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Synthesis, characterization and catalytic activity of a heterometallic Ni/Zn compound in the H/D exchange of salicylaldehyde

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Experimental

$Ni(NO_3)_2 \cdot 6H_2O$ was purchased from ORëC. 2,2′-Bipyridine and organic solvents were purchased from CARLO ERBA. Dimethyl sulfoxide (DMSO-h_6), $Zn(OAc)_2 \cdot 2H_2O$ and NaOCN were purchased from Sigma Aldrich. Salicylaldehyde and dimethyl sulfoxide (DMSO-d_6) were purchased from Aldrich.

Elemental analysis of carbon, hydrogen and nitrogen was performed on a Perkin Elmer model 2400 elemental analyzer. FT-IR spectrum was recorded as KBr dics in the region 4000-400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Solid–state (diffuse reflectance) electronic spectrum was measured as polycrystalline sample on a Perkin-Elmer Lambda 2s spectrometer, over the range 8000-18000 cm^{-1}. Melting point was observed in capillary tube on Electrothermal 9100.

The progress of the reaction was monitored by ^1H NMR spectroscopy at 27 °C. ^1H–NMR spectra were recorded on a Varian Mecury Plus 400 spectrometer. The organic product was confirmed by gas chromatography-mass spectrometry (GC-MS) using a Trace GC chromatography equipped with a Finnigan Polaris Q mass spectrometer (Thermo Finnigan, USA). 1 μl of the sample was injected into the gas chromatograph using splitless mode. Organic product was achieved with ZB-5 column (30m×0.25mm i.d., 0.25 μm film thickness). The oven was programmed with step temperature program starting at 60 °C for 5 min and increased to 280 °C with a heating rate of 3 °C/min. Helium gas was used as carrier gas at a flow rate of 1.0 ml/min (constant flow). The GC injector temperature was 200 °C and the transfer line temperature was held at 275 °C. The mass spectrometer presented an electronic impact source (EI) to promote electron ionization operated at the ionization energy of 70 eV and temperature of the ion source of 250 °C.

Synthesis of compound **1**

A methanol solution of 2,2′-bipyridine 0.2652 g (1.7000 mmol) was added to a methanol solution of $Ni(NO_3)_2 \cdot 6H_2O$ 0.1474 g (0.5060 mmol). The mixture was stirred for 30 min at room temperature followed by adding a solution of NaOCN 0.0749 g (1.1523 mmol) in 5 ml of DI. After the mixture solution was stirred for 30 min, a methanol solution of $Zn(OAc)_2 \cdot 2H_2O$ 0.1208 g (0.4729 mmol) was added and stirred continuously for 5 h. The red powder was precipitated and crystallized in DMSO. The red crystals were obtained after 3 days by slow evaporation at room temperature. Yield 83.16 %. Mp > 250 ^{o}C. Anal. Calc. for $NiZnC_{34}H_{26}N_{10}O_5$ (%): C, 52.44, H, 3.37, N, 17.99. Found (%): C, 52.03, H, 2.86, N, 17.97. IR (KBr, cm^{-1}): 3535 (br), 3080 (w), 2205 (s), 1599 (m), 1493 (m), 1473 (m), 1443 (m), 1337 (w), 1314 (w), 1158 (w), 1022 (w), 771 (s). Electronic diffuse reflectance: 523 nm and 801 nm.

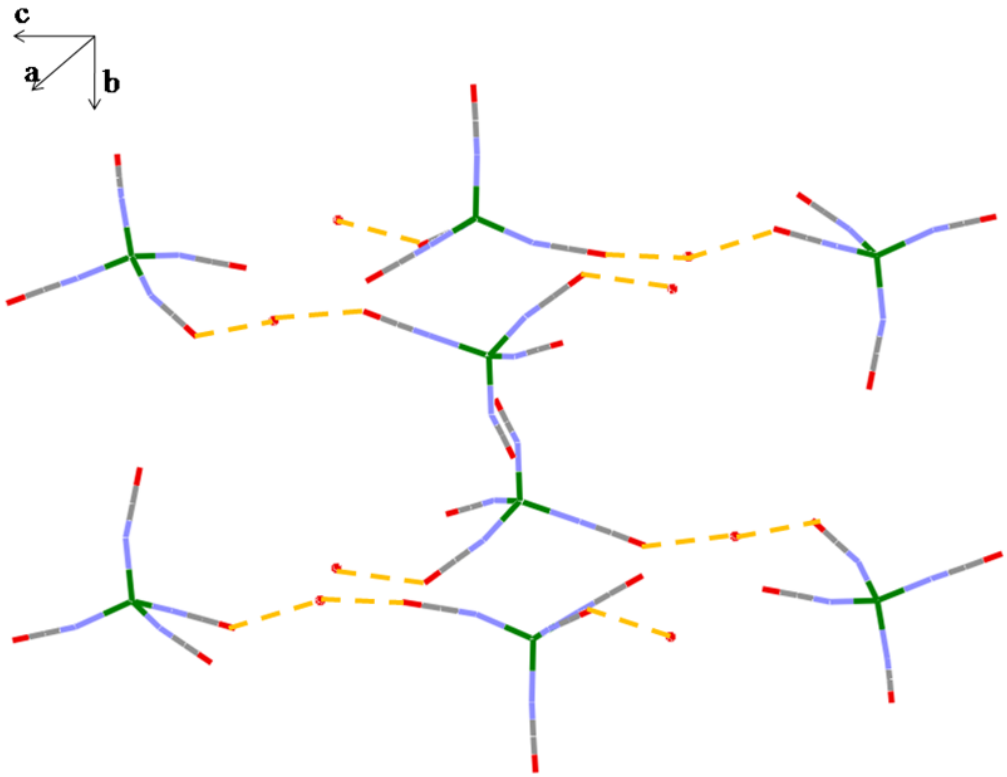

Figure S1 Packing diagram show one-dimension chain of **1** along c axis.

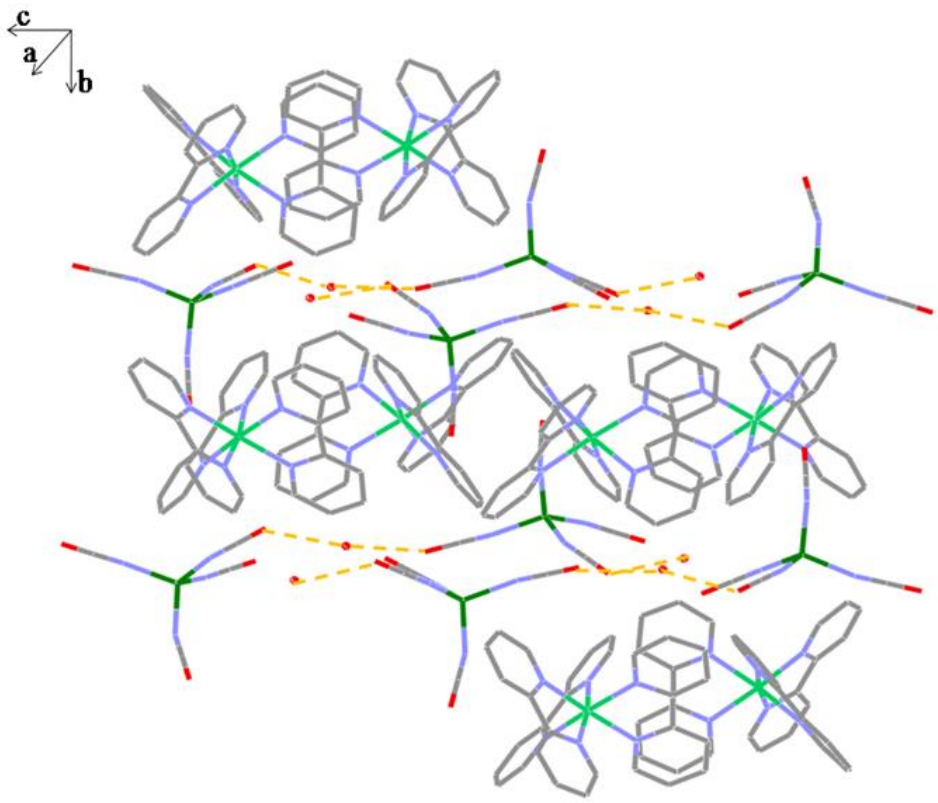

Figure S2 Packing diagram show cationic units are resides in cavities between anionic chains.

Table S1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	2179(1)	9952(1)	3473(1)	38(1)
Zn(1)	8658(1)	6925(1)	4630(1)	60(1)
O(1)	7479(2)	5047(1)	4562(1)	84(1)
O(2)	6652(3)	7796(2)	3558(2)	132(1)
O(3)	8373(4)	7595(2)	6303(2)	150(2)
O(4)	10546(2)	7523(2)	3370(1)	108(1)
N(1)	1444(2)	9362(1)	4039(1)	42(1)
N(2)	902(2)	10434(1)	3491(1)	46(1)
N(3)	1840(2)	9396(1)	2756(1)	43(1)
N(4)	2741(2)	10537(1)	2826(1)	48(1)
N(5)	3485(2)	9506(1)	3569(1)	45(1)
N(6)	2751(2)	10524(1)	4116(1)	43(1)
N(7)	8467(2)	5957(2)	4683(1)	74(1)

N(8)	7564(2)	7312(2)	4262(2)	78(1)
N(9)	8818(3)	7295(2)	5387(2)	91(1)
N(10)	9711(2)	7132(2)	4143(1)	82(1)
C(1)	1753(2)	8808(1)	4291(1)	51(1)
C(2)	1207(3)	8431(2)	4648(1)	64(1)
C(3)	319(3)	8630(2)	4754(1)	71(1)
C(4)	-6(2)	9204(2)	4500(1)	63(1)
C(5)	569(2)	9560(1)	4146(1)	43(1)
C(6)	279(2)	10182(2)	3857(1)	47(1)
C(7)	-555(2)	10490(2)	3950(2)	66(1)
C(8)	-762(3)	11068(2)	3665(2)	81(1)
C(9)	-137(3)	11325(2)	3292(2)	72(1)
C(10)	683(2)	10995(2)	3221(2)	60(1)
C(11)	1362(2)	8825(2)	2749(1)	54(1)
C(12)	1175(2)	8483(2)	2260(2)	63(1)
C(13)	1493(2)	8724(2)	1759(2)	64(1)
C(14)	1987(2)	9314(2)	1754(1)	59(1)
C(15)	2154(2)	9639(1)	2264(1)	45(1)
C(16)	2688(2)	10267(2)	2310(1)	48(1)
C(17)	3107(3)	10561(2)	1846(2)	81(1)
C(18)	3584(3)	11144(2)	1918(2)	102(2)
C(19)	3635(3)	11420(2)	2440(2)	86(1)
C(20)	3199(3)	11108(2)	2890(2)	64(1)
C(21)	3814(2)	8987(2)	3287(1)	56(1)
C(22)	4724(2)	8774(2)	3325(2)	69(1)
C(23)	5307(2)	9118(2)	3676(2)	78(1)
C(24)	4979(2)	9649(2)	3973(2)	69(1)
C(25)	4065(2)	9837(2)	3921(1)	47(1)
C(26)	3649(2)	10401(1)	4231(1)	46(1)
C(27)	4139(3)	10779(2)	4622(2)	65(1)
C(28)	3700(3)	11290(2)	4896(2)	73(1)
C(29)	2785(3)	11413(2)	4794(2)	69(1)
C(30)	2336(2)	11020(2)	4396(1)	55(1)
C(31)	7965(2)	5518(2)	4625(1)	53(1)
C(32)	7128(3)	7543(2)	3922(2)	68(1)
C(33)	8621(4)	7437(2)	5832(2)	89(1)
C(34)	10112(2)	7327(2)	3765(2)	56(1)
O(1W)	3782(5)	7455(4)	2546(3)	226(3)

Table S2 Anisotropic displacement parameters ($Å^2$ x 10^3) for **1**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	39(1)	34(1)	41(1)	4(1)	-1(1)	-2(1)
Zn(1)	66(1)	56(1)	59(1)	-2(1)	3(1)	-7(1)
O(1)	87(2)	76(2)	89(2)	14(1)	-31(2)	-22(2)
O(2)	138(3)	128(3)	129(3)	15(2)	-46(3)	25(3)
O(3)	272(5)	109(3)	69(2)	-7(2)	-19(3)	18(3)
O(4)	139(3)	106(2)	79(2)	16(2)	33(2)	-22(2)
N(1)	48(1)	39(1)	39(1)	3(1)	-2(1)	-3(1)
N(2)	44(1)	44(1)	51(1)	6(1)	-7(1)	3(1)
N(3)	45(1)	40(1)	45(1)	2(1)	-2(1)	-5(1)
N(4)	53(1)	40(1)	50(1)	7(1)	0(1)	-7(1)
N(5)	43(1)	41(1)	49(1)	3(1)	2(1)	3(1)
N(6)	44(1)	40(1)	45(1)	2(1)	-2(1)	-2(1)
N(7)	66(2)	58(2)	98(2)	-1(2)	17(2)	-8(2)
N(8)	86(2)	80(2)	68(2)	-2(2)	-10(2)	8(2)
N(9)	123(3)	91(3)	59(2)	-3(2)	-8(2)	-7(2)
N(10)	78(2)	86(2)	80(2)	6(2)	12(2)	-27(2)
C(1)	60(2)	45(2)	49(2)	10(1)	-8(1)	-5(1)
C(2)	92(3)	47(2)	53(2)	15(1)	-10(2)	-16(2)
C(3)	88(3)	70(2)	54(2)	8(2)	9(2)	-34(2)
C(4)	59(2)	72(2)	59(2)	-5(2)	12(2)	-20(2)
C(5)	44(2)	48(2)	38(1)	-5(1)	1(1)	-7(1)
C(6)	41(2)	50(2)	49(2)	-8(1)	-4(1)	-3(1)
C(7)	44(2)	71(2)	84(2)	-11(2)	8(2)	2(2)
C(8)	57(2)	74(3)	111(3)	-15(2)	-11(2)	25(2)
C(9)	72(2)	61(2)	84(2)	2(2)	-20(2)	23(2)
C(10)	58(2)	56(2)	65(2)	12(2)	-7(2)	8(2)
C(11)	59(2)	47(2)	56(2)	-1(1)	2(2)	-14(1)
C(12)	72(2)	48(2)	69(2)	-7(2)	-9(2)	-13(2)
C(13)	70(2)	62(2)	59(2)	-14(2)	-8(2)	-2(2)
C(14)	66(2)	66(2)	45(2)	0(2)	-1(2)	1(2)
C(15)	44(2)	45(2)	47(2)	4(1)	1(1)	1(1)
C(16)	47(2)	52(2)	45(2)	10(1)	1(1)	-5(1)
C(17)	93(3)	98(3)	52(2)	15(2)	4(2)	-37(2)
C(18)	123(4)	116(4)	67(3)	27(3)	6(2)	-64(3)

C(19)	105(3)	74(2)	79(3)	26(2)	-6(2)	-46(2)
C(20)	78(2)	47(2)	67(2)	10(2)	-6(2)	-21(2)
C(21)	57(2)	51(2)	60(2)	-3(2)	1(2)	6(1)
C(22)	63(2)	62(2)	82(2)	3(2)	16(2)	21(2)
C(23)	43(2)	88(3)	103(3)	4(2)	2(2)	15(2)
C(24)	43(2)	81(3)	81(2)	-2(2)	-8(2)	1(2)
C(25)	41(2)	51(2)	49(2)	6(1)	0(1)	-5(1)
C(26)	47(2)	45(2)	46(2)	4(1)	0(1)	-8(1)
C(27)	56(2)	65(2)	75(2)	-3(2)	-14(2)	-11(2)
C(28)	87(3)	62(2)	70(2)	-17(2)	-15(2)	-13(2)
C(29)	91(3)	49(2)	67(2)	-15(2)	-7(2)	3(2)
C(30)	60(2)	45(2)	59(2)	-3(1)	-6(2)	6(1)
C(31)	51(2)	59(2)	47(2)	9(2)	1(1)	10(2)
C(32)	73(2)	58(2)	73(3)	-8(2)	-2(2)	-4(2)
C(33)	151(4)	54(2)	62(3)	7(2)	-28(3)	-14(2)
C(34)	61(2)	44(2)	64(2)	-2(2)	-8(2)	-5(1)
O(1W)	317(8)	255(7)	105(3)	-5(4)	13(4)	118(6)

Table S3 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1**.

	x	y	z	U(eq)
H(1)	2365	8670	4221	62
H(2)	1444	8044	4817	77
H(3)	-65	8381	4995	85
H(4)	-615	9350	4569	76
H(7)	-983	10307	4207	80
H(8)	-1330	11284	3728	97
H(9)	-267	11717	3090	87
H(10)	1119	11174	2967	71
H(11)	1146	8652	3094	65
H(12)	830	8087	2271	76
H(13)	1380	8494	1420	77
H(14)	2205	9492	1412	71
H(17)	3065	10364	1486	97
H(18)	3874	11350	1608	123

H(19)	3962	11819	2497	103
H(20)	3226	11303	3251	77
H(21)	3408	8753	3048	67
H(22)	4934	8405	3118	83
H(23)	5931	8989	3711	93
H(24)	5377	9887	4214	82
H(27)	4765	10684	4698	78
H(28)	4029	11556	5154	88
H(29)	2469	11752	4987	83
H(30)	1708	11107	4320	65
H(1A)	3540(60)	7650(50)	2240(20)	271
H(2A)	3290(40)	7480(50)	2790(30)	271

Table S4 Hydrogen bonds for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(2A)...O(3)#1	0.91(2)	2.16(7)	2.785(7)	125(7)
O(1W)-H(1A)...O(2)#2	0.90(2)	1.92(4)	2.768(7)	156(9)

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,-z+1 #2 -x+1,y,-z+1/2

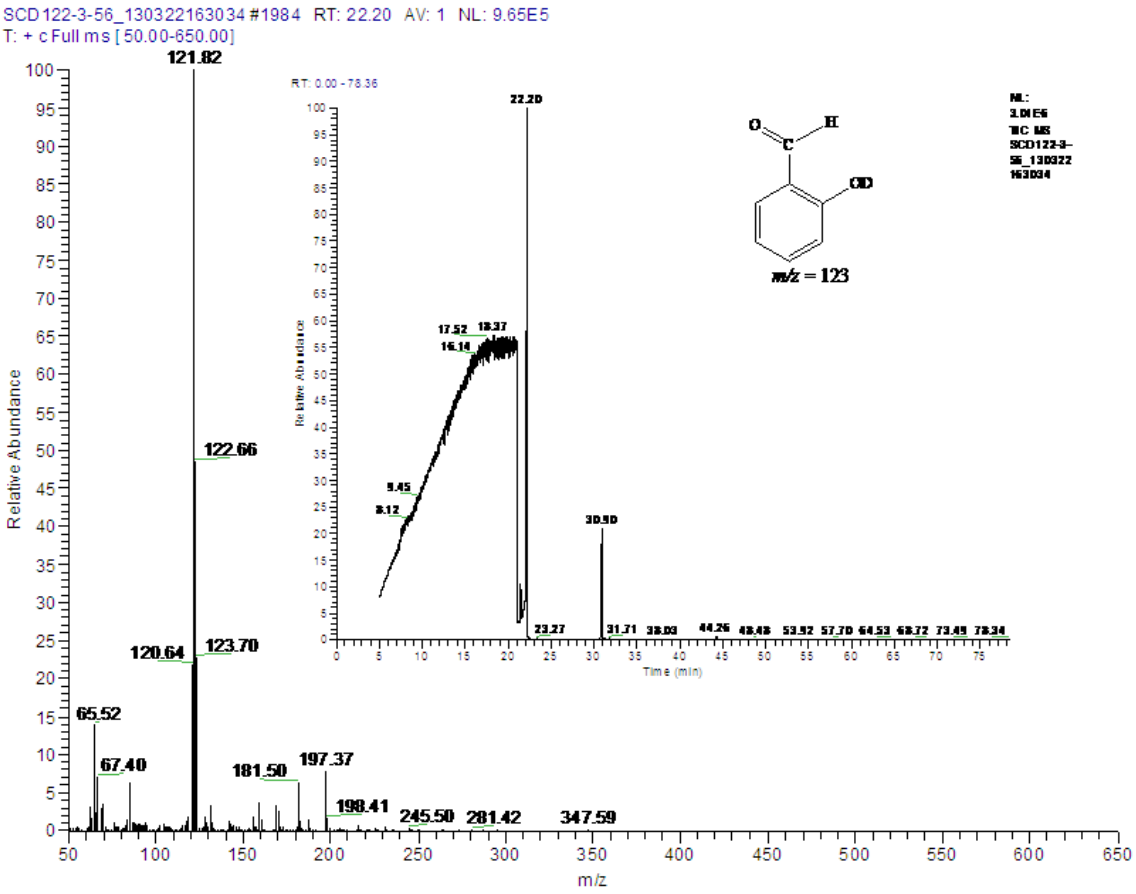

Figure S3 GC-MS spectrum of salicylaldehyde in DMSO-d_6 in the presence of **1**.

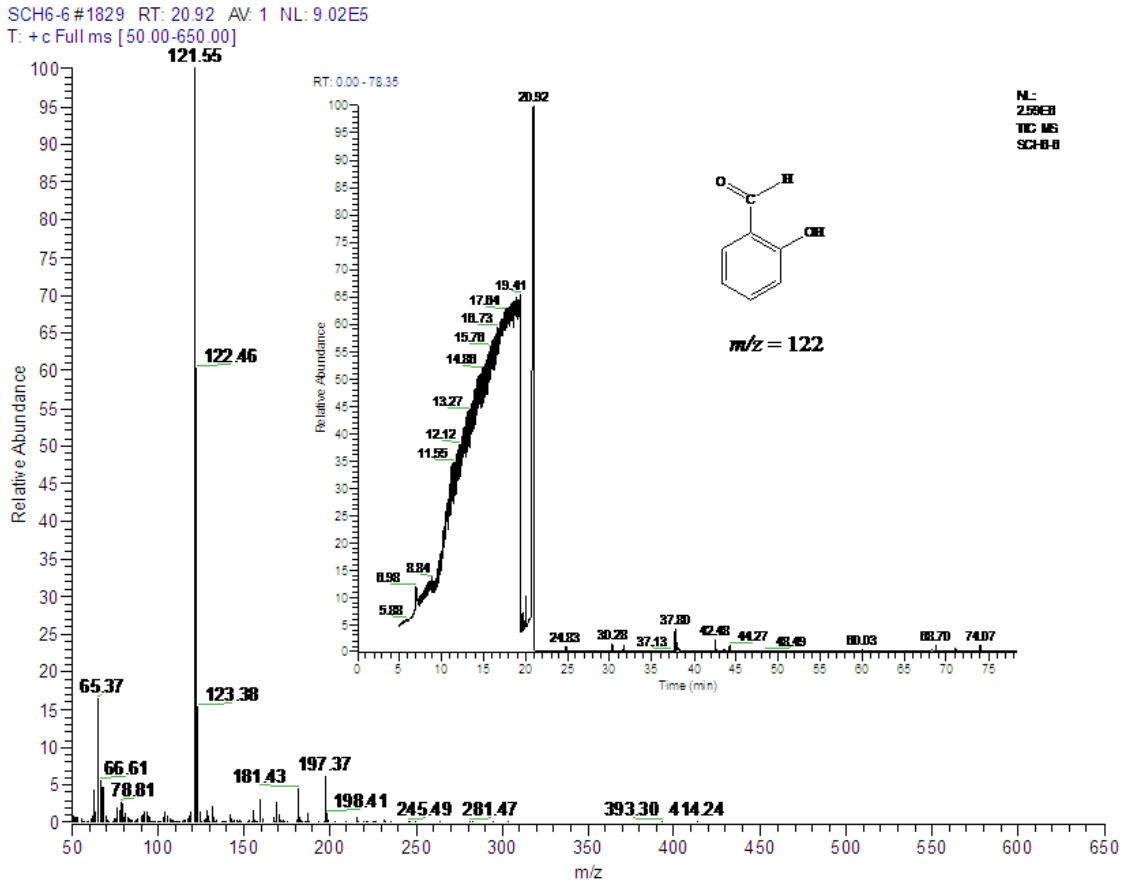

Figure S4 GC-MS spectrum of salicylaldehyde in DMSO-h_6 in the presence of **1**.