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Zwitterionic Liquid (ZIL) Coated CuO as an Efficient Catalyst for the Green Syntheses of Bis-Coumarins derivatives *via* One-Pot Multi-component Reactions Using Mechanochemistry

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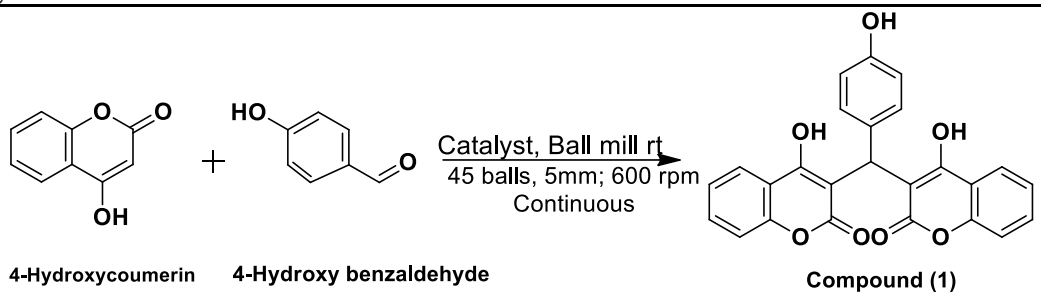
Table ST1. Eco scale calculation for the reaction of 4-hydroxybenzaldehyde and 4-hydroxycoumarin on 10 mmol scale.[1]

	Detail of parameters	Penalty Points
1. Yield		5
	90%	
2. Cost of reactants to obtain 10 mmol of product		
		0
	4-Hydroxybenzaldehyde	0
	4-Hydroxycoumarin	0
	Zil@CuO1	0
	Methanol (10 ml)	0
3. Safety		
	4-Hydroxybenzaldehyde	5 (T)
	4-Hydroxycoumarin	5 (T)
	ZIL@CuO1	5 (N)
	Methanol (10 ml)	10 (F, T)
4. Technical Setup		
	Ball-mill	2
5. Temperature Time		
	Room temperature, 3 h	1
	Annealing for CuO, Heating > 1 h	3
6. Work-up and purification		
	Solvent added	0
	Simple Filtration	0

Total of all penalties was 36, the total score was found to be 64 (100-36) indicating acceptable synthesis

Table ST2. Calculation of E-factor for the reaction of 4-Hydroxybenzaldehyde and 4-Hydroxycoumarin.[1]



Total amount of reactant: 1.22 g + 3.34 g = 4.56 g
Amount of final product: 4.1 g
Amount Of waste: 4.56 – 3.852 = 0.46 g
E factor = Amount of waste/Amount of product = 0.46/4.1 = 0.18.

Table ST3. Advancements of developed method over the methods documented in literature.

S. No	Reaction Time	Energy Source	Solvent Used	Catalyst Reusability	Yield	References
1	2.5 h	Reflux	Methanol	No	86%	[2]
2	24 h	Reflux	Methanol	No	83%	[3]
3	1 h	Reflux	Water	No	84%	[4]
4	24 h	Reflux	Ethanol	No	82%	[5]
5	5 h	Reflux	Acetic acid	No	78%	[6]
6	5H	Reflux	Ethanol	No	91%	[7]
7	24 h	Reflux	Ethanol	No	97%	[8]
8	1 h	Reflux	Water	No	88%	[9]
9	**180 min**	**Mechanical**	**No Solvent used**	**Recyclable**	**94%**	**-**

Table ST4. Selected bond lengths and angles (Å,°) for ZIL1

Bond lengths(Å)					
O(1)-C(9)	1.2101(16)	O(4)-C(11)	1.227(6)	O(7)-C(22)	1.2781(17)
O(2)-C(9)	1.2816(17)	O(5)-C(20)	1.211(12)	O(8)-C(22)	1.2051(17)
O(3)-C(11)	1.2636(18)	O(6)-C(20)	1.2701(17)		
Bond angles(°)					
C(1)-N(1)-C(2)	108.36(11)	C(1)-N(2)-C(8)	126.33(12)	C(13)-N(3)-C(21)	126.10(11)
C(1)-N(1)-C(10)	126.60(14)	C(7)-N(2)-C(8)	124.90(11)	C(12)-N(4)-C(18)	108.30(11)
C(2)-N(1)-C(10)	125.04(13)	C(12)-N(3)-C(13)	108.29(11)	C(12)-N(4)-C(19)	125.15(13)
C(1)-N(2)-C(7)	108.53(11)	C(12)-N(3)-C(21)	125.44(12)	C(18)-N(4)-C(19)	126.55(13)

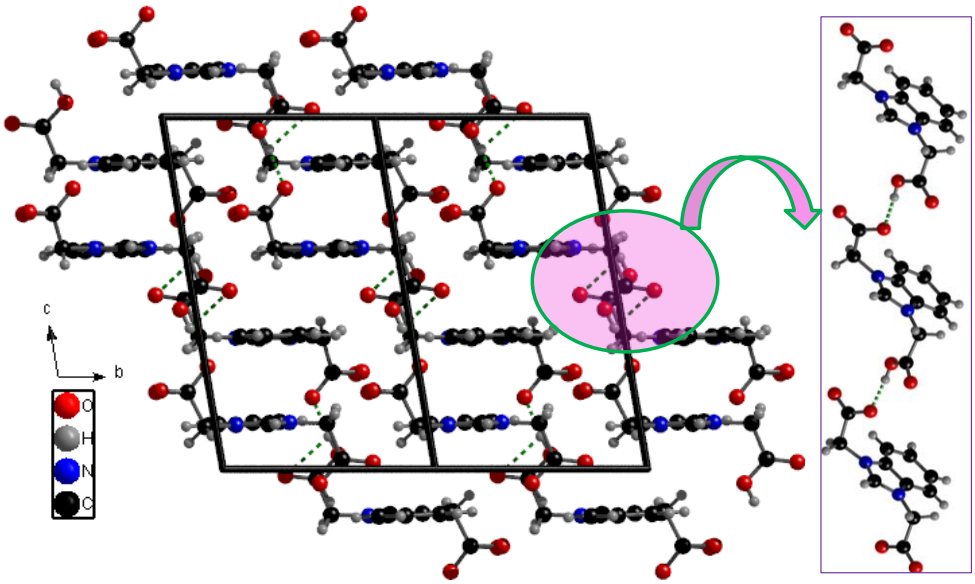


Figure SF1. The packing diagram of compound ZIL1

Table ST5. Hydrogen bonding parameters (Å, º) for Compound ZIL1

D-H···A	**D···A/ Å**	**H···A/ Å**	**D-H···A/º**
O2-H2A ...O6 [i]	2.479(2)	1.662(1)	174.3(1)
O7-H7A ...O3 [ii]	2.468(2)	1.649(1)	175.9(1)
C1-H1A...O1 [iii]	3.145(2)	2.501(1)	126.6(1)
C1-H1A...O6 [iv]	3.316(2)	2.498(1)	146.9(1)
C3-H3A...O2 [v]	3.439(2)	2.584(1)	153.0(1)
C4-H4A...O1[vi]	3.289(2)	2.490(1)	144.1(1)
C5-H5A...O6	3.224(3)	2.577(1)	127.1(1)
C12-H12A...O8[vii]	3.000(2)	2.405(1)	121.7(1)
C15-H15A...O8[ii]	3.399(3)	2.661(1)	136.8(1)
C15-H15A...O3	3.188(3)	2.520(1)	129.0(1)
C16-H16A...O8[viii]	3.179(2)	2.540(1)	126.2(1)
C17-H17A...O7[ix]	3.465(2)	2.596(1)	155.7(1)
C19-H19A...O7 [ix]	3.587(2)	2.617(1)	178.2(1)

Equivalent positions: (i) -x+1,-y+1,-z, (ii) -x+1,-y,-z+1, (iii) -x+2,-y+1,-z, (iv) x+1,+y,+z, (v)-x+1,-y,-z, (vi) x-1,+y-1,+z, (vii) -x,-y,-z+1, (viii) x+1,+y+1,+z, (ix)-x+1,-y+1,-z+1.

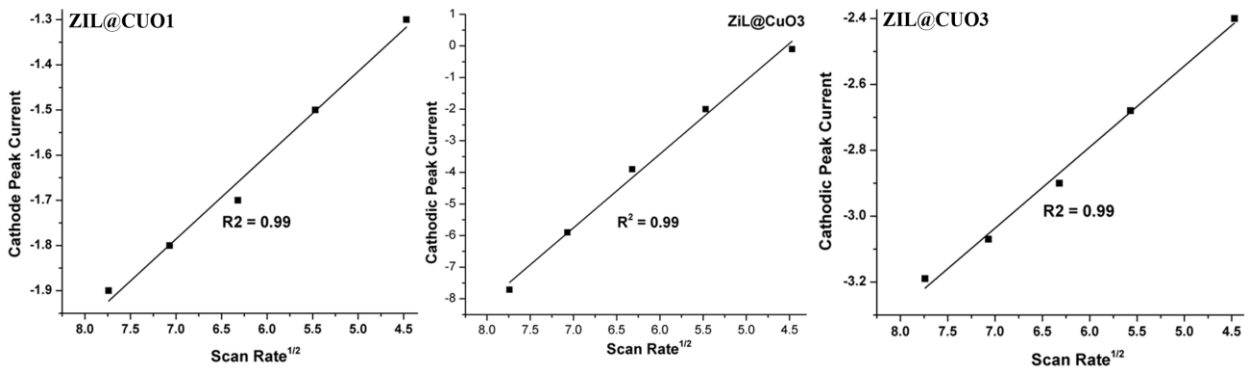


Figure SF2. Linear correlation was observed between cathodic peak current and the square root in CV study for **ZIL@CuO1-3** with subsequent increase in scan rate.

Table ST6. Multiple CV based parameters obtained during study

S. No	Catalyst	$E1_{pc}$ mV	$E1_{pa}$ mV	$\Delta E1$ mV	$E1_{1/2}$ mV	$I1_c/I1_a$	$E2_{pc}$	$E2_{pa}$	ΔE_2 mV	$E2_{1/2}$	$I2_c/I2_a$
1	ZIL1	-0.477	-0.444	0.33	-0.460	1.17	-	-	–	–	-
2	ZIL2	-0.605	-0.587	0.18	-0.596	0.37	0.094	0.029	65	0.615	1.12
3	ZIL3	-0.515	-0.451	0.64	-0.483	1.24	-	-	–	–	-
4	CuO	-0.500	-0.420	0.80	-0.460	3	-	-	–	–	-
5	ZIL1 + Cu	0.344	0.547	0.203	0.445	6	0.675	0.211	464	0.443	1.26
6	ZIL3 + Cu	-0.558	-0.414	0.144	-0.486	1.19	-	-	–	–	-
7	ZIL2 + Cu	-0.980	-0.897	0.83	-0.938	3.2	0.295	0.161	134	0.228	0.57
8	ZIL@CuO1	-0.549	-0.308	0.241	-0.428	0.30	-	-	–	–	-
9	ZIL@CuO2	-.507	-0.476	0.31	-0.491	1.2	-	-	–	–	-
10	ZIL@CuO3	-0.638	0.457	1.281	-0.547	6.03	-	-	–	–	-

$E1_{pc}$: Electrode potential at first cathodic peak

$E1_{pa}$: Electrode potential at first anodic peak

$\Delta E1$: Electrode Potential for first peak

$E1_{1/2}$: Half electrode potential for first peak

$I1_C$: Cathodic peak current for first peak

$I1_a$: Cathodic peak current for first peak

$E2_{pc}$: Electrode potential at second cathodic peak

$E2_{pa}$: Electrode potential at second anodic peak

ΔE_2: Electrode Potential for second peak

$E2_{1/2}$: Half electrode potential for second peak

$I2_c$: Cathodic peak current for second peak

$I2_a$: Cathodic peak current for second peak

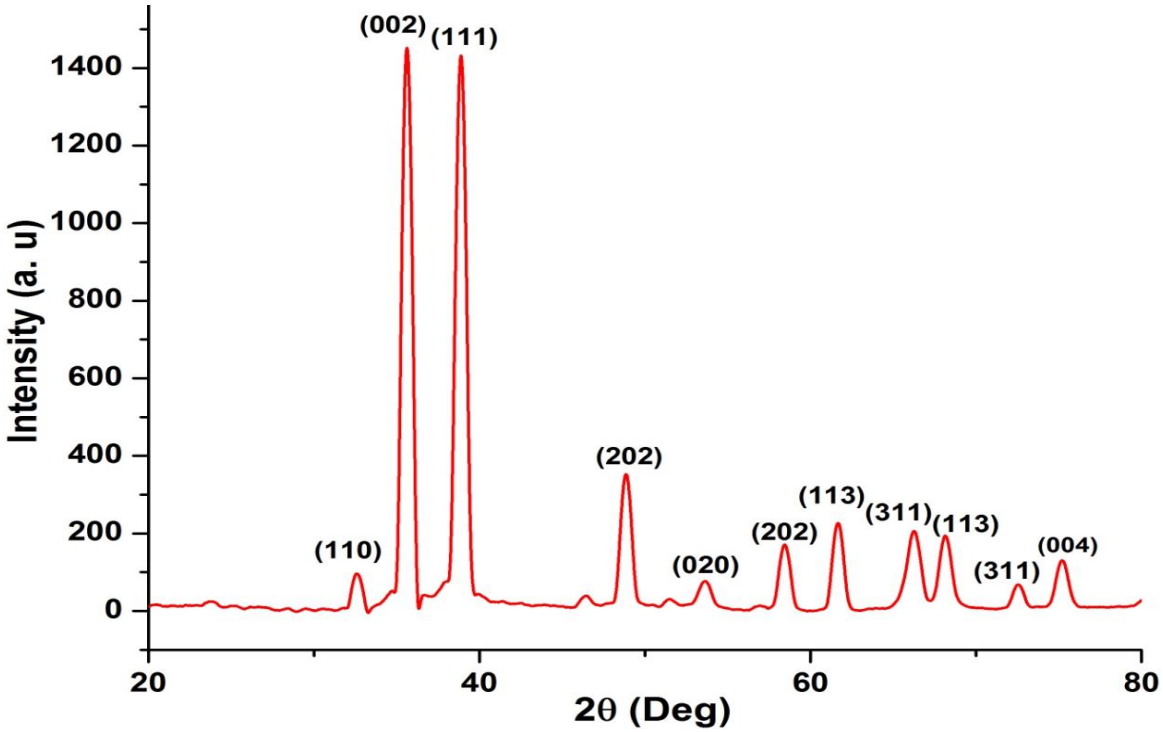


Figure SF3. PXRD pattern of **ZIL@CuO1** after calcined at 500 ºC for 5h. Typical CuO based pattern was obtained.

Table ST7. Effect of milling time and milling speed on the yield of reaction.

Sr. No	Time (Min)	Speed (rpm)	Yield (%)
1	30	600	25
2	40	600	32
3	50	600	40
4	60	600	40
5	80	600	55
6	100	600	75
7	120	600	78
8	150	600	82
9	**180**	**600**	**86**
10	210	600	86
11	240	600	85
12	180	400	68
13	180	500	75
14	180	800	67

Table ST8. Effect of milling time on the heat produced inside the milling jar

Sr. No	Time (Min)	Temp (º C)[#]
1	0	22.4
2	5	25.8
3	10	28.5
4	15	31.3
5	20	35.2
6	30	38.7
7	45	41.6
8	60	47.2

Table ST9. Effect of ball number on the yield of reaction

Sr. No	No Of Balls	Yield %
1	20	45.5
2	25	45.1
3	30	55.0
4	35	62.2
5	40	75.6
6	45	86.3
7	50	85.8
8	55	79.3
9	60	73.8

Table ST10. Selected bond lengths and angles (Å,º) for compound **(12)**

Bond lengths(Å)					
O(1)-C(10)	1.350(6)	O(4)-C(19)	1.347(6)	O(7)-N(1)	1.215(6)
O(1)-C(9)	1.383(6)	O(4)-C(18)	1.392(7)	O(8)-N(1)	1.208(6)
O(2)-C(10)	1.235(6)	O(5)-C(19)	1.228(7)	O(9)-C(35)	1.359(6)
O(3)-C(3)	1.326(6)	O(6)-C(12)	1.334(6)	O(9)-C(34)	1.380(6)
O(10)-C(35)	1.216(6)	O(12)-C(44)	1.348(6)	O(13)-C(44)	1.227(6)
O(11)-C(28)	1.338(5)	O(12)-C(43)	1.382(6)	O(14)-C(37)	1.341(5)
O(15)-N(2)	1.207(7)	O(16)-N(2)	1.209(7)		
Bond angles(º)					
C(10)-O(1)-C(9)	122.0(4)	O(8)-N(1)-O(7)	122.4(6)	O(5)-C(19)-O(4)	115.6(5)
C(19)-O(4)-C(18)	121.0(5)	O(8)-N(1)-C(24)	119.2(5)	O(5)-C(19)-C(11)	125.0(5)
C(35)-O(9)-C(34)	121.6(4)	O(7)-N(1)-C(24)	118.5(6)	O(4)-C(19)-C(11)	119.3(5)
C(44)-O(12)-C(43)	122.0(4)	O(15)-N(2)-O(16)	122.3(7)	O(11)-C(28)-C(27)	124.3(5)
O(8)-N(1)-O(7)	122.4(6)	O(15)-N(2)-C(49)	118.5(7)	O(11)-C(28)-C(29)	115.2(5)
O(8)-N(1)-C(24)	119.2(5)	O(16)-N(2)-C(49)	119.2(6)	O(10)-C(35)-O(9)	116.2(4)

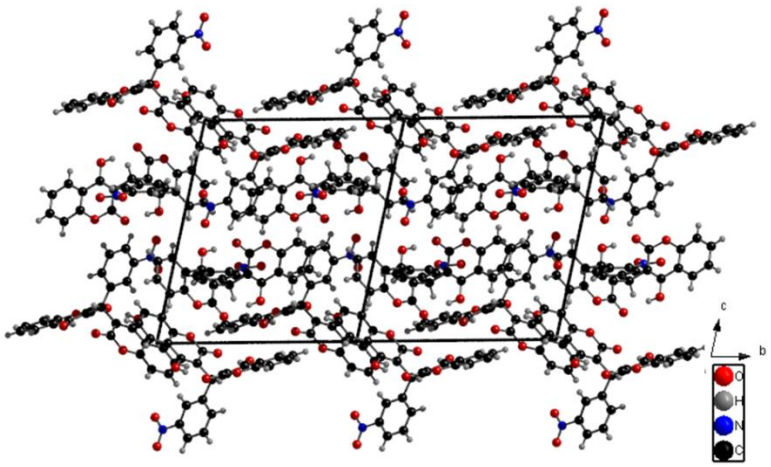


Figure SF4. Packing diagram of compound **(12)** shown down a axis.

Table ST11. Hydrogen bonding parameters (Å, º) for Compound (12)

D-H···A	**D···A/ Å**	**H···A/ Å**	**D-H···A/º**
O3-H3A...O5	2.646(6)	1.852(4)	162.4(4)
O6-H6B...O2	2.701(6)	1.888(4)	171.0(3)
O11-H11A...O13	2.600(5)	1.783(4)	174.1(3)
O14-H14B...O10	2.712(5)	1.955(4)	153.1(3)
C5-H5A...O3 [i]	3.269(7)	2.557(4)	133.6(4)
C6-H6A...O5 [i]	3.577(7)	2.663(4)	167.8(4)
C21-H21A...O16 [ii]	3.287(8)	2.608(5)	130.3(4)
C31-H31A...O13 [iii]	3.365(7)	2.512(4)	152.6(4)
C39-H39A...O10 [iv]	3.189(6)	2.354(3)	149.1(4)
C41-H41A...O1 [v]	3.334(7)	2.553(3)	141.8(4)
C42-H42A...O2 [v]	3.293(7)	2.630(4)	128.8(4)
C42-H42A...O6 [v]	3.461(6)	2.552(3)	165.9(4)
C46-H46A...O8	3.490(9)	2.635(5)	153.0(4)

Equivalent positions: (i) -x,-y+2,-z+1, (ii) x,+y+1,+z, (iii) -x+1,-y,-z+2, (iv) -x,-y+1,-z+2, (v) x+1,+y,+z

Table ST12. NMR data of compounds synthesized during experimental procedure

1,3-bis(carboxymethyl)-1H-benzo[d]imidazol-3-ium bromide (ZIL1) ^{1}H NMR (DMSO-d_6, 9:1, 400 MHz) δ 10.04 (s, 1H), 8.45–8.40 (m, 2H, Ar–H), 8.30–8.20 (m, 2H, Ar–H), 5.77 (s, 4H, CH_2);^{13}C NMR (D_2O, 9:1, 100 MHz)δ 48.8, 113.8, 127.4, 131.6, 143.7, 168.4. Anal.Calcd for$C_{11}H_{11}BrN_2O_4^-$: C, 41.93; H, 3.52; N, 8.89; Found: C, 41.89; H, 3.55 N, 8.88.

3-(carboxymethyl)-1-methyl-1H-imidazol-3-ium (ZIL2) ^{1}H NMR (400 MHz, DMSO-d_6, ppm)δ : 3.90 (s, 3H), 5.12 (s, 2H), 7.57-7.74 (d, 2H,), 9.41 (s, 1H,); ^{13}C NMR (100 MHz, D_2O, ppm) δ: 36.39, 50.07, 123.66, 124.13, 137.89, 168.58.Anal.Calcd for $C_6H_9N_2O_2^+$: C, 51.06; H, 6.43; N, 19.85; Found: C, 51.01; H, 6.42 N, 19.84.

2-(1-methyl-1H-imidazol-3-ium-3-yl)ethanesulfonate (ZIL3). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (t, J = 1.8 Hz, 1H), 7.65 (s, 1H), 7.59 (s, 0H), 7.11 (s, 1H), 6.89 (d, J = 6.0 Hz, 1H), 4.33 (t, 1H), 2.93 (t, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.66, 123.57, 123.10, 50.74, 46.59, 36.12. Anal.Calcd for$C_6H_{10}N_2O_3S$: C, 37.88; H, 5.30; N, 14.37; Found: C, 37.76; H, 5.35 N, 14.33.

3,3'-((4-hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (1). ^{1}H NMR (400 MHz, DMSO-D_6) δ 8.93 (s, 1H), 7.77 (d, J = 7.8 Hz, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.28 – 7.07 (m, 4H), 6.83 (d, J = 8.2 Hz, 2H), 6.52 (d, J = 8.7 Hz, 2H), 6.12 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 168.07, 165.09, 155.14, 152.99, 132.81, 131.30, 128.04, 124.61, 123.33, 120.54, 115.92, 115.01, 104.32, 35.83.Anal.Calcd for$C_{25}H_{16}O_7$: C, 70.09; H, 3.76;. Found: C, 70.23; H, 3.69.

3,3'-(pyridin-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) (2). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (s, 1H), 7.75 (d, 2H), 7.41 (td, J = 7.3, 1.8 Hz, 2H), 7.16 (d, J = 7.9 Hz, 5H), 7.08 (d, J = 7.9 Hz, 1H), 6.83 (t, J = 7.6 Hz, 1H), 6.54 (d, 2H), 6.10 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 167.64, 164.67, 155.54, 152.86, 130.95, 129.61, 126.45, 124.47, 123.22, 120.75, 118.21, 115.79, 115.09, 104.24, 33.37.Anal.Calcd for $C_{24}H_{15}NO_6$: C, 69.73; H, 3.66;. N,3.39; Found: C, 69.65; H, 3.71; N, 3.44.

3,3'-((2-hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3). ^{1}H NMR (400 MHz, DMSO-d_6) δ 17.11 (s, 1H), 8.28 (d, J = 4.9 Hz, 1H), 8.12 (s, 2H), 7.74 (dd, J = 7.6, 2.1 Hz, 2H), 7.51 (dd, J = 7.9, 2.1 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.23 – 7.14 (m, 4H), 7.11 (d, J = 7.9 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.21 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 168.09, 165.05, 162.35, 153.04, 148.82, 136.26, 131.35, 124.60, 123.36, 121.43, 120.82, 120.53, 115.96, 103.89, 72.79, 39.92.Anal.Calcd for $C_{25}H_{16}O_7$: C, 70.09; H, 3.76;. Found: C, 69.89; H, 3.78.

3,3'-((3-hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (4) ^{1}H NMR (400 MHz, DMSO-d_6) δ 17.58 (s, 1H), 8.88 (s, 1H), 7.77 (dd, J = 7.6, 2.1 Hz, 2H), 7.45 (td, J = 8.5, 7.9, 2.1 Hz, 2H), 7.19 (dd, J = 15.0, 7.6 Hz, 4H), 6.88 (t, J = 7.9 Hz, 1H), 6.56 – 6.33 (m, 3H), 6.13 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 168.19, 165.08, 157.45, 153.01, 144.48, 131.39, 128.97, 124.66, 123.38, 120.50, 117.96, 115.96, 114.21, 112.34, 103.95, 36.55.Anal.Calcd for $C_{25}H_{16}O_7$: C, 70.09; H, 3.76;. Found: C, 70.14; H, 3.81.

3,3'-(pyridin-4-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) (5). ^{1}H NMR (400 MHz, DMSO-d_6) δ

17.40 (s, 1H), 8.28 (d, 2H), 8.13 (s, 1H), 7.76 (dd, *J* = 7.9, 2.4 Hz, 2H), 7.54 – 7.41 (m, 2H), 7.27 – 7.12 (m, 4H), 7.02 (d, *J* = 4.9 Hz, 2H), 6.20 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 168.35, 164.90, 153.09, 152.32, 149.59, 131.68, 124.69, 123.52, 122.77, 120.22, 116.08, 102.76, 36.48.Anal.Calcd for $C_{24}H_{15}NO_6$: C, 69.73; H, 3.66;. N,3.39; Found: C, 69.74; H, 3.59; N, 3.72.

3,3'-(pyridin-3-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) (6) ^{1}H NMR (400 MHz, DMSO-d_6) δ 17.45 (s, 1H), 8.79 (s, 1H), 8.24 (dd, *J* = 6.7, 3.7 Hz, 2H), 7.77 (d, *J* = 7.9, 2H), 7.58 – 7.33 (m, 3H), 7.27 – 7.00 (m, 5H), 6.25 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 168.31, 164.86, 153.07, 148.69, 146.55, 138.23, 134.99, 131.63, 124.64, 123.54, 123.51, 120.26, 116.07, 103.11, 34.76.Anal.Calcd for $C_{24}H_{15}NO_6$: C, 69.73; H, 3.66;. N,3.39; Found: C, 69.61; H, 3.70; N, 3.36.

3,3'-((2-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7) ^{1}H NMR (400 MHz, DMSO-d_6) δ 16.72 (s, 1H), 8.79 (s, 1H), 7.71 (d, 2H), 7.51 – 7.41 (m, 4H), 7.30 (q, *J* = 7.3, 3.7 Hz, 2H), 7.18 (d, 4H), 6.43 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 168.40, 164.01, 153.04, 150.09, 135.87, 131.91, 131.52, 130.09, 127.11, 124.60, 124.37, 123.44, 120.05, 116.03, 102.71, 34.40.Anal.Calcd for $C_{25}H_{15}NO_8$: C, 65.65; H, 3.31;. N,3.06; Found: C, 65.61; H, 3.26; N, 3.05.

3,3'-((2,3-dihydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (8)^{1}H NMR (400 MHz, DMSO-d_6) δ 12.38 (s, 1H), 8.81 (s, 2H), 7.75 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.46 – 7.33 (m, 2H), 7.21 – 7.07 (m, 5H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.48 (q, *J* = 7.9, 1.7 Hz, 1H), 6.35 (t, *J* = 7.8, 1.7 Hz, 1H), 6.12 (s, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 167.59, 164.64, 152.86, 144.66, 143.70, 130.86, 130.10, 124.48, 123.15, 120.81, 120.63, 117.53, 115.76, 113.05, 104.46, 33.41.Anal.Calcd for $C_{24}H_{15}O_6$: C, 67.57; H, 3.63;. Found: C, 67.49; H, 3.69.

3,3'-(phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (9) ^{1}H NMR (400 MHz, DMSO-d_6) δ 17.55 (s, 2H), 7.76 (d, *J* = 7.9 Hz, 2H), 7.45 (t, *J* = 7.9 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.11 (t, *J* = 7.3 Hz, 2H), 7.06 – 6.98 (m, 3H), 6.22 (s, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ 168.22, 165.09, 153.02, 142.89, 131.43, 128.21, 127.16, 125.32, 124.64, 123.41, 120.45, 115.98, 103.92, 36.65.Anal.Calcd for $C_{25}H_{16}O_6$: C, 72.81; H, 3.91;. Found: C, 72.88; H, 3.88.

3,3'-((2,4-dihydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (10) ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.69 (s, 1H), 7.74 (dd, *J* = 8.1, 1.7 Hz, 3H), 7.43 – 7.34 (m, 3H), 7.18 – 7.09 (m, 5H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.02 (d, *J* = 2.7 Hz, 1H), 5.99 (s, 1H), 5.96 (dd, *J* = 8.2, 2.4 Hz, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 167.46, 164.66, 156.18, 156.07, 152.83, 130.80, 129.86, 124.44, 123.13, 120.85, 119.99, 115.74, 105.09, 104.69, 102.81, 32.63.Anal.Calcd for C25H16O8: C, 67.57; H, 3.63;. Found: C, 67.62; H, 3.59.

3,3'-((4-chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (11) ^{1}H NMR (400 MHz, chloroform-*D*) δ 17.17 (s, 1H), 8.04 (d, *J* = 7.3 Hz, 2H), 7.44 (td, *J* = 7.6, 1.8 Hz, 2H), 7.34 – 7.03 (m, 8H), 6.27 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*D*) δ 170.65, 167.43, 152.94, 139.53, 131.17, 131.3, 128.33, 128.26, 125.36, 123.41, 120.44, 115.68, 103.58, 36.42. Anal.Calcd for $C_{25}H_{15}ClO_6$: C, 67.20; H, Found: C, 67.25; H, 3.34.

3,3'-((3-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (12): ^{1}H NMR (400 MHz, chloroform-*D*) δ 11.37 (s, 1H), 11.37 (s, 1H), 8.13 (dd, *J* = 7.6, 2.7 Hz, 1H), 8.10 – 8.03 (m, 2H), 8.01 – 7.95 (m, 1H), 7.65 (t, *J* = 7.9 Hz, 2H), 7.59 – 7.46 (m, 3H), 7.45 – 7.35 (m, 4H), 6.11 (s, 1H).^{13}C NMR (101 MHz, chloroform-*D*) δ 169.23, 167.07, 166.68, 164.95, 152.67, 152.41, 148.80, 138.03, 133.45, 132.88, 129.69, 125.30, 125.25, 124.58, 122.23, 121.84, 116.94, 116.82, 116.76, 116.33, 104.68, 103.29, 36.25. Anal.Calcd for $C_{25}H_{15}NO_8$: C, 65.65; H, 3.31; N, 3.06. Found: C, 65.60; H, 3.35; N, 3.09.

3,3'-((2,4-dimethoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (13) ^{1}H NMR (400 MHz, chloroform-*D*) δ 11.74 (s, 1H), 8.00 (d, *J* = 7.9 Hz, 2H), 7.58 (t, *J* = 7.9 Hz, 2H), 7.45 – 7.29 (m, 5H), 6.94 (d, *J* = 9.2 Hz, 1H), 6.60 (d, *J* = 9.2 Hz, 1H), 6.08 (s, 1H), 3.83 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*D*) δ 176, 164.07, 153.55, 153.09, 152.20, 132.20, 124.85, 124.37, 122.56, 121.17, 116.63, 106.49, 60.78.25, 60.43. 33.12. Anal.Calcd for $C_{27}H_{20}O_8$: C, 68.64; H, 4.27; Found: C, 68.60; H, 4.30.

3,3'-((4-oxo-4H-chromen-3-yl)methylene)bis(4-hydroxy-2H-chromen-2-one) (14) ^{1}H NMR (400 MHz, chloroform-*D*) δ 11.50 (s, 2H), 8.08 (d, *J* = 9.4 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 1.5 Hz, 1H), 7.68 – 7.56 (m, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 5H), 5.99 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*D*) δ 177.00, 168.22, 164.52, 156.29, 153.51, 152.34, 133.83, 132.93, 125.99, 125.32, 125.00, 124.46, 123.48, 118.71, 118.05, 103.99, 30.58. Anal.Calcd for $C_{28}H_{16}O_8$: C, 70.00; H, 3.36; Found: C, 69.98; H, 3.39

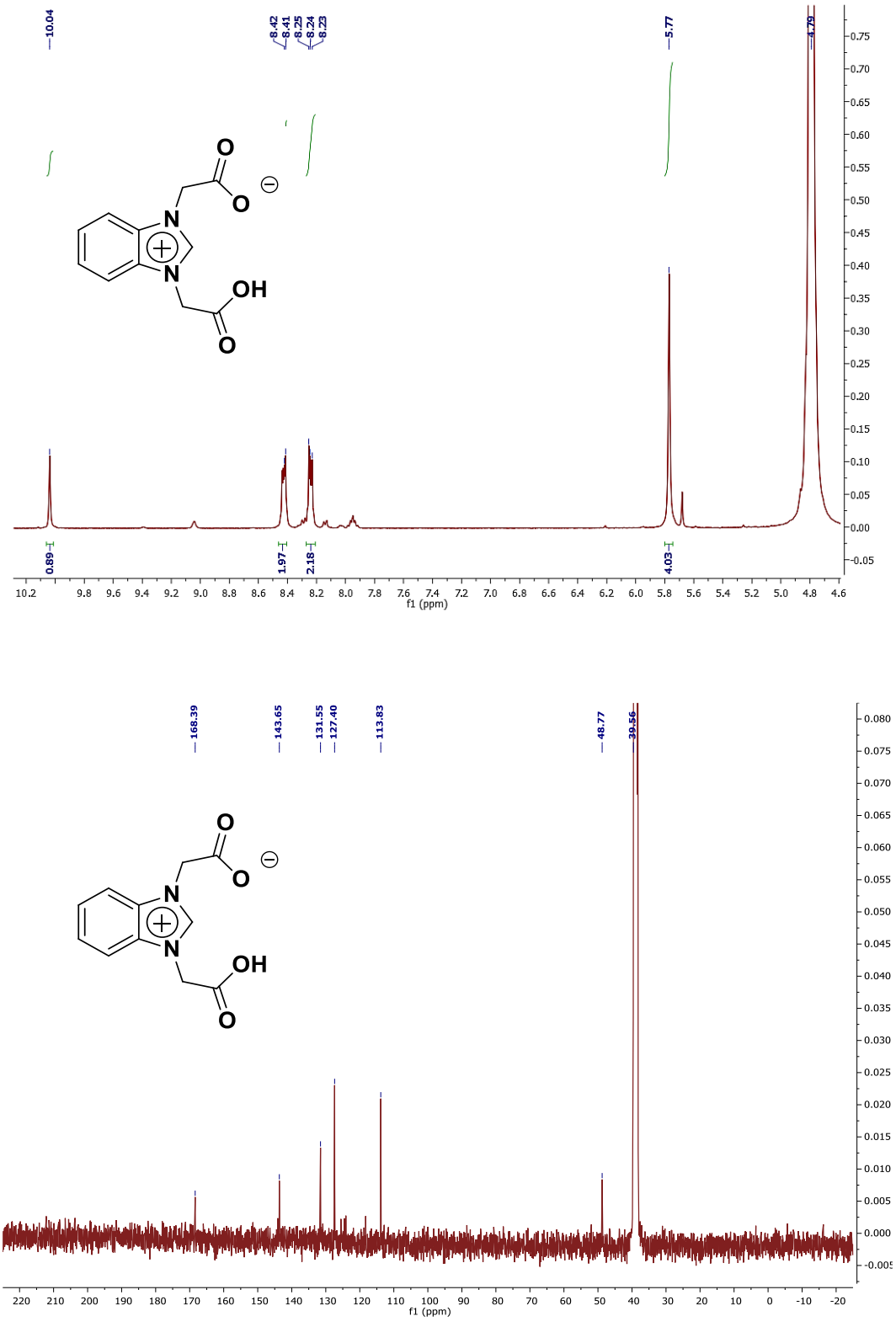


Figure SF5. ^{1}H and ^{13}C NMR of ZIL1

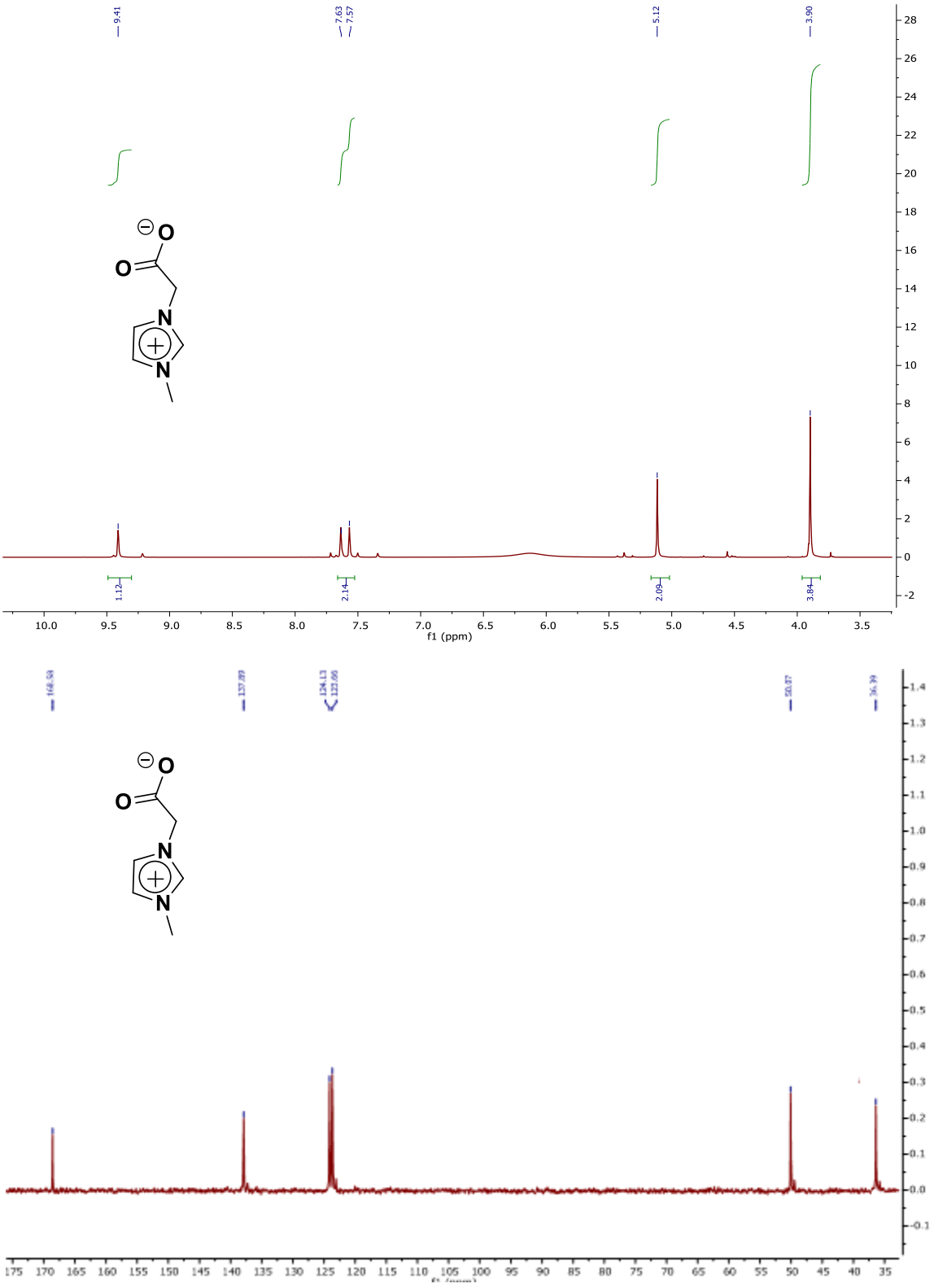


Figure SF6. ^{1}H and ^{13}C NMR of ZIL2

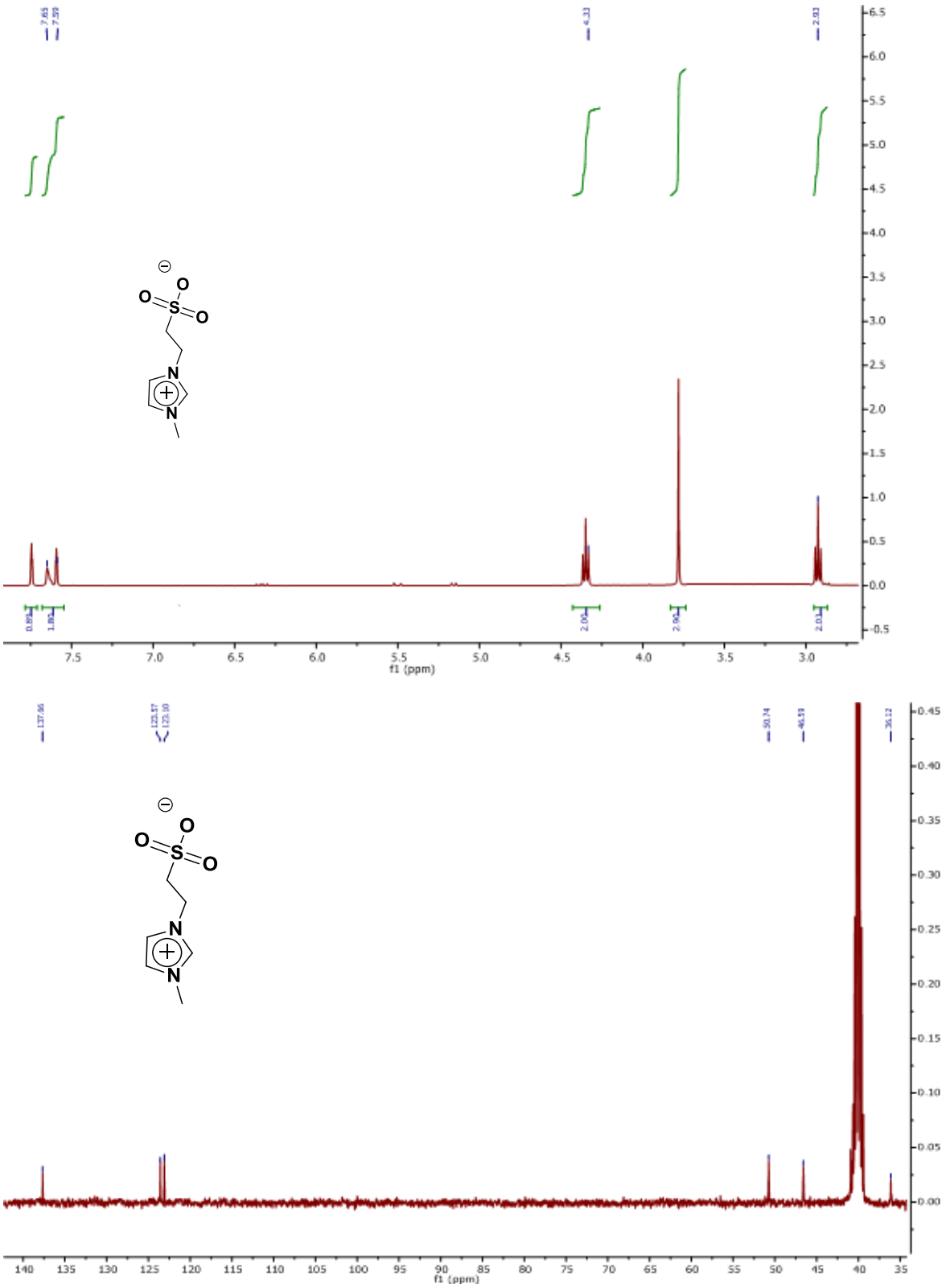
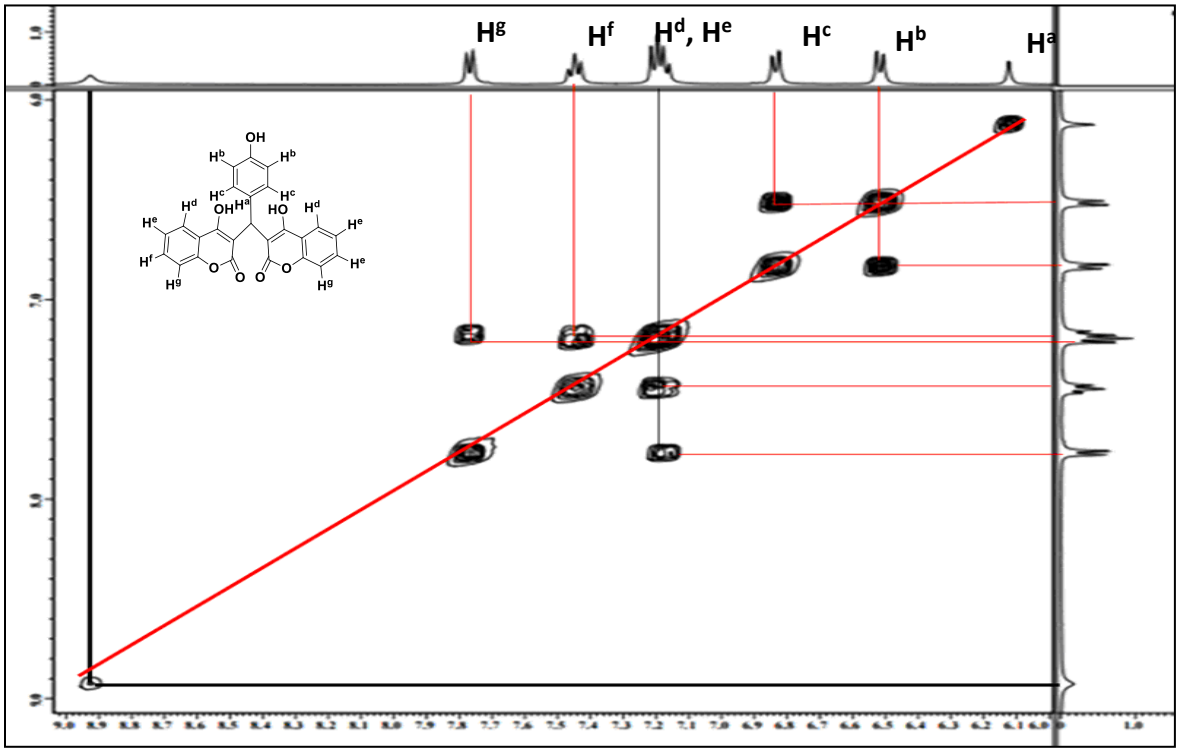


Figure SF7. ^{1}H and ^{13}C NMR of ZIL3



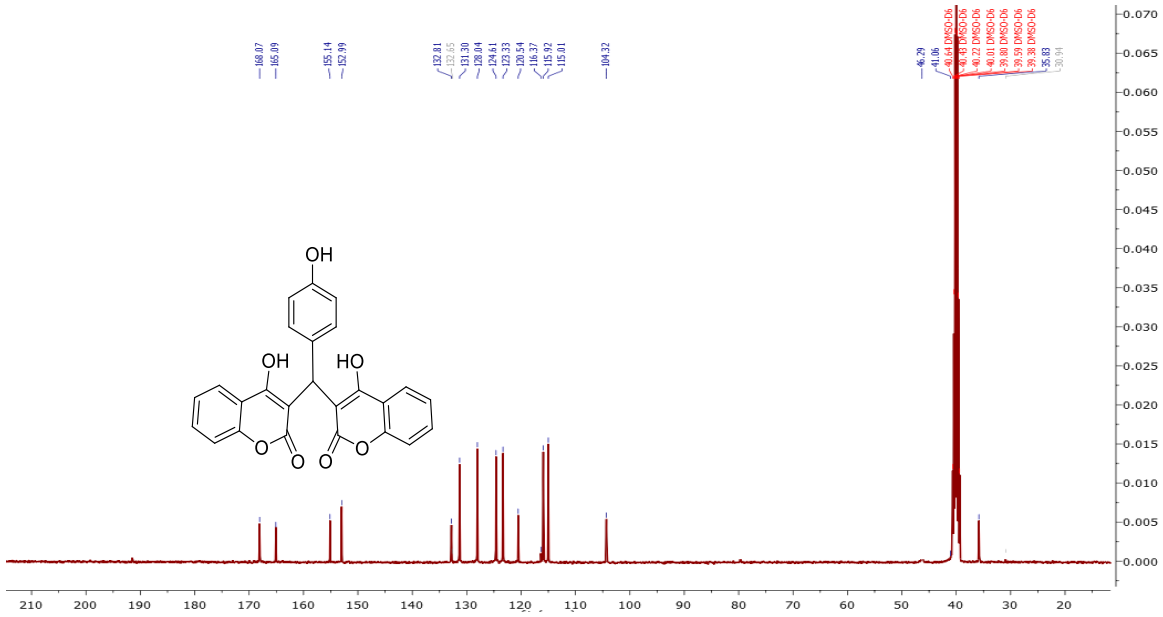


Figure SF8. H-H cosy and ^{13}C NMR of 3,3'-((4-hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

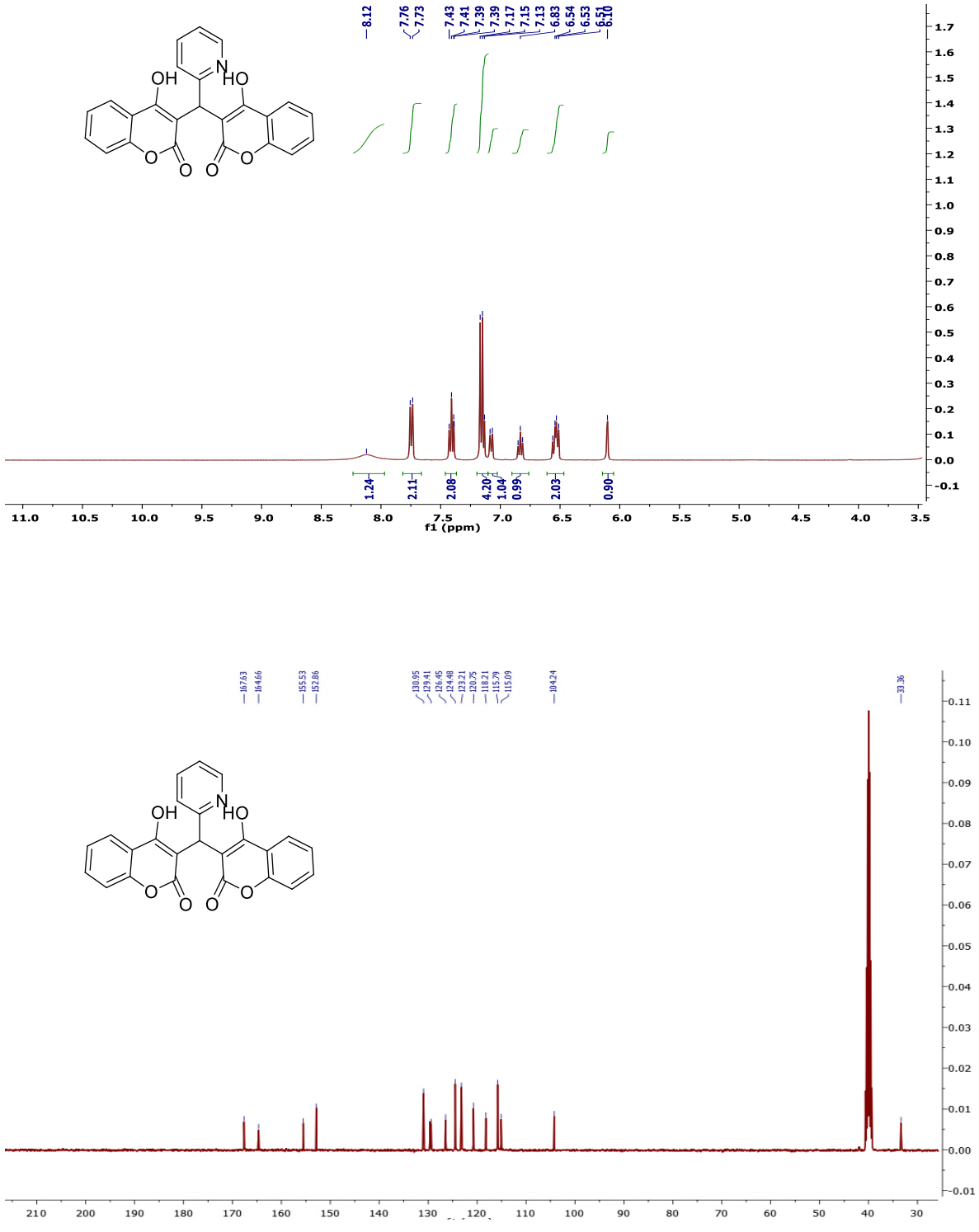


Figure SF9. ^{1}H and ^{13}C NMR of 3,3'-(pyridin-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one)

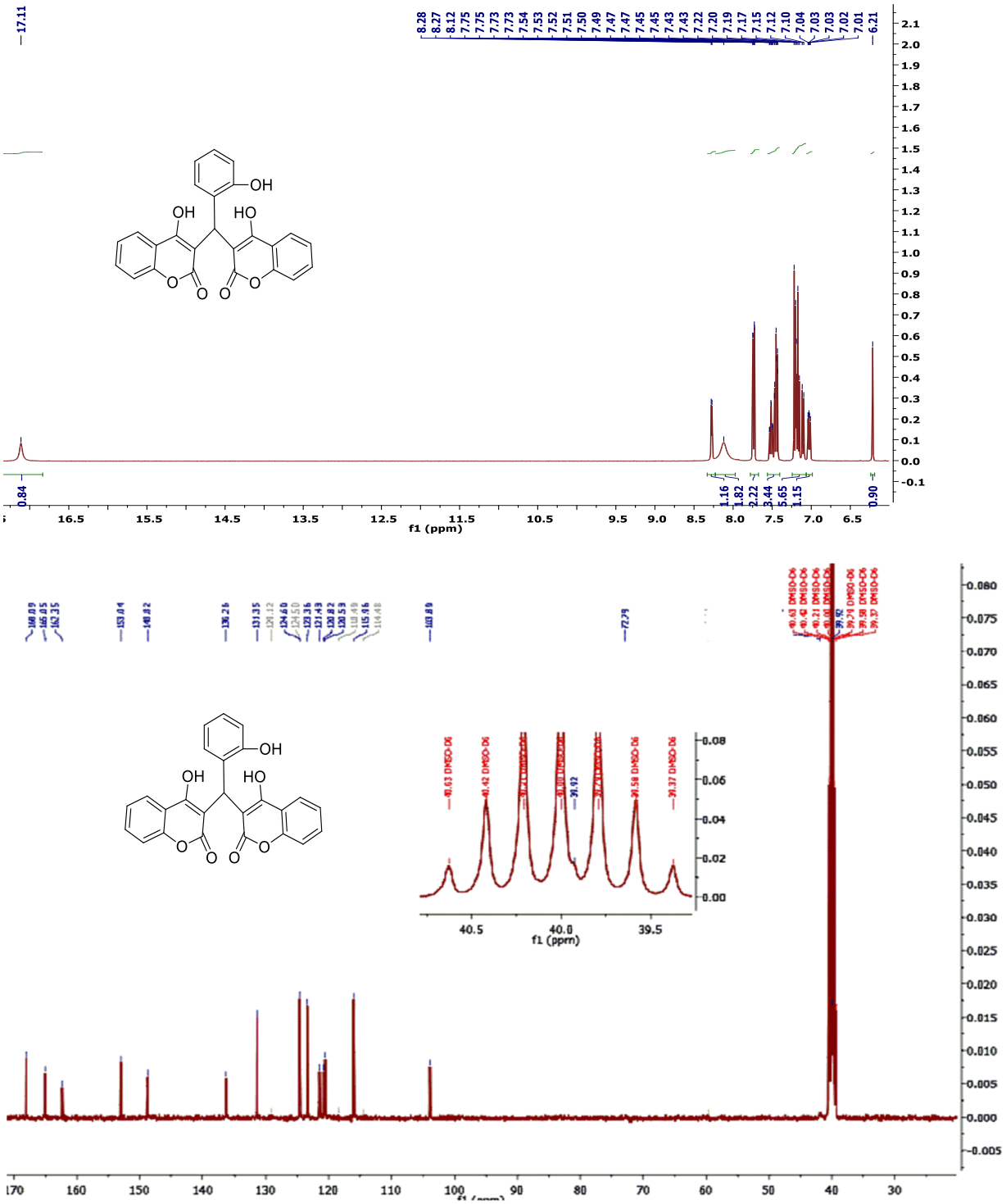


Figure SF10. ^{1}H and ^{13}C NMR of 3,3'-((2-hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

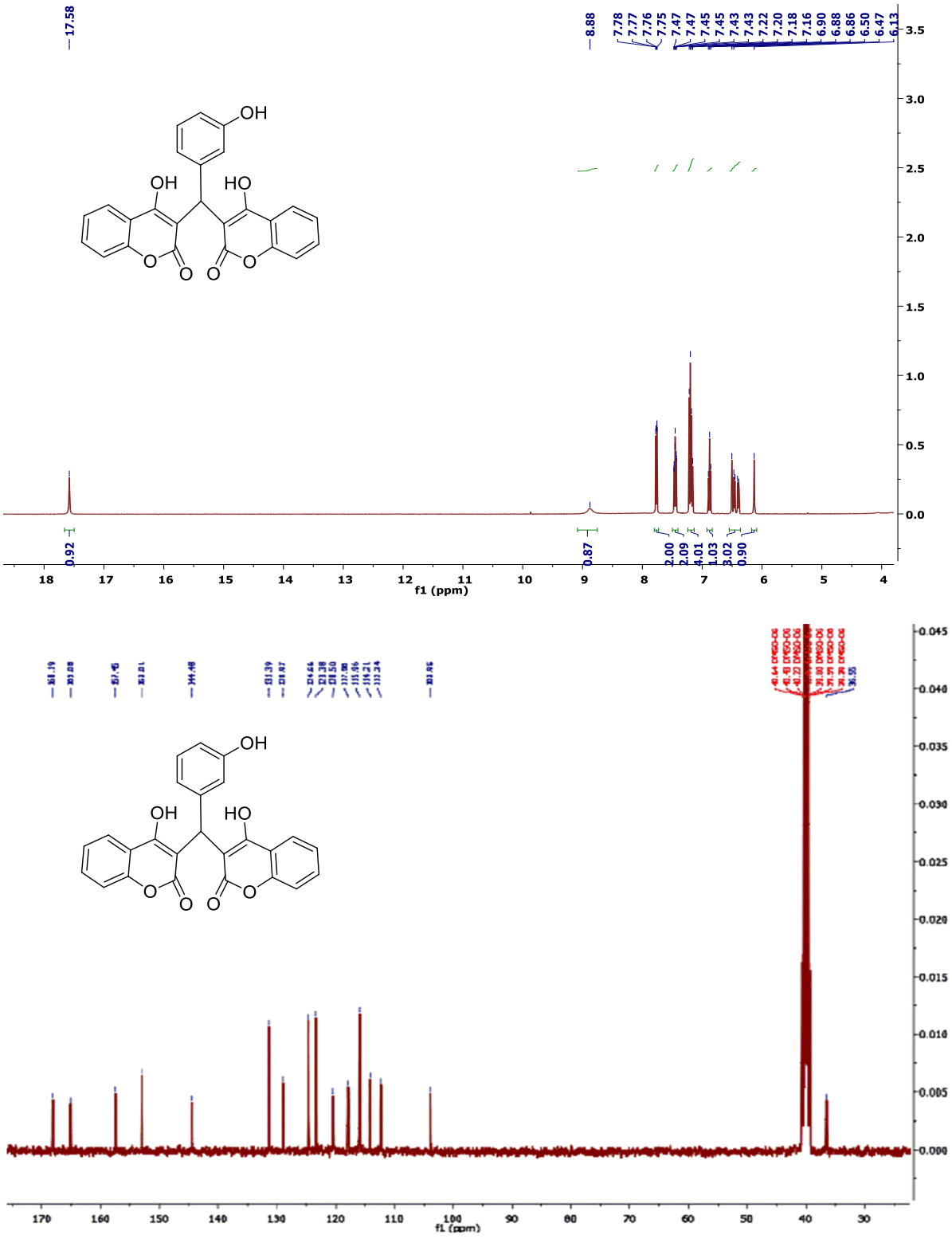


Figure SF11. ^{1}H and ^{13}C NMR of 3,3'-((3-hydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

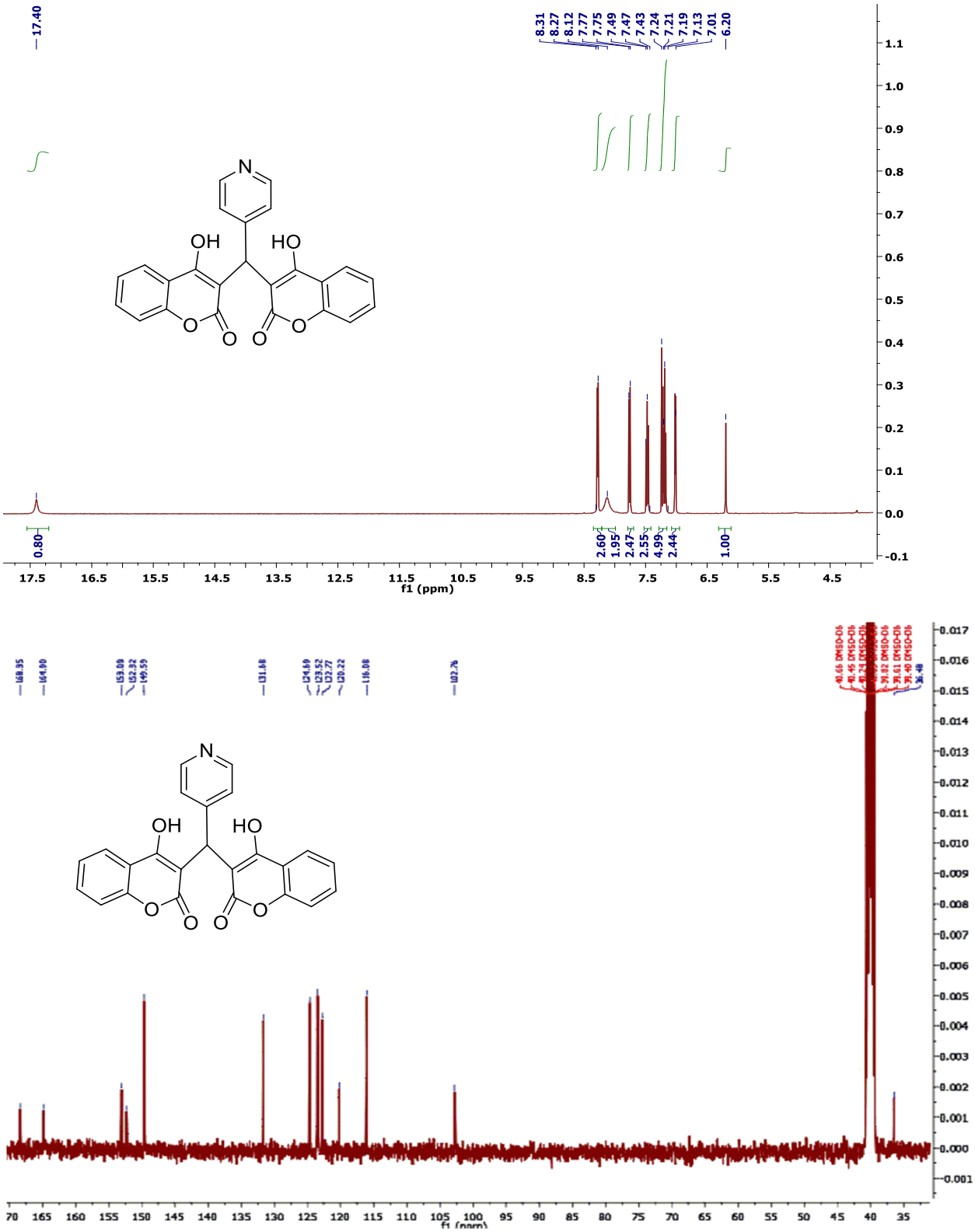


Figure SF12. ^{1}H and ^{13}C NMR of 3,3'-(pyridin-4-ylmethylene)bis(4-hydroxy-2H-chromen-2-one)

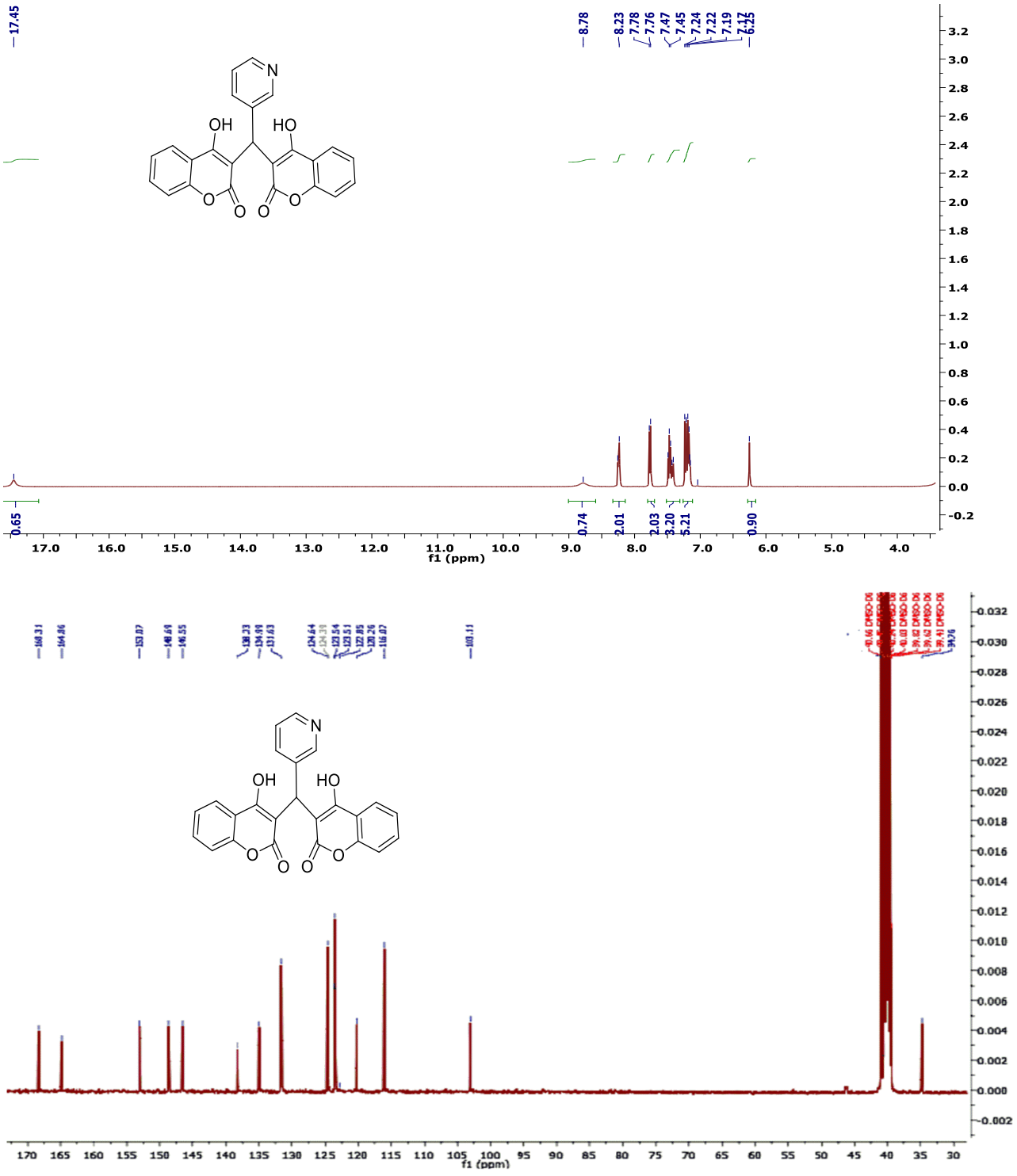


Figure SF13. ^{1}H and ^{13}C NMR of 3,3'-(pyridin-3-ylmethylene)bis(4-hydroxy-2H-chromen-2-one)

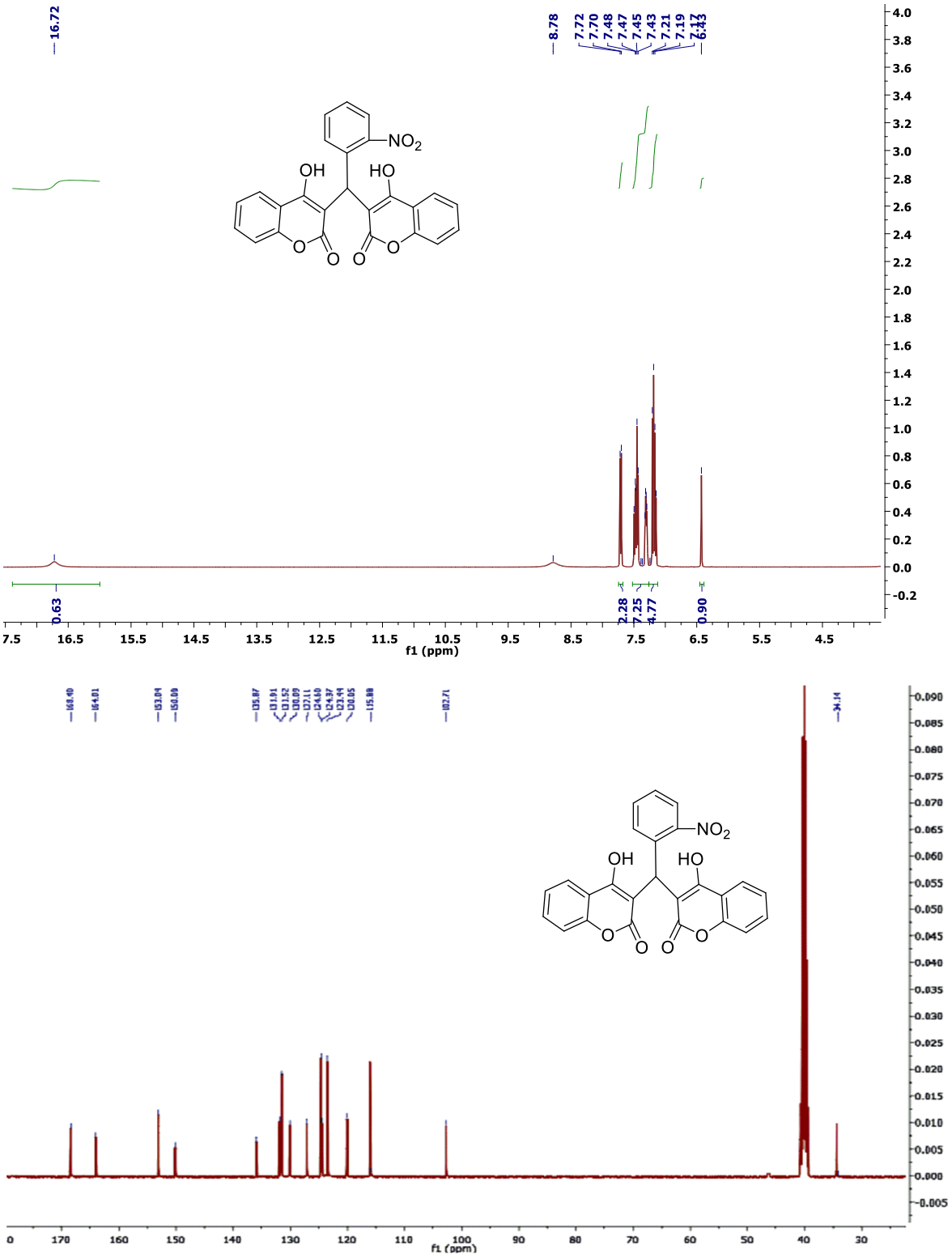


Figure SF14. ^{1}H and ^{13}C NMR of 3,3'-((2-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

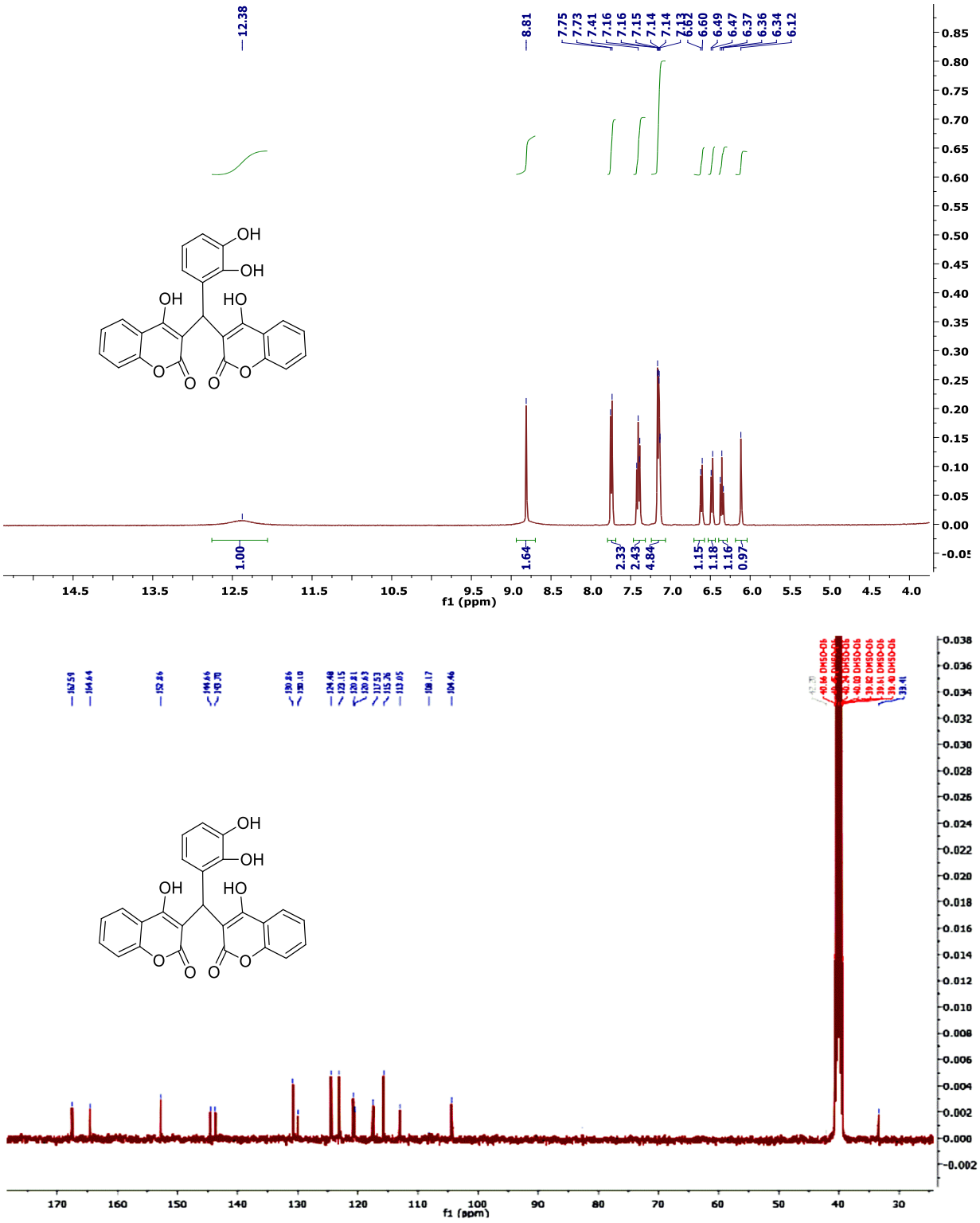


Figure SF15. ^{1}H and ^{13}C NMR of 3,3'-((2,3-dihydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

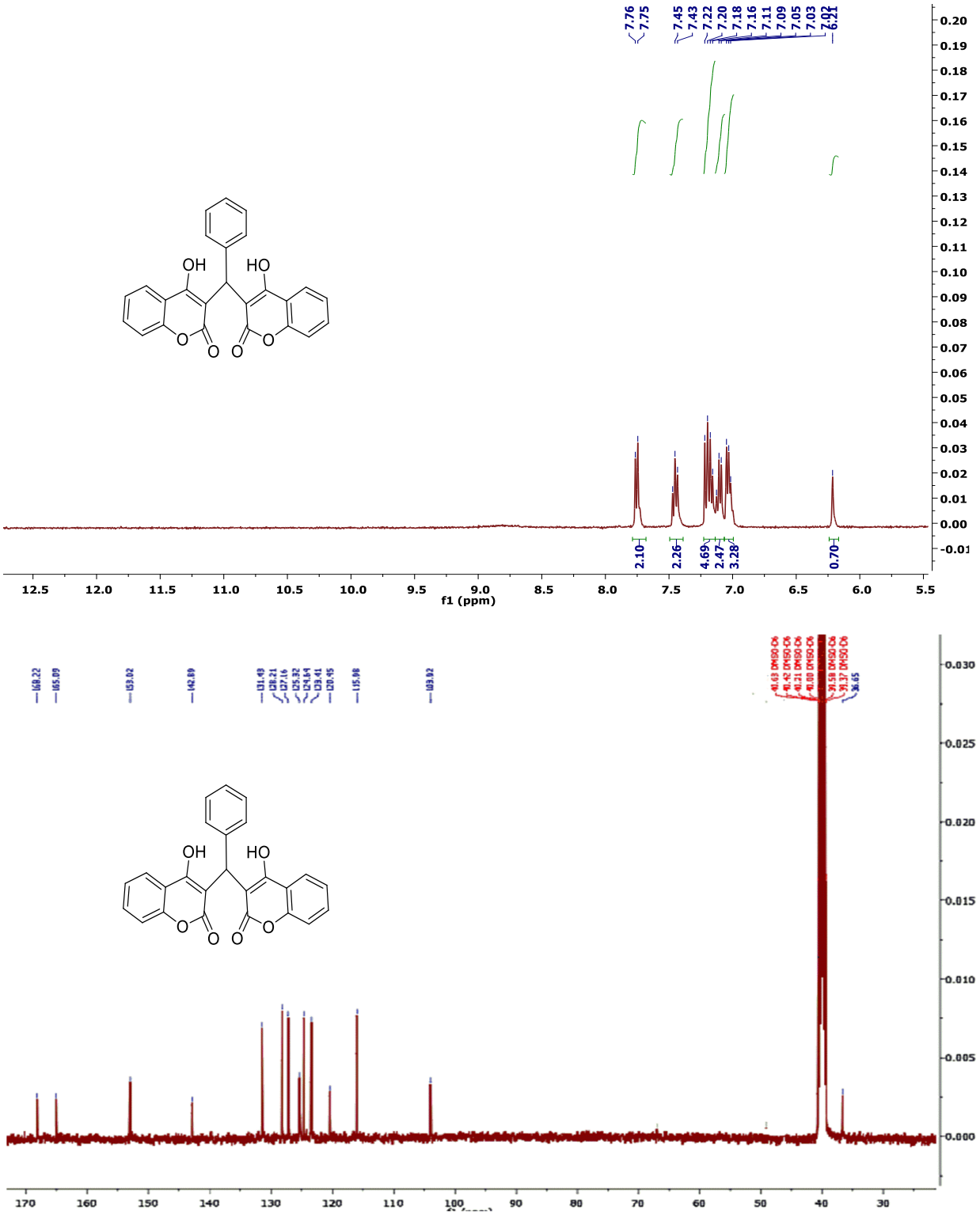


Figure SF16. ^{1}H and ^{13}C NMR of 3,3'-(phenylmethylene)bis(4-hydroxy-2H-chromen-2-one)

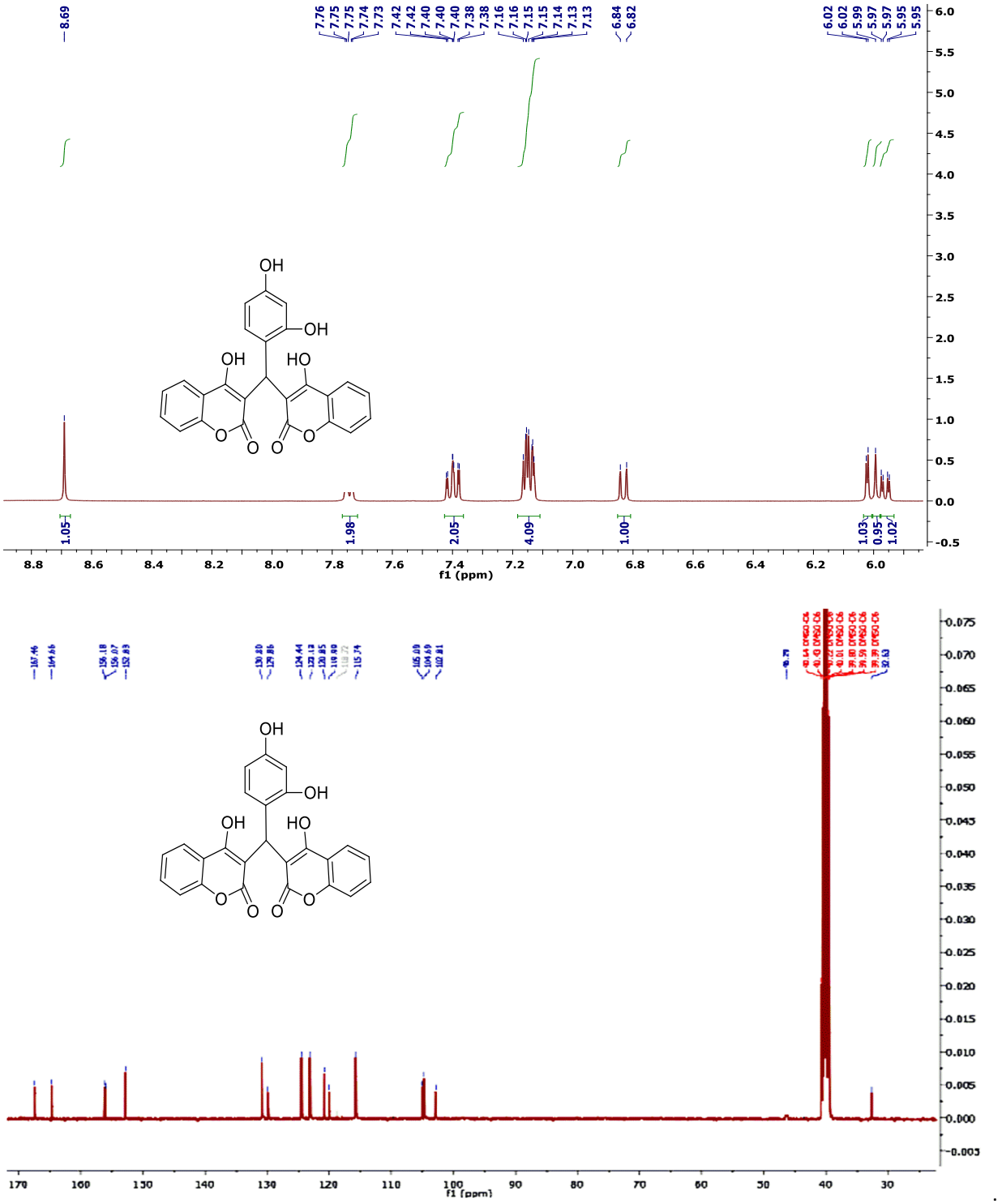


Figure SF17. ^{1}H and ^{13}C NMR of 3,3'-((2,4-dihydroxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

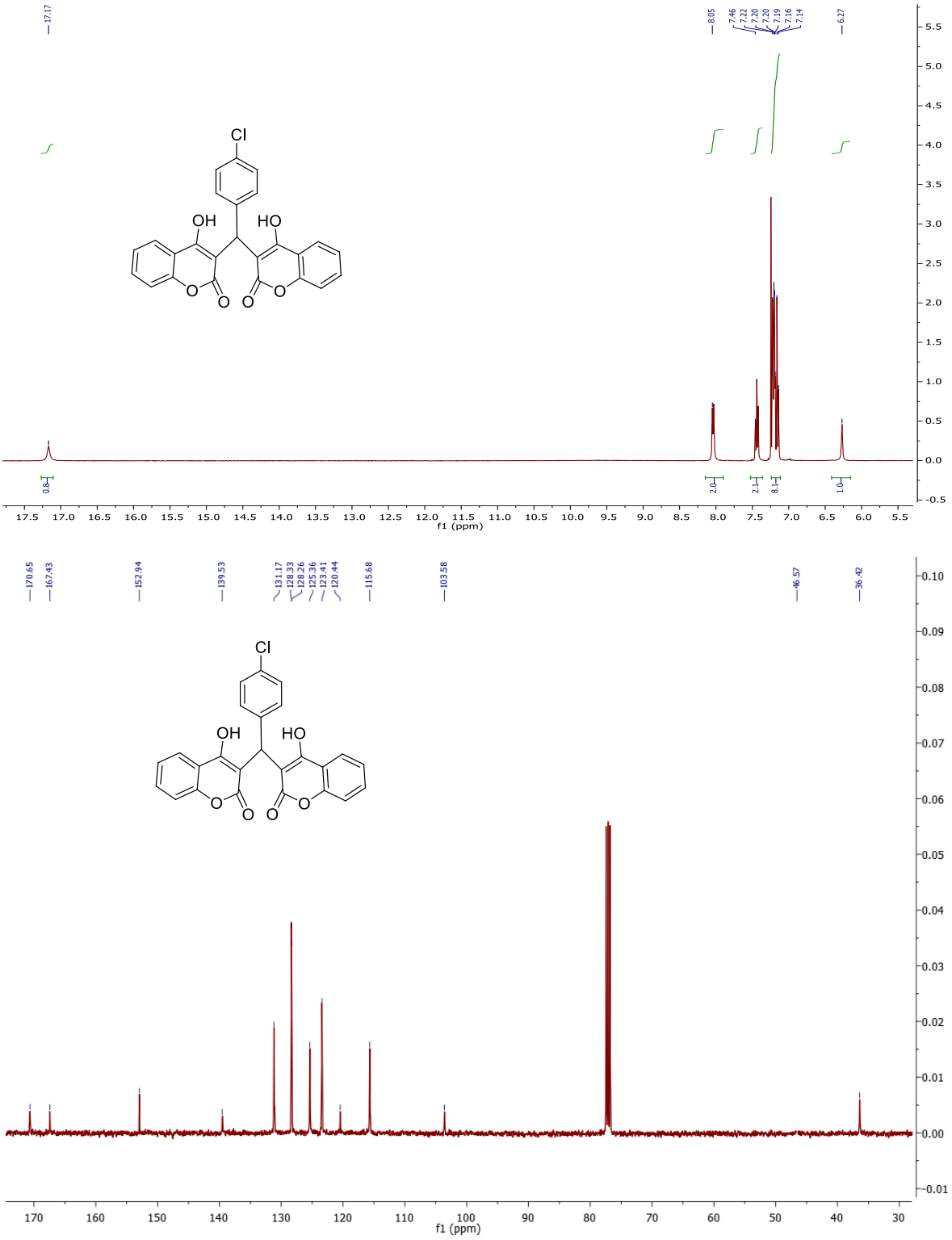


Figure SF18. ^{1}H and ^{13}C NMR of 3,3'-((4-chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

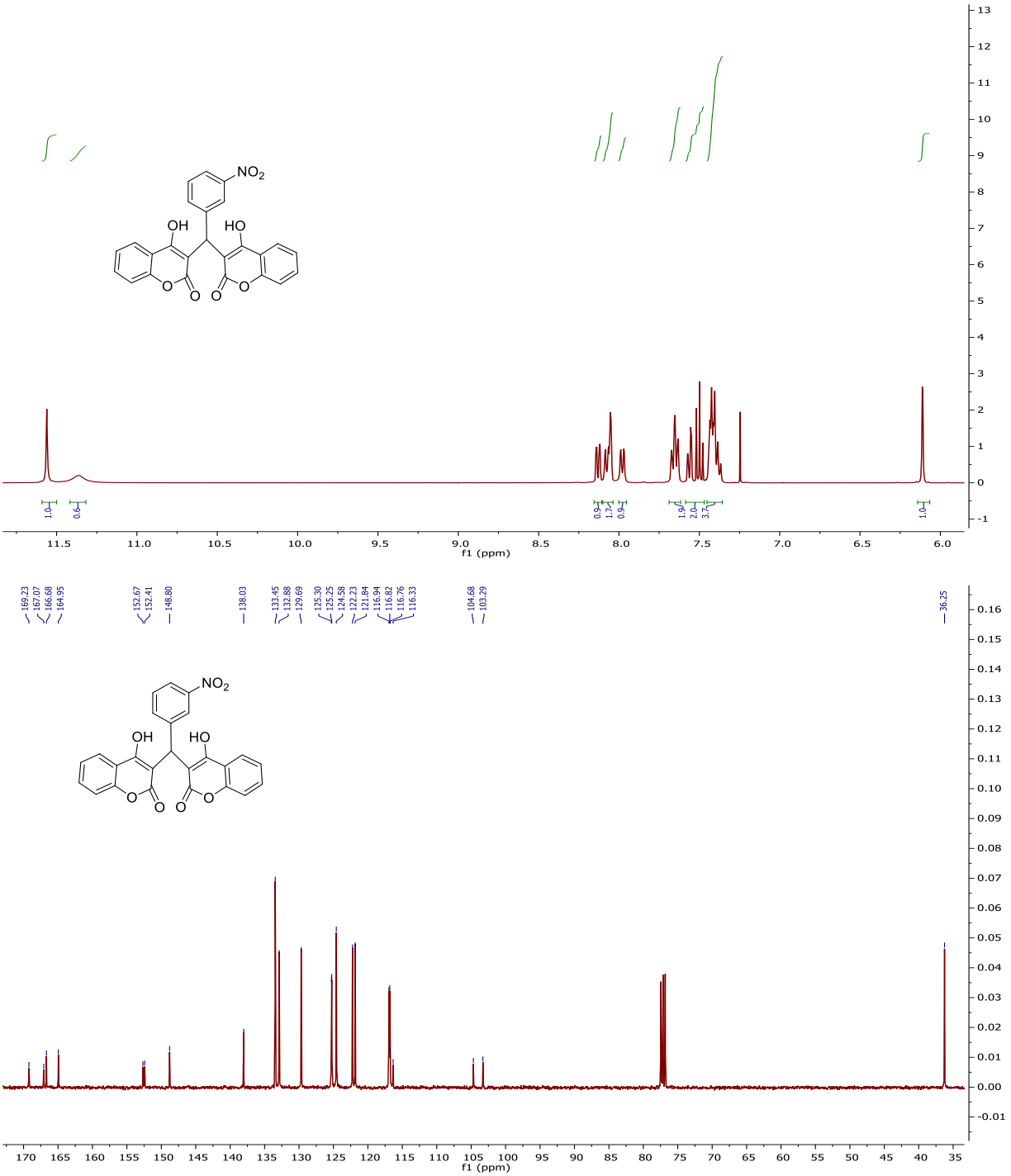


Figure SF19. ^{1}H and ^{13}C NMR of 3,3'-((3-nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

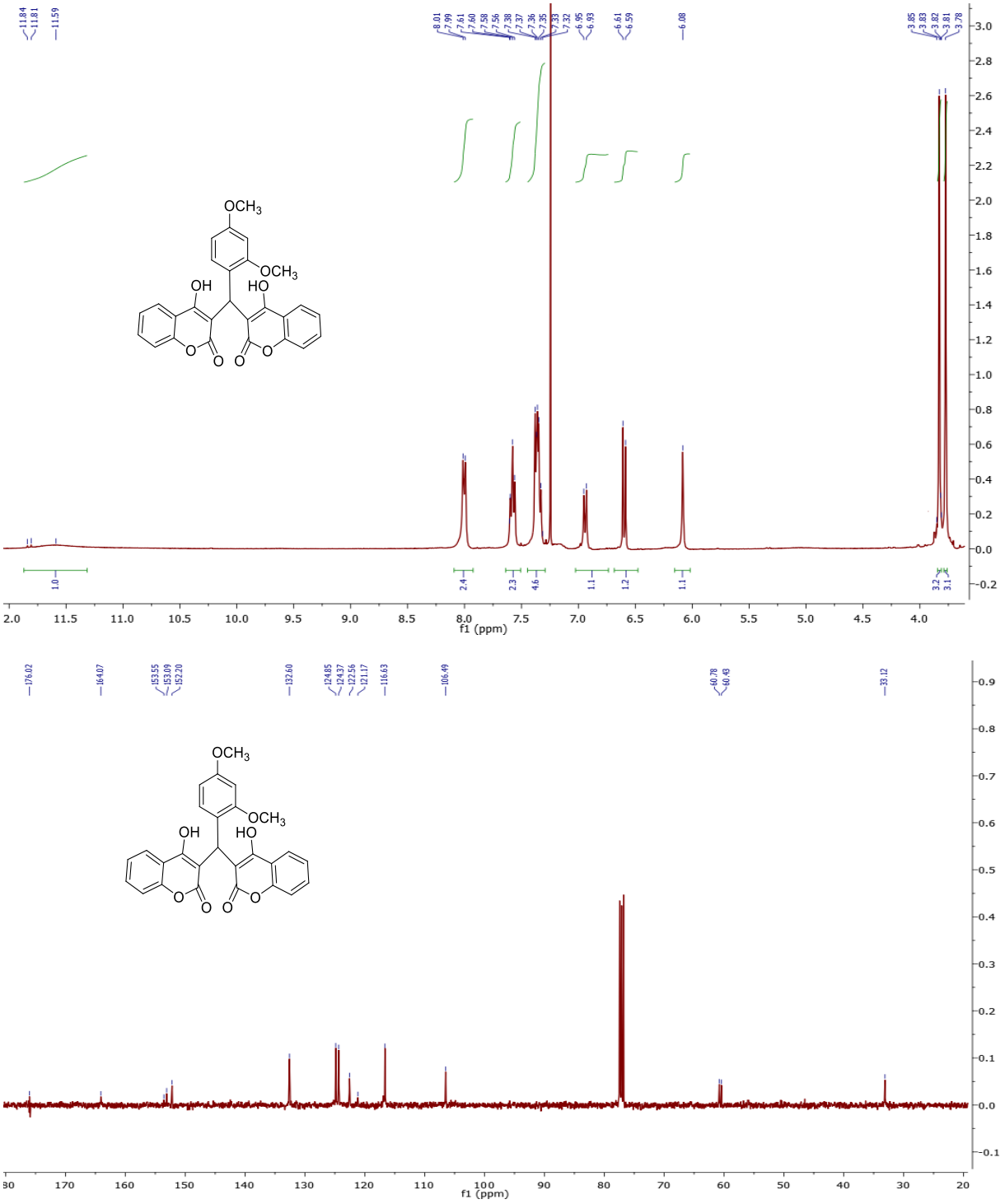


Figure SF20. ^{1}H and ^{13}C NMR of 3,3'-((2,4-dimethoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one)

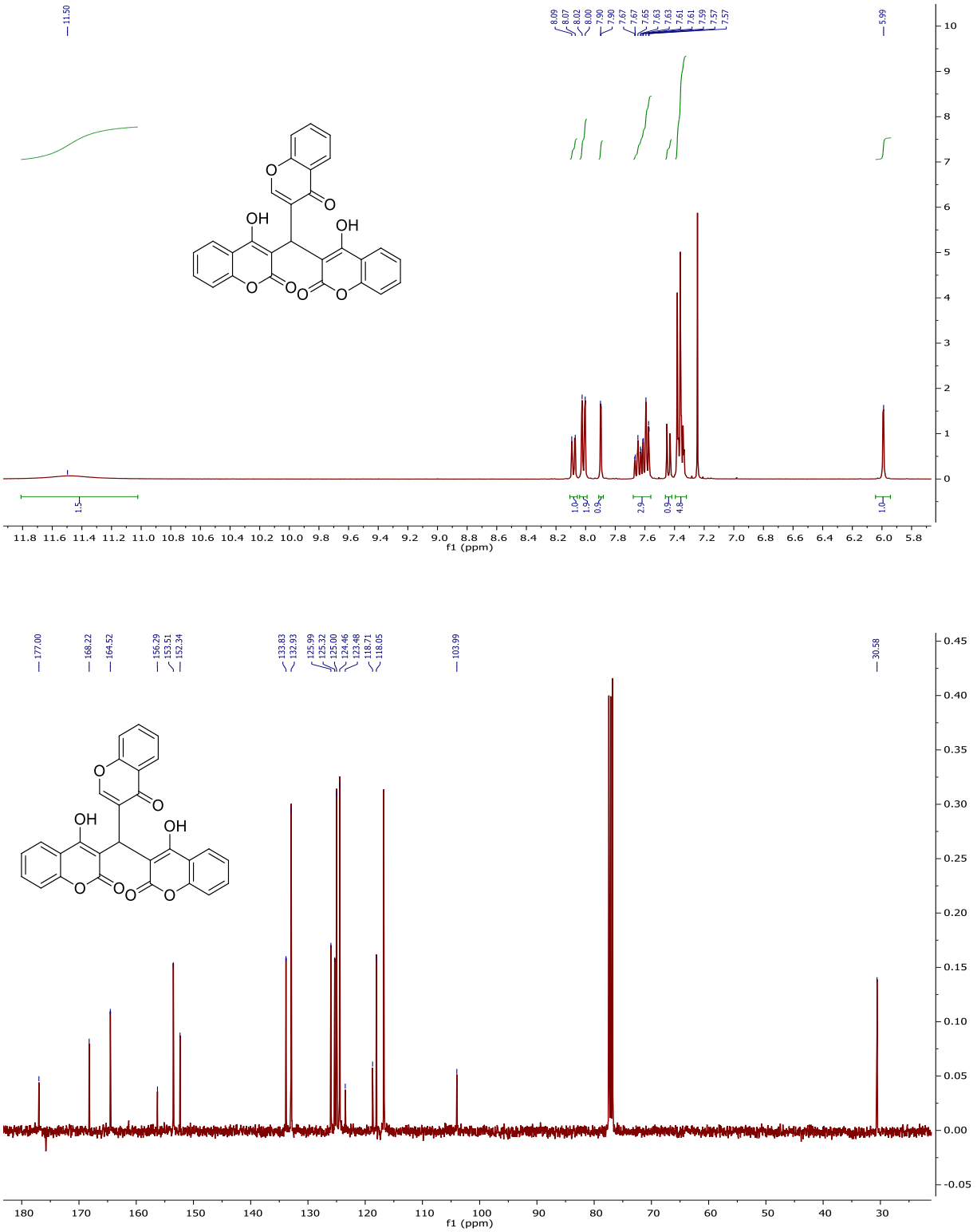


Figure SF21. ^{1}H and ^{13}C NMR of 3,3'-((4-oxo-4H-chromen-3-yl)methylene)bis(4-hydroxy-2H-chromen-2-one)

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