for $C_{39}H_{32}O_9Na$ $[M+Na]^+$ 667.1939, found 667.1949. **9β**: $[\alpha]_D^{27}$ = -2.59 (*c* 0.95, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.96 (dd, *J* = 14.5, 7.8 Hz, 5H), 7.56–7.47 (m, 4H), 7.45–7.35 (m, 7H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.29 (dd, *J* = 9.5, 1.7 Hz, 1H), 5.70 (t, *J* = 9.4 Hz, 1H), 5.59–5.53 (m, 1H), 4.66 (dd, *J* = 12.2, 2.8 Hz, 1H), 4.52 (dd, *J* = 12.2, 4.9 Hz, 1H), 4.28–4.22 (m, 1H), 2.80 (ddd, *J* = 12.4, 4.8, 1.9 Hz, 1H), 2.26 (dd, *J* = 21.6, 11.7 Hz, 1H), 1.53–1.47 (m, 1H), 0.86 (d, *J* = 7.7 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.16, 165.67, 165.38, 163.92, 134.21, 133.40, 133.30, 132.97, 132.12, 130.65, 130.39, 129.77, 129.75, 129.73, 129.67, 129.24, 129.01, 128.41, 128.27, 126.97, 125.17, 99.93, 91.83, 74.29, 73.07, 71.05, 69.31, 63.25, 35.04, 8.85, 0.63. HRMS-MALDI: calcd for $C_{39}H_{32}O_9Na$ $[M+Na]^+$ 667.1939, found 667.1955.
14	Y. Li, X. Yang, Y. Liu, C. Zhu, Y. Yang, B. Yu, *Chem. Eur. J.*, 2010, **16**, 1871-1882.
15	M. A. Oberli, P. Bindschädler, D. B. Werz, P. H. Seeberger, *Org. Lett.*, 2008, **10**, 905-908.
16	**16α**: $[\alpha]_D^{26}$ = 42.7 (*c* 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08–8.04 (m, 2H), 8.00–7.93 (m, 4H), 7.57–7.53 (m, 1H), 7.52–7.47 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 4H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.75 (ddd, *J* = 11.4, 9.6, 5.3 Hz, 1H), 5.58 (t, *J* = 9.8 Hz, 1H), 5.09–5.03 (m, 2H), 4.99 (dd, *J* = 10.1, 1.6 Hz, 1H), 4.59 (dd, *J* = 12.0, 2.7 Hz, 1H), 4.47 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.36 (ddd, *J* = 9.8, 5.4, 2.7 Hz, 1H), 3.76 (dt, *J* = 9.6, 6.7 Hz, 1H), 3.47 (dt, *J* = 9.6, 6.5 Hz, 1H), 2.53 (dd, *J* = 12.8, 5.3 Hz, 1H), 2.18 (q, *J* = 6.9 Hz, 1H), 2.06–1.98 (m, 2H), 1.80–1.73 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.17, 165.72, 165.55, 137.96, 133.23, 133.02, 132.98, 129.80, 129.74, 129.66, 129.62, 129.19, 128.34, 128.29, 114.99, 97.00, 70.36, 70.11, 68.18, 67.15, 63.53, 35.39, 30.32, 28.57. HRMS-ESI$^+$: calcd for $C_{31}H_{32}O_8Na$ $[M+Na]^+$ 567.1989, found 567.2002. **16β**: $[\alpha]_D^{28}$ = -27.0 (*c* 0.67, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.94 (t, *J* = 8.2 Hz, 4H), 7.51 (dt, *J* = 20.6, 7.0 Hz, 3H), 7.37 (dt, *J* = 14.9, 7.8 Hz, 6H), 5.80 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.55 (t, *J* = 9.5 Hz, 1H), 5.48–5.38 (m, 1H), 5.02 (d, *J* = 17.4 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.76 (d, *J* = 8.8 Hz, 1H), 4.61 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.49 (dd, *J* = 11.9, 5.5 Hz, 1H), 4.00 (ddd, *J* = 9.0, 5.2, 3.5 Hz, 1H), 3.93 (dd, *J* = 15.9, 6.6 Hz, 1H), 3.55 (dd, *J* = 16.2, 6.8 Hz, 1H), 2.59 (dd, *J* = 12.4, 4.4 Hz, 1H), 2.12 (q, *J* = 7.1 Hz, 2H), 1.96 (dd, *J* = 21.8, 12.0 Hz, 1H), 1.77–1.67 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.20, 165.85, 165.49, 137.93, 133.29, 133.22, 132.99, 129.77, 129.73, 129.72, 129.70, 129.38, 129.15, 128.37, 128.29, 114.95, 99.67, 72.10, 71.55, 70.30, 69.09, 63.73, 36.50, 30.08, 28.70. HRMS-ESI$^+$: calcd for $C_{31}H_{32}O_8Na$ $[M+Na]^+$ 567.1989, found 567.1995.
17	**17α**: $[\alpha]_D^{26}$ = 14.9 (*c* 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 2H), 7.96 (dd, *J* = 9.9, 8.7 Hz, 4H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.51–7.46 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36 (dd, *J* = 10.9, 4.4 Hz, 4H), 5.78–5.69 (m, 1H), 5.61 (t, *J* = 9.7 Hz, 1H), 5.56 (d, *J* = 4.9 Hz, 1H), 5.13 (d, *J* = 2.7 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.0 Hz,

	1H), 4.56 (d, *J* = 9.6 Hz, 1H), 4.49 (dd, *J* = 11.6, 5.5 Hz, 2H), 4.34 (dd, *J* = 4.8, 2.1 Hz, 1H), 4.30 (d, *J* = 7.9 Hz, 1H), 4.07 (t, *J* = 6.2 Hz, 1H), 3.89 (dd, *J* = 10.2, 6.4 Hz, 1H), 3.77 (dd, *J* = 10.2, 6.6 Hz, 1H), 2.57 (dd, *J* = 12.9, 5.2 Hz, 1H), 2.02 (td, *J* = 12.7, 3.5 Hz, 1H), 1.61 (s, 3H), 1.44 (s, 3H), 1.35 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.22, 165.73, 165.46, 133.17, 133.00, 132.88, 129.81, 129.72, 129.61, 129.25, 128.29, 128.28, 109.28, 108.61, 97.03, 96.33, 70.95, 70.63, 70.60, 70.15, 70.12, 68.22, 66.33, 66.28, 63.40, 35.25, 26.14, 25.95, 24.93, 24.50. HRMS-ESI$^+$: calcd for $C_{39}H_{42}O_{13}Na$ $[M+Na]^+$ 741.2518, found 741.2517. **17β**: $[\alpha]_D^{28}$ = -47.2 (*c* 0.39, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.93 (dd, *J* = 9.4, 7.9 Hz, 4H), 7.51 (dt, *J* = 13.3, 7.3 Hz, 3H), 7.37 (ddd, *J* = 15.5, 11.6, 7.9 Hz, 6H), 5.57–5.53 (m, 2H), 5.45 (ddd, *J* = 11.5, 9.5, 5.2 Hz, 1H), 4.88 (dd, *J* = 9.5, 1.8 Hz, 1H), 4.60 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.57 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.47 (dd, *J* = 12.0, 5.4 Hz, 1H), 4.31 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.17 (dd, *J* = 7.9, 1.6 Hz, 1H), 4.07–3.98 (m, 2H), 3.79 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.65 (ddd, *J* = 12.3, 5.0, 1.5 Hz, 1H), 1.98 (td, *J* = 12.0, 9.7 Hz, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.19, 165.74, 165.48, 133.27, 133.15, 132.95, 129.77, 129.74, 129.72, 129.71, 129.44, 129.15, 128.36, 128.34, 128.27, 109.38, 108.68, 100.26, 96.29, 72.08, 71.41, 71.37, 70.71, 70.40, 70.33, 69.13, 67.84, 63.71, 36.39, 29.69, 26.05, 25.96, 24.97, 24.39. HRMS-ESI$^+$: calcd for $C_{39}H_{42}O_{13}Na$ $[M+Na]^+$ 741.2518, found 741.2521.
18	S. Lee, S. Maharjan, K. Kim, N.-J. Kim, H.-J. Choi, Y.-G. Kwon, Y.-G. Suh, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 7102-7105.
19 & **20**	N. Ghosh, S. Nayak, A. K. Sahoo, *J. Org. Chem.*, 2011, **76**, 500-511
21 & **22**	A. S. K. Hashmi, M. C. Blanco, E. Kurpejović, W. Frey, J. W. Bats, *Adv. Synth. Catal.*, 2006, **348**, 709-713.
23 & **24**	C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.*, 2006, **12**, 1677-1693.
25 & **26**	L. Zhang, S. Wang, *J. Am. Chem. Soc.*, 2006, **128**, 1442-1443.

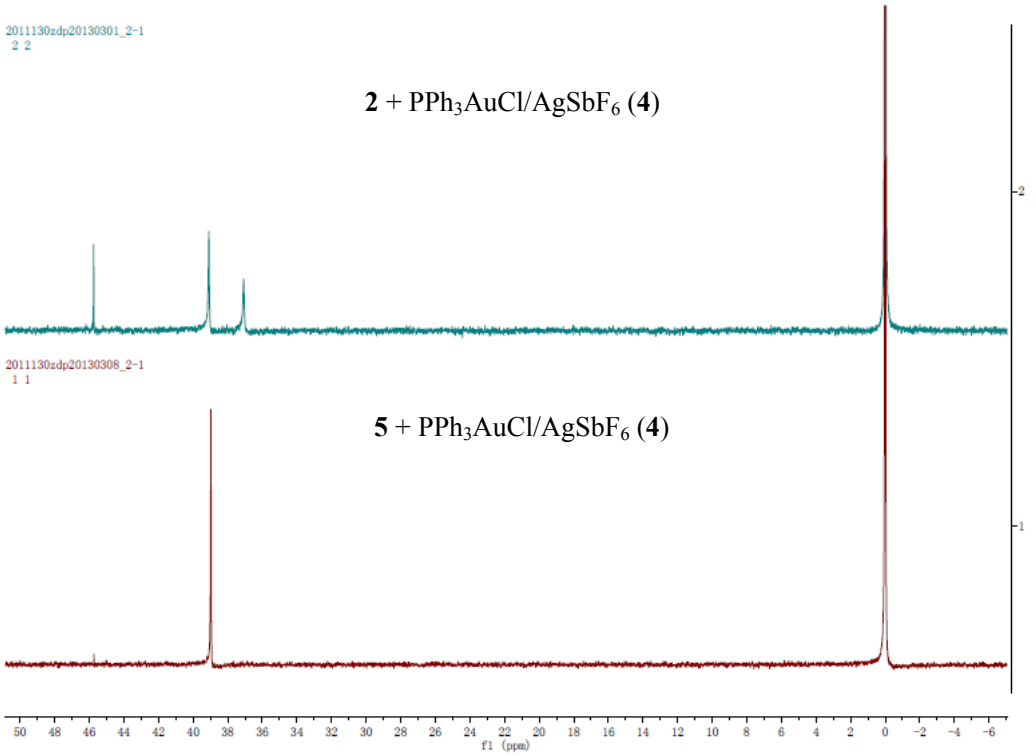


Figure S1. ^{31}P NMR spectra of the mixtures of the alkynes (**2** and **5**) and $PPh_3AuCl/AgSbF_6$.

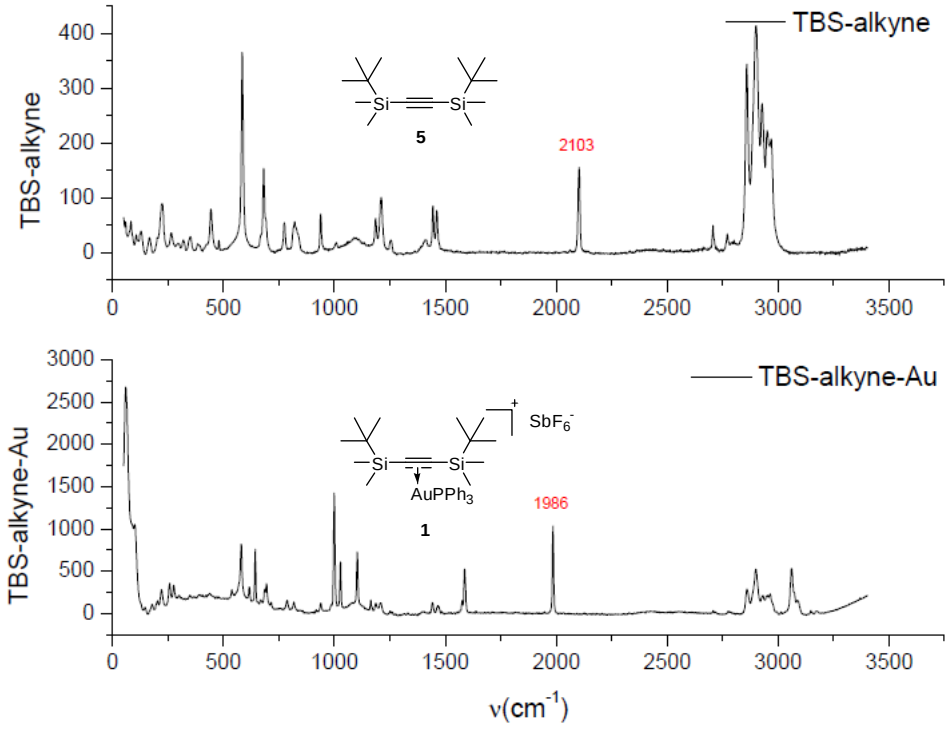
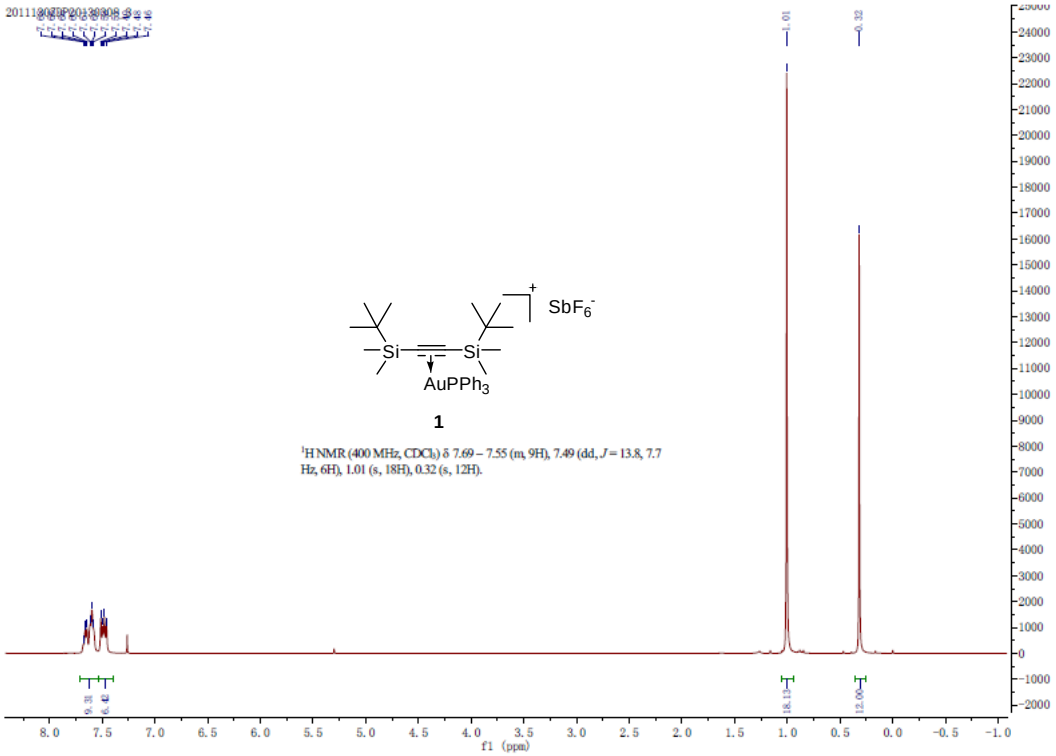
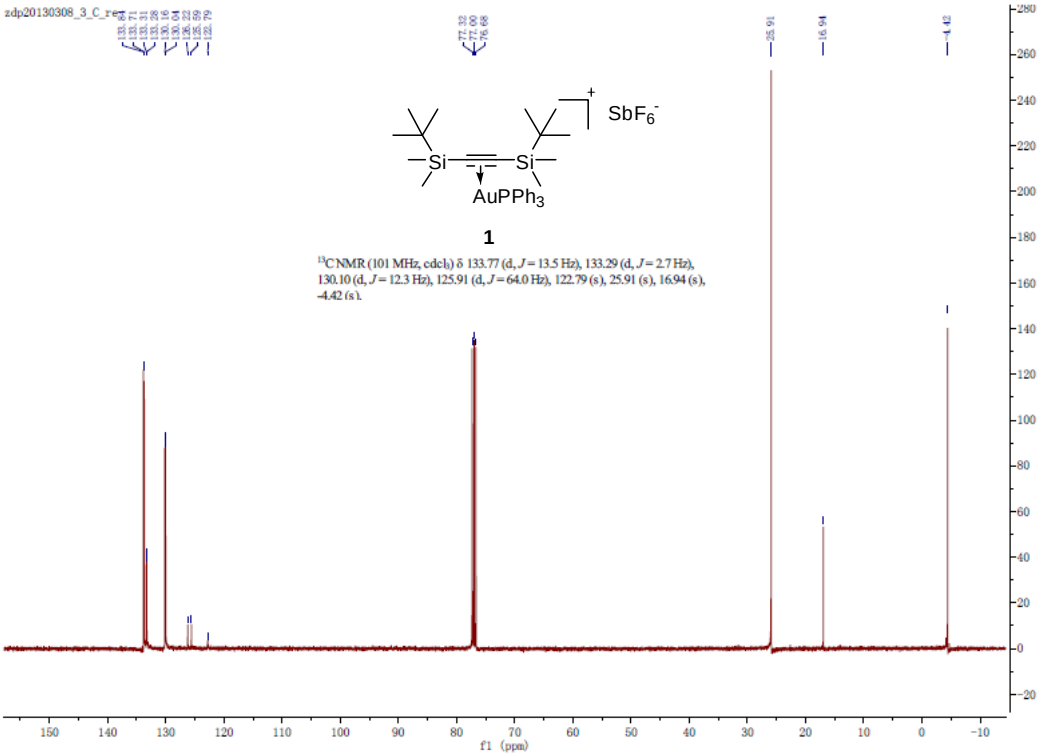


Figure S2. Raman spectra of compounds **1** and **5**.

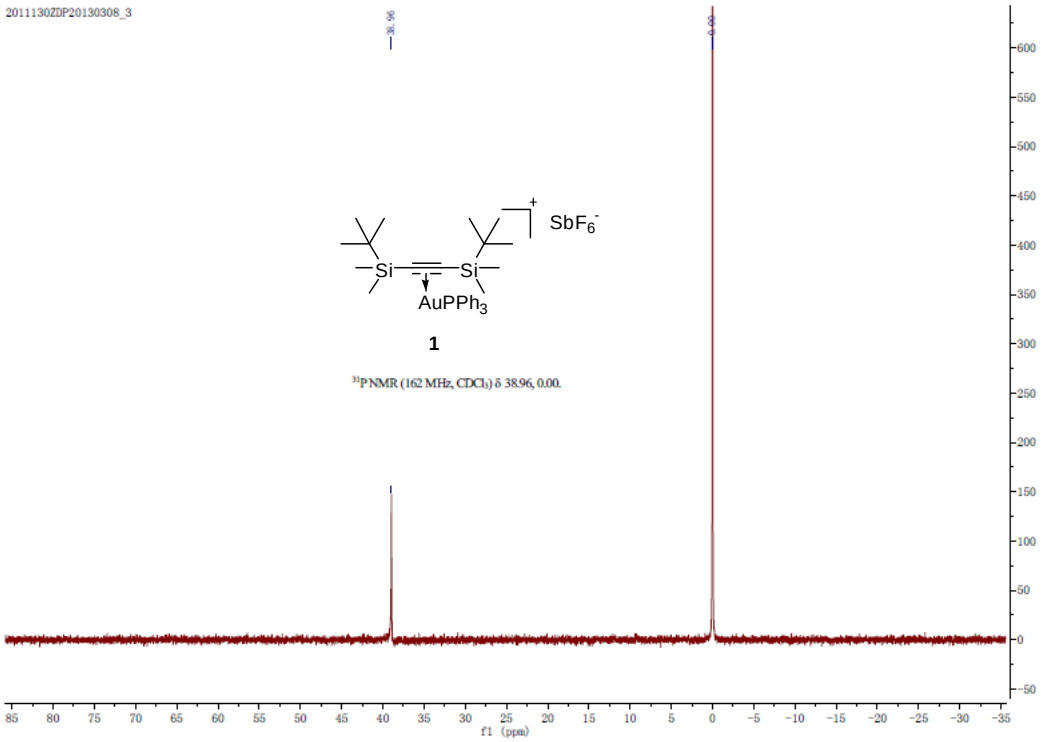
^{1}H NMR of compound **1**



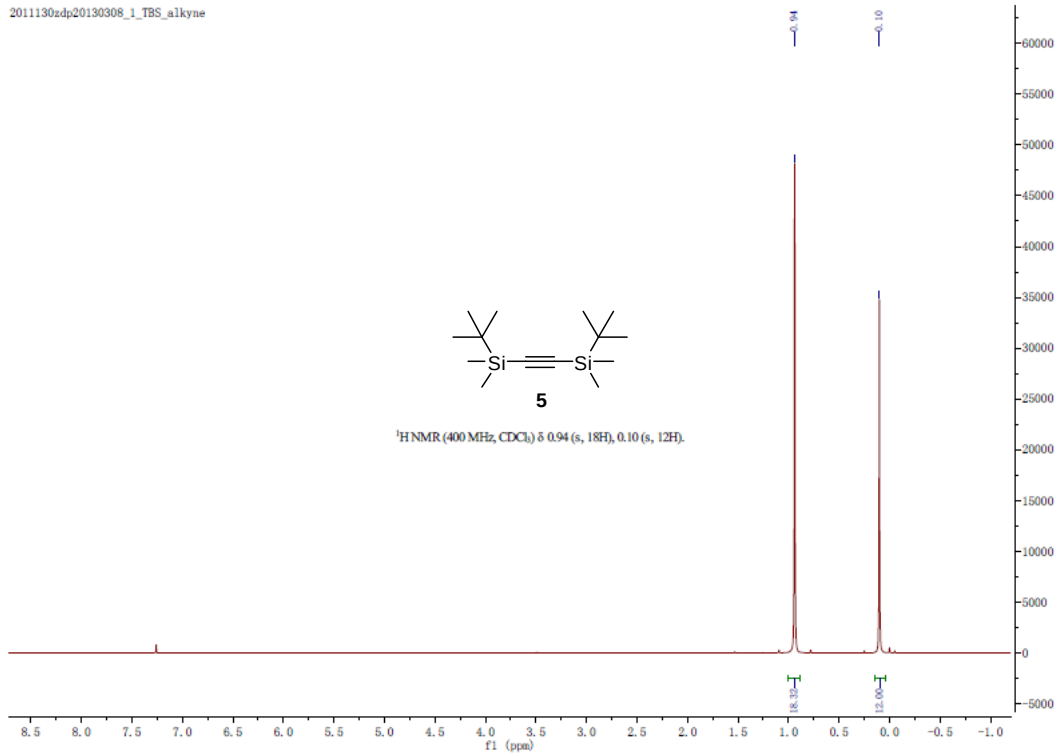
^{13}C NMR of compound **1**



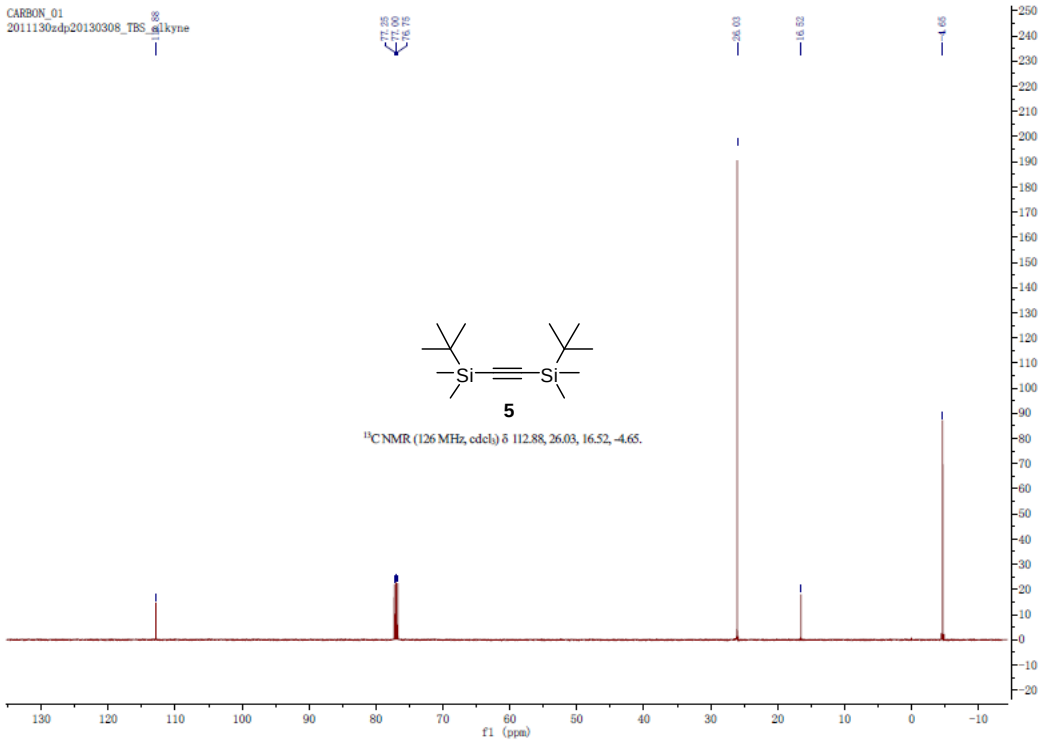
^{31}P NMR of compound **1**



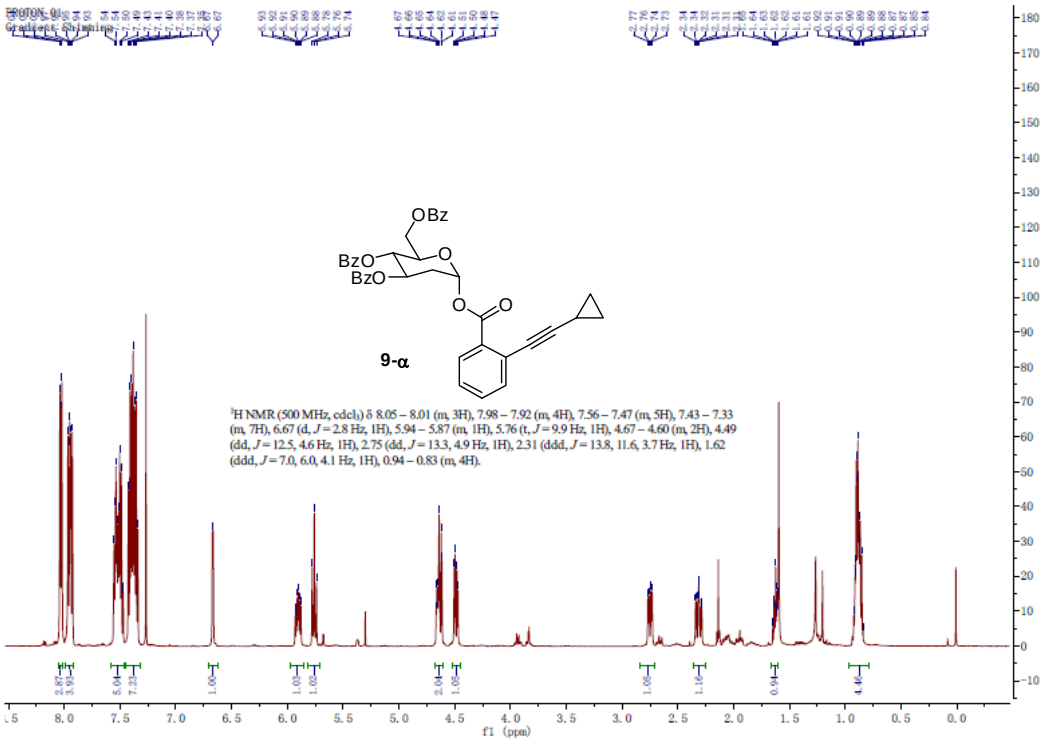
^{1}H NMR of compound **5**



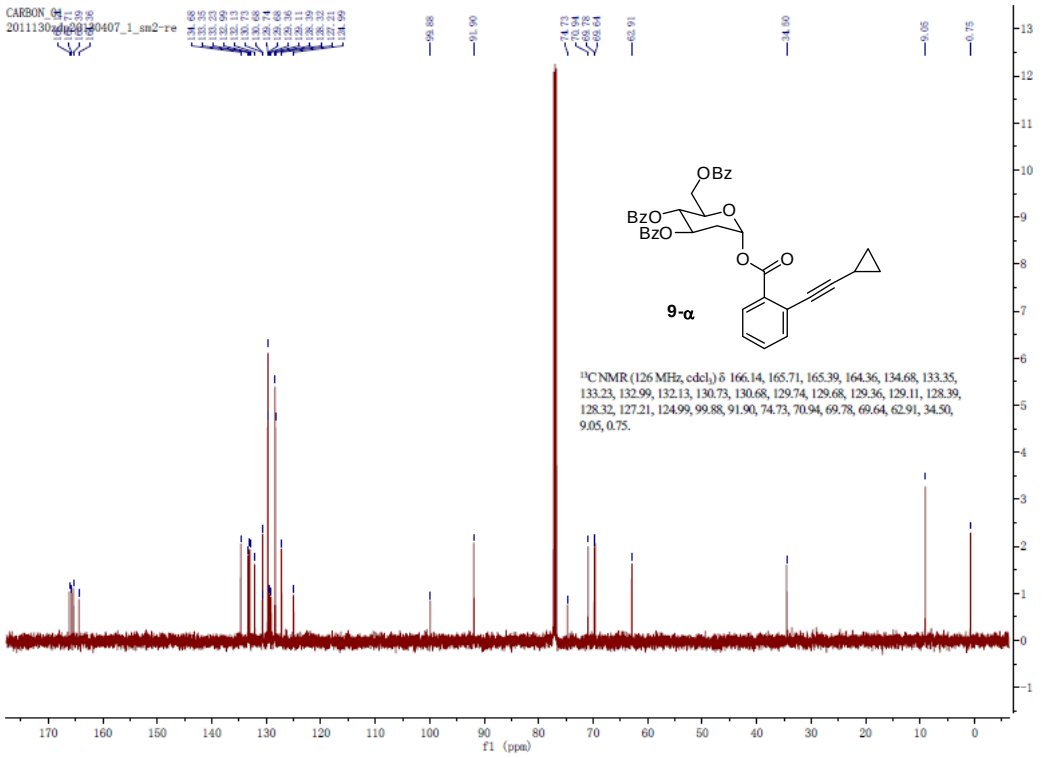
^{13}C NMR of compound **5**



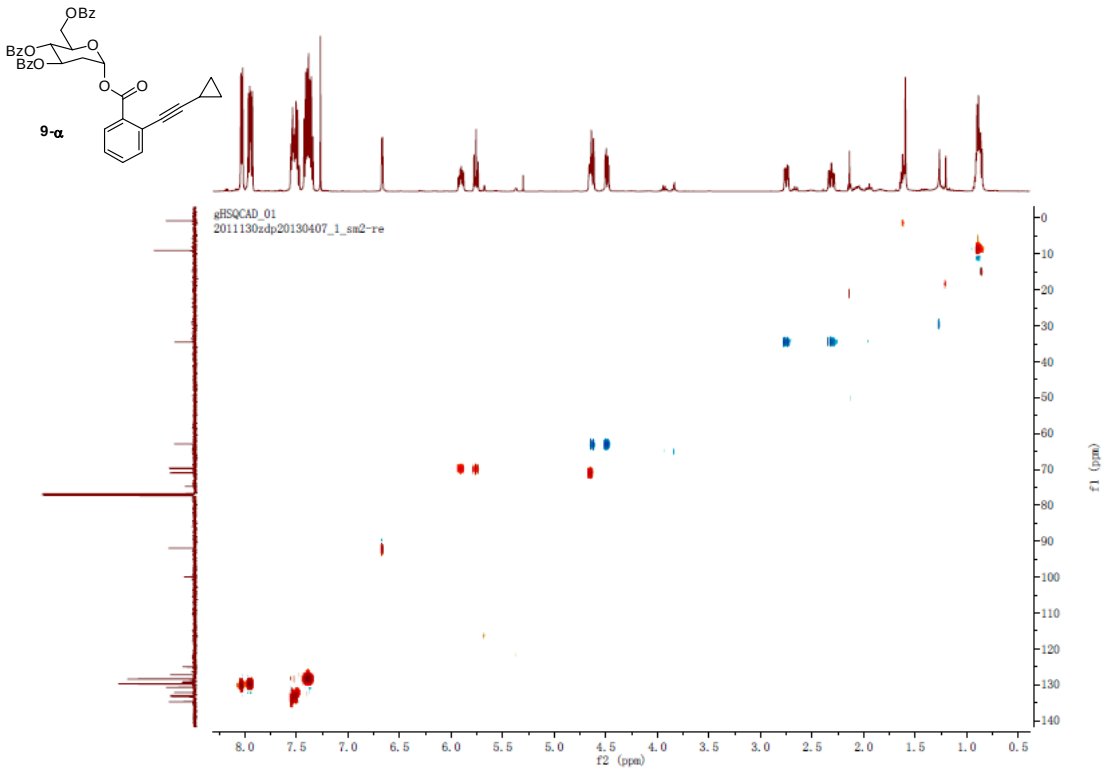
^{1}H NMR of compound **9α**



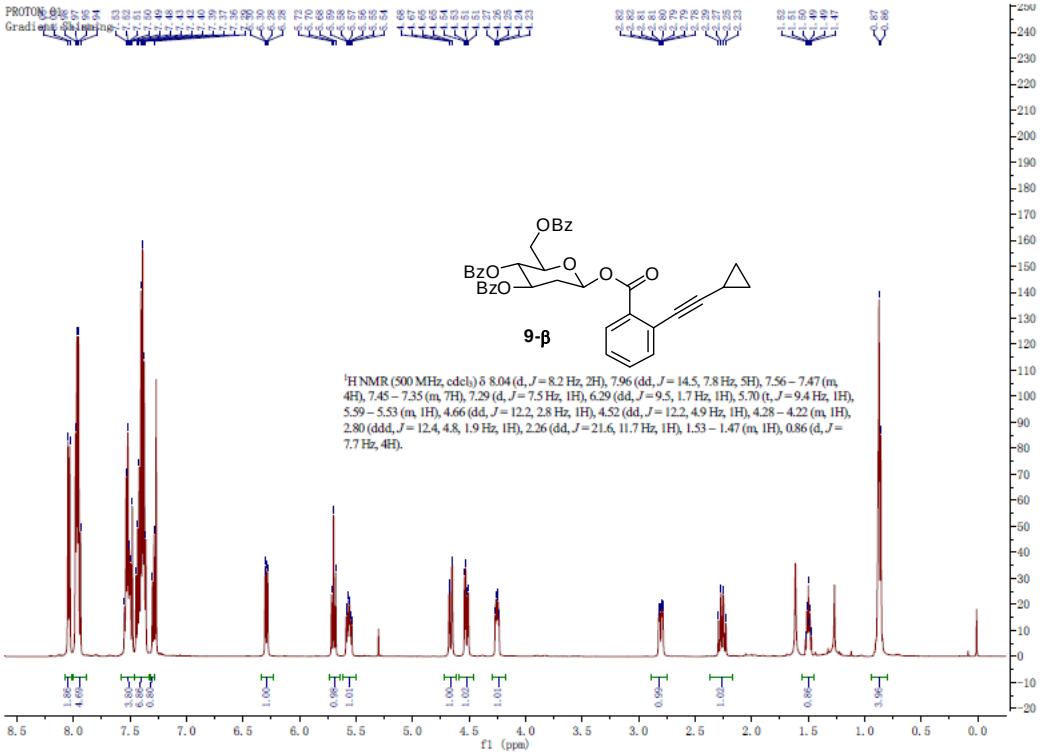
^{13}C NMR of compound **9α**



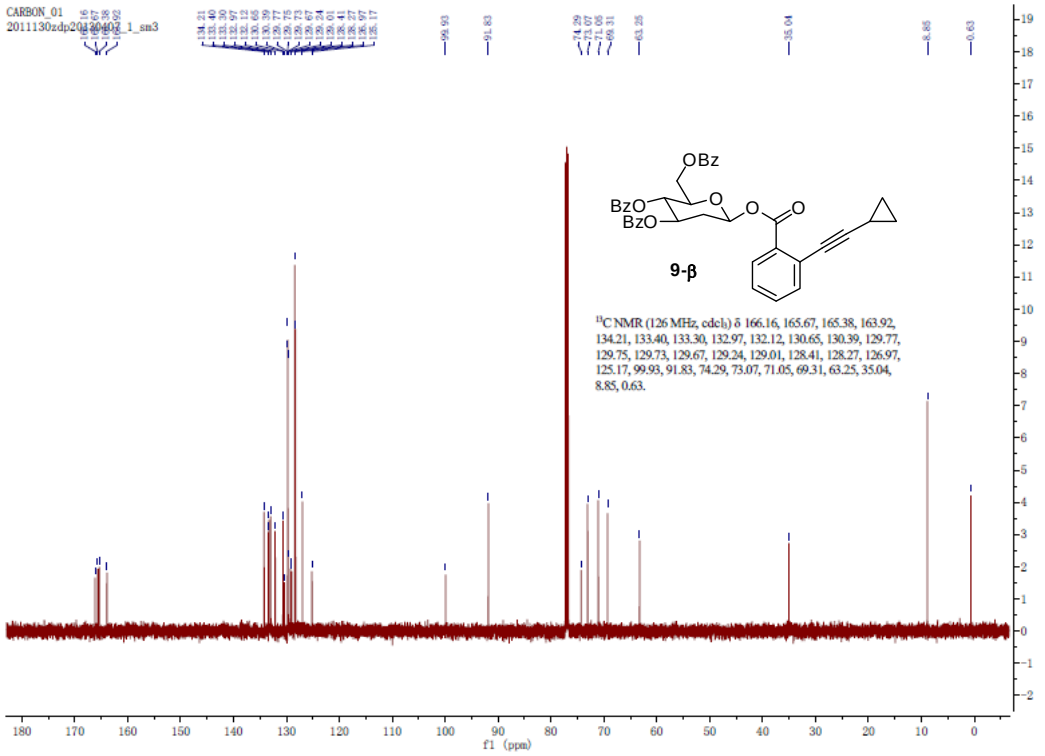
^{1}H-^{13}C COSY NMR of compound **9α**



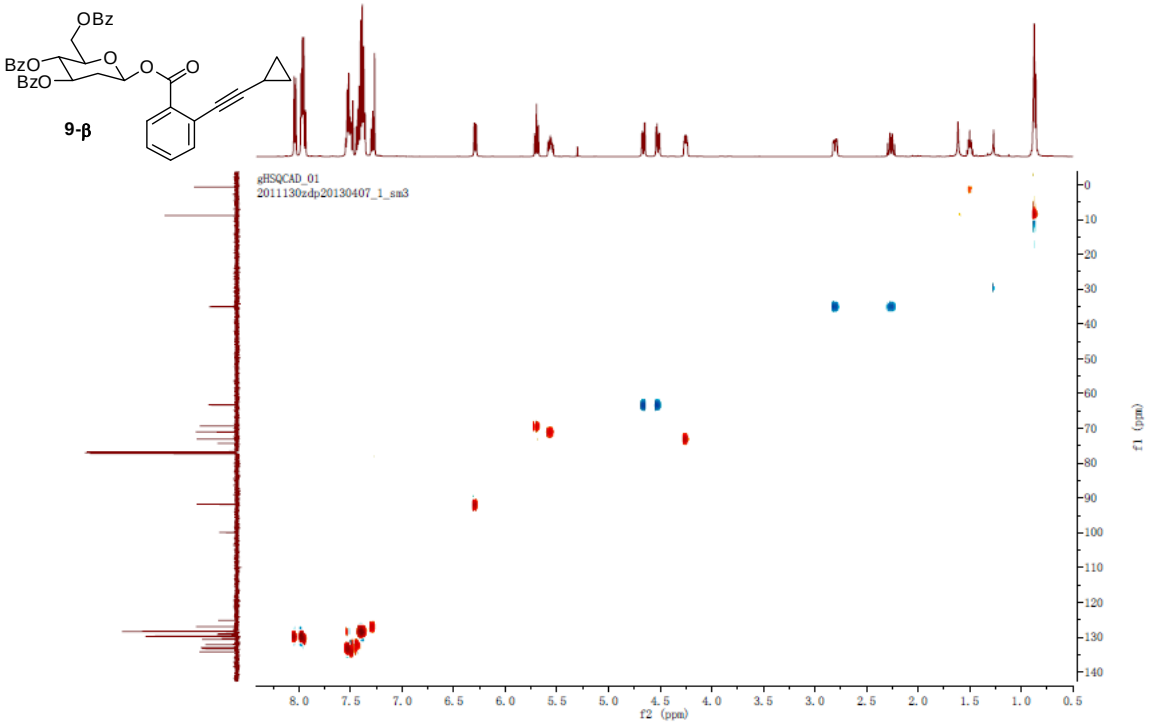
^{1}H NMR of compound **9β**



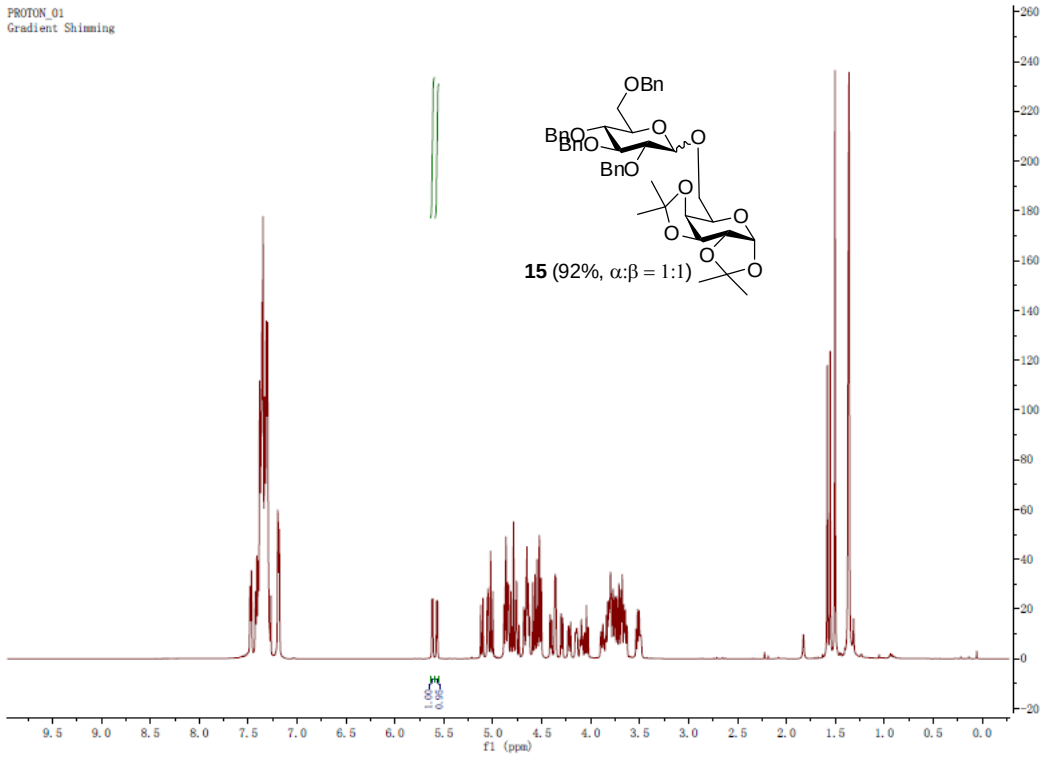
^{13}C NMR of compound **9β**



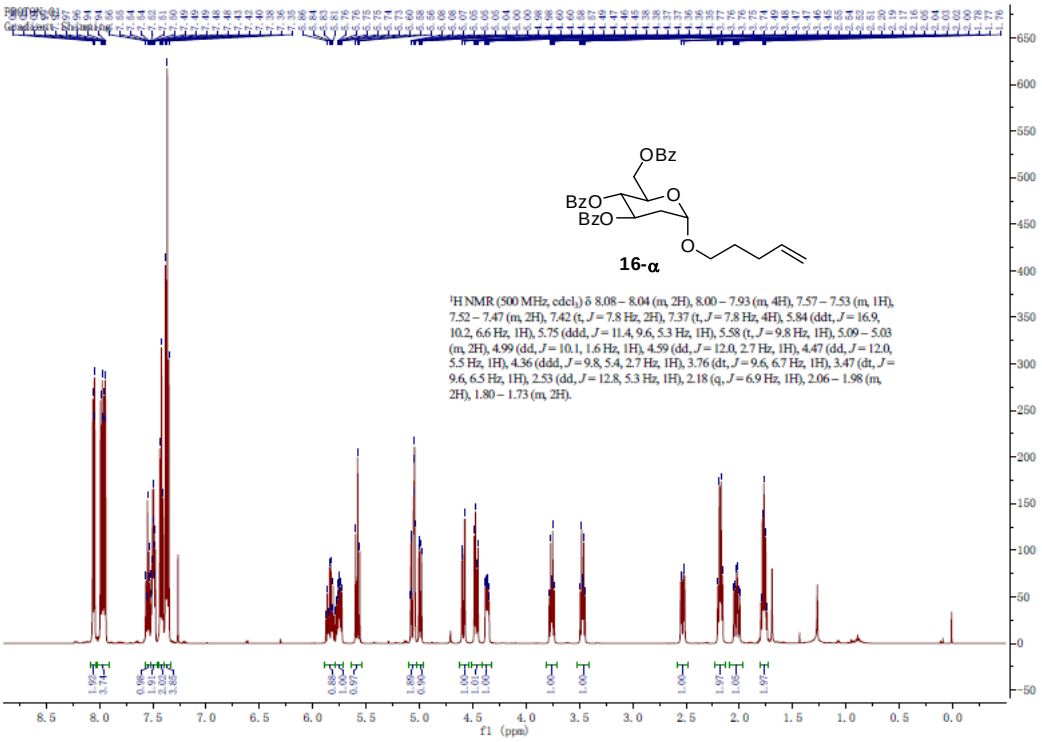
^{1}H-^{13}C COSY NMR of compound **9β**



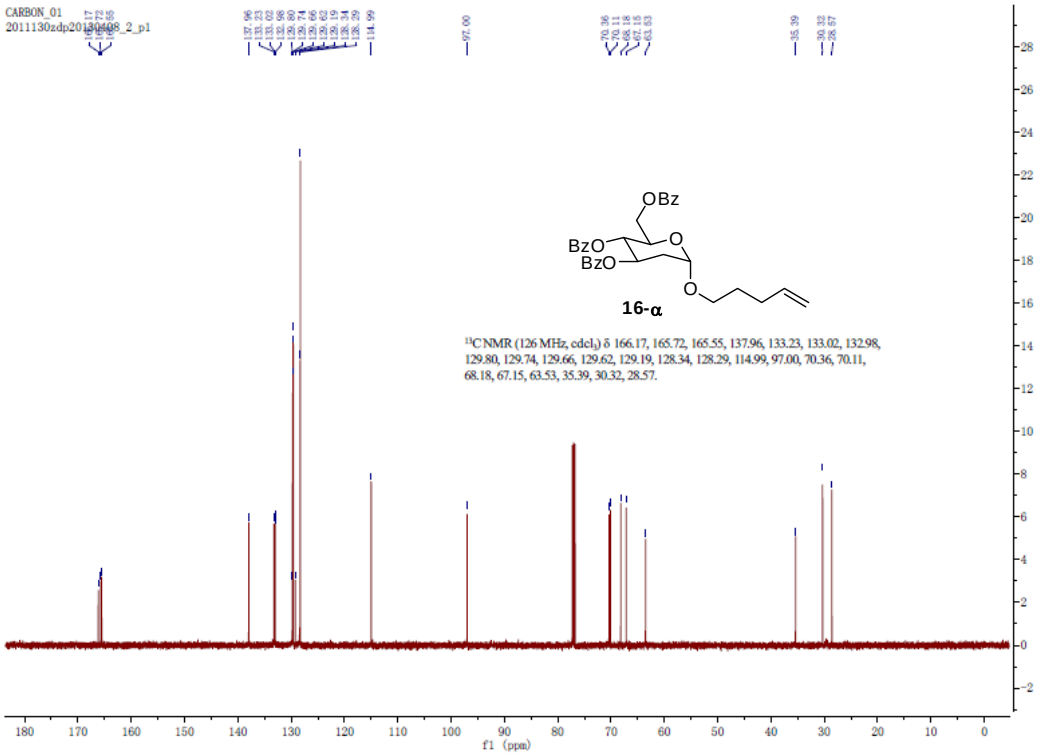
^{1}H NMR of compound **15**



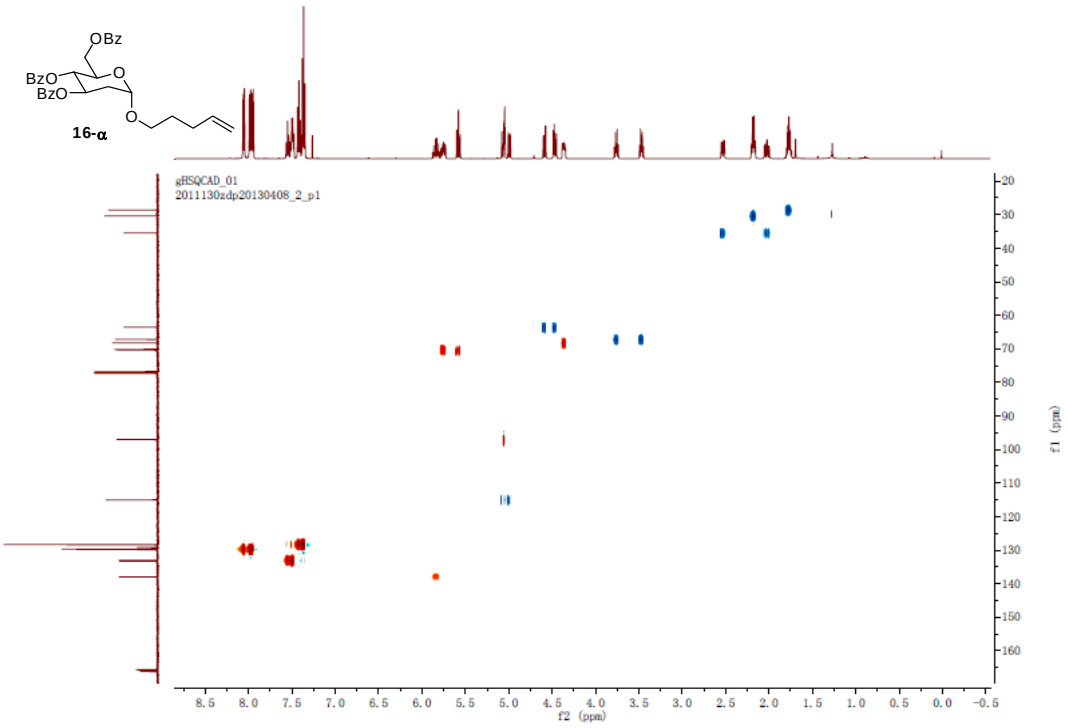
^{1}H NMR of compound **16α**



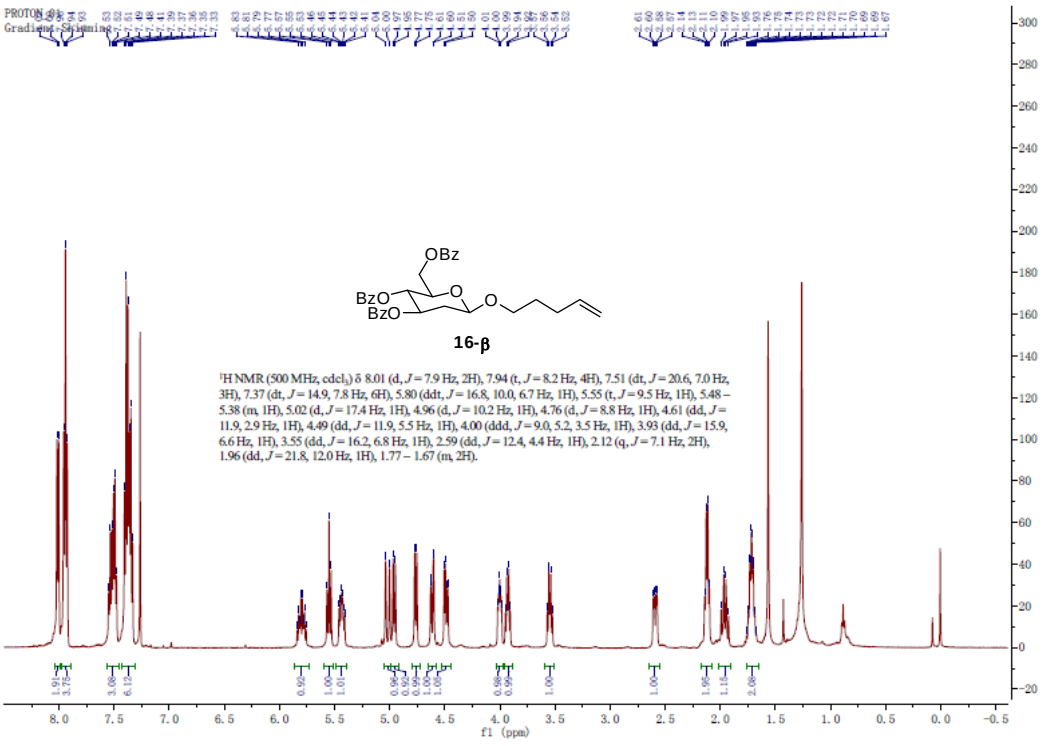
^{13}C NMR of compound **16α**



^{1}H-^{13}C COSY NMR of compound **16α**

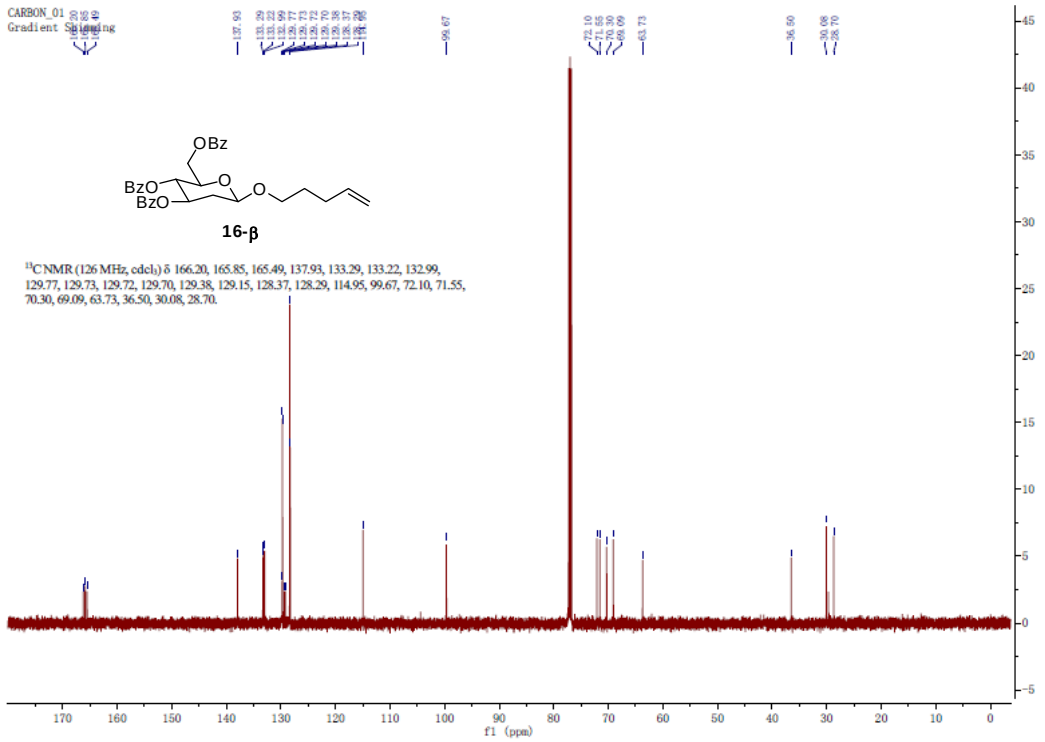


^{1}H NMR of compound **16β**

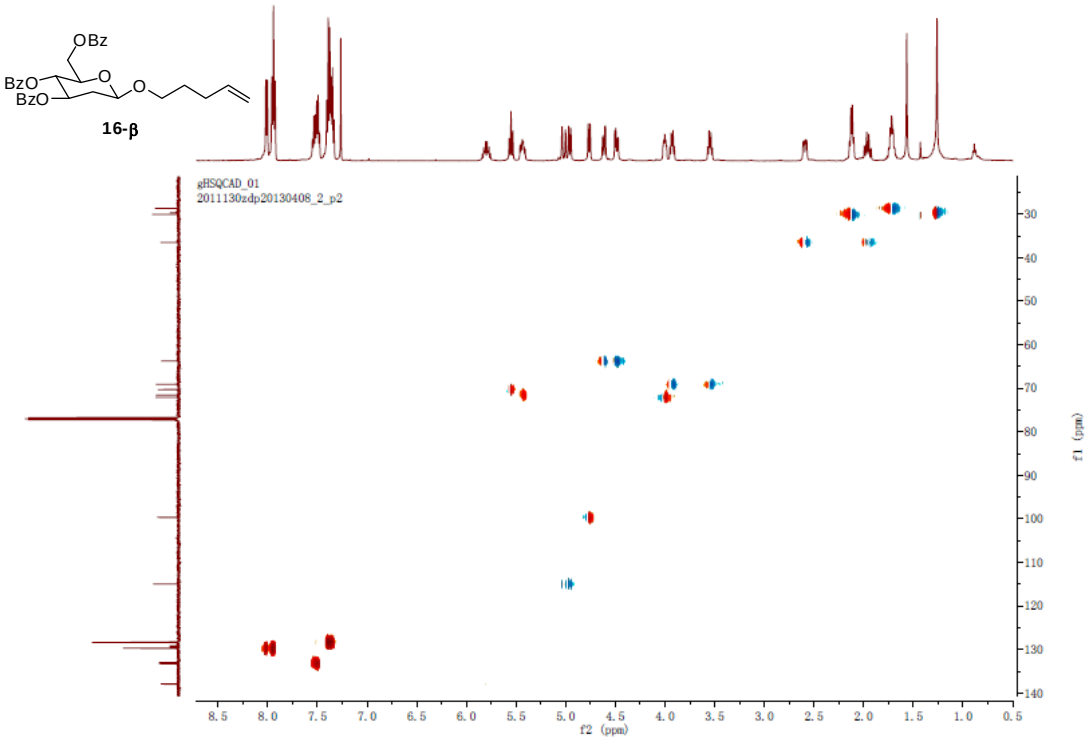


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.01 (d, J = 7.9 Hz, 2H), 7.94 (t, J = 8.2 Hz, 4H), 7.51 (dt, J = 20.6, 7.0 Hz, 3H), 7.37 (dt, J = 14.9, 7.8 Hz, 6H), 5.80 (ddt, J = 16.8, 10.0, 6.7 Hz, 1H), 5.55 (t, J = 9.5 Hz, 1H), 5.48 – 5.38 (m, 1H), 5.02 (d, J = 17.4 Hz, 1H), 4.96 (d, J = 10.2 Hz, 1H), 4.76 (d, J = 8.8 Hz, 1H), 4.61 (dd, J = 11.9, 2.9 Hz, 1H), 4.49 (dd, J = 11.9, 5.5 Hz, 1H), 4.00 (ddd, J = 9.0, 5.2, 3.5 Hz, 1H), 3.93 (dd, J = 15.9, 6.6 Hz, 1H), 3.55 (dd, J = 16.2, 6.8 Hz, 1H), 2.59 (dd, J = 12.4, 4.4 Hz, 1H), 2.12 (q, J = 7.1 Hz, 2H), 1.96 (dd, J = 21.8, 12.0 Hz, 1H), 1.77 – 1.67 (m, 2H).

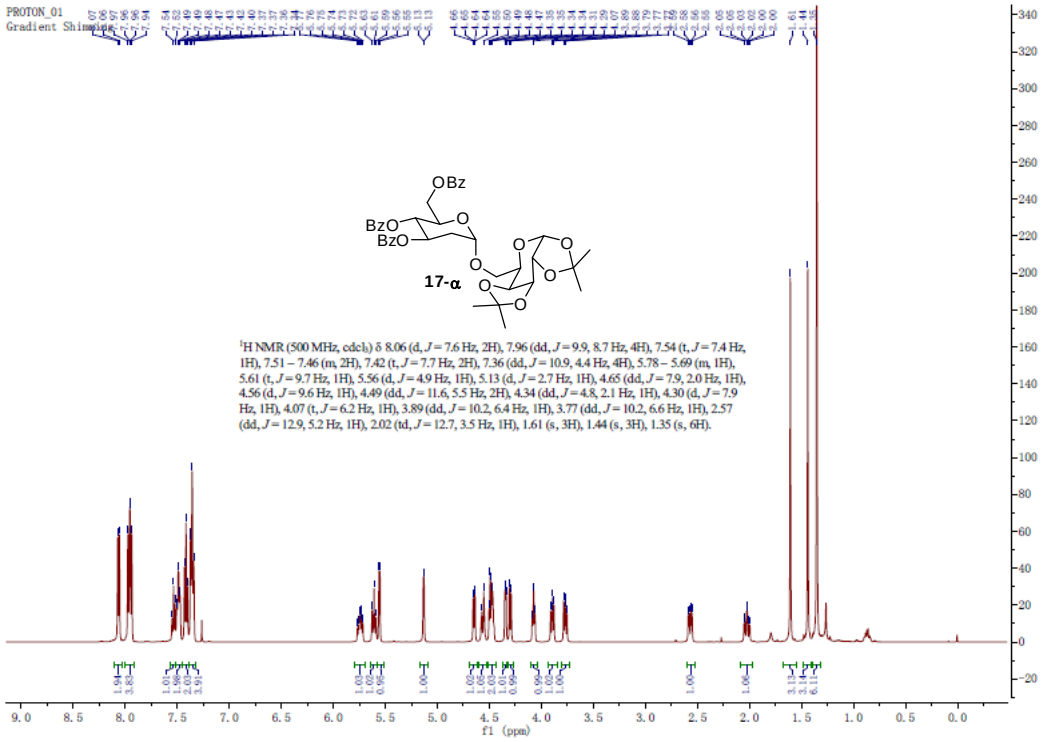
^{13}C NMR of compound **16β**



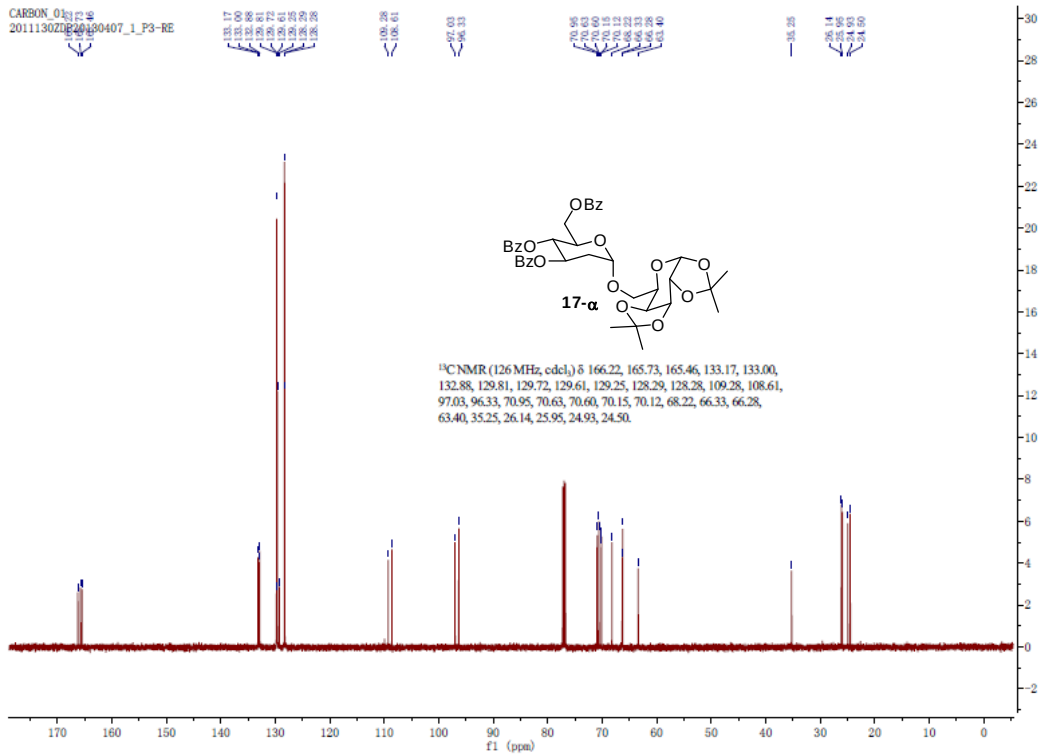
^{1}H-^{13}C COSY NMR of compound **16β**



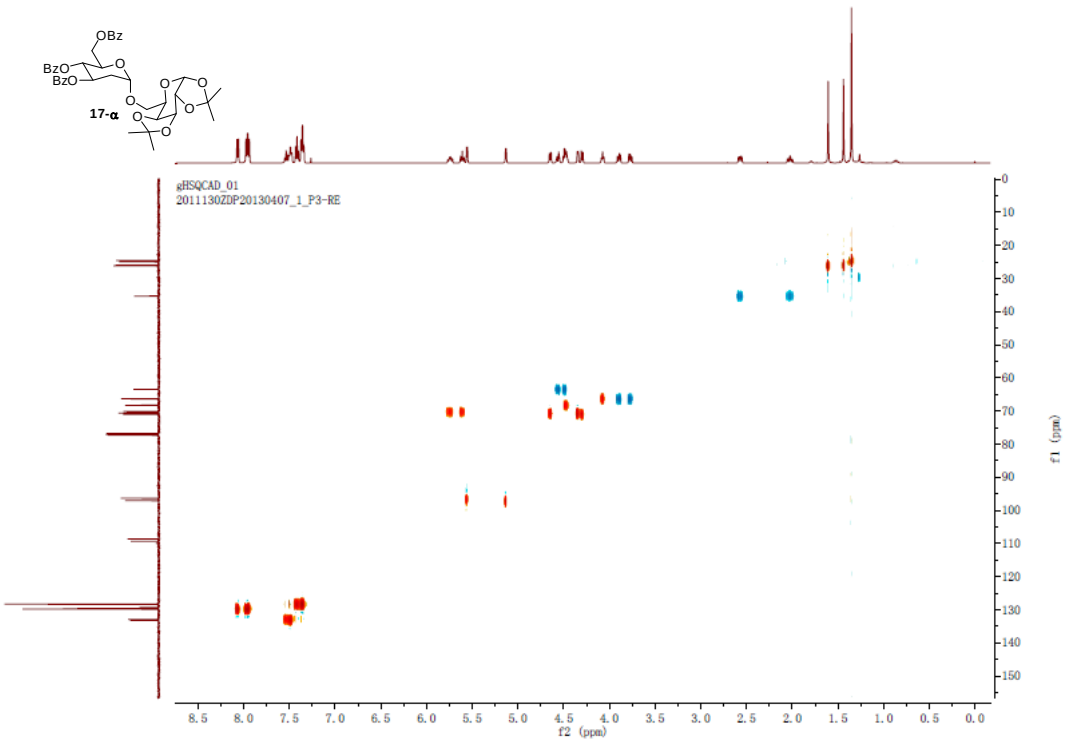
^{1}H NMR of compound **17α**



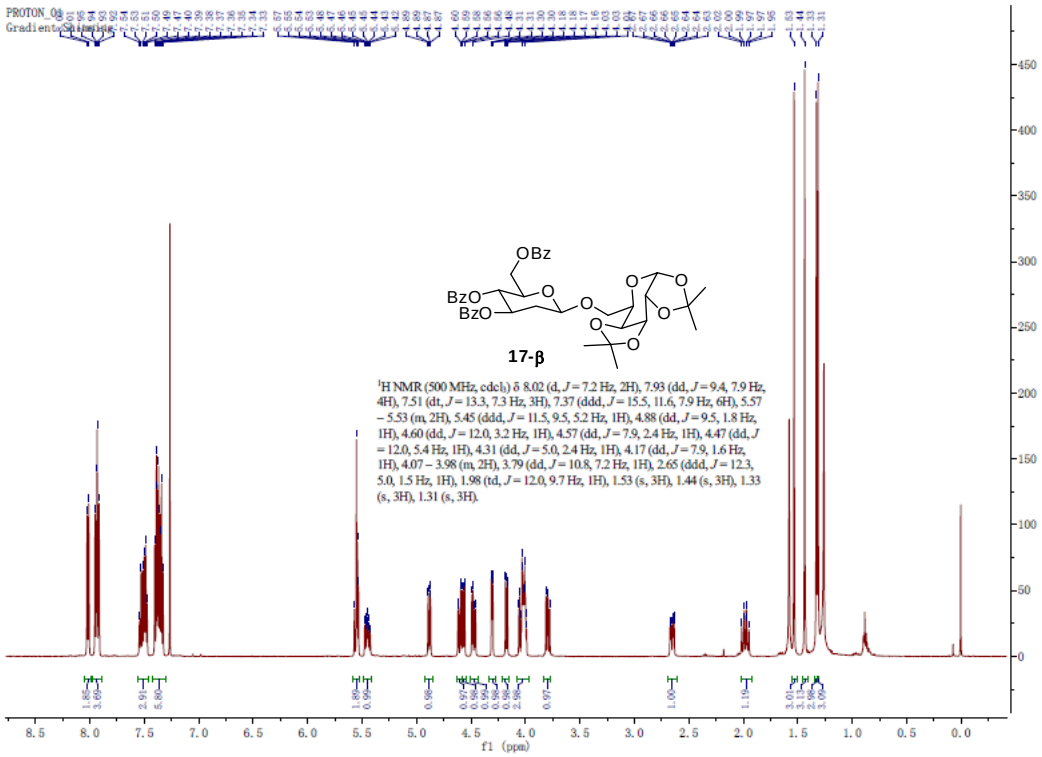
^{13}C NMR of compound **17α**



^{1}H-^{13}C COSY NMR of compound **17α**

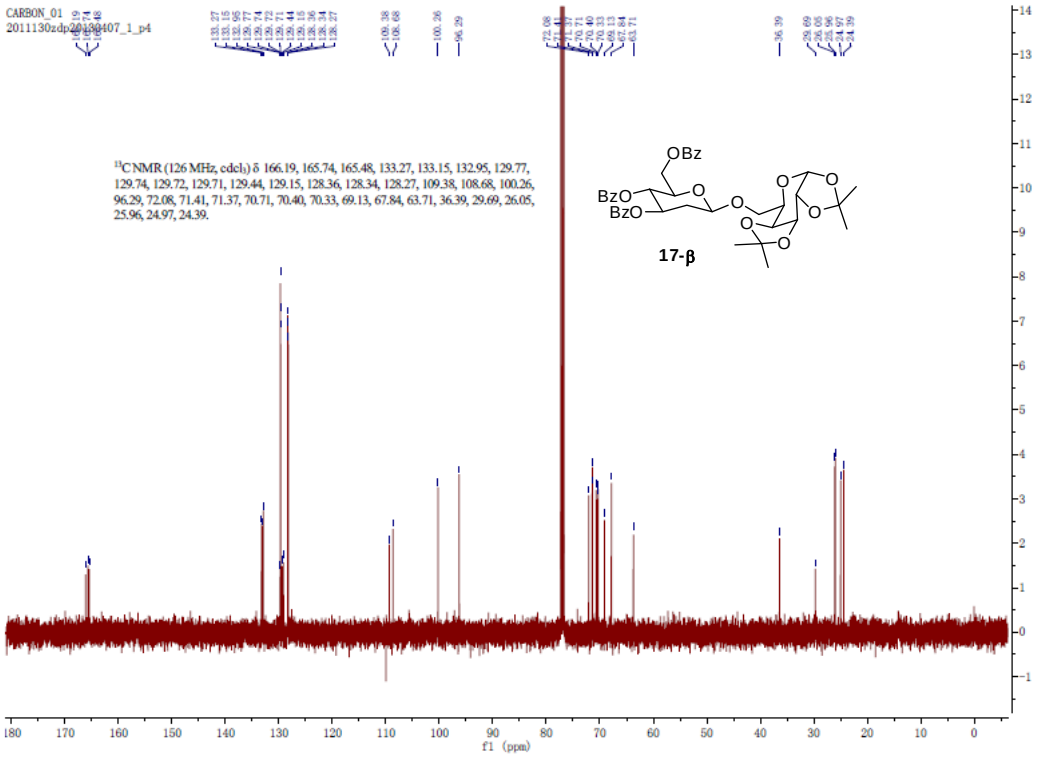


^{1}H NMR of compound **17β**

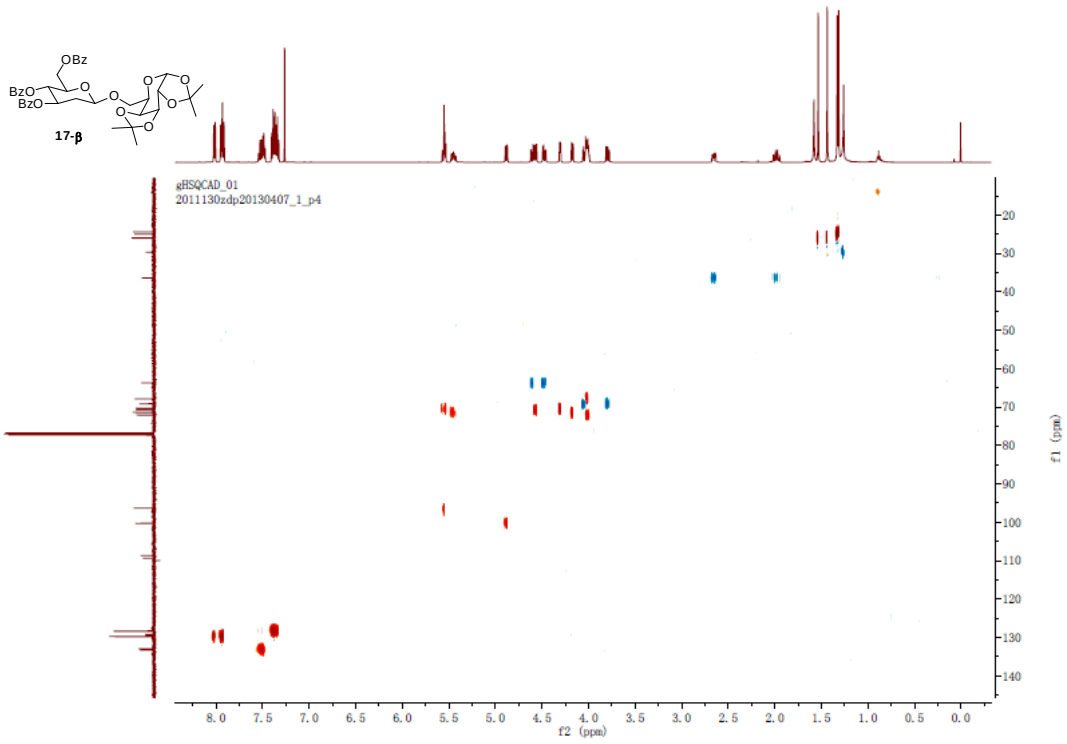


^{1}H NMR (500 MHz, cdcl$_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.93 (dd, J = 9.4, 7.9 Hz, 4H), 7.51 (dt, J = 13.3, 7.3 Hz, 3H), 7.37 (ddd, J = 15.5, 11.6, 7.9 Hz, 6H), 5.57 – 5.53 (m, 2H), 5.45 (ddd, J = 11.5, 9.5, 5.2 Hz, 1H), 4.88 (dd, J = 9.5, 1.8 Hz, 1H), 4.60 (dd, J = 12.0, 3.2 Hz, 1H), 4.57 (dd, J = 7.9, 2.4 Hz, 1H), 4.47 (dd, J = 12.0, 5.4 Hz, 1H), 4.31 (dd, J = 5.0, 2.4 Hz, 1H), 4.17 (dd, J = 7.9, 1.6 Hz, 1H), 4.07 – 3.98 (m, 2H), 3.79 (dd, J = 10.8, 7.2 Hz, 1H), 2.65 (ddd, J = 12.3, 5.0, 1.5 Hz, 1H), 1.98 (td, J = 12.0, 9.7 Hz, 1H), 1.53 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H).

^{13}C NMR of compound **17β**



^{1}H-^{13}C COSY NMR of compound **17β**



^{1}H NMR of compound **18**