Electronic Supplementary Material (ESI) for ChemComm.

A Facile Method for the Synthesis of Fused Perhydro-pyrano[2,3-*b*]pyrans Promoted by $Yb(OTf)_3$

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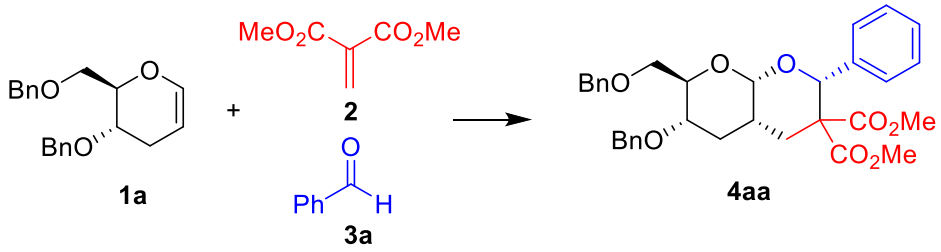
1. General information

All commercially sourced reagents were used as supplied unless otherwise stated. Thin-layer chromatography (TLC) was performed using silica gel GF254 precoated plates (0.20 mm thickness). Visualization on TLC was achieved by UV light (254 nm). Flash chromatography was performed on silica gel 90, 200-300 mesh. ^{1}H and ^{13}C NMR spectra (400 and 101 MHz, respectively) were recorded on a Bruker Avance 400 spectrometer with tetramethylsilane (TMS) as the internal standard. ESI-HRMS spectra were recorded on a BioTOF Q instrument. ECD spectra were recorded in MeOH using a Applied Photophysics *q*CD at room temperature.

2. Screening the reaction conditions

Table 1. Screening studies of reaction of 3-deoxy glycal **1a**, alkylidene malonate **2** and benzaldehyde **3a**.[a]



Entry	Lewis Acid	Solvent	T(°C)	Time(h)	Yield(%)[b]
1	$Sc(OTf)_3$	DCM	-10	12	66
2	**$Yb(OTf)_3$**	**DCM**	**-10**	**12**	**88**
3	$Zn(OTf)_2$	DCM	-10	12	ND
4	$Cu(OTf)_2$	DCM	-10	12	60
5	$InCl_3$	DCM	-10	12	36
6	$BiCl_3$	DCM	-10	12	40
7	$Yb(OTf)_3$	THF	-10	18	32
8	$Yb(OTf)_3$	$Cl_2C_2H_4$	-10	18	79
9	$Yb(OTf)_3$	CH_3CN	-10	18	46

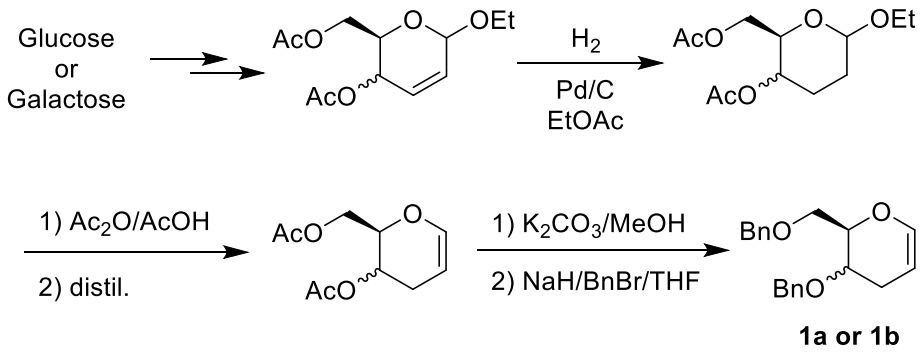
10	$Yb(OTf)_3$	Toluene	-10	18	60
11	$Yb(OTf)_3$	DCM	-20	18	85
12	$Yb(OTf)_3$	DCM	-30	18	82
13	$Yb(OTf)_3$	DCM	0	12	76
14	$Yb(OTf)_3$	DCM	r.t.	10	60
15[c]	$Yb(OTf)_3$	DCM	-10	12	51

[a] General conditions: **1a** (1.0 equiv), **2** (1.2 equiv), **3a** (1.2 equiv)，Lewis acid (0.2 equiv)，3 Å molecular sieve; [b] Isolated yield; [c] No 3 Å molecular sieve.

We began our studies by testing several readily available Lewis acids as the catalyst in the reaction (Table 1, entries 1-6). Fortunately, excellent isolated yield is observed by using 20 mol % of $Yb(OTf)_3$ as catalyst in DCM (Table 1, entry 2) at -10 °C. To improve the yield, we try to change the solvent (table 1, entries 7-10) and the temperature (Table 1, entries 11-14). To our delight, the reaction works very well in DCM at -10 °C by using 1.0 equiv of **1a**, 1.2 equiv of **2** and 1.2 equiv of **3a** under the catalysis of 20 mol% of $Yb(OTf)_3$ to give the product **4aa** in 88% (Table 1, entry 2). Finally, the lack of molecular sieve was investigated (table 1, entries 15), but the result let us disappointed because the yield are reduced. So we choose the entry 2 as the best reaction condition.

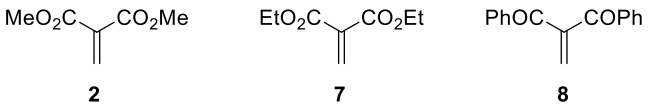
3. Synthesis of 3-deoxy glycal and alkylidene malonate

1) Synthesis of 3-deoxy glycal:[1]



1a or 1b

2) Synthesis of substrate 2, 7, 8: [2]



2 **7** **8**

Material **2, 7**: Following a modified procedure, to a mixture of a carbonyl compound (1.0 equiv) and paraformaldehyde (2.0 equiv) in dry THF is added the catalyst (1.0 equiv) and trifluoroacetic acid (0.1 equiv). The reaction mixture is stirred, open to the atmosphere, at reflux for 2 h. The mixture will become clear, then the reaction mixture is cooled down to room temperature and a second addition of paraformaldehyde (2.0 equiv) is performed. Next, the reaction mixture is stirred at reflux for an additional 6 h open to the atmosphere. The reaction mixture is cooled down and the solvent is removed under reduced pressure, dissolved in Et_2O and washed with 1N HCl, 1N NaOH, and brine. The solution mixture is dried (Na_2SO_4) and concentrated under vacuum. The crude product is purified by silica gel column chromatography using 5% EtOAc/petroleum ether as the eluent.

Material **8**: 1,3-diphenylpropane-1,3-dione (1.0 equiv), $FeCl_3 \cdot 6H_2O$ (0.1 equiv), $K_2S_2O_8$ (2.0 equiv) and DMA (solvent) were sequentially added to a tube under air. The tube was sealed and stirred at 110 ºC for 4 h. Upon completion (monitored by TLC), the resulting mixture was diluted with Et_2O and washed by brine (× 3). The organic layer was dried over Na_2SO_4, filtered, and then evaporated in vacuo, the residue was purified via column chromatography on silica gel by using petroleum ether-EtOAc as eluent to yield the desired product **8**.

4. General experimental procedure for the MCR

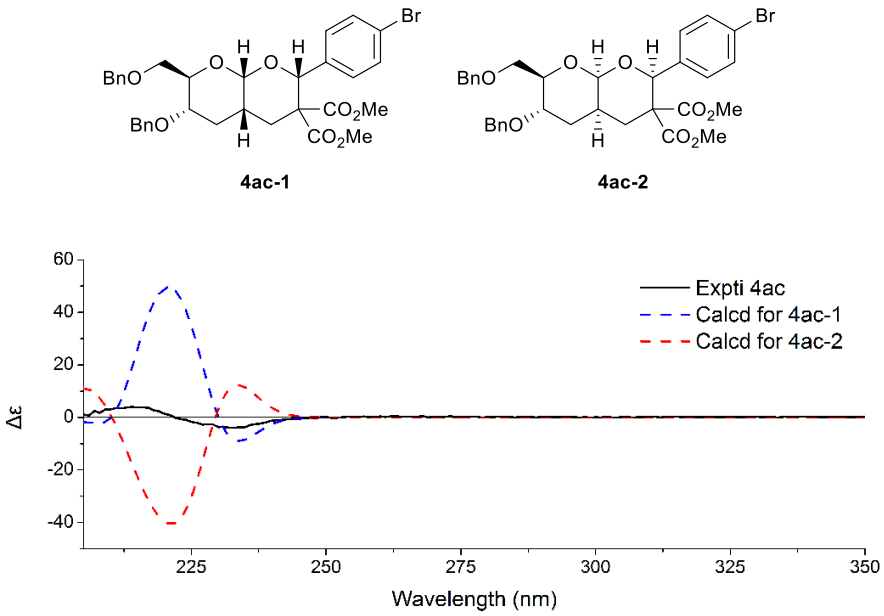
A solution of 3-deoxy glycal **1**, alkylidene malonate **2** and aldehyde **3** in dry DCM was added dropwise to a vigorously stirred solution of 20 mol% $Yb(OTf)_3$ and 3 Å in dry DCM at -10 or 0 ºC under N_2 environment. The mixture was then stirred for 12 or 20 hours and quenched with H_2O. Then the 3 Å molecular sieve was filtered out. The phases were separated and the aqueous phase extracted with DCM. The organic phases were dried over Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by silica gel chromatography with a mixture of EtOAc/petroleum ether to give the corresponding product **4**.

5. Quantum chemical ECD calculations of 4ac.

All the DFT calculations were carried out with the GAUSSIAN 09 series of programs. DFT method B3-LYP with a standard 6–31G(d) basis set (SDD2 basis set for Cu) was used for geometry optimizations. Harmonic vibrational frequency calculations were performed for all of the stationary points to confirm them as a local minimum. The polarizable continuum model (PCM) was employed to represent the actual solvent environment, and methanol was chosen in this study. Optimized geometries of ground states (S_0) were further used in TD-DFT calculation in the same level. Comparisons of the experimental and calculated spectra were done with SpecDis

software.[3] It was also used to apply a UV shift to the ECD spectra, Gaussian broadening of the excitations, and Boltzmann weighting of the spectra.

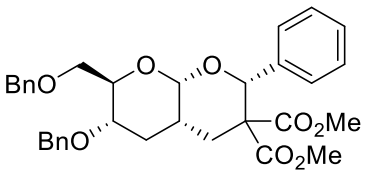
Figure 1. Experimental ECD spectra of **4ac** and calculated ECD spectra of **4ac-1** and **4ac-2.**



The calculated ECD of **4ac-1** matches very well with the experimental ECD, while the calculated ECD of its enantiomer **4ac-2** is opposite to the experimental one. So the absolute configurations were determined.

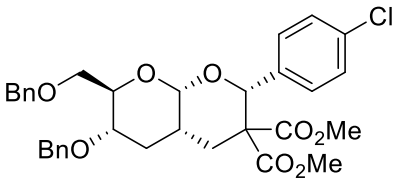
6. Characterization data of MCR products

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-phenyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4aa



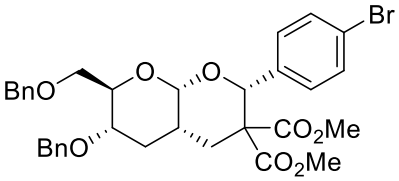
Yield: 88%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 15H), 5.11 (d, *J* = 2.5 Hz, 1H), 5.01 (s, 1H), 4.68 (d, *J* = 12.4 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 12.4 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.02 (dt, *J* = 2.0, 9.4 Hz, 1H), 3.83 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.73 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.68 (s, 3H), 3.64 (dd, *J* = 10.2, 3.7 Hz, 1H), 3.55 (s, 3H), 2.63 (qd, *J* = 14.4, 3.8 Hz, 2H), 2.18 – 2.09 (m, 1H), 2.01 (dt, *J* = 12.1, 4.1 Hz, 1H), 1.72 (dd, *J* = 24.2, 12.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.02, 169.67, 138.50, 138.27, 138.17, 128.35, 128.33, 127.65, 127.59, 127.55, 127.20, 127.15, 98.83, 81.76, 73.73, 73.53, 72.58, 70.99, 68.66, 56.67, 52.80, 51.89, 35.69, 32.59, 29.66. ESI-HRMS: m/z calcd for $C_{33}H_{36}NaO_8$ [M + Na]$^+$: 583.2302, found 583.2319.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-chlorophenyl) tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ab



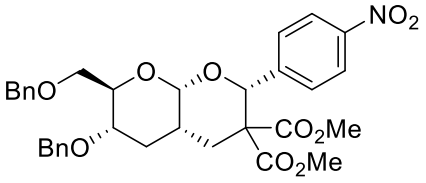
Yield: 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 10H), 7.27 (m, 4H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.95 (s, 1H), 4.64 (dd, *J* = 25.1, 12.4 Hz, 2H), 4.52 (dd, *J* = 41.1, 12.4Hz, 2H), 4.00 – 3.98 (m, 1H), 3.82 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.72 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.68 (s, 3H), 3.67 – 3.60 (m, 1H), 3.57 (s, 3H), 2.64 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.54 (dd, *J* = 14.3, 1.5 Hz, 1H), 2.16 – 2.08 (m, 1H), 2.00 (dt, *J* = 12.3, 3.9Hz, 1H), 1.68 (dd, *J* = 24.1, 12.3Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.86, 169.56, 138.43, 138.21, 136.71, 133.41, 128.62, 128.37, 128.35, 127.87, 127.64, 127.60, 127.38, 98.93, 81.21, 73.80, 73.55, 72.53, 71.04, 68.63, 56.51, 52.90, 51.97, 35.63, 32.54, 29.57. ESI-HRMS: m/z calcd for $C_{33}H_{35}ClNaO_8$ $[M + Na]^+$: 617.1913, found 617.1903.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-bromophenyl) tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ac



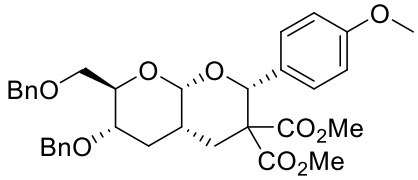
Yield: 82%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.29 (m, 10H), 7.27 – 7.25 (m, 4H), 5.09 (d, *J* = 2.4 Hz, 1H), 4.93 (s, 1H), 4.64 (dd, *J* = 25.3, 12.4 Hz, 2H), 4.52 (dd, *J* = 40.3, 12.4 Hz, 2H), 3.99 – 3.97 (m, 1H), 3.82 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.73 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.68 (s, 3H), 3.67 – 3.60 (m, 1H), 3.58 (s, 3H), 2.67 – 2.57 (m, 2H), 2.14 – 2.10 (m, 1H), 2.02 – 1,97 (dt, *J* = 12.4, 4.0 Hz, 1H), 1.67 (dd, *J* = 24.2, 12.4 Hz 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.84, 169.53, 138.42, 138.20, 137.24, 130.30, 128.95, 128.36, 128.33, 127.86, 127.63, 127.59, 121.66, 98.92, 81.23, 73.80, 73.55, 72.53, 71.03, 68.63, 56.46, 52.90, 51.97, 35.64, 32.54, 29.56. ESI-HRMS: m/z calcd for $C_{33}H_{35}BrNaO_8$ $[M + Na]^+$: 661.1408, found 661.1403.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-nitrophenyl) tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ad



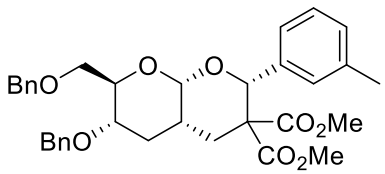
Yield: 61%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.30 (m, 8H), 7.29 – 7.25 (m, 2H), 5.12 (d, *J* = 2.6 Hz, 1H), 5.07 (s, 1H), 4.65 (dd, *J* = 24.9, 12.4 Hz, 2H), 4.53 (dd, *J* = 43.0, 12.5 Hz, 1H), 4.04 – 3.98 (m, 1H), 3.83 (dd, *J* = 10.6, 3.6 Hz, 1H), 3.75 (dd, *J* = 5.0, 1.8Hz, 1H), 3.72 (s, 3H), 3.67 – 3.61 (m, 1H), 3.58 (s, 3H), 2.75 – 2.59 (m, 2H), 2.19 -2.12 (m, 1H), 2.02 (dt, *J* = 12.2, 4.1 Hz, 1H), 1.66 (dd, *J* = 24.2, 12.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 169.26, 147.30, 145.63, 138.35, 138.15, 128.41, 128.38, 128.10, 127.89, 127.71, 127.65, 127.63, 122.41, 99.00, 80.83, 73.96, 73.58, 72.49, 71.12, 68.64, 56.56, 53.13, 52.11, 35.69, 32.49, 29.49. ESI-HRMS: m/z calcd for $C_{33}H_{35}NNaO_{10}$ $[M + Na]^+$: 628.2153, found 628.2150.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-methoxyphenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ae



Yield: 89%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 11H), 7.29 – 7.25 (m, 3H), 5.09 (d, *J* = 2.6 Hz, 1H), 4.94 (s, 1H), 4.69 – 4.45 (m, 5H), 4.01 – 3.99 (m, 1H), 3.85 – 3.80 (m, 4H), 3.72 (dd, *J* = 10.5, 1.7 Hz, 1H), 3.67 (s, 3H), 3.63 (m, 1H), 3.58 (s, 3H), 2.68 – 2.56 (m, 2H), 2.13 – 2.07 (m, 1H), 2.00 (dt, *J* = 12.3, 8.48 Hz, 1H), 1.71 (d, *J* = 24.1, 12.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.02, 169.77, 158.95, 138.49, 138.26, 130.24, 128.42, 128.35, 128.33, 127.86, 127.59, 112.57, 98.87, 81.65, 73.68, 73.52, 72.58, 70.99, 68.62, 56.62, 55.15, 52.81, 51.91, 35.59, 32.60, 29.63. ESI-HRMS: m/z calcd for $C_{33}H_{35}BrNaO_8$ $[M + Na]^+$: 661.1408, found 661.1393.

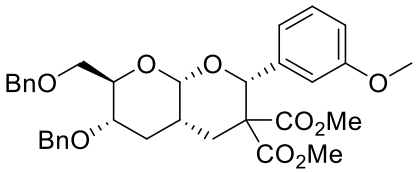
Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(m-tolyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4af



Yield: 84%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 8H), 7.29 – 7.26 (m, 3H), 7.21 (s, 1H), 7.16 (m, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 5.09 (d, *J* = 2.6 Hz, 1H), 4.96 (s, 1H), 4.65 (dd, *J* = 25.8, 12.4 Hz, 2H), 4.52 (dd, *J* = 39.9, 12.4 Hz, 2H), 4.03 (m, 1H), 3.84 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.74 (dd, *J* = 10.6, 1.6 Hz, 1H), 3.68 (s, 3H), 3.64 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.57 (s, 3H), 2.63 (qd, *J* = 14.4, 3.8 Hz, 2H), 2.35 (s, 3H), 2.17 – 2.08 (m, 1H), 2.01 (dt, *J* = 12.1, 4.1 Hz, 1H), 1.71 (dd, *J* = 24.0, 12.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.05, 169.68, 138.48, 138.26, 138.03, 136.63,

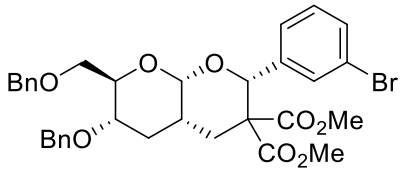
128.37, 128.35, 128.32, 127.86, 127.60, 127.55, 127.04, 124.17, 98.86, 81.81, 73.70, 73.53, 72.57, 71.02, 68.62, 56.67, 52.75, 51.88, 35.72, 32.60, 29.72, 29.64, 21.54. ESI-HRMS: m/z calcd for $C_{34}H_{38}NaO_8$ [M + Na]$^+$: 597.2459, found 597.2455.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-methoxyphenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ag



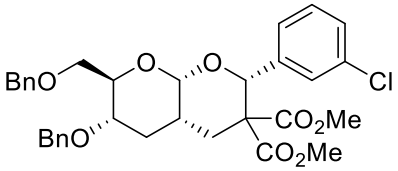
Yield: 85%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 8H), 7.25 – 7.21 (m, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 24.1 Hz, 1H), 6.88 (d, *J* = 7.7 Hz, 1H), 6.78 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.07 (d, *J* = 2.7 Hz, 1H), 4.96 (s, 1H), 4.62 (dd, *J* = 25.1, 12.4 Hz, 2H), 4.49 (dd, *J* = 25.1, 12.4 Hz, 2H), 3.98 (dt, *J* = 9.1, 2.7 Hz 1H), 3.85 – 3.79 (m, 4H), 3.70 (dd, *J* = 10.6, 1.7 Hz, 1H), 3.65 – 3.59 (m, 4H), 3.54 (s, 3H), 2.60 (qd, *J* = 21.1, 10.9, 5.1 Hz, 2H), 2.13 – 2.06 (m, 1H), 1.98 (dt, *J* = 12.3, 4.2 Hz, 1H), 1.68 (dd, *J* = 24.0, 12.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 169.59, 158.80, 139.71, 138.44, 138.26, 128.36, 128.32, 128.06, 127.86, 127.63, 127.55, 119.42, 113.23, 113.15, 98.85, 81.60, 73.72, 73.52, 72.58, 71.04, 68.62, 56.72, 55.19, 52.83, 51.92, 35.76, 32.60, 29.64. ESI-HRMS: m/z calcd for $C_{34}H_{38}NaO_9$ [M + Na]$^+$: 613.2408, found 613.2400.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-bromophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ah



Yield: 81%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 1.7 Hz, 1H), 7.36 – 7.27 (m, 10H), 7.24 – 7.22 (m, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.06 (d, *J* = 2.6 Hz, 1H), 4.91 (s, 1H), 4.61 (dd, *J* = 26.4, 12.4 Hz, 2H), 4.49 (dd, *J* = 41.9, 12.4 Hz, 2H), 3.98 (dt, *J* = 9.2, 2.4 Hz, 1H), 3.80 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.71 (dd, *J* = 10.7, 1.7 Hz, 1H), 3.67(s, 3H), 3.62 (td, *J* = 10.3, 4.1 Hz, 1H), 3.56 (s, 3H), 2.65 – 2.55 (m, 2H), 2.14 – 2.06 (m, 1H), 1.97 (dt, *J* = 12.4, 4.1 Hz, 1H), 1.4 (dd, *J* = 25.9, 12.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.83, 169.50, 140.42, 138.41, 138.21, 130.66, 130.35, 128.72, 128.38, 128.35, 127.89, 127.65, 127.63, 127.60, 125.80, 121.33, 98.98, 81.03, 73.81, 73.56, 72.49, 71.07, 68.59, 56.59, 52.96, 52.04, 35.65, 32.54, 29.57. ESI-HRMS: m/z calcd for $C_{33}H_{35}BrNaO_8$ [M + Na]$^+$: 661.1408, found 661.1393.

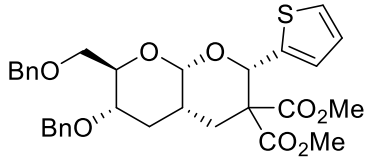
Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-chlorophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ai



Yield: 67%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.36 – 7.30 (m, 10H), 7.28 – 7.24 (m, 3H), 5.24 (s, 1H), 5.10 (d, *J* = 3.0 Hz, 1H), 4.63 (dd, *J* = 22.6, 12.4 Hz 2H), 4.56 (d, *J* = 12.4 Hz 1H), 4.49 (d, *J* = 11.6 Hz 1H), 4.00 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.82 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.72 – 3.66 (m, 2H), 3.64 (s, 3H), 3.61 (s, 3H), 2.83 (dd, *J* = 14.8, 5.4 Hz, 1H), 2.51 (dd, *J* = 14.8, 2.6 Hz, 1H), 2.20 -2.11 (m, 1H), 1.98 (dt, *J* = 12.2, 4.5 Hz, 1H), 1.71 (dd, *J* = 23.9, 12.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.80, 169.10, 138.52, 138.25, 135.20, 132.66, 129.14, 128.37, 128.33, 127.98, 127.86, 127.70, 127.62, 127.58, 125.88, 98.78, 73.77, 73.54, 72.51, 71.07, 68.63, 55.04, 53.24, 52.06, 35.48, 32.76, 29.35. ESI-HRMS: m/z calcd for $C_{33}H_{35}ClNaO_8$ $[M + Na]^+$: 617.1913, found 617.1917.

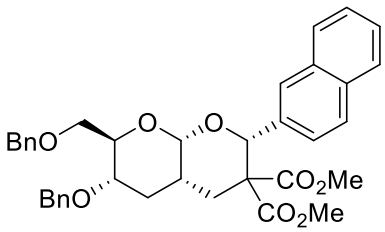
Dimethyl(2S,4aR,6S,7R,8aR)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(thiophen-2-

yl)tetrahydro-2H,5H-pyrano[2,3-b]pyran-3,3(4H)-dicarboxylate 4aj



Yield: 82%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 9H), 7.25 – 7.21 (m, 3H), 6.91 (d, *J* = 3.0 Hz, 2H), 5.26 (s, 1H), 5.08 (d, *J* = 2.0 Hz, 1H), 4.66 – 4.43 (m, 5H), 3.95 – 3.93 (m, 1H), 3.79 (m, 1H), 3.73 – 3.67 (m, 4H), 3.63 – 3.55 (m, 4H), 2.63 – 2.48 (m, 2H), 2.10 – 2.05 (m, 1H), 2.00 – 1.96 (m, 1H), 1.72 – 1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.70, 169.43, 140.79, 138.48, 138.25, 128.44, 128.37, 128.34, 127.89, 127.60, 127.58, 125.63, 125.27, 125.26, 98.95, 79.04, 73.69, 73.51, 72.46, 71.00, 68.54, 56.87, 53.02, 52.19, 35.45, 32.58, 29.72. ESI-HRMS: m/z calcd for $C_{31}H_{34}NaO_8S$ $[M + Na]^+$: 589.1867, found 589.1863.

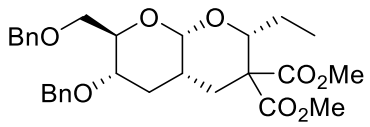
Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(naphthalene-2-yl) tetrahydro-2H,5H-pyrano[2,3-b]pyran-3,3(4H)-dicarboxylate 4ak



Yield: 69%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.73 (m, 4H), 7.67 – 7.59 (m, 1H), 7.50 – 7.44 (m, 2H), 7.41 – 7.32 (m, 7H), 7.32 – 7.29 (m, 2H), 5.19 (s, 1H), 5.18 (d, *J* = 2.6 Hz, 1H), 4.70 (d, *J* = 12.3 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H),

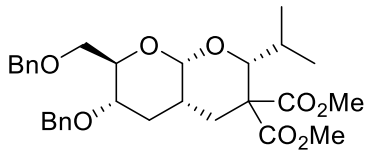
4.60 (d, *J* = 12.3 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.11 (dt, *J* = 9.4, 2.5Hz, 1H), 3.87 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.78 (dd, *J* = 10.5, 1.4 Hz, 1H), 3.73 – 3.65 (m, 4H), 3.53 (s, 3H), 2.74 (dd, *J* = 14.4, 5.2 Hz, 1H), 2.66 (dd, *J* = 14.3, 2.0 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.05 (dt, *J* = 12.1, 4.1 Hz, 1H), 1.78 (dd, *J* = 24.2, 12.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.10, 169.75, 138.48, 138.27, 135.79, 132.99, 132.63, 128.38, 128.35, 128.06, 127.89, 127.64, 127.58, 126.53, 125.94, 125.83, 125.79, 125.58, 98.99, 81.99, 73.81, 73.57, 72.62, 71.05, 68.68, 56.89, 52.88, 51.95, 35.76, 32.64, 29.67. ESI-HRMS: m/z calcd for $C_{37}H_{38}NaO_8$ $[M + Na]^+$: 633.2459, found 633.2465.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-ethyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4al



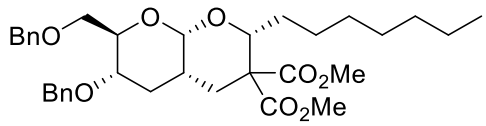
Yield: 70%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.29 (m, 8H), 7.26 - 7.21 (m, 2H), 4.90 (d, *J* = 2.4 Hz, 1H), 4.66 (d, *J* = 12.3 Hz, 1H), 4.56 (t, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 3.89 – 3.83 (dt, *J* = 9.6, 3.2 Hz, 1H), 3.81 – 3.77 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.59 (dd, *J* = 9.8, 2.2 Hz, 1H), 3.54 (dd, *J* = 9.9, 3.8 Hz, 1H), 2.50 (dd, *J* = 14.3, 1.7 Hz, 1H), 2.42 (dd, *J* = 14.3, 5.2 Hz, 1H), 2.37 – 2.25 (m, 1H), 2.05 – 1.96 (m, 1H), 1.90 (dt, *J* = 12.1, 4.0 Hz, 1H), 1.62 – 1.45 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.14, 170.36, 138.59, 138.29, 128.31, 127.90, 127.55, 127.53, 127.51, 98.74, 83.34, 73.51, 72.71, 70.81, 68.76, 55.12, 52.90, 52.09, 35.67, 32.86, 29.59, 25.07, 12.06. ESI-HRMS: m/z calcd for $C_{29}H_{36}NaO_8$ $[M + Na]^+$: 535.2302, found 535.2314.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-isopropyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4am



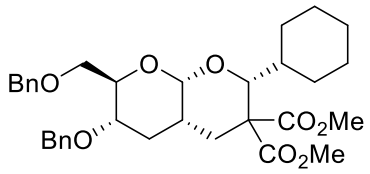
Yield: 64%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 8H), 7.26 - 7.21 (m, 2H), 4.87 (d, *J* = 2.2 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.60 - 4.62 (m, 2H), 4.43 (d, *J* = 11.6 Hz, 1H), 3.88 – 3.81 (m, 1H), 3.80 - 3.77 (m, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.71 – 3.66 (m, 1H), 3.59 – 3.49 (m, 2H), 2.66 – 2.54 (m, 2H), 2.31 (dd, *J* = 14.3, 5.2 Hz, 1H), 2.02 – 1.95 (m, 1H), 1.91 (dt, *J* = 12.3, 4.0 Hz, 1H), 1.51 (dd, *J* = 24.4, 12.2 Hz, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.03, 170.16, 138.56, 138.31, 128.32, 128.32, 127.92, 127.56, 98.67, 86.70, 77.38, 77.06, 76.75, 73.47, 73.38, 72.77, 70.87, 68.78, 54.32, 52.74, 52.04, 36.87, 32.89, 31.40, 29.62, 20.81, 19.15. ESI-HRMS: m/z calcd for $C_{30}H_{38}NaO_8$ $[M + Na]^+$: 549.2459, found 549.2463.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-hepty-ltetrahydro-2H,5H-pyrano[2,3-b]pyran-3,3(4H)-dicarboxylate 4ao



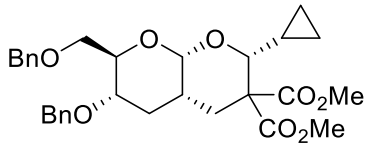
Yield: 78%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 8H), 7.26 – 7.21 (m, 2H), 4.90 (d, *J* = 2.5 Hz, 1H), 4.66 (d, *J* = 12.3 Hz, 1H), 4.56 (t, *J* = 12.1 Hz, 2H), 4.44 (d, *J* = 11.7 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.81 – 3.76 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.70 (dd, *J* = 10.6, 1.8 Hz, 1H), 3.65 (dd, *J* = 9.7, 1.8 Hz, 1H), 3.55 (td, *J* = 10.8, 4.0 Hz, 1H), 2.50 (dd, *J* = 14.3, 2.0 Hz, 1H), 2.43 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.06 – 1.95 (m, 1H), 1.89 (dt, *J* = 12.0, 4.0 Hz, 1H), 1.64 - 1.60 (m, 1H), 1.54 - 1.44 (m, 2H), 1.41 – 1.14 (m, 10H), 0.90 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.09, 170.39, 138.59, 138.28, 128.30, 127.89, 127.53, 127.51, 127.49, 98.68, 81.73, 73.49, 72.69, 70.80, 68.73, 55.20, 52.88, 52.08, 35.65, 32.82, 31.92, 31.85, 29.57, 29.35, 29.18, 27.40, 22.68, 14.13. ESI-HRMS: m/z calcd for $C_{34}H_{46}NaO_8$ [M + Na]$^+$: 605.3085, found 605.3093.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-cyclo-hexyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ap



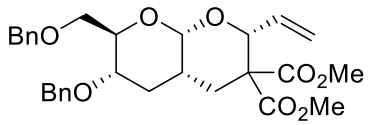
Yield: 75%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 8H), 7.23 (d, *J* = 6.8 Hz, 2H), 4.85 (d, *J* = 2.0 Hz, 1H), 4.65 (d, *J* = 12.3 Hz, 1H), 4.56 (t, *J* = 12.8 Hz, 2H), 4.43 (d, *J* = 11.7 Hz, 1H), 3.85 - 3.80 (m, 1H), 3.80 – 3.74 (m, 4H), 3.74 – 3.66 (m, 4H), 3.59 (d, *J* = 8.0 Hz, 1H), 3.53 (td, *J* = 10.5, 3.9 Hz, 1H), 2.56 (d, *J* = 14.1 Hz, 1H), 2.29 (dd, *J* = 14.1, 5.2 Hz, 2H), 2.22 - 2.16 (m, 1H), 2.00 - 1.94 m, 1H), 1.90 (dt, *J* = 12.0, 3.9 Hz, 1H), 1.75 - 1.64 m, 4H), 1.54 – 1.48 (m, 1H), 1.31 – 1.24 (m, 2H), 1.19 – 1.10 (m, 1H), 1.02 – 0.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.95, 170.18, 138.59, 138.29, 128.30, 127.91, 127.53, 127.50, 98.66, 85.72, 73.47, 73.38, 72.75, 70.81, 68.76, 54.15, 52.75, 52.02, 41.02, 36.87, 32.94, 30.62, 29.61, 29.42, 26.58, 26.47, 26.10. ESI-HRMS: m/z calcd for $C_{33}H_{42}NaO_8$ [M + Na]$^+$: 589.2772, found 589.2782.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-cyclo-propyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4aq



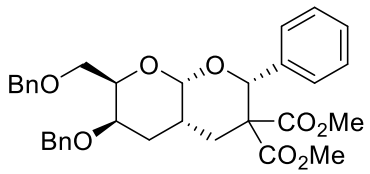
Yield: 71%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 8H), 7.26 - 7.20 (m, 2H), 4.85 (d, *J* = 2.4 Hz, 1H), 4.66 (d, *J* = 12.3 Hz, 1H), 4.59 - 4.52 m, 2H), 4.45 (d, *J* = 11.7 Hz, 1H), 3.91 - 3.86 (m, 1H), 3.81 - 3.77 (m, 4H), 3.75 (s, 3H), 3.70 (dd, *J* = 10.7, 1.5 Hz, 1H), 3.58 (td, *J* = 10.3, 4.1 Hz, 1H), 2.74 (d, *J* = 9.7 Hz, 1H), 2.46 (d, *J* = 3.6 Hz, 2H), 2.08 – 1.96 (m, 2H), 1.88 (dt, *J* = 11.9, 4.0 Hz, 1H), 1.53 – 1.43 (m, 1H), 0.70 - 0.63 (m, 1H), 0.55 – 0.47 (m, 1H), 0.37 - 0.31 (m, 1H), 0.08 - 0.03(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90 (s), 170.55 (s), 138.61 (s), 138.28 (s), 128.32 (s), 127.88 (s), 127.64 – 127.40 (m), 98.99 (s), 86.56 (s), 73.61 (d, *J* = 12.5 Hz), 72.59 (s), 70.87 (s), 68.63 (s), 55.04 (s), 52.85 (s), 52.18 (s), 35.50 (s), 32.74 (s), 29.53 (s), 12.22 (s), 3.91 (s), 3.59 (s). ESI-HRMS: m/z calcd for $C_{30}H_{36}NaO_8$ [M + Na]$^+$: 547.2302, found 547.2324.

Dimethyl(2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-vinyl-tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ar



Yield: 61%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 8H), 7.25 - 7.21 (m, 2H), 6.51 – 6.39 (m, 1H), 5.18 (dd, *J* = 14.1, 6.7 Hz, 2H), 4.99 (d, *J* = 2.4 Hz, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.56 (t, *J* = 10.1 Hz, 2H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.23 (d, *J* = 7.4 Hz, 1H), 3.88 (dt, *J* =3.1, 9.5 Hz, 1H), 3.81 – 3.77 (m, 1H), 3.76 (s, 3H), 3.75 – 3.70 (m, 1H), 3.70 (s, 3H), 3.58 (td, *J* = 10.5, 4.1 Hz, 1H), 2.58 – 2.47 (m, 2H), 2.08 – 1.99 (m, 1H), 1.91 (dt, *J* = 12.1, 4.1 Hz, 1H), 1.50 (dd, *J* = 24.3, 12.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.43, 170.06, 138.54, 138.27, 135.10, 128.41, 128.33, 128.32, 127.84, 127.67, 127.56, 127.54, 127.51, 127.48, 117.35, 98.41, 82.70, 73.65, 73.51, 72.56, 70.91, 68.58, 56.25, 52.82, 52.22, 34.92, 32.54, 29.49. ESI-HRMS: m/z calcd for $C_{29}H_{34}NaO_8$ [M + Na]$^+$: 533.2146, found 533.2146.

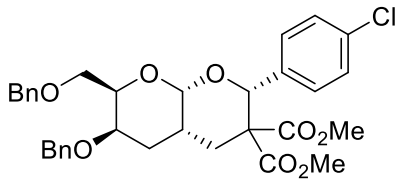
Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-phenyltet-rahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4ba



Yield: 69%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 - 7,36 (m, 2H), 7.35 - 7.25 (m, 13H), 5.16 (d, *J* = 1.9 Hz, 1H), 5.00 (s, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.59 (d, *J* = 11.8 Hz, 1H), 4.49 (t, *J* = 11.5 Hz, 1H), 4.27 (t, *J* = 6.5 Hz, 1H), 3.75 – 3.70 (m, 2H), 3.68 (s, 3H), 3.68 – 3.63 (m, 1H), 3.57 (s, 3H), 2.67 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.55 (dd, *J* = 14.4, 1.5 Hz, 1H), 2.50 – 2.38 (m, 1H), 1.92 (dt, *J* = 13.6, 3.6 Hz, 1H), 1.80 (td, *J* = 13.8, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.99, 170.01, 138.37, 138.22, 138.18, 128.38, 127.85, 127.80, 127.69, 127.64, 127.18, 99.39,

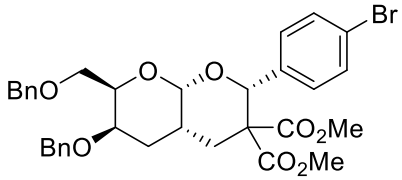
81.69, 73.49, 71.52, 71.20, 70.95, 69.22, 56.63, 52.77, 51.86, 35.79, 27.24, 26.30. ESI-HRMS: m/z calcd for $C_{33}H_{36}NaO_8$ $[M + Na]^+$: 583.2302, found 583.2313.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-chlorophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bb



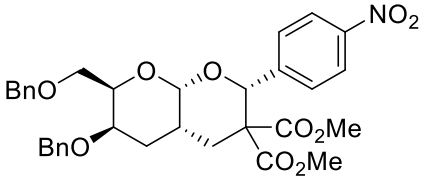
Yield: 72%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 14H), 5.14 (d, *J* = 2.0 Hz, 1H), 4.93 (s, 1H), 4.62 (dd, *J* = 32.5, 11.9 Hz, 2H), 4.46 (t, *J* = 12.6 Hz, 2H), 4.23 (t, *J* = 6.5 Hz, 1H), 3.71 – 3.69 (m, 2H), 3.67 (s, 3H), 3.66 – 3.63 (m, 1H), 3.58 (s, 3H), 2.64 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.54 (dd, *J* = 14.3, 1.5 Hz, 1H), 2.49 – 2.39 (m, 1H), 1.90 (dt, *J* = 14.0, 3.34 Hz, 1H), 1.75 (td, *J* = 13.7, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.83, 169.89, 138.29, 138.11, 136.76, 133.37, 128.65, 128.40, 127.88, 127.81, 127.74, 127.69, 127.36, 99.48, 81.12, 73.53, 71.62, 71.21, 70.88, 69.21, 56.49, 52.89, 51.96, 35.73, 27.19, 26.19. ESI-HRMS: m/z calcd for $C_{33}H_{35}ClNaO_8$ $[M + Na]^+$: 617.1913, found 617.1910.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-bromophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bc



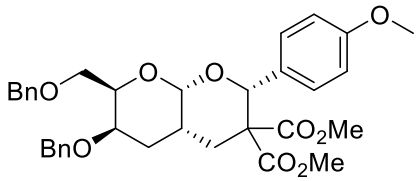
Yield: 64%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.28 (m, 12H), 5.14 (d, *J* = 1.8 Hz, 1H), 4.92 (s, 1H), 4.62 (dd, *J* = 32.2, 11.9 Hz, 2H), 4.47 (t, *J* = 12.9 Hz, 2H), 4.23 (t, *J* = 6.4 Hz, 1H), 3.71 – 3.69 (m, 2H), 3.67 (s, 3H), 3.64 (dd, *J* = 9.3, 5.9 Hz, 1H), 3.58 (s, 3H), 2.64 (dd, *J* = 14.6, 5.4 Hz, 1H), 2.54 (dd, *J* = 14.3, 1.4 Hz, 1H), 2.50 – 2.38 (m, 1H), 1.90 (dt, *J* = 10.4, 3.4 Hz,1H), 1.74 (td, *J* = 13.7, 1.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.82, 169.88, 138.29, 138.10, 137.29, 130.30, 128.99, 128.40, 127.88, 127.81, 127.74, 127.70, 121.64, 99.48, 81.15, 73.53, 71.62, 71.21, 70.88, 69.21, 56.44, 52.90, 51.97, 35.74, 27.18, 26.18. ESI-HRMS: m/z calcd for $C_{33}H_{35}BrNaO_8$ $[M + Na]^+$: 661.1408, found 661.1395.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-nitrophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bd



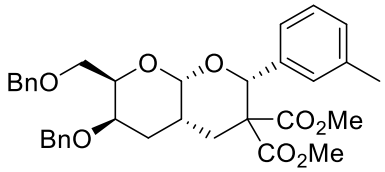
Yield: 58%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.28 (m, 10H), 5.14 (d, *J* = 2.2 Hz, 1H), 5.03 (s, 1H), 4.64 (dd, *J* = 29.6, 11.9 Hz, 2H), 4.45 (dd, *J* = 14.4, 12.0 Hz, 2H), 4.22 (t, *J* = 6.6 Hz, 1H), 3.75 – 3.70 (m, 1H), 3.69 (s, 3H), 3.67 – 3.62 (m, 2H), 3.56 (s, 3H), 2.65 (dd, *J* = 14.5, 5.2 Hz, 1H), 2.56 (dd, *J* = 14.5, 2.0 Hz, 1H), 2.50 – 2.40 (m, 1H), 1.89 (dt, *J* = 13.9, 3.6 Hz, 1H), 1.70 (td, *J* = 13.8, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.64, 169.58, 147.27, 145.65, 138.19, 138.02, 128.42, 128.11, 127.89, 127.81, 127.74, 122.40, 99.55, 80.73, 73.57, 71.82, 71.26, 70.82, 69.23, 56.54, 53.11, 52.09, 35.77, 27.13, 26.12. ESI-HRMS: m/z calcd for $C_{33}H_{35}NNaO_{10}$ $[M + Na]^+$: 628.2153, found 628.2150.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(4-methoxyphenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4be



Yield: 84%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 12H), 6.83 – 6.79 (m, 2H), 5.12 (d, *J* = 2.4 Hz, 1H), 4.90 (s, 1H), 4.60 (dd, *J* = 35.4, 11.9 Hz, 2H), 4.45 (t, *J* = 11.0 Hz, 2H), 4.27 – 4.19 (m, 1H), 3.79 (s, 3H), 3.71 – 3.66 (m, 2H), 3.64 (s, 3H), 3.63 – 3.59 (m, 1H), 3.57 (s, 3H), 2.63 (dd, *J* =14.5, 5.5 Hz, 1H), 2.50 (dd, *J* =14.5, 2.1 Hz, 1H), 2.46 – 2.36 (m, 1H), 1.88 (dt, *J* = 13.9, 3.8 Hz, 1H), 1.76 (td, *J* = 13.7, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.00, 170.12, 158.93, 138.37, 138.17, 130.29, 128.45, 128.38, 127.85, 127.80, 127.69, 127.65, 112.55, 99.42, 73.48, 71.46, 71.18, 70.93, 69.19, 56.60, 55.15, 52.78, 51.89, 35.69, 27.24, 26.25. ESI-HRMS: m/z calcd for $C_{34}H_{38}NaO_9$ $[M + Na]^+$: 613.2408, found 613.2386.

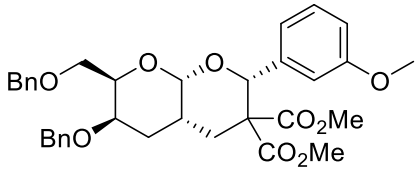
Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(m-tolyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bf



Yield: 76%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 10H), 7.26 – 7.15 (m, 3H), 7.10 – 7.06 (m, 1H), 5.15 (d, *J* = 2.4 Hz, 1H), 4.96 (s, 1H), 4.64 (dd, *J* = 33.2, 11.9 Hz, 2H), 4.49 (t, *J* = 11.5 Hz, 2H), 4.31 – 4.26 (m, 1H), 3.75 – 3.70 (m, 2H), 3.70 – 3.64 (m, 4H), 3.59 (s, 3H), 2.68 (dd, *J* = 14.5, 5.5 Hz, 1H), 2.54 (dd, *J* = 14.5, 2.1 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.37 (s, 3H), 1.92 (dt, *J* = 13.9, 3.5 Hz, 1H), 1.80 (td, *J* = 13.7, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.02, 170.04, 138.39, 138.18, 138.08, 136.62, 128.39, 127.89, 127.86, 127.80, 127.69, 127.66, 127.04, 124.23, 99.42, 81.75, 73.50, 71.49, 71.20, 70.94, 69.18, 56.64, 52.73, 51.86, 35.84, 27.25,

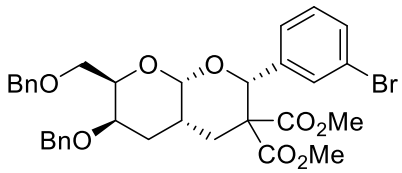
26.28, 21.57. ESI-HRMS: m/z calcd for $C_{34}H_{38}NaO_8$ [M + Na]$^+$: 597.2459, found 597.2441.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-methoxyphenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bg



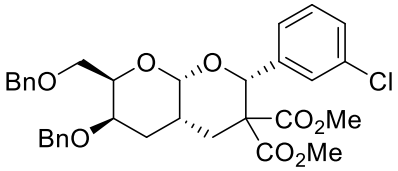
Yield: 73%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 10H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.06 (t, *J* = 2.1 Hz,1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.15 (d, *J* = 2.2 Hz, 1H), 4.98 (s, 1H), 4.64 (dd, *J* = 36.3, 12.0 Hz, 2H), 4.49 (dd, *J* = 11.6, 9.8 Hz, 2H), 4.27 (t, *J* = 6.6 Hz, 1H), 3.83 (s, 3H), 3.74 – 3.70 (m, 2H), 3.69 (s, 3H), 3.65 (dd, *J* = 9.6, 5.7 Hz, 1H), 3.59 (s, 3H), 2.66 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.55 (dd, *J* = 14.4, 1.8 Hz, 1H), 2.50 – 2.39 (m, 1H), 1.92 (dt, *J* = 13.8, 3.6 Hz, 1H), 1.80 (td, *J* = 13.7, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.00, 169.95, 158.79, 139.76, 138.36, 138.15, 128.39, 128.07, 127.87, 127.82, 127.70, 127.67, 119.50, 113.35, 113.01, 99.41, 81.54, 73.49, 71.49, 71.19, 70.87, 69.13, 56.67, 55.22, 52.84, 51.93, 35.88, 27.24, 26.26. ESI-HRMS: m/z calcd for $C_{34}H_{38}NaO_9$ [M + Na]$^+$: 613.2408, found 613.2420.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-bromophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bh



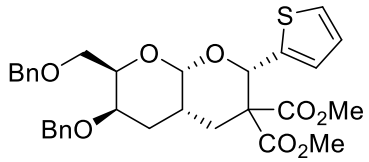
Yield: 61%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 1.9 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.35 – 7.27 (m, 11H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.12 (d, *J* = 2.2 Hz, 1H), 4.91 (s, 1H), 4.61 (dd, *J* = 27.5, 11.9 Hz, 2H), 4.46 (dd, *J* = 15.3, 11.9 Hz, 2H), 4.25 – 4.20 (m, 1H), 3.71 – 3.61 (m, 6H), 3.57 (s, 3H), 2.63 (dd, *J* = 14.6, 5.4 Hz, 1H), 2.52 (dd, *J* = 14.4, 1.9 Hz, 1H), 2.47 – 2.37 (m, 1H), 1.88 (dt, *J* = 13.9, 3.6 Hz, 1H), 1.73 (td, *J* = 13.7, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.80, 169.81, 140.48, 138.31, 138.12, 130.64, 130.39, 128.71, 128.40, 127.89, 127.80, 127.73, 127.69, 125.83, 121.34, 99.52, 80.95, 73.54, 71.62, 71.23, 70.89, 69.17, 56.58, 52.93, 52.00, 35.74, 27.18, 26.23. ESI-HRMS: m/z calcd for $C_{33}H_{35}BrNaO_8$ [M + Na]$^+$: 661.1408, found 661.1394.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-chlorophenyl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bi



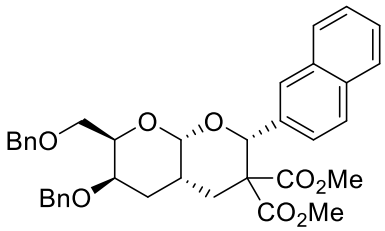
Yield: 62%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.26 (m, 12H), 7.25 – 7.17 (m, 2H), 5.18 (s, 1H), 5.11 (d, *J* = 1.4 Hz, 1H), 4.59 (dd, *J* = 39.5, 12.0 Hz, 2H), 4.45 (dd, *J* = 11.8, 6.2 Hz, 2H), 4.22 (t, *J* = 6.4 Hz, 1H), 3.71 – 3.65 (m, 2H), 3.63 – 3.56 (m, 7H), 2.81 (dd, *J* = 15.2, 5.7 Hz, 1H), 2.48 – 2.38 (m, 2H), 1.87 (dt, *J* = 13.4, 3.1 Hz, 1H), 1.75 (td, *J* = 13.4, 0.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.14, 169.02, 138.29, 138.11, 135.16, 132.76, 132.70, 129.10, 128.38, 128.37, 127.93, 127.84, 127.80, 127.71, 127.64, 125.84, 99.39, 73.49, 71.50, 71.23, 70.75, 69.11, 54.86, 53.23, 52.05, 35.60, 27.44, 25.79. ESI-HRMS: m/z calcd for $C_{33}H_{35}ClNaO_8$ $[M + Na]^+$: 617.1913, found 617.1921.

Dimethyl(2S,4aR,6R,7R,8aR)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(thiophen-2-yl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bj



Yield: 71%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 10H), 7.24 (dd, *J* = 4.1, 2.2 Hz, 1H), 6.92 – 6.88 (m, 2H), 5.25 (s, 1H), 5.13 (d, *J* = 2.4 Hz, 1H), 4.59 (dd, *J* = 33.8, 11.9 Hz, 2H), 4.45 (dd, *J* = 11.6, 9.8 Hz, 2H), 4.23 – 4.17 (m, 1H), 3.70 – 3.64 (m, 5H), 3.64 – 3.59 (m, 4H), 2.60 – 2.48 (m, 2H), 2.45 – 2.36 (m, 1H), 1.88 (dt, *J* = 13.9, 3.8 Hz, 1H), 1.74 (td, *J* = 13.7, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.67, 169.76, 140.80, 138.33, 138.15, 128.39, 128.38, 127.85, 127.81, 127.71, 127.64, 125.61, 125.29, 125.27, 99.49, 78.97, 73.42, 71.42, 71.21, 70.84, 69.07, 56.84, 53.01, 52.18, 35.52, 27.22, 26.30. ESI-HRMS: m/z calcd for $C_{31}H_{34}NaO_8S$ $[M + Na]^+$: 589.1867, found 589.1869.

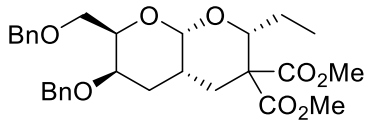
Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(naphthaalene-2-yl)tetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bk



Yield: 63%, colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.73 (m, 4H), 7.62 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.37 – 7.27 (m, 10H), 5.21 (d, *J* = 2.4 Hz, 1H), 5.15 (s, 1H), 4.64 (dd, *J* = 33.2, 11.9 Hz, 2H), 4.48 (t, *J* = 11.8 Hz, 2H), 4.36 – 4.30 (m, 1H), 3.77 – 3.70 (m, 2H), 3.69 – 3.66 (m, 1H), 3.65 (s, 3H), 3.52 (s, 3H), 2.72 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.58 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.52 – 2.43 (m, 1H), 1.93 (dt,

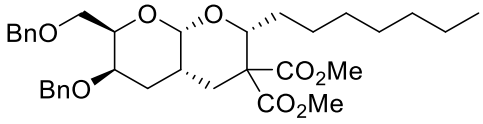
J = 13.9, 3.8 Hz, 1H), 1.82 (td, *J* = 13.7, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.08, 170.10, 138.37, 138.16, 135.82, 132.99, 132.64, 128.42, 128.09, 127.90, 127.84, 127.74, 127.70, 127.63, 126.51, 125.97, 125.83, 125.80, 125.62, 99.55, 81.91, 73.55, 71.61, 71.22, 70.94, 69.23, 56.86, 52.88, 51.95, 35.86, 27.28, 26.28. ESI-HRMS: m/z calcd for $C_{37}H_{38}NaO_8$ [M + Na]$^+$: 633.2459, found 633.2449.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-ethyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bl



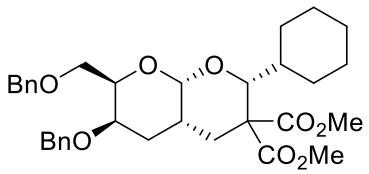
Yield: 61%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 10H), 4.95 (d, *J* = 1.3 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.45 (dd, *J* = 16.3, 11.9 Hz, 1H), 4.10 (t, *J* = 6.4 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.66 - 3.61 (m, 3H), 3.59 (dd, *J* = 9.7, 1.9 Hz, 1H), 2.50 – 2.37 (m, 2H), 2.36 – 2.24 (m, 2H), 1.80 (dt, *J* = 13.8, 3.5 Hz, 1H), 1.64 – 1.53 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.14, 170.68, 138.37, 138.23, 128.35, 128.32, 127.82, 127.66, 127.57, 99.21, 83.13, 73.38, 71.29, 71.10, 71.06, 69.36, 55.13, 52.88, 52.06, 35.64, 27.41, 26.20, 25.08, 12.06, 1.03. ESI-HRMS: m/z calcd for $C_{29}H_{36}NaO_8$ [M + Na]$^+$: 535.2302, found 535.2313.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-heptyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bo



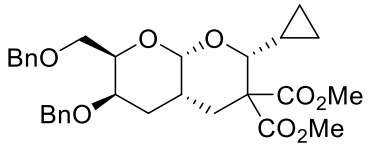
Yield: 60%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 4.94 (d, *J* = 1.8 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.42 (d, *J* = 12 Hz, 1H), 4.10 (t, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.66 – 3.59 (m, 4H), 2.49 – 2.39 (m, 2H), 2.36 – 2.23 (m, 2H), 1.80 (dt, *J* = 13.6, 3.5 Hz, 1H), 1.62 – 1.54 (m, 1H), 1.53 – 1.44 (m, 1H), 1.36 - 1.18 (s, 10H), 0.90 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.11, 170.72, 138.37, 138.23, 128.34, 128.32, 127.82, 127.66, 127.57, 99.16, 81.54, 73.38, 71.26, 71.10, 71.06, 69.34, 55.21, 52.86, 52.05, 35.62, 31.98, 31.86, 29.41, 29.19, 27.40, 27.36, 26.17, 22.68, 14.12. ESI-HRMS: m/z calcd for $C_{34}H_{46}NaO_8$ [M + Na]$^+$: 605.3085, found 605.3102.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-cyclohexyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bp



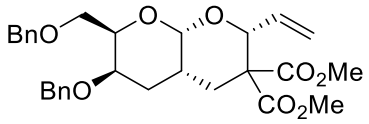
Yield: 57%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 10H), 4.90 (s, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.45 (dd, *J* = 15.6, 11.9 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.65 – 3.58 (m, 4H), 2.52 (q, *J* = 4.0 Hz, 1H), 2.34 – 2.17 (m, 4H), 1.82 (dt, *J* = 14.1, 6.8 Hz, 1H), 1.77 - 1.62 (m, 4H), 1.61 - 1.50 (m, 2H), 1.29 – 1.08 (m, 3H), 1.04 – 0.84 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.96, 170.53, 138.40, 138.24, 128.34, 128.32, 127.84, 127.81, 127.65, 127.58, 99.18, 85.52, 73.38, 71.23, 71.11, 71.08, 69.44, 54.20, 52.73, 52.02, 41.07, 36.90, 30.60, 29.49, 27.49, 26.61, 26.48, 26.24, 26.12. ESI-HRMS: m/z calcd for $C_{33}H_{42}NaO_8$ $[M + Na]^+$: 589.2772, found 589.2782.

Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-cyclopropyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4bq



Yield: 70%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 10H), 4.90 (d, *J* = 2.1 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.50 – 4.41 (m, 21H), 4.14 (t, *J* = 6.6 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.68 – 3.58 (m, 3H), 2.75 (d, *J* = 9.6 Hz, 1H), 2.44 (qd, *J* = 14.4, 3.6 Hz, 2H), 2.35 – 2.28 (m, 1H), 2.07 – 1.96 (m, 1H), 1.79 (dt, *J* = 13.7, 3.7 Hz, 1H), 1.55 (td, *J* = 13.6, 1.9 Hz, 1H), 0.70 - 0.59 (m, 1H), 0.55 - 0.45 (m, 1H), 0.41 - 0.32 (m, 1H), 0.11 – 0.01 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.90, 170.86, 138.37, 138.21, 128.34, 128.32, 127.80, 127.80, 127.66, 127.58, 99.43, 86.37, 73.40, 71.25, 71.18, 70.88, 69.03, 55.05, 52.82, 52.13, 35.48, 27.29, 26.08, 12.21, 3.86, 3.62. ESI-HRMS: m/z calcd for $C_{30}H_{36}NaO_8$ $[M + Na]^+$: 547.2302, found 547.2325.

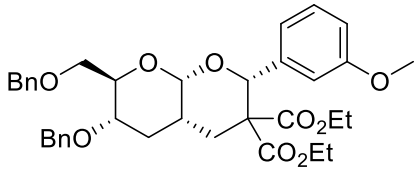
Dimethyl(2R,4aR,6R,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-vinyltetrahydro-2H,5H-pyrano[2,3-*b*]pyran-3,3(4H)-dicarboxylate 4br



Yield: 51%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 10H), 6.50 – 6.37 (m, 1H), 5.23 – 5.13 (m, 2H), 5.04 (d, *J* = 2.4 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.51 – 4.40 (m, 2H), 4.23 (d, *J* = 7.3 Hz, 1H), 4.17 – 4.10 (m, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.68 - 3.56 (m, 3H), 2.53 (dd, *J* = 14.4, 5.3 Hz, 1H), 2.46 (dd, *J* = 14.4, 2.2 Hz, 1H), 2.41 – 2.32 (m, 1H), 1.82 (dt, *J* = 13.7, 3.6

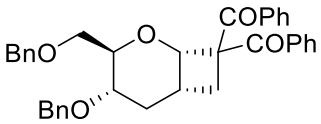
Hz, 1H), 1.58 (td, *J* = 13.7, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.42, 170.36, 138.34, 138.19, 135.08, 128.35, 128.33, 127.79, 127.77, 127.67, 127.59, 117.32, 98.89, 82.49, 73.39, 71.32, 71.17, 70.89, 69.09, 56.22, 52.80, 52.18, 34.91, 27.13, 26.12. ESI-HRMS: m/z calcd for $C_{29}H_{34}NaO_8$ [M + Na]$^+$: 533.2146, found 533.2151.

Diethyl (2R,4aR,6S,7R,8aS)-6-(benzyloxy)-7-((benzyloxy)methyl)-2-(3-methoxyphenyl)tetrahydro-2H,5H-pyrano[2,3-b]pyran-3,3(4H)-dicarboxylate 9



Yield: 72%, colorless oil. ^{1}H NMR (400 MHz, CDCl3) δ 7.35 – 7.22 (m, 10H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.77 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.06 (d, *J* = 2.6 Hz, 1H), 5.00 (s, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.56 (dd, *J* = 21.0, 11.9 Hz, 2H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.22 – 4.07 (m, 2H), 4.05 – 3.91 (m, 3H), 3.80 (dd, *J* = 10.7, 3.4 Hz, 1H), 3.77 (s, 3H), 3.70 (dd, *J* = 10.6, 1.7 Hz, 1H), 3.62 (td, *J* = 10.6, 4.1 Hz, 1H), 2.63 – 2.49 (m, 2H), 2.14 – 2.04 (m, 1H), 2.00 (dt, *J* = 12.0, 4.1 Hz, 1H), 1.79 (dd, *J* = 24.1, 12.5 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.79, 169.16, 158.72, 139.97, 138.43, 138.27, 128.36, 128.33, 127.98, 127.88, 127.67, 127.62, 127.55, 119.62, 113.38, 112.91, 98.77, 81.39, 73.68, 73.52, 72.57, 71.00, 68.62, 61.91, 60.85, 56.70, 55.19, 35.62, 32.64, 29.81, 13.83, 13.72. ESI-HRMS: m/z calcd for $C_{36}H_{42}NaO_9$ [M + Na]$^+$: 641.2721, found 641.2726.

((1S,3R,4S,6R)-4-(Benzyloxy)-3-((benzyloxy)methyl)-2-oxabicyclo[4.2.0]octane-8,8-diyl)bis(phenylmethanone) 10

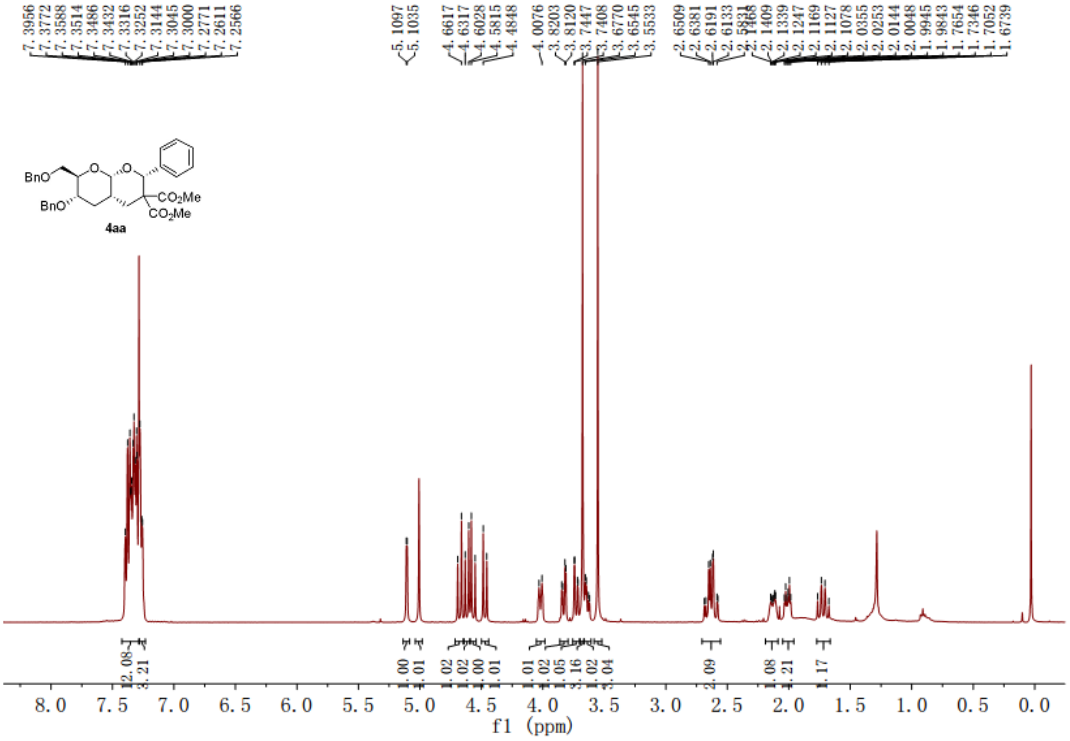


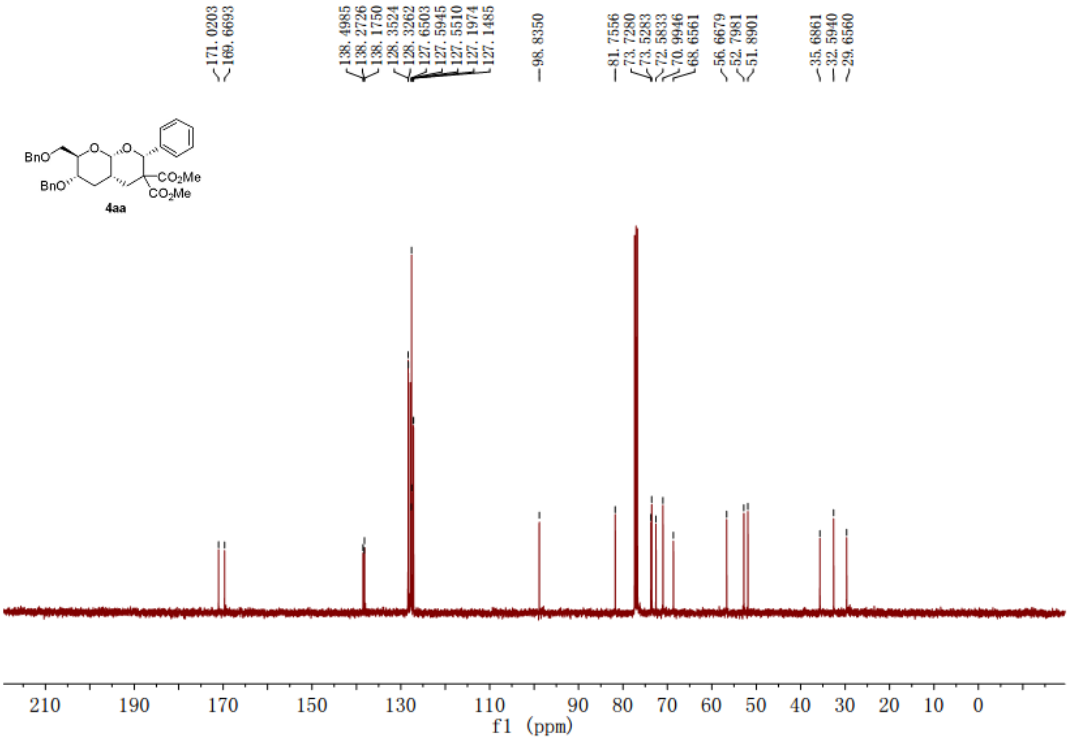
Yield: 72%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.42 – 7.30 (m, 8H), 7.27 – 7.20 (m, 5H), 7.15 – 7.02 (m, 5H), 5.60 (d, *J* = 2.5 Hz, 1H), 4.70 (d, *J* = 12.3 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.58 (d, *J* = 12.3 Hz, 1H), 4.46 (d, *J* = 11.3 Hz, 1H), 3.99 – 3.92 (m, 1H), 3.86 – 3.73 (m, 3H), 2.78 – 2.72 (m, 2H), 2.42 – 2.34 (m, 1H), 2.21 (dt, *J* = 12.0, 4.2 Hz, 1H), 1.75 (dd, *J* = 24.2, 12.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.41, 158.16, 138.79, 138.15, 138.05, 134.65, 131.59, 129.46, 129.42, 129.25, 128.43, 128.39, 127.94, 127.79, 127.77, 127.72, 127.66, 109.38, 96.82, 73.55, 72.94, 71.85, 71.18, 68.56, 31.01, 29.51, 29.34. ESI-HRMS: m/z calcd for $C_{33}H_{36}NaO_5$ [M + Na]$^+$: 569.2298, found 569.2305.

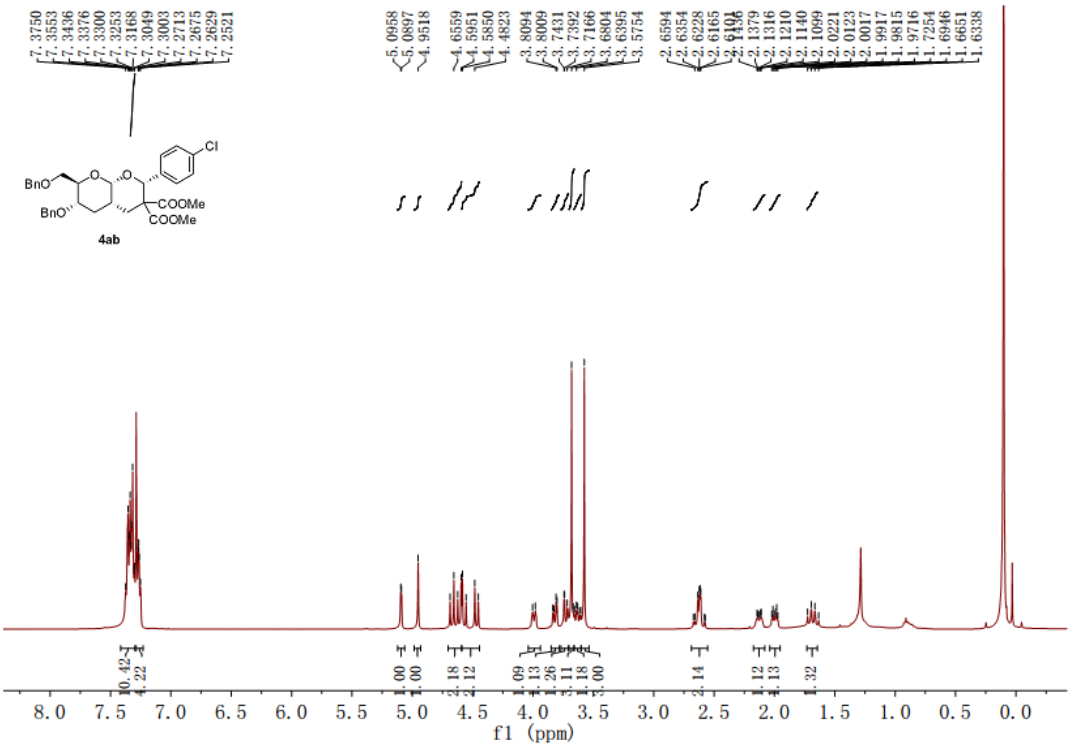
7. Notes and References

[1]. M. Okakbe and R. C. Sun, *Tetrahedron Lett.*, 1989, **30**, 2203.
[2]. a) A. Bugarin, K. D. Jones, B. T. Connell, *Chem. Commun.,* 2010**, 46**, 1715; b) Y. M. Li, S. J. Lou, Q. H. Zhou, L. W. Zhu, L. F. Zhu and L. Li, *Eur. J. Org. Chem.*, 2015, 3044.
[3]. a) T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann, Version 1.61 ed.; University of Würzburg: Würzburg, Germany, 2013; b) T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Bringmann, *Chirality* 2013, **25**, 243.

8. NMR spectra



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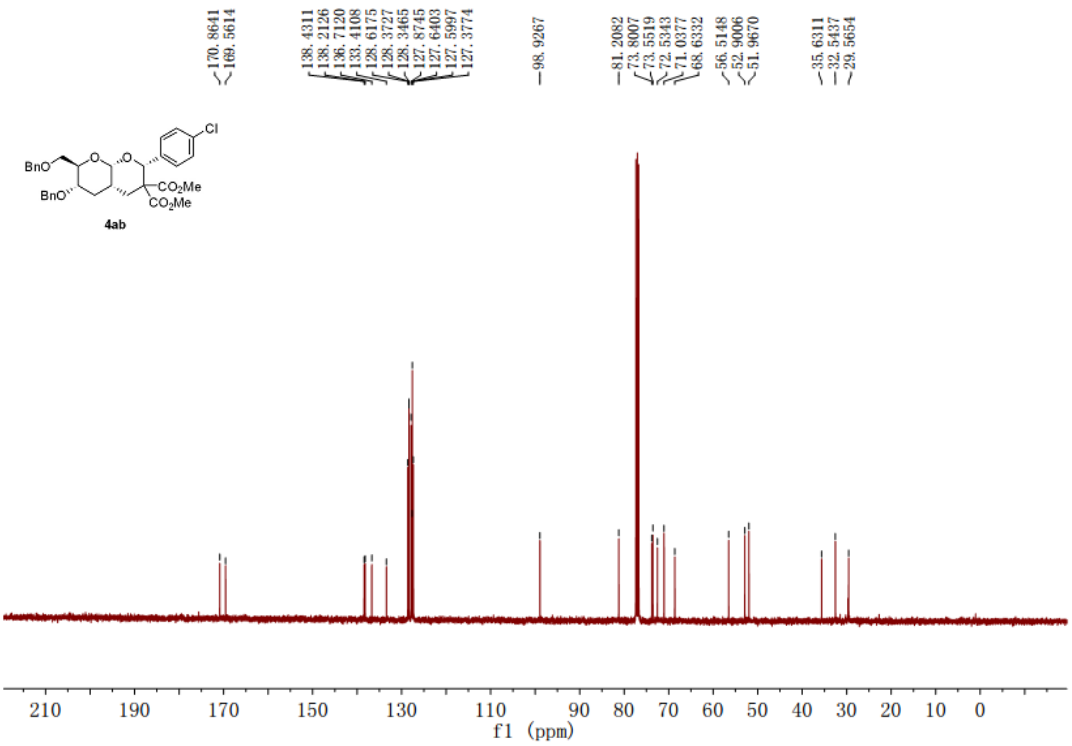
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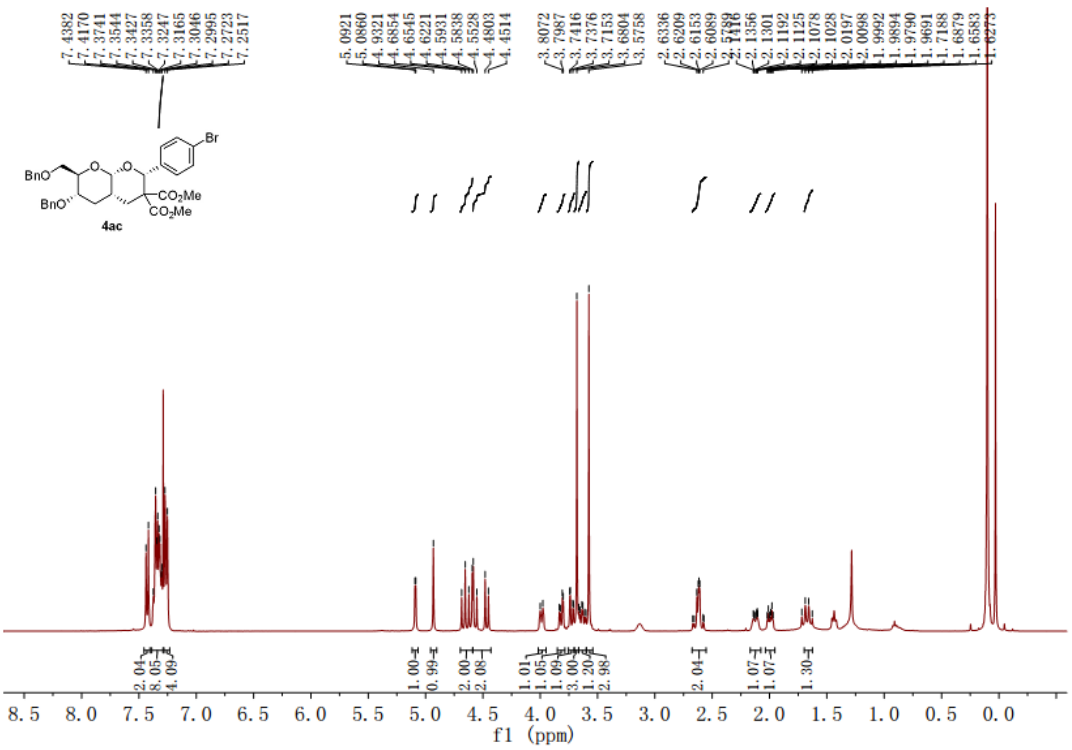
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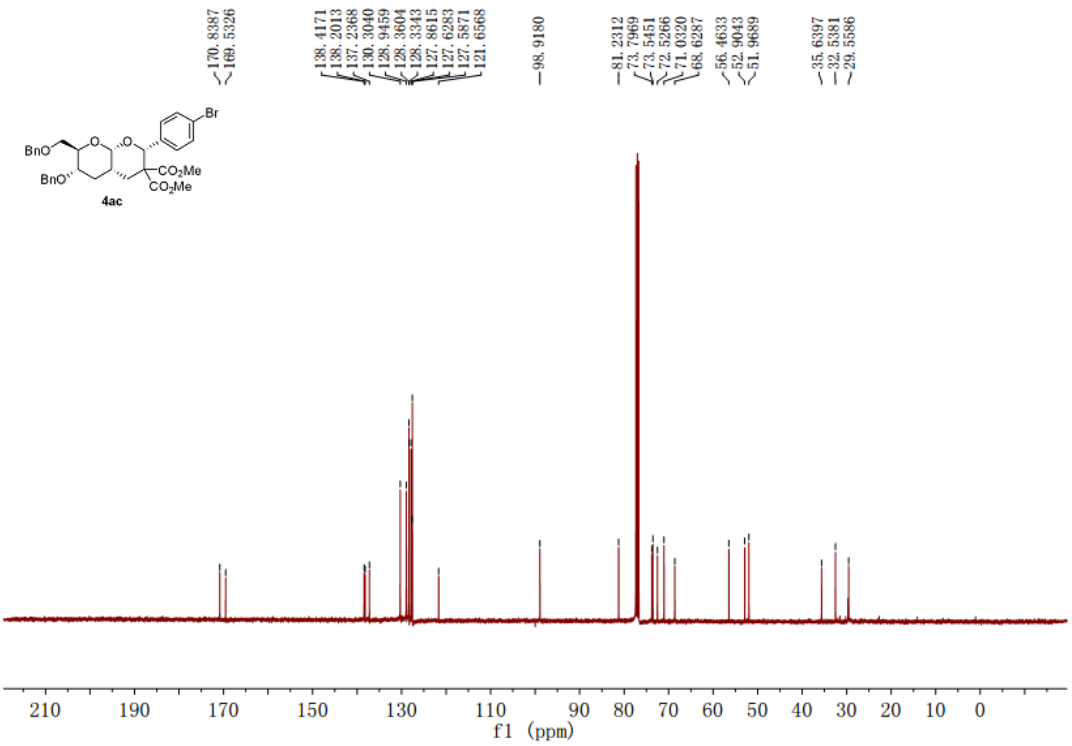
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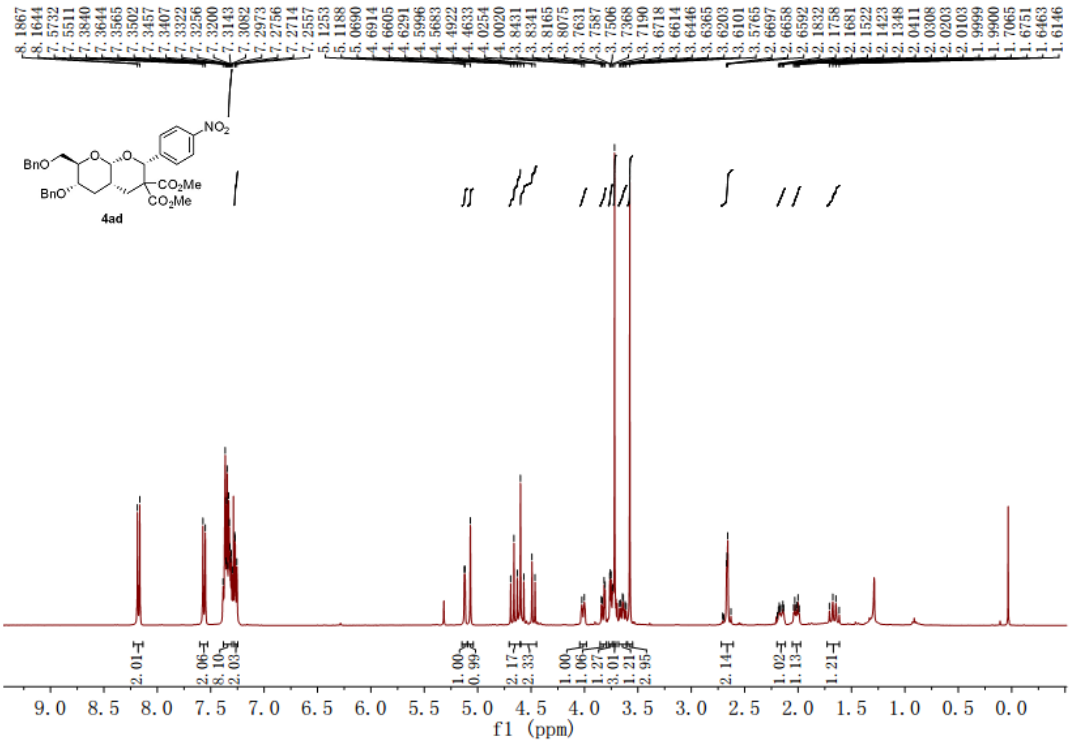
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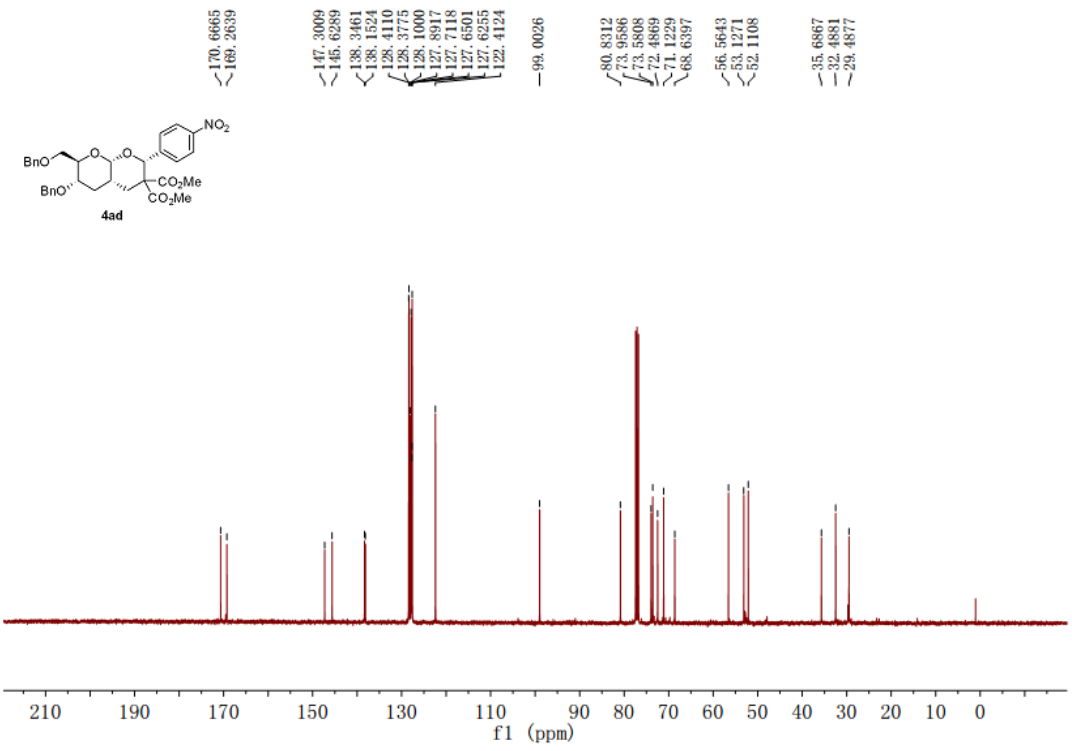
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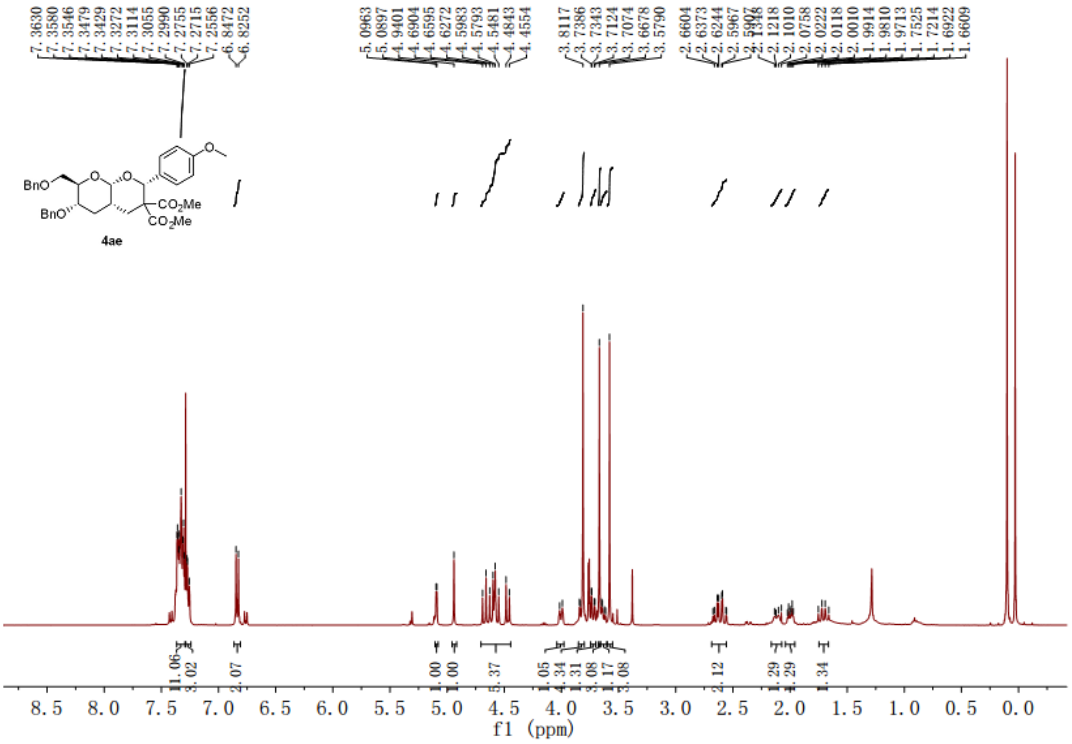
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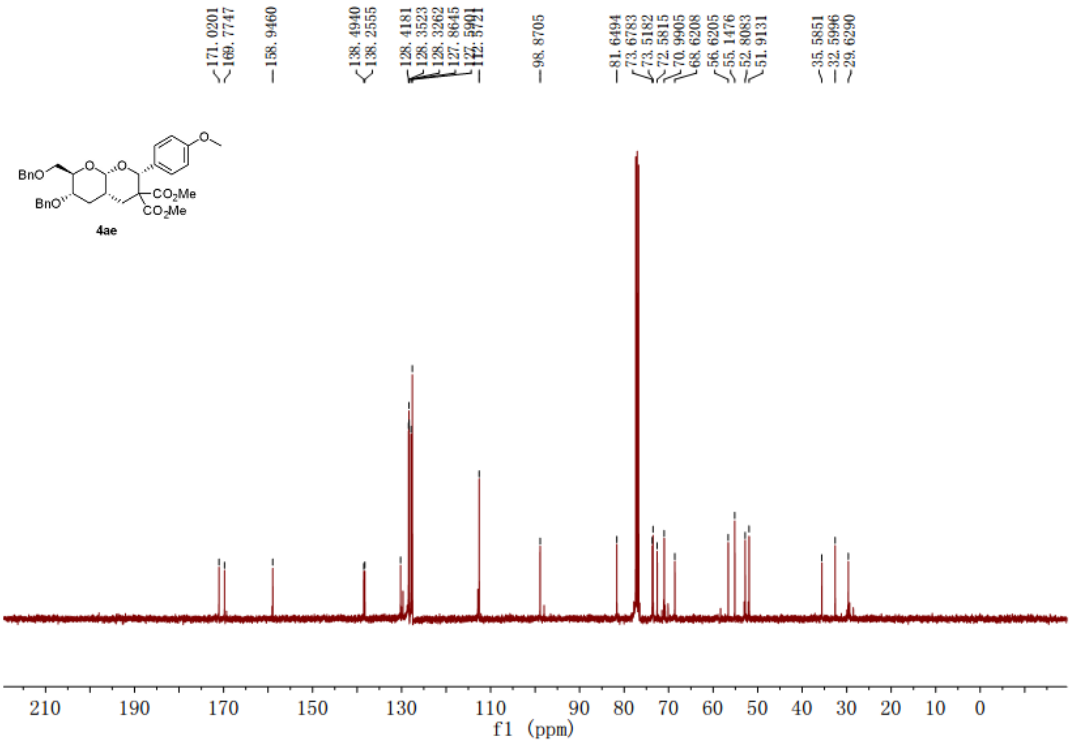
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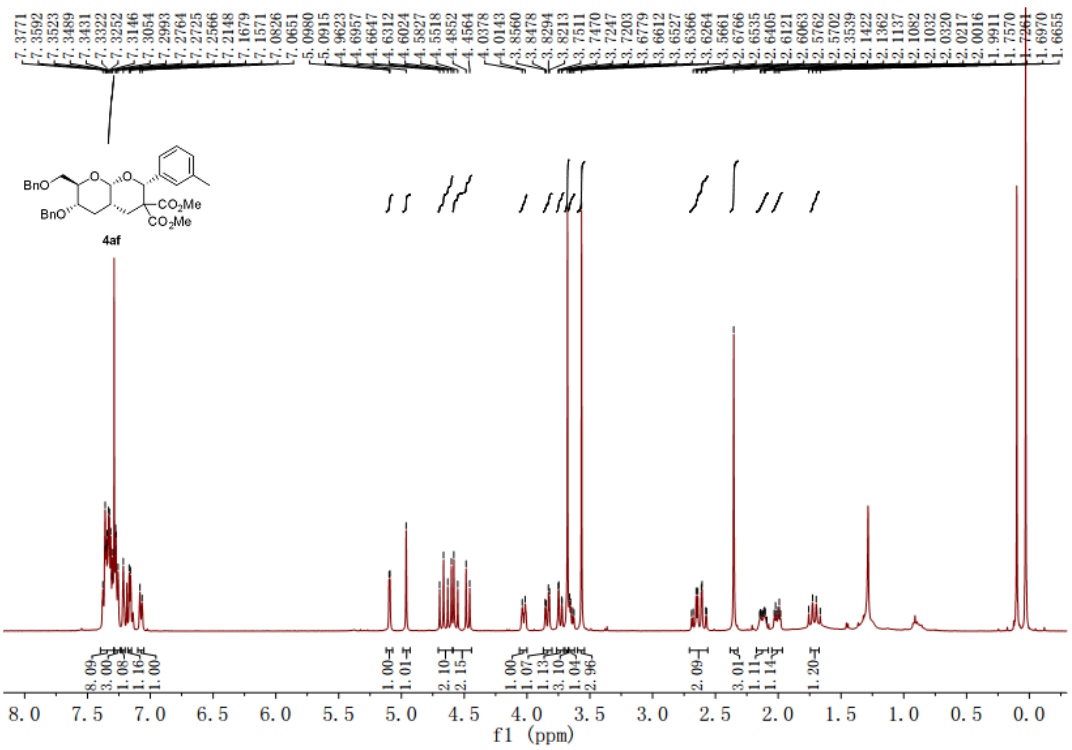
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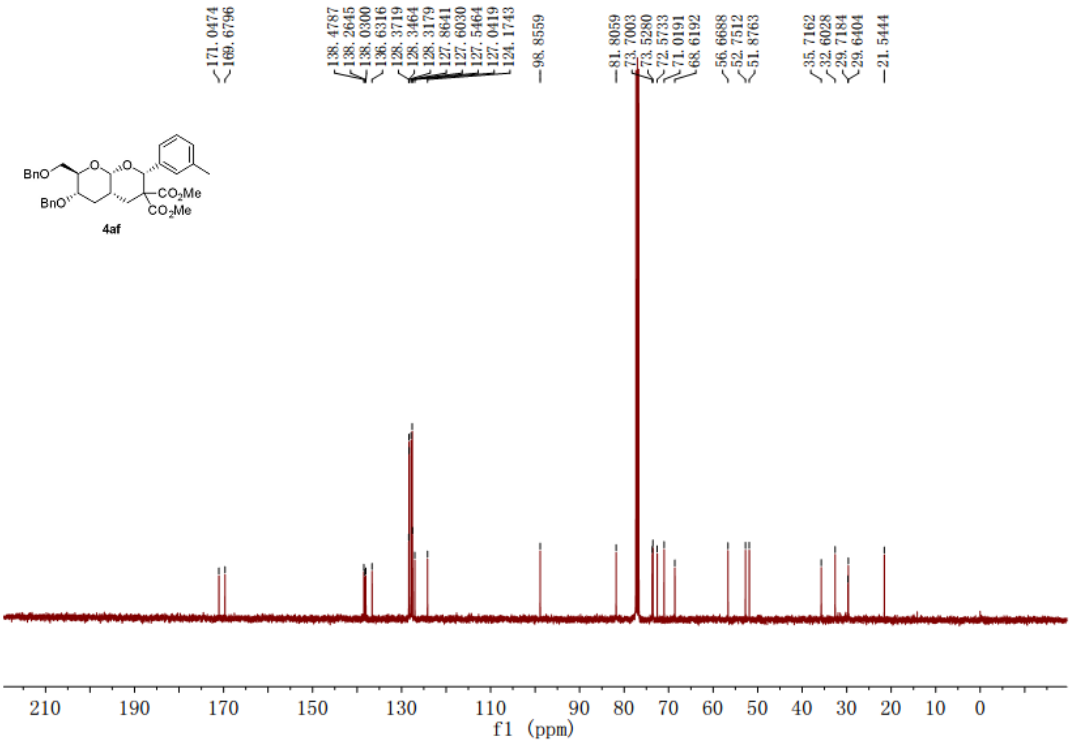
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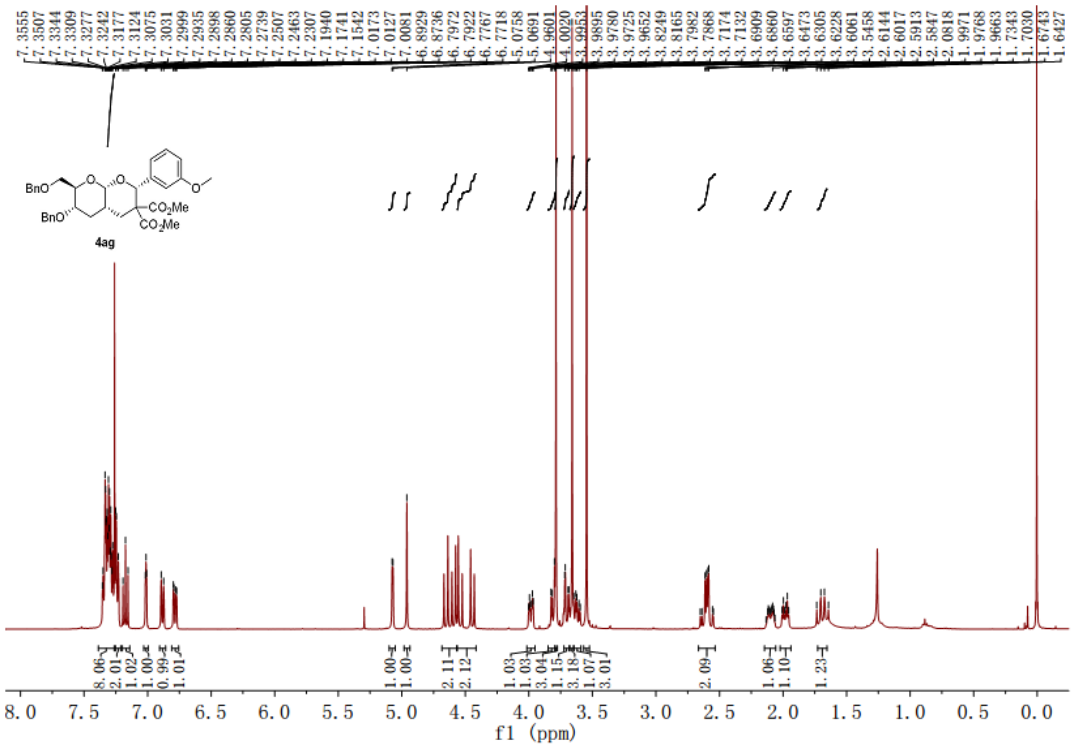
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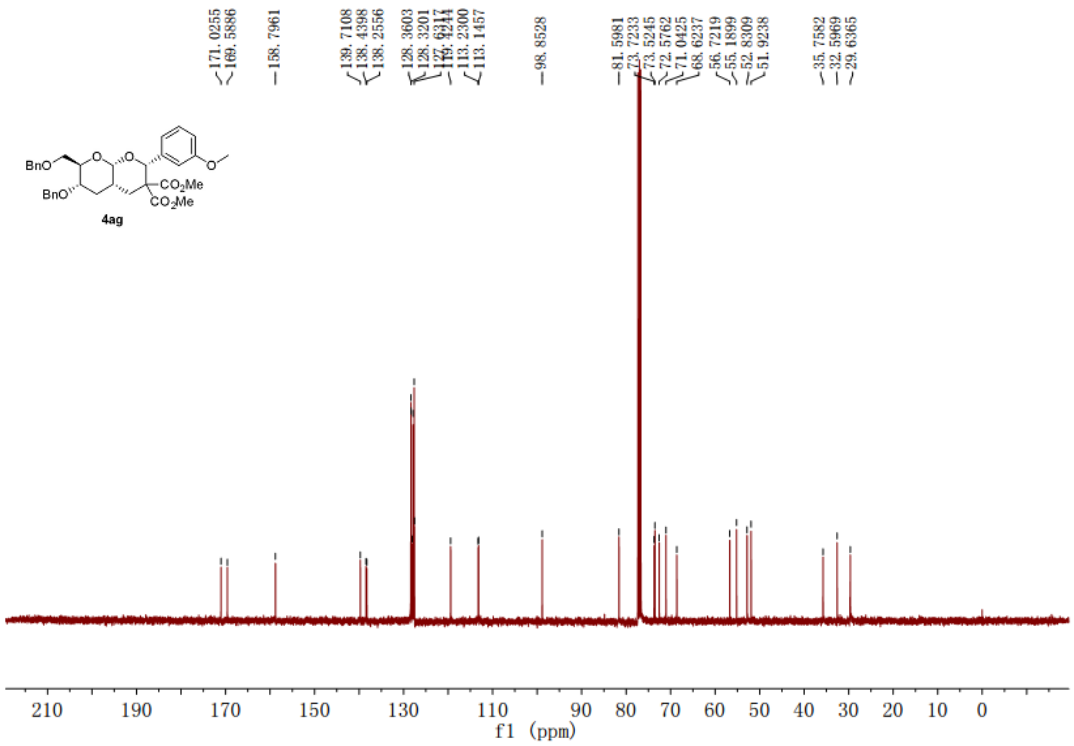
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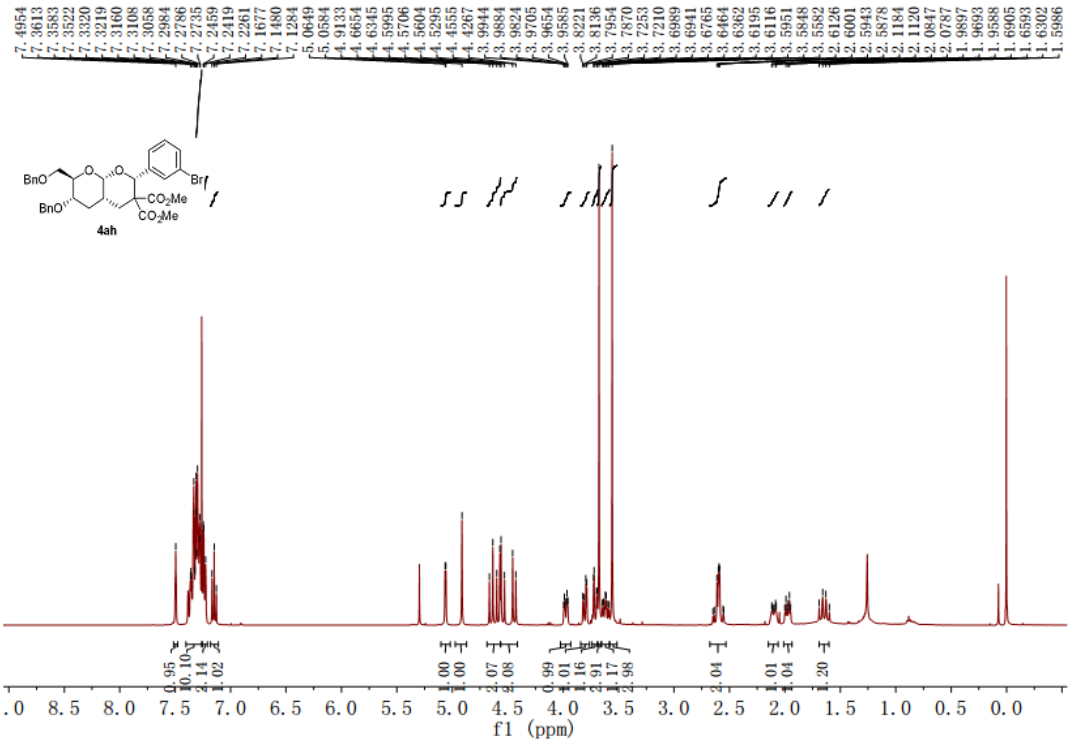
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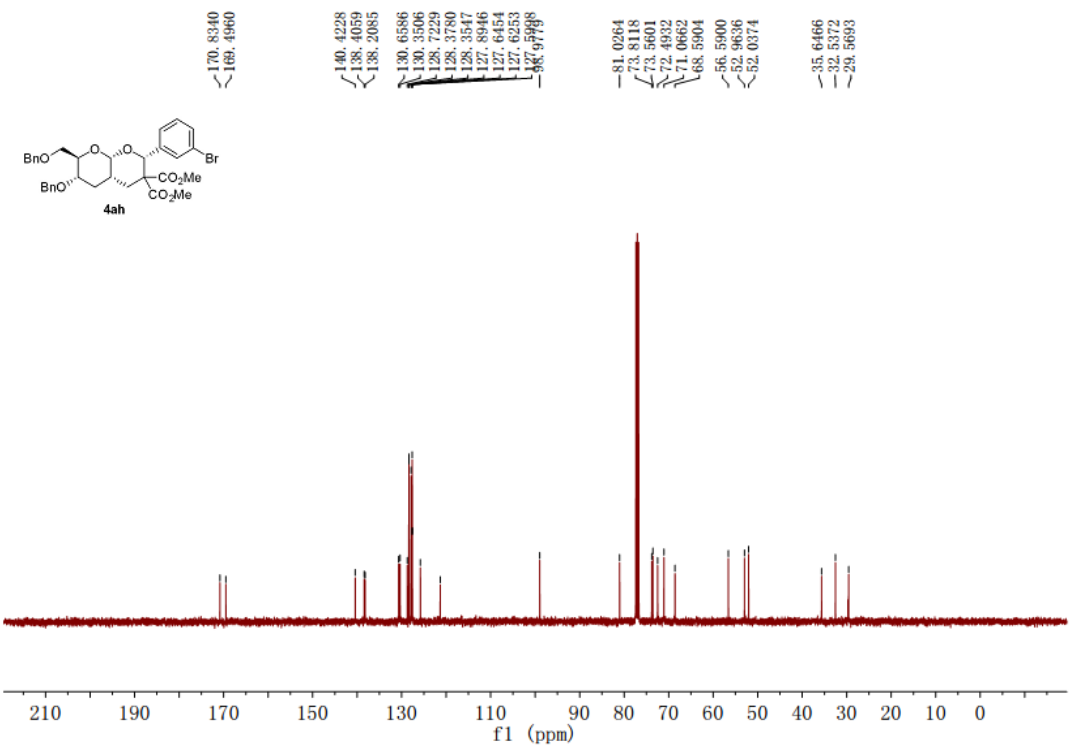
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CO2Me
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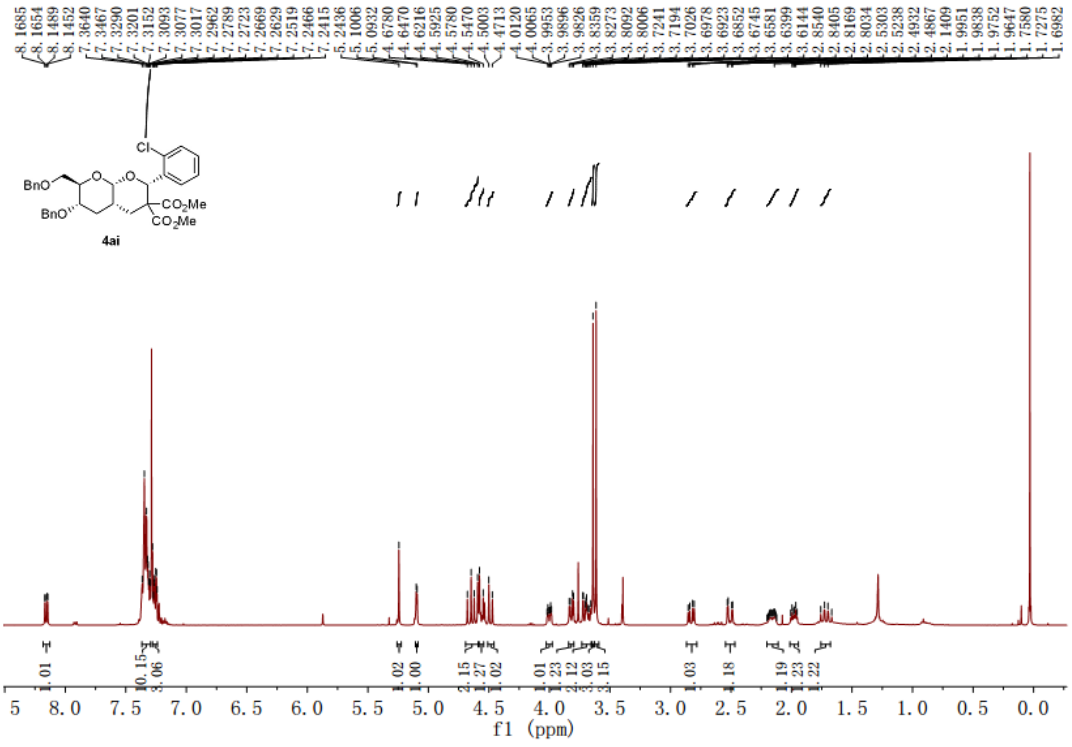
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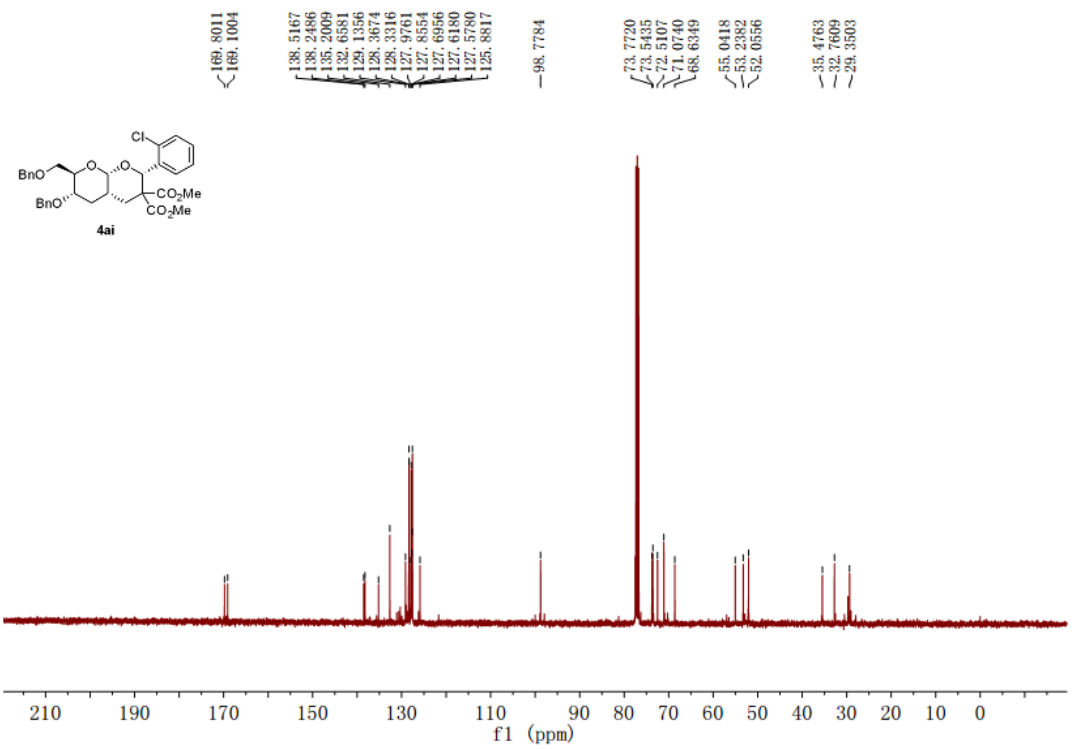
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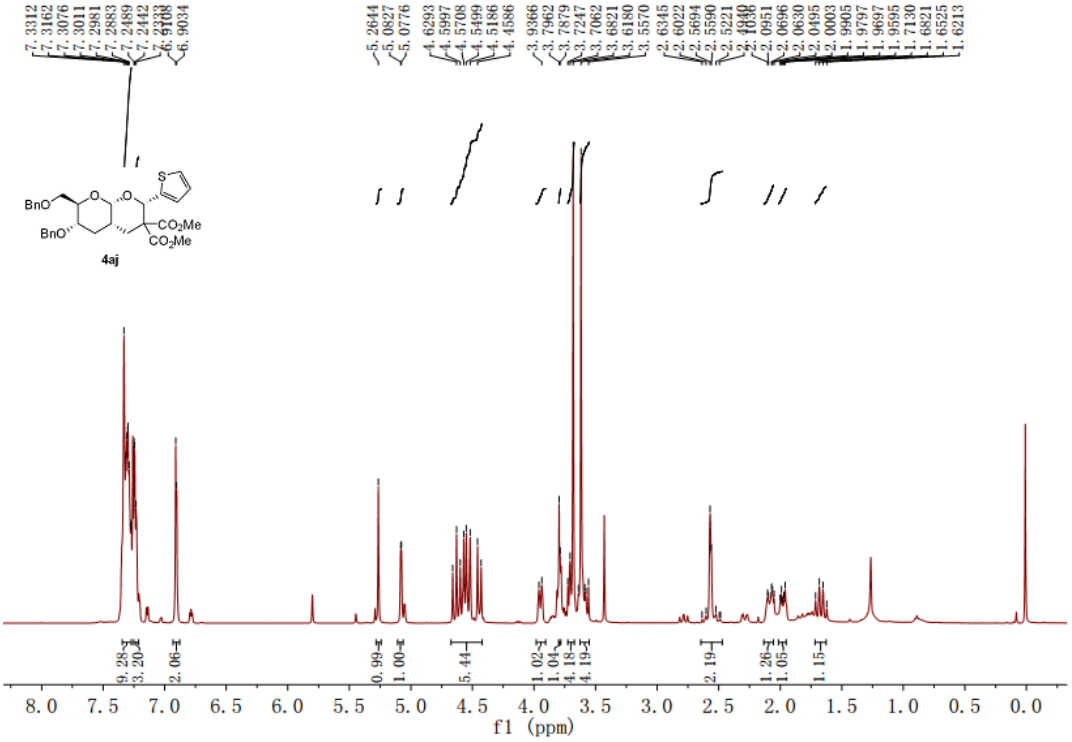
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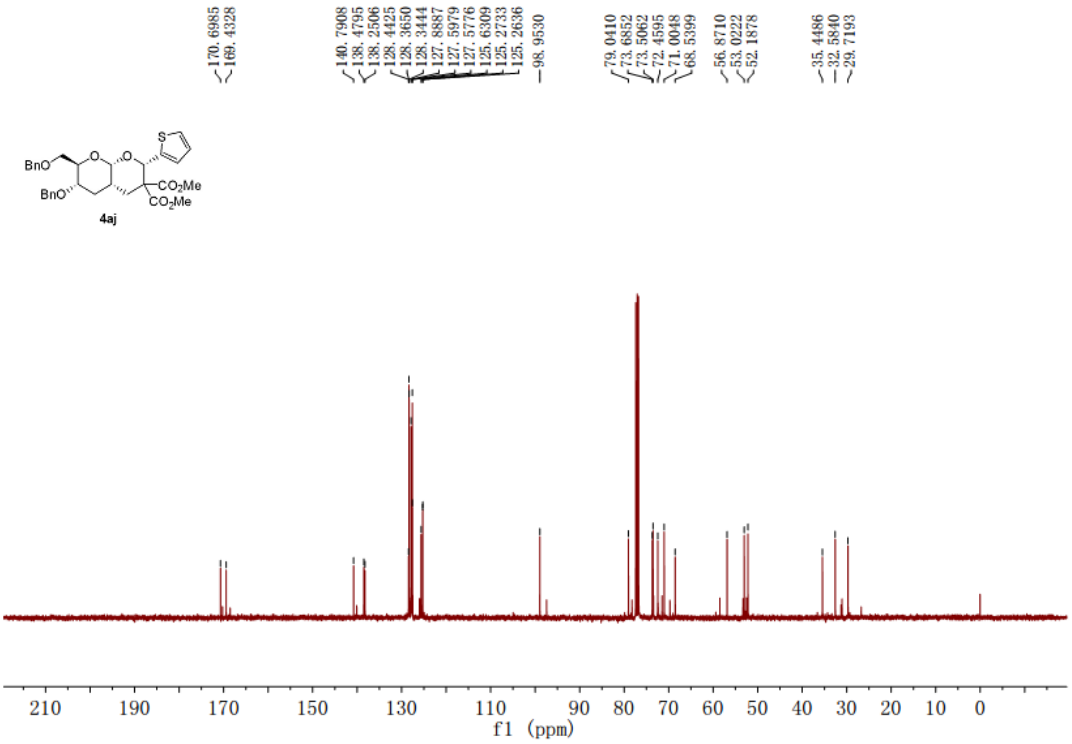
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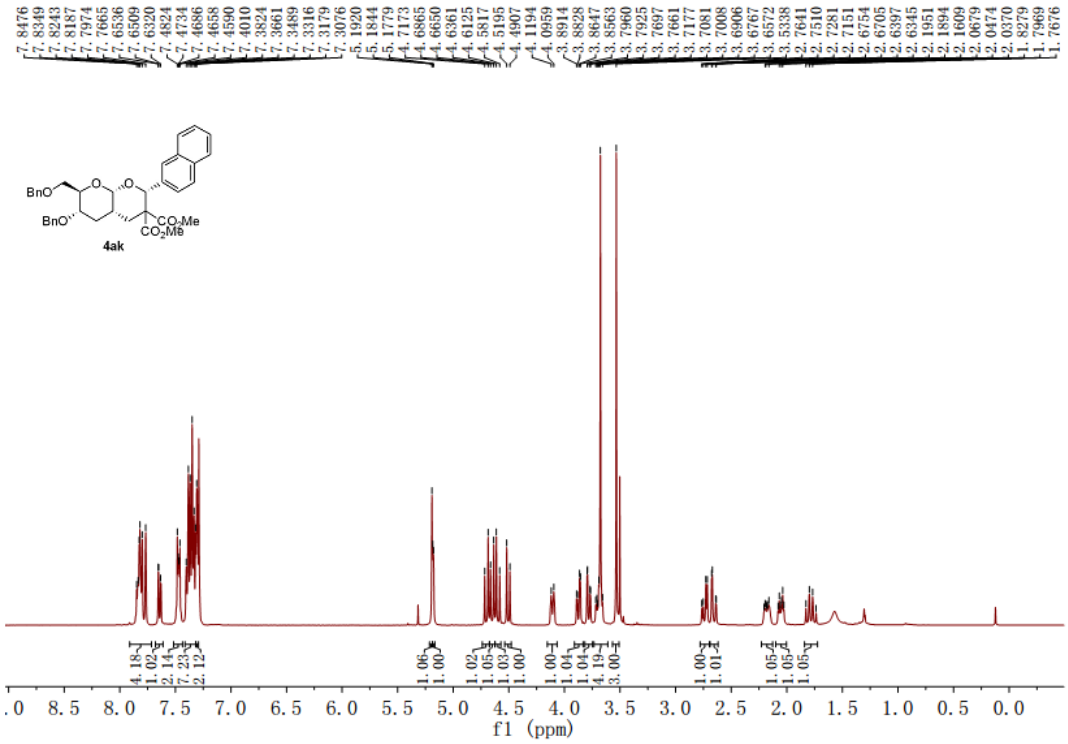
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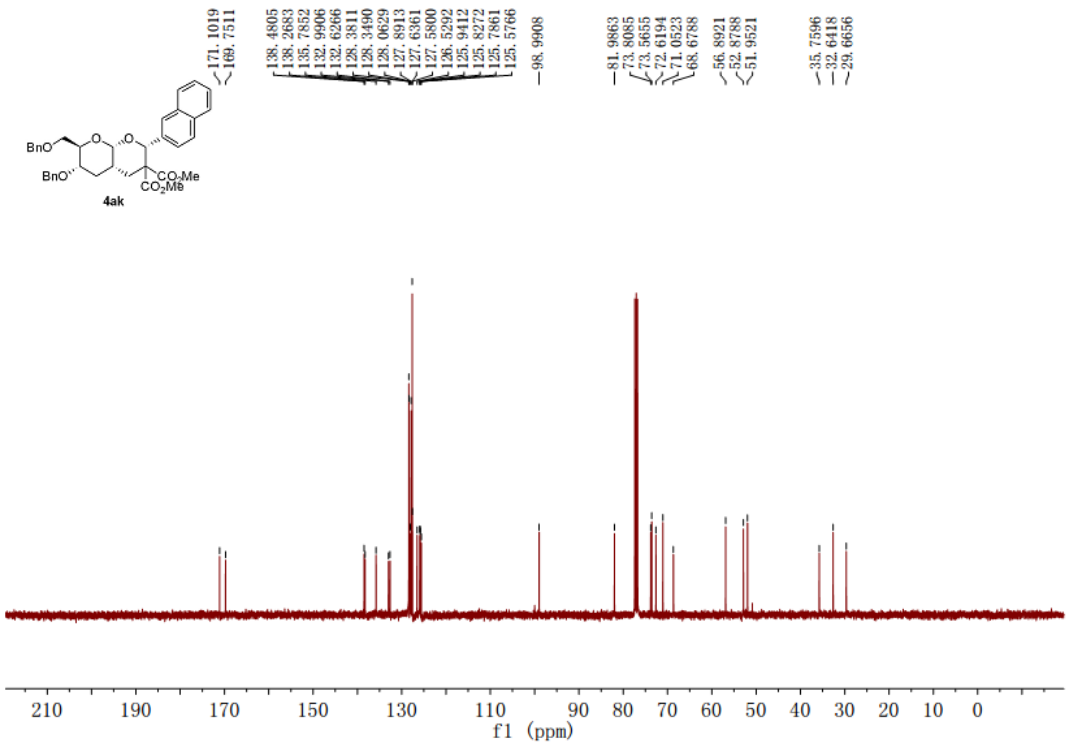
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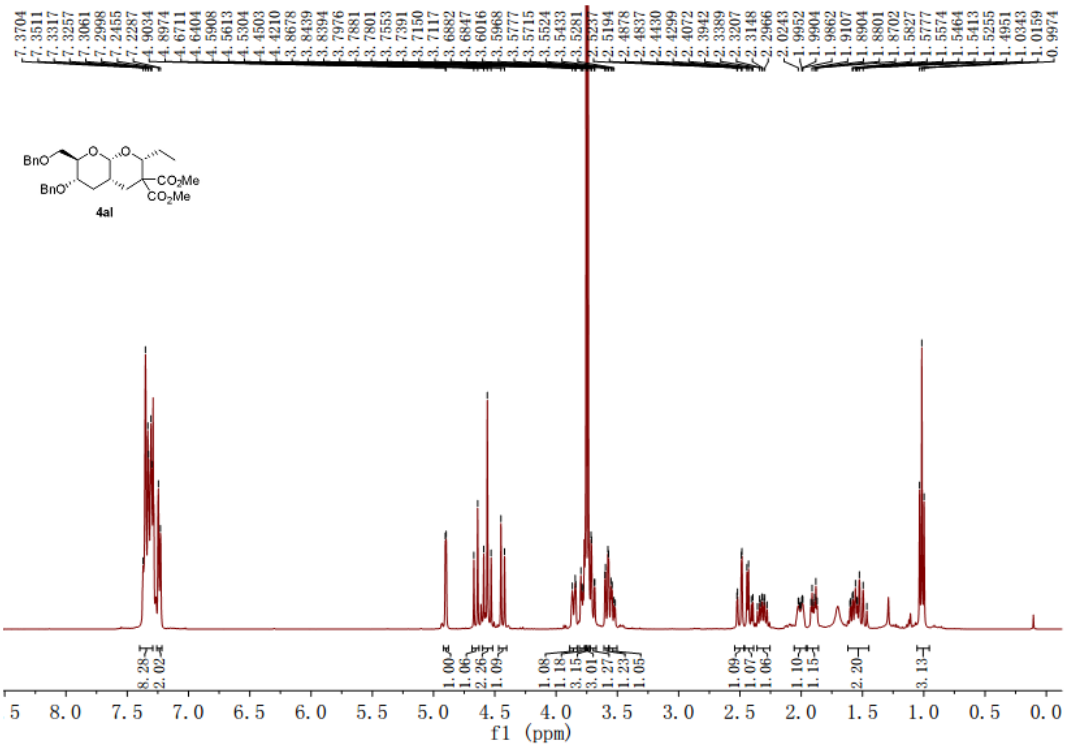
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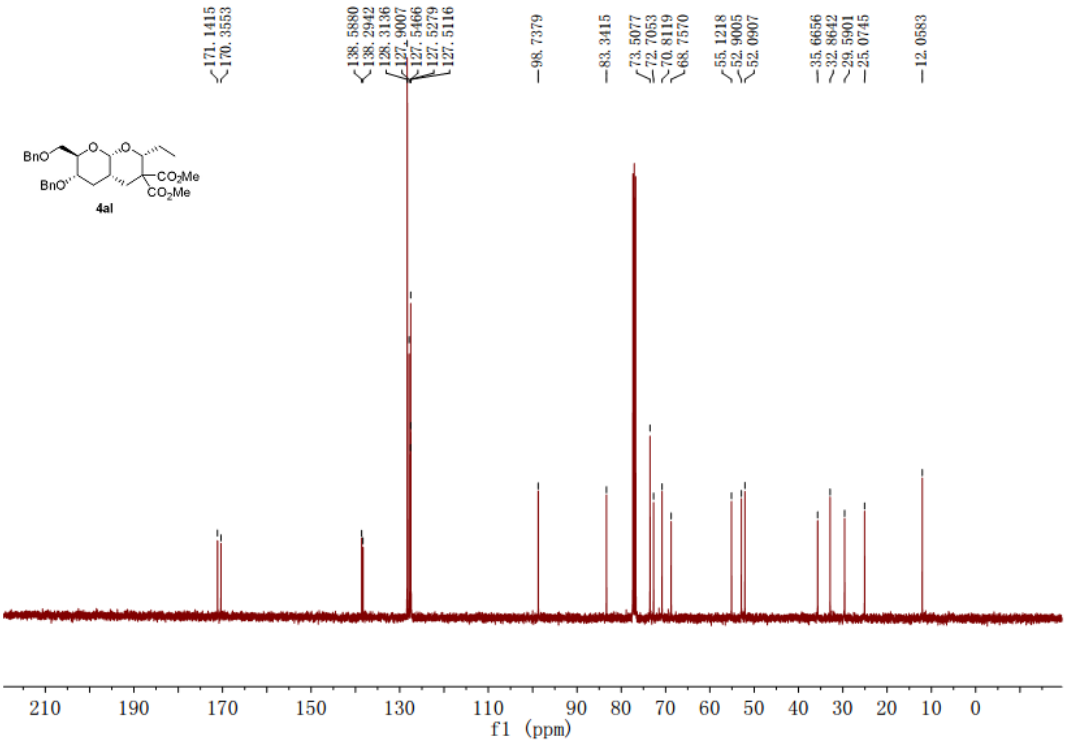
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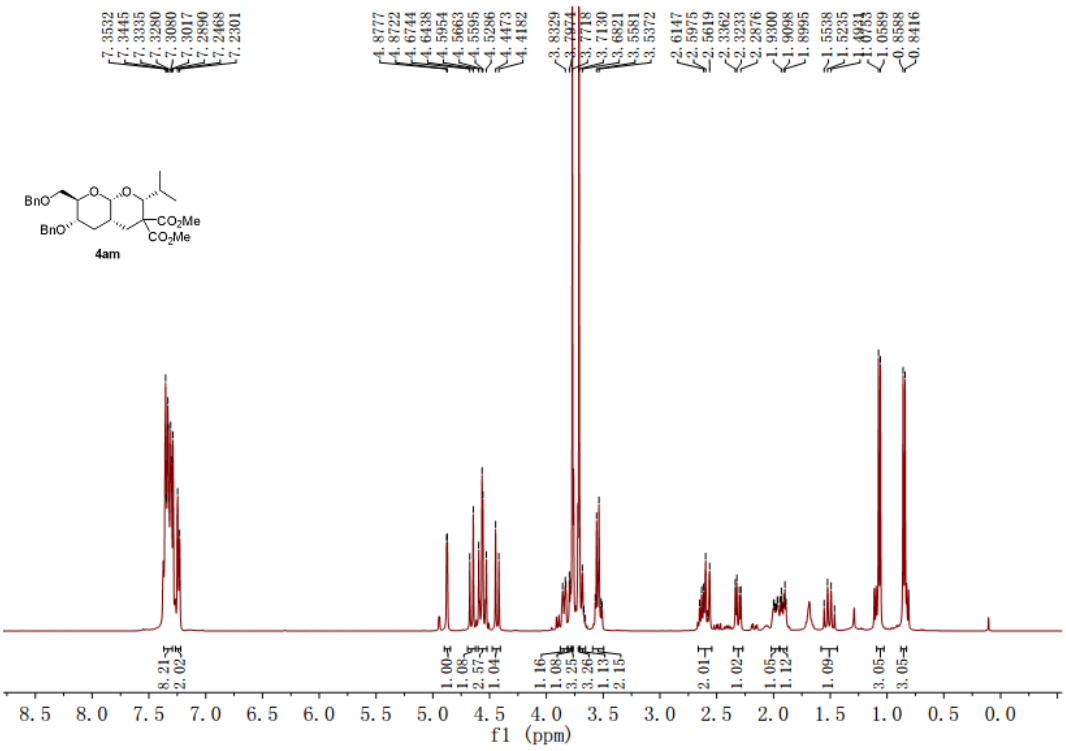
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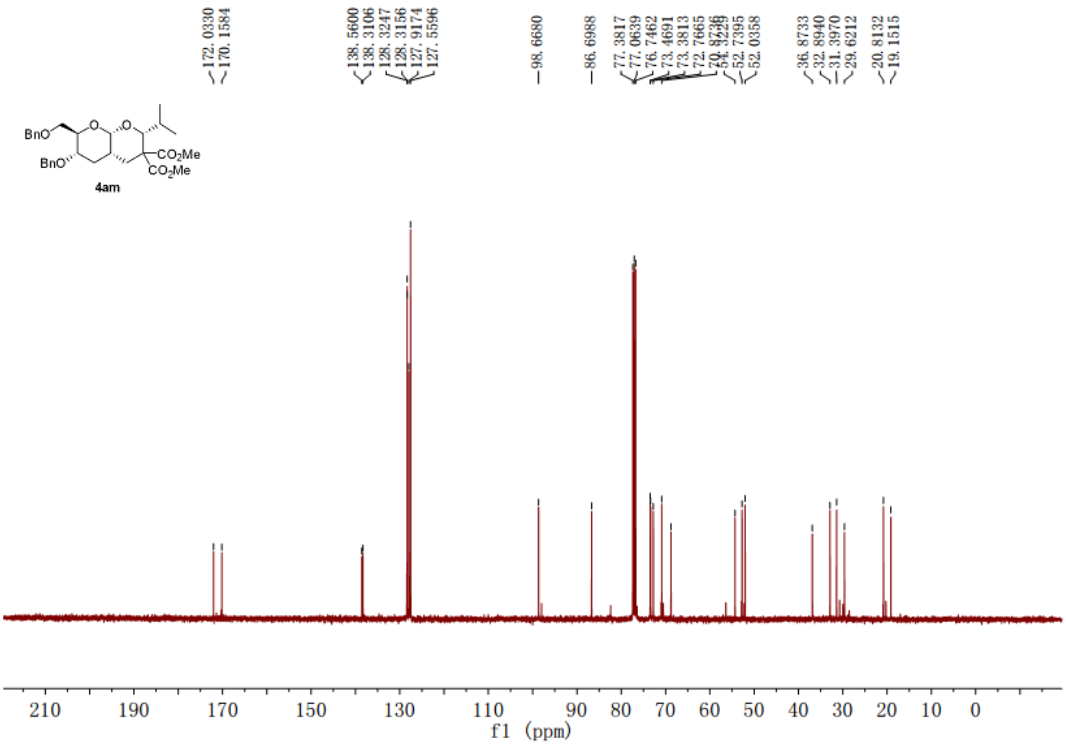
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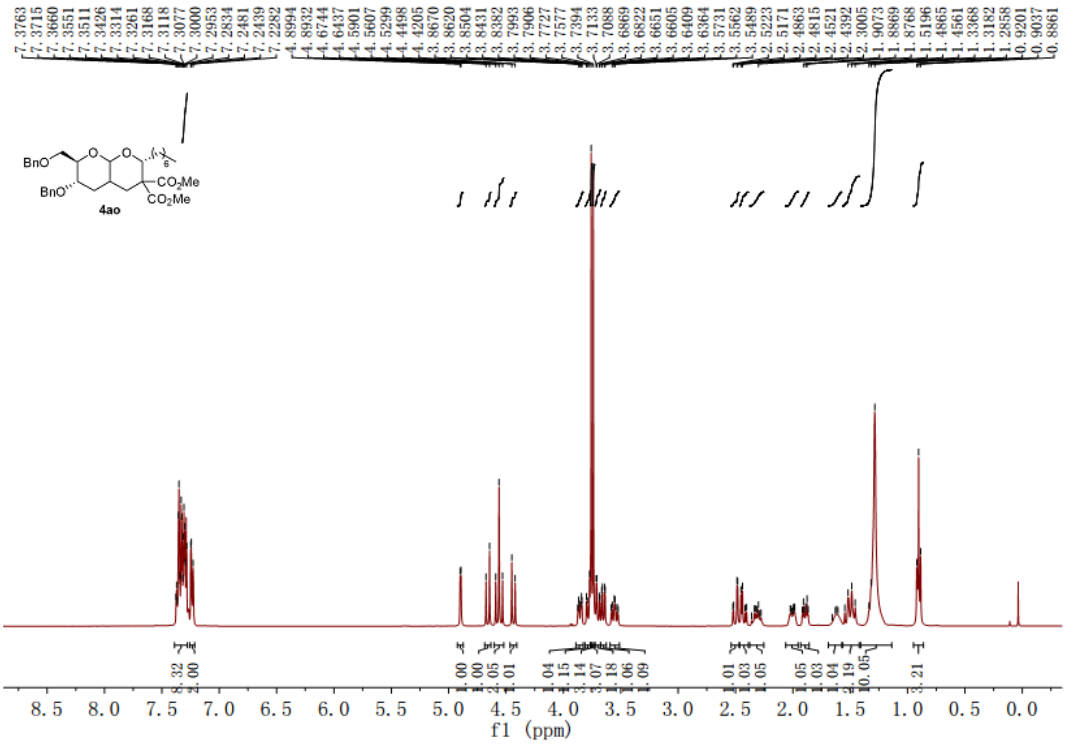
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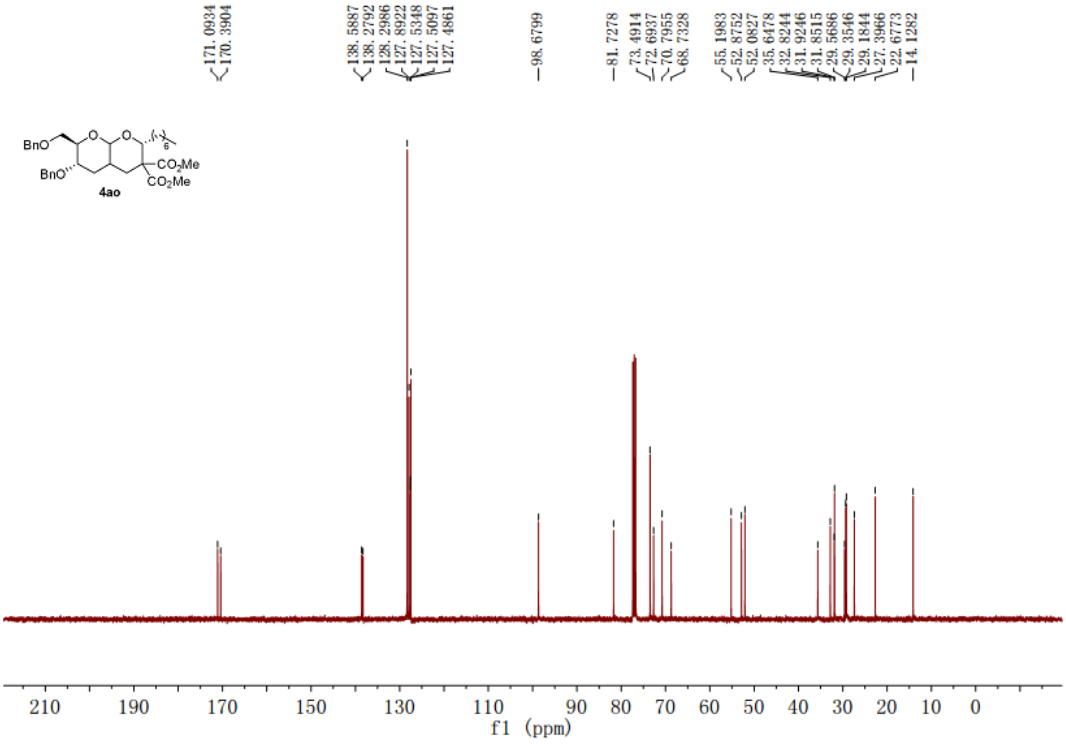
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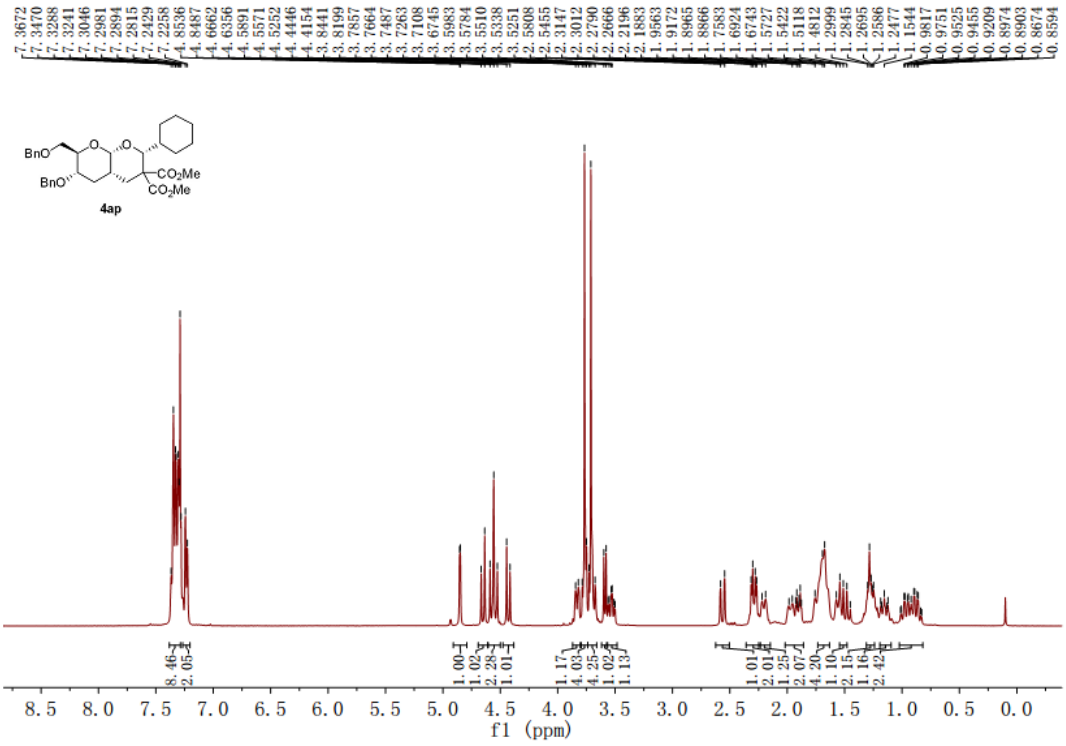
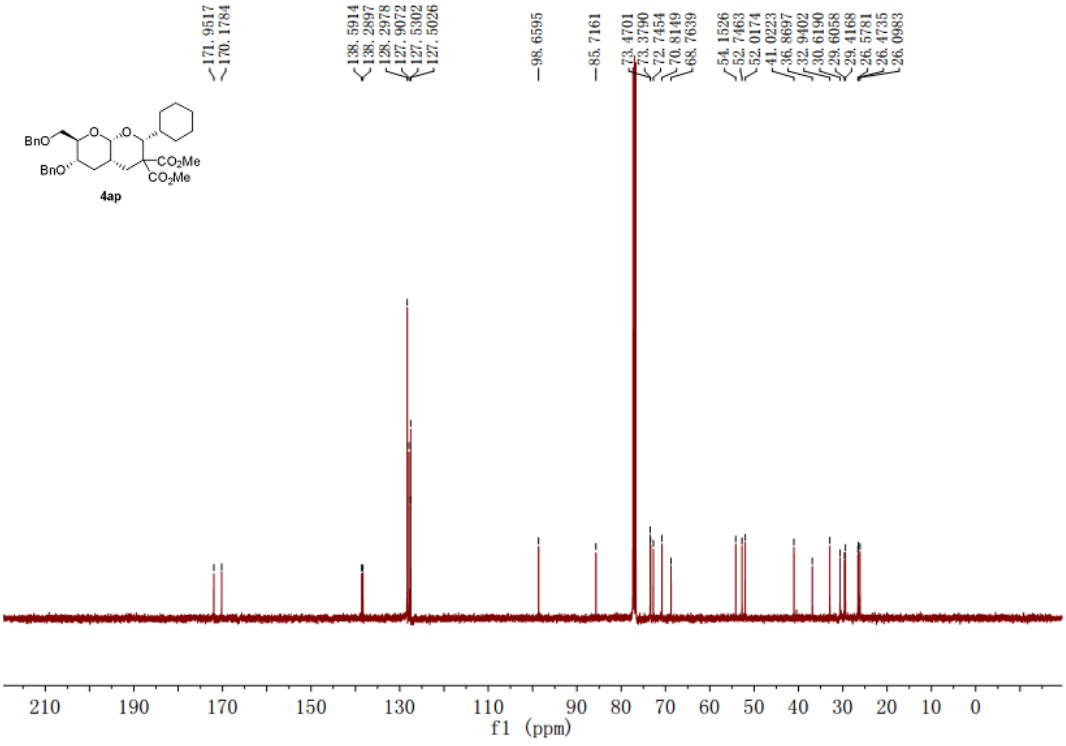

BnO
BnO
CO2Me
CO2Me
4ap
f1 (ppm)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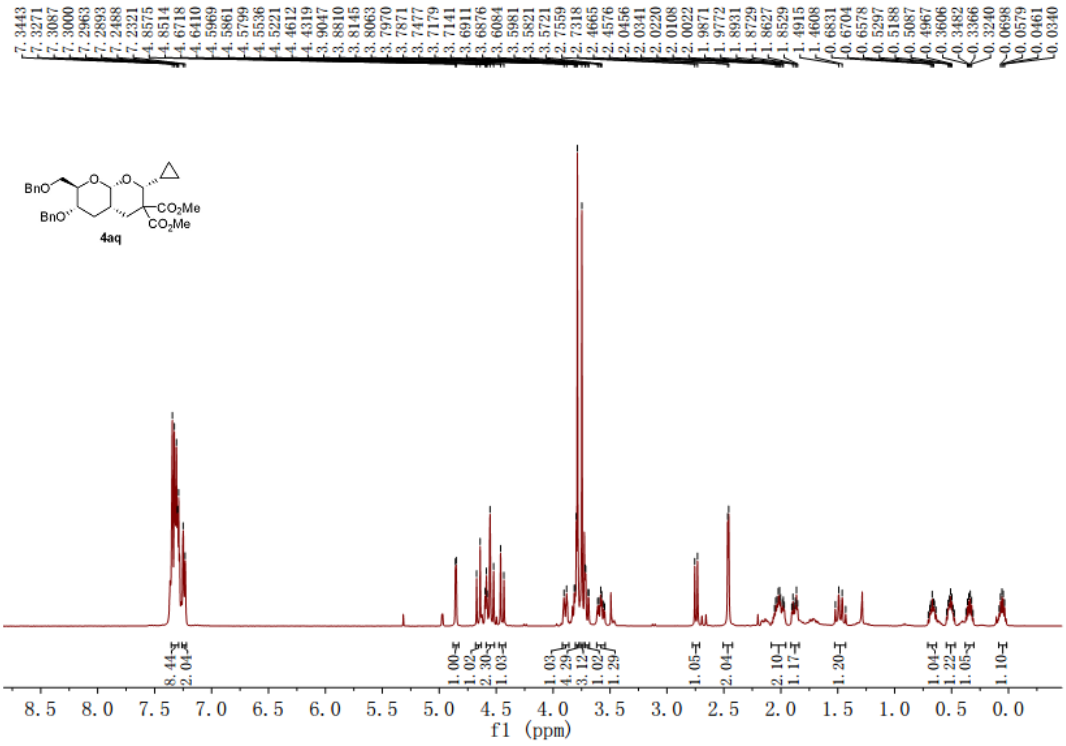
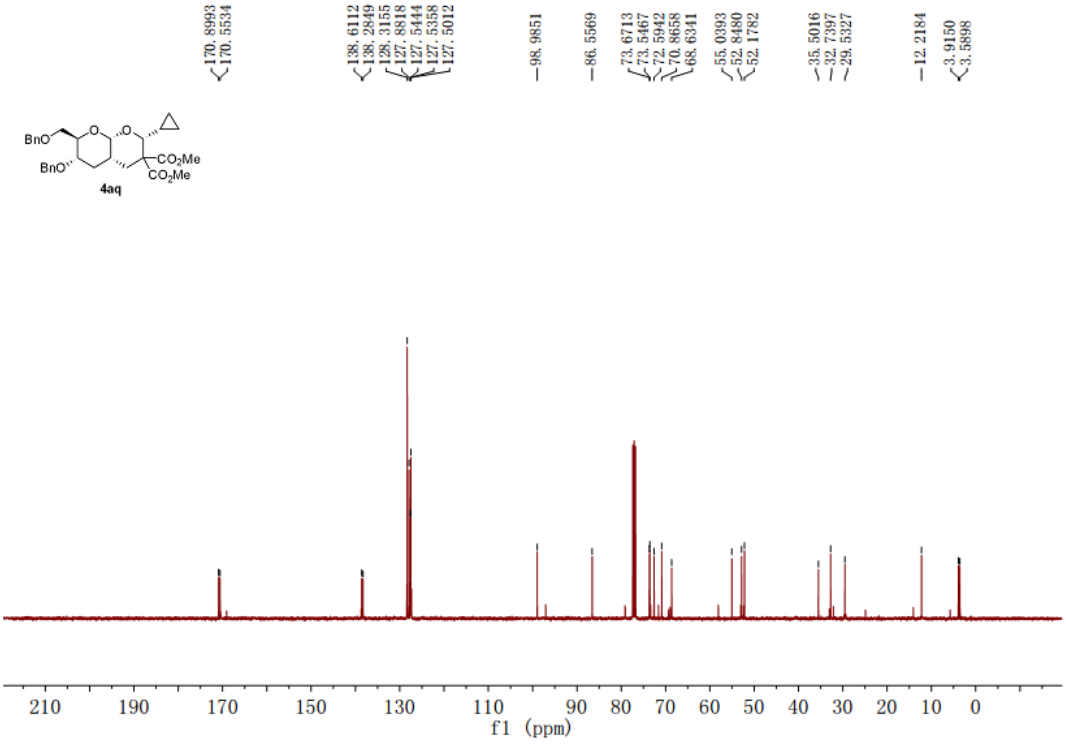
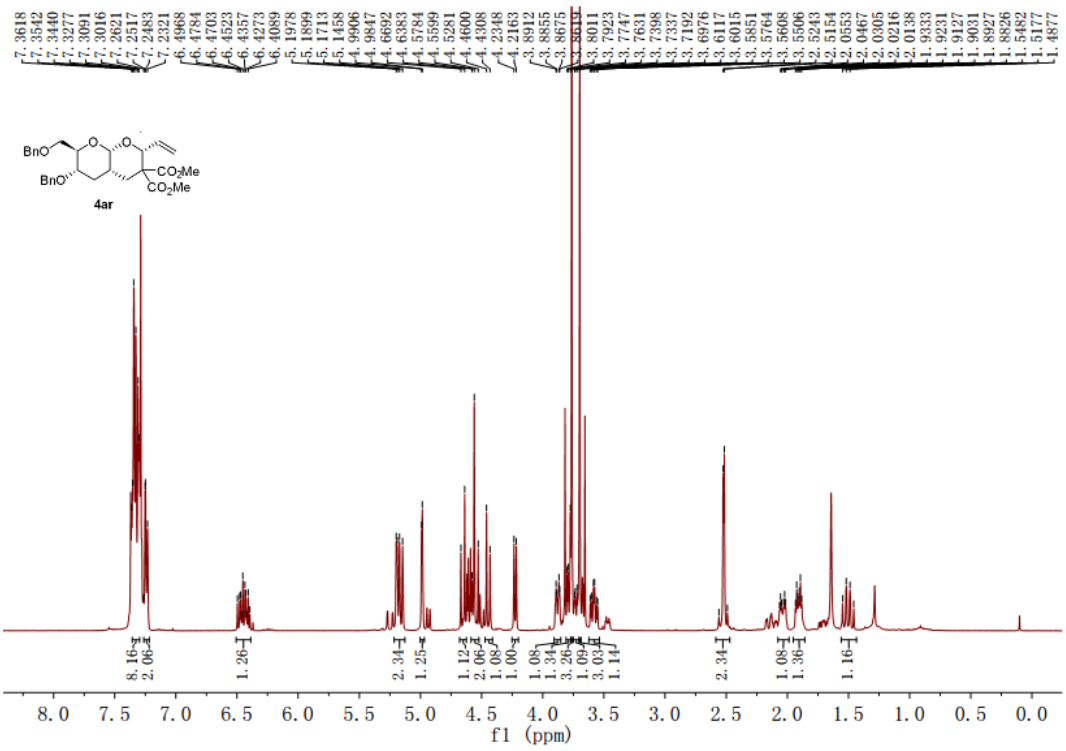
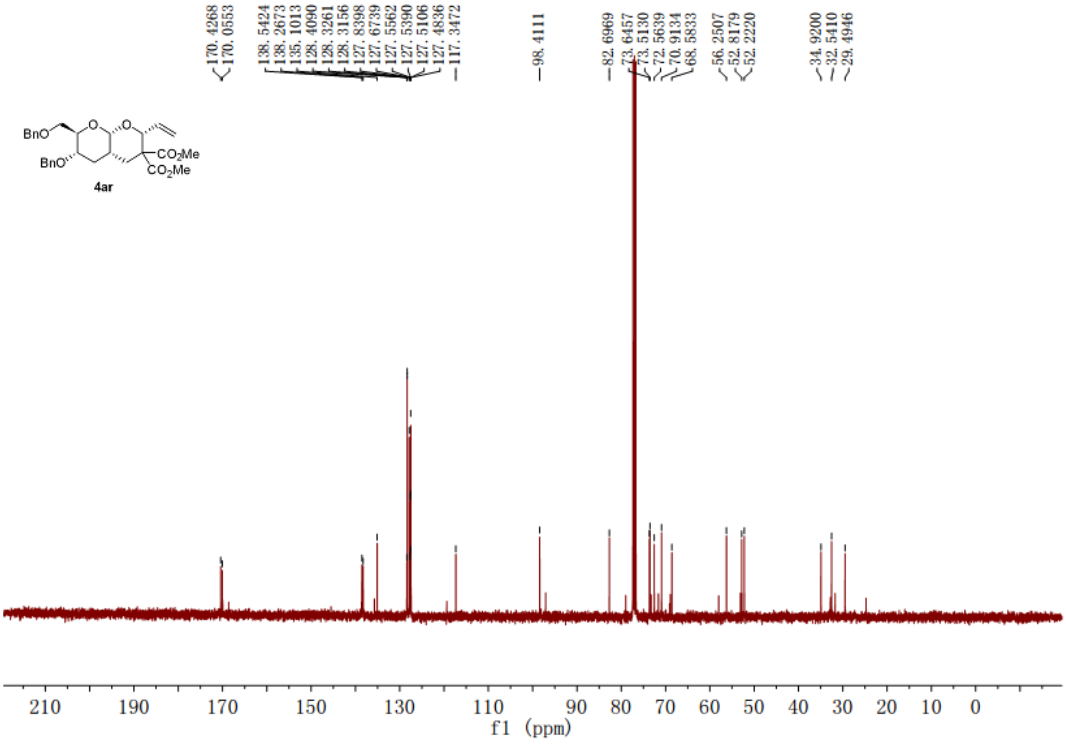
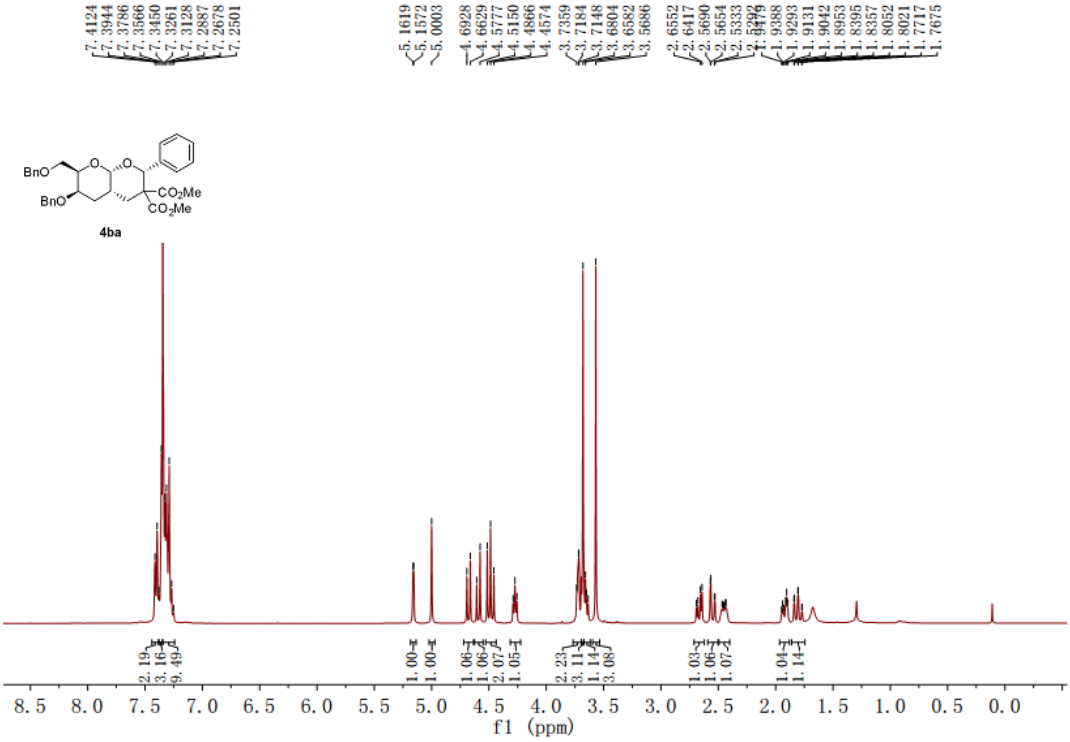
BnO
CO2Me
CO2Me
4ap
f1 (ppm)


4aq
f1 (ppm)


4aq
f1 (ppm)


BnO
BnO
CO2Me
CO2Me
4ar
f1 (ppm)


BnO
BnO
CO2Me
CO2Me
4ar
f1 (ppm)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5.1572
5.0003
4.6928
4.6629
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4.5150
4.4866
4.4574
3.7359
3.7184
3.7148
3.6804
3.6582
3.5686
2.6552
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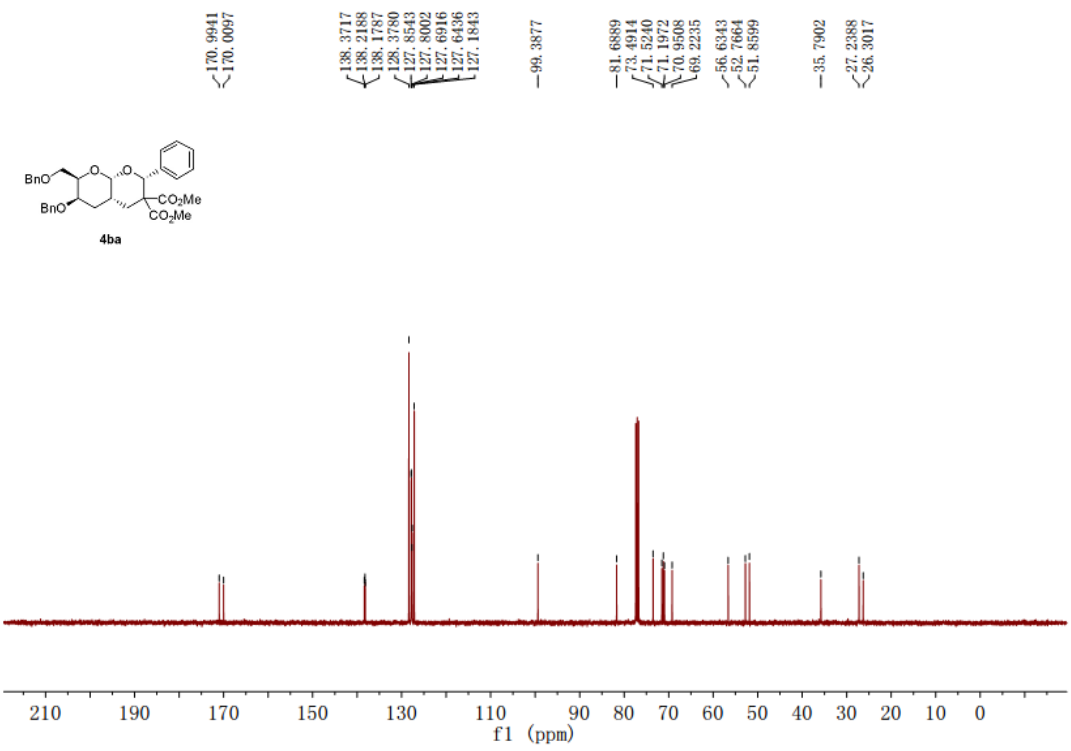
2.5690
2.5654
2.5333
2.5292
1.9388
1.9293
1.9131
1.9042
1.8953
1.8395
1.8357
1.8052
1.8021
1.7717
1.7675
BnO
BnO
CO2Me
CO2Me
4ba
2.19
3.16
9.49
1.00
1.00
1.06
1.06
2.07
1.05
2.23
3.11
1.14
3.08
1.03
1.06
1.07
1.04
1.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.1787
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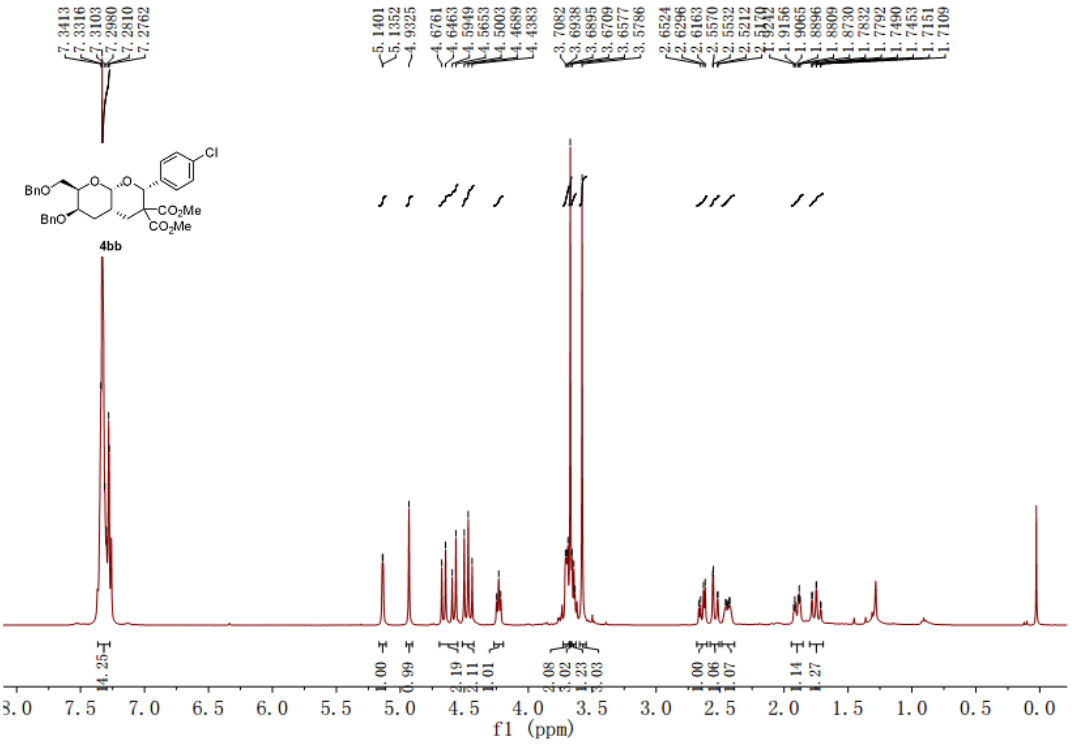
127.6916
127.6436
127.1843
99.3877
81.6889
73.4914
71.5240
71.1972
70.9508
69.2235
56.6343
52.7664
51.8599
35.7902
27.2388
26.3017
BnO
BnO
CO2Me
CO2Me
4ba
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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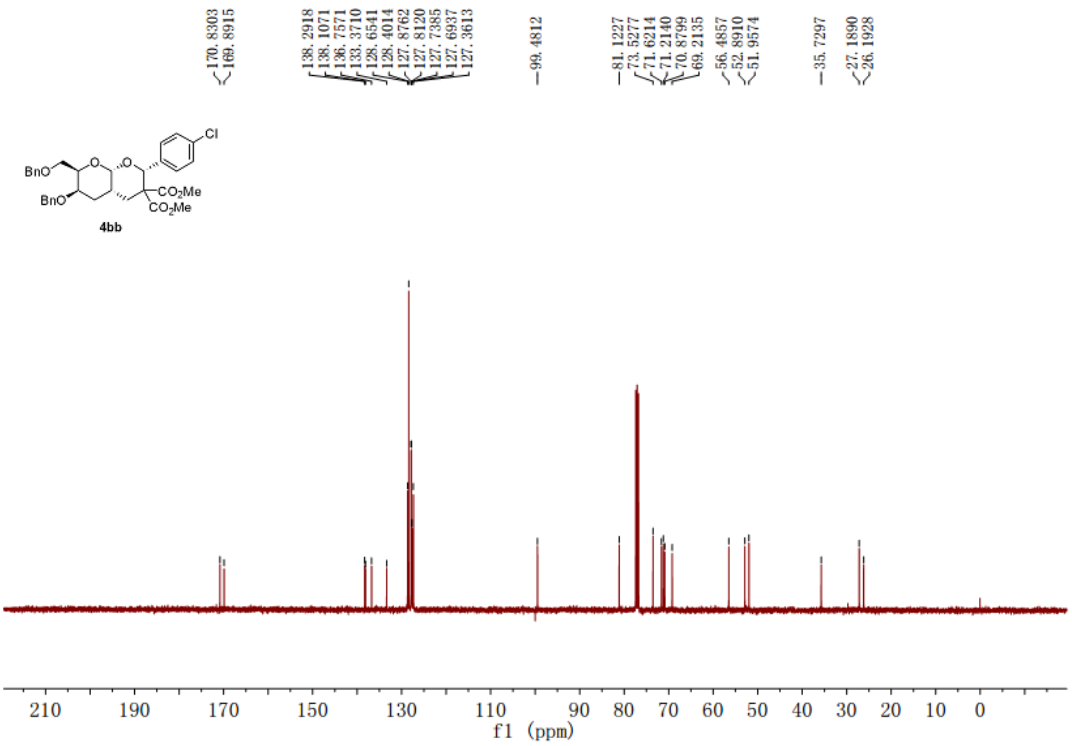
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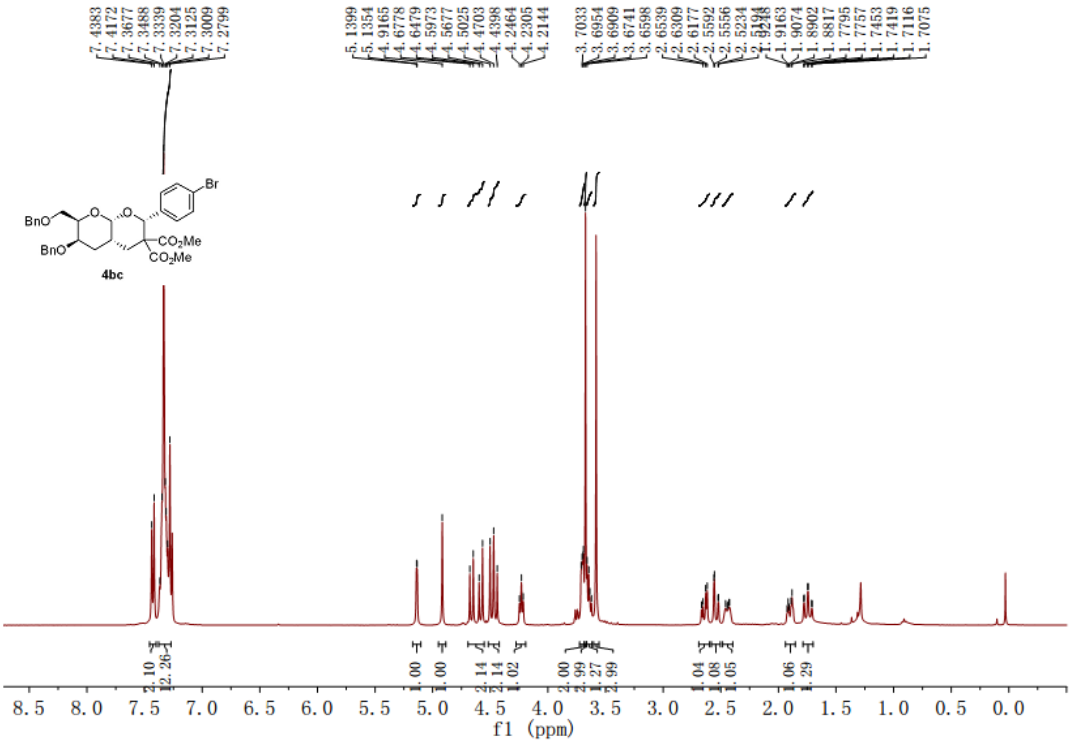
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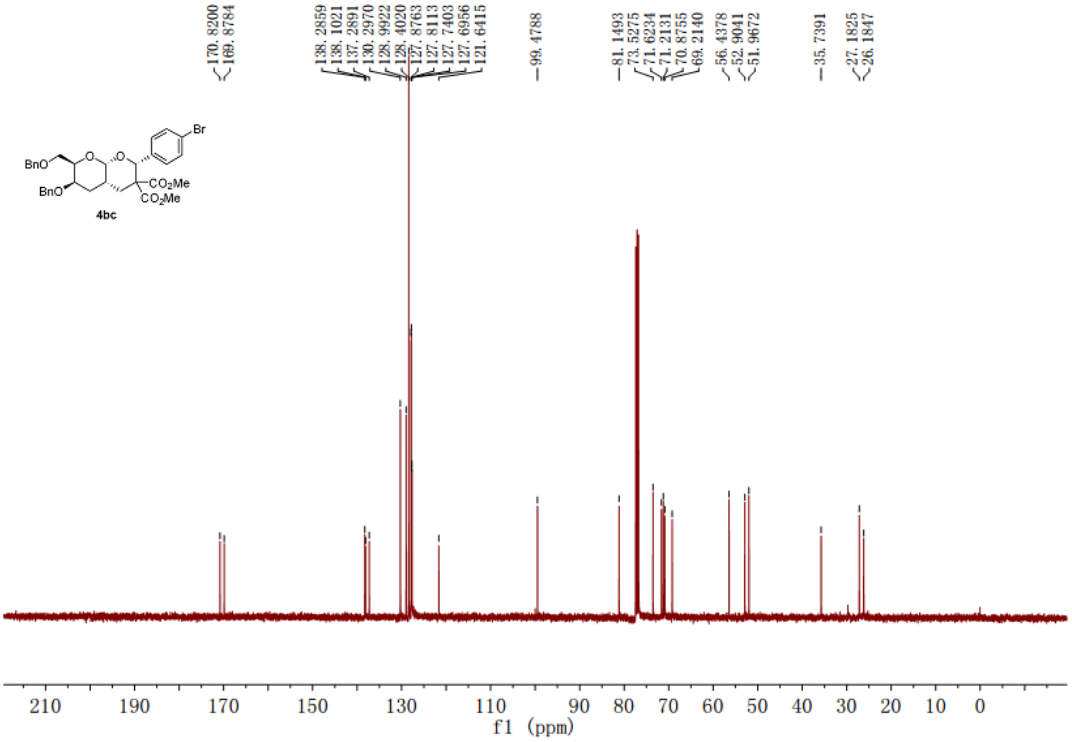
f1 (ppm)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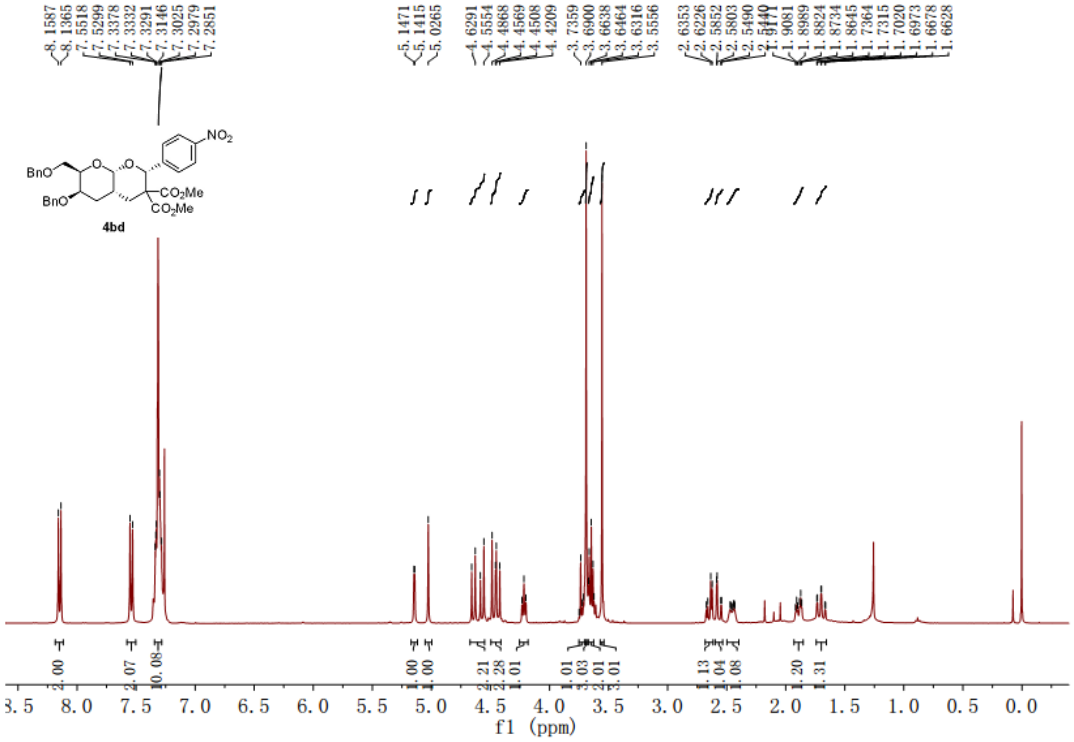
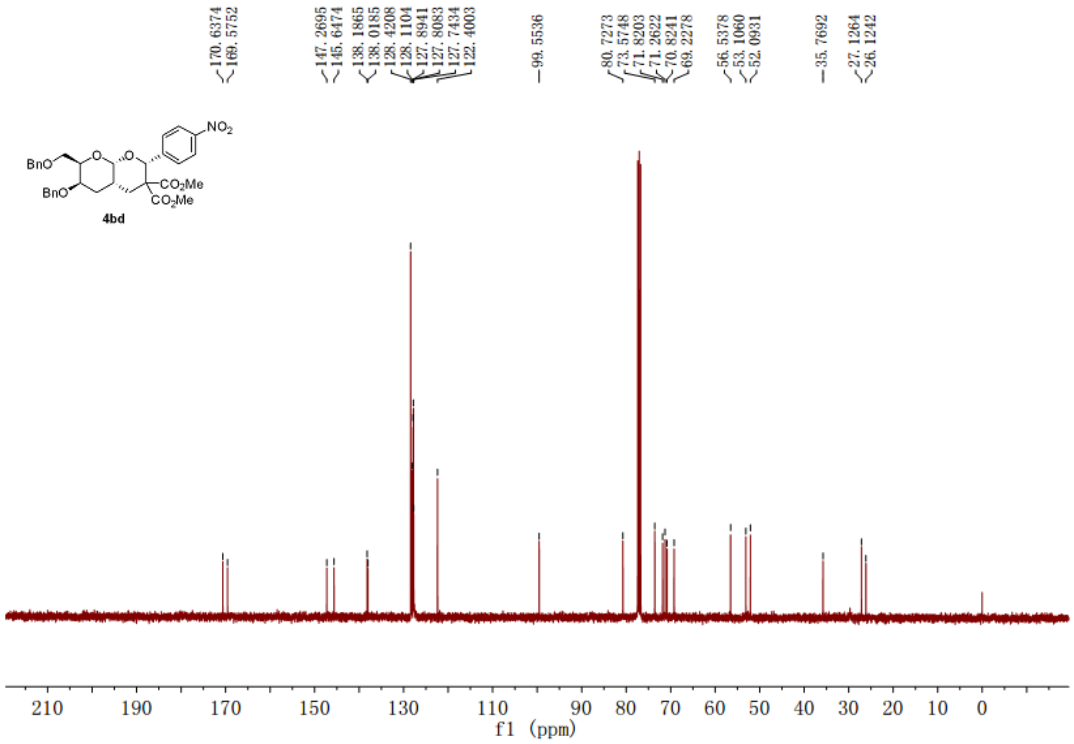
f1 (ppm)


4bd
f1 (ppm)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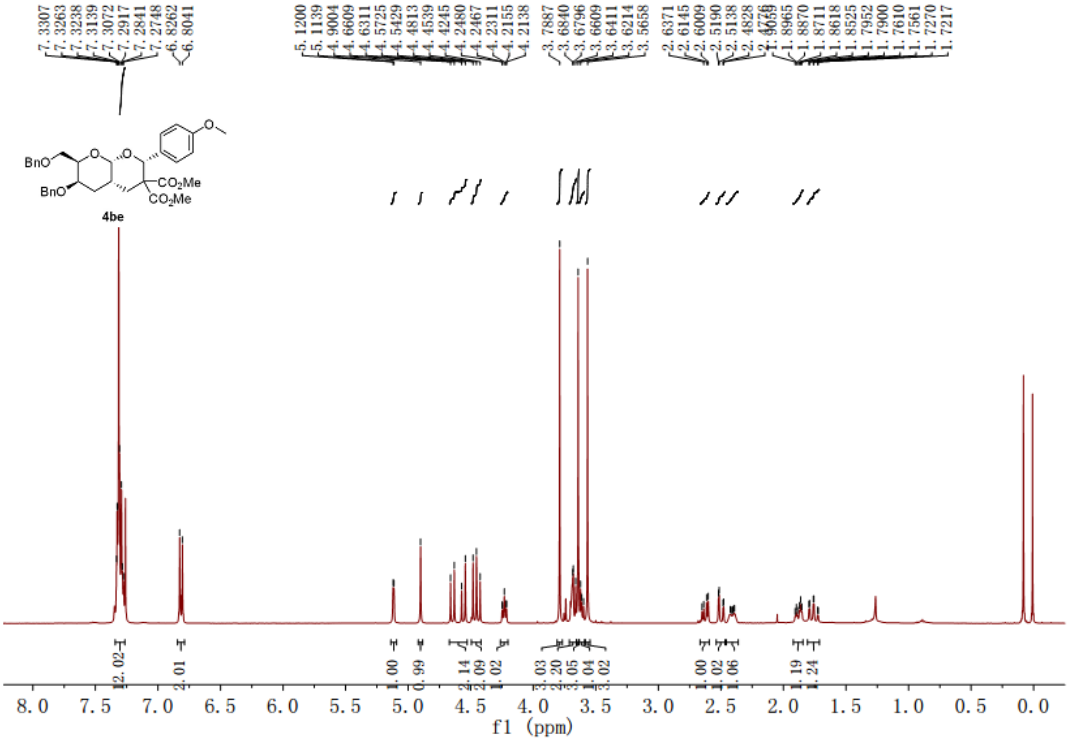
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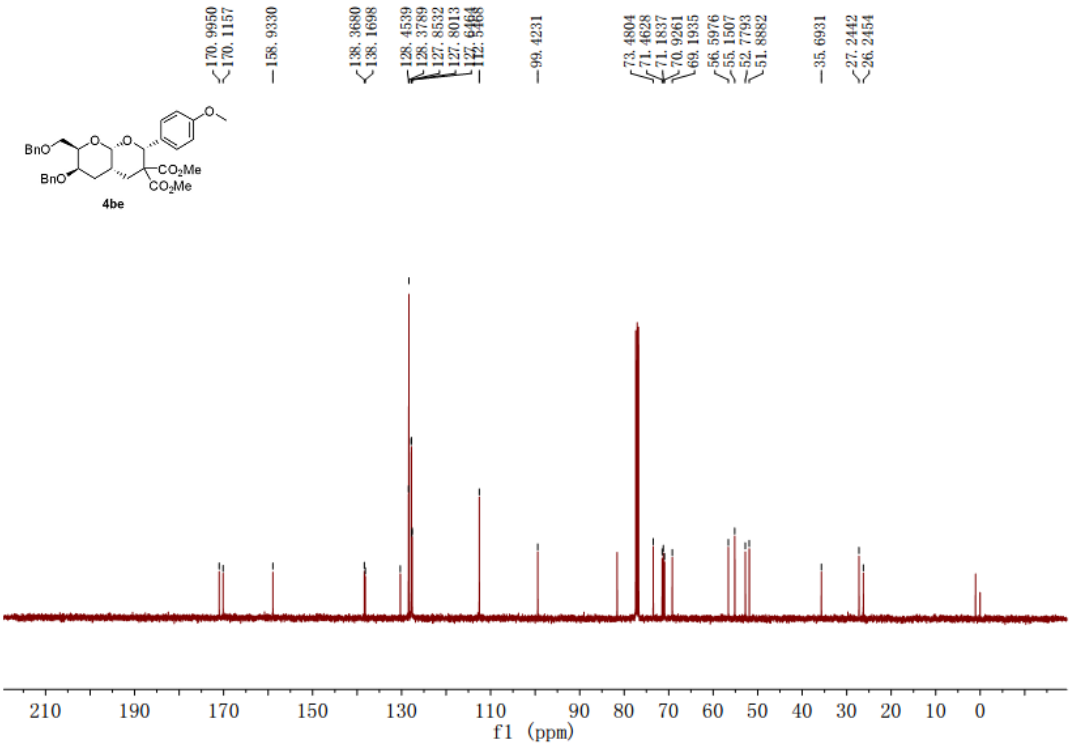
f1 (ppm)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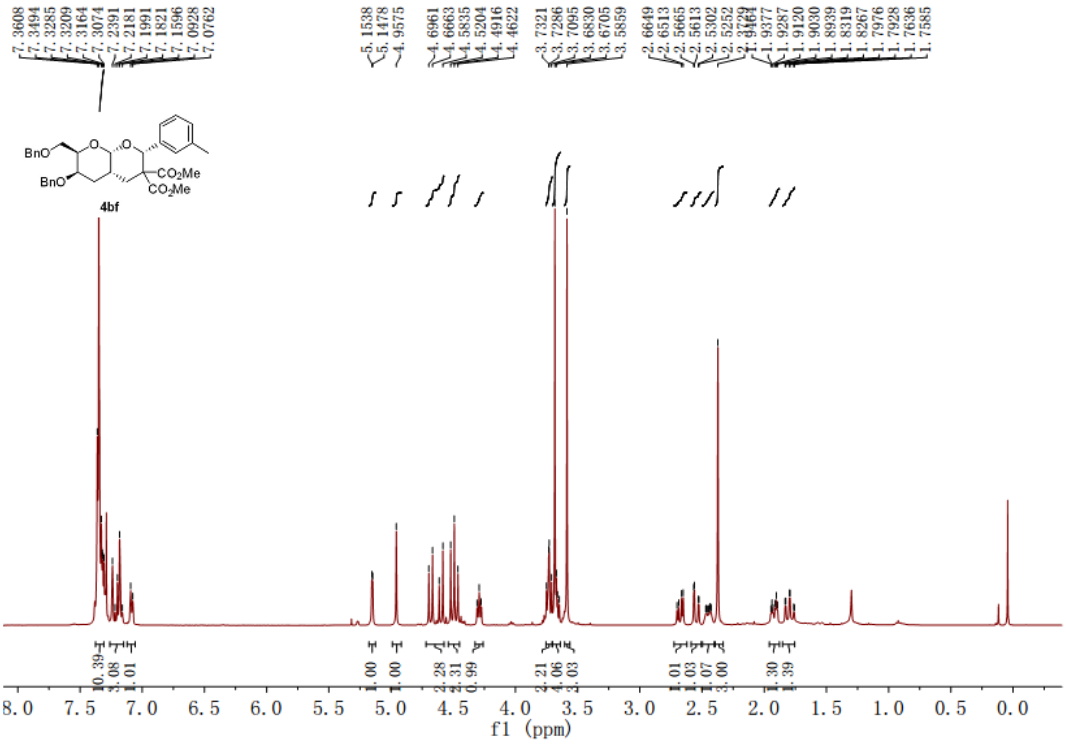
f1 (ppm)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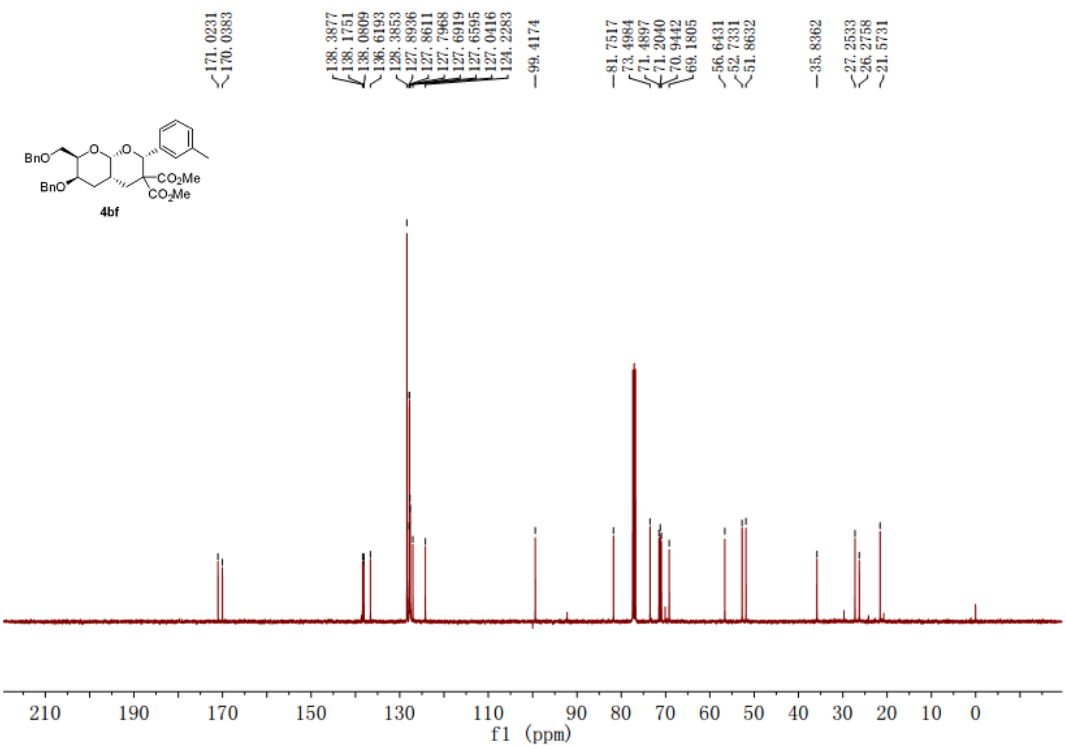
f1 (ppm)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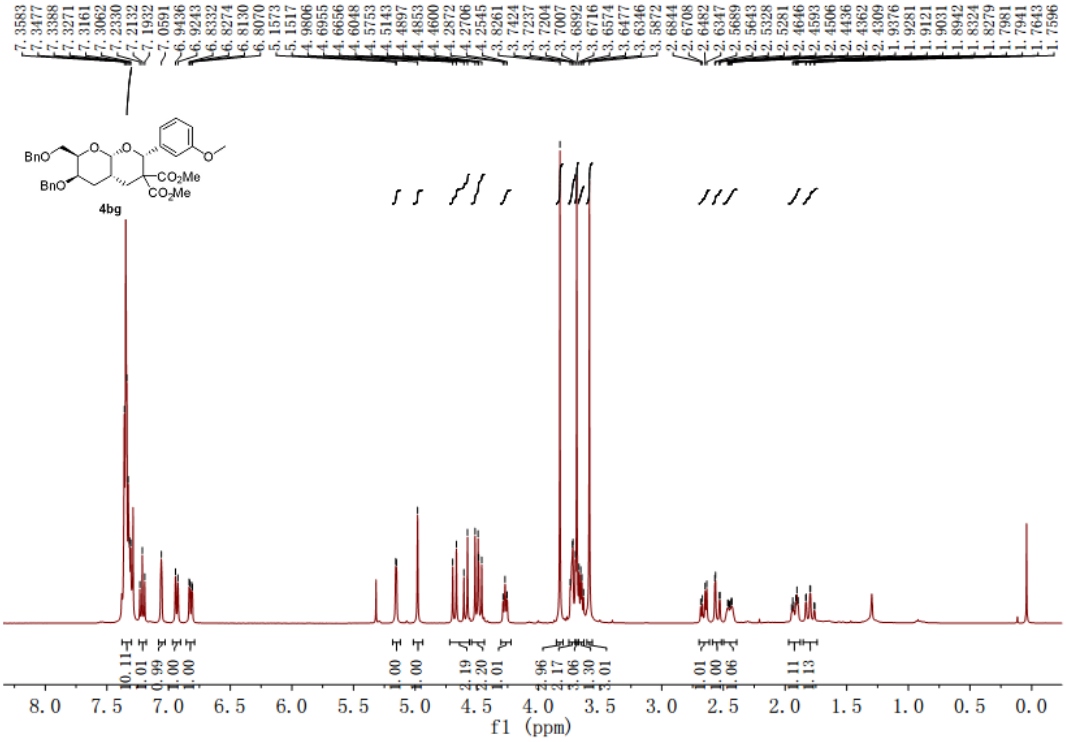
f1 (ppm)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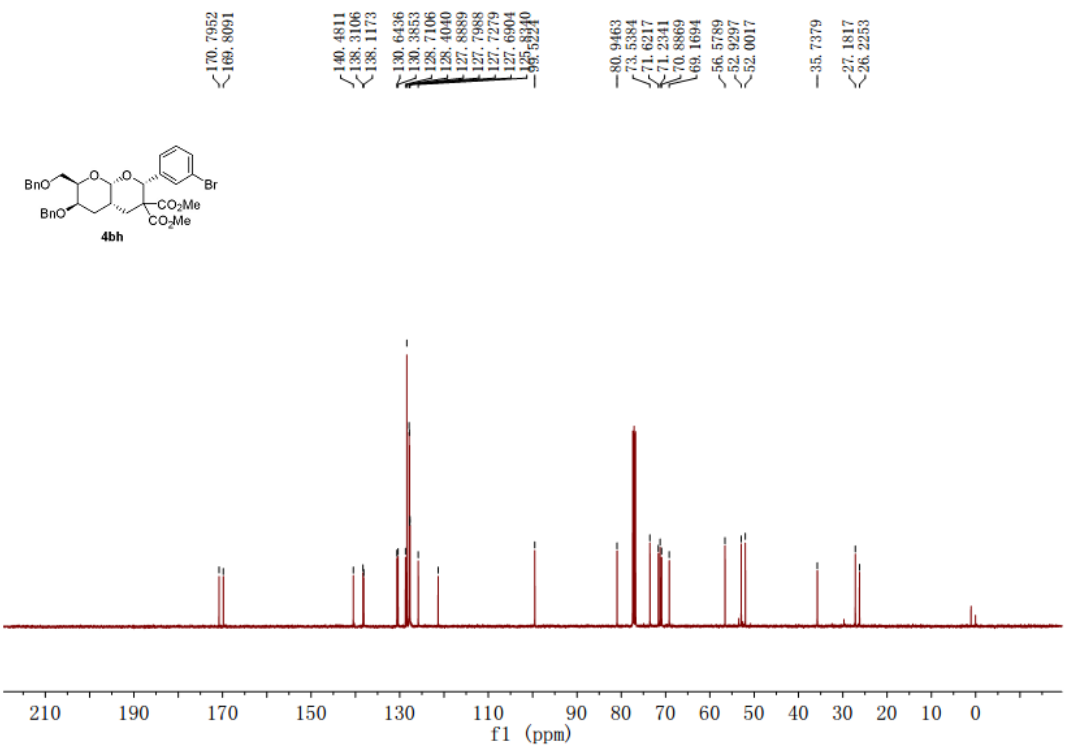
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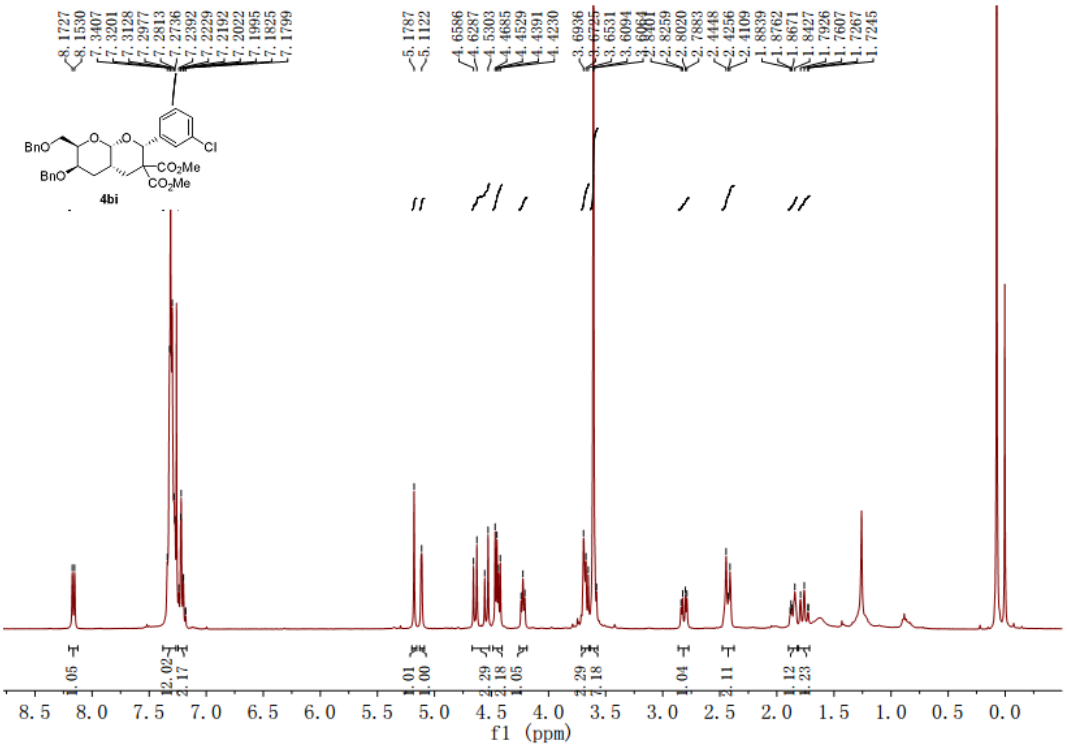
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7.2022
7.1995
7.1825
7.1799
5.1787
5.1122
4.6586
4.6287
4.5303
4.4685
4.4529
4.4391
4.4230
3.6936
3.6725
3.6531
3.6094
3.6061
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2.8020
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2.4448
2.4256
2.4109
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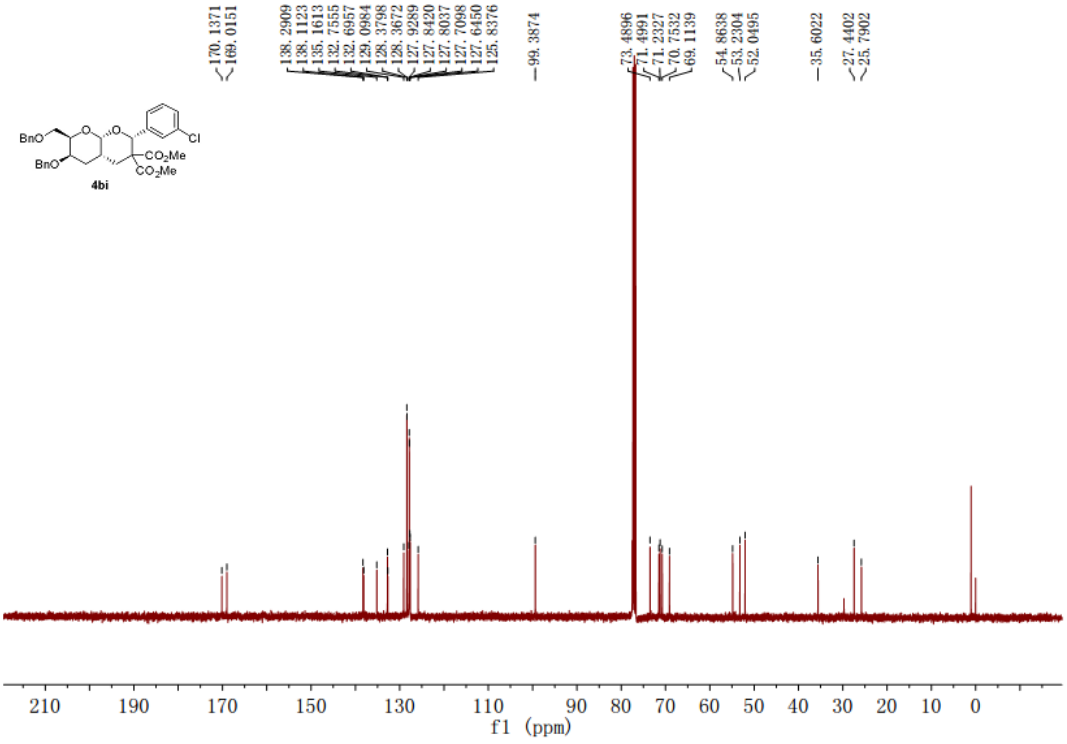
1.8762
1.8671
1.8427
1.7926
1.7607
1.7267
1.7245
BnO
BnO
CO2Me
CO2Me
Cl
4bi
1.05
12.02
2.17
1.01
1.00
2.29
2.18
1.05
2.29
7.18
1.04
2.11
1.12
1.23
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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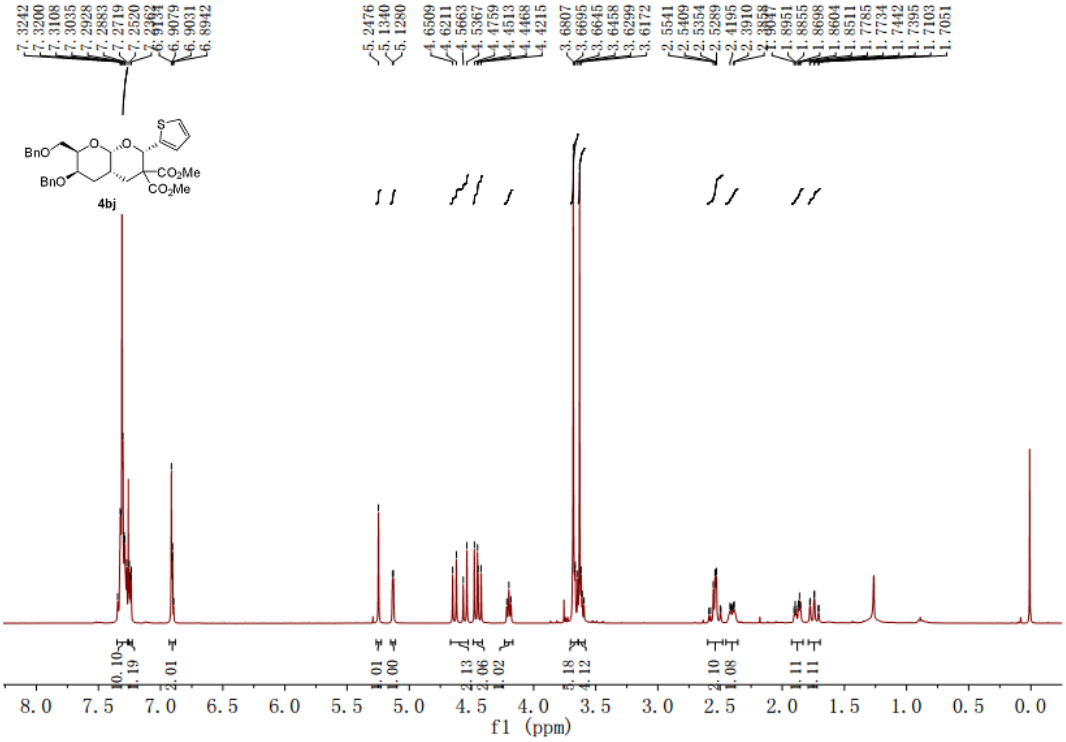
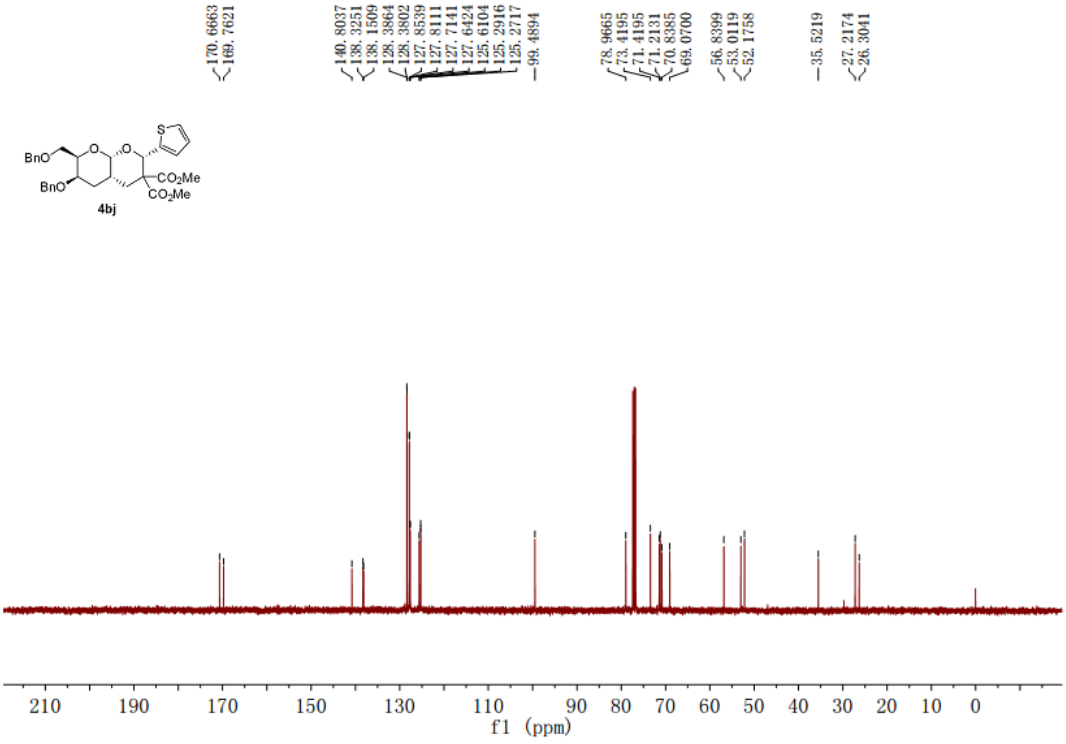
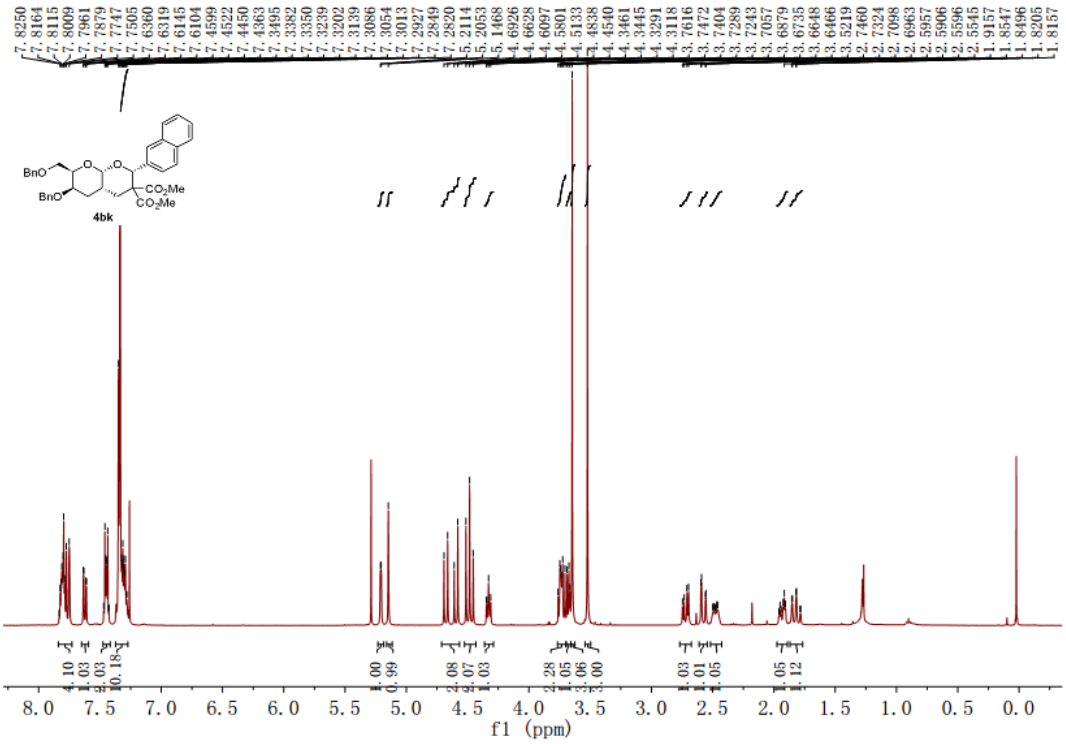
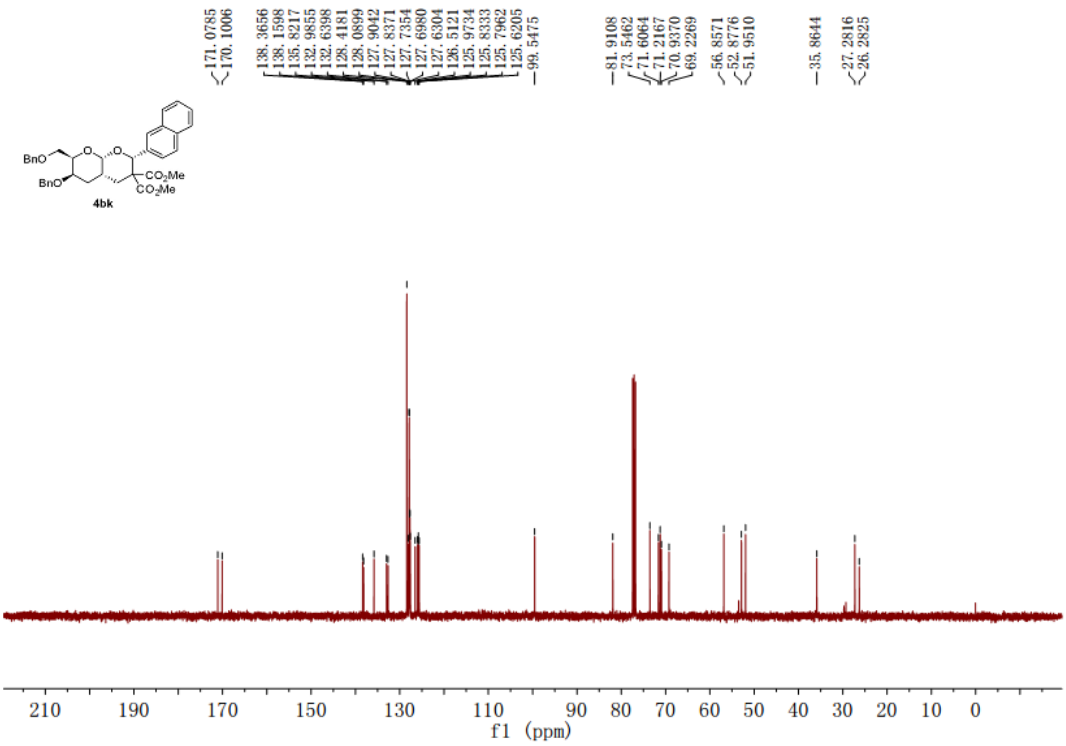
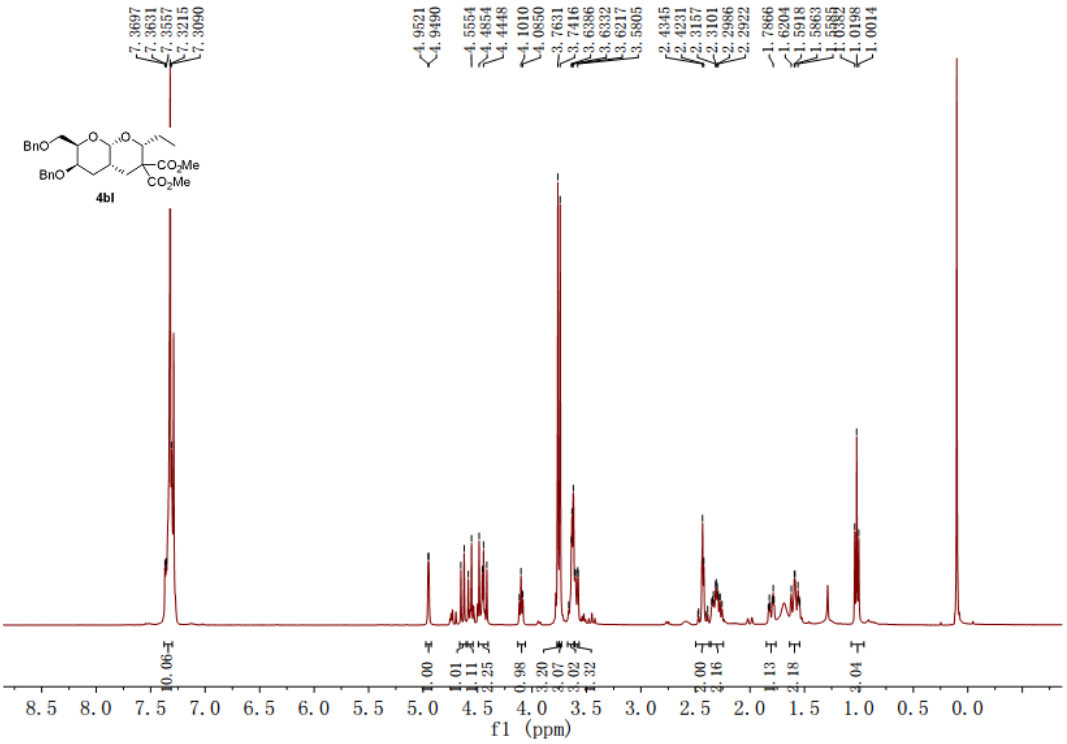
127.9289
127.8420
127.8037
127.7098
127.6450
125.8376
99.3874
73.4896
71.4991
71.2327
70.7532
69.1139
54.8638
53.2304
52.0495
35.6022
27.4402
25.7902
BnO
BnO
CO2Me
CO2Me
Cl
4bi
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


4bj
f1 (ppm)


4bj
f1 (ppm)


4bk
f1 (ppm)


4bk
f1 (ppm)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4.1010
4.0850
3.7631
3.7416
3.6386
3.6332
3.6217
3.5805
2.4345
2.4231
2.3157
2.3101
2.2986
2.2922
1.7866
1.6204
1.5918
1.5863
1.0198
1.0014
10.06
1.00
1.01
1.11
2.25
0.98
7.20
3.07
3.02
1.32
2.00
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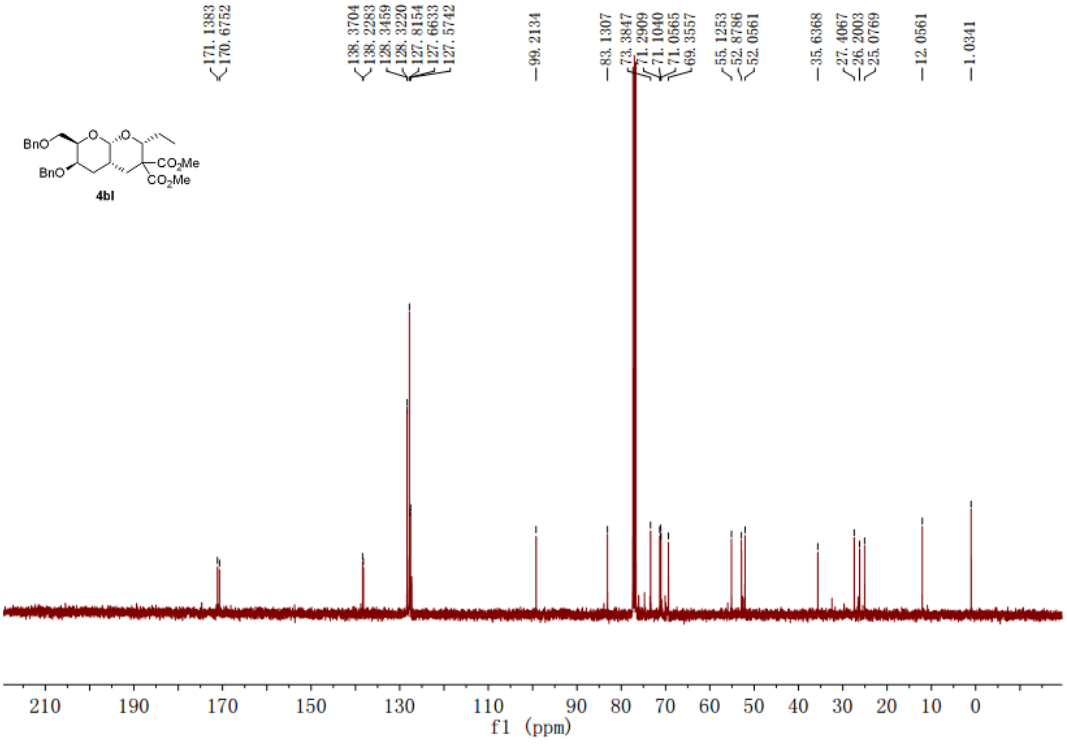
1.13
2.18
3.04
BnO
BnO
CO2Me
CO2Me
4bl
f1 (ppm)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52.0561
35.6368
27.4067
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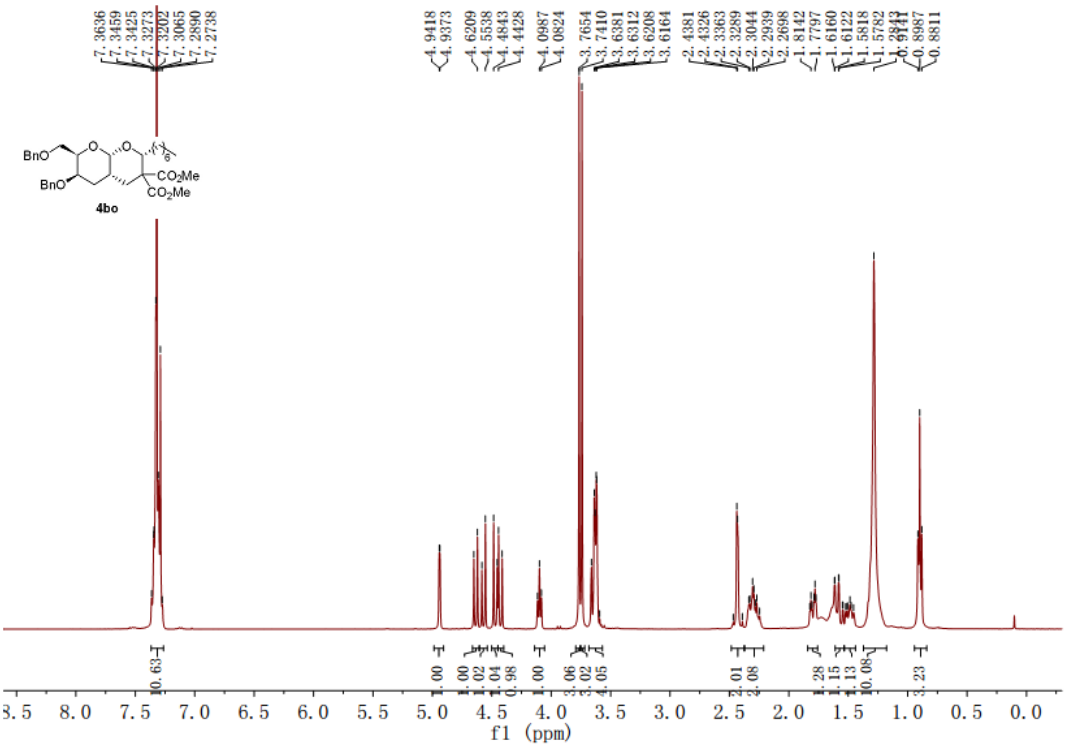
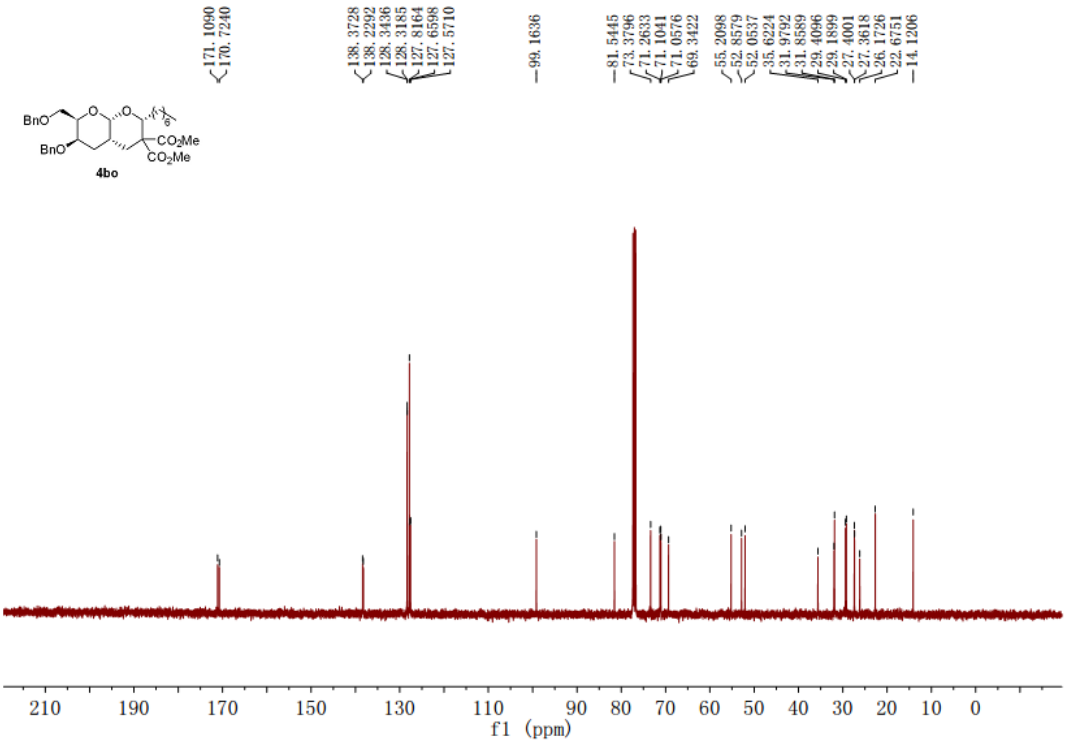
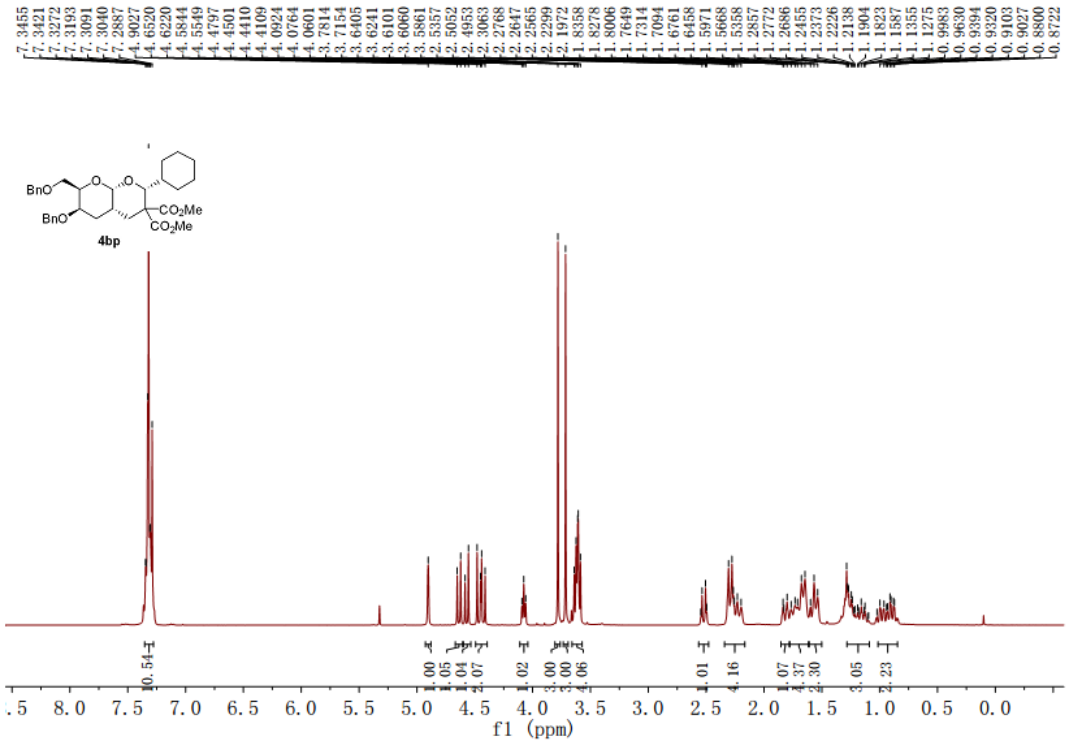
25.0769
12.0561
1.0341
BnO
BnO
CO2Me
CO2Me
4bl
f1 (ppm)


4bo
f1 (ppm)


4bo
f1 (ppm)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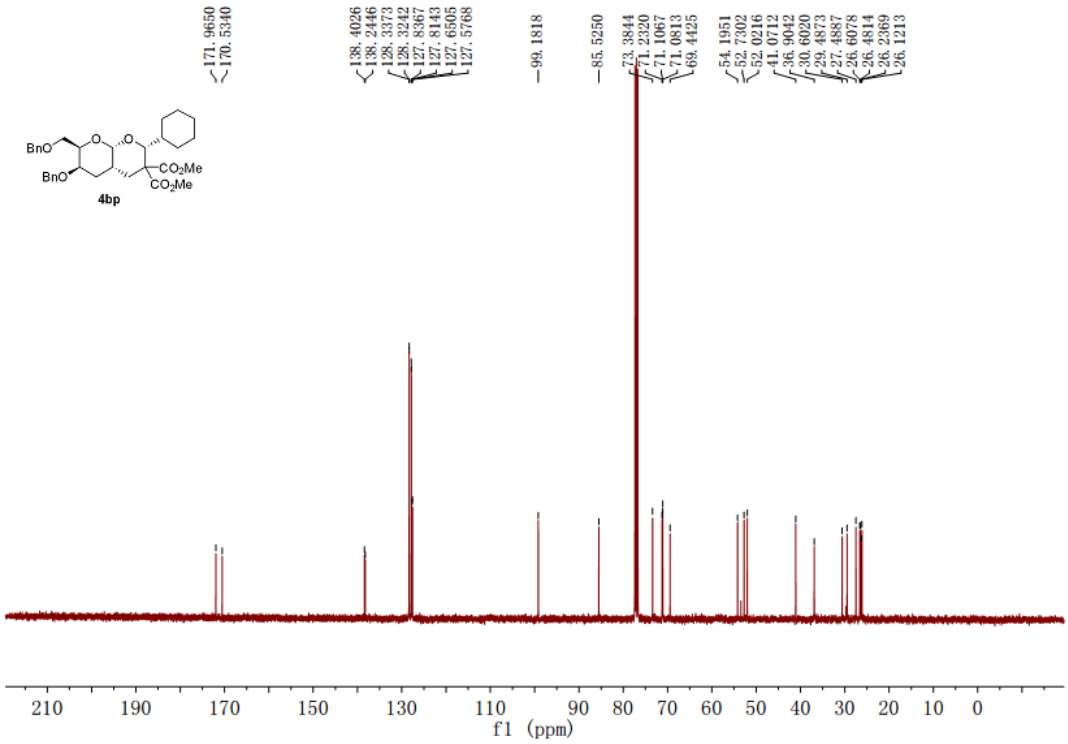
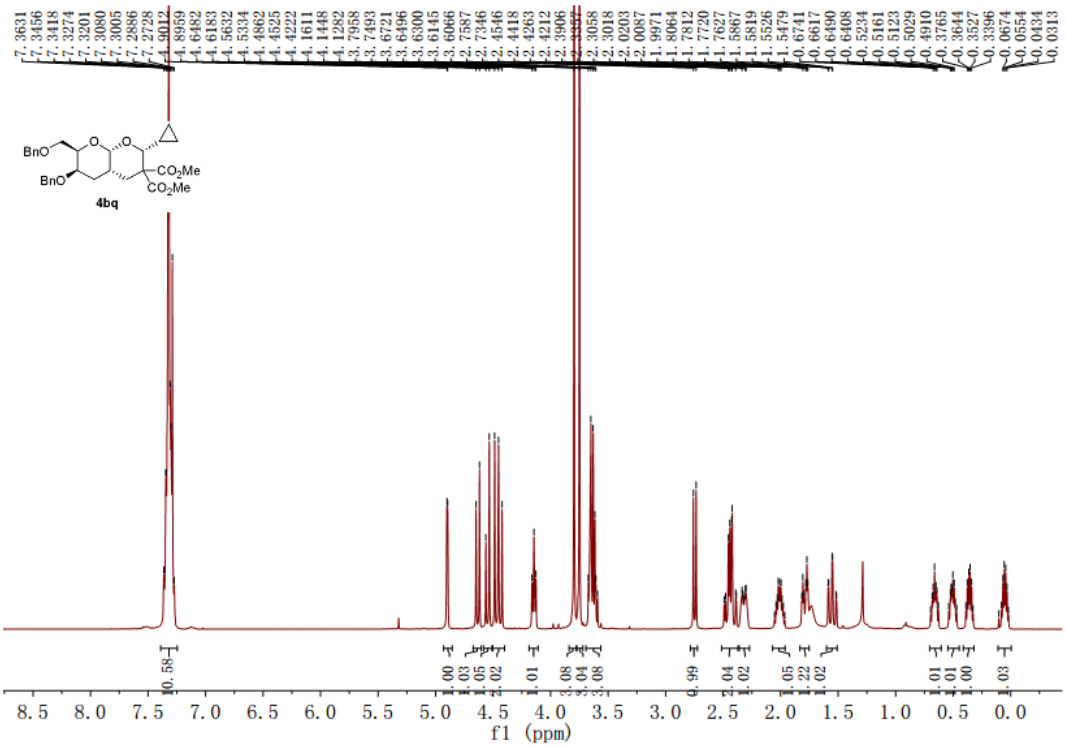
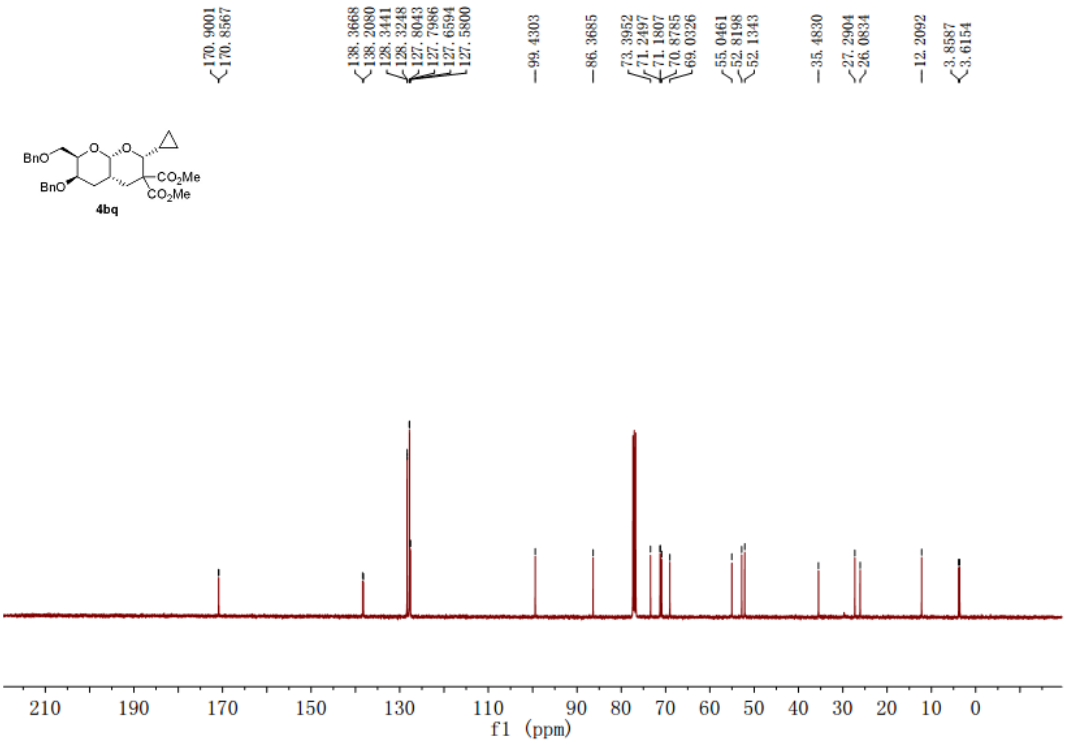

4bp
f1 (ppm)


BnO
BnO
CO2Me
CO2Me
4bq
f1 (ppm)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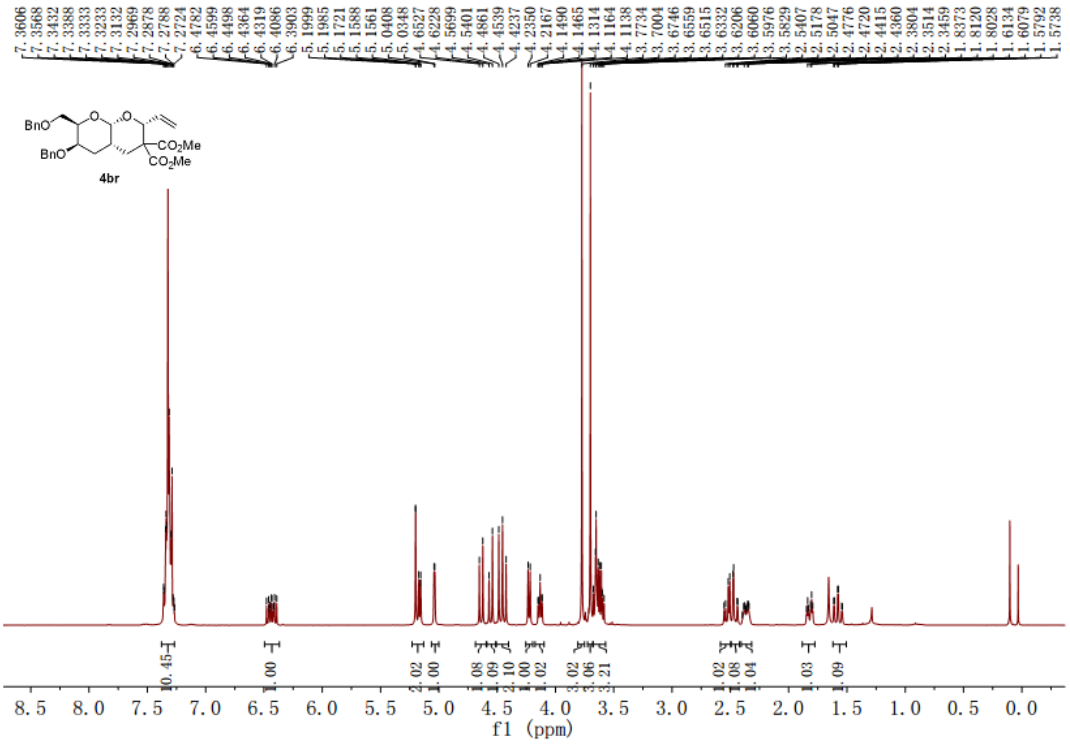
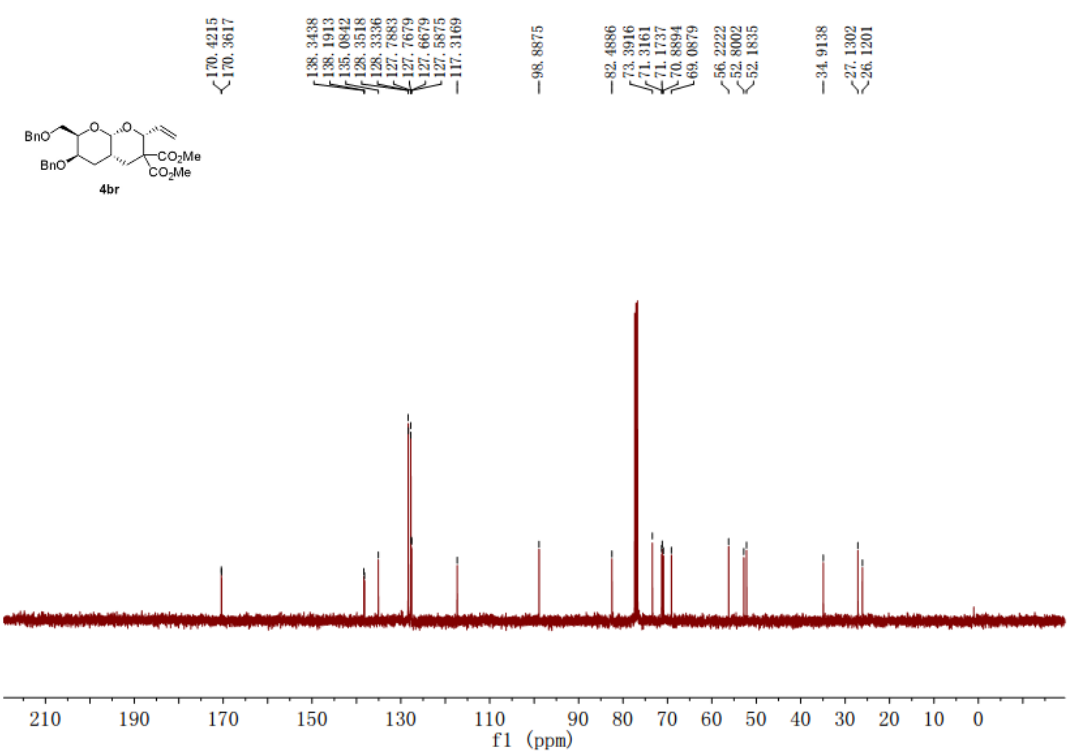
BnO
CO2Me
CO2Me
4bq
f1 (ppm)


BnO
BnO
CO2Me
CO2Me
4br
f1 (ppm)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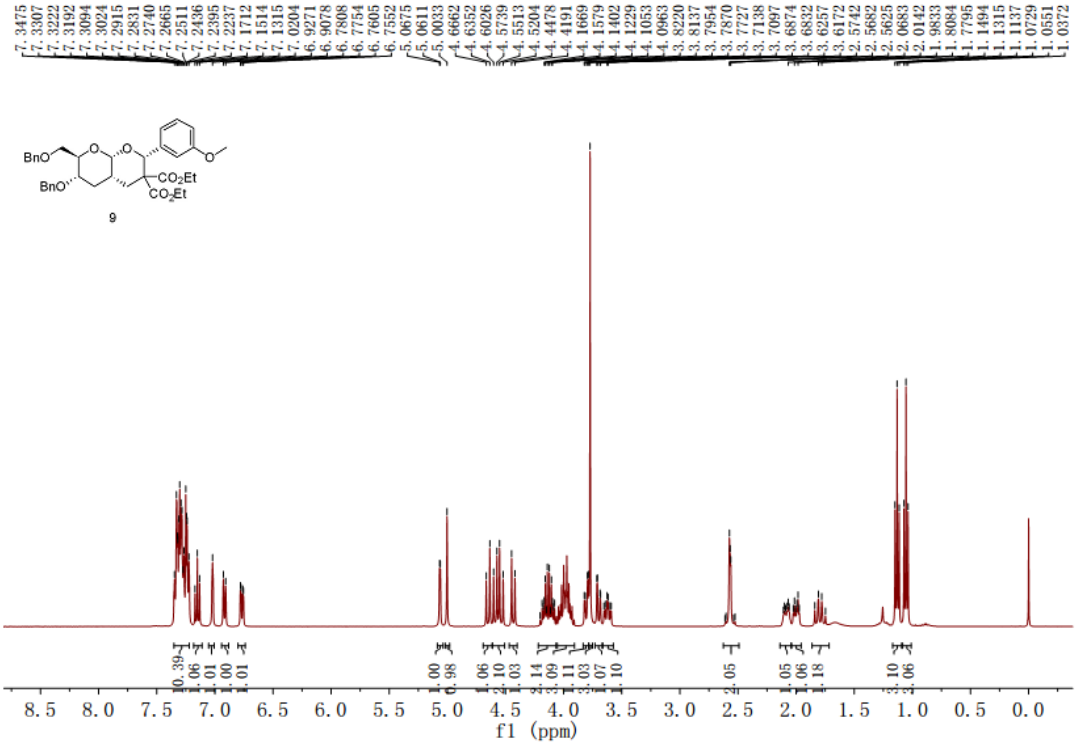
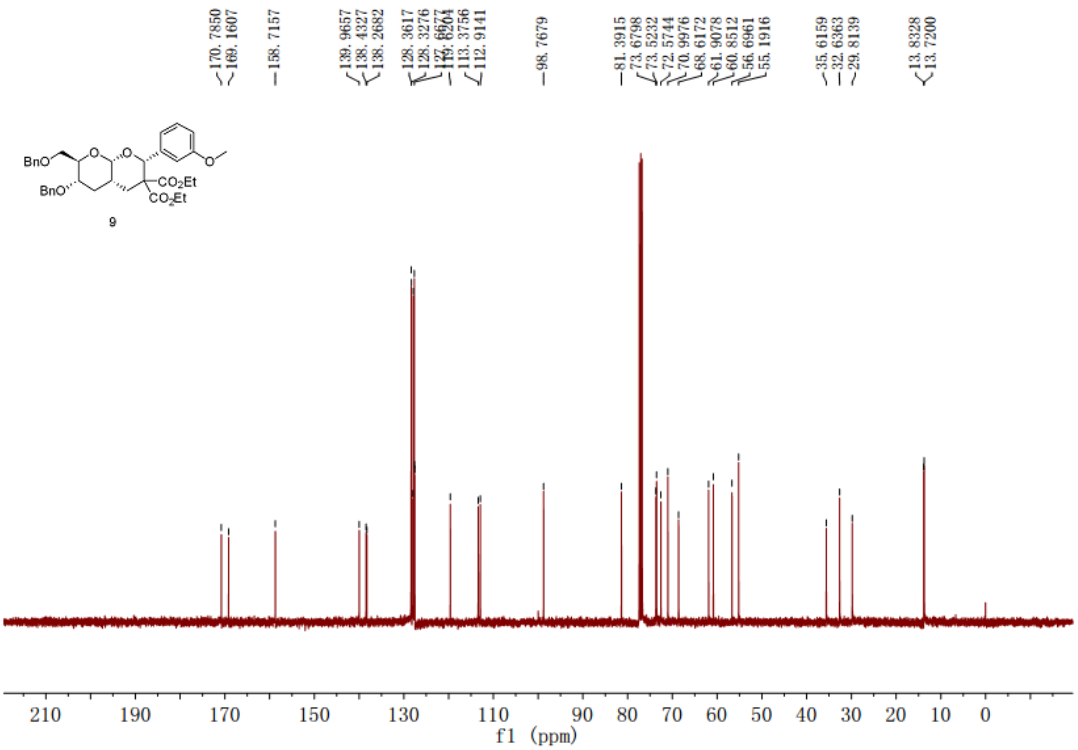
BnO
CO2Me
CO2Me
4br
f1 (ppm)


BnO
BnO
CO2Et
CO2Et
9
f1 (ppm)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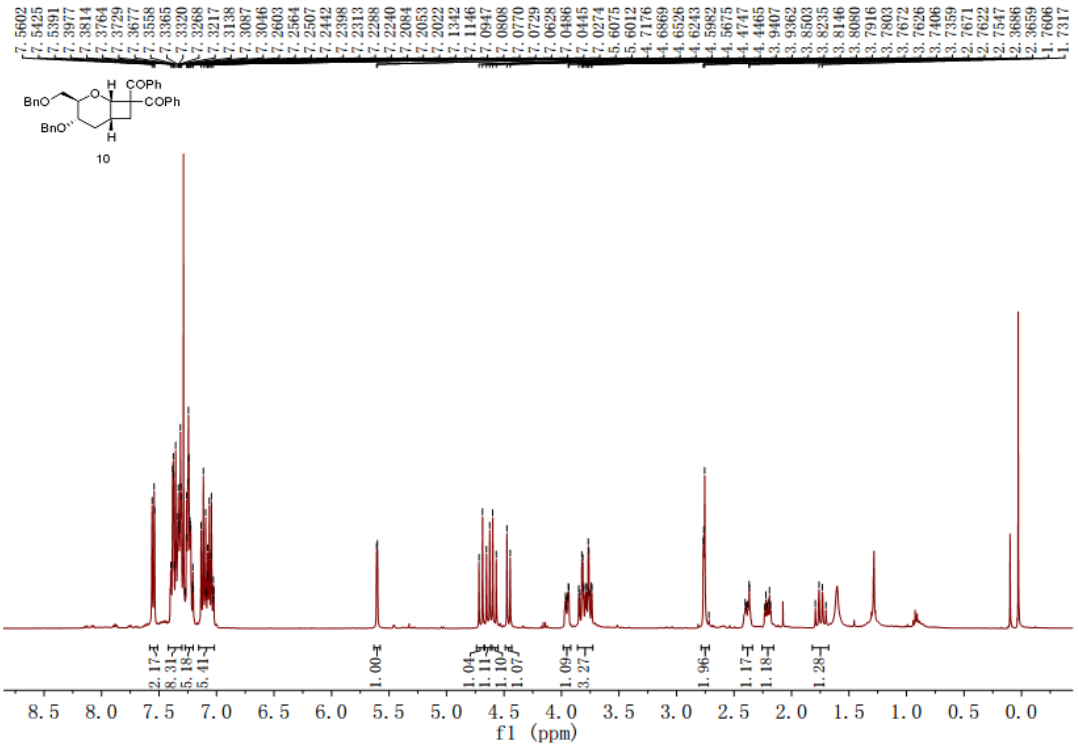
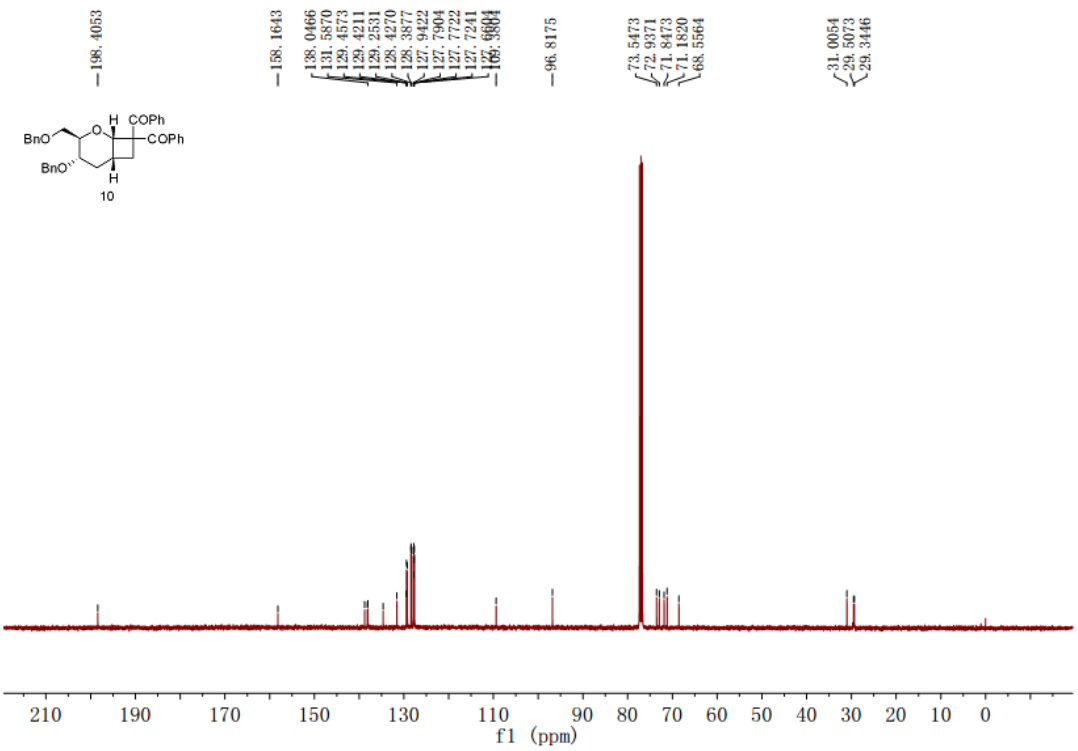
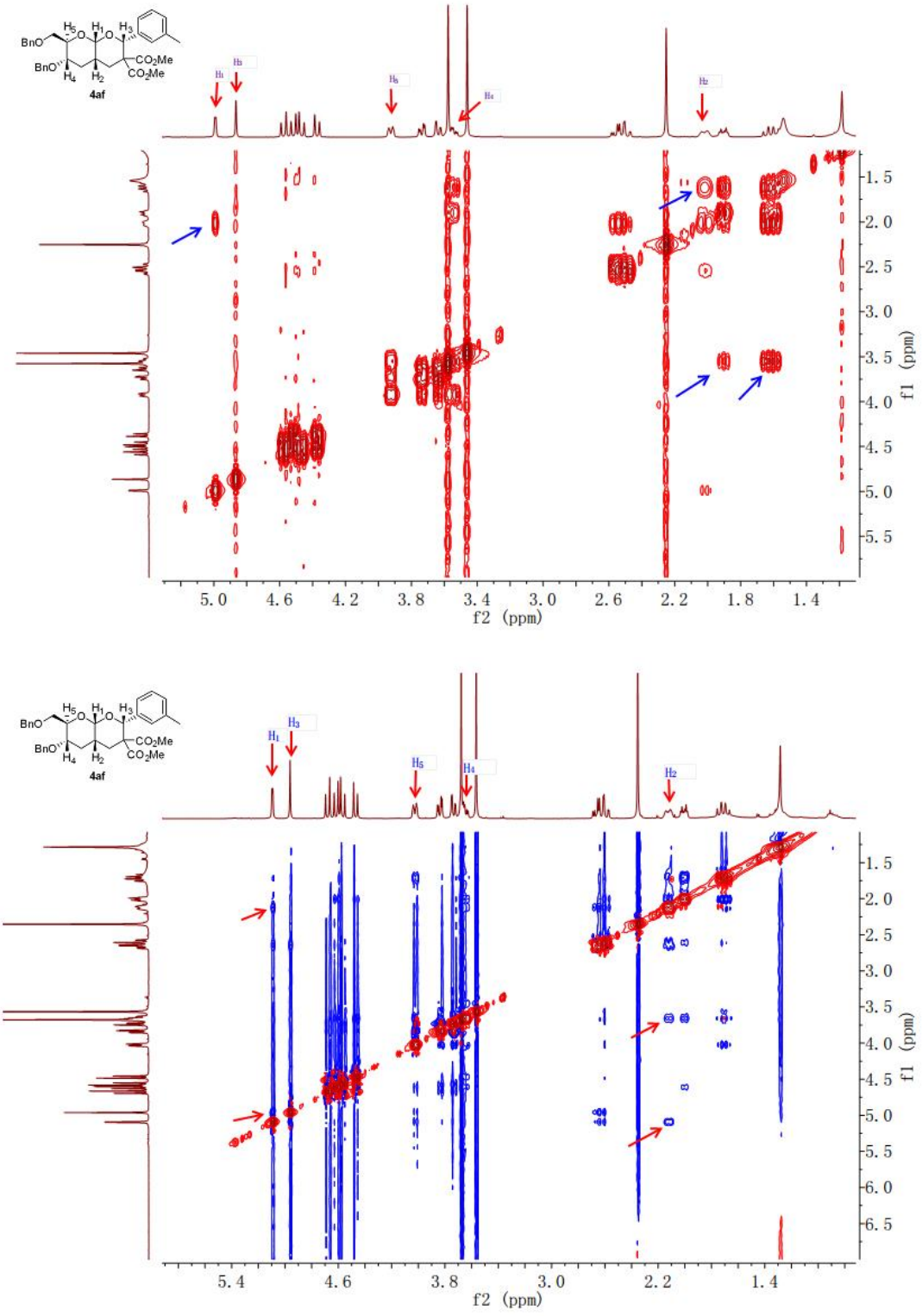
BnO
CO2Et
CO2Et
9
f1 (ppm)


10
f1 (ppm)

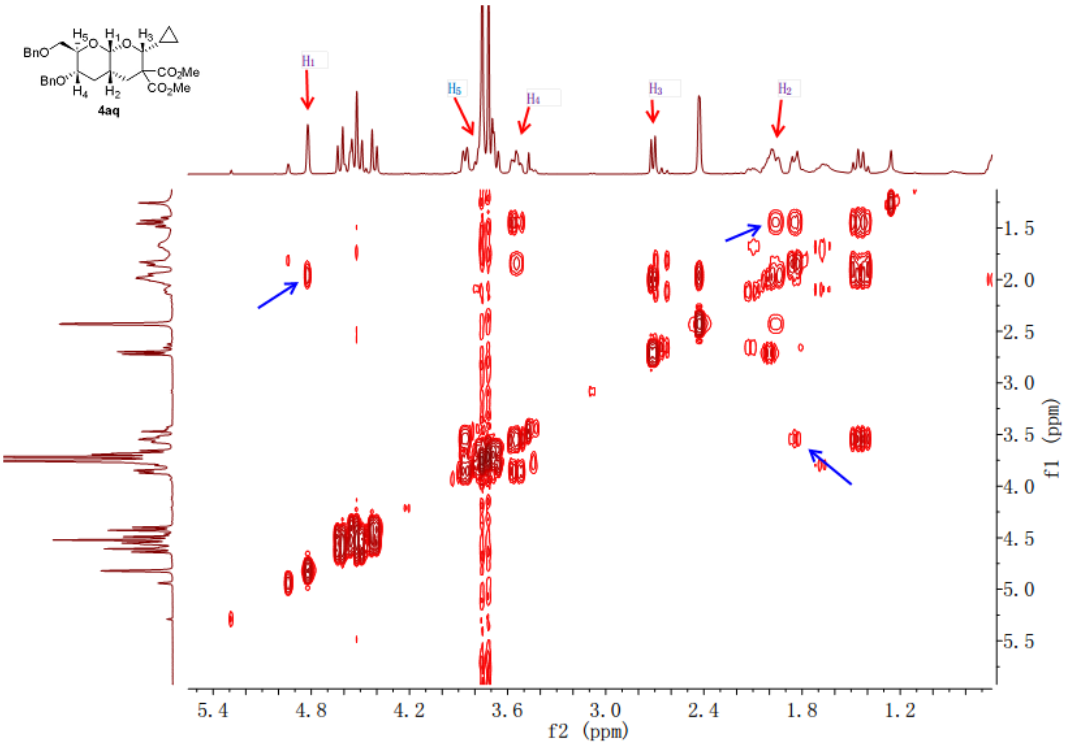

10
f1 (ppm)

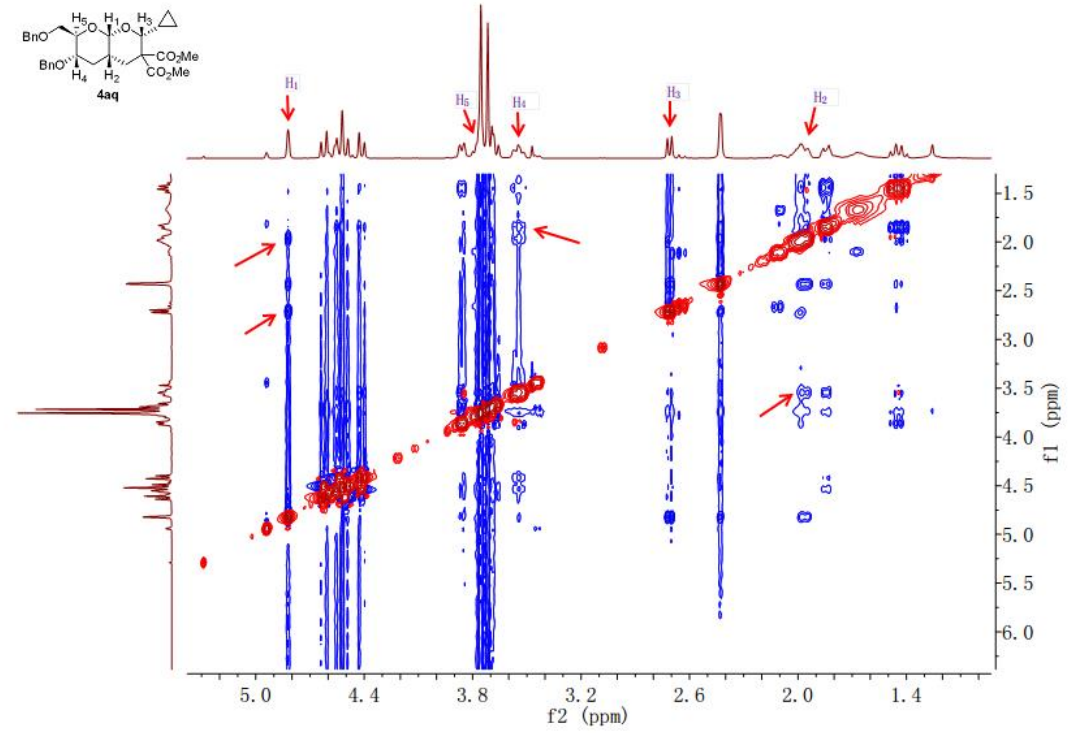
9. ^{1}H-^{1}H COSY and NOESY

^{1}H-^{1}H COSY and NOESY of **4af**

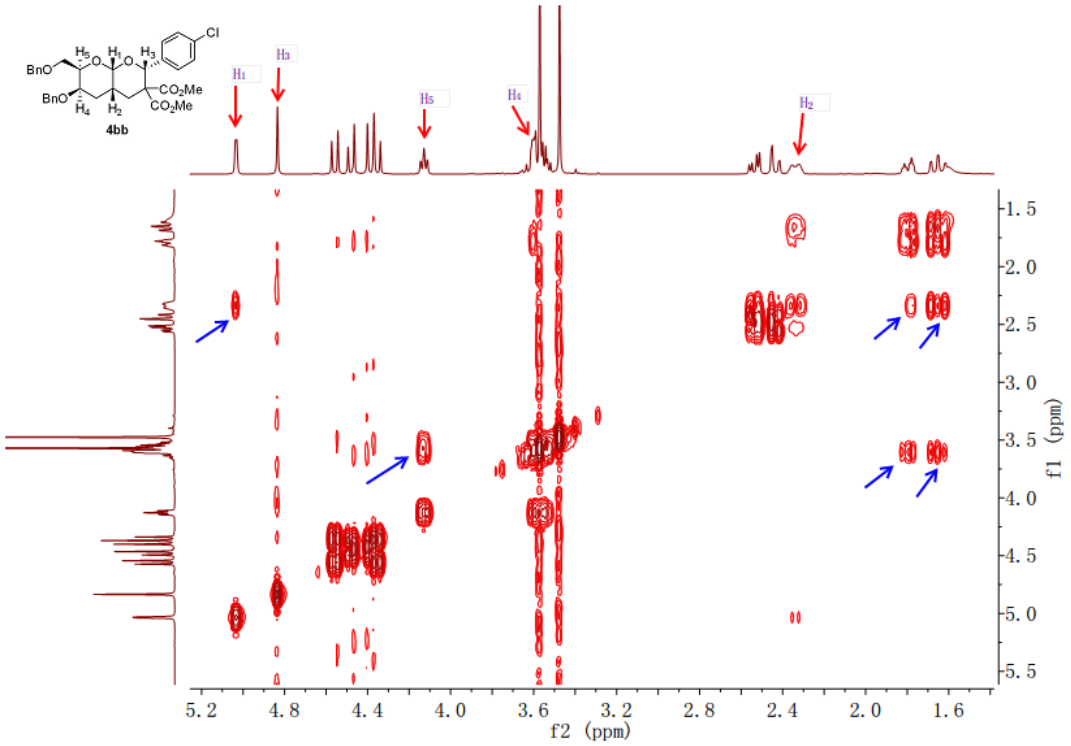


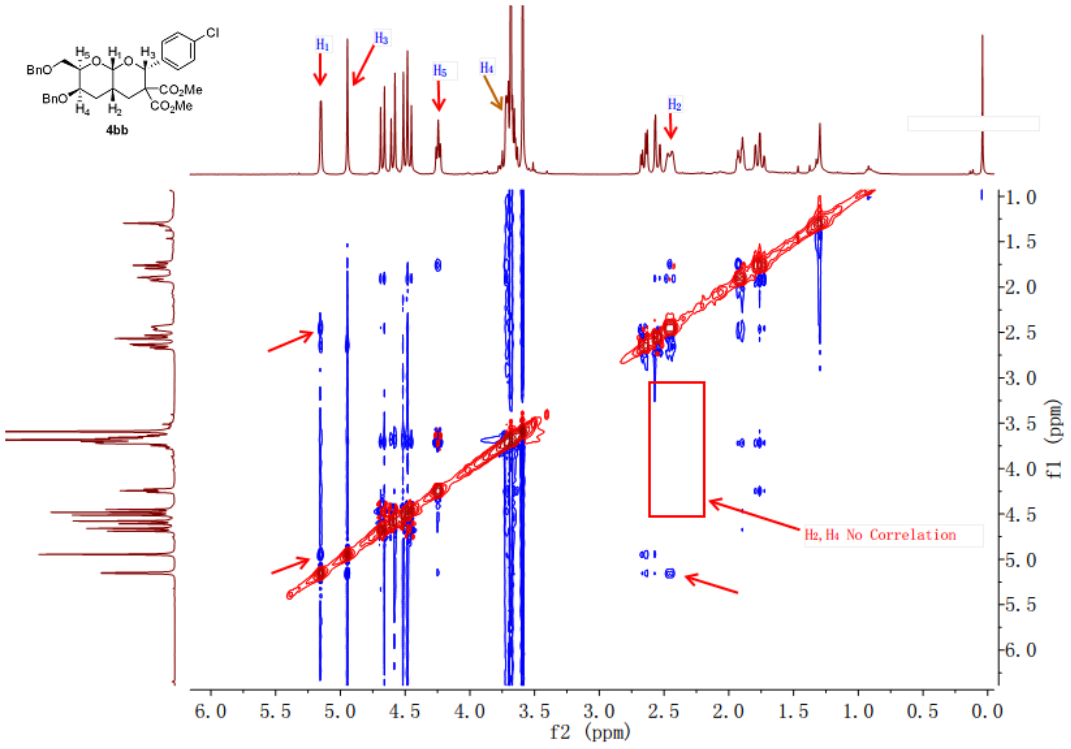
^{1}H-^{1}H COSY and NOESY of **4aq**





^{1}H-^{1}H COSY and NOESY of **4bb**





^{1}H-^{1}H COSY and NOESY of **4bq**