

Supplemental information

**Synthesis of C-glycosides by Ti-catalyzed
stereoselective glycosyl radical functionalization**

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1. General information

All commercial reagents were used without additional purification, unless otherwise stated. Anhydrous solvent was purchased from commercial sources and transferred under an argon atmosphere. NMR spectra were recorded on Bruker 400 MHz and Bruker DPX 500 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard (CDCl_3 : δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, dt = doublet of triplet, dd = double doublet, ddd = doublet of a double doublet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on Bruker 400 MHz and Bruker DPX 500 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.20 ppm). ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometer with complete proton decoupling or proton coupling. High-resolution mass spectrometric data (HRMS) were obtained using Agilent 7200 Q-TOF and Bruker MicroTOF-QII (APCI, or Electrospray ionization, ESI). GC-MS analysis was performed on Shimadzu GCMS-QP2020 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. Values for α/β , *d.r.* and *E/Z* of products were determined by ^1H NMR analysis.

Solvents

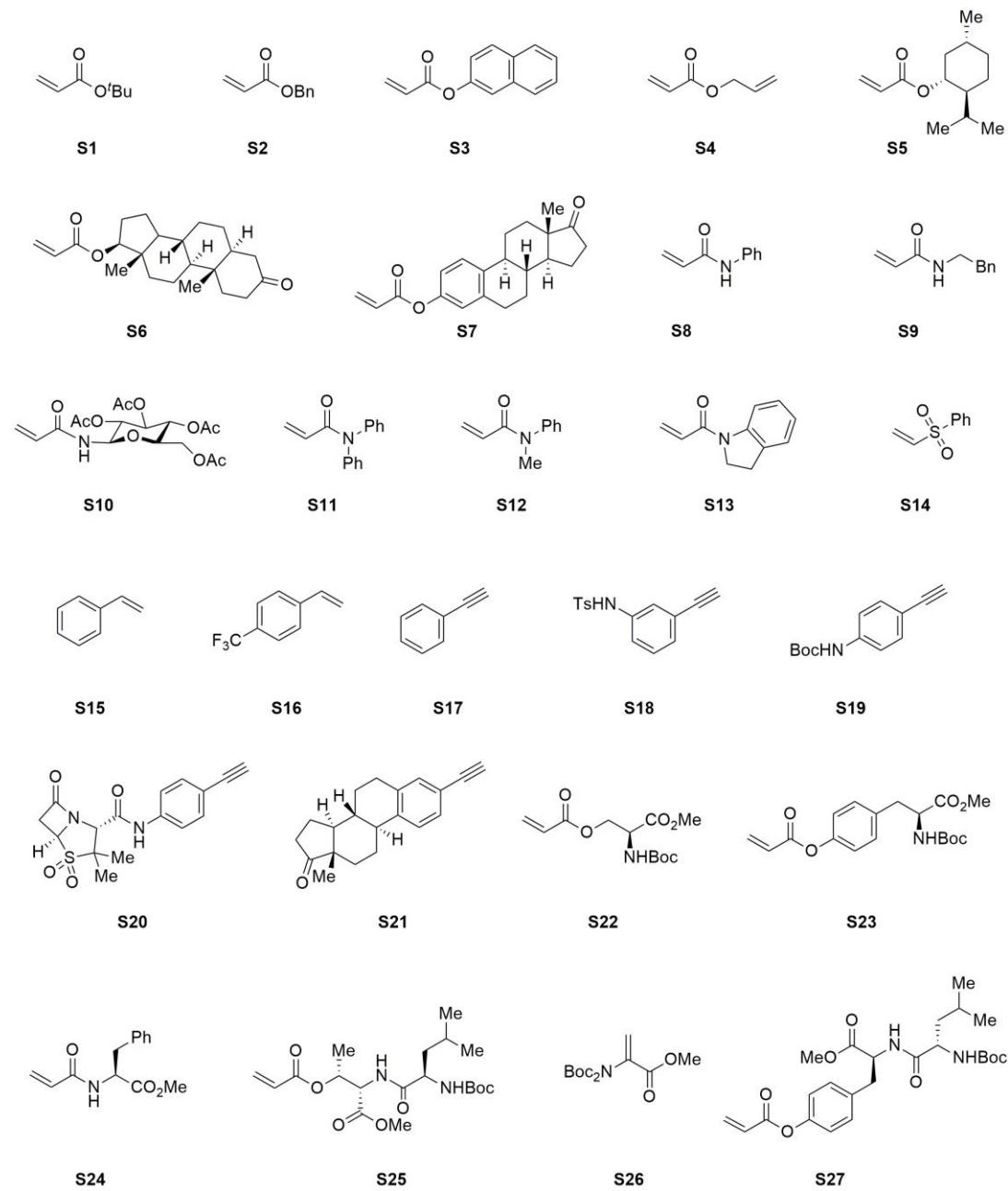
Solvents (acetonitrile, CH_2Cl_2 , tetrahydrofuran, ethyl acetate and toluene) were fetched under a positive pressure of dry nitrogen gas by a modified Innovative Technologies purification system, and further dried by molecular sieves before they were transferred into the glovebox. *N,N*-Dimethylacetamide (anhydrous), *N,N*-dimethylformamide (anhydrous), dimethyl sulfoxide (anhydrous), 1,2-dimethoxyethane (anhydrous) were used as received. All purification procedures of products were carried out with reagent grade solvents.

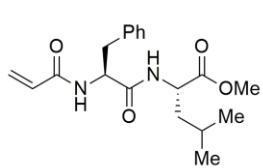
Materials

Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, or other commercial suppliers and were used as received. Cp_2TiCl_2 , CpTiCl_3 , $\text{Et}_3\text{N}\cdot\text{HCl}$ and Mn (powder, $\geq 99.9\%$ trace metals basis) were purchased from Sigma Aldrich. Cp^*TiCl_3 was purchased from Strem Chemicals.

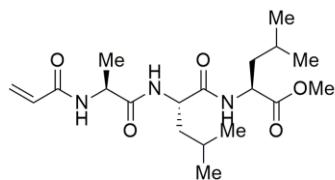
2. Preparation of substrates

Scheme S1. Substrate scope of acrylic esters/amides, alkynes and peptides

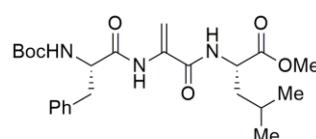




S28



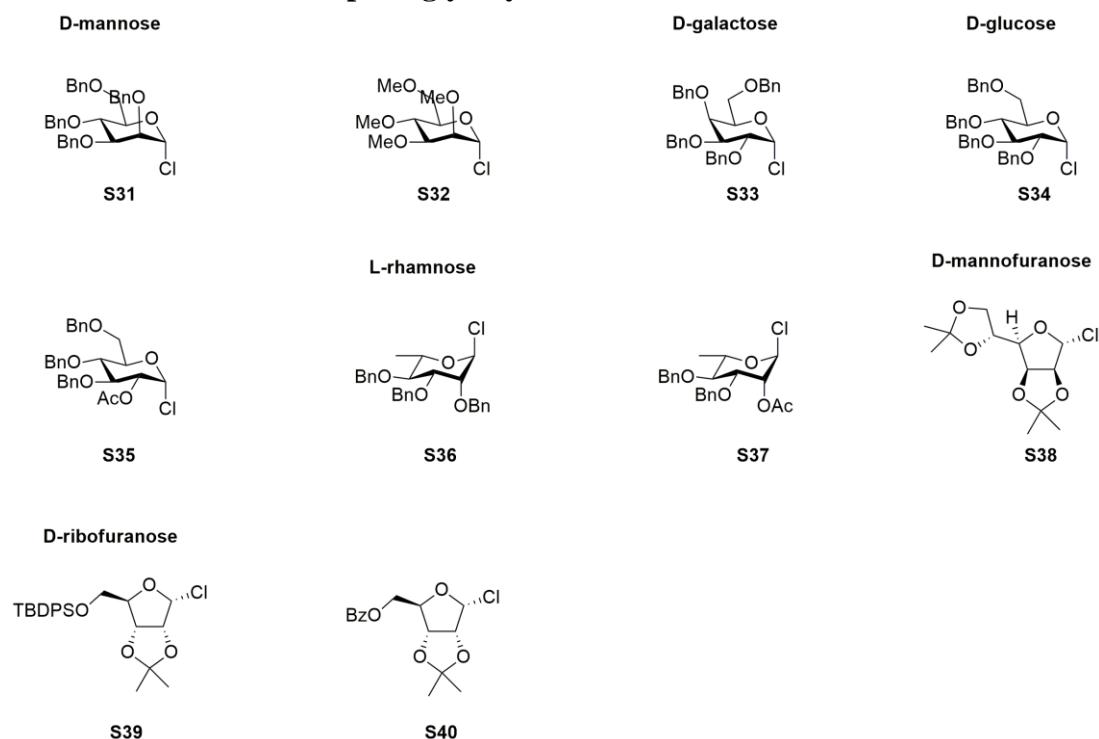
S29



S30

Alkene/alkyne **S1**, **S2**, **S14**, **S15–S17** are commercially available substrates. Alkynes **S18–S21** are known compounds.¹ **S3–S13** are prepared from reported methods.² Amino acids/peptides **S22–S30** are known compounds and prepared according to reported methods.³

Scheme S2. Substrate scope of glycosyl donors



All glycosyl donors **S31–S40** are known compounds and prepared according to reported methods.⁴

References:

1. Jiang, Y., Pan, J., Yang, T., Zhao, Y., Koh, M. J. (2021). Nickel-catalyzed site- and stereoselective reductive alkylalkynylation of alkynes. *Chem* 7, 993-1005.
2. Shang, W., Su, S.-N., Shi, R., Mou, Z.-D., Yu, G.-Q., Zhang, X., Niu, D. (2021). Generation of Glycosyl Radicals from Glycosyl Sulfoxides and Its Use in the Synthesis of C-linked Glycoconjugates. *Angew. Chem. Int. Ed.* 60, 385-390.

3. (a) Bao, G., Wang, P., Li, G., Yu, C., Li, Y., Liu, Y., He, Z., Zhao, T., Rao, J., Xie, J., Hong, L., Sun, W., Wang, R. (2021). 1,3-Dipolar Cycloaddition between Dehydroalanines and *C,N*-Cyclic Azomethine Imines: Application to Late-stage Peptide Modification. *Angew. Chem. Int. Ed.* **60**, 5331 - 5338. (b) Aycock, R. A., Pratt, C. J., Jui, N. T. (2018). Aminoalkyl Radicals as Powerful Intermediates for the Synthesis of Unnatural Amino Acids and Peptides. *ACS Catal.* **8**, 9115-9119.
4. Wang, Q., An, S., Deng, Z., Zhu, W., Huang, Z., He, G., Chen, G. (2019). Palladium-catalysed C–H glycosylation for synthesis of *C*-aryl glycosides. *Nat. Catal.* **2**, 793-800.

3. Analytical data of substrates

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl acrylate (S5):

¹H NMR (400 MHz, Chloroform-*d*) δ 6.37 (dd, *J* = 17.3, 1.6 Hz, 1H), 6.10 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.79 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.76 (td, *J* = 10.9, 4.4 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.87 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.72 – 1.65 (m, 2H), 1.57 – 1.46 (m, 1H), 1.45 – 1.38 (m, 1H), 1.13 – 0.99 (m, 2H), 0.93 – 0.85 (m, 7H), 0.76 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.0, 130.3, 129.3, 74.5, 47.3, 41.1, 34.5, 31.6, 26.5, 23.8, 22.2, 20.9, 16.6; HRMS (EI) m/z calcd for C₁₃H₂₂O₂ [M⁺]: 210.1620, found: 210.1605.

(5*S*,8*R*,9*S*,10*S*,13*S*,17*S*)-10,13-dimethyl-3-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acrylate (S6):

¹H NMR (400 MHz, Chloroform-*d*) δ 6.37 (dd, *J* = 17.4, 1.6 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.79 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.67 (dd, *J* = 9.2, 7.7 Hz, 1H), 2.42 – 2.25 (m, 3H), 2.23 – 2.15 (m, 1H), 2.11 – 2.06 (m, 1H), 2.01 (ddd, *J* = 13.2, 6.5, 2.4 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.67 – 1.60 (m, 2H), 1.58 – 1.45 (m, 3H), 1.39 – 1.28 (m, 5H), 1.19 (td, *J* = 12.9, 4.1 Hz, 1H), 1.12 – 1.04 (m, 1H), 1.01 (s, 3H), 0.97 – 0.87 (m, 1H), 0.83 (s, 3H), 0.77 – 0.72 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 212.1, 166.4, 130.4, 129.0, 83.0, 53.9, 50.8, 46.8, 44.8, 43.0, 38.7, 38.3, 37.0, 35.9, 35.4,

31.4, 28.9, 27.7, 23.7, 21.1, 12.3, 11.6; HRMS (EI) m/z calcd for C₂₂H₃₂O₃ [M⁺]: 344.2351, found: 344.2357.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl acrylate (S7):

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.4 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.59 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.31 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.00 (dd, *J* = 10.4, 1.3 Hz, 1H), 2.94 – 2.90 (m, 2H), 2.54 – 2.47 (m, 1H), 2.44 – 2.39 (m, 1H), 2.33 – 2.26 (m, 1H), 2.15 (dt, *J* = 18.5, 8.6 Hz, 1H), 2.09 – 1.94 (m, 3H), 1.67 – 1.57 (m, 3H), 1.55 – 1.40 (m, 3H), 0.91 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 221.0, 165.0, 148.6, 138.2, 137.6, 132.6, 128.2, 126.6, 121.7, 118.9, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 26.5, 25.9, 21.8, 14.0; HRMS (EI) m/z calcd for C₂₁H₂₄O₃ [M⁺]: 324.1725, found: 324.1732.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-acrylamidotetrahydro-2*H*-pyran-3,4,5-triyl triacetate (S10):

¹H NMR (400 MHz, Chloroform-*d*) δ 6.71 (d, *J* = 9.3 Hz, 1H), 6.26 (dd, *J* = 17.1, 1.1 Hz, 1H), 6.03 (dd, *J* = 17.0, 10.4 Hz, 1H), 5.69 (dd, *J* = 10.3, 1.1 Hz, 1H), 5.30 (q, *J* = 9.7 Hz, 2H), 5.02 (t, *J* = 9.7 Hz, 1H), 4.92 (t, *J* = 9.6 Hz, 1H), 4.27 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.04 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.82 (ddd, *J* = 10.2, 4.5, 2.2 Hz, 1H), 2.02 (s, 3H), 1.98 (d, *J* = 1.5 Hz, 6H), 1.97 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 170.7, 169.9, 169.7, 165.6, 130.1, 128.6, 78.4, 73.7, 72.9, 70.7, 68.3, 61.8, 20.8, 20.7, 20.63, 20.61; HRMS (ESI) m/z calcd for C₁₇H₂₃NNaO₁₀ [(M+Na)⁺]: 424.1214, found: 424.1215.

(*S*)-2-((*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl acrylate (S22):

¹H NMR (400 MHz, Chloroform-*d*) δ 6.40 (dt, *J* = 17.3, 1.1 Hz, 1H), 6.09 (ddd, *J* = 17.4, 10.5, 0.8 Hz, 1H), 5.86 (dt, *J* = 10.5, 1.1 Hz, 1H), 5.31 (d, *J* = 7.5 Hz, 1H), 4.61 (dt, *J* = 8.5, 3.8 Hz, 1H), 4.51 (dd, *J* = 11.4, 4.0 Hz, 1H), 4.41 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.76 (s, 3H), 1.44 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 170.4, 165.7, 155.3,

131.9, 127.8, 80.5, 64.6, 53.1, 52.9, 28.4; HRMS (ESI) m/z calcd for C₁₂H₁₉NNaO₆ [(M+Na)⁺]: 296.1105, found: 296.1105.

Methyl acryloyl-L-phenylalaninate (S24):

¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 3H), 7.03 – 7.00 (m, 2H), 6.21 (dd, *J* = 17.0, 1.4 Hz, 1H), 6.02 (dd, *J* = 17.0, 10.3 Hz, 2H), 5.59 (dd, *J* = 10.3, 1.4 Hz, 1H), 4.90 (dt, *J* = 7.8, 5.7 Hz, 1H), 3.66 (s, 3H), 3.15 – 3.04 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 172.1, 165.1, 135.9, 130.5, 129.4, 128.7, 127.4, 127.3, 53.3, 52.5, 38.0; HRMS (EI) m/z calcd for C₁₃H₁₅NO₃ [M⁺]: 233.1052, found: 233.1042.

Methyl *O*-acryloyl-*N*-((*tert*-butoxycarbonyl)-*L*-leucyl)-*L*-threoninate (S25):

¹H NMR (400 MHz, Chloroform-*d*) δ 6.79 (d, *J* = 9.4 Hz, 1H), 6.40 (d, *J* = 17.3 Hz, 1H), 6.07 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.84 (dt, *J* = 10.4, 1.2 Hz, 1H), 5.48 (qd, *J* = 6.4, 2.7 Hz, 1H), 4.93 – 4.91 (m, 1H), 4.80 (dd, *J* = 9.3, 2.7 Hz, 1H), 4.19 – 4.14 (m, 1H), 3.70 (s, 3H), 1.75 – 1.64 (m, 2H), 1.54 – 1.46 (m, 1H), 1.42 (s, 9H), 1.27 (d, *J* = 6.4 Hz, 3H), 0.94 (t, *J* = 6.4 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 170.1, 165.0, 155.9, 131.8, 128.0, 80.3, 70.9, 55.5, 53.3, 52.8, 40.8, 28.4, 24.9, 23.0, 22.2, 17.0; HRMS (ESI) m/z calcd for C₁₉H₃₂N₂NaO₇ [(M+Na)⁺]: 423.2102, found: 423.2100.

4-((*S*)-2-((*S*)-2-((*tert*-Butoxycarbonyl)amino)-4-methylpentanamido)-3-methoxy-3-oxopropylphenyl acrylate (S27):

¹H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 7.11 (m, 2H), 7.06 – 7.03 (m, 2H), 6.60 – 6.55 (m, 2H), 6.30 (dd, *J* = 17.3, 10.4 Hz, 1H), 6.00 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.84 (dt, *J* = 7.8, 5.9 Hz, 2H), 4.12 – 4.07 (m, 1H), 3.70 (s, 3H), 3.18 – 3.05 (m, 2H), 1.68 – 1.57 (m, 2H), 1.43 (s, 10H), 0.91 (dd, *J* = 6.3, 5.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 171.7, 164.6, 155.7, 149.8, 133.6, 132.7, 130.5, 128.1, 121.7, 80.2, 53.3, 52.5, 41.2, 37.5, 28.4, 24.9, 23.0, 22.1; HRMS (ESI) m/z calcd for C₂₄H₃₄N₂NaO₇ [(M+Na)⁺]: 485.2258, found: 485.2254.

Methyl acryloyl-L-phenylalanyl-L-leucinate (S28):

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.10 (m, 5H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.19 (dd, *J* = 17.0, 1.6 Hz, 1H), 6.06 (dd, *J* = 17.0, 10.1 Hz,

1H), 5.55 (dd, $J = 10.1, 1.7$ Hz, 1H), 4.85 (q, $J = 6.9$ Hz, 1H), 4.45 (td, $J = 8.3, 5.3$ Hz, 1H), 3.63 (s, 3H), 3.07 – 2.96 (m, 2H), 1.55 – 1.37 (m, 3H), 0.79 (d, $J = 6.2$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 171.4, 165.5, 136.7, 130.6, 129.6, 128.6, 127.2, 127.0, 54.5, 52.4, 51.1, 41.3, 38.6, 24.9, 22.8, 22.0; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{26}\text{N}_2\text{O}_4$ [M^+]: 346.1893, found: 346.1901.

Methyl acryloyl-L-alanyl-L-leucyl-L-leucinate (S29):

^1H NMR (400 MHz, Chloroform-*d*) δ 6.97 (d, $J = 8.3$ Hz, 1H), 6.85 (d, $J = 8.3$ Hz, 1H), 6.63 (d, $J = 7.7$ Hz, 1H), 6.32 (dd, $J = 17.0, 1.7$ Hz, 1H), 6.20 (dd, $J = 17.0, 10.1$ Hz, 1H), 5.68 (dd, $J = 10.1, 1.7$ Hz, 1H), 4.71 (p, $J = 7.1$ Hz, 1H), 4.62 – 4.57 (m, 1H), 4.53 (td, $J = 8.5, 6.0$ Hz, 1H), 3.73 (s, 3H), 1.71 – 1.54 (m, 6H), 1.39 (d, $J = 6.9$ Hz, 3H), 0.92 – 0.89 (m, 12H); ^{13}C NMR (101 MHz, DMSO) δ 173.7, 173.0, 172.9, 165.2, 132.5, 126.3, 52.7, 51.7, 51.1, 49.1, 41.6, 25.1, 23.9, 23.7, 22.7, 22.2, 19.1; HRMS (EI) m/z calcd for $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}_5$ [M^+]: 383.2420, found: 383.2413.

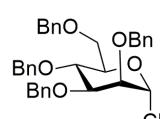
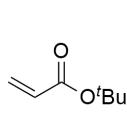
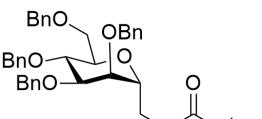
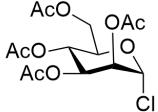
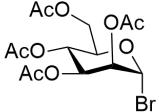
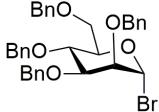
Methyl

(2-((*S*)-2-((*tert*-butoxycarbonyl)amino)-3-phenylpropanamido)acryloyl)-L-leucinate (S30):

^1H NMR (400 MHz, Chloroform-*d*) δ 8.56 (br, 1H), 7.32 – 7.23 (m, 3H), 7.10 – 7.08 (m, 2H), 6.64 (d, $J = 4.6$ Hz, 1H), 6.45 (s, 1H), 5.19 (s, 1H), 4.92 – 4.86 (m, 2H), 4.22 (br, 1H), 3.75 (s, 3H), 3.21 – 3.11 (m, 2H), 1.73 – 1.67 (m, 2H), 1.56 – 1.46 (m, 1H), 1.44 (s, 9H), 0.95 (dd, $J = 6.2, 2.4$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.0, 171.7, 163.5, 155.8, 135.6, 133.8, 129.4, 128.9, 127.5, 102.6, 80.5, 53.8, 52.7, 41.6, 37.8, 28.4, 25.0, 23.2, 21.9; HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{35}\text{N}_3\text{NaO}_6$ [(M+Na) $^+$]: 484.2418, found: 484.2424.

4. Optimization studies and experimental procedures

Table S1. Optimization of reaction conditions

 3a 1.0 equiv.		 4a 1.5 equiv.		 5a , 93% yield 2 mmol scale: 78% yield	
Entry	Cat. (10 mol%)	Red. (2.0 eq)	"H" source (1.5 eq)	Sol.	Yield (%) ^b
1	Cp ₂ TiCl ₂	Zn	Et ₃ N·HCl	THF	69
2	Cp*TiCl ₃	Zn	Et ₃ N·HCl	THF	47
3	CpTiCl ₃	Zn	Et ₃ N·HCl	THF	trace
4	Cp ₂ TiCl ₂	Zn	Et ₃ N·HCl	toluene	87
5	Cp*TiCl ₃	Zn	Et ₃ N·HCl	toluene	64
6	Cp ₂ TiCl ₂	Mn	Et ₃ N·HCl	THF	80
7	Cp*TiCl₃	Mn	Et₃N·HCl	THF	93
8	Cp*TiCl ₃	Mn	Et ₃ N·HCl	toluene	trace
9	Cp*TiCl ₃	Mn	Et ₃ N·HCl	DME	< 10
10	Cp*TiCl ₃	Mn	Et ₃ N·HCl	MeCN	< 10
11	Cp*TiCl ₃	Mn	Et ₃ N·HCl	DMSO	< 2
12	Cp*TiCl ₃	Mn	Et ₃ N·HCl	DCM	52
13	Cp*TiCl ₃	Mn	Coll·HCl	THF	28
14	Cp*TiCl ₃	Mn	i-PrOH	THF	trace
15	Cp*TiCl ₃	Mn	t-BuOH	THF	trace
16	Cp*TiCl ₃	Mn	Ph ₂ CHOH	THF	trace
17	Cp*TiCl ₃	Mn	HCl (dioxane)	THF	< 10
18	Cp*TiCl ₃	Mn	H ₂ O	THF	< 2
19 ^c	Cp*TiCl ₃	Mn	Et ₃ N·HCl	THF	< 2
20 ^d	Cp*TiCl ₃	Mn	Et ₃ N·HCl	THF	40
21 ^e	Cp*TiCl ₃	Mn	Et ₃ N·HCl	THF	48
 glycosyl donor 3b		 glycosyl donor 3c	 glycosyl donor 3d		

Otherwise noted^a: **1a** (0.1 mmol, 1.0 equiv.), **2a** (0.15 mmol, 1.5 equiv), Ti catalyst (10 mol%), reductant (0.2 mmol, 2.0 equiv.), proton source (0.15 mmol, 1.5 equiv.), solvent (0.5 mL), r.t.. ^bIsolated yields.

^cGlycosyl donor **3b** was used. ^dGlycosyl donor **3c** was used. ^eGlycosyl donor **3d** was used.

Abbreviations: r.t., room temperature; Coll·HCl, 2,4,6-trimethylpyridine, hydrochloride; THF, tetrahydrofuran; DME, dimethoxyethane; DMSO, dimethyl sulfoxide; DCM, dichloromethane; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl.

4.1 General procedures for Ti-catalyzed stereoselective glycosyl radical functionalization

For activated alkene substrates (General procedure A): In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar was added glycosyl donor (1.0 equiv., 0.1 mmol), Cp*TiCl₃ (10 mol%), Mn powder (2.0 equiv., 0.2 mmol), Et₃N·HCl (1.5 equiv., 0.15 mmol) and alkene (1.5 equiv., 0.15 mmol). The mixture

was then dissolved in 0.5 mL dry THF (unless otherwise noted). The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 16 h. After the reaction was complete, the volatiles were evaporated and the mixture was purified by flash silica gel column chromatography to afford the pure product.

For alkyne substrates (General procedure B): In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar was added glycosyl donor (2.0 equiv., 0.2 mmol), Cp₂TiCl₂ (10 mol%), Mn powder (2.0 equiv., 0.2 mmol), Et₃N•HCl (1.5 equiv., 0.15 mmol) and alkyne (1.0 equiv., 0.10 mmol). The mixture was then dissolved in 0.5 mL dry EtOAc (unless otherwise noted). The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 16 h. After the reaction was complete, the volatiles were evaporated and the mixture was purified by flash silica gel column chromatography to afford the pure product.

5. Synthetic applications and transformations

Procedure for synthesis of **10:** To a solution of **8** (1.0 mmol, 1.0 equiv.) in dry DCM (20 mL) was added acryloyl chloride solution (1.05 mmol dissolved in 10 mL DCM) dropwise under nitrogen atmosphere. The reaction mixture was allowed to stir at 0 °C for 30 min. After that, the reaction was quenched by adding aqueous NaHCO₃ (5 mL) and the mixture was extracted with DCM (3*15 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue was purified by flash silica gel column chromatography using hexanes/EtOAc (1/1) as eluent to give **9** (0.17 g, 72%) as light yellowish solid. The obtained **9** (0.5 mmol, 1.0 eq) was dissolved in acetone (5 mL). BnBr (0.75 mmol, 1.5 eq) and K₂CO₃ (0.75 mmol, 1.5 eq) were added subsequently. The reaction mixture was refluxed for 24 h, after which the volatiles were removed and the residue was subjected to flash silica gel column chromatography using hexanes/EtOAc (1/1) as eluent to give **10** (0.148 g, 91%) as light yellowish solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.82 (d, *J* = 2.8 Hz, 1H), 7.71 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.27 – 7.17 (m, 3H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.30 (dd, *J* = 17.0, 1.7 Hz, 1H), 6.19 (dd, *J* = 16.9, 10.0 Hz, 1H), 5.58 (dd, *J* = 10.0, 1.7 Hz, 1H), 5.00 (s, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 164.1, 154.9, 136.7, 131.3, 131.2, 128.6, 128.0, 127.7, 127.1, 125.8, 123.7, 121.2, 114.6, 71.1, 61.3, 14.3.

Procedure for synthesis of **11:** The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as colorless oil (α only, 62.8 mg, 74% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.55 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.30 – 7.26 (m, 2H), 7.25 – 7.15 (m, 19H), 7.12 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 1H), 5.04 (s, 2H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.50 – 4.39 (m, 7H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.92 (ddd, *J* = 11.0, 5.0, 3.6 Hz, 1H), 3.80 – 3.70 (m, 3H), 3.63 (t, *J* = 6.2 Hz, 1H), 3.54 – 3.50 (m, 2H), 2.33 – 2.29 (m, 1H), 1.96 – 1.88 (m, 1H), 1.83 – 1.74 (m, 2H), 1.25 (t, *J* = 7.1 Hz,

3H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.3, 166.1, 154.6, 138.19, 138.17, 138.1, 137.9, 137.0, 131.6, 128.60, 128.58, 128.56, 128.5, 128.2, 128.04, 127.99, 127.96, 127.94, 127.92, 127.91, 127.2, 125.4, 123.5, 121.3, 114.7, 77.0, 76.1, 75.2, 73.8, 73.6, 73.4, 72.5, 72.0, 71.6, 71.3, 69.0, 61.1, 33.8, 25.8, 14.4; Optical rotation: $[\alpha]_D^{25}$: +21.78 ($c = 1.0, \text{CHCl}_3$).

Procedure for synthesis of **2**: To a solution of **11** (0.05 mmol, 1.0 eq) in MeOH (2 mL) was added Pd/C (10 mol%). The reaction mixture was allowed to stir at room temperature overnight under H_2 atmosphere (balloon). The volatiles were then removed and the residue was purified by flash silica gel chromatography using DCM/MeOH (5/1) as eluent to give **2** (19.8 mg, 99%) as colorless oil. ^1H NMR (500 MHz, Methanol- d_4) δ 8.09 (d, $J = 2.7$ Hz, 1H), 7.62 (dd, $J = 8.9, 2.7$ Hz, 1H), 6.90 (d, $J = 8.9$ Hz, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), **3.89 (dt, $J = 11.1, 3.3$ Hz, 1H)**, 3.81 – 3.74 (m, 3H), 3.73 – 3.70 (m, 1H), 3.63 (t, $J = 8.4$ Hz, 1H), 3.49 (ddd, $J = 8.6, 6.1, 2.8$ Hz, 1H), 3.35 (s, 1H), 2.54 – 2.43 (m, 2H), 2.16 – 2.07 (m, 1H), 1.91 – 1.84 (m, 1H), 1.40 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (126 MHz, MeOD) δ 173.7, 170.9, 159.2, 131.4, 129.5, 122.3, 118.3, 113.1, 77.4, 76.0, 72.7, 72.6, 69.2, 62.7, 62.5, 33.7, 25.6, 14.3; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_9$ [(M+H) $^+$]: 400.1602, found: 400.1605.

Procedure for synthesis of **12**: To a solution of **5a** (2.0 mmol, 1.0 equiv.) in dry DCM (20 mL) was added $\text{CF}_3\text{CO}_2\text{H}$ (30 mmol, 15.0 eq) dropwise under nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature overnight. After that the volatiles were removed and the corresponding alkyl acid was used directly for the next step without purification. The obtained acid (2.0 mmol, 1.0 eq) and *N*-hydroxyphthalimide (2.0 mmol, 1.0 eq) were dissolved in DCM (8 mL) and DMAP (10 mol%) was added. DIC (2.4 mmol, 1.2 eq) was then added dropwise. The reaction mixture was allowed to stir at room temperature for 30 min. The insoluble materials were filtered off and the filtrate was then evaporated. The crude residue was subjected to flash silica gel column chromatography using hexanes/EtOAc (5/1) as eluent to give **12** (1.12 g, 76%) as colorless oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.89 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.79 (dd, $J = 5.5, 3.1$ Hz, 2H), 7.34 – 7.24 (m, 18H),

7.22 (dd, $J = 7.6$, 1.9 Hz, 2H), 4.63 – 4.60 (m, 1H), 4.57 – 4.50 (m, 7H), **4.02 (ddd, $J = 9.9, 6.2, 3.9$ Hz, 1H)**, 3.91 (q, $J = 5.1$ Hz, 1H), 3.86 – 3.83 (m, 1H), 3.80 (dd, $J = 6.0$, 2.8 Hz, 2H), 3.73 (dd, $J = 10.2$, 4.6 Hz, 1H), 3.59 (dd, $J = 6.2$, 2.9 Hz, 1H), 2.83 (ddd, $J = 16.9$, 9.3, 5.7 Hz, 1H), 2.69 (ddd, $J = 16.5$, 9.2, 6.6 Hz, 1H), 2.10 – 1.95 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 162.0, 138.5, 138.4, 138.3, 138.2, 134.9, 129.2, 128.60, 128.57, 128.5, 128.3, 128.1, 128.0, 127.91, 127.89, 127.7, 124.1, 76.0, 75.9, 74.7, 74.0, 73.5, 73.3, 72.5, 71.6, 70.6, 68.9, 27.4, 25.6; HRMS (ESI) m/z calcd for $\text{C}_{45}\text{H}_{43}\text{NNaO}_9$ [(M+Na) $^+$]: 764.2830, found: 764.2831.

Procedure for synthesis of 13: The title compound was prepared from a reported procedure⁵. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as colorless oil (0.1 mmol scale, 53.9 mg, 73% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.26 (m, 21H), 7.24 – 7.21 (m, 2H), 7.19 – 7.17 (m, 1H), 4.69 (d, $J = 11.4$ Hz, 1H), 4.59 – 4.50 (m, 7H), **3.91 (dt, $J = 9.1, 4.5$ Hz, 1H)**, 3.87 – 3.83 (m, 1H), 3.82 – 3.73 (m, 3H), 3.71 – 3.67 (m, 1H), 3.53 (dd, $J = 5.1$, 3.0 Hz, 1H), 2.41 – 2.37 (m, 2H), 1.60 – 1.48 (m, 3H), 1.41 – 1.34 (m, 1H); ^{19}F NMR (377 MHz, Chloroform-*d*) δ -90.04 (s, 1F), -90.08 (s, 1F); ^{13}C NMR (126 MHz, CDCl_3) δ 153.9 (t, $J = 290.7$ Hz), 138.5, 138.40, 138.37, 138.3, 135.6, 134.5, 129.9, 128.6, 128.52, 128.47, 128.4, 128.14, 128.11, 128.05, 128.0, 127.9, 127.8, 127.7, 127.63, 127.58, 126.6, 91.7 (dd, $J = 21.5$, 13.6 Hz), 76.9, 76.2, 75.0, 73.8, 73.7, 73.4, 72.4, 72.2, 71.7, 69.1, 29.4, 27.4, 24.0; HRMS (ESI) m/z calcd for $\text{C}_{45}\text{H}_{45}\text{ClF}_2\text{NaO}_5$ [(M+Na) $^+$]: 761.2816, found: 761.2810; Optical rotation: $[\alpha]_D^{25}$: +3.88 (c = 1.0, CHCl_3).

Procedure for synthesis of 14: The title compound was prepared from a reported procedure⁶. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as colorless oil (0.1 mmol scale, 54.1 mg, 62% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 20H), 7.13 (dd, $J = 7.4$, 2.1 Hz, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 5.16 (d, $J = 11.9$ Hz, 1H), 5.06 (d, $J = 11.9$ Hz, 1H), 4.60 (d, $J = 11.4$ Hz, 1H), 4.54 – 4.41 (m, 8H), 4.32 (s, 1H), **3.90 (dt, $J = 9.6, 4.5$ Hz, 1H)**, 3.82 – 3.75 (m, 2H), 3.74 – 3.68 (m, 2H), 3.64 (dd, $J = 10.2$, 3.5

Hz, 1H), 3.50 (dd, J = 5.1, 3.0 Hz, 1H), 3.42 – 3.32 (m, 2H), 2.72 (ddd, J = 14.5, 10.1, 5.1 Hz, 1H), 2.51 (ddd, J = 13.9, 9.7, 6.8 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.76 – 1.67 (m, 1H), 1.47 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.9, 167.0, 143.2, 138.5, 138.33, 138.28, 132.0, 129.22, 129.16, 128.59, 128.58, 128.54, 128.52, 128.2, 128.1, 128.0, 127.94, 127.93, 127.89, 127.86, 127.7, 77.1, 76.2, 75.1, 73.9, 73.8, 73.5, 72.4, 71.9, 71.8, 69.3, 68.3, 63.4, 63.0, 61.2, 38.5, 31.9, 31.7, 20.3, 18.8; HRMS (ESI) m/z calcd for $\text{C}_{51}\text{H}_{55}\text{NNaO}_{10}\text{S}$ [(M+Na) $^+$]: 896.3439, found: 896.3433.

Procedure for synthesis of 15: The title compound was prepared from a reported procedure⁷. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as colorless oil (0.1 mmol scale, 49.8 mg, 79% yield). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 23H), 7.25 – 7.23 (m, 2H), 4.73 (d, J = 11.4 Hz, 1H), 4.69 – 4.65 (m, 2H), 4.62 – 4.55 (m, 5H), **4.22 (dt, J = 9.5, 4.6 Hz, 1H)**, 3.92 (t, J = 6.4 Hz, 1H), 3.87 (q, J = 5.8, 5.3 Hz, 1H), 3.84 – 3.81 (m, 2H), 3.79 (dd, J = 10.2, 3.9 Hz, 1H), 3.69 (dd, J = 4.8, 3.1 Hz, 1H), 2.60 – 2.47 (m, 2H), 1.96 – 1.81 (m, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 138.5, 138.43, 138.37, 138.35, 131.7, 128.54, 128.52, 128.48, 128.4, 128.2, 128.1, 128.0, 127.9, 127.84, 127.81, 127.75, 127.7, 124.0, 89.6, 81.2, 77.3, 76.0, 75.1, 73.91, 73.87, 73.6, 72.3, 71.7, 71.6, 69.3, 29.2, 16.0; HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{45}\text{O}_5$ [(M+H) $^+$]: 653.3262, found: 653.3256.

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6. Mechanistic studies

6.1 Radical homocoupling experiment

Procedure for synthesis of **16a and **16b**:** The title compounds were prepared from the **General procedure A** without addition of Et₃N•HCl and alkene. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure products as a colorless oil (**16a**: 22.4 mg, 46% yield; **16b**: 14.1 mg, 29% yield). For **16a**: ¹H NMR (400 MHz, Chloroform-*d*) δ 4.81 – 4.77 (m, 4H), 4.35 (ddd, *J* = 7.6, 6.2, 4.4 Hz, 2H), **4.09 – 4.05 (m, 4H; H₁ and H_{1'})**, 3.98 (dd, *J* = 8.7, 4.5 Hz, 2H), 3.89 (dd, *J* = 7.6, 3.1 Hz, 2H), 1.49 (s, 6H), 1.43 (s, 6H), 1.36 (s, 6H), 1.35 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 113.3, 109.5, 86.0, 83.6, 82.8, 81.4, 73.8, 66.9, 27.1, 26.7, 25.6, 25.1; HRMS (EI) m/z calcd for C₂₄H₃₈O₁₀ [M⁺]: 486.2465, found: 486.2479. For **16b**: ¹H NMR (400 MHz, Chloroform-*d*) δ 5.02 (dd, *J* = 6.2, 0.7 Hz, 1H), 4.77 – 4.71 (m, 3H), **4.41 – 4.36 (m, 3H; H₁)**, **4.09 – 4.05 (m, 3H; H_{1'})**, 4.01 (dd, *J* = 8.7, 4.9 Hz, 1H), 3.88 (dd, *J* = 7.8, 3.8 Hz, 1H), 3.59 – 3.54 (m, 2H), 1.50 (s, 6H), 1.44 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 113.0, 112.5, 109.3, 83.3, 82.3, 82.2, 82.1, 81.3, 81.13, 81.11, 80.3, 73.8, 73.2, 67.1, 66.8, 27.2, 27.1, 26.3, 25.6, 25.5, 25.3, 24.8, 24.2; HRMS (EI) m/z calcd for C₂₄H₃₈O₁₀ [M⁺]: 486.2465, found: 486.2477.

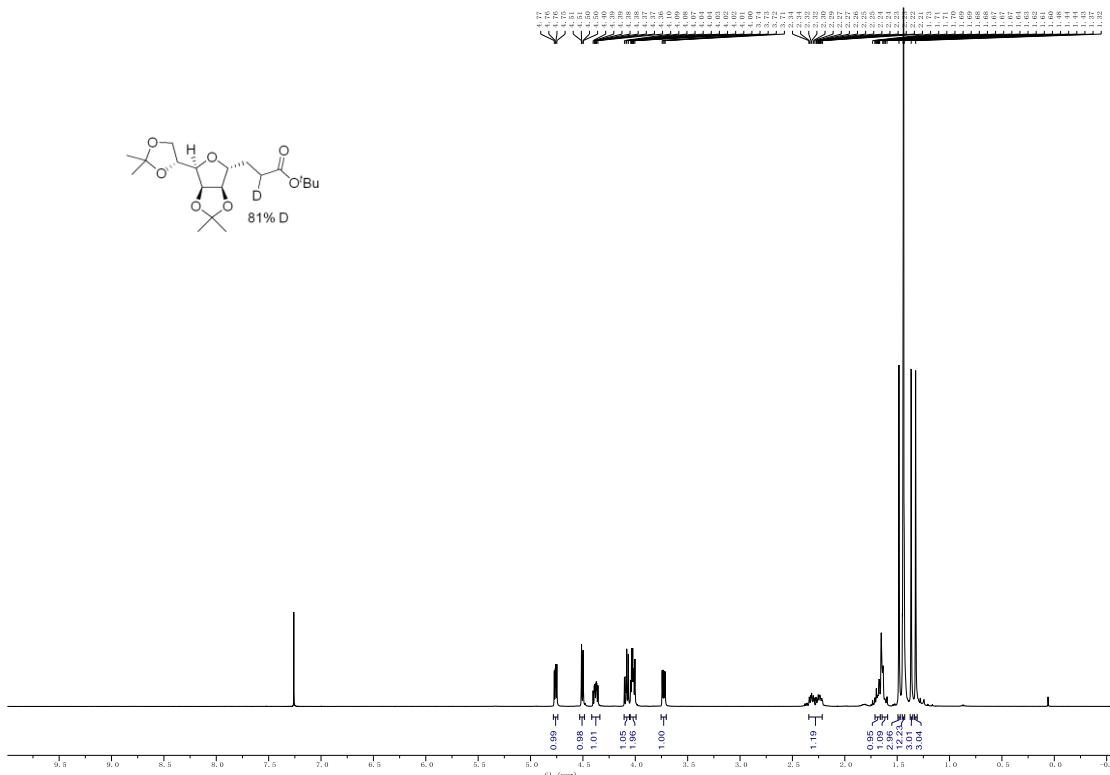
6.2 Deuterium labelling studies

Procedure for synthesis of **5ab with *d*₈-THF:** The title compound was prepared from the **General procedure A** with *d*₈-THF as solvent. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 17.5 mg, 47% yield, <5% D). Hydrogenation byproduct **17** was detected in <5% yield.

Procedure for synthesis of **d-5ab with Et₃N•DCl:** The title compound was prepared from the **General procedure A** with Et₃N•DCl as deuteron source. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 31.6 mg, 85% yield, 81% D). Hydrogenation byproduct **17** was detected in 5% yield. ¹H NMR spectrum of **d-5ab** was recorded to

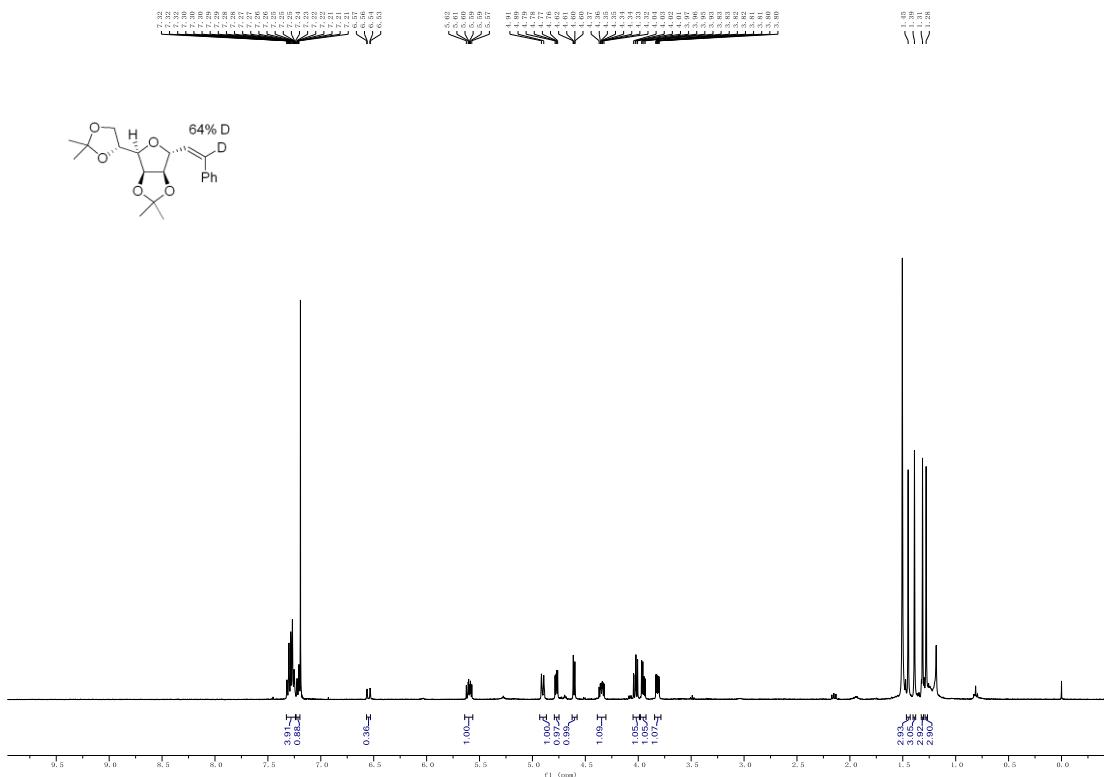
determine the degree of deuterium incorporation.

¹H NMR spectrum of *d*-5ab



Procedure for synthesis of *d*-7a with Et₃N•DCl: The title compound was prepared from the **General procedure B** with Et₃N•DCl used as deuterium source. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, >98:2 Z:E, 8.3 mg, 24% yield, 64% D). Hydrogenation byproduct **17** was detected in 51% yield. ¹H NMR spectrum of **d**-7a was recorded to determine the degree of deuterium incorporation.

¹H NMR spectrum of *d*-7a



6.3 Competition experiments

Procedure for synthesis of 19a: In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar was added tertiary alkyl chloride **18** (1.0 equiv., 0.1 mmol), Cp*TiCl₃ (10 mol%), Mn powder (2.0 equiv., 0.2 mmol), Et₃N•HCl (1.5 equiv., 0.15 mmol) and acrylate **4a** (1.5 equiv., 0.15 mmol). The mixture was then dissolved in 0.5 mL dry THF. The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 16 h. After the reaction was complete, the volatiles were evaporated and the residues were purified by flash silica gel column chromatography (eluent: hexanes : EtOAc = 20:1) gave the pure product as a colorless oil (25.4 mg, 92% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.25 (m, 2H), 7.19 – 7.15 (m, 3H), 2.58 – 2.54 (m, 2H), 2.23 – 2.19 (m, 2H), 1.61 – 1.59 (m, 1H), 1.59 – 1.57 (m, 1H), 1.52 – 1.47 (m, 2H), 1.45 (s, 9H), 0.94 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 174.0, 143.4, 128.5, 128.5, 125.8, 80.2, 44.3, 36.7, 32.8, 31.0, 30.8, 28.3, 26.9.

Procedure for synthesis of 19b: In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar was added tertiary alkyl chloride **18** (1.0 equiv., 0.1

mmol), Cp^{*}TiCl₃ (10 mol%), Mn powder (2.0 equiv., 0.2 mmol), Et₃N•HCl (1.5 equiv., 0.15 mmol) and acrylamide **4b** (1.5 equiv., 0.15 mmol). The mixture was then dissolved in 0.5 mL dry THF. The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 16 h. After the reaction was complete, the volatiles were evaporated and the residues were purified by flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (5.3 mg, 18% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.18 (dd, *J* = 8.2, 6.8 Hz, 3H), 7.16 – 7.08 (m, 2H), 2.61 – 2.57 (m, 2H), 2.34 – 2.30 (m, 2H), 1.75 – 1.71 (m, 2H), 1.56 – 1.52 (m, 2H), 0.99 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 171.9, 143.3, 138.1, 129.2, 128.6, 128.5, 125.8, 124.4, 119.9, 44.2, 37.3, 33.2, 33.0, 30.8, 27.1.

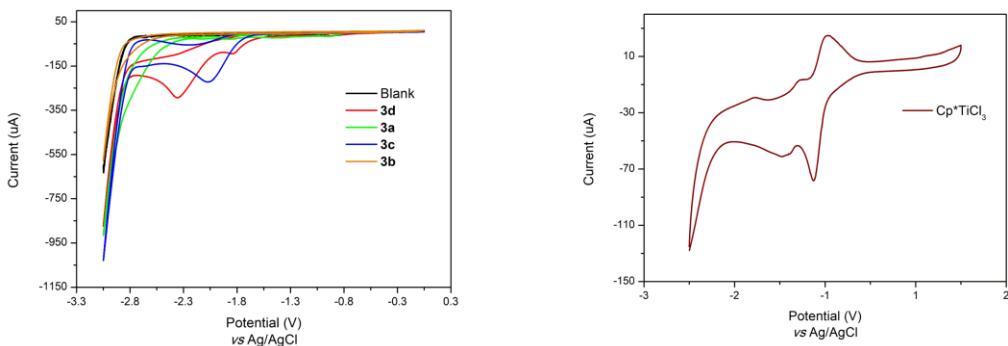
Competition experiment between 3a and 18 (in the presence of 4a): In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar were added glycosyl chloride **3a** (1.0 equiv., 0.1 mmol), tertiary alkyl chloride **18** (1.0 equiv., 0.1 mmol), Cp^{*}TiCl₃ (10 mol%), Mn powder (2.0 equiv., 0.2 mmol), Et₃N•HCl (1.5 equiv., 0.15 mmol) and acrylate **4a** (1.0 equiv., 0.10 mmol). The mixture was then dissolved in 0.5 mL dry THF. The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 16 h. After the reaction was complete, the volatiles were evaporated and the residues were purified by flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product **5a** as a colorless oil (α only, 46.9 mg, 72% yield). The conversion of **18** was observed to be <10% and the corresponding alkylated product **19a** was detected in <5% yield.

Competition experiment between 3a and 18 (in the presence of 4b): In a N₂-filled glovebox, to an oven-dried 5 mL vial equipped with a magnetic stir bar were added glycosyl chloride **3a** (1.0 equiv., 0.1 mmol), tertiary alkyl chloride **18** (1.0 equiv., 0.1 mmol), Cp^{*}TiCl₃ (10 mol%), Mn powder (2.0 equiv., 0.2 mmol), Et₃N•HCl (1.5 equiv., 0.15 mmol) and acrylamide **4b** (1.0 equiv., 0.10 mmol). The mixture was then

dissolved in 0.5 mL dry THF. The vial was tightly capped and removed from the glovebox. The mixture was allowed to vigorously stir at room temperature for 16 h. After the reaction was complete, the volatiles were evaporated and the residues were purified by flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product **5h** as a colorless oil (α only, 42.3 mg, 63% yield). The conversion of **18** was observed to be <10% and the corresponding alkylated product **19b** was detected in <5% yield.

6.4 Cyclic voltammetry studies

Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a Ag/AgCl reference electrode, and a platinum tablet counter electrode. The solution of interest was sparged with nitrogen for 3–5 minutes before data collection. Current was reported in μA , while all potentials were reported in V. Cyclic voltammograms of **3a–3d** and Cp^*TiCl_3 (10 mM) in MeCN (0.1 M *n*-Bu₄NClO₄) with a scan rate of 100 mV/s are shown below.



7. Computational studies

7.1 Computational methods

Kohn-Sham Density functional theory (KS-DFT) calculations were performed with *Gaussian 16* rev. B.01.¹ Geometry optimizations were performed using the B3LYP hybrid functional^{2–5} with Grimme's D3 dispersion correction with Becke-Jonson damping⁶ (herein denoted B3LYP-D3BJ) and the def2-SVP⁷ Karlsruhe-family basis

set. Minima and transition structures on the potential energy surface (PES) were confirmed using harmonic frequency analysis at the same level of theory, showing respectively zero and one imaginary frequency. Single point (SP) corrections were performed using B3LYP-D3BJ and def2-TZVP⁷ basis set for all atoms. The SMD implicit continuum solvation model⁸ was used to account for the effect of tetrahydrofuran (THF) solvent on the computed Gibbs energy profile. Gibbs energies were evaluated at the room temperature, using a quasi-RRHO treatment of vibrational entropies,⁹ using the GoodVibes code.¹⁰ Vibrational entropies of frequencies below 100 cm⁻¹ were obtained according to a free rotor description, using a smooth damping function to interpolate between the two limiting descriptions. The free energies were further corrected using standard concentration of 1 mol/L, which were used in solvation calculations. Unless otherwise stated, the final SMD (THF)-B3LYP-D3BJ/def2-TZVP//B3LYP-D3BJ/def2-SVP Gibbs energies are used for discussion throughout. *All Gibbs energy values in the text and figures are quoted in kcal mol⁻¹.*

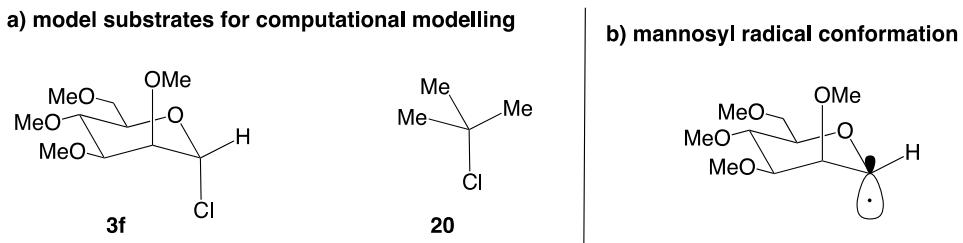
For species involving open-shell characteristics, including doublet radicals, radical ions and closed-shell diradicals, we performed above-mentioned DFT methodologies using the unrestricted formalism of Kohn-Sham theory (UKS). Wavefunction stability in the cases of closed-shell diradicals were checked using Gaussian keyword “stable=opt, guess=mix”. The eigenvalues of the spin operator \mathbf{S}^2 after annihilation of spin contamination were checked to ensure that they comply with the expected value of $S(S+1) = 0.75$ for a doublet wavefunction and $S(S+1) = 0$ for closed shell diradical, indicating that spin contamination is not a problem for the present methodology.

Non-covalent interactions (NCIs) were analyzed using NCIPILOT¹¹ calculations. The *.wfn* files for NCIPILOT were generated at B3LYP-D3BJ/def2-SVP level of theory. NCI indices calculated with NCIPILOT were visualized at a gradient isosurface value of $s = 0.5$ au. These are colored according to the sign of the second eigenvalue (λ_2) of the Laplacian of the density ($\nabla^2\rho$) over the range of -0.1 (blue = attractive) to +0.1 (red = repulsive). All molecular structures and molecular orbitals were visualized

using *PyMOL* software.¹² Geometries of all optimized structures (in .xyz format with their associated energy in Hartrees) are included in a separate folder named *structures_xyz* with an associated README file. All these data have been deposited with this Supporting Information.

7.2 Model simplification and conformational considerations

Mannosyl chloride **3f** and ^tBu–Cl **20** are used in computational modelling (Scheme S3 a)). The mannosyl radical generated from the homolytic cleavage of mannosyl chloride adopts a chair-like conformer (Scheme S3, b)), as described in literature by computational studies.^{13,14}



Scheme S3. a) Model substrates used in computational modelling, and b) chair-like conformation for mannosyl radical.

7.3 Gibbs energy profile without Ti-participation for radical addition step

Figure S1 shows the overall Gibbs energy profiles for the Ti-catalyzed radical alkylation reaction. The reaction energy profiles compare the relative reactivities for ^tBu–Cl (pathway in blue) vs glycosyl chloride (pathway in black). The overall transformation proceeds with first the generation of radical, followed by radical addition to the acrylamide, and finally the reduction of the radical intermediate to the neutral product.

The DFT-optimized key TSs are shown in Figure S2. The generation of ^tBu[·] radical (**TS1'**) has a barrier of 9.2 kcal mol⁻¹, which is 2.7 kcal mol⁻¹ higher than the generation of the glycosyl/mannosyl radical (**TS1**, at 6.5 kcal mol⁻¹). This implies a kinetic preference for the generation of glycosyl/mannosyl radical over ^tBu[·] radical by *ca.* 95 times at room temperature, using simple transition state theory. This step is

exergonic as the radicals formed have lower Gibbs energy than the starting material. In addition, this step is irreversible, as the subsequent radical addition (step from R^\bullet to acrylamide adduct via **TS2/TS2'**) has lower barriers than reversible addition of radical to Cp^*TiCl_3 (step from R^\bullet back to substrate **iii** and **iii'** via **TS1/TS1'**): for the glycosyl/mannosyl pathway, the forward barrier is 8.8 kcal mol⁻¹ while the reverse barrier is 9.9 kcal mol⁻¹; for the ^tBuCl pathway, the forward barrier is 10.5 kcal mol⁻¹ while the reverse barrier is 13.6 kcal mol⁻¹.

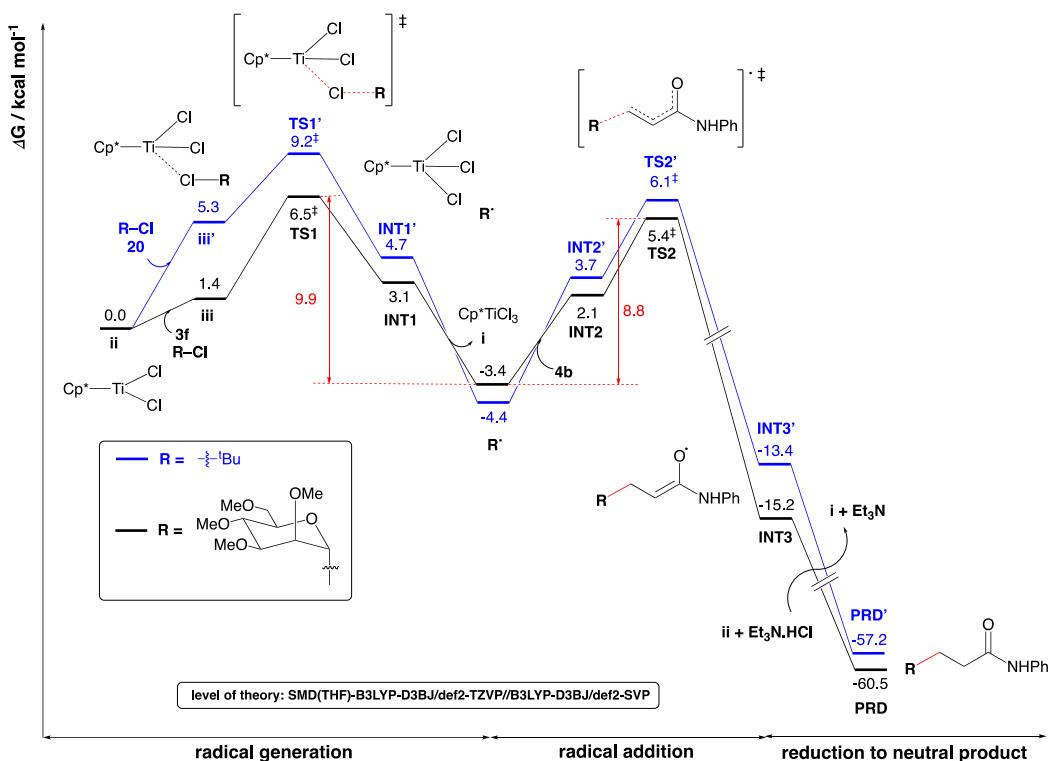


Figure S1. Overall Gibbs energy profile. Relative Gibbs energies are given in kcal mol⁻¹.

For the radical addition to acrylamide **4b**, in the absence of any coordination of acrylamide **4b** to Ti-catalyst, which could act as a Lewis acid (considered in section 6.4), the addition of glycosyl/mannosyl radical to acrylamide has a barrier of 8.8 kcal mol⁻¹ (**TS2**) whereas the addition of ^tBu[•] radical to acrylamide has a barrier of 10.5 kcal mol⁻¹ (**TS2'**). The activation energy difference, $\Delta\Delta G^\ddagger = 1.7$ kcal mol⁻¹ translates to a kinetic preference for glycosyl/mannosyl radical addition over ^tBu[•] radical addition to acrylamide by 18 times at room temperature. We will see that with

Ti-catalyst coordination to acrylamide, the radical addition step is not the overall rate-determining step and instead the radical generation step is the overall rate-determining step (*vide infra*).

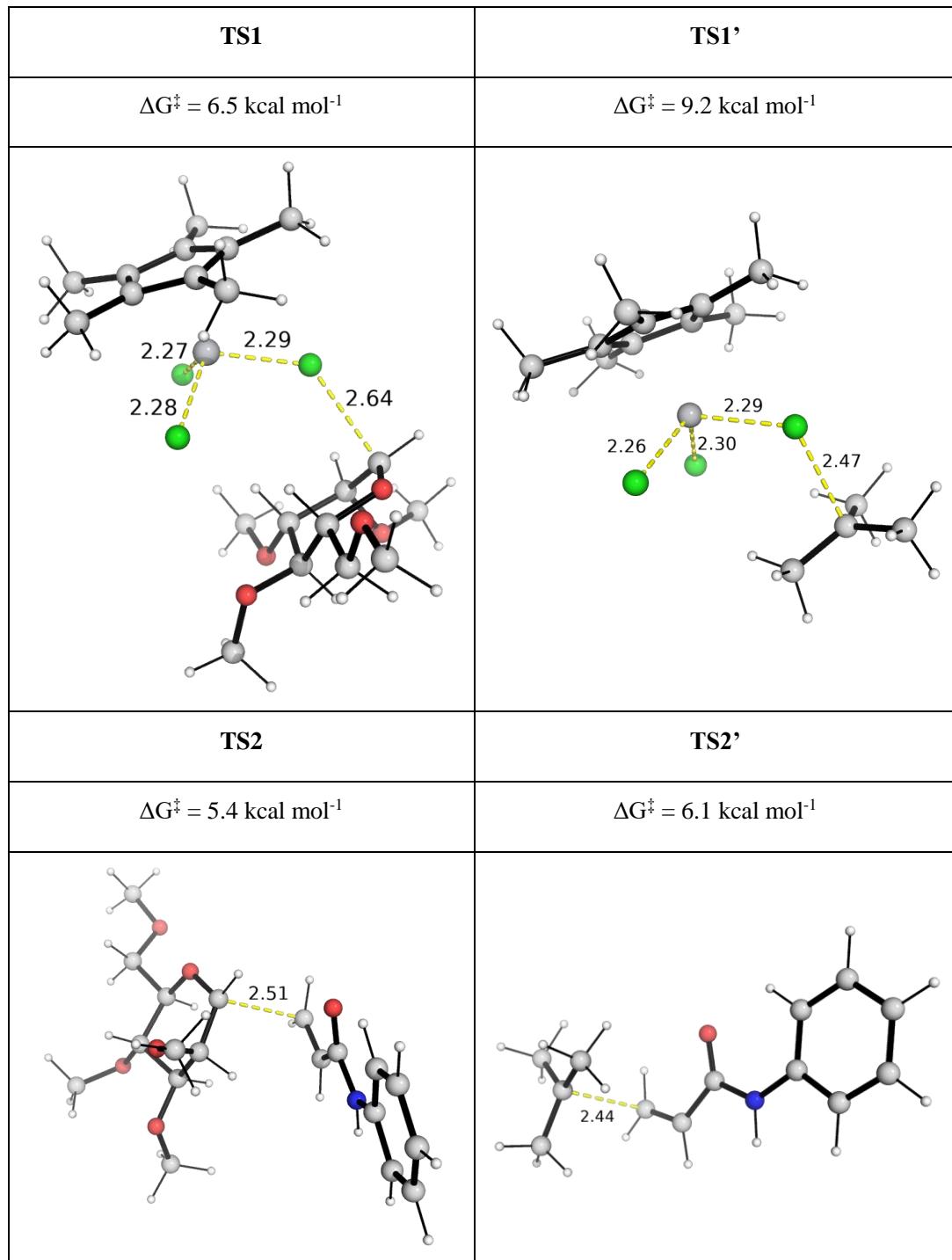


Figure S2. DFT optimized TS structures for the radical generation step (TS1 and TS1') and the radical addition to acrylamide (TS2 and TS2').

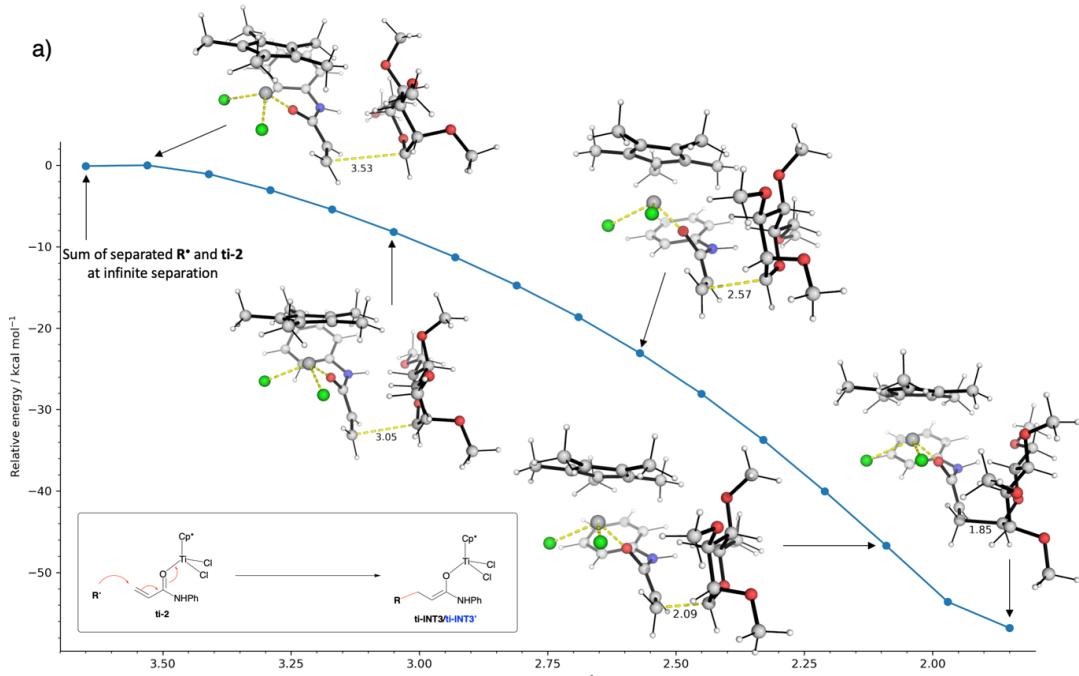
The reduction of the radical adduct **INT3/INT3'** by $\text{Cp}^*\text{Ti}^{(\text{III})}\text{Cl}_2$ and subsequent

protonation of the resultant enolate to give the final neutral product is highly exergonic and irreversible.

7.4 Gibbs energy profile with Ti-participation for radical addition step

The radical generation step in this case is the same as discussed in section 6.3. For the addition of the resultant radical to the $\text{Cp}^*\text{Ti}^{(\text{III})}\text{Cl}_2$ -coordinated acrylamide, no transition state structures were found – the optimization of reactant complex (with the forming C–C bond separation of $> 3.5\text{\AA}$) yields the product directly, indicating no barrier for the radical addition to the Ti(III)-activated acrylamide.

We further performed relaxed potential energy surface (PES) scans along the forming C–C bond and the result is shown in Figure S3, note that the C–C bond length range scanned cover the bond distances of **TS2** (2.51\AA) and **TS2'** (2.44\AA) shown in Figure S2. From Figure S3, we can see that no activation barrier exists for the addition of glycosyl/mannosyl radical to the Ti(III)-activated acrylamide. For the addition of ${}^{\text{'}}\text{Bu}^{\cdot}$ radical to the Ti(III)-activated acrylamide, there exists a small barrier for the complex formation (point 1 to point 2 in Figure S2b)). However, this barrier is much smaller compared to the transition state for radical generation (**TS1'**), shown in Figure S1.



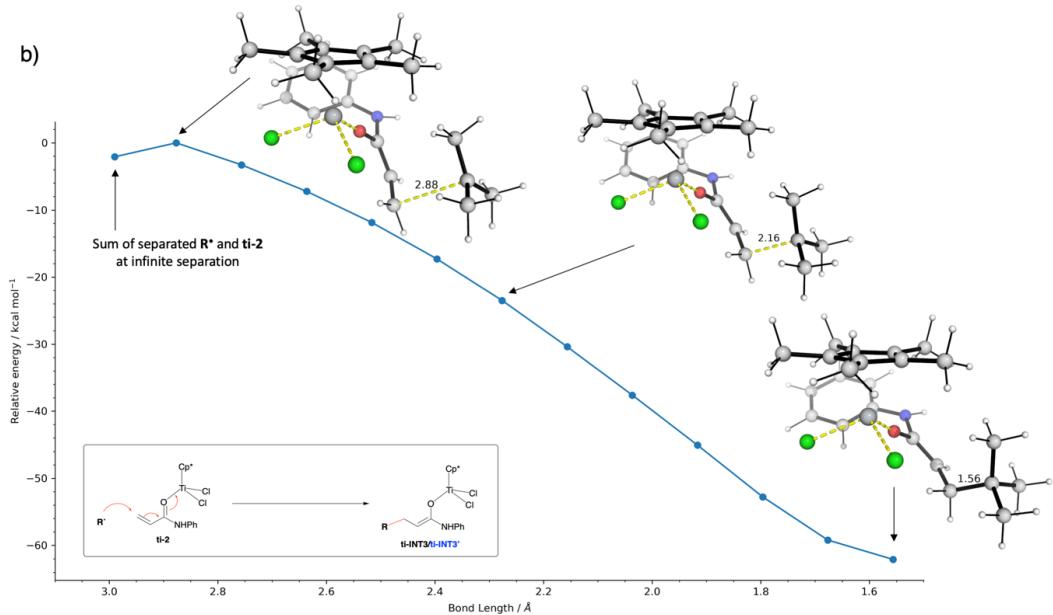


Figure S3. Relaxed potential energy surface (PES) scan in gas phase using UB3LYP-D3BJ/def2-SVP (*guess=mix*) for openshell-diradical system for a) the addition of glycosyl/mannosyl radical and b) the addition of tBu radical to Cp^{*}Ti^(III)Cl₂-coordinated acrylamide (named **ti-2** herein). Energy values are used without further corrections.

Figure S4 shows the Gibbs energy changes for the radical addition to Ti(III)-activated acrylamide, followed by the reduction to neutral product. We can see that these steps are highly exergonic and irreversible, as a strong C–C bond is formed. As a result of this analysis, we conclude that the rate-limiting step for the present Ti-catalyzed radical alkylation is the generation of radical step (**TS1** vs **TS1'**).

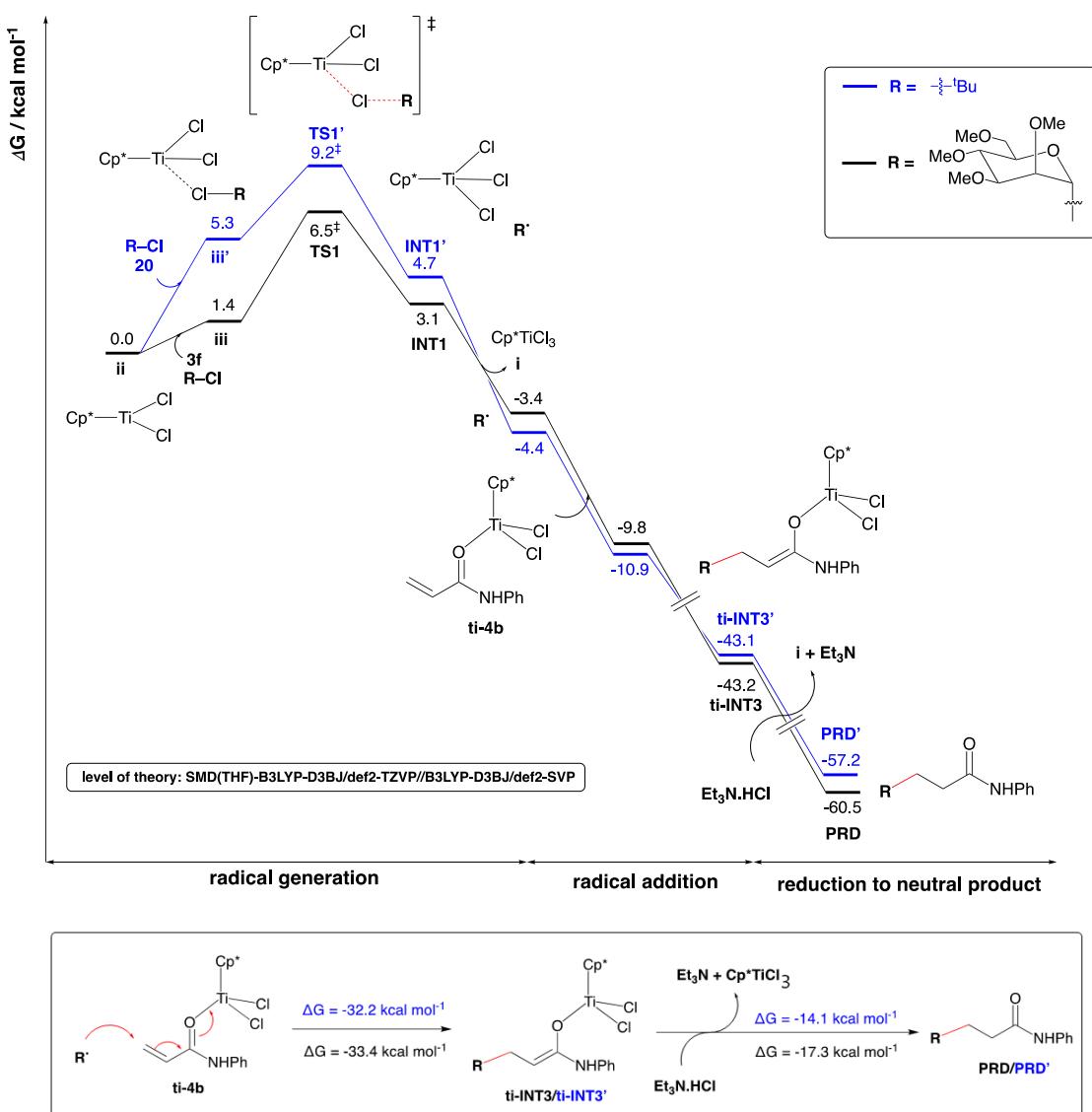


Figure S4. SMD(THF)-UB3LYP-D3BJ/def2-TZVP//UB3LYP-D3BJ/def2-SVP Gibbs energy change for the addition of radical to Ti(III)-coordinated acrylamide.

7.5 C–Cl bond strength and Radical stability

The bond dissociation enthalpies (BDEs) of the substrate can be computed. The corresponding radicals where a chlorine atom is removed were optimized, using unrestricted KS-DFT formalism, in addition to a chlorine atom. The BDE is calculated as

$$\text{BDE (R-Cl)} = H(\text{R}^\bullet) + H(\text{R}^\bullet) - H(\text{R-Cl})$$

where $H(X)$ is the enthalpy of chemical species X.

The calculations show that the C–Cl bond strengths in mannosyl chloride and ^tBuCl are similar, at 80.4 kcal mol⁻¹ and 80.3 kcal mol⁻¹, respectively.

Looking at the spin densities of the mannosyl and ^tBu• radicals, we can see that the spin density in the former is localized on the anomeric carbon atom where chlorine is removed, as well as on the anomeric oxygen atom, which stabilizes the mannosyl radical. On the other hand, the ^tBu• radical has spin density mostly on the carbon atom from which chlorine is abstracted. The stabilization by anomeric oxygen in mannosyl radical is likely to contribute to the stabilizing of the TS for mannosyl radical generation (**TS1**), resulting in lower activation barrier than ^tBu• radical generation (**TS1'**).

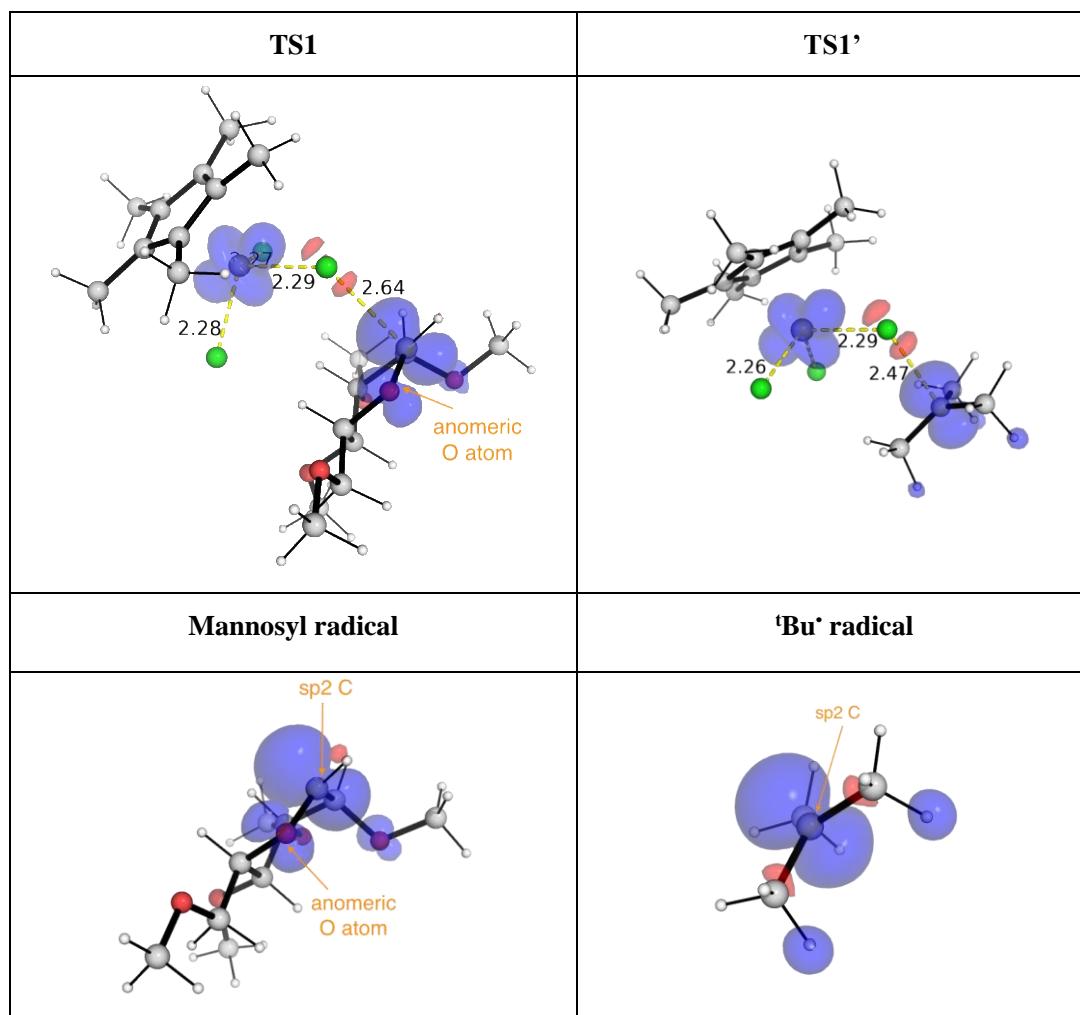


Figure S5. Spin density plots for the transition structures for the generation of mannosyl radical (**TS1**) and *tert*-butyl radical (**TS1'**), as well as for mannosyl radical and ^tBu• radical at isosurface value of 0.005 au.

7.6 Binding energies

The Gibbs energy change for the binding of glycosyl chloride **3f**, *tert*-butyl chloride **20**, acrylate **4a** and acrylamide **4b** were evaluated and the results are shown in Figure S6.

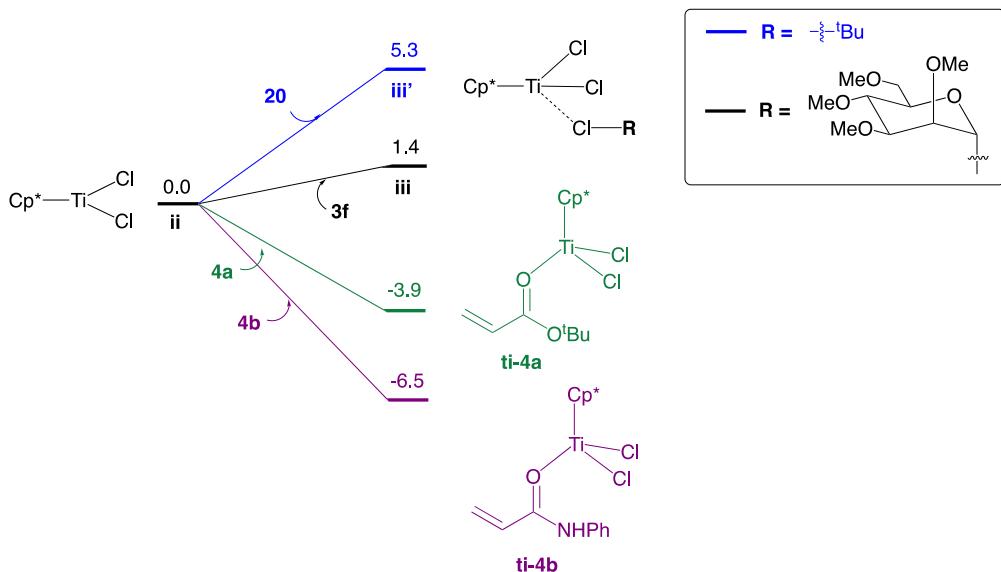


Figure S6. Gibbs energies of reaction (ΔG_r) for the binding of each chemical species to Cp^*TiCl_2 . Values are given in kcal mol⁻¹.

Comparing the binding energies of acrylate **4a** and acrylamide **4b**, we see that in the presence of both species, acrylamide **4b** will preferentially bind to Cp^*TiCl_2 catalyst over acrylate **4a**, possibly due to the more electron rich nature of acrylamide.

Comparing the binding of glycosyl chloride **3f** and *tert*-butyl chloride **20**, the binding of the former is more favorable. Their singly occupied molecular orbital (SOMO), spin density and non-covalent interactions (NCIs) appear to be similar. It is possible that the binding of glycosyl chloride **3f** gives a more stable complex due to its more favorable CH–Cl non-covalent interaction (NCI) between the CH group of the anomeric carbon and the Cl atom on Cp^*TiCl_2 (circled in orange, Figure S7) than the NCI between the CH group of the methyl group of *tert*-butyl chloride **20** and the Cl atom on Cp^*TiCl_2 (circled in orange, Figure S7) as suggested by the shorter CH–Cl distance in **iii** (2.36 Å) than in **iii'** (2.66 Å).

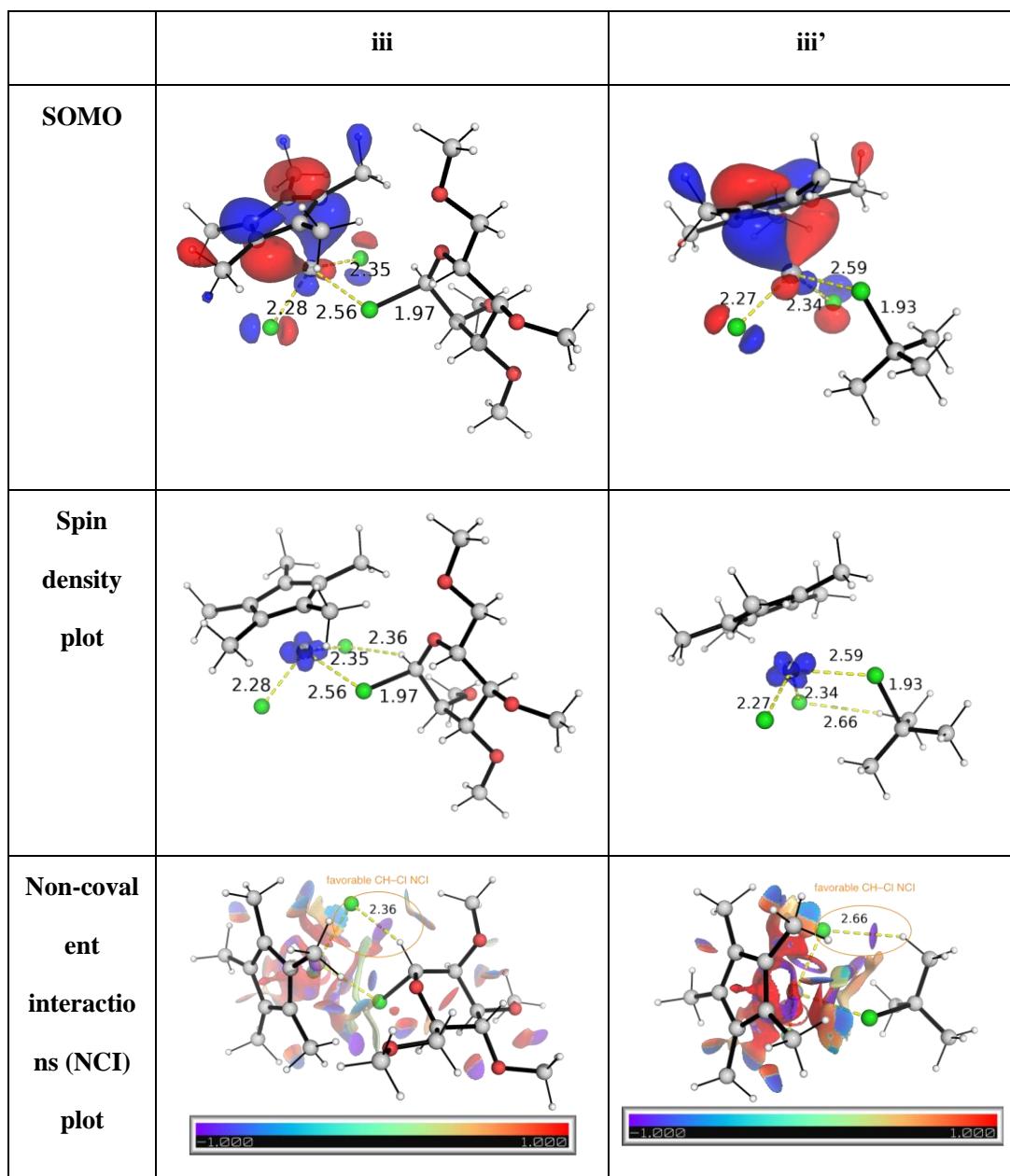


Figure S7. Plots of singly occupied molecular orbital (SOMO), spin density and non-covalent interactions (NCIs) for glycosyl chloride coordinated species **iii** and *tert*-butyl chloride coordinated species **iii'**.

7.7 Optimized structures and absolute energies, zero-point energies

Geometries of all optimized structures have been uploaded to zenodo.org (DOI: 10.5281/zenodo.4876297).

Absolute values (in Hartrees) for SCF energy, zero-point vibrational energy (ZPE), enthalpy and quasi-harmonic Gibbs free energy (at 25°C/298.15 K) for optimized

structures are given below. Single point corrections in SMD THF using B3LYP-D3BJ/def2-TZVP level of theory are also included.

Structure	E/au	ZPE/au	H/au	T.S/au	qh-G/au	SP
						SMD(THF)-B3L
						YP-D3BJ/def2-
						TZVP
3f	-1228.11276	0.298136	-1227.7952	0.064182	-1227.856406	-1229.162048
3f_radical	-767.973917	0.293565	-767.662	0.061974	-767.721294	-768.8612967
4b	-478.0418	0.160972	-477.87033	0.043071	-477.912412	-478.5851475
cl_radical	-460.006005	0	-460.00364	0.015019	-460.018663	-460.1693831
4a	-424.139369	0.178611	-423.9494	0.043465	-423.992287	-424.6282267
ti-4a	-2583.783389	0.40486	-2583.3488	0.084895	-2583.430251	-2585.120437
20	-617.834462	0.121784	-617.70522	0.033985	-617.739217	-618.1784793
20_radical	-157.698291	0.115668	-157.57528	0.033823	-157.608987	-157.8772053
Et3N	-292.233259	0.204717	-292.01814	0.041414	-292.058876	-292.5640443
Et3N.HCl	-752.936735	0.217374	-752.70719	0.04607	-752.752387	-753.4462825
ti-4b	-2637.689686	0.387051	-2637.2738	0.084821	-2637.354219	-2639.081438
INT2'	-635.749282	0.278047	-635.45258	0.065112	-635.513259	-636.4666674
TS2'	-635.747939	0.278951	-635.45187	0.060005	-635.508774	-636.4660296
INT3'	-635.787759	0.283086	-635.48838	0.057368	-635.543019	-636.5026895
PRD'	-636.441707	0.297008	-636.1286	0.056243	-636.182219	-637.1570993
INT2	-1246.028953	0.452402	-1245.5464	0.092676	-1245.631009	-1247.453595
TS2	-1246.025363	0.452582	-1245.5437	0.090627	-1245.626234	-1247.449656
INT3	-1246.065228	0.455673	-1245.581	0.087488	-1245.661851	-1247.48671
PRD	-1246.720113	0.469903	-1246.2219	0.085683	-1246.301338	-1248.144169
i	-2619.74185	0.226168	-2619.4959	0.066057	-2619.55869	-2620.765433
ii	-2159.592283	0.22385	-2159.35	0.063217	-2159.410307	-2160.461864
iii	-3387.74607	0.520302	-3387.187	0.108829	-3387.28797	-3389.641458
TS1-c2	-3387.736893	0.518484	-3387.1801	0.107315	-3387.279997	-3389.631774

INT1	-3387.742765	0.517875	-3387.1857	0.110467	-3387.287702	-3389.635633
iii-c2	-3387.743851	0.519803	-3387.185	0.109666	-3387.286677	-3389.635573
TS1	-3387.734389	0.517512	-3387.1781	0.110794	-3387.279756	-3389.629838
INT1-c2	-3387.735305	0.517288	-3387.1786	0.113087	-3387.281834	-3389.632017
iii'	-2777.457579	0.346941	-2777.084	0.080627	-2777.160208	-2778.652096
TS1'	-2777.4482	0.34413	-2777.0773	0.081363	-2777.154137	-2778.642486
INT1'	-2777.451233	0.342676	-2777.0802	0.087621	-2777.161266	-2778.645645
ti-INT3'	-2795.483614	0.511114	-2794.9383	0.095185	-2795.027824	-2797.040988
ti-INT3	-3405.764902	0.684272	-3405.0344	0.123764	-3405.148502	-3408.024217

7.8 References:

Full reference Gaussian 16:

Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

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8. Analytical data of products

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5a):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (α only, 60.7 mg, 93% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.19 (m, 18H), 7.12 (dd, J = 7.5, 2.1 Hz, 2H), 4.61 (d, J = 11.4 Hz, 1H), 4.56 – 4.48 (m, 3H), 4.46 – 4.42 (m, 4H), **3.90 (dt, J = 9.4, 4.6 Hz, 1H)**, 3.79 (t, J = 6.4 Hz, 1H), 3.72 – 3.69 (m, 2H), 3.65 (td, J = 10.0, 9.5, 4.4 Hz, 2H), 3.51 (dd, J = 4.8, 3.0 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.17 (ddd, J = 16.2, 8.7, 7.0 Hz, 1H), 1.81 – 1.67 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 138.54, 138.47, 138.40, 138.38, 128.53, 128.50, 128.48, 128.13, 128.07, 128.0, 127.9, 127.83, 127.82, 127.79, 127.7, 80.4, 77.4, 76.2, 75.0, 73.9, 73.6, 73.5, 72.3, 72.1, 71.7, 69.3, 31.8, 28.3, 25.2; HRMS (ESI) m/z calcd for $\text{C}_{41}\text{H}_{48}\text{NaO}_7$ [(M+Na) $^+$]: 675.3292, found: 675.3291.

Benzyl

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5b):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (α only, 62.4 mg, 91% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.16 (m, 23H), 7.13 – 7.10 (m, 2H), 5.02 (s, 2H), 4.58 (d, J = 11.4 Hz, 1H), 4.48 (d, J = 4.1 Hz, 2H), 4.49 – 4.40 (m, 5H), **3.90 (dt, J = 9.5, 4.8 Hz, 1H)**, 3.77 (t, J = 6.3 Hz, 1H), 3.74 – 3.6 (m, 2H), 3.62 (td, J = 11.8, 10.2, 4.7 Hz, 2H), 3.49 (dd, J = 5.2, 3.0 Hz, 1H), 2.45 (ddd, J = 15.3, 8.7, 6.1 Hz, 1H), 2.32 (dt, J = 16.3, 7.7 Hz, 1H), 1.88 – 1.74 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.3, 138.5, 138.4, 138.32, 138.30, 136.2, 128.7, 128.53, 128.51, 128.47, 128.4, 128.3, 128.13, 128.06, 128.0, 127.9, 127.84, 127.81, 127.7, 79.0, 76.2, 74.9, 73.7,

73.6, 73.5, 72.4, 71.8, 71.7, 69.2, 66.4, 30.6, 25.3; HRMS (ESI) m/z calcd for C₄₄H₄₆NaO₇ [(M+Na)⁺]: 709.3136, found: 709.3135.

Naphthalen-2-yl

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5c):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 67.1 mg, 93% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.72 (m, 2H), 7.69 – 7.66 (m, 1H), 7.44 (d, *J* = 2.3 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.28 – 7.26 (m, 2H), 7.25 – 7.16 (m, 16H), 7.14 – 7.10 (m, 3H), 4.57 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 1.3 Hz, 2H), 4.47 – 4.42 (m, 5H), **4.00 (q, J = 6.4 Hz, 1H)**, 3.82 – 3.77 (m, 2H), 3.75 – 3.70 (m, 2H), 3.65 (dd, *J* = 10.2, 3.8 Hz, 1H), 3.55 (dd, *J* = 5.5, 2.9 Hz, 1H), 2.73 – 2.65 (m, 1H), 2.58 (dt, *J* = 16.7, 7.7 Hz, 1H), 1.94 (q, *J* = 7.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 148.5, 138.5, 138.34, 138.26, 138.2, 133.9, 131.6, 129.5, 128.53, 128.48, 128.2, 128.04, 127.98, 127.88, 127.86, 127.8, 127.7, 126.6, 125.8, 121.3, 118.6, 76.6, 76.2, 74.9, 73.8, 73.6, 73.5, 72.4, 71.7, 71.4, 69.1, 30.7, 25.4; HRMS (ESI) m/z calcd for C₄₇H₄₆NaO₇ [(M+Na)⁺]: 745.3136, found: 745.3135.

Allyl

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5d):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (α only, 47.7 mg, 75% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.16 (m, 18H), 7.13 – 7.10 (m, 2H), 5.82 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.24 – 5.12 (m, 2H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.51 – 4.42 (m, 9H), **3.90 (dt, J = 9.5, 4.7 Hz, 1H)**, 3.79 – 3.76 (m, 1H), 3.74 – 3.66 (m, 3H), 3.62 (dd, *J* = 10.0, 3.8 Hz, 1H), 3.50 (dd, *J* = 5.0, 3.0 Hz, 1H), 2.43 (ddd, *J* = 16.5, 9.0, 5.9 Hz, 1H), 2.30 (ddd, *J* = 16.3, 8.6, 7.1 Hz, 1H), 1.87 – 1.74 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 138.5, 138.4, 138.3, 132.4, 128.52, 128.50, 128.47,

128.4, 128.13, 128.10, 128.06, 128.0, 127.87, 127.85, 127.83, 127.81, 127.7, 118.3, 77.1, 76.2, 74.9, 73.8, 73.6, 73.5, 72.3, 71.8, 71.7, 69.2, 65.2, 30.5, 25.2; HRMS (ESI) m/z calcd for C₄₀H₄₄NaO₇ [(M+Na)⁺]: 659.2979, found: 659.2974.

**(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl
3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5e):**

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (α only, 64.6 mg, 88% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.18 (m, 18H), 7.13 – 7.11 (m, 2H), 4.63 – 4.56 (m, 2H), 4.53 – 4.48 (m, 3H), 4.44 (dd, *J* = 11.7, 1.8 Hz, 4H), **3.90 (td, *J* = 7.0, 5.2 Hz, 1H)**, 3.79 – 3.74 (m, 2H), 3.72 – 3.70 (m, 1H), 3.65 (td, *J* = 10.2, 4.6 Hz, 2H), 3.50 (dd, *J* = 5.2, 3.0 Hz, 1H), 2.39 (dt, *J* = 16.3, 7.5 Hz, 1H), 2.23 (dt, *J* = 16.2, 7.9 Hz, 1H), 1.91 – 1.86 (m, 1H), 1.82 – 1.73 (m, 3H), 1.59 (ddd, *J* = 13.2, 6.8, 3.3 Hz, 3H), 1.44 – 1.34 (m, 1H), 1.31 – 1.24 (m, 1H), 1.02 – 0.94 (m, 1H), 0.92 – 0.85 (m, 1H), 0.81 (t, *J* = 6.9 Hz, 6H), 0.66 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 173.1, 138.5, 138.4, 138.34, 138.33, 128.53, 128.50, 128.47, 128.12, 128.08, 128.0, 127.9, 127.84, 127.79, 127.7, 76.2, 74.9, 74.3, 73.73, 73.67, 73.5, 72.4, 71.73, 71.69, 69.2, 47.2, 41.1, 34.4, 31.5, 30.8, 26.4, 25.4, 23.6, 22.2, 20.9, 16.5; HRMS (ESI) m/z calcd for C₄₇H₅₈NaO₇ [(M+Na)⁺]: 757.4075, found: 757.4078.

(5*S*,8*R*,9*S*,10*S*,13*S*,17*S*)-10,13-dimethyl-3-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5f):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 46.9 mg, 54% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 18H), 7.22 – 7.19 (m, 2H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.61 – 4.57 (m, 3H), 4.57 – 4.50 (m, 5H), **3.97 (q, *J* = 6.6, 6.1 Hz, 1H)**, 3.87 – 3.81 (m, 2H), 3.80 – 3.75 (m, 2H), 3.71 (dd, *J* = 10.1, 3.8 Hz, 1H),

3.58 (dd, $J = 5.2$, 3.0 Hz, 1H), 2.50 – 2.42 (m, 1H), 2.40 – 2.29 (m, 3H), 2.19 – 2.07 (m, 2H), 2.01 (ddd, $J = 13.3$, 6.5, 2.4 Hz, 1H), 1.86 (q, $J = 7.6$ Hz, 2H), 1.73 (dt, $J = 13.9$, 4.4 Hz, 2H), 1.62 (s, 3H), 1.59 – 1.53 (m, 1H), 1.51 – 1.42 (m, 2H), 1.39 – 1.26 (m, 5H), 1.15 (td, $J = 12.9$, 4.0 Hz, 1H), 1.08 – 1.03 (m, 1H), 1.02 (s, 3H), 0.91 (qd, $J = 12.4$, 5.5 Hz, 1H), 0.79 (s, 3H), 0.77 – 0.71 (m, 1H), ^{13}C NMR (126 MHz, CDCl_3) δ 212.1, 173.6, 138.5, 138.4, 138.3, 128.6, 128.52, 128.50, 128.13, 128.08, 128.0, 127.9, 127.8, 127.7, 82.8, 76.9, 76.2, 75.0, 73.73, 73.68, 73.5, 72.4, 71.8, 71.7, 69.2, 53.9, 50.7, 46.8, 44.8, 42.9, 38.7, 38.3, 37.0, 35.9, 35.4, 31.4, 30.7, 29.0, 27.7, 25.4, 23.7, 21.1, 12.4, 11.6; HRMS (ESI) m/z calcd for $\text{C}_{56}\text{H}_{68}\text{NaO}_8$ [(M+Na) $^+$]: 891.4806, found: 891.4800.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5g):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 73.8 mg, 87% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.16 (m, 19H), 7.13 (dd, $J = 7.5$, 2.0 Hz, 2H), 6.76 – 6.71 (m, 2H), 4.58 (d, $J = 11.5$ Hz, 1H), 4.51 – 4.43 (m, 7H), **3.98 (q, $J = 6.4$ Hz, 1H)**, 3.80 – 3.77 (m, 2H), 3.74 – 3.69 (m, 2H), 3.66 – 3.63 (m, 1H), 3.54 (dd, $J = 5.4$, 2.9 Hz, 1H), 2.81 (dd, $J = 8.2$, 3.5 Hz, 2H), 2.63 (dt, $J = 16.6$, 7.3 Hz, 1H), 2.52 (q, $J = 8.6$, 8.2 Hz, 1H), 2.42 (dd, $J = 18.9$, 8.6 Hz, 1H), 2.35 – 2.30 (m, 1H), 2.20 (td, $J = 10.8$, 4.2 Hz, 1H), 2.06 (dt, $J = 18.6$, 8.7 Hz, 1H), 2.00 – 1.85 (m, 5H), 1.57 – 1.46 (m, 3H), 1.45 – 1.33 (m, 3H), 0.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 221.0, 172.4, 148.7, 138.5, 138.4, 138.3, 138.2, 138.1, 137.4, 128.53, 128.49, 128.2, 128.1, 128.0, 127.9, 127.7, 126.5, 121.7, 118.9, 76.7, 76.1, 74.9, 73.7, 73.6, 73.5, 72.4, 71.6, 71.5, 69.1, 50.6, 48.1, 44.3, 38.1, 36.0, 31.7, 30.6, 29.5, 26.5, 25.9, 25.4, 21.7, 14.0; HRMS (ESI) m/z calcd for $\text{C}_{55}\text{H}_{60}\text{NaO}_8$ [(M+Na) $^+$]: 871.4180, found: 871.4177.

N-phenyl-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propenamide (5h):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 55.0 mg, 82% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.36 (d, J = 7.9 Hz, 2H), 7.25 – 7.16 (m, 20H), 7.13 (dd, J = 7.3, 2.2 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 4.61 (d, J = 11.5 Hz, 1H), 4.52 – 4.48 (m, 3H), 4.44 – 4.40 (m, 4H), **3.95 (dt, J = 11.0, 4.3 Hz, 1H)**, 3.79 (td, J = 6.8, 5.8, 2.8 Hz, 1H), 3.75 – 3.71 (m, 2H), 3.65 (t, J = 6.3 Hz, 1H), 3.57 – 3.52 (m, 2H), 2.34 (t, J = 7.0 Hz, 2H), 1.98 – 1.89 (m, 1H), 1.86 – 1.77 (m, 1H); ^{13}C NMR (126 MHz, CDCl₃) δ 171.4, 138.3, 138.2, 138.1, 138.0, 129.0, 128.61, 128.57, 128.3, 128.1, 127.97, 127.93, 127.9, 124.1, 120.1, 76.9, 76.1, 75.2, 73.9, 73.6, 73.5, 72.5, 72.0, 71.6, 69.1, 34.0, 25.8; HRMS (ESI) m/z calcd for C₄₃H₄₆NO₆ [(M+H)⁺]: 672.3320, found: 672.3319.

N-phenethyl-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanamide (5i):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:1) gave the pure product as a colorless oil (α only, 53.8 mg, 77% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.17 (m, 20H), 7.14 – 7.06 (m, 5H), 5.74 (s, 1H), 4.62 (d, J = 11.4 Hz, 1H), 4.54 – 4.49 (m, 2H), 4.47 – 4.37 (m, 5H), **3.88 (dt, J = 8.5, 3.8 Hz, 1H)**, 3.72 – 3.64 (m, 4H), 3.58 – 3.54 (m, 1H), 3.49 (dd, J = 4.7, 2.7 Hz, 1H), 3.33 (dq, J = 14.0, 7.2, 6.7 Hz, 2H), 2.63 (t, J = 7.1 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.85 – 1.78 (m, 1H), 1.74 – 1.68 (m, 1H); ^{13}C NMR (126 MHz, CDCl₃) δ 172.8, 139.2, 138.30, 138.26, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.91, 127.87, 126.6, 77.3, 76.2, 75.2, 74.0, 73.39, 73.35, 72.4, 71.9, 71.7, 69.3, 40.9, 35.9, 32.7, 25.8; HRMS (ESI) m/z calcd for C₄₅H₅₀NO₆ [(M+H)⁺]: 700.3633, found: 700.3626.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-(3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanamido)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5j):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 55.5 mg, 60% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.19 (m, 16H), 7.18 – 7.11 (m, 4H), 6.55 (d, J = 9.4 Hz, 1H), 5.18 (dt, J = 15.5, 9.4 Hz, 2H), 4.98 (t, J = 9.7 Hz, 1H), 4.83 (t, J = 9.6 Hz, 1H), 4.54 (dd, J = 14.9, 11.9 Hz, 2H), 4.47 – 4.40 (m, 6H), 4.20 (dd, J = 12.5, 4.3 Hz, 1H), **3.96 (dd, J = 12.5, 2.2 Hz, 1H)**, 3.84 (ddd, J = 9.6, 5.5, 3.6 Hz, 1H), 3.78 – 3.70 (m, 3H), 3.68 – 3.67 (m, 2H), 3.50 – 3.45 (m, 2H), 2.18 (td, J = 7.2, 2.3 Hz, 2H), 1.95 (s, 3H), 1.94 (s, 6H), 1.89 (s, 3H), 1.81 – 1.72 (m, 2H); ^{13}C NMR (126 MHz, CDCl₃) δ 173.4, 171.1, 170.8, 170.1, 169.7, 138.4, 138.3, 138.23, 138.18, 128.6, 128.5, 128.2, 128.03, 128.00, 127.95, 127.91, 127.88, 127.8, 78.3, 76.5, 76.3, 74.9, 73.6, 73.4, 73.1, 72.4, 71.7, 71.4, 70.7, 68.7, 68.3, 61.9, 33.1, 25.6, 20.9, 20.78, 20.76; HRMS (ESI) m/z calcd for C₅₁H₅₉NNaO₁₅ [(M+Na)⁺]: 948.3777, found: 948.3775.

N,N-Diphenyl-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanamide (5k):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 52.3 mg, 70% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.35 (m, 3H), 7.34 – 7.28 (m, 20H), 7.25 – 7.23 (m, 5H), 7.20 (dd, J = 7.6, 1.9 Hz, 2H), 4.75 (d, J = 11.3 Hz, 1H), 4.66 (d, J = 12.2 Hz, 1H), 4.60 – 4.46 (m, 6H), **4.02 (dt, J = 10.7, 3.7 Hz, 1H)**, 3.89 (t, J = 7.5 Hz, 1H), 3.78 (dd, J = 7.7, 3.0 Hz, 1H), 3.69 (dd, J = 10.1, 5.3 Hz, 1H), 3.65 – 3.63 (m, 1H), 3.62 (d, J = 3.6 Hz, 1H), 3.59 (dd, J = 10.2, 3.1 Hz, 1H), 2.45 (ddd, J = 16.4, 8.7, 5.4 Hz, 1H), 2.32 (ddd, J = 16.2, 8.3, 7.1 Hz, 1H), 2.01 – 1.93 (m, 1H), 1.90 – 1.84 (m, 1H); ^{13}C NMR (101 MHz, CDCl₃) δ 172.6, 142.9, 138.6, 138.5, 138.4, 128.51, 128.48, 128.46, 128.1, 128.0, 127.94, 127.89, 127.8, 127.74, 127.70, 127.6, 78.2, 76.4, 75.2, 74.2, 73.4, 73.3, 72.8, 72.2, 71.7, 69.4, 31.7, 25.1; HRMS (ESI) m/z calcd for C₄₉H₄₉NNaO₆ [(M+Na)⁺]: 770.3452, found: 770.3455.

N-Methyl-N-phenyl-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanamide (5l):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 51.4 mg, 75% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 21H), 7.18 (dd, J = 20.7, 7.3 Hz, 4H), 4.77 (d, J = 11.2 Hz, 1H), 4.66 (d, J = 12.3 Hz, 1H), 4.60 – 4.45 (m, 6H), **3.95 (d, J = 10.6 Hz, 1H)**, 3.88 (t, J = 7.8 Hz, 1H), 3.76 (dd, J = 8.0, 2.8 Hz, 1H), 3.68 (dd, J = 11.0, 5.4 Hz, 1H), 3.59 – 3.55 (m, 3H), 3.26 (s, 3H), 2.30 – 2.24 (m, 1H), 2.15 – 2.08 (m, 1H), 1.95 – 1.87 (m, 1H), 1.79 – 1.73 (m, 1H); ^{13}C NMR (126 MHz, CDCl₃) δ 172.5, 144.1, 138.61, 138.57, 138.5, 138.4, 129.9, 128.50, 128.46, 128.4, 128.1, 128.0, 127.93, 127.88, 127.8, 127.72, 127.68, 127.6, 127.5, 78.4, 76.3, 75.2, 74.3, 73.4, 73.1, 72.1, 71.7, 69.4, 37.5, 30.5, 25.1; HRMS (ESI) m/z calcd for C₄₄H₄₇NNaO₆ [(M+Na)⁺]: 708.3296, found: 708.3291.

1-(Indolin-1-yl)-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propan-1-one (5m):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:1) gave the pure product as a colorless oil (α only, 36.2 mg, 52% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.23 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.3 Hz, 2H), 7.34 – 7.29 (m, 16H), 7.25 – 7.17 (m, 4H), 7.02 (t, J = 7.4 Hz, 1H), 4.78 (d, J = 11.3 Hz, 1H), 4.69 – 4.62 (m, 2H), 4.59 (d, J = 8.2 Hz, 2H), 4.56 – 4.52 (m, 3H), **4.11 (dt, J = 9.4, 4.5 Hz, 1H)**, 3.94 – 3.89 (m, 1H), 3.87 – 3.82 (m, 4H), 3.77 – 3.73 (m, 2H), 3.69 (t, J = 3.4 Hz, 1H), 3.07 (t, J = 8.5 Hz, 2H), 2.61 – 2.55 (m, 1H), 2.45 (dt, J = 16.1, 7.7 Hz, 1H), 2.04 – 1.98 (m, 2H); ^{13}C NMR (126 MHz, CDCl₃) δ 170.7, 143.1, 138.4, 138.32, 138.26, 138.2, 131.2, 128.40, 128.39, 128.35, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.53, 127.48, 124.5, 123.5, 116.9, 78.0, 76.1, 75.2, 74.1, 73.3, 73.2, 72.5, 72.1, 71.7, 69.6, 47.9, 31.6, 28.0, 24.3; HRMS (ESI) m/z calcd for C₄₅H₄₇NNaO₆ [(M+Na)⁺]: 720.3296, found: 720.3288.

(2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-Tris(benzyloxy)-2-((benzyloxy)methyl)-6-(2-(phenylsulfo

(nyl)ethyl)tetrahydro-2*H*-pyran (5n):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 63.0 mg, 91% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.77 (dd, J = 8.4, 1.3 Hz, 2H), 7.55 – 7.50 (m, 1H), 7.44 – 7.40 (m, 2H), 7.24 – 7.16 (m, 16H), 7.14 – 7.10 (m, 4H), 4.42 – 4.31 (m, 8H), **3.80 – 3.74 (m, 2H)**, 3.68 – 3.61 (m, 3H), 3.52 (dd, J = 10.2, 5.0 Hz, 1H), 3.41 (dd, J = 7.2, 2.8 Hz, 1H), 3.20 (ddd, J = 14.1, 11.6, 4.7 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.00 (dddd, J = 13.7, 11.6, 4.8, 3.3 Hz, 1H), 1.80 (dddd, J = 14.3, 11.3, 9.8, 4.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl₃) δ 139.3, 138.3, 138.1, 138.0, 137.9, 133.7, 129.4, 128.57, 128.55, 128.5, 128.20, 128.17, 128.1, 128.00, 127.98, 127.81, 127.78, 76.0, 74.7, 74.4, 74.2, 73.3, 72.9, 72.6, 71.6, 69.3, 68.4, 53.0, 24.4; HRMS (ESI) m/z calcd for C₄₂H₄₄NaO₇S [(M+Na)⁺]: 715.2700, found: 715.2701.

(3aS,4R,6R,6aR)-4-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-phenethyl tetrahydrofuro[3,4-d][1,3]dioxole (5o):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 9.7 mg, 28% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 4.77 (dd, J = 6.1, 3.8 Hz, 1H), **4.52 (d, J = 6.0 Hz, 1H)**, 4.41 (ddd, J = 7.8, 6.3, 4.4 Hz, 1H), 4.11 (dd, J = 8.7, 6.3 Hz, 1H), 4.06 (dd, J = 9.8, 5.5 Hz, 1H), 4.03 (dd, J = 8.7, 4.4 Hz, 1H), 3.75 (dd, J = 7.7, 3.7 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.68 – 2.62 (m, 1H), 1.83 – 1.75 (m, 1H), 1.69 – 1.61 (m, 1H), 1.49 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (126 MHz, CDCl₃) δ 141.4, 128.8, 128.6, 126.2, 112.8, 109.4, 85.5, 83.6, 81.0, 80.2, 73.6, 67.3, 32.3, 32.1, 27.1, 26.3, 25.4, 24.8; HRMS (EI) m/z calcd for C₂₀H₂₈O₅ [M⁺]: 348.1937, found: 348.1923.

(3aS,4R,6R,6aR)-4-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-(4-(trifluoromethyl)phenethyl)tetrahydrofuro[3,4-d][1,3]dioxole (5p):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 19.1 mg, 46% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 4.78 (dd, J = 6.0, 3.5 Hz, 1H), **4.51 (d, J = 6.1 Hz, 1H)**, 4.43 – 4.39 (m, 1H), 4.12 (dd, J = 8.5, 6.5 Hz, 1H), 4.04 – 4.01 (m, 2H), 3.75 (dd, J = 7.6, 3.6 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.74 – 2.68 (m, 1H), 1.84 – 1.77 (m, 1H), 1.69 – 1.62 (m, 1H), 1.49 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H), 1.33 (s, 3H); ^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.36 (s, 3F); ^{13}C NMR (101 MHz, CDCl₃) δ 145.4, 129.0, 125.8 (q, J = 267.8), 125.6 (q, J = 3.8 Hz), 112.9, 109.4, 85.5, 83.3, 80.9, 80.3, 73.6, 67.2, 32.0, 31.97, 27.1, 26.3, 25.4, 24.8; HRMS (EI) m/z calcd for C₂₁H₂₇F₃O₅ [M⁺]: 416.1811, found: 416.1821.

(3a*S*,4*R*,6*R*,6a*R*)-4-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-((*Z*)-styryl)tetrahydrofuro[3,4-*d*][1,3]dioxole (7a):

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 95:5 Z:E, 12.8 mg, 37% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 4H), 7.29 – 7.27 (m, 1H), 6.62 (dd, J = 12.0, 1.5 Hz, 1H), 5.67 (dd, J = 11.9, 8.7 Hz, 1H), **4.97 (d, J = 8.7 Hz, 1H)**, 4.84 (dd, J = 6.0, 3.7 Hz, 1H), 4.67 (dd, J = 6.0, 1.1 Hz, 1H), 4.41 (ddd, J = 7.6, 6.2, 4.4 Hz, 1H), 4.09 (dd, J = 8.7, 6.2 Hz, 1H), 4.02 (dd, J = 8.7, 4.4 Hz, 1H), 3.89 (dd, J = 7.8, 3.7 Hz, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (126 MHz, CDCl₃) δ 135.9, 133.2, 129.4, 128.6, 127.72, 127.7, 113.1, 109.4, 86.4, 81.5, 81.1, 81.0, 73.6, 67.2, 27.2, 26.3, 25.4, 25.0; HRMS (EI) m/z calcd for C₂₀H₂₆O₅ [M⁺]: 346.1780, found: 346.1778.

N-(3-((*Z*)-2-((3a*R*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)vinyl)phenyl)-4-methylbenzenesulfonamide (7b):

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure

product as a colorless oil (α only, 94:6 Z:E, 21.6 mg, 42% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.65 (m, 2H), 7.24 – 7.21 (m, 3H), 7.12 (ddd, J = 8.1, 2.3, 1.0 Hz, 1H), 7.05 (dt, J = 7.7, 1.5 Hz, 1H), 7.00 (d, J = 1.9 Hz, 1H), 6.96 (t, J = 2.0 Hz, 1H), 6.52 (dd, J = 11.8, 1.5 Hz, 1H), 5.65 (dd, J = 11.8, 8.7 Hz, 1H), 4.84 (dd, J = 6.0, 3.9 Hz, 1H), **4.76 (dd, J = 8.8, 1.6 Hz, 1H)**, 4.61 (dd, J = 6.0, 1.5 Hz, 1H), 4.41 (ddd, J = 7.1, 6.3, 4.3 Hz, 1H), 4.08 (dd, J = 8.8, 6.3 Hz, 1H), 4.00 (dd, J = 8.8, 4.4 Hz, 1H), 3.92 (dd, J = 7.1, 3.8 Hz, 1H), 2.37 (s, 3H), 1.50 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃) δ 144.0, 137.1, 137.0, 136.4, 132.8, 129.8, 129.6, 128.4, 127.4, 126.1, 121.8, 120.2, 113.3, 109.4, 86.3, 81.24, 81.16, 81.0, 73.7, 67.0, 27.1, 26.4, 25.2, 25.0, 21.7; HRMS (EI) m/z calcd for C₂₇H₃₃NO₇S [M⁺]: 515.1978, found: 515.1976.

tert-Butyl

(4-((Z)-2-((3a*R*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)vinyl)phenyl)carbamate (7c):

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 96:4 Z:E, 20.3 mg, 44% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.54 – 6.50 (m, 2H), 5.59 (dd, J = 11.9, 8.5 Hz, 1H), **4.95 (d, J = 8.5 Hz, 1H)**, 4.82 (dd, J = 6.0, 3.7 Hz, 1H), 4.66 (dd, J = 6.0, 1.0 Hz, 1H), 4.42 (ddd, J = 7.8, 6.2, 4.5 Hz, 1H), 4.10 (dd, J = 8.7, 6.2 Hz, 1H), 4.04 (dd, J = 8.7, 4.5 Hz, 1H), 3.88 (dd, J = 7.8, 3.7 Hz, 1H), 1.52 (s, 12H), 1.45 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃) δ 152.8, 137.9, 132.5, 130.9, 130.2, 126.8, 118.4, 113.1, 109.4, 86.5, 81.7, 81.1, 81.0, 80.9, 73.6, 67.2, 28.5, 27.2, 26.4, 25.4, 25.0; HRMS (ESI) m/z calcd for C₂₅H₃₅NNaO₇ [(M+Na)⁺]: 484.2306, found: 484.2307.

(2*S*,5*R*)-*N*-(4-((Z)-2-((3a*R*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)vinyl)phenyl)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxamide 4,4-dioxide (7d):

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 98:2 Z:E, 27.0 mg, 47% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.56 (dd, *J* = 12.0, 1.6 Hz, 1H), 5.66 (dd, *J* = 11.9, 8.5 Hz, 1H), **4.92 (d, J = 8.6 Hz, 1H)**, 4.83 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.70 (t, *J* = 3.4 Hz, 1H), 4.65 (dd, *J* = 5.9, 1.1 Hz, 1H), 4.41 (ddd, *J* = 7.6, 6.2, 4.5 Hz, 1H), 4.33 (s, 1H), 4.09 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.02 (dd, *J* = 8.7, 4.5 Hz, 1H), 3.89 (dd, *J* = 7.6, 3.7 Hz, 1H), 3.61 (d, *J* = 3.3 Hz, 2H), 1.75 (s, 3H), 1.51 (d, *J* = 2.9 Hz, 6H), 1.45 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.5, 164.5, 135.6, 133.3, 132.1, 130.3, 128.1, 120.2, 113.2, 109.4, 86.4, 81.6, 81.1, 81.0, 73.6, 67.1, 64.7, 64.1, 60.7, 38.6, 27.2, 26.4, 25.4, 25.0, 19.7, 18.6; HRMS (ESI) m/z calcd for C₂₈H₃₆N₂NaO₉S [(M+Na)⁺]: 599.2034, found: 599.2032.

(8*R*,9*S*,13*S*,14*S*)-2-((*Z*)-2-((3*aR*,4*R*,6*R*,6*aS*)-6-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)vinyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (7e):

The title compound was prepared from the **General procedure B**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 4:1) gave the pure product as a colorless oil (α only, 97:3 *Z:E*, 18.8 mg, 36% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.1 Hz, 1H), 7.14 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.54 (dd, *J* = 11.9, 1.6 Hz, 1H), 5.62 (dd, *J* = 11.9, 8.6 Hz, 1H), **4.98 (d, J = 8.5 Hz, 1H)**, 4.83 (dd, *J* = 6.0, 3.7 Hz, 1H), 4.67 (dd, *J* = 6.0, 1.1 Hz, 1H), 4.41 (ddd, *J* = 7.8, 6.2, 4.6 Hz, 1H), 4.10 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.03 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.89 (dd, *J* = 7.7, 3.7 Hz, 1H), 2.94 – 2.92 (m, 2H), 2.51 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.33 – 2.29 (m, 1H), 2.20 – 2.13 (m, 1H), 2.11 – 1.95 (m, 3H), 1.67 – 1.60 (m, 2H), 1.55 – 1.48 (m, 6H), 1.45 – 1.42 (m, 4H), 1.38 (s, 3H), 1.35 (s, 3H), 0.92 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 221.1, 139.4, 136.7, 133.6, 132.7, 130.1, 127.5, 126.8, 125.6, 113.0, 109.4, 86.5, 81.7, 81.2, 81.0, 73.6, 67.2, 50.7, 48.2, 44.6, 38.3, 36.0, 31.8, 29.5, 27.2, 26.7, 26.4, 25.9, 25.4, 25.1, 21.8, 14.0; HRMS (EI) m/z calcd for C₃₂H₄₂O₆ [M⁺]: 522.2981, found: 522.2973.

tert-Butyl

3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5q):

The title compound was prepared from the **General procedure A**. Purification using

flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 29.6 mg, 85% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ **3.94 (dt, *J* = 10.3, 3.9 Hz, 1H)**, 3.59 – 3.56 (m, 3H), 3.50 (dd, *J* = 7.6, 3.1 Hz, 1H), 3.47 – 3.42 (m, 7H), 3.40 (s, 3H), 3.38 – 3.36 (m, 4H), 2.44 – 2.36 (m, 1H), 2.28 (ddd, *J* = 16.8, 8.8, 6.9 Hz, 1H), 1.93 – 1.83 (m, 1H), 1.79 – 1.71 (m, 1H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, CDCl₃) δ 172.8, 80.5, 79.8, 78.6, 76.7, 72.6, 71.9, 71.8, 59.9, 59.3, 58.0, 57.8, 31.8, 28.3, 24.8; HRMS (ESI) m/z calcd for C₁₇H₃₂NaO₇ [(M+Na)⁺]: 371.2040, found: 371.2045.

N-Phenyl-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-trimethoxy-6-(methoxymethyl)tetrahydro-2*H*-pyran-2-yl)propanamide (5r):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:2) gave the pure product as a colorless oil (α only, 23.5 mg, 64% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), **4.01 (dt, *J* = 10.9, 4.2 Hz, 1H)**, 3.71 – 3.66 (m, 2H), 3.57 – 3.51 (m, 2H), 3.48 (s, 3H), 3.48 (s, 3H), 3.42 – 3.38 (m, 7H), 3.36 – 3.33 (m, 1H), 2.49 – 2.46 (m, 2H), 2.01 – 1.92 (m, 2H); ^{13}C NMR (101 MHz, CDCl₃) δ 171.2, 138.5, 129.0, 124.1, 119.9, 79.7, 78.5, 77.0, 72.6, 71.9, 71.3, 60.0, 59.2, 58.1, 58.0, 33.9, 25.4; HRMS (EI) m/z calcd for C₁₉H₂₉NO₆ [M⁺]: 367.1995, found: 367.1999.

tert-Butyl

3-((2*R*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5s):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (> 95:5 $\alpha:\beta$, 61.3 mg, 94% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.19 (m, 20H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.64 – 4.47 (m, 5H), 4.46 – 4.36 (m, 2H), 3.92 – 3.88 (m, 3H), **3.79 – 3.75 (m, 1H)**, 3.69 – 3.63 (m, 2H), 3.56 (dd, *J* = 10.3, 4.9 Hz, 1H), 2.27 (ddd, *J* = 16.2, 9.1, 5.7 Hz, 1H), 2.13 (ddd, *J* = 16.2, 8.6, 7.2 Hz, 1H), 1.90 – 1.73 (m, 2H), 1.35 (s, 9H); ^{13}C

NMR (126 MHz, CDCl₃) δ 173.1, 138.8, 138.7, 138.5, 128.5, 128.4, 128.11, 128.07, 128.0, 127.9, 127.8, 127.70, 127.65, 80.3, 76.8, 74.6, 73.6, 73.5, 73.24, 73.15, 72.2, 71.4, 68.1, 32.0, 28.3, 22.6; HRMS (ESI) m/z calcd for C₄₁H₄₈NaO₇ [(M+Na)⁺]: 675.3292, found: 675.3286.

tert-Butyl

3-((2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5t):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (> 95:5 α:β, 60.0 mg, 92% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 18H), 7.06 – 7.04 (m, 2H), 4.84 (t, *J* = 9.8 Hz, 1H), 4.72 (t, *J* = 11.1 Hz, 2H), 4.59 (s, 2H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.39 (dd, *J* = 11.4, 5.0 Hz, 2H), **3.98 (ddd, J = 11.3, 5.5, 3.9 Hz, 1H)**, 3.72 (dd, *J* = 9.5, 7.8 Hz, 1H), 3.66 (dd, *J* = 9.5, 5.6 Hz, 1H), 3.61 (dd, *J* = 10.5, 3.4 Hz, 1H), 3.57 – 3.52 (m, 2H), 3.51 – 3.47 (m, 1H), 2.28 (ddd, *J* = 16.1, 8.9, 5.8 Hz, 1H), 2.18 (ddd, *J* = 16.0, 8.5, 7.0 Hz, 1H), 2.00 – 1.84 (m, 2H), 1.37 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 172.8, 138.9, 138.41, 138.37, 138.2, 128.6, 128.52, 128.49, 128.1, 128.02, 128.01, 127.9, 127.82, 127.79, 127.7, 82.5, 80.4, 80.0, 78.2, 75.6, 75.2, 73.7, 73.5, 73.1, 71.3, 69.1, 31.5, 28.3, 20.5; HRMS (ESI) m/z calcd for C₄₁H₄₈NaO₇ [(M+Na)⁺]: 675.3292, found: 675.3288.

N-phenyl-3-((2*R*,3*S*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanamide (5u):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (> 95:5 α:β, 40.3 mg, 60% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.36 – 7.29 (m, 20H), 7.18 (dd, *J* = 7.0, 2.6 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.83 (dd, *J* = 20.7, 10.9 Hz, 2H), 4.67 (s, 2H), 4.60 – 4.49 (m, 3H), **4.13 (dt, J = 11.2, 4.7 Hz, 1H)**, 3.84 (t, *J* = 8.9 Hz, 1H), 3.77 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.71 – 3.66 (m, 2H), 3.59 (dd, *J* = 10.4, 6.1 Hz, 1H), 3.51 – 3.44 (m, 1H), 2.45 (dd, *J*

= 8.3, 5.8 Hz, 2H), 2.25 – 2.18 (m, 1H), 2.16 – 2.07 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.1, 138.8, 138.3, 138.2, 137.9, 129.0, 128.65, 128.61, 128.60, 128.14, 128.11, 128.09, 128.05, 128.0, 127.8, 124.2, 119.9, 82.4, 80.0, 78.4, 75.7, 75.2, 73.7, 73.1, 72.6, 71.4, 69.8, 33.3, 21.5; HRMS (ESI) m/z calcd for $\text{C}_{43}\text{H}_{45}\text{NNaO}_6$ [(M+Na) $^+$]: 694.3139, found: 694.3136.

tert-Butyl

3-((2*R*,3*S*,4*S*,5*R*,6*R*)-3-acetoxy-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5v):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as white solid (91:9 $\alpha:\beta$, 42.3 mg, 70% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.18 (m, 13H), 7.09 – 7.07 (m, 2H), 4.98 (dd, J = 8.9, 5.5 Hz, 1H), 4.71 – 4.62 (m, 3H), 4.53 (d, J = 12.1 Hz, 1H), 4.42 (dd, J = 11.5, 4.1 Hz, 2H), 4.02 (ddd, J = 11.7, 5.6, 3.5 Hz, 1H), 3.77 – 3.73 (m, 1H), 3.66 – 3.56 (m, 4H), 2.31 (ddd, J = 16.5, 9.8, 5.3 Hz, 1H), 2.16 (ddd, J = 16.1, 9.1, 6.5 Hz, 1H), 1.96 – 1.84 (m, 4H), 1.74 – 1.63 (m, 1H), 1.36 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.7, 170.2, 138.5, 138.2, 128.59, 128.56, 128.5, 128.11, 128.06, 128.0, 127.93, 127.86, 127.8, 80.6, 80.1, 77.7, 75.0, 74.8, 73.7, 72.9, 72.0, 71.9, 69.0, 31.3, 28.3, 21.5, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{36}\text{H}_{44}\text{NaO}_8$ [(M+Na) $^+$]: 627.2928, found: 627.2924.

(2*R*,3*S*,4*S*,5*R*,6*R*)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)-2-(3-(diphenylamino)-3-oxopropyl)tetrahydro-2*H*-pyran-3-yl acetate (5w):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (91:9 $\alpha:\beta$, 37.0 mg, 53% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.13 (m, 23H), 7.08 – 7.05 (m, 2H), 4.95 (dd, J = 9.2, 5.7 Hz, 1H), 4.70 – 4.61 (m, 3H), 4.48 – 4.34 (m, 3H), 3.98 (ddd, J = 11.8, 5.7, 3.3 Hz, 1H), 3.73 (dd, J = 9.2, 8.3 Hz, 1H), 3.58 – 3.55 (m, 1H), 3.54 – 3.51 (m, 1H), 3.44 (ddd, J = 9.3, 4.0, 2.3 Hz, 1H), 3.38 (dd, J = 10.4, 2.2 Hz, 1H), 2.34 (ddd, J = 16.0, 9.2, 5.4 Hz, 1H), 2.17 (ddd, J = 15.9, 8.7, 6.5 Hz, 1H), 2.06 – 1.98 (m,

1H), 1.88 (s, 3H), 1.80 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.6, 170.2, 142.9, 138.6, 138.3, 138.2, 128.6, 128.54, 128.52, 127.97, 127.95, 127.89, 127.85, 127.8, 80.3, 77.9, 75.1, 74.8, 73.6, 73.0, 72.3, 71.7, 68.8, 31.3, 21.7, 21.1; HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{45}\text{NNaO}_7$ [(M+Na) $^+$]: 722.3088, found: 722.3085.

tert-Butyl

3-((2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)propanoate (5x):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (α only, 51.9 mg, 95% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 2H), 7.27 – 7.17 (m, 13H), 4.73 (d, J = 11.2 Hz, 1H), 4.61 – 4.46 (m, 5H), **3.87 (dt, J = 10.6, 3.8 Hz, 1H)**, 3.67 (dd, J = 7.7, 3.1 Hz, 1H), 3.60 – 3.53 (m, 1H), 3.52 – 3.48 (m, 2H), 2.25 (ddd, J = 16.4, 9.2, 5.6 Hz, 1H), 2.13 (ddd, J = 16.2, 8.8, 6.8 Hz, 1H), 1.78 (dddd, J = 14.3, 10.6, 8.8, 5.7 Hz, 1H), 1.65 – 1.60 (m, 1H), 1.35 (s, 9H), 1.25 (d, J = 6.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.7, 138.7, 138.50, 138.45, 128.54, 128.52, 128.50, 128.2, 128.1, 127.9, 127.82, 127.79, 80.5, 80.3, 78.5, 76.3, 74.6, 72.8, 72.3, 71.9, 69.6, 31.9, 28.3, 24.8, 18.3; HRMS (ESI) m/z calcd for $\text{C}_{34}\text{H}_{42}\text{NaO}_6$ [(M+Na) $^+$]: 569.2874, found: 569.2870.

N-Methyl-N-phenyl-3-((2S,3S,4R,5S,6S)-3,4,5-tris(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)propanamide (5y):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 38.8 mg, 67% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 18H), 7.19 (d, J = 7.7 Hz, 2H), 4.89 (d, J = 11.1 Hz, 1H), 4.70 (d, J = 12.4 Hz, 1H), 4.62 – 4.54 (m, 4H), **3.88 (d, J = 10.9 Hz, 1H)**, 3.71 (dd, J = 8.5, 3.0 Hz, 1H), 3.60 – 3.54 (m, 2H), 3.43 – 3.37 (m, 1H), 3.28 (s, 3H), 2.23 – 2.17 (m, 1H), 2.11 – 2.05 (m, 1H), 1.94 – 1.86 (m, 1H), 1.72 – 1.65 (m, 1H), 1.19 (d, J = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.5, 144.2, 138.8, 138.5, 129.9, 128.5, 128.4, 128.1, 128.01, 127.97, 127.9, 127.74, 127.71, 127.5,

80.6, 79.3, 76.4, 75.0, 73.8, 72.1, 71.9, 69.0, 37.5, 30.5, 24.8, 18.3; HRMS (ESI) m/z calcd for C₃₇H₄₁NNaO₅ [(M+Na)⁺]: 602.2877, found: 602.2871.

tert-Butyl

3-((2S,3S,4R,5S,6S)-3-acetoxy-4,5-bis(benzyloxy)-6-methyltetrahydro-2H-pyran-2-yl)propanoate (5z):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a foam solid (α only, 44.8 mg, 90% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.27 (m, 10H), 5.27 (dd, *J* = 3.4, 2.3 Hz, 1H), 4.88 (d, *J* = 10.9 Hz, 1H), 4.68 (d, *J* = 11.3 Hz, 1H), 4.60 (d, *J* = 11.0 Hz, 1H), 4.52 (d, *J* = 11.3 Hz, 1H), **3.89 – 3.85 (m, 1H)**, 3.84 – 3.82 (m, 1H), 3.62 (dq, *J* = 8.6, 6.0 Hz, 1H), 3.43 (t, *J* = 8.7 Hz, 1H), 2.35 (ddd, *J* = 16.5, 9.0, 5.7 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.14 (s, 3H), 2.03 – 1.93 (m, 1H), 1.80 – 1.72 (m, 1H), 1.44 (s, 9H), 1.32 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.3, 170.7, 138.6, 138.0, 128.59, 128.55, 128.2, 128.1, 128.0, 127.9, 80.7, 80.3, 78.0, 75.3, 75.0, 72.0, 70.9, 69.0, 31.7, 28.3, 24.1, 21.4, 18.5; HRMS (ESI) m/z calcd for C₂₉H₃₈NaO₇ [(M+Na)⁺]: 521.2510, found: 521.2511.

(2S,3S,4R,5S,6S)-4,5-Bis(benzyloxy)-6-methyl-2-(3-oxo-3-(phenylamino)propyl)tetrahydro-2H-pyran-3-yl acetate (5aa):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 32.1 mg, 62% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.47 (s, 1H), 7.36 – 7.27 (m, 12H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.27 (t, *J* = 3.0 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 11.1 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), **3.93 (ddd, J = 10.7, 4.5, 2.7 Hz, 1H)**, 3.86 (dd, *J* = 8.6, 3.4 Hz, 1H), 3.71 – 3.63 (m, 1H), 3.45 (t, *J* = 8.5 Hz, 1H), 2.49 – 2.35 (m, 2H), 2.14 (s, 4H), 1.97 – 1.90 (m, 1H), 1.30 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 170.3, 138.5, 138.0, 137.9, 129.1, 128.6, 128.5, 128.2, 128.03, 127.99, 127.9, 124.4, 119.9, 80.0, 77.7,

75.1, 74.7, 72.1, 70.9, 69.5, 33.9, 24.6, 21.4, 18.4; HRMS (ESI) m/z calcd for C₃₁H₃₅NNaO₆ [(M+Na)⁺]: 540.2357, found: 540.2359.

tert-Butyl

3-((3a*R*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrafuro[3,4-*d*][1,3]dioxol-4-yl)propanoate (5ab):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (α only, 33.1 mg, 89% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 4.76 (dd, *J* = 6.0, 3.8 Hz, 1H), 4.51 (d, *J* = 6.0 Hz, 1H), **4.38 (ddd, J = 7.8, 6.2, 4.4 Hz, 1H)**, 4.09 (dd, *J* = 8.7, 6.2 Hz, 1H), 4.02 (ddd, *J* = 8.7, 5.0, 2.3 Hz, 2H), 3.73 (dd, *J* = 7.8, 3.8 Hz, 1H), 2.38 – 2.21 (m, 2H), 1.72 – 1.60 (m, 2H), 1.49 (s, 3H), 1.44 (s, 12H), 1.37 (s, 3H), 1.33 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.5, 112.8, 109.4, 85.4, 83.7, 80.8, 80.7, 80.2, 73.6, 67.2, 31.9, 28.3, 27.1, 26.3, 25.9, 25.4, 24.8; HRMS (ESI) m/z calcd for C₁₉H₃₂NaO₇ [(M+Na)⁺]: 395.2040, found: 395.2042.

tert-Butyl

3-((3a*S*,4*S*,6*R*,6a*R*)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydrafuro[3,4-*d*][1,3]dioxol-4-yl)propanoate (5ac):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (β only, 41.0 mg, 76% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.67 (m, 4H), 7.43 – 7.36 (m, 6H), 4.70 (dd, *J* = 6.7, 3.7 Hz, 1H), 4.31 (dd, *J* = 6.7, 5.0 Hz, 1H), 4.02 (q, *J* = 3.7 Hz, 1H), **3.86 (dt, J = 8.0, 5.2 Hz, 1H)**, 3.76 (d, *J* = 3.8 Hz, 2H), 2.45 – 2.30 (m, 2H), 1.99 – 1.80 (m, 2H), 1.52 (s, 3H), 1.43 (s, 9H), 1.34 (s, 3H), 1.06 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 172.4, 135.7, 135.6, 133.4, 133.2, 129.74, 129.70, 127.72, 127.68, 114.1, 84.8, 84.2, 83.5, 81.9, 80.2, 64.2, 31.8, 29.1, 28.1, 27.5, 26.9, 25.6, 19.3; HRMS (ESI) m/z calcd for C₃₁H₄₄NaO₆Si [(M+Na)⁺]: 563.2799, found: 563.2796.

((3a*R*,4*R*,6*S*,6a*S*)-6-(3-(*tert*-Butoxy)-3-oxopropyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methyl benzoate (5ad):

The title compound was prepared from the **General procedure A**. Purification using

flash silica gel column chromatography (eluent: hexanes : EtOAc = 10:1) gave the pure product as a colorless oil (β only, 31.3 mg, 77% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dd, J = 8.3, 1.4 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 4.62 (dd, J = 6.8, 4.3 Hz, 1H), 4.48 (dd, J = 11.8, 4.1 Hz, 1H), 4.41 – 4.37 (m, 2H), 4.23 (q, J = 4.5 Hz, 1H), **3.92 (dt, J = 7.7, 5.3 Hz, 1H)**, 2.41 – 2.29 (m, 2H), 1.98 – 1.91 (m, 1H), 1.89 – 1.82 (m, 1H), 1.54 (s, 3H), 1.42 (s, 9H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, CDCl₃) δ 172.5, 166.5, 133.3, 130.0, 129.9, 128.6, 115.0, 84.8, 83.9, 82.2, 81.9, 80.5, 64.9, 31.7, 29.0, 28.3, 27.6, 25.7; HRMS (ESI) m/z calcd for C₂₂H₃₀NaO₇ [(M+Na)⁺]: 429.1884, found: 429.1885.

((3a*R*,4*R*,6*S*,6a*S*)-2,2-Dimethyl-6-(3-(methyl(phenyl)amino)-3-oxopropyl)tetrahydrafuro[3,4-*d*][1,3]dioxol-4-yl)methyl benzoate (5ae):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:1) gave the pure product as a colorless oil (β only, 31.6 mg, 72% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.30 – 7.26 (m, 1H), 7.15 (d, J = 7.6 Hz, 2H), 4.56 (t, J = 5.4 Hz, 1H), 4.39 – 4.29 (m, 3H), 4.15 (q, J = 4.7 Hz, 1H), **3.82 (dt, J = 9.1, 5.0 Hz, 1H)**, 3.24 (s, 3H), 2.27 – 2.20 (m, 1H), 2.18 – 2.12 (m, 1H), 2.01 – 1.94 (m, 1H), 1.84 – 1.77 (m, 1H), 1.50 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (126 MHz, CDCl₃) δ 172.4, 166.4, 144.1, 133.3, 130.0, 129.92, 129.86, 128.6, 128.0, 127.5, 114.7, 85.0, 84.0, 82.2, 81.9, 64.9, 37.5, 30.5, 29.7, 27.6, 25.7; HRMS (ESI) m/z calcd for C₂₅H₂₉NNaO₆ [(M+Na)⁺]: 462.1887, found: 462.1880.

Methyl

***N*-(*tert*-butoxycarbonyl)-*O*-(3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyl oxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl)-*L*-serinate (5af):**

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 74.9 mg, 94% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.16 (m, 18H), 7.13 – 7.11 (m, 2H), 5.28 (d, J = 8.5 Hz, 1H), 4.56 (d, J = 11.5 Hz, 1H), 4.50 – 4.42 (m, 8H), 4.36 (dd, J = 11.1,

3.8 Hz, 1H), 4.23 (dd, $J = 11.2, 3.5$ Hz, 1H), **3.86 (q, $J = 6.4$ Hz, 1H)**, 3.76 – 3.73 (m, 2H), 3.71 – 3.66 (m, 2H), 3.65 (s, 3H), 3.61 (dd, $J = 9.8, 3.1$ Hz, 1H), 3.49 (dd, $J = 5.5, 2.9$ Hz, 1H), 2.43 – 2.35 (m, 1H), 2.31 – 2.23 (m, 1H), 1.77 (q, $J = 7.3$ Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.1, 170.4, 155.4, 138.4, 138.3, 138.2, 128.6, 128.5, 128.2, 128.1, 128.0, 127.91, 127.87, 127.7, 80.5, 76.5, 76.1, 74.8, 73.7, 73.6, 73.4, 72.4, 71.7, 71.4, 69.0, 64.4, 53.1, 52.9, 30.2, 28.5, 25.3; HRMS (ESI) m/z calcd for $\text{C}_{46}\text{H}_{55}\text{NNaO}_{11}$ [(M+Na) $^+$]: 820.3667, found: 820.3665.

Methyl

(S)-2-((tert-butoxycarbonyl)amino)-3-(4-((3-((2R,3R,4R,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)propanoyl)oxy)phenyl)propionate (5ag):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 5:1) gave the pure product as a colorless oil (α only, 76.8 mg, 88% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.17 (m, 18H), 7.13 (dd, $J = 7.5, 2.0$ Hz, 2H), 7.04 (d, $J = 8.2$ Hz, 2H), 6.92 – 6.90 (m, 2H), 4.92 (d, $J = 8.3$ Hz, 1H), 4.57 (d, $J = 11.5$ Hz, 1H), 4.51 – 4.43 (m, 8H), **3.96 (q, $J = 6.5$ Hz, 1H)**, 3.78 (q, $J = 5.5$ Hz, 2H), 3.74 – 3.69 (m, 2H), 3.65 (d, $J = 3.4$ Hz, 1H), 3.62 (s, 3H), 3.53 (dd, $J = 5.6, 2.9$ Hz, 1H), 2.99 (qd, $J = 14.1, 6.1$ Hz, 2H), 2.67 – 2.59 (m, 1H), 2.55 – 2.47 (m, 1H), 1.90 (q, $J = 7.4$ Hz, 2H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.4, 172.0, 155.2, 149.9, 138.5, 138.34, 138.26, 138.2, 133.7, 130.4, 128.54, 128.49, 128.14, 128.05, 128.0, 127.88, 127.86, 127.7, 121.8, 80.2, 76.5, 76.2, 74.9, 73.8, 73.6, 73.5, 72.4, 71.7, 71.3, 69.1, 54.5, 52.4, 37.9, 30.6, 28.4, 25.4; HRMS (ESI) m/z calcd for $\text{C}_{52}\text{H}_{59}\text{NNaO}_{11}$ [(M+Na) $^+$]: 896.3980, found: 896.3981.

Methyl

(3-((2R,3R,4R,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)propanoyl)-L-phenylalaninate (5ah):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 60.6 mg, 80% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.11 (m, 23H), 6.99 (d, *J* = 6.8 Hz, 2H), 6.09 (d, *J* = 7.9 Hz, 1H), 4.75 (q, *J* = 6.6 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.53 – 4.40 (m, 7H), **3.91 (dt, *J* = 10.6, 4.3 Hz, 1H)**, 3.72 – 3.64 (m, 4H), 3.62 – 4.57 (m, 4H), 3.48 (dd, *J* = 5.0, 2.0 Hz, 1H), 3.02 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.91 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.24 – 2.08 (m, 2H), 1.83 – 1.66 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 172.5, 172.2, 138.4, 138.34, 138.27, 136.2, 129.3, 128.7, 128.52, 128.49, 128.2, 128.04, 127.98, 127.88, 127.85, 127.8, 127.7, 127.2, 77.1, 76.0, 75.0, 73.8, 73.5, 73.3, 72.3, 71.7, 71.6, 69.1, 53.3, 52.4, 38.0, 32.4, 25.7; HRMS (ESI) m/z calcd for C₄₇H₅₁NNaO₈ [(M+Na)⁺]: 780.3507, found: 780.3504.

Methyl

(3-((2*R*,3*S*,4*R*,5*S*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl-*L*-phenylalaninate (**5ai**):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 47.7 mg, 63% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.09 (m, 23H), 6.96 – 6.94 (m, 2H), 6.14 (d, *J* = 7.9 Hz, 1H), 4.74 (q, *J* = 6.7 Hz, 1H), 4.63 – 4.52 (m, 3H), 4.51 – 4.40 (m, 5H), **3.89 (ddd, *J* = 12.9, 6.7, 3.3 Hz, 4H)**, 3.67 – 3.59 (m, 2H), 3.55 (s, 3H), 3.47 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.00 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.84 (dd, *J* = 13.9, 6.7 Hz, 1H), 2.19 – 2.08 (m, 2H), 1.89 – 1.81 (m, 1H), 1.80 – 1.74 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 172.9, 172.2, 138.7, 138.5, 138.4, 138.3, 136.3, 129.3, 128.63, 128.58, 128.54, 128.51, 128.47, 128.2, 128.1, 128.0, 127.93, 127.85, 127.8, 127.7, 127.1, 76.9, 76.4, 74.4, 73.24, 73.17, 73.1, 72.0, 69.9, 67.6, 53.3, 52.3, 37.9, 32.8, 29.9, 24.0; HRMS (ESI) m/z calcd for C₄₇H₅₁NNaO₈ [(M+Na)⁺]: 780.3507, found: 780.3499.

Methyl

(3-((3*aR*,4*R*,6*R*,6*aS*)-6-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)propanoyl-*L*-phenylalaninate (**5aj**):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 40.0 mg, 84% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 3H), 7.12 – 7.11 (m, 2H), 5.94 (d, *J* = 7.8 Hz, 1H), 4.90 (dt, *J* = 7.9, 5.9 Hz, 1H), 4.78 (dd, *J* = 6.1, 3.8 Hz, 1H), 4.52 (d, *J* = 6.0 Hz, 1H), **4.40 (ddd, J = 7.6, 6.3, 4.5 Hz, 1H)**, 4.10 (dd, *J* = 8.6, 6.3 Hz, 1H), 4.06 – 4.01 (m, 2H), 3.76 – 3.74 (m, 4H), 3.19 – 3.10 (m, 2H), 2.33 – 2.19 (m, 2H), 1.76 – 1.71 (m, 2H), 1.50 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 172.2, 171.7, 136.0, 129.4, 128.8, 127.4, 112.8, 109.4, 85.3, 83.6, 80.8, 80.1, 73.6, 67.1, 53.2, 52.5, 38.1, 32.7, 27.1, 26.3, 26.1, 25.4, 24.8; HRMS (ESI) m/z calcd for C₂₅H₃₅NNaO₈ [(M+Na)⁺]: 500.2255, found: 500.2254.

Methyl

(3-((3a*S*,4*S*,6*R*,6a*R*)-6-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyltetrahydropyran-3*a*-yl)[1,3]dioxol-4-yl)propanoyl)-*L*-phenylalaninate (**5ak**):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (β only, 45.8 mg, 71% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.70 (tt, *J* = 6.1, 1.5 Hz, 4H), 7.46 – 7.37 (m, 6H), 7.31 – 7.23 (m, 3H), 7.12 – 7.10 (m, 2H), 6.00 (d, *J* = 7.9 Hz, 1H), 4.91 (dt, *J* = 7.9, 5.8 Hz, 1H), 4.71 (dd, *J* = 6.7, 3.8 Hz, 1H), 4.31 (dd, *J* = 6.8, 5.1 Hz, 1H), 4.02 (q, *J* = 3.9 Hz, 1H), **3.85 (dt, J = 8.1, 5.4 Hz, 1H)**, 3.79 (d, *J* = 3.9 Hz, 2H), 3.73 (s, 3H), 3.13 (qd, *J* = 13.9, 5.8 Hz, 2H), 2.37 – 2.27 (m, 2H), 2.03 – 1.96 (m, 1H), 1.92 – 1.85 (m, 1H), 1.53 (s, 3H), 1.36 (s, 3H), 1.08 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 172.1, 172.0, 136.1, 135.9, 135.8, 133.6, 133.4, 129.94, 129.92, 129.4, 128.8, 127.89, 127.86, 127.3, 114.4, 84.9, 84.3, 83.5, 82.0, 64.3, 53.2, 52.4, 38.1, 32.7, 29.4, 27.6, 27.0, 25.7, 19.4; HRMS (ESI) m/z calcd for C₃₇H₄₇NNaO₇Si [(M+Na)⁺]: 668.3014, found: 668.3015.

Methyl

N-((tert-butoxycarbonyl)-*L*-leucyl)-*O*-(3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl)-*L*-threoninate (**5al**):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:1) gave the pure product as a colorless oil (α only, 77.6 mg, 84% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.16 (m, 18H), 7.11 (dd, *J* = 7.4, 2.1 Hz,

2H), 6.64 (d, J = 9.1 Hz, 1H), 5.34 (qd, J = 6.4, 2.8 Hz, 1H), 4.87 (d, J = 8.1 Hz, 1H), 4.68 (dd, J = 9.2, 2.8 Hz, 1H), 4.58 – 4.42 (m, 8H), 4.08 – 4.03 (m, 1H), **3.87 (q, J = 6.4 Hz, 1H)**, 3.79 – 3.72 (m, 2H), 3.71 – 3.67 (m, 2H), 3.64 (dd, J = 10.0, 4.1 Hz, 1H), 3.59 (s, 3H), 3.50 (dd, J = 5.5, 2.9 Hz, 1H), 2.38 (dt, J = 15.4, 7.5 Hz, 1H), 2.24 (dt, J = 16.2, 7.7 Hz, 1H), 1.77 (q, J = 7.4 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.44 – 1.38 (m, 1H), 1.36 (s, 9H), 1.15 (d, J = 6.5 Hz, 3H), 0.86 (t, J = 6.3 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 173.2, 172.3, 170.1, 155.8, 138.4, 138.32, 138.28, 138.25, 128.51, 128.48, 128.09, 128.05, 128.0, 127.9, 127.84, 127.80, 127.7, 80.2, 76.6, 76.3, 74.7, 73.7, 73.6, 73.4, 72.4, 71.7, 71.4, 70.5, 69.0, 55.5, 53.4, 52.8, 41.0, 30.4, 28.4, 25.3, 24.8, 23.0, 22.2, 17.0; HRMS (ESI) m/z calcd for $\text{C}_{53}\text{H}_{68}\text{N}_2\text{NaO}_{12}$ [(M+Na) $^+$]: 947.4664, found: 947.4657.

Methyl

(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)-3-(4-((3-((2R,3R,4R,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl)oxy)phenyl)propanoate (5am):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:1) gave the pure product as a colorless oil (α only, 81.8 mg, 83% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.28 (m, 18H), 7.24 (dd, J = 7.7, 1.8 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 7.03 – 7.00 (m, 2H), 6.63 (d, J = 7.8 Hz, 1H), 4.90 – 4.85 (m, 2H), 4.68 (d, J = 11.5 Hz, 1H), 4.62 – 4.54 (m, 7H), 4.14 – 4.10 (m, 1H), **4.07 (q, J = 6.5 Hz, 1H)**, 3.92 – 3.87 (m, 2H), 3.85 – 3.81 (m, 2H), 3.75 (dd, J = 10.2, 3.9 Hz, 1H), 3.73 (s, 3H), 3.64 (dd, J = 5.6, 3.0 Hz, 1H), 3.20 – 3.09 (m, 2H), 2.74 (dt, J = 16.7, 7.4 Hz, 1H), 2.62 (dt, J = 16.7, 7.8 Hz, 1H), 2.01 (q, J = 7.6 Hz, 2H), 1.91 – 1.87 (m, 1H), 1.73 – 1.62 (m, 2H), 1.47 (s, 9H), 0.95 (t, J = 6.1 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.4, 172.0, 171.7, 155.7, 149.9, 138.4, 138.3, 138.22, 138.19, 133.4, 130.4, 128.52, 128.47, 128.1, 128.03, 127.98, 127.9, 127.8, 127.7, 121.8, 80.2, 76.5, 76.1, 74.8, 73.8, 73.5, 73.4, 72.4, 71.6, 71.3, 69.0, 53.2, 52.5, 41.2, 37.5, 30.6, 28.4, 25.4, 24.8, 23.0, 22.0; HRMS (ESI) m/z calcd for $\text{C}_{58}\text{H}_{70}\text{N}_2\text{NaO}_{12}$ [(M+Na) $^+$]: 1009.4821, found: 1009.4822.

Methyl

(3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl-L-phenylalanyl-L-leucinate (5an):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:1) gave the pure product as a colorless oil (α only, 62.6 mg, 72% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.14 (m, 20H), 7.12 – 7.06 (m, 5H), 6.40 (d, J = 7.8 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 4.60 (d, J = 11.4 Hz, 1H), 4.57 – 4.52 (m, 1H), 4.49 – 4.36 (m, 8H), **3.94 (dt, J = 8.5, 3.7 Hz, 1H)**, 3.72 – 3.67 (m, 2H), 3.64 – 3.61 (m, 2H), 3.58 (s, 3H), 3.57 – 3.53 (m, 1H), 3.48 – 3.46 (m, 1H), 3.03 (dd, J = 13.9, 6.2 Hz, 1H), 2.85 (dd, J = 14.0, 7.4 Hz, 1H), 2.17 – 2.07 (m, 2H), 1.85 – 1.74 (m, 1H), 1.71 – 1.63 (m, 1H), 1.47 – 1.36 (m, 3H), 0.78 (d, J = 4.7 Hz, 6H); ^{13}C NMR (126 MHz, CDCl₃) δ 173.0, 172.8, 171.2, 138.2, 138.0, 137.1, 129.4, 128.69, 128.65, 128.6, 128.5, 128.2, 128.1, 128.04, 127.99, 127.93, 127.91, 127.8, 127.0, 77.3, 75.9, 75.0, 73.9, 73.5, 72.3, 71.8, 71.7, 69.1, 54.6, 52.3, 51.2, 41.1, 37.8, 32.6, 25.5, 24.9, 22.9, 22.0; HRMS (ESI) m/z calcd for C₅₃H₆₂N₂NaO₉ [(M+Na)⁺]: 893.4348, found: 893.4342.

Methyl

(3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl-L-alanyl-L-leucyl-L-leucinate (1):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:2) gave the pure product as a colorless oil (α only, 53.5 mg, 59% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 18H), 7.20 (dd, J = 7.2, 2.4 Hz, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.55 (d, J = 7.1 Hz, 1H), 4.75 (d, J = 11.3 Hz, 1H), 4.62 – 4.51 (m, 8H), 4.35 (ddd, J = 9.5, 7.8, 5.4 Hz, 1H), 4.30 (t, J = 7.1 Hz, 1H), **4.07 (dt, J = 11.2, 4.3 Hz, 1H)**, 3.81 (dd, J = 7.2, 3.3 Hz, 2H), 3.72 (s, 3H), 3.70 – 3.67 (m, 3H), 3.59 – 3.58 (m, 1H), 2.36 – 2.25 (m, 2H), 1.99 – 1.93 (m, 1H), 1.88 – 1.81 (m, 2H), 1.69 – 1.63 (m, 3H), 1.59 – 1.53 (m, 2H), 1.18 (d, J = 7.2 Hz, 3H), 0.95 (dd, J = 7.9, 6.0 Hz, 6H), 0.84 (dd, J = 9.6, 6.2 Hz, 6H); ^{13}C NMR (101 MHz, CDCl₃) δ 173.2, 172.8, 172.0, 138.14, 138.10, 138.06, 137.8, 128.8, 128.62,

128.60, 128.5, 128.4, 128.3, 128.2, 128.04, 128.00, 127.97, 127.9, 78.0, 75.9, 74.8, 74.3, 73.9, 73.6, 72.4, 72.1, 71.9, 69.6, 52.4, 52.2, 51.0, 49.6, 41.2, 39.9, 32.3, 25.4, 25.0, 24.9, 23.08, 23.07, 22.0, 21.8, 17.4; HRMS (ESI) m/z calcd for C₅₃H₆₉N₃NaO₁₀ [(M+Na)⁺]: 930.4875, found: 930.4872.

Methyl

2-(bis(*tert*-butoxycarbonyl)amino)-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoate (5ao):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 2:1) gave the pure product as a colorless oil (α only, 90:10 d.r., 64.4 mg, 78% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.25 (m, 20H), 5.20 (dd, *J* = 10.4, 2.7 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.63 – 4.50 (m, 7H), 4.04 (t, *J* = 5.6 Hz, 1H), **3.99 (ddd, *J* = 11.2, 5.1, 2.3 Hz, 1H)**, 3.93 – 3.87 (m, 2H), 3.85 (dd, *J* = 6.8, 2.9 Hz, 1H), 3.82 – 3.78 (m, 1H), 3.73 (s, 3H), 3.63 – 3.61 (m, 1H), 2.46 (ddd, *J* = 14.7, 11.1, 3.5 Hz, 1H), 2.23 (td, *J* = 12.1, 11.4, 5.2 Hz, 1H), 1.51 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 171.6, 152.3, 138.7, 138.5, 138.4, 138.3, 128.49, 128.46, 128.42, 128.39, 128.1, 128.0, 127.9, 127.79, 127.76, 127.74, 127.69, 127.5, 83.2, 76.7, 76.4, 74.4, 73.6, 73.4, 72.2, 71.6, 69.3, 68.9, 55.0, 52.4, 30.8, 28.1; HRMS (ESI) m/z calcd for C₄₈H₅₉NNaO₁₁ [(M+Na)⁺]: 848.3980, found: 848.3982.

Methyl

(2-((S)-2-((*tert*-butoxycarbonyl)amino)-4-methylpentanamido)-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl-L-phenylalaninate (5ap):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:2) gave the pure product as a colorless oil (α only, 57:43 d.r., 76.8 mg, 78% yield for two isomers in total).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.18 (m, 16H), 7.16 – 7.08 (m, 8H), 7.02 – 7.00 (m, 2H), 6.96 (d, *J* = 6.4 Hz, 1H), 5.18 (d, *J* = 8.7 Hz, 1H), 4.67 (td, *J* = 7.4, 5.9 Hz, 1H), 4.55 – 4.36 (m, 9H), **4.15 (dt, *J* = 9.8, 5.4 Hz, 1H)**, 4.10 – 4.01 (m, 1H), 4.00 – 3.96 (m, 1H), 3.82 (t, *J* = 9.5 Hz, 1H), 3.67 (dd, *J* = 6.4, 3.0 Hz, 1H), 3.57

-3.53 (m, 4H), 3.46 (dd, $J = 5.7$, 3.0 Hz, 1H), 3.41 (d, $J = 10.6$ Hz, 1H), 2.99 (dd, $J = 13.9$, 5.9 Hz, 1H), 2.82 (dd, $J = 13.9$, 7.3 Hz, 1H), 1.91 – 1.85 (m, 2H), 1.60 – 1.51 (m, 2H), 1.35 (s, 9H), 1.28 (d, $J = 9.9$ Hz, 1H), 0.83 (dd, $J = 12.3$, 6.2 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.6, 171.7, 170.8, 155.8, 138.2, 138.1, 138.0, 136.3, 129.3, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.1, 80.0, 76.2, 75.9, 75.2, 73.7, 73.5, 72.8, 72.7, 71.7, 69.2, 68.6, 53.8, 53.1, 52.3, 51.6, 41.7, 37.8, 32.5, 28.5, 24.9, 23.3, 21.9; HRMS (ESI) m/z calcd for $\text{C}_{58}\text{H}_{71}\text{N}_3\text{NaO}_{11}$ [(M+Na) $^+$]: 1008.4981, found: 1008.4978.

Methyl

(2-((S)-2-((tert-butoxycarbonyl)amino)-4-methylpentanamido)-3-((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)propanoyl-L-phenylalaninate (5ap'):

The title compound was prepared from the **General procedure A**. Purification using flash silica gel column chromatography (eluent: hexanes : EtOAc = 1:2) gave the pure product as a colorless oil (α only, 57:43 d.r., 76.8 mg, 78% yield for two isomers in total).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, $J = 7.5$ Hz, 1H), 7.25 – 7.16 (m, 18H), 7.15 – 7.06 (m, 8H), 5.09 (d, $J = 7.4$ Hz, 1H), 4.73 (q, $J = 7.0$ Hz, 1H), 4.56 – 4.31 (m, 9H), **4.22 (dd, $J = 10.6$, 6.7 Hz, 1H)**, 3.92 – 3.90 (m, 1H), 3.87 – 3.78 (m, 2H), 3.62 (dd, $J = 5.9$, 2.8 Hz, 1H), 3.57 – 3.48 (m, 4H), 3.47 – 3.42 (m, 2H), 3.02 (qd, $J = 13.8$, 6.6 Hz, 2H), 2.22 (d, $J = 14.6$ Hz, 1H), 1.73 – 1.69 (d, $J = 14.7$ Hz, 1H), 1.56 – 1.43 (m, 2H), 1.36 – 1.26 (s, 10H), 0.78 (dd, $J = 6.5$, 4.8 Hz, 6H); ^{13}C NMR (126 MHz, CDCl_3) δ 173.2, 171.9, 171.2, 155.7, 138.24, 138.16, 138.1, 136.5, 129.5, 128.69, 128.65, 128.6, 128.5, 128.3, 128.02, 127.97, 127.94, 127.89, 127.85, 127.1, 80.0, 76.1, 75.2, 75.1, 74.6, 73.2, 72.6, 71.6, 69.4, 68.9, 54.0, 53.7, 52.2, 41.2, 37.9, 30.9, 28.5, 25.0, 23.2, 22.0; HRMS (ESI) m/z calcd for $\text{C}_{58}\text{H}_{71}\text{N}_3\text{NaO}_{11}$ [(M+Na) $^+$]: 1008.4981, found: 1008.4979.

9. X-ray crystallographic information

X-ray structure of **5v** (CCDC 2080694)

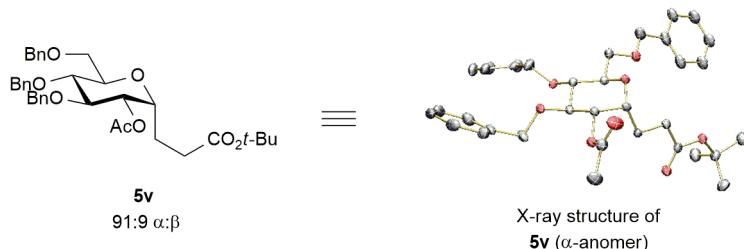


Table S2. Crystal data and structure refinement for **5v.**

Identification code	5v					
Empirical formula	C ₃₆ H ₄₄ O ₈					
Formula weight	604.71					
Temperature	100(2) K					
Wavelength	1.54178 Å					
Crystal system	Orthorhombic					
Space group	P ₂ 1 ₂ 1 ₂ 1					
Unit cell dimensions	a = 9.3756(2) Å	a = 90°.	b = 16.0708(3) Å	b = 90°.	c = 22.2902(5) Å	g = 90°.
Volume	3358.54(12) Å ³					
Z	4					
Density (calculated)	1.196 Mg/m ³					
Absorption coefficient	0.679 mm ⁻¹					
F(000)	1296					
Crystal size	0.468 x 0.462 x 0.294 mm ³					
Theta range for data collection	3.390 to 66.672°.					
Index ranges	-11 <= h <= 11, -19 <= k <= 19, -26 <= l <= 26					
Reflections collected	49948					
Independent reflections	5932 [R(int) = 0.0375]					
Completeness to theta = 66.672°	99.9 %					
Absorption correction	Semi-empirical from equivalents					
Max. and min. transmission	0.7528 and 0.6744					
Refinement method	Full-matrix least-squares on F ²					

Data / restraints / parameters	5932 / 216 / 447
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0249, wR2 = 0.0632
R indices (all data)	R1 = 0.0263, wR2 = 0.0635
Absolute structure parameter	0.01(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.124 and -0.206 e. \AA^{-3}

X-ray structure of **5z** (CCDC 2080693)

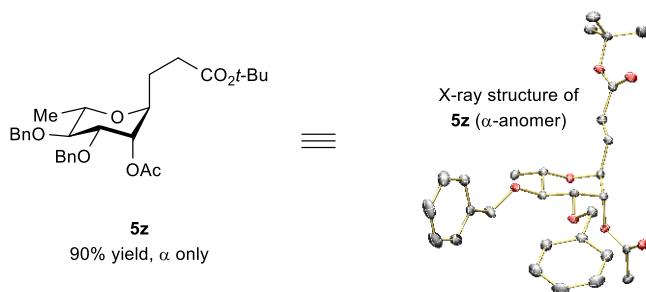


Table S3. Crystal data and structure refinement for **5z.**

Identification code	5z				
Empirical formula	C ₂₉ H ₃₈ O ₇				
Formula weight	498.59				
Temperature	100(2) K				
Wavelength	1.54178 Å				
Crystal system	Triclinic				
Space group	P1				
Unit cell dimensions	a = 9.5855(2) Å	a =			
	88.1520(10)°.				
	b = 9.6814(3) Å	b =			
	86.9020(10)°.				
	c = 33.0457(6) Å	g =			
	60.4370(10)°.				
Volume	2663.48(11) Å ³				
Z	4				
Density (calculated)	1.243 Mg/m ³				
Absorption coefficient	0.715 mm ⁻¹				
F(000)	1072				
Crystal size	0.498 x 0.444 x 0.276 mm ³				
Theta range for data collection	2.678 to 66.657°.				
Index ranges	-11≤h≤11, -11≤k≤11, -39≤l≤39				
Reflections collected	70092				
Independent reflections	17541 [R(int) = 0.0363]				
Completeness to theta = 66.657°	99.2 %				
Absorption correction	Semi-empirical from equivalents				
Max. and min. transmission	0.7528 and 0.6841				

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	17541 / 3 / 1317
Goodness-of-fit on F ²	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0788
R indices (all data)	R1 = 0.0361, wR2 = 0.0873
Absolute structure parameter	0.01(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.210 and -0.178 e. \AA^{-3}

10. NMR spectra

Figure S8. ^1H NMR spectrum of S5

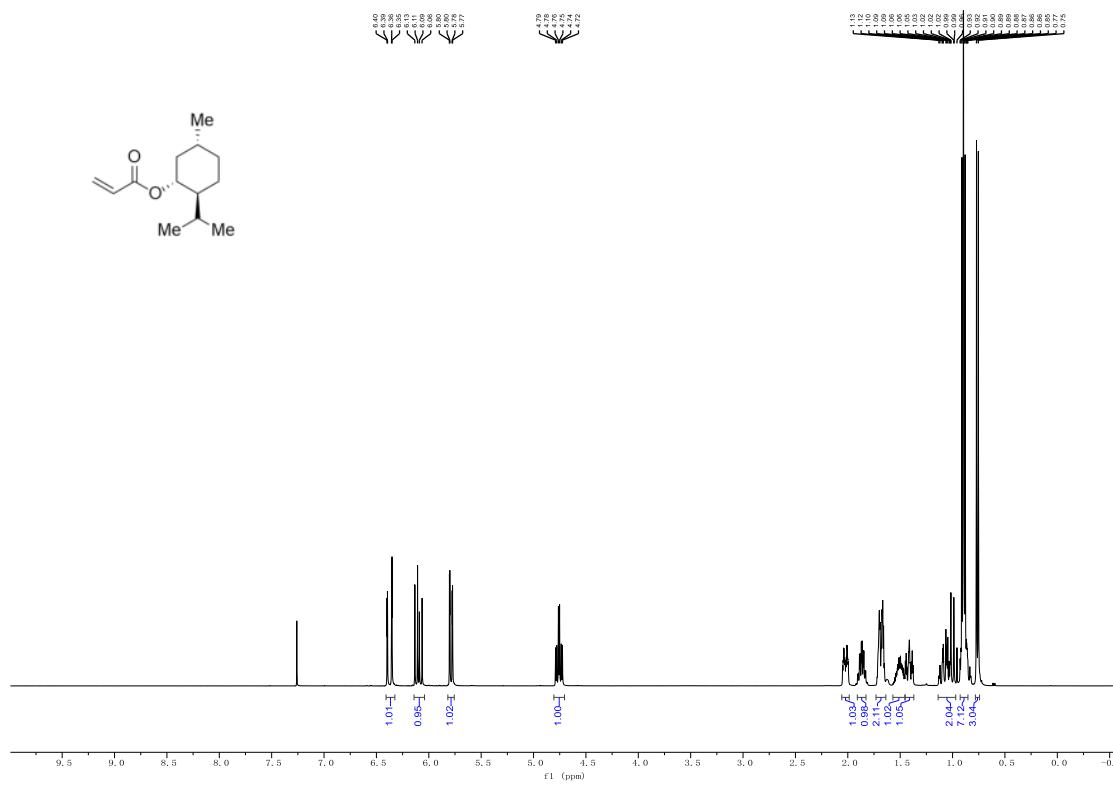


Figure S9. ^{13}C NMR spectrum of S5

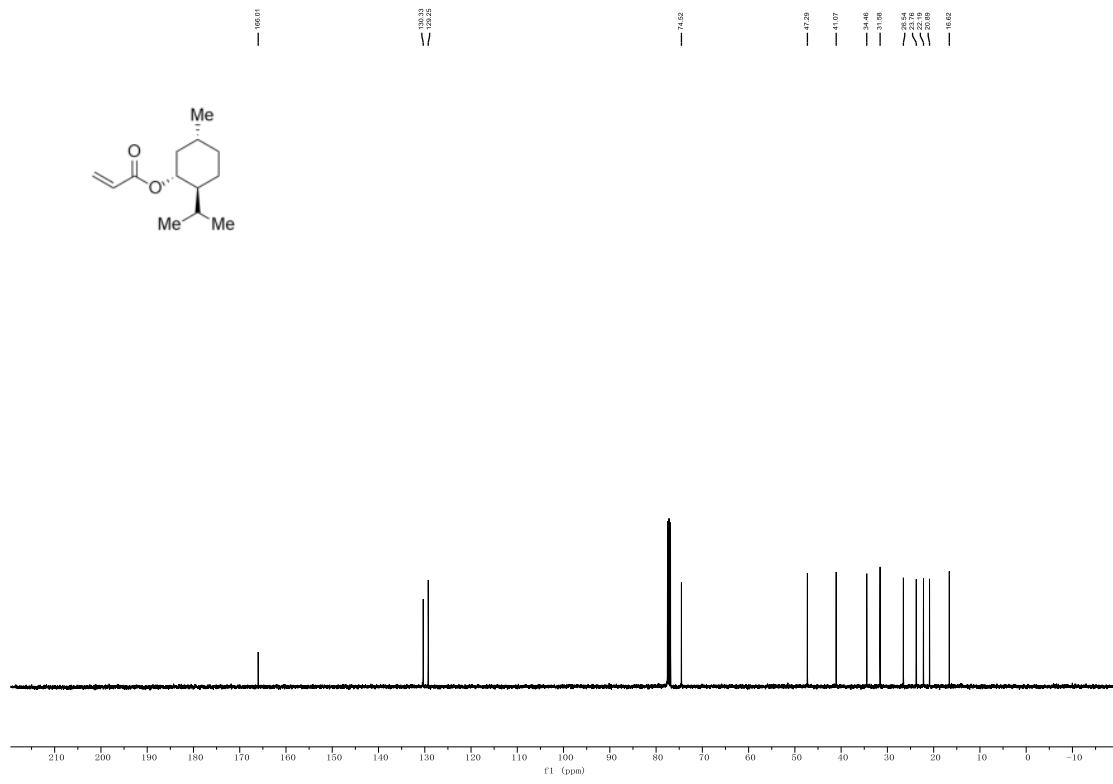


Figure S10. ^1H NMR spectrum of S6

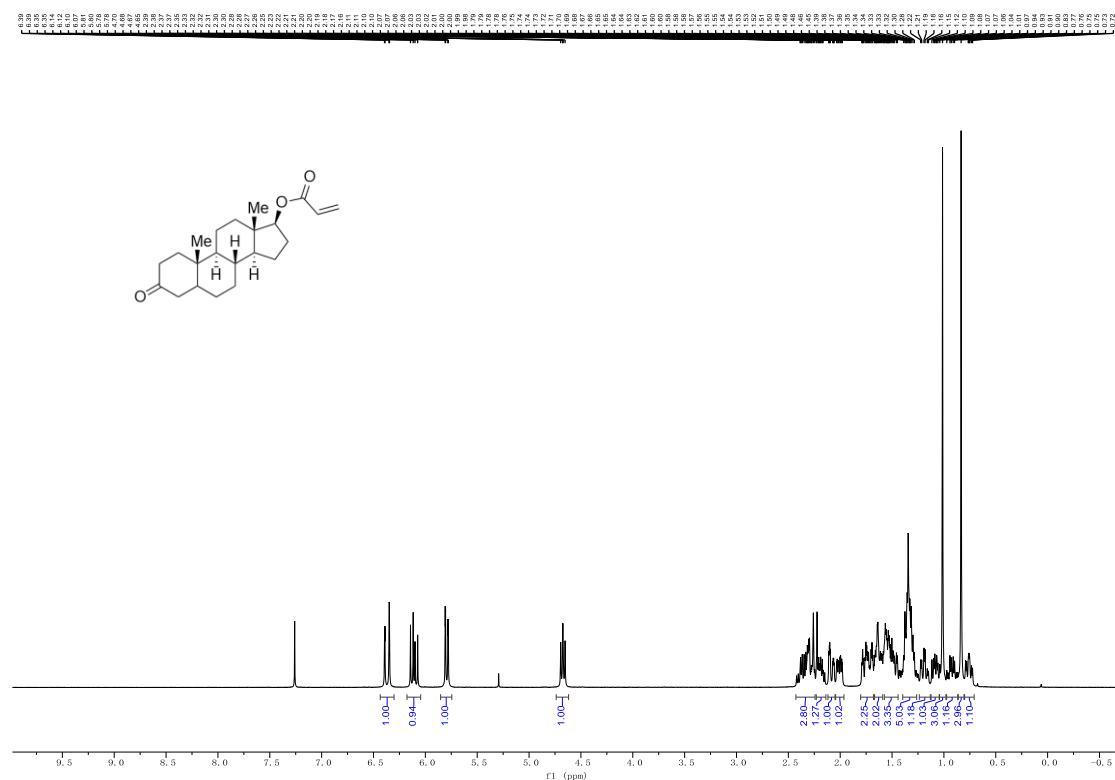


Figure S11. ^{13}C NMR spectrum of S6

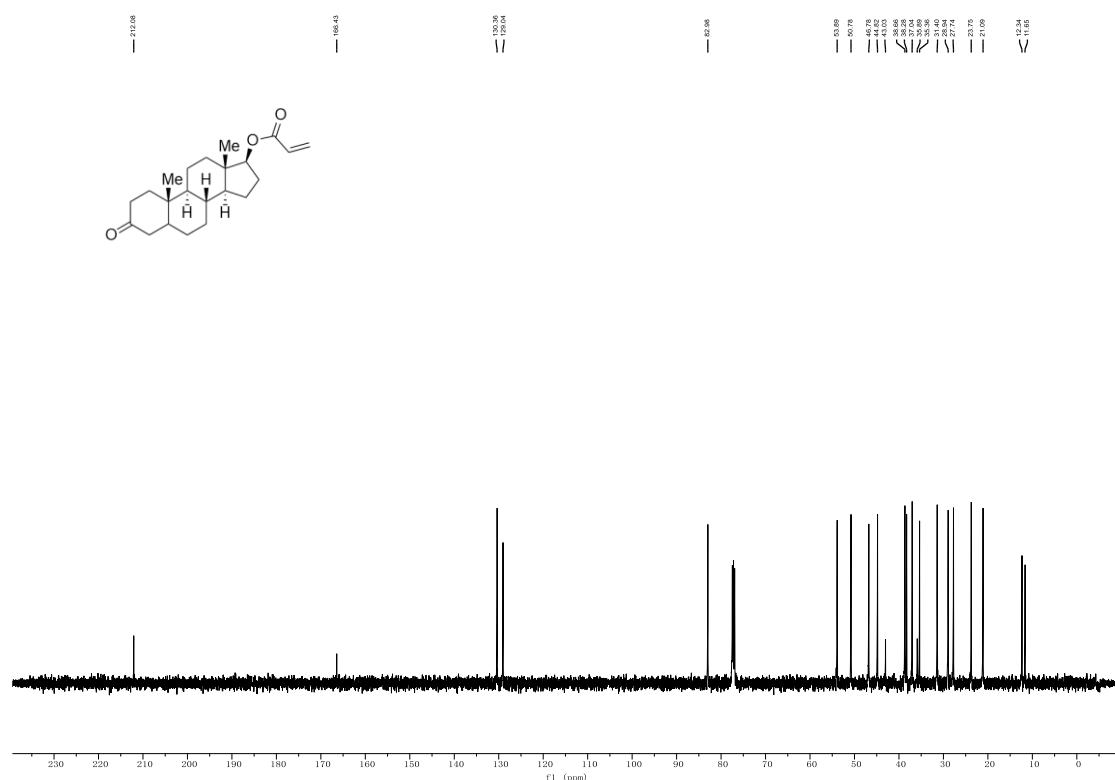


Figure S12. ^1H NMR spectrum of compound S7

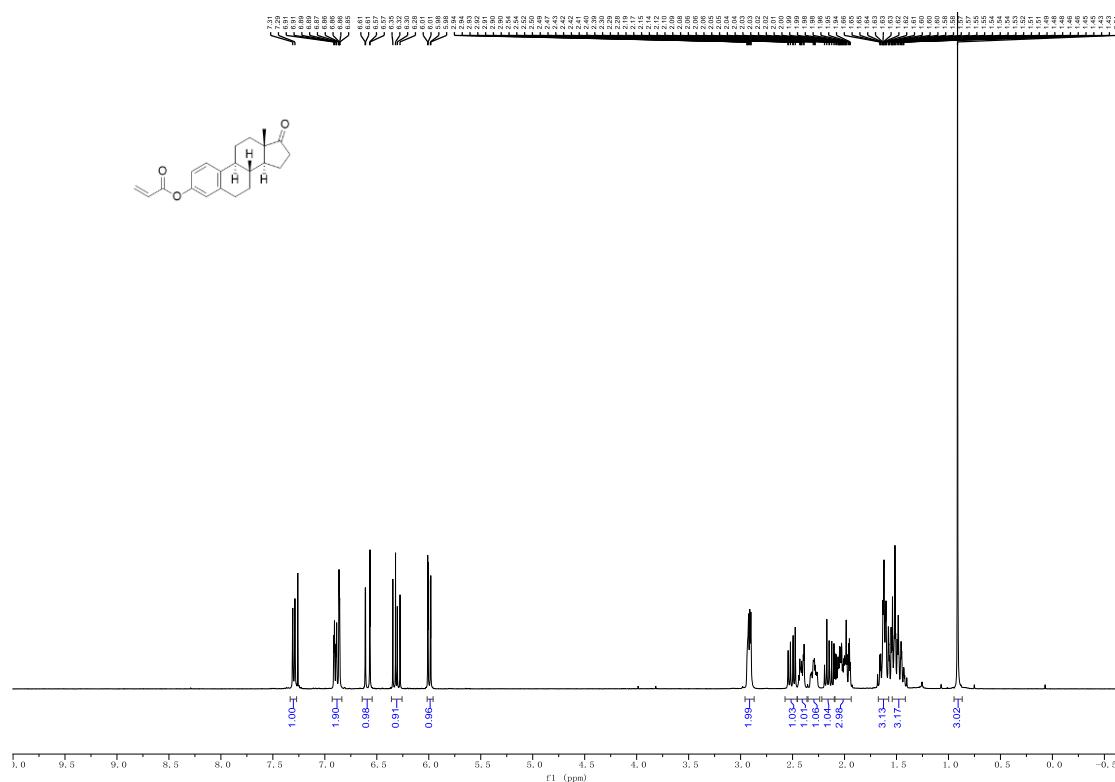


Figure S14. ^1H NMR spectrum of S10

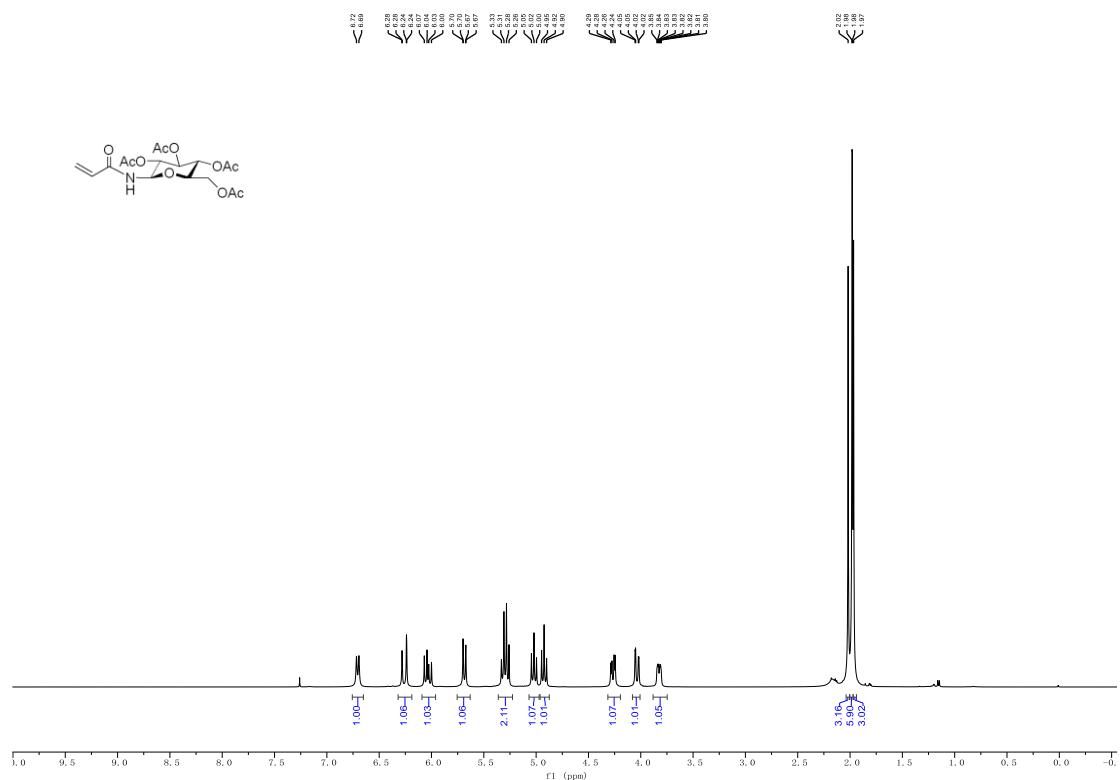


Figure S15. ^{13}C NMR spectrum of S10

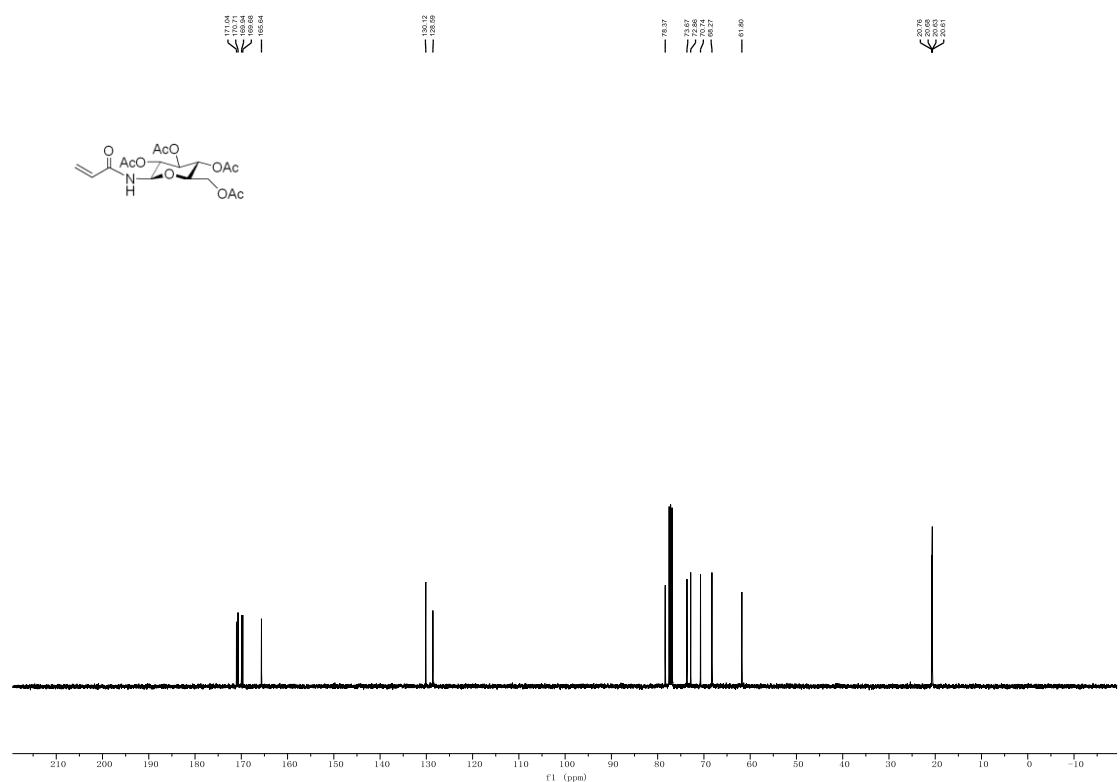


Figure S16. ^1H NMR spectrum of S22

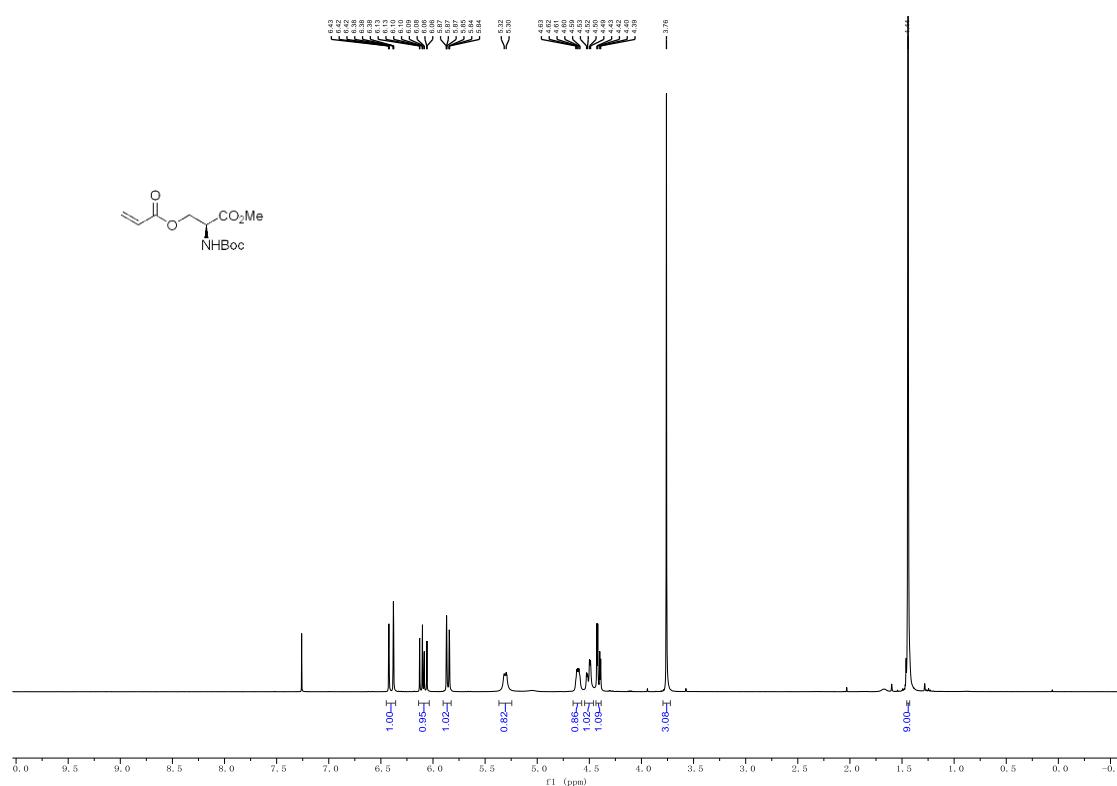


Figure S17. ^{13}C NMR spectrum of S22

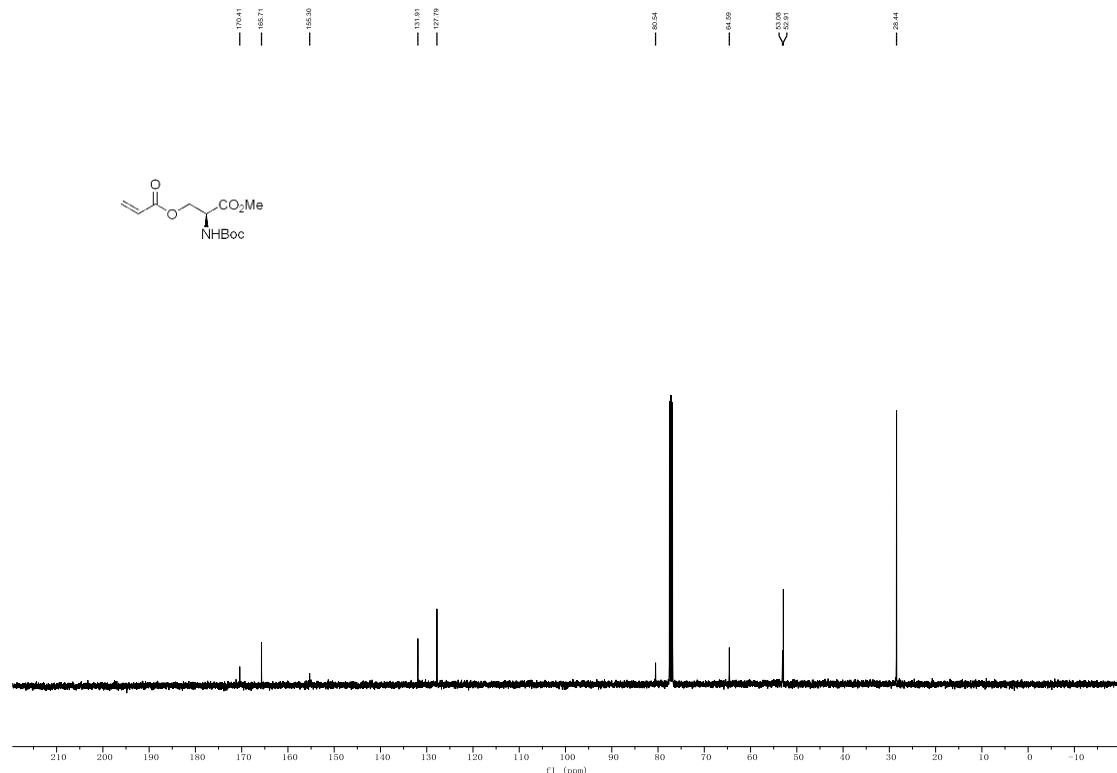


Figure S18. ^1H NMR spectrum of S24

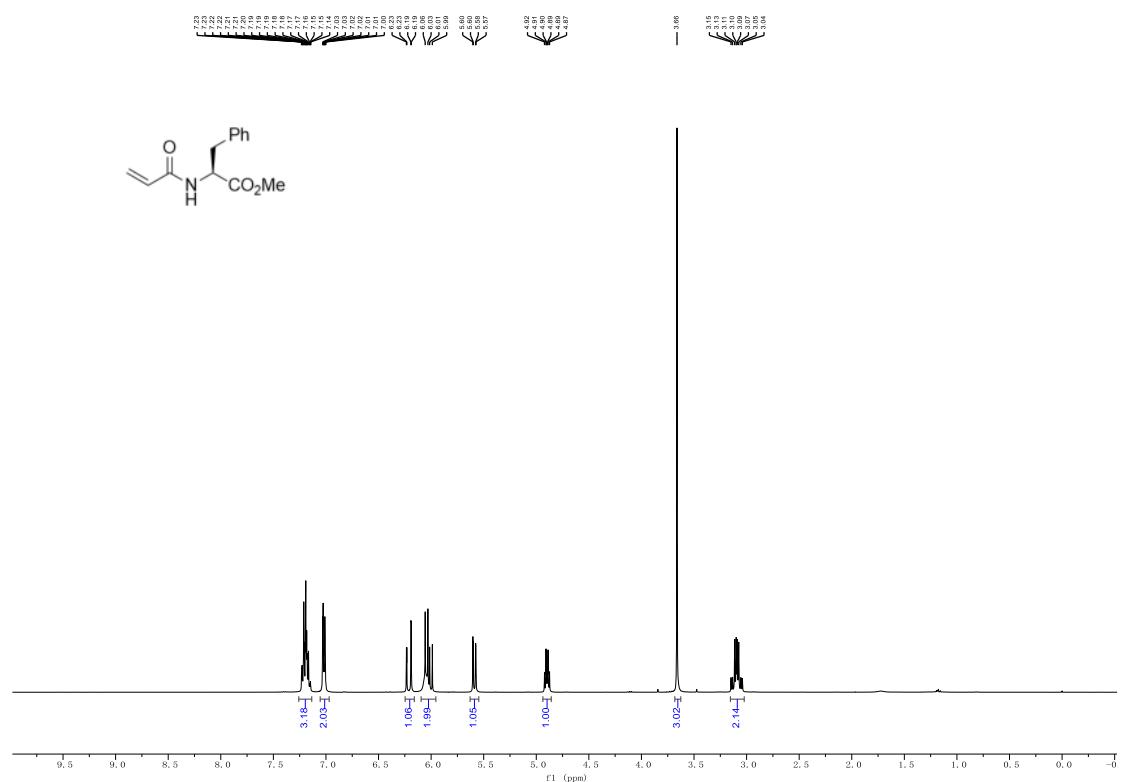


Figure S19. ^{13}C NMR spectrum of S24

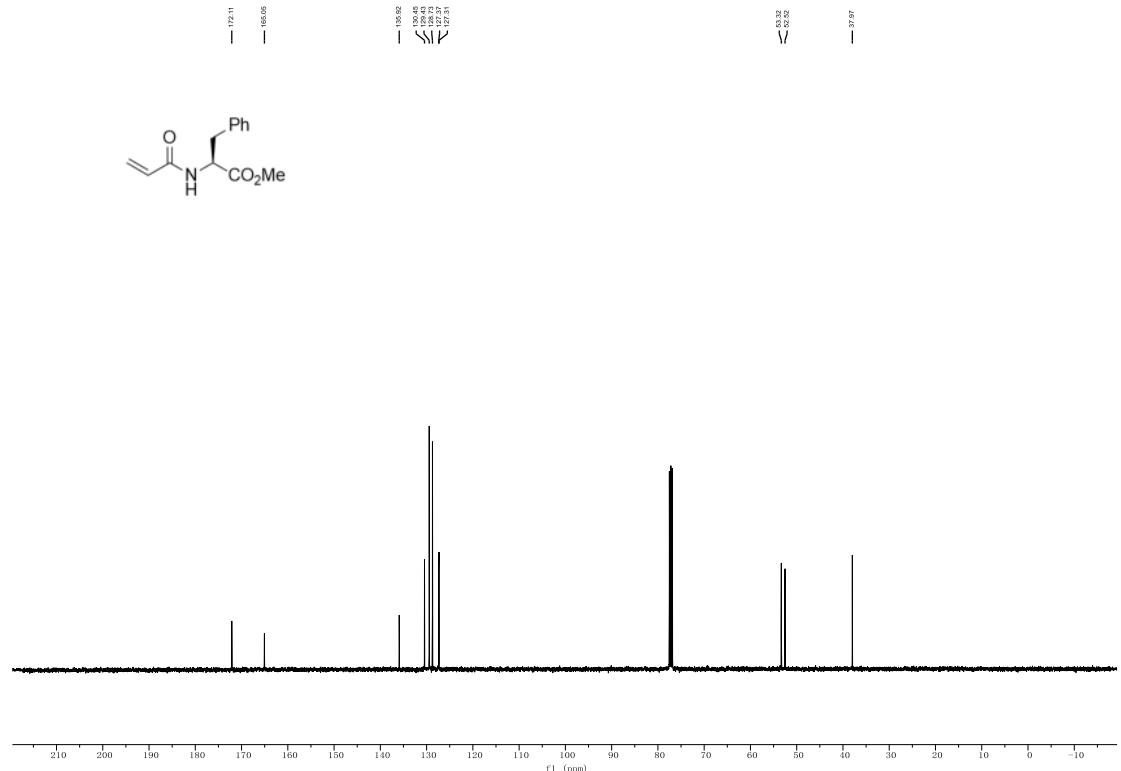


Figure S20. ^1H NMR spectrum of S25

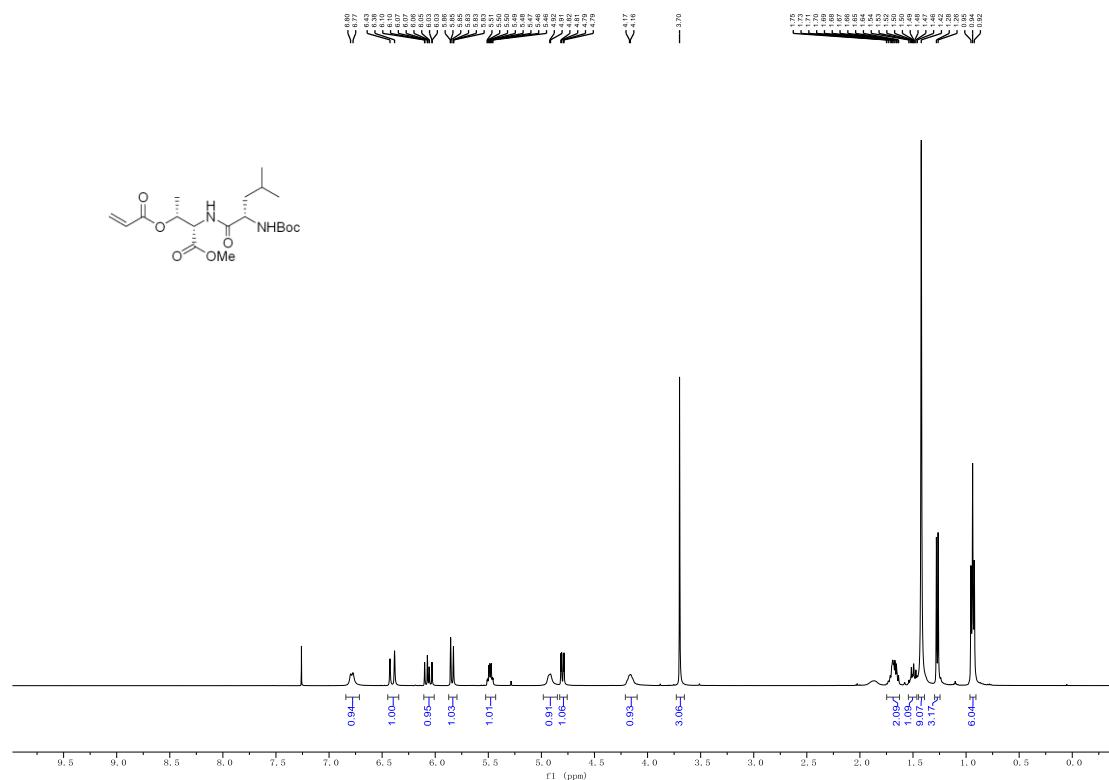


Figure S21. ^{13}C NMR spectrum of S25

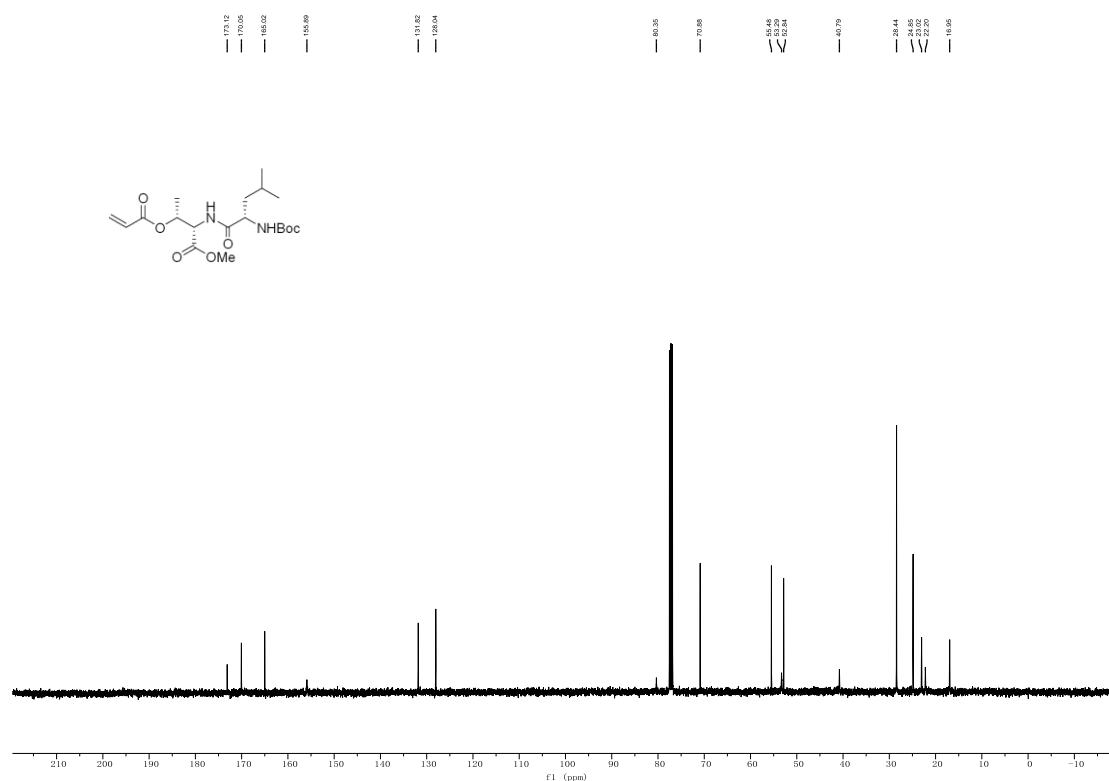


Figure S22. ^1H NMR spectrum of S27

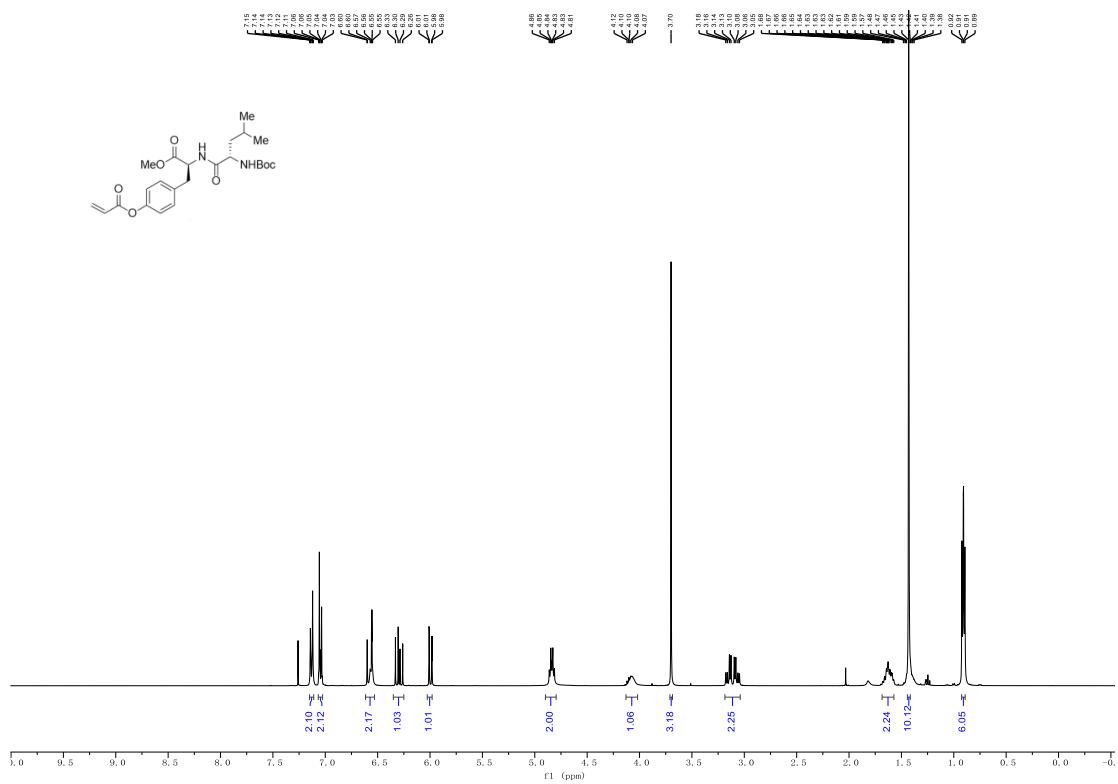


Figure S23. ^{13}C NMR spectrum of S27

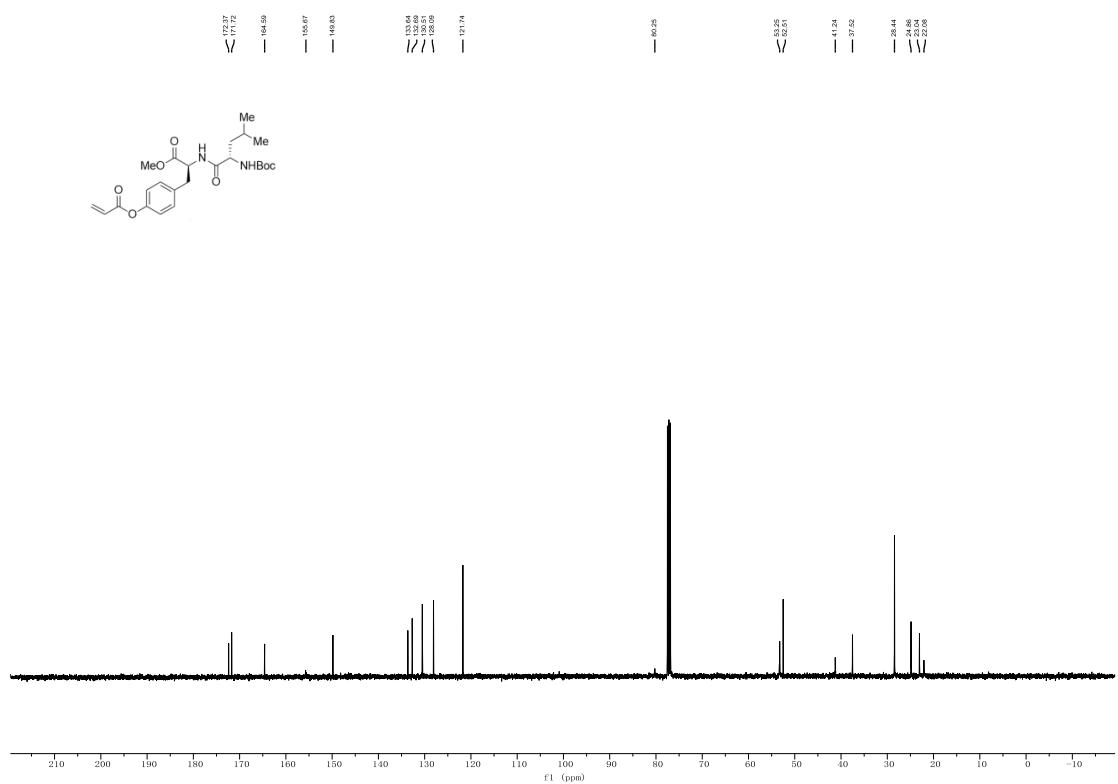


Figure S24. ^1H NMR spectrum of S28

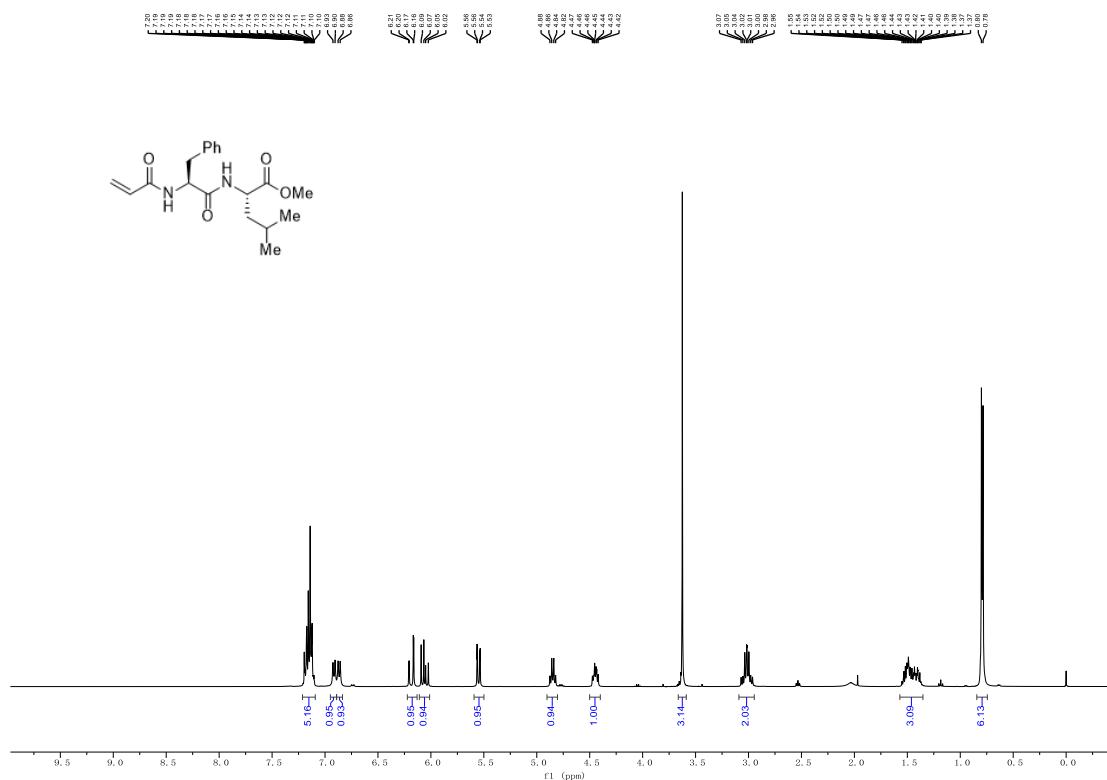


Figure S25. ^{13}C NMR spectrum of S28

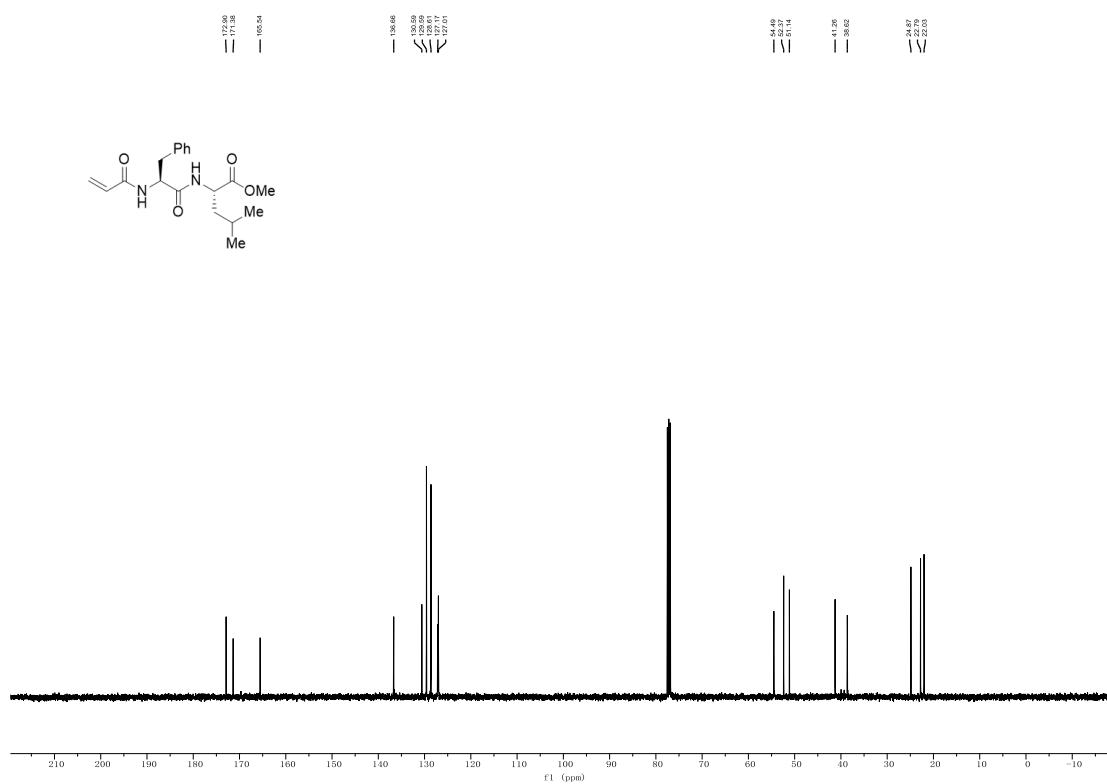


Figure S26. ^1H NMR spectrum of S29

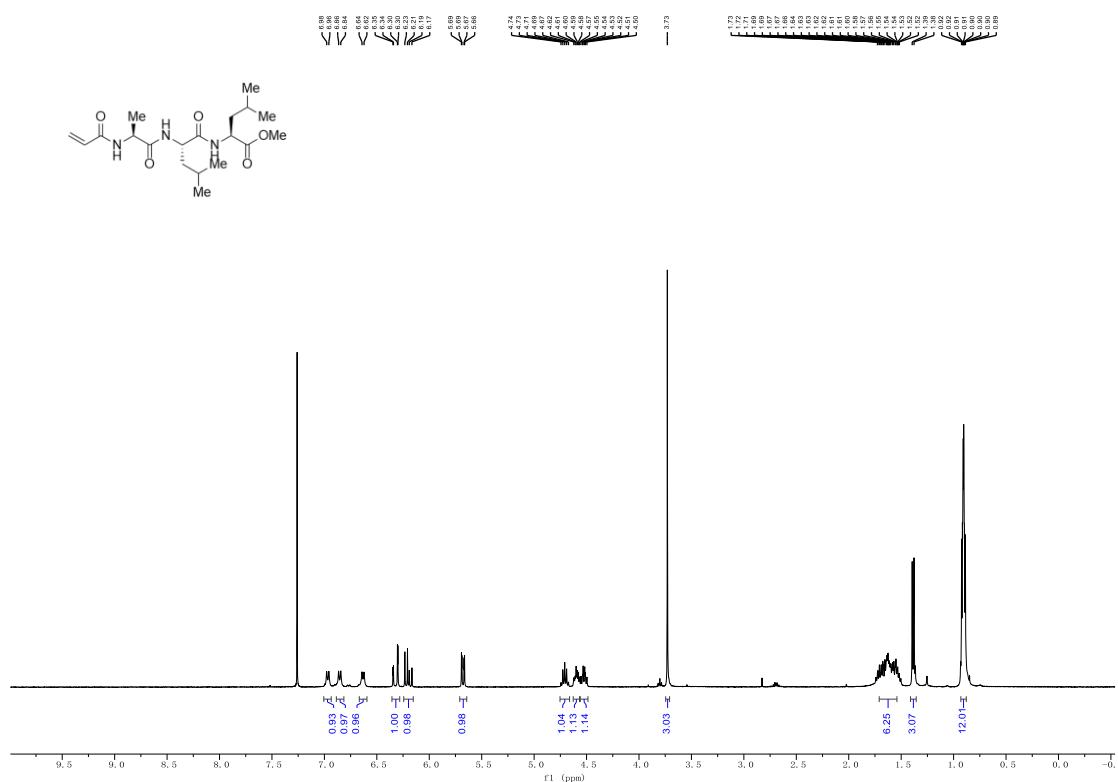


Figure S27. ^{13}C NMR spectrum of S29

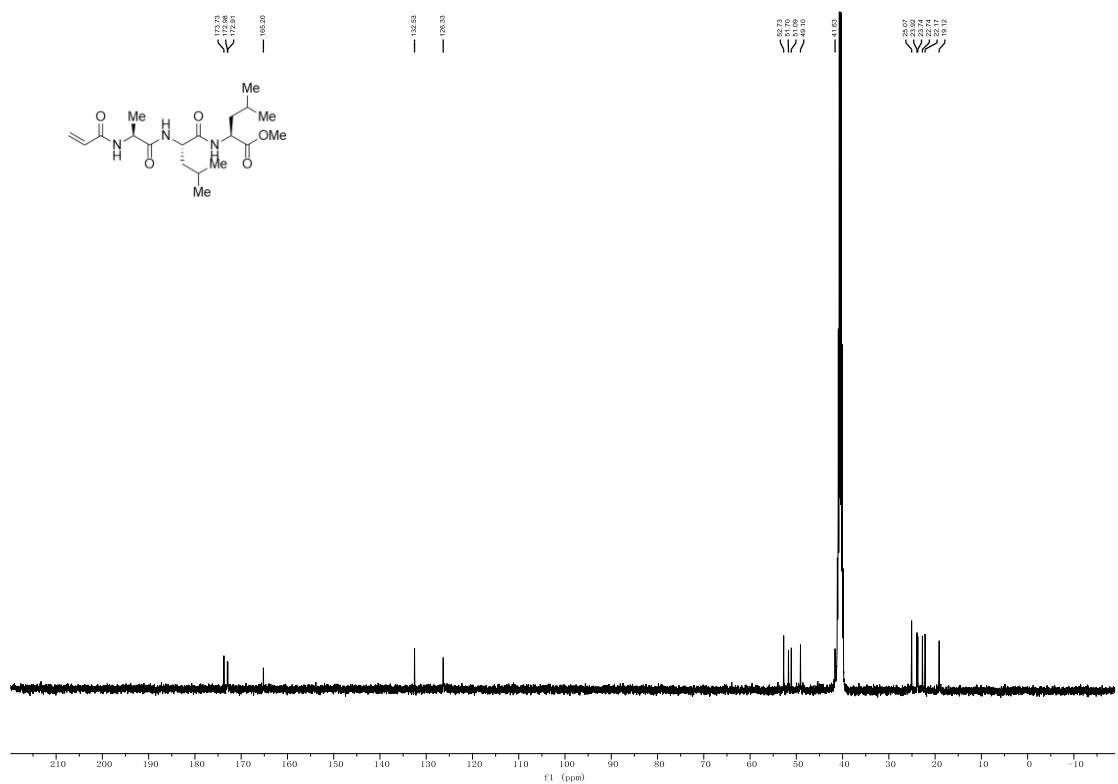


Figure S28. ^1H NMR spectrum of S30

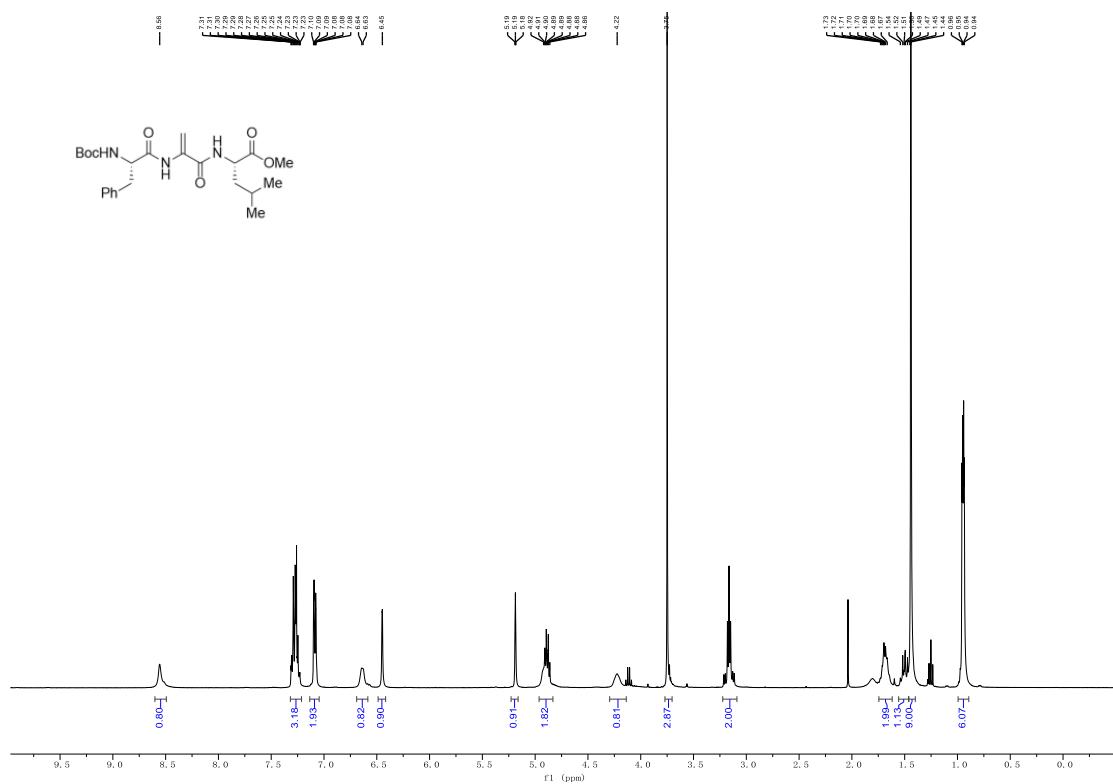


Figure S29. ^{13}C NMR spectrum of S30

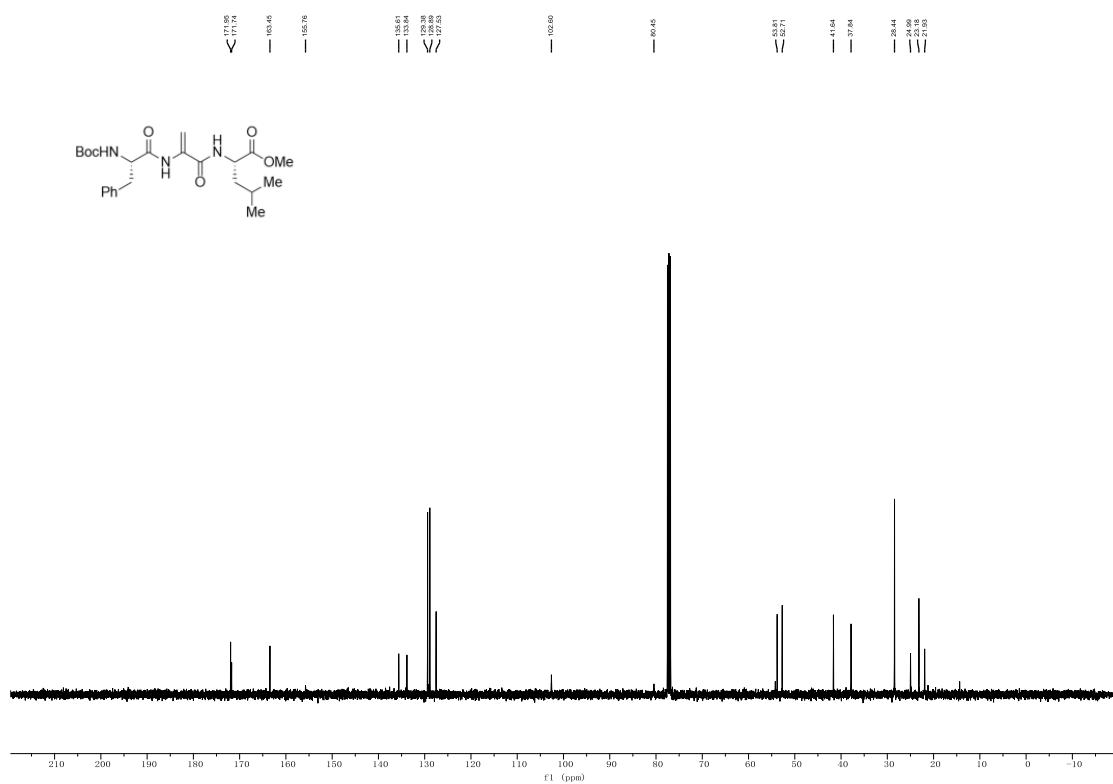


Figure S30. ^1H NMR spectrum of compound 1

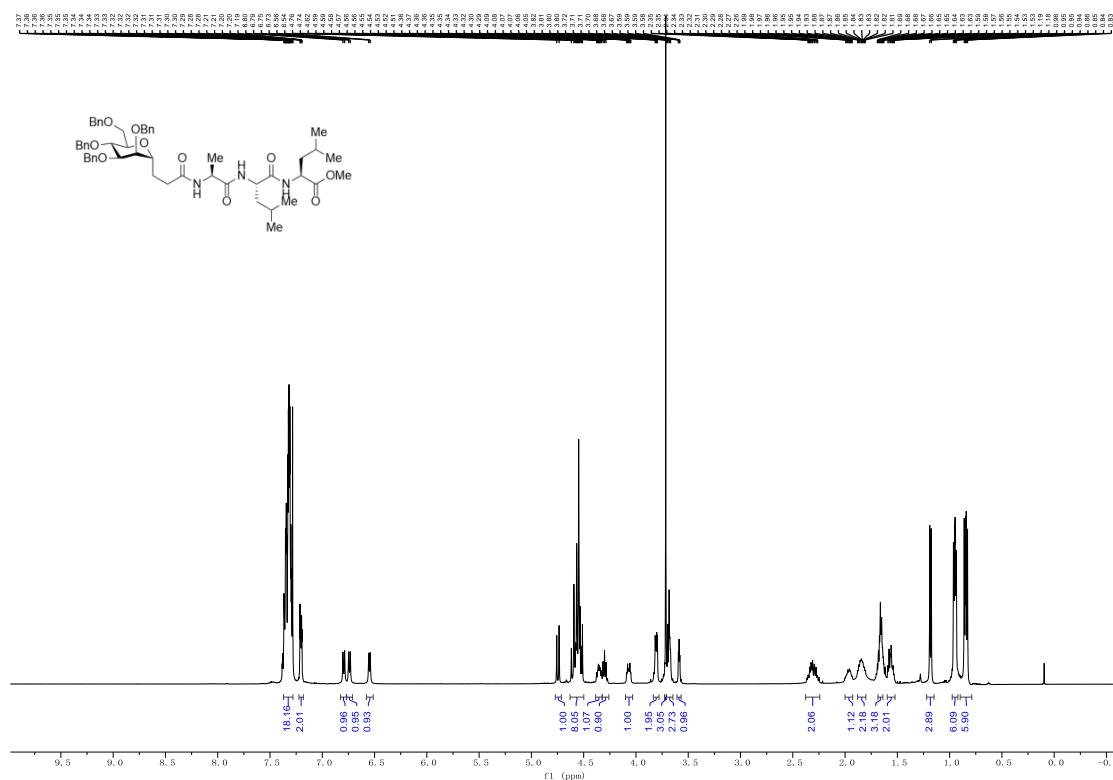


Figure S31. ^{13}C NMR spectrum of compound 1

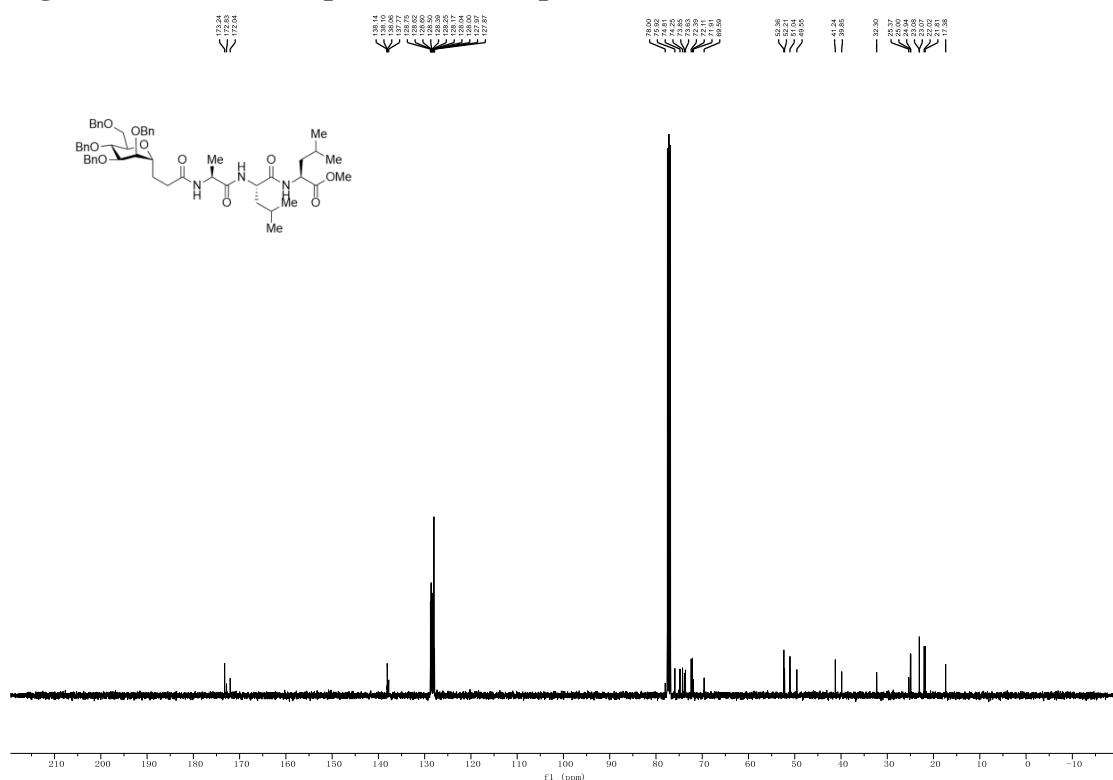


Figure S32. ^1H NMR spectrum of compound 2

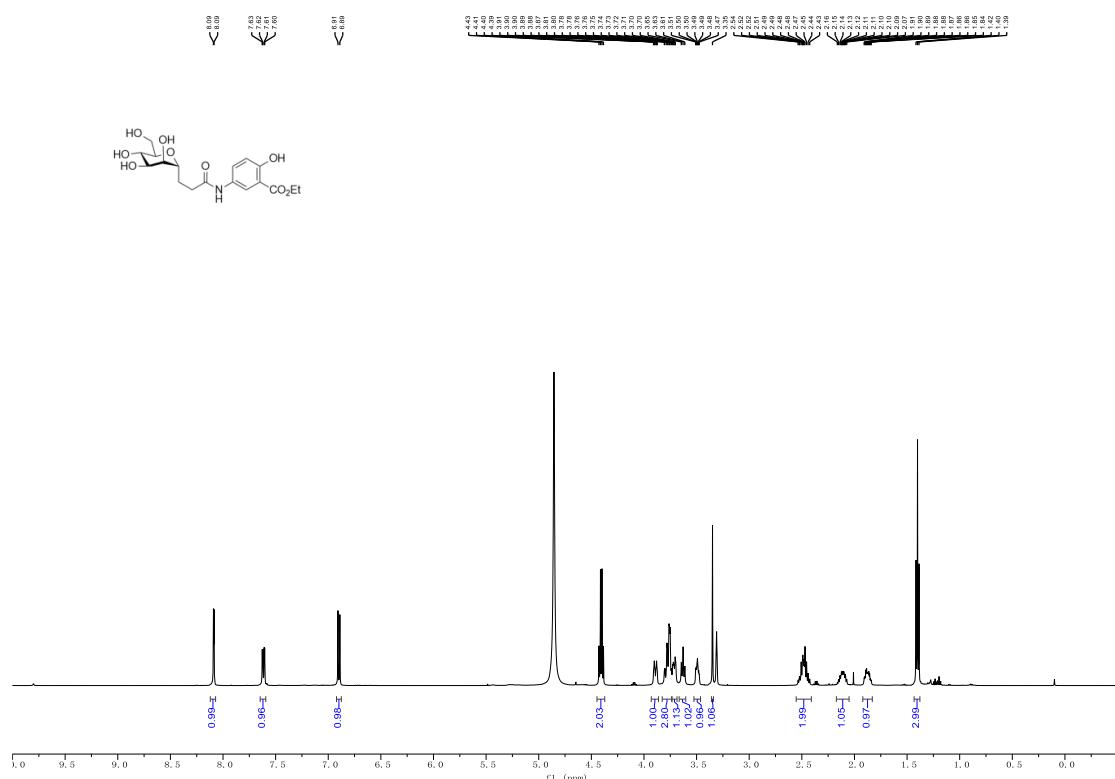


Figure S33. ^{13}C NMR spectrum of compound 2

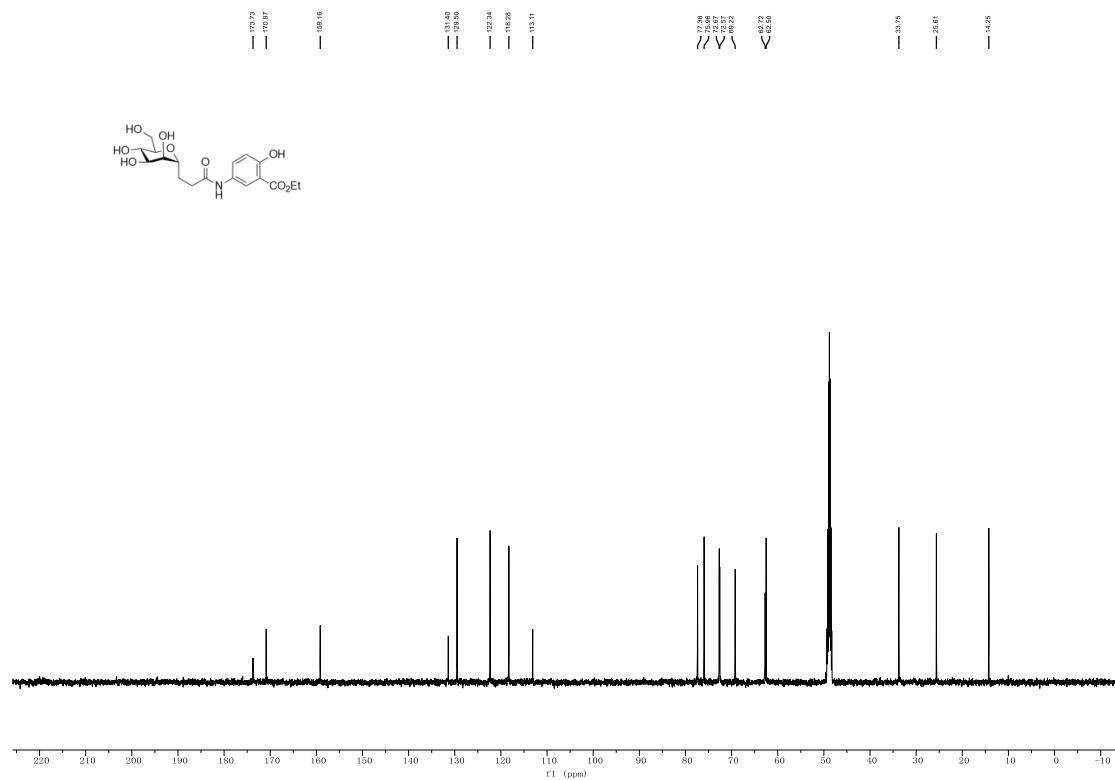


Figure S34. ^1H NMR spectrum of compound 5a

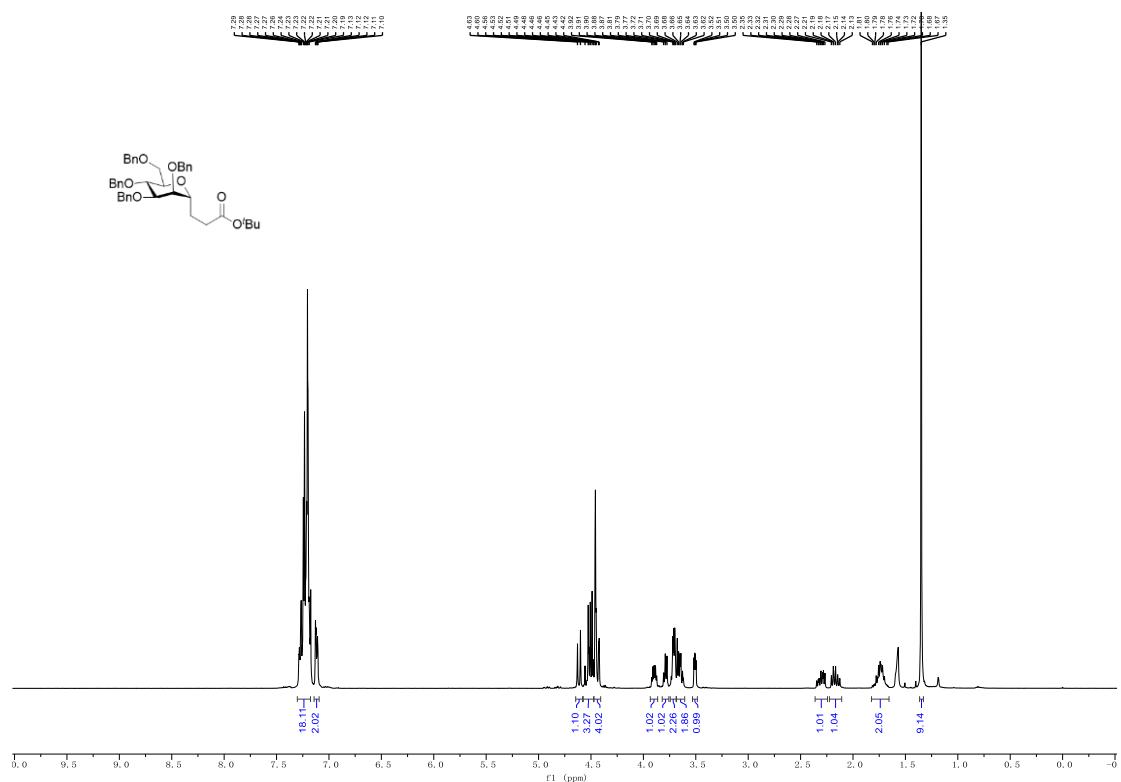


Figure S35. ^{13}C NMR spectrum of compound **5a**

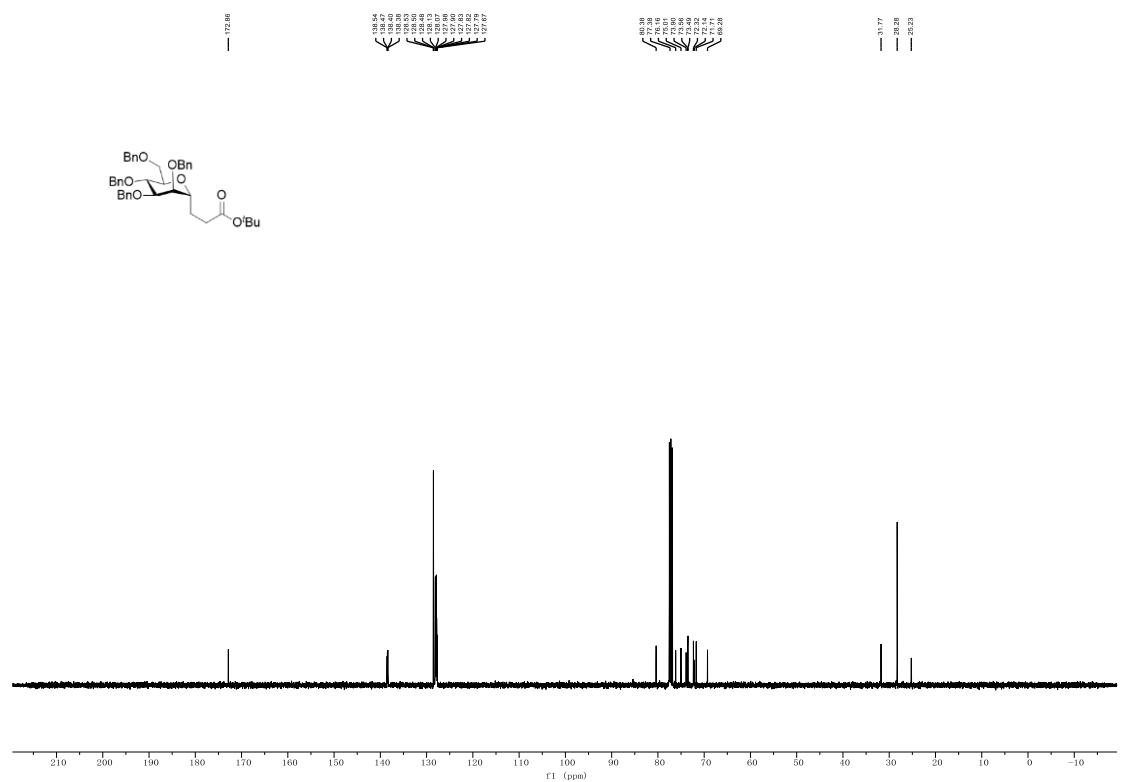


Figure S36. ^1H NMR spectrum of compound 5b

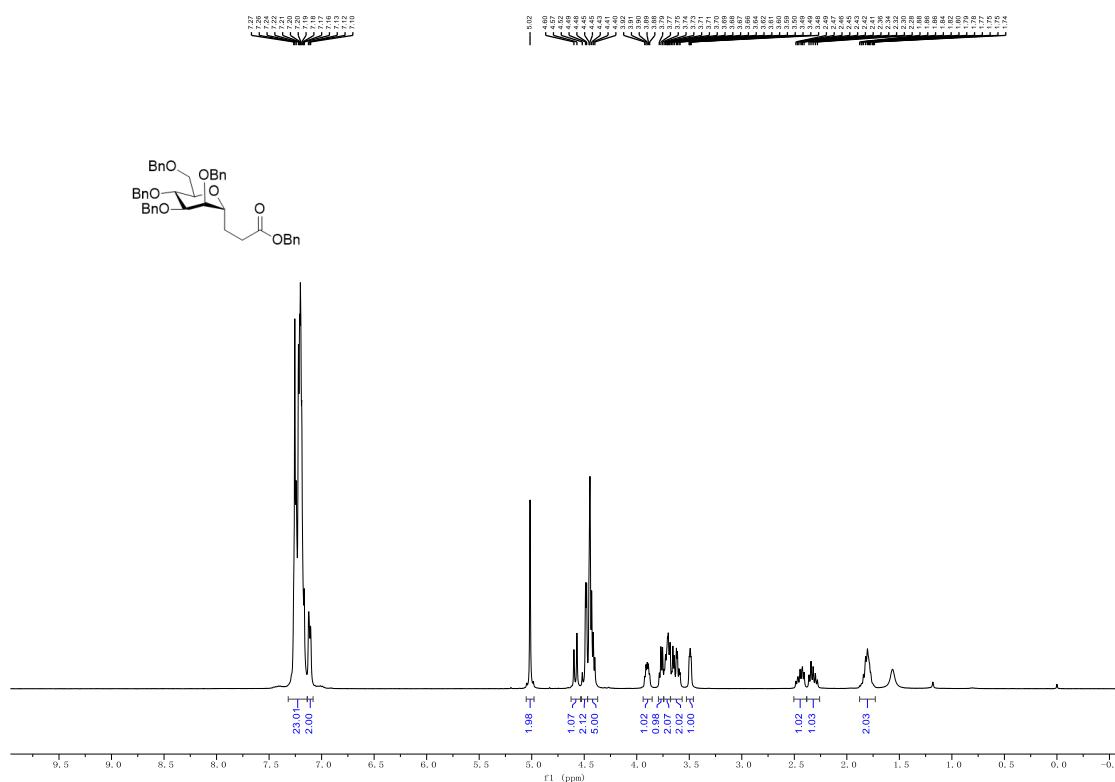


Figure S37. ^{13}C NMR spectrum of compound 5b

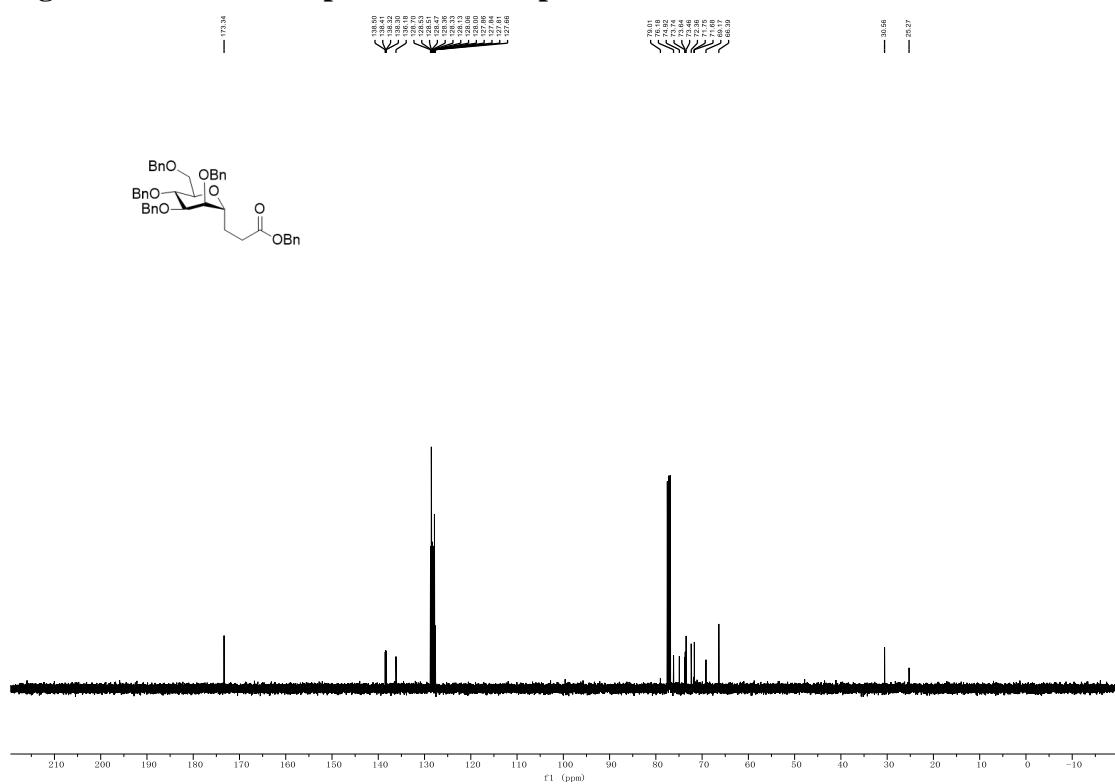


Figure S38. ^1H NMR spectrum of compound 5c

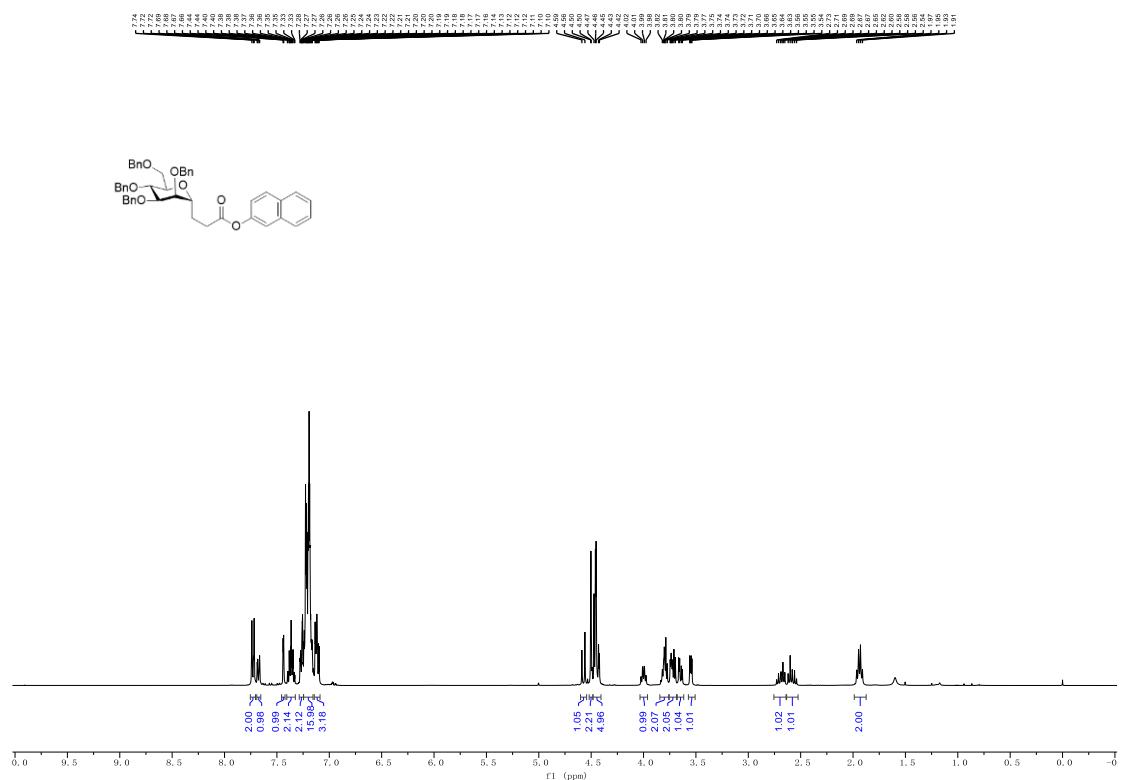


Figure S39. ^{13}C NMR spectrum of compound 5c

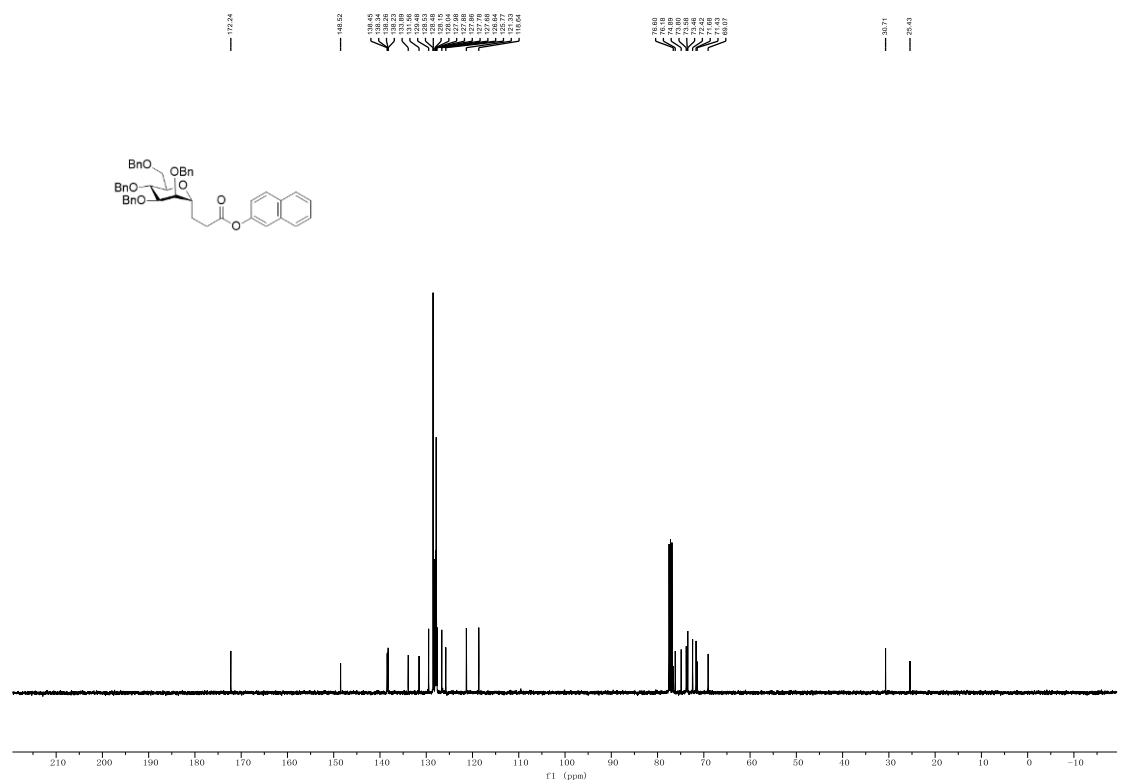


Figure S40. ^1H NMR spectrum of compound 5d

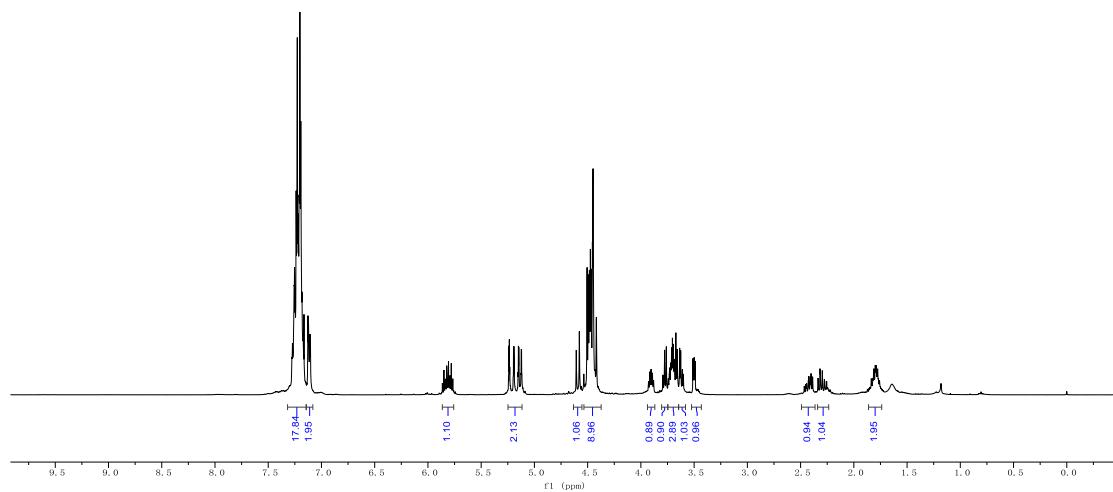
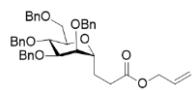


Figure S41. ^{13}C NMR spectrum of compound 5d

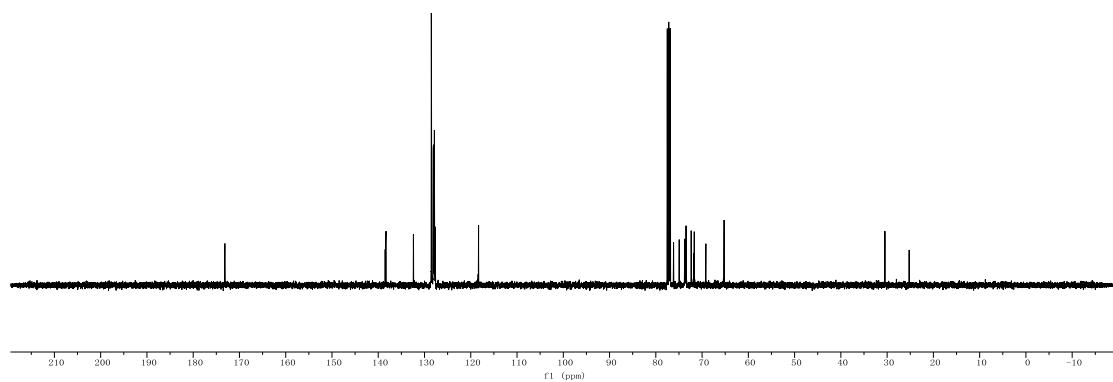
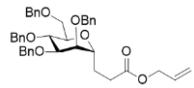


Figure S42. ^1H NMR spectrum of compound 5e

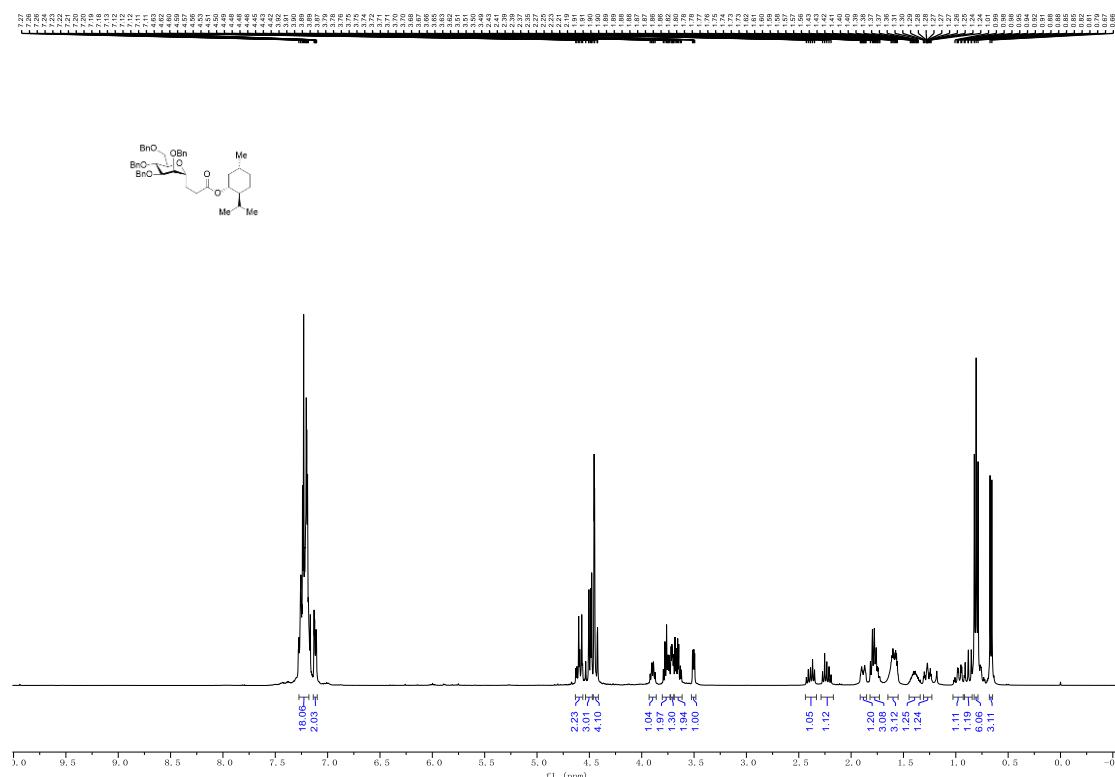


Figure S43. ^{13}C NMR spectrum of compound 5e

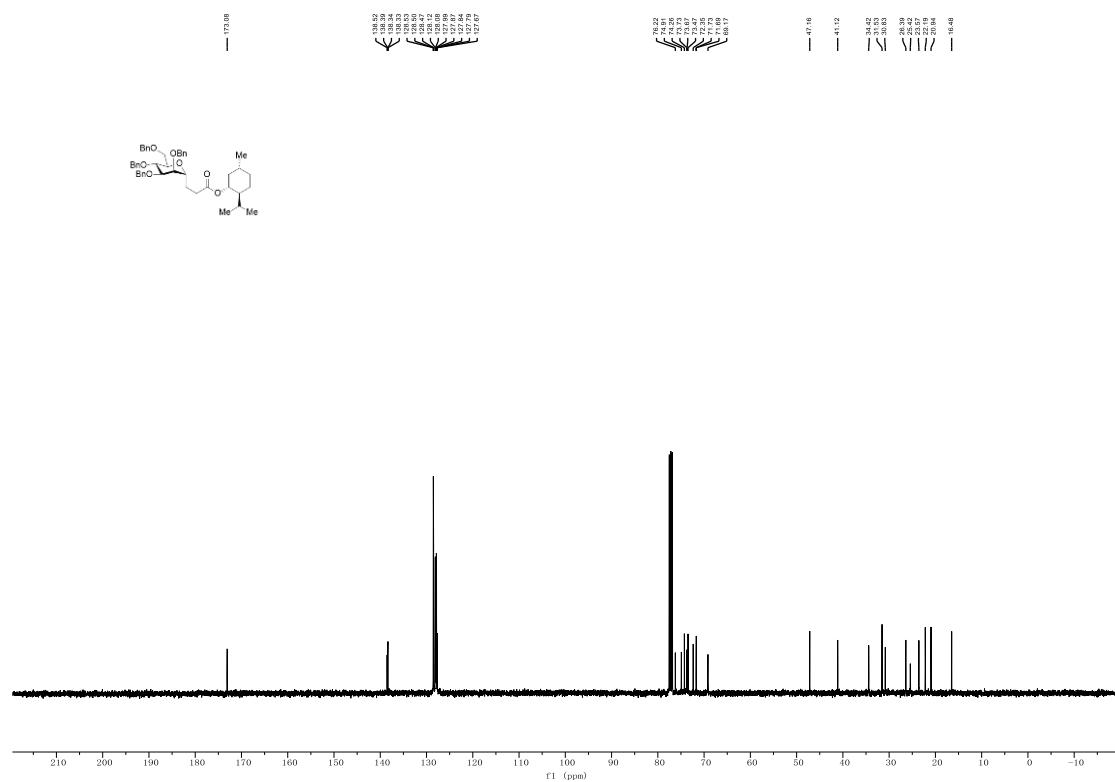


Figure S44. ^1H NMR spectrum of compound 5f

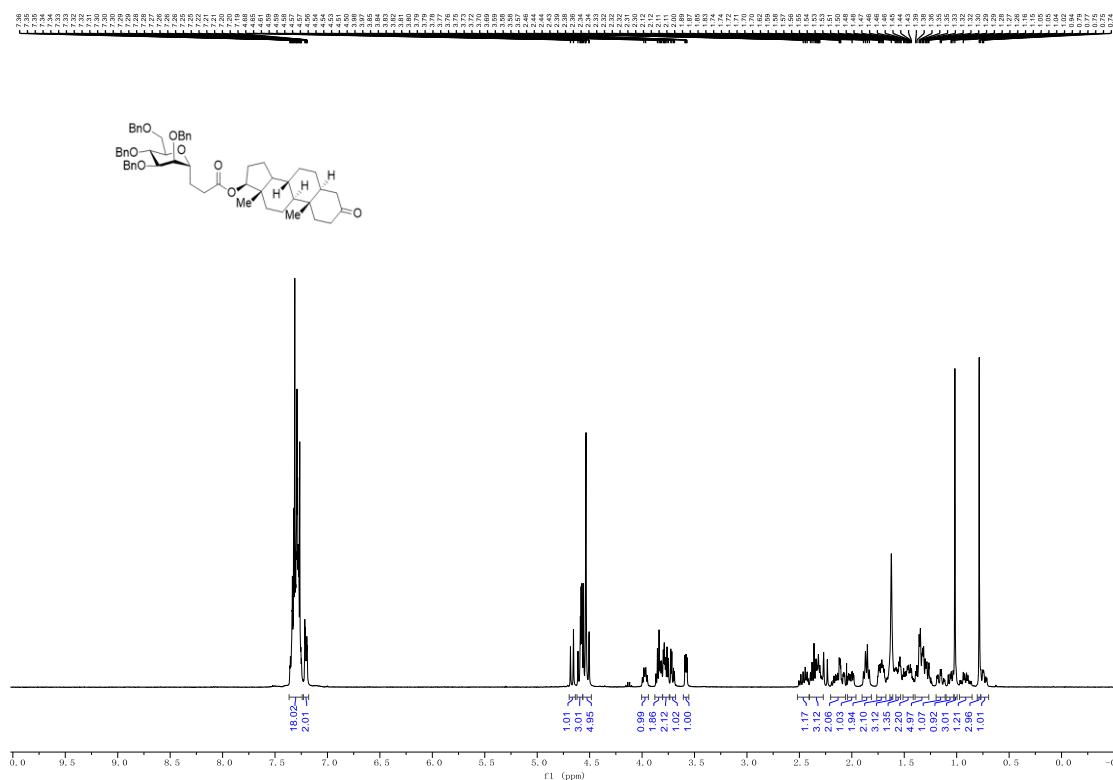


Figure S45. ^{13}C NMR spectrum of compound 5f

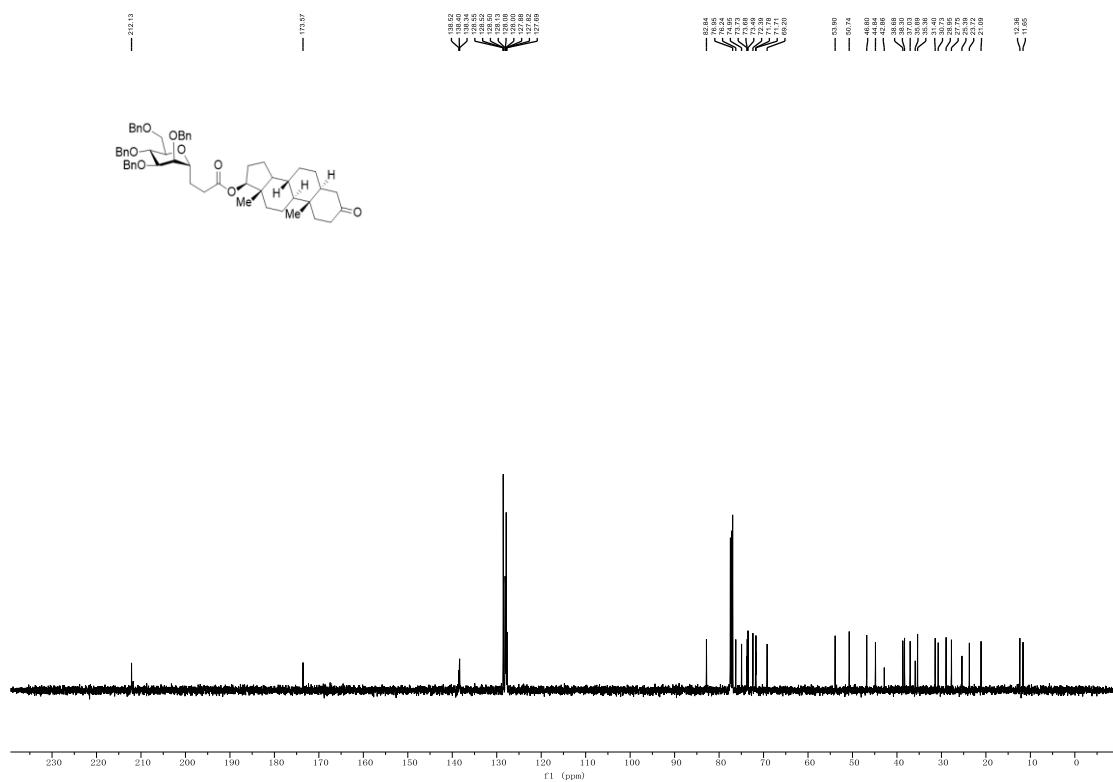


Figure S46. ^1H NMR spectrum of compound 5g

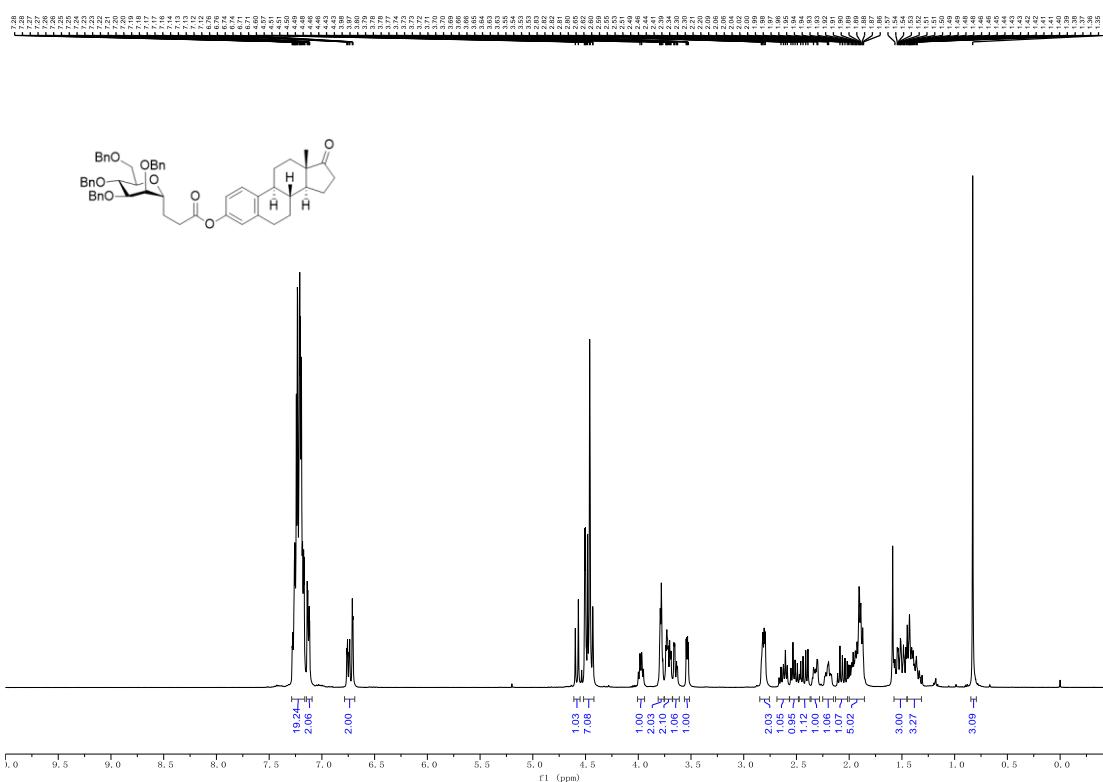


Figure S47. ^{13}C NMR spectrum of compound 5g

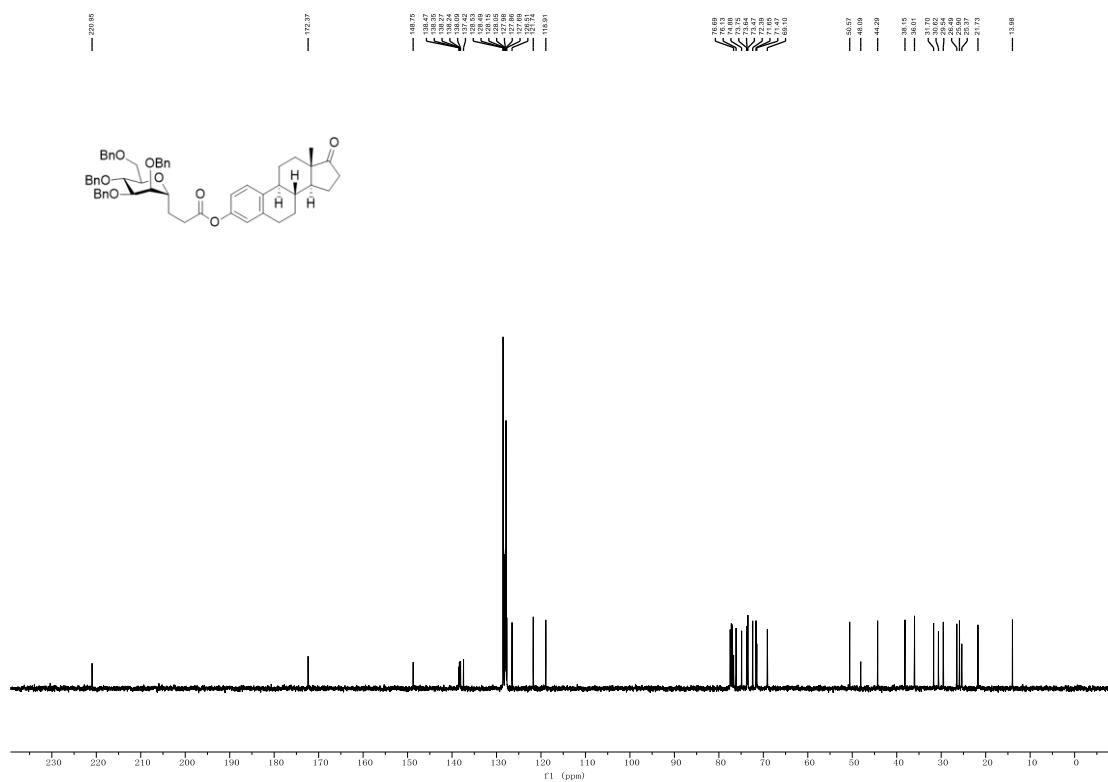


Figure S48. ^1H NMR spectrum of compound 5h

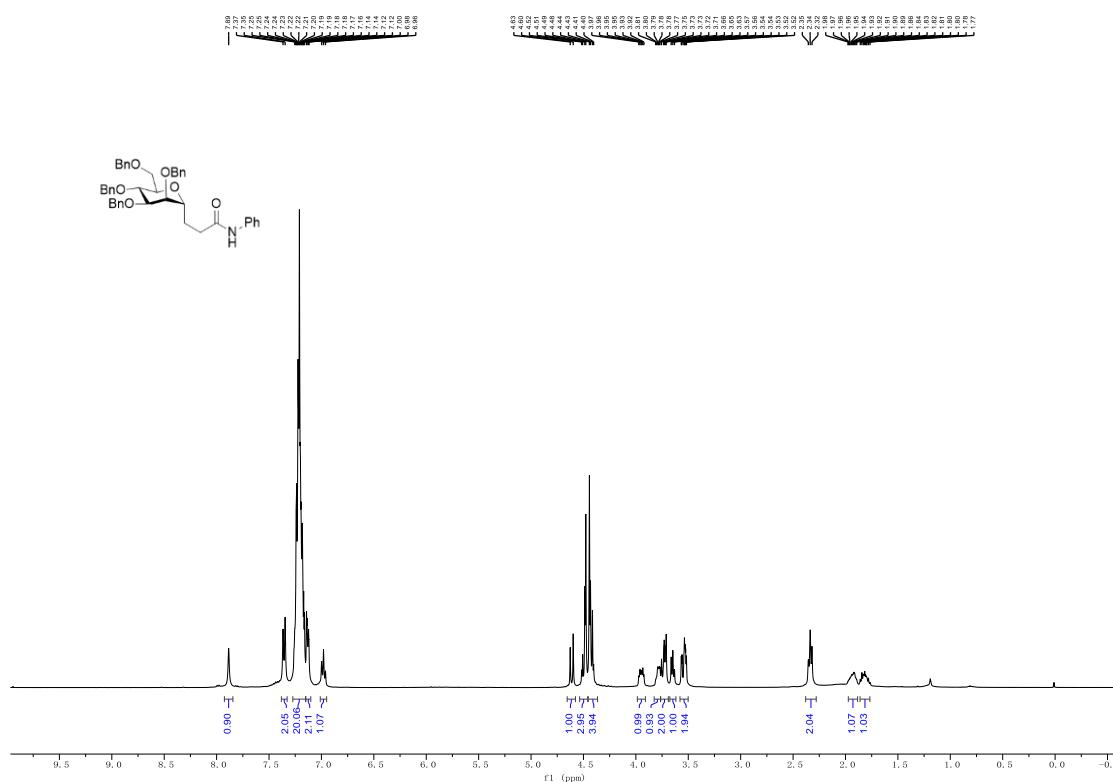


Figure S49. ^{13}C NMR spectrum of compound 5h

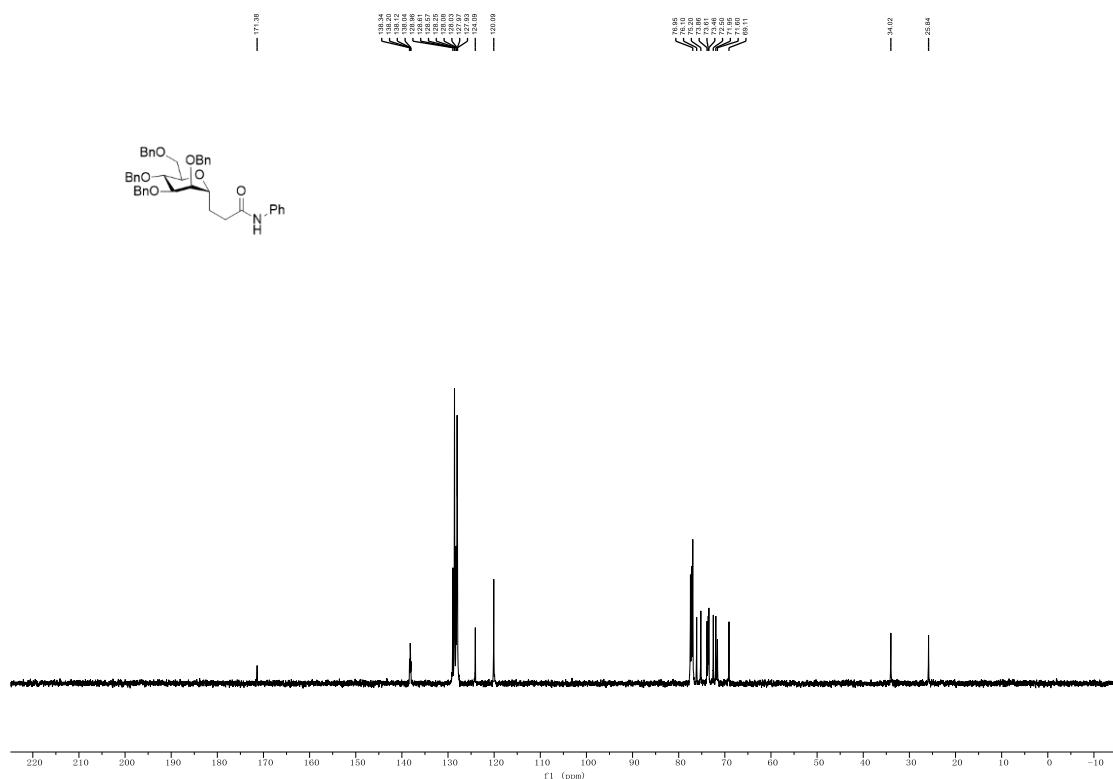


Figure S50. ^1H NMR spectrum of compound **5i**

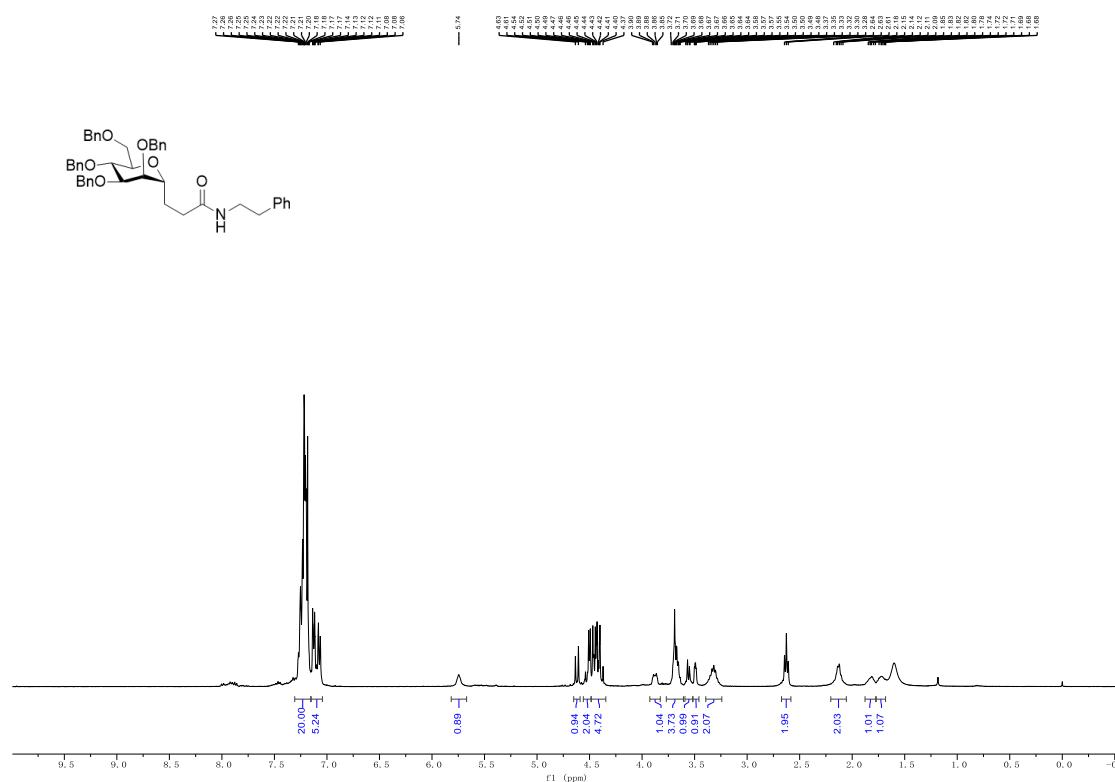


Figure S52. ^1H NMR spectrum of compound 5j

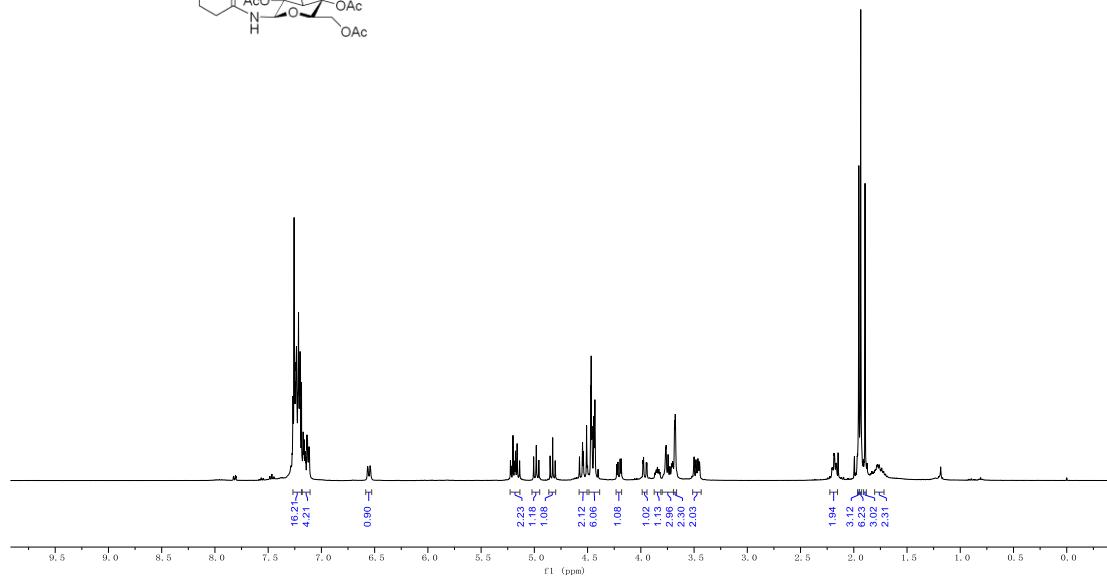
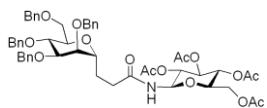


Figure S53. ^{13}C NMR spectrum of compound 5j

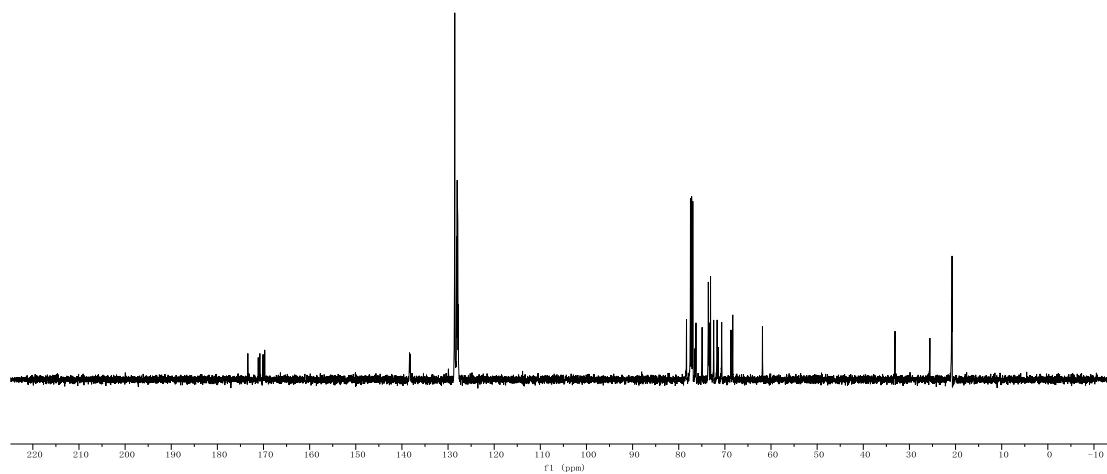
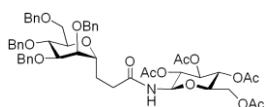


Figure S54. ^1H NMR spectrum of compound **5k**

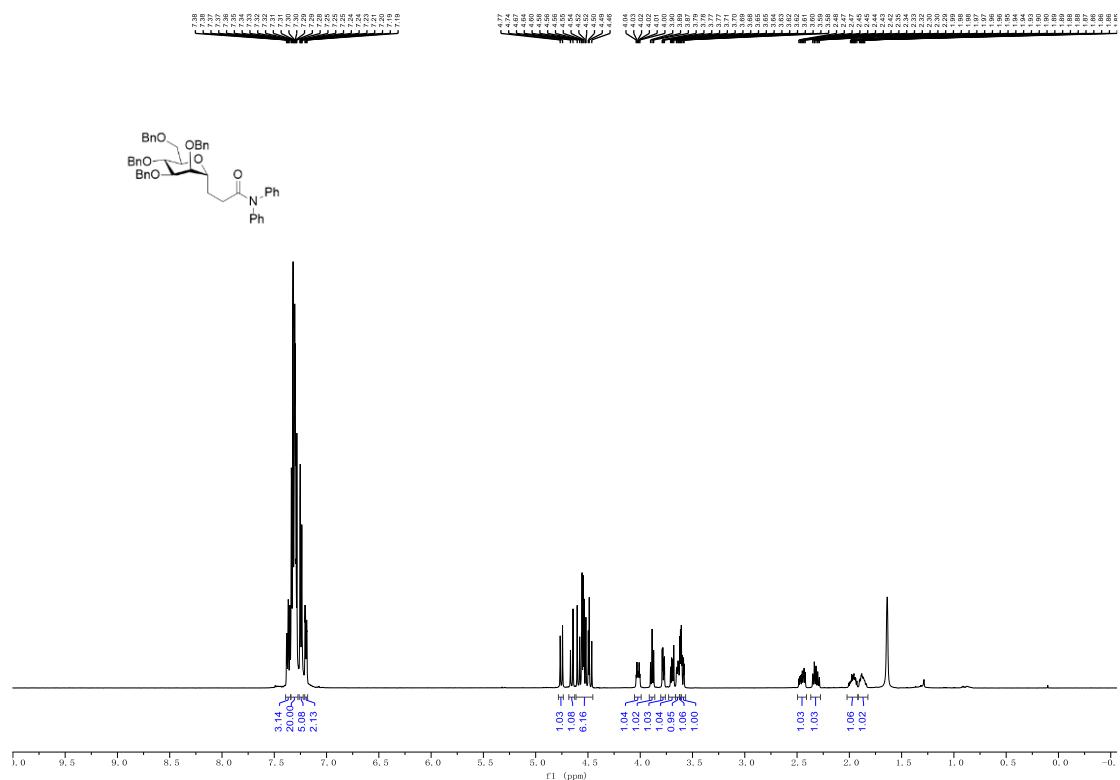


Figure S55. ^{13}C NMR spectrum of compound **5k**

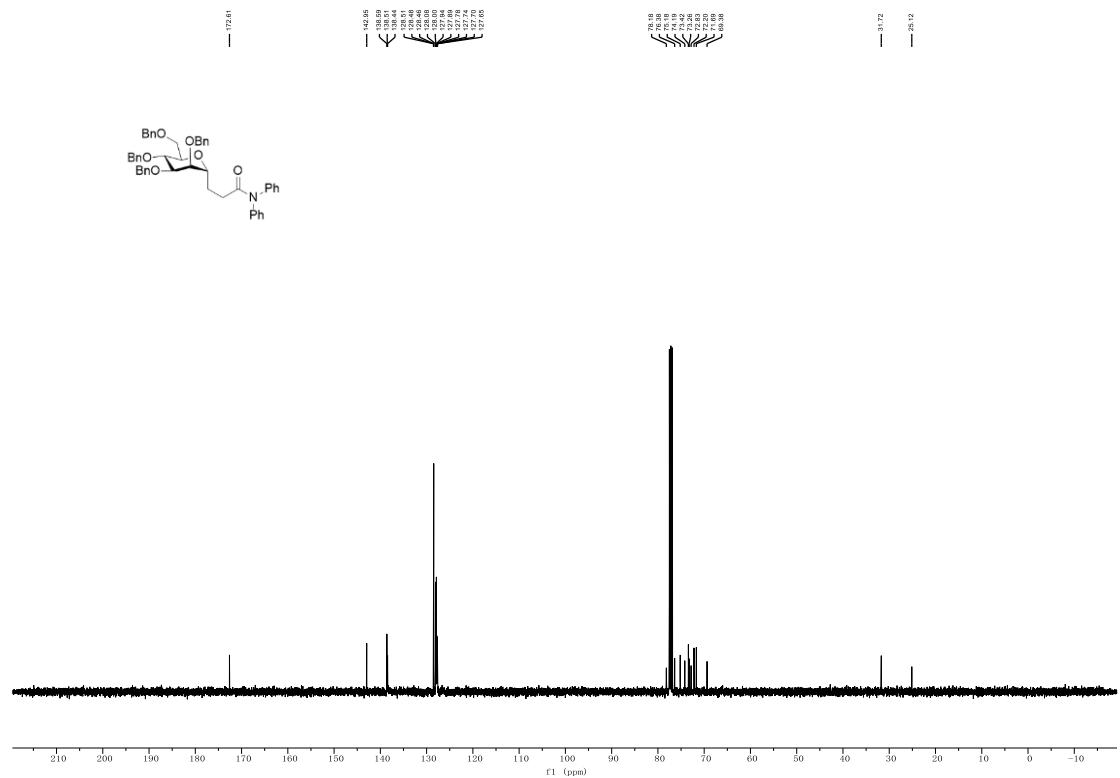


Figure S56. COSY spectrum of compound 5k

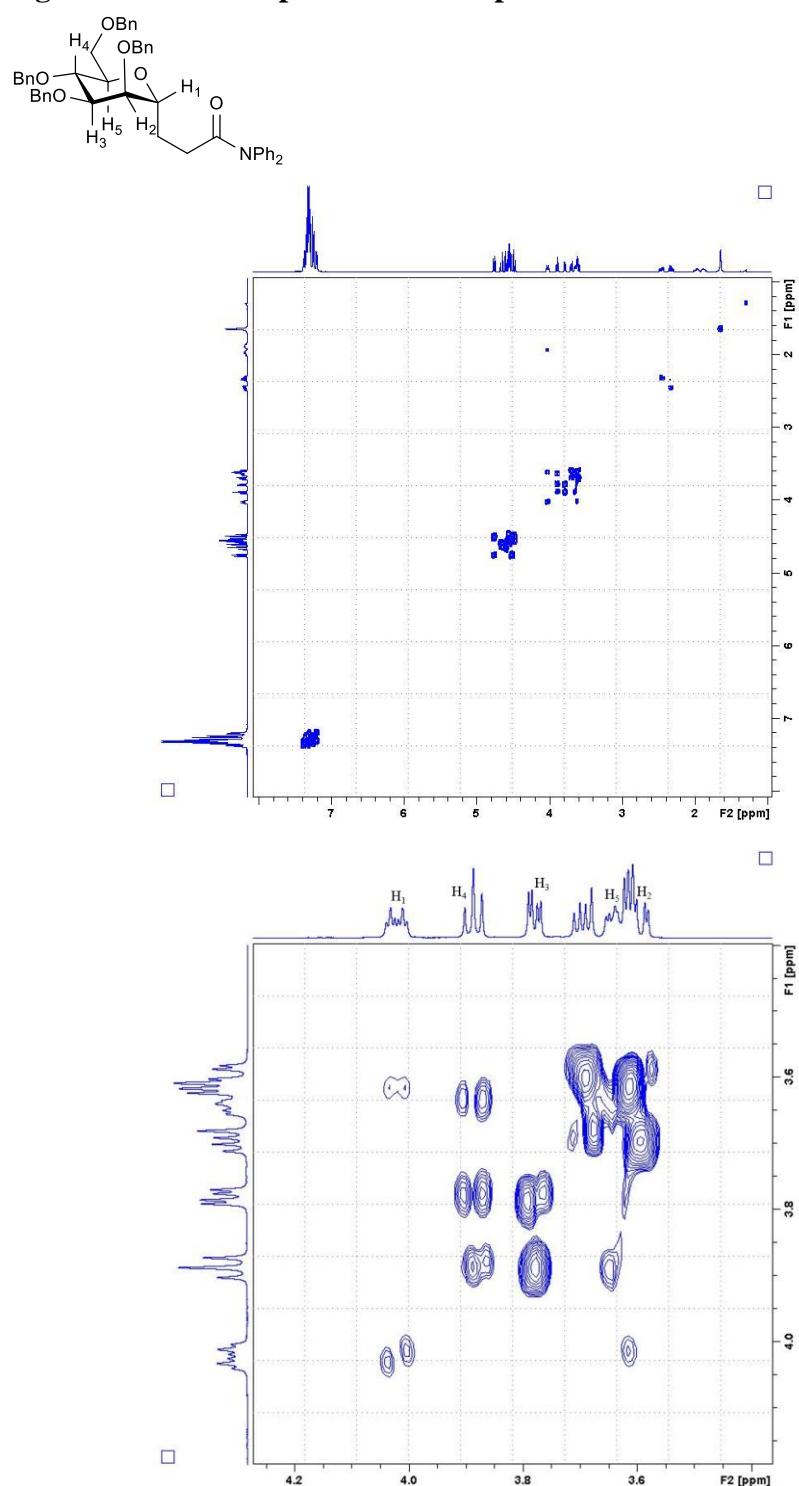


Figure S57. NOE spectrum of compound 5k

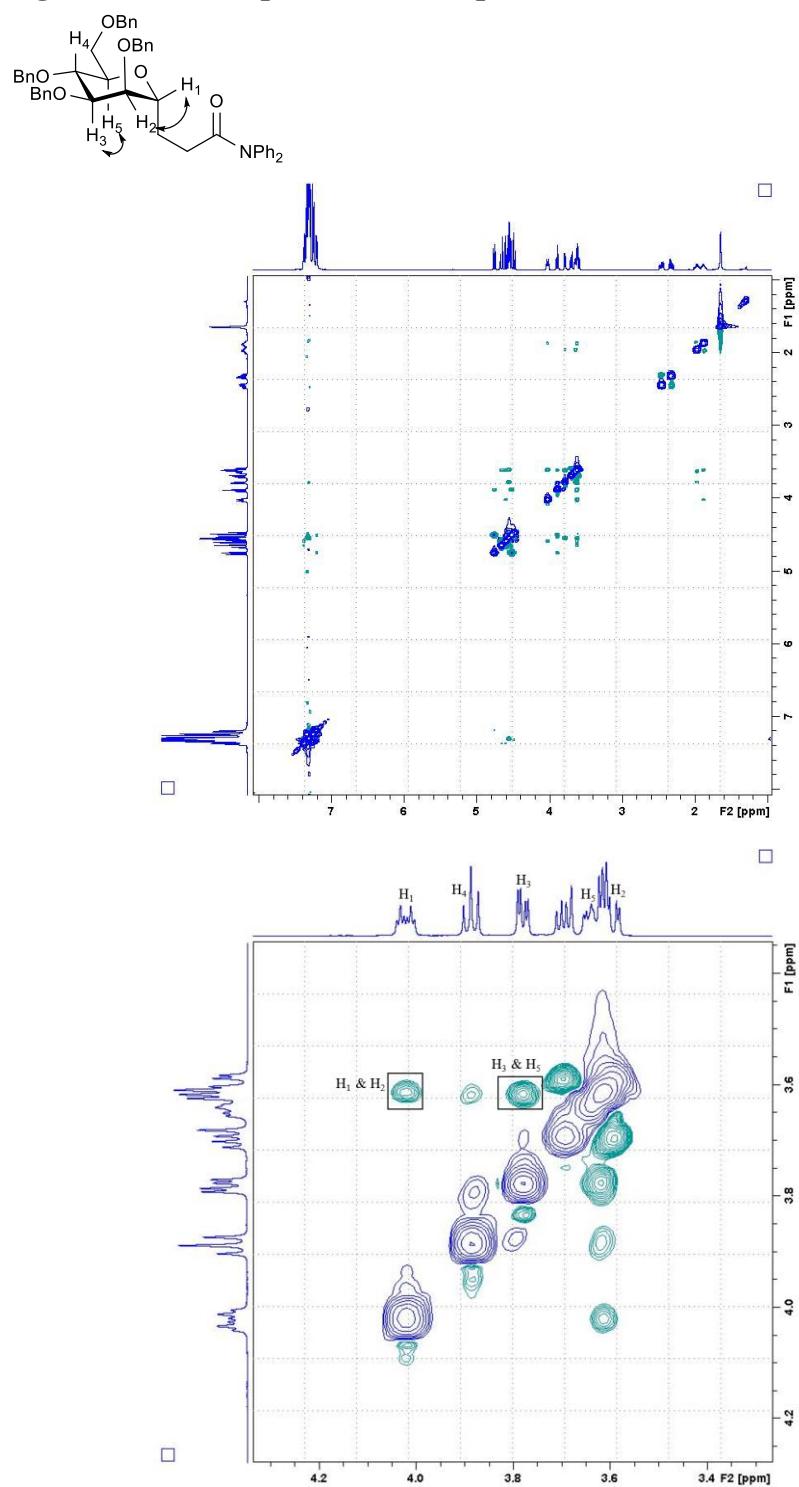


Figure S58. ^1H NMR spectrum of compound 5l

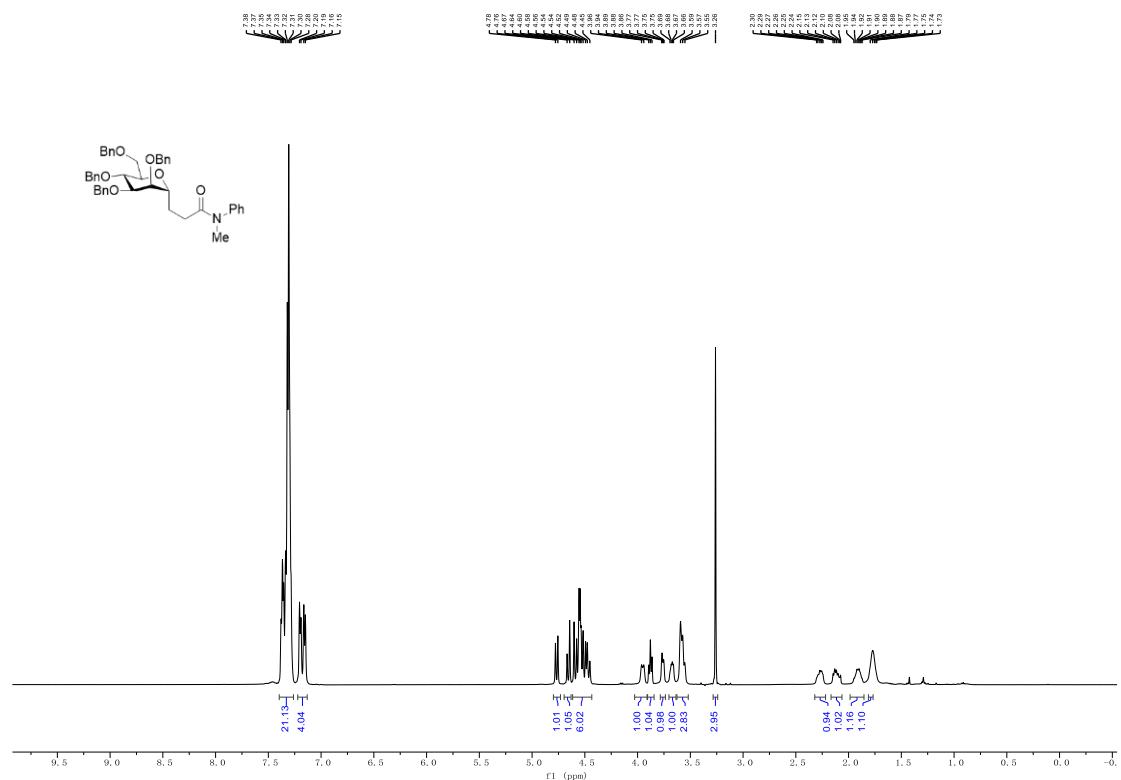


Figure S59. ^{13}C NMR spectrum of compound 5l

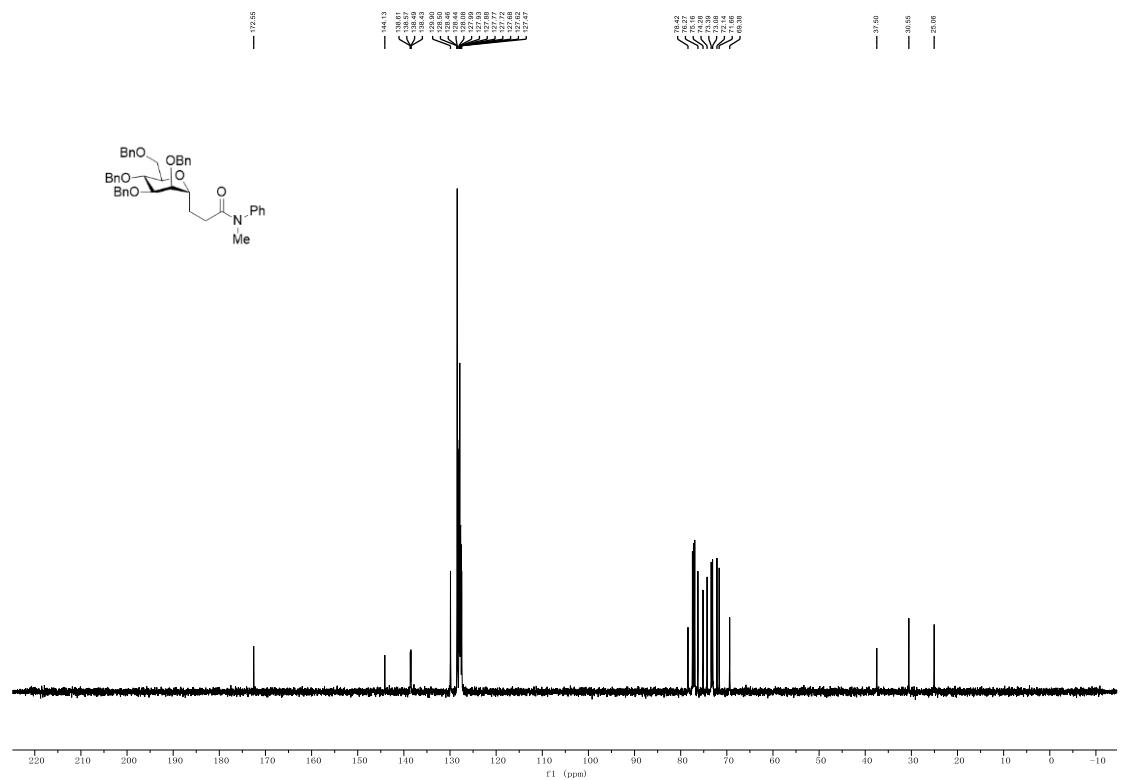


Figure S60. ^1H NMR spectrum of compound 5m

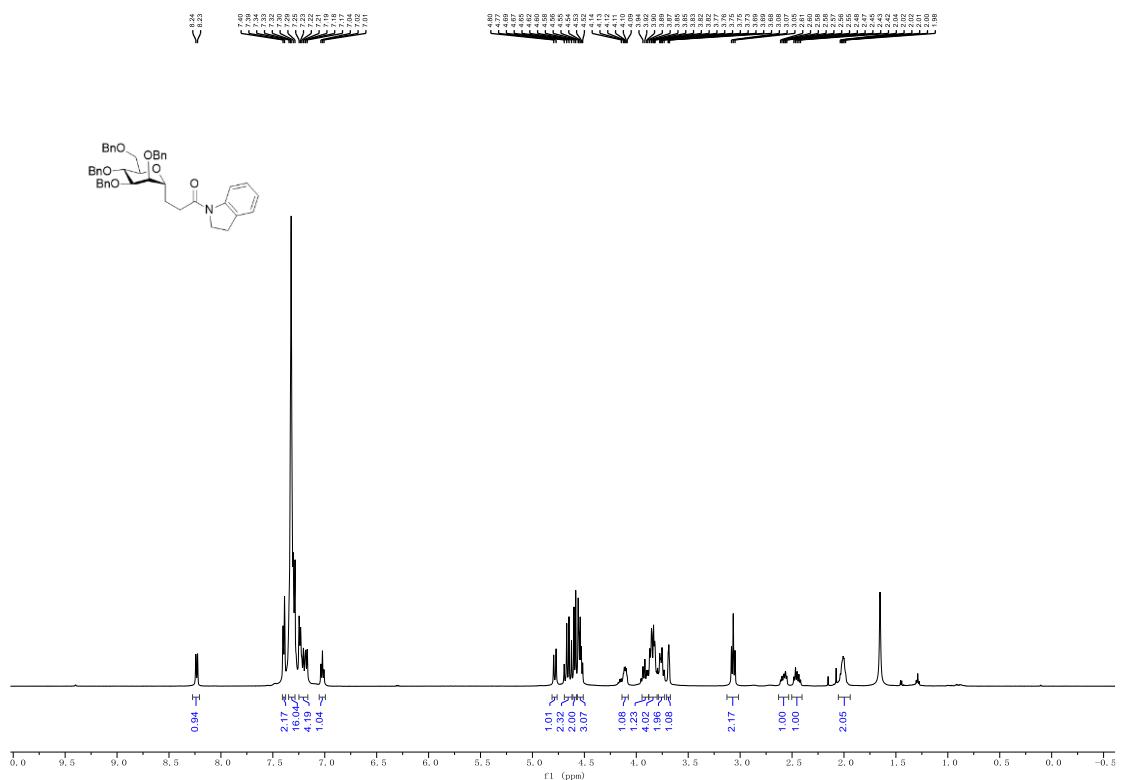


Figure S61. ^{13}C NMR spectrum of compound 5m

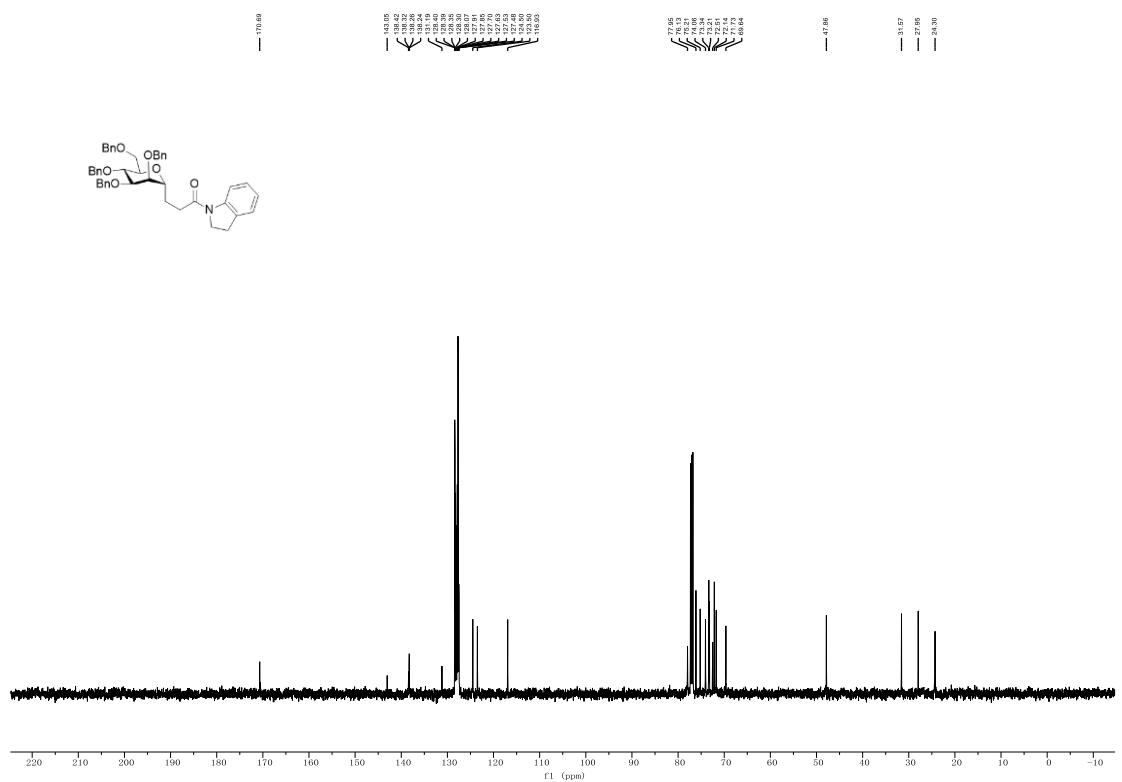


Figure S62. ^1H NMR spectrum of compound 5n

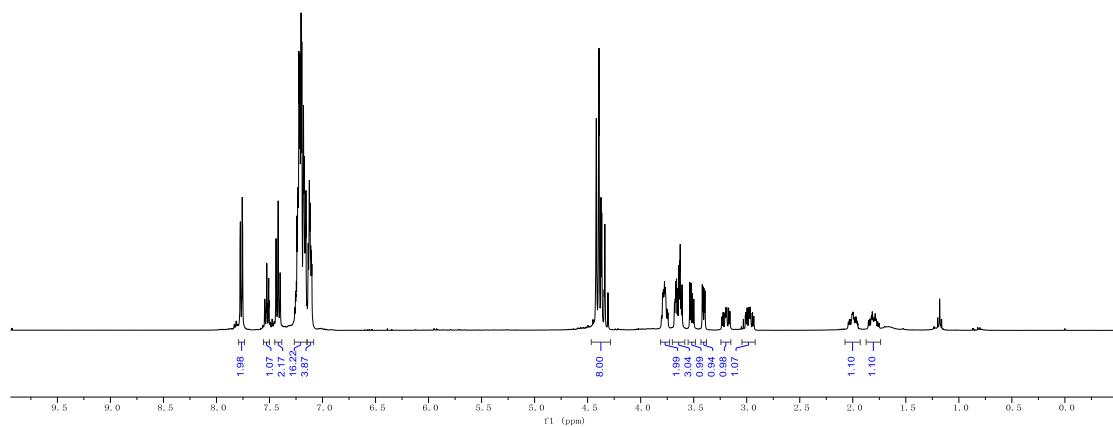
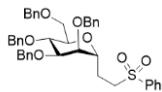


Figure S63. ^{13}C NMR spectrum of compound 5n

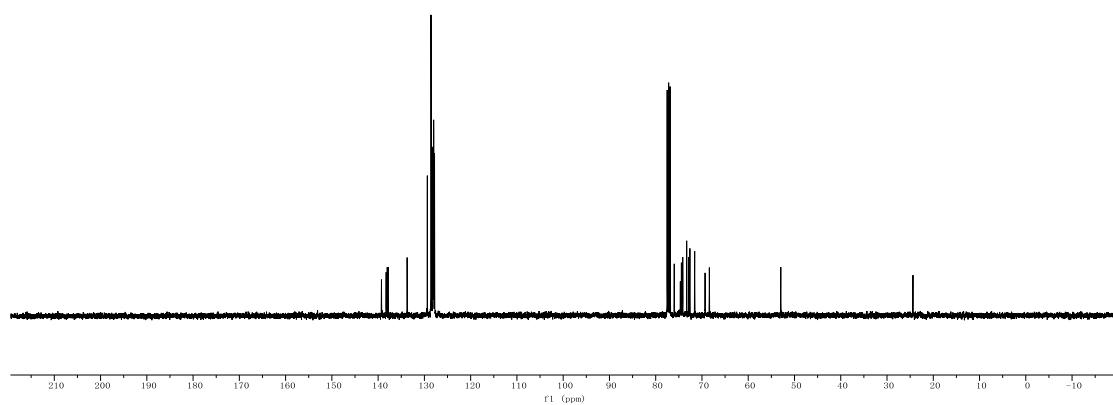
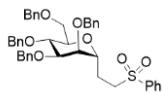


Figure S64. ^1H NMR spectrum of compound 5o

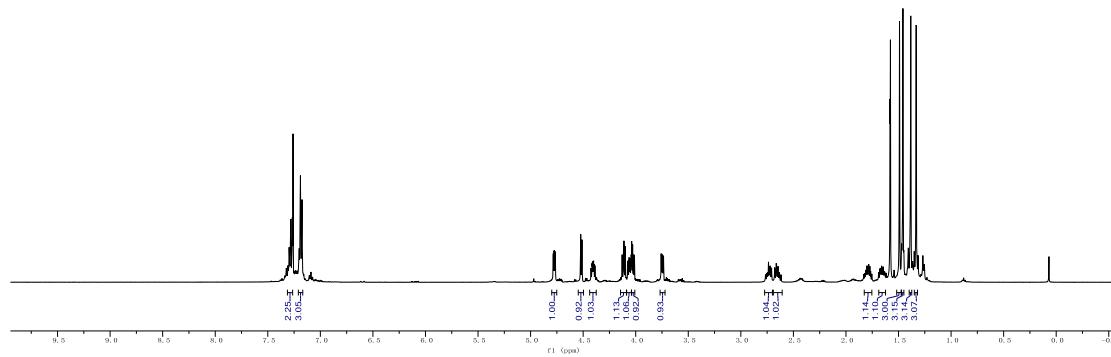
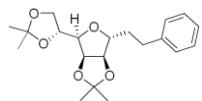


Figure S65. ^{13}C NMR spectrum of compound 5o

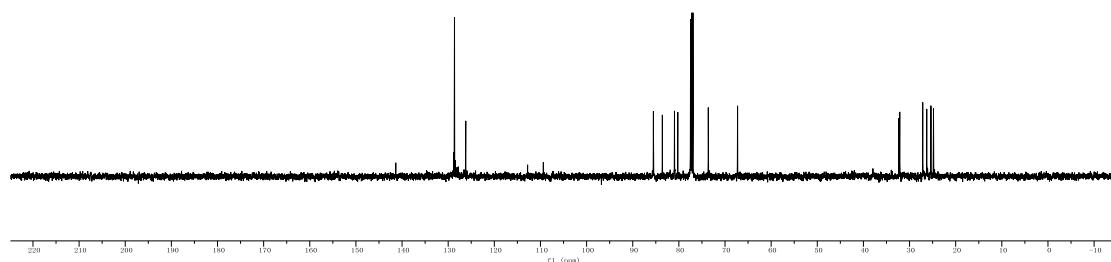
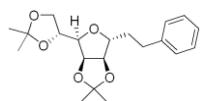


Figure S66. ^1H NMR spectrum of compound **5p**

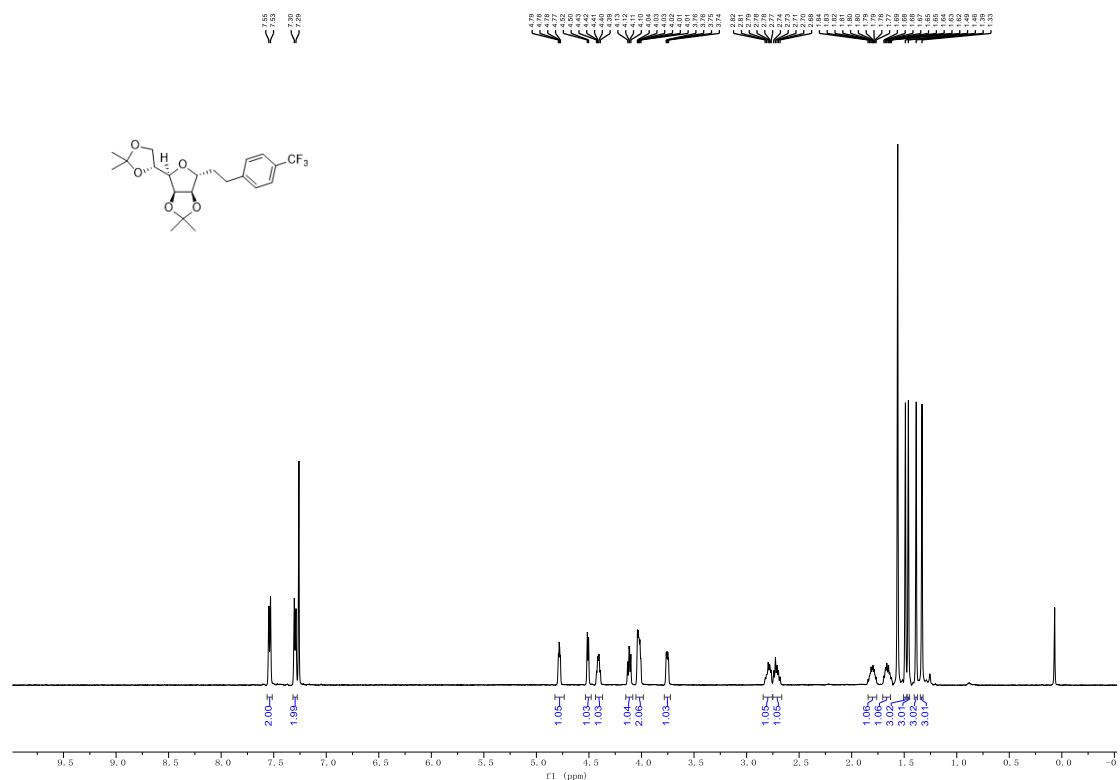


Figure S67. ^{19}F NMR spectrum of compound **5p**

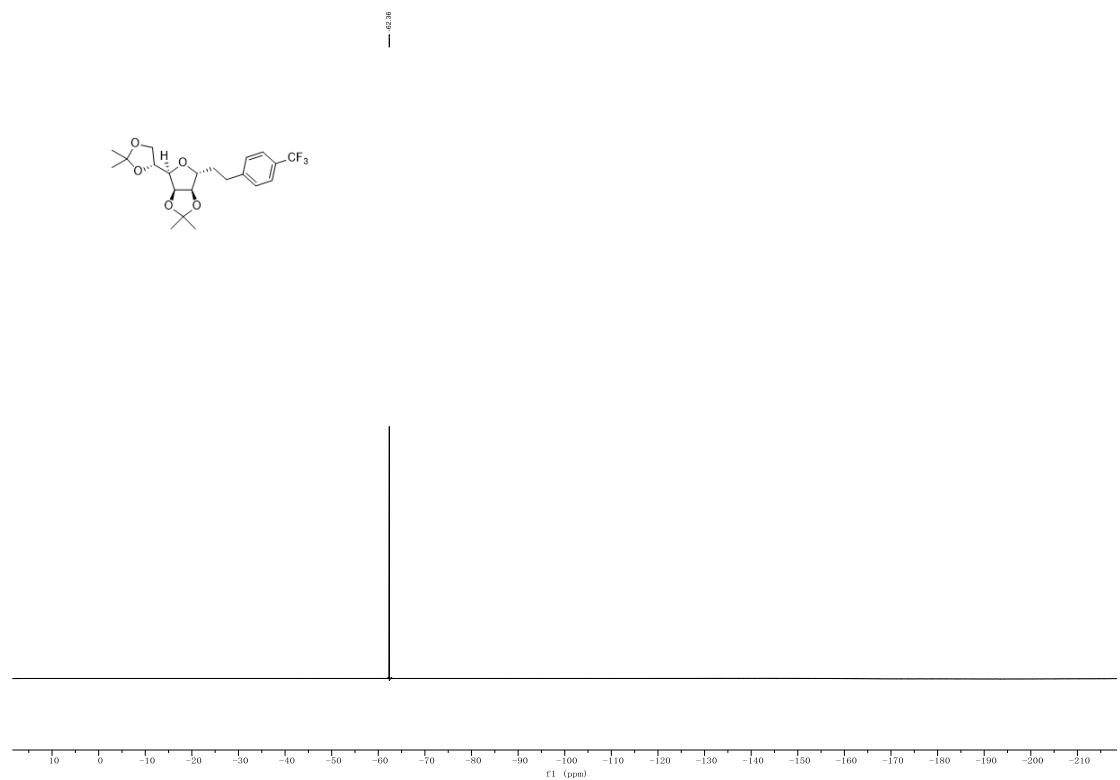


Figure S68. ^{13}C NMR spectrum of compound 5p

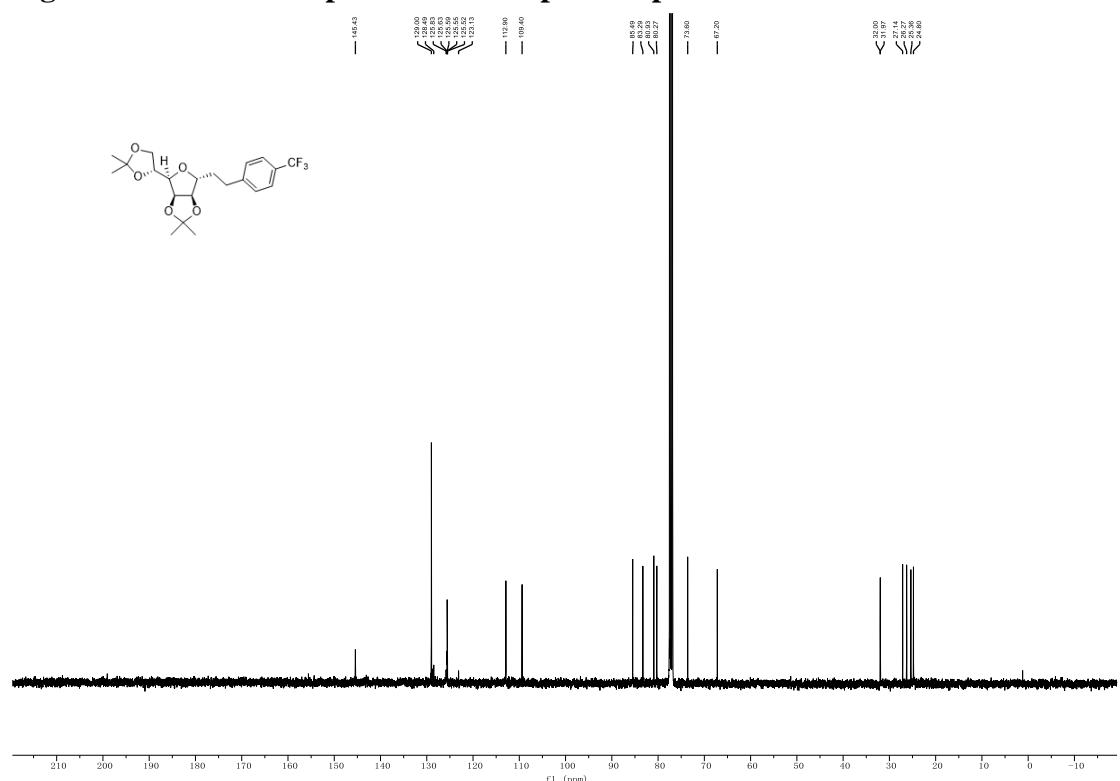


Figure S69. ^1H NMR spectrum of compound 5q

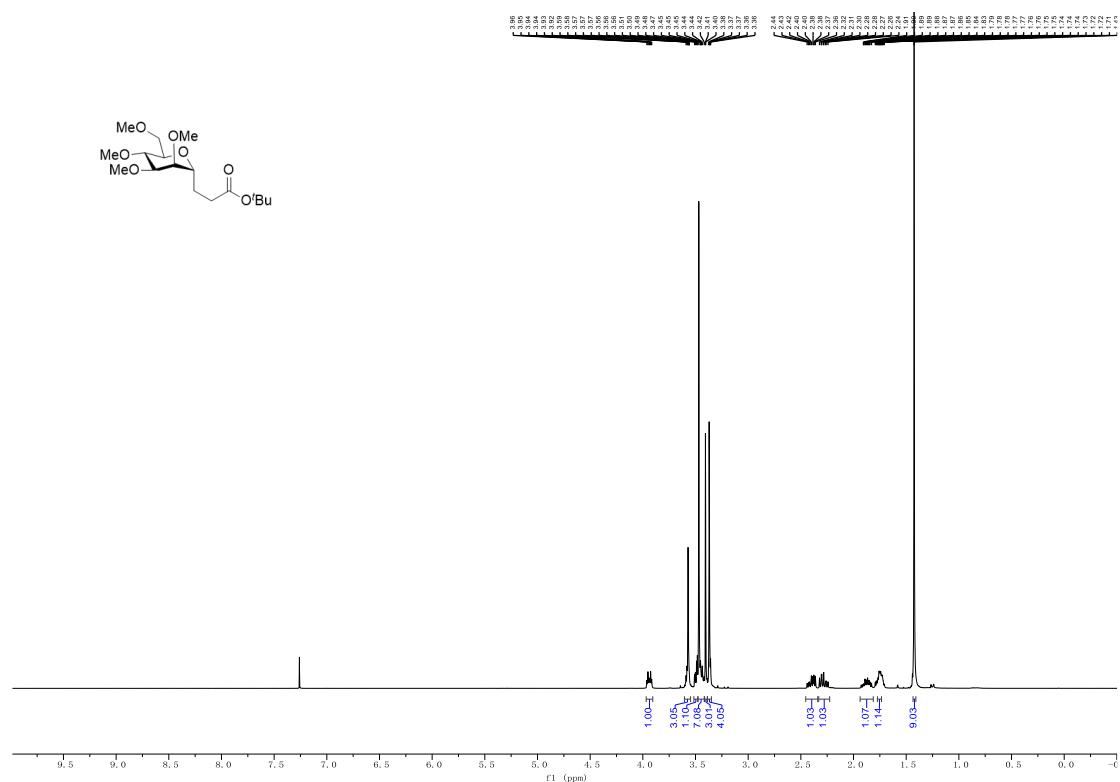


Figure S70. ^{13}C NMR spectrum of compound 5q

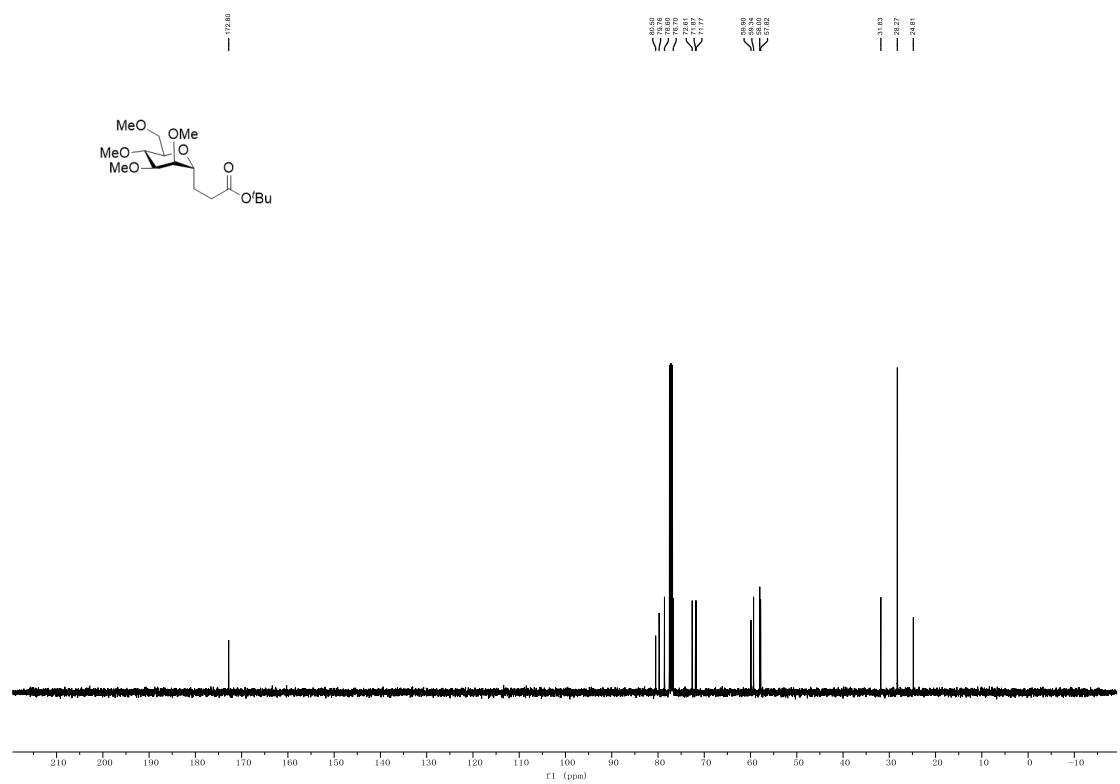


Figure S71. ^1H NMR spectrum of compound 5r

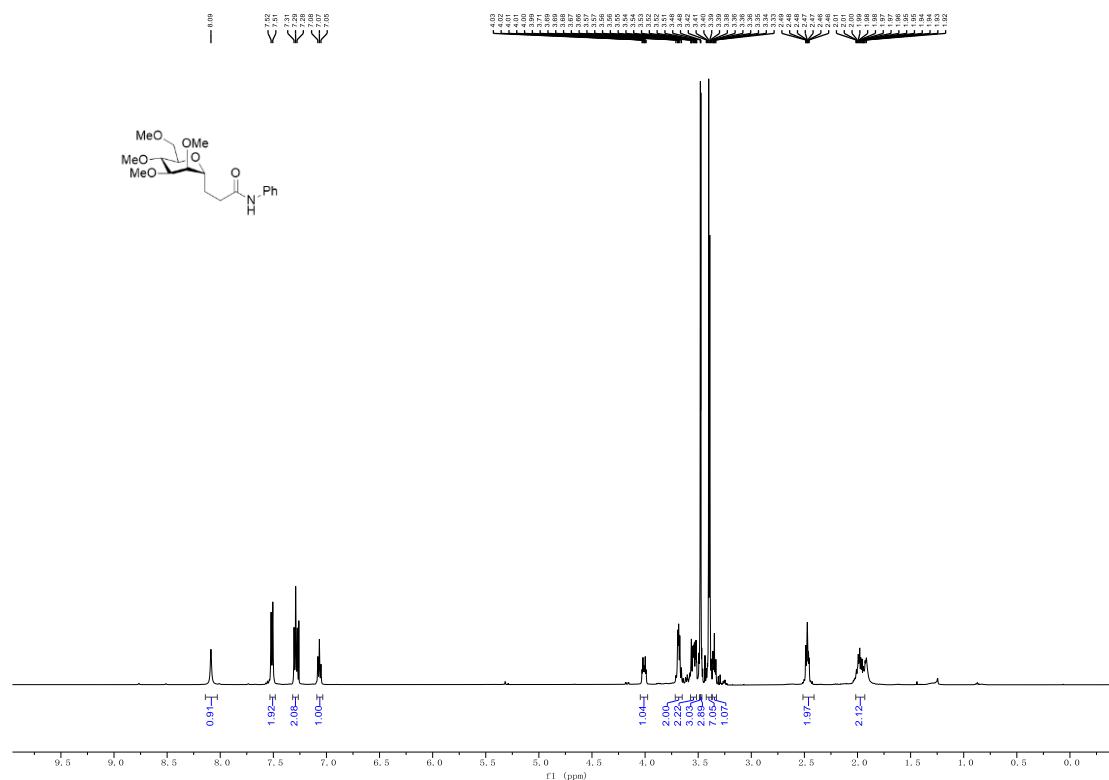


Figure S72. ^{13}C NMR spectrum of compound 5r

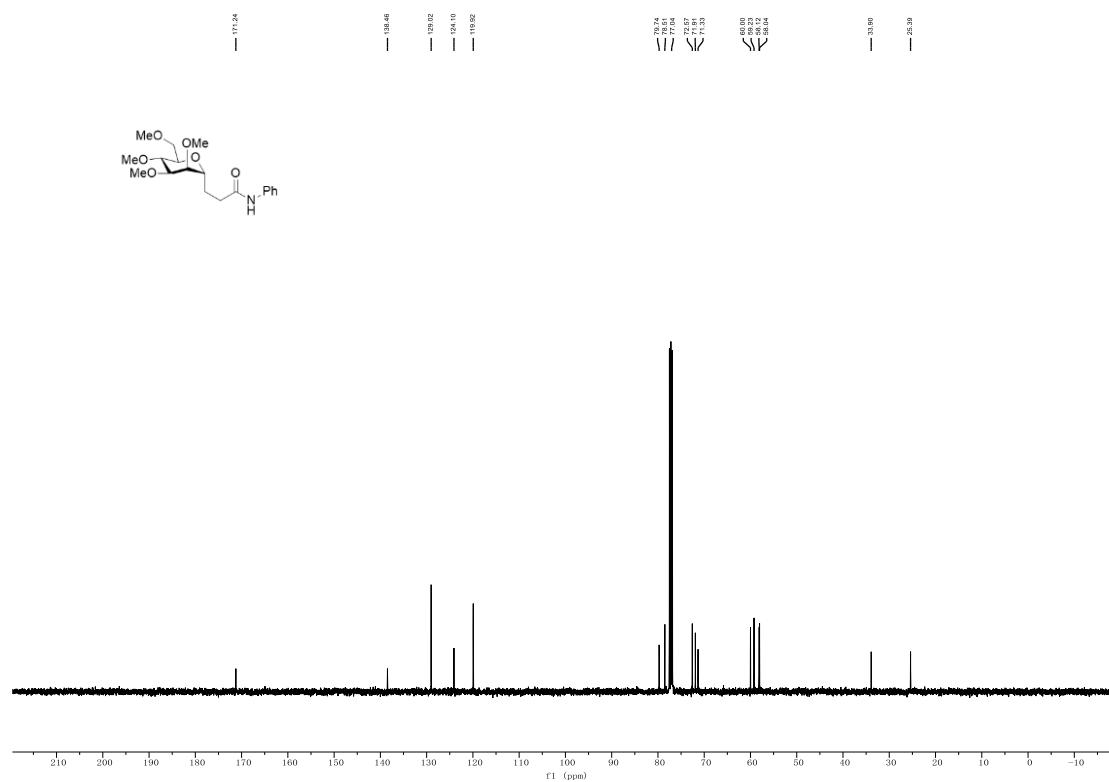


Figure S73. ^1H NMR spectrum of compound **5s**

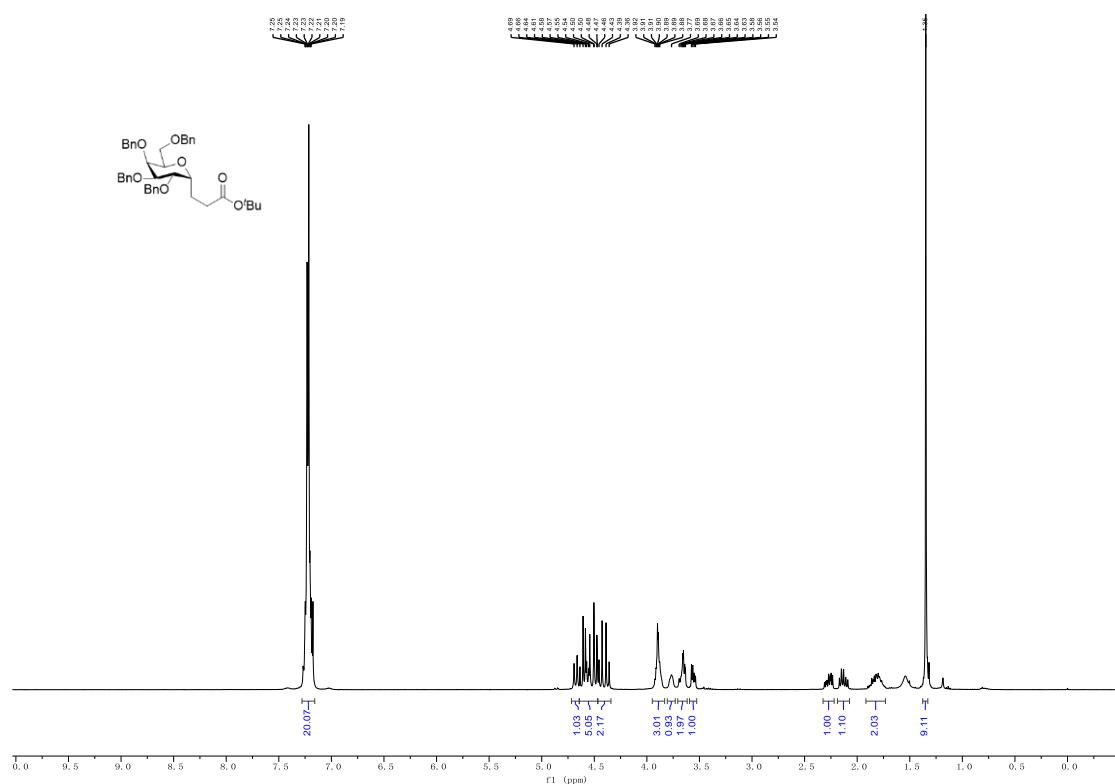


Figure S74. ^{13}C NMR spectrum of compound **5s**

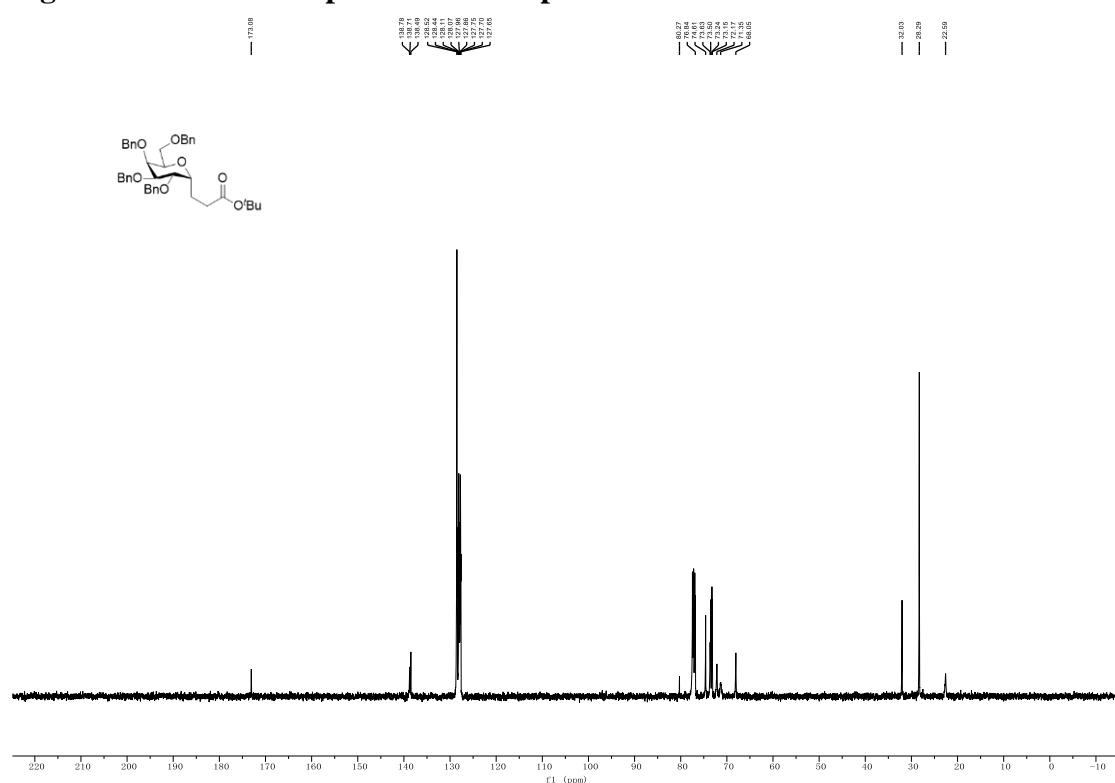


Figure S75. ^1H NMR spectrum of compound 5t

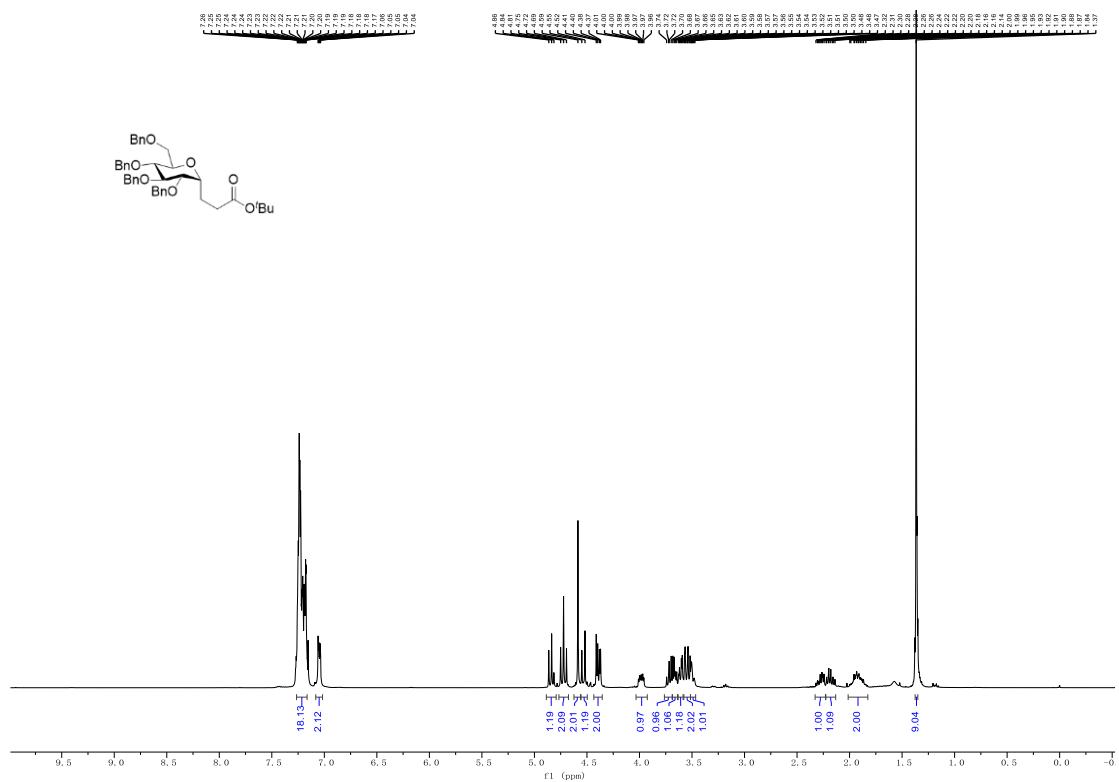


Figure S76. ^{13}C NMR spectrum of compound 5t

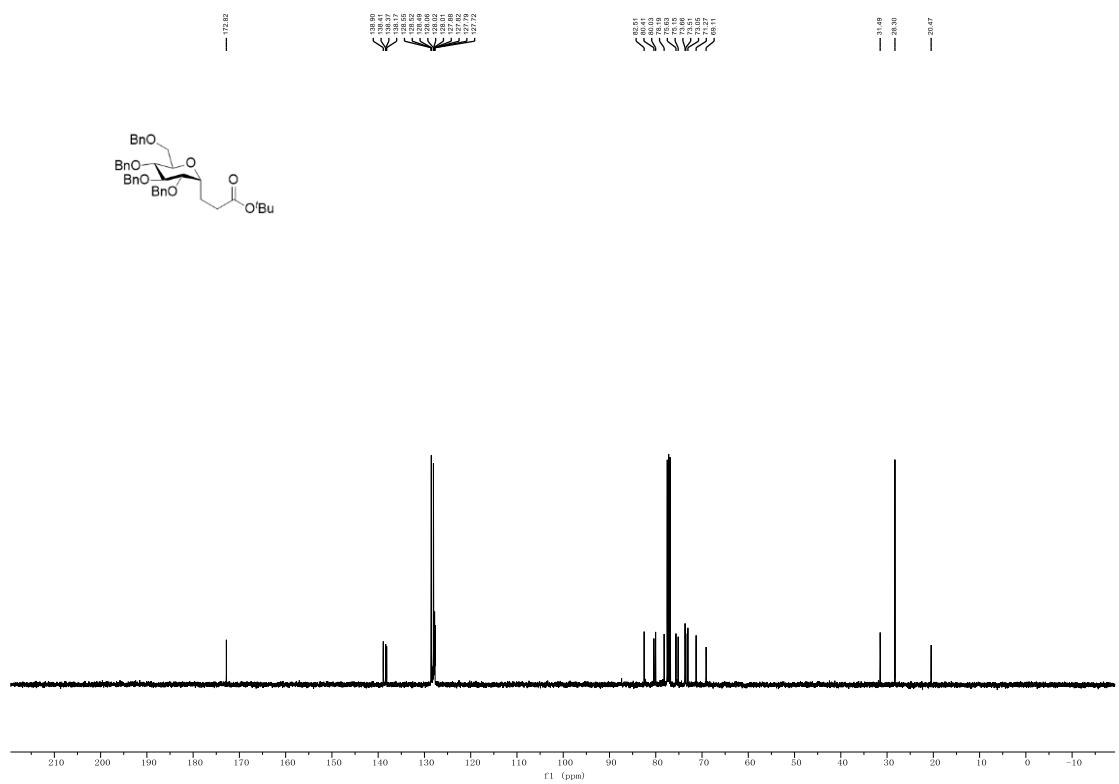


Figure S77. ^1H NMR spectrum of compound **5u**

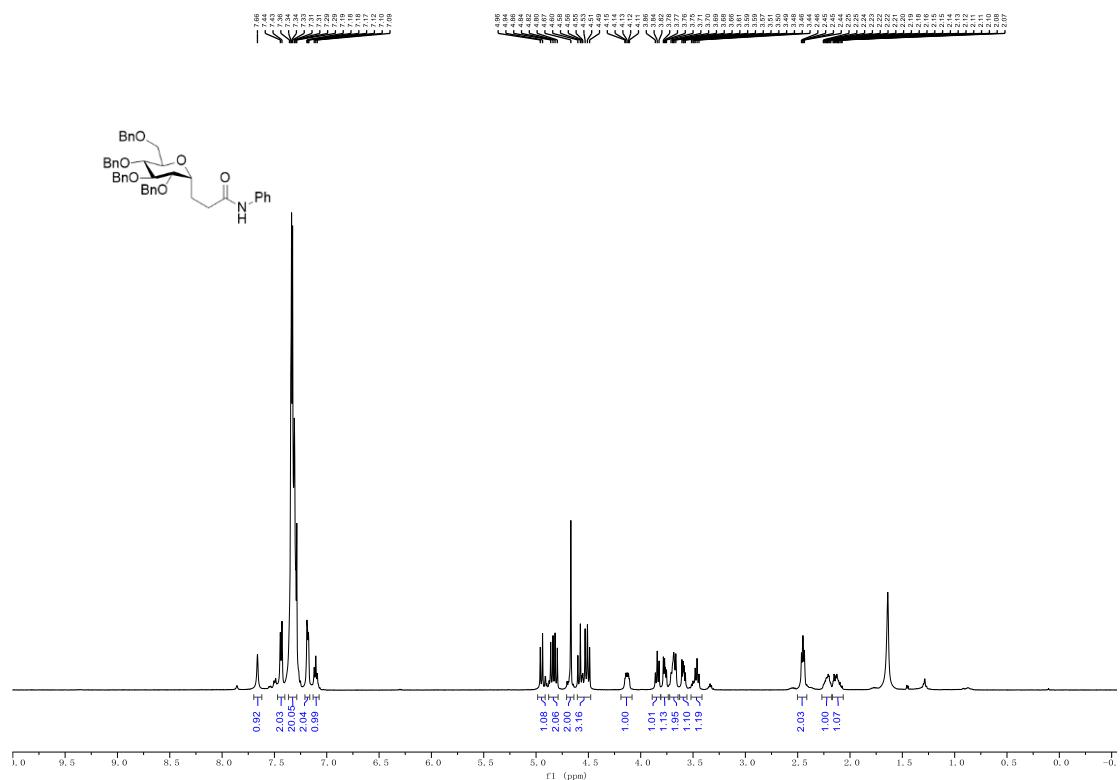


Figure S78. ^{13}C NMR spectrum of compound **5u**

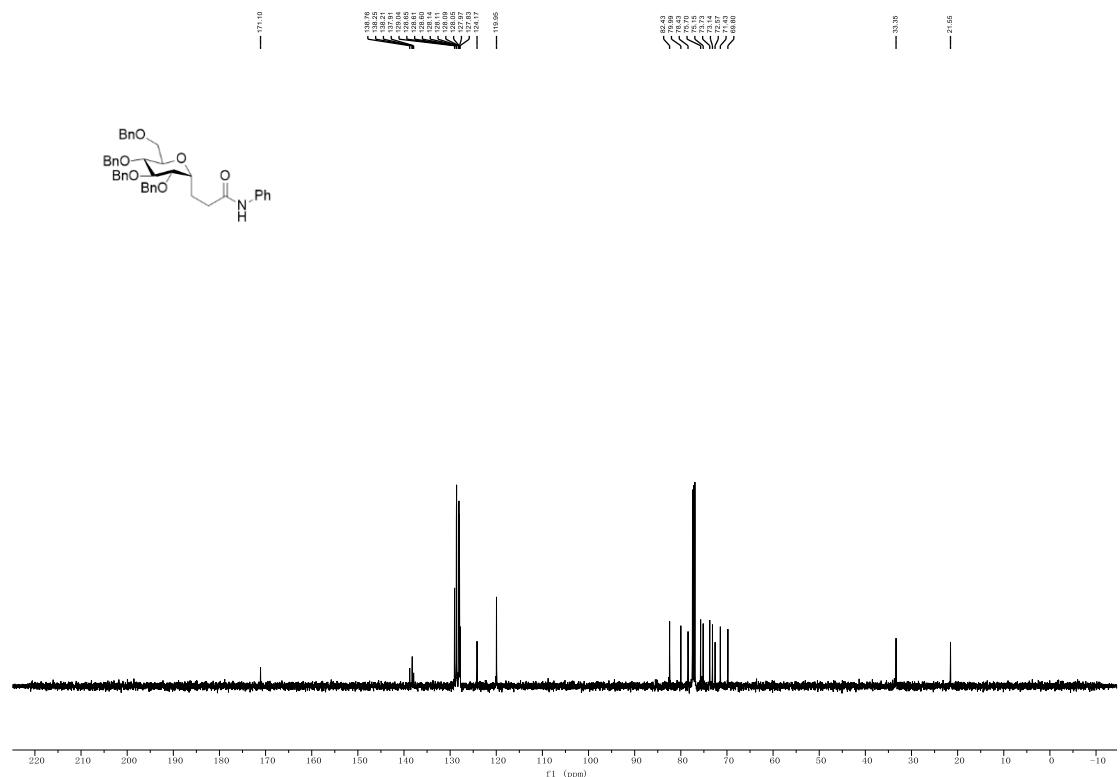


Figure S79. ^1H NMR spectrum of compound 5v

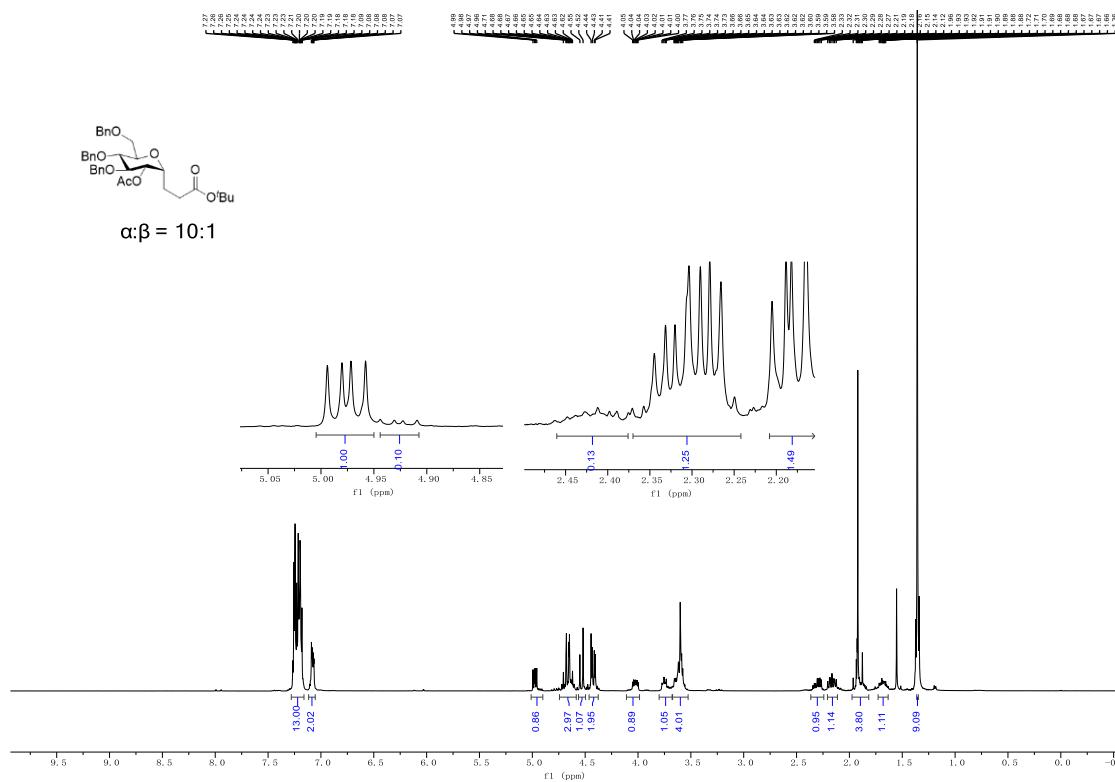


Figure S80. ^{13}C NMR spectrum of compound 5v

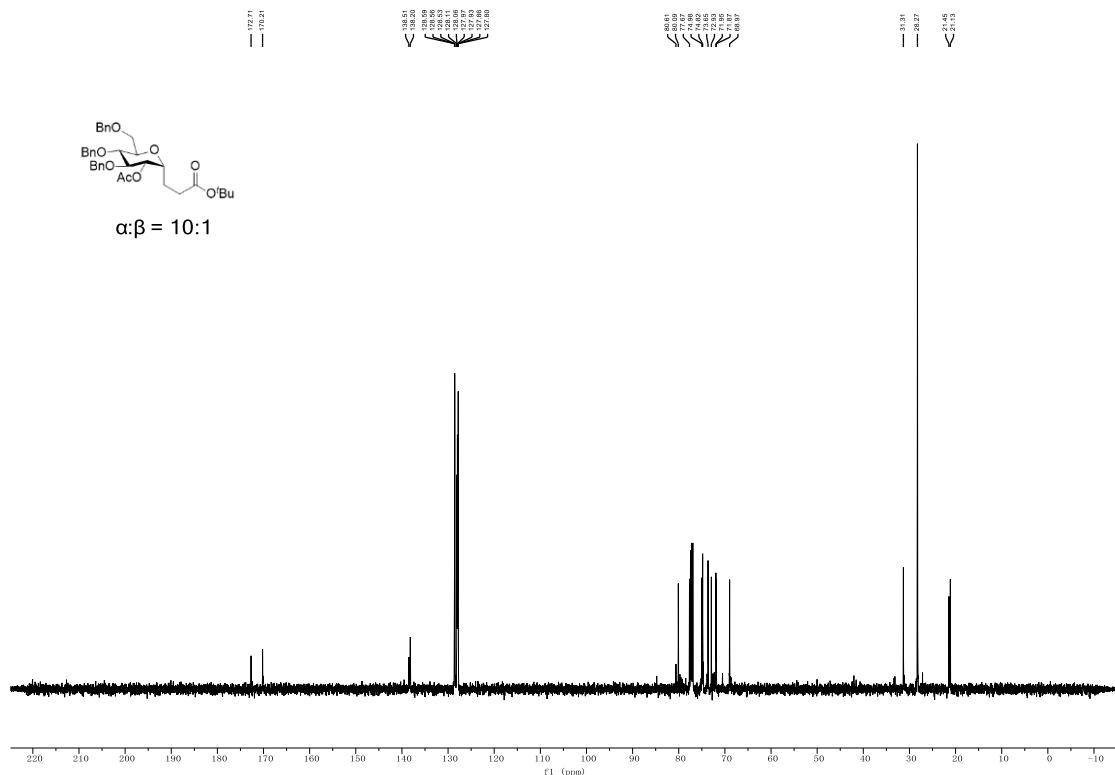


Figure S81. ^1H NMR spectrum of compound **5w**

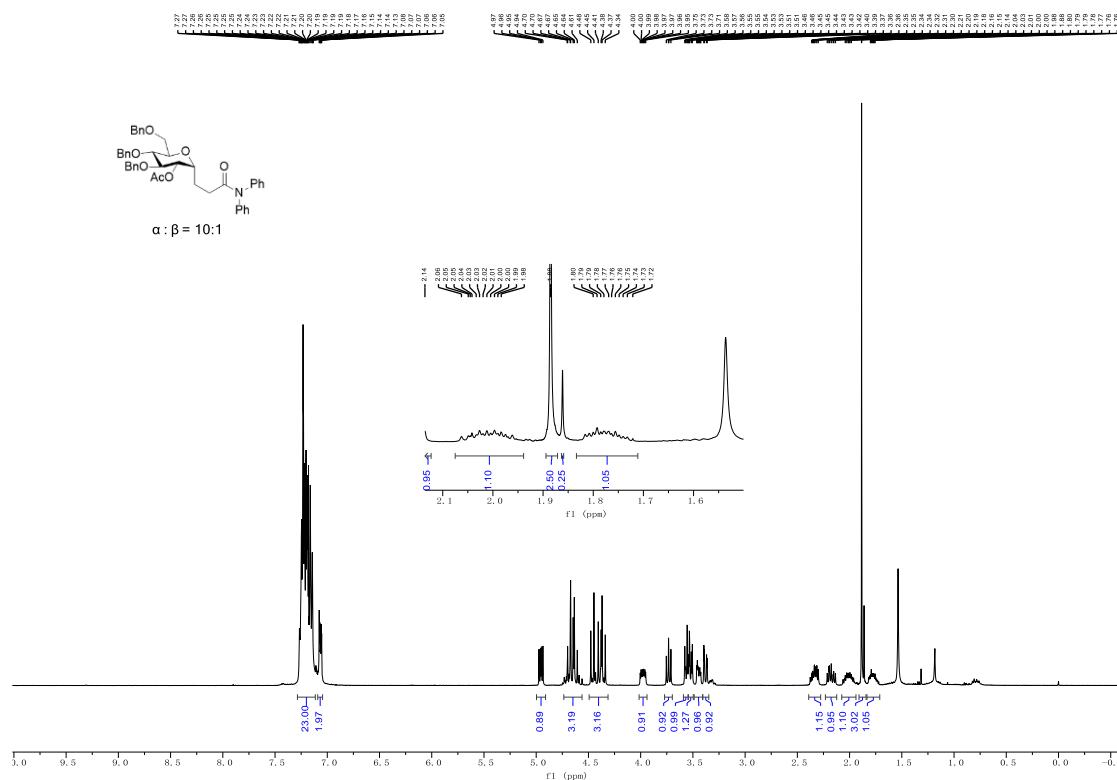


Figure S82. ^{13}C NMR spectrum of compound **5w**

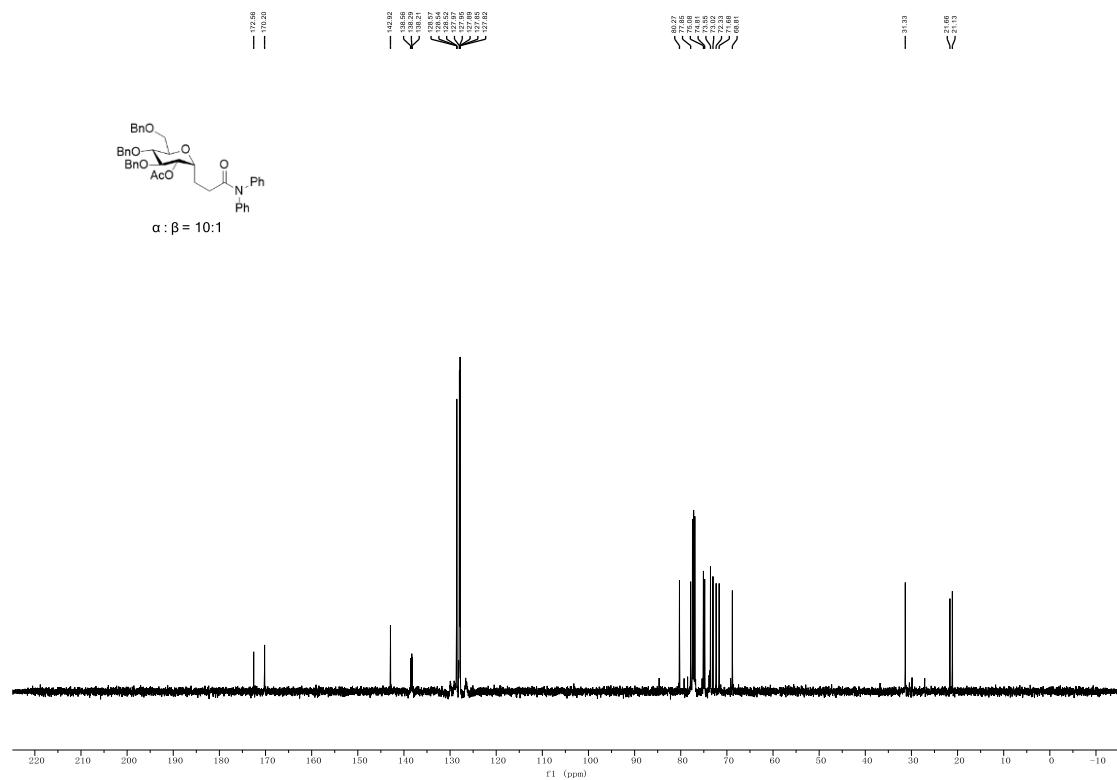


Figure S83. COSY spectrum of compound 5w

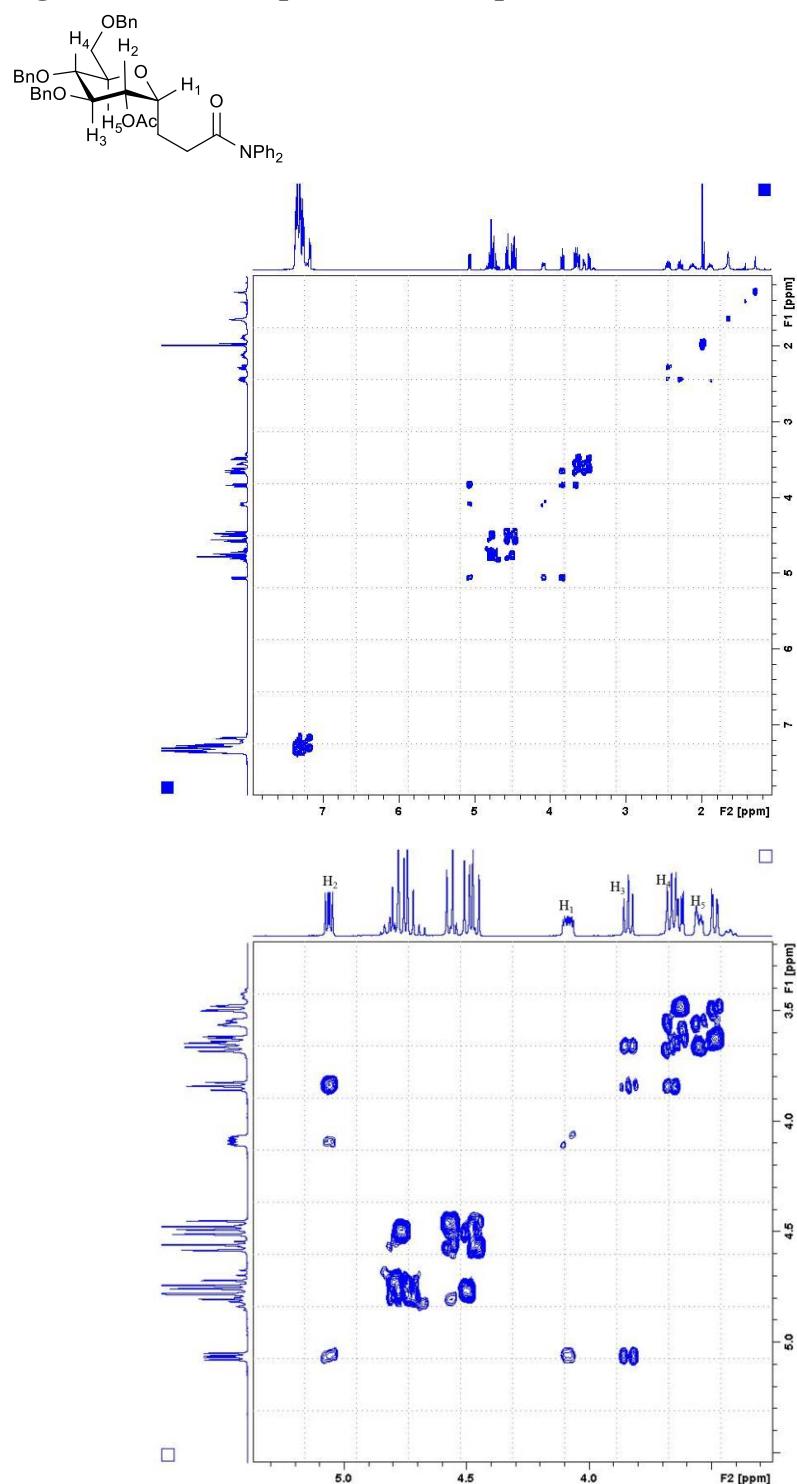


Figure S84. NOE spectrum of compound 5w

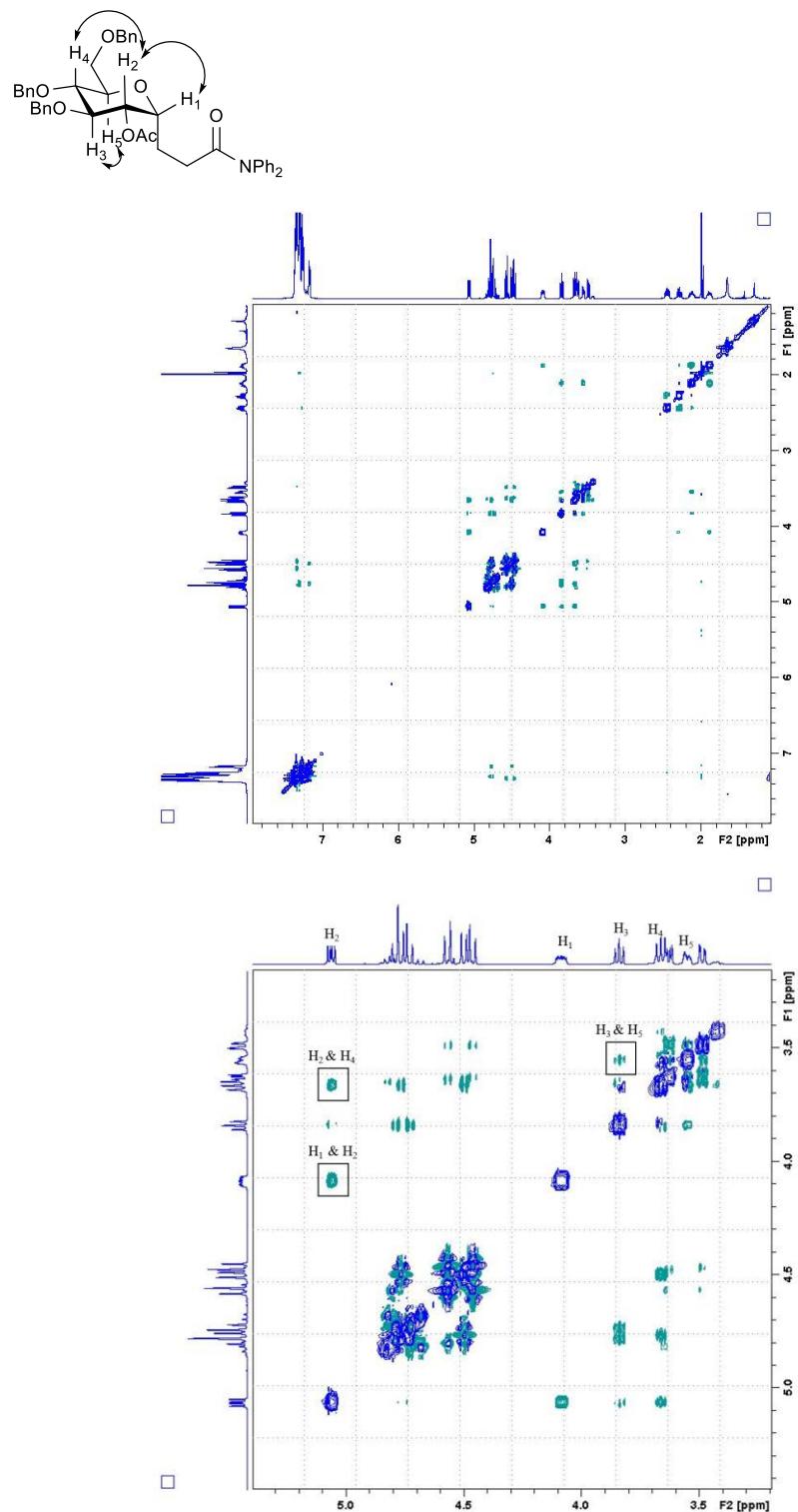


Figure S85. ^1H NMR spectrum of compound 5x

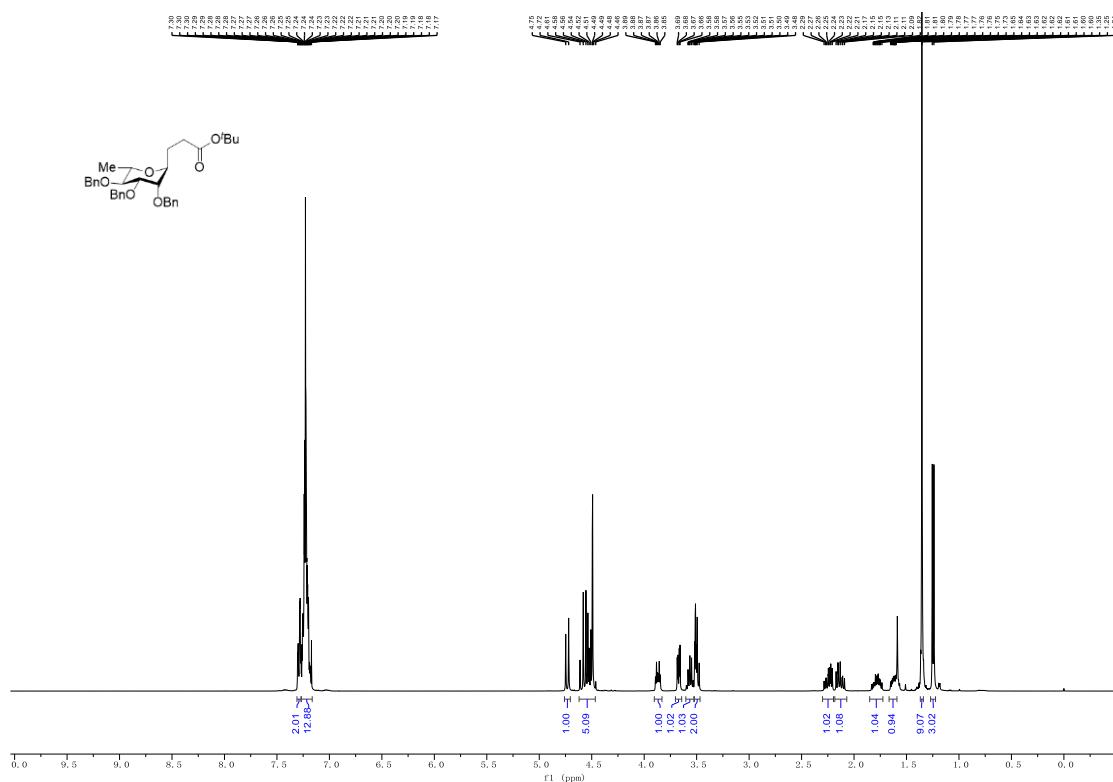


Figure S86. ^{13}C NMR spectrum of compound 5x

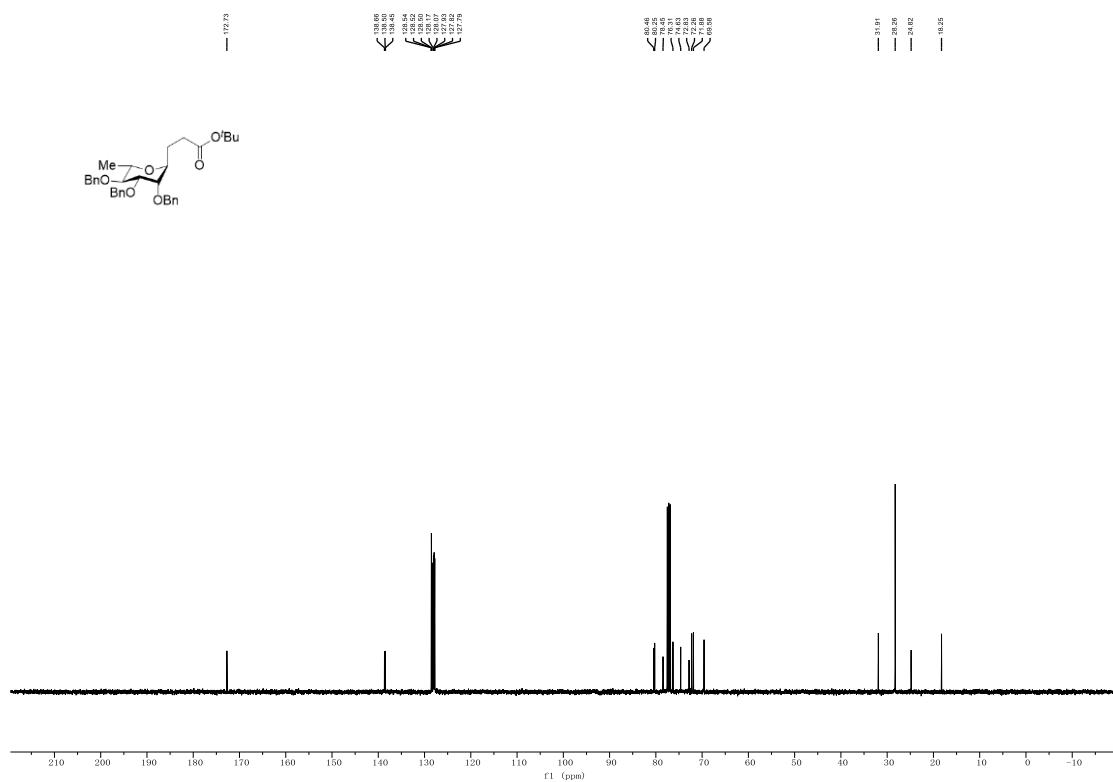


Figure S87. ^1H NMR spectrum of compound 5y

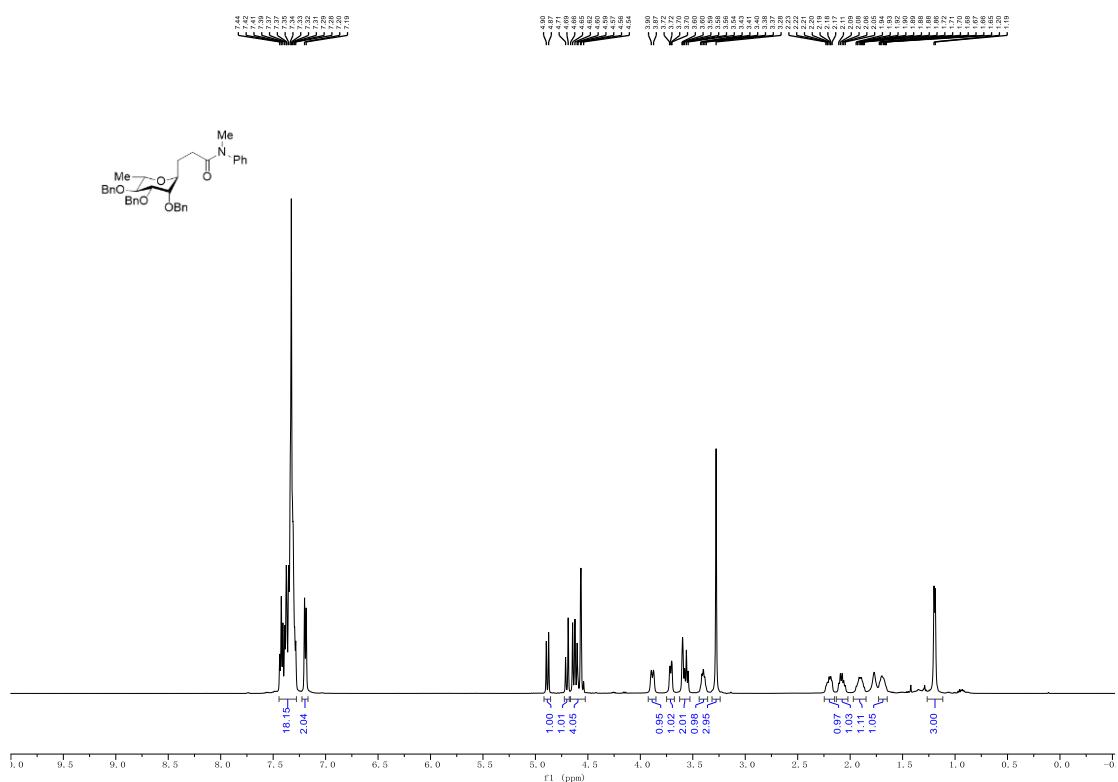


Figure S88. ^{13}C NMR spectrum of compound 5y

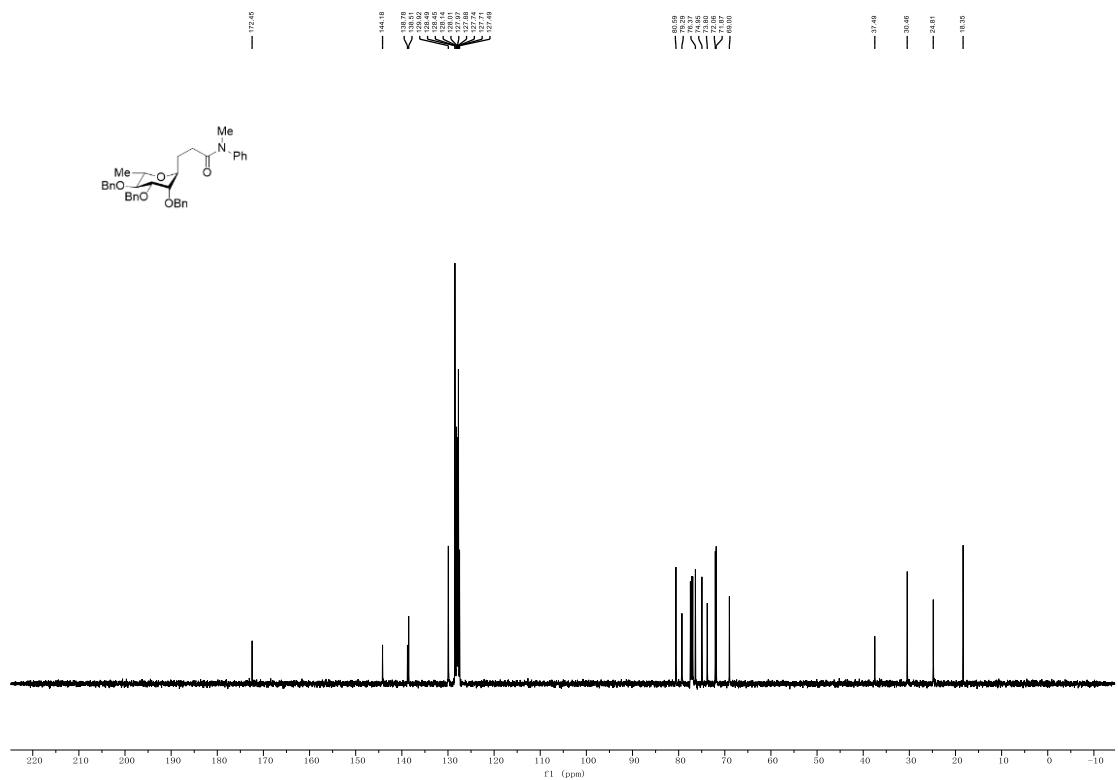


Figure S89. ^1H NMR spectrum of compound 5z

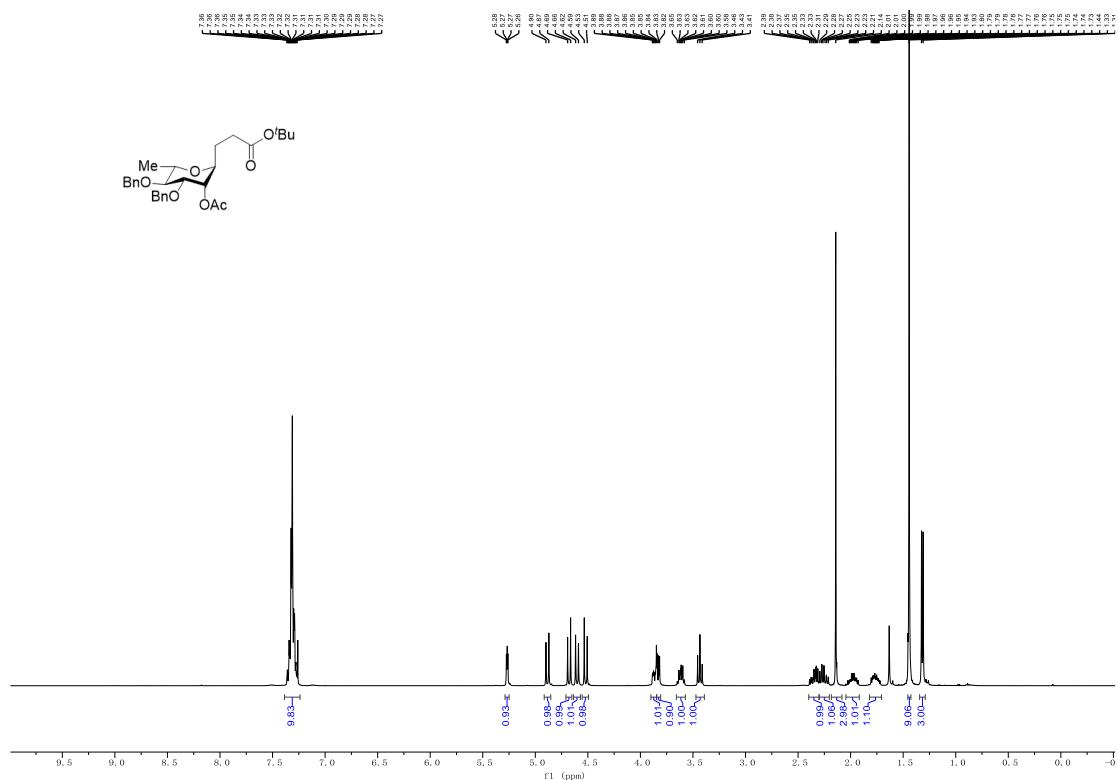


Figure S90. ^{13}C NMR spectrum of compound 5z

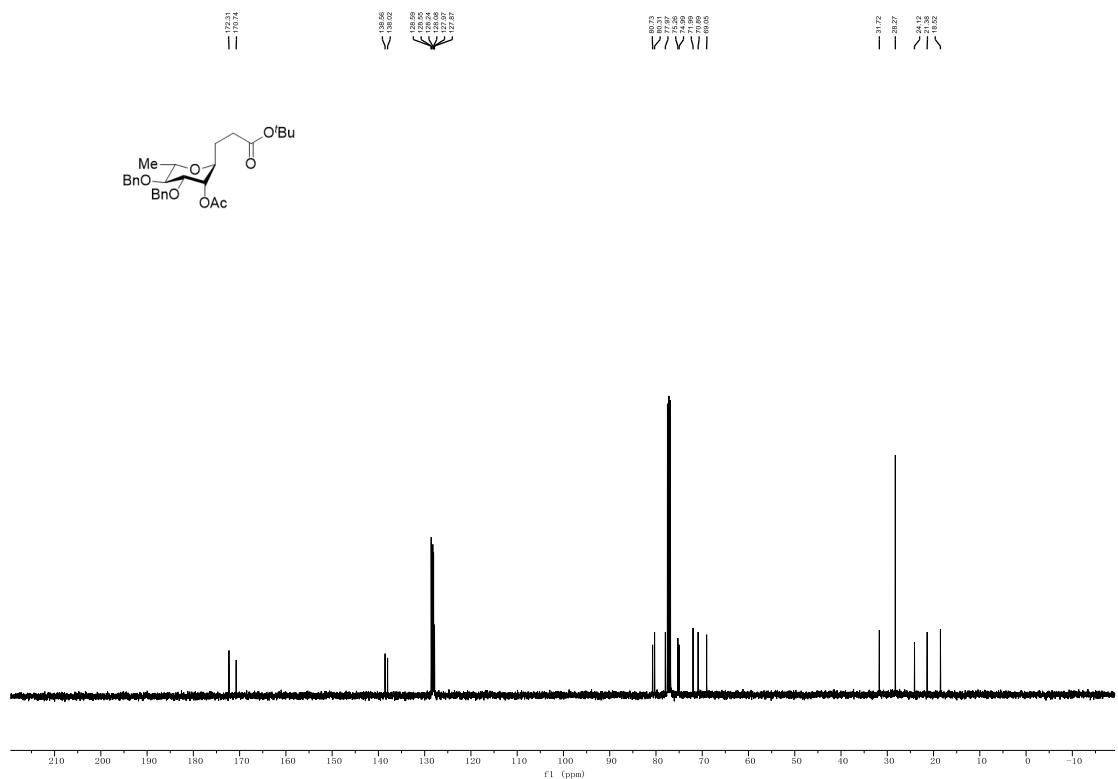


Figure S91. COSY spectrum of compound 5z

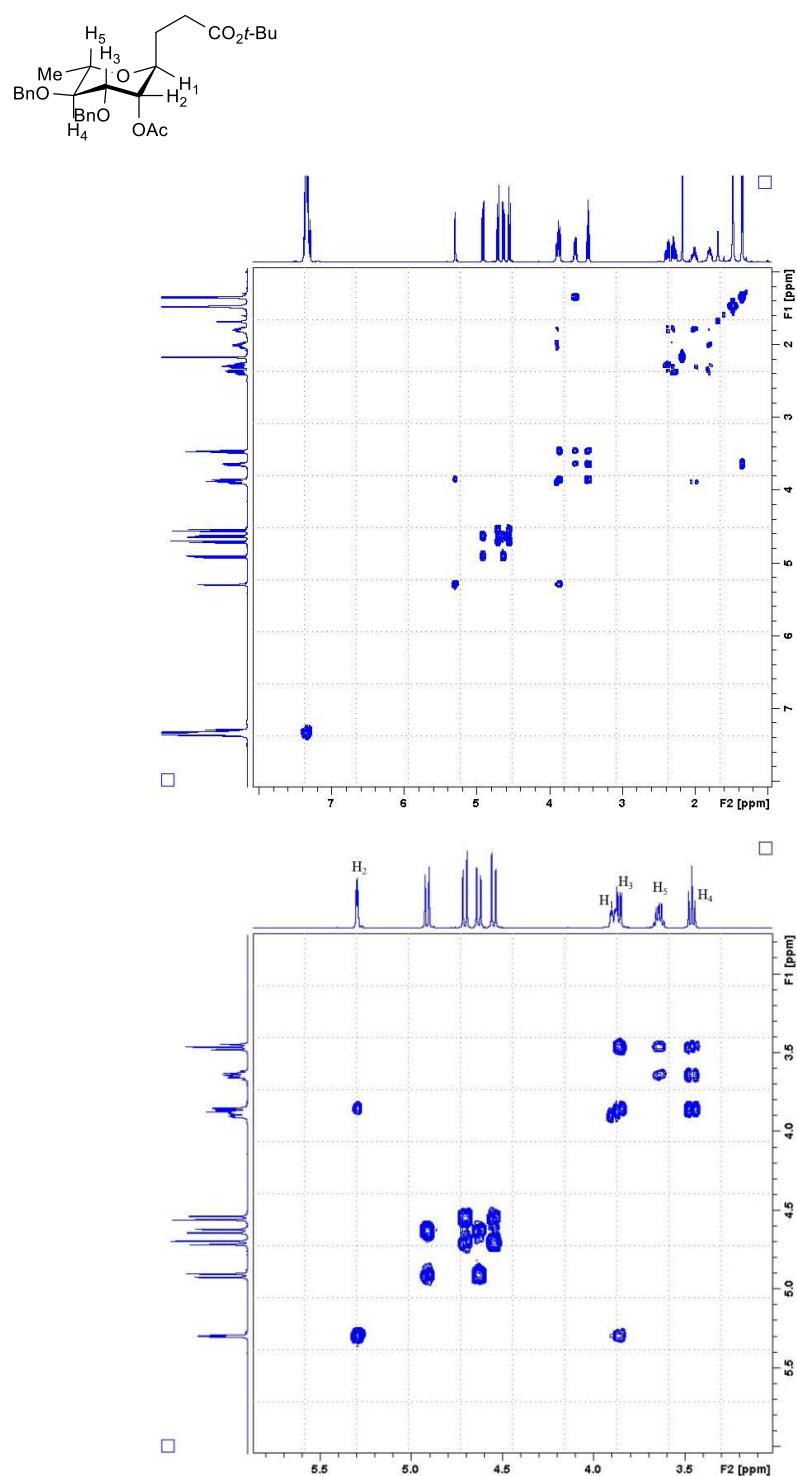


Figure S92. NOE spectrum of compound 5z

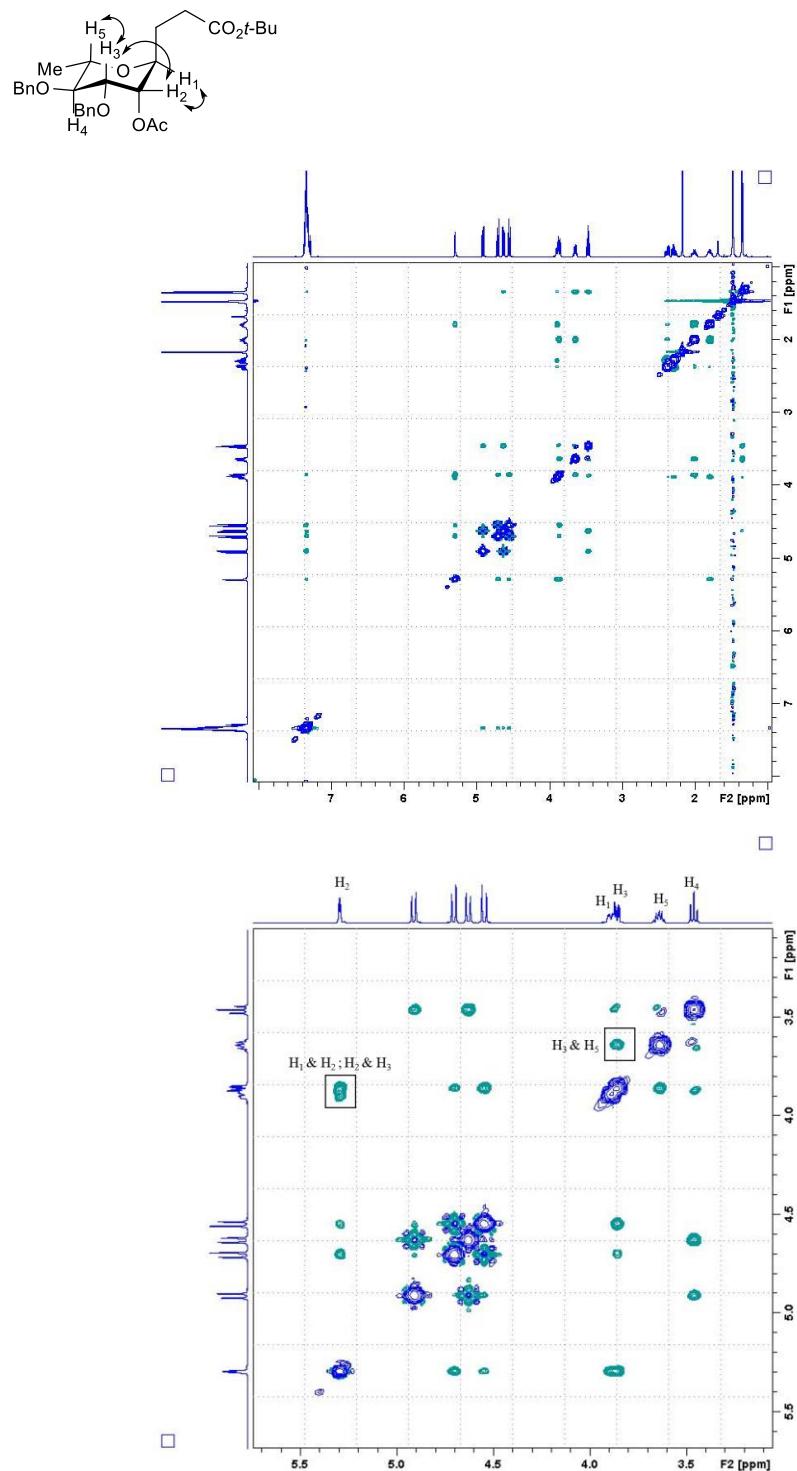


Figure S93. ^1H NMR spectrum of compound 5aa

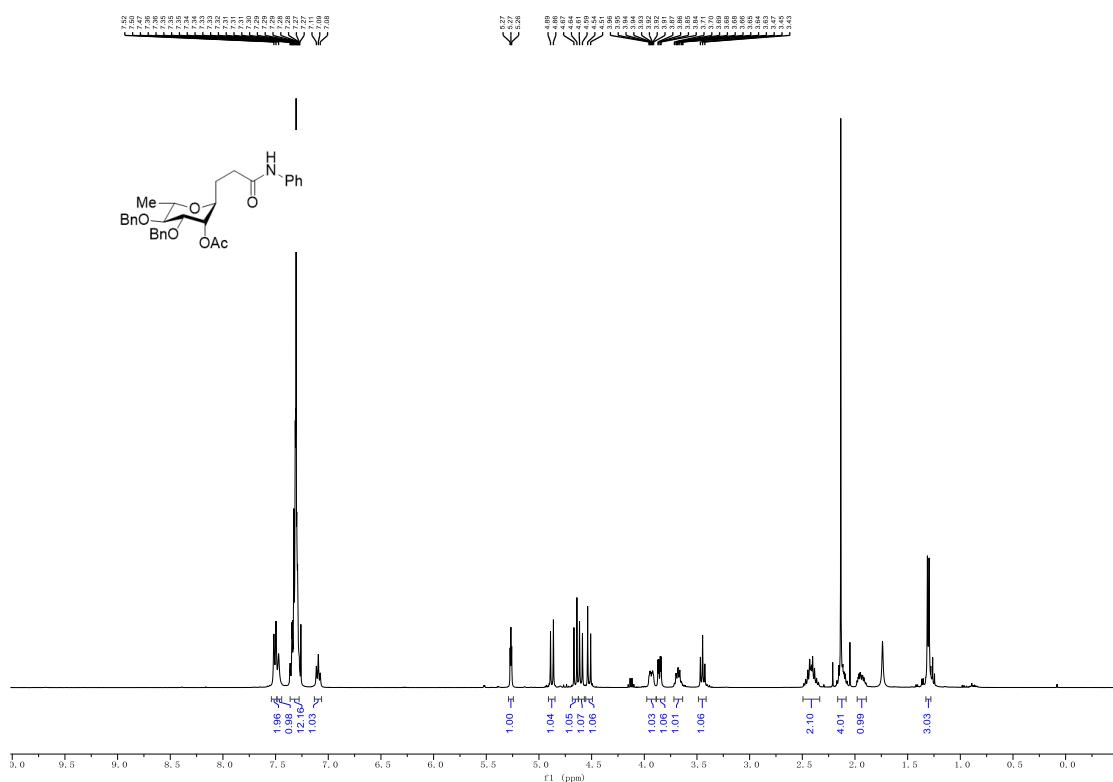


Figure S94. ^{13}C NMR spectrum of compound 5aa

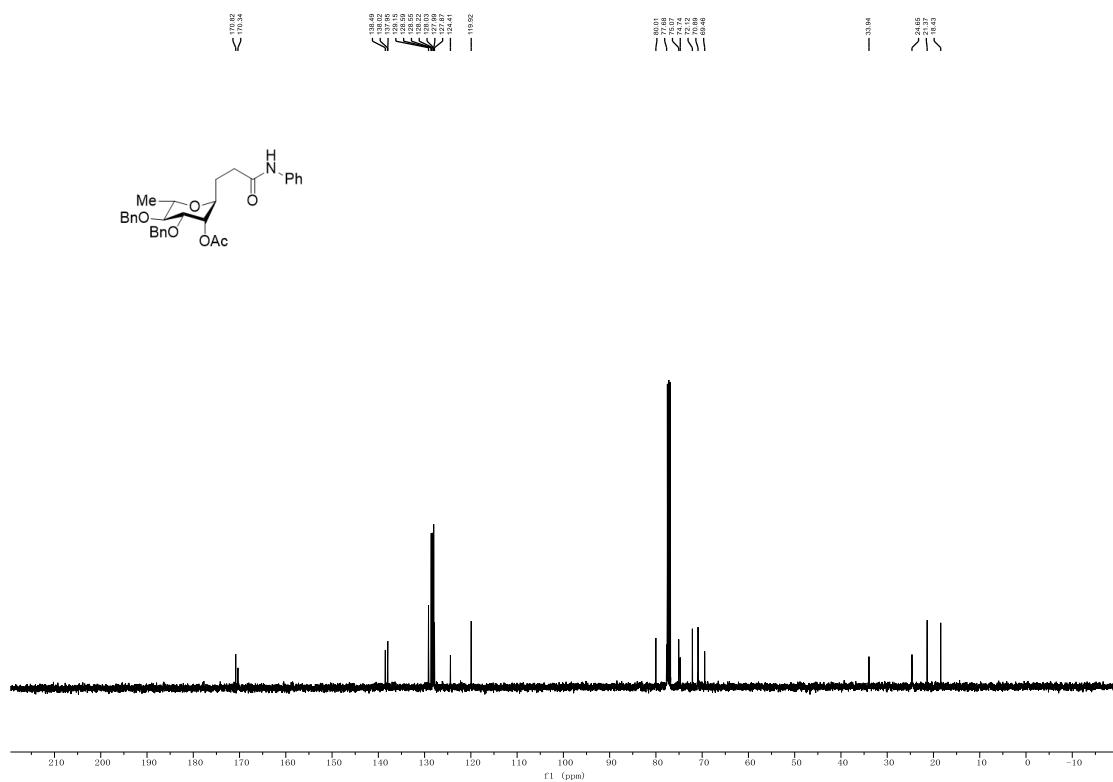


Figure S95. ^1H NMR spectrum of compound 5ab

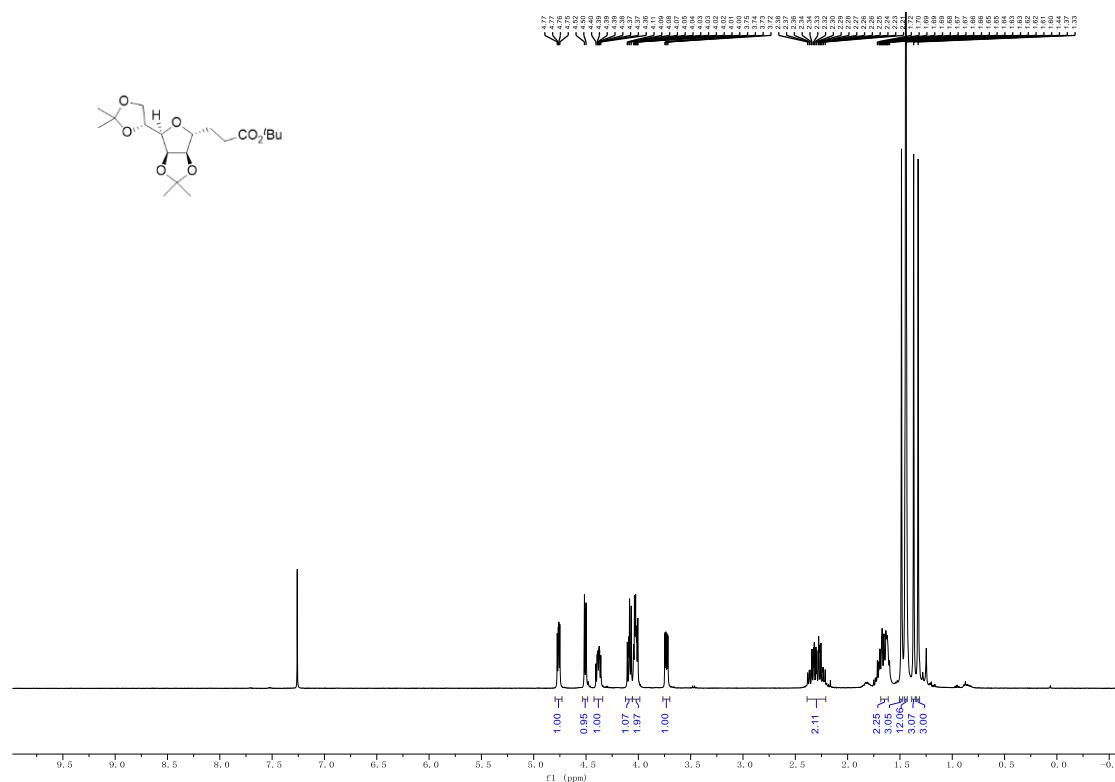


Figure S96. ^{13}C NMR spectrum of compound 5ab

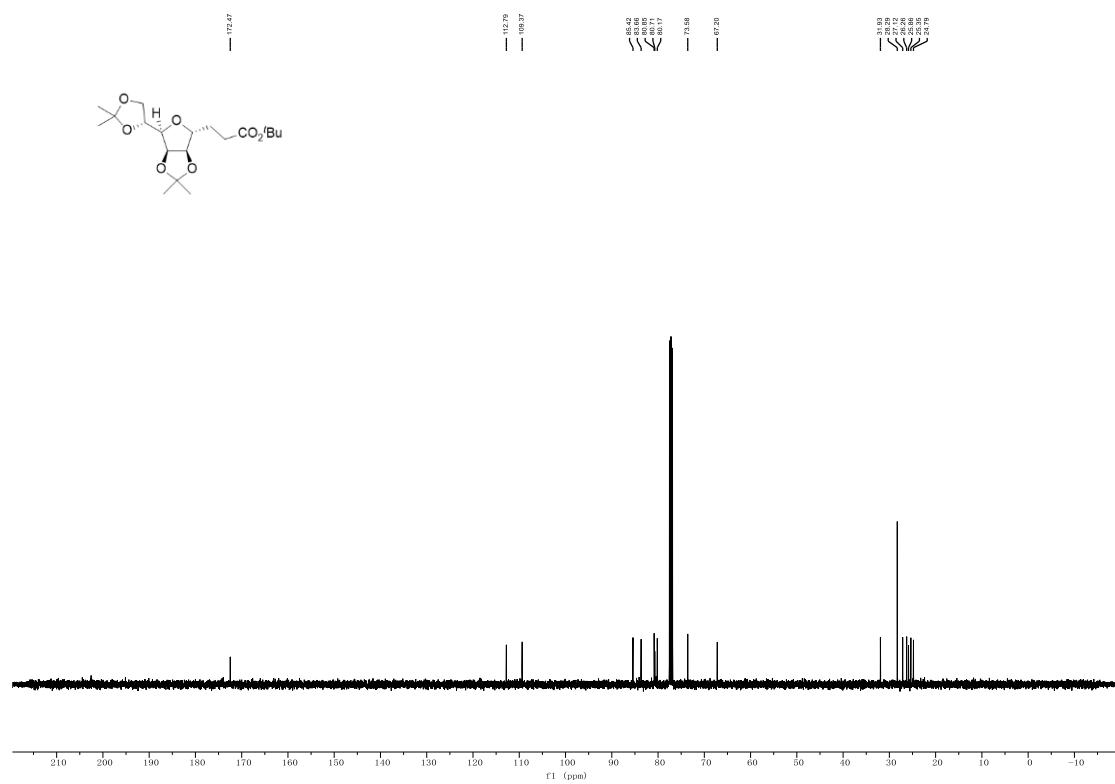


Figure S97. ^1H NMR spectrum of compound 5ac

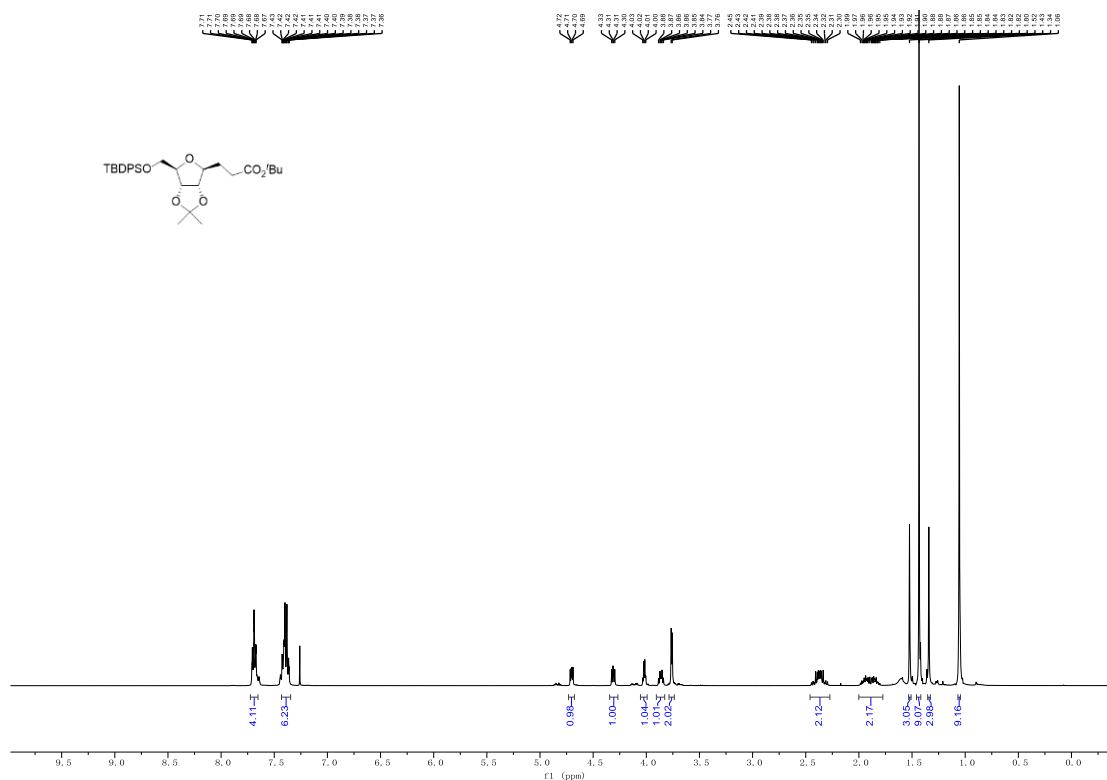


Figure S98. ^{13}C NMR spectrum of compound 5ac

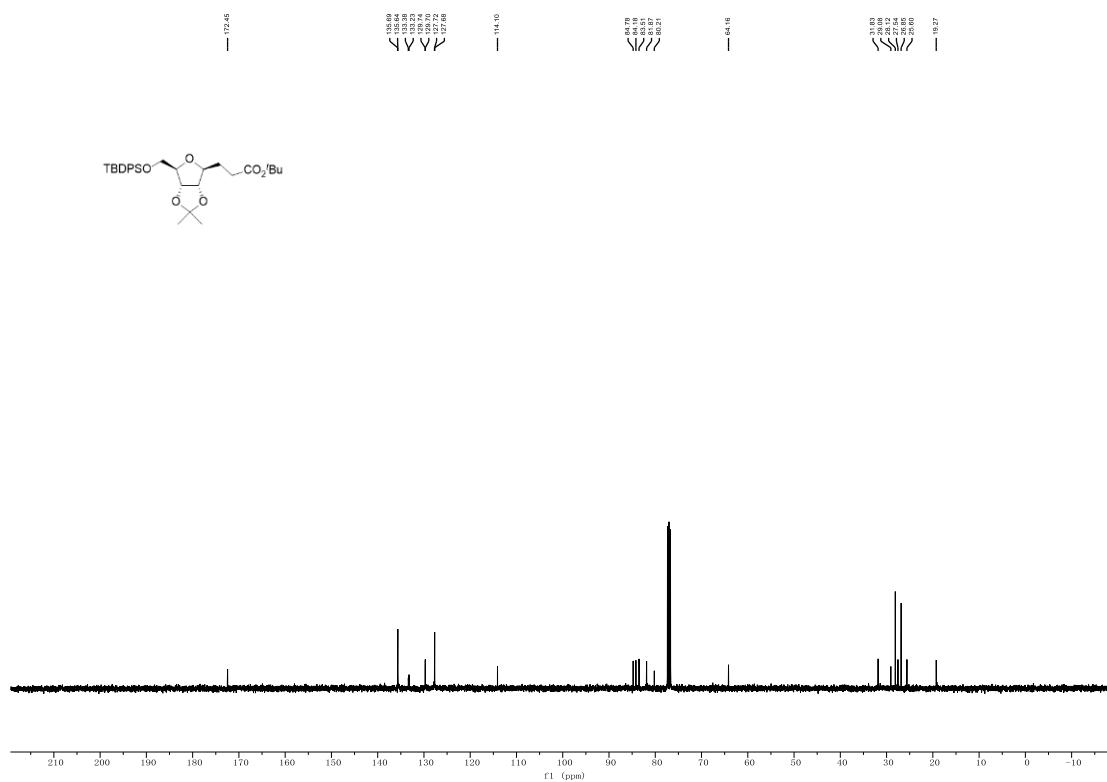


Figure S99. ^1H NMR spectrum of compound 5ad

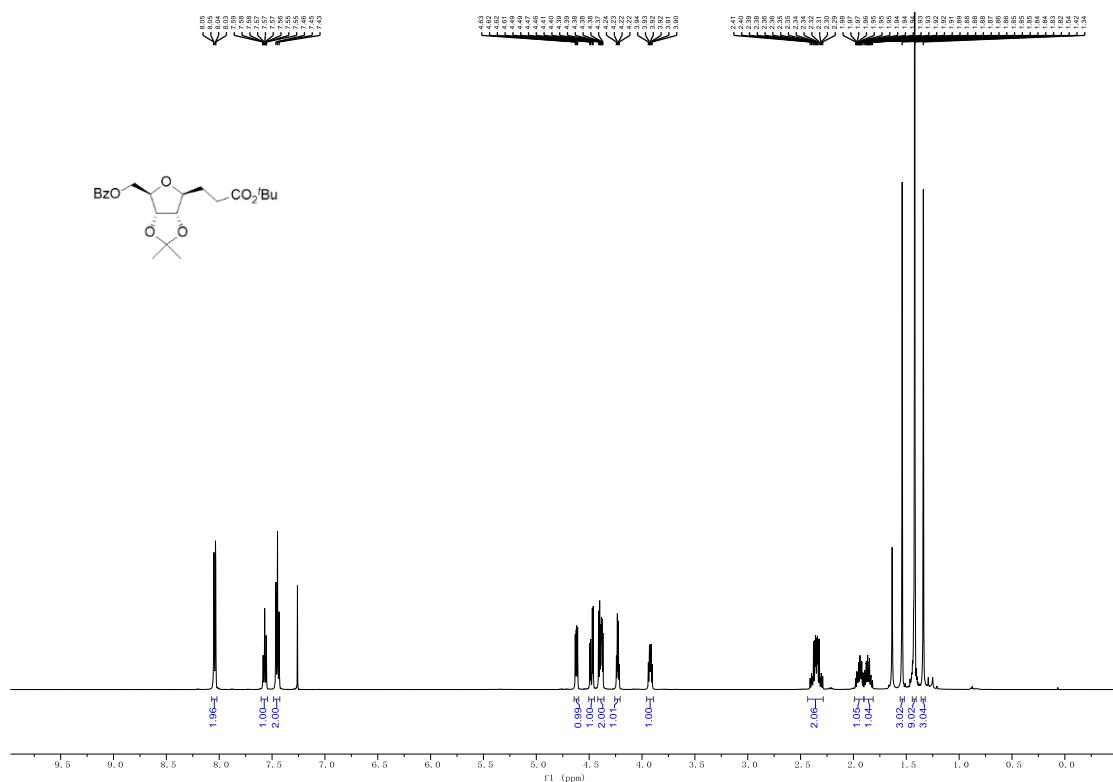


Figure S100. ^{13}C NMR spectrum of compound 5ad

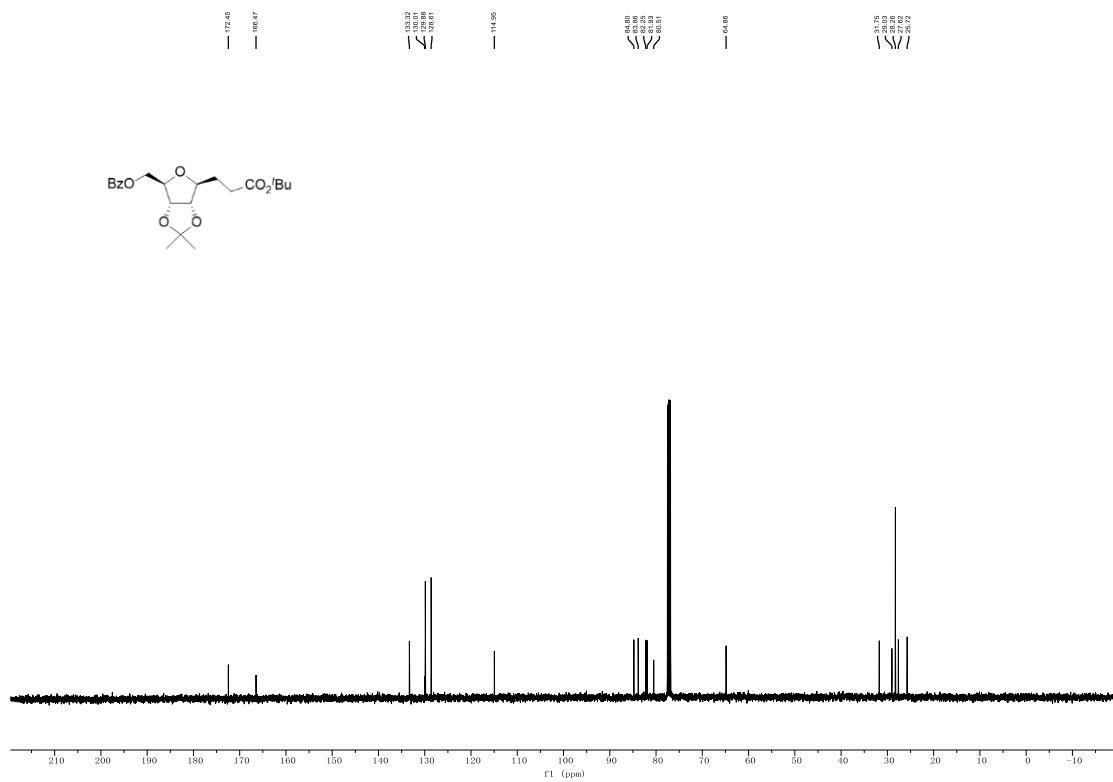


Figure S101. ^1H NMR spectrum of compound 5ae

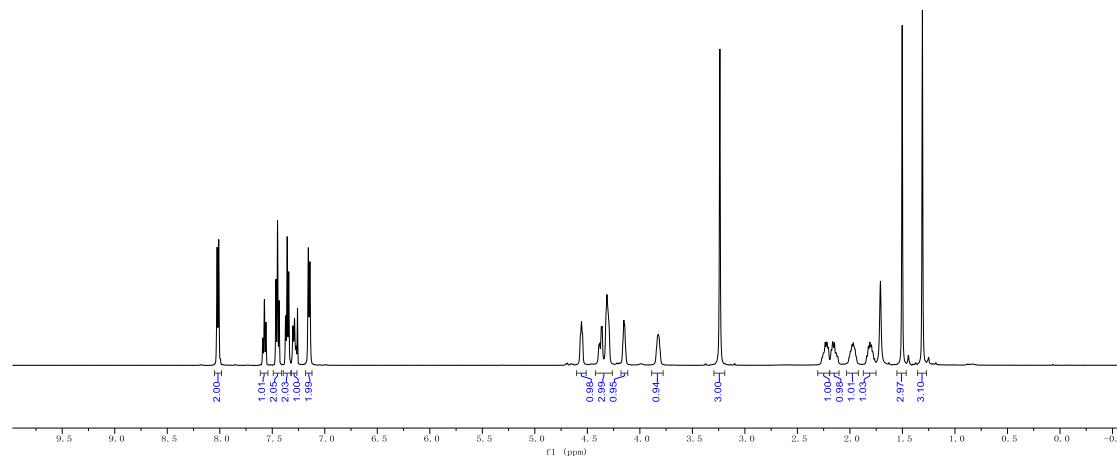
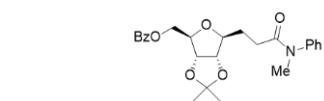


Figure S102. ^{13}C NMR spectrum of compound 5ae

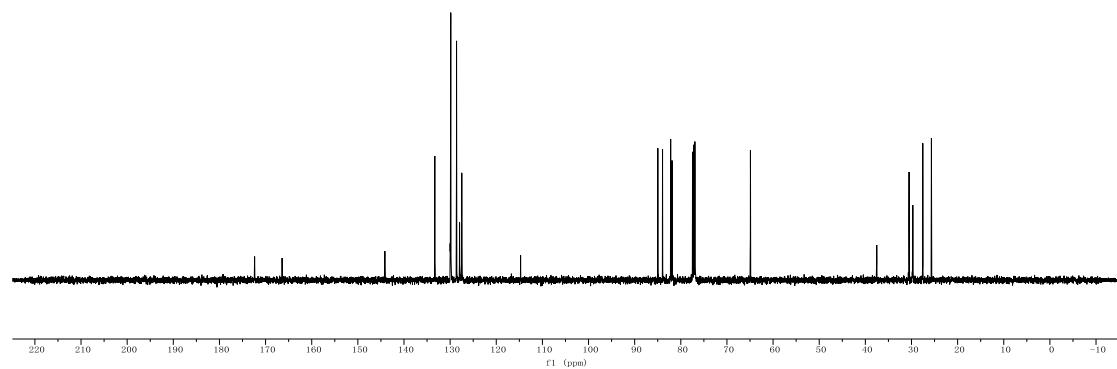
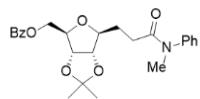


Figure S103. ^1H NMR spectrum of compound 5af

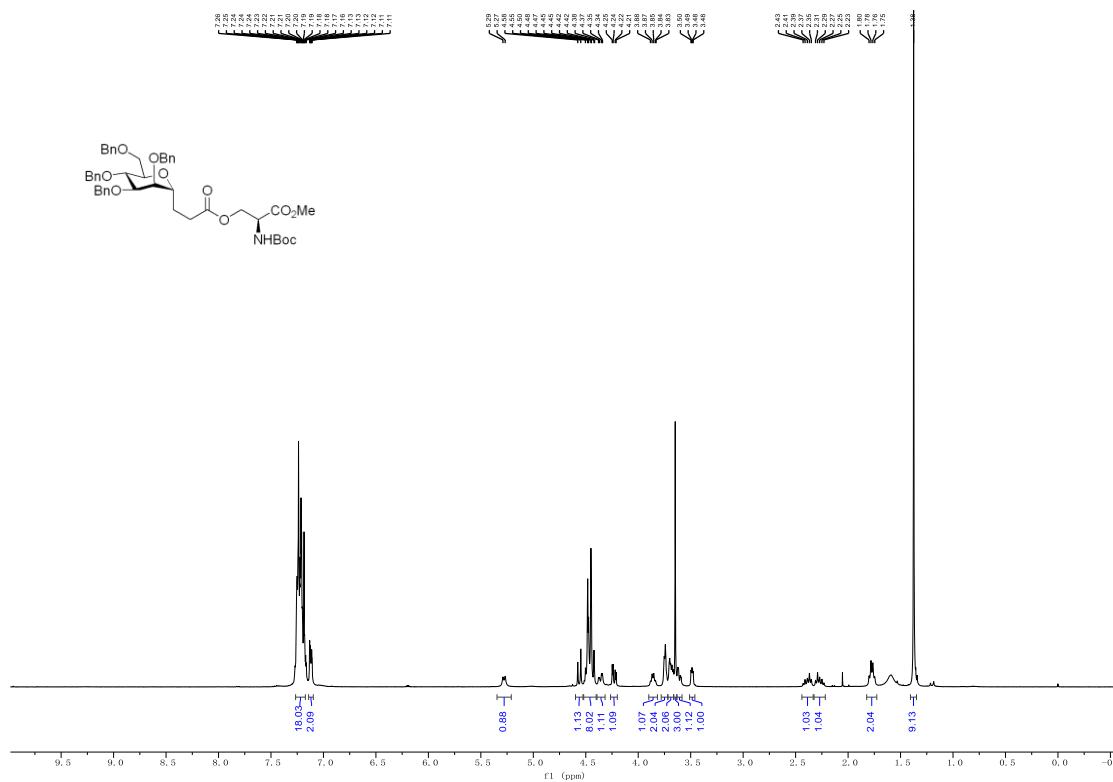


Figure S104. ^{13}C NMR spectrum of compound 5af

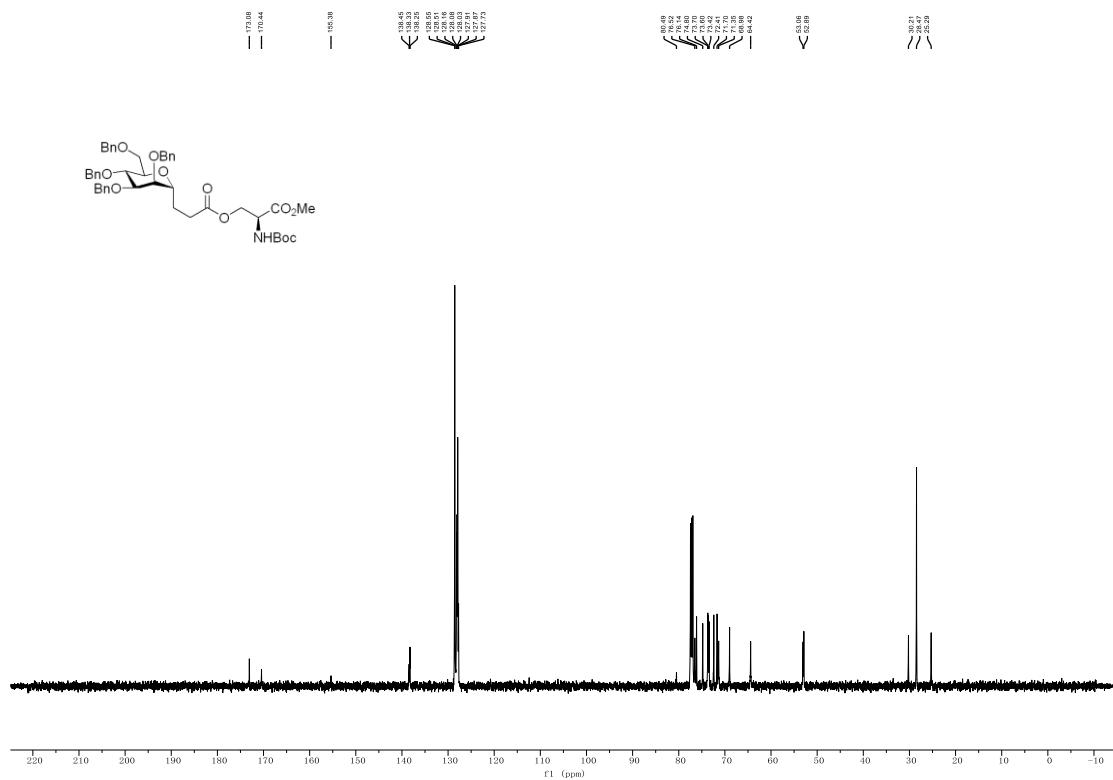


Figure S105. ^1H NMR spectrum of compound 5ag

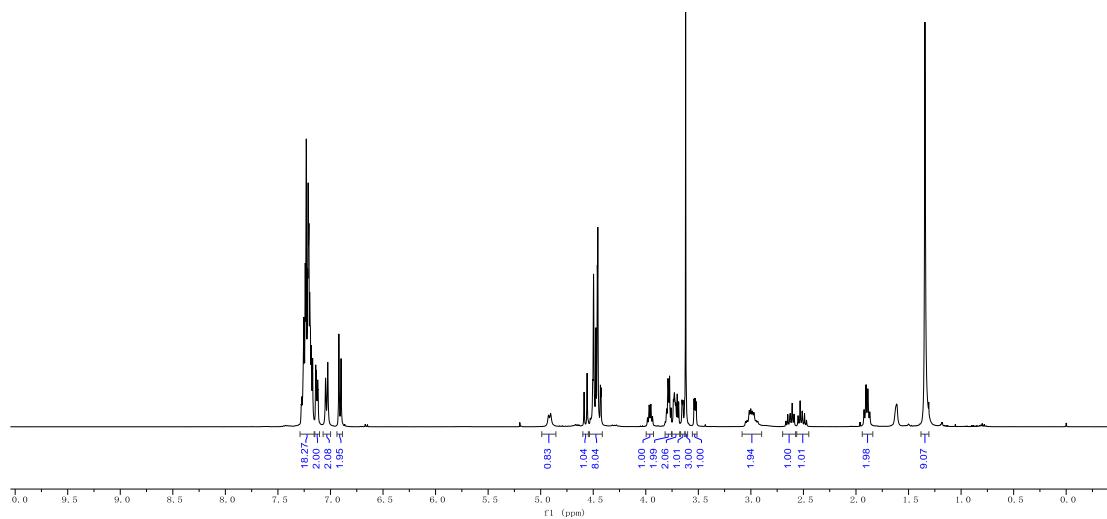
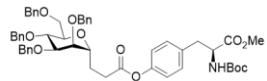


Figure S106. ^{13}C NMR spectrum of compound 5ag

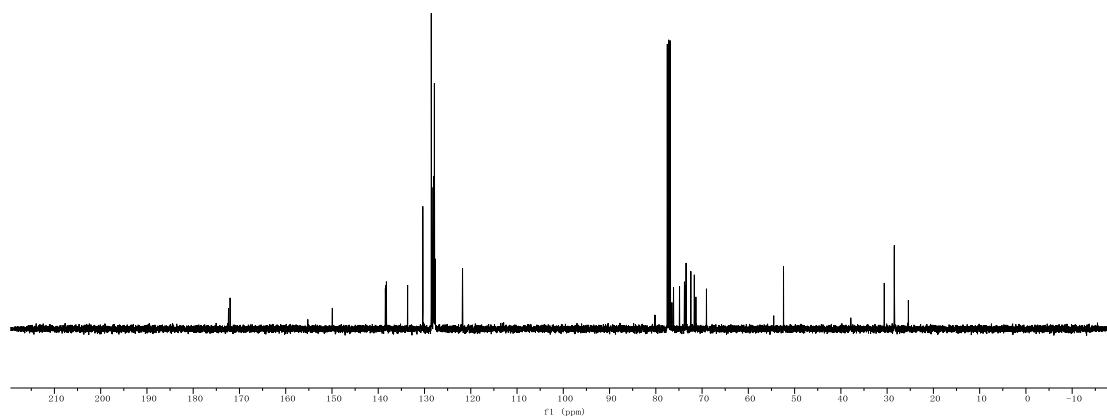
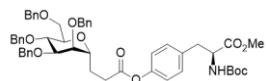


Figure S107. ^1H NMR spectrum of compound 5ah

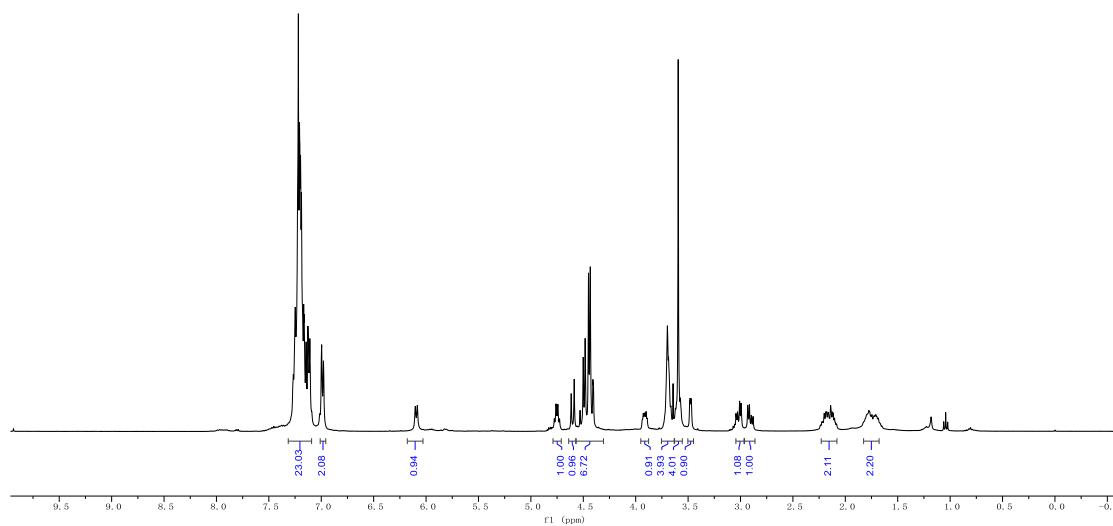
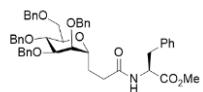


Figure S108. ^{13}C NMR spectrum of compound 5ah

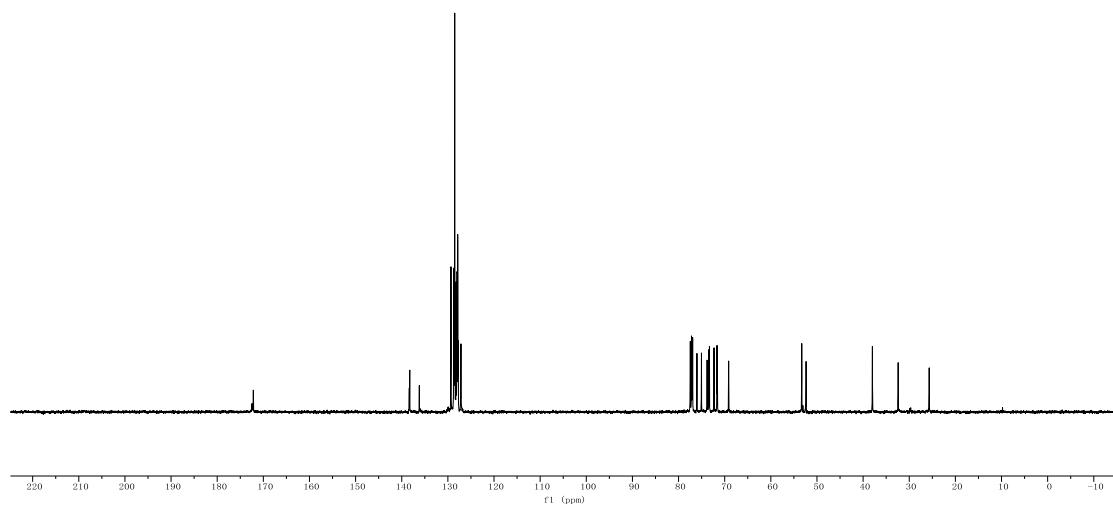
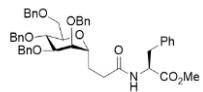


Figure S109. ^1H NMR spectrum of compound 5ai

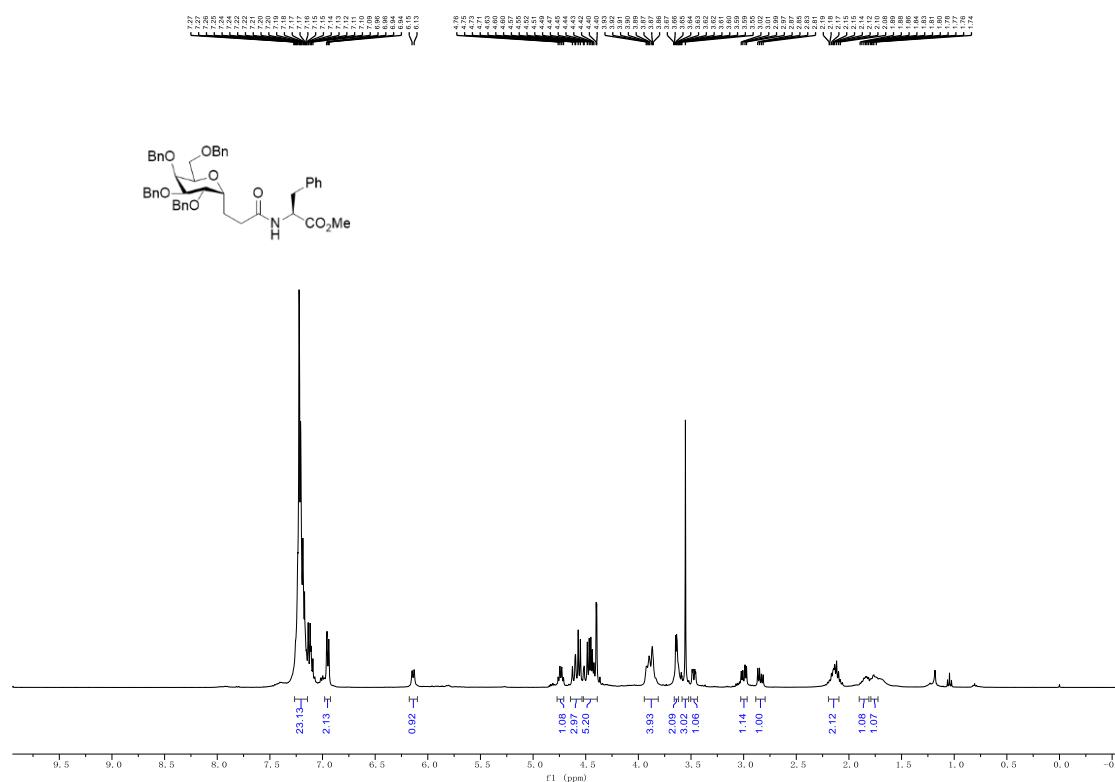


Figure S110. ^{13}C NMR spectrum of compound 5ai

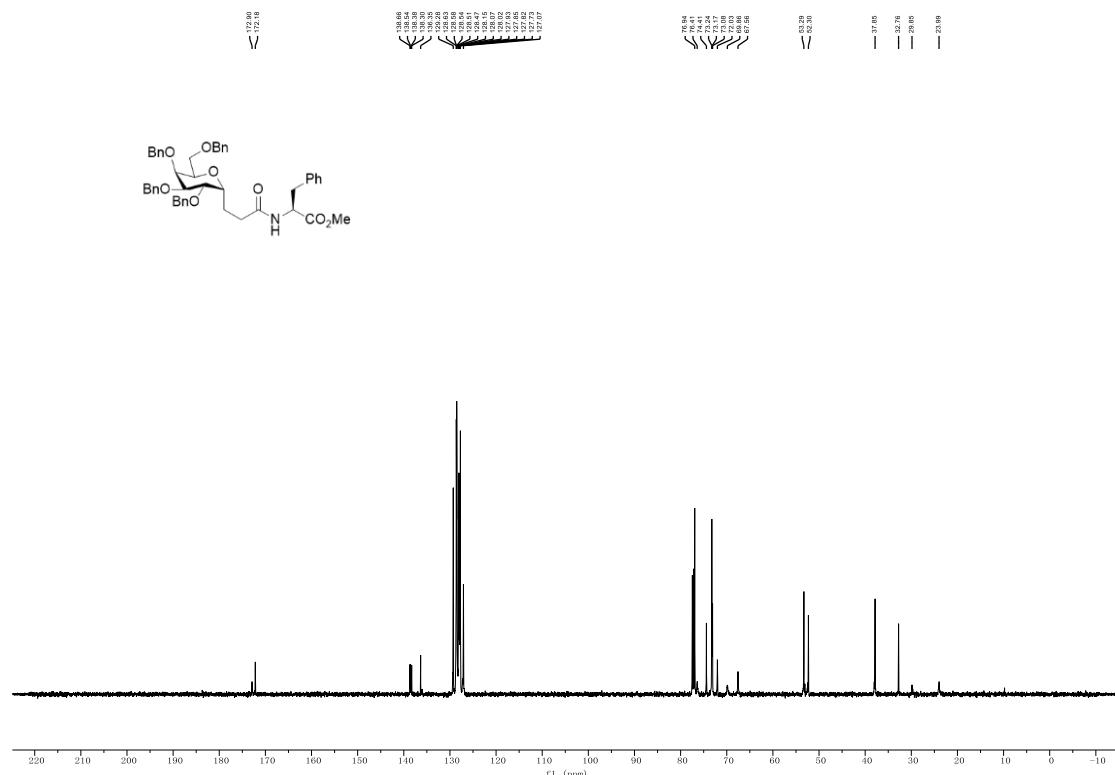


Figure S111. ^1H NMR spectrum of compound 5aj

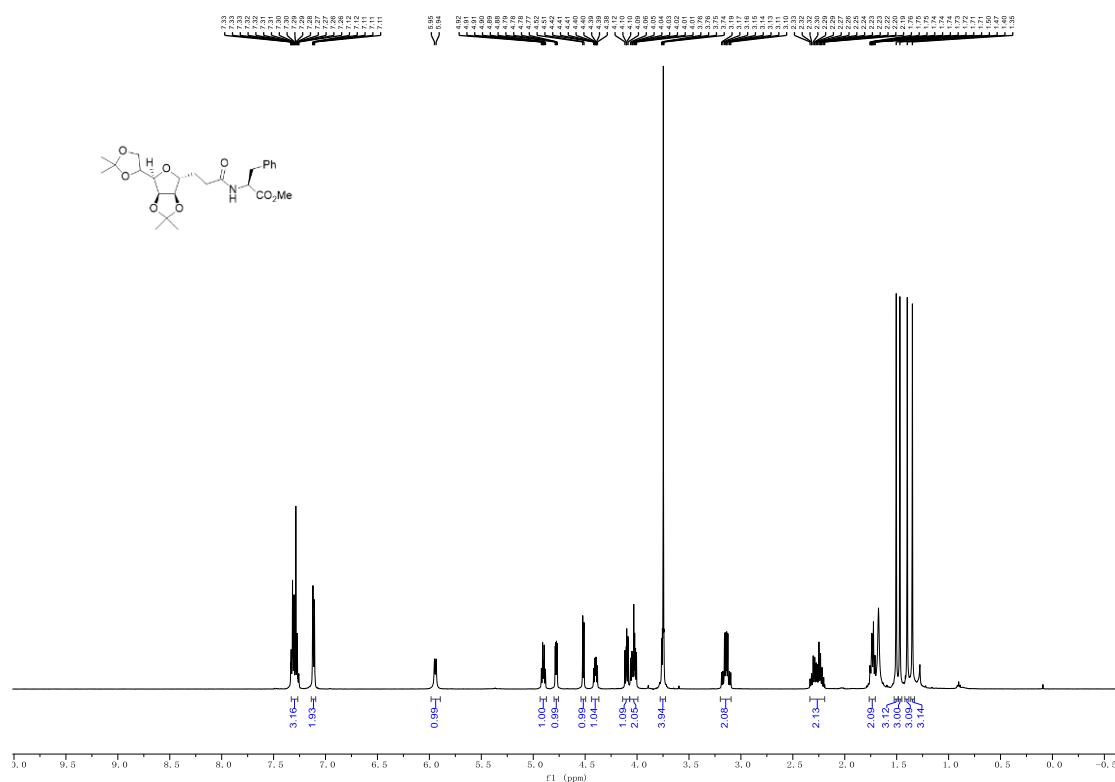


Figure S112. ^{13}C NMR spectrum of compound 5aj

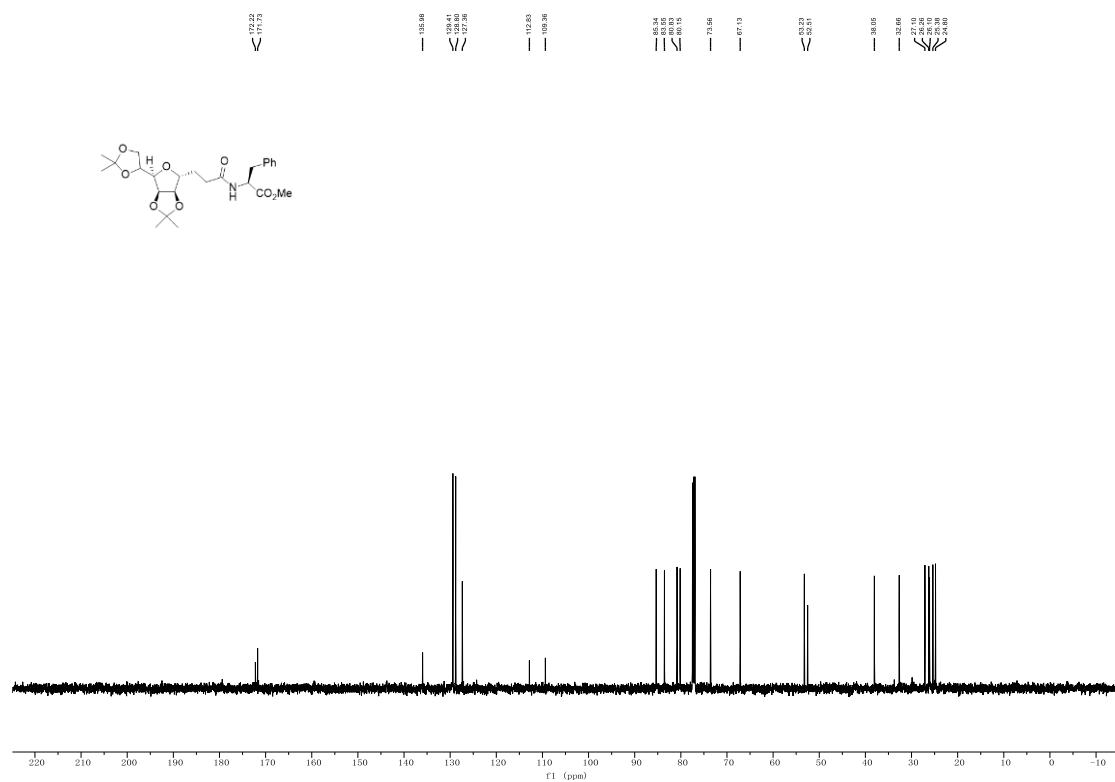


Figure S113. ^1H NMR spectrum of compound 5ak

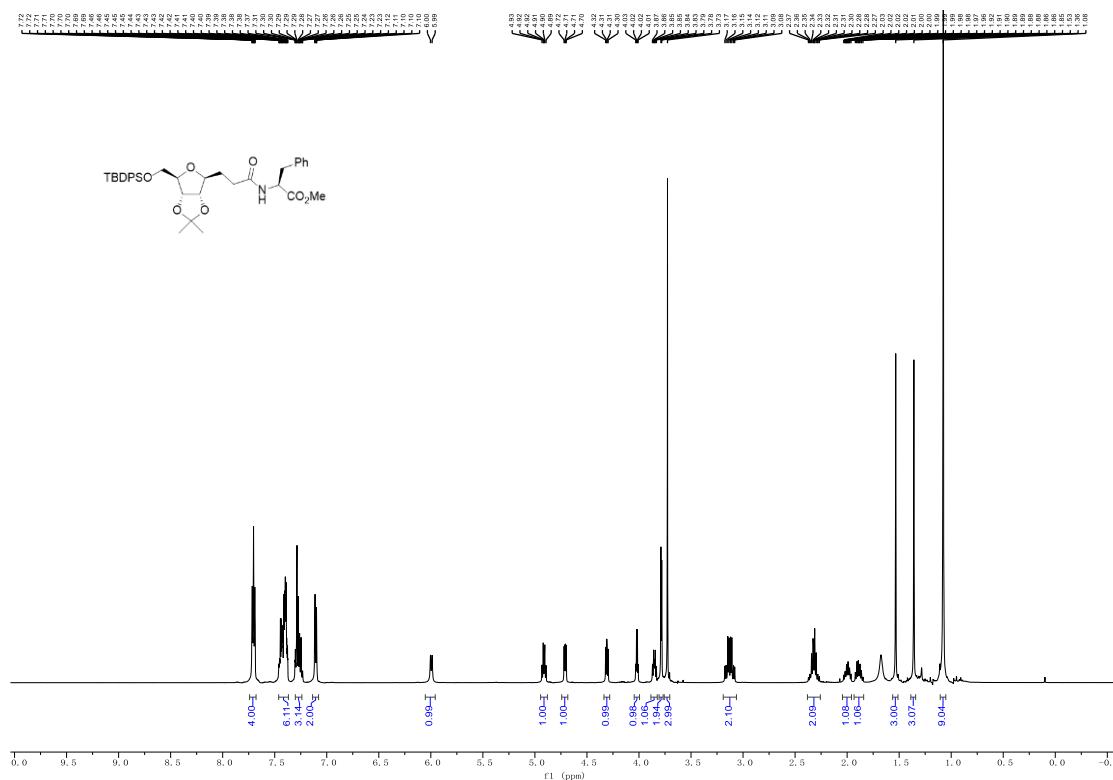


Figure S114. ^{13}C NMR spectrum of compound 5ak

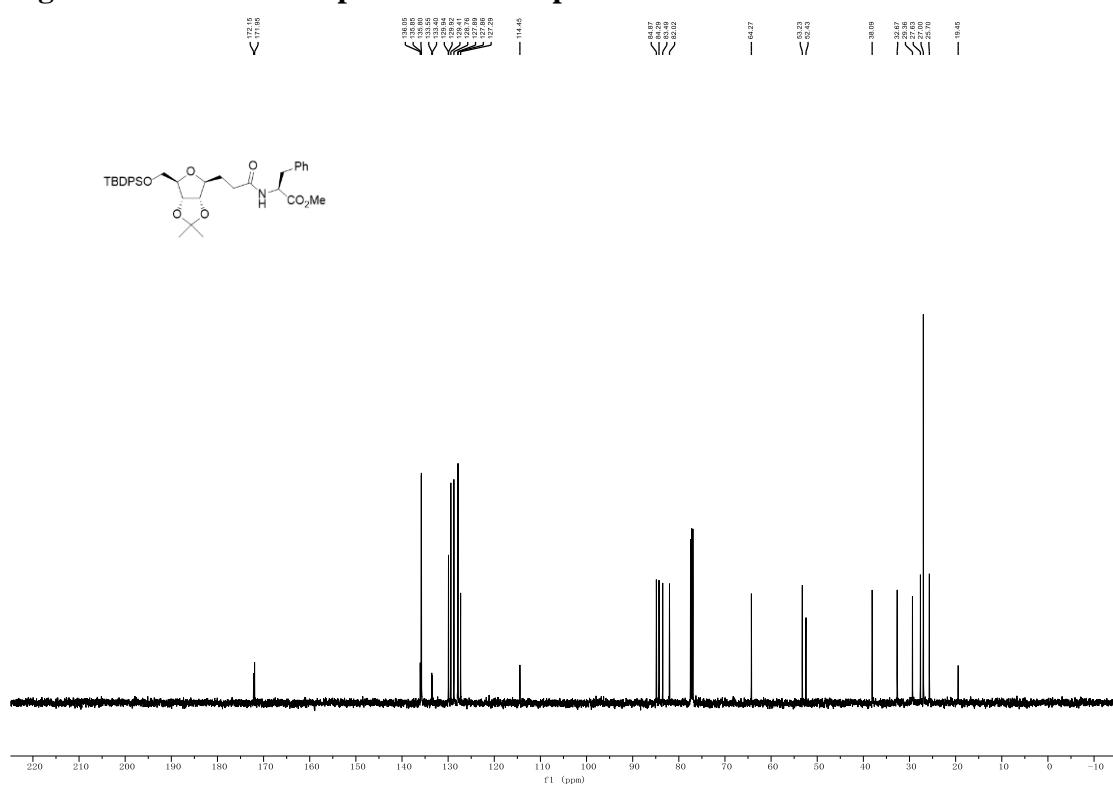


Figure S115. COSY spectrum of compound 5ak

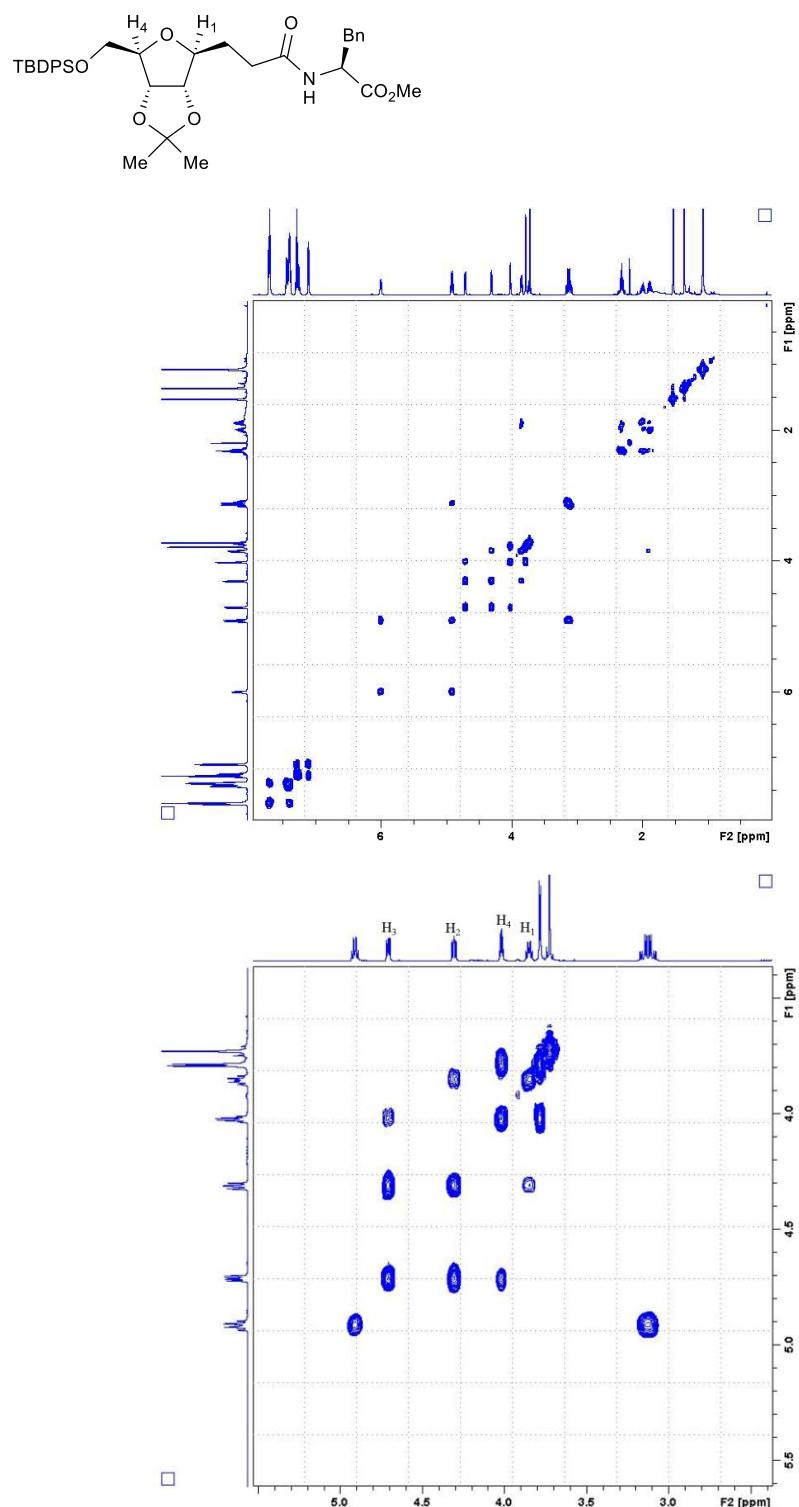


Figure S116. NOE spectrum of compound 5ak

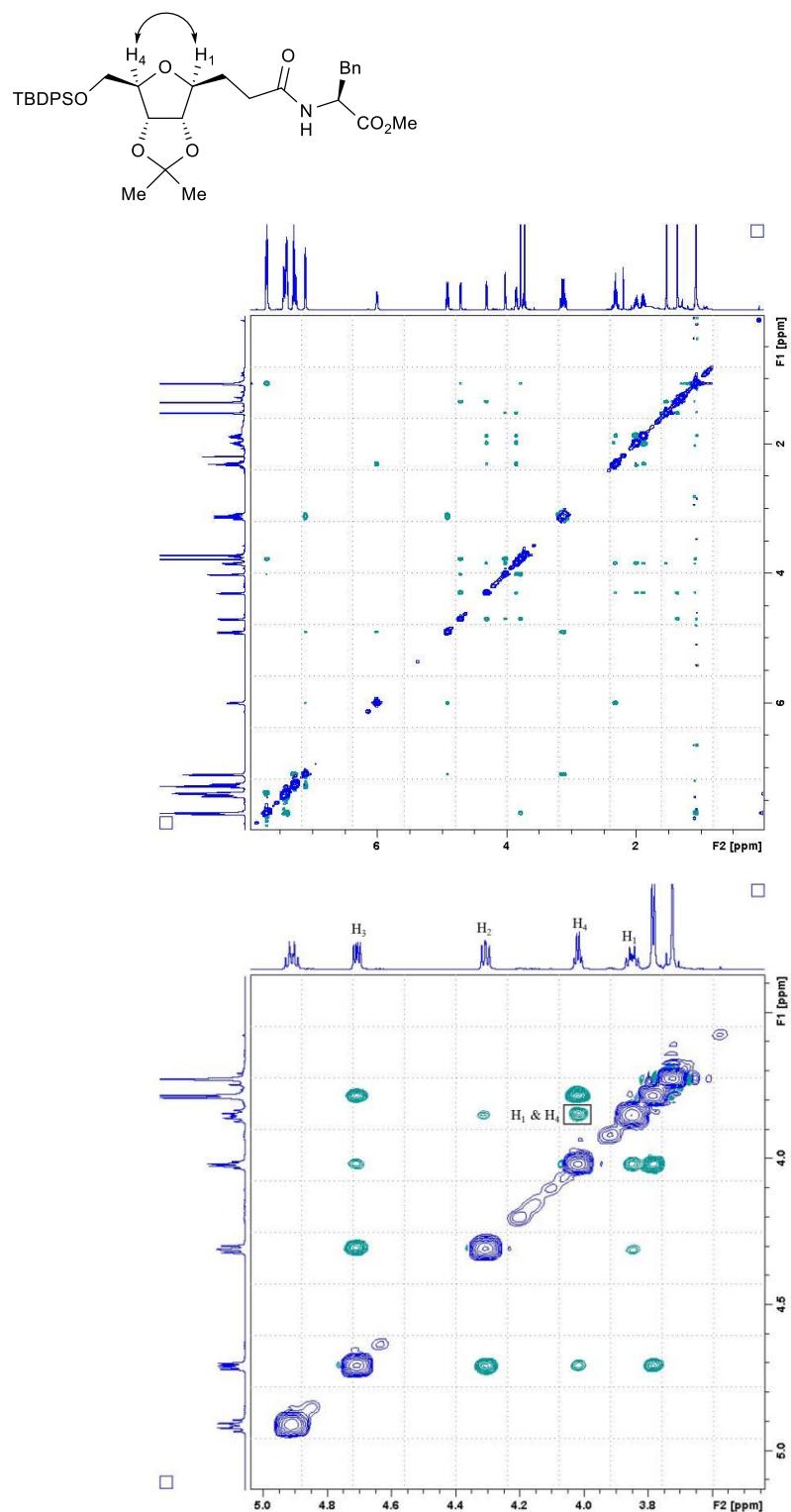


Figure S117. ^1H NMR spectrum of compound 5al

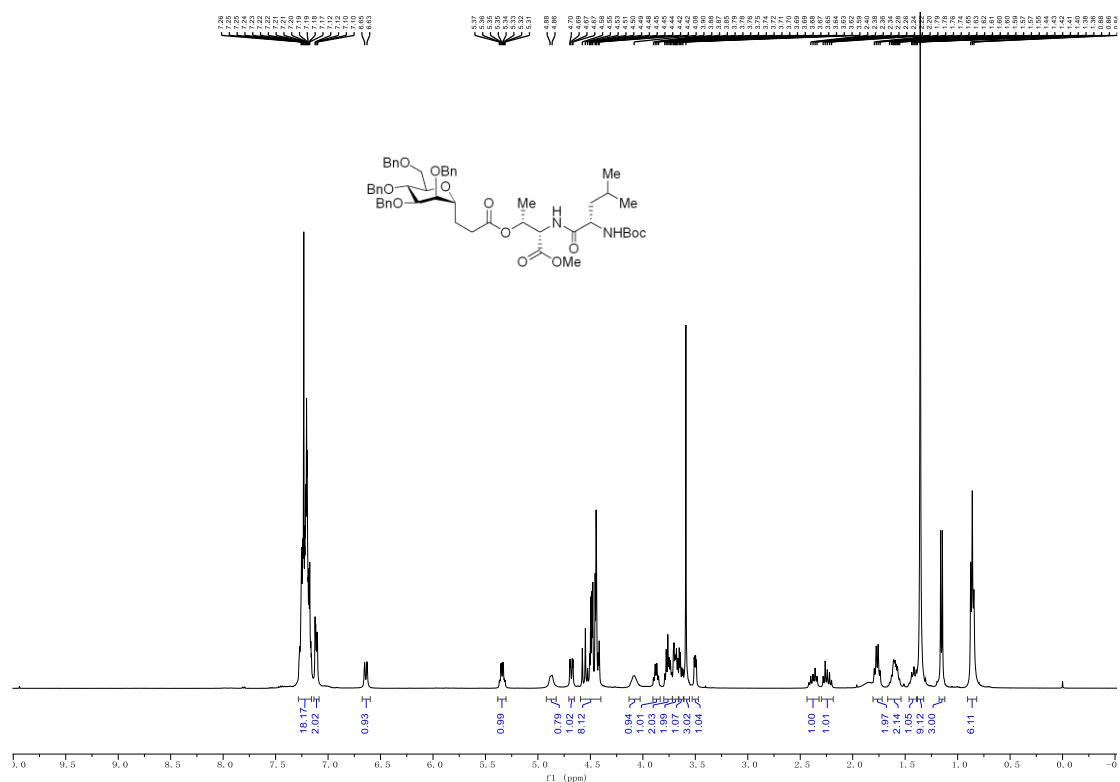


Figure S118. ^{13}C NMR spectrum of compound 5al

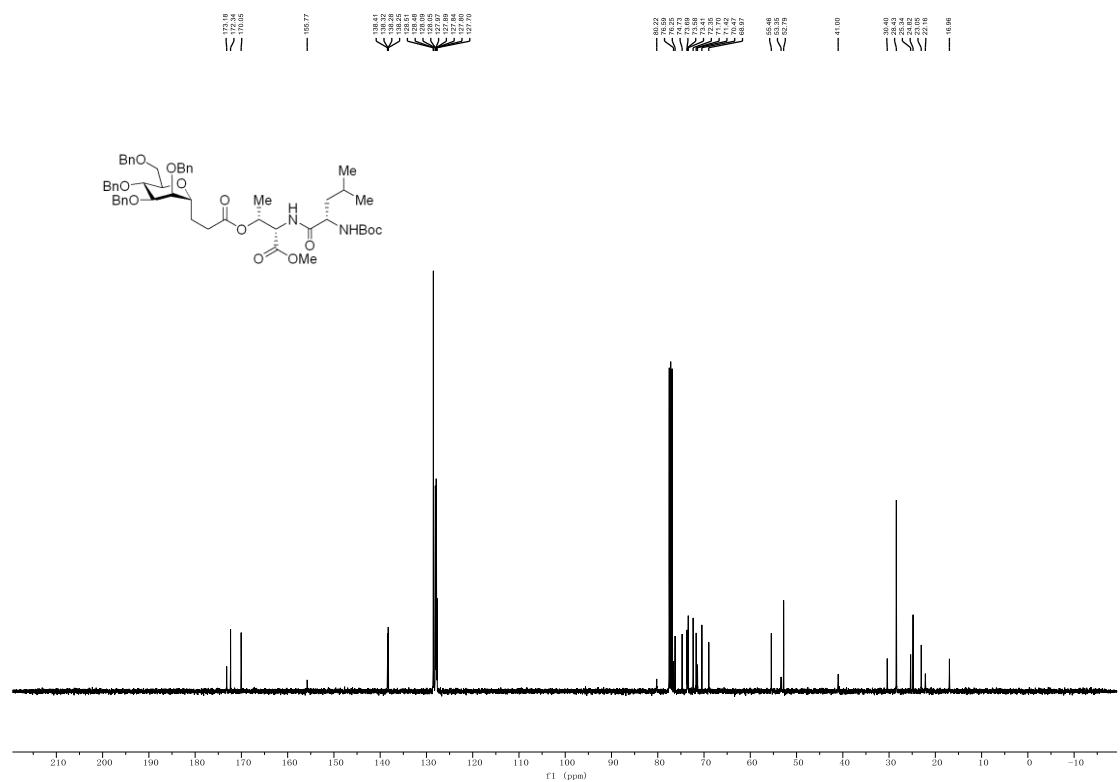


Figure S119. ^1H NMR spectrum of compound 5am

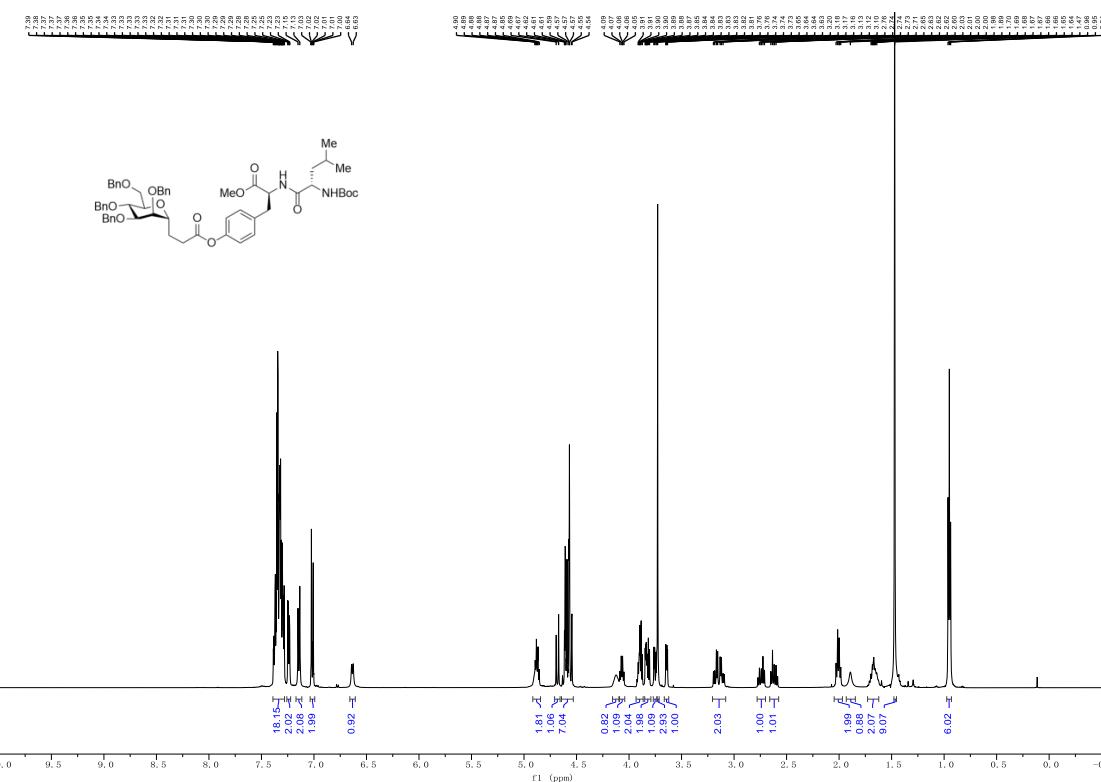


Figure S120. ^{13}C NMR spectrum of compound 5am

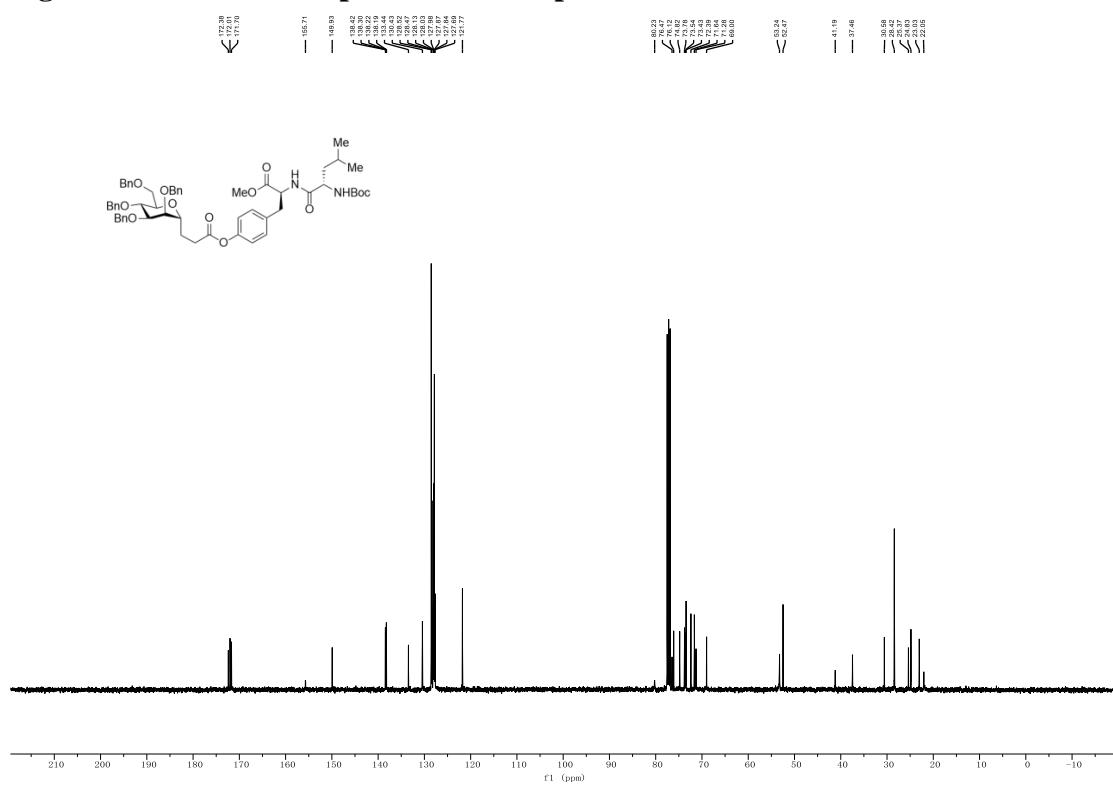


Figure S121. ^1H NMR spectrum of compound 5an

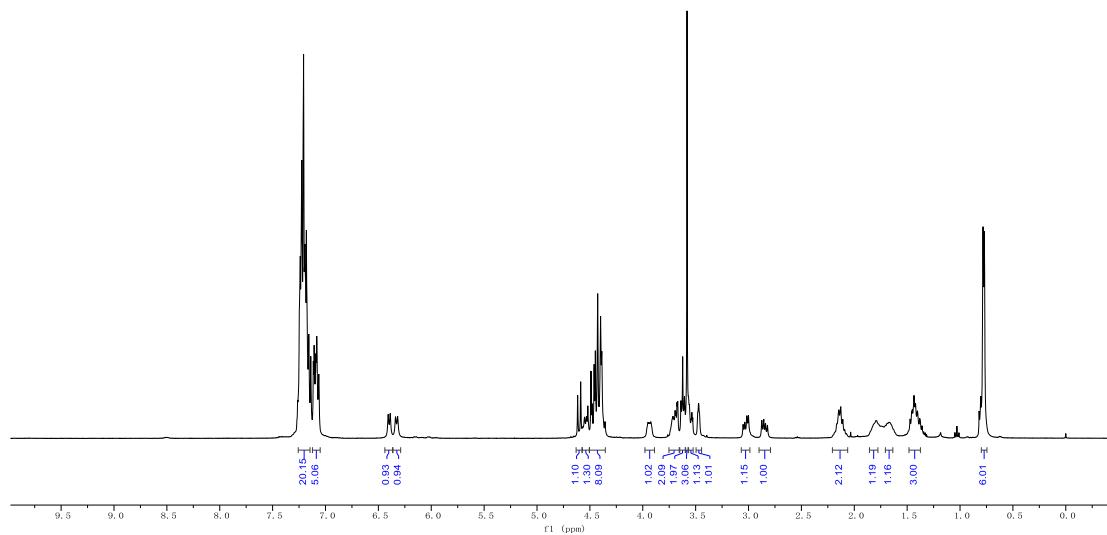
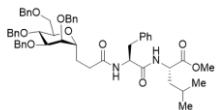


Figure S122. ^{13}C NMR spectrum of compound 5an

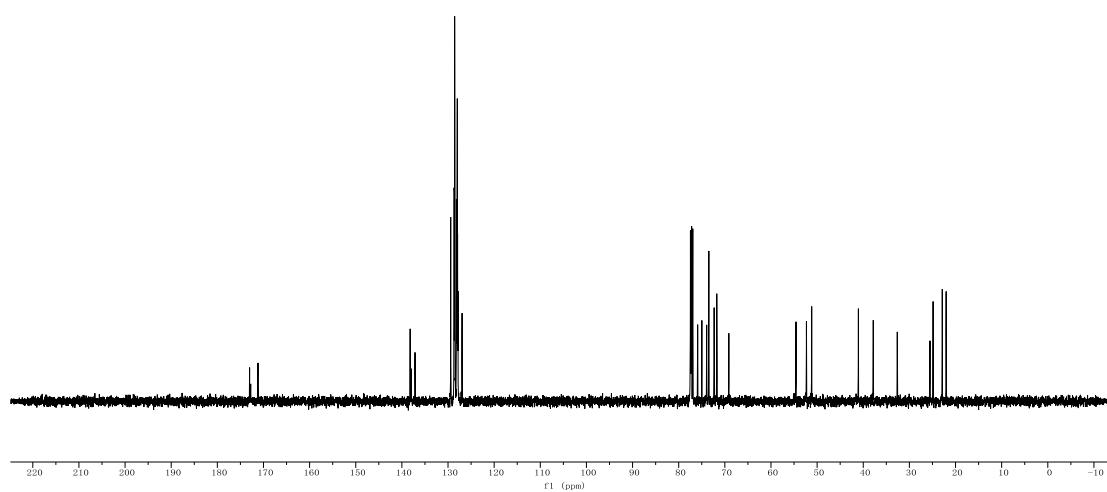
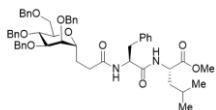
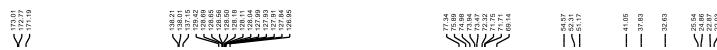


Figure S123. ^1H NMR spectrum of compound 5ao

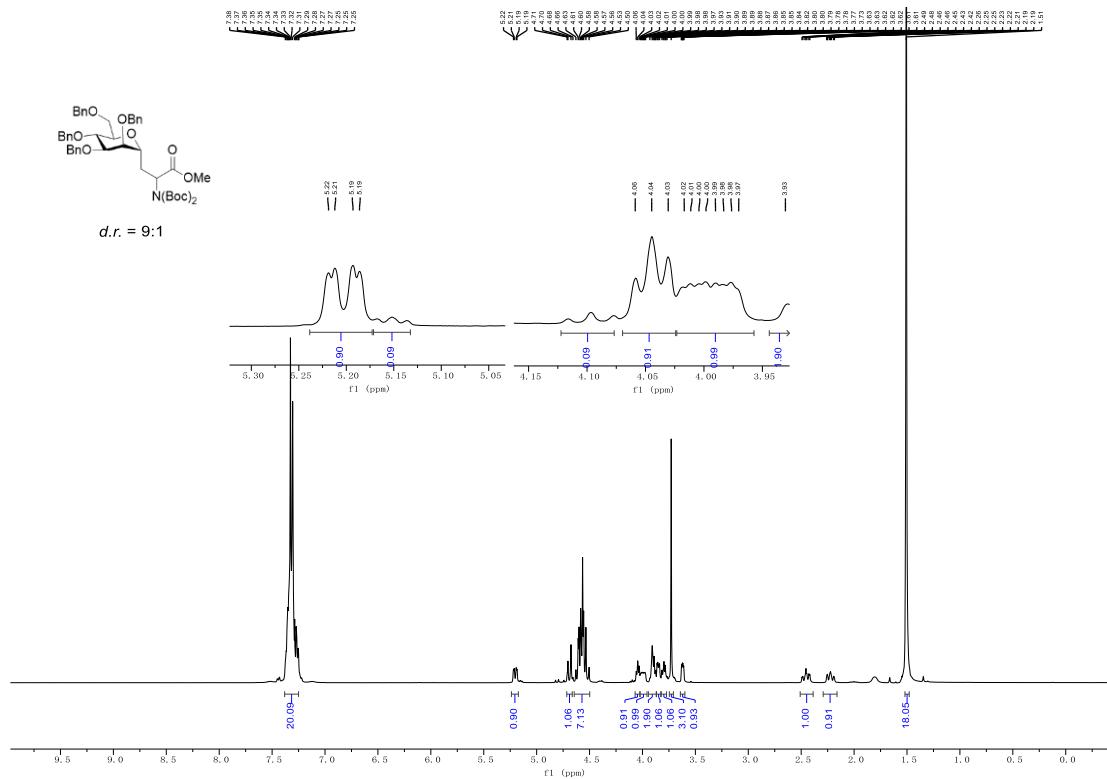


Figure S124. ^{13}C NMR spectrum of compound 5ao

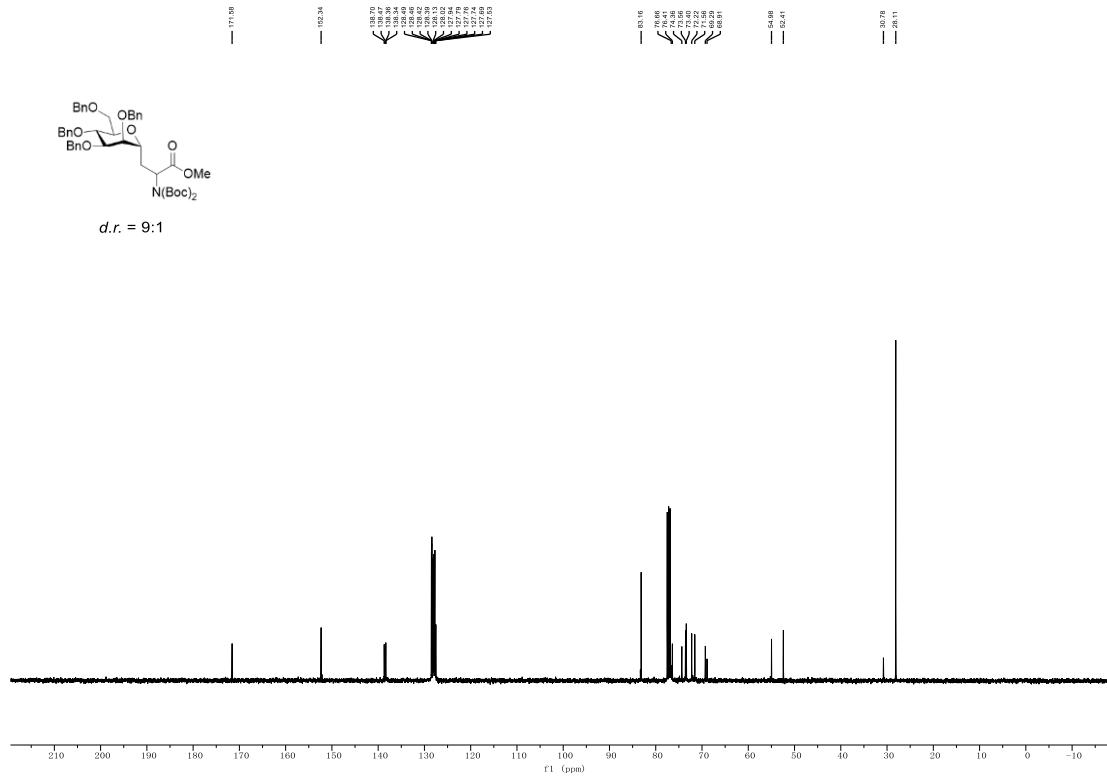


Figure S125. ^1H NMR spectrum of compound 5ap

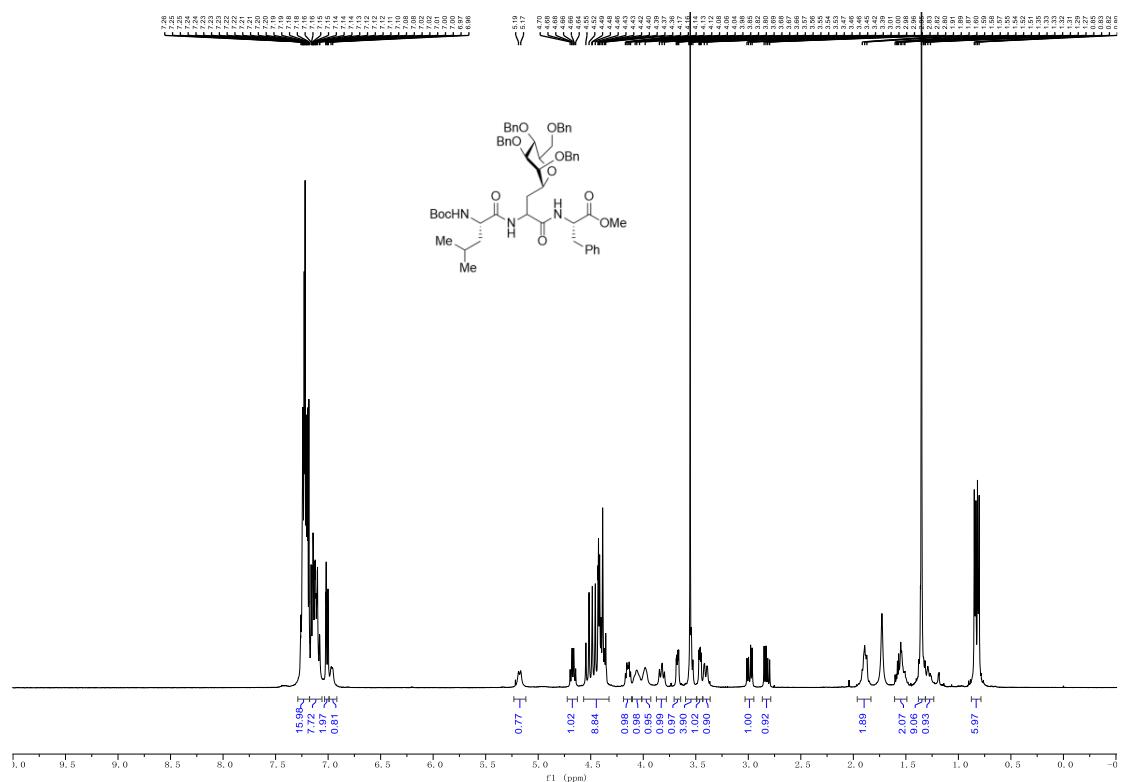


Figure S126. ^{13}C NMR spectrum of compound 5ap

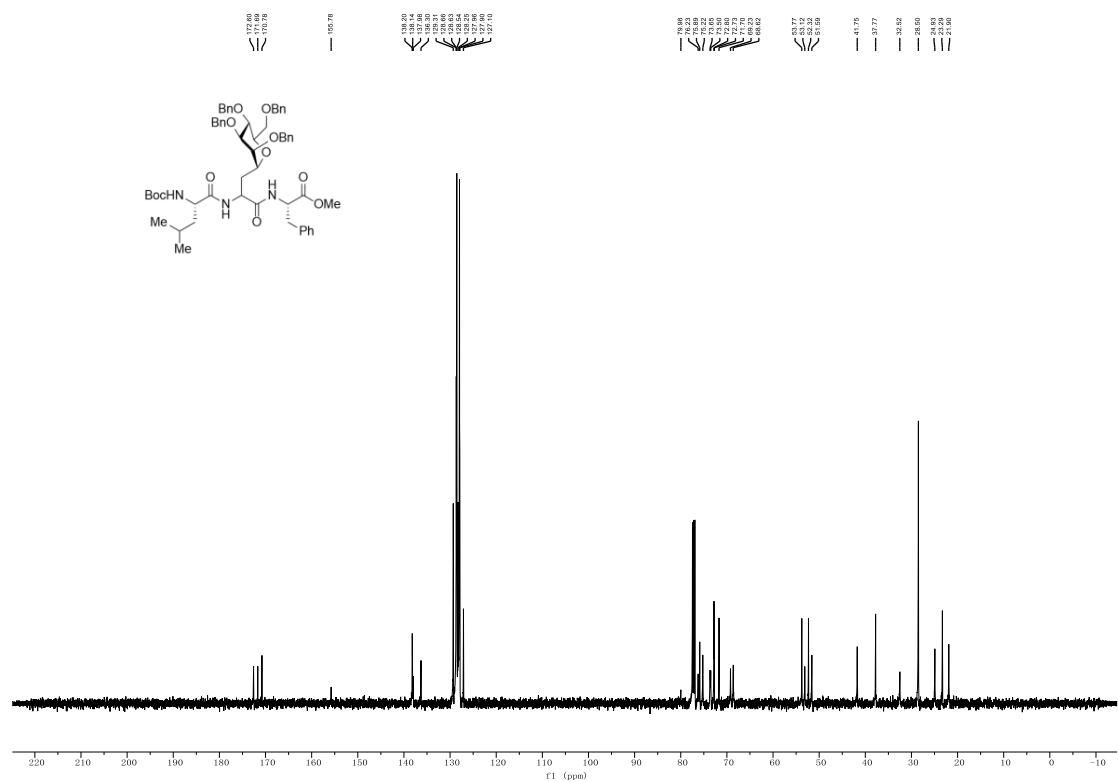


Figure S127. ^1H NMR spectrum of compound 5ap'

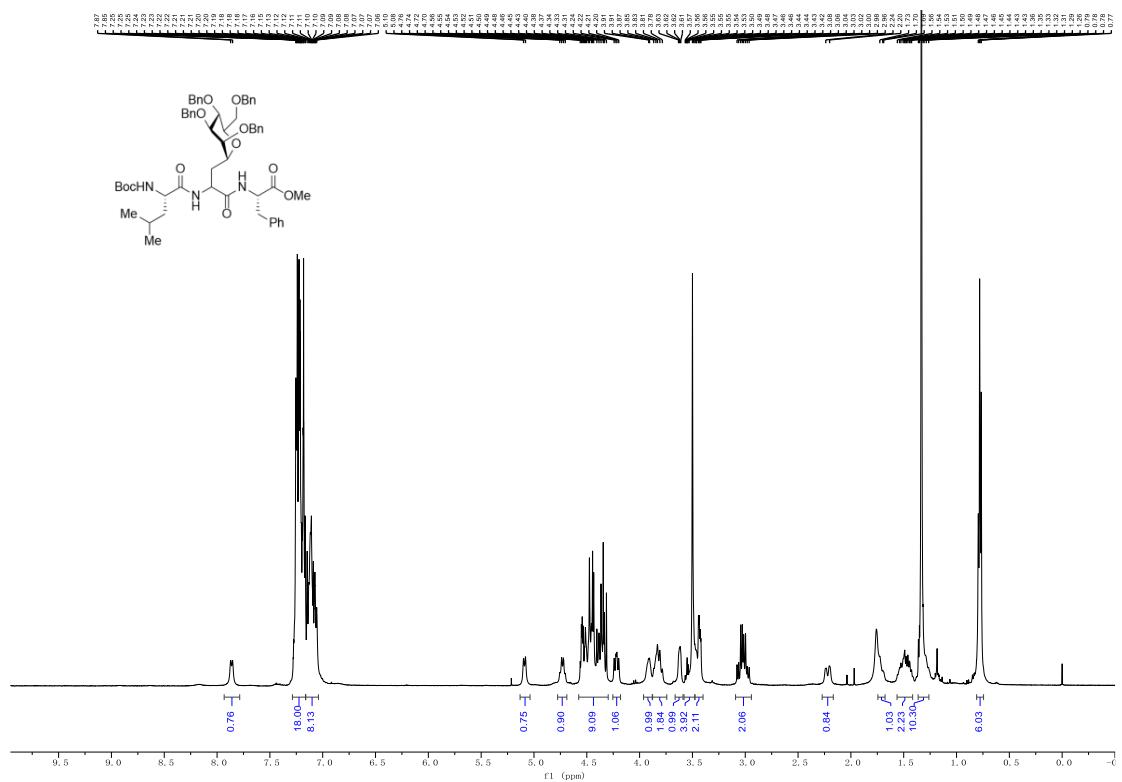


Figure S128. ^{13}C NMR spectrum of compound 5ap'

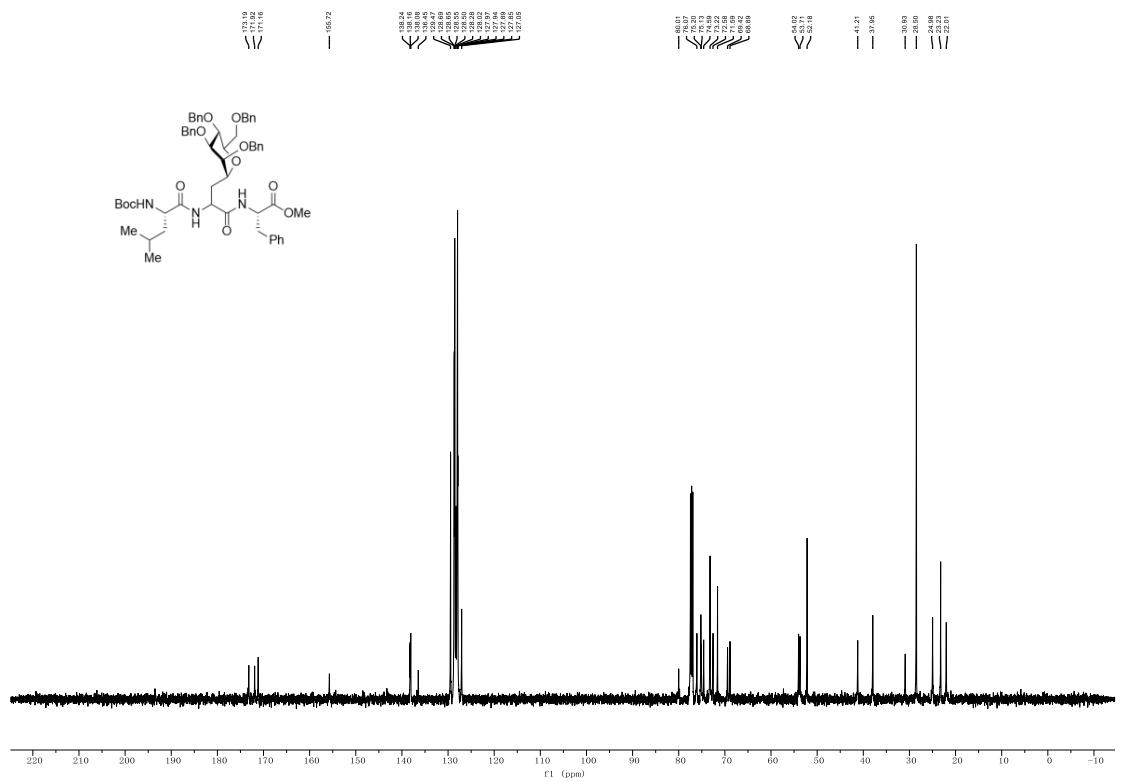


Figure S129. ^1H NMR spectrum of compound 7a

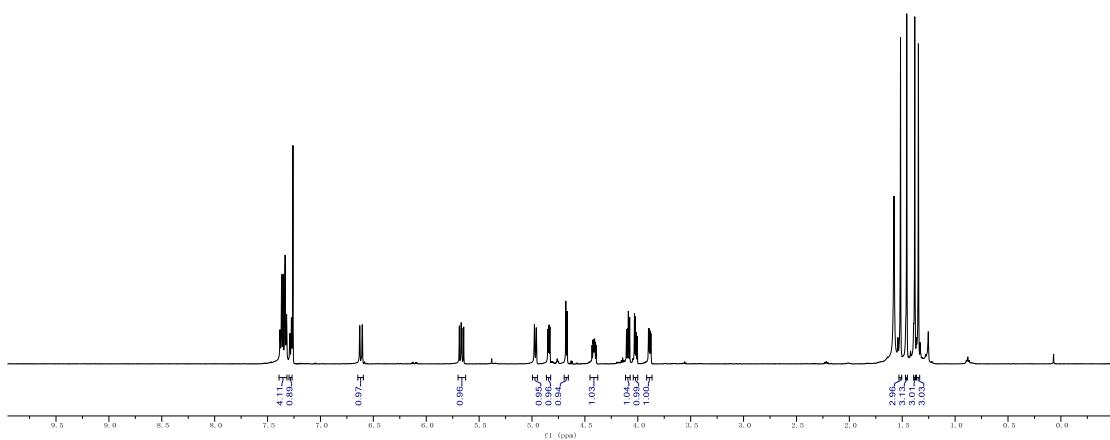
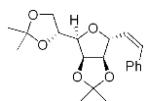


Figure S130. ^{13}C NMR spectrum of compound 7a

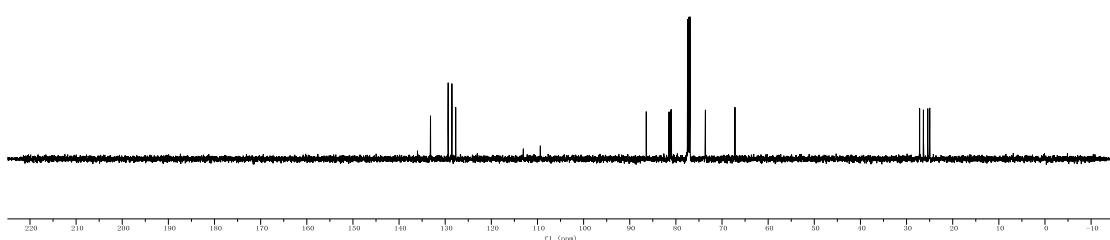
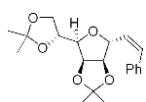


Figure S131. COSY spectrum of compound 7a

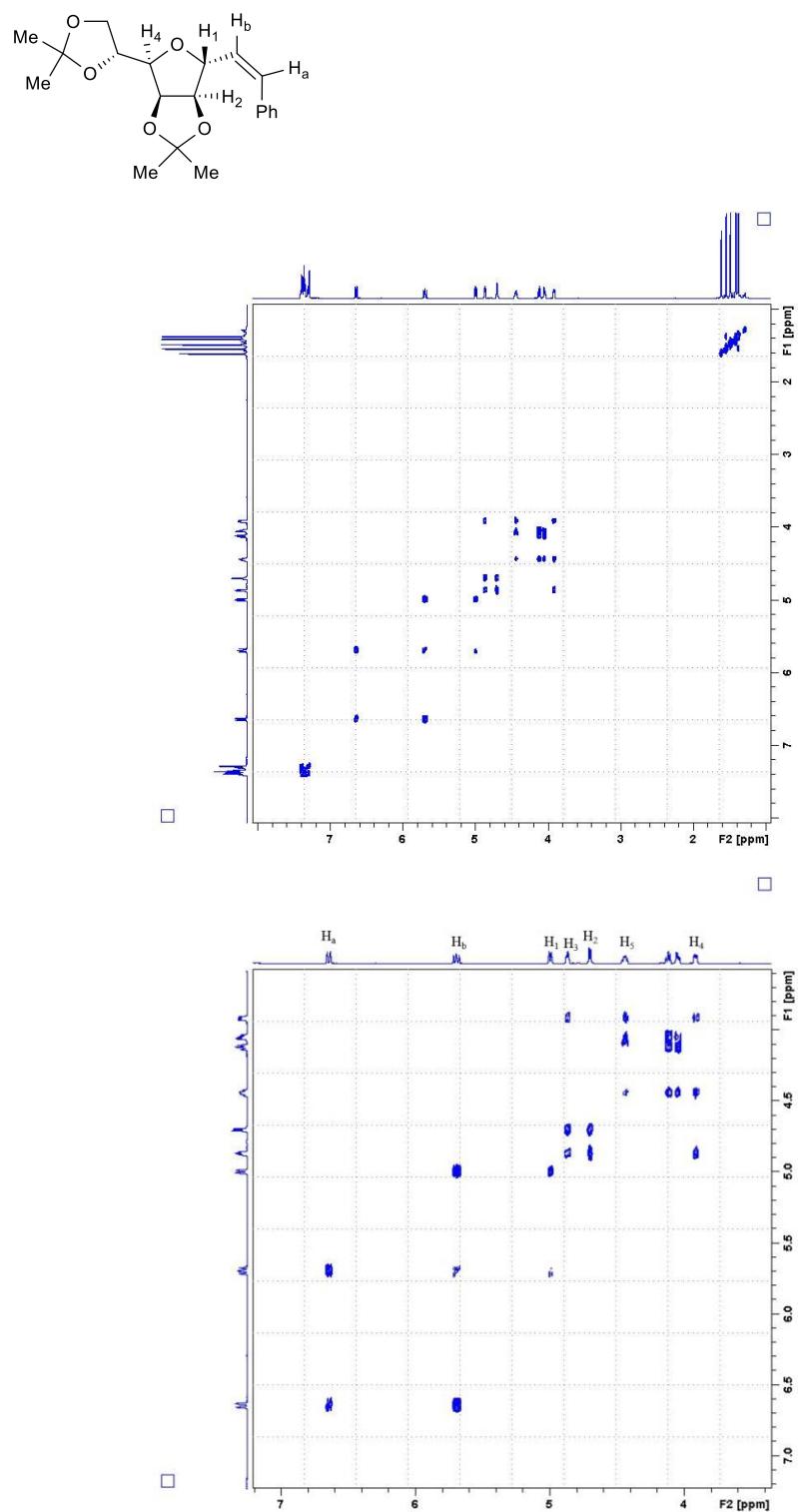


Figure S132. NOE spectrum of compound 7a

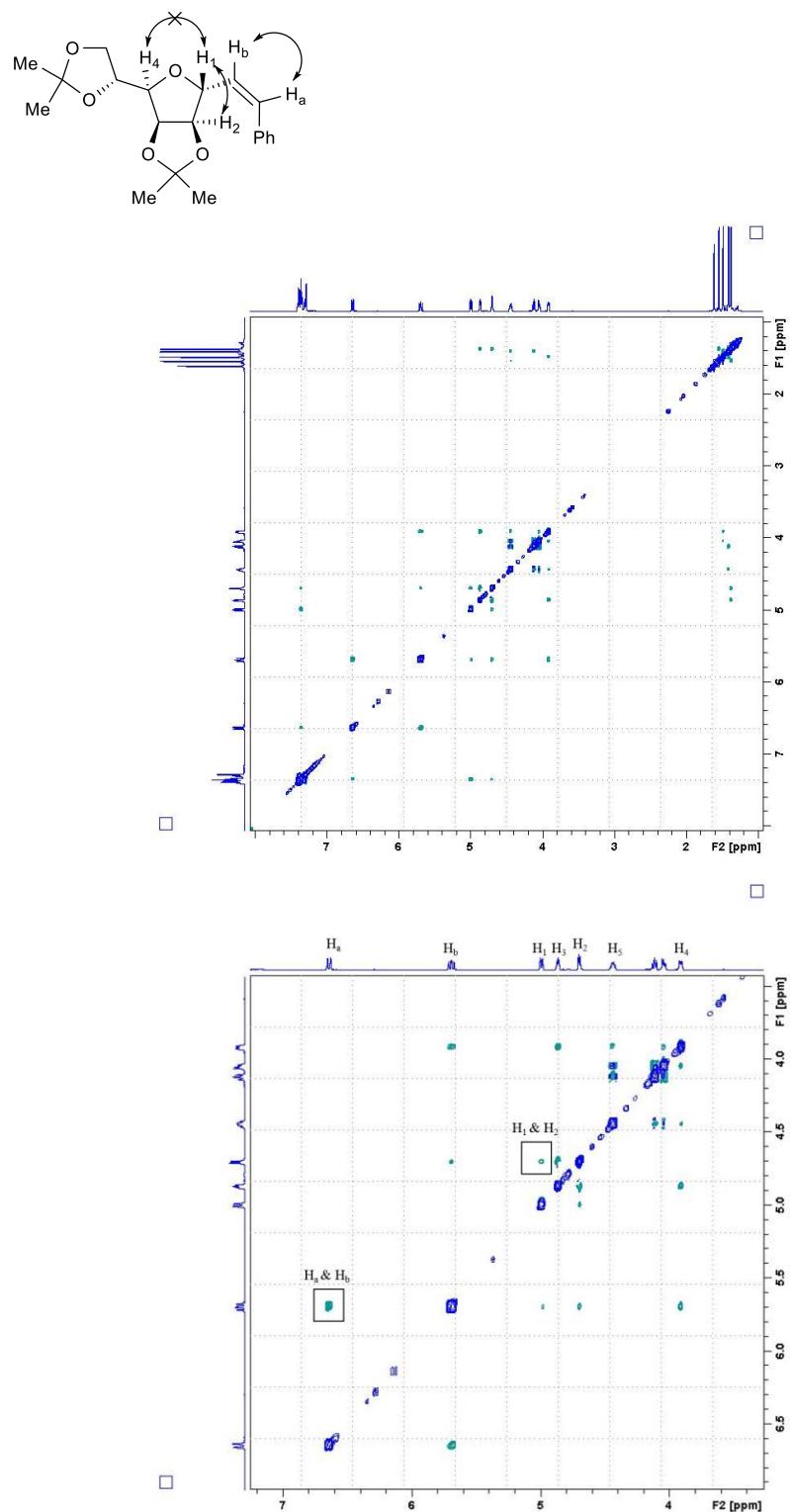


Figure S133. ^1H NMR spectrum of compound 7b

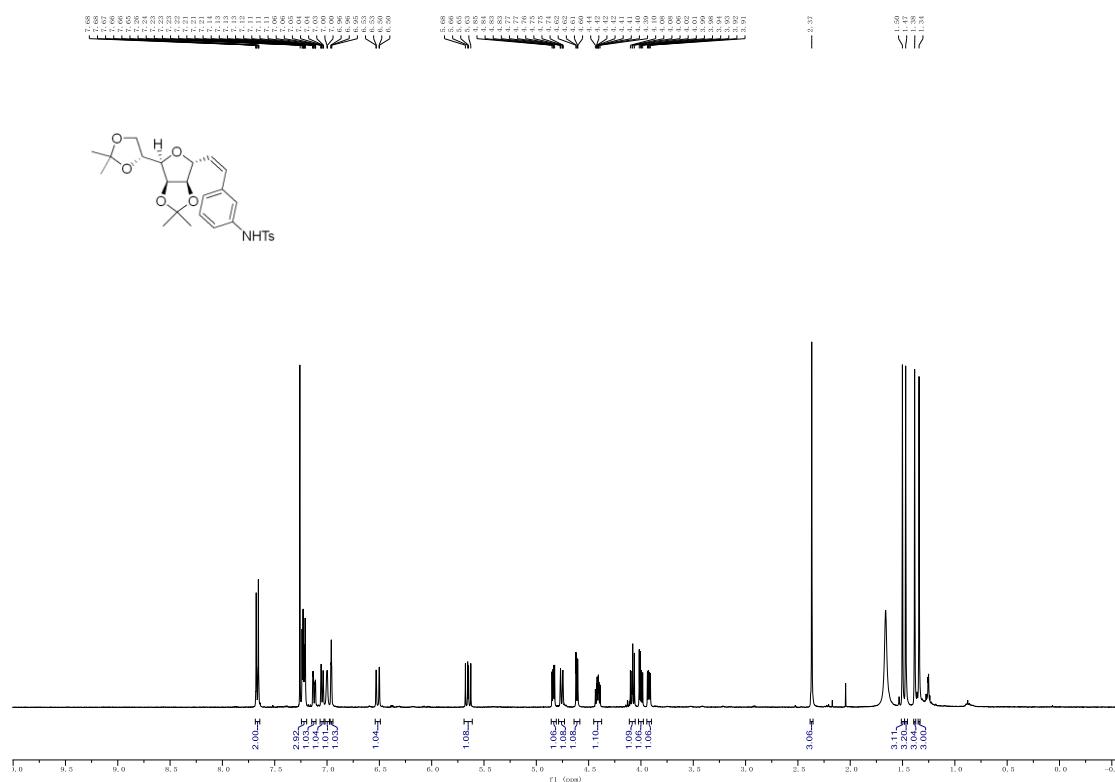


Figure S134. ^{13}C NMR spectrum of compound 7b

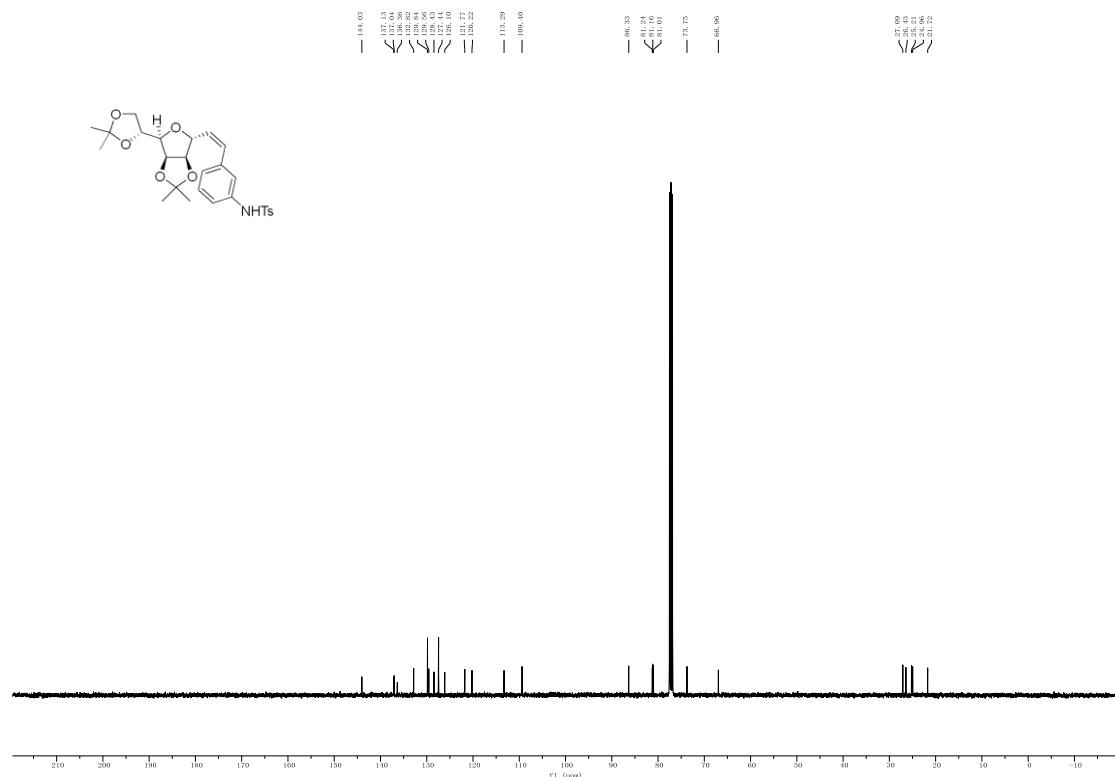


Figure S135. ^1H NMR spectrum of compound 7c

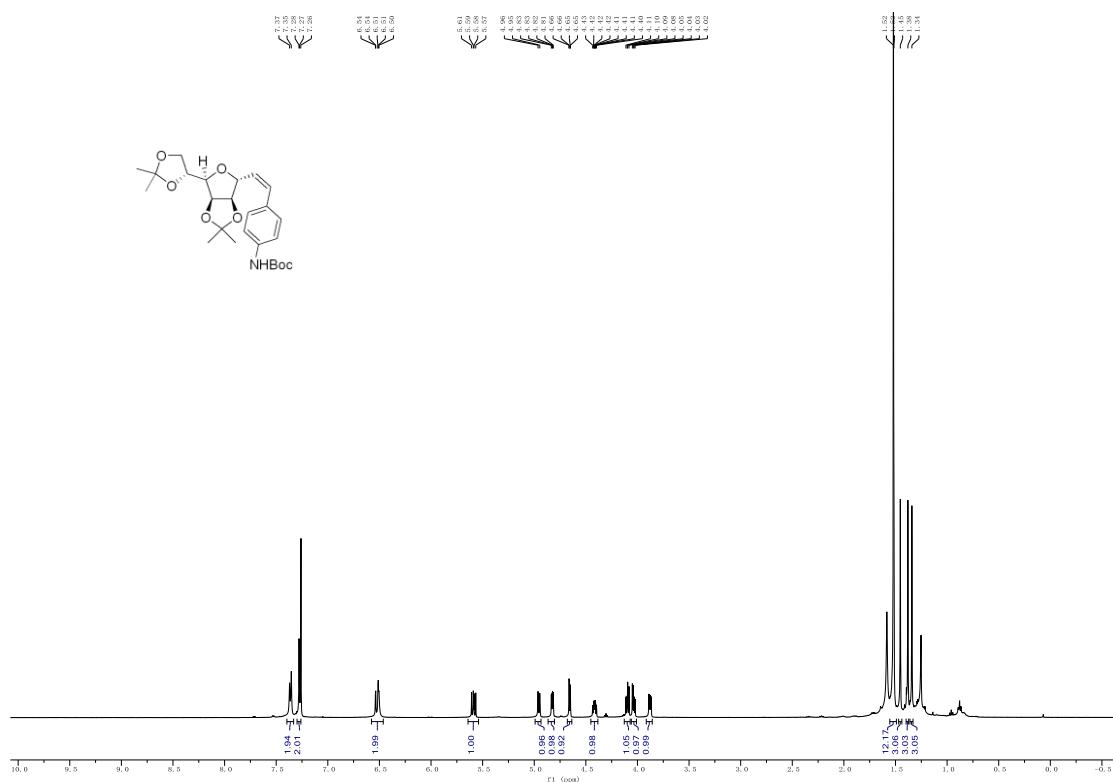


Figure S136. ^{13}C NMR spectrum of compound 7c

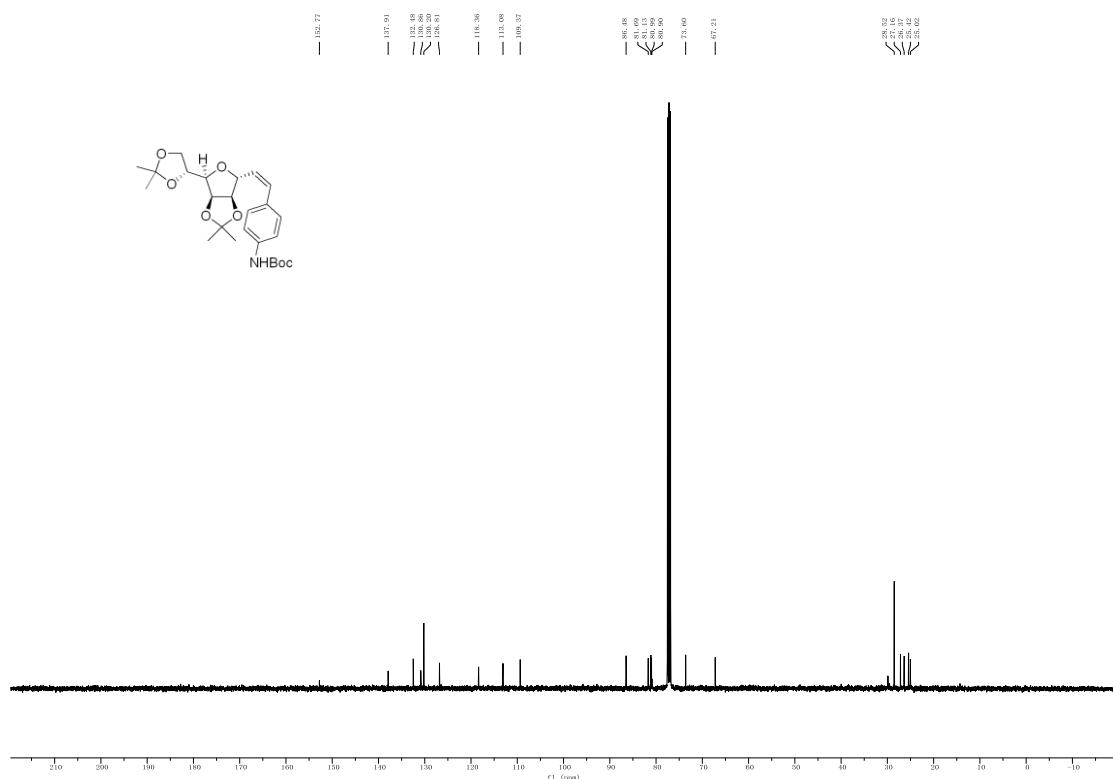


Figure S137. ^1H NMR spectrum of compound 7d

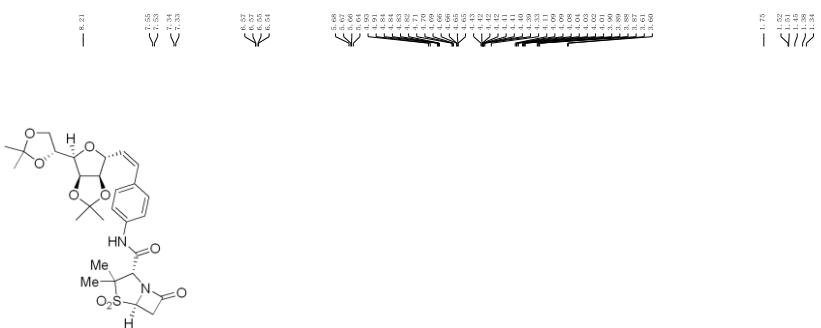


Figure S138. ^{13}C NMR spectrum of compound 7d

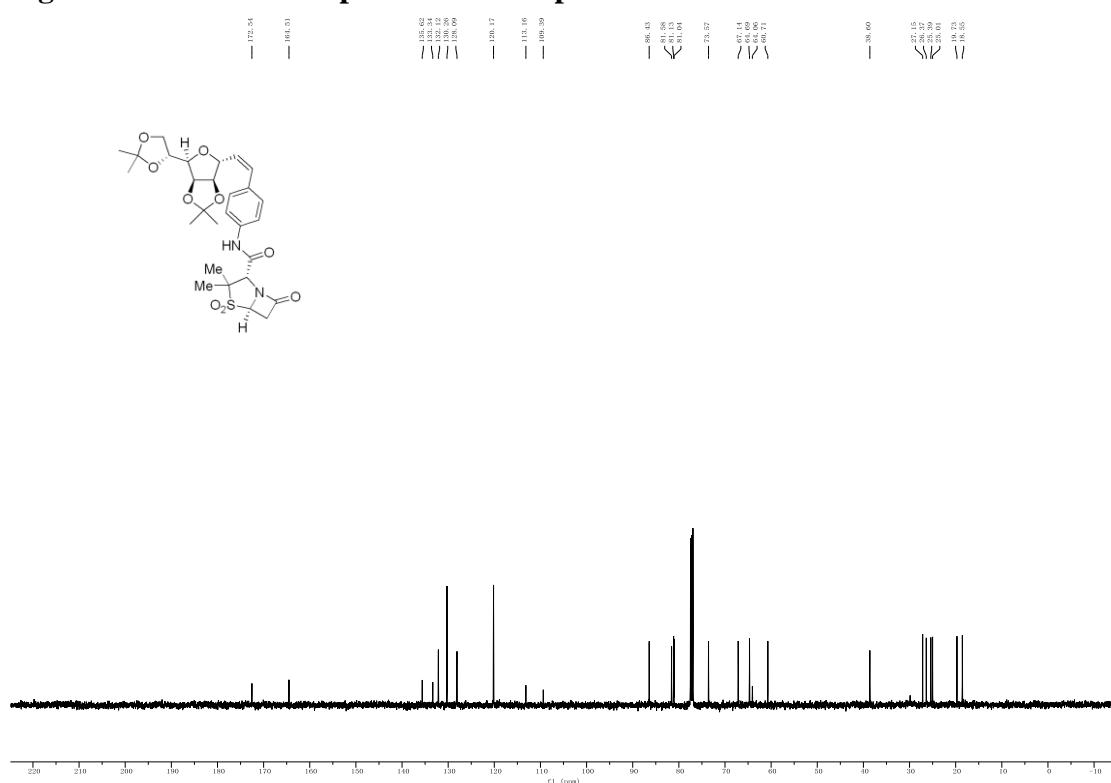


Figure S139. ^1H NMR spectrum of compound 7e

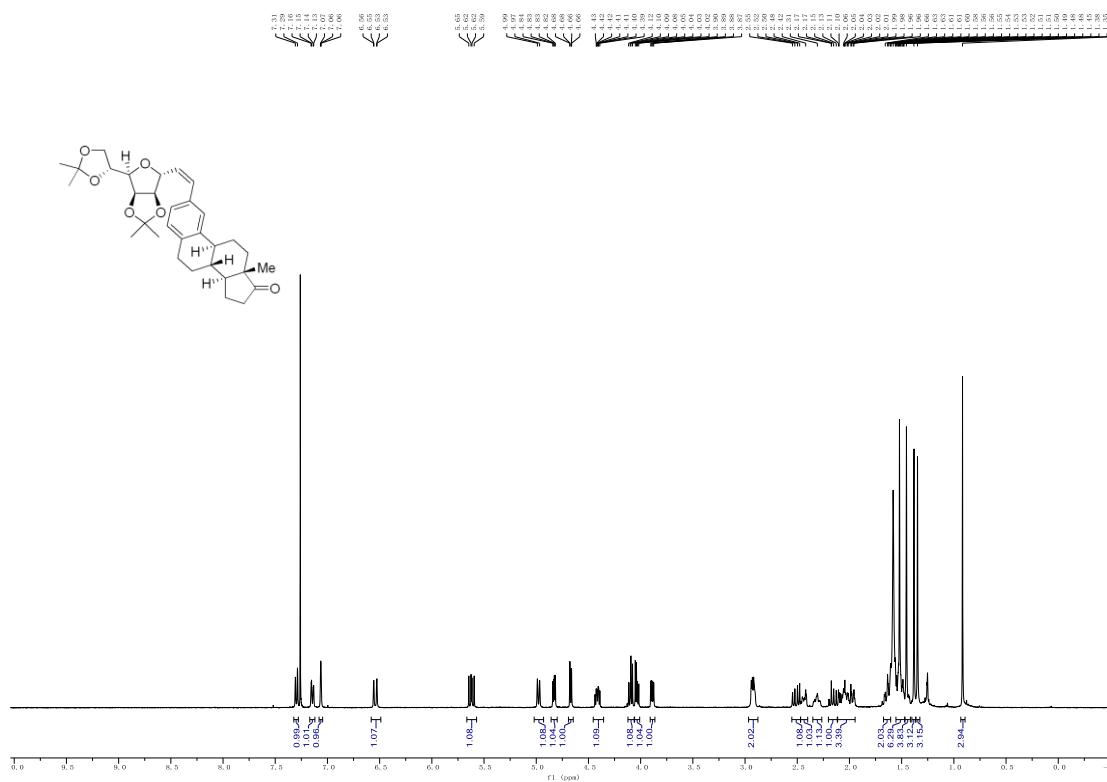


Figure S140. ^{13}C NMR spectrum of compound 7e

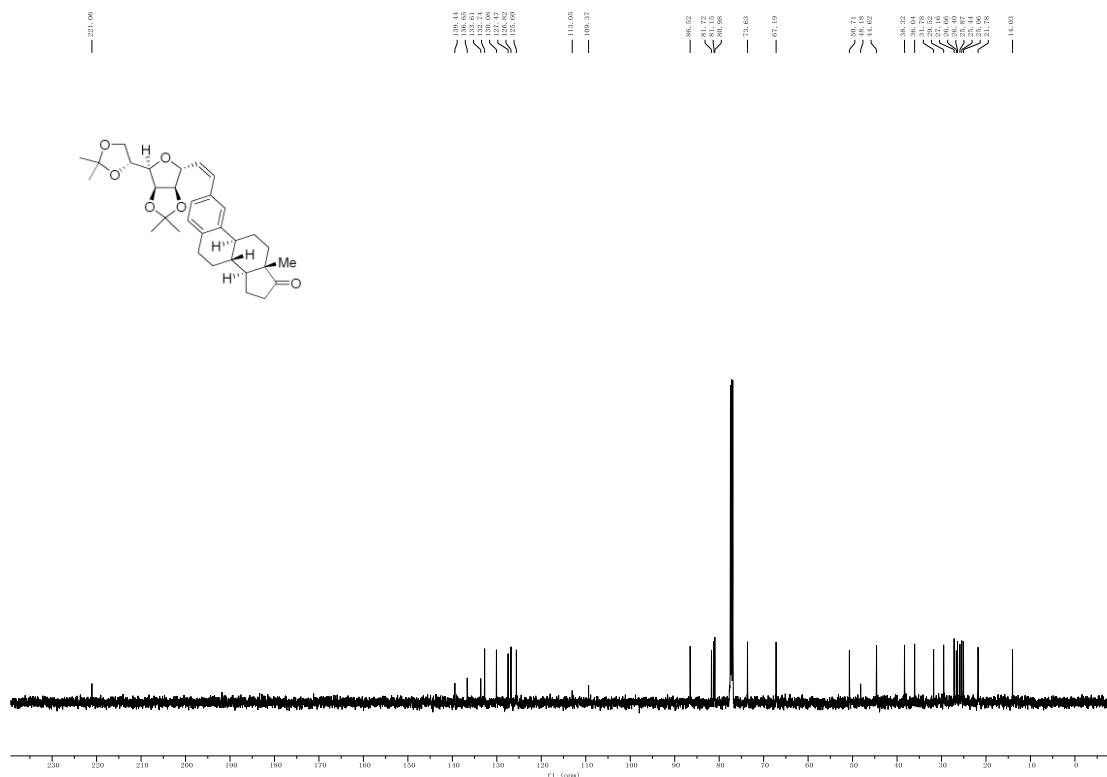


Figure S141. ^1H NMR spectrum of compound 10

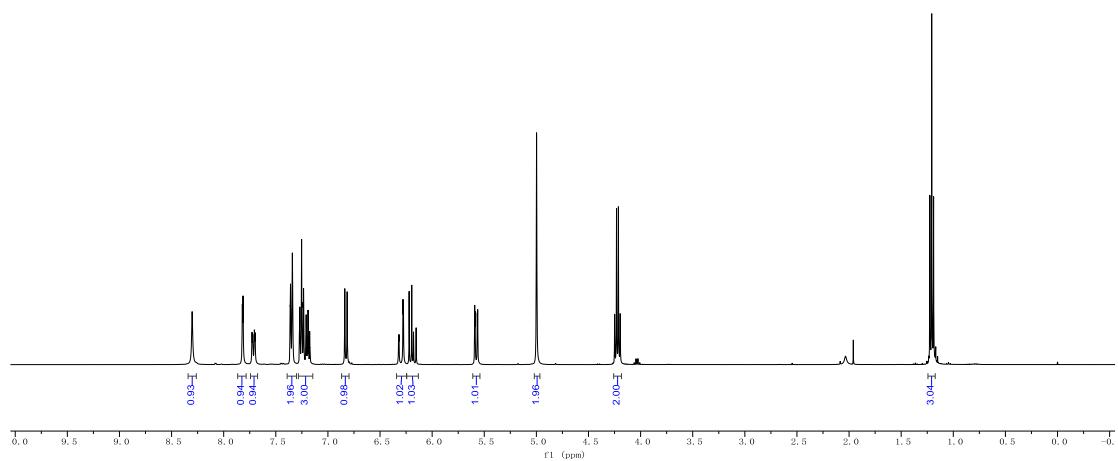
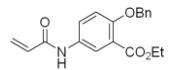


Figure S142. ^{13}C NMR spectrum of compound 10

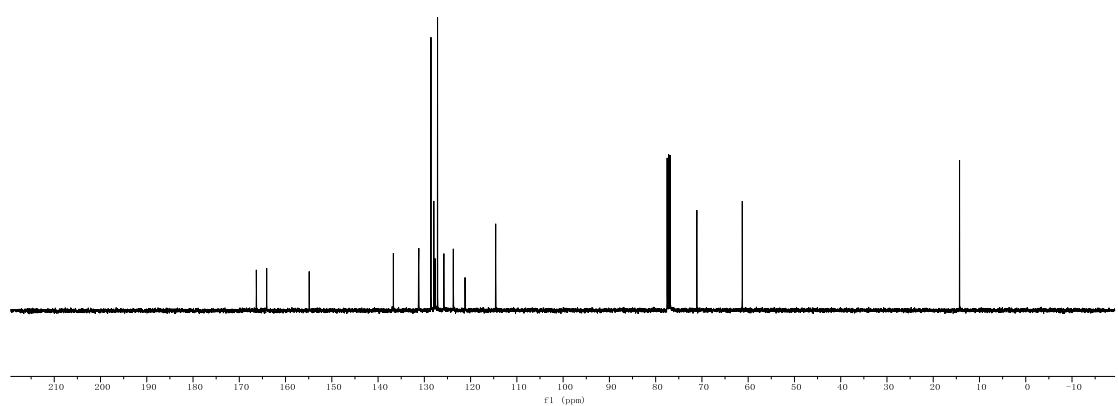
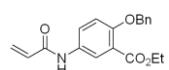


Figure S143. ^1H NMR spectrum of compound 11

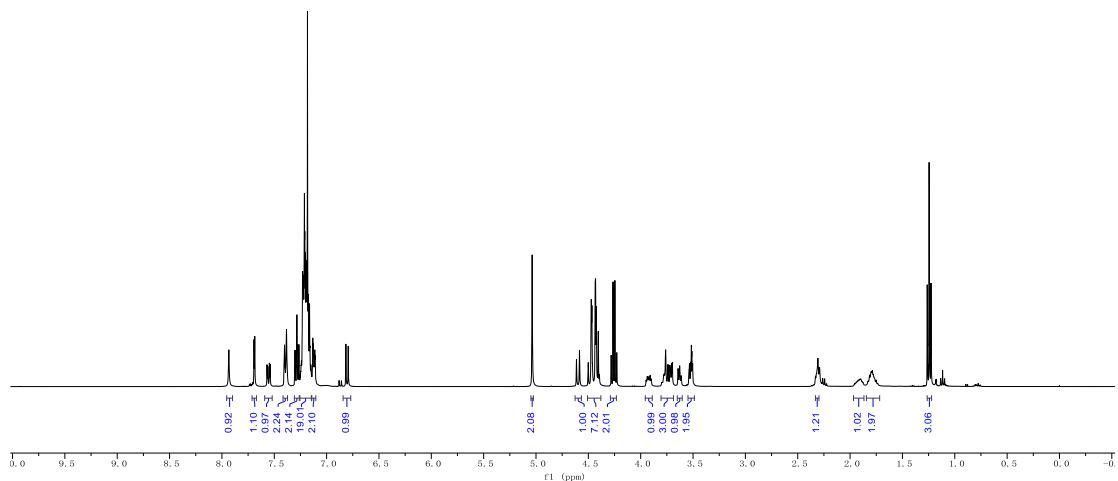
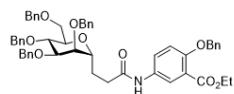


Figure S144. ^{13}C NMR spectrum of compound 11

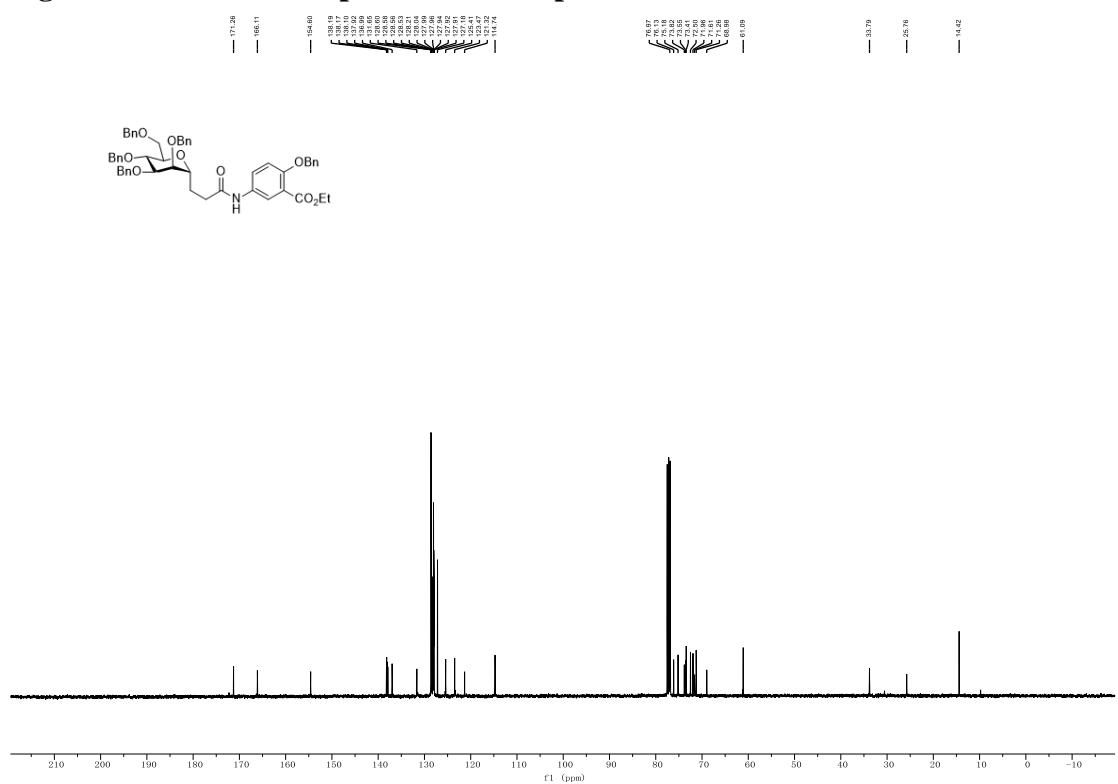


Figure S145. ^1H NMR spectrum of compound 12

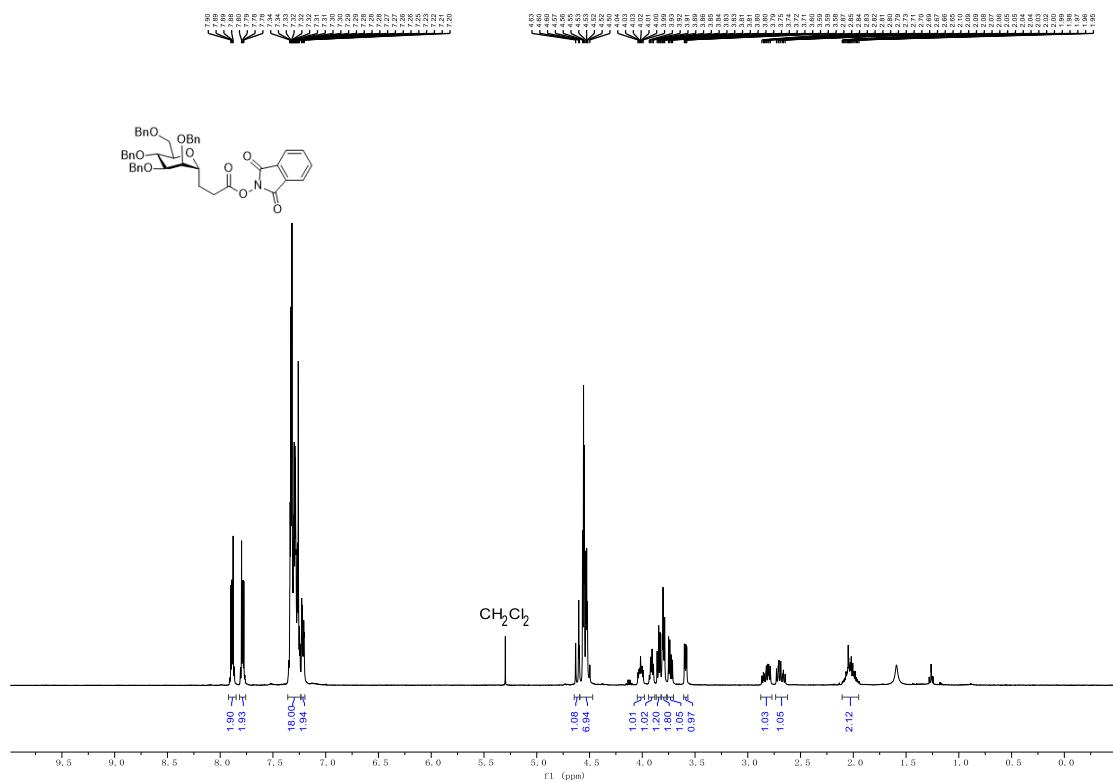


Figure S146. ^{13}C NMR spectrum of compound 12

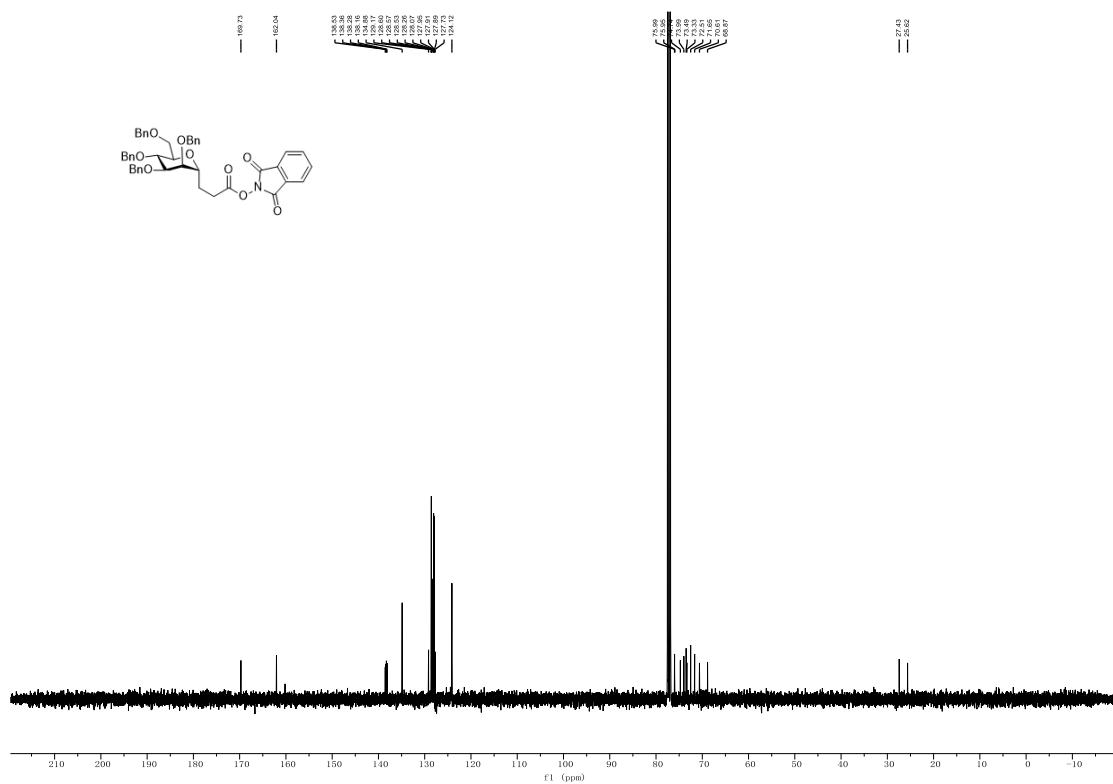


Figure S147. ^1H NMR spectrum of compound 13

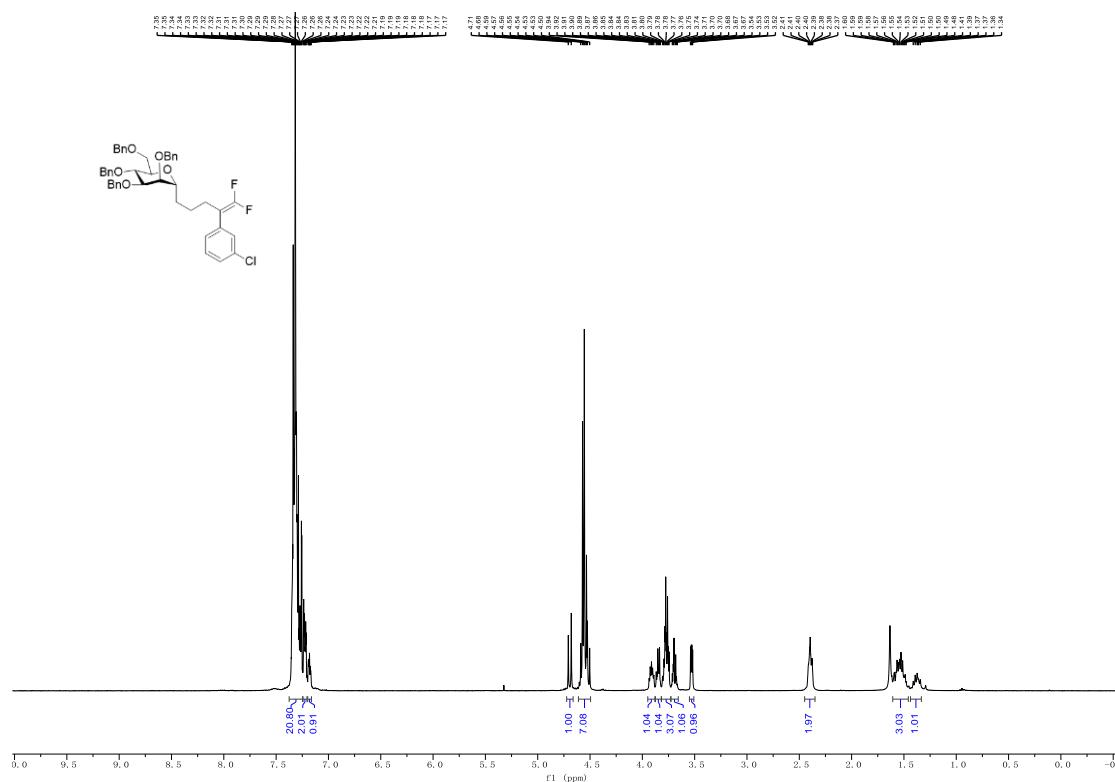


Figure S148. ^{19}F NMR spectrum of compound 13

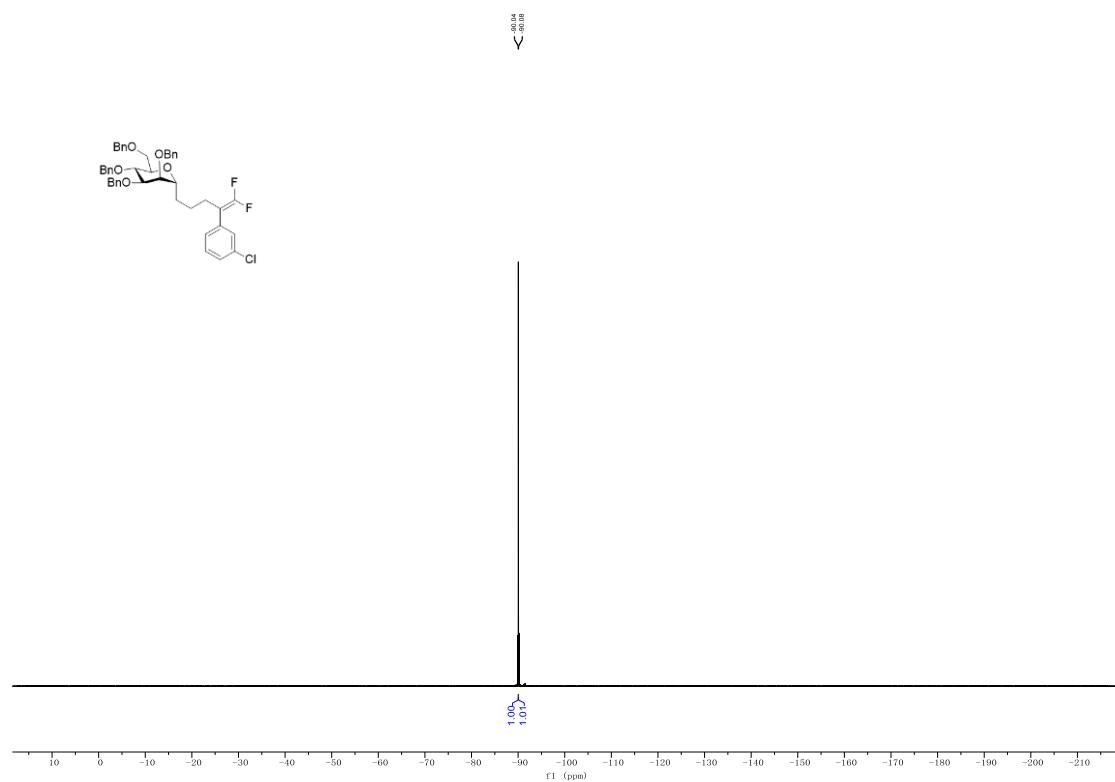


Figure S149. ^{13}C NMR spectrum of compound 13

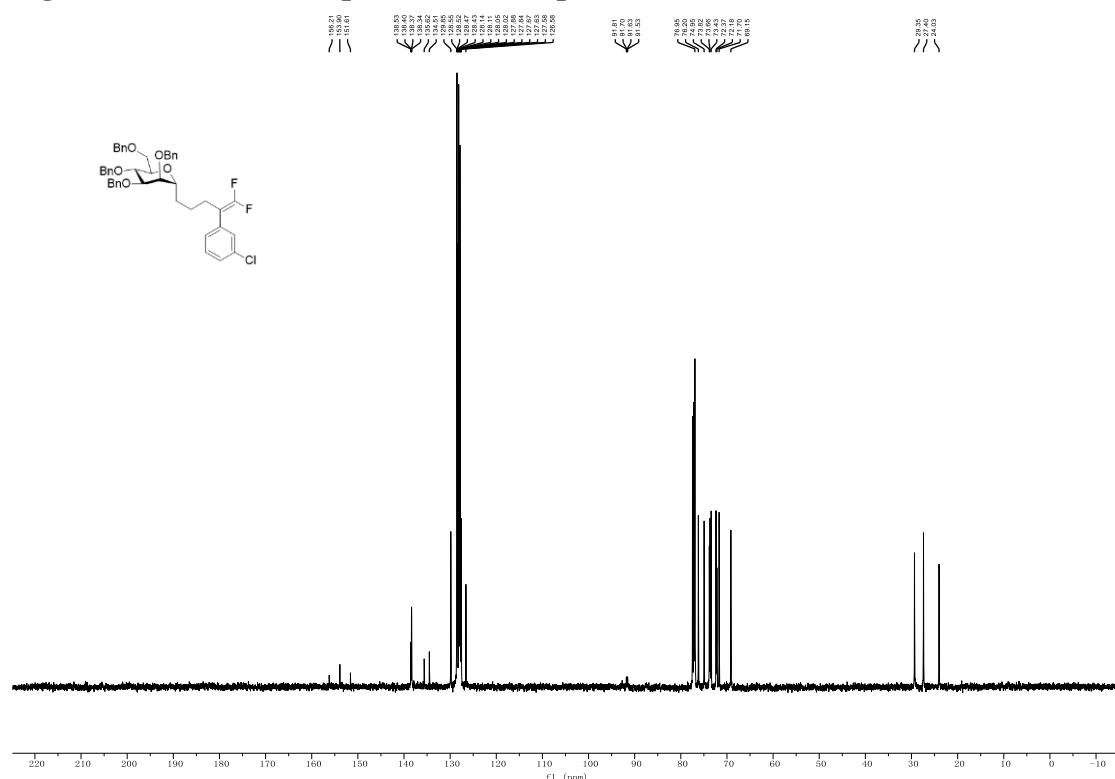


Figure S150. ^1H NMR spectrum of compound 14

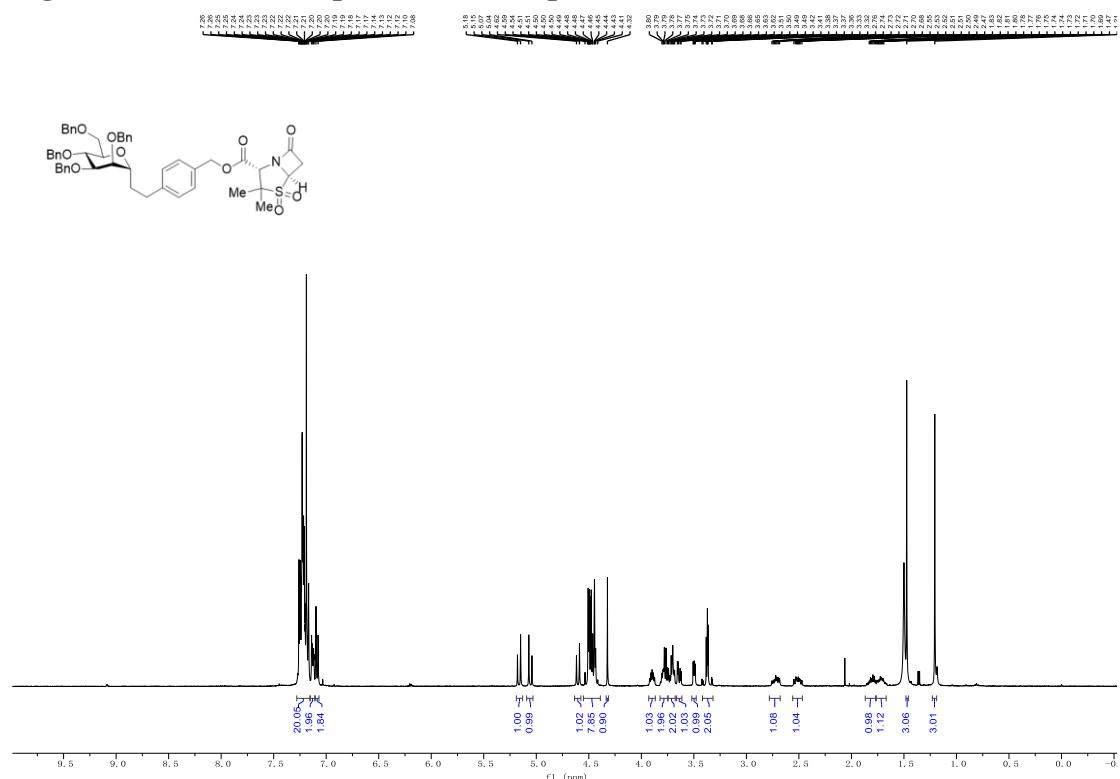


Figure S151. ^{13}C NMR spectrum of compound 14

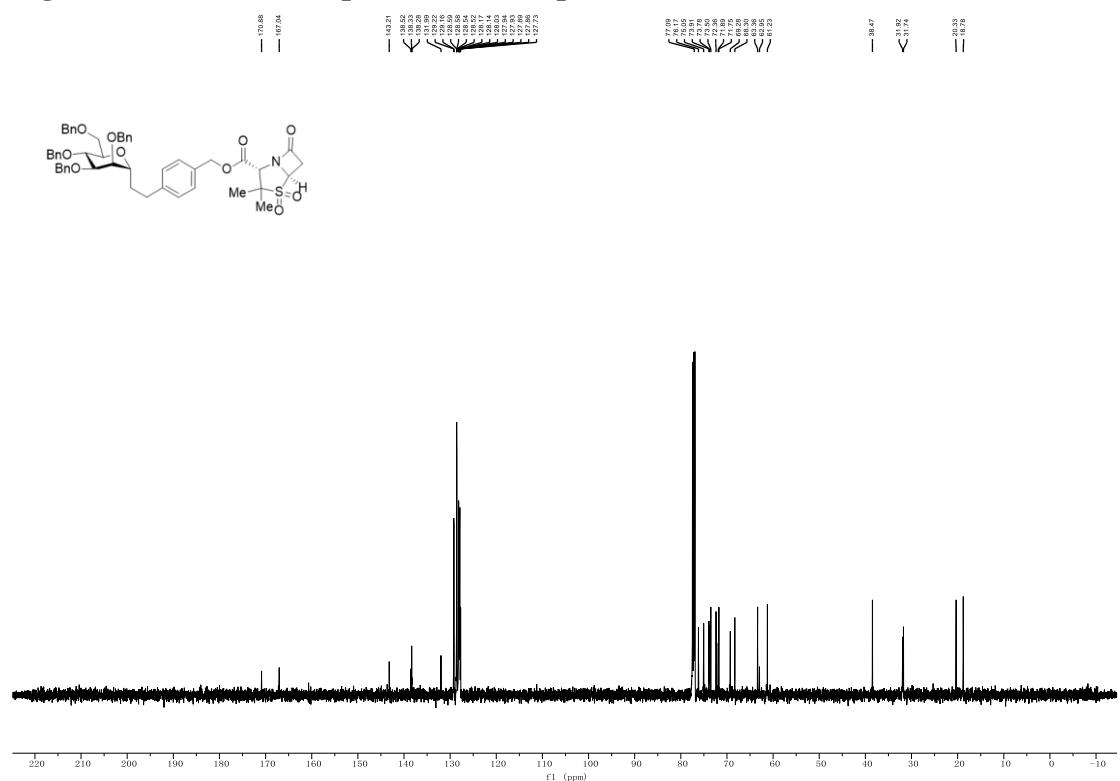


Figure S152. ^1H NMR spectrum of compound 15

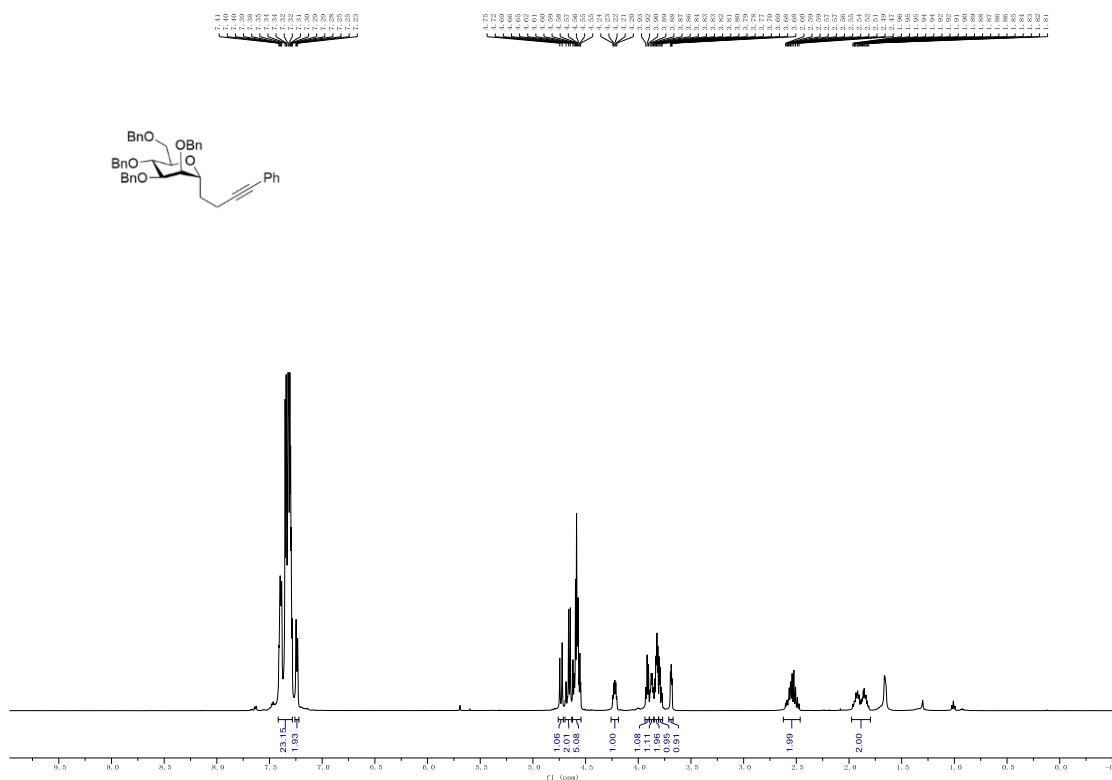


Figure S153. ^{13}C NMR spectrum of compound 15

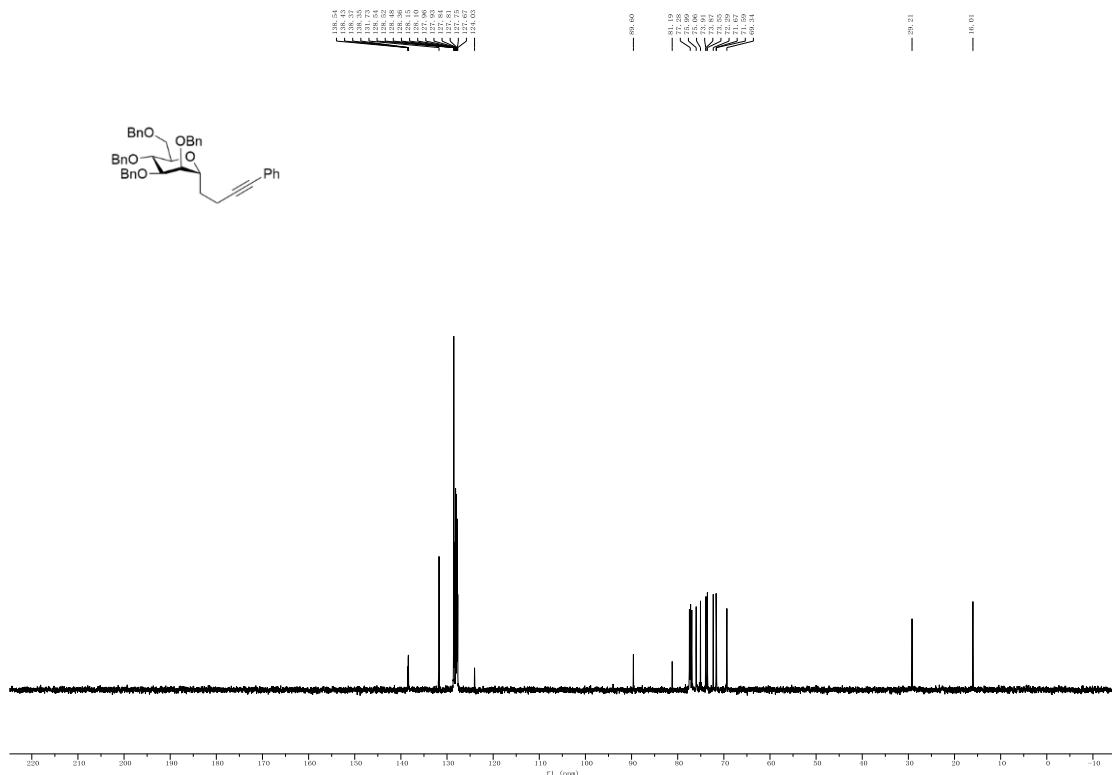


Figure S154. ^1H NMR spectrum of compound 16a

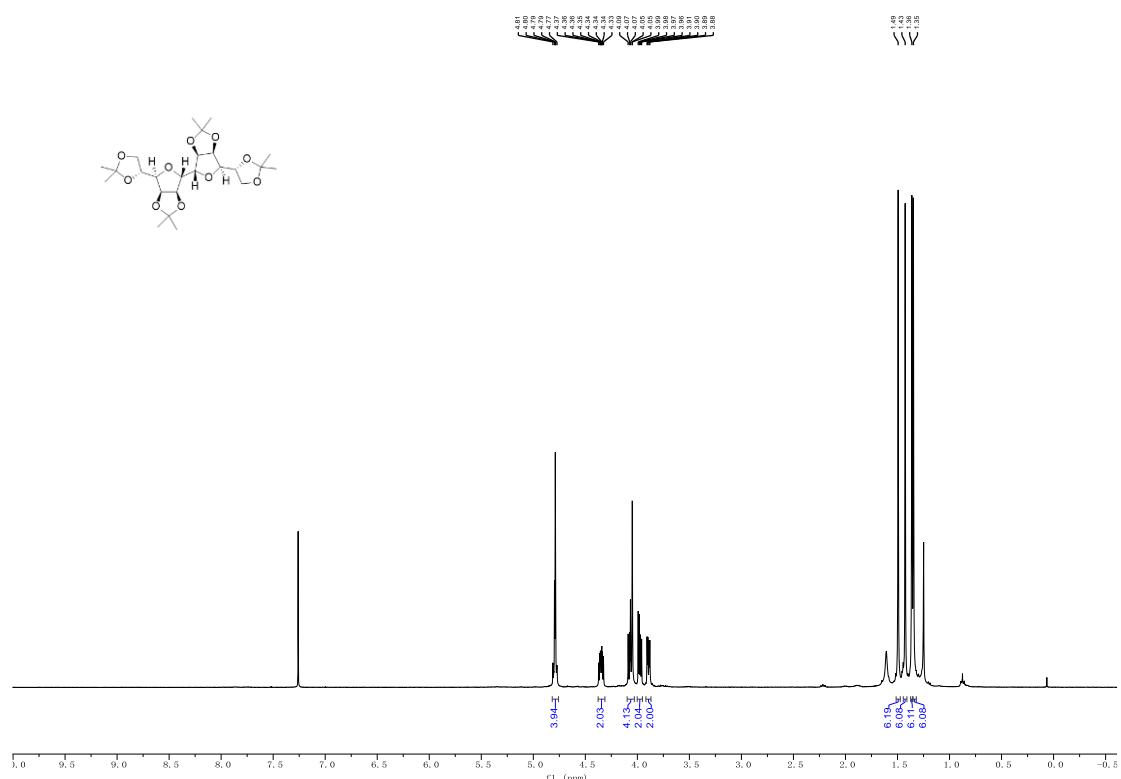


Figure S155. ^{13}C NMR spectrum of compound 16a

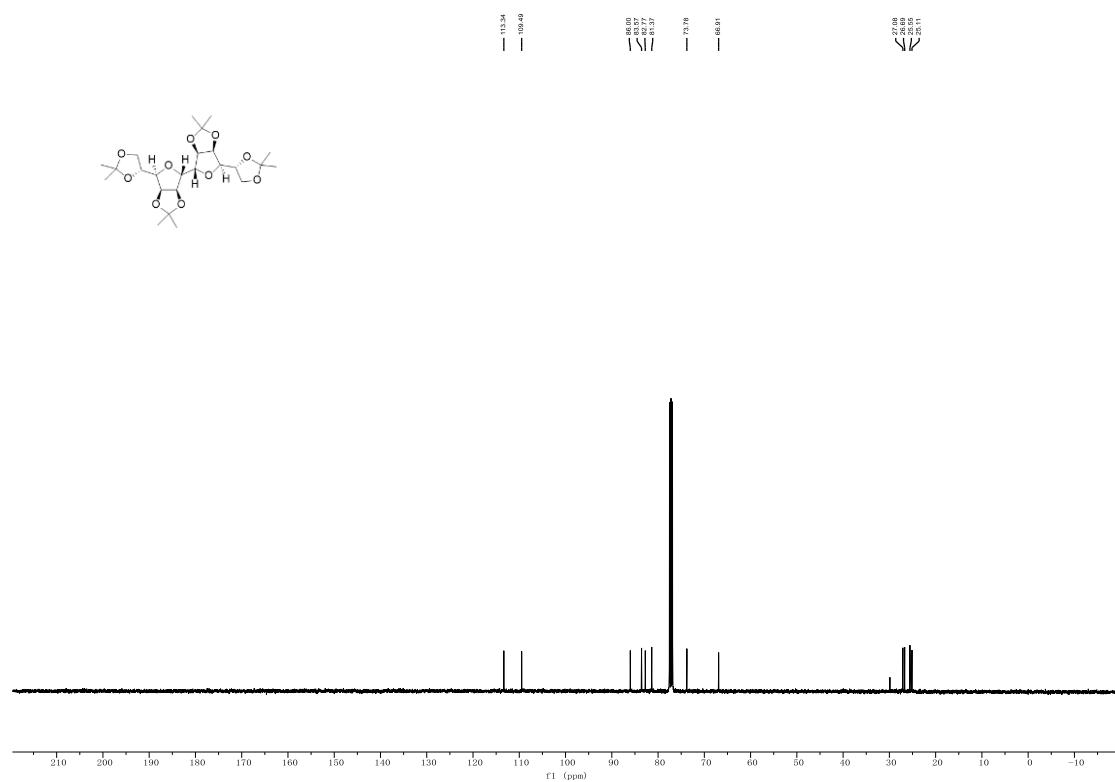


Figure S156. COSY spectrum of compound 16a

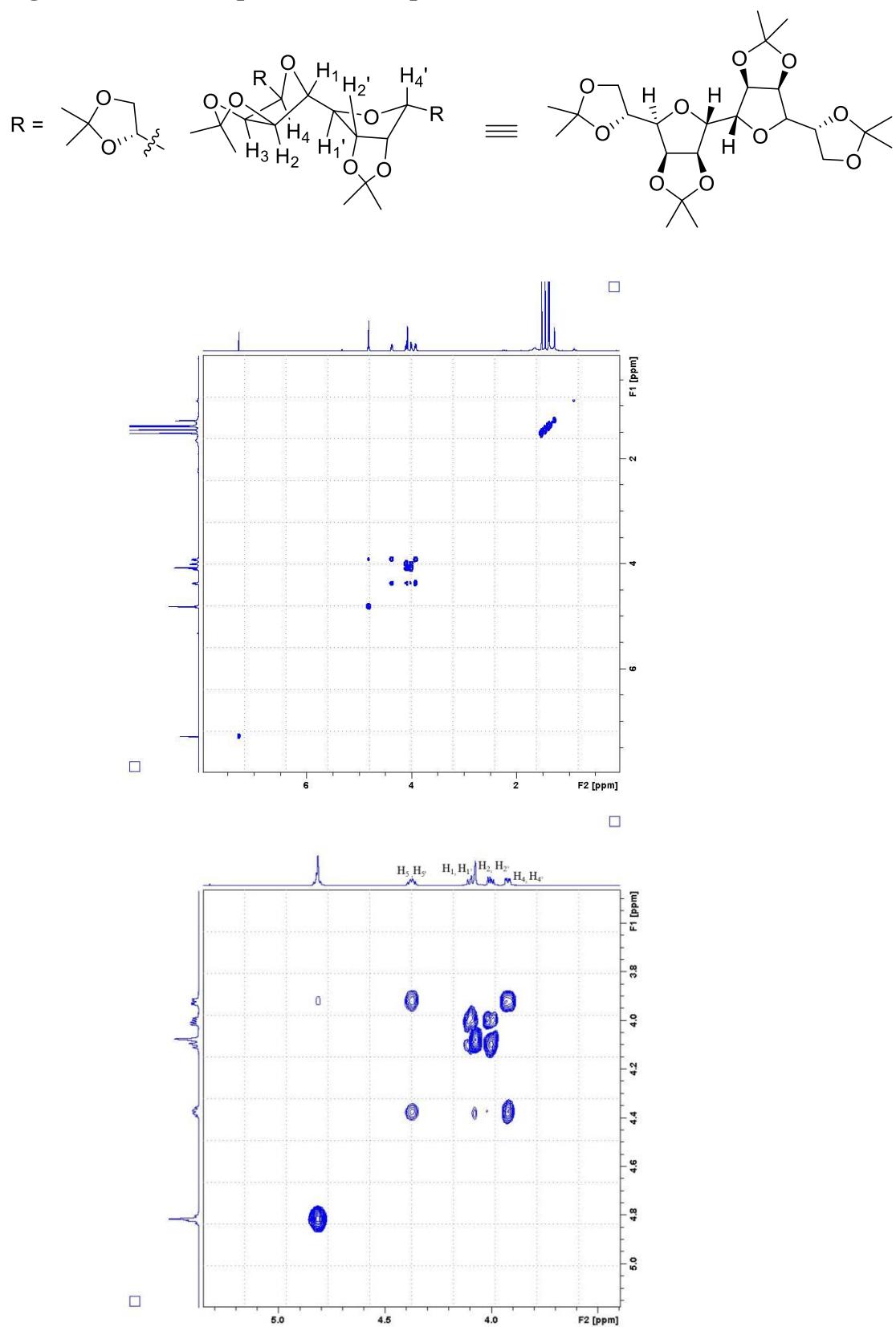


Figure S157. NOE spectrum of compound 16a

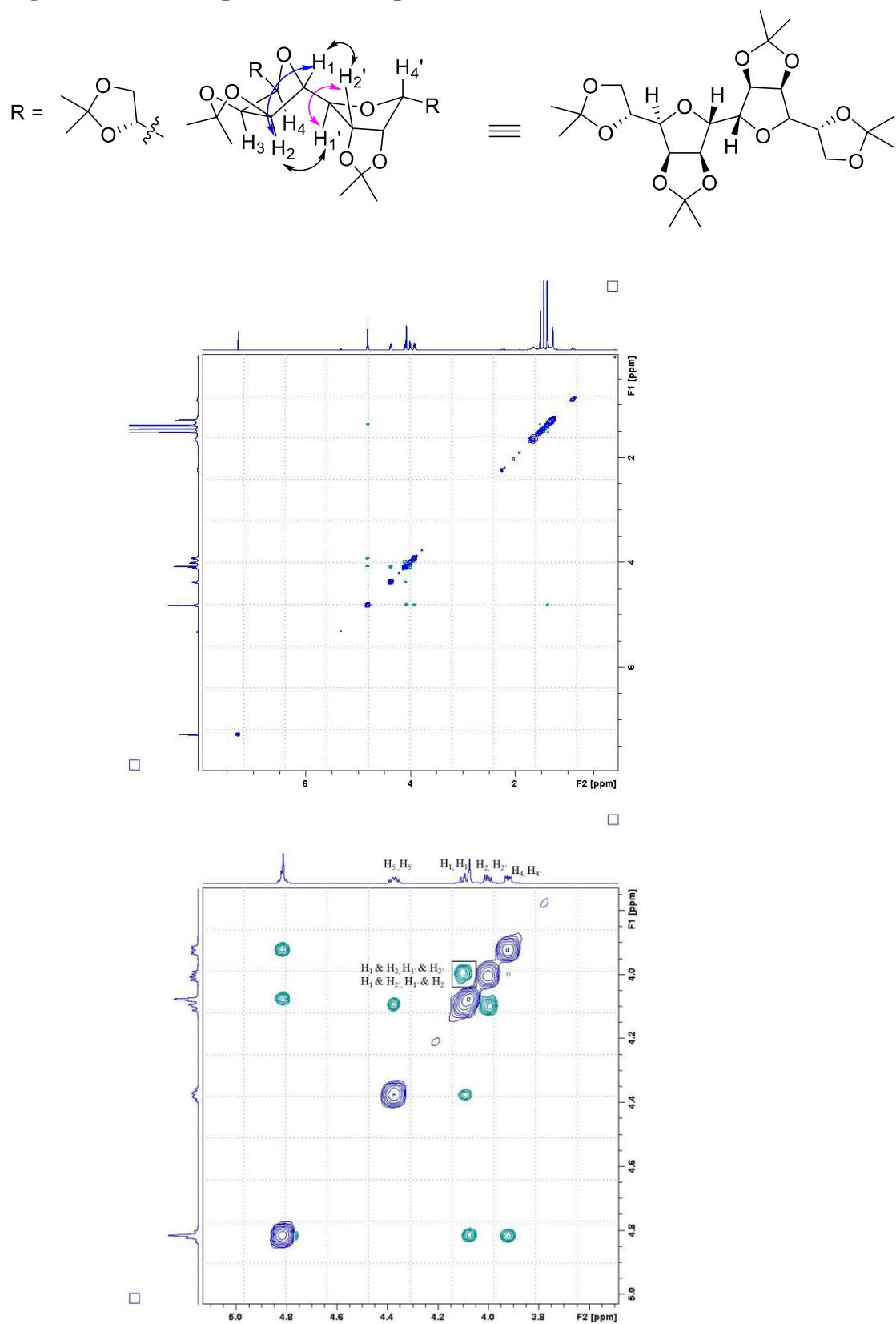


Figure S158. ^1H NMR spectrum of compound 16b

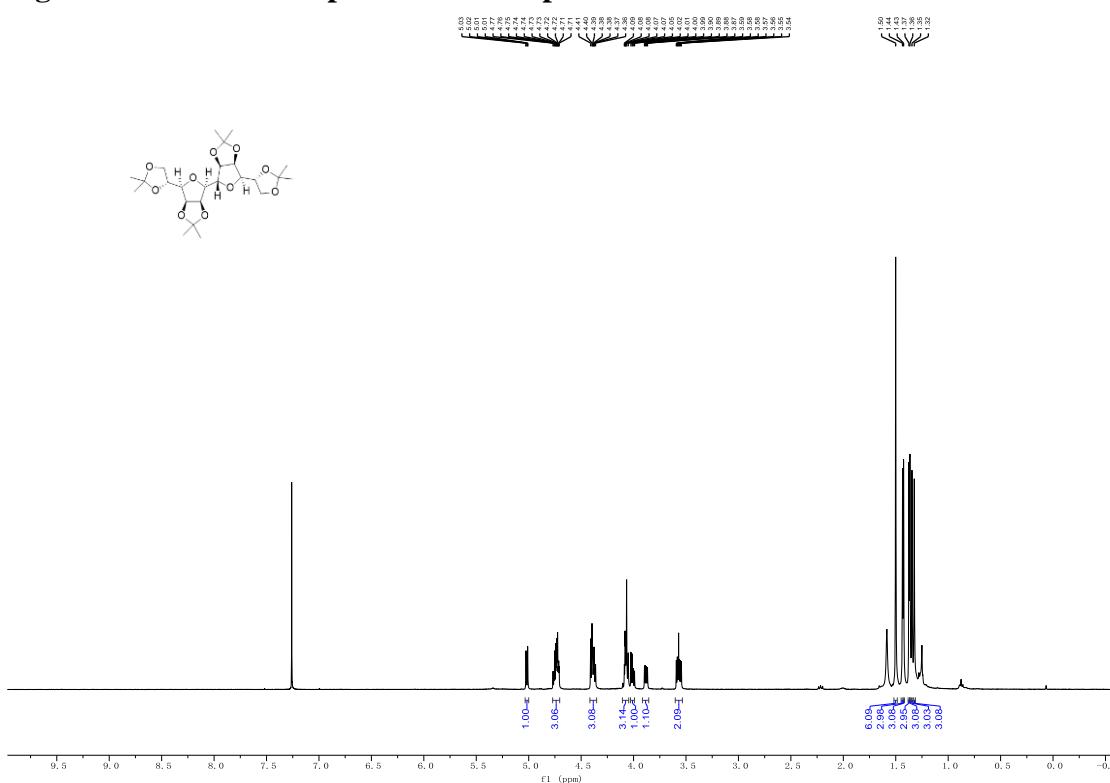


Figure S159. ^{13}C NMR spectrum of compound 16b

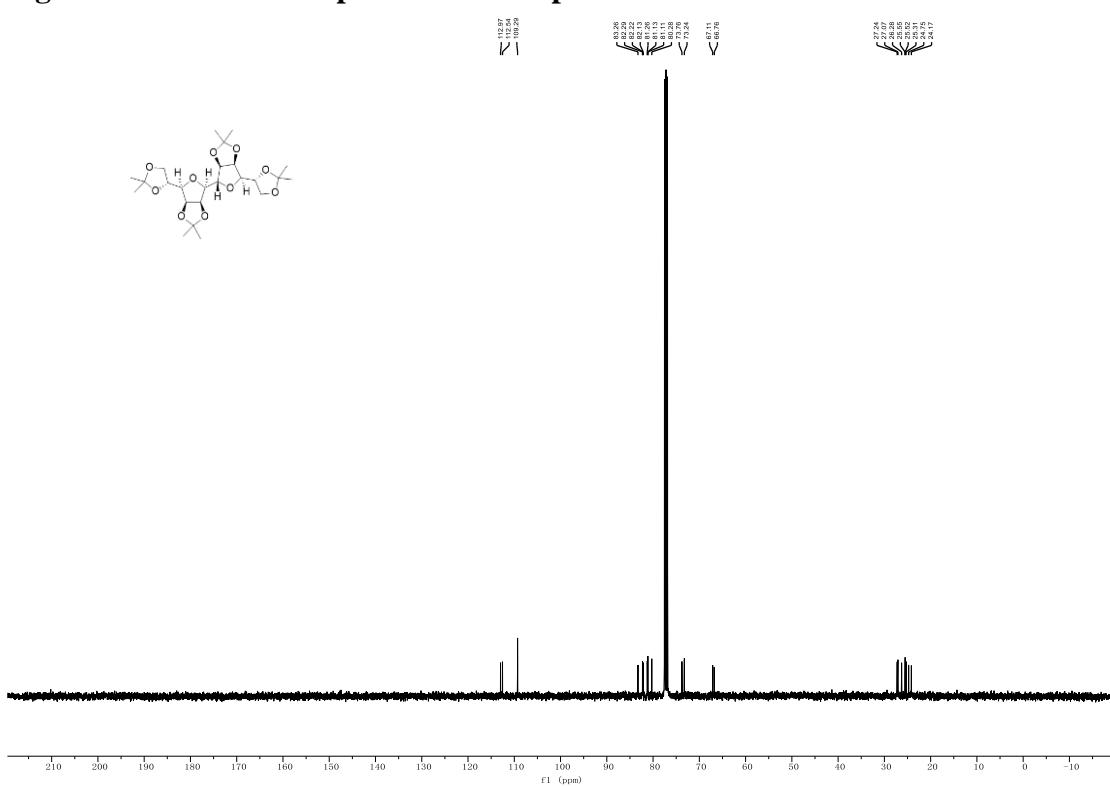


Figure S160. COSY spectrum of compound 16b

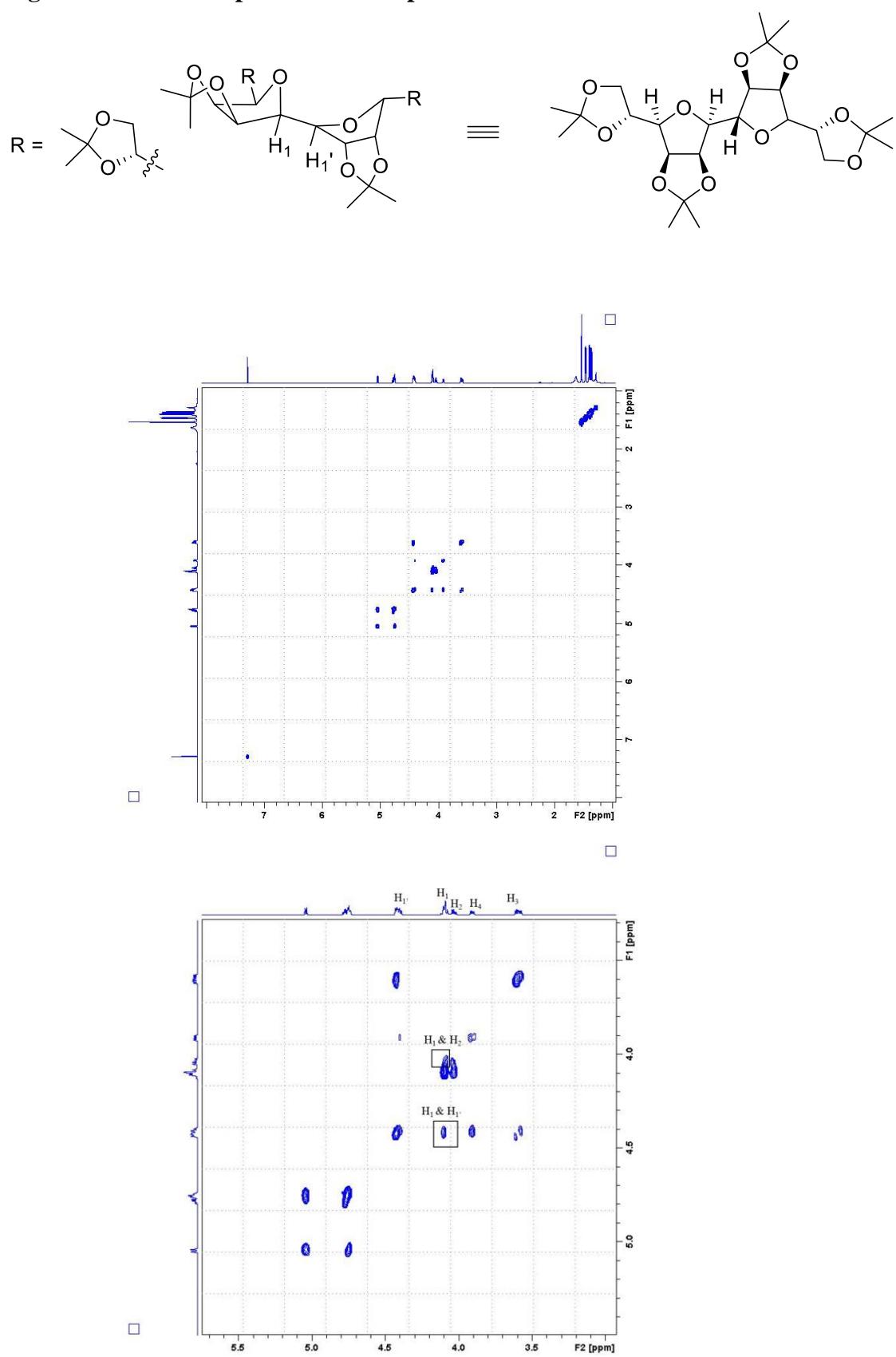


Figure S161. NOE spectrum of compound 16b

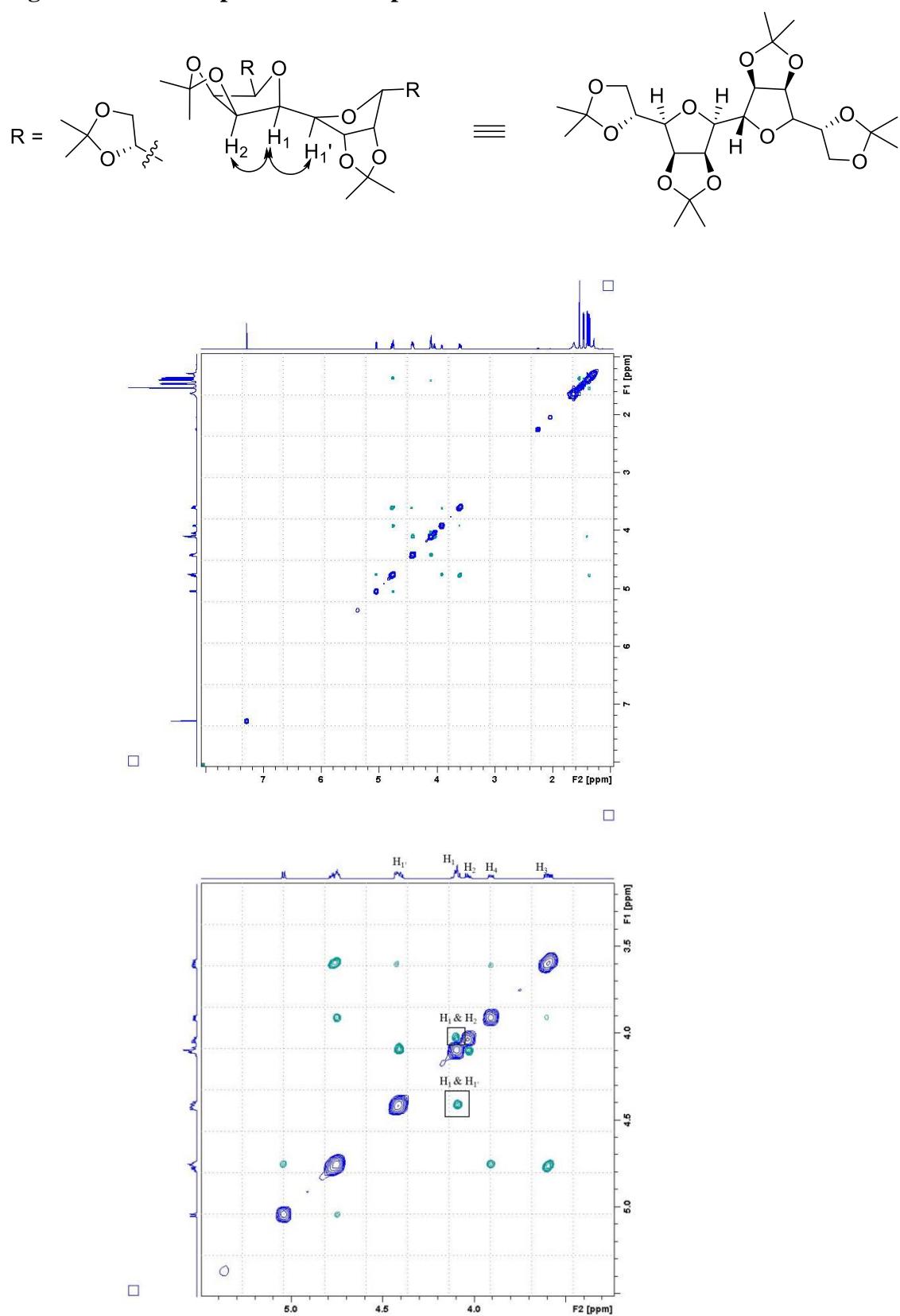


Figure S162. ^1H NMR spectrum of compound 19a

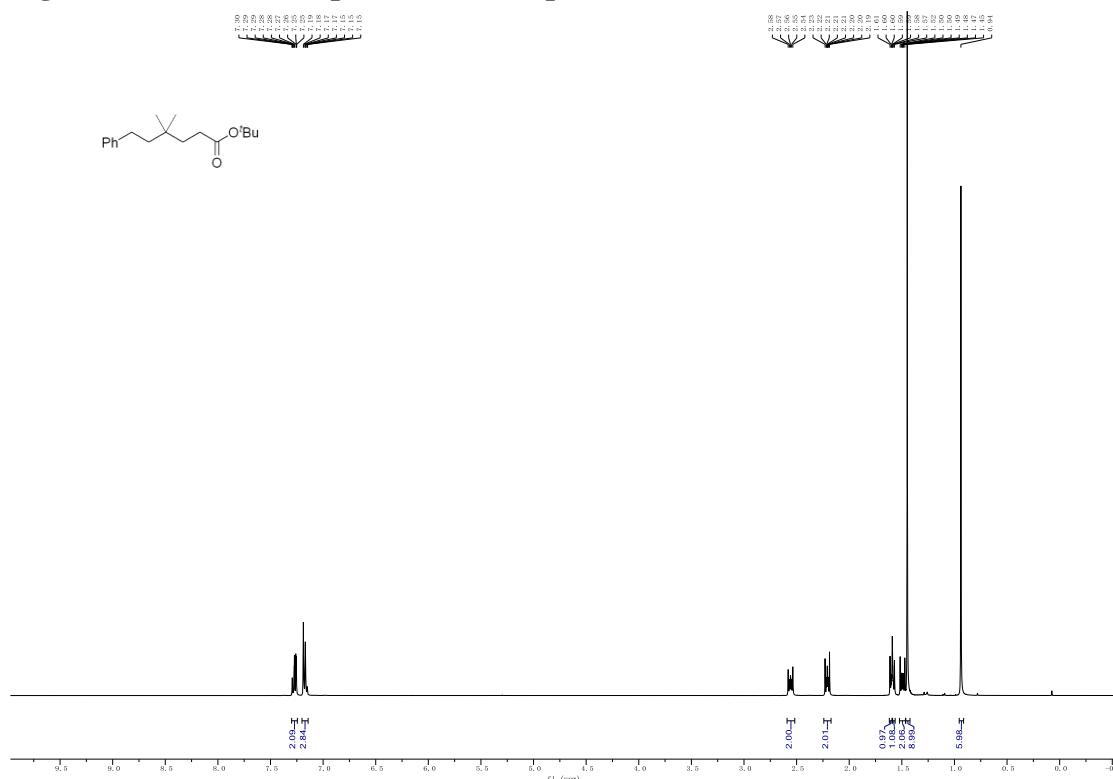


Figure S163. ^{13}C NMR spectrum of compound 19a

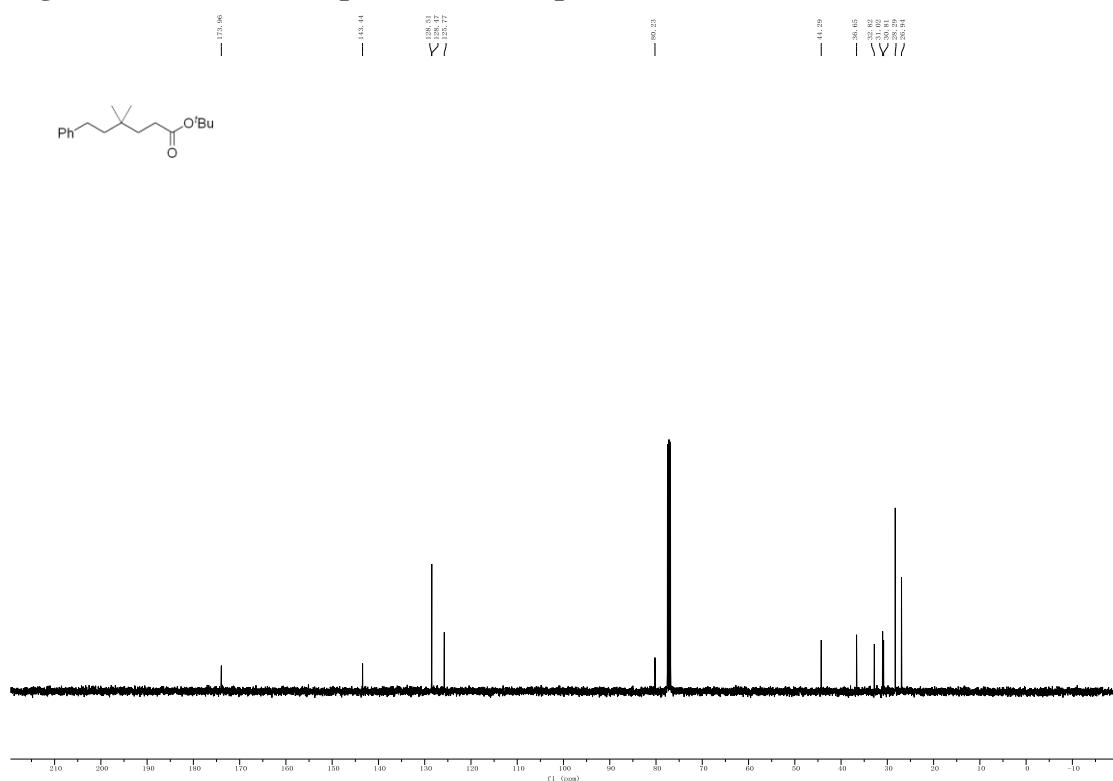


Figure S164. ^1H NMR spectrum of compound 19b

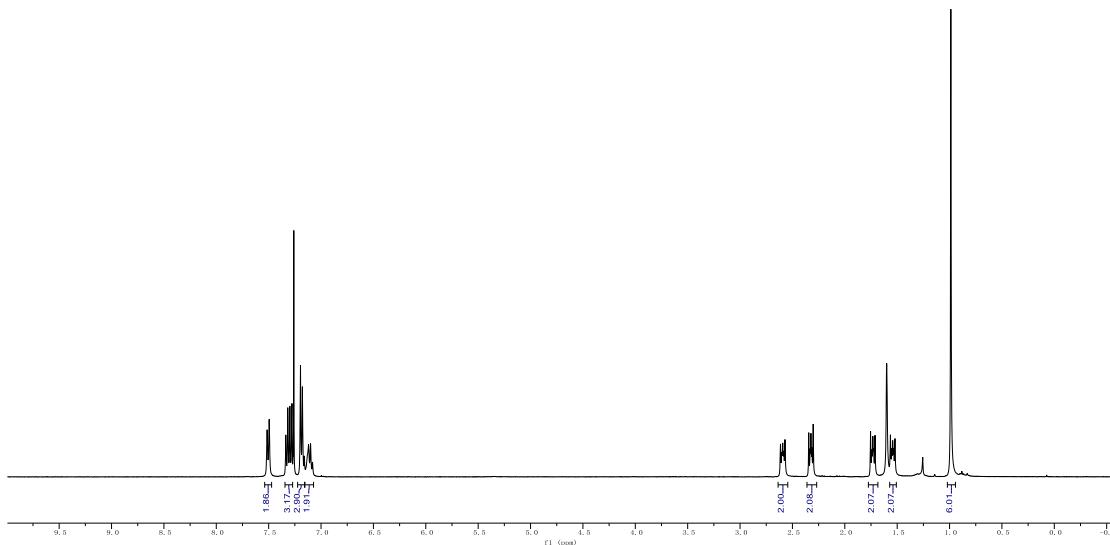
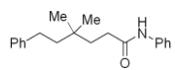


Figure S165. ^{13}C NMR spectrum of compound 19b

