Electronic Supplementary Material (ESI) for RSC Advances

Tosyl cyanide as a *C*-sulfinylating agent: 3-sulfinylation of 4-hydroxycoumarins and related heterocycles

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Supporting Information

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General Remarks

NMR spectra were recorded on Varian Inova 400 MHz FT spectrometer at room temperature. All NMR spectra are referenced relative to the solvent residual peak. High resolution mass spectra were measured on a Waters/Micromass GCT and Waters 2996 Photodiode Array Detector instruments. Melting points were recorded in open capillaries and are uncorrected. Infrared spectra were recorded on a Varian 3100 FT-IR spectrometer at room temperature using KBr pellets.

Materials

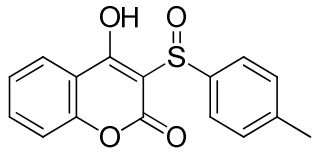
All reagents were obtained from commercial suppliers and used without further purification. 1,4-Dioxane, *N,N'*-dimethylformamide and potassium carbonate were purchased from Sigma-Aldrich and used as received. Tosyl cyanide was purchased from Waterstone Technologies (US) and used as received. Thin layer chromatography was performed on Merck aluminium-backed sheets (silica gel 60 F_{254}). Detection was by UV and/or by coloration with ceric ammonium molybdate (CAM) or vanillin. Flash column chromatography was performed using Merck silica gel 60 (230-400 mesh).

The following compounds were synthesized according to literature procedures: 4-hydroxy-1,6-dimethylpyridin-2(1*H*)-one,[1] 1-benzyl-4-hydroxy-6-methylpyridin-2(1*H*)-one,[2] 4-hydroxy-6-methyl-1-phenylpyridin-2(1*H*)-one,[3] 4-hydroxy-1-methylquinolin-2(1*H*)-one[4] and 4-methylphenyl (4-methylphenyl)sulfinyl sulfone.[5]

General procedure for the *C*-sulfinylation of 4-hydroxy heterocycles

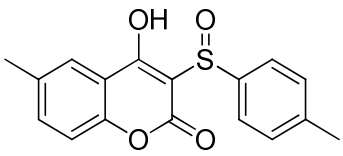
Tosyl cyanide (217 mg, 1.2 mmol) was added to a suspension of substrate (1.0 mmol) and K_2CO_3 (168 mg, 1.2 mmol) in 1,4-dioxane (5 mL) or a 1,4-dioxane/DMF mixture (1:1 v/v, 5 mL). The reaction mixture was stirred at rt and the progress of the reaction was monitored by TLC analysis. After the disappearance of the starting material, the reaction mixture was diluted with water (10 mL), the pH was adjusted to ~2 with 1 M aq. HCl and the resulting mixture was stirred for 5 min to allow for complete precipitation. The solid was collected by filteration, washed with water (20 mL) and dried overnight *in vacuo* to give the *C*-sulfinylated product. In the case of 4-hydroxy-6-methyl-2*H*-pyran-2-one, after pH adjustment, the aq. layer was extracted with EtOAc (2 x 10 mL) and the combined organic layers were washed with water (10 mL) and sat. aq. NaCl solution. The organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography.

4-Hydroxy-3-(*p*-tolylsulfinyl)-2*H*-chromen-2-one



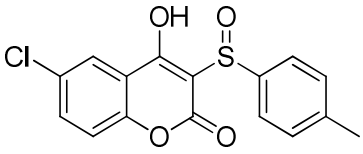
Isolated as a white solid (270 mg, 90%); Mp: 144-148 ^{o}C; IR (KBr, cm^{-1}): υ 2920, 1699, 1614, 1557, 1325, 1200; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3 H, CH_3), 7.24-7.32 (m, 2 H, Ar-H), 7.35 (d, *J* = 8.0 Hz, 2 H, Tol), 7.59-7.63 (m, 1 H, Ar-H), 7.85 (d, *J* = 8.0 Hz, 2 H, Tol), 7.89-7.93 (m, 1 H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 100.0, 116.3, 117.0, 123.6, 124.5, 125.6, 130.3, 134.2, 139.1, 143.3, 154.2, 158.5, 170.6; HRMS (ESI): $C_{16}H_{12}O_4NaS$ $[M + Na]^+$ calculated: 323.0354, found: 323.0341.

4-Hydroxy-6-methyl-3-(*p*-tolylsulfinyl)-2*H*-chromen-2-one



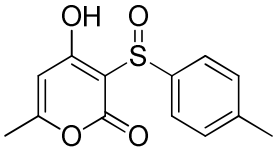
Isolated as a white solid (286 mg, 91%); Mp: 148-153 ^{o}C; IR (KBr, cm^{-1}): υ 2920, 1698, 1627, 1357, 1203; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 7.15 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.33 (d, *J* = 8.0 Hz, 2 H, Tol), 7.40 (dd, *J* = 8.5, 2.1 Hz, 1 H, Ar-H), 7.67-7.68 (m, 1 H, Ar-H), 7.45 (d, *J* = 8.0 Hz, 2 H, Tol); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 21.5, 99.9, 115.9, 116.8, 123.0, 125.5, 130.3, 134.4, 135.2, 139.2, 143.2, 152.4, 158.6, 170.6; HRMS (ESI): $C_{17}H_{14}O_4NaS$ $[M + Na]^+$ calculated: 337.0511, found: 337.0521.

6-Chloro-4-hydroxy-3-(*p*-tolylsulfinyl)-2*H*-chromen-2-one



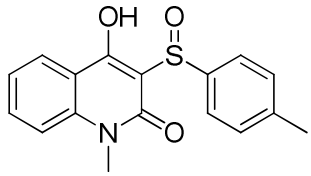
Isolated as a white solid (307 mg, 92%); Mp: 171-174 ^{o}C; IR (KBr, cm^{-1}): υ 3067, 2923, 1716, 1617, 1554, 1325, 1270; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3 H, CH_3), 7.21 (d, *J* = 8.8 Hz, 1 H, Ar-H), 7.35 (d, *J* = 8.0 Hz, 2 H, Tol), 7.55 (dd, *J* = 8.8, 2.6 Hz, 1 H, Ar-H), 7.83 (d, *J* = 8.0 Hz, Tol), 7.87 (d, *J* = 2.5 Hz, 1 H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 101.0, 117.4, 118.5, 123.1, 125.6, 130.3, 130.4, 134.1, 138.8, 143.6, 152.5, 157.9, 169.4; HRMS (ESI): $C_{16}H_{11}O_4NaSCl$ $[M + Na]^+$ calculated: 356.9964, found: 356.9959.

4-Hydroxy-6-methyl-3-(*p*-tolylsulfinyl)-2*H*-pyran-2-one



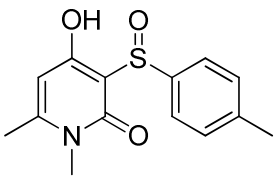
The title compound was isolated by flash column chromatography (SiO_2; pentane/EtOAc, 40:60) as a cream colored solid (224 mg, 85%); Mp: 110-114 ^{o}C; IR (KBr, cm^{-1}): υ 2922, 1699, 1639, 1557, 1315, 1170; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 5.79 (br s, 1 H, C=CH), 7.34 (d, *J* = 7.9 Hz, 2 H, Tol), 7.79 (d, *J* = 7.9 Hz, 2 H, Tol); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.1, 21.5, 97.6, 102.6, 125.3, 130.2, 139.5, 143.1, 159.6, 166.2, 174.7; HRMS (ESI): $C_{13}H_{12}O_4NaS$ $[M + Na]^+$ calculated: 287.0354, found: 287.0362.

4-Hydroxy-1-methyl-3-(*p*-tolylsulfinyl)quinolin-2(1*H*)-one



Isolated as a pale brown solid (291 mg, 93%); Mp: 177-182 ^{o}C; IR (KBr, cm^{-1}): υ 2921, 1629, 1566, 1503, 1335, 1176; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3 H, CH_3), 3.56 (s, 3 H, NCH_3), 7.25-7.33 (m, 4 H, Ar-H), 7.61-7.66 (m, 1 H, Ar-H), 7.88 (d, *J* = 8.2 Hz, 2 H, Tol), 8.07 (dd, *J* = 8.5, 1.5 Hz, 1 H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 28.7, 105.5, 114.2, 116.8, 122.2, 123.9, 125.8, 130.1, 132.9, 140.3, 140.6, 142.7, 159.3, 166.4; HRMS (ESI): $C_{17}H_{15}NO_3NaS$ $[M + Na]^+$ calculated: 336.0670, found: 336.0678.

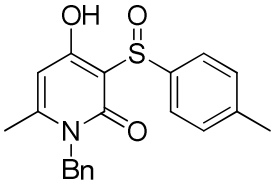
4-Hydroxy-1,6-dimethyl-3-(*p*-tolylsulfinyl)pyridin-2(1*H*)-one



Isolated as a cream colored solid (263 mg, 95%); Mp: 181-185 ^{o}C; IR (KBr, cm^{-1}): υ 3073, 1637, 1570, 1557, 1339, 1220; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 3.36 (s, 3 H, NCH_3), 5.77 (s, 1 H, C=CH), 7.30 (d, *J* = 7.9 Hz, 2 H, Tol), 7.83 (d, *J*

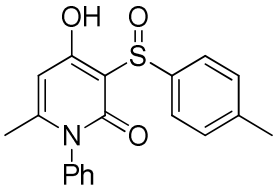
= 7.9 Hz, 2 H, Tol), 12.79 (s, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 21.5, 30.2, 102.6, 103.7, 125.6, 130.0, 140.7, 142.4, 150.2, 160.2, 169.6; HRMS (ESI): $C_{14}H_{15}NO_3NaS$ $[M + Na]^+$ calculated 300.0670, found: 300.0683.

1-Benzyl-4-hydroxy-6-methyl-3-(*p*-tolylsulfinyl)pyridin-2(1*H*)-one



Isolated as a cream colored solid (297 mg, 84%); Mp: 189-195 °C; IR (KBr, cm^{-1}): υ 3070, 1635, 1573, 1560, 1335, 1225; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 4.97 (d, *J* = 15.8 Hz, 1 H, PhCH*H*), 5.30 (d, *J* = 15.8 Hz, 1 H, PhC*H*H), 5.75 (s, 1 H, C=CH), 7.05 (d, *J* = 7.2 Hz, 2 H, Tol), 7.15-7.43 (m, 5 H, Ph-H), 7.85 (d, *J* = 7.2 Hz, 2 H, Tol), 12.87 (s, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.5, 46.3, 103.1, 104.0, 125.4, 126.3, 127.5, 128.8, 129.9, 135.9, 140.7, 142.3, 150.5, 160.3, 170.0; HRMS (ESI): $C_{20}H_{19}NO_3S$ $[M + Na]^+$ calculated: 376.0983, found: 376.0991.

4-Hydroxy-6-methyl-1-phenyl-3-(*p*-tolylsulfinyl)pyridin-2(1*H*)-one



Isolated as a cream colored solid (312 mg, 92%); Mp: 171-175 °C; IR (KBr, cm^{-1}): υ 3071, 1642, 1562, 1338, 1226; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 3 H, CH_3), 2.39 (s, 3 H, Tol-CH_3), 5.84 (bs, 1 H, C=CH), 7.01-7.07 (m, 1 H, Ph-H), 7.17-7.24 (m, 1 H, Ph-H), 7.30 (d, *J* = 7.9 Hz, 2 H, Tol), 7.38-7.54 (m, 3 H, Ph-H), 7.84 (d, *J* = 7.9 Hz, 2 H, Tol), 12.98 (s, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 21.5, 102.6, 104.0, 125.4, 128.0, 128.1, 129.1, 129.7, 129.7, 129.9, 137.1, 140.5, 142.2, 150.3, 160.4, 170.5; HRMS (ESI): $C_{19}H_{18}NO_3NaS$ $[M + Na]^+$ calculated 340.1007, found: 340.1022.

4-Hydroxy-3-(*p*-tolylsulfinyl)-2*H*-chromen-2-one using TsCN/Et_3N

To a solution of 4-hydroxycoumarin (162 mg, 1.0 mmol) and Et_3N (122 mg, 1.2 mmol) in 1,4-dioxane (5 mL) was added tosyl cyanide (217 mg, 1.2 mmol) in one portion at rt. The reaction mixture was stirred at rt until TLC analysis indicatied the disappearance of the starting material (2 h). The reaction mixture was diluted with water (10 mL), the pH was adjusted to ~2 with 1 M aq. HCl and the aq. layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with water (10 mL) and aq. sat. NaCl solution, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was

purified by flash column chromatography (SiO_2: pentane/EtOAc, 40/60) to give the title compound as a white solid (270 mg, 90%).

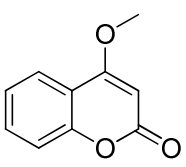
4-Hydroxy-3-(*p*-tolylsulfinyl)-2*H*-chromen-2-one using sulfinyl sulfone (2)/Et_3N

To a solution of 4-hydroxycoumarin (162 mg, 1.0 mmol) and Et_3N (122 mg, 1.2 mmol) in 1,4-dioxane (5 mL) was added sulfinyl sulfone **2** (353 mg, 1.2 mmol) in one portion at rt. After stirring the reaction mixture at rt for 6 h, the pH was adjusted to ~2 with 1 M aq. HCl and the aq. layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2: pentane/EtOAc, 40/60) to give the sulfinylated product as a white solid (234 mg, 78%).

4-Hydroxy-1,6-dimethyl-3-(*p*-tolylsulfinyl)pyridin-2(1*H*)-one using TsCN/Et_3N

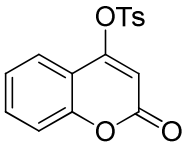
To a solution of 4-hydroxy-1,6-dimethylpyridin-2(1*H*)-one (139 mg, 1.0 mmol) and Et_3N (122 mg, 1.2 mmol) in 1,4-dioxane/DMF mixture (1:1 v/v, 5 mL) was added tosyl cyanide (272 mg, 1.5 mmol) in one portion at rt. After stirring the reaction mixture at rt for 2 h, the pH was adjusted to ~2 with 1 M aq. HCl and the aq. layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with water (10 mL) and sat. aq. NaCl solution, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to afford the crude product. ^{1}H NMR analysis of this material indicated a 70% conversion to the title compound.

4-Methoxy-2*H*-chromen-2-one



This compound was prepared by a modified procedure. To a suspension of 4-hydroxycoumarin (1.00 g, 12 mmol) and K_2CO_3 (2.06 g, 15 mmol) in 1,4-dioxane (20 mL) was added dimethyl sulphate (1.86 g, 1.40 mL, 15 mmol) slowly drop wise at rt and stirring was continued at rt for 14 h. The reaction mixture pH was adjusted to ~2 with 1 M aq. HCl and the aq. layer was extracted with DCM (2 x 20 mL). The combined organic layers were washed with water (10 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure to give the title compound as a white solid (0.98 g, 90%). The spectroscopic data are consistent with those reported in the literature.[6]

2-Oxo-2*H*-chromen-4-yl 4-methylbenzenesulfonate



To a solution of 4-hydroxycoumarin (162 mg, 1.0 mmol) and Et_3N (122 mg, 1.2 mmol) in 1,4-dioxane (5 mL) was added tosyl chloride (229 mg, 1.2 mmol) in one portion at rt. The reaction mixture was stirred at rt for 1 h. Water (10 mL) was added, the pH was adjusted to ~2 with 1 M aq. HCl and the mixture was stirred for 5 min to allow for complete precipitation. The solid was collected by filtration, washed with water (20 mL) and recrystallized from DCM/pentane to give the title compound as a white solid (282 mg, 89%). The spectroscopic data are consistent with those reported in the literature.[7]

References

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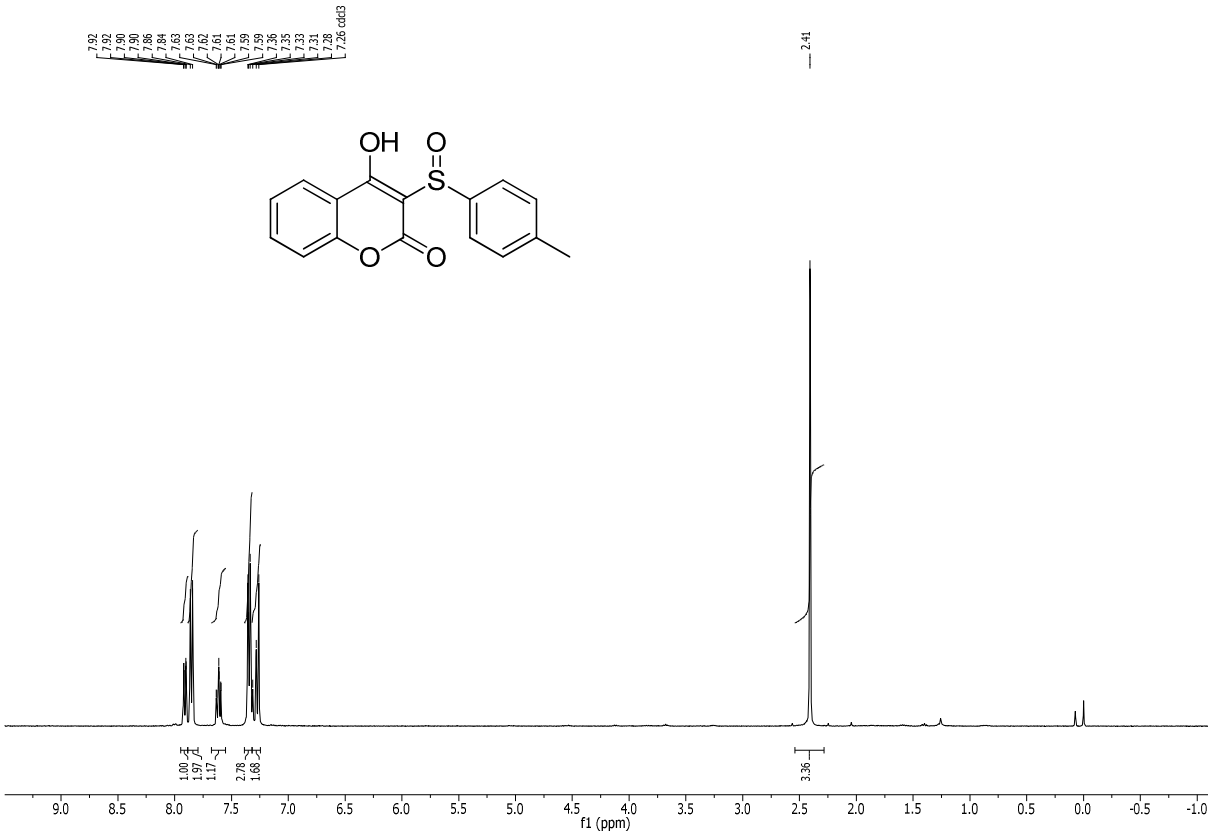
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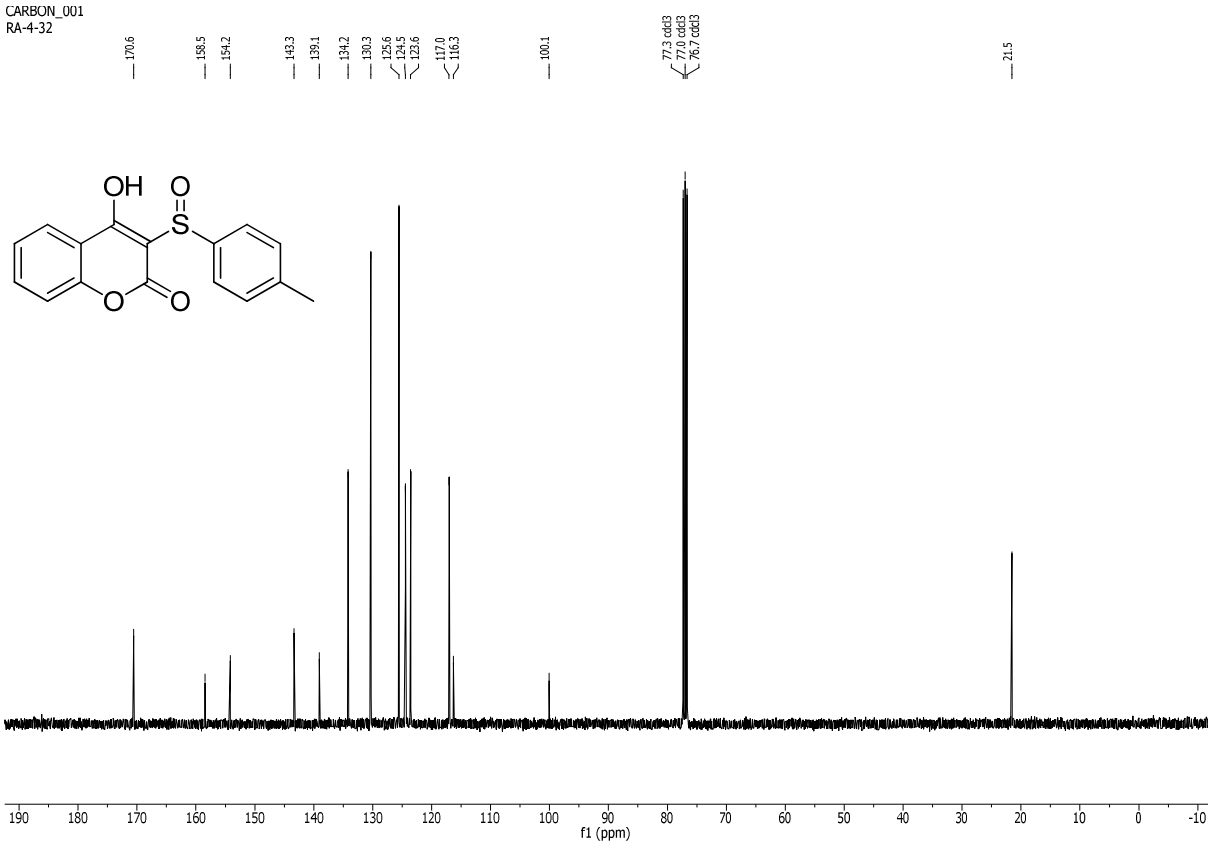
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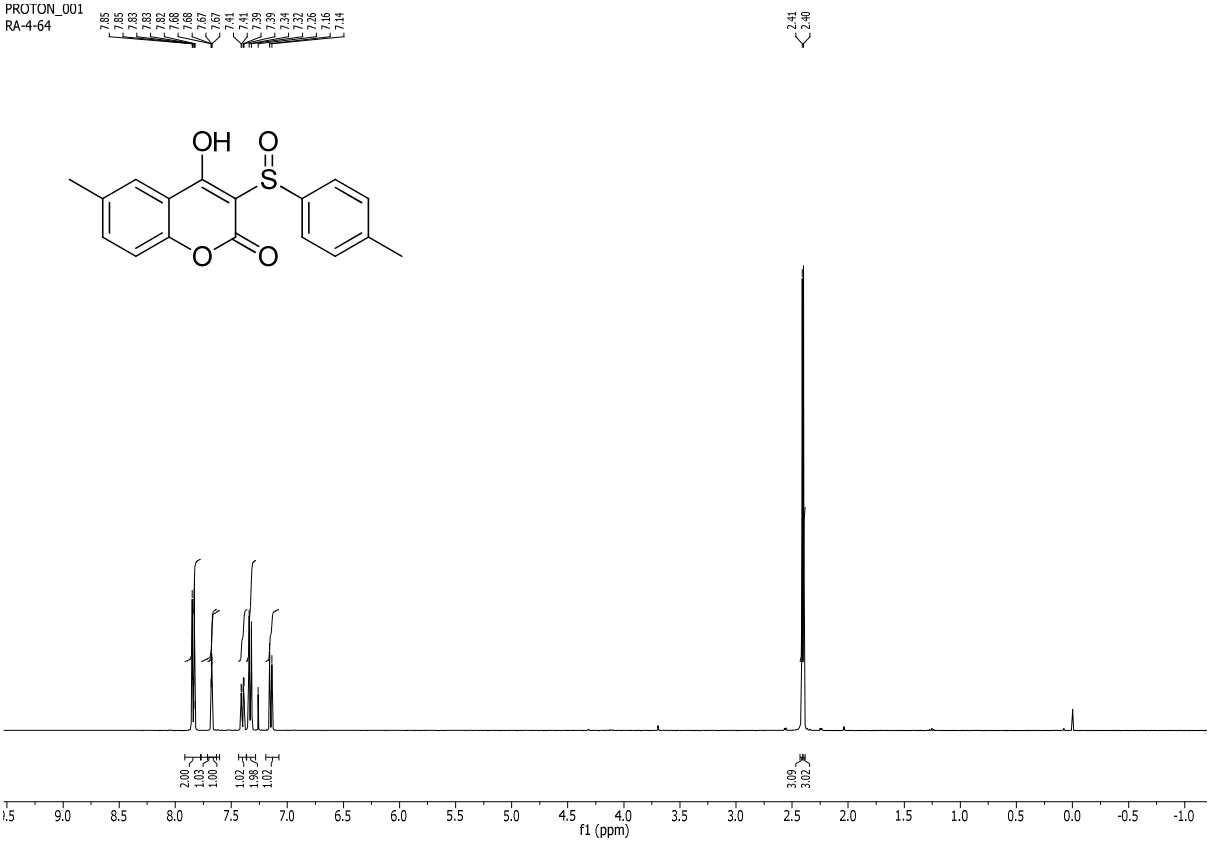
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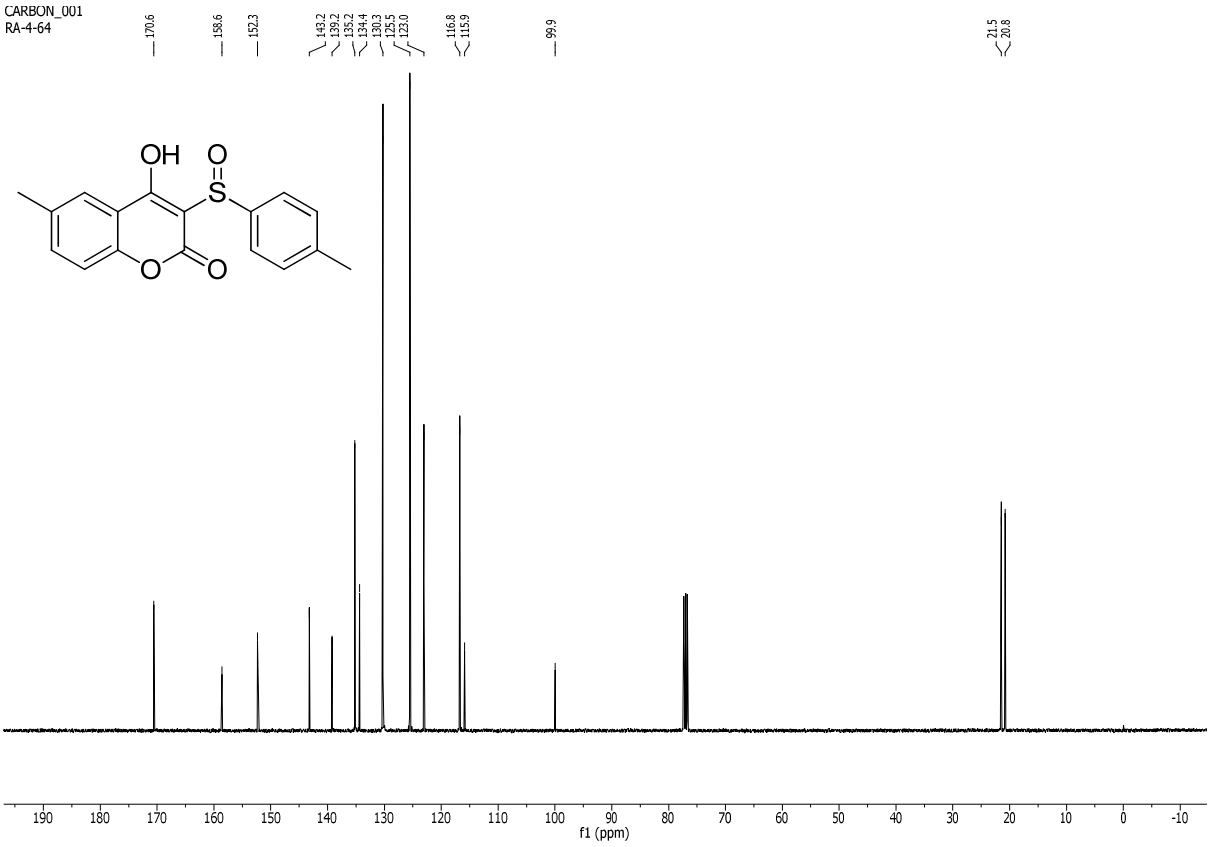
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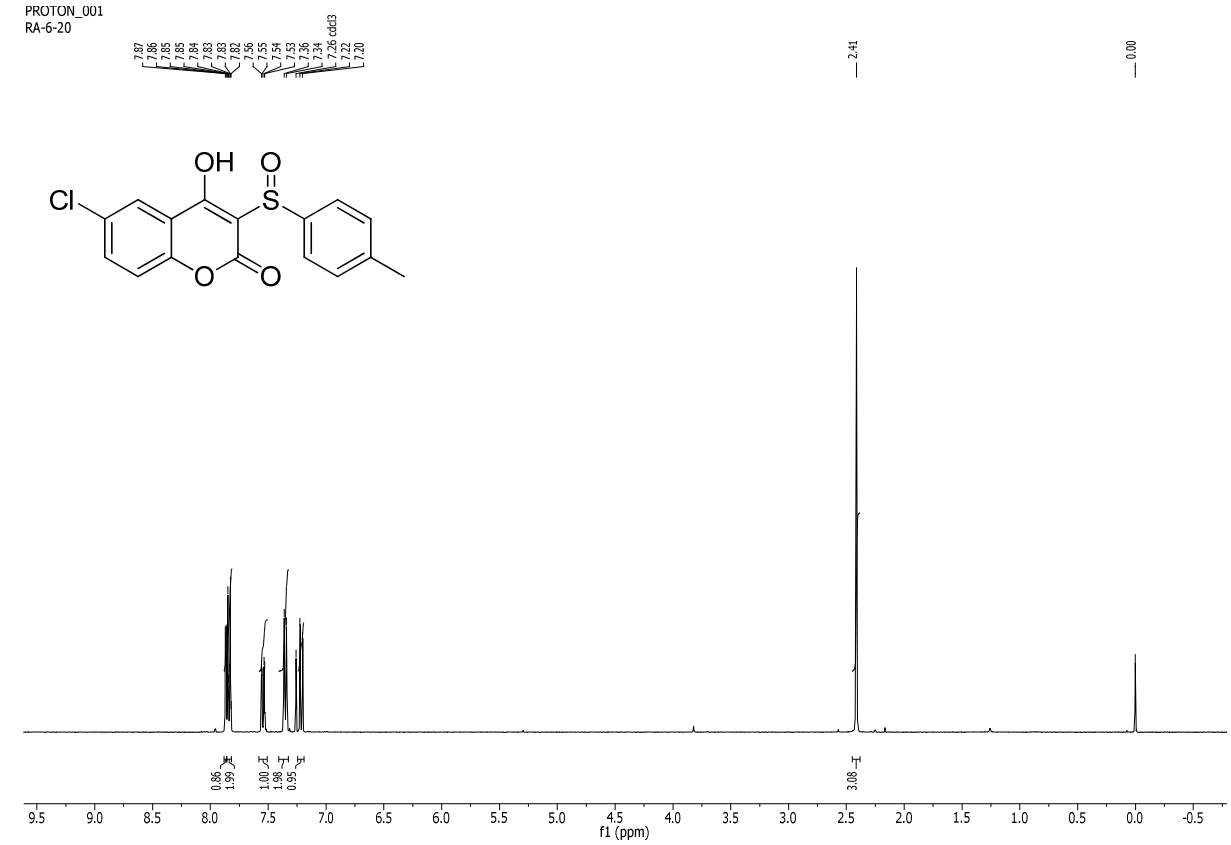
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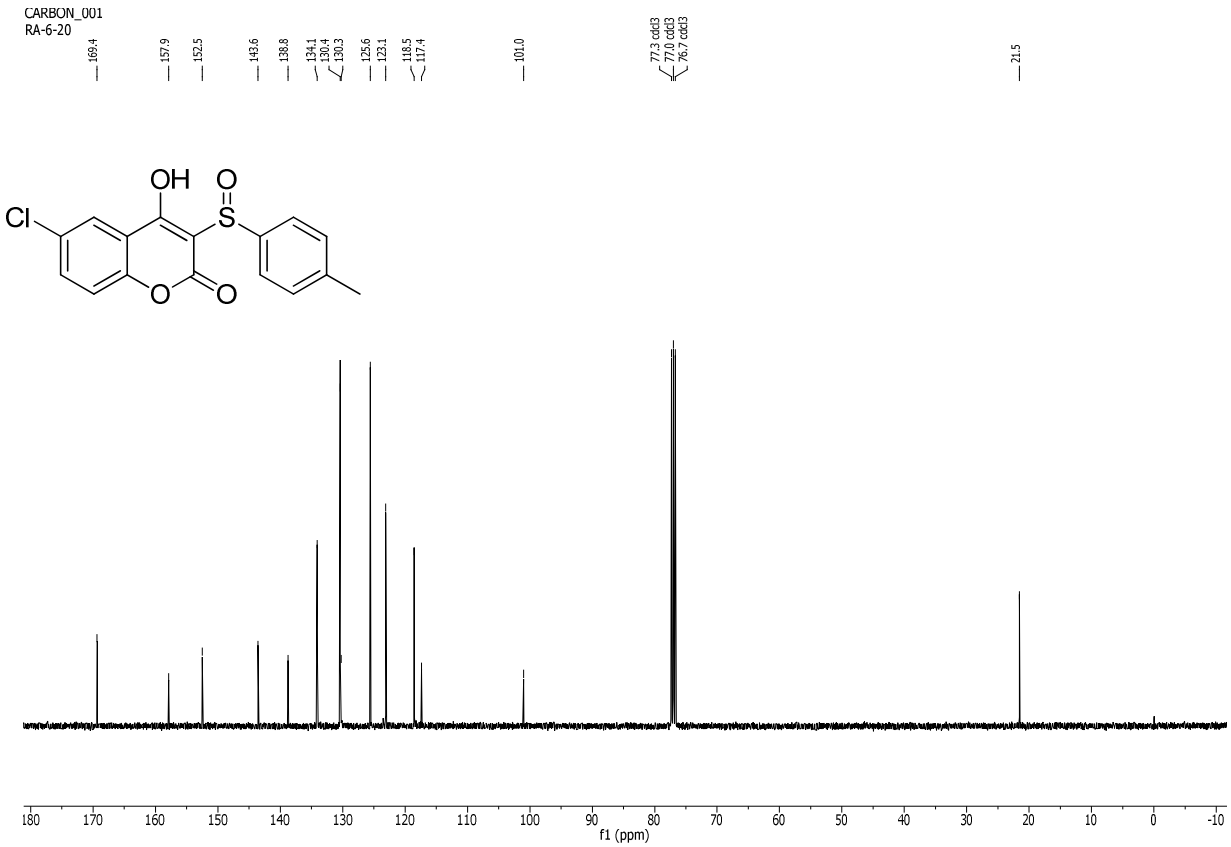
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117.4
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76.7 cdcl3
21.5
OH
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Cl
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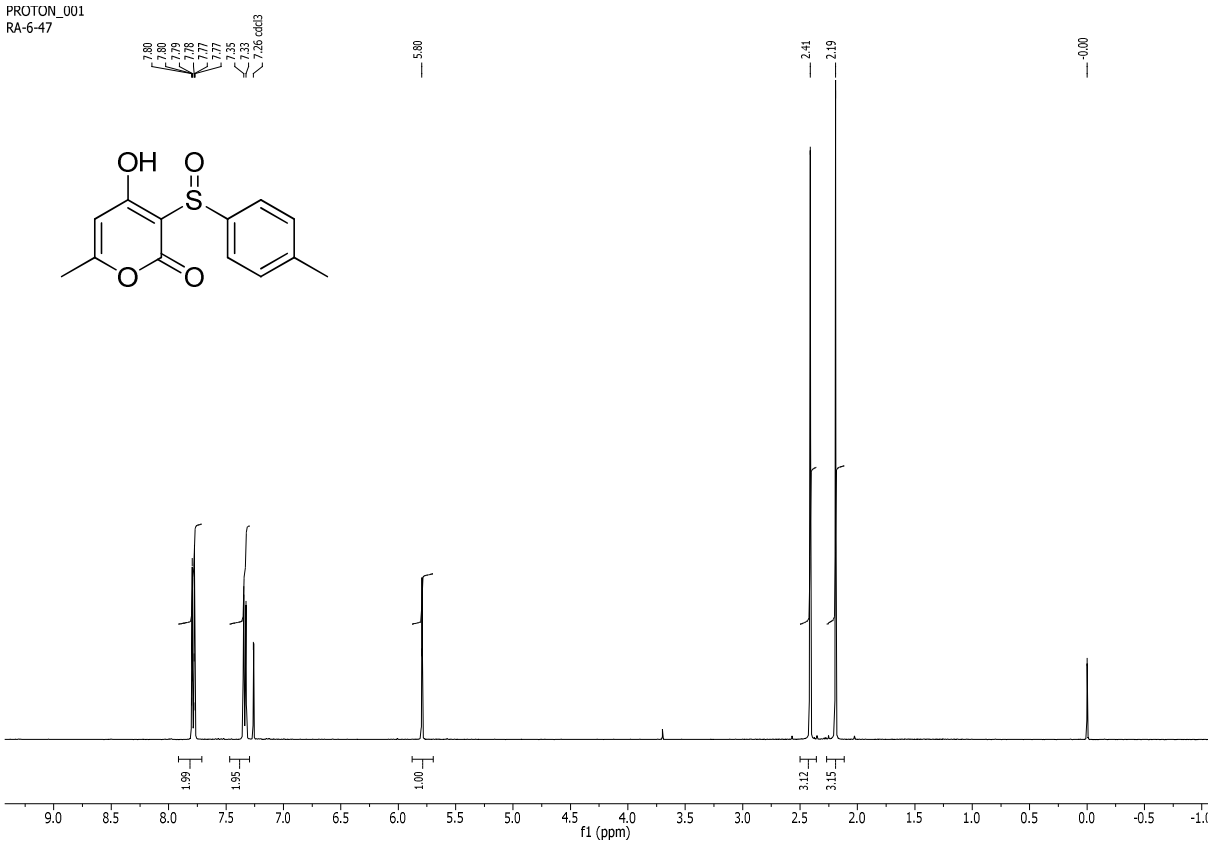
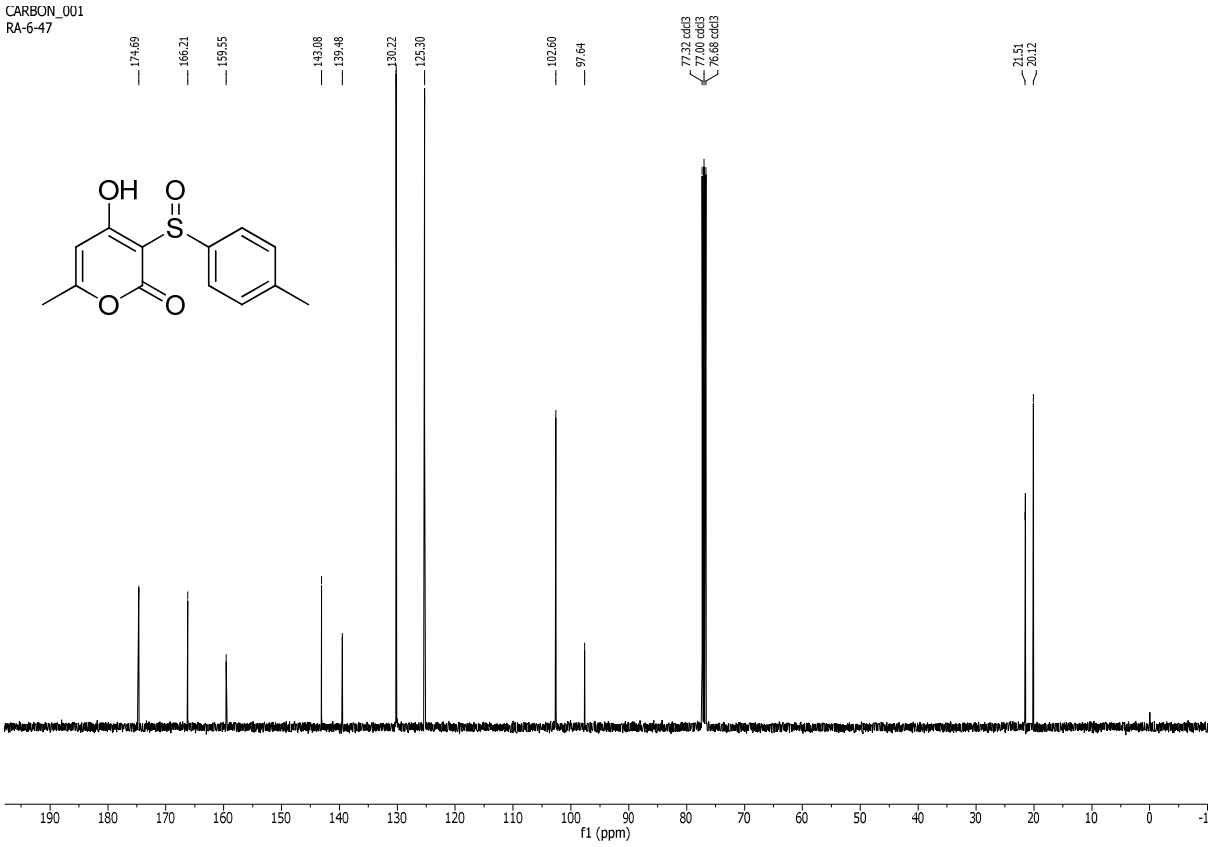
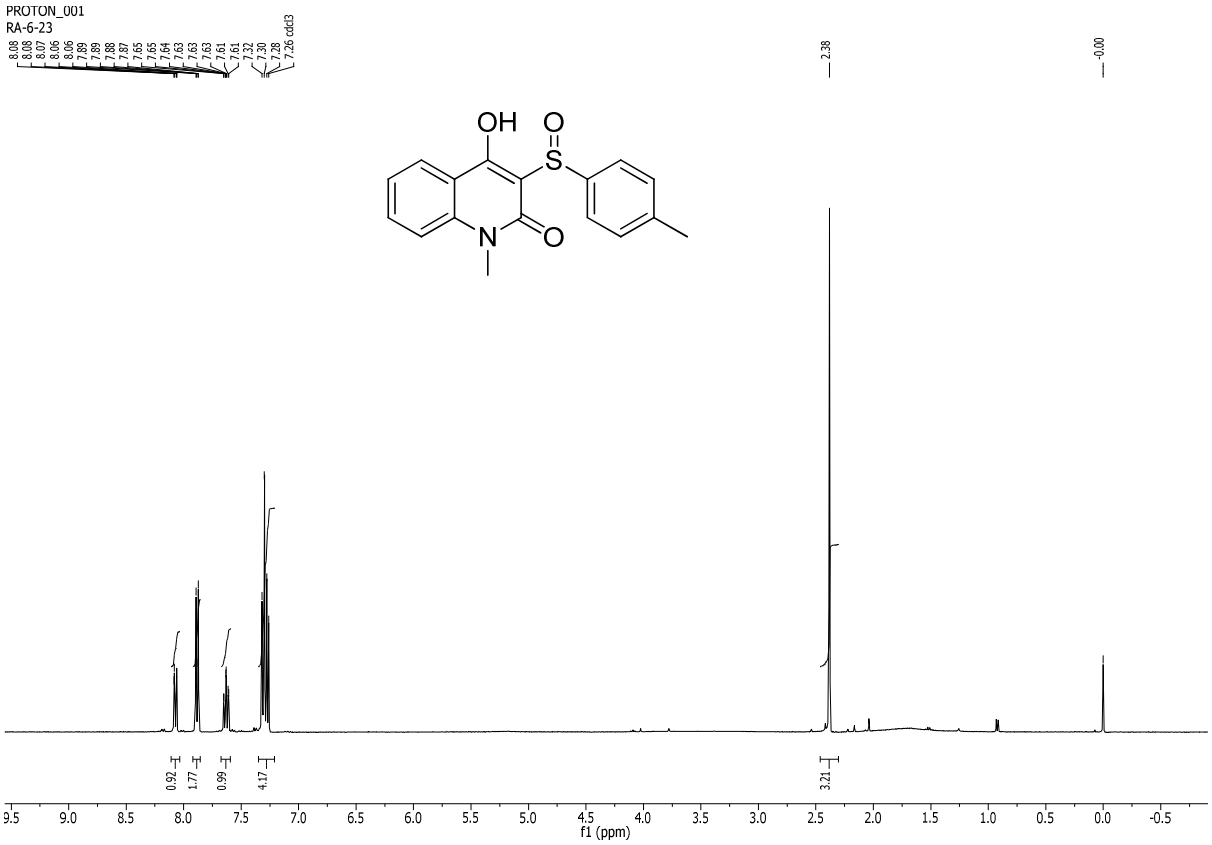
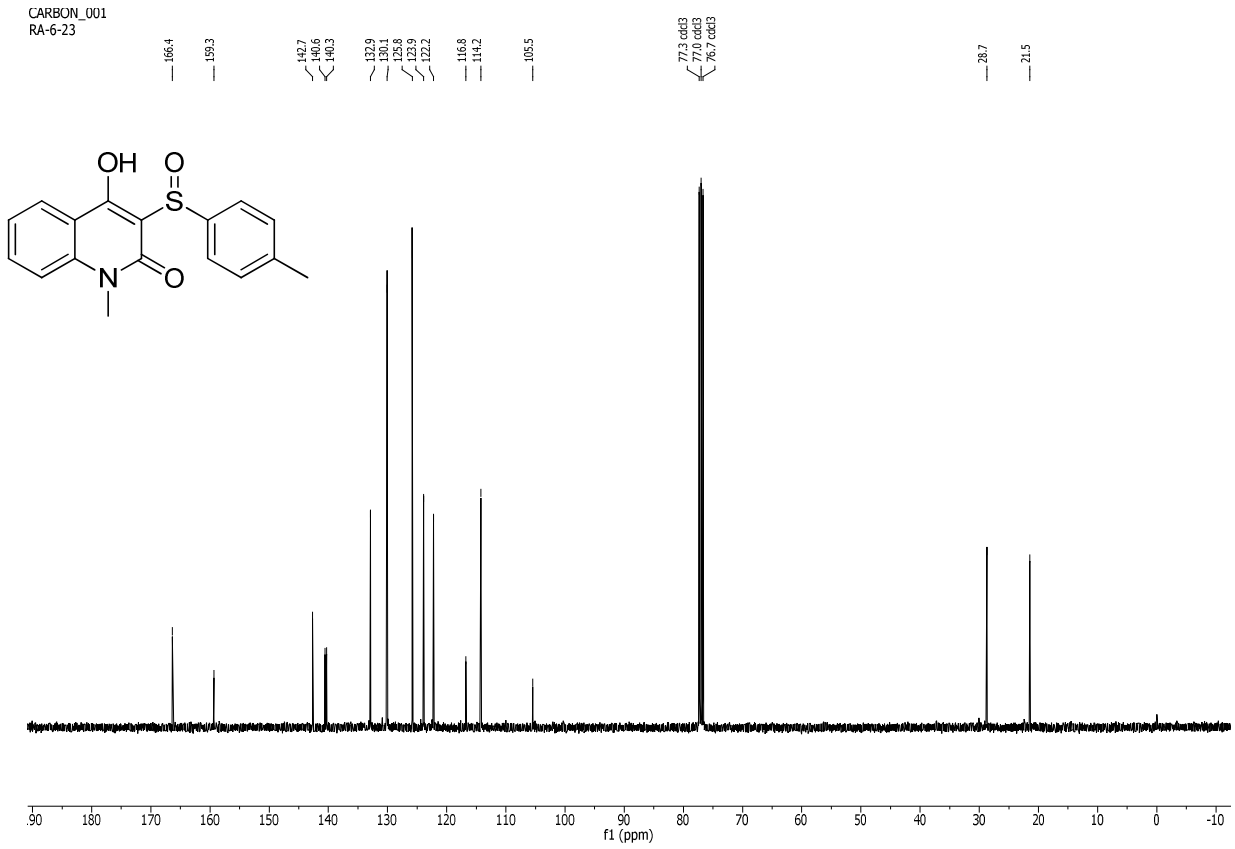
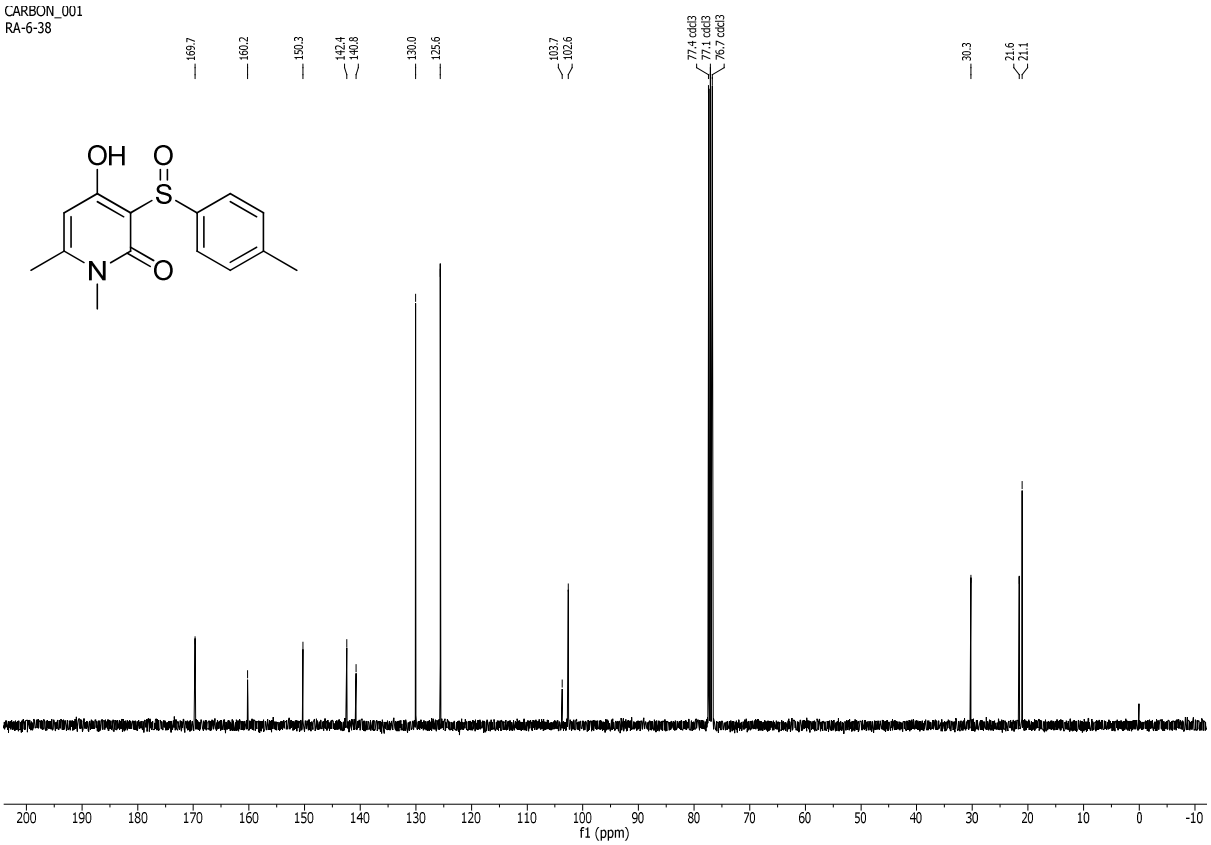
O
f1 (ppm)

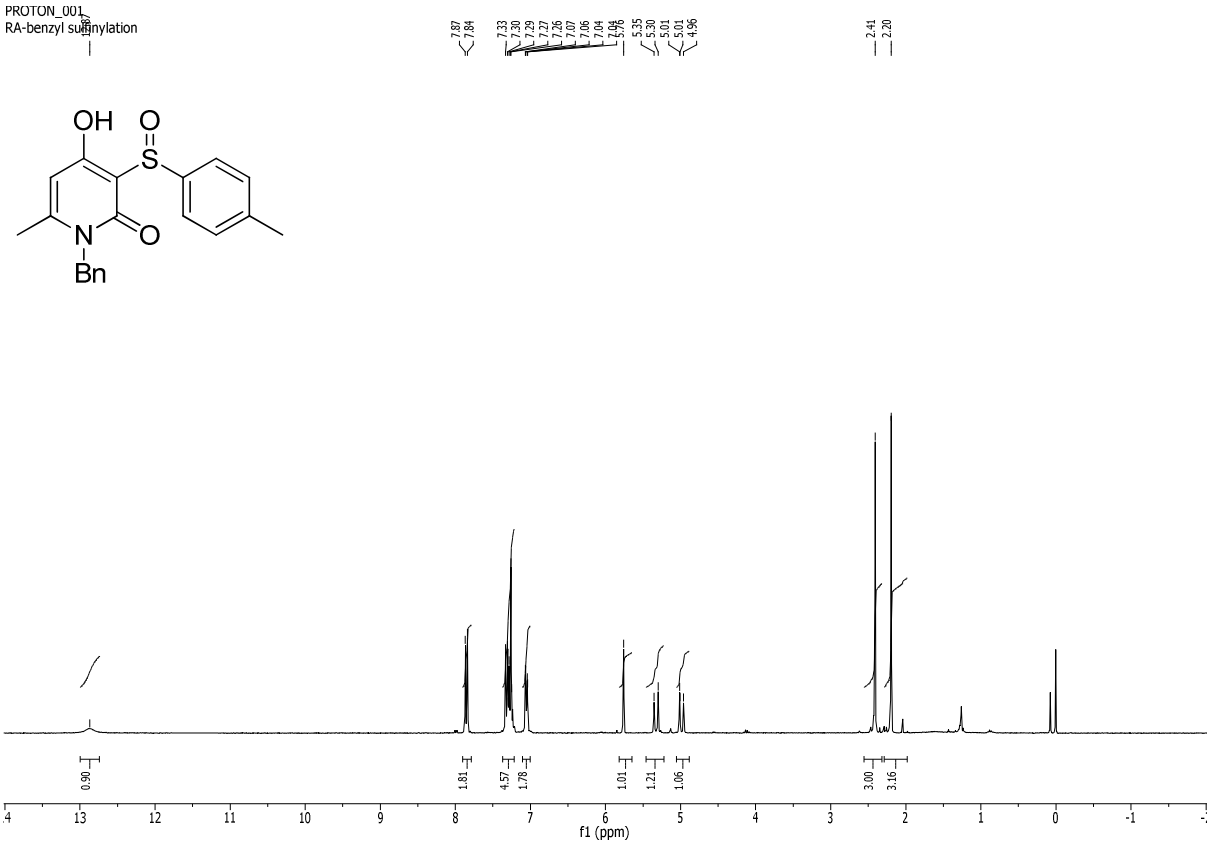

PROTON_001
RA-6-47
7.80
7.80
7.79
7.78
7.77
7.77
7.35
7.33
7.26 cdcl3
5.80
2.41
2.19
-0.00
OH
O
S
O
O
1.99
1.95
1.00
3.12
3.15
f1 (ppm)

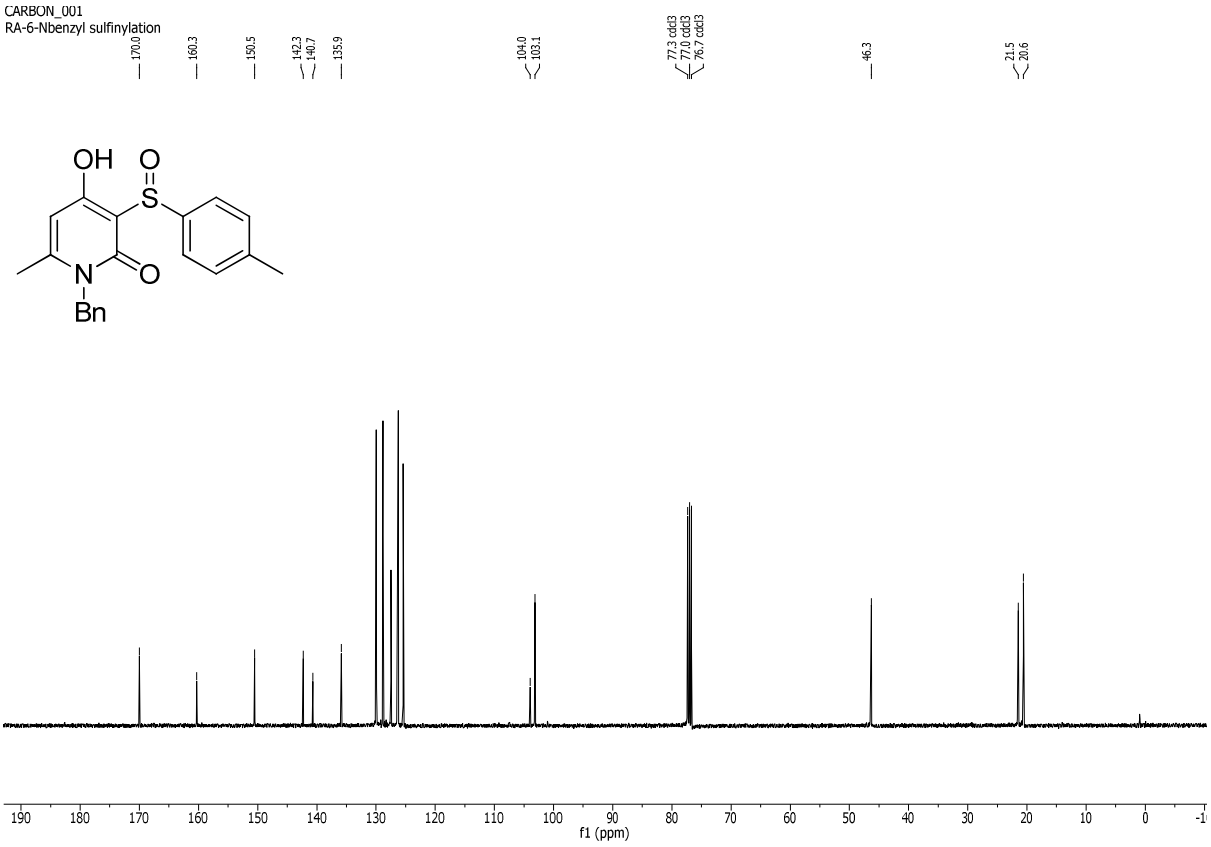

CARBON_001
RA-6-47
174.69
166.21
159.55
143.08
139.48
130.22
125.30
102.60
97.64
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
21.51
20.12
OH
O
S
O
O
f1 (ppm)

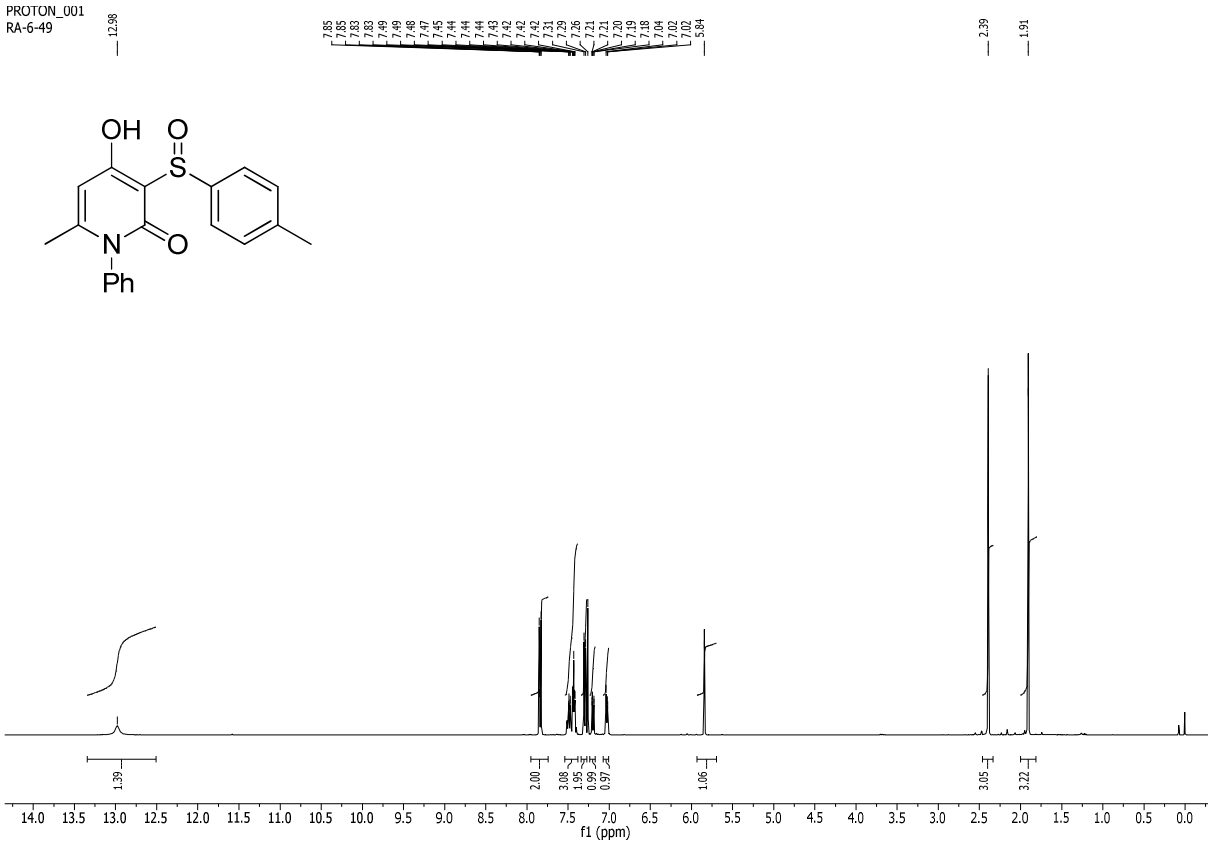

PROTON_001
RA-6-23
8.08
8.08
8.07
8.06
8.06
7.89
7.89
7.88
7.87
7.65
7.65
7.64
7.63
7.63
7.63
7.61
7.61
7.32
7.30
7.28
7.26 cdcl3
2.38
-0.00
OH
O
S
N
O
0.92
1.77
0.99
4.17
3.21
f1 (ppm)

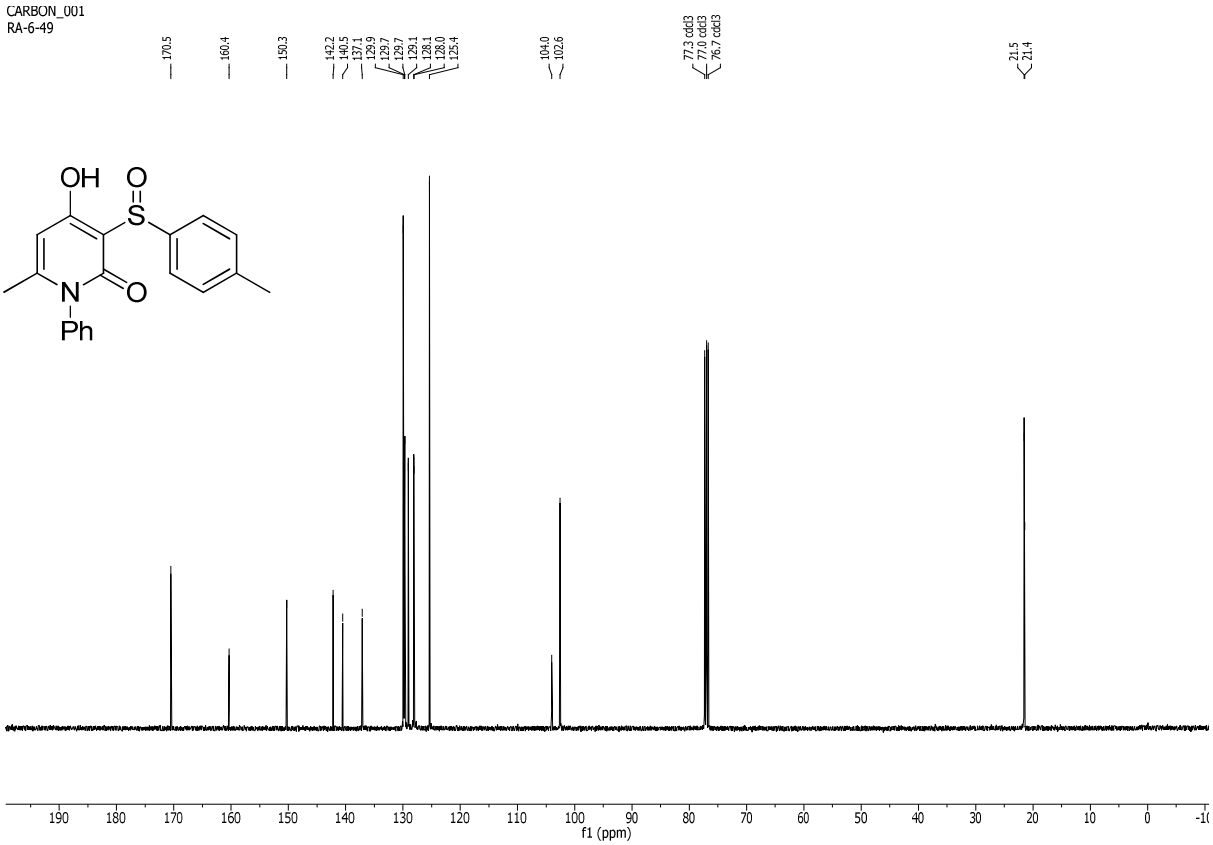

CARBON_001
RA-6-23
166.4
159.3
142.7
140.6
140.3
132.9
130.1
125.8
123.9
122.2
116.8
114.2
105.5
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
28.7
21.5
OH
O
S
N
O
f1 (ppm)



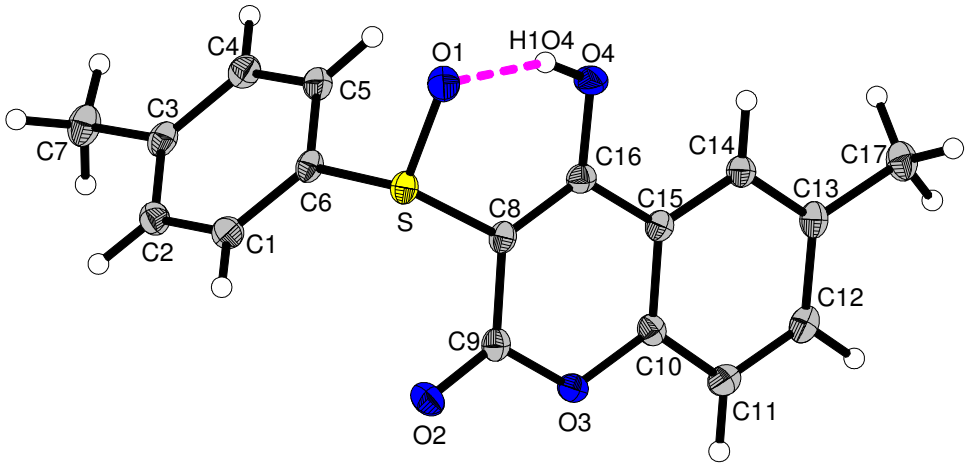

PROTON_001
RA-benzyl sulfinylation
7.87
7.84
7.33
7.30
7.29
7.27
7.26
7.07
7.06
7.04
6.96
5.35
5.30
5.01
4.96
2.41
2.20
OH
O
S
N
O
Bn
0.90
1.81
4.57
1.78
1.01
1.21
1.06
3.00
3.16
f1 (ppm)


CARBON_001
RA-6-Nbenzyl sulfinylation
170.0
160.3
150.5
142.3
140.7
135.9
104.0
103.1
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
46.3
21.5
20.6
OH
O
S
N
O
Bn
f1 (ppm)


PROTON_001
RA-6-49
12.98
7.85
7.85
7.83
7.83
7.49
7.49
7.48
7.47
7.45
7.44
7.44
7.44
7.43
7.42
7.42
7.42
7.31
7.29
7.26
7.21
7.21
7.20
7.19
7.18
7.04
7.02
7.02
5.84
2.39
1.91
OH
O
S
N
O
Ph
1.39
2.00
3.08
1.95
0.99
0.97
1.06
3.05
3.22
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


CARBON_001
RA-6-49
170.5
160.4
150.3
142.2
140.5
137.1
129.9
129.7
129.7
129.1
128.1
128.0
125.4
104.0
102.6
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
21.5
21.4
OH
O
S
N
O
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Crystal structure of 4-hydroxy-6-methyl-3-(*p*-tolylsulfinyl)-2*H*-chromen-2-one



(thermal ellipsoids are drawn on the 50% probability level)

Crystal data and structure refinement

Identification code	has27
Empirical formula	$C_{17}\ H_{14}\ O_4\ S$
Formula weight	314.34
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 14.2101(6) Å α= 90°.
	b = 7.1147(2) Å β= 114.959(5)°.
	c = 15.2952(7) Å γ = 90°.
Volume	1401.94(10) $Å^3$
Z	4
Density (calculated)	1.489 Mg/m^3
Absorption coefficient	2.204 mm^{-1}
F(000)	656
Crystal size	0.1946 x 0.1512 x 0.0507 mm^3
Theta range for data collection	3.43 to 77.01°.

Index ranges	–17<=h<=17, –8<=k<=8, –17<=l<=13
Reflections collected	16011
Independent reflections	2820 [R(int) = 0.0209]
Completeness to theta = 77.01°	95.6 %
Absorption correction	Analytical
Max. and min. transmission	0.904 and 0.744
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	2820 / 0 / 202
Goodness–of–fit on F^2	1.060
Final R indices [I>2sigma(I)]	R1 = 0.0302, wR2 = 0.0820
R indices (all data)	R1 = 0.0305, wR2 = 0.0824
Largest diff. peak and hole	0.267 and –0.392 e.Å^{-3}

Bond lengths [Å] and angles [°]

C(1)–C(6)	1.3881(17)
C(1)–C(2)	1.3923(18)
C(1)–H(1)	0.9500
C(2)–C(3)	1.3940(18)
C(2)–H(2)	0.9500
C(3)–C(4)	1.3984(18)
C(3)–C(7)	1.5064(17)
C(7)–H(7A)	0.9800
C(7)–H(7B)	0.9800
C(7)–H(7C)	0.9800
C(4)–C(5)	1.3880(18)
C(4)–H(4)	0.9500
C(5)–C(6)	1.3920(17)
C(5)–H(5)	0.9500
C(6)–S	1.7909(12)
S–O(1)	1.5204(9)
S–C(8)	1.7821(12)

C(8)–C(16)	1.3701(16)
C(8)–C(9)	1.4371(18)
C(9)–O(2)	1.2135(15)
C(9)–O(3)	1.3770(15)
O(3)–C(10)	1.3826(14)
C(10)–C(11)	1.3877(17)
C(10)–C(15)	1.3938(18)
C(11)–C(12)	1.3888(18)
C(11)–H(11)	0.9500
C(12)–C(13)	1.3976(19)
C(12)–H(12)	0.9500
C(13)–C(14)	1.3899(17)
C(13)–C(17)	1.5103(16)
C(17)–H(17A)	0.9800
C(17)–H(17B)	0.9800
C(17)–H(17C)	0.9800
C(14)–C(15)	1.4034(16)
C(14)–H(14)	0.9500
C(15)–C(16)	1.4487(16)
C(16)–O(4)	1.3250(15)
O(4)–H(1O4)	0.8400
C(6)–C(1)–C(2)	119.13(12)
C(6)–C(1)–H(1)	120.4
C(2)–C(1)–H(1)	120.4
C(1)–C(2)–C(3)	120.96(12)
C(1)–C(2)–H(2)	119.5
C(3)–C(2)–H(2)	119.5
C(2)–C(3)–C(4)	118.57(12)
C(2)–C(3)–C(7)	120.53(12)
C(4)–C(3)–C(7)	120.89(12)
C(3)–C(7)–H(7A)	109.5
C(3)–C(7)–H(7B)	109.5

H(7A)–C(7)–H(7B)	109.5
C(3)–C(7)–H(7C)	109.5
H(7A)–C(7)–H(7C)	109.5
H(7B)–C(7)–H(7C)	109.5
C(5)–C(4)–C(3)	121.32(12)
C(5)–C(4)–H(4)	119.3
C(3)–C(4)–H(4)	119.3
C(4)–C(5)–C(6)	118.77(11)
C(4)–C(5)–H(5)	120.6
C(6)–C(5)–H(5)	120.6
C(1)–C(6)–C(5)	121.18(11)
C(1)–C(6)–S	118.34(10)
C(5)–C(6)–S	120.48(9)
O(1)–S–C(8)	104.07(5)
O(1)–S–C(6)	106.34(6)
C(8)–S–C(6)	98.76(5)
C(16)–C(8)–C(9)	122.84(11)
C(16)–C(8)–S	122.10(10)
C(9)–C(8)–S	114.98(9)
O(2)–C(9)–O(3)	117.79(11)
O(2)–C(9)–C(8)	124.75(12)
O(3)–C(9)–C(8)	117.46(10)
C(9)–O(3)–C(10)	121.02(10)
O(3)–C(10)–C(11)	116.80(11)
O(3)–C(10)–C(15)	122.26(11)
C(11)–C(10)–C(15)	120.94(11)
C(10)–C(11)–C(12)	118.56(12)
C(10)–C(11)–H(11)	120.7
C(12)–C(11)–H(11)	120.7
C(11)–C(12)–C(13)	122.16(11)
C(11)–C(12)–H(12)	118.9
C(13)–C(12)–H(12)	118.9

C(14)–C(13)–C(12)	118.28(11)
C(14)–C(13)–C(17)	120.76(11)
C(12)–C(13)–C(17)	120.96(11)
C(13)–C(17)–H(17A)	109.5
C(13)–C(17)–H(17B)	109.5
H(17A)–C(17)–H(17B)	109.5
C(13)–C(17)–H(17C)	109.5
H(17A)–C(17)–H(17C)	109.5
H(17B)–C(17)–H(17C)	109.5
C(13)–C(14)–C(15)	120.69(11)
C(13)–C(14)–H(14)	119.7
C(15)–C(14)–H(14)	119.7
C(10)–C(15)–C(14)	119.37(11)
C(10)–C(15)–C(16)	118.08(11)
C(14)–C(15)–C(16)	122.55(11)
O(4)–C(16)–C(8)	124.18(11)
O(4)–C(16)–C(15)	117.55(10)
C(8)–C(16)–C(15)	118.27(11)
C(16)–O(4)–H(1O4)	109.5

Hydrogen bonds [Å and °]

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(4)–H(1O4)...O(1)	0.84	1.76	2.5435(12)	154.1