# Identification and analytical characterization of a novel synthetic cannabinoid-type substance in herbal material in Europe

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**SUPPLEMENTARY MATERIAL**

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**Figure S2 :** Chemoidentifiers and IUPAC name of 2F-MPSBA

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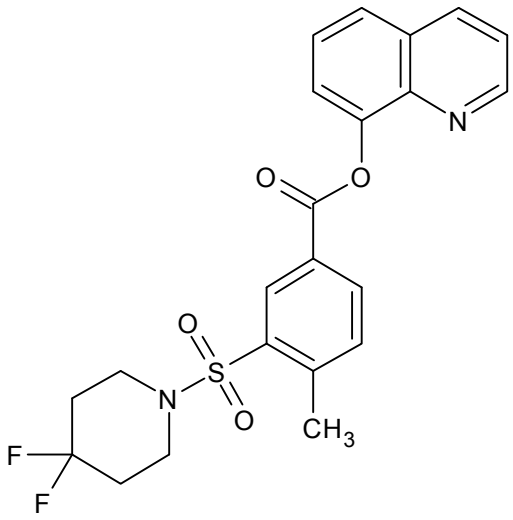
**Figure S14 :** 2D-NMR TOCSY $^{1}$H, $^{1}$H in DMSO-d6 (Sample 8)

**Note:** *Electronic data can be obtained upon request to the authors.*



Molecular Formula: $C_{22}H_{20}F_2N_2O_4S$
Formula Weight: 446.4670064
Monoisotopic Mass: 446.111184 Da
Nominal Mass: 446 Da
Average Mass: 446.467 Da

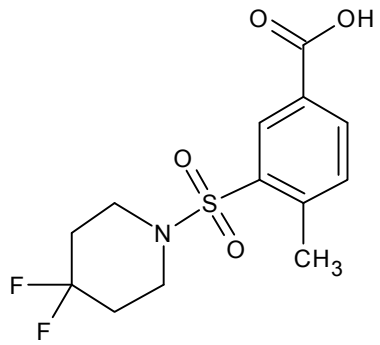
quinolin-8-yl 3-(4,4-difluoropiperidine-1-sulfonyl)-4-methylbenzoate

InChI=1S/C22H20F2N2O4S/c1-15-7-8-17(14-19(15)31(28,29)26-12-9-22(23,24)10-13-26)21(27)30-18-6-2-4-16-5-3-11-25-20(16)18/h2-8,11,14H,9-10,12-13H2,1H3

InChiKey: JOSWCKYCXJMLNM-UHFFFAOYSA-N

SMILES: FC1(F)CCN(CC1)S(=O)(=O)c1cc(ccc1C)C(=O)Oc1cccc2cccnc21

**Figure S1 :** Chemoidentifiers and IUPAC name of 2F-QMPSB



Molecular Formula: $C_{13}H_{15}F_2NO_4S$
Formula Weight: 319.3243064
Monoisotopic Mass: 319.068984 Da
Nominal Mass: 319 Da
Average Mass: 319.3243 Da

3-(4,4-difluoropiperidine-1-sulfonyl)-4-methylbenzoic acid

InChI=1S/C13H15F2NO4S/c1-9-2-3-10(12(17)18)8-11(9)21(19,20)16-6-4-13(14,15)5-7-16/h2-3,8H,4-7H2,1H3,(H,17,18)

InChiKey: VRCWMNIBLGREDC-UHFFFAOYSA-N

SMILES: FC1(F)CCN(CC1)S(=O)(=O)c1cc(ccc1C)C(=O)O

**Figure S2 :** Chemoidentifiers and IUPAC name of 2F-MPSBA

**Table S1.** Fragments of the two compounds identified by GC-IT-MS

| 1st peak $t_R$ = 5.38 min | | | | | | |
|---|---|---|---|---|---|---|
| **No.** | **Formula** | **Fragment** | **m/z Calc** | **m/z Exp.** | **RI Exp.(%)** | **TIC Exp.(%)** |
| 1 | C14H17F2NO4S(+) | M | 333.084 | 333 | 9.713 | 2.289 |
| 2 | C13H14F2NO3S(+) | M - CH3O | 302.066 | 302.1 | 5.863 | 1.362 |
| 3 | C12H13FNO2S(+) | M - C2H4FO2 | 254.065 | 254.1 | 8.45 | 1.926 |
| 4 | C9H10O2(+) | M - C5H7F2NO2S | 150.068 | 150.1 | 9.527 | 2.001 |
| 5 | C9H9O2(+) | M - C5H8F2NO2S | 149.06 | 149.1 | 21.646 | 4.545 |
| 6 | C9H8O2(+) | M - C5H9F2NO2S | 148.052 | 148.1 | 18.189 | 3.819 |
| 7 | C8H6O2(+) | M - C6H11F2NO2S | 134.036 | 134.1 | 6.716 | 1.394 |
| 8 | C5H9F2N(+) | M - C9H8O4S | 121.07 | 121.1 | 23.869 | 4.791 |
| 9 | C5H8F2N(+) | M - C9H9O4S | 120.062 | 120.1 | 100 | 20.069 |
| 10 | C5H7F2N(+) | M - C9H10O4S | 119.054 | 119.2 | 17.513 | 3.514 |
| 11 | C5H6F2N(+) | M - C9H11O4S | 118.046 | 118.2 | 10.607 | 2.128 |
| 12 | C5H5F2N(+) | M - C9H12O4S | 117.038 | 117.2 | 19.572 | 3.927 |
| 13 | C5H7FN(+) | M - C9H10FO4S | 100.056 | 100.1 | 13.504 | 2.71 |
| 14 | C4H5F2(+) | M - C10H12NO4S | 91.035 | 91.1 | 14.374 | 2.842 |
| 15 | C7H6(+) | M - C7H11F2NO4S | 90.046 | 90.1 | 16.578 | 3.388 |
| 16 | C7H5(+) | M - C7H12F2NO4S | 89.039 | 89.1 | 32.206 | 6.582 |
| **2nd-peak $t_R$ = 17.54 min ; 2F-QMPSB** | | | | | | |
| **No.** | **Formula** | **Fragment** | **m/z Calc** | **m/z Exp.** | **RI Exp.(%)** | **TIC Exp.(%)** |
| 1 | C13H15F2NO3S(+) | M - C9H5NO | 303.074 | 303.1 | 12.405 | 1.403 |
| 2 | C13H14F2NO3S(+) | M - C9H6NO | 302.066 | 302.1 | 100 | 11.307 |
| 3 | C13H13FNO3S(+) | M - C9H7FNO | 282.059 | 282.1 | 10.651 | 1.204 |
| 4 | C13H12FNO3S(+) | M - C9H8FNO | 281.052 | 281.1 | 26.457 | 2.991 |
| 5 | C17H13NO2(+) | M - C5H7F2NO2S | 263.094 | 263.2 | 59.35 | 6.651 |
| 6 | C15H10NO2(+) | M - C7H10F2NO2S | 236.071 | 236.1 | 6.326 | 0.693 |
| 7 | C7H9F2NO2S(+) | M - C15H11NO2 | 209.032 | 209 | 14.662 | 1.547 |
| 8 | C5H7F2NO2S(+) | M - C17H13NO2 | 183.016 | 183 | 27.875 | 2.877 |
| 9 | C9H7NO(+) | M - C13H13F2NO3S | 145.052 | 145.1 | 7.155 | 0.732 |
| 10 | C8H7O2(+) | M - C14H13F2N2O2S | 135.044 | 135.1 | 25.457 | 2.572 |
| 11 | C8H6O2(+) | M - C14H14F2N2O2S | 134.036 | 134.1 | 6.944 | 0.701 |
| 12 | C8H5O2(+) | M - C14H15F2N2O2S | 133.028 | 133.1 | 6.678 | 0.675 |
| 13 | C5H7F2N(+) | M - C17H13NO4S | 119.054 | 119.1 | 18.368 | 1.793 |
| 14 | C5H6F2N(+) | M - C17H14NO4S | 118.046 | 118.1 | 37.785 | 3.689 |
| 15 | C5H5F2N(+) | M - C17H15NO4S | 117.038 | 117.1 | 14.133 | 1.38 |
| 16 | C8H4O(+) | M - C14H16F2N2O3S | 116.026 | 116.1 | 17.799 | 1.793 |
| 17 | C5H7F2(+) | M - C17H13N2O4S | 105.051 | 105.1 | 5.835 | 0.568 |
| 18 | C4H5F2(+) | M - C18H15N2O4S | 91.035 | 91.1 | 13.439 | 1.293 |
| 19 | C7H6(+) | M - C15H14F2N2O4S | 90.046 | 90 | 12.351 | 1.228 |
| 20 | C7H5(+) | M - C15H15F2N2O4S | 89.039 | 89 | 20.054 | 1.994 |

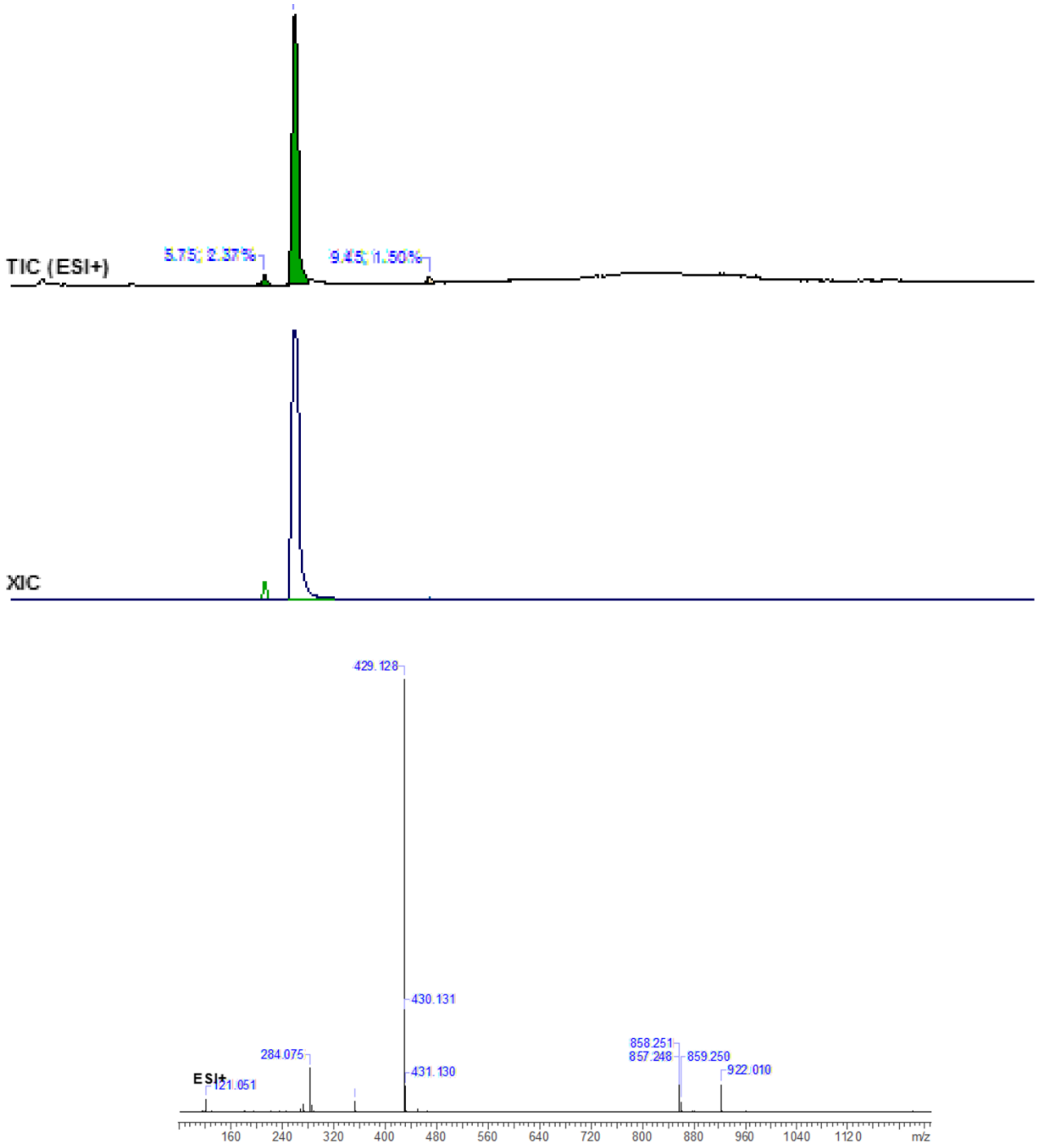



**Figure S3 :** UHPLC-qTOF-MS, minor compound 1 at $t_R$ = 5.75 min (monofluorinated QMPSB)

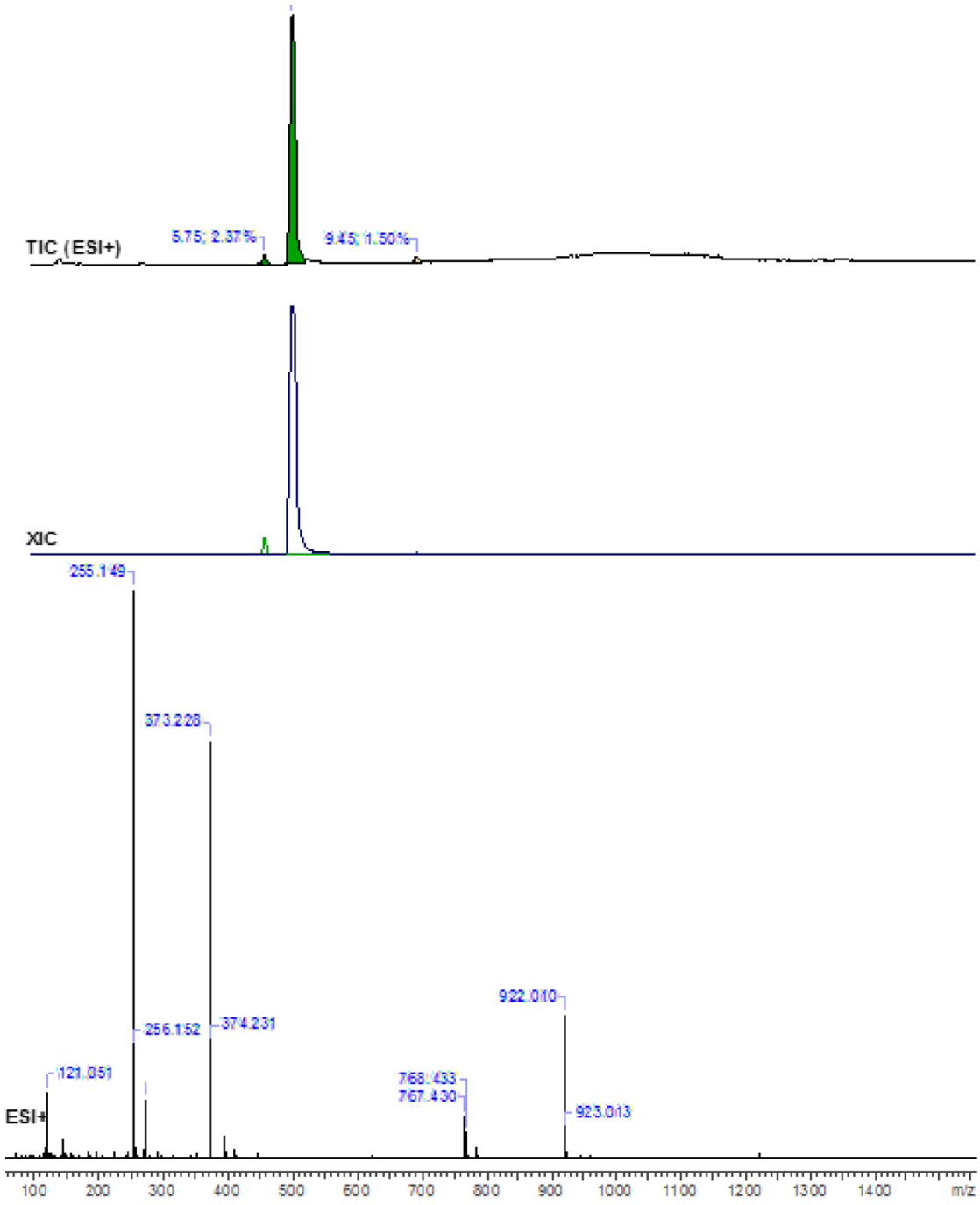



**Figure S4 :** UHPLC-qTOF-MS, minor compound 2 at $t_R$=9.45 min (AM-2201)

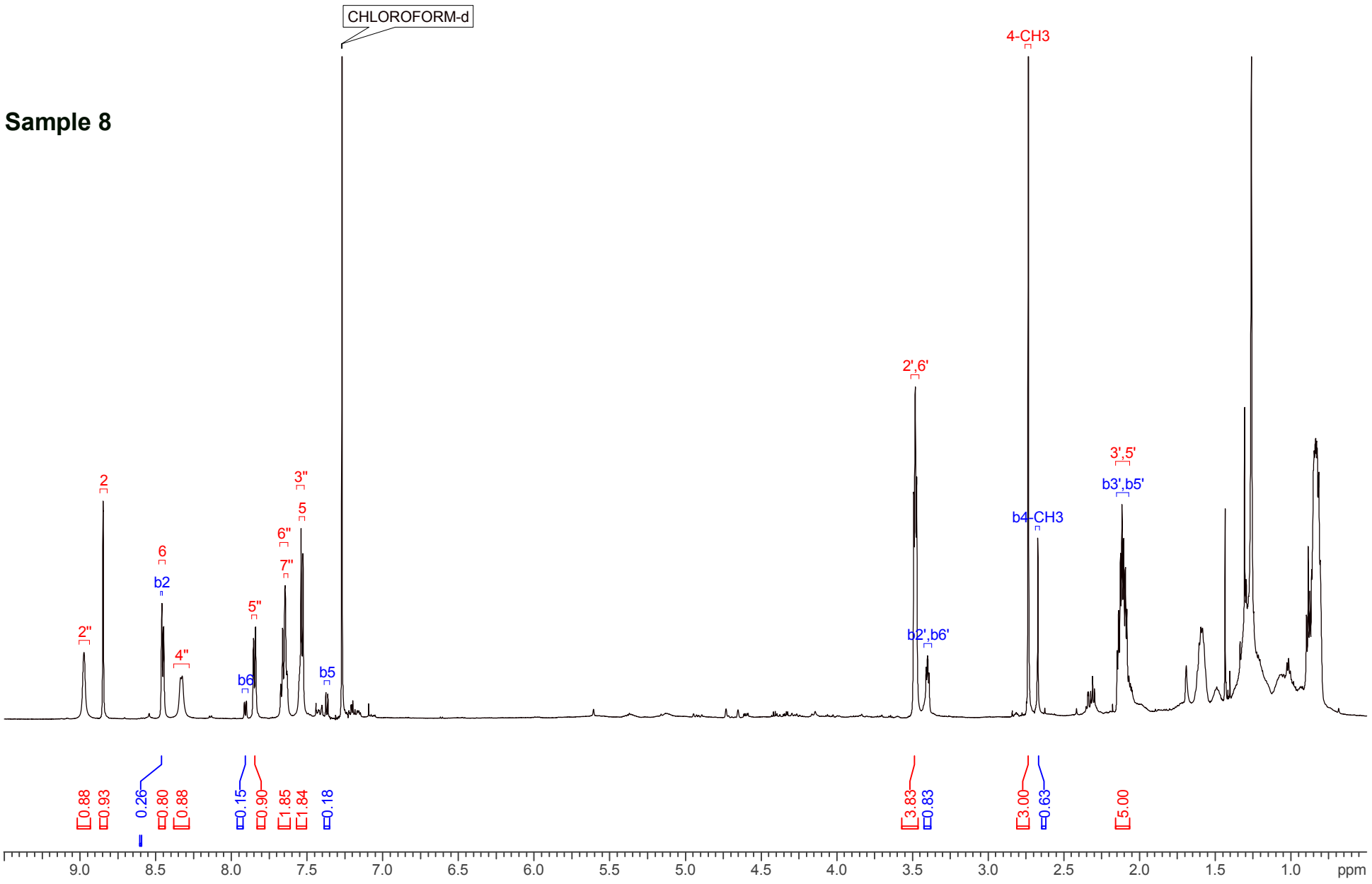



**Figure S5 :** $^{1}$H NMR spectrum of Sample 8 in $CDCl_3$

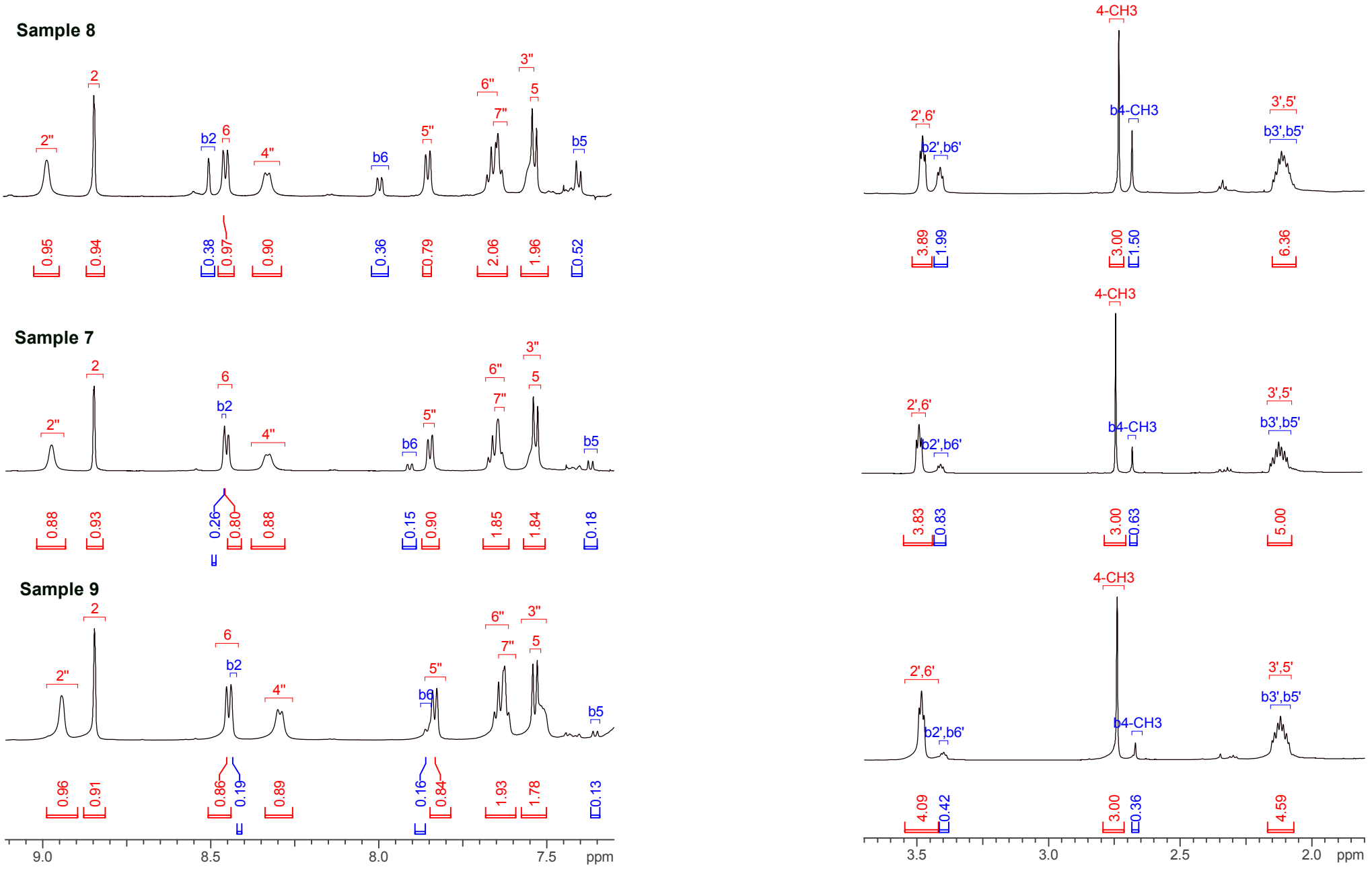



**Figure S6 :** Comparison of $^{1}H$ NMR spectra in $CDCl_3$ of the three samples ( zooms on aromatic and aliphatic areas **)**

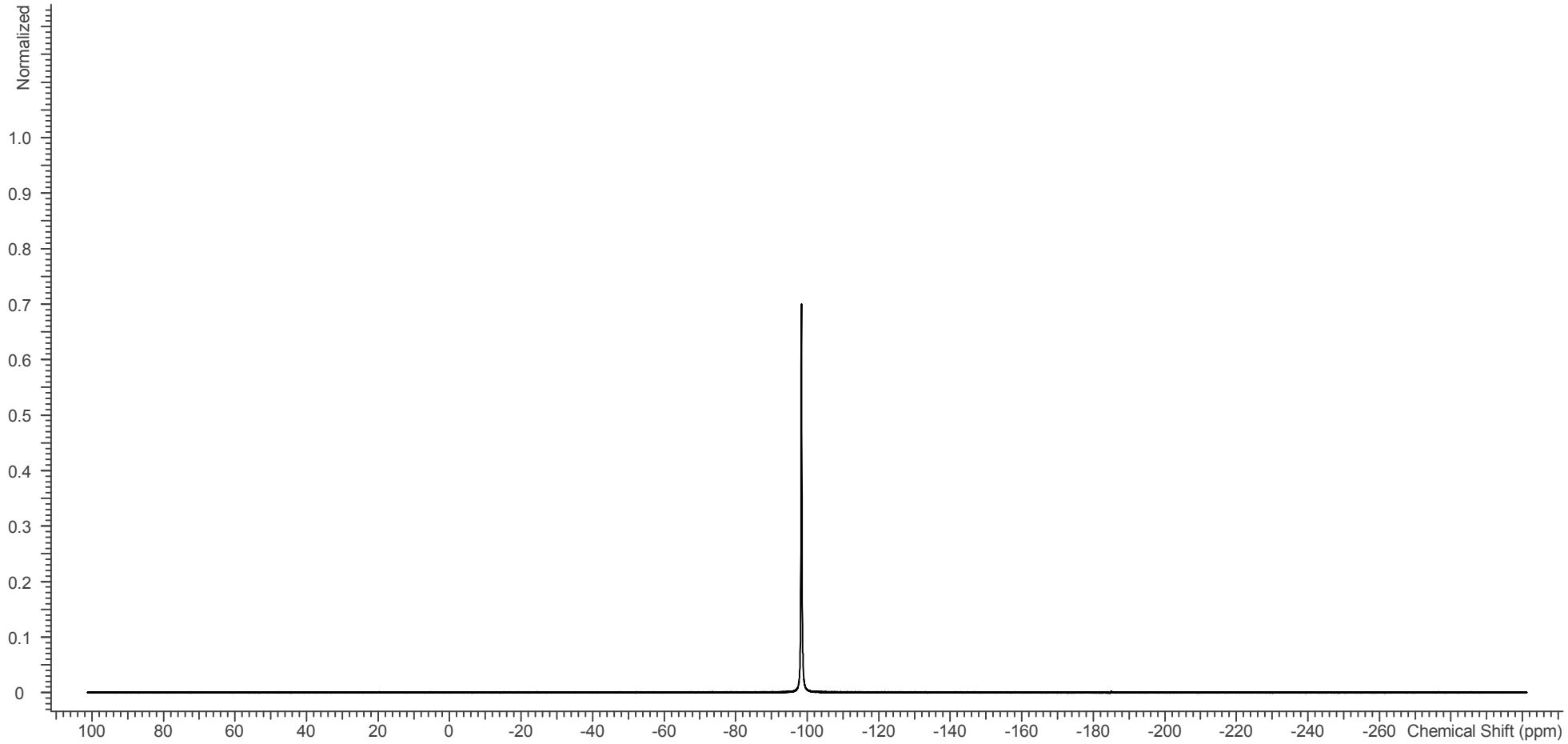



**Figure S7 :** $^{19}F$ spectrum in $CDCl_3$ (measured at 295 K , Inverse Gate Decoupling from $^{1}H$ )

**Sample 8**

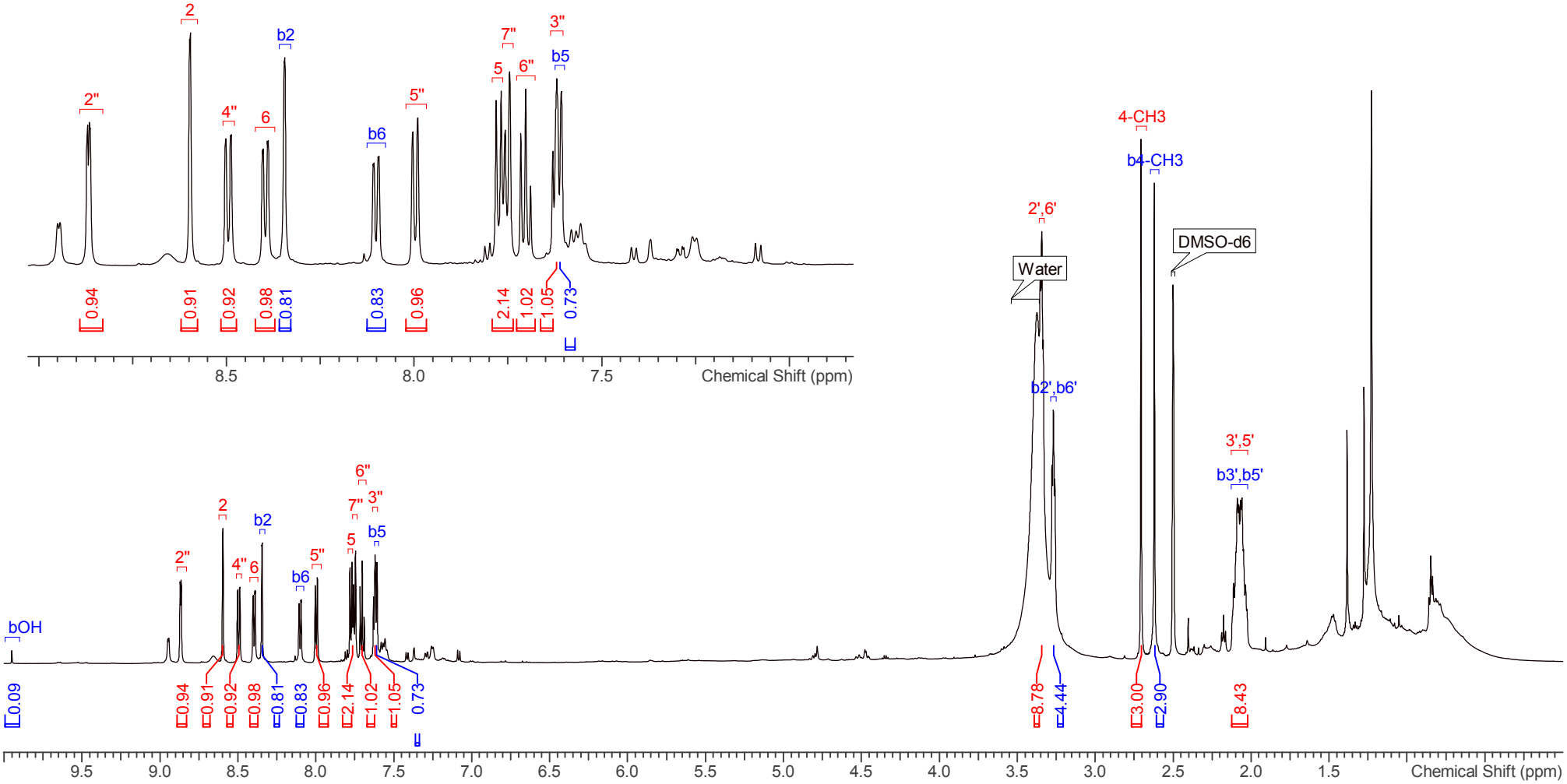



**Figure S8 :** $^{1}$H NMR spectrum of Sample 8 in DMSO-d6

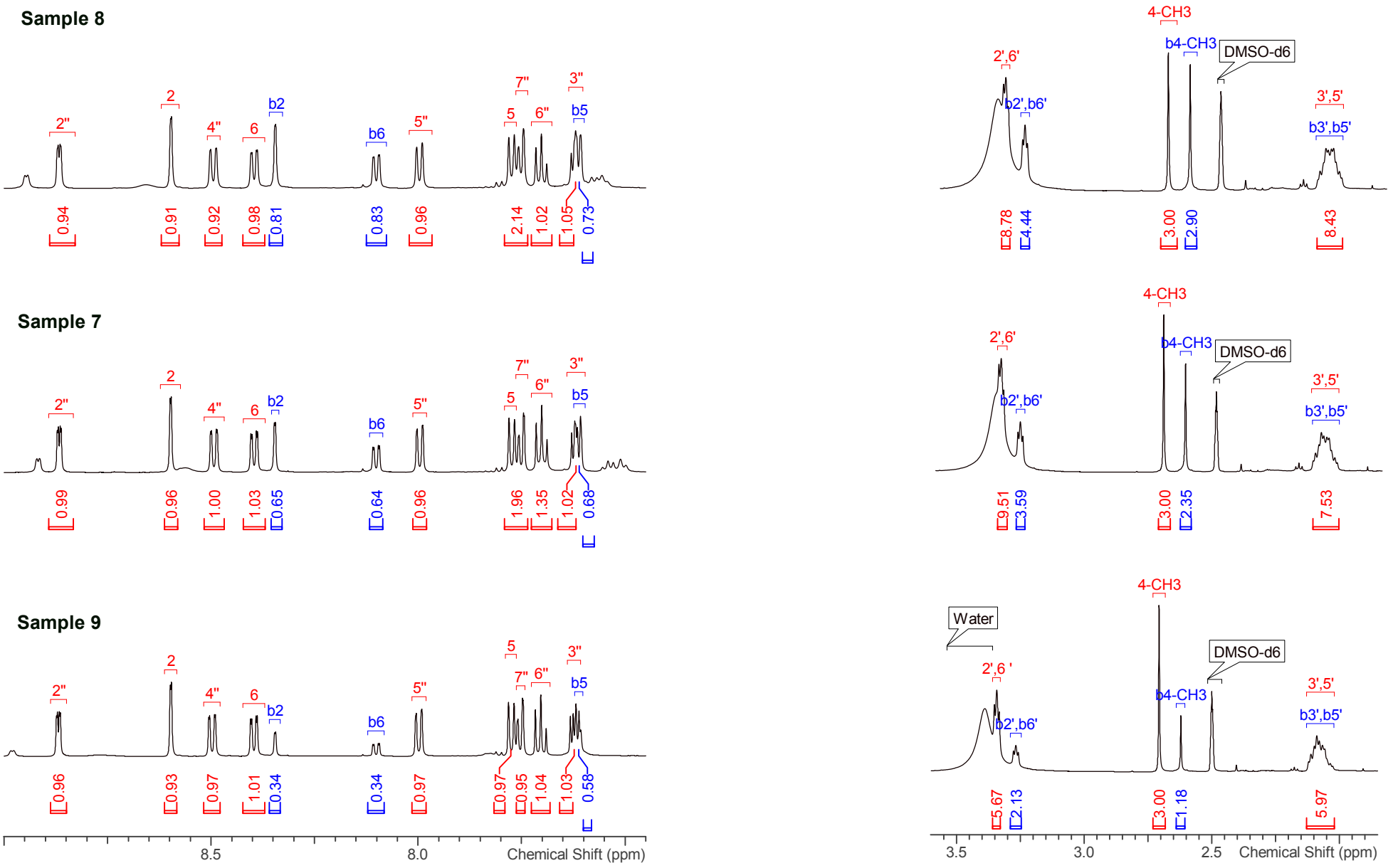


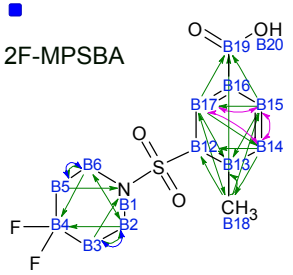

**Figure S9 :** Comparison of $^{1}$H NMR spectra in DMSO-d6 of the three samples ( zooms on aromatic and aliphatic areas **)**

## **Table S2 :** ACD/labs NMR summary table (Sample 8)

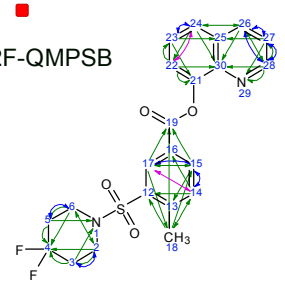
The columns C Label and H Label give the correspondence with the convention of numbering of atoms of QMPSB as in Blakey *et al*, 2016.

COSY
TOCSY
HMBC

2F-MPSBA



2F-QMPSB



| Atom# | C Label | C Shift | X Shift | XHn | H Label | H Shift | H Multiplicity | COSY | TOCSY | H HMBC | C HMBC | X HMBC | Component |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B20 | | | | OH | bOH | 9.950 | s | | | | | | B |
| B19 | C=O | 165.984 | | C | | | | | | B18, B15, B17 | | | B |
| B18 | b4-CH3 | 20.157 | | CH3 | b4-CH3 | 2.621 | s | | | B14, B17 | B17, B15, B12, B13, B19 | | B |
| B17 | b2 | 130.220 | | CH | b2 | 8.345 | d (1.56) | | B14, B15 | B18, B15 | B18, B14, B13, B19 | | B |
| B15 | b6 | 133.664 | | CH | b6 | 8.101 | dd (7.89, 1.28) | | B14, B17 | B18 | B17, B13, B19 | | B |
| B14 | b5 | 133.702 | | CH | b5 | 7.611 | br d (7.56) | | B15, B17 | B17 | B18, B12 | | B |
| B13 | b4 | 142.508 | | C | | | | | | B18, B15, B17 | | | B |
| B12 | b3 | 135.994 | | C | | | | | | B18, B14 | | | B |
| B4 | b4' | 121.900 | | C | | | | | | B2, B6 | | | B |
| B3, B5 | b3',b5' | 33.116 | | CH2 | b3',b5' | 2.055 | m | B2, B6 | B2, B6 | B2, B6 | B2, B6 | B1 | B |
| B2, B6 | b2',b6' | 42.319 | | CH2 | b2',b6' | 3.268 | t (5.73, 5.73) | B3, B5 | B3, B5 | B3, B5 | B3, B5, B4 | | B |
| B1 | bN | | 92.700 | N | | | | | | B3, B5 | | | B |
| 30 | 8a'' | 140.251 | | C | | | | | | 22, 24, 26, 28 | | | A |
| 29 | N2 | | 300.740 | N | | | | | | 27, 28 | | | A |
| 28 | 2'' | 150.846 | | CH | 2'' | 8.867 | dd (4.10, 1.40) | 27, 26 | 27, 26 | 27, 26 | 27, 26, 30 | 29 | A |
| 27 | 3'' | 122.294 | | CH | 3'' | 7.620 | dd (8.30, 4.10) | 26, 28 | 26, 28 | 28 | 25, 28 | 29 | A |
| 26 | 4''' | 136.399 | | CH | 4'' | 8.494 | dd (8.30, 1.40) | 27, 28 | 27, 28 | 24, 28 | 24, 30, 28 | | A |
| 25 | 4a'' | 129.194 | | C | | | | | | 27, 23 | | | A |
| 24 | 5'' | 126.556 | | CH | 5'' | 7.996 | br dd (8.10, 1.10) | 23 | 22 | 26 | 22, 26, 30 | | A |
| 23 | 6'' | 126.505 | | CH | 6'' | 7.702 | br dd (8.10, 7.30) | 24 | | 22 | 25, 21 | | A |
| 22 | 7'' | 121.801 | | CH | 7'' | 7.751 | dd (7.30, 1.10) | | 24 | 24 | 23, 30, 21 | | A |
| 21 | 8'' | 146.809 | | C | | | | | | 23, 22 | | | A |
| 19 | C=O | 163.456 | | C | | | | | | 18, 15, 17 | | | A |
| 18 | 4-CH3 | 20.303 | | CH3 | 4-CH3 | 2.706 | s | | | 14, 17 | 14, 15, 12, 19 | | A |
| 17 | 2 | 130.684 | | CH | 2 | 8.597 | d (1.65) | 15 | 14, 15 | 15 | 18, 15, 19 | | A |
| 16 | 1 | 127.333 | | C | | | | | | 14 | | | A |
| 15 | 6 | 134.311 | | CH | 6 | 8.396 | dd (7.90, 1.65) | 14, 17 | 14, 17 | 18, 17 | 17, 13, 19 | | A |
| 14 | 5 | 134.191 | | CH | 5 | 7.774 | d (7.90) | 15 | 15, 17 | 18 | 18, 16, 12 | | A |
| 13 | 4 | 143.959 | | C | | | | | | 15 | | | A |
| 12 | 3 | 136.631 | | C | | | | | | 18, 14 | | | A |
| 4 | 4' | 121.920 | | C | | | | | | 3, 5, 2, 6 | | | A |
| 3, 5 | 3',5' | 33.172 | | CH2 | 3',5' | 2.078 | m | 2, 6 | 2, 6 | 2, 6 | 4 | 1 | A |
| 2, 6 | 2',6' | 42.324 | | CH2 | 2',6' | 3.343 | t (5.30, 5.30) | 3, 5 | 3, 5 | | 3, 5, 4 | | A |
| 1 | N1 | | 92.802 | N | | | | | | 3, 5 | | | A |

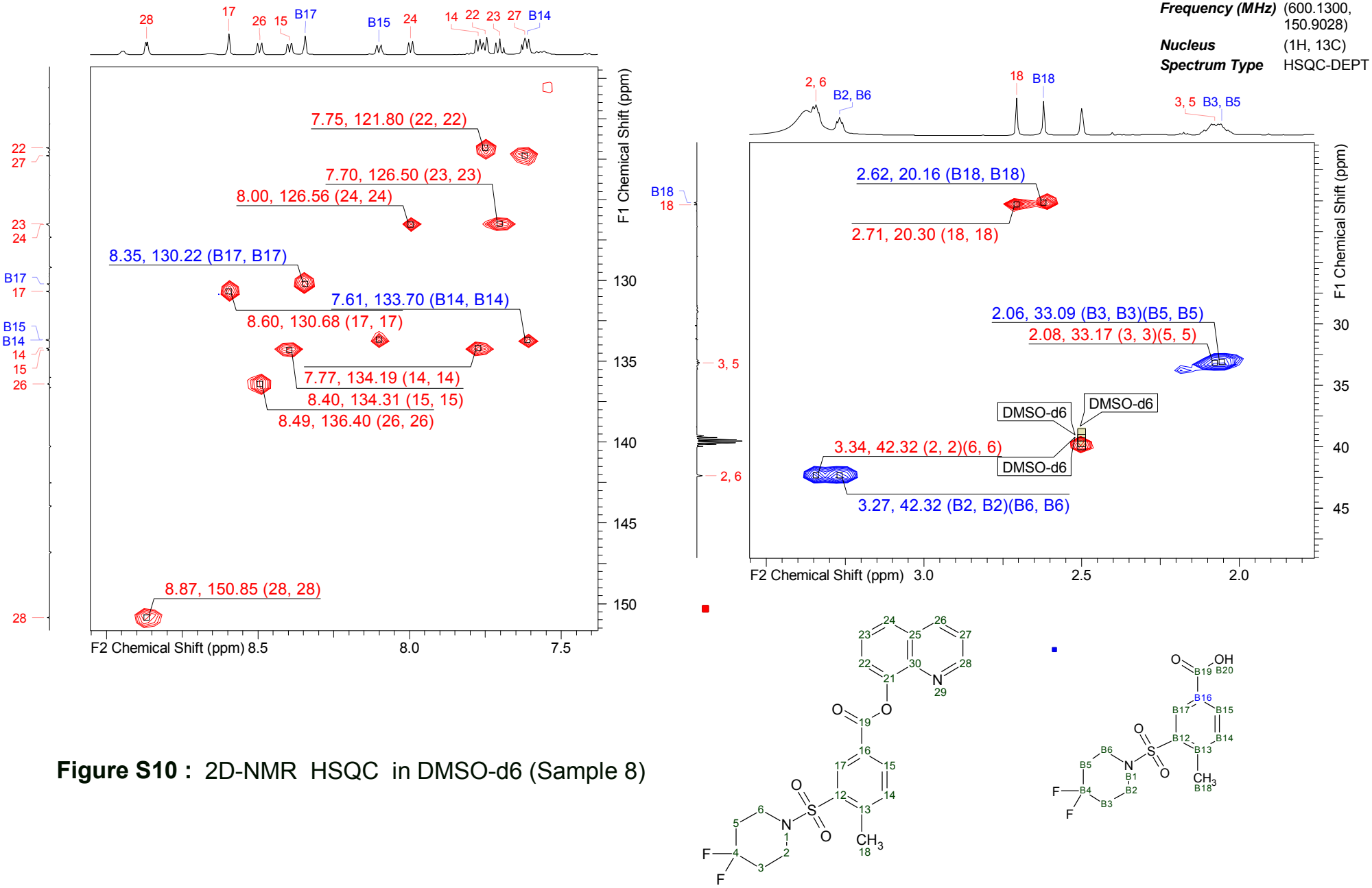
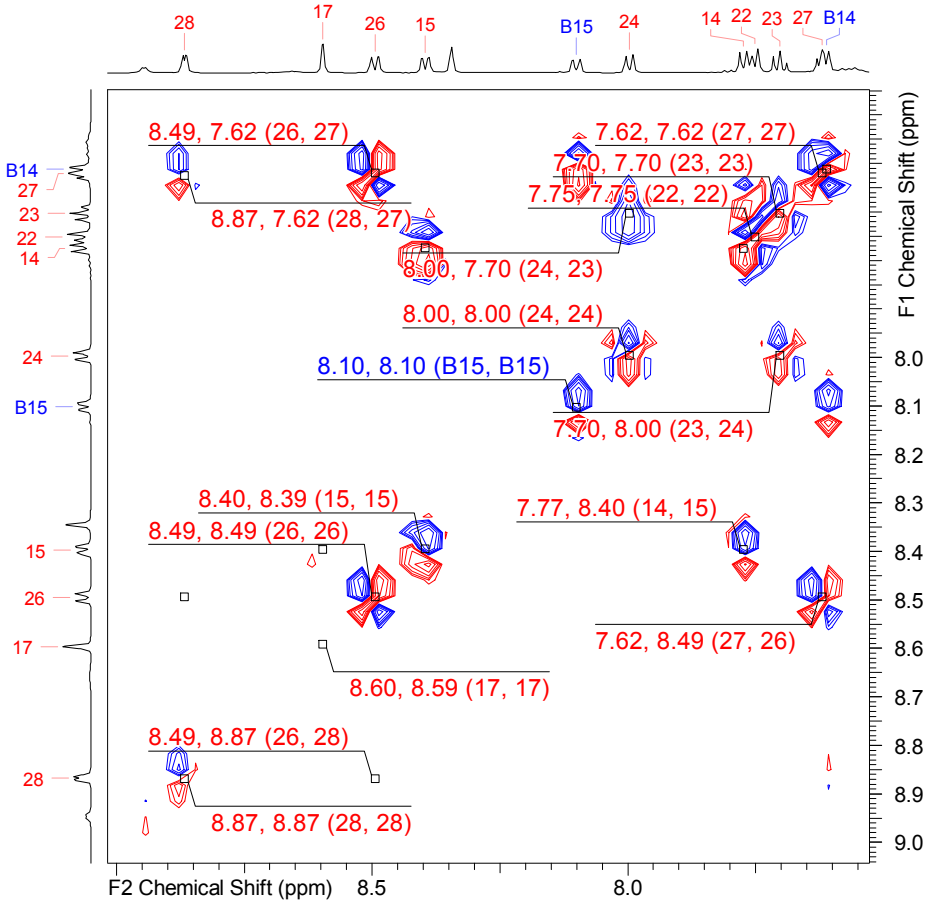
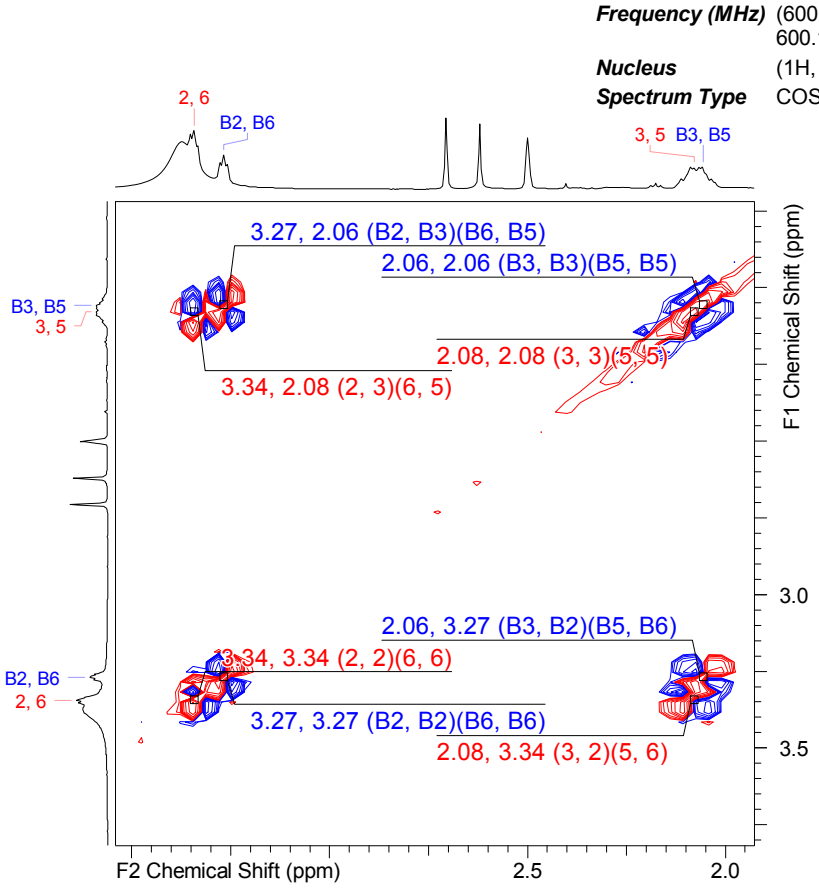
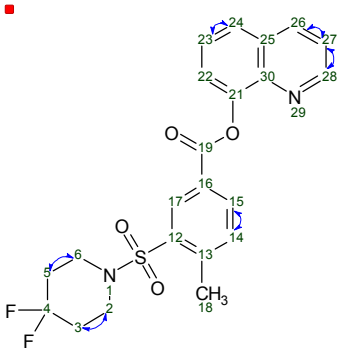



**Figure S10 :** 2D-NMR HSQC in DMSO-d6 (Sample 8)



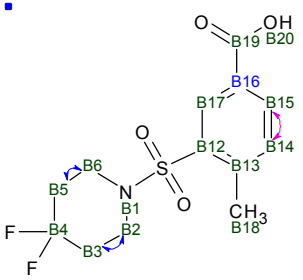
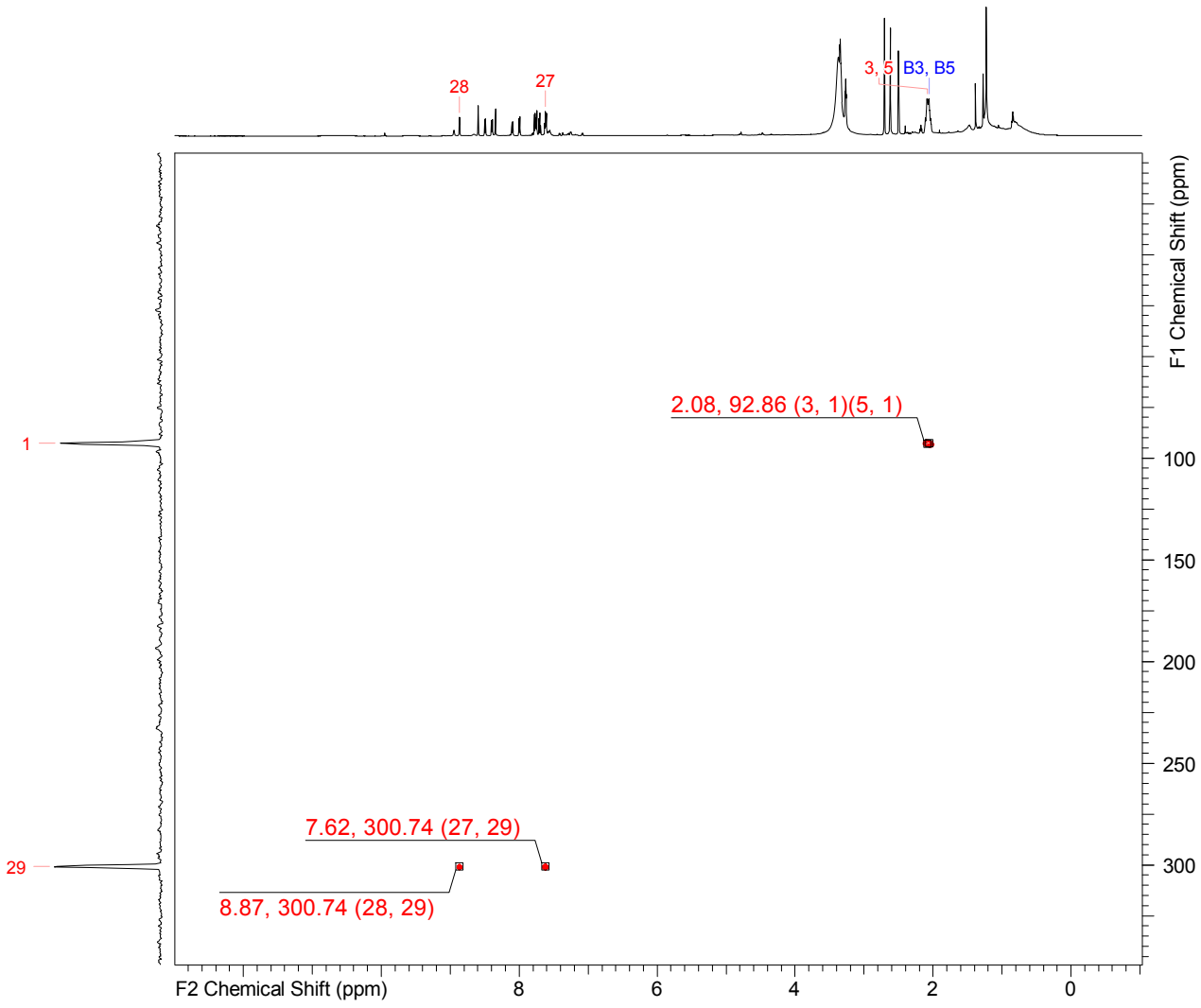


**Figure S11 :** 2D-NMR COSY in DMSO-d6 (Sample 8)



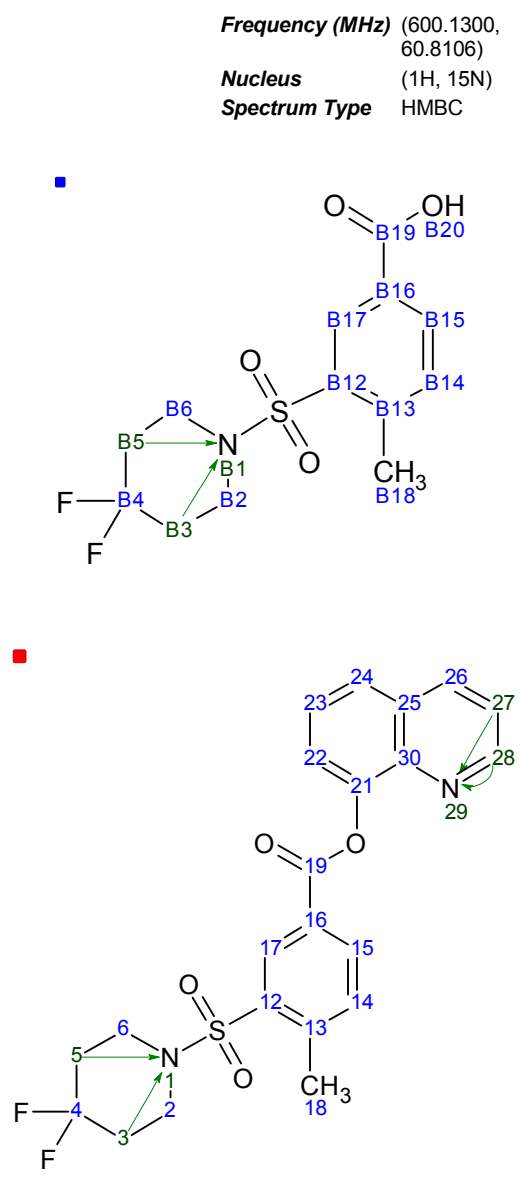
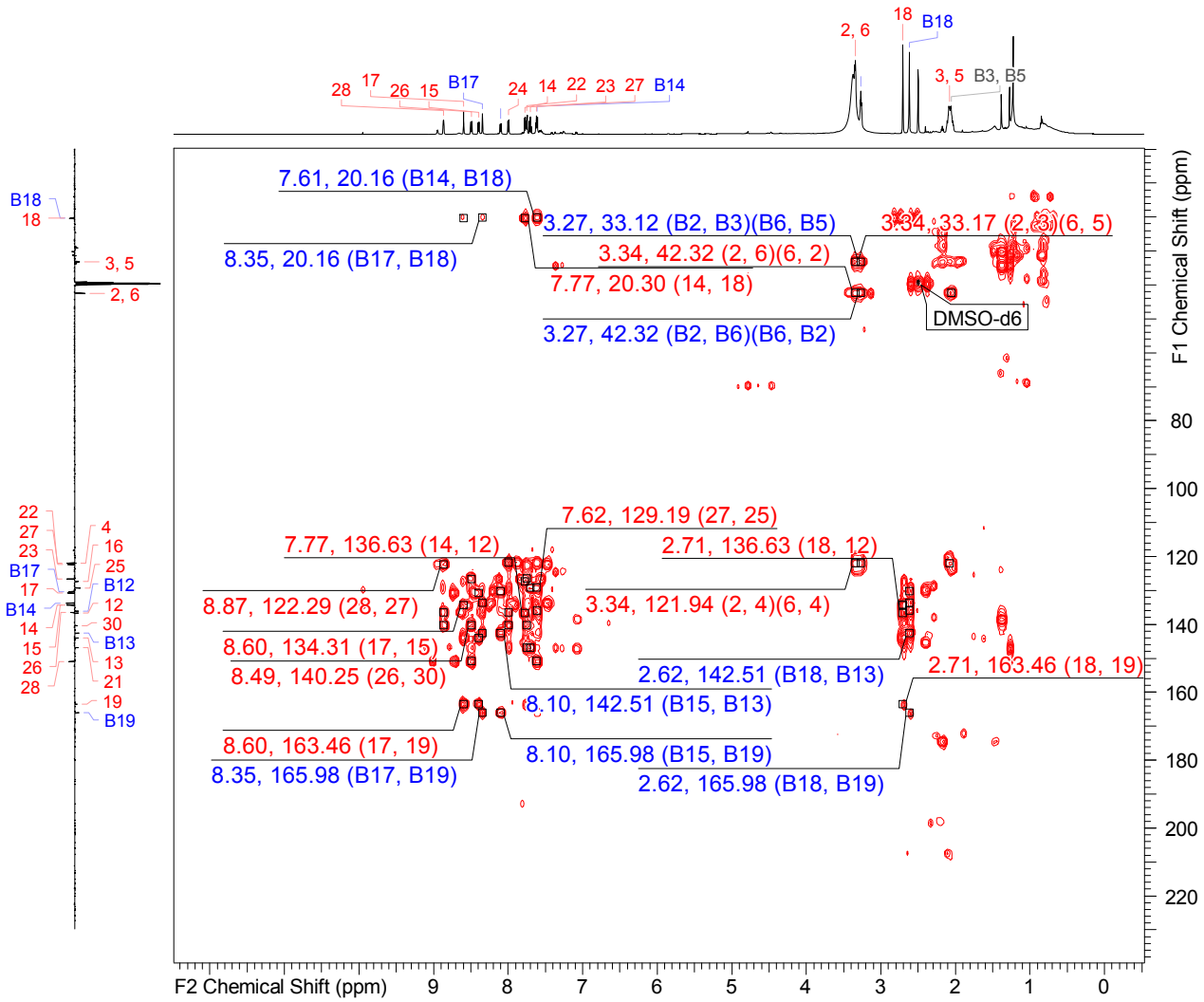
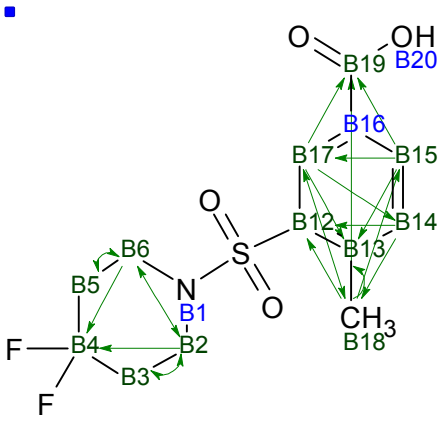




**Figure S12 :** 2D-NMR HMBC $^{15}N$, $^{1}H$ in DMSO-d6 (Sample 8)




***Frequency (MHz)*** (600.1300, 150.9028)
***Nucleus*** (1H, 13C)
***Spectrum Type*** HMBC



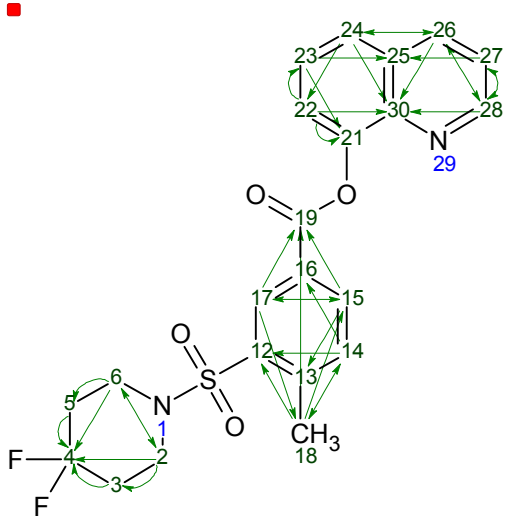




**Figure S13 :** 2D-NMR HMBC $^{13}C$, $^{1}H$ in DMSO-d6 (Sample 8)

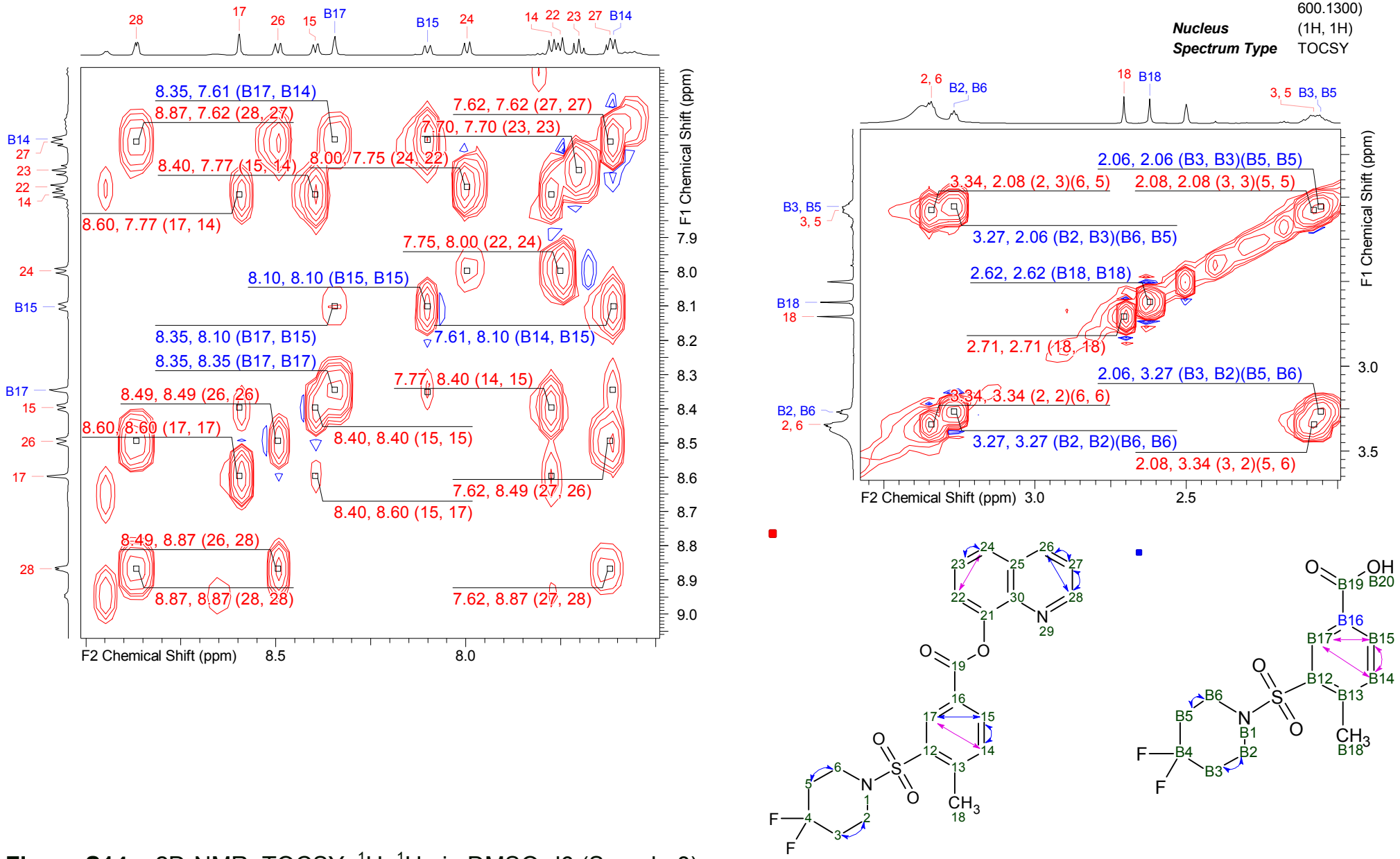



**Figure S14 :** 2D-NMR TOCSY $^{1}H$, $^{1}H$ in DMSO-d6 (Sample 8)