Supplementary Information

A sustainable gateway to access 1,8-dioxo-octahydroxanthene scaffolds *via* surface engineered halloysite based magnetically responsive catalyst.

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1. Experimental

1.1. Chemicals and Methods

Halloysite nanotubes, 3-Chloropropyltrimethoxysilane (CPTMS) (>97%) and 1,2-diaminocyclohexane (DCH) were obtained from Sigma Aldrich and TCI chemicals respectively. Ferrous sulphate and ferric sulphate were commercially acquired from Sisco Research Laboratory (SRL). Anhydrous sodium sulphate, dichloromethane (DCM) and ethanol were purchased from Merck. Other reagents were obtained from Spectrochem Pvt. Ltd and are of analytical grade.

1.2. Instrumentation

For determining the detailed information related to morphological, functionalization and magnetization attributes of newly designed nanocomposites, a number of distinctive physico-chemical techniques were employed. Fourier transform infrared (FT-IR) spectroscopy analysis was executed on a Perkin-Elmer Spectrum BX II spectrophotometer with germanium waveguide using KBr pellet technique having an operating range of 4000–400 cm^{-1} at atmospheric conditions. Powder X-ray diffraction (P-XRD) spectra determines the structure and phase of nanocopmosites and obtained through Rigaku XRD Miniflex 600/600-C in 2θ range of 5−80° (λ = 0.15405 nm, 40 kV, 40 mA) at a scanning range of 3° min^{-1}. Moreover, energy dispersive X-ray fluorescence (ED-XRF) spectroscopy was recorded employing Fischerscope X-ray XAN-FAD BC apparatus in order to corroborate the metalation of final nanocatalyst. A Tekmar Sonic Disruptor TM300 sonicator was utilized to disperse the aggregated nanoparticles. Furthermore, the magnetic characteristics of modified and unmodified nanoparticles was deduced by using EV-9, Microsense, ADE, vibrating sample magnetometer (VSM) at room temperature. To shed light on the shape and morphological attributes of synthesized nanocomposites, field emission scanning electron microscopy (FE-SEM) analysis was carried out by employing Hitachi-SU 8010 FE-SEM. In addition, to gain an insight into the shape and size of nanocomposites transmission electron microscopy (TEM) images were acquired using Thermo Scientific, Talos instrument. Besides, by using an efficient Jeol- JSM-6610/LV, EDS as well as elemental mapping images were acquired. X-ray photoelectron spectroscopic (XPS) studies were conducted through Physical Electronics, PHI

5000 VersaProbe III. Further, flame atomic absorption spectrometer (model no. N3180021 PinAAcle 500) was employed to estimate the copper content in nanocatalyst utilizing an acetylene flame. Moreover, the N_2 adsorption-desorption isotherm was measures using NOVA touch 4LX [s/n:1050020628] surface area analyzer instrument at liquid nitrogen temperature (77.35 K). The specific surface area was obtained by Brunauer–Emmett–Teller (BET) equation and the pore width distribution was calculated using Barrett–Joyner–Halenda (BJH) method. Finally, the ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra of synthesized organic compounds/products were recorded using a JEOL JNM-AXCP 400.

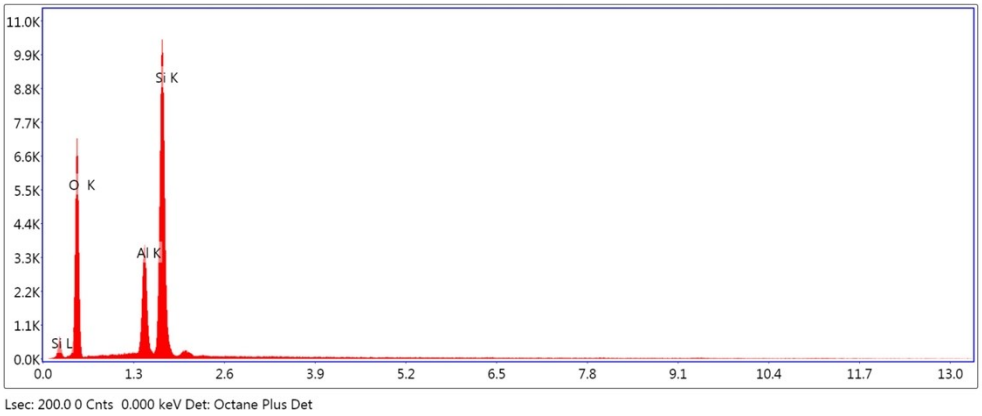


Fig S1. EDS spectra of HNTs.

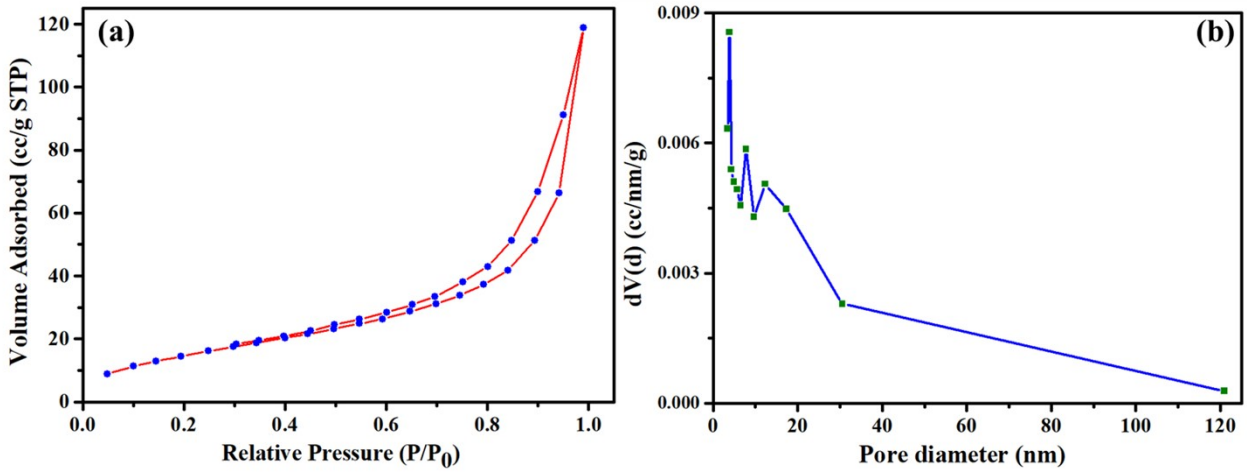


Fig S2. (a) N_2 adsorption-desorption isotherms and (b) the pore width distribution curve obtained using the BJH method.

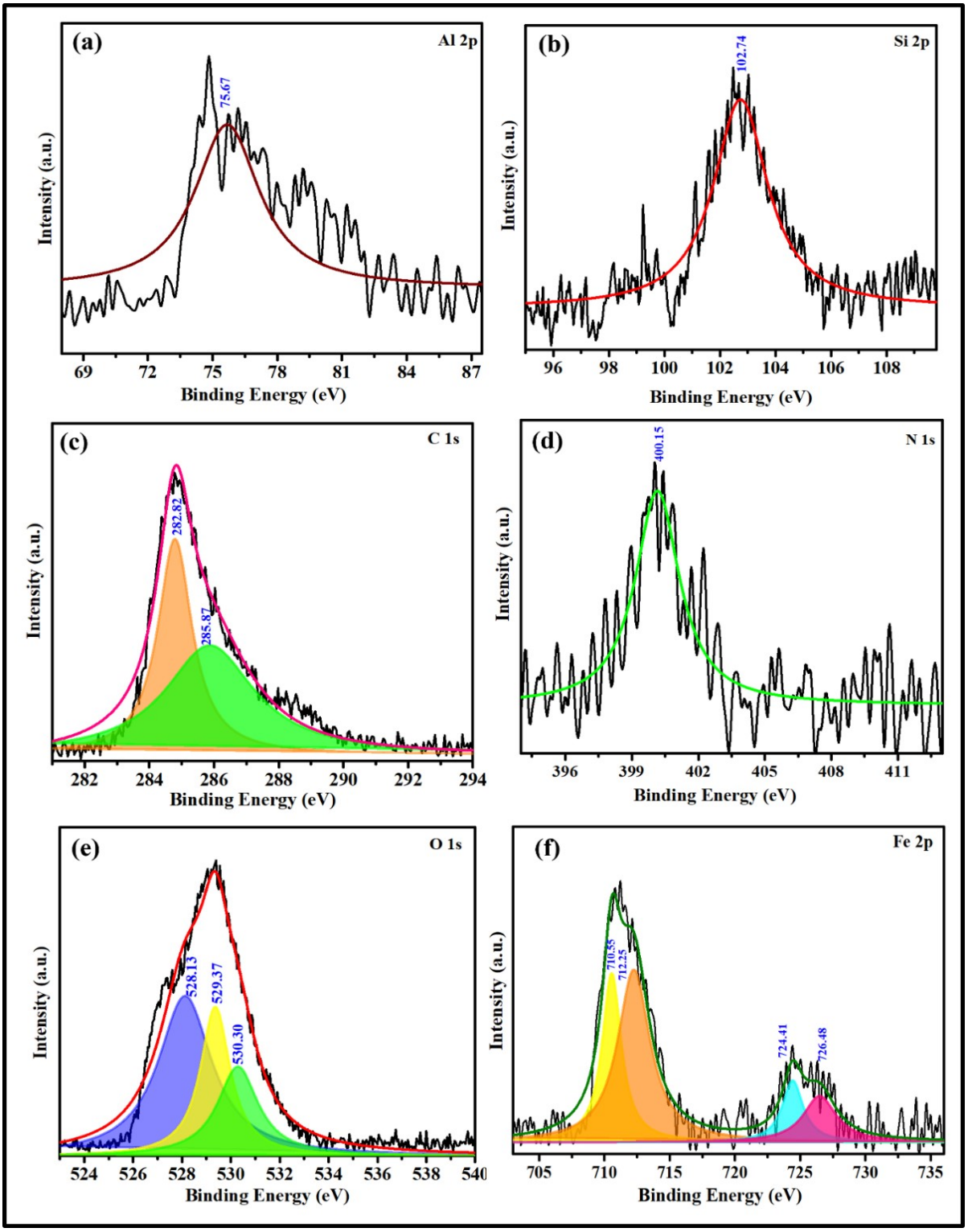


Fig S2. Core level XPS spectra of (a) Al 2p (b) Si 2p, (c) C 1s (d) N 1s (e) O 1s and (f) Fe 2p.

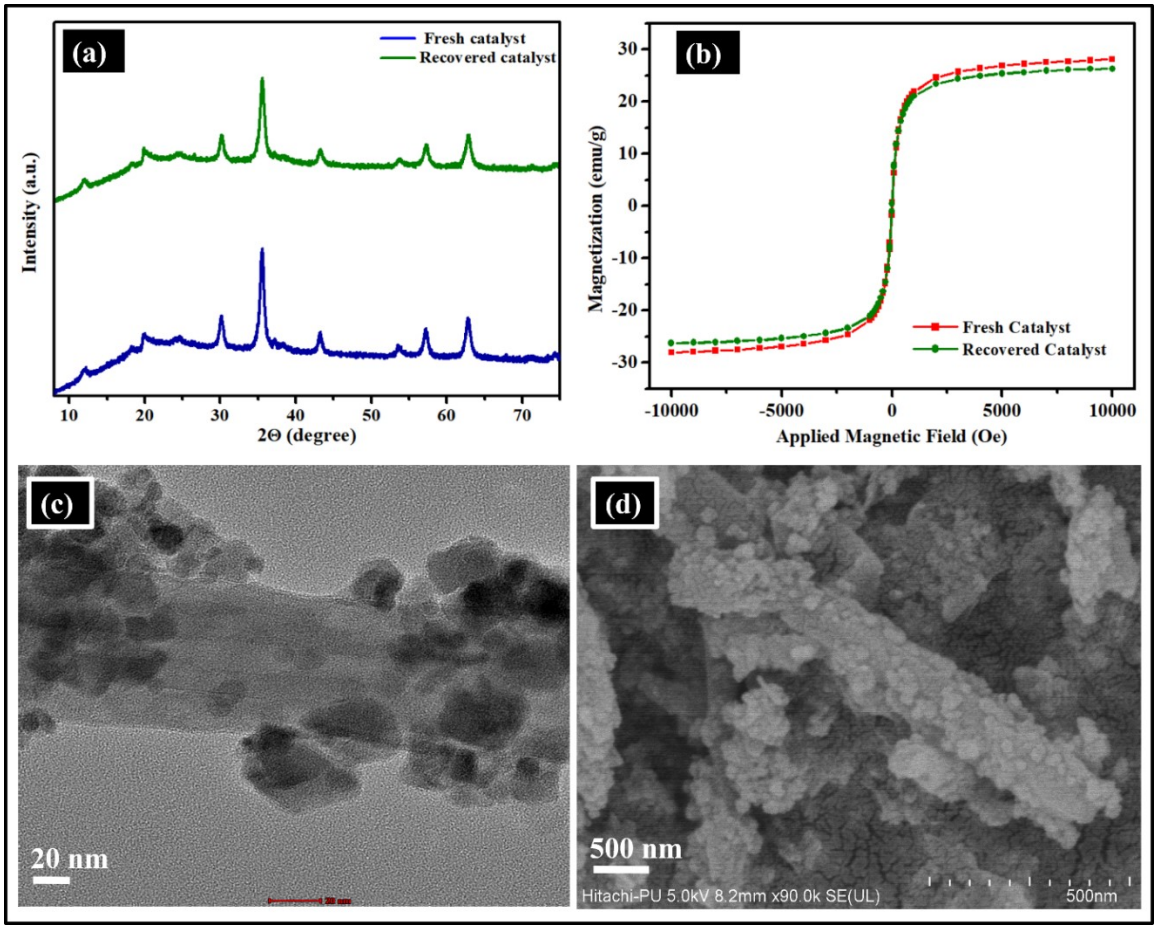


Fig S3. (a) XRD, (b) VSM, (c) TEM and (d) FE-SEM analysis of the recovered Cu(II)@DCH@CPTMS@MHNTs after fifth run.

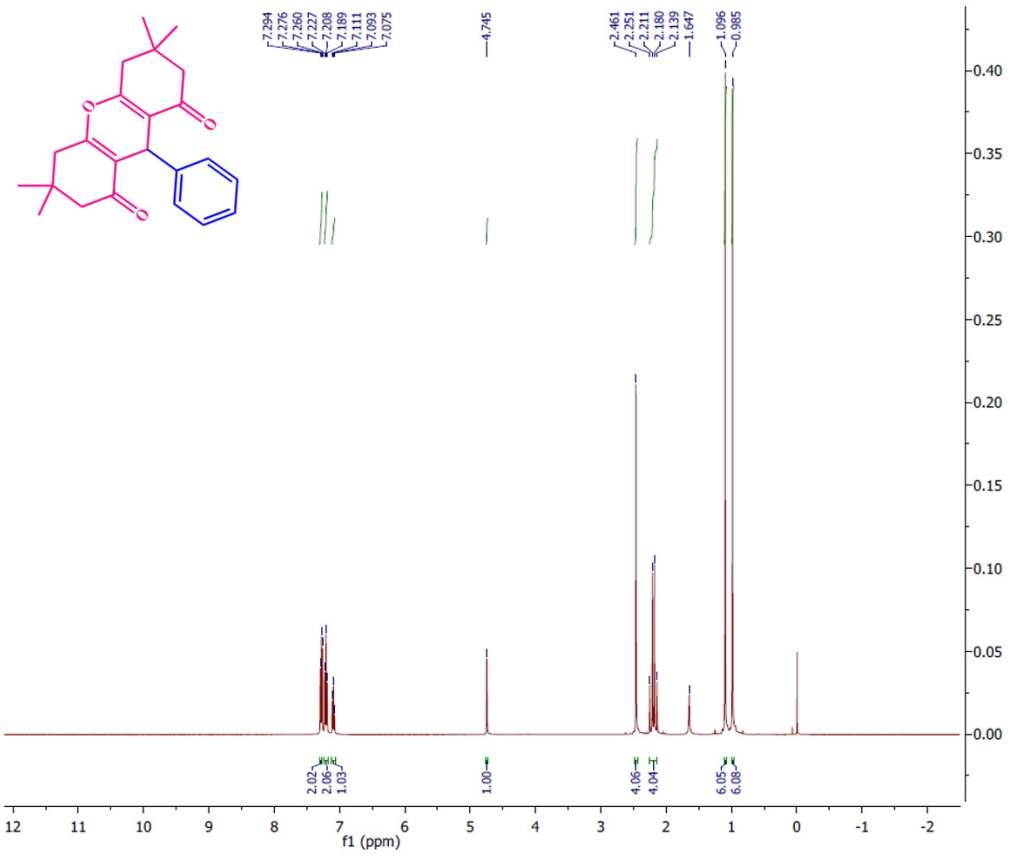
Table S1 Screening of catalyst[a]

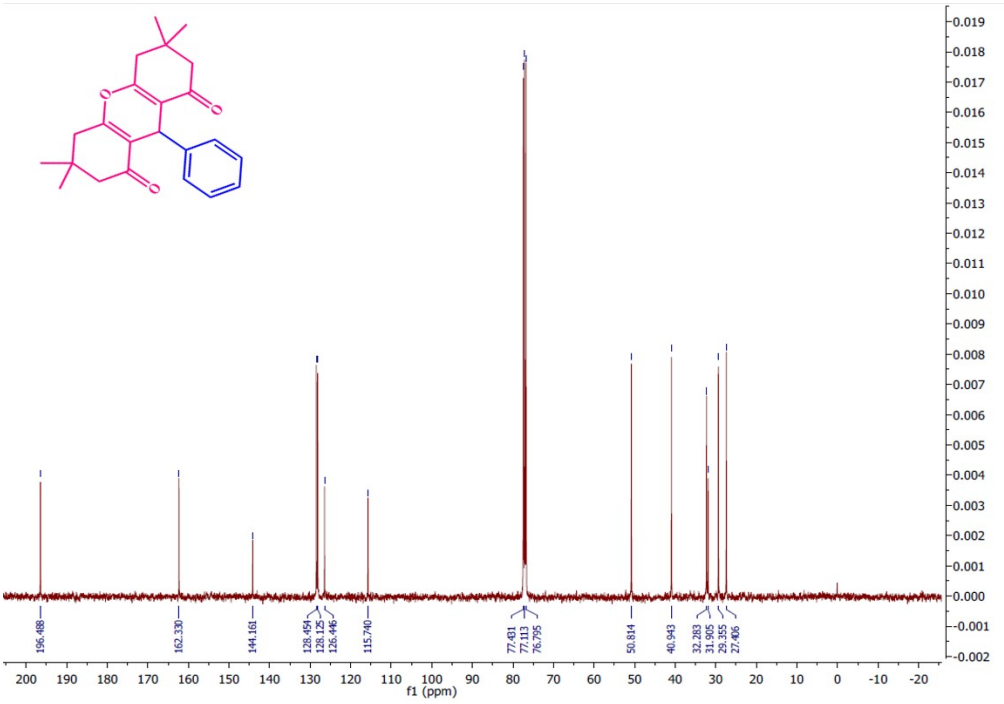
Entry No	Catalyst	Yield[b] (%)
1.	No catalyst	trace
2.	HNTs	trace
3.	MHNTs	23
4.	CPTMS@MHNTs	15
5.	DCH@CPTMS@MHNTs	trace
6.	Cu(II)@DCH@CPTMS@MHNTs	97

[a]Reaction conditions: dimedone (2 mmol), benzaldehyde (1 mmol), catalyst (15 mg), EtOH: H_2O (1:1, 3mL), stirring, 40 °C, 20 min. [b]Isolated yield.

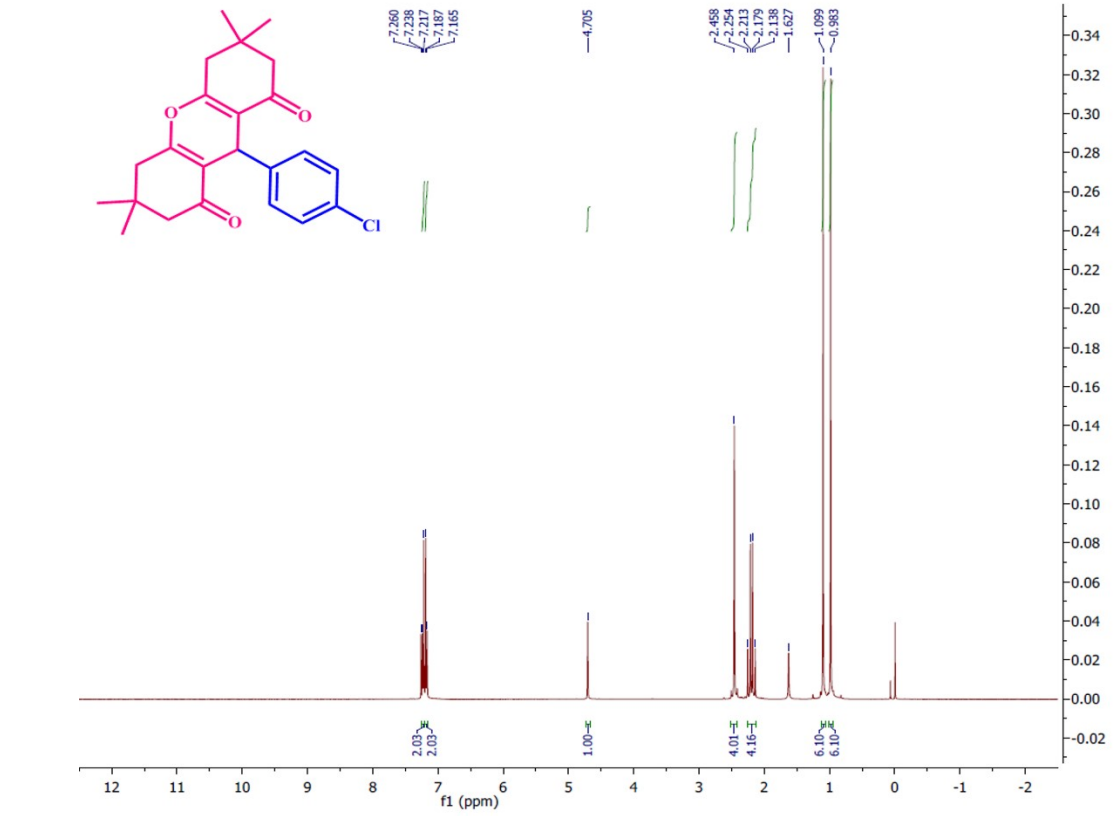
^{1}H and ^{13}C spectra of compounds

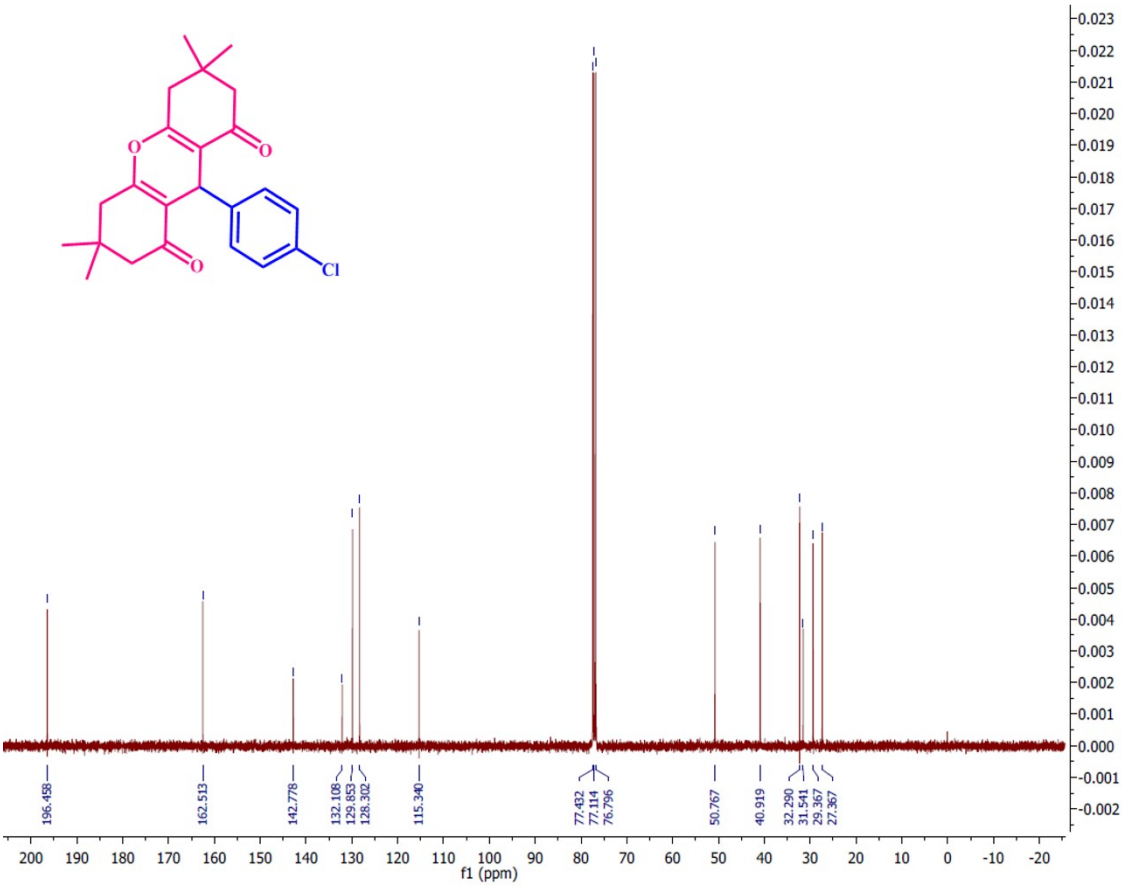
3a, 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



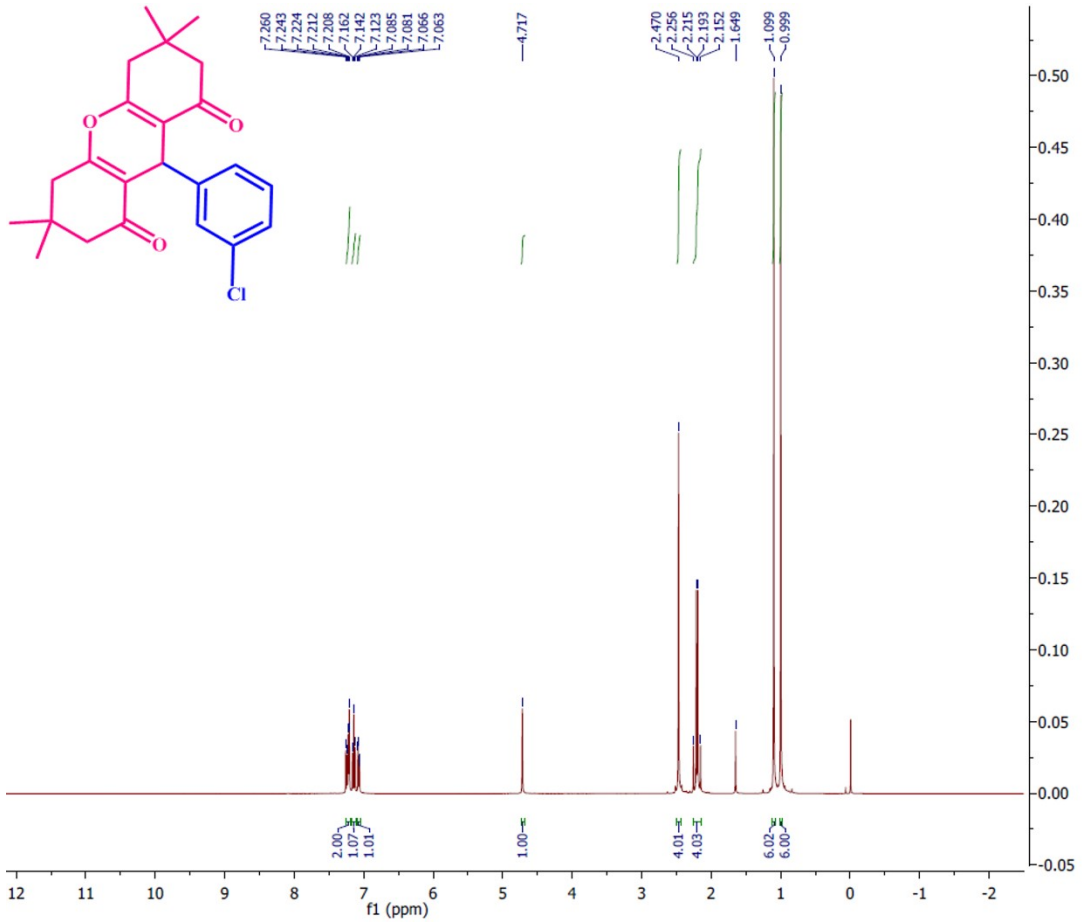


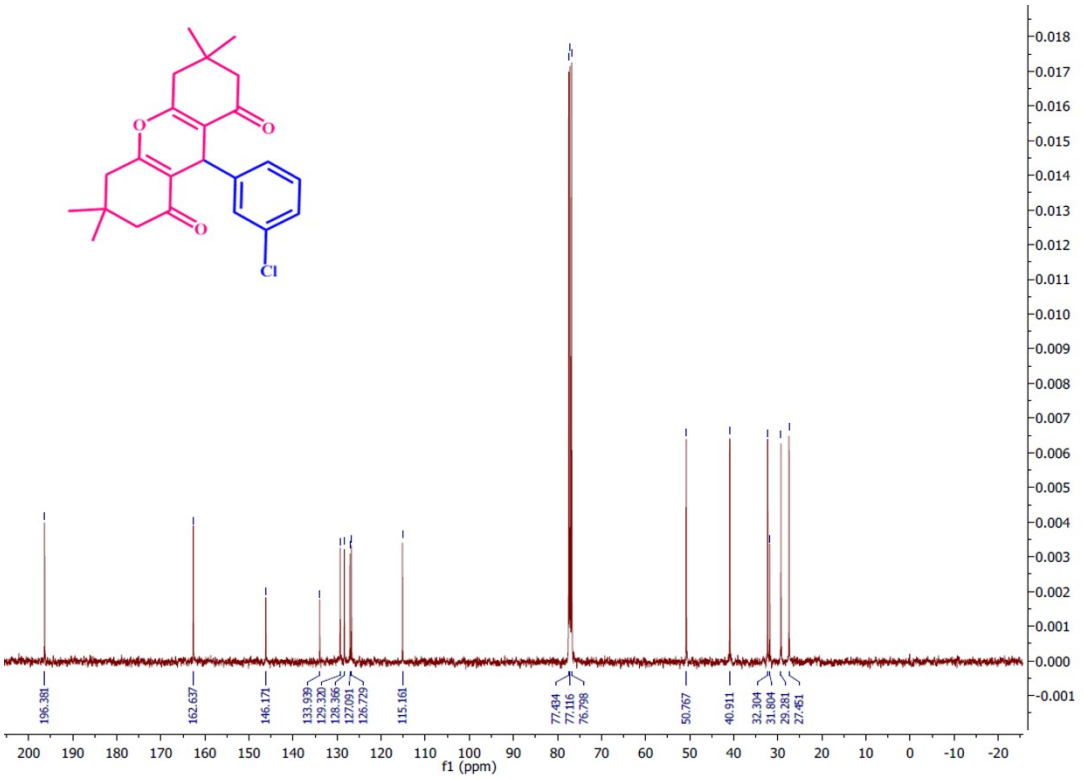
3b, 9-(4-chlorophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



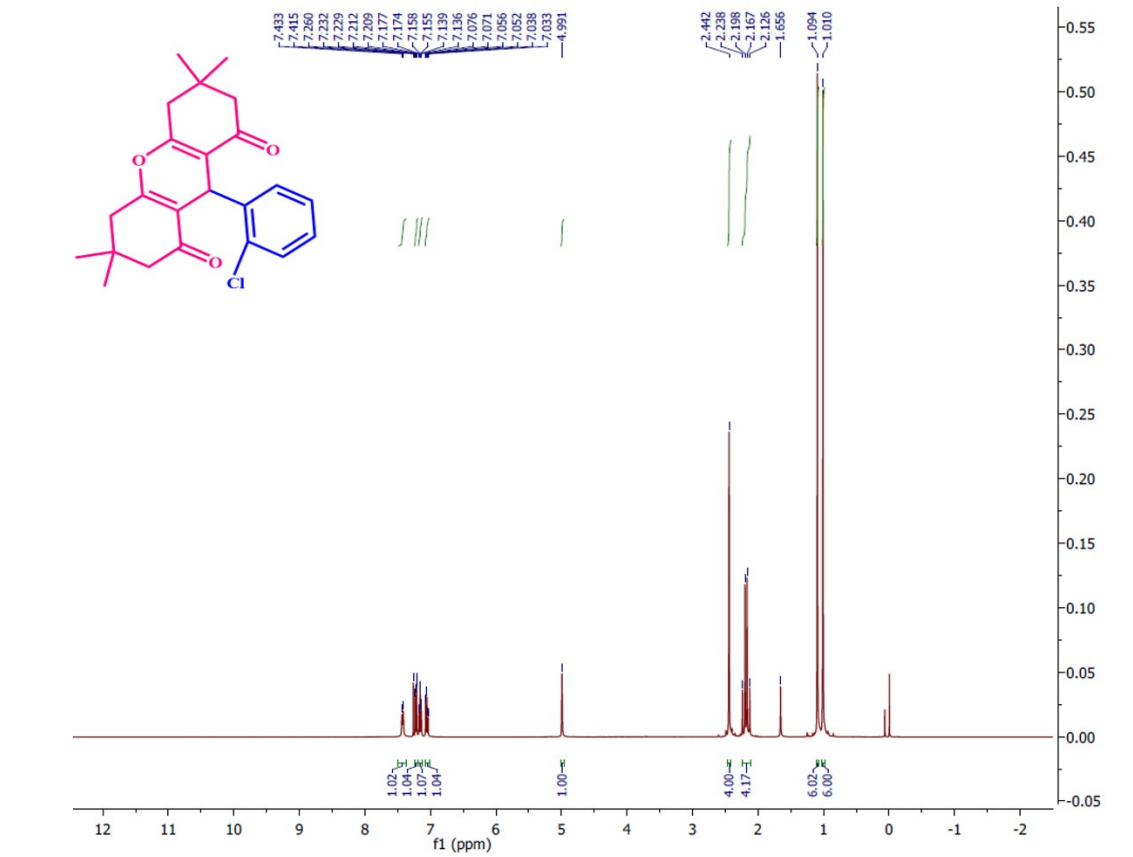


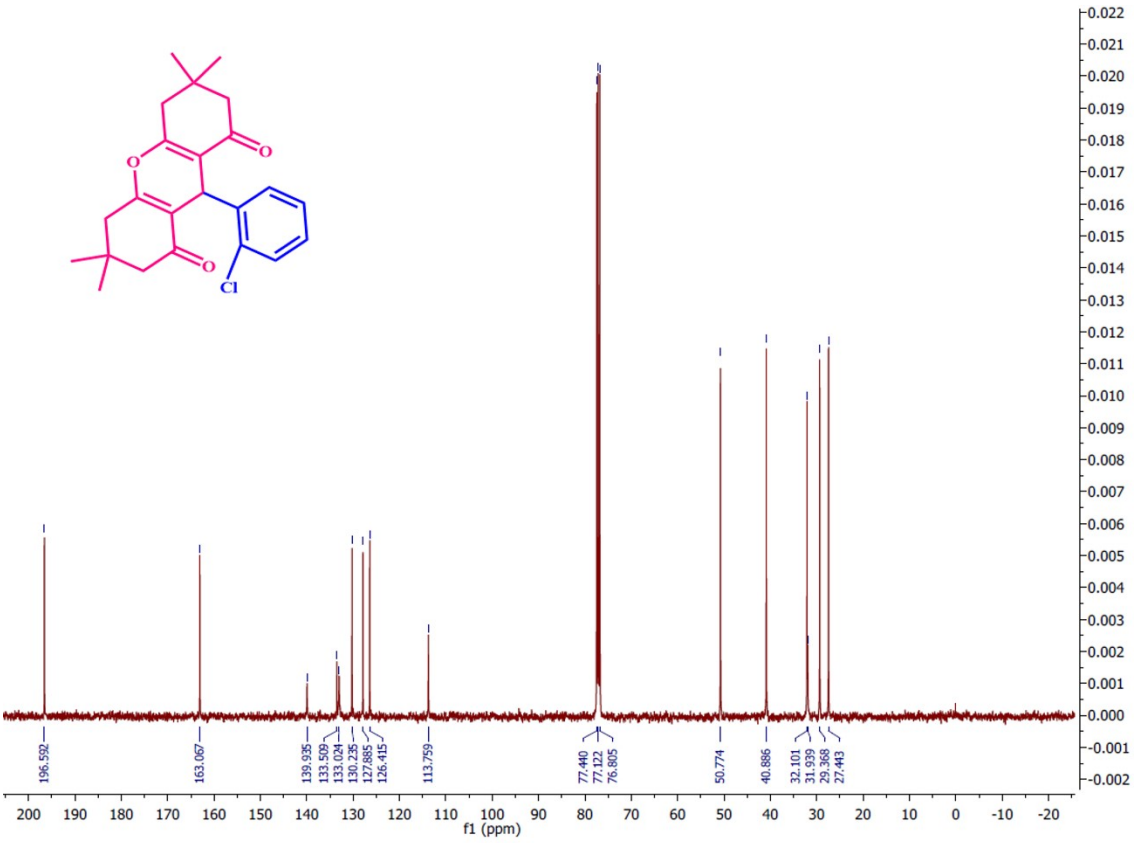
3c, 9-(3-chlorophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



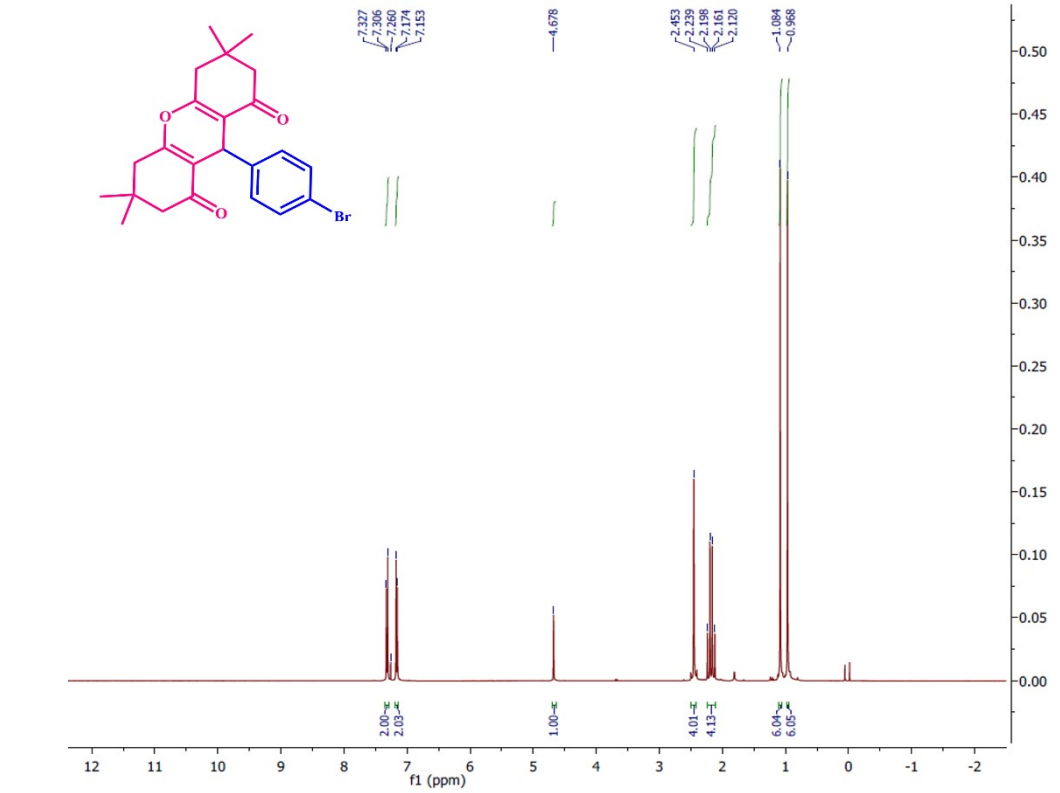


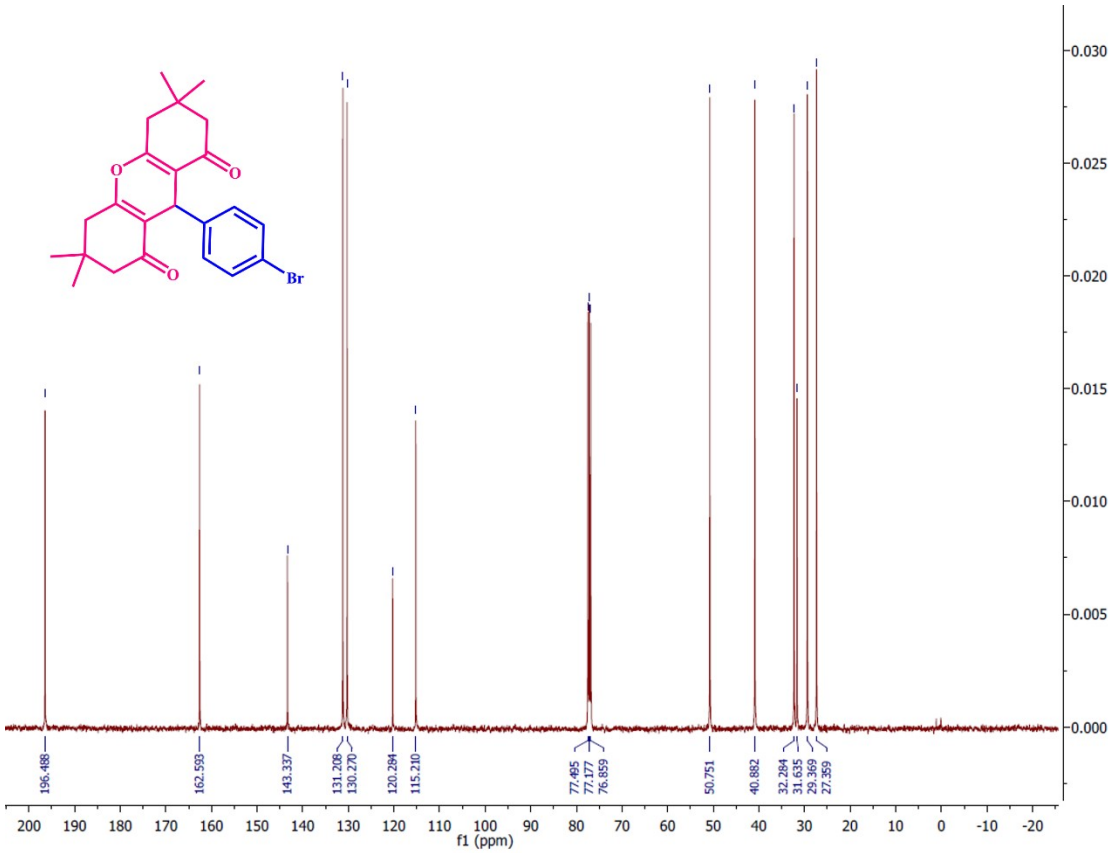
3d, 9-(2-chlorophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



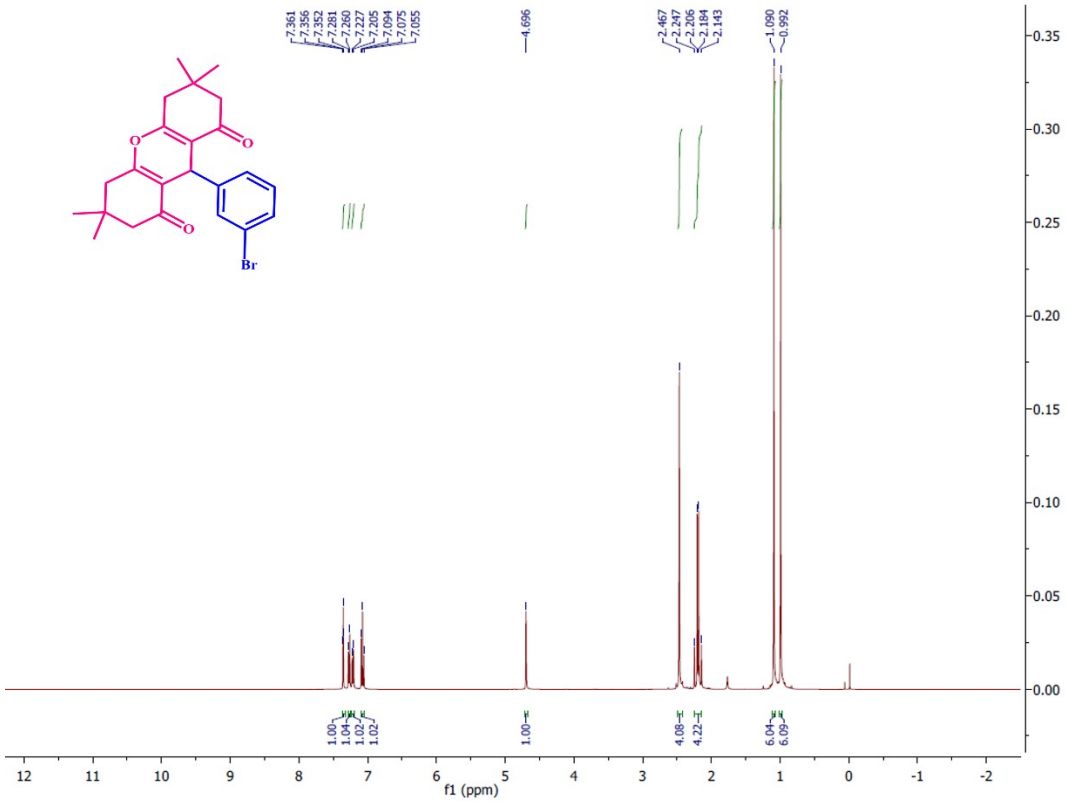


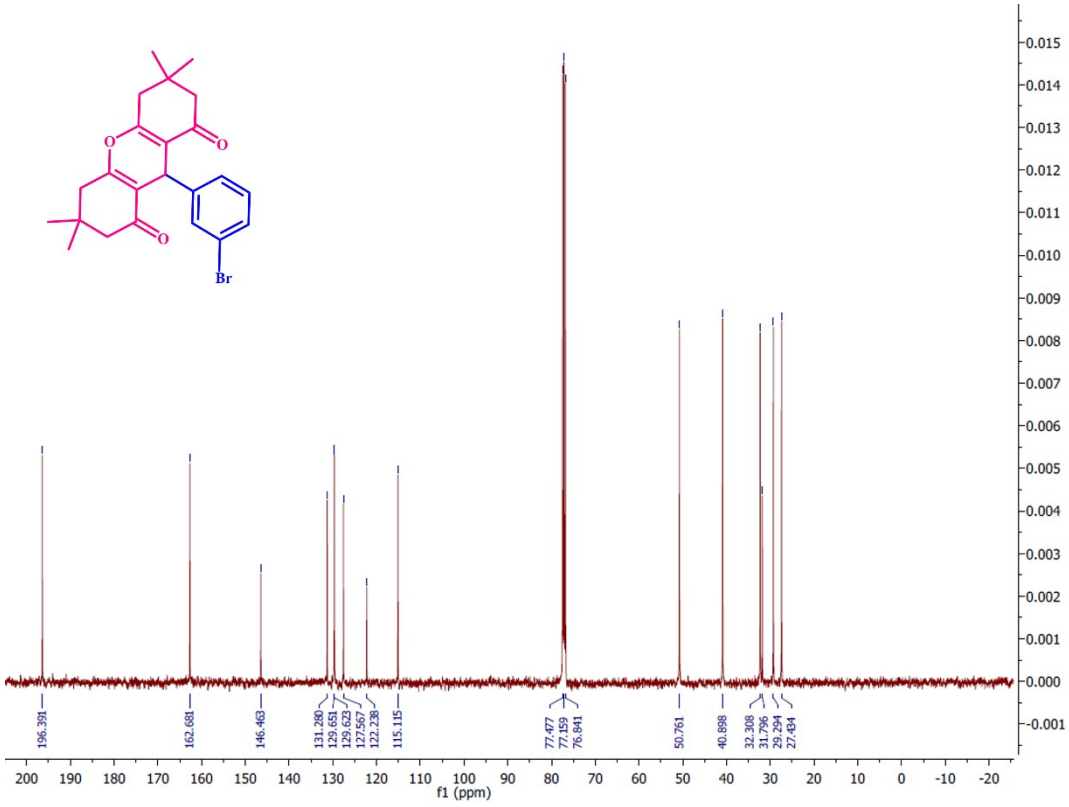
3e, 9-(4-bromophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.





3f, 9-(3-bromophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.





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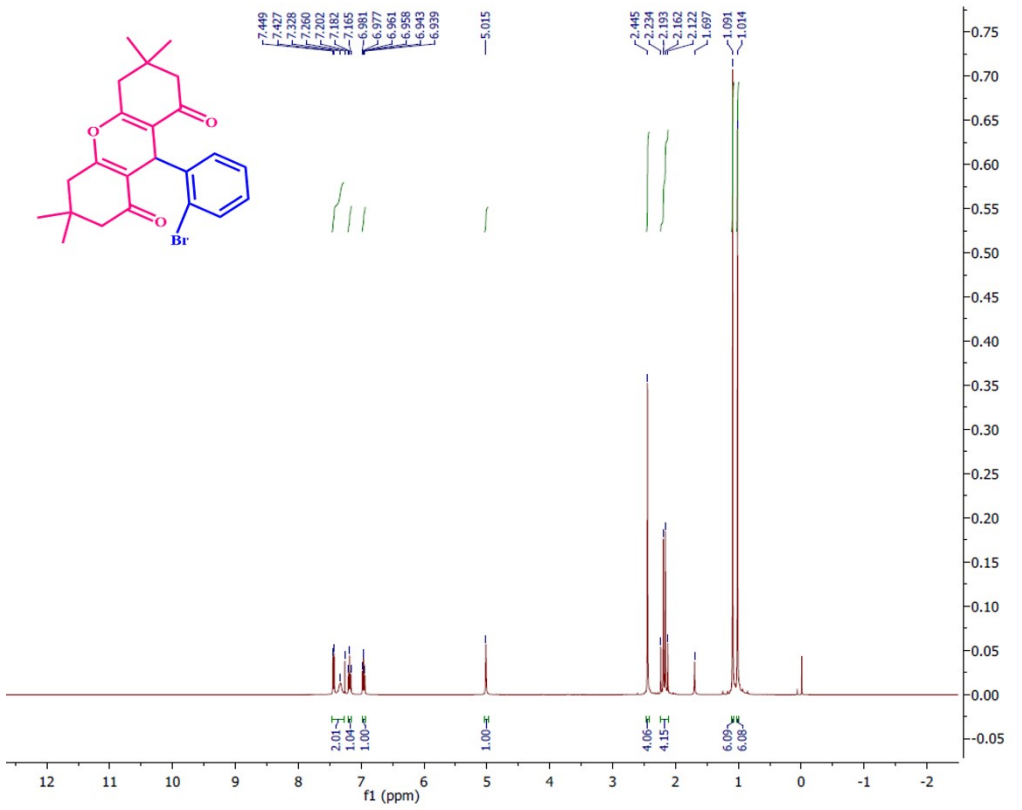
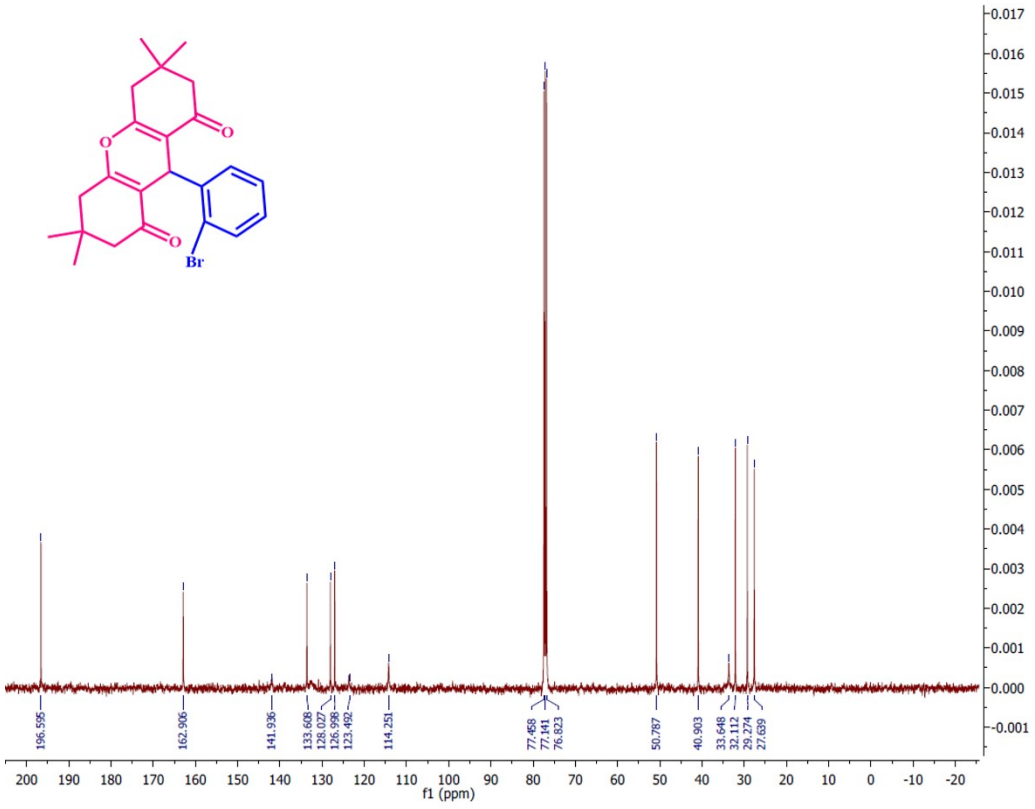
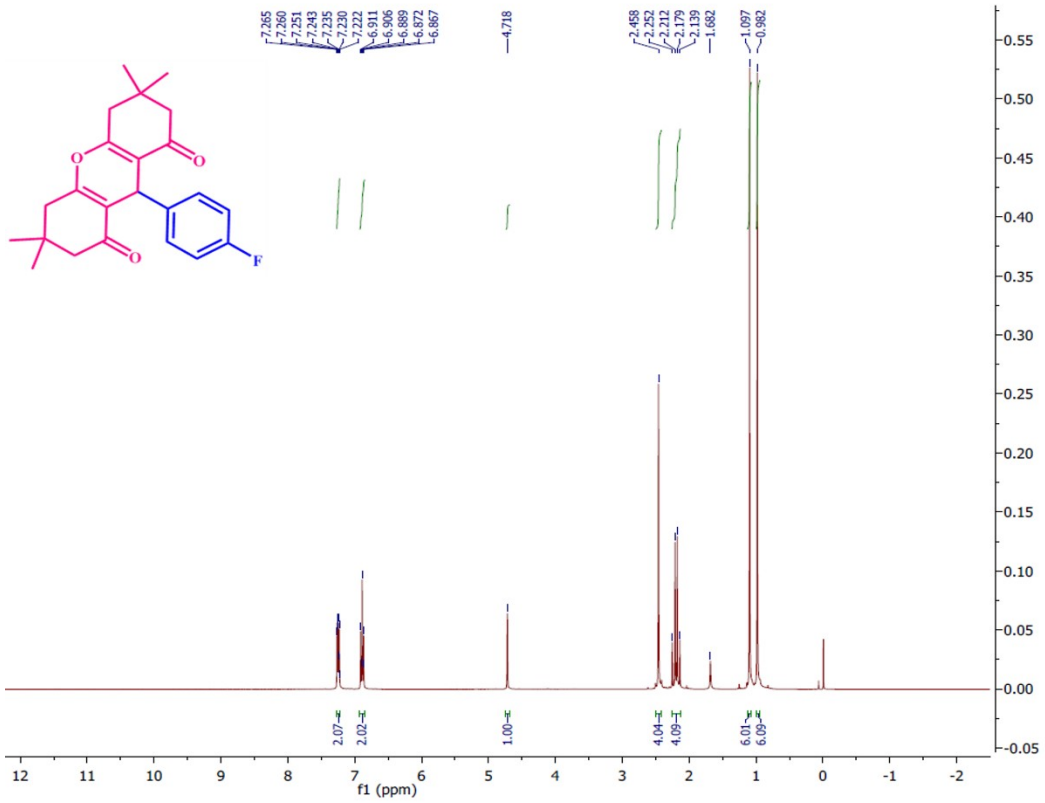
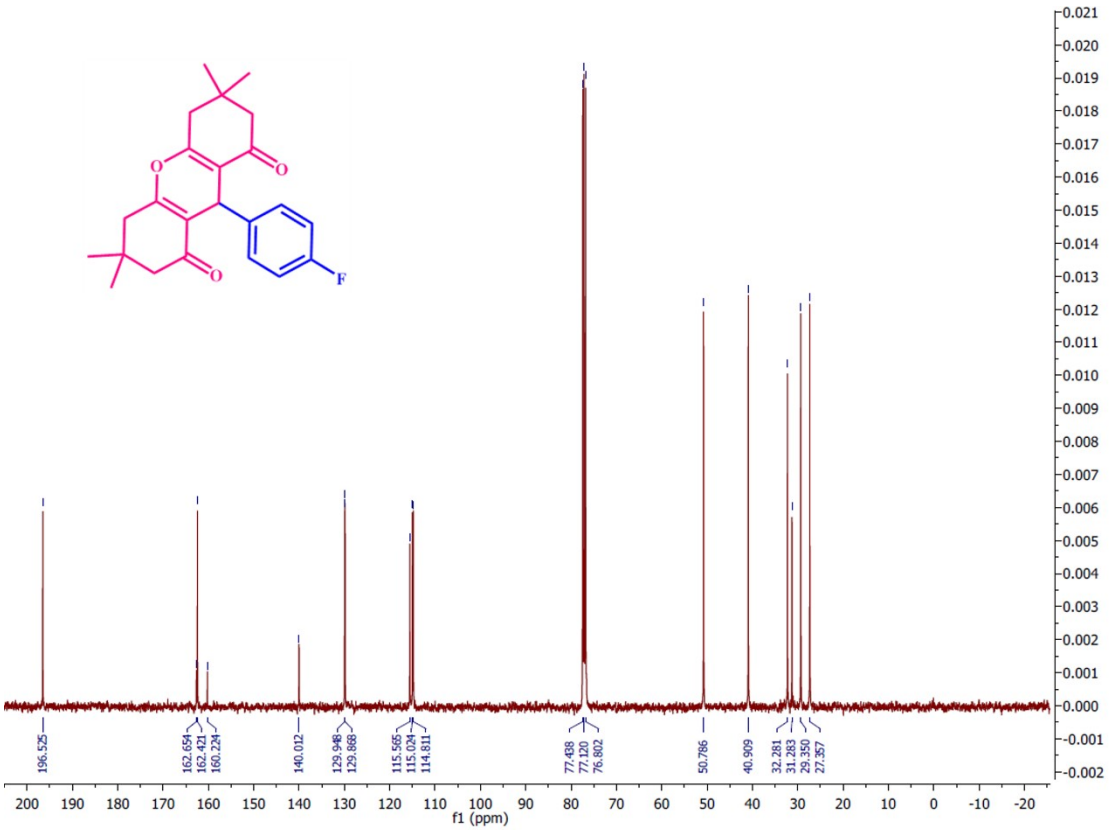


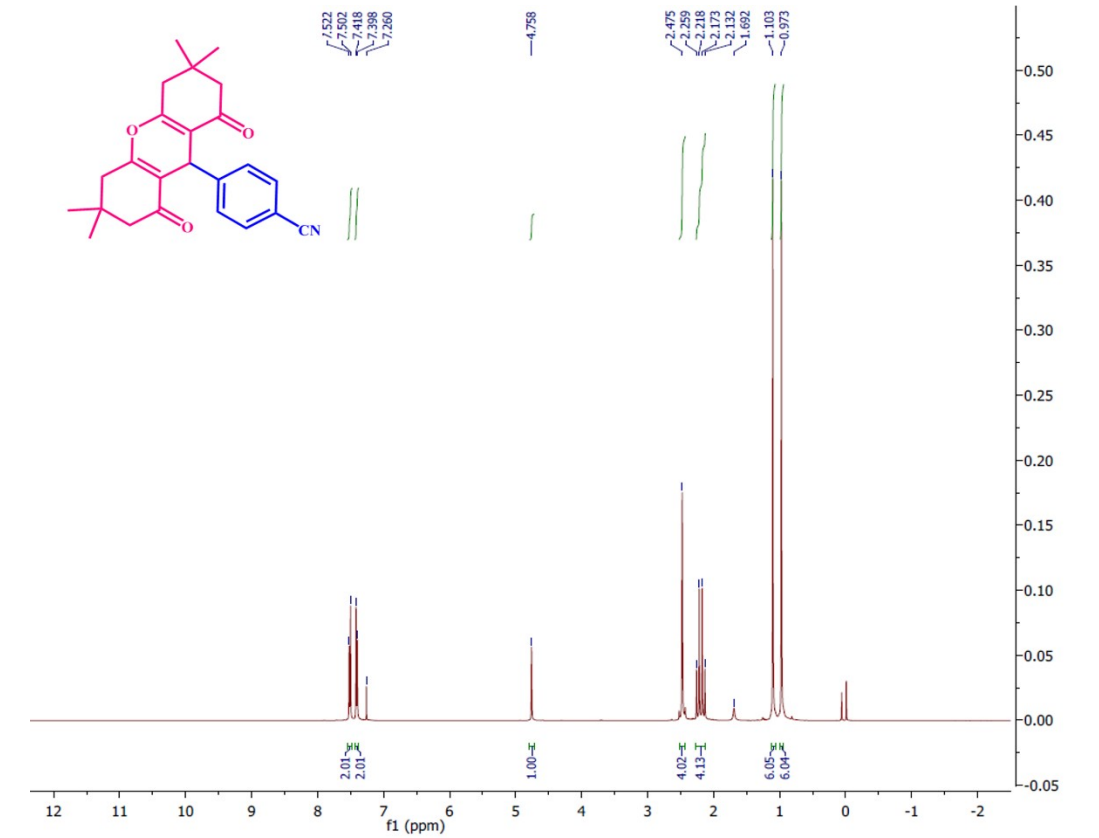


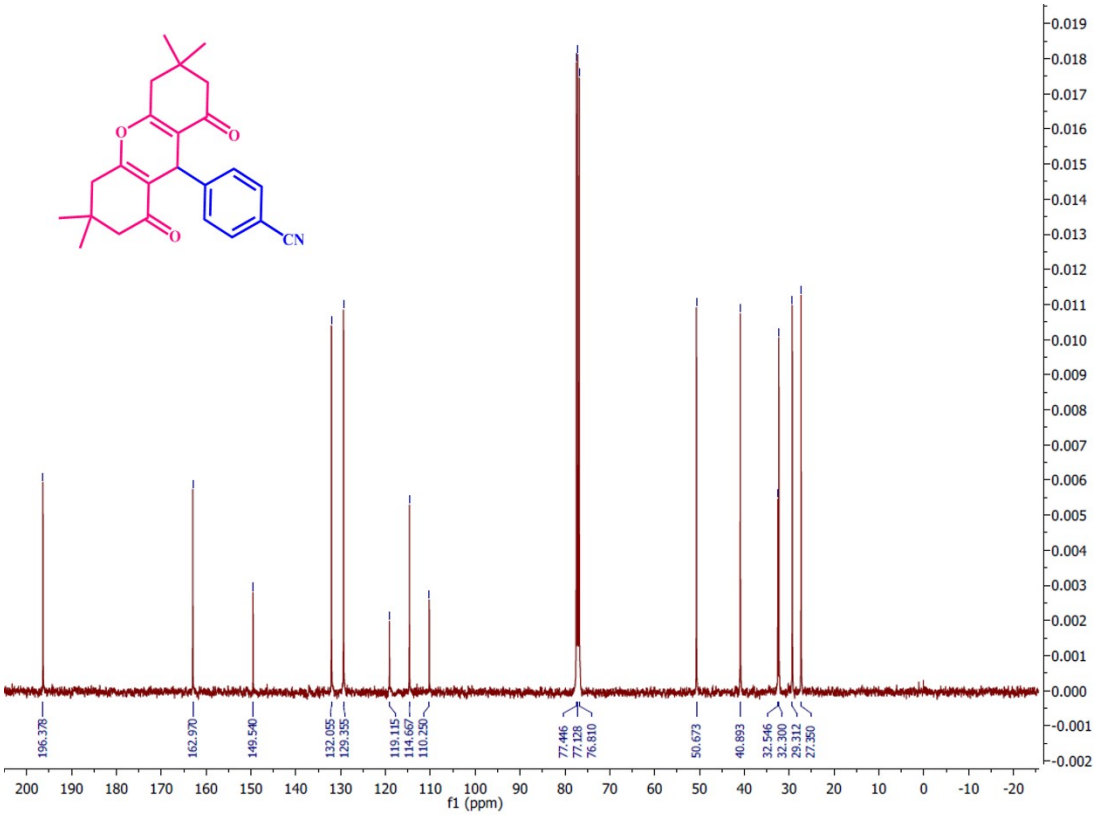
3h,9-(4-florophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



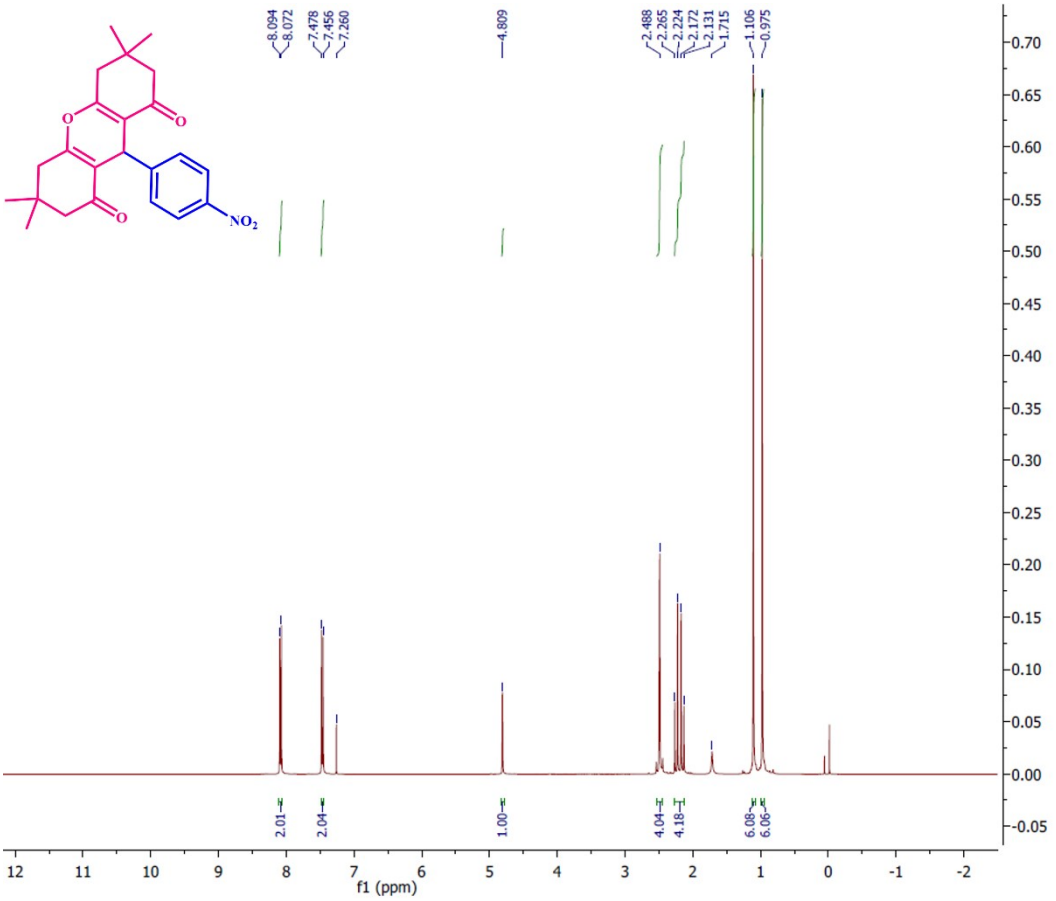


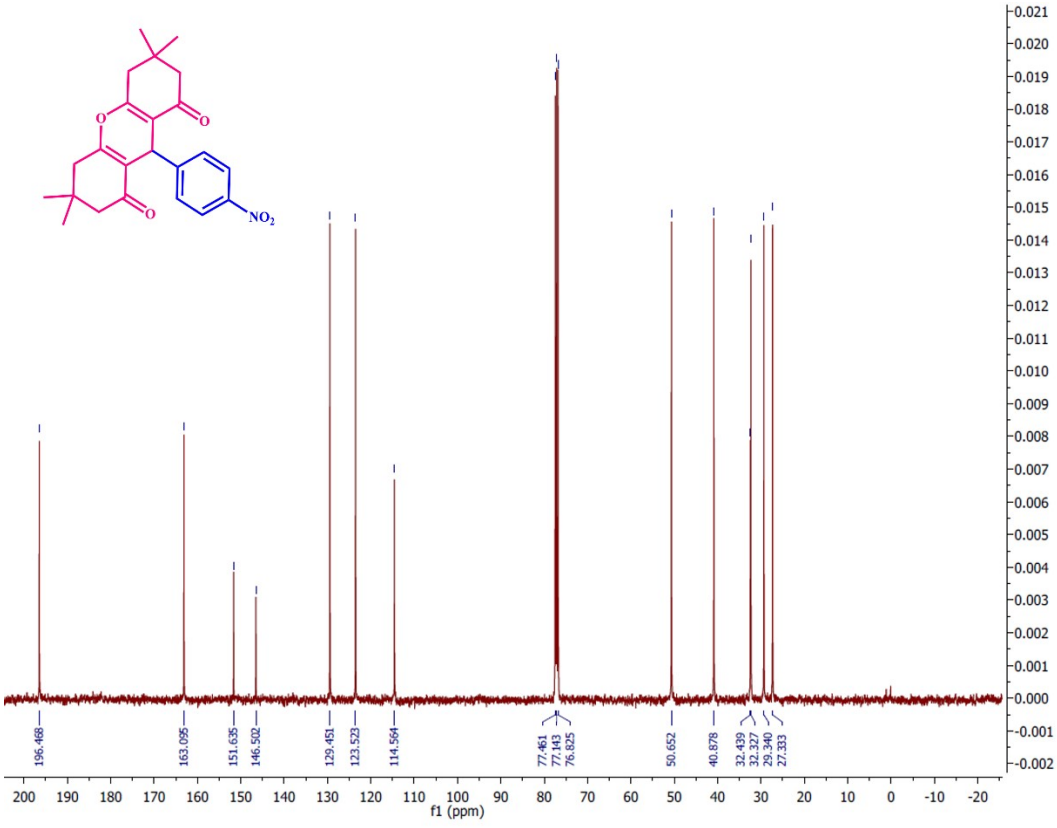
3i,9-(4-formylbenzonitrile)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



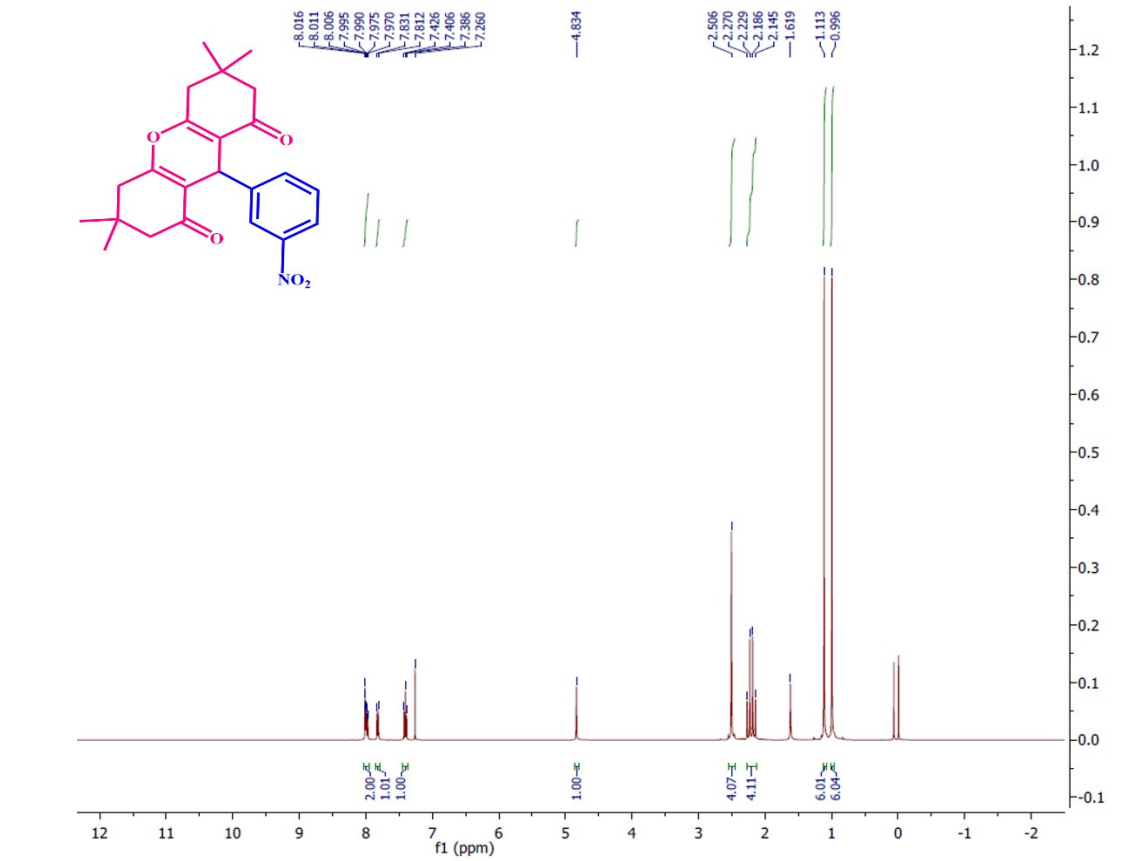


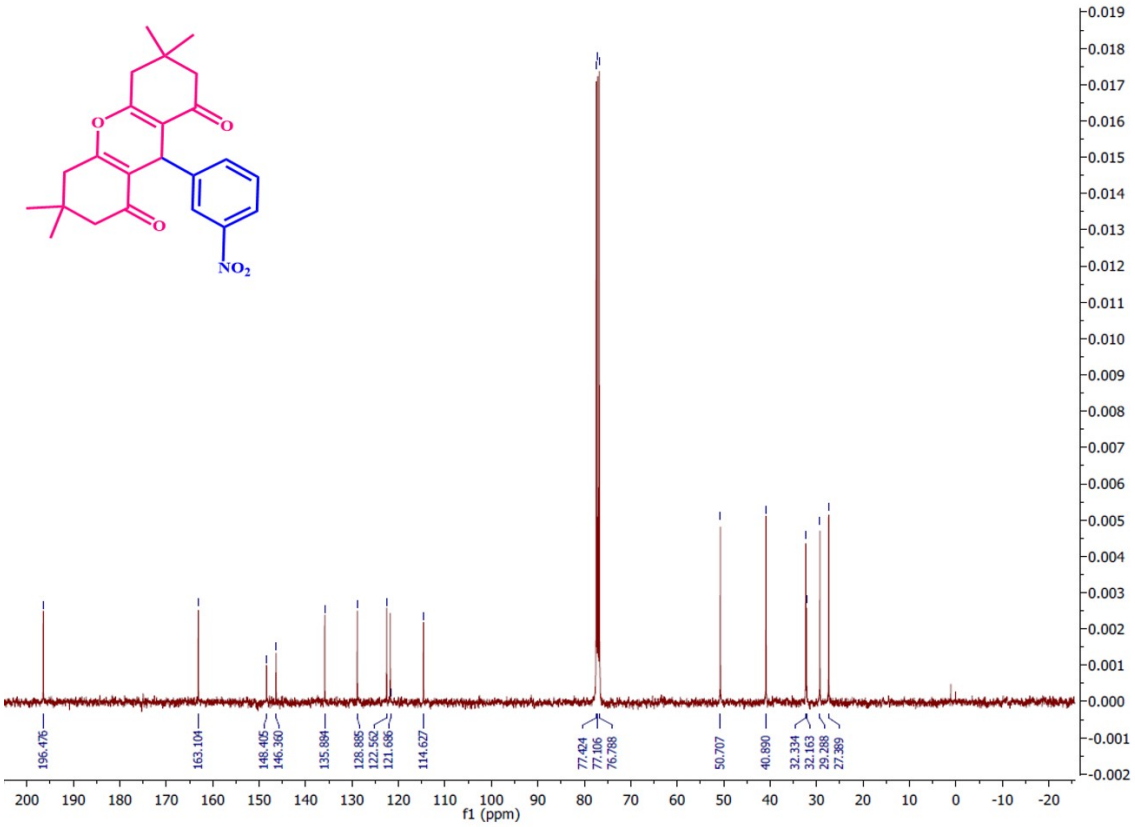
3j,9-(4-nitrophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



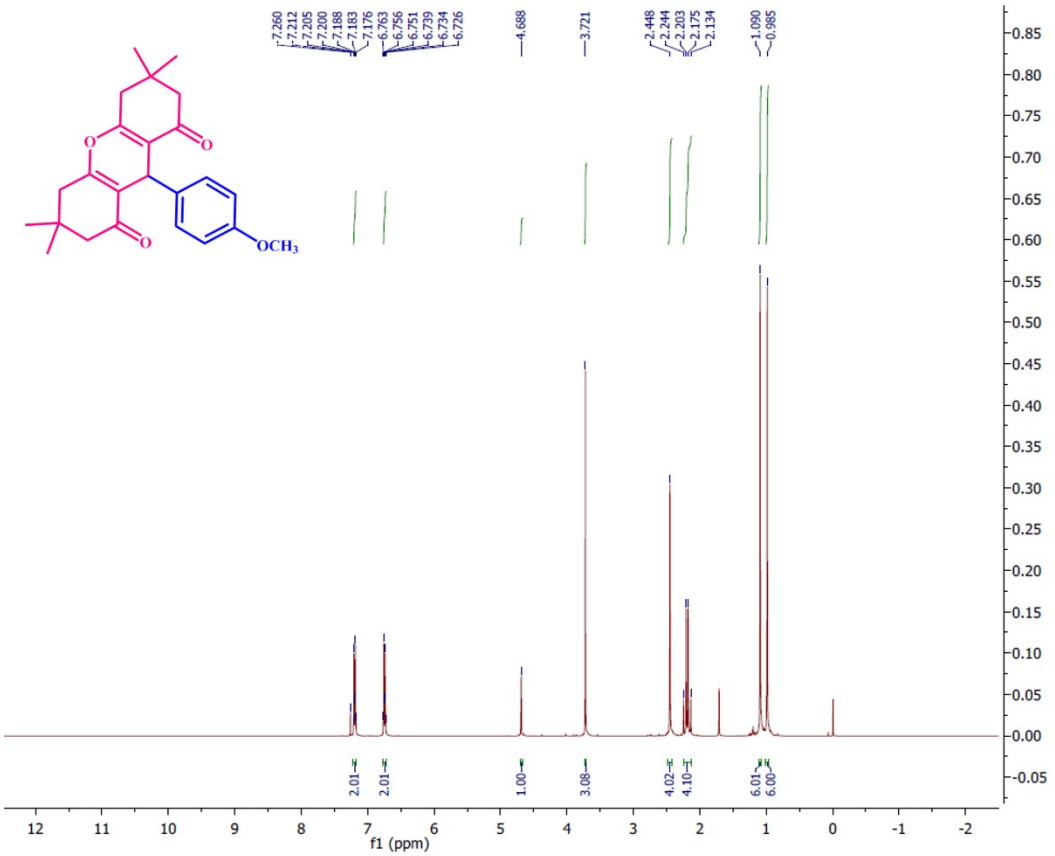


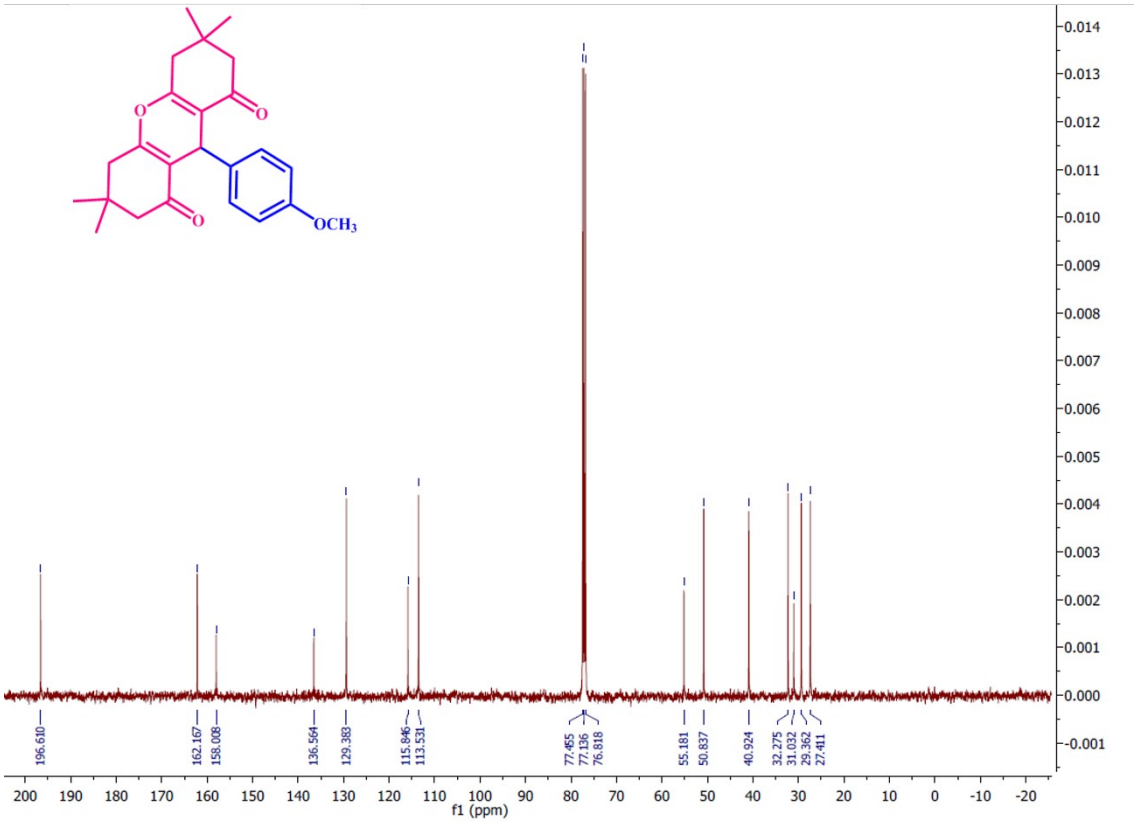
3k,9-(3-nitrophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.





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





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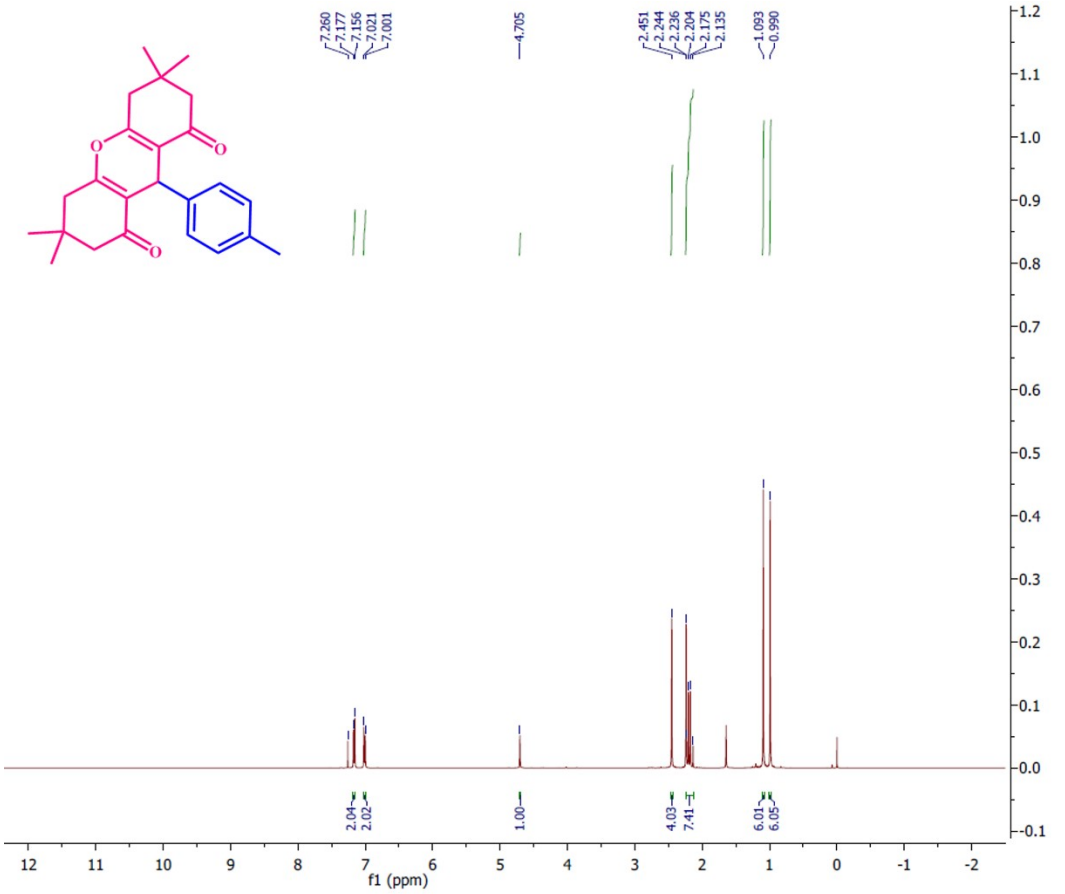
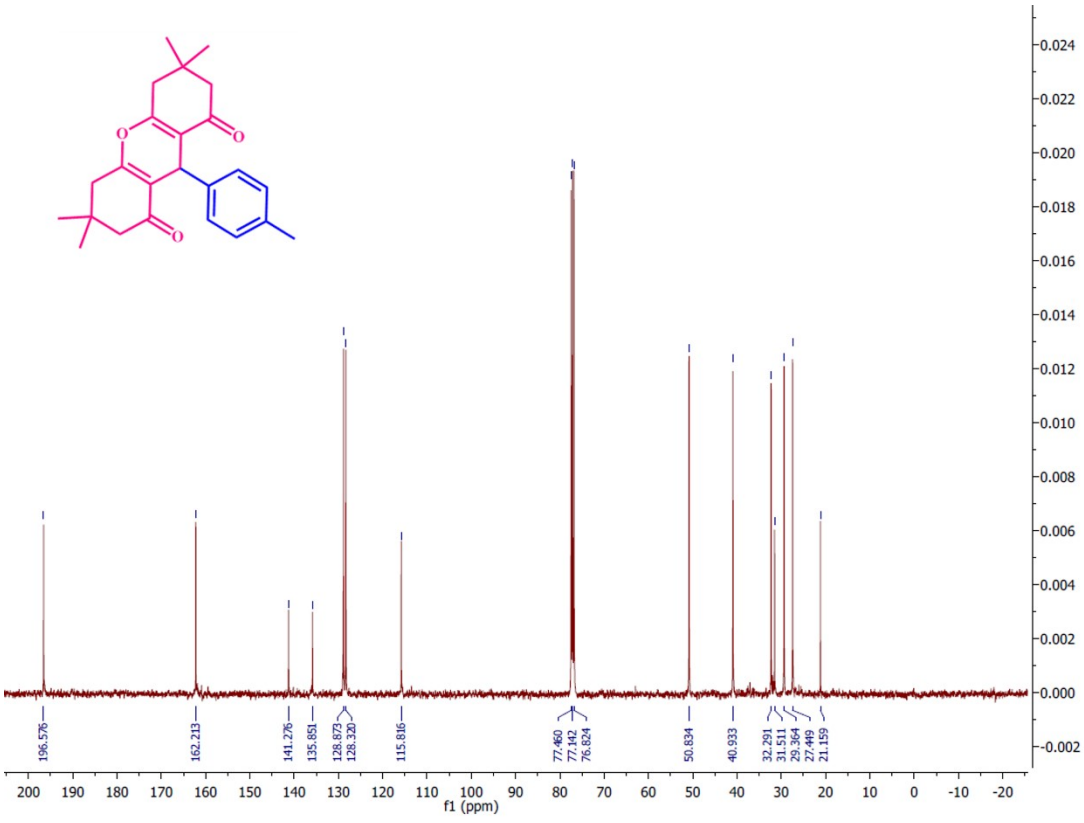
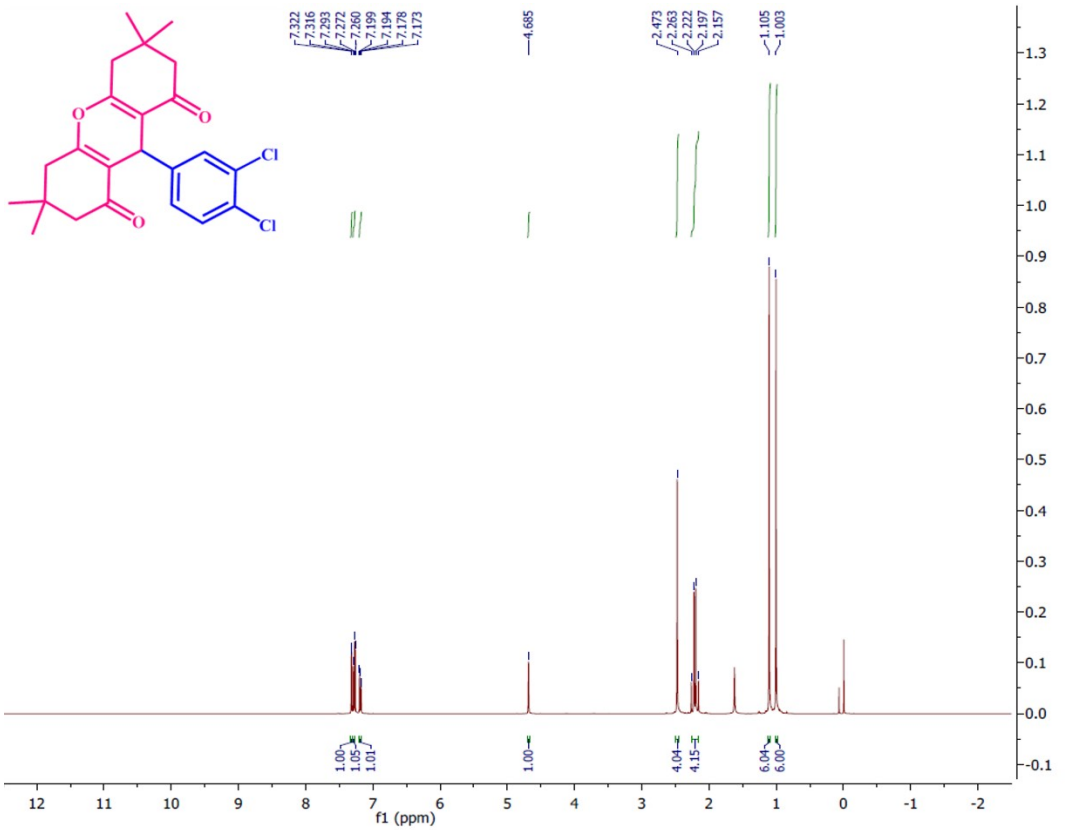
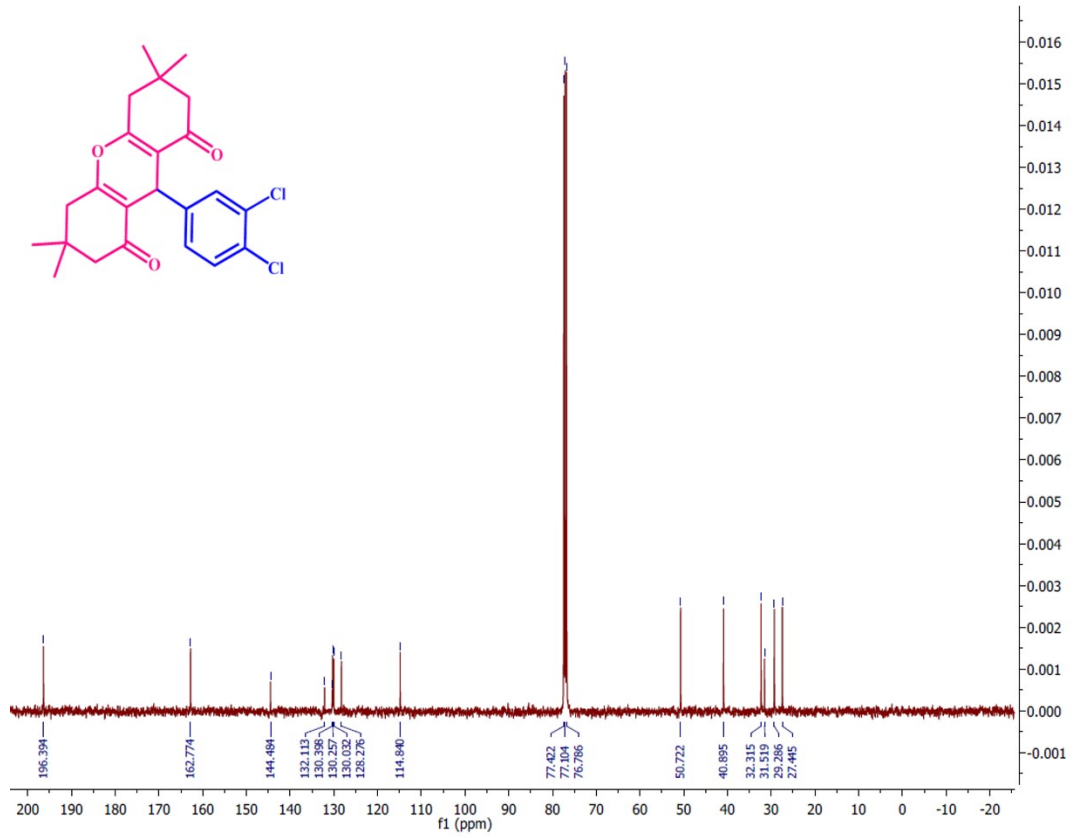


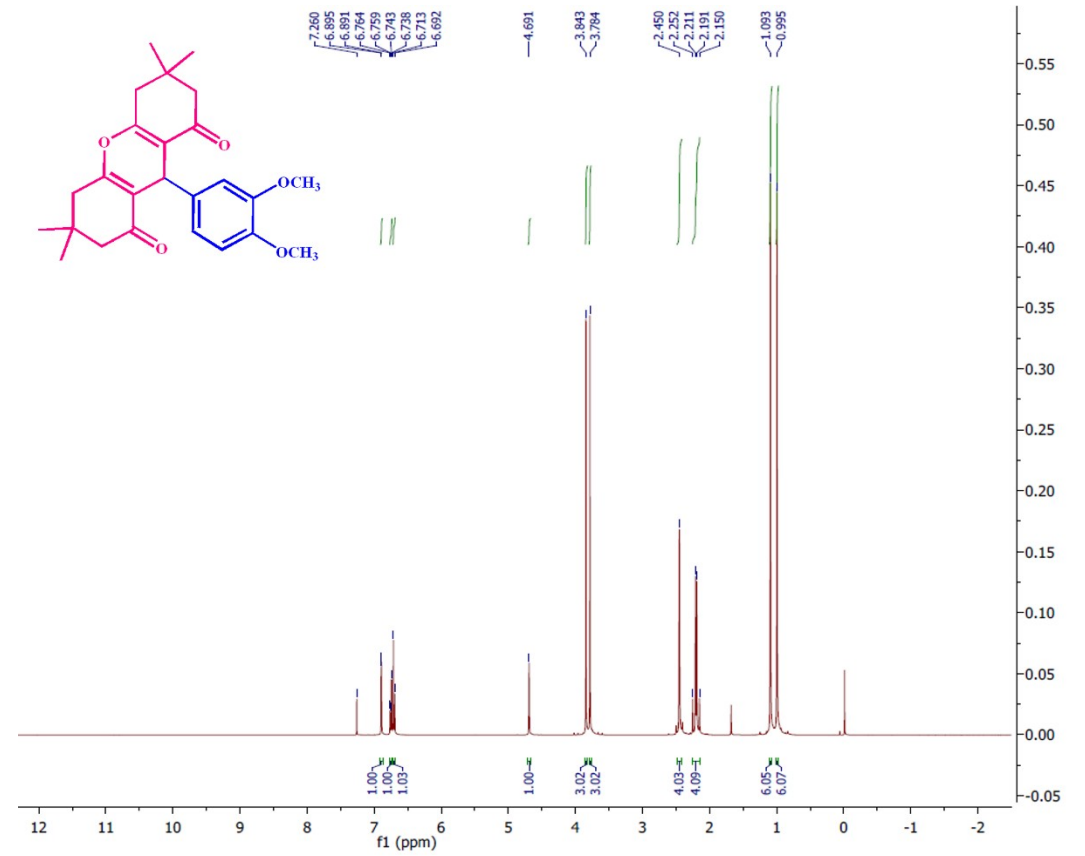


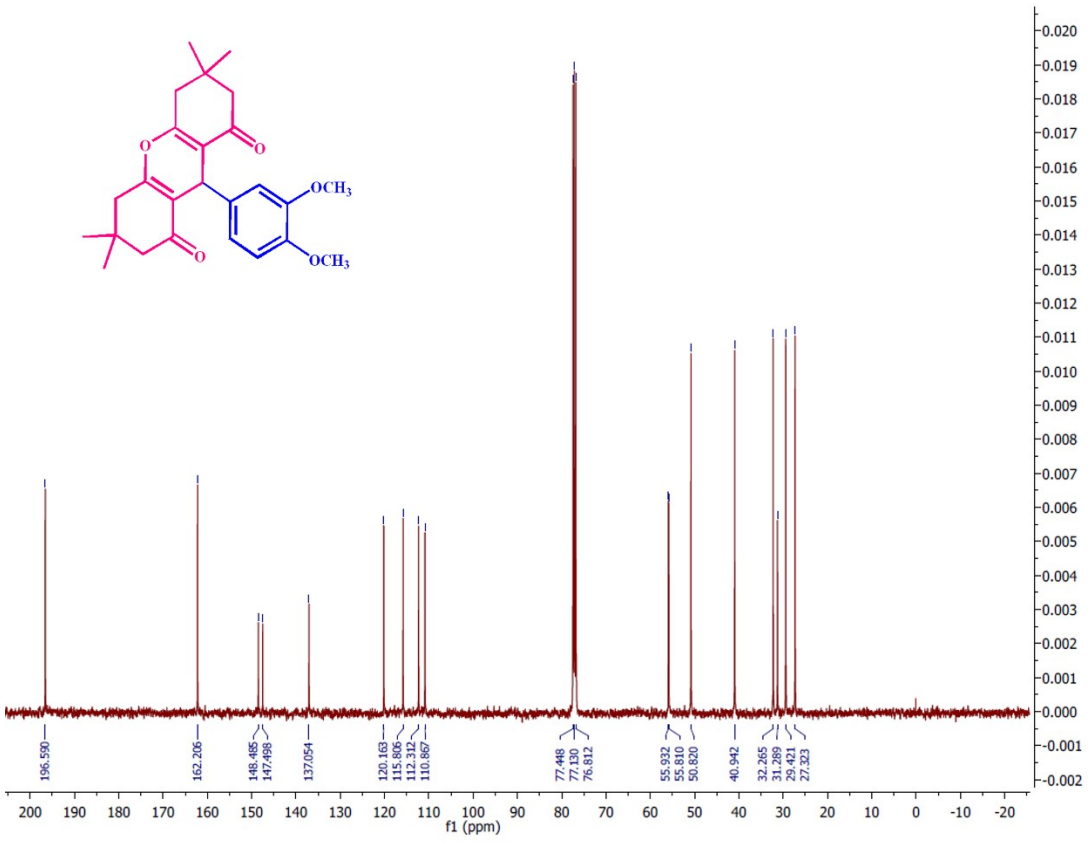
3n,9-(3,4-dichlorophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.



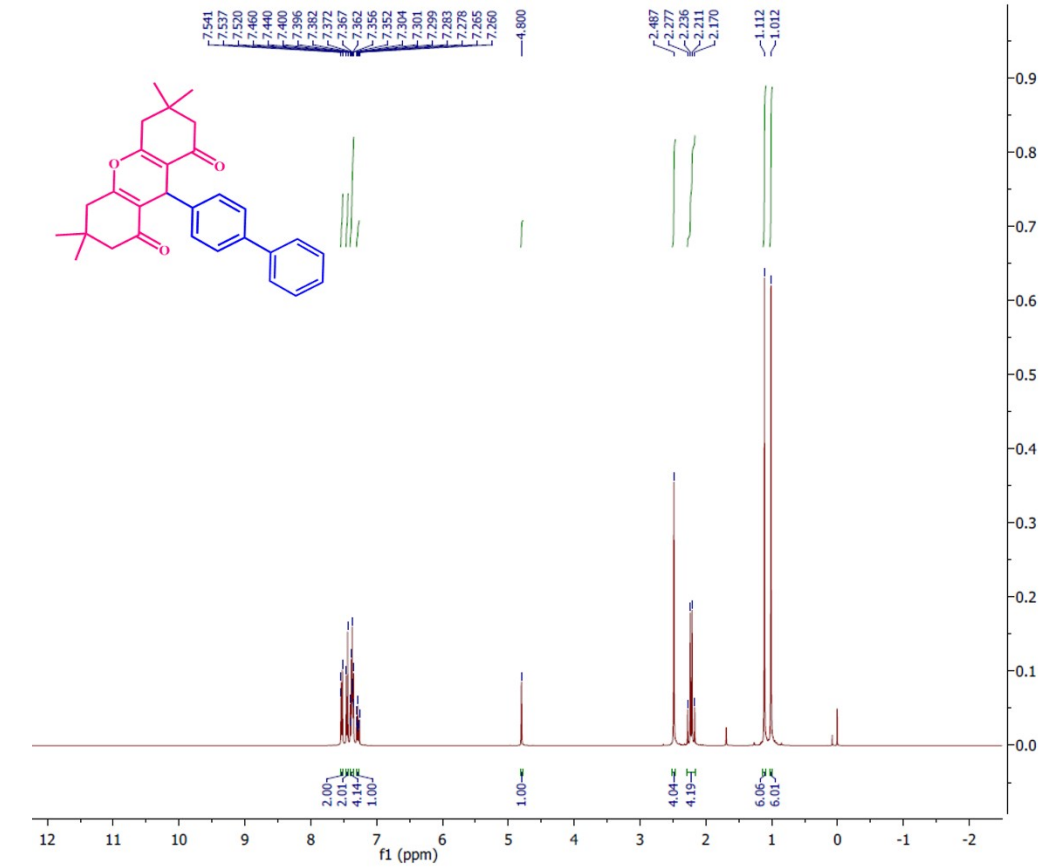


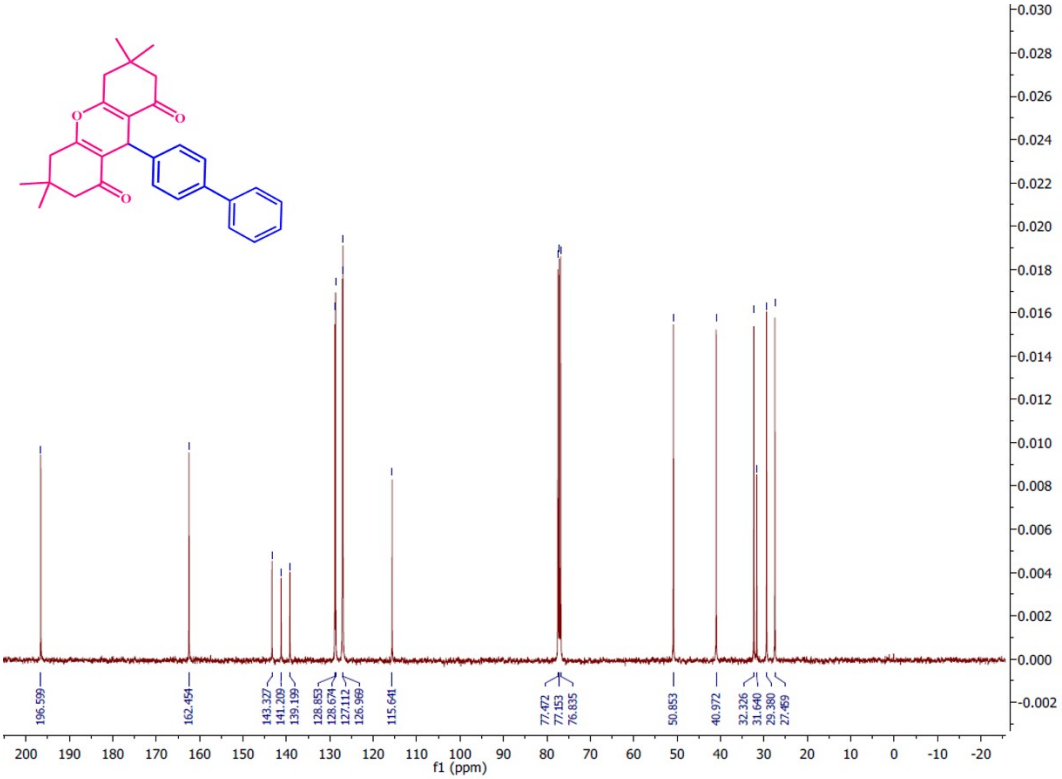
3o,9-(3,4-dimethoxyphenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.





3p, 9-([1,1'-biphenyl]-4-yl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.





Data information of NMR spectra

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

White solid, ^{1}H-NMR (400 MHz,) δH ppm 7.29 (d *J* = 7.0 Hz, 2H), 7.21 (dd, *J* = 10.4, 4.9 Hz,2H), 7.12 – 7.07 (t, J= 7.3Hz, 1H), 4.74 (s,1H), 2.46 (s,4H), 2.20 (q, *J* = 16.3 Hz,4H), 1.10 (s,6H), 0.98 (s,6H); ^{13}C-NMR (101 MHz,) δ C ppm 196.49 (s), 162.33 (s), 144.16 (s), 128.45 (s), 128.13 (s), 126.45 (s), 115.74 (s), 77.32 (s), 77.11 (s), 76.80 (s), 50.81 (s), 40.94 (s), 32.28 (s), 31.90 (s), 29.36 (s), 27.41 (s).

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

White solid, ^{1}H-NMR (400 MHz,) δH ppm 7.21 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 4.70 (s,1H), 2.46 (s,4H), 2.20 (q, *J* = 16.3 Hz,4H), 1.10 (s.6H), 0.98 (s,6H); ^{13}C-NMR (101 MHz,) δC ppm 196.5, 162.5, 142.8, 132.1, 129.9, 128.3, 115.3, 77.4, 77.1, 76.8, 50.8, 40.9, 32.3, 31.5, 29.4, 27.4

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

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δH ppm 7.28 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 7.6 Hz, 2H), 7.07 (t, *J* = 7.3 Hz,1H), 4.72 (s,1H), 2.47 (s,4H), 2.20 (q, *J* = 16.3 Hz, 4H), 1.10 (s,6H), 1.00 (s,6H); ^{13}C-NMR (101 MHz, $CdCl_3$) δC ppm 196.38, 162.64, 146.17, 133.94, 129.32, 128.37, 127.09, 126.73, 115.16, 77.43, 77.22, 76.80, 50.77, 40.91, 32.30, 31.80, 29.28, 27.45.

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

White solid,^{1}H NMR (400 MHz, $CdCl_3$) δ 7.42 (d, *J* = 7.4 Hz,1H), 7.24 – 7.20 (m,1H), 7.17 (dd, *J* = 7.5, 1.2 Hz,1H), 7.05 (td, *J* = 7.6, 1.7 Hz,1H), 4.99 (s,1H), 2.44 (s,4H), 2.18 (q, *J* = 16.3 Hz,4H), 1.09 (s,6H), 1.01 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.6, 163.1, 139.9, 133.5, 133.0, 130.2, 127.9, 126.4, 113.8, 77.4, 77.1, 76.8, 50.8, 40.9, 32.1, 31.9, 29.4, 27.4.

3e, 9-(4-bromophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz,2H), 4.68 (s,1H), 2.45 (s,2H), 2.18 (q, *J* = 16.3 Hz, 4H), 1.08 (s,6H), 0.97 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.5, 162.6, 143.3, 131.2, 130.3, 120.3, 115.2, 77.5, 77.2, 76.9, 50.8, 40.9, 32.3, 31.6, 29.4, 27.4

3f, 9-(3-bromophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.36 (t, *J* = 1.8 Hz,1H), 7.27 (d, *J* = 8.6 Hz,1H), 7.22 (d, *J* = 8.7 Hz,1H), 7.07 (t, *J* = 7.8 Hz,1H), 4.70 (s,1H), 2.47 (s,1H), 2.20 (q, *J* = 16.3

Hz,1H), 1.09 (s,6H), 0.99 (s,6H).^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.4, 162.7, 146.5, 131.3, 129.7, 127.6, 122.2, 115.1, 77.5, 77.2, 76.8, 50.8, 40.9, 32.3, 31.8, 29.3, 27.4

3g, 9-(2-bromophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.40 (t, *J* = 24.1 Hz,2H), 7.18 (t, *J* = 7.5 Hz,1H), 6.96 (td, *J* = 7.8, 1.6 Hz,1H), 5.02 (s,1H), 2.44 (s,4H), 2.18 (q, *J* = 16.2 Hz,4H), 1.09 (s,6H), 1.01 (s,6H). ^{13}C-NMR (101 MHz,$CdCl_3$) δ 196.6, 162.9, 141.9, 133.6, 128.1, 127.1, 114.3, 77.5, 77.2, 76.8, 50.8, 40.9, 33.6, 32.1, 29.2, 27.6

3h,9-(4-florophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.27 – 7.22 (m,2H), 6.93 – 6.85 (m,2H), 4.72 (s,1H), 2.46 (s,4H), 2.20 (q, *J* = 16.3 Hz,4H), 1.10 (s,6H), 0.98 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.5, 162.7, 162.4, 160.2, 140.0, 140.0, 130.0, 129.9, 115.6, 115.0, 114.8, 77.4, 77.1, 76.8, 50.8, 40.9, 32.3, 31.3, 29.4, 27.4

3i,9-(4-formylbenzonitrile)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.51 (d, *J* = 8.1 Hz,2H), 7.41 (d, *J* = 8.2 Hz,2H), 4.76 (s,1H), 2.47 (s,4H), 2.20 (q, *J* = 16.3 Hz,4H), 1.10 (s,6H), 0.97 (s,6H).^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.4, 163.0, 149.5, 132.1, 129.4, 119.1, 114.7, 110.3, 77.5, 77.1, 76.8, 50.7, 40.9, 32.5, 32.3, 29.3, 27.4

3j,9-(4-nitrophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 8.08 (d, *J* = 8.8 Hz,2H), 7.47 (d, *J* = 8.8 Hz,2H), 4.81 (s,1H), 2.49 (s,4H), 2.20 (q, *J* = 16.4 Hz,4H), 1.11 (s,6H), 0.97 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.5, 163.1, 151.6, 146.5, 129.5, 123.5, 114.6, 77.5, 77.1, 76.8, 50.7, 40.9, 32.4, 32.3, 29.3, 27.3

3k,9-(3-nitrophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 8.03 – 7.95 (m,2H), 7.82 (d, *J* = 7.7 Hz,1H), 7.41 (t, *J* = 7.9 Hz,1H), 4.83 (s,1H), 2.51 (s,4H), 2.21 (q, *J* = 16.3 Hz,4H), 1.11 (s,6H), 1.00 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.5, 163.1, 148.4, 146.4, 135.9, 128.9, 122.6, 121.8, 114.6, 77.4, 77.1, 76.8, 50.7, 40.9, 32.3, 32.2, 29.3, 27.4

3l,9-(4-methoxyphenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.21 – 7.17 (m,2H), 6.76 – 6.72 (m,2H), 4.69 (s,1H), 3.72 (s,3H), 2.45 (s,4H), 2.19 (q, *J* = 16.3 Hz,4H), 1.09 (s,6H), 0.98 (s,6H). ^{13}C-NMR (101

MHz, $CdCl_3$) δ 196.6, 162.2, 158.0, 136.6, 129.4, 115.8, 113.5, 77.5, 77.1, 76.8, 55.2, 50.8, 40.9, 32.3, 31.0, 29.4, 27.4

3m, 9-(p-tolyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.17 (d, *J* = 8.0 Hz,2H), 7.01 (d, *J* = 7.8 Hz,2H), 4.70 (s,1H), 2.45 (s,4H), 2.25 – 2.13 (m,7H), 1.09 (s,6H), 0.99 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.6, 162.2, 141.3, 135.9, 128.9, 128.3, 115.8, 77.5, 77.1, 76.8, 50.8, 40.9, 32.3, 31.5, 29.4, 27.5, 21.2

3n,9-(3,4-dichlorophenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.32 (d, *J* = 2.1 Hz,1H), 7.28 (d, *J* = 8.3 Hz,1H), 7.19 (dd, *J* = 8.3, 2.1 Hz,1H), 4.68 (s,1H), 2.47 (s,4H), 2.21 (q, *J* = 16.3 Hz,4H), 1.10 (s,6H), 1.00 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.39, 162.77, 144.48, 132.11, 130.40, 130.14, 128.28, 114.84, 77.42, 77.10, 76.79, 50.72, 40.89, 32.31, 31.52, 29.29, 27.44.

3o,9-(3,4-dimethoxyphenyl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 6.89 (d, *J* = 1.9 Hz,1H), 6.75 (dd, *J* = 8.3, 1.9 Hz,1H), 6.70 (d, *J* = 8.3 Hz,1H), 4.69 (s,1H), 3.84 (s,3H), 3.78 (s,3H), 2.45 (s,4H), 2.20 (q, *J* = 16.3 Hz,4H), 1.09 (s,6H), 1.00 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.59, 162.21, 148.48, 147.50, 137.05, 120.16, 115.81, 112.31, 110.87, 77.45, 77.13, 76.81, 55.87, 50.82, 40.94, 32.27, 31.29, 29.42, 27.32.

3p, 9-([1,1'-biphenyl]-4-yl)-3,3,6,6-tetramethyl--3,4,5,6,7,9-hexahydro-1H-xanthene-1,8-(2H)-dione.

White solid, ^{1}H-NMR (400 MHz, $CdCl_3$) δ 7.55 – 7.51 (m,2H), 7.45 (d, *J* = 8.3 Hz,2H), 7.41 – 7.35 (m,4H), 7.31 – 7.26 (m,1H), 4.80 (s,1H), 2.49 (s,4H), 2.22 (q, *J* = 16.3 Hz,4H), 1.11 (s,6H), 1.01 (s,6H). ^{13}C-NMR (101 MHz, $CdCl_3$) δ 196.60, 162.45, 143.33, 141.21, 139.20, 128.76, 127.04, 115.64, 77.31, 77.12, 76.92, 76.83, 50.85, 40.97, 32.33, 31.64, 29.38, 27.46