Supporting information

One-Pot Synthesis of 1,3-oxazine derivatives catalyzed by a green nanocomposite of lacunary phosphomolybdate on TiO_2/g-C_3N_4 under mild solvent-free conditions

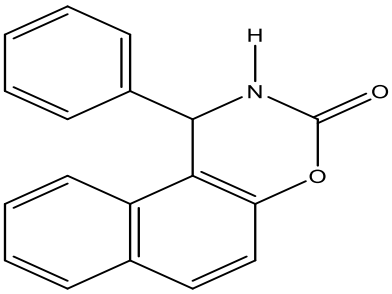
Maryam Bahmanziyari, Hossein Naeimi*

[a] *Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, 87317-51167, I.R. Iran; Tel: 98-31-55912388; Fax: 983155912397; E-mail: Naeimi@kashanu.ac.ir*

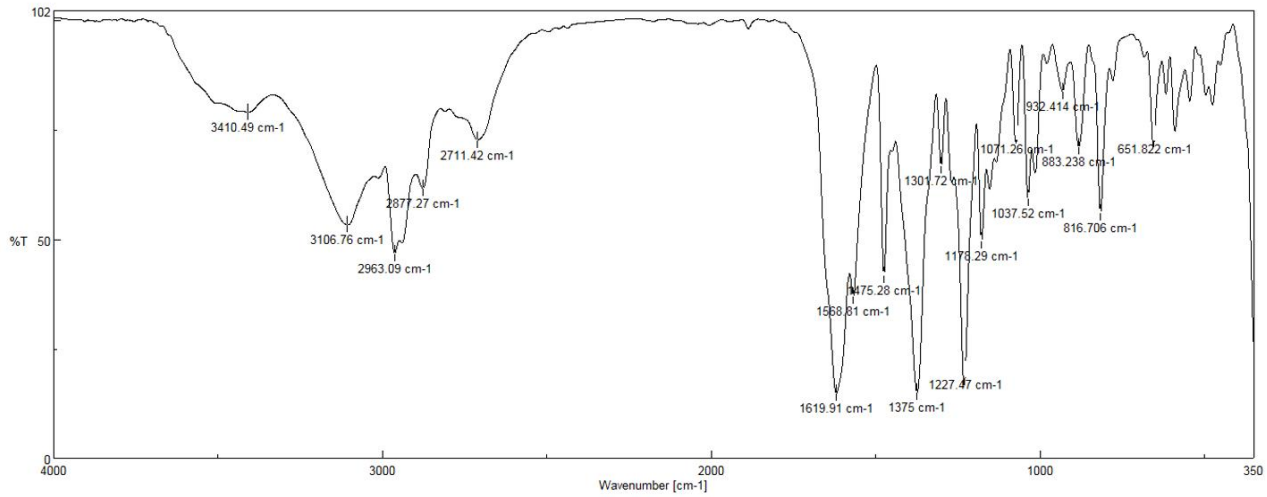
General procedure for the synthesis of 1,3-oxazine derivatives

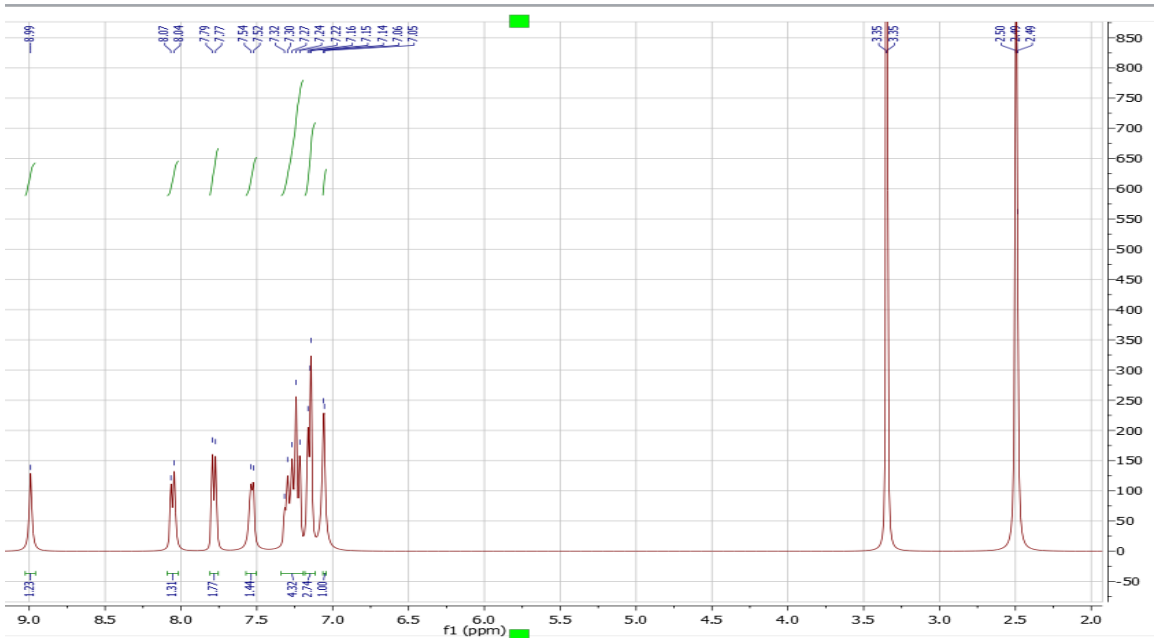
In a test tube stirred in an oil bath at a temperature of 80 °C with 1 mmol aromatic aldehydes, 1mmol 2-naphthol, and 1.2 mmol urea, 3 mg nanocomposite $H_3PMo_{11}O_{39}$@TiO_2@*g*-C_3N_4 was used. The progress of the reaction was monitored through thin layer chromatography (Ethyl acetate/n-hexane, 1/3). In order to separate the catalyst from the mixture, the mixture was cooled before adding ethanol 25 mL, centrifuged, and then filtered. With the help of recrystallization, the pure product was prepared to evaluate the melting point, FT-IR and ^{1}H NMR.

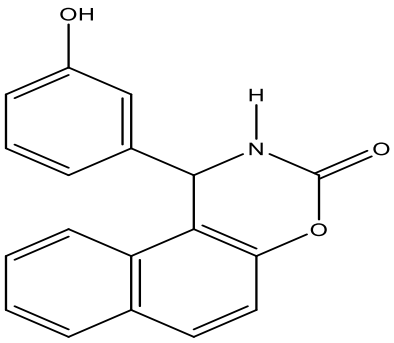
The spectral data:



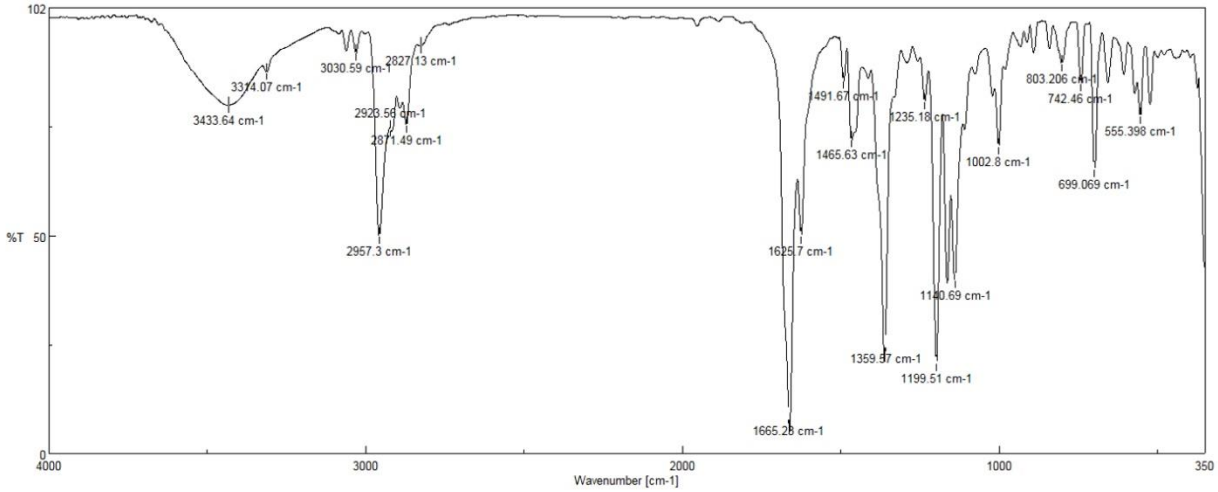
1-(phenyl) -1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4a);** White solid; m.p.: 220-225 °C; IR (KBr) v = 3410, 3107, 2963, 2872, 1619, 1568, 1375, 1227/cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.05 (s, 1H), 7.15 (d, J=8.0 Hz, 3H), 7.22-7.32 (m, 4H), 7.53 (d, J=8.0 Hz, 1H), 7.78 (d, J=8.0 Hz, 2H), 8.05 (d, J= 12.0 Hz, 1H), 8.99 (s, 1H).

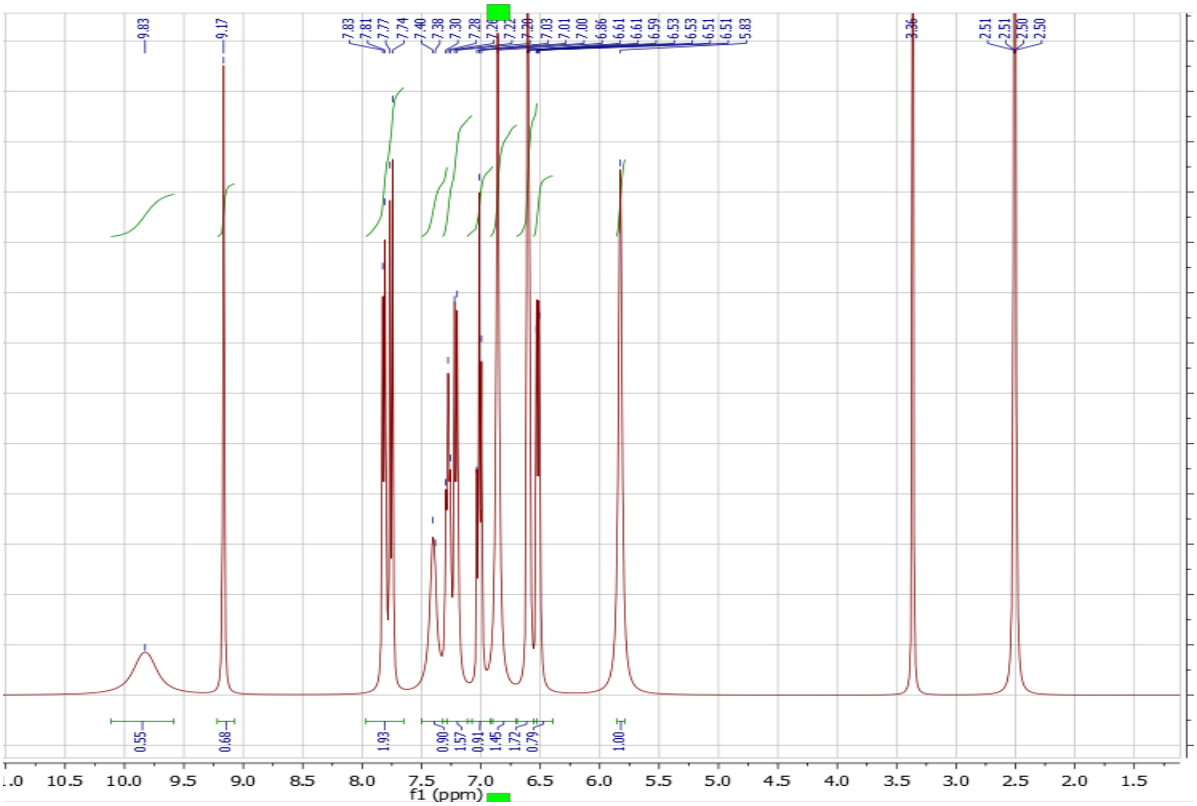

102
%T 50
0
4000
3000
2000
1000
350
Wavenumber [cm-1]
3410.49 cm-1
3106.76 cm-1
2963.09 cm-1
2877.27 cm-1
2711.42 cm-1
1619.91 cm-1
1568.81 cm-1
1475.28 cm-1
1375 cm-1
1301.72 cm-1
1227.47 cm-1
1178.29 cm-1
1071.26 cm-1
1037.52 cm-1
932.414 cm-1
883.238 cm-1
816.706 cm-1
651.822 cm-1

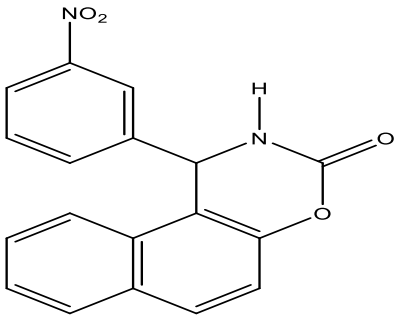

f1 (ppm)



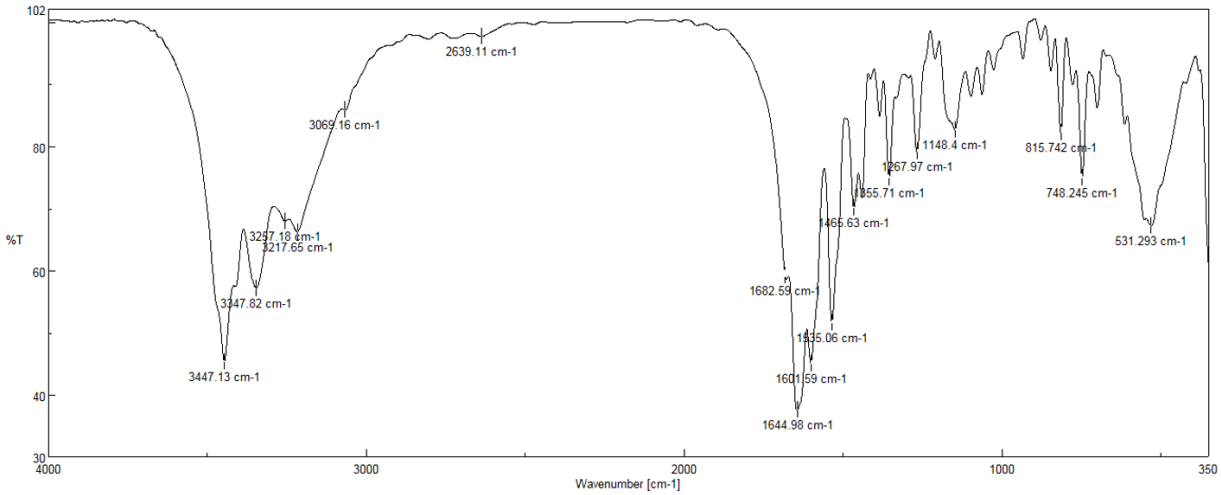
1-(3-hydroxyphenyl) -1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4b);** White solid; m.p.: 188-200 °C; IR (KBr) ν = 3434, 3314, 2957, 1665, 1625, 1359, 1199 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.83 (s, 1H), 6.52 (d, *J*= 8.0 Hz, 2H), 6.59 (d, *J*= 8.0 Hz, 2H), 6.86 (s, 1H), 7.02 (t, *J*=12.0 Hz, 1H), 7.20 (d, *J*=8.0 Hz, 1H), 7.28 (t, *J*=16.0 Hz, 1H), 7.40 (s, 1H), 7.74 (d, *J*=12.0 Hz, 1H), 7.81 (d, *J*=8.0 Hz, 1H), 9.17 (s, 1H), 9.83 (s, 1H).

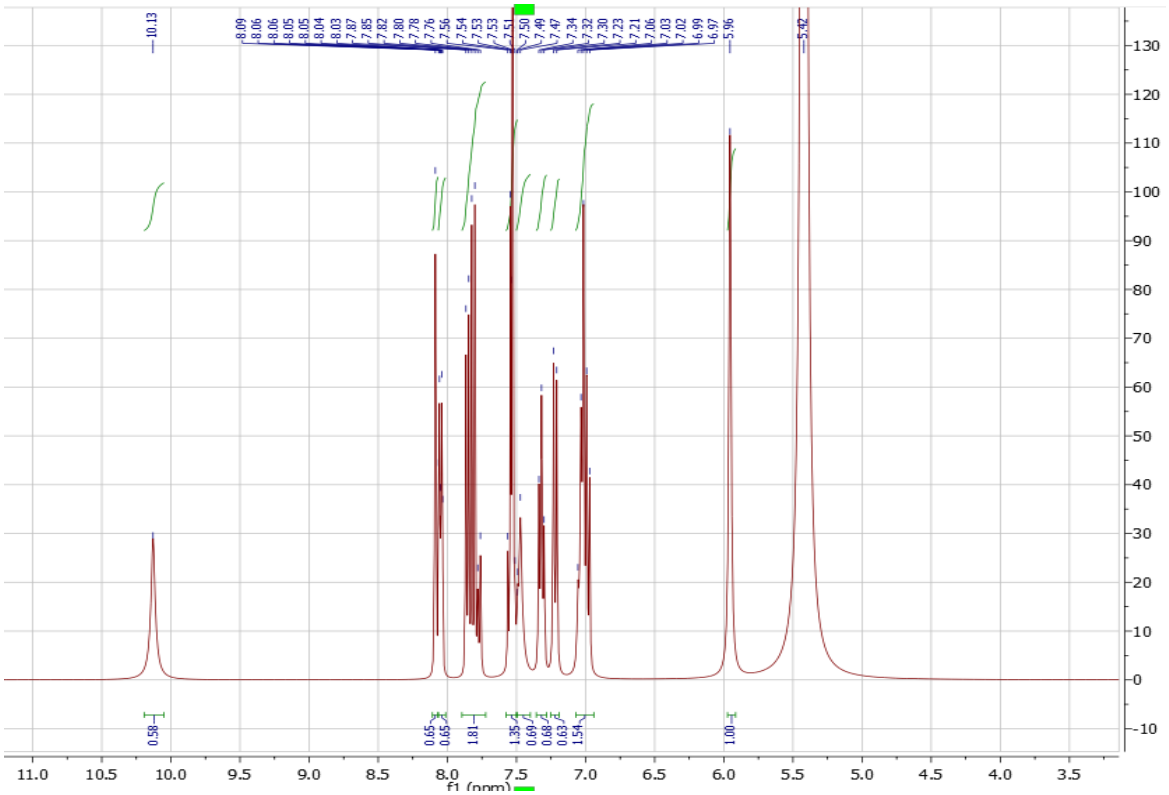


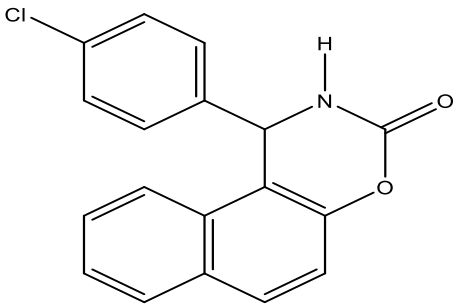




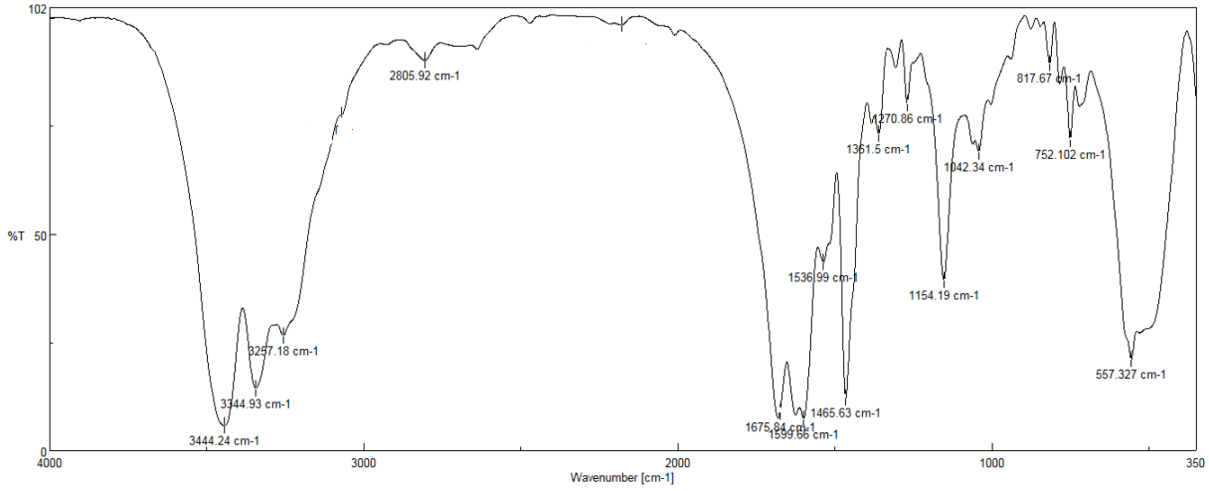
1-(3-nitrophenyl) -1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4c);** Yellow solid; m.p.: 224-228°C; IR (KBr) ν = 3447, 3347, 1644, 1602, 1535, 1466, 1356 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 5.96 (s, 1H), 6.97-7.06 (m, 2H), 7.21 (d, *J*= 8.0 Hz, 1H), 7.32 (t, *J*= 16.0 Hz, 1H), 7.47-7.56 (m, 2H), 8.09 (s, 1H), 10.13 (s, 1H).

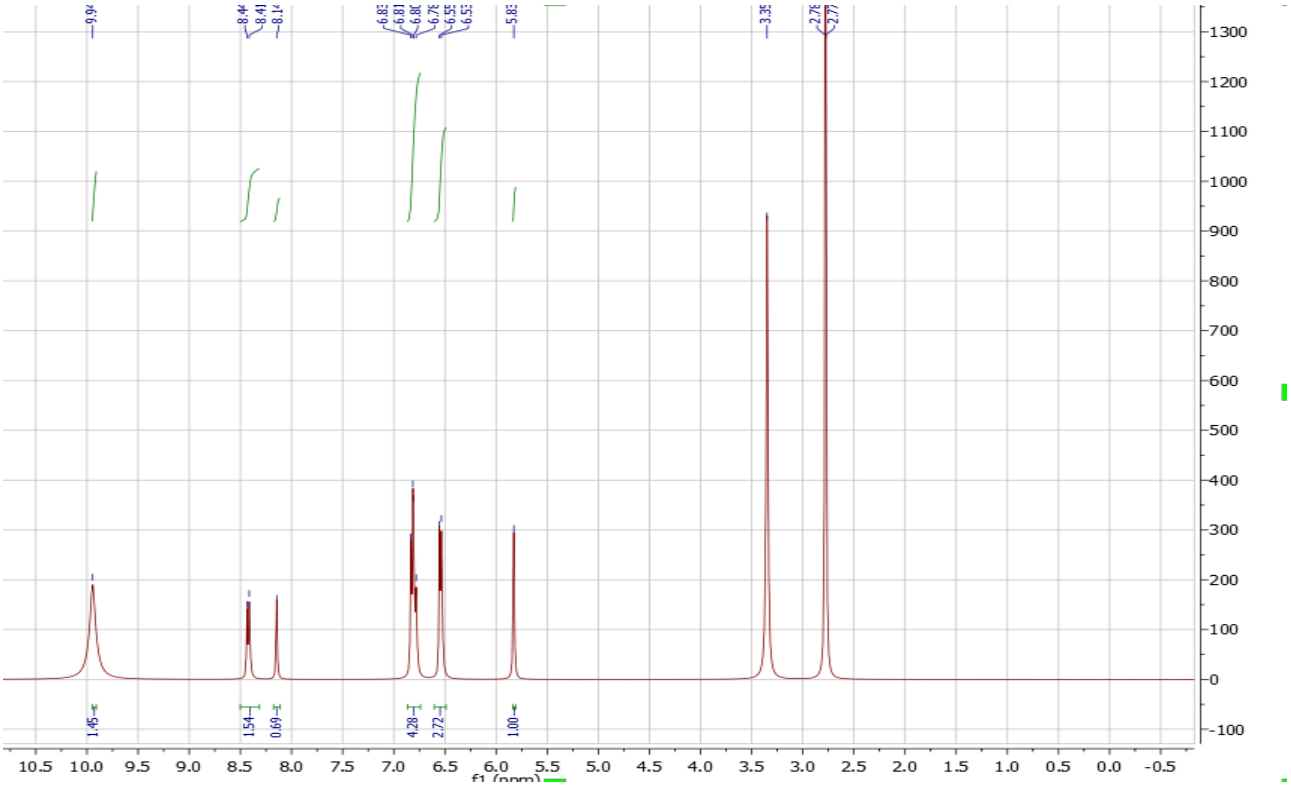

%T
Wavenumber [cm-1]
3447.13 cm-1
3247.82 cm-1
3297.18 cm-1
3217.65 cm-1
3069.16 cm-1
2639.11 cm-1
1682.59 cm-1
1644.98 cm-1
1601.59 cm-1
1535.06 cm-1
1465.63 cm-1
1355.71 cm-1
1267.97 cm-1
1148.4 cm-1
815.742 cm-1
748.245 cm-1
531.293 cm-1

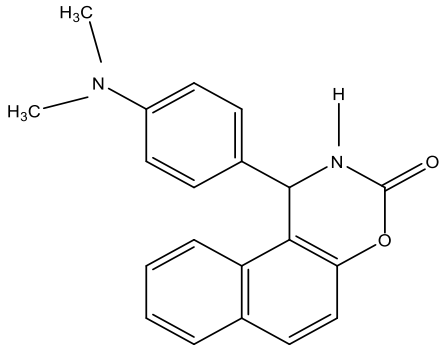

f1 (ppm)



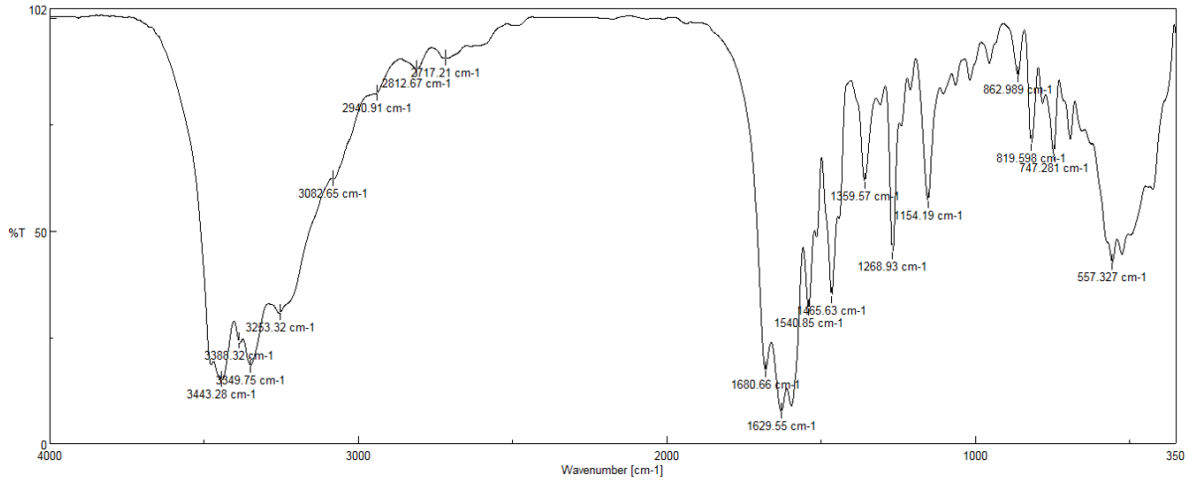
1-(4-chlorophenyl)-1H-naphtho[1,2-e] [1,3] oxazin-3(2H)-one **(4d);** White solid; m.p.: 210-215°C; IR (KBr) ν = 3444, 3344, 3257, 1675, 1599, 1465, 1154 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) ; 5.83 (s, 1H), 6.54 (d, J= 8.0 Hz, 3H), 6.80 (t, J= 20.0 Hz, 4H), 8.14 (s, 1H), 8.42 (d, J= 12.0 Hz, 2H), 9.94 (s, 1H).

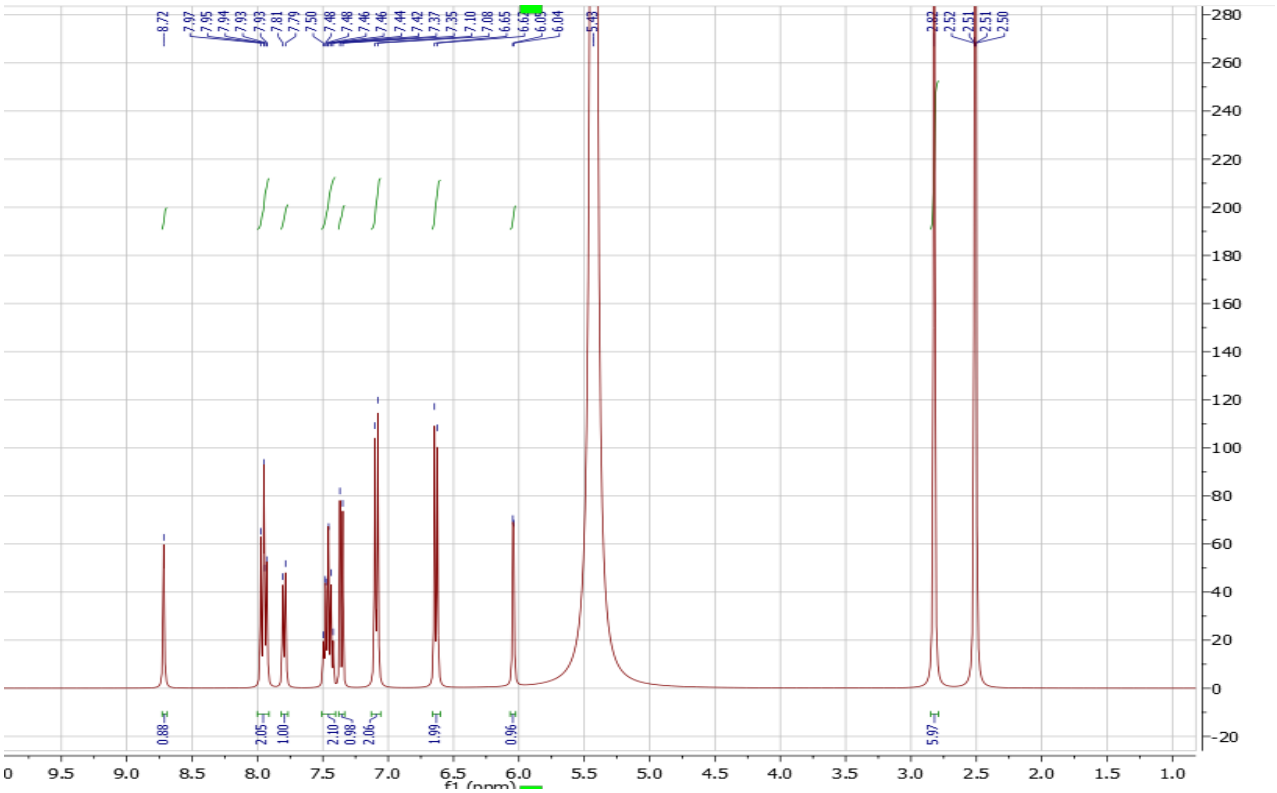


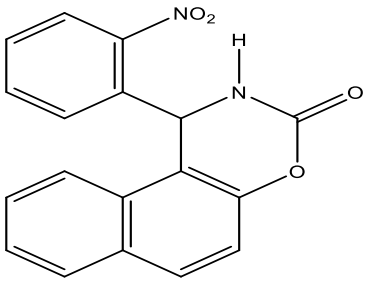




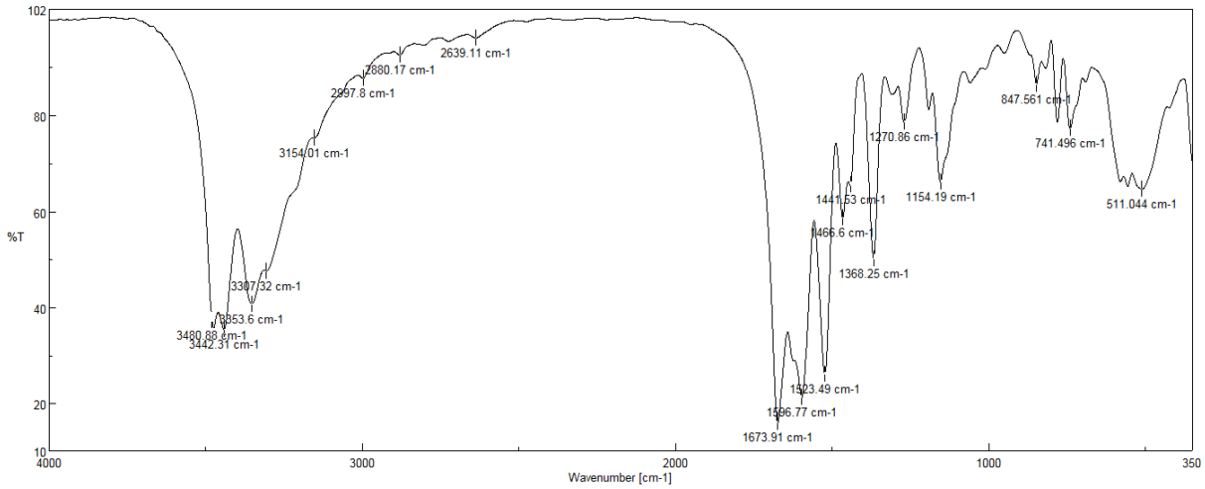
1-(*N*,*N*-dimethylphenyl) -1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4e);** White solid; m.p.: 220-228 °C; IR (KBr) ν = 3443, 3388, 3253, 1681, 1629, 1541, 1466, 1269, 557 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 2.82 (s, 6H), 6.04 (d, *J*=4.0 Hz,1H), 6.29 (d, *J*= 12.0 Hz, 2H), 7.08 (d, *J*= 8.0 Hz, 2H), 7.35 (d, *J*= 8.0 Hz,1H), 7.42-7.50 (m, 2H), 7.79 (d, *J*= 8.0 Hz, 1H), 7.94 (t, *J*= 16.0 Hz, 2H), 8.72 (s, 1H).

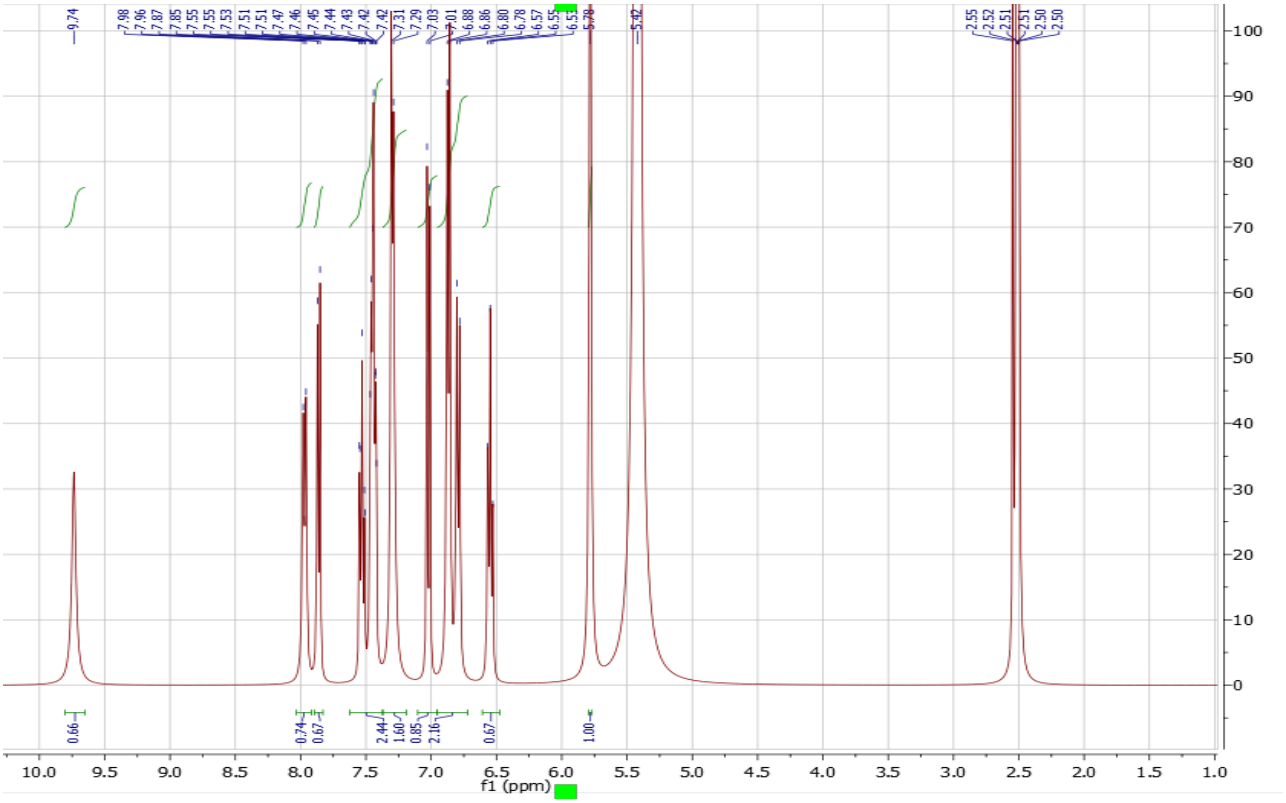

102
%T 50
0
4000
3000
2000
1000
350
Wavenumber [cm-1]
3443.28 cm-1
3388.32 cm-1
3349.75 cm-1
3253.32 cm-1
3082.65 cm-1
2940.91 cm-1
2812.67 cm-1
2717.21 cm-1
1680.66 cm-1
1629.55 cm-1
1540.85 cm-1
1465.63 cm-1
1359.57 cm-1
1268.93 cm-1
1154.19 cm-1
862.989 cm-1
819.598 cm-1
747.281 cm-1
557.327 cm-1

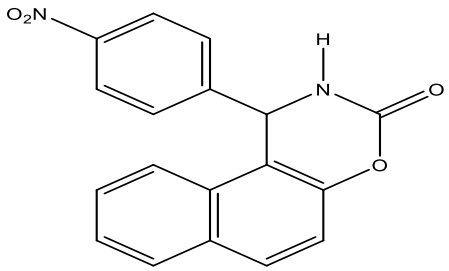




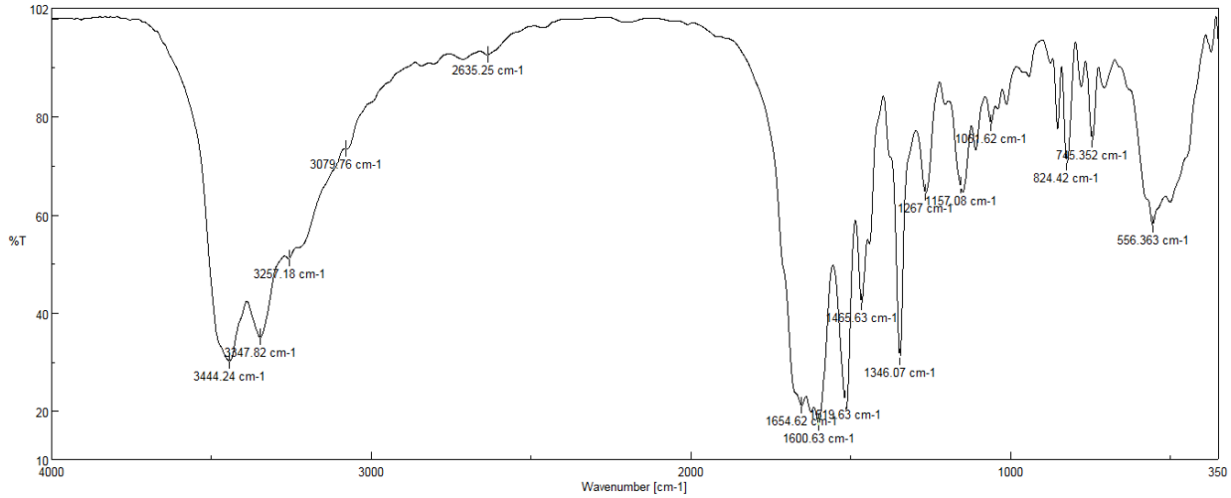
1-(2-nitroophenyl)-1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4f);** White solid; m.p.: 103-108 °C; IR (KBr) ν = 3481, 3442, 3307, 1673, 1597, 1524, 1368, 1154, 511 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 5.78 (s,1H), 6.55 (t, J=16.0 Hz, 1H), 6.78 (d, J= 8.0 Hz, 1H), 6.86 (d, J=8.0 Hz, 1H), 7.01 (d, J=8.0 Hz, 2H), 7.29 (d, J=8.0 Hz, 2H), 7.42-7.55 (m, 2H), 7.58 (d, J= 8.0 Hz, 1H), 7.96 (d, J=8.0 Hz, 1H), 9.74 (s, 1H).

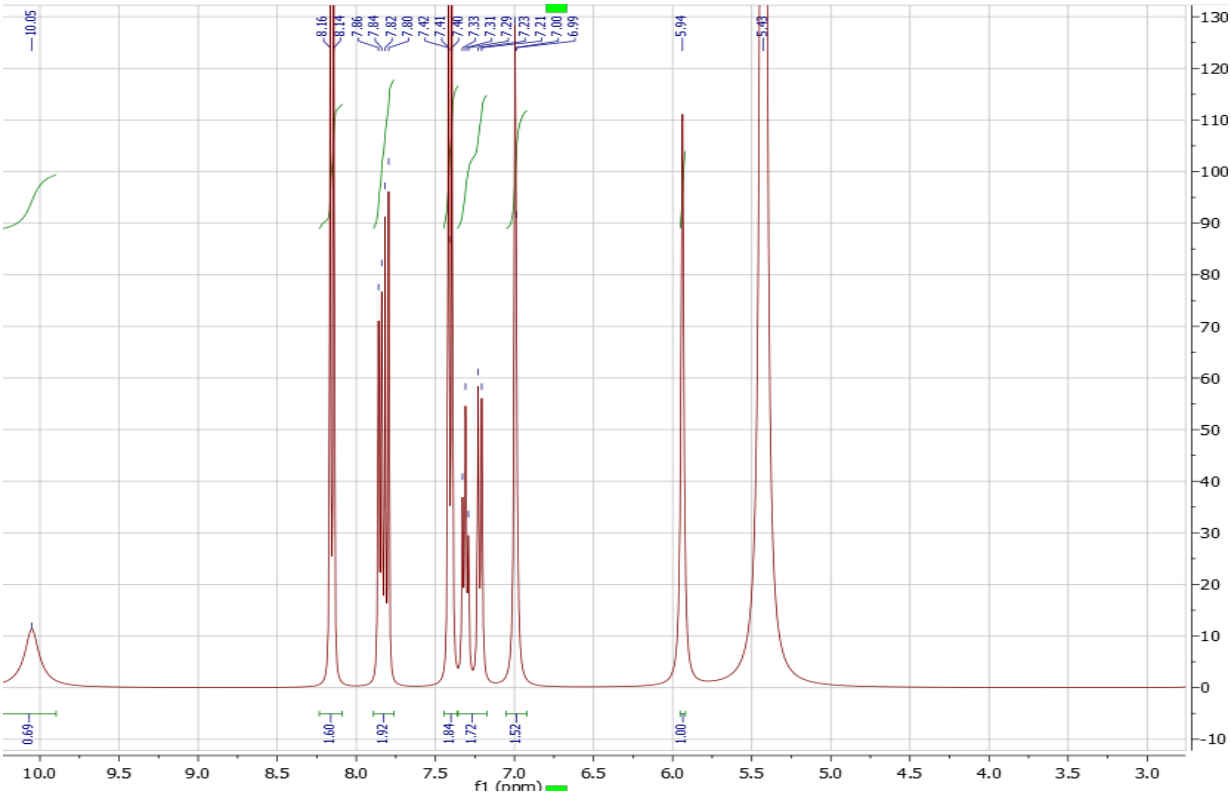

%T
Wavenumber [cm-1]
3480.88 cm-1
3442.31 cm-1
3307.32 cm-1
3353.6 cm-1
3154.01 cm-1
2997.8 cm-1
2880.17 cm-1
2639.11 cm-1
1673.91 cm-1
1596.77 cm-1
1523.49 cm-1
1466.6 cm-1
1441.53 cm-1
1368.25 cm-1
1270.86 cm-1
1154.19 cm-1
847.561 cm-1
741.496 cm-1
511.044 cm-1

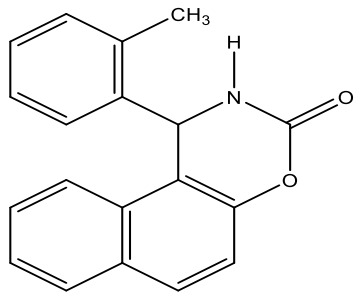

f1 (ppm)



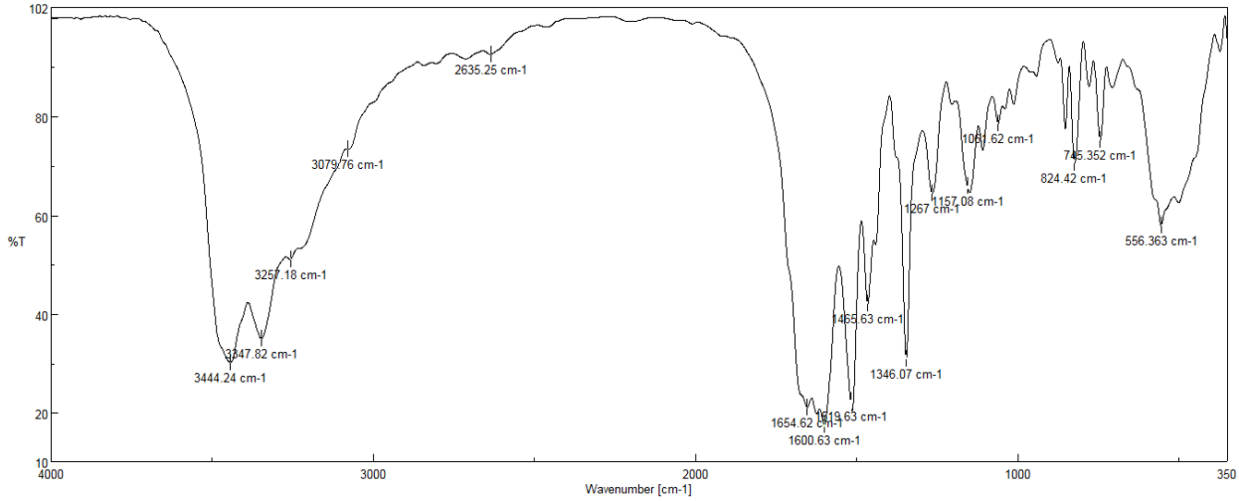
1-(4-nitroophenyl)-1H-naphtho[1,2-e] [1,3]oxazin-3(2H)-one **(4g);** Yellow solid; m.p.: 187-190 °C; IR (KBr) ν = 3444, 3348, 3257, 1655, 1600, 1466, 1346, 556 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 5.94 (s, 1H), 7.00 (s, 2H), 7.22 (d, *J*= 8.0 Hz, 1H), 7.31 (t, *J*= 16.0 Hz, 1H), 7.41 (d, *J*= 8.0 Hz, 2H), 7.80-7.86 (m, 2H), 8.15 (d, *J*= 8.0 Hz, 2H), 10.05 (s, 1H).

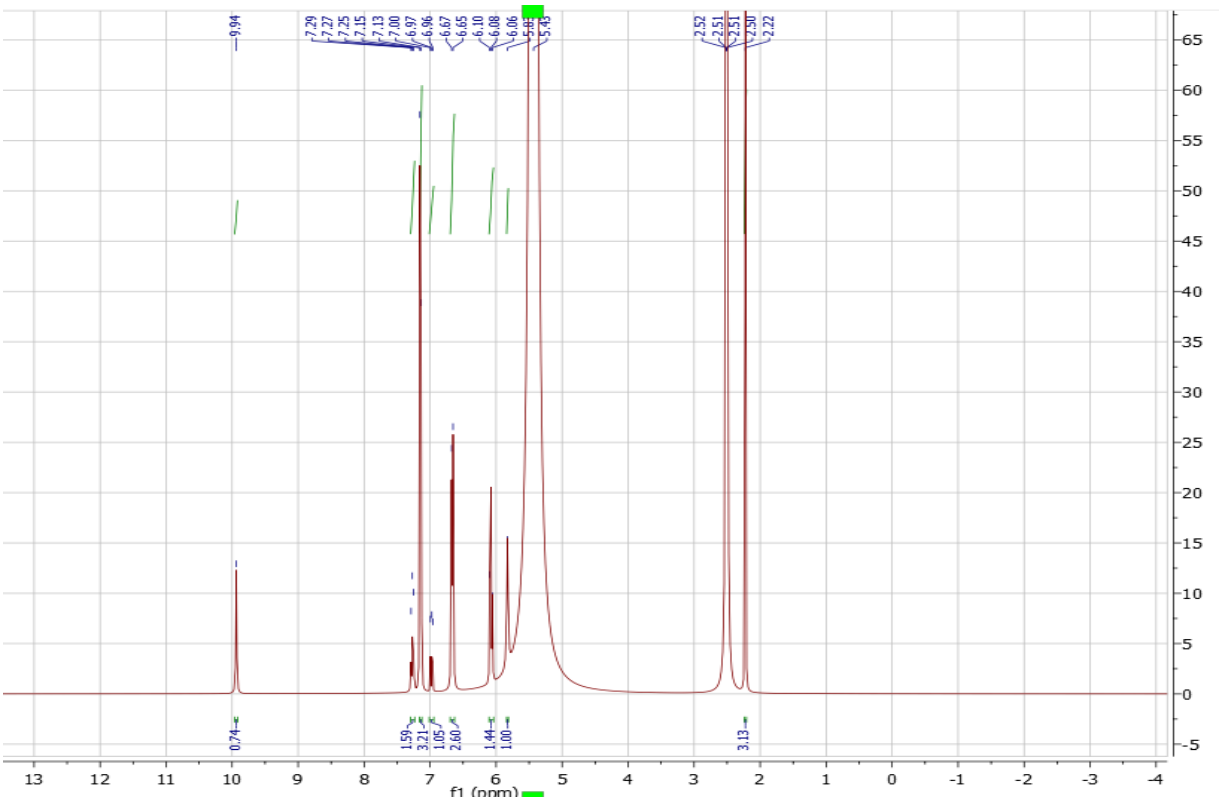

%T
Wavenumber [cm-1]
3444.24 cm-1
3347.82 cm-1
3257.18 cm-1
3079.76 cm-1
2635.25 cm-1
1654.62 cm-1
1619.63 cm-1
1600.63 cm-1
1465.63 cm-1
1346.07 cm-1
1267 cm-1
1157.08 cm-1
1081.62 cm-1
824.42 cm-1
745.352 cm-1
556.363 cm-1

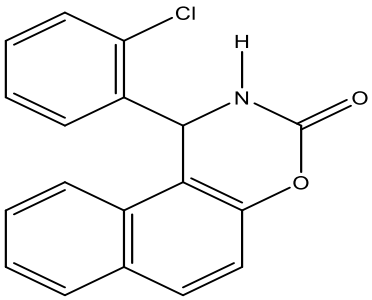

10.05
8.16
8.14
7.86
7.84
7.82
7.80
7.42
7.41
7.40
7.33
7.31
7.29
7.23
7.21
7.00
6.99
5.94
5.43
0.69
1.60
1.92
1.84
1.72
1.52
1.00
f1 (ppm)



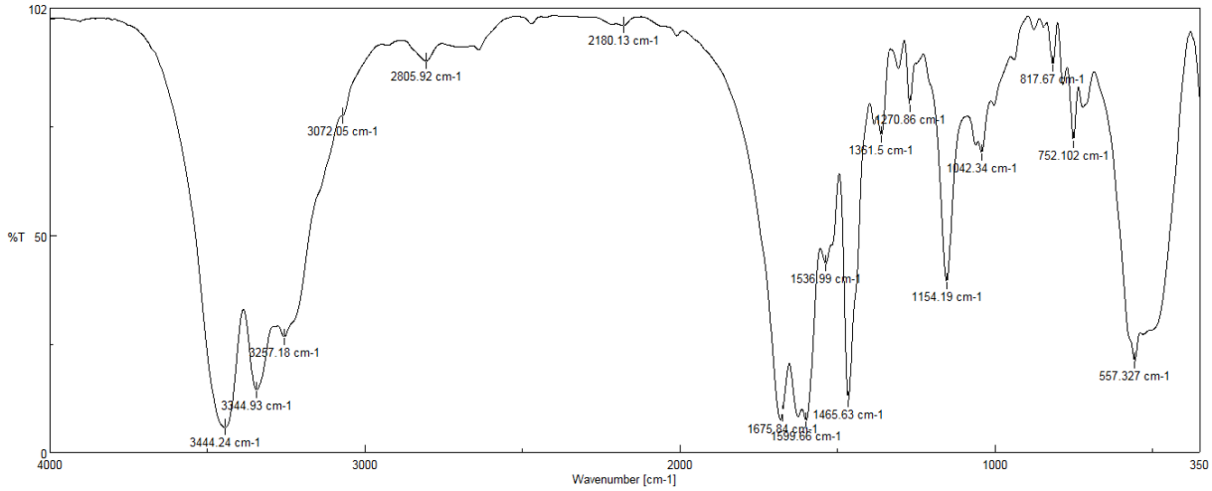
1-(2-methylphenyl)-1H-naphtho[1,2-e] [1,3] oxazin-3(2H)-one **(4h);** White solid; m.p.: 225-230 °C; IR (KBr) ν = 3444.2, 3347.8, 3225.3, 1686.4, 1593.8, 1465.6, 1158, 536.1 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 2.22 (s, 3H), 5.83 (s, 1H), 6.06 (d, j=8Hz, 3H), 6.97 (t, j=16Hz, 1H), 7.14 (d, j=8Hz, 3H), 7.27 (t, j=16Hz, 2H), 9.94 (s, 1H).

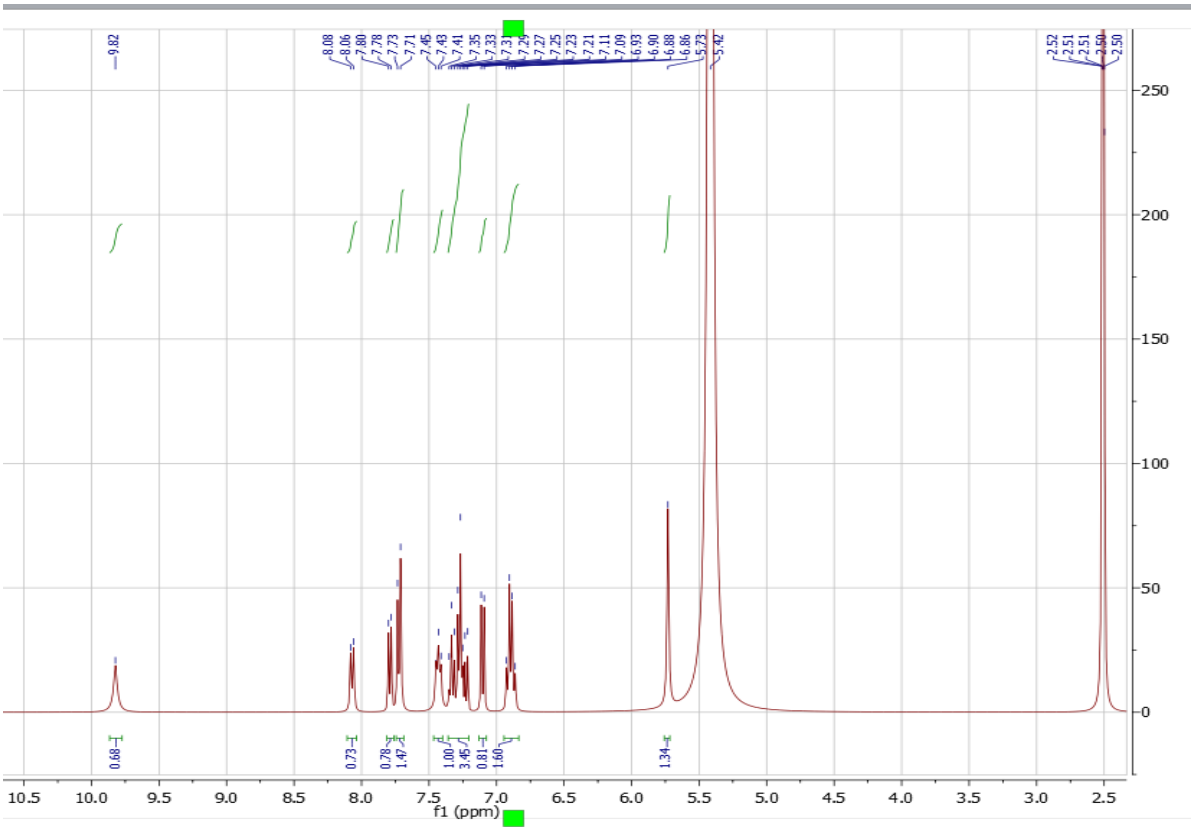

%T
Wavenumber [cm-1]
3444.24 cm-1
3347.82 cm-1
3257.18 cm-1
3079.76 cm-1
2635.25 cm-1
1654.62 cm-1
1619.63 cm-1
1600.63 cm-1
1485.63 cm-1
1346.07 cm-1
1267 cm-1
1157.08 cm-1
1081.62 cm-1
824.42 cm-1
745.352 cm-1
556.363 cm-1

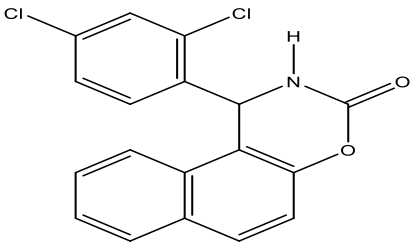

9.94
7.29
7.27
7.25
7.15
7.13
7.00
6.97
6.96
6.67
6.65
6.10
6.08
6.06
5.43
2.52
2.51
2.51
2.30
2.22
0.74
1.59
3.21
1.05
2.60
1.44
1.00
3.13
f1 (ppm)



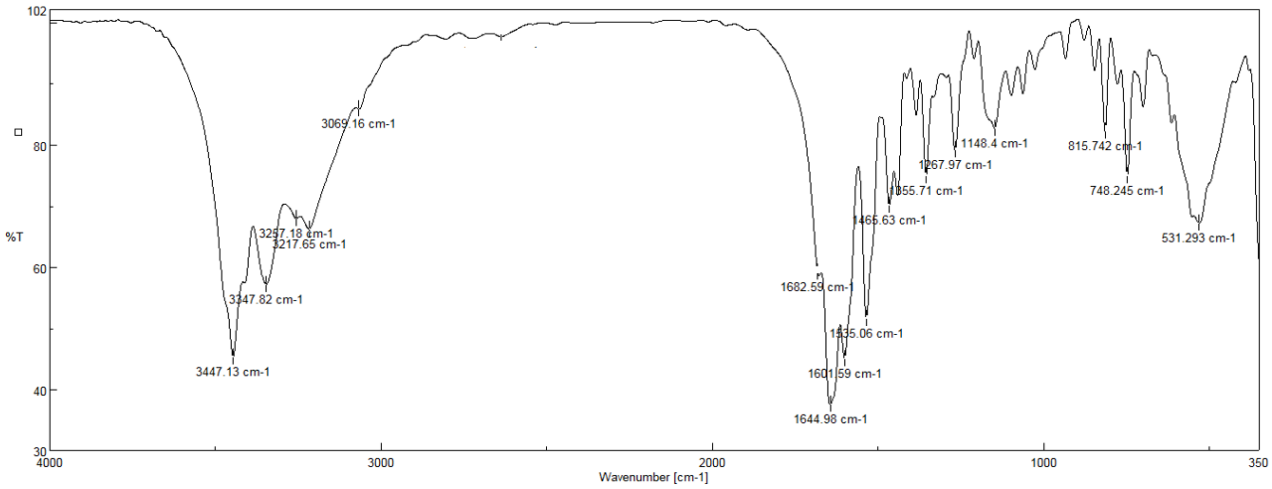
1-(2-chlorophenyl)-1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4i);** White solid; m.p.: (1-250 -255°C; IR (KBr) ν = 3444, 3345, 3257, 1654, 1600, 1464, 1157, 557 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 5.73 (s, 1H), 6.86 (q, 2H), 7.09 (d, *J*=8.0 Hz, 1H), 7.21-7.35 (m, 3H), 7.41 (t, *J*=16.0 Hz, 1H), 7.71 (d, *J*=8.0 Hz, 1H), 7.78 (d, *J*=8.0 Hz, 1H), 8.06 (d, *J*=8.0 Hz, 1H), 9.82 (s, 1H).

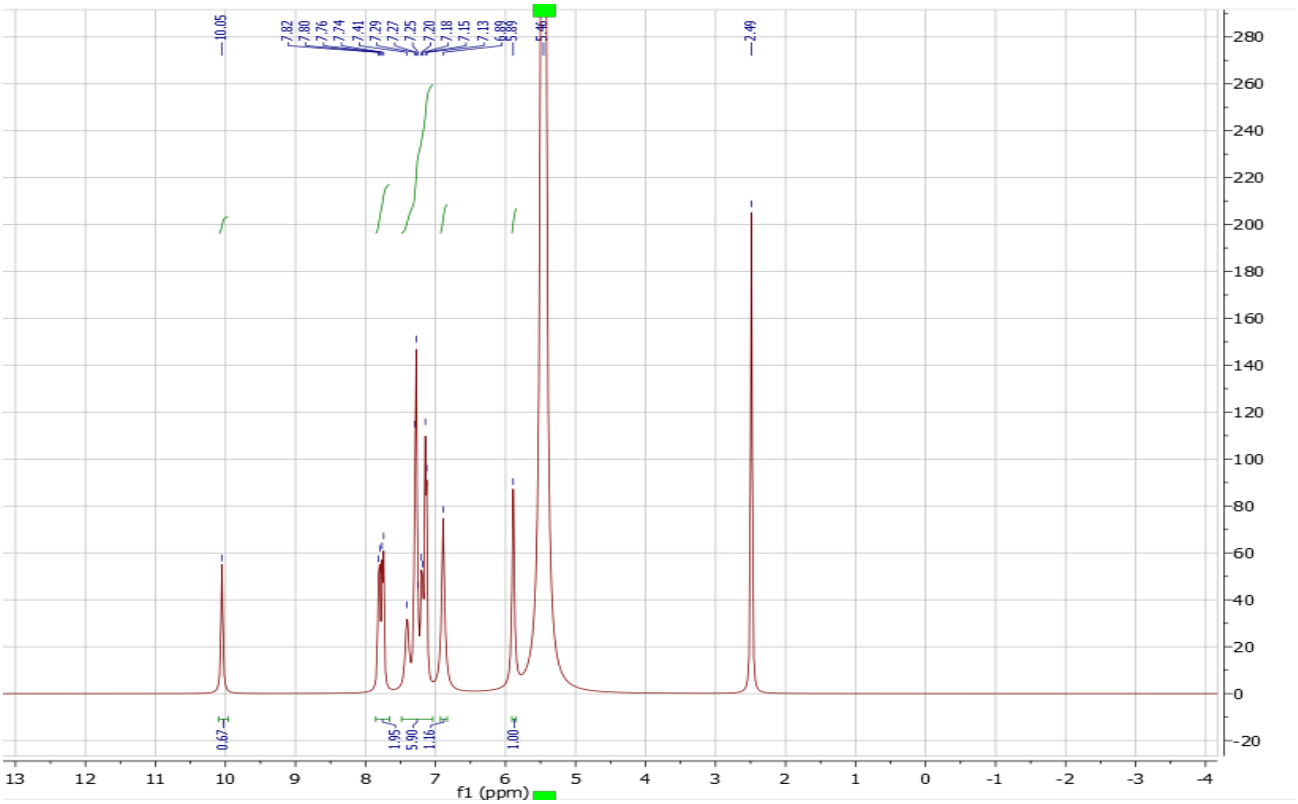

102
%T 50
0
4000
3000
2000
1000
350
Wavenumber [cm-1]
3444.24 cm-1
3344.93 cm-1
3257.18 cm-1
3072.05 cm-1
2805.92 cm-1
2180.13 cm-1
1675.84 cm-1
1599.66 cm-1
1536.99 cm-1
1465.63 cm-1
1361.5 cm-1
1270.86 cm-1
1154.19 cm-1
1042.34 cm-1
817.67 cm-1
752.102 cm-1
557.327 cm-1

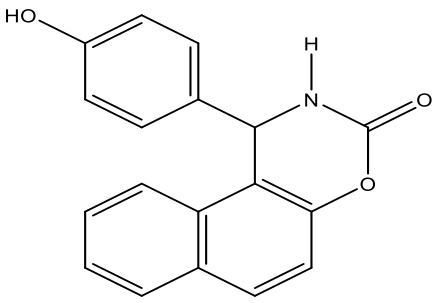

9.82
8.08
8.06
7.80
7.78
7.73
7.71
7.45
7.43
7.41
7.35
7.33
7.31
7.29
7.27
7.25
7.23
7.21
7.11
7.09
6.93
6.90
6.88
6.86
5.73
5.42
2.52
2.51
2.51
2.50
2.50
250
200
150
100
50
0
0.68
0.73
0.78
1.47
1.00
3.45
0.81
1.60
1.34
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)



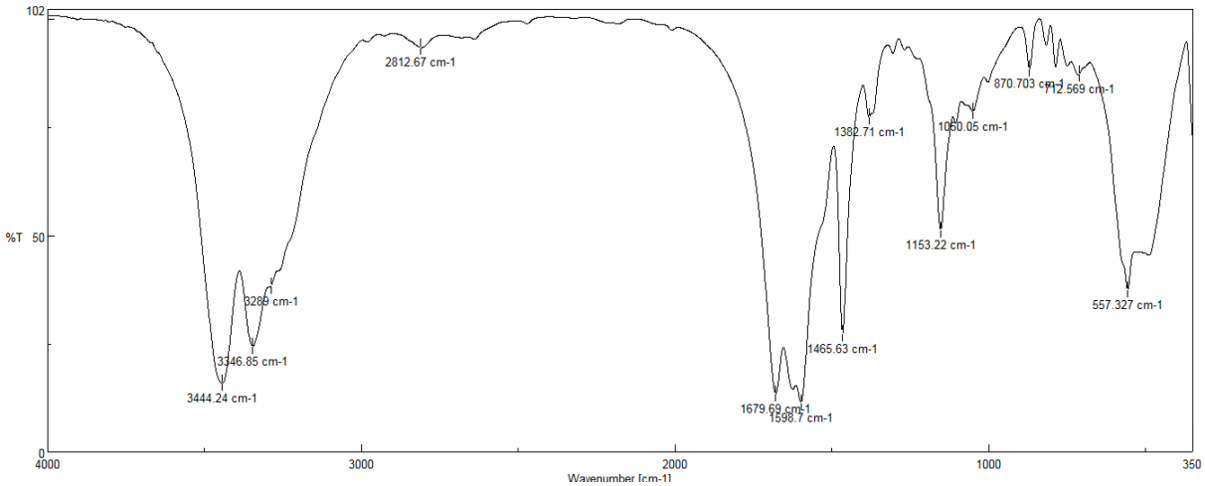
1-(2,4-dichlorophenyl)-1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4j);** White solid; m.p.: 258-260 °C; IR (KBr) ν = 3447, 3347, 3257, 1644, 1535, 1466, 1148 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 5.89 (s, 1H), 6.89 (s, 1H), 7.13-7.41 (m, 6H), 7.74 (q, 2H), 10.05 (s, 1H).

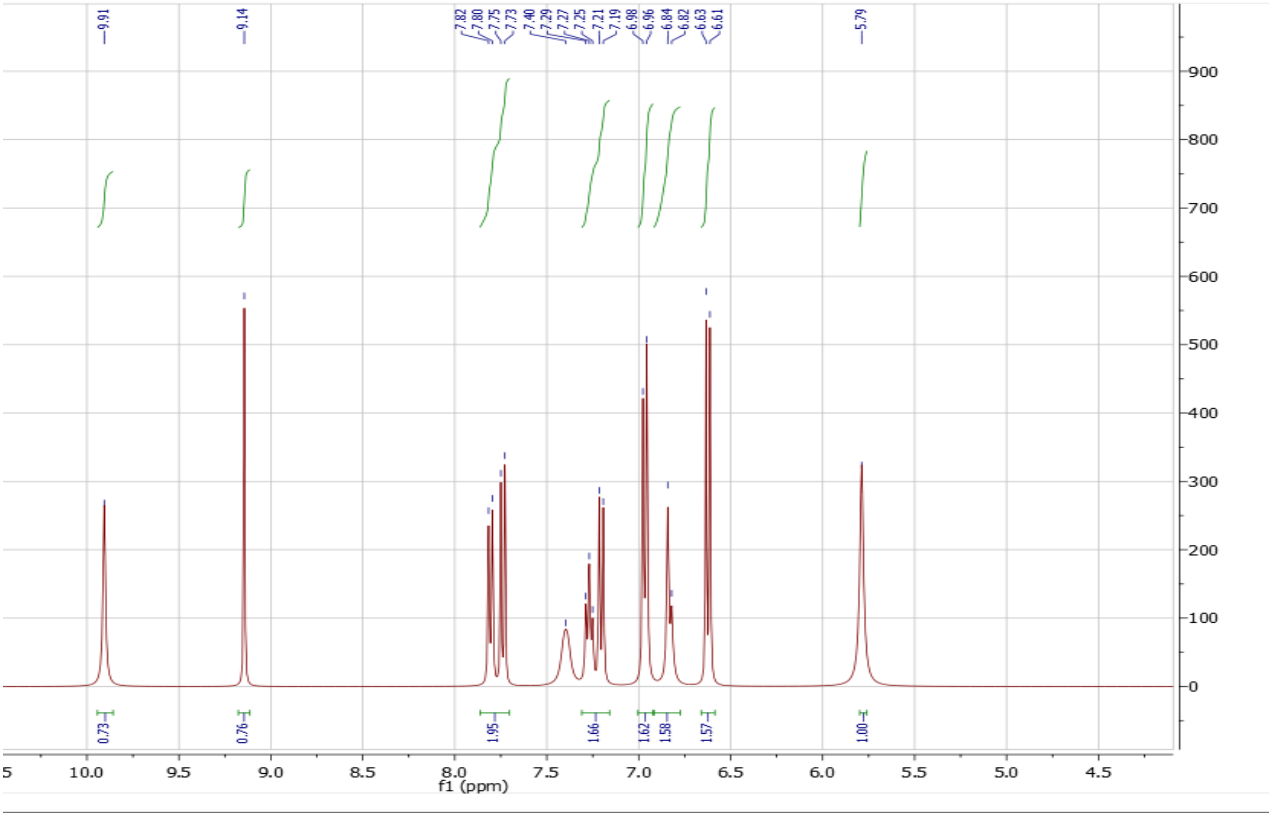


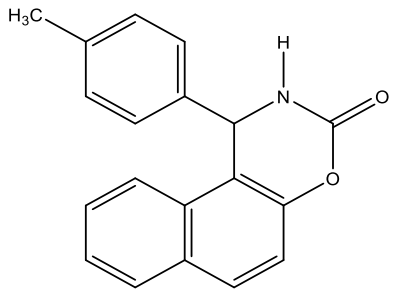




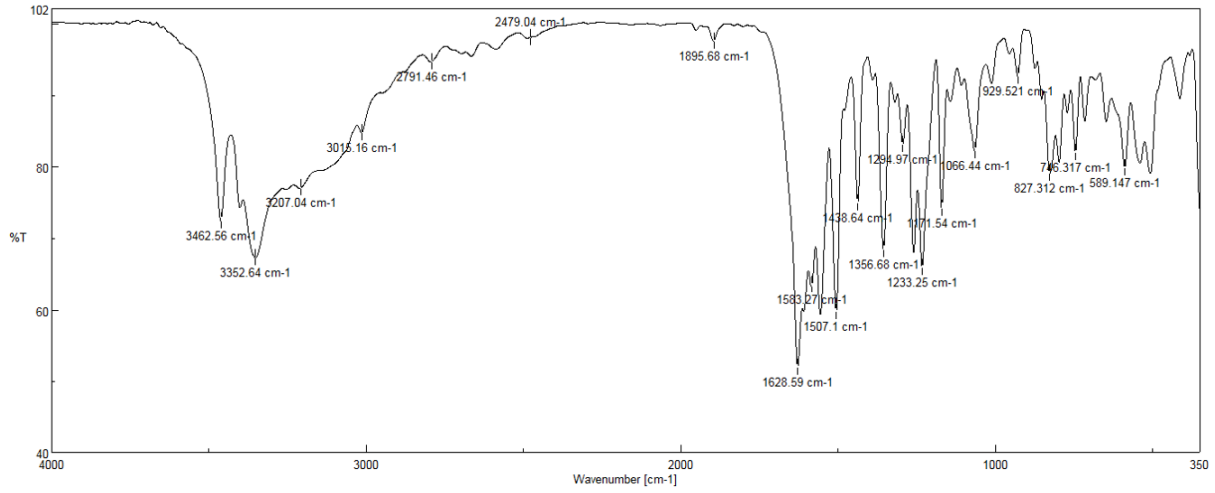
1-(4-hydroxyphenyl)-1H-naphtho[1,2-e][1, 3] oxazin-3(2H)-one**(4k);** White solid; m.p.: 180-184 °C; IR (KBr) ν = 3442, 3347, 3289, 1680, 1599, 1466, 1153, 557 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 5.79 (s, 1H), 6.61 (d, J=8.0 Hz, 2H), 6.83 (d, J=8.0 Hz, 2H), 6.96 (d, J=8.0 Hz, 1H), 7.19 (d, J=8.0 Hz, 1H), 7.27 (t, J=16.0 Hz, 1H), 7.73 (d, J=8.0 Hz, 1H), 7.80 (d, J=8.0 Hz, 1H), 9.14 (s, 1H), 9.91 (s, 1H).

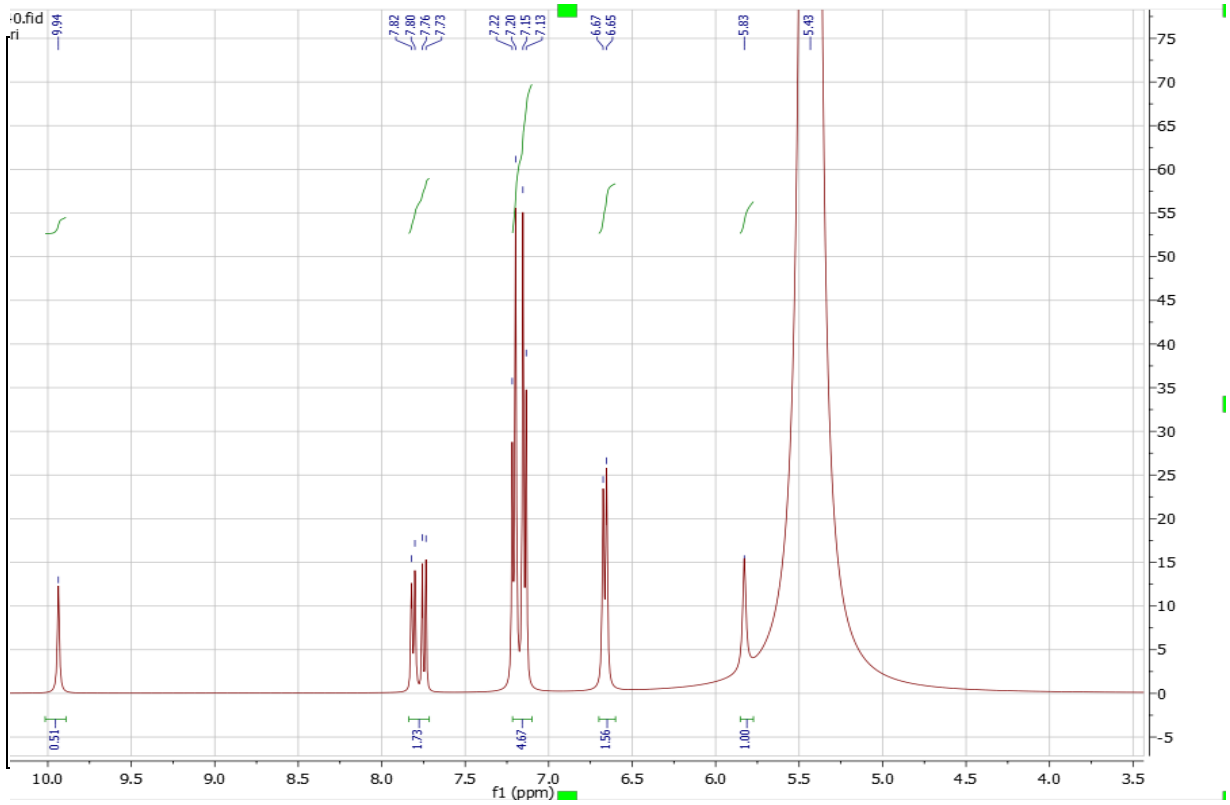

102
%T 50
0
4000
3000
2000
1000
350
Wavenumber [cm-1]
2812.67 cm-1
3289 cm-1
3346.85 cm-1
3444.24 cm-1
1679.69 cm-1
1598.7 cm-1
1465.63 cm-1
1382.71 cm-1
1153.22 cm-1
1030.05 cm-1
870.703 cm-1
712.569 cm-1
557.327 cm-1


9.91
9.14
7.82
7.80
7.75
7.73
7.40
7.29
7.27
7.25
7.21
7.19
6.98
6.96
6.84
6.82
6.63
6.61
5.79
900
800
700
600
500
400
300
200
100
0
0.73
0.76
1.95
1.66
1.62
1.58
1.57
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)



1-(4-methylphenyl)-1H-naphtho[1,2-e] [1, 3] oxazin-3(2H)-one **(4l);** White solid; m.p.: 165-168 °C; IR (KBr) ν = 3463, 3352, 3207, 1629, 1583, 1507, 1357, 1233 /cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm) ; 2.28 (s, 3H), 5.83 (s, 1H), 6.65 (d, J=8.0 Hz, 2H), 7.20 (q, 5H), 7.76 (d, J=12.0 Hz, 1H), 7.80 (d, J=8.0 Hz, 1H), 9.94 (s, 1H).


102
80
60
40
%T
4000
3000
2000
1000
350
Wavenumber [cm-1]
3462.56 cm-1
3352.64 cm-1
3207.04 cm-1
3015.16 cm-1
2791.46 cm-1
2479.04 cm-1
1895.68 cm-1
1628.59 cm-1
1583.27 cm-1
1507.1 cm-1
1438.64 cm-1
1356.68 cm-1
1294.97 cm-1
1233.25 cm-1
1171.54 cm-1
1066.44 cm-1
929.521 cm-1
827.312 cm-1
746.317 cm-1
589.147 cm-1


9.94
7.82
7.80
7.76
7.73
7.22
7.20
7.15
7.13
6.67
6.65
5.83
5.43
0.51
1.73
4.67
1.56
1.00
f1 (ppm)