One-pot synthesis of Bis-spiro Piperidines Using Nanocellulose/BF_3/Fe_3O_4 as a Natural Based Catalyst

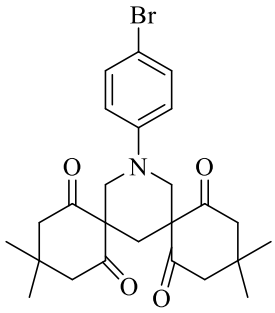
Parisa Moharrami Korblagh [1], Abdolhamid Bamoniri [1*], Bi Bi Fatemeh Mirjalili [2]

[1] *Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan, I.R.Iran*

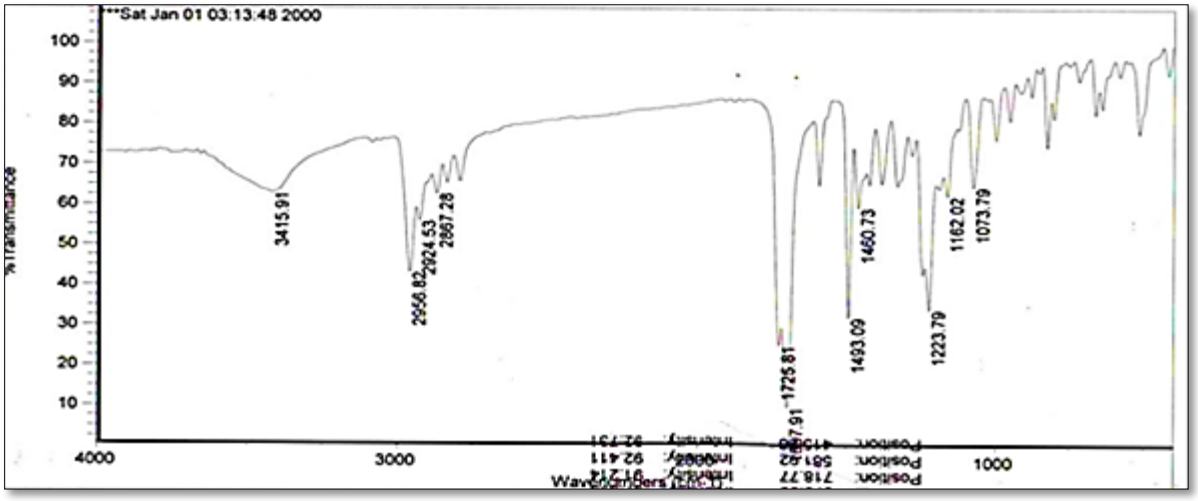
[2] *Department of Organic Chemistry, College of Science, Yazd University, Yazd, I.R.Iran*

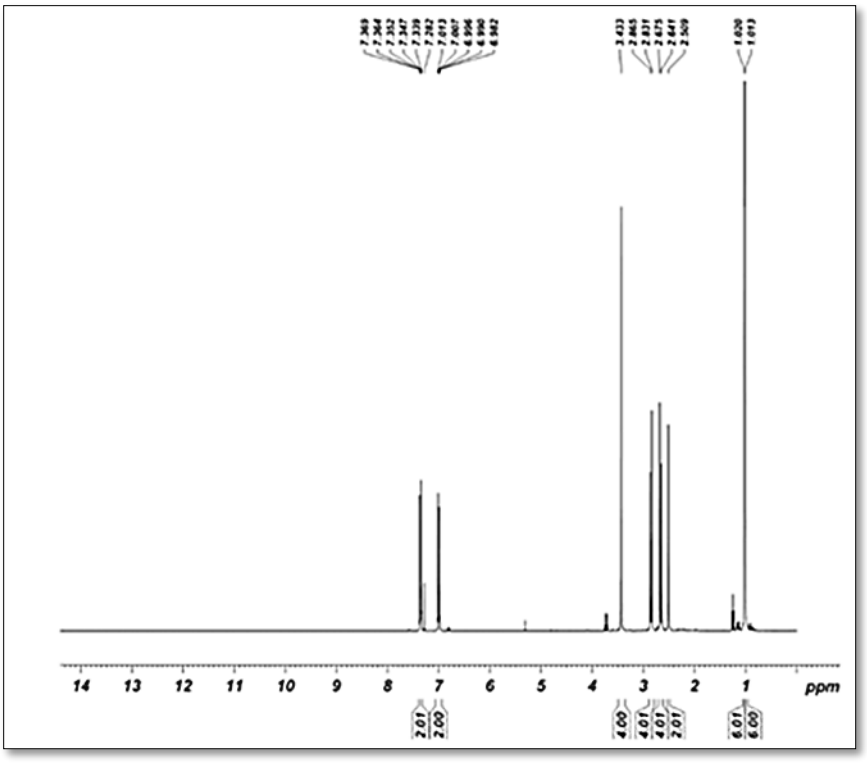
bamoniri@kashanu.ac.ir

(15-(4-Boromophenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 1)

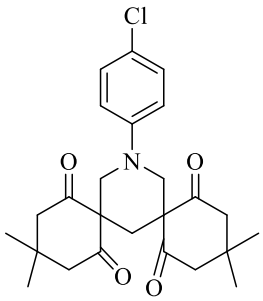


(15-(4-Boromophenyl)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone Compound **1a** (table 2, Entry 1): mp: 207-208 ºC; FTIR (KBr) ῡ: 1073, 1223, 1375, 1600-1460, 1725, 2924, 3039 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.35 (2H, d, ^3J=6.8 Hz, ArH), 7.00 (2H, d, ^3J =6.8Hz, ArH), 3.43 (4H, s, NCH_2), 2.84 (4H, d, ^2J =13.6 Hz, $COCH_2$), 2.65 (4H, d, ^2J =13.6 Hz, $COCH_2$), 2.50 (2H, s, CH_2), 1.02 (6H, s, CH_3),1.01 (6H, s, CH_3).

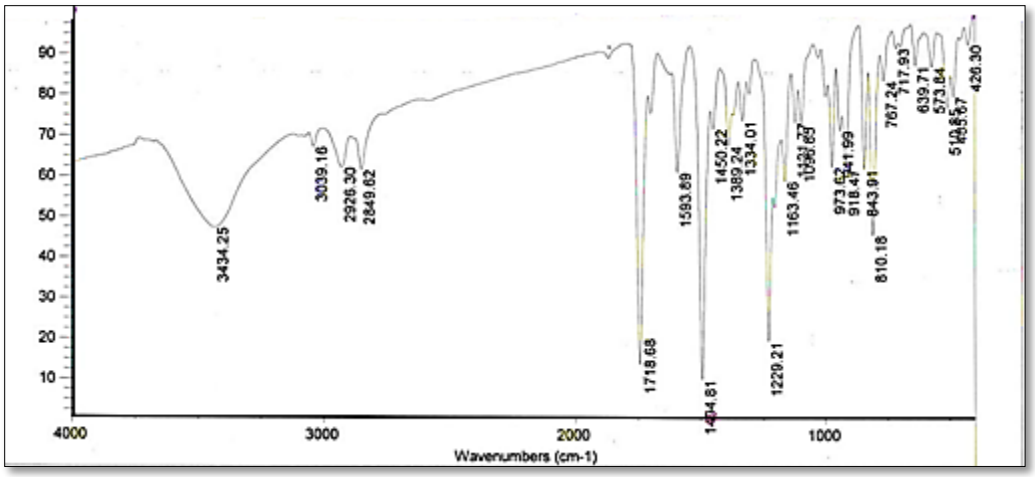


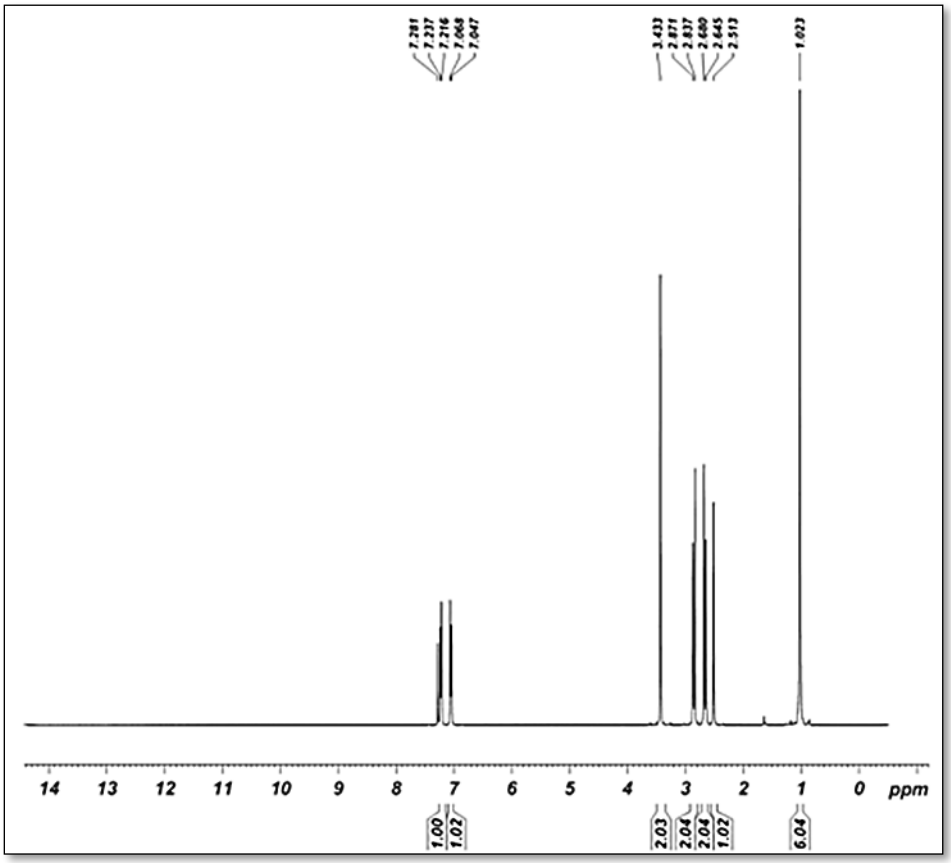


(15-(4-Chlorophenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 2)

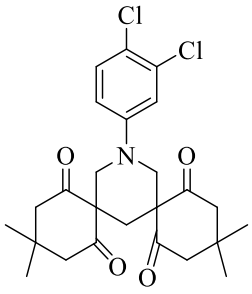


(15-(4-Chlorophenyl)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone Compound **2a** (table 2, Entry 2) mp: 215-217 ºC; FTIR (KBr) ῡ: 767, 1229, 1389, 1593-1450, 1718, 2926, 3039 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.22 (2H, d, ^3J =8.4 Hz, ArH), 7.05 (2H, d, ^3J =8.4 Hz, ArH), 3.43 (4H, s, NCH_2), 2.85 (4H, d, ^2J =13.6 Hz, $COCH_2$), 2.66 (4H, d, ^2J =14 Hz, $COCH_2$), 2.51 (2H, s, CH_2),1.02 (12H, s, CH_3).

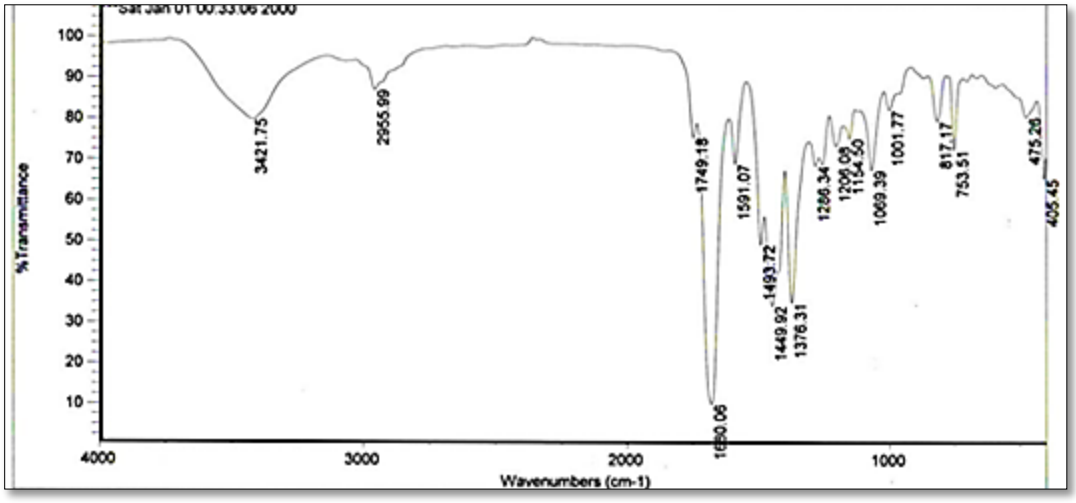

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3039.16
2926.30
2849.62
1718.68
1593.69
1404.81
1450.22
1389.24
1334.01
1229.21
1163.46
973.62
941.99
918.47
843.91
810.18
767.24
717.93
639.71
573.84
426.30
Wavenumbers (cm-1)

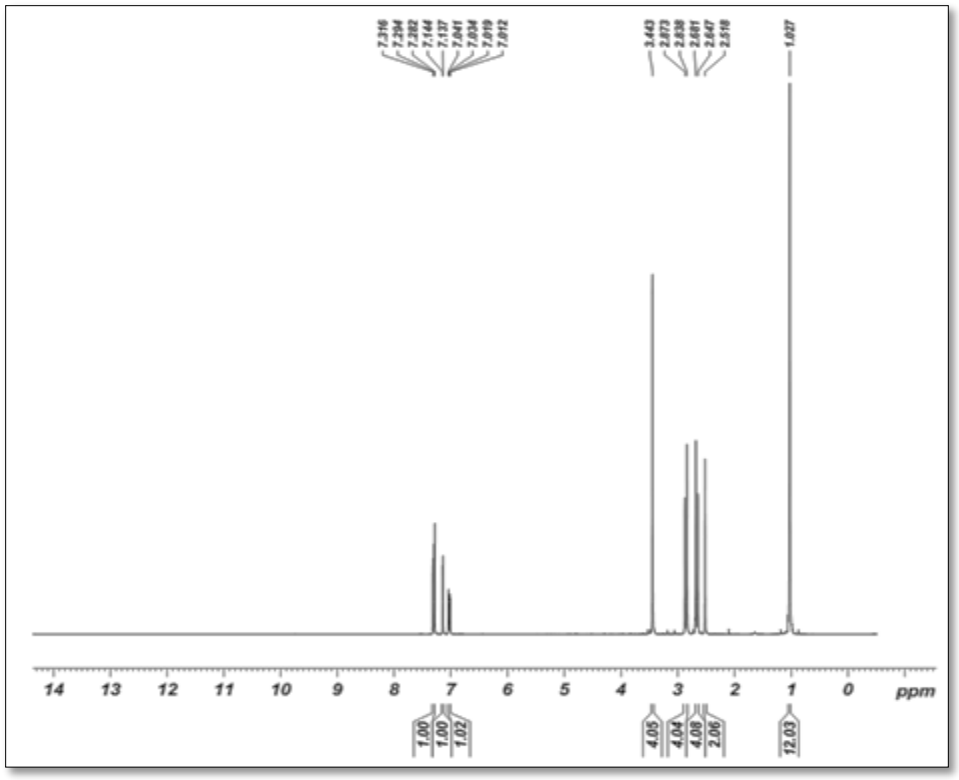

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7.337
7.316
7.068
7.047
3.433
2.871
2.837
2.680
2.645
2.513
1.023
ppm
1.00
1.02
2.03
2.04
2.04
1.02
6.04

(15-(3,4-Dichlorophenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,1-tetrone (table 4, Entry 3)

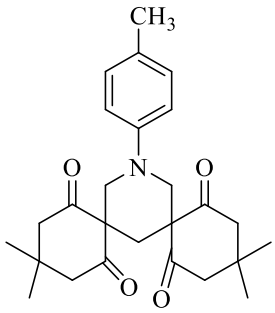


(15-(3,4-Dichlorophenyl)-3,3,11,11-tetramethyl-15 azadispiro[5.1.5.3]hexadecne-1,5,9,1-tetrone Compound **3a** (table 2, Entry 3) mp: 236-238 ºC; FTIR (KBr) ῡ: 1001, 1286, 1376, 1660-1493, 1749, 2955, 3050 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.30 (1H, d, ^{3}J =8.8 Hz, ArH), 7.13 (1H, d, ^{3}J =2.8 Hz, ArH), 7.02 (1H, dd, ^{3}J =8.8, 2.8 Hz, ArH), 3.44 (4H, s, CH_2), 2.85 (4H, d, ^{2}J =14 Hz, $COCH_2$), 2.66 (4H, d, ^{2}J =13.6 Hz, CH_2), 2.51 (2H, s, CH_2), 1.02 (12H, s, CH_3).

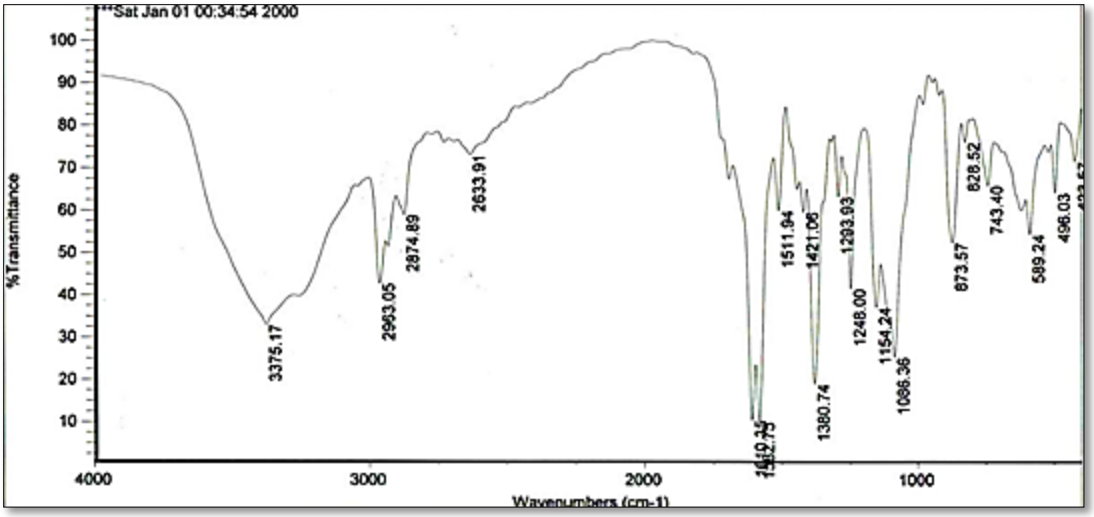


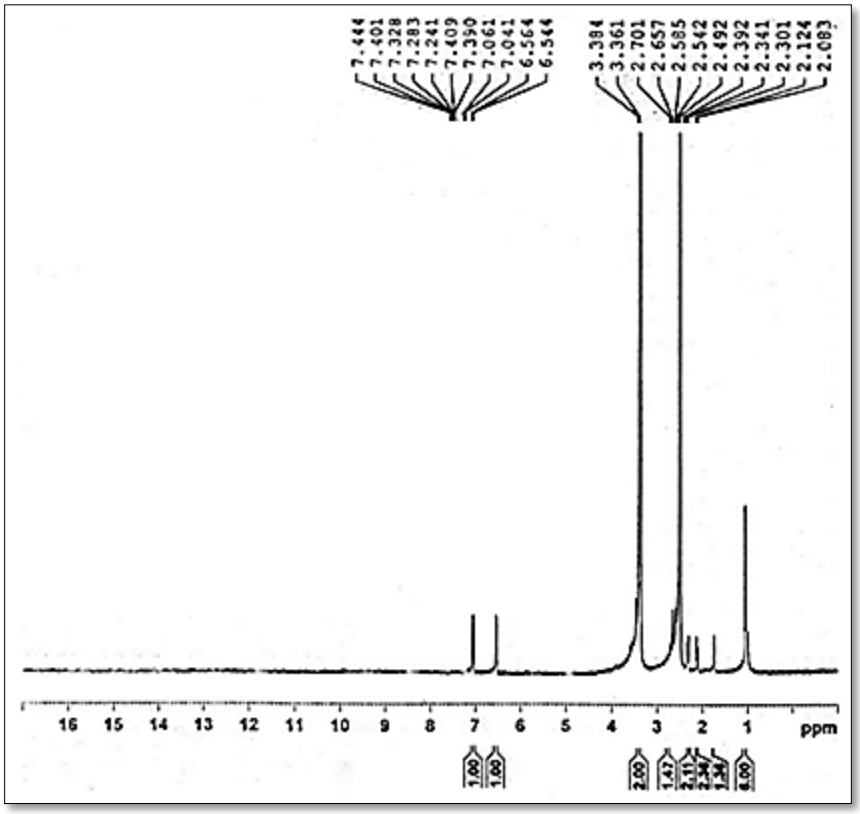


(15-(p-Tolyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 4)

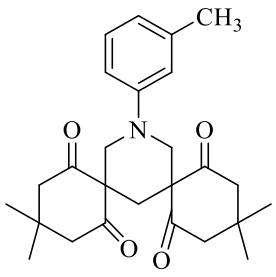


(15-(p-Tolyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone
Compound **4a** (table 2, Entry 4) mp: 250-253 ºC; FTIR (KBr) ῡ: 1248, 1380, 1610-1421, 1718, 3039, 2963 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 7.05 (2H, d, ^3J =8 Hz, ArH), 6.55 (2H, d, ^3J =8 Hz, ArH), 3.38 (4H, s, CH_2), 2.66 (3H, s, CH_3), 2.32 (4H, d, ^2J =16 Hz, CH_2), 2.10 (4H, d, ^2J =16.4 Hz, CH_2), 1.74 (2H, s, CH_2),1.05 (12H, s, CH_3).

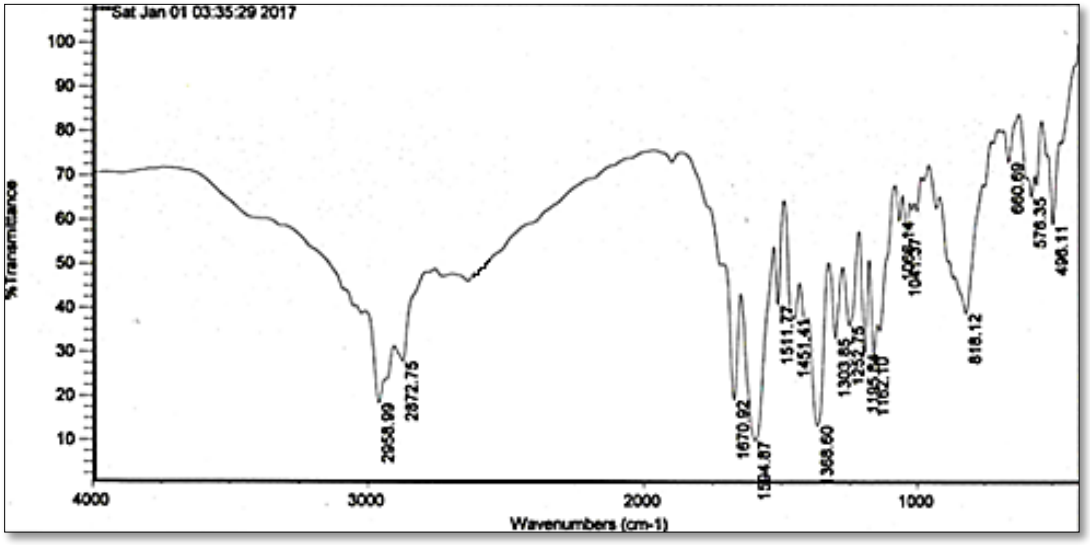

***Sat Jan 01 00:34:54 2000
%Transmittance
Wavenumbers (cm-1)
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2000
1000
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2963.05
2874.89
2633.91
1511.94
1421.06
1380.74
1293.93
1248.00
1154.24
1066.36
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743.40
589.24
496.03

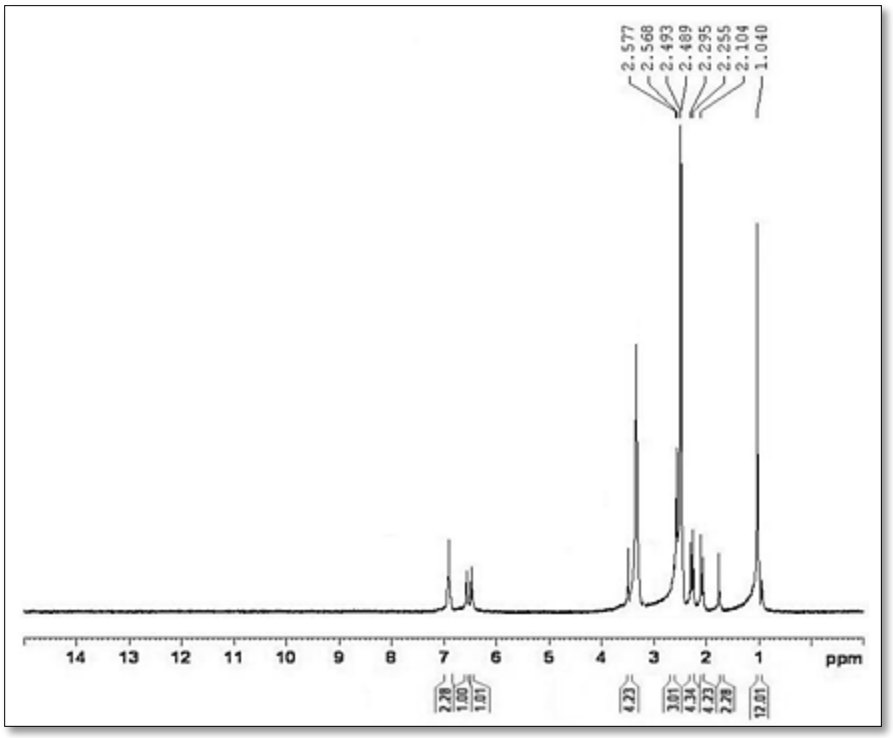

7.444
7.401
7.328
7.283
7.241
7.409
7.390
7.061
7.041
6.564
6.544
3.384
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2.701
2.657
2.585
2.542
2.492
2.392
2.341
2.301
2.124
2.083
ppm
1.00
1.00
2.00
1.47
2.11
2.34
1.34
6.00

(15-(m-Tolyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 5)

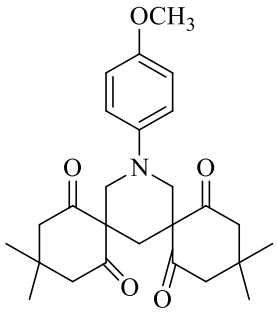


(15-(m-Tolyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone
Compound **5a** (table 2, Entry 5) mp: 188-190 ºC; FTIR (KBr) ῡ: 1255, 1374, 1596-1417, 1667, 2958, 3015 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 6.90 (1H, s, ArH), 6.85 (1H, d, ^3J =8 Hz, ArH), 6.64 (1H, d, ^3J =8 Hz, ArH), 6.54 (1H, t, ^3J =8.4 Hz, ArH), 2.57 (3H, s, CH_3), 3.4 (4H, s, CH_2), 2.27 (4H, d, ^2J =16.4 Hz, CH_2), 2.12 (4H, d, ^2J =16.4 Hz, CH_2), 1.75 (2H, s, CH_2), 1.04 (12H, s, CH_3).



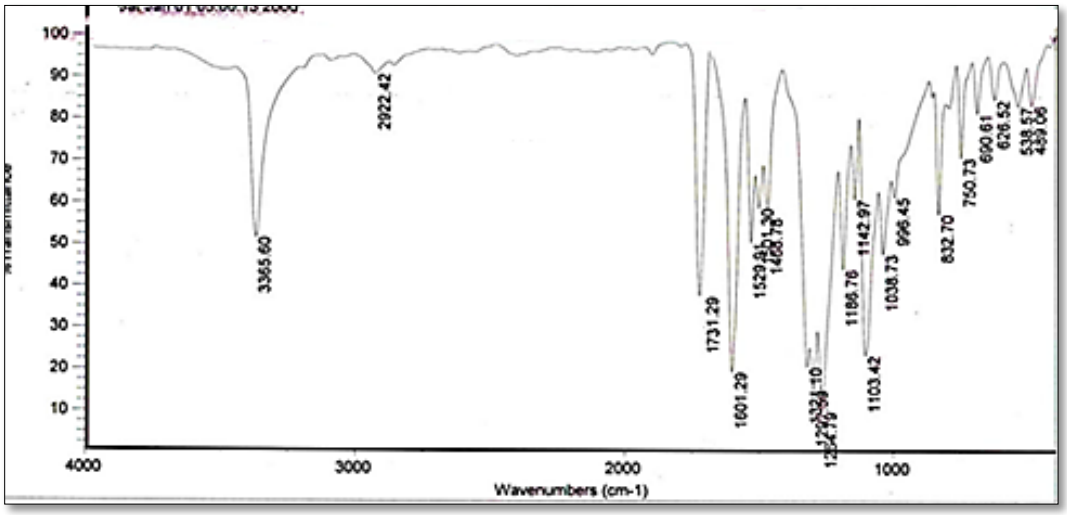


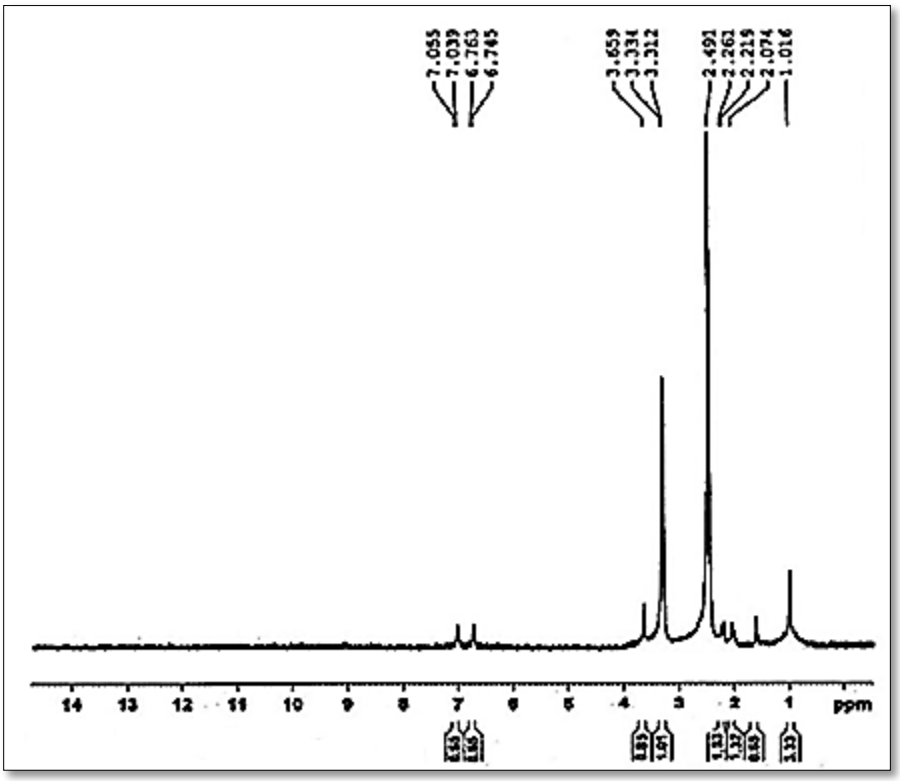
(15-(4-Methoxyphenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 6)



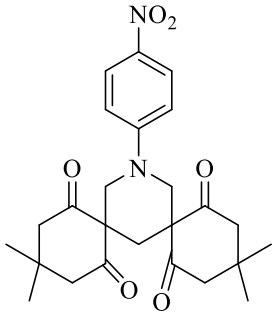
(15-(4-Methoxyphenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone Compound **6a** (table 2, Entry 6) mp: 188–190 ºC; FTIR (KBr) ῡ: 3030, 2922, 1731, 1601-1468, 1350, 1264, 1038, 1264 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.05 (2H, d, ^{3}J =6.4 Hz,

ArH), 6.75 (2H, d, ^{3}J =7.2 Hz, ArH), 3.66 (4H, s, CH_2), 3.33 (3H, s, OCH_3), 2.23 (4H, d, 2 J =17.2 Hz, CH_2), 2.07 (4H, d, ^{2}J =17.2 Hz, CH_2), 1.72 (2H, s, CH_2),1.00 (12H, s, CH_3).

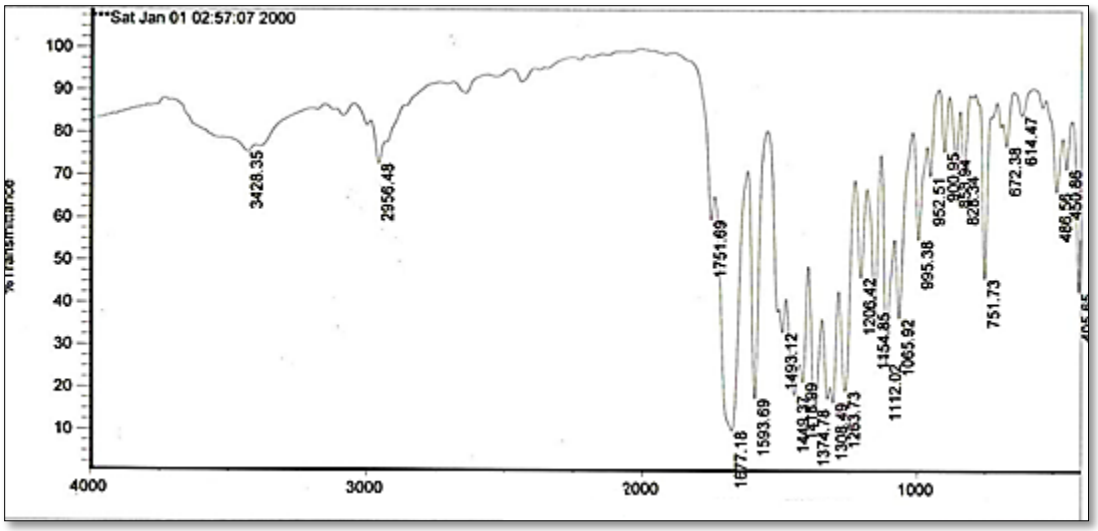


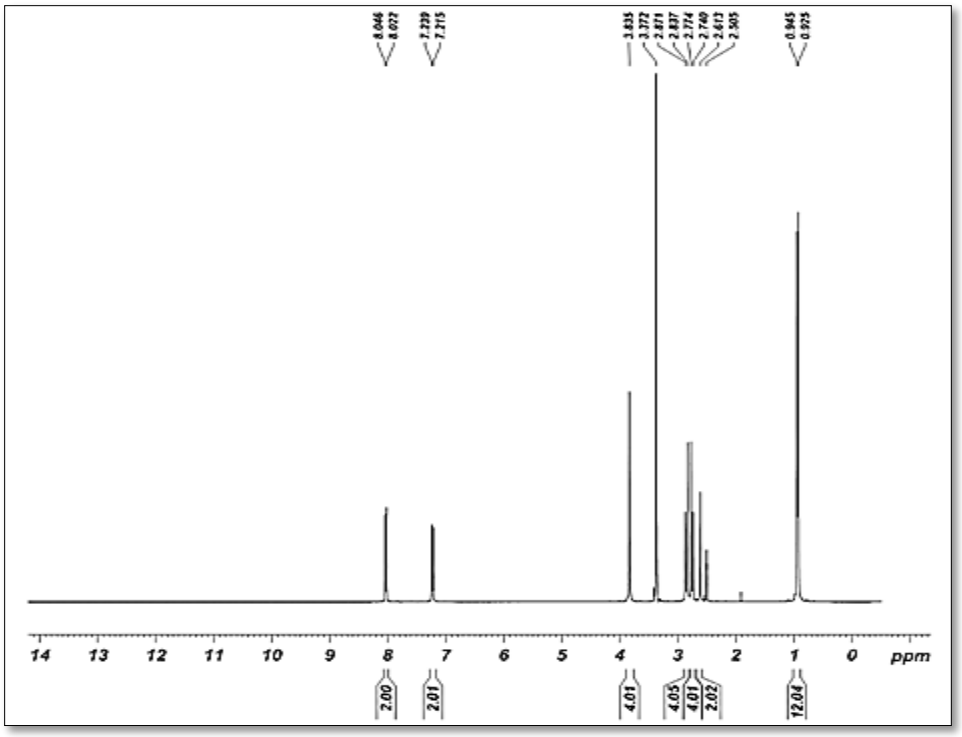


(15-(4-Nitrophenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 7)

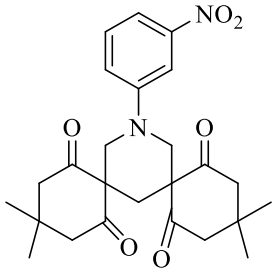


(15-(4-Nitrophenyl)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone Compound **7a** (table 2, Entry 7) mp: 220-222 ºC; FTIR (KBr) ῡ: 1263, 1374, 1593, 1677-1418, 1751, 2956, 3030 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 8.03 (2H, d, ^3J =9.6 Hz, ArH), 7.22 (2H, d, ^3J =9.6 Hz, ArH), 3.83 (4H, s, NCH_2), 2.85 (4H, d, ^2J =13.6 Hz, $COCH_2$), 2.75 (4H, d, ^2J =13.6 Hz, $COCH_2$), 2.61 (2H, s, CH_2), 0.94 (6H, s, CH_3),0.92 (6H, s, CH_3).



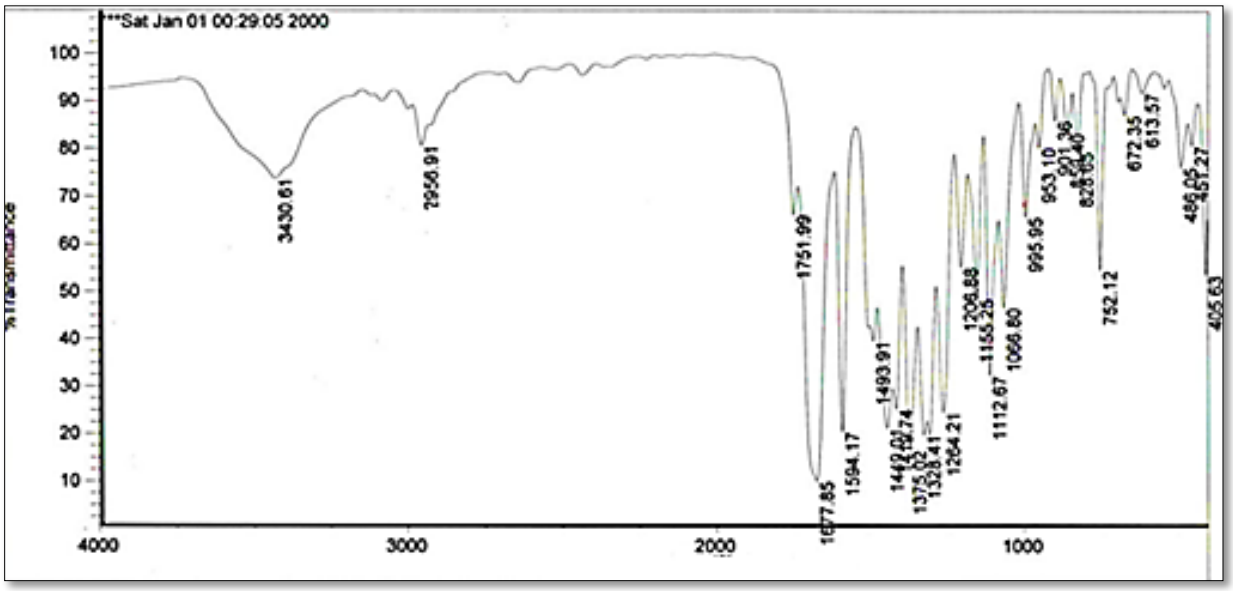


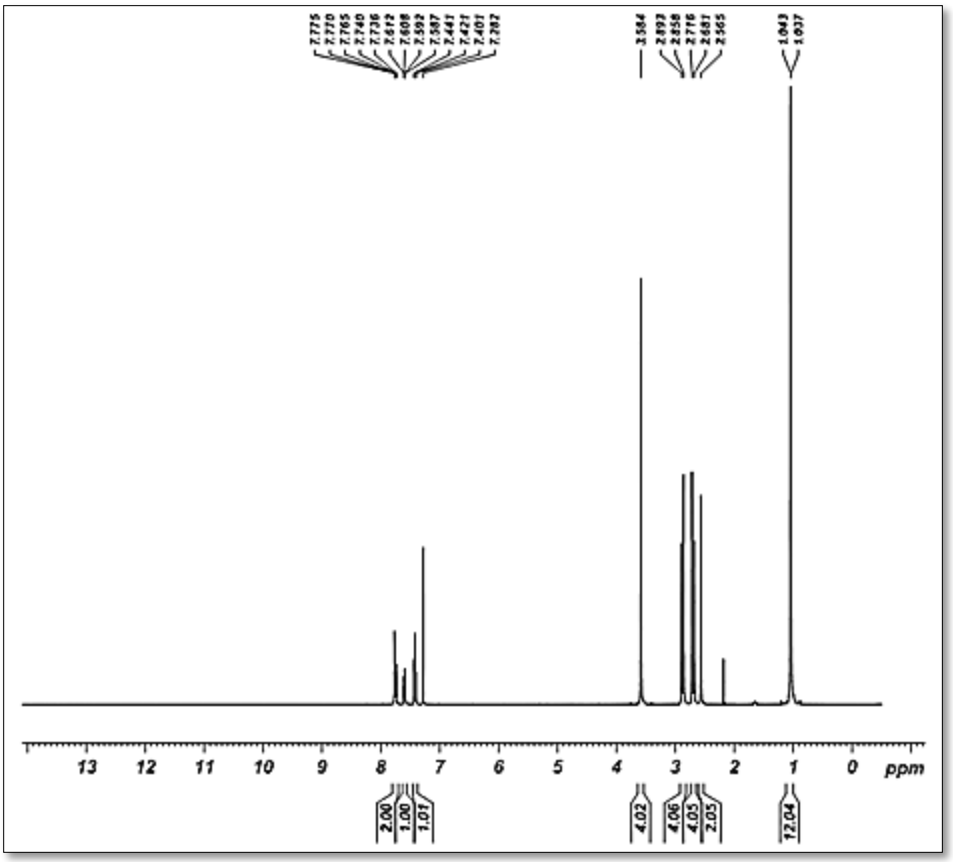
(15-(3-Nitrophenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 8)



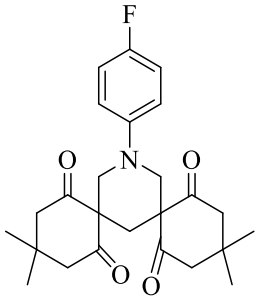
(15-(3-Nitrophenyl)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone Compound **8a** (table 2, Entry 8) mp: 186–188 ºC; FTIR (KBr) ῡ: 1264, 1375, 1594, 1677-1449,

1751, 2956, 3030 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.75 (1H, dd, ^3J =8.2, 2.0, ArH), 7.59 (1H, dd, ^3J =8.2, 2.0 Hz, ArH), 7.42 (1H, t, ^3J =8.0 Hz, ArH), 3.57 (4H, s, NCH_2), 2.87 (4H, d, ^2J =14.0 Hz, $COCH_2$), 2.69 (4H, d, ^2J =14.0 Hz, $COCH_2$), 2.56 (2H, s, CH_2), 1.04 (6H, s, CH_3), 1.03 (6H, s, CH_3).

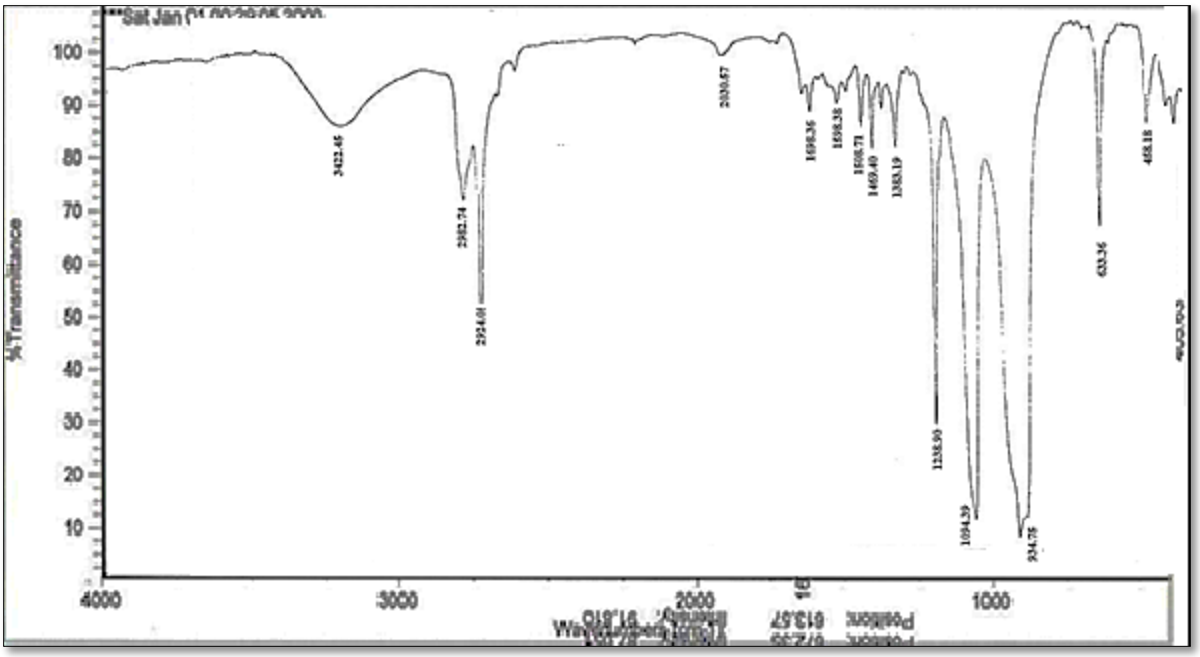


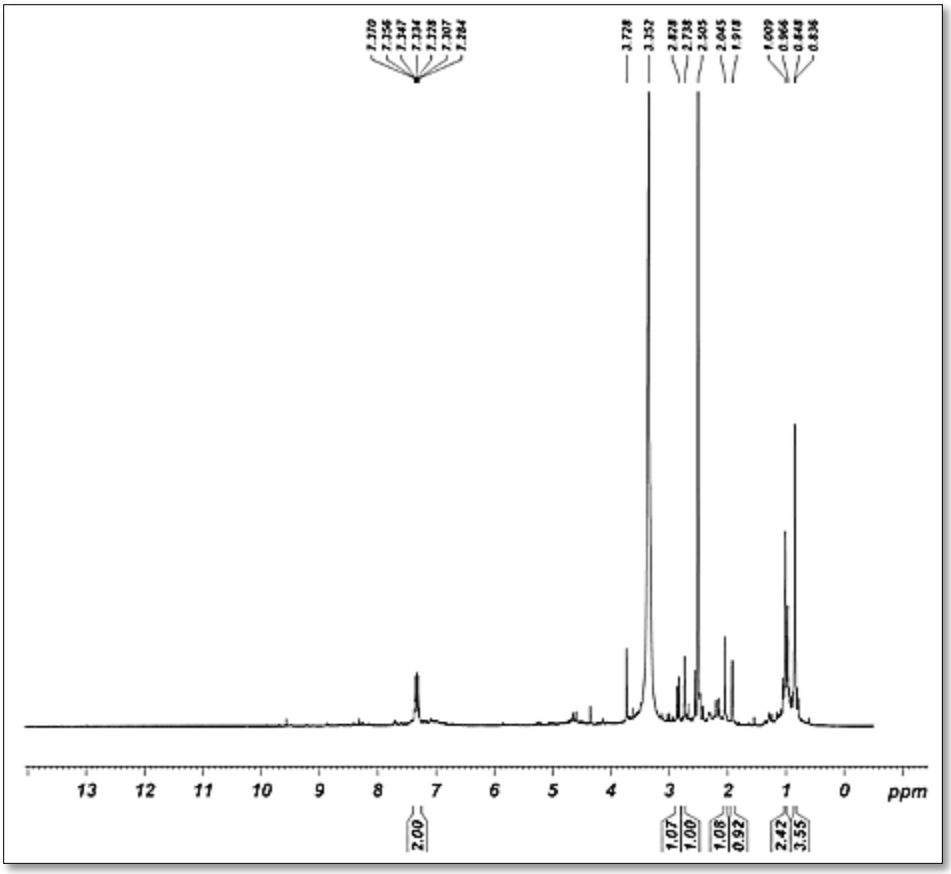


(15-(4-Fluorine)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 9)

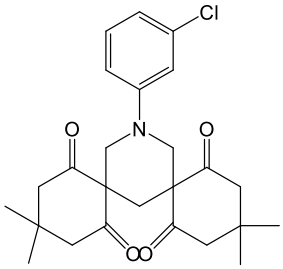


(15-(4-Fluorine)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone Compound **9a** (table 2, Entry 9) mp: 140–142 ºC; FTIR (KBr) ῡ: 1094, 1238, 1381, 1598-1469, 1698, 2924 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, δ ppm): 7.28-7.37 (4H, m, ArH), 3.35 (4H, s, NCH_2), 2.82 (4H, s, $COCH_2$), 2.73 (4H, s, $COCH_2$), 2.04 (2H, s, CH_2), 1.00 (6H, s, CH_3),0.96 (6H, s, CH_3).

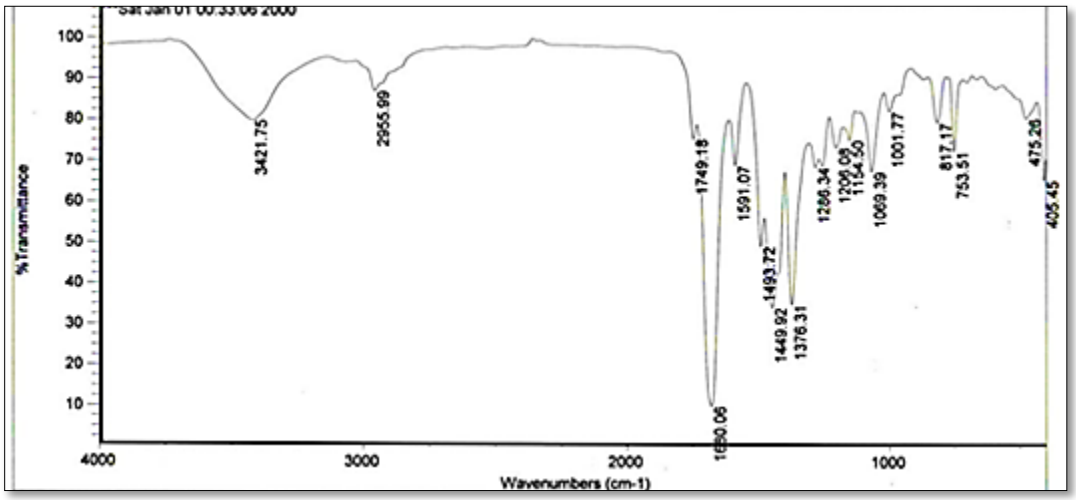

%Transmittance
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10
4000
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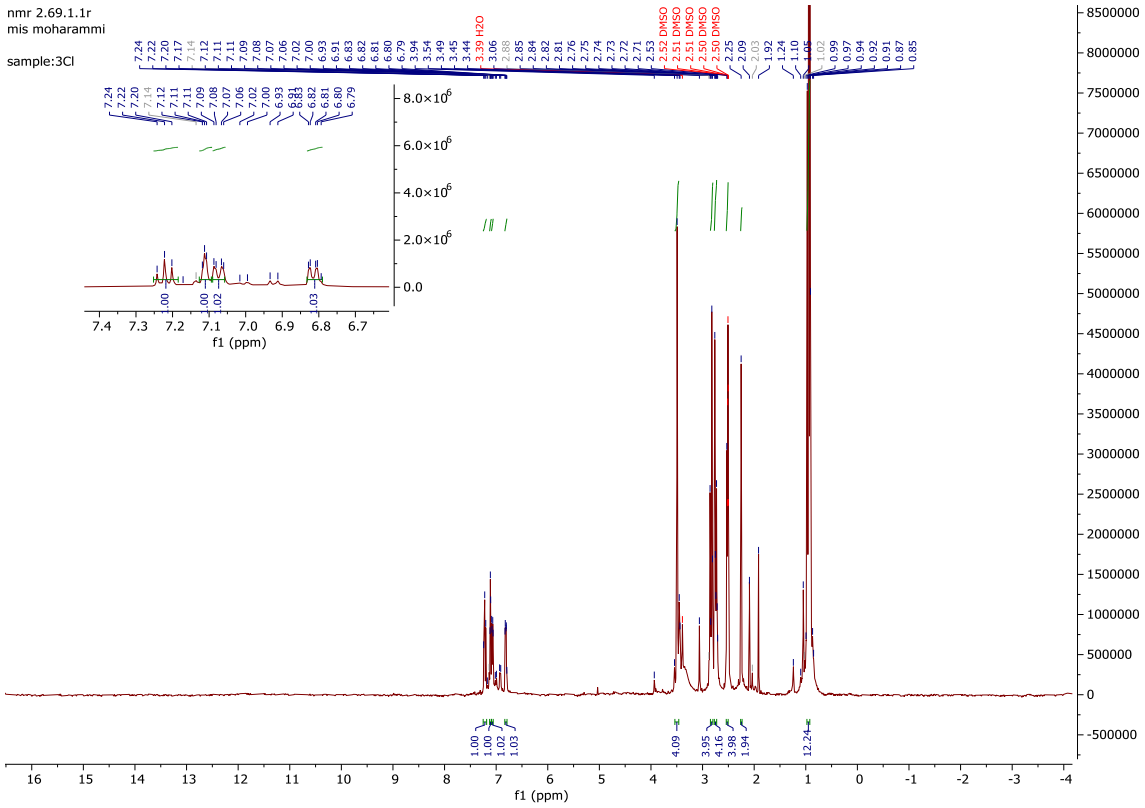

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7.347
7.334
7.328
7.307
7.284
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3.352
2.828
2.758
2.505
2.045
1.918
1.009
0.966
0.848
0.836
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.07
1.00
1.08
0.92
2.42
3.55

(15-(3- Chlorophenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 9)

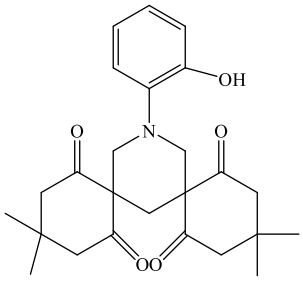


(15-(3-Chlorophenyl)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,1-tetrone Compound **10a** (table 2, Entry 10) mp: 189–191 ºC; FTIR (KBr) ῡ: 1264, 1375, 1594, 1677-1449, 1751, 2956, 3030 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.86 (1H, s, ArH), 7.59 (1H, t, ^3J =8.0 Hz, ArH), 7.48 (1H, t, ^3J =8.0 Hz, ArH), 3.62 (4H, s, NCH_2), 2.87 (4H, d, ^2J =14.0 Hz, $COCH_2$), 2.69 (4H, d, ^2J =14.0 Hz, $COCH_2$), 2.59 (2H, s, CH_2), 0.96 (12H, s, CH_3).

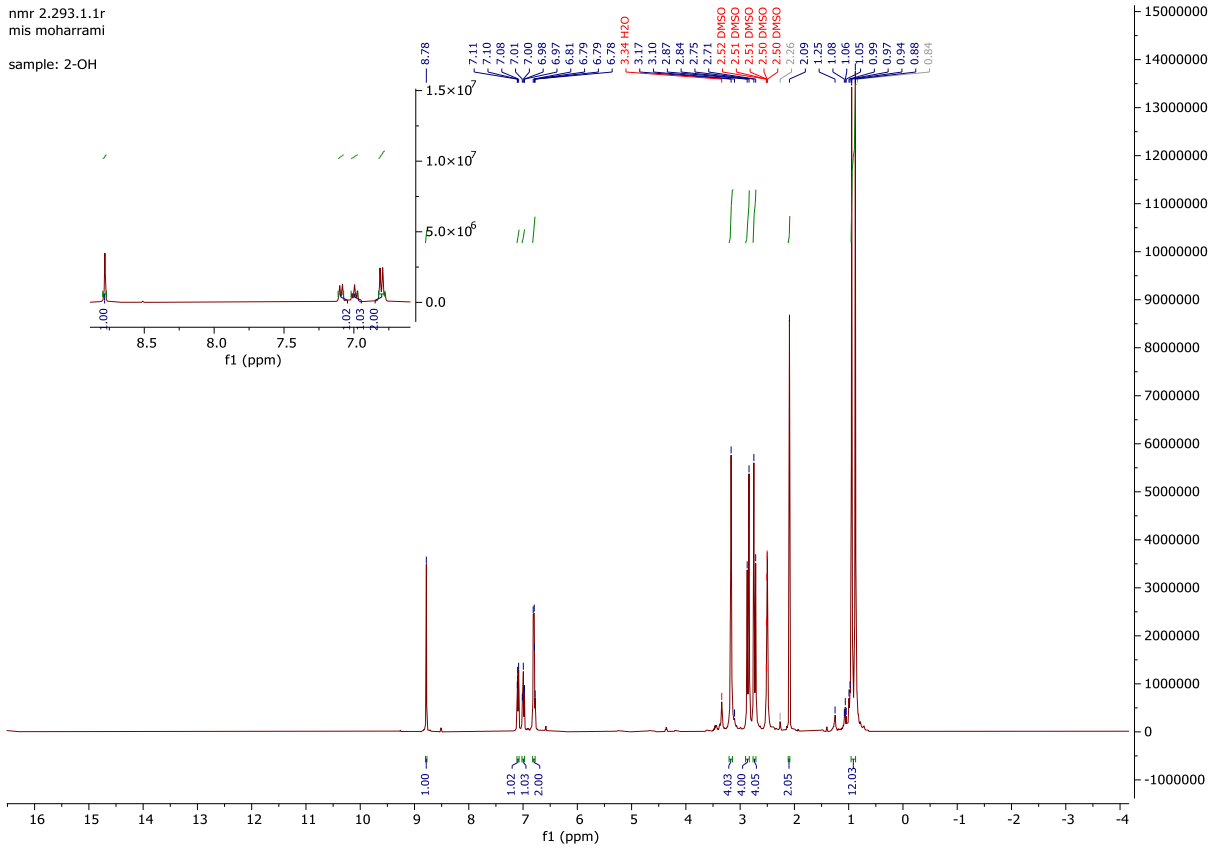




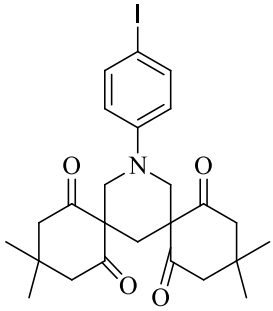
(15-(2-Hydroxyphenyl)-3,3,11,11-tetramethyl-15–azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 12)



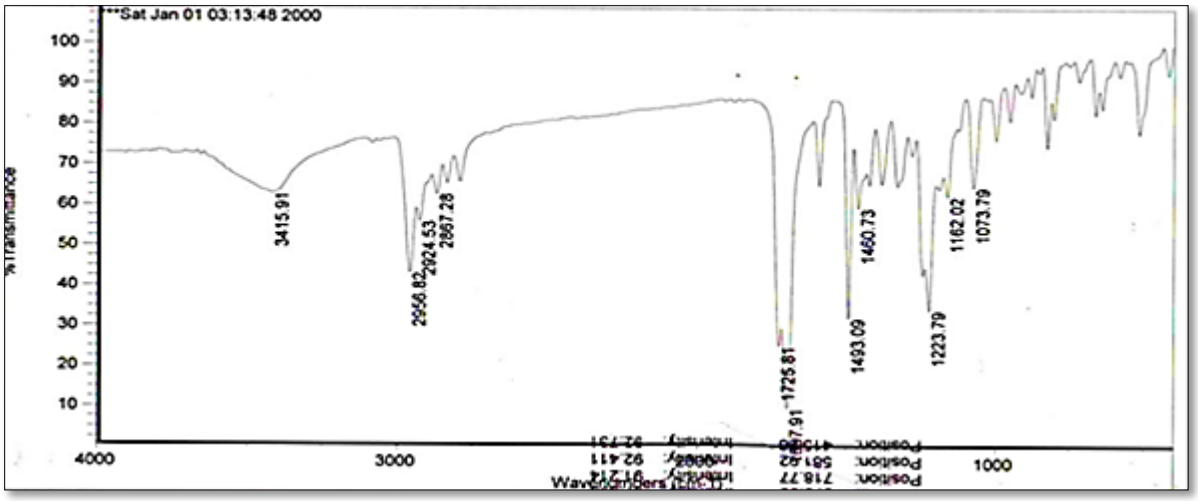
Compound **11a** (table 2, Entry 11) mp: 189–191 ºC; FTIR (KBr) ῡ: 1264, 1375, 1594, 1677-1449, 1751, 2956, 3030 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.86 (1H, s, OH), 7.86 (1H, d, ArH), 7.59 (1H, d, ^{3}J =8.0 Hz, ArH), 7.48 (2H, t, ^{3}J =8.0 Hz, ArH), 3.62 (4H, s, NCH_2), 2.87 (4H, d, ^{2}J =14.0 Hz, $COCH_2$), 2.69 (4H, d, 2 J =14.0 Hz, $COCH_2$), 2.59 (2H, s, CH_2), 0.96 (12H, s, CH_3).

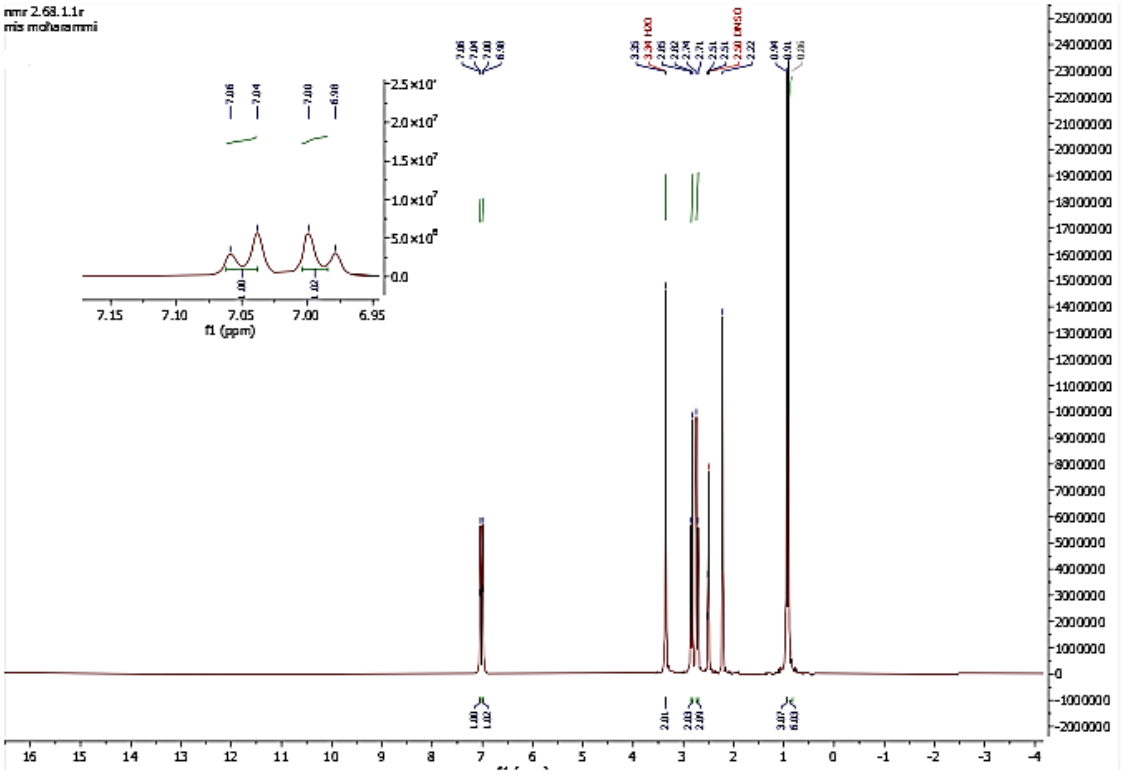


(15-(4-Iodophenyl)-3,3,11,11-tetramethyl-15-azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 12)



(15-(4- Iodien)-3,3,11,11-tetramethyl-15– azadispiro[5.1.5.3]hexadecne-1,5,9,13-tetrone (table 4, Entry 1) mp: 208-209 ºC; FTIR (KBr) ῡ: 1073, 1223, 1375, 1600-1460, 1725, 2924, 3039 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm) 7.05 (d, J = 8.2 Hz, 1H), 7.00 (s, 1H), 3.35 (s, 2H), 2.82 (s, 2H), 2.72 (d, J = 13.5 Hz, 2H), 0.94 (s, 3H), 0.91 (s, 6H).


**Sat Jan 01 03:13:48 2000
%Transmittance
3415.91
2956.82
2924.53
2867.28
1725.81
1493.09
1460.73
1223.79
1162.02
1073.79
4000
3000
1000


nmr 2.68.1.1r
mis mohesammi
f1 (ppm)