Electronic supplementary information for

AIE-Active β-diketones Containing Pyridiniums: Fluorogenic Binding to Cellulose and Water-Vapour-Recoverable Mechanochromic Luminescence

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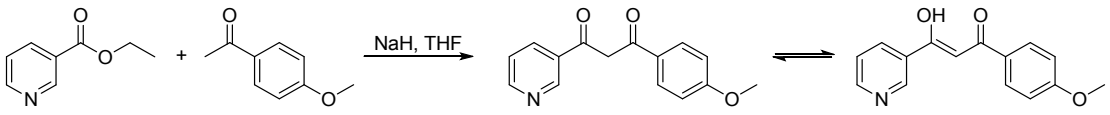
Materials

Tetrahydrofuran (THF) and toluene were distilled by refluxing with sodium for 3 h before use. Sodium hydride (95%) and boron trifluoride diethyl etherate (99.8%, purified by redistillation) were purchased from Sigma–Aldrich. All other reagents and solvents were obtained from Aladdin Reagent (Shanghai) and were used as received.

Methods

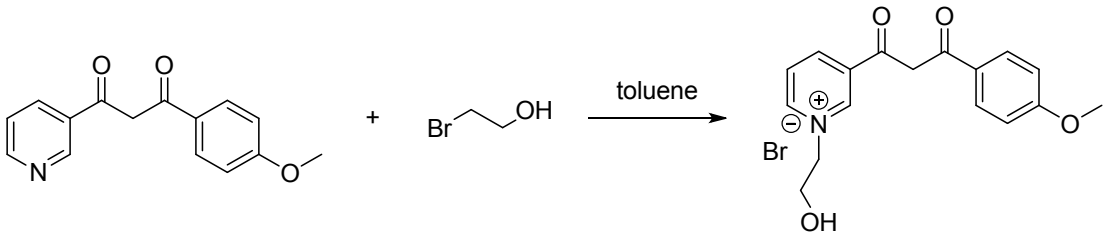
^{1}H NMR (400 MHz) spectra were recorded on a Bruker AV300 NMR spectrometer operated in the Fourier transform mode. ^{1}H NMR spectra were referenced to the signal for residual protiochloroform at 7.26 ppm and coupling constants are given in hertz. UV–vis absorption spectra were recorded on a Beijing Persee TU-1901 UV–vis spectrometer. Photographs were taken by a Cannon 500D digital camera. Steady-state emission spectra were recorded on a Horiba FluoroMax-4 spectrofluorometer (Japan). Fluorescence lifetime data were acquired with a 1 MHz LED laser with the excitation peak at 372 nm (NanoLED-370). Lifetime data were analyzed with DataStation v6.6 (Horiba Scientific).

Synthesis



To a dried round-bottom flask, 4-methoxyacetophenone (1.50 g, 10 mmol), ethyl nicotinate (6.05 g, 40 mmol), THF (10 mL) and sodium hydride (95%, 0.51 g, 20 mmol) were added successively at room tempreture. The mixture was refluxed for 6 h. After cooling to room temperature, the reaction was quenched with saturated $NaHCO_3$ aqueous solution and the solvent was removed in vacuo. The mixture was extracted with ethyl acetate (50 mL × 3). The organic phase were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The final product was

obtained by recrystallization in ethyl acetate (2.30 g, 90%).



1-(4-Methoxyphenyl)-3-(pyridin-3-yl)propane-1,3-dione (0.51 g, 2.0 mmol) and 2-bromoethanol (98%, 0.51 g, 4.0 mmol) were dissolved in toluene (10 mL) and the mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtered and the residue was washed with toluene to afford the product as a pale green solid (0.70 g, 92%).
1: δ (400 MHz, DMSO-d_6) 16.93 (1 H, s), 9.70 (1 H, s), 9.27 (1 H, d, *J* 8.3), 9.18 (1 H, d, *J* 6.0), 8.36 (1 H, dd, *J* 8.1, 6.1), 8.23 (2 H, d, *J* 8.9), 7.55 (1 H, s), 7.18 (2 H, d, *J* 8.9), 5.30 (1 H, s), 4.79 (2 H, t), 3.94 (2 H, t), 3.89 (3 H, s). HRMS (APCI) m/z calcd for $C_{17}H_{18}NO_4^+$, 300.12303; found 300.12271.

Compounds **2**, **3**, **4**, **5**, **6** were synthesized following the same procedure as **1**.

2 (yield 90%)**:** δ (400 MHz, DMSO-d_6) 16.90 (1 H, s), 9.81 (1 H, s), 9.29 (1 H, d, *J* 6.0), 9.21 (1 H, d, *J* 8.2), 8.35 (1 H, dd, *J* 8.0, 6.2), 8.24 (2 H, d, *J* 8.9), 7.56 (1 H, s), 7.18 (2 H, d, *J* 8.9), 4.76 (2 H, q, *J* 7.3), 3.91 (3 H, s), 1.62 (3 H, t, *J* 7.3). HRMS (APCI) m/z calcd for $C_{17}H_{18}NO_3^+$, 284.12812; found 284.12778.

3 (yield 87%)**:** δ (400 MHz, DMSO-d_6) 16.59 (1 H, s), 9.76 (1 H, s), 9.25 (2 H, dd, *J* 30.2, 7.1), 8.38 (1 H, dd, *J* 8.0, 6.1), 8.24 (2 H, d, *J* 7.4), 7.75 (1 H, t, *J* 7.3), 7.70-7.61 (3 H, m), 5.30 (1 H, s), 4.81 (2 H, t), 3.95 (2 H, t). HRMS (APCI) m/z calcd for $C_{16}H_{16}NO_3^+$, 270.11247; found 270.12212.

4 (yield 90%)**:** δ (400 MHz, DMSO-d_6) 16.89 (1 H, s), 9.67 (1 H, s), 9.27 (1 H, d, *J* 8.5), 9.18 (1 H, d, *J* 6.1), 8.39-8.33 (1 H, m), 8.22 (2 H, d, *J* 8.9), 7.54 (1 H, s), 7.19 (2 H, d, *J* 9.0), 5.29 (1 H, t, *J* 5.3), 4.78 (2 H, t), 3.97-3.92 (2 H, m), 3.89 (3 H, s). HRMS (APCI) m/z calcd for $C_{17}H_{18}NO_4^+$, 300.12303; found 300.12283.

5 (yield 83%)**:** δ (400 MHz, DMSO-d_6) 16.76 (1 H, s), 9.76 (1 H, s), 9.31 (1 H, d, *J* 8.2), 9.21 (1 H, d, *J* 6.0), 8.86 (1 H, s), 8.39 (1 H, dd, *J* 8.0, 6.2), 8.21 (1 H, dd, *J* 8.7, 1.6), 8.06 (2 H, dd, *J* 20.2, 8.9), 7.73 (1 H, s), 7.49 (1 H, d, *J* 2.1), 7.33 (1 H, dd, *J* 9.0, 2.4), 5.32 (1 H, s), 4.82 (2 H, t), 3.95 (5 H, s). HRMS (APCI) m/z calcd for $C_{21}H_{20}NO_4^+$, 350.13868; found 350.13846.

6 (yield 85%)**:** δ (400 MHz, DMSO-d_6) 9.76 (1 H, s), 9.30 (1 H, d, *J* 8.1), 9.21 (1 H, d, *J* 6.0), 8.96 (1 H, d, *J* 9.4), 8.64 (1 H, d, *J* 8.1), 8.54-8.29 (7 H, m), 8.21 (1 H, t, *J* 7.6), 7.60 (1 H, s), 5.31 (1 H, s), 4.80 (2 H, t), 3.95 (2 H, s). HRMS (APCI) m/z calcd for $C_{26}H_{20}NO_3^+$, 394.14377; found 394.14349.

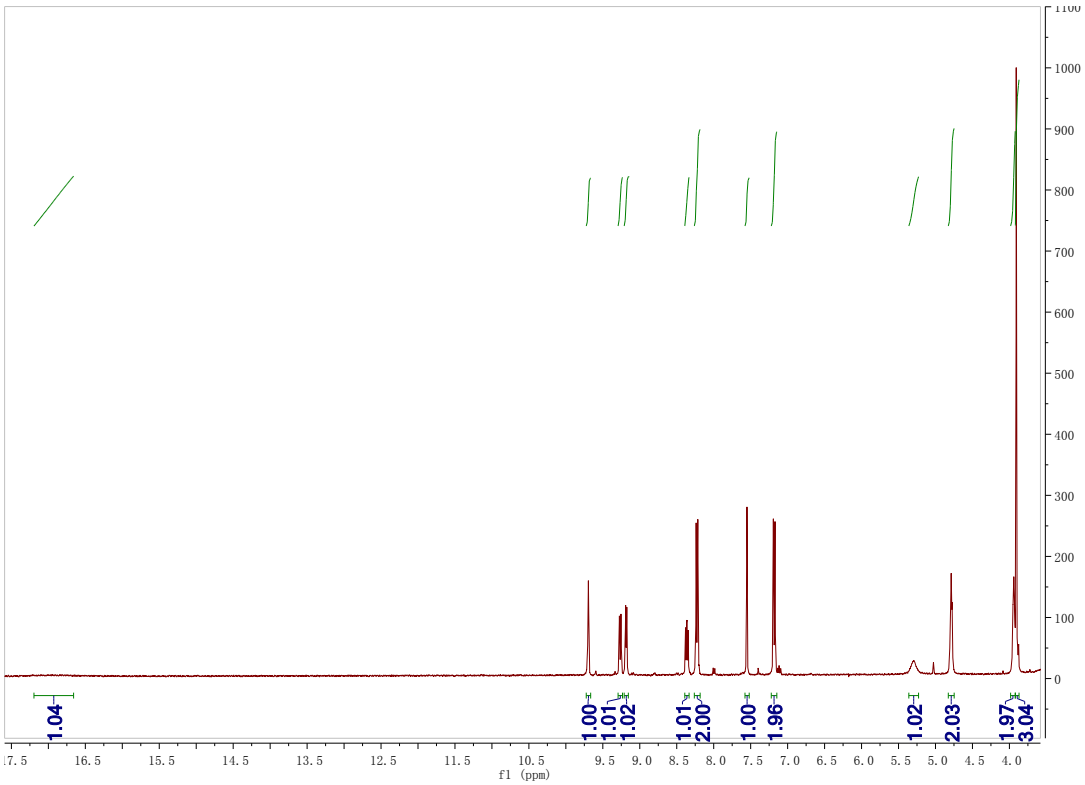


Figure S1. ^{1}H NMR spectra of **1** in DMSO-d_6.

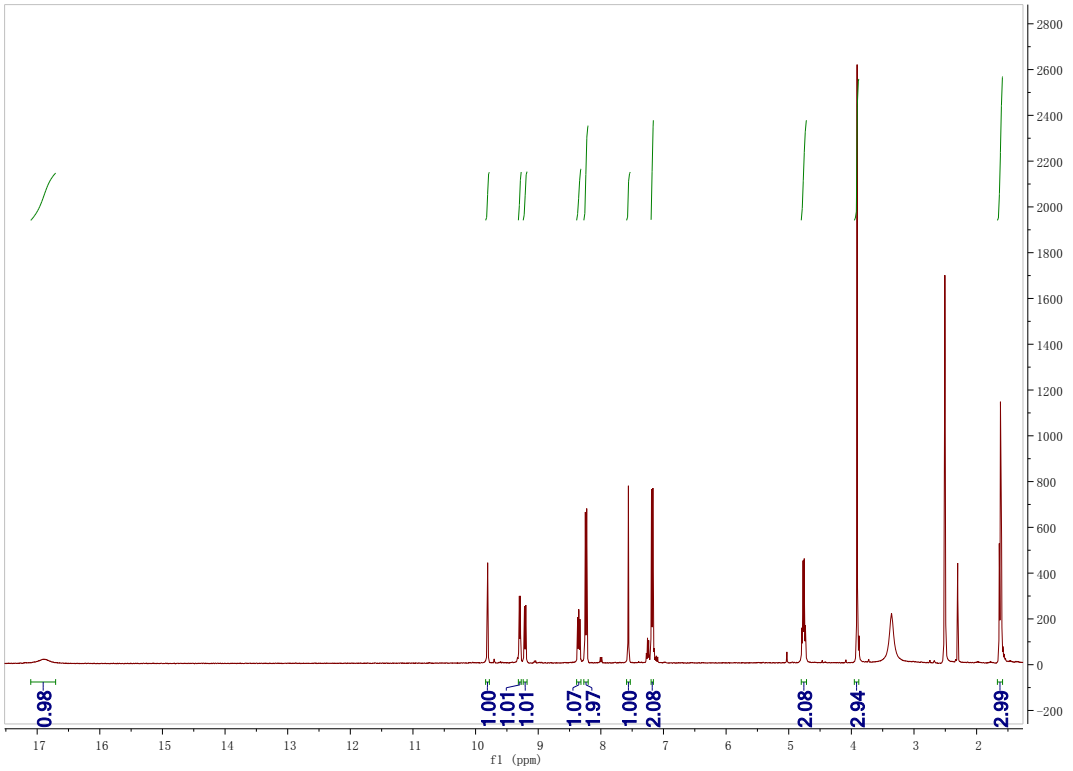


Figure S2. ^{1}H NMR spectra of **2** in DMSO-d_6.

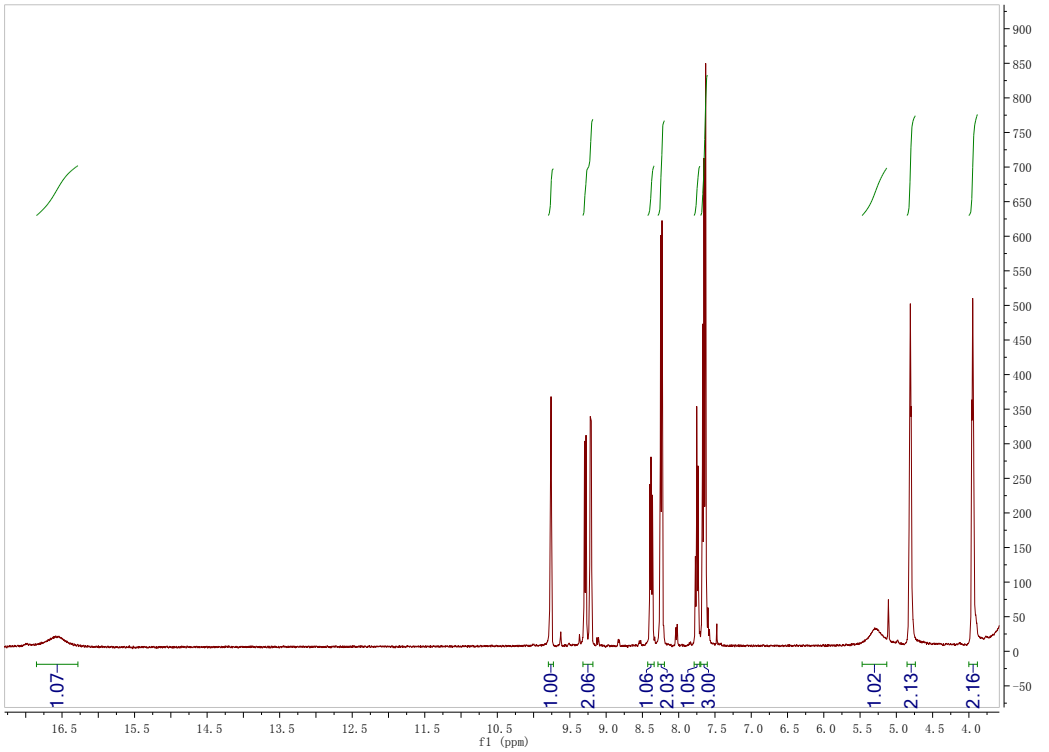


Figure S3. ^{1}H NMR spectra of **3** in DMSO-d_6.

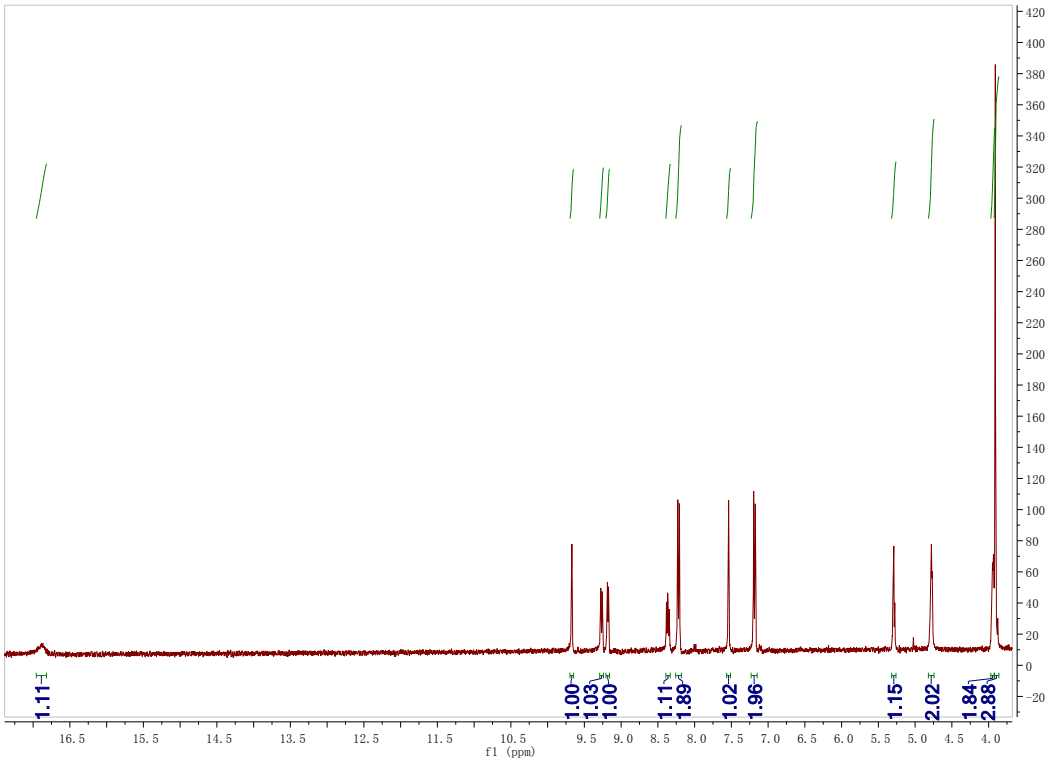


Figure S4. ^{1}H NMR spectra of **4** in DMSO-d_6.

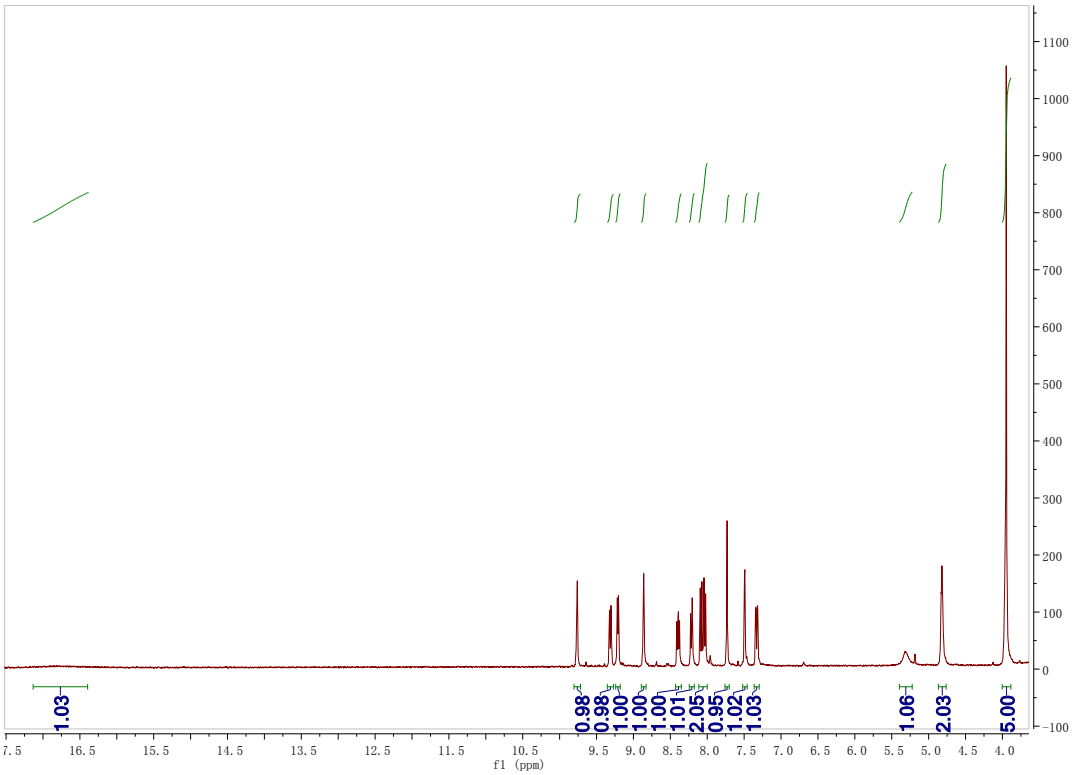


Figure S5. ^{1}H NMR spectra of **5** in DMSO-d_6.

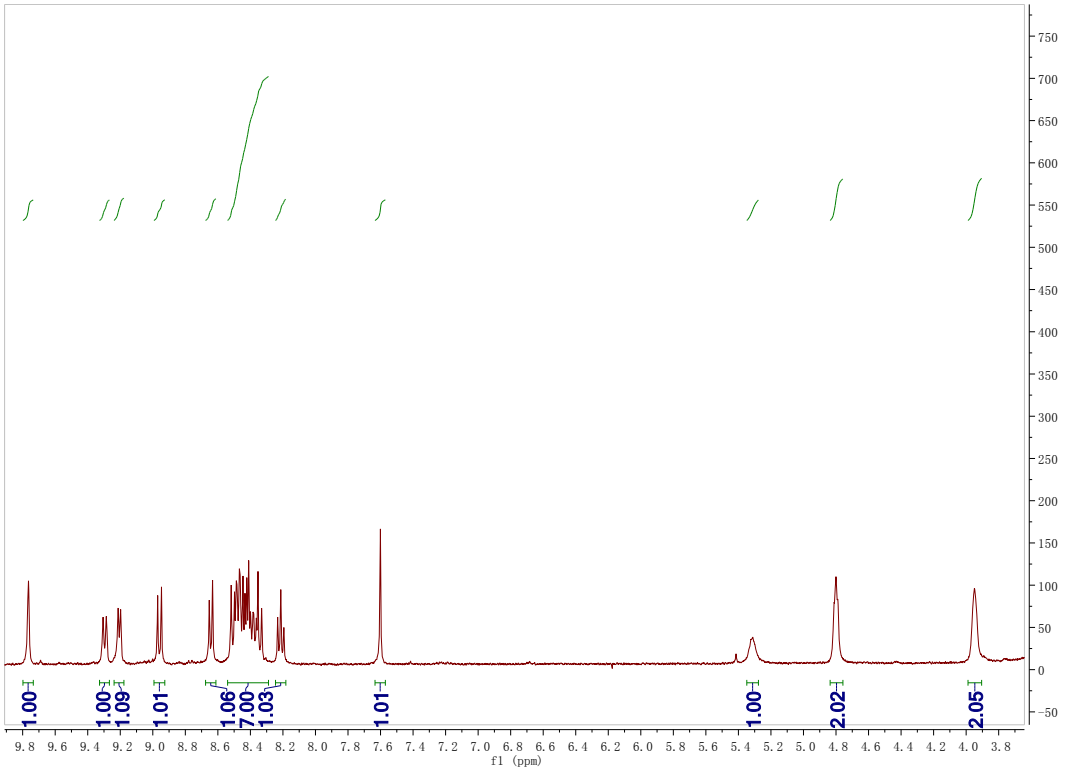


Figure S6. ^{1}H NMR spectra of **6** in DMSO-d_6.

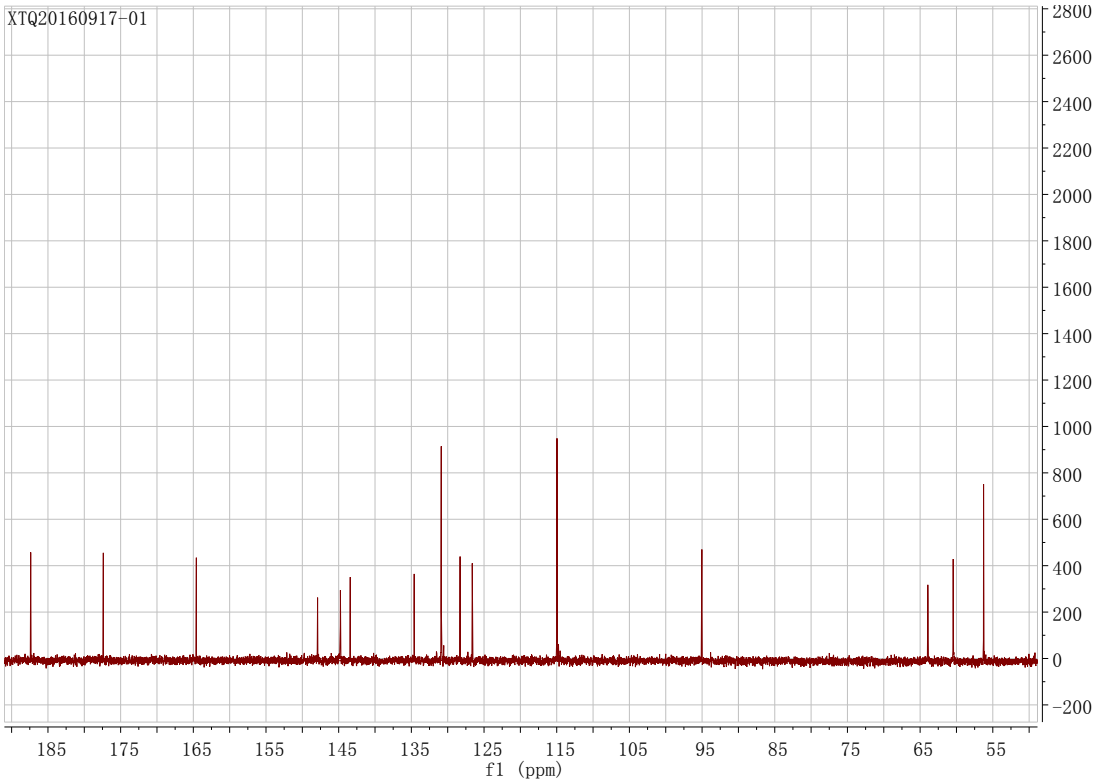


Figure S7. ^{13}C NMR spectra of **1** in DMSO-d_6.

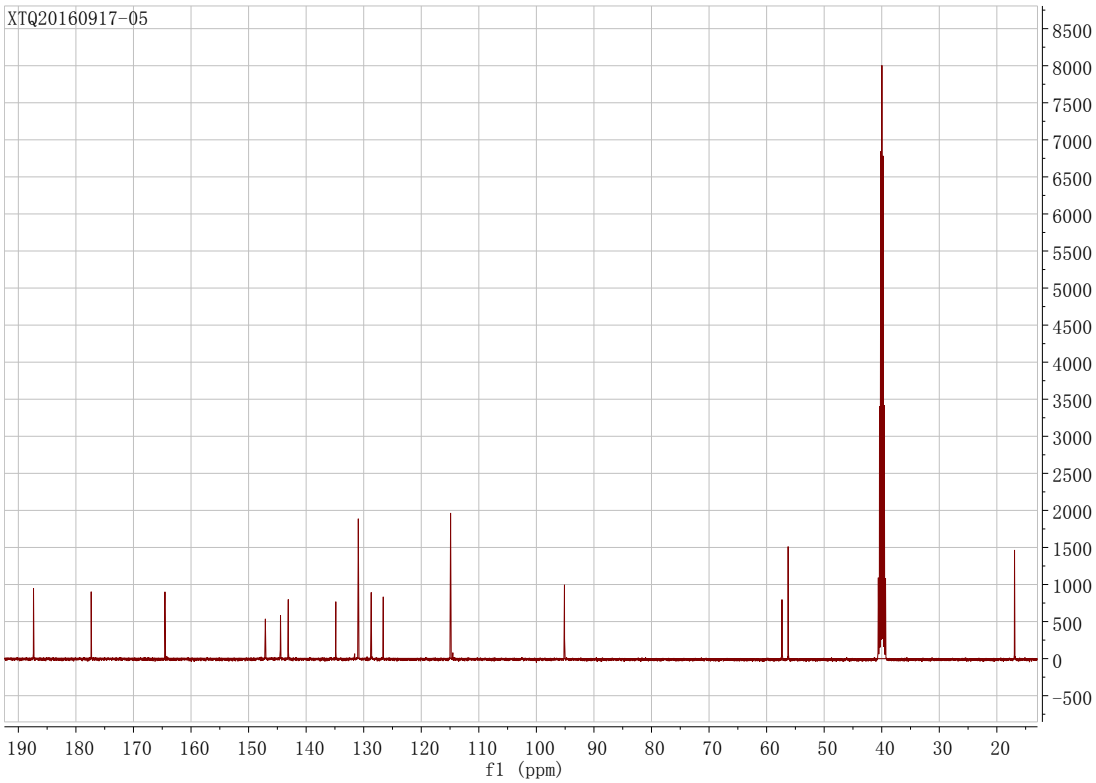


Figure S8. ^{13}C NMR spectra of **2** in DMSO-d_6.

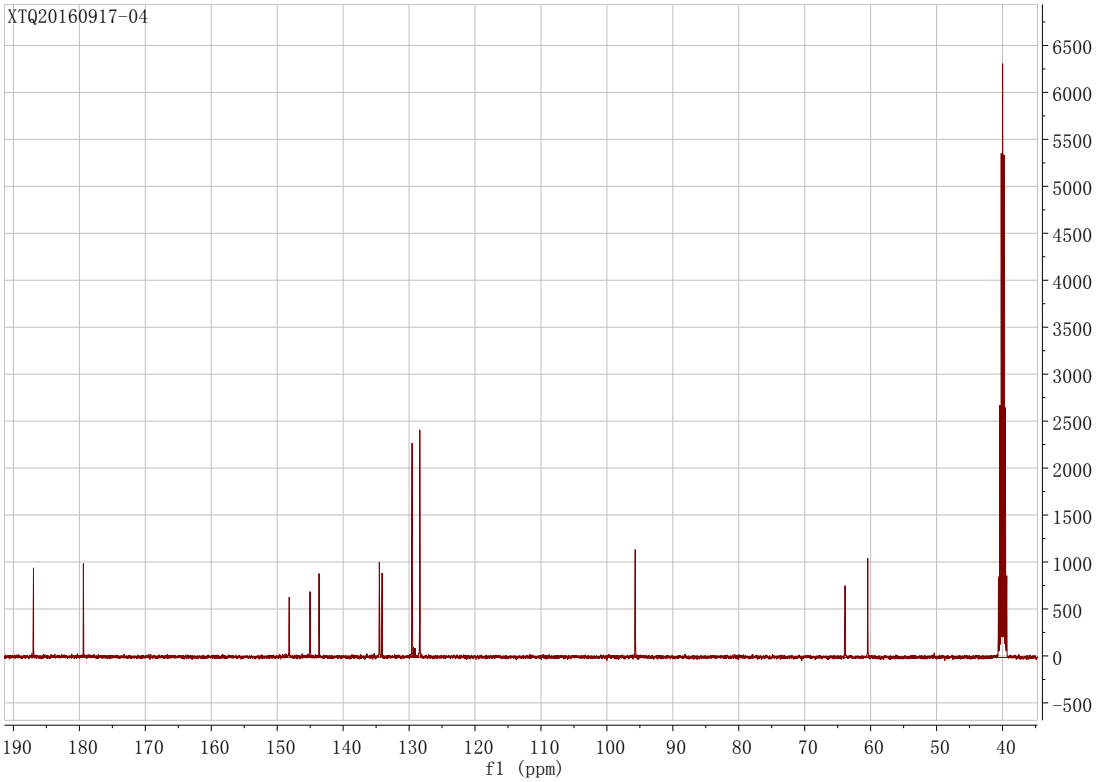


Figure S9. ^{13}C NMR spectra of **3** in DMSO-d_6.

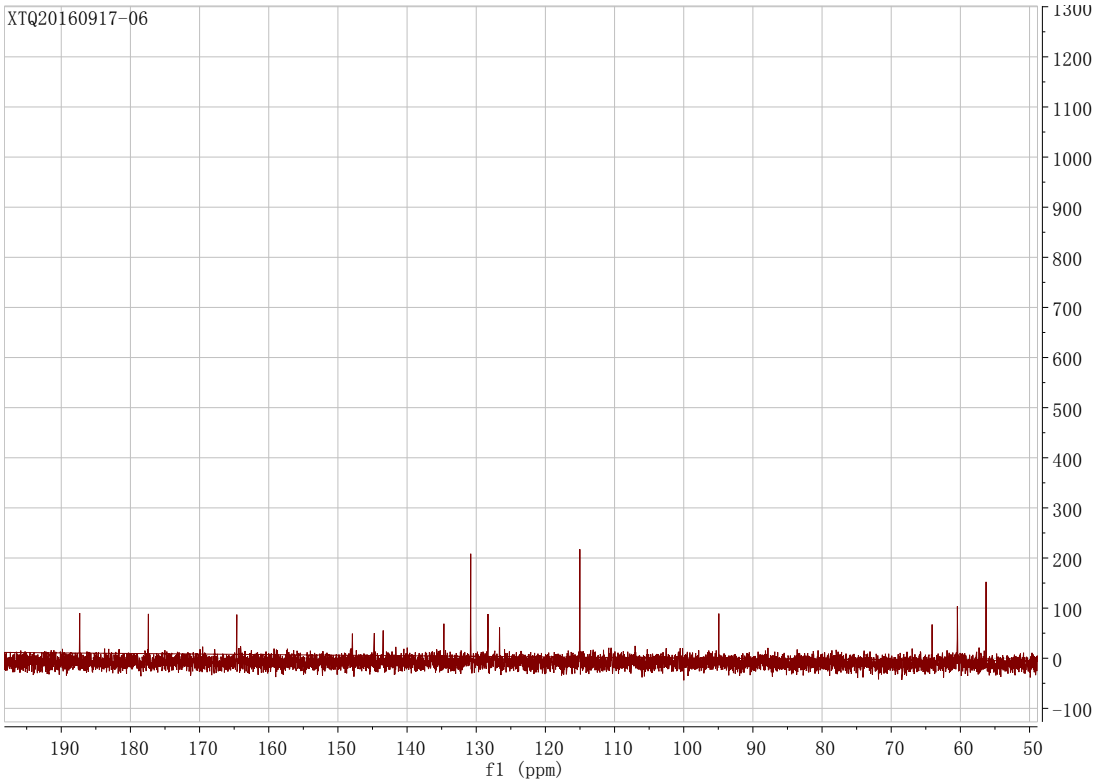


Figure S10. ^{13}C NMR spectra of **4** in DMSO-d_6.

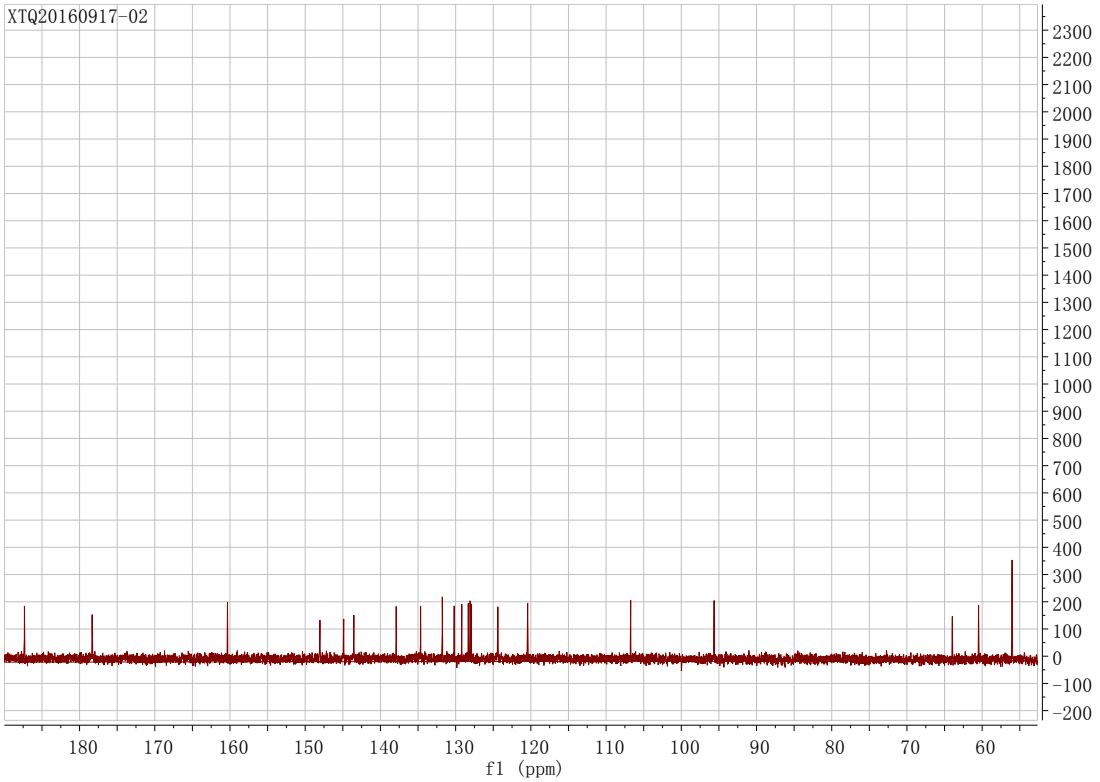


Figure S11. ^{13}C NMR spectra of **5** in DMSO-d_6.

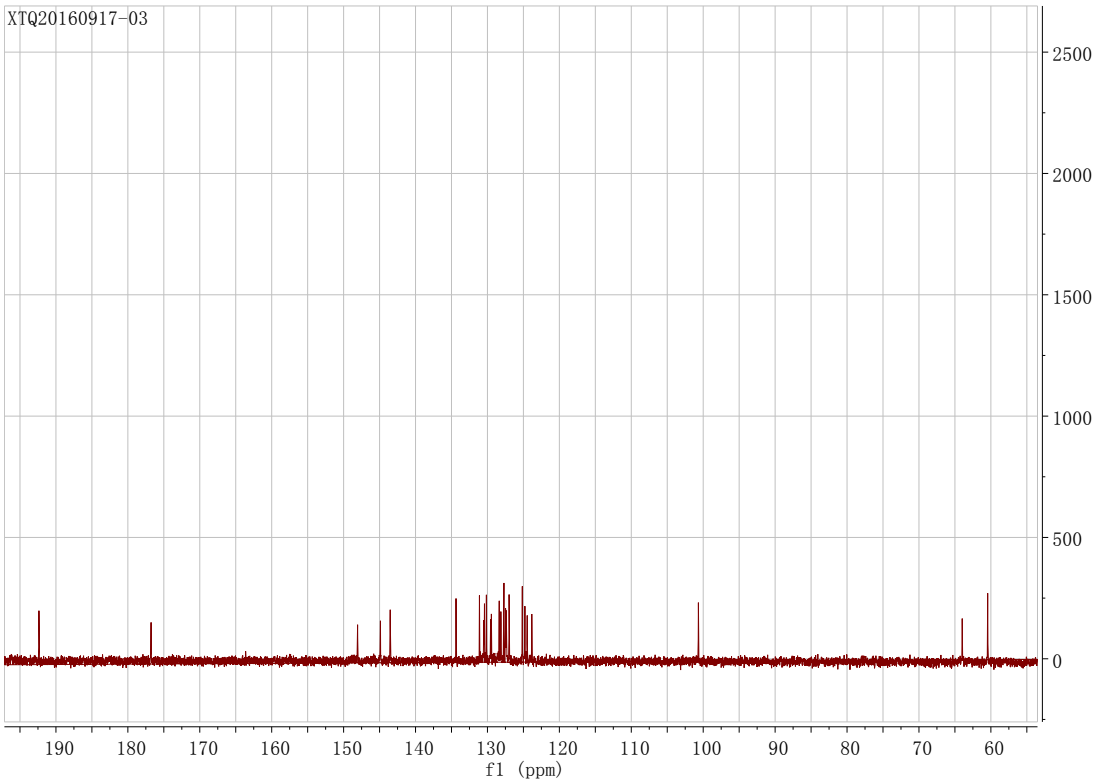


Figure S12. ^{13}C NMR spectra of **6** in DMSO-d_6.

Table S1 Crystal data and structure refinement for **1.**

Identification code	xtq0427
Empirical formula	$C_{17}H_{20}BrNO_5$
Formula weight	398.25
Temperature/K	290(2)
Crystal system	triclinic
Space group	P-1
a/Å	5.2286(5)
b/Å	8.3500(6)
c/Å	20.2441(18)
α/°	79.956(7)
β/°	89.888(8)
γ/°	81.369(7)
Volume/Å^3	860.17(13)
Z	2
ρ_{calc}mg/mm^3	1.538
m/mm^{-1}	2.416
F(000)	408.0
Crystal size/mm^3	0.35 × 0.32 × 0.31
2Θ range for data collection	5.74 to 52.74°
Index ranges	-6 ≤ h ≤ 6, -10 ≤ k ≤ 10, -25 ≤ l ≤ 20
Reflections collected	7194
Independent reflections	3460[R(int) = 0.0513]
Data/restraints/parameters	3460/4/232
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0586, wR_2 = 0.1258
Final R indexes [all data]	R_1 = 0.0965, wR_2 = 0.1487
Largest diff. peak/hole / e Å^{-3}	0.52/-0.62

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1.** U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	1788.9(9)	1712.7(6)	1297.6(2)	68.3(2)
O3	1077(6)	3576(4)	3693.9(14)	56.4(8)
O2	11388(6)	-1514(4)	4193.2(14)	55.3(8)
O1	14547(6)	-3270(4)	3622.1(15)	56.7(8)
N1	13478(7)	-3946(4)	1382.7(16)	45.9(8)
O4	15809(8)	-2996(6)	124.1(19)	103.6(15)
O5	7400(7)	9217(5)	1500(2)	83.7(11)
C6	13034(8)	-2858(5)	3096(2)	45.5(10)
C3	16239(8)	-4720(5)	2558(2)	53.6(11)
C4	13980(7)	-3603(5)	2508.3(19)	41.5(9)
C11	3809(8)	1818(5)	3137(2)	49.3(10)
C7	10743(8)	-1797(5)	3081(2)	45.6(10)
C8	9990(8)	-1096(5)	3647(2)	43.9(10)
C5	12646(8)	-3243(5)	1906(2)	46.2(10)
C9	7636(8)	113(5)	3662.5(19)	42.5(9)
C12	3244(8)	2430(5)	3720(2)	45.1(10)
C14	7024(9)	733(5)	4244(2)	49.2(10)
C13	4860(8)	1882(5)	4281(2)	51.5(11)
C1	15678(9)	-5049(5)	1436(2)	54.6(11)
C15	365(10)	4173(6)	4296(2)	62.7(13)
C16	12048(9)	-3463(6)	730(2)	60.9(13)
C10	5980(8)	682(5)	3107(2)	47.1(10)
C17	13308(10)	-2221(7)	261(2)	70.7(14)
C2	17085(9)	-5436(6)	2014(2)	58.7(12)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1.** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Br1	64.5(4)	71.7(4)	67.4(4)	-20.4(2)	9.0(2)	3.2(3)
O3	63(2)	48.4(18)	54.4(19)	-15.8(13)	3.3(14)	9.5(15)
O2	62(2)	56(2)	43.8(18)	-13.7(14)	-4.3(15)	9.0(16)
O1	59(2)	55(2)	52(2)	-13.8(15)	-2.4(16)	9.3(15)
N1	50(2)	42(2)	44(2)	-12.1(15)	5.8(16)	0.8(16)
O4	94(3)	114(4)	82(3)	17(2)	29(2)	11(3)

O5	64(3)	65(3)	113(3)	-3(2)	-8(2)	7(2)
C6	49(3)	37(2)	49(3)	-6.3(17)	0(2)	-3.8(19)
C3	54(3)	52(3)	49(3)	-4(2)	4(2)	6(2)
C4	44(2)	34(2)	44(2)	-4.6(16)	6.0(18)	-1.2(18)
C11	57(3)	49(3)	39(2)	-9.8(18)	-3.3(19)	3(2)
C7	47(2)	42(2)	46(2)	-12.8(17)	0.2(18)	4.7(19)
C8	51(3)	37(2)	44(2)	-7.4(17)	1.7(19)	-7.6(19)
C5	47(2)	38(2)	53(3)	-12.5(18)	7.7(19)	3.3(18)
C9	50(2)	37(2)	41(2)	-8.4(16)	3.7(18)	-3.2(18)
C12	47(2)	35(2)	50(3)	-5.2(17)	2.8(19)	-0.5(18)
C14	60(3)	47(3)	40(2)	-10.9(18)	-4.1(19)	-1(2)
C13	60(3)	48(3)	48(3)	-19.4(19)	4(2)	1(2)
C1	59(3)	46(3)	59(3)	-16(2)	15(2)	-1(2)
C15	67(3)	56(3)	63(3)	-19(2)	12(2)	8(2)
C16	61(3)	68(3)	54(3)	-23(2)	-5(2)	5(3)
C10	59(3)	45(2)	38(2)	-12.8(17)	3.1(19)	-2(2)
C17	87(4)	67(3)	52(3)	-10(2)	2(3)	7(3)
C2	58(3)	48(3)	63(3)	-6(2)	10(2)	9(2)

Table S4 Bond Lengths for **1.**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O3	C12	1.364(5)	C4	C5	1.370(6)
O3	C15	1.423(5)	C11	C12	1.380(5)
O2	C8	1.293(5)	C11	C10	1.374(5)
O1	C6	1.293(5)	C7	C8	1.405(5)
N1	C5	1.340(5)	C8	C9	1.474(5)
N1	C1	1.353(5)	C9	C14	1.385(5)
N1	C16	1.482(5)	C9	C10	1.390(5)
O4	C17	1.418(6)	C12	C13	1.386(5)
C6	C4	1.487(5)	C14	C13	1.381(6)
C6	C7	1.376(5)	C1	C2	1.347(6)
C3	C4	1.383(5)	C16	C17	1.507(7)
C3	C2	1.383(6)			

Table S5 Bond Angles for **1.**

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C12	O3	C15	117.4(3)	C7	C8	C9	123.6(4)
C5	N1	C1	120.6(4)	N1	C5	C4	121.6(4)
C5	N1	C16	120.0(3)	C14	C9	C8	119.9(4)
C1	N1	C16	119.4(3)	C14	C9	C10	117.7(4)
O1	C6	C4	114.8(3)	C10	C9	C8	122.4(3)
O1	C6	C7	122.4(4)	O3	C12	C11	115.9(4)
C7	C6	C4	122.8(4)	O3	C12	C13	124.2(4)
C2	C3	C4	120.4(4)	C11	C12	C13	119.8(4)
C3	C4	C6	120.6(4)	C13	C14	C9	122.0(4)
C5	C4	C6	121.9(3)	C14	C13	C12	119.0(4)
C5	C4	C3	117.5(4)	C2	C1	N1	120.4(4)
C10	C11	C12	120.4(4)	N1	C16	C17	110.9(4)
C6	C7	C8	120.1(4)	C11	C10	C9	120.9(4)
O2	C8	C7	119.9(4)	O4	C17	C16	107.6(4)
O2	C8	C9	116.6(3)	C1	C2	C3	119.5(4)

Table S6 Hydrogen Bonds for **1.**

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O4	H4	Br1[1]	0.82	2.42	3.213(4)	163.5
O2	H2	O1	0.85(2)	1.64(4)	2.464(4)	163(10)
O1	H1	O2	0.85(2)	1.74(7)	2.464(4)	143(10)
O5	H5A	Br1[2]	0.846(19)	2.47(2)	3.303(4)	169(5)
O5	H5B	Br1[3]	0.852(19)	2.50(3)	3.315(4)	161(5)

[1]2-X,-Y,-Z; [2]1+X,1+Y,+Z; [3]+X,1+Y,+Z

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **1.**

Atom	*x*	*y*	*z*	U(eq)
H4	16345	-2473	-215	124
H3	17194	-4992	2959	64
H11	2713	2176	2762	59
H7	9692	-1543	2695	55
H5	11125	-2491	1859	55
H14	8105	364	4621	59

H13	4491	2283	4677	62
H1A	16223	-5543	1072	66
H15A	-1189	4960	4214	94
H15B	1733	4690	4441	94
H15C	72	3272	4638	94
H16A	10277	-2997	802	73
H16B	12008	-4431	527	73
H10	6348	288	2710	57
H17A	12288	-1855	-152	85
H17B	13439	-1272	468	85
H2A	18614	-6179	2048	70
H2	12660(140)	-2130(110)	4060(50)	70
H1	13980(190)	-2820(120)	3950(40)	70
H5A	8380(90)	9940(50)	1400(30)	88
H5B	5820(50)	9650(70)	1430(30)	88