

SUPPORTING INFORMATION

for

Design of an Aryne-Platform for the Synthesis of Heterocyclic Allocolchicinoids

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(5*S*,11*aR*)-5-(*N*-(*tert*-Butoxycarbonyl)acetamido)-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene-3-yl trifluoromethanesulfonate (6)

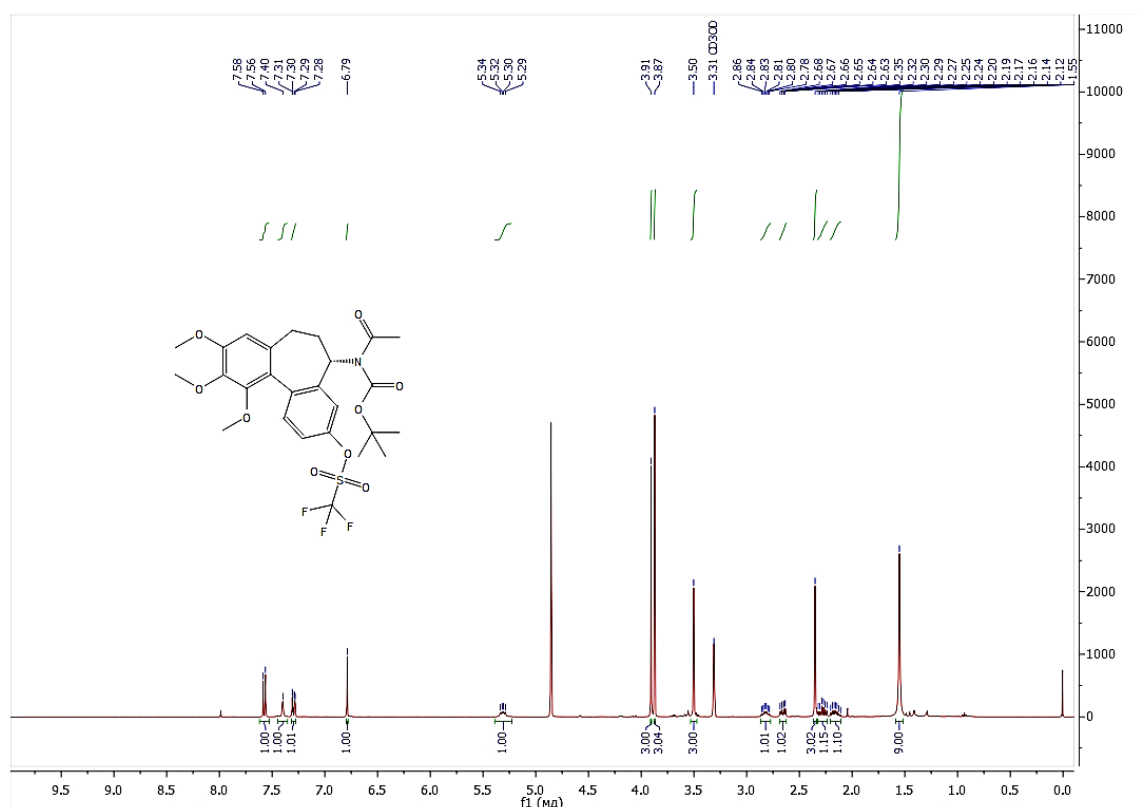


Figure S1. ¹H NMR (400 MHz, CD₃OD) spectrum of compound 6

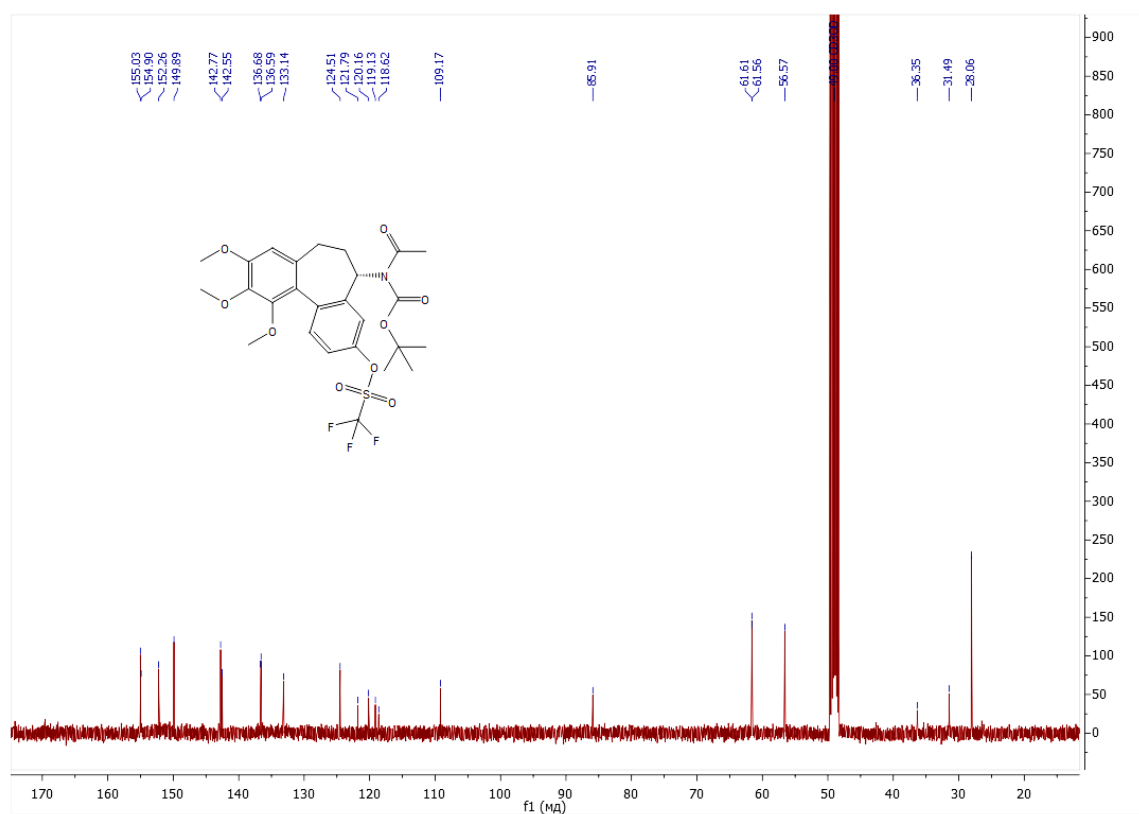


Figure S2. ¹³C NMR (400 MHz, CD₃OD) spectrum of compound 6

(5*S*,11*aR*)-5-Acetamido-2-iodo-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cycloheptene-3-yl trifluoromethanesulfonate (7a**)**

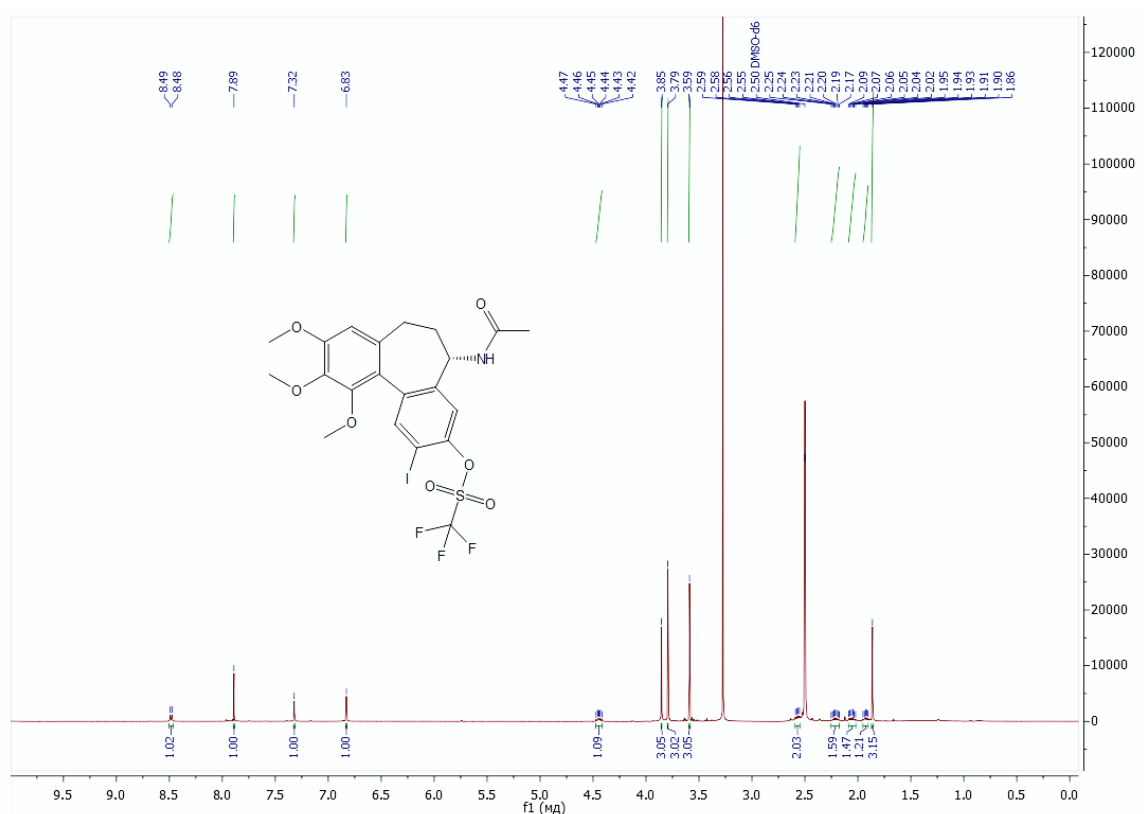


Figure S3. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **7a**

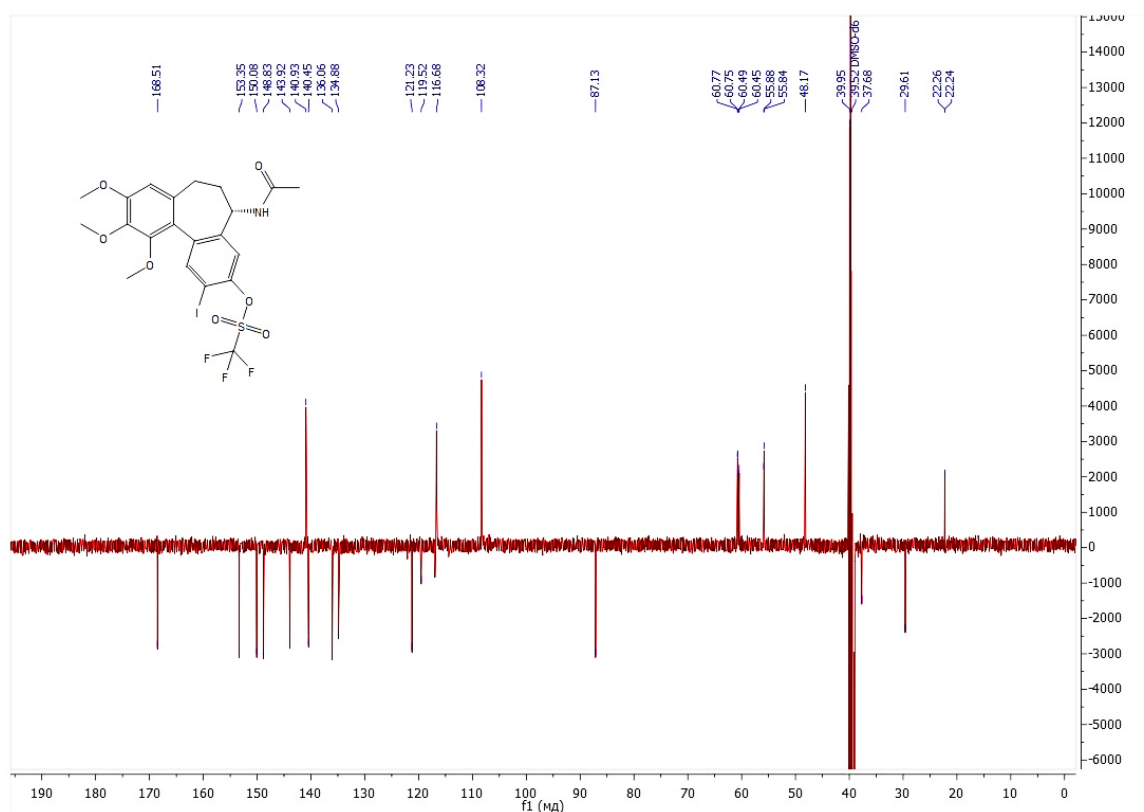


Figure S4. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound **7a**

(5S)-5-Acetamido-2-iodo-9,10,11-trimethoxy-6,7-dihydro-5H-dibenzo[a,c]cyclohepten-3-yl 4-methylbenzenesulfonate (7b)

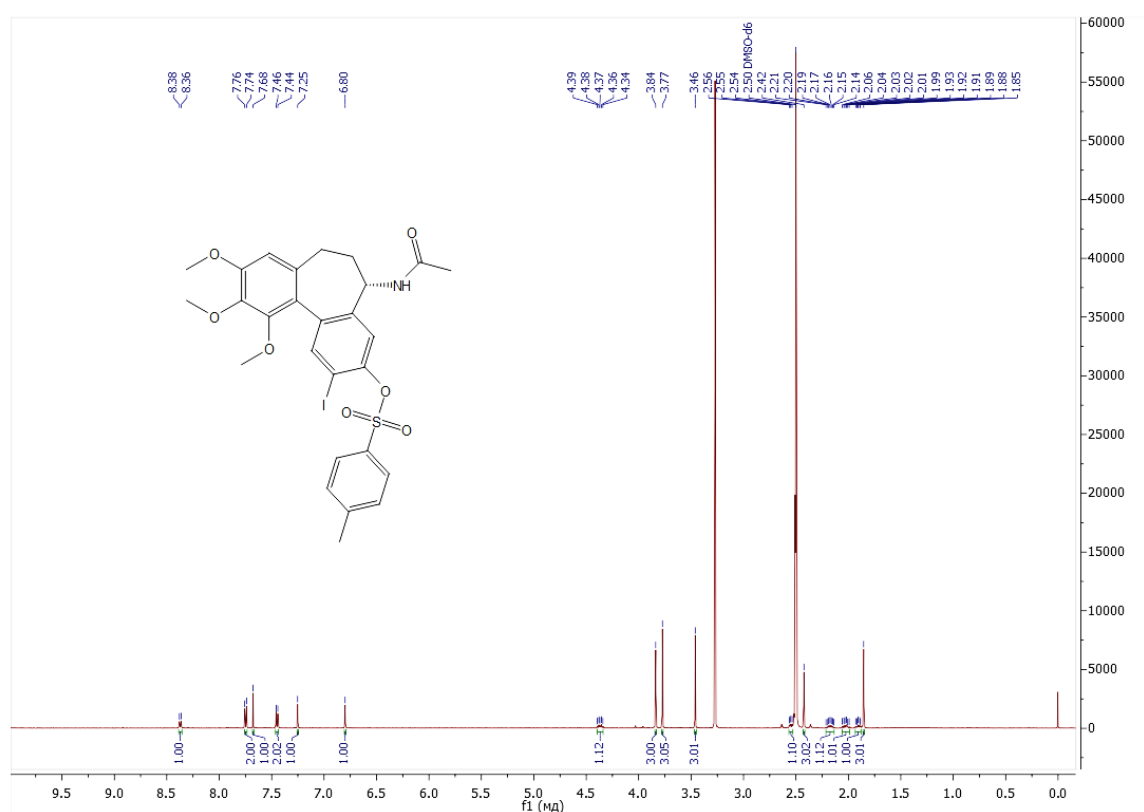


Figure S5. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **7b**

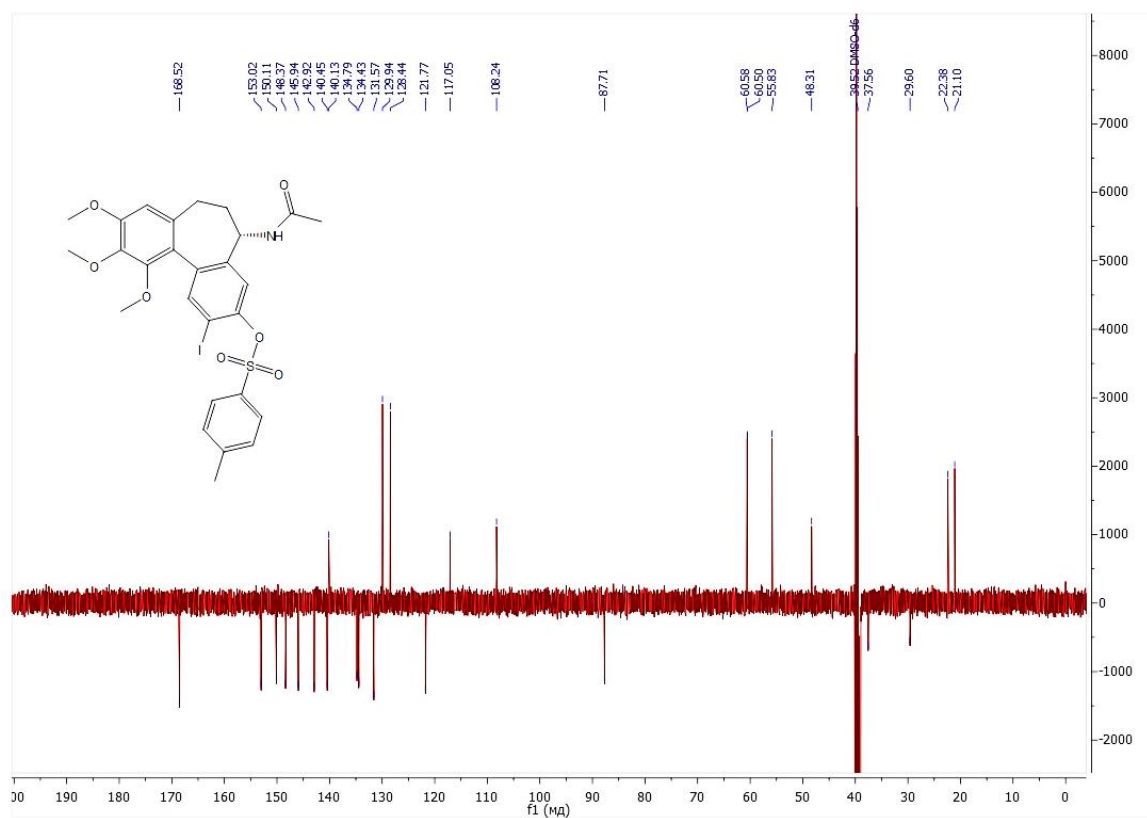


Figure S6. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound **7b**

***N*-((7*S*,13*bR*)-1,2,3,9-Tetramethoxy-6,7,9,12-tetrahydro-5*H*-9,12-epoxybenzo[3,4]cyclohepta[1,2-*b*]naphthalen-7-yl)acetamide (8')** and ***N*-((7*S*,13*bR*)-1,2,3,12-tetramethoxy-6,7,9,12-tetrahydro-5*H*-9,12-epoxybenzo[3,4]cyclohepta[1,2-*b*]naphthalen-7-yl)acetamide (8'')** isomers

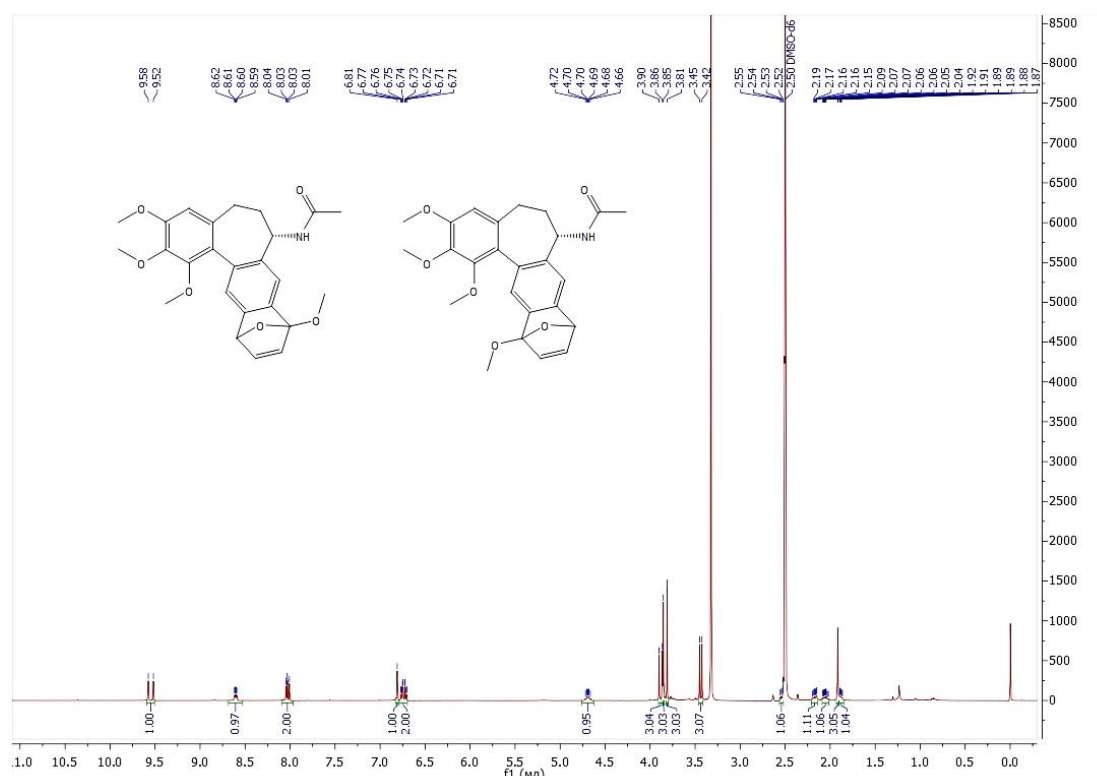


Figure S7. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) spectrum of compounds **8**

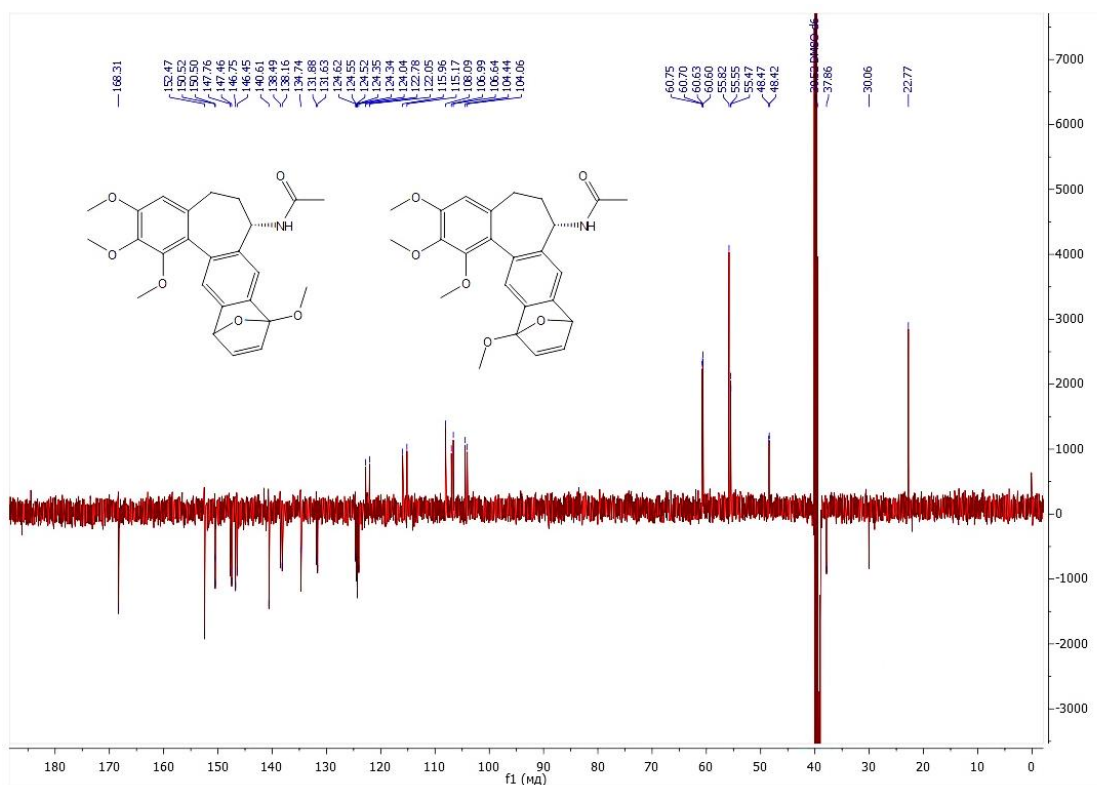


Figure S8. ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) spectrum of compounds **8**

***N*-((5*S*)-3-Hydroxy-2-iodo-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)-2-(trimethylsilyl)acetamide (10)**

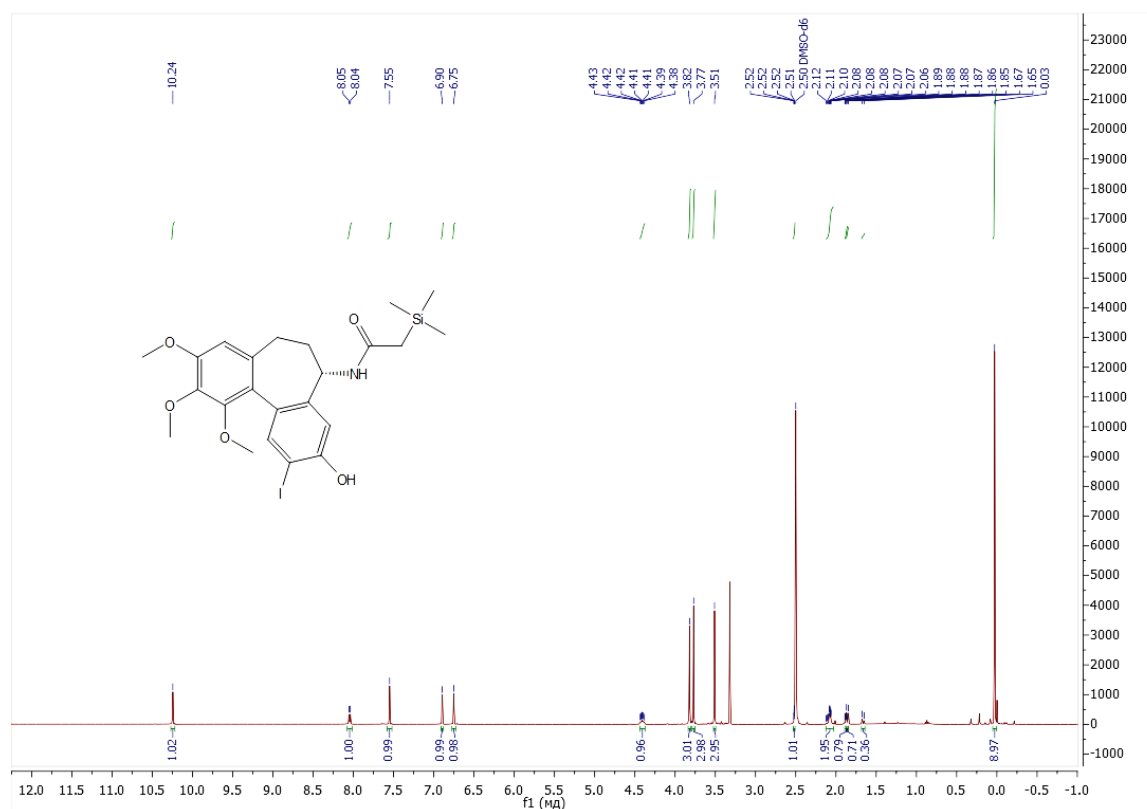


Figure S9. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) spectrum of compound **10**

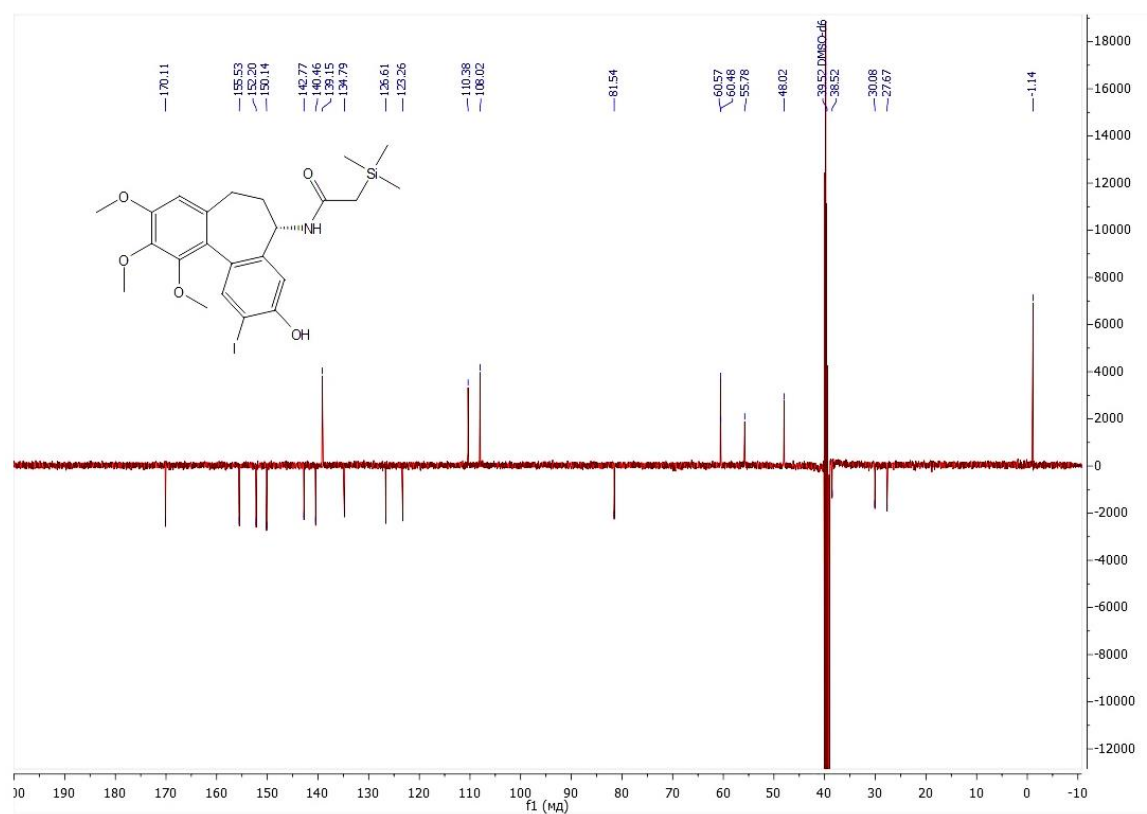


Figure S10. ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) spectrum of compound **10**

***N*-((5*S*,11*aR*)-2-iodo-9,10,11-trimethoxy-3-((triethylsilyl)oxy)-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)acetamide (**11**)**

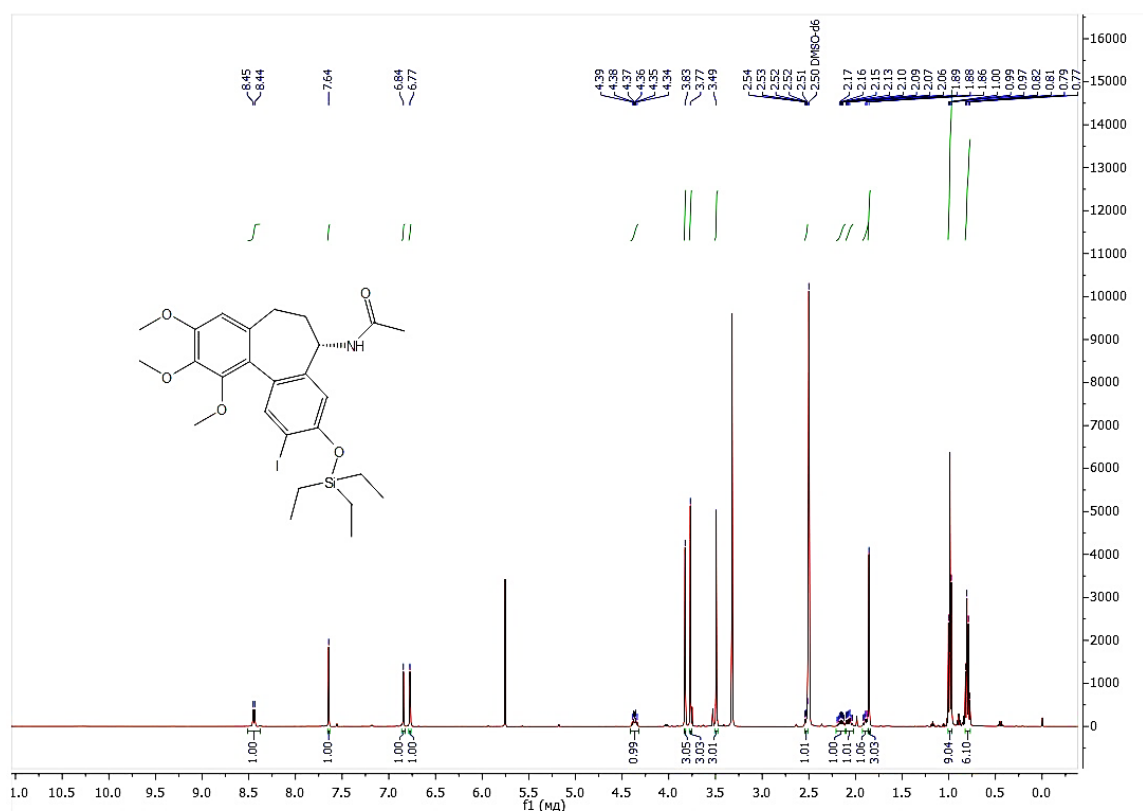


Figure S11. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **11**

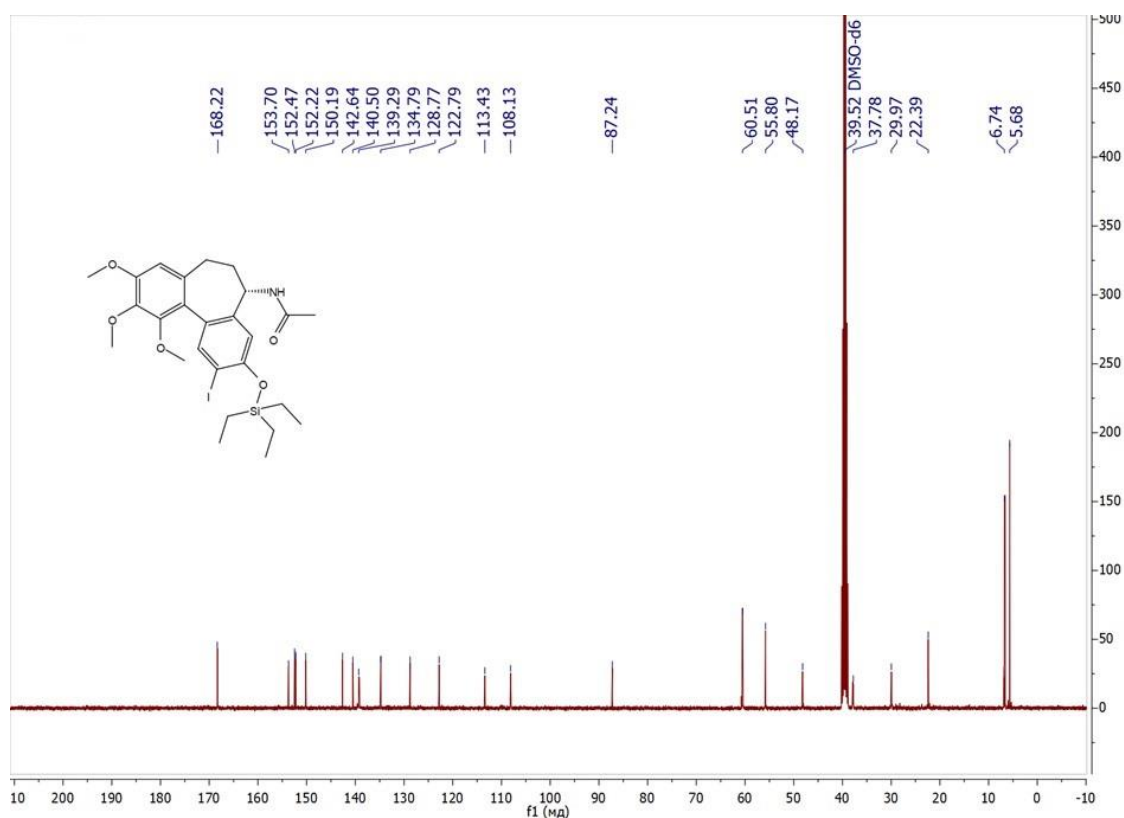


Figure S12. ¹³C NMR (400 MHz, DMSO-*d*₆) spectrum of compound **11**

***N*-((5*S*,11*aR*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-iodo-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)acetamide (**12**)**

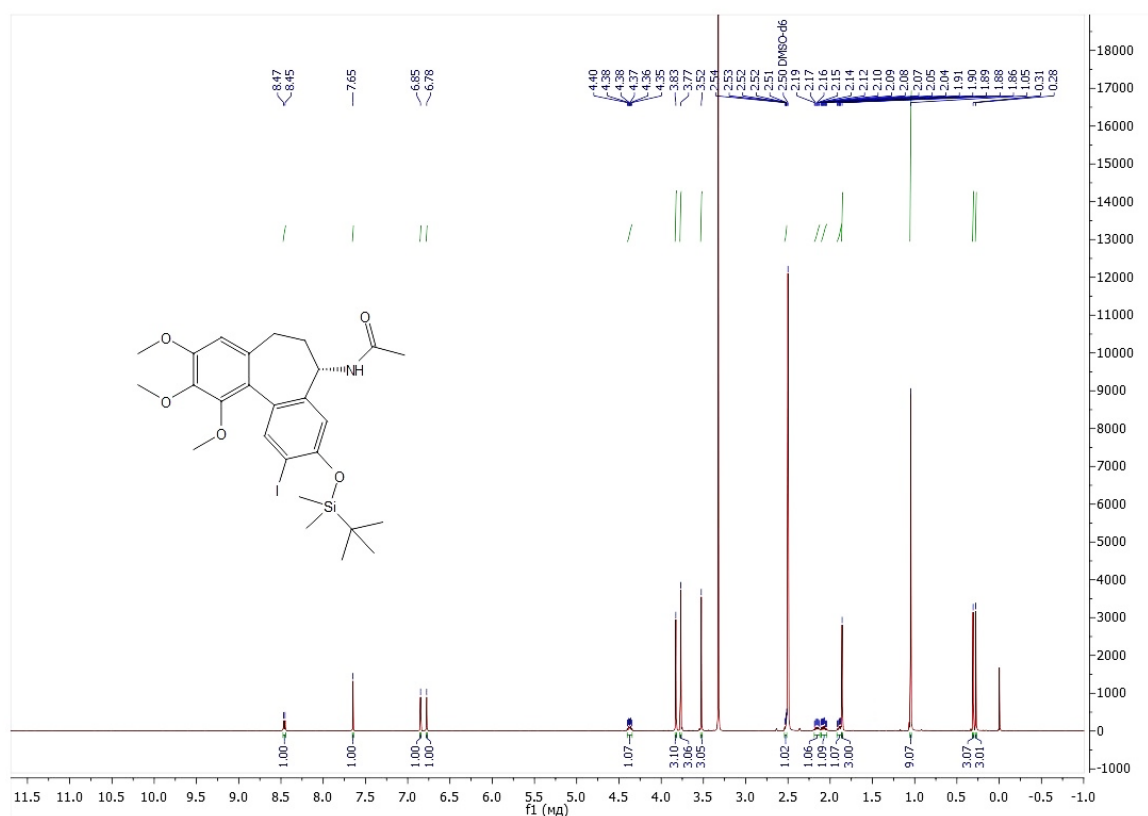


Figure S13. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **12**

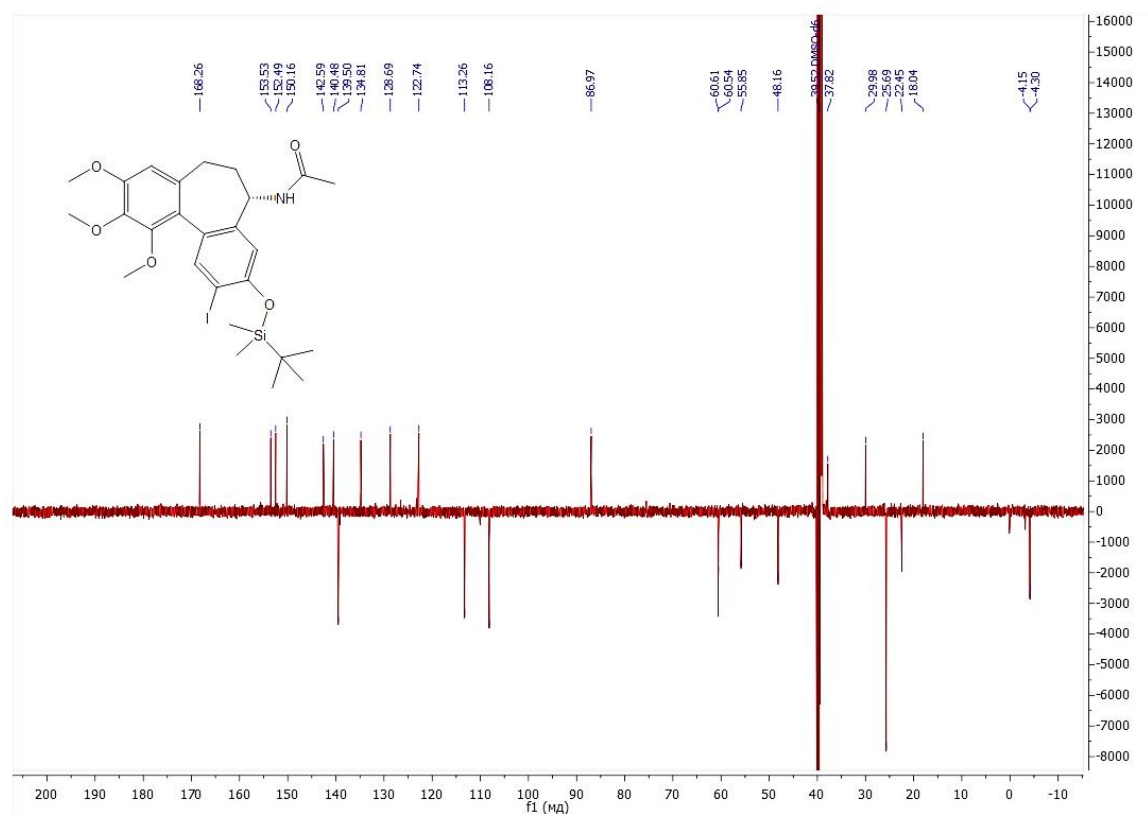


Figure S14. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound **12**

***N*-((5*S*,11*aR*)-3-Hydroxy-2-iodo-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)-*N*-(triethylsilyl)acetamide (**13**)**

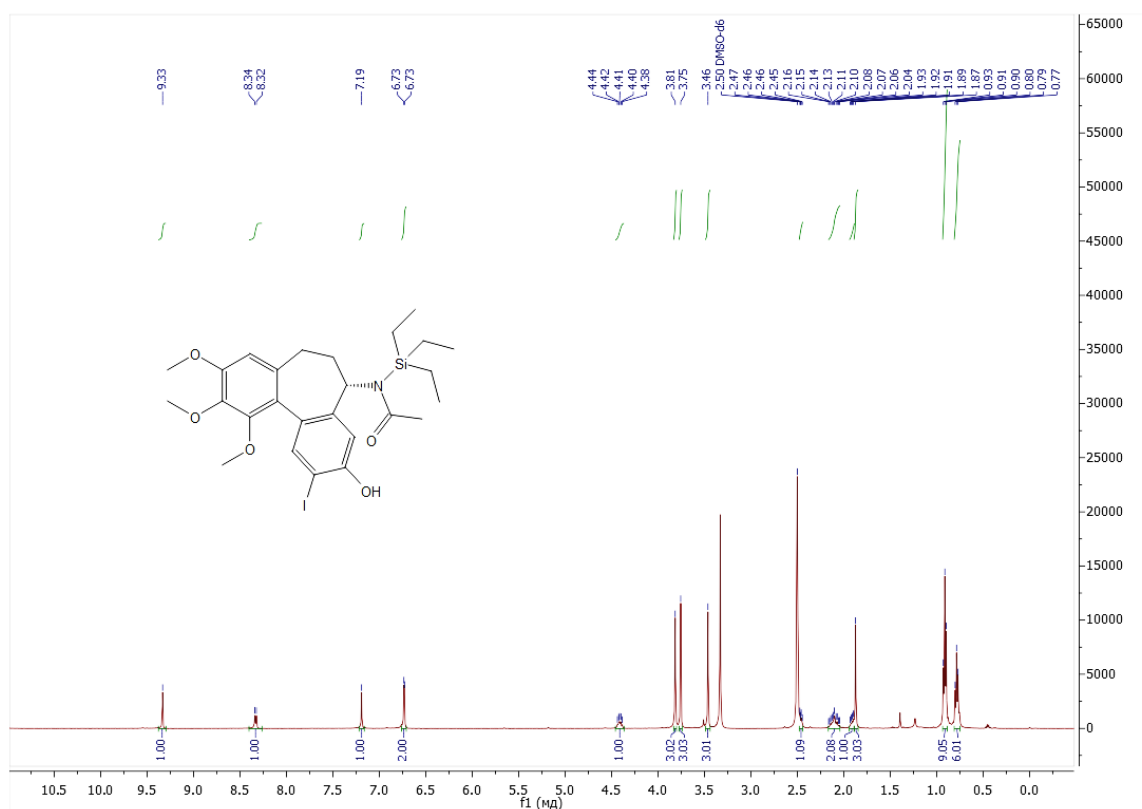


Figure S15. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **13**

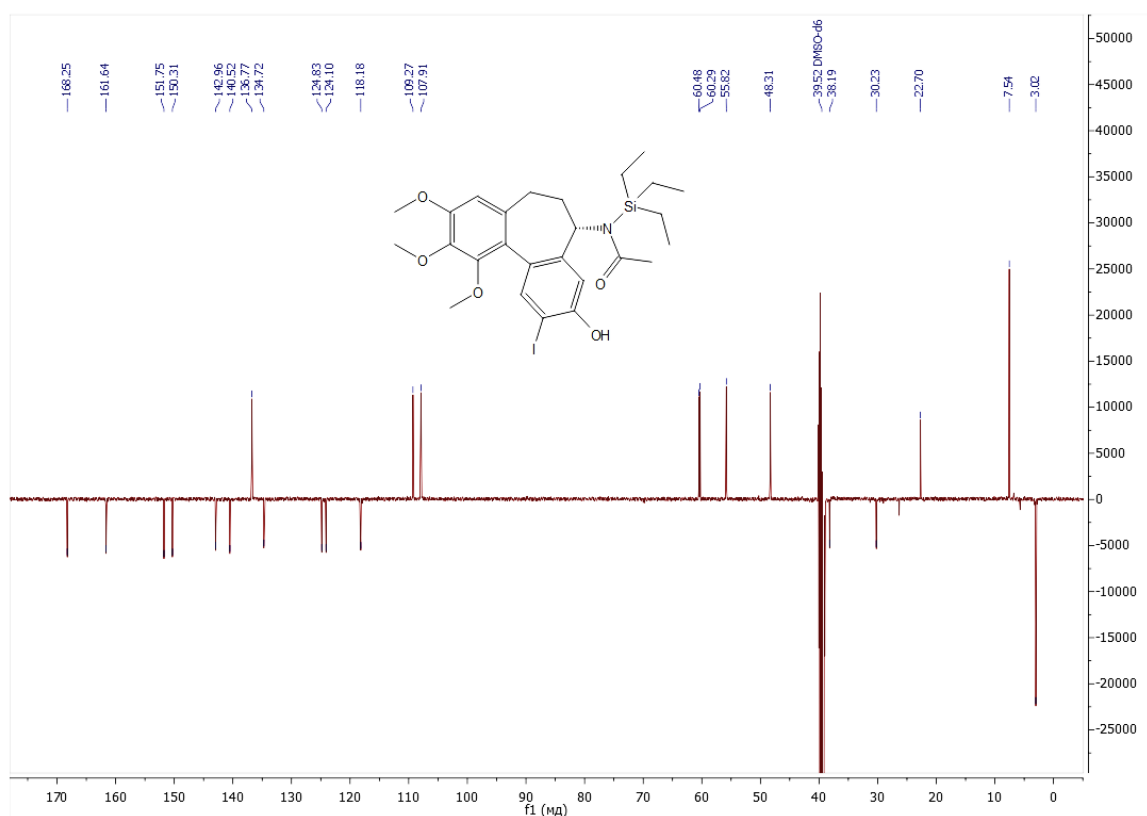


Figure S16. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound **13**

***N*-((5*S*,11*aR*)-2-(*tert*-Butyldimethylsilyl)-3-hydroxy-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)acetamide (**14**)**

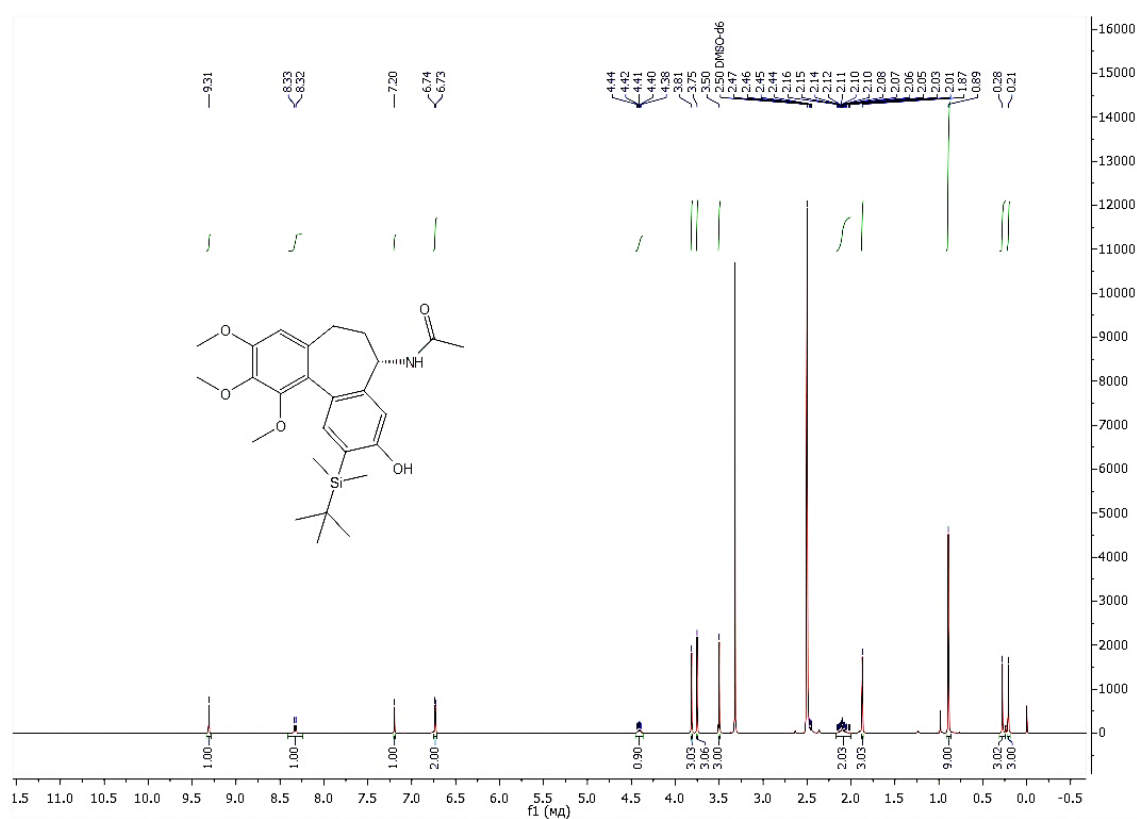


Figure S17. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) spectrum of compound **14**

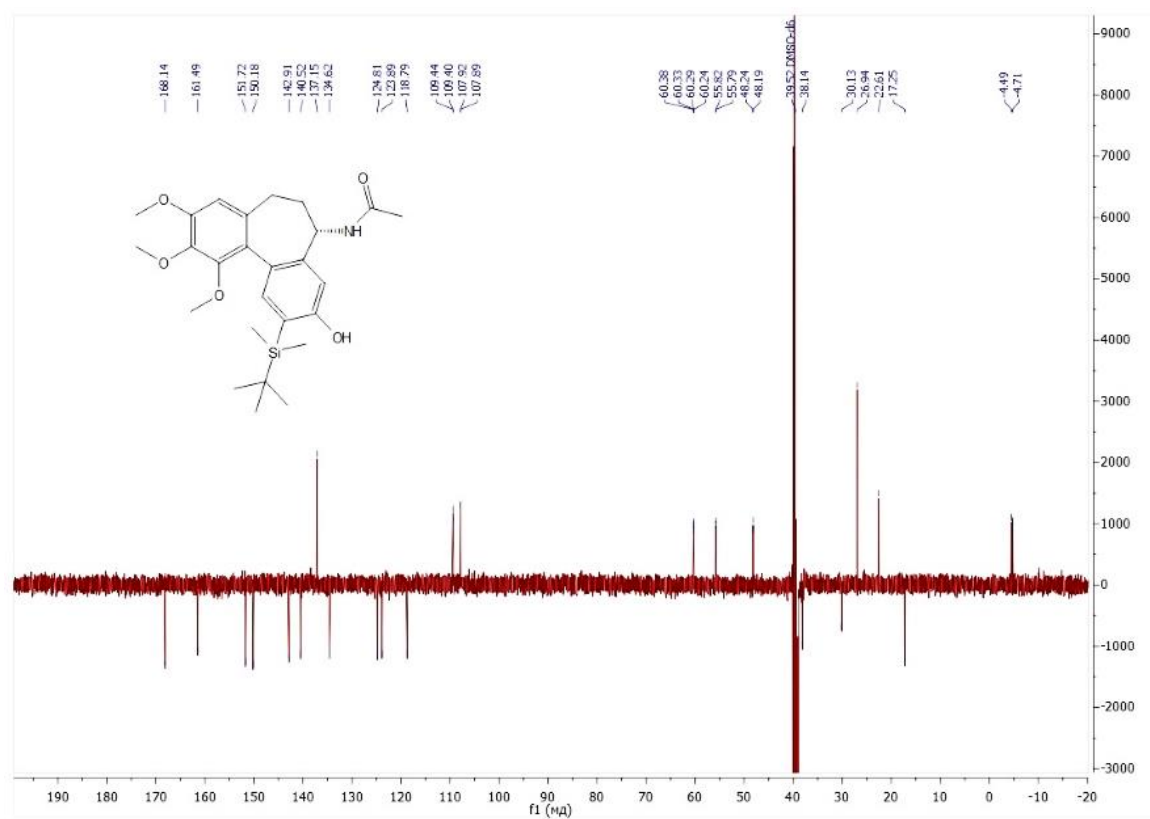


Figure S18. ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) spectrum of compound **14**

(5*S*,11*aR*)-5-Acetamido-2-(*tert*-butyldimethylsilyl)-9,10,11-trimethoxy-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-3-yl trifluoromethanesulfonate (15**)**

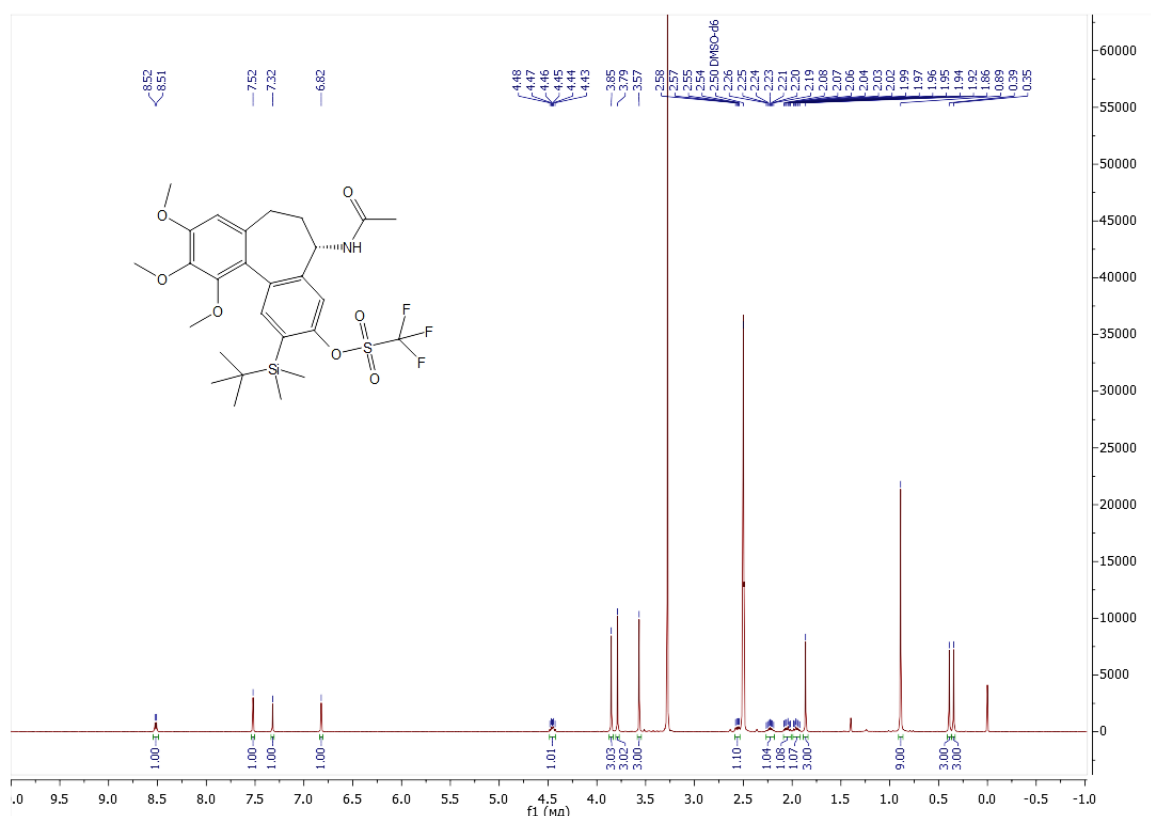


Figure S19. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) spectrum of compound **15**

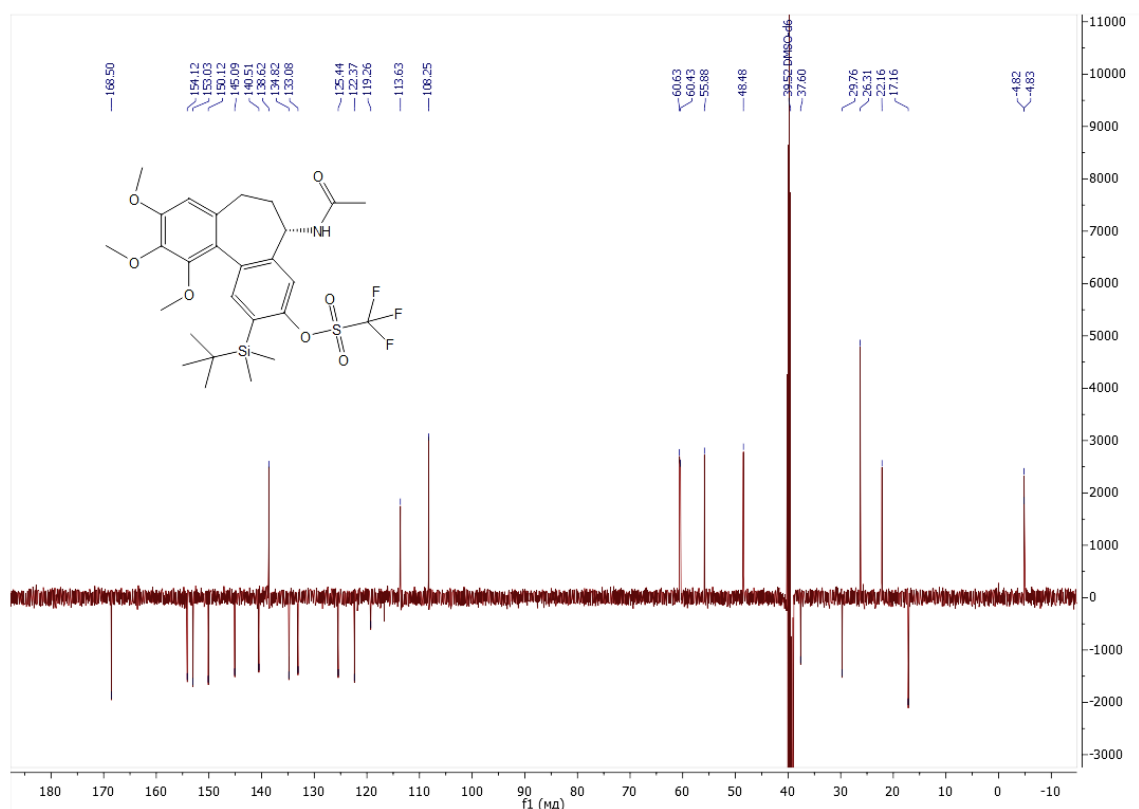


Figure S20. ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) spectrum of compound **15**

***N*-((7*S*)-9-Benzyl-1,2,3-trimethoxy-5,6,7,9-tetrahydrobenzo[3',4']cyclohepta[1',2':4,5]benzo[1,2-*d*][1,2,3]triazol-7-yl)acetamide (**16**)**

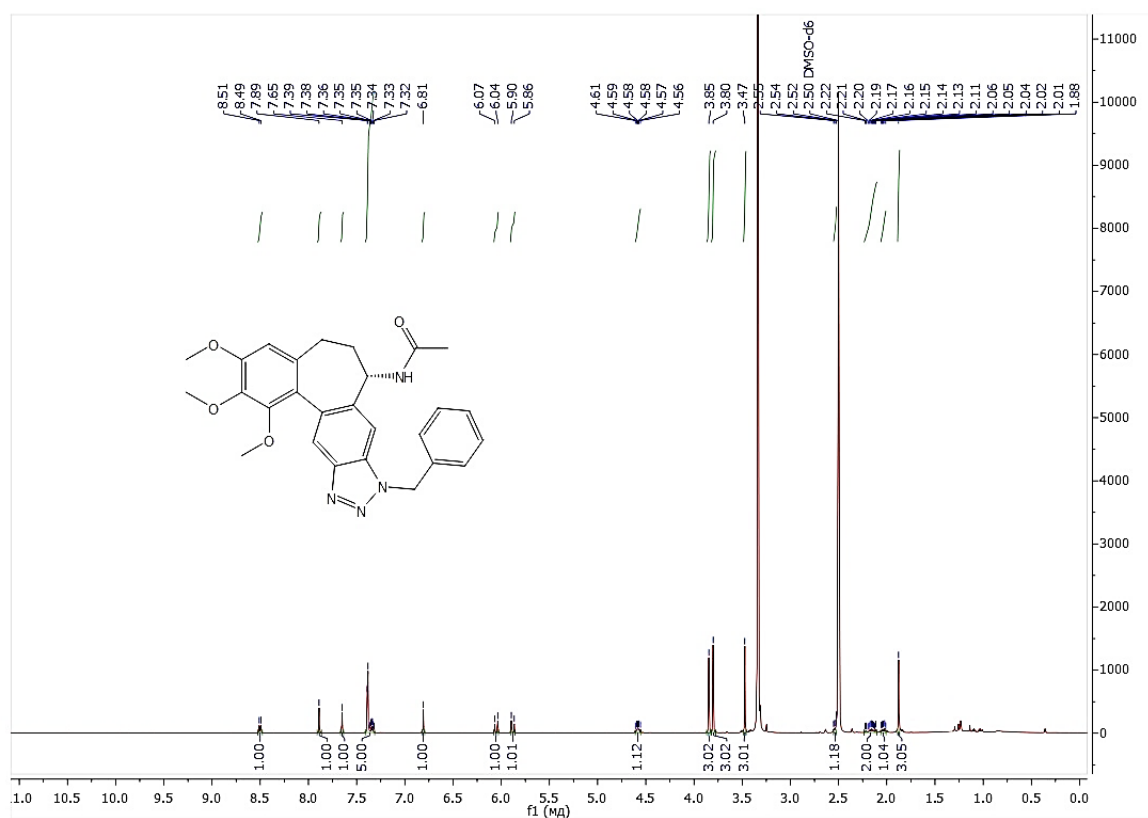


Figure S21. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **16**

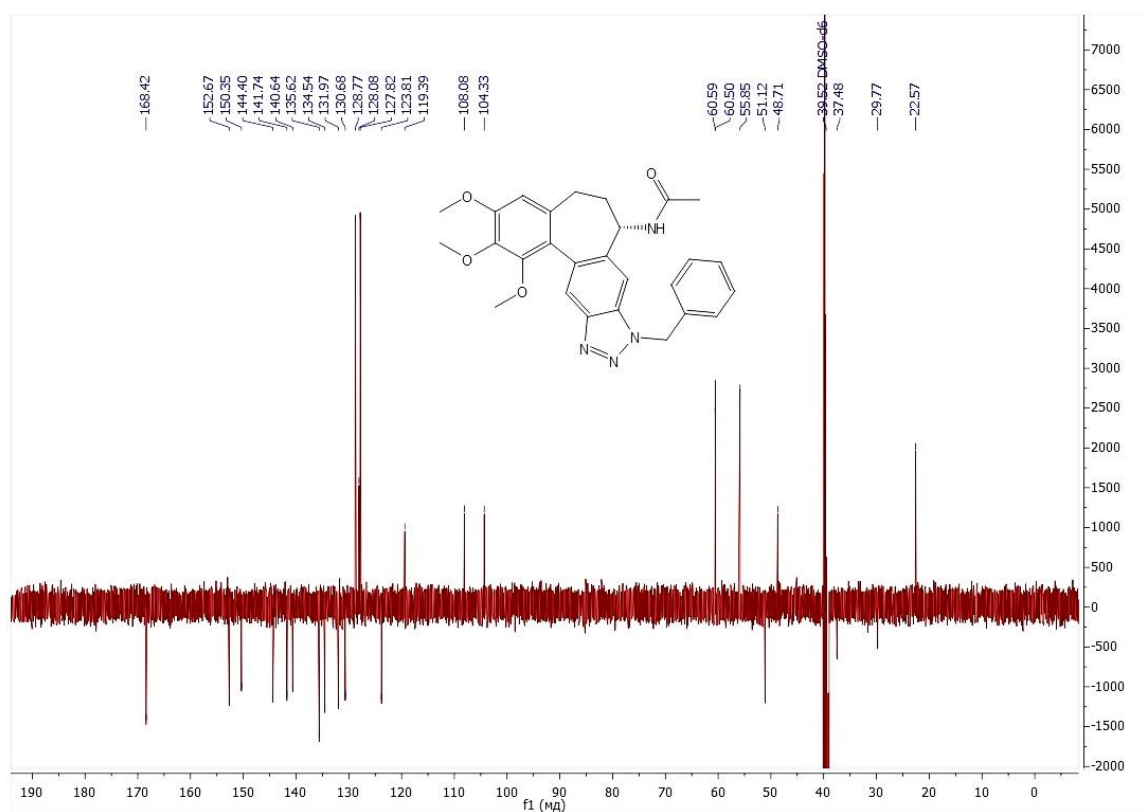


Figure S22. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound **16**

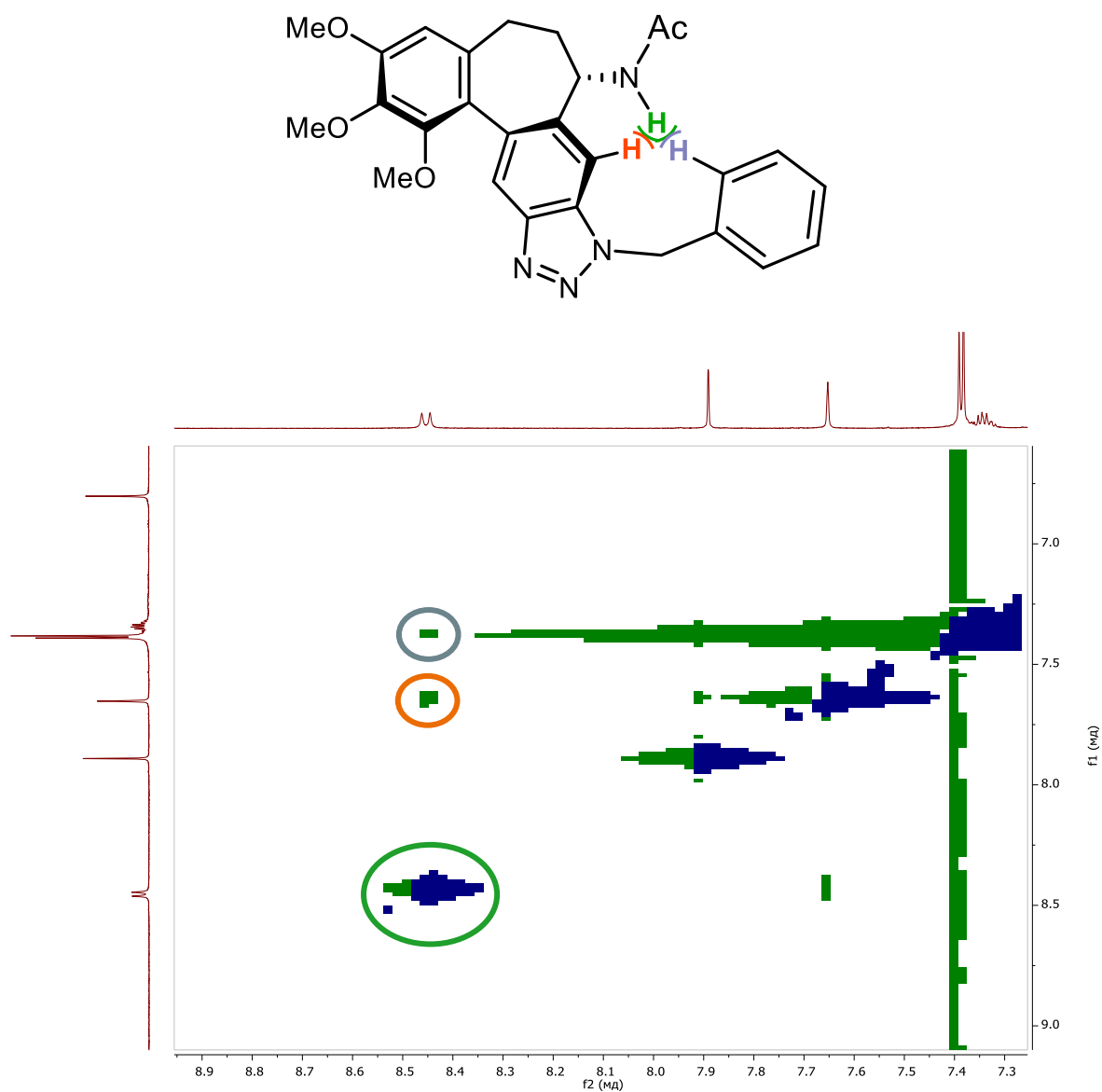


Figure S23. H,H-NOESY NMR (500 MHz, DMSO-*d*₆) spectrum of compound **16**

***N*-((5*S*,11*aR*)-3-Hydroxy-9,10,11-trimethoxy-2-(trimethylsilyl)-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)acetamide (**17**)**

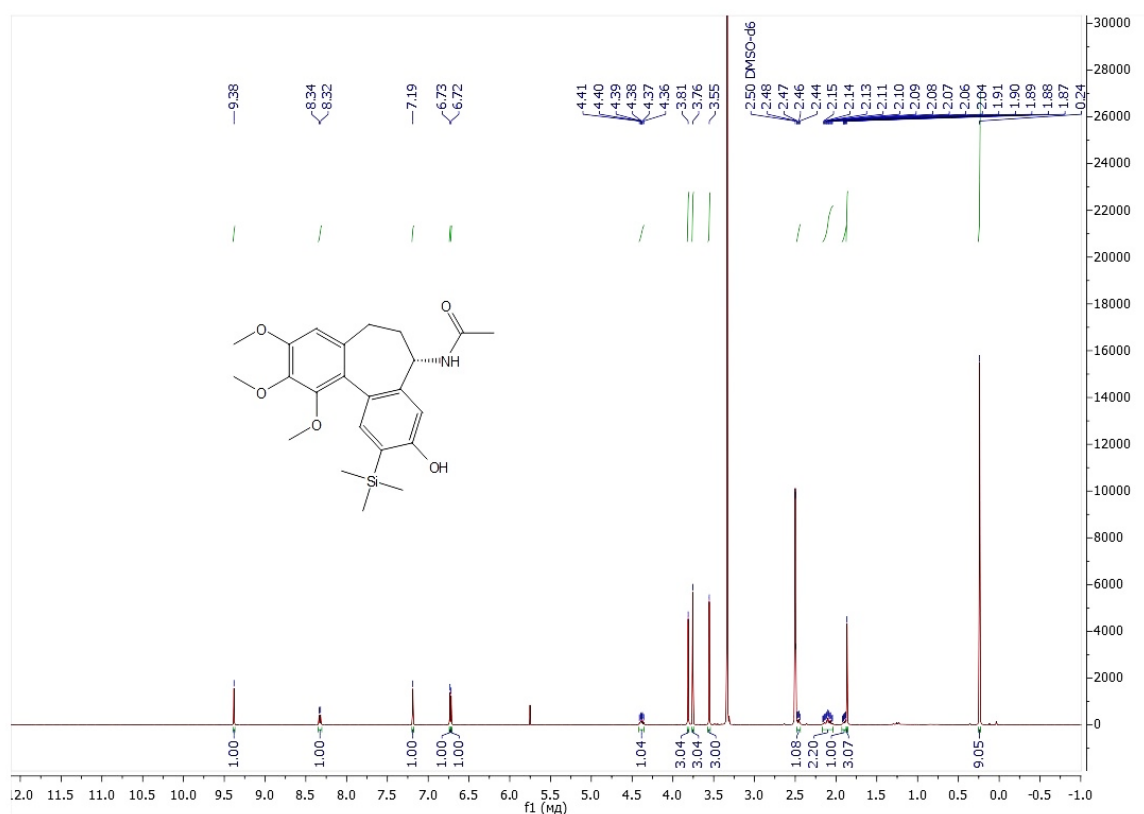


Figure S24. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound **17**

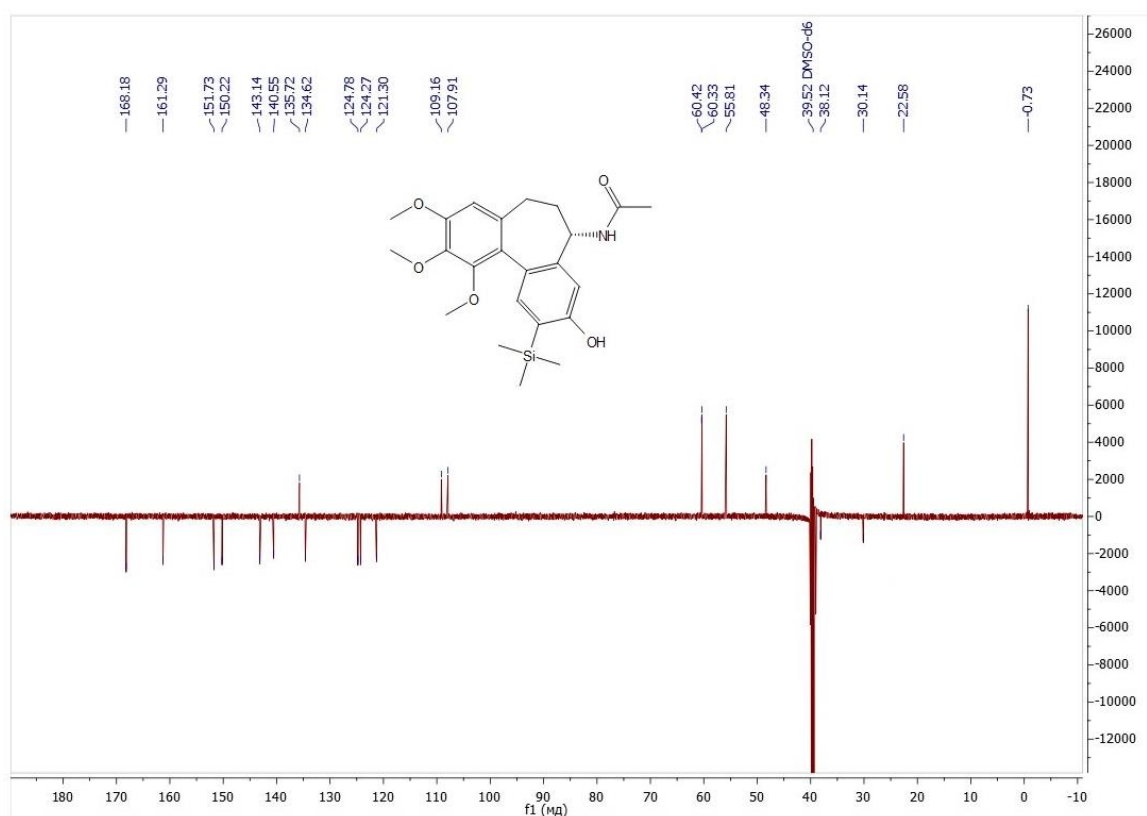


Figure S25. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound **17**

***N*-((5*S*,11*aR*)-9,10,11-Trimethoxy-2-(trimethylsilyl)-3-((trimethylsilyl)oxy)-6,7-dihydro-5*H*-dibenzo[*a,c*]cyclohepten-5-yl)acetamide (18)**

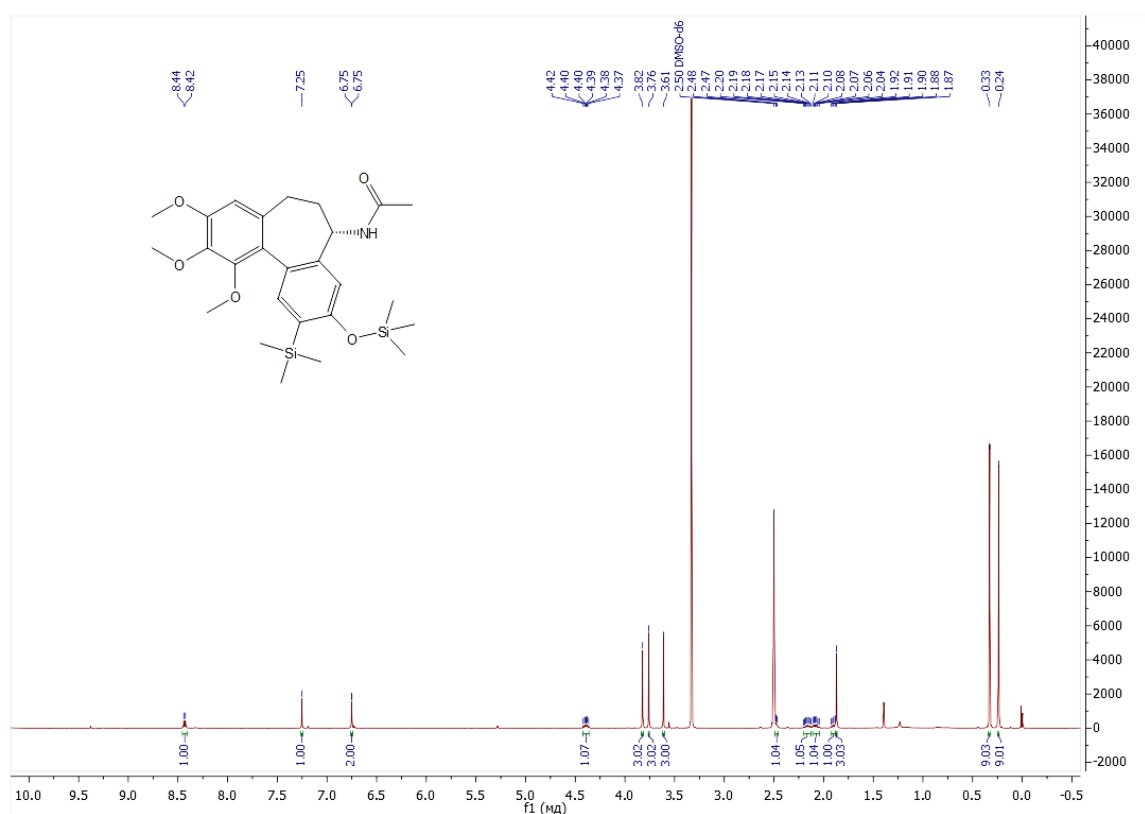


Figure S26. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) spectrum of compound **18**

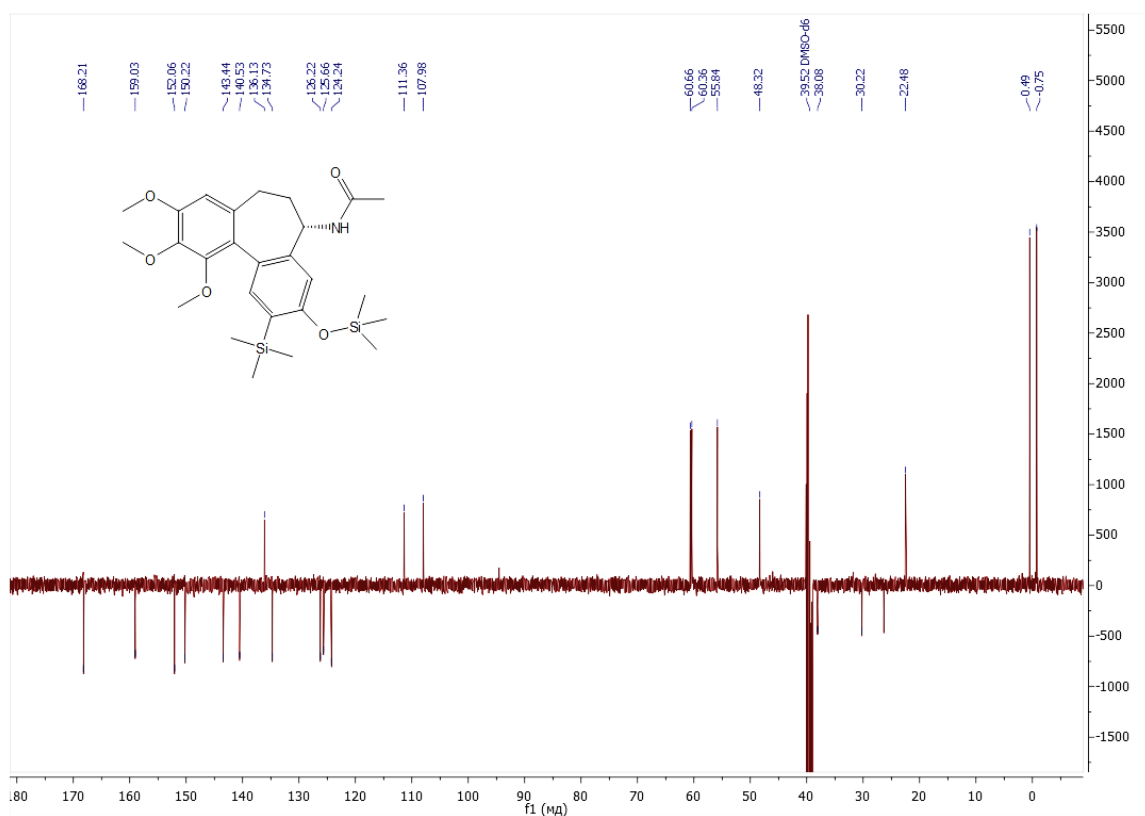


Figure S27. ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) spectrum of compound **18**

***N*-((7*S*,13*bR*)-1,2,3-Trimethoxy-6,7,9,12-tetrahydro-5*H*-9,12-epoxybenzo[3,4]cyclohepta[1,2-*b*]naphthalen-7-yl)acetamide (**19**)**

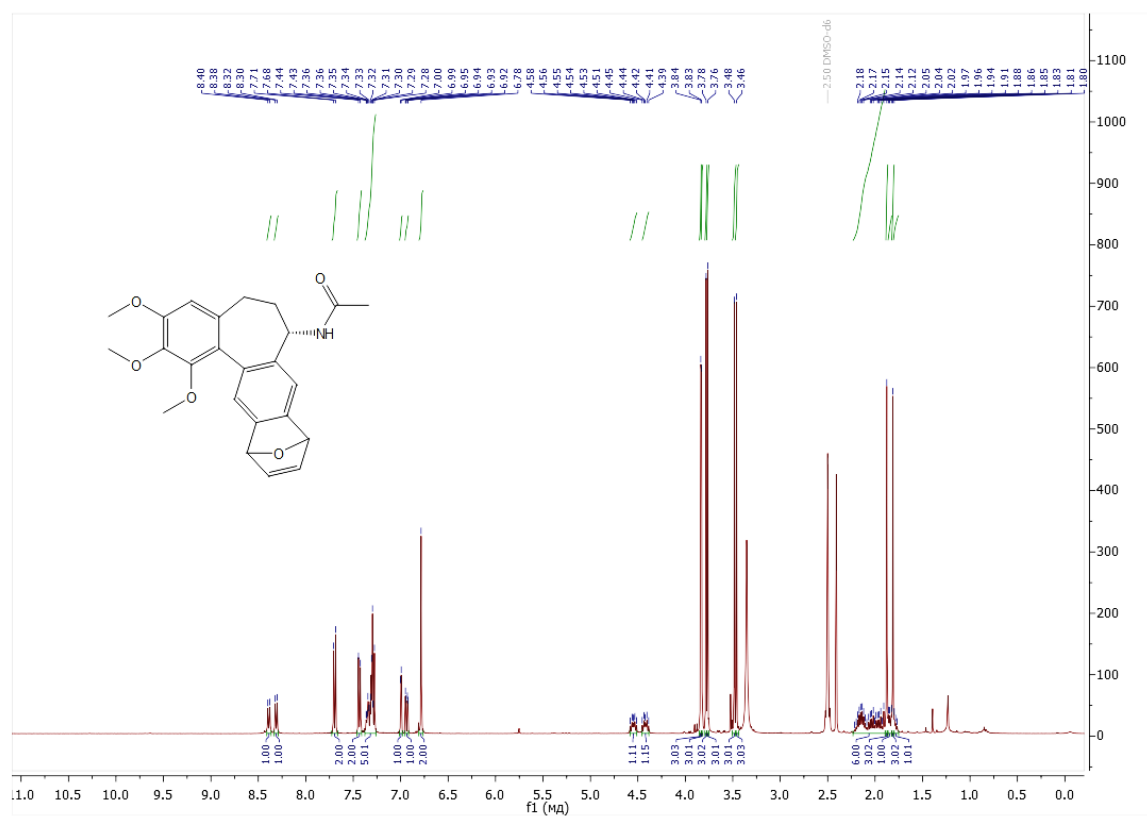


Figure S28. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectrum of compound **19**

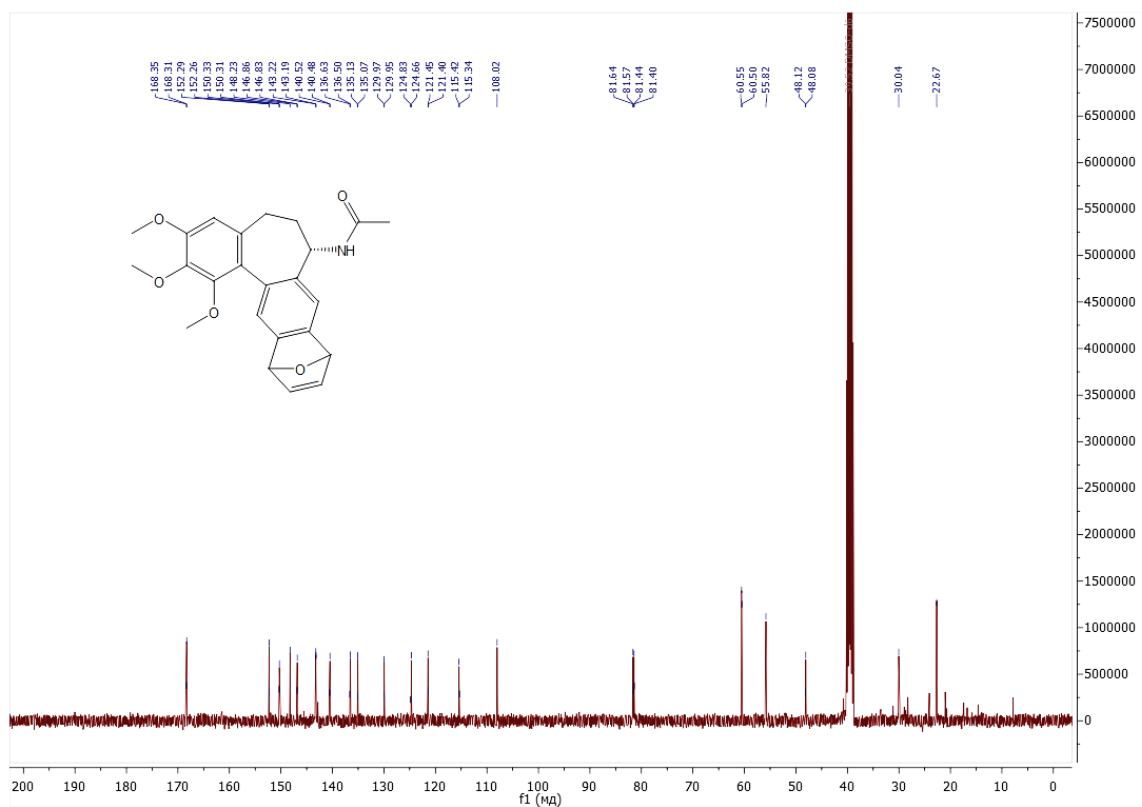


Figure S29. ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) spectrum of compound **19**

***N*-((7*S*,14*bR*)-1,2,3-Trimethoxy-10,13-dimethyl-9-oxo-5,6,7,9,10,11,12,13-octahydrobenzo[3',4']cyclohepta[1',2':4,5]benzo[1,2-*e*][1,4]diazepin-7-yl)acetamide (**20**)**

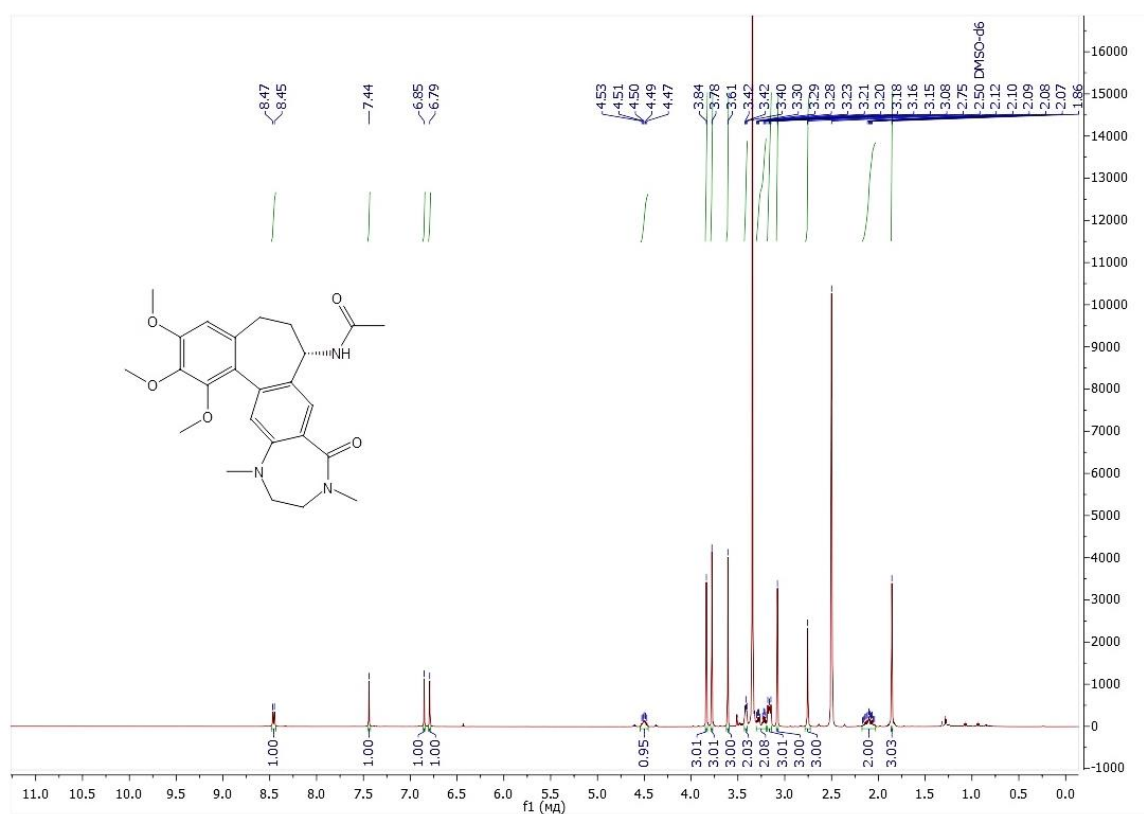


Figure S30. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) spectrum of compound **20**

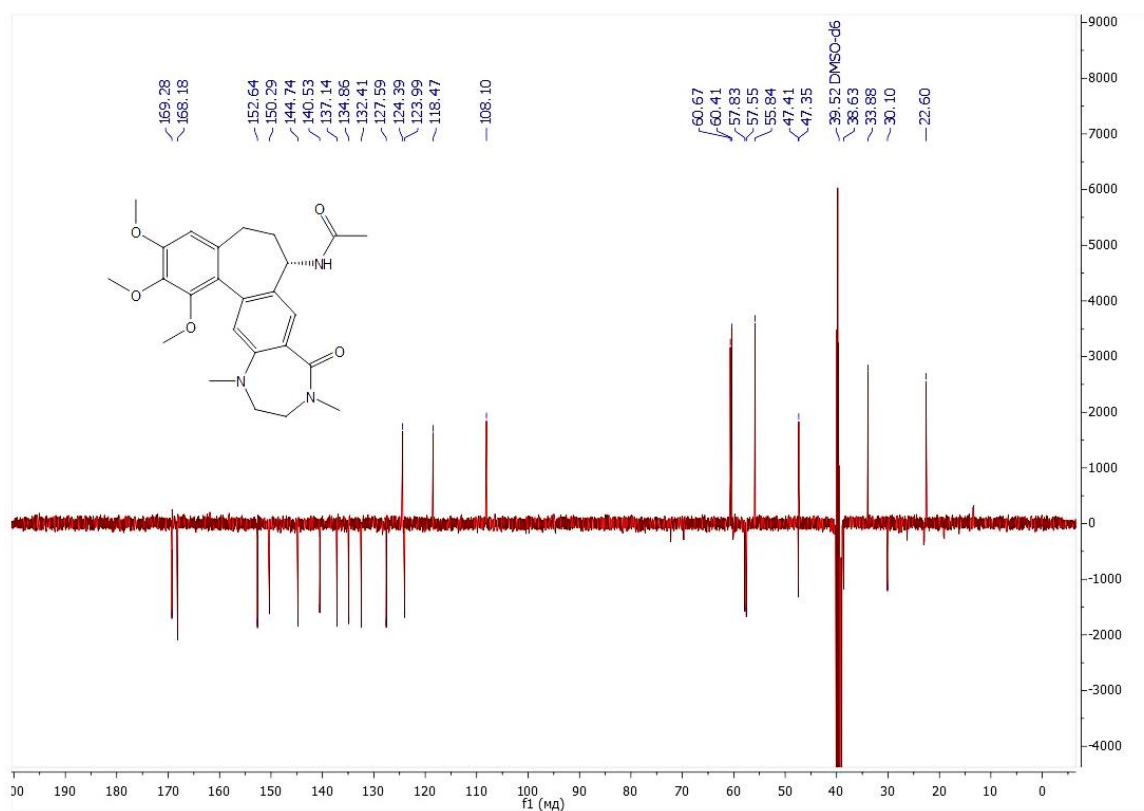


Figure S31. ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) spectrum of compound **20**

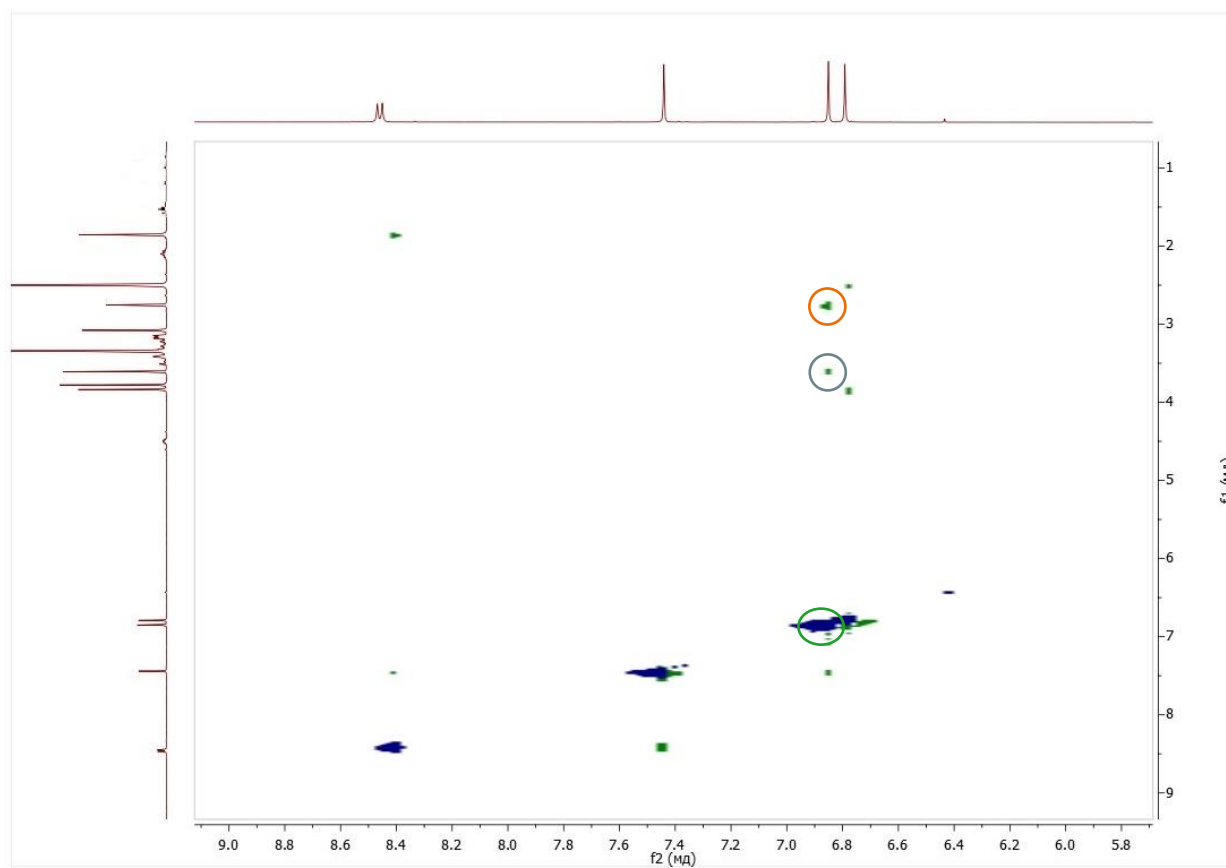
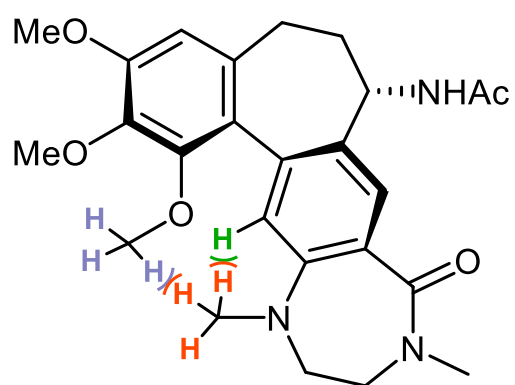


Figure S32. H,H-NOESY NMR (500 MHz, DMSO- d_6) spectrum of compound **20**

Ethyl (7S)-7-acetamido-1,2,3-trimethoxy-5,6,7,11-tetrahydrobenzo[3,4]cyclohepta[1,2-f]indazole-9-carboxylate (21)

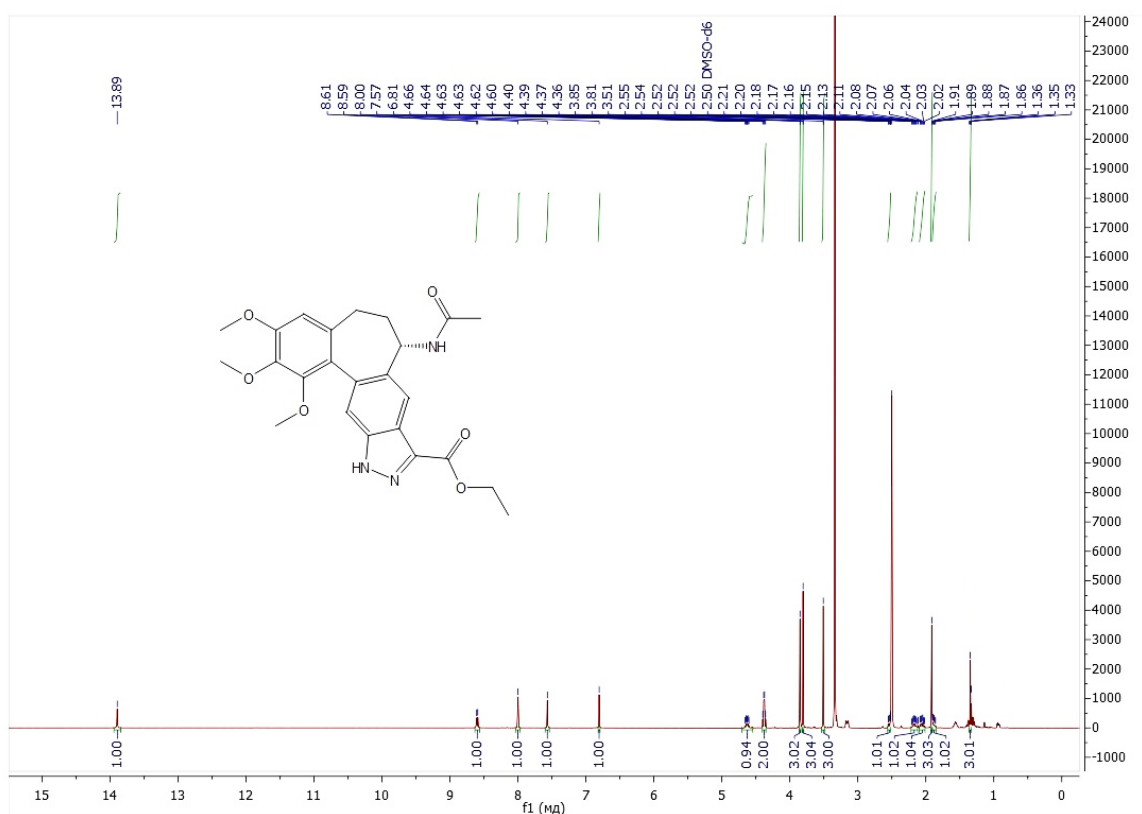


Figure S33. ¹H NMR (500 MHz, DMSO-*d*₆) spectrum of compound 21

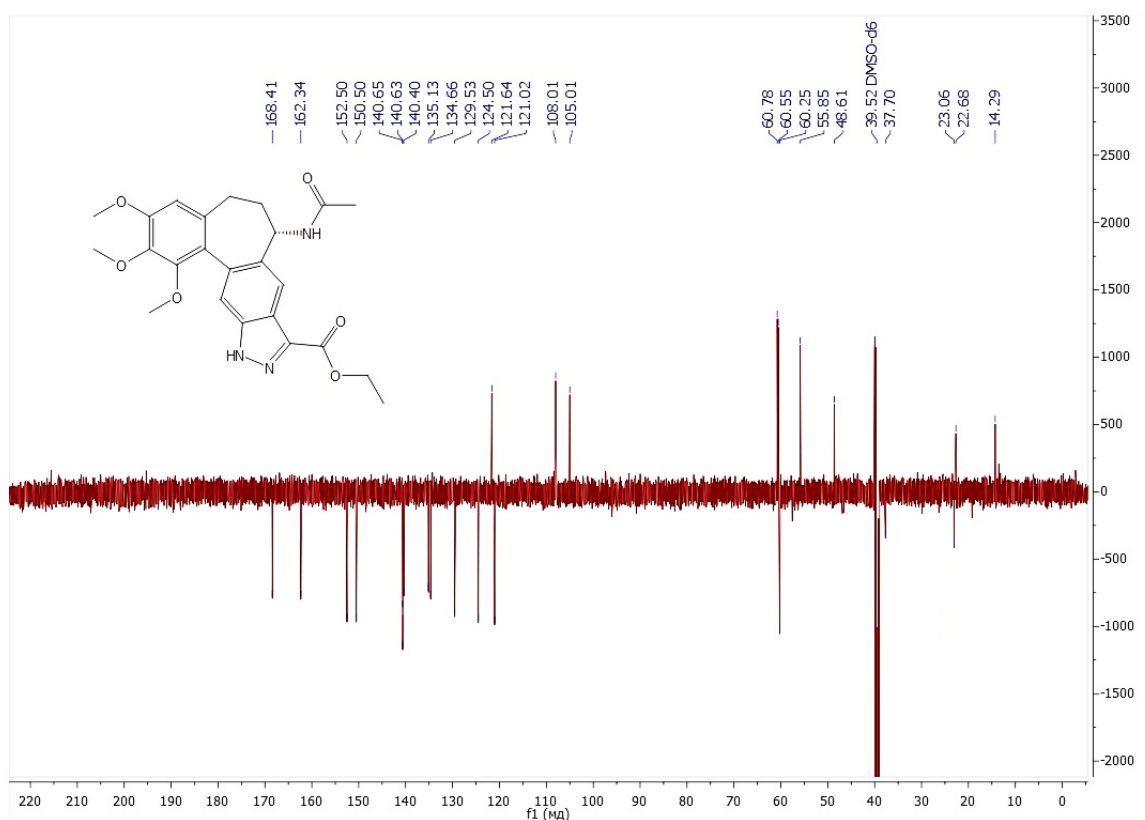


Figure S34. ¹³C NMR (126 MHz, DMSO-*d*₆) spectrum of compound 21

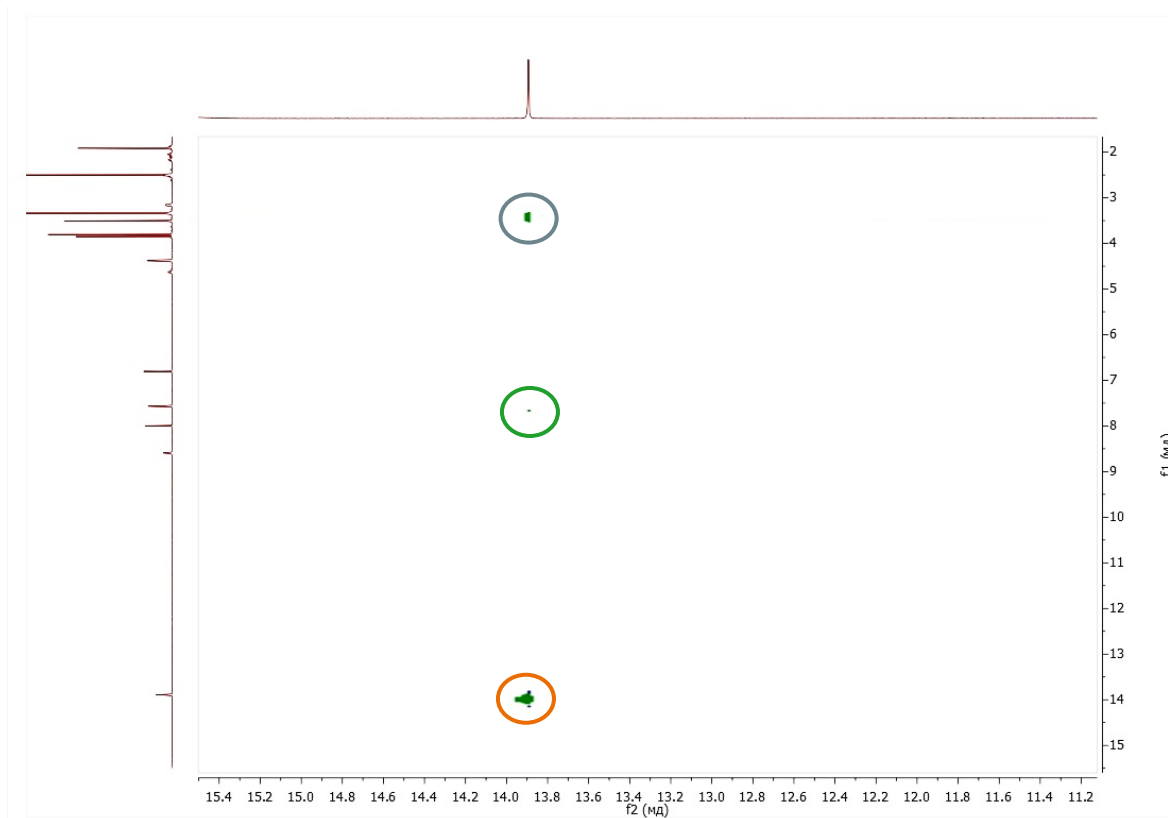
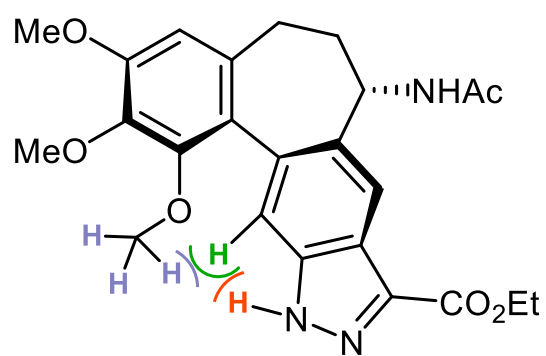


Figure S35. H,H-NOESY NMR (500 MHz, DMSO-*d*₆) spectrum of compound **21**