Supporting Information

Total Synthesis of (-)-Penicimutanin A and Related Congeners.

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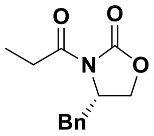
General Information

Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

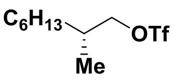
Reactions were monitored by Thin Layer Chromatography on plates (GF254) supplied by Yantai Chemicals (China) visualized by UV or stained with ethanolic solution of phosphomolybdic acid and cerium sulfate, basic solution of $KMnO_4$, and iodine vapor. If not specially mentioned, flash column chromatography was performed using E. Merck silica gel (60, particle size 0.040–0.063 mm). NMR spectra were recorded on JEOL 400, Bruker AV500 instruments and calibrated by using residual undeuterated chloroform (δ H = 7.26 ppm) and $CDCl_3$ (δ C = 77.16 ppm), or Methanol-d_4 (δ H = 3.31 ppm, δ C = 49.00 ppm) as internal references. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, b = broad, td = triple doublet, dt = double triplet, dq = double quartet, m = multiplet. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization) as ionization method.

For experiments using 10 mL IKA ElectraSyn pro vial, the dimensions of the glassy carbon anode were 55 mm x 8 mm x 2 mm; the dimensions of Pt Sheet cathode were 55 mm x 8 mm x 2 mm.

Experimental procedures:



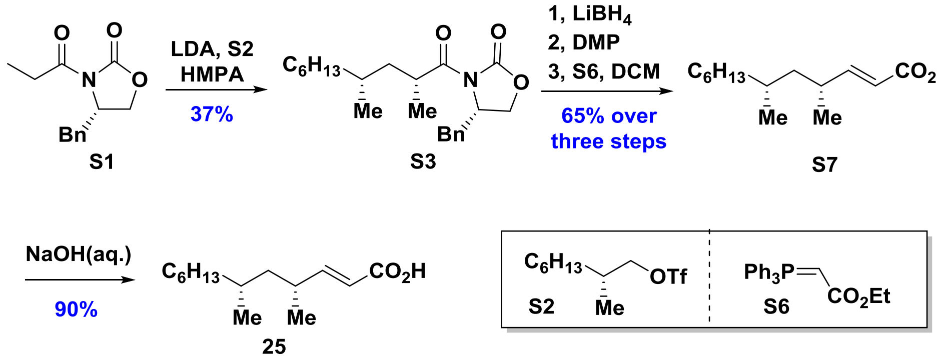
S1



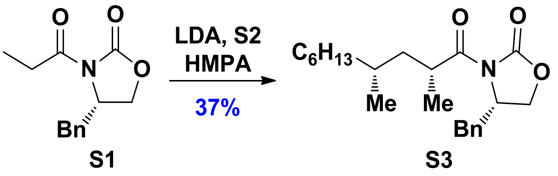
S2

*Compound **S1** and **S2** are known products.*[1, 2]

Synthetic route toward side chain 25:



*Synthesis of compound **S3***



To a flamed-dried flask containing **S1** (4.1 g, 17.8 mmol) in THF (60 mL) was added LDA (2 M, 11.0 mL, 22 mmol) dropwise at -78 °C. The reaction was stirred for 40 mins at -78 °C. HMPA (4.2 mL, 21.1 mmol) was added dropwise to the mixture, followed by the addition of **S2** (4.97 g, 18 mmol). Stirring was continued at -78 °C for 4 hours, then cooling bath was removed and the reaction was stirred at room temperature for an additional 0.5 hours. Saturated aqueous NH_4Cl (60 mL) was added to quench the reaction, extracted with EtOAc (50 mL × 3) and washed with brine (50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to give a yellow oil, which was chromatographed on silica gel to give the amide **S3** (2.4 g, 37% yield) as a yellow oil. **R*f*** = 0.65 (petroleum ether / EtOAc = 5/1);

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.21 (dd, *J* = 6.9, 1.8 Hz, 2H), 4.68 (ddt, *J* = 10.6, 7.0, 3.3 Hz, 1H), 4.20 –

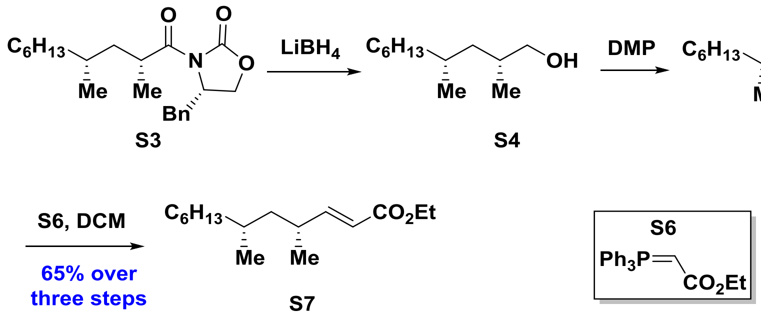
4.11 (m, 2H), 3.94 (dt, J = 8.4, 6.5 Hz, 1H), 3.29 (dd, J = 13.3, 3.4 Hz, 1H), 2.72 (dd, J = 13.3, 9.7 Hz, 1H), 1.87 (ddd, J = 13.9, 8.4, 5.9 Hz, 1H), 1.45-1.41 (m, 1H), 1.35-1.32 (m, 2H), 1.31 – 1.21 (m, 8H), 1.21 – 1.17 (m, 1H), 1.16 (d, J = 6.8 Hz, 3H), 1.14 – 1.06 (m, 1H), 0.91 (d, J = 6.6 Hz, 3H), 0.86 (t, J = 6.7 Hz, 3H);

^{13}C NMR (125 MHz, Chloroform-*d*) δ 177.8, 153.2, 135.5, 129.5, 129.0, 127.4, 66.0, 55.5, 41.5, 38.2, 36.9, 35.4, 32.0, 30.9, 29.7, 27.0, 22.8, 20.1, 18.2, 14.2.

IR: ν_{max} 2925, 1786, 1693, 1384, 1210, 704 cm^{-1};

HRMS calcd. for $C_{22}H_{33}NO_3Na^+$ [M+Na]$^+$: 382.2358. Found: 382.2358.

*Synthesis of compound **S8***



To a stirred solution of $LiBH_4$ (1.8 g, 79.4 mmol) in THF (100 mL) at 0 ^{o}C was added a THF (10 mL) solution of compound **S3** (3.8 g, 10.6 mmol) dropwise. The mixture was stirred at room temperature for 1.5 hours. MeOH (10 mL) was slowly added followed by aqueous NH_4Cl (30 mL). The mixture was extracted by EtOAc (100 mL × 3) and washed with brine (100 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated to give crude **S4** (1.6 g) as colorless oil, which was used directly in the next step.

To a stirred DCM (30 mL) solution of **S4** (1.6 g, 8.5 mmol) and $NaHCO_3$ (2.9 g, 34.0 mmol) was added DMP (5.2 g, 12.8 mmol) in three potions. The reaction was stirred at room temperature for 3 hours. Saturated solution of $Na_2S_2O_3$ (30 mL) was added and the mixture was extracted with DCM (40 mL × 3). The combined organic layers were washed with brine (40 mL) and dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified via quick flash column chromatography on silica gel to give crude aldehyde **S5** (1.57 g) as a colorless oil.

The freshly prepared crude **S5** (1.57 g) was dissolved in DCM (50 mL), followed by pouring Ethyl (triphenylphosphoranylidene) acetate **S6** (11.8 g, 34.0 mmol) into the mixture. The formed system was refluxed overnight. The reaction was monitored by TLC. After removing the volatiles in vacuo, the residue was chromatographed on silica gel to give **S7** as a colorless oil. (1.7 g, 65 % yield from **S3**). $\mathbf{R}_f$ = 0.9 (petroleum ether / EtOAc = 5/1);

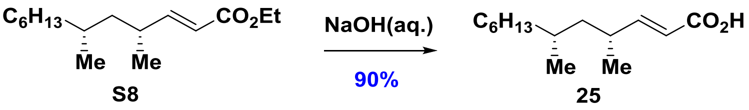
^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 6.80 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.76 (dd, *J* = 15.7, 1.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.46 – 2.34 (m, 1H), 1.41 – 1.33 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.31 – 1.18 (m, 9H), 1.13 – 1.05 (m, 2H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H);

^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 167.1, 154.9, 119.7, 60.3, 43.9, 37.5, 34.4, 32.0, 30.5, 29.8, 26.9, 22.8, 20.5, 19.5, 14.4, 14.2.

IR: ν_{max} 3421, 1746, 1634, 1374, 1192, 1010, 761cm^{-1};

HRMS calcd. for $C_{16}H_{30}O_2Na^+$ $[M+Na]^+$: 277.2144. Found: 277.2144.

*Synthesis of compound **25***



Compound **S8** (800.0 mg, 3.2 mmol) was dissolved in MeOH (50 mL) and H_2O (5 mL). Sodium hydroxide (512.0 mg, 12.8 mmol) was added. The reaction mixture was stirred at 60 ^{o}C until the ester **S8** was completely consumed. The reaction was diluted with water and the volatiles were removed under vacuum, extracted by Et_2O (50 mL × 3). The organic phase was extracted with water (50 mL). Then, the combined water phase was added aqueous HCl (2 N) until pH = 1. Finally, the aqueous phase was extracted with EtOAc (80 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give acid **25** (640.0 mg, 90 % yield) as a pale oil. $\mathbf{R}_f$ = 0.1 (petroleum ether / EtOAc = 5/1);

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 6.93 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.79 (d, *J*

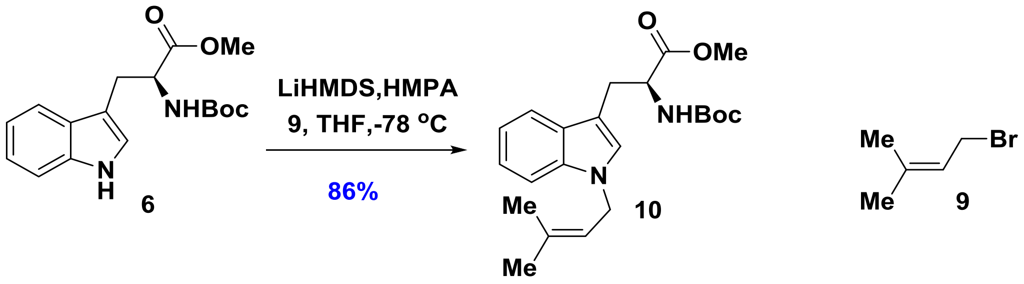
= 15.6 Hz, 1H), 2.51 – 2.39 (m, 1H), 1.43 – 1.34 (m, 2H), 1.29 – 1.21 (m, 9H), 1.12-1.10 (m, 2H), 1.04 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 7.7 Hz, 3H), 0.84 (d, *J* = 6.2 Hz, 3H);

^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 172.2, 157.9, 119.1, 43.8, 37.5, 34.6, 32.1, 30.5, 29.8, 26.9, 22.8, 20.4, 19.6, 14.3.

IR: ν_{max} 3421, 2962, 2922, 1696, 1651, 1419, 1282, 990, 931cm^{-1};

HRMS calcd. for $C_{14}H_{25}O_2^-$ [M-H]$^-$: 225.1855. Found: 225.1855. $[\alpha]^{20}_D$ -28.10 (c 1.0, CH_2Cl_2).

*Synthesis of compound **10***



To a flamed-dried flask containing **6** (1 g, 3.14 mmol) in THF (40 mL) was added LiHMDS (1 M, 3.8 mL, 3.8 mmol) dropwise at -78 °C. The reaction was stirred for 40 mins at -78 °C. HMPA (0.6 mL, 3.45 mmol) was added dropwise to the mixture, followed by the addition of **9** (2 mL, 3.30 mmol). Stirring was continued at -78 °C for 1 hours, then cooling bath was removed and the reaction was stirred at room temperature for an additional 10 hours. Saturated aqueous NH_4Cl (60 mL) was added and the mixture was extracted with EtOAc (30 mL × 3) and washed with brine (20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to give a yellow oil, which was chromatographed on silica gel to give the compound **10** (1 g, 86% yield) as a white solid. **R*f*** = 0.75 (petroleum ether / EtOAc = 2/1);

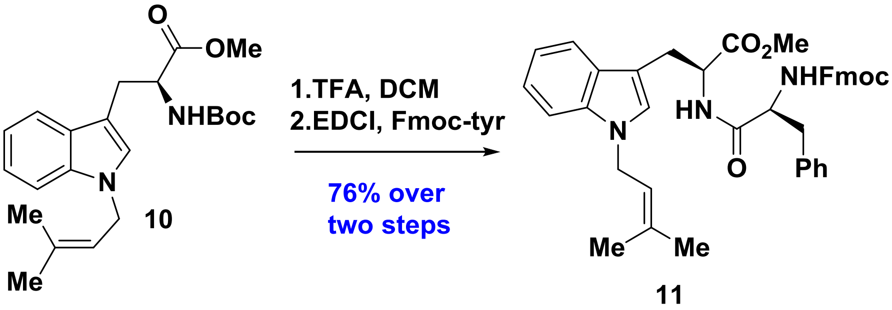
^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 5.35 (dt, *J* = 8.9, 4.2 Hz, 1H), 5.06 (d, *J* = 8.1 Hz, 1H), 4.64 (d, *J* = 6.9 Hz, 2H), 4.61 (d, *J* = 5.2 Hz, 1H), 3.68 (s, 3H), 3.32 – 3.19 (m, 2H), 1.82 (s, 3H), 1.76 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.9, 155.4, 136.5, 136.3, 126.2, 121.7, 120.0, 119.2, 119.0, 109.7, 108.67, 108.65, 79.9, 54.4, 52.3, 44.1, 29.8, 28.5, 28.1, 25.8, 18.2.

IR: ν_{max} 2920, 2345, 1734, 1646, 1547, 1457, 1360 cm^{-1}.

HRMS calcd. for $C_{22}H_{30}N_2O_4Na^+$ [M+Na]$^+$: 409.2103. Found: 409.2100. **mp.**:93-96 °C.

Synthesis of compound ***11***



To a stirred solution of **10** (1.5 g, 4.0 mmol) in DCM (20 mL) at 0 °C was added TFA (4.6 mL, 40 mmol). The reaction was stirred at room temperature for overnight. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted by DCM (20 mL × 3) and washed with brine (20 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated to give crude product **S8** as colorless oil, which was used directly in the next step.

To a stirred solution of above **S8** (1.1 g) and Fmoc-L-Phenylalanine (1.7 g, 4.4 mmol) in DCM (25 ml) was added Et_3N (0.83 ml, 6 mmol), HOBt (0.6 g, 4.4 mmol) and EDCI (0.84 g, 4.4 mmol) at 0 °C sequentially. Then cooling bath was removed and the reaction was stirred at room temperature for an additional 10 hours. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted by DCM (30 mL × 3) and washed with brine (30 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford rotamers **11** (1.9 g, 76% yield) as a white solid. **R*f*** = 0.65 (petroleum ether / EtOAc = 2/1);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (t, *J* = 6.8 Hz, 2H), 7.60 – 7.46 (m, 2H), 7.41 (q, *J* = 7.7, 7.3 Hz, 3H), 7.29 (dt, *J* = 11.0, 5.6 Hz, 4H), 7.25 – 7.21 (m, 3H), 7.20 – 7.13 (m, 2H), 7.06 (dt, *J* = 30.4, 6.8 Hz, 2H), 6.73 (d, *J* = 37.4 Hz, 1H), 6.43 – 6.19

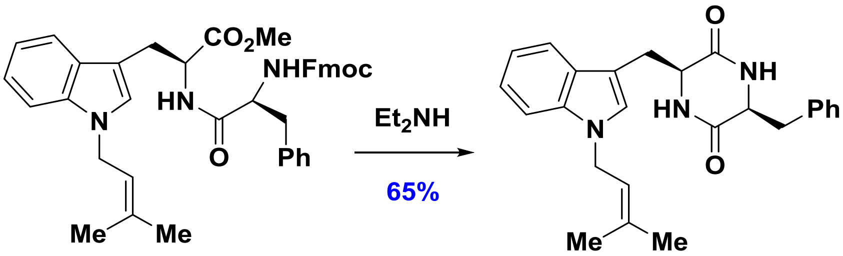
(m, 1H), 5.34 – 5.24 (m, 2H), 4.85 (dd, *J* = 7.7, 5.4 Hz, 1H), 4.57 (t, *J* = 7.1 Hz, 2H), 4.41 (q, *J* = 8.2, 7.3 Hz, 2H), 4.25 (d, *J* = 9.3 Hz, 1H), 4.19 – 4.10 (m, 1H), 3.70 – 3.59 (m, 3H), 3.24 (d, *J* = 5.4 Hz, 2H), 3.04 (d, *J* = 7.5 Hz, 2H), 1.78 (s, 3H), 1.73 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 170.3, 155.8, 143.9, 141.4, 136.4, 136.3, 129.6, 129.5, 128.79, 128.76, 128.3, 127.8, 127.2, 126.4, 126.3, 125.3, 125.2, 121.8, 120.1, 120.0, 119.4, 118.6, 109.9, 67.2, 67.1, 56.3, 56.1, 53.4, 52.4, 47.2, 47.1, 44.2, 38.8, 38.6, 25.7, 18.1.

IR: ν_{max} 3852, 3652, 3313, 2923, 2355, 1731, 1652, 1545, 1446, 1262, 740, 694 cm^{-1}.

HRMS calcd. for $C_{41}H_{42}N_3O_5^+$ $[M+H]^+$: 655.3124. Found: 655.3120. **mp.:** 177-179 ^{o}C;

*Synthesis of penicimutain (**5**)*



11

penicimutatin (5)

To a stirred solution of compound **11** (1.5 g, 2.37 mmol) in THF (8 mL) at 0 ^{o}C was added Et_2NH (2 mL). The mixture was stirred at the room temperature for 8 hours. Then saturated aqueous NH_4Cl (10 mL) was added. The solution was extracted with EtOAc (20 mL ×3) incorporating a brine (20 mL) wash. The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **5** (0.6 g, 65% yield) as a white solid. **R*f*** = 0.15 (petroleum ether / EtOAc = 2/1) ;

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.99 (d, *J* = 2.7 Hz, 1H), 7.76 (d, *J* = 2.8 Hz, 1H), 7.50 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.34(dt, *J* = 7.9, 1.0 Hz, 1H), 7.18 – 7.10 (m, 4H), 7.02 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.99 (s, 1H), 6.71 – 6.61 (m, 2H), 5.25 (dddd, *J* =

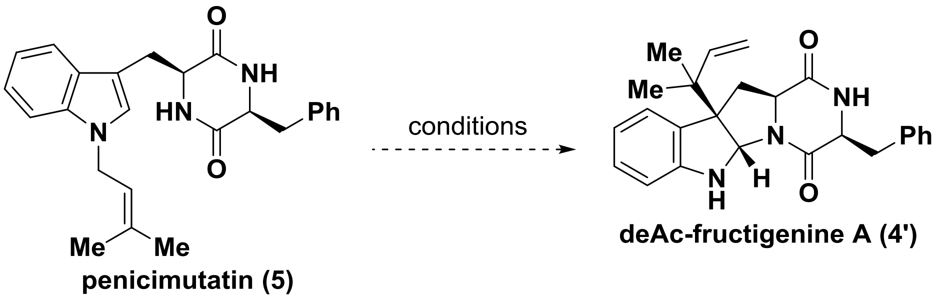
8.3, 5.6, 2.9, 1.4 Hz, 1H), 4.69 (d, J = 6.9 Hz, 2H), 3.97 (dtd, J = 5.3, 3.7, 2.1 Hz, 1H), 3.83 (ddd, J = 7.4, 4.4, 2.5 Hz, 1H), 2.79 (dd, J = 14.5, 4.4 Hz, 1H), 2.54 (dd, J = 7.9, 1H), 2.45 (dd, J = 13.4, 4.7 Hz, 1H), 1.83 (dd, J = 13.5, 7.1 Hz, 1H), 1.79 (s, 3H), 1.63 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 166.2, 136.6, 135.7, 135.1, 129.7, 128.13, 128.05, 127.5, 126.4, 121.0, 120.6, 119.2, 118.6, 109.8, 108.4, 55.7, 55.3, 43.4, 29.7, 25.4, 17.8.

IR: ν_{max} 2355, 1714, 1680, 1629, 1562, 1508, 1316 cm $^{-1}$.

HRMS calcd. for $C_{25}H_{26}N3O_2^-[M-H]^-$: 400.2025. Found: 400.2031. **mp.:** 227-229 ^{o}C;

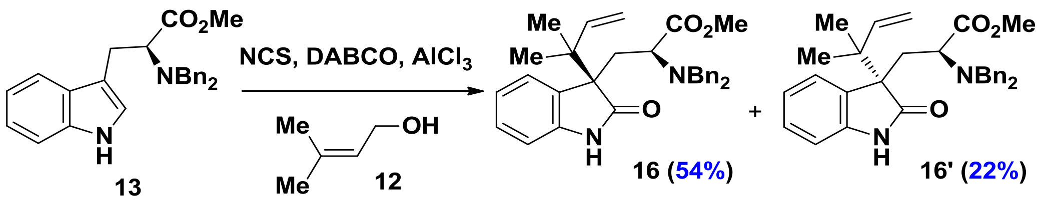
Table of S1: attempts of biomimetic aza-Claisen rearrangement



Entry[a]	Lewis acids	Temperature / ℃	Solvent	Conversion[b]	result
1	**PTSA**	**150**	**DMF**	**> 90%**	**decomposed**
2	**$SnCl_2$**	**150**	**DMF**	**> 90%**	**decomposed**
3	**$BF_3{\cdot}Et_2O$**	**140**	**DMF**	**> 90%**	**decomposed**
4	**$AlMe_3$**	**110**	**tol**	**< 5%**	**5 recycled**
5	**$AuCl_3$**	**80−110**	**tol**	**< 5%**	**5 recycled**

[a] All reaction were run on a 0.08 mmol scale at indicated temperature for 10 hours in a flamed dried flask under N_2 balloon; [b] conversion was determined based on isolated **5**;

Synthesis of compound ***16***



To a flame-dried round-bottom flask was added **13** (1 g, 2.52 mmol) and DCM (5 mL). The solution was cooled to 0 ℃ and DABCO (170 mg, 1.51 mmol) was added followed by NCS (370 mg, 2.77 mmol). The resultant solution was stirred at 0 ℃ for 5 min, followed by addition of compound **12** (0.52 mL, 5.04 mmol) , then added $AlCl_3$ (202 mg, 1.5 mmol) in three portions every 8 hours.[3] This mixture was stirred for 1 h at 0 ℃, then the mixture was warmed to room temperature and stirred for 24 hours. The reaction mixture was concentrated under vacuum and purified by flash chromatography on silica gel to afford **16** (630 mg, 54% yield) and **16'** (250 mg, 22% yield) both as a white solid.

16: Rf = 0.7 (petroleum ether / EtOAc = 2/1) ;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.25 (m, 9H), 7.24 – 7.15 (m, 2H), 7.09 (td, *J* = 7.7, 1.3 Hz, 1H), 7.02 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.86 (td, *J* = 7.6, 1.1 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.04 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.07 (dd, *J* = 10.8, 1.3 Hz, 1H), 4.95 (dd, *J* = 17.4, 1.3 Hz, 1H), 3.79 (d, *J* = 11.9 Hz, 2H), 3.35 (s, 3H), 3.32 (d, *J* = 15.9 Hz, 2H), 2.76 – 2.61 (m, 2H), 2.42 (dd, *J* = 11.9, 1.2 Hz, 1H), 1.12 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.6, 172.4, 143.3, 141.7, 139.4, 129.1, 129.0, 128.2, 128.0, 127.2, 126.9, 121.0, 113.9, 109.2, 58.4, 57.3, 54.7, 51.0, 42.1, 32.3, 22.4, 21.8.

IR: ν_{max} 3847, 3652, 2364, 1643, 1499, 1129 cm $^{-1}$.

HRMS calcd. for $C_{31}H_{35}N_2O_3^+$ $[M+H]^+$: 483.2648. Found: 483.2570. **mp.:** 117-119 °C;

16': Rf = 0.4 (petroleum ether / EtOAc = 2/1) ;

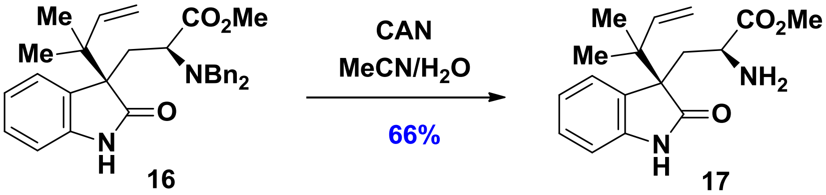
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 2.4 Hz, 1H), 7.24 – 7.16 (m, 10H), 7.09 (tdd, *J* = 5.7, 3.2, 1.3 Hz, 1H), 6.78 – 6.66 (m, 3H), 5.99 (ddd, *J* = 17.5, 10.8, 1.4 Hz, 1H), 5.08 (dt, *J* = 10.8, 1.3 Hz, 1H), 4.97 (dt, *J* = 17.4, 1.3 Hz, 1H), 3.81 (d, *J* = 14.0, 2H), 3.80 (s, 1H), 3.53 (s, 3H), 3.31(d, *J* = 13.2, 2H), 2.90 (ddd, *J* = 10.0, 2.6, 1.2 Hz, 1H), 2.75 (ddd, *J* = 13.6, 10.0, 1.3 Hz, 1H), 2.15 (dt, *J* = 13.8, 1.9 Hz, 1H), 1.13 – 1.02 (m, 3H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 180.0, 172.3, 143.1, 141.5, 139.4, 129.7, 128.7, 128.6, 128.2, 127.9, 126.9, 126.0, 121.7, 114.1, 109.0, 58.2, 56.6, 54.9, 51.1, 42.6, 32.9, 21.9, 21.7.

IR: ν_{max} 3033, 2951, 2847, 2245, 1731, 1700, 1468, 1231, 1169, 912, 745 cm $^{-1}$.

HRMS calcd. for $C_{31}H_{33}N_2O_3^-$ [M-H]$^-$: 481.2491. Found: 481.2495. **mp.:** 100-102 ^{o}C;

*Synthesis of compound **17***



To a stirred solution of **16** (345 mg, 0.72 mmol) in MeCN / H_2O (2 mL / o.4 mL) at 0 ^{o}C, was added CAN (824 mg, 1.5 mmol). The mixture was stirred at the room temperature for 6 hours. Saturated aqueous $NaHCO_3$ (10 mL) was added and the mixture was extracted by DCM (30 mL × 3) and washed with brine (30 mL). Dried over $MgSO_4$, and evaporate the filtrate in vacuum. The compound was dissolved again in MeCN/H_2O (2 mL/0.4 mL). To the formed solution was added CAN (824 mg, 1.5 mmol). The mixture was stirred at the room temperature for 8 hours. Saturated aqueous $NaHCO_3$ (10 mL) was added and the mixture was extracted by DCM (30 mL × 3) and washed with brine (30 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **17** (170 mg, 66% yield) as a brown solid. **R$_f$** = 0.1 (petroleum ether / EtOAc = 2/1);

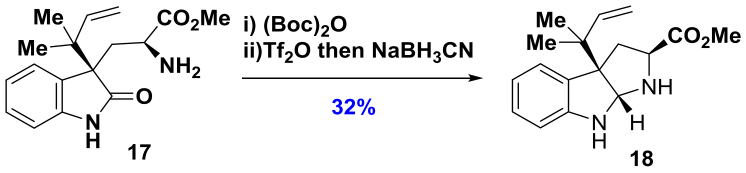
^{1}H NMR (400 MHz,) δ 7.64 (s, 1H), 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.12 (ddt, *J* = 7.5, 1.4, 0.7 Hz, 1H), 6.96 (td, *J* = 7.5, 1.1 Hz, 1H), 6.88 – 6.78 (m, 1H), 6.02 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.08 (dd, *J* = 10.8, 1.3 Hz, 1H), 4.97 (dd, *J* = 17.4, 1.3 Hz, 1H), 3.56 (s, 3H), 2.79 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.29 (dd, *J* = 11.3, 7.1 Hz, 1H), 2.24 (d, *J* = 2.8 Hz, 1H), 2.22 (s, 1H), 1.75 (dd, *J* = 11.3, 7.2 Hz, 1H), 1.11 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.0, 176.0, 143.4, 142.7, 129.6, 127.9, 126.5, 120.9, 113.9, 109.1, 58.8, 56.6, 51.8, 42.24, 42.19, 34.6, 22.0, 21.8, 14.5.

IR: ν_{max} 3861, 3649, 2947, 2364, 1655, 1556, 1457, 751 cm $^{-1}$.

HRMS calcd. for $C_{17}H_{23}N_2O_3^+$ $[M+H]^+$: 303.1709. Found: 303.1700. **mp.**: 60 – 62 ℃.

*Synthesis of compound **18***



To a stirred solution of the compound **17** (100 mg, 0.33 mmol) in DCM (3 mL) at 0 ^{o}C was added Et_3N (60 μL, 0.83 mmol) and $(Boc)_2O$ (84 μL, 0.37 mmol). The mixture was stirred at the room temperature for 4 hours. Then saturated NH_4Cl (aq.) (2 mL) was added, extracted with DCM (3 mL × 3) and wished with brine (3 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to give crude product **17’** (91 mg) as a colorless oil product.

To a stirred solution of **17’** (91 mg) in DCM (3 ml) was added Tf_2O (0.11 mL, 0.67 mmol) at 0 ℃. The reaction flask was stirred at the same temperature for 10 min, at which time the reaction mixture was concentrated under vacuum. After that was dissolved in MeOH (4 mL) and cooled to 0 ℃, $NaBH_3CN$ (140 mg, 2.2 mmol) was added. The mixture was stirred at the room temperature for 30 min. Saturated aqueous $NaHCO_3$ (5 mL) was added and the mixture was extracted by EtOAc (10 mL ×3) and washed with brine (10 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **18**[5] (30 mg, 32% yield from **17**) as a colorless oil. **R$_f$** = 0.5 (petroleum ether / EtOAc = 2/1)；

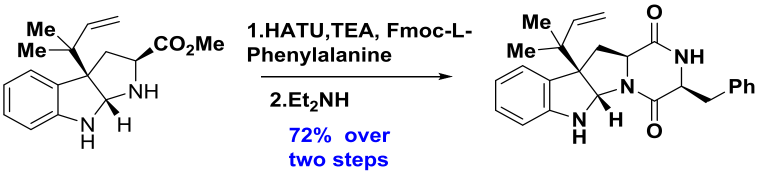
^{1}H NMR (400 MHz, Chloroform-*d*) 7.13-7.11 (m, 1H), 7.06 (td, *J* = 7.6, 1.3 Hz, 1H), 6.71 (td, *J* = 7.5, 1.1 Hz, 1H), 6.56-6.54 (m, 1H), 5.99 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.10 (dd, *J* = 10.8, 1.3 Hz, 1H), 5.04 (dd, *J* = 17.6 Hz, 1H), 4.99 (s, 1H), 3.70 (s, 3H), 3.59 (dd, *J* = 10.9, 5.5 Hz, 1H), 2.28 (dd, *J* = 12.0, 5.6 Hz, 1H), 2.16 (t, *J* = 11.5 Hz, 1H), 1.11 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 151.1, 144.5, 130.9, 128.5, 125.5, 118.6, 113.9, 109.1, 80.1, 65.8, 59.9, 52.3, 41.4, 41.2, 23.4, 23.0.

IR: ν_{max} 3734, 2917, 2364, 1759, 1505, 1194, 912, 742 cm -1.

HRMS calcd. for $C_{17}H_{23}N_2O_2^+$ $[M+H]^+$: 287.1760. Found: 287.1755.

Synthesis of compound 4'



18

deAc-fructigenine A (4')

A mixture of **18** (220 mg, 0.77 mmol) and N-Fmoc-L- **Phenylalanine** (450 mg, 1.15 mmol) was stirred in anhydrous DMF (5 mL) at −20 ℃ for 10 min, HATU (322 mg, 0.85 mmol) and Et_3N (0.23 mL, 1.54 mmol) were added into the above solution at −20 ℃. After stirring for 18 hours, brine (5 mL) was added and the mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash chromatography to give a yellow oil product (420 mg).

To a stirred solution of above compound (420 mg) in THF (2 mL) at 0 °C, then added Et_2NH (0.5 mL). The mixture was stirred at the room temperature for 8 hours. Then saturated NH_4Cl (3 mL) was added, extracted with EtOAc (5 mL × 3) and washed with brine (5 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **4'** (222 mg, 72% yield from **18**) as a white solid. **R$_f$** = 0.15 (petroleum ether / EtOAc = 2/1);

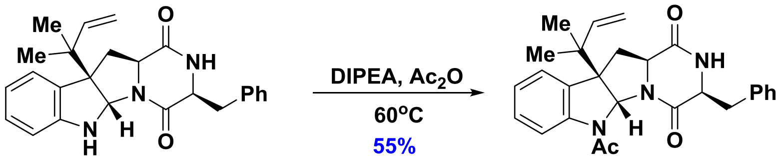
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.11 (m, 1H), 7.09 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.75 (td, *J* = 7.5, 1.1 Hz, 1H), 6.62 – 6.55 (m, 1H), 5.95 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.70 (s, 1H), 5.53 (s, 1H), 5.16 – 5.04 (m, 2H), 5.02 (s, 1H), 4.21 (ddd, *J* = 10.3, 3.7, 1.9 Hz, 1H), 3.91 (ddd, *J* = 11.4, 6.2, 2.0 Hz, 1H), 3.56 (dd, *J* = 14.4, 3.8 Hz, 1H), 2.82 (dd, *J* = 14.4, 10.3 Hz, 1H), 2.51 (dd, *J* = 12.6, 6.2 Hz, 1H), 2.37 (dd, *J* = 12.6, 11.1 Hz, 1H), 1.10 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.2, 165.6, 150.1, 143.6, 135.7, 129.4, 129.2, 129.1, 127.8, 125.2, 119.1, 114.7, 109.3, 77.8, 61.7, 59.0, 56.4, 41.0, 37.1, 36.3, 23.0, 22.6.

IR: ν_{max} 3645, 2920, 2341,1660, 1569, 1460,1192 cm $^{-1}$.

HRMS calcd. for $C_{25}H_{26}N_3O_2^-$[M-H]$^-$: 400.2027. Found: 400.2025. **mp.:** 83-85 ^{o}C;

Synthesis of compound ***4***



deAc-fructigenine A (4')

fructigenine A (4)

To a solution of compound **4’** (40 mg, 0.1 mmol) in acetic anhydride (3 mL) and DIPEA (0.05 mL, 3 mmol) was added under N_2. Then the reaction mixture was warmed to 60 ℃ and stirred for 36 h. The mixture was evaporated under reduced pressure. The residue was dissolved in DCM (5 mL), washed with saturated $NaHCO_3$ (5 mL × 3) and brine (5 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **4** (24 mg, 55% yield) as a white solid. **R*f*** = 0.15 (petroleum ether / EtOAc = 2/1);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.33 – 7.31 (m, 1H), 7.31 – 7.29 (m, 1H), 7.29 – 7.27 (m, 1H), 7.24 (d, *J* = 1.3 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.12 (td, *J* = 7.5, 1.1 Hz, 1H), 6.04 (s, 1H), 5.80 – 5.70 (m, 2H), 5.15 – 5.12 (m, 1H), 5.10 (dd, *J* = 11.2, 1.0 Hz, 1H), 4.23 (ddd, *J* = 10.2, 3.8, 1.6 Hz, 1H), 3.79 (ddd, *J* = 11.5, 5.6, 1.7 Hz, 1H), 3.53 (dd, *J* = 14.3, 3.7 Hz, 1H), 2.82 (dd, *J* =

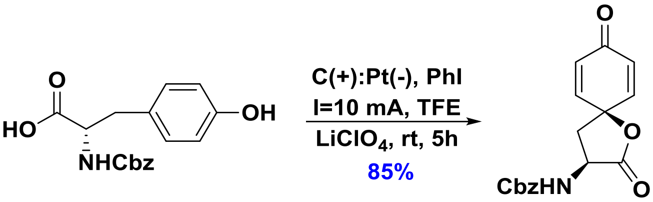
14.4, 10.1 Hz, 1H), 2.65 (s, 3H), 2.55 (dd, *J* = 12.5, 5.6 Hz, 1H), 2.23 (t, *J* = 12.0 Hz, 1H), 1.12 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.2, 168.3, 164.9, 143.4, 143.2, 135.4, 129.4, 129.3, 129.2, 127.8, 124.7, 119.3, 114.7, 61.1, 59.2, 56.1, 40.5, 37.1, 36.2, 23.7, 23.3, 22.5.

IR: ν_{max} 3849, 3742, 2923, 2367, 1675, 1482, 1375, 1145, 1098, 923, 728 cm $^{-1}$.

HRMS calcd. for $C_{27}H_{28}N_3O_3^-$[M-H]$^-$: 442.2231. Found: 442.2137. **mp.:** 90-92 ^{o}C; **[α]$^{20}_D$** -128.0 (c 0.35, MeOH).

*Synthesis of compound **19***



(S)-Cbz-tyrosine (8) **19**

A solution of an ArI (0.21ml, 1.9 mmol) in TFE (7 mL) containing $LiClO_4$ (530 mg, 5.0 mmol). The ElectraSyn vial cap equipped with anode (glassy carbon) and cathode (Pt sheet) were inserted into the mixture.[4] The reaction mixture was electrolyzed under a constant current of 10 mA for 5 hours, but stirring was continued for 5 hours. After the reaction, the ElectraSyn vial cap was removed and electrodes were rinsed with a mixture of organic solvents (EtOAc 5 mL), which was combined with the crude mixture. The reaction mixture was diluted with H_2O (5 mL) and extracted with EtOAc (10 mL × 3) and washed with brine (5 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **18** (85 mg, 85% yeild) as a white solid. **R$_f$** = 0.25 (petroleum ether / EtOAc = 2/1)；

We performed cumulative reaction products through multiple parallel reactions to accumulate **18** in 5 grams for further study.

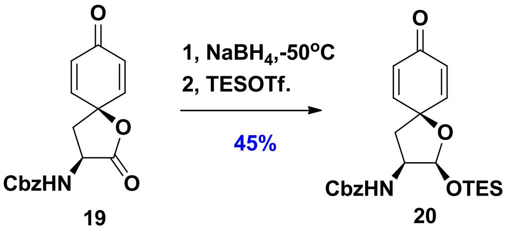
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 6.86 (d, *J* = 9.8 Hz, 2H), 6.26 (t, *J* = 8.5 Hz, 2H), 5.80 (d, *J* = 7.0 Hz, 1H), 5.11 (d, *J* = 2.8 Hz, 2H), 4.63 (q, *J* = 9.3 Hz, 1H), 2.67 (dd, *J* = 13.2, 9.2 Hz, 1H), 2.48 (t, *J* = 12.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.2, 173.6, 156.1, 146.2, 144.3, 135.7, 129.8, 129.2, 128.8, 128.7, 128.5, 128.3, 76.2, 67.6, 50.5, 38.2.

IR: ν_{max} 3852, 3626, 2923, 2358, 1785, 1669, 1251, 1025, 793 cm $^{-1}$.

HRMS calcd. for $C_{17}H_{14}NO_5^{-}$[M-H]$^{-}$: 313.0872. Found: 312.0950. **mp.:** 126-128 ^{o}C;

*Synthesis of compound **20***



To a stirred solution of compound **19** (2 g, 6.4 mmol) in THF (30 mL) at -50 ^{o}C was added $NaBH_4$ (484 mg, 12.8 mmol). The mixture was stirred at same temperature for 1 hour and the volatile was removed under vacuum. The residue was directly purified by a quick flash column chromatography on silica gel to give the compound **19’** (1.28 g).

To a stirred solution of the compound **19’** (1.28g) in DCM (20 mL) at 0 ^{o}C, then added 2,6-lutidine (0.57 mL, 4.92 mmol) and TESOTf (1.02 mL, 4.51 mmol). The mixture was stirred at the same temperature for 45 min. Then saturated $NaHCO_3$ (aq.) (10 mL) was added, extracted with DCM (15 mL × 3) and wished with brine (15 mL). The organic phase was combined and dried over Na_2SO_4, filtered and purified by flash chromatography on silica gel to afford **20** (1.25 g, 45% yield from **19**) as a white solid. **R*f*** = 0.9 (EtOAc/petroleum ether = 1/1);

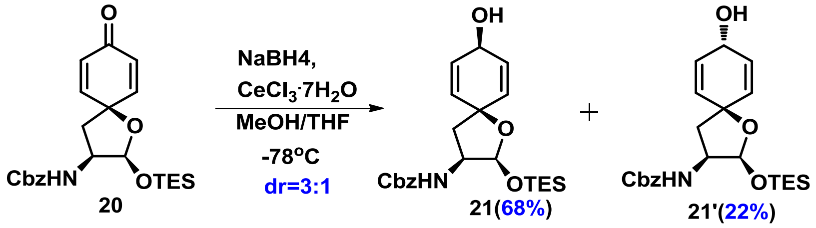
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.31 (m, 5H), 6.80 (td, *J* = 9.8, 8.7, 3.3 Hz, 2H), 6.18 – 6.08 (m, 2H), 5.43 (d, *J* = 4.2 Hz, 1H), 5.13 (s, 2H), 5.08 (d, *J* = 9.0 Hz, 1H), 4.47 (d, *J* = 10.0 Hz, 1H), 2.37 (dd, *J* = 12.7, 7.9 Hz, 1H), 2.07 (t, *J* = 12.0 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (125 MHz, Chloroform-d) δ 185.3, 155.8, 150.9, 148.5, 136.3, 128.7, 128.5, 128.3, 127.6, 127.5, 96.8, 67.3, 54.8, 38.8, 6.7, 4.9.

IR: ν_{max} 2937, 1683, 1592, 1511, 1456, 1156, 791 cm^{-1};

HRMS calcd. for $C_{23}H_{30}NO_5Si^-$ $[M-H]^-$: 428.1893. Found: 428.1898. **mp.:** 64-66 ^{o}C;

*Synthesis of compound **21***



To a flame dried flask (100 mL) was added MeOH (30 mL), followed by pouring into $NaBH_4$ (212 mg, 5.6 mmol) and $CeCl_3$ (840 mg, 3.4 mmol) at -78 ^{o}C. The stirring was continued for additional 5 min, then compound **20** (1.2 g, 2.8 mmol) dissolved in THF (30 mL) was added dropwise. The reaction was monitored by TLC. Upon starting material consumption, saturated NH_4Cl (40 mL) was added and the resulting mixture was extracted with EtOAc (30 mL × 3), and washed with brine (30 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was chromatographed on silica gel to give **21** (0.82 g, 68% yield) and **21'** (0.26 g, 22% yield) both as colorless oil.

Compound **21**: **R*f*** = 0.7 (EtOAc/Petroleum ether = 1/1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 5H), 5.92 (ddt, *J* = 8.0, 5.2, 2.5 Hz, 2H), 5.82 (ddd, *J* = 9.9, 4.6, 2.8 Hz, 2H), 5.30 (d, *J* = 4.2 Hz, 1H), 5.14 – 5.04 (m, 3H), 4.37 (dp, *J* = 12.1, 4.4 Hz, 2H), 2.16 (dd, *J* = 12.4, 7.7 Hz, 1H), 1.84 (t, *J* = 12.0 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.64 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.8, 136.4, 133.1, 131.4, 128.9, 128.7, 128.6, 128.3, 128.2, 95.8, 76.0, 67.0, 62.0, 54.3, 41.1, 6.8, 4.8.

IR: ν_{max} 3441,3321, 2952, 2872,1718, 1693, 1516, 1454,1409, 1255, 1018, 744 cm^{-1};

HRMS calcd. for $C_{23}H_{32}NO_5Si^-$$[M-H]^-$: 430.2050. Found: 430.2128.

Compound **21'**: **R*f*** = 0.6 (EtOAc/Petroleum ether = 1/1)

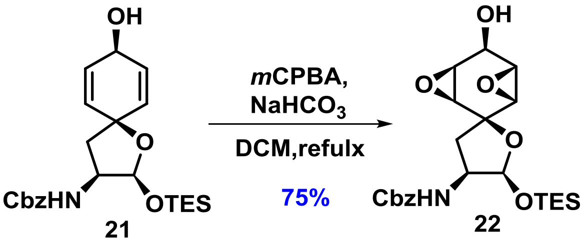
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 5H), 6.06 – 5.95 (m, 2H), 5.91 – 5.80 (m, 2H), 5.30 (d, *J* = 4.2 Hz, 1H), 5.13 – 5.04 (m, 3H), 4.47 (dt, *J* = 3.7, 1.9 Hz, 1H), 4.42 – 4.32 (m, 1H), 2.21 (dd, *J* = 12.4, 7.8 Hz, 1H), 1.89 (t, *J* = 12.0 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.67 – 0.60 (m, 6H);

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.9, 136.5, 134.6, 131.9, 129.9, 129.6, 128.7, 128.3, 128.2, 95.9, 75.8, 67.0, 62.1, 54.7, 40.6, 6.8, 4.8.

IR: ν_{max} 3441,3314, 2952, 2880,1716, 1698, 1534, 1457,1412, 1255, 1103, 793 cm^{-1};

HRMS calcd. for $C_{23}H_{32}NO_5Si^-$[M-H]$^-$: 430.2050. Found: 430.2050.

Synthesis of compound ***22***



To a 40 ml flask was added compound **21** (2 g, 4.6 mmol) and diluted with DCM (50 mL), m-CPBA (5.64 g, 27.8 mmol) and NaHCO$_3$ (3.86 g, 46 mmol) were added. The reaction mixture was stirred at 40 °C overnight. Saturated $Na_2S_2O_3$ (50 mL) was added and extracted with DCM (100 mL × 3) incorporating a brine wash (100 mL). The combined organic layers were dried over MgSO$_4$ and chromatographed on silica gel to give (1.6 g, 75% yield) as a white solid. **R$_f$** = 0.1 (EtOAc/Petroleum ether = 1/1);

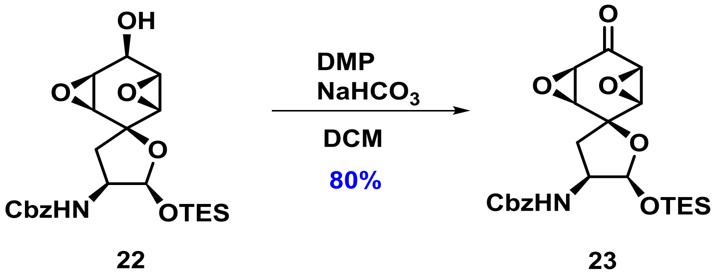
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 5H), 5.43 (d, *J* = 4.0 Hz, 1H), 5.17 – 5.05 (m, 3H), 4.40 (d, *J* = 9.9 Hz, 1H), 4.25 – 4.15 (m, 1H), 3.42 (q, *J* = 3.3, 2.8 Hz, 2H), 3.27 (t, *J* = 3.0 Hz, 1H), 3.23 (d, *J* = 3.6 Hz, 1H), 2.48 (d, *J* = 11.8 Hz, 1H), 2.35 (dd, *J* = 12.6, 8.4 Hz, 1H), 1.88 (t, *J* = 11.8 Hz, 1H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 136.3, 128.7, 128.5, 128.4, 96.7, 78.7, 67.2, 64.2, 61.7, 60.2, 56.5, 56.2, 54.4, 36.8, 6.8, 4.8.

IR: ν_{max} 3344, 2960, 2875,1726, 1531, 1454, 1262, 1023, 936, 801 cm^{-1};

HRMS calcd. for $C_{23}H_{32}NO_7Si^-$[M-H]$^-$: 462.1948. Found: 462.2026. **mp.:** 35-36 ^{o}C;

*Synthesis of compound **23***



To a stirred solution of compound **22** (1.1 g, 2.37 mmol) in DCM (20 ml) was added $NaHCO_3$ (795 mg, 9.48 mmol) and Dess-Martin periodinane (1.52 g, 3.6 mmol) portionwise. The reaction was stirred at room temperature for 0.5 hours. Saturated solution of Na_2SO_3 (20 mL) was added and the mixture was extracted with DCM (40 mL × 3). The combined organic layers were washed with brine (40 mL), dried over Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel to give **23** (0.86 g, 80% yield) as a white solid. **R*f*** = 0.5 (EtOAc / Petroleum ether = 1/1);

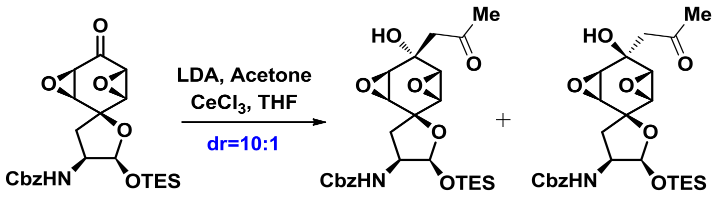
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.30 (m, 5H), 5.47 (d, *J* = 4.1 Hz, 1H), 5.17 – 5.03 (m, 3H), 4.43 (dtd, *J* = 10.6, 8.6, 4.0 Hz, 1H), 3.52 – 3.49 (m, 1H), 3.47 (t, *J* = 2.7 Hz, 1H), 3.41 (dd, *J* = 4.1, 1.7 Hz, 2H), 2.42 (dd, *J* = 12.9, 8.4 Hz, 1H), 1.96 (dd, *J* = 12.9, 10.9 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.6 Hz, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.8, 155.8, 136.2, 128.7, 128.5, 128.4, 96.9, 78.6, 67.3, 64.2, 63.0, 55.7, 55.5, 54.3, 35.9, 6.7, 4.8.

IR: ν_{max} 2960, 2920, 2870, 2850, 1863, 1843, 1828, 1726, 1696, 1616, 1457, 1422, 1113, 721, 671 cm^{-1};

HRMS calcd. for $C_{23}H_{30}NO_7Si^-$[M-H]$^-$: 460.1792. Found: 460.1869. **mp.:** 67-69 ^{o}C。

*Synthesis of compound **24***



23 **24** (72%) **24'**(7%)

To a flamed-dried flask was added dried acetone (0.6 mL, 8.6 mmol), dropwise to a stirring of LDA (2M, 4.3 mL, 8.6 mmol) in THF (50 mL). Stirring was continued for additional 40 min at -78 °C. Then $CeCl_3$ (1.92 g, 7.8 mmol) was added to the system in one portion, followed by the addition of compound **23** (1.8 g, 3.9 mmol) dissolved in THF at -78 °C in drop-wise manner. After the addition was completed, the reaction mixture was stirred at -78 °C for 30 min, then warmed to 0 °C and stirred for an additional 10 min. Saturated NH_4Cl (20 mL) was added and the mixture was extracted with EtOAc (100 mL × 3), and washed with brine (100 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated, which was chromatographed on silica gel to give **24** (1.45 g, 72% yield) and **24’** (140 mg, 7% yield) both as white solids.

Compound **24**: **R*f*** = 0.4 (EtOAc/Petroleum ether = 2/1);

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39-7.31 (m, 5H), 5.42 (d, *J* = 4.2 Hz, 1H), 5.16 – 5.05 (m, 3H), 4.69 (br s, 1H), 4.44-4.34 (m, 1H), 3.24-3.20 (m, 2H), 3.16 (t, *J* = 3.1 Hz, 1H), 3.11 (t, *J* = 3.1 Hz, 1H), 3.07 (s, 2H), 2.44 (dd, *J* = 12.8, 8.1 Hz, 1H), 2.26 (s, 3H), 1.92 (t, *J* = 12.0 Hz, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.5, 155.9, 136.4, 128.7, 128.4, 128.3, 96.7, 78.6, 67.2, 66.5, 59.3, 58.4, 57.9, 57.5, 54.4, 47.0, 36.8, 31.8, 6.8, 4.8;

IR: ν_{max} 3439, 3349, 2960, 2878, 1723, 1696, 1516, 1459, 1382, 1260, 1132, 1020, 968, 868, 801,754, 696 cm^{-1};

HRMS calcd. for $C_{26}H_{36}NO_8Si^-$ $[M-H]^-$: 518.2210. Found: 518.2216; **mp.:** 47-49 °C.

Compound **24’**: **R*f*** = 0.2 (EtOAc/Petroleum ether = 1/1).

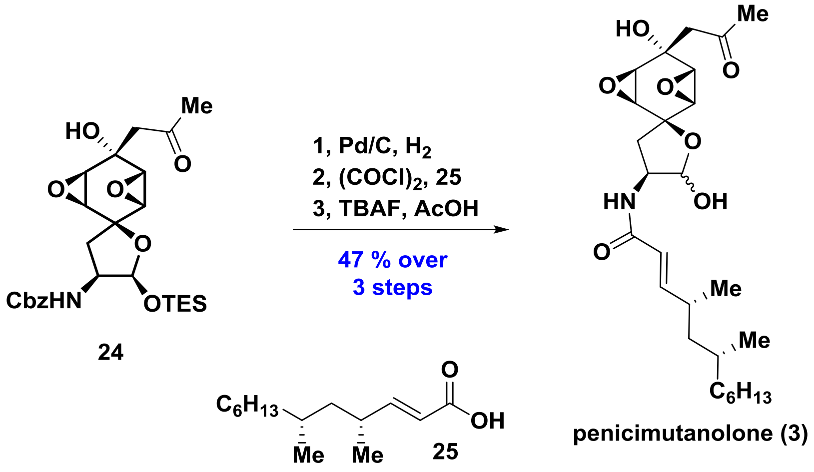
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.30 (m, 5H), 5.42 (d, *J* = 4.1 Hz, 1H), 5.11 (s, 2H), 5.09 (d, *J* = 9.0 Hz, 1H), 4.48 – 4.35 (m, 1H), 3.31 (t, *J* = 3.2 Hz, 1H), 3.25 (t, *J* = 3.3 Hz, 1H), 3.17-3.14 (m, 2H), 2.97 (s, 2H), 2.69 (dd, *J* = 13.2, 8.3 Hz, 1H), 2.22 (s, 3H), 2.10 – 1.96 (m, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.2, 155.9, 136.4, 128.7, 128.4, 128.3, 96.5, 78.8, 67.3, 67.2, 63.1, 61.0, 60.5, 60.1, 54.5, 50.7, 37.2, 31.3, 6.8, 4.8;

IR: ν_{max} 3444, 3356, 2965, 2932, 1718, 1696, 1521, 1452, 1377, 1262, 1010, 931, 793, 734,666 cm^{-1};

HRMS calcd. for $C_{26}H_{36}NO_8Si^-$ [M-H]$^-$: 518.2210. Found: 518.2210; **mp.:** 55-57 ^{o}C.

*Synthesis of penicimutanolone (**3**)*



Compound **24** (25 mg, 0.048 mmol) was dissolved in methanol (3 mL), after 10% Pd/C (13 mg) was added under a protective flow of nitrogen, the reaction vessel was sealed and purged by hydrogen. The reaction mixture was stirred under hydrogen atmosphere (balloon) for 1 hours. The reaction was monitored by TLC. Upon the complete consumption of starting material, the reaction solution was filtrated through a pad of celite and rinsed by DCM (5 mL). The combined filtrate was concentrated in vacuo to produce the desired amine as a white solid.

Compound **25** (11.65 mg, 0.053 mmol) was dissolved in DCM (2 mL) at room temperature, followed by the addition of oxalic acid (5 µL, 0.058 mmol) in DCM (1 mL). After a 5-minute stirring, one drop of DMF was added to the system, the mixture was stirred for 1 hours. The volatiles was removed in vacuo, which got acyl chloride as a yellow oil.

To the prepared amine in DCM (3 mL) at 0 ^{o}C was added TEA (14.6 μL, 0.106 mmol) dropwise, followed by the addition of the prepared acyl chloride dissolved in DCM (2 mL). The reaction was stirred at room temperature for 30 min. Saturated $NaHCO_3$ (2 mL) was added and the mixture was extracted with DCM (6 mL × 3) incorporating a brine (6 mL) wash. The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified through a quick flash chromatography to give a white solid.

To the above product dissolved in THF (3 mL) was added TBAF (40 μL, 0.144 mmol) and AcOH (8 μL, 0.144 mmol) in THF (1 mL) at 0^{o}C. The solution was warmed to room temperature and monitored by TLC. Saturated NH_4Cl (4 mL) was added and the mixture was extracted with EtOAc (10 mL × 3), and washed with brine (10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give a white solid, which was chromatographed on silica gel to give **3** (11 mg, 47% yield from **24**) as a white solid. **R*f*** = 0.65 (EtOAc / MeOH = 10/1);

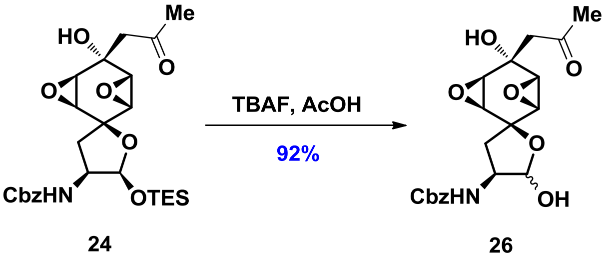
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (dd, *J* = 15.3, 8.4 Hz, 1H), 6.02 (d, *J* = 8.3 Hz, 1H), 5.75 (dd, *J* = 15.3, 0.9 Hz, 1H), 5.55 (d, *J* = 4.3 Hz, 1H), 4.77 – 4.70 (m, 1H), 4.68 (d, *J* = 8.5 Hz, 1H), 3.31 (t, *J* = 3.1 Hz, 1H), 3.26 (q, *J* = 2.7, 2.1 Hz, 2H), 3.19 (t, *J* = 3.1 Hz, 1H), 3.07 (s, 2H), 2.58 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.39 (p, *J* = 7.9 Hz, 1H), 2.27 (s, 3H), 2.01 (dd, *J* = 13.0, 10.7 Hz, 1H), 1.40 – 1.36 (m, 2H), 1.25 (s, 9H), 1.09 (td, *J* = 8.9, 8.4, 3.5 Hz, 3H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.4 Hz, 3H);

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.4, 166.1, 151.6, 121.4, 96.5, 79.2, 66.4, 59.4, 58.7, 58.2, 57.4, 52.1, 47.1, 44.1, 37.5, 37.0, 34.2, 32.1, 31.8, 30.5, 29.8, 27.0, 22.8, 20.7, 19.6, 14.3.

IR: ν_{max} 3329, 2957, 2932, 2855, 1703, 1668, 1634, 1539, 1257, 1018, 798 cm-1;

HRMS calcd. for $C_{26}H_{41}NO_7Na^+[M+Na]^+$: 502.2781. Found: 502.2883. **mp.**: 112-114 ^oC; $[\alpha]^{25}_D$ -1.0 (c 0.83, MeOH).

*Synthesis of compound **26***



To the compound **24** (25 mg, 0.048 mmol) dissolved in THF (3 mL) was added TBAF (40 μL, 0.144 mmol) and AcOH (8 μL, 0.144 mmol) in THF (1 mL) at 0^{o}C. The solution was then warmed to room temperature and indicated by TLC. Saturated NH_4Cl (4 mL) was added and the mixture was extracted with EtOAc (10 mL × 3), and washed with brine (10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give a white solid, which was chromatographed on silica gel to give **26** (18 mg, 92% yield) as a white solid. $\mathbf{R_f}$ = 0.65 (EtOAc / MeOH = 10/1);

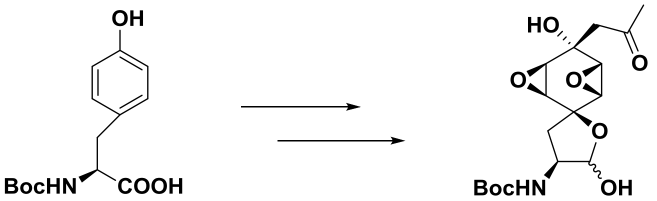
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 8.5 Hz, 5H), 5.56 – 5.44 (m, 2H), 5.09 (s, 2H), 4.85 (s, 1H), 4.69 (s, 1H), 4.39 (dq, *J* = 8.6, 4.6 Hz, 1H), 3.35 – 3.25 (m, 1H), 3.22 (q, *J* = 3.3 Hz, 2H), 3.12 (d, *J* = 3.4 Hz, 1H), 3.08 – 2.97 (m, 2H), 2.48 (dd, *J* = 13.0, 8.4 Hz, 1H), 2.25 (s, 3H), 1.98 (dd, *J* = 13.0, 10.7 Hz, 1H).

^{13}CNMR (100 MHz, Chloroform-*d*) δ 211.4, 156.0, 136.3, 128.7, 128.4, 128.3, 78.7, 67.2, 66.4, 59.4, 58.6, 58.1, 57.4, 53.8, 47.1, 36.9, 31.7.

IR: ν_{max} 3025, 2923, 2850, 2367, 1703, 1458, 745, 692 cm^{-1};

HRMS calcd. for $C_{20}H_{23}NO_8Na^+[M+Na]^+$: 428.1321. Found: 428.1316. **mp.**:132-134 ^oC.

*Synthesis of compound **27***



S9 **27**

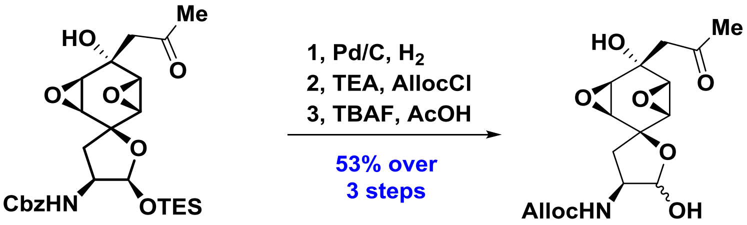
Compound **27** was prepared similar to that of Compound **26**.

^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 5.57 – 5.48 (m, 1H), 5.11 (d, *J* = 8.7 Hz, 1H), 4.37 (d, *J* = 9.9 Hz, 1H), 3.31 (d, *J* = 14.2 Hz, 1H), 3.24 (t, *J* = 3.1 Hz, 2H), 3.12 (d, *J* = 3.6 Hz, 1H), 3.07 (d, *J* = 3.4 Hz, 2H), 2.50 (dd, *J* = 12.8, 8.6 Hz, 1H), 2.28 (d, *J* = 2.8 Hz, 3H), 2.08 – 1.96 (m, 1H), 1.45 (s, 9H).

^{13}**C NMR** (100 MHz, Chloroform-*d*) δ 211.4, 155.4, 96.3, 80.1, 66.4, 59.4, 58.6, 58.0, 57.4, 53.5, 47.1, 37.0, 31.7, 28.4.

IR: ν_{max} 3847, 3748, 3645, 2355, 1684, 1502, 1367, 1166, 1014, 802 cm^{-1};
HRMS calcd. for $C_{17}H_{24}NO_8Na^{-}[M-H]^{-}$: 370.1502. Found: 370.1509. **mp.**:154-156 °C.

Synthesis of compound ***28***



24 **28**

Compound **24** (100 mg, 0.193 mmol) was dissolved in methanol (3 mL), after 10% Pd/C (41 mg) was added under a protective flow of nitrogen, the reaction vessel was sealed and purged by hydrogen. The reaction mixture was stirred under hydrogen atmosphere (balloon) for 1 hours. The reaction was monitored by TLC. Upon the complete consumption of starting material, the reaction solution was filtrated through a pad of celite and rinsed by DCM (5 mL). The combined filtrate was concentrated in vacuo to produce the desired amine as a white solid.

To the prepared amine in DCM (3 mL) at -10 °C was added TEA (62 μL, 0.444 mmol) and AllocCl (30 μL, 0.29 mmol) dropwise. The reaction was stirred at room temperature for 1 hour. Saturated $NaHCO_3$ (2 mL) was added and the mixture was extracted with DCM (6 mL × 3) incorporating a brine (6 mL) wash. The organic layers were dried over Na_2SO_4, filtered and concentrated in vacuum. The residue was purified through a quick flash chromatography to give a white solid.

To the above product dissolved in THF (3 mL) was added TBAF (73 µL, 0.288 mmol) and AcOH (16 µL, 0.288 mmol) in THF (1 mL) at $0^{o}C$. The solution was warmed to room temperature and monitored by TLC. Saturated NH_4Cl (4 mL) was added and the mixture was extracted with EtOAc (10 mL × 3), and washed with brine (10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give a white solid, which was chromatographed on silica gel to give **28** (36 mg, 53% yield from **24**) as a white solid. $\mathbf{R_{\mathit{f}}}$ = 0.7 (EtOAc / MeOH = 10/1);

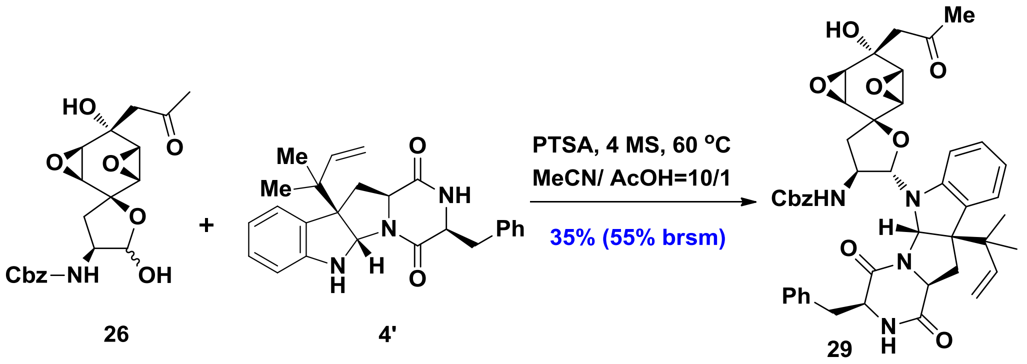
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.90 (ddt, *J* = 16.4, 10.8, 5.6 Hz, 1H), 5.59 – 5.49 (m, 1H), 5.44 (d, *J* = 8.7 Hz, 1H), 5.35 – 5.26 (m, 1H), 5.24 – 5.16 (m, 1H), 4.82 – 4.65 (m, 1H), 4.56 (d, *J* = 5.8 Hz, 2H), 4.44 – 4.33 (m, 1H), 3.32 (dt, *J* = 13.9, 3.0 Hz, 1H), 3.24 (q, *J* = 2.8 Hz, 2H), 3.17 – 3.09 (m, 1H), 3.05 (s, 2H), 2.55 – 2.43 (m, 1H), 2.27 (s, 3H), 2.04 – 1.96 (m, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.3, 155.9, 132.7, 118.1, 96.2, 78.7, 66.3, 65.97, 59.4, 58.6, 58.1, 57.4, 53.7, 47.1, 36.9, 31.7.

IR: ν_{max} 3855, 3813, 3748, 3645, 2355, 1833, 1677, 1652, 1559, 1457 cm-1;

HRMS calcd. for $C_{16}H_{20}NO_8Na^-[M-H]^-$: 354.1189. Found: 354.1200. **mp.**:86-88 ^{o}C.

*Synthesis of compound **29***



Compound **26** (20 mg, 0.05 mmol) and compound **4’** (25 mg, 0.06 mmol) were dissolved in MeCN (2 mL) at 0 °C, then AcOH (0.2 mL), 4Å MS (50 mg) and PTSA (3 mg, 0.012 mmol) were added. The mixture was stirred at 60 °C for 72 hours. Saturated aqueous $NaHCO_3$ (2 mL) was added and the mixture was extracted with EtOAc (5 ml × 3), washed with brine (5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated to give a white solid, which was chromatographed on silica gel to give **29** (13.5 mg, 35% yield) as a white solid and **26** (7.5 mg, 0.019 mmol) was recycled. **R_f** = 0.2 (petroleum ether / EtOAc = 1 / 1);

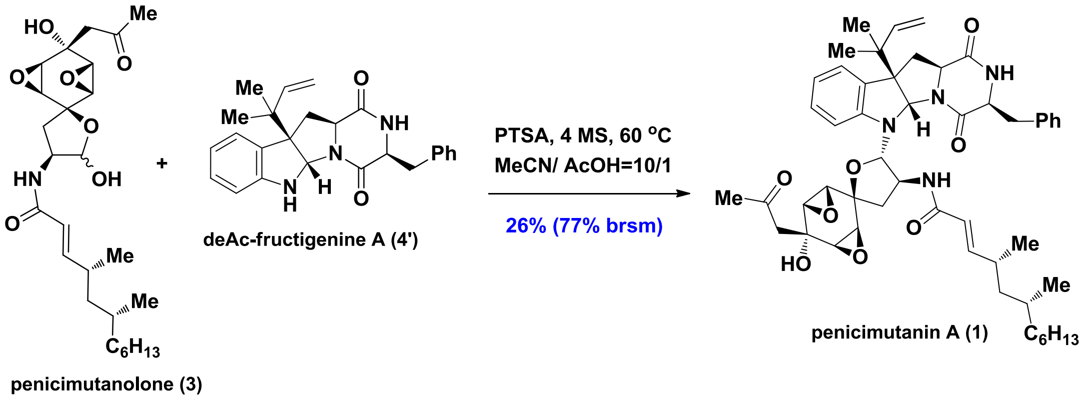
^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 (s, 7H), 7.18 – 7.04 (m, 5H), 6.76 (t, J = 7.4 Hz, 1H), 6.66 (d, J = 7.9 Hz, 1H), 6.03 (s, 1H), 5.88 (dd, J = 17.2, 10.8 Hz, 1H), 5.79 (s, 1H), 5.60 (d, J = 11.9 Hz, 1H), 5.57 – 5.50 (m, 1H), 5.14 – 5.00 (m, 4H), 4.69 (s, 1H), 4.25 (d, J = 7.7 Hz, 1H), 3.98 – 3.84 (m, 1H), 3.51 – 3.49 (m, 1H), 3.48 (s, 2H) 3.39 (t, J = 3.2 Hz, 1H), 3.32 – 3.19 (m, 4H), 3.06 (s, 2H), 2.85 (dd, J = 14.3, 9.1 Hz, 1H), 2.64 (dd, J = 13.4, 8.3 Hz, 1H), 2.41 (dd, J = 11.6, 5.2 Hz, 1H), 2.26 (s, 3H), 2.08 (dt, J = 14.3, 10.6 Hz, 2H), 1.01 (s, 3H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 211.4, 167.9, 163.8, 155.9, 148.7, 143.4, 136.1, 135.6, 129.7, 129.5, 129.1, 128.9, 128.7, 128.4, 128.3, 127.5, 125.4, 119.7, 114.8, 107.9, 88.7, 74.2, 67.1, 66.4, 60.7, 58.7, 58.5, 58.1, 57.7, 57.5, 56.1, 53.6, 50.9, 50.1, 47.1, 41.2, 39.1, 37.9, 37.6, 31.8, 23.0, 22.2, 15.4.

IR: ν_{max} 3334, 2370,2335, 1776, 1714, 1643, 1508, 1396, 1158 cm -1.

HRMS calcd. for $C_{45}H_{48}N_4O_9Na^+$ $[M+Na]^+$:811.3319. Found:811.3314. **mp.**: 107-109 °C;

*Synthesis of penicimutanin A (**1**)*



Compound **3** (20 mg, 0.037 mmol) and compound **4’** (16 mg, 0.041 mmol) were dissolved in MeCN (2 mL) at 0 °C, then AcOH (0.2 mL), 4Å MS (50 mg) and PTSA (1.5 mg, 0.01 mmol) were added. The mixture was stirred at 60 °C for 72 hours. Saturated aqueous NaHCO$_3$ (2 mL) was added and the mixture was extracted with EtOAc (5 ml × 3) and washed with brine (5 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated to give a white solid, which was chromatographed on silica gel to give **1** (9.5 mg, 26% yield) as a white solid and **3** (13 mg, 0.027 mmol) was recycled. **R_f** = 0.15 (petroleum ether / EtOAc = 1 / 1);

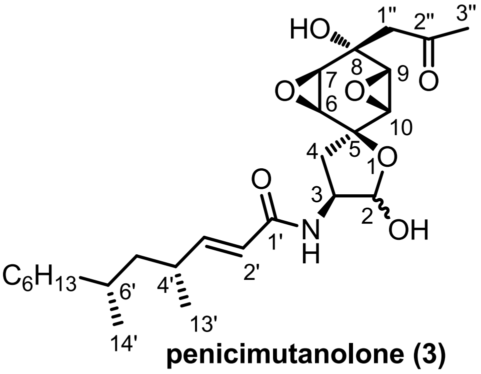
^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.10 (td, *J* = 7.8, 0.9 Hz, 1H), 6.78 (t, *J* = 7.8 Hz, 1H), 6.74 (dd, *J* = 15.7, 8.2 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.11 (br s, 1H), 5.95 (br s, 1H), 5.91 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.70 (d, *J* = 8.7 Hz, 1H), 5.70 (d, *J* = 8.7 Hz, 1H), 5.70 (s, 1H), 5.54 (s, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 5.07 (d, *J* = 17.3 Hz, 1H), 4.64 (s, 1H), 4.30 (ddd, *J* = 9.7, 3.9, 1.9 Hz, 1H), 3.96 (ddd, *J* = 11.7, 5.6, 1.9 Hz, 1H), 3.51 (dd, *J* = 3.9, 2.5 Hz, 1H), 3.40 (dd, *J* = 3.8, 2.5 Hz, 1H), 3.37 (d, *J* = 3.8 Hz, 1H), 3.29 (dd, *J* = 3.8, 3.0 Hz, 1H), 3.23 (dd, *J* = 3.9, 3.0 Hz, 1H), 3.08 (s, 2H), 2.89 (dd, *J* = 14.3, 9.6 Hz, 1H), 2.77 (dd, *J* = 13.6, 8.6 Hz, 1H), 2.46 (dd, *J* = 12.2, 5.6 Hz, 1H), 2.40 – 2.31 (m, 1H), 2.27 (s, 3H), 2.15 (dd, *J* = 12.3, 11.4 Hz, 1H), 2.12 (dd, *J* = 13.1, 8.7 Hz, 1H), 1.42 – 1.34 (m, 2H), 1.34 – 1.30 (m, 1H), 1.30 – 1.24 (m, 2 H),1.26 – 1.15 (m, 7H), 1.12 – 1.06 (m, 1H), 1.08 – 1.03 (m, 1H), 1.04 (s, 3H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.96 (s, 3H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.3, 168.0, 166.2, 164.1, 151.5, 148.1, 143.4, 135.4, 130.0, 129.3, 129.2, 128.8, 127.6, 125.3, 121.1, 119.8, 114.7, 108.9, 90.0, 79.7, 74.7, 66.4, 60.6, 58.6, 58.3, 57.9, 57.6, 57.4, 56.1, 49.7, 47.0, 44.0, 41.1, 38.4, 38.2, 37.5, 34.1, 31.9, 31.7, 30.3, 29.7, 26.8, 23.0, 22.7, 22.2, 20.4, 19.4, 14.1.

IR: ν_{max} 3629, 2905, 2383, 1703,1652, 1550, 1102, 734 cm $^{-1}$.

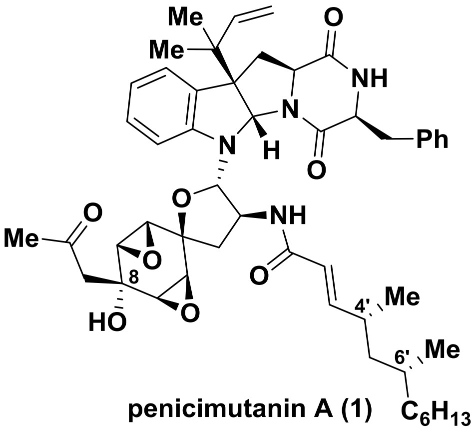
HRMS calcd. for $C_{51}H_{66}N_4O_5Na^+$ $[M+Na]^+$:855.4778. Found:855.4773. **mp.:** 130-133 ^{o}C; **$[\alpha]^{25}_{D}$** -91.1 (c 0.25, MeOH).

NMR Comparison:



penicimutanolone (3)

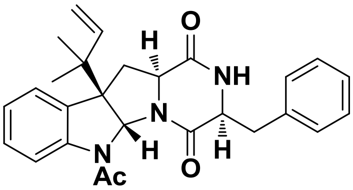
		^{1}HNMR			^{13}CNMR	
Position.	**Δ**	Natural-**3**	Synthetic-**3**	**Δ**	Natural-**3**	Synthetic-**3**
2	**-0.01**	5.55	5.56 d (4.3)	**0.00**	96.46	96.46
2-OH	**-**	-	-	**-**	-	-
3	**0.00**	4.73	4.73 m	**-0.02**	52.08	52.10
3-NH	**-0.01**	6.00	6.01 d (8.3)	**-**	-	-
4	**0.00**	2.00	2.00 dd (13.0)	**0.00**	37.54	37.54
	0.00	2.58	2.58 dd (13.0)	**-**	-	-
5	**-**	-	-	**0.06**	79.21	79.15
6	**-0.01**	3.30	3.31 t (3.1)	**-0.04**	59.39	59.43
7	**0.00**	3.25	3.25 q (2.7)	**-0.07**	58.67	58.74
8	**-**	-	-	**0.03**	66.39	66.36
8-OH	**0.01**	4.68	4.67 d (8.5)	**-**	-	-
9	**-0.01**	3.18	3.19 t (3.1)	**-0.07**	58.11	58.18
10	**0.00**	3.25	3.25 q (2.1)	**-0.02**	57.37	57.39
1’	**-**	-	-	**-0.03**	166.05	166.08
2’	**0.00**	5.75	5.75 dd (15.3)	**-0.02**	121.36	121.38
3’	**0.00**	6.73	6.73 dd (15.3)	**0.01**	151.59	151.58
4’	**0.00**	2.39	2.39 p (7.9)	**0.00**	34.24	34.24
4’-CH3	**0.00**	1.03	1.03 d (6.7)	**0.01**	20.67	20.66
			1.09 td (8.9)			
5’	**0.01**	1.09	1.37 m	**-0.01**	44.05	44.06
	-0.01	1.36	1.37 m			
6’	**-0.01**	1.36	0.83 d (6.4)	**0.00**	30.48	30.48
6’-CH3	**0.00**	0.83	1.25 s	**-0.01**	19.54	19.55
			1.25 s			
7’	**0.00**	1.25	1.25 s	**-0.01**	36.99	37.00
8’	**0.00**	1.25	1.25 s	**0.00**	26.95	26.95
9’	**0.00**	1.25	1.25 s	**0.00**	29.83	29.83
10’	**0.00**	1.25	0.88 t (6.8)	**0.00**	32.05	32.05
11’	**0.00**	1.25	3.07 s	**0.00**	22.82	22.82
12’	**0.00**	0.88	-	**0.01**	14.28	14.27
1’’	**0.00**	3.07	2.27 s	**0.00**	47.13	47.13
2’’	**-**	-		**0.02**	211.43	211.41
3’’	**0.01**	2.28		**0.02**	31.79	31.77



penicimutanin A (1)

			Penicimutanin A (**1**)			
	^{1}HNMR				^{13}CNMR	
Position	△	Natural-**1**	Synthetic-**1**	△	Natural-**1**	Synthetic-**1**
1		-	-		167.9	168.0
2（NH）	**0.00**	5.70	5.70 S	**0.0**	-	**-**
3	**0.00**	4.30	4.30 ddd (9.7, 3.9, 1.9)	**-**	56.1	56.1
4	**-**	**-**	-	**0.0**	164.1	164.1
5a	**0.01**	5.96	5.95 br s	**0.1**	79.8	79.7
6a	**-**	**-**	-	**0.0**	148.1	148.1
7	**0.01**	6.71	6.70 d (7.9)	**-0.1**	108.8	108.9
8	**0.00**	7.10	7.10 td (7.8, 0.9)	**0.0**	128.8	128.8
9	**0.00**	6.78	6.78 t (7.8)	**0.0**	119.8	119.8
10	**0.00**	7.13	7.13 br d (7.8)	**0.0**	125.3	125.3
10a	**-**	**-**	-	**0.0**	130.0	130.0
10b	**-**	**-**	**-**	**-0.1**	60.7	60.6
11	**-0.01**	2.45	2.46 dd (12.2, 5.6)	**0.0**	38.4	38.4
	-0.01	2.14	2.15 dd (12.3, 11.4)			
11a	**-0.01**	3.95	3.96 ddd (11.7, 5.6, 1.9)	**0.0**	58.6	58.6
12	**0.00**	3.37	3.37 d (3.8)	**0.0**	37.5	37.5
	0.01	2.90	2.89 dd (14.3, 9.6)			
13	**-**	**-**	**-**	**0.0**	135.4	135.4
14	**0.00**	7.17	7.17 br d (7.4)	**0.0**	129.2	129.2
15	**-0.01**	7.31	7.32 br t (7.4)	**0.0**	129.3	129.3
16	**0.00**	7.26	7.26 br t (7.4)	**0.0**	127.6	127.6
16-OH	**-**	**-**	-	**-**	-	**-**
17	**-0.01**	7.31	7.32 br t (7.4)	**0.0**	129.3	129.3
18	**0.00**	7.17	7.17 br d (7.4)	**0.0**	129.2	129.2
19	**-**	**-**	-	**0.0**	41.1	41.1
19a	**-0.01**	1.03	1.04 s	**0.0**	22.2	22.2
19b	**0.00**	0.96	0.96 s	**0.0**	23.0	23.0
20	**-0.01**	5.90	5.91 dd (17.3, 10.9)	**0.0**	143.4	143.4
21	**-0.01**	5.11	5.12 d (10.8)	**-0.1**	114.6	114.7

	-0.01	5.06	5.07 d (17.3)			
2'	**-0.01**	5.69	5.70 d (8.7)	**-0.1**	89.9	90.0
3'	**0.01**	5.55	5.54 s	**0.0**	49.7	49.7
3'-NH	**0.02**	6.13	6.11 br s	**-**	-	-
4'	**0.00**	2.12	2.12 dd (13.1, 8.7)	**0.0**	38.2	38.2
	-0.01	2.76	2.77 dd (13.6, 8.6)			
5'	**-**	-	-	**0.0**	74.7	74.7
6'	**0.00**	3.40	3.40 dd (3.8, 2.5)	**0.0**	57.4	57.4
7'	**0.00**	3.29	3.29 dd (3.8, 3.0)	**0.0**	58.3	58.3
8'	**-**	-	-	**0.0**	66.4	66.4
8'-OH	**-0.01**	4.63	4.64 s	**-**	-	-
9'	**0.00**	3.23	3.23 dd (3.9, 3.0)	**0.0**	57.9	57.9
10'	**-0.01**	3.50	3.51 dd (3.9, 2.5)	**0.0**	57.6	57.6
11'	**-0.01**	3.07	2H 3.08 s	**-0.1**	47.1	47.0
12'	**-**	-	-	**-0.1**	211.2	211.3
13'	**0.00**	2.27	3H 2.27 s	**0.0**	31.7	31.7
1"	**-**	-	-	**0.0**	166.2	166.2
2"	**0.00**	5.70	5.70 br d (8.7)	**-0.1**	121.2	121.1
3"	**-0.01**	6.73	6.74 dd (15.7, 8.2)	**-0.1**	151.4	151.5
4"	**0.00**	2.40-2.31	2.40-2.31 m	**0.0**	34.1	34.1
5"	**0.00**	1.34-1.30	1.34-1.30 m	**0.0**	44.0	44.0
	0.00	1.12-1.06	1.12-1.06 m			
6"	**0.00**	1.42-1.34	2H 1.42-1.34 m	**0.0**	30.3	30.3
7"	**0.00**	1.26-1.15	1.26-1.15 m	**-0.1**	37.4	37.5
	0.00	1.08-1.03	1.08-1.03 m			
8"	**0.00**	1.26-1.15	2H 1.26-1.15 m	**0.0**	26.8	26.8
9"	**0.00**	1.26-1.15	2H 1.26-1.15 m	**0.0**	29.7	29.7
10"	**0.00**	1.26-1.15	2H 1.26-1.15 m	**0.0**	31.9	31.9
11"	**0.00**	1.30-1.24	2H 1.30-1.24 m	**-0.1**	22.6	22.7
12"	**0.00**	0.87	3H 0.87 t (6.9)	**0.0**	14.1	14.1
13"	**0.00**	0.99	3H 0.99 d (6.6)	**0.0**	20.4	20.4
14"	**0.01**	0.81	3H 0.80 d (6.4)	**0.0**	19.4	19.4



fructigenine A (4)

			Fructigenine A			
	^{1}HNMR			^{13}CNMR		
Position	△	Natural-**4**	Synthetic-**4**	△	Natural-**4**	Synthetic-**4**
1	**-**	-	-	**0.0**	164.8	164.8
2 (NH)	**0.00**	5.77	5.77 s	**-**	-	-
3	**0.01**	4.24	4.23 dd (10.2, 1.5)	**0.0**	55.9	55.9
4	**-**	-	-	**0.0**	168.1	168.1
5	**-**	-	-	**-**	-	-
5a	**0.00**	6.04	6.04 br s	**0.0**	79.4	79.4
6 (N)	**-**	-	-	**-**	-	-
6a	**-**	-	-	**0.0**	143.0	143.0
7	**0.01**	8.01	8.00 br s	**0.0**	124.5	124.5
8	**0.00**	7.37-7.24	7.37-7.24 m	**0.0**	129.1	129.1
9	**0.00**	7.13	7.12 (7.5, 1.1)	**0.1**	119.2	119.1
10	**0.00**	7.37-7.24	7.37-7.24 m	**0.0**	129.1	129.1
10a	**-**	-	-	**0.1**	132.0	131.9
10b	**-**	-	-	**0.0**	60.9	60.9
11	**0.01**	2.56	2.55 dd (12.5, 5.6)	**-0.1**	36.9	37.0
	0.01	2.24	2.23 dd (12.7, 12.0)			
11a	**0.00**	3.79	3.79 br s (11.5, 5.6)	**0.0**	59.1	59.1
12	**0.01**	3.54	3.53 dd (14.3, 3.7)	**0.0**	36.1	36.1
	0.00	2.82	2.82 dd (14.4, 10.1)			
13	**-**	-	-	**0.0**	135.3	135.3
14	**0.01**	7.19	7.18 dd (6.9, 1.8)	**0.0**	129.2	129.2
15	**0.00**	7.37-7.24	7.37-7.24 m	**0.0**	129.3	129.3
16	**0.00**	7.37-7.24	7.37-7.24 m	**0.0**	127.7	127.7
17	**0.00**	7.37-7.24	7.37-7.24 m	**0.0**	129.3	129.3
18	**0.00**	7.19	7.18 dd (6.9, 1.8)	**0.0**	129.2	129.2
19	**-**	-	-	**0.0**	40.3	40.3
19a	**0.01**	1.13	1.12 s	**0.0**	23.6	23.6
19b	**0.00**	0.97	0.97 s	**0.0**	23.2	23.2
20	**0.00**	5.76	5.76 dd (17.5, 10.9)	**0.0**	143.3	143.3
21	**0.00**	5.13	5.13 d (4.2)	**0.0**	114.6	114.6
	0.01	5.11	5.10 d (11.2)			
22	**-**	-	-	**0.0**	170.1	170.1

23	**0.00**	2.66	2.66 br s	**0.1**	22.4	22.3

Reference:

[1]. Wipf, P.; Kim, Y.; Fritch, P. C. *J. Org. Chem.* **1993**, *58*, 7195.

[2]. Mckillop A.; Lee M.; Robert J. W.; Richard J. K. T.; Norman L. *Tetrahedron. Lett.* **1993**, *34*, 5519.

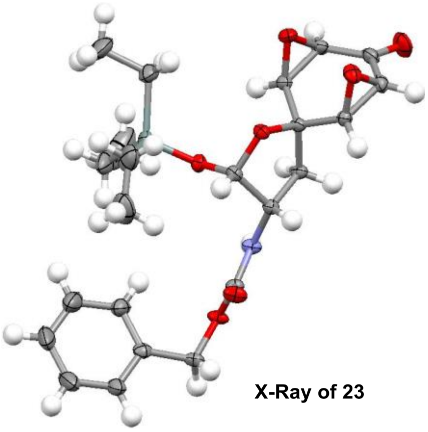
[3]. a) Booker-Milburn, K.; Fedouloff, M.;Paknoham, S.; Strachan, J.; Melville, J.; Voyle, M. *Tetrahedron Lett.* **2000**, *41*, 4657.

b) Linton, E. C.; Kozlowski, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 16162.

[4]. a) Amano, Y.;Nishiyama, S. *Tetrahedron Letters* , **2006** , *47* ,6505.
b) Kajiyama ,D .; Saiton, T.; Nishiyam, S. *Electrochemistry,* **2013,** *81*, 319.

[5]. Ruchti, J.; Carreira, E. M. *J. Am. Chem. Soc.* **2014**, *136*, 16756.

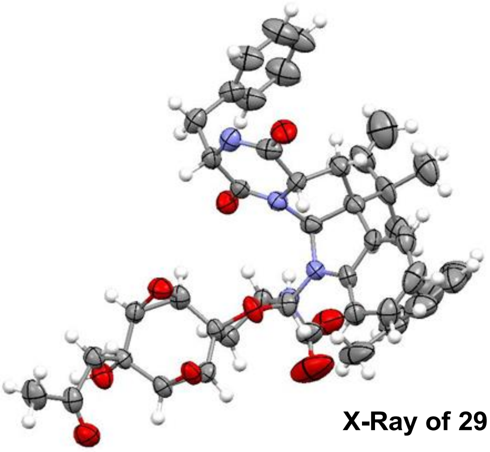
X-Ray data for compounds:



X-Ray of 23

Identification code	mx7026	
Empirical formula	C23 H31 N O7 Si	
Formula weight	461.58	
Temperature	173.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.936(4) Å	α= 90 °.
	b = 9.071(3) Å	β= 94.630(5) °.
	c = 12.562(5) Å	γ = 90 °.
Volume	1242.0(8) Å^3	
Z	2	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.135 mm^{-1}	
F(000)	492	
Crystal size	0.305 x 0.222 x 0.037 mm^3	
Theta range for data collection	1.626 to 27.475 °.	
Index ranges	-14<=h<=12, -9<=k<=11, -16<=l<=16	
Reflections collected	8505	
Independent reflections	5103 [R(int) = 0.0397]	
Completeness to theta = 25.242 °	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.80177	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5103 / 1 / 292
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1430
R indices (all data)	R1 = 0.0598, wR2 = 0.1458
Absolute structure parameter	0.02(11)
Extinction coefficient	n/a
Largest diff. peak and hole	0.520 and -0.313 e.$Å^{-3}$



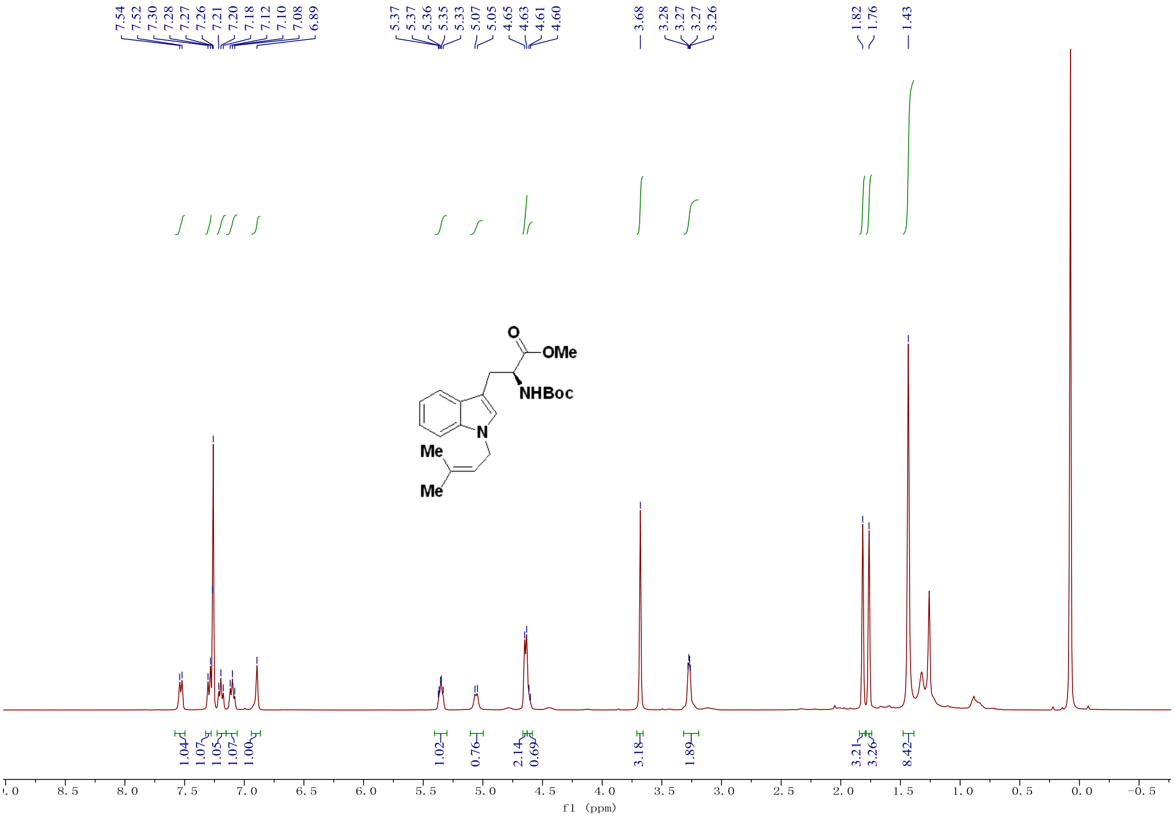
X-Ray of 29

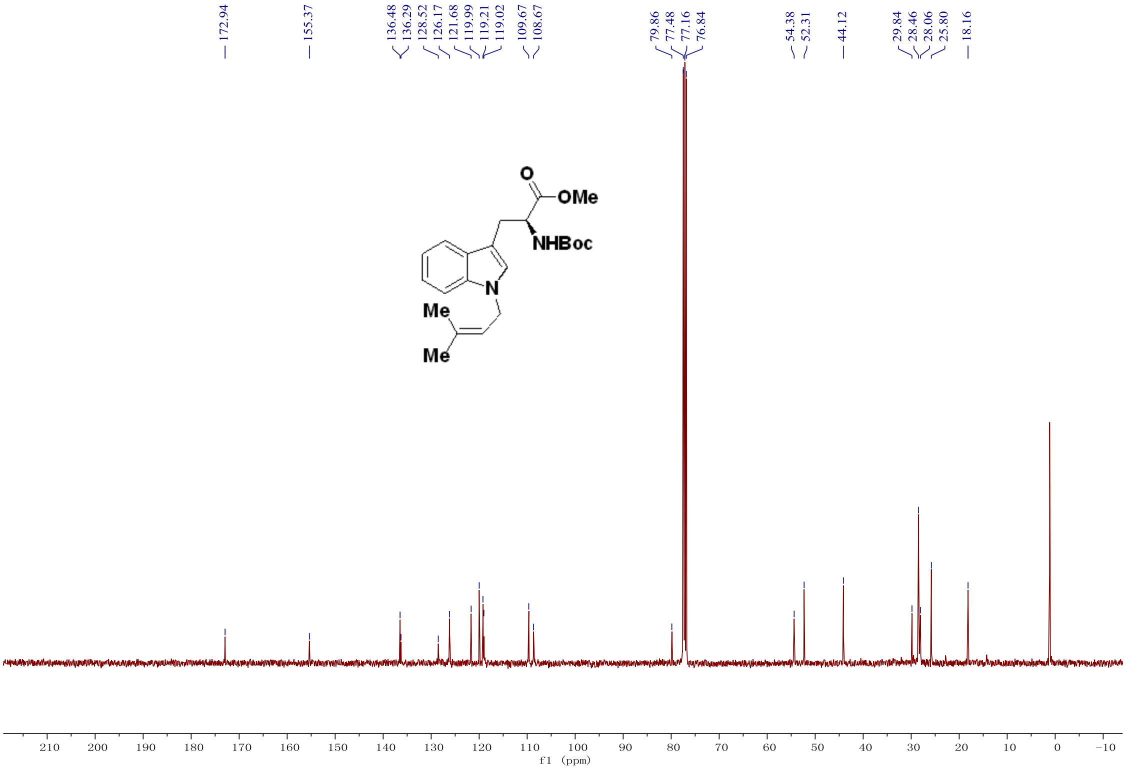
Identification code	190518d
Empirical formula	$C_{45}H_{47}N_4O_9$
Formula weight	787.87
Temperature/K	293(2)
Crystal system	N/A
Space group	$P2_1$
a/Å	8.7818(5)
b/Å	21.1435(13)
c/Å	10.5555(7)
α/°	90.00
β/°	92.327(2)
γ/°	90.00
Volume/$Å^3$	1958.3(2)
Z	2
ρ_{calc}g/cm^3	1.336
μ/mm^{-1}	0.766
F(000)	834.0

Crystal size/mm^3	0.25 × 0.20 × 0.10
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/ °	8.36 to 132.1
Index ranges	$-8 \leq h \leq 10$, $-14 \leq k \leq 25$, $-11 \leq l \leq 12$
Reflections collected	6536
Independent reflections	4692 [R_{int} = 0.0594, R_{sigma} = N/A]
Data/restraints/parameters	4692/1/535
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.1146
Final R indexes [all data]	R_1 = 0.1039, wR_2 = 0.1305
Largest diff. peak/hole / e Å^{-3}	0.29/-0.29
Flack parameter	0.0(4)

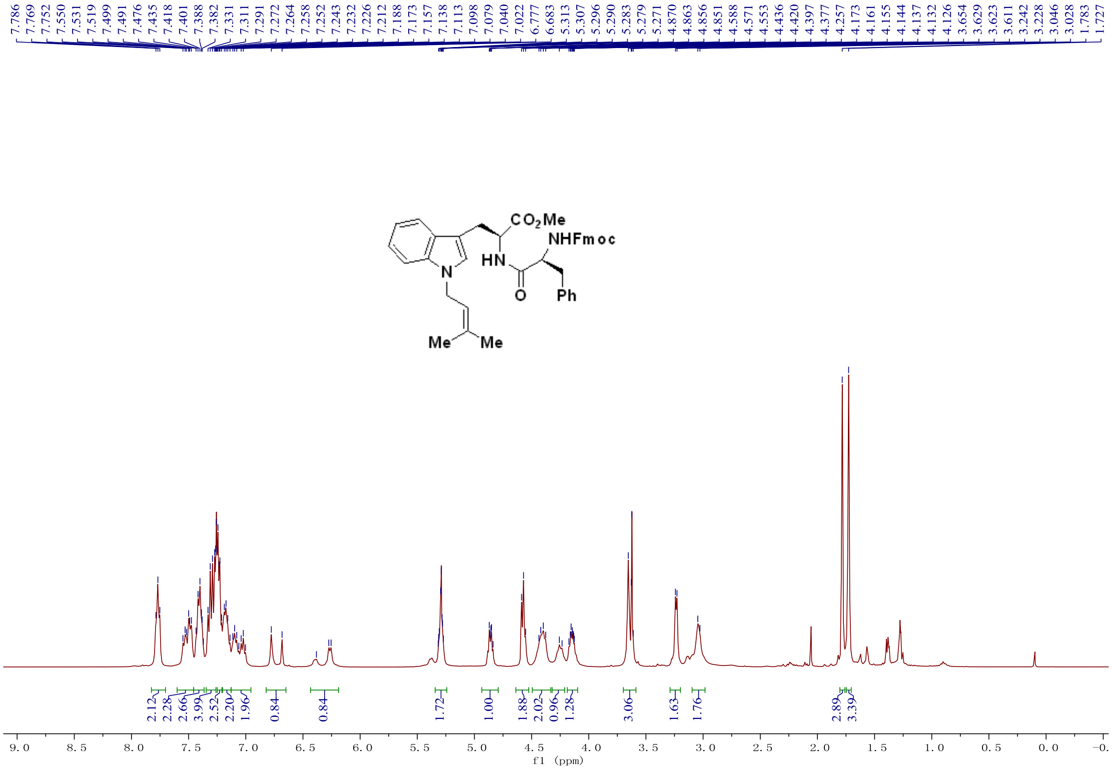
NMR Spectra:

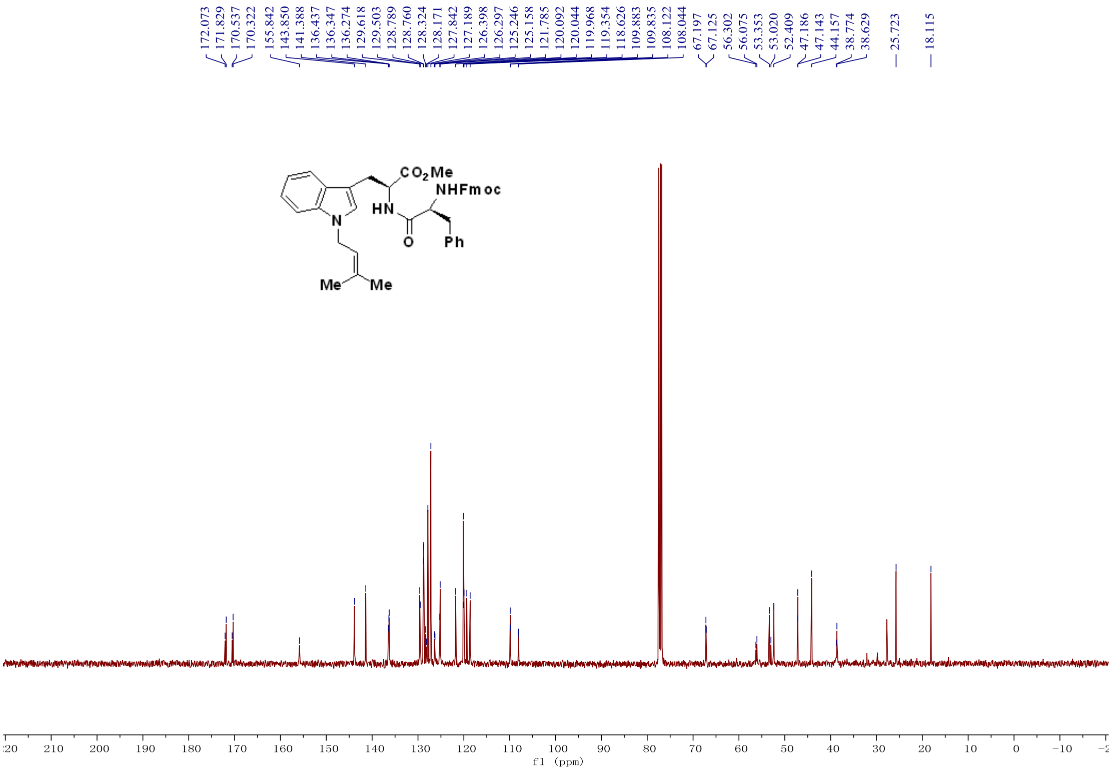
Compound **10**



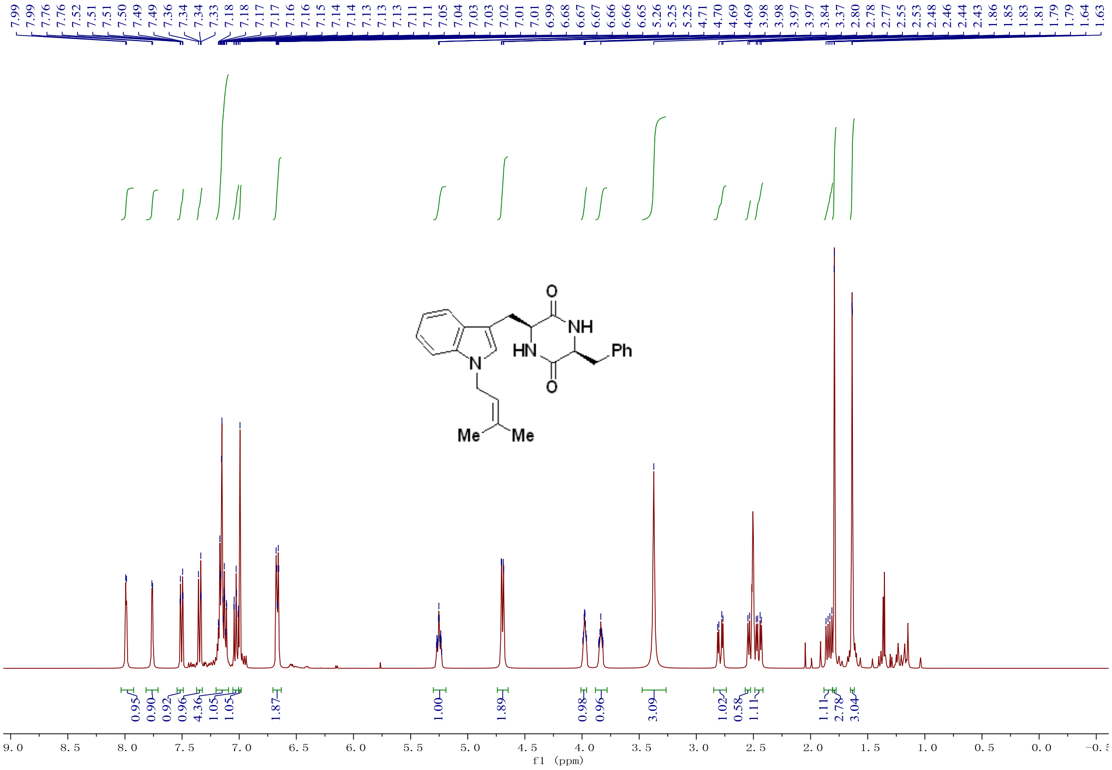


Compound **11** (rotamers)





Compound **5**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HN
Ph
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N
Me
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0.92
0.96
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1.00
1.89
0.98
0.96
3.09
1.02
0.58
1.11
1.11
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7.0
6.5
6.0
5.5
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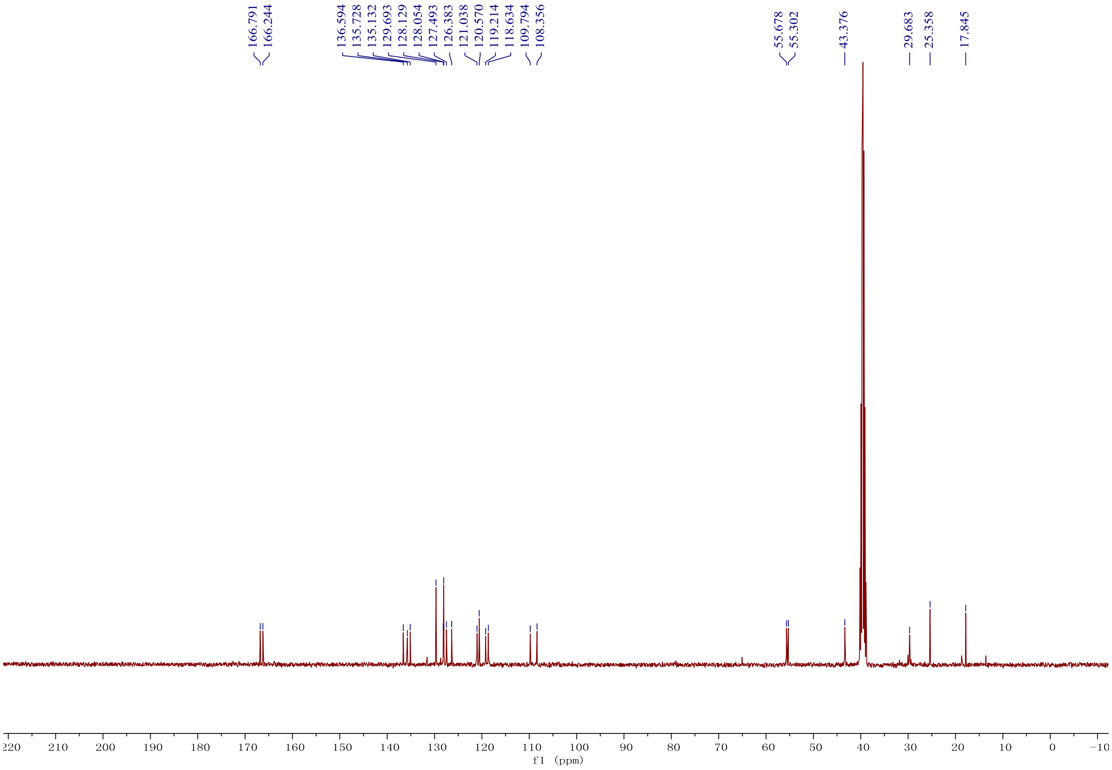
f1 (ppm)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60
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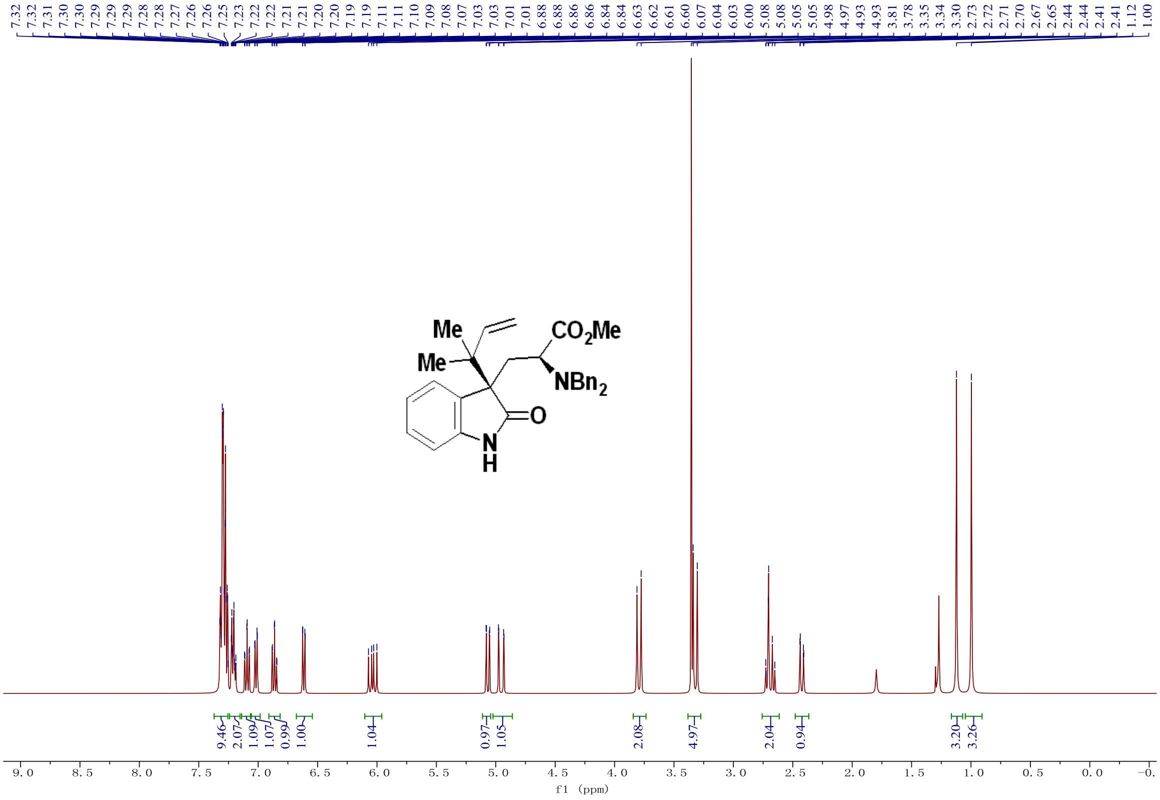
10
0
−10
f1 (ppm)

Compound **16**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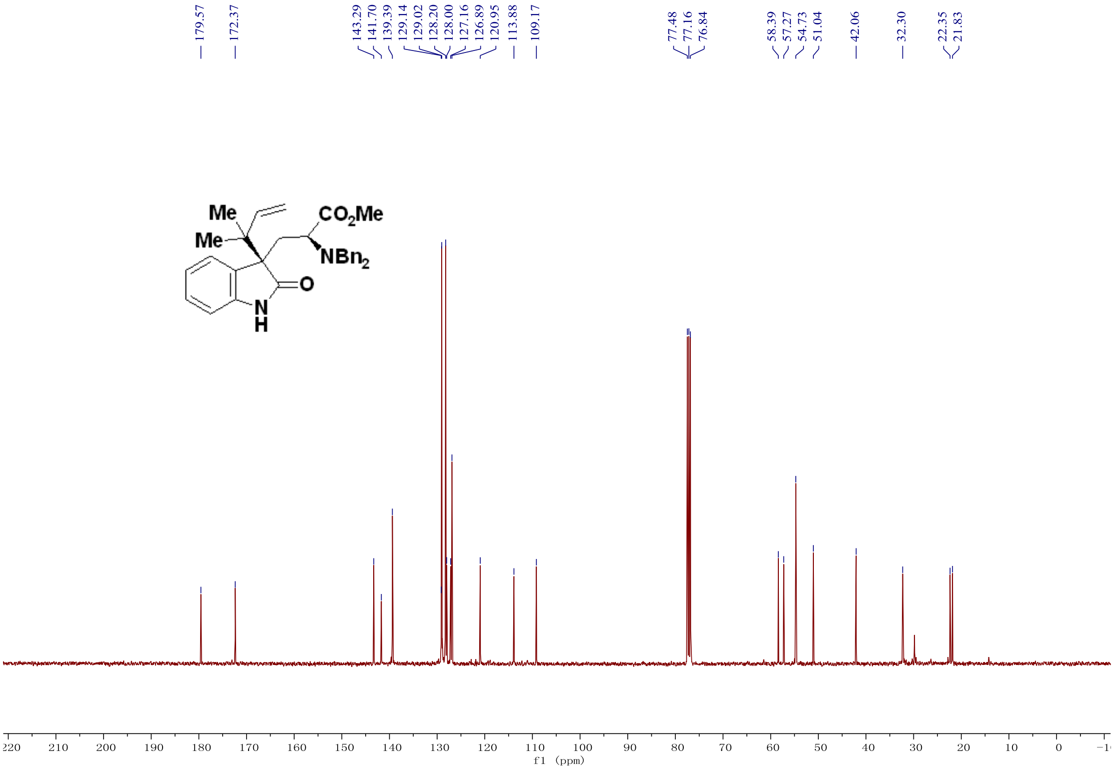
Me
Me
CO2Me
NBn2
O
N
H
9.46 2.07 1.09 1.07 0.99 1.00 1.04 0.97 1.05 2.08 4.97 2.04 0.94 3.20 3.26
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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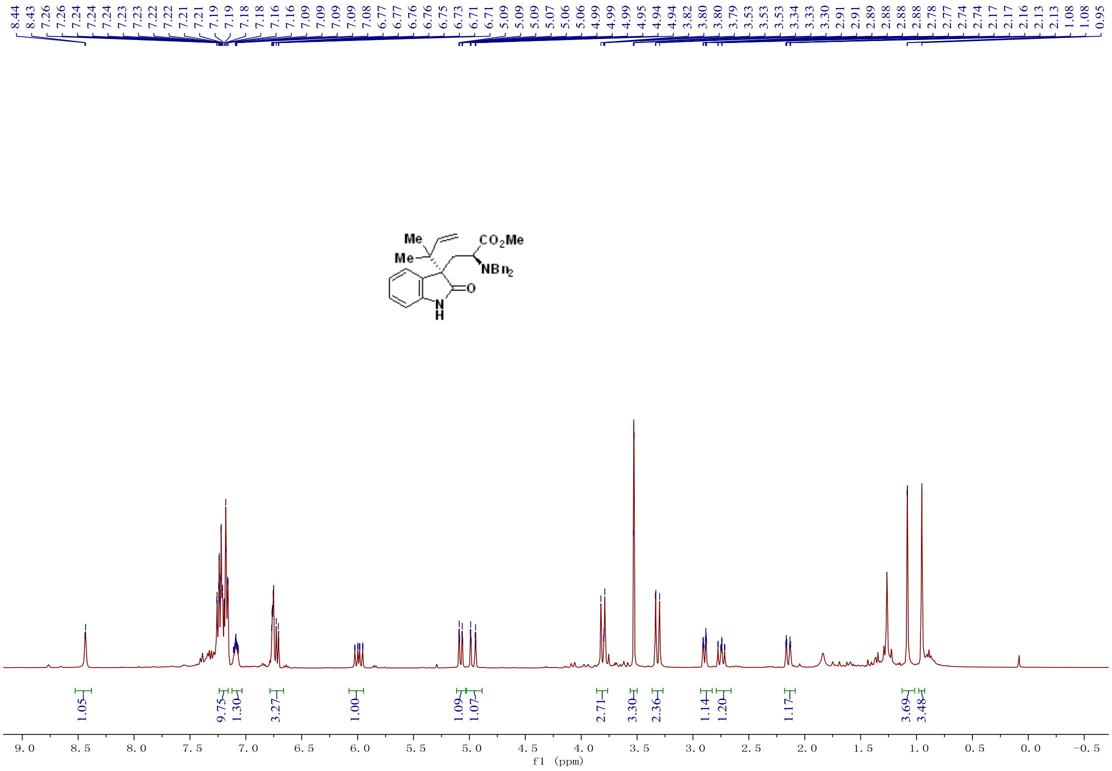
Me
Me
CO2Me
NBn2
O
N
H
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

Compound **16’**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2.74
2.17
2.17
2.16
2.13
2.13
1.08
1.08
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Me
Me
CO2Me
NBn2
O
N
H
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1.30
3.27
1.00
1.09
1.07
2.71
3.30
2.36
1.14
1.20
1.17
3.69
3.48
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
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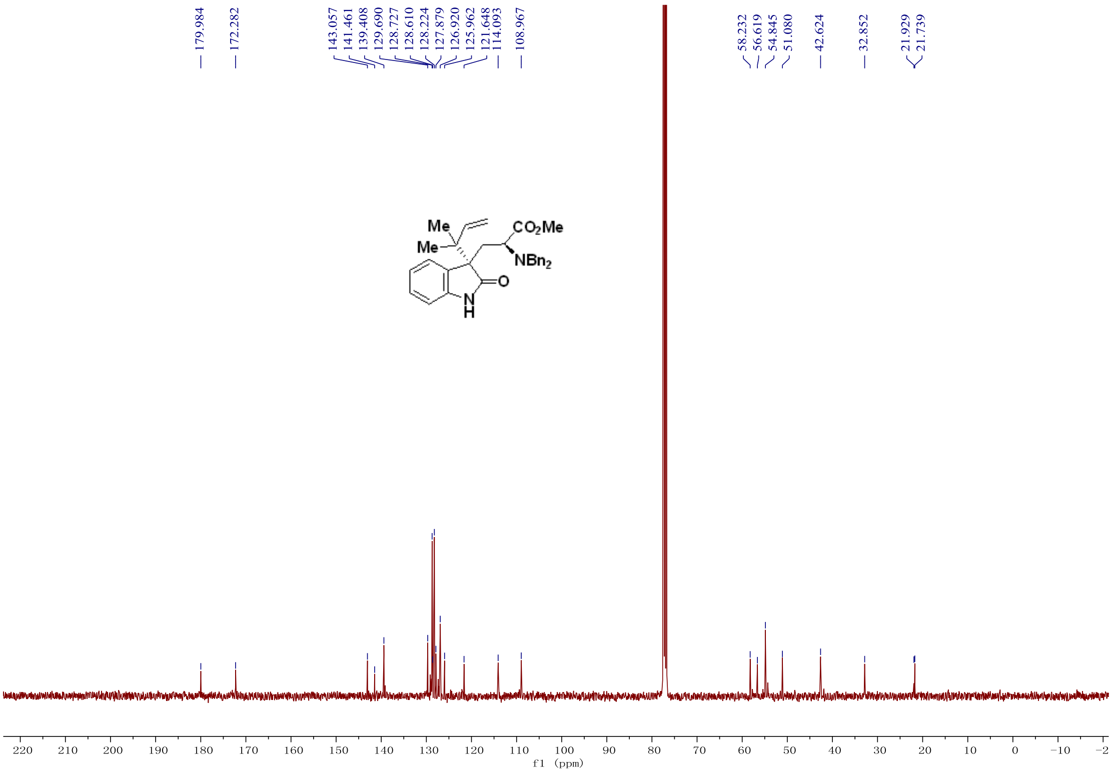
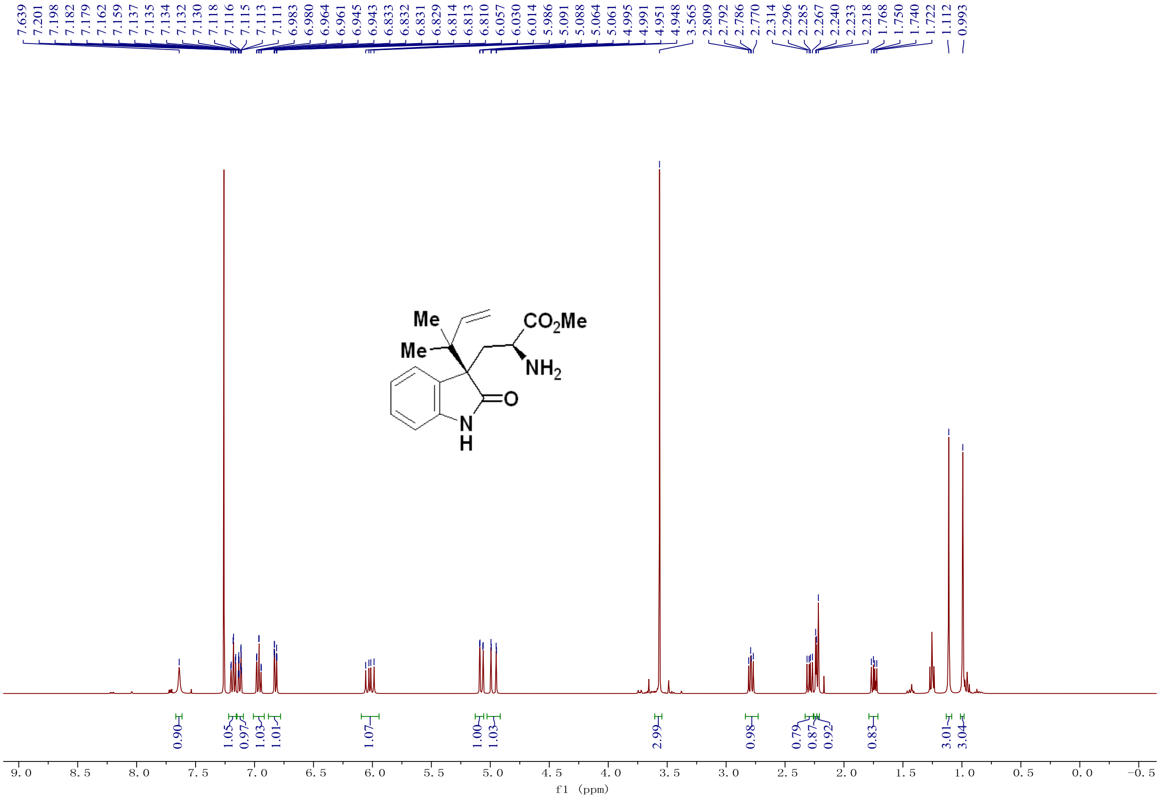
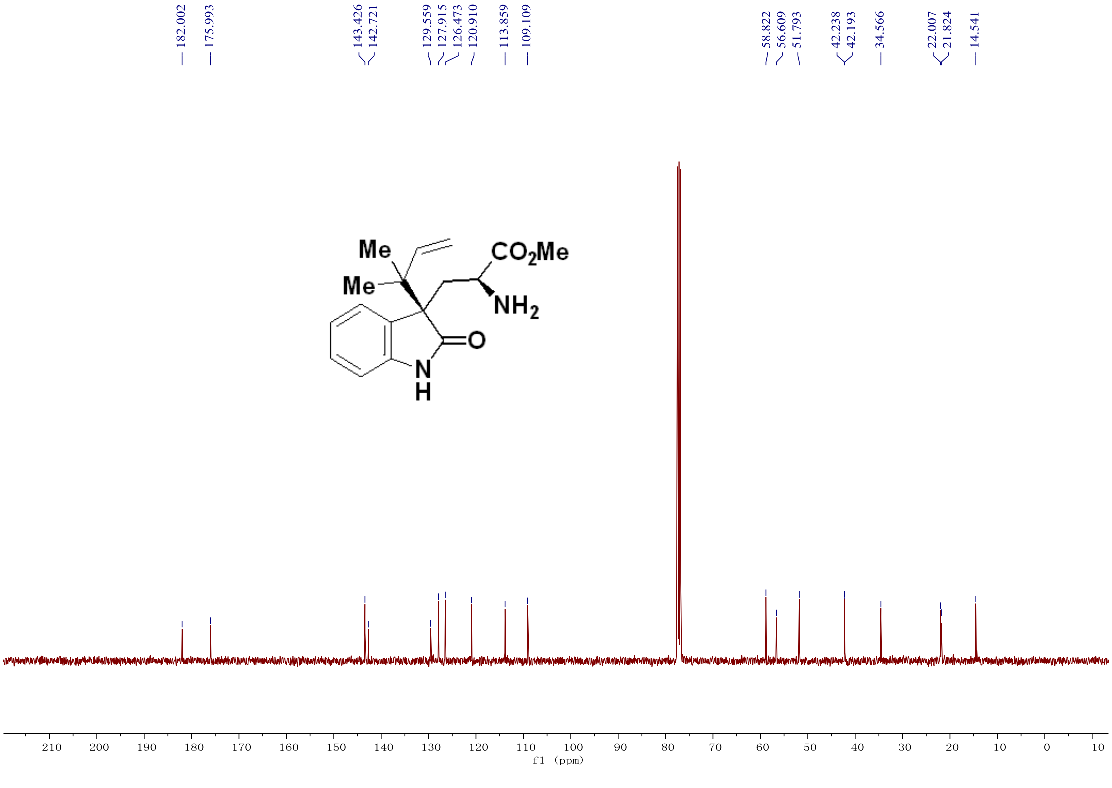
f1 (ppm)

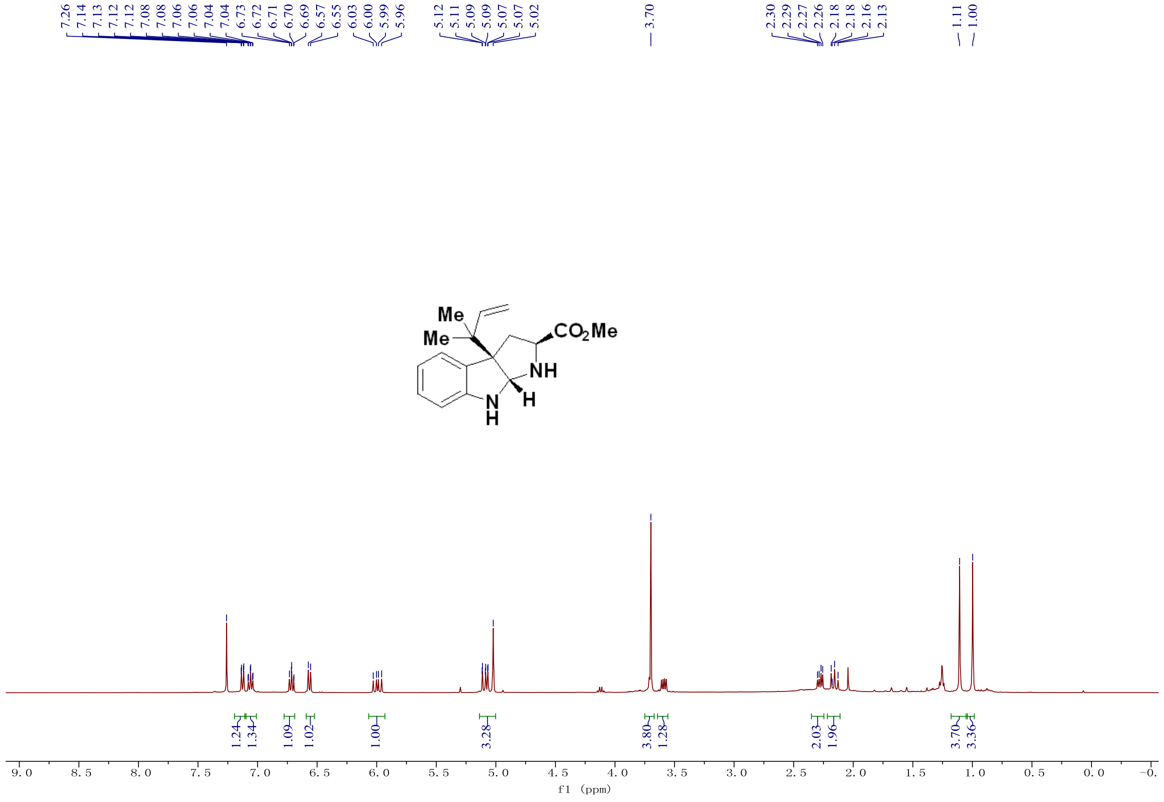

179.984
172.282
143.057
141.461
139.408
129.690
128.727
128.610
128.224
127.879
126.920
125.962
121.648
114.093
108.967
58.232
56.619
54.845
51.080
42.624
32.852
21.929
21.739
Me
Me
CO2Me
NBn2
O
N
H
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

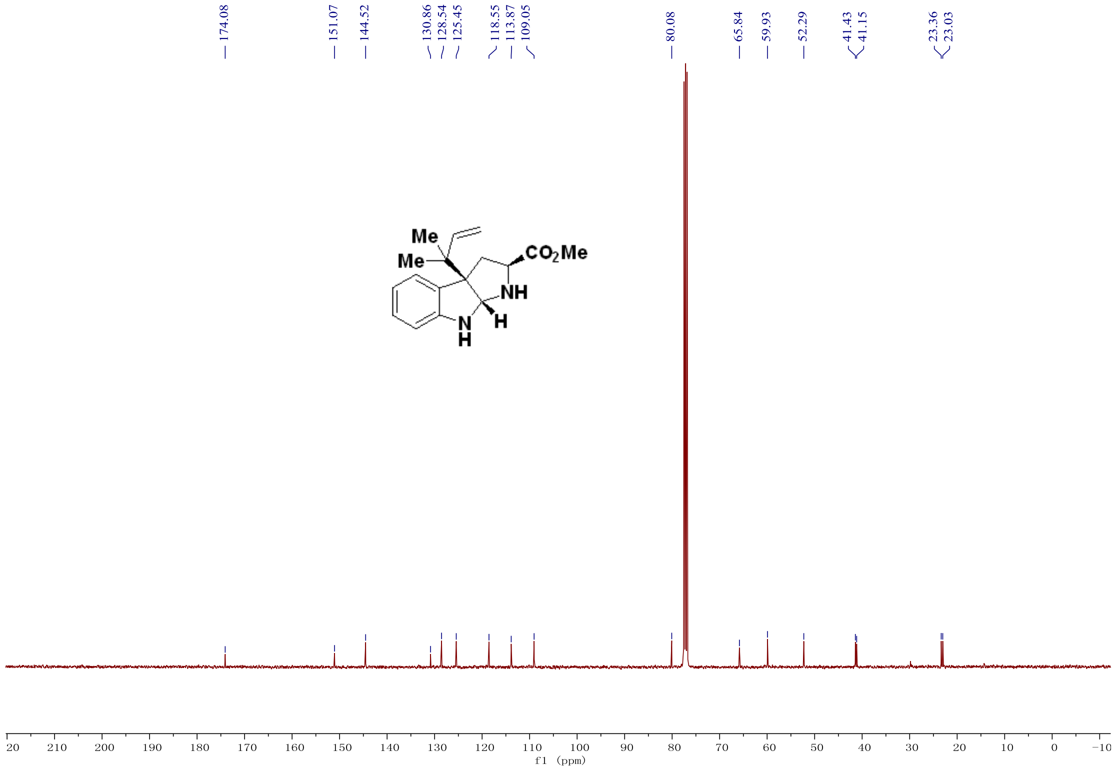
Compound **17**


7.639
7.201
7.198
7.182
7.179
7.162
7.159
7.137
7.135
7.134
7.132
7.130
7.118
7.116
7.115
7.113
7.111
6.983
6.980
6.964
6.961
6.945
6.943
6.833
6.832
6.831
6.829
6.814
6.813
6.810
6.057
6.030
6.014
5.986
5.091
5.088
5.064
5.061
4.995
4.991
4.951
4.948
3.565
2.809
2.792
2.786
2.770
2.314
2.296
2.285
2.267
2.240
2.233
2.218
1.768
1.750
1.740
1.722
1.112
0.993
Me
Me
CO2Me
NH2
O
N
H
0.90
1.05
0.97
1.03
1.01
1.07
1.00
1.03
2.99
0.98
0.79
0.87
0.92
0.83
3.01
3.04
9.0
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
-0.5
f1 (ppm)

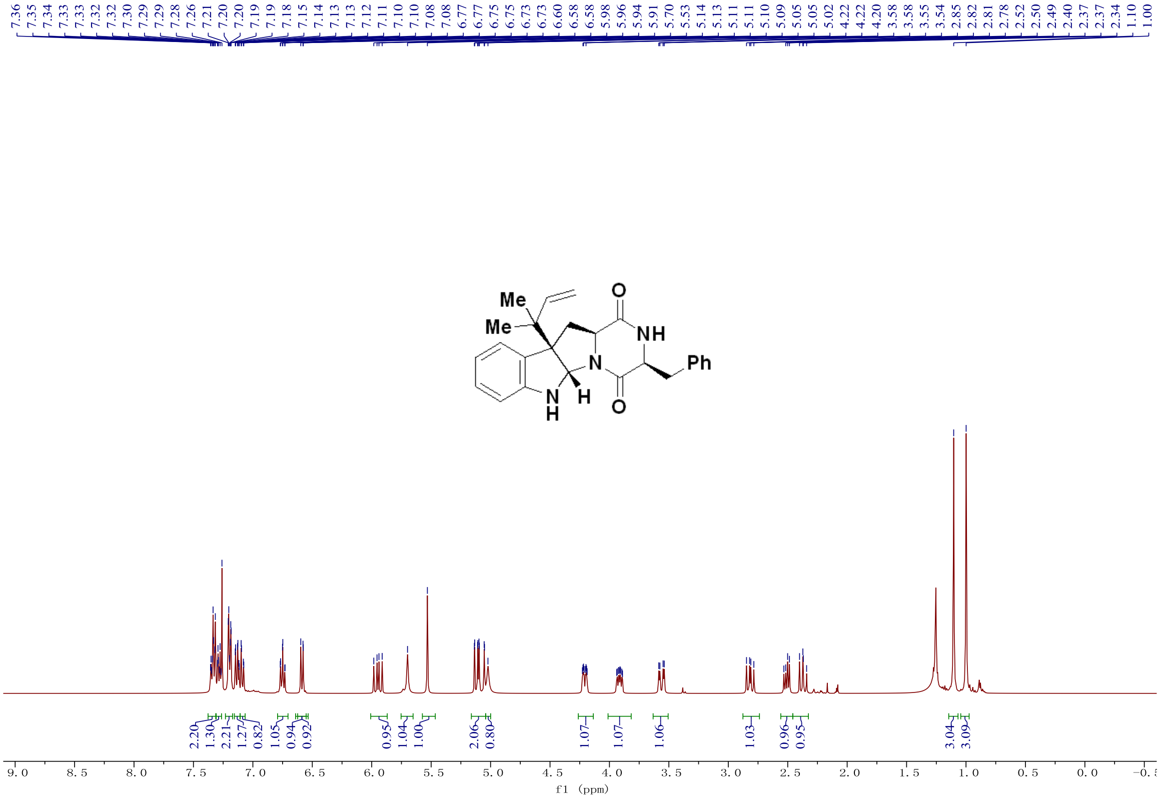

182.002
175.993
143.426
142.721
129.559
127.915
126.473
120.910
113.859
109.109
58.822
56.609
51.793
42.238
42.193
34.566
22.007
21.824
14.541
Me
Me
CO2Me
NH2
O
N
H
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

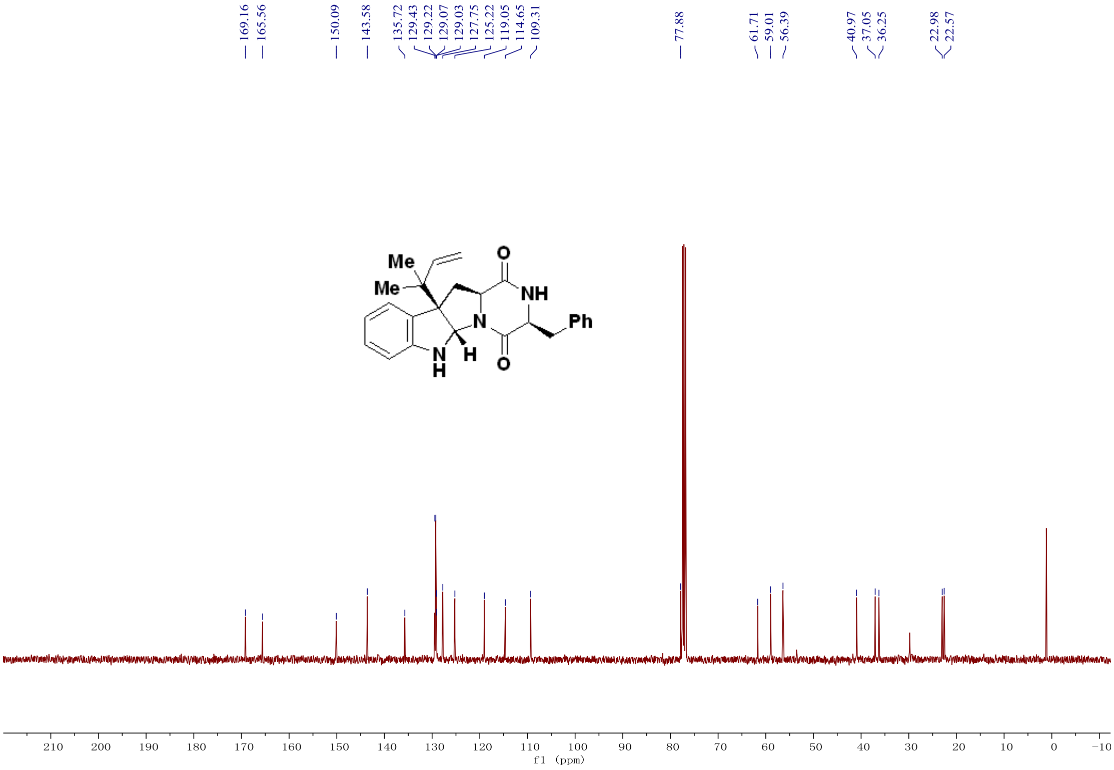
Compound **18**


7.26
7.14
7.13
7.12
7.12
7.08
7.08
7.06
7.06
7.04
7.04
6.73
6.72
6.71
6.70
6.69
6.57
6.55
6.03
6.00
5.99
5.96
5.12
5.11
5.09
5.09
5.07
5.07
5.02
3.70
2.30
2.29
2.27
2.26
2.18
2.18
2.16
2.13
1.11
1.00
Me
Me
CO2Me
NH
N
H
H
1.24
1.34
1.09
1.02
1.00
3.28
3.80
1.28
2.03
1.96
3.70
3.36
9.0
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
-0.
f1 (ppm)

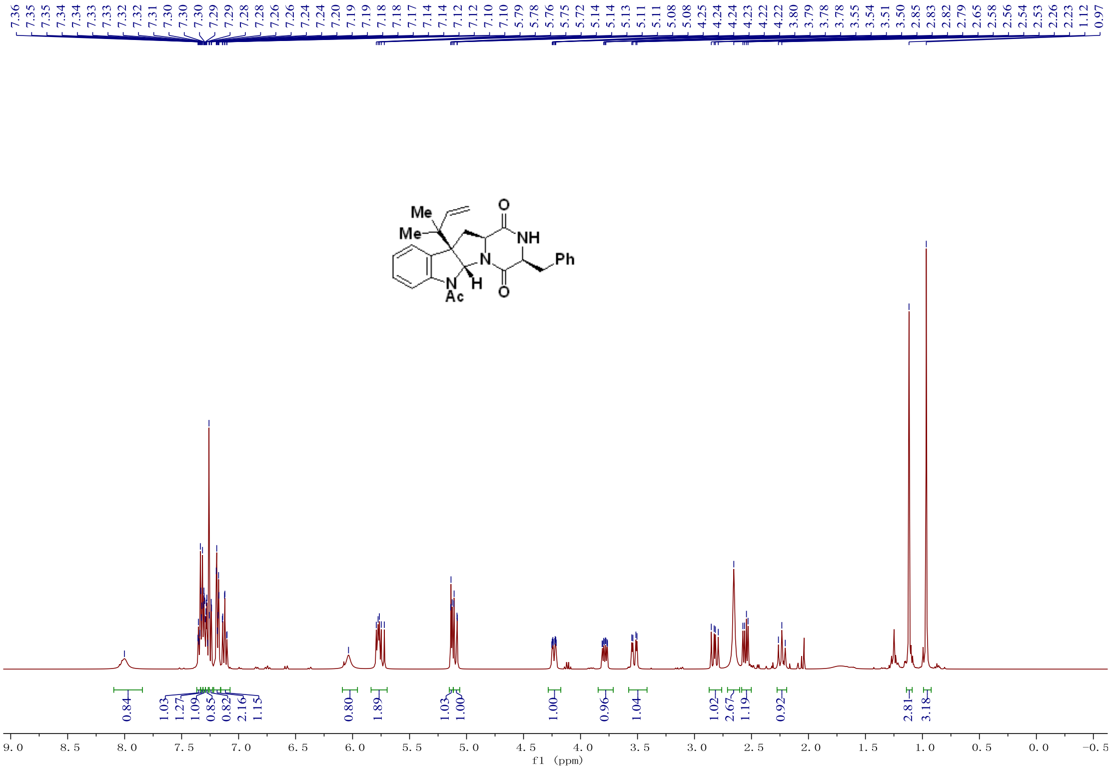

174.08
151.07
144.52
130.86
128.54
125.45
118.55
113.87
109.05
80.08
65.84
59.93
52.29
41.43
41.15
23.36
23.03
Me
Me
CO2Me
NH
N
H
H
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

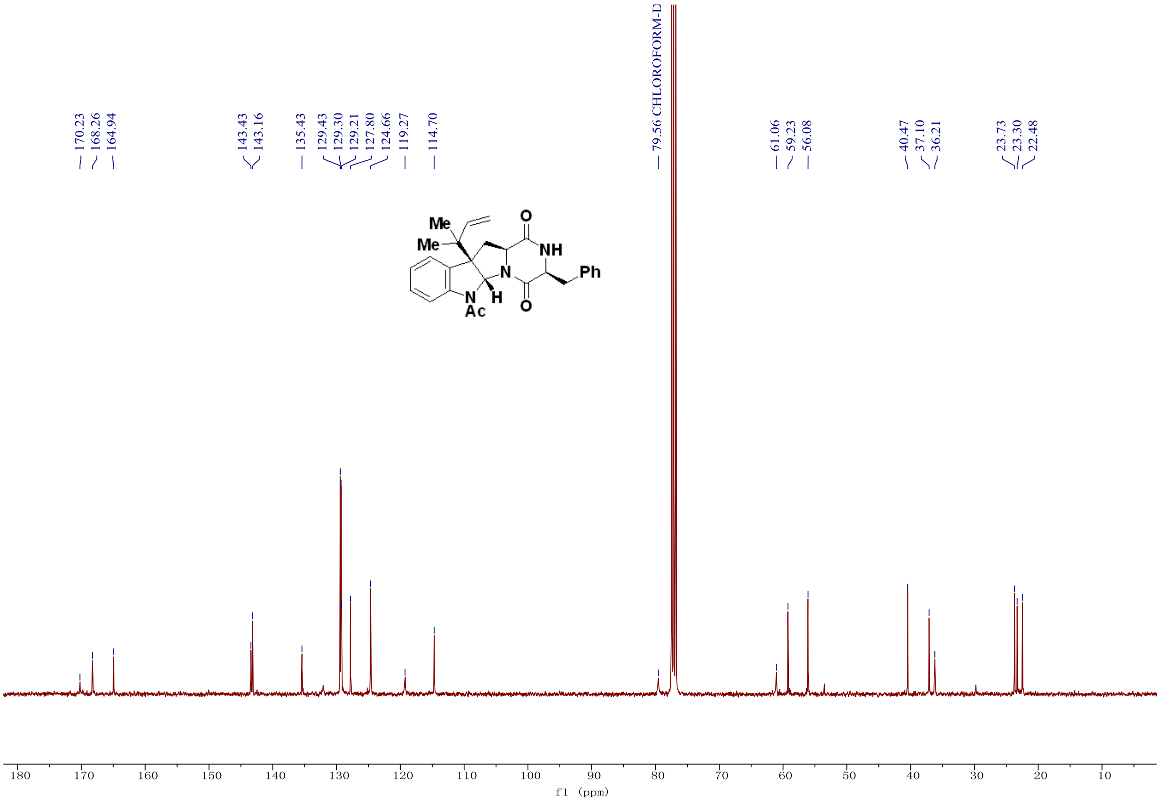
Compound **4’**


7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.30
7.29
7.29
7.28
7.26
7.21
7.20
7.20
7.19
7.19
7.18
7.15
7.14
7.13
7.13
7.12
7.11
7.10
7.10
7.08
7.08
6.77
6.77
6.75
6.75
6.73
6.73
6.60
6.58
6.58
5.98
5.96
5.94
5.91
5.70
5.53
5.14
5.13
5.11
5.11
5.10
5.09
5.05
5.05
5.02
4.22
4.22
4.20
3.58
3.58
3.55
3.54
2.85
2.82
2.81
2.78
2.52
2.50
2.49
2.40
2.37
2.37
2.34
1.10
1.00
Me
Me
O
NH
N
Ph
N
H
H
O
2.20
1.30
2.21
1.27
0.82
1.05
0.94
0.92
0.95
1.04
1.00
2.06
0.80
1.07
1.07
1.06
1.03
0.96
0.95
3.04
3.09
9.0
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
-0.5
f1 (ppm)

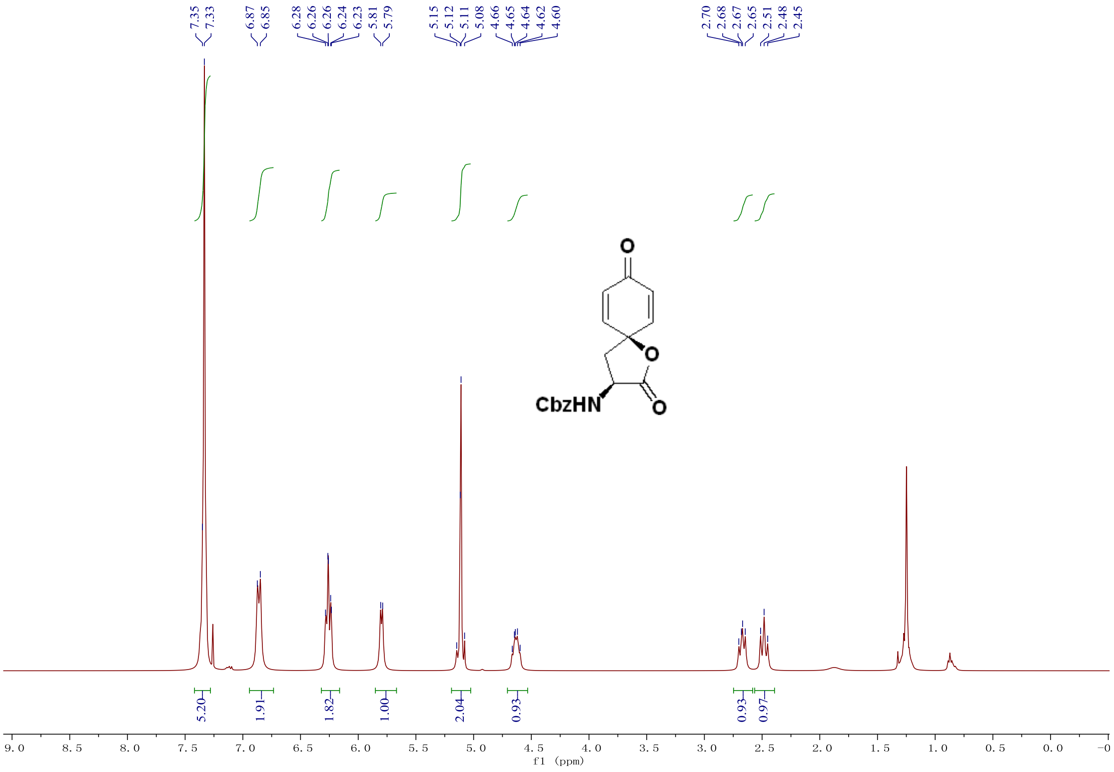

169.16
165.56
150.09
143.58
135.72
129.43
129.22
129.07
129.03
127.75
125.22
119.05
114.65
109.31
77.88
61.71
59.01
56.39
40.97
37.05
36.25
22.98
22.57
Me
Me
O
NH
N
Ph
N
H
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

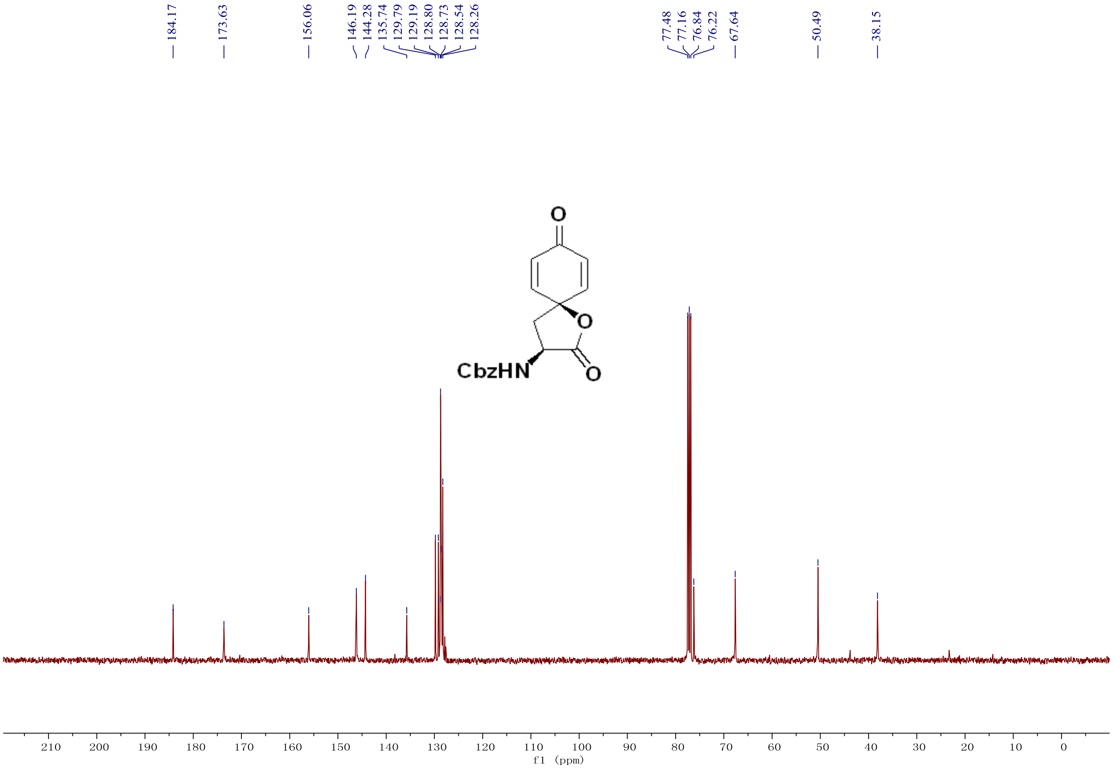
Compound **4**


7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.26
7.24
7.24
7.20
7.19
7.19
7.18
7.18
7.17
7.14
7.14
7.12
7.12
7.10
7.10
5.79
5.78
5.76
5.75
5.72
5.14
5.14
5.13
5.11
5.11
5.08
5.08
4.25
4.24
4.24
4.23
4.22
4.22
3.80
3.79
3.78
3.78
3.55
3.54
3.51
3.50
2.85
2.83
2.82
2.79
2.65
2.58
2.56
2.54
2.53
2.26
2.23
1.12
0.97
Me
Me
O
NH
N
Ph
N
H
Ac
O
0.84
1.03
1.27
1.09
0.85
0.82
2.16
1.15
0.80
1.89
1.03
1.00
1.00
0.96
1.04
1.02
2.67
1.19
0.92
2.81
3.18
9.0
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
-0.5
f1 (ppm)

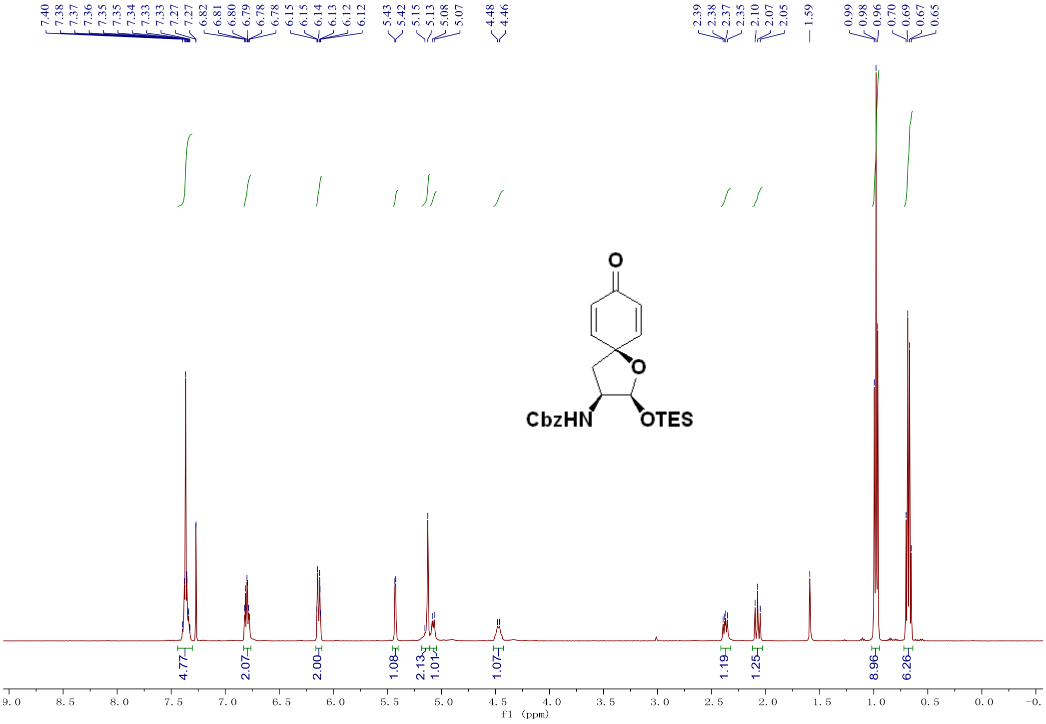

170.23
168.26
164.94
143.43
143.16
135.43
129.43
129.30
129.21
127.80
124.66
119.27
114.70
79.56 CHLOROFORM-D
61.06
59.23
56.08
40.47
37.10
36.21
23.73
23.30
22.48
Me
Me
O
NH
N
Ph
N
H
Ac
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

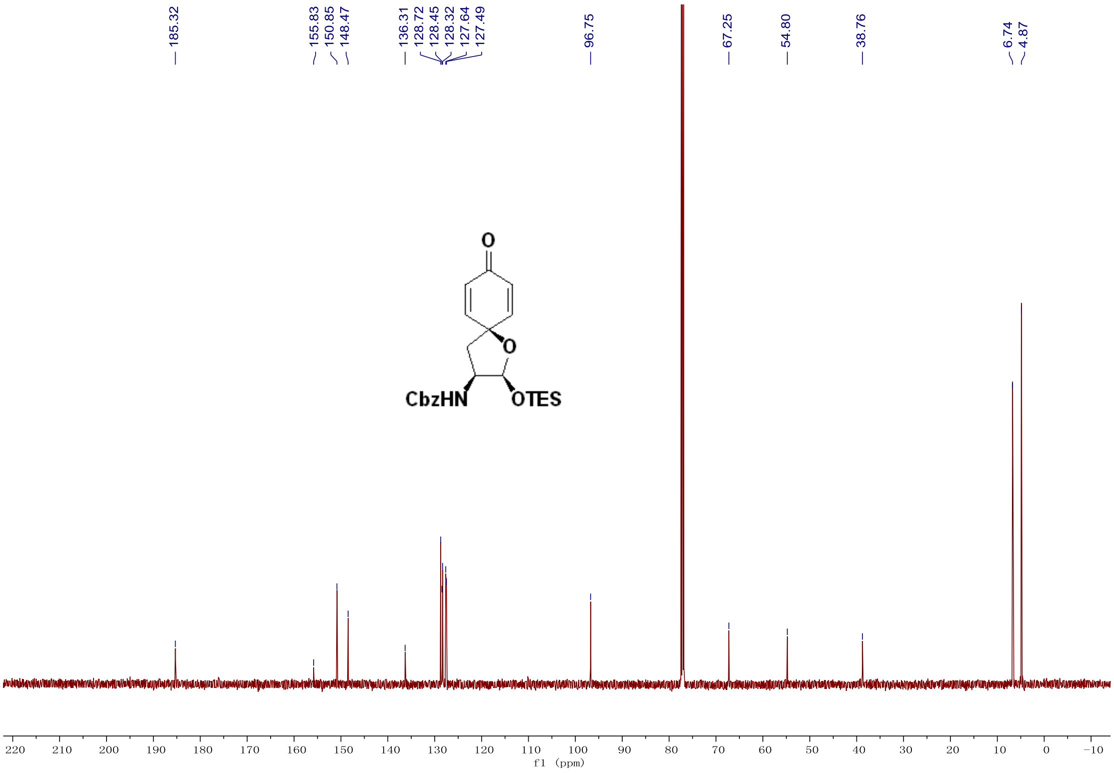
Compound **19**


7.35
7.33
6.87
6.85
6.28
6.26
6.26
6.24
6.23
5.81
5.79
5.15
5.12
5.11
5.08
4.66
4.65
4.64
4.62
4.60
2.70
2.68
2.67
2.65
2.51
2.48
2.45
5.20
1.91
1.82
1.00
2.04
0.93
0.93
0.97
CbzHN
O
O
O
9.0
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)

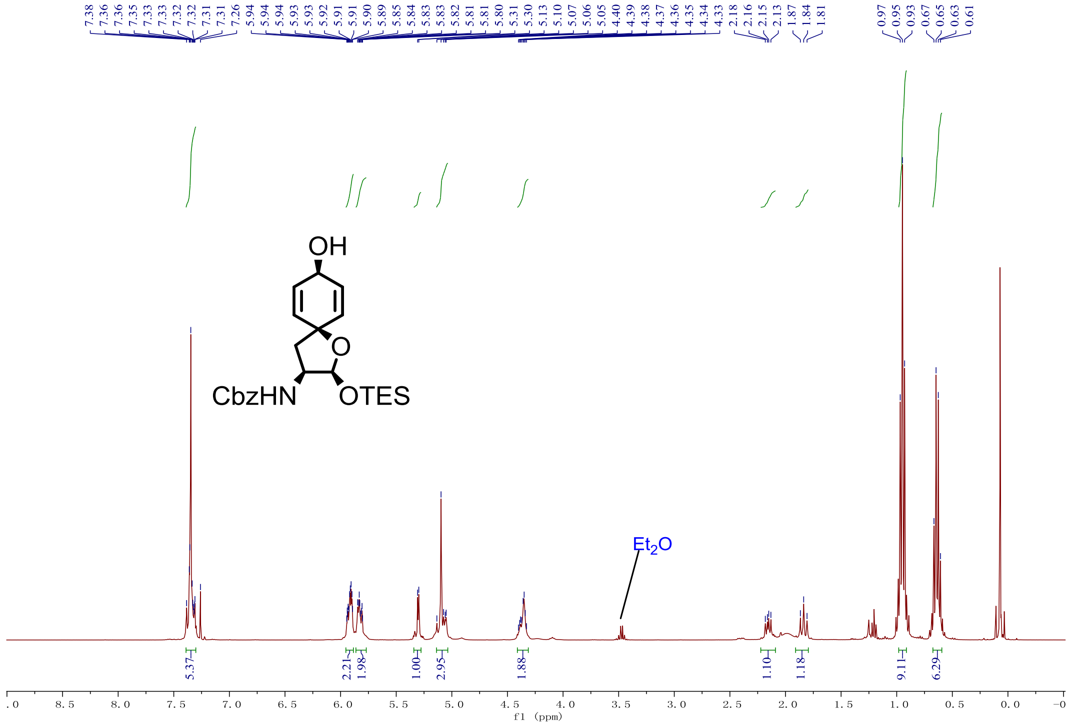

184.17
173.63
156.06
146.19
144.28
135.74
129.79
129.19
128.80
128.73
128.54
128.26
77.48
77.16
76.84
76.22
67.64
50.49
38.15
CbzHN
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

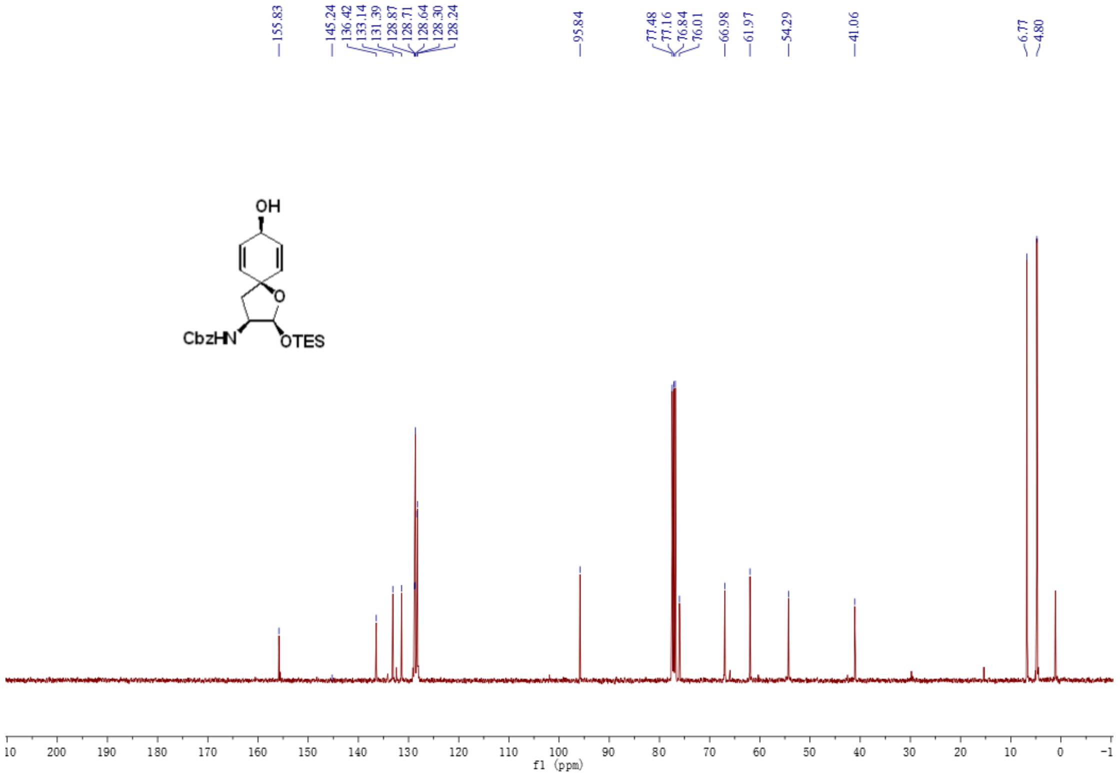
Compound **20**


7.40
7.38
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.27
7.27
7.27
6.82
6.81
6.80
6.79
6.78
6.78
6.15
6.15
6.14
6.13
6.12
6.12
5.43
5.42
5.15
5.13
5.08
5.07
4.48
4.46
2.39
2.38
2.37
2.35
2.10
2.07
2.05
1.59
0.99
0.98
0.96
0.70
0.69
0.67
0.65
O
O
CbzHN
OTES
4.77
2.07
2.00
1.08
2.13
1.01
1.07
1.19
1.25
8.96
6.26
9.0
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
-0.
f1 (ppm)

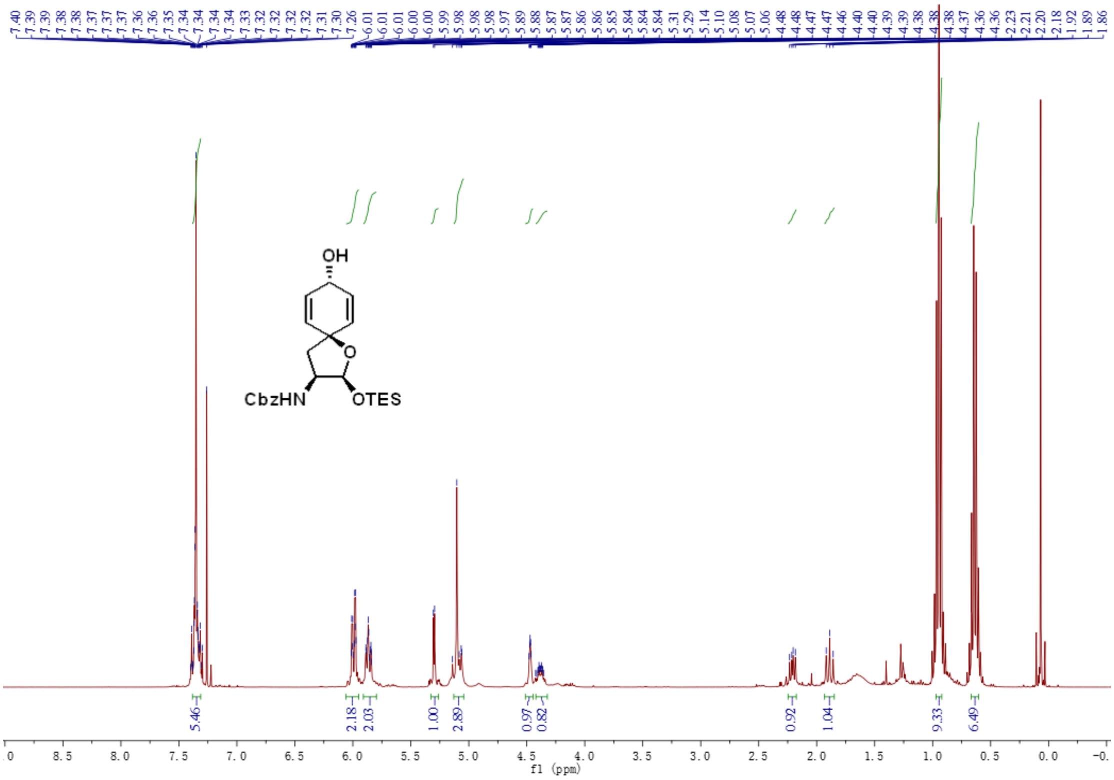

185.32
155.83
150.85
148.47
136.31
128.72
128.45
128.32
127.64
127.49
96.75
67.25
54.80
38.76
6.74
4.87
O
O
CbzHN
OTES
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

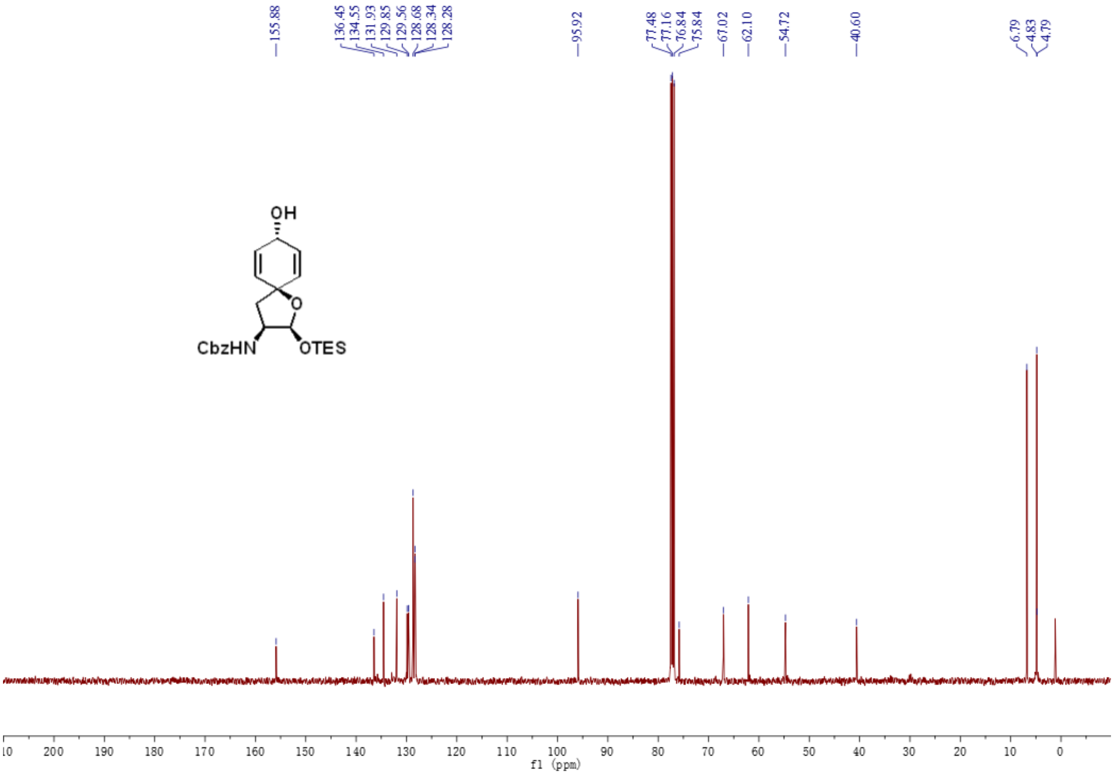
Compound **21**


7.38
7.36
7.36
7.35
7.33
7.33
7.32
7.31
7.26
5.94
5.94
5.93
5.93
5.92
5.91
5.91
5.90
5.89
5.85
5.84
5.83
5.83
5.82
5.81
5.81
5.80
5.31
5.30
5.13
5.10
5.07
5.06
5.05
4.40
4.39
4.38
4.37
4.36
4.35
4.34
4.33
2.18
2.16
2.15
2.13
1.87
1.84
1.81
0.97
0.95
0.93
0.67
0.65
0.63
0.61
OH
O
CbzHN
OTES
Et_2O
5.37
2.21
1.98
1.00
2.95
1.88
1.10
1.18
9.11
6.29
f1 (ppm)

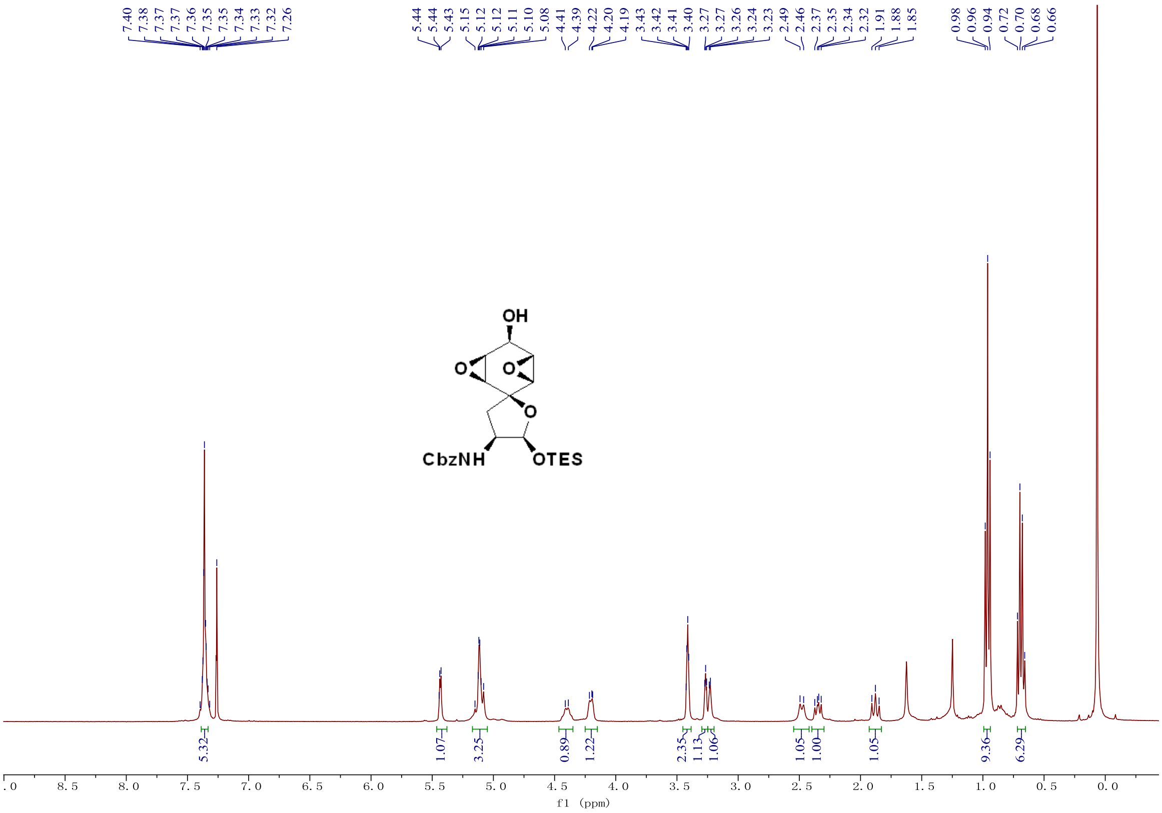

155.83
145.24
136.42
133.14
131.39
128.87
128.71
128.64
128.30
128.24
95.84
77.48
77.16
76.84
76.01
66.98
61.97
54.29
41.06
6.77
4.80
OH
O
CbzHN
OTES
f1 (ppm)

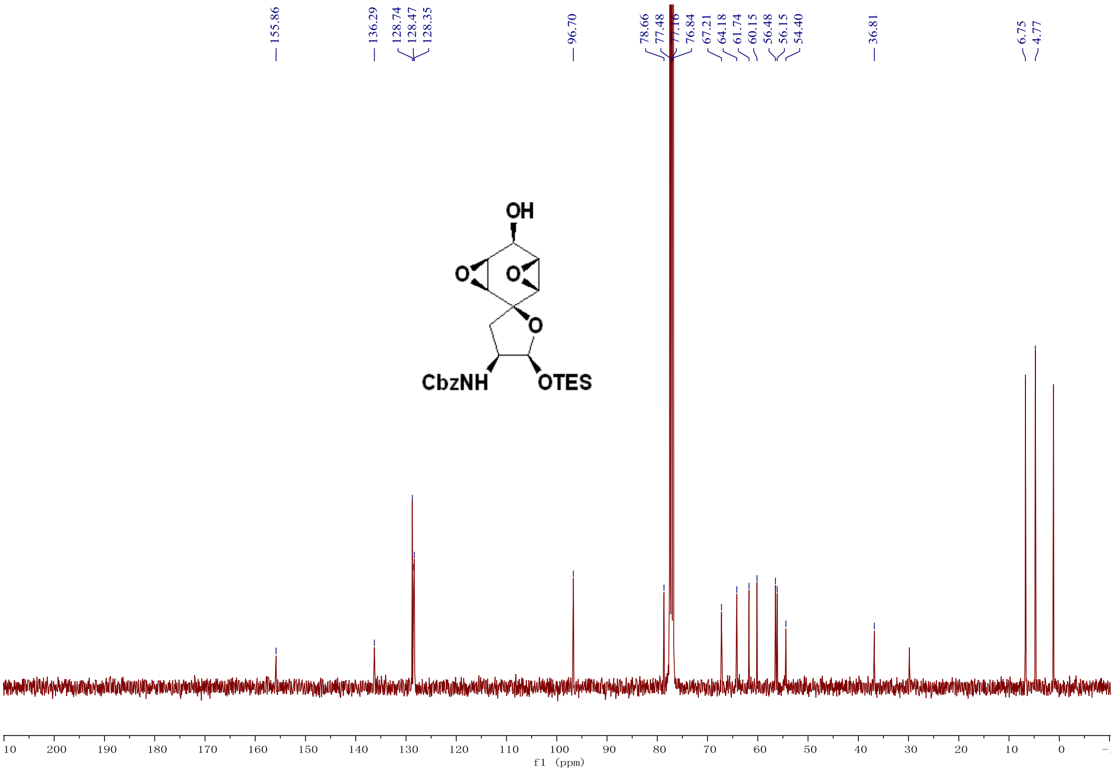
Compound **21’**


7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.34
7.34
7.33
7.32
7.32
7.32
7.32
7.31
7.30
7.26
6.01
6.01
6.01
6.00
6.00
5.99
5.98
5.98
5.98
5.97
5.89
5.88
5.87
5.87
5.86
5.86
5.85
5.84
5.84
5.84
5.31
5.29
5.14
5.10
5.08
5.07
5.06
4.48
4.48
4.47
4.47
4.46
4.40
4.40
4.39
4.39
4.38
4.38
4.38
4.37
4.36
4.36
2.23
2.21
2.20
2.18
1.92
1.89
1.86
OH
O
CbzHN
OTES
5.46
2.18
2.03
1.00
2.89
0.97
0.82
0.92
1.04
9.33
6.49
0
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
-0.
f1 (ppm)

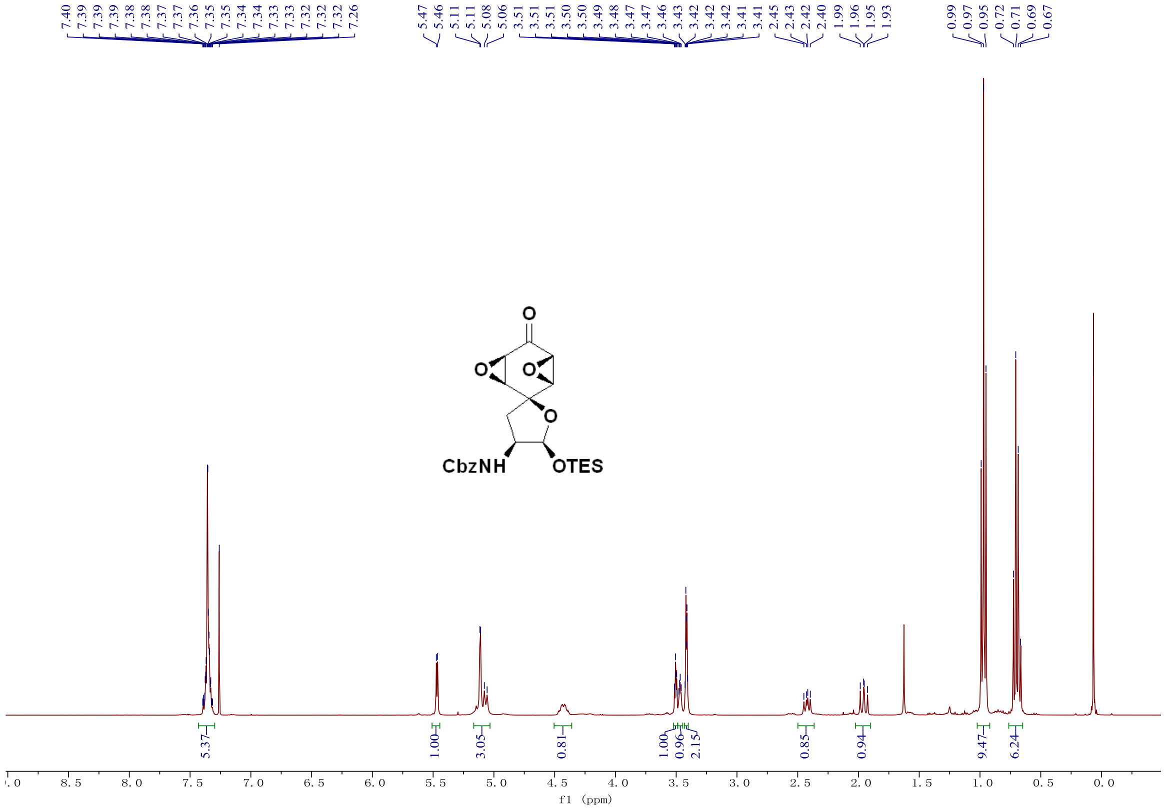

155.88
136.45
134.55
131.93
129.85
129.56
128.68
128.34
128.28
95.92
77.48
77.16
76.84
75.84
67.02
62.10
54.72
40.60
6.79
4.83
4.79
OH
O
CbzHN
OTES
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

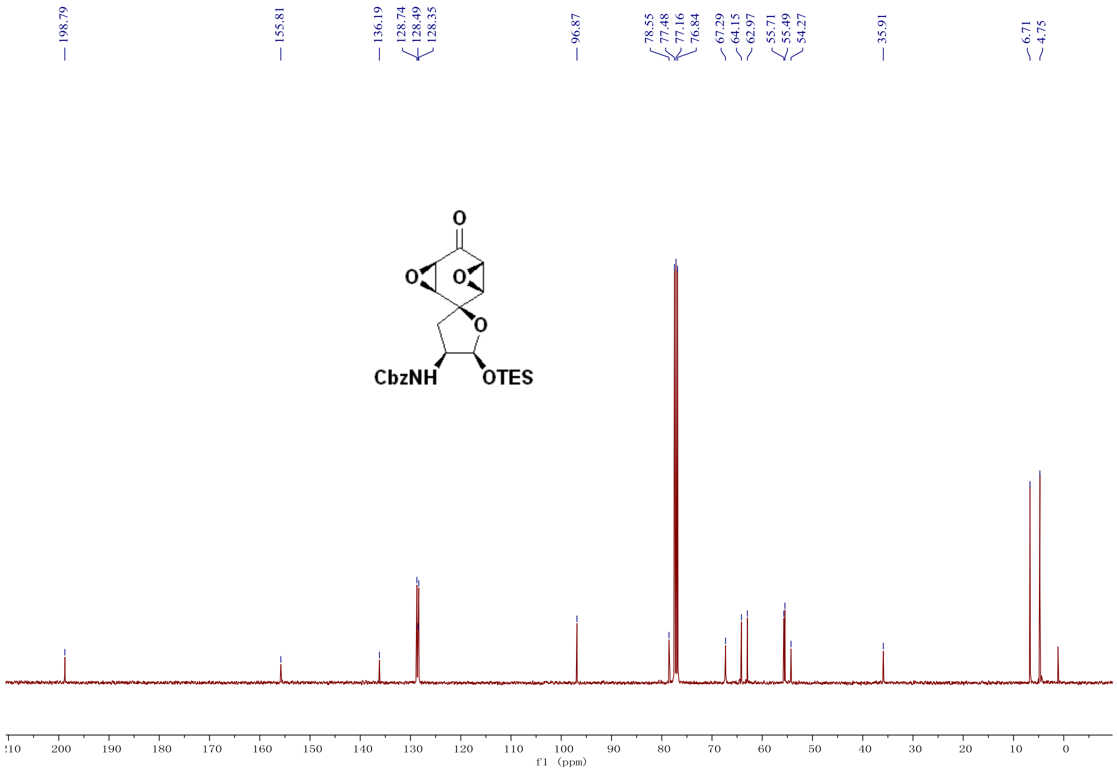
Compound **22**


7.40
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.26
5.44
5.44
5.43
5.15
5.12
5.12
5.11
5.10
5.08
4.41
4.39
4.22
4.20
4.19
3.43
3.42
3.41
3.40
3.27
3.27
3.26
3.24
3.23
2.49
2.46
2.37
2.35
2.34
2.32
1.91
1.88
1.85
0.98
0.96
0.94
0.72
0.70
0.68
0.66
OH
O
O
O
CbzNH
OTES
5.32
1.07
3.25
0.89
1.22
2.35
1.13
1.06
1.05
1.00
1.05
9.36
6.29
.0
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)

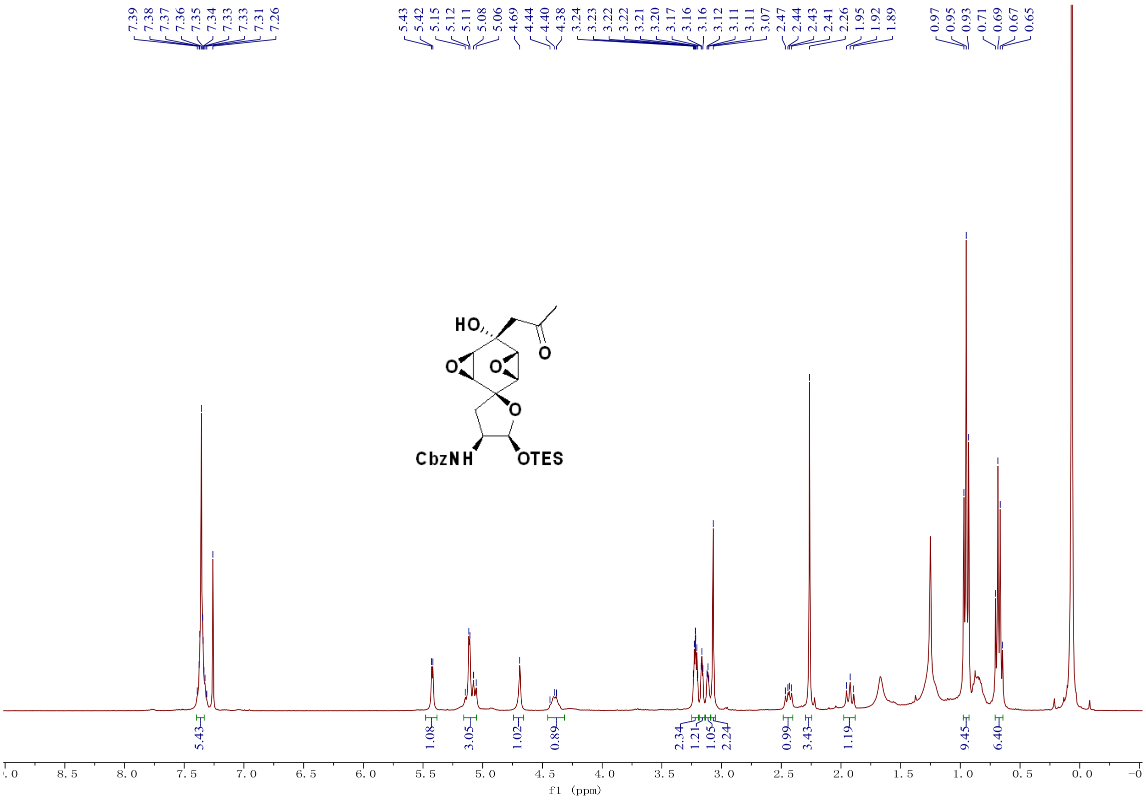

155.86
136.29
128.74
128.47
128.35
96.70
78.66
77.48
77.16
76.84
67.21
64.18
61.74
60.15
56.48
56.15
54.40
36.81
6.75
4.77
OH
O
O
O
CbzNH
OTES
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

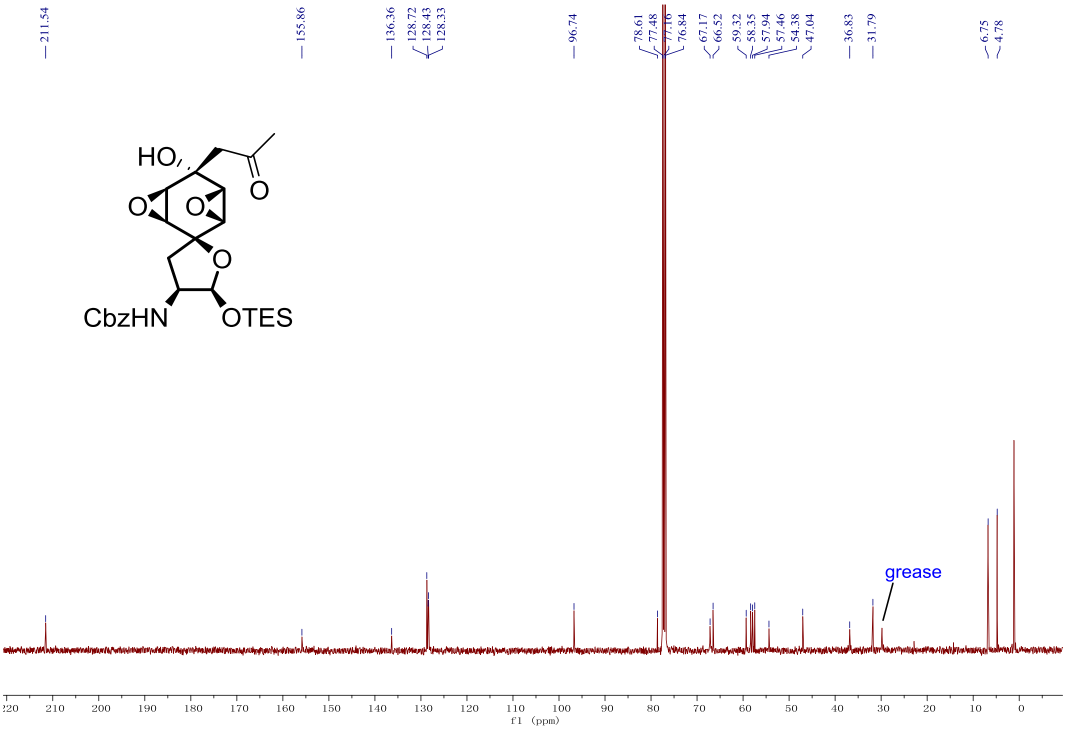
Compound **23**


7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.26
5.47
5.46
5.11
5.11
5.08
5.06
3.51
3.51
3.51
3.50
3.50
3.49
3.48
3.47
3.47
3.46
3.43
3.42
3.42
3.42
3.41
2.45
2.43
2.42
2.40
1.99
1.96
1.95
1.93
0.99
0.97
0.95
0.72
0.71
0.69
0.67
O
O
O
O
CbzNH
OTES
5.37
1.00
3.05
0.81
1.00
0.96
2.15
0.85
0.94
9.47
6.24
9.0
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)

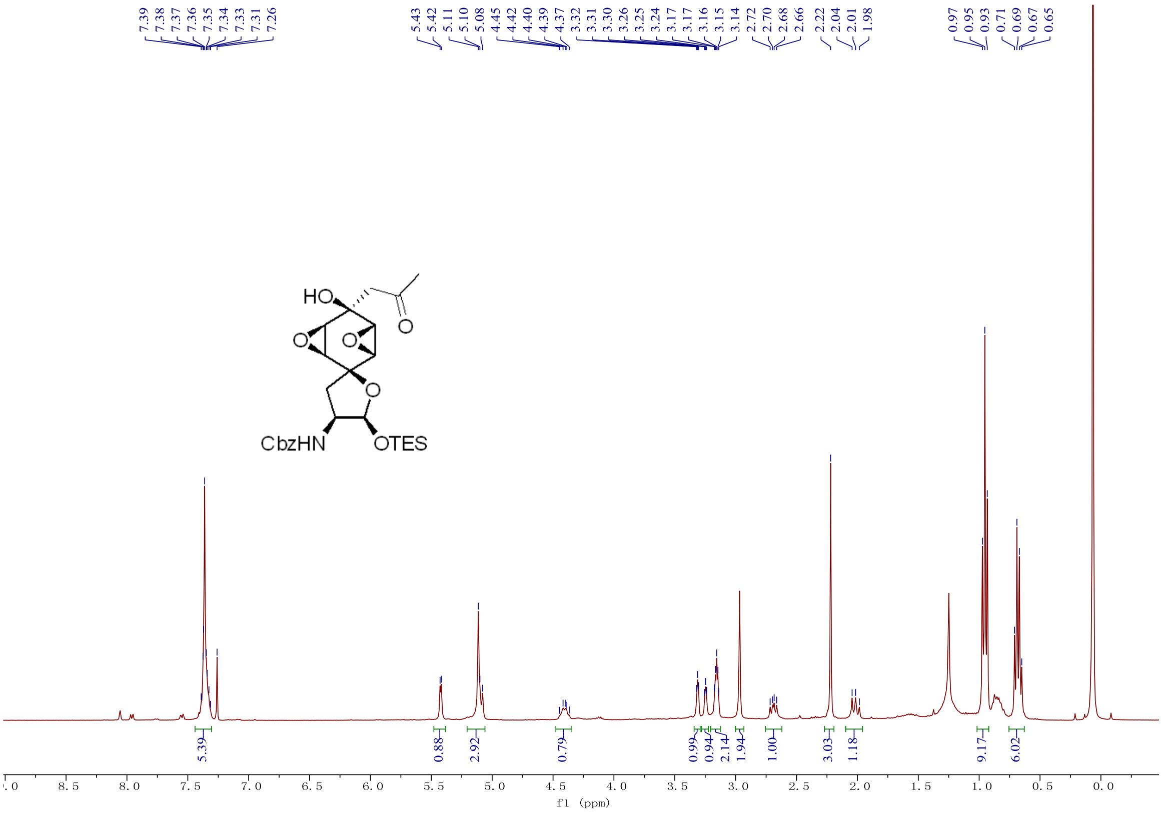

198.79
155.81
136.19
128.74
128.49
128.35
96.87
78.55
77.48
77.16
76.84
67.29
64.15
62.97
55.71
55.49
54.27
35.91
6.71
4.75
O
O
O
O
CbzNH
OTES
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

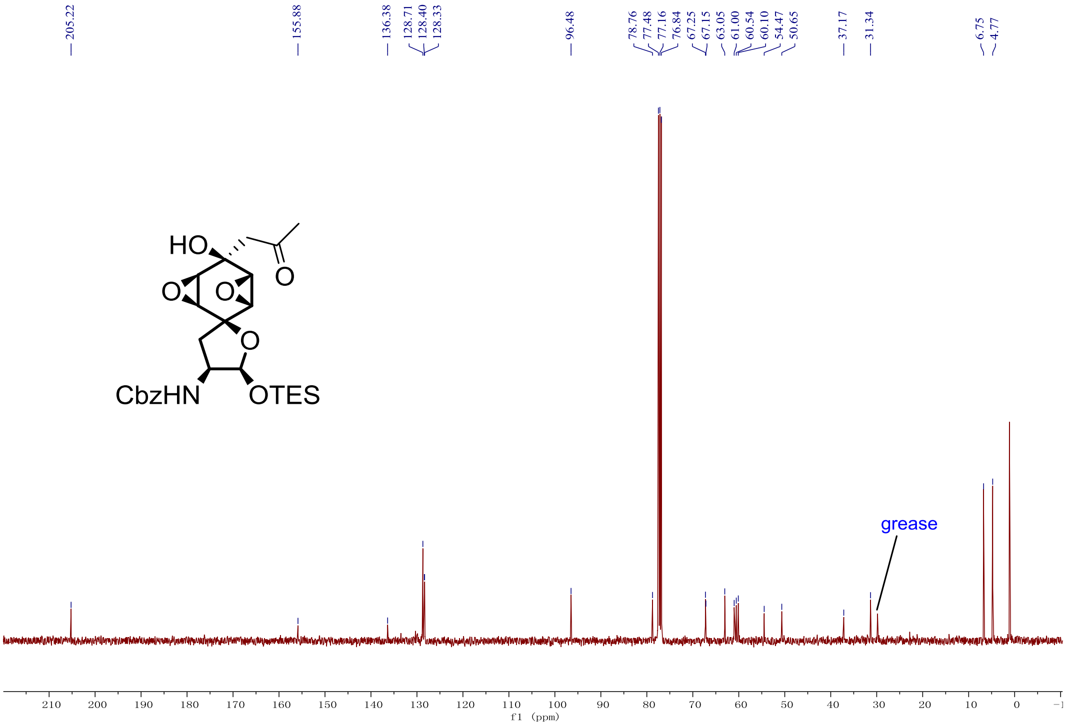
Compound **24**


7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.31
7.26
5.43
5.42
5.15
5.12
5.11
5.08
5.06
4.69
4.44
4.40
4.38
3.24
3.23
3.22
3.22
3.21
3.20
3.17
3.16
3.16
3.12
3.11
3.11
3.07
2.47
2.44
2.43
2.41
2.26
1.95
1.92
1.89
0.97
0.95
0.93
0.71
0.69
0.67
0.65
HO
O
O
O
CbzNH
OTES
5.43
1.08
3.05
1.02
0.89
2.34
1.21
1.05
2.24
0.99
3.43
1.19
9.45
6.40
9.0
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
-0
f1 (ppm)

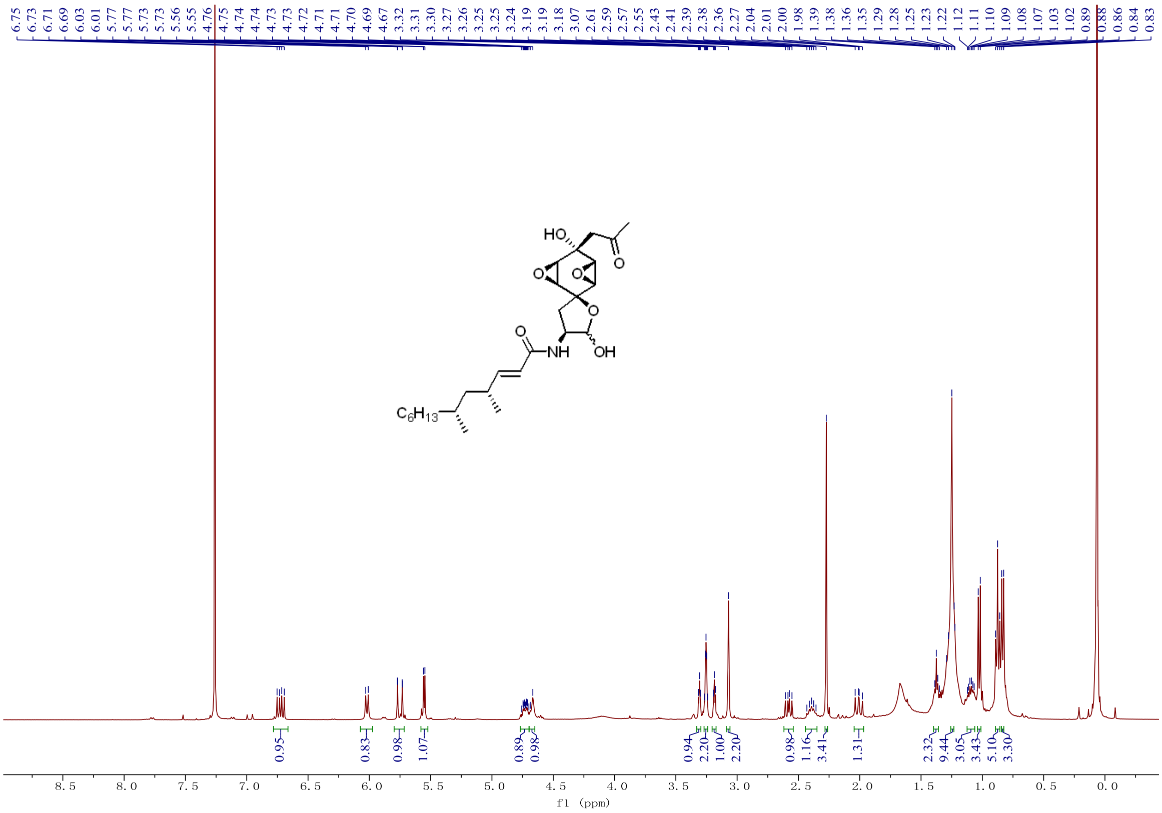

211.54
155.86
136.36
128.72
128.43
128.33
96.74
78.61
77.48
77.16
76.84
67.17
66.52
59.32
58.35
57.94
57.46
54.38
47.04
36.83
31.79
6.75
4.78
HO
O
O
O
CbzHN
OTES
grease
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

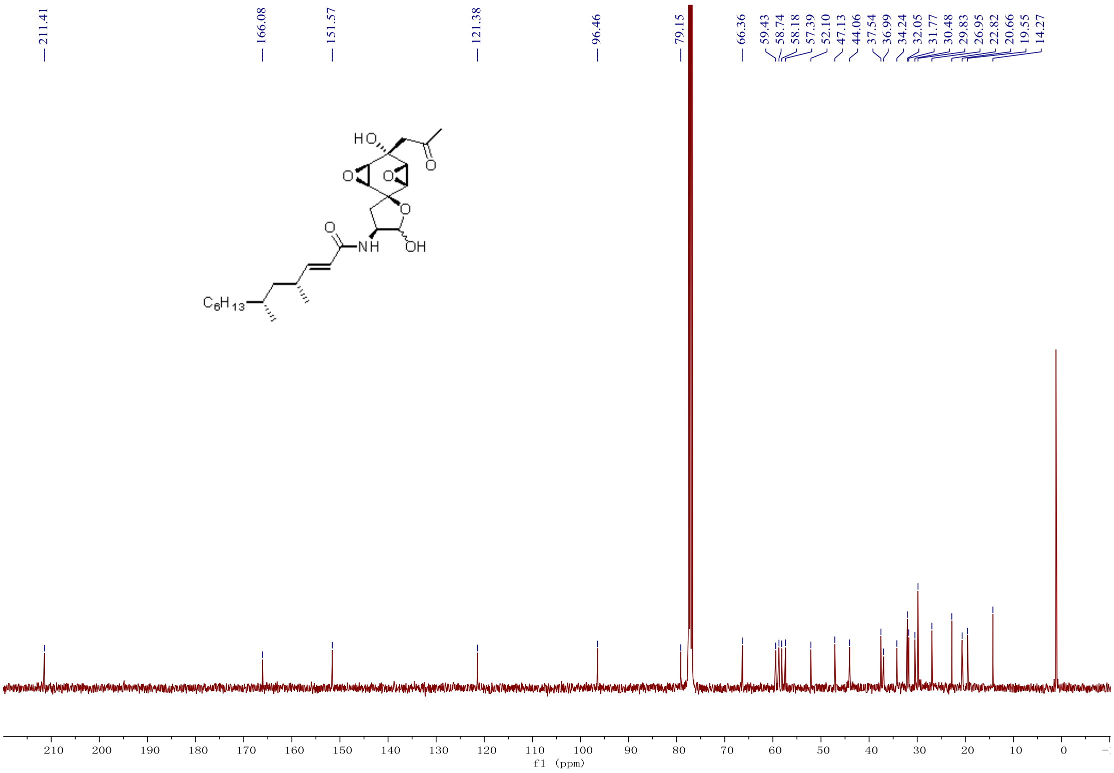
Compound **24’**


7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.31
7.26
5.43
5.42
5.11
5.10
5.08
4.45
4.42
4.40
4.39
4.37
3.32
3.31
3.30
3.26
3.25
3.24
3.17
3.17
3.16
3.15
3.14
2.72
2.70
2.68
2.66
2.22
2.04
2.01
1.98
0.97
0.95
0.93
0.71
0.69
0.67
0.65
HO
O
O
O
CbzHN
OTES
5.39
0.88
2.92
0.79
0.99
0.94
2.14
1.94
1.00
3.03
1.18
9.17
6.02
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)

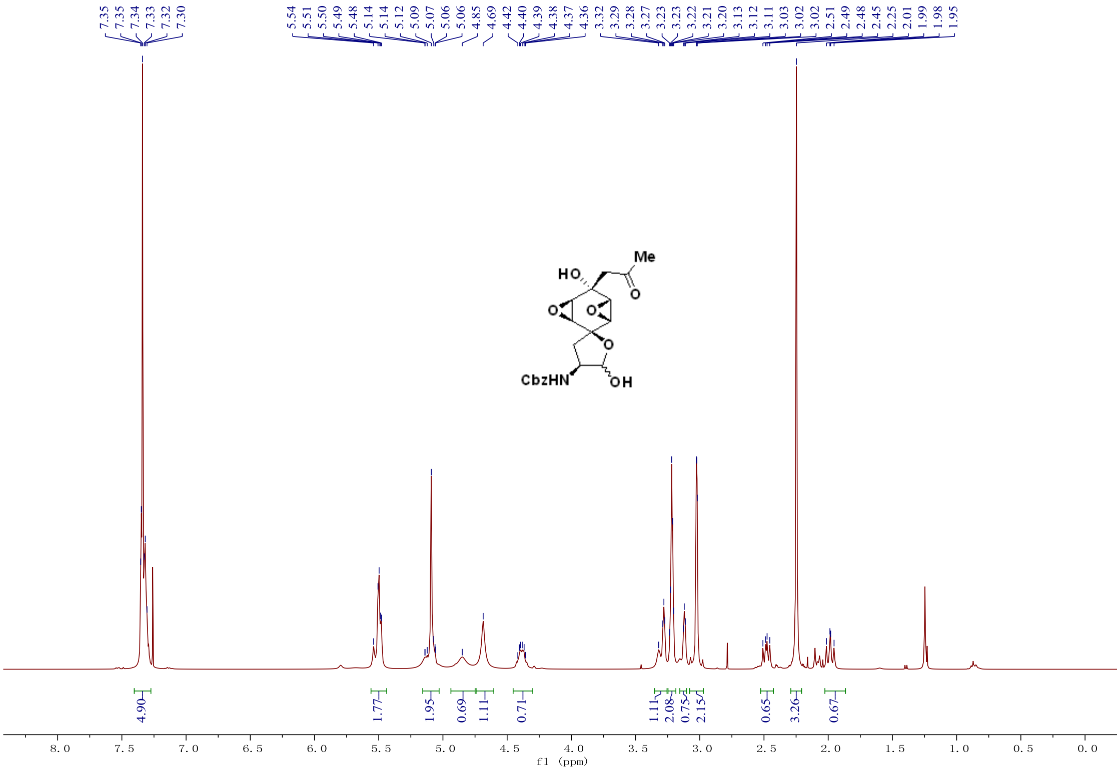

205.22
155.88
136.38
128.71
128.40
128.33
96.48
78.76
77.48
77.16
76.84
67.25
67.15
63.05
61.00
60.54
60.10
54.47
50.65
37.17
31.34
6.75
4.77
HO
O
O
O
CbzHN
OTES
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

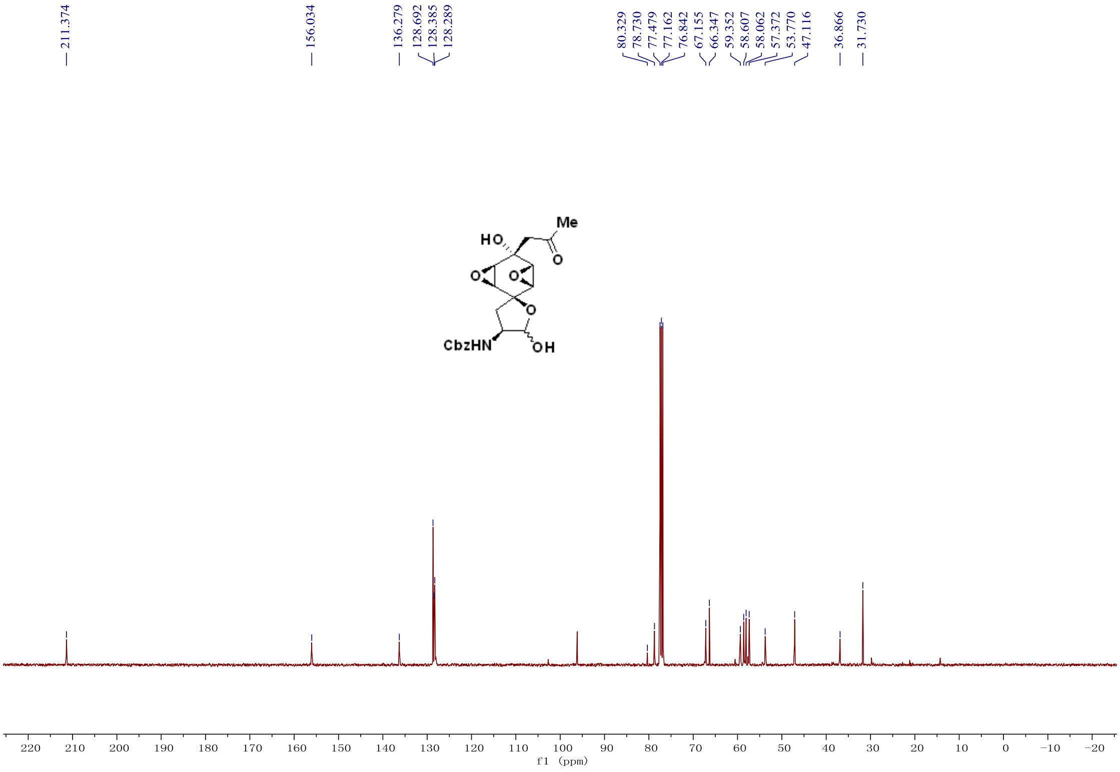
Compound **3**


6.75
6.73
6.71
6.69
6.03
6.01
5.77
5.77
5.73
5.73
5.56
5.55
4.76
4.75
4.74
4.74
4.73
4.73
4.72
4.71
4.71
4.70
4.69
4.67
3.32
3.31
3.30
3.27
3.26
3.25
3.25
3.24
3.19
3.19
3.18
3.07
2.61
2.59
2.57
2.55
2.43
2.41
2.39
2.38
2.36
2.27
2.04
2.01
2.00
1.98
1.39
1.38
1.36
1.35
1.29
1.28
1.25
1.23
1.22
1.12
1.11
1.10
1.09
1.08
1.07
1.03
1.02
0.89
0.88
0.86
0.84
0.83
HO
O
O
O
O
NH
OH
C6H13
0.95
0.83
0.98
1.07
0.89
0.98
0.94
2.20
1.00
2.20
0.98
1.16
3.41
1.31
2.32
9.44
3.05
3.43
5.10
3.30
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)

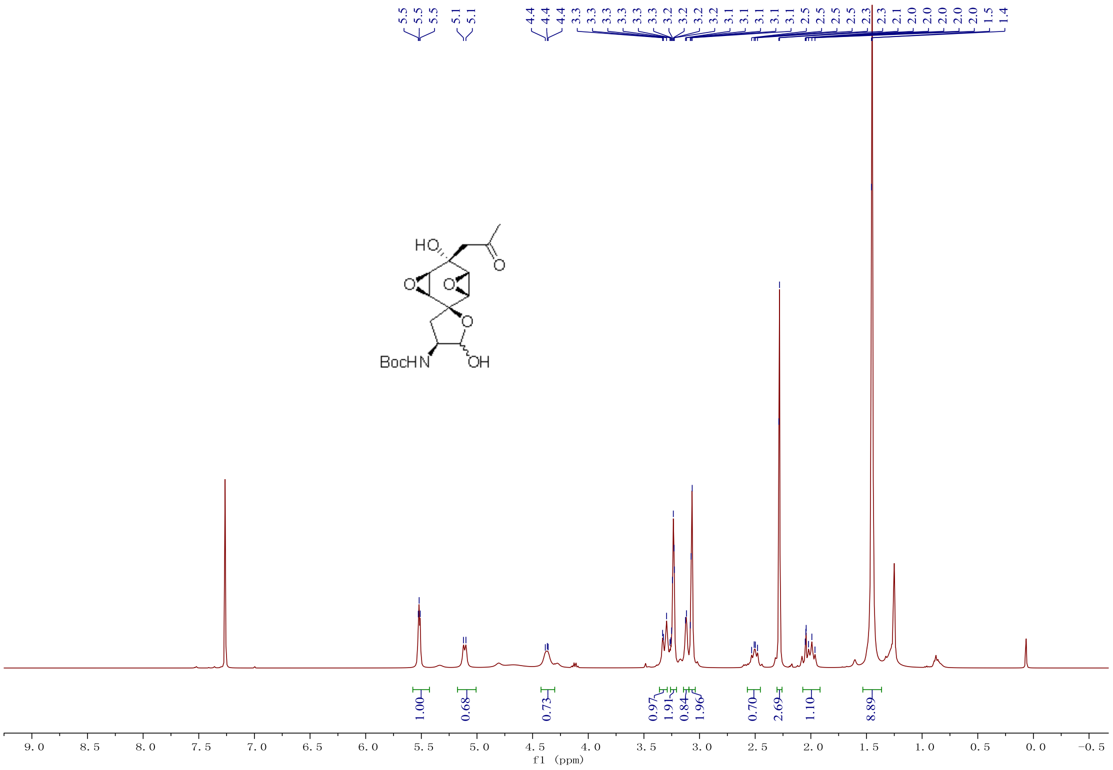

211.41
166.08
151.57
121.38
96.46
79.15
66.36
59.43
58.74
58.18
57.39
52.10
47.13
44.06
37.54
36.99
34.24
32.05
31.77
30.48
29.83
26.95
22.82
20.66
19.55
14.27
HO
O
O
O
O
NH
OH
C6H13
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

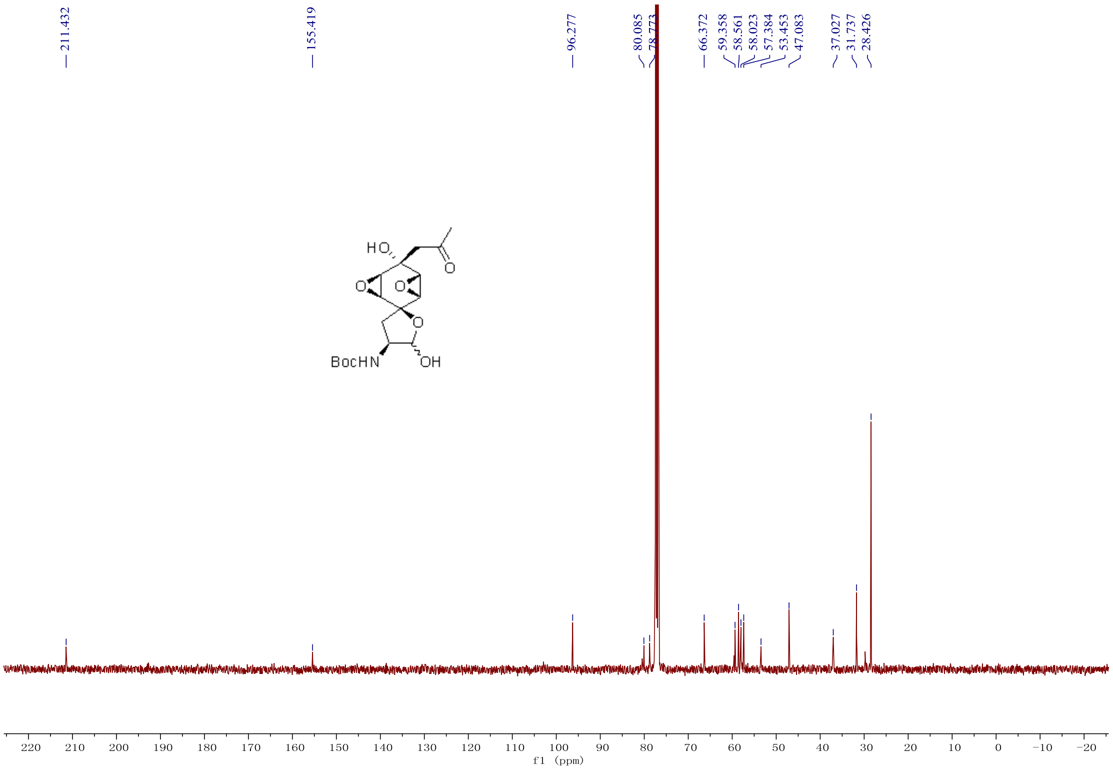
Compound **26**


7.35
7.35
7.34
7.33
7.32
7.30
5.54
5.51
5.50
5.49
5.48
5.14
5.14
5.12
5.09
5.07
5.06
5.06
4.85
4.69
4.42
4.40
4.39
4.38
4.37
4.36
3.32
3.29
3.28
3.27
3.23
3.23
3.22
3.21
3.20
3.13
3.12
3.11
3.03
3.02
3.02
2.51
2.49
2.48
2.45
2.25
2.01
1.99
1.98
1.95
Me
HO
O
O
O
CbzHN
OH
4.90
1.77
1.95
0.69
1.11
0.71
1.11
2.08
0.75
2.15
0.65
3.26
0.67
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)

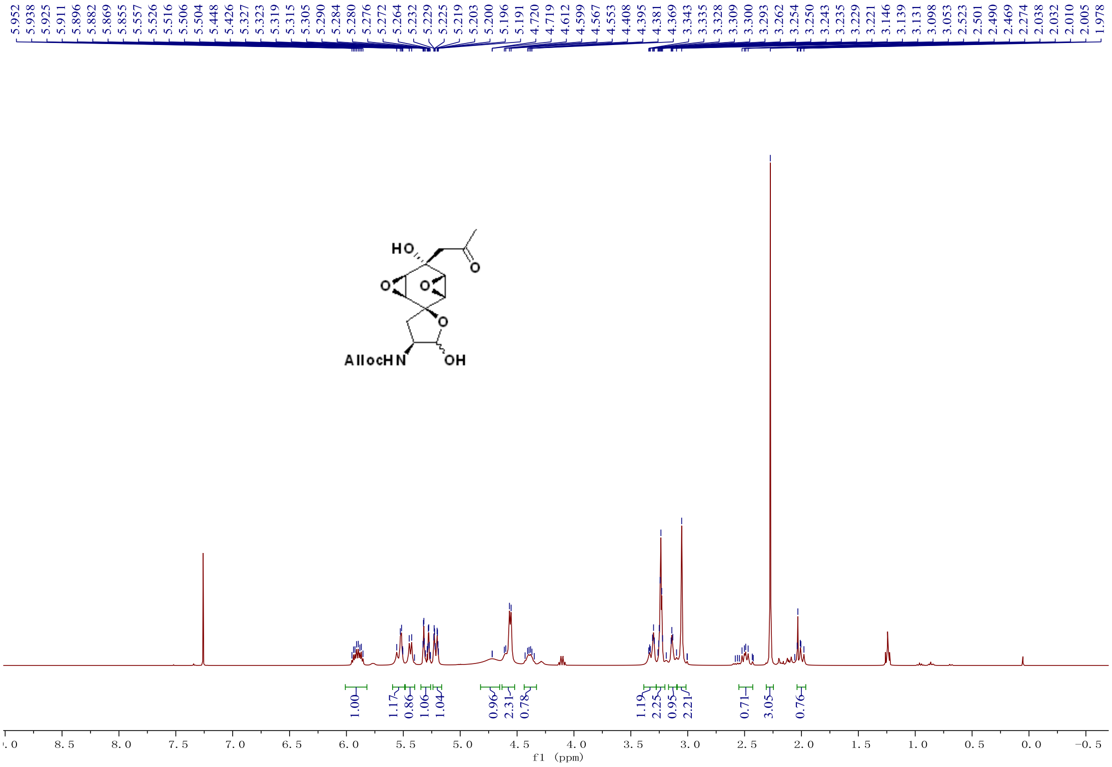

211.374
156.034
136.279
128.692
128.385
128.289
80.329
78.730
77.479
77.162
76.842
67.155
66.347
59.352
58.607
58.062
57.372
53.770
47.116
36.866
31.730
Me
HO
O
O
O
CbzHN
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

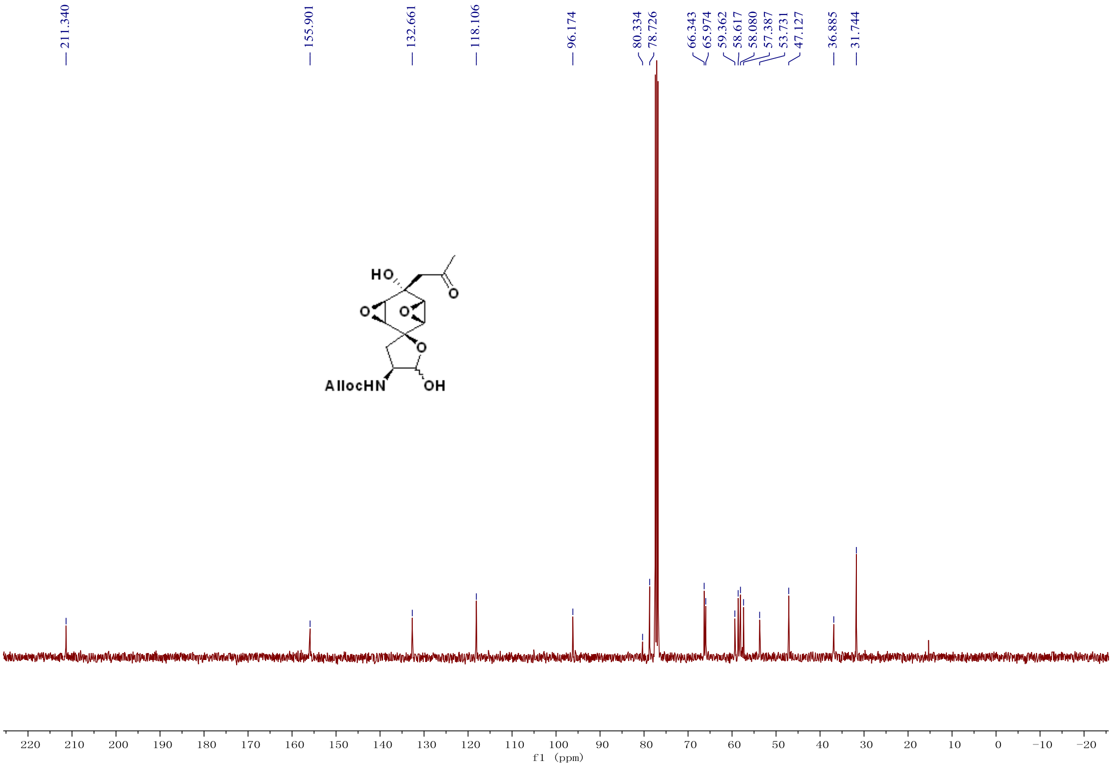
Compound **27**


5.5
5.5
5.5
5.1
5.1
4.4
4.4
4.4
3.3
3.3
3.3
3.3
3.3
3.3
3.2
3.2
3.2
3.2
3.1
3.1
3.1
3.1
3.1
2.5
2.5
2.5
2.5
2.3
2.3
2.1
2.0
2.0
2.0
2.0
2.0
1.5
1.4
HO
O
O
O
BocHN
OH
1.00
0.68
0.73
0.97
1.91
0.84
1.96
0.70
2.69
1.10
8.89
9.0
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
-0.5
f1 (ppm)

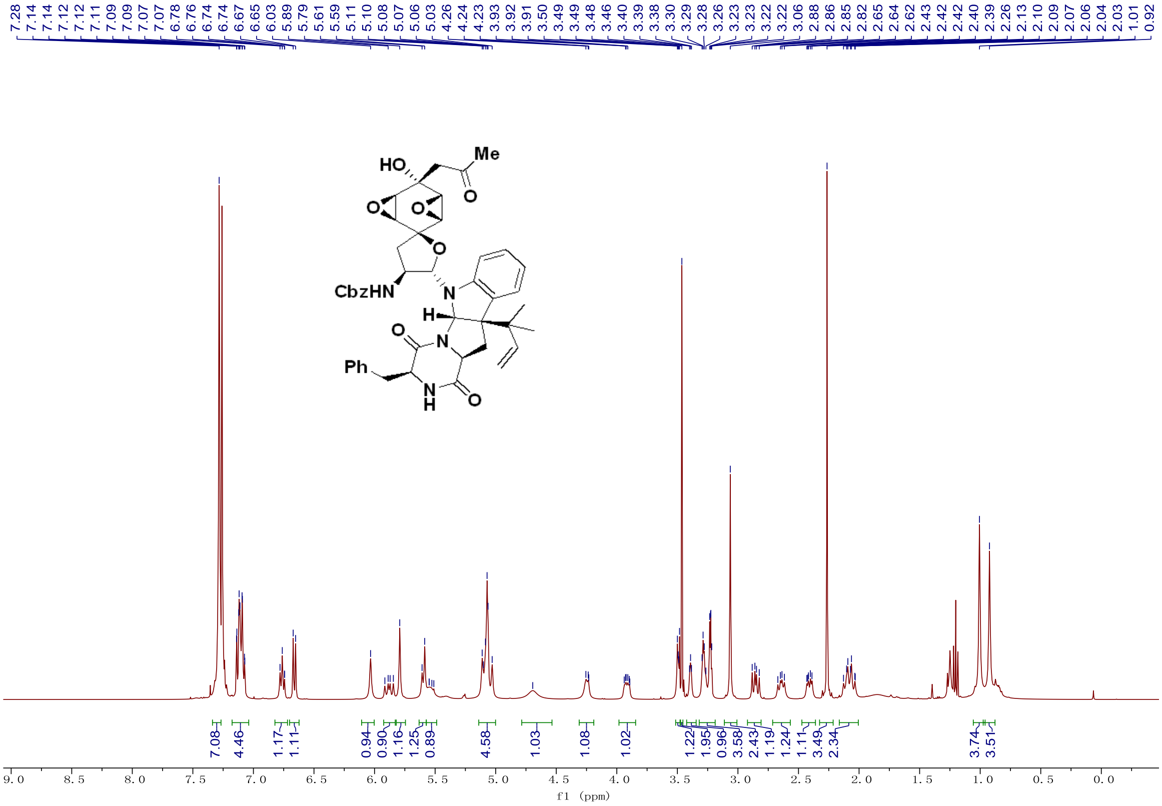

211.432
155.419
96.277
80.085
78.773
66.372
59.358
58.561
58.023
57.384
53.453
47.083
37.027
31.737
28.426
HO
O
O
O
BocHN
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

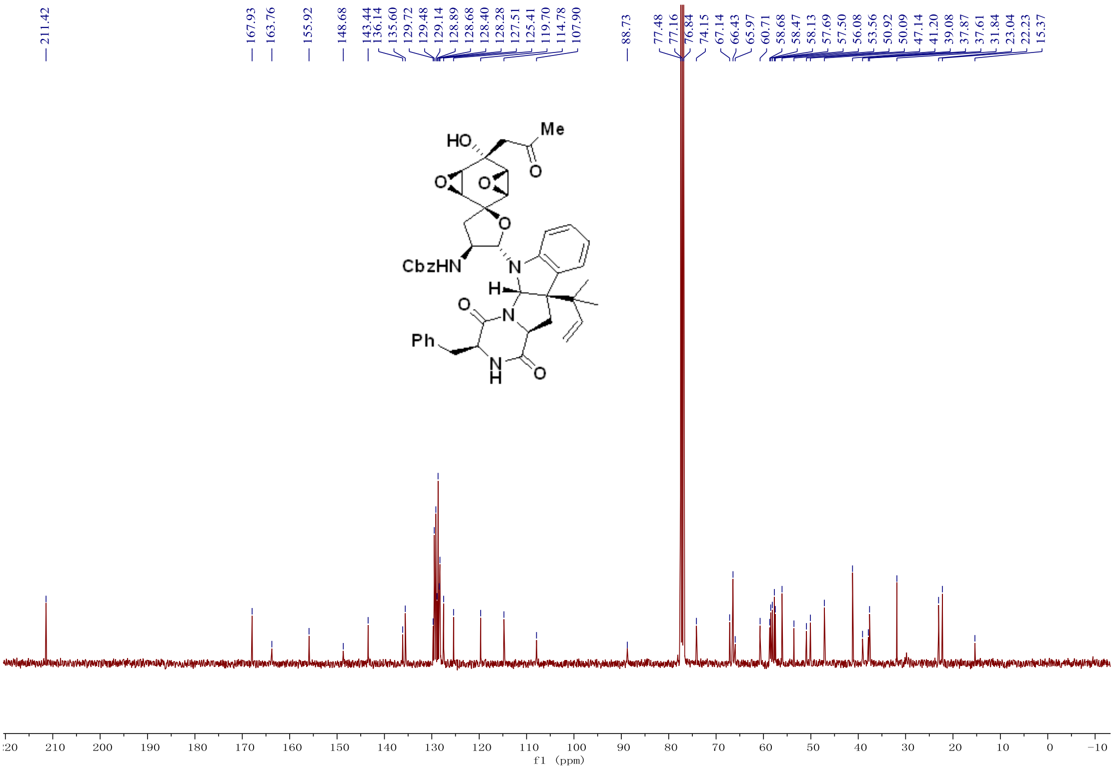
Compound **28**


5.952
5.938
5.925
5.911
5.896
5.882
5.869
5.855
5.557
5.526
5.516
5.506
5.504
5.448
5.426
5.327
5.323
5.319
5.315
5.305
5.290
5.284
5.280
5.276
5.272
5.264
5.232
5.229
5.225
5.219
5.203
5.200
5.196
5.191
4.720
4.719
4.612
4.599
4.567
4.553
4.408
4.395
4.381
4.369
3.343
3.335
3.328
3.309
3.300
3.293
3.262
3.254
3.250
3.243
3.235
3.229
3.221
3.146
3.139
3.131
3.098
3.053
2.523
2.501
2.490
2.469
2.274
2.038
2.032
2.010
2.005
1.978
HO
O
O
O
AllocHN
OH
1.00
1.17
0.86
1.06
1.04
0.96
2.31
0.78
1.19
2.25
0.95
2.21
0.71
3.05
0.76
. 0
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
−0.5
f1 (ppm)

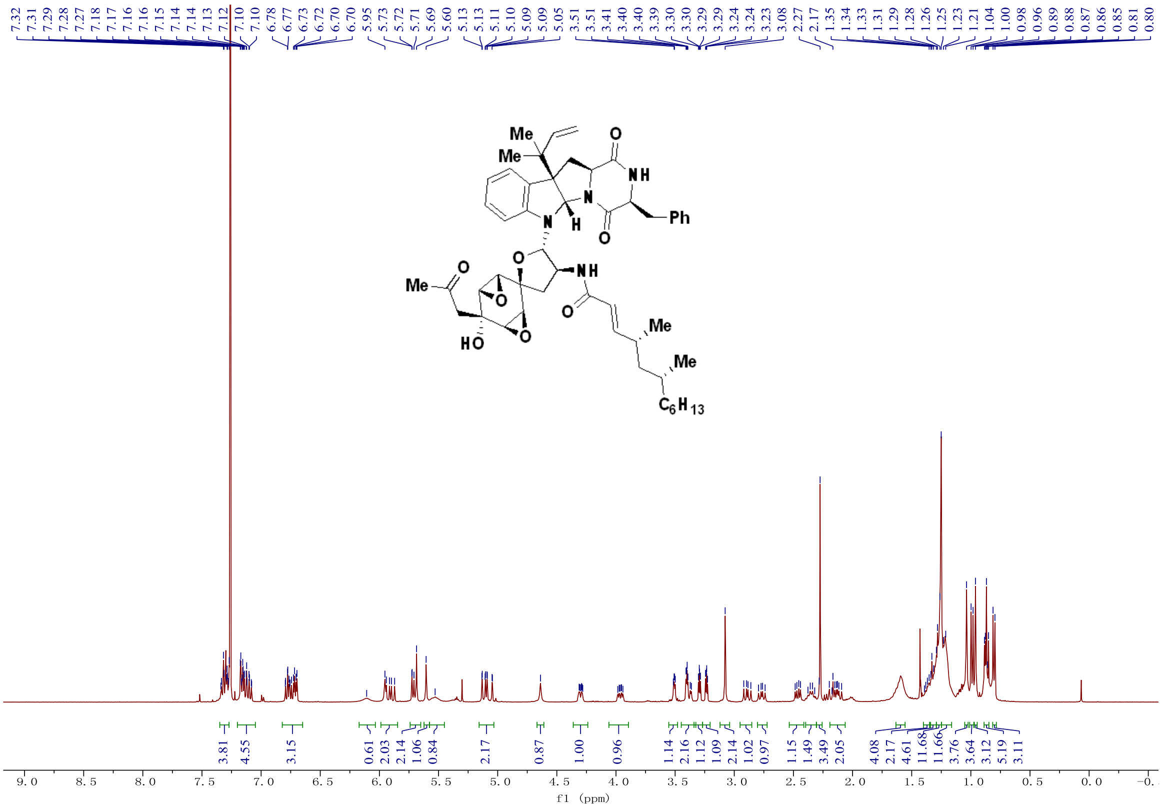

211.340
155.901
132.661
118.106
96.174
80.334
78.726
66.343
65.974
59.362
58.617
58.080
57.387
53.731
47.127
36.885
31.744
HO
O
O
O
AllocHN
OH
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

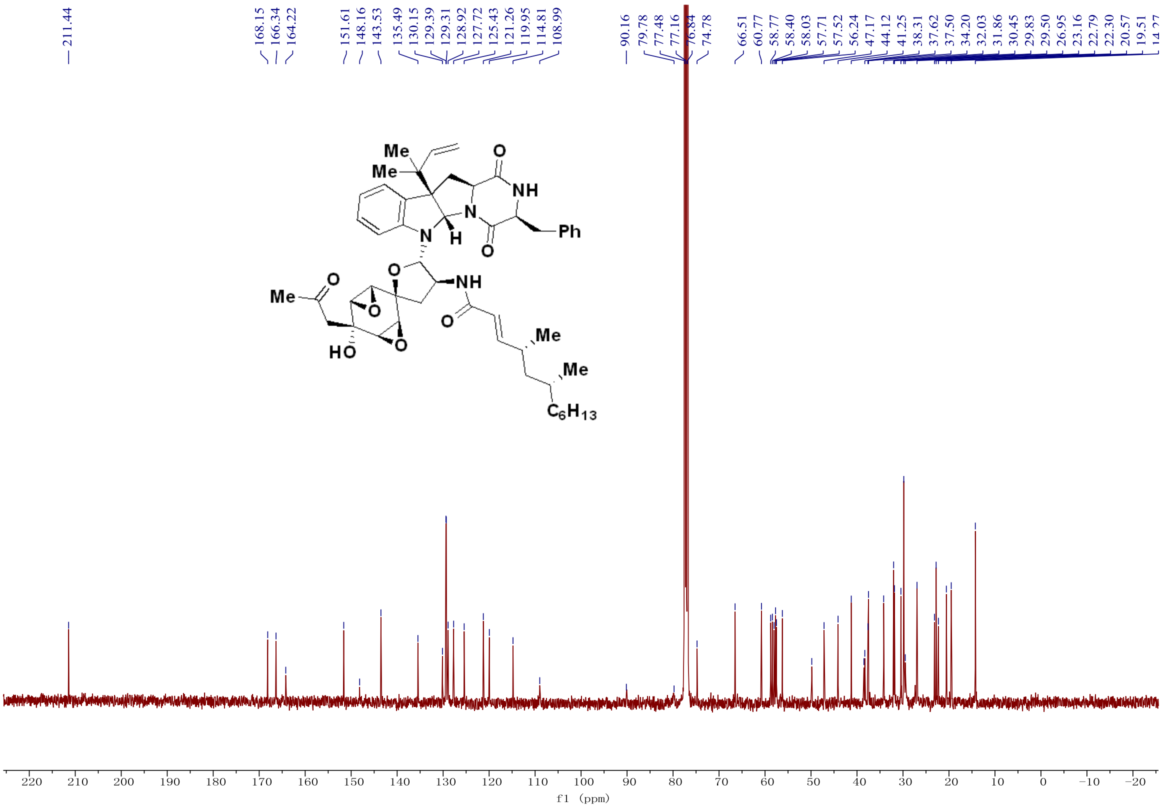
Compound **29**


7.28
7.14
7.14
7.12
7.12
7.11
7.09
7.09
7.07
7.07
6.78
6.76
6.74
6.74
6.67
6.65
6.03
5.89
5.79
5.61
5.59
5.11
5.10
5.08
5.07
5.06
5.03
4.26
4.24
4.23
3.93
3.92
3.91
3.50
3.49
3.49
3.48
3.46
3.40
3.39
3.38
3.30
3.29
3.28
3.26
3.23
3.23
3.22
3.22
3.06
2.88
2.86
2.85
2.82
2.65
2.64
2.62
2.43
2.42
2.42
2.40
2.39
2.26
2.13
2.10
2.09
2.07
2.06
2.04
2.03
1.01
0.92
HO
Me
O
O
O
O
CbzHN
N
H
N
O
Ph
N
H
O
7.08
4.46
1.17
1.11
0.94
0.90
1.16
1.25
0.89
4.58
1.03
1.08
1.02
1.22
1.95
0.96
3.58
2.43
1.19
1.24
1.11
3.49
2.34
3.74
3.51
9.0
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)

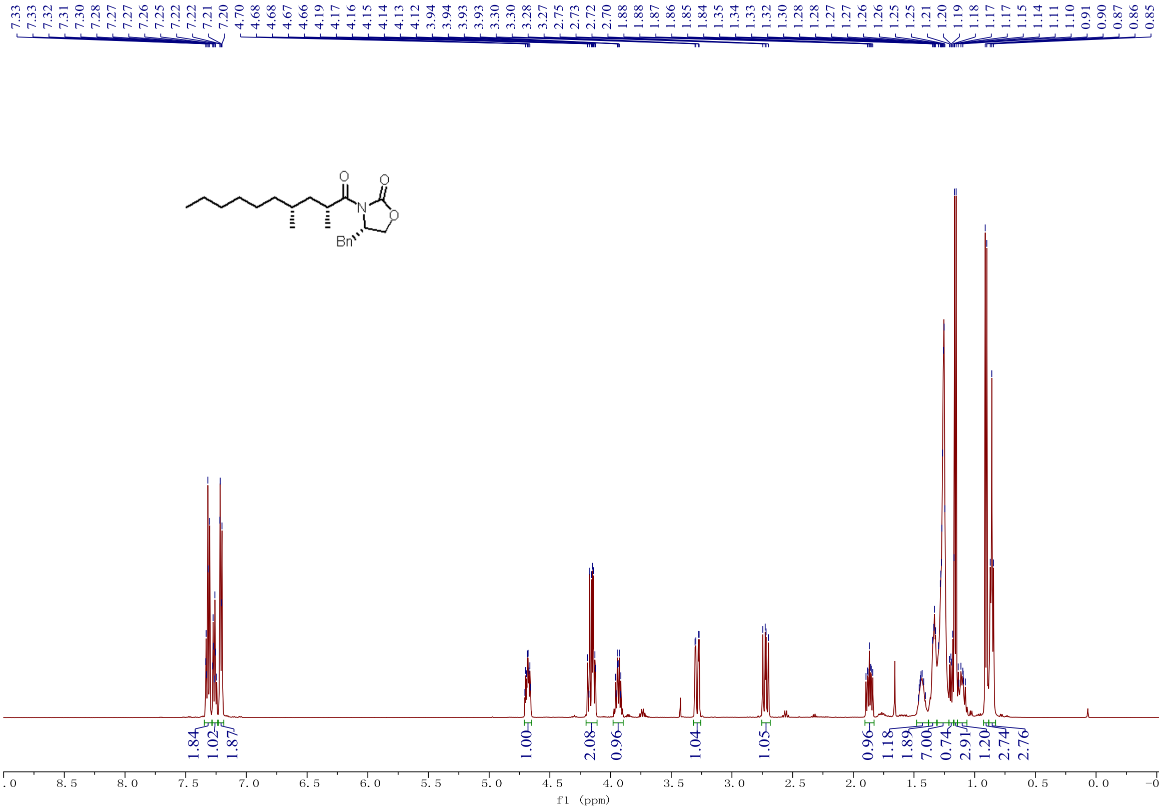

211.42
167.93
163.76
155.92
148.68
143.44
136.14
135.60
129.72
129.48
129.14
128.89
128.68
128.40
128.28
127.51
125.41
119.70
114.78
107.90
88.73
77.48
77.16
76.84
74.15
67.14
66.43
65.97
60.71
58.68
58.47
58.13
57.69
57.50
56.08
53.56
50.92
50.09
47.14
41.20
39.08
37.87
37.61
31.84
23.04
22.23
15.37
HO
Me
O
O
O
O
CbzHN
N
H
O
N
Ph
N
H
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

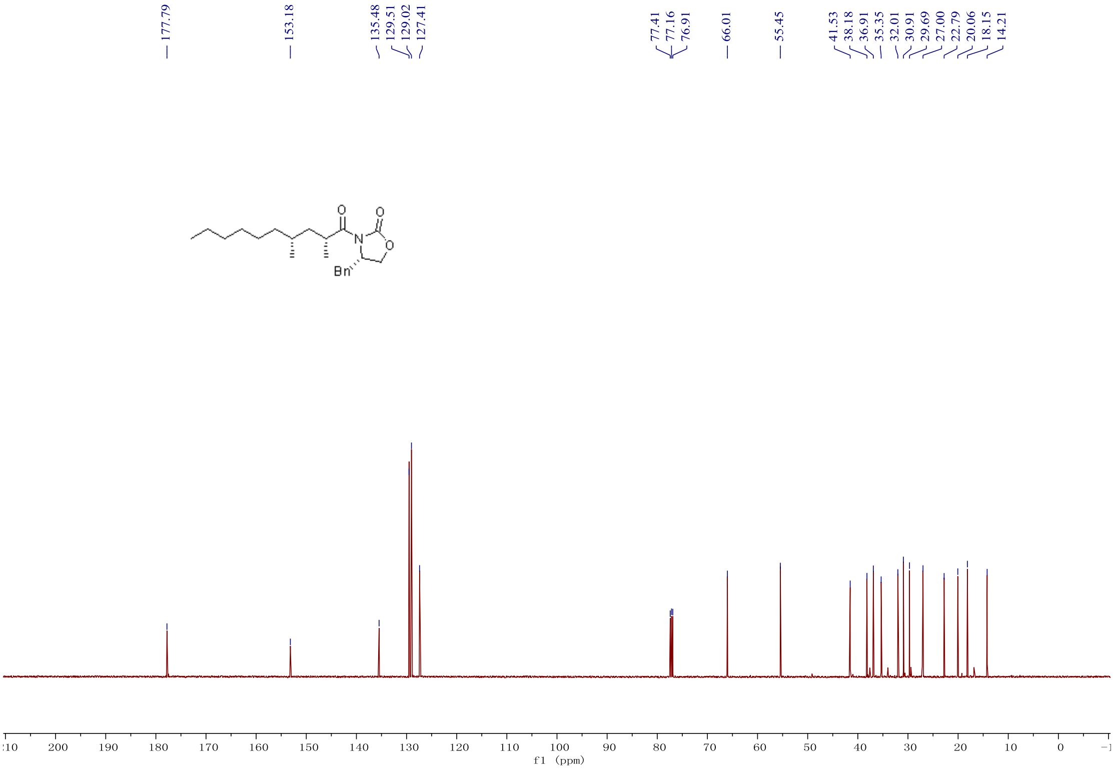
Compound **1**


7.32
7.31
7.29
7.28
7.27
7.18
7.17
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.10
7.10
6.78
6.77
6.73
6.72
6.72
6.70
5.95
5.73
5.72
5.71
5.69
5.60
5.13
5.13
5.11
5.10
5.09
5.09
5.05
3.51
3.51
3.41
3.40
3.40
3.39
3.30
3.30
3.29
3.29
3.24
3.24
3.23
3.08
2.27
2.17
1.35
1.34
1.33
1.31
1.29
1.28
1.26
1.25
1.23
1.21
1.04
1.00
0.98
0.96
0.89
0.88
0.87
0.86
0.85
0.81
0.80
Me
Me
O
NH
N
N
H
Ph
O
O
NH
Me
O
O
O
HO
O
Me
Me
C6H13
3.81
4.55
3.15
0.61
2.03
2.14
1.06
0.84
2.17
0.87
1.00
0.96
1.14
2.16
1.12
1.09
2.14
1.02
0.97
1.15
1.49
3.49
2.05
4.08
2.17
4.61
11.68
11.66
3.76
3.64
3.12
5.19
3.11
9.0
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
-0.
f1 (ppm)

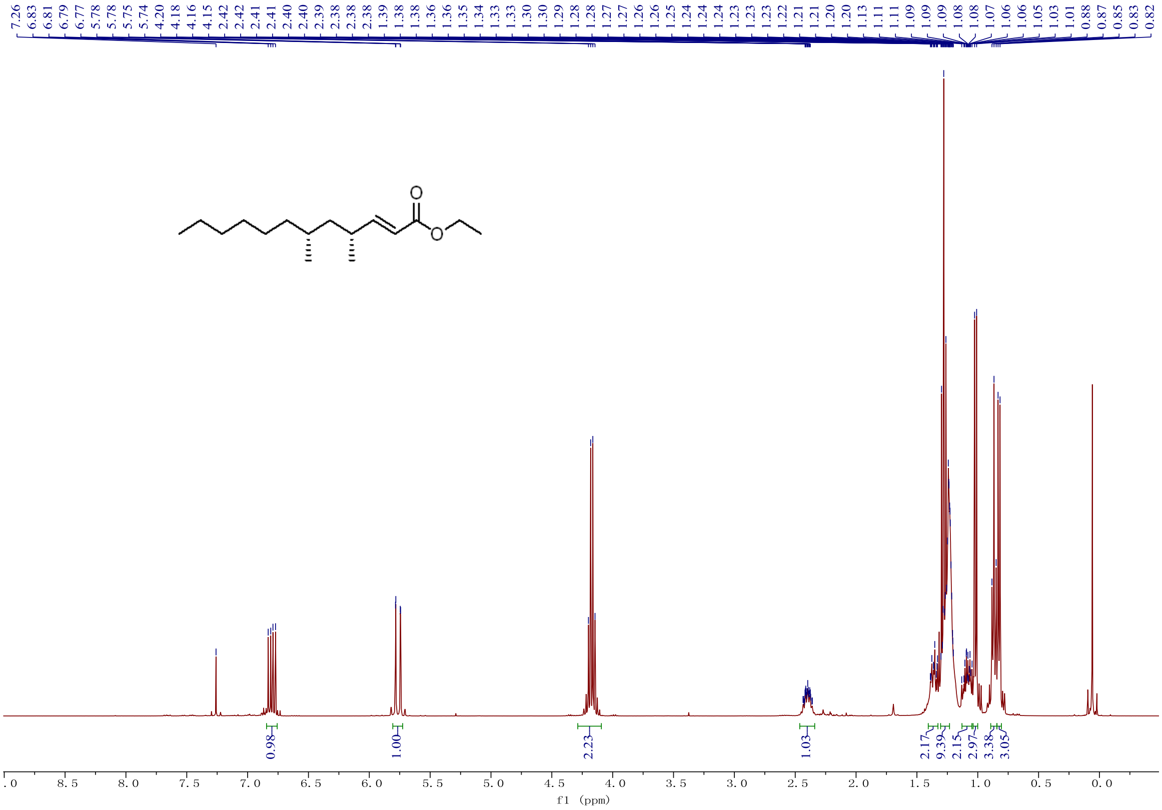

211.44
168.15
166.34
164.22
151.61
148.16
143.53
135.49
130.15
129.39
129.31
128.92
127.72
125.43
121.26
119.95
114.81
108.99
90.16
79.78
77.48
77.16
76.84
74.78
66.51
60.77
58.77
58.40
58.03
57.71
57.52
56.24
47.17
44.12
41.25
38.31
37.62
37.50
34.20
32.03
31.86
30.45
29.83
29.50
26.95
23.16
22.79
22.30
20.57
19.51
14.27
Me
Me
O
NH
N
N
H
Ph
O
O
NH
Me
O
O
O
HO
O
Me
Me
C6H13
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

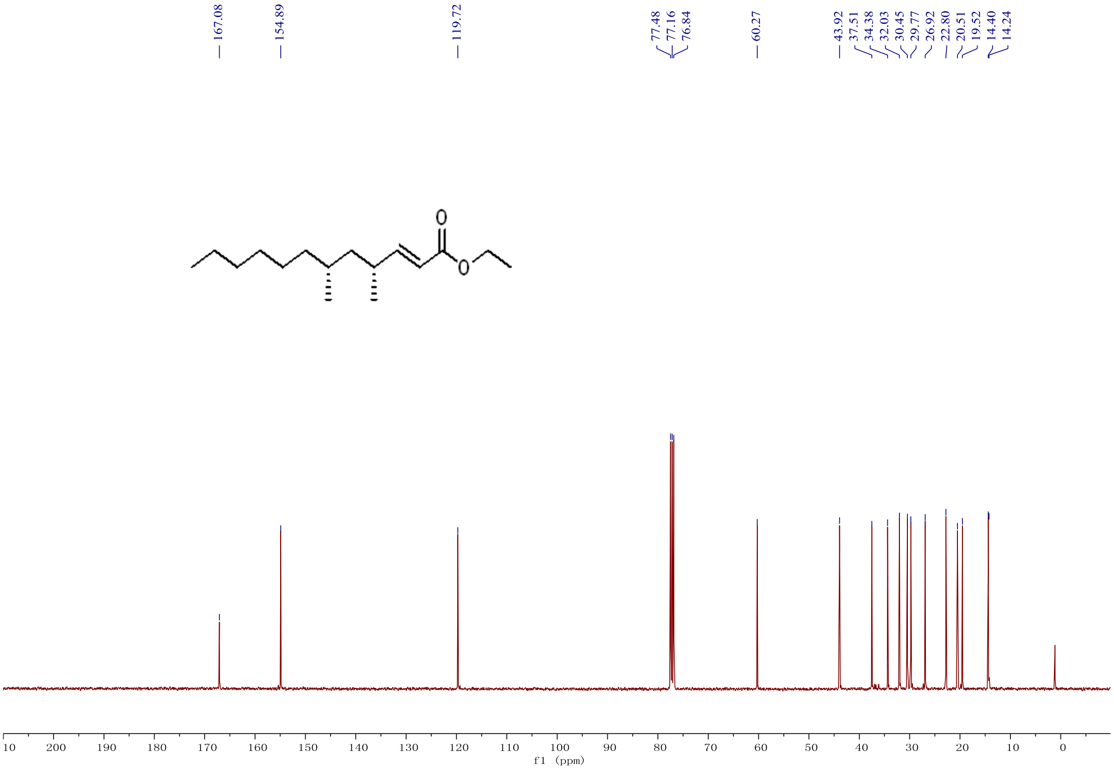
Compound **S3**


7.33
7.33
7.32
7.31
7.30
7.28
7.27
7.27
7.26
7.25
7.22
7.22
7.21
7.20
4.70
4.68
4.68
4.67
4.66
4.19
4.17
4.16
4.15
4.14
4.13
4.12
3.94
3.94
3.93
3.93
3.30
3.28
3.27
2.75
2.73
2.72
2.70
1.88
1.88
1.87
1.86
1.85
1.84
1.35
1.34
1.33
1.32
1.30
1.28
1.28
1.27
1.27
1.26
1.26
1.25
1.25
1.21
1.20
1.19
1.18
1.17
1.17
1.15
1.14
1.11
1.10
0.91
0.90
0.87
0.86
0.85
O
O
N
O
Bn
1.84
1.02
1.87
1.00
2.08
0.96
1.04
1.05
0.96
1.18
1.89
7.00
0.74
2.91
1.20
2.74
2.76
.0
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
-0
f1 (ppm)

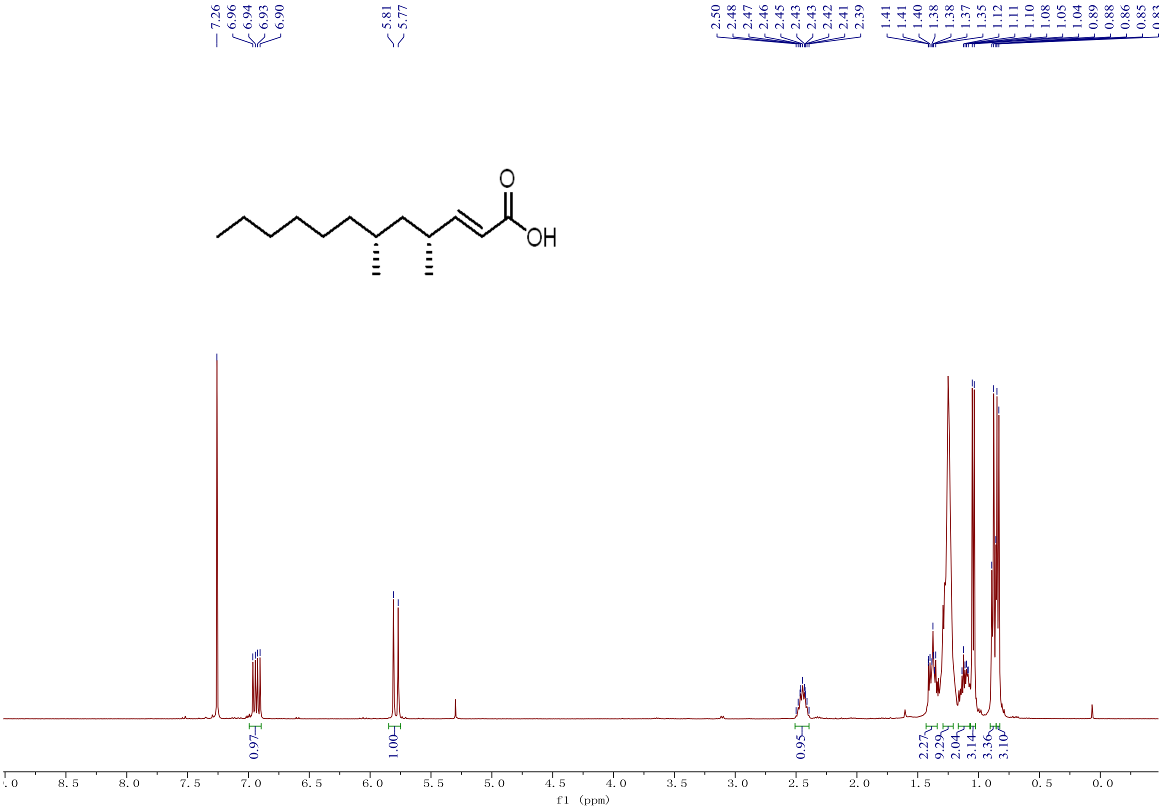

177.79
153.18
135.48
129.51
129.02
127.41
77.41
77.16
76.91
66.01
55.45
41.53
38.18
36.91
35.35
32.01
30.91
29.69
27.00
22.79
20.06
18.15
14.21
O
O
N
O
Bn
:10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

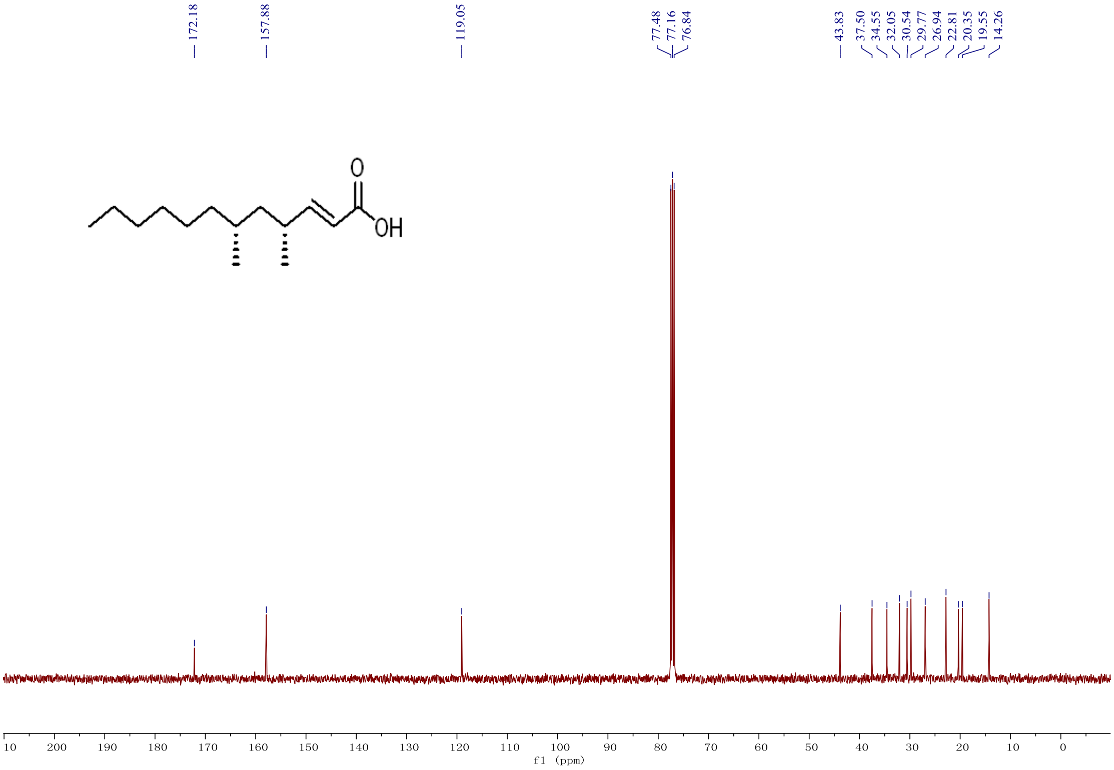
Compound **S8**


7.26
6.83
6.81
6.79
6.77
5.78
5.78
5.75
5.74
4.20
4.18
4.16
4.15
2.42
2.42
2.41
2.41
2.40
2.40
2.39
2.38
2.38
2.38
1.39
1.38
1.38
1.36
1.36
1.35
1.34
1.33
1.33
1.30
1.30
1.29
1.28
1.28
1.27
1.27
1.26
1.26
1.25
1.24
1.24
1.24
1.23
1.23
1.23
1.22
1.21
1.21
1.20
1.20
1.13
1.11
1.11
1.09
1.09
1.09
1.08
1.08
1.07
1.06
1.05
1.03
1.01
0.88
0.87
0.85
0.83
0.82
O
O
0.98
1.00
2.23
1.03
2.17
9.39
2.15
2.97
3.38
3.05
9.0
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)


167.08
154.89
119.72
77.48
77.16
76.84
60.27
43.92
37.51
34.38
32.03
30.45
29.77
26.92
22.80
20.51
19.52
14.40
14.24
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound **25**


7.26
6.96
6.94
6.93
6.90
5.81
5.77
2.50
2.48
2.47
2.46
2.45
2.43
2.43
2.42
2.41
2.39
1.41
1.41
1.40
1.38
1.38
1.37
1.35
1.12
1.11
1.10
1.08
1.05
1.04
0.89
0.88
0.86
0.85
0.83
O
OH
0.97
1.00
0.95
2.27
9.29
2.04
3.14
3.36
3.10
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)


172.18
157.88
119.05
77.48
77.16
76.84
43.83
37.50
34.55
32.05
30.54
29.77
26.94
22.81
20.35
19.55
14.26
O
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)