Introduction of a trinuclear catalyst manganese on the surface of magnetic cellulose as an eco-benign, efficient and reusable novel heterogeneous catalyst for the multi-component synthesis of new derivatives of Xanthene

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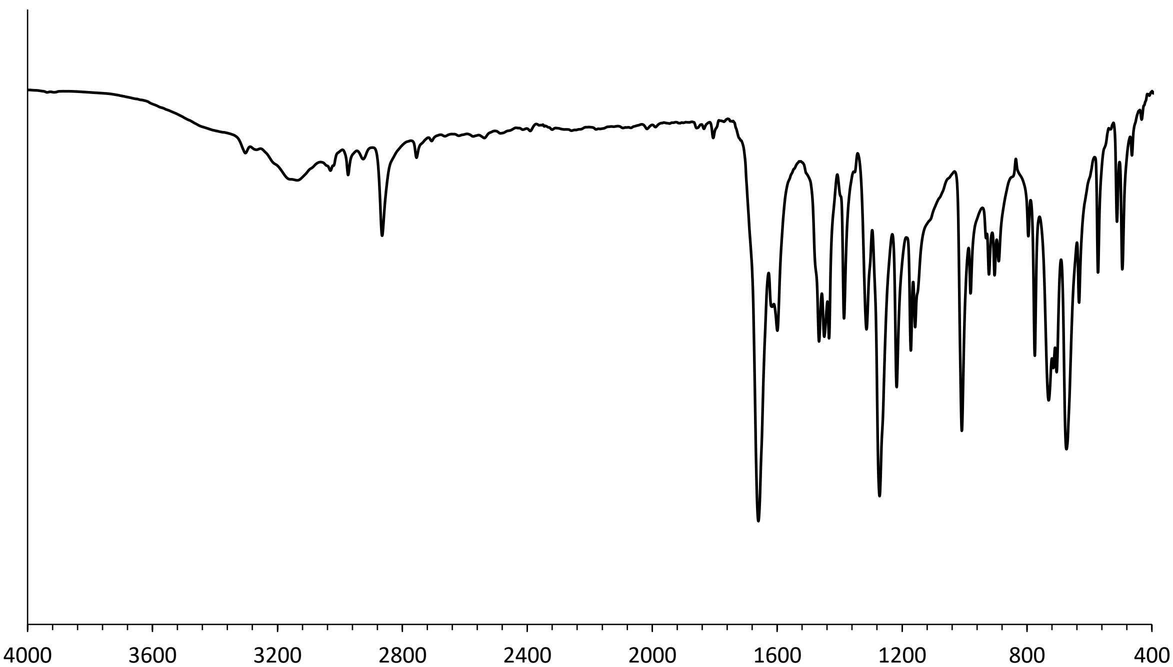
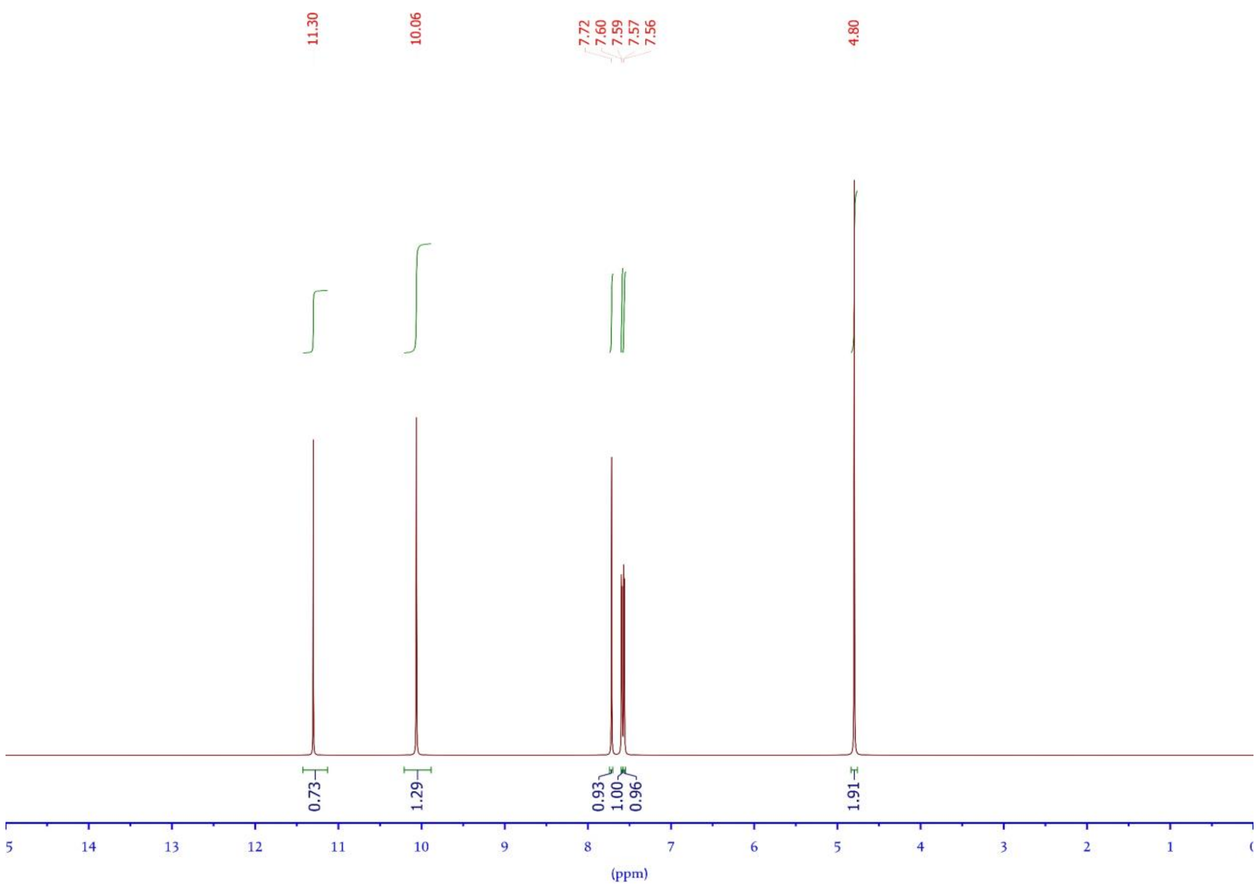
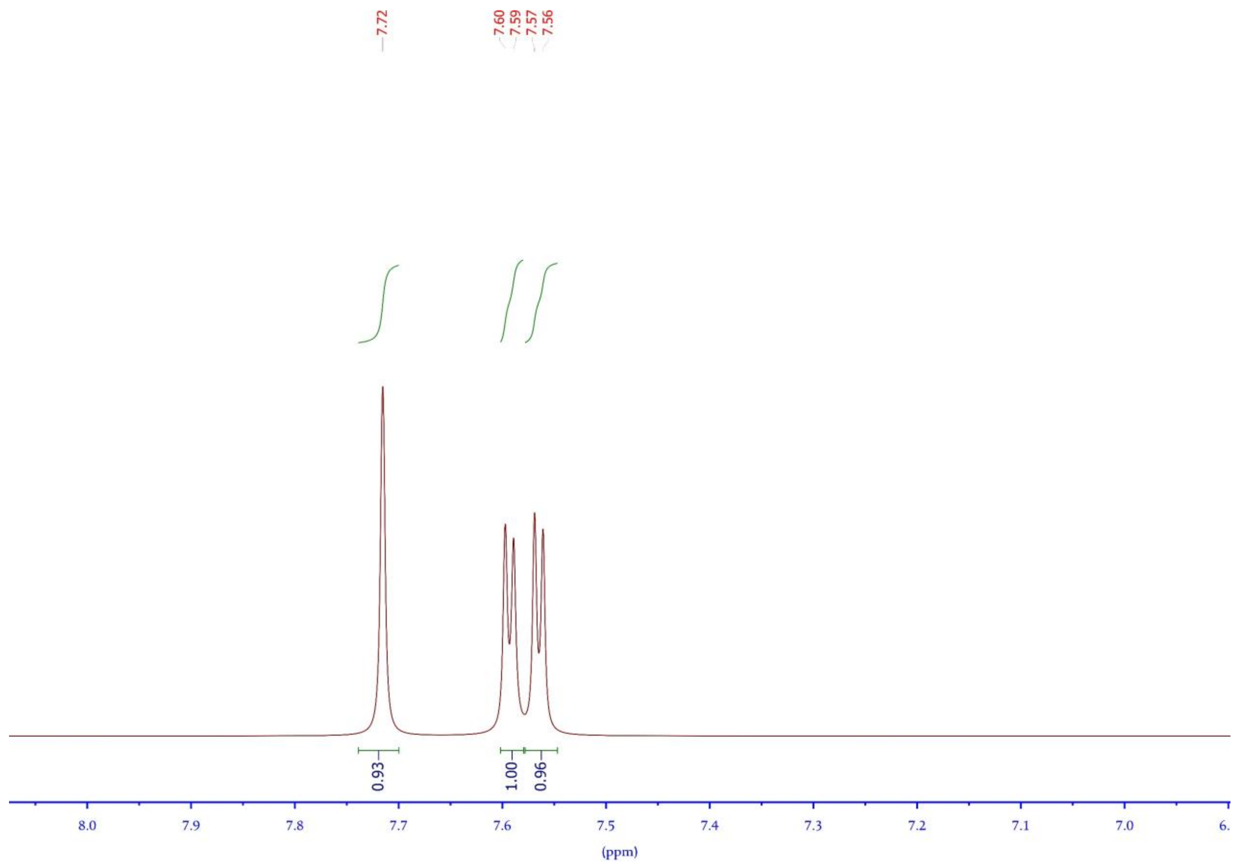
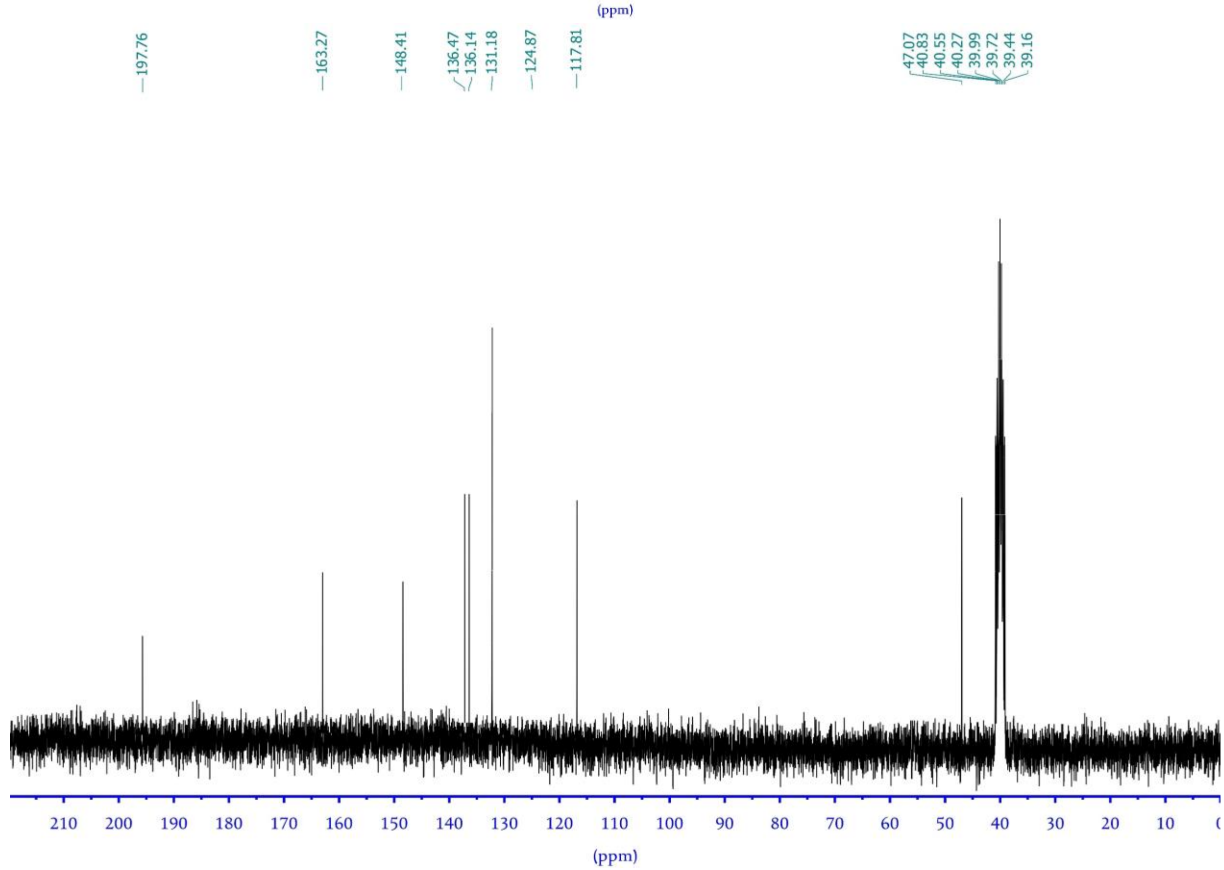
b. Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran.

5-(chloromethyl)-2-hydroxybenz aldehyde (IV)






7.72
7.60
7.59
7.57
7.56
0.93
1.00
0.96
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
(ppm)


197.76
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136.47
136.14
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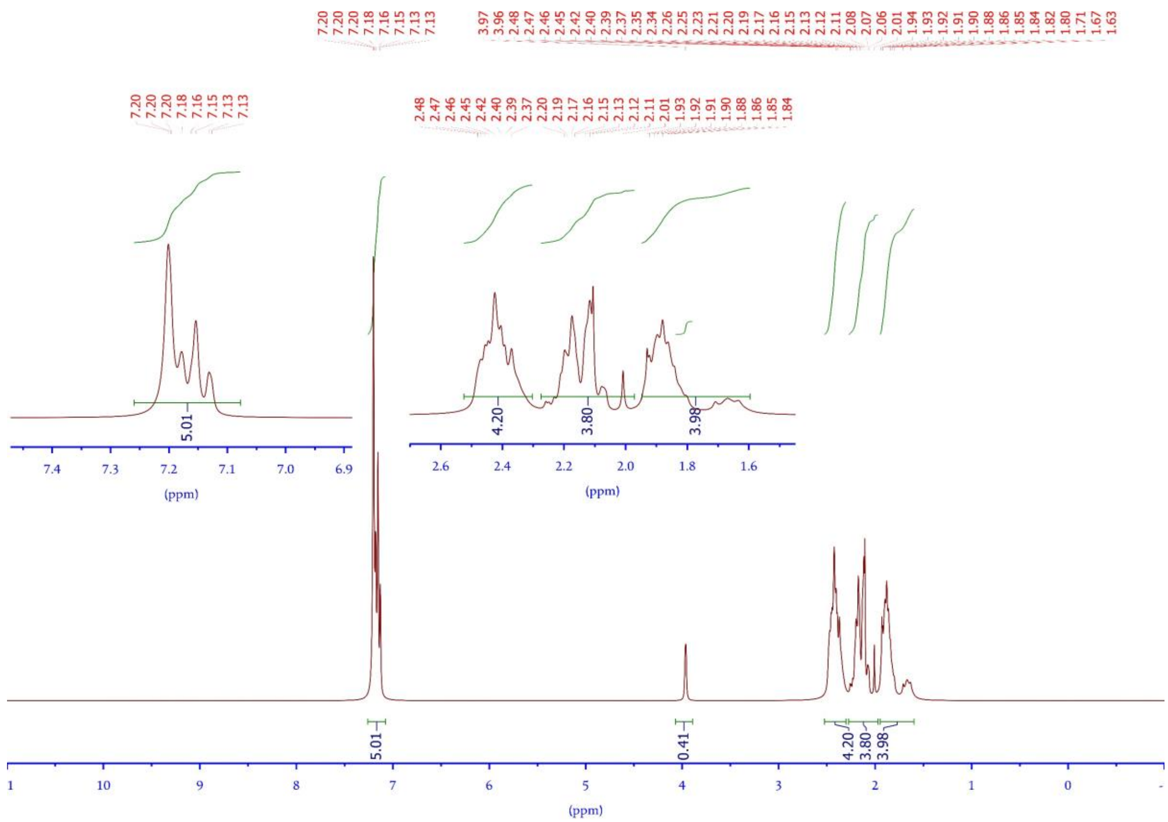
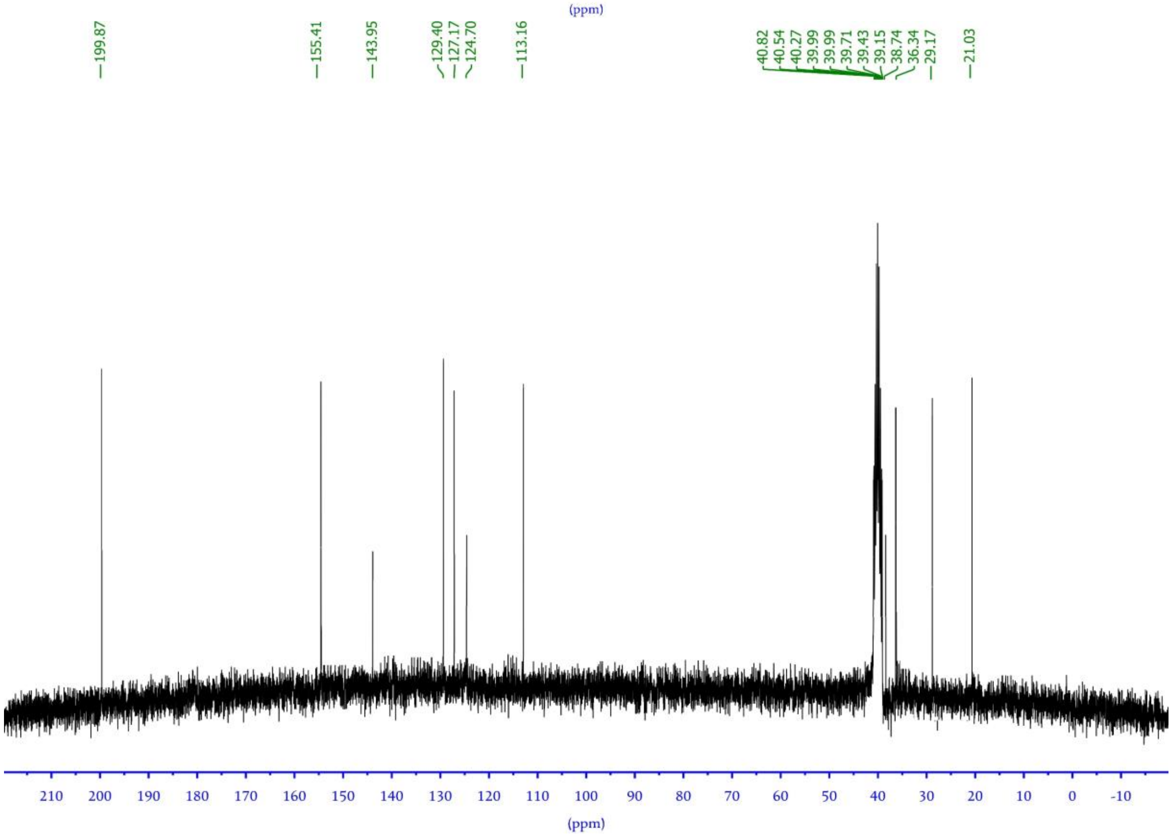
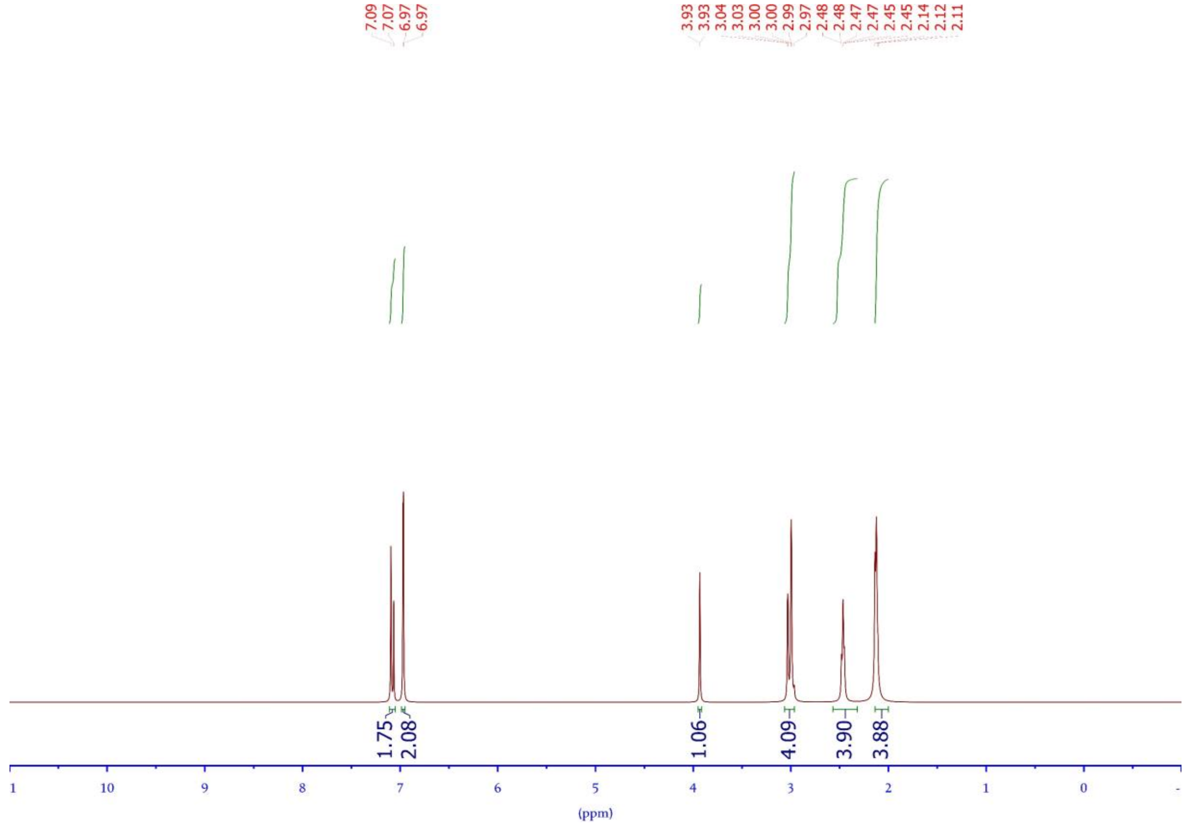
117.81
47.07
40.83
40.55
40.27
39.99
39.72
39.44
39.16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

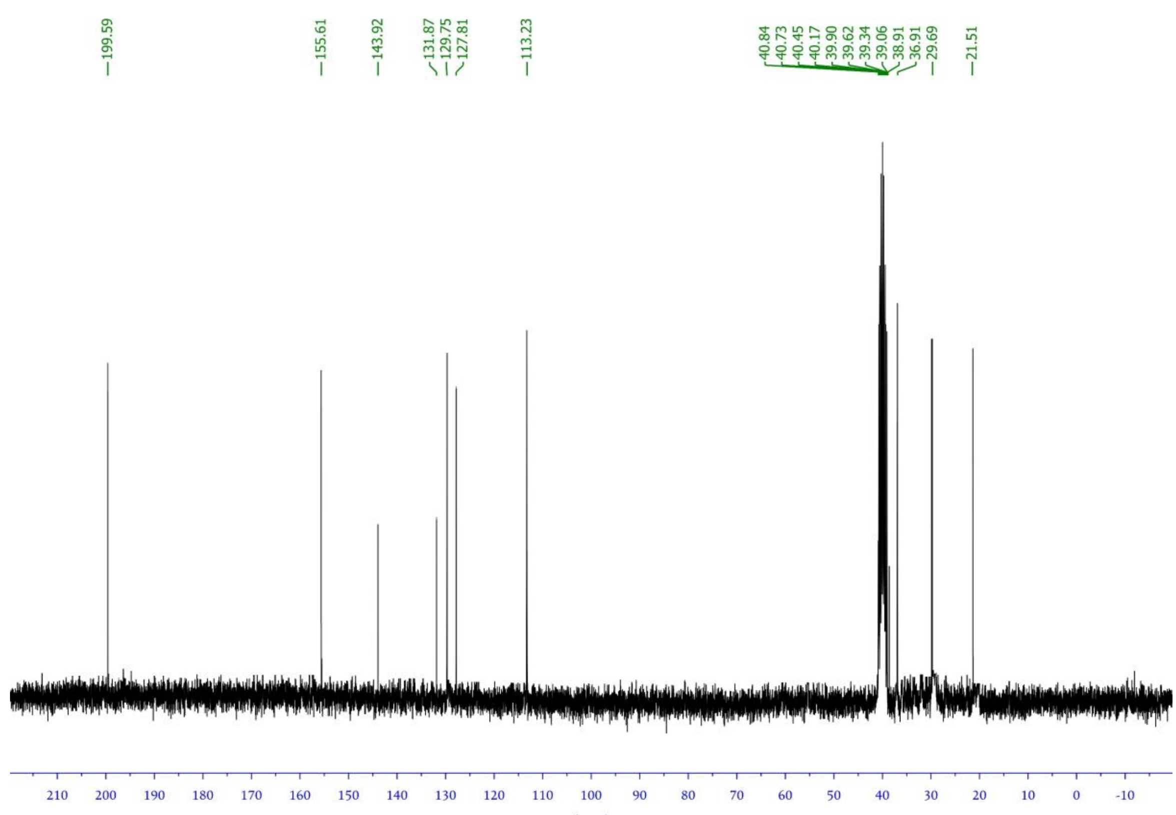
9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 1)



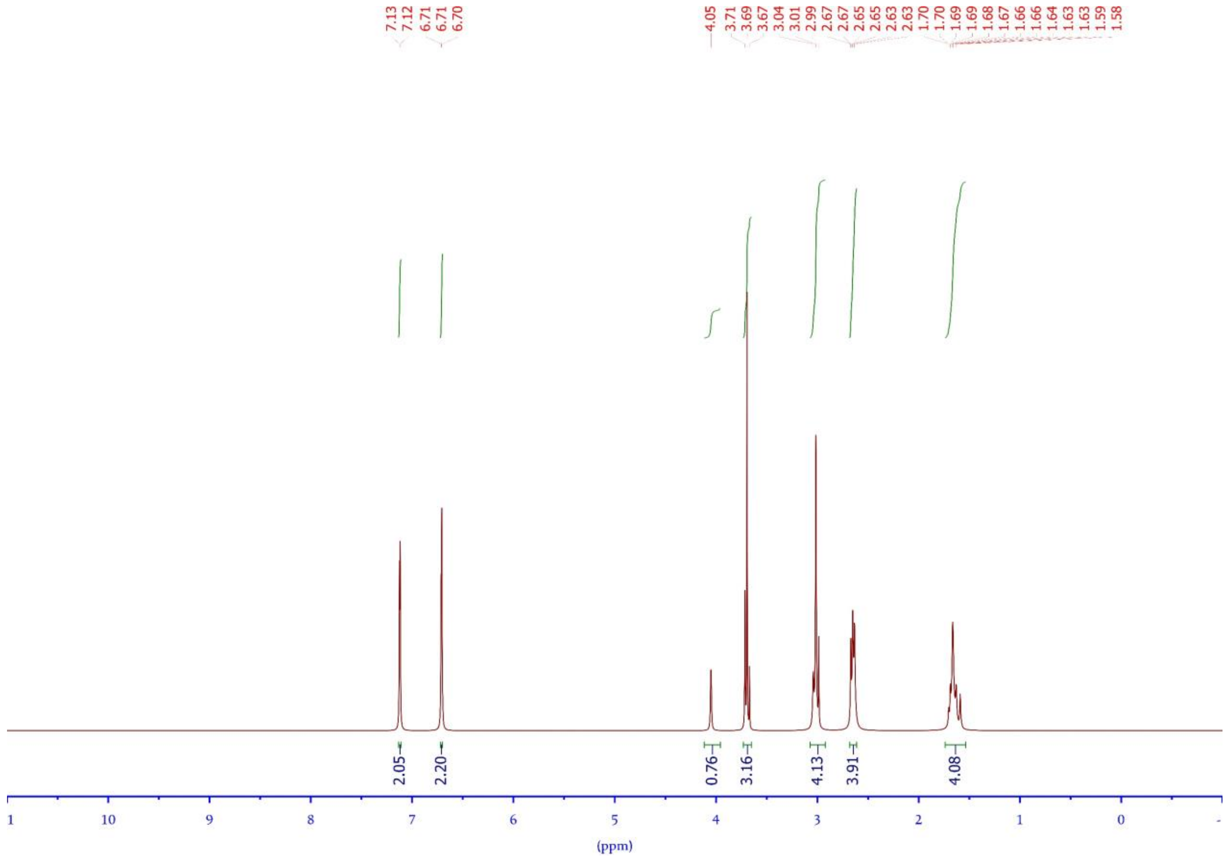


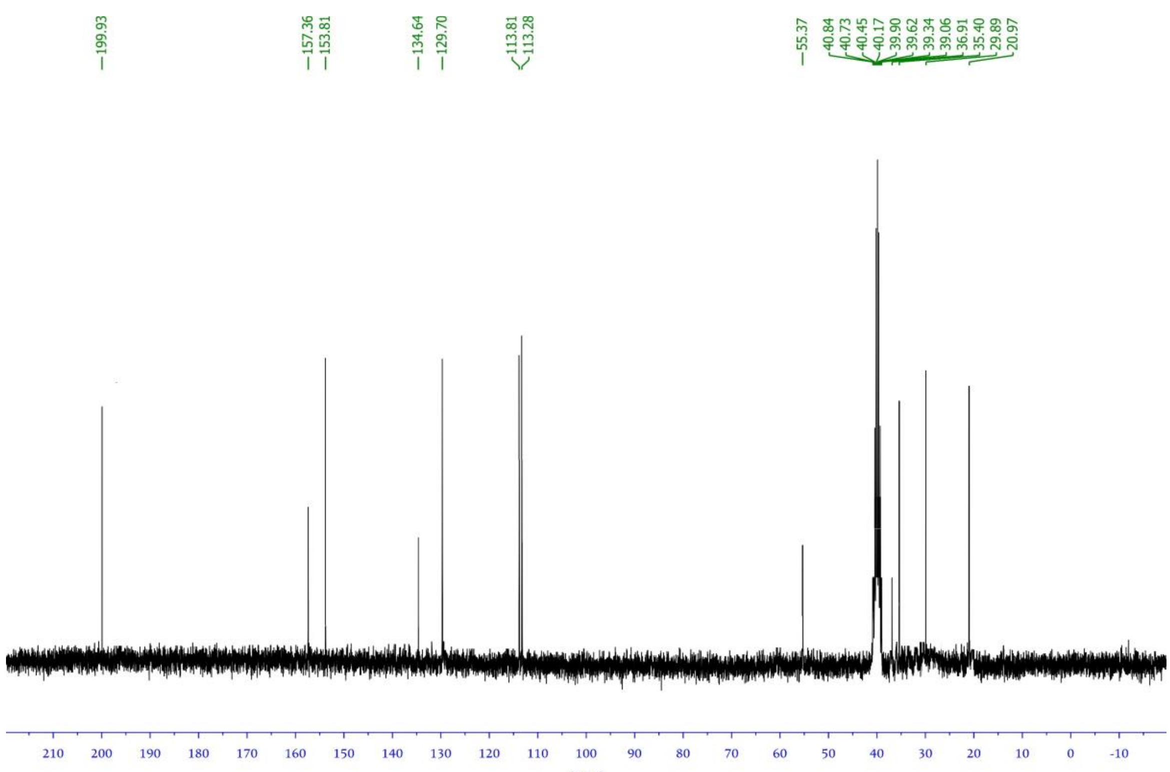
9-(4-chlorophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 2)



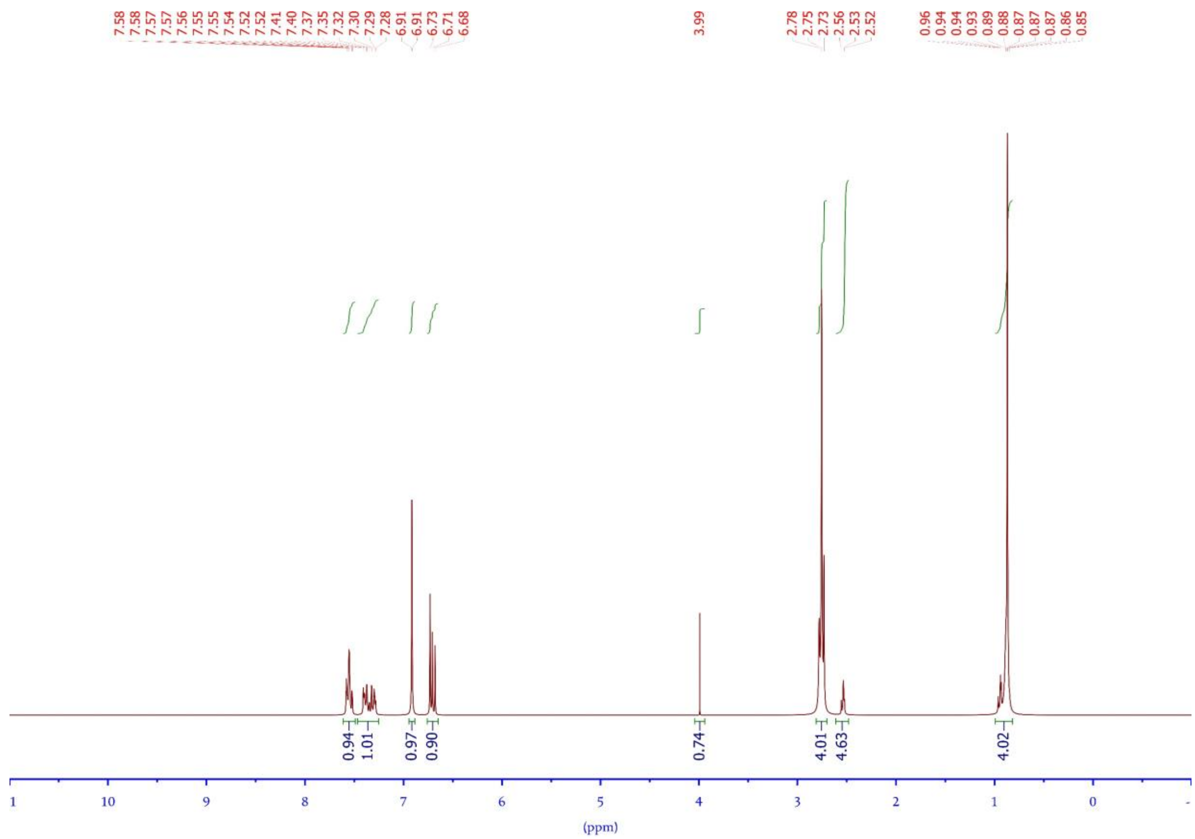


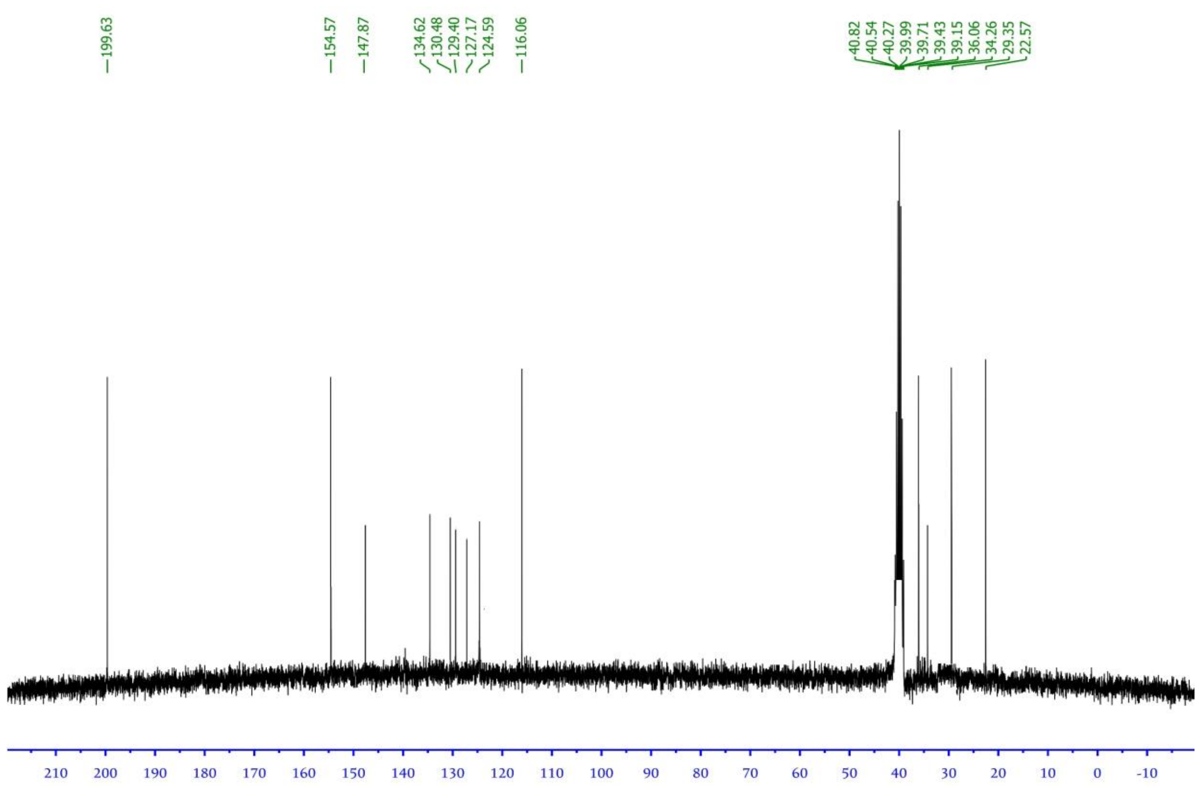
9-(4-methoxyphenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 3)



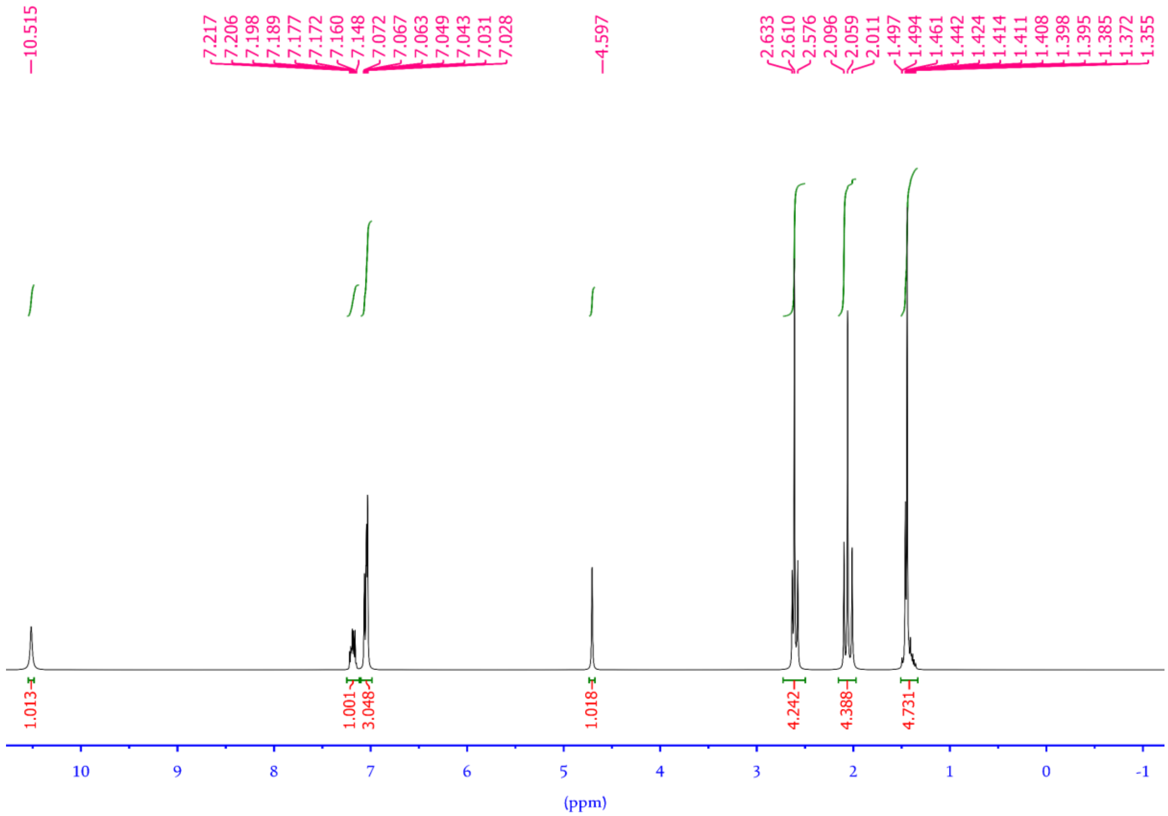


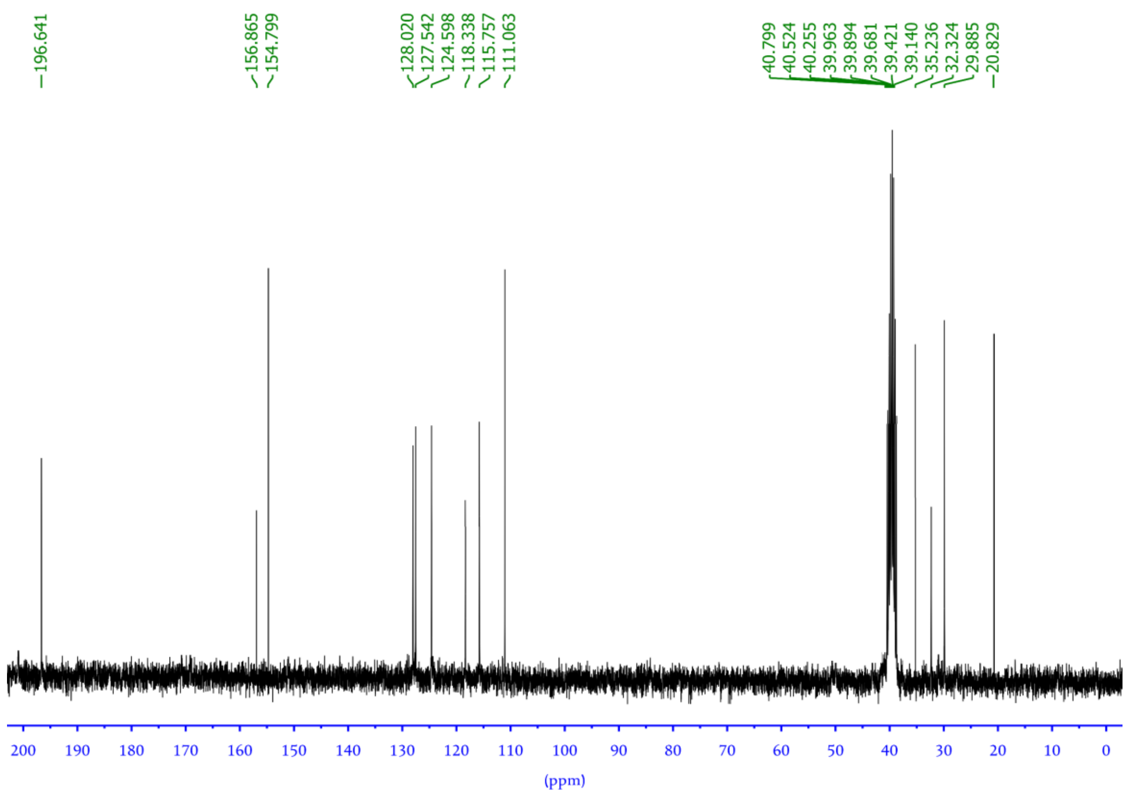
9-(2-nitrophenyl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 4)



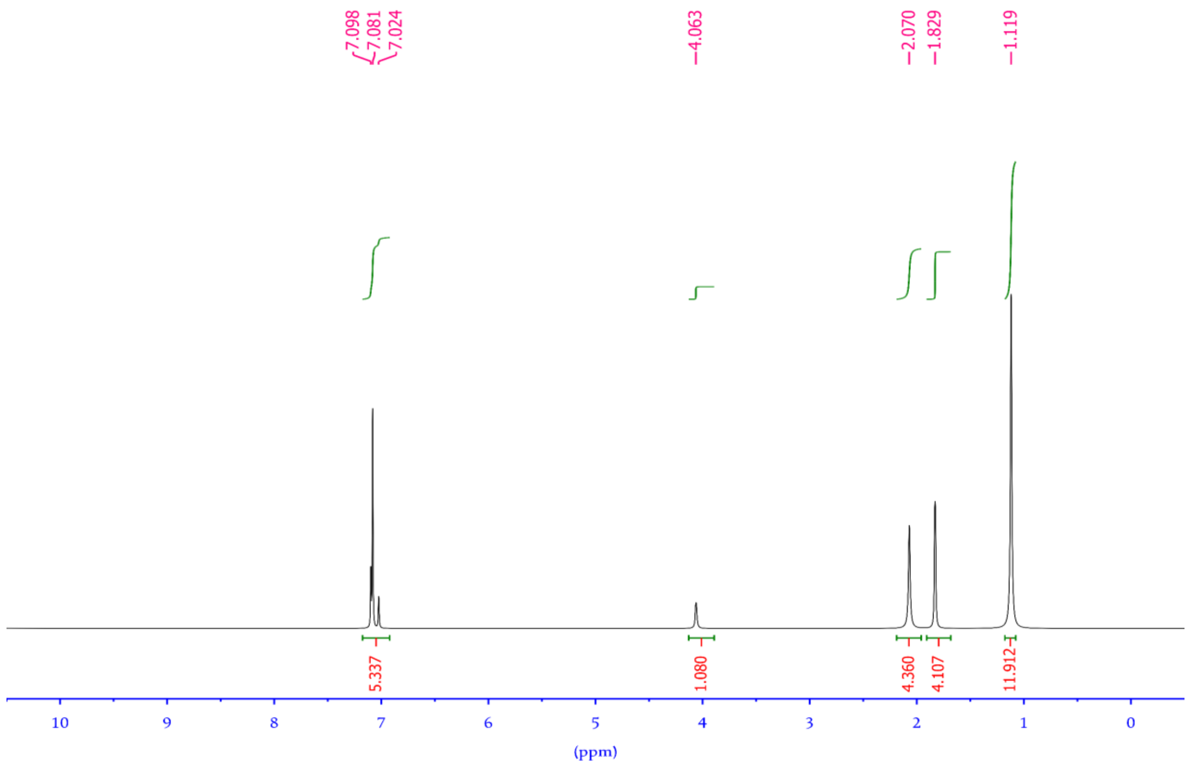


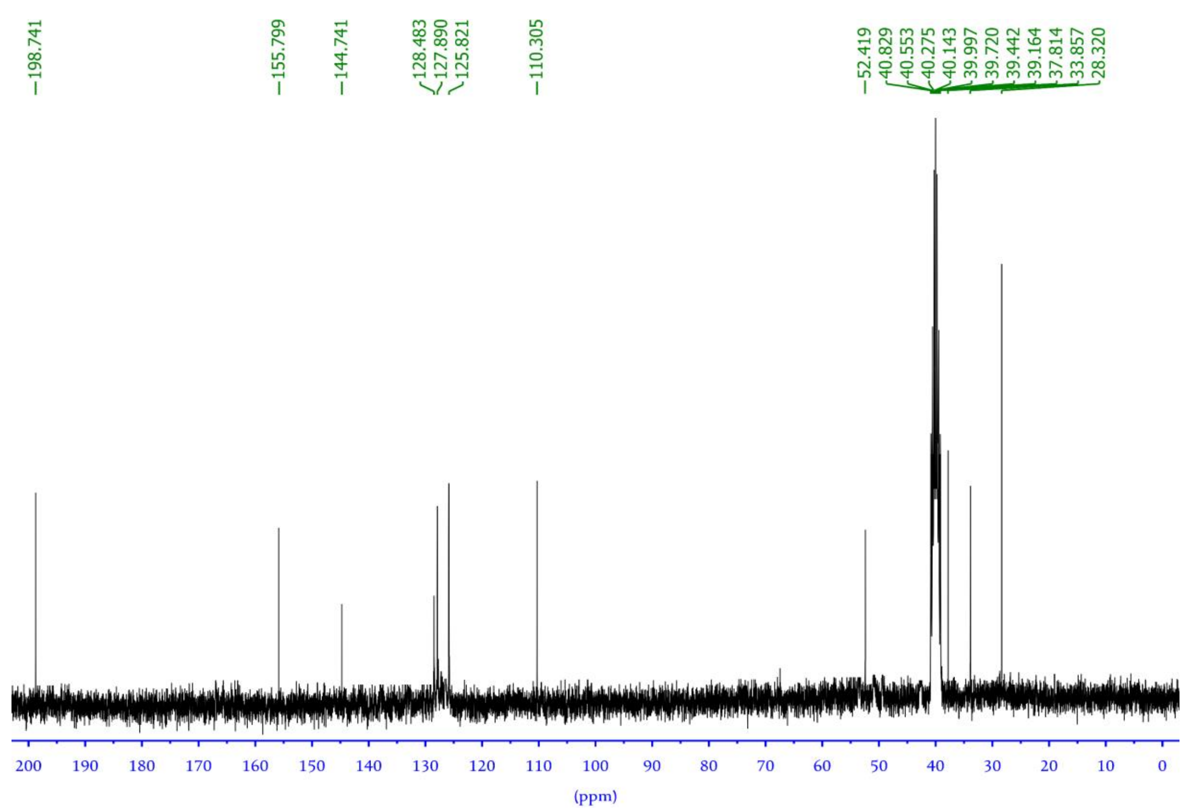
9-(2-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 5)



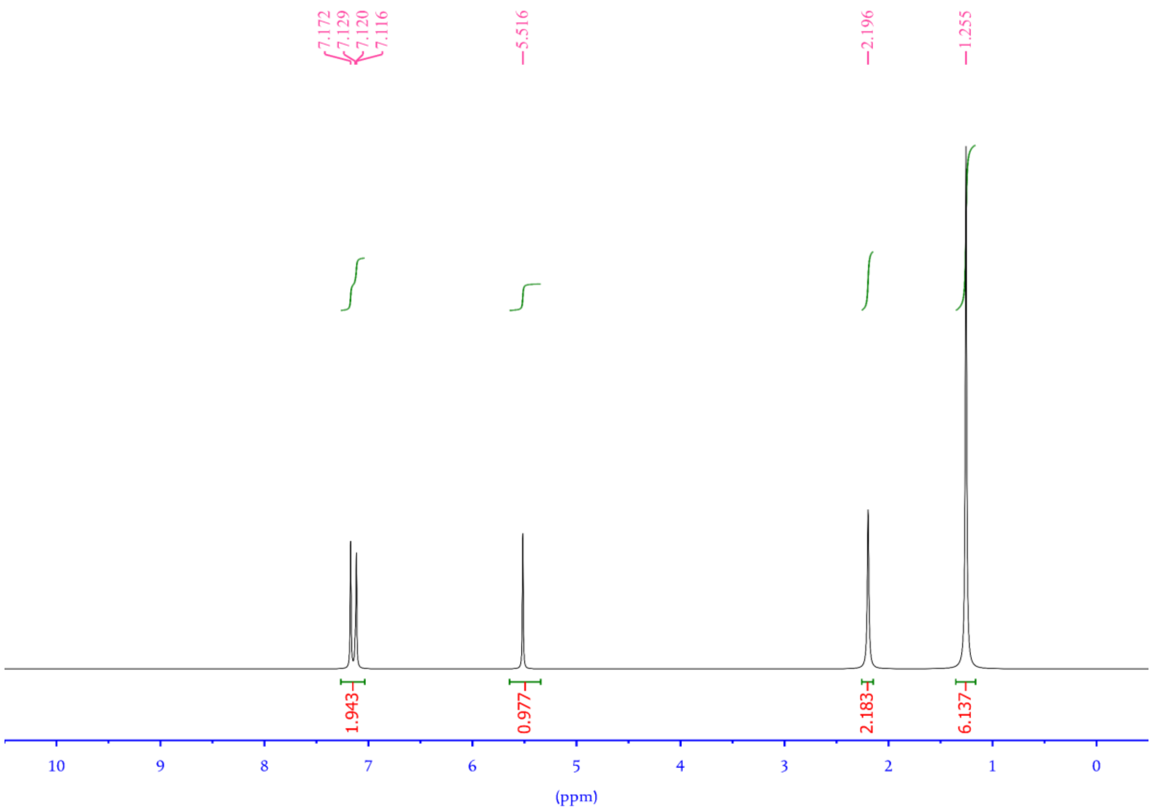


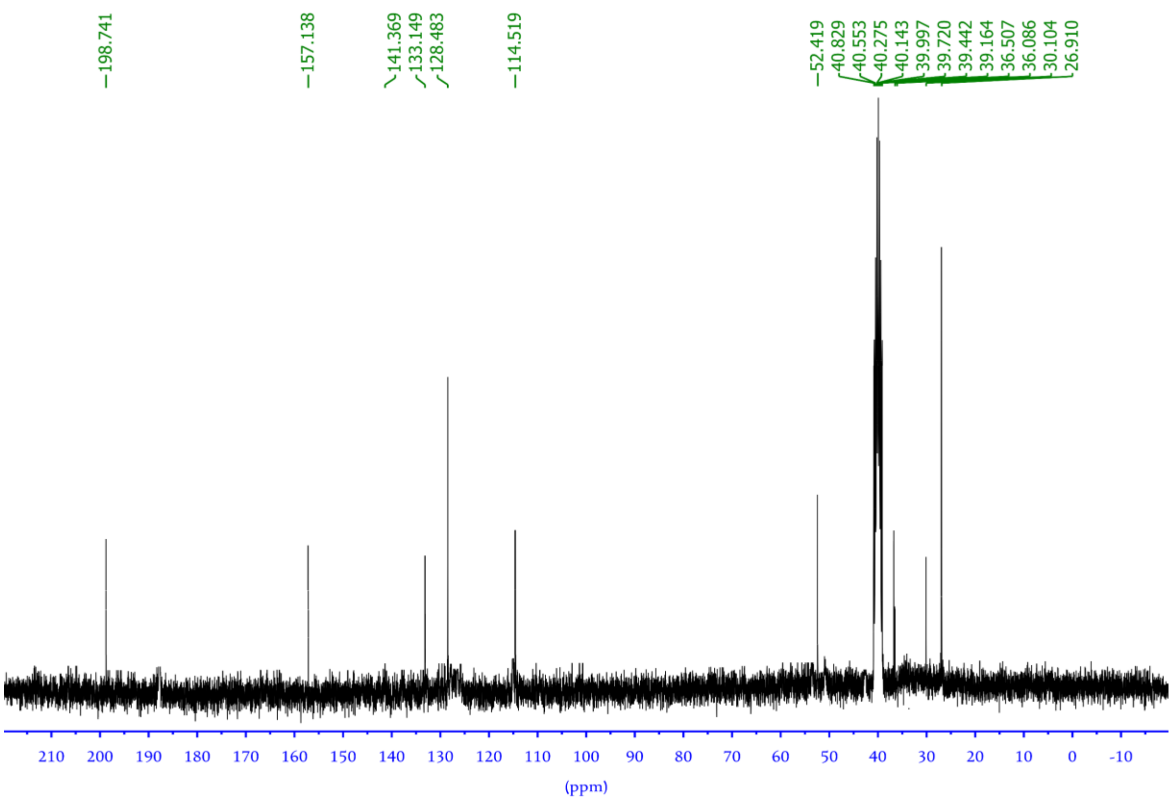
3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 6)



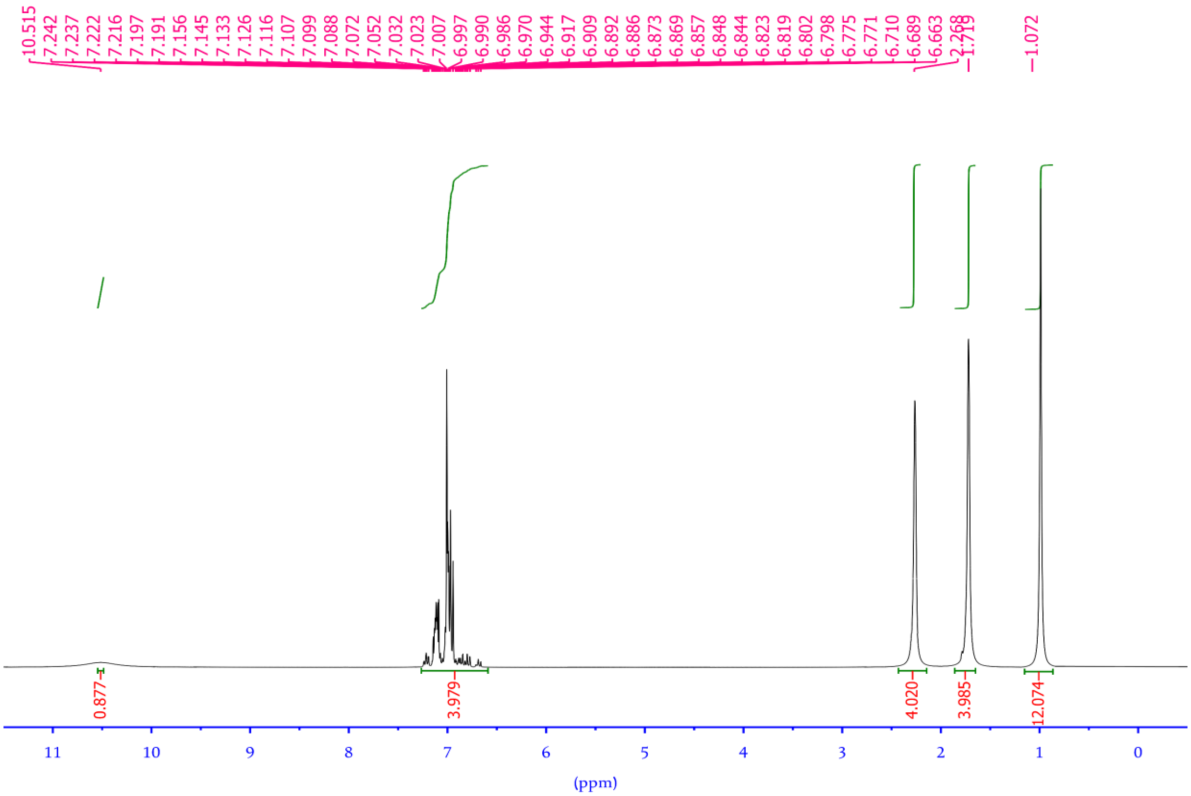


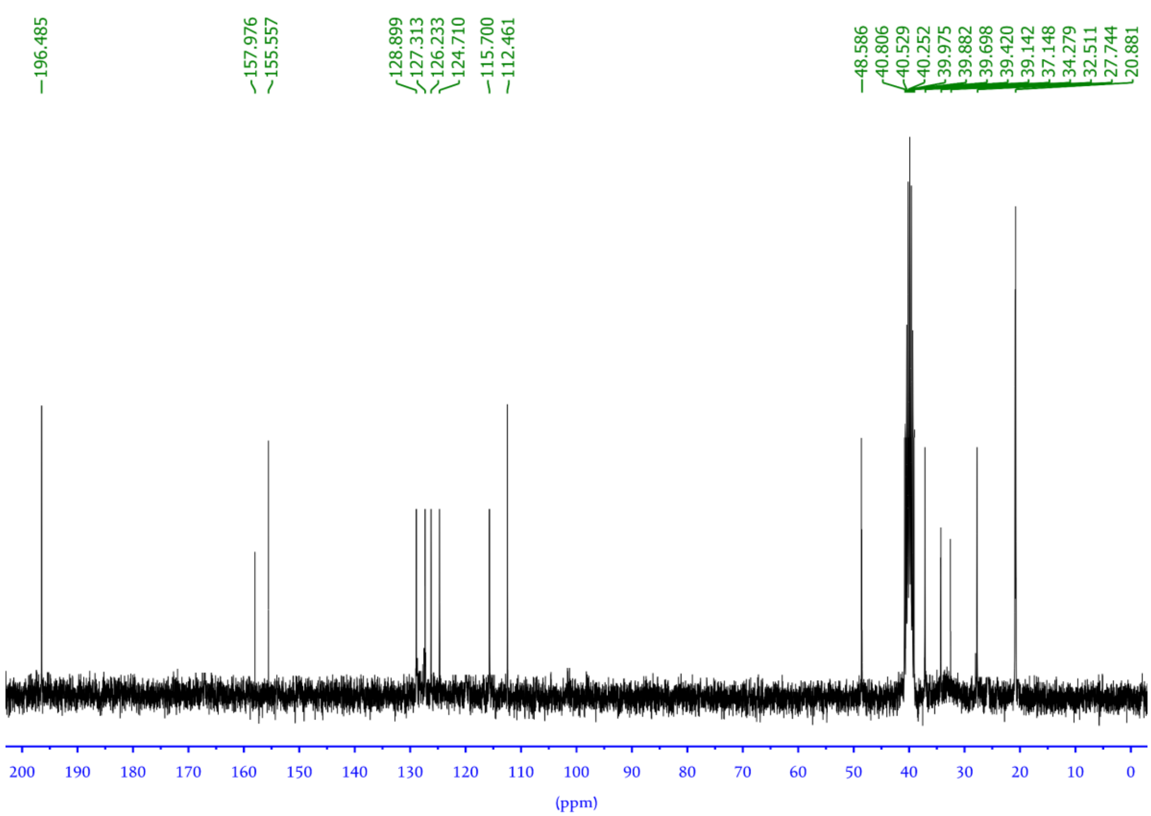
9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 7)



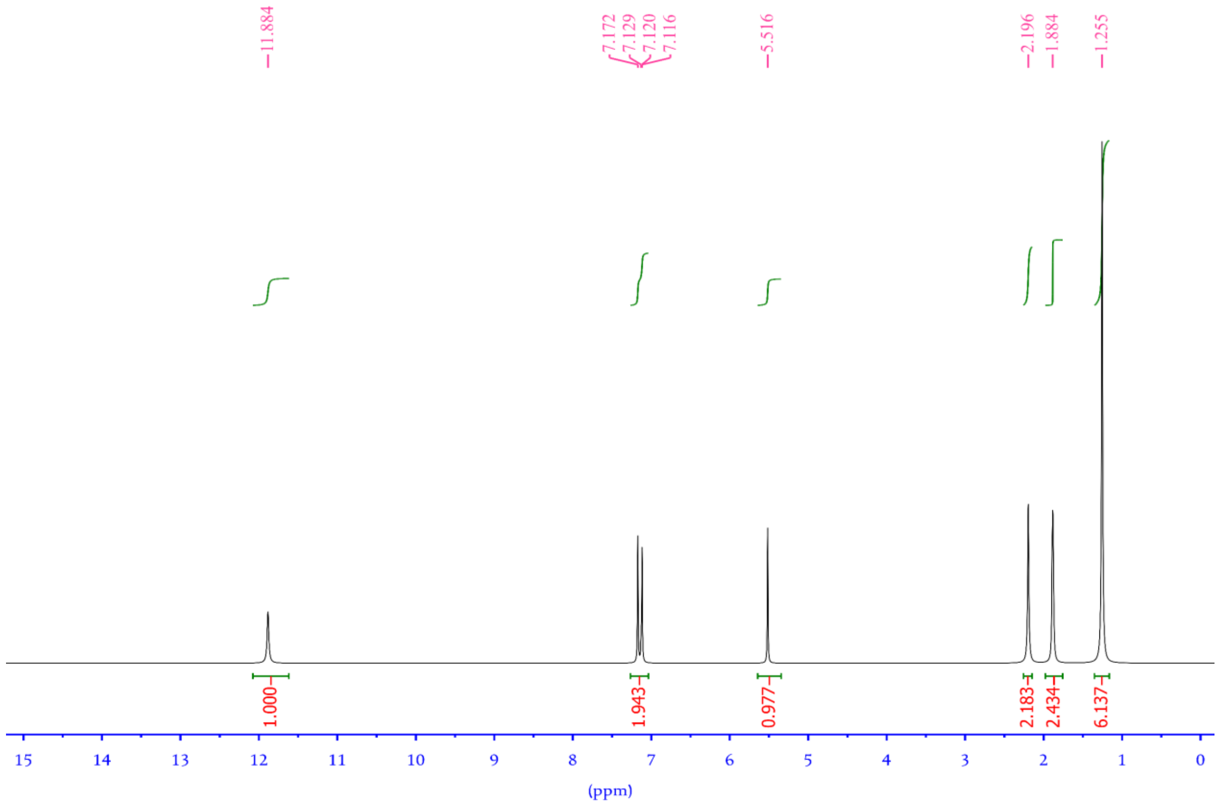


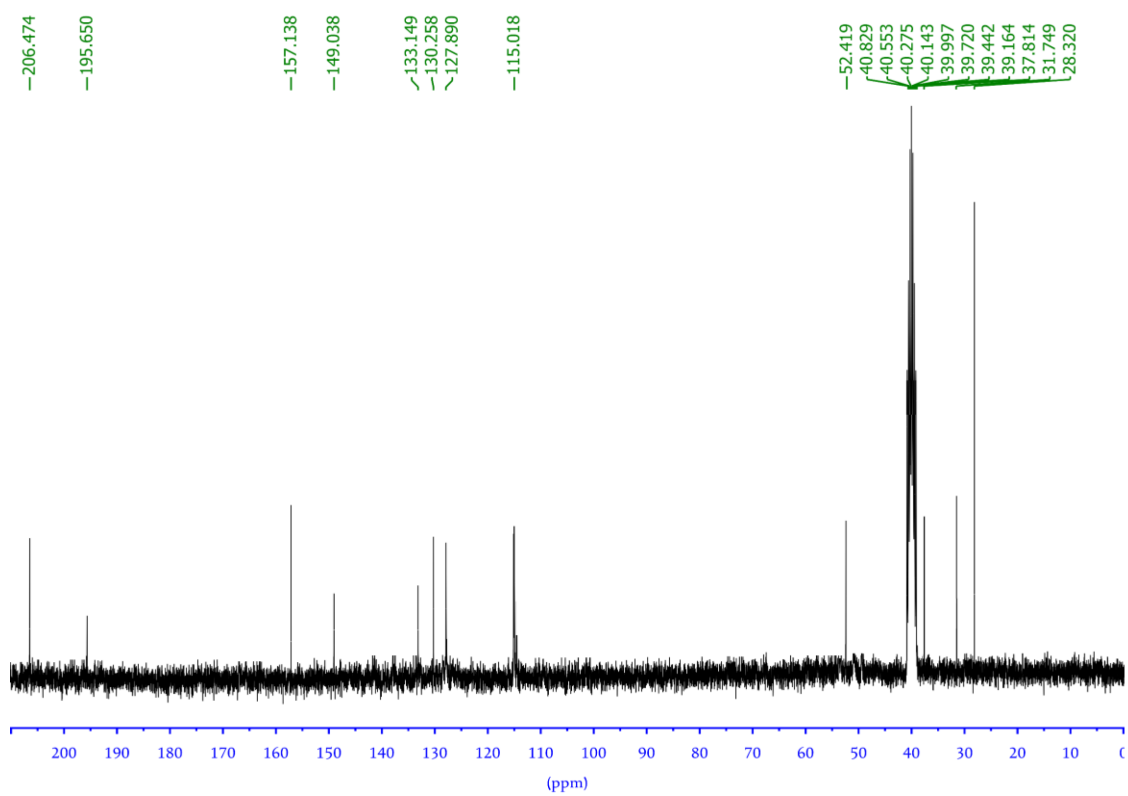
9-(2-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 8)



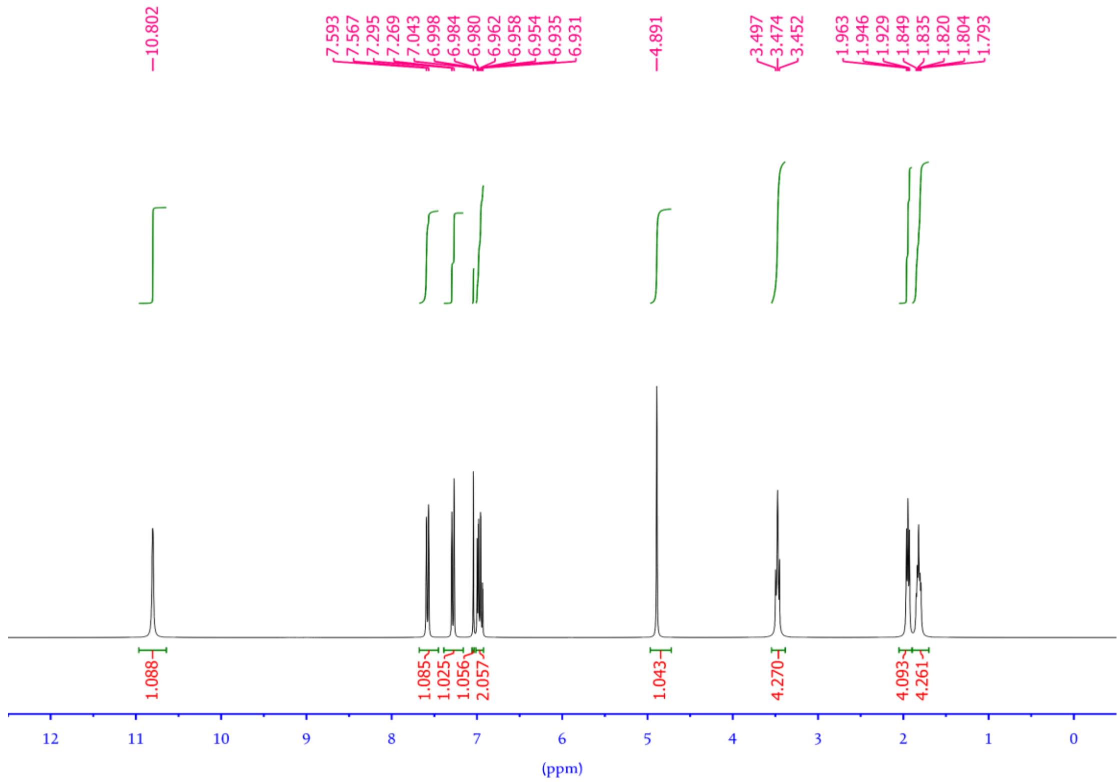


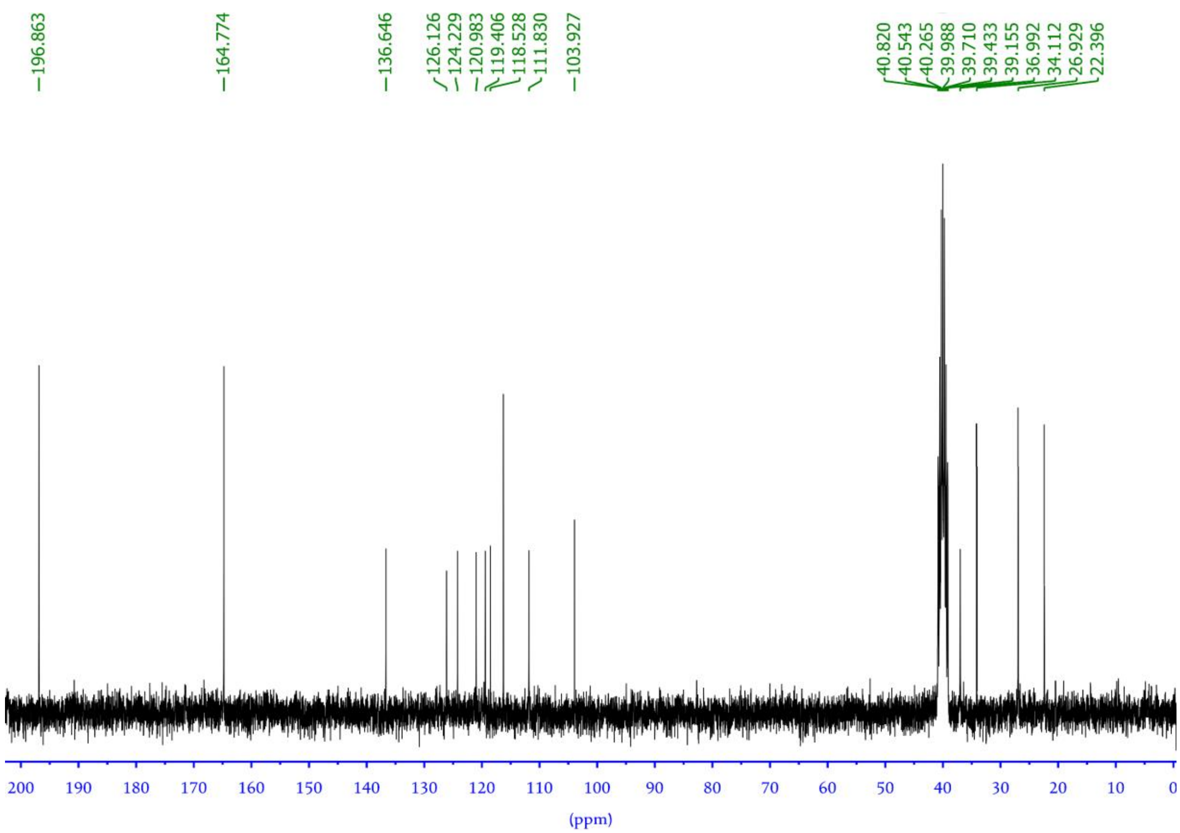
4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) benzaldehyde (Table 2, Entry 9)



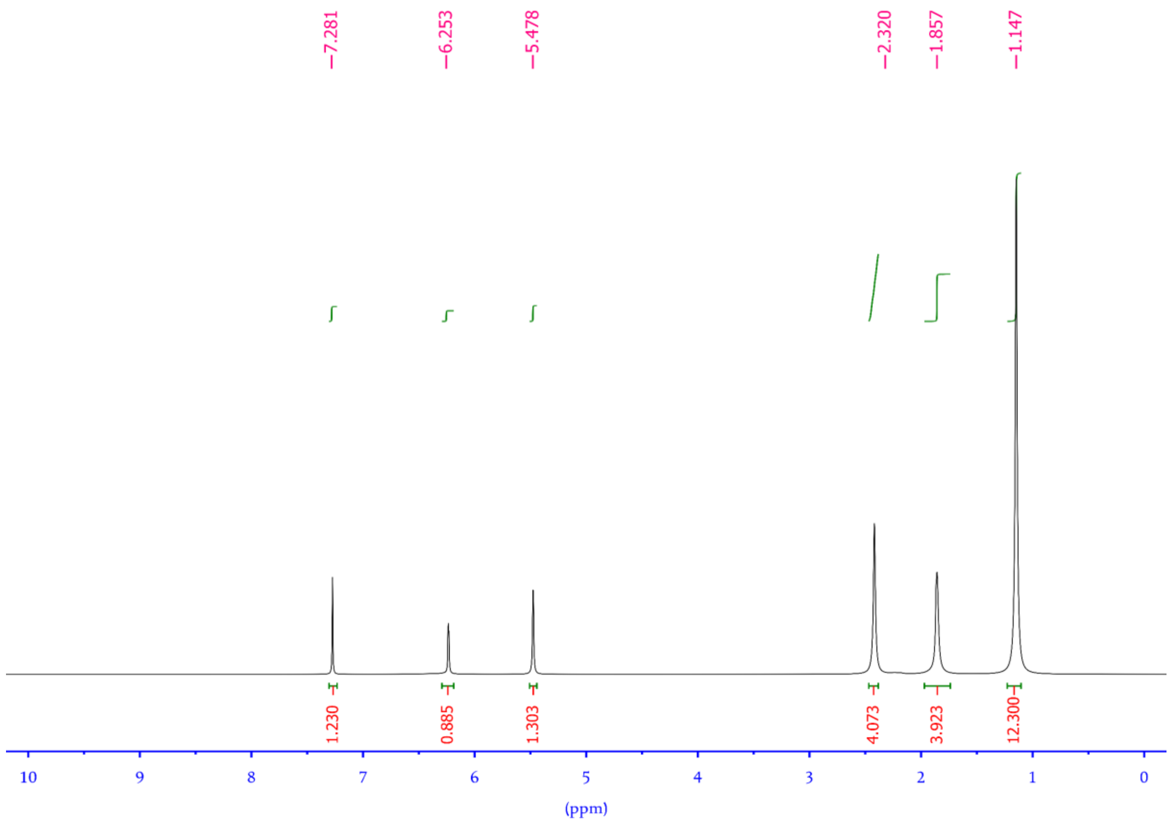


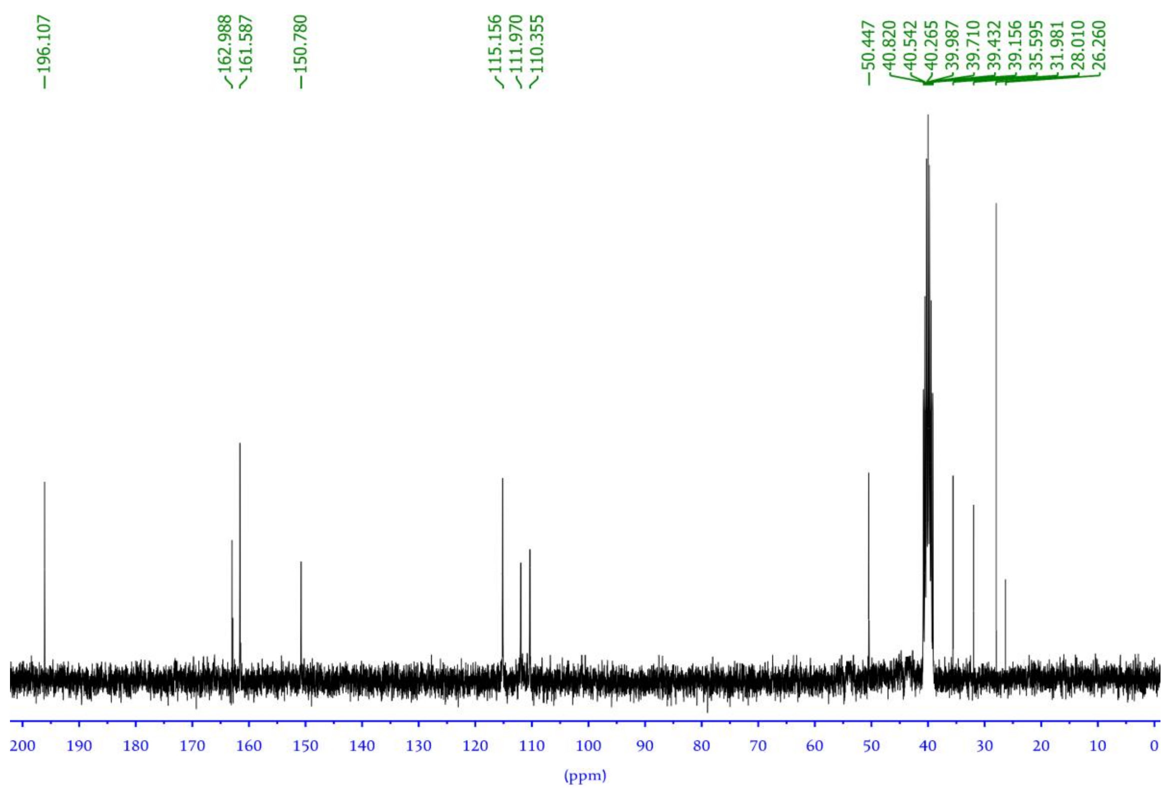
9-(1H-indol-3-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 10)



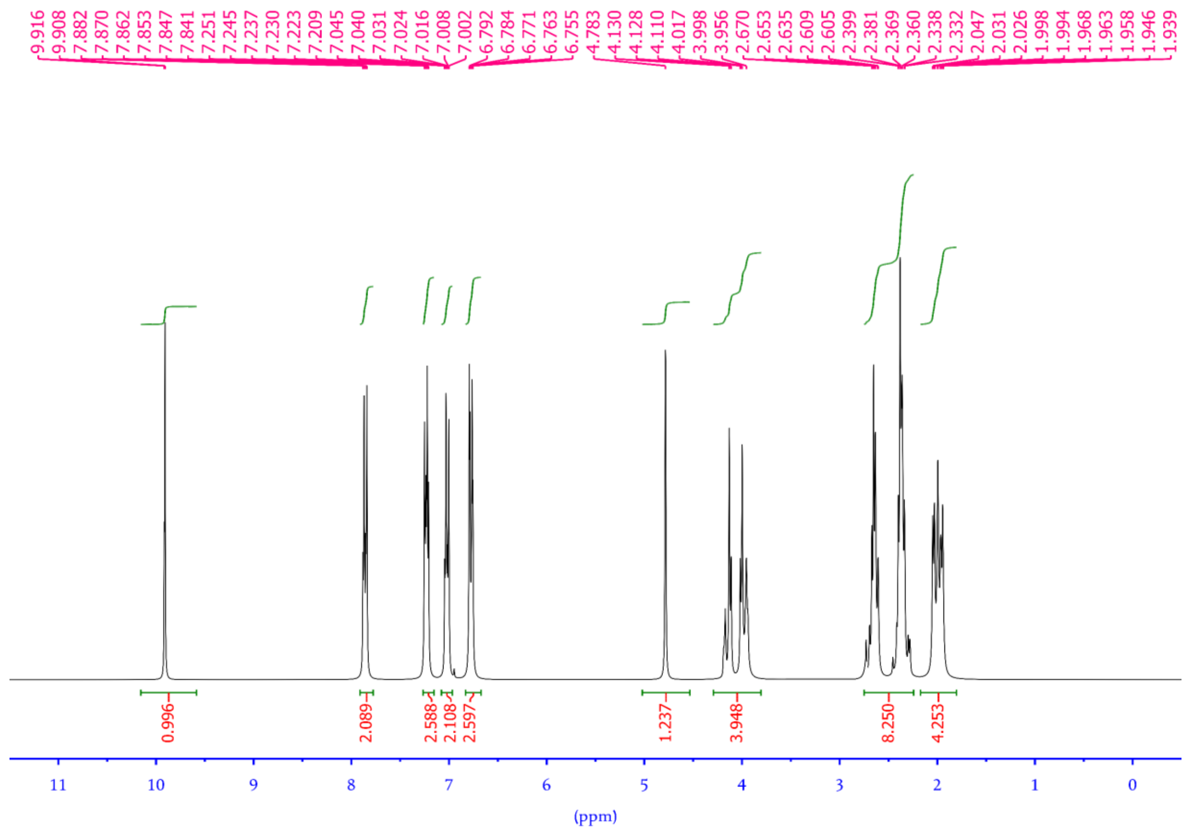


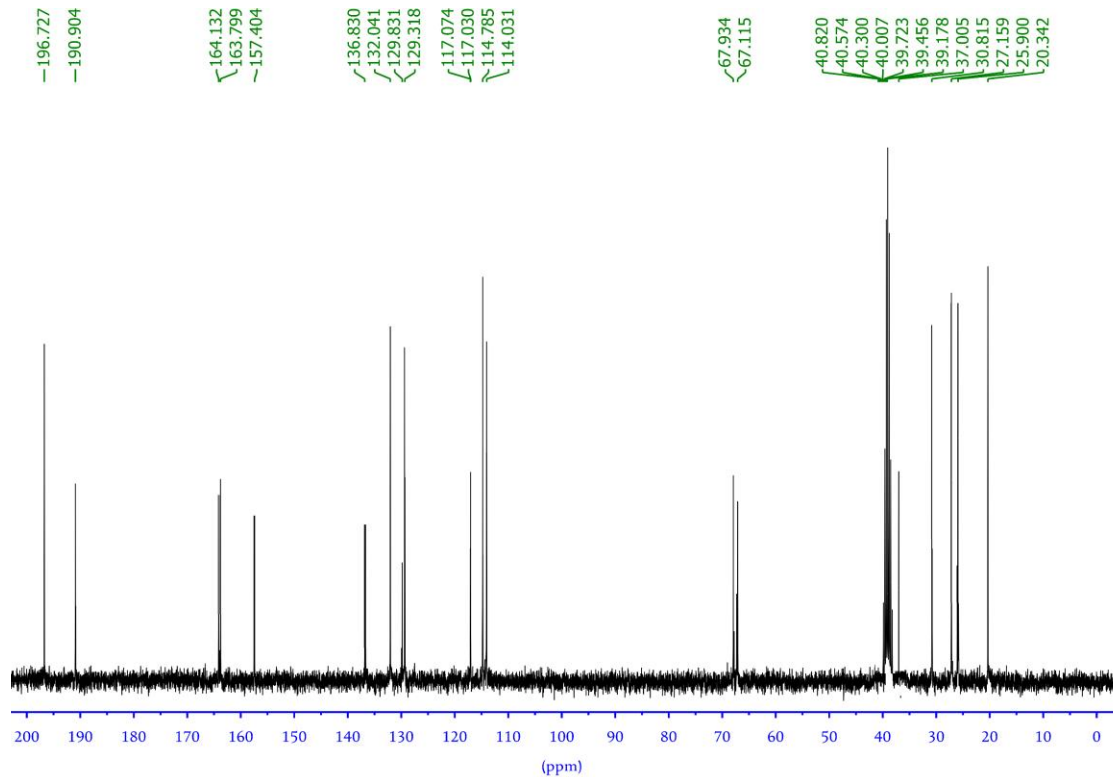
3,3,6,6-tetramethyl-9-(5-nitrofuran-2-yl)-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (Table 2, Entry 11)



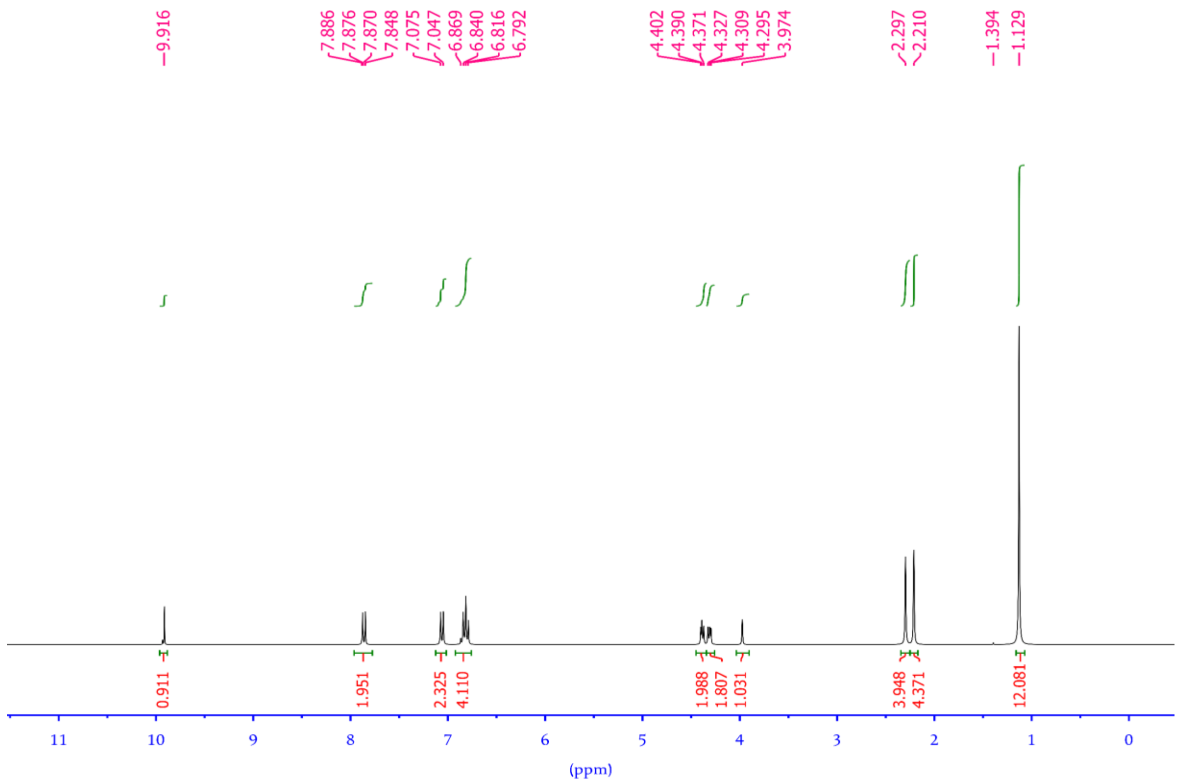


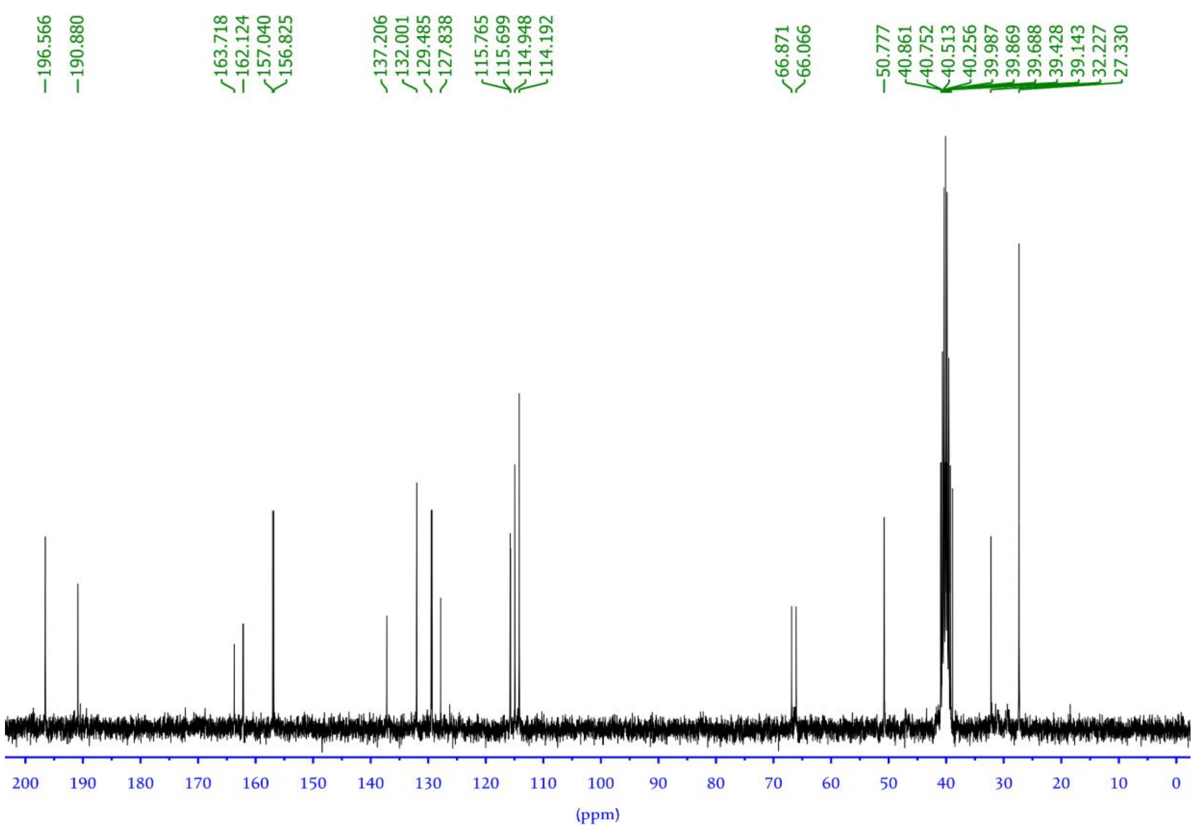
4-(4-(4-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenoxy) butoxy) benzaldehyde (Table 2, Entry 12)



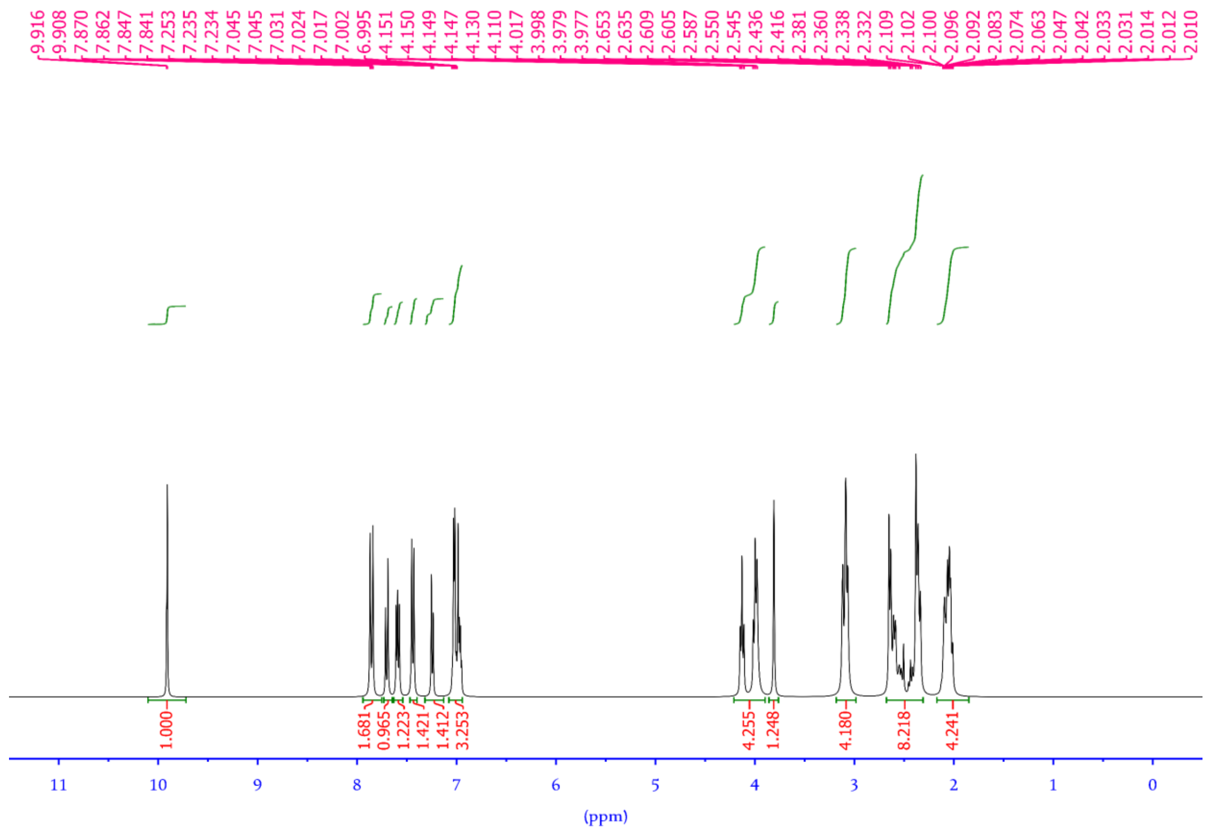


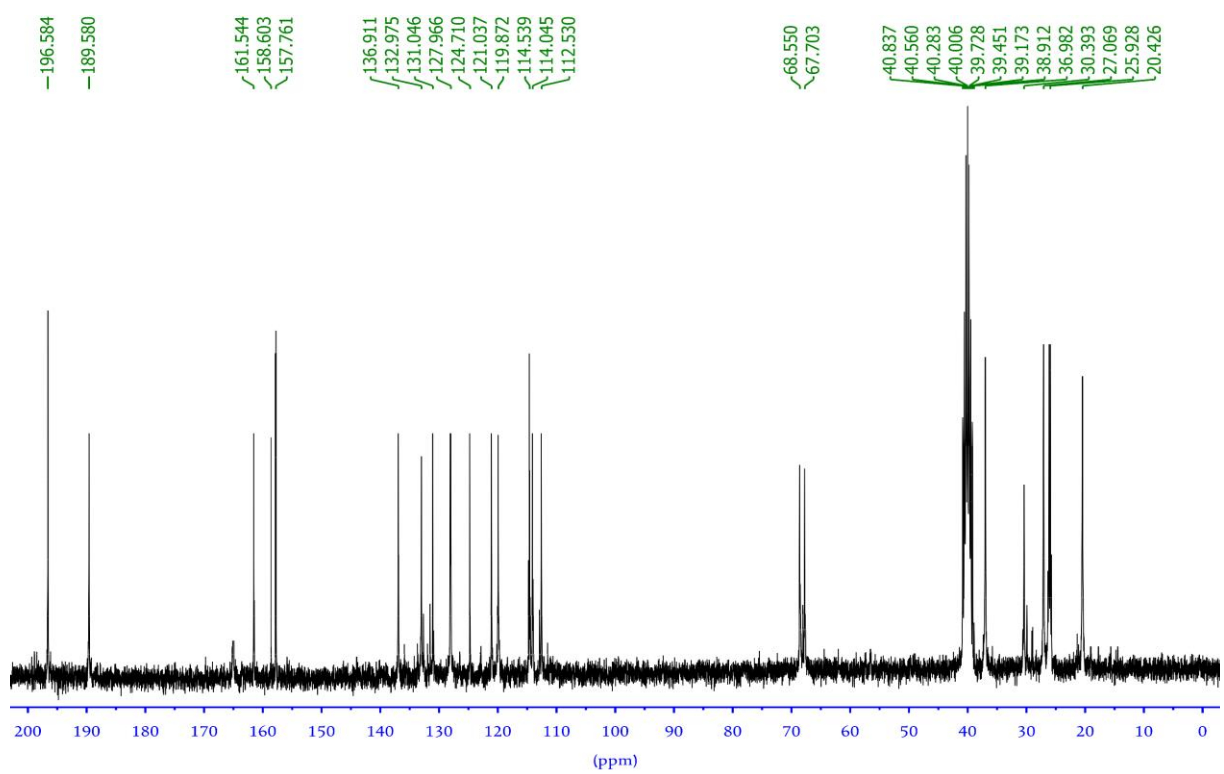
4-(2-(4-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenoxy) ethoxy) benzaldehyde (Table 2, Entry 13)



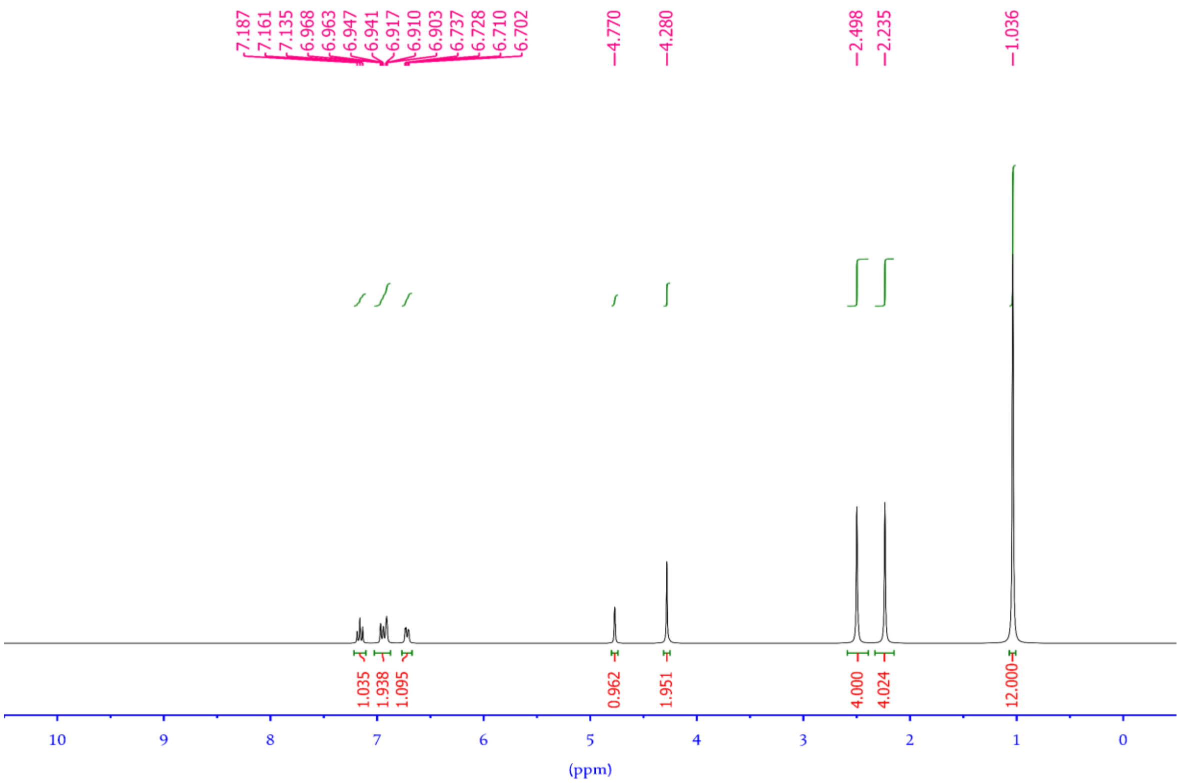


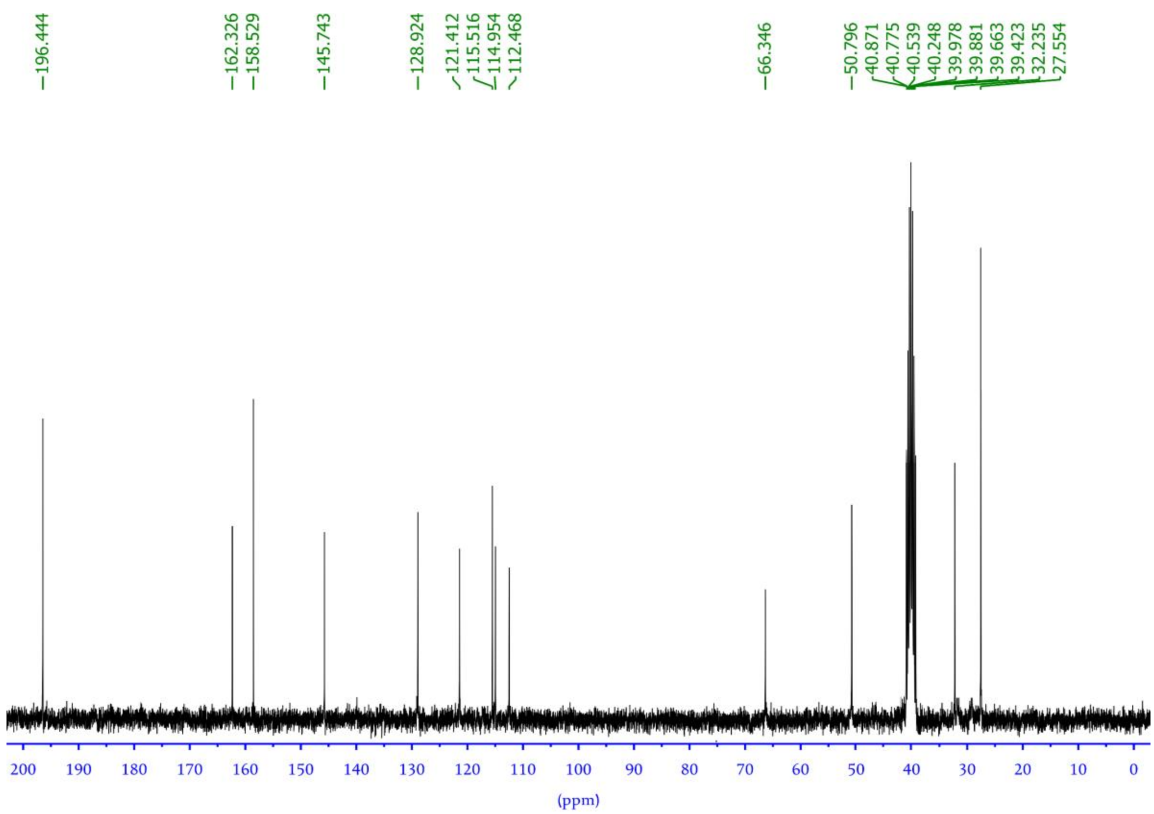
2-(4-(2-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenoxy) butoxy) benzaldehyde (Table 2, Entry 14)





9,9'-((ethane-1,2-diylbis(oxy)) bis(3,1-phenylene)) bis(3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione) (Table 2, Entry 15)





Green chemistry metrics analysis

The following formulae were used for calculating atom economy (AE), atom efficiency (AEf), carbon efficiency (CE), reaction mass efficiency (RME), optimum efficiency (OE), process mass intensity (PMI), E factor, solvent and water intensity (SI and WI).

$$AE = \frac{Molecular\ weight\ of\ the\ product}{Total\ molecular\ weight\ of\ reactants} \times 100$$

$$AE_f = AE{\cdot}Yield\ (\%)$$

$$CE = \frac{Amount\ of\ carbon\ in\ the\ product}{Total\ carbon\ present\ in\ reactants} \times 100$$

$$RME = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} \times 100$$

$$OE = \frac{RME}{AE} \times 100$$

$$PMI = \frac{Total\ mass\ of\ input\ material\ in\ the\ whole\ process}{Mass\ of\ product}$$

$$E\ factor = PMI - 1$$

$$SI = \frac{Total\ mass\ of\ solvents\ excluding\ water\ in\ the\ whole\ process}{Mass\ of\ product}$$

$$WI = \frac{Total\ mass\ of\ water\ used\ in\ the\ whole\ process}{Mass\ of\ product}$$

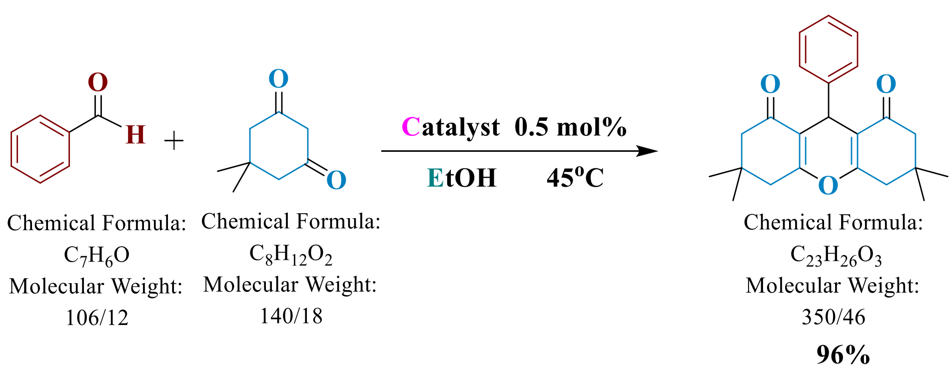
Synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 5)

Experimental procedure:

Benzaldehyde (1 mmol), dimedone (0.14 g, 2 mmol) were added to a mixture of Fe3O4@NFC@ NNSM-Mn (0.004) in EtOH (1 mL). The reaction mixture was heated at 45 °C and stirred until TLC monitoring indicated no further progress in the reaction. Then, the reaction mixture was cooled to room temperature. EtOH (4 mL) was added to the reaction mixture and the catalyst was separated by centrifugation, washed with EtOH (4 mL), dried and re-used for a consecutive run under the same reaction conditions. The solvent of the combined organic layer was evaporated under reduced pressure to obtain a residue, which was recrystallized in EtOH to produce the pure product.

Materials used for metrics calculations:

Benzaldehyde (0.106 g, 1 mmol), dimedone (0.28 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.336 g, 0.96 mmol).



$$AE = \frac{350.46}{106.12+140.18+140.18} \times 100 = 90.68$$

$$AE_f = 90.68 \times 96\% = 87.05$$

$$CE = \frac{23 \times 0.00096}{7 \times 0.001 + 16 \times 0.002} \times 100 = 56.41$$

$$RME = \frac{0.336}{0.106+0.140+0.140} \times 100 = 87.04$$

$$OE = \frac{87.04}{90.68} \; 100 = 95.99$$

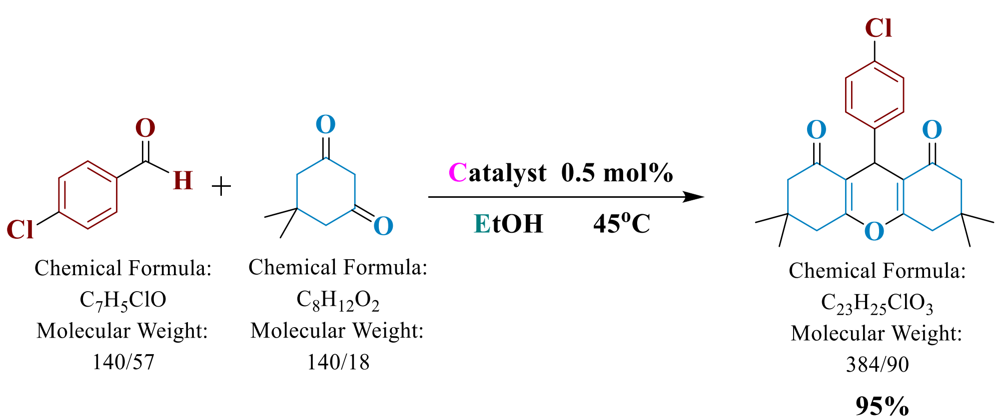
$$PMI = \frac{0.106+0.140+0.140+7.9}{0.336} = 24.66$$

$$E\ factor = 24.66 - 1 = 23.66$$

$$SI = \frac{10 \times 0.789}{0.336} = 23.48$$

$$WI = 0$$

Synthesis of 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8 (2H)-dione catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 6)



Materials used for metrics calculations:

4-Chlorobenzaldehyde (0.14 g, 1 mmol), dimedone (0.28 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.365 g, 0.95 mmol).

$$AE = \frac{384.90}{140.57+140.18+140.18} \times 100 = 91.44$$

$$AE_f = 91.44 \times 95\% = 86.86$$

$$CE = \frac{23 \times 0.00095}{7 \times 0.001 + 16 \times 0.002} \times 100 = 56.02$$

$$RME = \frac{0.365}{0.140+0.140+0.140} \times 100 = 86.90$$

$$OE = \frac{86.90}{91.44}\ 100 = 95.03$$

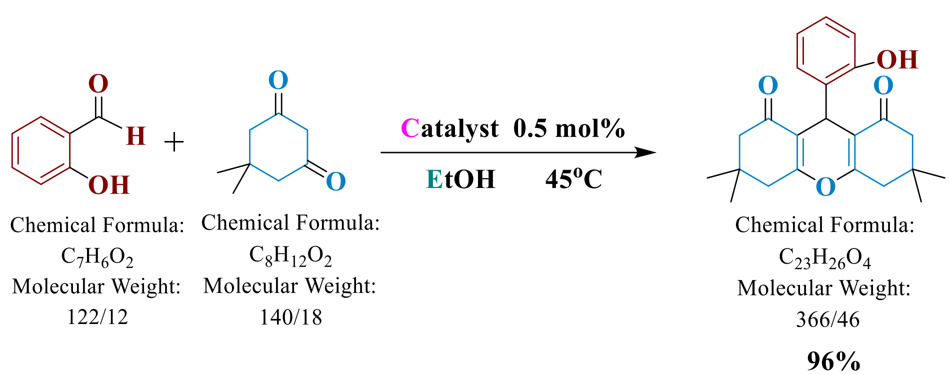
$$PMI = \frac{0.140+0.140+0.140+7.9}{0.365} = 22.84$$

$$E\ factor = 22.84 - 1 = 21.84$$

$$SI = \frac{10 \times 0.789}{0.365} = 21.61$$

$$WI = 0$$

Synthesis of 9-(2-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 6)



Materials used for metrics calculations:

2-Hydroxybenzaldehyde (0.14 g, 1 mmol), dimedone (0.28 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.351 g, 0.96 mmol).

$$AE = \frac{366.46}{122.12+140.18+140.18} \times 100 = 91.05$$

$$AE_f = 91.05 \times 96\% = 87.40$$

$$CE = \frac{23 \times 0.00096}{7 \times 0.001 + 16 \times 0.002} \times 100 = 56.61$$

$$RME = \frac{0.351}{0.122+0.140+0.140} \times 100 = 87.31$$

$$OE = \frac{87.31}{91.05}\ 100 = 95.89$$

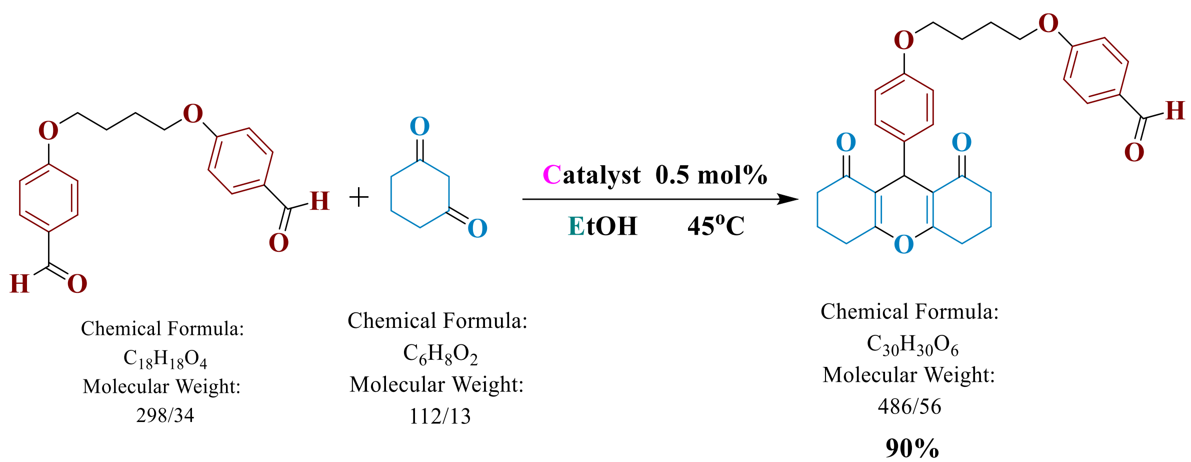
$$PMI = \frac{0.122+0.140+0.140+7.9}{0.351} = 23.65$$

$$E\ factor = 23.65 - 1 = 22.65$$

$$SI = \frac{10 \times 0.789}{0.351} = 22.47$$

$$WI = 0$$

Synthesis of 4-(4-(4-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenoxy) butoxy) benzaldehyde catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 11)



Materials used for metrics calculations:

4,4'-(butane-1,4-diylbis(oxy)) di-benzaldehyde (0.298 g, 1 mmol), 1,3-Cyclohexane Dione (0.224 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.437 g, 0.90 mmol).

$$AE = \frac{486.56}{298.34+112.13+112.13} \times 100 = 93.10$$

$$AE_f = 93.1 \times 90\% = 83.79$$

$$CE = \frac{30\times0.00090}{18\times0.001+12\times0.002}\times100 = 64.28$$

$$RME = \frac{0.437}{0.298+0.112+0.112}\times100 = 83.71$$

$$OE = \frac{83.71}{93.1}\ 100 = 89.92$$

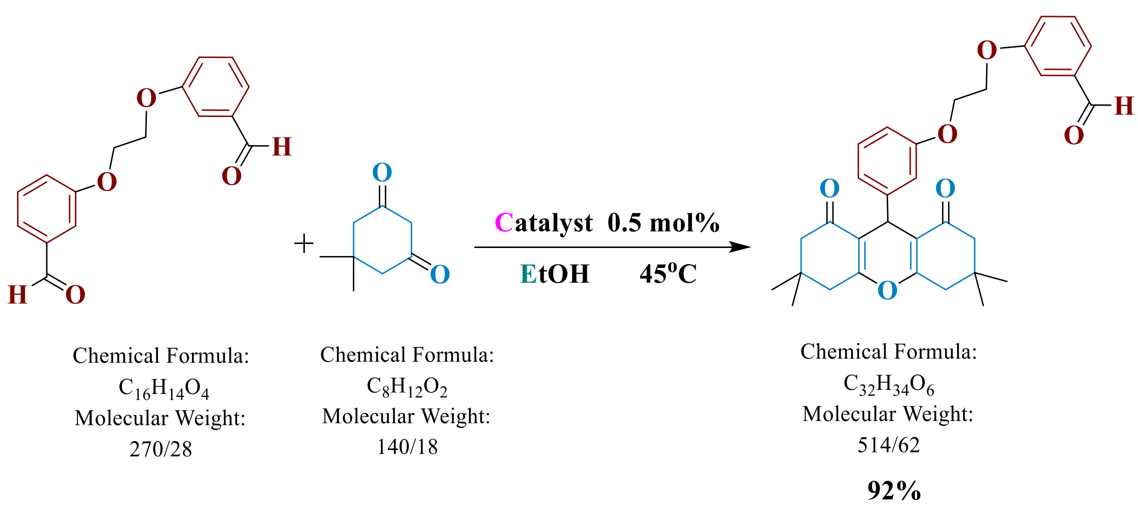
$$PMI = \frac{0.298+0.112+0.112+7.9}{0.437} = 19.27$$

$$E\ factor = 19.27 - 1 = 18.27$$

$$SI = \frac{10\times0.789}{0.437} = 18.05$$

$$WI = 0$$

Synthesis of 3-(3-(3,3,6,6-tetramethyl-1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenethyl) benzaldehyde catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 12)



Materials used for metrics calculations:

3,3'-(ethane-1,2-diyl) benzaldehyde (0.270 g, 1 mmol), dimedone (0.0.28 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.473 g, 0.92 mmol).

$$AE = \frac{514.62}{270.28+140.18+140.18} \times 100 = 93.45$$

$$AE_f = 93.45 \times 92\% = 85.98$$

$$CE = \frac{32 \times 0.00092}{16 \times 0.001 + 16 \times 0.002} \times 100 = 60.41$$

$$RME = \frac{0.473}{0.270+0.140+0.140} \times 100 = 86$$

$$OE = \frac{86}{93.45}\ 100 = 92.02$$

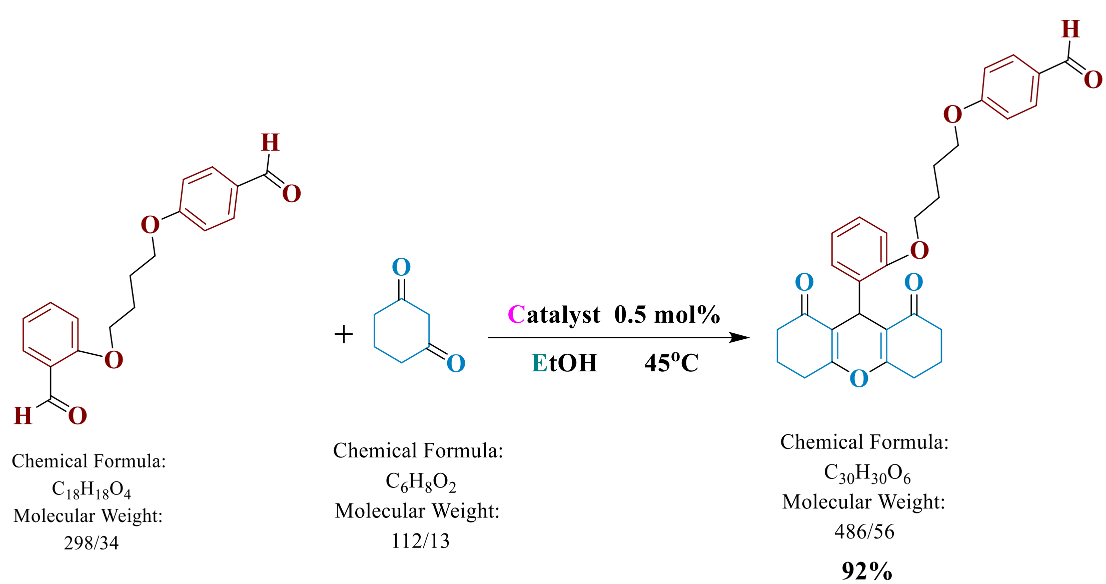
$$PMI = \frac{0.270+0.140+0.140+7.9}{0.473} = 17.86$$

$$E\ factor = 17.86 - 1 = 16.86$$

$$SI = \frac{10 \times 0.789}{0.473} = 16.68$$

$$WI = 0$$

Synthesis of 4-(4-(2-(1,8-dioxo-2,3,4,5,6,7,8,9-octahydro-1H-xanthen-9-yl) phenoxy) butoxy) benzaldehyde catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 13)



Materials used for metrics calculations:

2-(4-(4-formylphenoxy) butoxy) benzaldehyde (0.298 g, 1 mmol), 1,3-Cyclohexane Dione (0.224 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.447 g, 0.92 mmol).

$$AE = \frac{486.56}{298.34+112.13+112.13} \times 100 = 93.1$$

$$AE_f = 93.1 \times 92\% = 85.65$$

$$CE = \frac{30 \times 0.00090}{18 \times 0.001 + 12 \times 0.002} \times 100 = 64.28$$

$$RME = \frac{0.447}{0.298+0.112+0.112} \times 100 = 85.63$$

$$OE = \frac{85.63}{93.10}\ 100 = 91.97$$

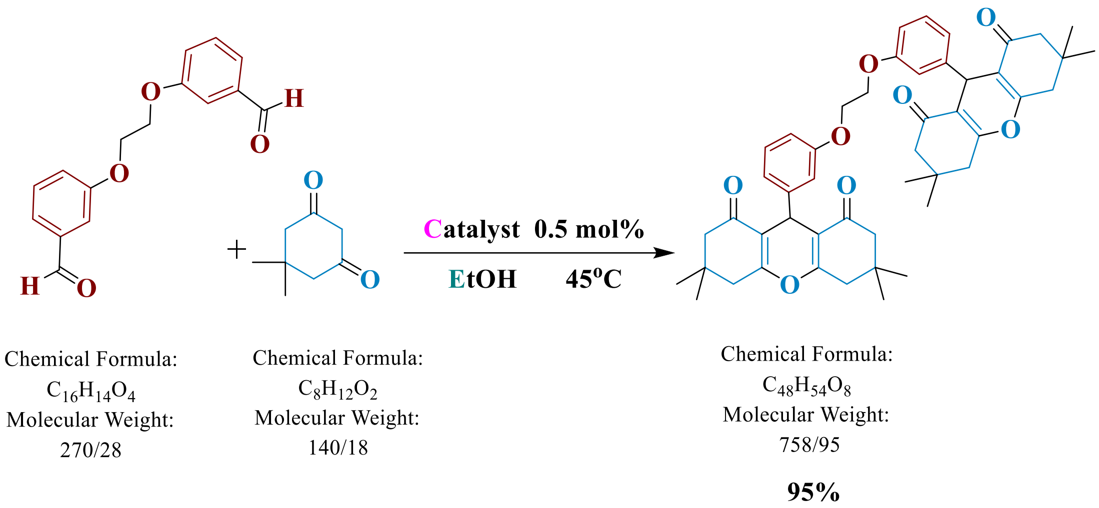
$$PMI = \frac{0.298+0.112+0.112+7.9}{0.447} = 18.84$$

$$E\ factor = 18.84 - 1 = 17.84$$

$$SI = \frac{10 \times 0.789}{0.447} = 17.65$$

$$WI = 0$$

Synthesis of 9,9'-(ethane-1,2-diylbis(3,1-phenylene)) bis (3,3,6,6-tetramethyl-3,4,5,6,7,9-hexa hydro-1H-xanthene-1,8(2H)-dione) catalyzed by Fe_3O_4@NFC@NNSM-Mn (Table 2, entry 15)



Materials used for metrics calculations:

3,3'-(ethane-1,2-diyl) benzaldehyde (0.270 g, 1 mmol), dimedone (0.28 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.721 g, 0.95 mmol).

$$AE = \frac{758.95}{270.28+140.18+140.18} \times 100 = 137.83$$

$$AE_f = 137.83 \times 95\% = 130.93$$

$$CE = \frac{48 \times 0.00095}{16 \times 0.001 + 16 \times 0.002} \times 100 = 95$$

$$RME = \frac{0.721}{0.270+0.140+0.140} \times 100 = 131.09$$

$$OE = \frac{131.09}{137.83} \times 100 = 95.11$$

$$PMI = \frac{0.270+0.140+0.140+7.9}{0.721} = 11.71$$

$$E\ factor = 11.71 - 1 = 10.71$$

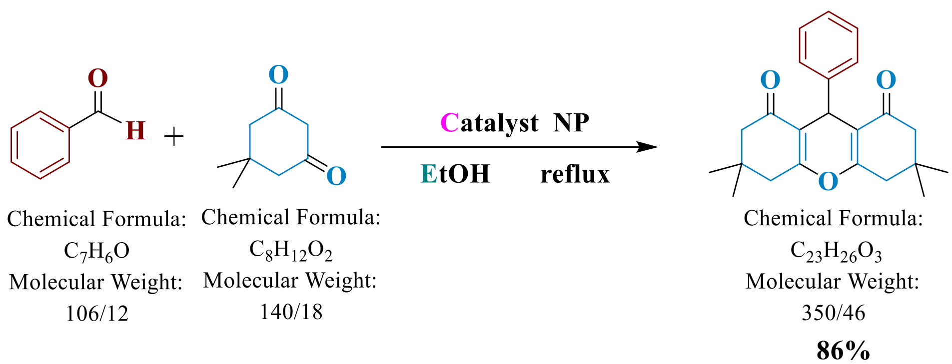
$$SI = \frac{10 \times 0.789}{0.721} = 10.94$$

$$WI = 0$$

Synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione catalyzed by NP (Table 5, entry 8)

Materials used for metrics calculations:

Benzaldehyde (0.106 g, 1 mmol), dimedone (0.28 g, 2 mmol), EtOH (10 mL, 7.9 g), product (0.301 g, 0.86 mmol).



$$AE = \frac{350.46}{106.12+140.18+140.18} \times 100 = 90.68$$

$$AE_f = 90.68 \times 86\% = 77.98$$

$$CE = \frac{23 \times 0.00086}{7 \times 0.001 + 16 \times 0.002} \times 100 = 50.71$$

$$RME = \frac{0.301}{0.106+0.140+0.140} \times 100 = 77.97$$

$$OE = \frac{77.97}{90.68} 100 = 85.99$$

$$PMI = \frac{0.106+0.140+0.140+7.9}{0.301} = 27.52$$

$$E\ factor = 27.52 - 1 = 26.52$$

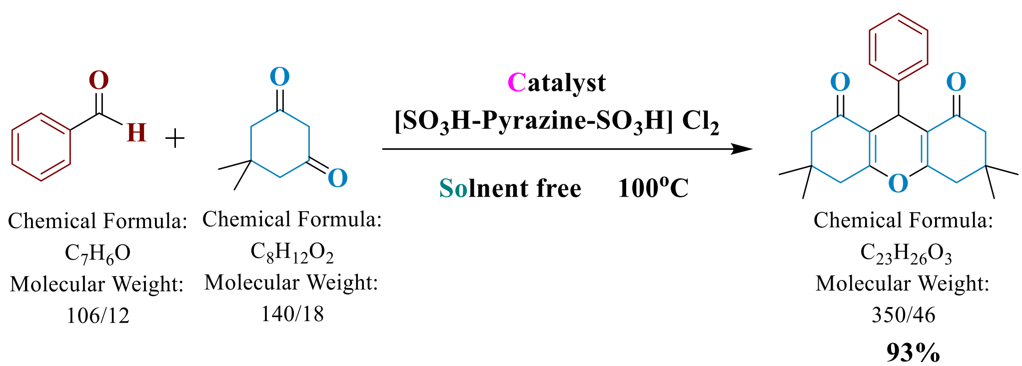
$$SI = \frac{10 \times 0.789}{0.301} = 26.24$$

$$WI = 0$$

Synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione catalyzed by [SO_3H–Pyrazine–SO_3H] Cl2 (Table 5, entry 1)

Materials used for metrics calculations:

Benzaldehyde (0.106 g, 1 mmol), dimedone (0.28 g, 2 mmol), EtOH (5 mL, 3.95 g), H_2O (10 mL, 10 g), product (0.325 g, 0.93 mmol).



$$AE = \frac{350.46}{106.12+140.18+140.18} \times 100 = 90.67$$

$$AE_f = 90.67 \times 93\% = 84.32$$

$$CE = \frac{23 \times 0.00093}{7 \times 0.001 + 16 \times 0.002} \times 100 = 54.84$$

$$RME = \frac{0.325}{0.106+0.140+0.140} \times 100 = 84.19$$

$$OE = \frac{84.19}{90.67} 100 = 92.85$$

$$PMI = \frac{0.106+0.140+0.140+3.95+10}{0.325} = 44.11$$

$$E\ factor = 44.11 - 1 = 43.11$$

$$SI = \frac{10 \times 0.789}{0.325} = 24.30$$

$$WI = \frac{10}{0.325} = 30.76$$

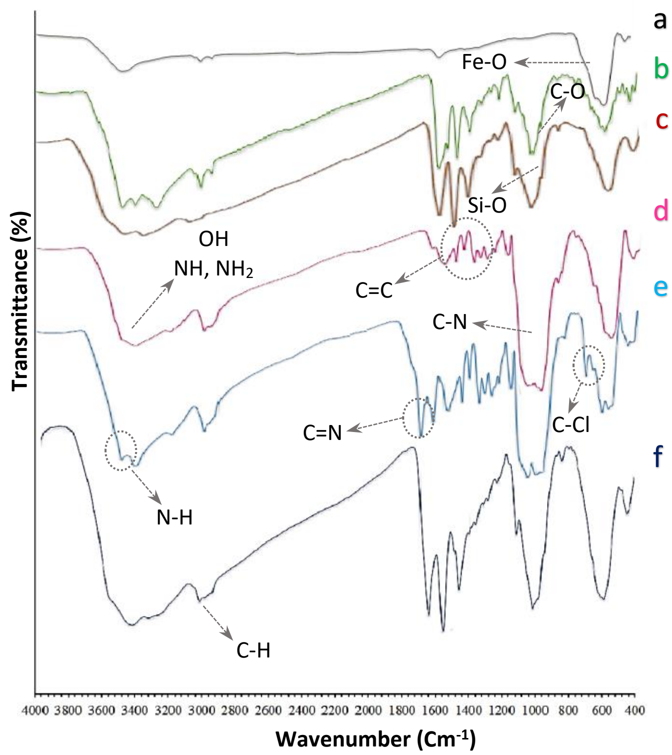


Figure S1: (a) Fe_3O_4, (b) Fe_3O_4@NFC, (c) Fe_3O_4@NFC-Cl, (d) Fe_3O_4@NFC-NN, (e) Fe_3O_4@NFC-NNS-Mn(III), (f) Fe_3O_4@NFC-NNSM-Mn(III)

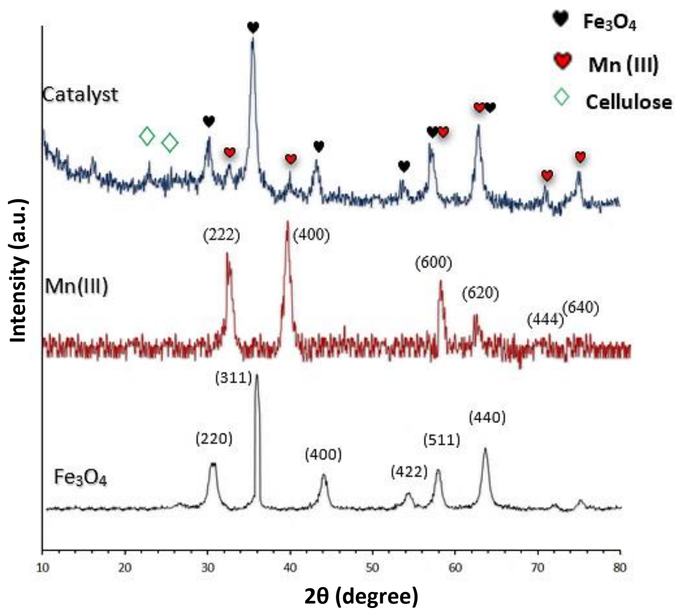


Figure S2: XRD spectra of (black) Fe_3O_4, (red) Mn_2O_3 and (blue) Fe_3O_4@NFC-NNSMMn(III)

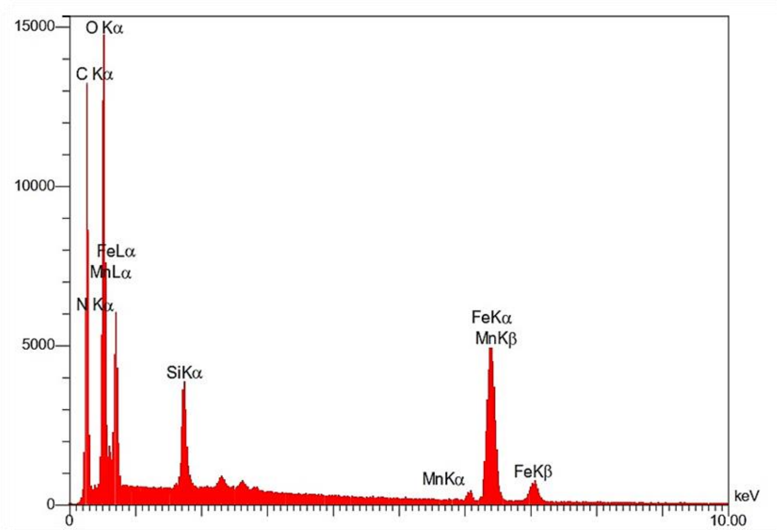
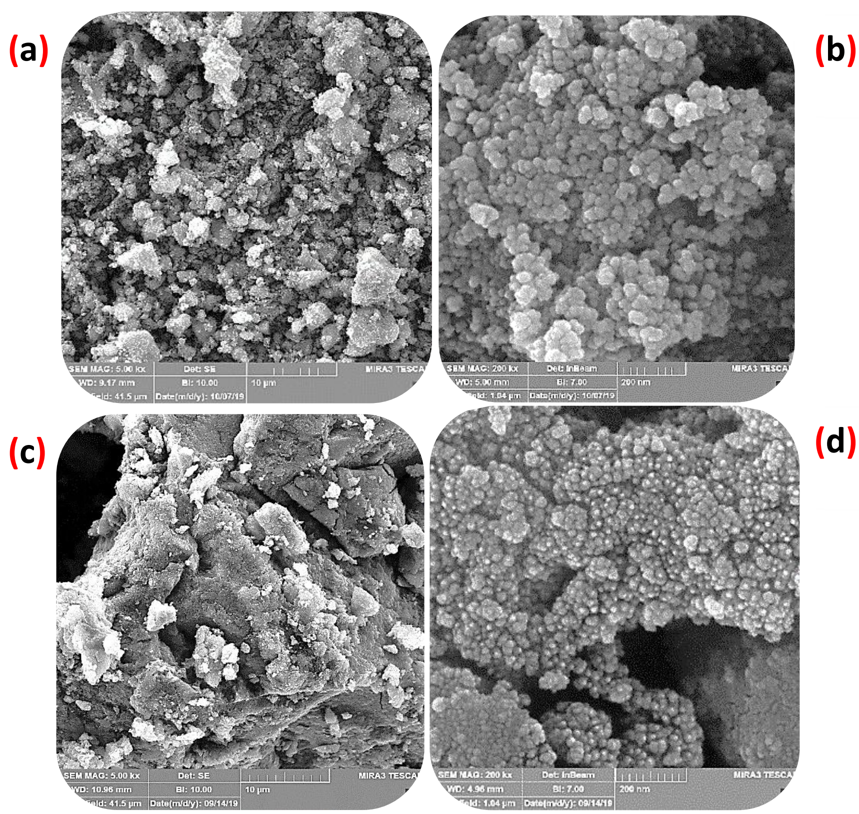


Figure S3: EDX image of Fe_3O_4@NFC@NNSM-Mn(III)



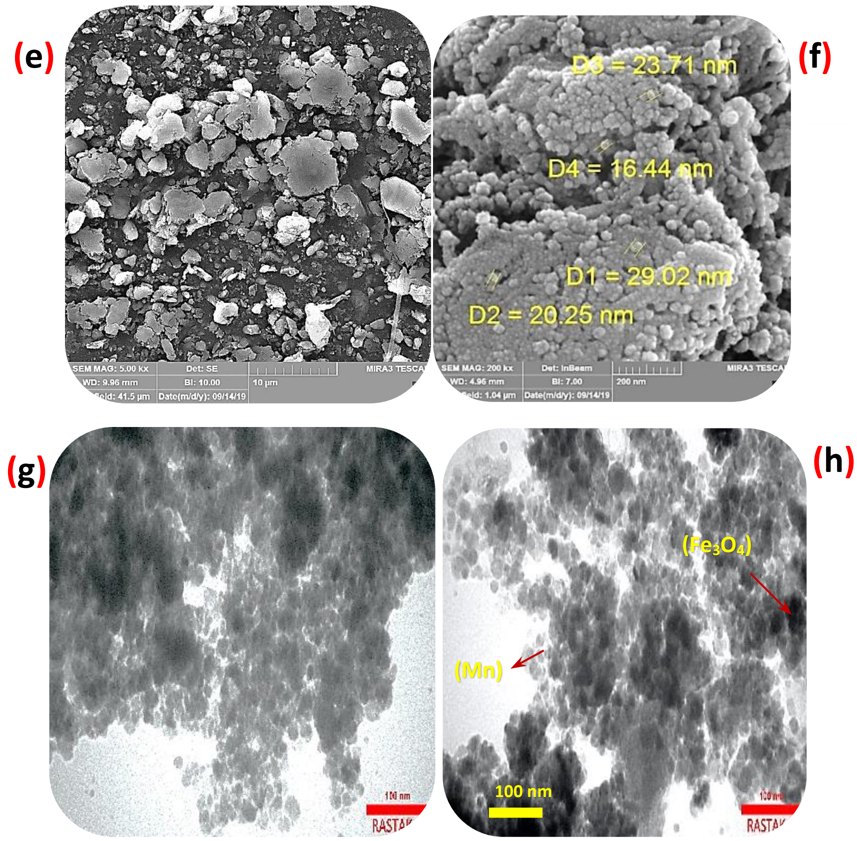


Figure S4: SEM image of (a,b) Fe_3O_4, of (c,d) Fe_3O_4@NFC, of (e,f) Fe_3O_4@NFC@NNSM-Mn(III) and (g,h) TEM image of the Fe_3O_4@NFC@NNSM-Mn(III)

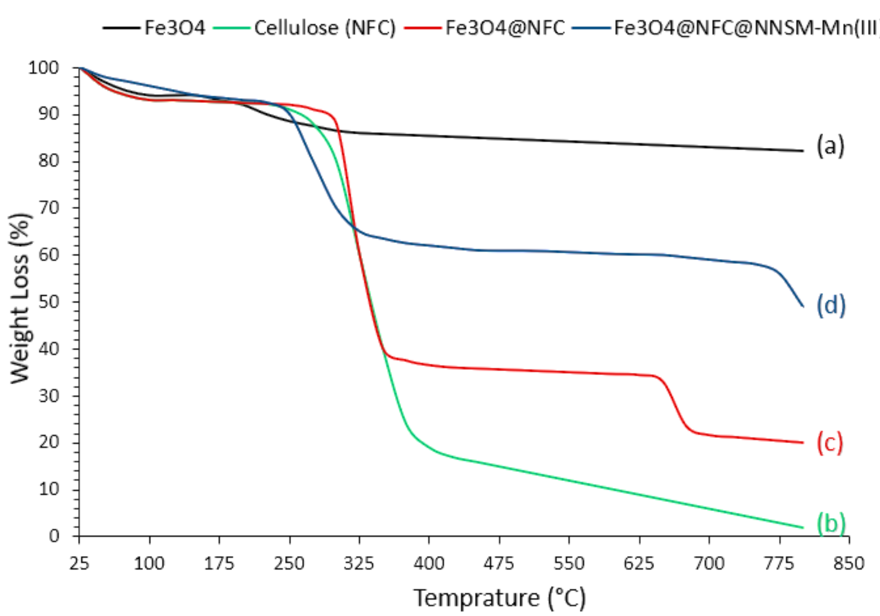


Figure S5: TGA curves for (a) Fe_3O_4, (b) Cellulose, (c) Fe_3O_4@NFC, and (d) Fe_3O_4@NFC@NNSM-Mn(III)

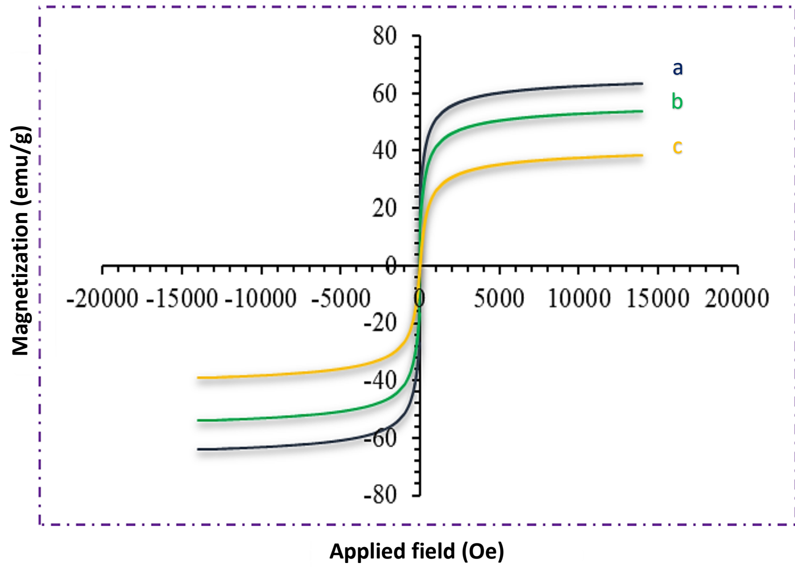


Figure S6: VSM pattern Fe_3O_4 (a), Fe_3O_4@NFC (b) and (c) Fe_3O_4@NFC@NNSM-Mn(III)

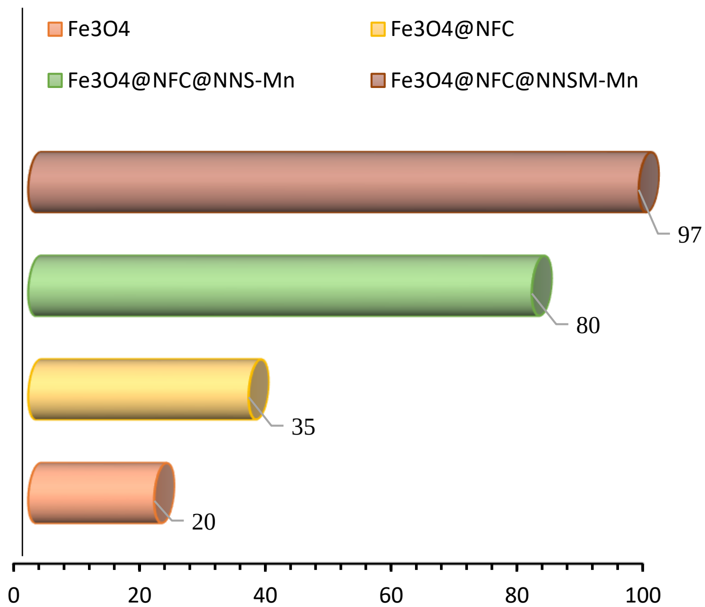


Figure S7: Comparison of the performance of catalysts with each other. Reaction conditions: Alcohols (1 mmol), TBHP (2 mmol), Catalyst (0.5 mol%), S. F., 40 °C.

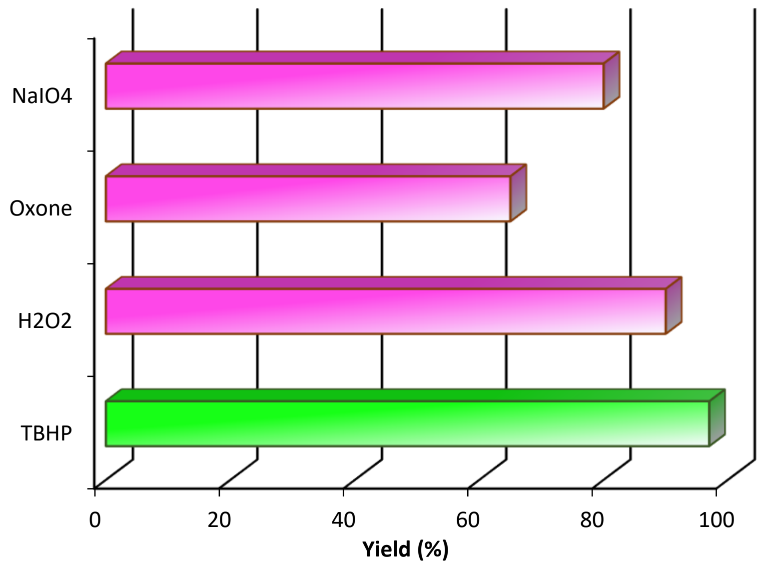


Figure S8: Reaction conditions: benzyl alcohol (1 mmol), oxidant (2 mmol), catalyst (0.5 mol%), S. F., 40 °C for 20 min.

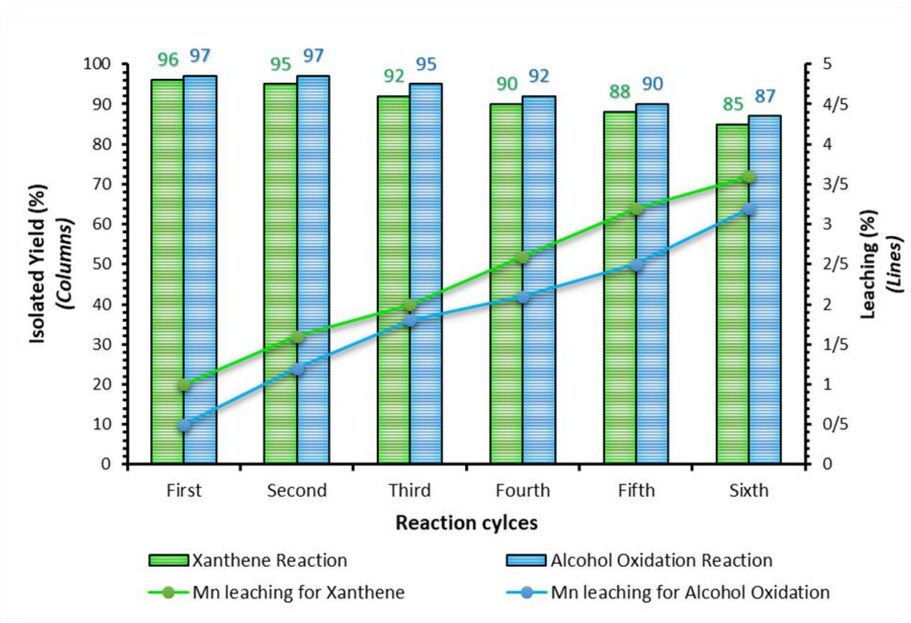


Figure S9. Recyclability of Fe_3O_4@NFC@NNSM-Mn(III) in the model Alcohol oxidation and Xanthene Multi-component reaction, under the optimized reaction conditions; Reaction times: 10 min (Xanthene Multi-component reaction) and 30 min (Alcohol oxidation)

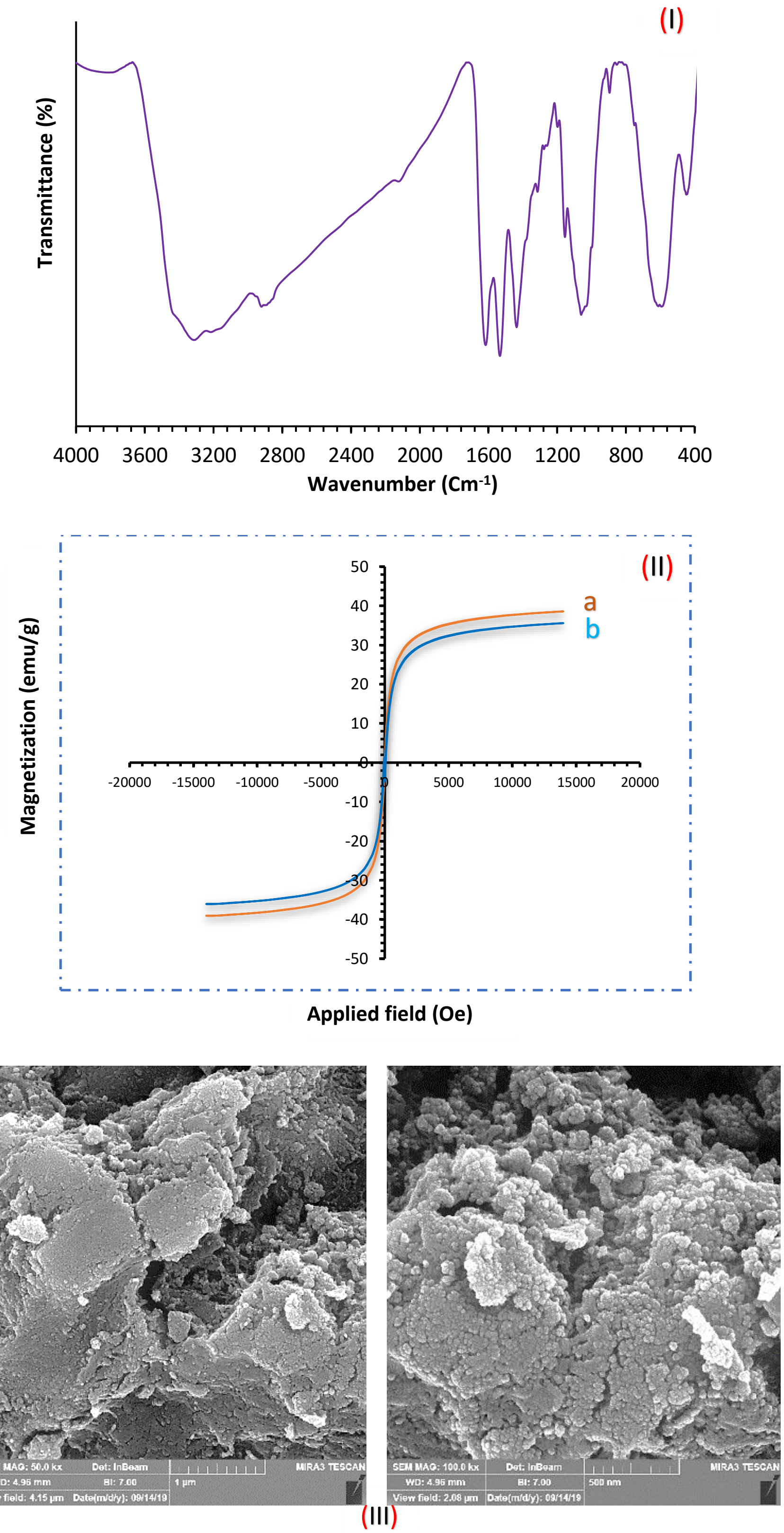


Figure S10: (I) FT-IR; (II) VSM (a: before recycling and b: after recycling); (III) Fe-SEM analysis of Fe_3O_4@NFC@NNSM-Mn(III) after six times

Comparative study

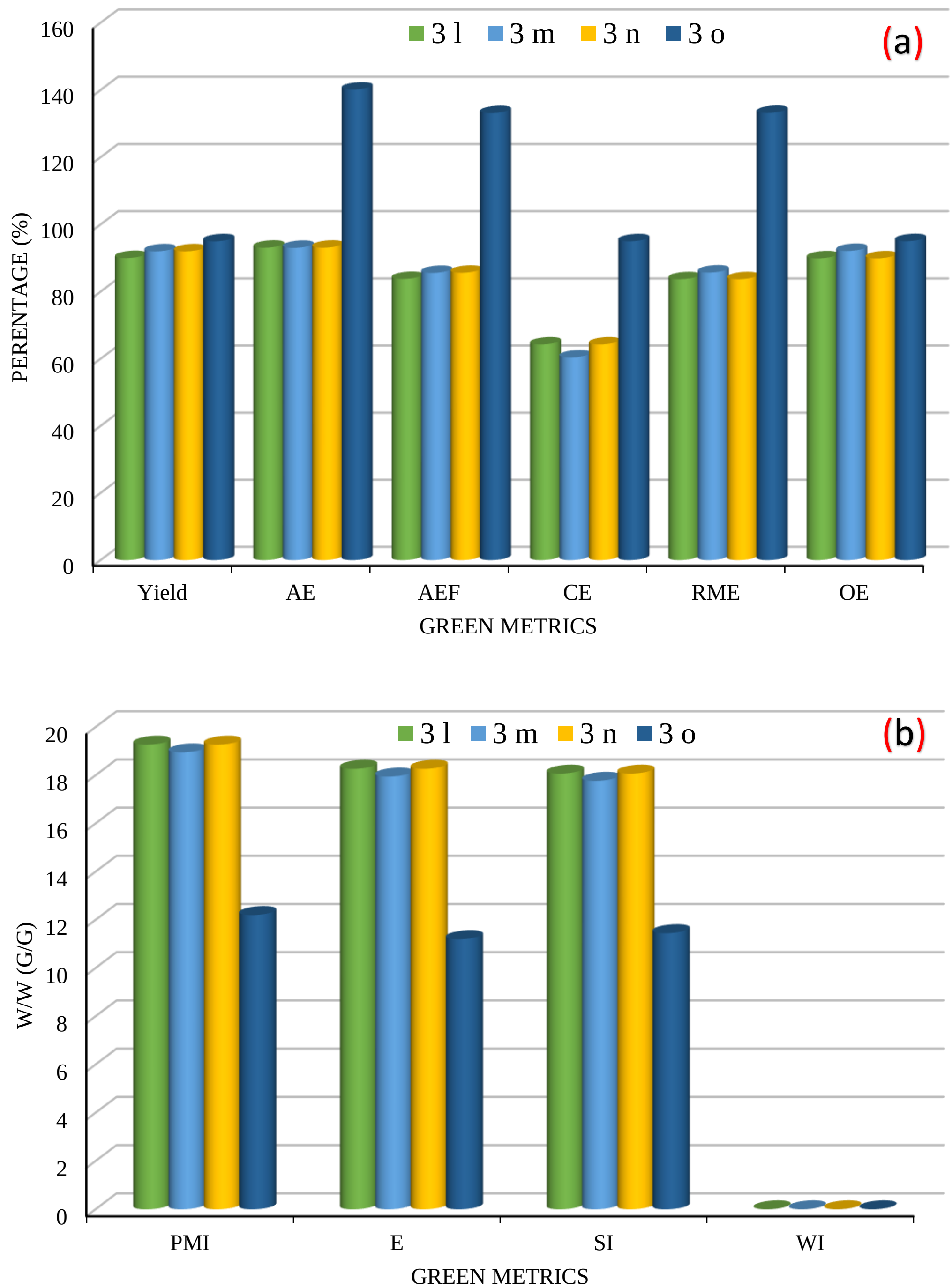
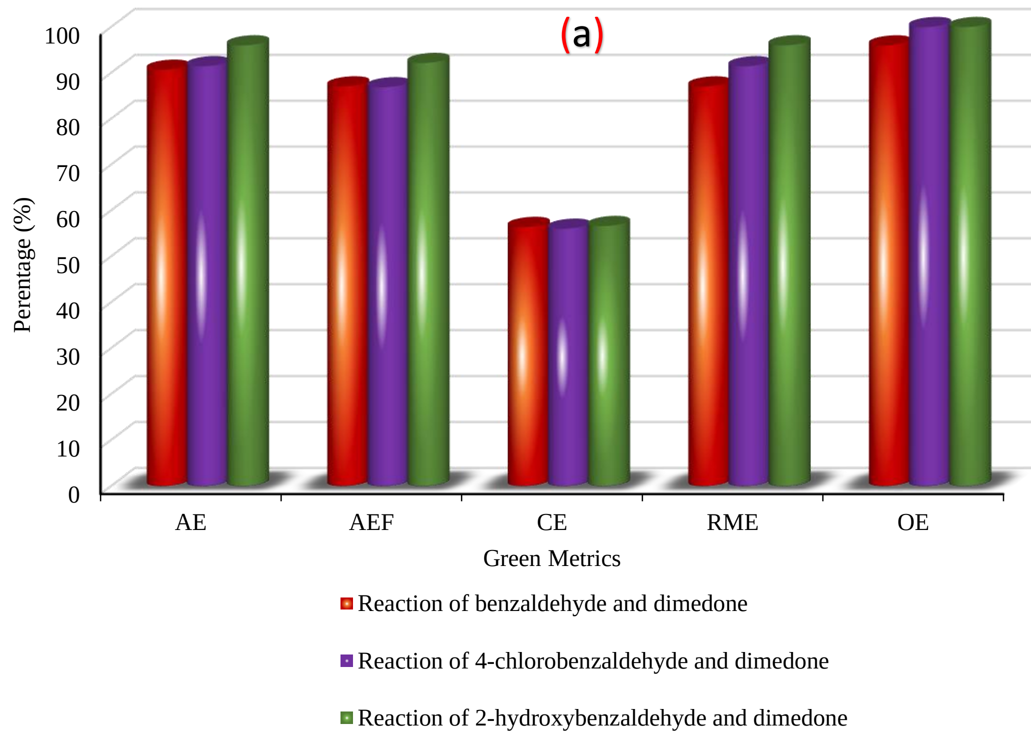


Figure S11: Green metrics including (a) AE, AEf, CE, RME, OE and (b) PMI, E, SI, and WI for the one-pot three-component reactions of aldehyde (3 l – 3 o) and dimedone (entries 11-15 in Table 2); W/W = Weight/Weight (g/g)



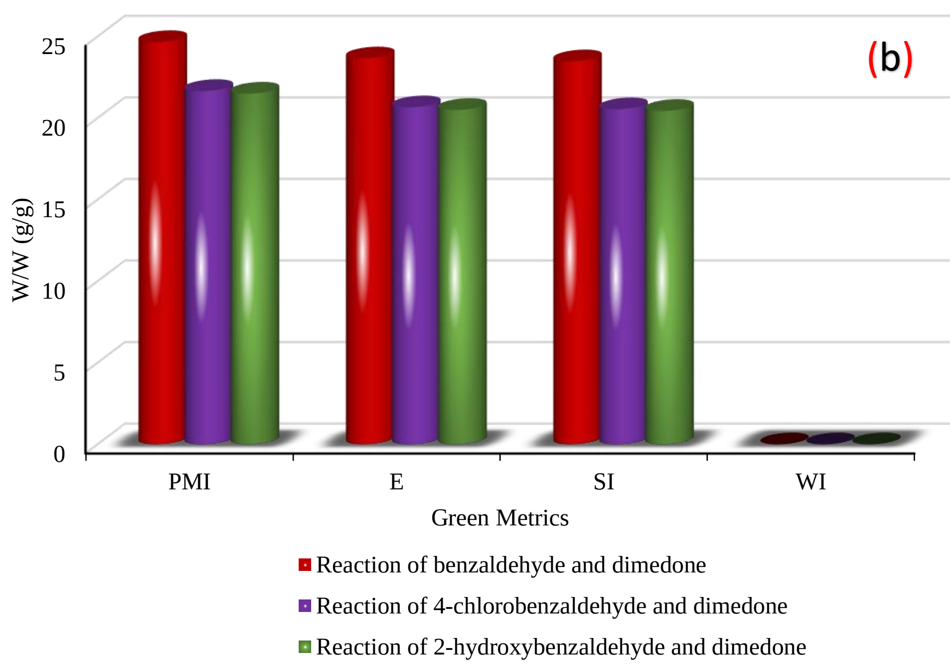


Figure S12: Green metrics including (a) AE, AEf, CE, RME, OE and (b) PMI, E, SI, and WI for the one-pot three-component reactions of aldehyde (benzaldehyde/4-chlorobenz aldehyde/2-hydroxybenzaldehyde) and dimedone (entries 5, 6 and 7 in Table 2); W/W = Weight/Weight (g/g)

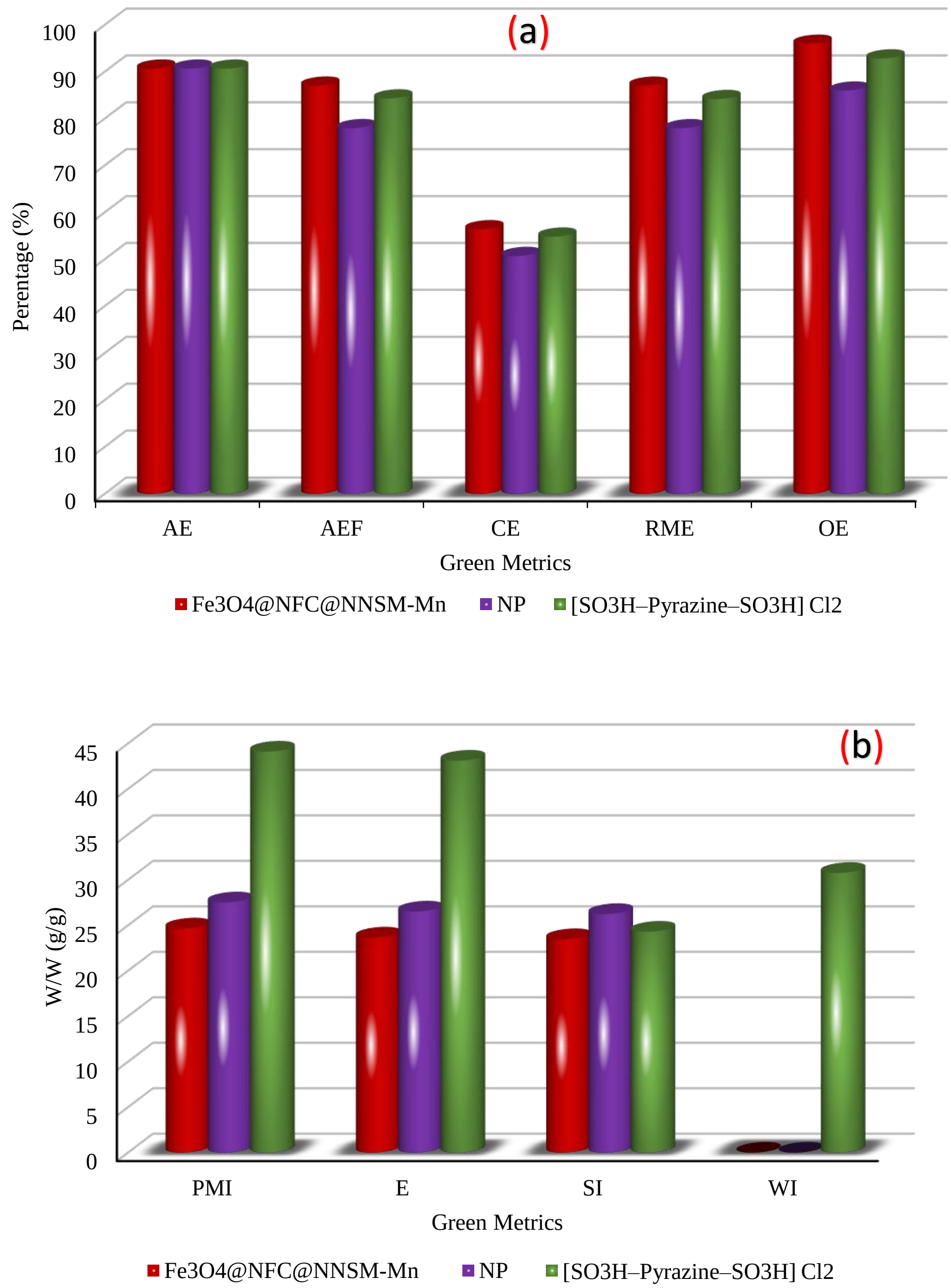


Figure S13: Green metrics including (a) AE, AEf, CE, RME, OE and (b) PMI, E, SI and WI for the one-pot three-component reaction of benzaldehyde and dimedone catalysed by Fe_3O_4@NFC@NNSM-Mn(III) (this study), [SO_3H–Pyrazine–SO_3H] Cl_2 (Table 5, entry 1) and NP (Table 5, entry 8); W/W = Weight/Weight (g/g)