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Engaging DBFO as a C1N1 "Two-Atom Synthon" in [3+2] Cycloaddition Reaction: Synthesis of energetic materials 5-Azidotetrazole 1*N*-Oxide

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Table of Contents

1 Crystallographic Data for 2, 5–9

Table S1 Crystal data and structure refinement details of 2, 5–9

Compound Name	**2**	**5·3H$_2$O**	**6·3H$_2$O**	**7·H$_2$O**	**8**	**9**
Empirical formula	CH_4BrN_5O	CH_6LiN7O_4	$CH_6N_7NaO_4$	$CH_2KN_7O_2$	CH_4N_8O	$C_2H_6N_{10}O$
Formula weight	182.00	187.07	203.12	183.2	144.12	186.17
Temperature [K]	298(2)	298(2)	296(2)	298(2)	298(2)	298(2)
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	*Pbca*	$P2_1/n$	*P*-1	*P*1	*P*21/c	C2/c
A [Å]	13.6300(12)	10.8794(11)	6.5213(10)	4.1780(5)	8.1819(8)	11.6030(11)
B [Å]	7.5726(7)	6.6298(7)	6.6446(10)	5.2749(6)	31.960(3)	7.7399(7)
C [Å]	21.2621(19)	12.4870(13)	10.3328(16)	8.0471(8)	7.6696(7)	17.4853(15)
α [°]	90.00	90.00	97.055(2)	97.332(3)	90	90.00
β [°]	90.00	111.646(5)	104.341(2)	91.810(2)	117.412(5)	101.915(3)
γ [°]	90.00	90.00	107.556(2)	91.691(2)	90	90.00
V [Å^3]	2194.6(3)	837.15(15)	404.01(11)	175.71(3)	1780.4(3)	1536.5(2)
Z	16	4	2	1	12	8
ρ [g·cm^{-3}]	2.203	1.484	1.67	1.731	1.613	1.610
F(000)	1408.0	384.0	208	92	888	768.0
Crystal size [mm^3]	0.40 × 0.11 × 0.05	0.20 × 0.13 × 0.10	0.12 × 0.10 × 0.08	0.40 × 0.30 × 0.16	0.49 × 0.32 × 0.11	0.47 × 0.35 × 0.30
Θ [°]	4.86 to 50.04	4.26 to 50.04	4.166 to 54.79	5.1 to 50	5.1 to 50.04	4.76 to 50.02
Index ranges	-16 ≤ h ≤ 16, -8 ≤ k ≤ 9, -25 ≤ l ≤ 9	-12 ≤ h ≤ 11, -7 ≤ k ≤ 7, -14 ≤ l ≤ 12	-8 ≤ h ≤ 8, -8 ≤ k ≤ 8, -7 ≤ l ≤ 13	-4 ≤ h ≤ 4, -6 ≤ k ≤ 6, -8 ≤ l ≤ 9	-7 ≤ h ≤ 9, -31 ≤ k ≤ 38, -9 ≤ l ≤ 9	-13 ≤ h ≤ 13, -7 ≤ k ≤ 9, -20 ≤ l ≤ 20
Reflections collected	9136	4055	2483	870	8850	3712
Independent reflections	1915	1467	1778	733	3108	1352
Goodness-of-fit on F^2	1.006	1.084	0.988	1.12	1.076	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0793, wR_2 = 0.2274	R_1 = 0.0636, wR_2 = 0.1340	R_1 = 0.0358, wR_2 = 0.1125	R_1 = 0.0577, wR_2 = 0.1571	R_1 = 0.0796, wR_2 = 0.1903	R_1 = 0.0523, wR_2 = 0.1263
Final R indexes [all data]	R_1 = 0.1114, wR_2 = 0.2504	R_1 = 0.1037, wR_2 = 0.1487	R_1 = 0.0379, wR_2 = 0.1144	R_1 = 0.0582, wR_2 = 0.1582	R_1 = 0.1100, wR_2 = 0.2066	R_1 = 0.0685, wR_2 = 0.1330
CCDC No.	2057903	2044151	2044152	2044153	2044154	2044155

Table S2 Selected bond lengths of 5·3H_2O

bond	Length[Å]	bond	Length[Å]
Li1–O2	1.897(6)	N2–N3	1.320(3)
Li1–O4	1.963(6)	N3–N4	1.355(3)
Li1–O1	1.964(6)	N4–C1	1.330(4)
Li1–O3	1.971(6)	N5–N6	1.259(4)
N1–C1	1.338(3)	N5–C1	1.386(4)
N1–O1	1.342(3)	N6–N7	1.112(3)
N1–N2	1.343(3)		

Table S3 Selected angles of 5·3H_2O

bond	Angle [°]	bond	Angle [°]
O2-Li1-O4	118.4(3)	N3-N2-N1	106.2(2)
O2-Li1-O1	108.7(3)	N2-N3-N4	110.7(2)
O4-Li1-O1	109.2(3)	C1-N4-N3	105.4(2)
O2-Li1-O3	111.7(3)	N6-N5-C1	112.2(2)
O4-Li1-O3	98.9(2)	N7-N6-N5	172.4(3)
O1-Li1-O3	109.4(3)	N1-O1-Li1	122.5(2)
C1-N1-O1	129.2(2)	N4-C1-N1	109.2(2)
C1-N1-N2	108.5(2)	N4-C1-N5	129.9(3)
O1-N1-N2	122.3(2)	N1-C1-N5	120.9(2)

Table S4 Hydrogen bonds present in 5·3H_2O

D–H•••A	d(D-H) [Å]	d(H•••A) [Å]	< DHA [°]	d(D..A) [Å]	
O2-H2A•••N4	0.850	2.05	172.93	2.896	-x+2, -y+1, -z
O2-H2B•••O3	0.850	1.982	176.22	2.83	-x+1, -y+1, -z
O3-H3A•••O1	0.850	1.932	175.86	2.781	-x+3/2, y+1/2, -z+1/2
O3-H3B•••N2	0.850	2.064	170.77	2.906	-x+3/2, y-1/2, -z+1/2
O4-H4A•••O1	0.850	1.96	178.06	2.809	-x+3/2, y-1/2, -z+1/2
O4-H4Cb•••N7	0.850	2.355	155.3	3.147	-x+2, -y, -z

Table S5 Selected bond lengths of 6·3H$_2$O

bond	Length[Å]	bond	Length[Å]
N1–C3	1.324(2)	Na1–Na1^2	3.6222(13)
N1–N2	1.357(2)	N2–N3	1.304(2)
Na1–O4	2.3579(14)	C3–N4	1.3334(19)
Na1–O5	2.3950(14)	C3–N5	1.388(2)
Na1–O3	2.4133(14)	N3–N4	1.3440(19)
Na1–O4^1	2.4288(14)	N4–O1	1.3280(17)
Na1–O3^2	2.4302(14)	N5–N6	1.2490(19)
Na1–N7	2.7388(18)	N6–N7	1.119(2)
Na1–Na11	3.5390(14)		

^{1}1-X, 2-Y, 2-Z; ^{2}1-X, 1-Y, 2-Z

Table S6 Selected angles of 6·3H$_2$O

bond	Angle [°]	bond	Angle [°]
C3–N1–N2	105.49(13)	N7–Na1–Na1^1	124.24(5)
O4–Na1–O5	97.10(5)	O4–Na1–Na1^2	110.58(4)
O4–Na1–O3	99.81(5)	O5–Na1–Na1^2	126.09(4)
O5–Na1–O3	162.34(5)	O3–Na1–Na1^2	41.77(3)
O4–Na1–O4^1	84.66(5)	O4^1–Na1–Na1^2	135.27(5)
O5–Na1–O4^1	91.09(5)	O3^2–Na1–Na1^2	41.42(3)
O3–Na1–O4^1	95.51(5)	N7–Na1–Na1^2	75.62(4)
O4–Na1–O3^2	110.78(5)	Na1^1–Na1–Na1^2	136.20(4)
O5–Na1–O3^2	86.09(5)	N3–N2–N1	110.38(13)
O3–Na1–O3^2	83.19(5)	N1–C3–N4	109.26(13)
O4^1–Na1–O3^2	164.52(5)	N1–C3–N5	129.51(14)
O4–Na1–N7	166.61(6)	N4–C3–N5	121.23(14)
O5–Na1–N7	87.94(5)	Na1–O3–Na1^2	96.81(5)
O3–Na1–N7	76.70(5)	N2–N3–N4	106.88(13)
O4^1–Na1–N7	82.84(5)	O1–N4–C3	129.04(13)
O3^2–Na1–N7	81.85(5)	O1–N4–N3	122.95(12)
O4–Na1–Na1^1	43.10(3)	C3–N4–N3	107.98(13)
O5–Na1–Na1^1	95.48(4)	Na1–O4–Na1^1	95.34(5)
O3–Na1–Na1^1	100.33(4)	N6–N5–C3	112.44(13)
O4^1–Na1–Na1^1	41.56(3)	N7–N6–N5	172.76(17)
O3^2–Na1–Na1^1	153.87(5)	N6–N7–Na1	156.59(16)

^{1}1-X, 2-Y, 2-Z; ^{2}1-X, 1-Y, 2-Z

Table S7 Hydrogen bonds present in 6·3H$_2$O

D–H•••A	d(D-H) [Å]	d(H•••A) [Å]	< DHA [°]	d(D..A) [Å]	
O2–H2A•••O1	0.850	1.946	166.68	2.780	-x, -y, -z
O2–H2B•••O4	0.850	2.059	169.87	2.899	-x, -y+1, -z+1
O3–H3A•••N4	0.850	2.129	152.65	2.910	-x+1, -y+1, -z+1
O3–H3B•••O1	0.850	1.943	169.92	2.784	x, y+1, z+1
O3–H3B•••N1	0.850	2.563	140.41	3.263	x, y+1, z+1
O4–H4C•••O1	0.850	1.945	166.34	2.778	-x, -y+1, -z
O4–H4D•••N2	0.850	2.132	172.81	2.977	-x, -y, -z

Table S8 Selected bond lengths of 7·H_2O

bond	Length[Å]	bond	Length[Å]
K1–O1	2.754(5)	N1–N2	1.375(8)
K1–O2[1]	2.764(6)	N1–K1[1]	3.372(5)
K1–O2	2.766(6)	N2–N3	1.316(8)
K1–O1[2]	2.793(6)	N2–K1[5]	2.893(6)
K1–N2[3]	2.893(6)	N3–N4	1.346(10)
K1–N7[4]	3.075(8)	N4–C1	1.341(9)
K1–N5	3.190(6)	N5–N6	1.273(9)
K1–N1[2]	3.372(6)	N5–C1	1.408(9)
K1–K1[2]	4.1780(5)	N6–N7	1.114(11)
K1–K1[1]	4.1780(5)	N7–K1[6]	3.075(8)
N1–O1	1.325(7)	O1–K1[1]	2.793(6)
N1–C1	1.345(9)	O2–K1[2]	2.764(6)

[1]1+X, +Y, +Z; [2]-1+X, +Y, +Z; [3]-1+X, 1+Y, +Z; [4]+X, +Y, 1+Z; [5]1+X, -1+Y, +Z; [6]+X, +Y, -1+Z

Table S9 Selected angles of 7·H_2O

bond	Angle [°]	bond	Angle [°]
O1–K1–O2[1]	78.86(15)	N5–K1–K1[2]	107.56(12)
O1–K1–O2	159.82(17)	N1[2]–K1–K1[2]	56.33(10)
O2[1]–K1–O2	98.14(15)	O1–K1–K11	41.48(11)
O1–K1–O1[2]	97.74(15)	O2[1]–K1–K1[1]	40.95(11)
O2[1]–K1–O1[2]	159.97(17)	O2–K1–K1[1]	139.09(11)
O2–K1–O1[2]	78.17(14)	O1[2]–K1–K1[1]	139.22(11)
O1–K1–N2[3]	129.46(15)	N2[3]–K1–K1[1]	114.30(11)
O2[1]–K1–N2[3]	106.87(18)	N7[4]–K1–K1[1]	87.24(19)
O2–K1–N2[3]	70.63(16)	N5–K1–K1[1]	72.44(12)
O1[2]–K1–N2[3]	90.63(16)	N1[2]–K1–K1[1]	123.67(10)
O1–K1–N7[4]	81.6(2)	K1[2]–K1–K1[1]	180.00(4)
O2[1]–K1–N7[4]	74.1(2)	O1–N1–C1	129.4(6)
O2–K1–N7[4]	78.4(2)	O1–N1–N2	123.0(6)
O1[2]–K1–N7[4]	85.9(2)	C1–N1–N2	107.7(5)
N2[3]–K1–N7[4]	148.9(2)	O1–N1–K1[1]	53.4(3)
O1–K1–N5	57.74(17)	C1–N1–K1[1]	114.9(4)
O2[1]–K1–N5	108.25(15)	N2–N1–K1[1]	105.2(4)
O2–K1–N5	140.24(17)	N3–N2–N1	106.0(6)
O1[2]–K1–N5	85.70(14)	N3–N2–K1[5]	120.7(4)
N2[3]–K1–N5	73.50(15)	N1–N2–K1[5]	132.6(4)
N7[4]–K1–N5	136.8(2)	N2–N3–N4	111.3(5)
O1–K1–N1[2]	84.46(15)	C1–N4–N3	106.0(6)
O2[1]–K1–N1[2]	163.21(17)	N6–N5–C1	111.6(5)
O2–K1–N1[2]	96.85(16)	N6–N5–K1	139.3(5)
O1[2]–K1–N1[2]	22.40(13)	C1–N5–K1	108.9(4)
N2[3]–K1–N1[2]	85.24(15)	N7–N6–N5	172.3(8)
N7[4]–K1–N1[2]	101.7(2)	N6–N7–K1[6]	166.3(8)
N5–K1–N1[2]	63.32(14)	N1–O1–K1	122.0(4)
O1–K1–K1[2]	138.52(11)	N1–O1–K1[1]	104.2(4)
O2[1]–K1–K1[2]	139.05(11)	K1–O1–K1[1]	97.74(15)
O2–K1–K1[2]	40.91(11)	K1[2]–O2–K1	98.14(15)
O1[2]–K1–K1[2]	40.78(11)	N4–C1–N1	109.0(6)

N2[3]–K1–K1[2]	65.70(11)	N4–C1–N5	131.0(6)
N7[4]–K1–K1[2]	92.76(19)	N1–C1–N5	120.0(6)

[1]1+X, +Y, +Z; [2]-1+X, +Y, +Z; [3]-1+X, 1+Y, +Z; [4]+X, +Y, 1+Z; [5]1+X, -1+Y, +Z; [6]+X, +Y, -1+Z

Table S10 Hydrogen bonds present in 7·H_2O

D–H•••A	d(D-H) [Å]	d(H•••A) [Å]	< DHA [°]	d(D..A) [Å]	
O2–H2A•••O1	0.850	2.069	141.85	2.788	x-1, y+1, z
O2–H2B•••N4	0.850	2.138	159.53	2.949	x-1, y+1, z+1

Table S11 Selected bond lengths of 8

bond	Length[Å]	bond	Length[Å]
N1–C1	1.320(5)	N13–N14	1.102(6)
N1–O1	1.322(4)	N15–O3	1.243(7)
N1–N2	1.327(5)	N15–C3	1.368(6)
N2–N3	1.291(5)	N15–N16	1.371(6)
N3–N4	1.339(5)	N16–N17	1.369(6)
N4–C1	1.315(5)	N17–N18	1.392(6)
N5–N6	1.232(5)	N18–C3	1.402(6)
N5–C1	1.374(5)	N15'–O3	1.296(19)
N6–N7	1.119(6)	N15'–C3'	1.407(9)
N8–O2	1.310(4)	N15'–N16'	1.417(9)
N8–C2	1.322(5)	N16'–N17'	1.422(9)
N8–N9	1.330(5)	N17'–N18'	1.429(9)
N9–N10	1.294(5)	N18'–C3'	1.398(9)
N10–N11	1.347(6)	N19–C3'	1.166(11)
N11–C2	1.315(6)	N19–N20	1.221(6)
N12–N13	1.245(6)	N19–C3	1.368(6)
N12–C2	1.350(6)	N20–N21	1.105(6)

Table S12 Selected angles of 8

bond	Angle [°]	bond	Angle [°]
C1–N1–O1	128.4(3)	O3'–N15'–C3'	133.6(17)
C1–N1–N2	108.5(3)	O3'–N15'–N16'	118.9(17)
O1–N1–N2	123.1(3)	C3'–N15'–N16'	106.9(6)
N3–N2–N1	106.5(3)	N15'–N16'–N17'	107.8(6)
N2–N3–N4	110.7(3)	N16'–N17'–N18'	108.4(6)
C1–N4–N3	105.6(3)	C3'–N18'–N17'	106.1(6)
N6–N5–C1	112.9(3)	C3'–N19–N20	133.4(9)
N7–N6–N5	172.5(5)	C3'–N19–C3	24.2(7)
O2–N8–C2	128.4(3)	N20–N19–C3	109.8(4)
O2–N8–N9	122.7(3)	N21–N20–N19	171.4(5)
C2–N8–N9	109.0(3)	N4–C1–N1	108.7(3)
N10–N9–N8	106.0(4)	N4–C1–N5	131.5(4)
N9–N10–N11	111.0(4)	N1–C1–N5	119.8(3)
C2–N11–N10	105.4(4)	N11–C2–N8	108.7(4)
N13–N12–C2	118.8(4)	N11–C2–N12	122.3(4)
N14–N13–N12	170.1(5)	N8–C2–N12	129.0(4)
O3–N15–C3	130.0(5)	N19–C3–N15	121.5(5)

O3–N15–N16	121.7(5)	N19–C3–N18	129.8(4)
C3–N15–N16	108.2(4)	N15–C3–N18	108.6(4)
N17–N16–N15	108.4(4)	N19–C3'–N18'	134.3(13)
N16–N17–N18	108.8(4)	N19–C3'–N15'	114.8(13)
N17–N18–C3	106.0(4)	N18'–C3'–N15'	110.7(6)

Table S13 Selected bond lengths of 9

bond	Angle [°]	bond	Angle [°]
N1–O1	1.308(2)	N5–N6	1.236(3)
N1–C1	1.314(3)	N5–C1	1.367(3)
N1–N2	1.329(3)	N6–N7	1.108(3)
N2–N3	1.285(3)	N8–C2	1.295(3)
N3–N4	1.332(3)	N9–C2	1.301(3)
N4–C1	1.300(3)	N10–C2	1.298(3)

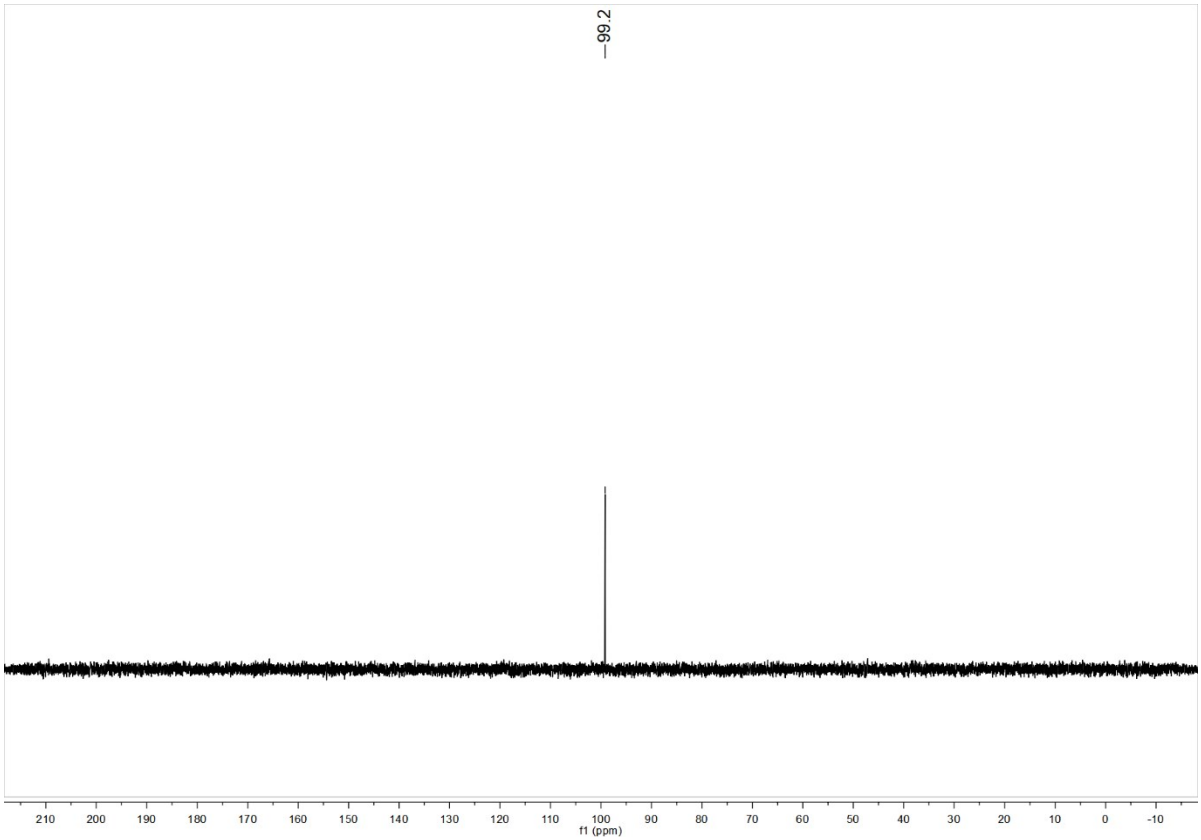
Table S14 Selected angles of 9

bond	Angle [°]	bond	Angle [°]
O1–N1–C1	130.4(2)	N7–N6–N5	172.2(3)
O1–N1–N2	121.71(19)	N4–C1–N1	109.0(2)
C1–N1–N2	107.9(2)	N4–C1–N5	129.9(2)
N3–N2–N1	106.8(2)	N1–C1–N5	121.1(2)
N2–N3–N4	110.1(2)	N8–C2–N10	121.0(2)
C1–N4–N3	106.2(2)	N8–C2–N9	120.2(2)
N6–N5–C1	112.7(2)	N10–C2–N9	118.7(2)
O1–N1–C1	130.4(2)	N7–N6–N5	172.2(3)

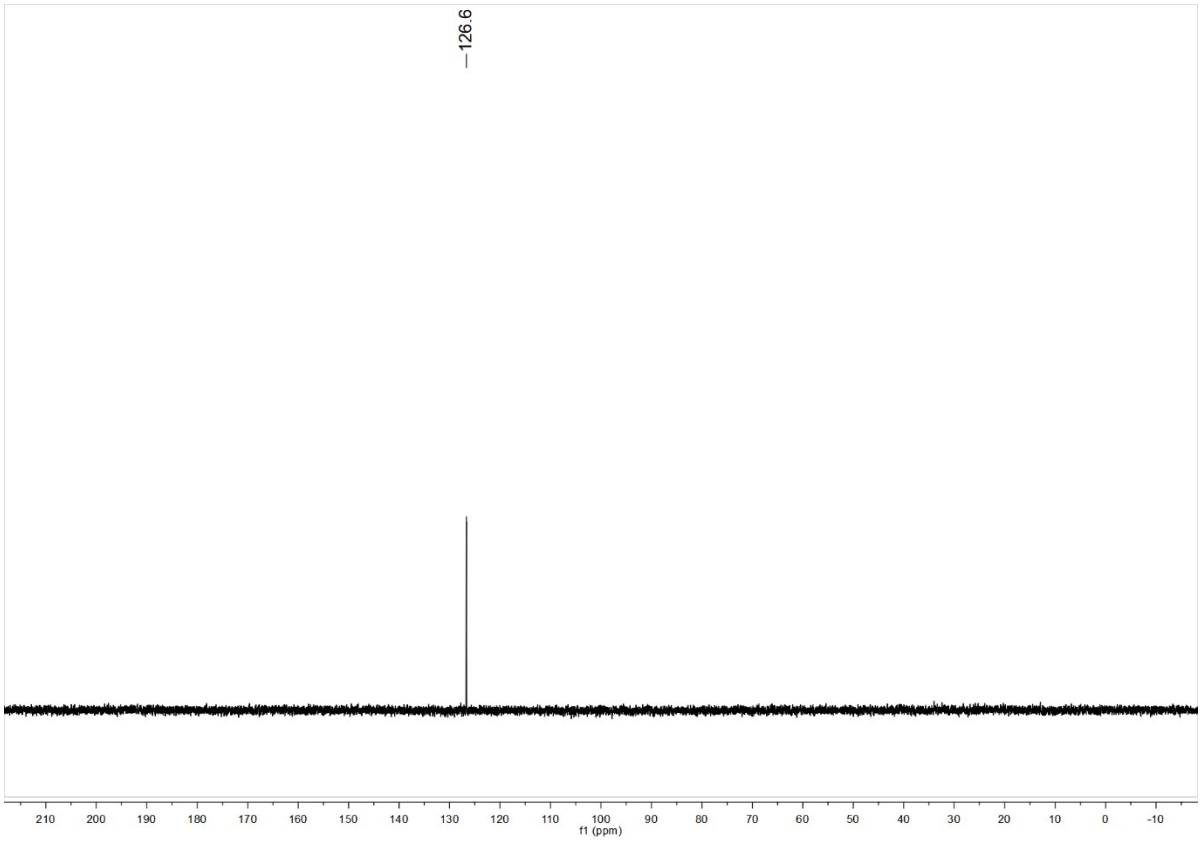
Table S15 Hydrogen bonds present in 9

D–H•••A	d(D-H) [Å]	d(H•••A) [Å]	< DHA [°]	d(D..A) [Å]	
N8–H8A•••O1	0.86	2.000	168.88	2.848	x-1/2, y+1/2, z
N8–H8B•••N2	0.86	2.235	149.72	3.009	x, y+1, z
N9–H9A•••O1	0.86	2.256	147.33	3.016	x, y+1, z
N9–H9B•••O1	0.86	2.153	139.36	2.861	-x+1, y+1, -z+3/2
N10–H10A•••O1	0.86	2.213	139.71	2.922	-x+1/2, y+1/2, -z+3/2
N10–H10B•••N4	0.86	2.052	173.82	2.908	x, -y+1, z+1/2

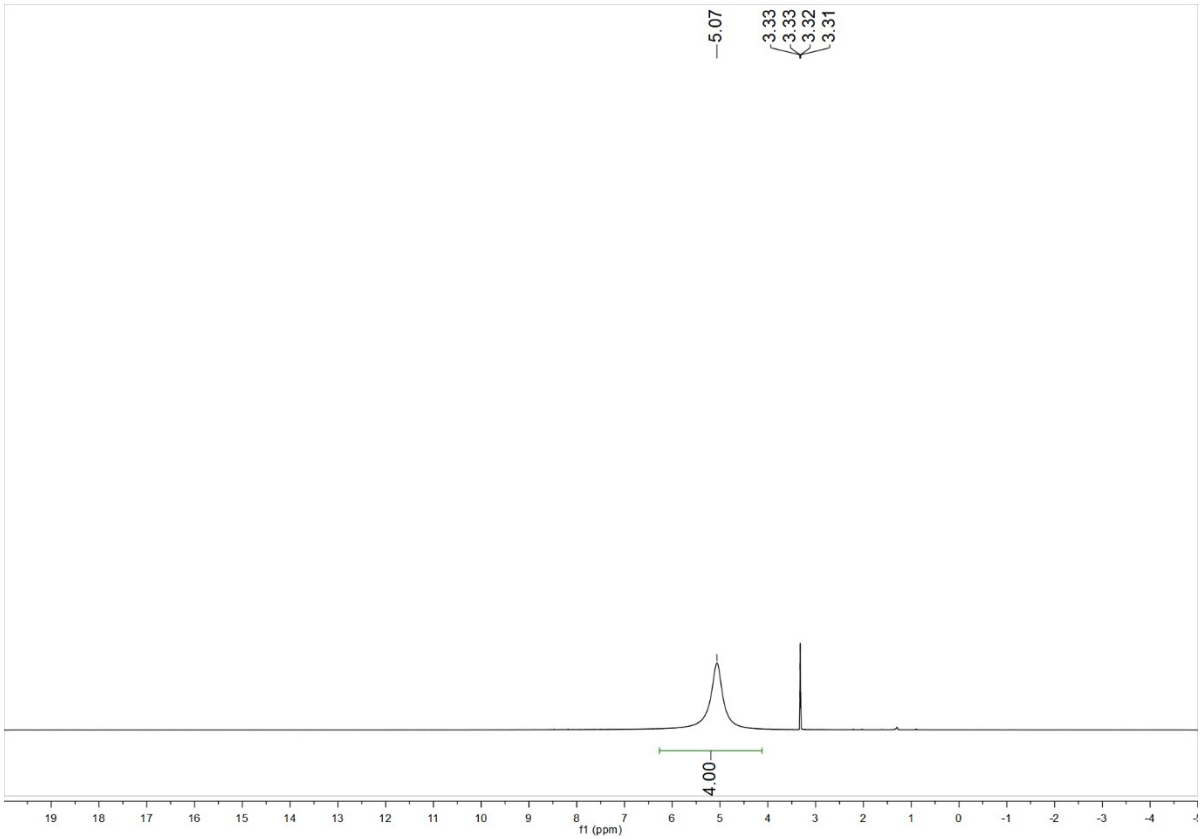
2 NMR spectra ^{1}H or ^{13}C NMR Spectra of product



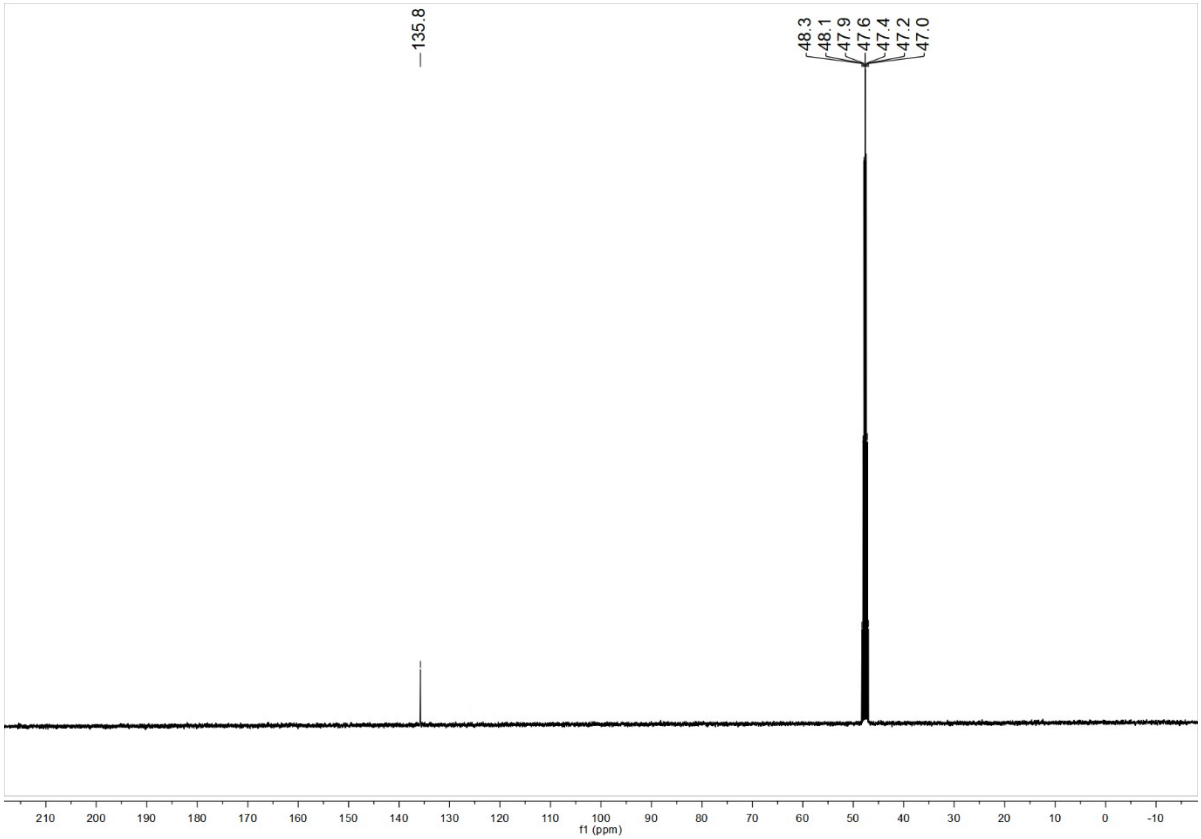
^{13}C NMR of **DBFO** in D_2O at 25 ^{o}C



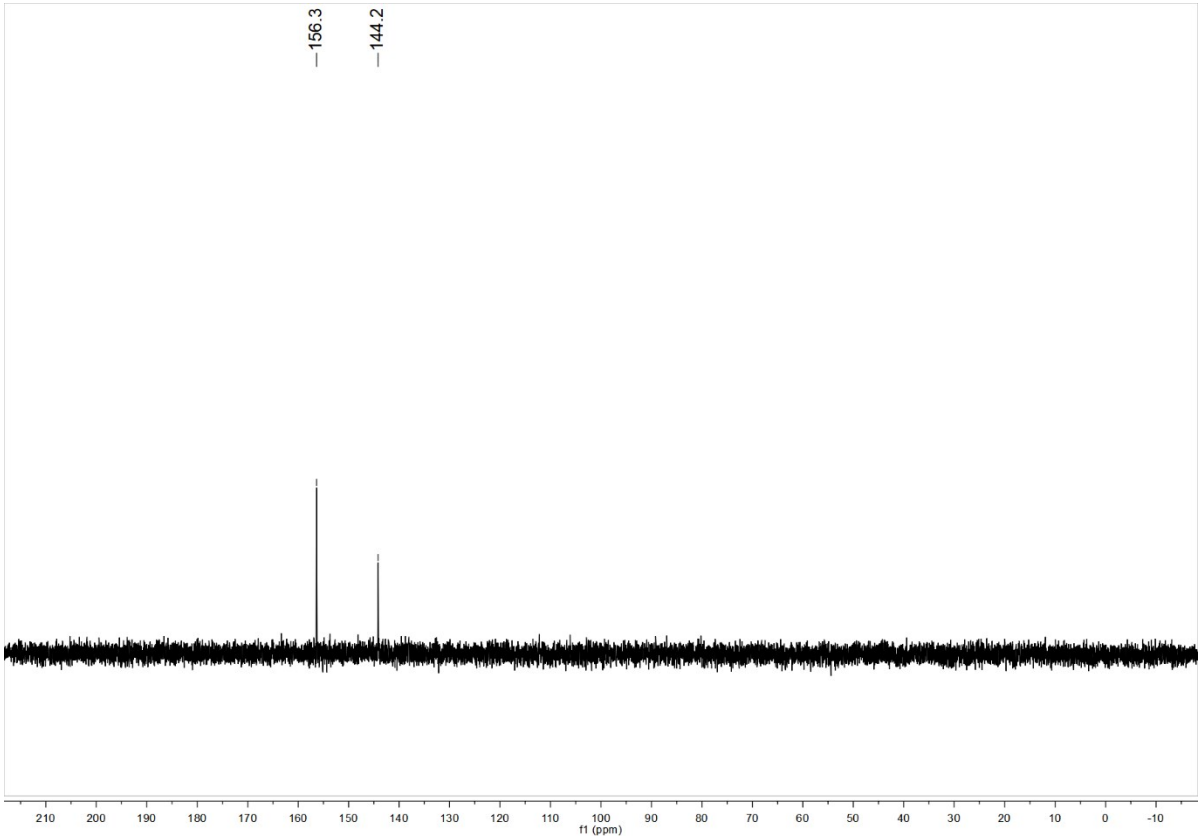
^{13}C NMR of intermediate **I** in D_2O at 25 ^{o}C



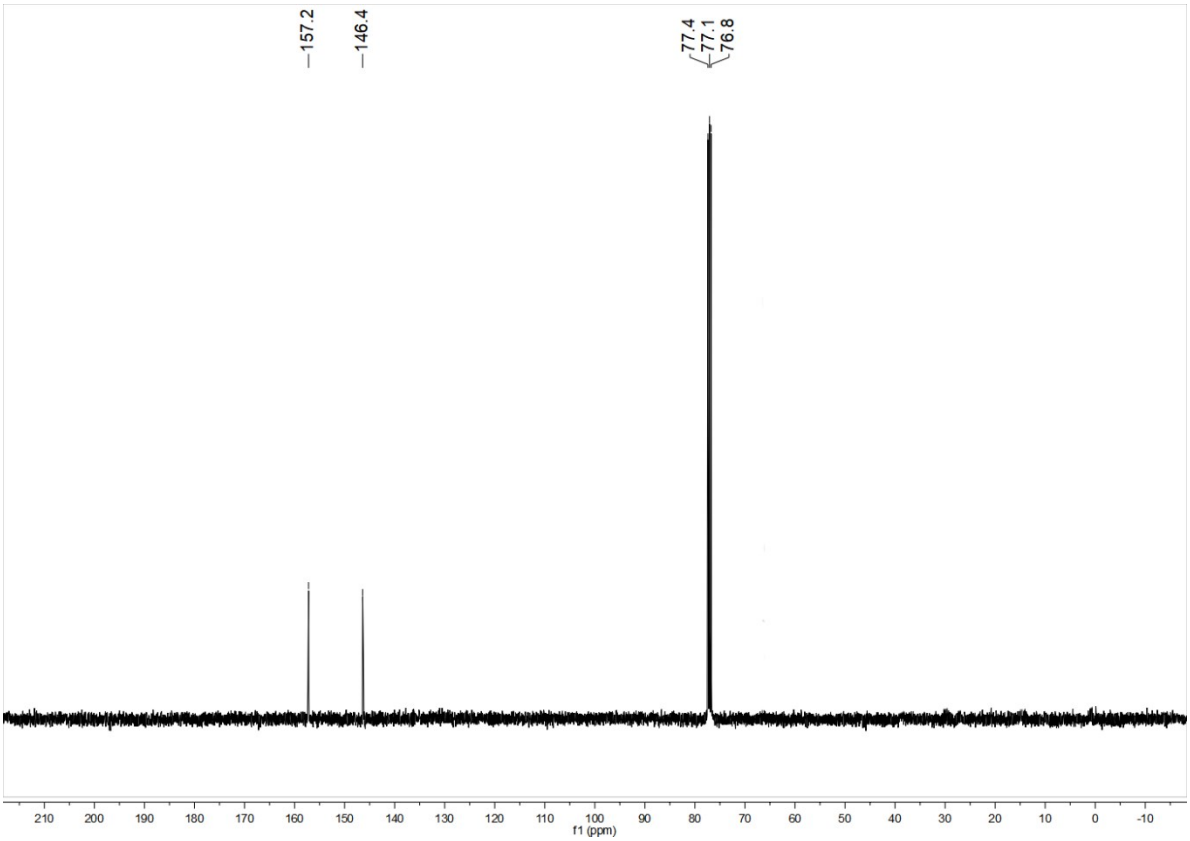
^{1}H NMR of **2** in Methanol-d_4 at 25 ˚C



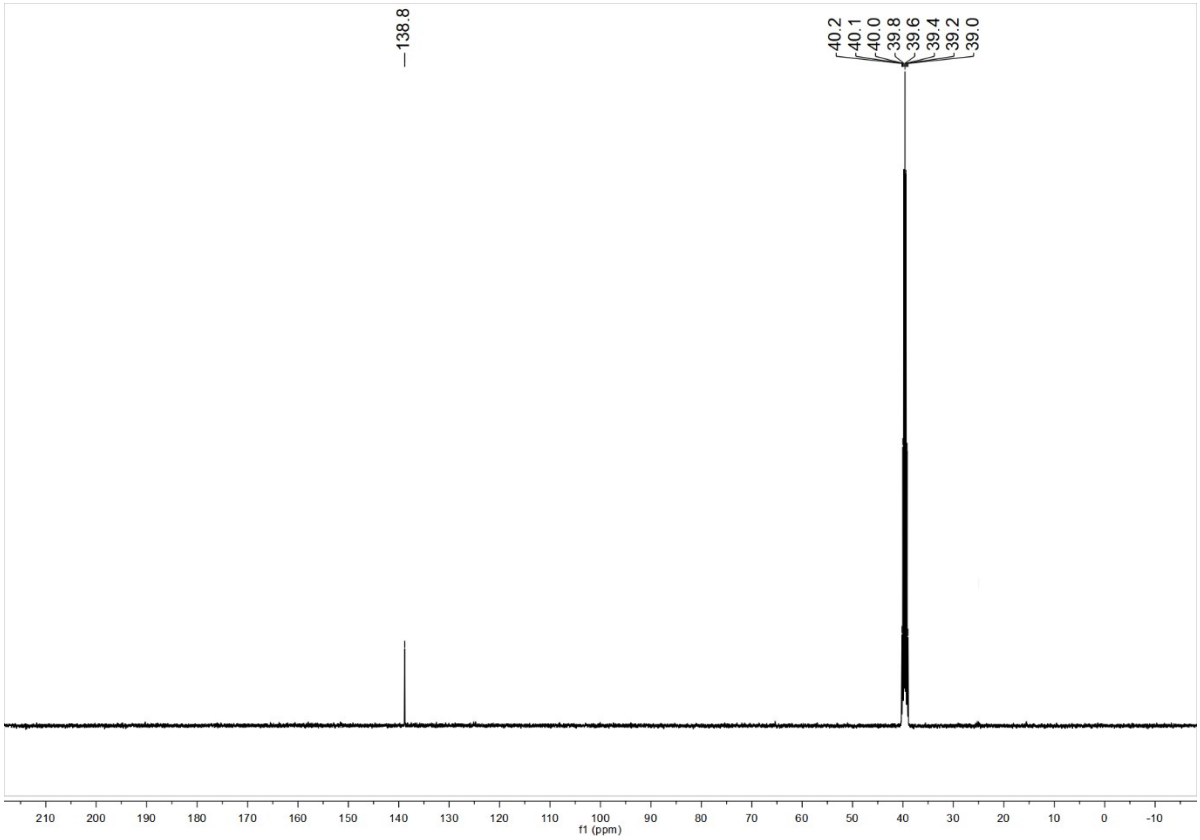
^{13}C NMR of **2** in Methanol-d_4 at 25 ˚C



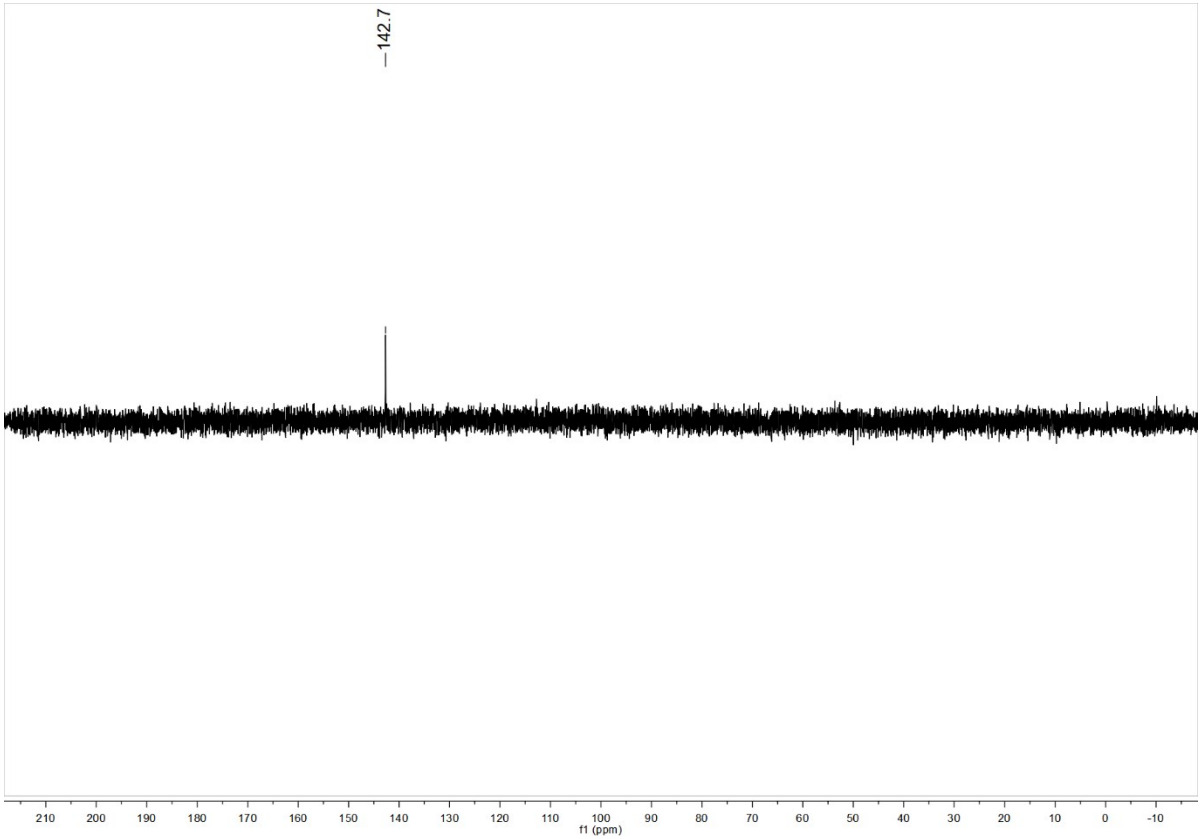
^{13}C NMR of **4** in D_2O at 25 ^oC



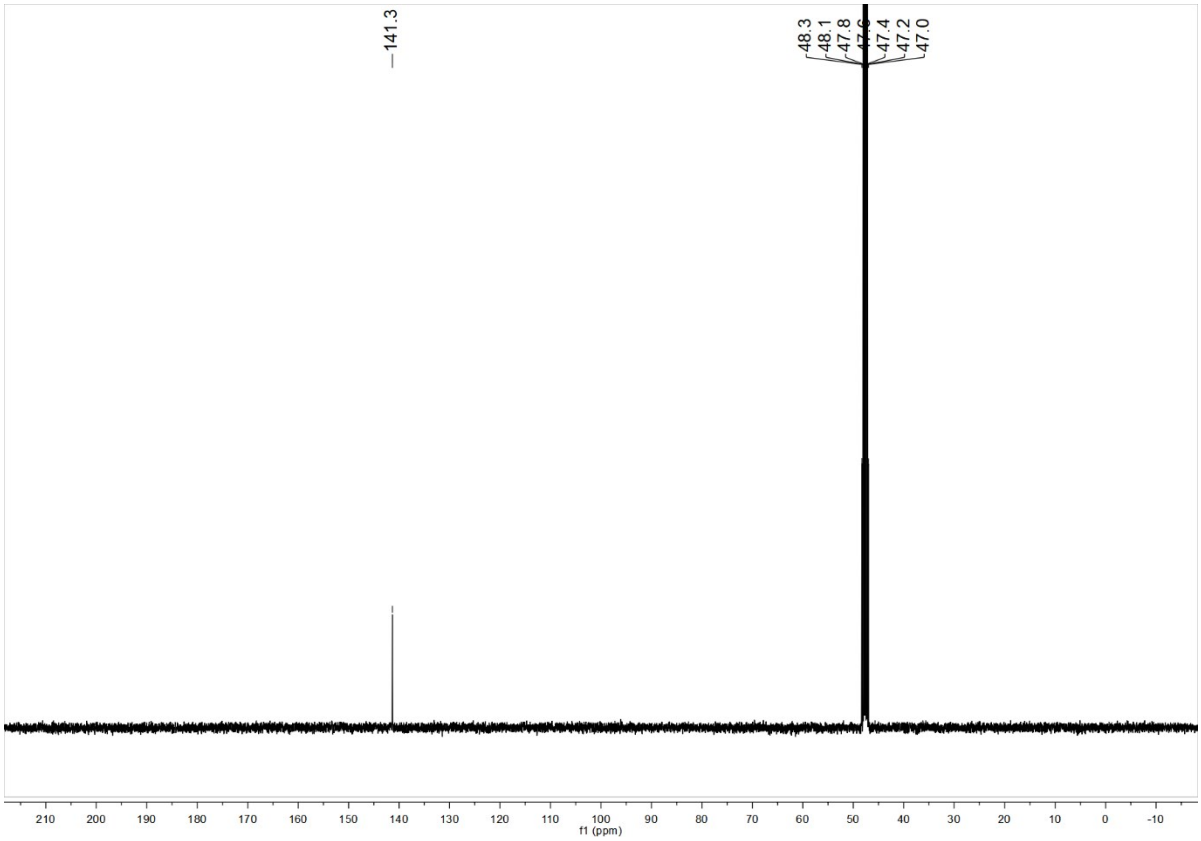
^{13}C NMR of **4** in $CDCl_3$ at 25 ^oC



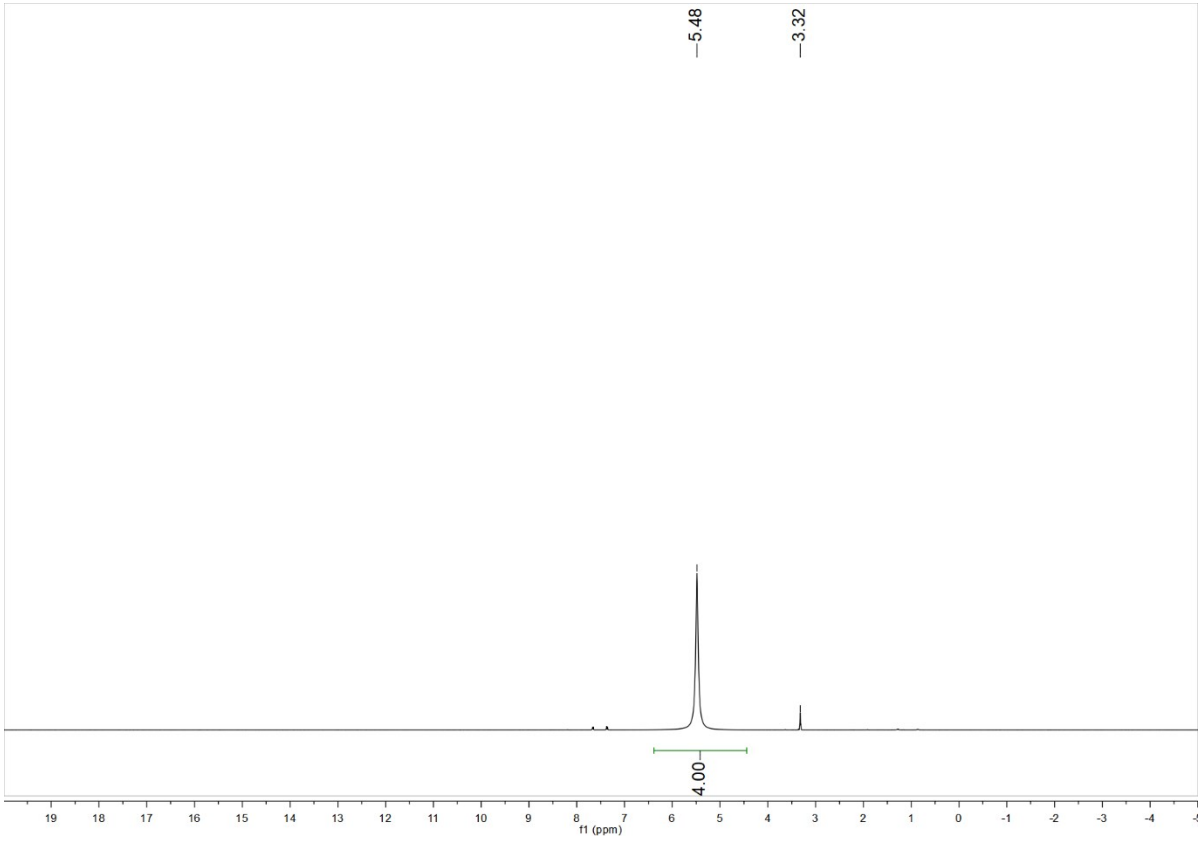
^{13}C NMR of **5·3H$_2$O** in DMSO-d_6 at 25 ^{o}C



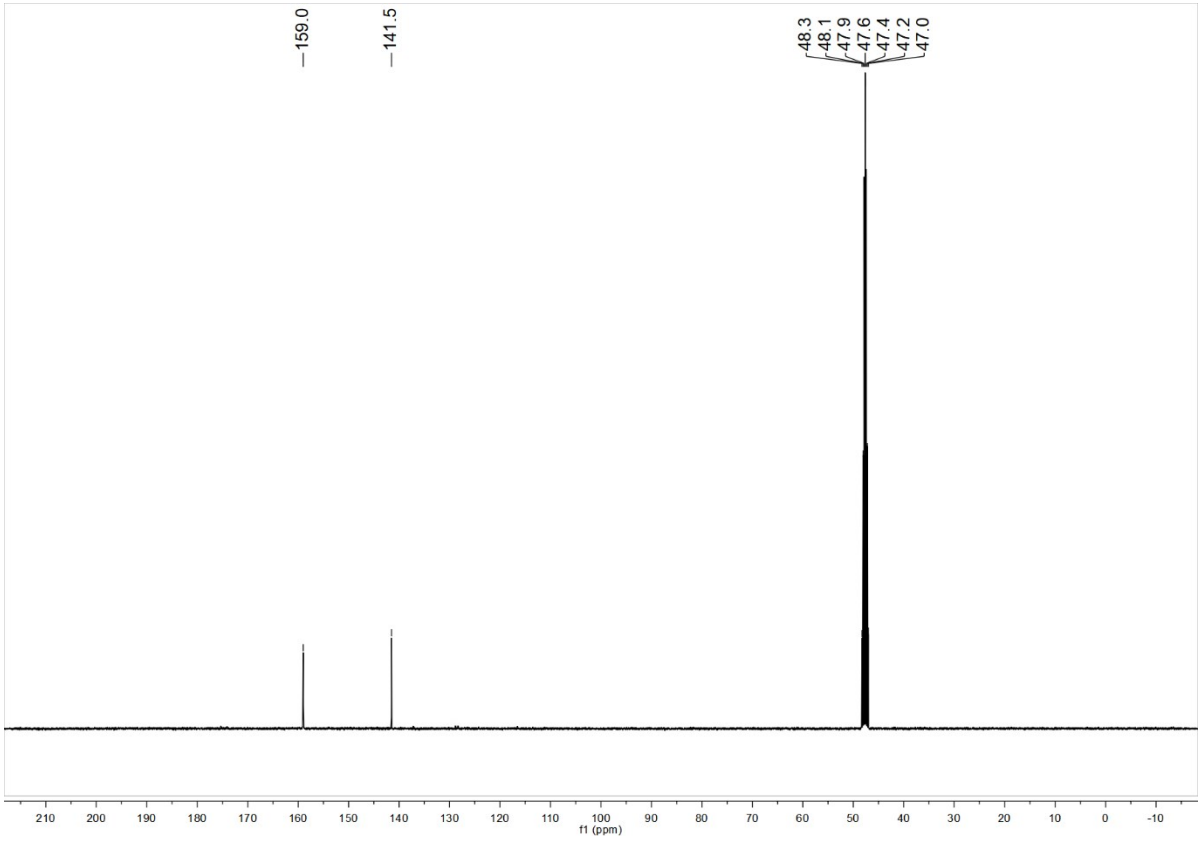
^{13}C NMR of **6·3H$_2$O** in D_2O at 25 ^{o}C



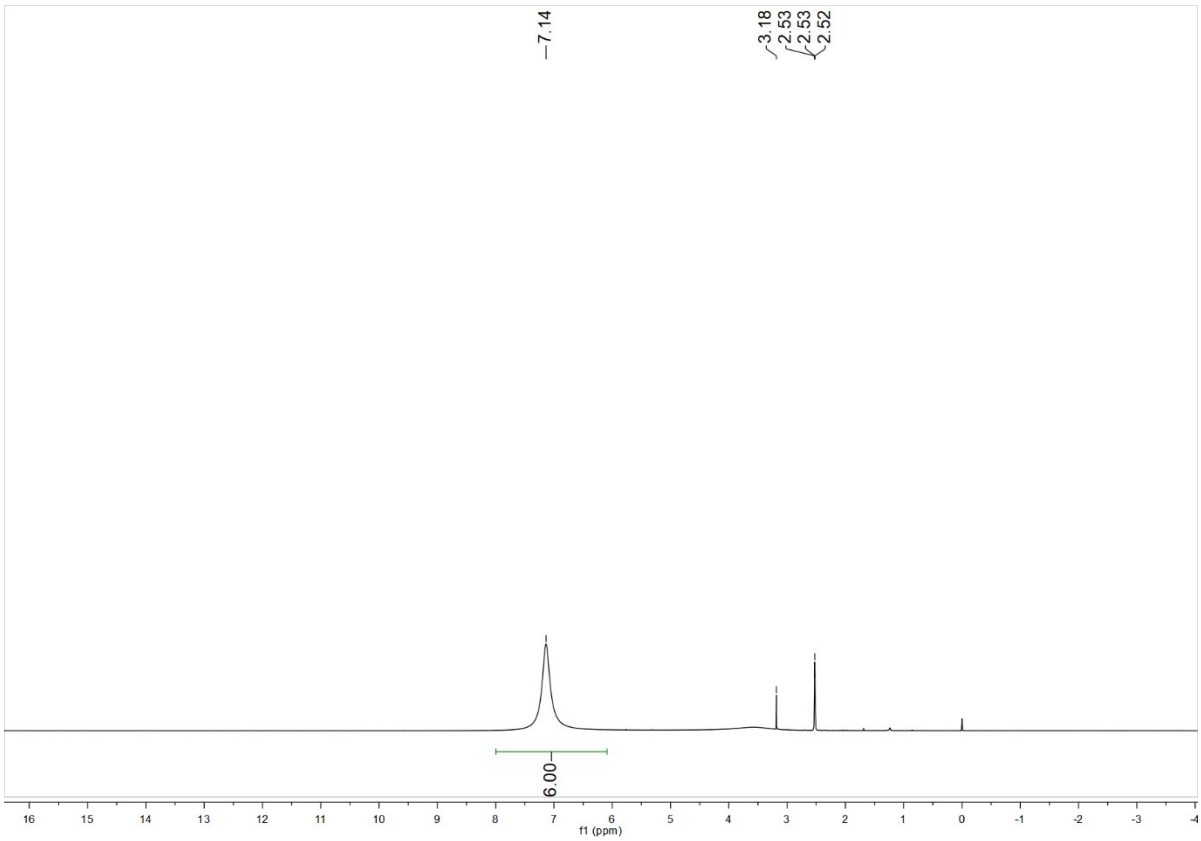
^{13}C NMR of **7·H_2O** in Methanol-d_4 at 25 ˚C



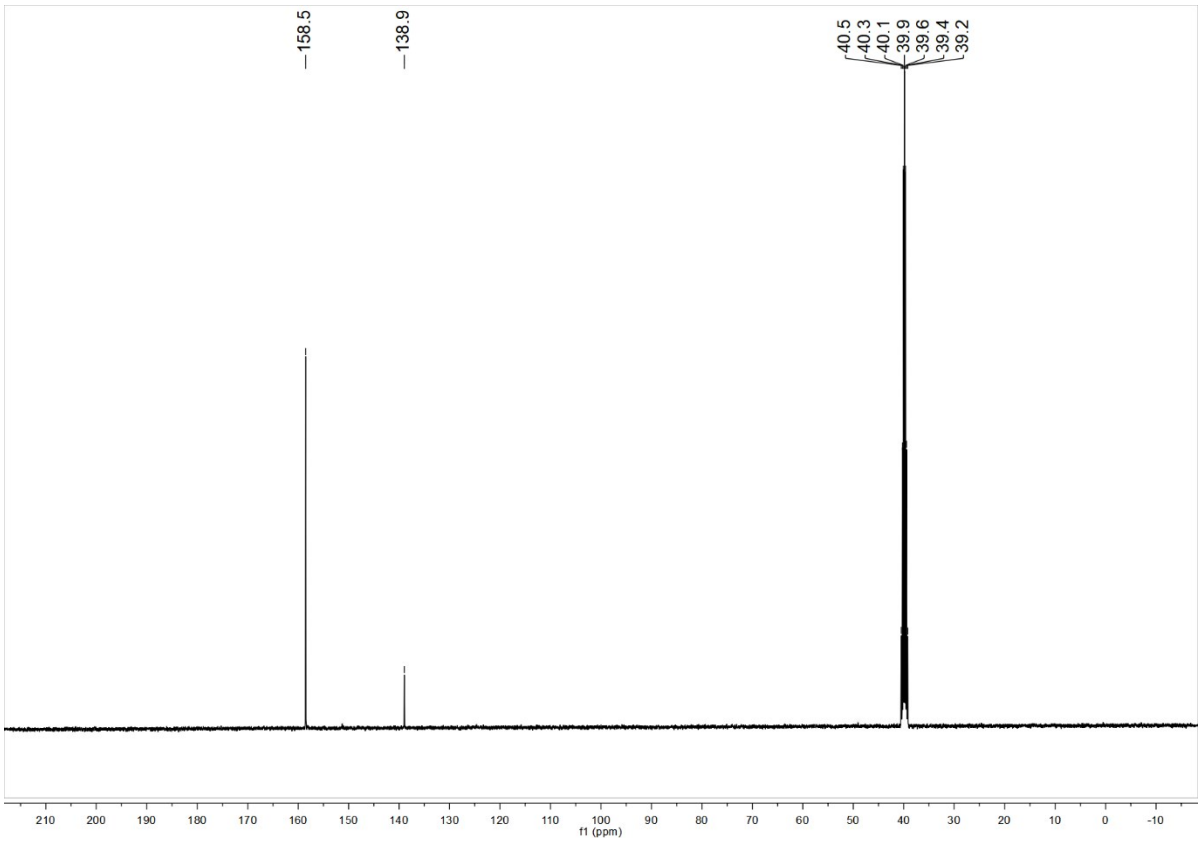
^{1}H NMR of **8** in Methanol-d_4 at 25 ˚C



^{13}C NMR of **8** in Methanol-d_4 at 25 ^{o}C

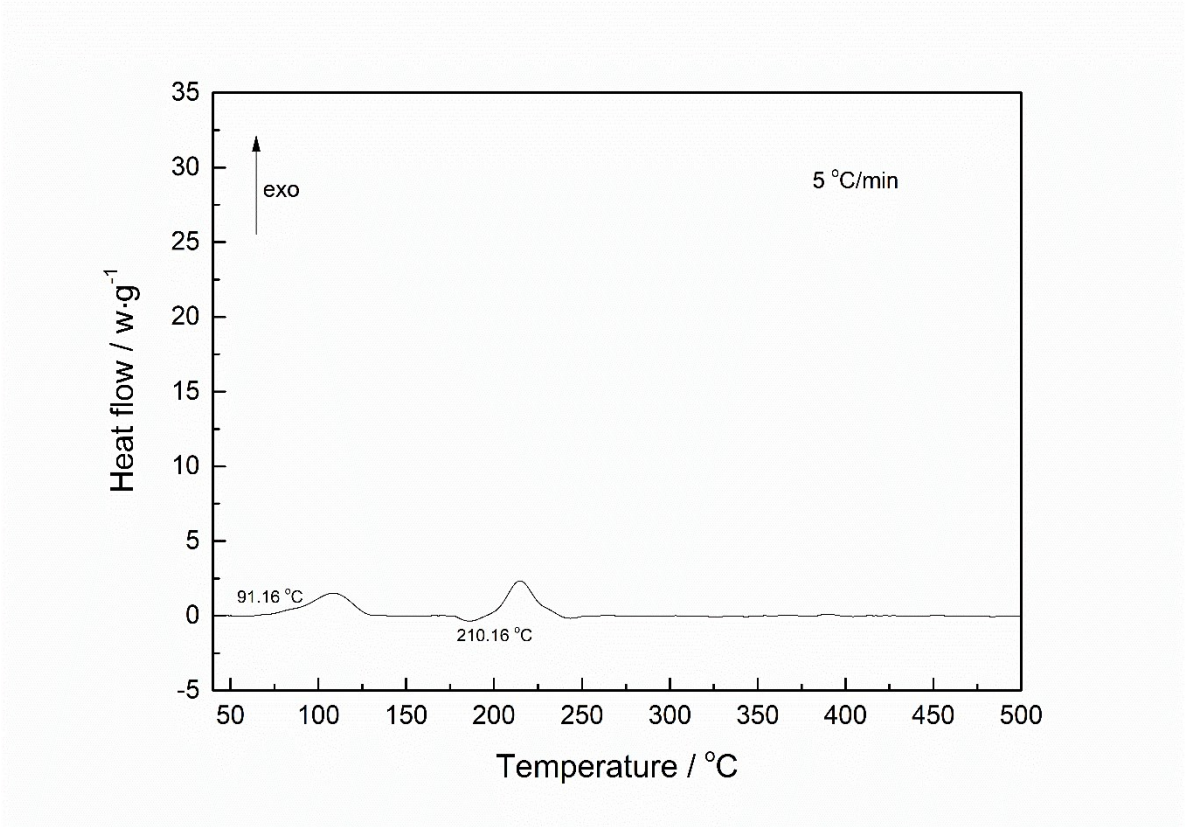


^{1}H NMR of **9** in DMSO-d_6 at 25 ^{o}C

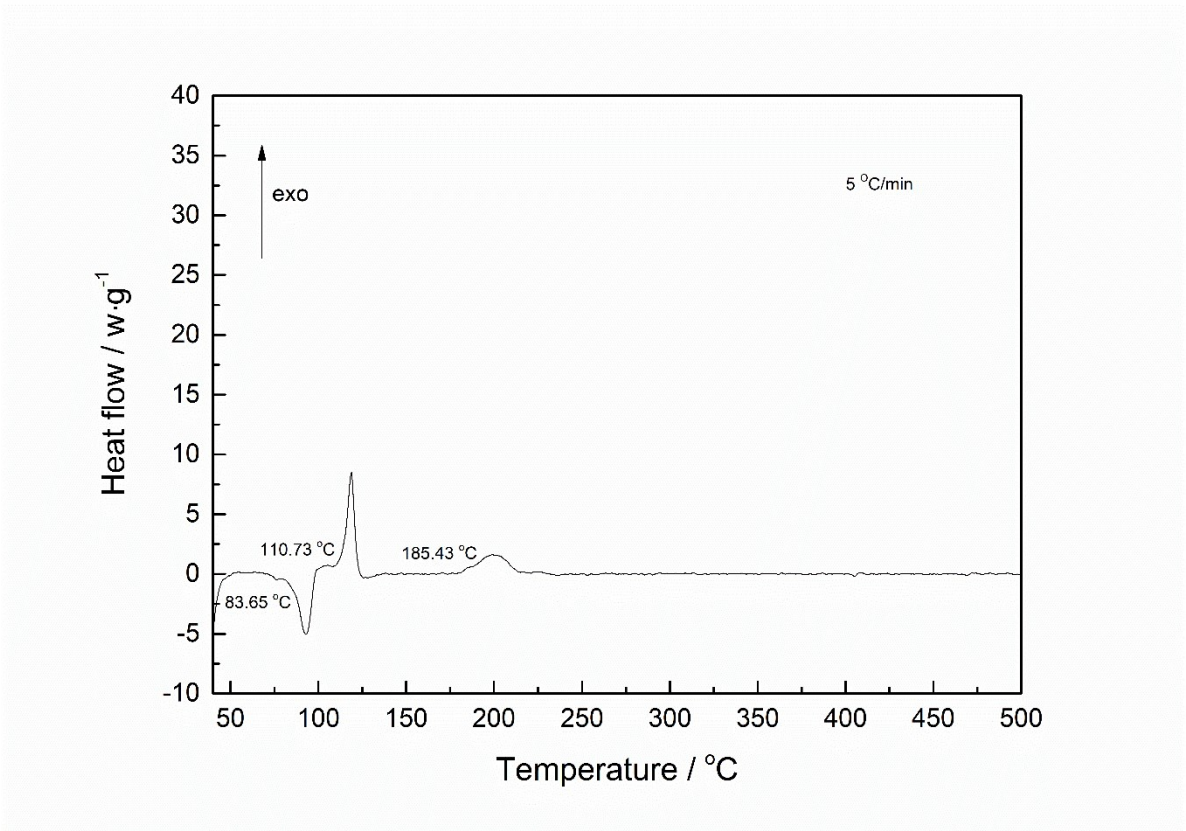


^{13}C NMR of **9** in DMSO-d_6 at 25 °C

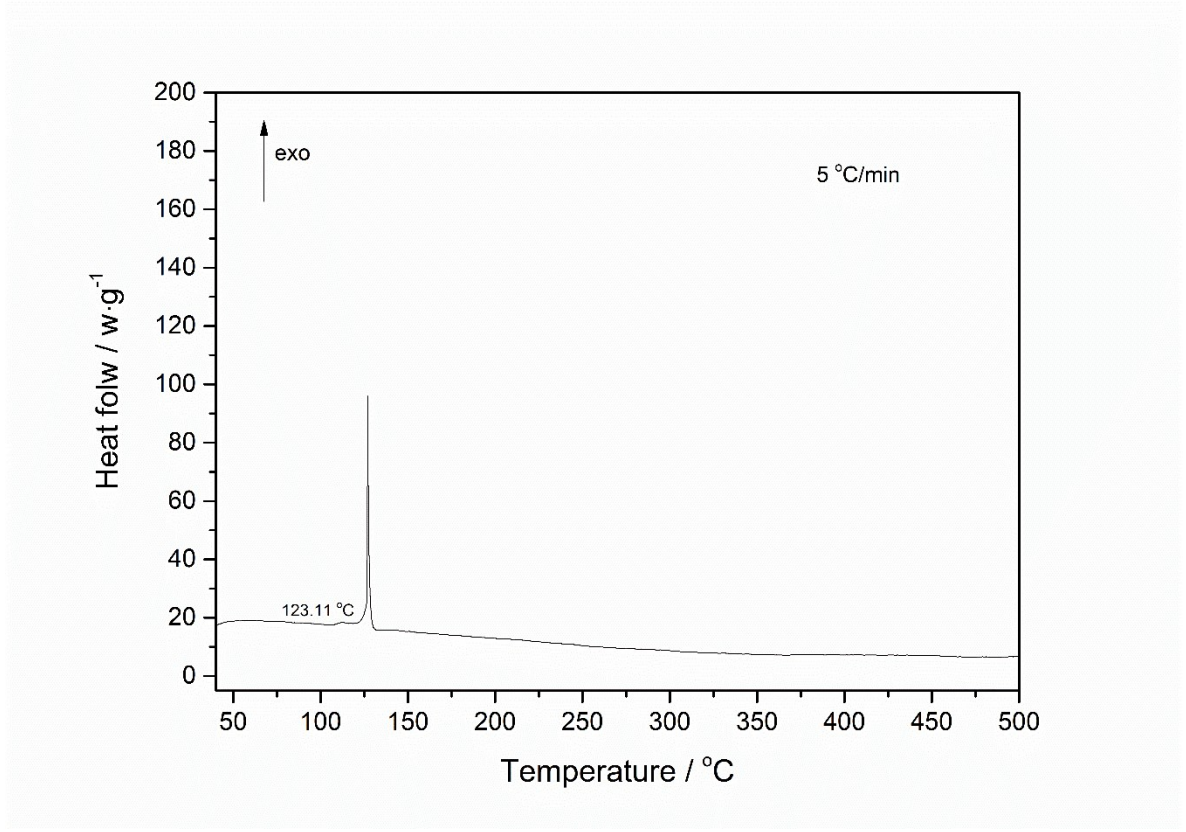
3 DSC spectra of 5–9



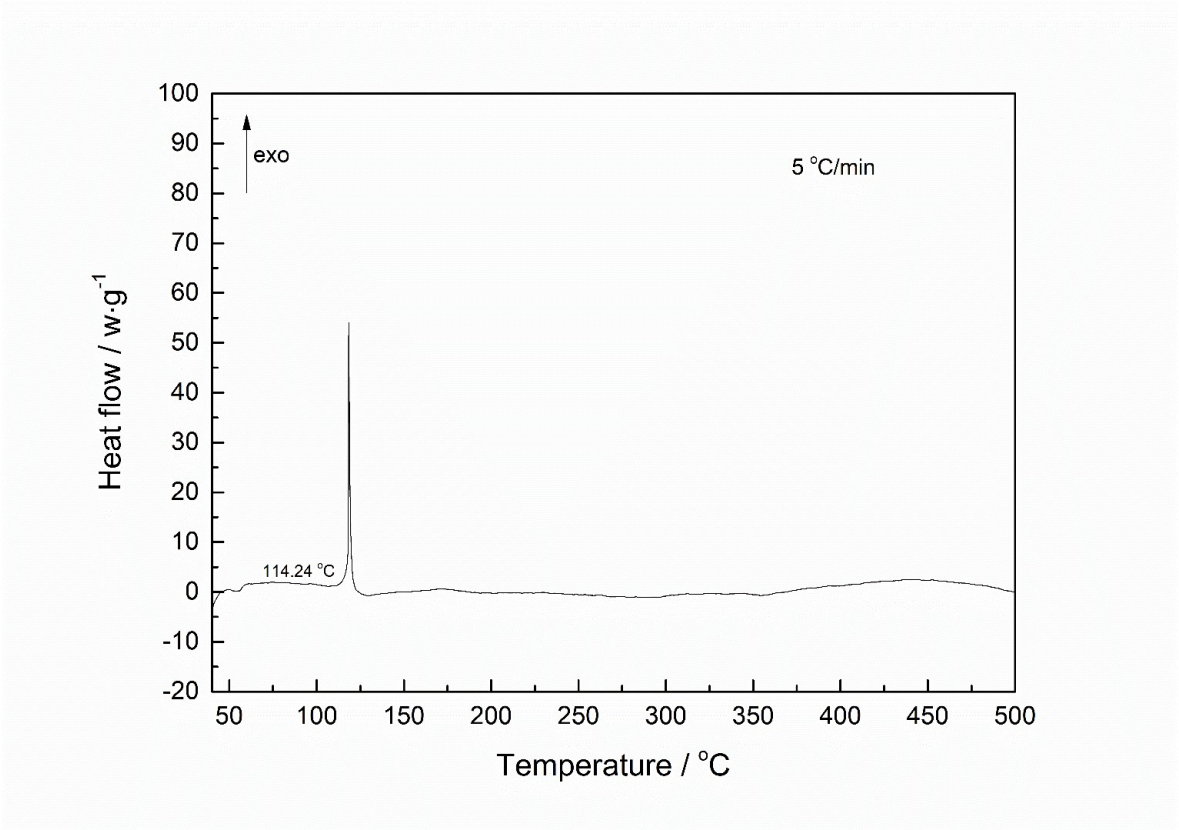
DSC plot of **5**



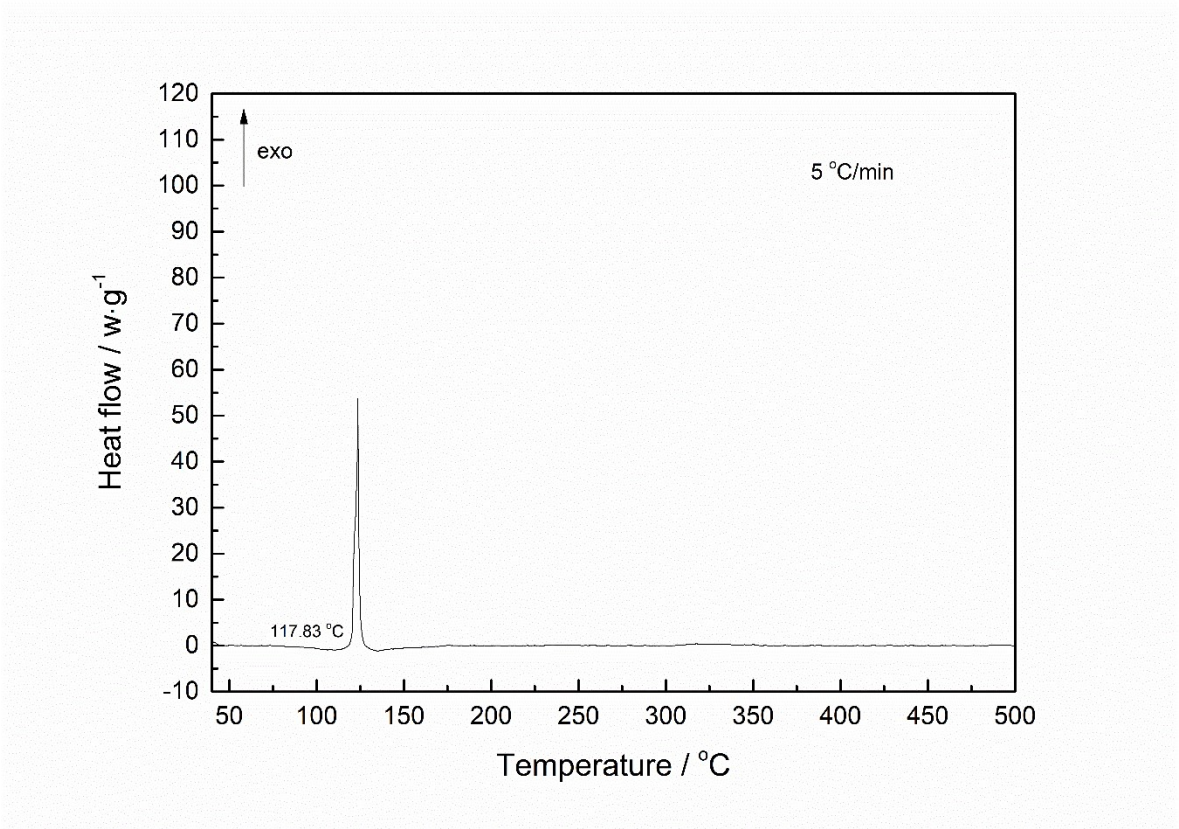
DSC plot of **6**•$3H_2O$



DSC plot of **7**•H_2O



DSC plot of **8**



DSC plot of **9**

4. Calculated rate constant k for 3 to 4

T	k
173.15	3.16388E-08
183.15	3.88357E-07
193.15	3.68977E-06
203.15	2.81753E-05
213.15	0.000177498
223.15	0.000953266
233.15	0.004424376
243.15	0.018137231
253.15	0.066637401
263.15	0.221634177
273.15	0.676154144
283.15	1.907240206
293.15	5.013881136
303.15	12.36959617
313.15	28.84095649
323.15	63.82197027
333.15	134.7954789
343.15	272.3210118
353.15	529.1634541
363.15	992.1665157
373.15	1798.595411