

Supporting information for

Asymmetric Synthesis of (-)-Solanidine and (-)-Tomatidenol

Yun Wang,^[a, b] Guanxin Huang,^[a] Yong Shi,^[c] Wei-sheng Tian,^[c] Chunlin Zhuang,^{*,[a, b]} and Fen-Er Chen^{*,[a, b, d]}

-
- [a] Dr. Y. Wang, G. Huang, Dr. C.-L. Zhuang, Prof. Dr. F.-E. Chen
Engineering Center of Catalysis and Synthesis for Chiral Molecules, Fudan University, Shanghai 200433, China
E-mail: rfchen@fudan.edu.cn (F.-E. Chen); zclnathan@163.com (C.-L. Zhuang)
- [b] Y. Wang, G. Huang, Dr. C.-L. Zhuang, Prof. Dr. F.-E. Chen
Shanghai Engineering Center of Industrial Asymmetric Catalysis for Chiral Drugs, Shanghai 200433, China
- [c] Dr. Y. Shi, Prof. Dr. W.-S. Tian
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.
- [d] Prof. Dr. F.-E. Chen
Institute of Pharmaceutical Science and Technology, Zhejiang University of Technology, 18 Chao Wang Road, 310014, Hangzhou, China

Table S1. Comparing the ^1H NMR Data of Synthetic **1** with Those Reported^[1]

Numbering	Our sample: (400 MHz, CDCl_3)	Reported by Zhang (400 MHz, CDCl_3)	$\Delta\delta/\text{ppm}$
3	3.46-3.57 (m, 1H)	3.46-3.57 (m, 1H)	0.00
6	5.35 (d, $J = 5.1$ Hz, 1H)	5.35 (d, $J = 4.7$ Hz, 1H)	0.00
16	2.81-2.91 (m, 1H)	2.85 (d, $J = 7.8$ Hz, 1H)	0.01
18	0.84 (s)	0.83 (s)	0.01
19	1.02 (s)	1.02 (s)	0.00
21	0.83 (d, $J = 6.8$ Hz, 3H)	0.83 (d, $J = 6.6$ Hz)	0.00
22	2.57-2.68 (m, 1H)	2.57-2.67 (m, 1H),	0.00
27	0.92 (d, $J = 6.6$ Hz)	0.92 (d, $J = 6.5$ Hz, 3H)	0.00

Table S2. Comparing the ^{13}C NMR Data of Synthetic **1** with Those Reported^[1]

numbering	Our sample (100 MHz, CDCl_3)	Reported by Zhang (CDCl_3)	$\Delta\delta/\text{ppm}$
1	37.4	37.4	0.0
2	31.5	31.5	0.0
3	71.9	71.9	0.0
4	42.5	42.5	0.0
5	140.9	140.9	0.0
6	121.8	121.8	0.0
7	31.8	31.8	0.0
8	32.2	32.2	0.0
9	50.4	50.4	0.0
10	36.8	36.8	0.0
11	21.1	21.1	0.0
12	40.1	40.1	0.0
13	40.4	40.4	0.0
14	57.8	57.8	0.0
15	33.5	33.5	0.0
16	69.2	69.2	0.0
17	63.2	63.2	0.0

18	17.1	17.0	0.1
19	19.7	19.7	0.0
20	36.8	36.8	0.0
21	18.5	18.4	0.1
22	74.8	74.8	0.0
23	29.5	29.8	0.3
24	31.2	31.2	0.0
25	31.2	31.2	0.0
26	60.4	60.4	0.0
27	19.6	19.6	0.0

Table S3. Comparing the ^1H NMR Data of Synthetic **2** with Those Reported^[2]

Numbering	Our sample: (400 MHz, CDCl_3)	Reported by Wu (400 MHz, CDCl_3)	$\Delta\delta/\text{ppm}$
3	3.46-3.57 (m, 1H)	3.46-3.57 (m, 1H)	0.00
6	5.35 (d, $J = 5.4$ Hz, 1H)	5.35 (d, $J = 4.6$ Hz, 1H)	0.00
16	4.14 (q, $J = 7.4$ Hz, 1H)	4.13 (q, $J = 7.4$ Hz, 1H)	0.01
18	0.85 (s)	0.85 (s)	0.00
19	1.03 (s, 3H)	1.03 (s)	0.00
21	0.86 (d, $J = 6.7$ Hz, 3H)	0.86 (d, $J = 7.0$ Hz, 3H)	0.00
24	2.66-2.76 (m, 2H)	2.67-2.80 (m, 2H)	0.02
26	2.20-2.37 (m, 2H)	2.30 (dd, $J = 12.8, 3.8$ Hz, 1H) 2.23 (t, $J = 12.2$ Hz, 1H)	0.02
27	0.98 (d, $J = 6.7$ Hz, 3H)	0.98 (d, $J = 6.6$ Hz, 3H)	0.00

Table S4. Comparing the ^{13}C NMR Data of Synthetic **2** with Those Reported^[3]

numbering	Our sample (100 MHz, CDCl_3)	Reported by Chhabra (CDCl_3)	$\Delta\delta/\text{ppm}$
1	36.8	36.9	0.1
2	31.8	31.6	0.2
3	71.9	71.7	0.2
4	42.4	42.3	0.1
5	141.0	141.0	0.0
6	121.5	121.0	0.5
7	32.3	32.1	0.2
8	31.5	31.4	0.1
9	50.3	50.1	0.2
10	37.4	37.3	0.1
11	21.0	20.9	0.1
12	40.1	40.0	0.1
13	40.8	40.6	0.2
14	56.2	56.0	0.2
15	32.9	32.8	0.1

16	78.6	78.5	0.1
17	62.0	61.9	0.1
18	16.9	16.8	0.1
19	19.5	19.4	0.1
20	43.2	43.0	0.2
21	16.1	15.9	0.2
22	100.1	99.1	1.0
23	26.8	26.7	0.1
24	28.7	28.6	0.1
25	31.2	31.1	0.1
26	50.4	50.2	0.2
27	19.6	19.4	0.2

Reference:

1. Z. D. Zhang, Y. Shi, J. J. Wu, J. R. Lin, W. S. Tian, *Org. Lett.* 2016, **18**, 3038-3040.
2. J. J. Wu, R. Gao, Y. Shi, W. S. Tian, *Tetrahedron Lett.* 2015, **56**, 6639-6642.
3. A. W. Wangyonyi, S. C. Ghhabra, G. Mkoji, U. Eilert, W. M. Njue, *Phytochemistry*. 2002, **59**, 79-84.

^1H and ^{13}C NMR spectra of all new compounds

Figure S1. ^1H NMR Spectrum of **9** (400 MHz, CDCl_3)

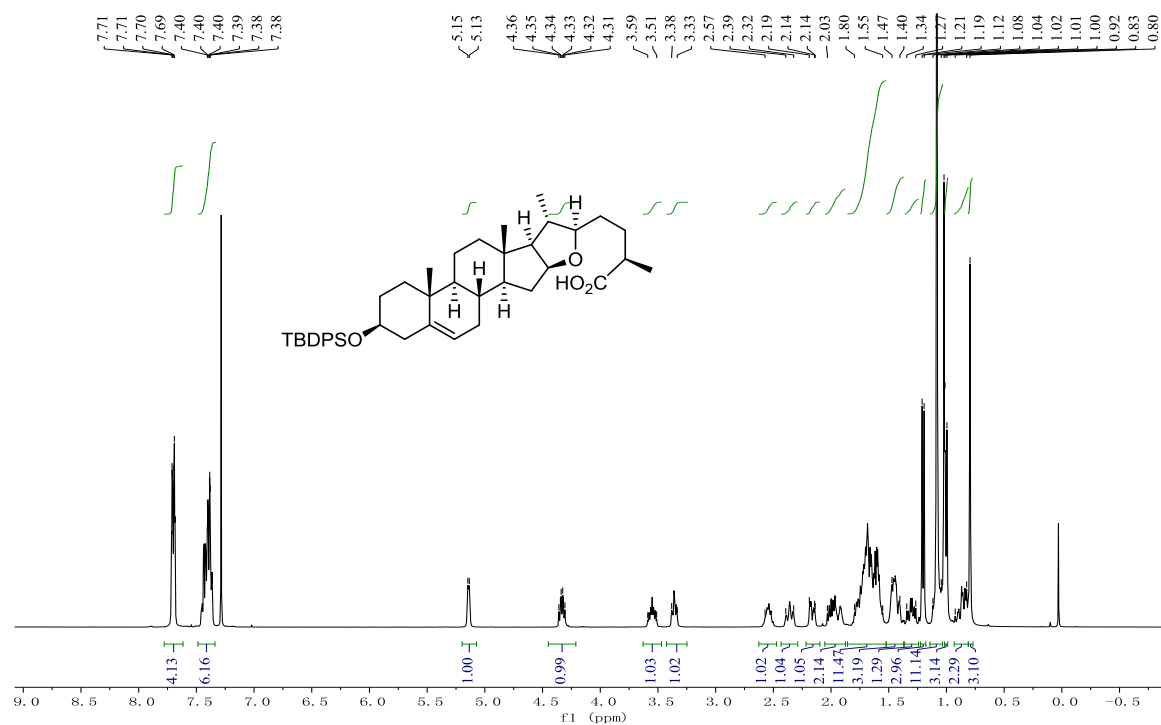


Figure S2. ^{13}C NMR Spectra of **9** (100 MHz, CDCl_3)

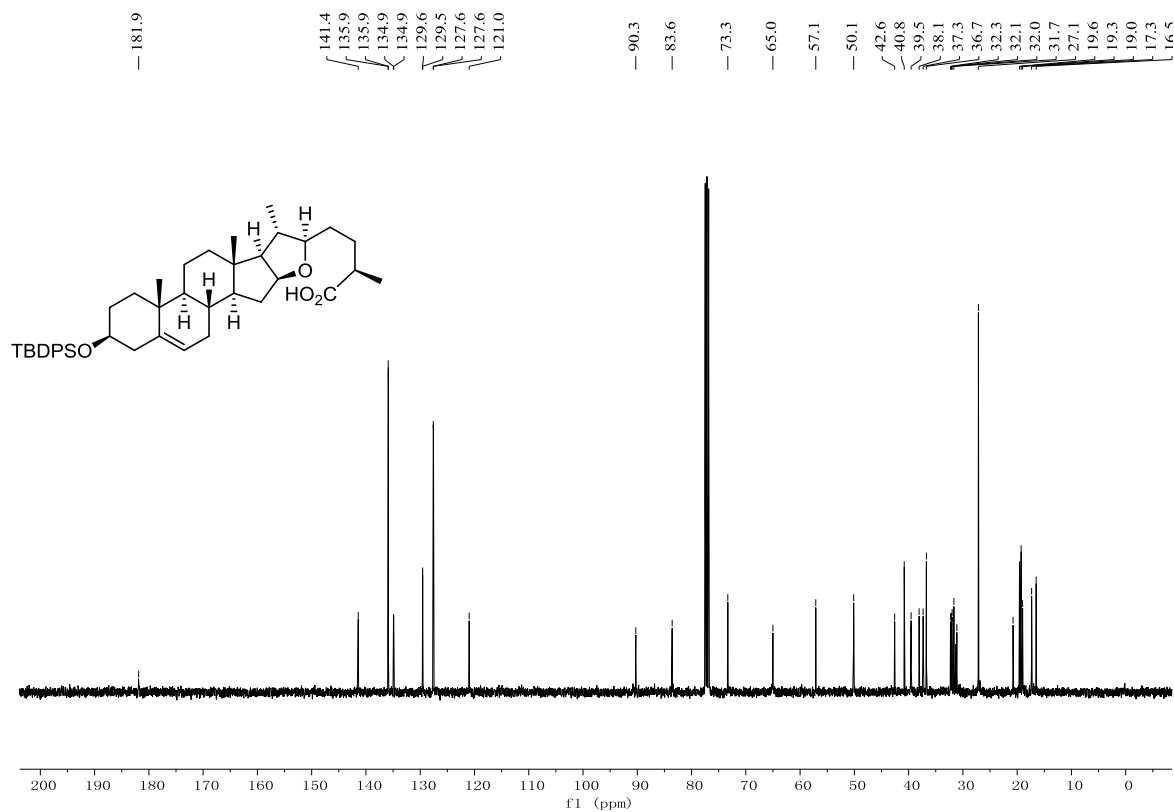


Figure S3. ^{13}C NMR Spectra of **9** (DEPT, 100 MHz, CDCl_3)

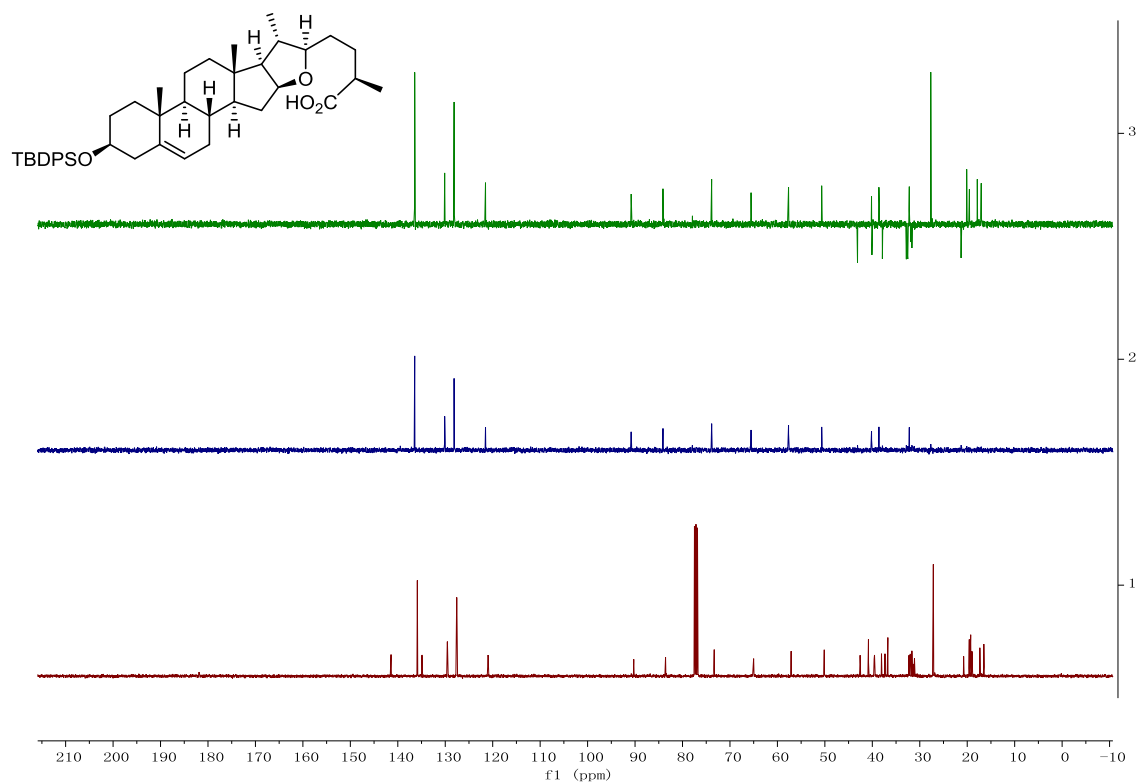


Figure S4. ^1H NMR Spectrum of **8** (400 MHz, CDCl_3)

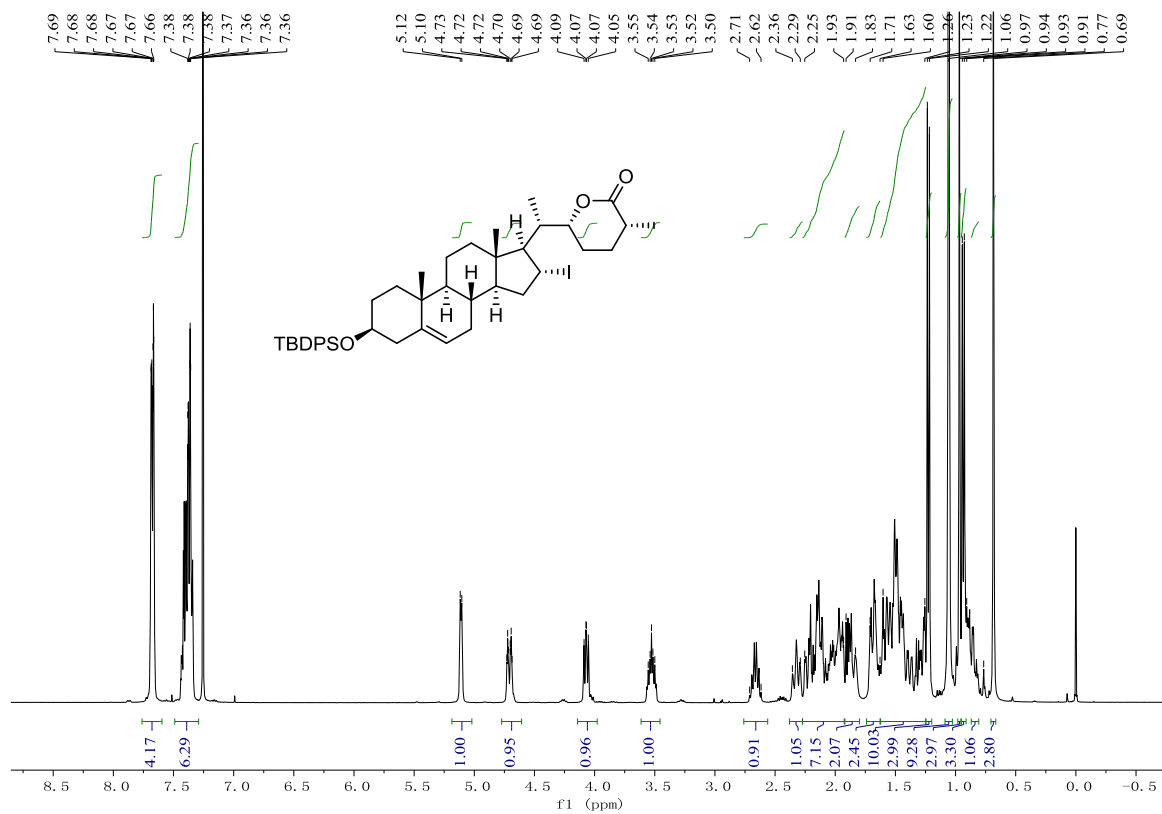


Figure S5. ^{13}C NMR Spectra of **8** (100 MHz, CDCl_3)

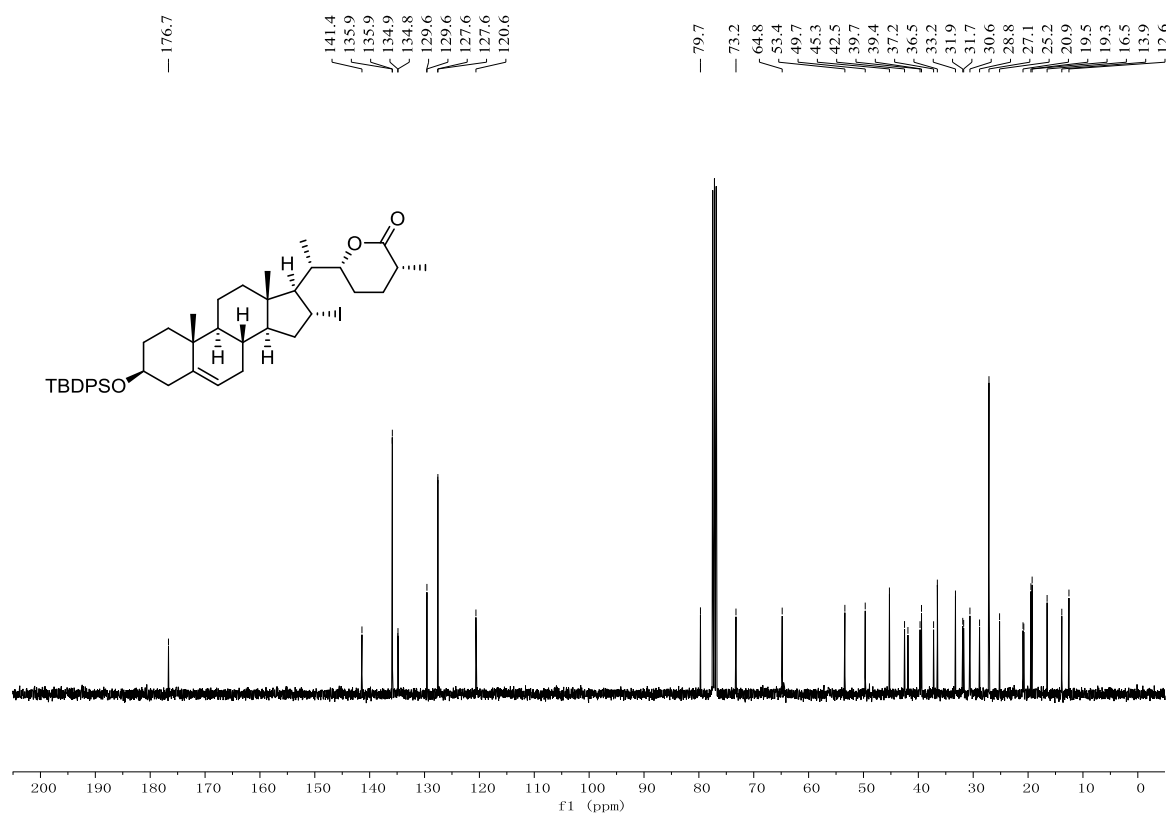


Figure S6. ^{13}C NMR Spectra of **8** (DEPT, 100 MHz, CDCl_3)

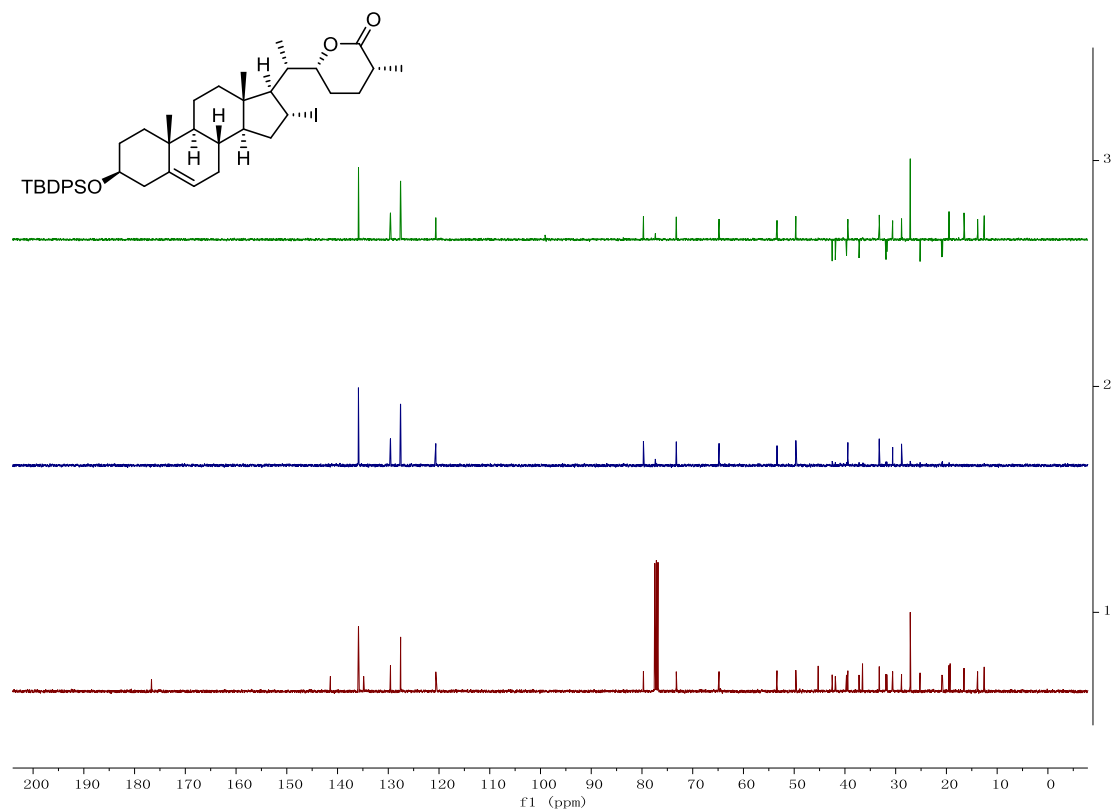


Figure S7. ^1H NMR Spectrum of **12** (400 MHz, CDCl_3)

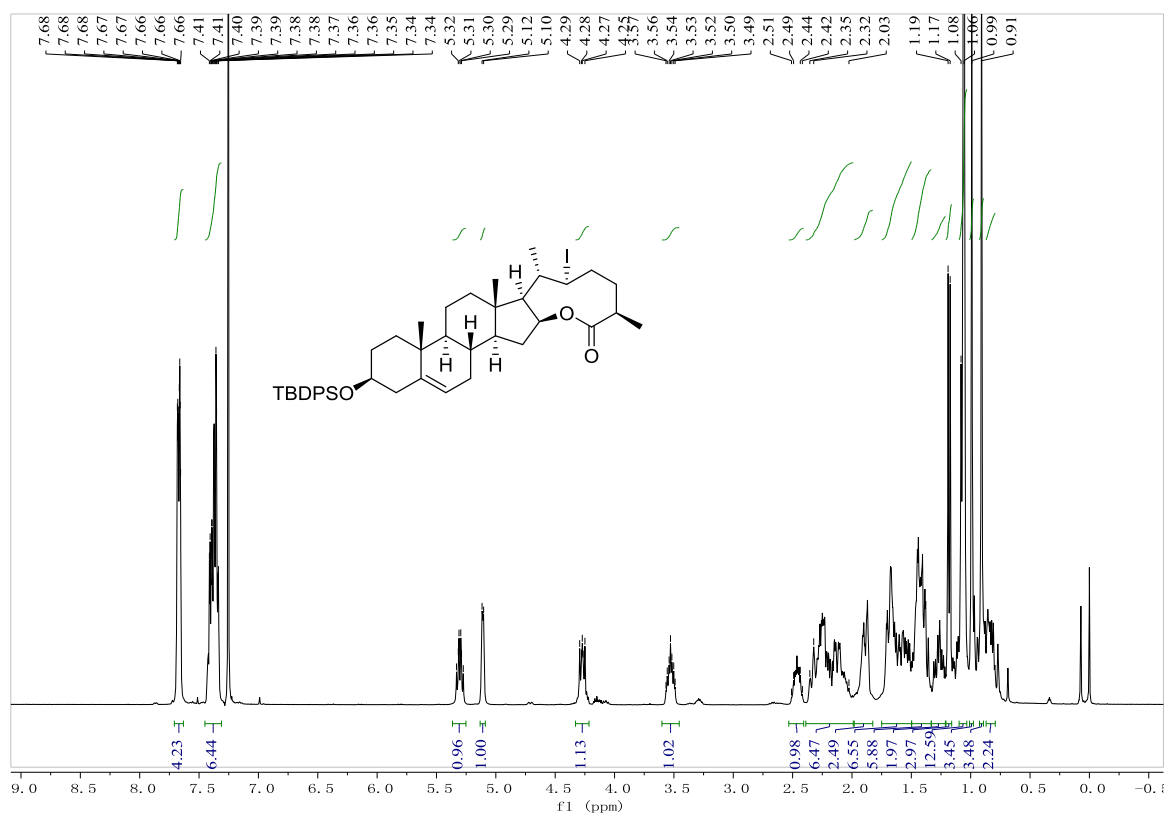


Figure S8. ^{13}C NMR Spectra of **12** (100 MHz, CDCl_3)

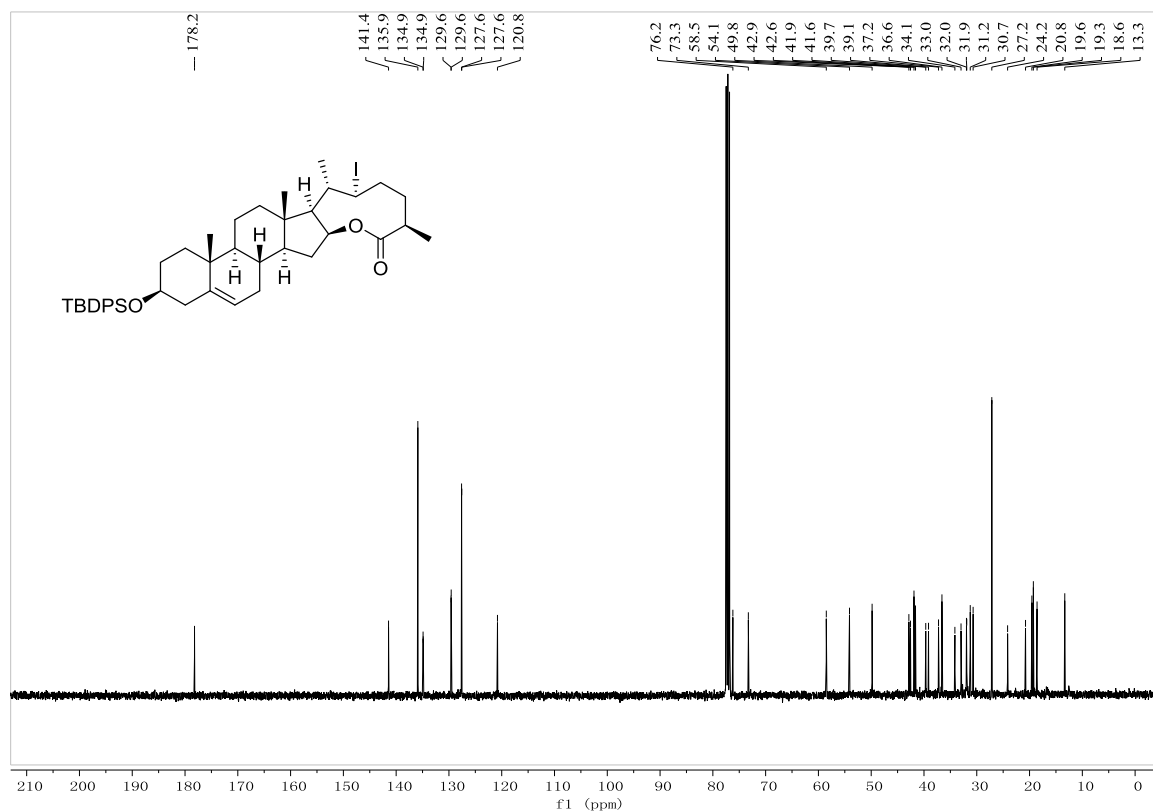


Figure S9. ^{13}C NMR Spectra of **12** (DEPT, 100 MHz, CDCl_3)

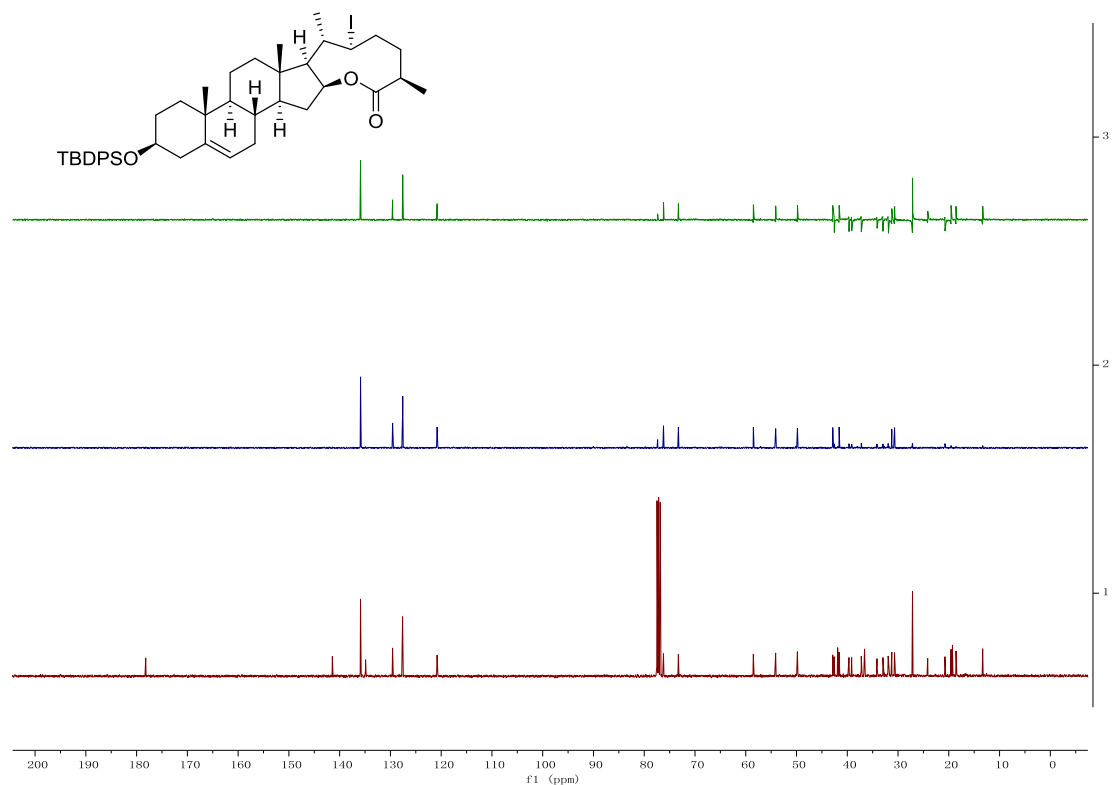


Figure S10. ^1H NMR Spectrum of **13** (400 MHz, CDCl_3)

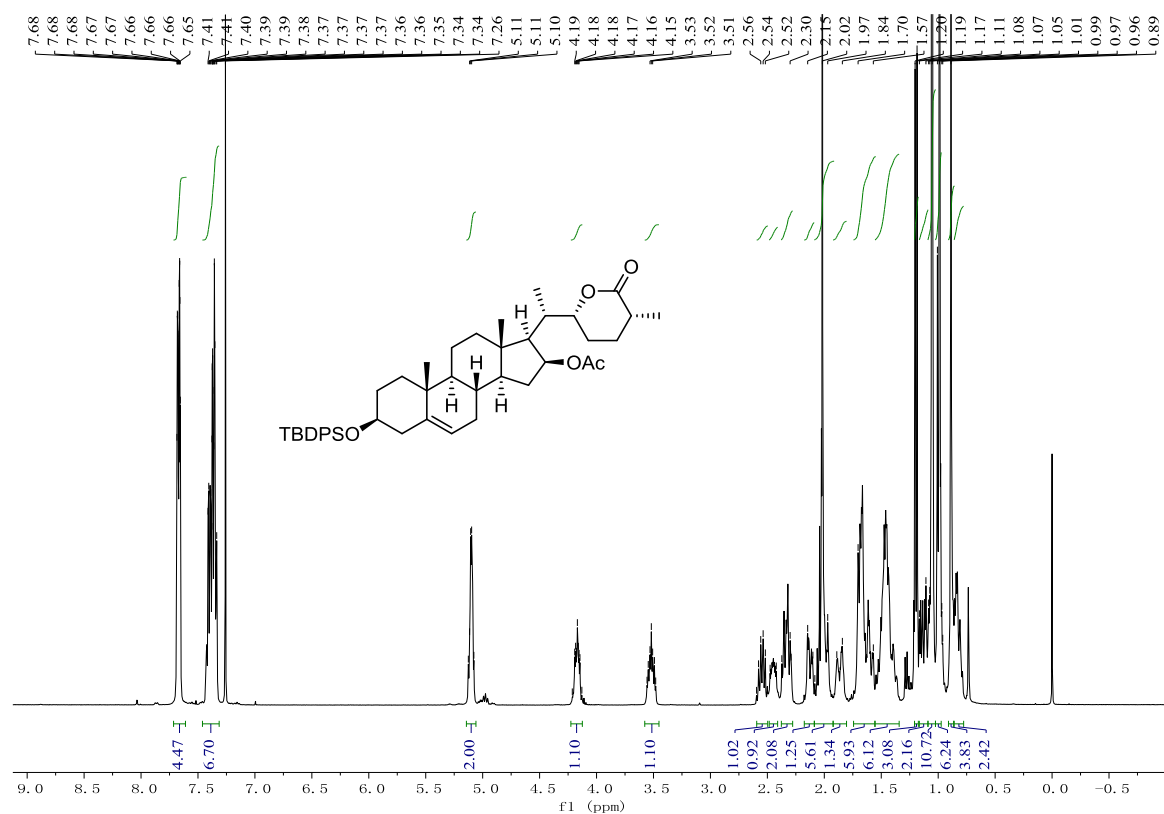


Figure S11. ^{13}C NMR Spectra of **13** (100 MHz, CDCl_3)

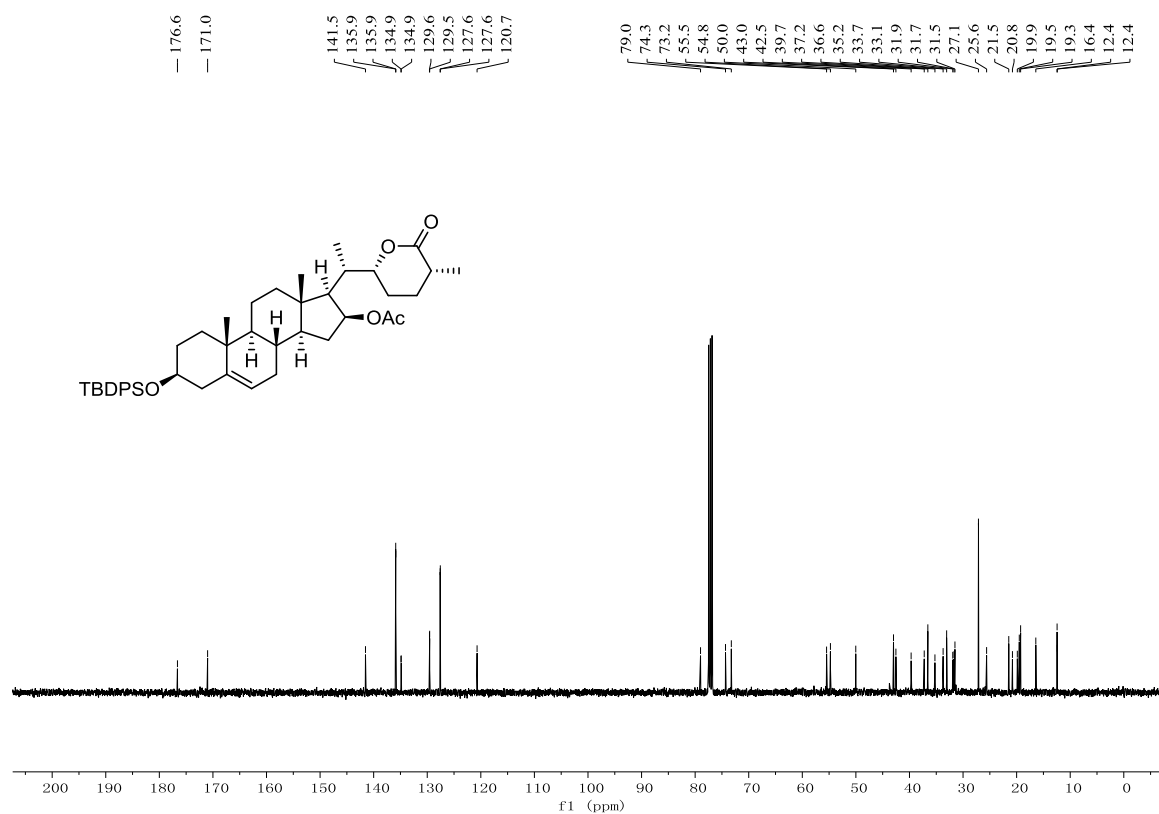


Figure S12. ^{13}C NMR Spectra of **13** (DEPT, 100 MHz, CDCl_3)

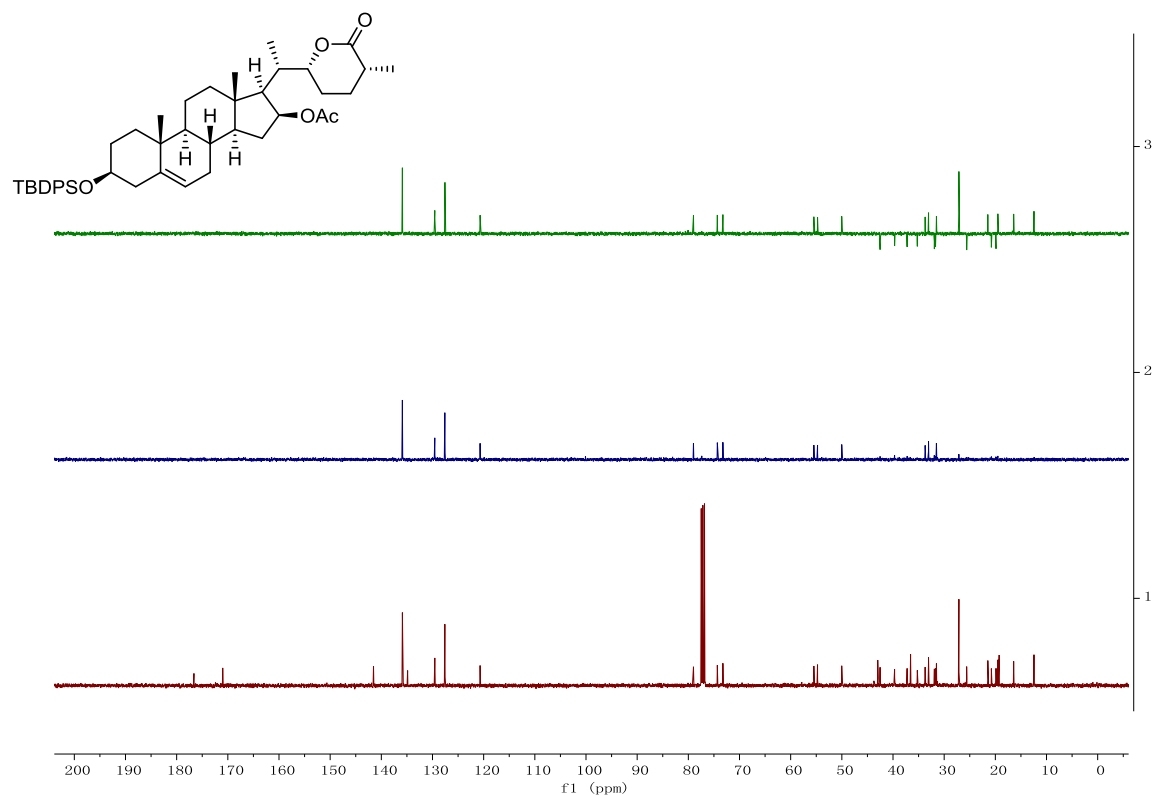


Figure S13. ^1H NMR Spectrum of 7 (400 MHz, CDCl_3)

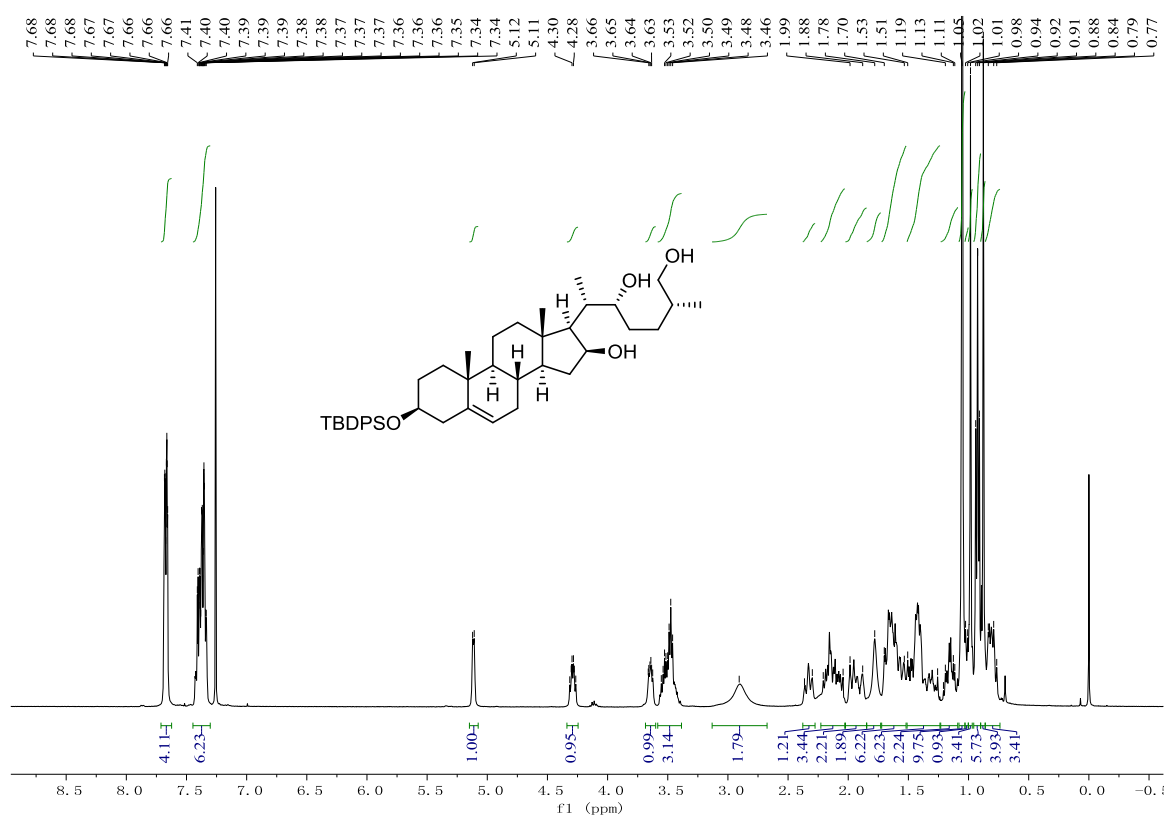


Figure S14. ^{13}C NMR Spectra of 7 (100 MHz, CDCl_3)

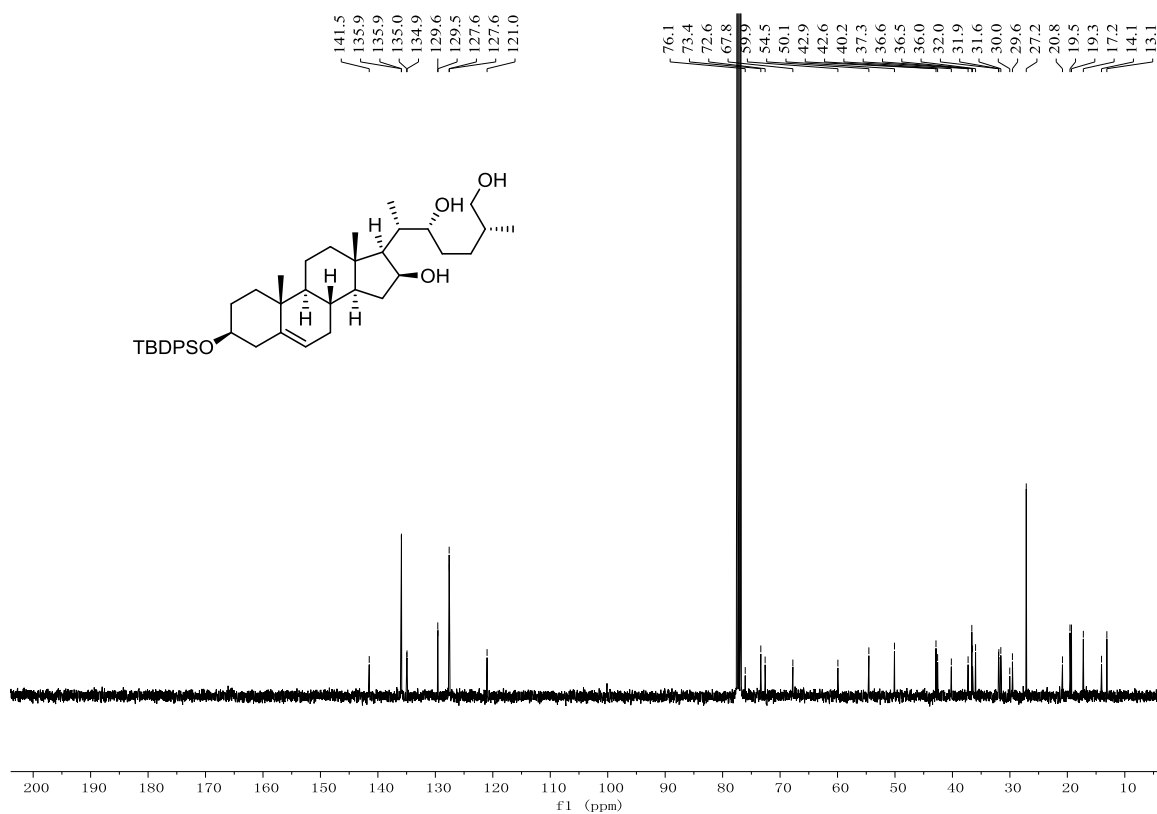


Figure S15. ^{13}C NMR Spectra of **7** (DEPT, 100 MHz, CDCl_3)

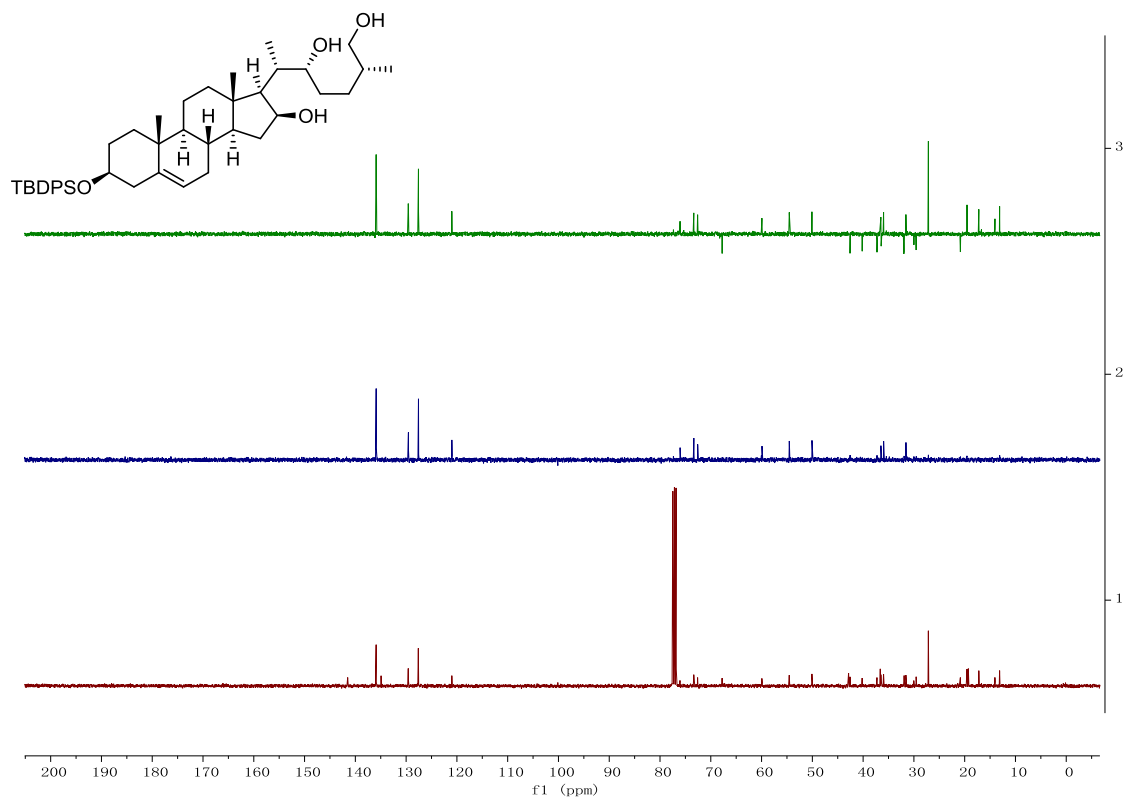


Figure S16. ^1H NMR Spectrum of **16** (400 MHz, CDCl_3)

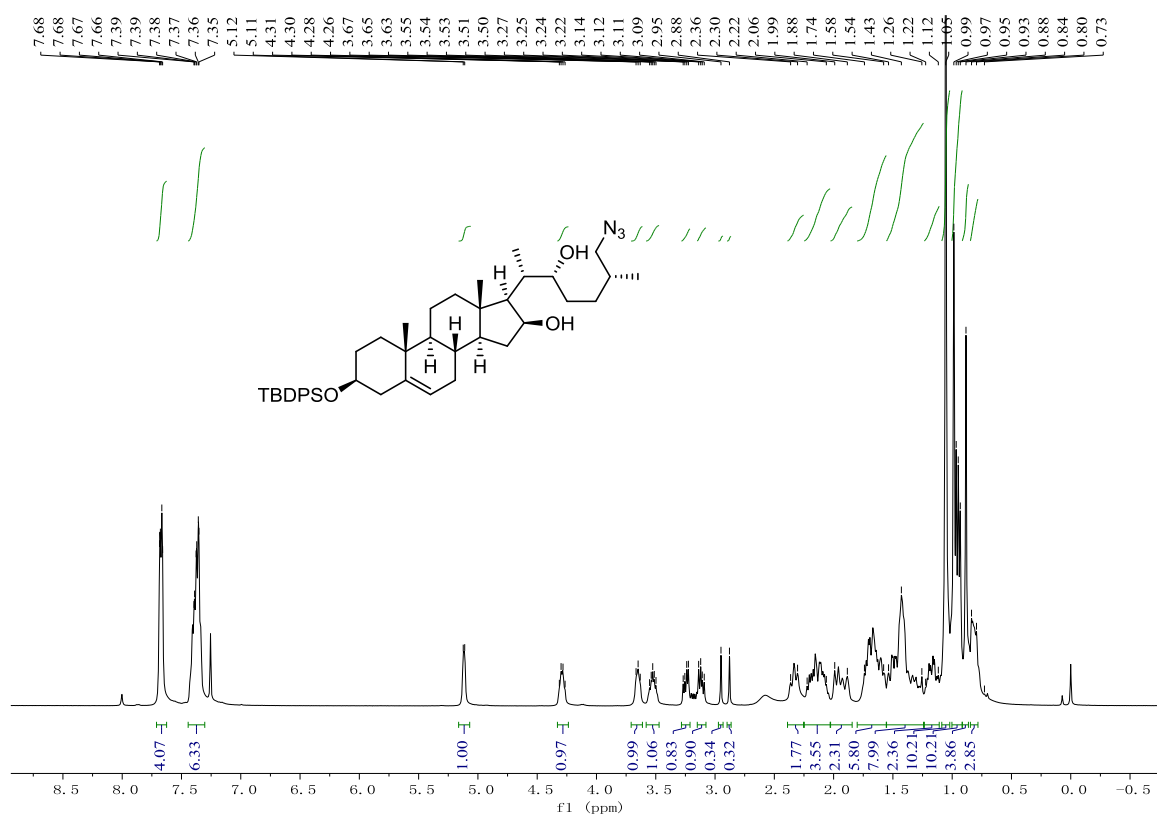


Figure S17. ^{13}C NMR Spectra of **16** (100 MHz, CDCl_3)

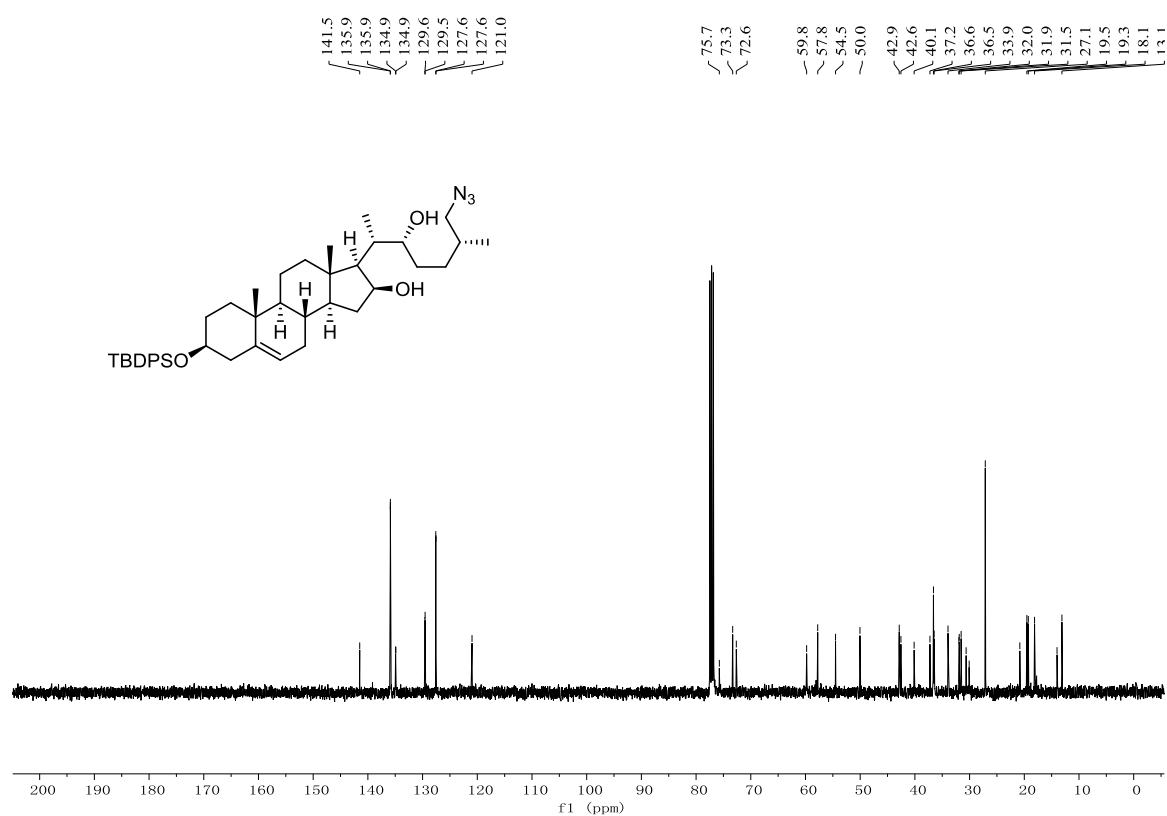


Figure S18. ^{13}C NMR Spectra of **16** (DEPT, 100 MHz, CDCl_3)

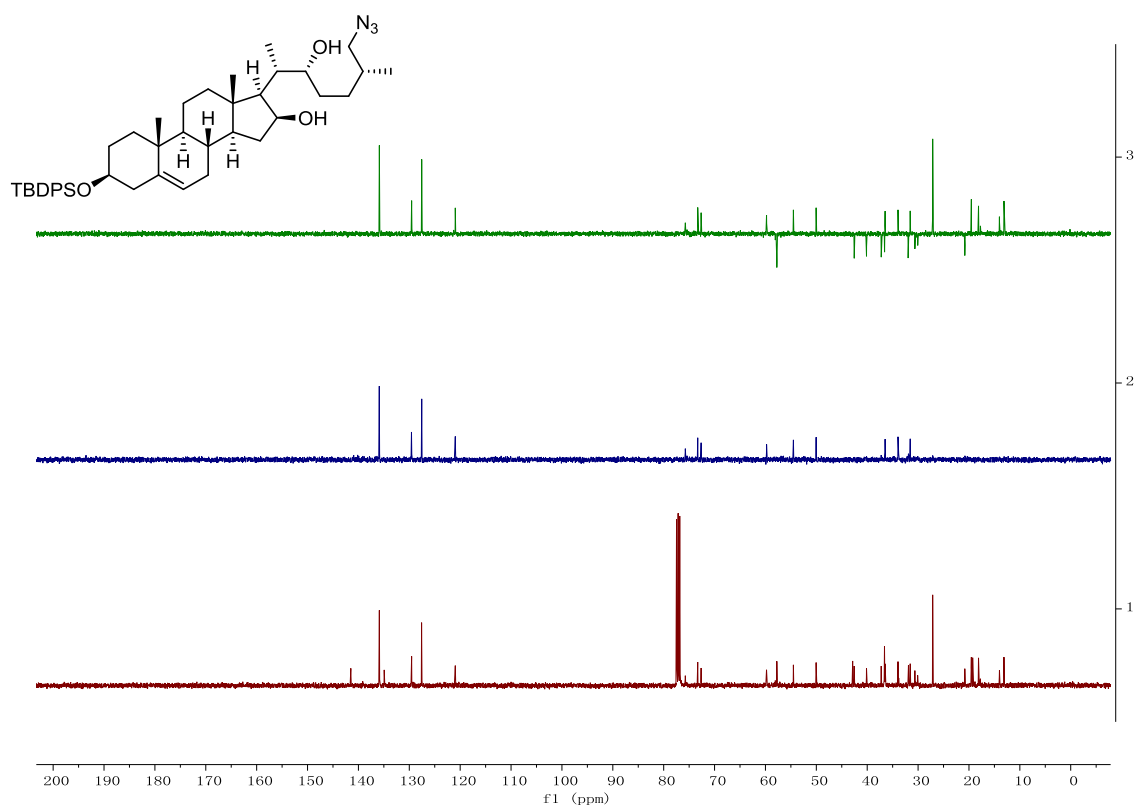


Figure S19. ^1H NMR Spectrum of **6** (400 MHz, CDCl_3)

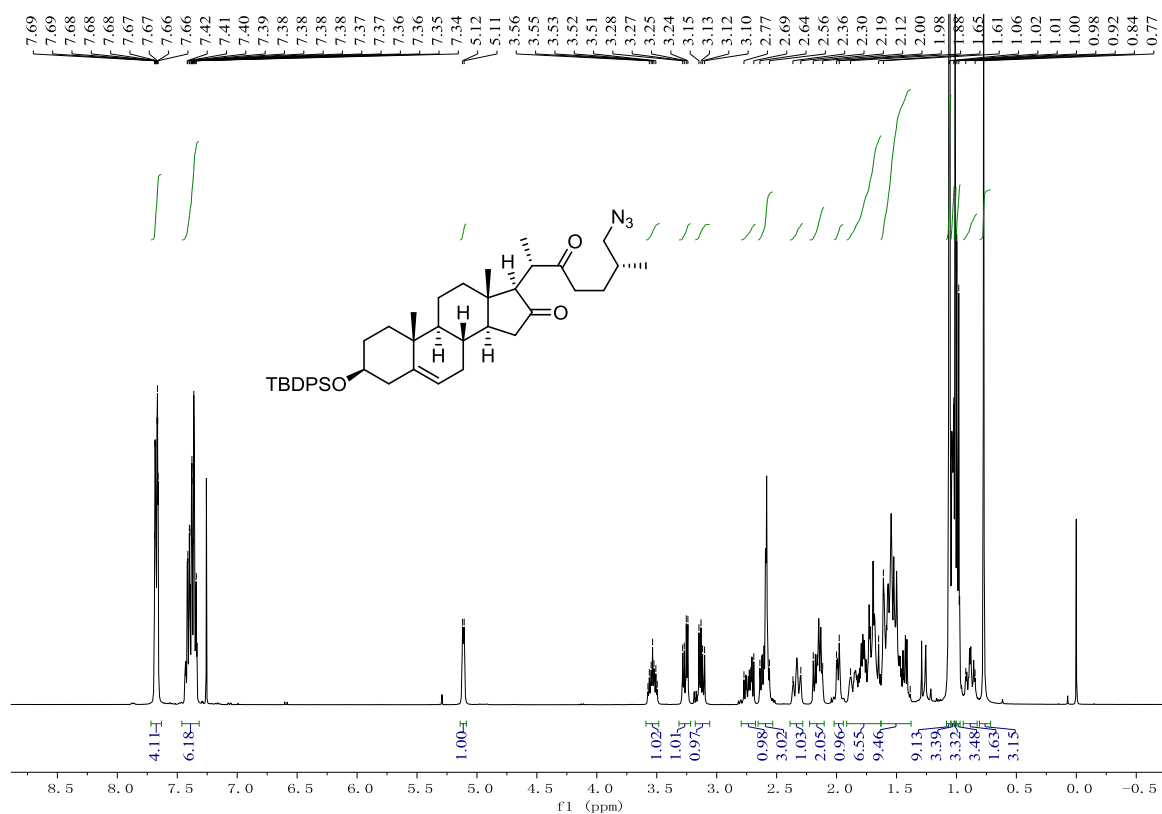


Figure S20. ^{13}C NMR Spectra of **6** (100 MHz, CDCl_3)

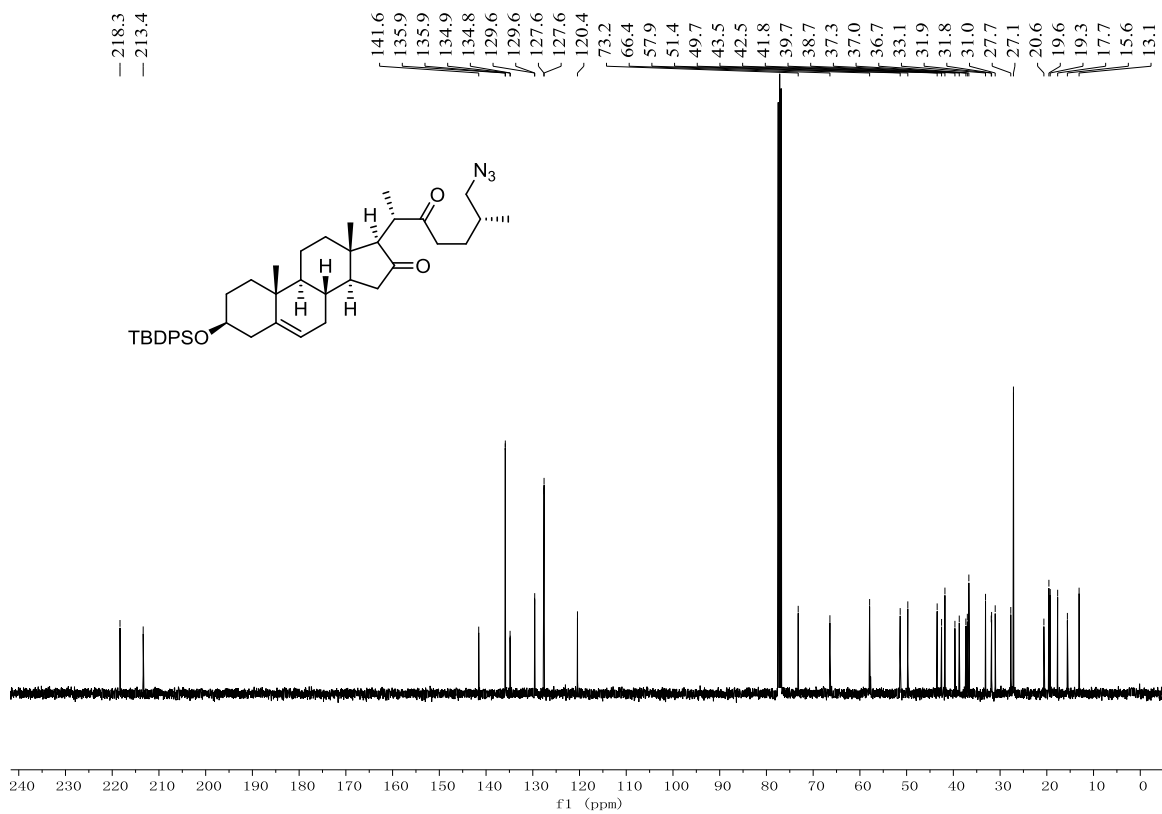


Figure S21. ^{13}C NMR Spectra of **6** (DEPT, 100 MHz, CDCl_3)

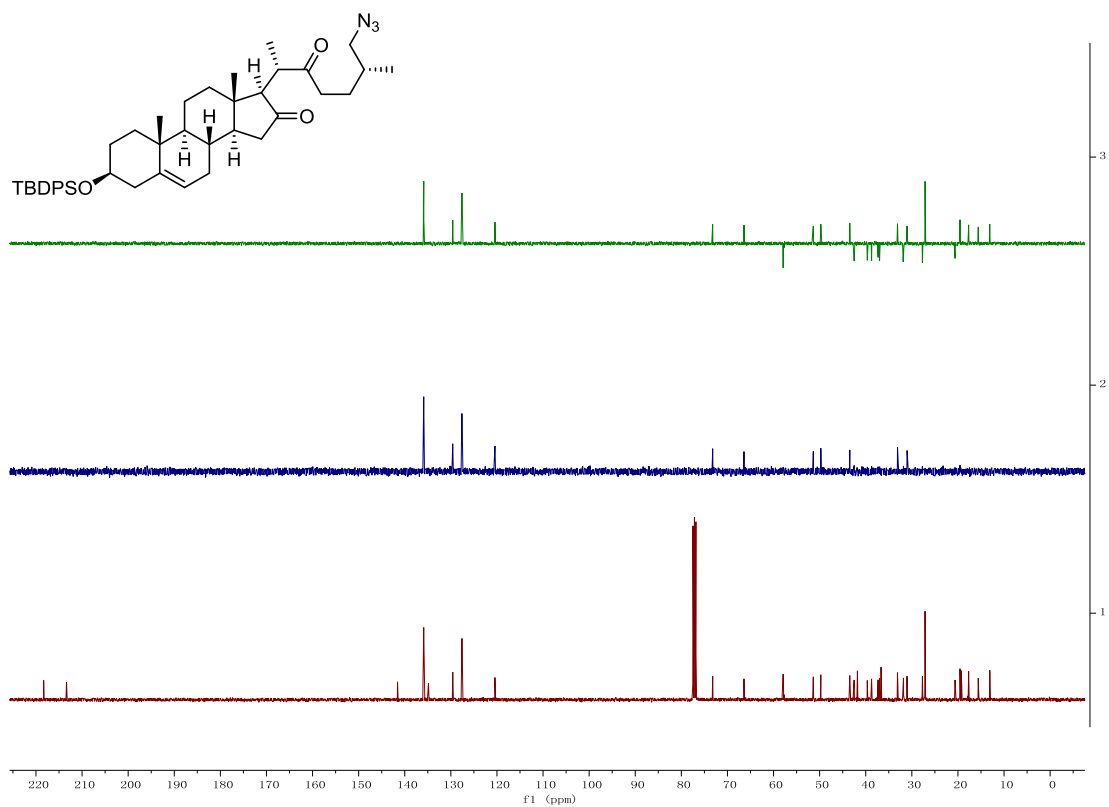


Figure S22. ^1H NMR Spectrum of **17** (400 MHz, CDCl_3)

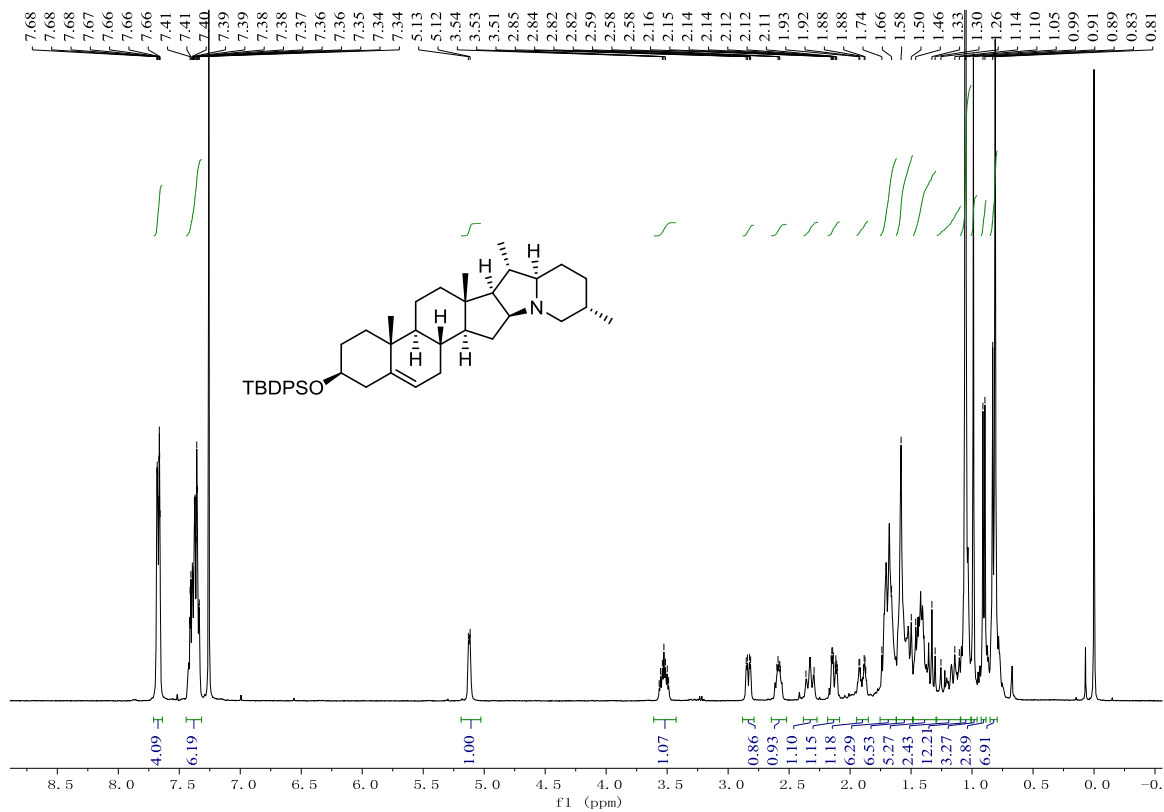


Figure S23. ^{13}C NMR Spectra of **17** (100 MHz, CDCl_3)

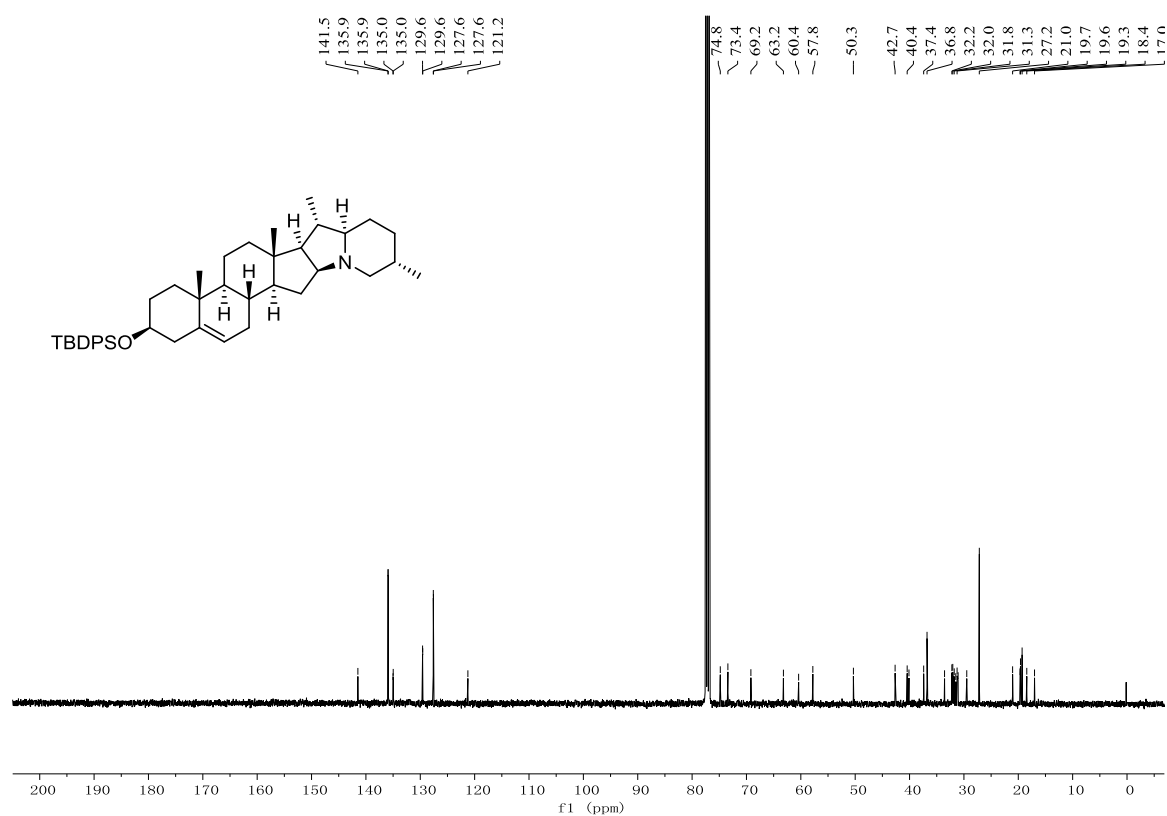


Figure S24. ^1H NMR Spectrum of **1** (400 MHz, CDCl_3)

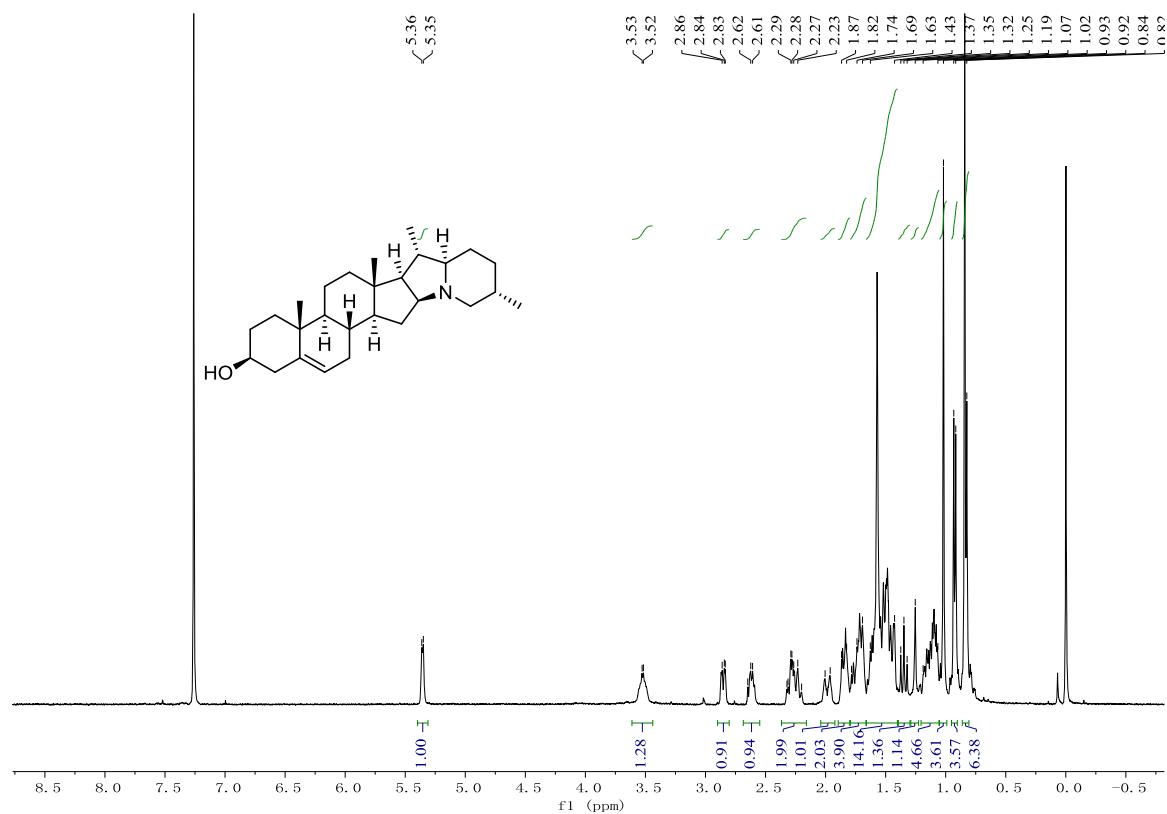


Figure S25. ^{13}C NMR Spectra of **1** (100 MHz, CDCl_3)

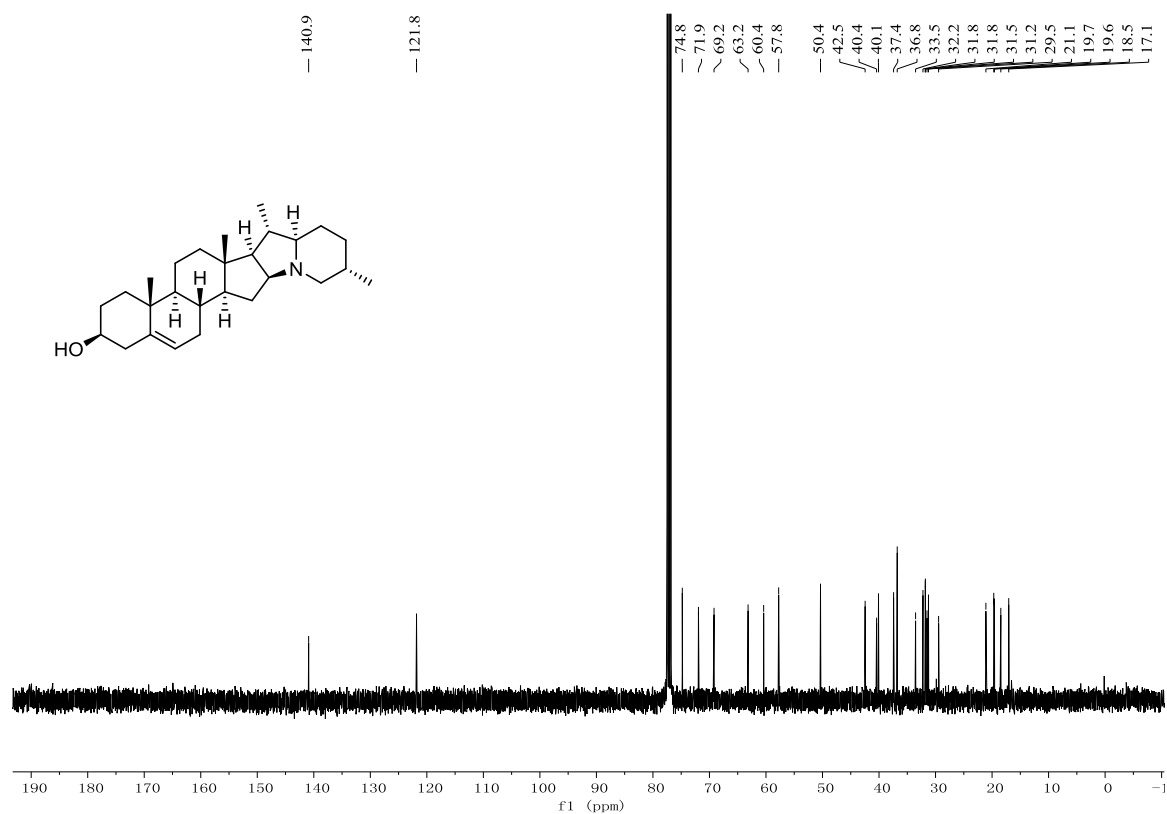


Figure S26. ^1H NMR Spectrum of **18** (400 MHz, CDCl_3)

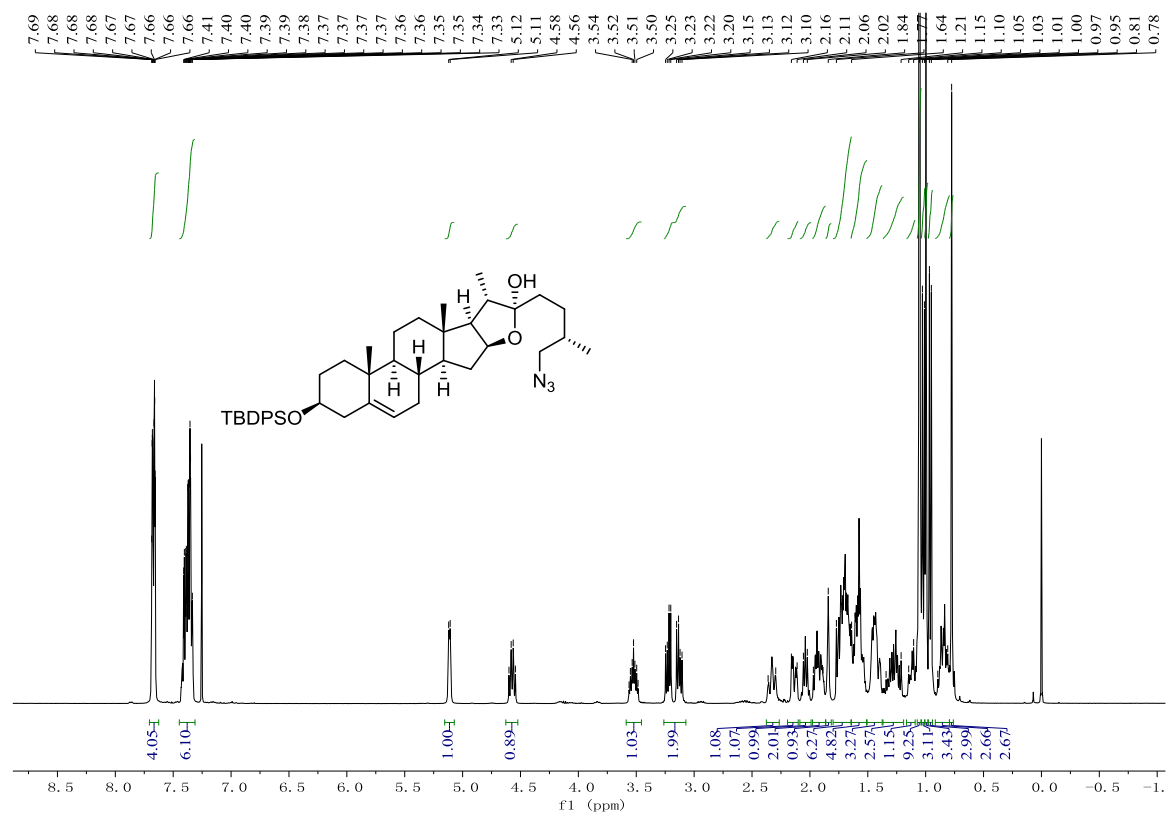


Figure S27. ^{13}C NMR Spectra of **18** (100 MHz, CDCl_3)

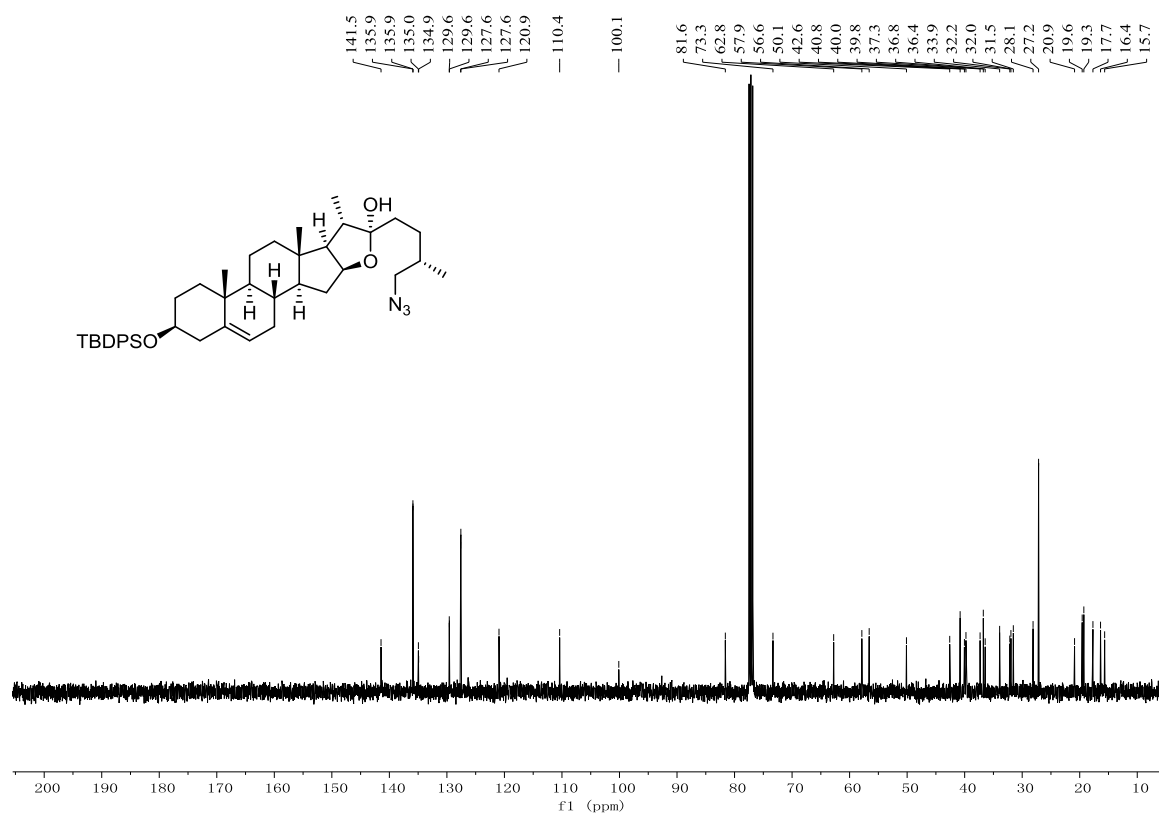


Figure S28. ^{13}C NMR Spectra of **18** (DEPT, 100 MHz, CDCl_3)

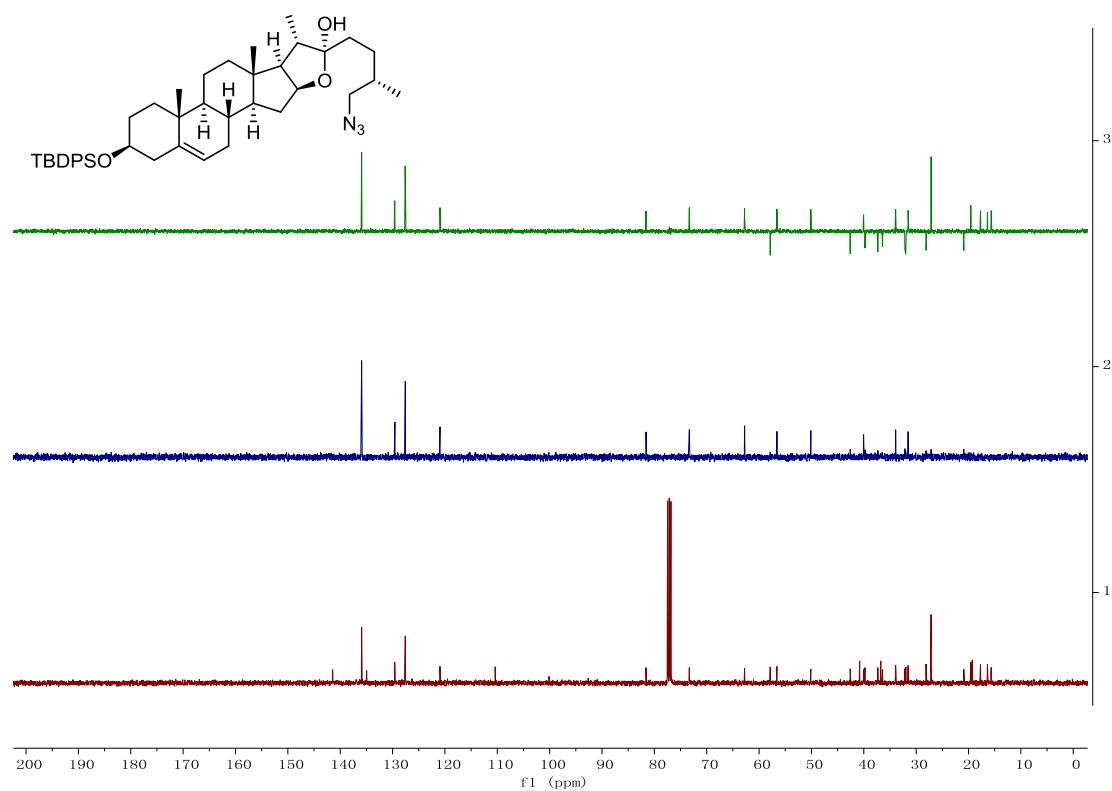


Figure S29. ^1H NMR Spectrum of **22-*epi*-16** (400 MHz, CDCl_3)

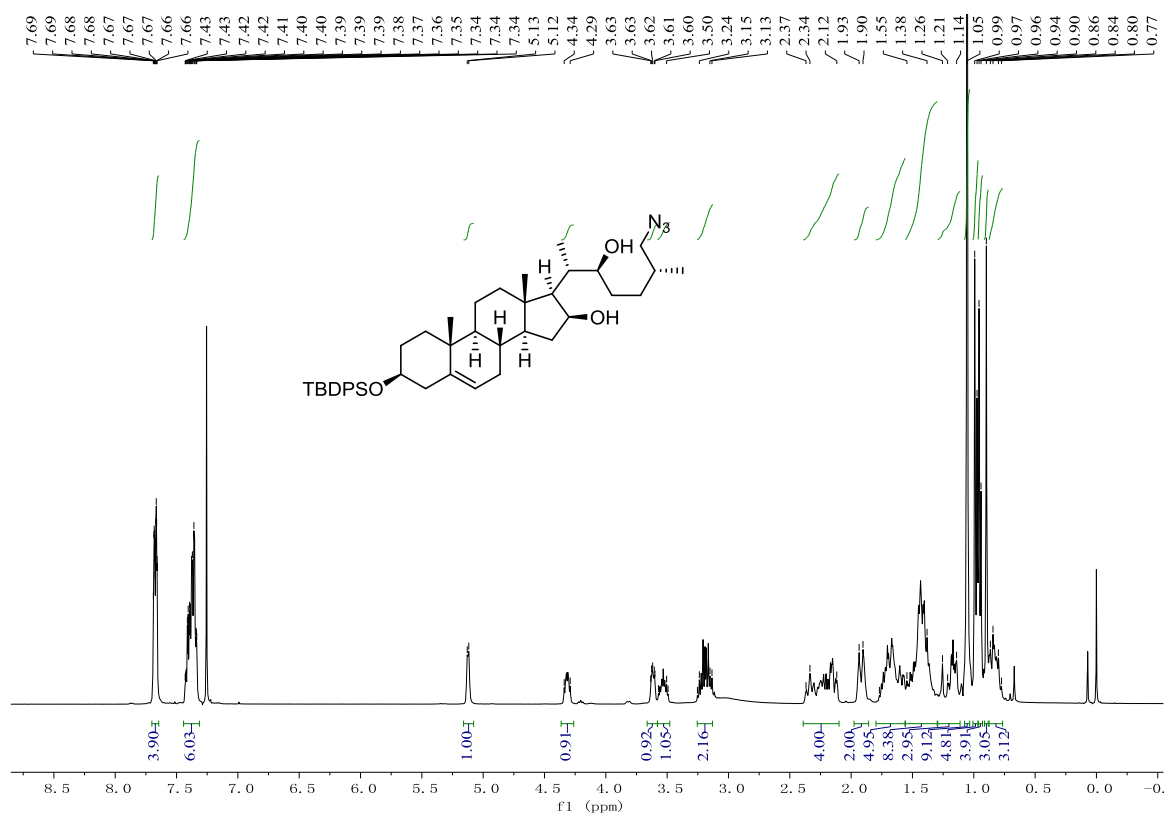


Figure S30. ^{13}C NMR Spectra of **22-*epi*-16** (100 MHz, CDCl_3)

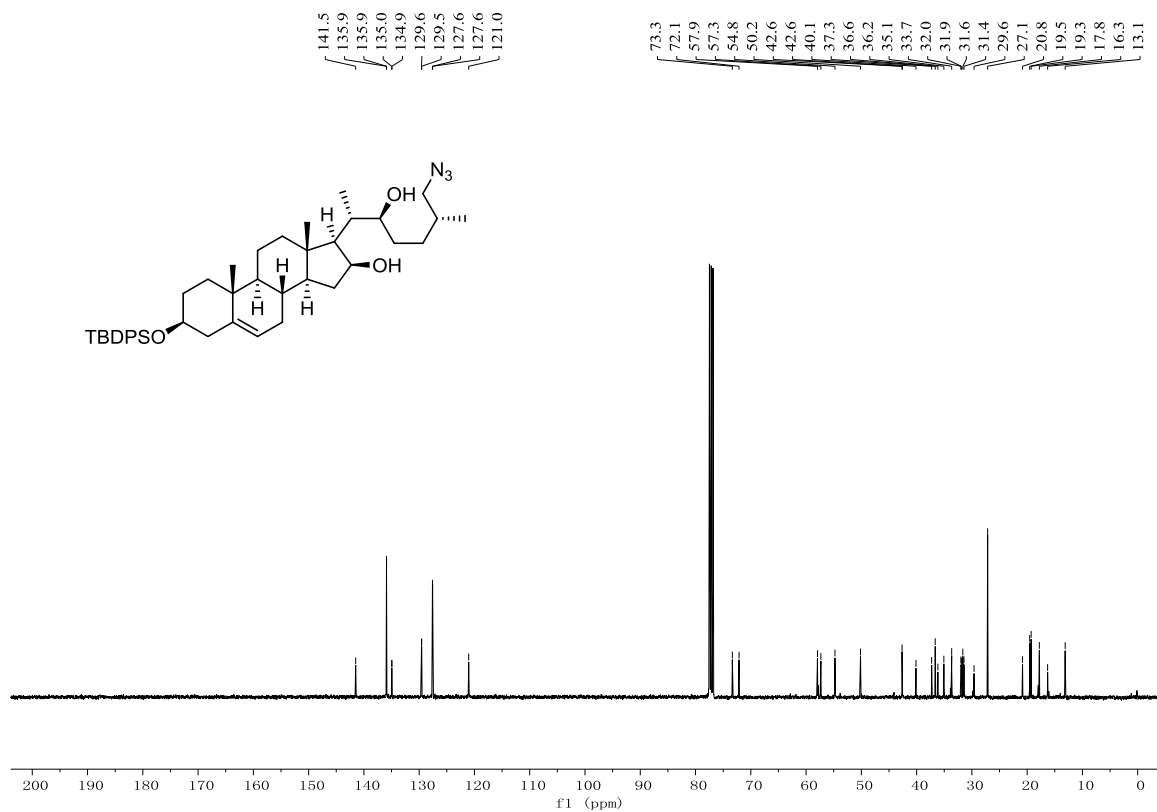


Figure S31. ^1H NMR Spectrum of **2** (400 MHz, CDCl_3)

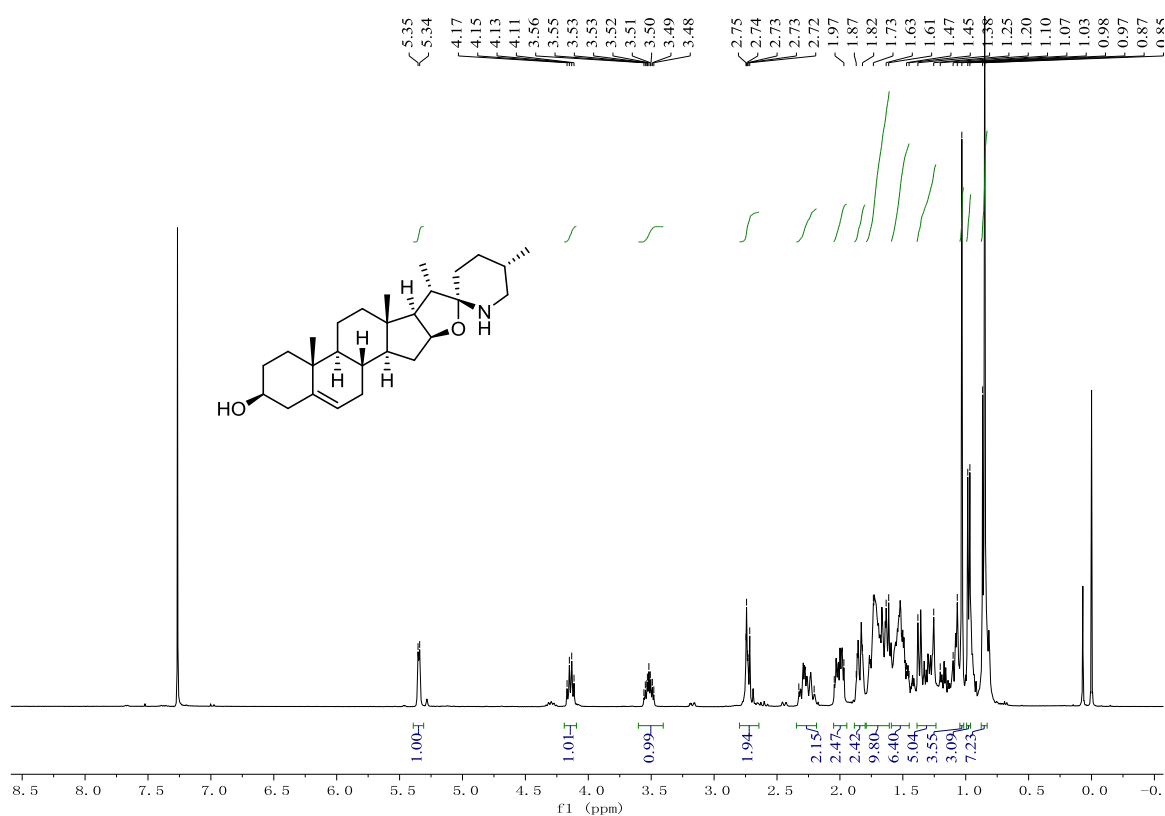


Figure S32. ^{13}C NMR Spectra of **2** (100 MHz, CDCl_3)

