Supplementary Information

Cytotoxic Indolocarbazoles from *Actinomadura melliaura* ATCC 39691

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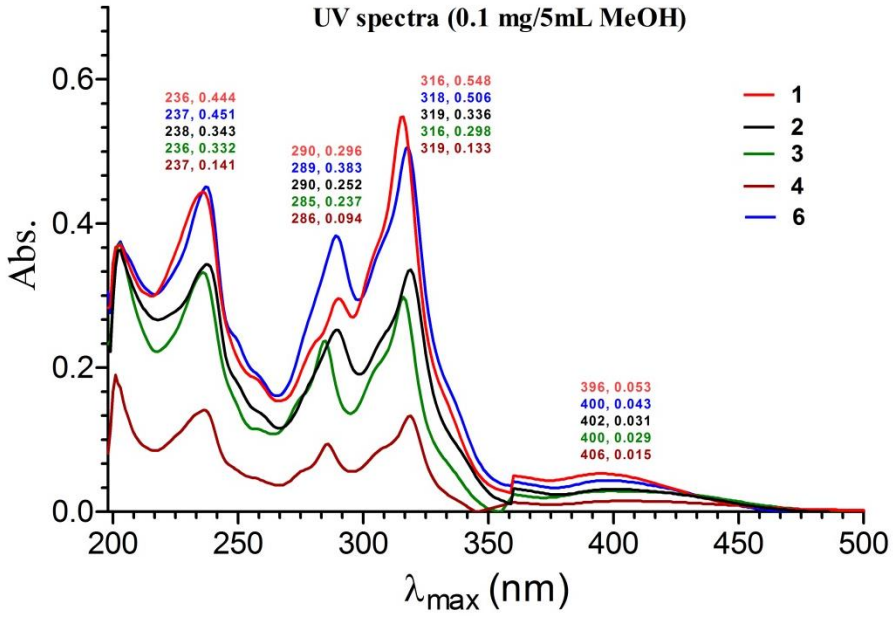

Figure S1. UV (MeOH) spectra of AT2433-A1 (**6**), A3, A4, A5 and B3 (**1**-**4**).

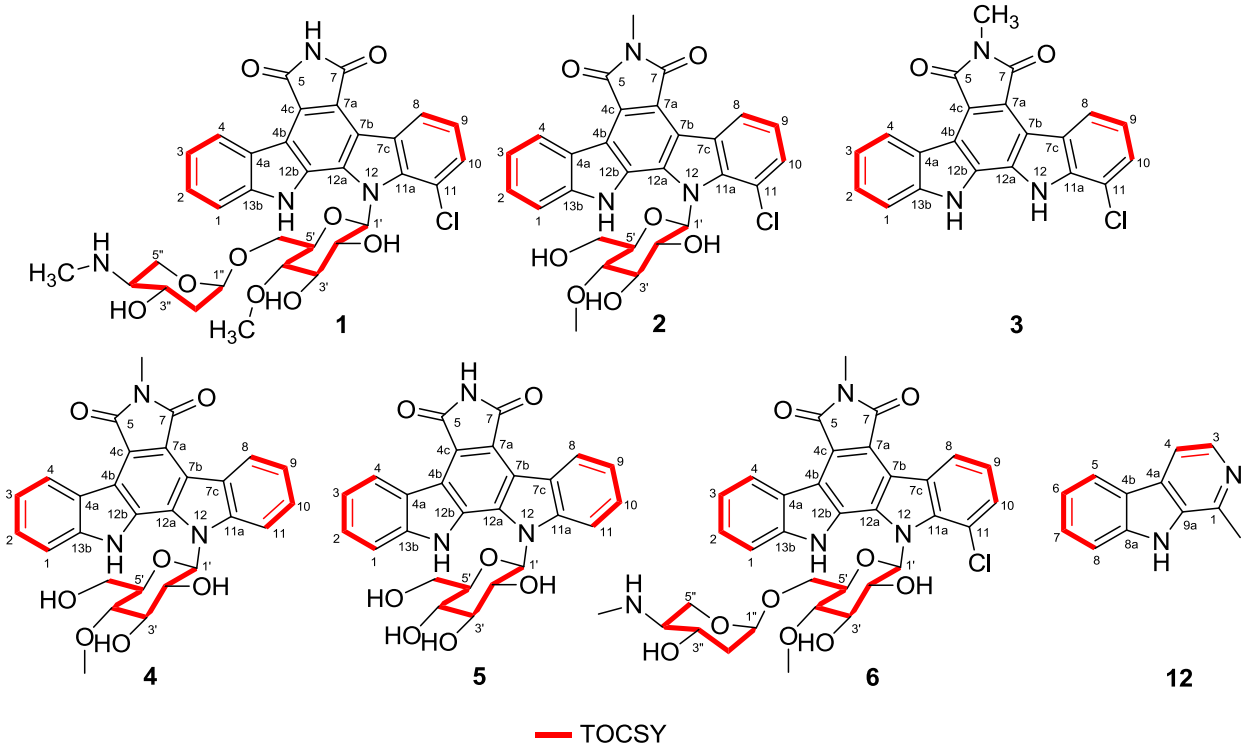

Figure S2. TOCSY (—) correlations in AT2433-A1 (**6**), A3, A4, A5, B3 (**1**-**4**), BMY-41219 (**5**) and harman (1-methyl-*β*-carboline, **12**).

Figure S3. *Actinomadura melliaura* ATCC 39691 culture broth after inoculation and cultivation on A-medium at 28 °C, and 200 rpm for 6 days

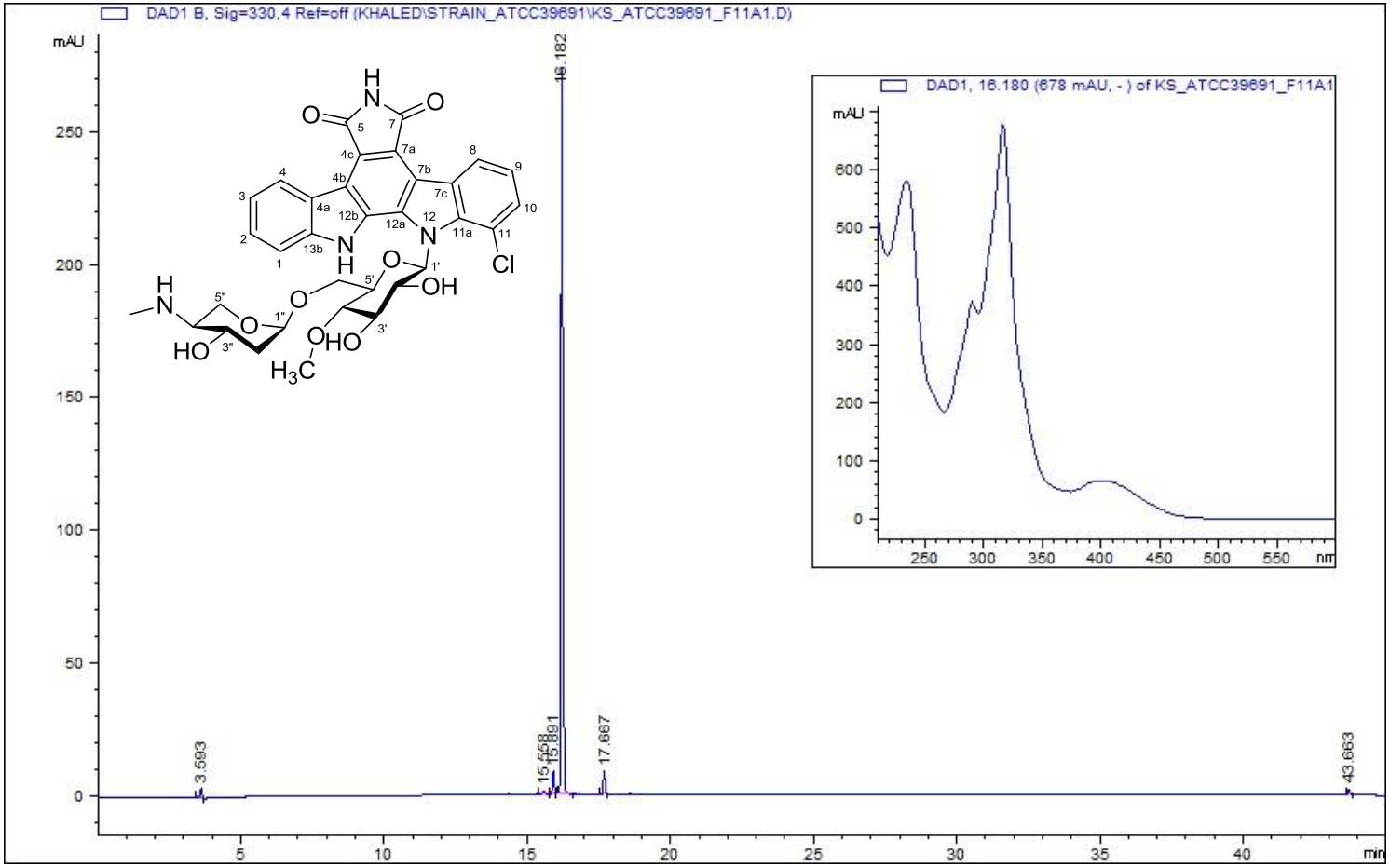

Figure S4. HPLC of AT2433-A3 (**1**). HPLC-conditions: Detection wavelength 254 nm; **solvent A:** H_2O/0.1% TFA; **solvent B:** CH_3CN; flow rate: 1.0 mL min^{-1}; 0-35 min, 5%-100% B; 35-40 min, 100% B; 40-41 min, 100%-5% B; 41-45 min, 5% B). UV-vis inset of full wavelength 190-600 nm.

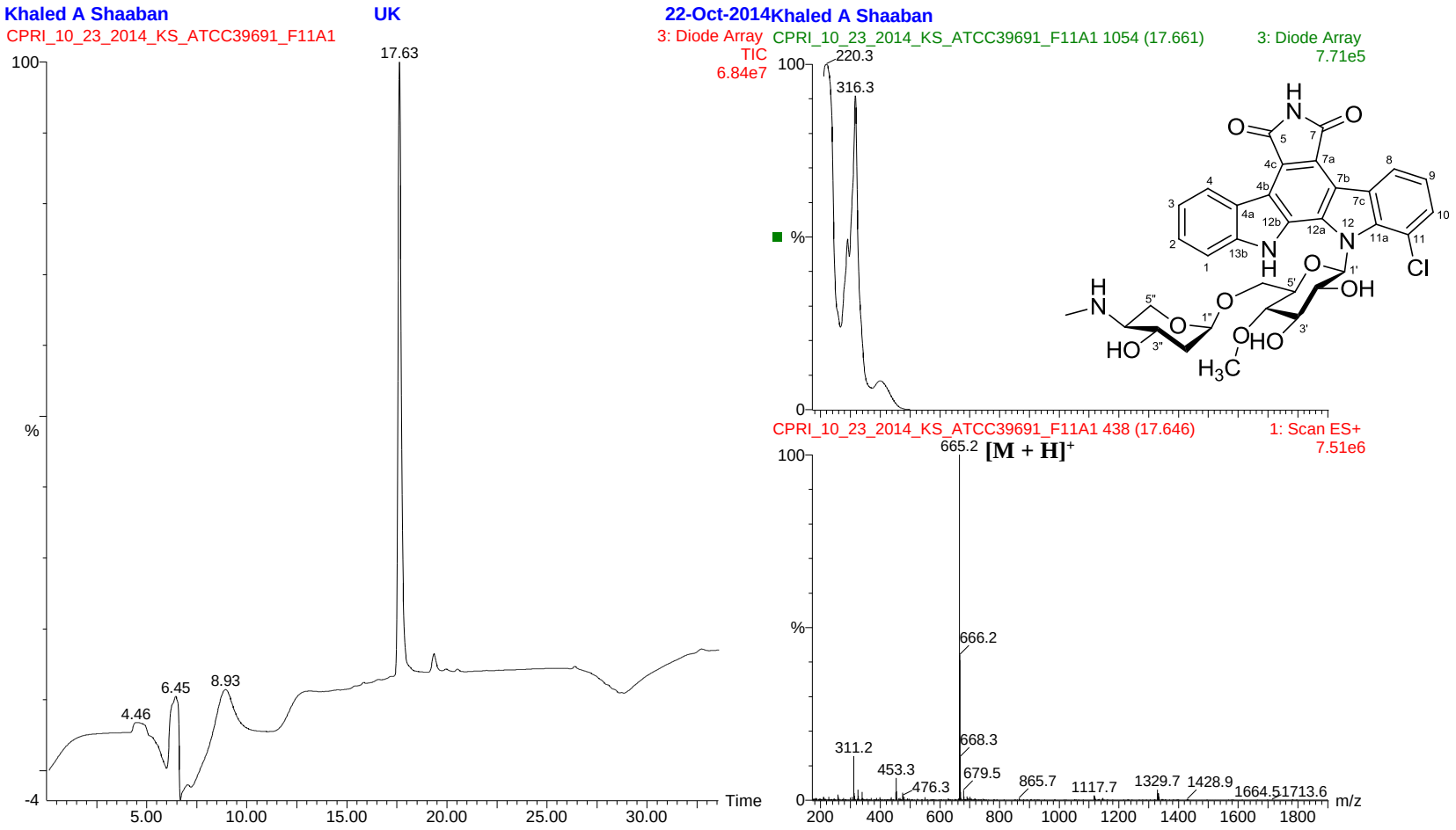

Figure S5. HPLC/UV/MS analyses of the purified AT2433-A3 (**1**). Detection wavelength: 210-500; **solvent A:** H_2O/0.1% Formic acid, **solvent B:** CH_3CN/0.1% Formic acid; flow rate: 0.5 mL min^{-1}; 0-4 min, 10% B; 4-22 min, 10-100% B; 22-27 min, 100% B; 27-29 min, 100%-10% B; 29-35 min, 10 % B.

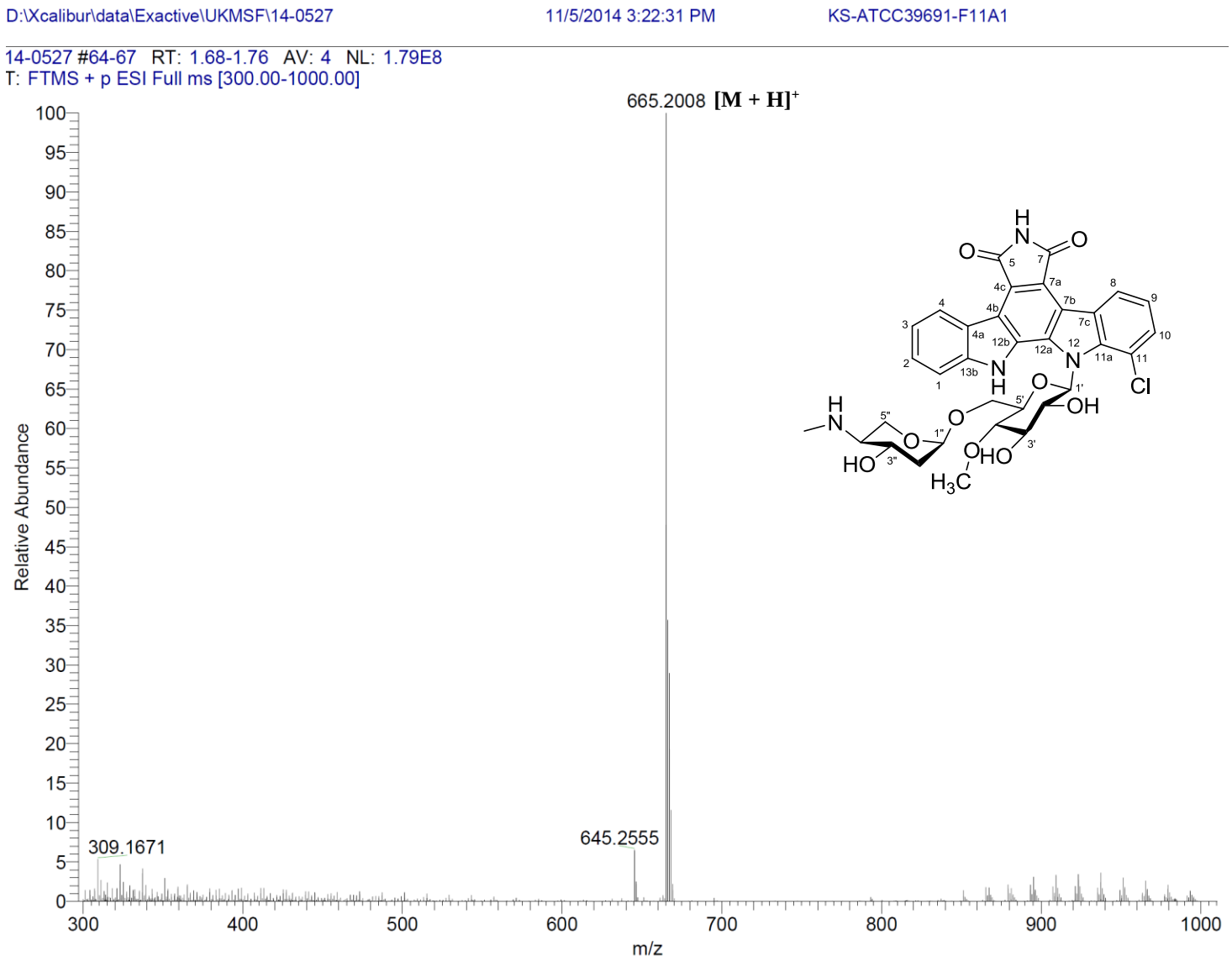

Figure S6. (+)-HRESI-MS spectrum of AT2433-A3 (**1**)

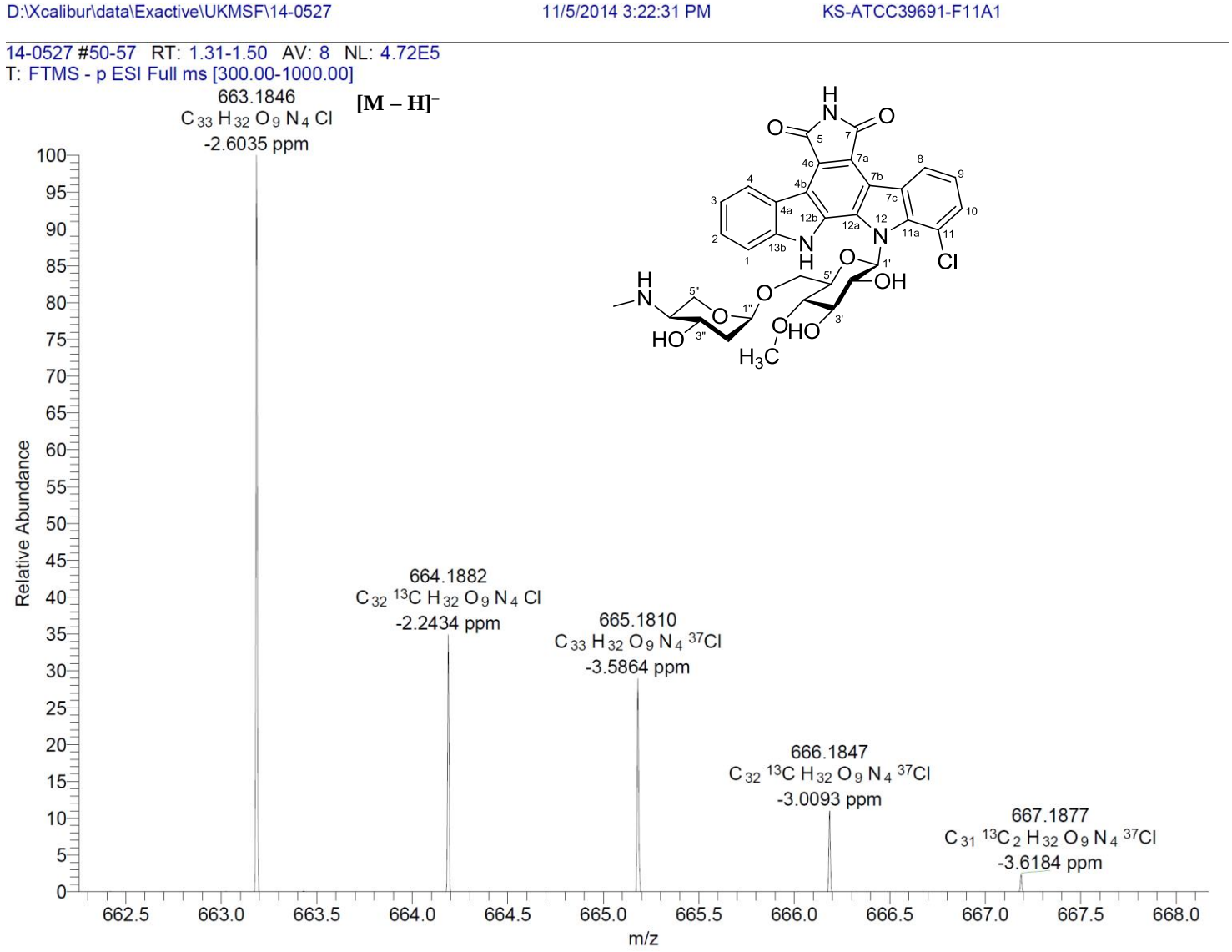

Figure S7. (–)-HRESI-MS spectrum of AT2433-A3 (**1**)

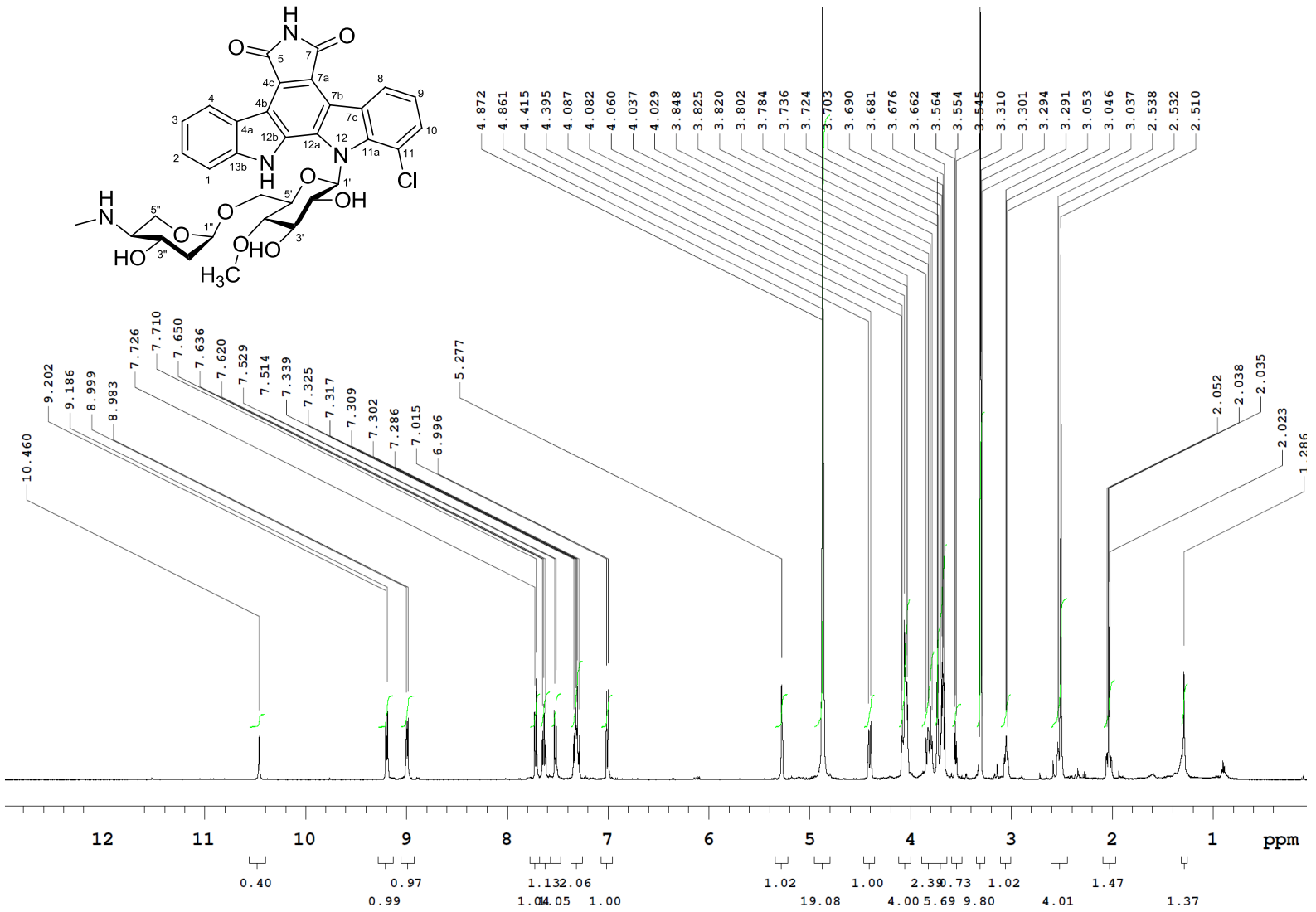

Figure S8. ^{1}H NMR spectrum (CD_3OD, 500 MHz) of AT2433-A3 (**1**)

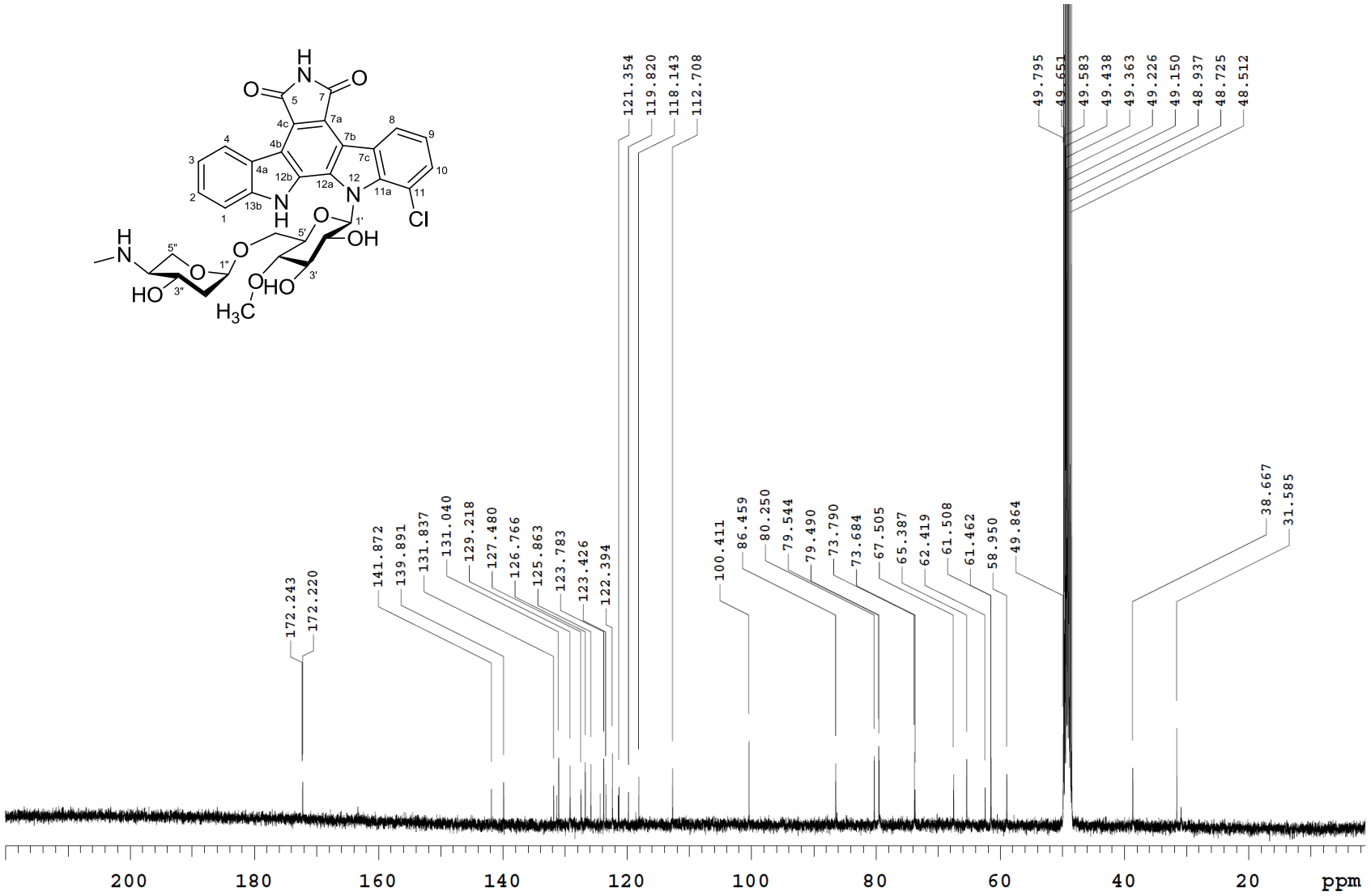

Figure S9. ^{13}C NMR spectrum (CD_3OD, 100 MHz) of AT2433-A3 (**1**)

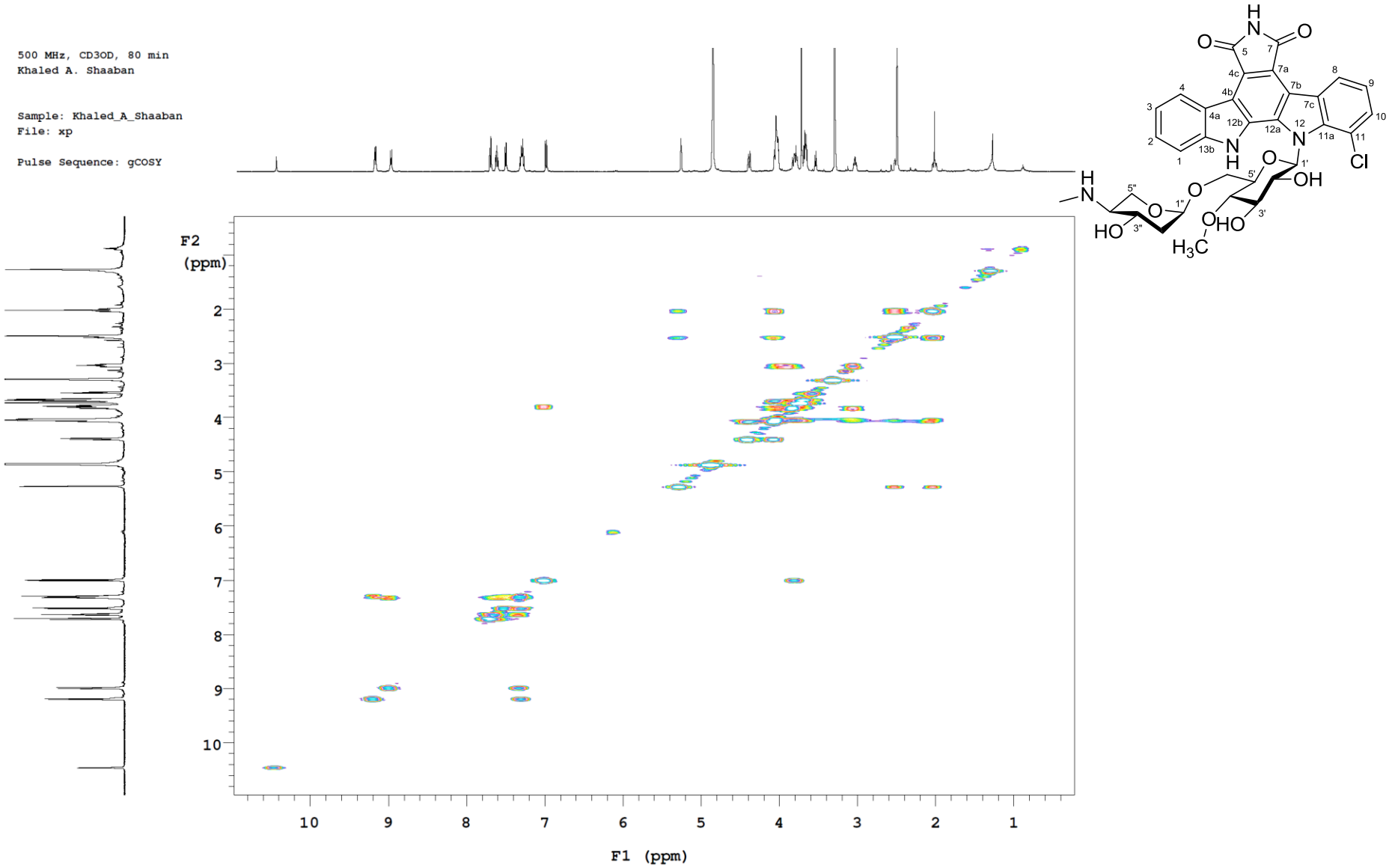

Figure S10. ^{1}H-^{1}H COSY spectrum (CD_3OD, 500 MHz) of AT2433-A3 (**1**)

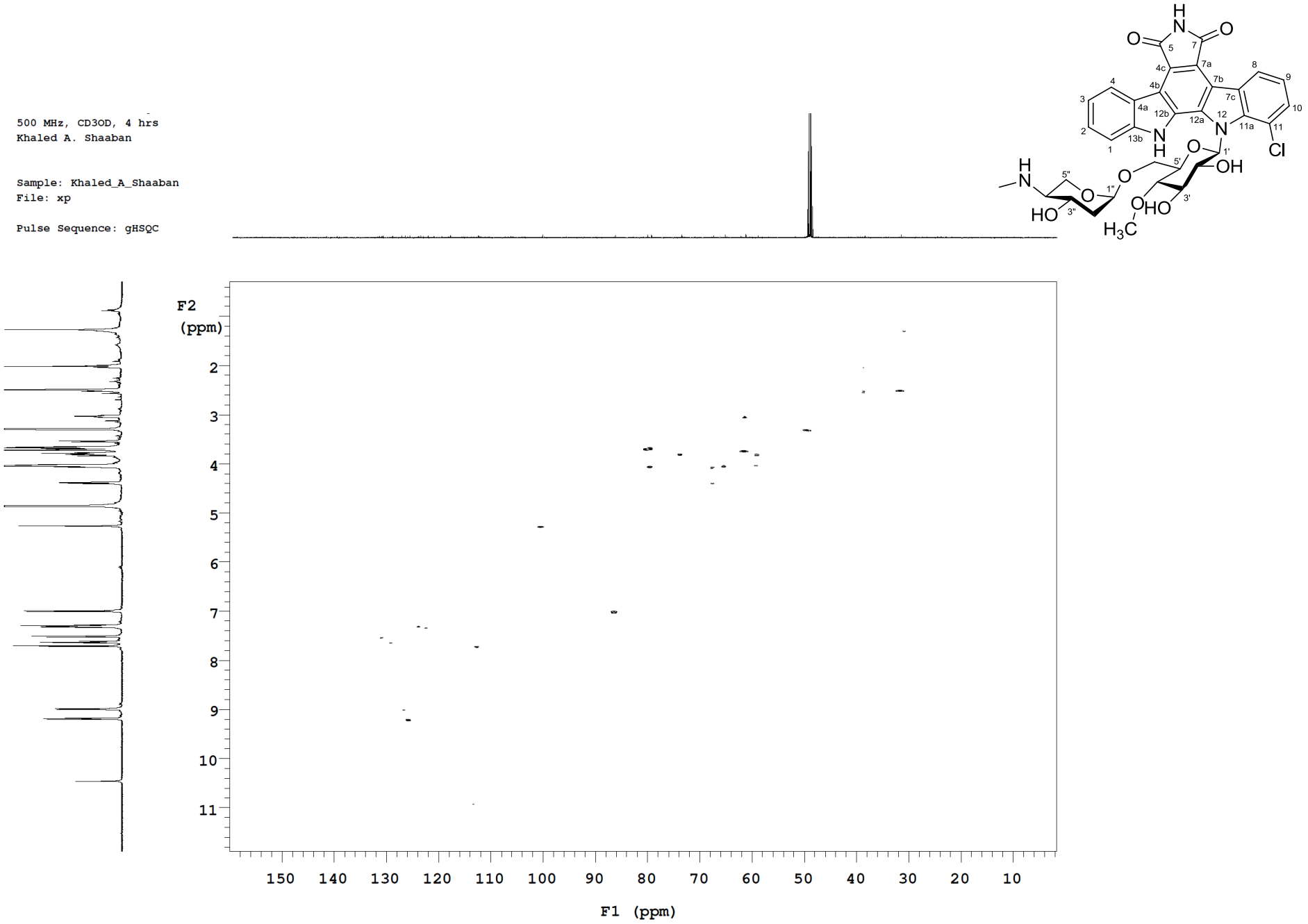

Figure S11. HSQC spectrum (CD_3OD, 500 MHz) of AT2433-A3 (**1**)

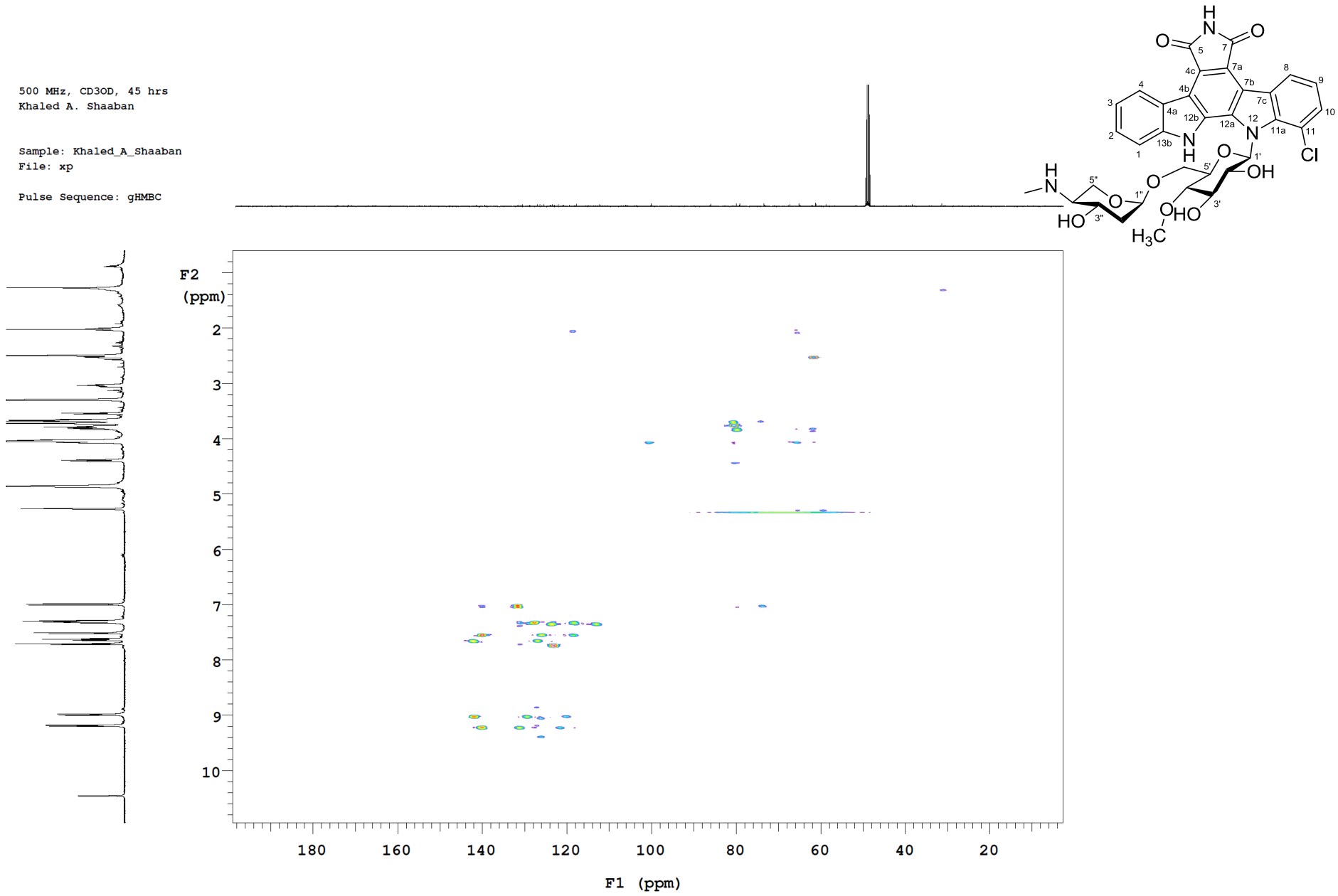

Figure S12. HMBC spectrum (CD_3OD, 500 MHz) of AT2433-A3 (**1**)

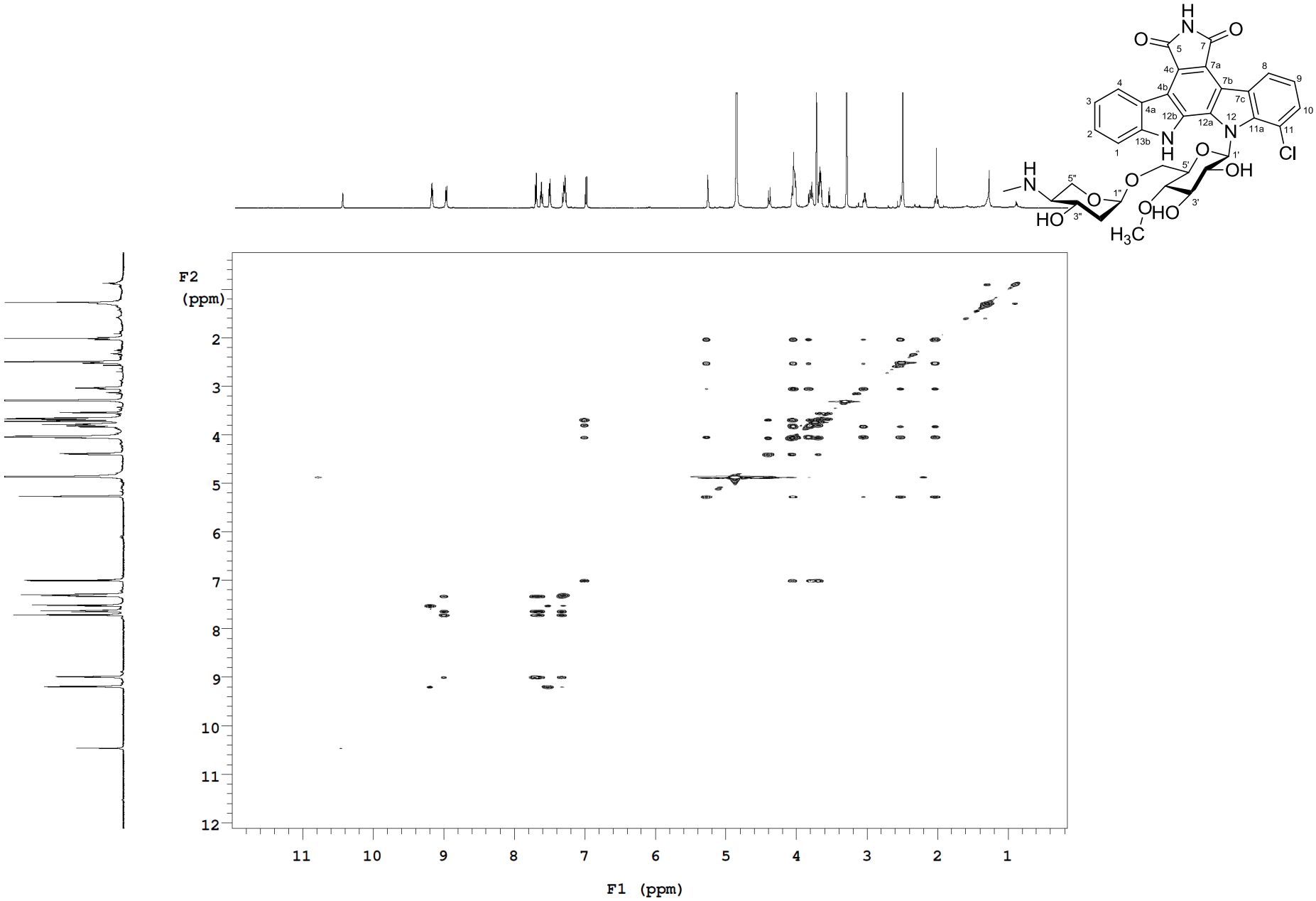

Figure S13. TOCSY spectrum (CD_3OD, 500 MHz) of AT2433-A3 (**1**)

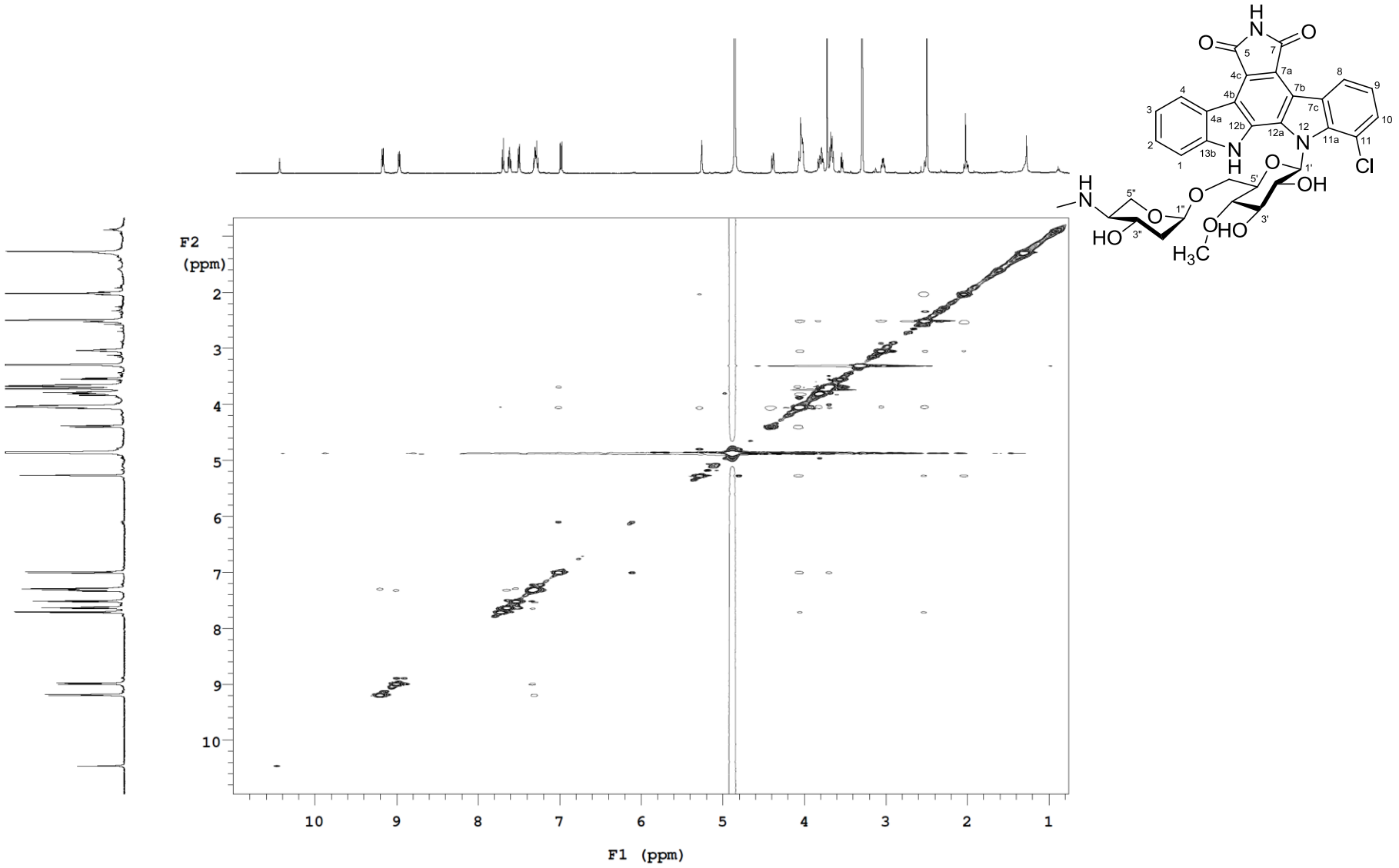

Figure S14. NOESY spectrum (CD_3OD, 500 MHz) of AT2433-A3 (**1**)

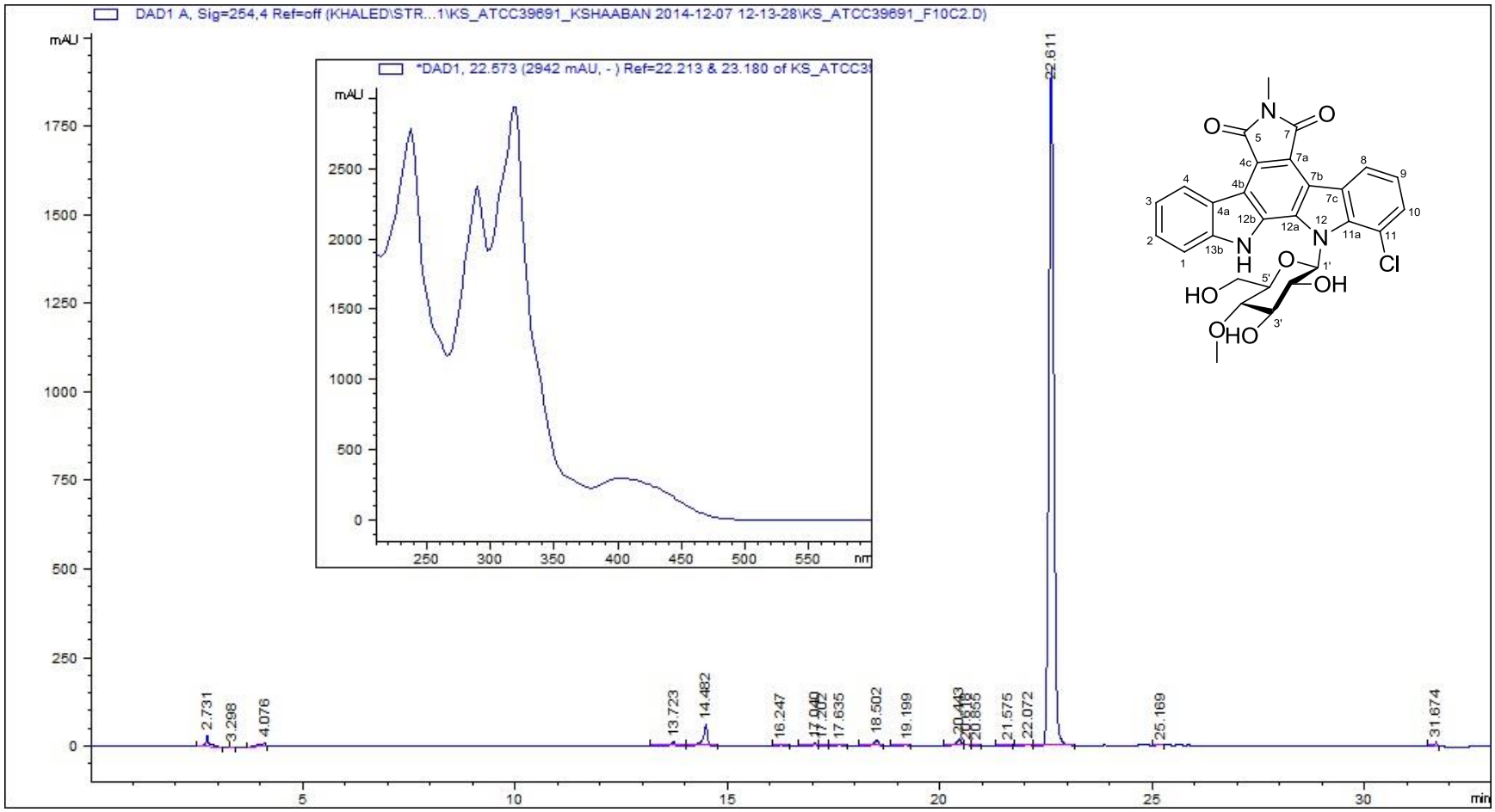

Figure S15. HPLC of AT2433-A4 (**2**). HPLC-conditions: Detection wavelength 254 nm; **solvent A:** H_2O/0.1% TFA; **solvent B:** CH_3CN; flow rate: 0.5 mL min^{-1}; 0-4 min, 10% B; 4-22 min, 10-100% B; 22-27 min, 100% B; 27-29 min, 100%-10% B; 29-35 min, 10 % B. UV-vis inset of full wavelength 190-600 nm.

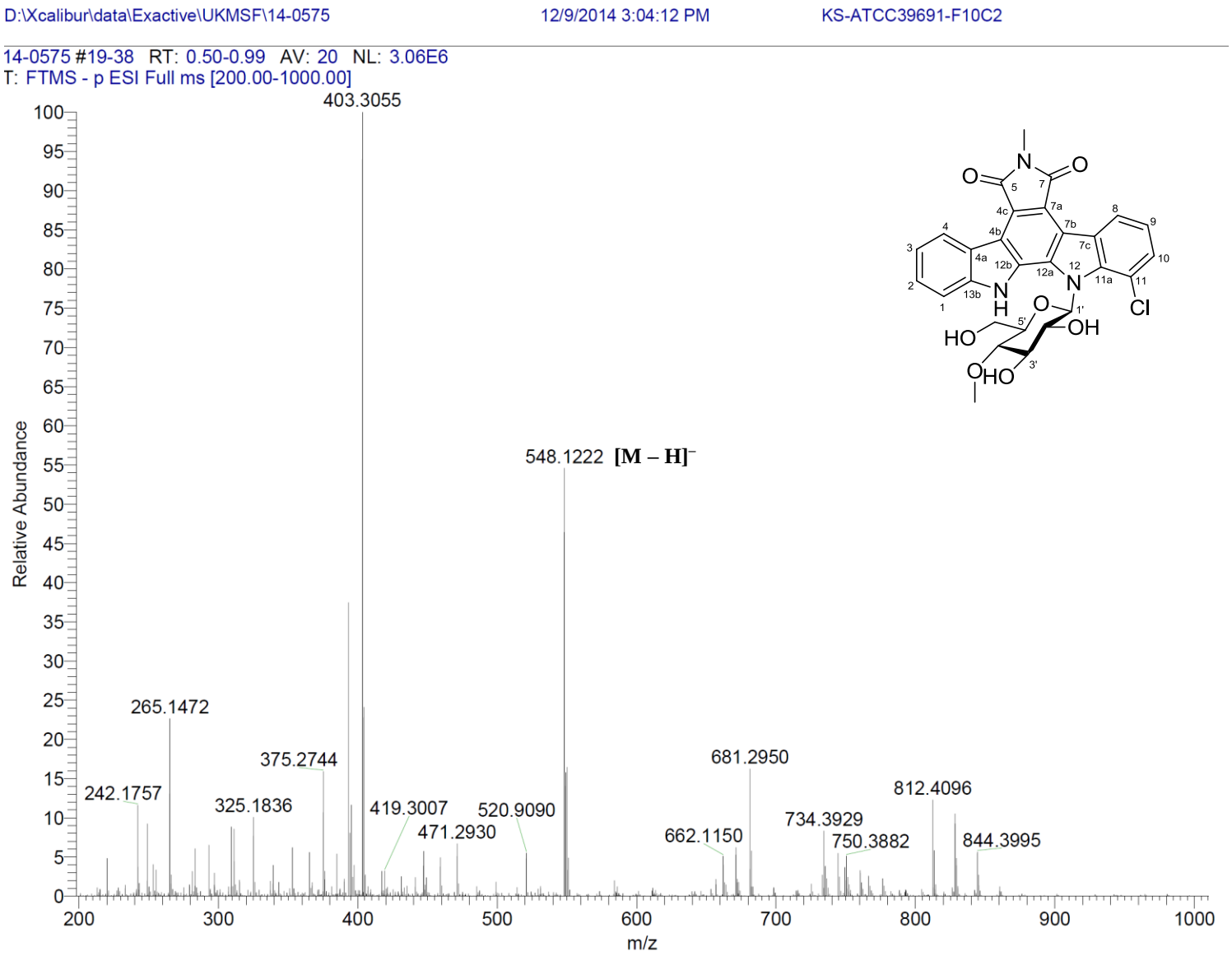

Figure S16: (–)-HRESI-MS spectrum of AT2433-A4 (**2**)

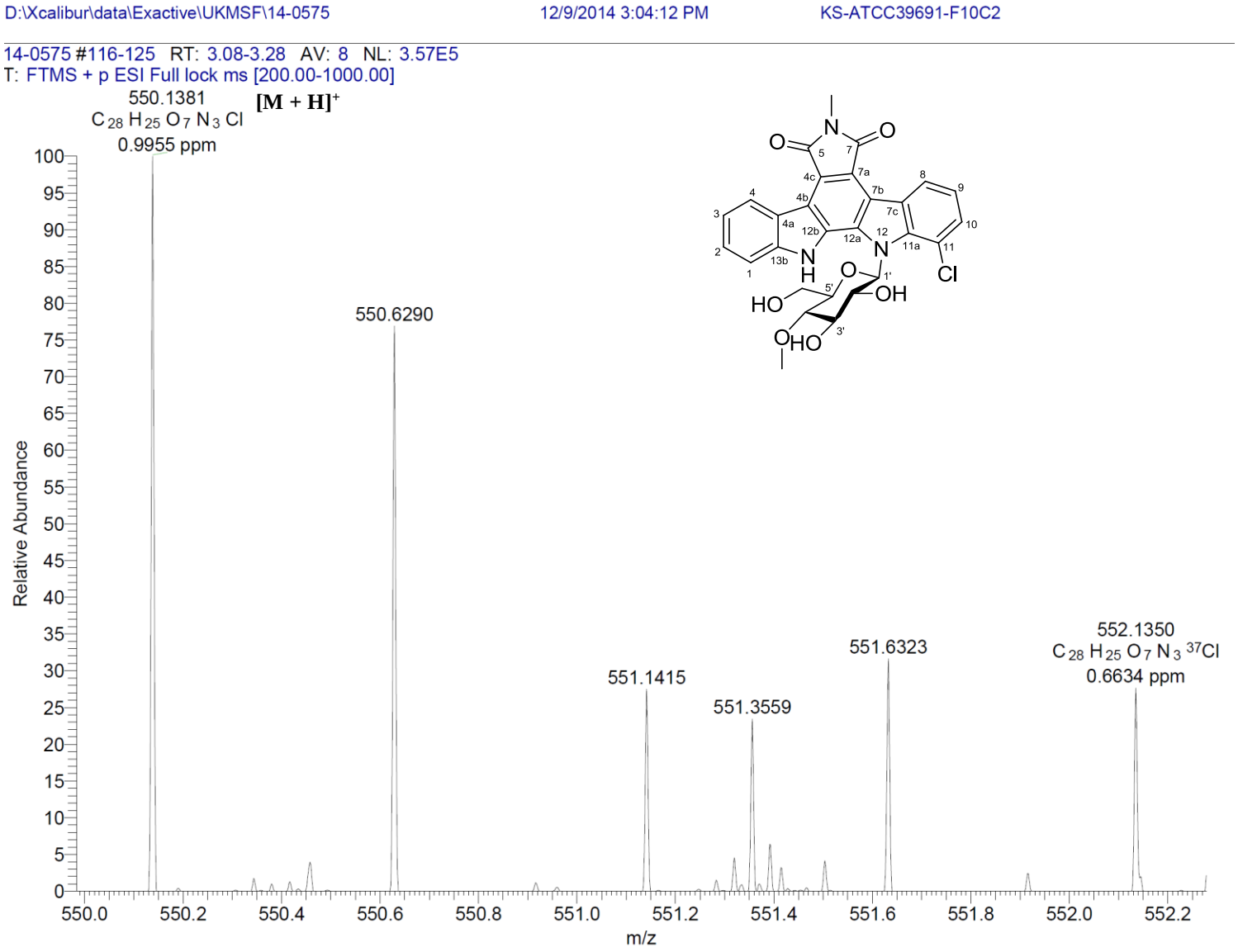

Figure S17: (+)-HRESI-MS spectrum of AT2433-A4 (**2**)

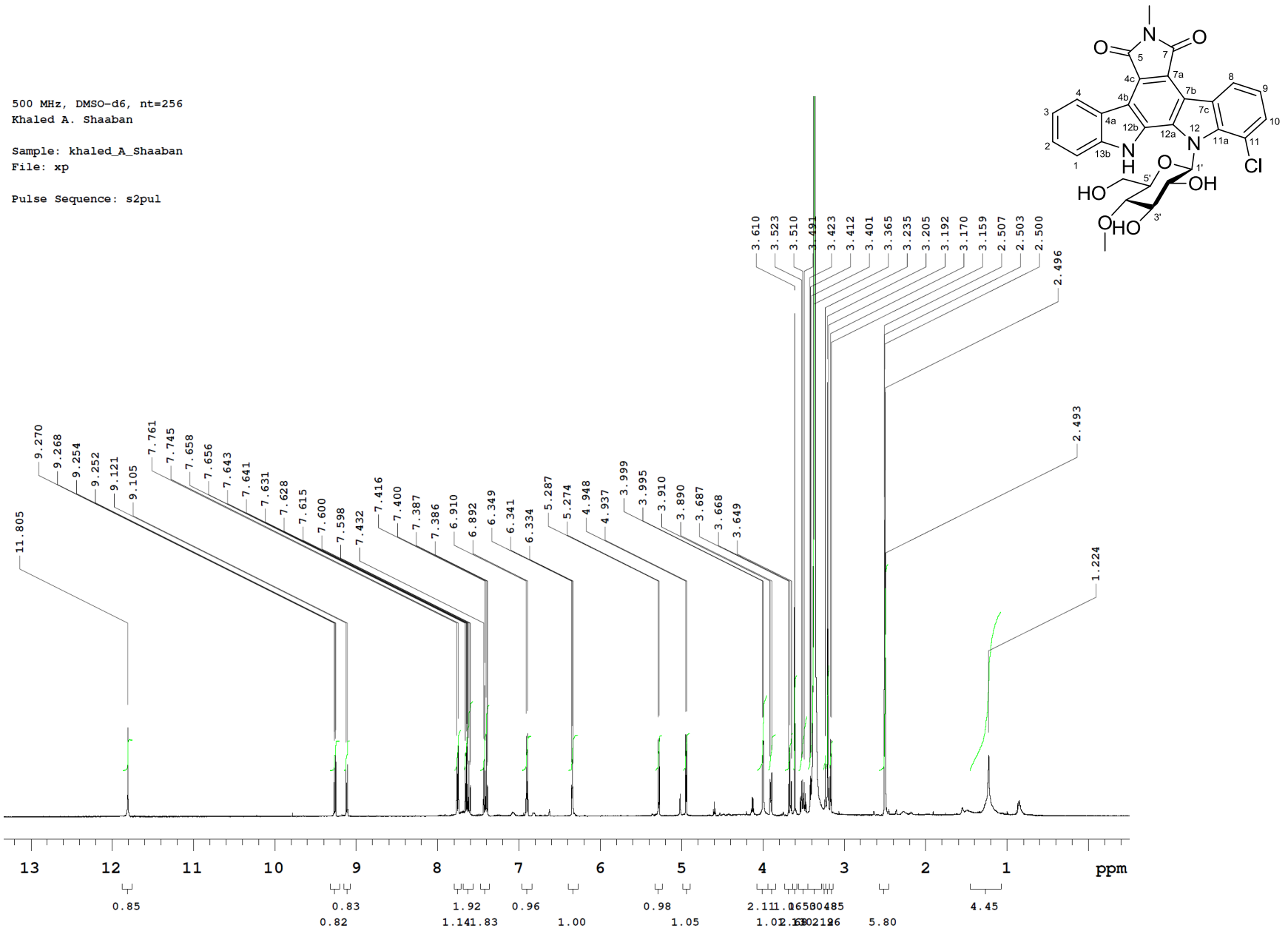

Figure S18: ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of AT2433-A4 (**2**)

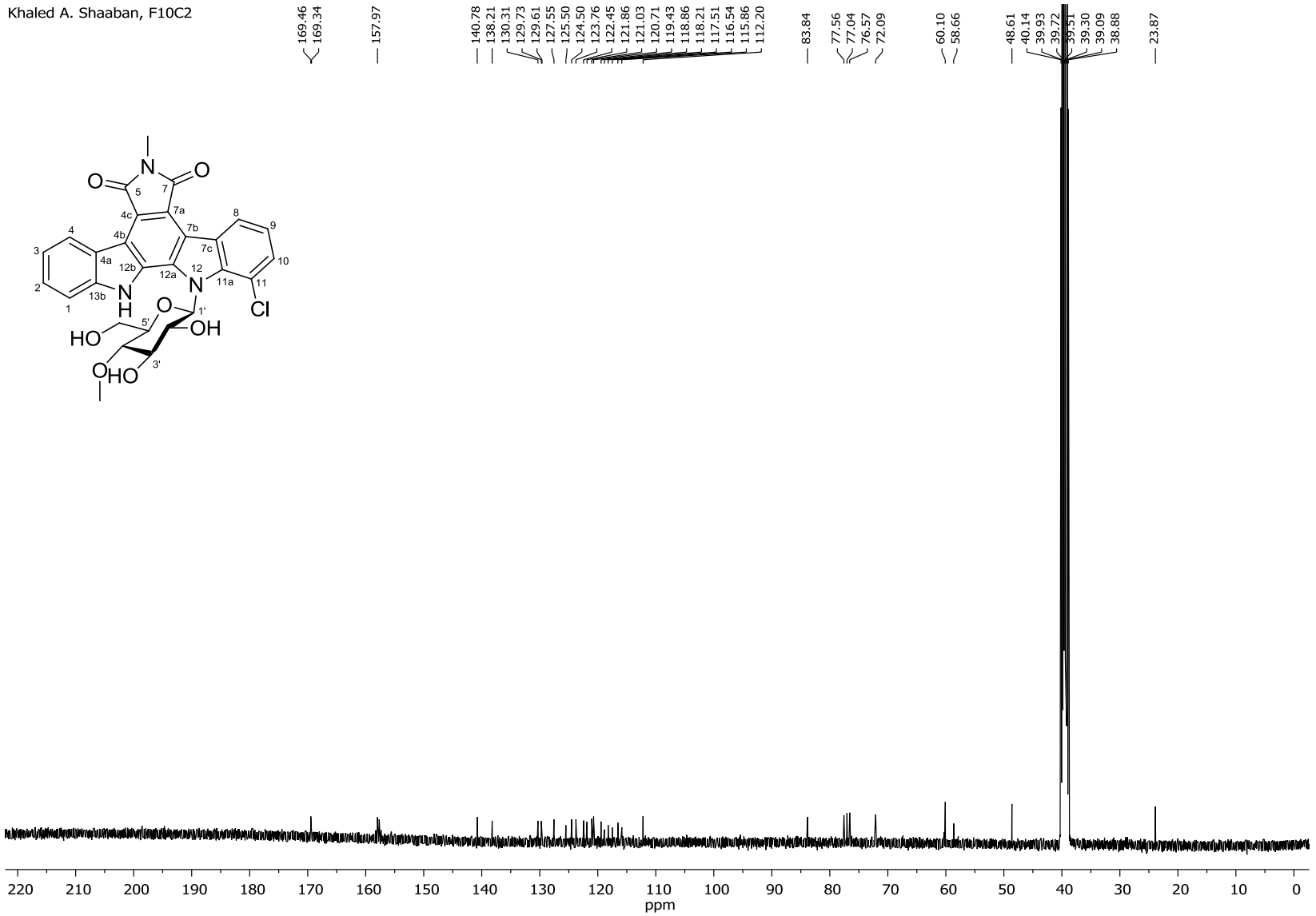

Figure S19: ^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of AT2433-A4 (**2**)

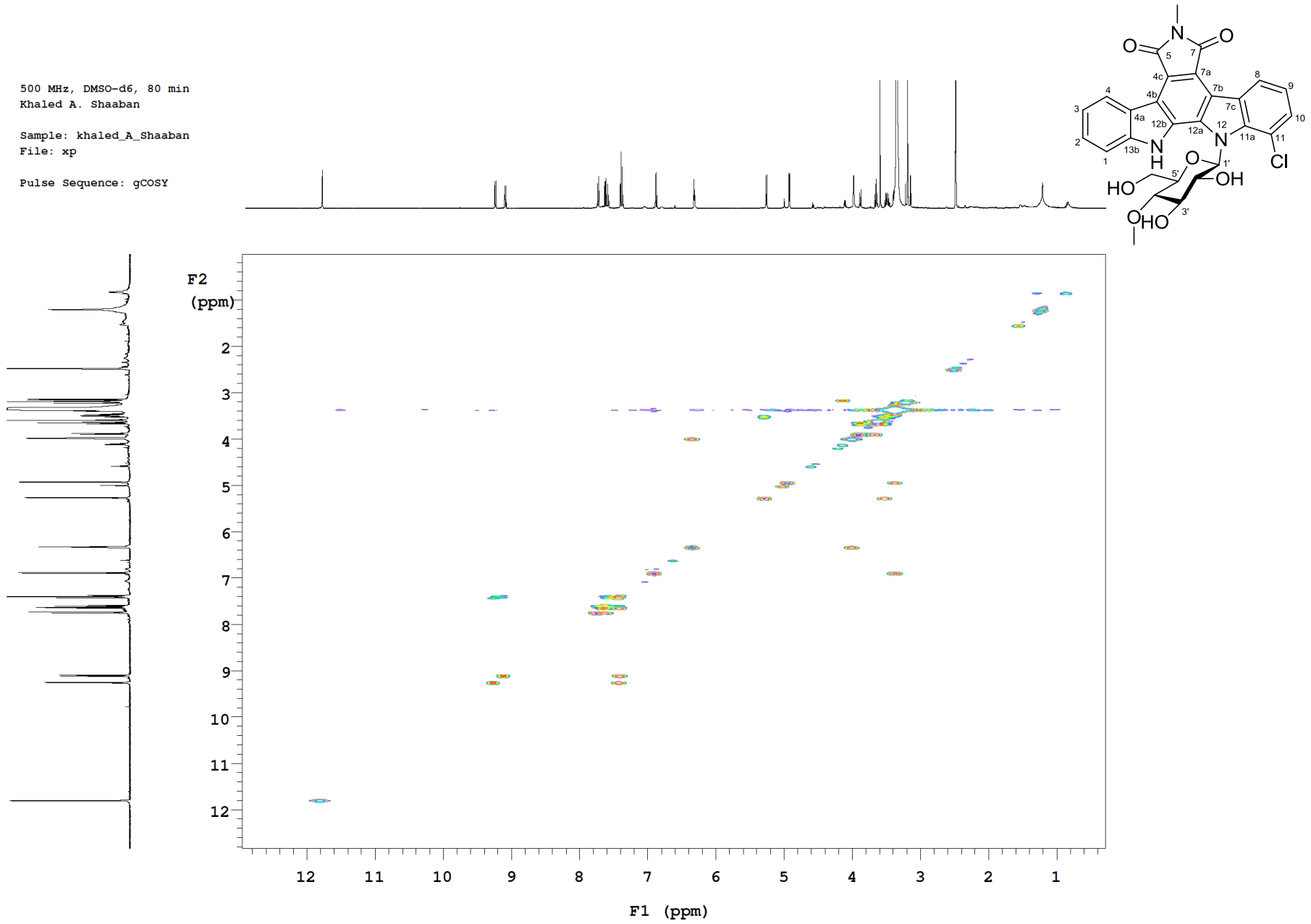

Figure S20: ^{1}H-^{1}H COSY spectrum (DMSO-d_6, 500 MHz) of AT2433-A4 (**2**)

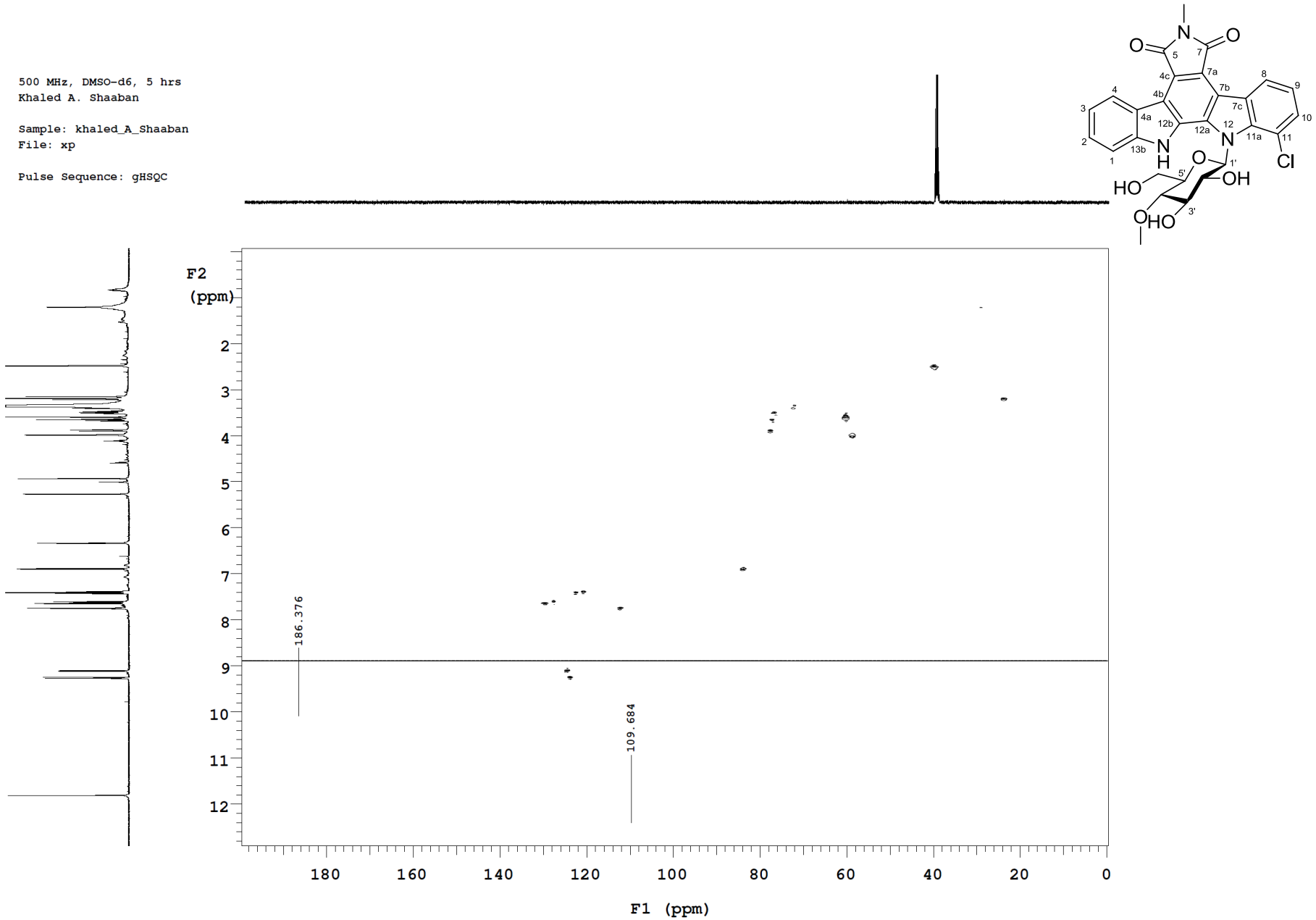

Figure S21: HSQC spectrum (DMSO-d_6, 500 MHz) of AT2433-A4 (**2**)

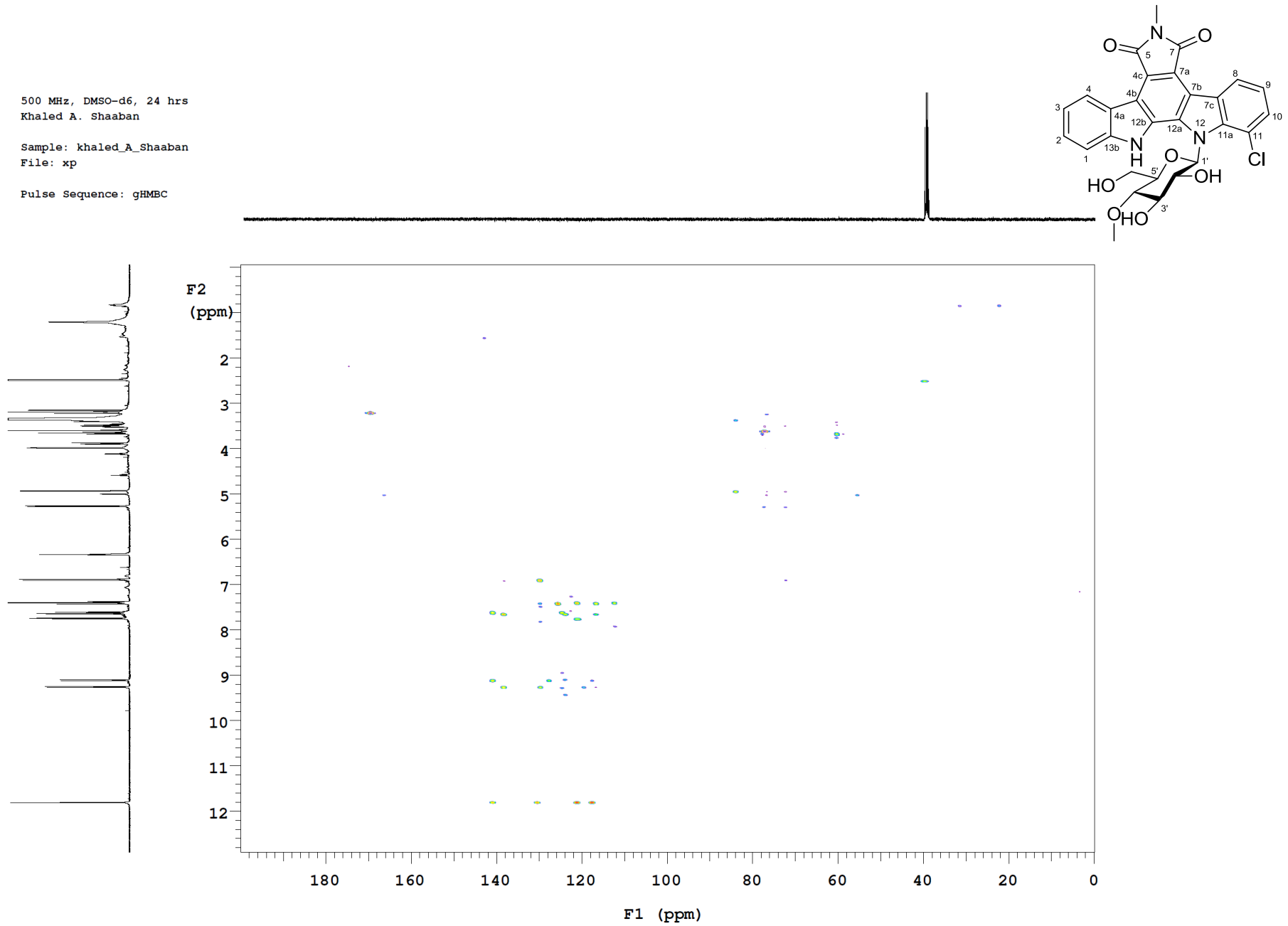

Figure S22: HMBC spectrum (DMSO-d_6, 500 MHz) of AT2433-A4 (**2**)

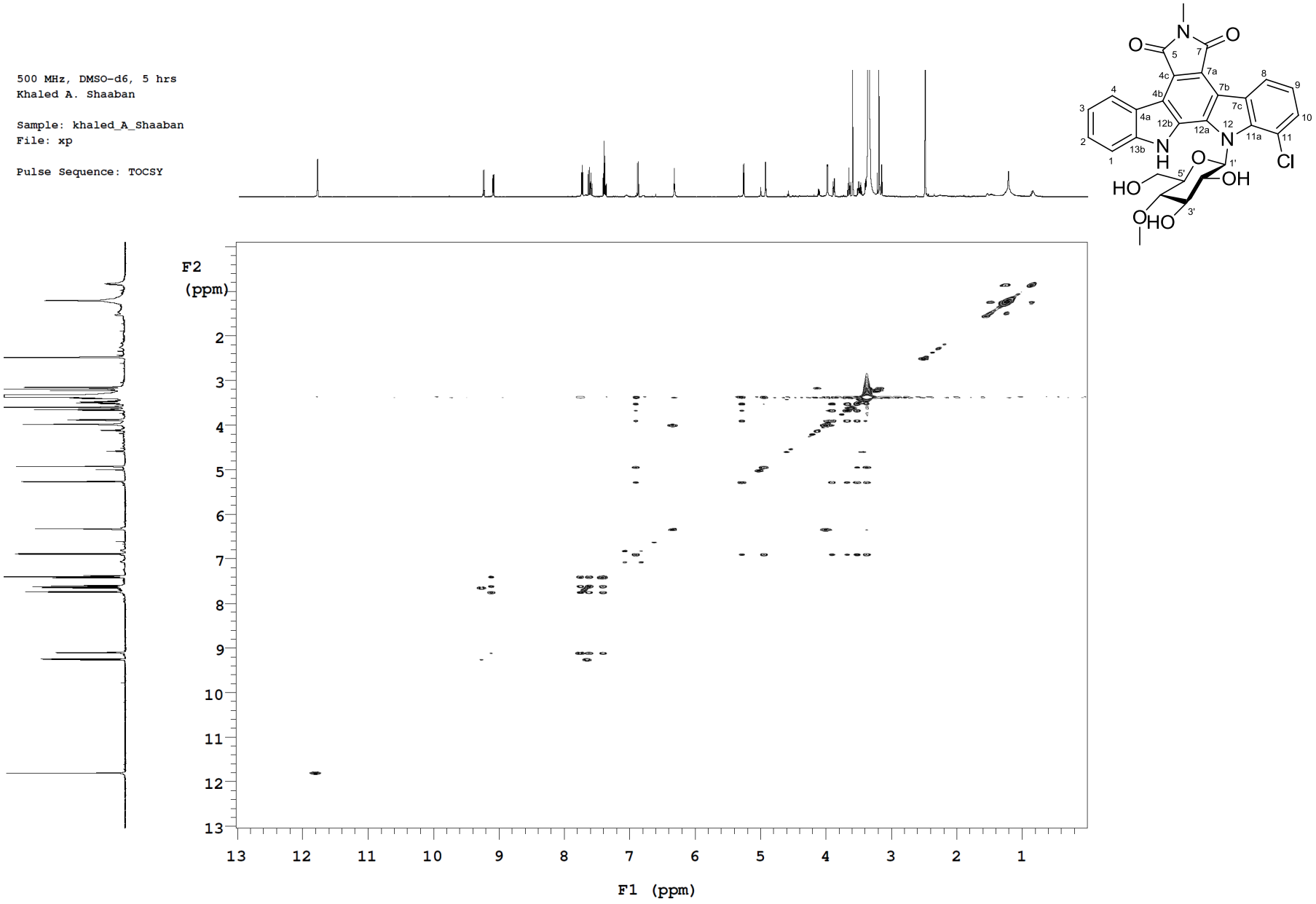

Figure S23: TOCSY spectrum (DMSO-d_6, 500 MHz) of AT2433-A4 (**2**)

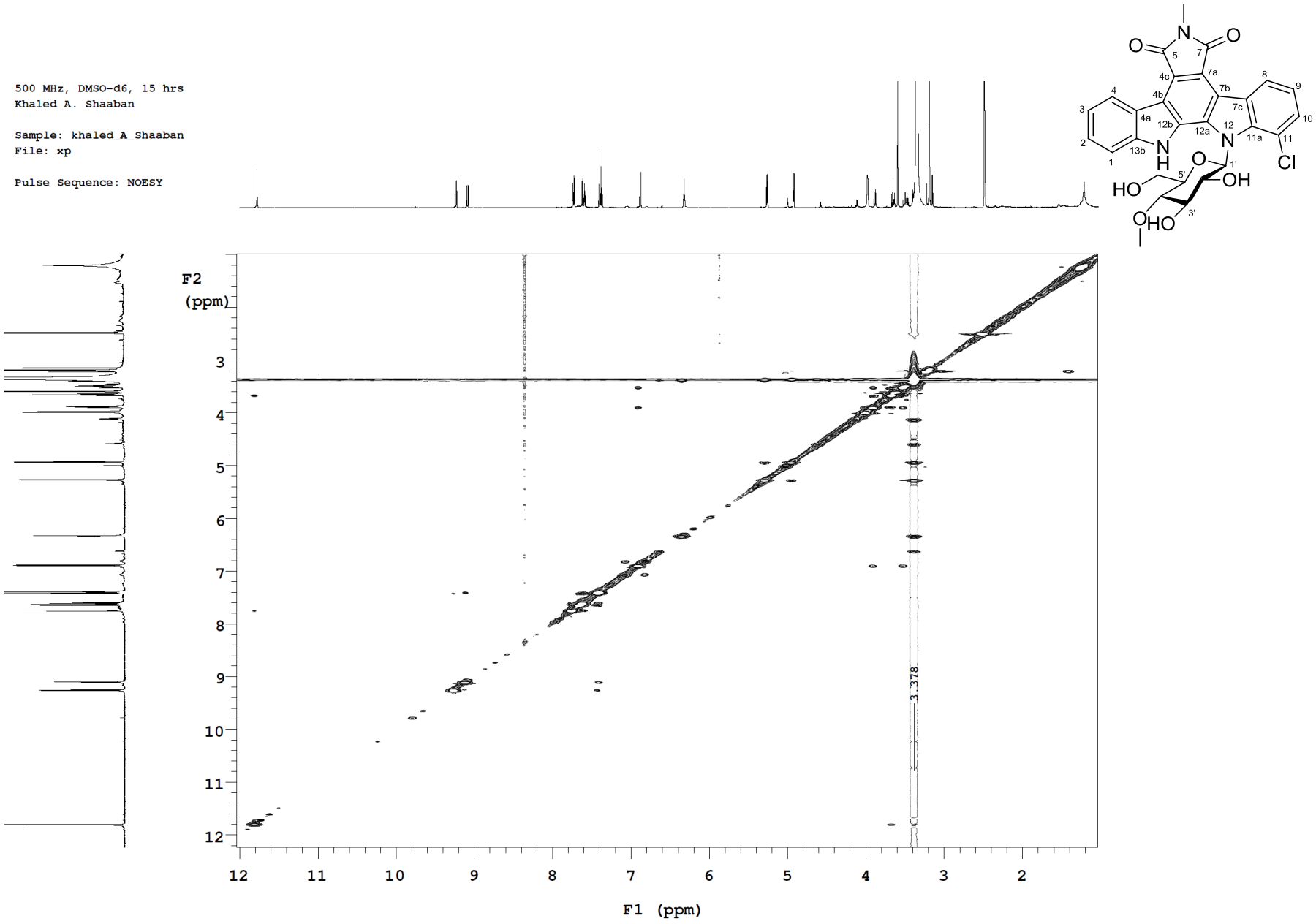

Figure S24: NOESY spectrum (DMSO-d_6, 500 MHz) of AT2433-A4 (**2**)

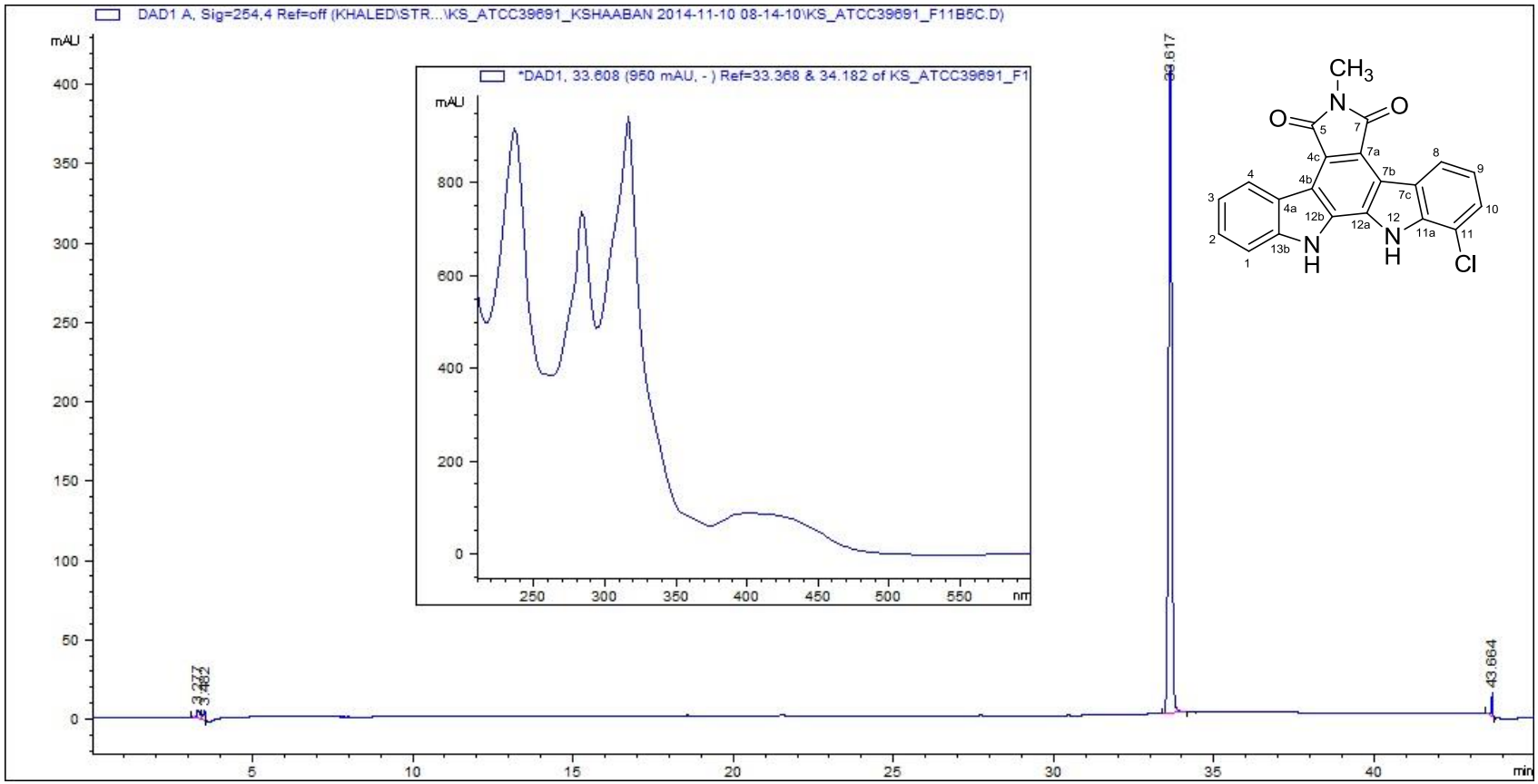

Figure S25: HPLC of AT2433-A5 (**3**). HPLC-conditions: Detection wavelength 254 nm; **solvent A:** H_2O/0.1% TFA; **solvent B:** CH_3CN; flow rate: 1.0 mL min^{-1}; 0-35 min, 5%-100% B; 35-40 min, 100% B; 40-41 min, 100%-5% B; 41-45 min, 5% B). UV-vis inset of full wavelength 190-600 nm.

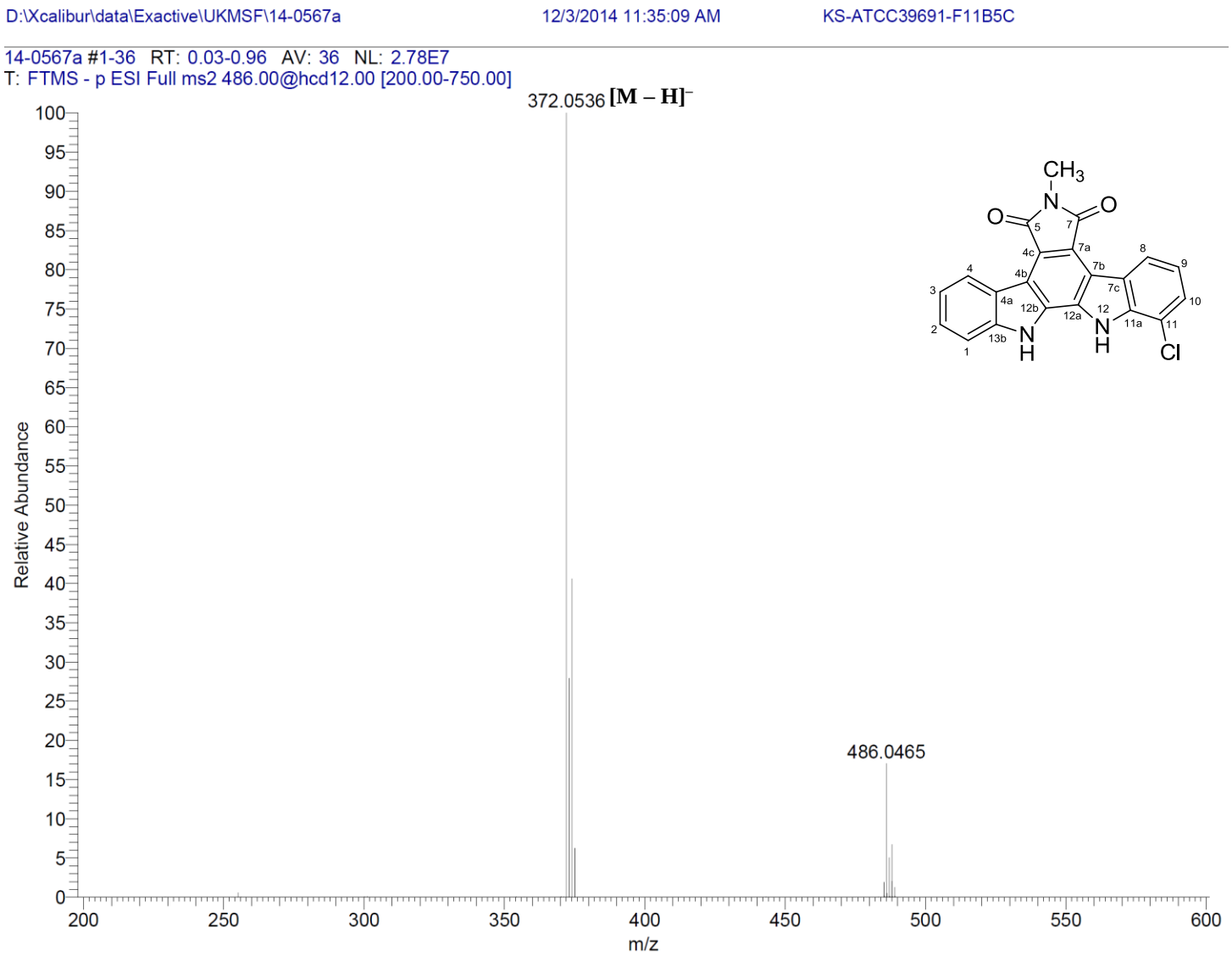

Figure S26: (–)-HRESI-MS spectrum of AT2433-A5 (**3**)

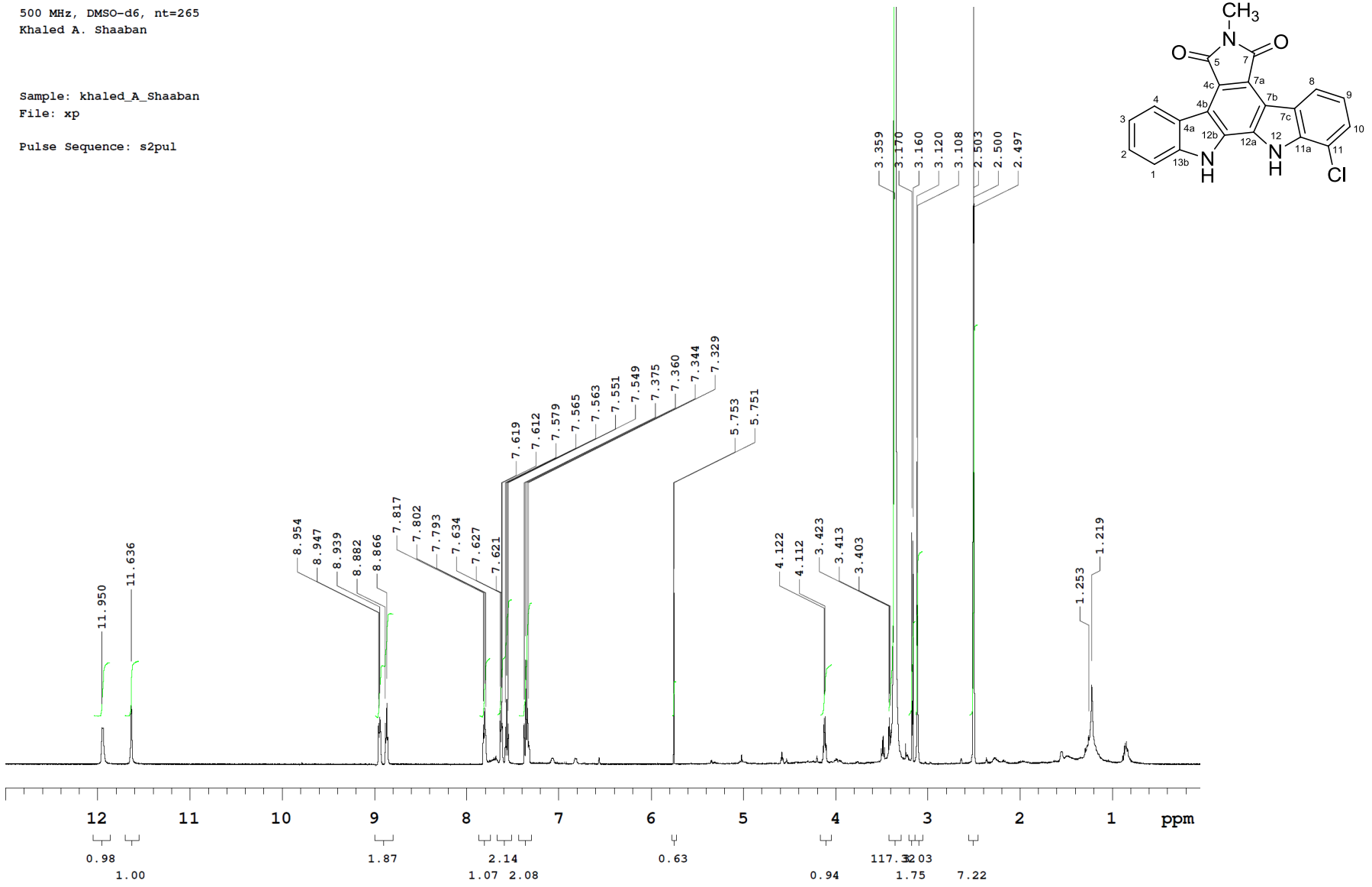

Figure S27: ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of AT2433-A5 (**3**)

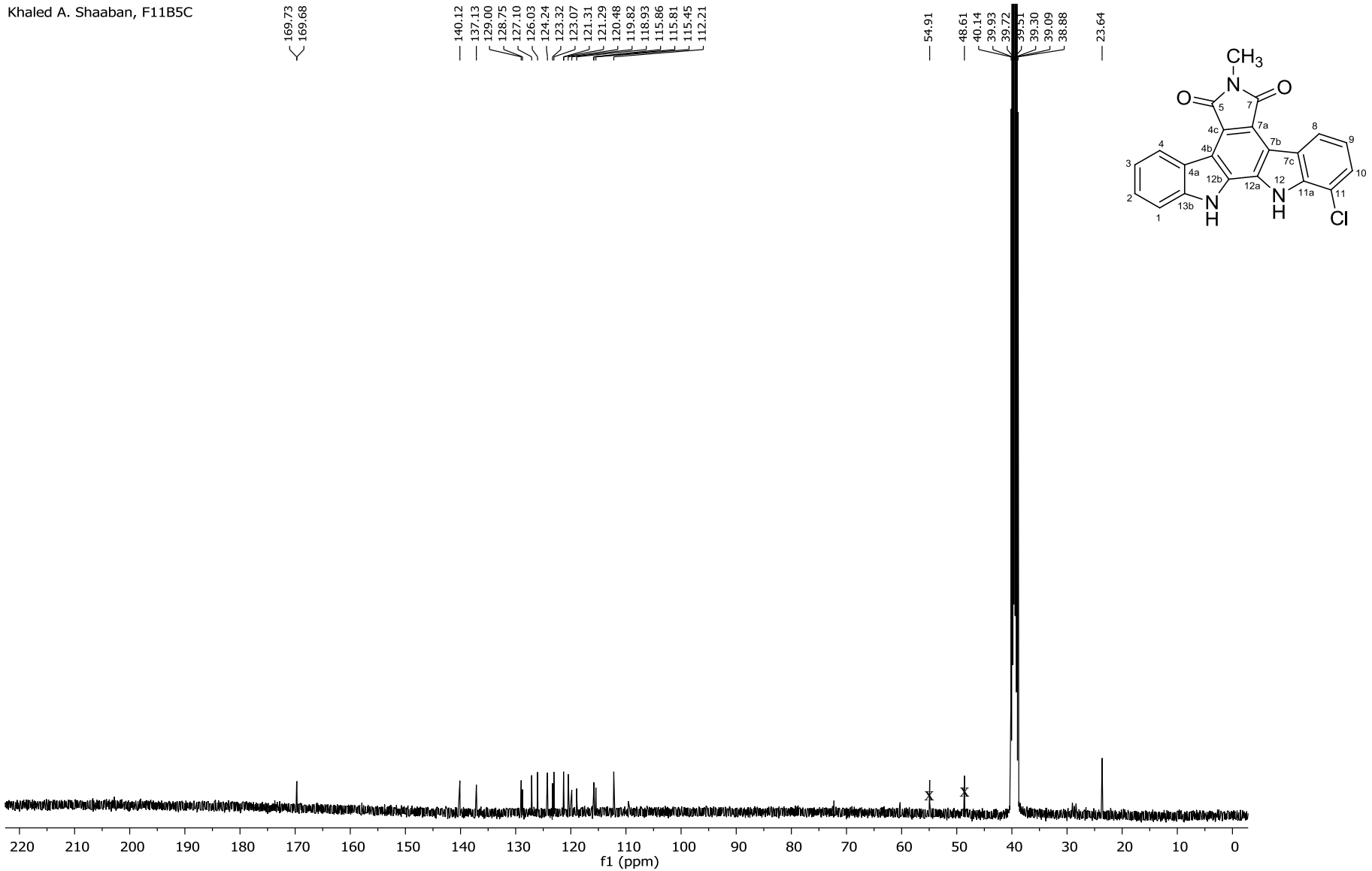

Figure S28: ^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of AT2433-A5 (**3**)

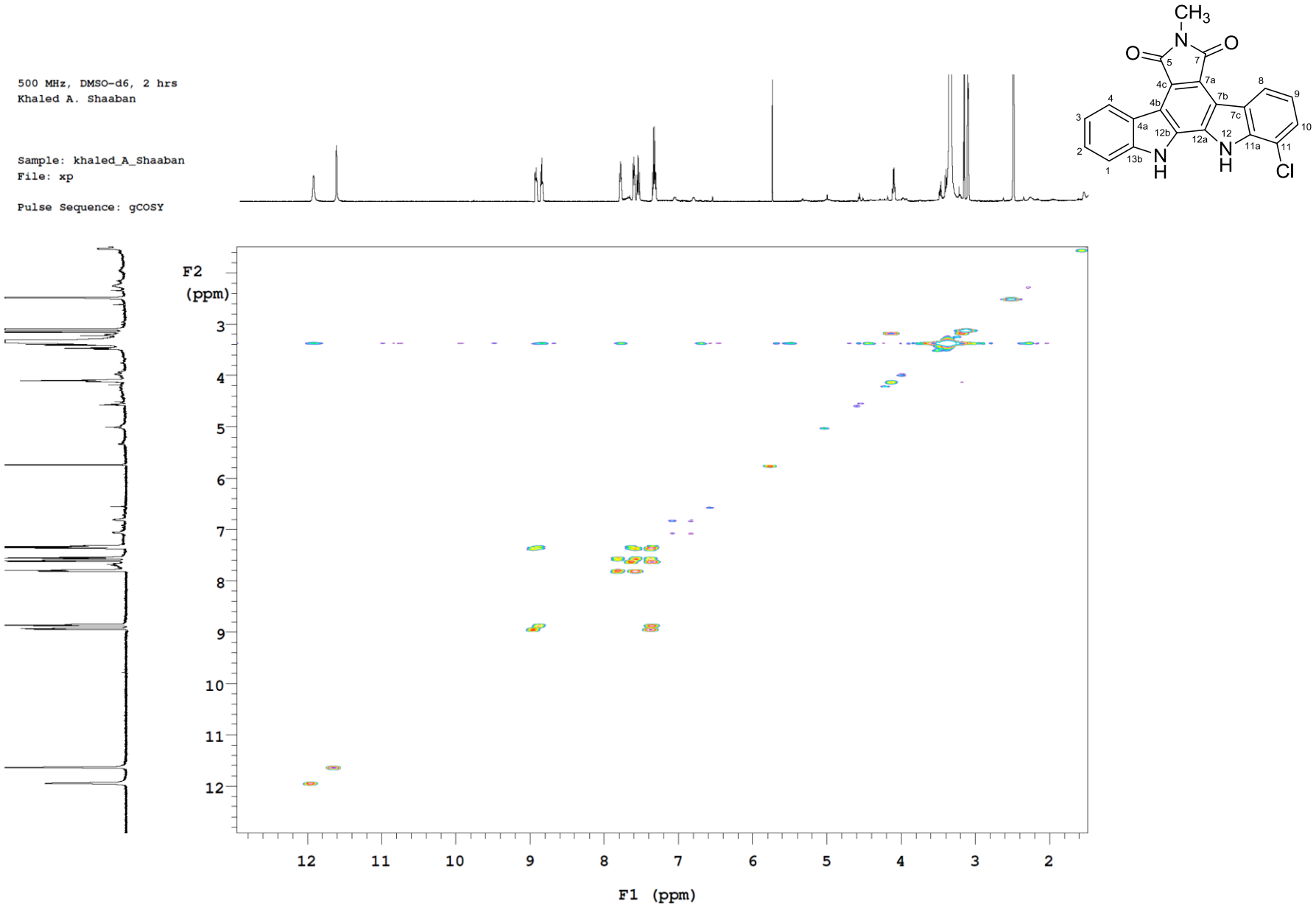

Figure S29: ^{1}H-^{1}H COSY spectrum (CD_3OD, 500 MHz) of AT2433-A5 (**3**)

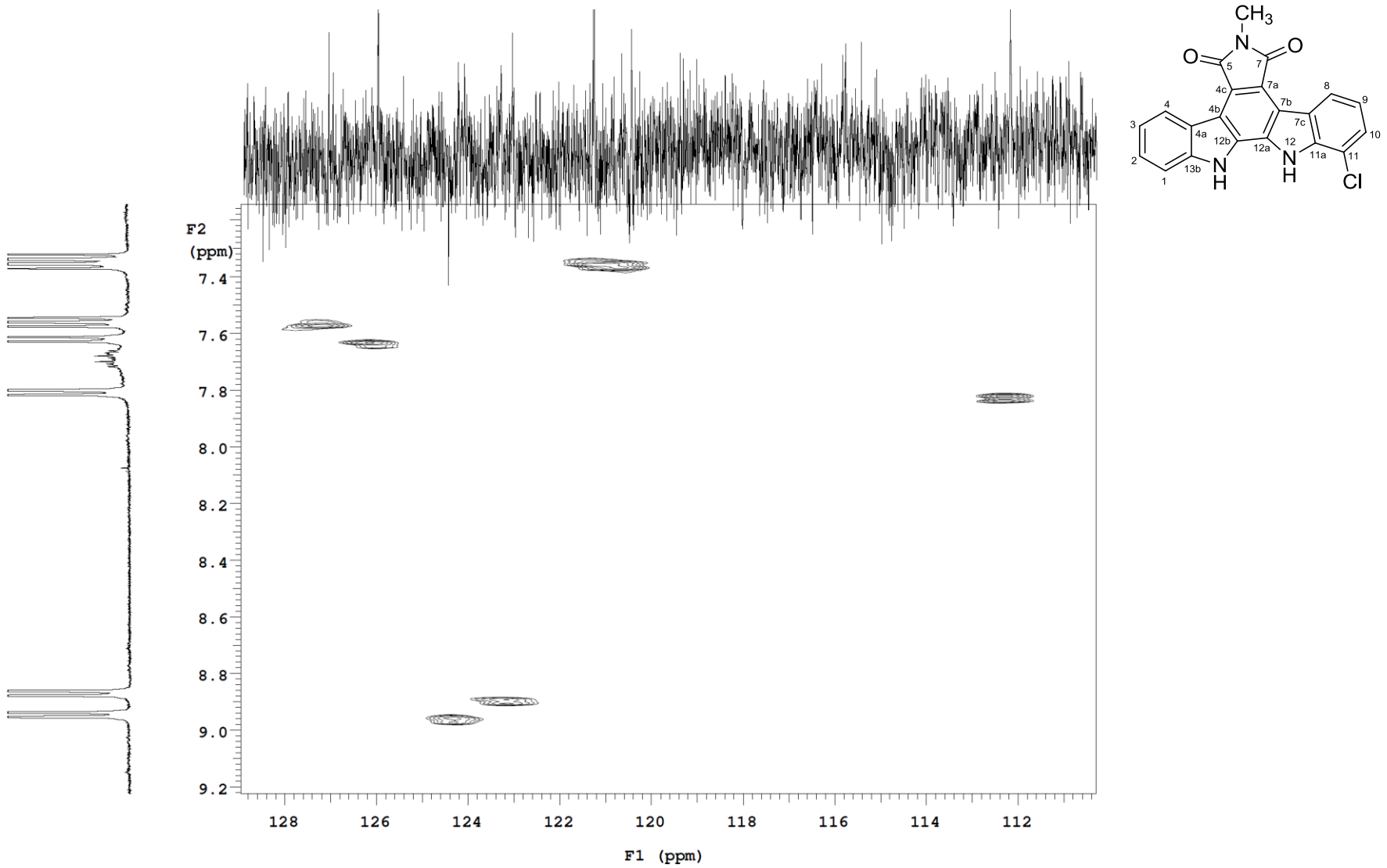

Figure S30: Enlarged HSQC spectrum (DMSO-d_6, 500 MHz) of AT2433-A5 (**3**)

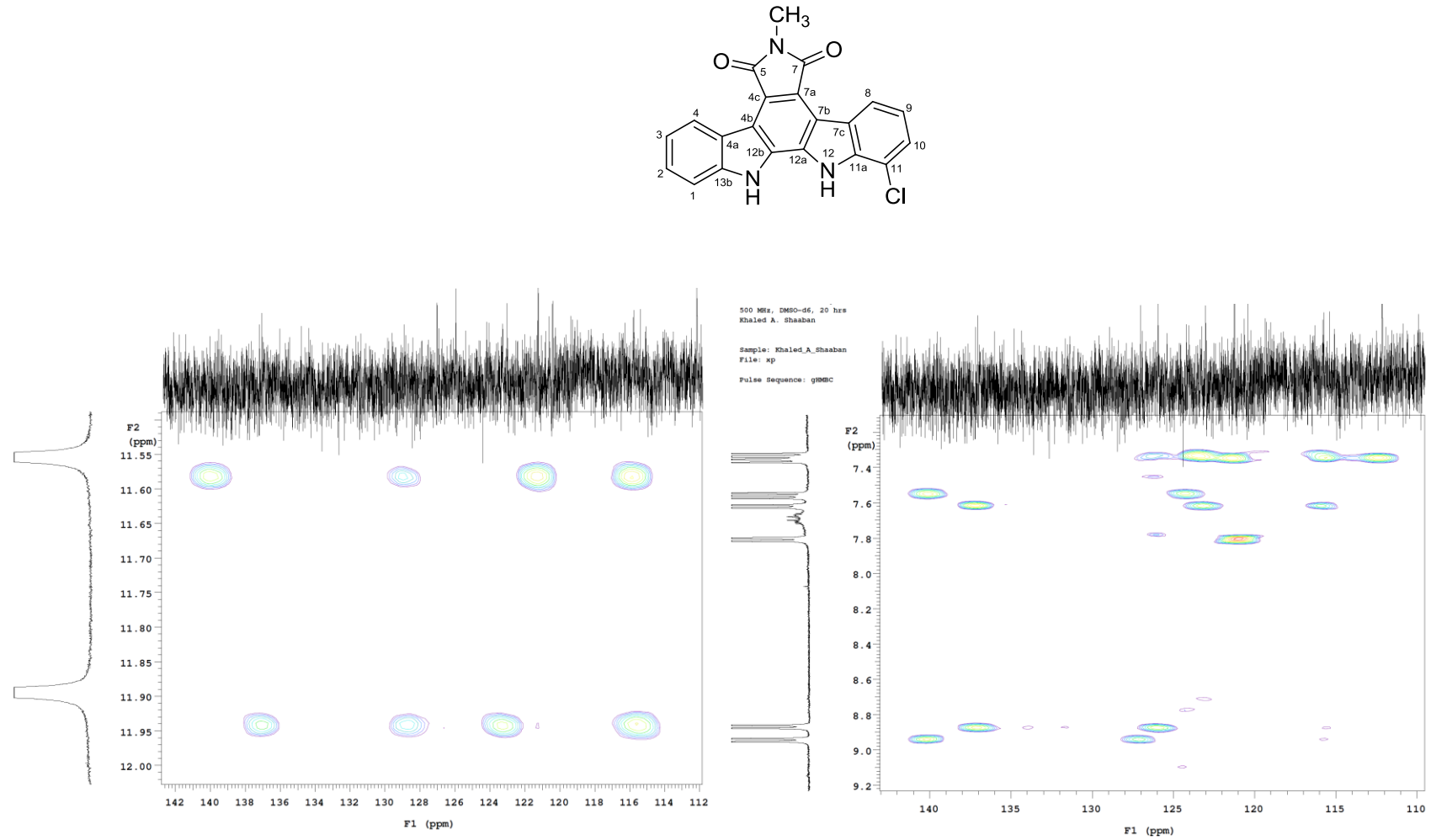

Figure S31: Enlarged HMBC spectrum (DMSO-d_6, 500 MHz) of AT2433-A5 (**3**)

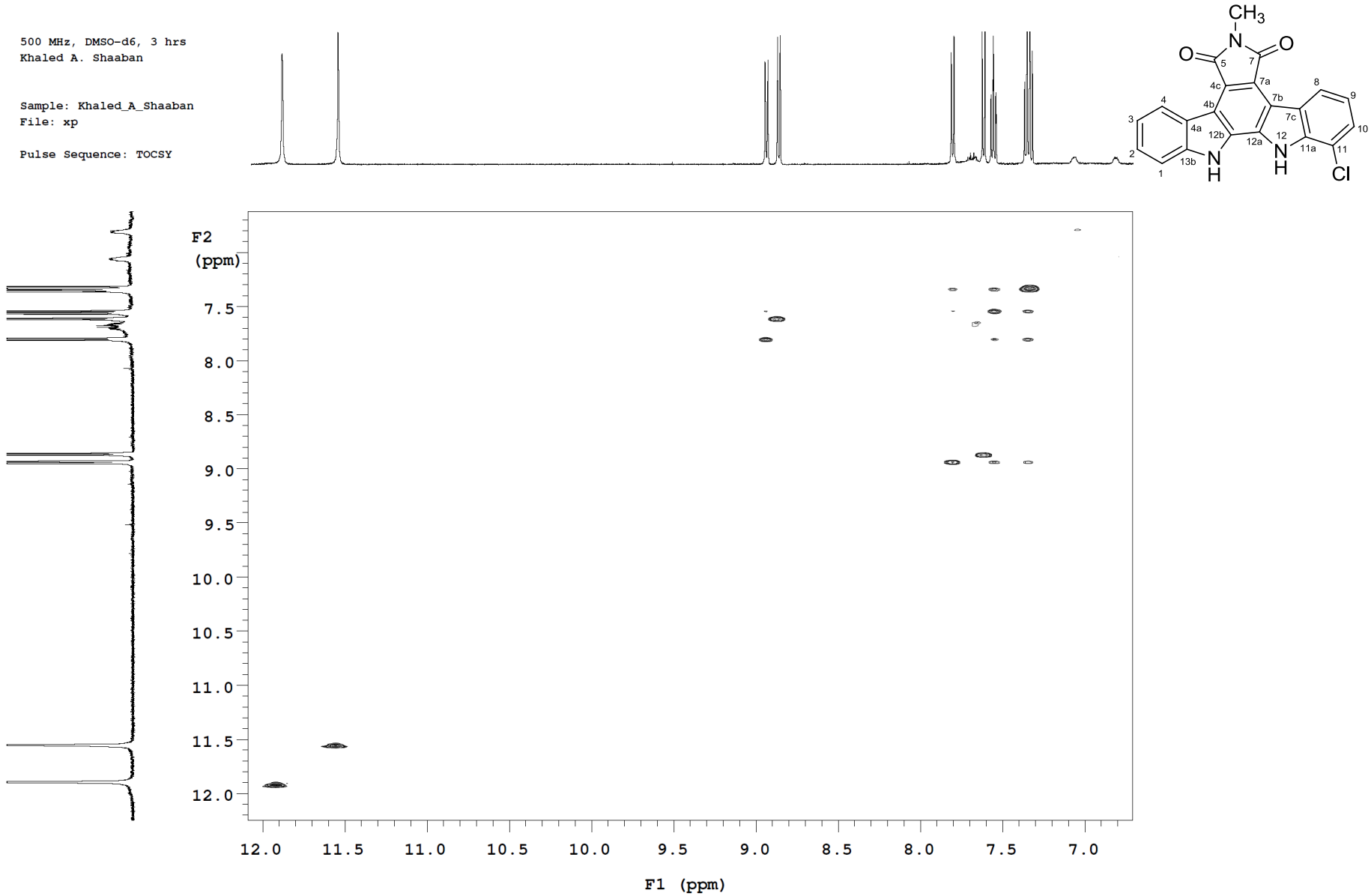

Figure S32: Enlarged TOCSY spectrum (DMSO-d_6, 500 MHz) of AT2433-A5 (**3**)

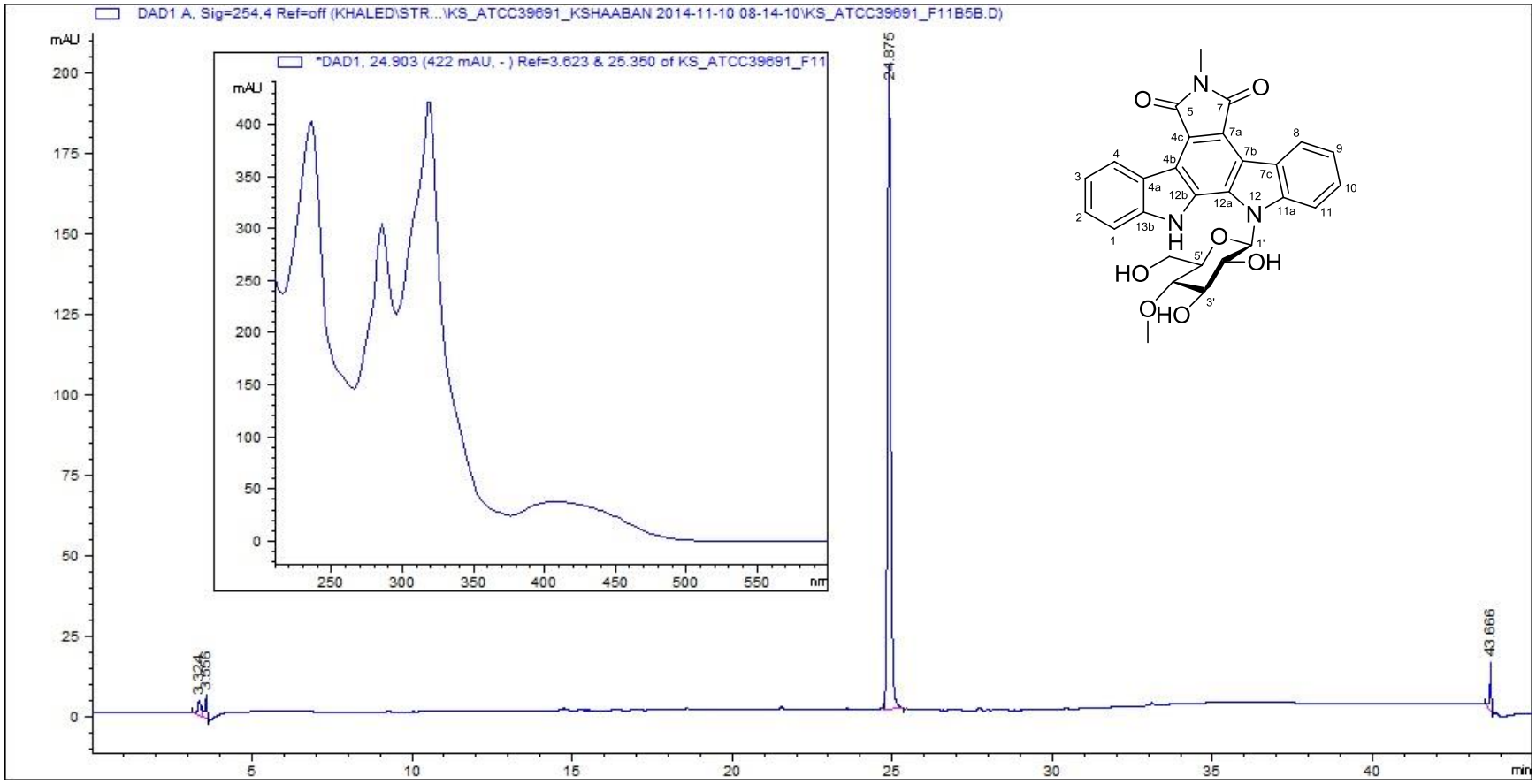

Figure S33: HPLC of AT2433-B3 (**4**). HPLC-conditions: Detection wavelength 254 nm; **solvent A:** H_2O/0.1% TFA; **solvent B:** CH_3CN; flow rate: 1.0 mL min^{-1}; 0-35 min, 5%-100% B; 35-40 min, 100% B; 40-41 min, 100%-5% B; 41-45 min, 5% B). UV-vis inset of full wavelength 190-600 nm.

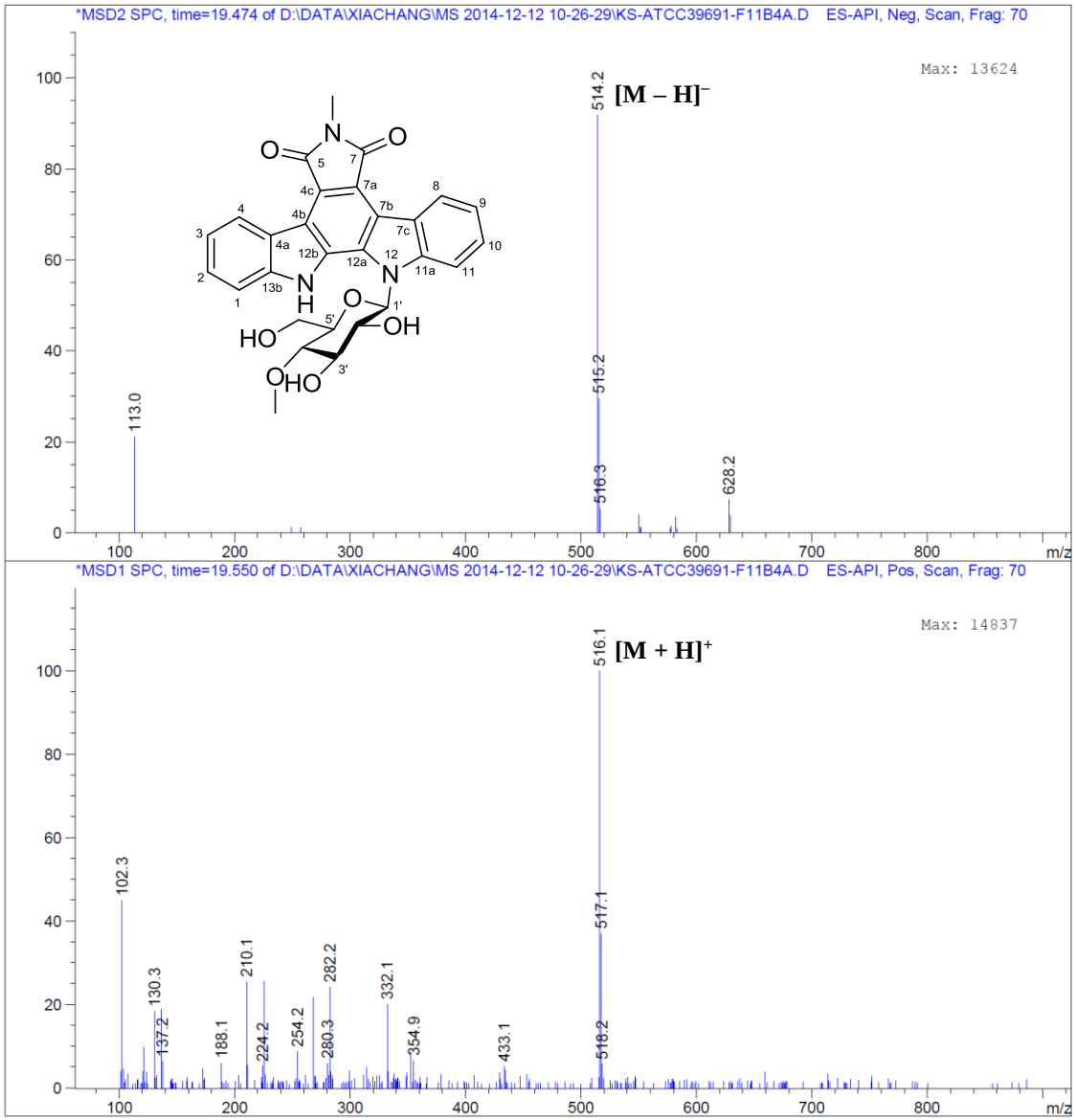

Figure S34: (+) and (–)-APCI-MS spectra of AT2433-B3 (**4**)

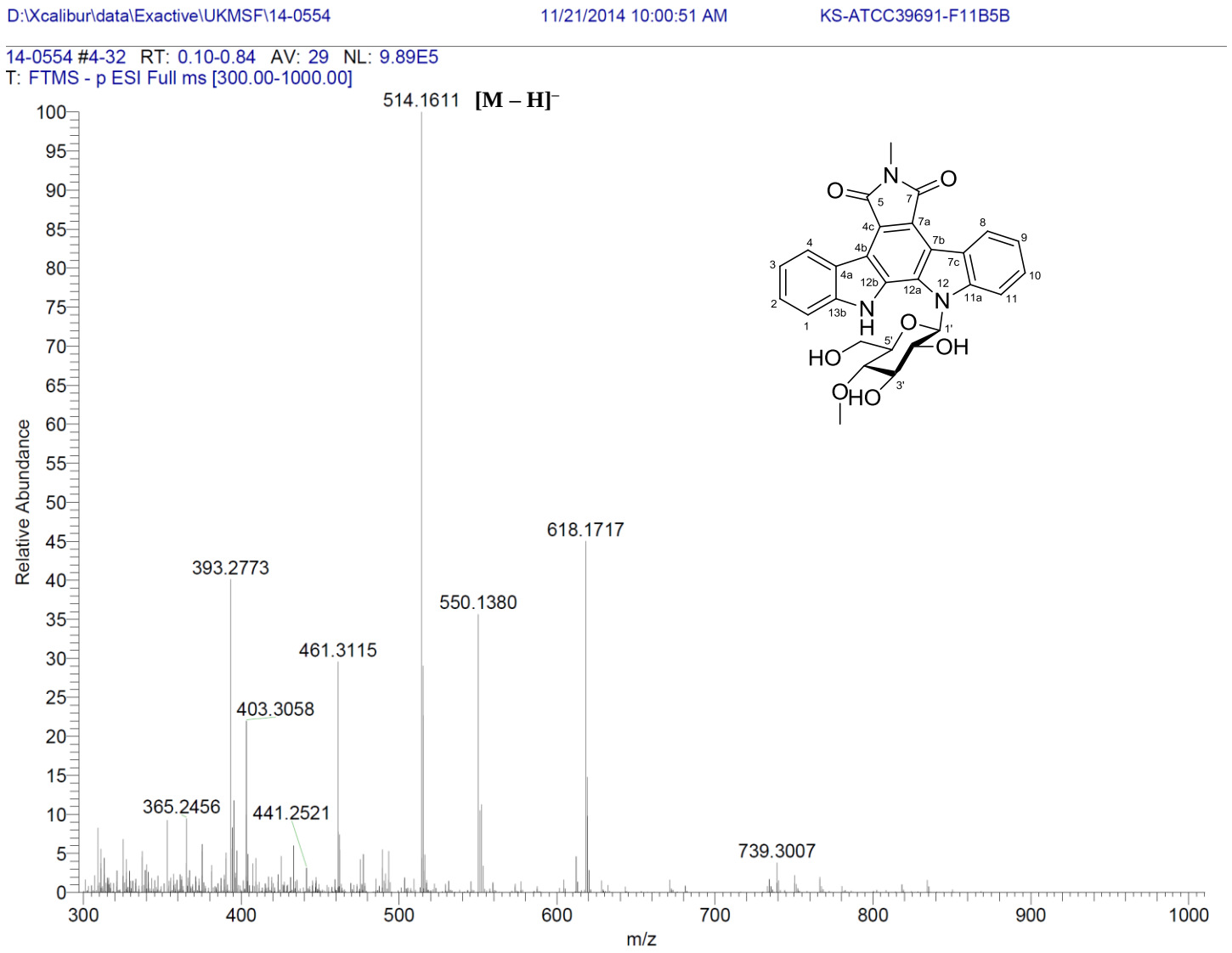

Figure S35: (–)-HRESI-MS spectrum of AT2433-B3 (**4**)

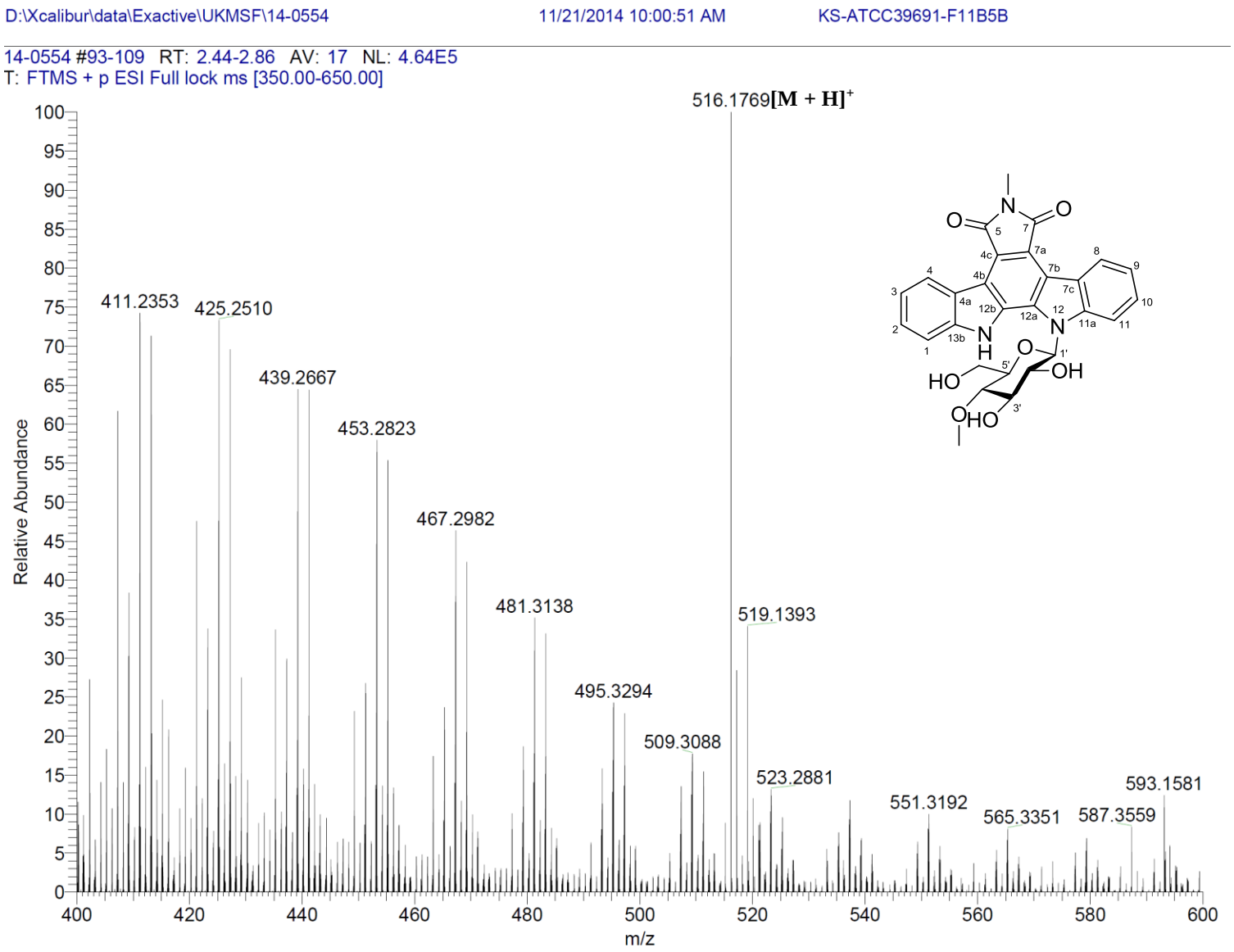

Figure S36: (+)-HRESI-MS spectrum of AT2433-B3 (**4**)

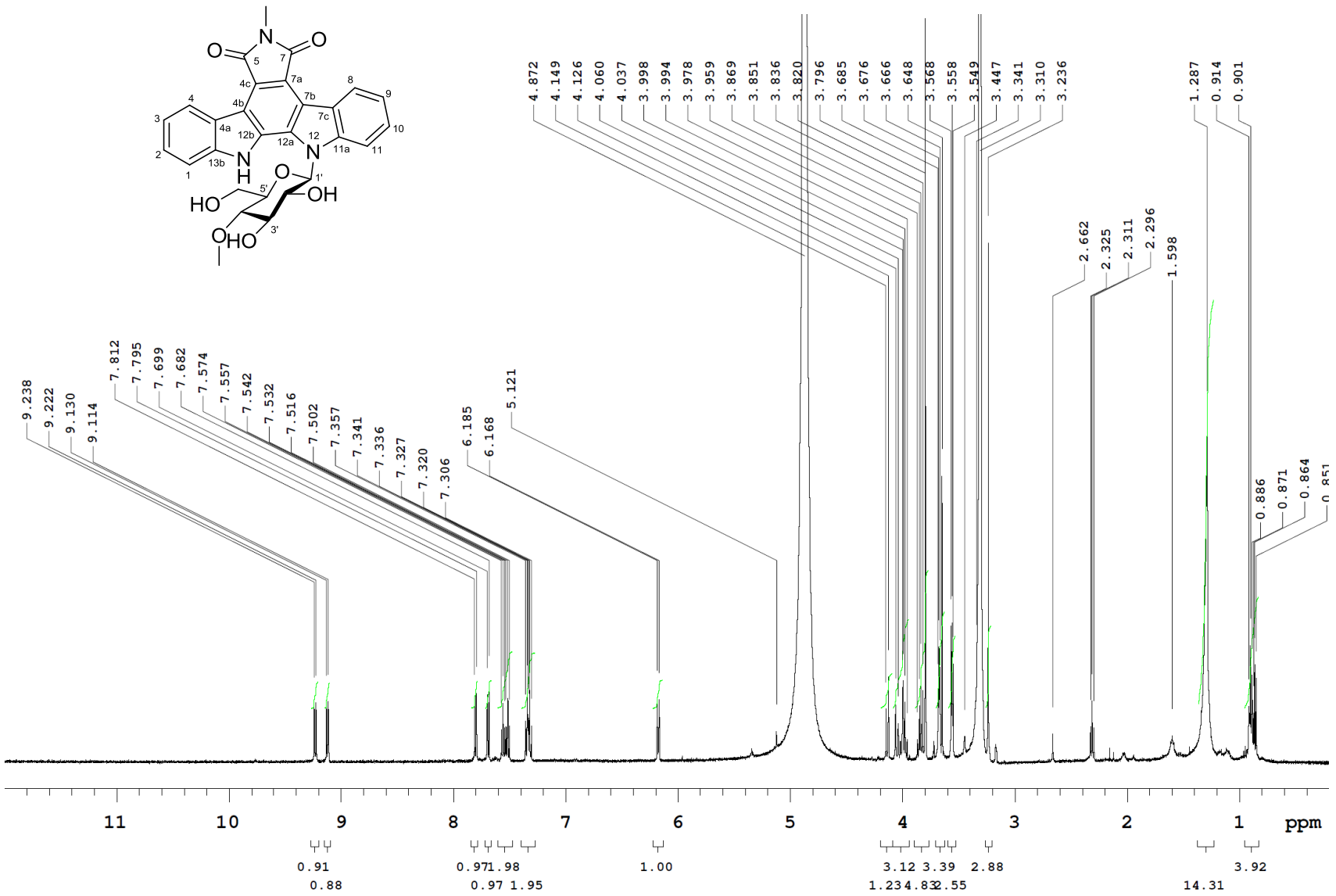

Figure S37: ^{1}H NMR spectrum (CD_3OD, 500 MHz) of AT2433-B3 (**4**)

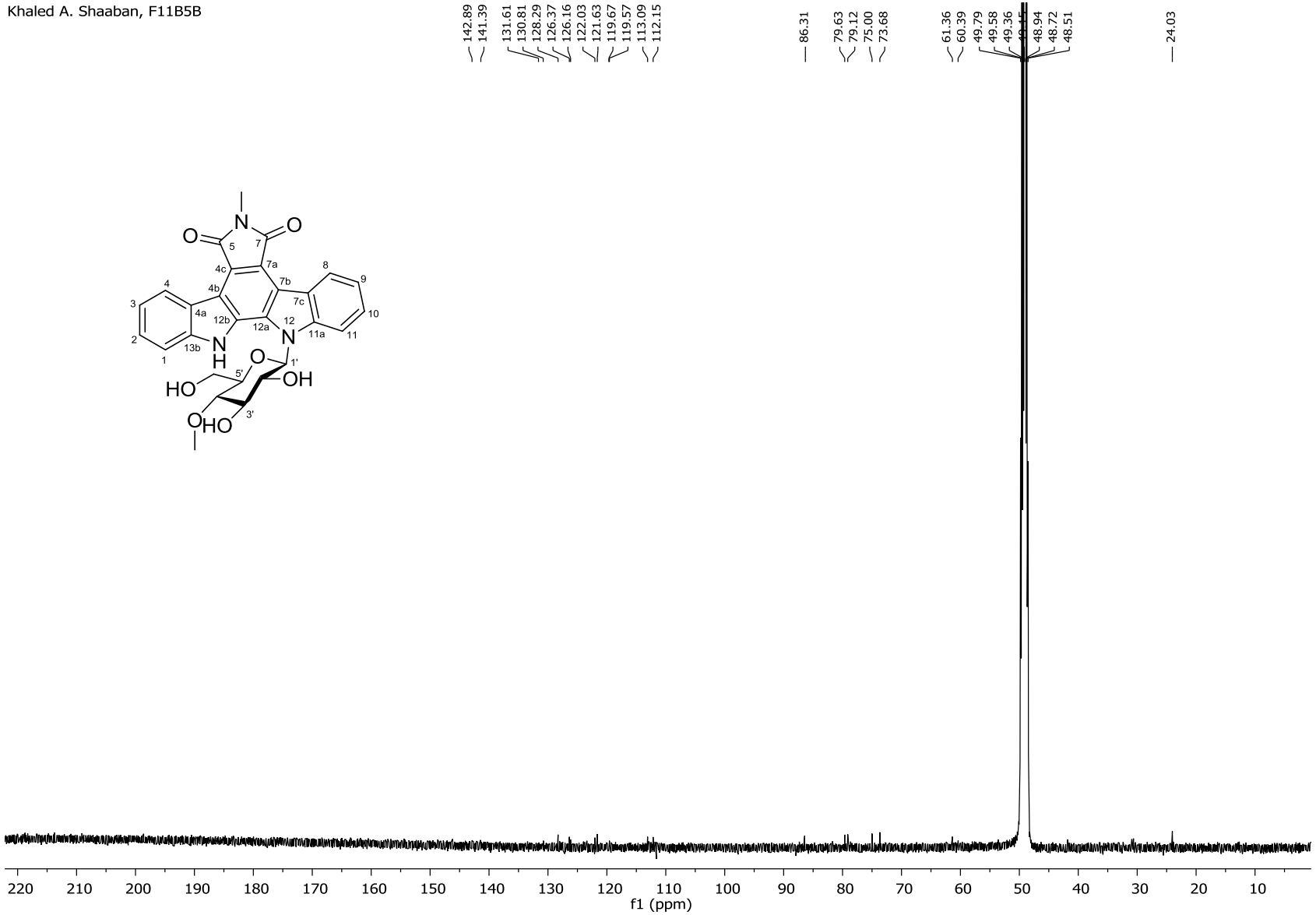

Figure S38: ^{13}C NMR spectrum (CD_3OD, 100 MHz) of AT2433-B3 (**4**)

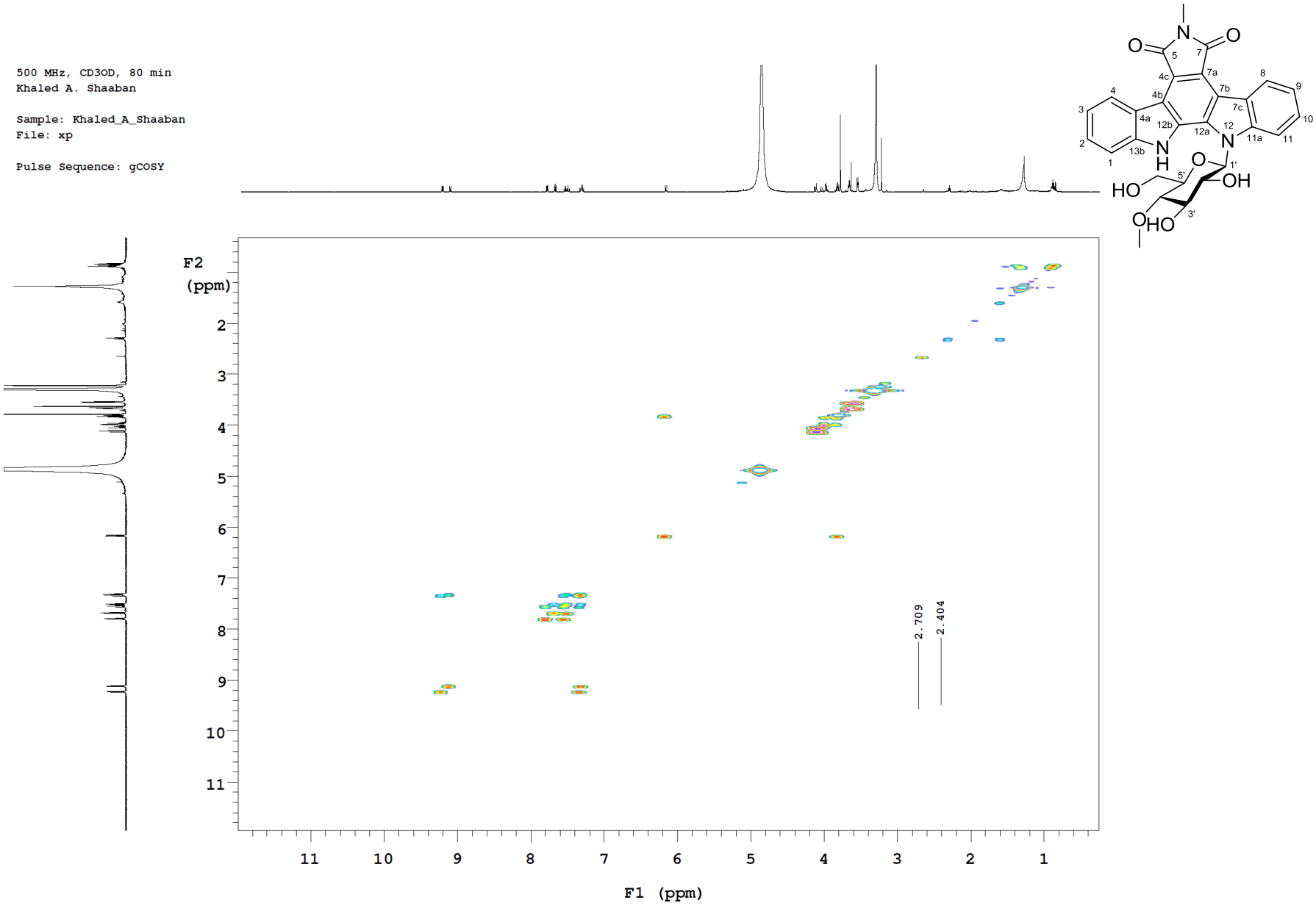

Figure S39: ^{1}H-^{1}H COSY spectrum (CD_3OD, 500 MHz) of AT2433-B3 (**4**)

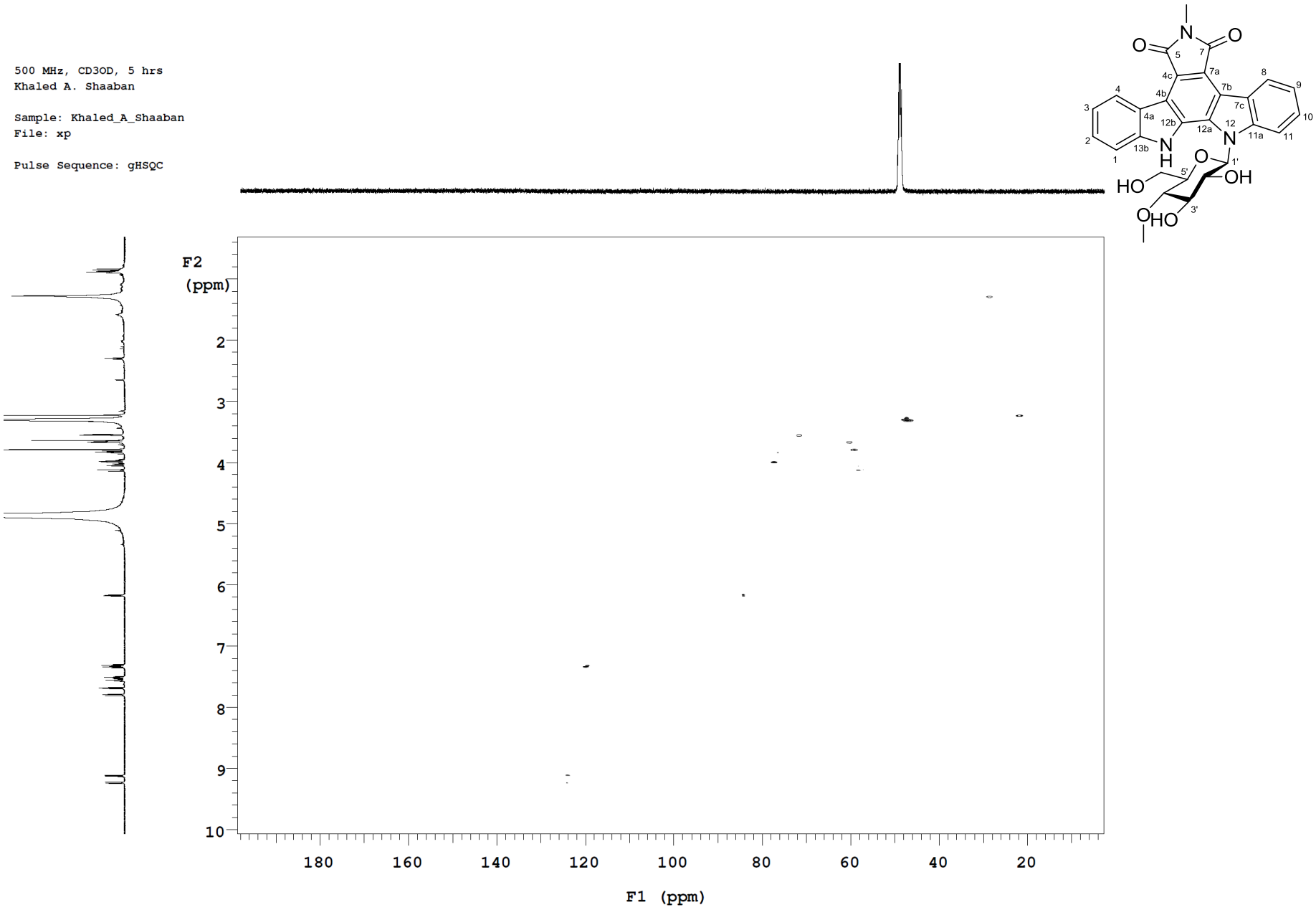

Figure S40: HSQC spectrum (CD_3OD, 500 MHz) of AT2433-B3 (**4**)

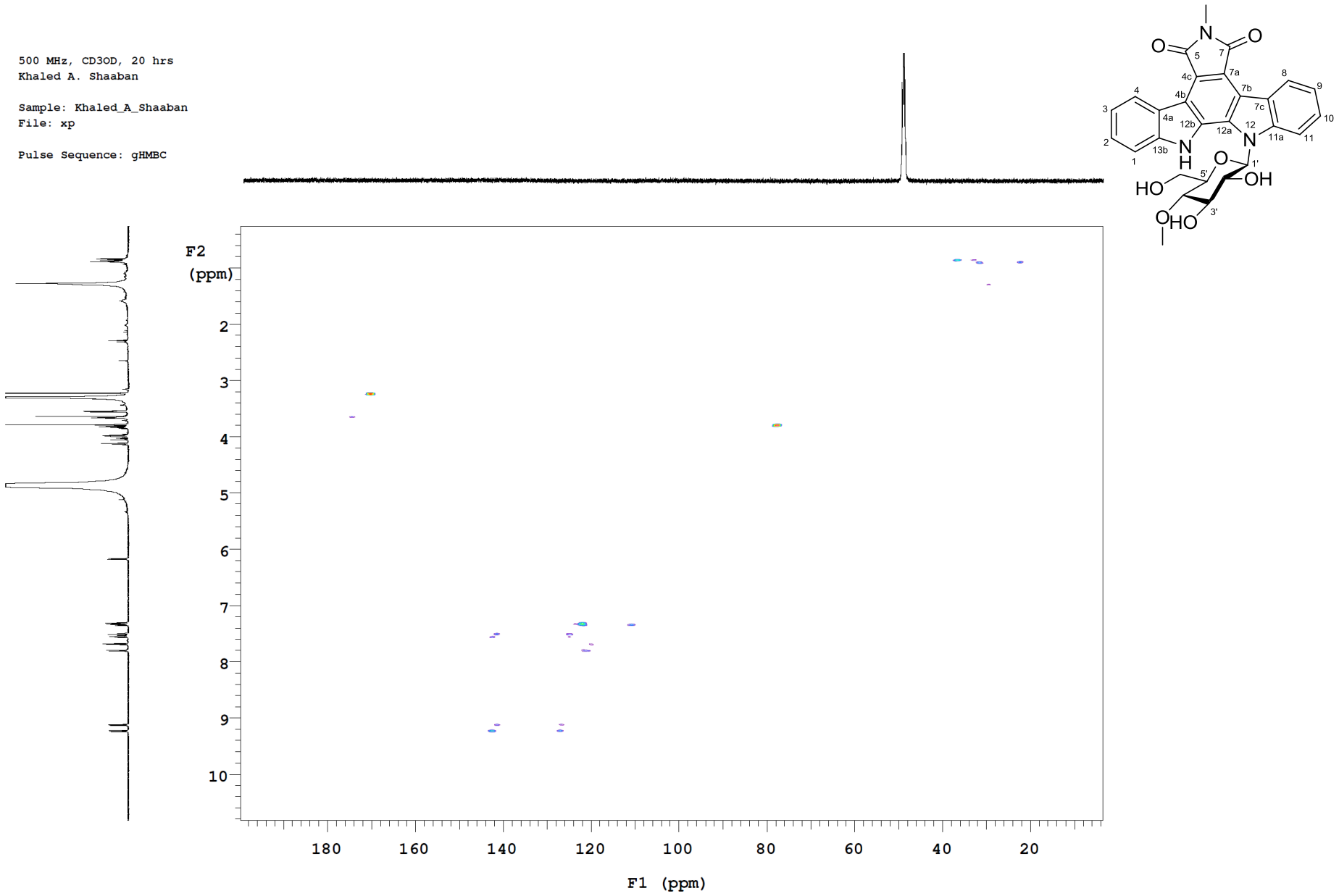

Figure S41: HMBC spectrum (CD_3OD, 500 MHz) of AT2433-B3 (**4**)

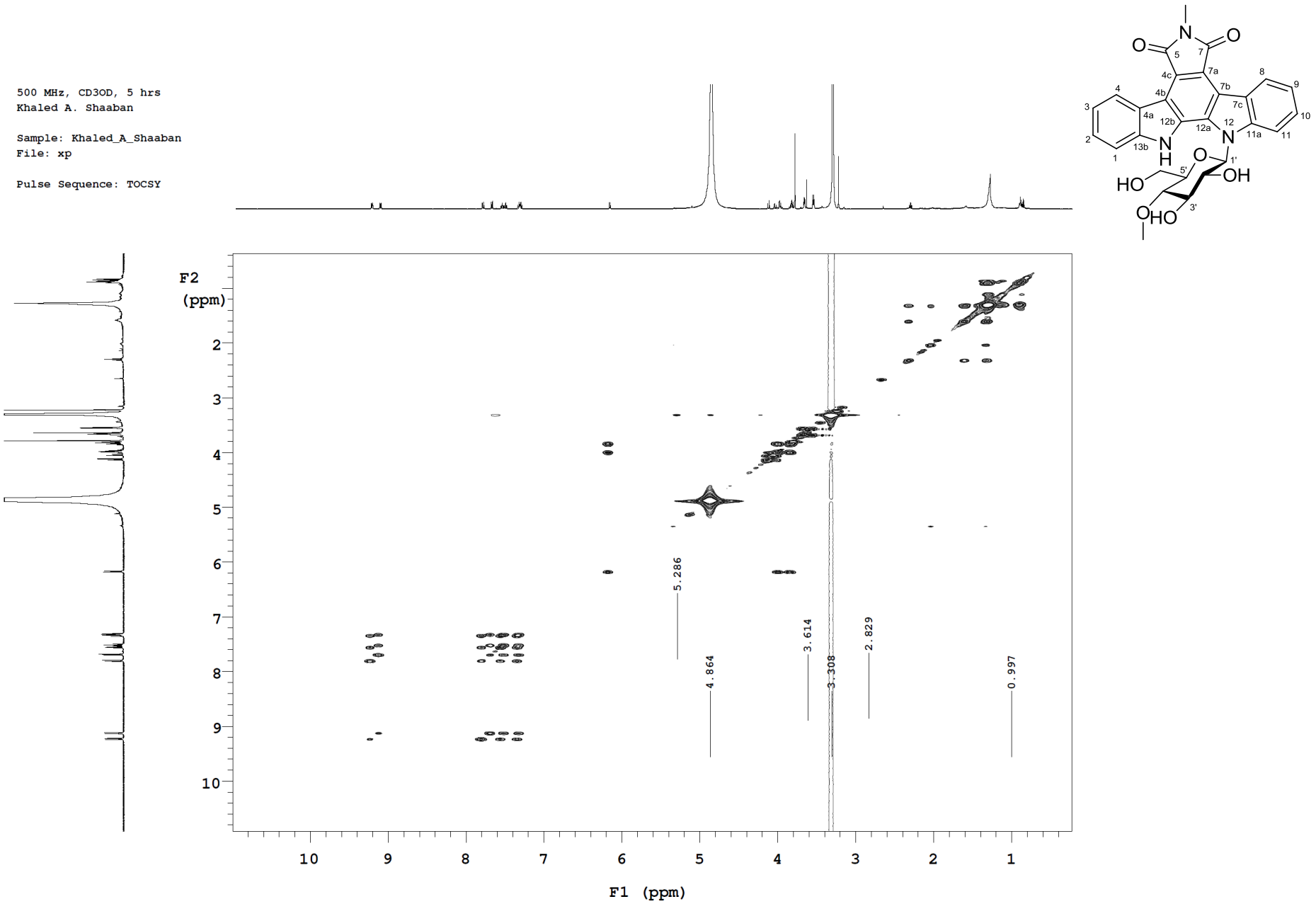

Figure S42: TOCSY spectrum (CD_3OD, 500 MHz) of AT2433-B3 (**4**)

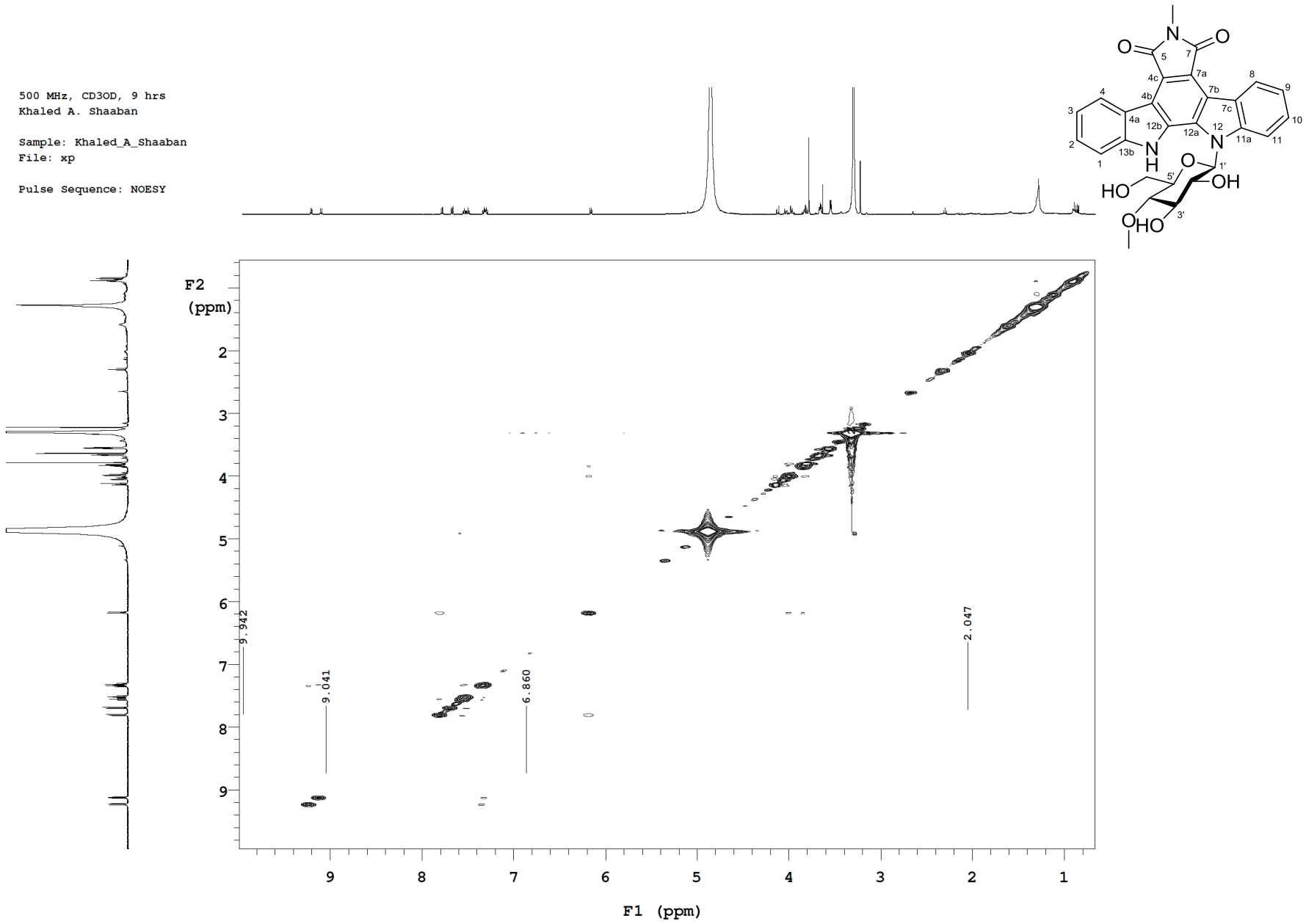

Figure S43: NOESY spectrum (CD_3OD, 500 MHz) of AT2433-B3 (**4**)

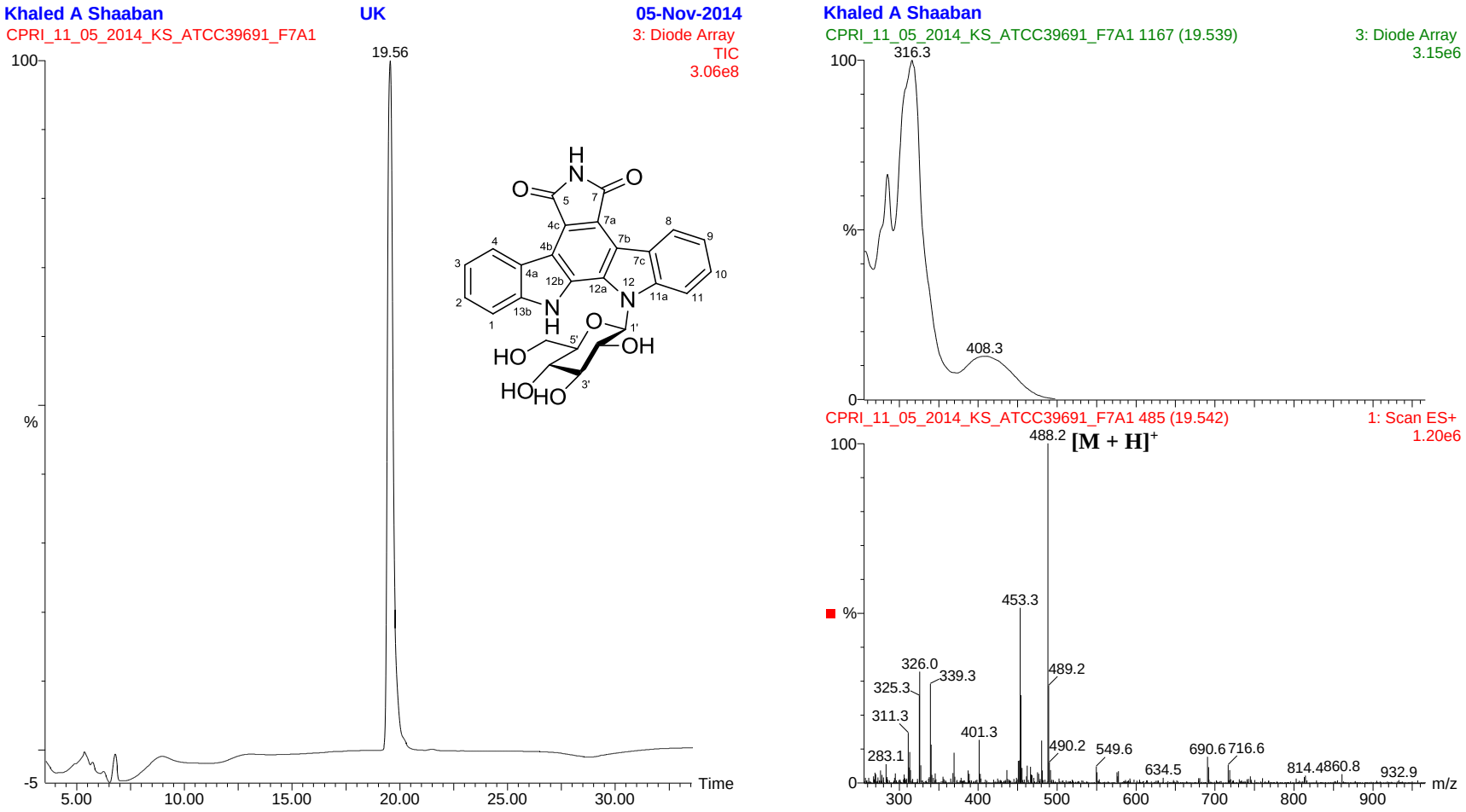

Figure S44: HPLC/UV/MS analyses of the purified BMY-41219 (**5**). Detection wavelength: 210-500; **solvent A:** H_2O/0.1% Formic acid, **solvent B:** CH_3CN/0.1% Formic acid; flow rate: 0.5 mL min^{-1}; 0-4 min, 10% B; 4-22 min, 10-100% B; 22-27 min, 100% B; 27-29 min, 100%-10% B; 29-35 min, 10 % B.

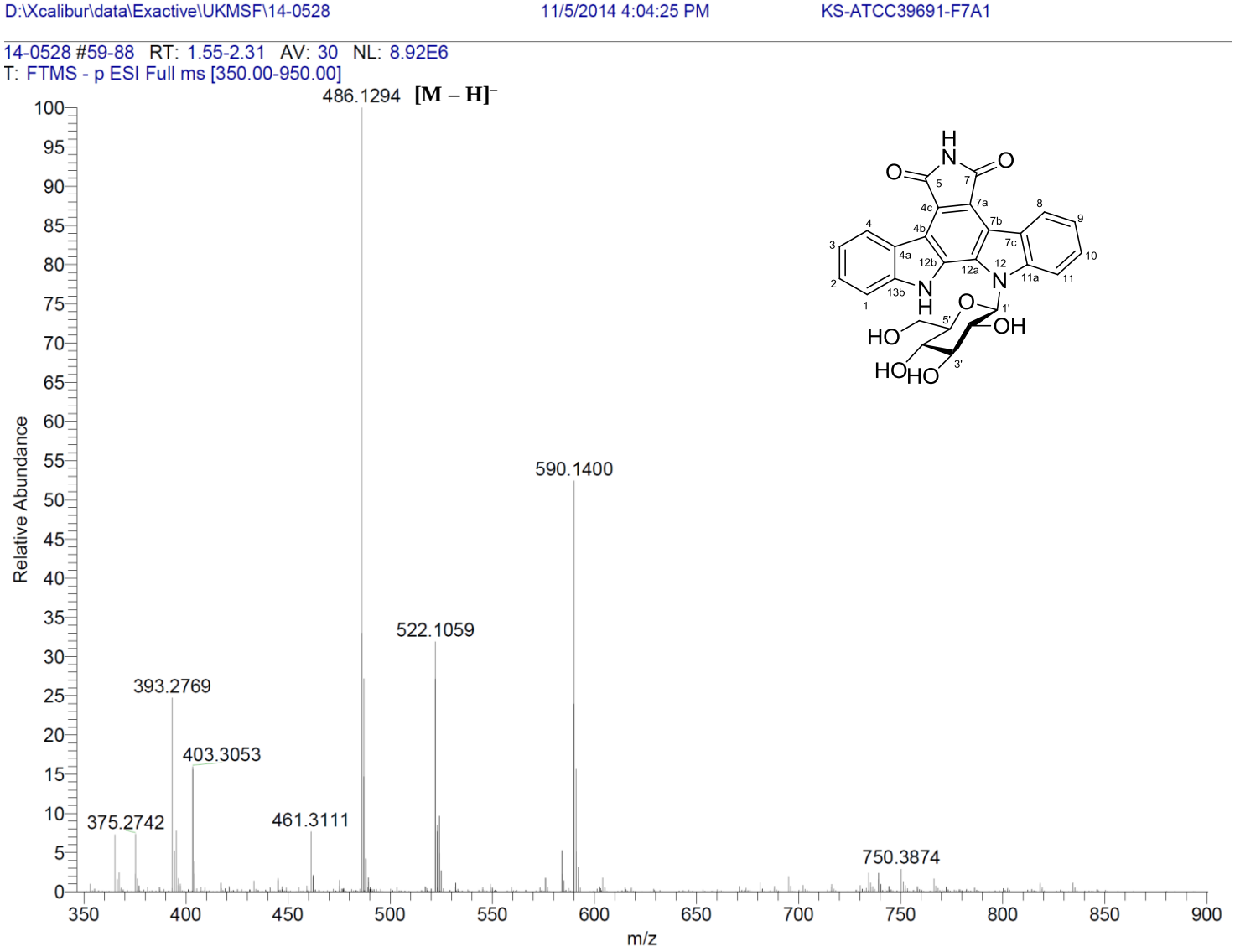

Figure S45: (–)-HRESI-MS spectrum of BMY-41219 (**5**)

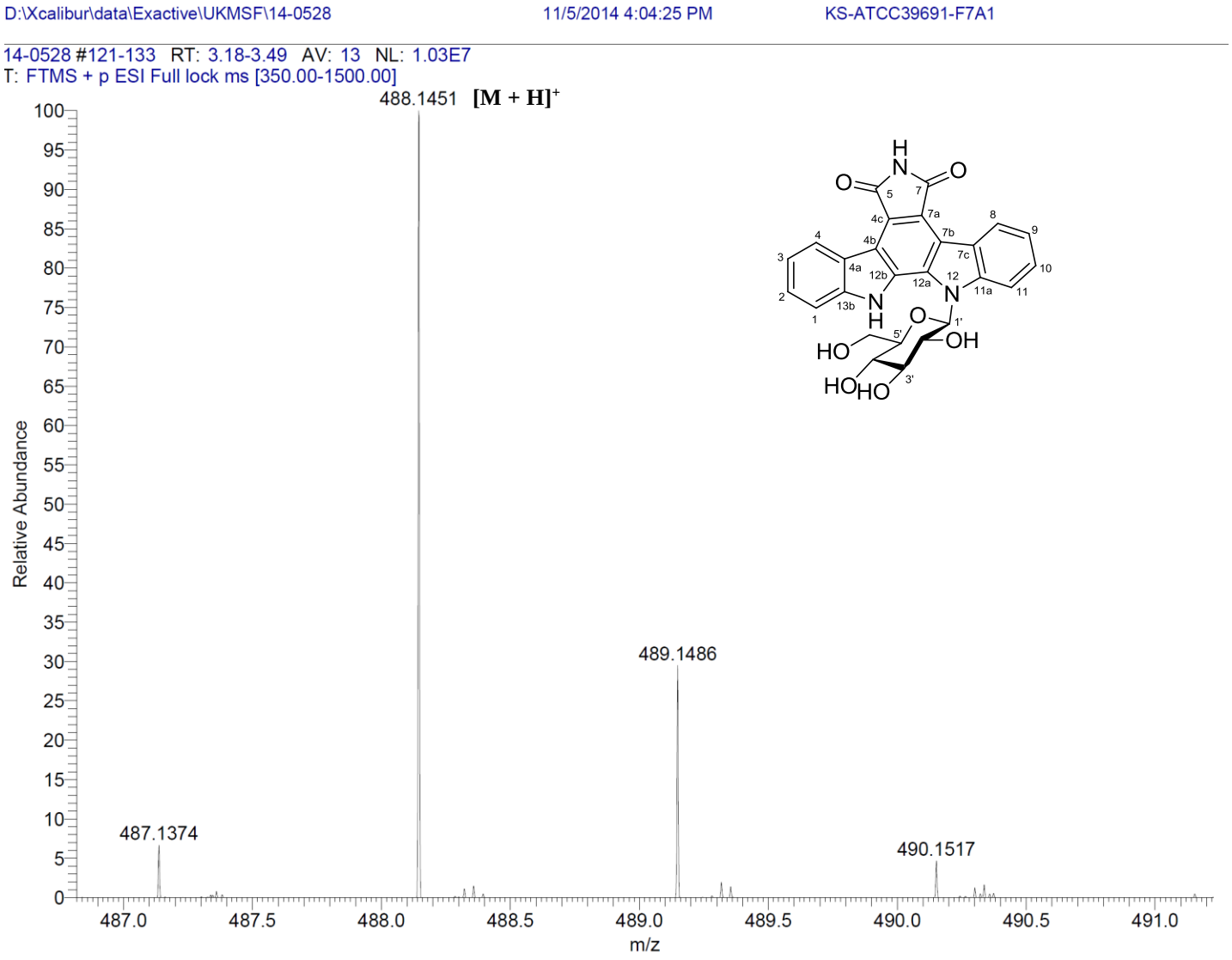

Figure S46: (+)-HRESI-MS spectrum of BMY-41219 (**5**)

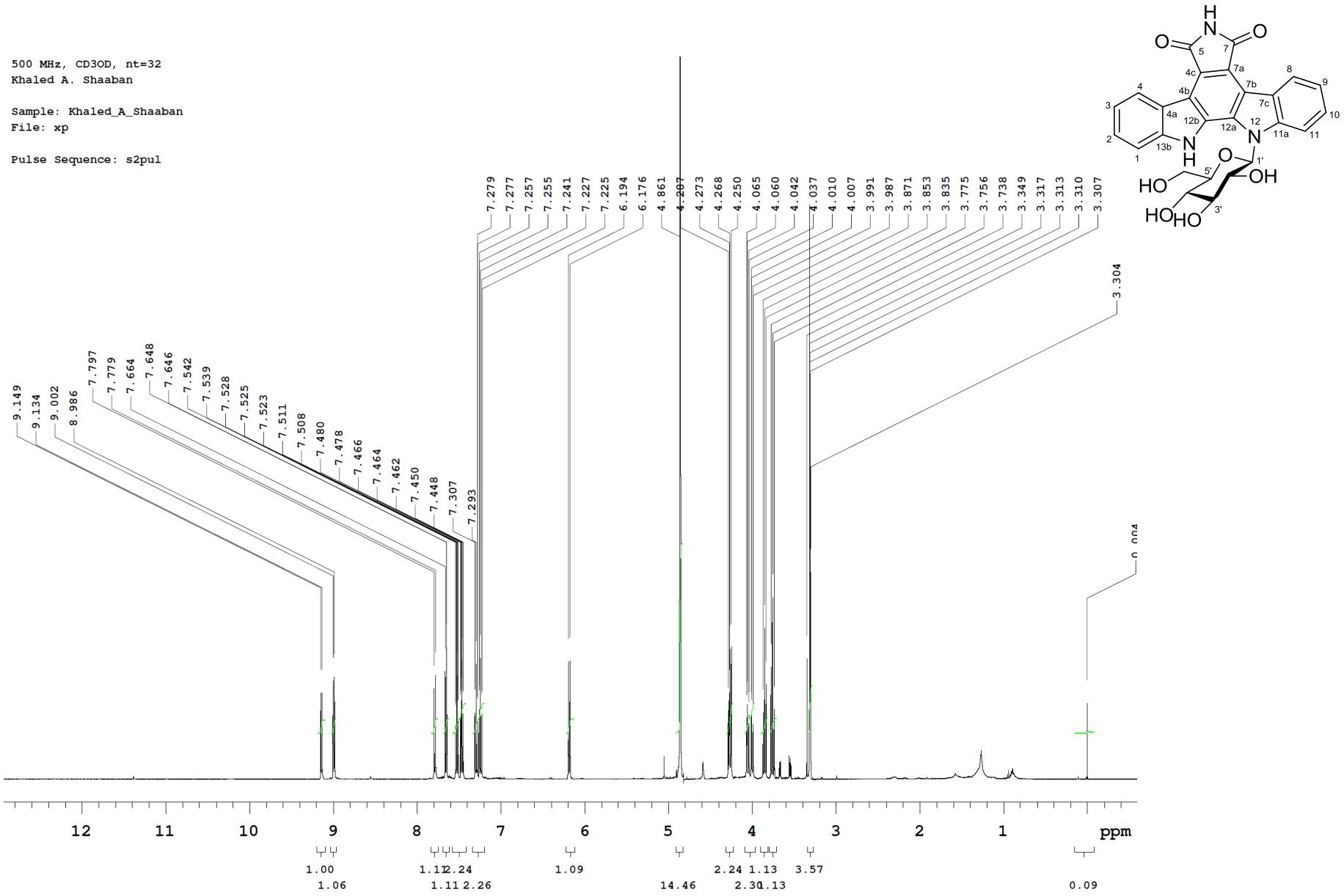

Figure S47: ^{1}H NMR spectrum (CD_3OD, 500 MHz) of BMY-41219 (**5**)

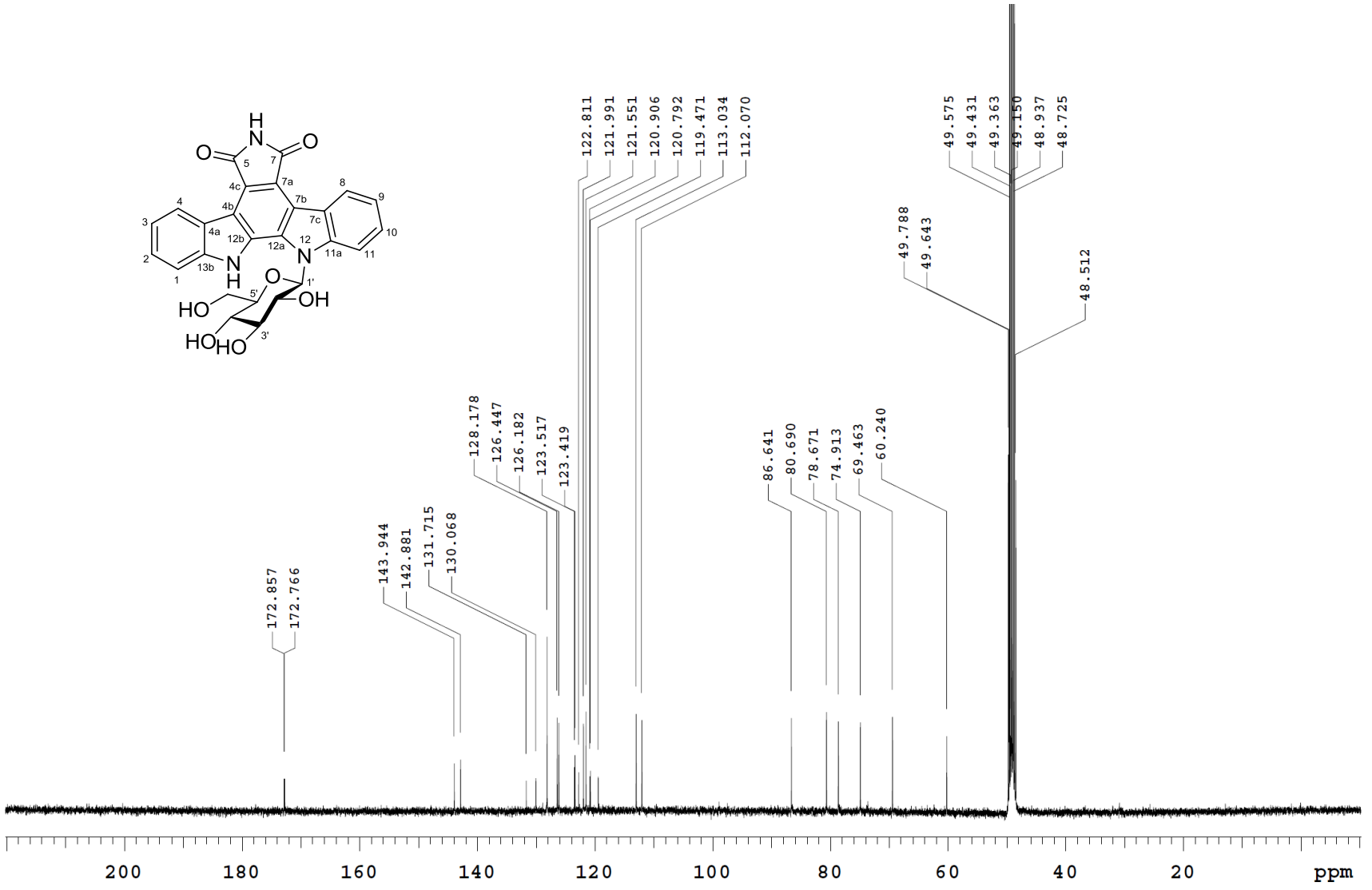

Figure S48: ^{13}C NMR spectrum (CD_3OD, 100 MHz) of BMY-41219 (**5**)

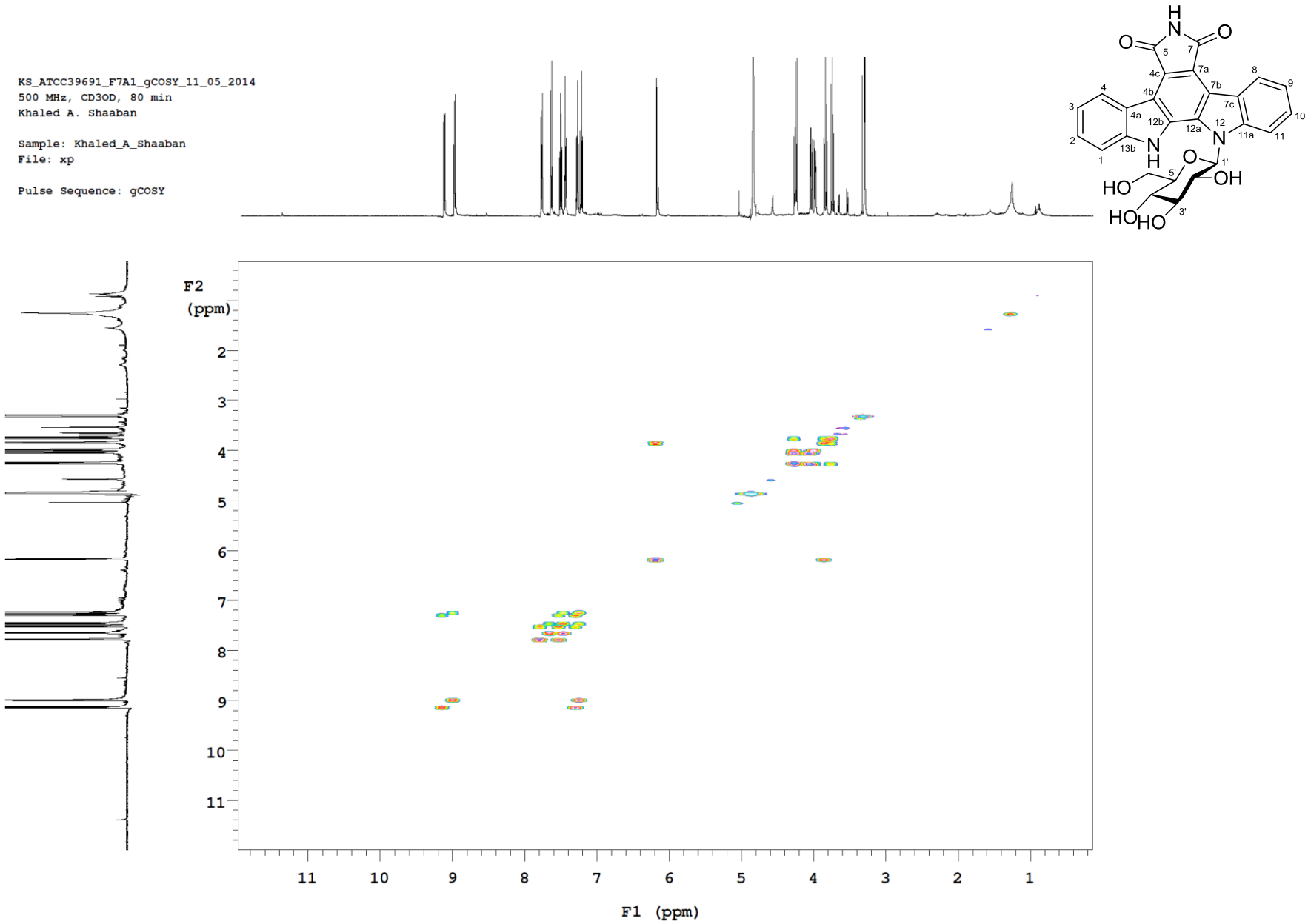

Figure S49: ^{1}H-^{1}H COSY spectrum (CD_3OD, 500 MHz) of BMY-41219 (**5**)

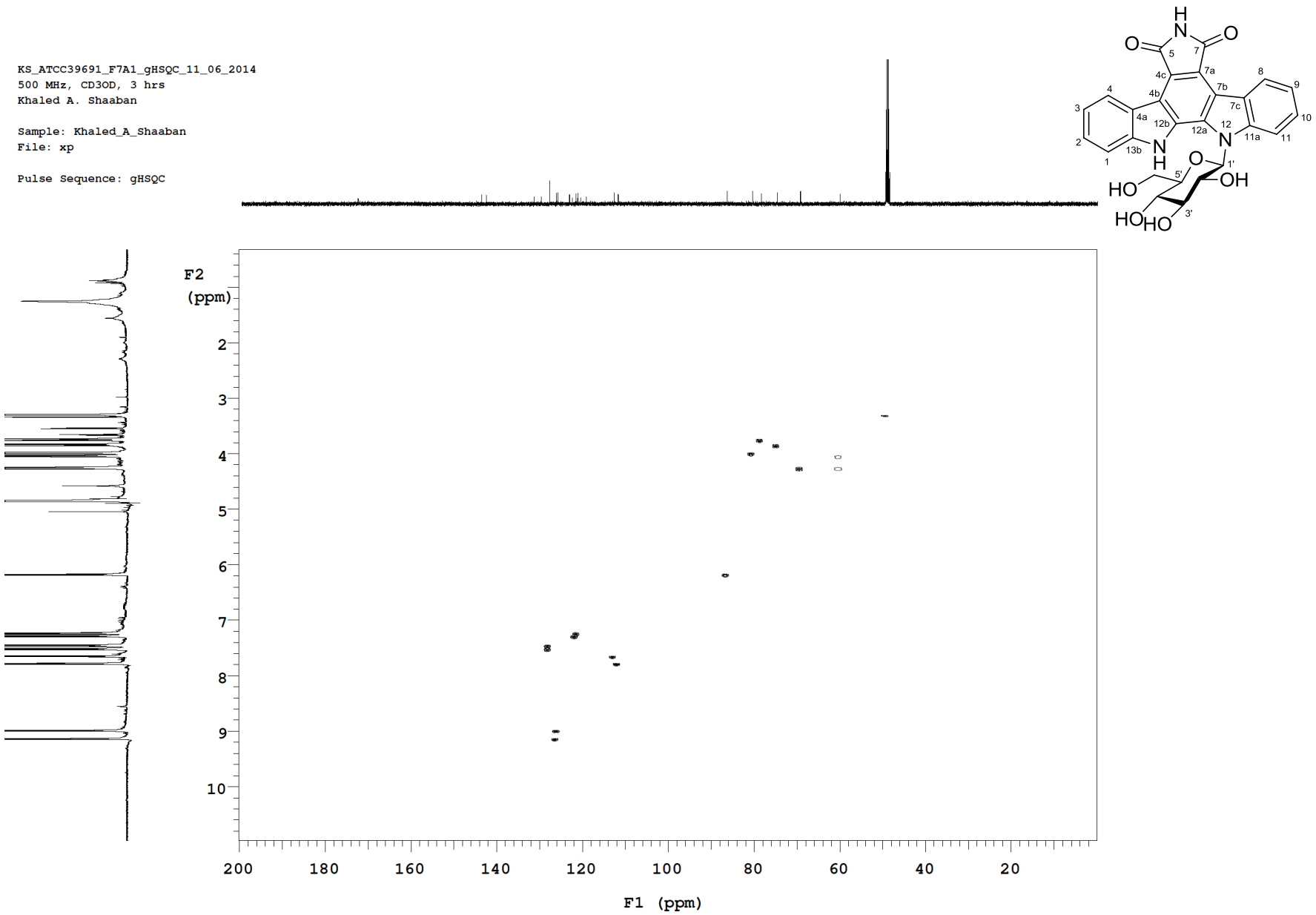

Figure S50: HSQC spectrum (CD_3OD, 100 MHz) of BMY-41219 (**5**)

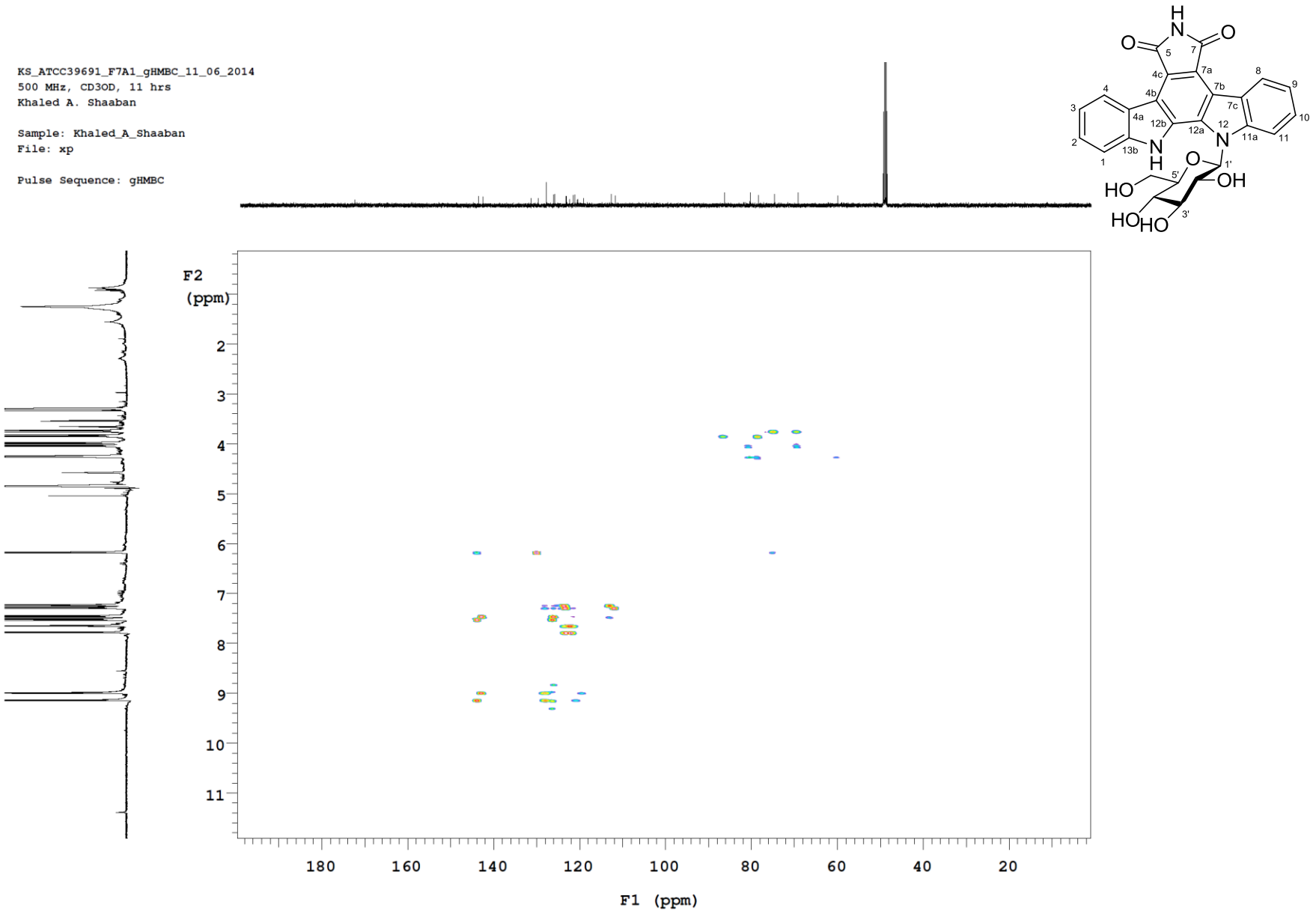

Figure S51: HMBC spectrum (CD_3OD, 100 MHz) of BMY-41219 (**5**)

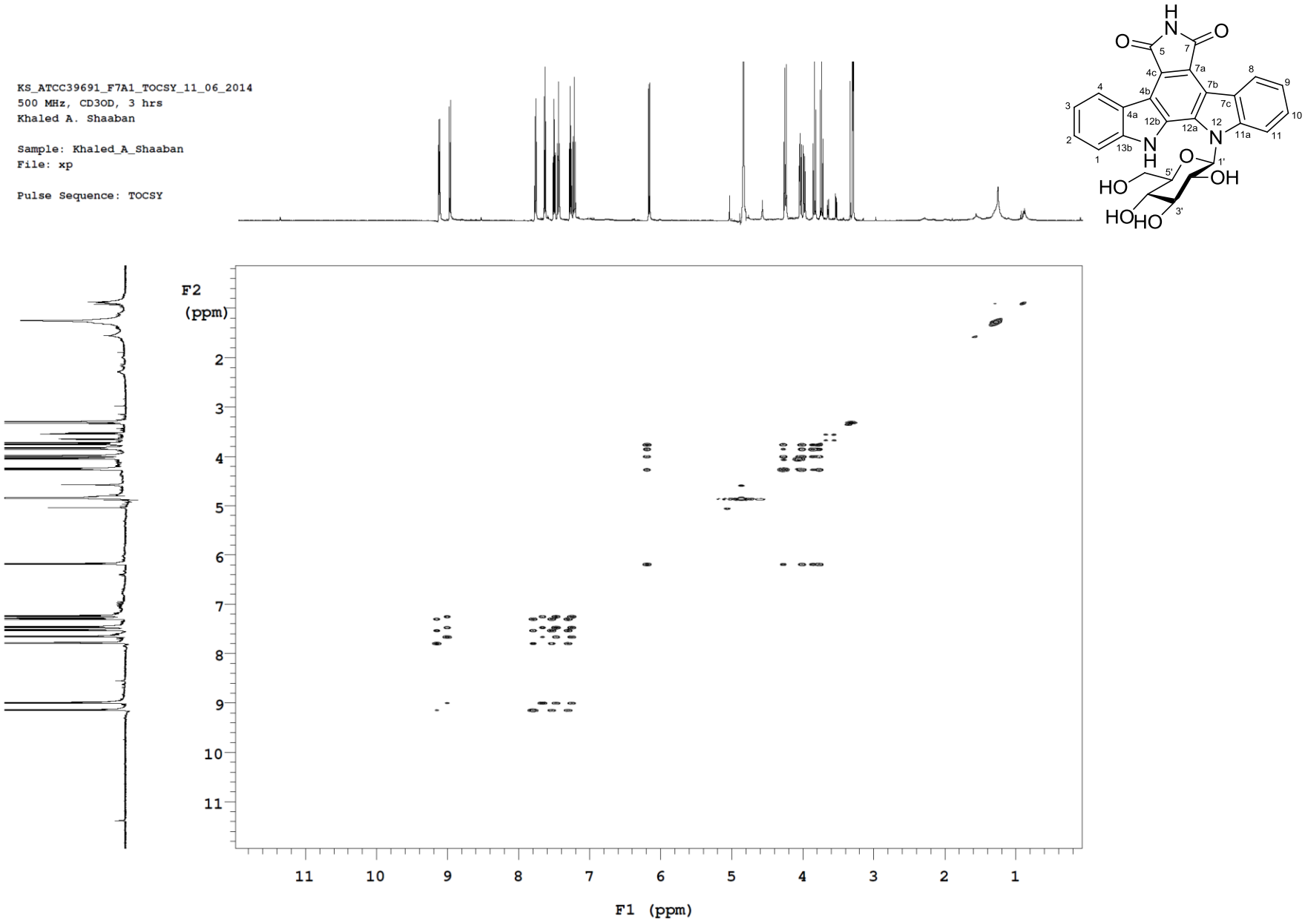

Figure S52: TOCSY spectrum (CD_3OD, 100 MHz) of BMY-41219 (**5**)

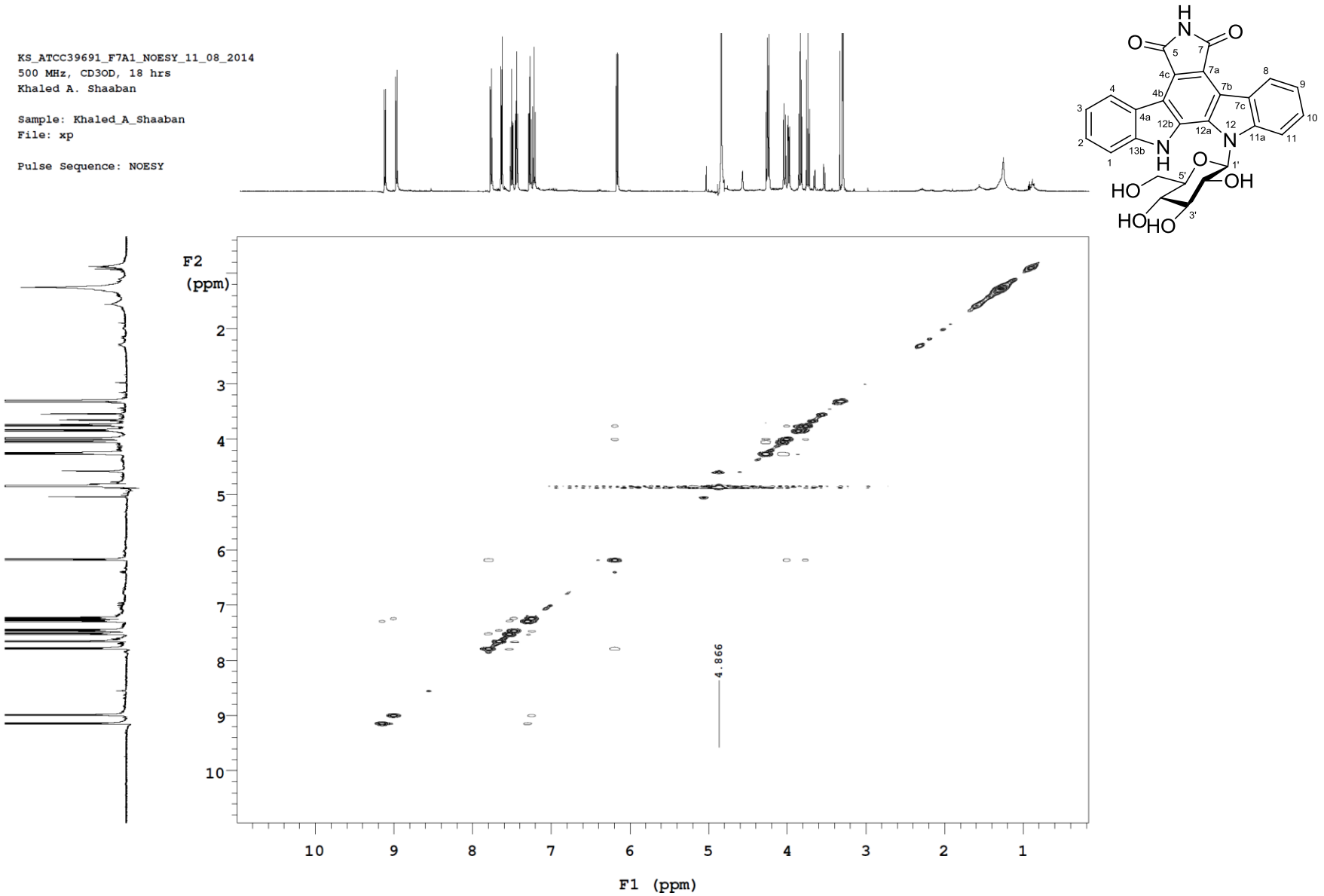

Figure S53: NOESY spectrum (CD_3OD, 100 MHz) of BMY-41219 (**5**)

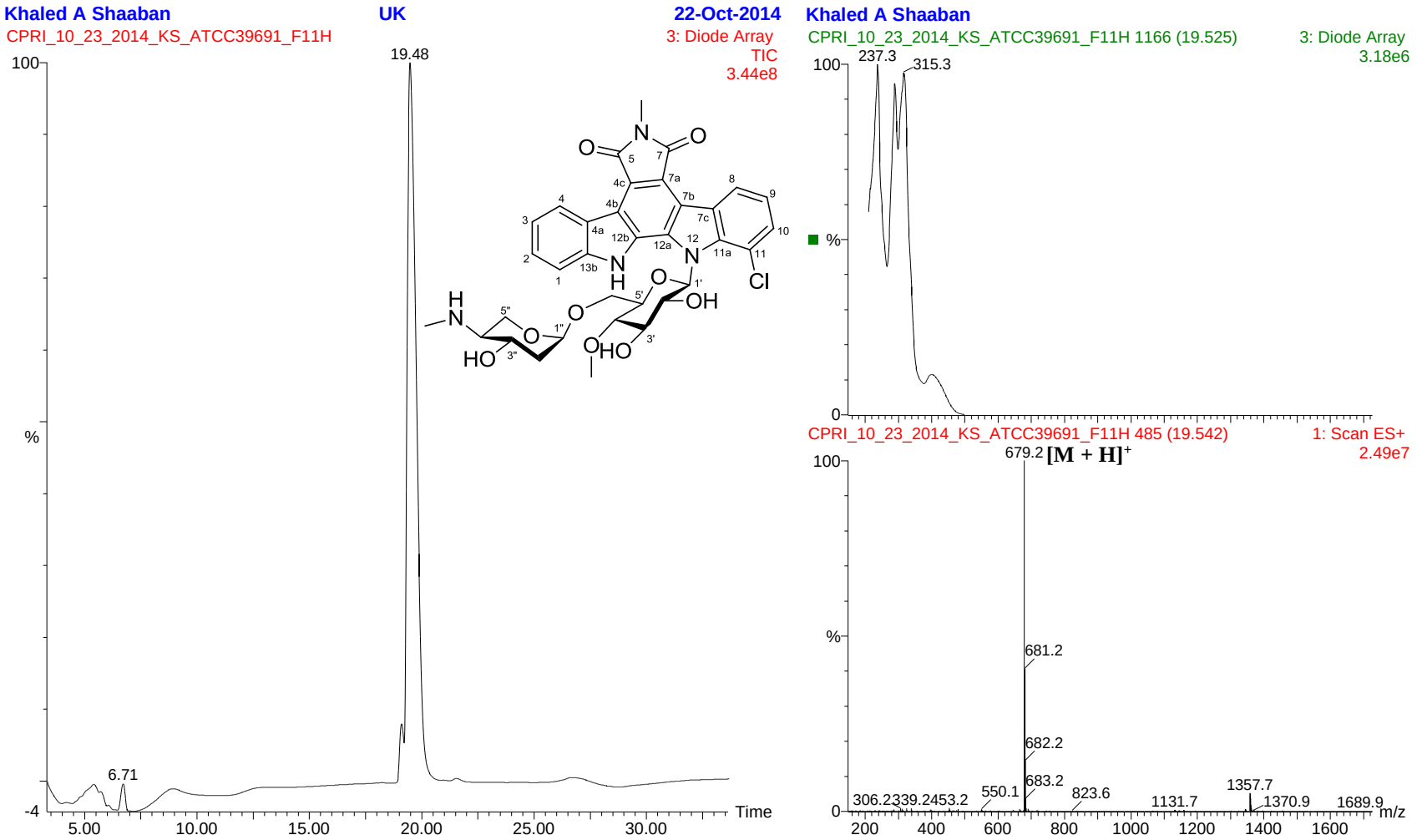

Figure S54: HPLC/UV/MS analyses of AT2433-A1 (**6**). Detection wavelength: 210-500; **solvent A:** H_2O/0.1% Formic acid, **solvent B:** CH_3CN/0.1% Formic acid; flow rate: 0.5 mL min^{-1}; 0-4 min, 10% B; 4-22 min, 10-100% B; 22-27 min, 100% B; 27-29 min, 100%-10% B; 29-35 min, 10 % B.

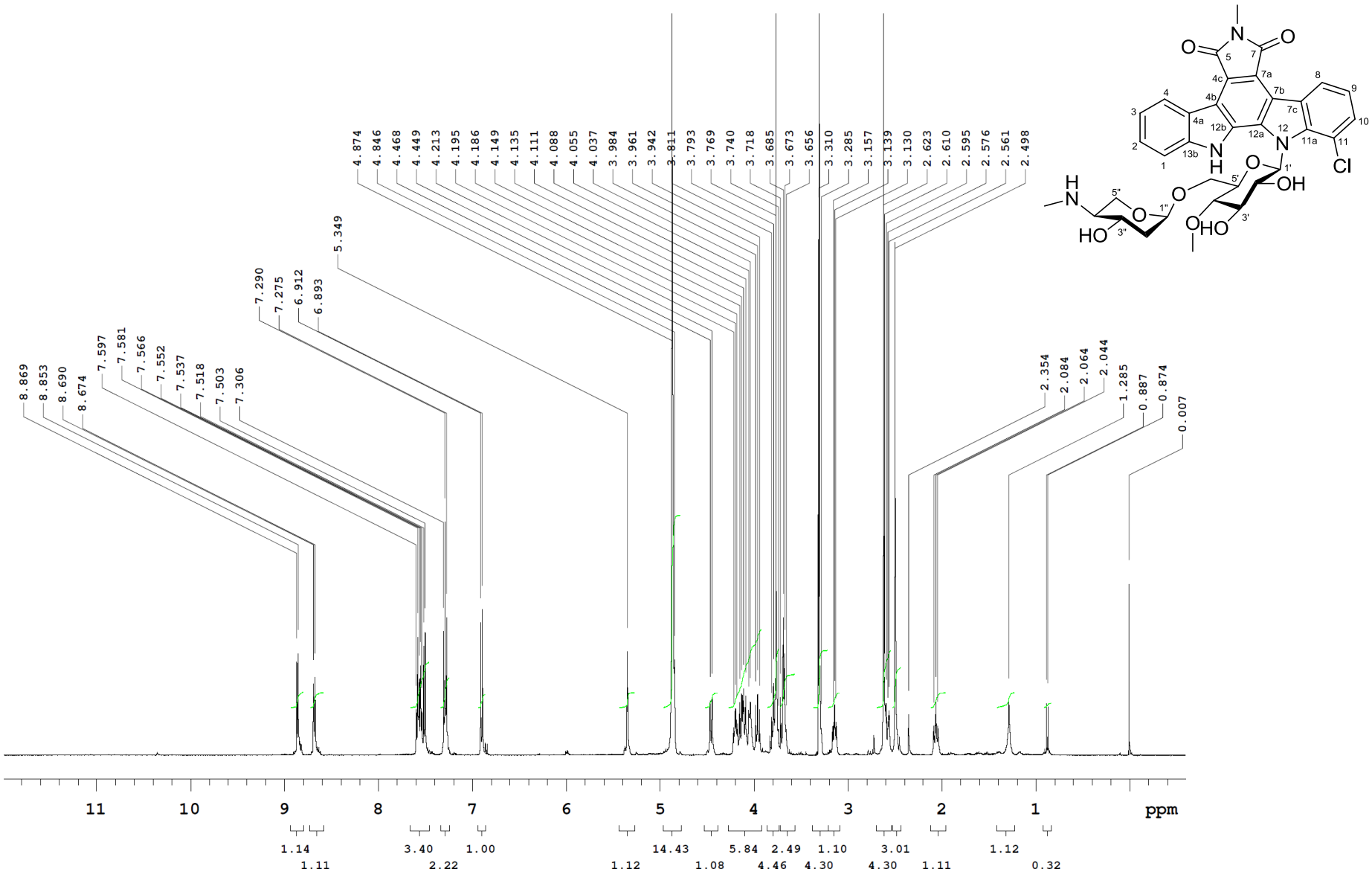

Figure S55: ^{1}H NMR spectrum (CD_3OD, 500 MHz) of AT2433-A1 (**6**)

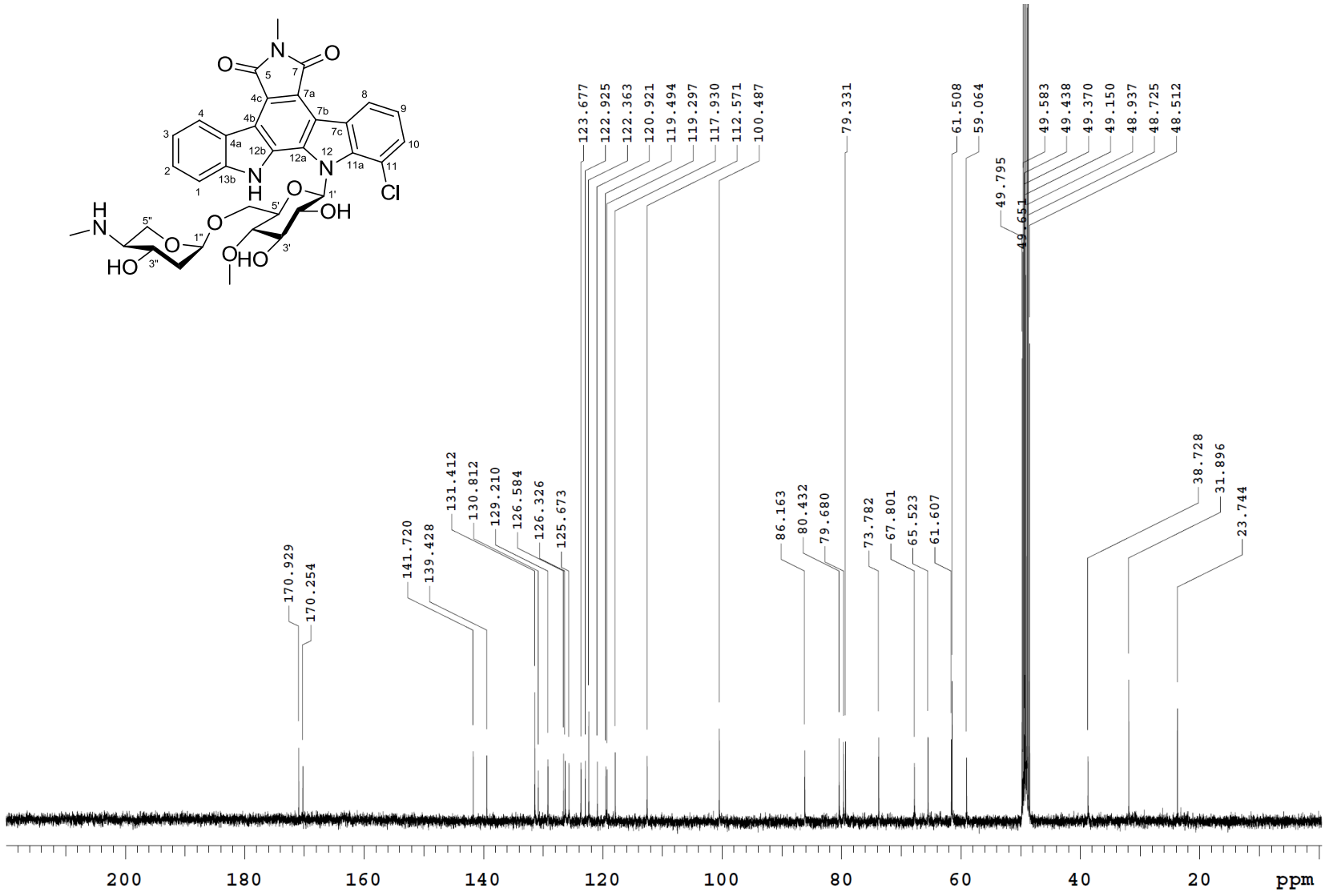

Figure S56: ^{13}C NMR spectrum (CD_3OD, 100 MHz) of AT2433-A1 (**6**)

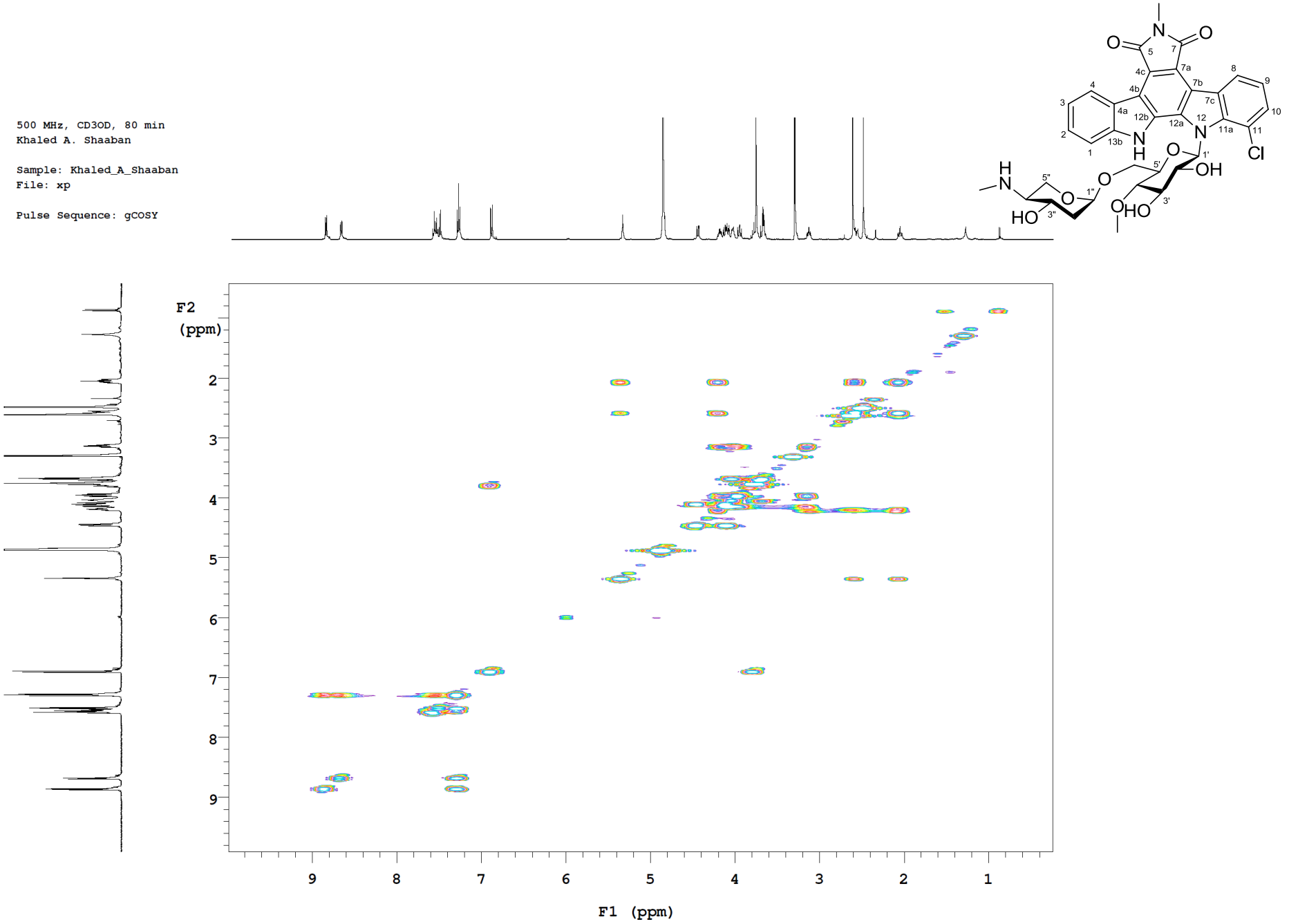

Figure S57: ^{1}H-^{1}H COSY spectrum (CD_3OD, 500 MHz) of AT2433-A1 (**6**)

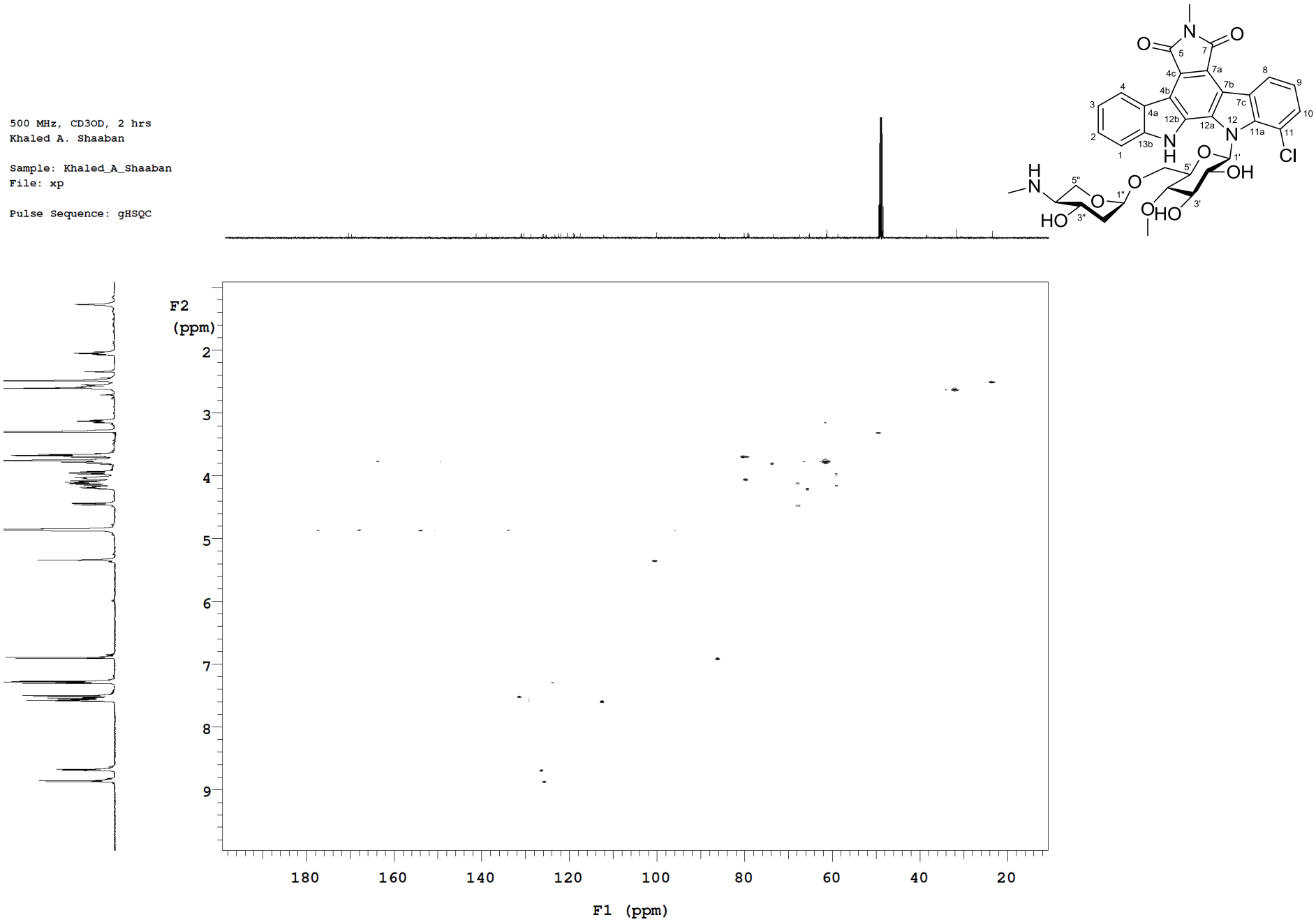

Figure S58: HSQC spectrum (CD_3OD, 500 MHz) of AT2433-A1 (**6**)

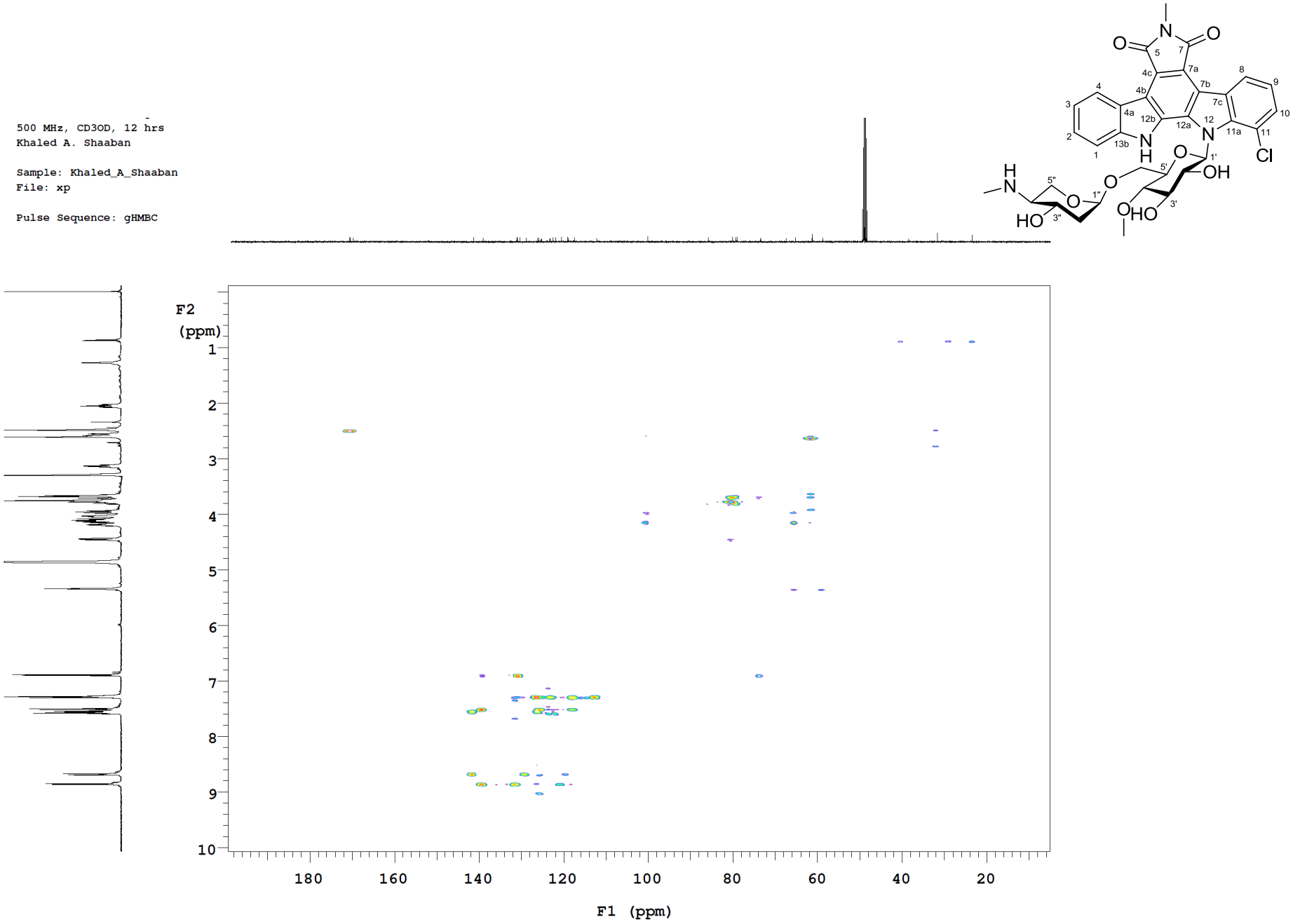

Figure S59: HMBC spectrum (CD_3OD, 500 MHz) of AT2433-A1 (**6**)

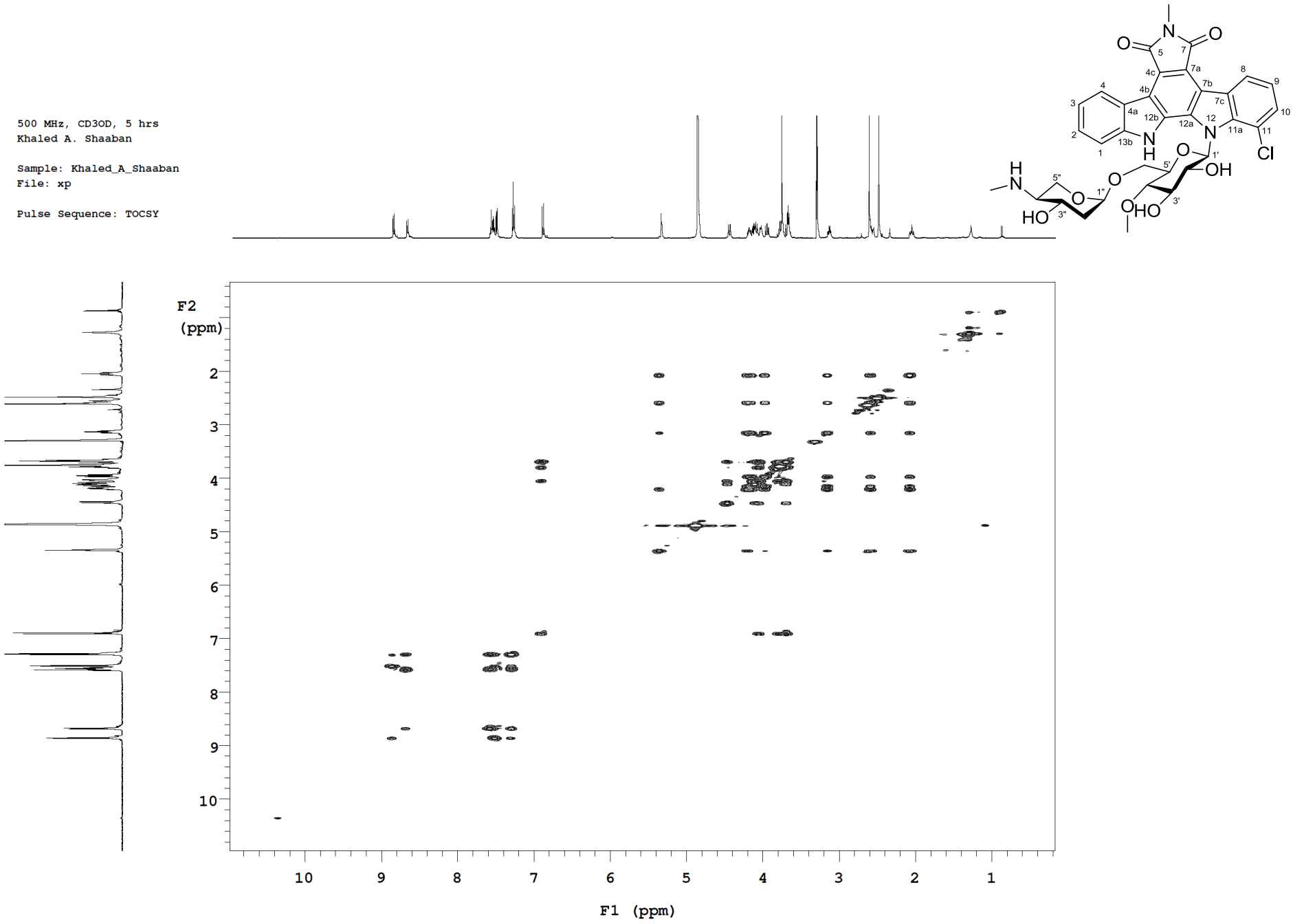

Figure S60: TOCSY spectrum (CD_3OD, 500 MHz) of AT2433-A1 (**6**)

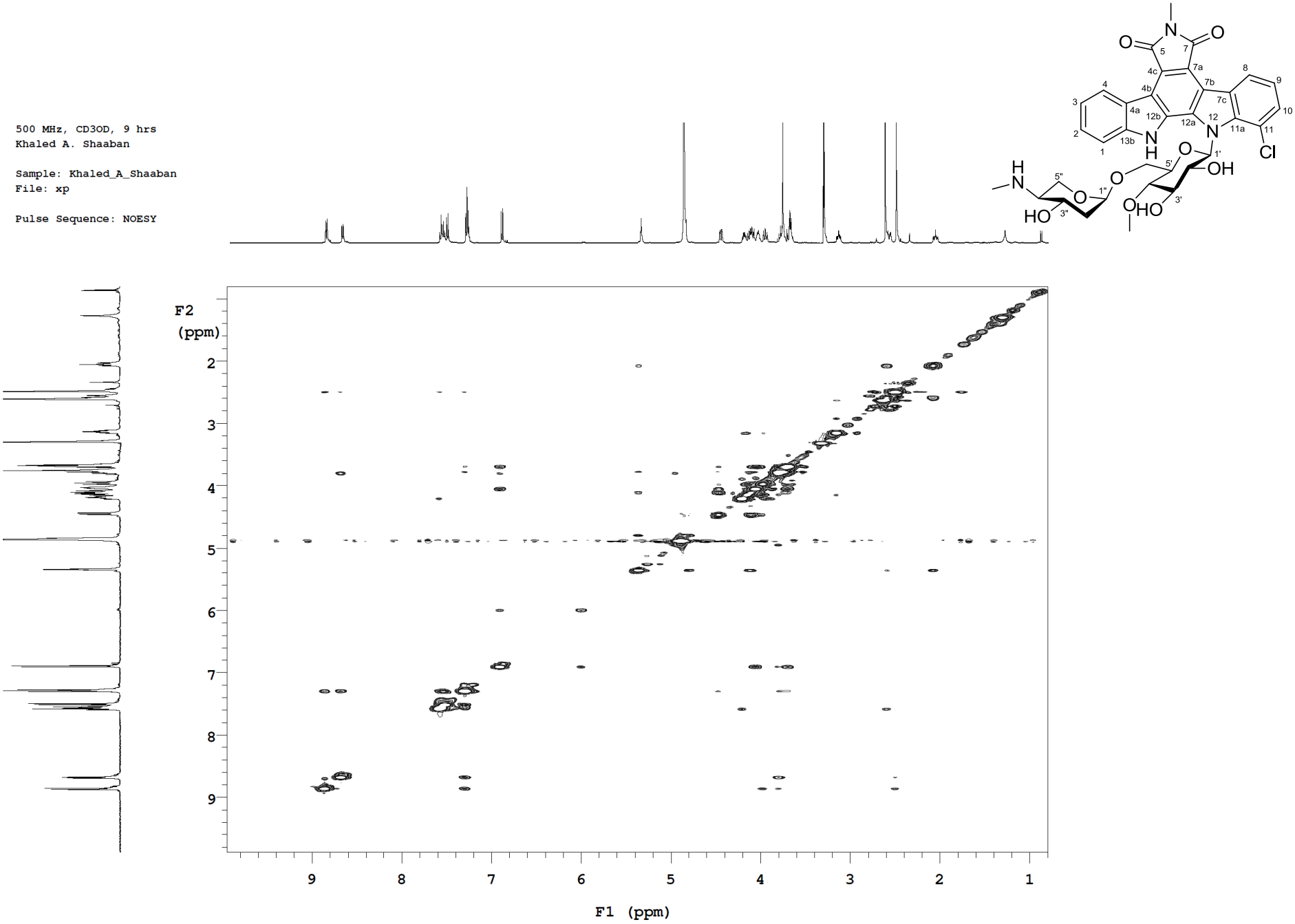

Figure S61: NOESY spectrum (CD_3OD, 500 MHz) of AT2433-A1 (**6**)

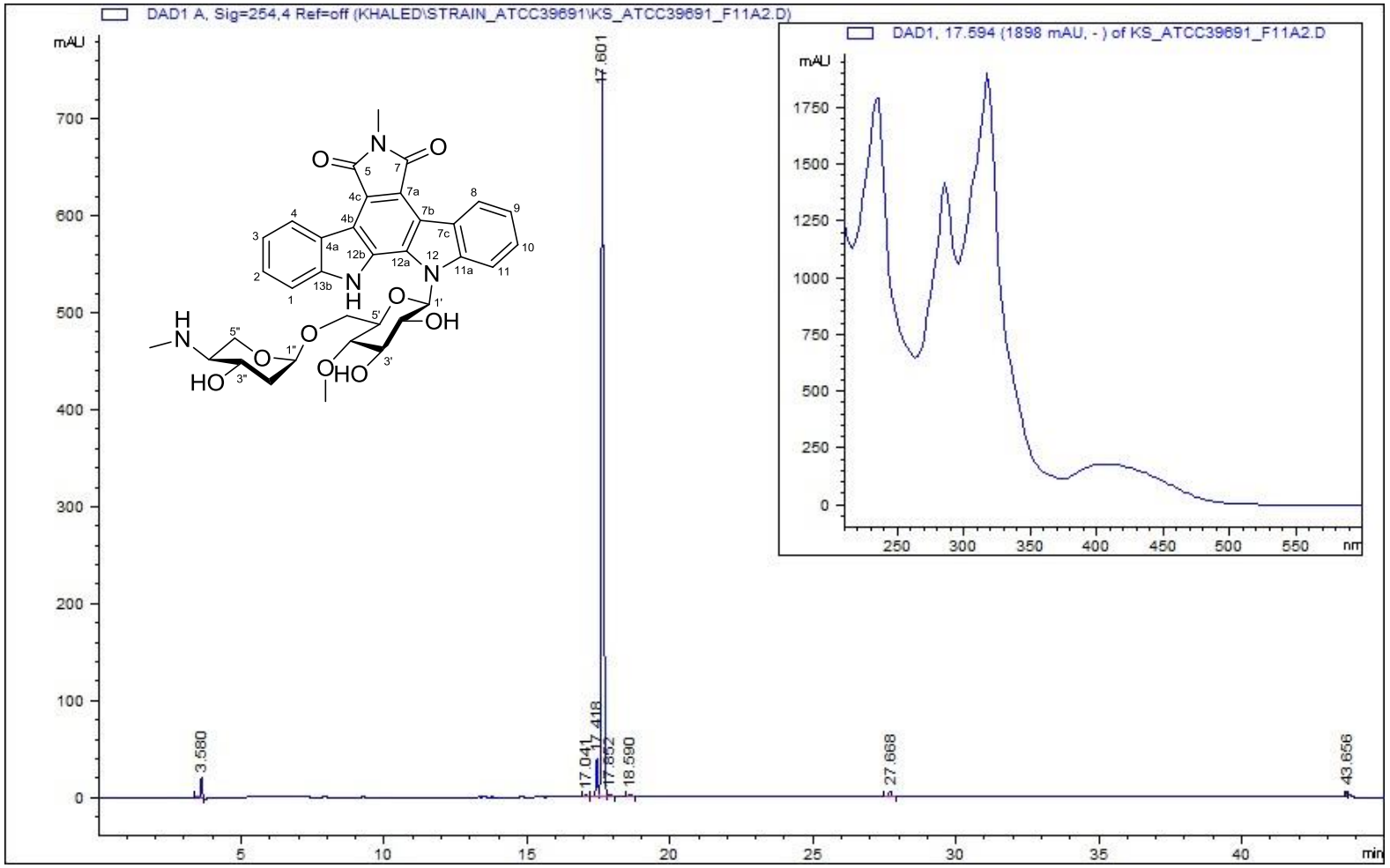

Figure S62: HPLC of AT2433-B1 (**7**). HPLC-conditions: Detection wavelength 254 nm; **solvent A:** H_2O/0.1% TFA; **solvent B:** CH_3CN; flow rate: 1.0 mL min^{-1}; 0-35 min, 5%-100% B; 35-40 min, 100% B; 40-41 min, 100%-5% B; 41-45 min, 5% B). UV-vis inset of full wavelength 190-600 nm.

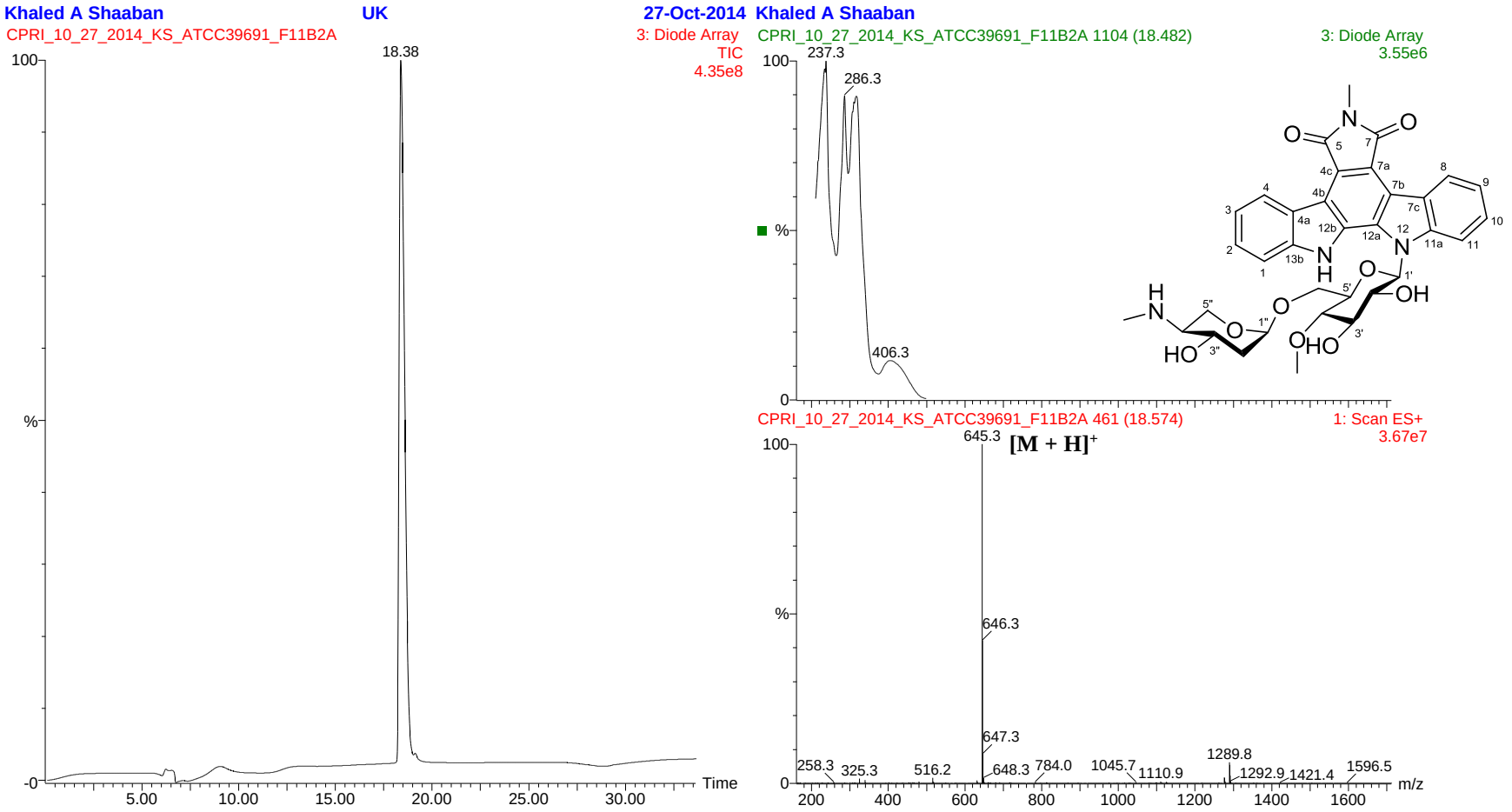

Figure S63: HPLC/UV/MS analyses of AT2433-B1 (**7**). Detection wavelength: 210-500; **solvent A:** H_2O/0.1% Formic acid; **solvent B:** CH_3CN/0.1% Formic acid; flow rate: 0.5 mL min^{-1}; 0-4 min, 10% B; 4-22 min, 10-100% B; 22-27 min, 100% B; 27-29 min, 100%-10% B; 29-35 min, 10 % B.

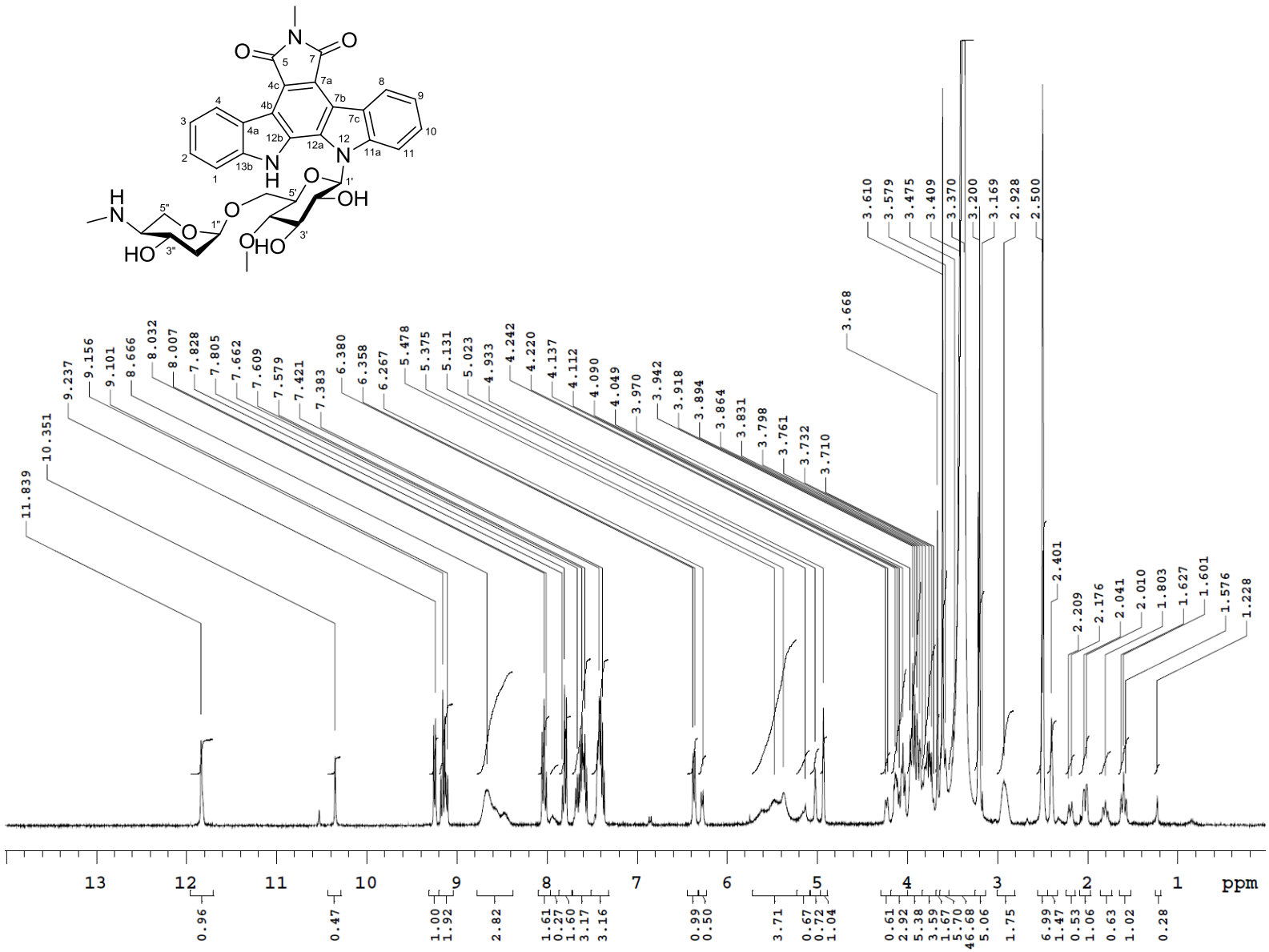

Figure S64: ^{1}H NMR spectrum (DMSO-d_6, 400 MHz) of AT2433-B1 (**7**)

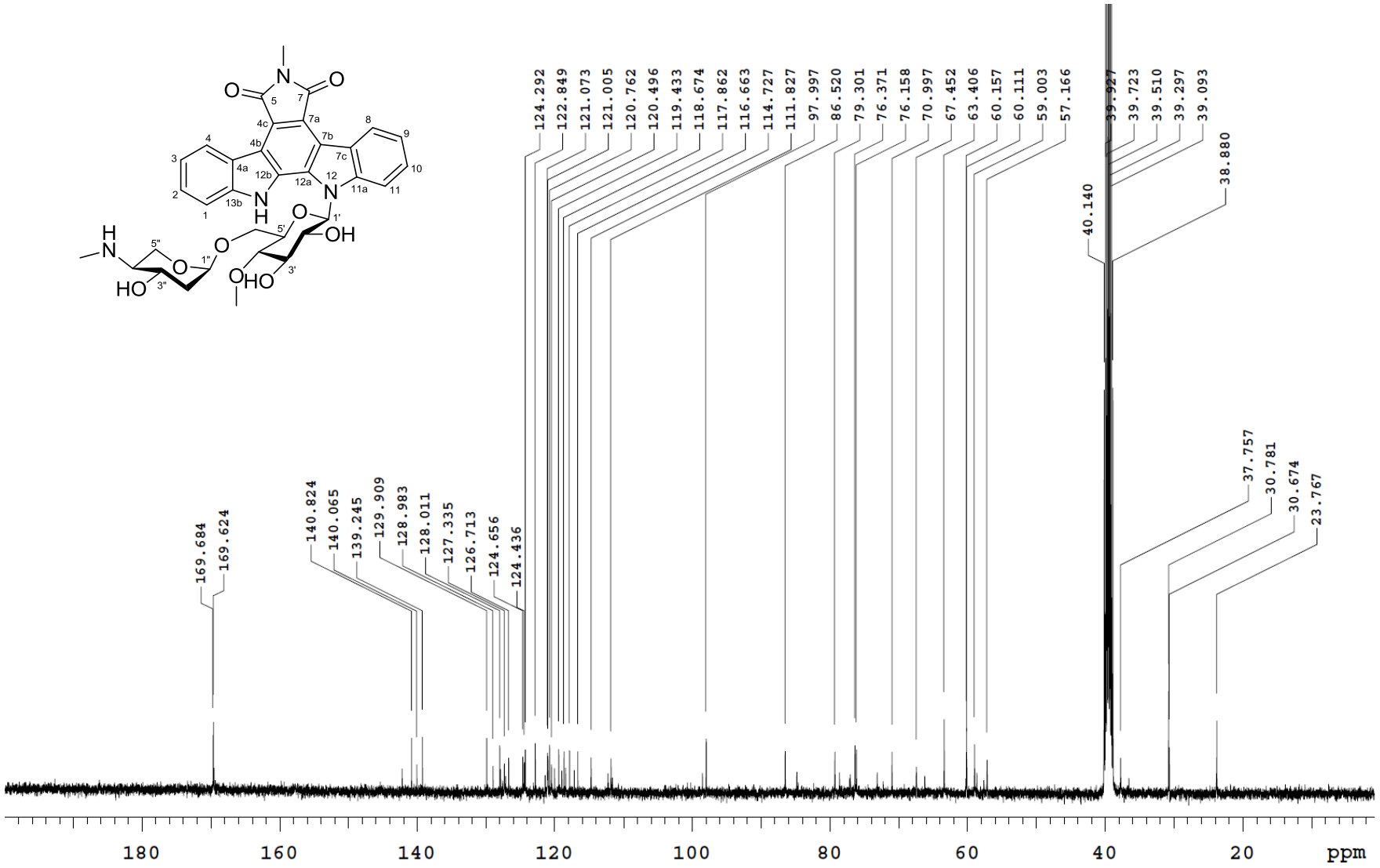

Figure S65: ^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of AT2433-B1 (**7**)

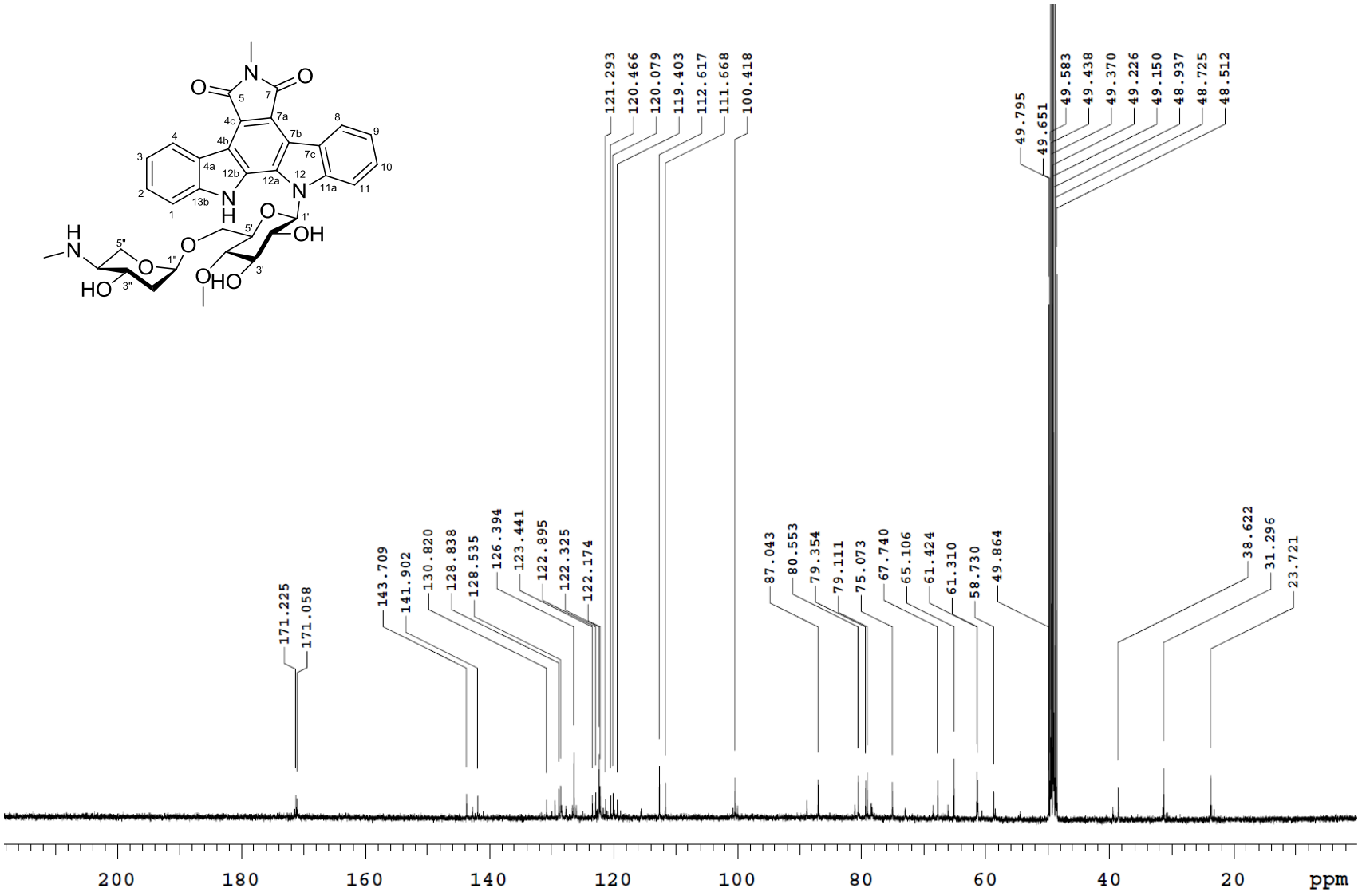

Figure S66: ^{13}C NMR spectrum (CD_3OD, 100 MHz) of AT2433-B1 (**7**)

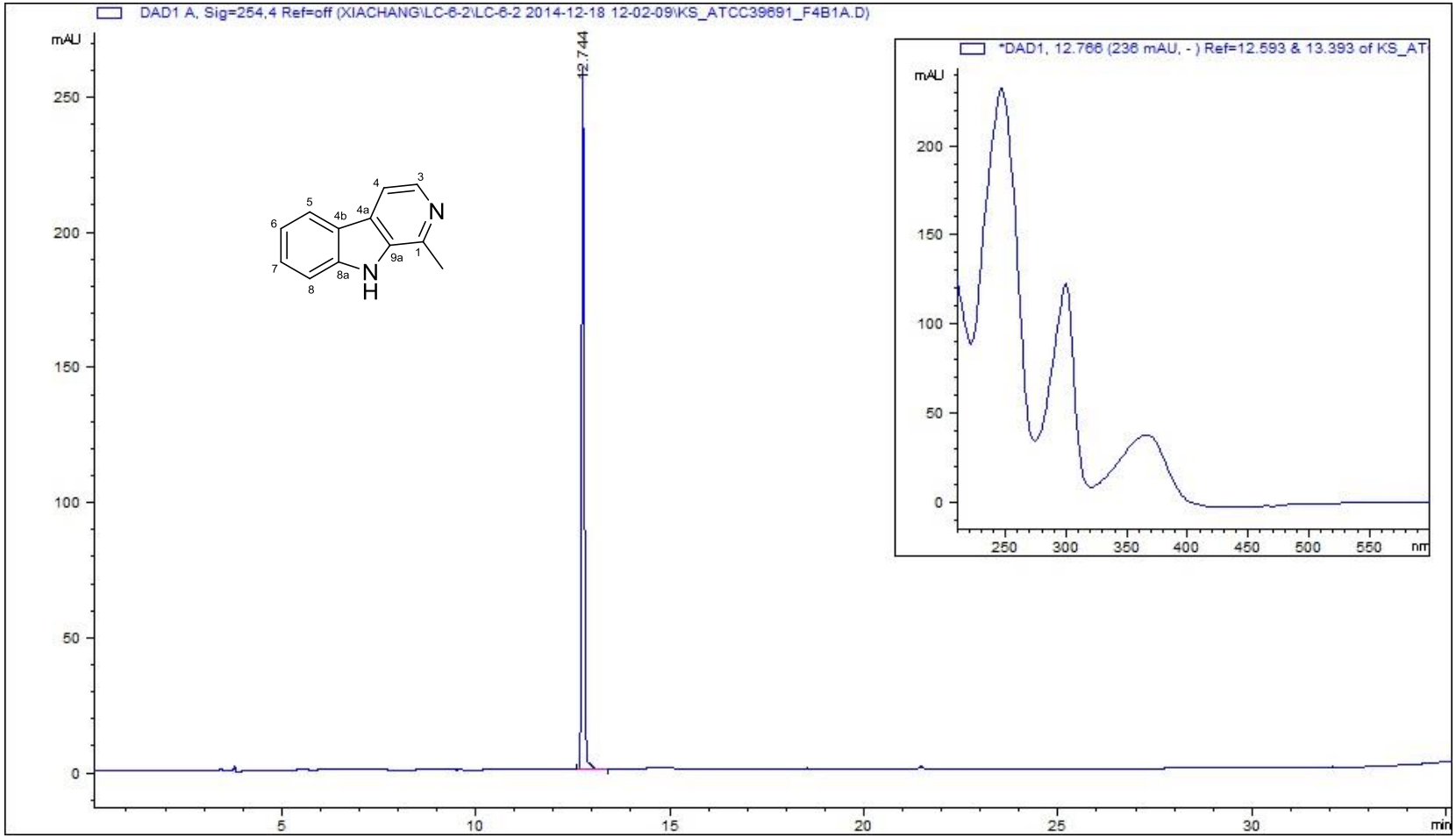

Figure S67: HPLC of harman "1-methyl-*β*-carboline" (**12**). HPLC-conditions: Detection wavelength 254 nm; **solvent A:** H_2O/0.1% TFA; **solvent B:** CH_3CN; flow rate: 0.5 mL min^{-1}; 0-4 min, 10% B; 4-22 min, 10-100% B; 22-27 min, 100% B; 27-29 min, 100%-10% B; 29-35 min, 10 % B. UV-vis inset of full wavelength 190-600 nm.

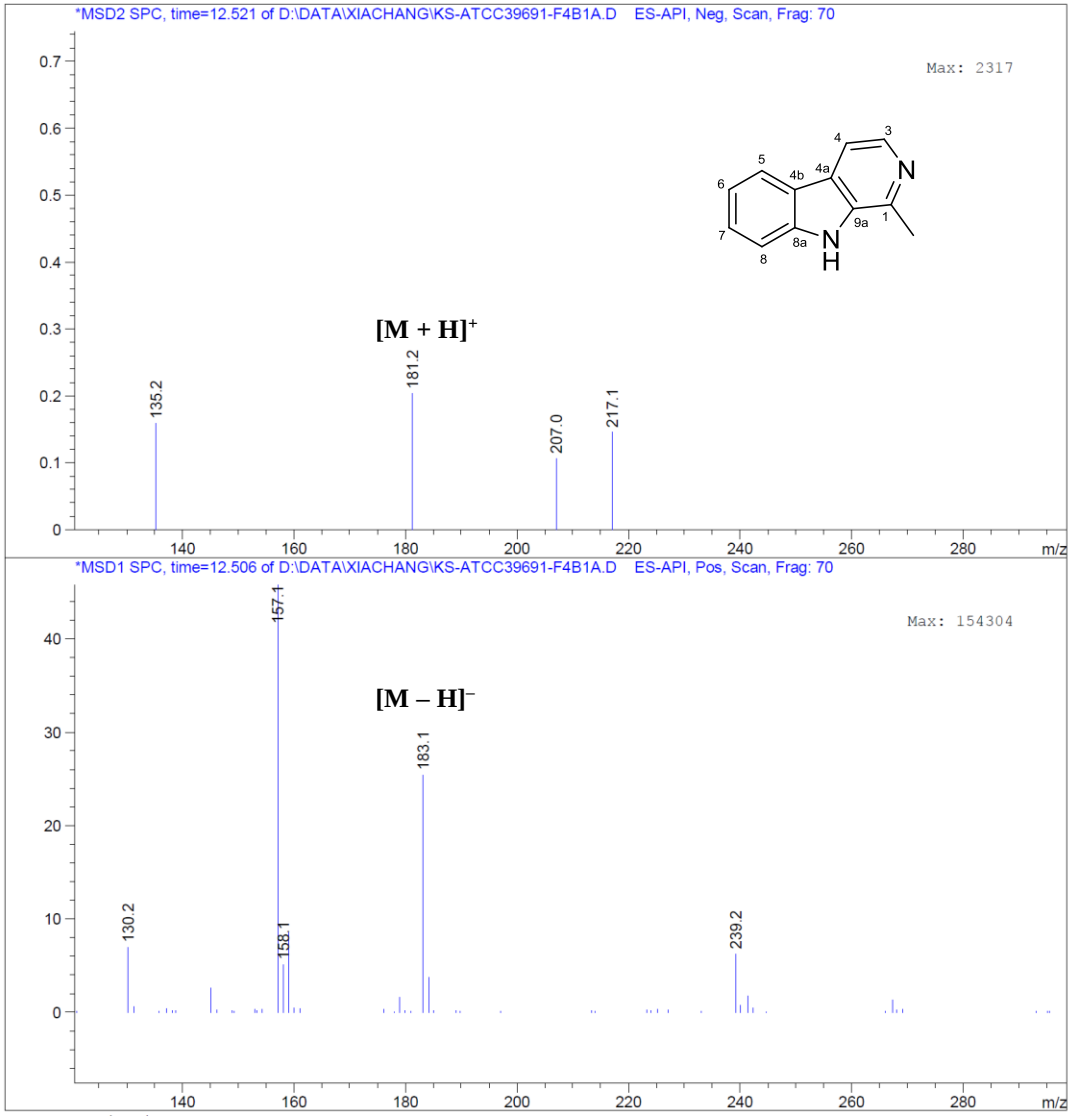

Figure S68: (+) and (–)-APCI-MS spectra of harman "1-methyl-*β*-carboline" (**12**)

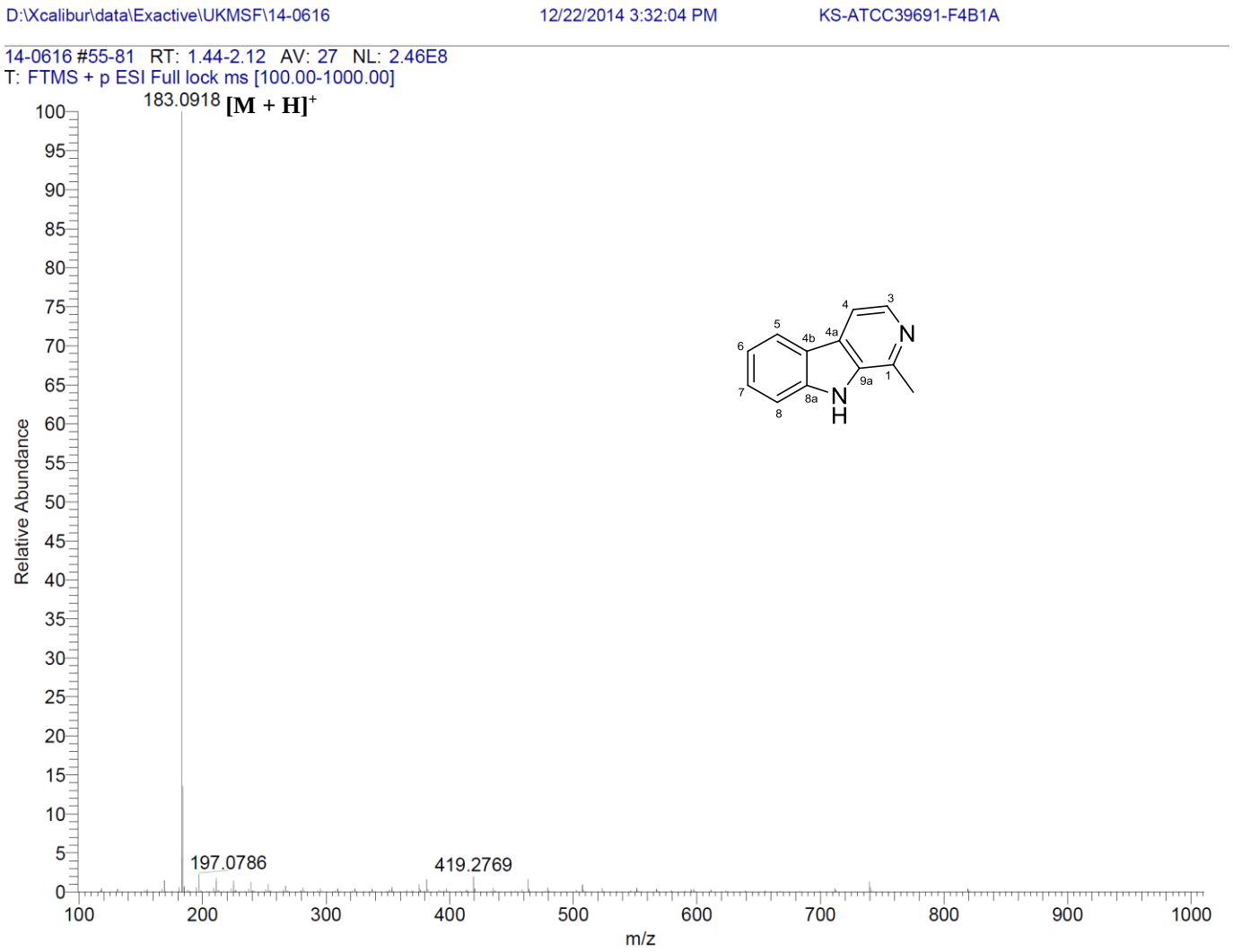

Figure S69: (+)-HRESI-MS spectrum of harman "1-methyl-*β*-carboline" (**12**)

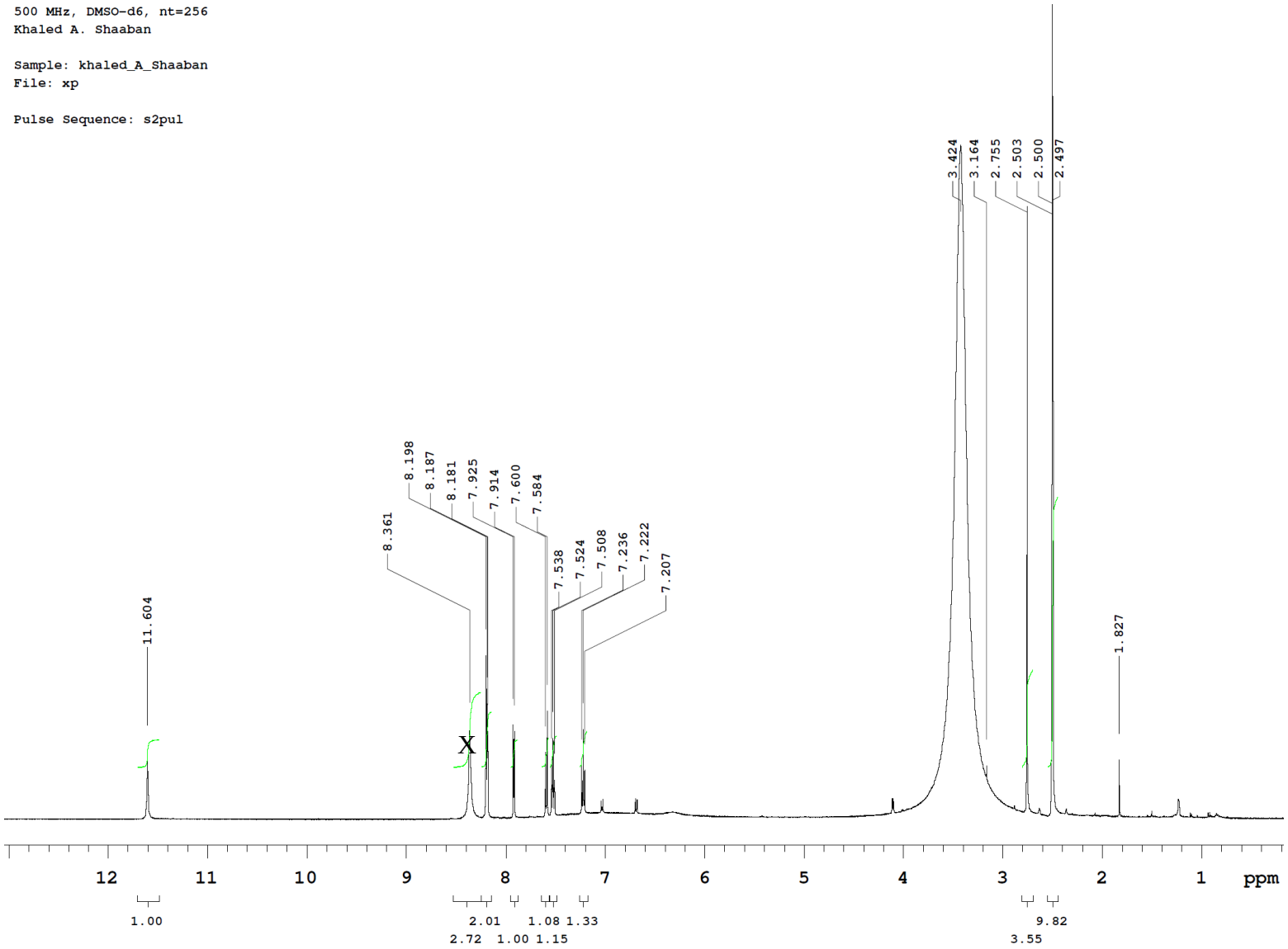

Figure S70: ^{1}H NMR spectrum (DMSO-d_6, 500 MHz) of harman "1-methyl-β-carboline" (**12**)

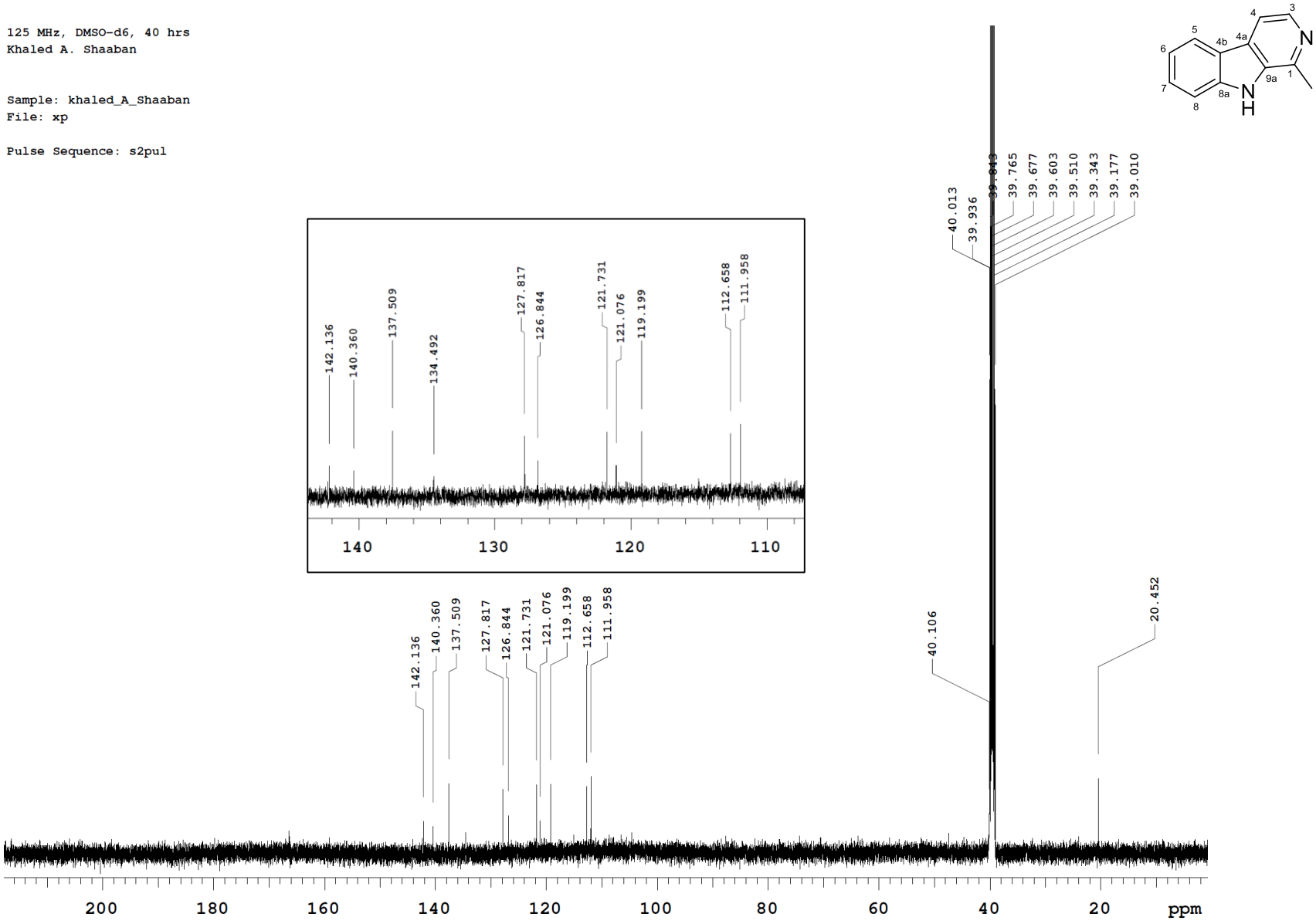

Figure S71: ^{13}C NMR spectrum (DMSO-d_6, 125 MHz) of harman "1-methyl-β-carboline" (**12**)

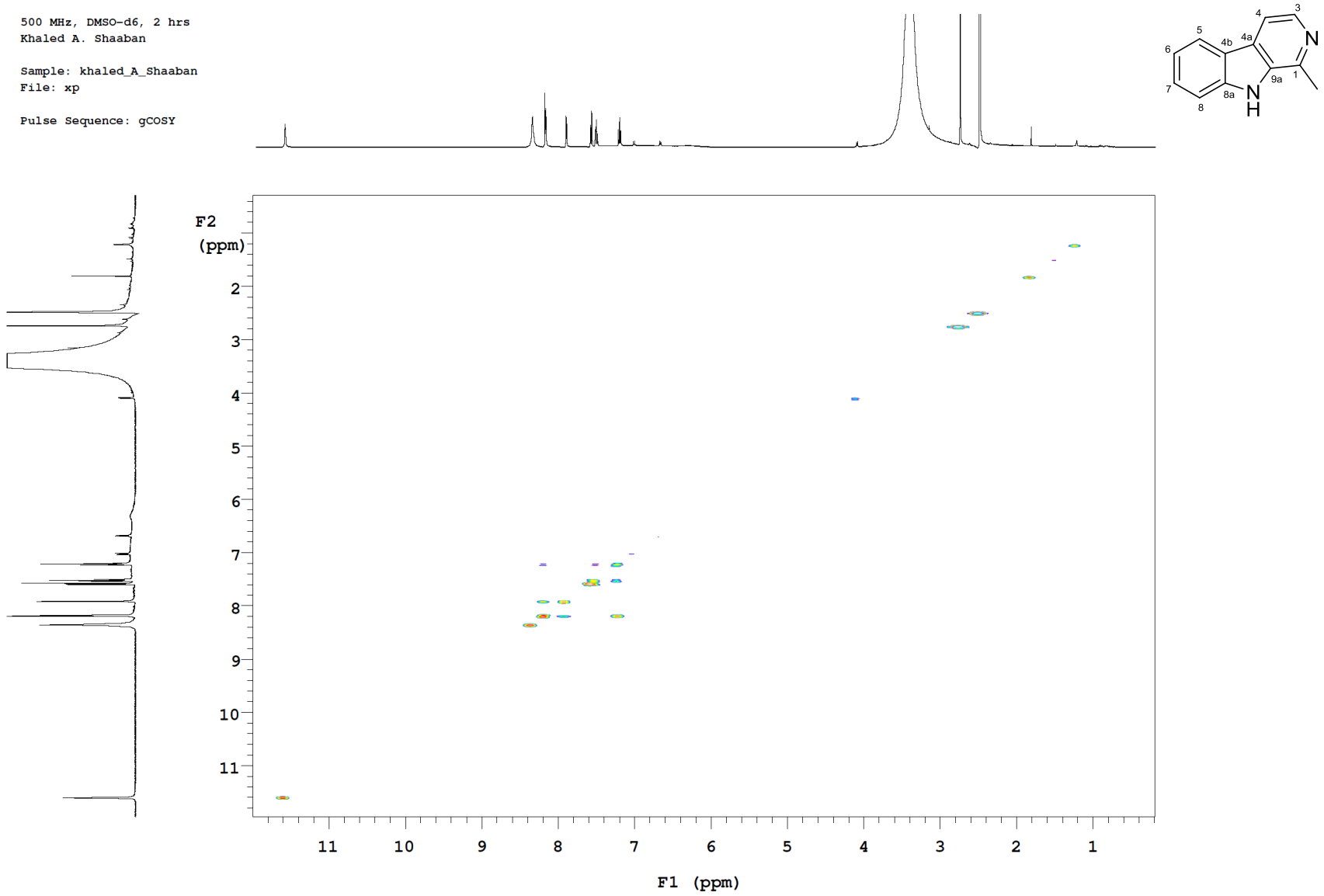

Figure S72: ^{1}H-^{1}H COSY spectrum (DMSO-d_6, 500 MHz) of harman "1-methyl-β-carboline" (**12**)

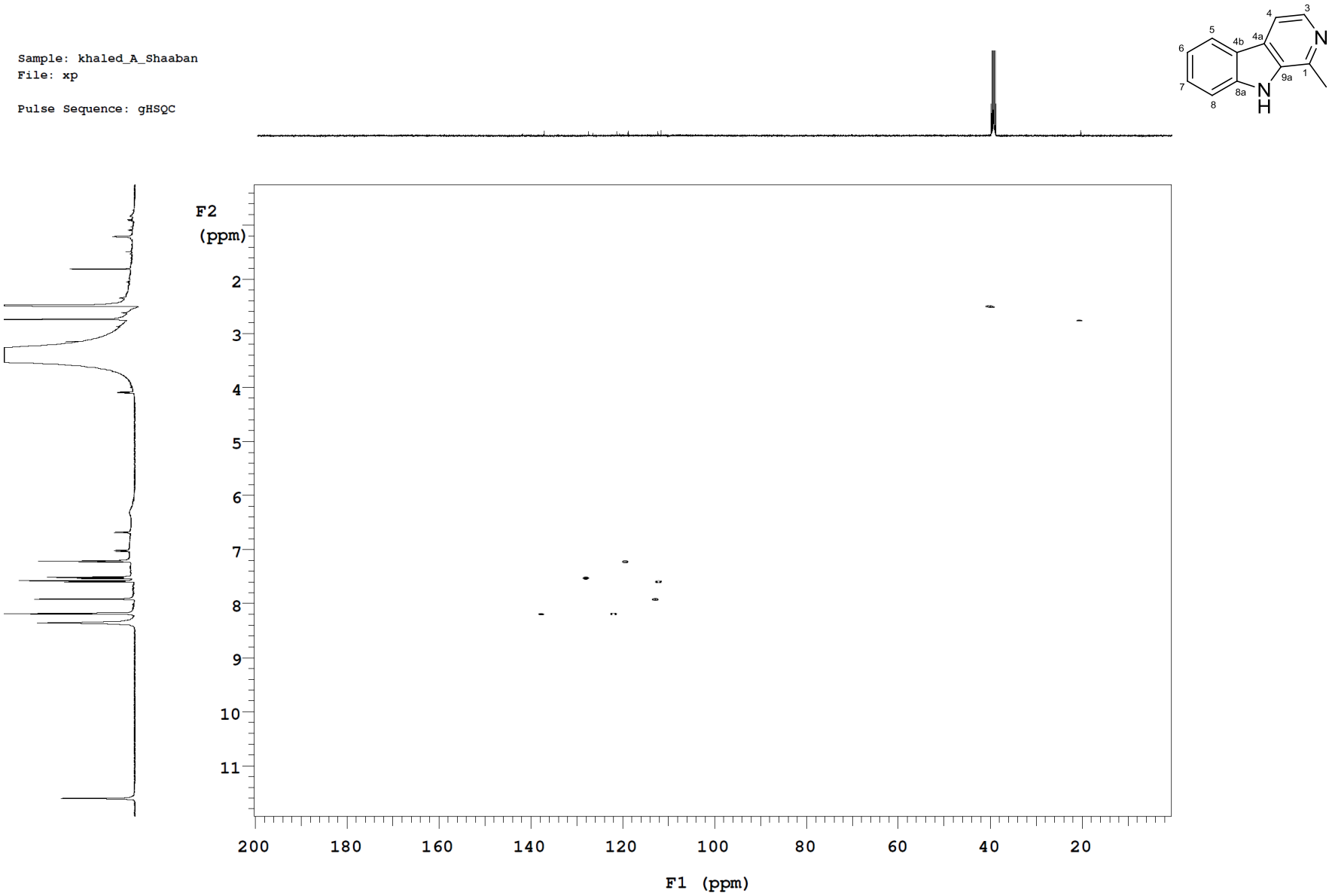

Figure S73: HSQC spectrum (DMSO-d_6, 500 MHz) of harman "1-methyl-β-carboline" (**12**)

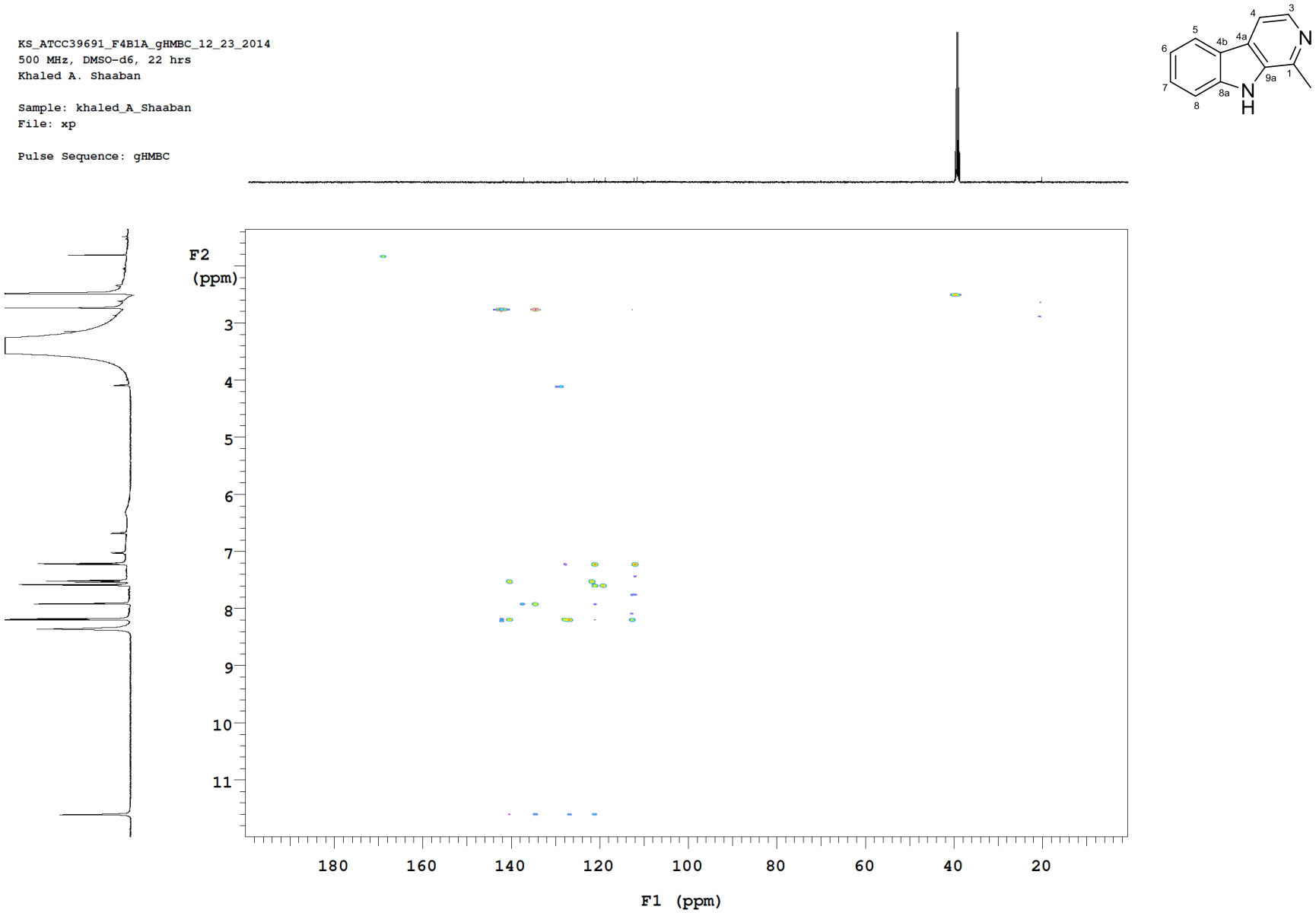

Figure S74: HMBC spectrum (DMSO-d_6, 500 MHz) of harman "1-methyl-β-carboline" (**12**)

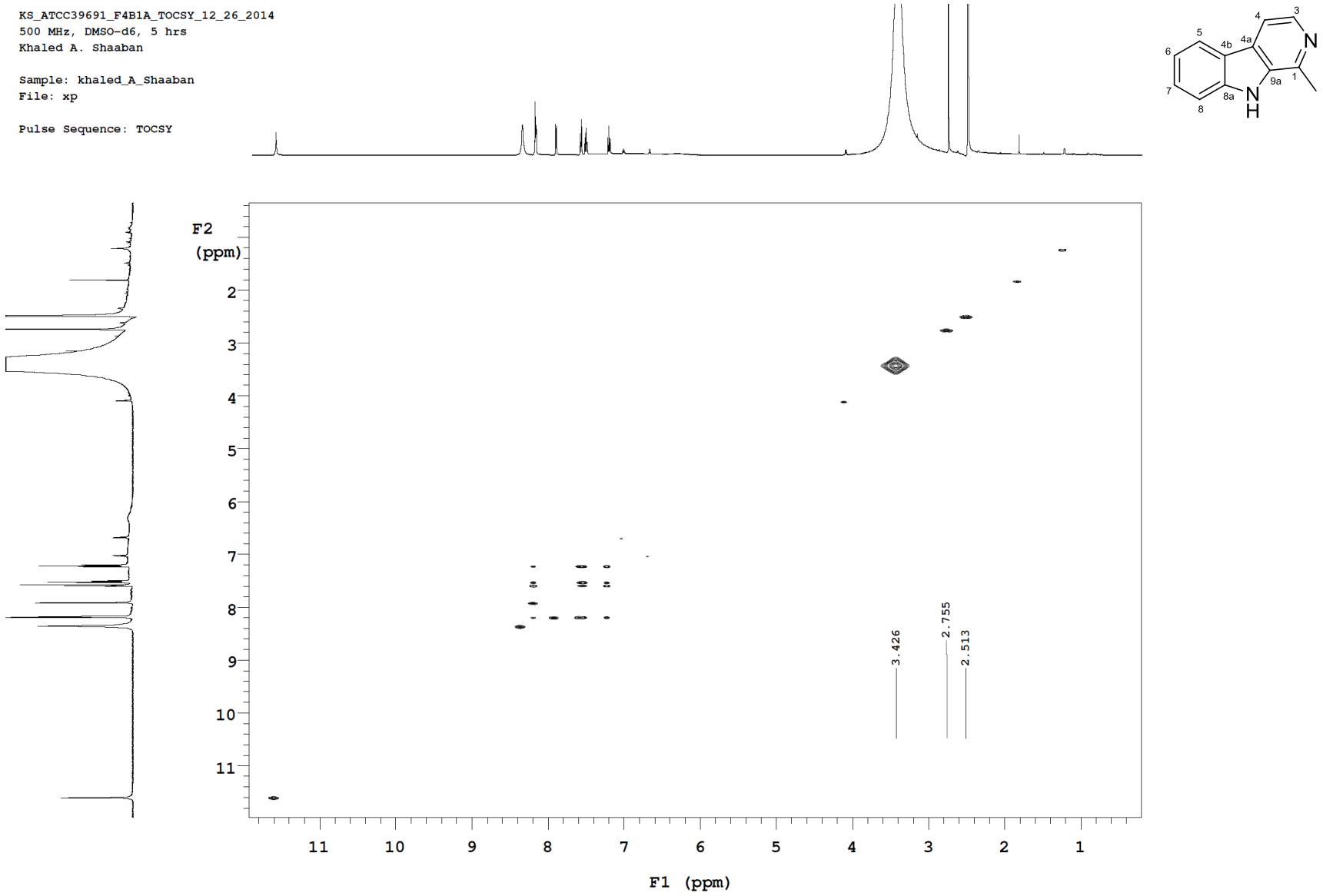

Figure S75: TOCSY spectrum (DMSO-d_6, 500 MHz) of harman "1-methyl-β-carboline" (**12**)

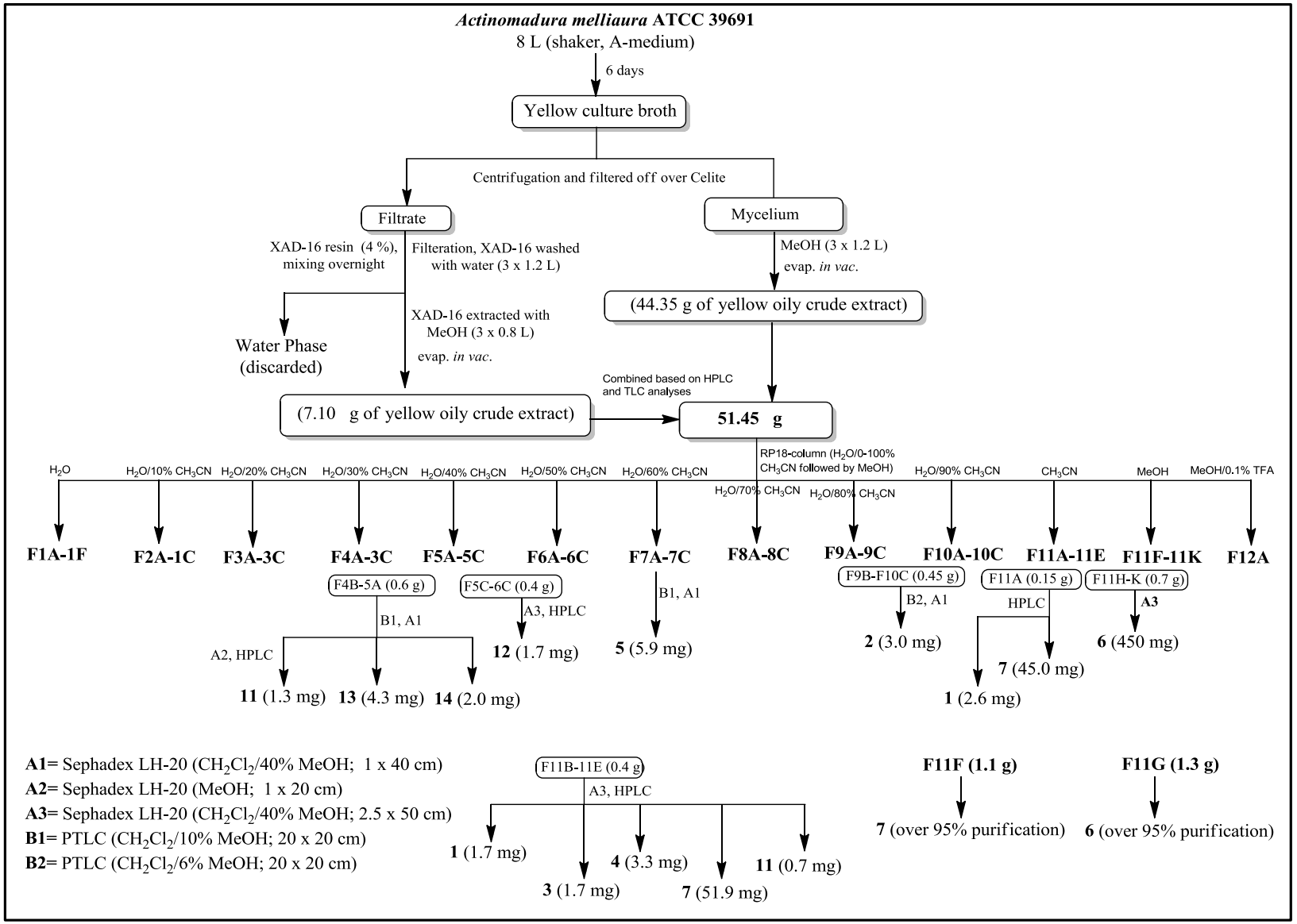

Figure S76. Isolation scheme of *Actinomadura melliaura* ATCC 39691 metabolites.

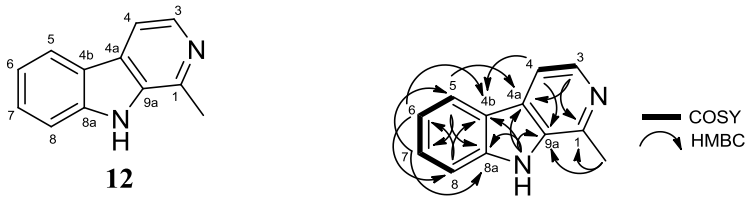

Figure S77. Chemical structure, ^{1}H–^{1}H-COSY and selected HMBC correlations in harman (**12**)

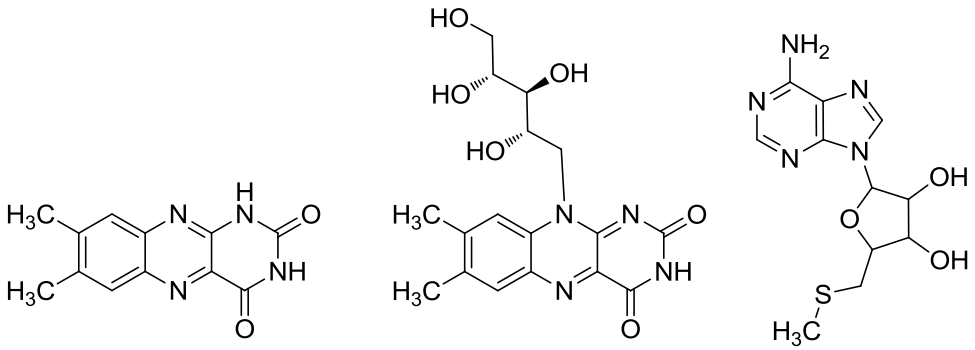

Figure S78: Chemical structures of lumichrome (**13**), riboflavin (**14**) and 5'-methyl-thioadenosine (**15**)

Table S1. Cytotoxic activities of compounds **1**-**7** at 10 µM (average of three independent replicates); see Figure 4.

Compounds	PC3		A549		U118	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**
Veh. Control	100.0	10.3	100.0	23.6	100.0	23.7
1	39.0	0.6	19.9	1.4	31.3	1.6
2	69.0	5.6	47.4	4.6	40.5	0.7
3	154.9	13.7	164.0	27.3	186.1	9.6
4	98.3	5.2	96.6	11.3	61.0	8.4
5	47.7	1.2	32.6	3.5	53.6	5.9
6	27.0	0.8	10.5	0.5	20.8	0.7
7	36.4	1.3	16.6	0.7	29.4	1.2

SD= Standard deviation, Vehicle control= 1% DMSO and media

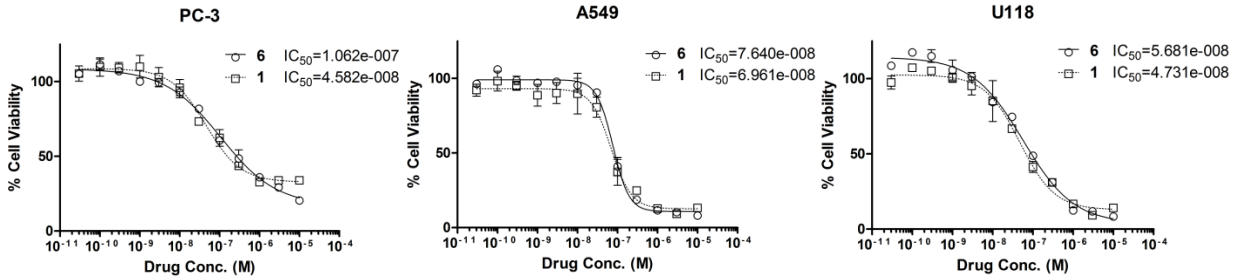

Figure S79. Dose–response curve of AT2433-A3 (**1**) and AT2433-A1 (**6**) in PC3 (Prostate), A549 (lung) and U118 (brain) human cancer cell lines at 72h; see Table 3.

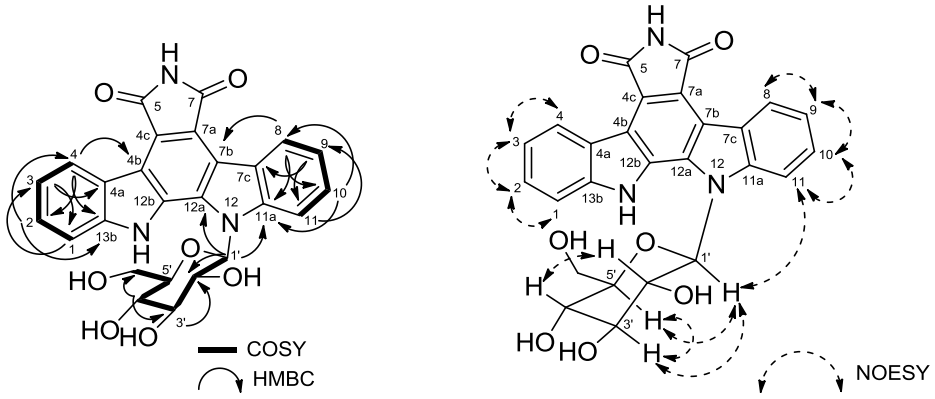

Figure S80. Selected $^{1}H–^{1}H$-COSY, HMBC and NOESY correlations in BMY-41219 (**5**)

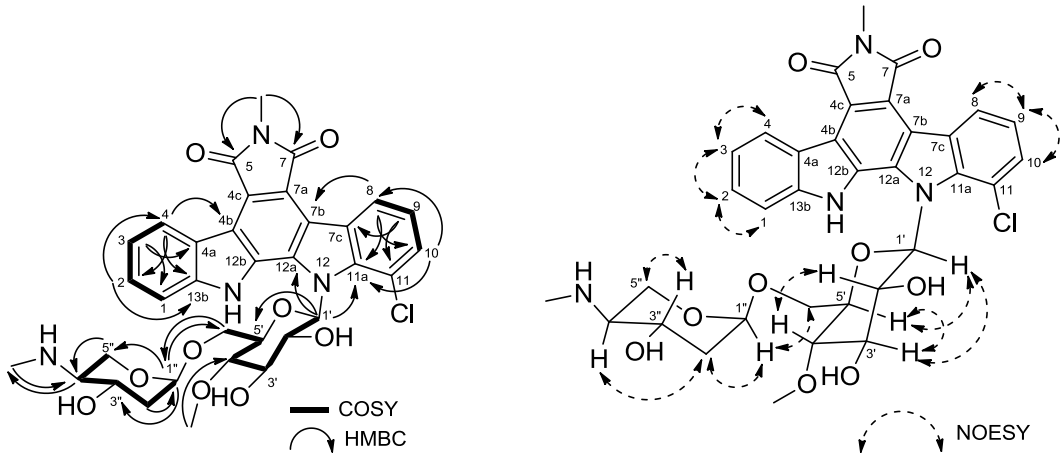

Figure S81. Selected $^{1}H–^{1}H$-COSY, HMBC and NOESY correlations in AT2433-A1 (**6**)

Table S2. ^{13}C (100 MHz) and ^{1}H NMR data of compounds **5**-**7**

Position	BMY-41219 **(5)** [a,b]		AT2433-A1 **(6)** [a,b]		AT2433-B1 (**7**) [a]		
	δ_C, type	δ_H [c], m (*J* in Hz)	δ_C, type	δ_H [c], m (*J* in Hz)	δ_C, type [d]	δ_C, type [b]	δ_H [d,e], m (*J* in Hz)
1	113.0, CH	7.66, dd (8.0, 1.0)	112.6, CH	7.58, d (8.0)	112.3, CH	112.6, CH	7.81, d (8.4)
2	128.2, CH	7.47, td (7.0, 1.0)	129.2, CH	7.55, td (7.0, 1.5)	127.9, CH	128.5, CH	7.67, t (7.6)
3	121.5, CH	7.24, td (7.0, 1.0)	122.4, CH	7.29, t (8.0)	121.4, CH	121.3, CH	7.42, t (7.6)
4	126.2, CH	9.00, dd (7.0, 1.0)	126.3, CH	8.68, d (8.0)	126.7, CH	126.4, CH	9.25, d (8.4)
4a	123.5, C	-	122.9, C	-	122.8, C	122.9, C	-
4b	119.5, C	-	119.5, C	-	119.4, C	119.1, C	-
4c	120.8, C	-	119.3, C	-	119.0, C	120.1, C	-
5	172.7, C	-	170.3, C	-	169.6, C	171.1, C	-
6-$\underline{CH_3}$	-	-	23.7, CH_3	2.50, s	23.8, CH_3	23.7, CH_3	3.20, s
7	172.8, C	-	170.9, C	-	169.7, C	171.2, C	-
7a	122.8, C	-	122.4, C	-	120.8, C	120.5, C	-
7b	120.8, C	-	120.9, C	-	120.8, C	119.4, C	-
7c	123.4, C	-	126.6, C	-	124.7, C	123.4, C	-
8	126.4, CH	9.13, dd (7.5, 0.5)	125.7, CH	8.87, dd (8.0, 1.0)	124.4, CH	126.4, CH	9.16, d (8.8)
9	122.0, CH	7.29, td (8.0, 1.0)	123.7, CH	7.29, t (7.5)	124.3, CH	122.3, CH	7.42, t (7.6)
10	128.2, CH	7.52, td (7.0, 1.5)	131.4, CH	7.51, dd (7.5, 1.0)	128.0, CH	128.8, CH	7.67, t (7.6)
11	112.0, C	7.78, d (9.0)	117.9, C	-	111.8, CH	111.7, CH	8.05, d (8.8)
11a	143.9, C	-	139.4, C	-	139.2, C	143.7, C	-
12	-	-	-	-	-	-	-
12a	130.0, C	-	130.8, C	-	129.0, C	129.5, C	-
12b	131.7, C	-	131.4, C	-	129.9, C	130.8, C	-
13	-	-	-	-	-	-	11.83, brs
13a	142.9, C	-	141.7, C	-	140.8, C	141.9, C	-
1'	86.6, CH	6.19, d (9.0)	86.2, CH	6.90, d (9.5)	86.5, CH	87.0, CH	6.38, d (8.8)
2'	74.9, CH	3.85, t (9.0)	73.8, CH	3.79, m	71.0, CH	75.1, CH	3.41, m
2'-OH						-	5.47-5.37, brs
3'	78.7, CH	3.76, t (9.5)	79.3, CH	3.69, m	76.2, CH	79.1, CH	3.50, m
3'-OH					-	-	5.28, d (6.5)
4'	69.5, CH	4.27, t (9.5)	80.4, CH	3.69, m	79.3, CH	80.6, CH	3.67, m
4'-O$\underline{CH_3}$	-	-	61.5, CH_3	3.77, s	59.0, CH_3	61.4, CH_3	3.63, s
5'	80.7, CH	4.00, dd (9.5, 2.0)	79.7, CH	4.05, m	76.4, CH	79.4, CH	3.94, m
6'	60.2, CH_2	4.26, d (9.0), 4.06, dd (11.5, 2.5)	67.8, CH_2	4.46, dd (11.5, 2.0), 4.12, dd (11.5, 3.5)	67.5, CH_2	67.7, CH_2	3.97, m
6'-OH	-	-	-	-	-	-	-
1"	-	-	100.4, CH	5.35, t (3.0)	100.0, CH	100.4, CH	4.93, brs
2"	-	-	38.7, CH_2	2.60 - 2.56, m 2.06, m	37.8, CH_2	38.6, CH_2	2.04, m 1.60, m
3"	-	-	65.5, CH	4.20, m	63.4, CH	65.1, CH	4.15, m
4"	-	-	61.6, CH	3.13, m	60.2, CH	61.3, CH	2.93, m
4"-NH$\underline{CH_3}$	-	-	31.9, CH_3	2.62, s	30.8, CH_3	31.3, CH_3	2.22, s
5"	-	-	59.1, CH_2	4.14, dd (11.0, 4.0) 3.96, dd (11.5, 9.5)	57.2, CH_2	58.7, CH_2	4.06, m 3.92, m

Assignments supported by 2D HSQC and HMBC experiments

[a] See supporting information for the NMR spectra; [b] CD_3OD; [c] 500 MHz; [d] DMSO-d_6; [e] 400 MHz

Physico-chemical properties of compounds 5-7 and harman (12)

*BMY-41219 (**5**)*: yellow solid; UV/vis (MeOH) λ_{max} 227, 285, 316, 408 nm; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 100 MHz), see Table S2; (+)-APCI-MS: *m/z* 488 $[M + H]^+$; (+)-HR-ESI-MS: *m/z* 488.1451 $[M + H]^+$ (calcd for $C_{26}H_{22}N_3O_7$, 488.1452); (–)-HR-ESI-MS: *m/z* 486.1294 $[M – H]^–$ (calcd for $C_{26}H_{20}N_3O_7$, 486.1295).

*AT2433-A1 (**6**)*: yellow solid; UV/vis (MeOH) λ_{max} (log ε) 237 (4.18), 289 (4.11), 318 (4.23), 400 (3.16) nm; ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 100 MHz), see Table S2; (+)-APCI-MS: *m/z* 679 $[M + H]^+$.

*AT2433-B1 (**7**)*: yellow solid; UV/vis (MeOH) λ_{max} 237, 286, 319, 406 nm; ^{1}H NMR (DMSO-d_6, 400 MHz) and ^{13}C NMR (DMSO-d_6, 100 MHz), (CD_3OD, 100 MHz), see Table S2; (+)-APCI-MS: *m/z* 645 $[M + H]^+$.

*Harman (1-Methyl-β-carboline, **12**)*: white powder; blue UV-absorbing (254 nm), fluorescence (365 nm); pale-yellow with anisaldehyde/H_2SO_4 spraying reagent; R_f 0.38 (silica gel, 10% MeOH-CH_2Cl_2); UV λ_{max} 238, 295, 368 nm; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 11.60 (brs, 1H, NH), 8.20 (d, *J* = 5.5 Hz, 1H, H-3), 8.19 (d, *J* = 8.5 Hz, 1H, H-5), 7.92 (d, *J* = 5.5 Hz, 1H, H-4), 7.59 (d, *J* = 8.0 Hz, 1H, H-8), 7.52 (t, *J* = 7.0 Hz, 1H, H-7), 7.22 (t, *J* = 7.0 Hz, 1H, H-6), 2.76 (s, 3H, 1-CH_3); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 142.1 (Cq-1), 140.4 (Cq-8a), 137.5 (CH-3), 134.5 (Cq-9a), 127.8 (CH-7), 126.8 (Cq-4a), 121.7 (CH-5), 121.1 (Cq-4b), 119.2 (CH-6), 112.7 (CH-4), 112.0 (CH-8), 20.5 (1-CH_3); (+)-APCI-MS: *m/z* 183 $[M + H]^+$; (–)-APCI-MS: *m/z* 181 $[M – H]^–$; (+)-HR-ESI-MS: *m/z* 183.0918 $[M + H]^+$ (calcd for $C_{12}H_{11}N_2$, 183.0917); (–)-HR-ESI-MS: *m/z* 181.0771 $[M – H]^–$ (calcd for $C_{12}H_9N_2$, 181.0771). See figure S77, for COSY and HMBC correlations.