



Supporting Information

for

Discovery of ianthelliformisamines D–G from the sponge *Suberea ianthelliformis* and the total synthesis of ianthelliformisamine D

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NMR data tables for compounds 4–7, 1D and 2D NMR spectra of compounds 4–7, ^1H NMR spectra of natural products 1–3 and 8 and ^1H and ^{13}C NMR spectra of synthetic compounds 4, 9, and 10

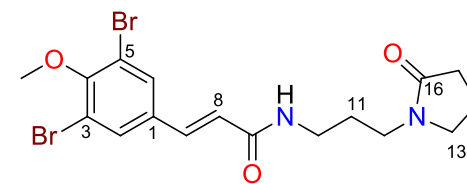
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Table S1: NMR data table for ianthelliformisamine D (**4**) in DMSO-*d*₆^a

| position | δ_C , type | δ_H , mult. (<i>J</i> in Hz) | COSY | HMBC | ROESY |
|--------------------|-----------------------|--------------------------------------|----------|---|--------------------|
| 1 | 134.5, C | | | | |
| 2 | 131.6, CH | 7.89, s | | 3, 4, 6, 7 | 7, 8 |
| 3 | 118.0, C | | | | |
| 4 | 153.9, C | | | | |
| 4-OCH ₃ | 60.6, CH ₃ | 3.81, s | | 4 | |
| 5 | 118.0, C | | | | |
| 6 | 131.6, CH | 7.89, s | | 2, 4, 5, 7 | 7, 8 |
| 7 | 135.2, CH | 7.33, d (15.8) | 8 | 1 ^w , 2, 6, 8 ^w , 9 | 2, 6 |
| 8 | 124.5, CH | 6.66, d (15.8) | 7 | 1, 9 | 2, 6, 9-NH |
| 9 | 164.4, C | | | | |
| 9-NH | | 8.04, t (5.7) | 10 | 9, 10 ^w | 8, 10 ^w |
| 10 | 36.5, CH ₂ | 3.14 dt (5.7, 6.5) | 9-NH, 11 | 9, 11 ^w , 12 | 9-NH, 11, 12 |
| 11 | 27.0, CH ₂ | 1.63, m | 10, 12 | 10 ^w , 12 | 10, 12 |
| 12 | 39.7, CH ₂ | 3.20, t (7.2) | 11 | 10, 11 ^w , 13 ^w | 10, 11 |
| 13 | 46.4, CH ₂ | 3.33, m | 14 | 12 ^w , 14 ^w , 15 | 14, 15 |
| 14 | 17.5, CH ₂ | 1.91, m | 13, 15 | 13, 15 ^w , 16 | 13, 15 |
| 15 | 30.5, CH ₂ | 2.21, t (8.0) | 14 | 13, 14, 16 | 13, 14 |
| 16 | 173.9 | | | | |



^aSpectra recorded at 25 °C (800 MHz for ¹H NMR and 200 MHz for ¹³C NMR); ^wWeak correlation.

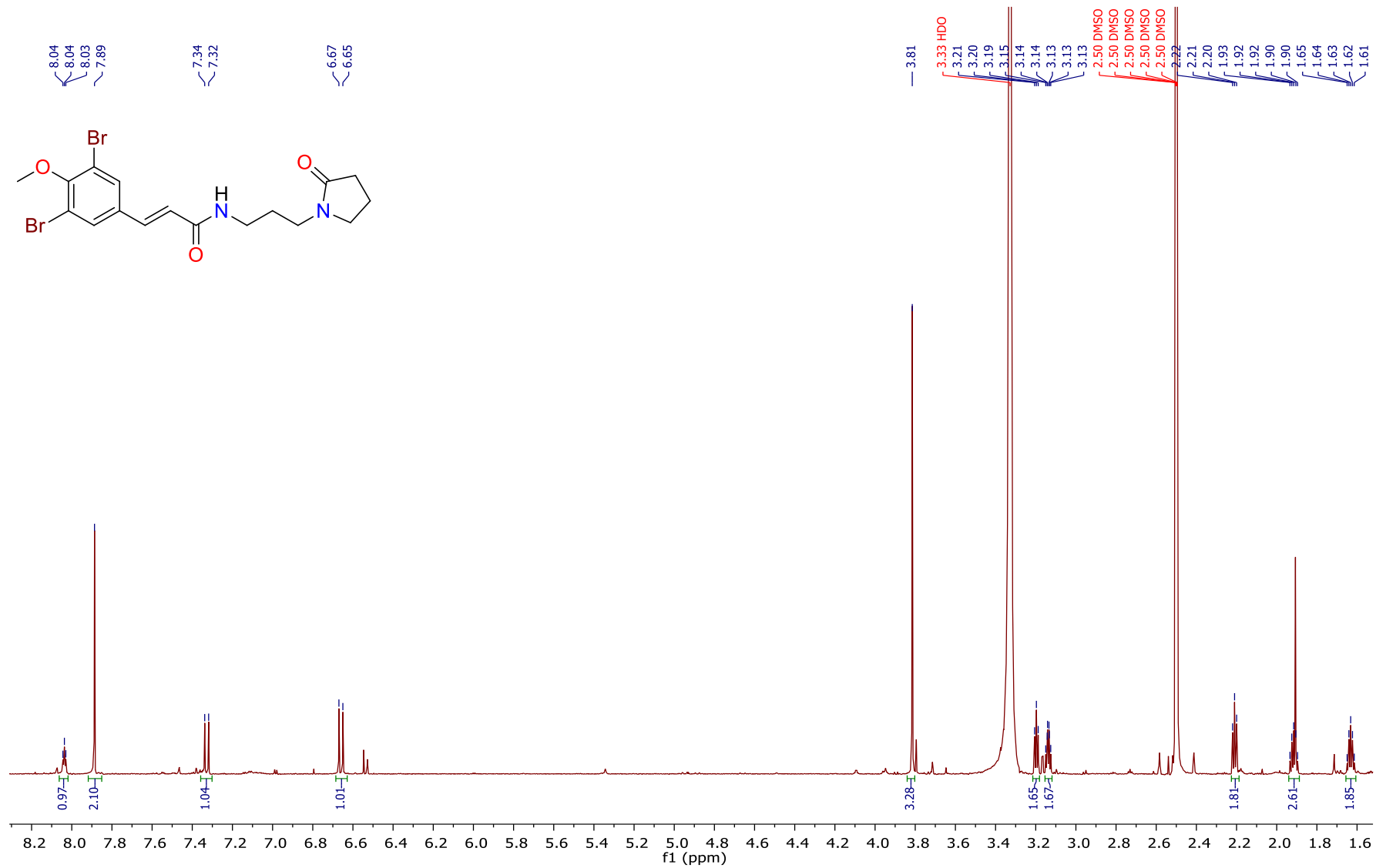


Figure S1: ¹H NMR (800 MHz) spectrum of ianthelliformisamine D (4) in DMSO-*d*₆

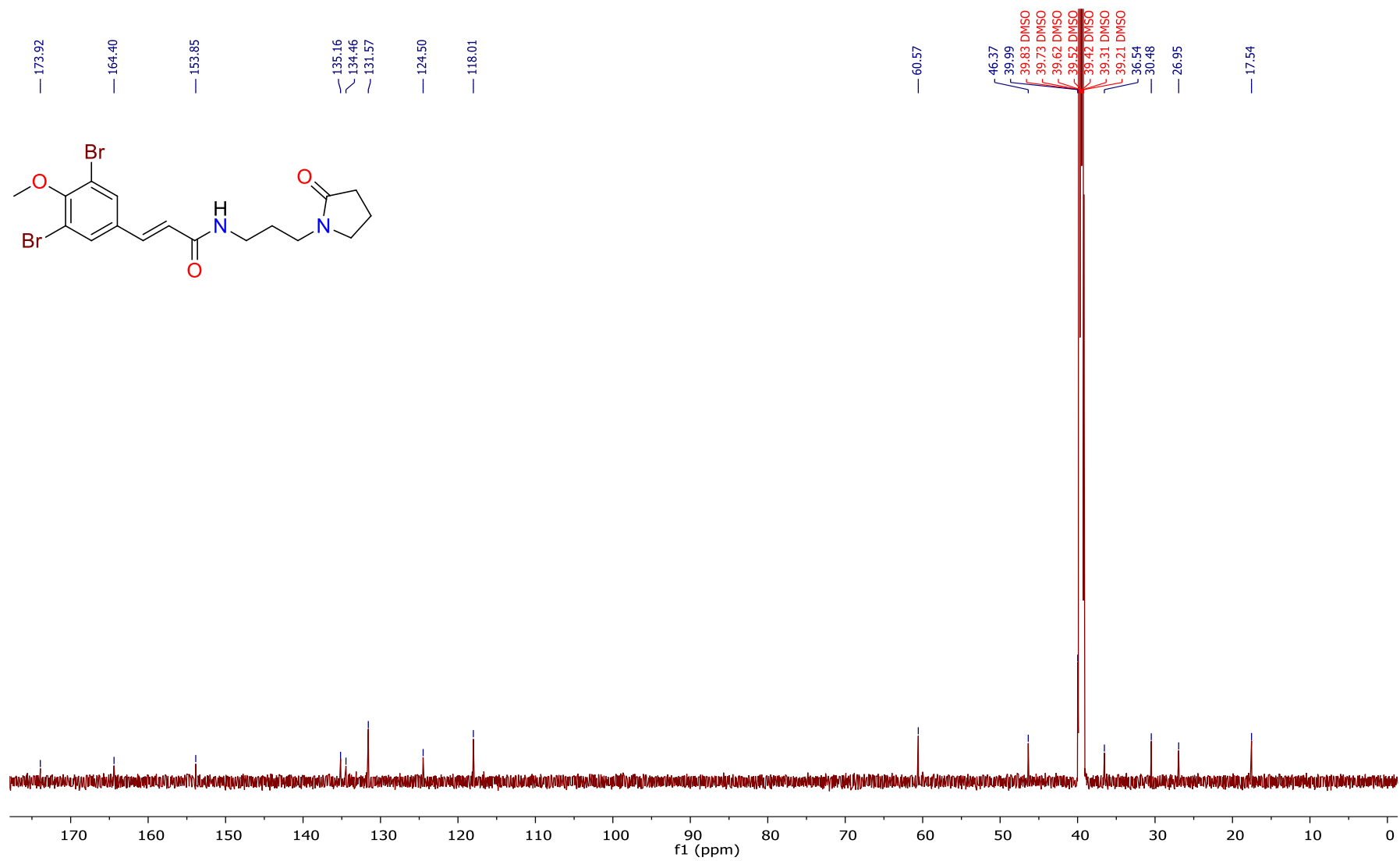


Figure S2: ^{13}C NMR (200 MHz) spectrum of ianthelliformisamine D (4) in $\text{DMSO-}d_6$

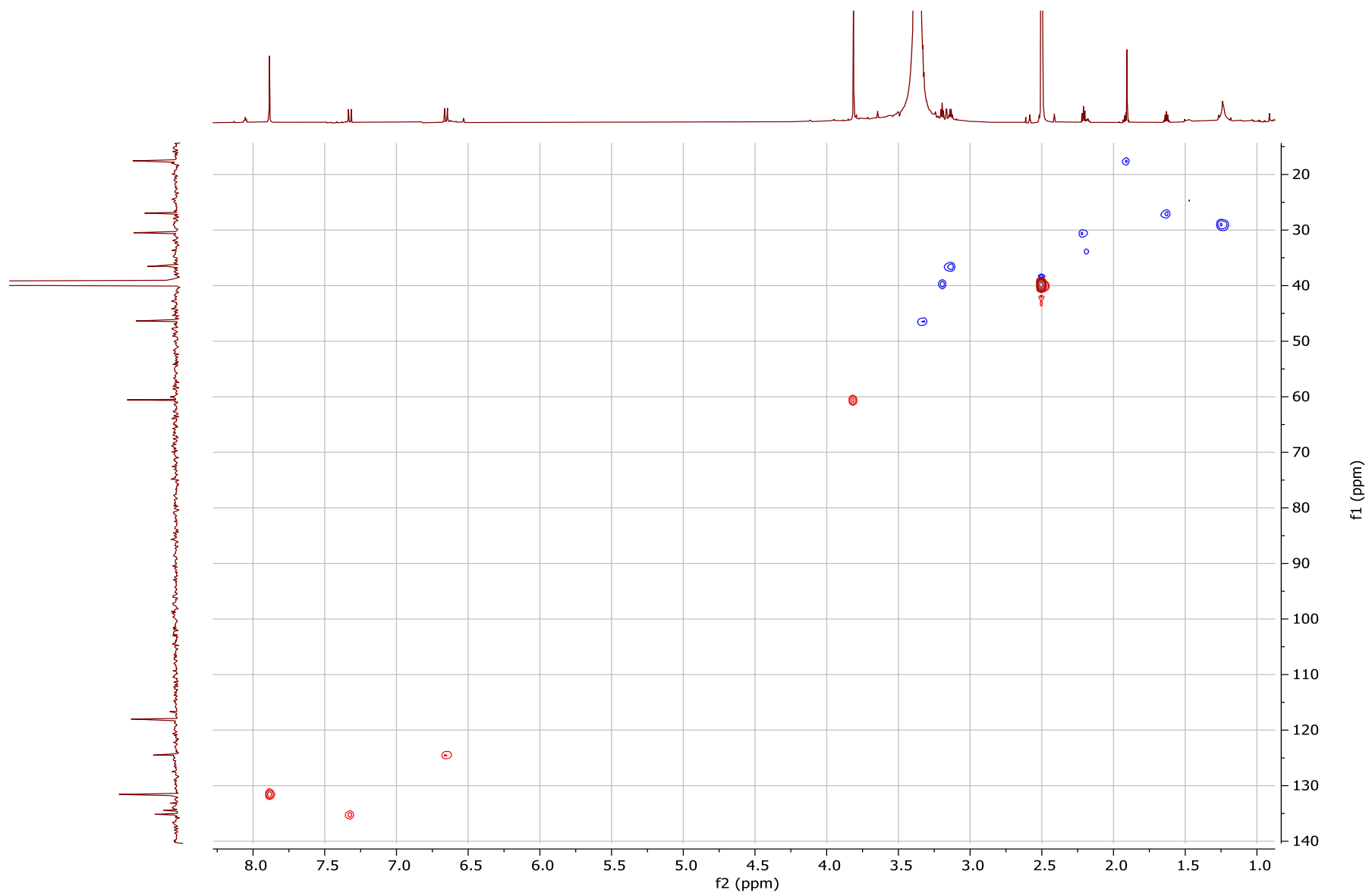


Figure S3: HSQC spectrum of ianthelliformisamine D (**4**) in DMSO-*d*₆

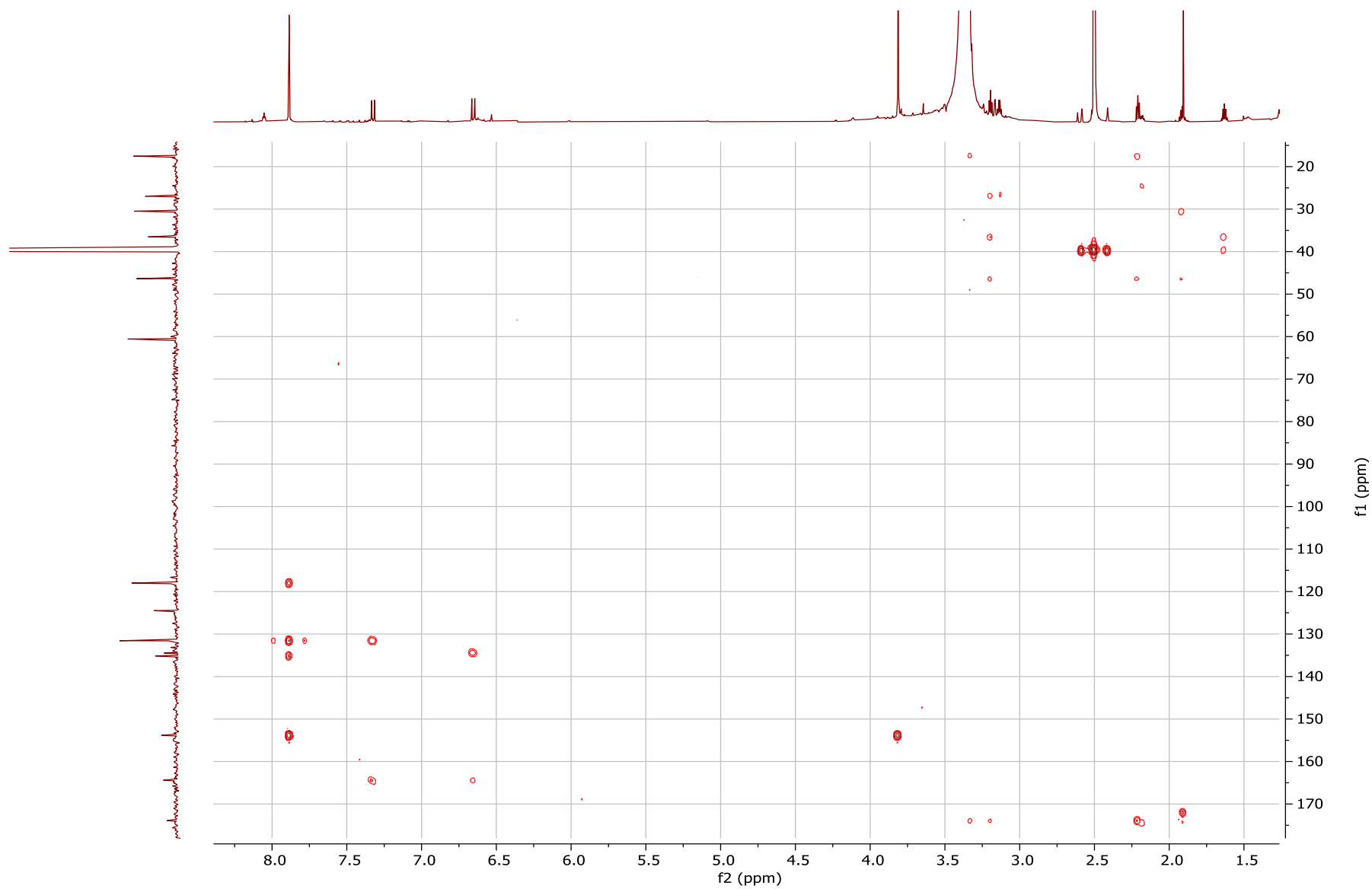


Figure S4: HMBC spectrum of ianthelliformisamine D (**4**) in DMSO-*d*₆

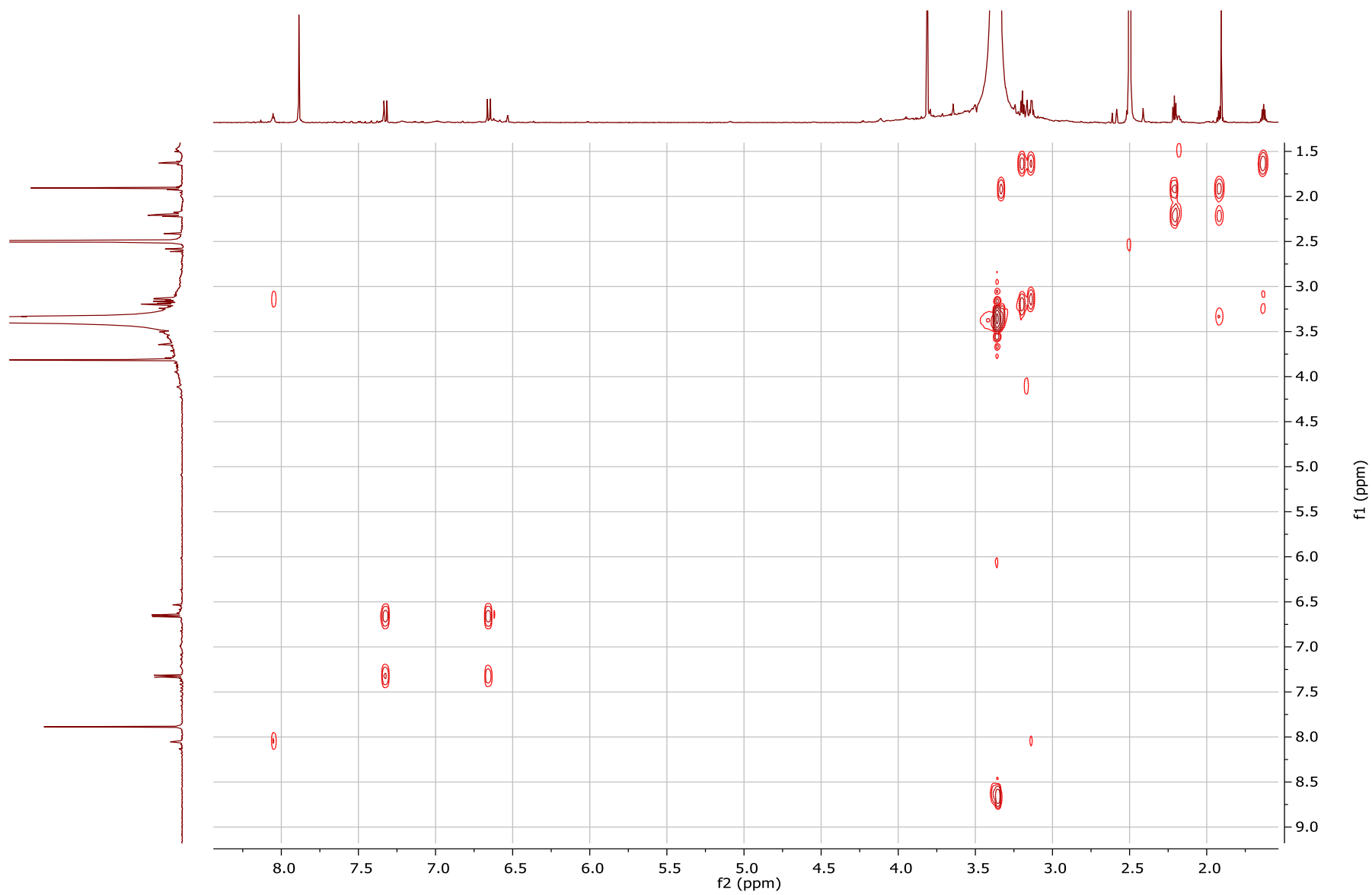


Figure S5: COSY spectrum of ianthelliformisamine D (**4**) in DMSO-*d*₆

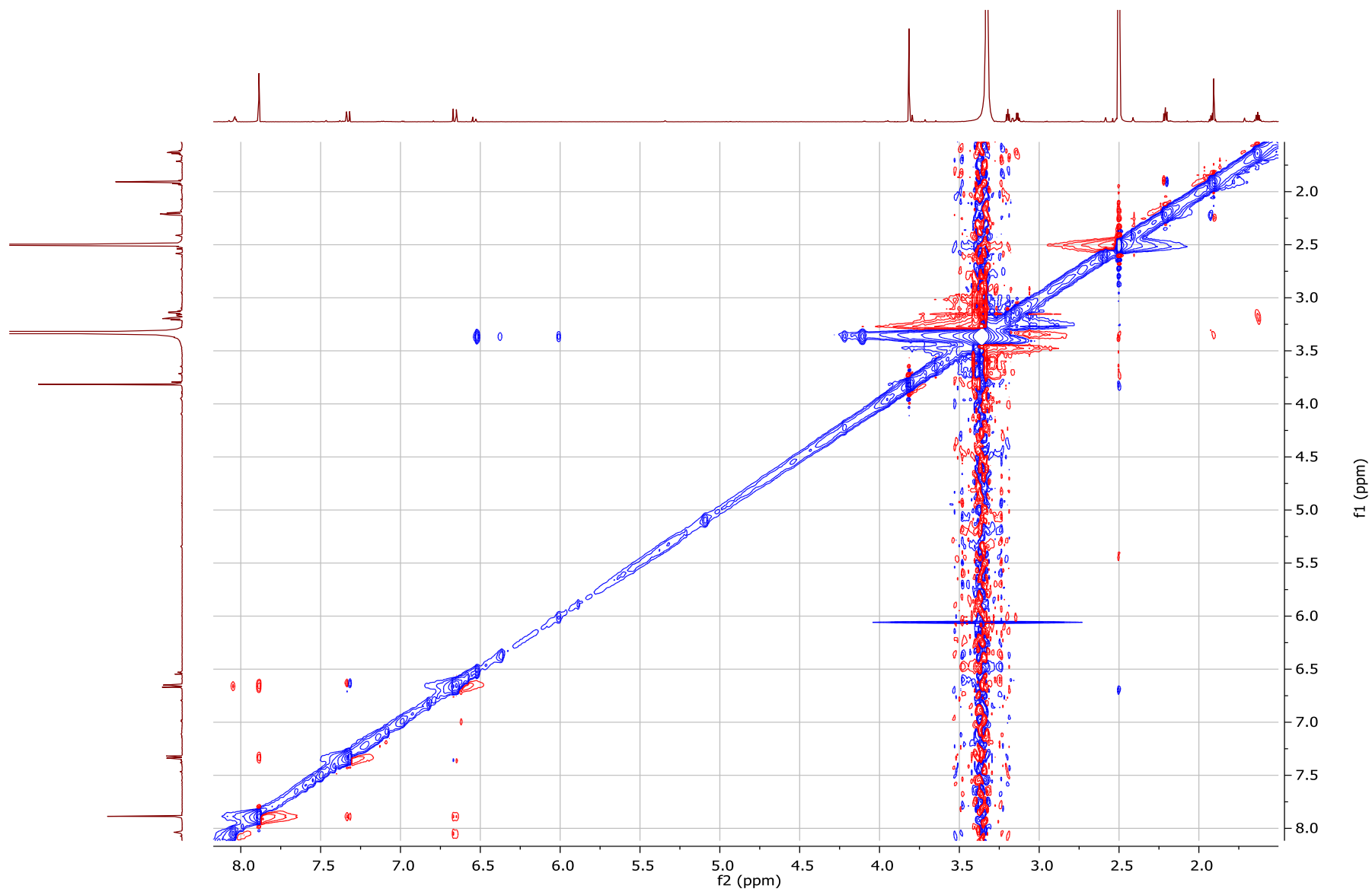
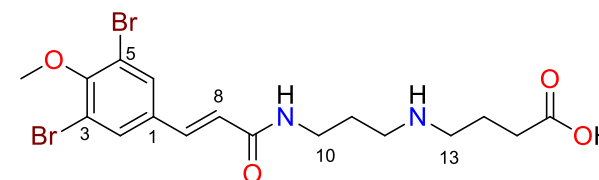


Figure S6: ROESY spectrum of ianthelliformisamine D (**4**) in DMSO-*d*₆

Table S2: NMR data table for ianthelliformisamine E (**5**) in DMSO-*d*₆^{a, b}

| position | δ_C , type | δ_H , mult. (<i>J</i> in Hz) | COSY | HMBC | ROESY |
|--------------------|-----------------------|--------------------------------------|-----------|---|--------|
| 1 | 134.3, C | | | | |
| 2 | 131.6, CH | 7.89, s | | 3, 4, 6, 7 | 7, 8 |
| 3 | 118.0, C | | | | |
| 4 | 153.9, C | | | | |
| 4-OCH ₃ | 60.6, CH ₃ | 3.82, s | | 4 | |
| 5 | 118.0, C | | | | |
| 6 | 131.6, CH | 7.89, s | | 2, 4, 5, 7 | 7, 8 |
| 7 | 135.5, CH | 7.36, d (15.8) | 8 | 1 ^w , 2, 6, 8 ^w , 9 | |
| 8 | 124.1, CH | 6.65, d (15.8) | 7 | 1, 9 | |
| 9 | 164.9, C | | | | |
| 9-NH | | 8.23, t (5.7) | 10 | 9, 10 ^w | 8, 10 |
| 10 | 35.9, CH ₂ | 3.25 dt (5.7, 6.5) | 9-NH, 11 | 9, 11 ^w , 12 | 11, 12 |
| 11 | 26.1, CH ₂ | 1.77, m | 10, 12 | 10 ^w , 12 | 10, 12 |
| 12 | 44.8, CH ₂ | 2.92, m | 11, 12-NH | 10, 11 ^w , 13 ^w | 10, 11 |
| 12-NH | | 8.35, brs | 12, 13 | | |
| 13 | 46.3, CH ₂ | 2.93, m | 12-NH, 14 | 12 ^w , 14 ^w , 15 | 14, 15 |
| 14 | 21.1, CH ₂ | 1.79, m | 13, 15 | 13, 15 ^w , 16 | 13, 15 |
| 15 | 30.4, CH ₂ | 2.36, t (7.3) | 14 | 13, 14, 16 | 13, 14 |
| 16 | 173.6, C | | | | |
| 16-OH | | c | | | |



^aSpectra recorded at 25 °C (800 MHz for ¹H NMR and 200 MHz for ¹³C NMR); ^bIsolated as a TFA salt; ^cNot observed; ^wWeak correlation.

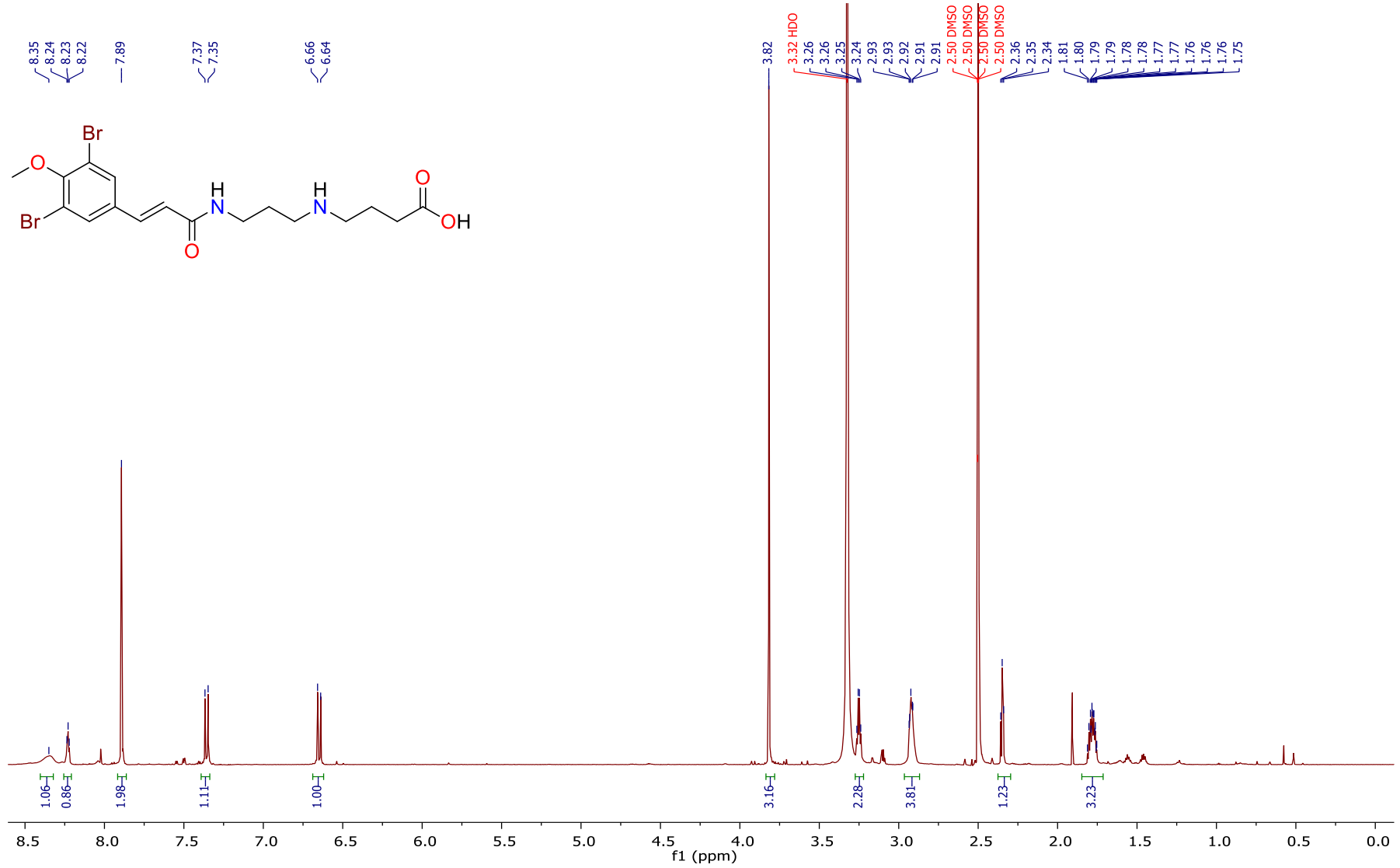


Figure S7: ¹H NMR (800 MHz) spectrum of ianthelliformisamine E (5) in DMSO-*d*₆

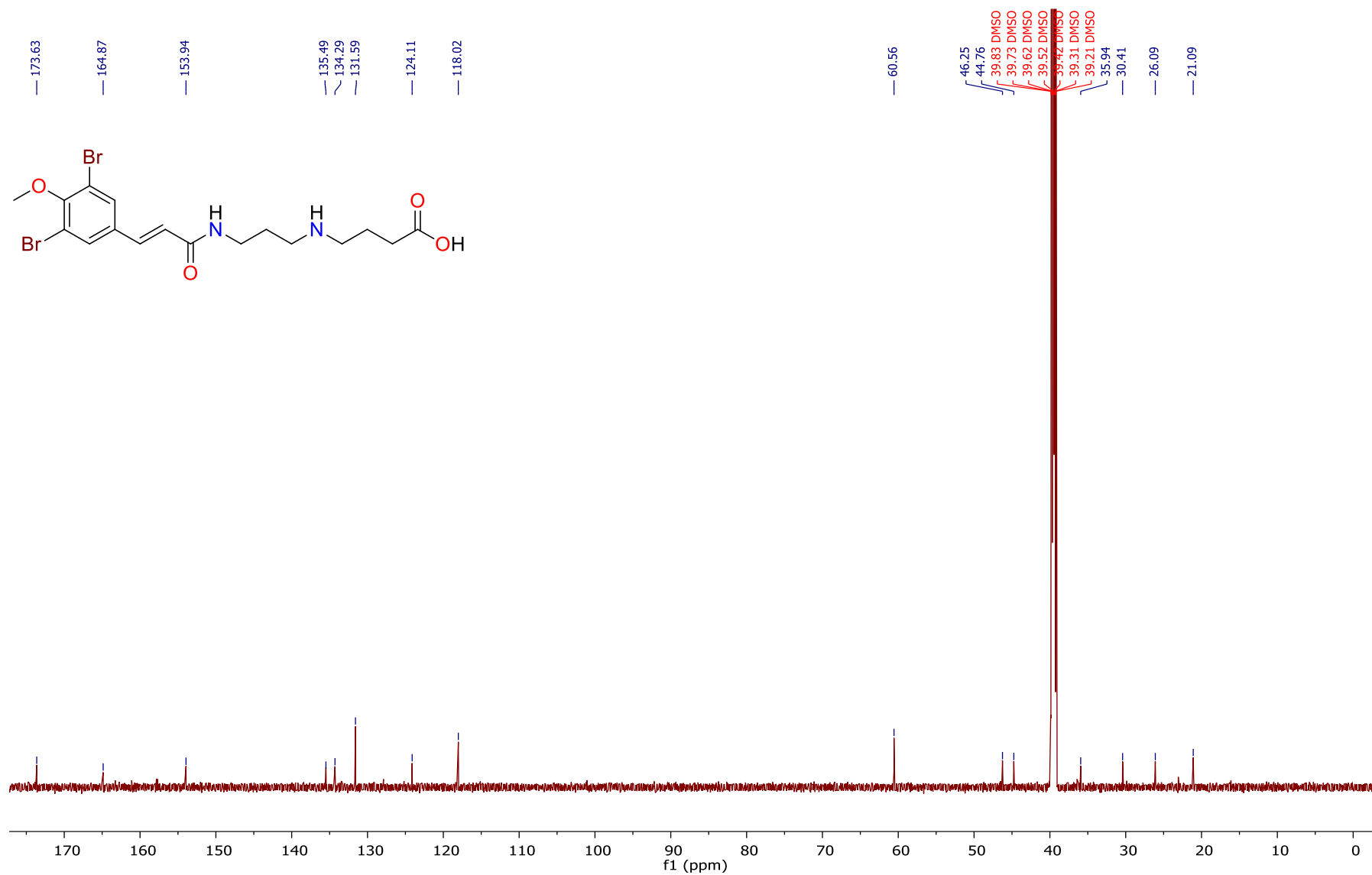


Figure S8: ^{13}C NMR (200 MHz) spectrum of ianthelliformisamine E (5) in $\text{DMSO-}d_6$

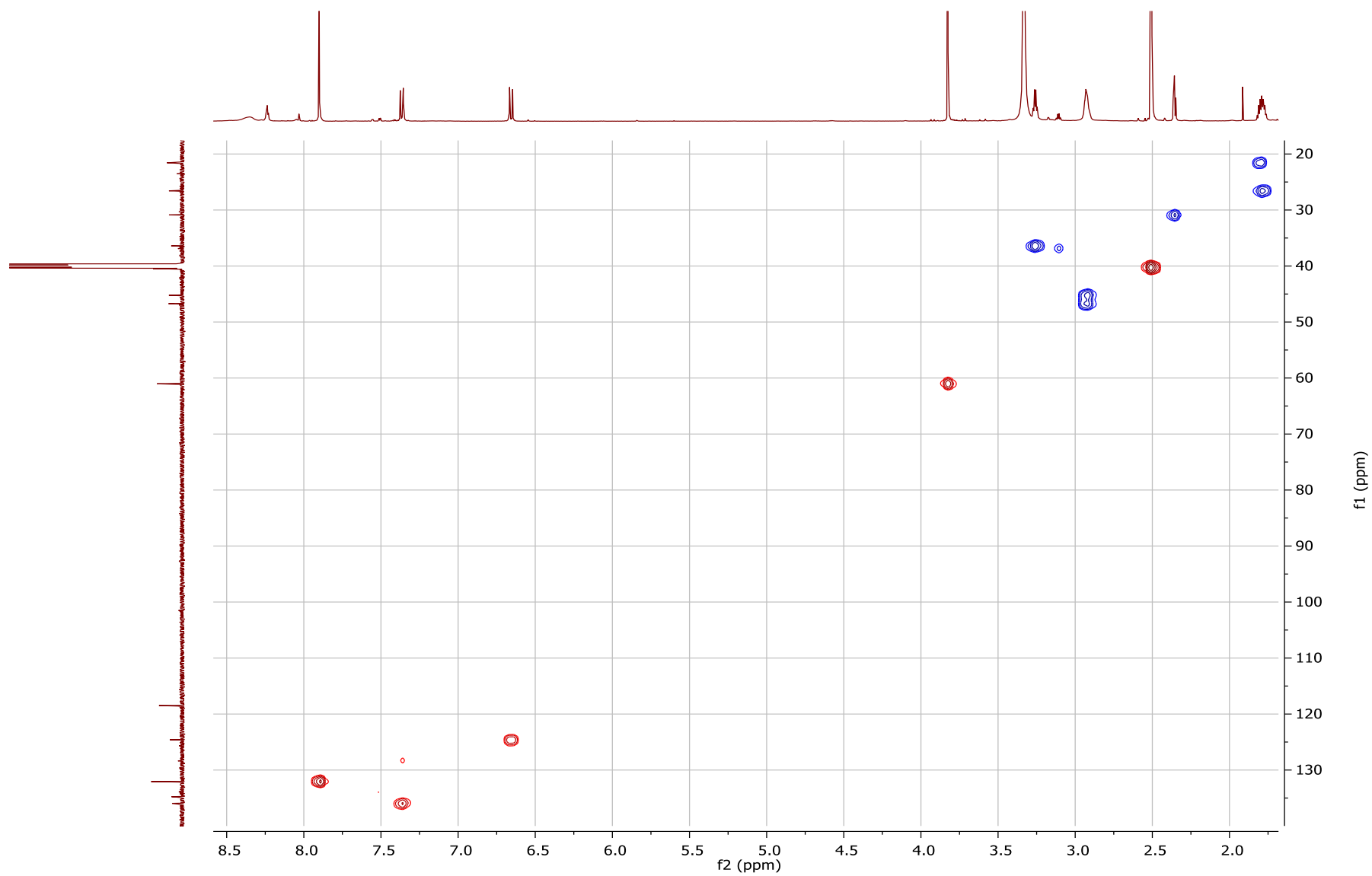


Figure S9: HSQC spectrum of ianthelliformisamine E (**5**) in DMSO-*d*₆

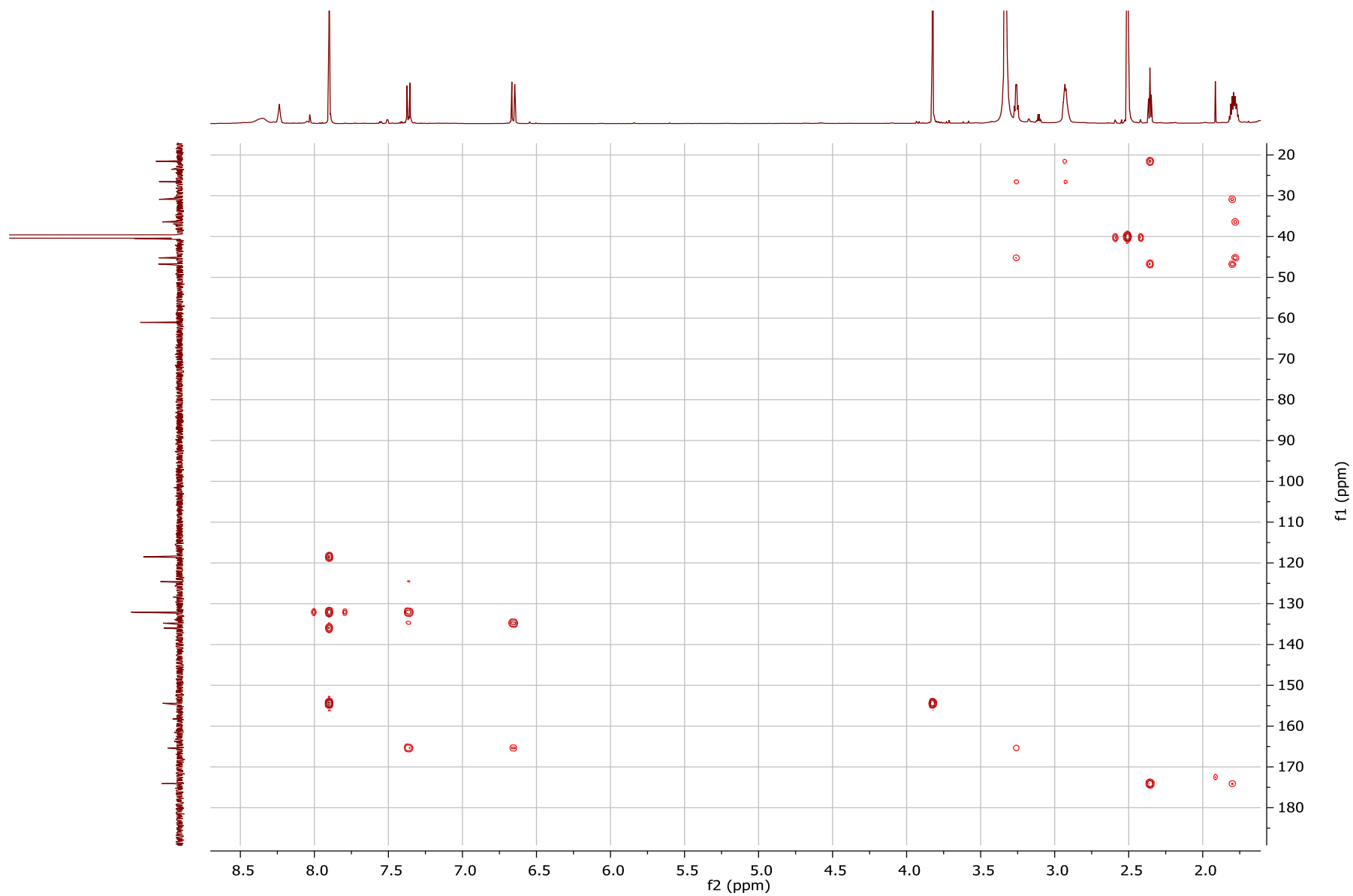


Figure S10: HMBC spectrum of ianthelliformisamine E (**5**) in DMSO-*d*₆

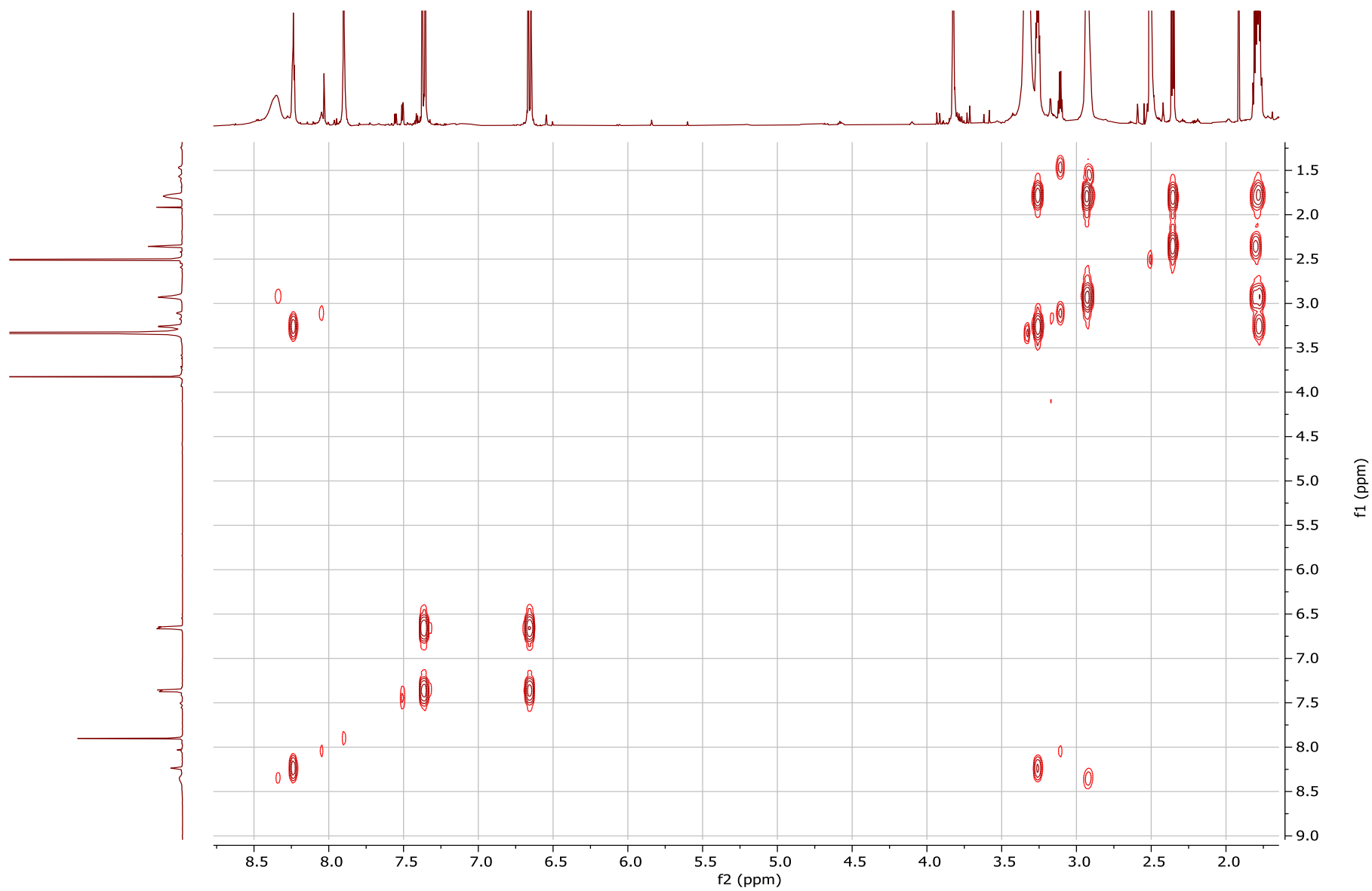


Figure S11: COSY spectrum of ianthelliformisamine E (**5**) in DMSO-*d*₆

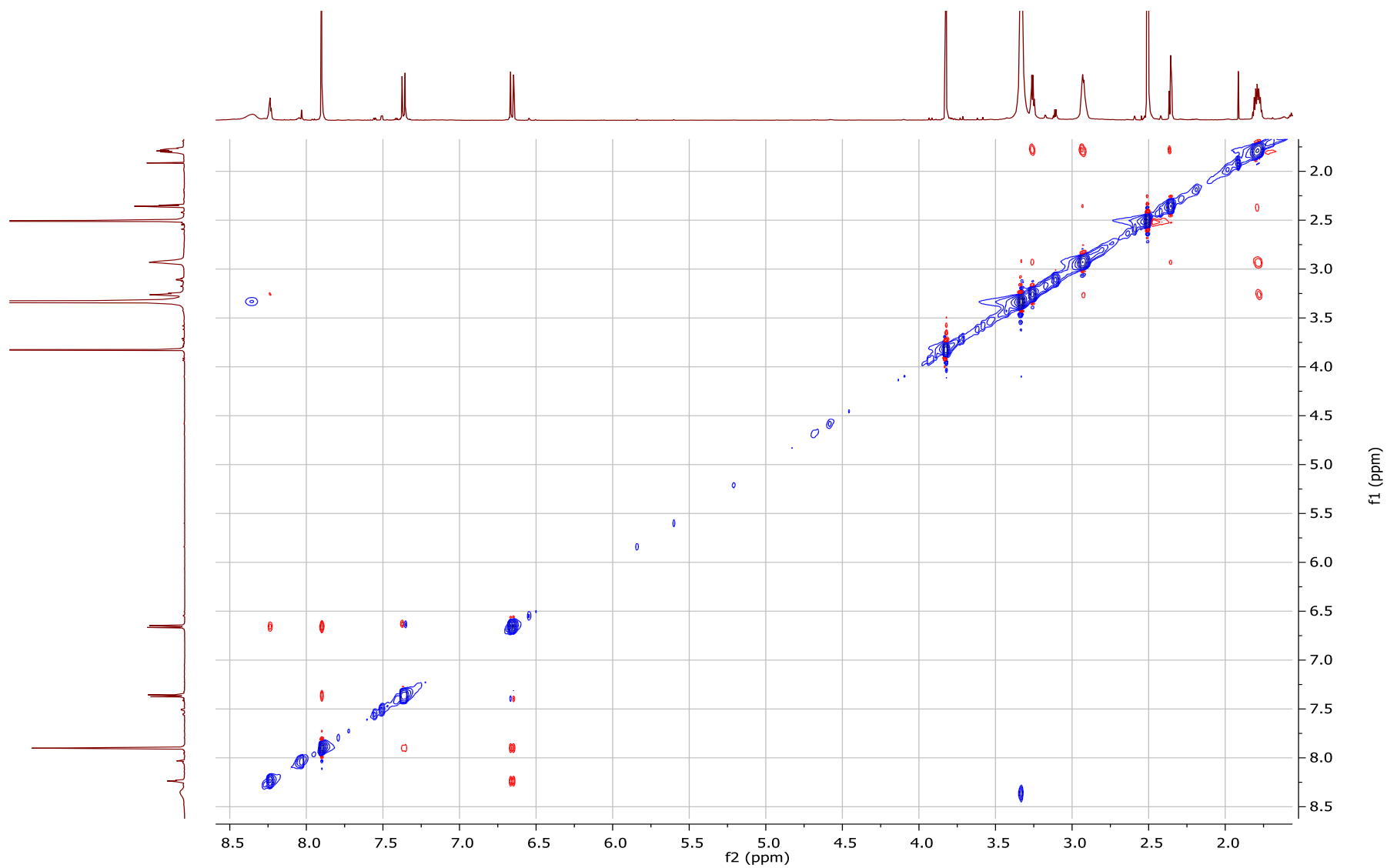
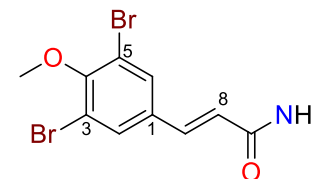


Figure S12: ROESY spectrum of ianthelliformisamine E (**5**) in DMSO-*d*₆

Table S3: NMR data table for ianthelliformisamine F (**6**) in DMSO-*d*₆^a

| position | δ_C , type | δ_H , mult. (<i>J</i> in Hz) | COSY | HMBC |
|--------------------|-----------------------|--------------------------------------|-------------------|-----------------------------|
| 1 | 134.4, C | | | |
| 2 | 131.6, CH | 7.88, s | | 1 ^w , 3, 4, 6, 7 |
| 3 | 118.0, C | | | |
| 4 | 153.9, C | | | |
| 4-OCH ₃ | 60.6, CH ₃ | 3.81, s | | 4 |
| 5 | 118.0, C | | | |
| 6 | 131.6, CH | 7.88, s | | 1 ^w , 2, 4, 5, 7 |
| 7 | 135.7, CH | 7.32, d (15.8) | 8 | 1, 2, 6, 8 ^w , 9 |
| 8 | 124.6, CH | 6.65, d (15.8) | 7 | 1, 7, 9 |
| 9 | 166.1, C | | | |
| 9-NH ₂ | | 7.19, brs | 9-NH ₂ | 8 |
| | | 7.46, brs | 9-NH ₂ | |

^aSpectra recorded at 25 °C (800 MHz for ¹H NMR and 200 MHz for ¹³C NMR).



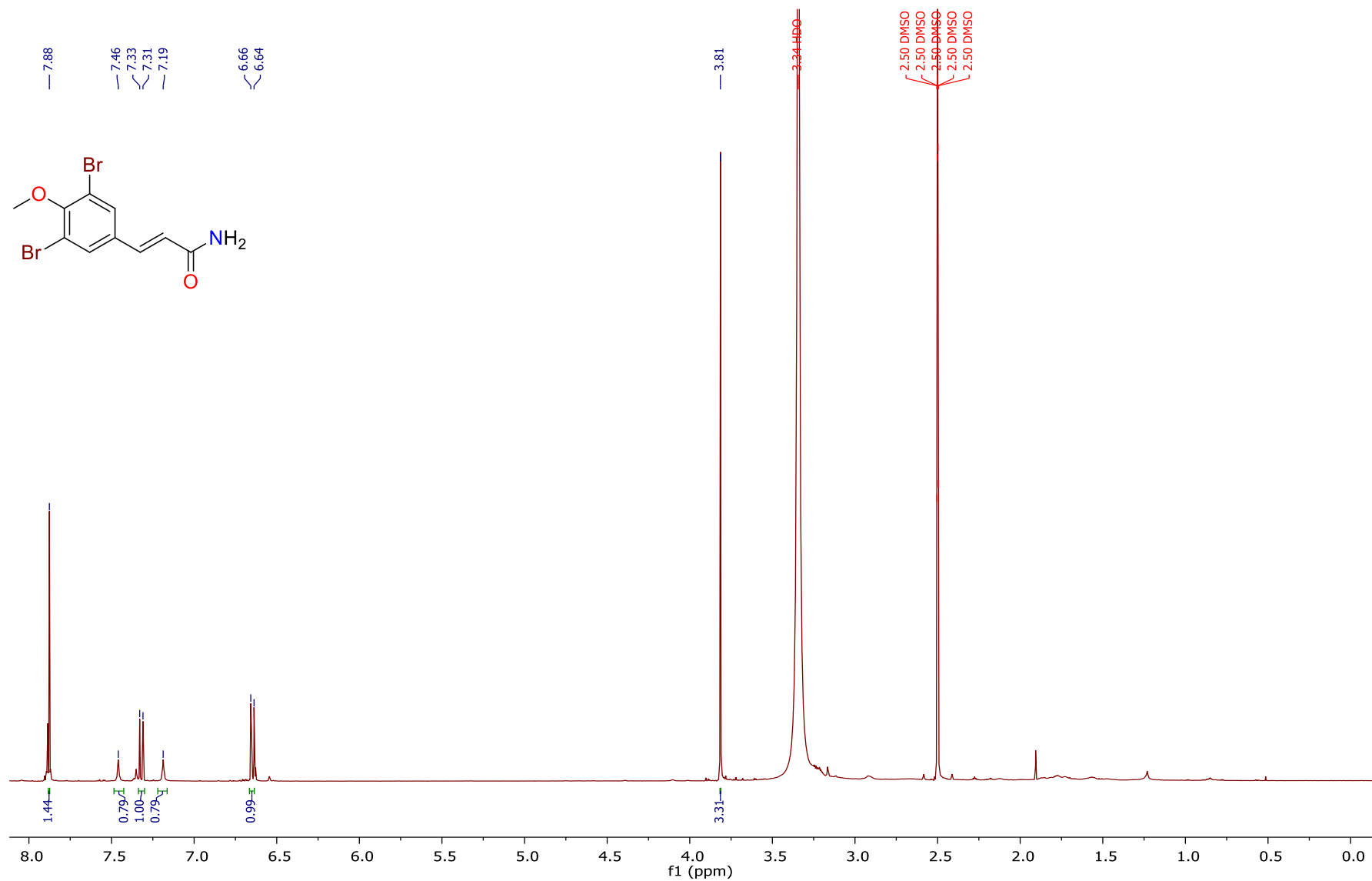


Figure S13: ¹H NMR (800 MHz) spectrum of ianthelliformisamine F (6) in DMSO-*d*₆

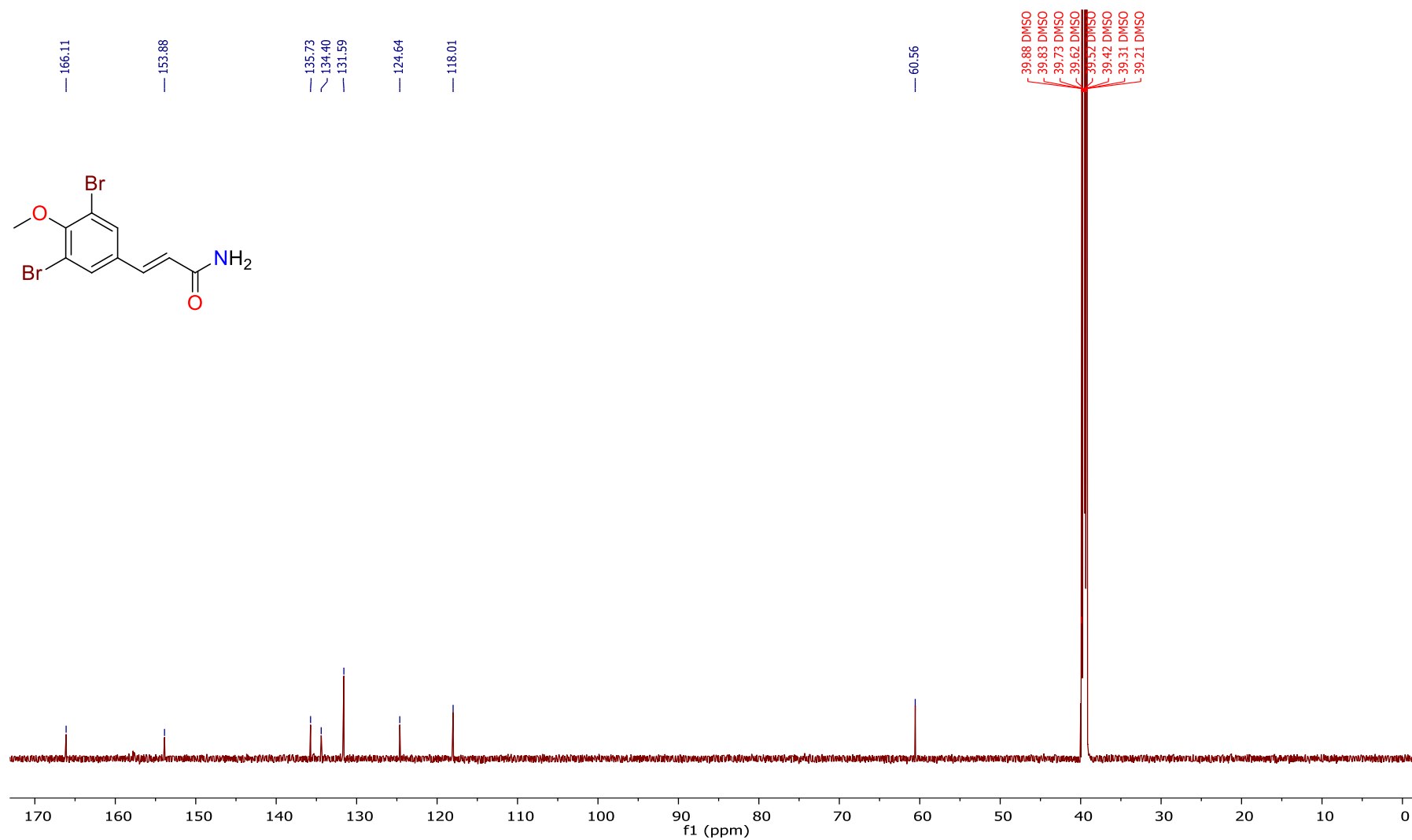


Figure S14: ¹³C NMR (200 MHz) spectrum of ianthelliformisamine F (**6**) in DMSO-*d*₆

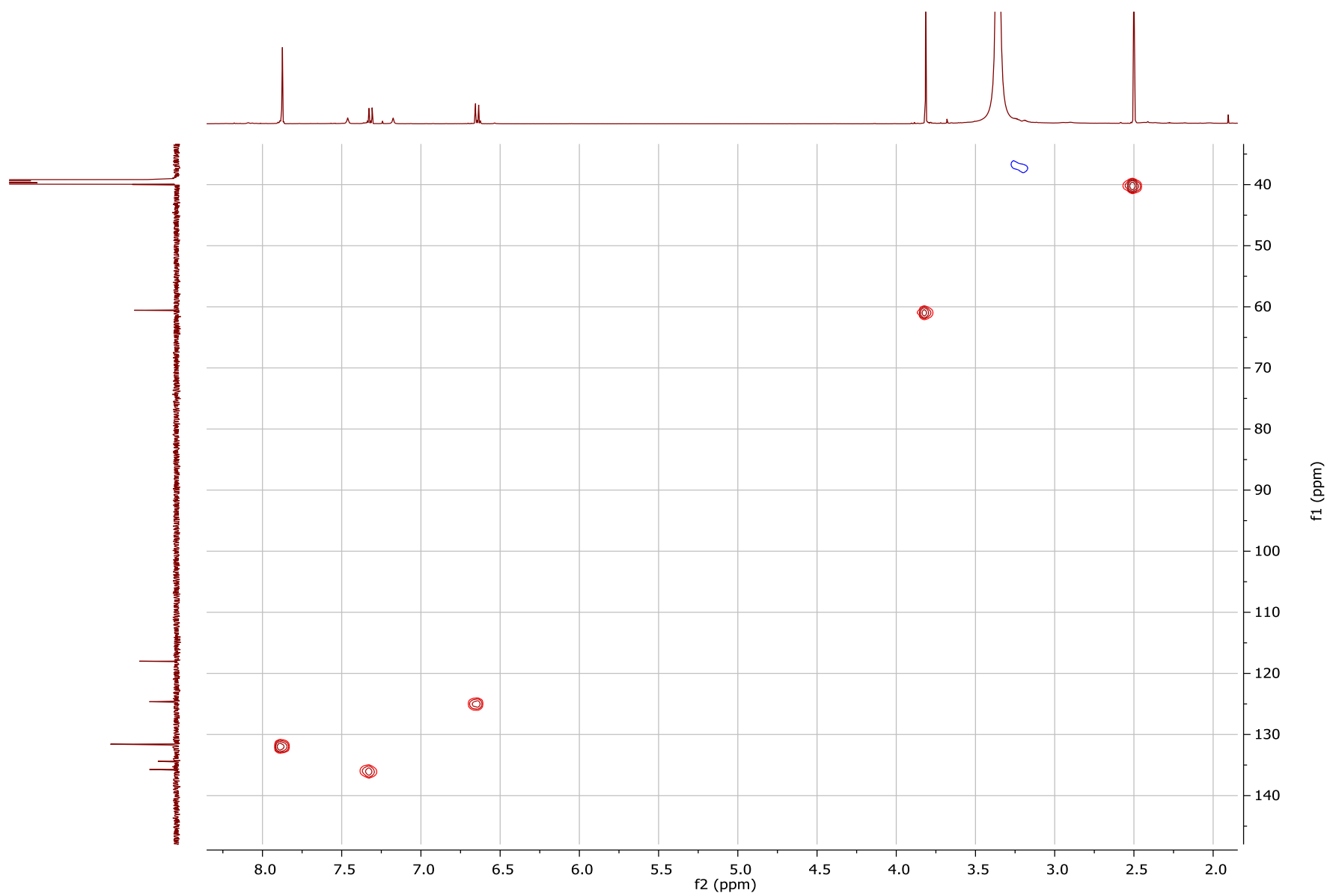


Figure S15: HSQC spectrum of ianthelliformisamine F (**6**) in DMSO-*d*₆

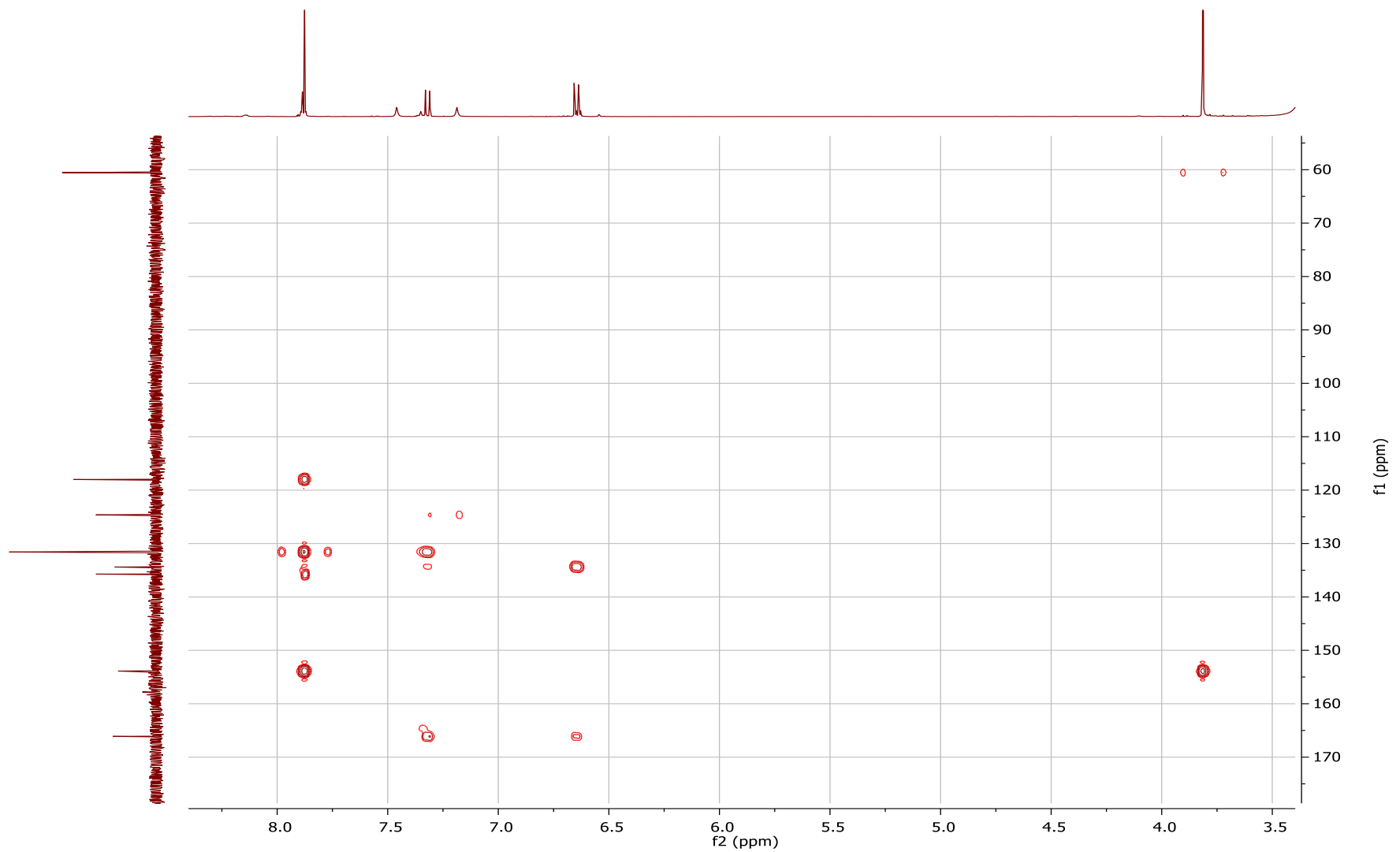


Figure S16: HMBC spectrum of ianthelliformisamine F (**6**) in DMSO-*d*₆

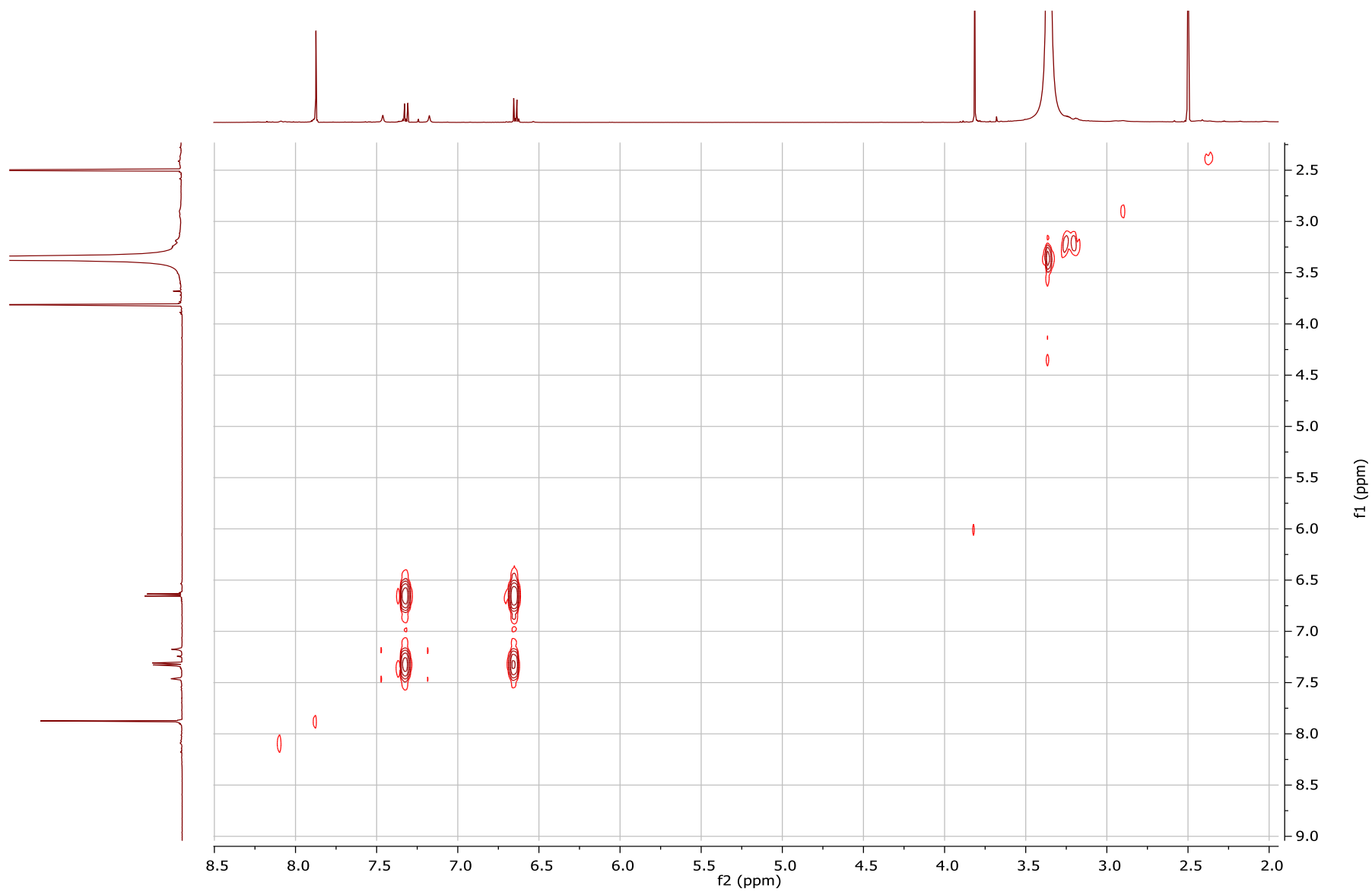
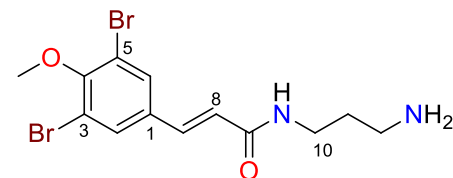


Figure S17: COSY spectrum of ianthelliformisamine F (**6**) in DMSO-*d*₆

Table S4: NMR data table for ianthelliformisamine G (**7**) in DMSO- $d_6^{a, b}$

| position | δ_C , type | δ_H , mult. (J in Hz) | COSY | HMBC |
|--------------------|-----------------------|------------------------------|----------|---|
| 1 | 134.3, C | | | |
| 2 | 131.6, CH | 7.89, s | | 3, 4, 6, 7 |
| 3 | 118.0, C | | | |
| 4 | 153.9, C | | | |
| 4-OCH ₃ | 60.6, CH ₃ | 3.82, s | | 4 |
| 5 | 118.0, C | | | |
| 6 | 131.6, CH | 7.89, s | | 2, 4, 5, 7 |
| 7 | 135.4, CH | 7.35, d (15.8) | 8 | 1 ^w , 2, 6, 8 ^w , 9 |
| 8 | 124.2, CH | 6.65, d (15.8) | 7 | 1, 9 |
| 9 | 164.9, C | | | |
| 9-NH | | 8.23, t (5.8) | 10 | 9 ^w |
| 10 | 35.9, CH ₂ | 3.25, dt (5.8, 6.8) | 9-NH, 11 | 9, 11 ^w , 12 ^w |
| 11 | 27.5, CH ₂ | 1.73, tt (6.8, 7.5) | 10, 12 | 10, 12 |
| 12 | 36.9, CH ₂ | 2.81, m | 11 | 10 ^w , 11 ^w |
| 12-NH ₂ | | 7.73, brs | | |



^aSpectra recorded at 25 °C (800 MHz for ¹H NMR and 200 MHz for ¹³C NMR); ^bIsolated as a TFA salt; ^wWeak correlation.

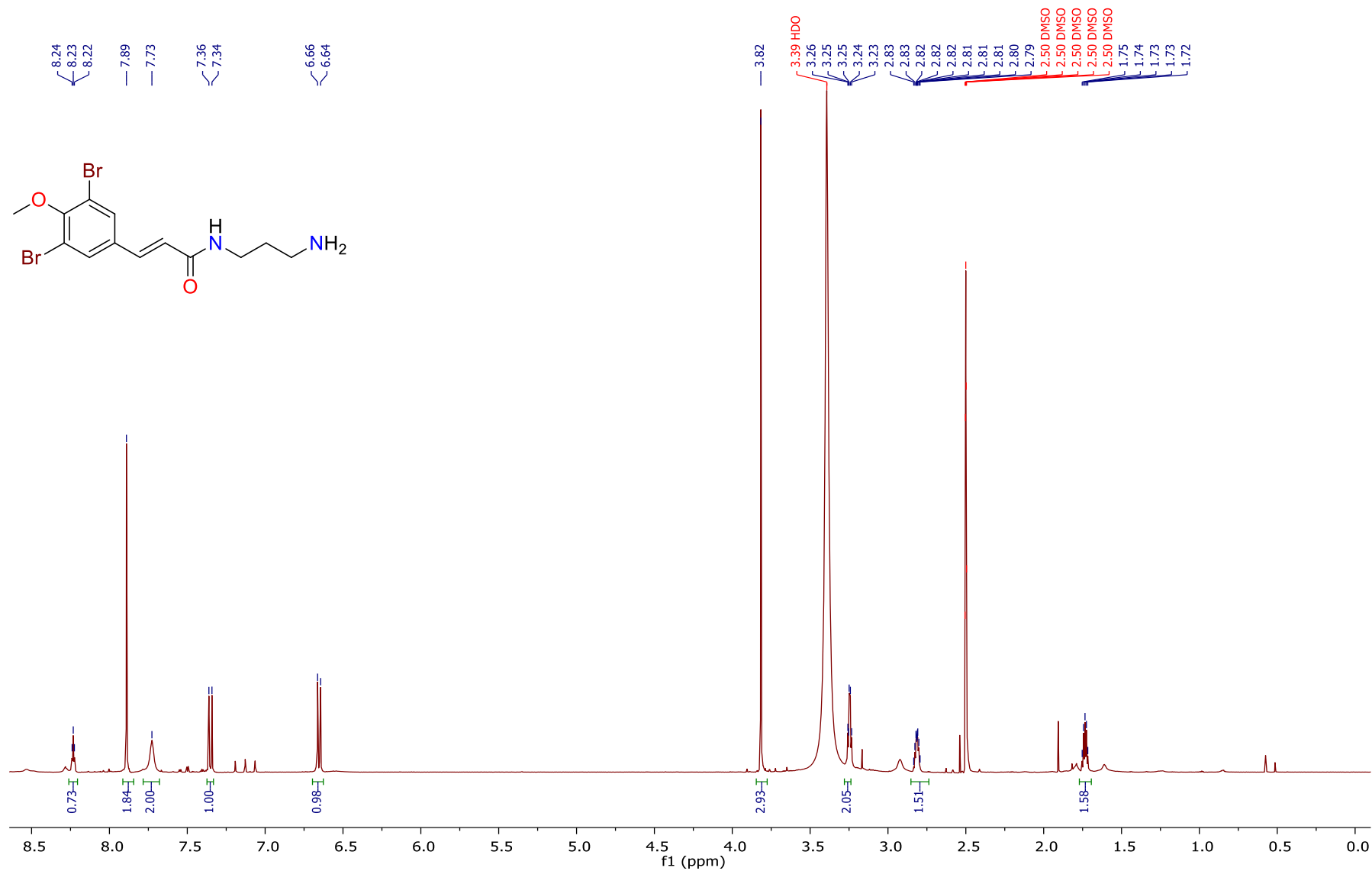


Figure S18: ¹H NMR (800 MHz) spectrum of ianthelliformisamine G (7) in DMSO-*d*₆

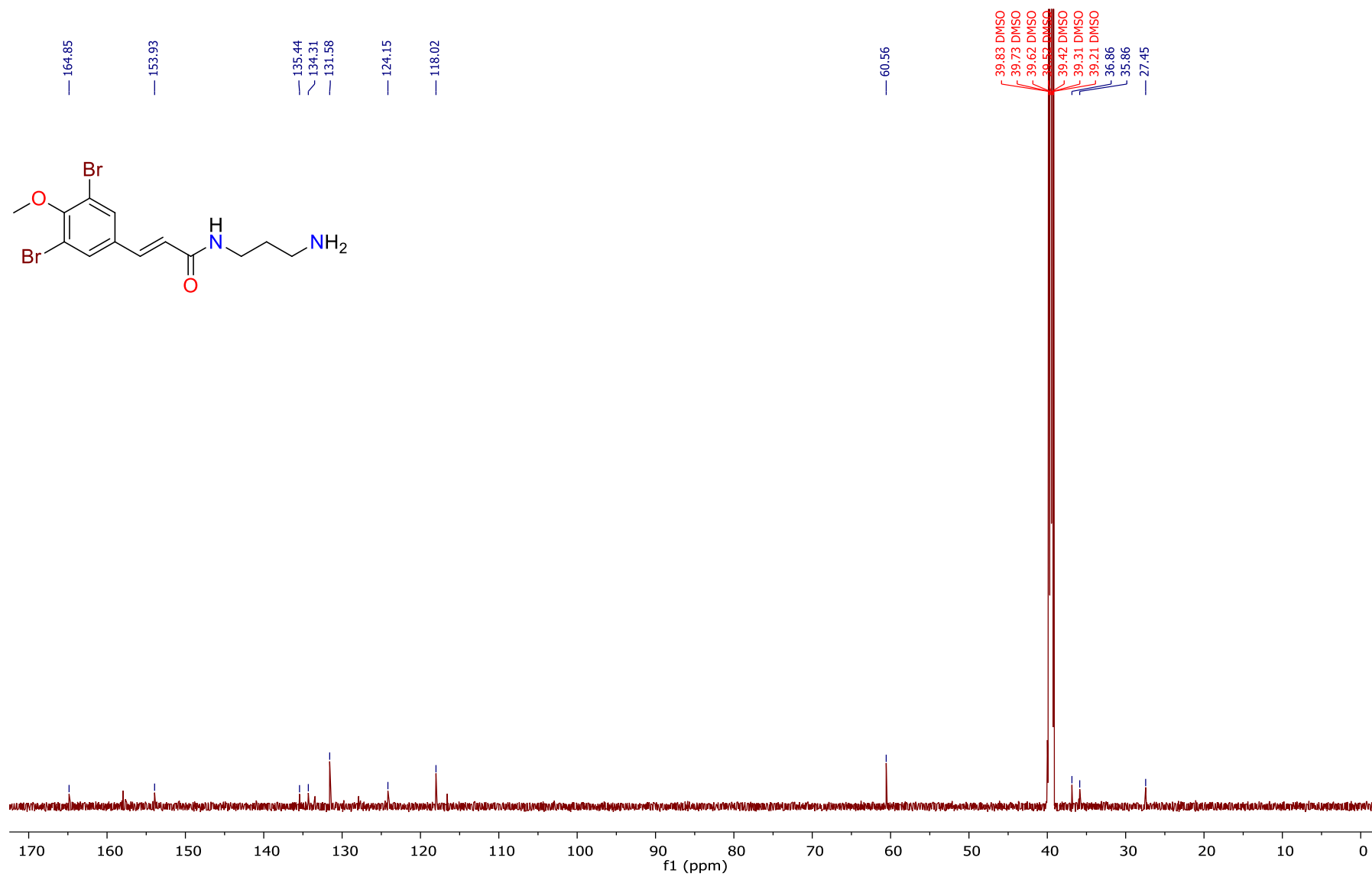


Figure S19: ^{13}C NMR (200 MHz) spectrum of ianthelliformisamine G (7) in $\text{DMSO-}d_6$

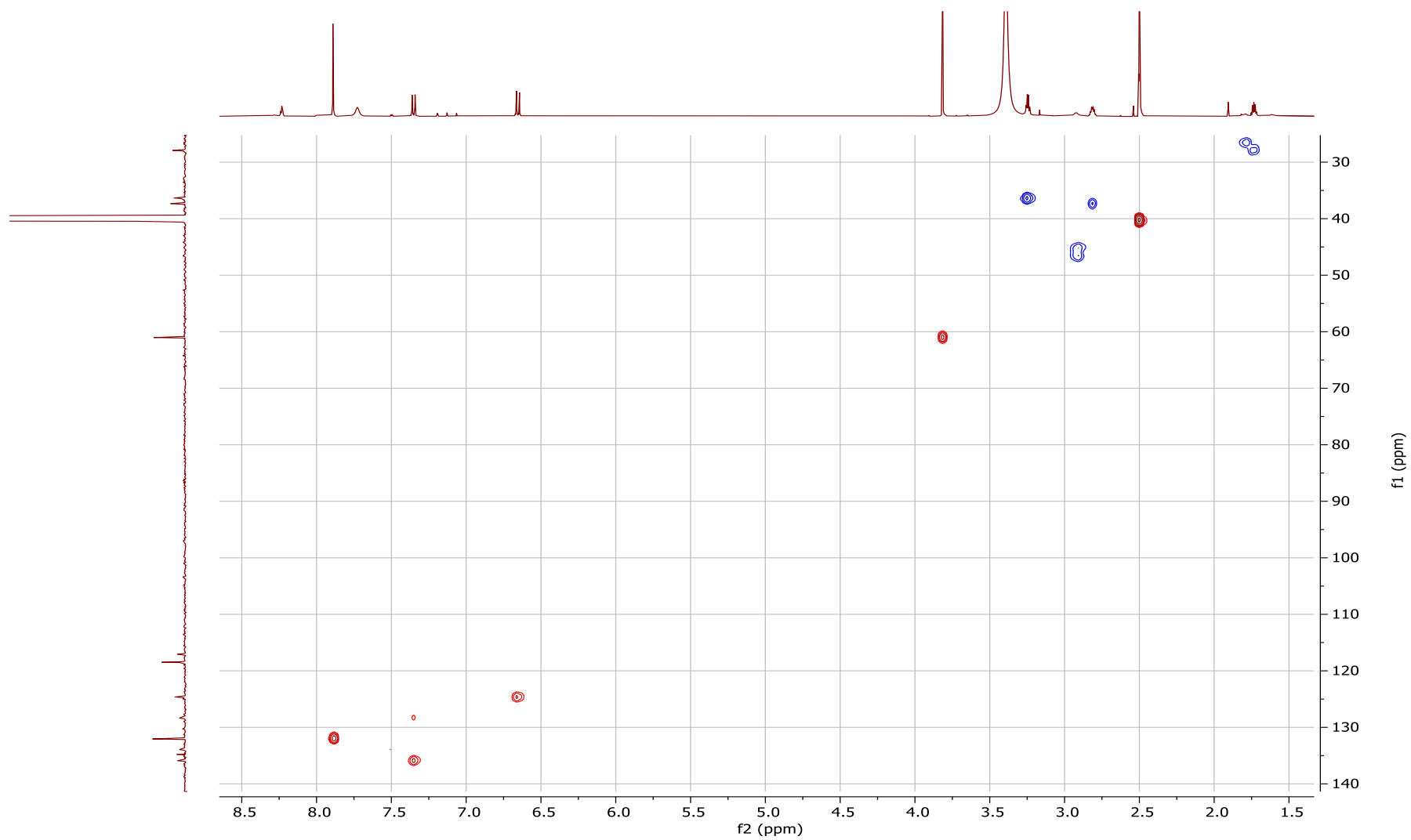


Figure S20: HSQC spectrum of ianthelliformisamine G (**7**) in DMSO-*d*₆

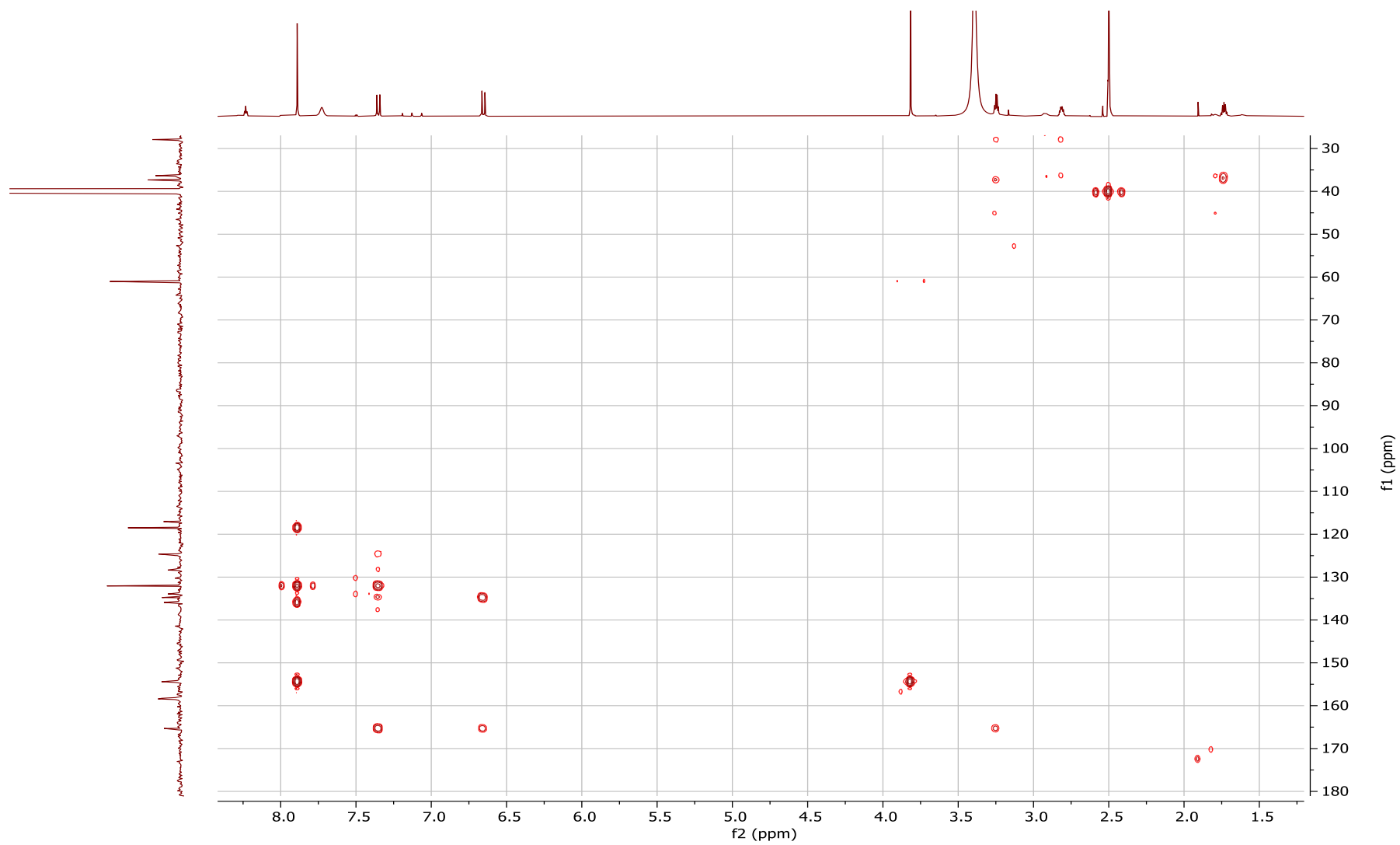


Figure S21: HMBC spectrum of ianthelliformisamine G (7) in DMSO-*d*₆



Figure S22: COSY spectrum of ianthelliformisamine G (7) in DMSO-*d*₆

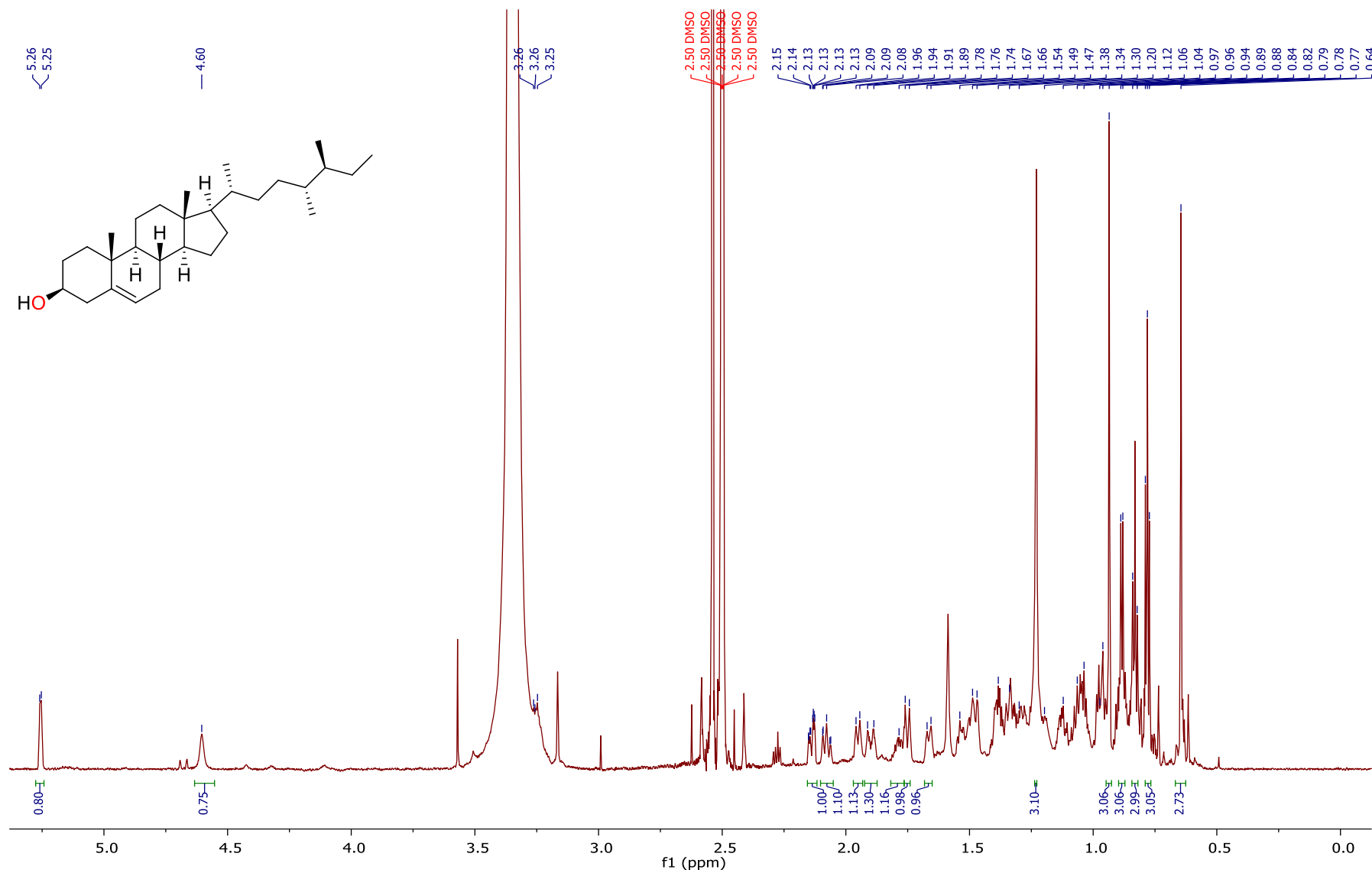


Figure S23: ¹H NMR (800 MHz) spectrum of aplysterol (**8**) in DMSO-*d*₆

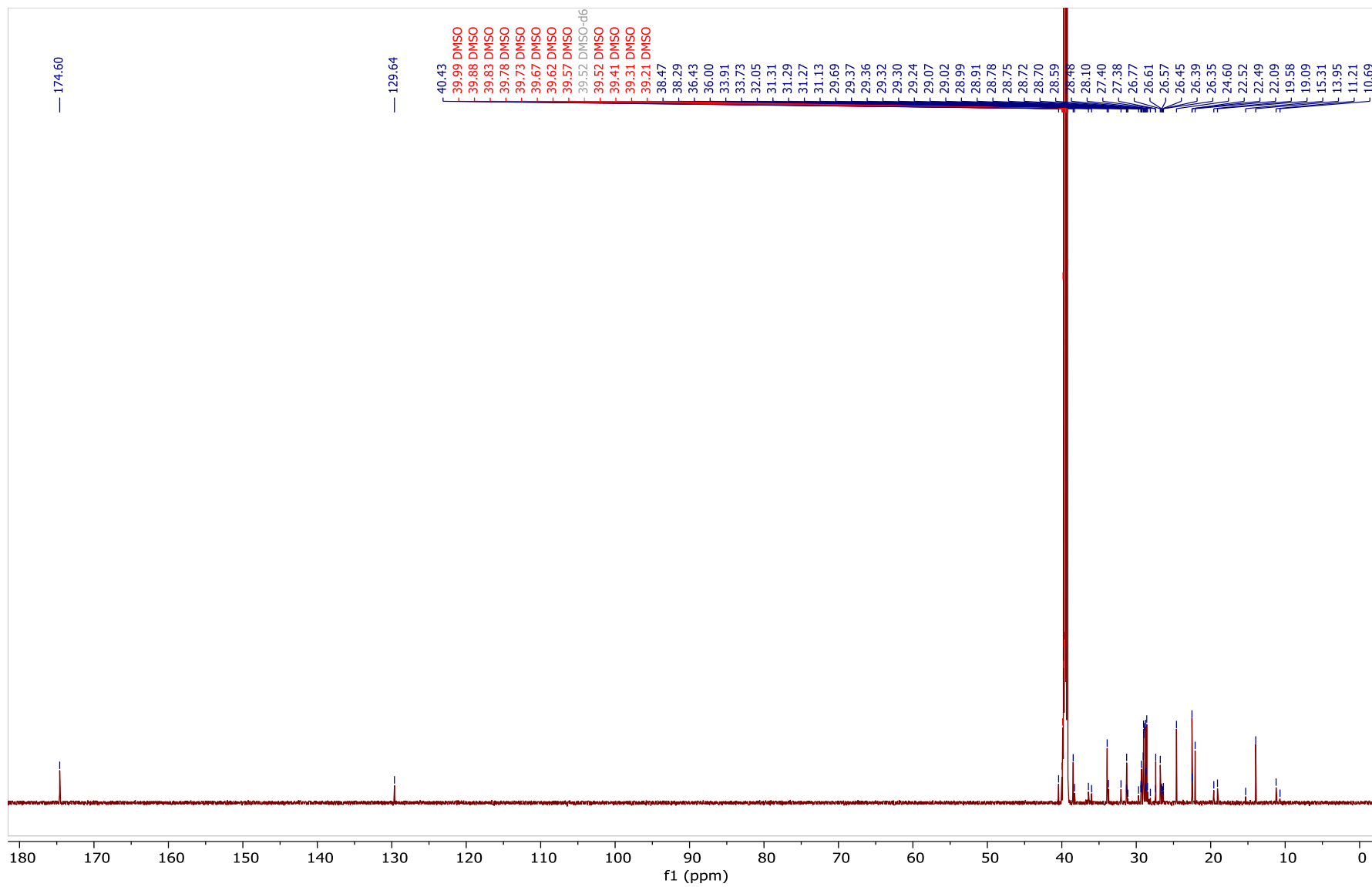


Figure S24: ^{13}C NMR (200 MHz) spectrum of alysterol (**8**) in $\text{DMSO-}d_6$

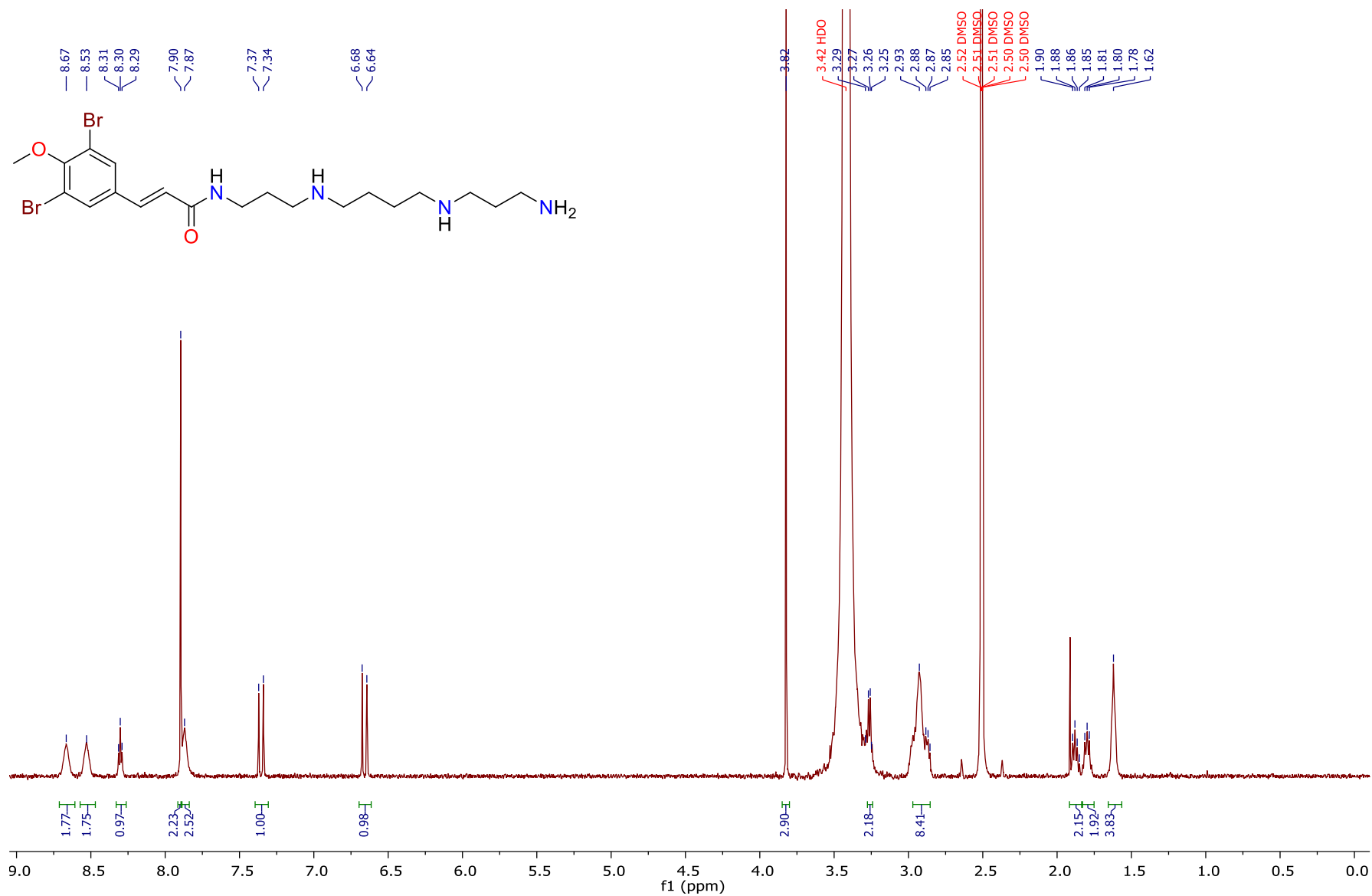


Figure S25: ¹H NMR (800 MHz) spectrum of ianthelliformisamine A (**1**) in DMSO-*d*₆

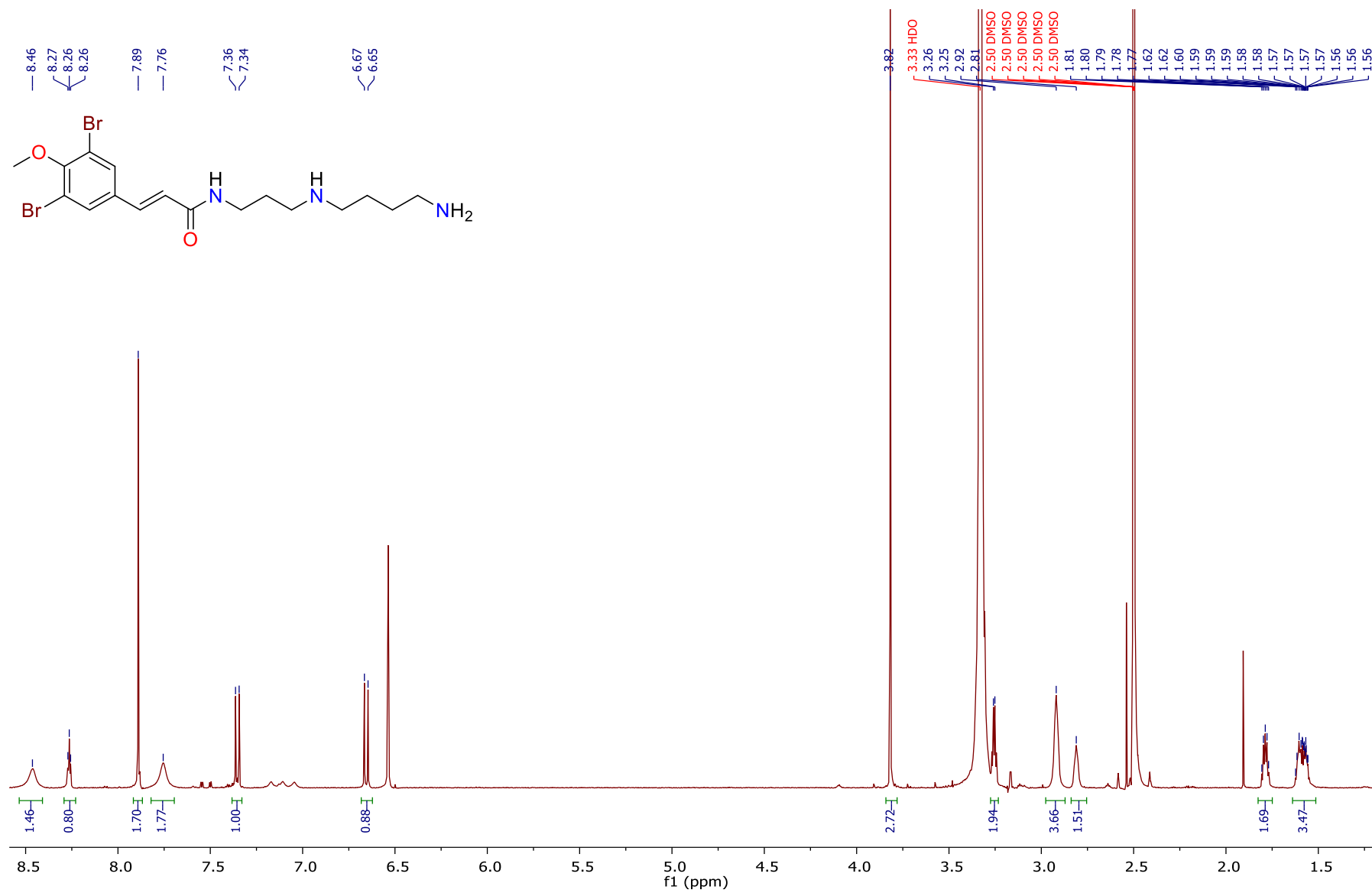


Figure S26: ¹H NMR (800 MHz) spectrum of ianthelliformisamine B (2) in DMSO-*d*₆

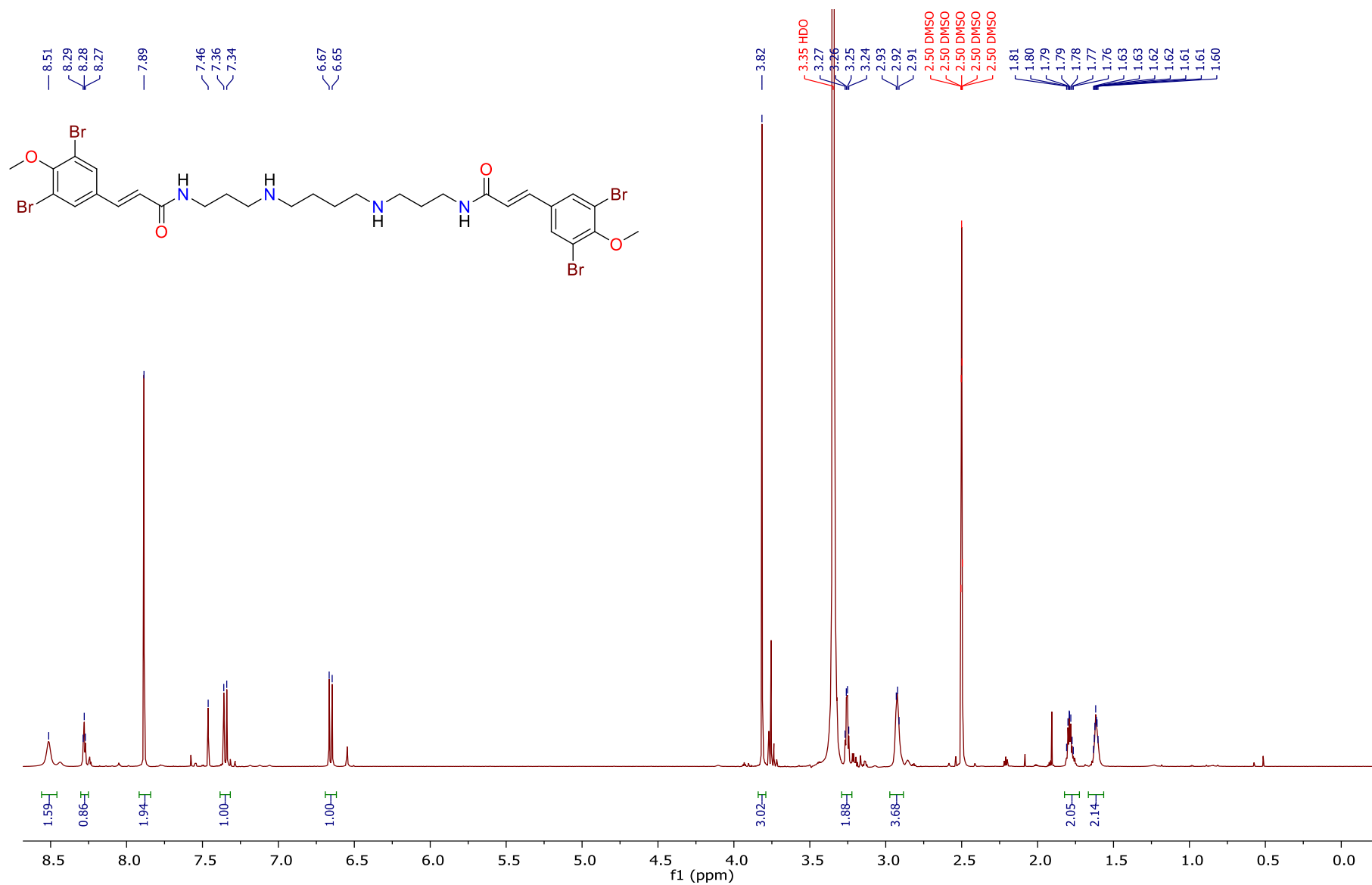


Figure S27: ¹H NMR (800 MHz) spectrum of ianthelliformisamine C (**3**) in DMSO-*d*₆

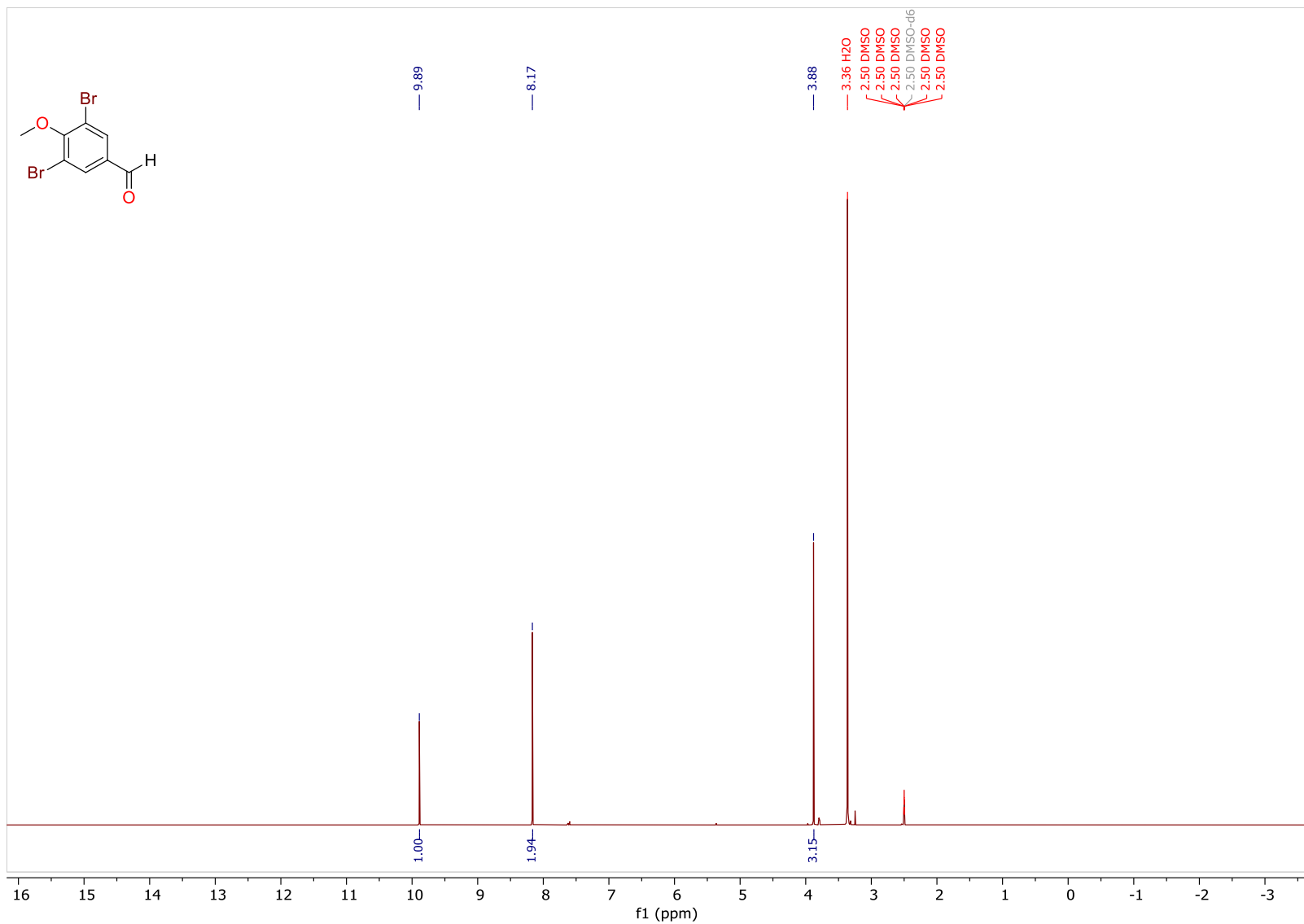


Figure S28: ¹H NMR (800 MHz) spectrum of 3,5-dibromo-4-methoxybenzaldehyde (**9**) in DMSO-*d*₆

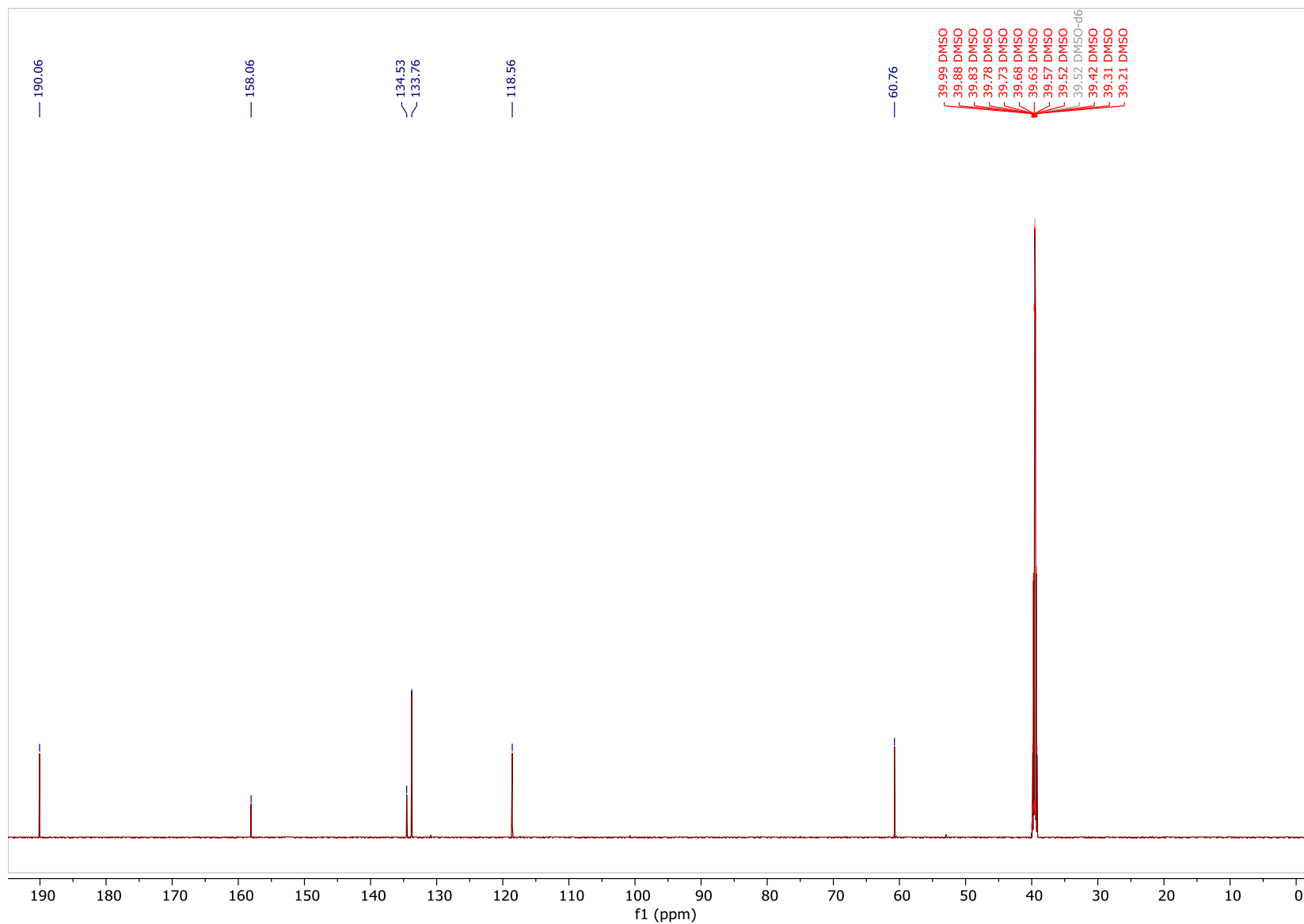


Figure S29: ^{13}C NMR (200 MHz) spectrum of 3,5-dibromo-4-methoxybenzaldehyde (**9**) in DMSO- d_6

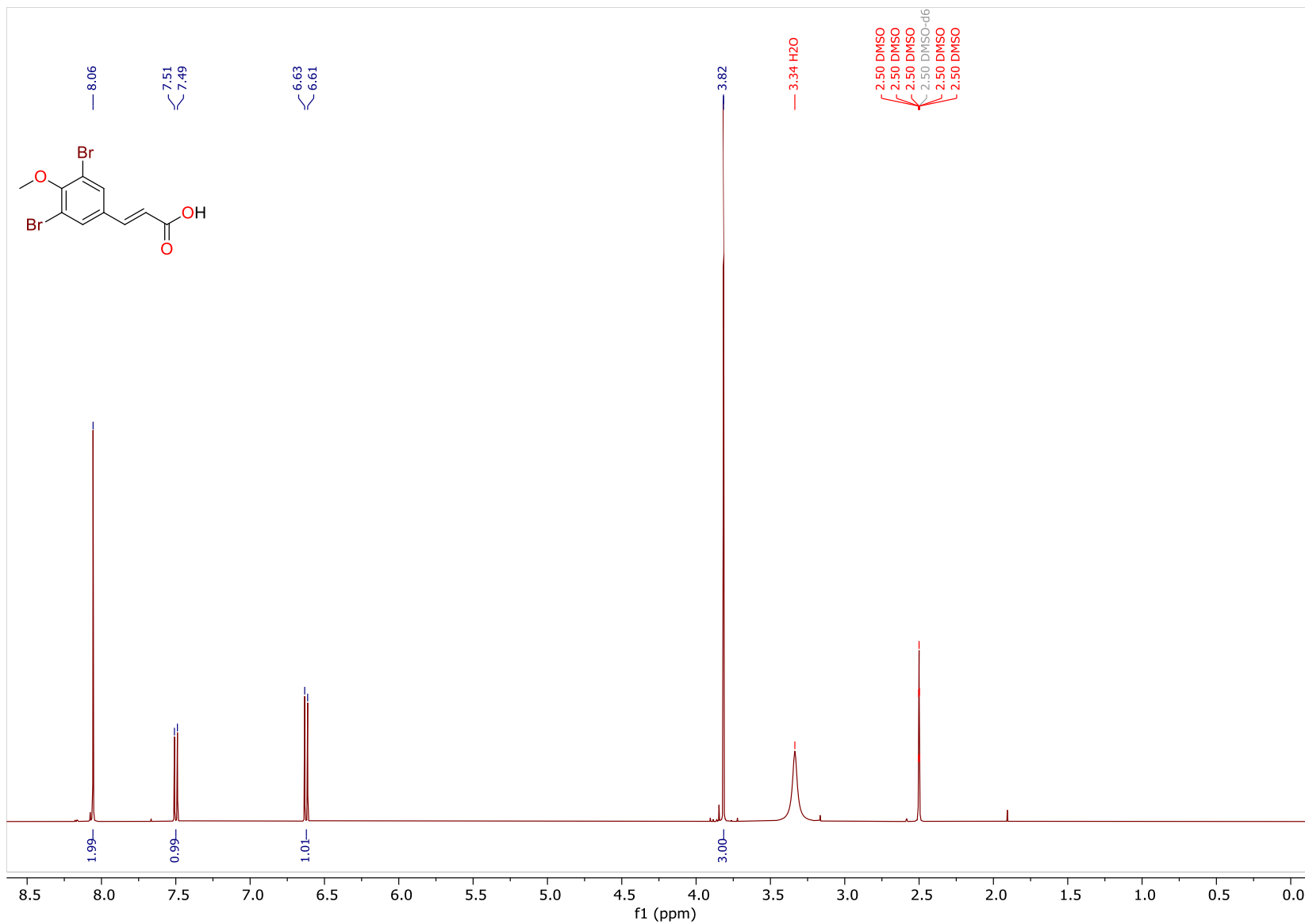


Figure S30: ¹H NMR (800 MHz) spectrum of (*E*)-3-(3,5-dibromo-4-methoxyphenyl)acrylic acid (**10**) in DMSO-*d*₆

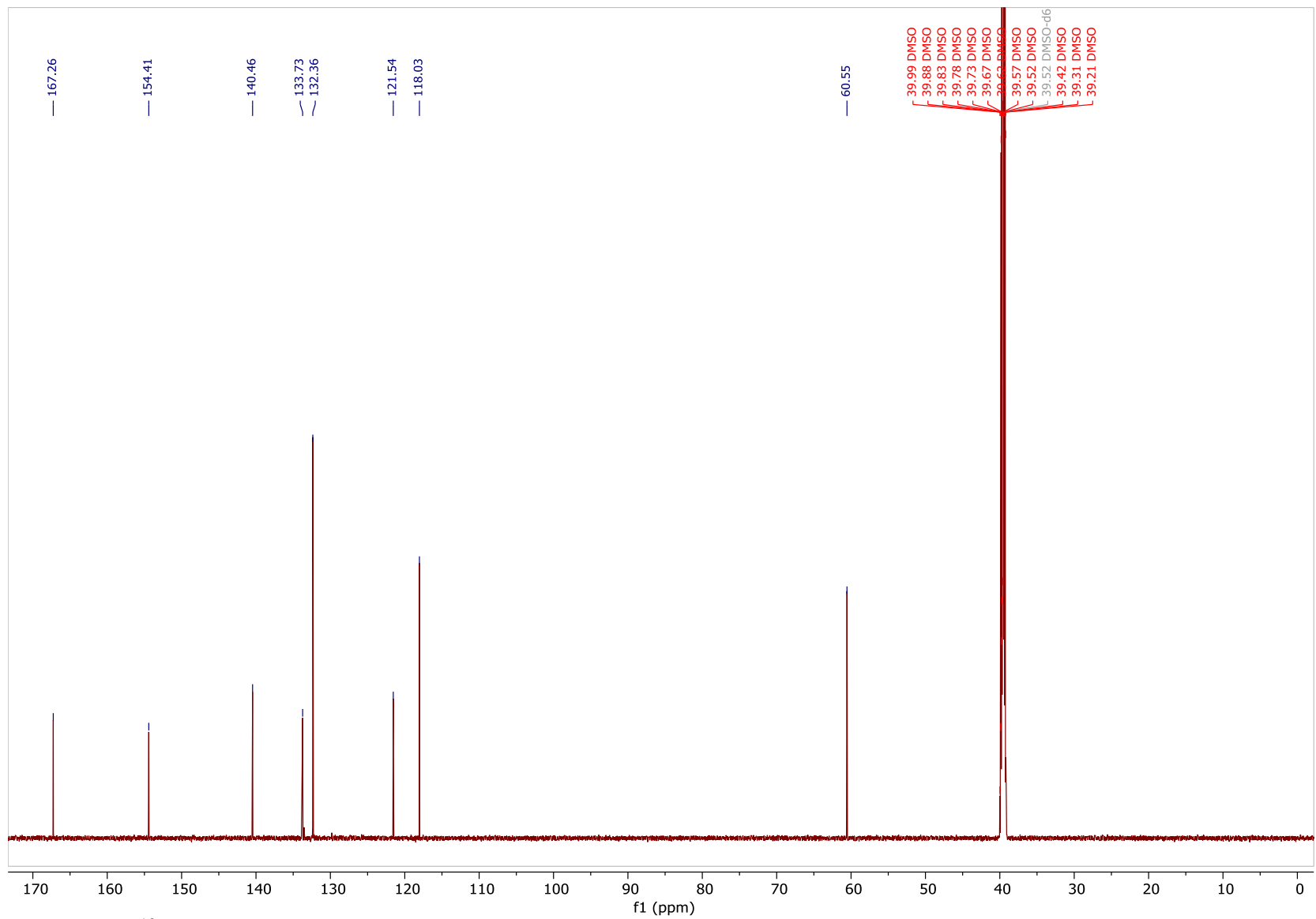


Figure S31: ^{13}C NMR (200 MHz) spectrum of (*E*)-3-(3,5-dibromo-4-methoxyphenyl)acrylic acid (**10**) in $\text{DMSO-}d_6$

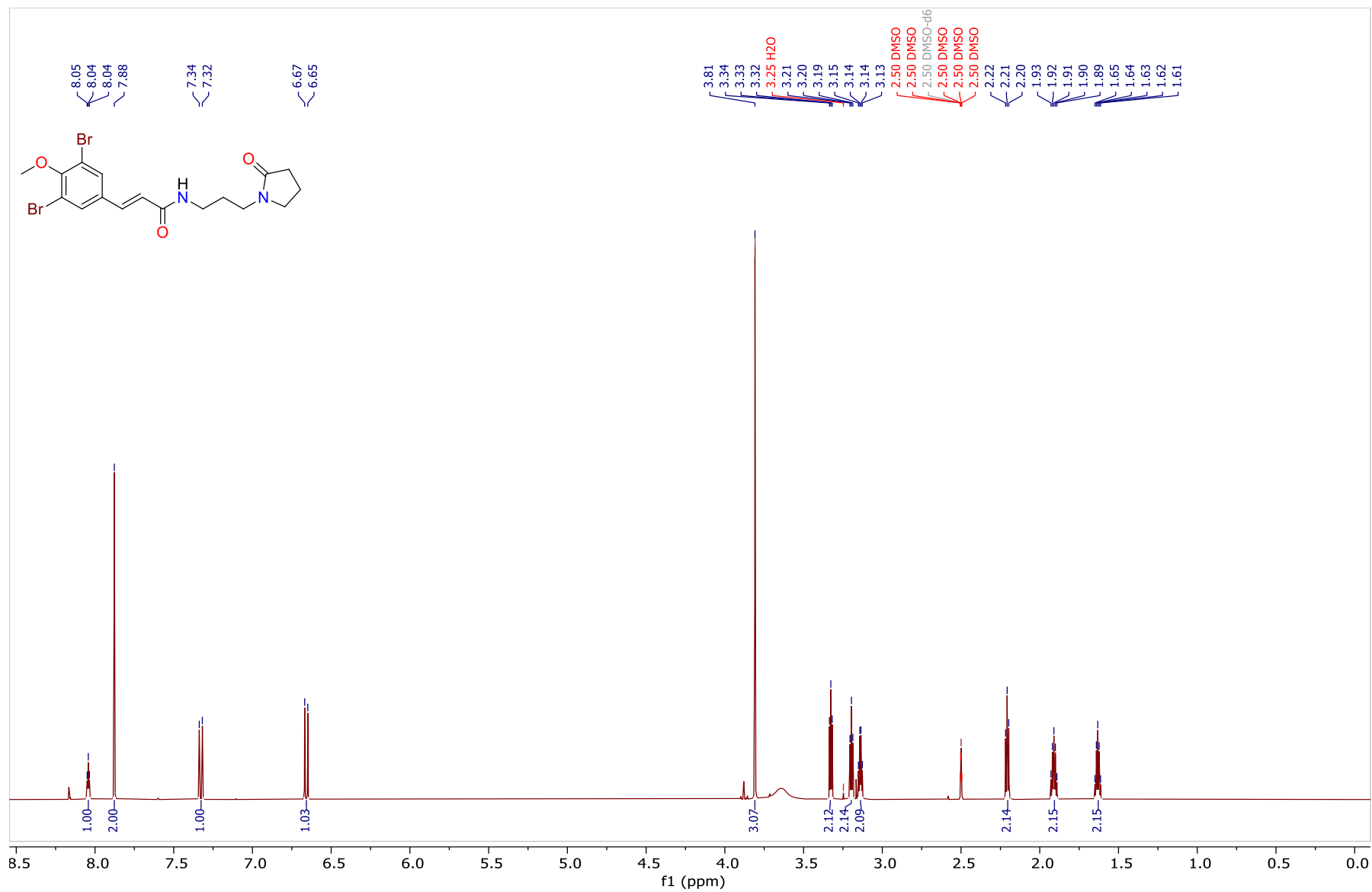


Figure S32: ¹H NMR (800 MHz) spectrum of synthetic ianthelliformisamine D (**4**) in DMSO-*d*₆

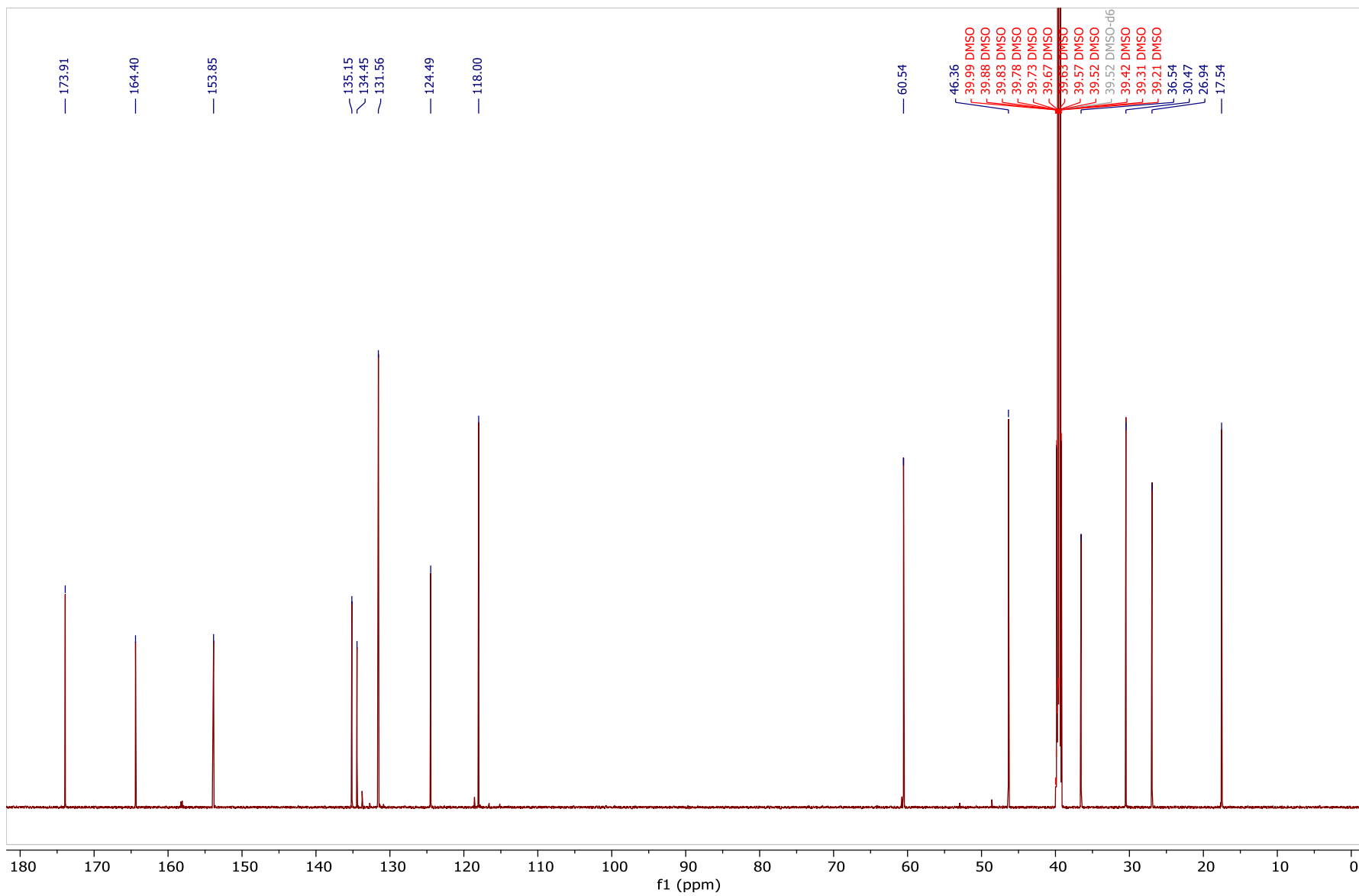


Figure S33: ^{13}C NMR (200 MHz) spectrum of synthetic ianthelliformisamine D (**4**) in $\text{DMSO-}d_6$

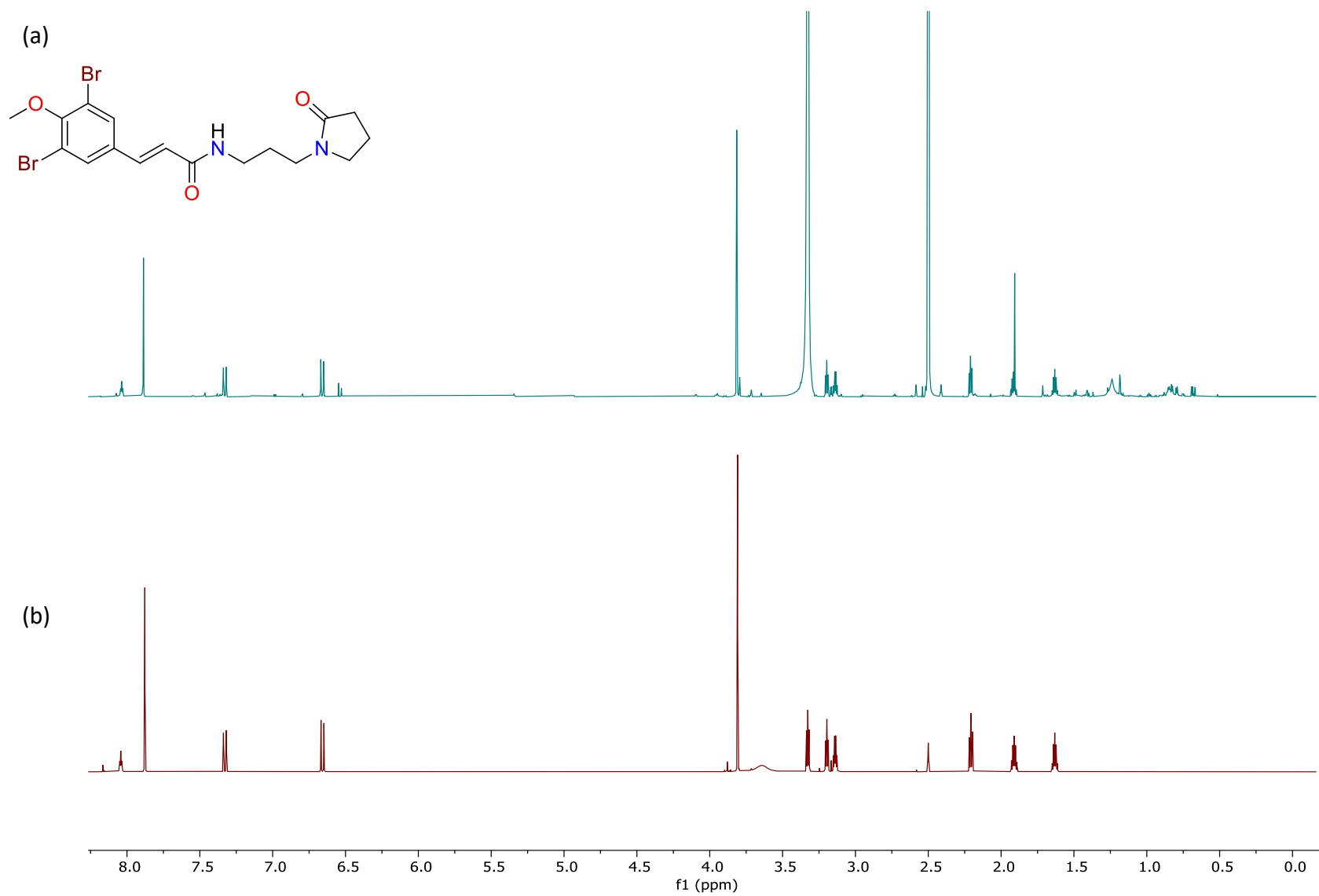
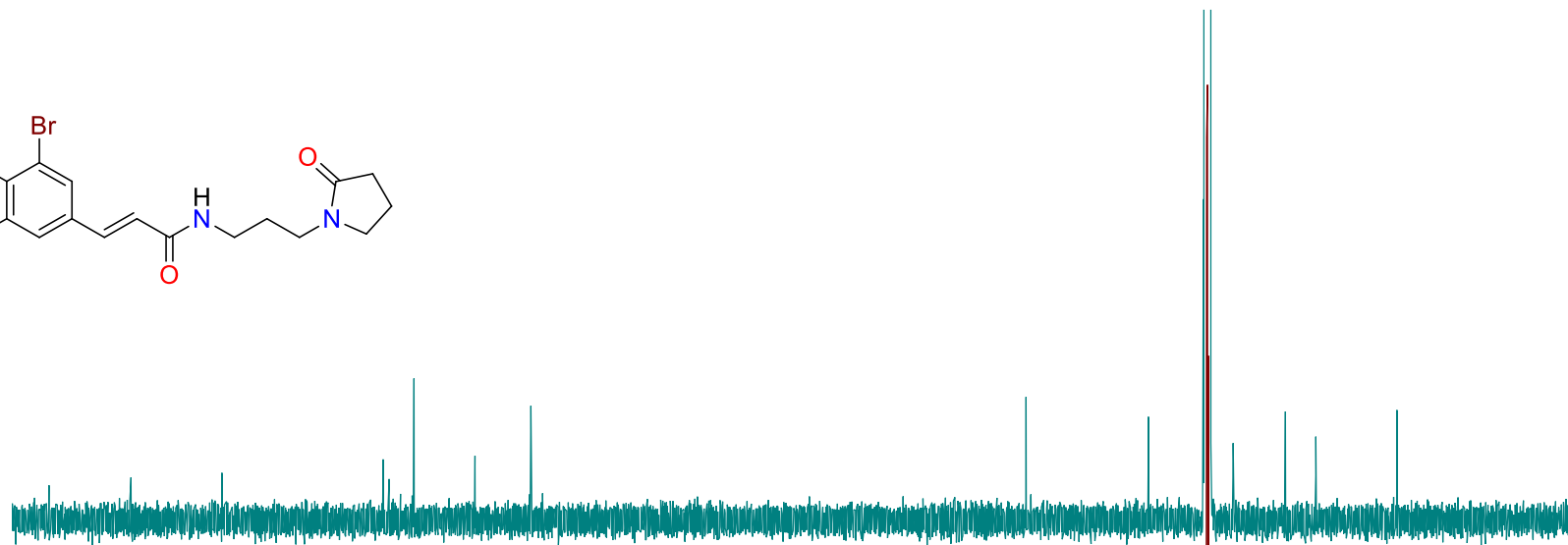
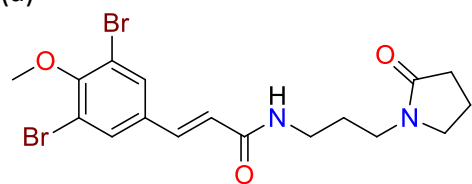


Figure S34: Stacked ^1H NMR (800 MHz) spectra of natural product (a) and synthetic (b), ianthelliformisamine D (**4**) in $\text{DMSO-}d_6$

(a)



(b)

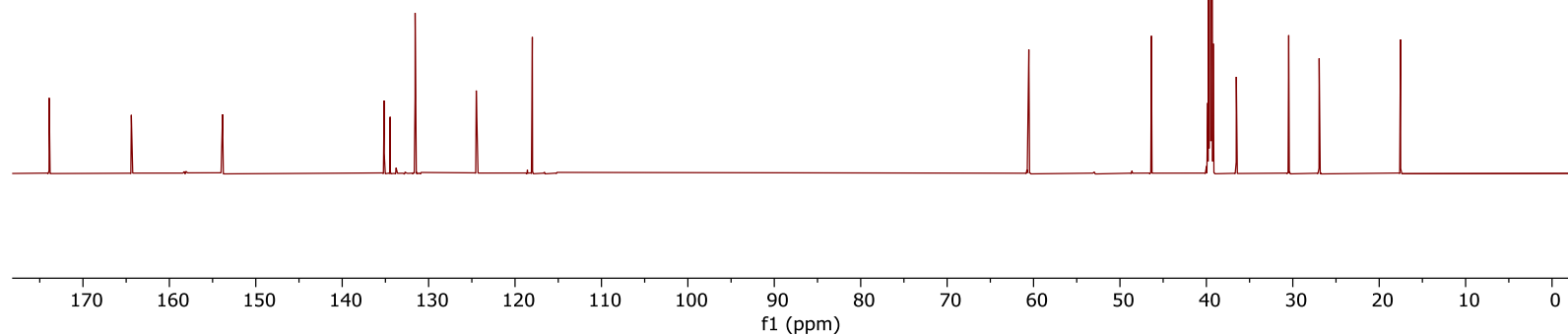


Figure S35: Stacked ^{13}C NMR (200 MHz) spectra of natural product (a) and synthetic (b), ianthelliformisamine D (**4**) in $\text{DMSO-}d_6$