Supplementary Information

Figure S1. ^{1}H NMR spectrum of Tanjungide A (500 MHz, DMSO-d_6).

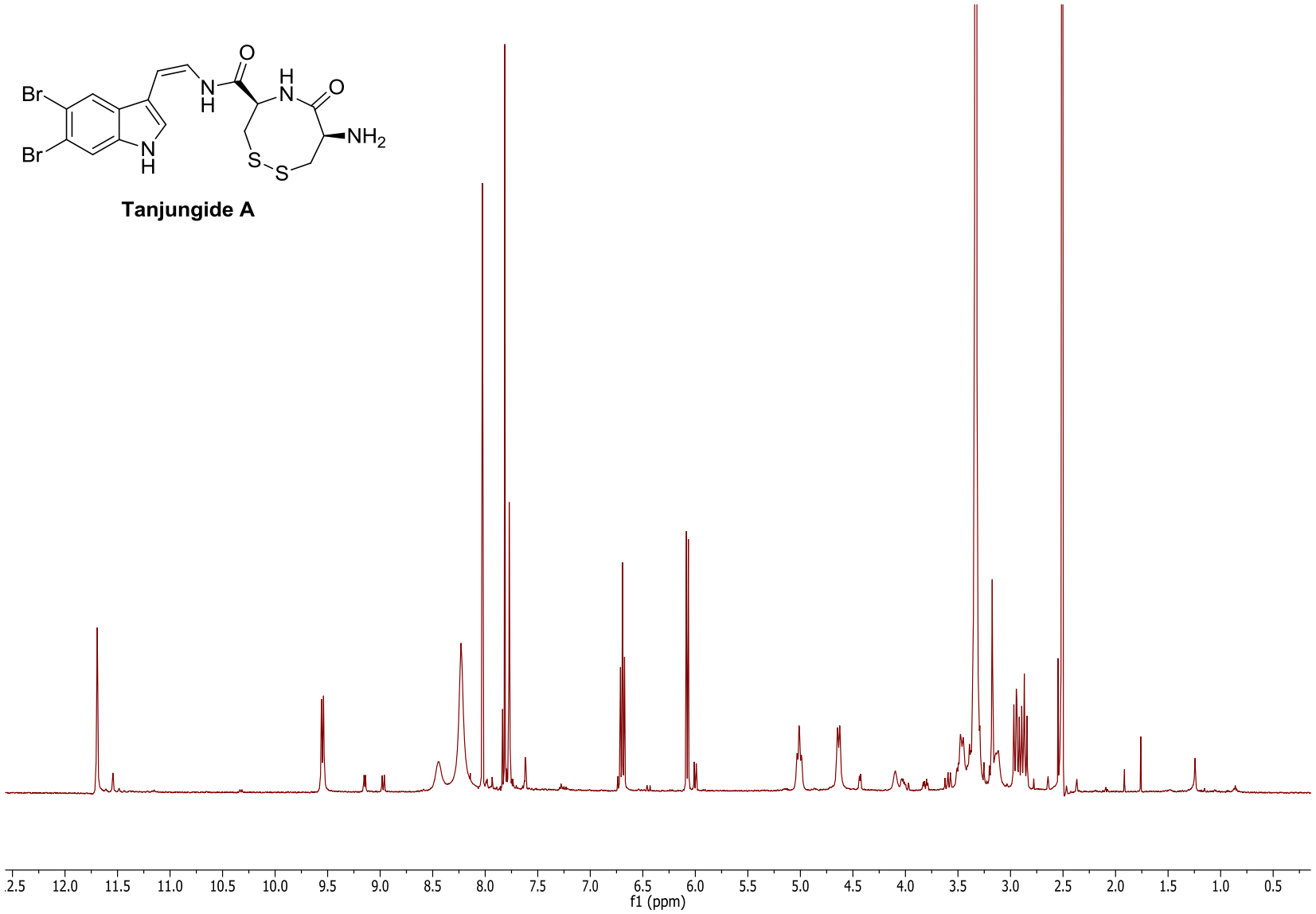


Figure S2. ^{13}C NMR spectrum of Tanjungide A (500 MHz, DMSO-d_6).

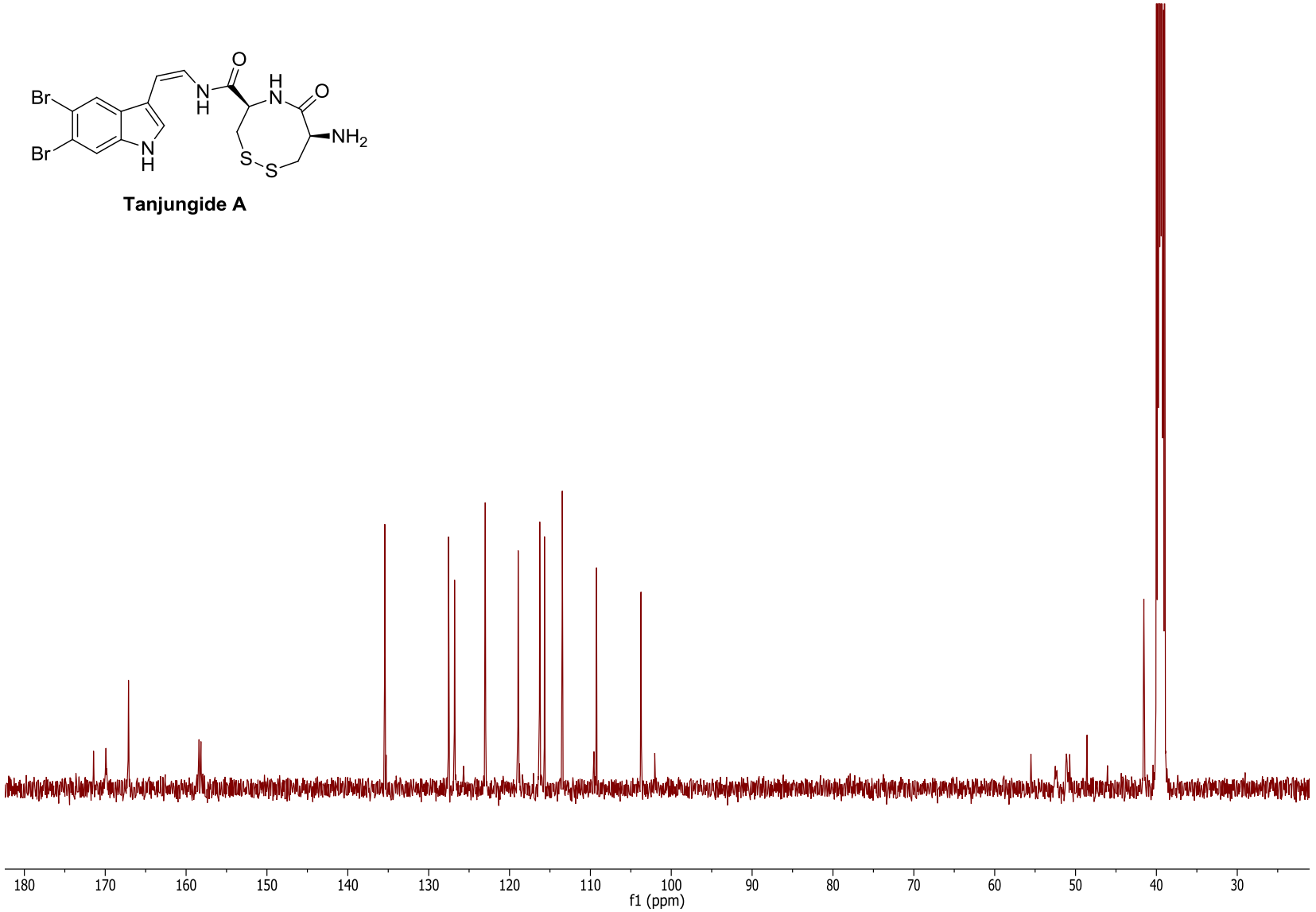


Figure S3. *g*-COSY spectrum of Tanjungide A.

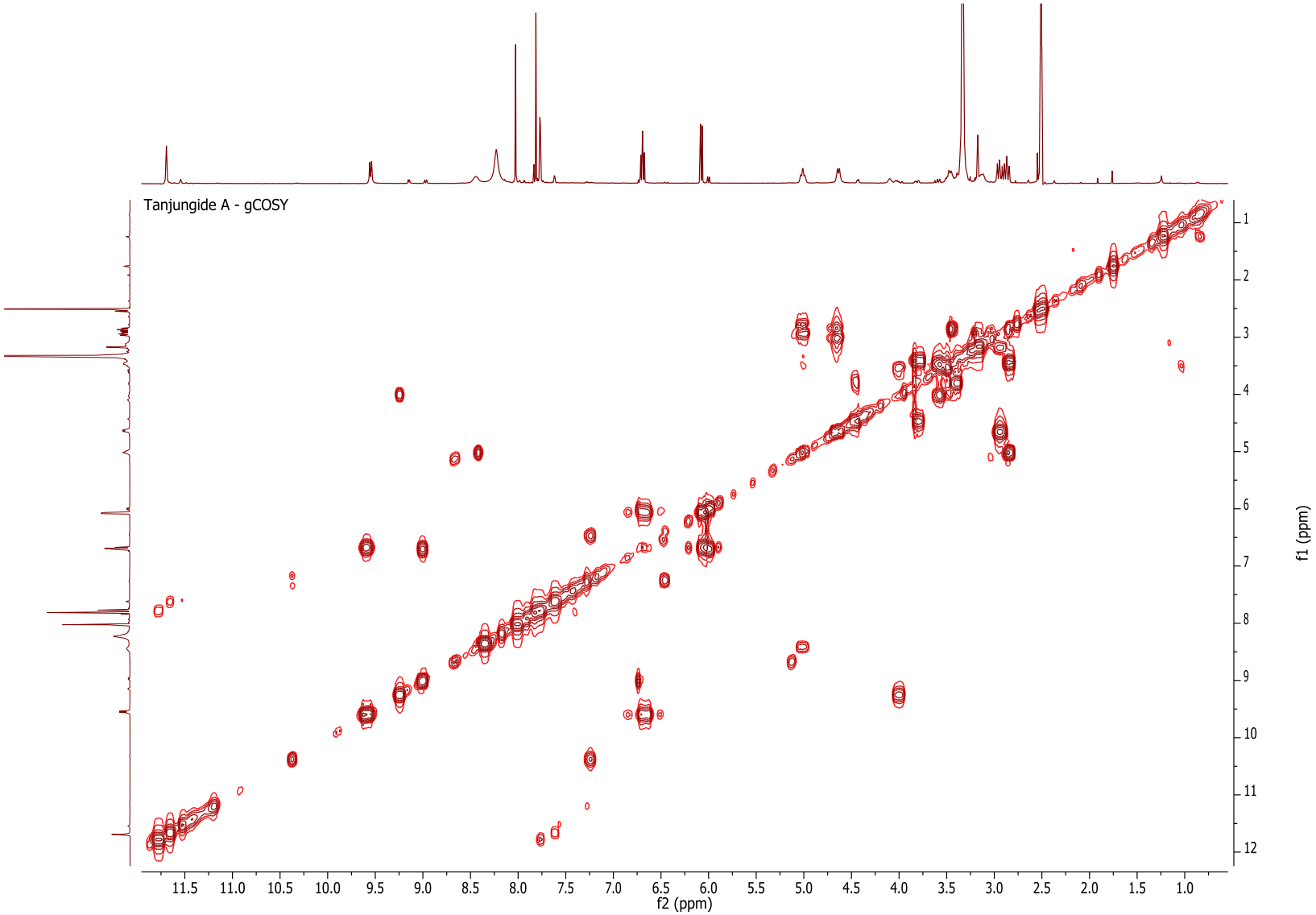


Figure S4. *g*-HSQC spectrum of Tanjungide A.

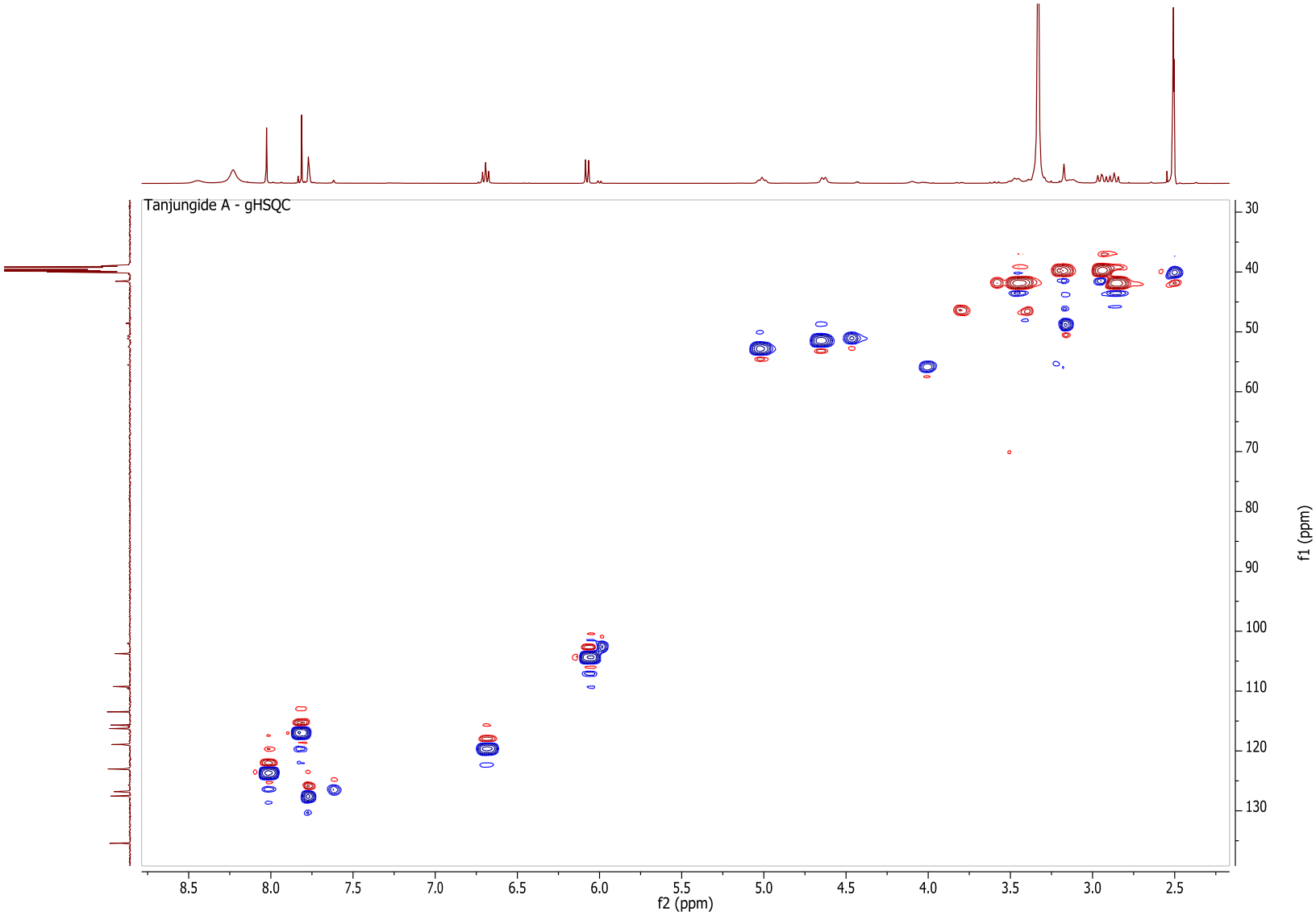


Figure S5. *g*-HMBC spectrum of Tanjungide A.

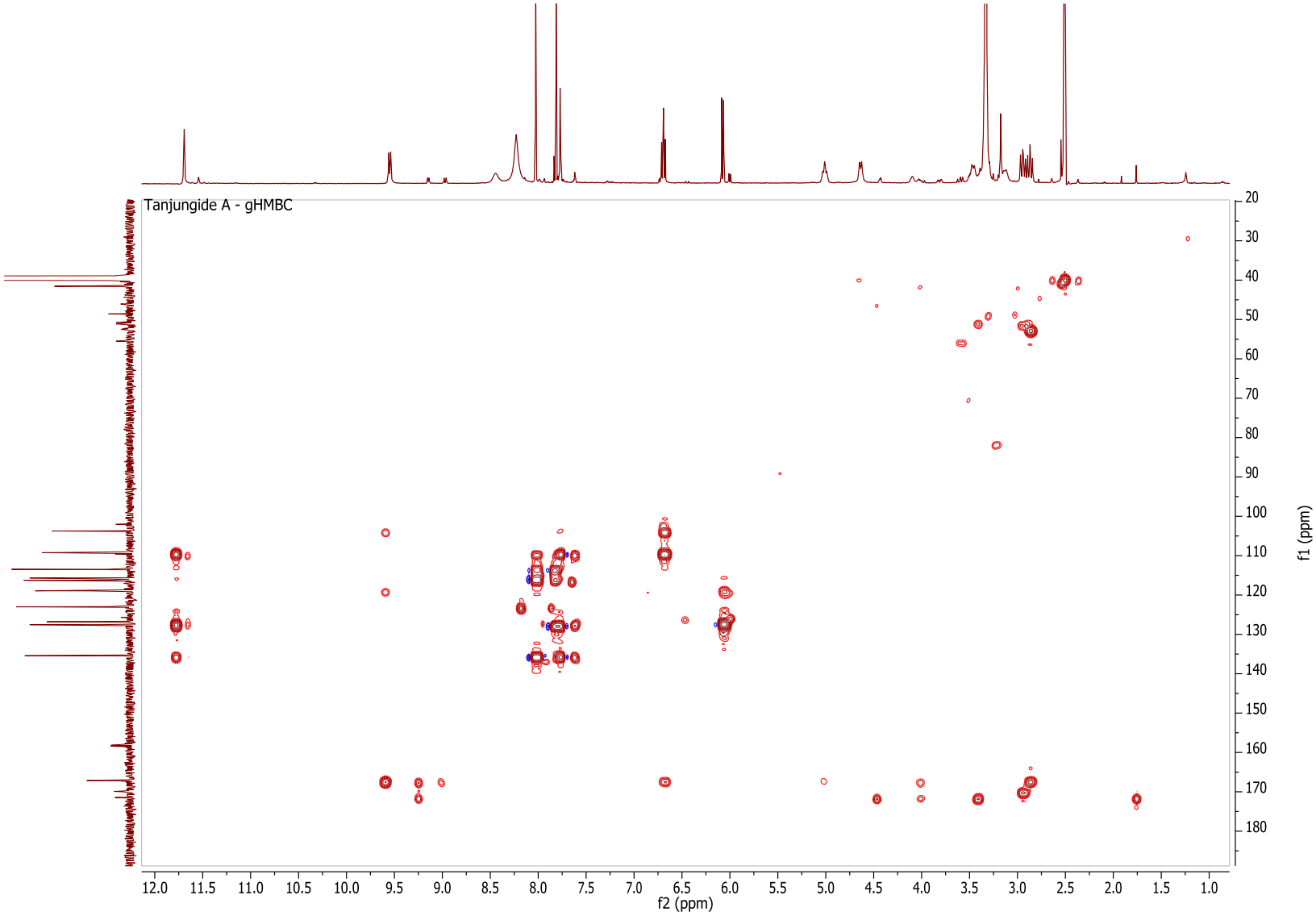


Figure S6. ROESY spectrum of Tanjungide A.

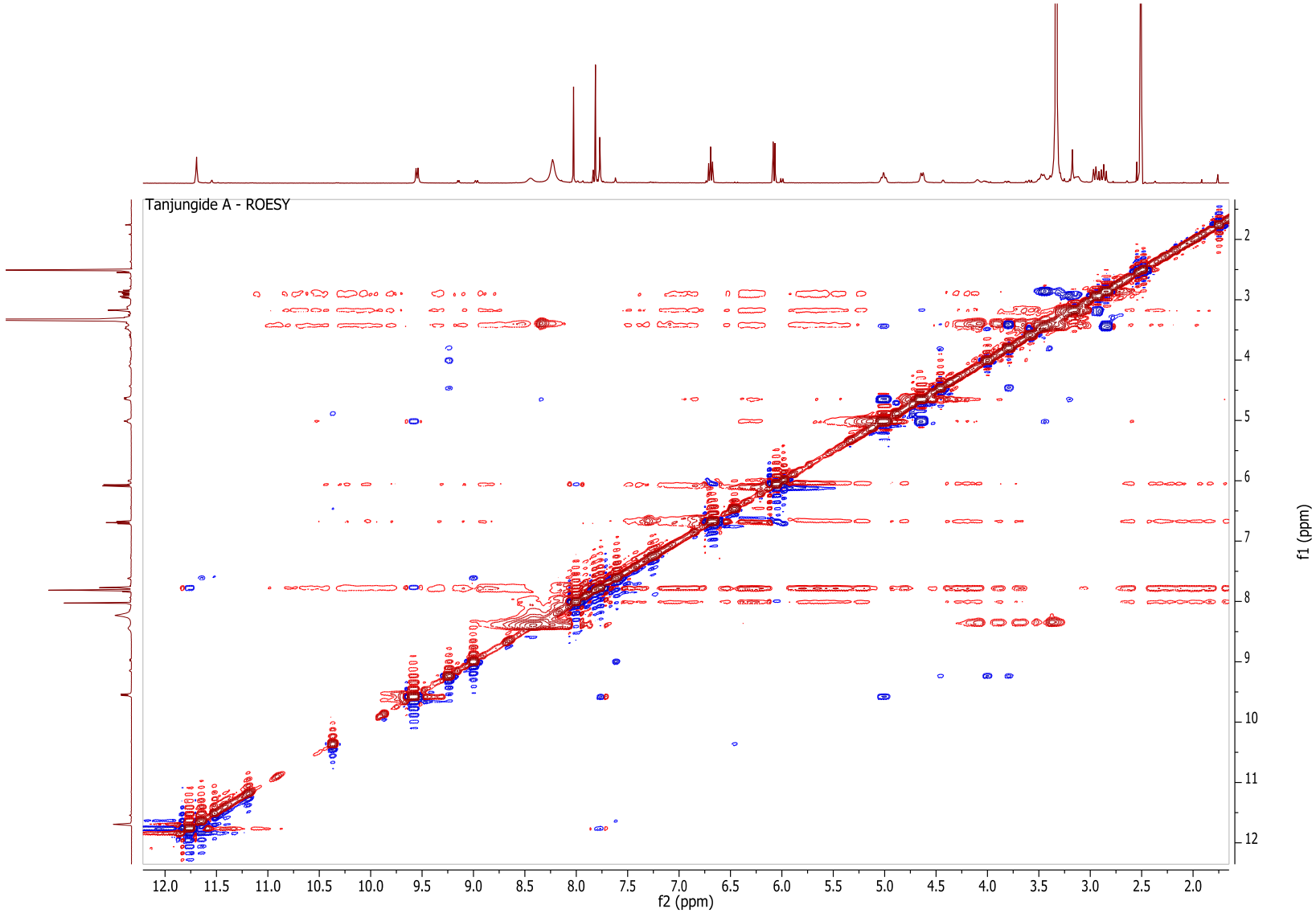


Figure S7. ^{1}H NMR spectrum of Tanjungide B (500 MHz, CD_3OD)

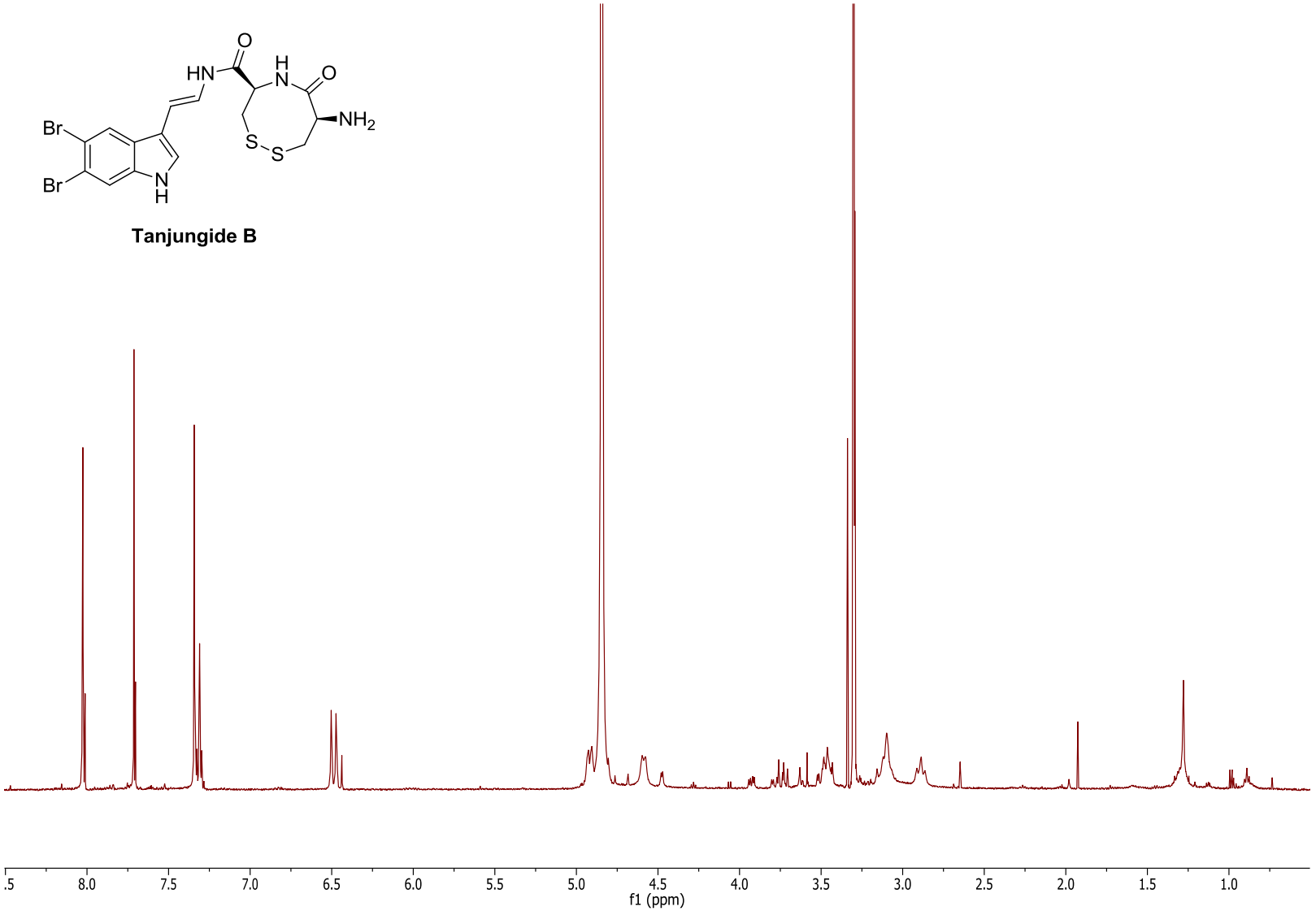


Figure S8. ^{13}C NMR spectrum of Tanjungide B (125 MHz, CD_3OD).

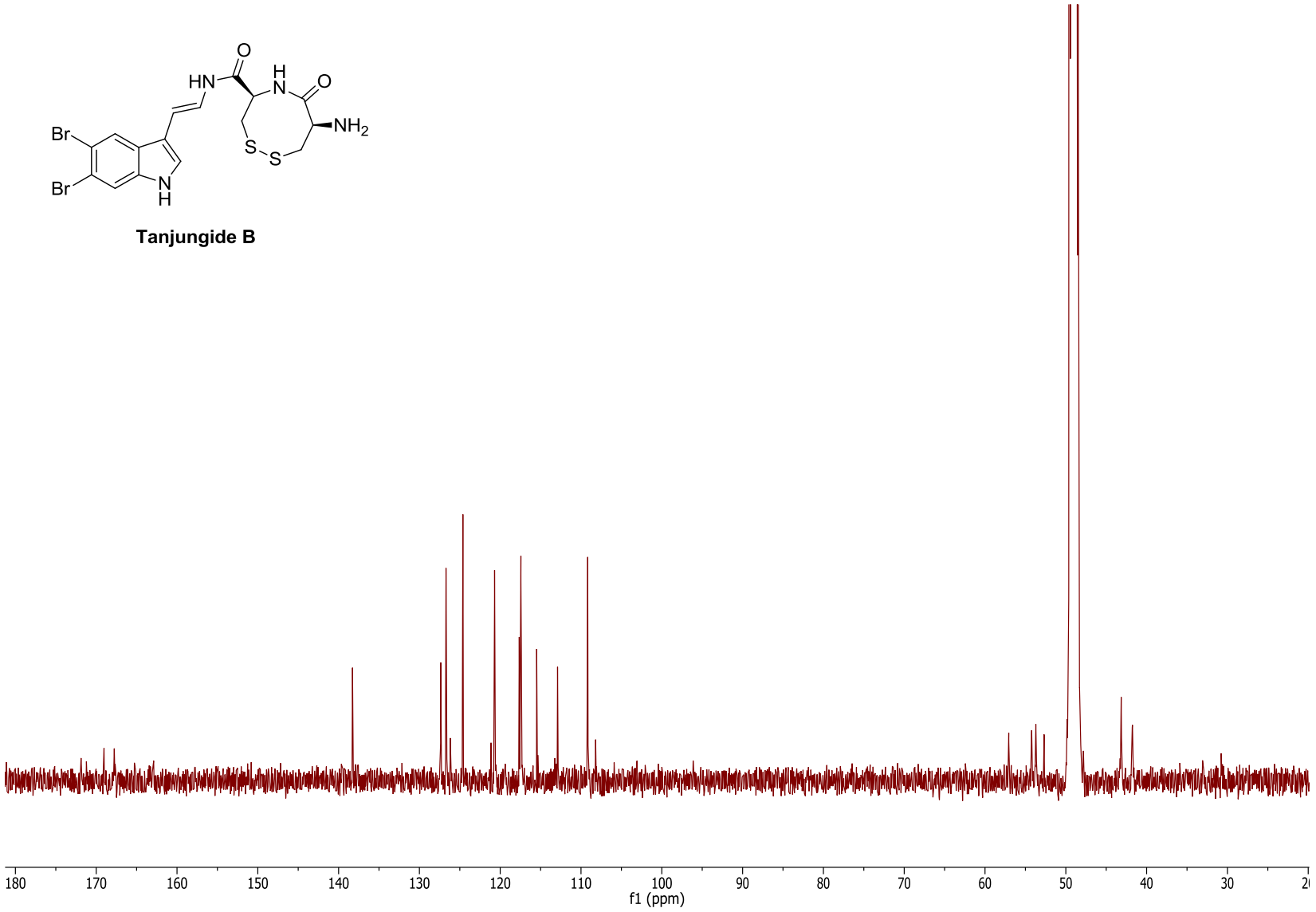


Figure S9. *g*-COSY spectrum Tanjungide B.

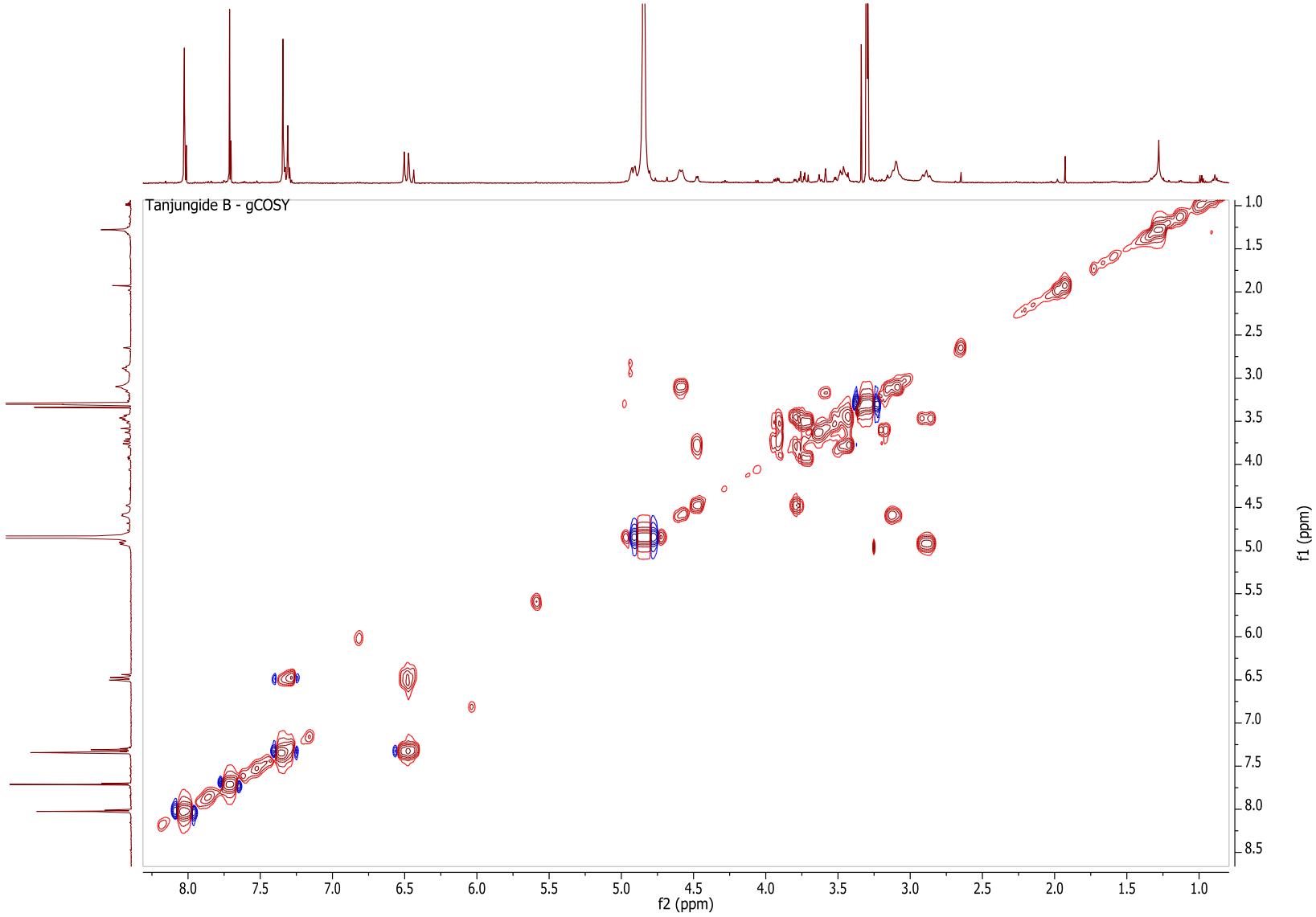


Figure S10. *g*-HSQC spectrum of Tanjungide B.

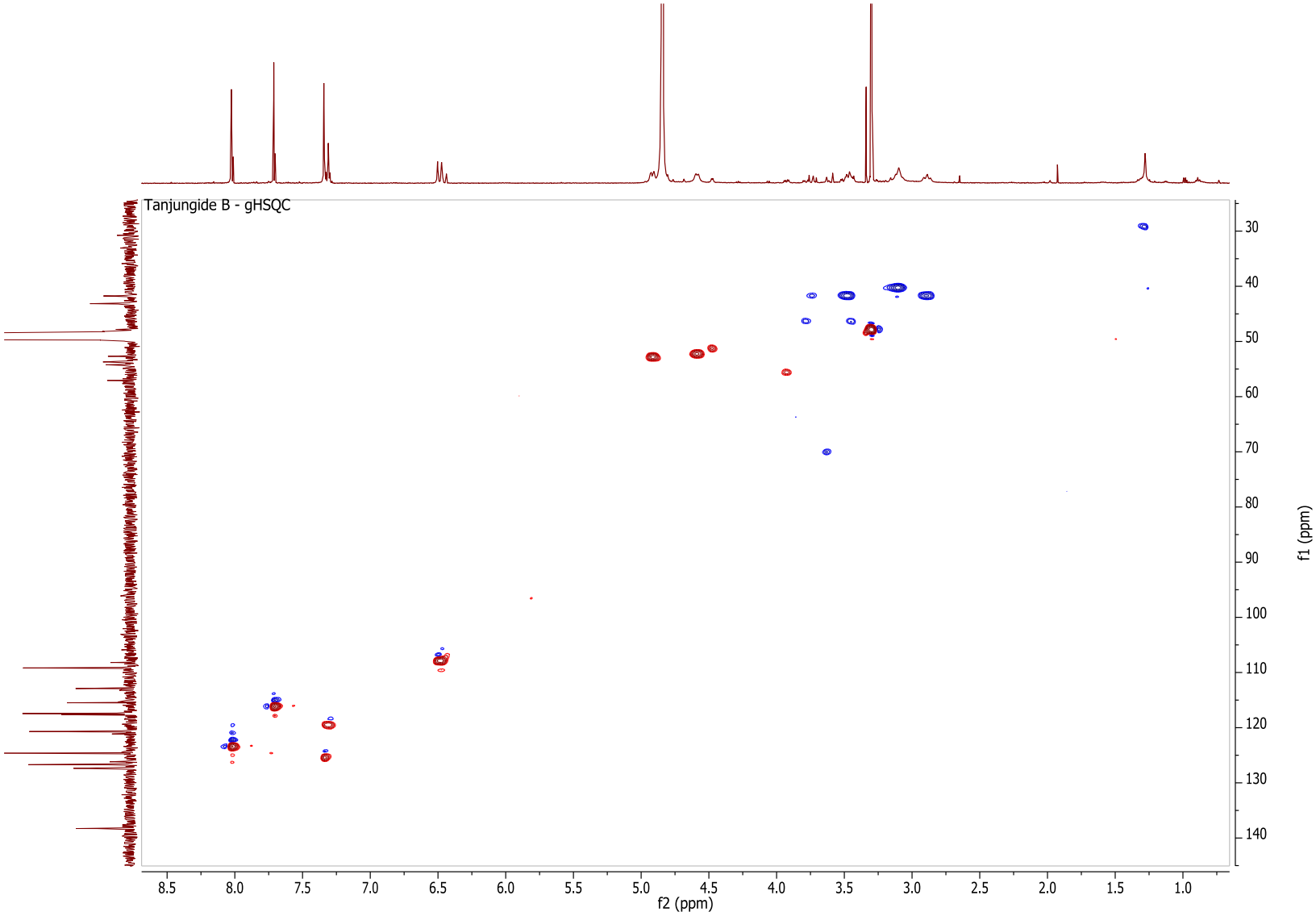


Figure S11. *g*-HMBC spectrum of Tanjungide B.

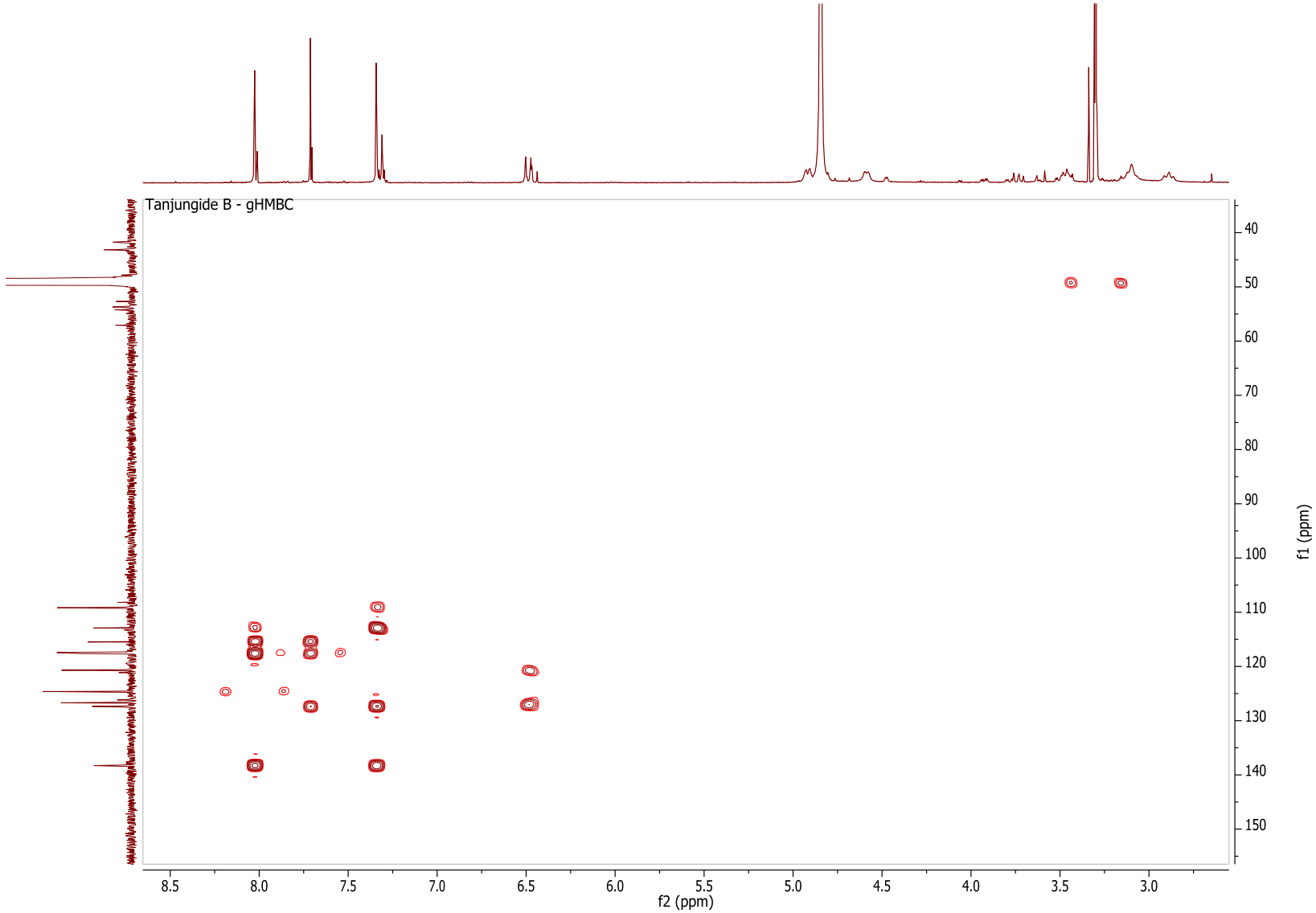


Figure S12. ROESY spectrum of Tanjungide B.

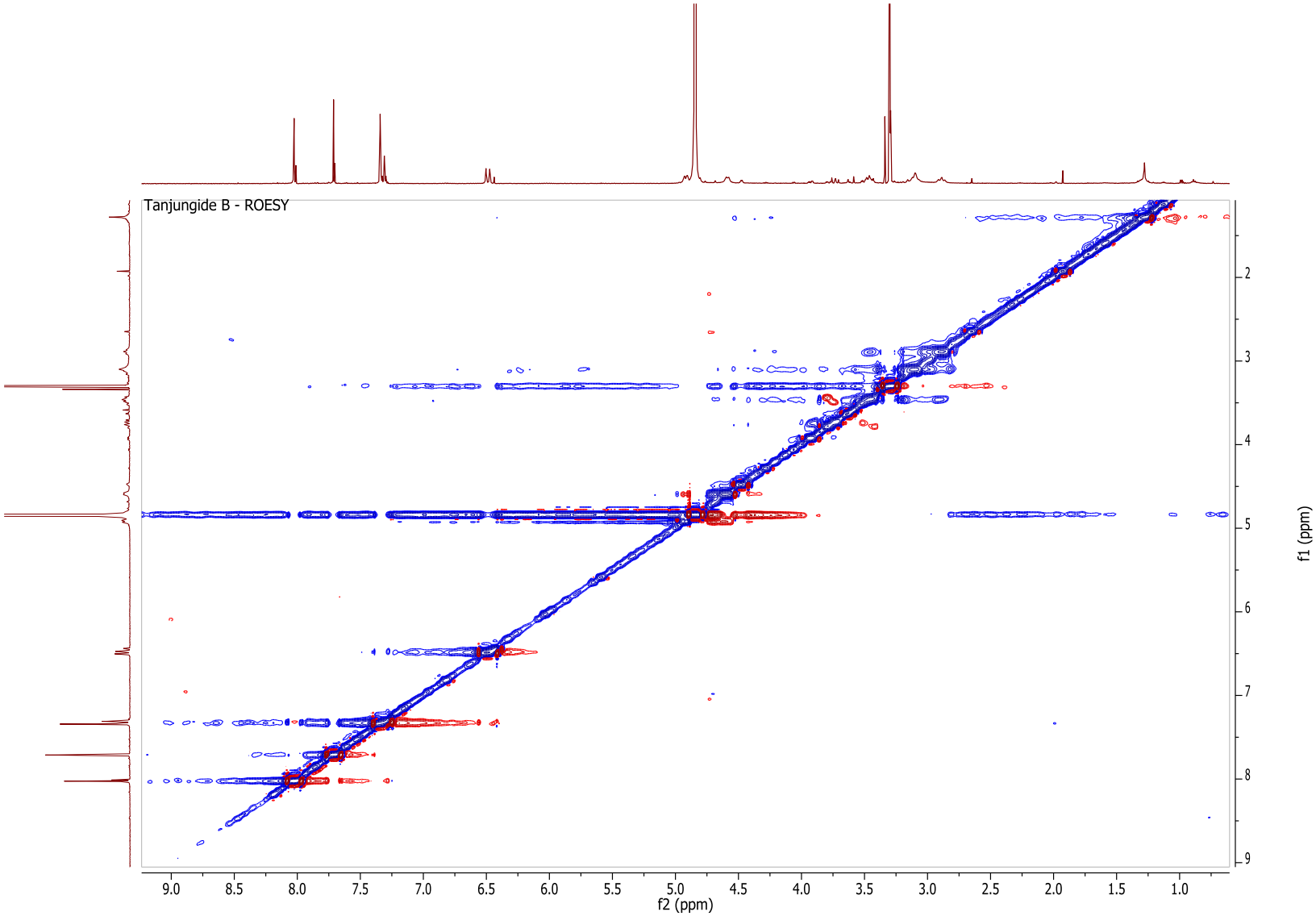


Figure S13. ^{1}H NMR spectrum of 5,6-dibromo-1*H*-indole-3-carboxylic acid (**4**) (300 MHz, CD_3OD).

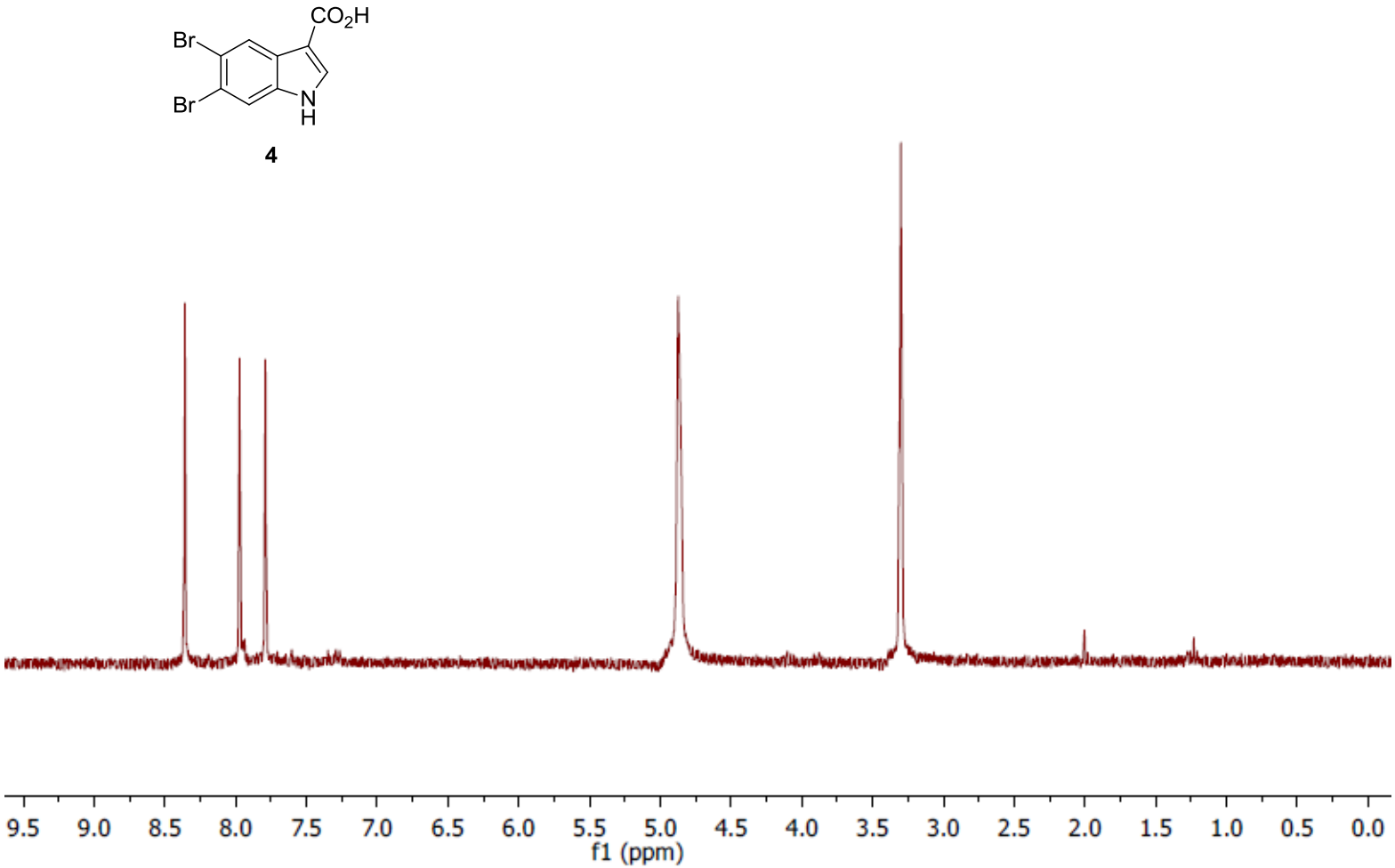


Figure S14. ^{13}C NMR spectrum of 5,6-dibromo-1*H*-indole-3-carboxylic acid (**4**) (75 MHz, CD_3OD).

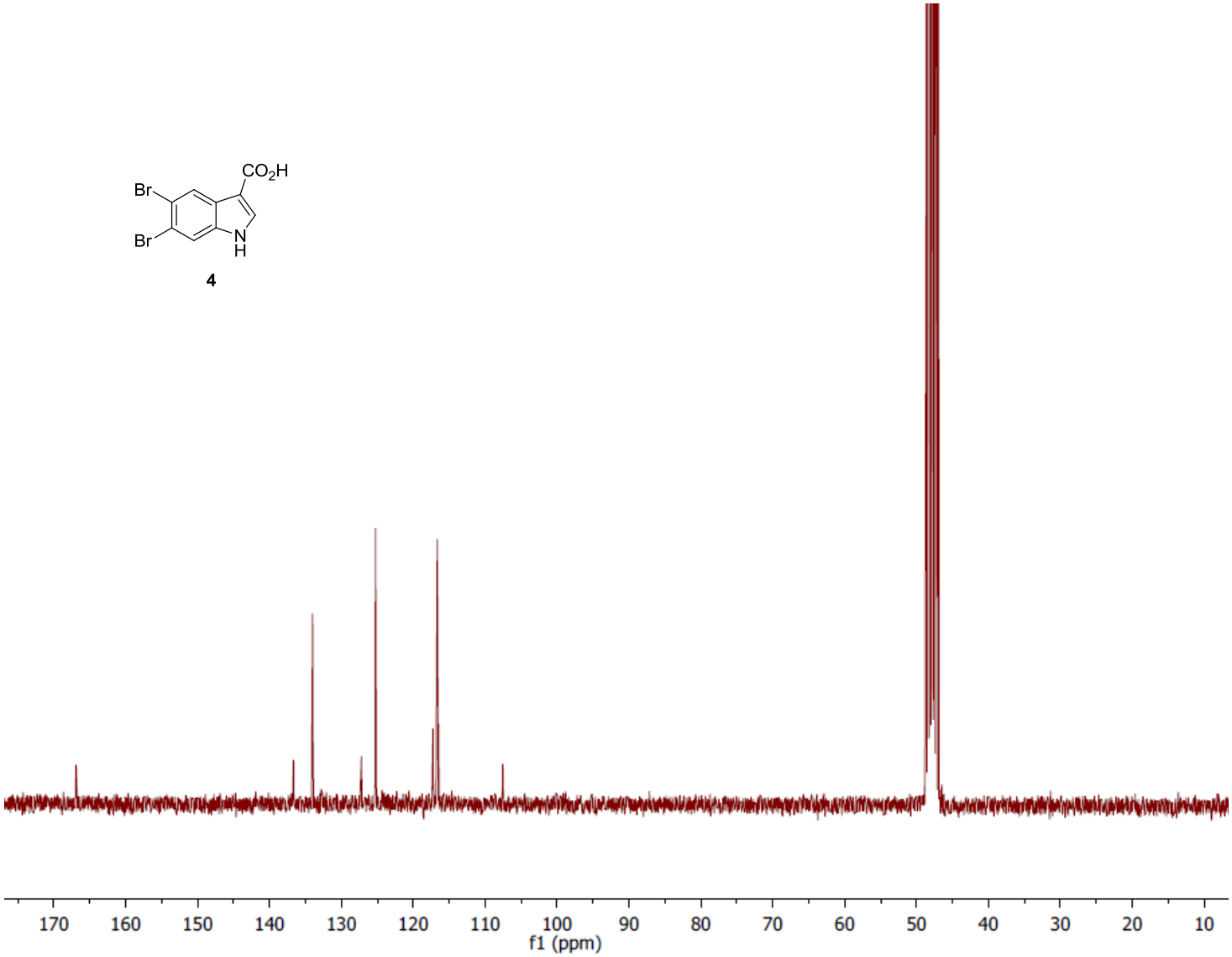
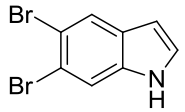


Figure S15. ^{1}H NMR spectrum of 5,6-dibromo-1*H*-indole (**5**) (300 MHz, $CDCl_3$).



5

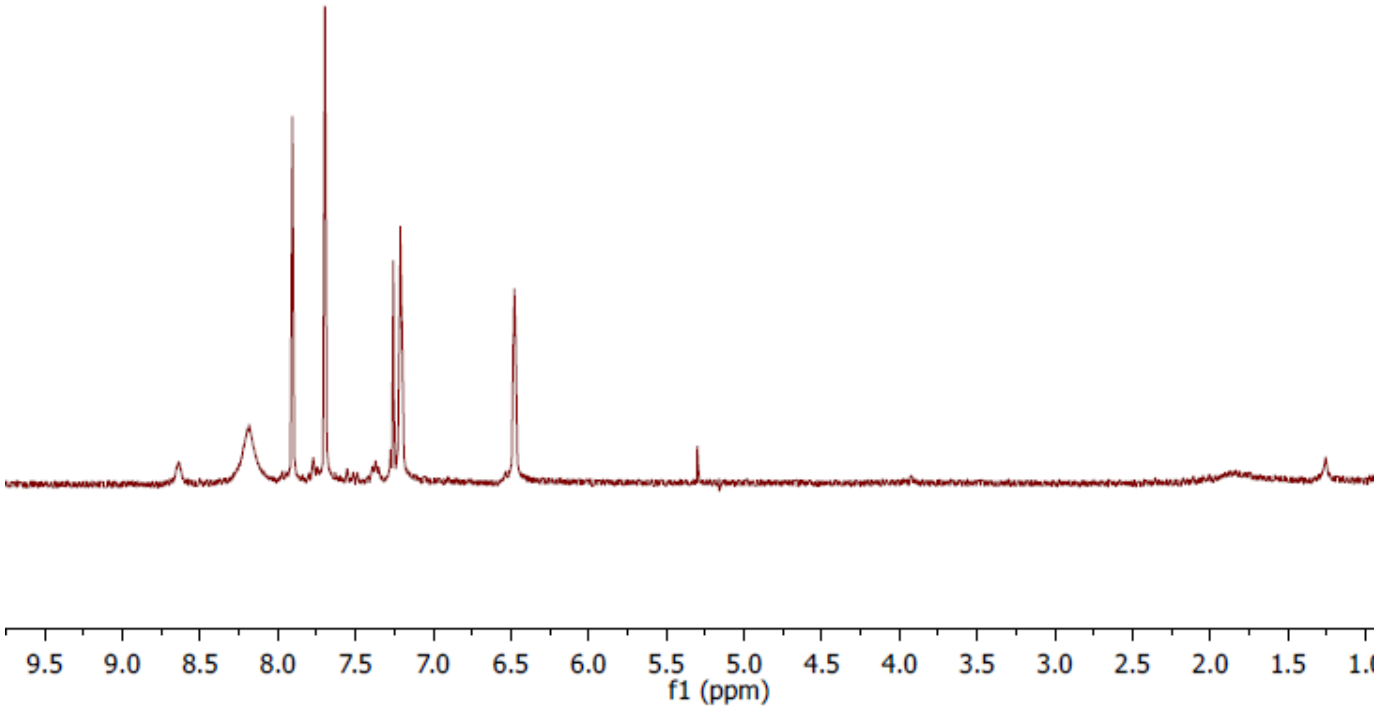


Figure S16. ^{13}C NMR spectrum of 5,6-dibromo-1*H*-indole (**5**) (75 MHz, $CDCl_3$).

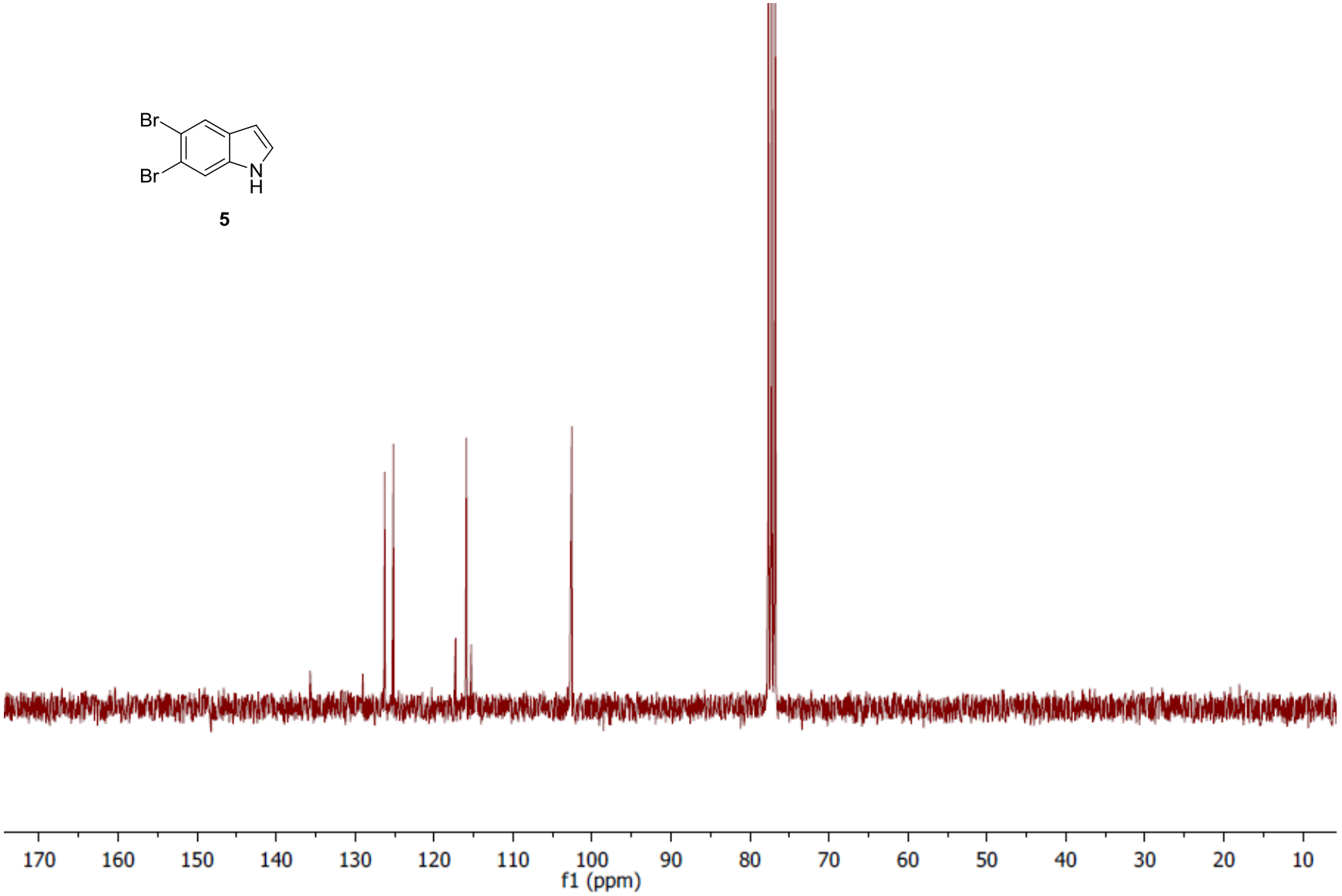


Figure S17. ^{1}H NMR spectrum of 5,6-dibromo-1*H*-indole-3-carbaldehyde (**6**) (300 MHz, DMSO-d_6).

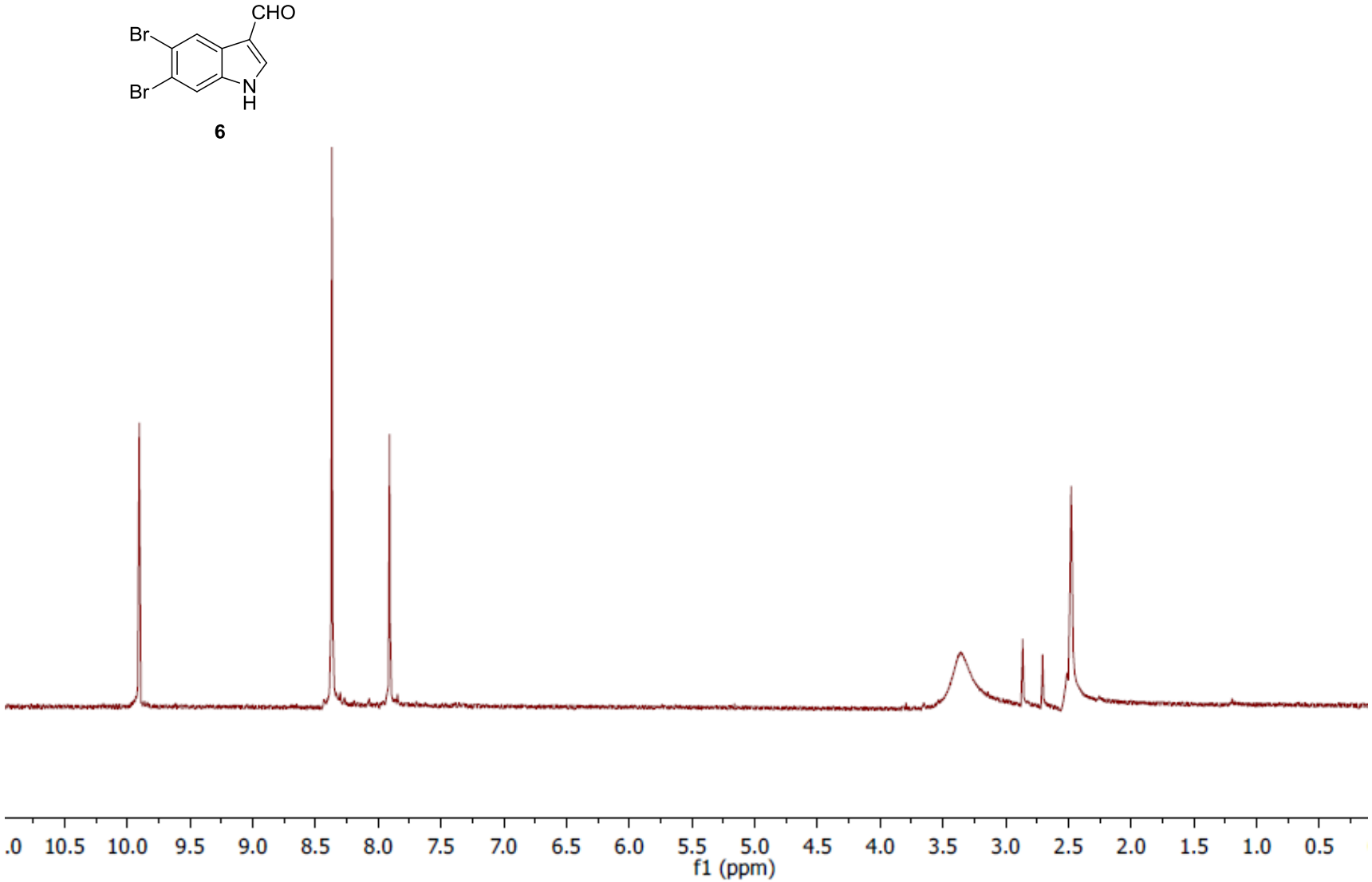


Figure S18. ^{13}C NMR spectrum of 5,6-dibromo-1*H*-indole-3-carbaldehyde (**6**) (75 MHz, DMSO-d_6).

6

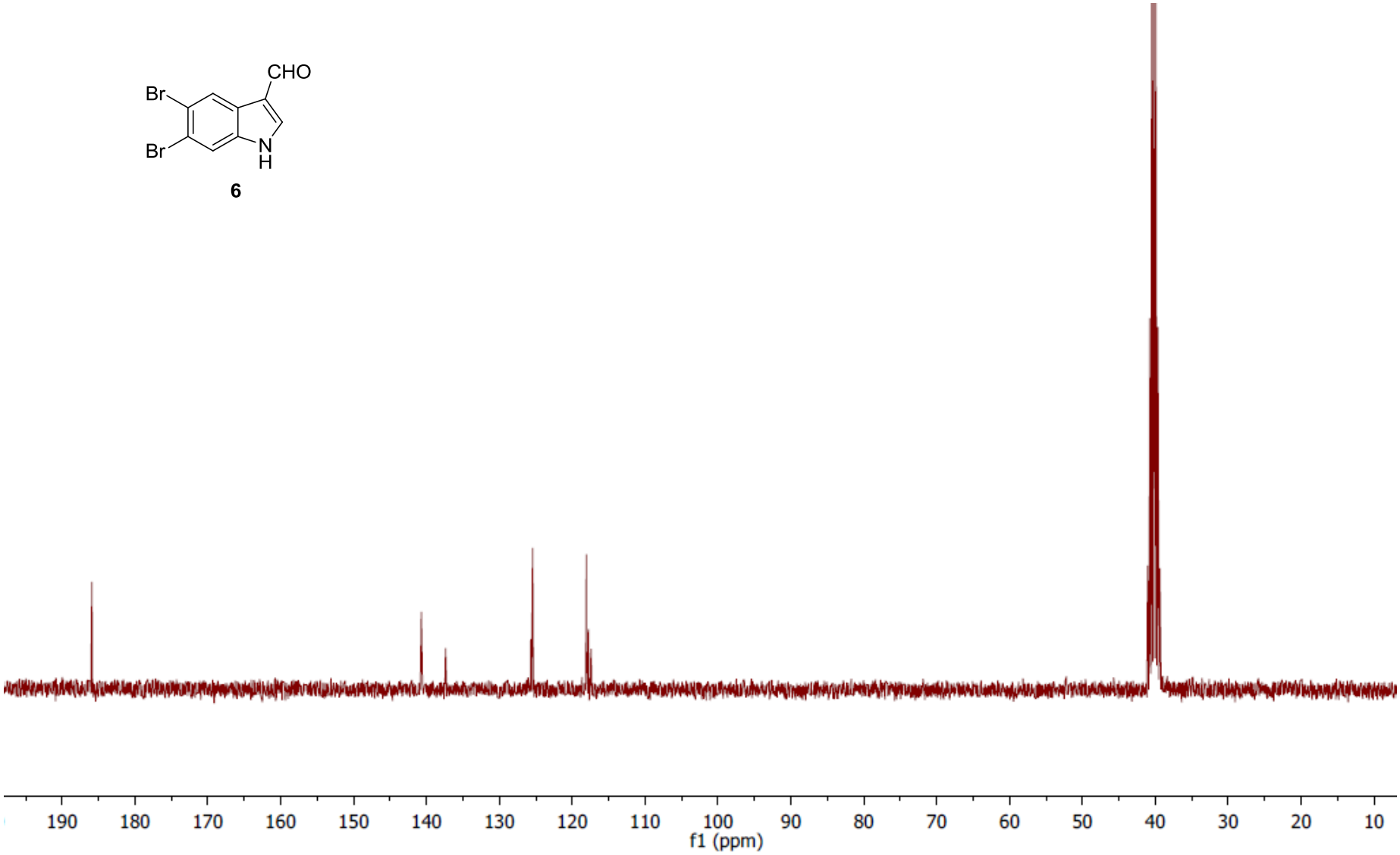


Figure S19. ^{1}H NMR spectrum of *tert*-butyl 5,6-dibromo-3-formyl-1*H*-indole-1-carboxylate (**7**) (300 MHz, $CDCl_3$).

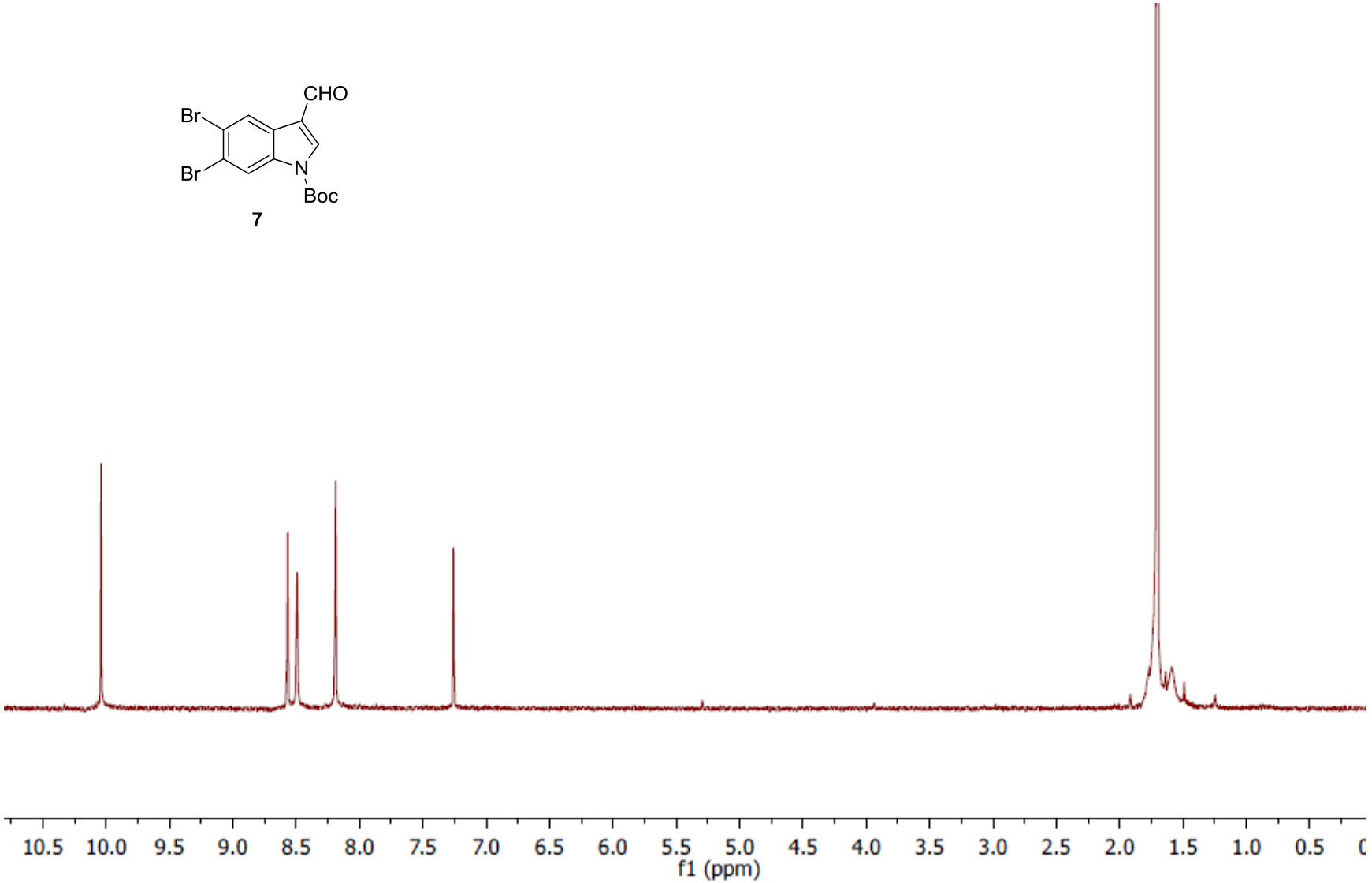


Figure S20. ^{13}C NMR spectrum of *tert*-butyl 5,6-dibromo-3-formyl-1*H*-indole-1-carboxylate (**7**) (75 MHz, $CDCl_3$).

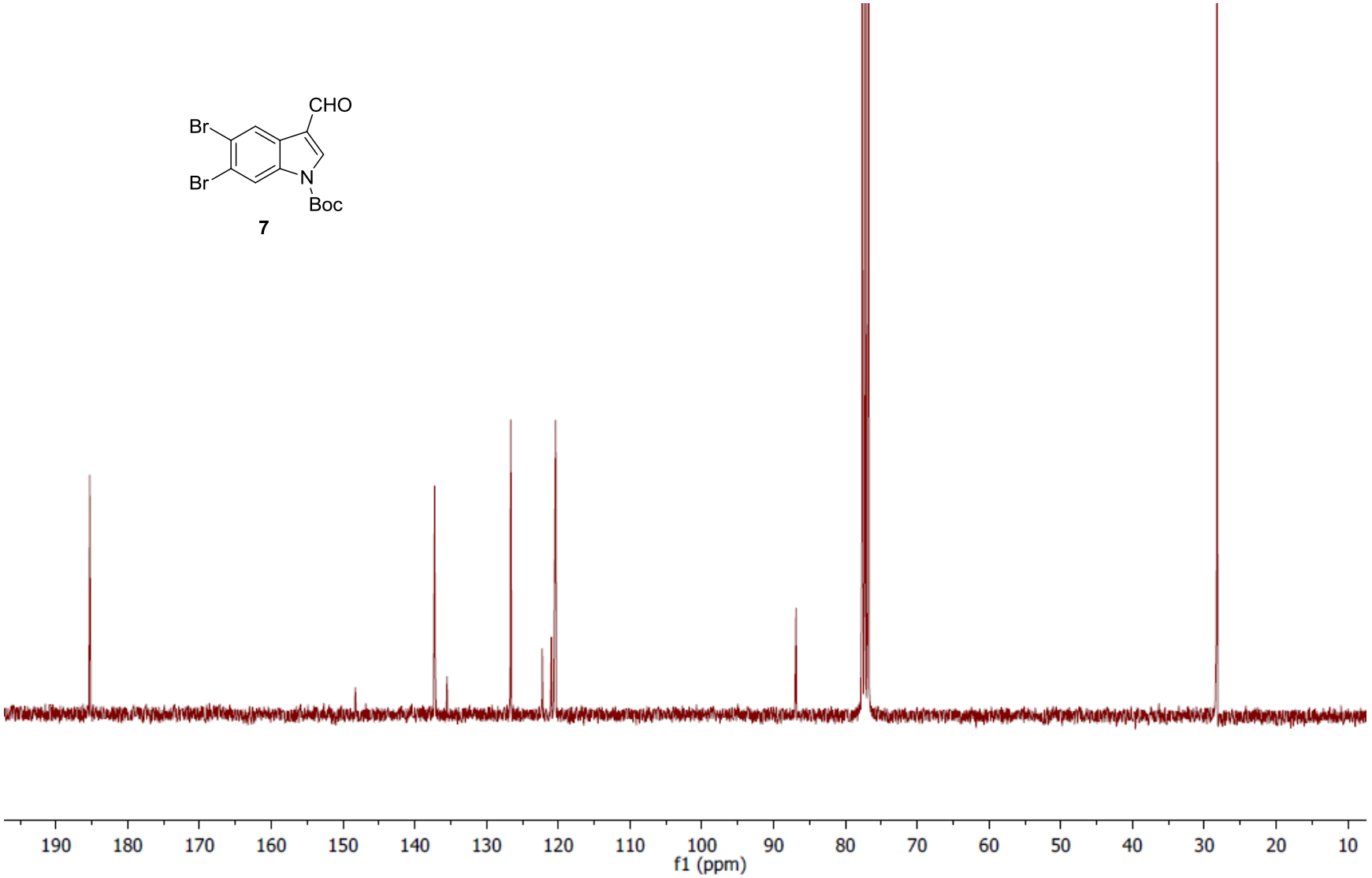


Figure S21. ^{1}H NMR spectrum of (*Z*)-*tert*-butyl 5,6-dibromo-3-(2-iodovinyl)-1*H*-indole-1-carboxylate (**8**) (300 MHz, $CDCl_3$).

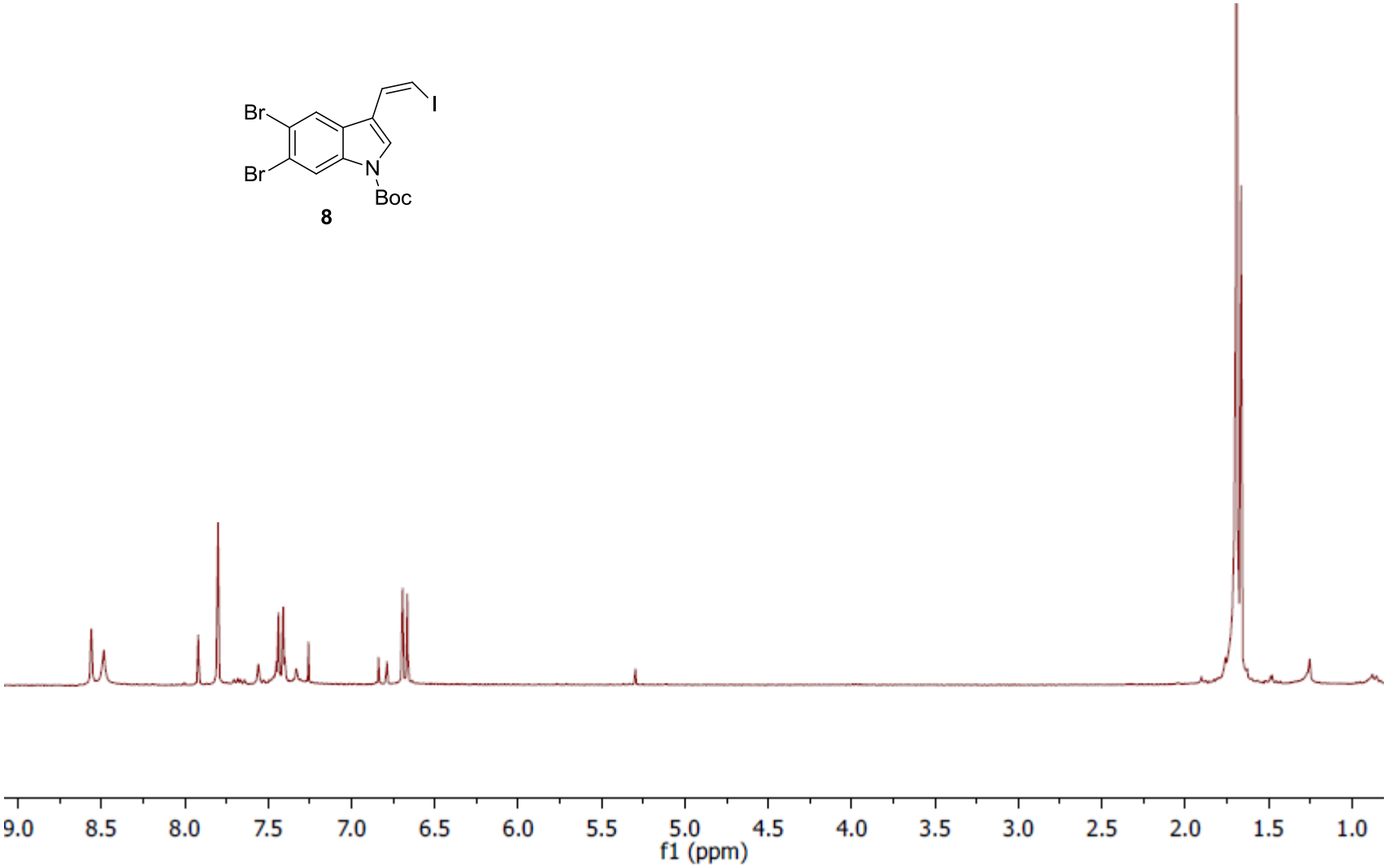


Figure S22. ^{13}C NMR spectrum of (*Z*)-*tert*-butyl 5,6-dibromo-3-(2-iodovinyl)-1*H*-indole-1-carboxylate (**8**) (75 MHz, $CDCl_3$).

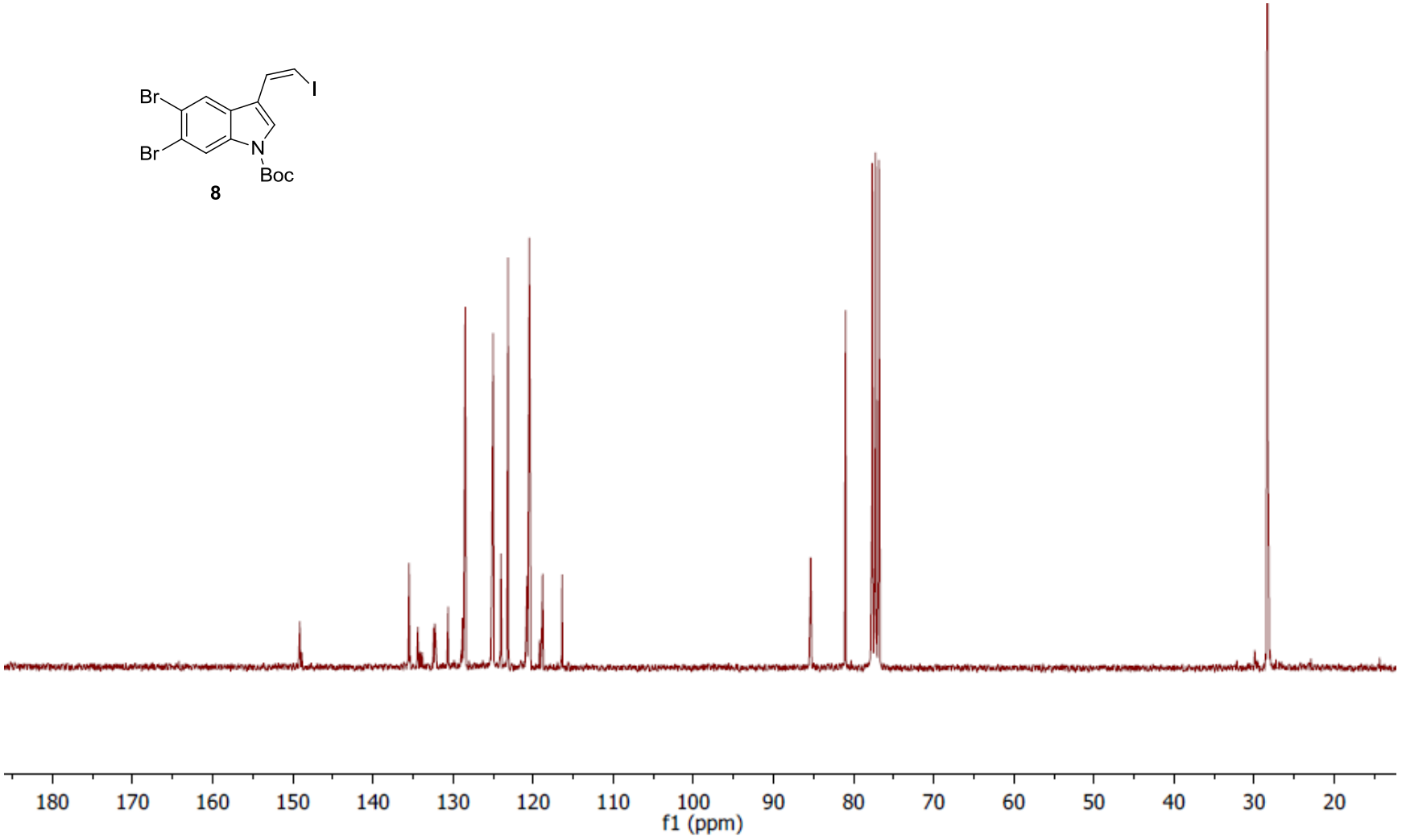


Figure S23. ^{1}H NMR spectrum of (*R*,*Z*)-*tert*-butyl 3-(2-(2-(((allyloxy)carbonyl)amino)-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*Z*-**10**) (300 MHz, $CDCl_3$).

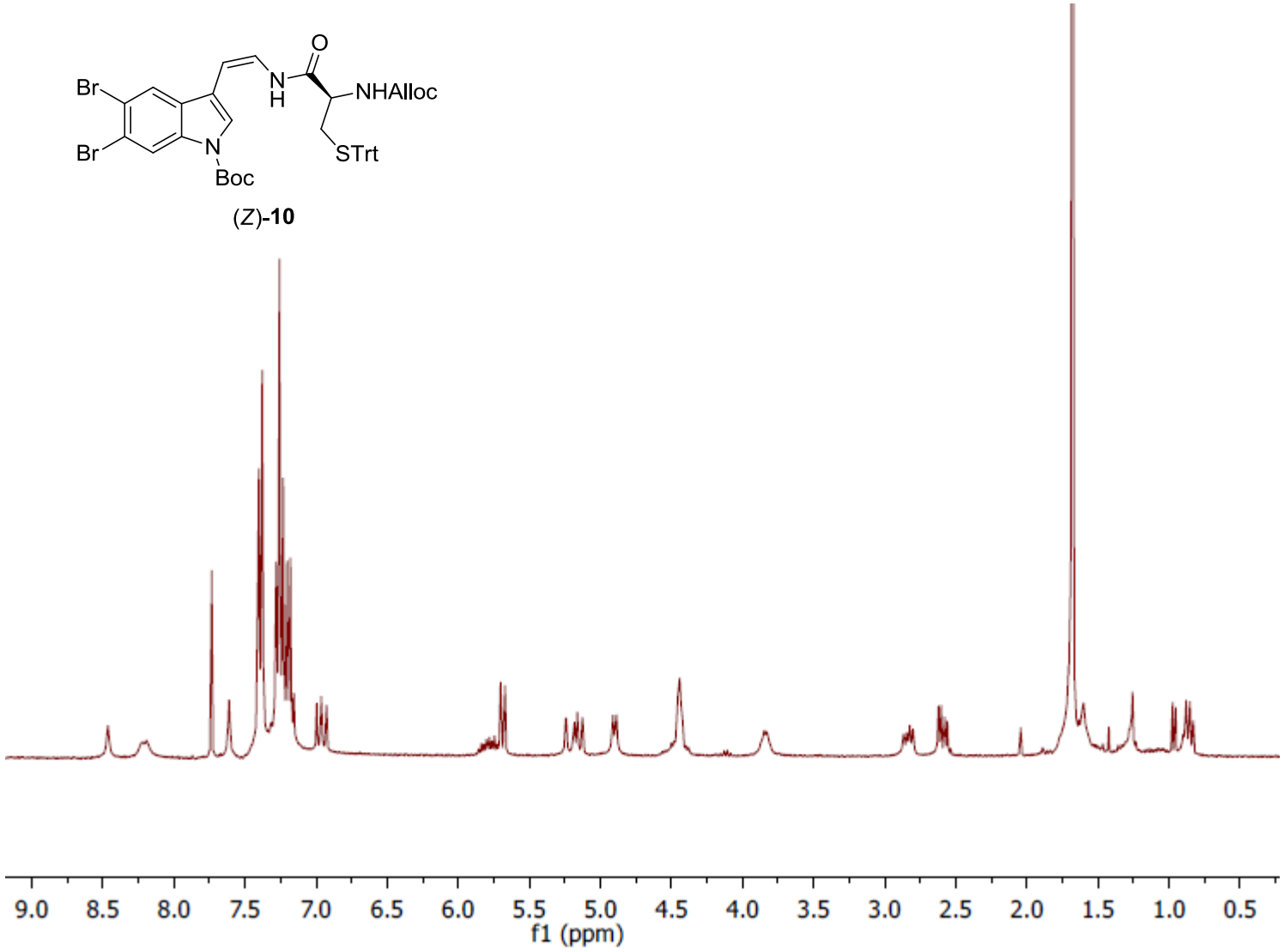


Figure S24. ^{13}C NMR spectrum of (*R*,*Z*)-*tert*-butyl 3-(2-(2-(((allyloxy)carbonyl)amino)-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*Z*-**10**) (75 MHz, $CDCl_3$).

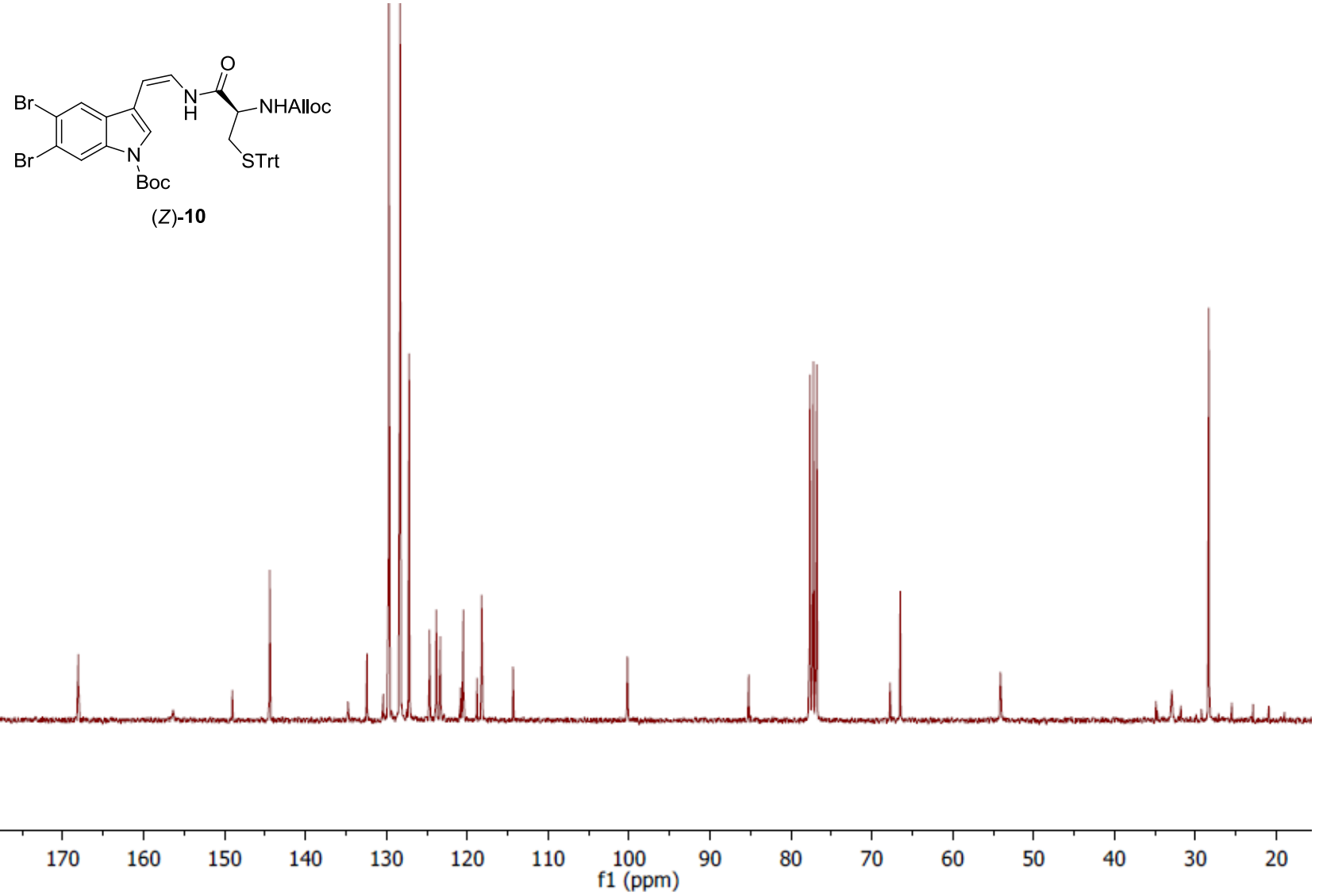


Figure S25. ^{1}H NMR spectrum of (*R*,*E*)-*tert*-butyl 3-(2-(2-(((allyloxy)carbonyl)amino)-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*E*-**10**) (300 MHz, $CDCl_3$).

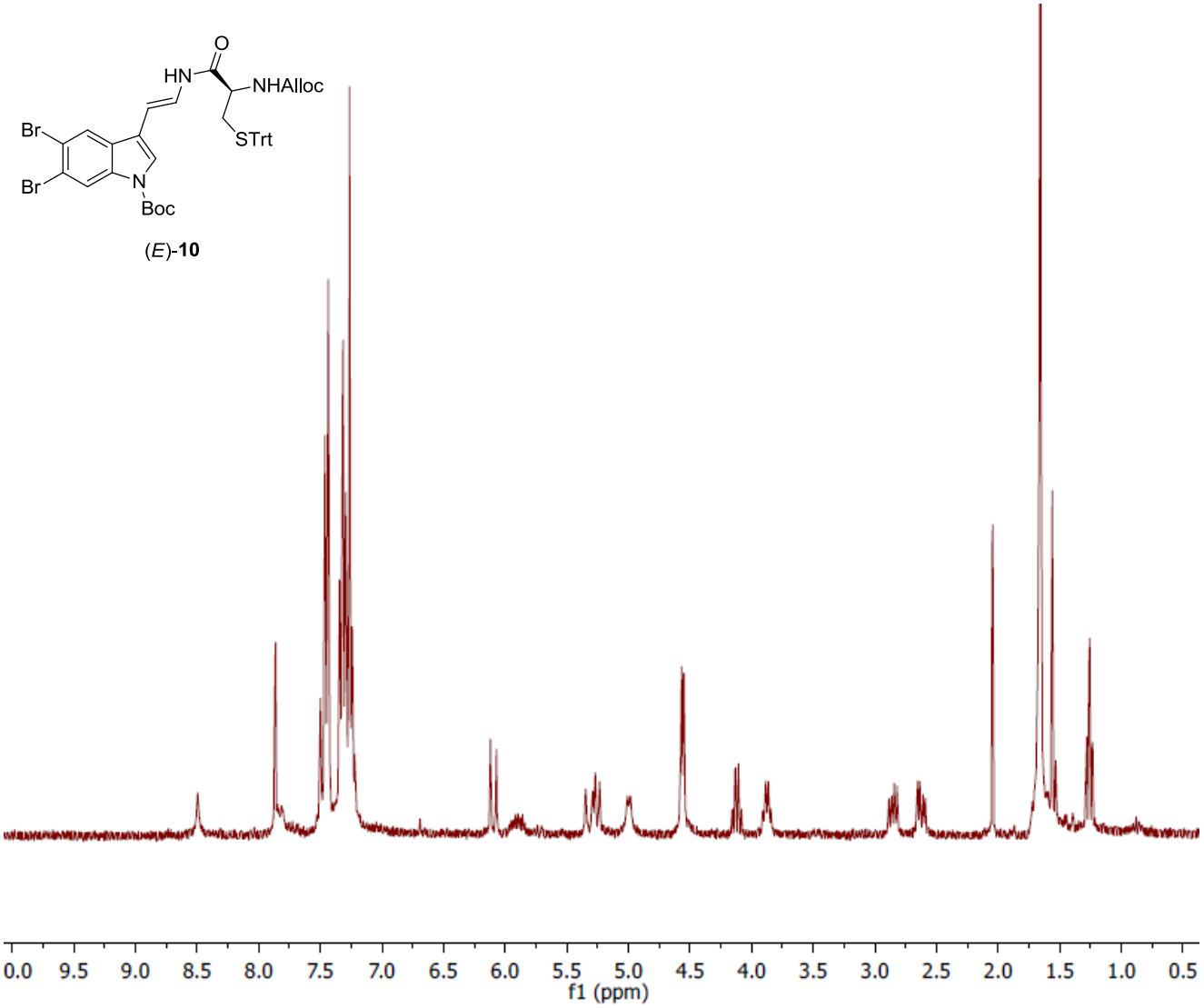


Figure S26. ^{13}C NMR spectrum of (*R*,*E*)-*tert*-butyl 3-(2-(2-(((allyloxy)carbonyl)amino)-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*E*-**10**) (75 MHz, $CDCl_3$).

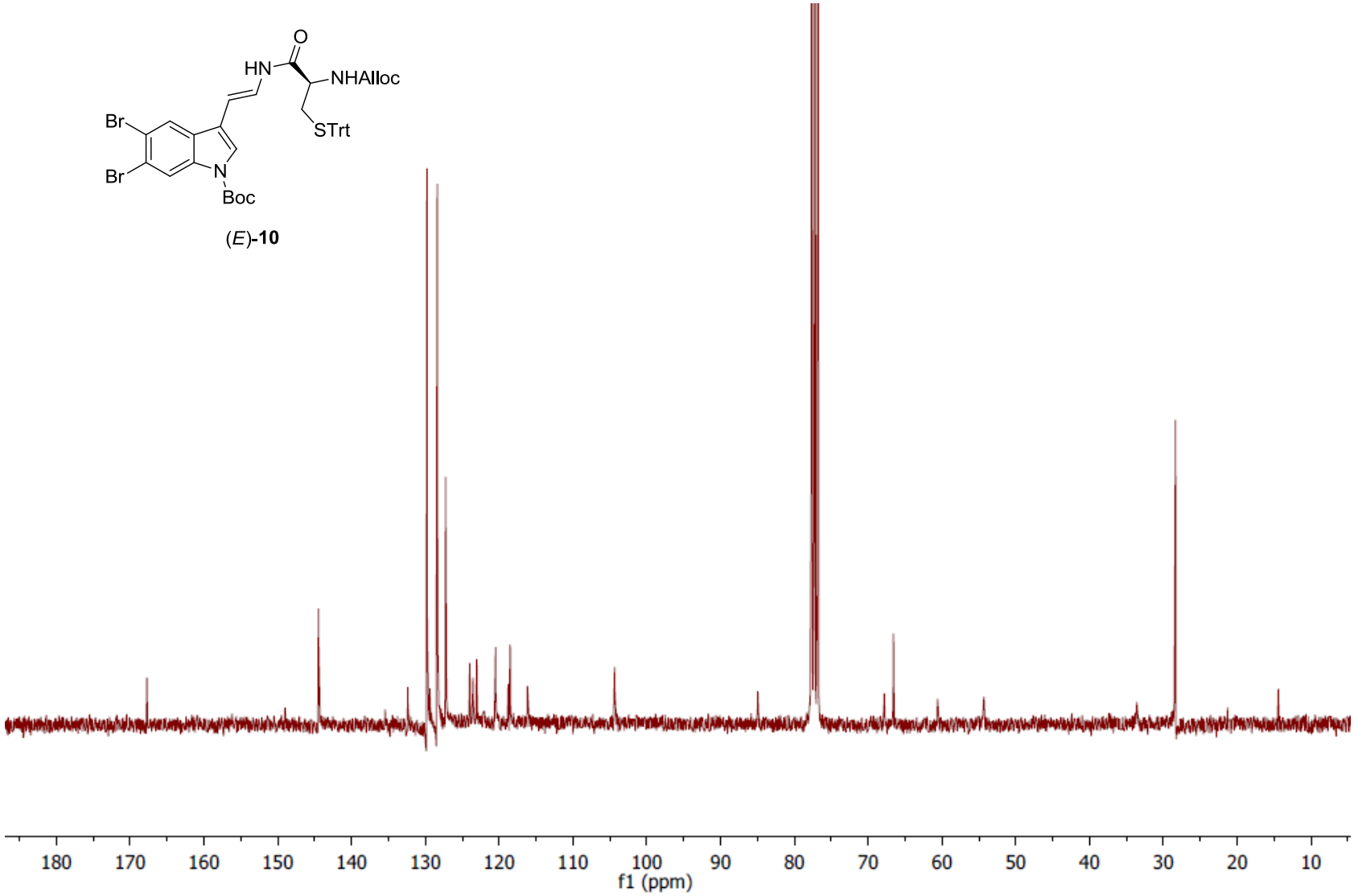


Figure S27. ^{1}H NMR spectrum of (*R*,*Z*)-*tert*-butyl 3-(2-(2-amino-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*Z*-**11**) (300 MHz, $CDCl_3$).

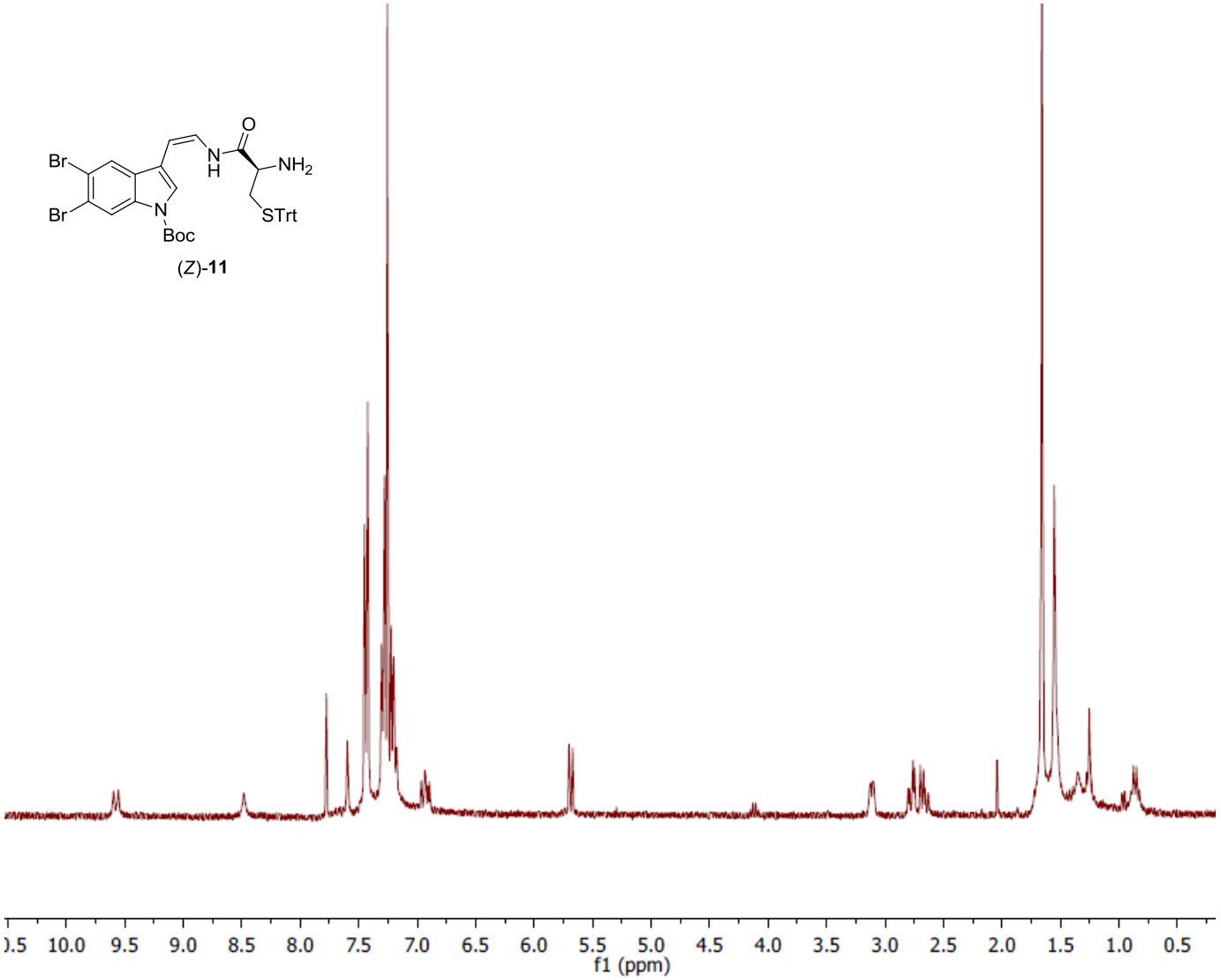


Figure S28. ^{13}C NMR spectrum of (*R*,*Z*)-*tert*-butyl 3-(2-(2-amino-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*Z*-**11**) (75 MHz, $CDCl_3$).

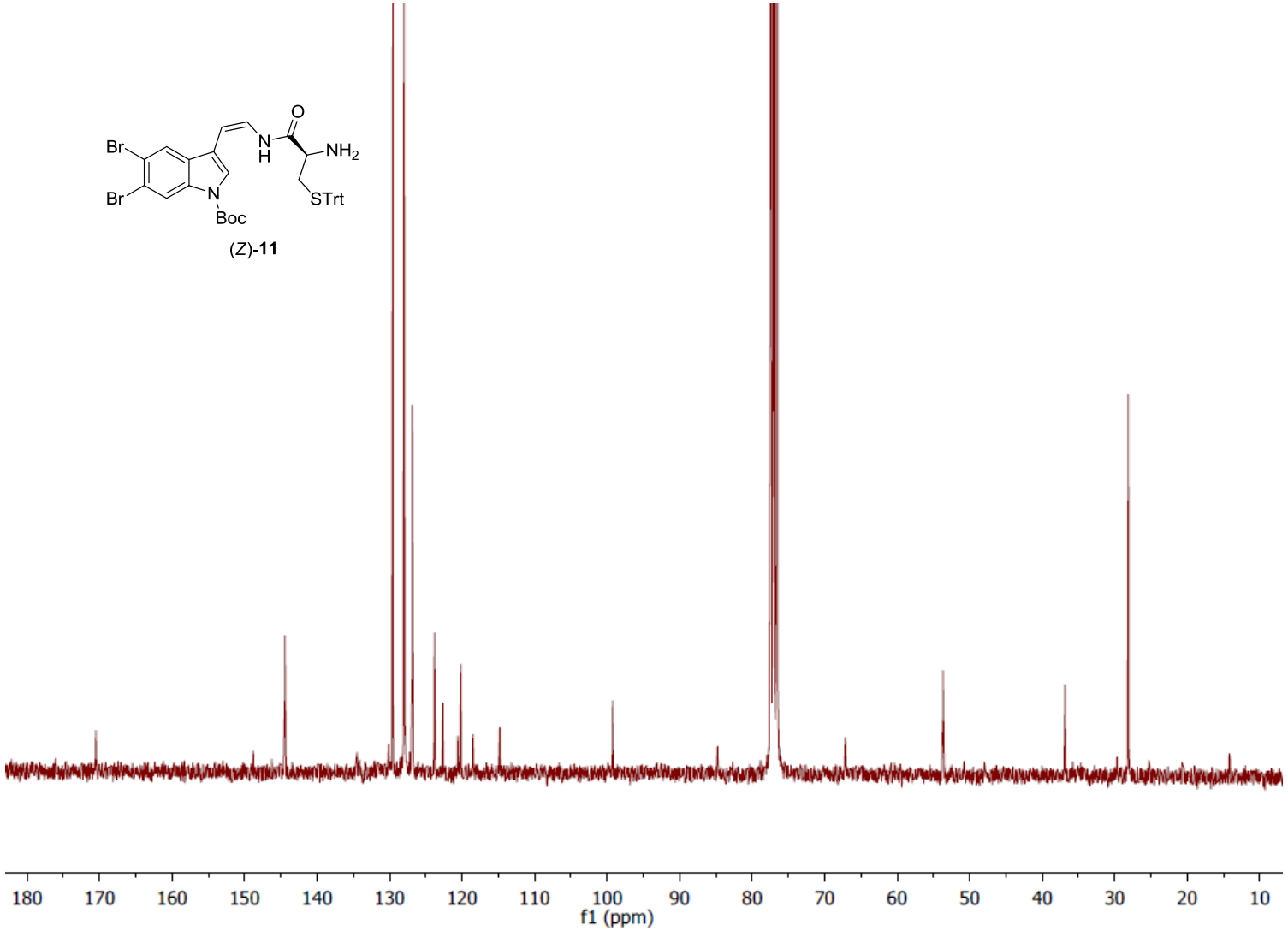


Figure S29. ^{1}H NMR spectrum of (*R*,*E*)-*tert*-butyl 3-(2-(2-amino-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*E*-**11**) (300 MHz, $CDCl_3$).

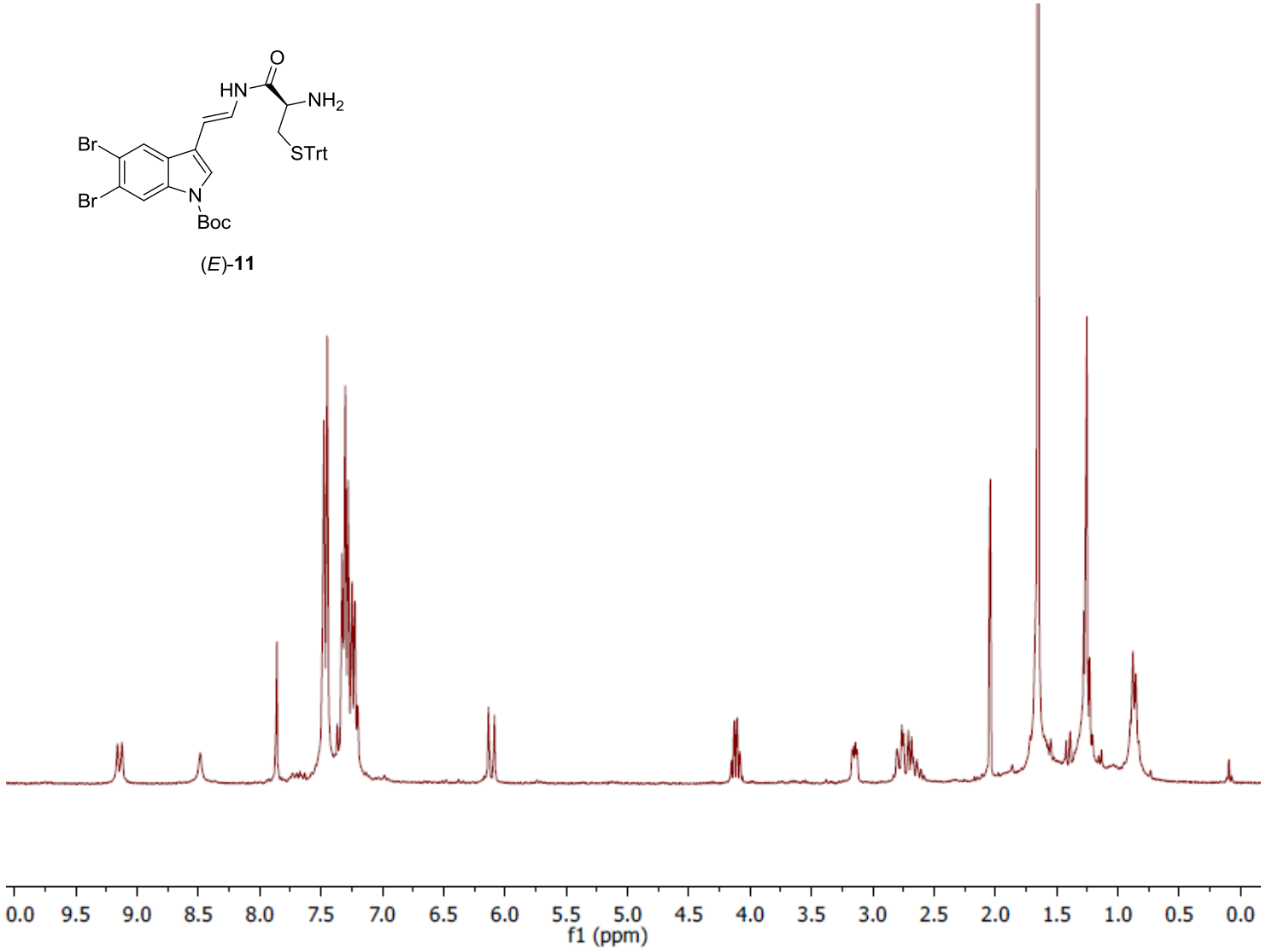


Figure S30. ^{13}C NMR spectrum of (*R*,*E*)-*tert*-butyl 3-(2-(2-amino-3-(tritylthio)propanamido)vinyl)-5,6-dibromo-1*H*-indole-1-carboxylate (*E*-**11**) (75 MHz, $CDCl_3$).

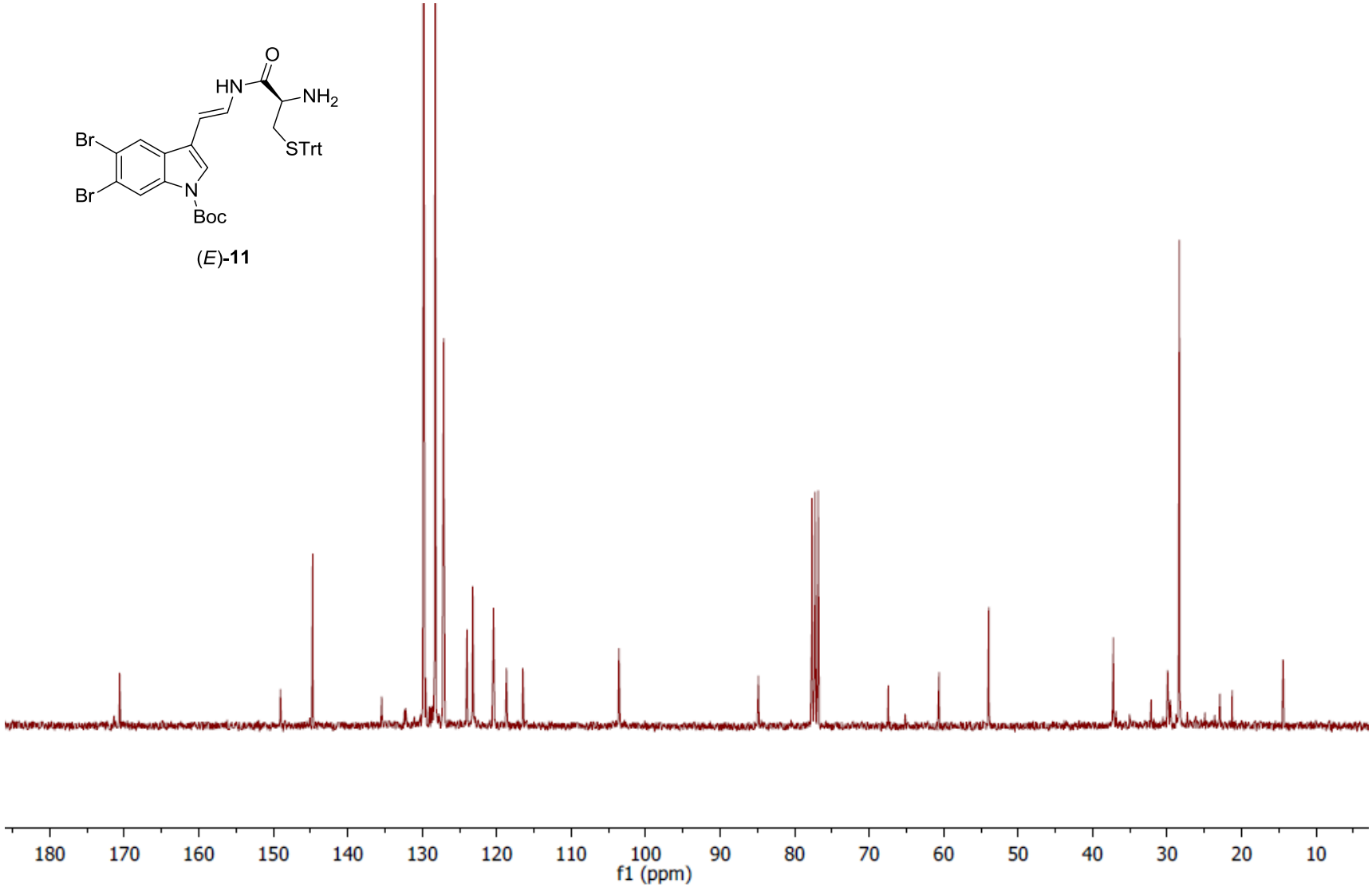


Figure S31. ^{1}H NMR spectrum of *tert*-butyl 5,6-dibromo-3-((6*R*,9*R*,*Z*)-2,2-dimethyl-4,7,10-trioxo-6,9-bis((tritylthio)methyl)-3-oxa-5,8,11-triazatridec-12-en-13-yl)-1*H*-indole-1-carboxylate (*Z*-**12**) (300 MHz, $CDCl_3$).

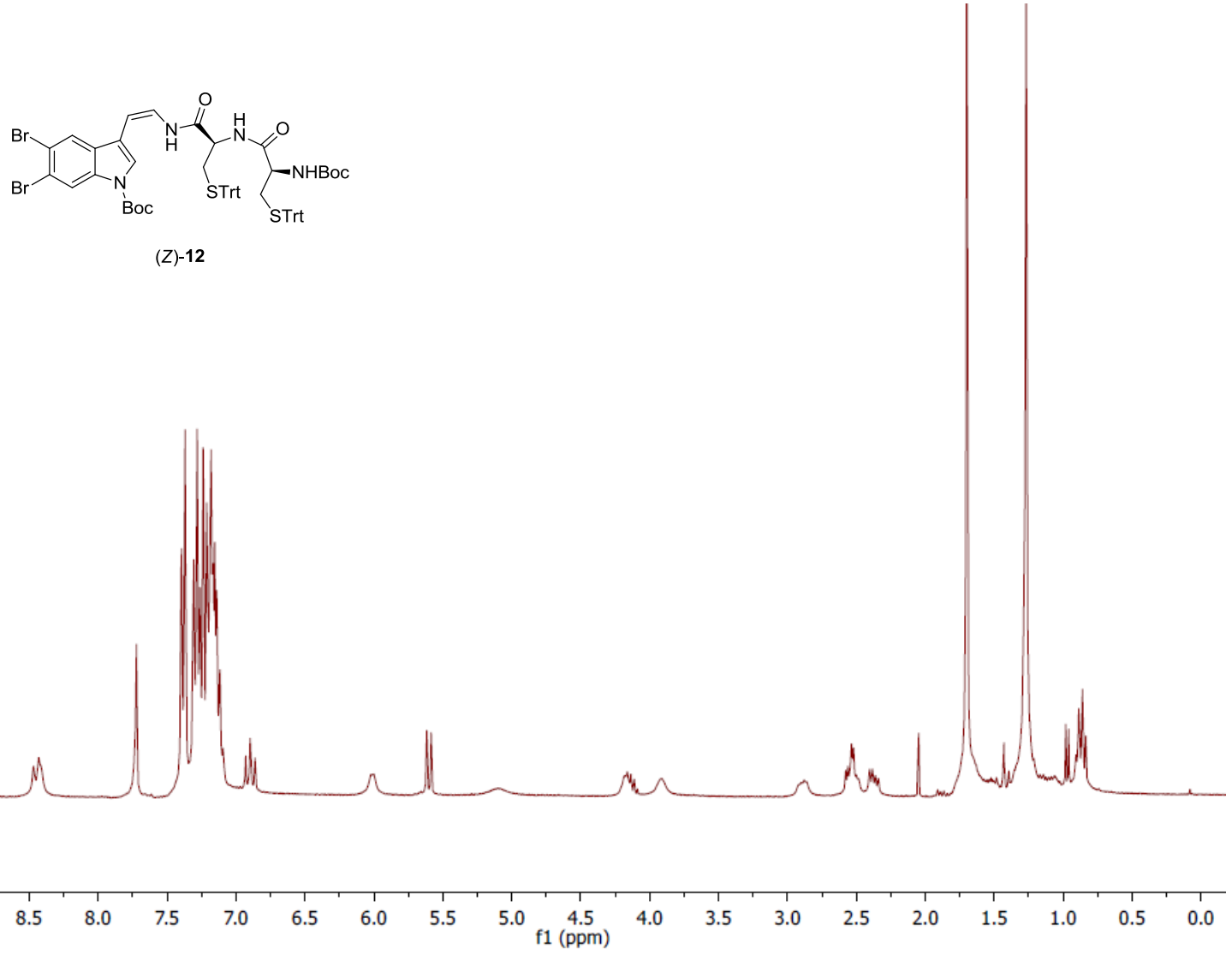


Figure S32. ^{13}C NMR spectrum of *tert*-butyl 5,6-dibromo-3-((6*R*,9*R*,*Z*)-2,2-dimethyl-4,7,10-trioxo-6,9-bis((tritylthio)methyl)-3-oxa-5,8,11-triazatridec-12-en-13-yl)-1*H*-indole-1-carboxylate (*Z*-**12**) (75 MHz, $CDCl_3$).

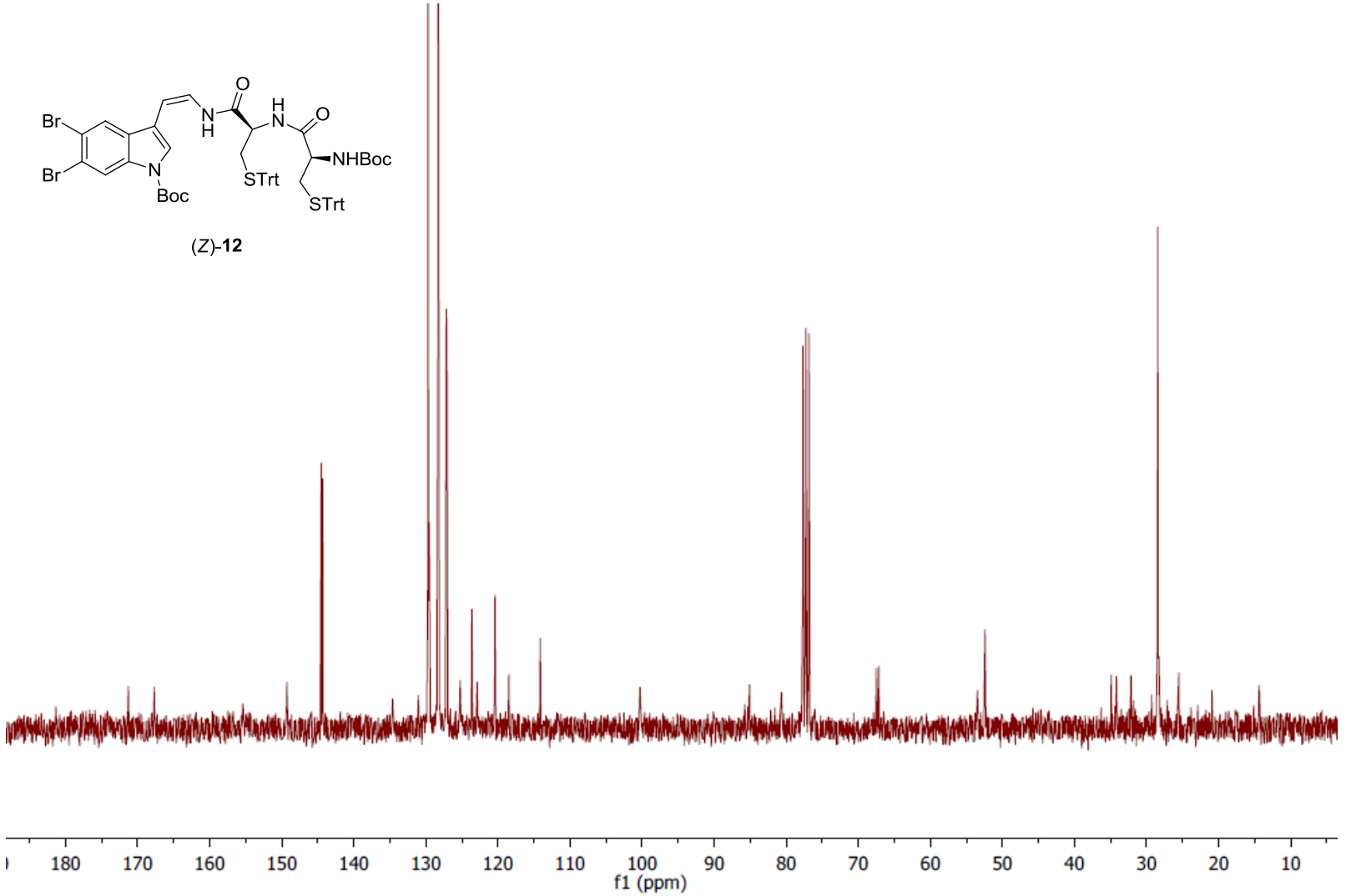


Figure S33. ^{1}H NMR spectrum of *tert*-butyl 5,6-dibromo-3-((6*R*,9*R*,*E*)-2,2-dimethyl-4,7,10-trioxo-6,9-bis((tritylthio)methyl)-3-oxa-5,8,11-triazatridec-12-en-13-yl)-1*H*-indole-1-carboxylate (*E*-**12**) (300 MHz, $CDCl_3$).

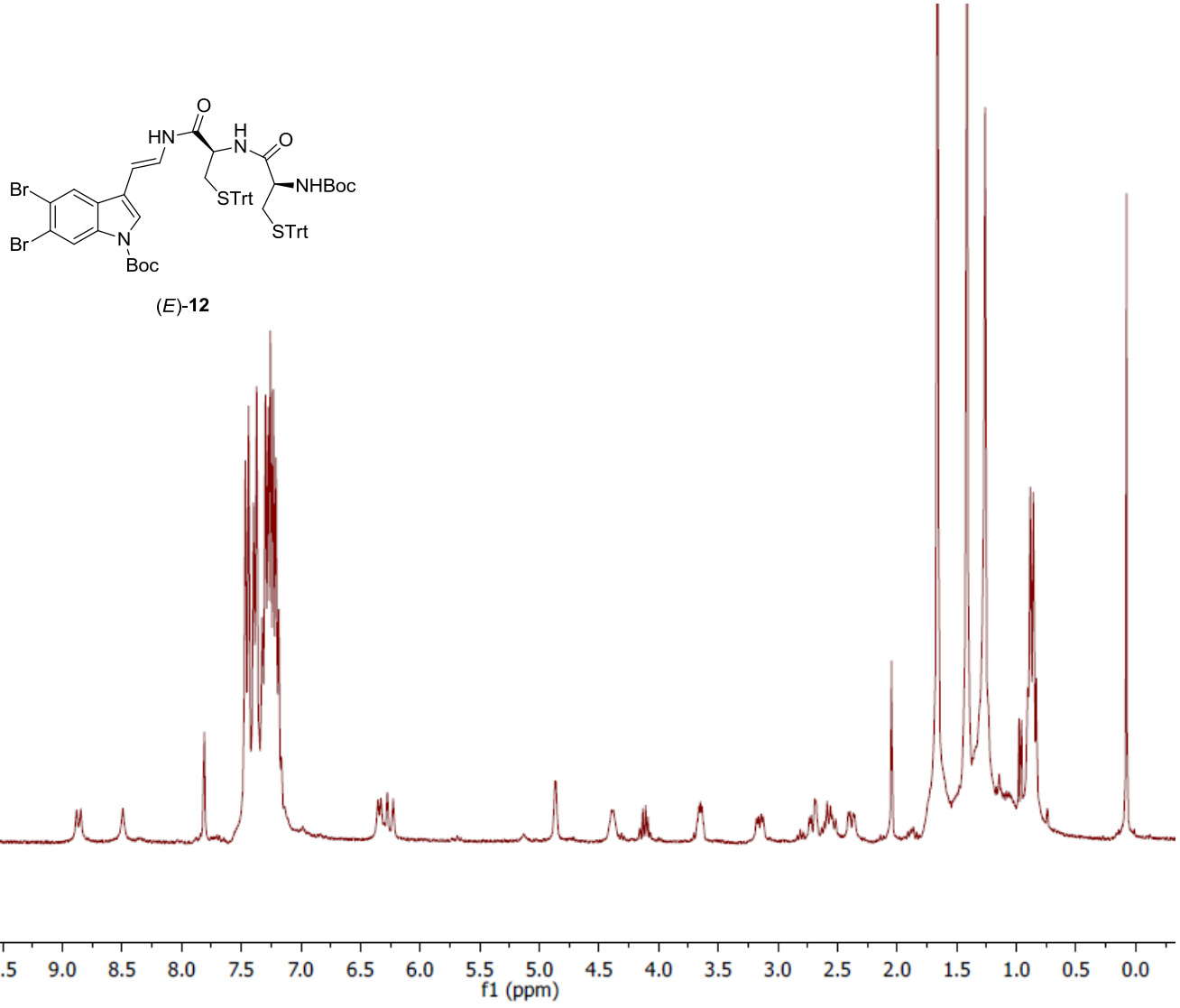


Figure S34. ^{1}H NMR spectrum of *tert*-butyl 5,6-dibromo-3-((*Z*)-2-((4*R*,7*R*)-7-((tert-butoxycarbonyl)amino)-6-oxo-1,2,5-dithiazocane-4-carboxamido)vinyl)-1*H*-indole-1-carboxylate (*Z*-**13**) (300 MHz, $CDCl_3$).

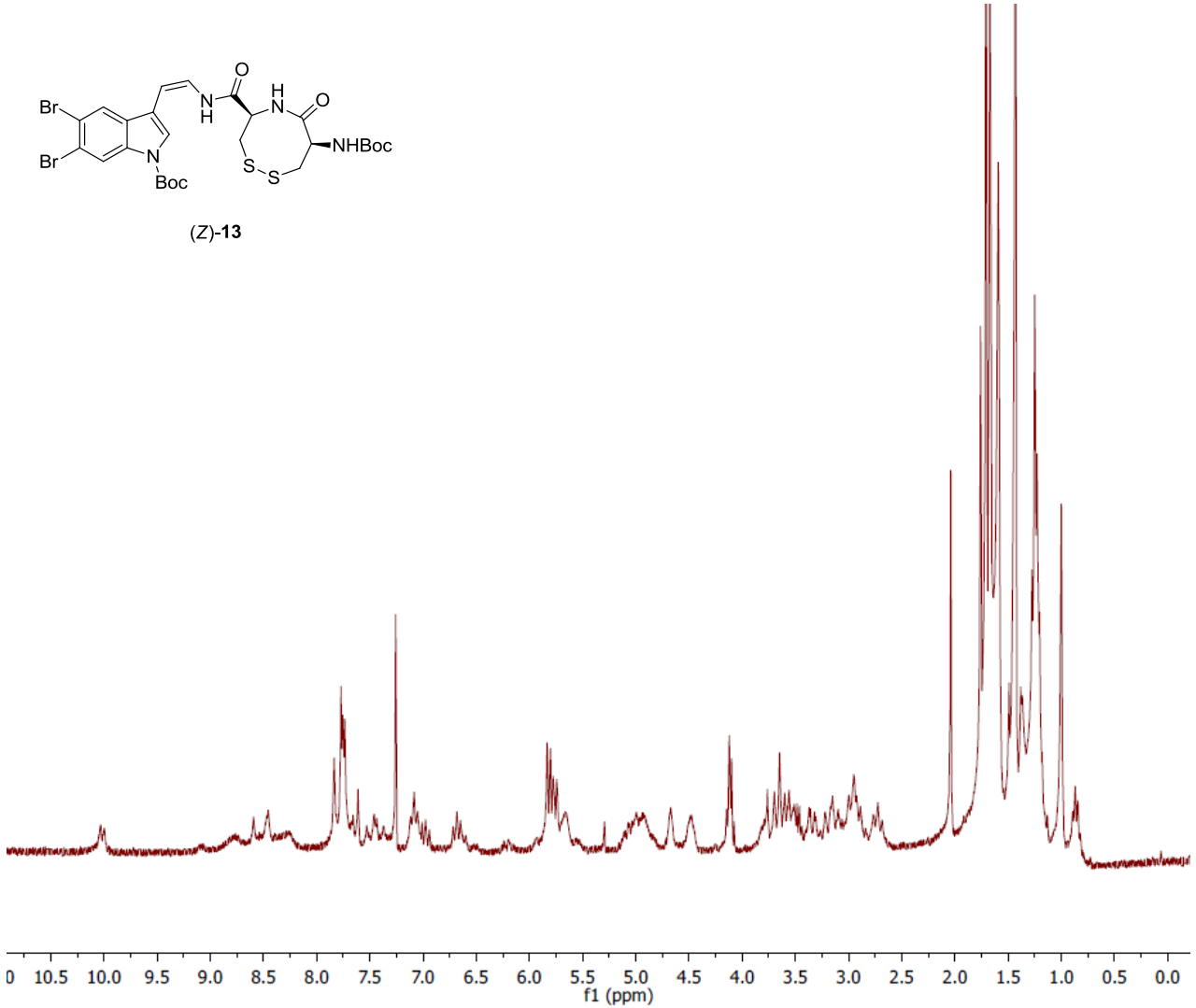


Figure S35. ^{13}C NMR spectrum of *tert*-butyl 5,6-dibromo-3-((*Z*)-2-((4*R*,7*R*)-7-((tert-butoxycarbonyl)amino)-6-oxo-1,2,5-dithiazocane-4-carboxamido)vinyl)-1*H*-indole-1-carboxylate (*Z*-**13**) (75 MHz, $CDCl_3$).

(*Z*)-**13**

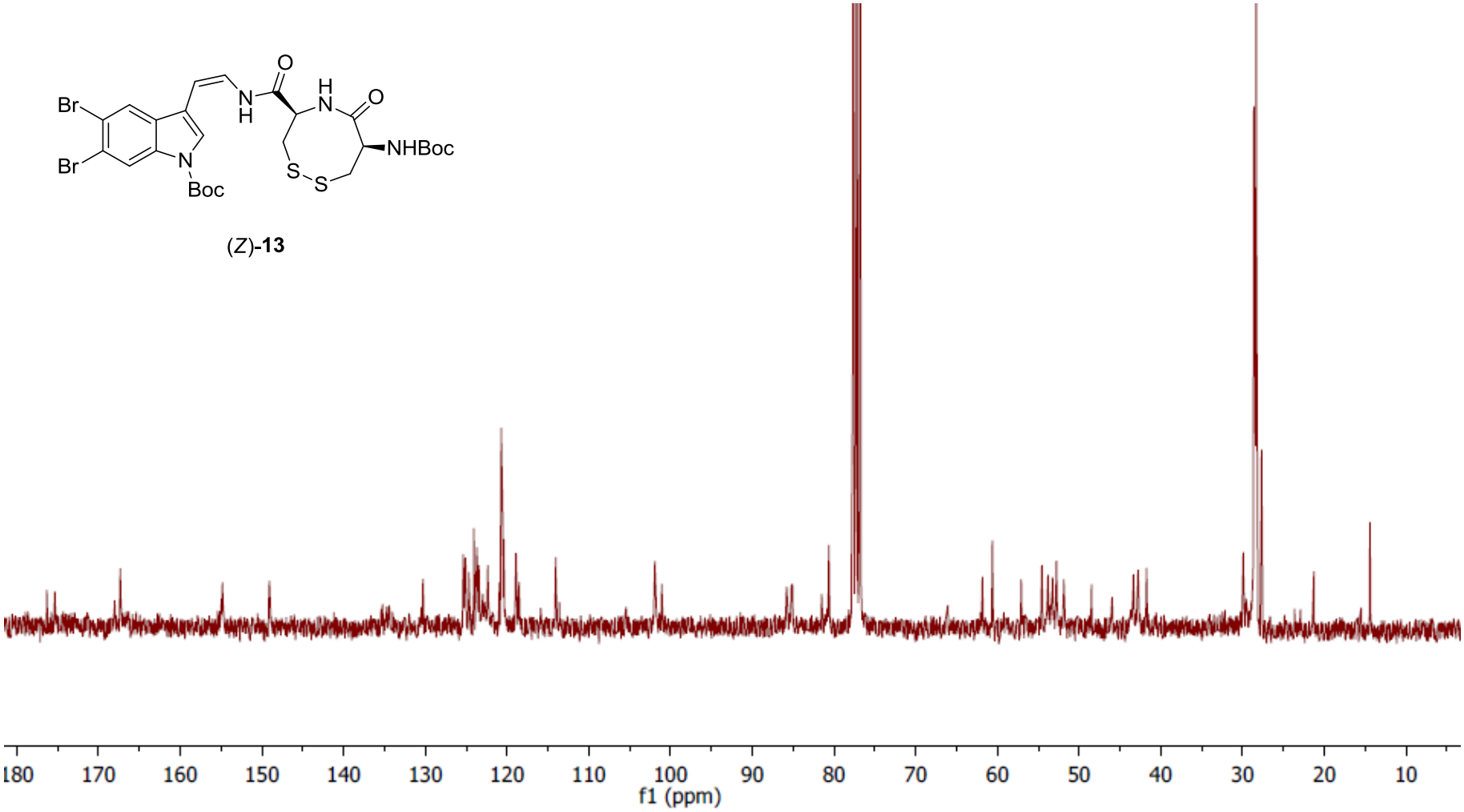


Figure S36. ^{1}H NMR spectrum of *tert*-butyl 5,6-dibromo-3-((*E*)-2-((4*R*,7*R*)-7-((tert-butoxycarbonyl)amino)-6-oxo-1,2,5-dithiazocane-4-carboxamido)vinyl)-1*H*-indole-1-carboxylate (*E*-**13**) (300 MHz, $CDCl_3$).

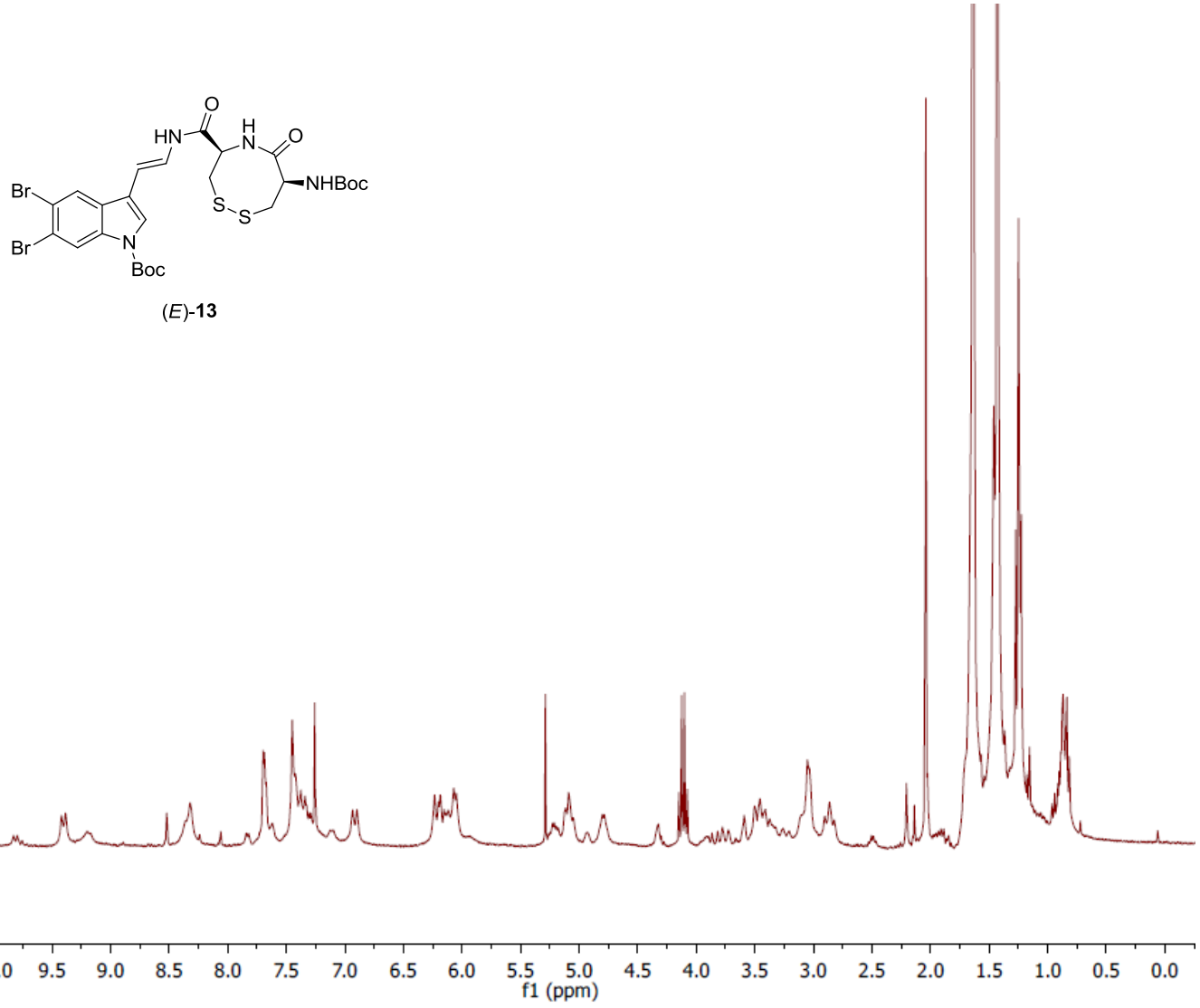


Figure S37. ^{13}C NMR spectrum of *tert*-butyl 5,6-dibromo-3-((*E*)-2-((4*R*,7*R*)-7-((tert-butoxycarbonyl)amino)-6-oxo-1,2,5-dithiazocane-4-carboxamido)vinyl)-1*H*-indole-1-carboxylate (*E*-**13**) (75 MHz, $CDCl_3$).

(*E*)-**13**

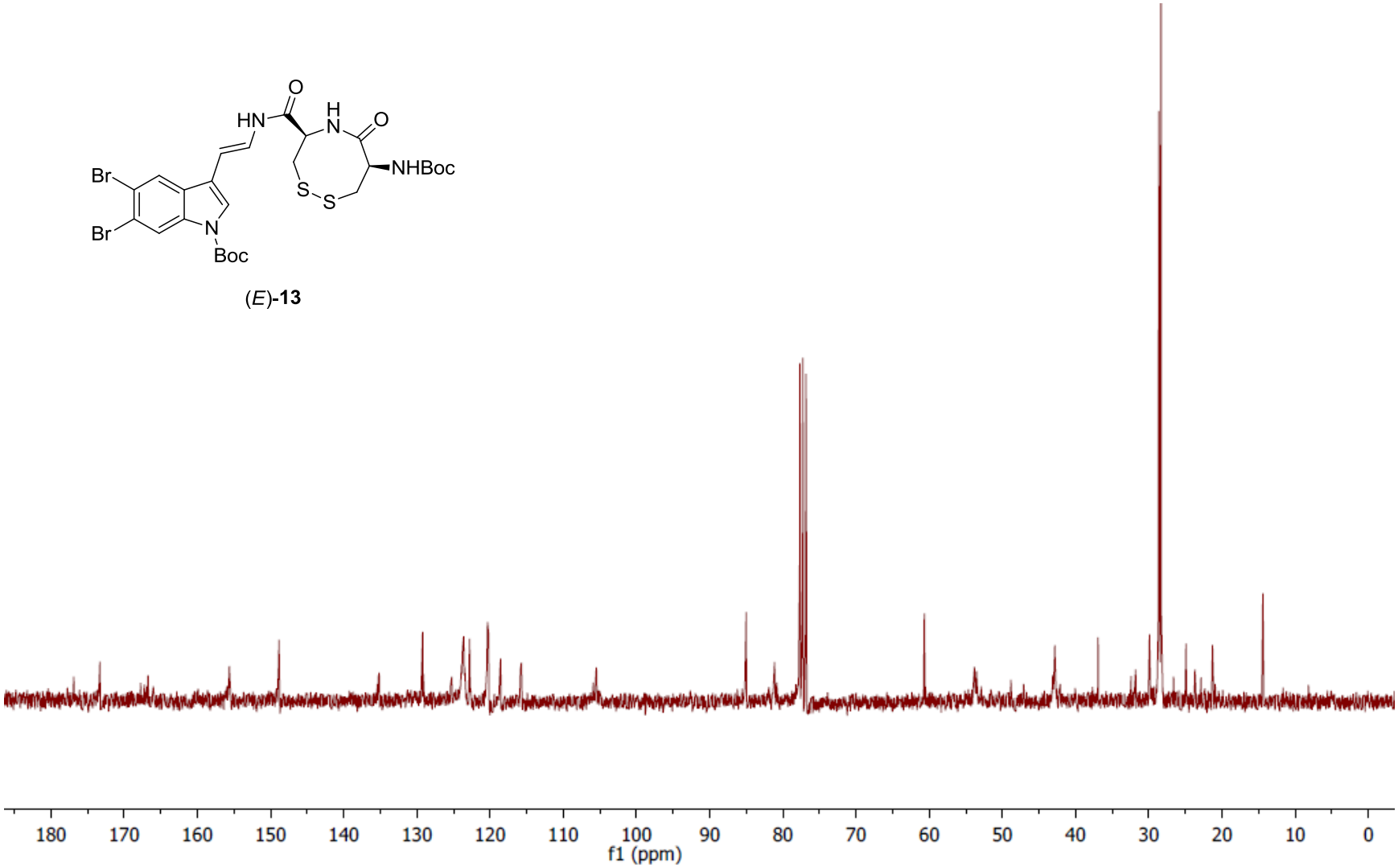


Figure S38. ^{1}H NMR spectra of synthetic *vs.* natural Tanjungide A.

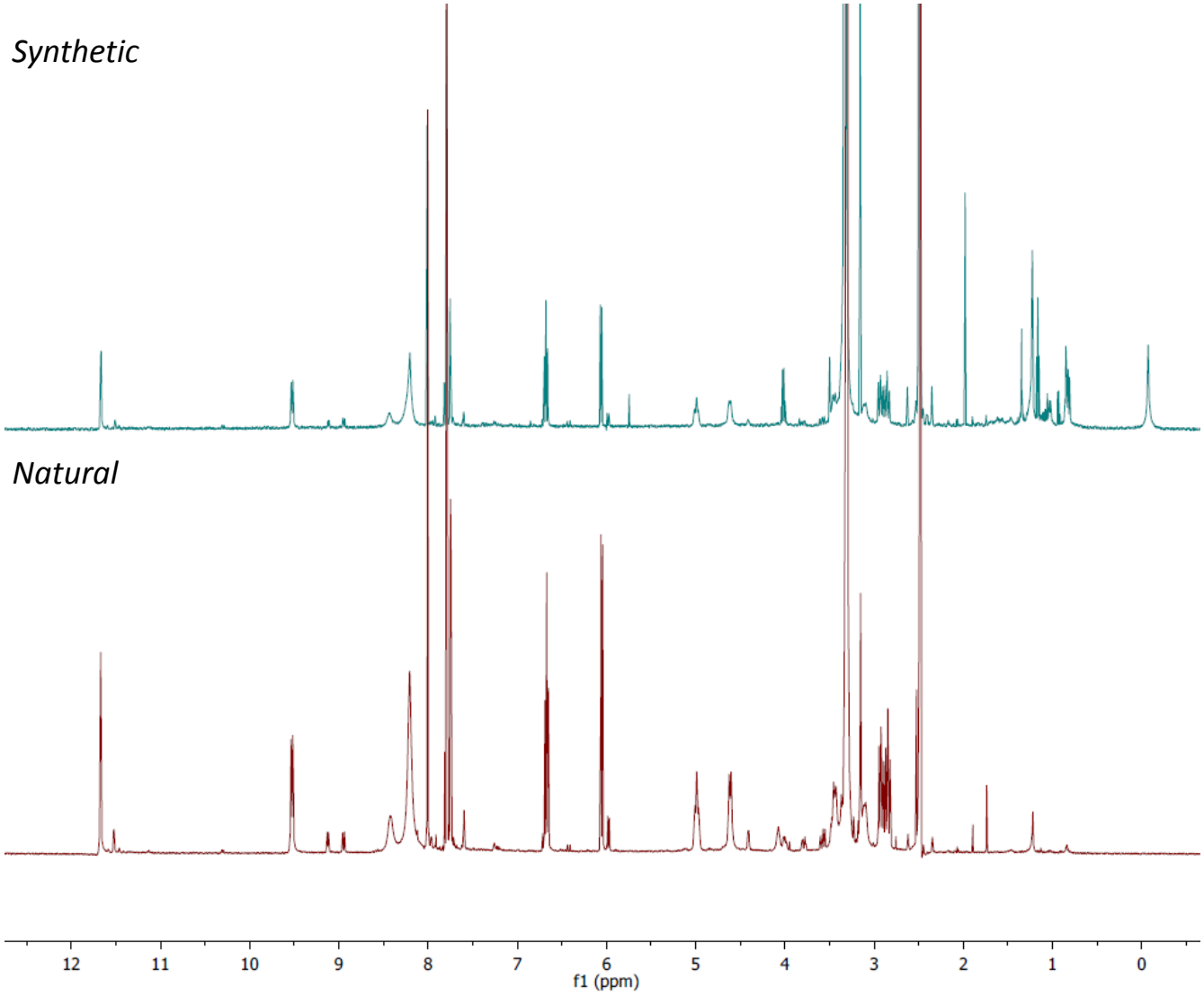


Figure S39. Marfey's reaction. Desthiotanjungide A.