Organometallic ciprofloxacin conjugates with dual action: synthesis, characterization, and antimicrobial and cytotoxicity studies

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Supplementary Information

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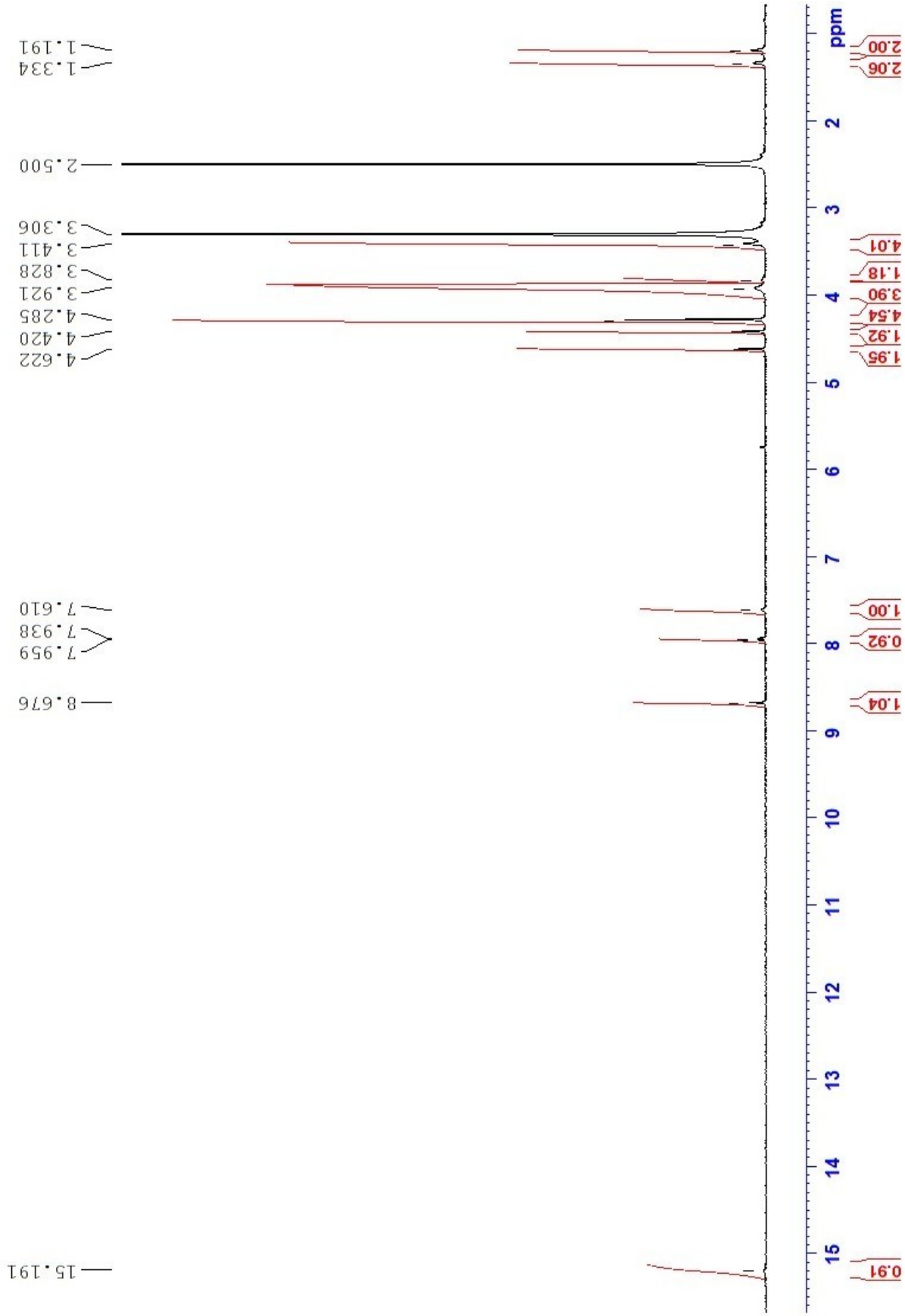

Fig. S1 ^{1}H NMR of compound **1**(600 MHz, DMSO-d_6)

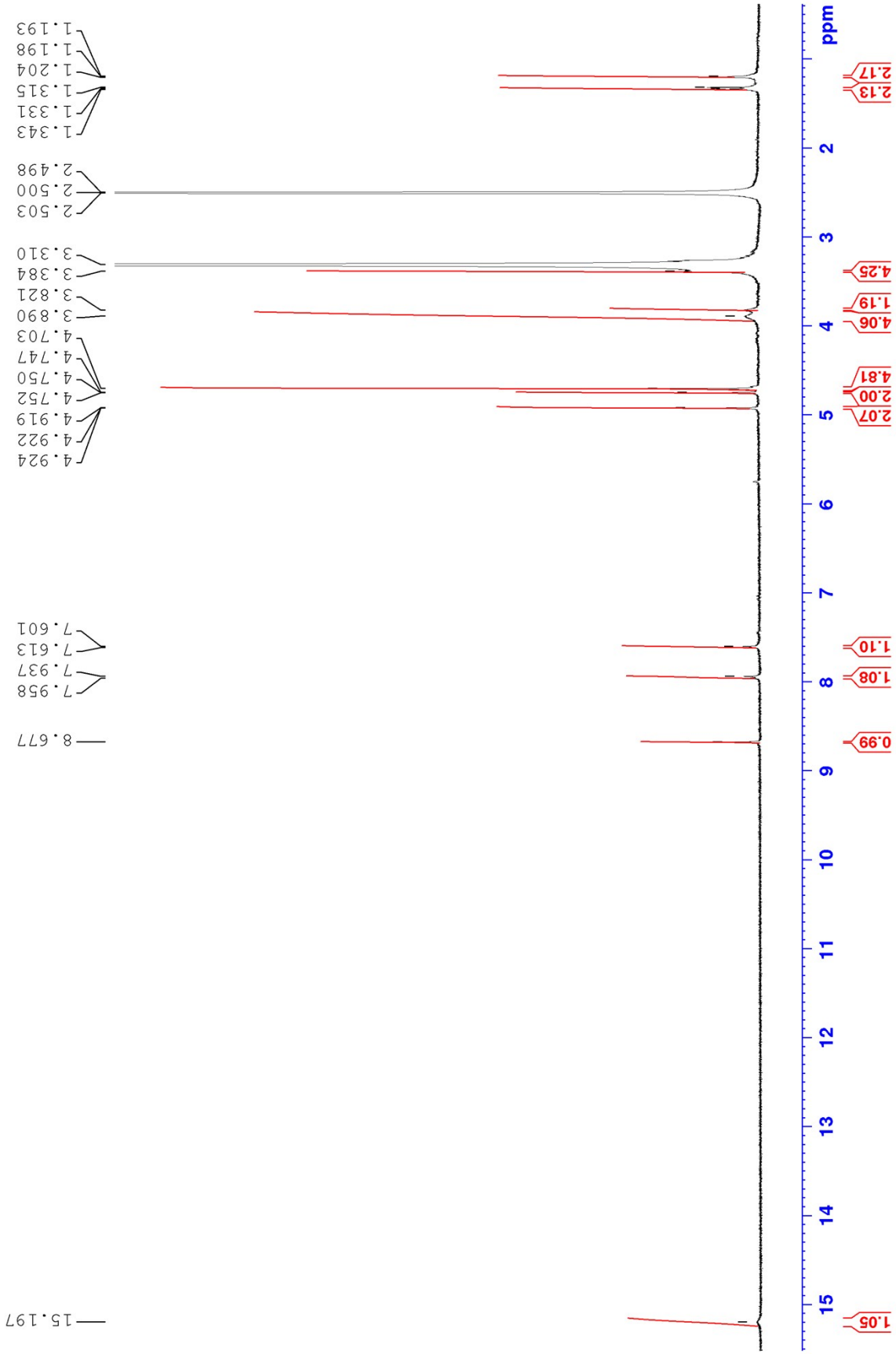

Fig. S2 ^{1}H NMR of compound **2** (600 MHz, DMSO-d_6)

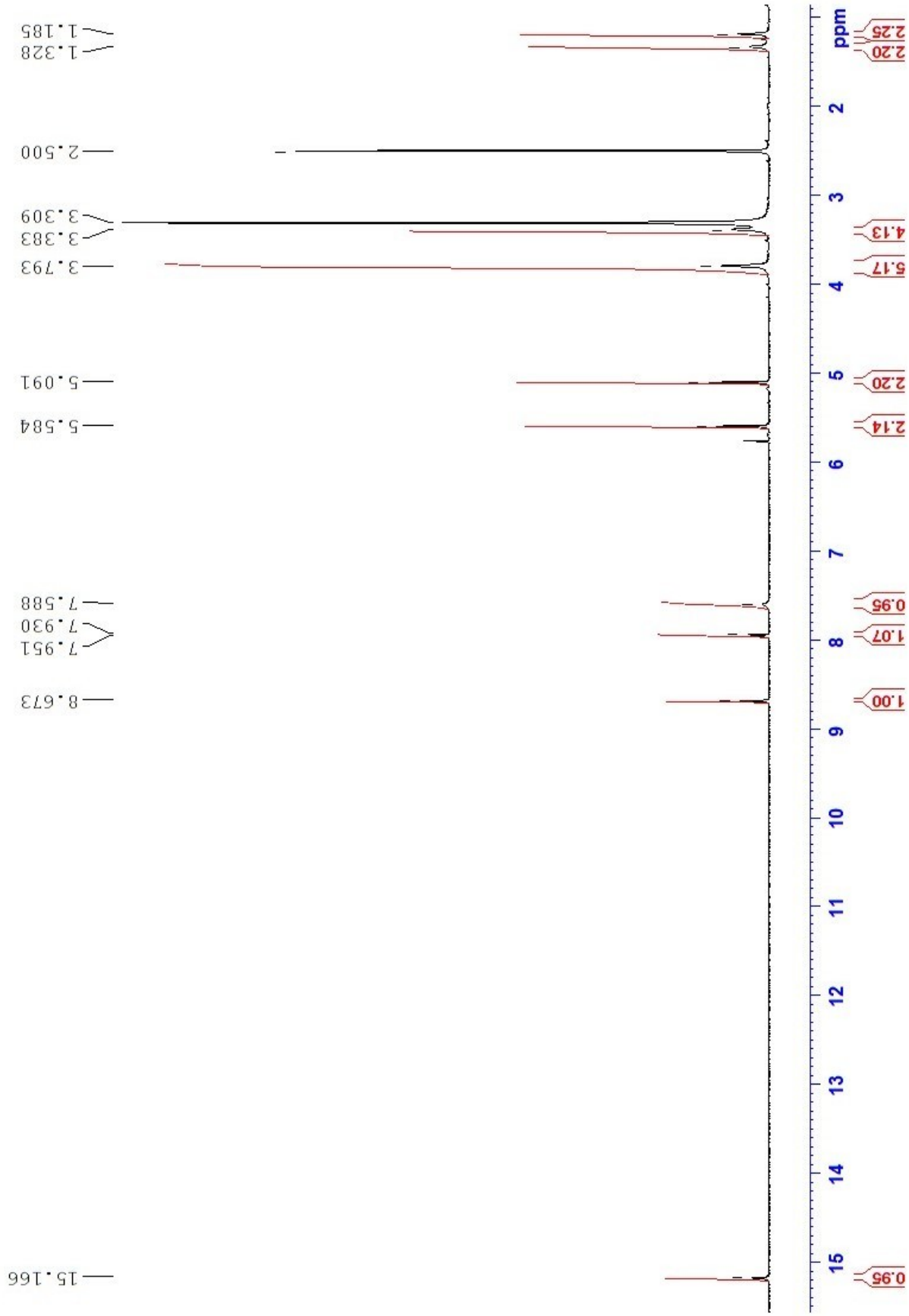

Fig. S3 ^{1}H NMR of compound **3** (600 MHz, DMSO-d_6)

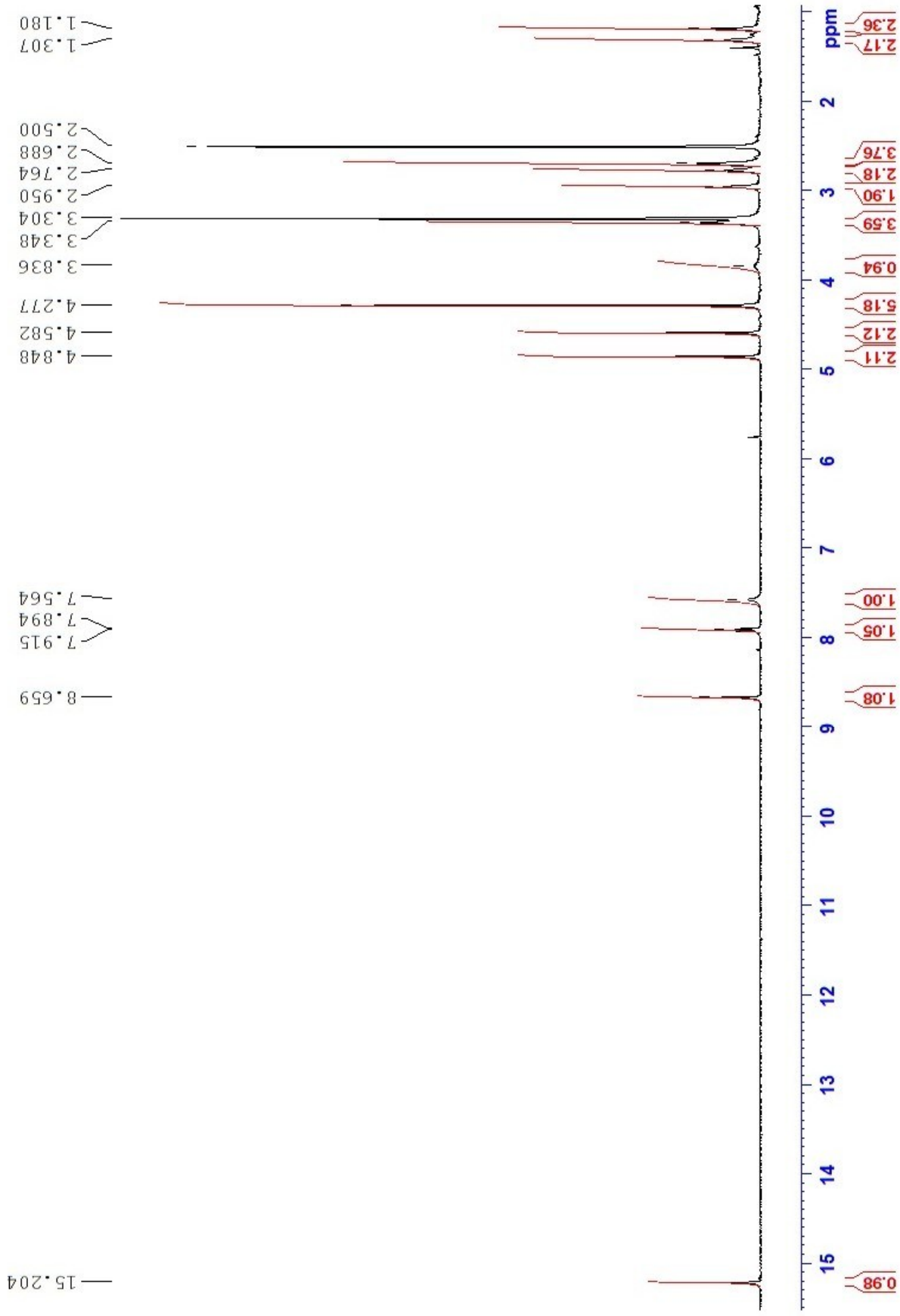

Fig. S4 ^{1}H NMR of compound **4** (600 MHz, DMSO-d_6)

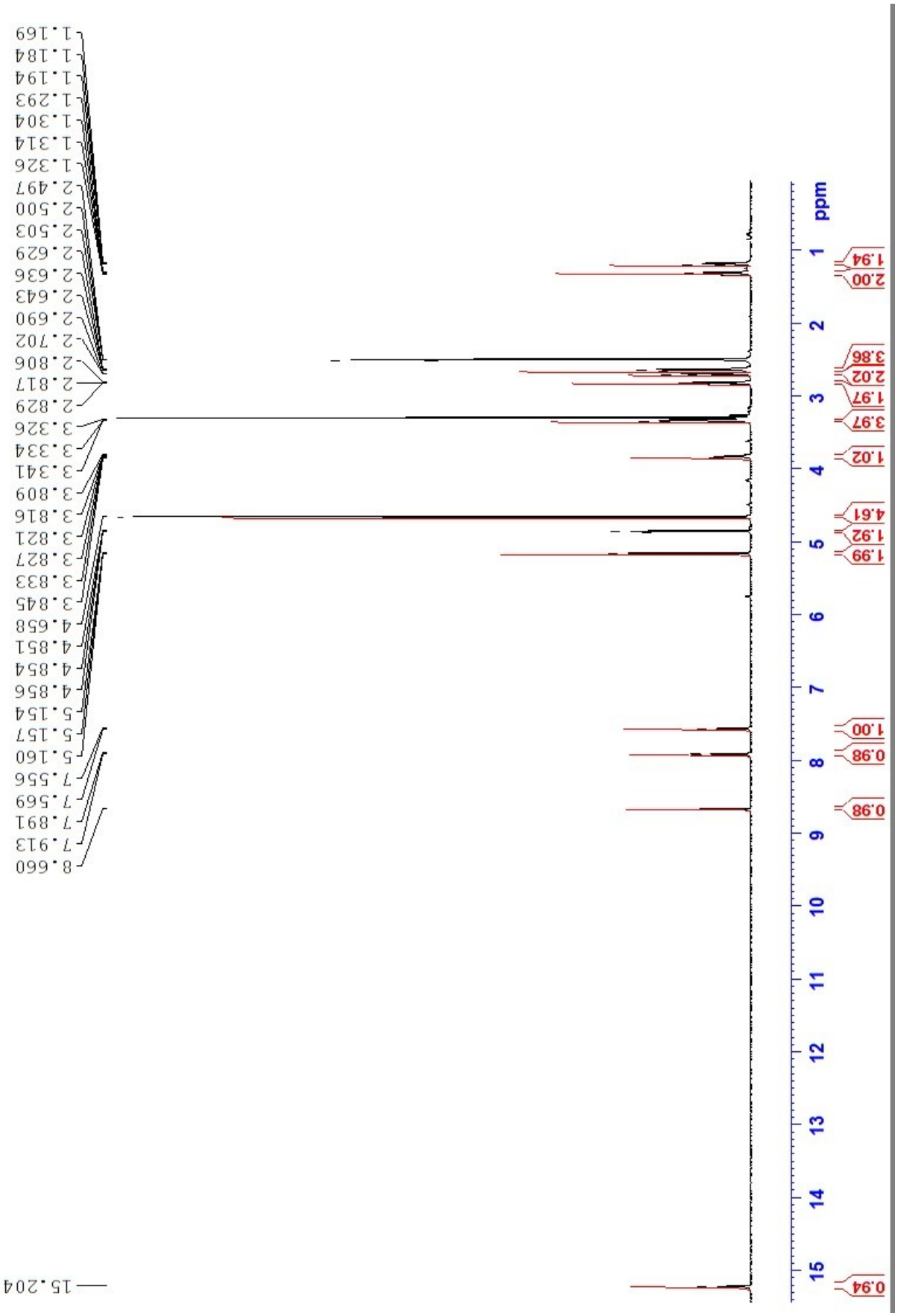

Fig. S5 ^{1}H NMR of compound **5** (600 MHz, DMSO-d_6)

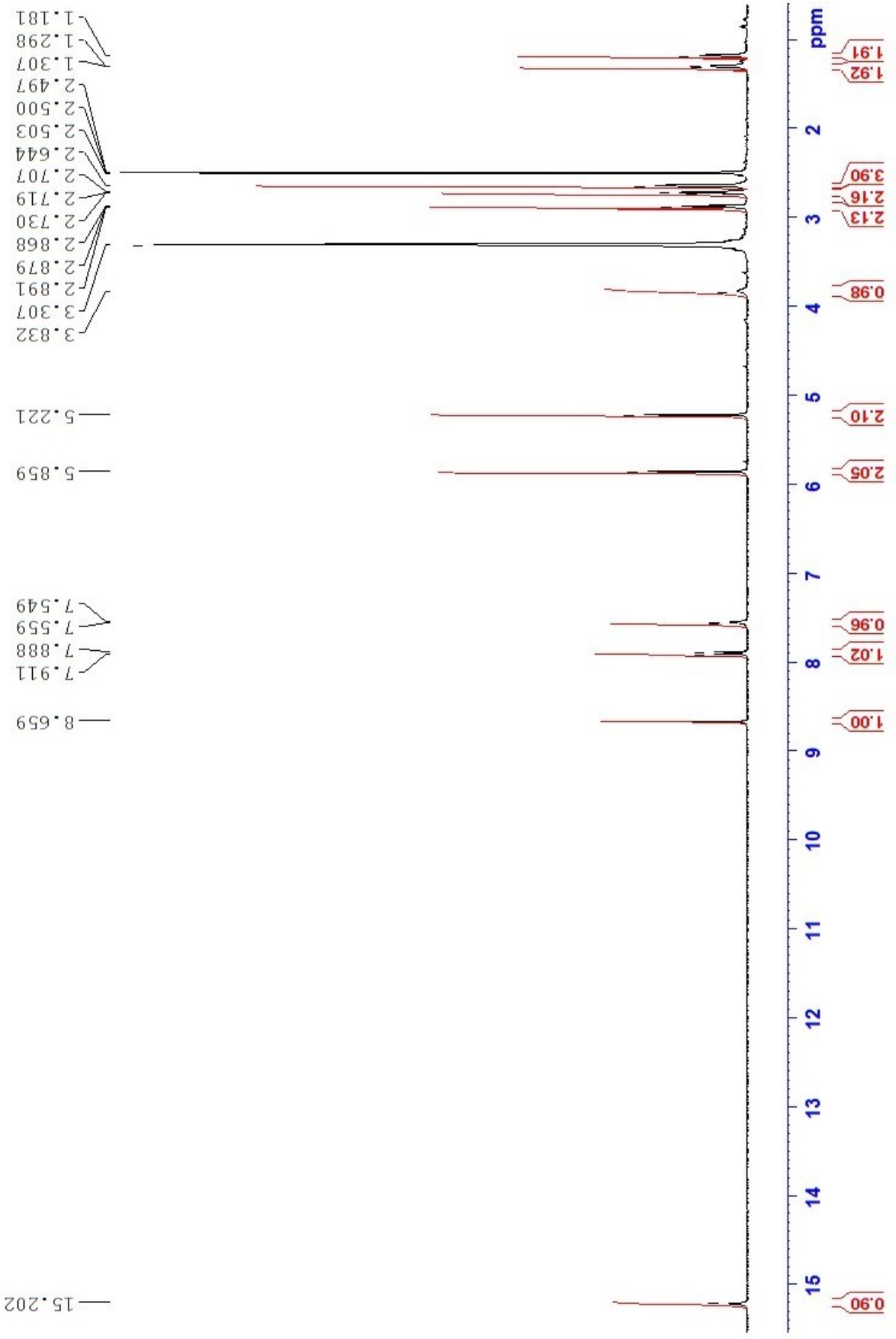

Fig. S6 ^{1}H NMR of compound **6** (600 MHz, DMSO-d_6)

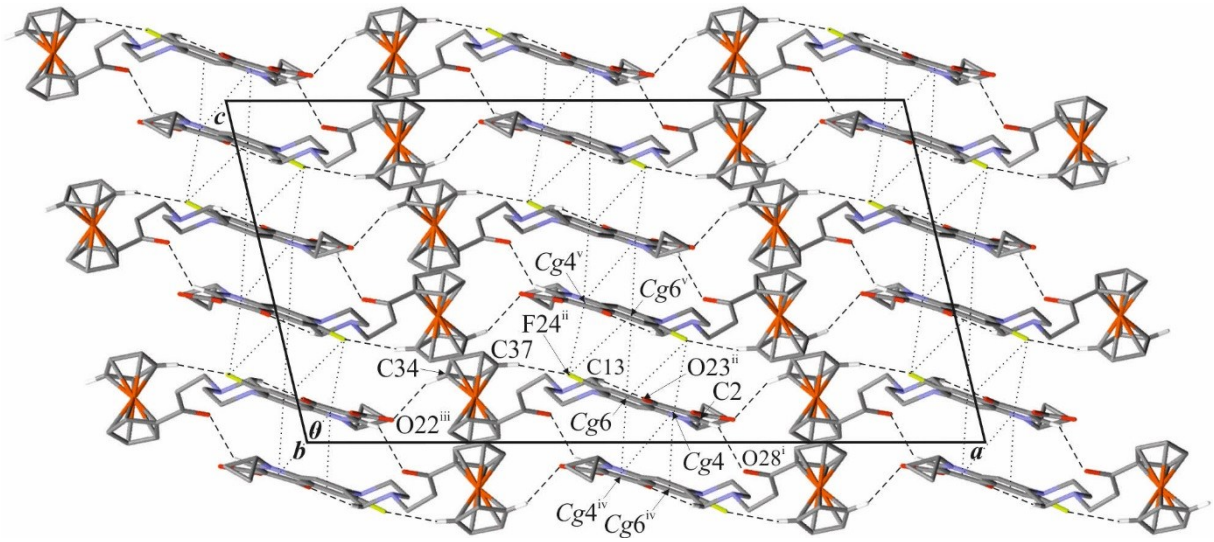

Fig. S7 Interactions of **4** in the crystal lattice, viewed along *b*-direction. The C−H···O and C−H···F hydrogen bonds are represented by dashed lines, while the π- π and C−F···π contacts by dotted lines. The H-atoms not involved in the intermolecular interactions have been omitted for clarity. Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $x, y + 1, z$; (iii) $x - 1/2, y + 3/2, z$; (iv) $-x + 1, -y - 1, -z$; (v) $-x + 1, y, -z + 1/2$.

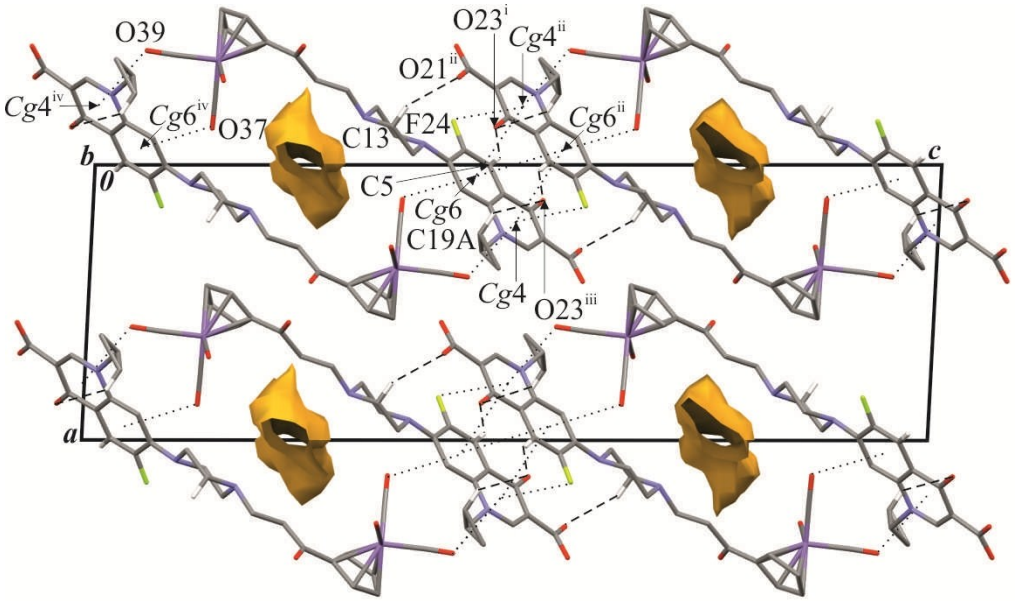

Fig. S8 Interactions of **6** in the crystal lattice. The C−H···O and C−H···F hydrogen bonds are represented by dashed lines, while the π- π, C−F···π and C=O··π contacts by dotted lines. The H-atoms not involved in the intermolecular interactions have been omitted for clarity. Solvent accessible voids colored in yellow. Symmetry codes: (i) $-x, -y - 1, -z + 1$; (ii) $-x, -y, -z + 1$; (iii) $x, y + 1, z$; (iv) $-x, y + 1/2, -z + 3/2$.

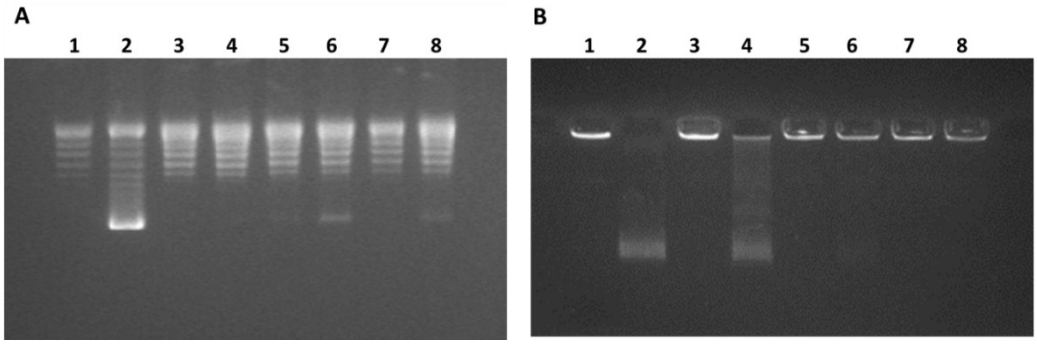

Fig. S9 Inhibition assay results for *E. coli* DNA gyrase (**A**) and *S. aureus* topoisomerase IV (**B**) treated with six organometallic ciprofloxacin derivatives at the concentration of 50 μM. [**A**: 1 – relaxed pBR322 - negative control; 2 – *E. coli* DNA gyrase - positive control; 3 – compound 4; 4 – compound 1; 5 – compound 5; 6 – compound 2; 7 – compound 6; 8 – compound 3; **B**: 1 –kinetoplast catenated DNA - negative control; 2 – *S. aureus* topoisomerase IV – positive control; 3 – compound 4; 4 – compound 1; 5 – compound 5; 6 – compound 2; 7 – compound 6; 8 – compound 3].

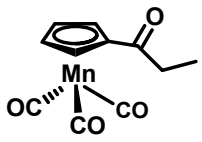

Fig. S10 Chemical structure of **Pp-Cym**

Table S1 Crystal data and structure refinement details for **4** and **6**.

Identification code	**4**	**6**
Empirical formula	$C_{30}H_{30}FFeN_3O_4$	$C_{28}H_{25}FMnN_3O_7$
Formula weight	571.42	589.45
Temperature/K	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	$P2_1/c$
a/Å	30.6129(10)	11.2786(5)
b/Å	10.5408(2)	7.2123(3)
c/Å	15.8947(5)	34.7213(9)
α/°	90	90
β/°	103.153(3)	93.113(3)
γ/°	90	90
Volume/Å^3	4994.4(3)	2820.24(18)
Z	8	4
ρ_{calc}g/cm^3	1.520	1.388
μ/mm^{-1}	5.278	4.294
F(000)	2384.0	1216.0
Crystal size/mm^3	0.19 × 0.11 × 0.04	0.32 × 0.14 × 0.10
Radiation	Cu*K*α (λ = 1.54184)	Cu*K*α (λ = 1.54184)
2*Θ* range for data collection/°	5.93 to 134.138	5.098 to 148.004
Index ranges	$-36 \le h \le 36$, $-12 \le k \le 12$, $-15 \le l \le 18$	$-14 \le h \le 13$, $-9 \le k \le 8$, $-42 \le l \le 43$
Reflections collected	19631	44790
Independent reflections	4466 [R_{int} = 0.0361, R_{sigma} = 0.0273]	5669 [R_{int} = 0.0590, R_{sigma} = 0.0352]
Data/restraints/parameters	4466/166/346	5669/5/384
Goodness-of-fit on F^2	1.046	1.069
Final *R* indexes [*I*>=2σ (*I*)]	R_1 = 0.0992, wR_2 = 0.2509	R_1 = 0.0755, wR_2 = 0.2055
Final *R* indexes [all data]	R_1 = 0.1076, wR_2 = 0.2579	R_1 = 0.0880, wR_2 = 0.2139
Largest diff. peak/hole / e Å^{-3}	1.83/-1.34	0.84/-0.64

Table S2 Bond lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe(39)	C(30)	2.063(8)	C(9)	C(8)	1.395(7)
Fe(39)	C(29)	2.033(7)	C(9)	C(10)	1.404(7)
Fe(39)	C(33)	2.035(8)	C(13)	C(12)	1.528(8)
Fe(39)	C(31)	2.069(9)	O(28)	C(27)	1.229(7)
Fe(39)	C(32)	2.047(9)	C(7)	C(8)	1.401(8)
Fe(39)	C(36)	2.030(7)	C(7)	C(6)	1.418(8)
Fe(39)	C(35)	2.016(7)	C(4)	C(10)	1.448(7)
Fe(39)	C(34)	2.021(7)	C(10)	C(5)	1.409(8)
Fe(39)	C(38)	2.035(7)	C(6)	C(5)	1.355(8)
Fe(39)	C(37)	2.041(7)	C(30)	C(29)	1.430(9)
F(24)	C(6)	1.361(6)	C(30)	C(31)	1.390(11)
O(21)	C(20)	1.339(7)	C(17)	C(18)	1.476(8)
O(23)	C(4)	1.265(6)	C(17)	C(19)	1.497(7)
O(22)	C(20)	1.209(7)	C(15)	C(16)	1.513(8)
N(1)	C(9)	1.408(7)	C(18)	C(19)	1.497(9)
N(1)	C(2)	1.338(7)	C(27)	C(29)	1.466(9)
N(1)	C(17)	1.456(6)	C(27)	C(26)	1.510(8)
N(14)	C(13)	1.462(7)	C(29)	C(33)	1.420(10)
N(14)	C(15)	1.464(7)	C(33)	C(32)	1.410(11)
N(14)	C(25)	1.471(7)	C(31)	C(32)	1.427(11)
N(11)	C(7)	1.386(7)	C(25)	C(26)	1.514(8)
N(11)	C(12)	1.460(7)	C(36)	C(35)	1.4182
N(11)	C(16)	1.470(7)	C(36)	C(37)	1.4180
C(3)	C(2)	1.373(7)	C(35)	C(34)	1.4180
C(3)	C(20)	1.490(7)	C(34)	C(38)	1.4187
C(3)	C(4)	1.428(8)	C(38)	C(37)	1.4187

Table S3 Valence angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(30)	Fe(39)	C(31)	39.3(3)	O(22)	C(20)	O(21)	121.2(5)
C(29)	Fe(39)	C(30)	40.8(3)	O(22)	C(20)	C(3)	124.1(5)
C(29)	Fe(39)	C(33)	40.8(3)	N(11)	C(7)	C(8)	122.9(5)
C(29)	Fe(39)	C(31)	67.2(3)	N(11)	C(7)	C(6)	121.3(5)
C(29)	Fe(39)	C(32)	67.7(3)	C(8)	C(7)	C(6)	115.7(5)
C(29)	Fe(39)	C(38)	146.6(3)	O(23)	C(4)	C(3)	122.7(5)
C(29)	Fe(39)	C(37)	119.1(3)	O(23)	C(4)	C(10)	121.5(5)
C(33)	Fe(39)	C(30)	68.9(3)	C(3)	C(4)	C(10)	115.7(5)
C(33)	Fe(39)	C(31)	68.2(3)	C(9)	C(8)	C(7)	121.3(5)
C(33)	Fe(39)	C(32)	40.4(3)	C(9)	C(10)	C(4)	121.5(5)
C(33)	Fe(39)	C(37)	148.7(3)	C(9)	C(10)	C(5)	117.8(5)
C(32)	Fe(39)	C(30)	67.7(3)	C(5)	C(10)	C(4)	120.7(5)
C(32)	Fe(39)	C(31)	40.6(3)	F(24)	C(6)	C(7)	117.5(5)
C(36)	Fe(39)	C(30)	139.4(3)	C(5)	C(6)	F(24)	118.5(5)
C(36)	Fe(39)	C(29)	115.0(3)	C(5)	C(6)	C(7)	123.9(5)
C(36)	Fe(39)	C(33)	116.6(3)	C(29)	C(30)	Fe(39)	68.4(4)
C(36)	Fe(39)	C(31)	174.9(3)	C(31)	C(30)	Fe(39)	70.6(5)
C(36)	Fe(39)	C(32)	144.2(3)	C(31)	C(30)	C(29)	107.2(6)
C(36)	Fe(39)	C(38)	68.75(16)	N(11)	C(12)	C(13)	109.2(5)
C(36)	Fe(39)	C(37)	40.78(13)	N(1)	C(17)	C(18)	119.1(5)
C(35)	Fe(39)	C(30)	177.7(3)	N(1)	C(17)	C(19)	118.9(5)
C(35)	Fe(39)	C(29)	137.2(3)	C(18)	C(17)	C(19)	60.5(4)
C(35)	Fe(39)	C(33)	108.9(3)	C(6)	C(5)	C(10)	120.0(5)
C(35)	Fe(39)	C(31)	140.6(3)	N(14)	C(15)	C(16)	111.0(5)
C(35)	Fe(39)	C(32)	110.9(3)	C(17)	C(18)	C(19)	60.5(4)
C(35)	Fe(39)	C(36)	41.04(13)	O(28)	C(27)	C(29)	121.9(6)
C(35)	Fe(39)	C(34)	41.13(13)	O(28)	C(27)	C(26)	121.3(6)
C(35)	Fe(39)	C(38)	68.99(16)	C(29)	C(27)	C(26)	116.7(5)
C(35)	Fe(39)	C(37)	68.88(17)	C(30)	C(29)	Fe(39)	70.7(4)
C(34)	Fe(39)	C(30)	140.6(3)	C(30)	C(29)	C(27)	124.0(6)
C(34)	Fe(39)	C(29)	171.7(3)	C(27)	C(29)	Fe(39)	119.5(5)
C(34)	Fe(39)	C(33)	131.1(3)	C(33)	C(29)	Fe(39)	69.7(4)
C(34)	Fe(39)	C(31)	109.5(3)	C(33)	C(29)	C(30)	108.9(6)
C(34)	Fe(39)	C(32)	104.7(3)	C(33)	C(29)	C(27)	126.6(6)
C(34)	Fe(39)	C(36)	69.03(16)	N(11)	C(16)	C(15)	110.4(5)
C(34)	Fe(39)	C(38)	40.94(12)	C(17)	C(19)	C(18)	59.0(4)
C(34)	Fe(39)	C(37)	68.82(16)	C(29)	C(33)	Fe(39)	69.5(4)
C(38)	Fe(39)	C(30)	113.3(3)	C(32)	C(33)	Fe(39)	70.2(5)
C(38)	Fe(39)	C(33)	169.9(3)	C(32)	C(33)	C(29)	106.8(6)
C(38)	Fe(39)	C(31)	106.8(3)	C(30)	C(31)	Fe(39)	70.1(5)
C(38)	Fe(39)	C(32)	130.2(3)	C(30)	C(31)	C(32)	108.7(7)
C(38)	Fe(39)	C(37)	40.74(12)	C(32)	C(31)	Fe(39)	68.9(5)
C(37)	Fe(39)	C(30)	112.8(3)	N(14)	C(25)	C(26)	114.2(5)
C(37)	Fe(39)	C(31)	134.2(3)	C(27)	C(26)	C(25)	114.9(5)
C(37)	Fe(39)	C(32)	170.8(3)	C(33)	C(32)	Fe(39)	69.4(5)
C(9)	N(1)	C(17)	119.7(4)	C(33)	C(32)	C(31)	108.3(7)

C(2)	N(1)	C(9)	120.5(4)	C(31)	C(32)	Fe(39)	70.6(5)
C(2)	N(1)	C(17)	119.7(4)	C(35)	C(36)	Fe(39)	69.0(3)
C(13)	N(14)	C(15)	108.0(4)	C(37)	C(36)	Fe(39)	70.0(3)
C(13)	N(14)	C(25)	108.8(4)	C(37)	C(36)	C(35)	108.0
C(15)	N(14)	C(25)	109.9(5)	C(36)	C(35)	Fe(39)	70.0(3)
C(7)	N(11)	C(12)	118.1(4)	C(34)	C(35)	Fe(39)	69.6(3)
C(7)	N(11)	C(16)	119.3(4)	C(34)	C(35)	C(36)	108.0
C(12)	N(11)	C(16)	109.5(4)	C(35)	C(34)	Fe(39)	69.3(3)
C(2)	C(3)	C(20)	117.8(5)	C(35)	C(34)	C(38)	108.0
C(2)	C(3)	C(4)	120.5(5)	C(38)	C(34)	Fe(39)	70.1(3)
C(4)	C(3)	C(20)	121.7(5)	C(34)	C(38)	Fe(39)	69.0(3)
C(8)	C(9)	N(1)	120.3(5)	C(37)	C(38)	Fe(39)	69.8(3)
C(8)	C(9)	C(10)	121.2(5)	C(37)	C(38)	C(34)	108.0
C(10)	C(9)	N(1)	118.5(5)	C(36)	C(37)	Fe(39)	69.2(3)
N(1)	C(2)	C(3)	123.1(5)	C(36)	C(37)	C(38)	108.0
N(14)	C(13)	C(12)	111.1(4)	C(38)	C(37)	Fe(39)	69.4(3)
O(21)	C(20)	C(3)	114.7(5)				

Table S4 Torsion angles for **4**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe(39)	C(30)	C(29)	C(27)	-113.1(7)	C(4)	C(3)	C(2)	N(1)	2.2(8)
Fe(39)	C(30)	C(29)	C(33)	59.4(6)	C(4)	C(3)	C(20)	O(21)	8.2(7)
Fe(39)	C(30)	C(31)	C(32)	-58.2(6)	C(4)	C(3)	C(20)	O(22)	-171.7(5)
Fe(39)	C(29)	C(33)	C(32)	60.6(6)	C(4)	C(10)	C(5)	C(6)	178.8(5)
Fe(39)	C(33)	C(32)	C(31)	60.0(6)	C(8)	C(9)	C(10)	C(4)	177.6(5)
Fe(39)	C(31)	C(32)	C(33)	-59.3(6)	C(8)	C(9)	C(10)	C(5)	-3.3(7)
Fe(39)	C(36)	C(35)	C(34)	-59.4(3)	C(8)	C(7)	C(6)	F(24)	174.1(4)
Fe(39)	C(36)	C(37)	C(38)	58.8(3)	C(8)	C(7)	C(6)	C(5)	-2.6(8)
Fe(39)	C(35)	C(34)	C(38)	-59.6(3)	C(10)	C(9)	C(8)	C(7)	4.0(8)
Fe(39)	C(34)	C(38)	C(37)	-59.1(3)	C(6)	C(7)	C(8)	C(9)	-1.1(7)
Fe(39)	C(38)	C(37)	C(36)	-58.6(3)	C(30)	C(29)	C(33)	Fe(39)	-60.1(5)
F(24)	C(6)	C(5)	C(10)	-173.4(5)	C(30)	C(29)	C(33)	C(32)	0.6(9)
O(23)	C(4)	C(10)	C(9)	-176.2(5)	C(30)	C(31)	C(32)	Fe(39)	58.9(6)
O(23)	C(4)	C(10)	C(5)	4.8(7)	C(30)	C(31)	C(32)	C(33)	-0.3(10)
N(1)	C(9)	C(8)	C(7)	-177.6(5)	C(12)	N(11)	C(7)	C(8)	-7.9(8)
N(1)	C(9)	C(10)	C(4)	-0.8(7)	C(12)	N(11)	C(7)	C(6)	167.2(5)
N(1)	C(9)	C(10)	C(5)	178.3(4)	C(12)	N(11)	C(16)	C(15)	-58.3(6)
N(1)	C(17)	C(18)	C(19)	-108.7(5)	C(17)	N(1)	C(9)	C(8)	-2.3(7)
N(1)	C(17)	C(19)	C(18)	109.1(6)	C(17)	N(1)	C(9)	C(10)	176.1(4)
N(14)	C(13)	C(12)	N(11)	-60.4(6)	C(17)	N(1)	C(2)	C(3)	-176.8(5)
N(14)	C(15)	C(16)	N(11)	58.9(6)	C(15)	N(14)	C(13)	C(12)	59.5(6)
N(14)	C(25)	C(26)	C(27)	-93.3(6)	C(15)	N(14)	C(25)	C(26)	-78.4(6)
N(11)	C(7)	C(8)	C(9)	174.3(5)	C(27)	C(29)	C(33)	Fe(39)	112.3(7)
N(11)	C(7)	C(6)	F(24)	-1.4(8)	C(27)	C(29)	C(33)	C(32)	172.9(7)
N(11)	C(7)	C(6)	C(5)	-178.1(5)	C(29)	C(30)	C(31)	Fe(39)	58.9(6)
C(3)	C(4)	C(10)	C(9)	3.5(7)	C(29)	C(30)	C(31)	C(32)	0.7(10)
C(3)	C(4)	C(10)	C(5)	-175.5(5)	C(29)	C(27)	C(26)	C(25)	-171.9(6)
C(9)	N(1)	C(2)	C(3)	0.8(7)	C(29)	C(33)	C(32)	Fe(39)	-60.2(6)
C(9)	N(1)	C(17)	C(18)	139.2(5)	C(29)	C(33)	C(32)	C(31)	-0.1(10)
C(9)	N(1)	C(17)	C(19)	68.9(6)	C(16)	N(11)	C(7)	C(8)	129.4(6)
C(9)	C(10)	C(5)	C(6)	-0.3(7)	C(16)	N(11)	C(7)	C(6)	-55.5(7)
C(2)	N(1)	C(9)	C(8)	-179.9(5)	C(16)	N(11)	C(12)	C(13)	58.4(6)
C(2)	N(1)	C(9)	C(10)	-1.5(7)	C(31)	C(30)	C(29)	Fe(39)	-60.2(6)
C(2)	N(1)	C(17)	C(18)	-43.1(7)	C(31)	C(30)	C(29)	C(27)	-173.4(7)
C(2)	N(1)	C(17)	C(19)	-113.5(6)	C(31)	C(30)	C(29)	C(33)	-0.8(9)
C(2)	C(3)	C(20)	O(21)	-170.4(5)	C(25)	N(14)	C(13)	C(12)	178.7(5)
C(2)	C(3)	C(20)	O(22)	9.7(8)	C(25)	N(14)	C(15)	C(16)	-177.2(5)
C(2)	C(3)	C(4)	O(23)	175.5(5)	C(26)	C(27)	C(29)	Fe(39)	84.7(6)
C(2)	C(3)	C(4)	C(10)	-4.2(7)	C(26)	C(27)	C(29)	C(30)	170.3(7)
C(13)	N(14)	C(15)	C(16)	-58.6(6)	C(26)	C(27)	C(29)	C(33)	-0.9(10)
C(13)	N(14)	C(25)	C(26)	163.5(5)	C(36)	C(35)	C(34)	Fe(39)	59.7(3)
O(28)	C(27)	C(29)	Fe(39)	-94.1(7)	C(36)	C(35)	C(34)	C(38)	0.0
O(28)	C(27)	C(29)	C(30)	-8.5(11)	C(35)	C(36)	C(37)	Fe(39)	-58.7(3)
O(28)	C(27)	C(29)	C(33)	-179.7(7)	C(35)	C(36)	C(37)	C(38)	0.0
O(28)	C(27)	C(26)	C(25)	6.9(8)	C(35)	C(34)	C(38)	Fe(39)	59.1(3)
C(20)	C(3)	C(2)	N(1)	-179.2(4)	C(35)	C(34)	C(38)	C(37)	0.0

C(20)	C(3)	C(4)	O(23)	-3.1(8)	C(34)	C(38)	C(37)	Fe(39)	58.6(3)
C(20)	C(3)	C(4)	C(10)	177.2(4)	C(34)	C(38)	C(37)	C(36)	0.0
C(7)	N(11)	C(12)	C(13)	-160.5(5)	C(37)	C(36)	C(35)	Fe(39)	59.4(3)
C(7)	N(11)	C(16)	C(15)	161.1(5)	C(37)	C(36)	C(35)	C(34)	0.0
C(7)	C(6)	C(5)	C(10)	3.3(8)					

Table S5 Bond lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C(2)	C(3)	1.353(6)	C(17B)	N(1)	1.509(10)
C(2)	N(1)	1.345(5)	C(18)	C(19A)	1.590(8)
C(3)	C(4)	1.432(5)	C(18)	C(19B)	1.567(10)
C(3)	C(20)	1.482(5)	C(20)	O(21)	1.319(5)
C(4)	C(10)	1.447(5)	C(20)	O(22)	1.212(5)
C(4)	O(23)	1.259(5)	C(25)	C(26)	1.526(6)
C(5)	C(6)	1.354(5)	C(25)	N(14)	1.470(6)
C(5)	C(10)	1.407(5)	C(26)	C(27)	1.501(6)
C(6)	C(7)	1.408(6)	C(27)	C(29)	1.498(7)
C(6)	F(24)	1.365(4)	C(27)	O(28)	1.198(8)
C(7)	C(8)	1.388(5)	C(29)	C(30)	1.403(8)
C(7)	N(11)	1.395(5)	C(29)	C(33)	1.427(6)
C(8)	C(9)	1.396(5)	C(29)	Mn(40)	2.118(5)
C(9)	C(10)	1.392(5)	C(30)	C(31)	1.425(6)
C(9)	N(1)	1.398(5)	C(30)	Mn(40)	2.139(5)
C(12)	C(13)	1.521(6)	C(31)	C(32)	1.389(9)
C(12)	N(11)	1.448(5)	C(31)	Mn(40)	2.142(6)
C(13)	N(14)	1.460(6)	C(32)	C(33)	1.412(9)
C(15)	C(16)	1.516(6)	C(32)	Mn(40)	2.135(6)
C(15)	N(14)	1.454(6)	C(33)	Mn(40)	2.114(6)
C(16)	N(11)	1.480(5)	C(34)	Mn(40)	1.773(7)
C(17A)	C(18)	1.448(8)	C(34)	O(35)	1.152(8)
C(17A)	C(19A)	1.483(12)	C(36)	Mn(40)	1.793(5)
C(17A)	N(1)	1.492(8)	C(36)	O(37)	1.160(6)
C(17B)	C(18)	1.395(10)	C(38)	Mn(40)	1.797(4)
C(17B)	C(19B)	1.502(13)	C(38)	O(39)	1.147(5)

Table S6 Valence angles for **6**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N(1)	C(2)	C(3)	124.4(4)	C(30)	C(31)	Mn(40)	70.4(3)
C(2)	C(3)	C(4)	119.4(3)	C(32)	C(31)	C(30)	107.5(5)
C(2)	C(3)	C(20)	119.4(3)	C(32)	C(31)	Mn(40)	70.8(4)
C(4)	C(3)	C(20)	121.2(4)	C(31)	C(32)	C(33)	109.2(4)
C(3)	C(4)	C(10)	116.2(3)	C(31)	C(32)	Mn(40)	71.3(3)
O(23)	C(4)	C(3)	122.5(3)	C(33)	C(32)	Mn(40)	69.8(4)
O(23)	C(4)	C(10)	121.3(3)	C(29)	C(33)	Mn(40)	70.5(3)
C(6)	C(5)	C(10)	120.0(3)	C(32)	C(33)	C(29)	107.2(6)
C(5)	C(6)	C(7)	123.5(3)	C(32)	C(33)	Mn(40)	71.4(3)
C(5)	C(6)	F(24)	118.2(3)	O(35)	C(34)	Mn(40)	179.0(8)
F(24)	C(6)	C(7)	118.3(3)	O(37)	C(36)	Mn(40)	178.7(4)
C(8)	C(7)	C(6)	116.0(3)	O(39)	C(38)	Mn(40)	177.7(6)
C(8)	C(7)	N(11)	122.2(3)	C(29)	Mn(40)	C(30)	38.5(2)
N(11)	C(7)	C(6)	121.6(3)	C(29)	Mn(40)	C(31)	65.1(2)
C(7)	C(8)	C(9)	121.7(4)	C(29)	Mn(40)	C(32)	64.99(19)
C(8)	C(9)	N(1)	120.5(3)	C(30)	Mn(40)	C(31)	38.89(16)
C(10)	C(9)	C(8)	120.6(3)	C(32)	Mn(40)	C(30)	64.2(2)
C(10)	C(9)	N(1)	118.9(3)	C(32)	Mn(40)	C(31)	37.9(2)
C(5)	C(10)	C(4)	120.6(3)	C(33)	Mn(40)	C(29)	39.40(18)
C(9)	C(10)	C(4)	121.3(3)	C(33)	Mn(40)	C(30)	65.0(3)
C(9)	C(10)	C(5)	118.1(3)	C(33)	Mn(40)	C(31)	64.9(3)
N(11)	C(12)	C(13)	110.2(4)	C(33)	Mn(40)	C(32)	38.8(2)
N(14)	C(13)	C(12)	112.3(5)	C(34)	Mn(40)	C(29)	97.5(3)
N(14)	C(15)	C(16)	111.3(4)	C(34)	Mn(40)	C(30)	132.8(2)
N(11)	C(16)	C(15)	108.2(4)	C(34)	Mn(40)	C(31)	156.4(3)
C(18)	C(17A)	C(19A)	65.7(5)	C(34)	Mn(40)	C(32)	121.5(3)
C(18)	C(17A)	N(1)	117.4(6)	C(34)	Mn(40)	C(33)	91.5(3)
C(19A)	C(17A)	N(1)	111.2(8)	C(34)	Mn(40)	C(36)	92.7(3)
C(18)	C(17B)	C(19B)	65.4(6)	C(34)	Mn(40)	C(38)	92.1(2)
C(18)	C(17B)	N(1)	119.8(8)	C(36)	Mn(40)	C(29)	111.58(18)
C(19B)	C(17B)	N(1)	109.8(9)	C(36)	Mn(40)	C(30)	91.7(2)
C(17A)	C(18)	C(19A)	58.2(4)	C(36)	Mn(40)	C(31)	108.2(2)
C(17B)	C(18)	C(19B)	60.6(5)	C(36)	Mn(40)	C(32)	145.7(2)
C(17A)	C(19A)	C(18)	56.1(4)	C(36)	Mn(40)	C(33)	151.0(2)
C(17B)	C(19B)	C(18)	54.0(5)	C(36)	Mn(40)	C(38)	93.1(2)
O(21)	C(20)	C(3)	115.4(4)	C(38)	Mn(40)	C(29)	152.9(2)
O(22)	C(20)	C(3)	123.6(4)	C(38)	Mn(40)	C(30)	134.6(2)
O(22)	C(20)	O(21)	120.8(4)	C(38)	Mn(40)	C(31)	97.5(2)
N(14)	C(25)	C(26)	113.2(5)	C(38)	Mn(40)	C(32)	88.4(2)
C(27)	C(26)	C(25)	113.1(5)	C(38)	Mn(40)	C(33)	115.4(2)
C(29)	C(27)	C(26)	116.7(5)	C(2)	N(1)	C(9)	119.7(3)
O(28)	C(27)	C(26)	122.0(5)	C(2)	N(1)	C(17A)	118.8(4)
O(28)	C(27)	C(29)	121.3(4)	C(2)	N(1)	C(17B)	120.5(4)
C(27)	C(29)	Mn(40)	125.0(4)	C(9)	N(1)	C(17A)	118.5(4)
C(30)	C(29)	C(27)	130.2(4)	C(9)	N(1)	C(17B)	116.2(4)
C(30)	C(29)	C(33)	107.7(5)	C(7)	N(11)	C(12)	118.4(3)
C(30)	C(29)	Mn(40)	71.6(3)	C(7)	N(11)	C(16)	116.8(4)

C(33)	C(29)	C(27)	122.1(5)	C(12)	N(11)	C(16)	110.2(4)
C(33)	C(29)	Mn(40)	70.1(3)	C(13)	N(14)	C(25)	108.8(4)
C(29)	C(30)	C(31)	108.3(5)	C(15)	N(14)	C(13)	108.0(4)
C(29)	C(30)	Mn(40)	70.0(3)	C(15)	N(14)	C(25)	111.2(4)
C(31)	C(30)	Mn(40)	70.7(3)				

Table S7 Torsion angles for **6**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C(2)	C(3)	C(4)	C(10)	0.4(7)	C(20)	C(3)	C(4)	C(10)	-178.0(4)
C(2)	C(3)	C(4)	O(23)	179.3(5)	C(20)	C(3)	C(4)	O(23)	0.9(7)
C(2)	C(3)	C(20)	O(21)	-170.2(5)	C(25)	C(26)	C(27)	C(29)	-174.8(5)
C(2)	C(3)	C(20)	O(22)	6.8(8)	C(25)	C(26)	C(27)	O(28)	2.8(9)
C(3)	C(2)	N(1)	C(9)	0.1(9)	C(26)	C(25)	N(14)	C(13)	176.4(5)
C(3)	C(2)	N(1)	C(17A)	-159.9(7)	C(26)	C(25)	N(14)	C(15)	-64.8(6)
C(3)	C(2)	N(1)	C(17B)	158.2(7)	C(26)	C(27)	C(29)	C(30)	-0.4(9)
C(3)	C(4)	C(10)	C(5)	-179.6(4)	C(26)	C(27)	C(29)	C(33)	177.5(6)
C(3)	C(4)	C(10)	C(9)	-0.4(7)	C(26)	C(27)	C(29)	Mn(40)	-95.4(6)
C(4)	C(3)	C(20)	O(21)	8.1(7)	C(27)	C(29)	C(30)	C(31)	178.8(6)
C(4)	C(3)	C(20)	O(22)	-174.9(5)	C(27)	C(29)	C(30)	Mn(40)	-120.7(6)
C(5)	C(6)	C(7)	C(8)	-1.6(8)	C(27)	C(29)	C(33)	C(32)	-178.1(6)
C(5)	C(6)	C(7)	N(11)	-177.1(5)	C(27)	C(29)	C(33)	Mn(40)	119.6(6)
C(6)	C(5)	C(10)	C(4)	178.5(4)	C(29)	C(30)	C(31)	C(32)	-1.3(6)
C(6)	C(5)	C(10)	C(9)	-0.7(7)	C(29)	C(30)	C(31)	Mn(40)	60.1(4)
C(6)	C(7)	C(8)	C(9)	-1.5(8)	C(30)	C(29)	C(33)	C(32)	0.2(8)
C(6)	C(7)	N(11)	C(12)	169.9(5)	C(30)	C(29)	C(33)	Mn(40)	-62.1(4)
C(6)	C(7)	N(11)	C(16)	-54.5(7)	C(30)	C(31)	C(32)	C(33)	1.4(7)
C(7)	C(8)	C(9)	C(10)	3.5(8)	C(30)	C(31)	C(32)	Mn(40)	61.2(4)
C(7)	C(8)	C(9)	N(1)	-178.5(5)	C(31)	C(32)	C(33)	C(29)	-1.0(8)
C(8)	C(7)	N(11)	C(12)	-5.4(8)	C(31)	C(32)	C(33)	Mn(40)	60.7(5)
C(8)	C(7)	N(11)	C(16)	130.3(5)	C(33)	C(29)	C(30)	C(31)	0.6(7)
C(8)	C(9)	C(10)	C(4)	178.5(5)	C(33)	C(29)	C(30)	Mn(40)	61.2(4)
C(8)	C(9)	C(10)	C(5)	-2.3(7)	F(24)	C(6)	C(7)	C(8)	176.8(5)
C(8)	C(9)	N(1)	C(2)	-178.3(5)	F(24)	C(6)	C(7)	N(11)	1.3(7)
C(8)	C(9)	N(1)	C(17A)	-18.2(8)	Mn(40)	C(29)	C(30)	C(31)	-60.5(4)
C(8)	C(9)	N(1)	C(17B)	22.8(8)	Mn(40)	C(29)	C(33)	C(32)	62.3(5)
C(10)	C(5)	C(6)	C(7)	2.7(8)	Mn(40)	C(30)	C(31)	C(32)	-61.4(4)
C(10)	C(5)	C(6)	F(24)	-175.7(4)	Mn(40)	C(31)	C(32)	C(33)	-59.7(5)
C(10)	C(9)	N(1)	C(2)	-0.2(8)	Mn(40)	C(32)	C(33)	C(29)	-61.7(5)
C(10)	C(9)	N(1)	C(17A)	159.9(6)	N(1)	C(2)	C(3)	C(4)	-0.2(8)
C(10)	C(9)	N(1)	C(17B)	-159.1(6)	N(1)	C(2)	C(3)	C(20)	178.1(5)
C(12)	C(13)	N(14)	C(15)	56.8(6)	N(1)	C(9)	C(10)	C(4)	0.4(7)
C(12)	C(13)	N(14)	C(25)	177.6(5)	N(1)	C(9)	C(10)	C(5)	179.6(4)
C(13)	C(12)	N(11)	C(7)	-164.6(5)	N(1)	C(17A)	C(18)	C(19A)	-102.3(9)
C(13)	C(12)	N(11)	C(16)	57.1(6)	N(1)	C(17A)	C(19A)	C(18)	111.5(6)
C(15)	C(16)	N(11)	C(7)	161.6(4)	N(1)	C(17B)	C(18)	C(19B)	99.6(11)
C(15)	C(16)	N(11)	C(12)	-59.3(6)	N(1)	C(17B)	C(19B)	C(18)	-114.6(8)
C(16)	C(15)	N(14)	C(13)	-59.8(6)	N(11)	C(7)	C(8)	C(9)	174.0(5)
C(16)	C(15)	N(14)	C(25)	-179.1(4)	N(11)	C(12)	C(13)	N(14)	-56.6(6)
C(18)	C(17A)	N(1)	C(2)	-50.7(10)	N(14)	C(15)	C(16)	N(11)	61.5(6)
C(18)	C(17A)	N(1)	C(9)	149.0(6)	N(14)	C(25)	C(26)	C(27)	-172.7(5)
C(18)	C(17B)	N(1)	C(2)	40.6(11)	O(23)	C(4)	C(10)	C(5)	1.4(7)
C(18)	C(17B)	N(1)	C(9)	-160.7(7)	O(23)	C(4)	C(10)	C(9)	-179.4(4)
C(19A)	C(17A)	N(1)	C(2)	-123.5(6)	O(28)	C(27)	C(29)	C(30)	-178.0(6)
C(19A)	C(17A)	N(1)	C(9)	76.2(7)	O(28)	C(27)	C(29)	C(33)	-0.1(10)
C(19B)	C(17B)	N(1)	C(2)	112.9(8)	O(28)	C(27)	C(29)	Mn(40)	87.0(7)

C(19B)	C(17B)	N(1)	C(9)	-88.4(8)

Table S8 Hydrogen-bond geometry in the crystal of **4**.

D−H···A	**d(D−H) (Å)**	**d(H···A) Å**	**d(D···A) Å**	**<D−H···A (°)**
O21−H21···O23*	0.82(5)	1.81(7)	2.534(6)	146(9)
C2−H2···O22*	0.93	2.51	2.823(7)	100
C2−H2···O28^{i}	0.93	2.46	3.206(7)	137
C13−H13B···O23^{ii}	0.97	2.45	3.341(7)	152
C16−H16A···F24*	0.97	2.26	2.909(6)	124
C25−H25A···O28*	0.97	2.45	2.808(8)	102
C34−H34···O22^{iii}	0.98	2.54	3.454(8)	156
C37−H37···F24^{ii}	0.93	2.40	3.262(7)	154

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $x, y + 1, z$; (iii) $x - 1/2, y + 3/2, z$; (*) intramolecular interaction.

Table S9 The geometry of π–π interactions in the crystal of **4**.

***Cg*I**	***Cg*J**	***Cg*I···*Cg*J (Å)**	**Dihedral angle (°)**	**Interplanar distance (Å)**	**Offset (Å)**
4	4^{iv}	3.530(3)	0	3.363(2)	1.073(3)
4	6^{iv}	3.739(3)	2.5(2)	3.366(2)	1.628(3)
6	4^{iv}	3.740(3)	2.5(2)	3.408(2)	1.540(3)
6	6^{v}	3.756(3)	13	3.576(2)	1.149(3)

*Cg*4 and *Cg*6 denote geometric centers of aromatic rings delineated by the N1/C2−C4/C10−C9 and C5−C10 atoms, respectively. Symmetry codes: (iv) −*x* + 1, −*y* − 1, −*z*; (v) −*x* + 1, *y*, −*z* + 1/2.

Table S10 The geometry of the C−F···π contacts in the crystal of **4**.

D−X	***Cg*I**	**d(X···*Cg*I) (Å)**	**<Y−X···*Cg*I (°)**
C6−F24	4^{v}	3.500(4)	103.0(3)
C6−F24	6^{v}	3.811(4)	70.2(3)

*Cg*4 and *Cg*6 denote geometric centers of aromatic rings delineated by the N1/C2−C4/C10−C9 and C5−C10 atoms, respectively. Symmetry code: (v) $-x + 1, y, -z + 1/2$.

Table S11 Hydrogen-bond geometry in the crystal of **6**.

D−H···A	**d(D−H) (Å)**	**d(H···A) Å**	**d(D···A) Å**	**<D−H···A (°)**
O21−H21···O23*	0.82(6)	1.74(6)	2.529(5)	162(8)
C2−H2···O22*	0.93	2.50	2.825(6)	100
C5−H5···O23^{i}	0.93	2.27	3.127(5)	153
C13−H13A···O21^{ii}	0.97	2.50	3.396(6)	154
C16−H16A···F24*	0.97	2.18	2.860(5)	126
C19A−H19A···O23^{iii}	0.97	2.51	3.264(10)	135

Symmetry codes: (i) $-x, -y-1, -z+1$; (ii) $-x, -y, -z+1$; (iii) $x, y+1, z$; (*) intramolecular interaction.

Table S12 The geometry of π–π interactions in the crystal of **6**.

***Cg*I**	***Cg*J**	***Cg*I···*Cg*J (Å)**	**Dihedral angle (°)**	**Interplanar distance (Å)**	**Offset (Å)**
4	6^{ii}	3.651(2)	0.9(2)	3.421(2)	1.275(2)
6	4^{ii}	3.651(2)	0.9(2)	3.440(2)	1.223(2)
6	6^{ii}	3.874(2)	0	3.437(2)	1.787(2)

*Cg*4 and *Cg*6 denote geometric centers of aromatic rings delineated by the N1/C2−C4/C10−C9 and C5−C10 atoms, respectively. Symmetry code: (ii) $-x, -y, -z + 1$.

Table S13 The geometry of the C−F···π contacts in the crystal of **6**.

D−X	***Cg*I**	**d(X···*Cg*I) (Å)**	**<Y−X···*Cg*I (°)**
C6−F24	4[ii]	3.659(3)	69.3(2)
C36−O37	6[iv]	3.779(4)	96.3(3)
C38−O39	4[iv]	3.153(4)	122.0(4)

*Cg*4 and *Cg*6 denote geometric centers of aromatic rings delineated by the N1/C2−C4/C10−C9 and C5−C10 atoms, respectively. Symmetry codes: (ii) $-x, -y, -z+1$; (iv) $-x, y+1/2, -z+3/2$.