# Supplementary Material

## Tedaniophorbasins A and B, novel fluorescent pteridine alkaloids incorporating a thiomorpholine from the sponge *Tedaniophorbas ceratosis*

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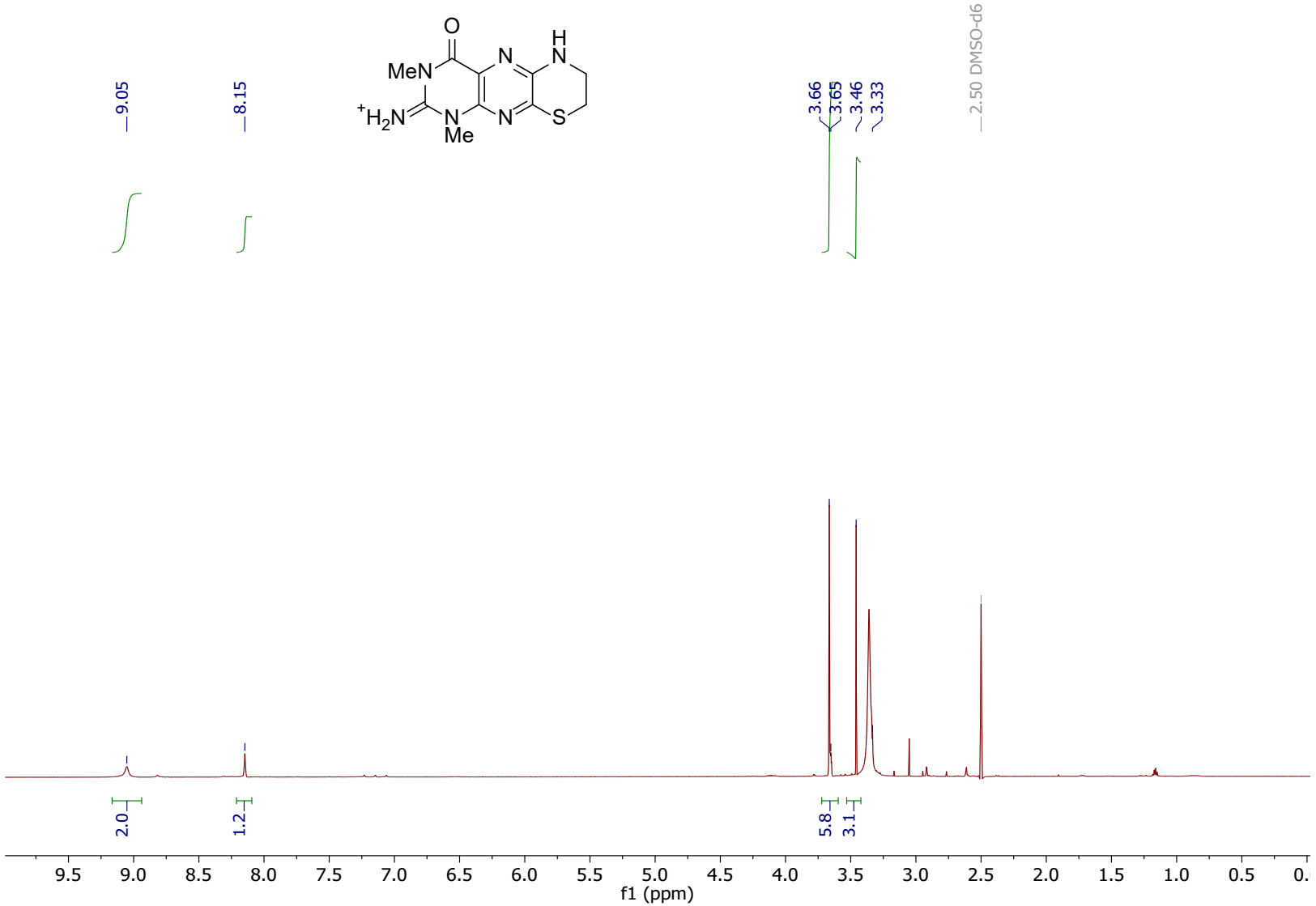



**Figure S1:** $^{1}$H NMR spectrum (600 MHz) of tedaniophorbasin A (**1**) in DMSO-$d_6$.

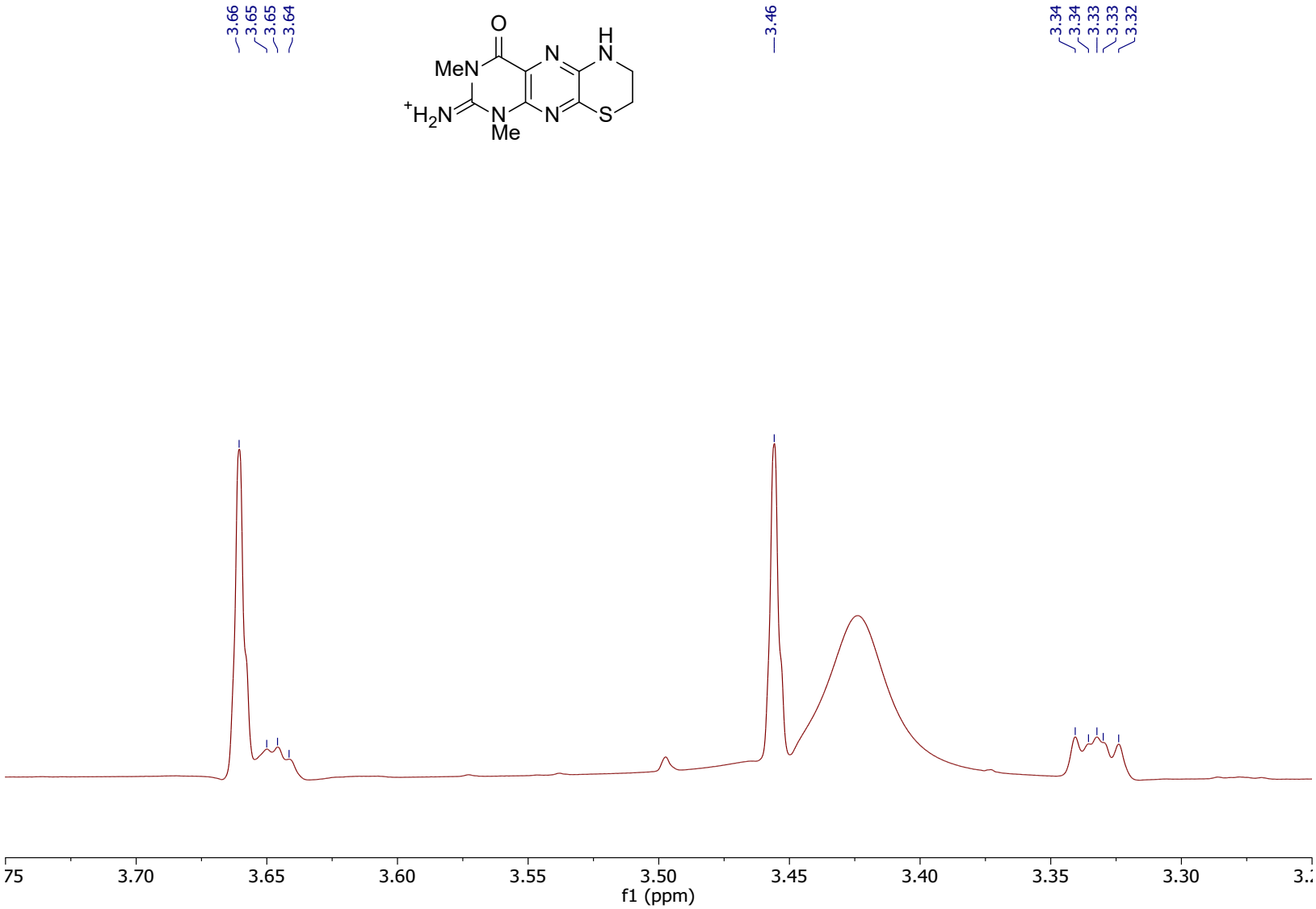



**Figure S2:** $^{1}$H NMR spectrum (600 MHz) expansion of tedaniophorbasin A (**1**) in DMSO-$d_6$.

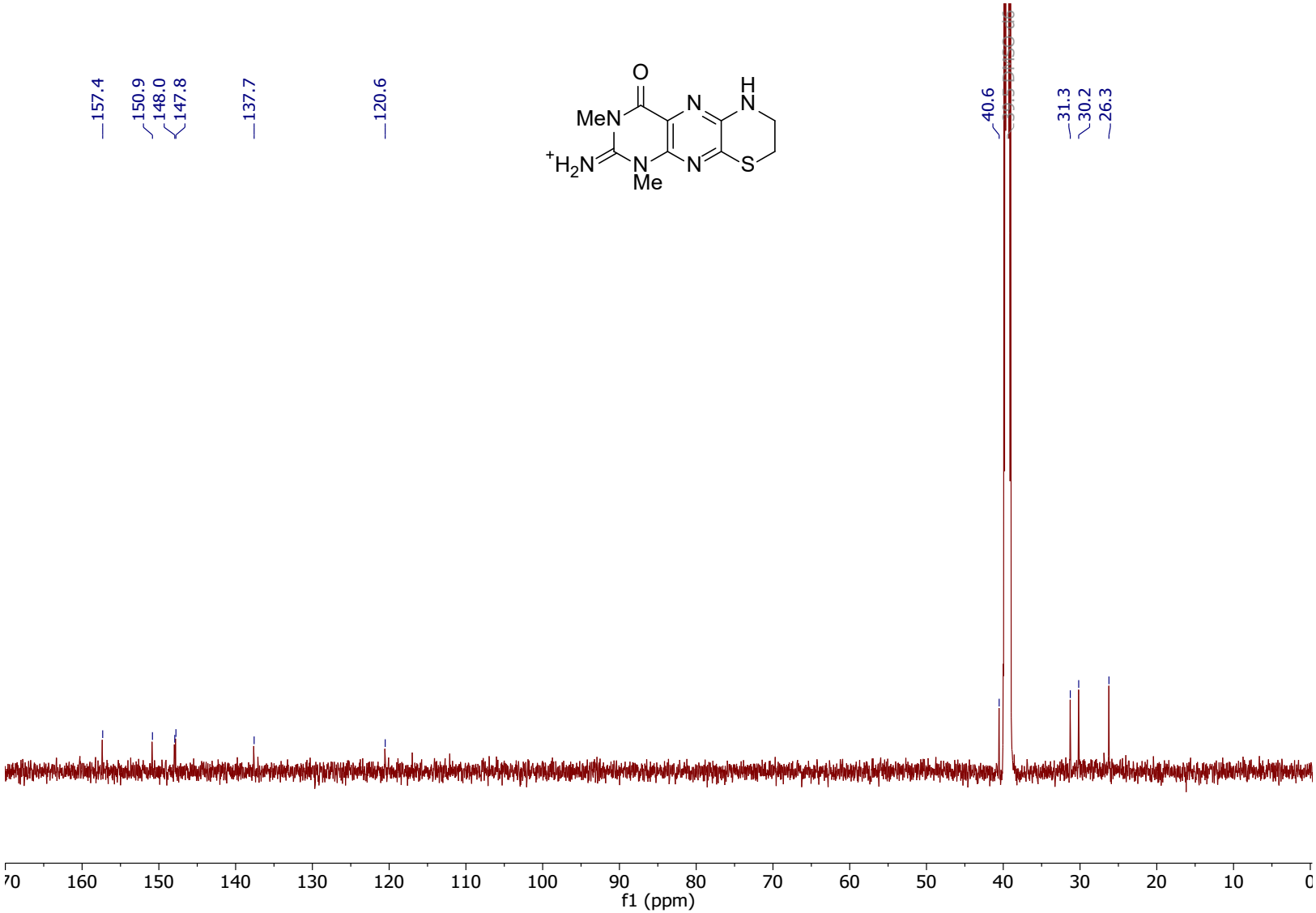



**Figure S3:** $^{13}$C NMR spectrum (150 MHz) of tedaniophorbasin A (**1**) in DMSO-$d_6$.

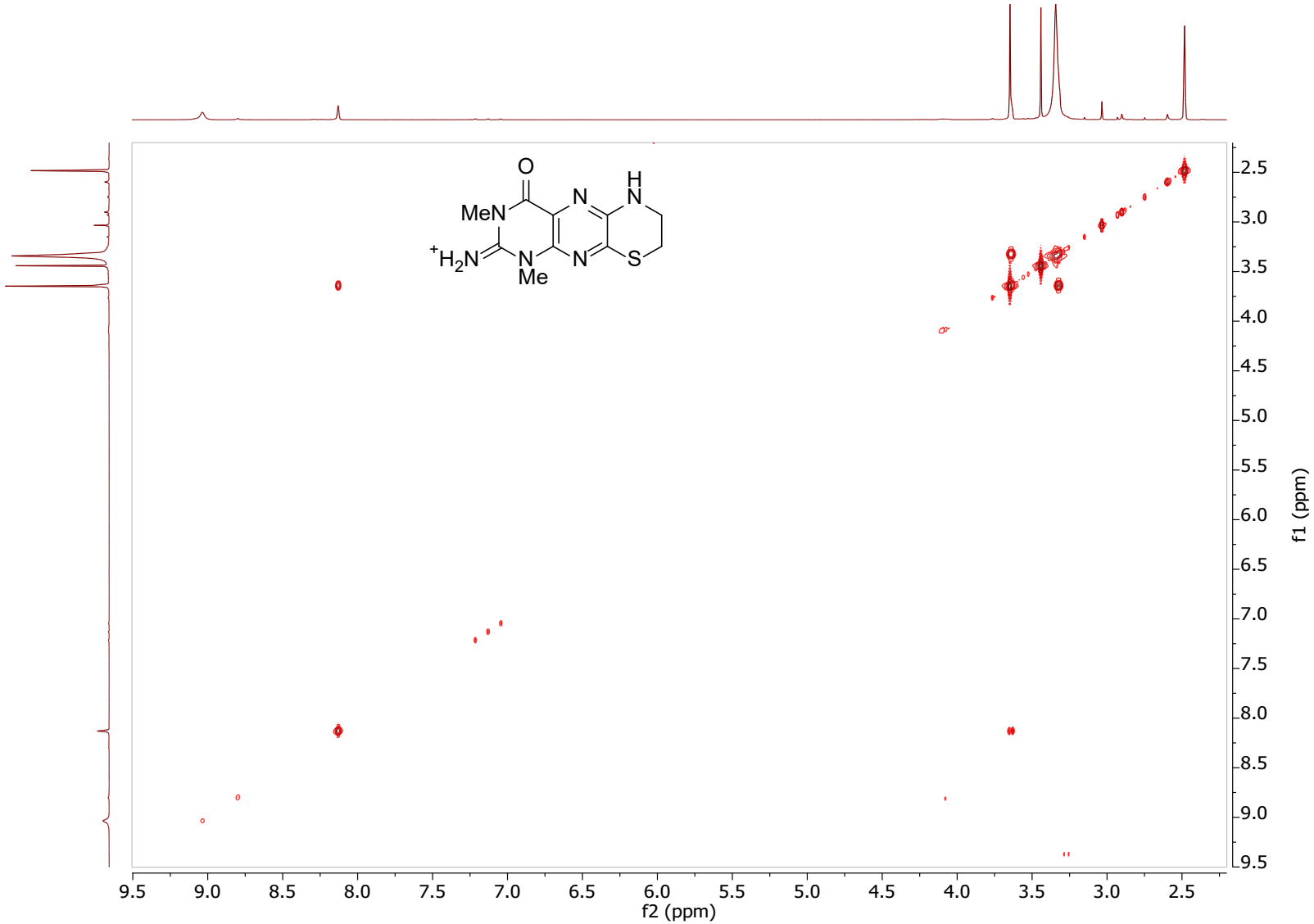



**Figure S4:** COSY NMR spectrum (600 MHz) of tedaniophorbasin A (**1**) in DMSO-$d_6$.

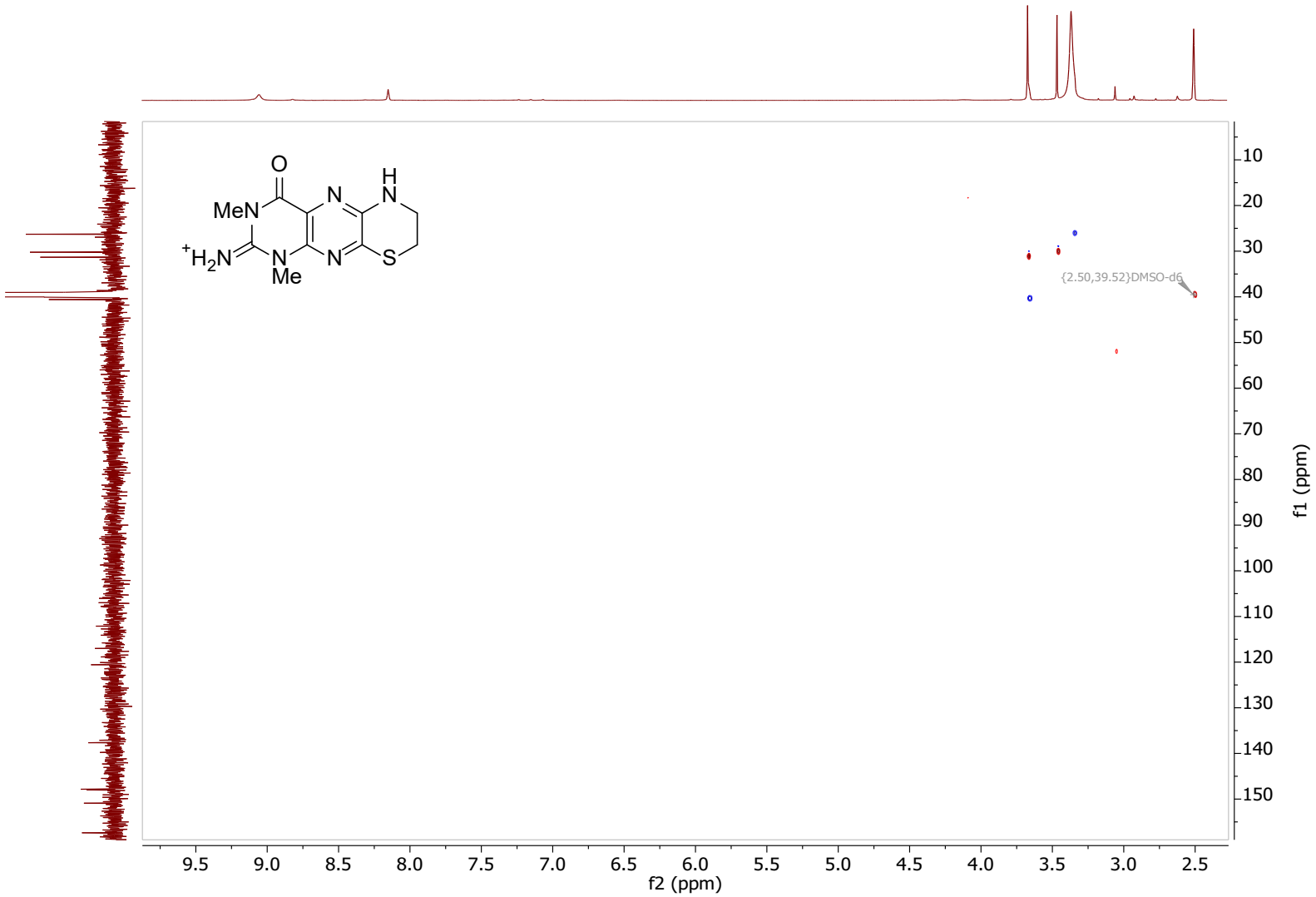



**Figure S5:** HSQC NMR spectrum (600 MHz) of tedaniophorbasin A (**1**) in DMSO-$d_6$.

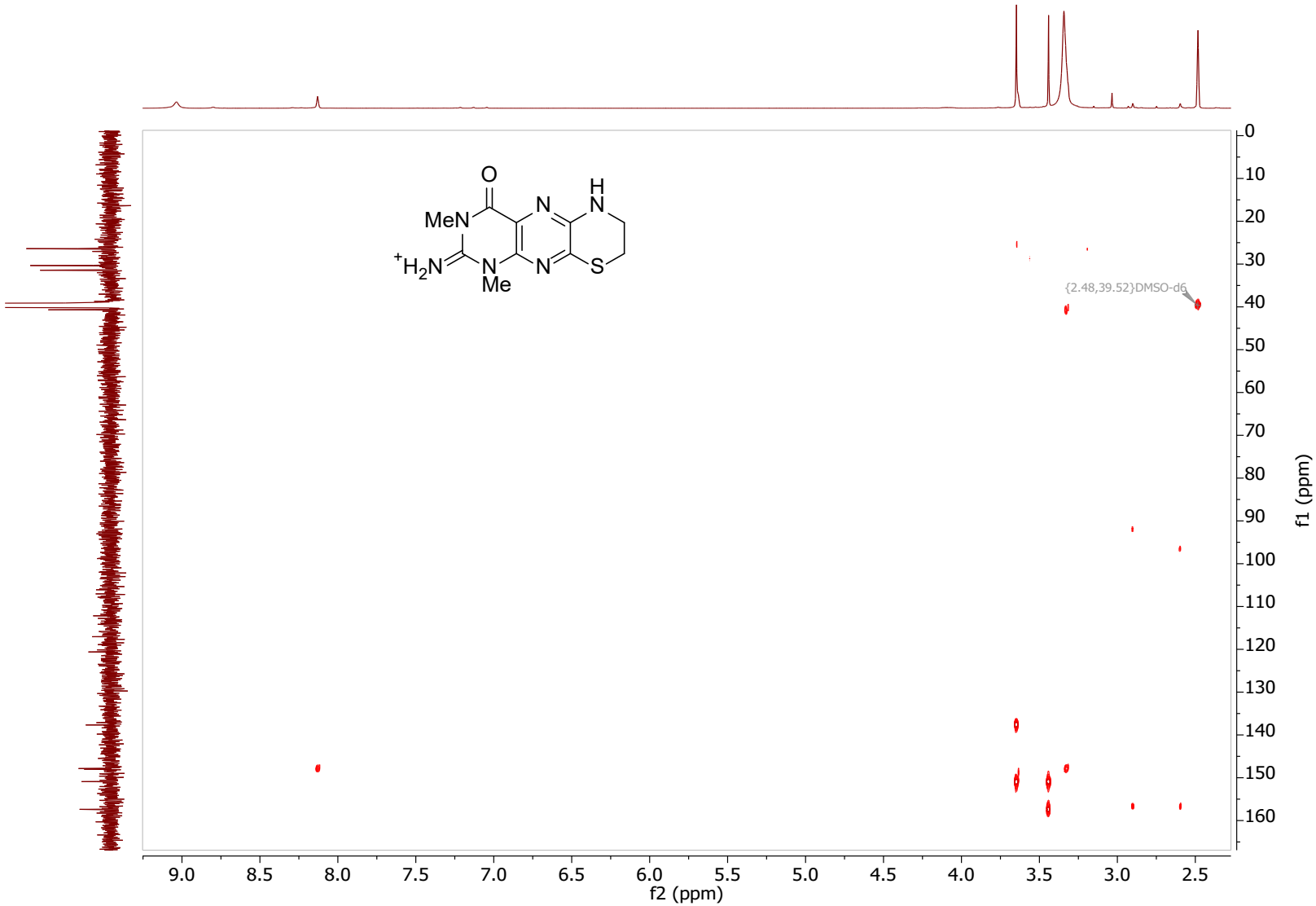



**Figure S6:** HMBC NMR spectrum (600 MHz) of tedaniophorbasin A (**1**) in DMSO-$d_6$.

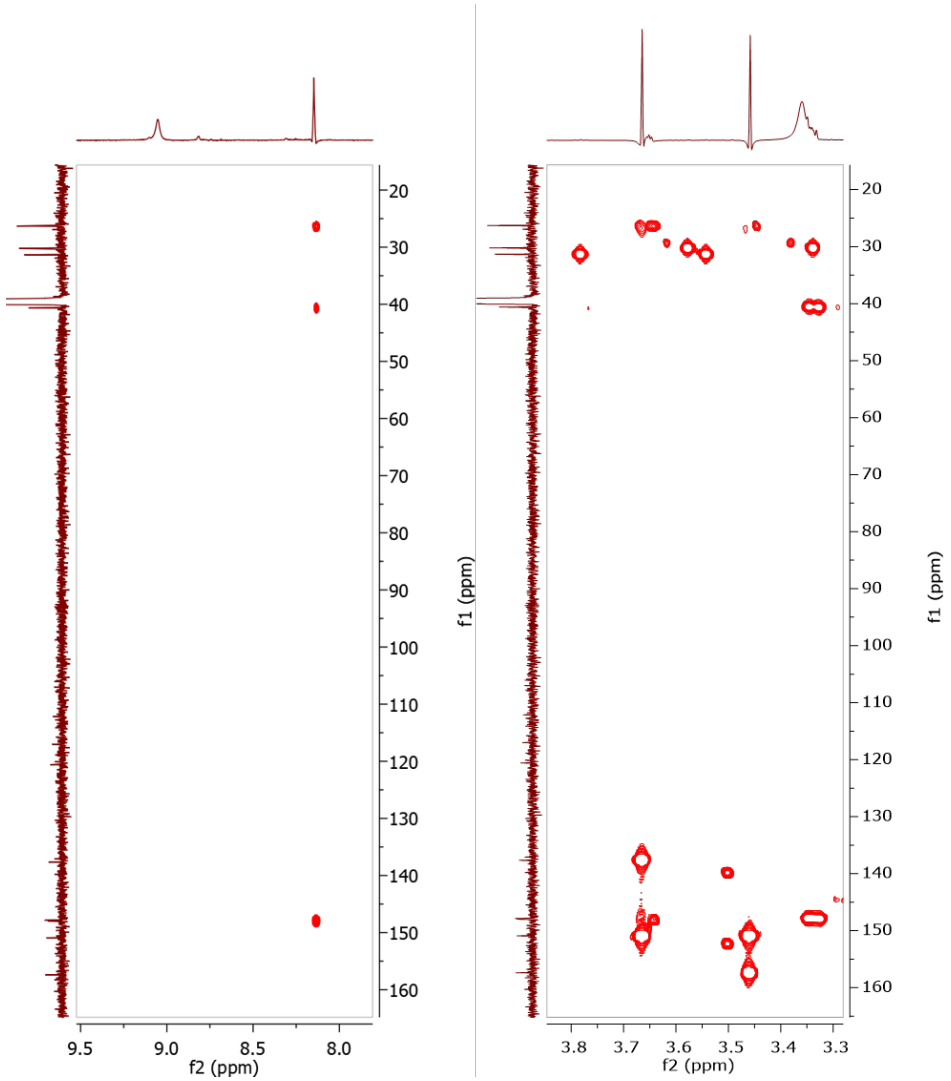



**Figure S7:** HMBC NMR spectrum (600 MHz) Expansions for tedaniophorbasin A (**1**) in DMSO-$d_6$.

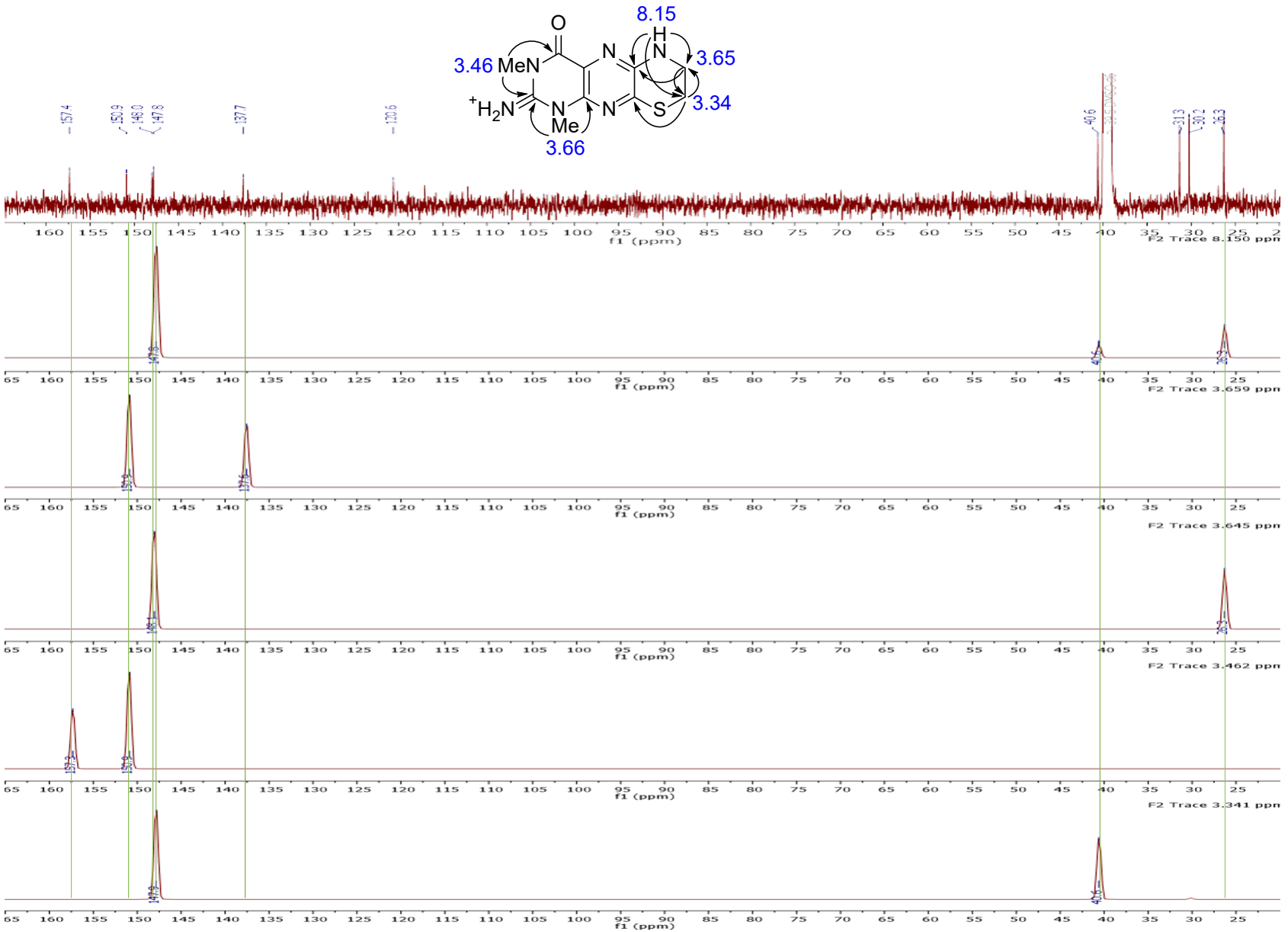



**Figure S8:** HMBC NMR Traces at each $^{1}$H resonance chemical shift (600 MHz) of tedaniophorbasin A (**1**) in DMSO-$d_6$.

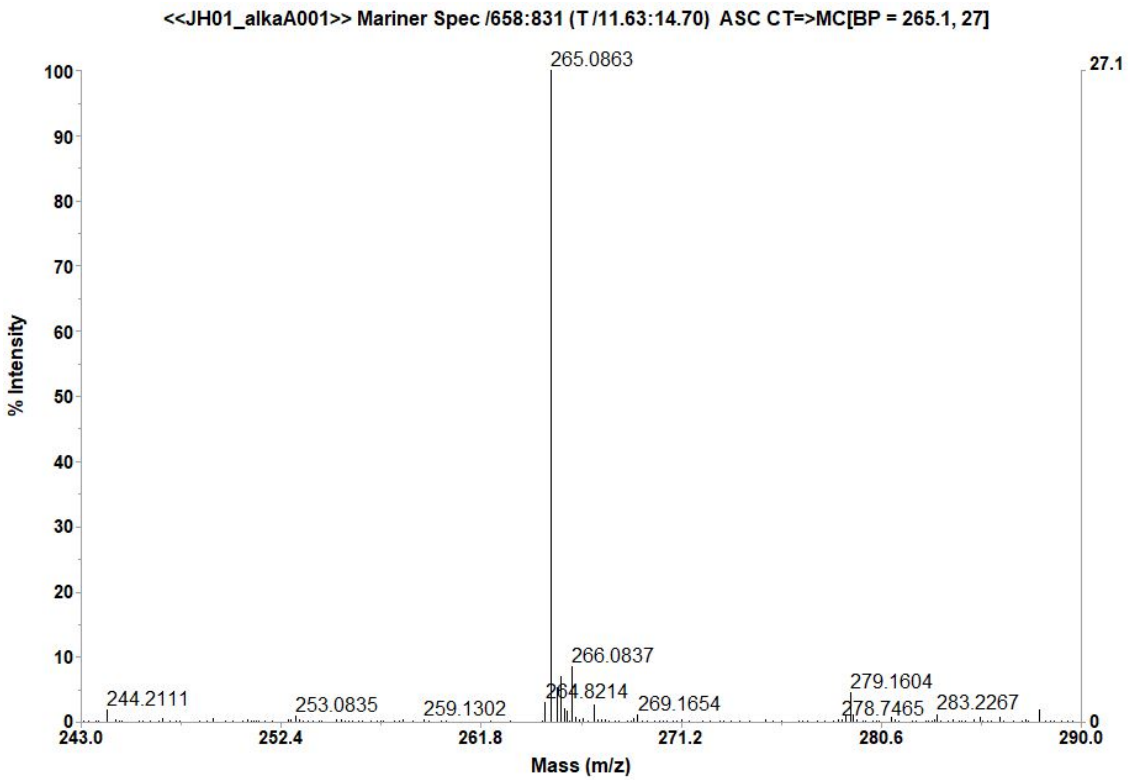



**Figure S9:** HRESIMS $[M+H]^+$ of tedaniophorbasin A (**1**)

| # | MF | Monoisotopic mass | Ionization | *m/z* | PPM | mDa | unsaturation |
|---|---|---|---|---|---|---|---|
| 1 | $C_2H_9N_{12}O_4$ | 265.0870 | $H^+$ | 265.0864 | -0.46 | -0.12 | 4.5 |
| 2 | $C_{10}H_{21}N_2S_3$ | 265.0867 | $H^+$ | 265.0861 | 0.61 | 0.16 | 1.5 |
| 3 | $C_{10}H_{13}N_6OS$ | 265.0872 | $H^+$ | 265.0866 | -1.16 | -0.31 | 7.5 |
| 4 | $C_{17}H_{13}O_3$ | 265.0865 | $H^+$ | 265.0859 | 1.43 | 0.38 | 11.5 |
| 5 | $C_9H_{17}N_2O_5S$ | 265.0858 | $H^+$ | 265.0853 | 3.89 | 1.03 | 2.5 |

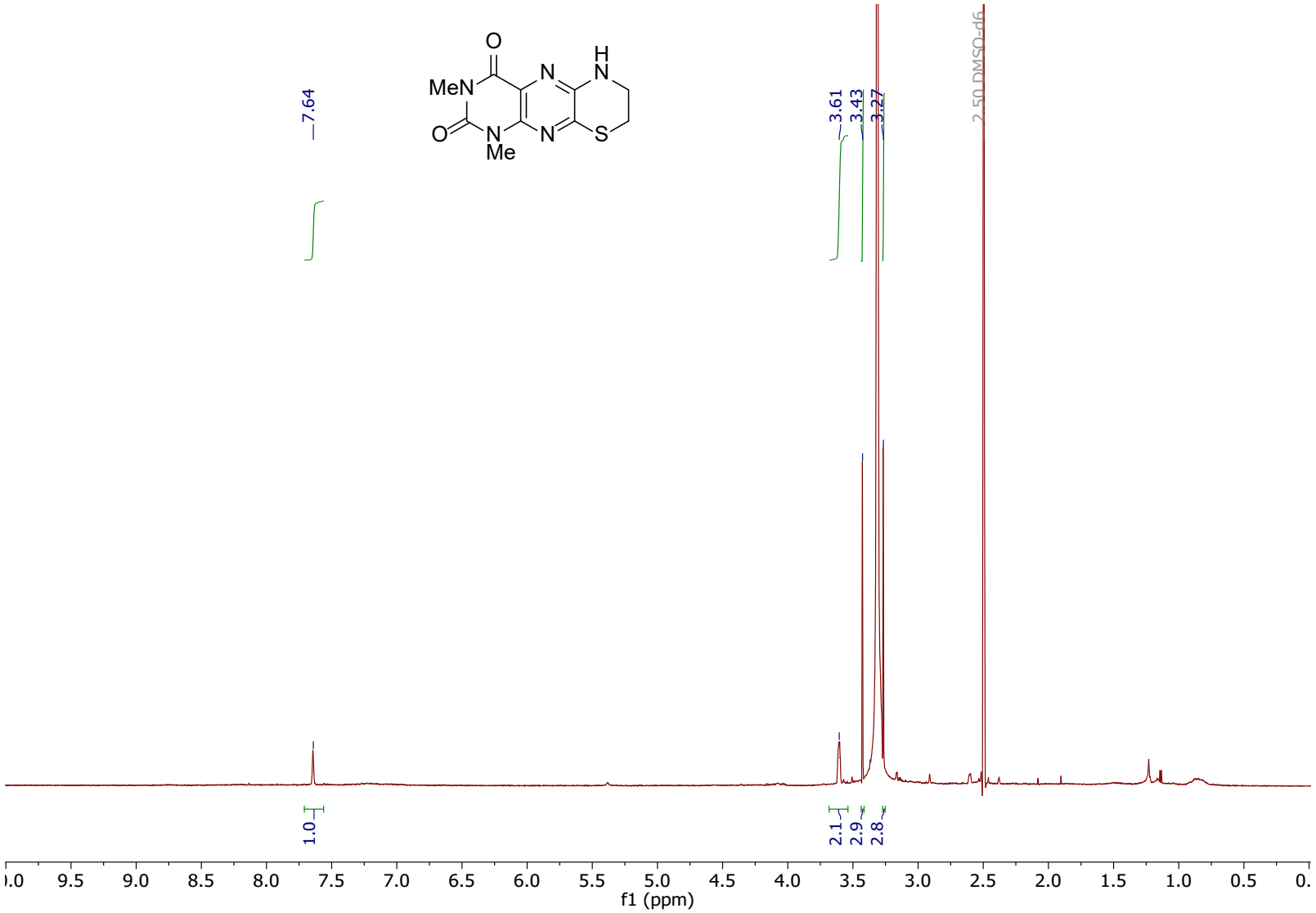



**Figure S10:** [1]H NMR spectrum (600 MHz) of tedaniophorbasin B (**2**) in DMSO-$d_6$.

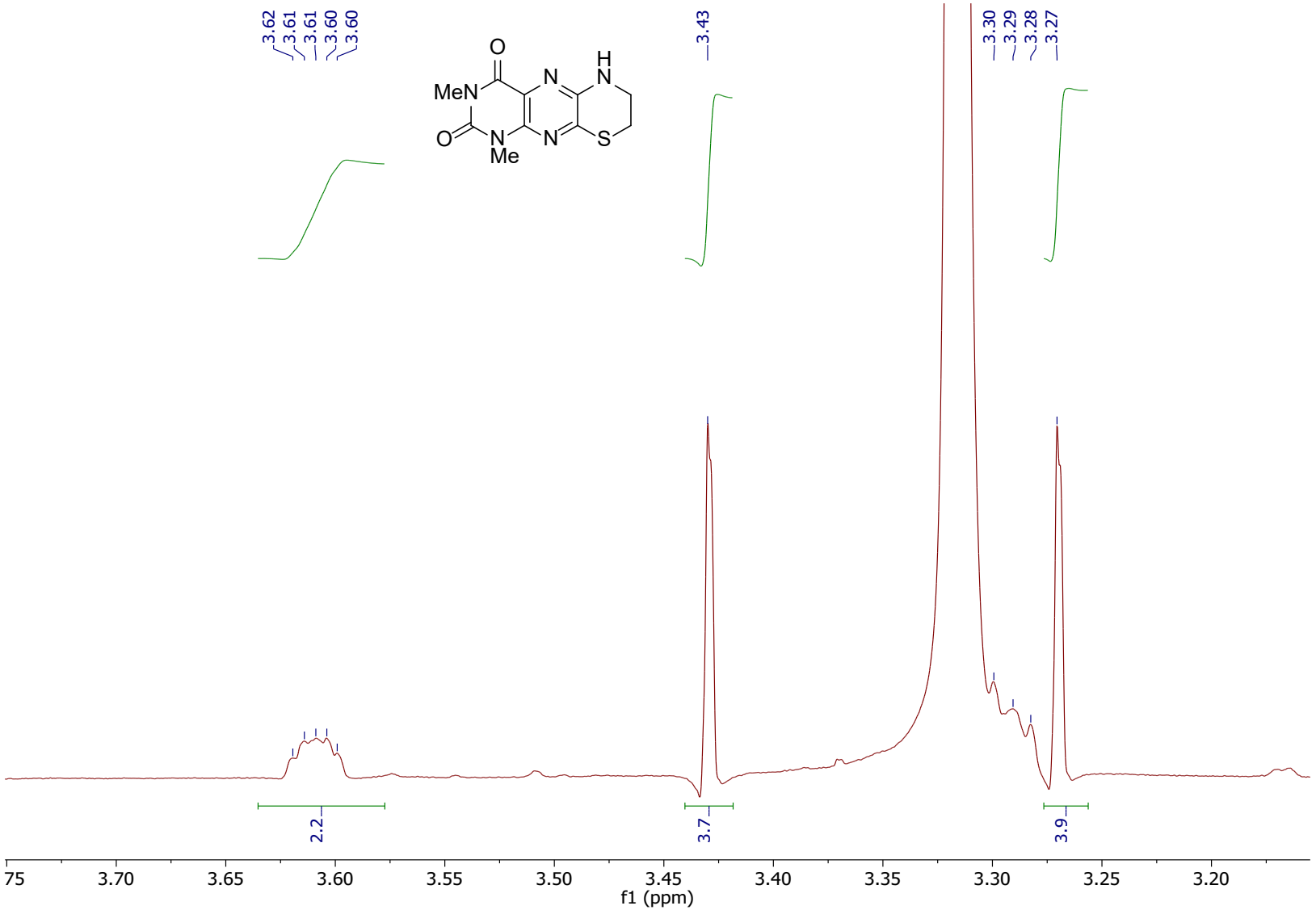



**Figure S11:** [1]H NMR spectrum (600 MHz) expansion of tedaniophorbasin B (**2**) in DMSO-$d_6$.

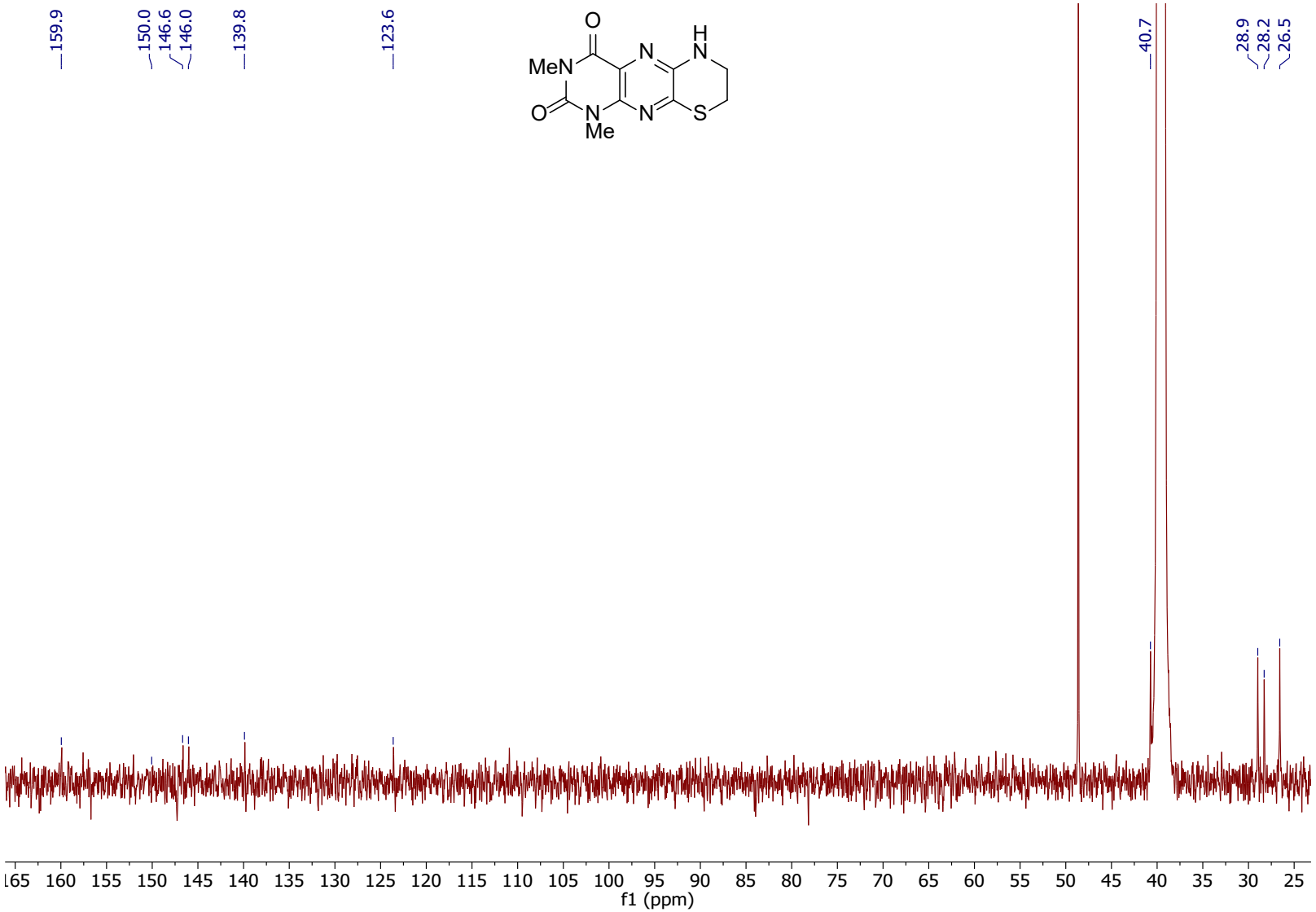



**Figure S12:** $^{13}$C NMR spectrum (150 MHz) of tedaniophorbasin B (**2**) in DMSO-$d_6$.

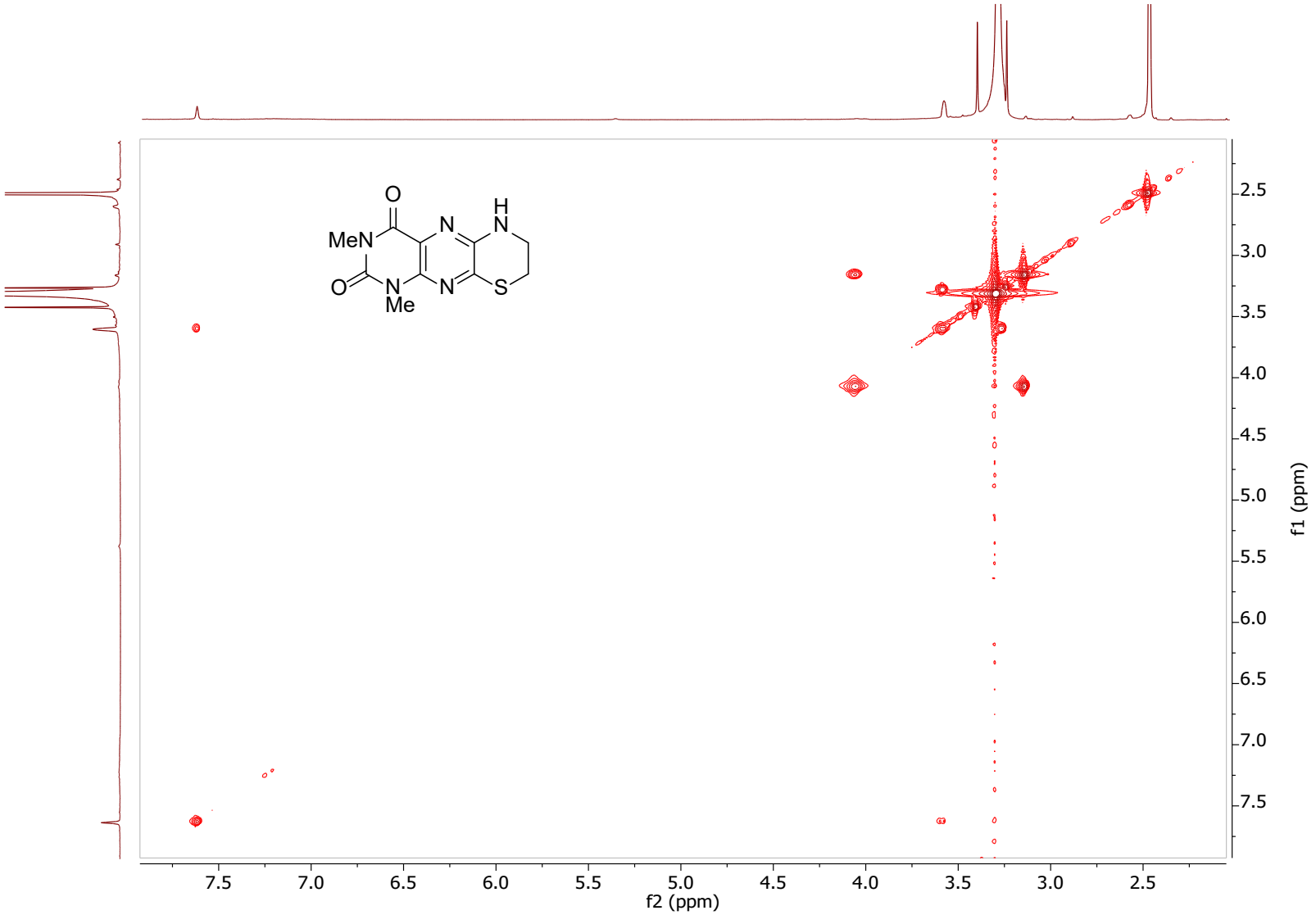



**Figure S13:** COSY NMR spectrum (600 MHz) of tedaniophorbasin B (**2**) in DMSO-$d_6$.

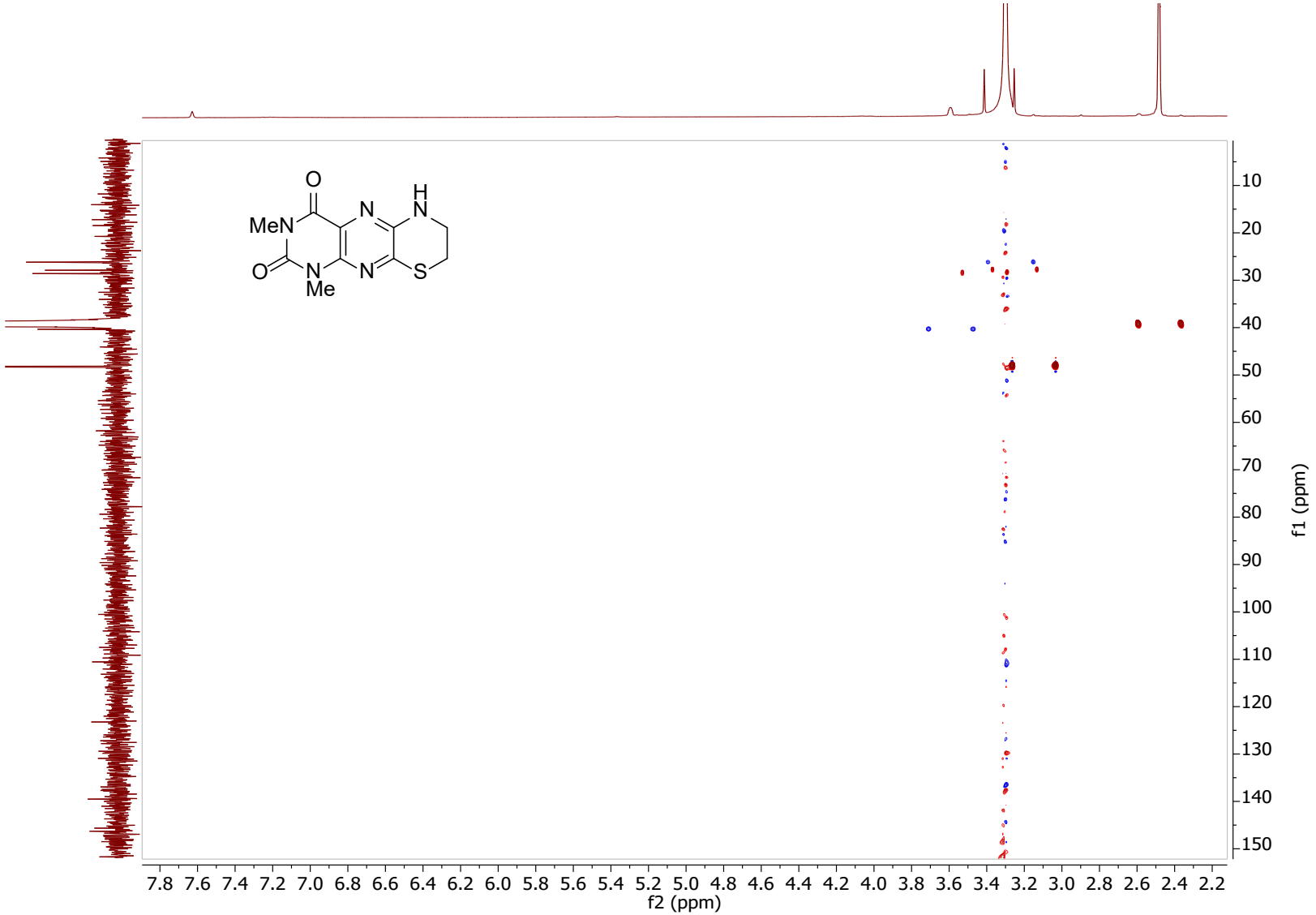



**Figure S14:** Coupled Edited HSQC NMR spectrum (600 MHz) of tedaniophorbasin B (**2**) in DMSO-$d_6$.

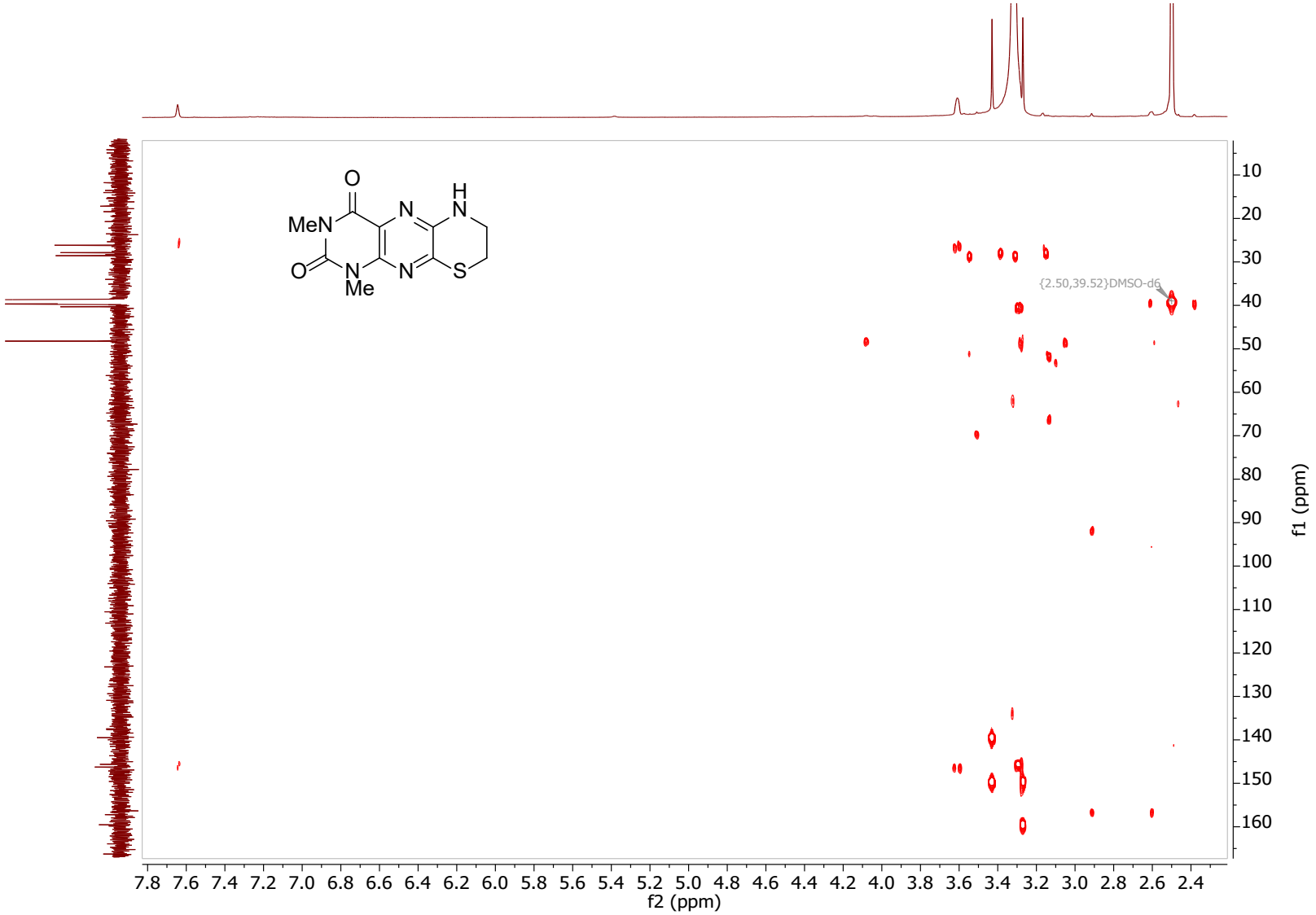



**Figure S15:** HMBC NMR spectrum (600 MHz) of tedaniophorbasin B (**2**) in DMSO-$d_6$.

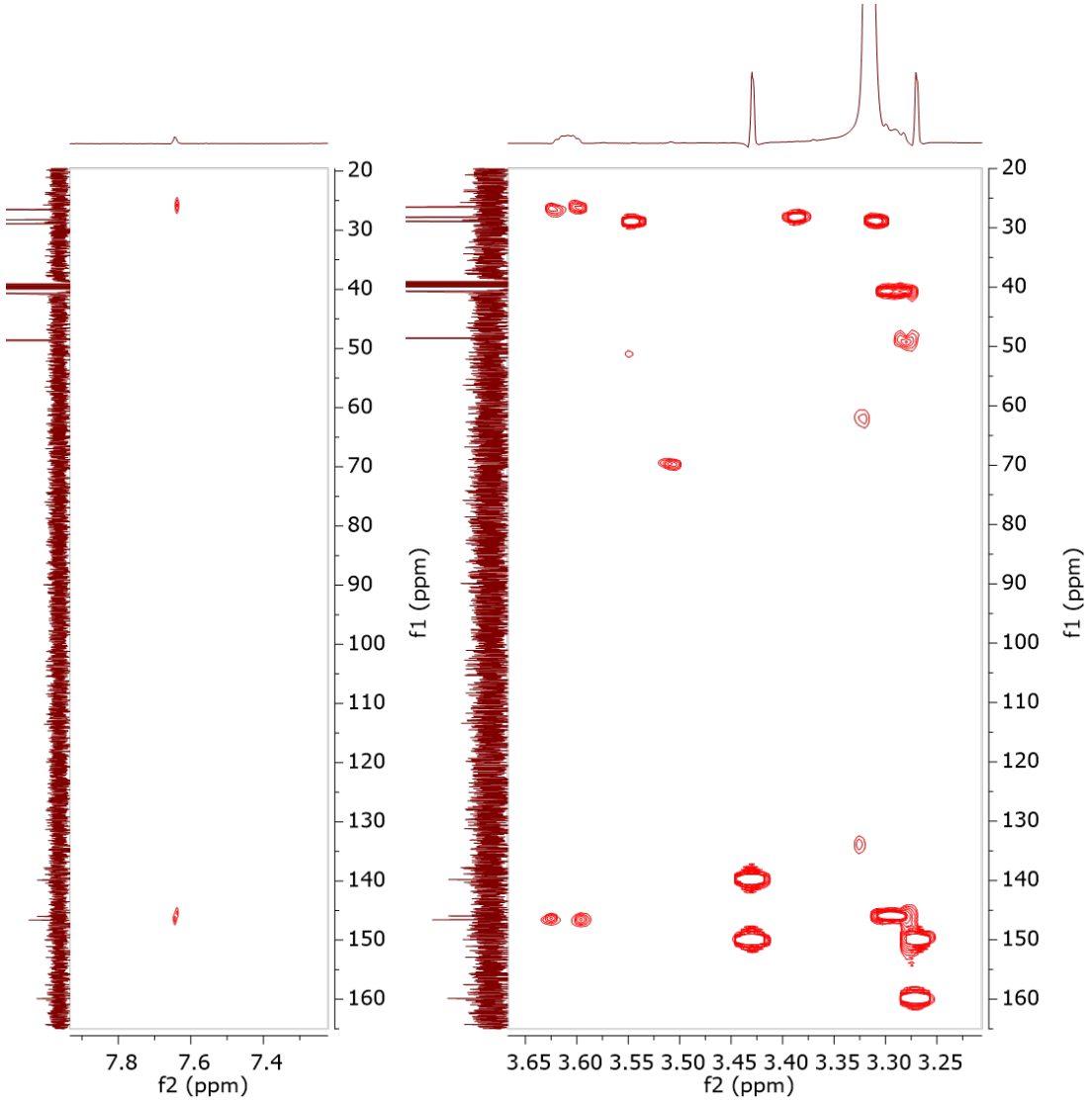



**Figure S16:** HMBC NMR spectrum (600 MHz) Expansions for tedaniophorbasin B (**2**) in DMSO-$d_6$.

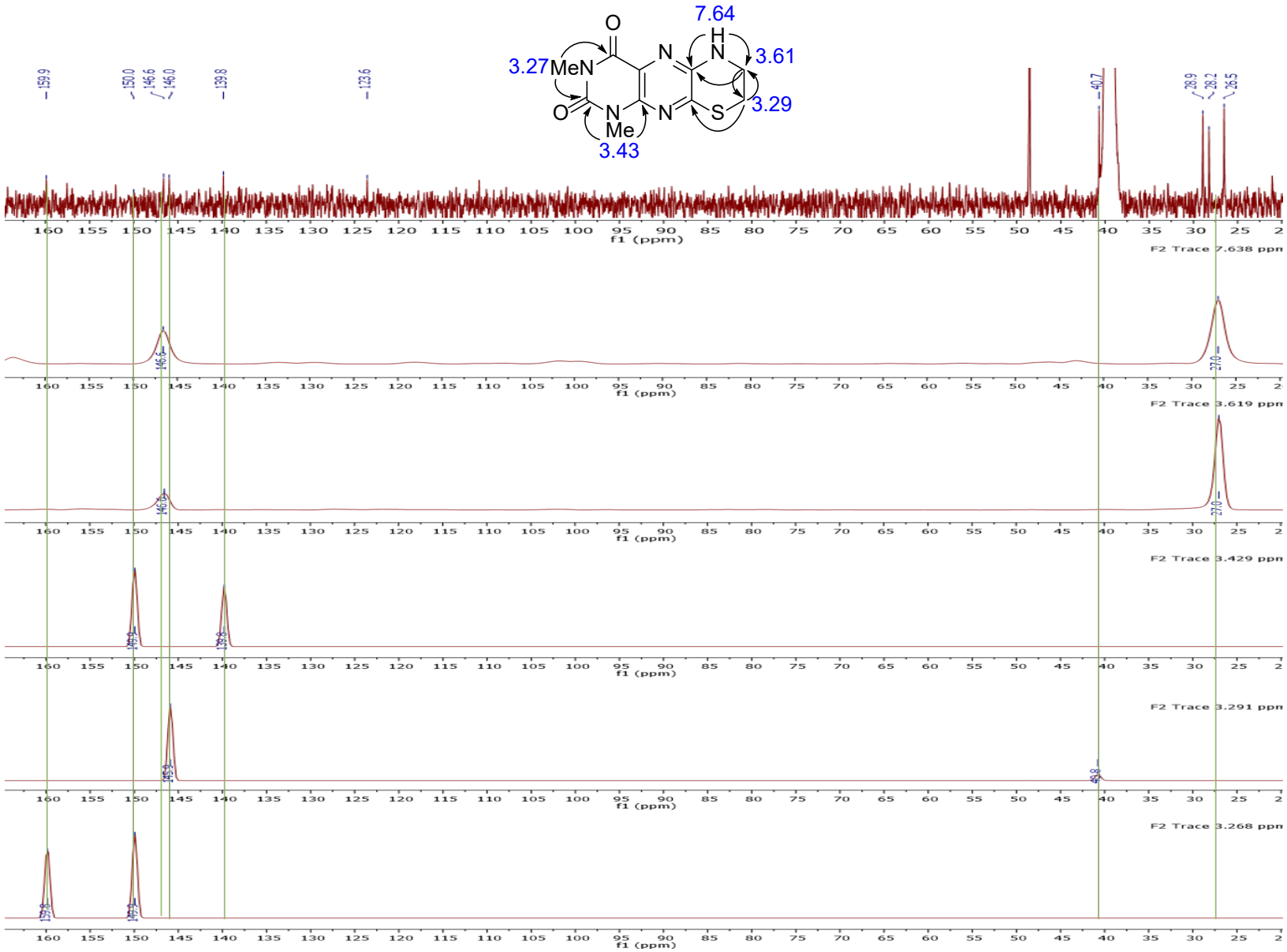



**Figure S17:** HMBC NMR Traces at each $^{1}$H resonance chemical shift (600 MHz) of tedaniophorbasin B (**2**) in DMSO-$d_6$

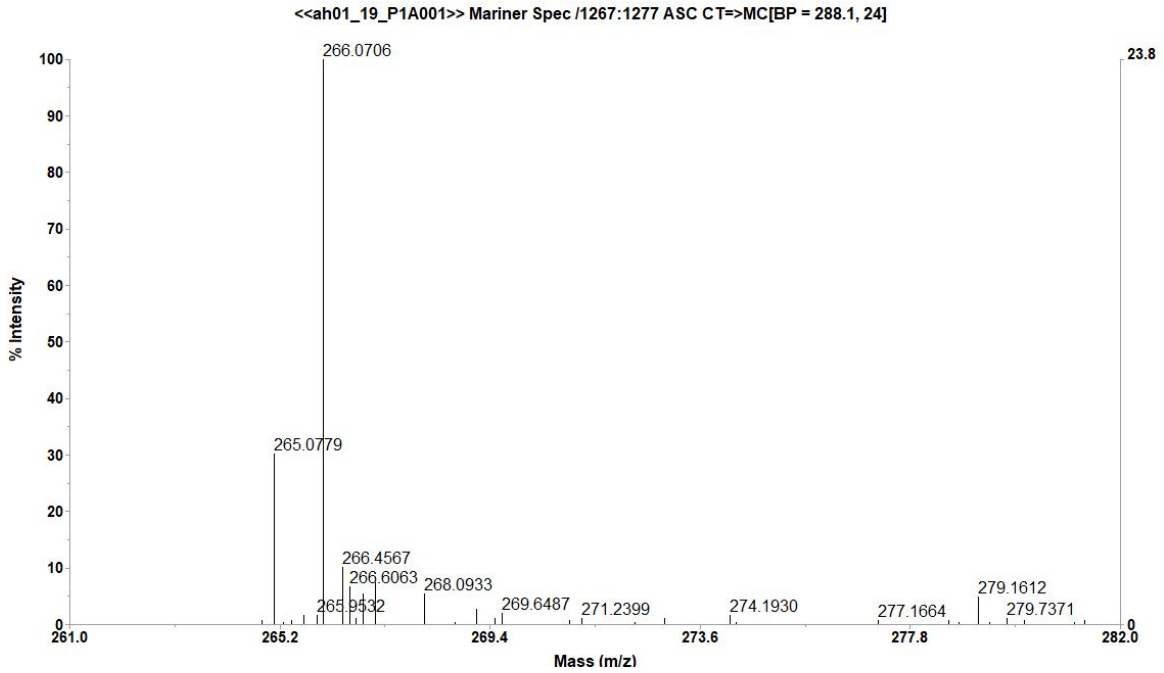
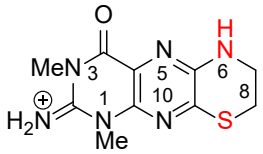



**Figure S18:** HRESIMS $[M+H]^+$ of tedaniophorbasin B (**2**)

| # | MF | Monoisotopic mass | Ionization | *m/z* | PPM | mDa | unsaturation |
|---|---|---|---|---|---|---|---|
| 1 | $C_{10}H_{12}N_5O_2S$ | 266.0712 | $H^+$ | 266.0706 | -0.08 | -0.02 | 7.5 |
| 2 | $C_2H_8N_{11}O_5$ | 266.0710 | $H^+$ | 266.0704 | 0.61 | 0.16 | 4.5 |
| 3 | $CH_2N_{18}$ | 266.0710 | $H^+$ | 266.0704 | 0.63 | 0.17 | 10 |
| 4 | $C_{10}H_{20}NOS_3$ | 266.0707 | $H^+$ | 266.0702 | 1.68 | 0.45 | 1.5 |
| 5 | $C_{18}H_8N_3$ | 266.0718 | $H^+$ | 266.0713 | -2.53 | -0.67 | 16.5 |

**Calculated DFT (GIAO) $^{13}$C NMR Chemical Shifts for 1a, 1a', 2a and 2a'.**

**Table S1. Tedaniophorbasin A (1a) DFT vs Experimental $^{13}$C NMR data for 1 (DMSO-$d_6$).**

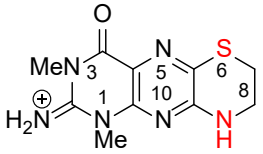



**1a**

| Atom numbers | Experimental $^{13}$C chemical shift | DFT Calcd. $^{13}$C chemical shifts[3] | Absolute Error values |
|---|---|---|---|
| 1 (N-$CH_3$) | 31.3 | 28.1 | 3.2 |
| 2 | 151.0 | 150.0 | 1.0 |
| 3 (N-$CH_3$) | 30.3 | 27.3 | 3.0 |
| 4 | 157.4 | 154.0 | 3.4 |
| 4a | 120.6 | 124.2 | 3.6 |
| 5a | 148.0* | 150.0 | 2.0 |
| 7 | 40.6 | 40.3 | 0.3 |
| 8 | 26.3 | 25.1 | 1.2 |
| 9a | 147.9* | 148.5 | 0.6 |
| 10a | 137.6 | 137.6 | 0.0 |

**$^{13}$C MAE = 1.8**

**Table S2. Tedaniophorbasin A (1a') DFT vs Experimental $^{13}$C NMR data for 1 (DMSO-$d_6$).**



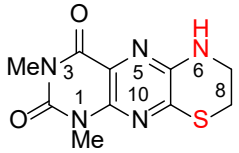

**1a'**

| Atom numbers | Experimental $^{13}$C chemical shift | DFT Calcd. $^{13}$C chemical shifts[3] | Absolute Error values |
|---|---|---|---|
| 1 (N-$CH_3$) | 31.3 | 27.4 | 3.9 |
| 2 | 151.0 | 151.2 | 0.2 |
| 3 (N-$CH_3$) | 30.3 | 27.0 | 3.3 |
| 4 | 157.4 | 151.7 | 5.7 |
| 4a | 120.6 | 118.5 | 2.1 |
| 5a | 147.9* | 140.7 | 7.2 |
| 7 | 26.3 | 22.7 | 3.6 |
| 8 | 40.6 | 42.5 | 1.9 |
| 9a | 148.0* | 150.1 | 2.1 |
| 10a | 137.6 | 144.2 | 6.6 |

**$^{13}$C MAE = 3.7**

***sDP4+ probability = tedaniophorbasin A (1a, proposed) 100% vs alternate (1a') 0%[1]**

**Table S3. Tedaniophorbasin B (2a) DFT vs Experimental $^{13}C$ NMR data for 2 (DMSO-$d_6$).**

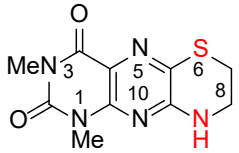


**2a**

| Atom numbers | Experimental $^{13}C$ chemical shift | DFT Calcd. $^{13}C$ chemical shifts[3] | Absolute Error values |
|---|---|---|---|
| 1 (N-$CH_3$) | 28.9 | 29.4 | 0.5 |
| 2 | 150.0 | 149.4 | 0.6 |
| 3 (N-$CH_3$) | 28.2 | 28.6 | 0.4 |
| 4 | 159.9 | 159.2 | 0.7 |
| 4a | 123.6 | 124.6 | 1.0 |
| 5a | 146.6 | 145.6 | 1.0 |
| 7 | 40.7 | 40.4 | 0.3 |
| 8 | 26.5 | 26.3 | 0.2 |
| 9a | 146.0 | 141.8 | 4.2 |
| 10a | 139.8 | 144.2 | 4.4 |

**$^{13}C$ MAE = 1.3**

**Table S4. Tedaniophorbasin B (2a') DFT vs Experimental $^{13}C$ NMR data for 2 (DMSO-$d_6$).**



**2a'**

| Atom numbers | Experimental $^{13}C$ chemical shift | DFT Calcd. $^{13}C$ chemical shifts[3] | Absolute Error values |
|---|---|---|---|
| 1 (N-$CH_3$) | 28.9 | 28.9 | 0.0 |
| 2 | 150.0 | 149.8 | 0.2 |
| 3 (N-$CH_3$) | 28.2 | 28.4 | 0.2 |
| 4 | 159.9 | 157.8 | 2.1 |
| 4a | 123.6 | 121.6 | 2.0 |
| 5a | 146.0 | 134.3 | 11.7 |
| 7 | 26.5 | 23.5 | 3.0 |
| 8 | 40.7 | 42.1 | 1.4 |
| 9a | 146.6 | 149.2 | 2.8 |
| 10a | 139.8 | 148.8 | 9.0 |

**$^{13}C$ MAE = 3.2**

***sDP4+ probability = tedaniophorbasin B (2a, proposed) 100.0% vs alternate (2a') 0.0%[1]**


1. Grimblat, N.; Zanardi, M. M.; Sarotti, A. M. Beyond DP4: An Improved Probability for the Stereochemical Assignment of Isomeric Compounds Using Quantum Chemical Calculations of NMR Shifts. *J. Org. Chem*. **2015**, *80*, 12526–125