# Design, Synthesis, and Biological Activities of Vibsanin B Derivatives: A New Class of HSP90 C-terminal Inhibitors

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**Table S1. Antiproliferative Activity of Compounds 6 – 10 and ViB-4-OH ($IC_{50}$, $\mu$M)**

| Compd. | MCF-7 | SMMC-7721 | A-549 | HL-60 | SW480 |
|---|---|---|---|---|---|
| **6** | 2.85 ± 0.03 | 3.25 ± 0.14 | 3.46 ± 0.21 | 2.64 ± 0.06 | 2.65 ± 0.17 |
| **7** | 0.24 ± 0.01 | 0.21 ± 0.01 | 0.14 ± 0.01 | 0.62 ± 0.01 | - |
| **8** | 4.51 ± 0.09 | 4.63 ± 0.23 | 3.75 ± 0.12 | 3.05 ± 0.23 | 2.95 ± 0.16 |
| **9** | 12.58 ± 0.43 | 8.67 ± 0.14 | 12.35 ± 0.93 | 3.15 ± 0.07 | 12.89 ± 0.24 |
| **10** | 16.08 ± 0.10 | 14.88 ± 0.63 | 20.89 ± 0.47 | 10.15 ± 0.54 | 17.49 ± 0.29 |
| **ViB-4-OH** | 17.38 ± 2.38 | 16.37 ± 0.59 | 18.65 ± 0.34 | 15.90 ± 0.61 | 19.67 ± 1.37 |
| **DDP**[a] | 16.80 ± 0.46 | 9.58 ± 0.24 | 14.09 ± 0.76 | 1.69 ± 0.03 | 25.46 ± 0.72 |

[a] cisplatin was used as positive control.

**Table S2. Primary toxicity of vibsanin B and its derivatives 7 and 12f on zebrafish embryo [a]**

| Compd. | Status of embryonic development [b] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 4 μM | | | 8 μM | | | 16 μM | | |
| | LoD [c] | SC [c] | BM [c] | LoD | SC | BM | LoD | SC | BM |
| **ViB** | (20/20) live | (20/20) yes | (20/20) yes | (20/20) live | (20/20) yes | (19/20) yes | 15/18 live | 9/15 yes | 1/15 yes |
| **12f** | (20/20) live | (20/20) yes | (20/20) yes | (20/20) live | (20/20) yes | (19/20) yes | 20/20 live | 20/20 yes | 16/20 yes |
| **7** | (20/20) live | (20/20) yes | (20/20) yes | (20/20) live | (20/20) yes | (19/20) yes | 9/17 live | 6/9 yes | 0/17 yes |

[a] All zebrafish embryos used in this work were bred in a standard condition of 28.5 °C egg water. 15-20 embryos were put into the one well of 12 well-plate and treated with vibsanin B (ViB) derivatives **7** and **12f** at concentration of 4, 8, 16 $\mu$M, for 12 hours, respectively;

[b] The primary toxicity of vibsanin B and its derivatives **7** and **12f** on zebrafish embryo (3 days post fertilization) was determined by observation of the embryonic phenotypes including systemic circulation and body movement;

[c] LoD (live or dead), SC (systemic circulation), BM (body movement).

**Table S3. In silico drug-like profiles of vibsanin B derivatives [a]**

| Compd. | Solubility [b] | Absorption [c] | PSA [d] | Hepatotoxicity [e] | Rat Oral $LD_{50}$ [f] |
|---|---|---|---|---|---|
| **7** | 1 | 1 | 64.347 | -9.8619 | 0.1762 |
| **12f** | 2 | 1 | 71.052 | -9.9846 | 0.7611 |

[a] Predicted properties were performed on ADMET and Toxicity Prediction modules of Discovery Studio 4.0. [b] aqueous solubility level in water at 25 °C. 0 (extremely low), 1 (very low), 2 (low), 3 (good), 4 (optimal). [c] human intestinal absorption (HIA) after oral administration. 0 (good), 1 (moderate), 2 (poor), 3 (very poor). [d] PSA: fast polar surface area (compounds with 10 or fewer rotatable bonds and PSA below 140 Å would have a higher chance of being orally bioavailable). [e] hepatotoxicity (< -0.4095: nontoxicity, > -0.4905: toxicity) .[f] the unit is g/kg (body weight).

**TableS4. Primers for pFlag-CMV-3/4-HSP90b-NTD, MD, CTD constructs.**

| Mutants | Primers: Forward primers(F), Reverse primers(R) |
|---|---|
| HSP90β-NTD (P2-S234) | F: 5'-ATAAGAATGCGGCCGCGCCTGAGGAAGTGCACCATGG-3' |
| | R: 5'-GCTCTAGACTATTTCTCTTCCTCTGCCTCAT-3' |
| HSP90β-MD (S261-K552) | F: 5'-ATAAGAATGCGGCCGCGAGCGGTAAGGATAAGAAGAA-3' |
| | R: 5'- GCTCTAGACTACTTCTTCTTCTCCTCCTCAT-3' |
| HSP90β-CTD (E547-D724) | F: 5'-ATAAGAATGCGGCCGCGGAGGAGGAGAAGAAGAAGAT-3' |
| | R: 5'- GCTCTAGACTAATCGACTTCTTCCATGCGAG-3' |

**TableS5. Primers for pET28a(+)-His-HSP90β-CTD construct.**

| **Mutants** | **Primers: Forward primers (F), Reverse primers (R)** |
|---|---|
| HSP90β-CTD (E547-D724) | F: 5'-GGAATTCCATATGGAGGAGGAGAAGAAGAAG-3' |
| | R: 5'-ACGCGTCGACCTAATCGACTTCTTCCAT-3' |

**Table S6. $IC_{50}$ ($\mu$M) of each compound in luciferase refolding assay.**

| | Novobiocin | 12a | 7 | 12f | 8f | 11 | ViB |
|---|---|---|---|---|---|---|---|
| $IC_{50}$ | 339±5.33 | 1.13±0.05 | 1.31±0.21 | 0.91±0.17 | 2.96±0.35 | 0.11±0.03 | 4.24±0.11 |

**HSP90β-NTD, MD, CTD cDNA sequences:**

**HSP90β-NTD**(P2-K234)**:**

CCTGAGGAAGTGCACCATGGAGAGGAGGAGGTGGAGACTTTTGCCTTTCAGGCAGA
AATTGCCCAACTCATGTCCCTCATCATCAATACCTTCTATTCCAACAAGGAGATTTT
CCTTCGGGAGTTGATCTCTAATGCTTCTGATGCCTTGGACAAGATTCGCTATGAGAG
CCTGACAGACCCTTCGAAGTTGGACAGTGGTAAAGAGCTGAAAATTGACATCATCC
CCAACCCTCAGGAACGTACCCTGACTTTGGTAGACACAGGCATTGGCATGACCAAA
GCTGATCTCATAAATAATTTGGGAACCATTGCCAAGTCTGGTACTAAAGCATTCATG
GAGGCTCTTCAGGCTGGTGCAGACATCTCCATGATTGGGCAGTTTGGTGTTGGCTTT
TATTCTGCCTACTTGGTGGCAGAGAAAGTGGTTGTGATCACAAAGCACAACGATGA
TGAACAGTATGCTTGGGAGTCTTCTGCTGGAGGTTCCTTCACTGTGCGTGCTGACCA
TGGTGAGCCCATTGGCAGGGGTACCAAAGTGATCCTCCATCTTAAAGAAGATCAGA
CAGAGTACCTAGAAGAGAGGCGGGTCAAAGAAGTAGTGAAGAAGCATTCTCAGTT
CATAGGCTATCCCATCACCCTTTATTTGGAGAAGGAACGAGAGAAGGAAATTAGTG
ATGATGAGGCAGAGGAAGAGAAA

**HSP90β-MD**(S261-K552)**:**

AGCGGTAAGGATAAGAAGAAGAAAACTAAGAAGATCAAAGAGAAATACATTGATC
AGGAAGAACTAAACAAGACCAAGCCTATTTGGACCAGAAACCCTGATGACATCAC
CCAAGAGGAGTATGGAGAATTCTACAAGAGCCTCACTAATGACTGGGAAGACCACT
TGGCAGTCAAGCACTTTTCTGTAGAAGGTCAGTTGGAATTCAGGGCATTGCTATTTA
TTCCTCGTCGGGCTCCCTTTGACCTTTTTGAGAACAAGAAGAAAAAGAACAACATC
AAACTCTATGTCCGCCGTGTGTTCATCATGGACAGCTGTGATGAGTTGATACCAGA
GTATCTCAATTTTATCCGTGGTGTGGTTGACTCTGAGGATCTGCCCCTGAACATCTC
CCGAGAAATGCTCCAGCAGAGCAAAATCTTGAAAGTCATTCGCAAAAACATTGTTA
AGAAGTGCCTTGAGCTCTTCTCTGAGCTGGCAGAAGACAAGGAGAATTACAAGAAA
TTCTATGAGGCATTCTCTAAAAATCTCAAGCTTGGAATCCACGAAGACTCCACTAAC
CGCCGCCGCCTGTCTGAGCTGCTGCGCTATCATACCTCCCAGTCTGGAGATGAGATG

ACATCTCTGTCAGAGTATGTTTCTCGCATGAAGGAGACACAGAAGTCCATCTATTAC
ATCACTGGTGAGAGCAAAGAGCAGGTGGCCAACTCAGCTTTTGTGGAGCGAGTGCG
GAAACGGGGCTTCGAGGTGGTATATATGACCGAGCCCATTGACGAGTACTGTGTGC
AGCAGCTCAAGGAATTTGATGGGAAGAGCCTGGTCTCAGTTACCAAGGAGGGTCTG
GAGCTGCCTGAGGATGAGGAGGAGAAGAAGAAG

**HSP90β-CTD**(E547-D724)**:**

GAGGAGGAGAAGAAGAAGATGGAAGAGAGCAAGGCAAAGTTTGAGAACCTCTGCA
AGCTCATGAAAGAAATCTTAGATAAGAAGGTTGAGAAGGTGACAATCTCCAATAGA
CTTGTGTCTTCACCTTGCTGCATTGTGACCAGCACCTACGGCTGGACAGCCAATATG
GAGCGGATCATGAAAGCCCAGGCACTTCGGGACAACTCCACCATGGGCTATATGAT
GGCCAAAAAGCACCTGGAGATCAACCCTGACCACCCCATTGTGGAGACGCTGCGGC
AGAAGGCTGAGGCCGACAAGAATGATAAGGCAGTTAAGGACCTGGTGGTGCTGCTG
TTTGAAACCGCCCTGCTATCTTCTGGCTTTTCCCTTGAGGATCCCCAGACCCACTCCA
ACCGCATCTATCGCATGATCAAGCTAGGTCTAGGTATTGATGAAGATGAAGTGGCA
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GGATGCGTCTCGCATGGAAGAAGTCGAT

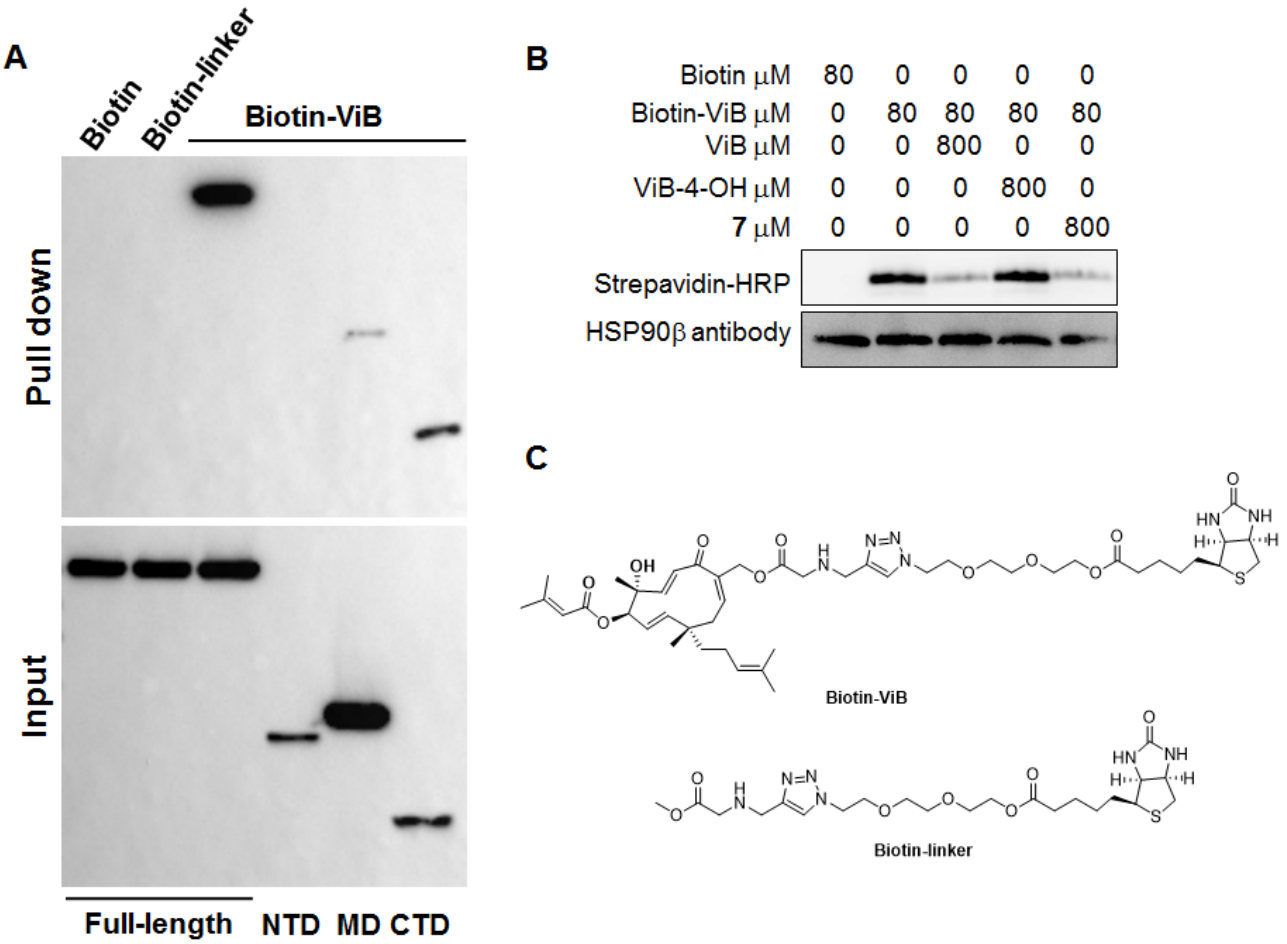



**Figure S1.** Vibsanin B targets Hsp90 CTD. (**A**) Lysates of 293T cells expressing Hsp90$\beta$ mutants including Hsp90$\beta$-NTD, MD and CTD were incubated with 30 $\mu$M Biotin-ViB, respectively, followed by pull down assay with strepavidin-argrose beads. The precipitates were analyzed by western blot assay against Flag antibodies. (**B**). Recombinant His-Hsp90$\beta$-CTD protein was incubated with Biotin-ViB, ViB, ViB-4-OH or **7** for 2 hours, and the mixtures were blotted with antibodies against His or biotin. (**C**) Structures of Biotin-ViB and Biotin-linker.

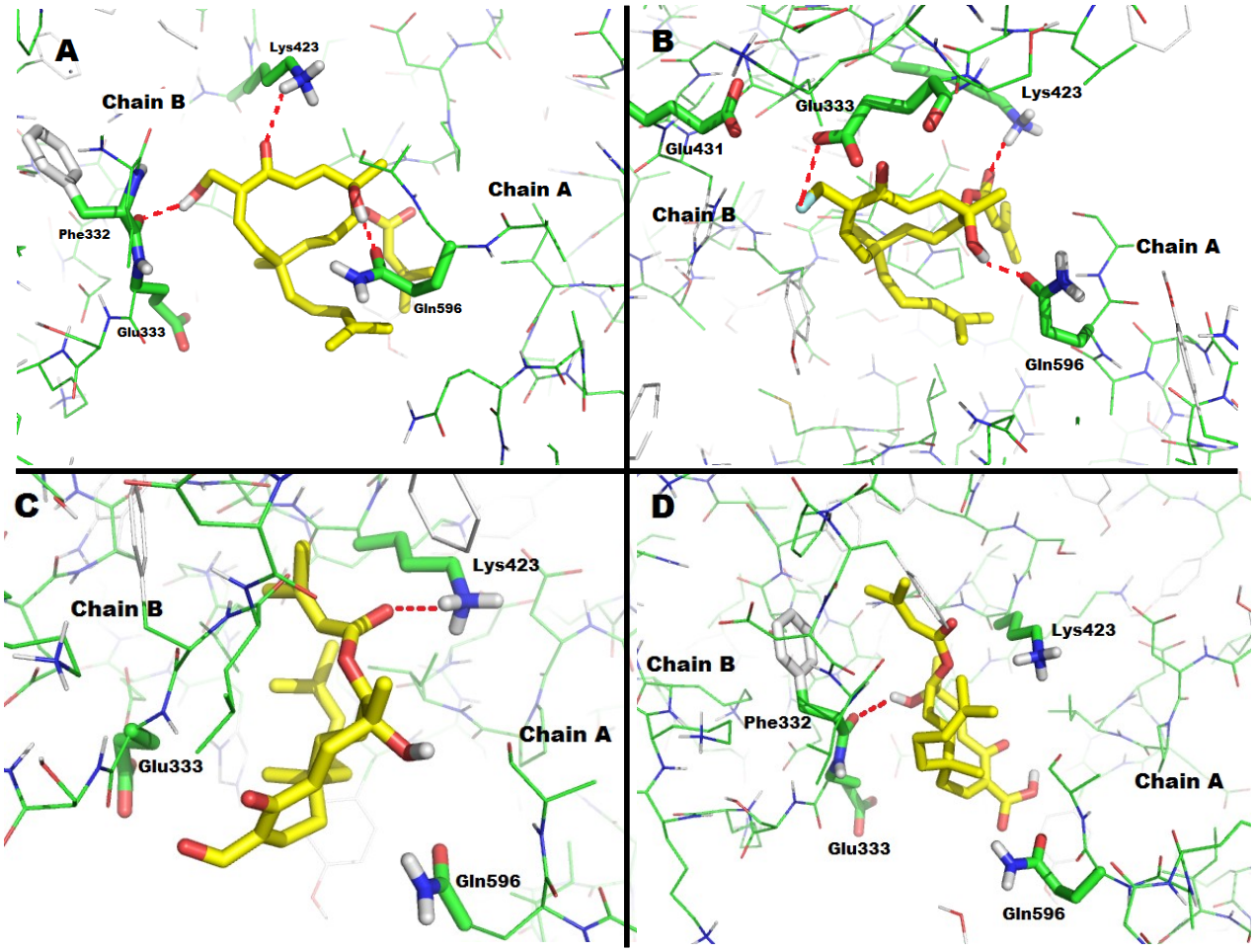



**Figure S2.** Predicted binding mode of **6** (**A**), **7** (**B**), **9** (**C**), **10** (**D**) at the interface of the C-terminal domain of Chain B (light cyan) and Chain A (light yellow) of the yeast Hsp90 (2cg9). Ligands colored by element type (C yellow, O red, F cyan, polar H white), key residues colored by element type (C green, O red, N blue, polar H white), key interactions were showed in red dot line. Docking was performed using AutoDock v4.01.

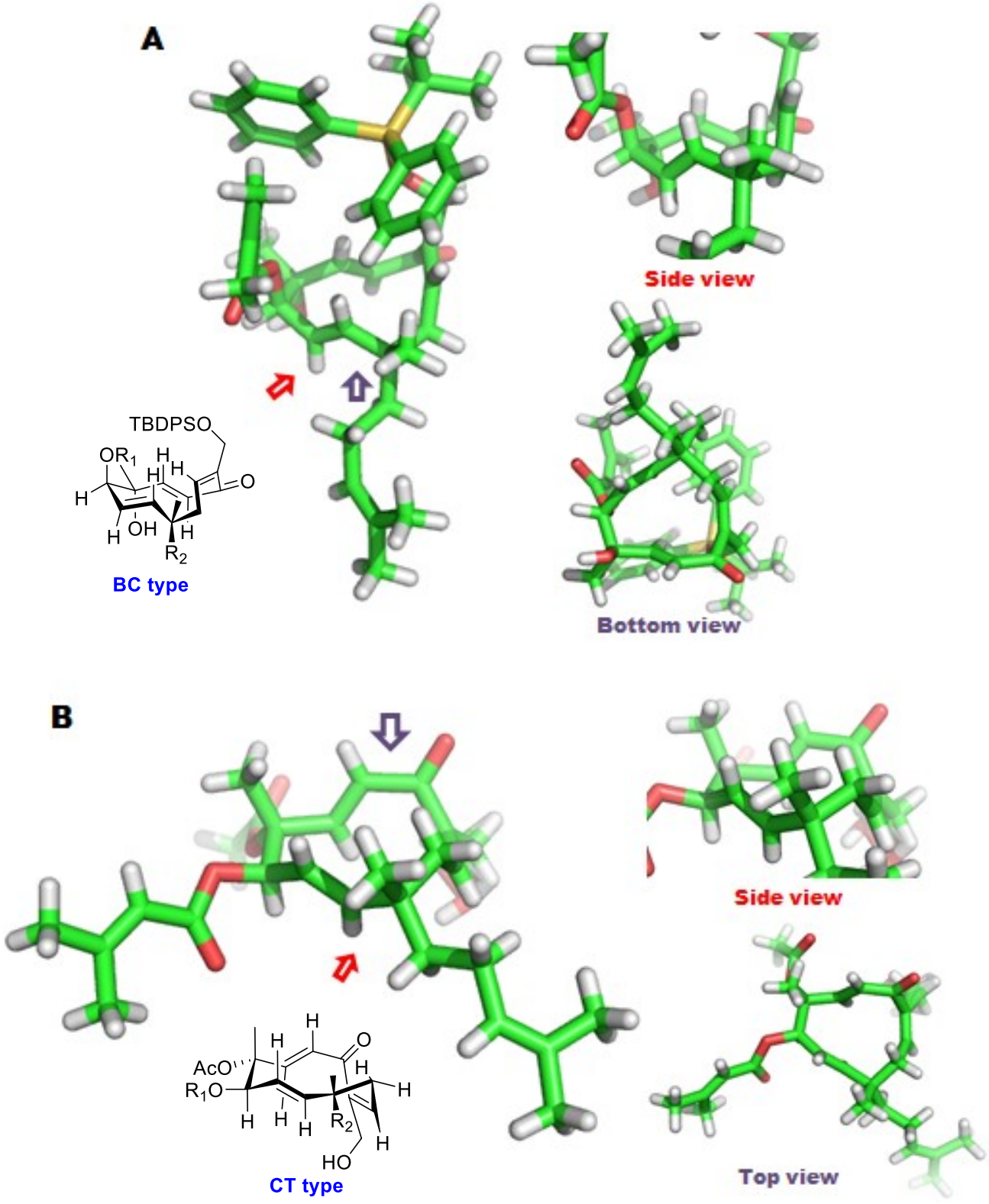



**Figure S3. Solid state conformations of compounds 13c and 8d. (A)** BC conformation of **13c**, red arrow is side view, gray arrow is bottom view, crystalline structure CCDC number: 981550; **(B)** CT conformation of **8d**, red arrow is side view, gray arrow is top view, crystalline structure CCDC number: 1517432.

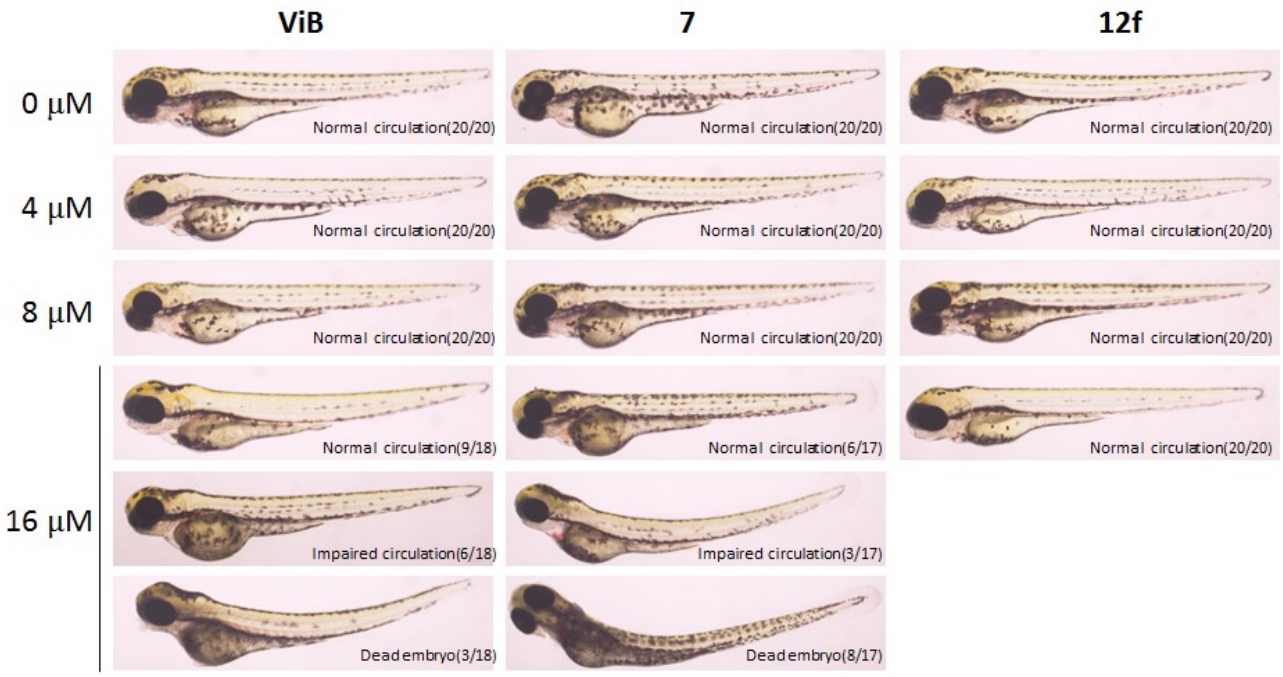



**Figure S4.** Status of embryonic development after treatment with ViB, **7**, and **12f** (0, 4, 8, 16 $\mu$M) for 12 h at 3dfp.

**The conformational instability of vibsanin B derivatives and its influence on NMR analysis and antiproliferative activity:**

**Note 1.** ViB exists in two major conformers (BC type and CT type)[1] which are resulted from its 11-membered ring. In NMR test, these two conformers could be always detected whether at high temperature (> 60 ℃) or low temperature (< 0 ℃). In this study, more conformationally stable CT type is about 2.8-fold (25 ℃) to BC type which was consistent with the reference.[2] The conformational isomerization in $^{13}$C NMR test is not so obvious as that in $^{1}$H NMR test, there are usually 3-9 carbon signals more than the real ones. This phenomenon makes the NMR spectra of ViB derivatives seem lack of purity. For convenience, only the CT type NMR data of ViB homologues are reported,[3] so does this work.

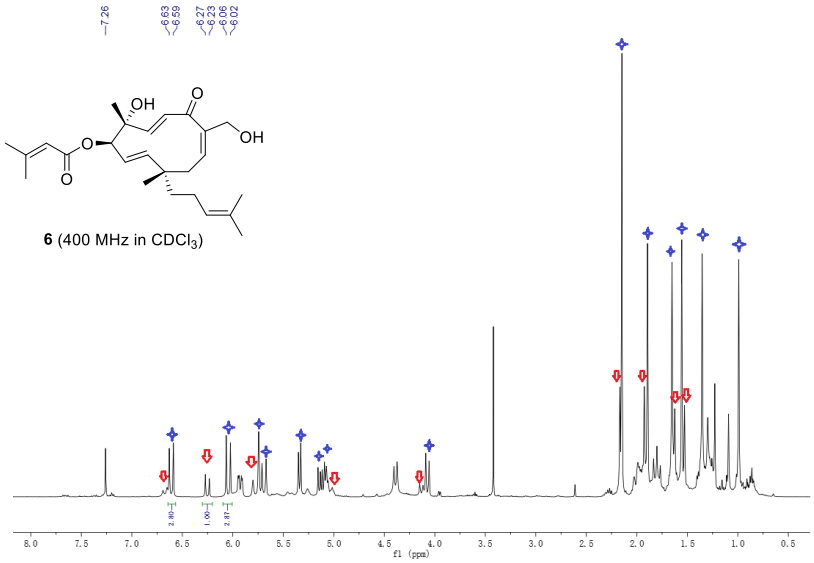



Figure **S5**. $^{1}$H NMR spectra of vibsanin B at 25 ℃. Red arrows are the signals of BC type, blue stars are the signals of CT type, the ratio of CT : BC is **2.8 : 1**

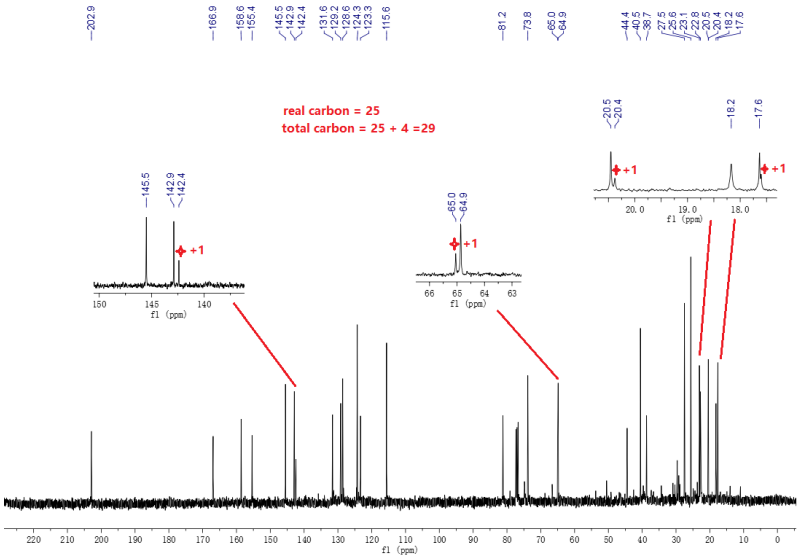



Figure **S6**. $^{13}$C NMR spectra of vibsanin B at 25 ℃. Red stars are the signals of BC type.

**Note 2.** The conformational instability of ViB could be improved by modification of its C7 hydroxyl group and C8 side chain. We found that C7 hydroxyl group acetylated compound **8d** exists in only CT conformer (see X-ray analysis Figure S4) (Figure S7), and the improvement was also found in C7 hydroxyl group methylated compound **8e**, which the ratio of CT:BC is 5.5 : 1. Similar observation was found in the $^{1}$H NMR spectra of compounds **8f** and **28f**. Obviously, enhancing the conformational stability did not improve the antiproliferative activity (**8f**, **28f**), suggesting that the conformational instable ligands (like compounds **7**, **11**, **12a** – **12f**, etc. in the present study) could also bind to the target protein well and then exhibit their biological functions like conformationally rigid ligands.

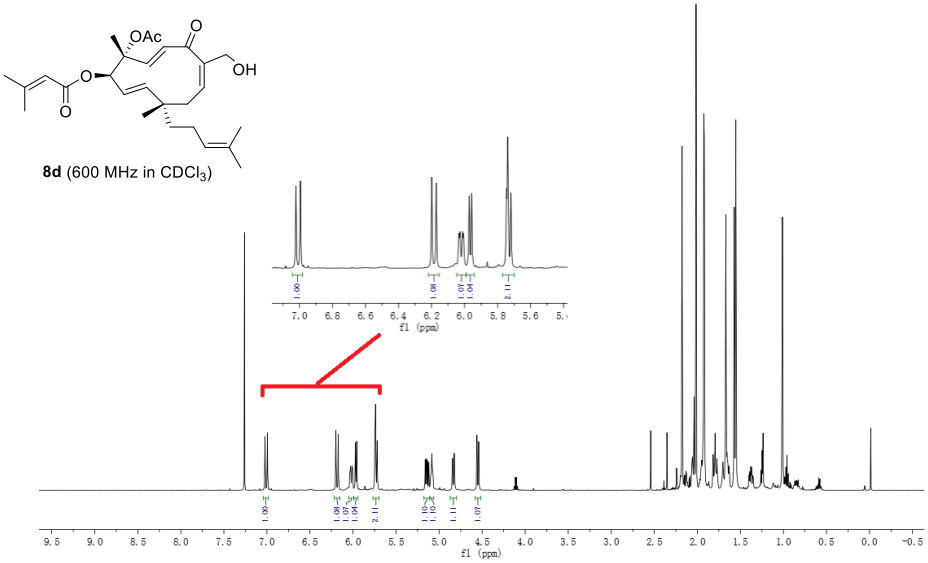



Figure **S7**. $^{1}$H NMR spectra of **8d** at 25 °C. The ratio of CT : BC is **1 : 0**

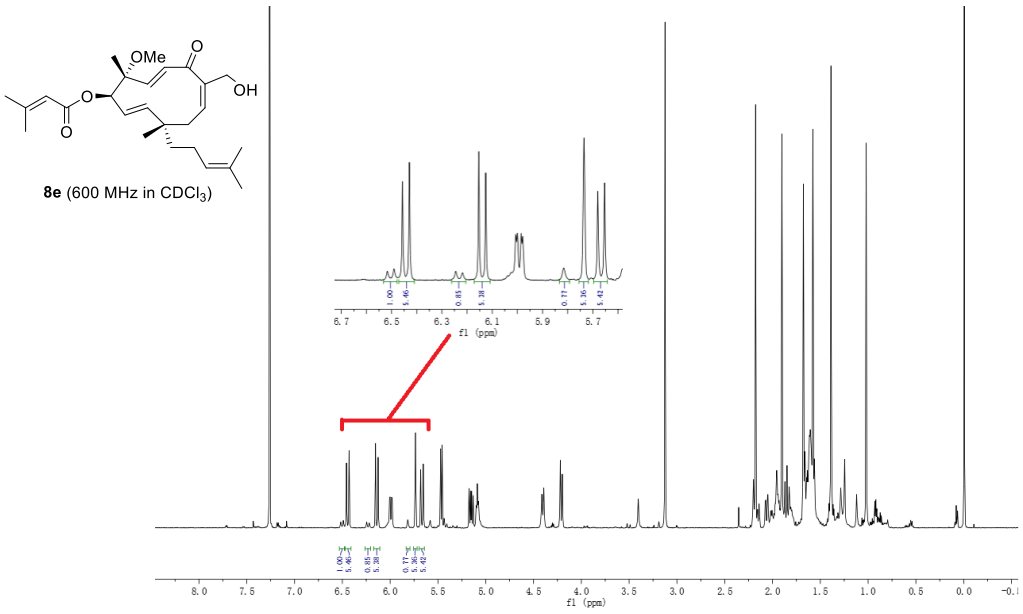



Figure **S8**. $^{1}$H NMR spectra of **8e** at 25 °C. The ratio of CT : BC is **5.5 : 1**

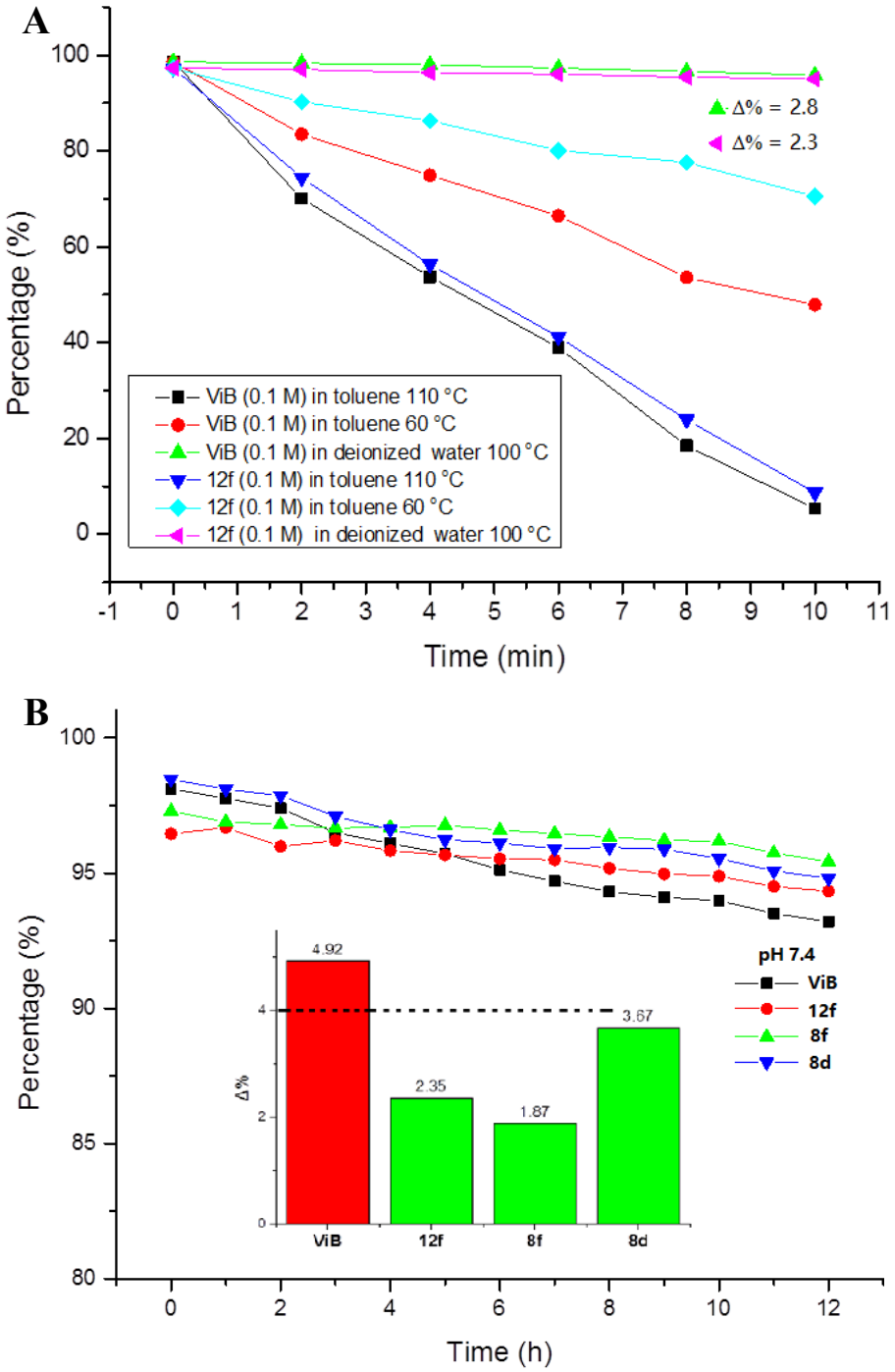



**Figure S9.** Solution stability of vibsanin B derivatives. (A) Thermostability of ViB and **12f** in toluene (110 °C and 60 °C) and deionized water (100 °C); (B) Stability of ViB, **12f**, **8f**, and **8d** in PBS pH 7.4 at 37.0 °C for 12 h, Δ% represents decomposition percentage, Δ% < 4 represents good solution stability. The decomposition behaviors of the compounds were measured by HPLC. Data for the percentage of remaining compound are expressed as values from one experiment for A or as means ± SD from three independent experiments for B.

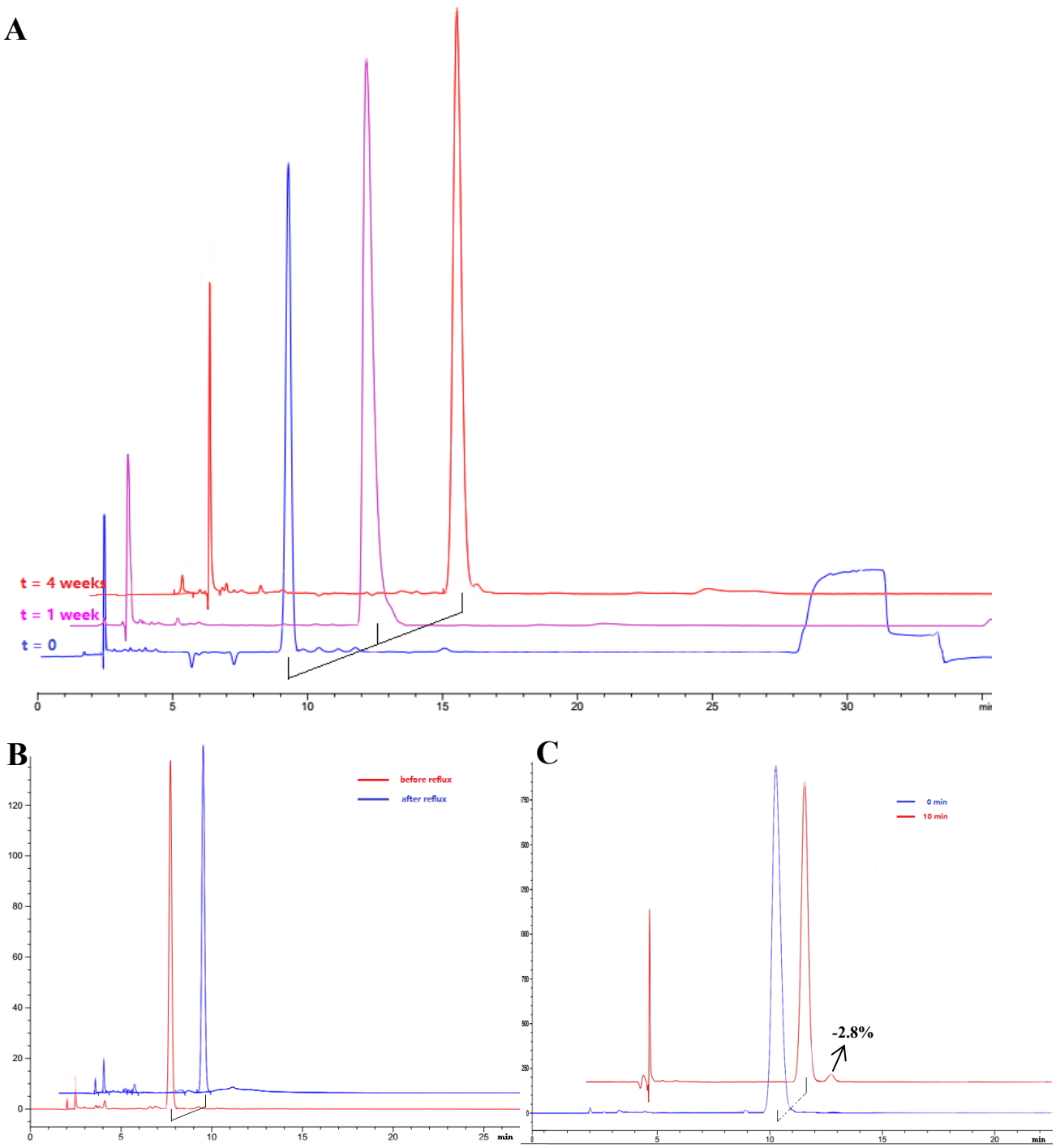
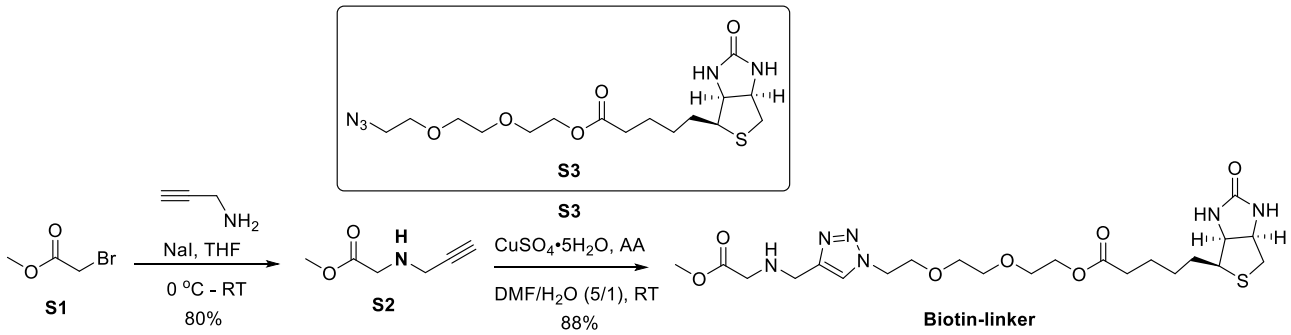



**Figure S10.** HPLC traces for solution stability of vibsanin B derivatives. (A) Stability of **12f** (0.1 M) in DMSO (4 $^{o}$C) for 4 weeks; (B) Thermostability of **8f** (0.1 M) in toluene (110 $^{o}$C) for 30 min; (100 $^{o}$C); (C) Stability of ViB (0.1 M) in deionized water (100 $^{o}$C) for 10 min.

**Procedure for preparation of Biotin-ViB:**

*Biotin-ViB.* Biotin-ViB was prepared according to the literature,[4] and was obtained as a colorless oil. $^1$H NMR (800 MHz, $CDCl_3$) $\delta$ 7.70 (d, $J$ = 12.7 Hz, 1H), 6.61 (d, $J$ = 16.3 Hz, 1H), 6.11 – 6.03 (m, 2H), 5.89 (s, 1H), 5.78 (s, 1H), 5.67 (d, $J$ = 16.1 Hz, 1H), 5.50 (d, $J$ = 9.2 Hz, 1H), 5.43 (s, 1H), 5.17 (dd, $J$ = 16.1, 9.2 Hz, 1H), 5.10 (t, $J$ = 6.8 Hz, 1H), 4.92 (d, $J$ = 11.9 Hz, 1H), 4.70 (d, $J$ = 11.9 Hz, 1H), 4.51 (ddt, $J$ = 17.5, 13.1, 6.5 Hz, 4H), 4.36 – 4.31 (m, 1H), 4.27 – 4.17 (m, 2H), 3.94 – 3.88 (m, 2H), 3.86 (t, $J$ = 5.2 Hz, 2H), 3.65 (p, $J$ = 7.4 Hz, 3H), 3.63 – 3.58 (m, 5H), 3.56 (d, $J$ = 17.2 Hz, 1H), 3.47 (d, $J$ = 17.2 Hz, 1H), 3.14 (dd, $J$ = 12.0, 7.3 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.72 (t, $J$ = 9.8 Hz, 1H), 2.31 (t, $J$ = 7.4 Hz, 2H), 2.17 (s, 3H), 1.91 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.40 (s, 3H), 1.02 (s, 3H); $^{13}$C NMR (200 MHz, $CDCl_3$) $\delta$ 200.6, 173.5, 171.6, 166.4, 163.4, 157.8, 156.6, 145.4, 145.0, 138.2, 132.6, 131.7, 128.1, 124.2, 124.1, 123.3, 116.1, 80.5, 73.3, 70.5, 70.5, 69.5, 69.2, 66.9, 63.3, 61.9, 60.1, 55.4, 50.3, 49.9, 44.6, 43.7, 40.6, 40.5, 38.9, 33.8, 28.3, 28.2, 27.5, 25.7, 24.7, 23.1, 22.8, 20.4, 17.9, 17.7; MS (ESI): $[M+H]^+$ calcd for $C_{46}H_{69}N_6O_{11}S$, 913; found, 913; $[M+Na]^+$ calcd for $C_{46}H_{68}N_6O_{11}SNa$, 935; found, 935.

**Procedure for preparation of Biotin-linker:**




*Compound S2.* To a solution of bromo methylacetate (**S1**) (120 mg) in THF (10 mL) was added NaI (180 mg), the resulting mixture was stirred at 0 ℃ for 10 min, then propargyl amine (50 mg in 2 mL THF) was added, the mixture was stirred at room temperature for 4 h after consumption of the starting materials. The reaction was quenched by adding water (2 mL). Then the mixture was portioned by adding ethyl acetate (20 mL), and the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 4:1 v/v) to afford compound **S2** (80 mg, 80%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.72 (s, 3H), 3.50 (s, 2H), 3.47 (d, $J$ = 2.4 Hz,

2H), 2.22 (t, $J$ = 2.3 Hz, 1H), 1.76 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 172.5, 81.2, 72.1, 52.0, 49.1, 37.8; MS (ESI): $[M+H]^+$ calcd for $C_6H_{10}NO_2$, 128; found, 128.

*Biotin-linker.* To a solution of compound S**2** (10 mg) and compound S**3** [4] (47 mg) in DMF/$H_2O$ (2.4 mL, 5:1, v/v) were added $CuSO_4$ (2 mg) and ascorbic acid (1.4 mg) successively. The mixture was stirred at the room temperature under nitrogen for 2.5 h after consumption of the starting materials. Then water (2 mL) was added to quench the reaction, and the aqueous phase was extracted with EtOAc (10 mL×3) for three times. The combined organic layers were washed with brine (10 mL × 3), dried over $Na_2SO_4$, and evaporated *in vacuo*. The resulting crude product was subjected to silica gel chromatography (DCM/MeOH 10:1, v/v) to give Biotin-linker (37 mg, 88% yield) as a colorless oil. $^1$H NMR (800 MHz, $CDCl_3$) $\delta$ 7.72 (s, 1H), 6.06 (s, 1H), 5.47 (s, 1H), 4.52 (d, $J$ = 29.3 Hz, 3H), 4.31 (s, 1H), 4.21 (m, 2H), 3.94 (brs, 2H), 3.86 (brs, 2H), 3.72 (s, 3H), 3.66 (t, $J$ = 4.5 Hz, 3H), 3.62 (s, 5H), 3.48 (brs, 2H), 3.14 (s, 1H), 2.89 (d, $J$ = 8.8 Hz, 1H), 2.74 (d, $J$ = 11.7 Hz, 1H), 2.34 (t, $J$ = 6.9 Hz, 3H), 1.77 – 1.68 (m, 2H), 1.65 (m, 4H), 1.43 (m, 3H); $^{13}$C NMR (200 MHz, $CDCl_3$) $\delta$ 173.8, 172.6, 163.7, 145.9, 123.3, 70.5, 70.4, 69.6, 69.2, 63.4, 62.0, 60.2, 55.7, 52.1, 50.3, 49.8, 44.1, 40.7, 33.8, 28.4, 28.3, 24.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{37}N_6O_7S$, 529.2444; found, 529.2454.

**Procedure for preparation of vibsanin B derivatives:**

*18-O-acetyl vibsanin B (**8**).* To a stirred solution of ViB (0.2 g) and TEA (200 $\mu$L) in DCM (5 mL) was added $Ac_2O$ (100 $\mu$L) and DMAP (6 mg), the mixture was stirred at room temperature for 4 h. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1 v/v) to afford compound **8** (215 mg, 98%) as a colorless oil: $[\alpha]^{17}_D$ +43 (*c* 2.0, $CH_2Cl_2$). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.46 (d, *J* = 16.4 Hz, 1H), 6.06 (d, *J* = 16.4 Hz, 1H), 6.02 (dd, *J* = 13.2, 3.8 Hz, 1H), 5.79 (s, 1H), 5.63 (d, *J* = 16.1 Hz, 1H), 5.36 (d, *J* = 9.2 Hz, 1H), 5.20 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.09 (t, *J* = 7.0 Hz, 1H), 4.85 (d, *J* = 12.1 Hz, 1H), 4.59 (d, *J* = 12.3 Hz, 1H), 2.20 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.03 (s, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 200.5, 170.9, 167.6, 159.7, 155.1, 145.5, 138.6, 132.0, 131.9, 128.6, 124.3, 123.6, 115.4, 82.1, 74.4, 66.3, 44.8, 40.8, 39.1, 27.7, 25.8, 23.3, 23.1, 21.0, 20.7, 18.7, 17.8; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{27}H_{38}O_6Cl$, 493.2362; found, 493.2359.

*7,18-di-O-acetyl vibsanin B (**8a**).* To a stirred solution of ViB (0.2 g) and TEA (670 $\mu$L) in DCM (10 mL) was added $Ac_2O$ (500 $\mu$L) and DMAP (0.6 g), the mixture was stirred at room temperature for 16 h. DCM (10 mL) and water (10 mL) were added to the mixture, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 20:1 v/v) to afford compound **8a** (216 mg, 90%) as a white amorphous powder: $[\alpha]^{23}_D$ +21 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.01 (d, *J* = 16.4 Hz, 1H), 6.19 (d, *J* = 16.4 Hz, 1H), 6.03 (dd, *J* = 12.9, 3.5 Hz, 1H), 5.97 (d, *J* = 9.1 Hz, 1H), 5.74 (d, *J* = 16.0 Hz, 1H), 5.74 (s, 1H), 5.15 (dd, *J* = 16.2, 9.1 Hz, 1H), 5.09 (t, *J* = 6.6 Hz, 1H), 4.84 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 2.18 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H), 1.93 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.56 (s, 3H), 1.02 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 200.4, 170.8, 169.8, 165.3, 158.2, 152.1, 146.7, 138.4, 132.0, 131.0, 124.2, 123.9, 122.8, 115.8, 81.5, 76.0, 66.5, 44.8, 40.9, 38.9, 27.7, 25.8, 23.3, 22.9, 21.9, 20.8, 20.5, 17.8, 16.7. HRMS (ESI): $[M-H]^-$ calcd for $C_{29}H_{39}O_7$, 499.2701; found, 499.2687.

*7,18-di-O-methyl vibsanin B (**8b**) and 18-O-methyl vibsanin B (**8c**).* To a stirred solution of ViB (50 mg) in MeI (2 mL) was added freshly prepared silver oxide (560 mg), the mixture was sealed and stirred at 40 °C for 24 h. The mixture was passed a pad of celite, the filter cake was washed by

DCM (5 mL × 3). The solvent was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1 – 10:1 v/v) to afford compound **8b** (16 mg, 30%) and **8c** (31 mg, 60%) as colorless oil.

**8b**, $[\alpha]^{20}_{D}$ +51 (*c* 2.5, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.49 (d, *J* = 16.4 Hz, 1H), 6.11 (d, *J* = 16.4 Hz, 1H), 5.93 (dd, *J* = 12.5, 2.9 Hz, 1H), 5.73 (s, 1H), 5.67 (d, *J* = 16.2 Hz, 1H), 5.49 (d, *J* = 9.1 Hz, 1H), 5.14 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.08 (t, *J* = 6.8 Hz, 1H), 4.21 (d, *J* = 11.3 Hz, 1H), 3.87 (d, *J* = 11.3 Hz, 1H), 3.33 (s, 3H), 3.13 (s, 3H), 2.17 (s, 3H), 1.90 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.39 (s, 3H), 1.01 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 201.5, 165.5, 157.4, 154.0, 145.6, 140.8, 132.0, 131.9, 129.7, 124.4, 123.8, 116.2, 78.9, 78.3, 74.8, 58.8, 51.6, 44.7, 40.7, 38.9, 27.6, 25.8, 23.3, 22.9, 20.5, 17.8, 14.2; HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{41}O_5$, 445.2949; found, 445.2952.

**8c**, $[\alpha]^{23}_{D}$ +40 (*c* 4.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.54 (d, *J* = 16.3 Hz, 1H), 6.05 (d, *J* = 16.3 Hz, 1H), 5.93 (dd, *J* = 12.8, 3.7 Hz, 1H), 5.78 (s, 1H), 5.66 (d, *J* = 16.2 Hz, 1H), 5.38 (d, *J* = 9.1 Hz, 1H), 5.19 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 4.18 (d, *J* = 11.6 Hz, 1H), 3.90 (d, *J* = 11.6 Hz, 1H), 3.35 (s, 3H), 2.19 (s, 3H), 2.06 – 2.01 (m, 1H), 1.93 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.36 (s, 3H), 1.02 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 201.8, 167.5, 159.6, 154.7, 145.7, 140.9, 131.9, 129.2, 128.8, 124.3, 123.4, 115.4, 81.9, 74.8, 74.5, 58.9, 44.7, 40.7, 39.0, 27.8, 25.8, 23.3, 23.0, 20.6, 18.6, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{38}O_5Na$, 453.2611; found, 453.2614.

*18-O-triethylsilyl vibsanin B (**13a**).* To a stirred solution of ViB (0.5 g) and TEA (330 $\mu$L) in DCM (10 mL) was added TESCl (300 $\mu$L), the mixture was stirred at room temperature for 6 h. The solvent was evaporated under vacuum and the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1 v/v) to afford compound **13a** (623 mg, 98% yield) as a white foam: $[\alpha]^{17}_{D}$ +68 (*c* 2.1, $CH_2Cl_2$). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.57 (d, *J* = 16.3 Hz, 1H), 6.05 (d, *J* = 16.3 Hz, 1H), 5.92 (d, *J* = 9.3 Hz, 1H), 5.79 (s, 1H), 5.68 (d, *J* = 16.2 Hz, 1H), 5.36 (d, *J* = 9.1 Hz, 1H), 5.19 (dd, *J* = 16.2, 9.1 Hz, 1H), 5.09 (d, *J* = 7.1 Hz, 1H), 4.44 (d, *J* = 12.9 Hz, 2H), 4.15 (dd, *J* = 19.4, 12.5 Hz, 1H), 2.20 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.37 (s, 3H), 1.03 (s, 3H), 0.96 (m, 9H), 0.60 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 202.3, 167.4, 159.5, 154.9, 145.8, 143.3, 131.8, 128.9, 126.7, 124.4, 123.2, 115.5, 82.0, 74.5, 64.5, 44.4, 40.6, 38.9, 27.7, 25.8,

23.2, 23.0, 20.6, 18.6, 17.8, 6.9, 4.5; HRMS (ESI): $[M+Na]^+$ calcd for $C_{31}H_{50}O_5SiNa$, 553.3320; found, 553.3324.

*18-O-t-butyldimethylsilyl vibsanin B (**13b**).* To a stirred solution of ViB (0.5 g) and imidazole (160 mg) in DCM (10 mL) was added TBSCl (270 mg) and DAMP (15 mg), the mixture was stirred at room temperature for 6 h. 10 mL of DCM and 10 mL of water were added to the mixture, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1 v/v) to afford compound **13b** (640 mg, 100% yield) as a white foam: $[\alpha]^{17}_D$ +61 (*c* 1.0, $CH_2Cl_2$). $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 6.56 (d, $J$ = 16.3 Hz, 1H), 6.04 (d, $J$ = 16.3 Hz, 1H), 5.95 – 5.86 (m, 1H), 5.78 (s, 2H), 5.67 (d, $J$ = 16.2 Hz, 1H), 5.35 (d, $J$ = 9.1 Hz, 1H), 5.18 (dd, $J$ = 16.2, 9.1 Hz, 1H), 5.09 (t, $J$ = 7.0 Hz, 1H), 4.42 (d, $J$ = 12.8 Hz, 1H), 4.16 (d, $J$ = 12.8 Hz, 1H), 2.20 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.02 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H). $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 202.3, 167.4, 159.4, 155.0, 145.9, 143.3, 131.8, 128.9, 126.7, 124.4, 123.2, 115.5, 82.0, 74.5, 64.9, 44.3, 40.6, 38.9, 27.7, 26.0, 25.8, 23.2, 23.0, 20.6, 20.5, 18.6, 18.4, 17.8, -3.5, -5.3; HRMS (ESI): $[M+Na]^+$ calcd for $C_{31}H_{50}O_5SiNa$, 553.3320; found, 553.3323.

*18-O-t-butyldiphenylsilyl vibsanin B (**13c**)*[3a]. To a solution of ViB (0.4 g), imidazole (140 mg) and DMAP (24 mg) in DCM (10 mL) was added TBDPSCl (390 $\mu$L), the mixture was stirred at room temperature for 24 h. The solvent was evaporated under vacuum and the residue was purified by flash chromatography on silica gel and further recrystallization (MeOH) to afford compound **13c** as a colorless bulk crystal: $[\alpha]^{17}_D$ +63 (*c* 1.2, $CH_2Cl_2$).

*7-O-acetyl vibsanin B (**8d**).* To a solution of compound **13a** (50 mg) and and TEA (670 $\mu$L) in DCM (10 mL) was added $Ac_2O$ (500 $\mu$L) and DMAP (0.6 g), the mixture was stirred at room temperature for 16 h. DCM (10 mL) and water (10 mL) were added to the mixture, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The crude product was dissolved in AcOH/THF/$H_2O$ (8 mL, 5/2/1, v/v), the resulting mixture was stirred at RT for 4 h. Ethyl acetate (10 mL) was added, the organic layer was washed with $NaHCO_3$ saturated aqueous solution (10 mL × 3), brine (10 mL × 1), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl

acetate 6:1 v/v) to afford compound **8d** (38 mg, 96%) as white powder, which further recrystallized from (petroleum ether/ethyl acetate 10:1 v/v) to yield needle crystal: $[\alpha]^{25}_{D}$ +100 (*c* 2.0, $CH_2Cl_2$). m.p. 210 -211 °C. $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.01 (d, *J* = 16.4 Hz, 1H), 6.18 (d, *J* = 16.4 Hz, 1H), 6.02 (dd, *J* = 12.9, 3.6 Hz, 1H), 5.96 (d, *J* = 9.1 Hz, 1H), 5.73 (d, *J* = 16.0 Hz, 1H), 5.73 (s, 1H), 5.14 (dd, *J* = 16.2, 9.1 Hz, 1H), 5.08 (t, *J* = 6.9 Hz, 1H), 4.83 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 12.1 Hz, 1H), 2.18 (s, 3H), 2.01 (s, 3H), 1.93 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.01 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 200.4, 170.8, 169.8, 165.3, 158.1, 152.0, 146.6, 138.3, 132.0, 131.0, 124.2, 122.8, 115.8, 81.5, 76.0, 66.5, 44.8, 40.8, 38.8, 27.6, 25.8, 23.3, 22.9, 21.9, 20.8, 20.5, 17.8, 16.7; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{27}H_{38}O_6Cl$, 493.2362; found, 493.2378.

*7-O-methyl vibsanin B (**8e**).* To a solution of compound **13a** (50 mg) in MeI (5 mL) was added freshly prepared silver oxide (220 mg), the mixture was sealed and stirred at 40 °C for 24 h. The mixture was passed a pad of celite, the filter cake was washed by DCM (5 mL × 3). The solvent was concentrated under vacuum. Similar to the synthesis of **8d**, the TES group was removed under the same condition to afford compound **8e** (13 mg, 32%, 65% based on the recovery of ViB 20 mg) as colorless oil: $[\alpha]^{23}_{D}$ +50 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.44 (d, *J* = 16.5 Hz, 1H), 6.14 (d, *J* = 16.5 Hz, 1H), 5.99 (dd, *J* = 12.9, 3.9 Hz, 1H), 5.74 (s, 1H), 5.67 (d, *J* = 16.2 Hz, 1H), 5.46 (d, *J* = 9.2 Hz, 1H), 5.15 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.09 (t, *J* = 6.8 Hz, 1H), 4.40 (d, *J* = 12.4 Hz, 1H), 4.21 (d, *J* = 12.5 Hz, 1H), 3.12 (s, 3H), 2.18 (s, 3H), 2.06 (d, *J* = 13.8 Hz, 1H), 1.90 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H), 1.02 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 202.2, 165.5, 157.6, 153.5, 145.6, 142.4, 132.0, 131.9, 130.2, 124.3, 123.8, 116.1, 78.8, 78.4, 65.4, 51.6, 44.9, 40.7, 38.9, 27.6, 25.8, 23.2, 22.9, 20.5, 17.8, 14.1; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{38}O_5Na$, 453.2611; found, 453.2610.

*7-methylene vibsanin B (**8f**).* To a solution of compound **13b** (50 mg) in pyridine (5 mL) was added dropwise of $SOCl_2$ (200 $\mu$L) at 0 °C, the mixture was stirred at 0 °C for 0.5 h. The reaction was then quenched by adding of water (0.2 mL) and ethylacetate (10 mL), the organic layer was washed with $CuSO_4$ saturated aqueous solution (10 mL × 3), brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The mixture was passed a pad of celite, the filter cake was washed by DCM (5 mL × 3). The crude product was dissolved in THF (4 mL), TBAF (100 $\mu$L, 1 M in THF)

to this solution at 0 °C, the resulting mixture was stirred at RT for 2 h. Ethyl acetate (10 mL) was added, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1 v/v) to afford compound **8f** (31 mg, 82%) as colorless oil: $[\alpha]^{17}_D$ -152 (*c* 0.2, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.98 (d, *J* = 16.1 Hz, 1H), 6.28 (d, *J* = 16.1 Hz, 1H), 6.05 (dd, *J* = 12.7, 4.0 Hz, 1H), 5.90 (d, *J* = 8.9 Hz, 1H), 5.80 (m, 1H), 5.74 (d, *J* = 16.3 Hz, 1H), 5.38 (s, 1H), 5.27 (dd, *J* = 16.3, 9.0 Hz, 1H), 5.18 (d, *J* = 1.7 Hz, 1H), 5.11 (t, *J* = 7.1 Hz, 1H), 4.39 (dd, *J* = 12.2, 4.1 Hz, 1H), 4.19 (d, *J* = 12.5 Hz, 1H), 2.20 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.42 (td, *J* = 12.8, 5.2 Hz, 1H), 1.05 (s, 3H); $^1$H NMR (100 MHz, $CDCl_3$) $\delta$ 201.6, 165.3, 158.8, 150.6, 143.5, 142.2, 131.9, 130.5, 130.2, 127.0, 124.5, 124.3, 115.5, 110.7, 74.8, 65.8, 41.0, 39.0, 31.1, 27.7, 25.8, 23.4, 22.9, 20.5, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{34}O_4Na$, 421.2349; found, 421.2351.

*Synthesis of Compound **14**.* To a solution of ViB (20 mg) in AcOH (2 mL), was added zinc powder (6 mg), the resulting suspension was stirred vigorously at RT for 12 h. The mixture was then passed a short pad of celite, the filter cake was washed with ethyl acetate (5 mL × 3), the combined organic layers were washed with $NaHCO_3$ saturated aqueous solution (5 mL × 3), brine (10 mL × 1), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate 4:1 – 2:1 v/v) to afford compound **14** (14 mg, 70%) as colorless oil: $[\alpha]^{17}_D$ +33 (*c* 2.1, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 5.79 (t, *J* = 8.4 Hz, 1H), 5.69 (s, 1H), 5.59 (d, *J* = 15.7 Hz, 1H), 5.25 (d, *J* = 8.5 Hz, 1H), 5.14 (dd, *J* = 15.7, 8.5 Hz, 1H), 5.04 (t, *J* = 5.7 Hz, 1H), 4.35 (d, *J* = 11.7 Hz, 1H), 4.18 (d, *J* = 12.8 Hz, 1H), 3.05 (brs, 1H), 2.72 (brs, 2H), 2.62 (brs, 1H), 2.14 (s, 3H), 2.00 (brs, 1H), 1.89 (s, 3H), 1.64 (s, 3H), 1.54 (s, 3H), 1.42 (td, *J* = 12.6, 4.2 Hz, 1H), 1.30 (td, *J* = 12.6, 5.4 Hz, 1H), 1.24 (s, 3H), 0.96 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 207.2, 166.5, 158.2, 146.5, 144.2, 132.4, 131.7, 124.5, 122.4, 115.9, 81.1, 74.1, 65.9, 42.2, 38.9, 38.8, 37.1, 33.7, 29.8, 27.7, 25.8, 24.3, 23.1, 20.5, 17.7; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{25}H_{38}O_5Cl$, 453.2413; found, 453.2409.

*18-methoxymethoxyl vibsanin B (**15**).* To a solution of ViB (20 mg) and DIPEA (24 $\mu$L) in DCM (2 mL) at 0 °C, was added MOMCl (8 $\mu$L), the reaction was allowed to warm to RT and stir for 2 h. The reaction was then quenched by adding of water (0.2 mL) and DCM (10 mL), the organic layer

was washed with brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 15:1 v/v) to afford compound **15** (20 mg, 90%) as slightly yellow oil: $[\alpha]^{20}_D$ +55 (*c* 6.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.55 (d, *J* = 16.3 Hz, 1H), 6.07 (d, *J* = 16.3 Hz, 1H), 5.95 (dd, *J* = 12.9, 3.9 Hz, 1H), 5.78 (s, 1H), 5.66 (d, *J* = 16.2 Hz, 1H), 5.38 (d, *J* = 9.1 Hz, 1H), 5.20 (dd, *J* = 16.2, 9.1 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 4.63 – 4.58 (m, 2H), 4.37 (d, *J* = 11.5 Hz, 1H), 4.02 (d, *J* = 11.5 Hz, 1H), 3.33 (s, 3H), 2.20 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 201.7, 167.5, 159.8, 154.6, 145.7, 140.8, 132.0, 129.7, 128.9, 124.3, 123.4, 115.4, 96.2, 81.9, 74.6, 69.5, 55.6, 44.8, 40.7, 39.0, 27.8, 25.8, 23.3, 23.1, 20.7, 18.6, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{27}H_{40}O_6Na$, 483.2723; found, 483.2727.

*18-O-p-nitrobenzoyl vibsanin B (**16**).* To a solution of ViB (40 mg) and TEA (16 $\mu$L) in DCM (2 mL) at 0 °C, was added *p*-nitrobenzoylchloride (20 mg), the reaction was allowed to warm to RT and stirred for 30 min. The reaction was then quenched by adding of water (0.2 mL) and DCM (10 mL), the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 12:1 v/v) to afford compound **16** (52 mg, 95%) as colorless oil: $[\alpha]^{23}_D$ +58 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.26 (m, 2H), 8.17 (m, 2H), 6.69 (d, *J* = 16.4 Hz, 1H), 6.13 (m, 2H), 5.80 (s, 1H), 5.67 (d, *J* = 16.1 Hz, 1H), 5.34 (d, *J* = 9.2 Hz, 1H), 5.24 (dd, *J* = 16.1, 9.2 Hz, 1H), 5.17 (d, *J* = 11.9 Hz, 1H), 5.08 (t, *J* = 7.0 Hz, 1H), 4.81 (d, *J* = 11.9 Hz, 1H), 2.21 (s, 1H), 1.95 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.39 (s, 3H), 1.07 (s, 3H). $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 200.4, 167.9, 164.4, 160.5, 156.2, 150.7, 145.3, 137.8, 135.0, 132.8, 132.1, 131.1 (×2), 128.2, 124.1, 123.8 (×2), 123.7, 115.1, 82.7, 74.4, 68.1, 44.7, 40.8, 39.2, 27.9, 25.8, 23.3, 23.1, 20.7, 18.8, 17.9; HRMS (ESI): $[M+Na]^+$ calcd for $C_{32}H_{39}NO_8Na$, 588.2568; found, 588.2566.

*18-azido vibsanin B (**17**).* To a solution of ViB (50 mg) in DMF/$CCl_4$ (5 mL, 1:4, v/v) was added $NaN_3$ (16 mg) and $PPh_3$ (63 mg), the reaction was warmed to 40 °C and stirred for 2 h. The reaction was then quenched by adding of water (1 mL) and ethyl acetate (10 mL), the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1 v/v) to afford

compound **17** (50 mg, 96%) as yellow foam: $[\alpha]^{20}_{D}$ +126 (*c* 2.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.46 (d, *J* = 16.4 Hz, 1H), 6.08 (d, *J* = 16.5 Hz, 1H), 5.98 (dd, *J* = 12.9, 4.0 Hz, 1H), 5.78 (d, *J* = 1.1 Hz, 2H), 5.66 (d, *J* = 16.2 Hz, 1H), 5.36 (d, *J* = 9.2 Hz, 1H), 5.21 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.10 (t, *J* = 7.0 Hz, 1H), 4.15 (d, *J* = 13.8 Hz, 1H), 3.93 (d, *J* = 13.7 Hz, 1H), 2.20 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 200.5, 167.5, 159.9, 154.4, 145.4, 138.0, 132.1, 131.6, 128.5, 124.2, 123.7, 115.3, 81.9, 74.3, 54.5, 44.9, 40.6, 39.0, 27.8, 25.8, 23.2, 23.0, 20.7, 18.6, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{35}N_3O_4Na$, 464.2520; found, 464.2519.

*Triazol **18**.* To a solution of **17** (20 mg) in DMF/$H_2O$ (5 mL, 4:1, v/v) was added propargyl alcohol (3 $\mu$L), sodium ascorbate (1 mg) and $CuSO_4$ (0.2 mg), the resulting mixture was sonicated for 30 min until the yellow solids were not precipitated any more. Water (2 mL) and ethyl acetate (20 mL) were added to the mixture, and the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 1:1 v/v) to afford compound **18** (20 mg, 88%) as white amorphous powder: $[\alpha]^{17}_{D}$ +80 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.50 (s, 1H), 6.19 (dd, *J* = 12.9, 3.8 Hz, 1H), 5.92 (d, *J* = 16.4 Hz, 1H), 5.75 (s, 1H), 5.55 (s, 1H), 5.25 (d, *J* = 14.5 Hz, 1H), 5.20 (d, *J* = 9.2 Hz, 1H), 5.14 – 5.08 (m, 2H), 5.03 (d, *J* = 14.3 Hz, 1H), 4.78 (d, *J* = 13.2 Hz, 1H), 4.66 (d, *J* = 13.1 Hz, 1H), 2.17 (s, 3H), 1.92 (s, 3H), 1.69 (s, 3H), 1.59 (s, 3H), 1.39 (td, *J* = 12.8, 5.2 Hz, 1H), 1.24 (s, 3H), 1.01 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 200.5, 167.3, 159.8, 154.9, 148.7, 144.9, 137.8, 133.5, 132.1, 127.7, 124.1, 123.9, 123.3, 115.3, 81.7, 73.9, 67.8, 56.3, 44.8, 40.9, 39.0, 27.8, 25.9, 23.2, 23.1, 20.7, 18.3, 17.9; HRMS (ESI): $[M+H]^+$ calcd for $C_{28}H_{40}N_3O_5$, 498.2962; found, 498.2966.

*Xanthate **19**.* To a solution of ViB (40 mg) in THF (2 mL) at -40 °C was added a suspension of NaH (4 mg) in THF (1 mL), the mixture was stirred for 5 min at the same temperature, freshly distilled $CS_2$ (7 $\mu$L) was added and the reaction was kept stirring for 30 min at -40 °C. To this solution, MeI (8 $\mu$L) was added, and the reaction was allowed to warm to RT and stirred for 10 h. After completion, water (1 mL) and ethyl acetate (20 mL) were added to the mixture, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The

residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 4:1 v/v) to afford compound **19** (35 mg, 72%) as colorless oil: $[\alpha]^{20}_{D}$ +53 (*c* 2.5, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.52 (d, *J* = 16.4 Hz, 1H), 6.14 (dd, *J* = 12.8, 3.9 Hz, 1H), 6.08 (d, *J* = 16.4 Hz, 1H), 5.78 (s, 1H), 5.64 (d, *J* = 16.1 Hz, 1H), 5.34 (d, *J* = 9.4 Hz, 2H), 5.24 – 5.16 (m, 2H), 5.09 (t, *J* = 6.9 Hz, 1H), 2.52 (s, 3H), 2.20 (s, 3H), 1.93 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 215.3, 200.2, 167.5, 159.8, 155.3, 145.4, 137.5, 134.1, 132.1, 128.3, 124.2, 123.6, 115.4, 82.0, 75.0, 74.7, 74.3, 44.7, 40.8, 39.0, 27.8, 25.8, 23.3, 23.0, 20.6, 18.6, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{27}H_{38}O_5S_2$, 529.2053; found, 529.2054.

*4R-hydroxyl vibsanin B (**20a**) and 4S-hydroxyl vibsanin B (**20b**).* To a solution of ViB (0.1 g) and $CeCl_3 \cdot 7H_2O$ (9 mg) in MeOH (5 mL) at 0 °C, was added portionwise of $NaBH_4$ (27 mg), the resulting mixture was stirred for 2 h at 0 °C. After completion, $NH_4Cl$ saturated aqueous solution (1 mL) and ethyl acetate (20 mL) were added, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate 3:1 – 2:1, v/v) to afford compound **20a** (48 mg, 48%) as white foam and compound **20b** (47 mg, 47%) as colorless wax.

**20a**: $[\alpha]^{23}_{D}$ +41 (*c* 2.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.82 – 5.75 (m, 1H), 5.74 (s, 1H), 5.59 (dd, *J* = 12.3, 3.7 Hz, 1H), 5.55 – 5.46 (m, 1H), 5.36 (d, *J* = 15.7 Hz, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 5.07 (t, *J* = 8.9 Hz, 3H), 4.28 (d, *J* = 12.1 Hz, 1H), 4.15 (d, *J* = 12.1 Hz, 1H), 2.16 (s, 3H), 1.90 (s, 3H), 1.64 (s, 3H), 1.54 (s, 3H), 1.26 (s, 3H), 1.02 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 167.7, 158.9, 147.7, 141.1, 140.4, 131.6, 129.4, 125.6, 124.6, 121.2, 115.7, 86.8, 75.8, 73.4, 66.7, 42.0, 40.7, 38.3, 27.7, 25.8, 23.4, 23.1, 22.7, 20.6, 17.8; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{25}H_{38}O_5Cl$, 453.2413; found, 453.2433.

**20b**: $[\alpha]^{23}_{D}$ +27 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 5.76 – 5.73 (m, 1H), 5.71 (d, *J* = 5.5 Hz, 1H), 5.68 (d, *J* = 5.3 Hz, 1H), 5.66 (d, *J* = 4.7 Hz, 1H), 5.43 (dd, *J* = 16.7, 1.1 Hz, 1H), 5.35 – 5.31 (m, 1H), 5.07 (d, *J* = 3.6 Hz, 1H), 4.87 (d, *J* = 4.2 Hz, 1H), 4.12 (s, 1H), 2.16 (d, *J* = 0.9 Hz, 2H), 2.09 – 2.05 (m, 1H), 1.91 (d, *J* = 0.9 Hz, 2H), 1.66 (s, 3H), 1.56 (s, 3H), 1.30 (d, *J* = 7.6 Hz, 3H), 1.05 (s, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 166.9, 158.2, 147.0, 144.2, 132.8, 131.6, 127.4,

124.7, 121.9, 120.8, 116.0, 76.9, 70.6, 69.3, 66.9, 43.6, 40.9, 38.3, 27.7, 25.8, 23.4, 23.0, 20.6, 20.1, 17.8; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{25}H_{38}O_5Cl$, 453.2413; found, 453.2433.

*Methyl oxime **22***. To a solution of mixed **20a** and **20b** (0.1 g) in DCM (7 mL) was added $MnO_2$ (0.21 g), the resulting suspension was stirred at RT for 2 h. The mixture was then passed a short pad of celite, the filter cake was washed with DCM (5 mL × 3), and the solvent was concentrated under vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 4:1, v/v) to afford compound **21** (85 mg, 89%) as yellow foam. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.42 (t, $J$ = 3.0 Hz, 1H), 6.63 (dd, $J$ = 12.7, 4.5 Hz, 1H), 5.80 (dd, $J$ = 15.6, 9.6 Hz, 1H), 5.74 (s, 1H), 5.32 (dd, $J$ = 15.7, 3.4 Hz, 2H), 5.28 – 5.16 (m, 1H), 5.05 (d, $J$ = 11.9 Hz, 1H), 5.00 (d, $J$ = 9.1 Hz, 1H), 4.53 (d, $J$ = 11.1 Hz, 1H), 4.48 (d, $J$ = 10.9 Hz, 1H), 2.17 (s, 3H), 1.91 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.29 (s, 3H), 1.16 (s, 3H); MS ESI (*m/z*): 439 $[M+Na]^+$

To a solution of compound **21** (20 mg) in 1.1 mL of pyridine/AcOH (10/1, v/v) was added *N*-methoxyhydroxylamine hydrochloride (8 mg), the reaction was allowed to warm to 40 °C and stirred for 12 h. After completion, 2 mL of water and 10 mL of ethyl acetate were added, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum to yield crude oxime intermediate. To a solution of this crude product in 2 mL of DCM was added TEMPO (0.8 mg) and PIDA (15 mg), the resulting mixture was stirred at RT for 2 h. The solvent was concentrated under vacuum, and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate 4:1, v/v) to afford compound **22** (13 mg, 60% over 2 steps) as colorless oil: $[\alpha]^{17}_D$ +20 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.71 (s, 1H), 6.49 (d, $J$ = 16.4 Hz, 1H), 6.07 (d, $J$ = 16.4 Hz, 1H), 6.03 (dd, $J$ = 13.0, 4.1 Hz, 1H), 5.78 (s, 1H), 5.59 (d, $J$ = 16.1 Hz, 1H), 5.32 (d, $J$ = 9.2 Hz, 1H), 5.17 (dd, $J$ = 16.1, 9.2 Hz, 1H), 5.09 (t, $J$ = 7.0 Hz, 1H), 3.83 (s, 3H), 2.20 (s, 3H), 1.94 (s, 3H), 1.68 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H), 1.03 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 198.4, 167.6, 160.0, 156.4, 149.5, 148.7, 145.4, 138.6, 134.6, 132.1, 128.5, 124.1, 115.3, 82.6, 74.6, 62.3, 44.9, 41.0, 39.4, 27.8, 25.8, 23.3, 20.7, 20.5, 18.8, 17.8; MS ESI (*m/z*): 444 $[M+H]^+$

*18-aldehyde vibsanin B (**9**)*[3a]. A 50 mL round bottom flask was charged with ViB (1 g) and DCM-DMSO (18 mL, 5 : 1, v/v), IBX (1.7 g) was added in. The mixture was stirred for 3 h at room

temperature. The mixture was passed through short pad of Celite. The solvent was concentrated under vacuum and the residue was purified by flash chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1, v/v) to afford the product as a colorless foam (yields: 95%): $[\alpha]^{20}_{D}$ +48 (*c* 2.2, $CH_2Cl_2$).

**General Procedure for Synthesis of Compounds 23a – 23c**[3a]. A solution of compound **7** (42 mg) in DCM (1 mL), the appropriate secondary amine (2 equiv.) and $NaBH(OAc)_3$ (42 mg) was stirred at RT. The progress of the reactions was monitored by TLC. The solvent was evaporated under vacuum and the mixture was purified by column chromatography on silica gel.

*18-carboxyl vibsanin B (**10**).* To a solution of compound **9** (0.2 g), 2-methyl-2-butene (1 mL) and $NaH_2PO_4$ (0.25 g) in *t*BuOH/$H_2O$ (4 mL, 3/1, v/v) was added portionwise of $NaClO_2$ (0.43 g), the resulting mixture was vigorously stirred at RT for 10 min. 5 mL of NaCl saturated aqueous solution was added, the mixture was extracted with ethyl acetate (5 mL × 3), and combined organic layers were washed with brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate 1:1 – 1:2, v/v) to afford compound **10** (0.18 g, 88%) as white foam: $[\alpha]^{17}_{D}$ +22 (*c* 2.5, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.21 (dd, *J* = 13.1, 3.5 Hz, 1H), 6.54 (d, *J* = 16.4 Hz, 1H), 6.11 (d, *J* = 16.5 Hz, 1H), 5.77 (s, 1H), 5.61 (d, *J* = 16.0 Hz, 1H), 5.37 (d, *J* = 9.4 Hz, 1H), 5.17 (dd, *J* = 16.2, 9.0 Hz, 1H), 5.10 (t, *J* = 6.0 Hz, 1H), 2.19 (s, 3H), 1.93 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.06 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 211.0, 196.8, 167.4, 159.9, 156.3, 145.1, 144.5, 134.9, 132.0, 131.6, 124.1, 123.9, 115.1, 82.2, 74.3, 53.7, 44.9, 41.2, 39.1, 27.6, 25.6, 23.1, 20.5, 18.4, 17.6; HRMS (ESI): $[M+Cl]^-$ calcd for $C_{25}H_{34}O_6Cl$, 465.2049; found, 465.2067.

**General Procedure for Synthesis of 18-*N*,*N*-dialkyl formamide vibsanin B (24b – 24f)**. To a solution of compound **10** (20 mg), corresponding amine (2 equiv.), DMAP (3 mg) in DCM (2 mL) was added EDCI (9 mg), the resulting mixture was stirred at RT for 12 – 24 h. After completion, water (2 mL) and DCM (10 mL) were added, and the organic layer was washed with brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum. The residue was purified by chromatography on silica gel.

*18-N,N-dimethyl formamide vibsanin B (**24a**)* (71%), slightly yellow oil: $[\alpha]^{17}_{D}$ +8 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.94 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.3 Hz, 1H), 6.01 (dd, *J* = 12.9, 3.9 Hz, 1H), 5.76 (s, 1H), 5.66 (d, *J* = 16.1 Hz, 1H), 5.43 (d, *J* = 9.1 Hz, 1H), 5.17 (dd, *J* = 16.1, 9.2 Hz, 1H), 5.05 (t, *J* = 7.1 Hz, 1H), 3.11 (s, 3H), 2.96 (s, 3H), 2.18 (s, 3H), 2.11 (dd, *J* = 13.8, 4.0 Hz, 1H), 1.92 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H), 1.09 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 197.5, 167.3, 166.9, 158.9, 158.0, 145.0, 139.7, 131.9, 131.8, 128.2, 124.2, 124.0, 115.6, 81.3, 74.2, 44.5, 40.8, 39.3, 39.1, 35.2, 27.7, 25.8, 23.2, 23.0, 20.6, 18.3, 17.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{40}NO_5$, 458.2901; found, 458.2901.

*18-N,N-diethyl formamide vibsanin B (**24b**)* (78%), slightly yellow oil: $[\alpha]^{17}_{D}$ +30 (*c* 3.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 7.02 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.3 Hz, 1H), 5.94 (dd, *J* = 12.9, 3.8 Hz, 1H), 5.76 (s, 1H), 5.69 (d, *J* = 16.1 Hz, 1H), 5.44 (d, *J* = 9.1 Hz, 1H), 5.17 (dd, *J* = 16.1, 9.1 Hz, 1H), 5.07 (t, *J* = 7.0 Hz, 1H), 3.67 (m, 1H), 3.44 (m, 1H), 3.37 (m, 2H), 2.19 (s, 3H), 1.93 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H), 1.12 (m, 6H), 1.03 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 197.4, 167.0, 166.7, 159.0, 158.4, 145.1, 140.5, 131.9, 130.1, 128.3, 124.2, 124.0, 115.6, 81.5, 74.3, 44.5, 43.2, 40.8, 39.4, 39.1, 27.7, 25.8, 23.3, 23.0, 20.6, 18.3, 17.8, 14.3, 12.8; HRMS (ESI): $[M-H]^-$ calcd for $C_{29}H_{42}NO_5$, 484.3068; found, 484.3100.

*18-N,N-diisopropyl formamide vibsanin B (**24c**)* (70%), slightly yellow oil: $[\alpha]^{17}_{D}$ +12 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.49 (d, *J* = 16.2 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 5.78 (d, *J* = 15.8 Hz, 1H), 5.76 (s, 1H), 5.37 (d, *J* = 9.8 Hz, 1H), 5.15 (dd, *J* = 16.4, 8.9 Hz, 1H), 5.05 (t, *J* = 7.0 Hz, 1H), 4.07 (dt, *J* = 13.2, 6.7 Hz, 1H), 3.44 (dt, *J* = 13.6, 6.7 Hz, 1H), 2.32 (dd, *J* = 14.4, 10.1 Hz, 1H), 2.17 (s, 3H), 2.01 (dd, *J* = 14.4, 3.8 Hz, 1H), 1.92 (s, 3H), 1.68 (s, 3H), 1.56 (s, 3H), 1.47 (d, *J* = 6.8 Hz, 6H), 1.38 (s, 3H), 1.12 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 197.9, 167.0, 165.3, 159.1, 155.5, 145.1, 144.1, 141.0, 138.3, 131.9, 124.2, 123.8, 115.6, 83.2, 76.5, 51.4, 45.9, 42.8, 41.7, 40.0, 37.1, 35.4, 27.7, 25.8, 23.4, 21.1, 21.0, 20.7, 20.6, 20.4, 17.7; HRMS (ESI): $[M+H]^+$ calcd for $C_{31}H_{48}NO_5$, 514.3527; found, 514.3529.

*18-pyrrolidinyl formamide vibsanin B (**24d**)* (68%), slightly yellow oil: $[\alpha]^{16}_{D}$ +15 (*c* 2.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.82 (d, *J* = 16.3 Hz, 1H), 6.37 (dd, *J* = 13.0, 3.8 Hz, 1H), 6.19 (dd, *J* = 12.5, 4.6 Hz, 1H), 6.10 (t, *J* = 12.7 Hz, 1H), 5.77 (s, 1H), 5.64 (d, *J* = 16.2 Hz, 1H), 5.40 (d, *J* = 9.1

Hz, 1H), 5.18 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.07 (t, *J* = 7.1 Hz, 1H), 3.64 (dd, *J* = 10.5, 5.2 Hz, 1H), 3.49 (m, 1H), 3.42 (dd, *J* = 16.9, 6.9 Hz, 1H), 3.36 (m, 1H), 2.19 (s, 3H), 1.94 (s, 3H), 1.66 (s, 3H), 1.57 (s, 3H), 1.37 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 198.2, 167.1, 166.5, 159.3, 157.4, 145.1, 140.3, 134.6, 132.0, 128.7, 124.2, 124.0, 115.5, 81.6, 74.3, 48.7, 46.5, 44.7, 41.0, 39.1, 27.8, 26.3, 25.8, 24.3, 23.3, 23.1, 20.6, 18.5, 17.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{29}H_{42}NO_5$, 484.3057; found, 484.3058.

*18-morpholinyl formamide vibsanin B* ***(24e)*** (82%), slightly yellow oil: $[\alpha]^{16}_D$ +11 (*c* 5.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.96 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.3 Hz, 1H), 5.99 (dt, *J* = 13.2, 6.6 Hz, 1H), 5.76 (s, 1H), 5.67 (d, *J* = 16.1 Hz, 1H), 5.44 (d, *J* = 9.1 Hz, 1H), 5.18 (dd, *J* = 16.1, 9.2 Hz, 1H), 5.05 (t, *J* = 7.1 Hz, 1H), 3.95 – 3.34 (m, 8H), 2.19 (s, 3H), 2.10 (dd, *J* = 13.8, 3.9 Hz, 1H), 1.93 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H), 1.10 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 197.1, 167.0, 165.9, 159.2, 158.3, 145.0, 139.5, 139.2, 132.0, 131.9, 128.1, 124.1, 115.5, 81.4, 74.2, 67.2, 66.7, 48.0, 44.5, 42.5, 40.9, 39.1, 27.7, 25.8, 23.3, 23.0, 20.6, 18.3, 17.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{29}H_{42}NO_6$, 484.3057; found, 484.3058.

*18-(N-methylpiperazinyl) formamide vibsanin B* ***(24f)*** (75%), yellow oil: $[\alpha]^{23}_D$ +35 (*c* 13.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.98 (d, *J* = 16.3 Hz, 1H), 6.06 (d, *J* = 16.3 Hz, 1H), 5.97 (dd, *J* = 12.9, 3.9 Hz, 1H), 5.77 (s, 1H), 5.67 (d, *J* = 16.2 Hz, 1H), 5.44 (d, *J* = 9.1 Hz, 1H), 5.18 (dd, *J* = 16.1, 9.2 Hz, 1H), 5.06 (t, *J* = 7.1 Hz, 1H), 3.84 (m, 4H), 3.52 (brs, 2H), 3.42 (brs, 2H), 2.30 (s, 3H), 2.19 (s, 3H), 2.10 (dd, *J* = 13.8, 3.9 Hz, 1H), 1.93 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.37 (s, 3H), 1.10 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 197.2, 167.1, 165.7, 159.2, 158.4, 145.0, 139.8, 132.0, 131.4, 128.2, 124.2, 124.0, 115.5, 81.5, 74.3, 55.4, 54.6, 47.5, 46.1, 44.5, 42.0, 40.9, 39.1, 27.7, 25.8, 23.3, 23.0, 20.6, 18.4, 17.8; HRMS (ESI): $[M+H]^+$ calcd for $C_{30}H_{45}N_2O_5$, 513.3328; found, 513.3329.

**General Procedure for Synthesis of Compounds 26b and 26c.** To a solution of compound **13b** (0.5 g), $CeCl_3 \cdot 7H_2O$ (35 mg) or compound **13c** (0.5 g), $CeCl_3 \cdot 7H_2O$ (28 mg) in MeOH (10 mL) at -78 °C, was added portionwise of $NaBH_4$ (0.11 g) or (86 mg), the resulting mixture was stirred at -78 °C for 2 h. After completion, $NH_4Cl$ saturated aqueous solution (1 mL) and ethyl acetate (20 mL) were added, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and

concentrated under vacuum to yield crude **25b** or **25c** which was used in next step without further purification.

The crude **25b** or **25c** was dissolved in DCM (10 mL), to this solution was added TEA (390 $\mu$L) or (320 $\mu$L) and TESCl (315 $\mu$L) or (255 $\mu$L), the resulting mixture was stirred at RT for 8 h. After completion, water (1 mL) and DCM (20 mL) were added, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum to yield crude disilane intermediate. This crude product was dissolved in THF/$Et_2O$ (10 mL, 1/1, v/v) at 0 °C, to this solution was added $LiBH_4$ (41 mg) or (33 mg), the reaction was allowed to warm to RT and stirred for 12 h. After completion, $NH_4Cl$ saturated aqueous solution (1 mL) and ethyl acetate (20 mL) were added, the organic layer was washed with brine (10 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate 6:1, v/v) to afford compound **26b** (0.395 g, 75% over 3 steps) as colorless oil and compound **26c** (0.365 g, 70% over 3 steps). **26b**: MS ESI (*m/z*): 586 $[M+Na]^+$; **26c**: MS ESI (*m/z*): 711 $[M+Na]^+$.

**General Procedure for Synthesis of compounds 28b – 28e**. To a solution of compound **26b** (50 mg), corresponding acid (0.18 mmol), DMAP (5mg) in DCM (5 mL) at 0 °C was added DCC (37 mg), the reaction was allowed to warm to RT and stirred for 12 – 24 h. After completion, water (1 mL) and ethyl acetate (10 mL) were added, and the organic layer was washed with brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum to give crude ester. This crude product was dissolved in AcOH/THF/$H_2O$ (6.5 mL, 8/2/1, v/v) and stirred for 2 – 4 h. After completion, ethyl acetate (10 mL) was added, the organic layer was washed with $NaHCO_3$ saturated aqueous solution (10 mL × 2), brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum to give the crude C4-OTES removed intermediate. This crude product was dissolved in DCM/DMSO (6 mL, 5/1, v/v), to this solution was added IBX (75 mg), the resulting mixture was stirred at RT for 2 – 6 h. After completion, the mixture was passed a short pad of celite, the filter cake was washed with ethyl acetate (5 mL × 3), and the combined organic layers were washed with brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum to give crude ketones **27b** – **27e**. This crude product was dissolved in THF/AcOH (2.1 mL, 20/1, v/v), to this solution was added TBAF (90 $\mu$L, 2 M in THF), the resulting mixture was stirred 1 – 4 h. After completion, water (1 mL) and ethyl acetate (10 mL)

were added, and the organic layer was washed with brine (5 mL × 3), dried over $Na_2SO_4$, and concentrated under vacuum, and the residue was purified by chromatography on silica gel.

**28b**, (32% over 4 steps), colorless oil: $[\alpha]^{17}_D$ +9 (*c* 4.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.55 (d, *J* = 16.3 Hz, 1H), 6.08 (d, *J* = 16.3 Hz, 1H), 5.97 (dd, *J* = 12.9, 3.8 Hz, 1H), 5.70 (d, *J* = 16.2 Hz, 1H), 5.33 (d, *J* = 9.1 Hz, 1H), 5.14 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.10 (t, *J* = 7.0 Hz, 1H), 4.42 (d, *J* = 12.6 Hz, 1H), 4.12 (d, *J* = 12.7 Hz, 1H), 2.15 (s, 3H), 2.04 (brd, *J* = 10.9 Hz, 1H), 1.68 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H), 1.02 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 202.9, 171.8, 154.8, 146.1, 142.9, 131.9, 129.8, 129.0, 124.3, 123.0, 82.0, 74.0, 65.3, 44.8, 41.0, 40.8, 38.9, 25.8, 22.9, 21.4, 18.3, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{32}O_5Na$, 399.2147; found, 399.2141.

**28c**, (26% over 4 steps), colorless oil: $[\alpha]^{20}_D$ +28 (*c* 2.1, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.56 (d, *J* = 16.3 Hz, 1H), 6.07 (d, *J* = 16.3 Hz, 1H), 5.97 (dd, *J* = 12.8, 3.8 Hz, 1H), 5.69 (d, *J* = 16.2 Hz, 1H), 5.33 (d, *J* = 9.1 Hz, 1H), 5.15 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.09 (t, *J* = 7.0 Hz, 1H), 4.41 (d, *J* = 12.5 Hz, 1H), 4.14 (d, *J* = 12.7 Hz, 1H), 2.64 (m, 1H), 1.67 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.03 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 202.8, 178.0, 154.9, 146.0, 142.9, 131.9, 129.7, 128.8, 124.3, 123.0, 81.9, 74.2, 65.2, 44.7, 40.8, 38.9, 34.3, 25.8, 23.3, 23.0, 19.2, 18.9, 18.3, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{36}O_5Na$, 427.2460; found, 427.2462.

**28d**, (35% over 4 steps), colorless oil: $[\alpha]^{17}_D$ +27 (*c* 2.1, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.53 (d, *J* = 16.3 Hz, 1H), 6.08 (d, *J* = 16.4 Hz, 1H), 5.98 (dd, *J* = 12.8, 3.9 Hz, 1H), 5.68 (d, *J* = 16.2 Hz, 1H), 5.35 (d, *J* = 9.2 Hz, 1H), 5.16 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.09 (t, *J* = 7.0 Hz, 1H), 4.41 (d, *J* = 12.7 Hz, 1H), 4.16 (d, *J* = 12.7 Hz, 1H), 2.40 (m, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.37 (s, 3H), 1.03 (s, 3H), 0.98 (td, *J* = 7.4, 2.3 Hz, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 202.6, 174.7, 154.5, 146.0, 142.8, 132.0, 129.8, 128.9, 124.3, 123.1, 82.1, 74.2, 65.3, 44.8, 40.8, 38.9, 36.5, 25.9, 23.3, 23.0, 18.6, 18.5, 17.8, 13.8; HRMS (EI): $[M]^+$ calcd for $C_{24}H_{36}O_5$, 404.2563; found, 404.2562.

**28e**, (42% over 4 steps), colorless oil: $[\alpha]^{18}_D$ +50 (*c* 2.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 8.09 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 6.61 (d, *J* = 16.4 Hz, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 6.01 (dd, *J* = 12.8, 4.0 Hz, 1H), 5.78 (d, *J* = 16.2 Hz, 1H), 5.61 (d, *J* = 9.1 Hz, 1H), 5.31 (dd, *J* = 16.2, 9.2 Hz, 1H), 5.10 (t, *J* = 7.0 Hz, 1H), 4.43 (d, *J* = 12.6 Hz, 1H), 4.19 (d, *J* = 12.6

Hz, 1H), 1.68 (s, 3H), 1.58 (s, 3H), 1.50 (s, 3H), 1.06 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 202.5, 167.2, 154.3, 146.3, 142.8, 133.7, 132.0, 130.0, 129.8, 129.7, 129.0, 128.7, 124.3, 123.1, 82.8, 74.5, 65.3, 44.9, 40.9, 39.0, 25.8, 23.3, 23.0, 18.7, 17.9; HRMS (EI): $[M]^+$ calcd for $C_{27}H_{34}O_5$, 438.2406; found, 438.2399.

*Synthesis of Compounds **28f***. Prepared by using **26c** (50 mg), diisopropylethylamine (38 $\mu$L) and MOMCl (11 $\mu$L) following the general procedure for synthesis of compounds **28b** – **28e** to afford **28f** (28% over 4 steps) as colorless oil: $[\alpha]^{16}_D$ +11 (*c* 5.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 6.46 (d, *J* = 16.4 Hz, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 5.99 (dd, *J* = 12.8, 3.8 Hz, 1H), 5.61 (d, *J* = 16.1 Hz, 1H), 5.21 (dd, *J* = 16.1, 9.0 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 4.71 (d, *J* = 7.3 Hz, 1H), 4.62 (d, *J* = 7.4 Hz, 1H), 4.43 (dd, *J* = 12.2, 3.9 Hz, 1H), 4.28 (d, *J* = 9.0 Hz, 1H), 4.17 (d, *J* = 12.3 Hz, 1H), 3.38 (s, 3H), 1.68 (s, 3H), 1.59 (s, 3H), 1.39 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 202.2, 153.6, 144.9, 142.7, 131.9, 130.4, 130.1, 125.1, 124.4, 92.2, 80.6, 80.5, 65.5, 55.8, 45.1, 40.8, 39.0, 25.8, 23.4, 23.0, 17.8, 14.4; HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{34}O_5Na$, 401.2298; found, 401.2301.

*4R-methoxyl vibsanin B (**29a**) and 4S-methoxyl vibsanin B (**29b**)*. Prepared by using crude **25b** (0.1 g), silver oxide (220 mg) and MeI (60 $\mu$L) following the general procedure for synthesis of compounds **28b** – **28e** to afford **29a** (42% over 2 steps) and **29b** (41% over 2 steps) as colorless oil.

**29a**: $[\alpha]^{15}_D$ +26 (*c* 1.3, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 5.75 (s, 1H), 5.63 (m, 2H), 5.50 (d, *J* = 15.8 Hz, 1H), 5.39 (d, *J* = 15.7 Hz, 1H), 5.16 (dd, *J* = 15.8, 9.4 Hz, 1H), 5.06 (d, *J* = 9.3 Hz, 2H), 4.69 (d, *J* = 9.6 Hz, 1H), 4.31 (t, *J* = 9.6 Hz, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.27 (s, 3H), 2.18 (s, 3H), 1.99 (dd, *J* = 13.0, 4.2 Hz, 1H), 1.92 (s, 3H), 1.65 (s, 3H), 1.55 (s, 3H), 1.28 (s, 3H), 1.05 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$ 166.8, 158.1, 146.5, 141.3, 139.2, 130.5, 125.2, 124.6, 123.4, 120.0, 114.4, 86.6, 81.9, 74.9, 65.5, 55.0, 40.8, 39.6, 37.1, 30.0, 26.6, 24.7, 22.3, 22.0, 19.4, 16.6; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{40}O_5Na$, 455.2768; found, 455.2770.

**29b**: $[\alpha]^{15}_D$ +22 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) $\delta$ 5.75 (s, 1H), 5.73 (d, *J* = 4.7 Hz, 1H), 5.63 (d, *J* = 5.2 Hz, 1H), 5.50 (d, *J* = 0.9 Hz, 1H), 5.35 (m, 1H), 5.21 (d, *J* = 7.3 Hz, 1H), 5.07 (s, 1H), 4.35 (d, *J* = 4.6 Hz, 1H), 4.10 (s, 1H), 3.28 (s, 2H), 2.31 (t, *J* = 13.0 Hz, 1H), 2.17 (s, 3H), 1.91 (s, 3H), 1.66 (s, 3H), 1.56 (s, 3H), 1.32 (s, 3H), 1.04 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) $\delta$

166.9, 158.3, 147.3, 141.6, 135.1, 134.0, 131.5, 127.2, 124.7, 120.7, 115.9, 79.5, 76.8, 69.3, 66.8, 56.7, 43.1, 40.7, 38.4, 31.1, 27.7, 25.8, 23.4, 23.0, 20.6, 17.8; HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{40}O_5Na$, 455.2768; found, 455.2769.

**Precedure for preparation of plasimids and recobinant HSP90β-CTD protein**

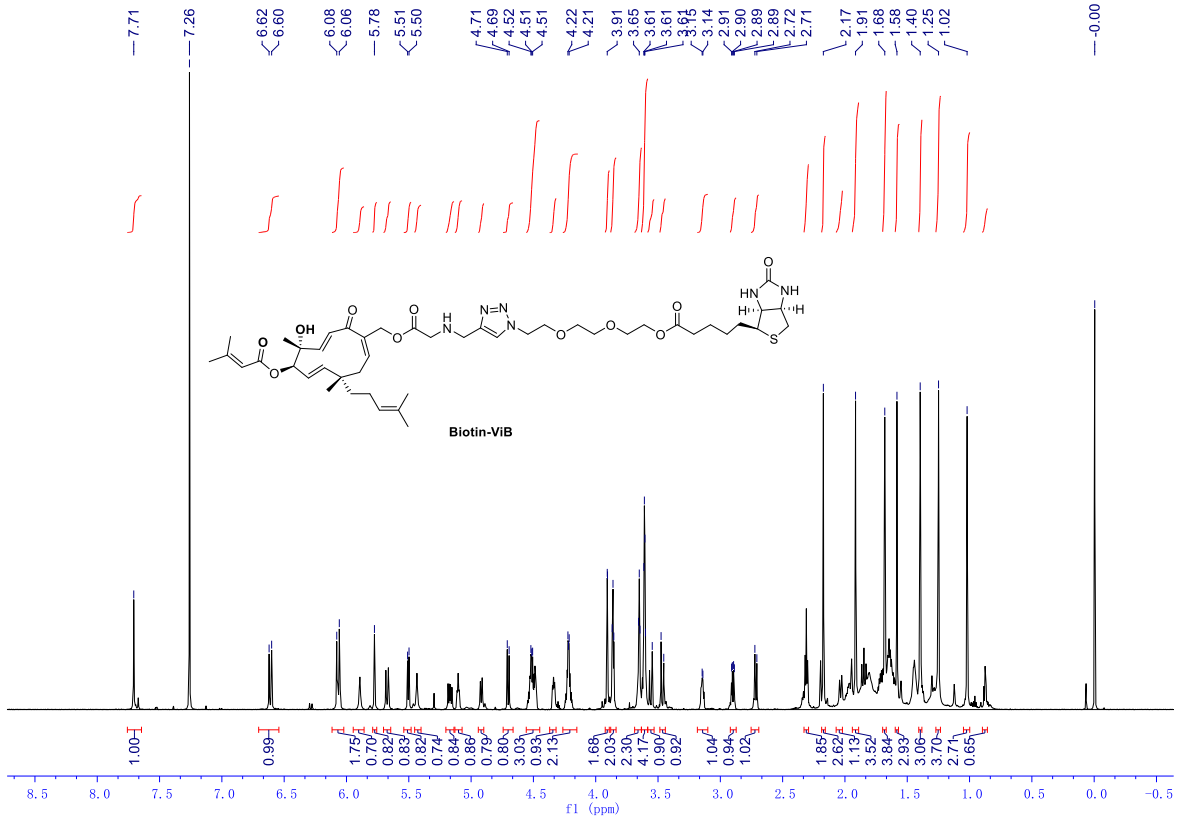
*Plasimids.* Human HSP90β gene coding sequnece is cloned from the plasmid vector pcDNA3.1-Flag-HSP90β in Chen's lab,[5] and subcloned into pET28a(+) vector to generate a 6×His-tagged fusion protein. The HSP90β CTD coding sequence(E547-D724) is also cloned from vector pcDNA3.1-Flag-HSP90β and then subcloned into the pET28a(+) vector, producing the vector called pET-28a(+)-HSP90β-CTD. HSP90β NTD (amino acid: P2-K234), MD (amino acid: S261-K552) and CTD (amino acid: E547-D724) sequences were also cloned from pcDNA3.1-Flag-HSP90β vector and subcloned into pcDAN3.1-Flag empity vector, generating pcDNA3.1-Flag-HSP90β-NTD, pcDNA3.1-Flag-HSP90β-MD and pcDNA3.1-Flag-HSP90β-CTD vectors, respectively. The specific primers used to amplify the coding sequence for the specific vectors are listed in the TableS4 and TableS5. All of the coding genes in above vectors were sequenced and convinced a 100% identies match.

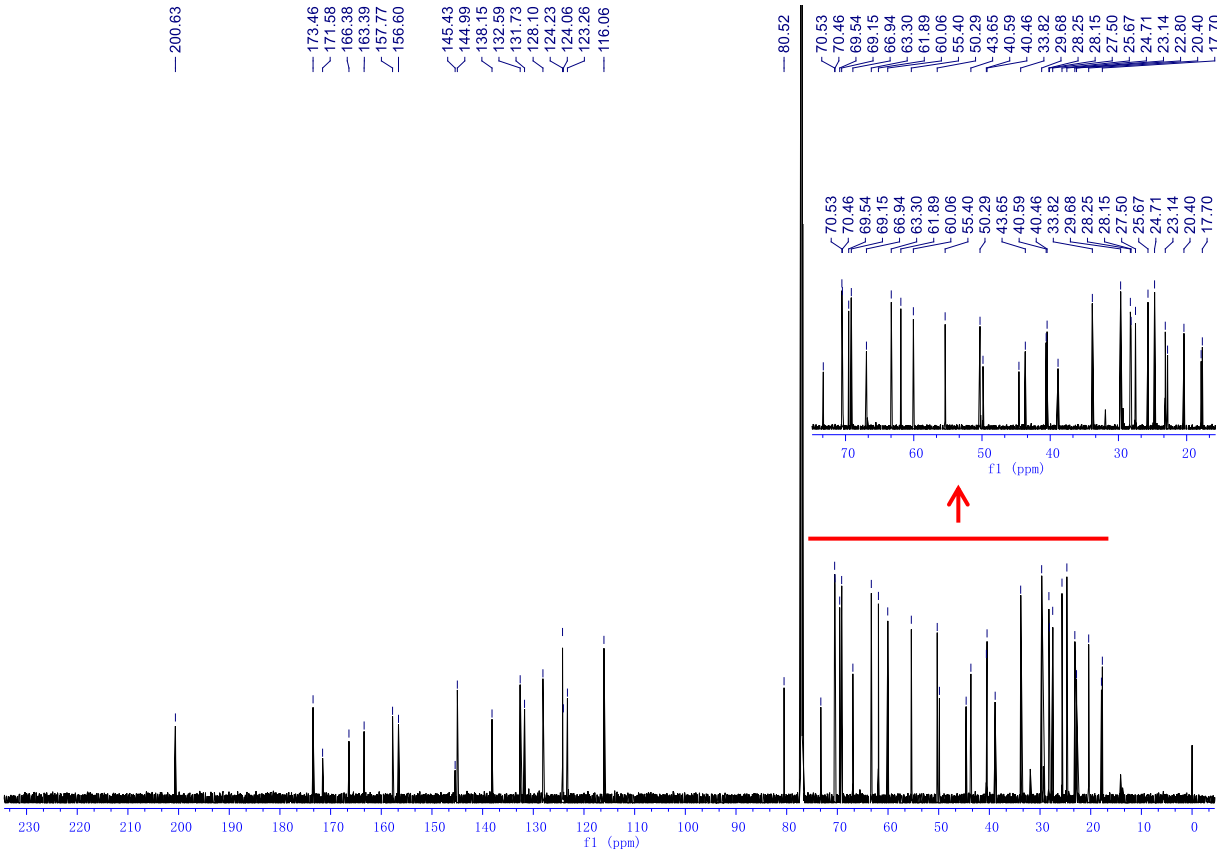
*Preparation of recombinant HSP90β-CTD protein.* The *E. coli* strain BL21(DE3) was transformed with pET28a-HSP90β-C, and cultured in LB medium containing 100μg/mL kanamycin at 37℃. When the absorbance of culturing medium is from 0.6 to 1.0 at 600 nm, the BL21 *E. coli* with transformed vectors was induced with 0.5 mM isopropyl-D-1-thiogalactopyranoside (IPTG) for 4 hours before being harvested by centrifugation. Then the cell pellets were suspended in equilibration buffer (20 mM TrisHCl, 100 mM NaCl, pH 8.0，5mM β-Mercaptoethanol (β-ME), 1mM PMSF) and homonized by sonication. After centrifugation(25000rpm, 45min), the supernatant was loaded to a HisTrap column (GE Healthcare) and washed with washing buffer (20mM Tris, 300mM NaCl, 25mM imidazole, 5mM β-ME, pH 8.0). Then the column was eluted with elution buffer (20 mM TrisHCl, 100 mM NaCl, 150mM imidazole, 1mM PMSF, 5mM β-ME, pH 8.0) and the expressed proteins were collected according to the absorbance peak at 280 nm on the FPLC (GE Healthcare). Then the protein within elution buffer was subject to dialysis in the dialysis buffer (20mM TrisHCl, 20mM NaCl, EDTA 5mM, pH 8.0 ) at 4℃ overnight. After dialysis, the protein exchanged with dialysis buffer was loaded to ion exchange column Q (GE Healthcare) and washed

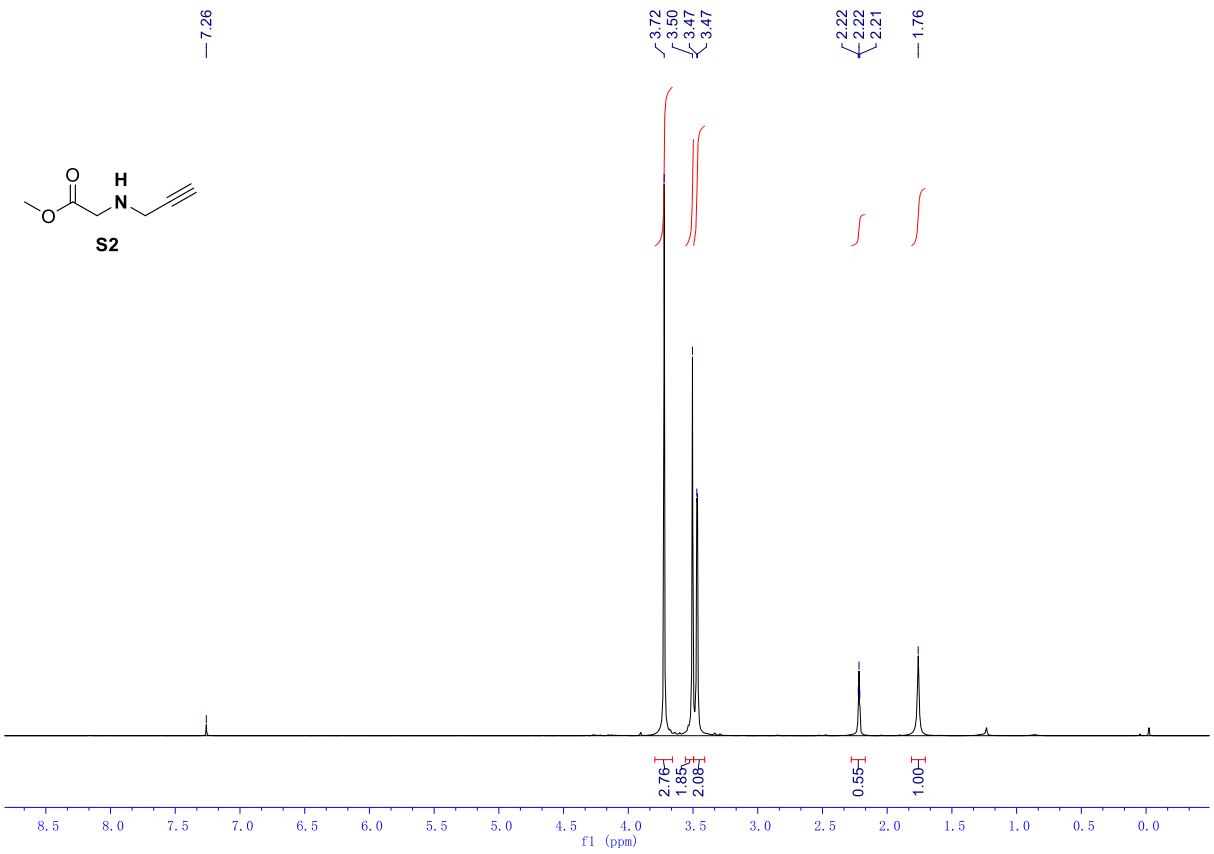
with low salt buffer (20 mM Tris, 20 mM NaCl, 5mM EDTA, 5mM β-ME, pH 8.0). The HSP90β-CTD protein was eluted with a NaCl gradient (20 mM Tris, pH 8.0, 0 - 1 M NaCl).

*Western blot analysis.* Cell lysates were subjected to be electrophoresed and seperated in the 10% SDS-PAGE, and then the proteins in the gel were transferred to enhanced chemiluminescence-nitrocellulose membranes (Bio-Rad, catlog: 162-0112). After blocking with 5% nonfat milk in Tris-buffered saline, the membranes were incubated with the antibody against His or Flag tags（Cell signaling Technology）overnight at 4 °C, followed by incubation of horseradish peroxidase (HRP)-linked secondary antibody (Cell Signaling Technology ) for 1 hour at room temperature. Detection was performed by Immobilon Western Chemiluminescent HRP substrate Kit (Millipore, cat. No. WBKLS0100) according to the chemoiluminal manufacturer's instruction (LAS-4000, FUJIFILM). Signal intensity of protein was normalized against ubiquitously expressed proteins GAPDH or actin using Quantity One (Bio-Rad, Hercules, CA, USA) software.

## $^{1}H$ and $^{13}C$ NMR spectra of tested compounds

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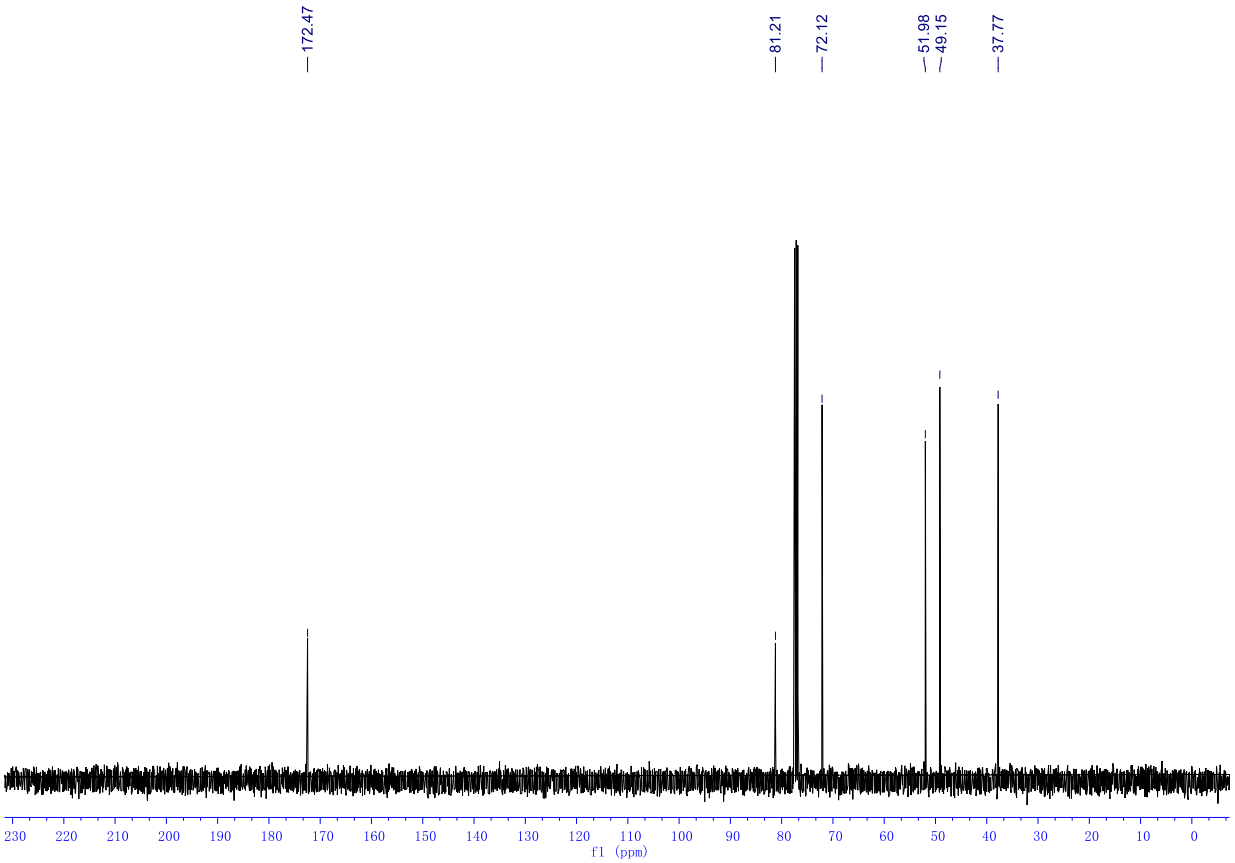
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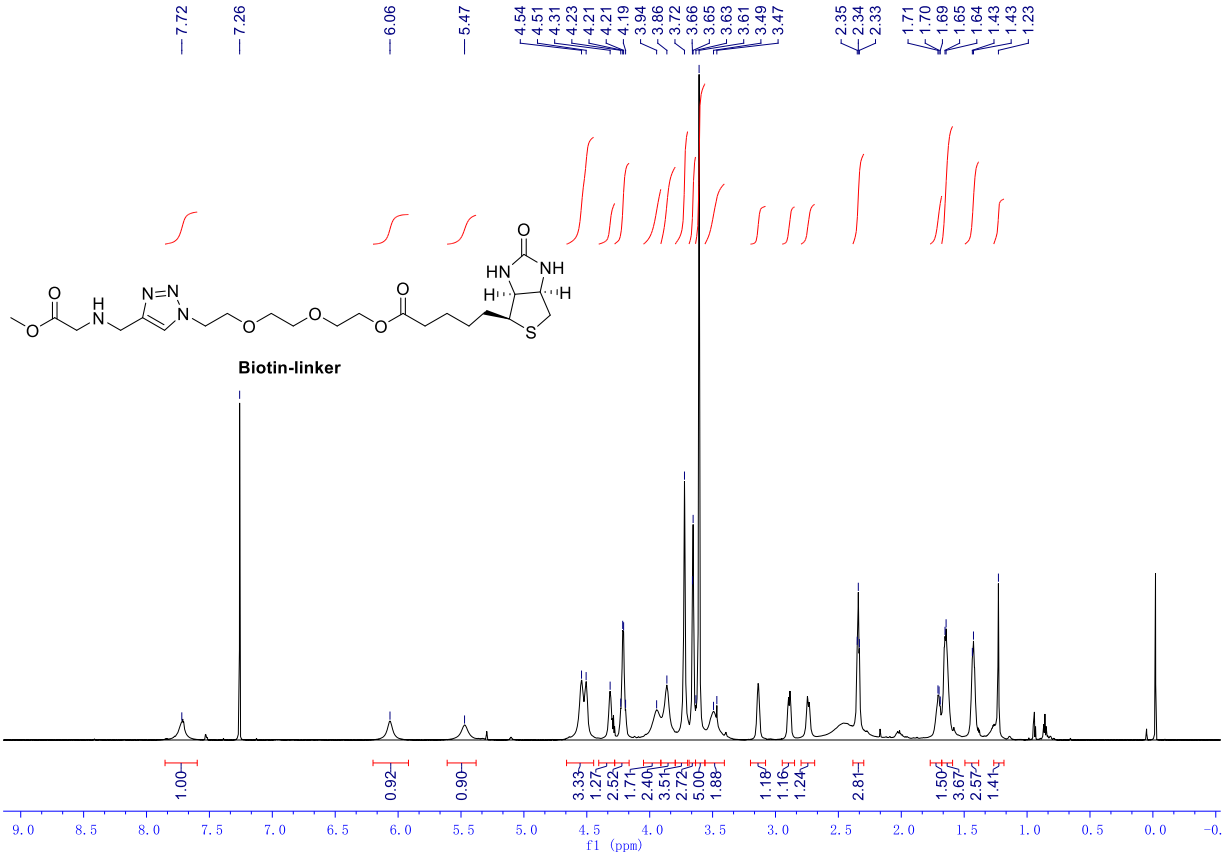
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1.70
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1.43
1.23
Biotin-linker
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0.90
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1.27
2.52
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2.40
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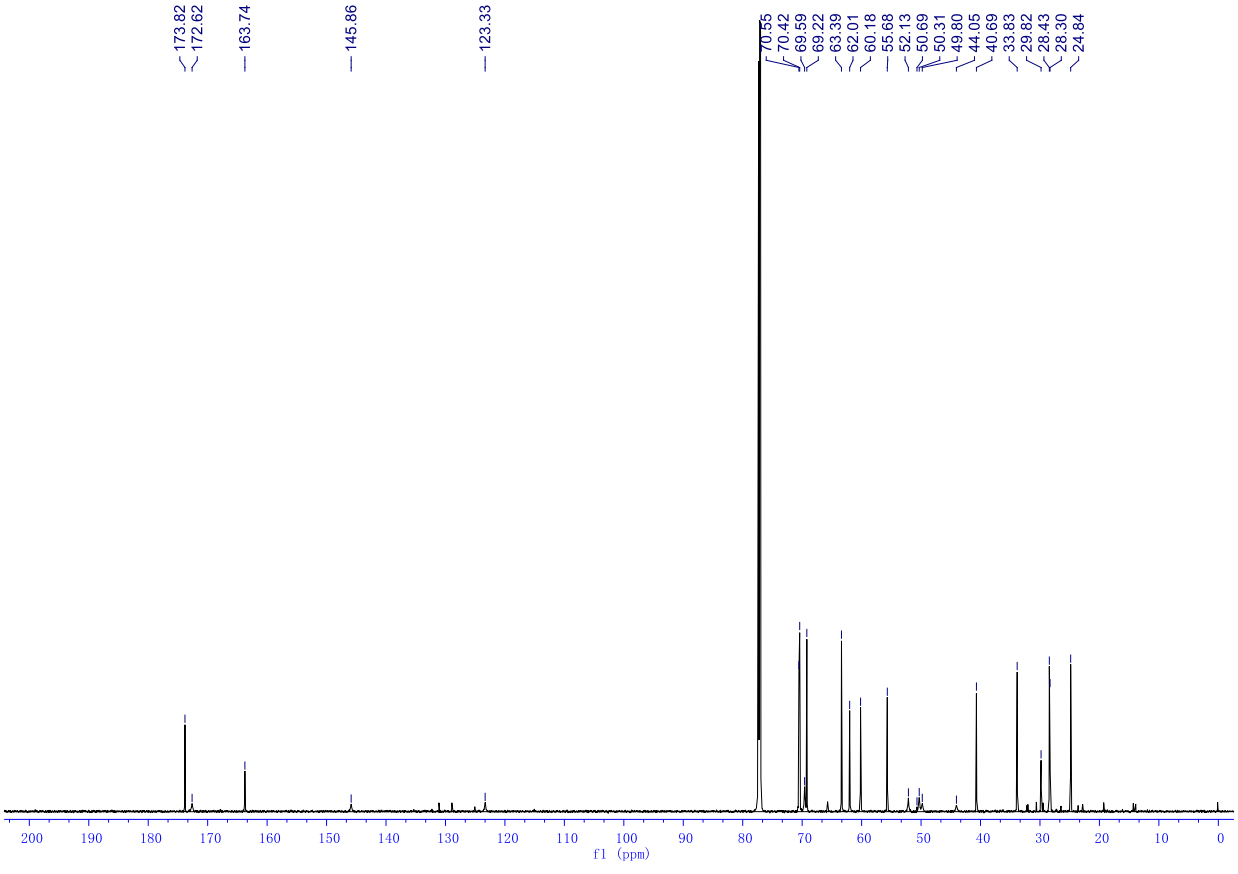
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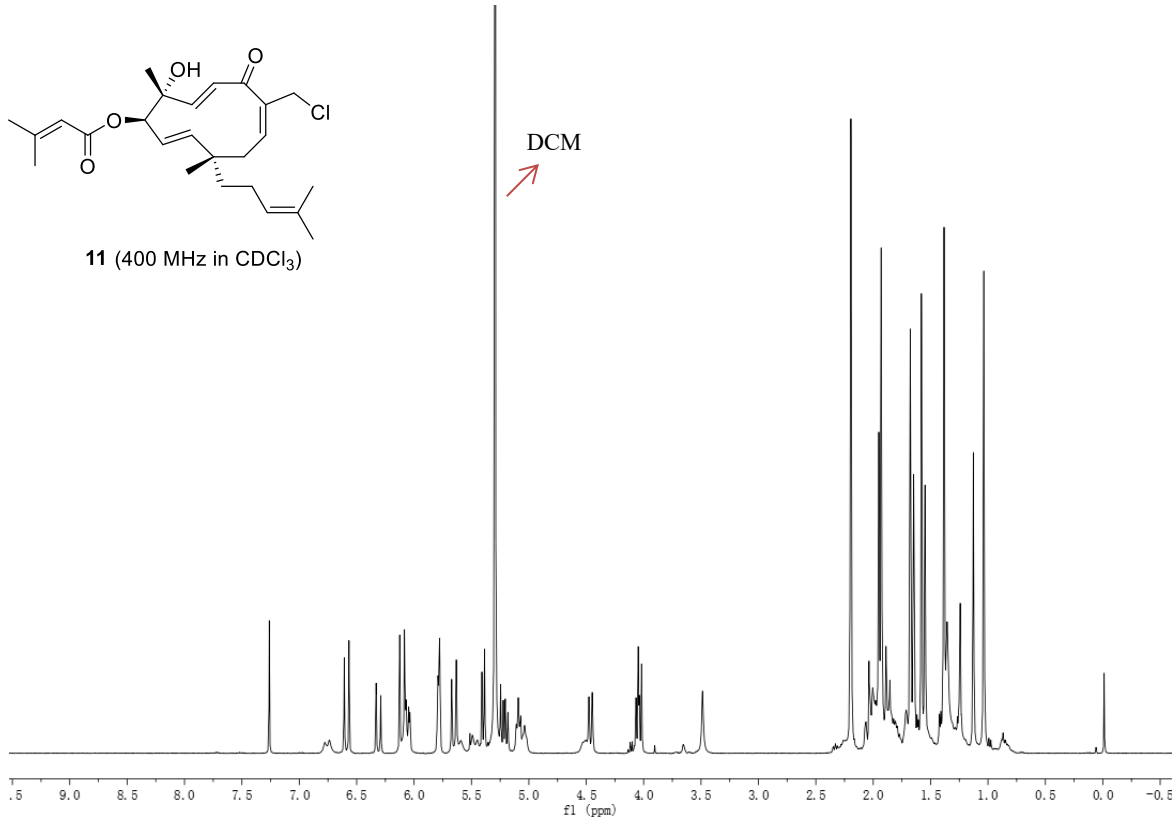
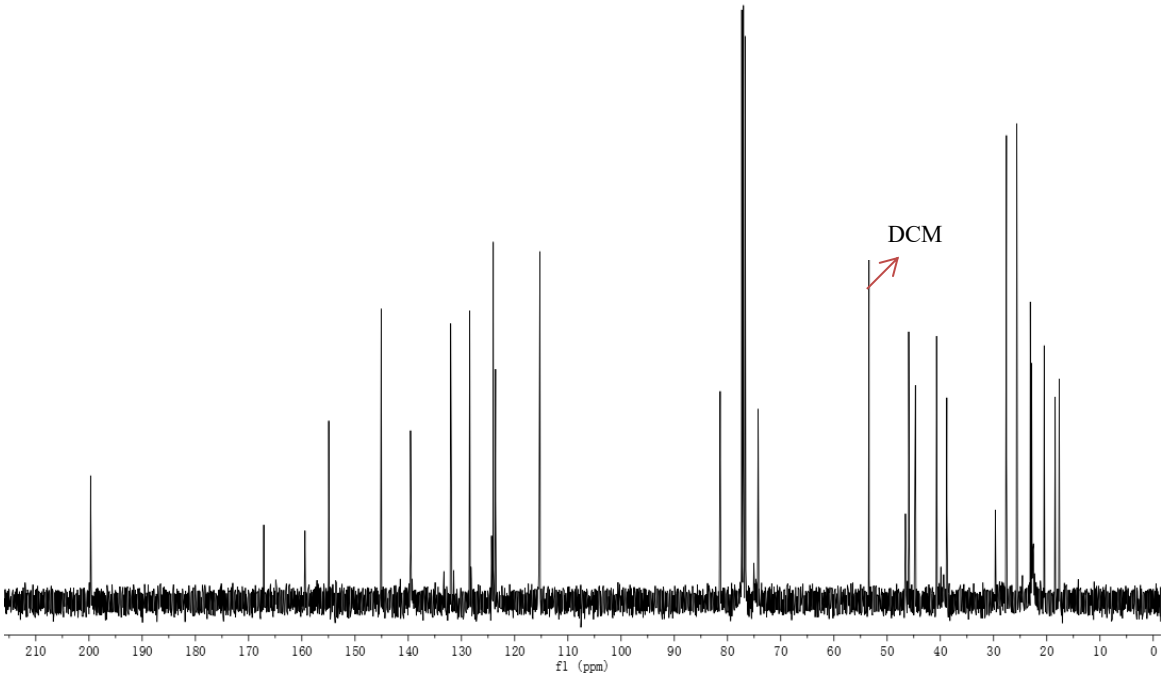
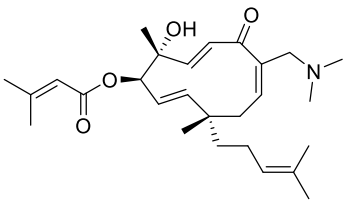


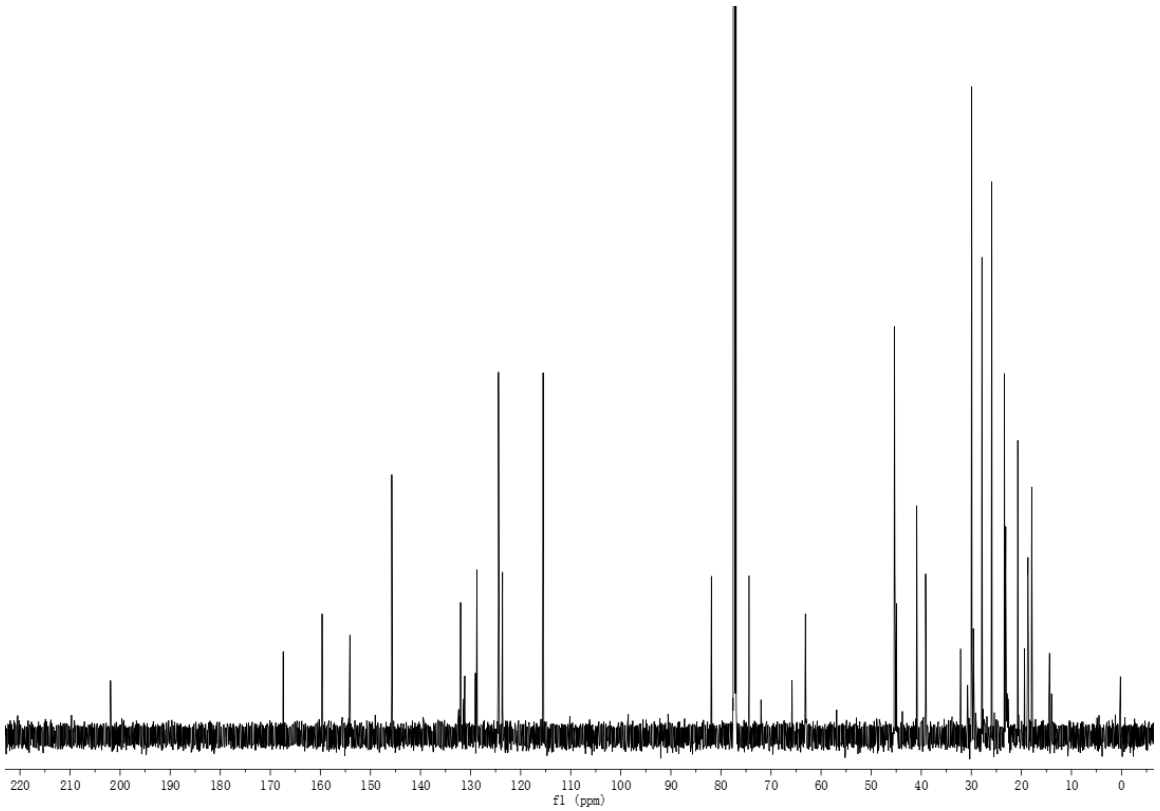

**11** (400 MHz in $CDCl_3$)

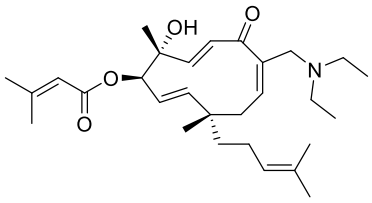





**12a** (600 MHz in $CDCl_3$)

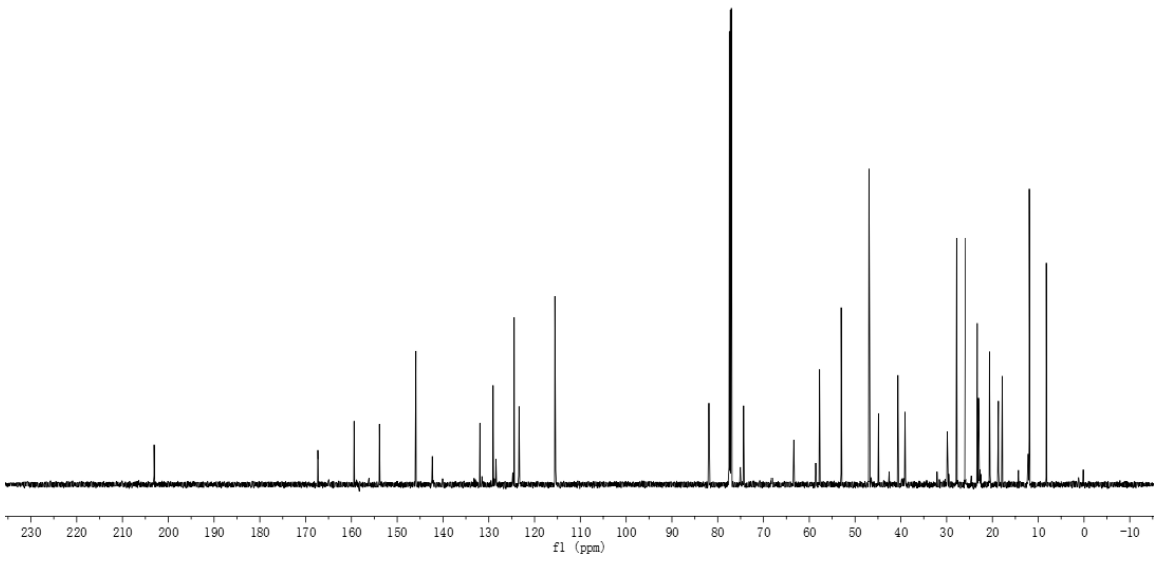


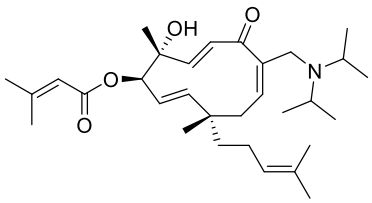






**12b** (600 MHz in $CDCl_3$)

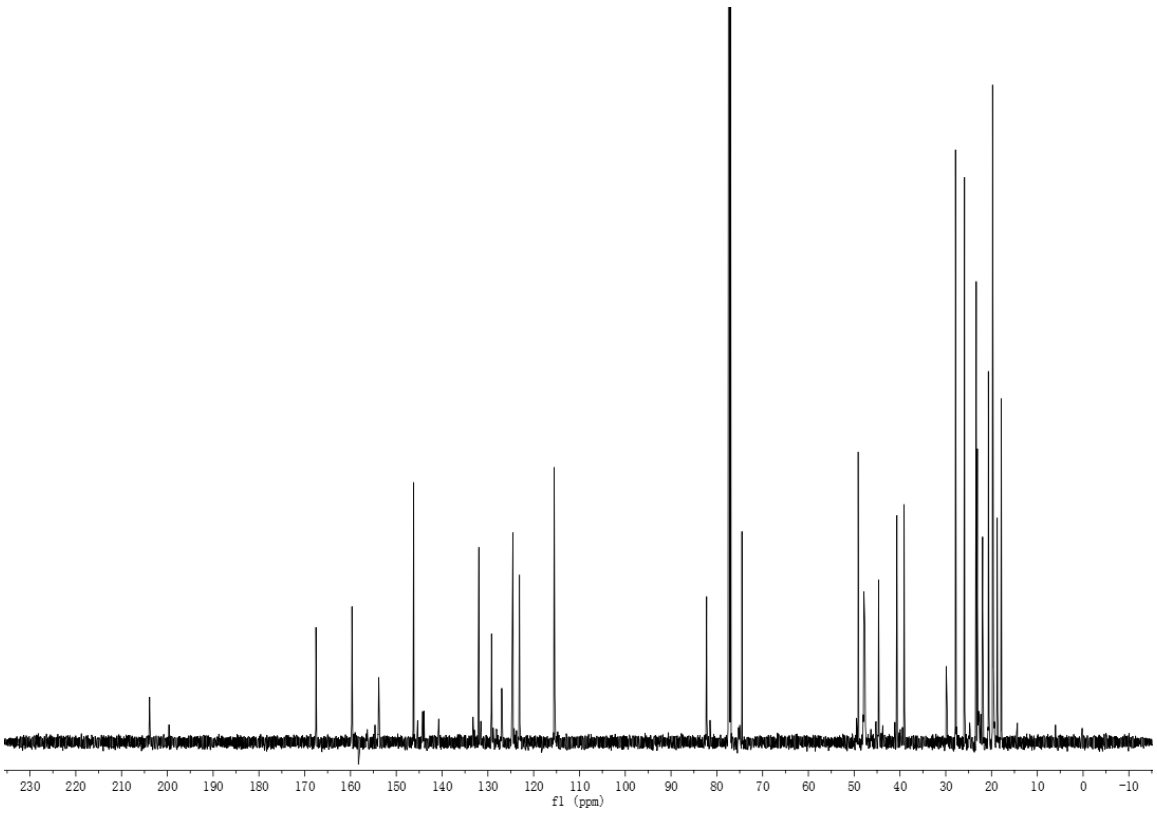


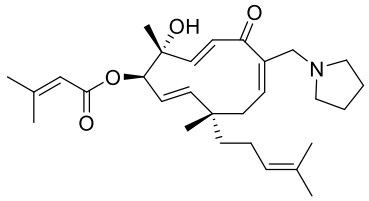






**12c** (600 MHz in $CDCl_3$)

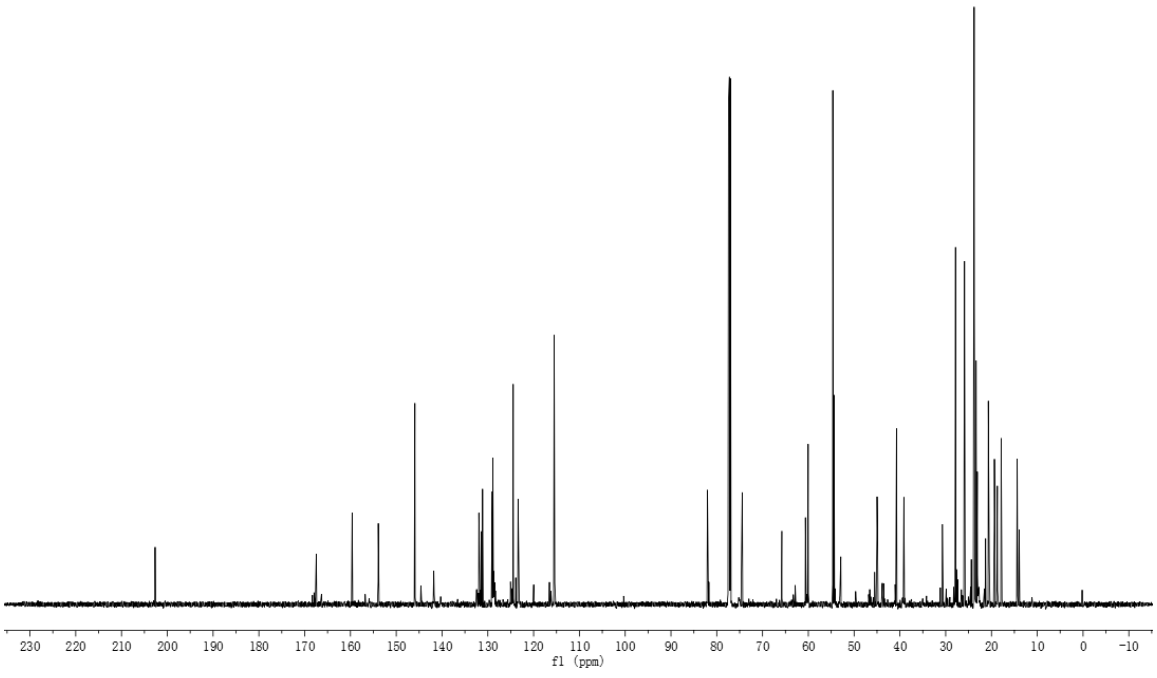


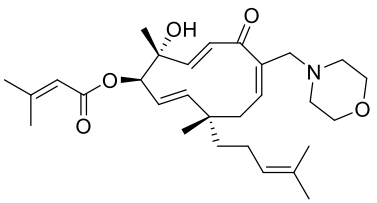






**12d** (600 MHz in $CDCl_3$)

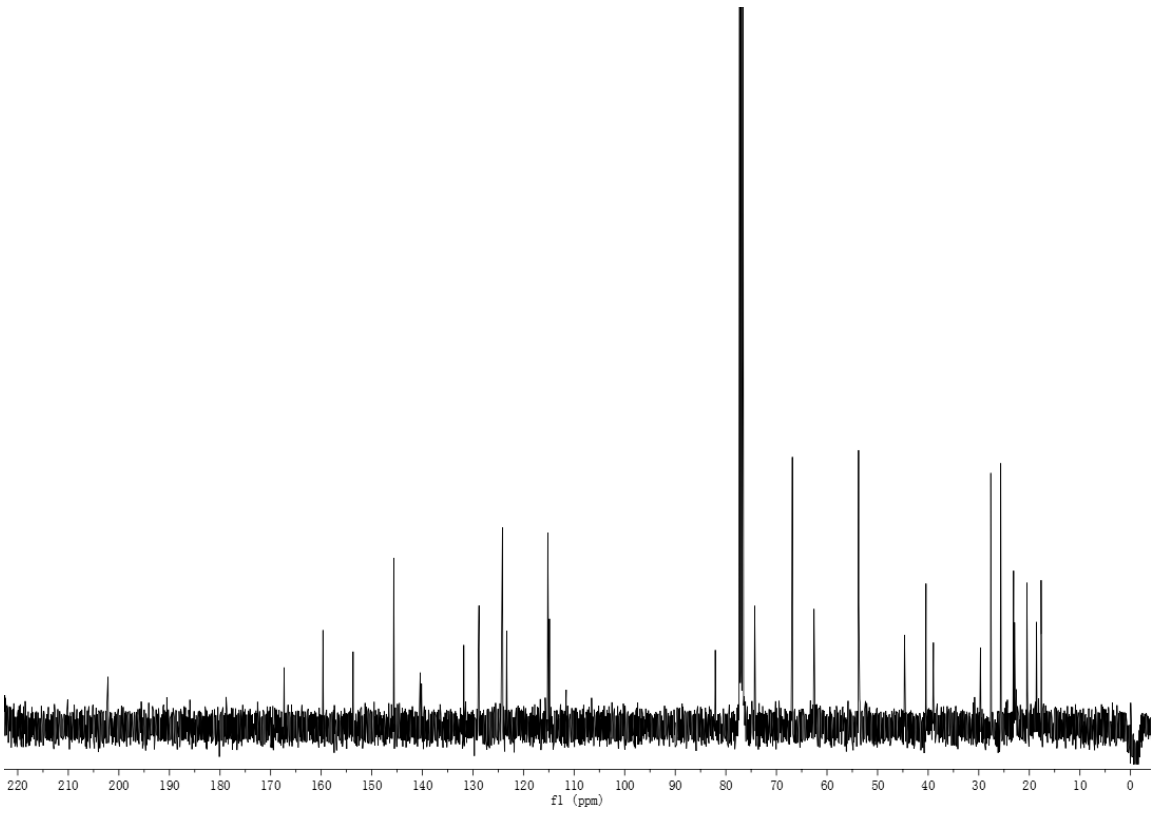


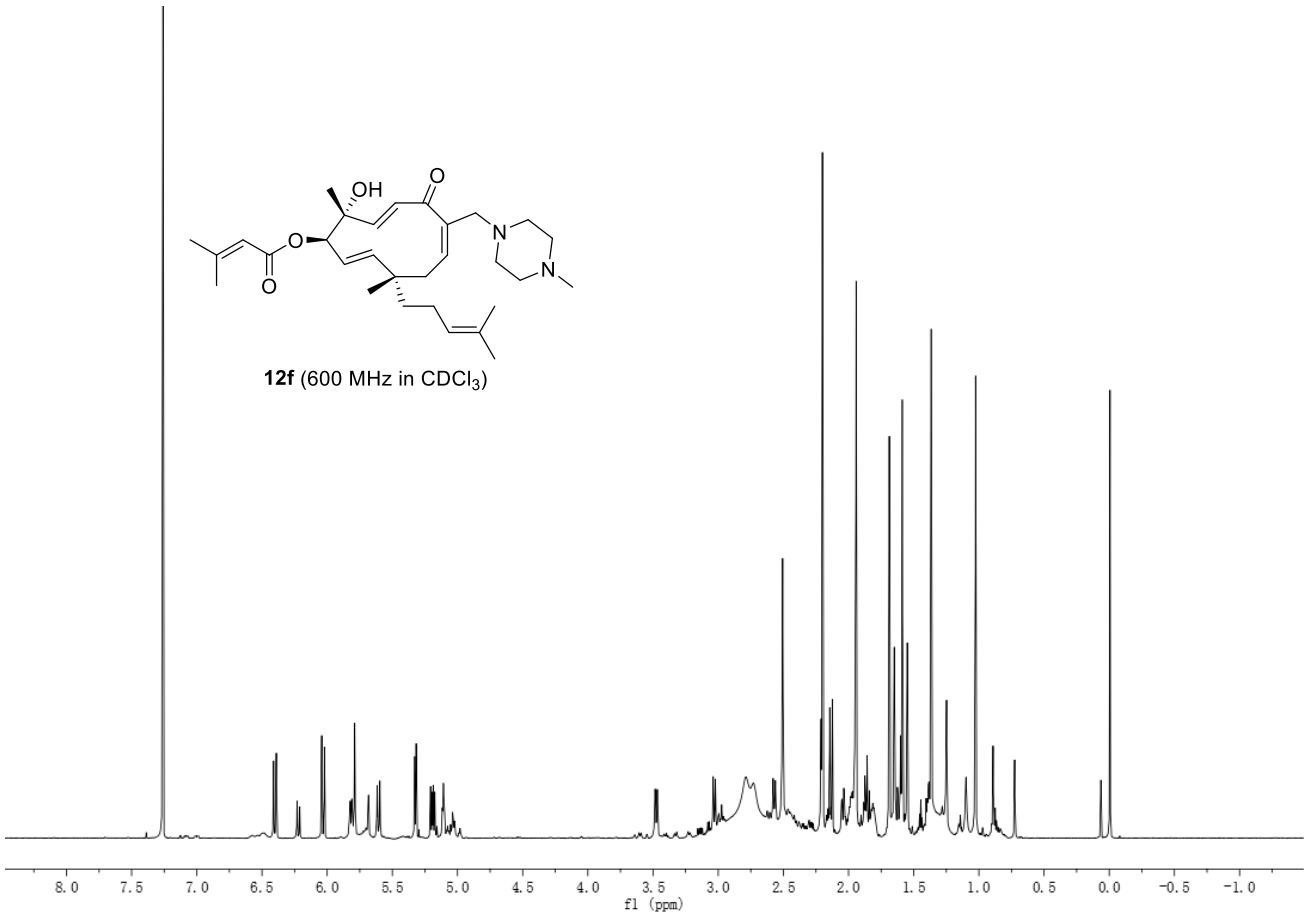





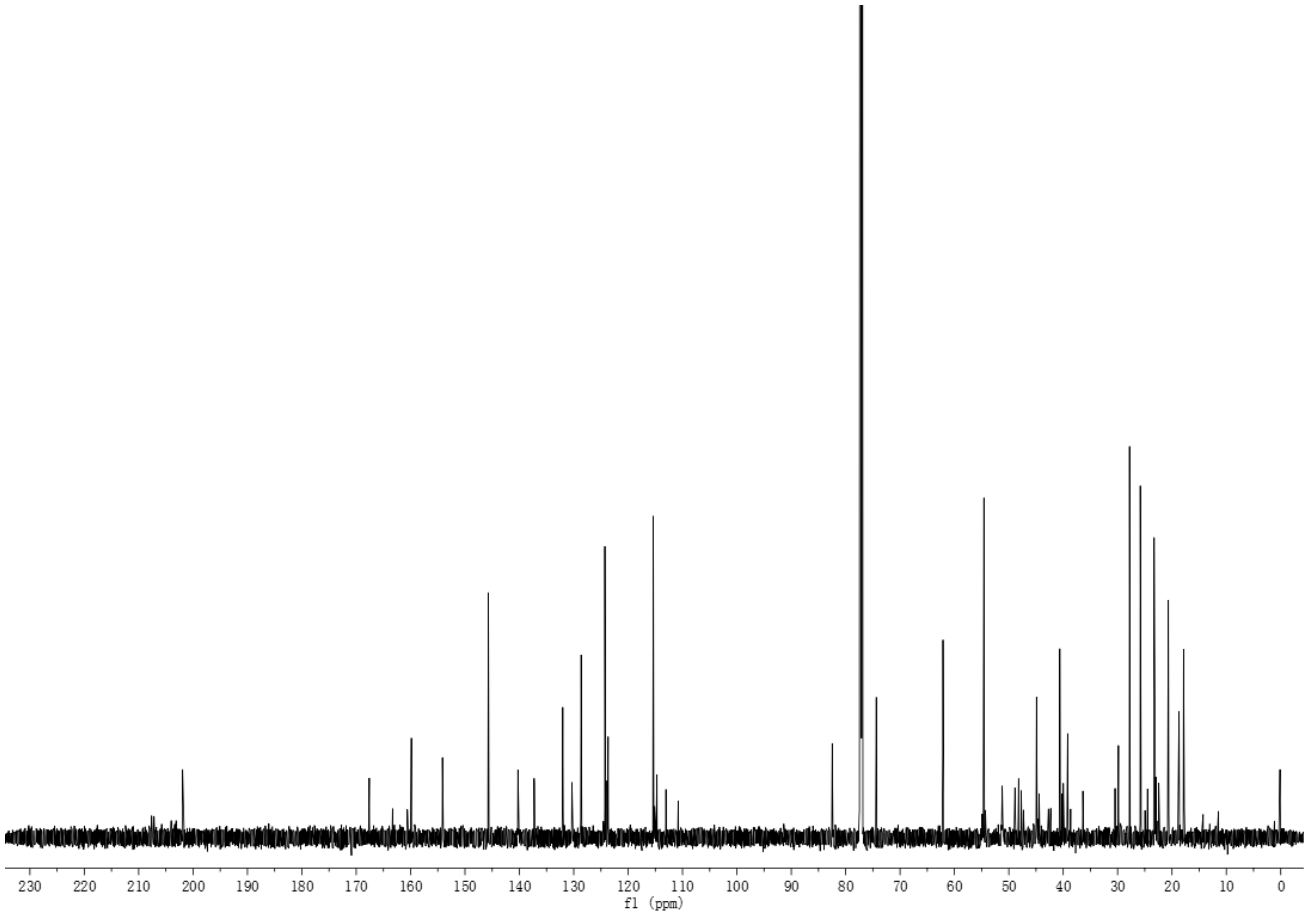

**12e** (600 MHz in $CDCl_3$)

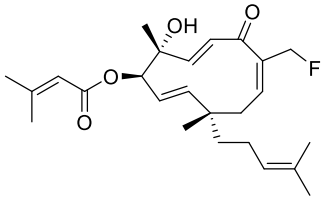




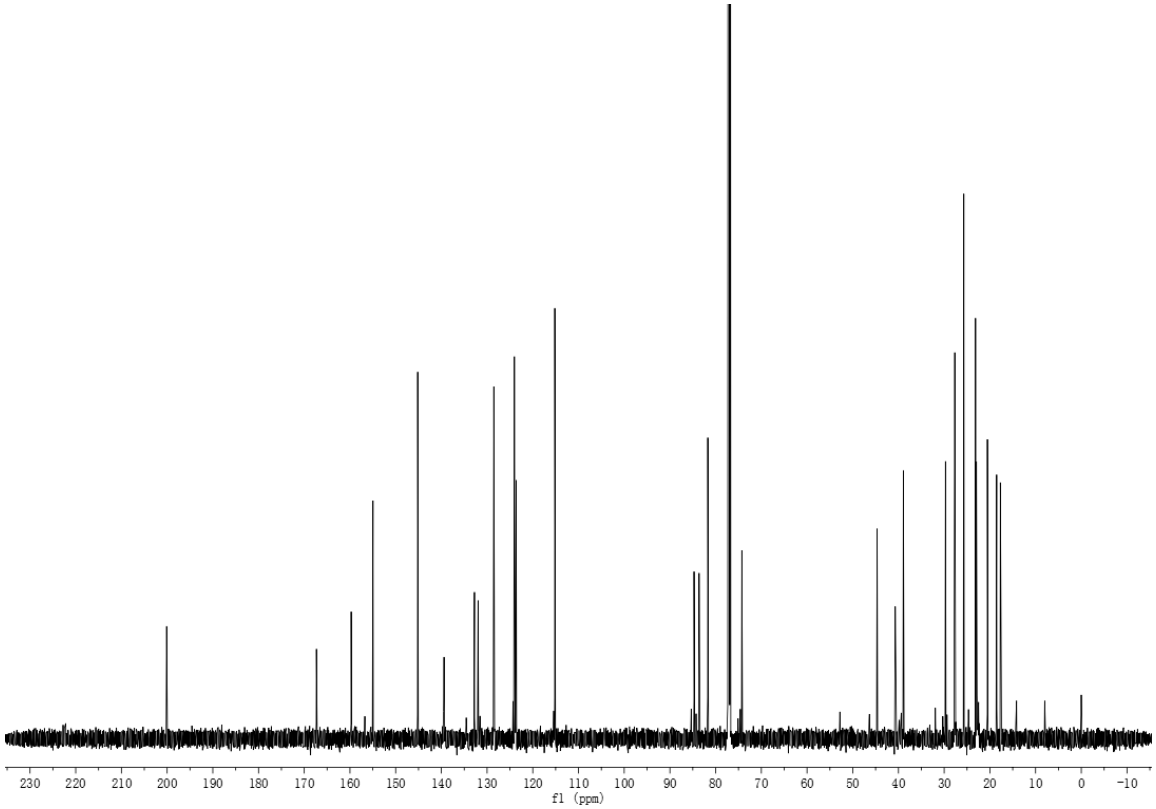

**12f** (600 MHz in $CDCl_3$)

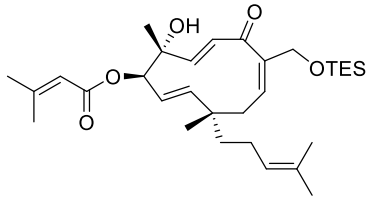





**7** (600 MHz in $CDCl_3$)

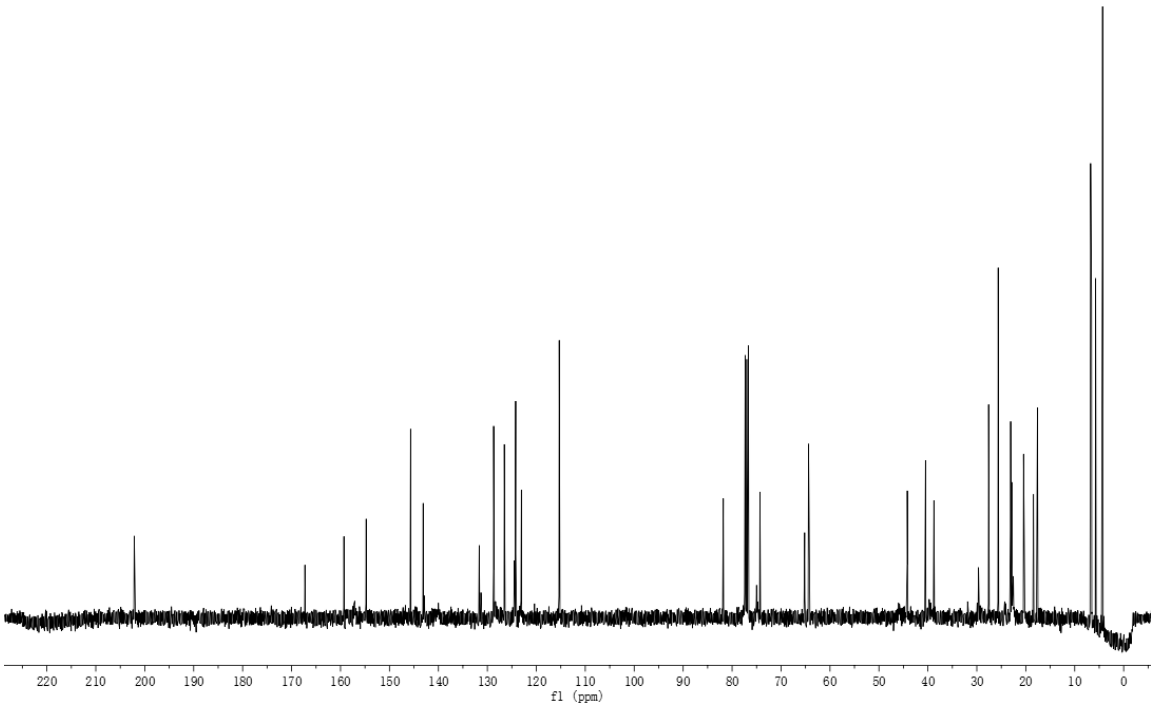


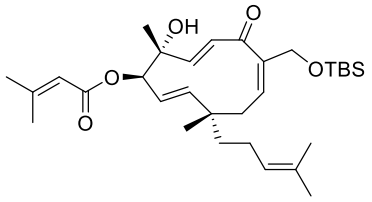






**13a** (500 MHz in $CDCl_3$)

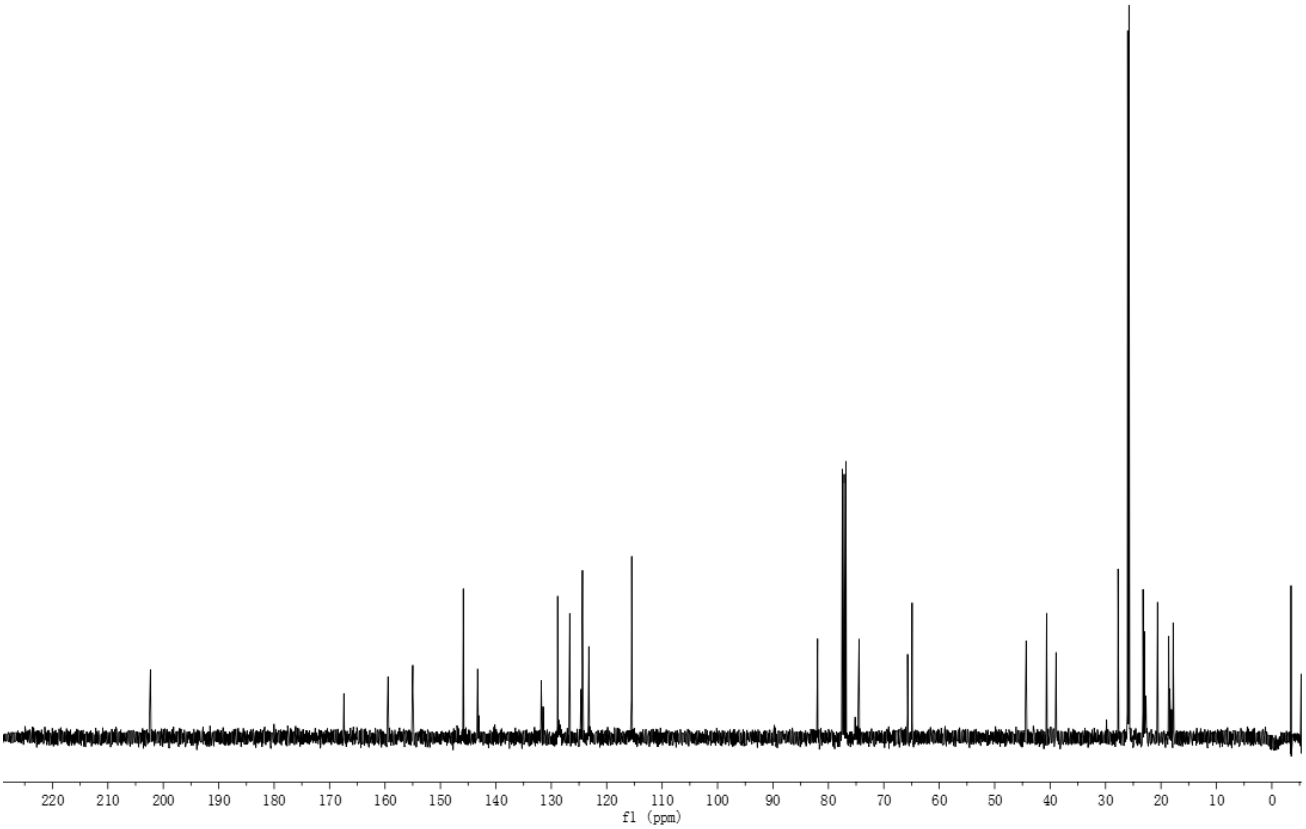


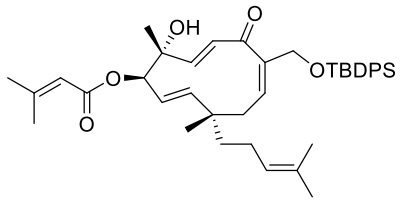






**13b** (500 MHz in $CDCl_3$)

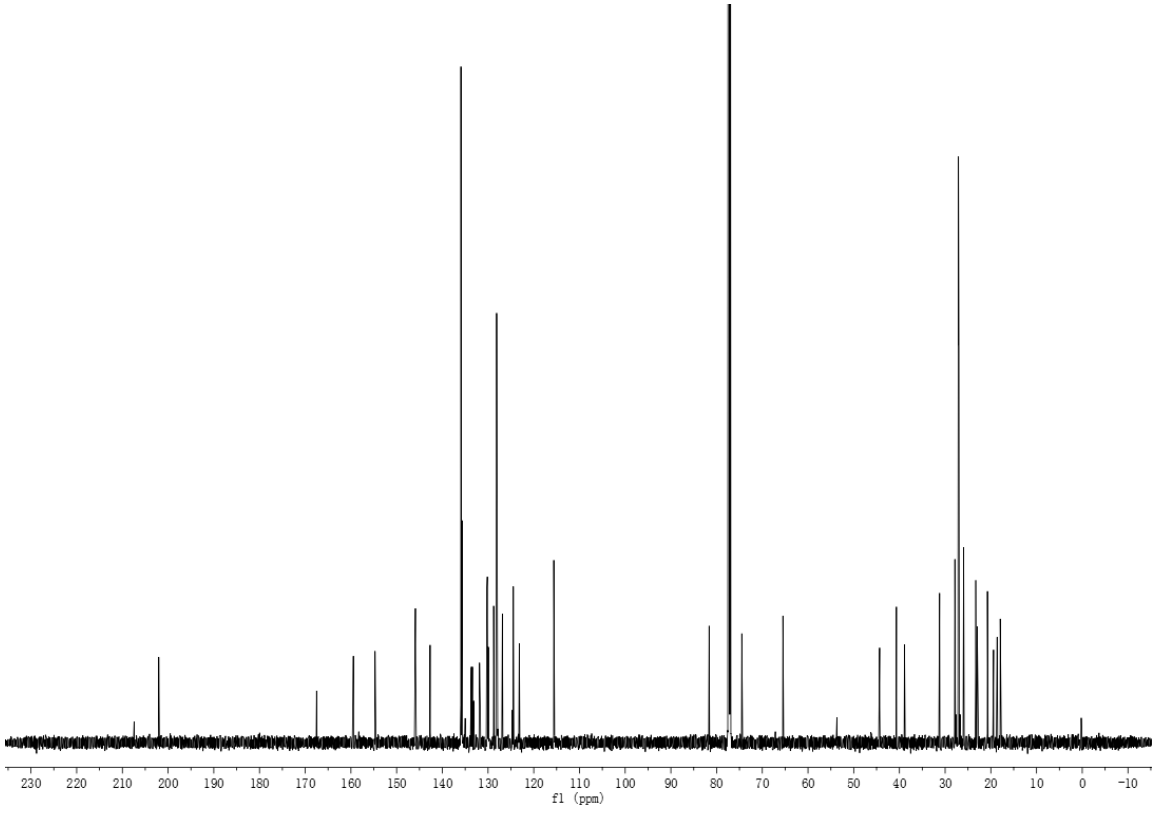


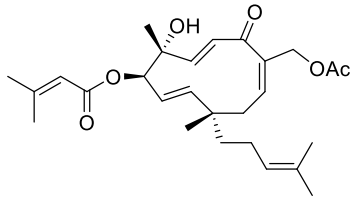






**13c** (600 MHz in $CDCl_3$)

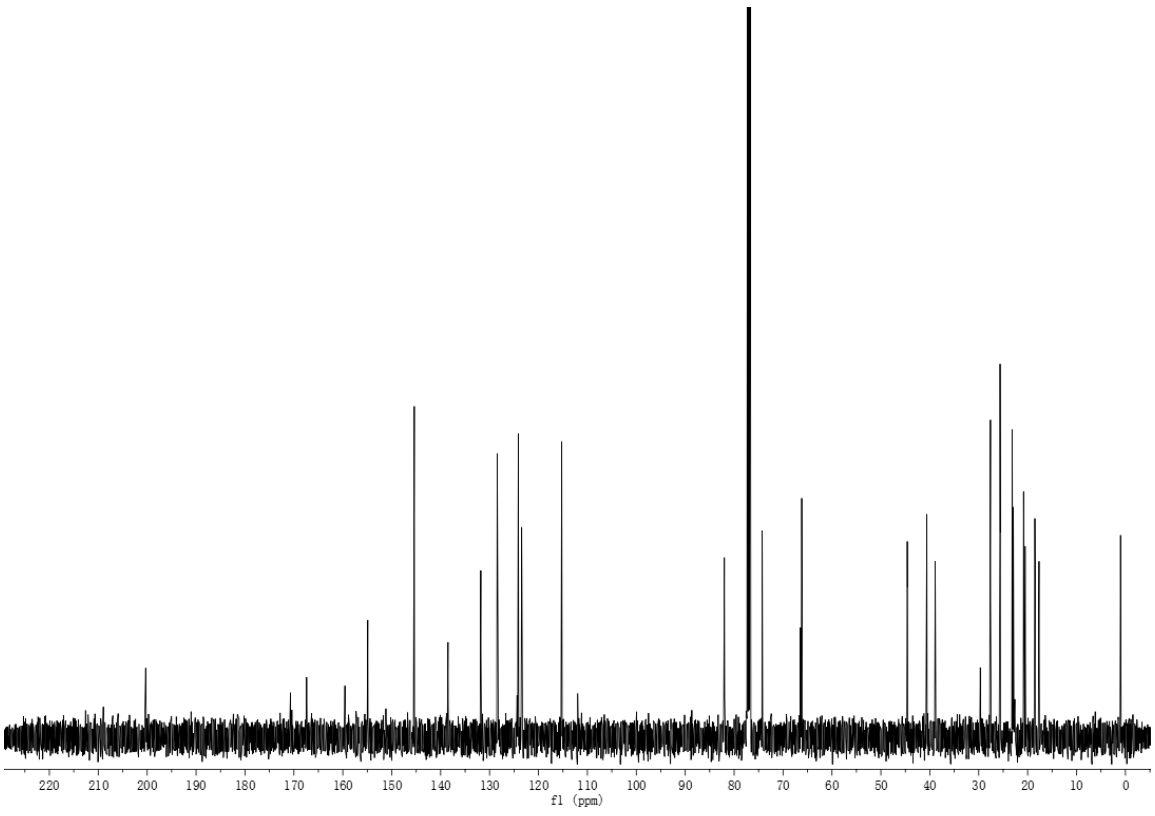


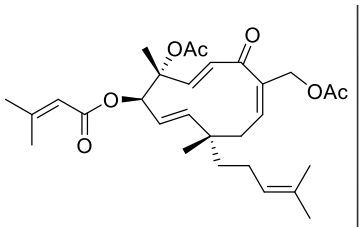






**8** (500 MHz in $CDCl_3$)

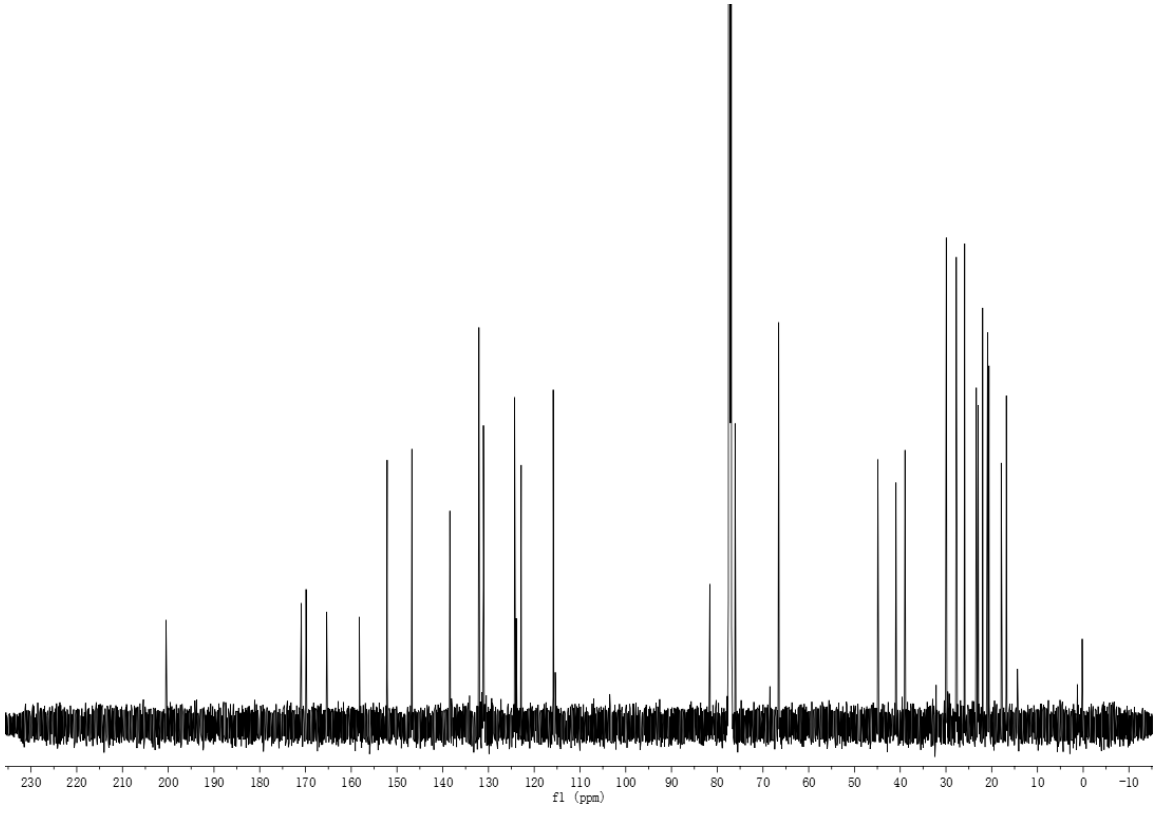


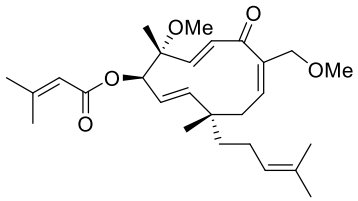





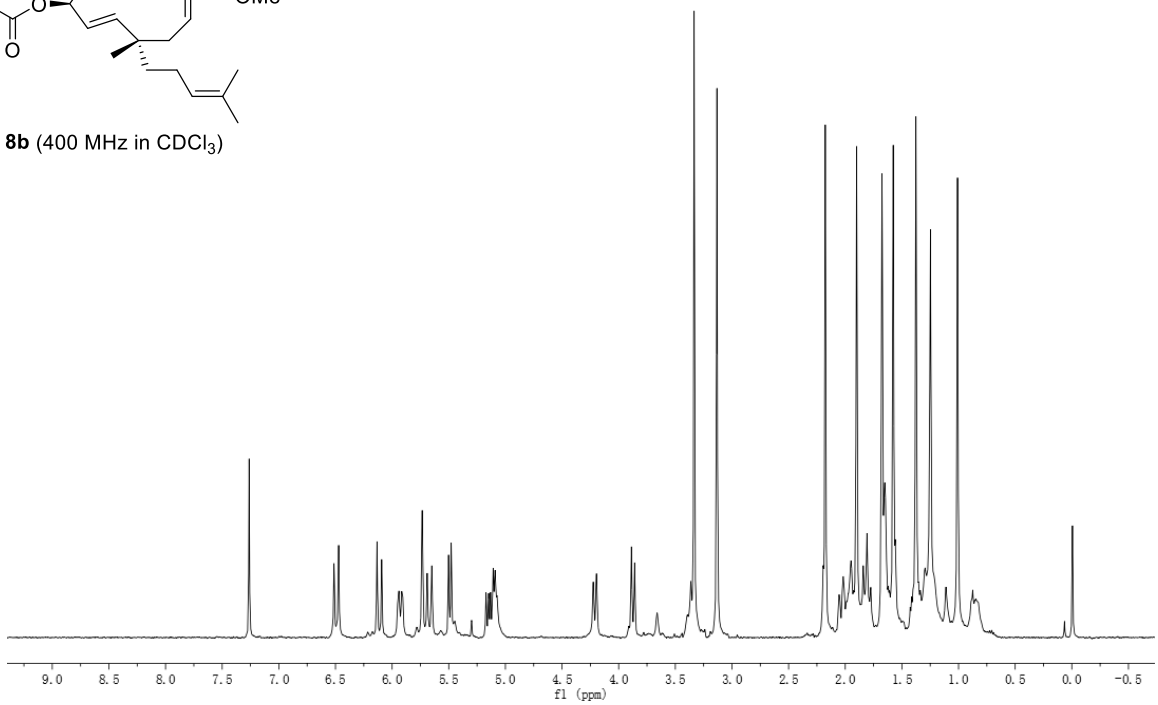

**8a** (600 MHz in $CDCl_3$)

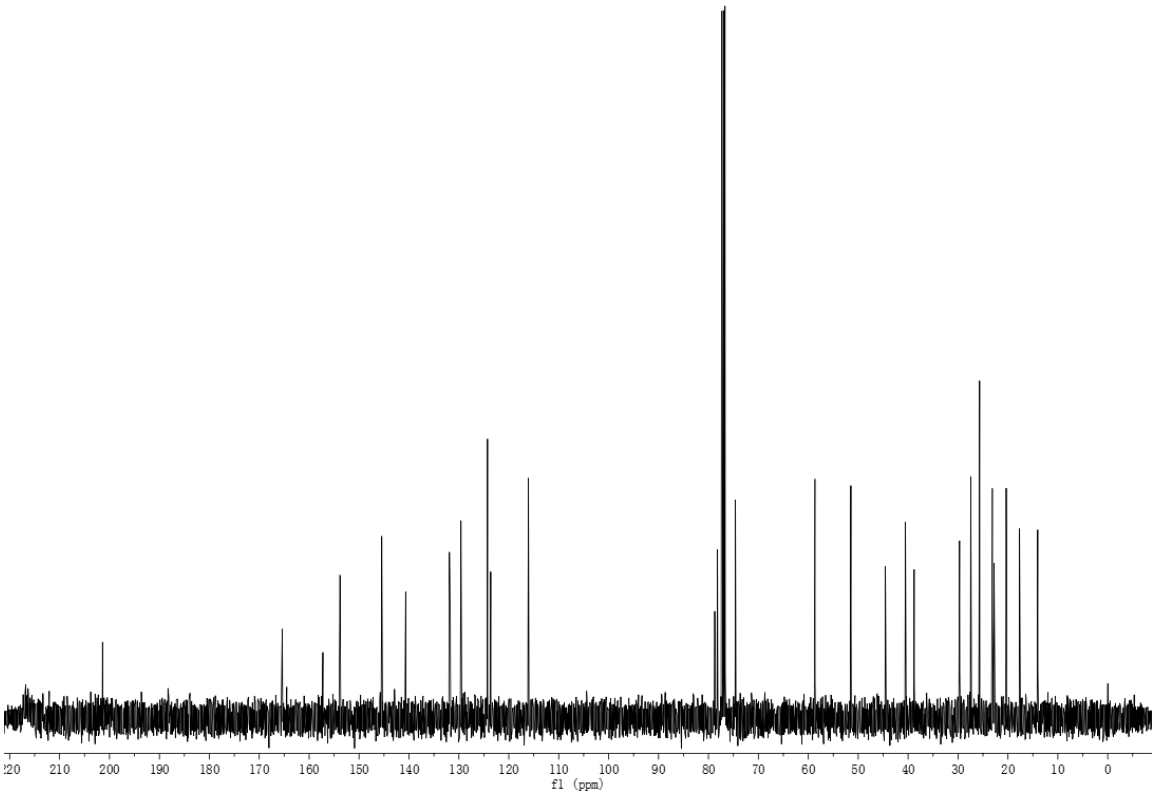


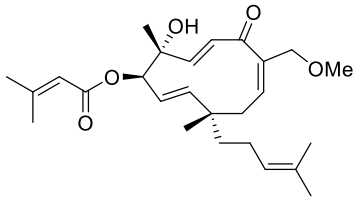





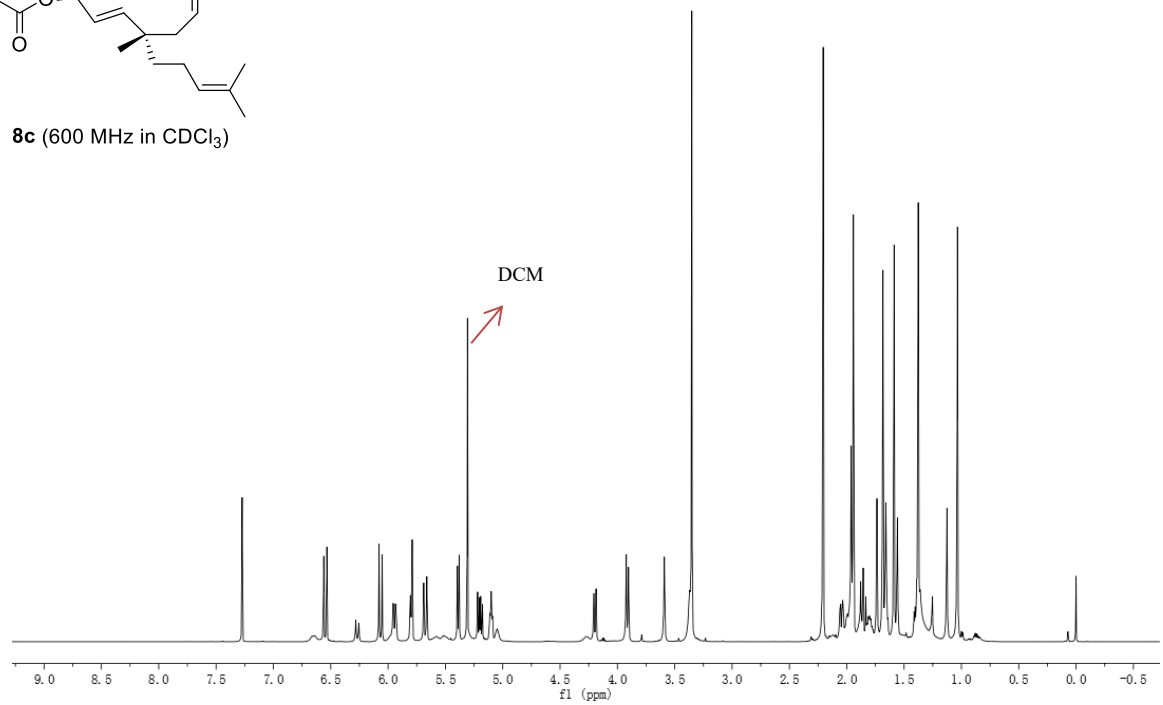

**8b** (400 MHz in $CDCl_3$)

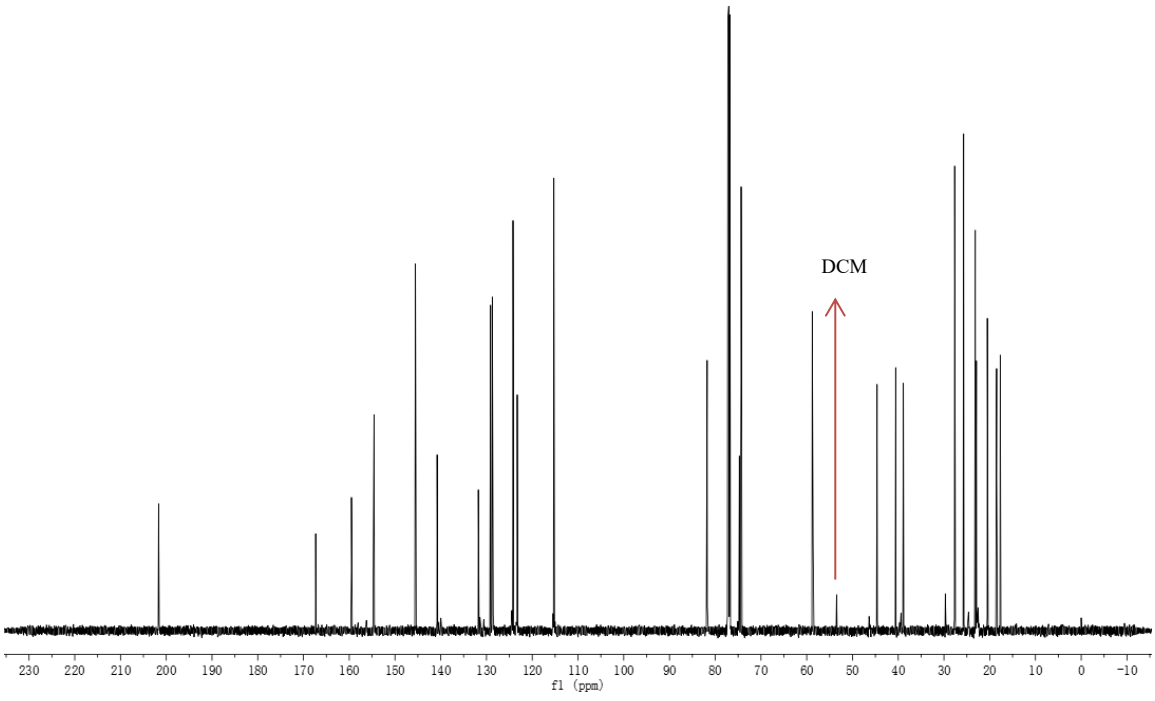


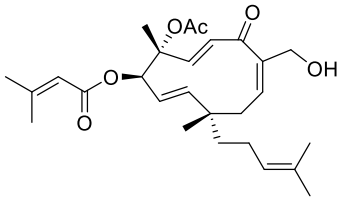





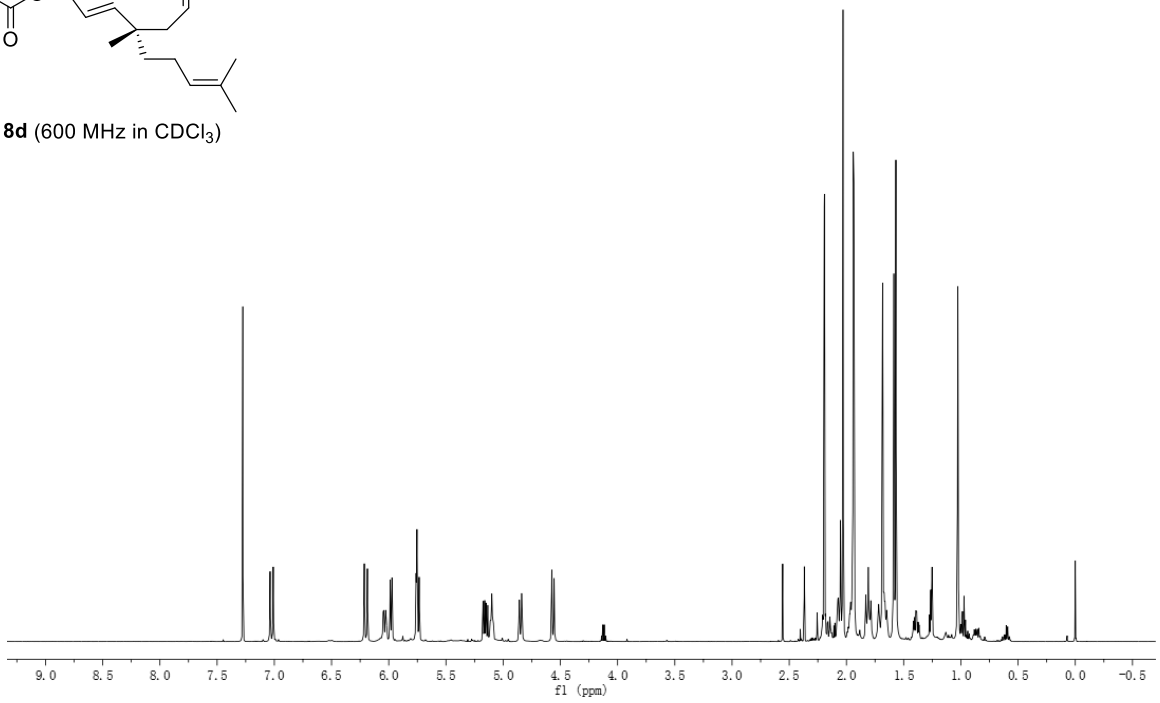

**8c** (600 MHz in $CDCl_3$)

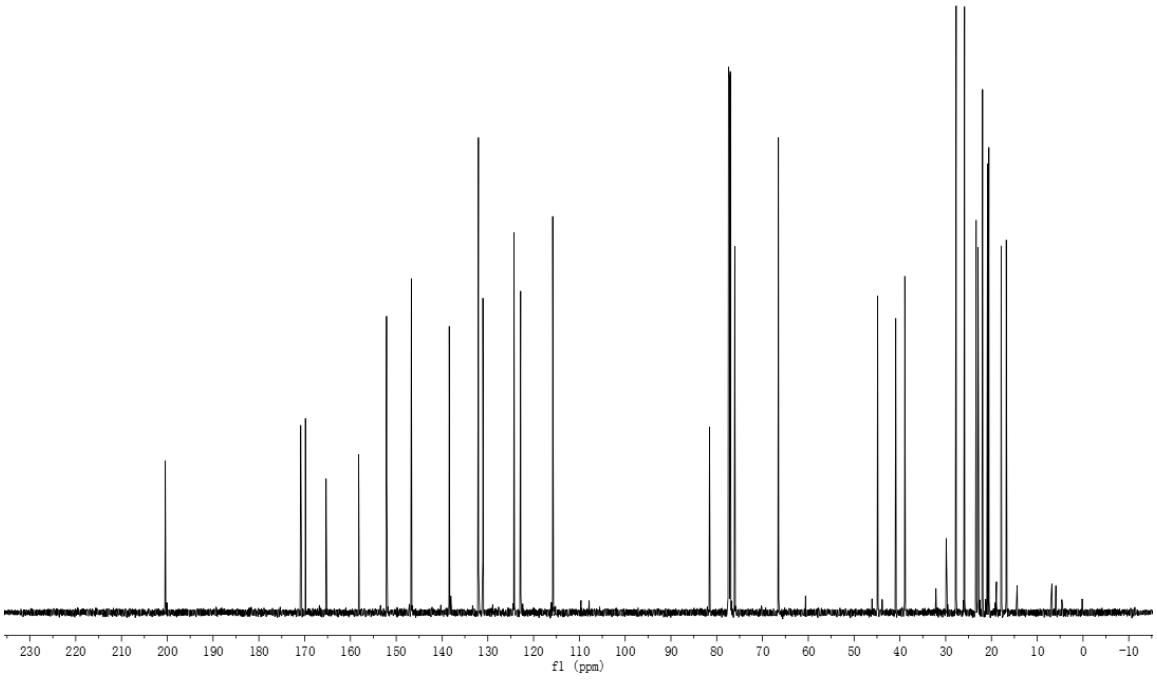


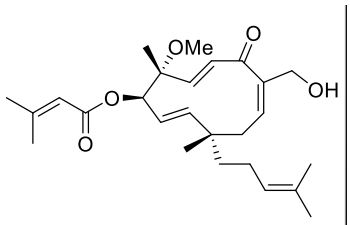





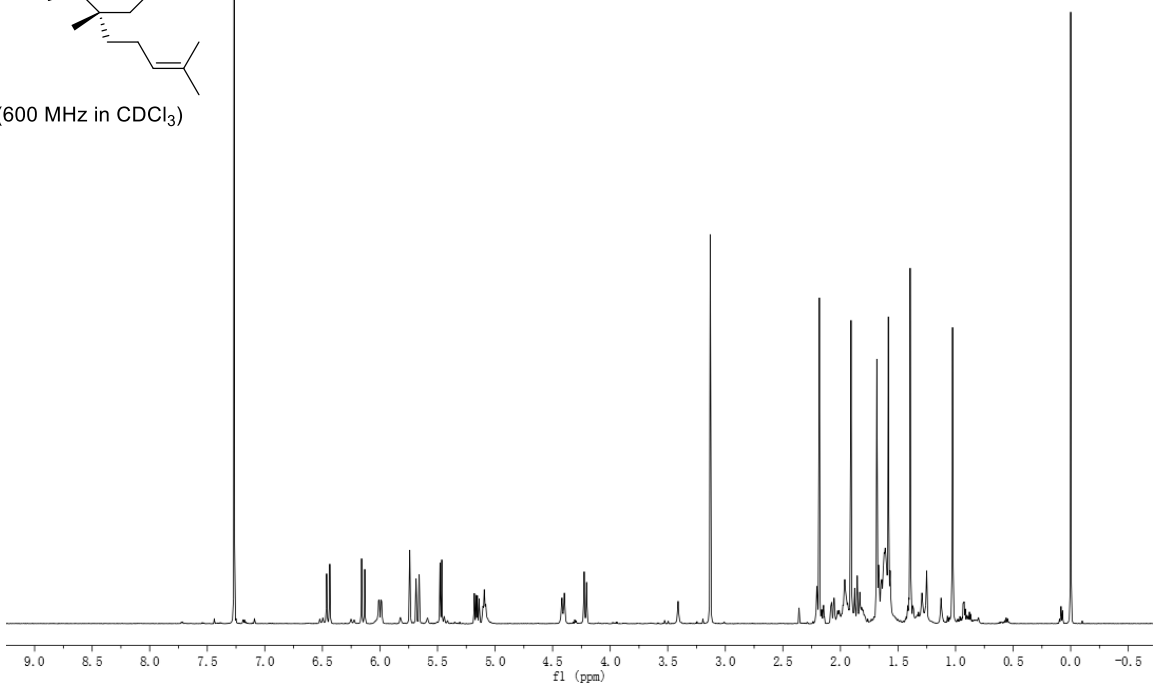

**8d** (600 MHz in $CDCl_3$)

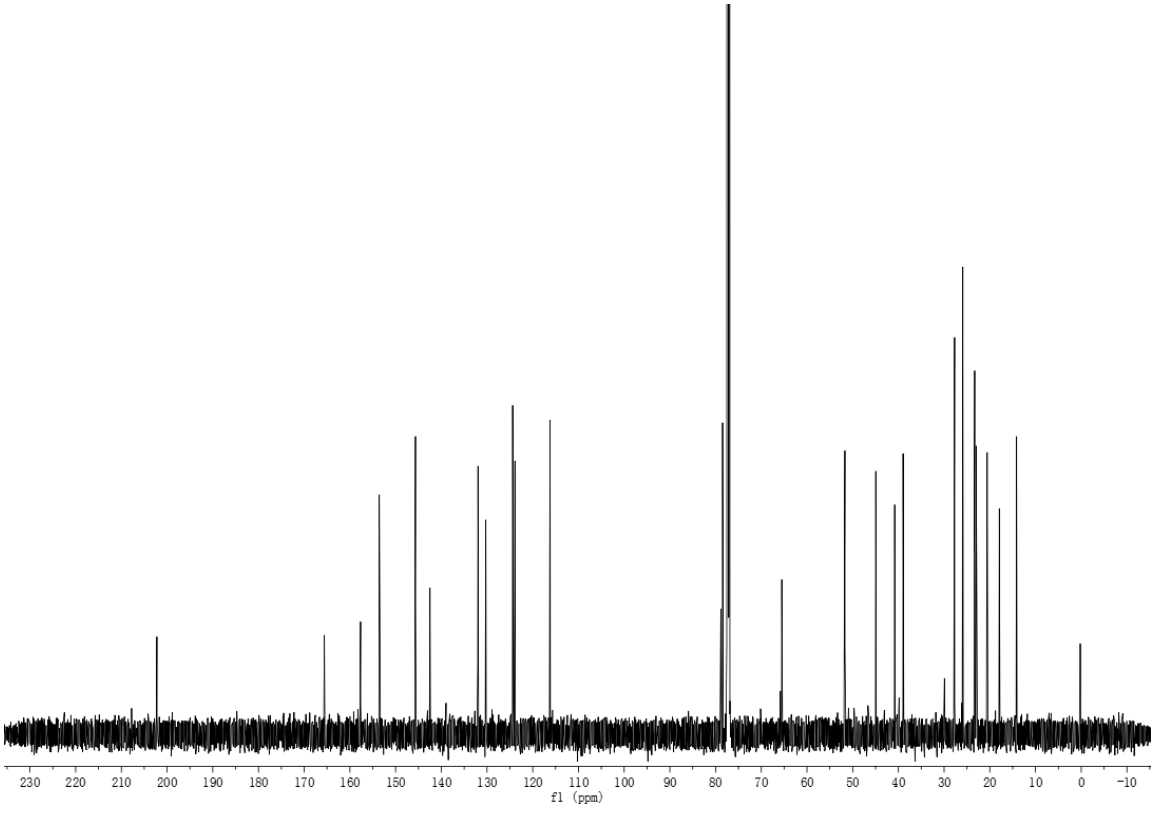


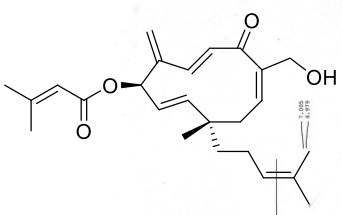






**8e** (600 MHz in $CDCl_3$)

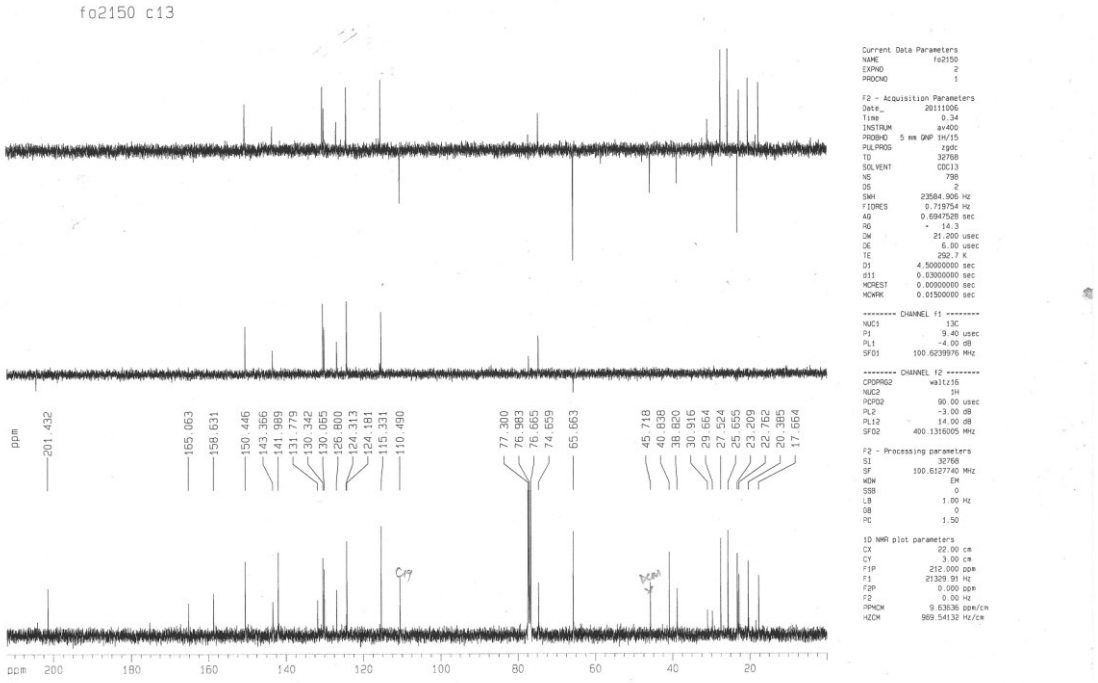


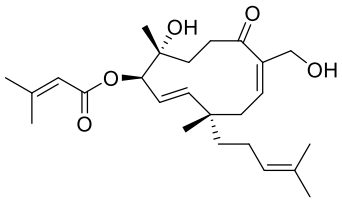





**8f** (600 MHz in $CDCl_3$)

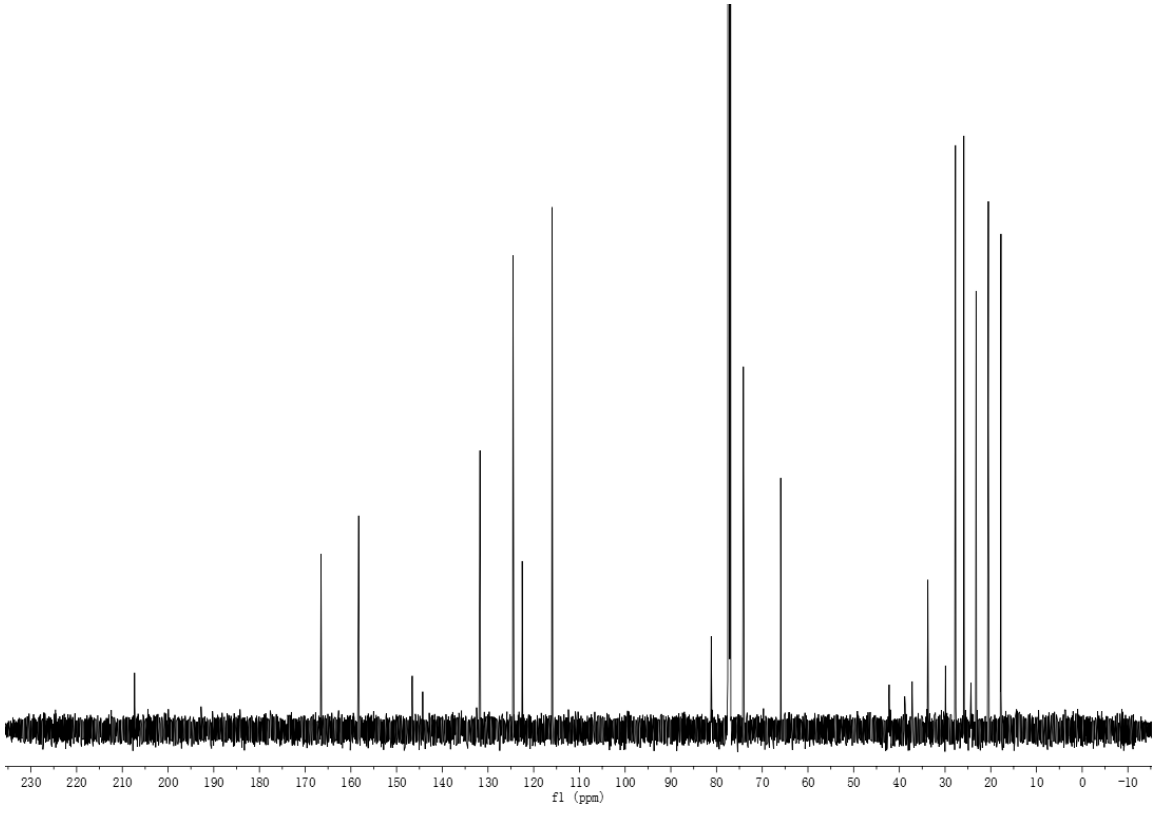


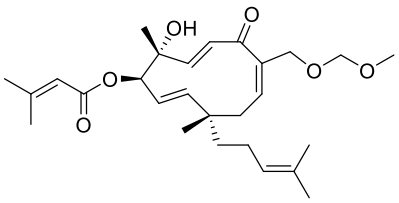





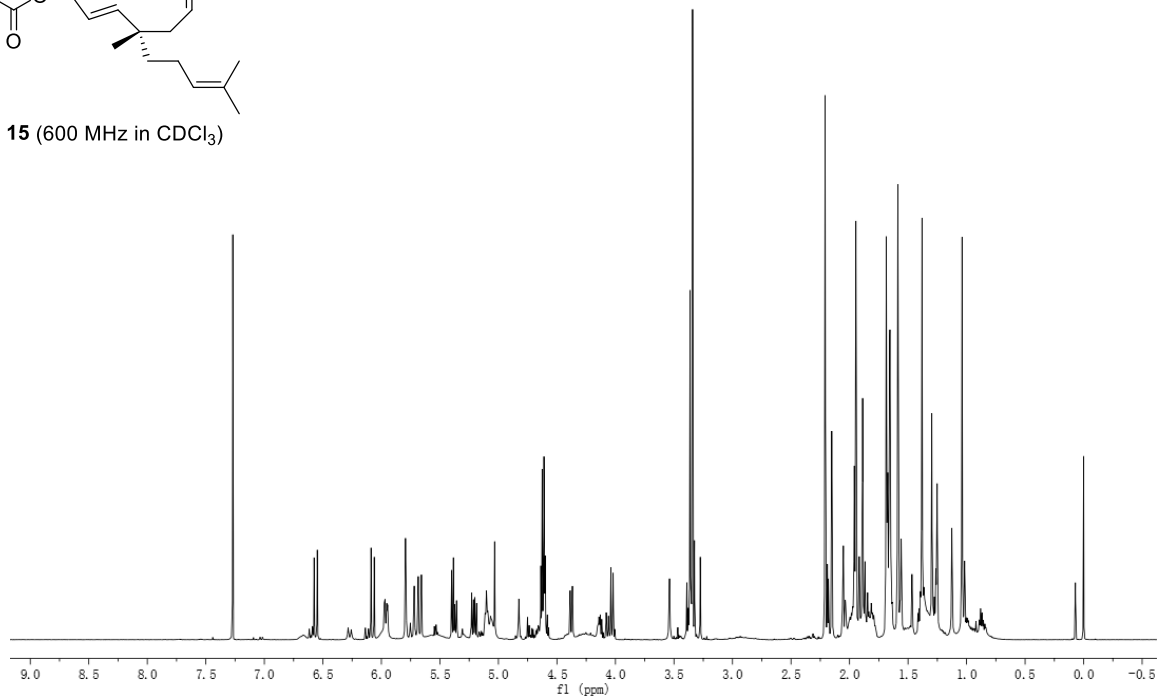

**14** (600 MHz in $CDCl_3$)

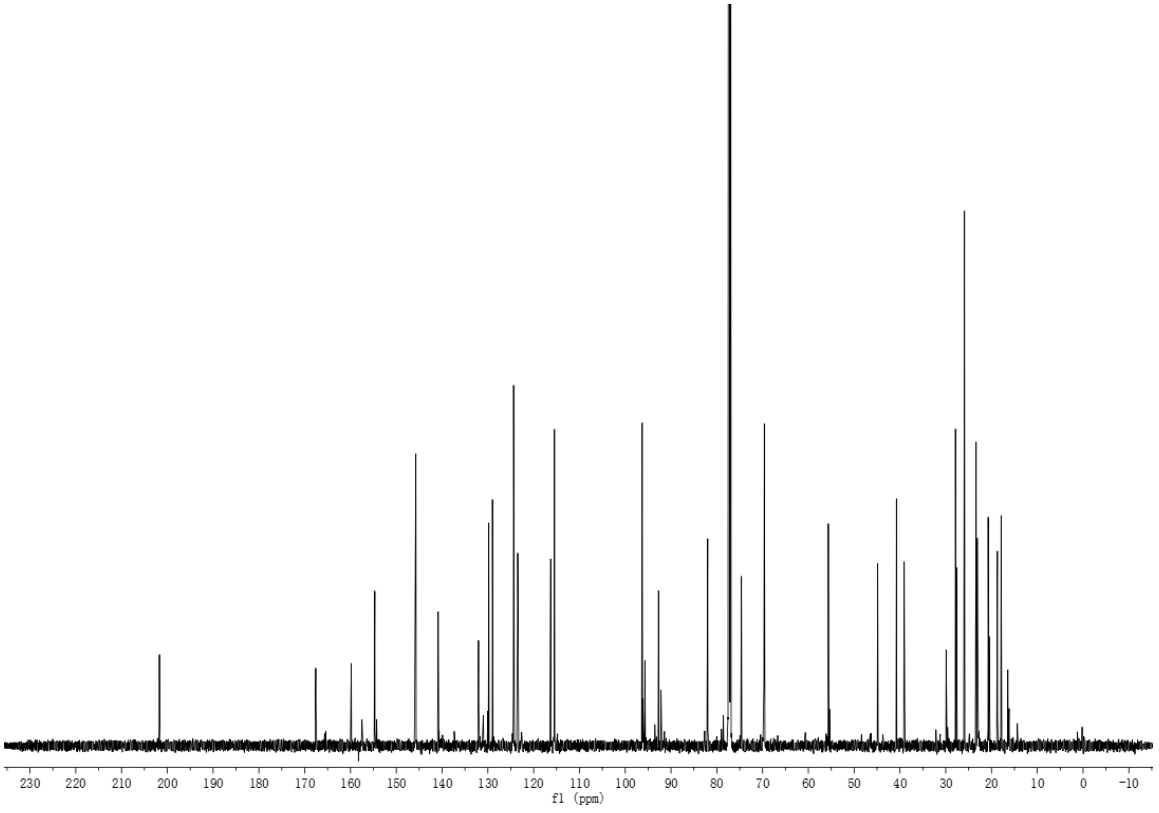


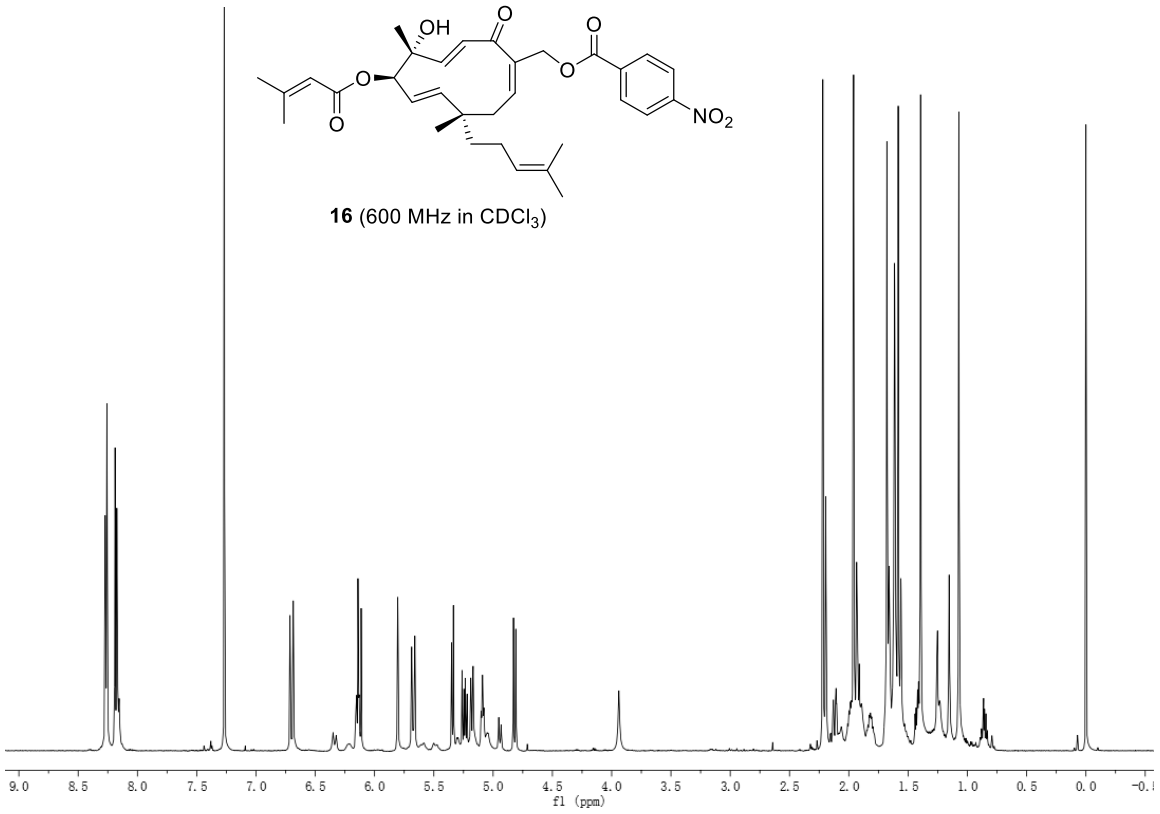





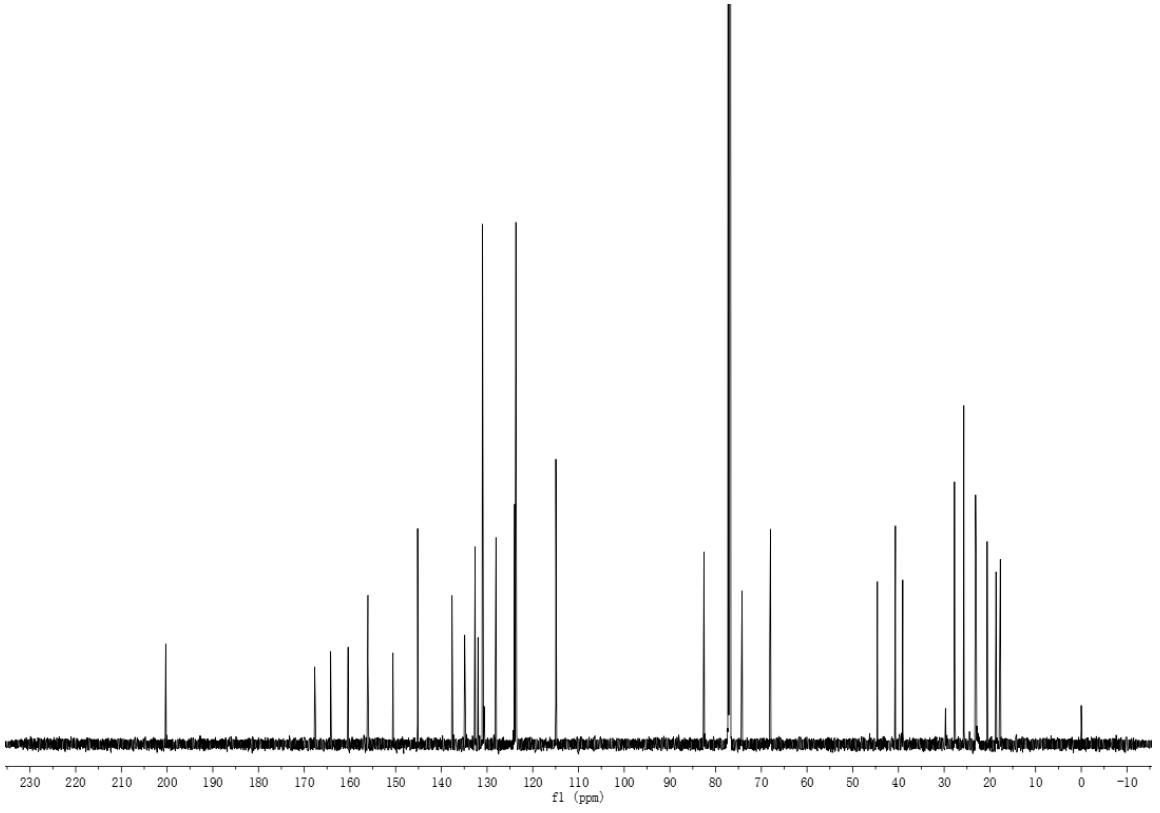

**15** (600 MHz in $CDCl_3$)

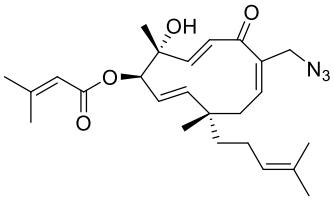


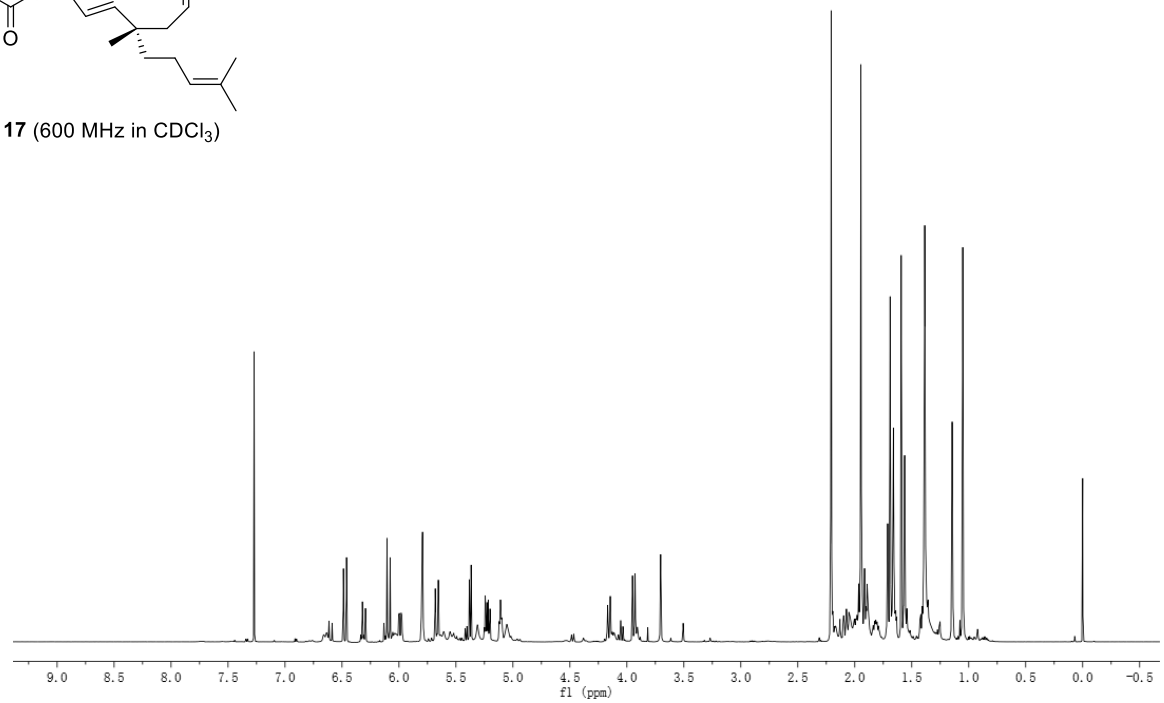


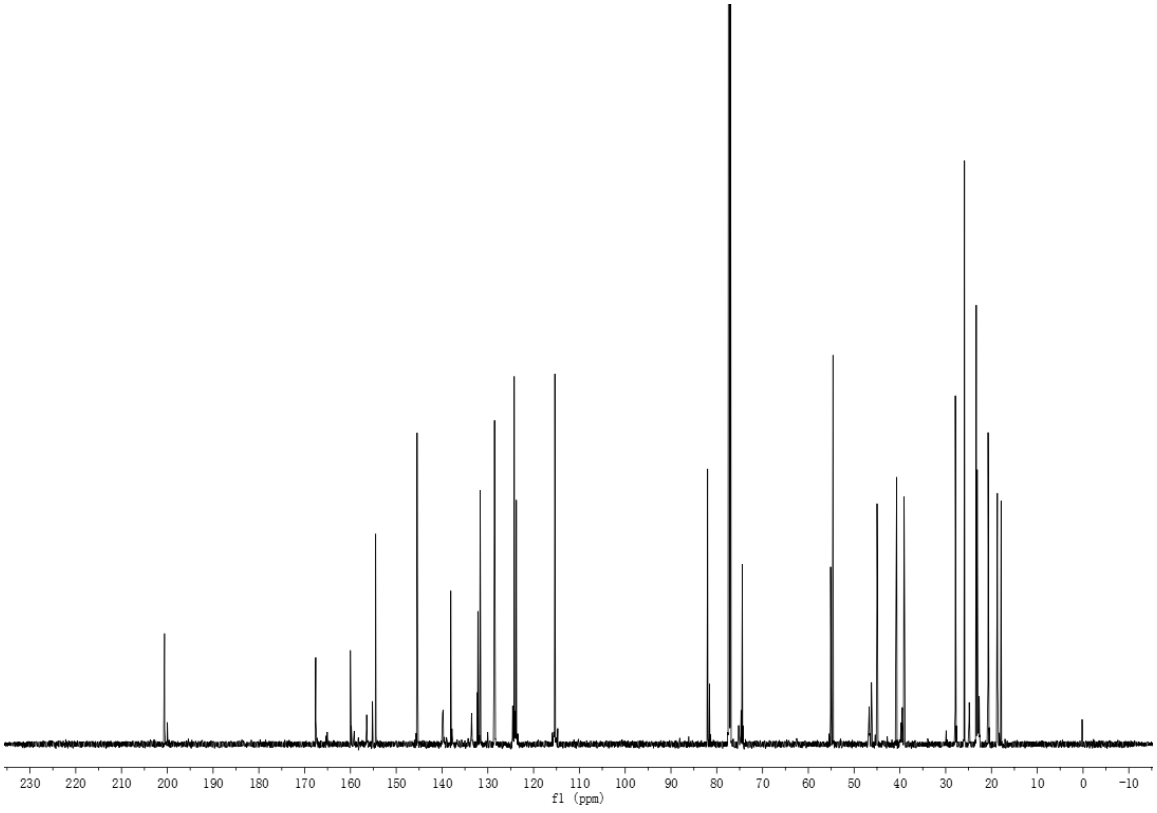

**16** (600 MHz in $CDCl_3$)

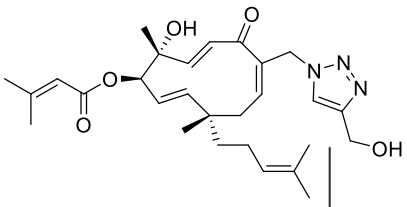




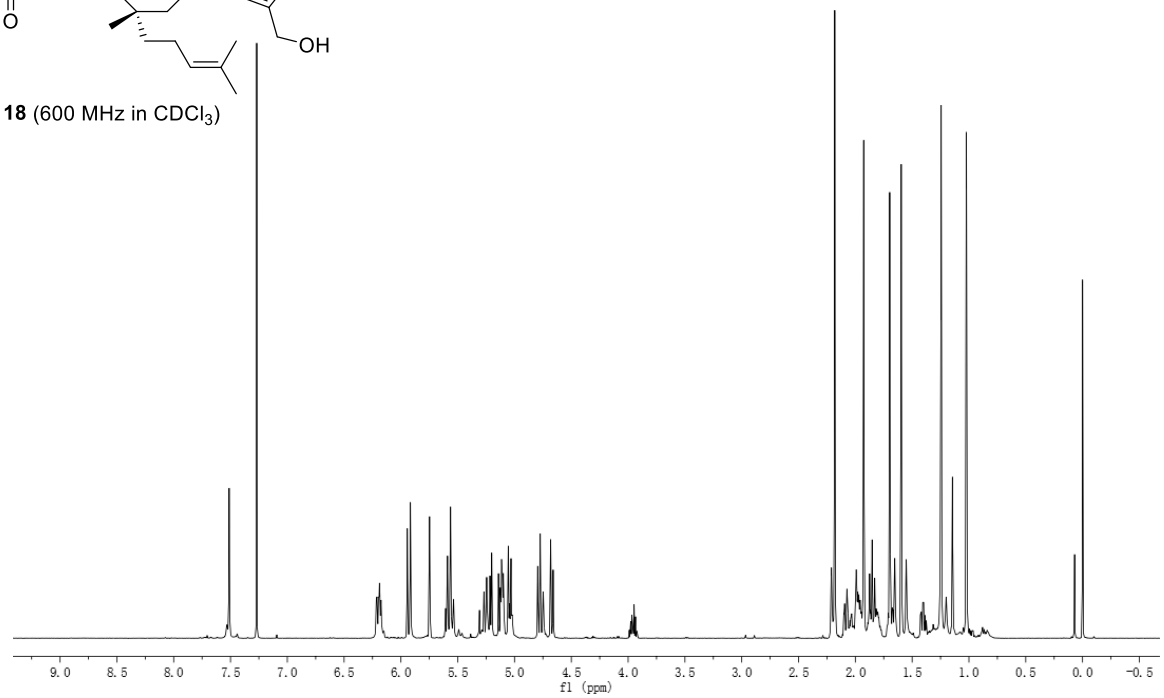

**17** (600 MHz in $CDCl_3$)

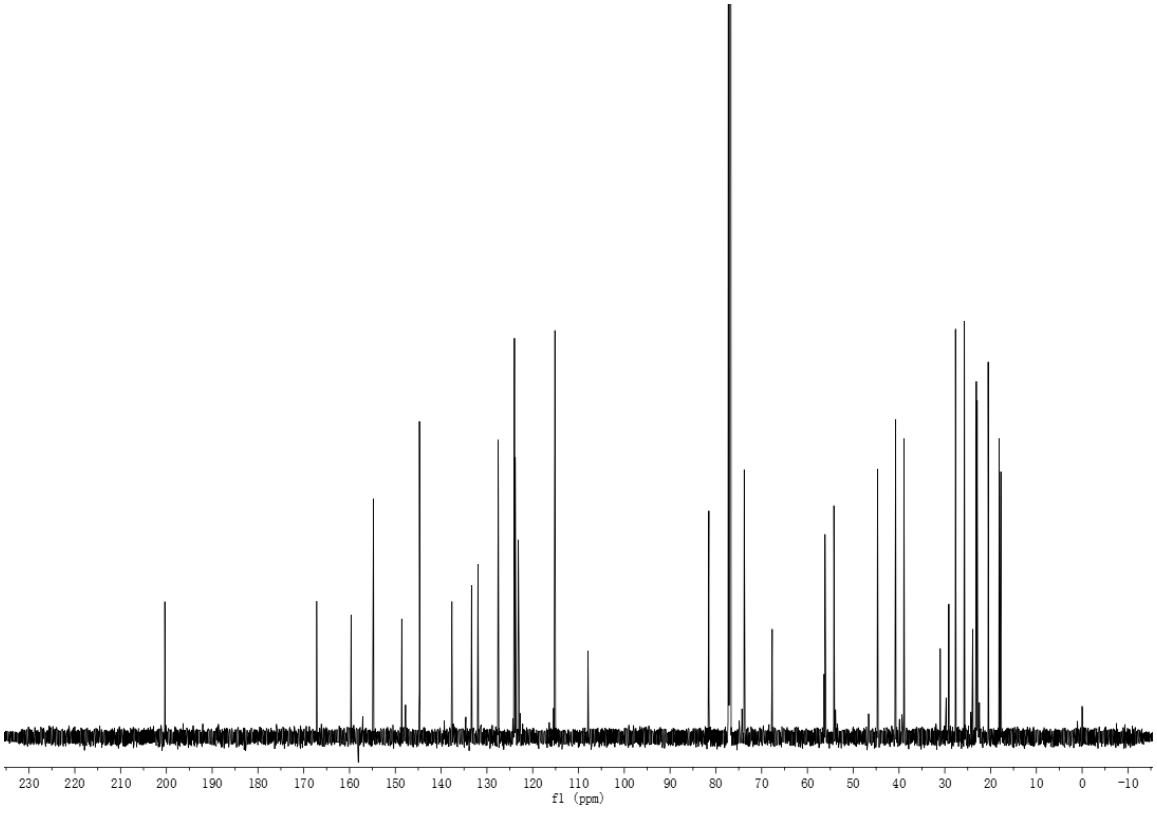


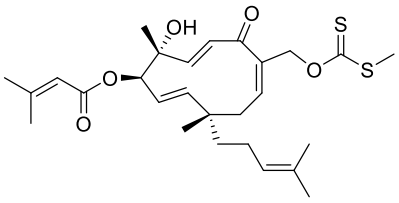






**18** (600 MHz in $CDCl_3$)

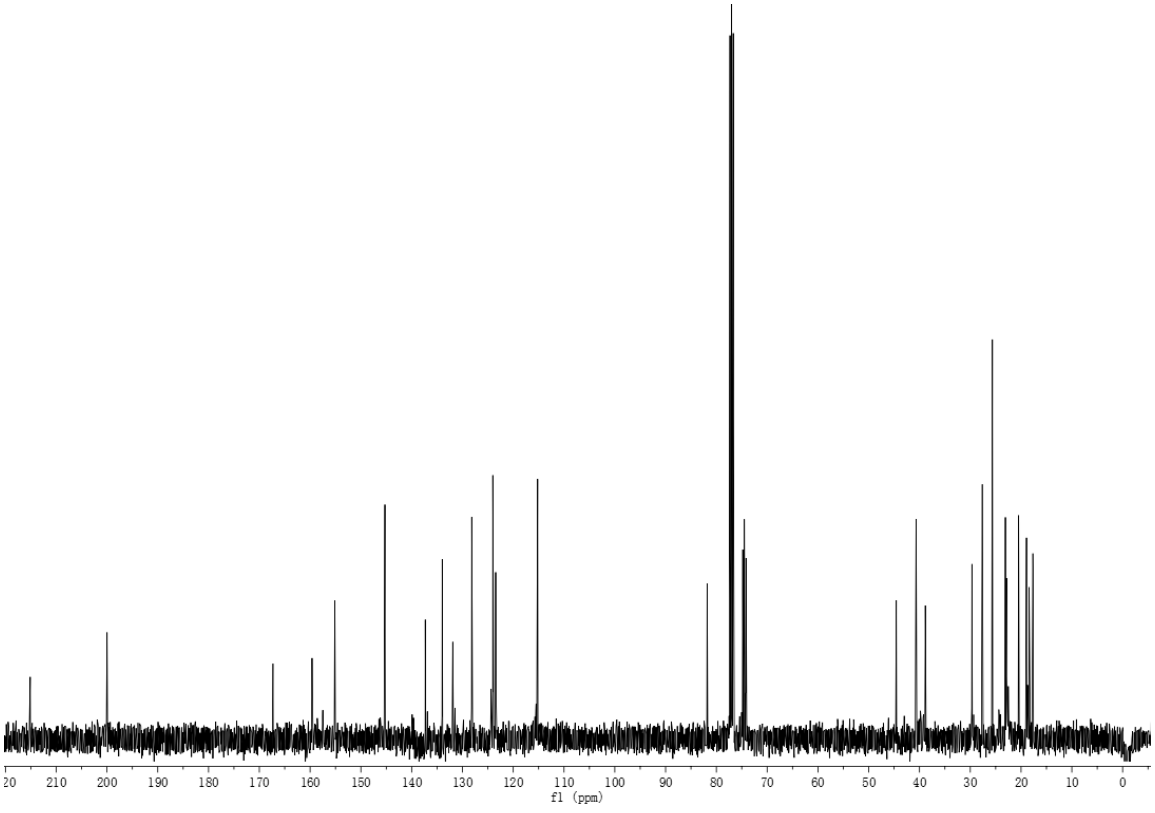


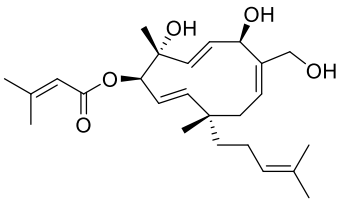





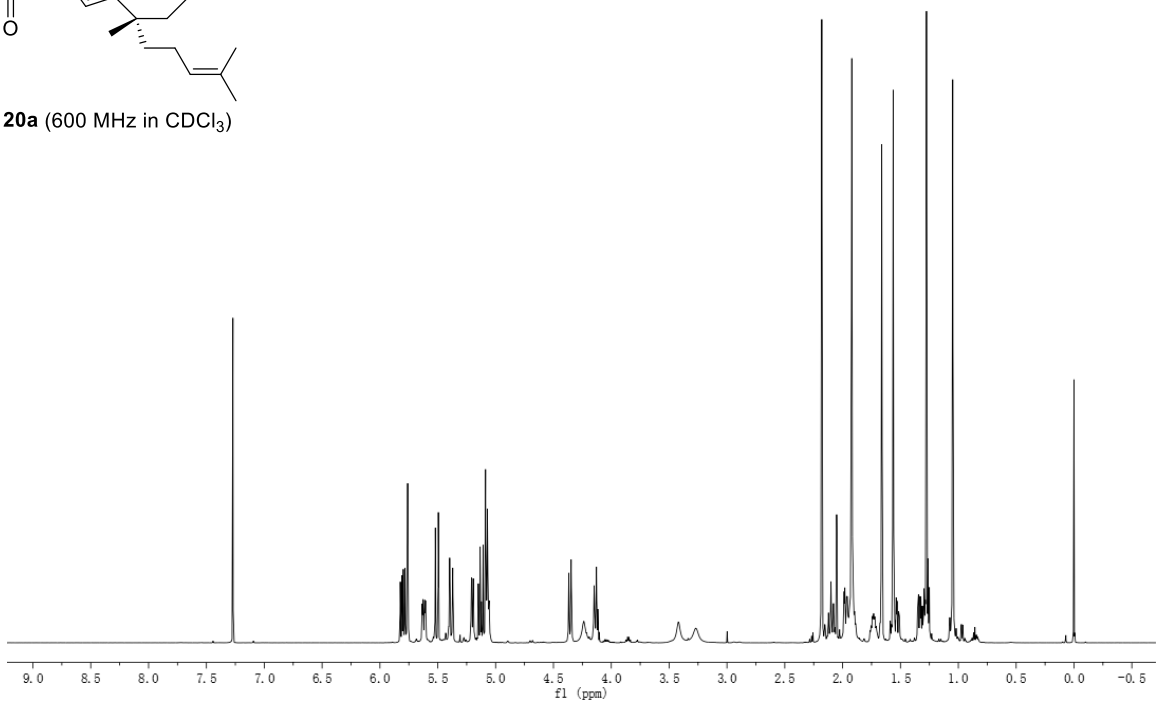

**19** (500 MHz in $CDCl_3$)

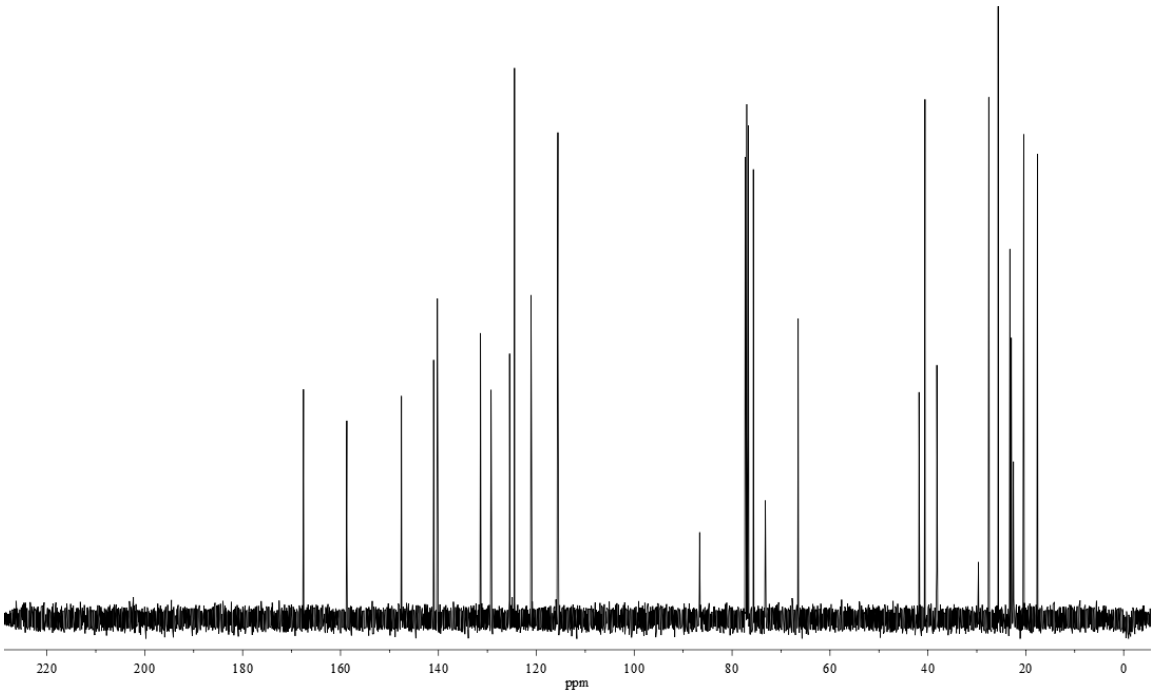


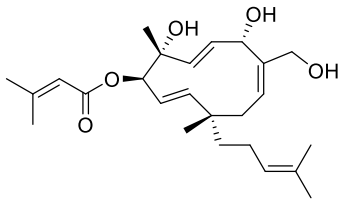





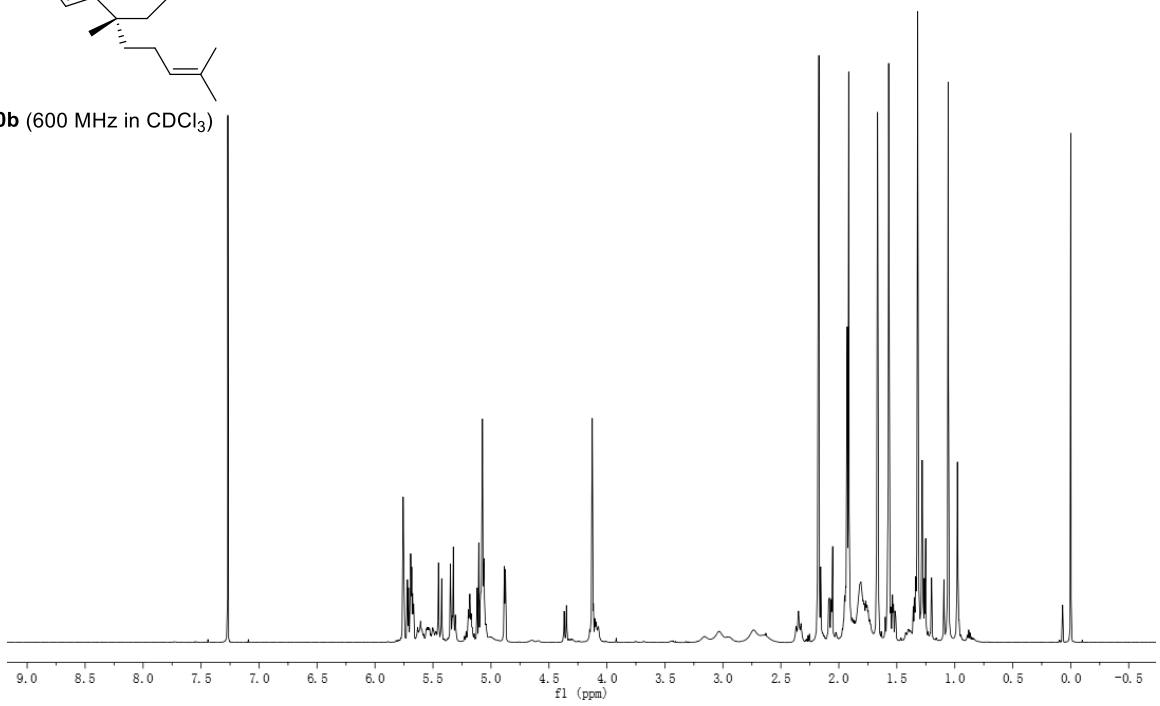

**20a** (600 MHz in $CDCl_3$)

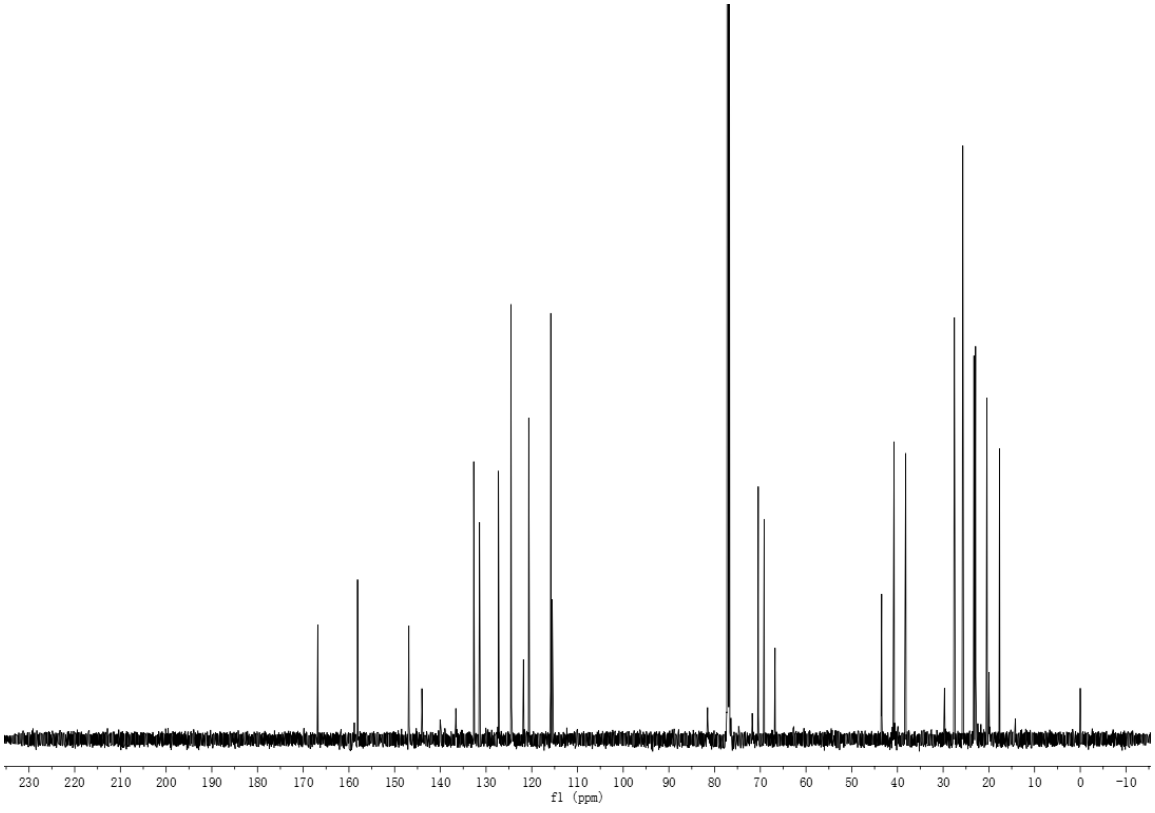


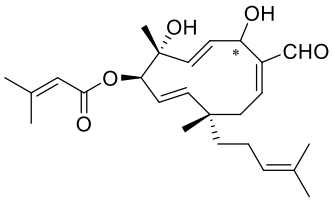





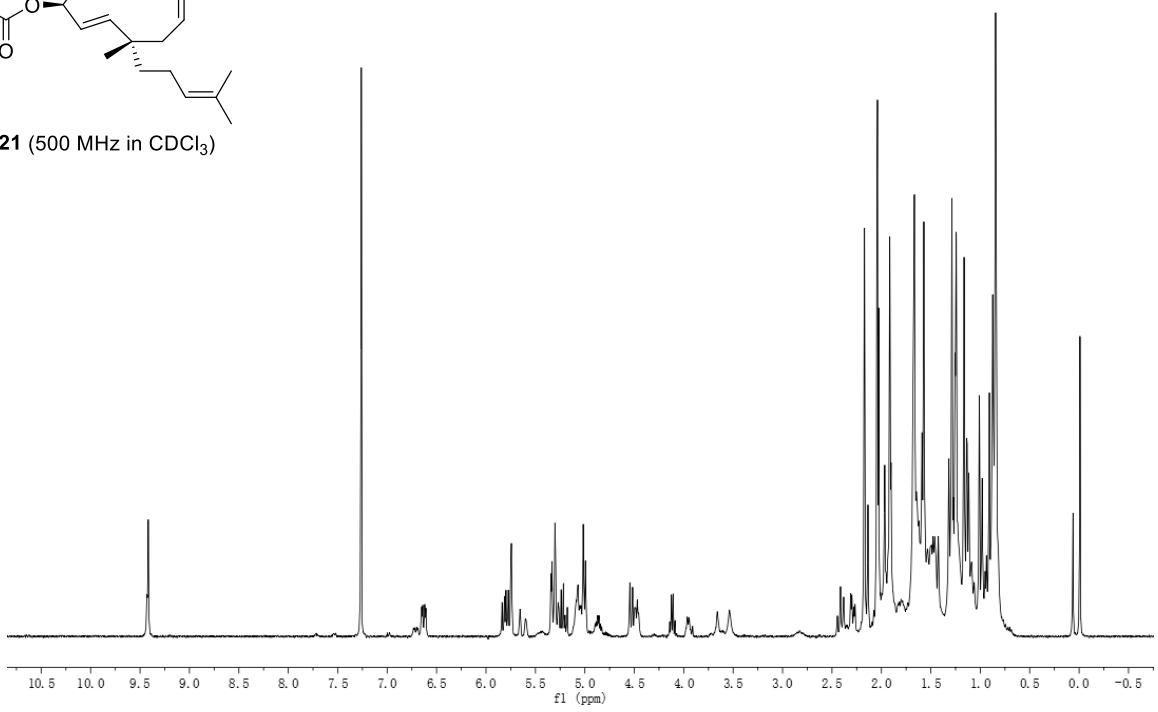

**20b** (600 MHz in $CDCl_3$)

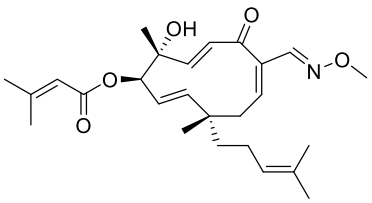


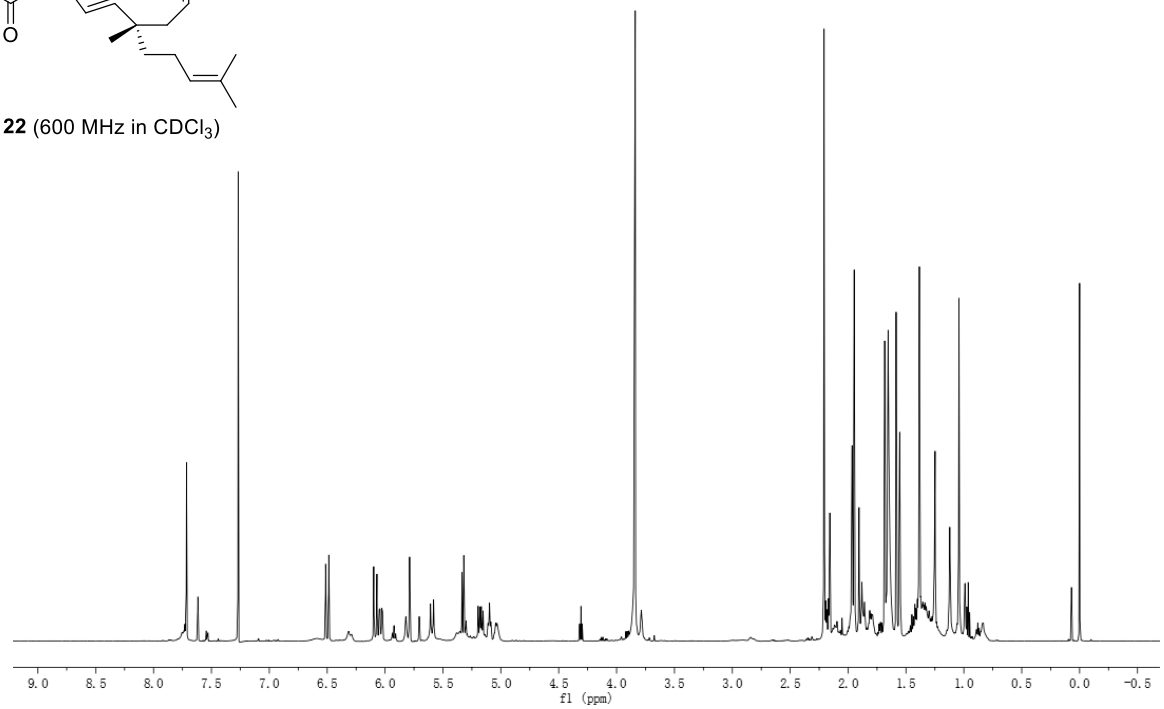


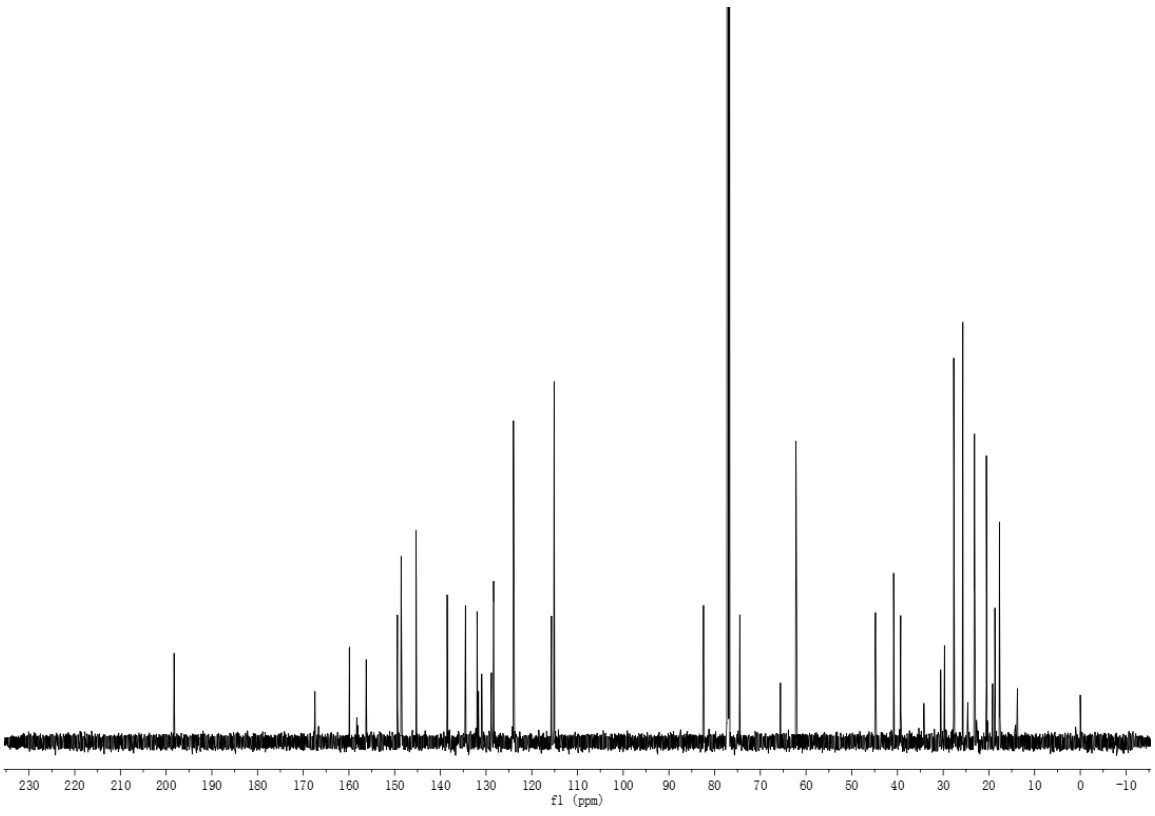

**21** (500 MHz in $CDCl_3$)

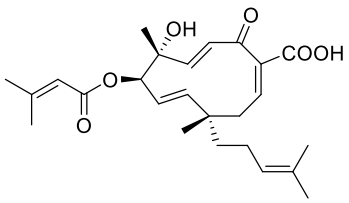





**22** (600 MHz in $CDCl_3$)

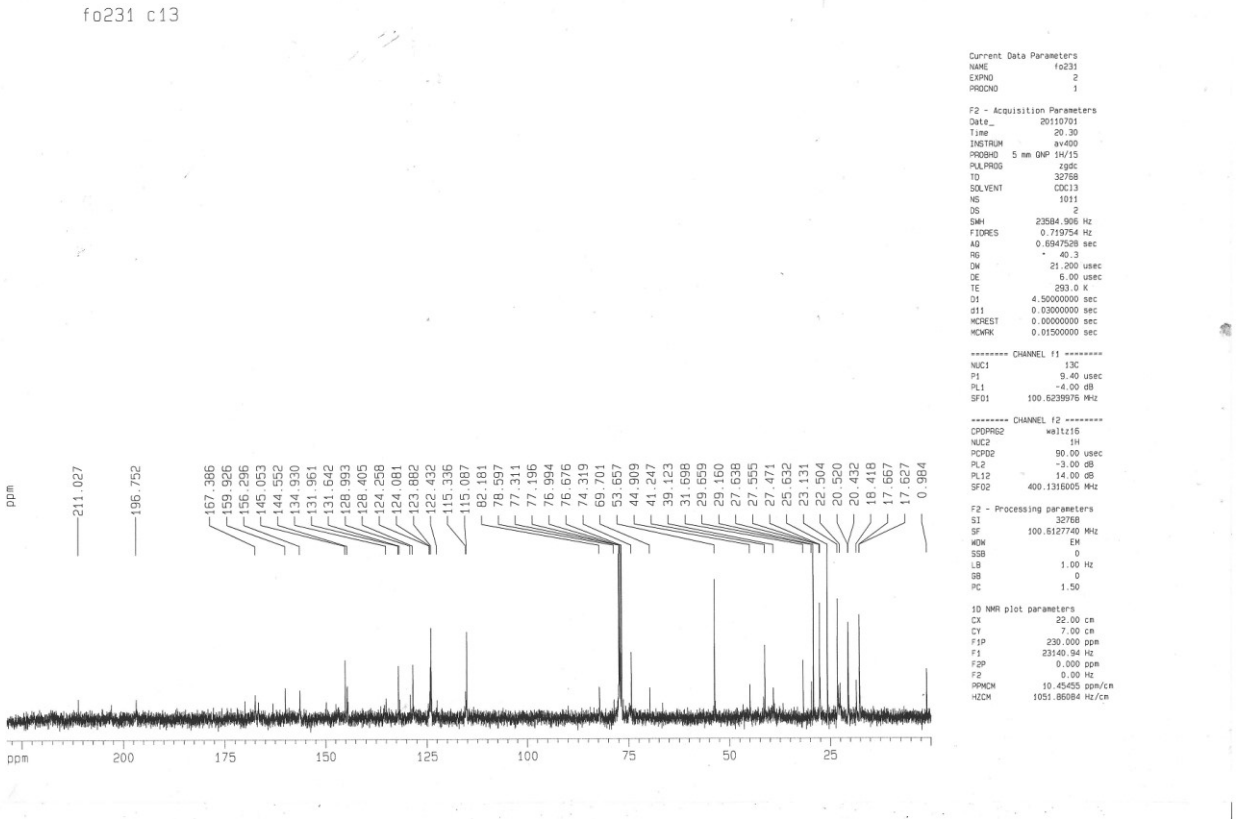





**10** (400 MHz in $CDCl_3$)

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Current Data Parameters
NAME                  fo231
EXPNO                     2
PROCNO                    1

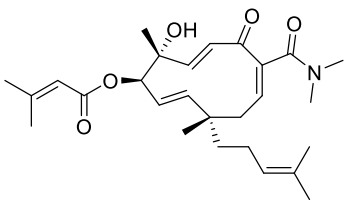
F2 - Acquisition Parameters
Date_              20110701
Time                  20.30
INSTRUM               av400
PROBHD   5 mm QNP 1H/15
PULPROG               zgdc
TD                   32768
SOLVENT               CDCl3
NS                     1011
DS                        2
SWH                23584.906 Hz
FIDRES             0.719754 Hz
AQ                 0.6947528 sec
RG                      40.3
DW                   21.200 usec
DE                    6.00 usec
TE                  293.0 K
D1                 4.50000000 sec
d11                0.03000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                    9.40 usec
PL1                  -4.00 dB
SFO1            100.6239975 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                90.00 usec
PL2                  -3.00 dB
PL12                 14.00 dB
SFO2            400.1316005 MHz

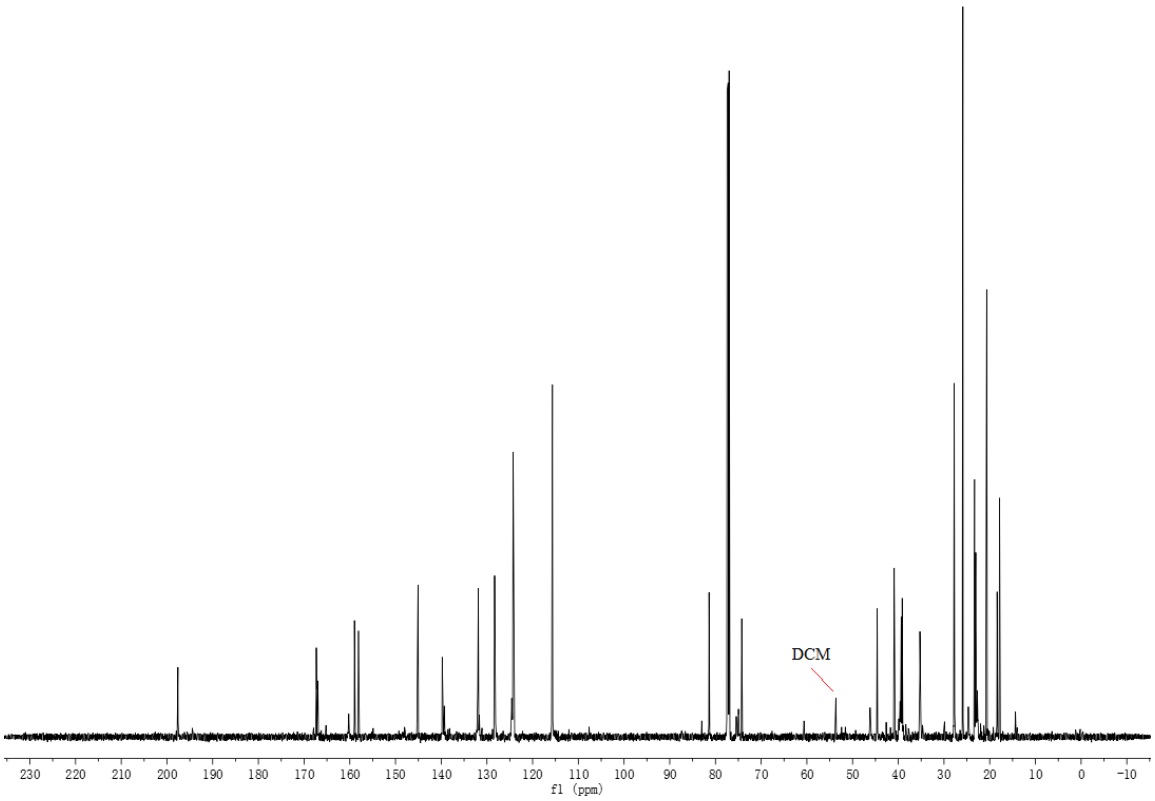
F2 - Processing parameters
SI                       32768
SF              100.6127740 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.50

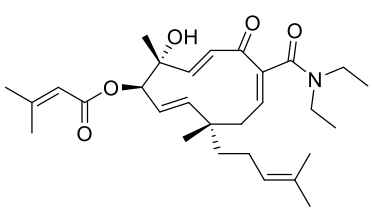
1D NMR plot parameters
CX                   22.00 cm
CY                    7.00 cm
F1P                 230.000 ppm
F1                23140.94 Hz
F2P                   0.000 ppm
F2                    0.00 Hz
PPMCM             10.45455 ppm/cm
HZCM              1051.86084 Hz/cm
```




**24a** (600 MHz in $CDCl_3$)

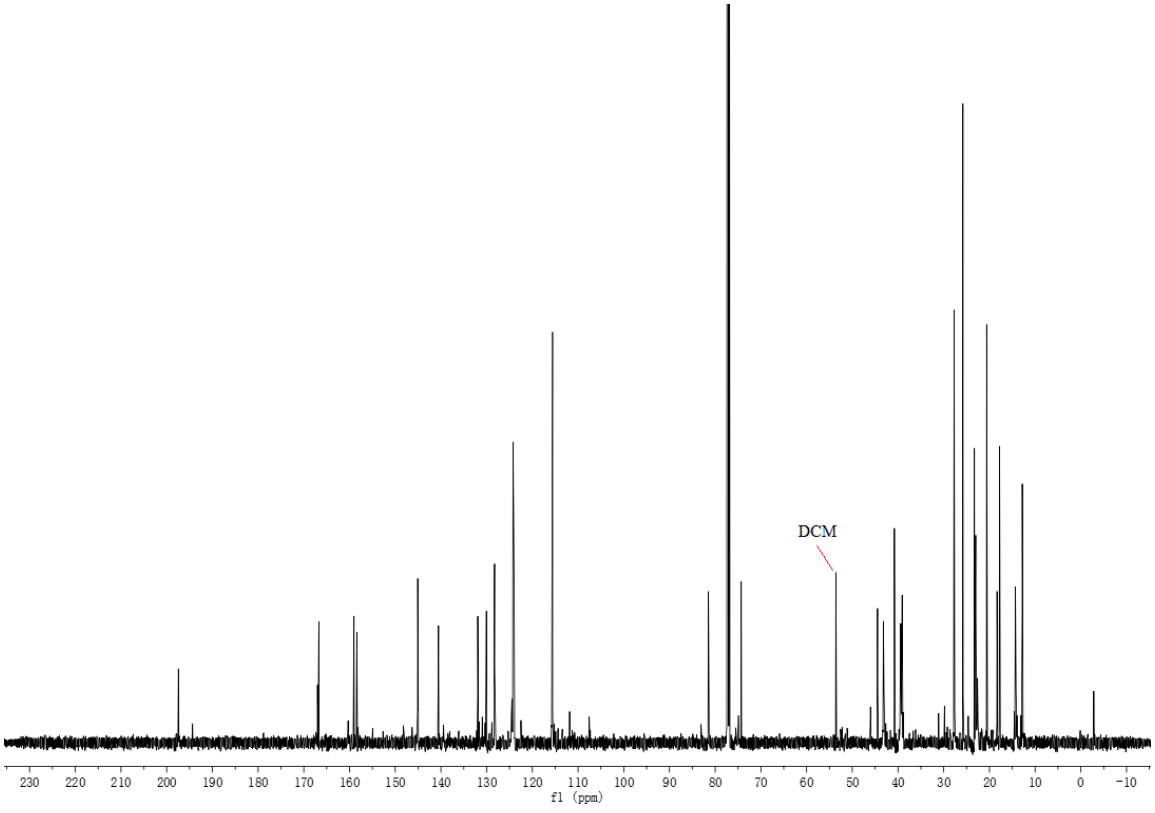


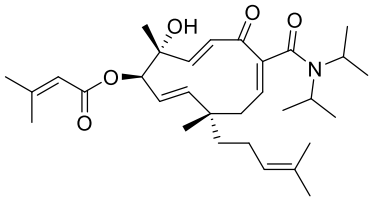






**24b** (600 MHz in $CDCl_3$)

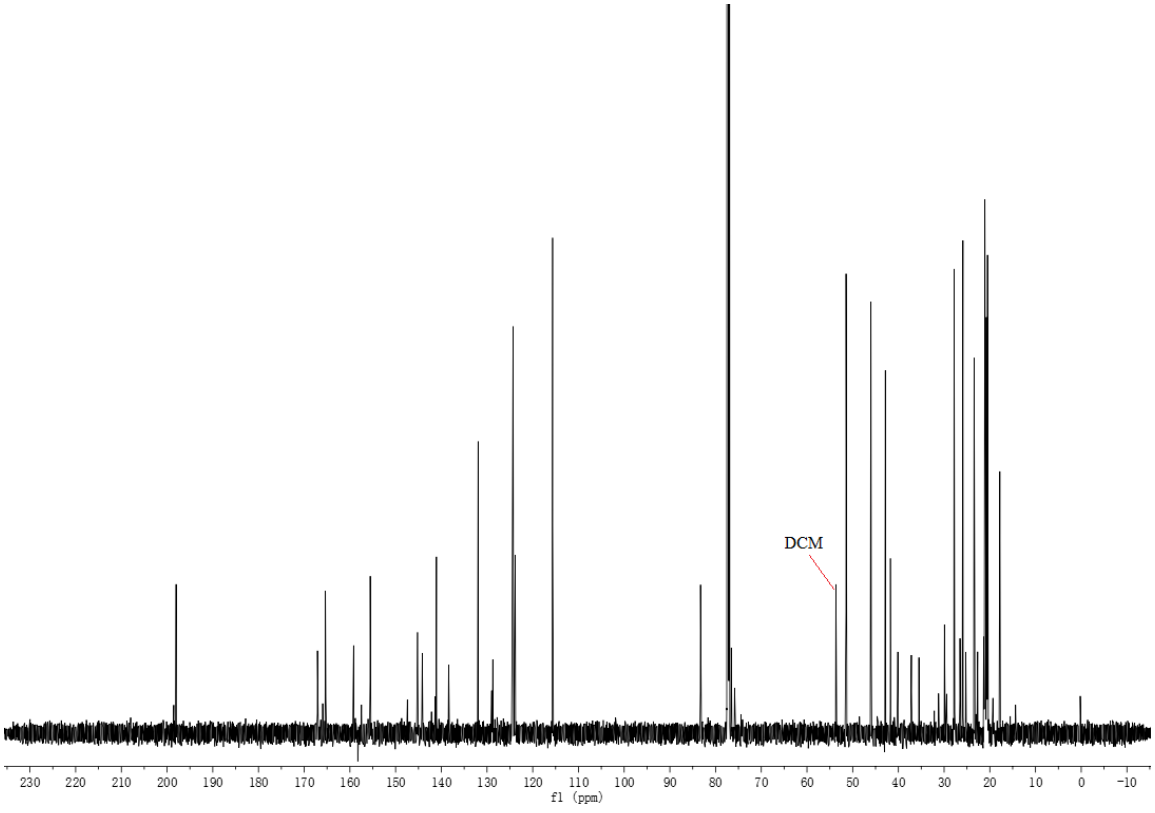


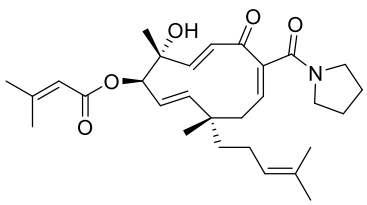






**24c** (600 MHz in $CDCl_3$)

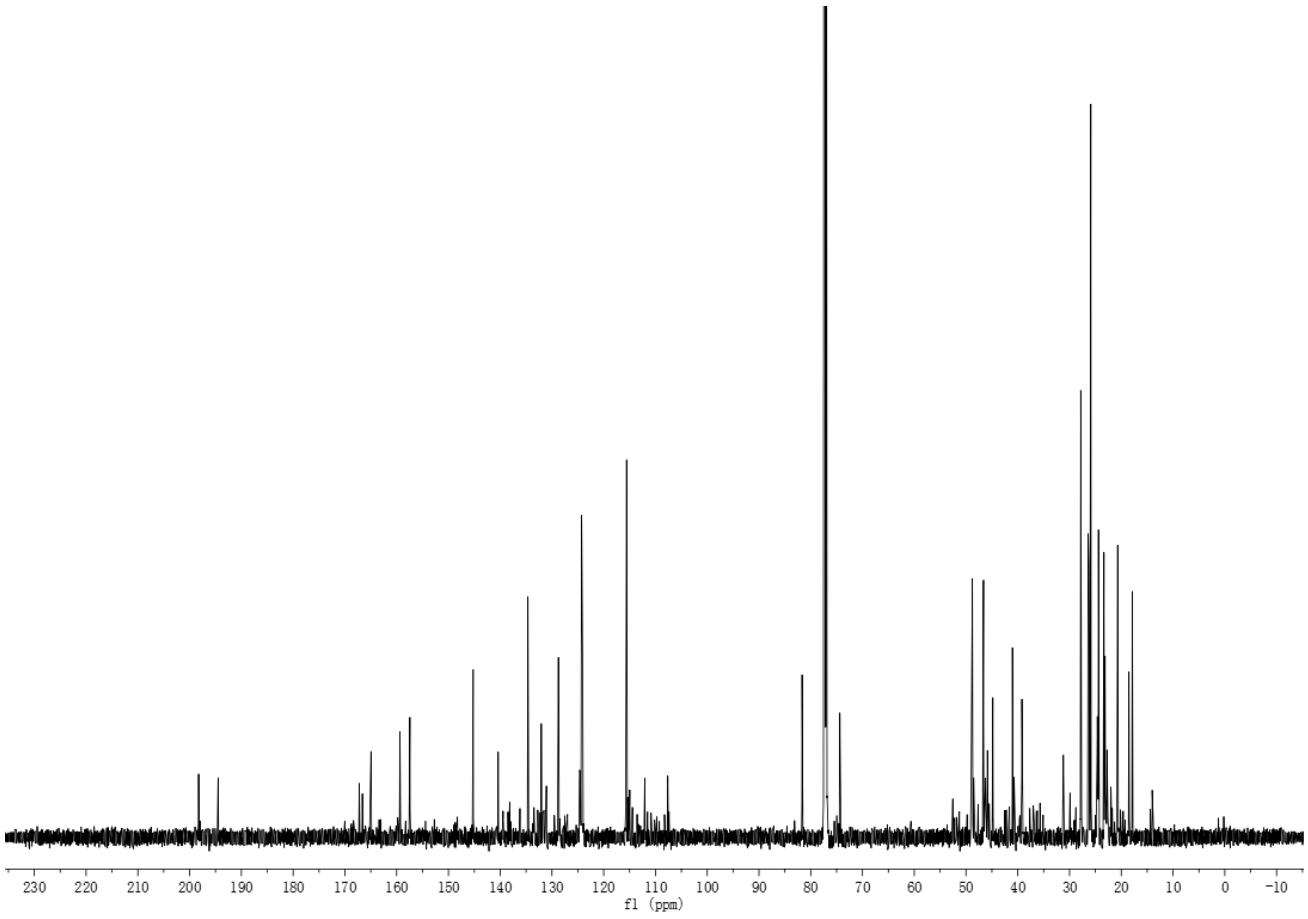


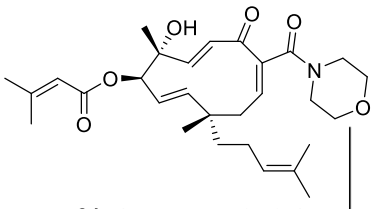





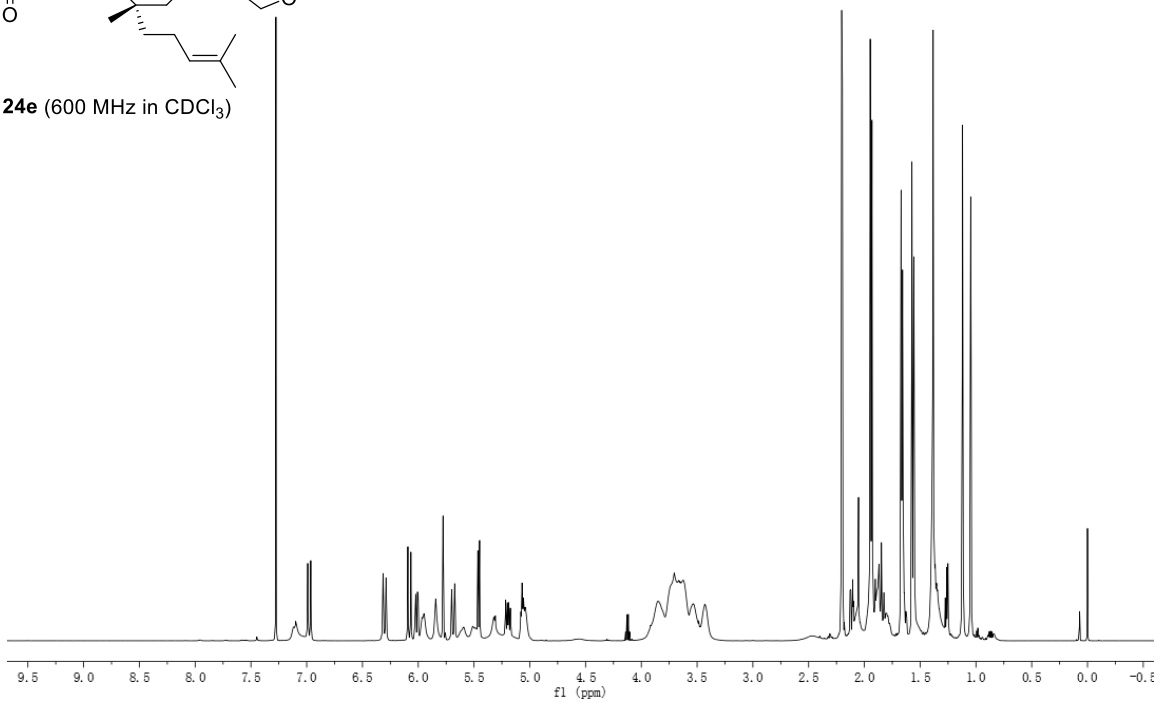

**24d** (600 MHz in $CDCl_3$)

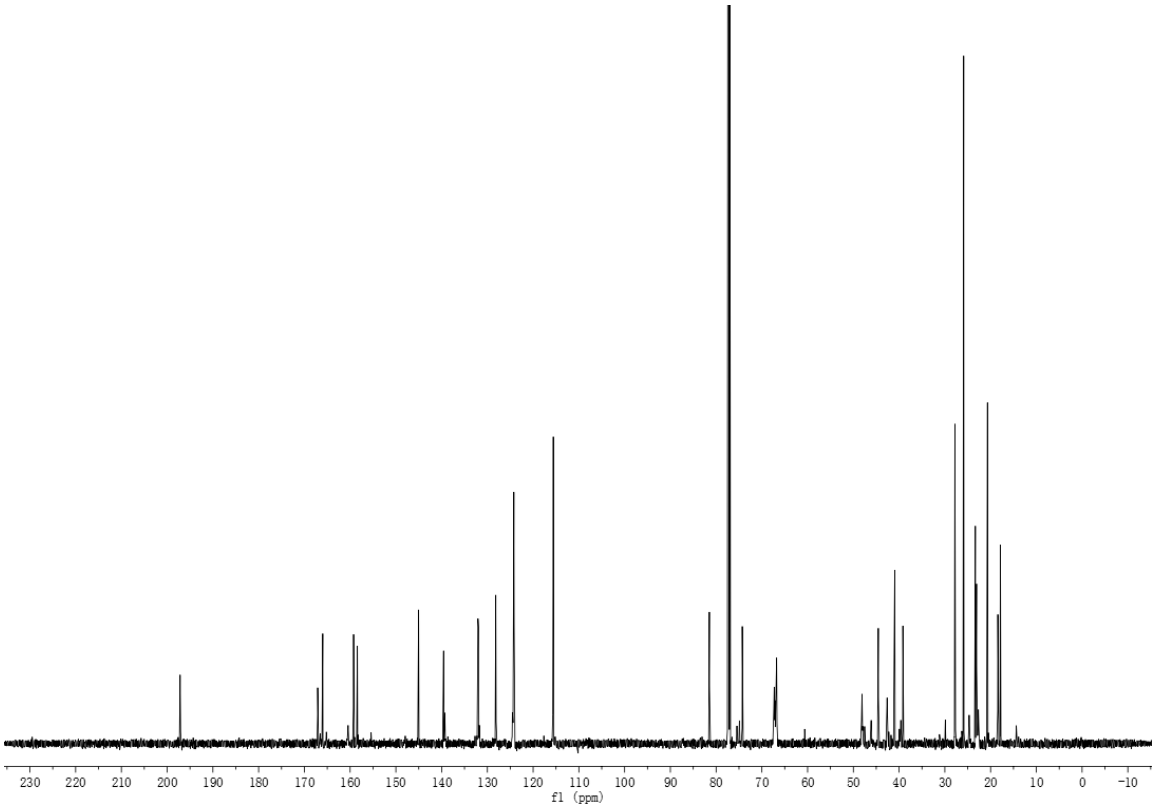


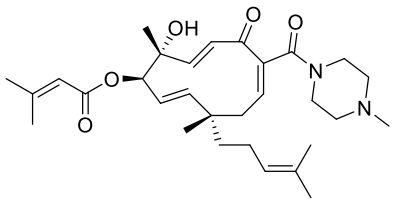





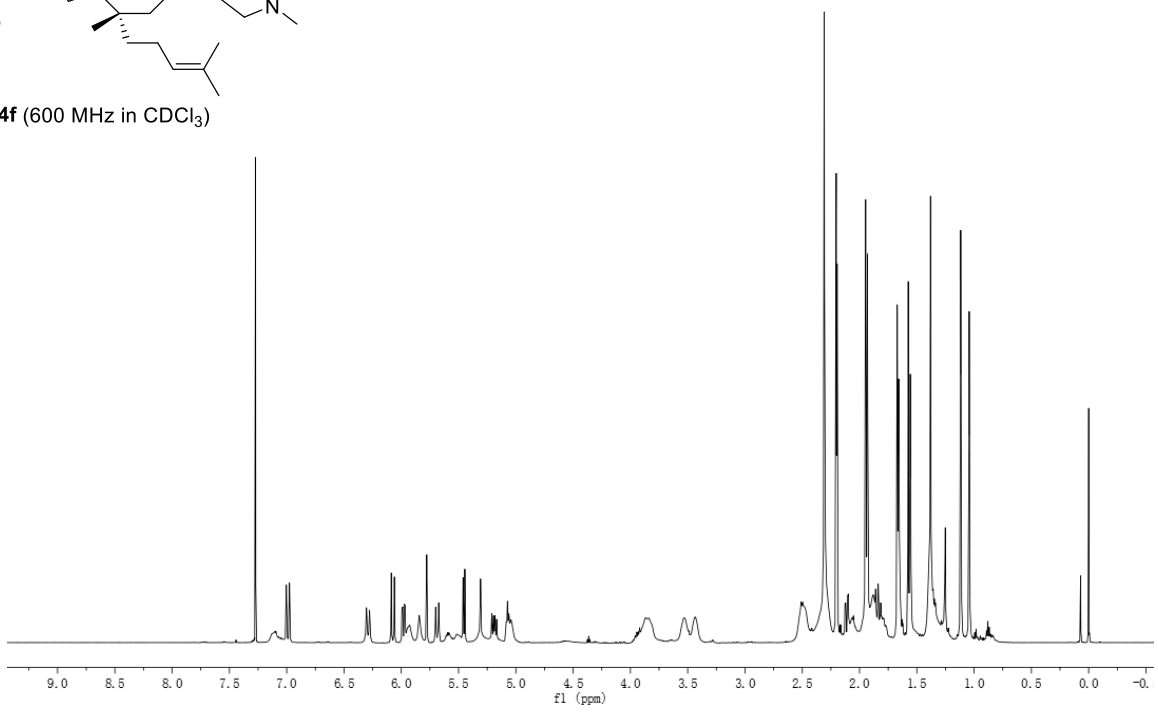

**24e** (600 MHz in $CDCl_3$)

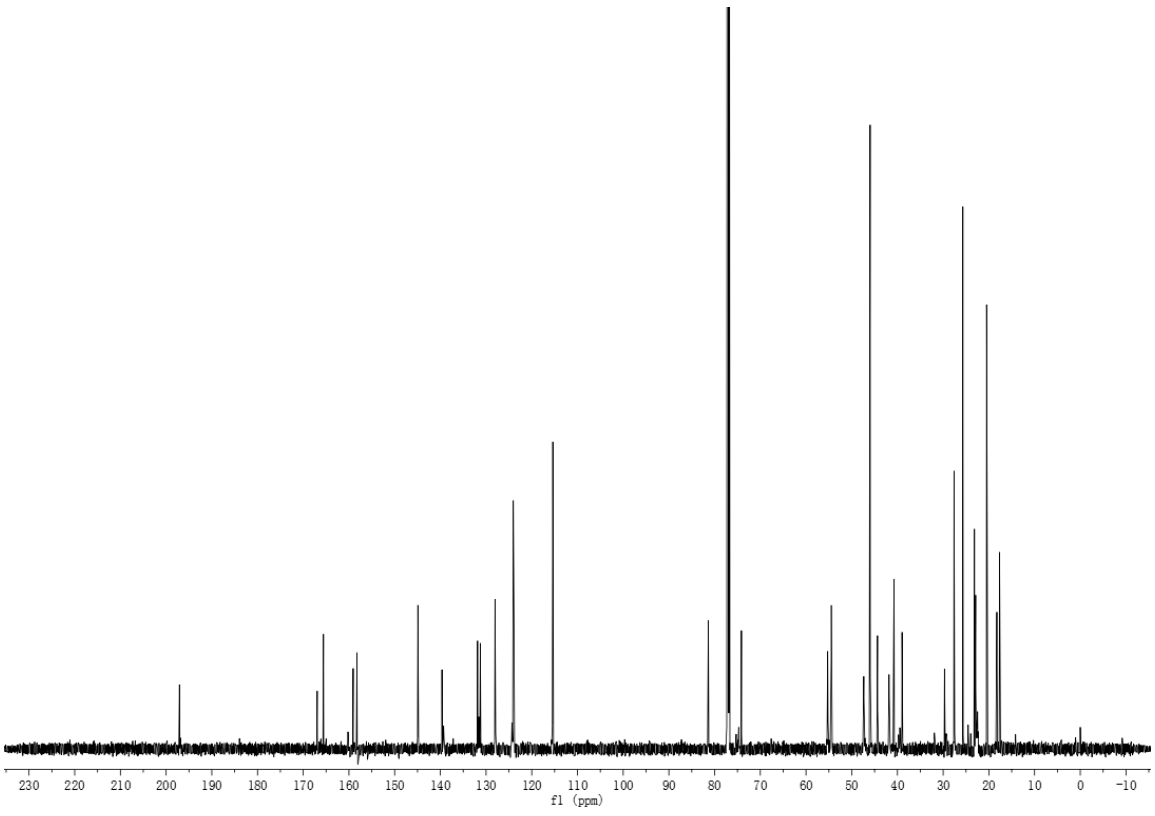


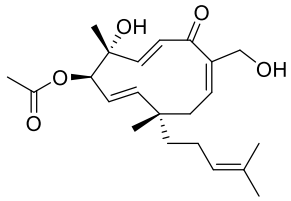





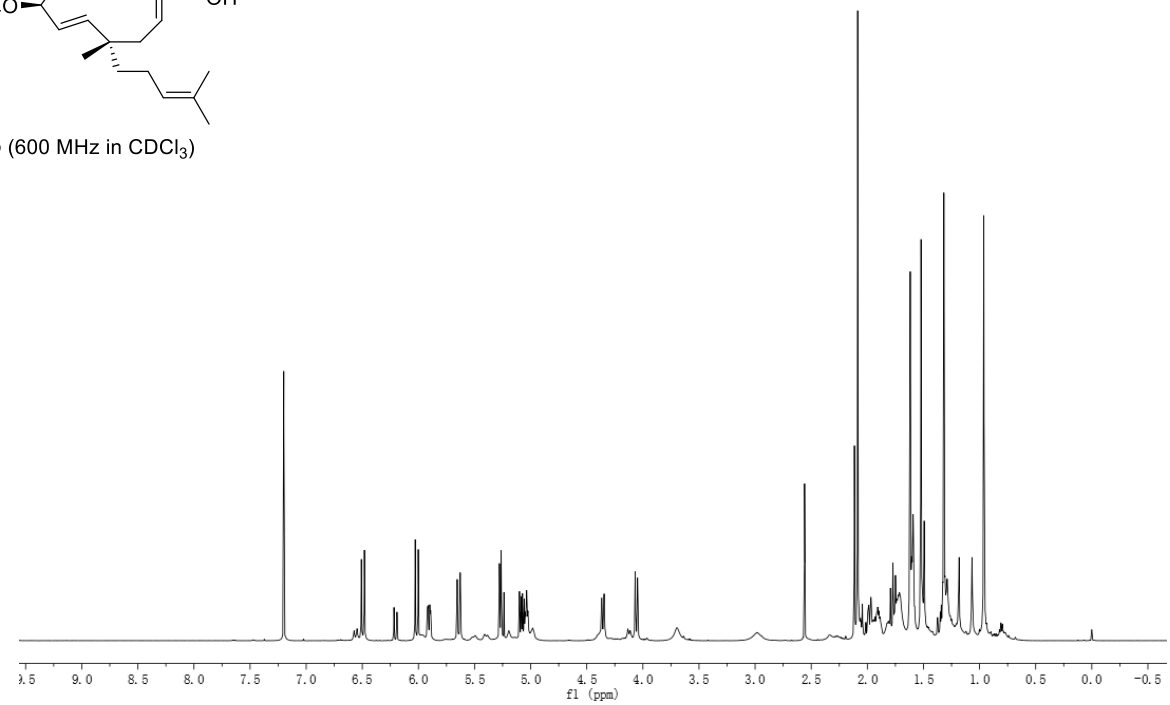

**24f** (600 MHz in $CDCl_3$)

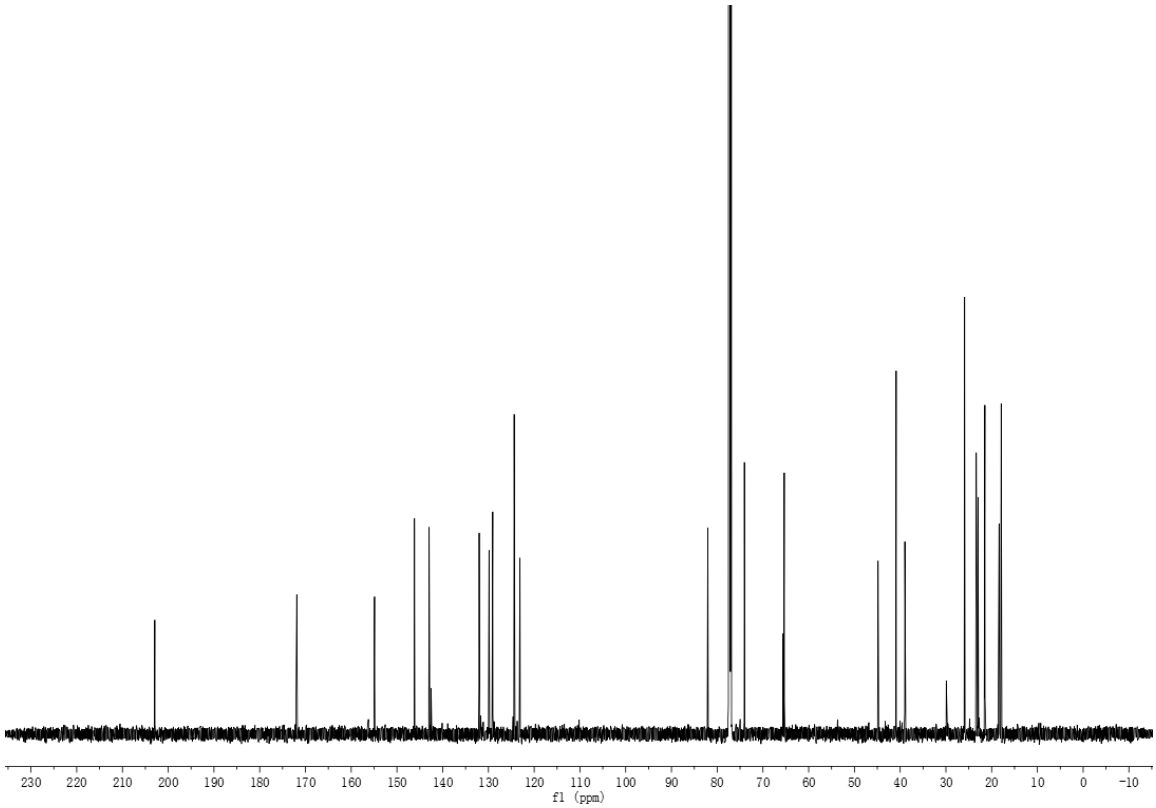


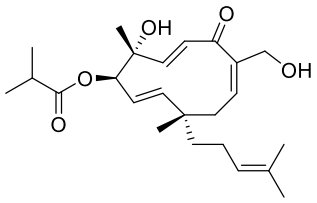





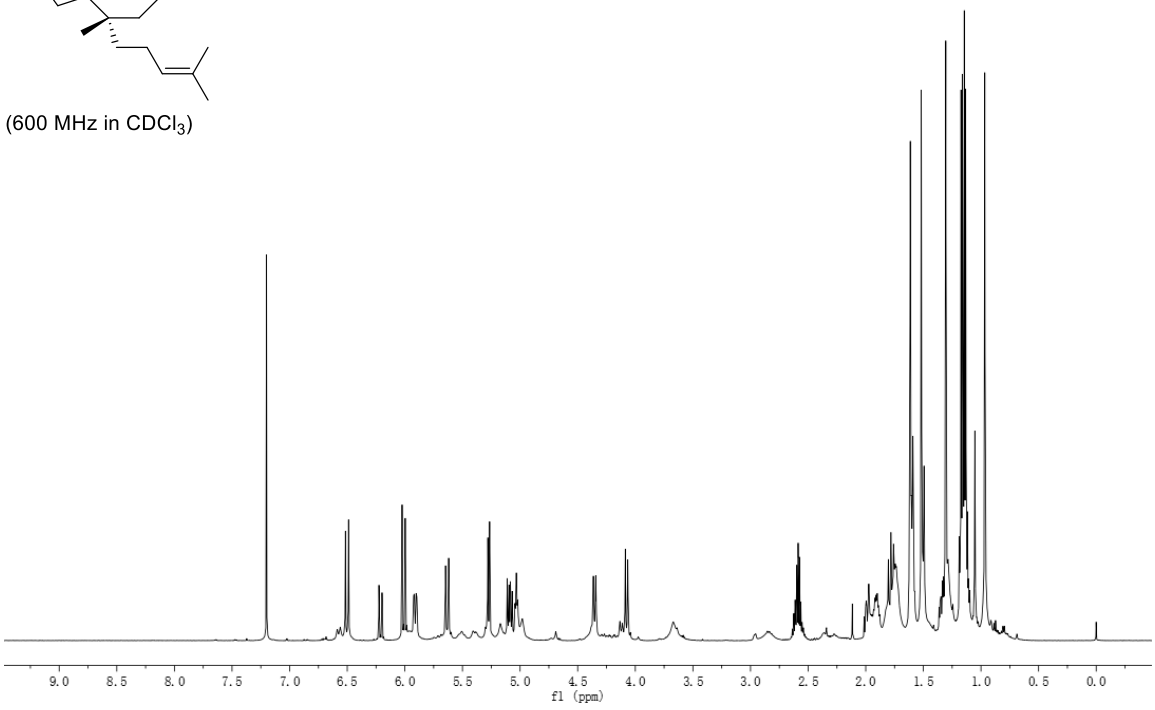

**28b** (600 MHz in $CDCl_3$)

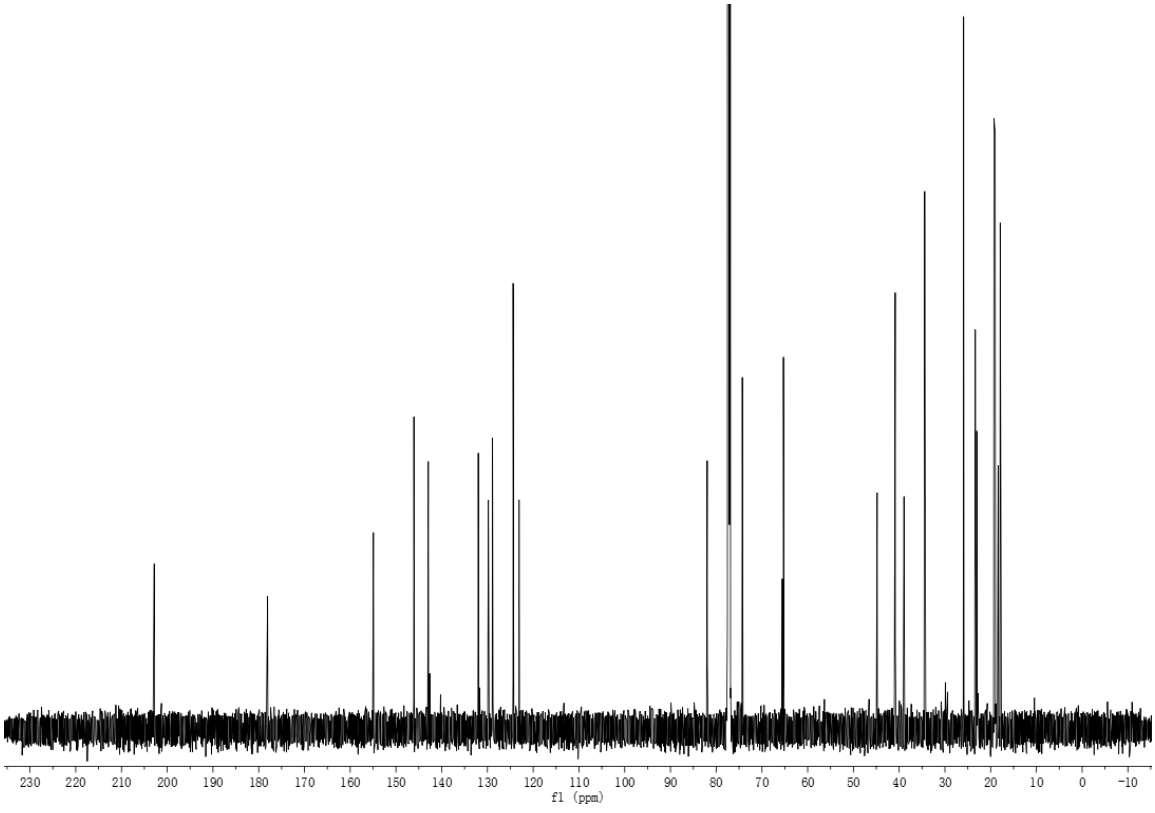


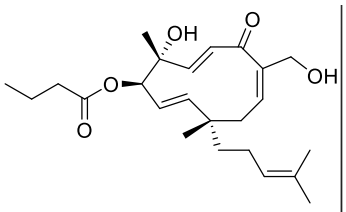





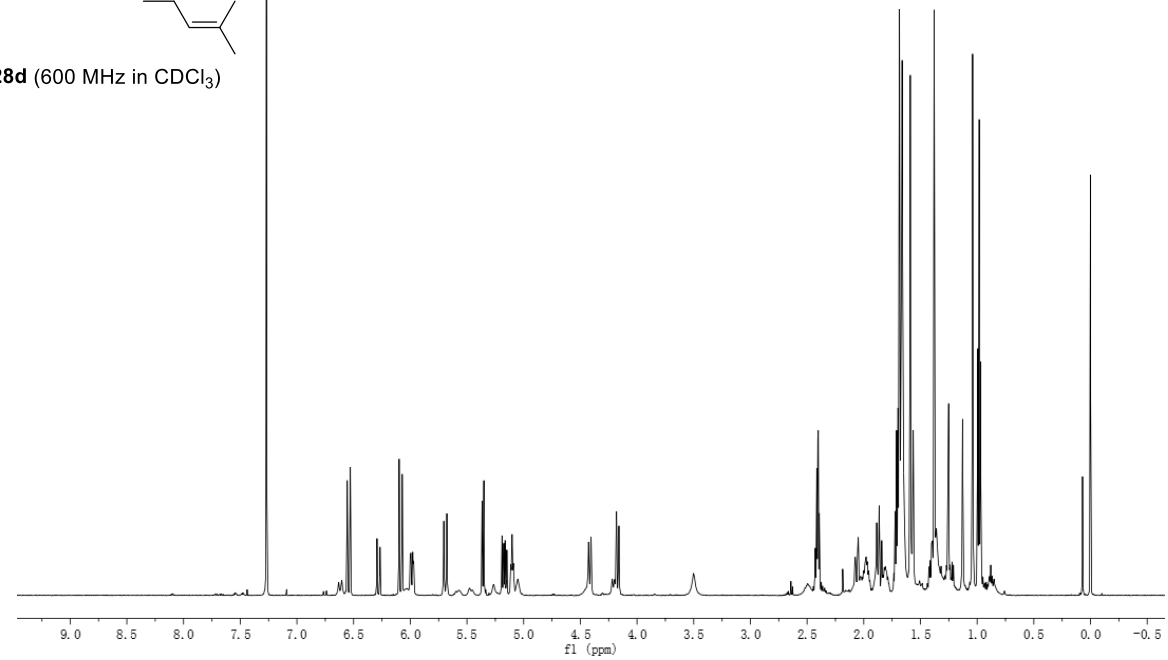

**28c** (600 MHz in $CDCl_3$)

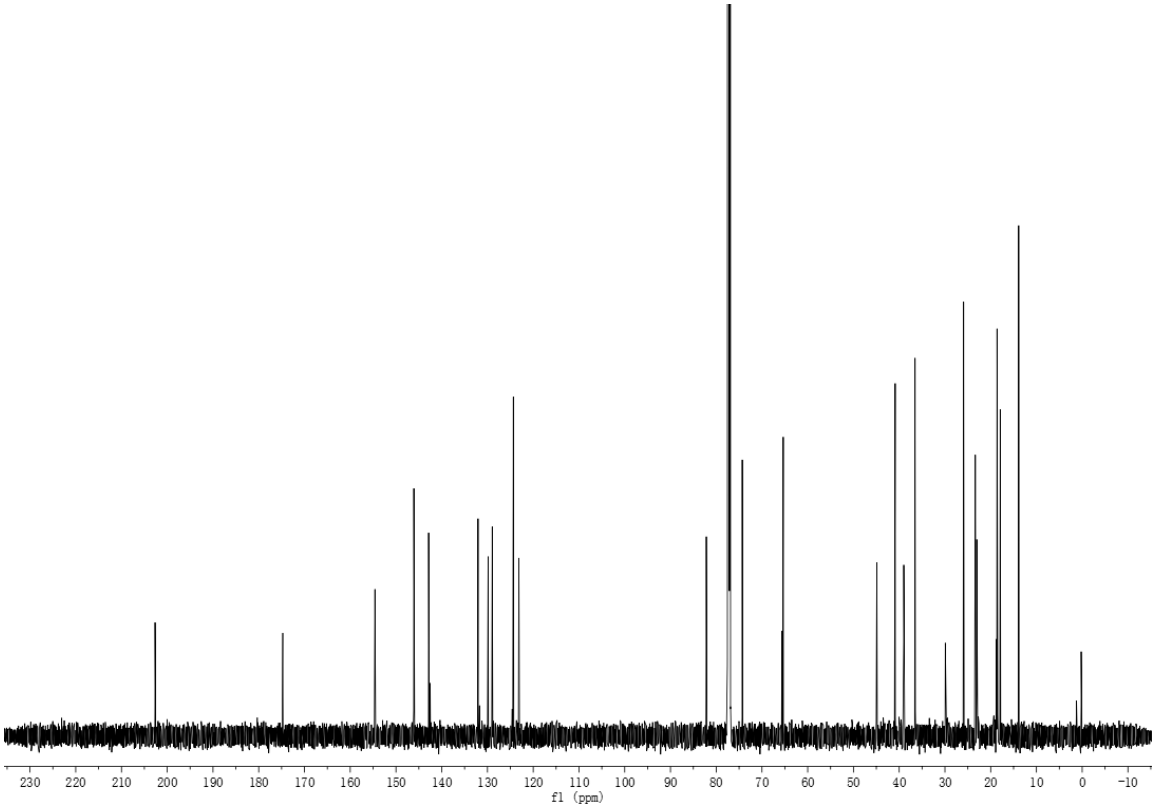


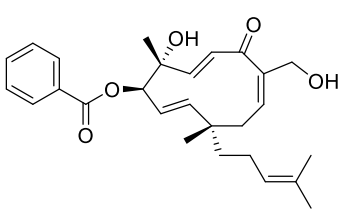






**28d** (600 MHz in $CDCl_3$)

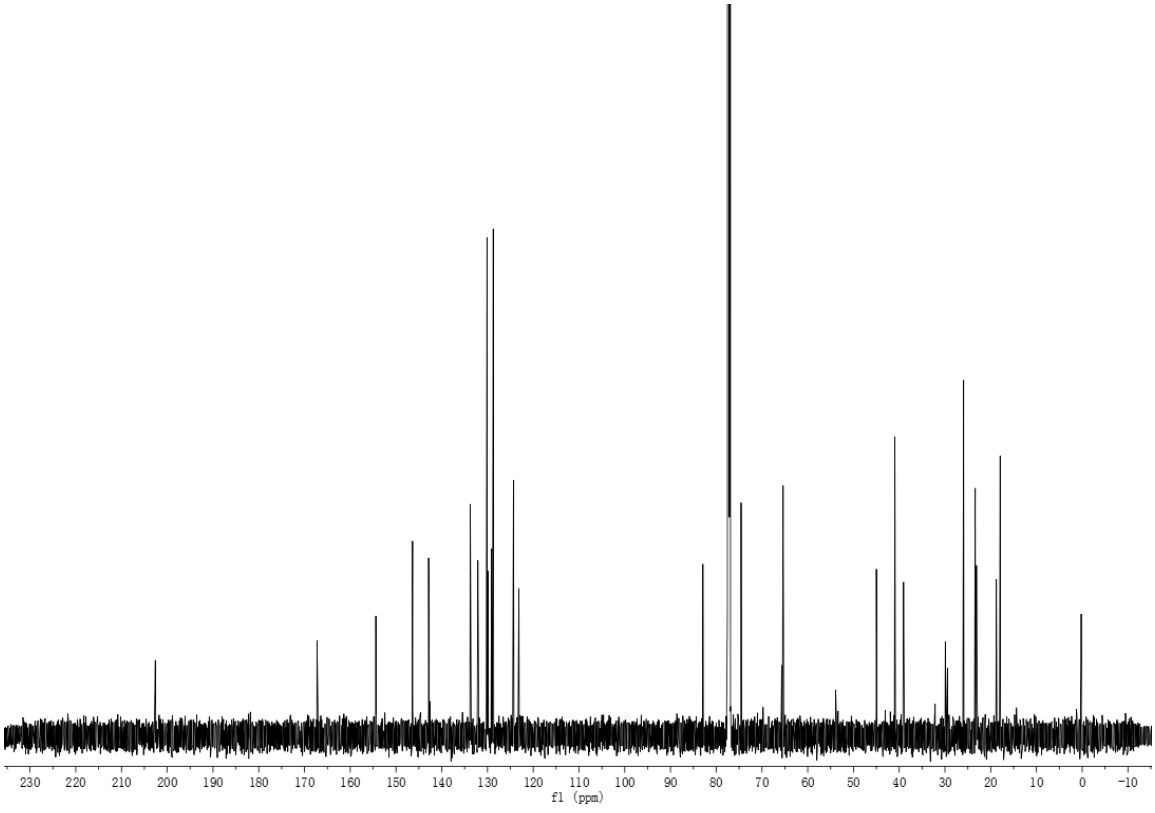


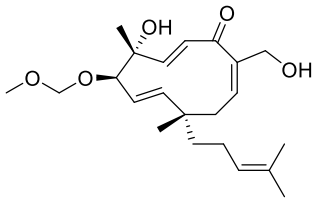





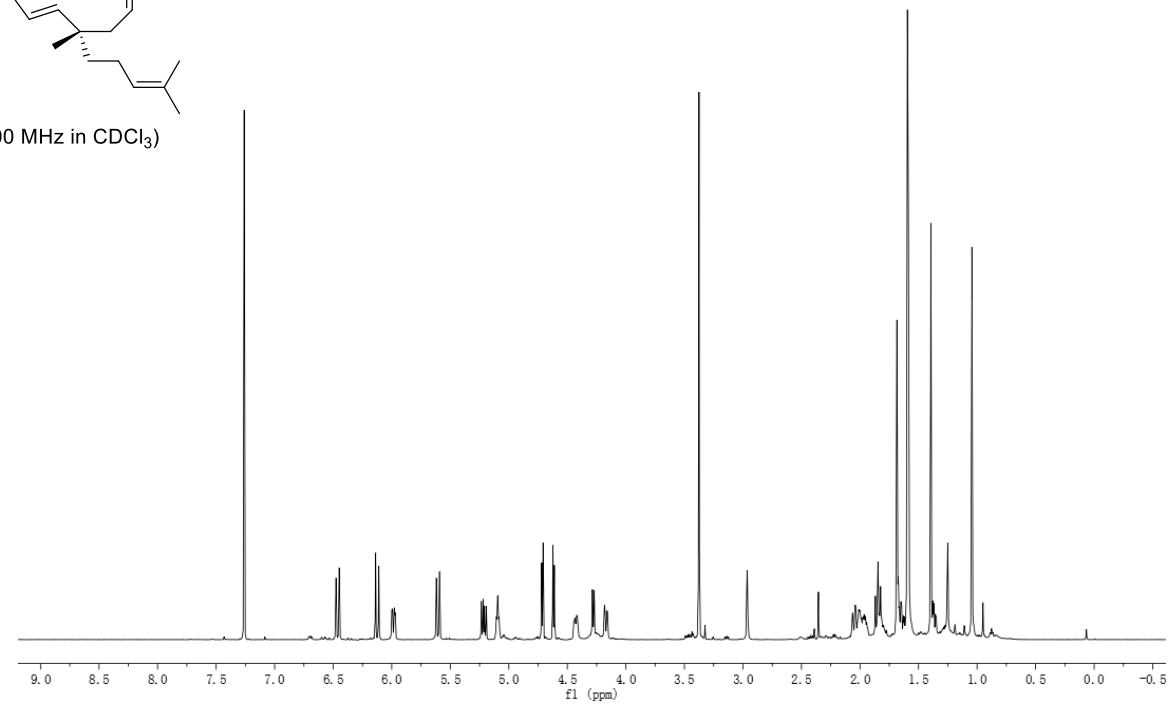

**28e** (600 MHz in $CDCl_3$)

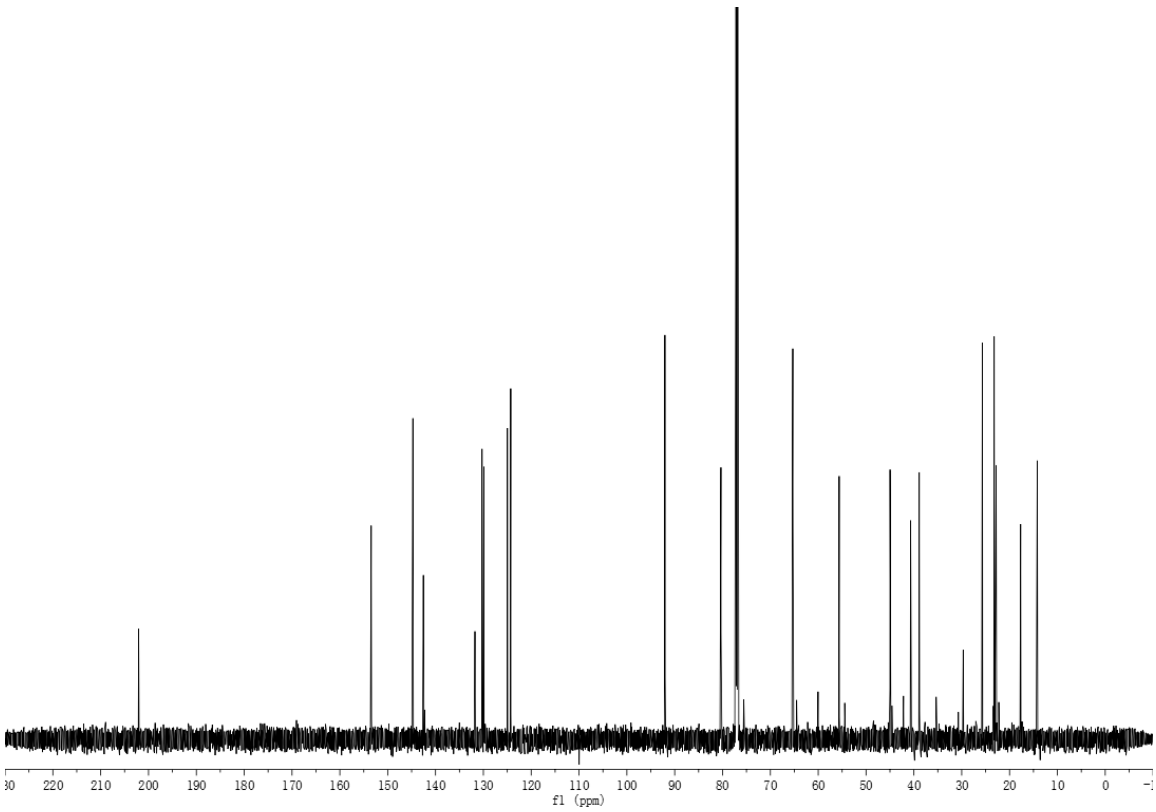


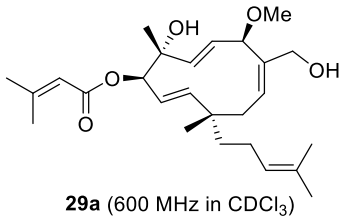






**28f** (600 MHz in $CDCl_3$)

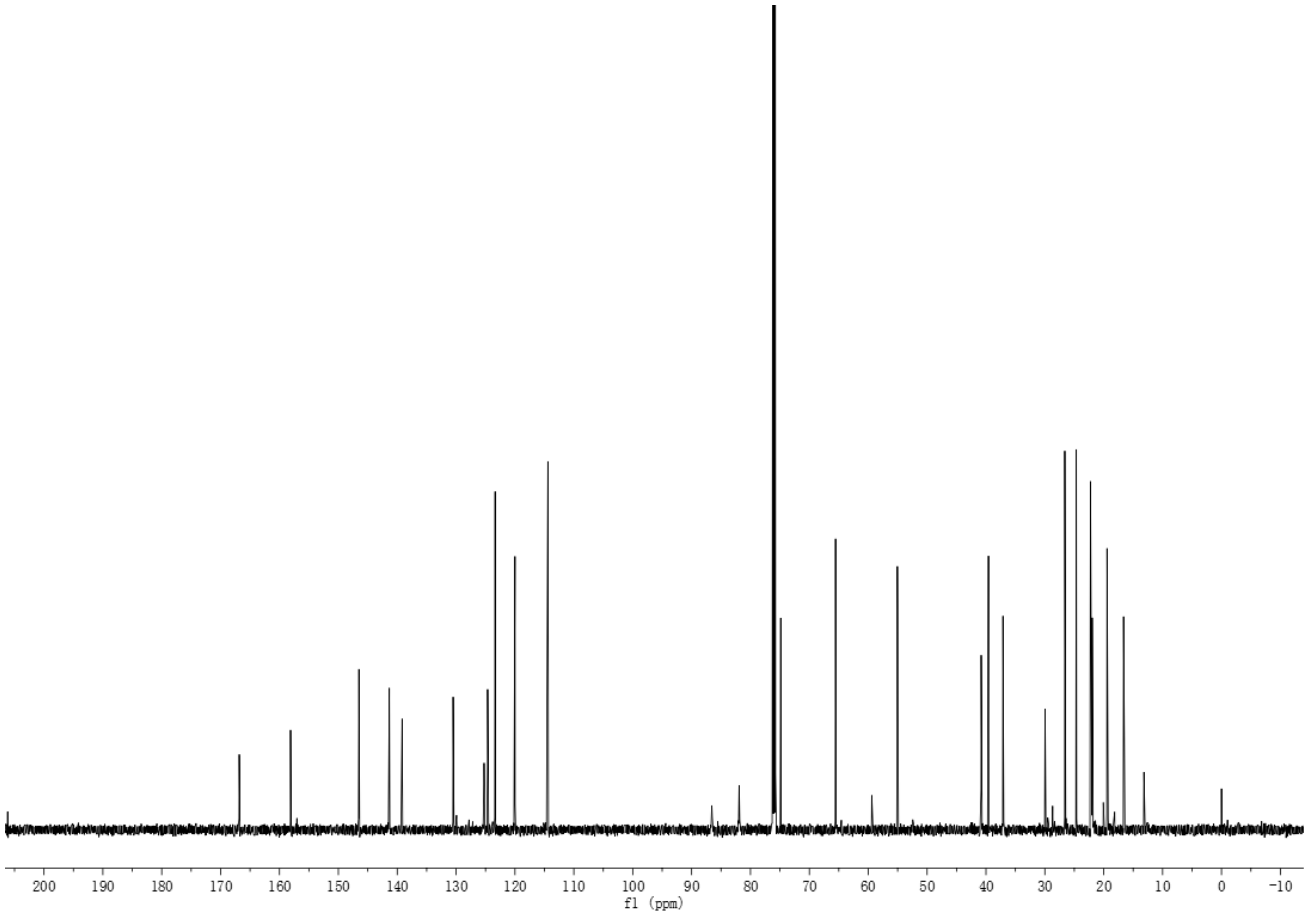


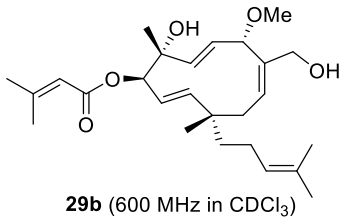






**29a** (600 MHz in $CDCl_3$)

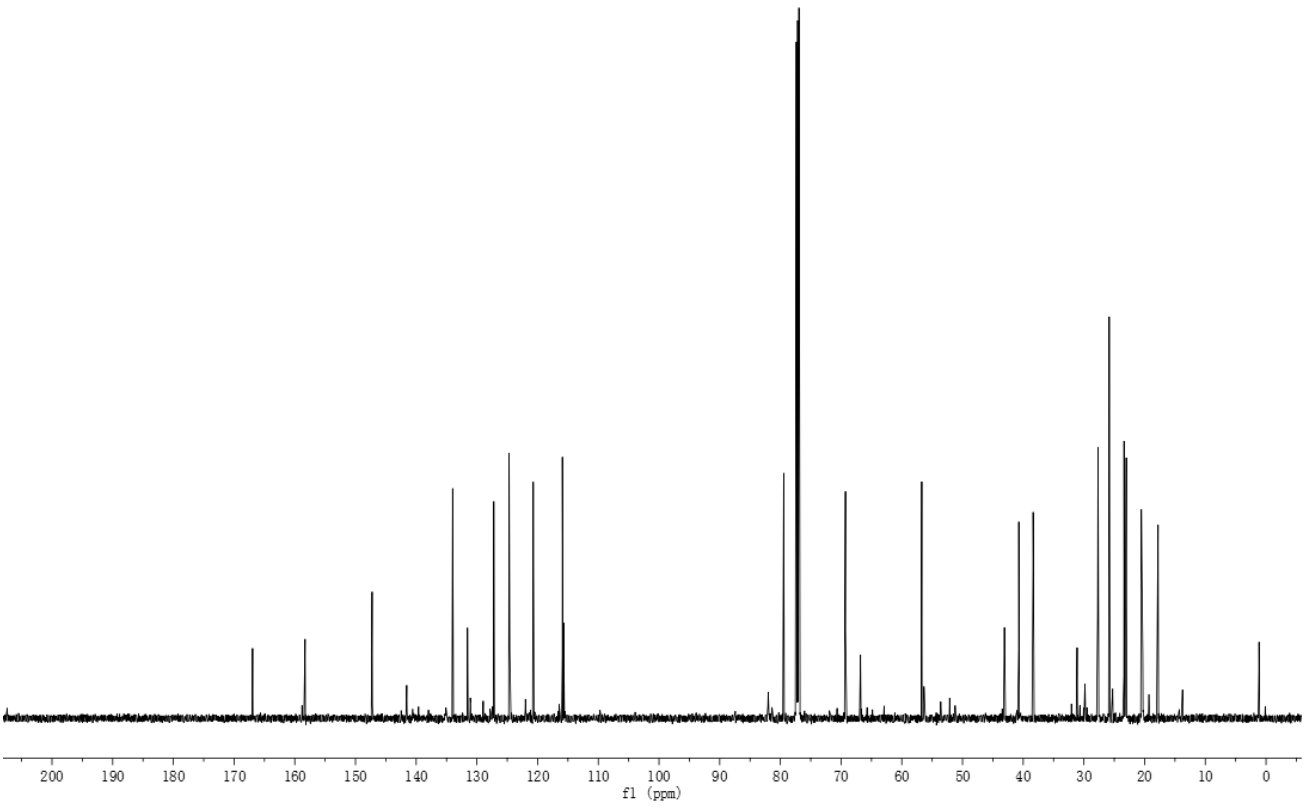


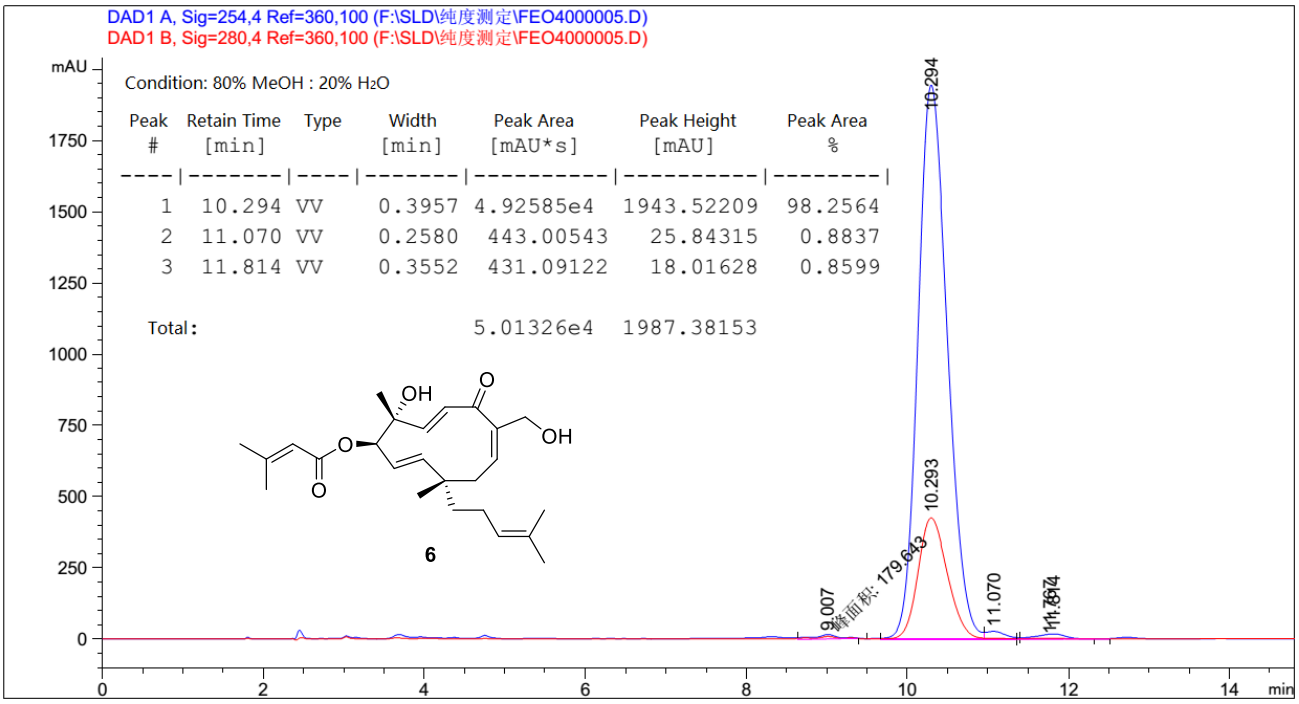


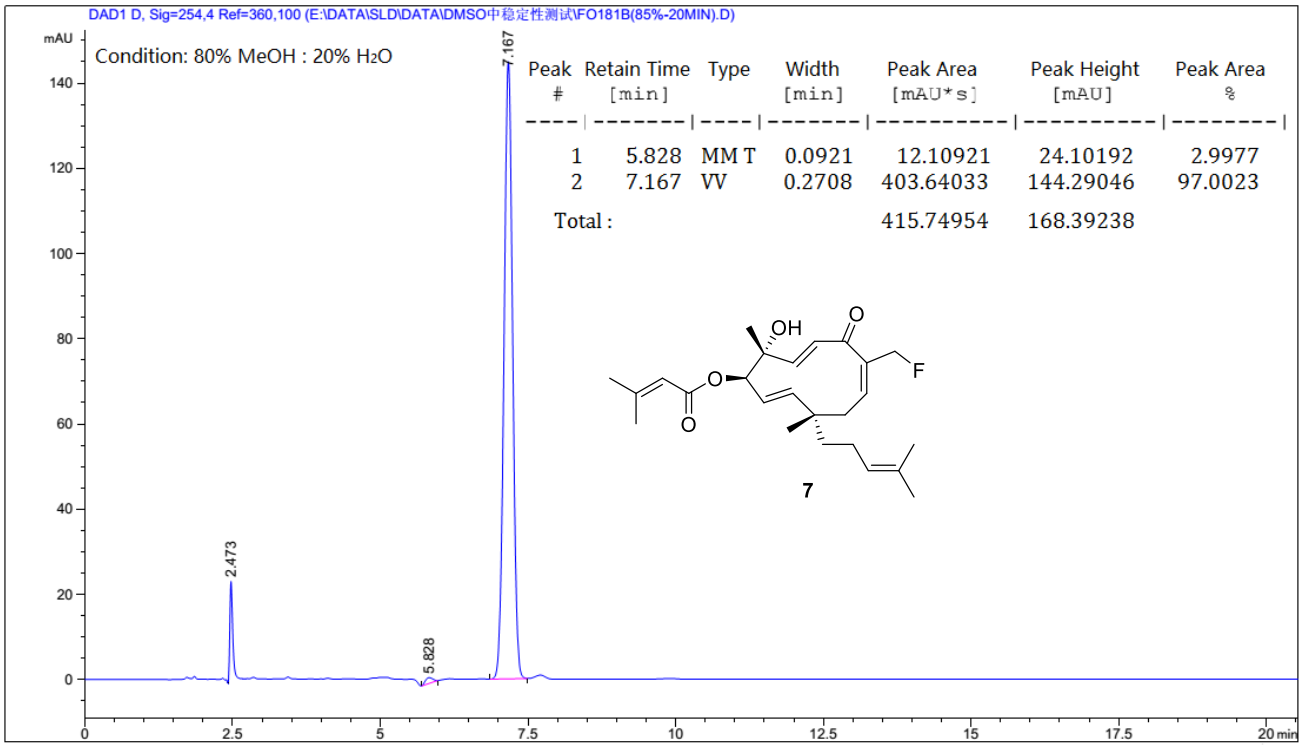

**29b** (600 MHz in $CDCl_3$)

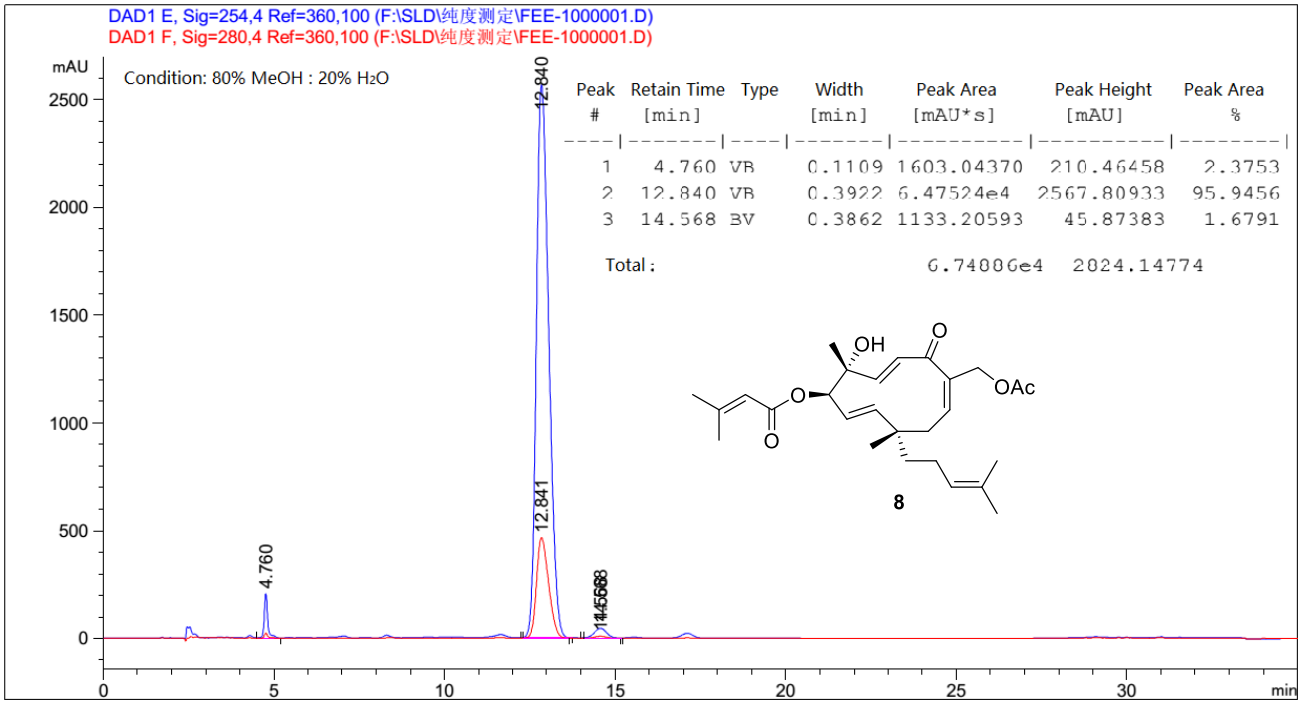


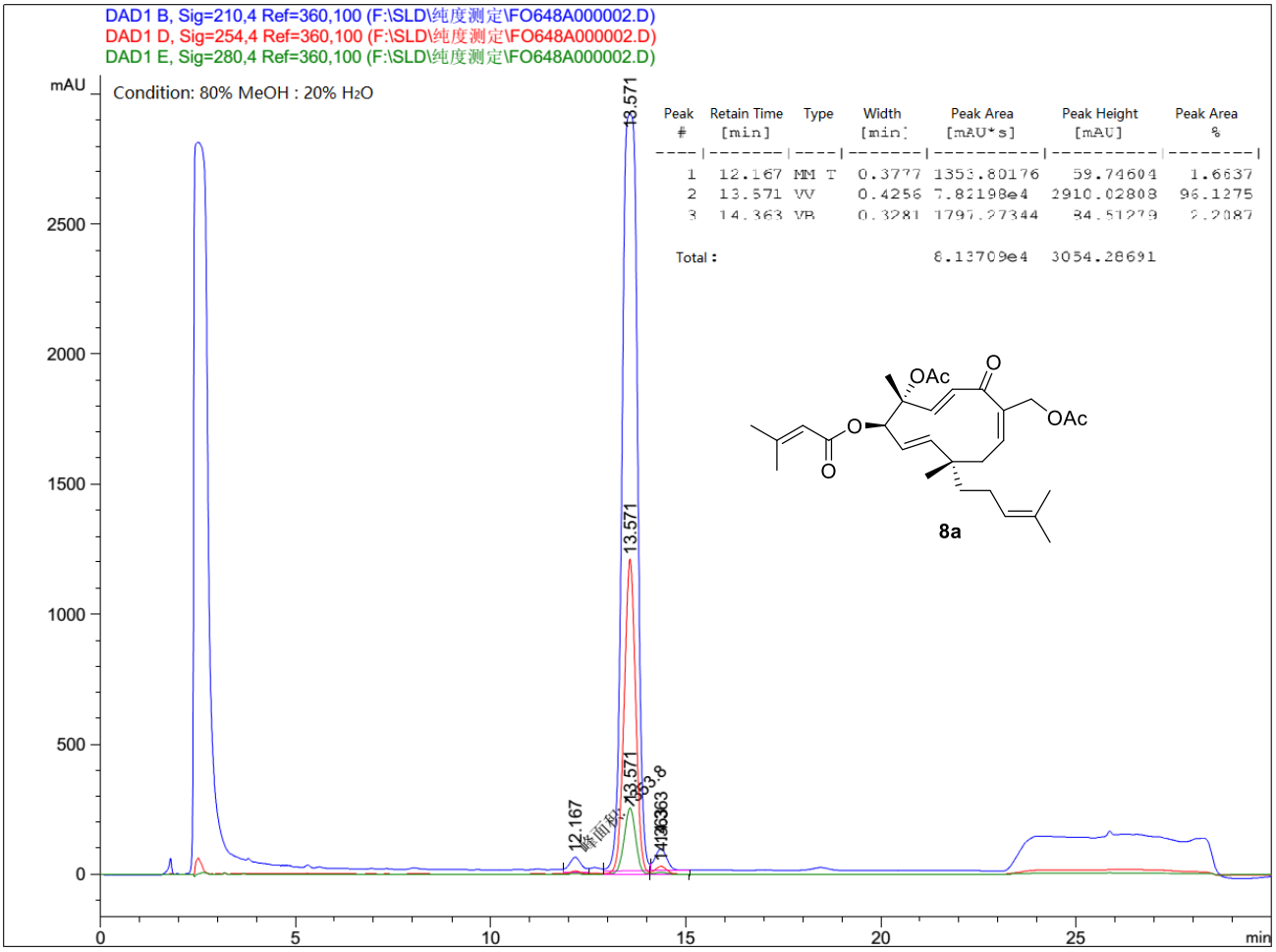



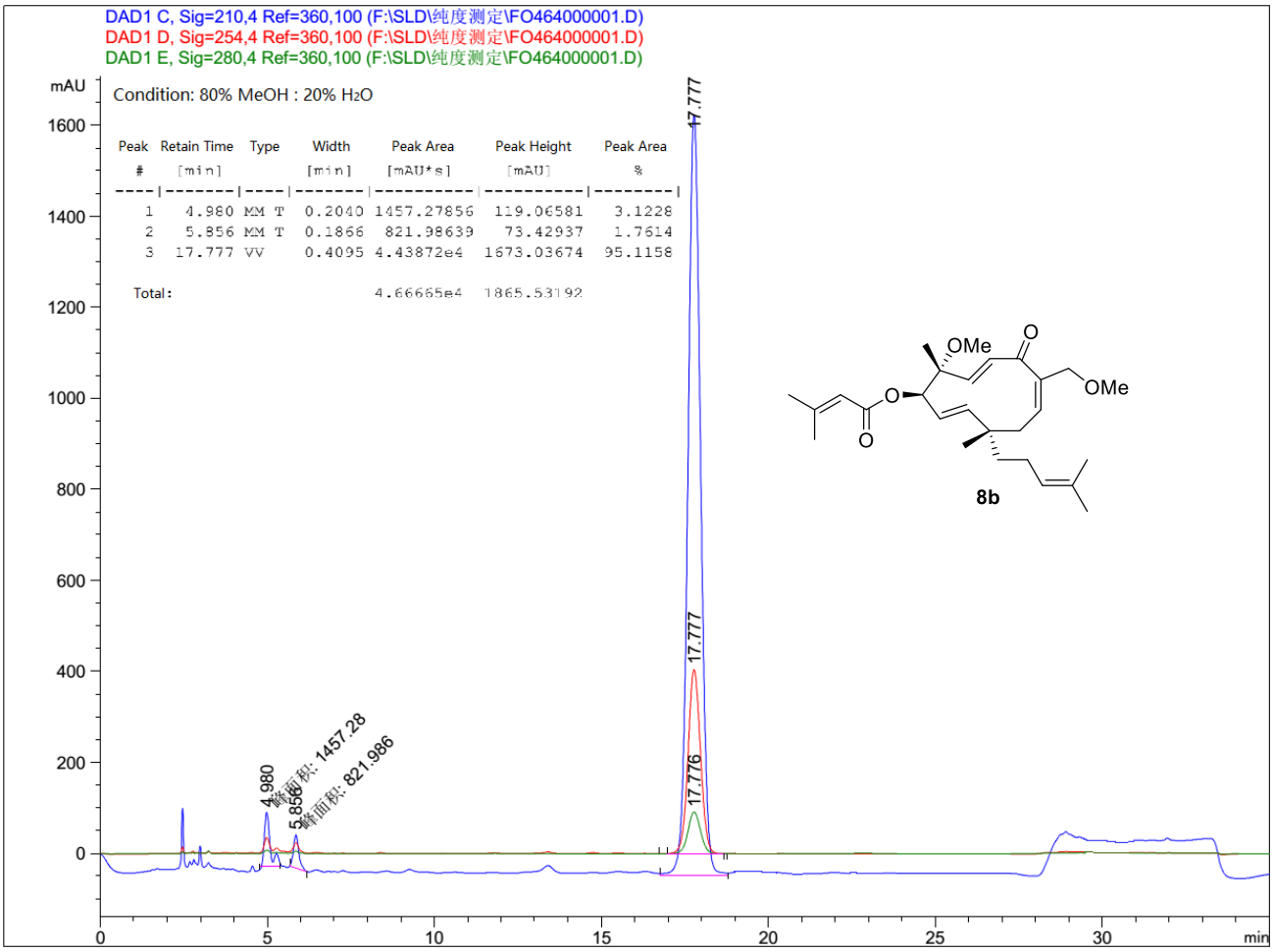
## HPLC chromatograms of tested vibsanin B derivatives

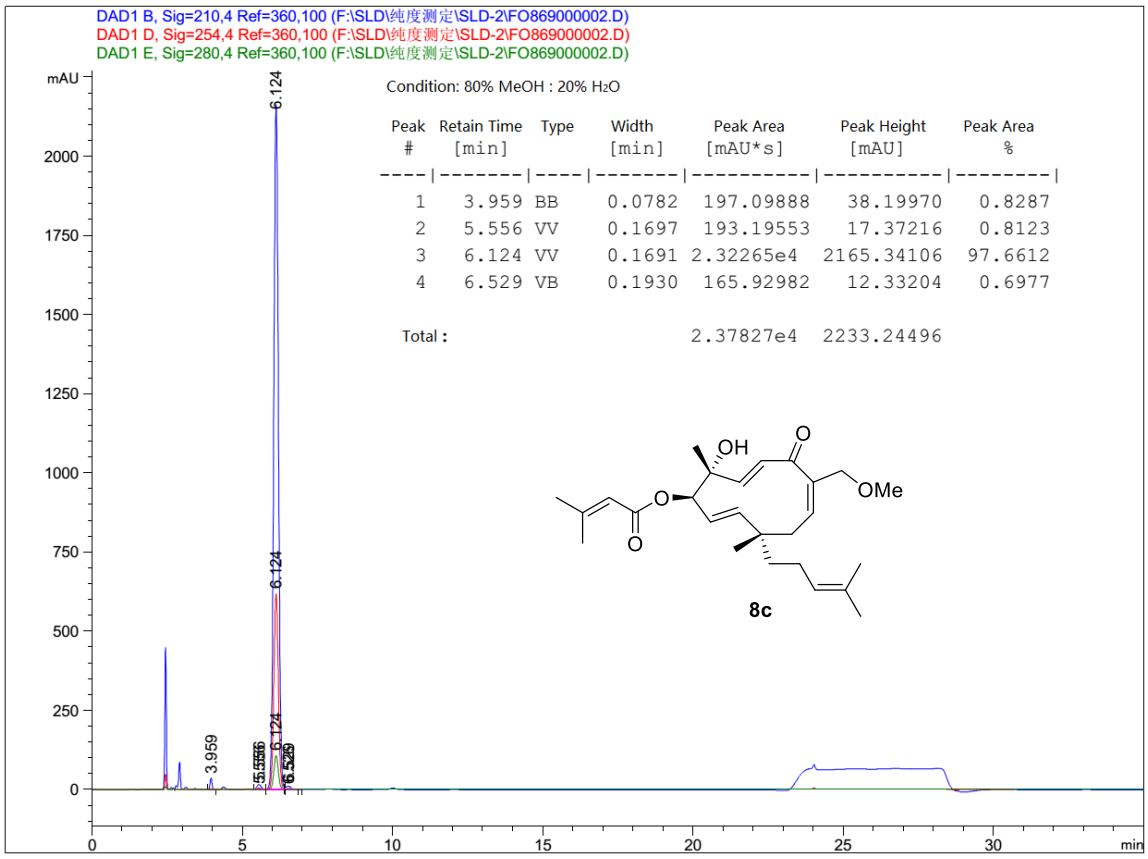



DAD1 E, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\FEE-1000001.D)
DAD1 F, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\FEE-1000001.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 4.760 | VB | 0.1109 | 1603.04370 | 210.46458 | 2.3753
2 | 12.840 | VB | 0.3922 | 6.47524e4 | 2567.80933 | 95.9456
3 | 14.568 | BV | 0.3862 | 1133.20593 | 45.87383 | 1.6791
Total : | | | | 6.74806e4 | 2824.14774
OH
O
OAc
O
O
8
4.760
12.841
min


DAD1 B, Sig=210,4 Ref=360,100 (F:\SLD\纯度测定\FO648A000002.D)
DAD1 D, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\FO648A000002.D)
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\FO648A000002.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 12.167 | MM T | 0.3777 | 1353.80176 | 59.74604 | 1.6637
2 | 13.571 | VV | 0.4256 | 7.82198e4 | 2910.02808 | 96.1275
3 | 14.363 | VB | 0.3281 | 1797.27344 | 84.51279 | 2.2087
Total : | | | | 8.13709e4 | 3054.28691
OAc
O
OAc
O
O
8a
13.571
12.167
min


DAD1 C, Sig=210,4 Ref=360,100 (F:\SLD\纯度测定\FO464000001.D)
DAD1 D, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\FO464000001.D)
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\FO464000001.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 4.980 | MM T | 0.2040 | 1457.27856 | 119.06581 | 3.1228
2 | 5.856 | MM T | 0.1866 | 821.98639 | 73.42937 | 1.7614
3 | 17.777 | VV | 0.4095 | 4.43872e4 | 1673.03674 | 95.1158
Total: 4.66665e4 1865.53192
17.777
4.980
峰面积: 1457.28
5.856
峰面积: 821.986
17.777
17.776
OMe
O
OMe
O
O
8b
min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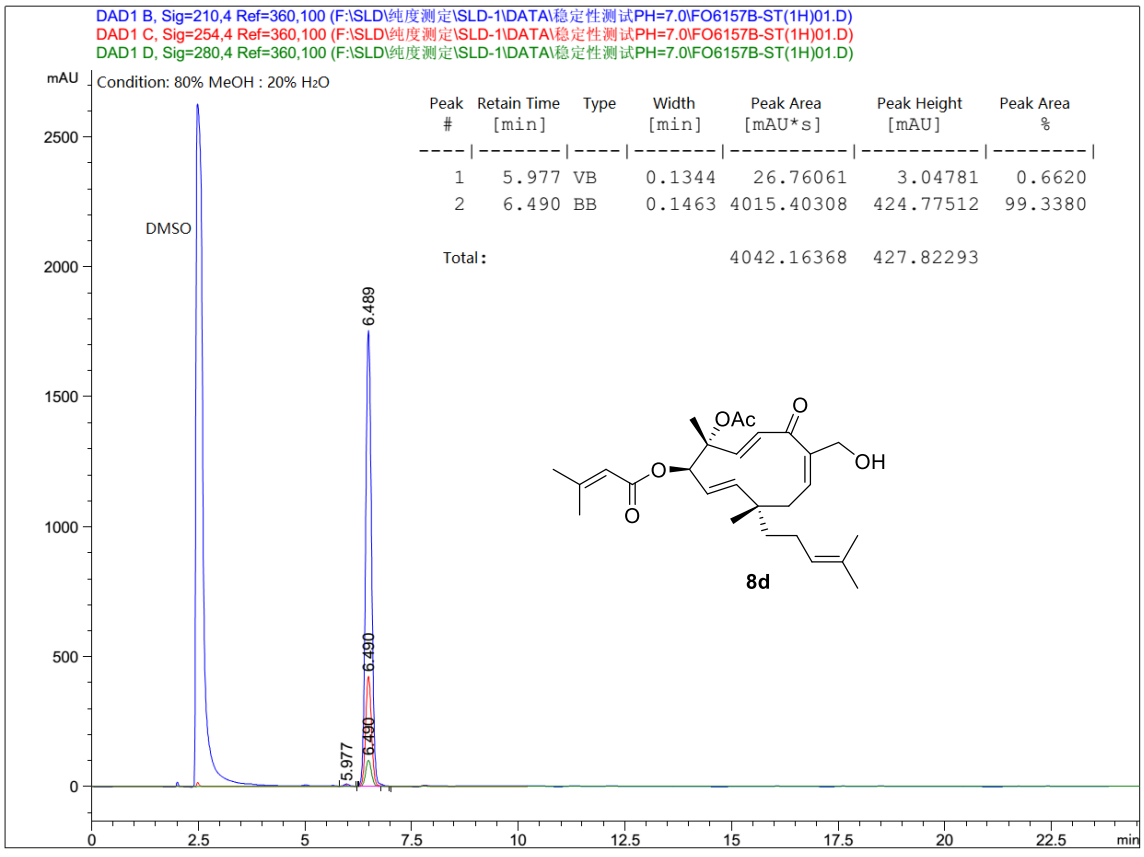
DAD1 D, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\SLD-2\FO869000002.D)
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-2\FO869000002.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 3.959 | BB | 0.0782 | 197.09888 | 38.19970 | 0.8287
2 | 5.556 | VV | 0.1697 | 193.19553 | 17.37216 | 0.8123
3 | 6.124 | VV | 0.1691 | 2.32265e4 | 2165.34106 | 97.6612
4 | 6.529 | VB | 0.1930 | 165.92982 | 12.33204 | 0.6977
Total: | | | | 2.37827e4 | 2233.24496 |
OH
O
OMe
8c
min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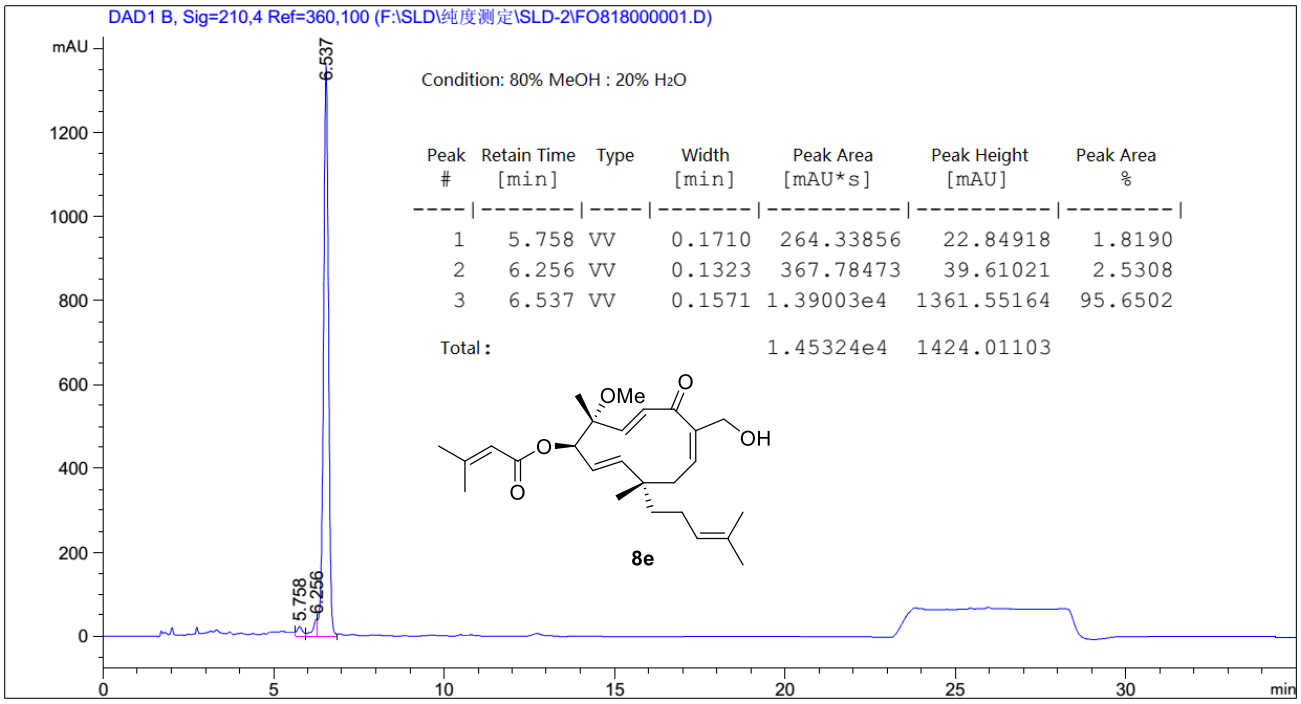
DAD1 C, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\SLD-1\DATA\稳定性测试PH=7.0\FO6157B-ST(1H)01.D)
DAD1 D, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-1\DATA\稳定性测试PH=7.0\FO6157B-ST(1H)01.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 5.977 | VB | 0.1344 | 26.76061 | 3.04781 | 0.6620
2 | 6.490 | BB | 0.1463 | 4015.40308 | 424.77512 | 99.3380
Total: | | | | 4042.16368 | 427.82293 |
DMSO
OAc
O
OH
8d
min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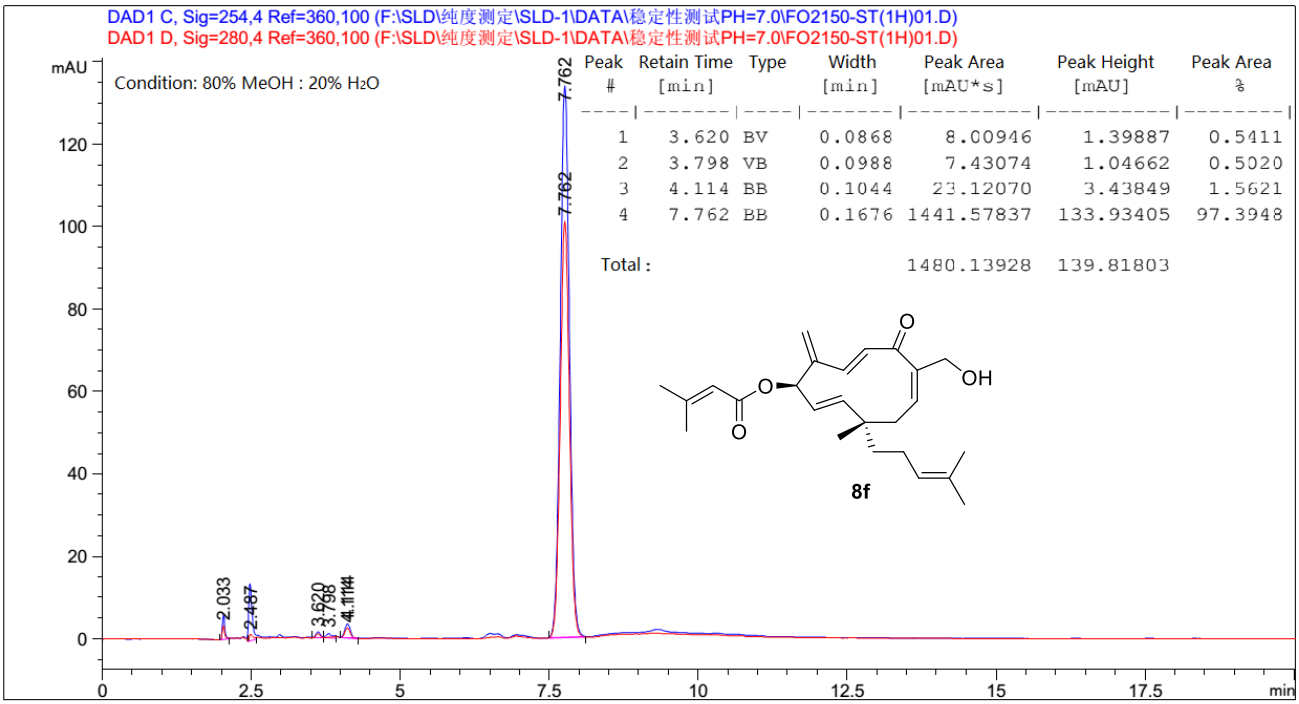
mAU
Condition: 80% MeOH : 20% H2O
6.537
5.758
6.256
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 5.758 | VV | 0.1710 | 264.33856 | 22.84918 | 1.8190
2 | 6.256 | VV | 0.1323 | 367.78473 | 39.61021 | 2.5308
3 | 6.537 | VV | 0.1571 | 1.39003e4 | 1361.55164 | 95.6502
Total: | | | | 1.45324e4 | 1424.01103
OMe
O
OH
O
O
8e
min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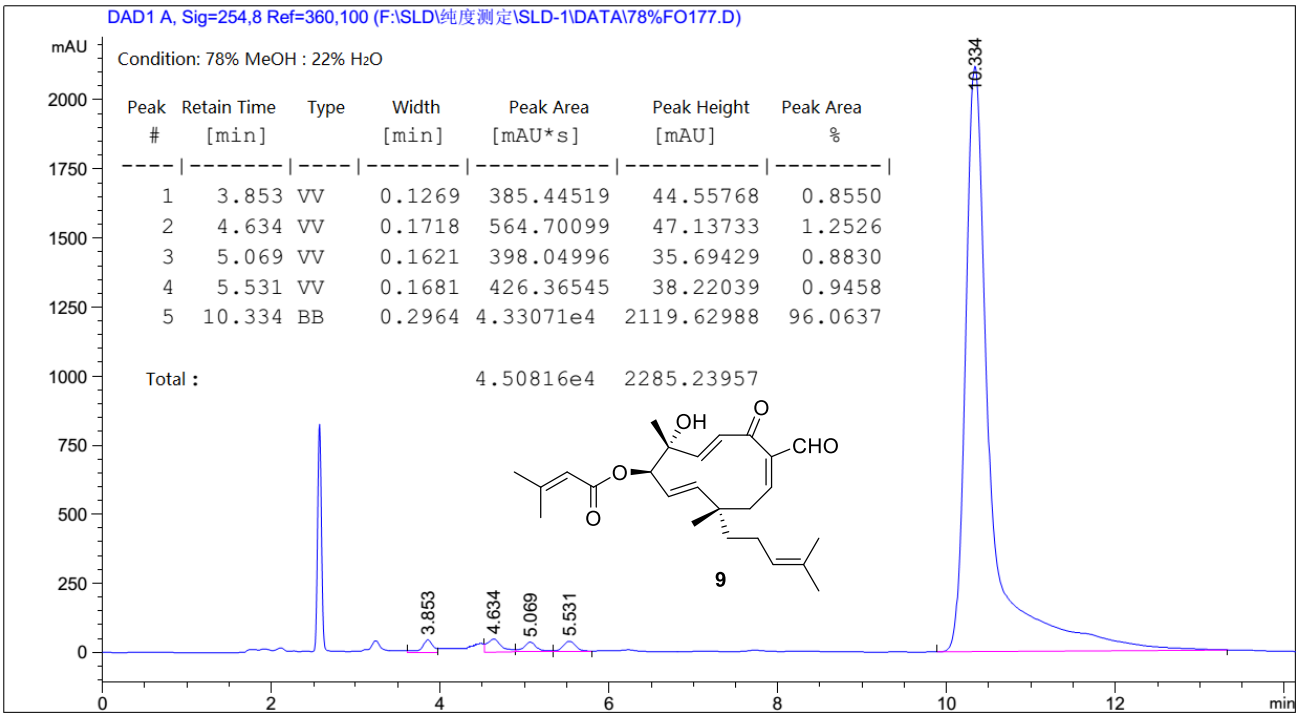
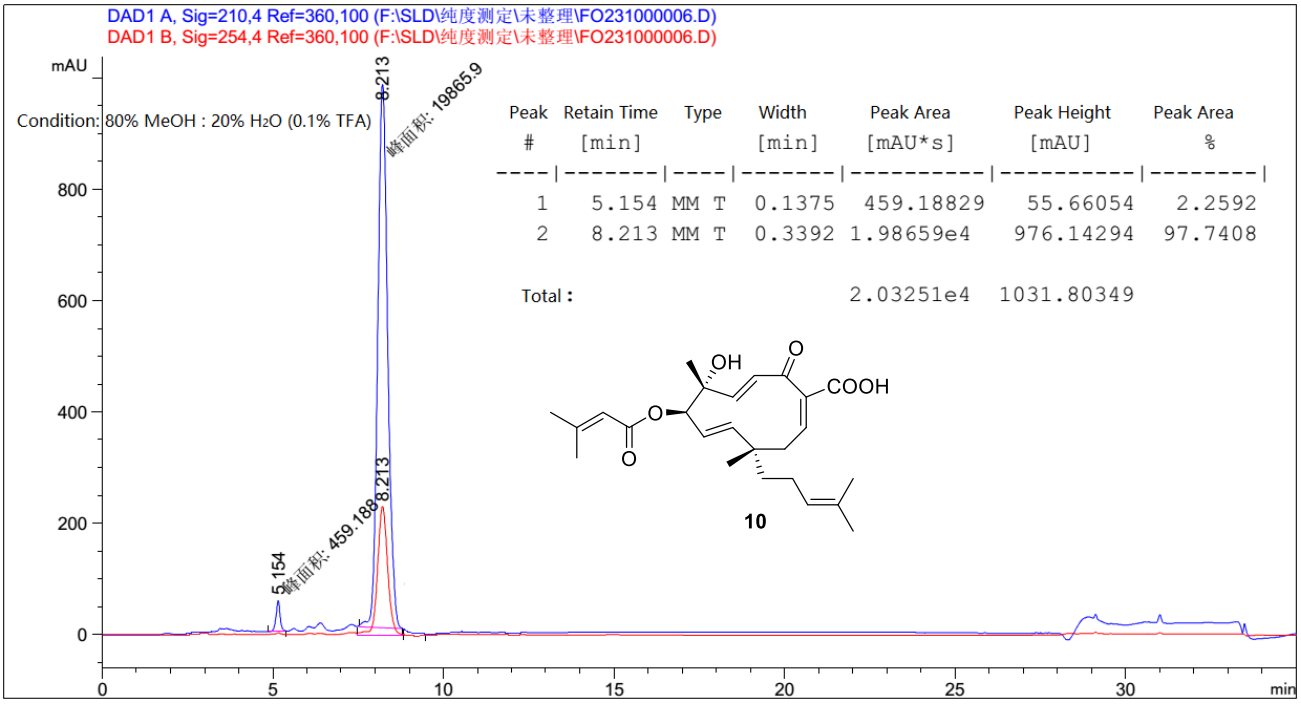
DAD1 D, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-1\DATA\稳定性测试PH=7.0\FO2150-ST(1H)01.D)
mAU
Condition: 80% MeOH : 20% H2O
7.762
7.762
2.033
2.487
3.620
3.798
4.114
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 3.620 | BV | 0.0868 | 8.00946 | 1.39887 | 0.5411
2 | 3.798 | VB | 0.0988 | 7.43074 | 1.04662 | 0.5020
3 | 4.114 | BB | 0.1044 | 23.12070 | 3.43849 | 1.5621
4 | 7.762 | BB | 0.1676 | 1441.57837 | 133.93405 | 97.3948
Total: | | | | 1480.13928 | 139.81803
O
OH
O
O
8f
min


DAD1 A, Sig=254,8 Ref=360,100 (F:\SLD\纯度测定\SLD-1\DATA\78%FO177.D)
Condition: 78% MeOH : 22% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 3.853 VV 0.1269 385.44519 44.55768 0.8550
2 4.634 VV 0.1718 564.70099 47.13733 1.2526
3 5.069 VV 0.1621 398.04996 35.69429 0.8830
4 5.531 VV 0.1681 426.36545 38.22039 0.9458
5 10.334 BB 0.2964 4.33071e4 2119.62988 96.0637
Total : 4.50816e4 2285.23957
OH
O
CHO
O
O
9
mAU
min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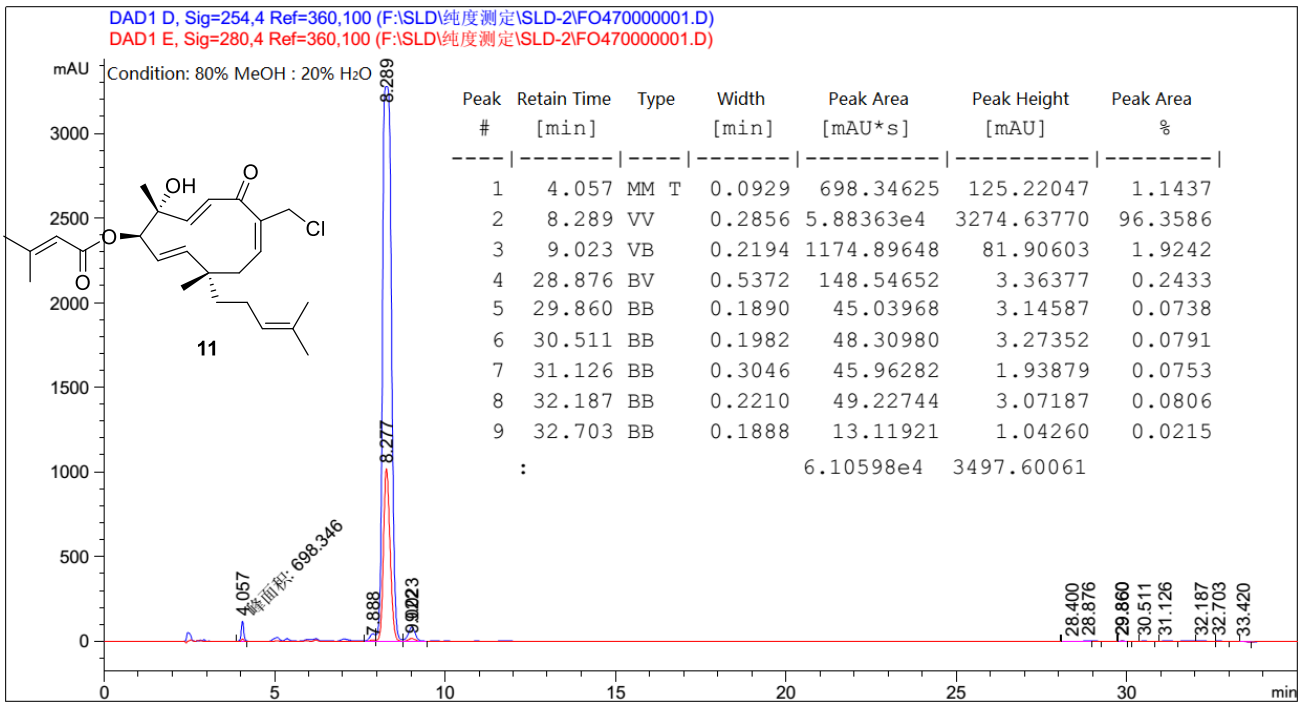
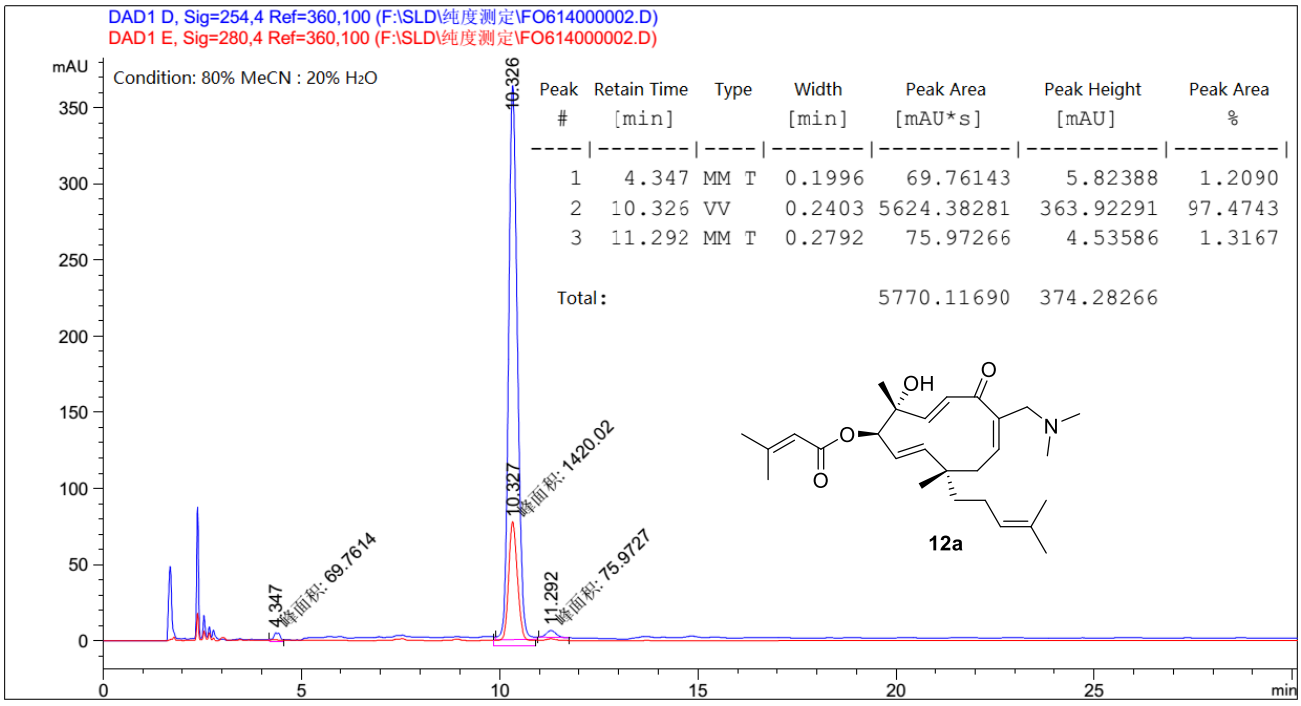
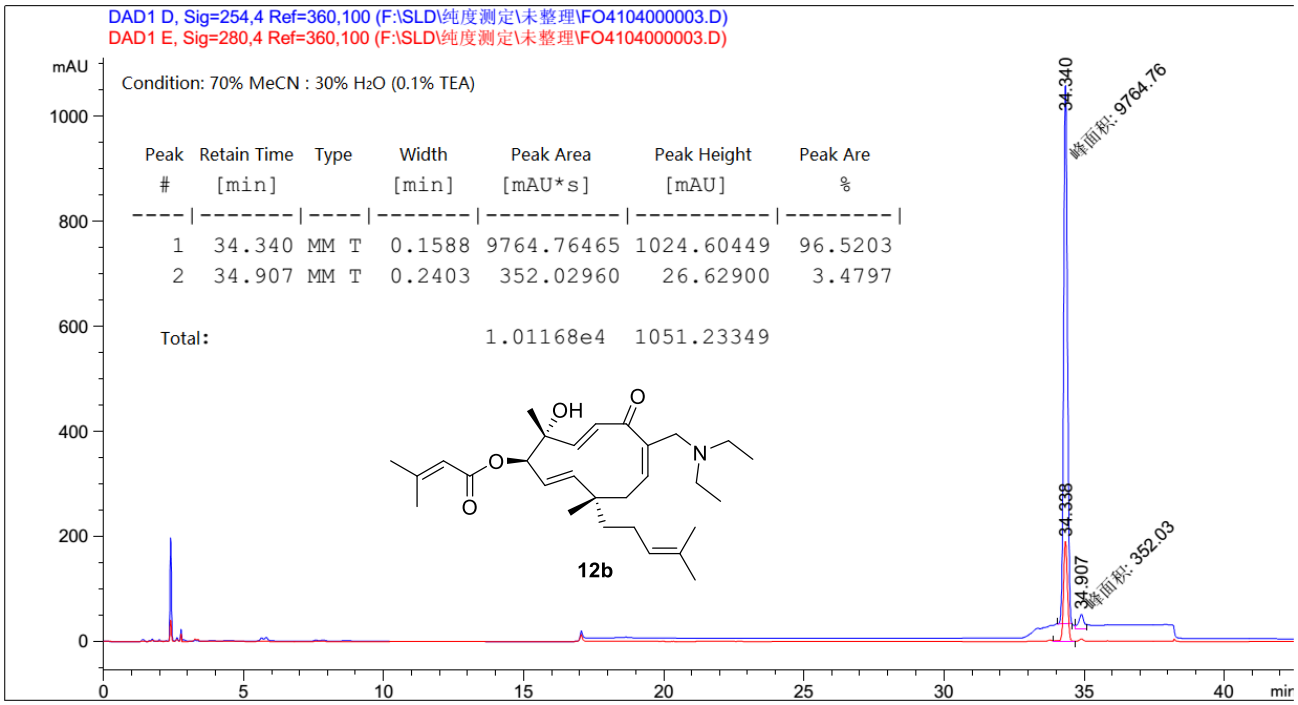
DAD1 B, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO231000006.D)
Condition: 80% MeOH : 20% H2O (0.1% TFA)
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 5.154 MM T 0.1375 459.18829 55.66054 2.2592
2 8.213 MM T 0.3392 1.98659e4 976.14294 97.7408
Total : 2.03251e4 1031.80349
峰面积: 19865.9
峰面积: 459.188
OH
O
COOH
O
O
10
mAU
min




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 4.057 | MM T | 0.0929 | 698.34625 | 125.22047 | 1.1437 |
| 2 | 8.289 | VV | 0.2856 | 5.88363e4 | 3274.63770 | 96.3586 |
| 3 | 9.023 | VB | 0.2194 | 1174.89648 | 81.90603 | 1.9242 |
| 4 | 28.876 | BV | 0.5372 | 148.54652 | 3.36377 | 0.2433 |
| 5 | 29.860 | BB | 0.1890 | 45.03968 | 3.14587 | 0.0738 |
| 6 | 30.511 | BB | 0.1982 | 48.30980 | 3.27352 | 0.0791 |
| 7 | 31.126 | BB | 0.3046 | 45.96282 | 1.93879 | 0.0753 |
| 8 | 32.187 | BB | 0.2210 | 49.22744 | 3.07187 | 0.0806 |
| 9 | 32.703 | BB | 0.1888 | 13.11921 | 1.04260 | 0.0215 |
| : | | | | 6.10598e4 | 3497.60061 | |




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 4.347 | MM T | 0.1996 | 69.76143 | 5.82388 | 1.2090 |
| 2 | 10.326 | VV | 0.2403 | 5624.38281 | 363.92291 | 97.4743 |
| 3 | 11.292 | MM T | 0.2792 | 75.97266 | 4.53586 | 1.3167 |
| Total: | | | | 5770.11690 | 374.28266 | |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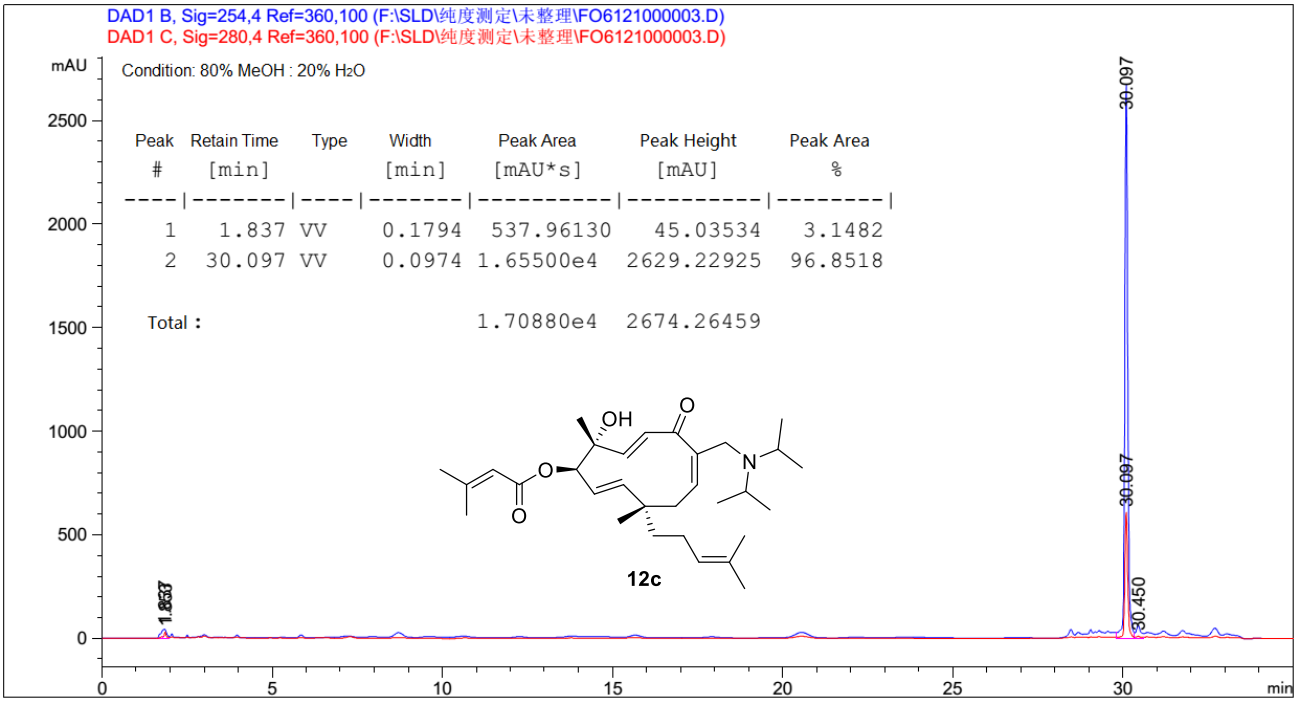
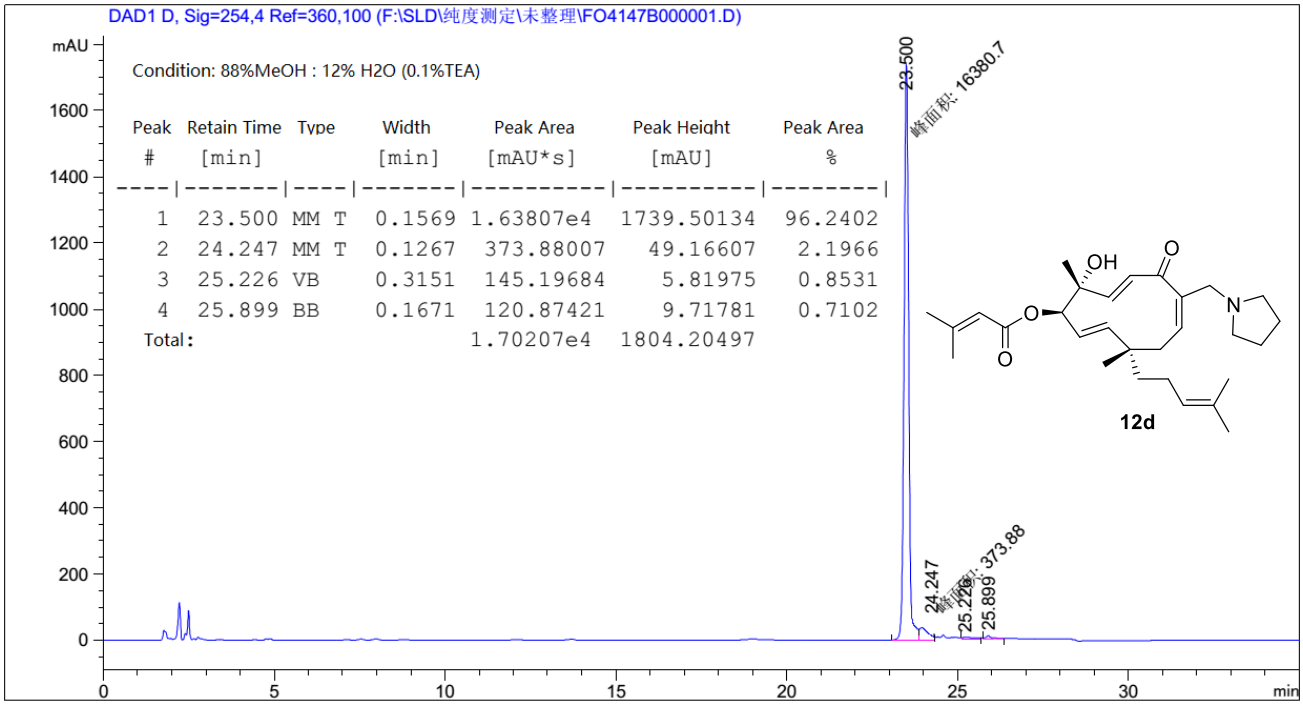
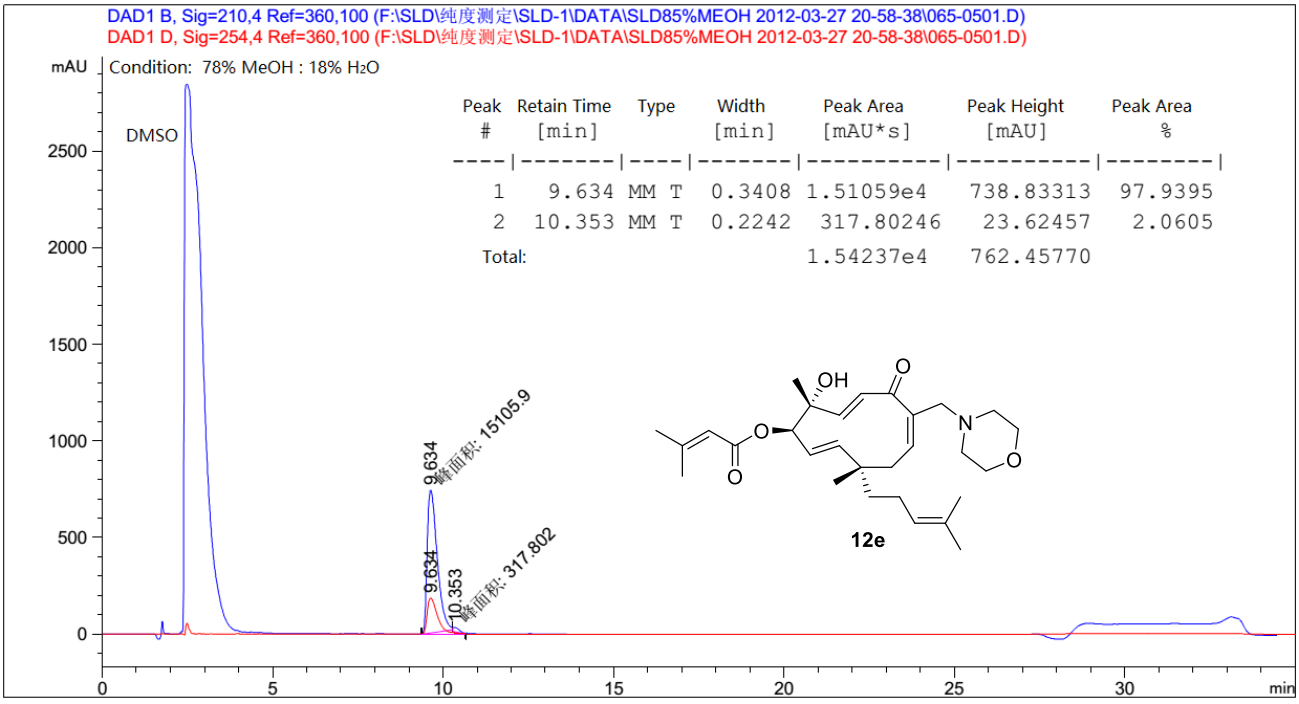
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO4104000003.D)
mAU
Condition: 70% MeCN : 30% H2O (0.1% TEA)
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Are %
1 | 34.340 | MM T | 0.1588 | 9764.76465 | 1024.60449 | 96.5203
2 | 34.907 | MM T | 0.2403 | 352.02960 | 26.62900 | 3.4797
Total: 1.01168e4 1051.23349
OH
O
O
O
N
12b
34.340
峰面积: 9764.76
34.338
34.907
峰面积: 352.03
min


DAD1 B, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO6121000003.D)
DAD1 C, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO6121000003.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 1.837 | VV | 0.1794 | 537.96130 | 45.03534 | 3.1482
2 | 30.097 | VV | 0.0974 | 1.65500e4 | 2629.22925 | 96.8518
Total : 1.70880e4 2674.26459
OH
O
O
O
N
12c
30.097
30.097
30.450
min


DAD1 D, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO4147B000001.D)
mAU
Condition: 88%MeOH : 12% H2O (0.1%TEA)
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 23.500 | MM T | 0.1569 | 1.63807e4 | 1739.50134 | 96.2402
2 | 24.247 | MM T | 0.1267 | 373.88007 | 49.16607 | 2.1966
3 | 25.226 | VB | 0.3151 | 145.19684 | 5.81975 | 0.8531
4 | 25.899 | BB | 0.1671 | 120.87421 | 9.71781 | 0.7102
Total: | | | | 1.70207e4 | 1804.20497 |
23.500
峰面积: 16380.7
24.247
峰面积: 373.88
25.226
25.899
OH
O
N
12d
min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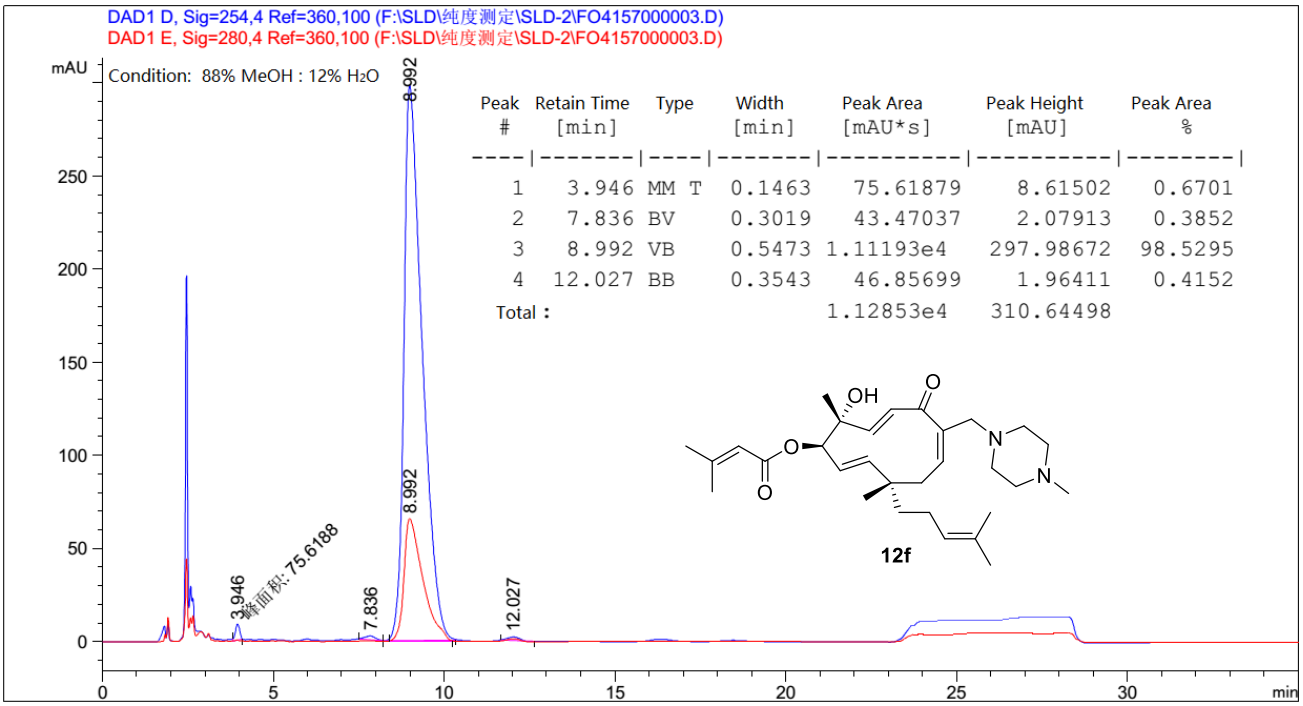
DAD1 D, Sig=254,4 Ref=360,100 (F:\SLD\纯度测定\SLD-1\DATA\SLD85%MEOH 2012-03-27 20-58-38\065-0501.D)
mAU
Condition: 78% MeOH : 18% H2O
DMSO
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 9.634 | MM T | 0.3408 | 1.51059e4 | 738.83313 | 97.9395
2 | 10.353 | MM T | 0.2242 | 317.80246 | 23.62457 | 2.0605
Total: | | | | 1.54237e4 | 762.45770
9.634
峰面积: 15105.9
9.634
10.353
峰面积: 317.802
OH
O
N
O
12e
min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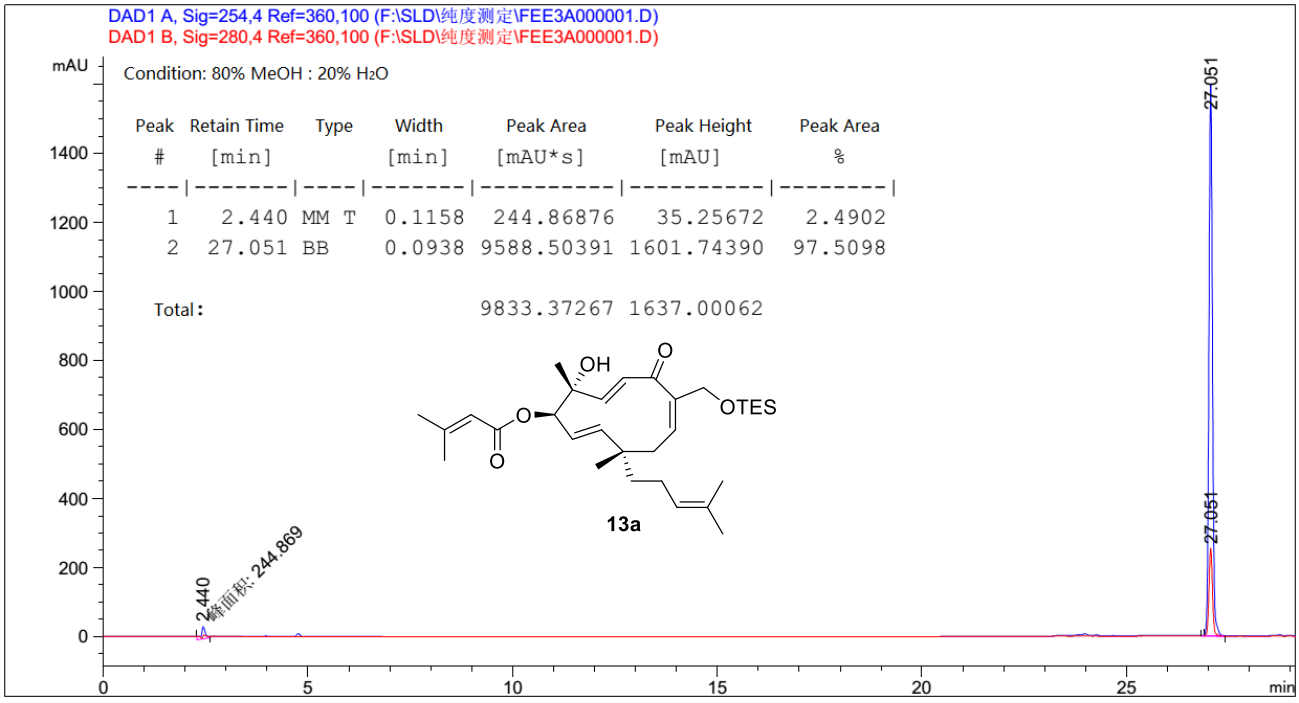
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-2\FO4157000003.D)
mAU
Condition: 88% MeOH : 12% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 3.946 | MM T | 0.1463 | 75.61879 | 8.61502 | 0.6701
2 | 7.836 | BV | 0.3019 | 43.47037 | 2.07913 | 0.3852
3 | 8.992 | VB | 0.5473 | 1.11193e4 | 297.98672 | 98.5295
4 | 12.027 | BB | 0.3543 | 46.85699 | 1.96411 | 0.4152
Total : | | | | 1.12853e4 | 310.64498 |
8.992
3.946
峰面积: 75.6188
7.836
12.027
OH
O
O
O
N
N
12f
min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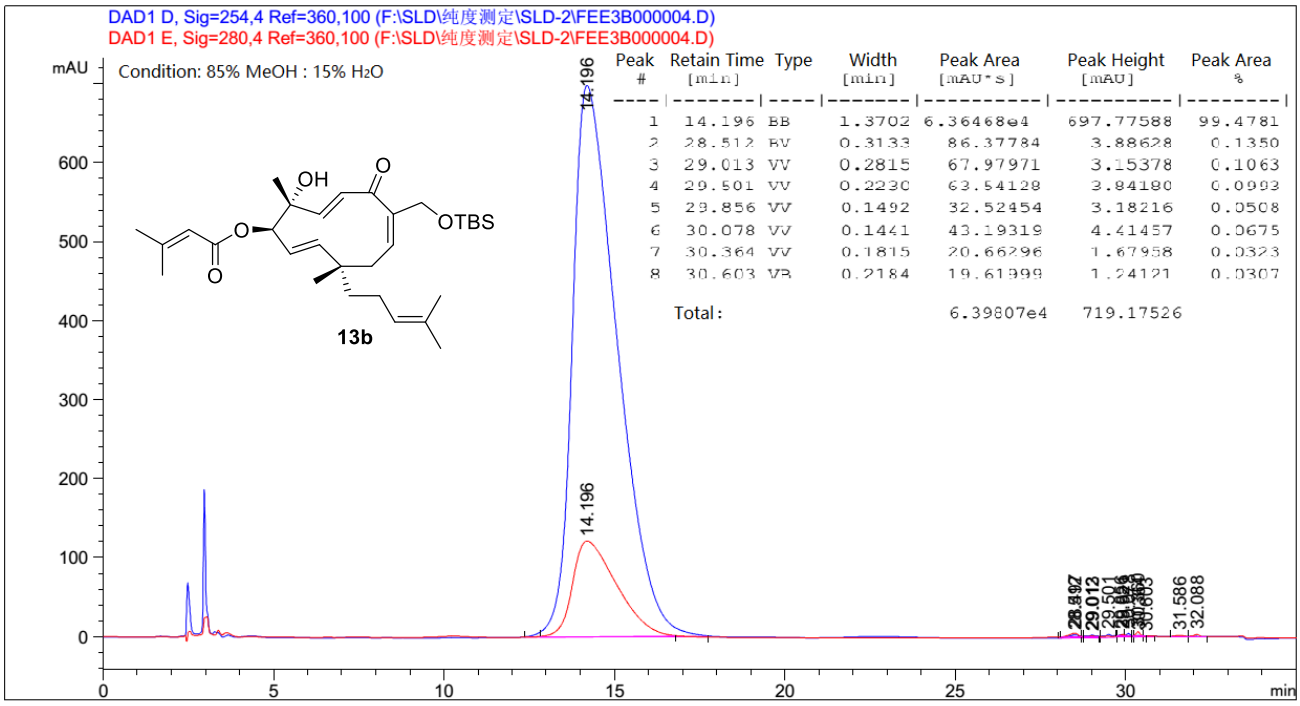
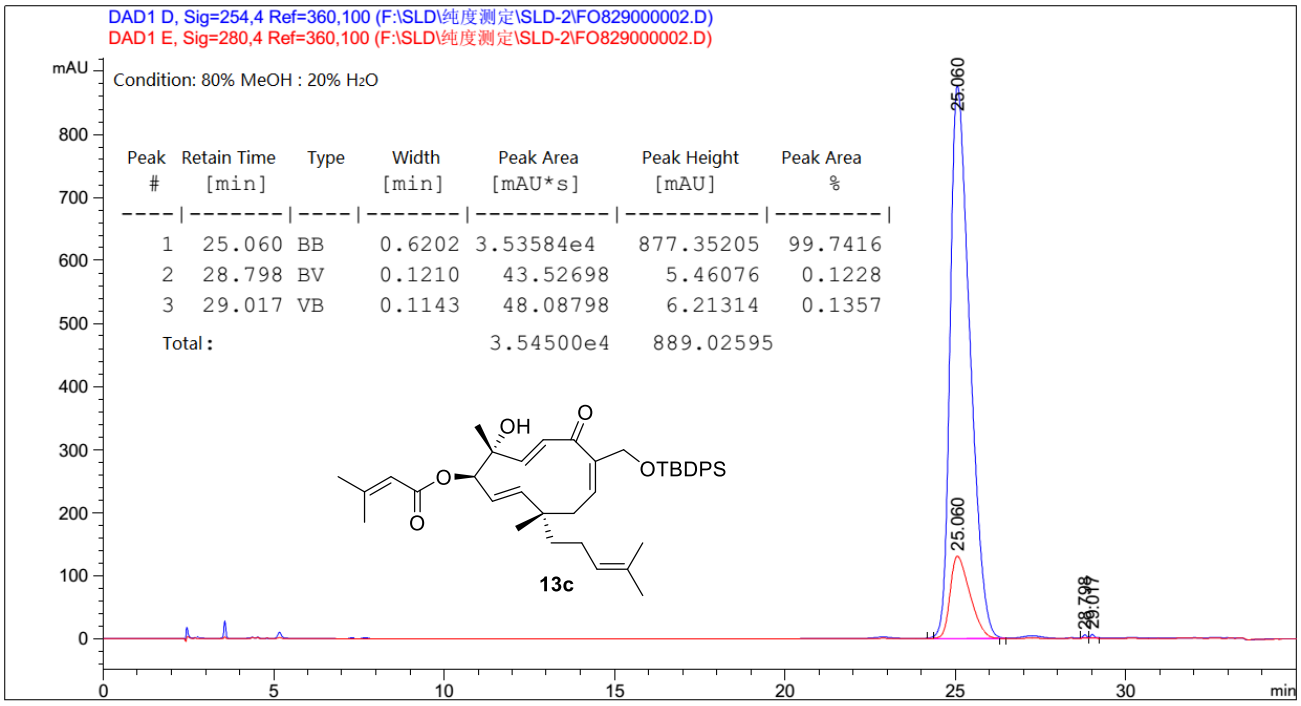
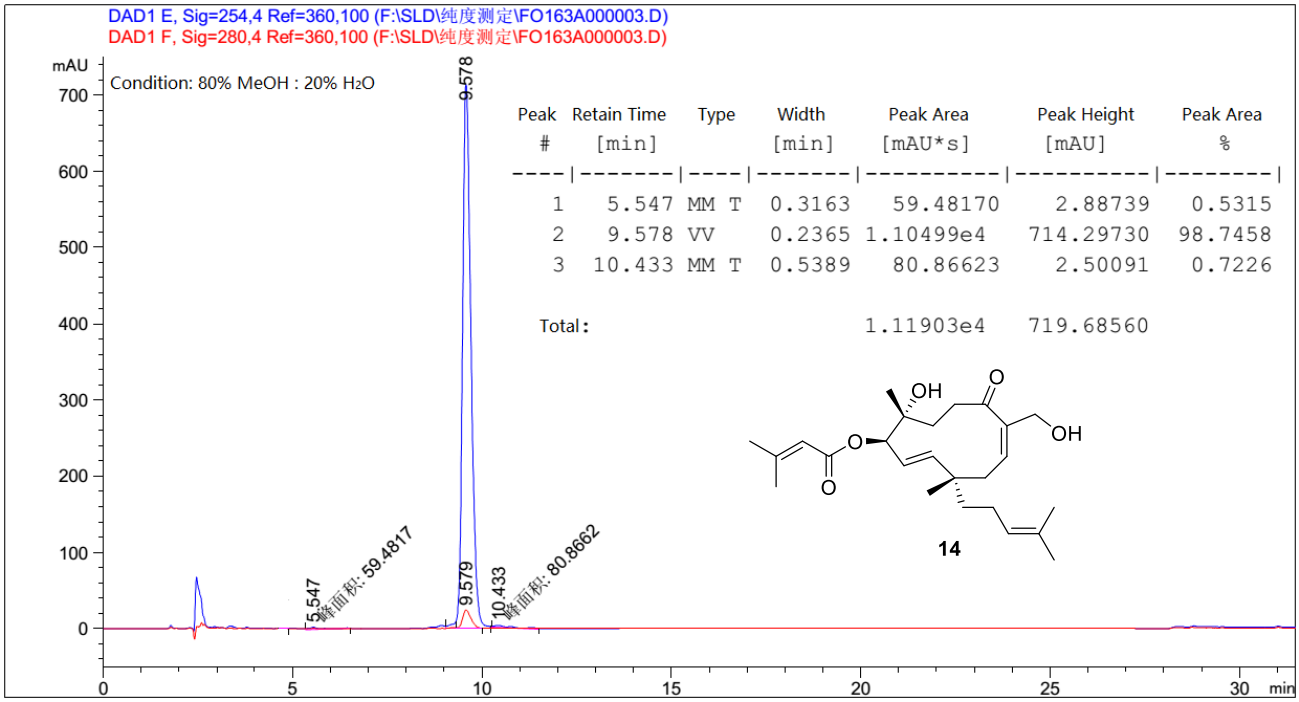
DAD1 B, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\FEE3A000001.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.440 | MM T | 0.1158 | 244.86876 | 35.25672 | 2.4902
2 | 27.051 | BB | 0.0938 | 9588.50391 | 1601.74390 | 97.5098
Total: | | | | 9833.37267 | 1637.00062 |
27.051
2.440
峰面积: 244.869
OH
O
O
O
OTES
13a
min




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 14.196 | BB | 1.3702 | 6.36468e4 | 697.77588 | 99.4781 |
| 2 | 28.512 | BV | 0.3133 | 86.37784 | 3.88628 | 0.1350 |
| 3 | 29.013 | VV | 0.2815 | 67.97971 | 3.15378 | 0.1063 |
| 4 | 29.501 | VV | 0.2230 | 63.54128 | 3.84180 | 0.0993 |
| 5 | 29.856 | VV | 0.1492 | 32.52454 | 3.18216 | 0.0508 |
| 6 | 30.078 | VV | 0.1441 | 43.19319 | 4.41457 | 0.0675 |
| 7 | 30.364 | VV | 0.1815 | 20.66296 | 1.67958 | 0.0323 |
| 8 | 30.603 | VB | 0.2184 | 19.61999 | 1.24121 | 0.0307 |
| Total: | | | | 6.39807e4 | 719.17526 | |



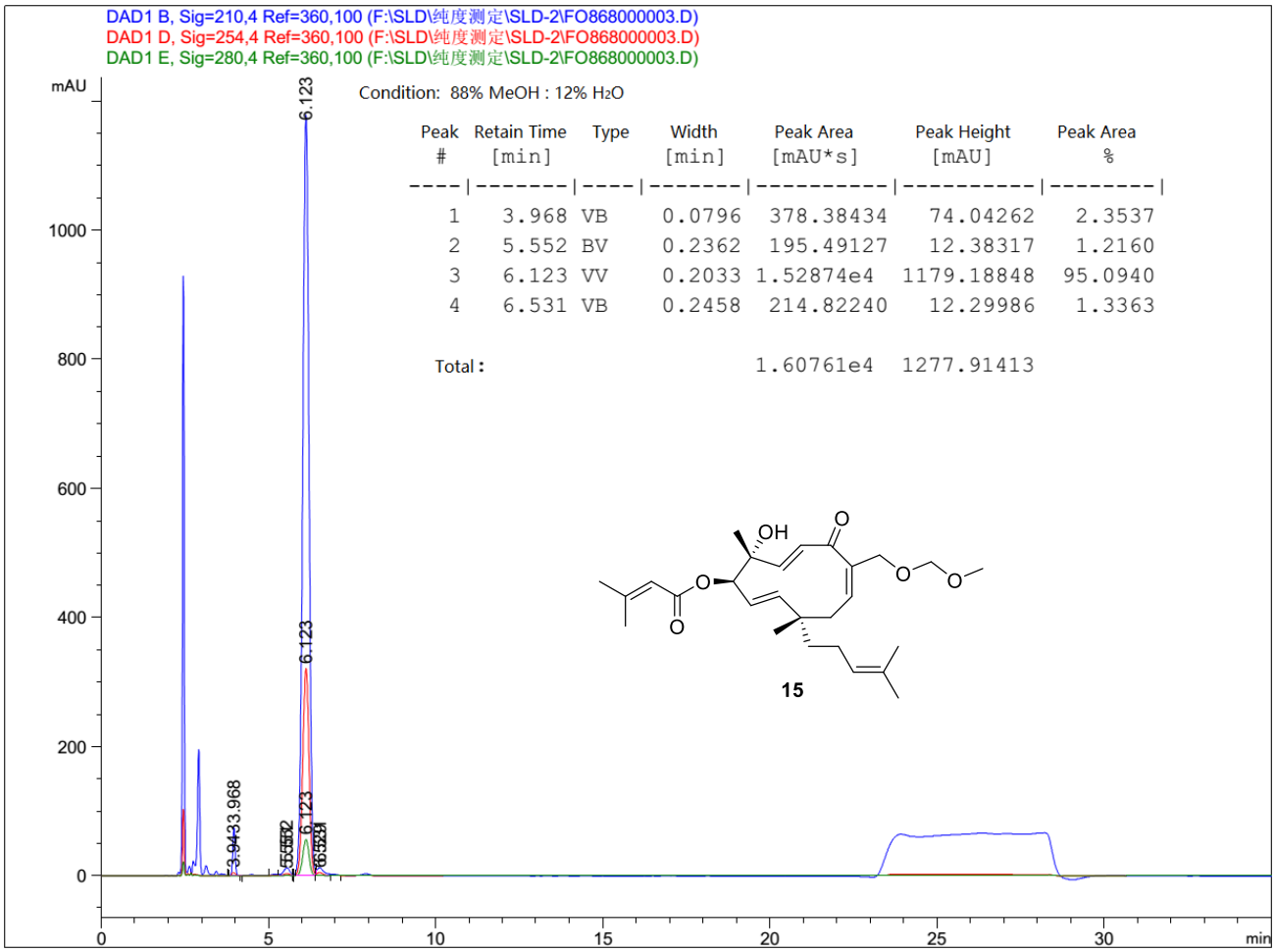

| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 25.060 | BB | 0.6202 | 3.53584e4 | 877.35205 | 99.7416 |
| 2 | 28.798 | BV | 0.1210 | 43.52698 | 5.46076 | 0.1228 |
| 3 | 29.017 | VB | 0.1143 | 48.08798 | 6.21314 | 0.1357 |
| Total: | | | | 3.54500e4 | 889.02595 | |




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 5.547 | MM T | 0.3163 | 59.48170 | 2.88739 | 0.5315 |
| 2 | 9.578 | VV | 0.2365 | 1.10499e4 | 714.29730 | 98.7458 |
| 3 | 10.433 | MM T | 0.5389 | 80.86623 | 2.50091 | 0.7226 |
| Total: | | | | 1.11903e4 | 719.68560 | |



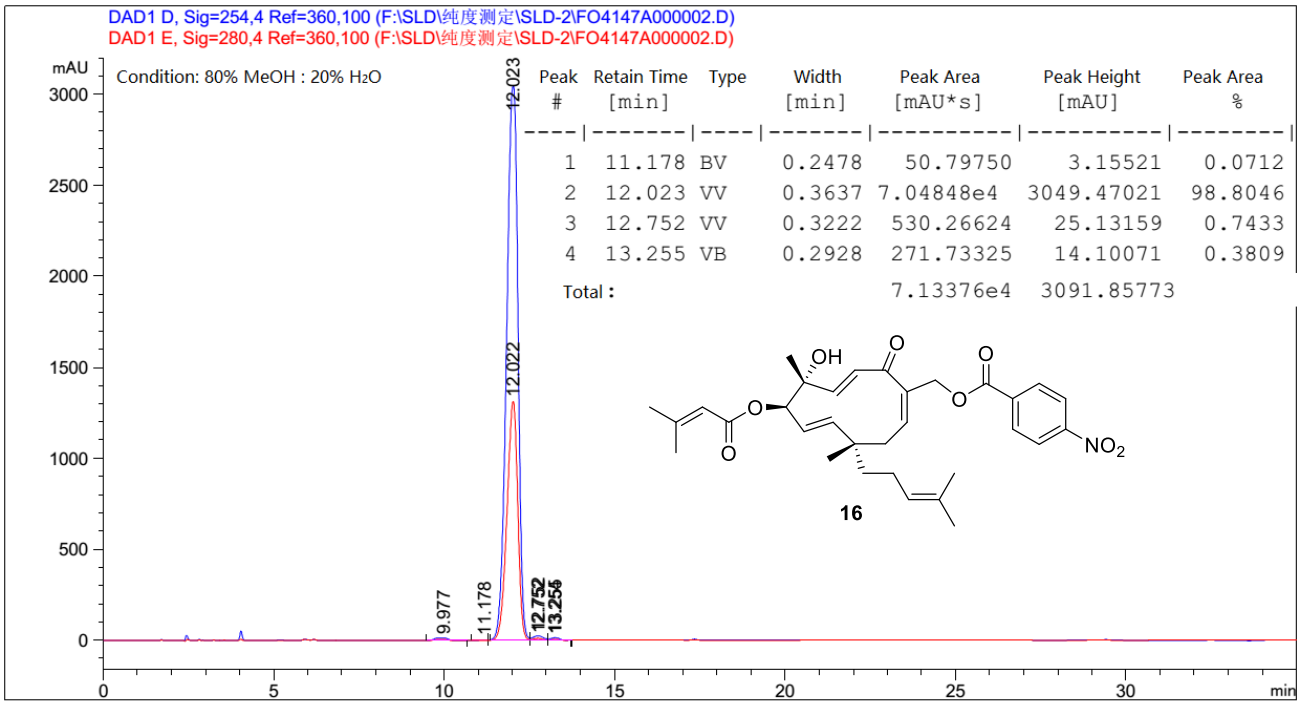
**14**




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 3.968 | VB | 0.0796 | 378.38434 | 74.04262 | 2.3537 |
| 2 | 5.552 | BV | 0.2362 | 195.49127 | 12.38317 | 1.2160 |
| 3 | 6.123 | VV | 0.2033 | 1.52874e4 | 1179.18848 | 95.0940 |
| 4 | 6.531 | VB | 0.2458 | 214.82240 | 12.29986 | 1.3363 |
| Total: | | | | 1.60761e4 | 1277.91413 | |



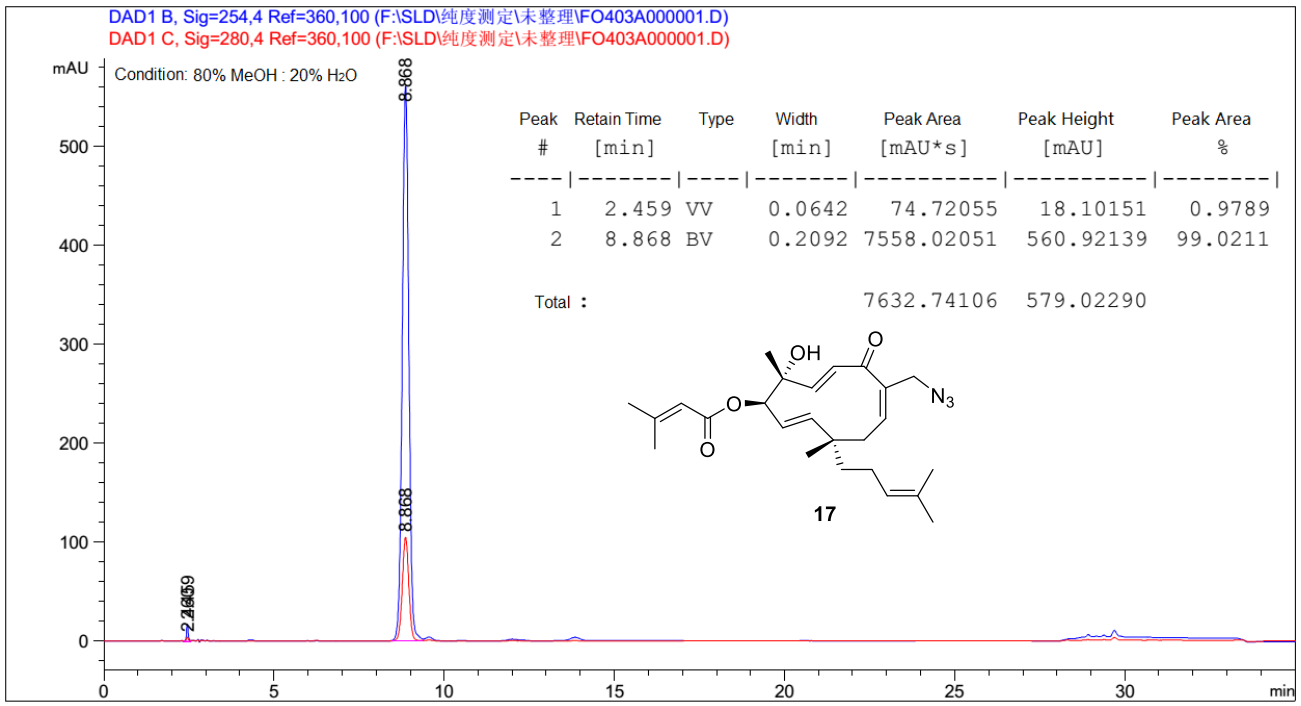
**15**




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 11.178 | BV | 0.2478 | 50.79750 | 3.15521 | 0.0712 |
| 2 | 12.023 | VV | 0.3637 | 7.04848e4 | 3049.47021 | 98.8046 |
| 3 | 12.752 | VV | 0.3222 | 530.26624 | 25.13159 | 0.7433 |
| 4 | 13.255 | VB | 0.2928 | 271.73325 | 14.10071 | 0.3809 |
| Total : | | | | 7.13376e4 | 3091.85773 | |



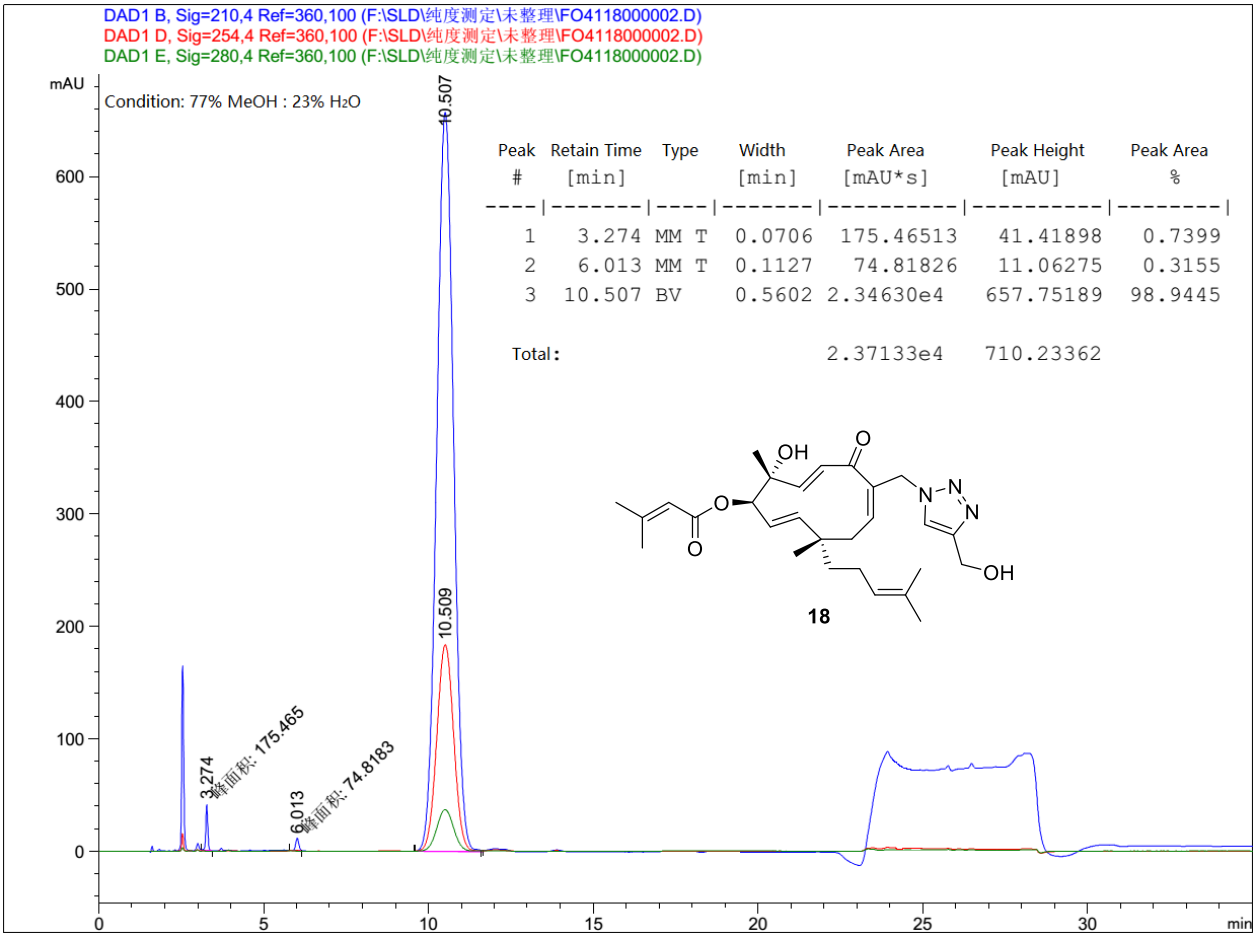

**16**




| Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area % |
|---|---|---|---|---|---|---|
| 1 | 2.459 | VV | 0.0642 | 74.72055 | 18.10151 | 0.9789 |
| 2 | 8.868 | BV | 0.2092 | 7558.02051 | 560.92139 | 99.0211 |
| Total : | | | | 7632.74106 | 579.02290 | |




**17**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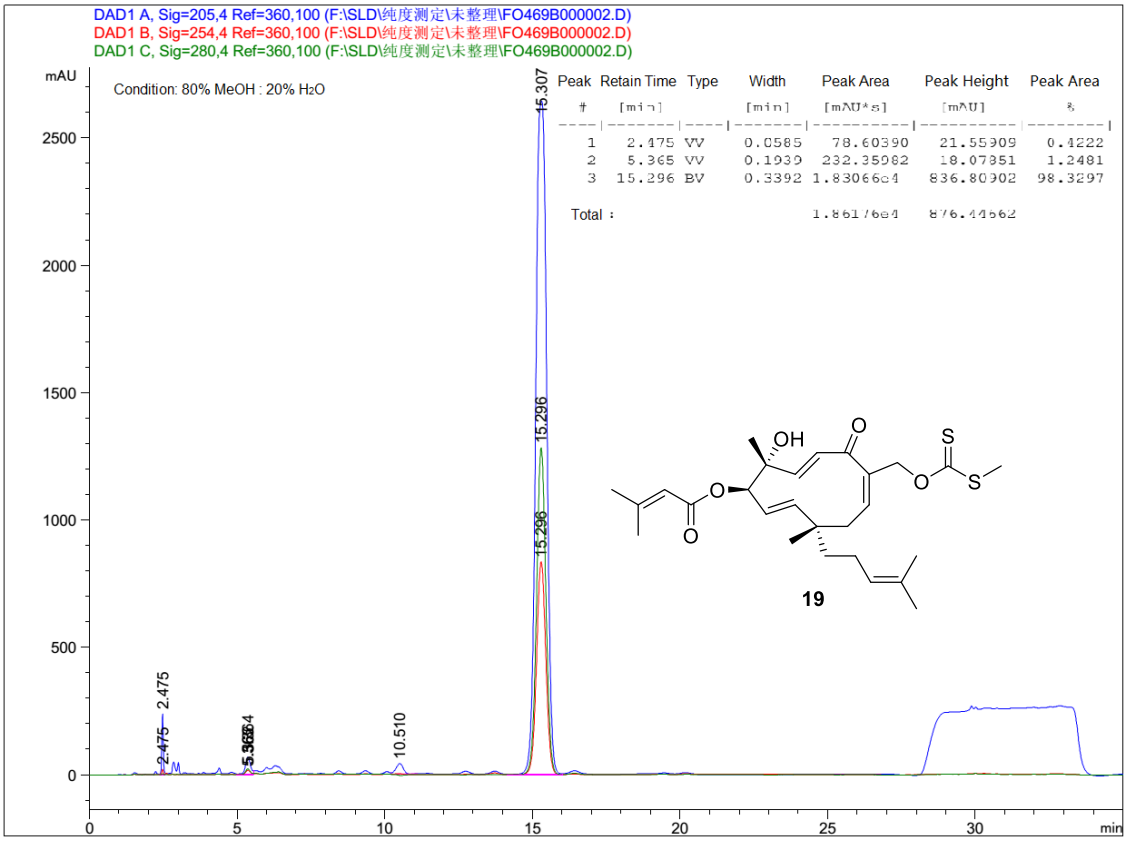
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO4118000002.D)
mAU
Condition: 77% MeOH : 23% H2O
10.507
10.509
3.274
峰面积: 175.465
6.013
峰面积: 74.8183
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 3.274 | MM T | 0.0706 | 175.46513 | 41.41898 | 0.7399
2 | 6.013 | MM T | 0.1127 | 74.81826 | 11.06275 | 0.3155
3 | 10.507 | BV | 0.5602 | 2.34630e4 | 657.75189 | 98.9445
Total: | | | | 2.37133e4 | 710.23362
OH
O
O
N
N
N
OH
18
min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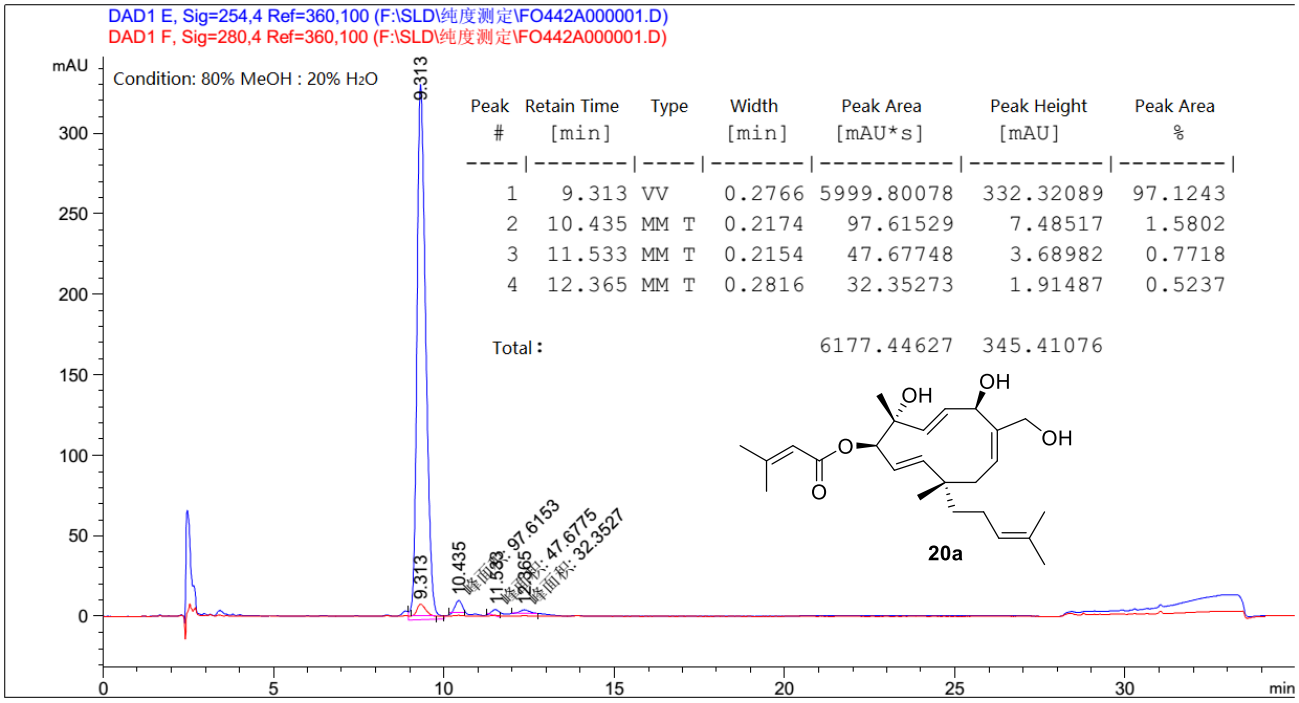
DAD1 C, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO469B000002.D)
mAU
Condition: 80% MeOH : 20% H2O
15.307
15.296
15.296
2.475
10.510
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.475 | VV | 0.0585 | 78.60390 | 21.55909 | 0.4222
2 | 5.365 | VV | 0.1939 | 232.35082 | 18.07351 | 1.2481
3 | 15.296 | BV | 0.3392 | 1.83066e4 | 836.80902 | 98.3297
Total : | | | | 1.86176e4 | 876.44162
OH
O
O
S
O
S
19
min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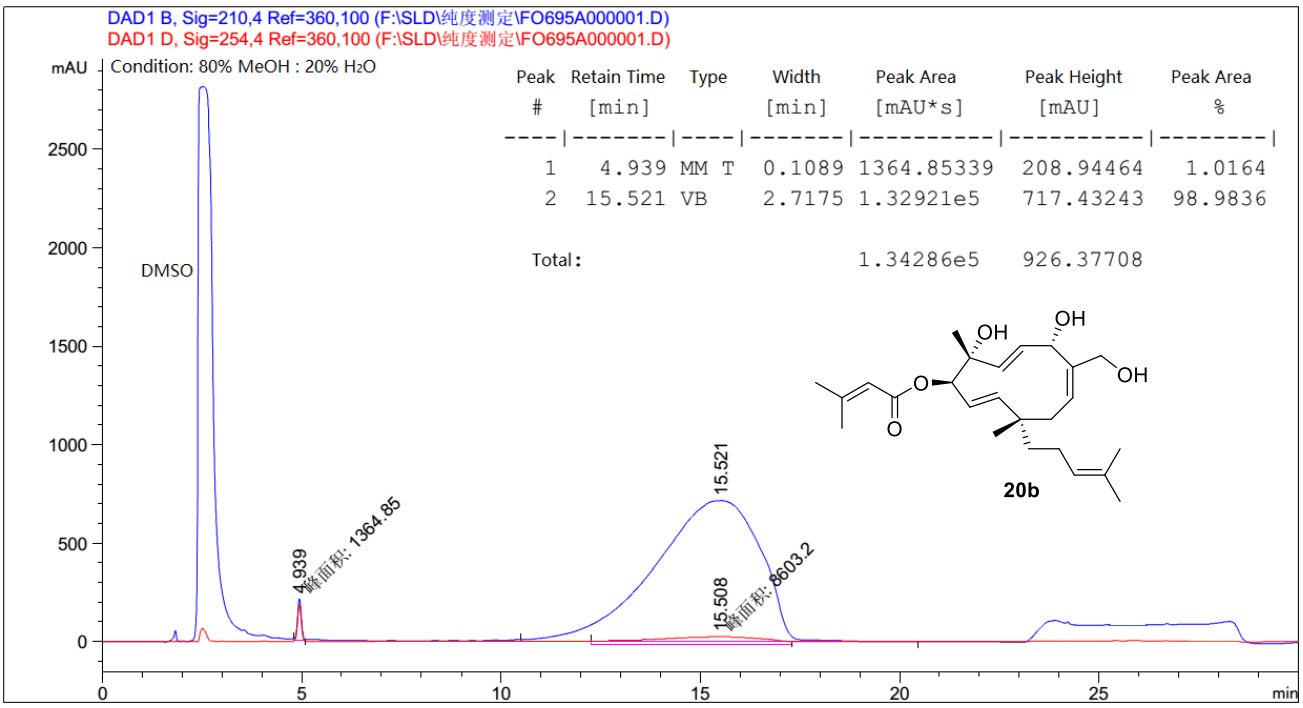
mAU
Condition: 80% MeOH : 20% H2O
9.313
10.435
11.533
12.365
峰面积: 97.6153
峰面积: 47.6775
峰面积: 32.3527
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 9.313 | VV | 0.2766 | 5999.80078 | 332.32089 | 97.1243
2 | 10.435 | MM T | 0.2174 | 97.61529 | 7.48517 | 1.5802
3 | 11.533 | MM T | 0.2154 | 47.67748 | 3.68982 | 0.7718
4 | 12.365 | MM T | 0.2816 | 32.35273 | 1.91487 | 0.5237
Total: 6177.44627 345.41076
OH
OH
OH
O
O
20a
min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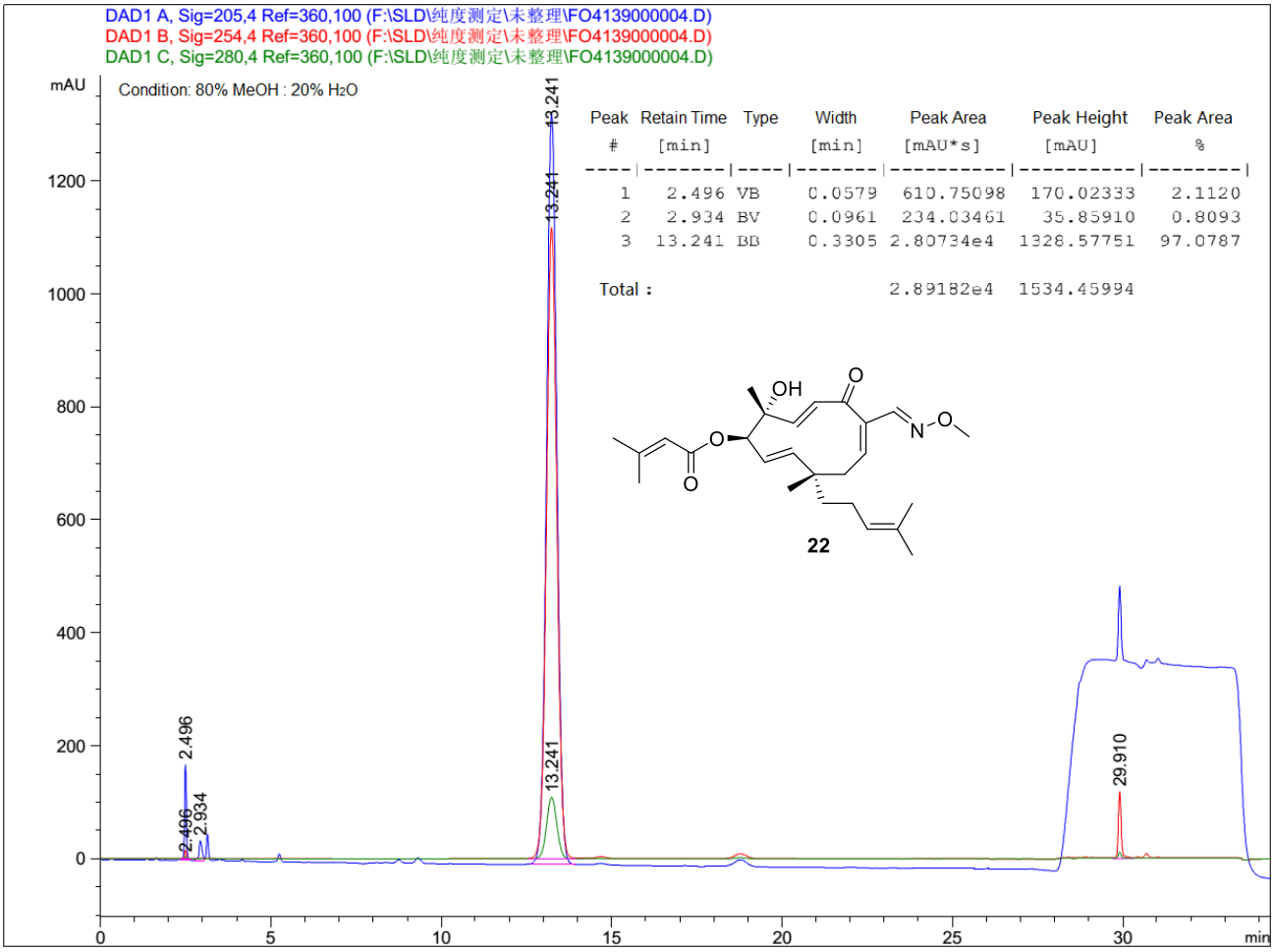
mAU
Condition: 80% MeOH : 20% H2O
DMSO
4.939
15.521
15.508
峰面积: 1364.85
峰面积: 8603.2
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 4.939 | MM T | 0.1089 | 1364.85339 | 208.94464 | 1.0164
2 | 15.521 | VB | 2.7175 | 1.32921e5 | 717.43243 | 98.9836
Total: 1.34286e5 926.37708
OH
OH
OH
O
O
20b
min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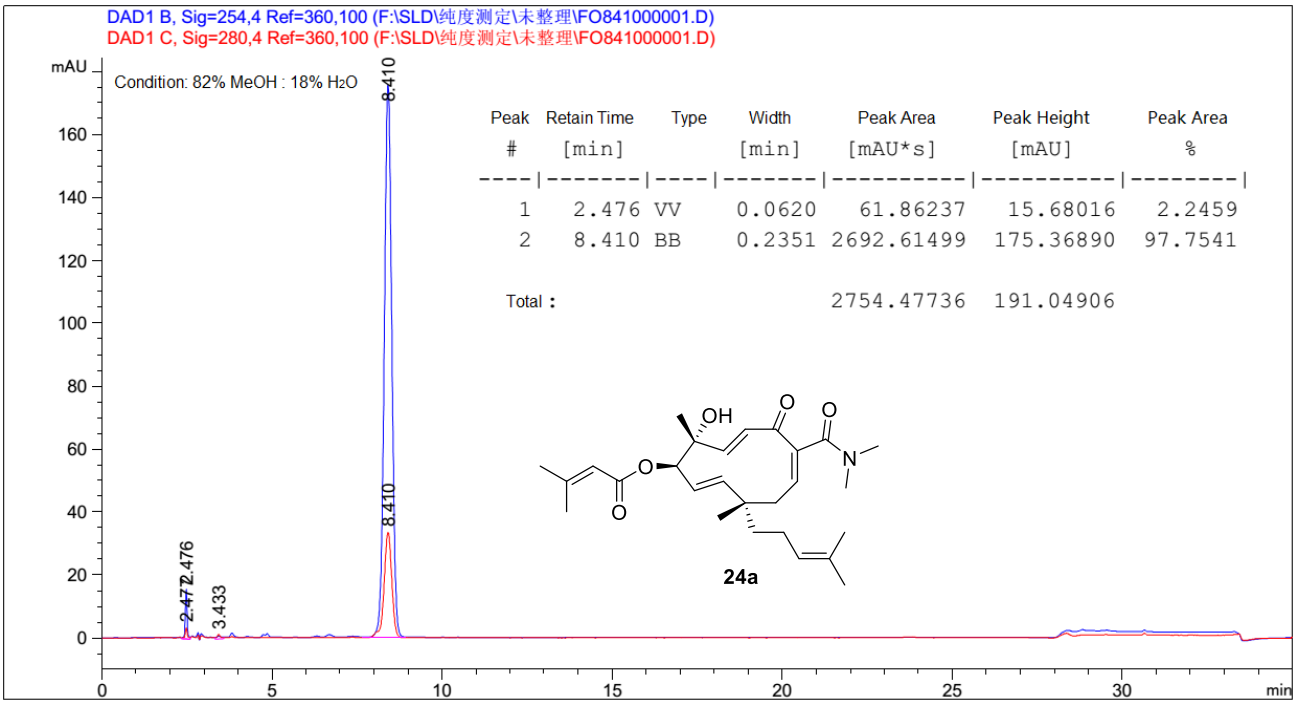
DAD1 C, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO4139000004.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.496 | VB | 0.0579 | 610.75098 | 170.02333 | 2.1120
2 | 2.934 | BV | 0.0961 | 234.03461 | 35.85910 | 0.8093
3 | 13.241 | BB | 0.3305 | 2.80734e4 | 1328.57751 | 97.0787
Total : 2.89182e4 1534.45994
22
2.496
2.934
13.241
29.910
min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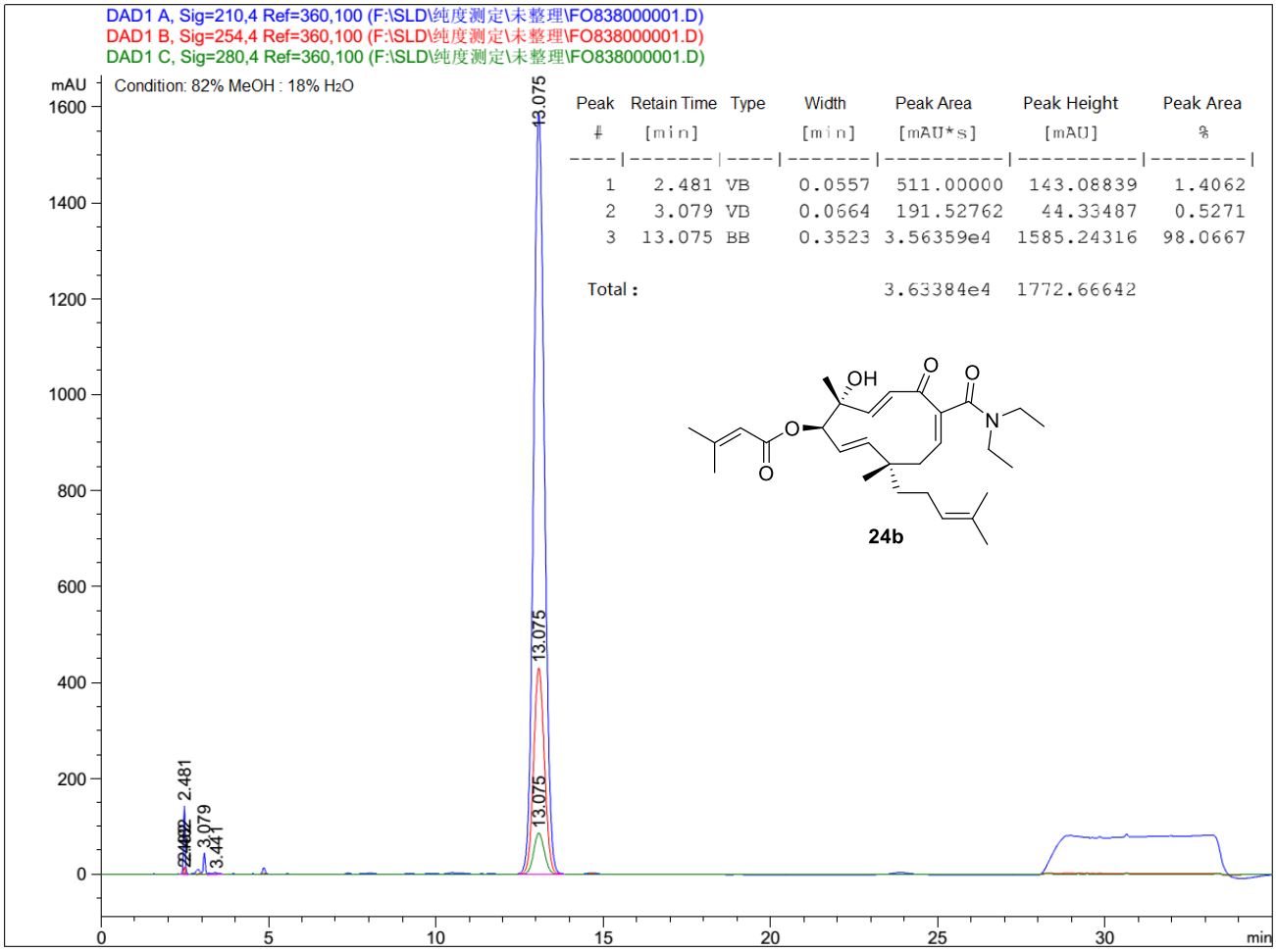
mAU
Condition: 82% MeOH : 18% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.476 | VV | 0.0620 | 61.86237 | 15.68016 | 2.2459
2 | 8.410 | BB | 0.2351 | 2692.61499 | 175.36890 | 97.7541
Total : 2754.47736 191.04906
24a
2.476
3.433
8.410
min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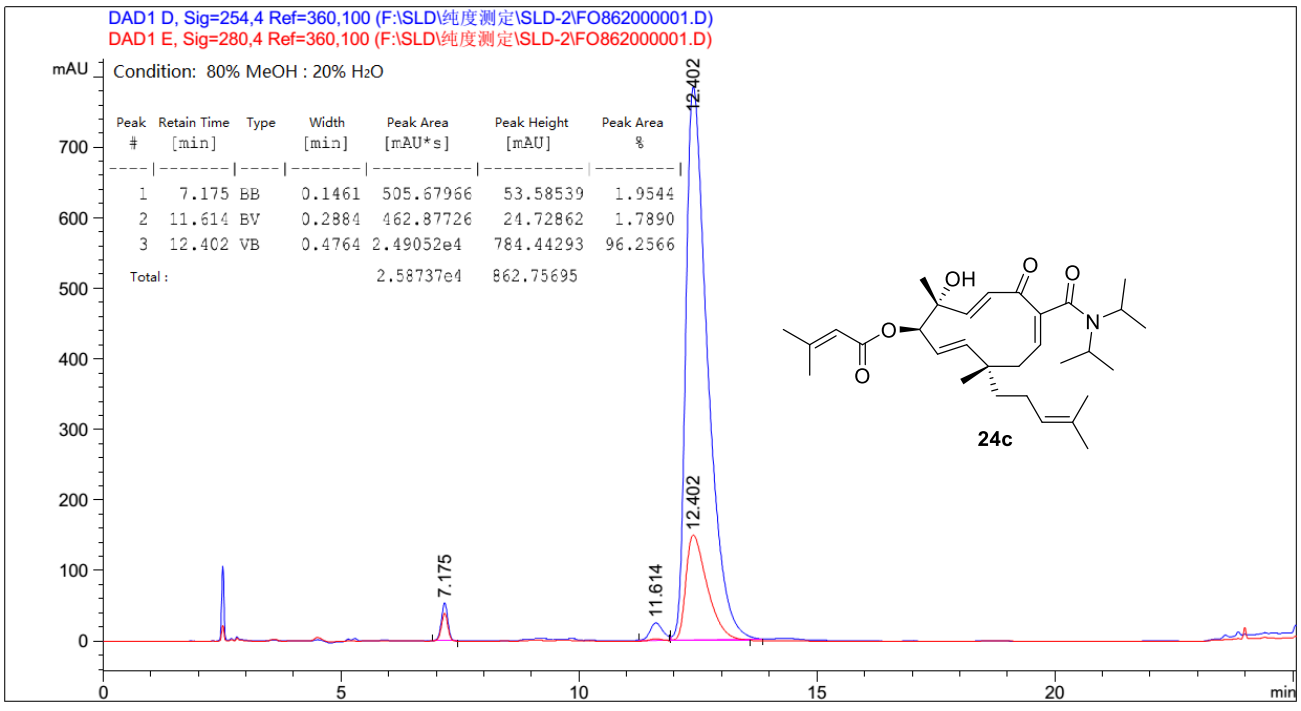
DAD1 C, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO838000001.D)
mAU
Condition: 82% MeOH : 18% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.481 | VB | 0.0557 | 511.00000 | 143.08839 | 1.4062
2 | 3.079 | VB | 0.0664 | 191.52762 | 44.33487 | 0.5271
3 | 13.075 | BB | 0.3523 | 3.56359e4 | 1585.24316 | 98.0667
Total : 3.63384e4 1772.66642
24b
min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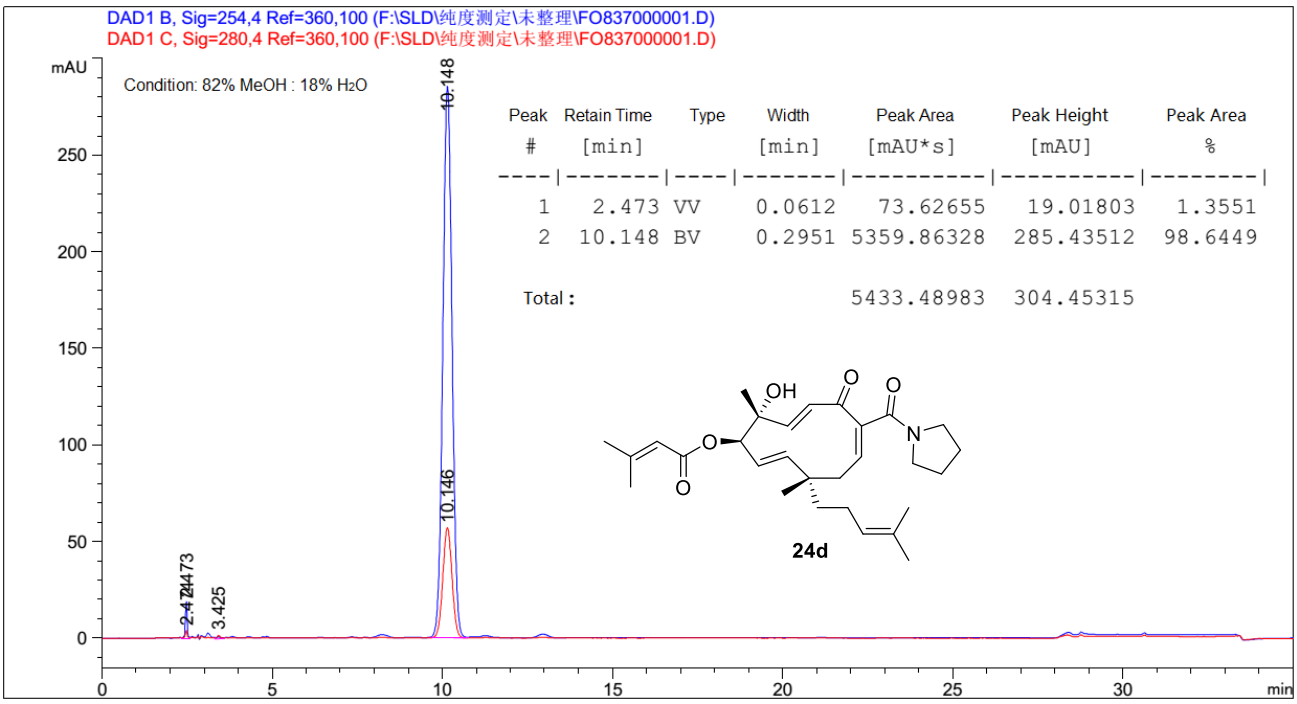
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-2\FO862000001.D)
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 7.175 | BB | 0.1461 | 505.67966 | 53.58539 | 1.9544
2 | 11.614 | BV | 0.2884 | 462.87726 | 24.72862 | 1.7890
3 | 12.402 | VB | 0.4764 | 2.49052e4 | 784.44293 | 96.2566
Total : 2.58737e4 862.75695
24c
min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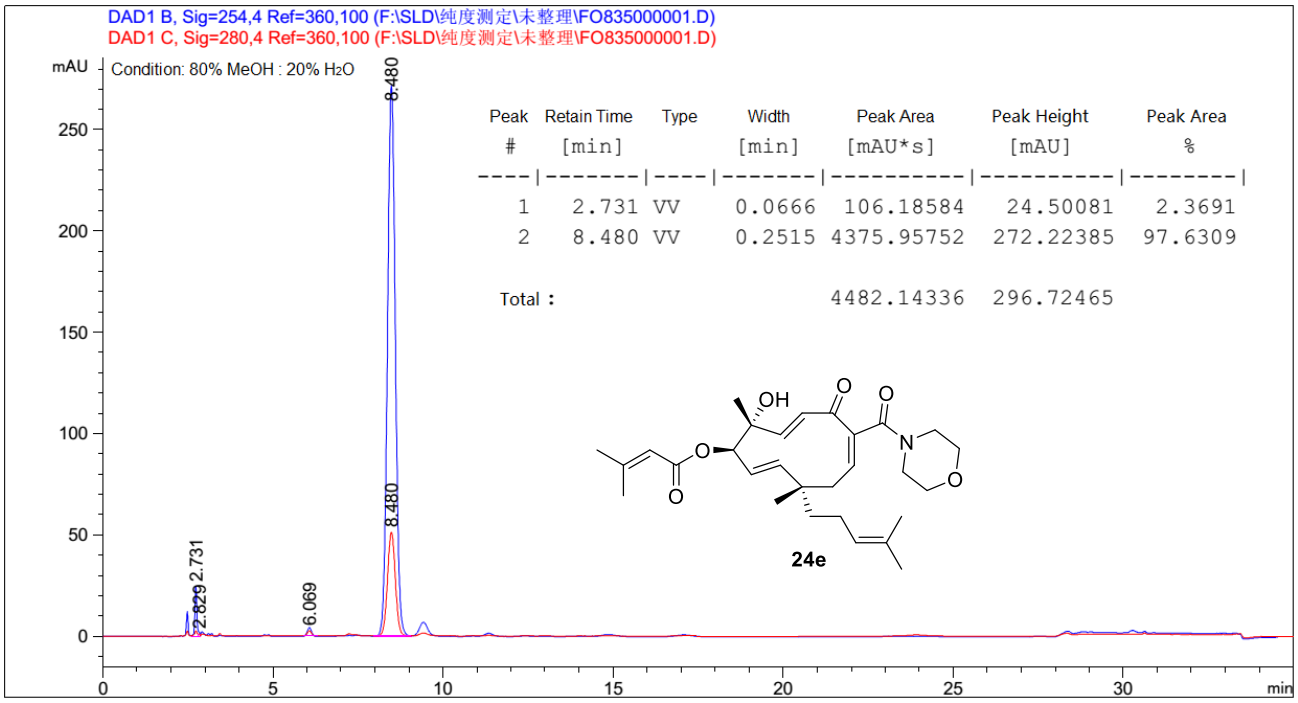
mAU
Condition: 82% MeOH : 18% H2O
10.148
10.146
2.473
3.425
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.473 | VV | 0.0612 | 73.62655 | 19.01803 | 1.3551
2 | 10.148 | BV | 0.2951 | 5359.86328 | 285.43512 | 98.6449
Total : 5433.48983 304.45315
OH
O
O
N
O
O
24d
min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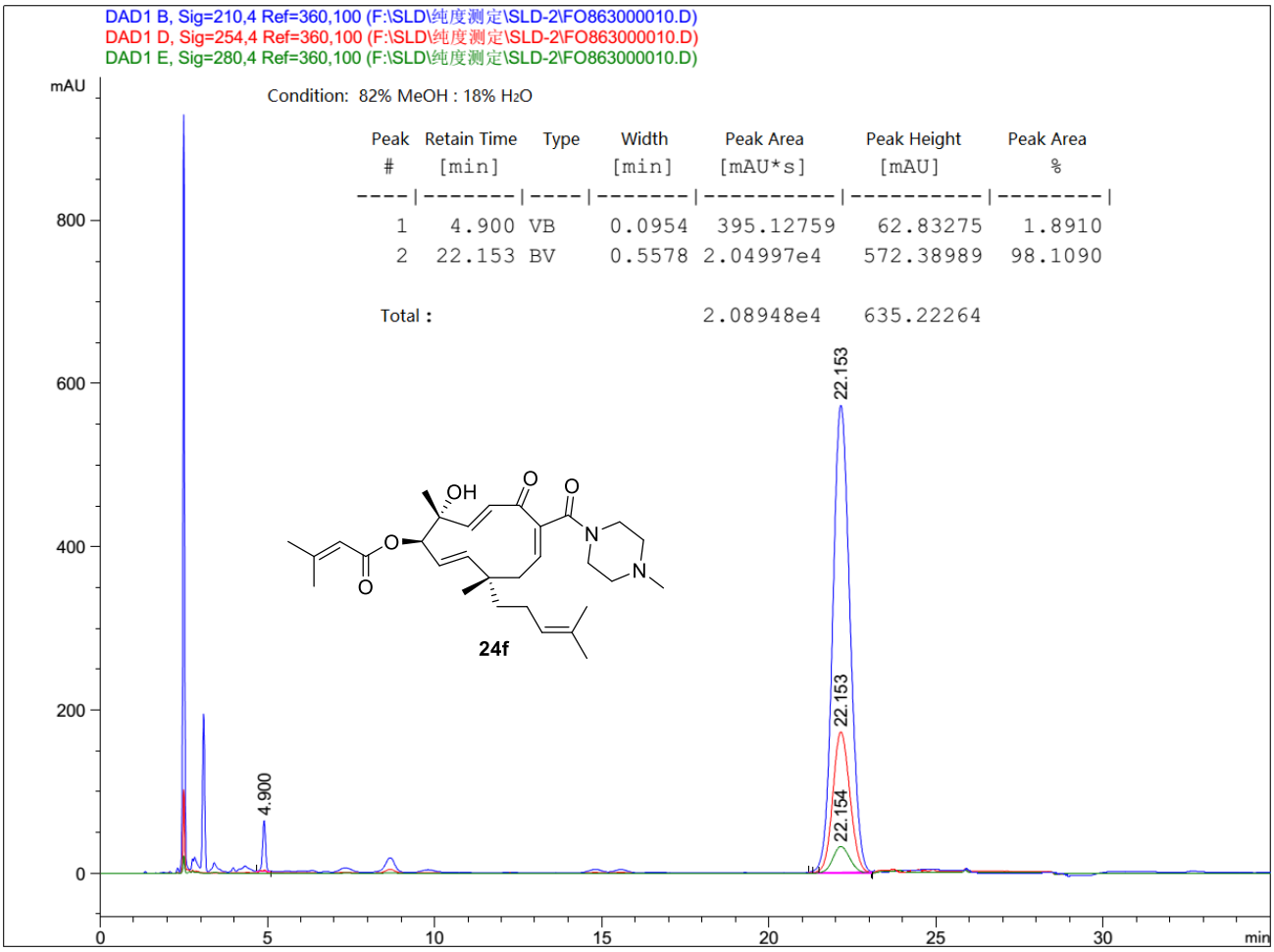
mAU
Condition: 80% MeOH : 20% H2O
8.480
8.480
2.731
2.829
6.069
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.731 | VV | 0.0666 | 106.18584 | 24.50081 | 2.3691
2 | 8.480 | VV | 0.2515 | 4375.95752 | 272.22385 | 97.6309
Total : 4482.14336 296.72465
OH
O
O
N
O
O
24e
min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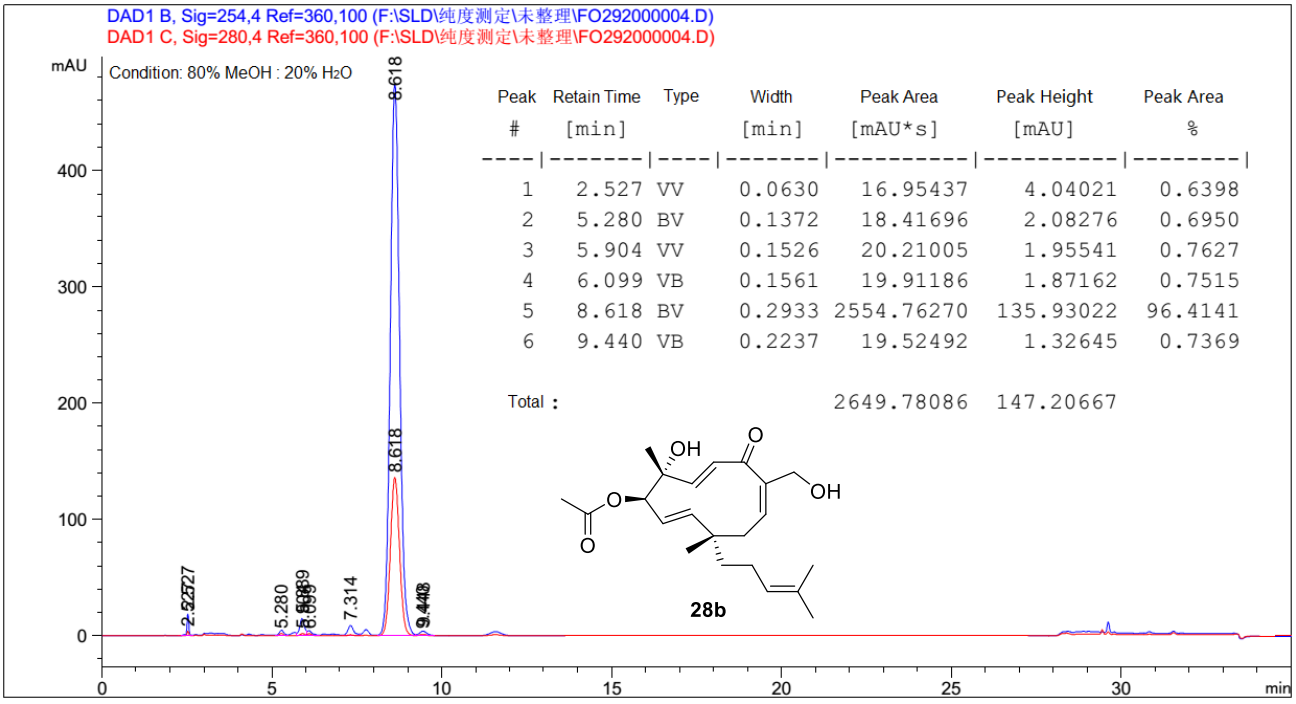
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-2\FO863000010.D)
mAU
Condition: 82% MeOH : 18% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 4.900 | VB | 0.0954 | 395.12759 | 62.83275 | 1.8910
2 | 22.153 | BV | 0.5578 | 2.04997e4 | 572.38989 | 98.1090
Total : 2.08948e4 635.22264
22.153
22.153
22.154
4.900
OH
O
O
O
O
N
N
24f
0
200
400
600
800
0
5
10
15
20
25
30
min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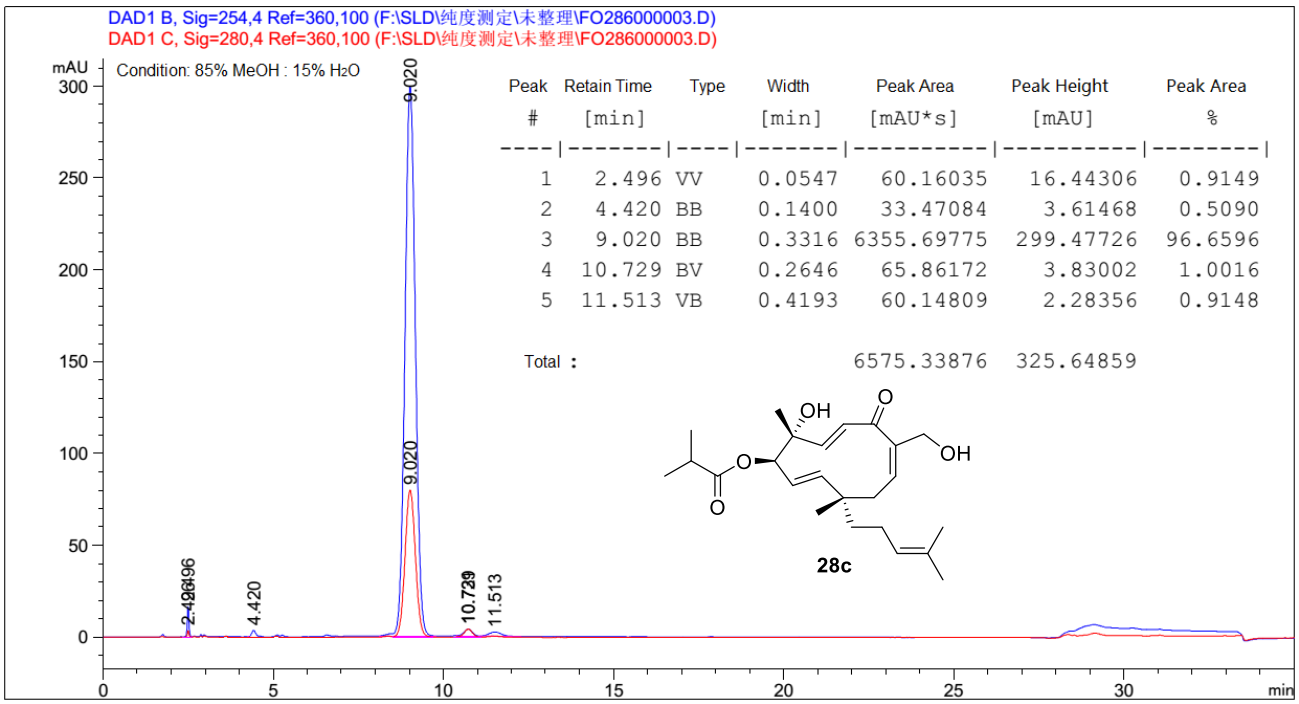
mAU
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.527 | VV | 0.0630 | 16.95437 | 4.04021 | 0.6398
2 | 5.280 | BV | 0.1372 | 18.41696 | 2.08276 | 0.6950
3 | 5.904 | VV | 0.1526 | 20.21005 | 1.95541 | 0.7627
4 | 6.099 | VB | 0.1561 | 19.91186 | 1.87162 | 0.7515
5 | 8.618 | BV | 0.2933 | 2554.76270 | 135.93022 | 96.4141
6 | 9.440 | VB | 0.2237 | 19.52492 | 1.32645 | 0.7369
Total : 2649.78086 147.20667
8.618
8.618
7.314
5.280
OH
OH
O
O
28b
0
100
200
300
400
0
5
10
15
20
25
30
min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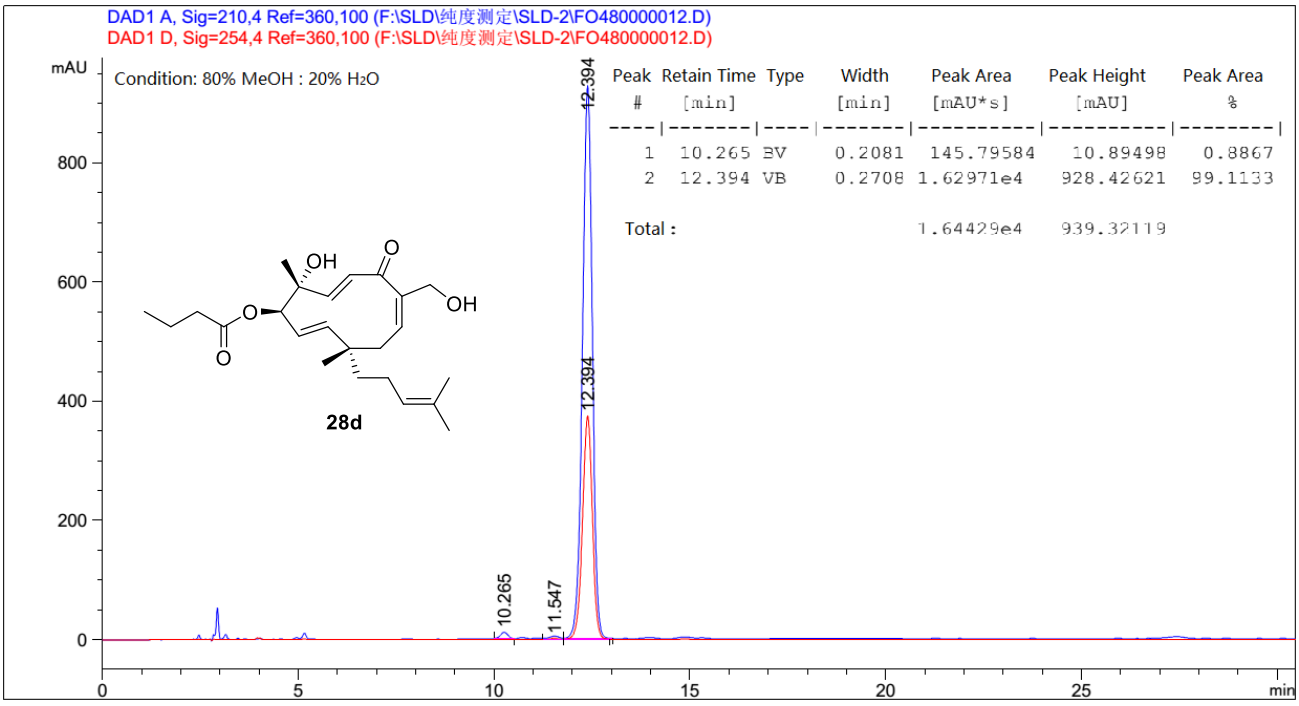
mAU
Condition: 85% MeOH : 15% H2O
9.020
4.420
10.729
11.513
min
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.496 | VV | 0.0547 | 60.16035 | 16.44306 | 0.9149
2 | 4.420 | BB | 0.1400 | 33.47084 | 3.61468 | 0.5090
3 | 9.020 | BB | 0.3316 | 6355.69775 | 299.47726 | 96.6596
4 | 10.729 | BV | 0.2646 | 65.86172 | 3.83002 | 1.0016
5 | 11.513 | VB | 0.4193 | 60.14809 | 2.28356 | 0.9148
Total : 6575.33876 325.64859
28c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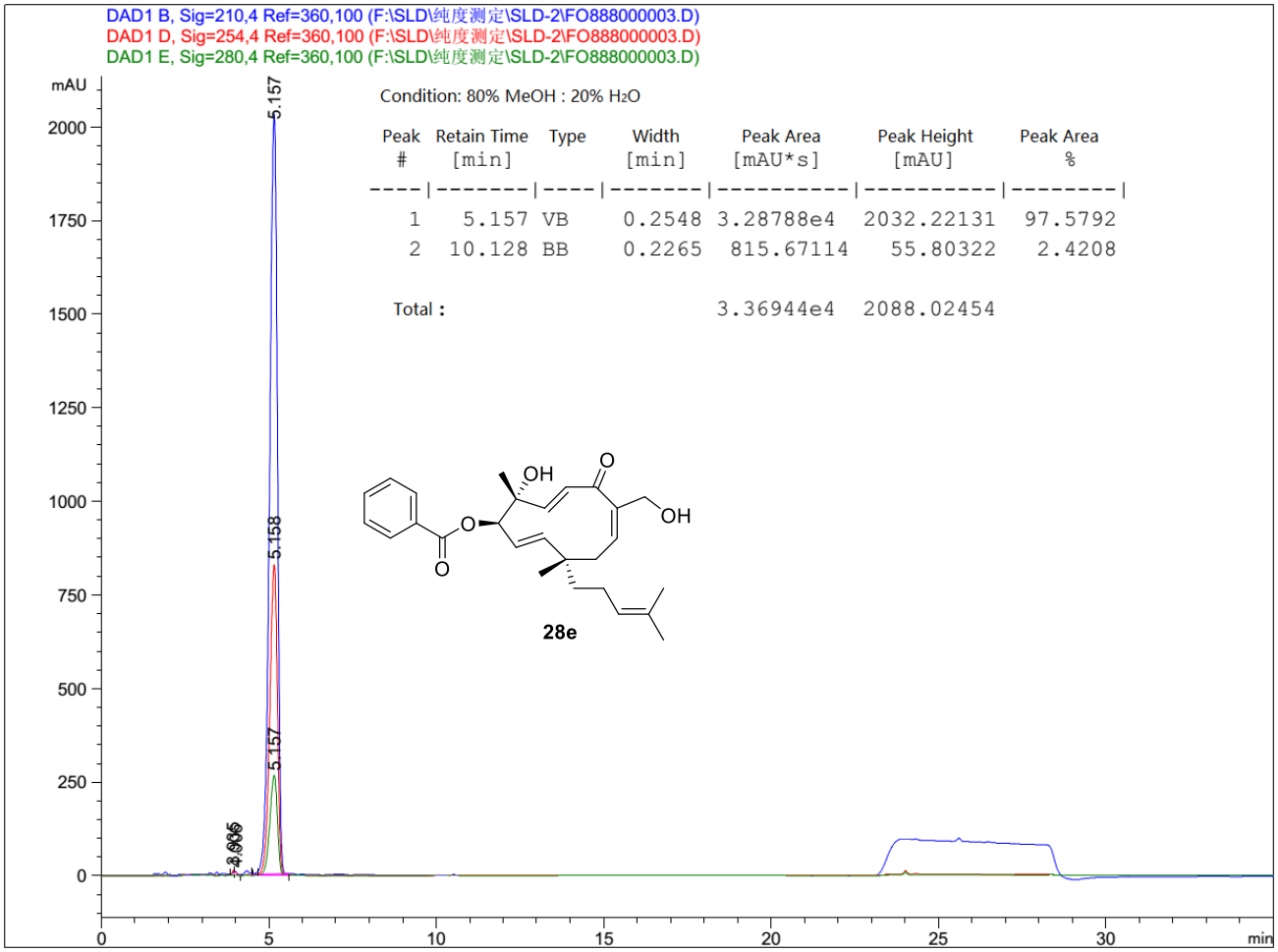
mAU
Condition: 80% MeOH : 20% H2O
12.394
10.265
11.547
min
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 10.265 | BV | 0.2081 | 145.79584 | 10.89498 | 0.8867
2 | 12.394 | VB | 0.2708 | 1.62971e4 | 928.42621 | 99.1133
Total : 1.64429e4 939.32119
28d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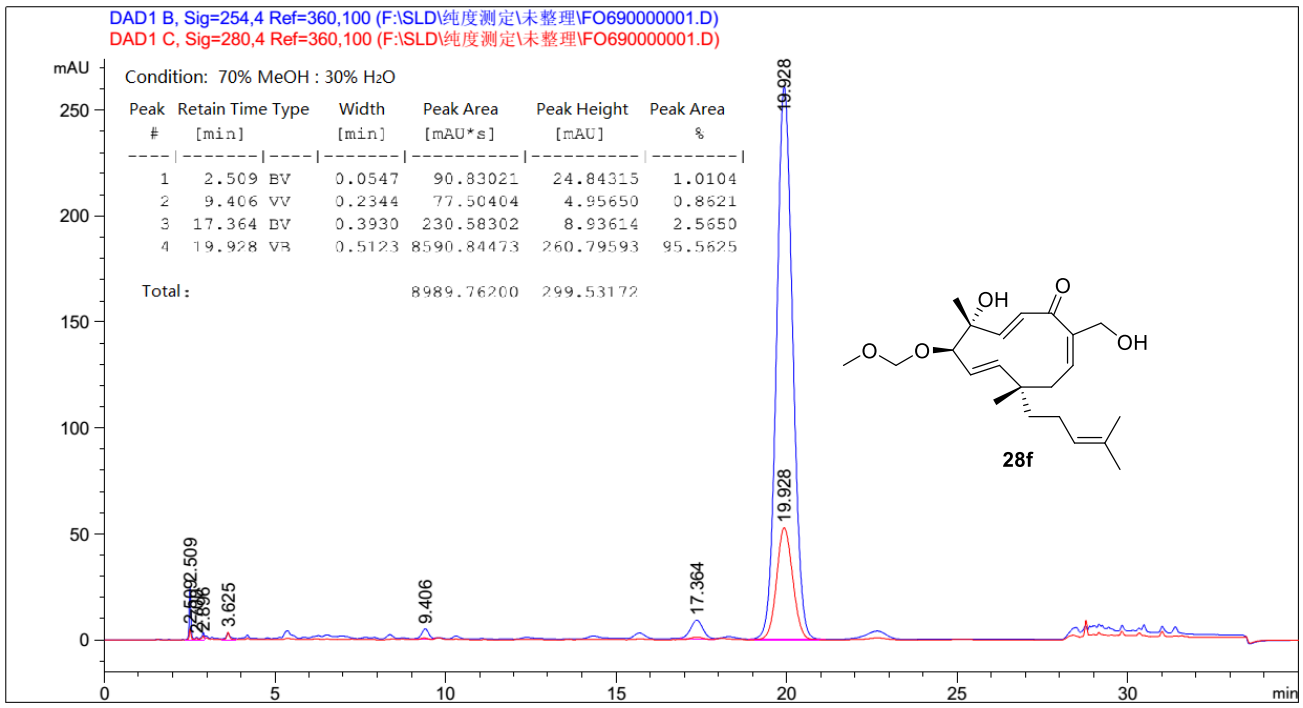
DAD1 E, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\SLD-2\FO888000003.D)
Condition: 80% MeOH : 20% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 5.157 | VB | 0.2548 | 3.28788e4 | 2032.22131 | 97.5792
2 | 10.128 | BB | 0.2265 | 815.67114 | 55.80322 | 2.4208
Total : 3.36944e4 2088.02454
28e
mAU
min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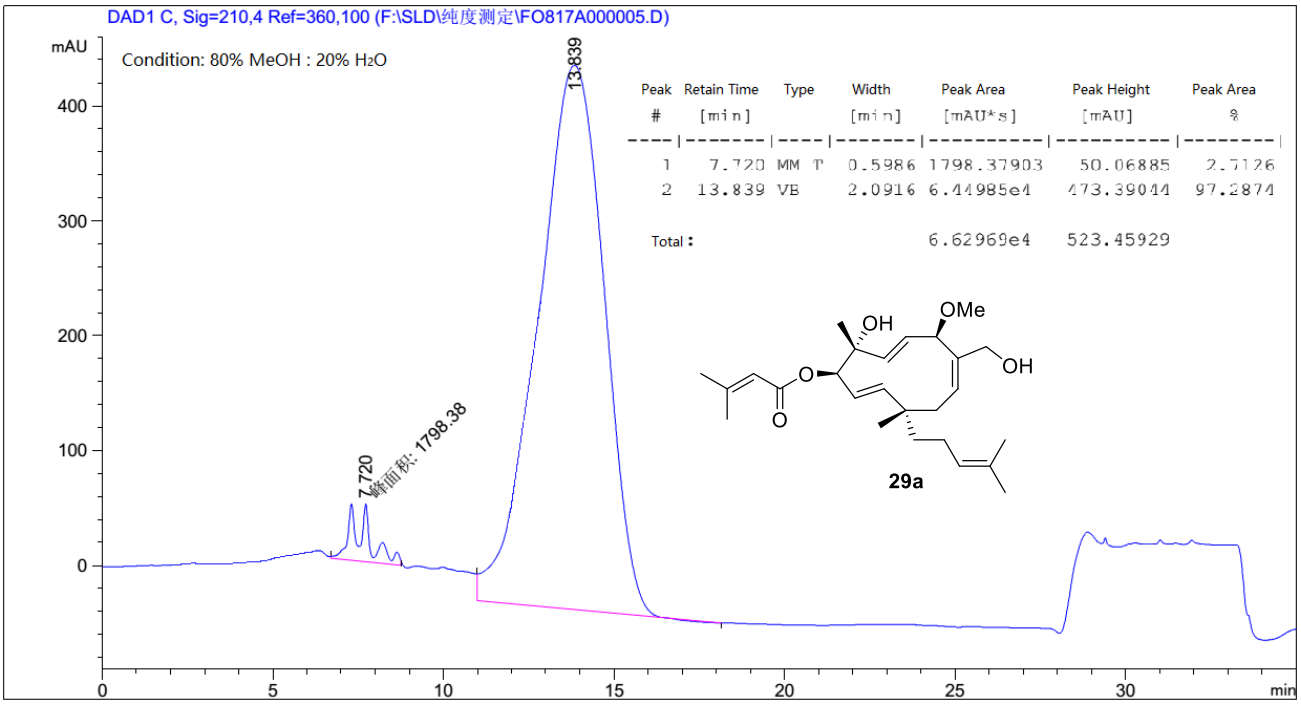
DAD1 C, Sig=280,4 Ref=360,100 (F:\SLD\纯度测定\未整理\FO690000001.D)
Condition: 70% MeOH : 30% H2O
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 2.509 | BV | 0.0547 | 90.83021 | 24.84315 | 1.0104
2 | 9.406 | VV | 0.2344 | 77.50404 | 4.95650 | 0.8621
3 | 17.364 | BV | 0.3930 | 230.58302 | 8.93614 | 2.5650
4 | 19.928 | VB | 0.5123 | 8590.84473 | 260.79593 | 95.5625
Total : 8989.76200 299.53172
28f
mAU
min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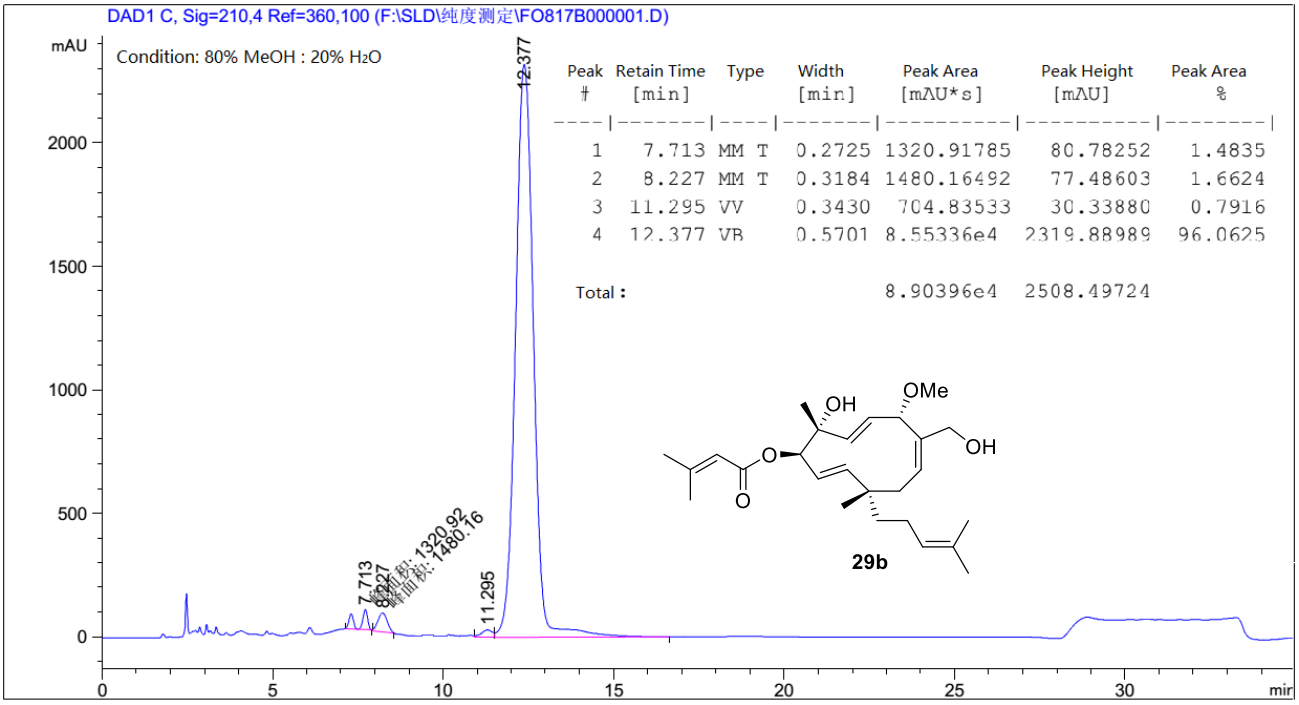
mAU
Condition: 80% MeOH : 20% H2O
13.839
7.720
峰面积: 1798.38
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 7.720 | MM T | 0.5986 | 1798.37903 | 50.06885 | 2.7126
2 | 13.839 | VB | 2.0916 | 6.44985e4 | 473.39044 | 97.2874
Total: 6.62969e4 523.45929
OH
OMe
OH
O
O
29a
min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mAU
Condition: 80% MeOH : 20% H2O
12.377
7.713
8.227
11.295
峰面积: 1320.92
峰面积: 1480.16
Peak # | Retain Time [min] | Type | Width [min] | Peak Area [mAU*s] | Peak Height [mAU] | Peak Area %
1 | 7.713 | MM T | 0.2725 | 1320.91785 | 80.78252 | 1.4835
2 | 8.227 | MM T | 0.3184 | 1480.16492 | 77.48603 | 1.6624
3 | 11.295 | VV | 0.3430 | 704.83533 | 30.33880 | 0.7916
4 | 12.377 | VB | 0.5701 | 8.55336e4 | 2319.88989 | 96.0625
Total: 8.90396e4 2508.49724
OH
OMe
OH
O
O
29b
min

## Reference

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