Electronic Supplementary Information

Efficient Preparation of 9-Aryl-1,8-dioxo-octahydroxanthenes Catalyzed by Nano-TiO2 with High Recyclability

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General methods. All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Nano-TiO_2 was prepared according to the reported procedure.[36] Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100) were run on a Bruker Avance DPX, FT-NMR spectrometers, δ in ppm. Mass spectra were obtained with Shimadzu GC-MS-QP 1100 EX model.

General procedure for the synthesis of 9-aryl-1,8-dioxo-octahydroxanthenes

A mixture of dimedone (0.28 g, 2 mmol), arylaldehyde (1 mmol) and nano-TiO_2 (0.1 mmol, 10 mol%) in a test tube was firstly stirred magnetically. After solidification of the reaction mixture with a small rod at 100 °C and completion the reaction monitored by TLC, the mixture was cooled to room temperature and warm EtOH (30 mL) was added to it. Then the reaction mixture was concentrated to 10 mL and centrifuged for 20 min to separate the Nano-TiO_2. After evaporation of the solvent from the supernatant, the resulting solid was recrystallized from EtOH (95%) to give the pure product. EtOAc (10 mL) was added to the recycled Nano-TiO_2 and centrifuged (two times). Finally, the Nano-TiO_2 was dried and reused for the next run.

Spectral data and original spectrums of the products

3,3,6,6-Tetramethyl-9-phenyl-1,8-dioxo-octahydroxanthene (1a)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.90 (s, 6H), 1.04 (s, 6H), 2.09 (d, *J* = 16.1 Hz, 2H), 2.27 (d, *J* = 16.2 Hz, 2H), 2.53 (d, *J* = 17.1 Hz, 2H), 2.58 (d, *J* = 17.7 Hz, 2H), 4.53 (s, 1H), 7.10 (t, *J* = 7.0 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 7.20 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 27.3, 29.3, 31.8, 32.2, 40.9, 50.7, 115.6, 126.4, 128.0, 128.4, 144.1, 162.3, 196.4. Anal. calcd. for $C_{23}H_{26}O_3$: C 78.83, H 7.48; found: C 78.60, H 7.57.

3,3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene (1b)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.01 (s, 6H), 1.12 (s, 6H), 2.18 (d, *J* = 16.4 Hz, 2H), 2.25 (d, *J* = 16.4 Hz, 2H), 2.48 (s, 4H), 3.75 (s, 3H), 4.72 (s, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.3, 29.3, 30.9, 32.2, 40.9, 50.8, 55.1, 113.5, 115.8, 129.3, 136.5, 157.9, 162.1, 196.5. Anal. calcd. for $C_{24}H_{28}O_4$: C 75.76, H 7.42; found: C 75.94, H 7.31.

3,3,6,6-Tetramethyl-9-(3-methoxyphenyl)-1,8-dioxo-octahydroxanthene (1c)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.02 (s, 6H), 1.11 (s, 6H), 2.16-2.26 (Distorted AB system, 4H), 2.48 (s, 4H), 3.77 (s, 3H), 6.66 (dd, *J* = 1.6, 7.2 Hz, 1H), 6.88-6.90 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 27.4, 29.2, 31.8, 32.2, 40.9, 50.8, 55.13, 111.8, 114.3, 115.5, 120.9, 128.9, 145.7, 159.3, 162.3, 196.4. Anal. calcd. for $C_{24}H_{28}O_4$: C 75.76, H 7.42; found: C 75.98, H 7.54.

3,3,6,6-Tetramethyl-9-(3,4-dimethoxyphenyl)-1,8-dioxo-octahydroxanthene (1d)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.92 (s, 6H), 1.04 (s, 6H), 2.10 (d, *J* = 16.1 Hz, 2H), 2.27 (d, *J* = 16.1 Hz, 2H), 2.51 (d, *J* = 17.6 Hz, 2H), 2.57 (d, *J* = 17.4 Hz, 2H), 3.68 (s, 6H), 4.48 (s, 1H), 6.67 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.72 (d, *J* = 1.9 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 27.2, 29.6, 31.4, 32.7, 50.9, 56.3, 56.3, 112.2, 112.9, 115.4, 120.9, 137.7, 148.1, 148.9, 163.6, 196.9. Anal. calcd. for $C_{25}H_{30}O_5$: C 73.15, H 7.37; found: C 72.96, H 7.47.

3,3,6,6-Tetramethyl-9-(3,4,5-trimethoxyphenyl)-1,8-dioxo-octahydroxanthene (1e)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.96 (s, 6H), 1.05 (s, 6H), 2.14 (d, J = 16.2 Hz, 2H), 2.29 (d, J = 16.2 Hz, 2H), 2.50-2.54 (Distorted AB system, 4H), 3.32 (s, 3H), 3.60 (s, 3H), 3.69 (s, 3H), 4.50 (s, 1H), 6.42 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 27.2, 29.4, 31.8, 32.2, 40.9, 50.7, 56.1, 60.7, 105.6, 115.5, 136.5, 139.7, 152.8, 162.4, 196.5. Anal. calcd. for $C_{26}H_{32}O_6$: C 70.89, H 7.32; found: C 70.68, H 7.40.

3,3,6,6-Tetramethyl-9-(4-benzyloxyphenyl)-1,8-dioxo-octahydroxanthene (1f)

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 1.01 (s, 6H), 1.09 (s, 6H), 2.13-2.27 (m, 4H), 2.45 (s, 4H), 4.69 (s, 1H), 4.82 (s, 2H), 6.80 (d, J = 8.7 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 7.29-7.43 (m, 5H); ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 27.2, 29.4, 31.8, 32.2, 40.9, 50.7, 69.0, 114.8, 115.6, 126.9, 127.3, 128.4, 129.3, 136.5, 139.7, 152.8, 162.4, 196.5. Anal. calcd. for $C_{30}H_{32}O_4$: C 78.92, H 7.06; found: C 78.68, H 7.19.

3,3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8-dioxo-octahydroxanthene (1g)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.02 (s, 6H), 1.25 (s, 6H), 2.17-2.27 (m, 7H), 2.49 (s, 4H), 4.74 (s, 1H), 7.04 (d , J = 7.5 Hz, 2H), 7.20 (d, J = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 21.5, 27.8, 29.7, 31.9, 32.6, 41.3, 51.2, 116.2, 128.7, 129.2, 136.1, 141.6, 162.5, 196.8. Anal. calcd. for $C_{24}H_{28}O_3$: C 79.09, H 7.74; found: C 79.27, H 7.66.

3,3,6,6-Tetramethyl-9-(4-hydroxyphenyl)-1,8-dioxo-octahydroxanthene (1h)

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.97 (s, 6H), 1.07 (s, 6H), 2.09-2.25 (m, 4H), 2.44 (s, 4H), 4.64 (s, 1H), 6.51 (d, J = 7.4 Hz, 2H), 7.04 (d, J = 7.4 Hz, 2H), 7.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 27.4, 29.2, 30.9, 32.3, 40.8, 50.7, 115.3, 115.9, 129.3, 135.4, 154.8, 162.5, 197.4. Anal. calcd. for $C_{23}H_{26}O_4$: C 75.38, H 7.15; found: C 75.61, H 7.25.

3,3,6,6-Tetramethyl-9(5-bromo-2-hydroxyphenyl)-1,8-dioxo-octahydroxanthene (1i)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.90 (s, 6H), 0.97 (s, 3H), 1.05 (s, 3H), 2.04 (d, J = 15.8 Hz, 2H), 2.25 (d, J = 15.9 Hz, 2H), 2.34 (d, J = 17.3 Hz, 2H), 2.55 (d, J = 17.4 Hz, 2H), 5.04 (s, 1H), 6.95 (d, J = 8.64 Hz, 1H), 7.04 (s, 1H), 7.28 (d, J = 8.60 Hz, 1H), 10.59 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) 26.9, 28.4, 30.0, 32.5, 51.2, 100.4, 111.3, 116.3, 118.6, 129.1, 130.6, 131.4, 149.8, 165.3, 196.5. Anal. calcd. for $C_{23}H_{25}BrO_4$: C 62.03, H 5.66; found: C 61.84, H 5.54.

3,3,6,6-Tetramethyl-9-(4-bromophenyl)-1,8-dioxo-octahydroxanthene (1J)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.91 (s, 6H), 1.04 (s, 6H), 2.07 (d, *J* = 16.1 Hz, 2H), 2.25 (d, *J* = 16.1 Hz, 2H), 2.50-2.59 (Distorted AB system, 4H), 4.49 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 27.3, 29.3, 31.5, 32.2, 40.8, 50.7, 115.1, 120.2, 130.2, 131.1, 143.3, 162.5, 196.4. Anal. calcd. for $C_{23}H_{25}BrO_3$: C 64.34, H 5.87; found: C 64.50, H 5.76.

3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene (1k)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.90 (s, 6H), 1.04 (s, 6H), 2.09 (d, *J* = 16.1 Hz, 2H), 2.27 (d, *J* = 16.1 Hz, 2H), 2.52 (d, 2H), 2.57 (d, *J* = 17.6 Hz, 2H), 4.51 (s, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 27.3, 29.3, 31.5, 32.2, 40.8, 50.7, 115.2, 128.2, 129.8.2, 131.9, 142.8, 162.5, 196.4. Anal. calcd. for $C_{23}H_{25}ClO_3$: C 71.77, H 6.55; found: C 71.92, H 6.63.

3,3,6,6-Tetramethyl-9-(3-chlorophenyl)-1,8-dioxo-octahydroxanthene (1l)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.02 (s, 6H), 1.12 (s, 6H), 2.18-2.27 (Distorted AB system, 4H), 2.52 (t, *J* = 14.0 Hz, 4H), 4.74 (s, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 7.25 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 27.8, 29.6, 32.2, 32.6, 41.2, 51.1, 115.5, 127.0, 127.4, 128.8, 129.6, 134.3, 146.6, 163.1, 196.7. Anal. calcd. for $C_{23}H_{25}ClO_3$: C 71.77, H 6.55; found: C 71.56, H 6.43.

3,3,6,6-Tetramethyl-9-(2-chlorophenyl)-1,8-dioxo-octahydroxanthene (1m)

^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 0.88 (s, 6H), 1.04 (s, 6H), 2.02 (d, *J* = 16.1 Hz, 2H), 2.26 (d, *J* = 16.0 Hz, 2H), 2.43-2.60 (m, 4H), 4.82 (s, 1H), 7.12 (t, *J* = 7.1 Hz, 1H), 7.19-7.27 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 27.3, 29.3, 31.8, 32.0, 40.8, 50.7, 113.7, 126.3, 127.8, 130.1, 132.9, 133.4, 139.9, 163.0, 196.5. Anal. calcd. for $C_{23}H_{25}ClO_3$: C 71.77, H 6.55; found: C 71.52, H 6.68.

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (1n)

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 0.99 (s, 6H), 1.12 (s, 6H), 2.16 (d, *J* = 16.3 Hz, 2H), 2.26 (d, *J* = 16.3 Hz, 2H), 2.51 (t, *J* = 18.7 Hz, 4H), 4.83 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 8.08 (2H, *J* = 8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 27.7, 29.6, 32.6, 32.8, 41.2, 51.0, 114.9, 123.8, 129.8, 146.8, 152.0, 163.5, 196.7. Anal. calcd. for $C_{23}H_{25}NO_5$: C 69.86, H 6.37, N 3.54; found: C 69.73, H 6.28, N 3.61.

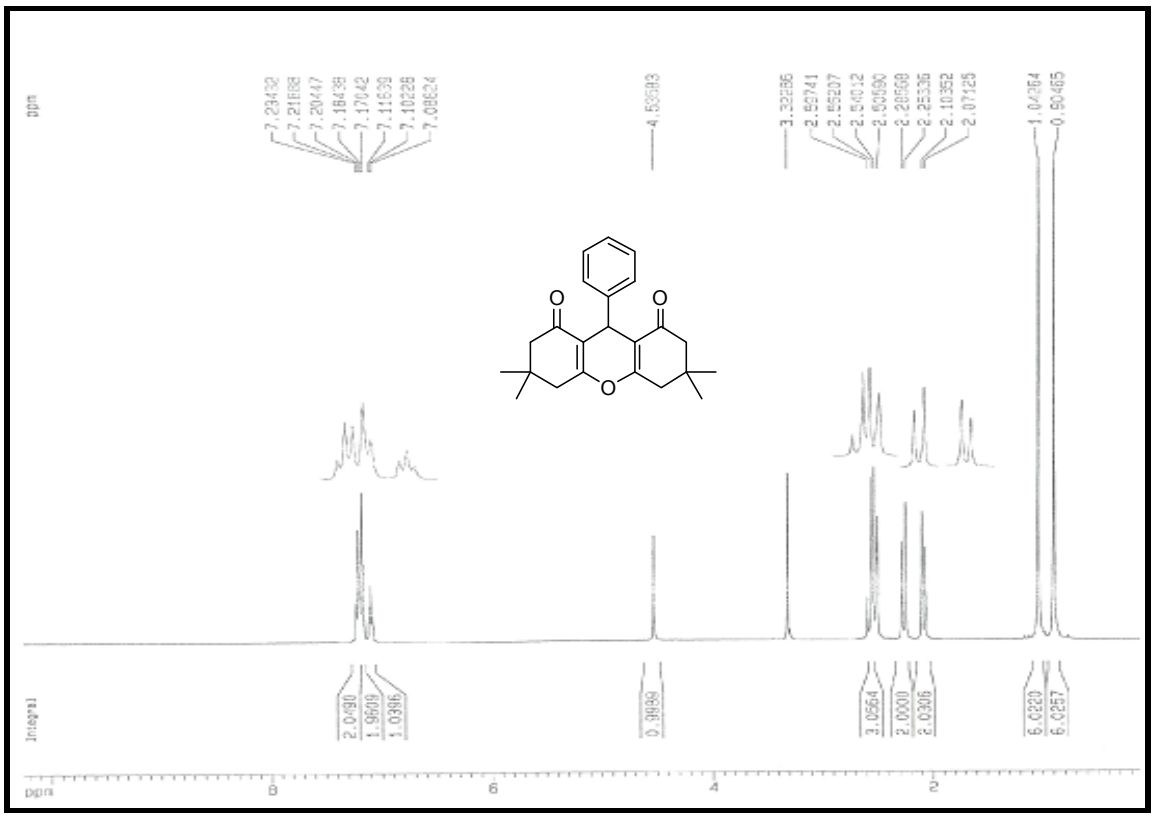
3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-1,8-dioxo-octahydroxanthene (1o)

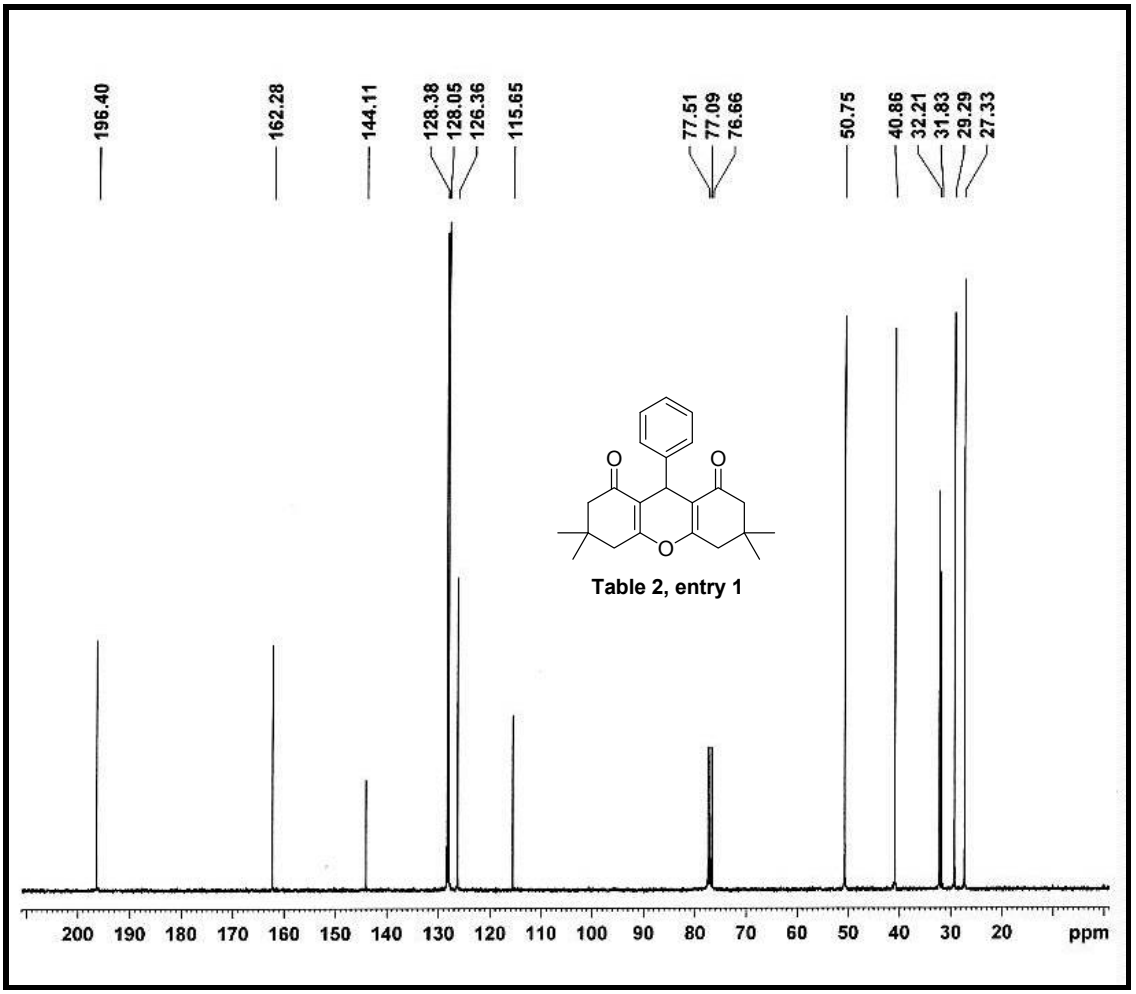
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.01 (s, 6H), 1.13 (s, 6H), 2.18 (d, *J* = 16.3 Hz, 2H), 2.27 (d, *J* = 16.3 Hz, 2H), 2.53 (t, *J* = 18.5 Hz, 4H), 4.85 (s, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.81 (d, *J* =7.5 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 8.06 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 27.7, 29.6, 32.5, 32.7, 41.2, 51.0, 114,9, 122.0, 123.1, 129.2, 136.0, 146.8, 148.7, 163.5, 196.8. Anal. calcd. for $C_{23}H_{25}NO_5$: C 69.86, H 6.37, N 3.54; found: C 69.67, H 6.48, N 3.45.

3,3,6,6-Tetramethyl-9-(4-cyanophenyl)-1,8-dioxo-octahydroxanthene (1p)

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.99 (s, 6H), 1.13 (s, 6H), 2.17 (d, *J* = 16.4 Hz, 2H), 2.26 (d, *J* = 16.4, 2H), 2.52 (t, *J* = 15.4 Hz, 4H), 4.78 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.53 (2H, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 27.3, 29.2, 32.2, 32.4, 40.8, 50.6, 110.2, 114.6, 119.1, 129.3, 131.9, 149.5, 162.9, 196.3. Anal. calcd. for $C_{24}H_{25}NO_3$: C 76.77, H 6.71, N 3.73; found: C 76.99, H 6.61, N 3.65.

3,3,6,6-Tetramethyl-9-phenyl-1,8-dioxo-octahydroxanthene (1a)





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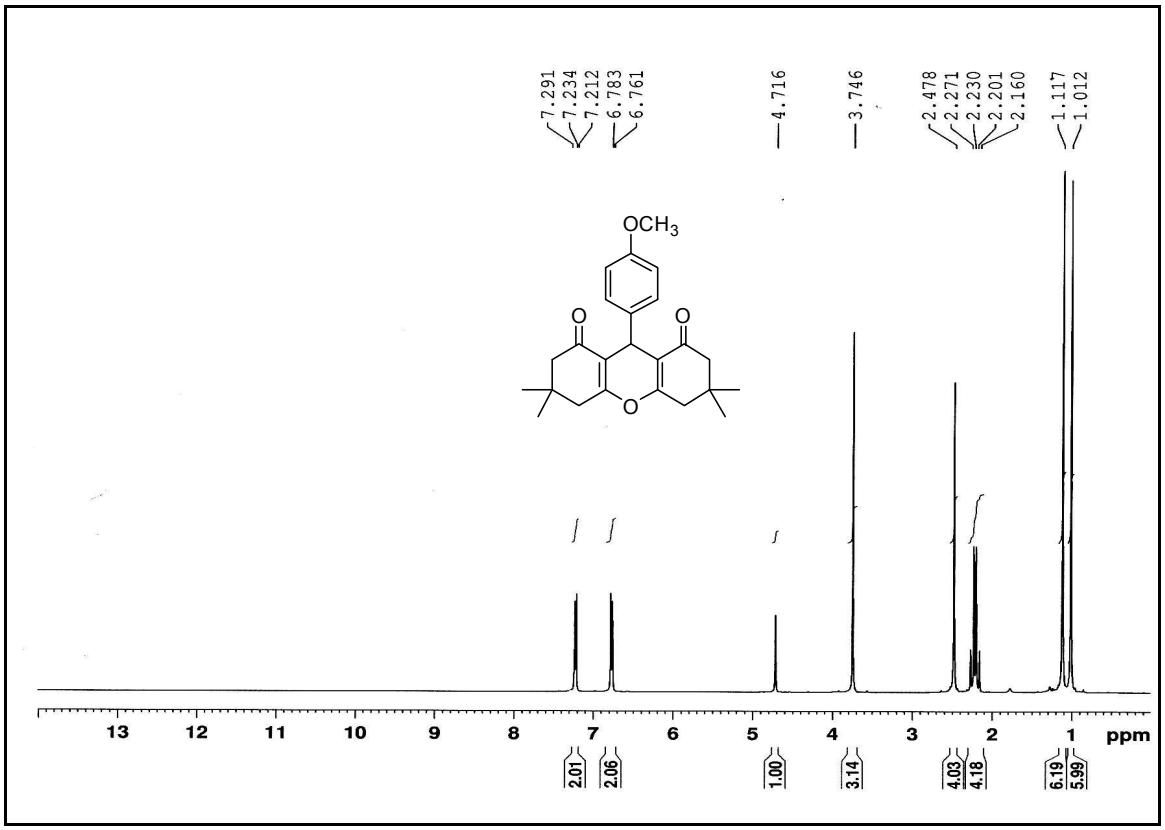

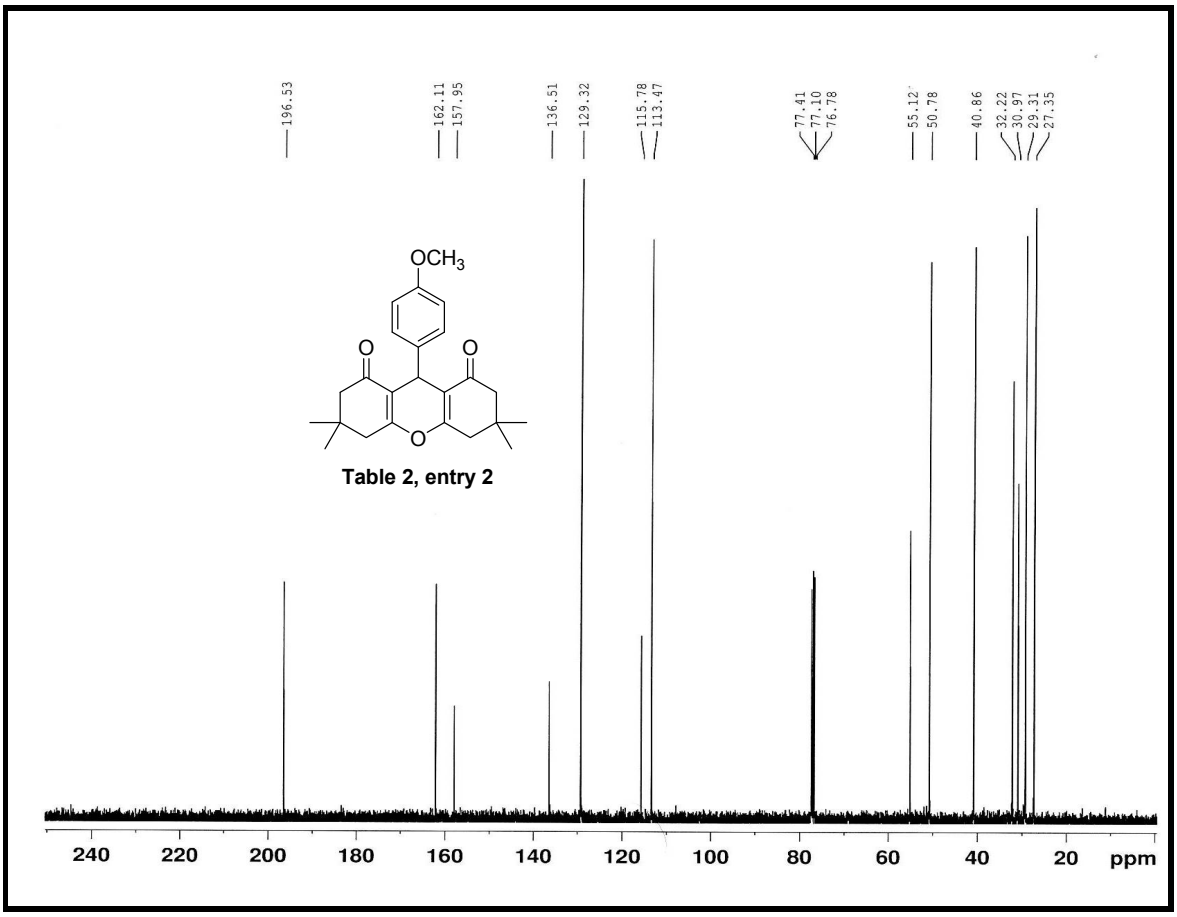

Table 2, entry 2

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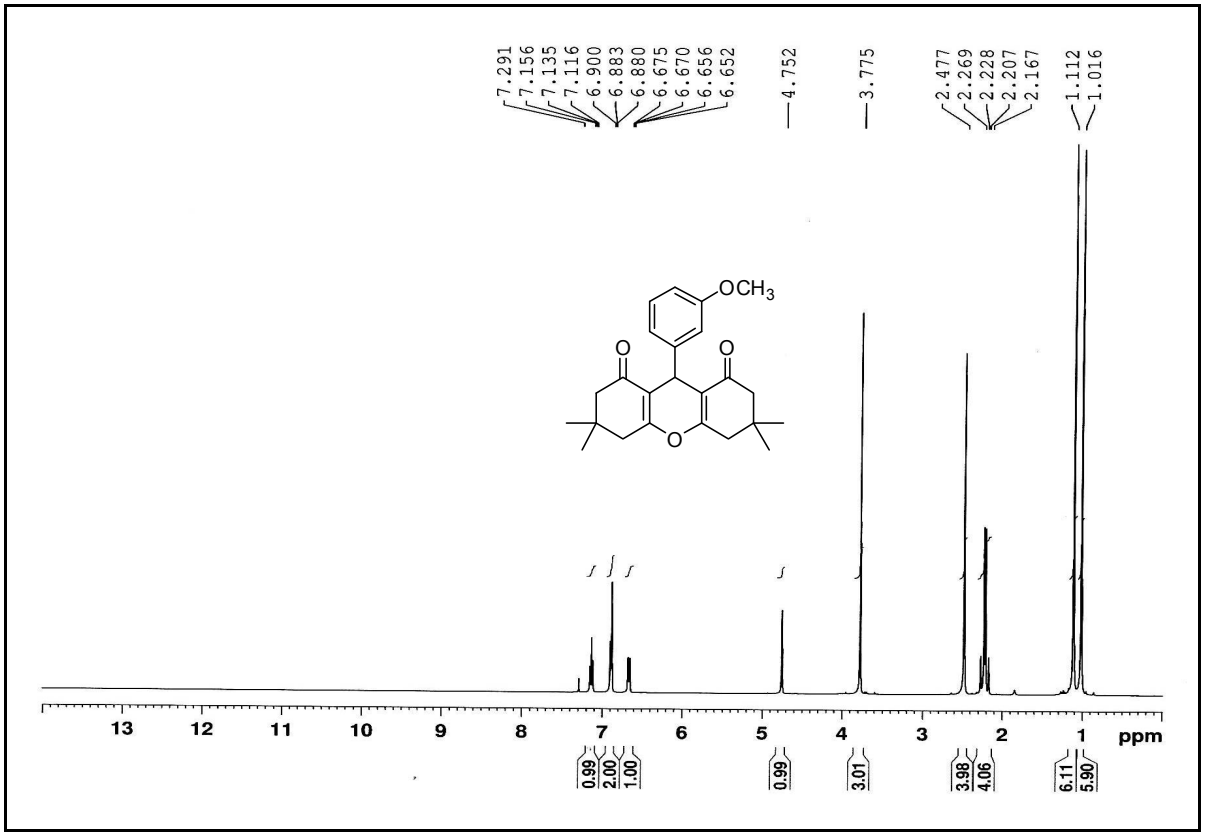
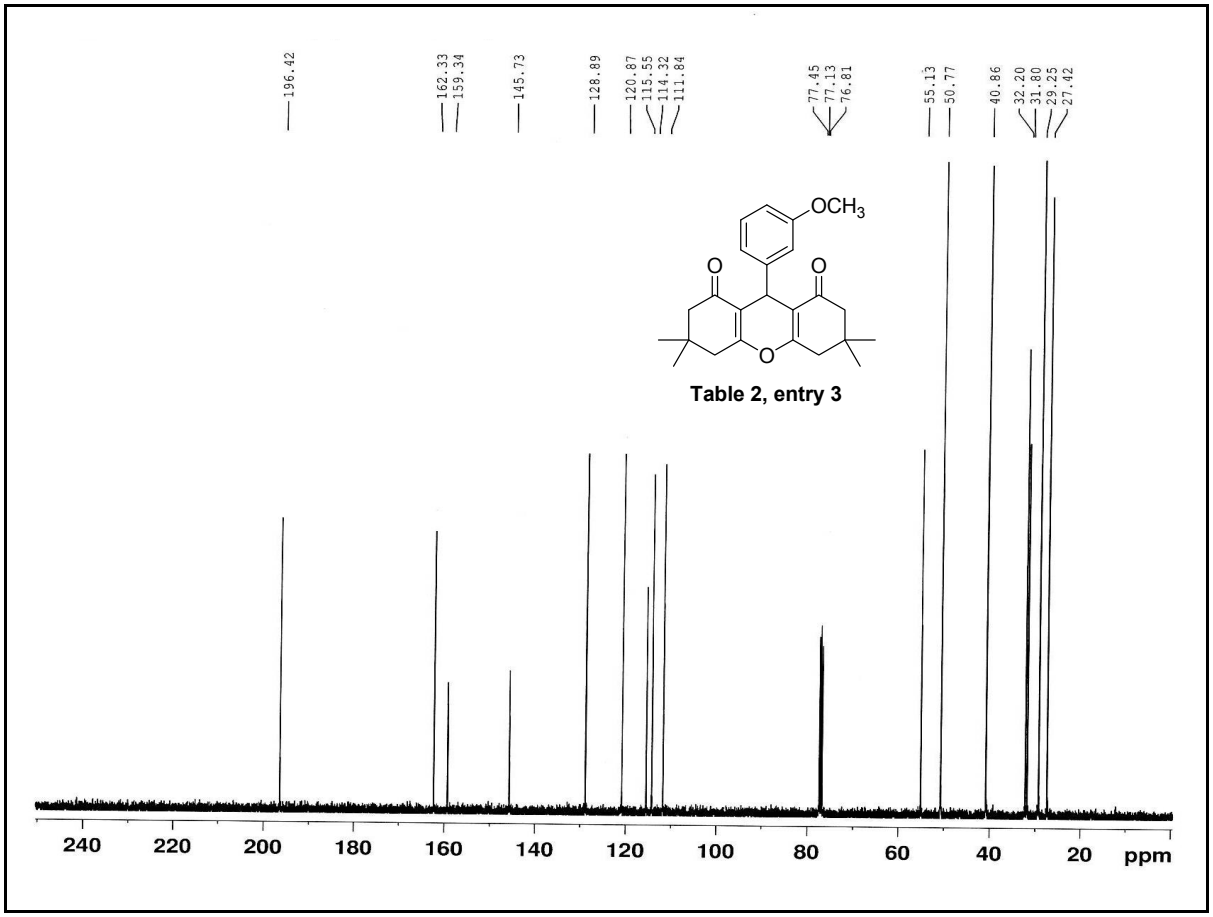
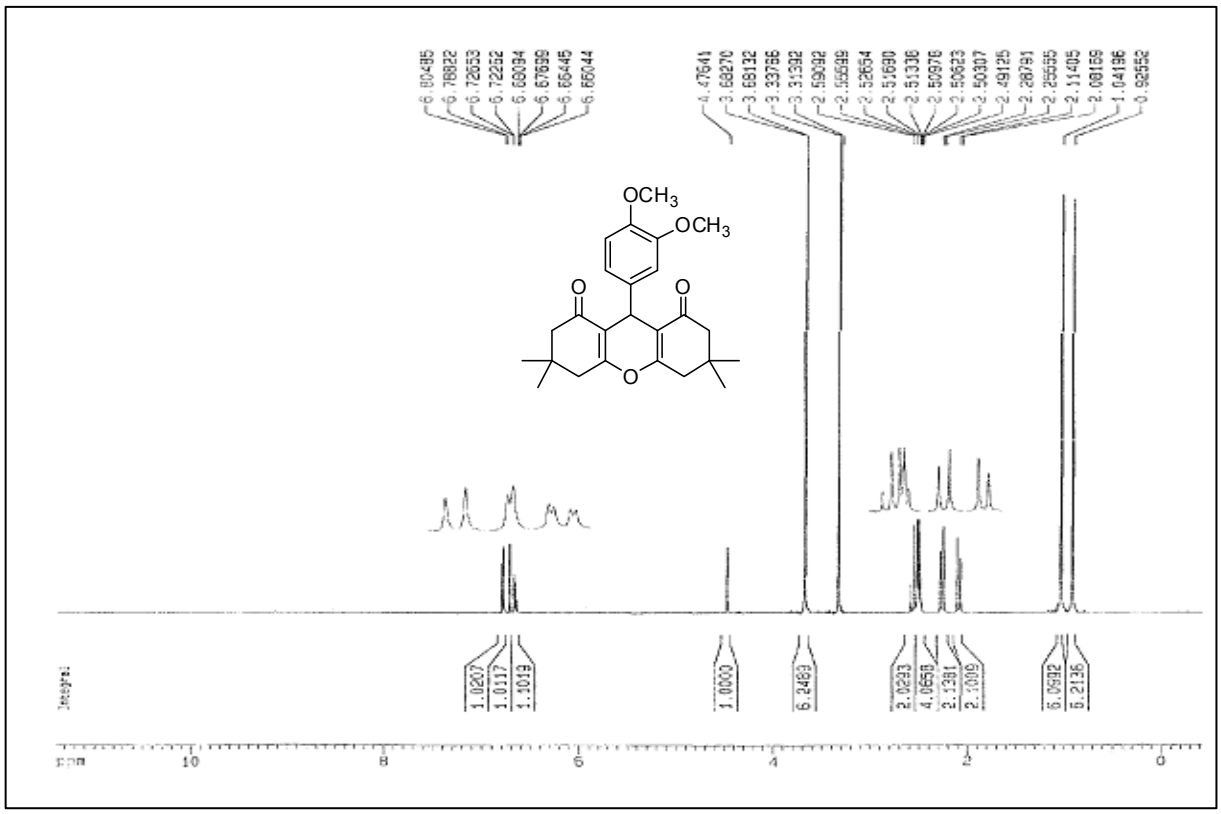




3,3,6,6-Tetramethyl-9-(3,4-dimethoxyphenyl)-1,8-dioxo-octahydroxanthene (1d)



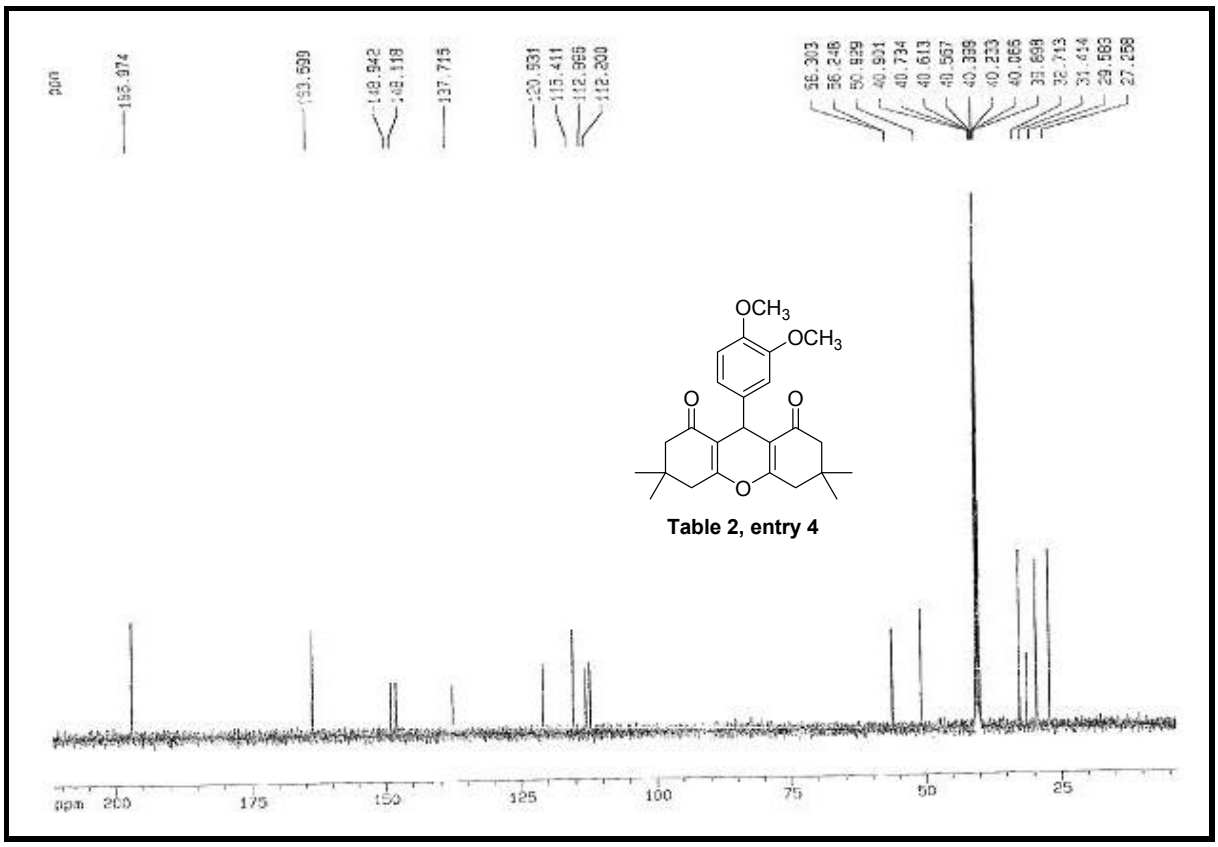
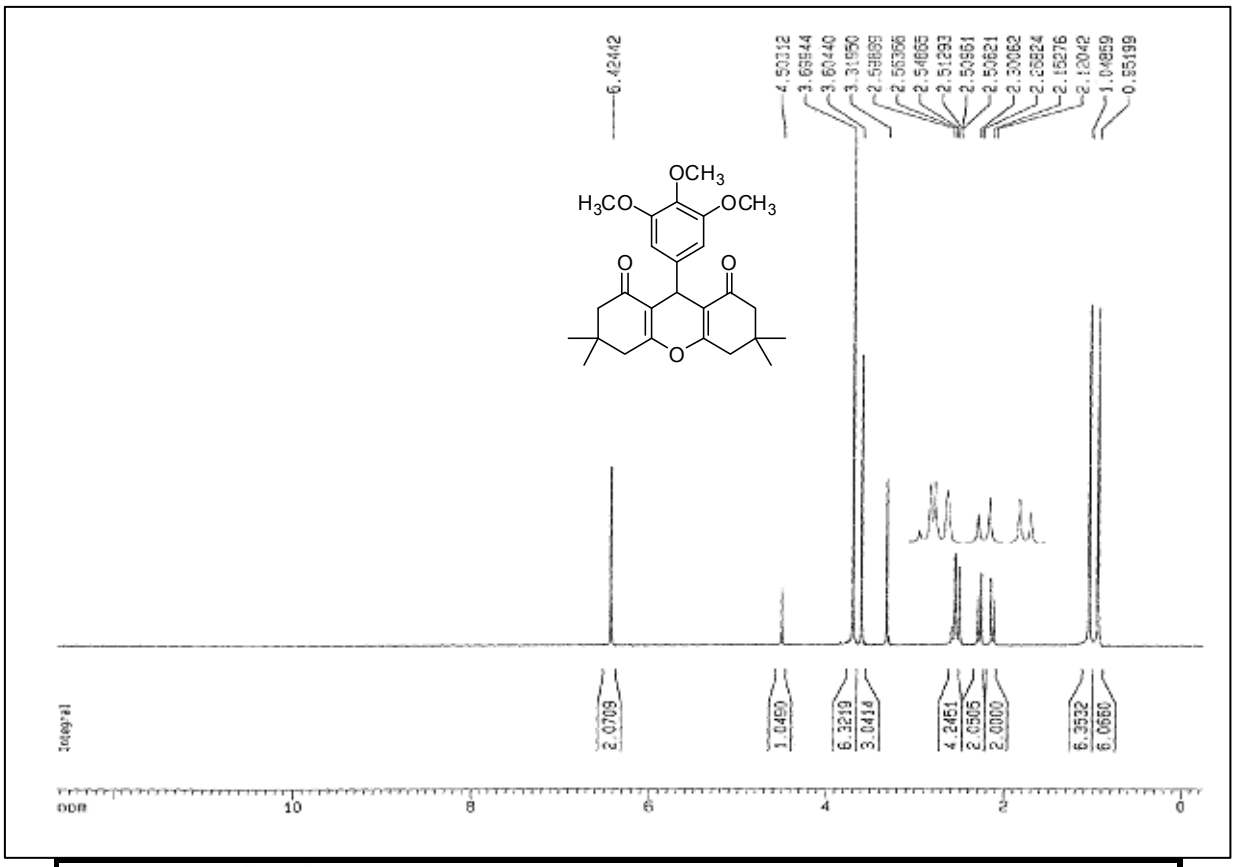
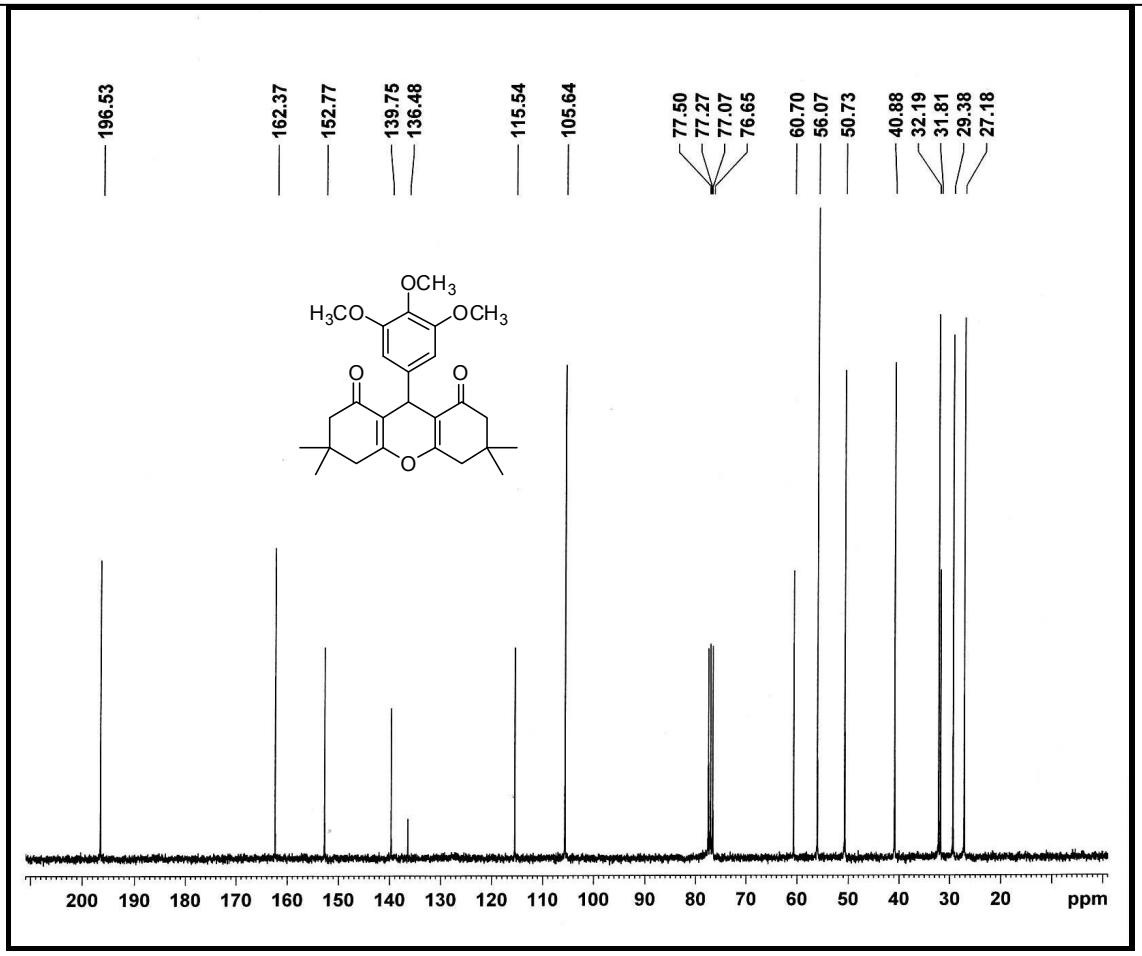


Table 2, entry 4

3,3,6,6-Tetramethyl-9-(3,4,5-trimethoxyphenyl)-1,8-dioxo-octahydroxanthene (1e)





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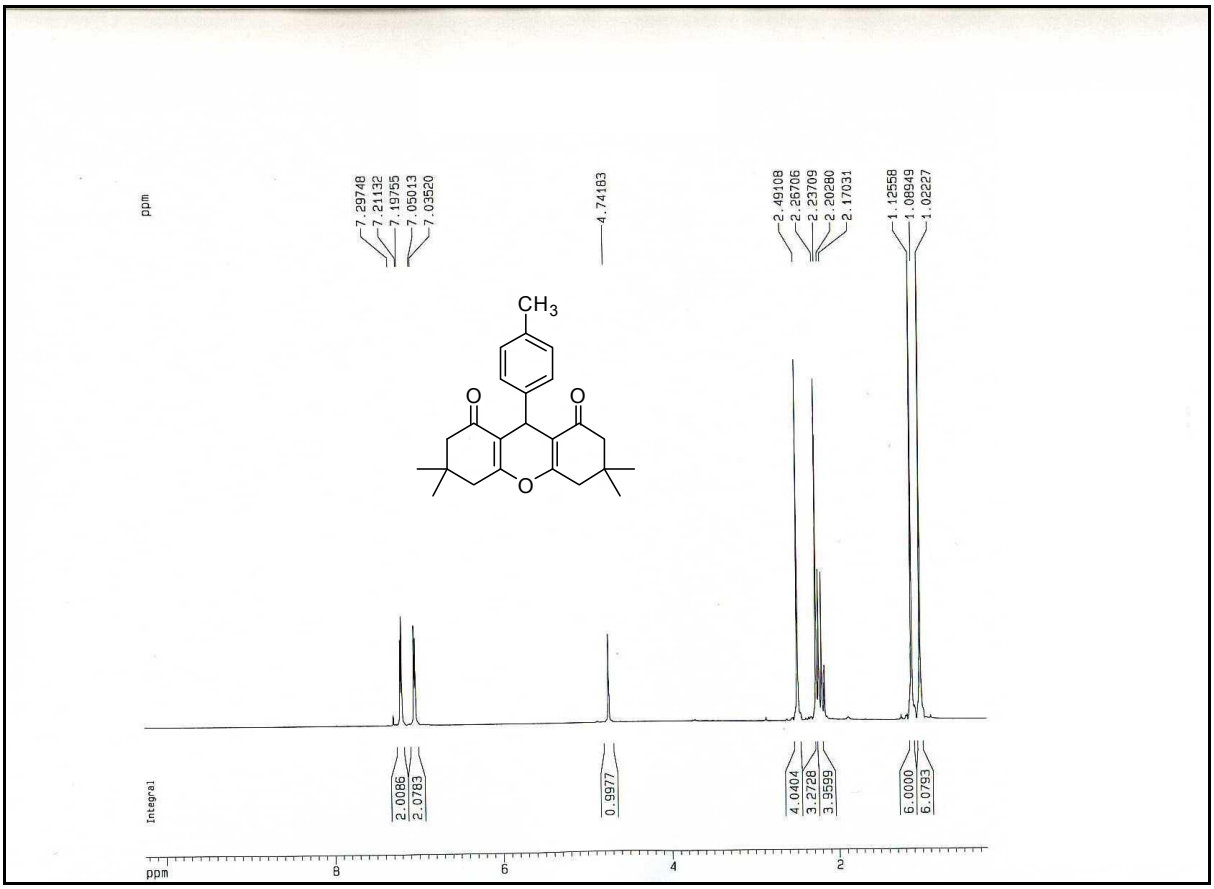

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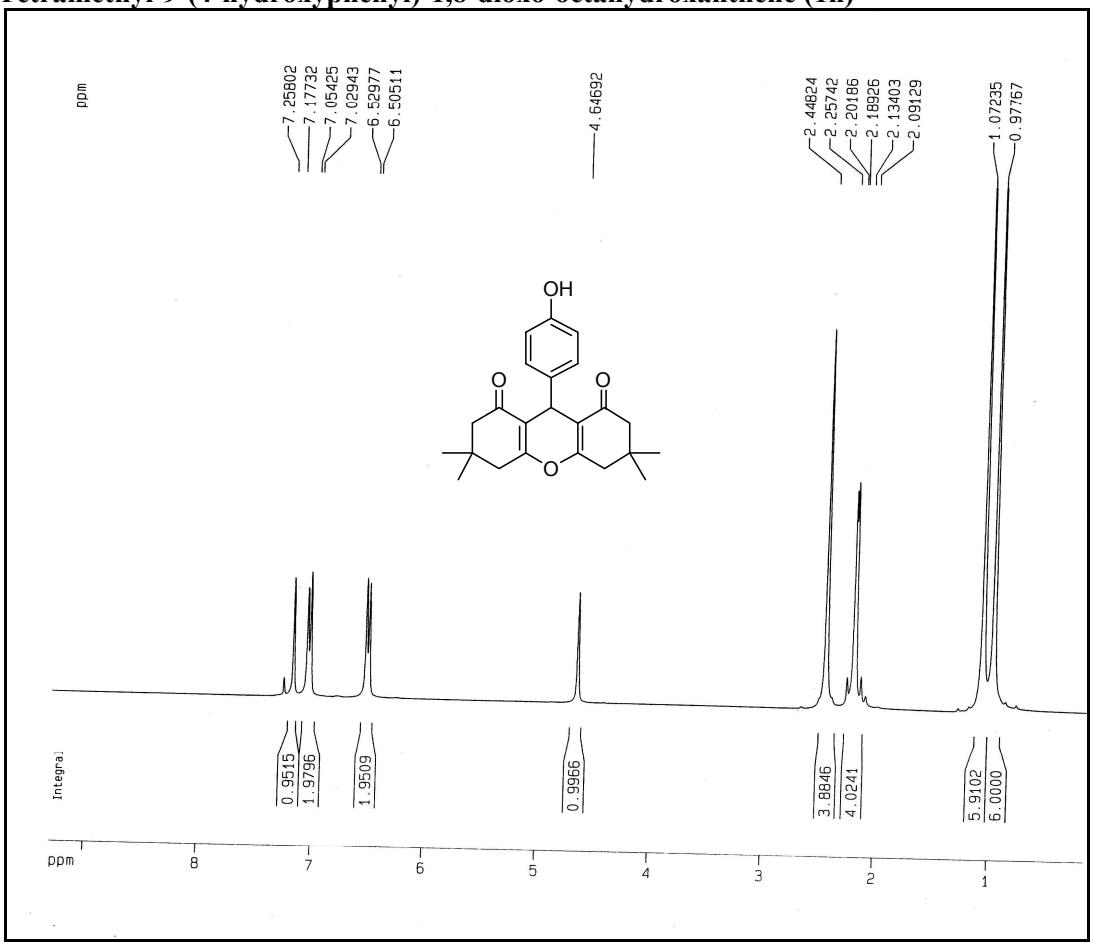
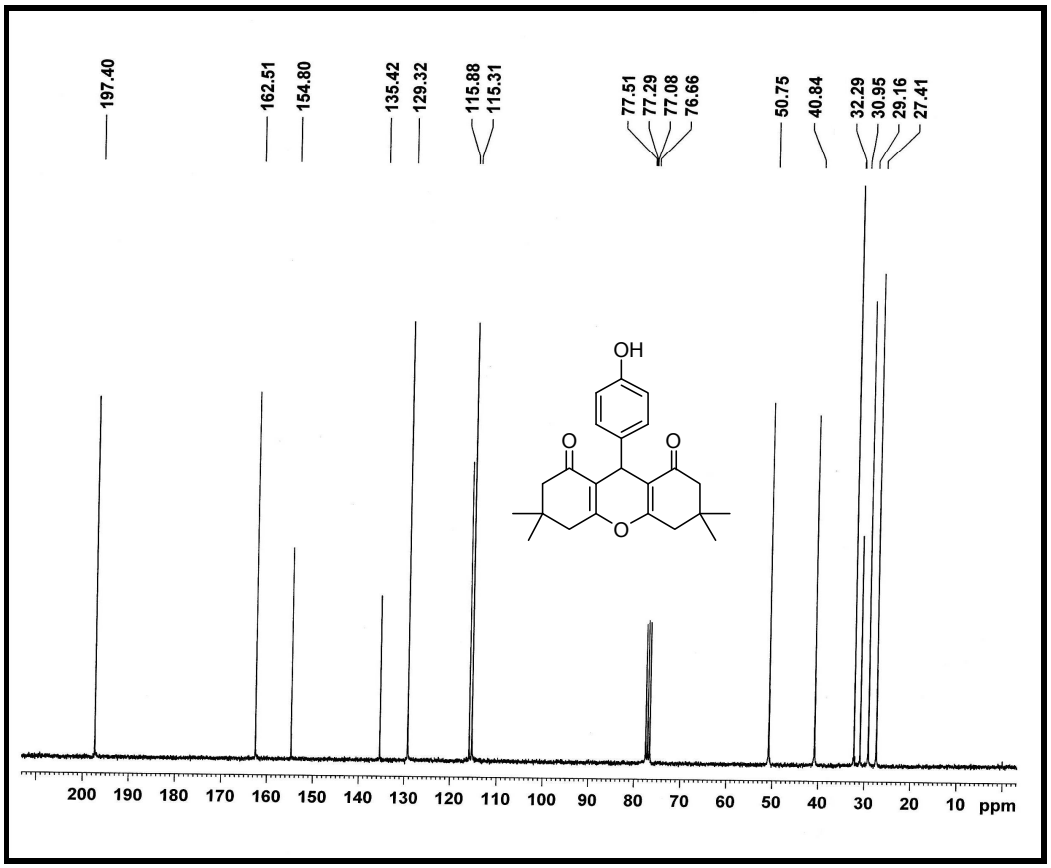
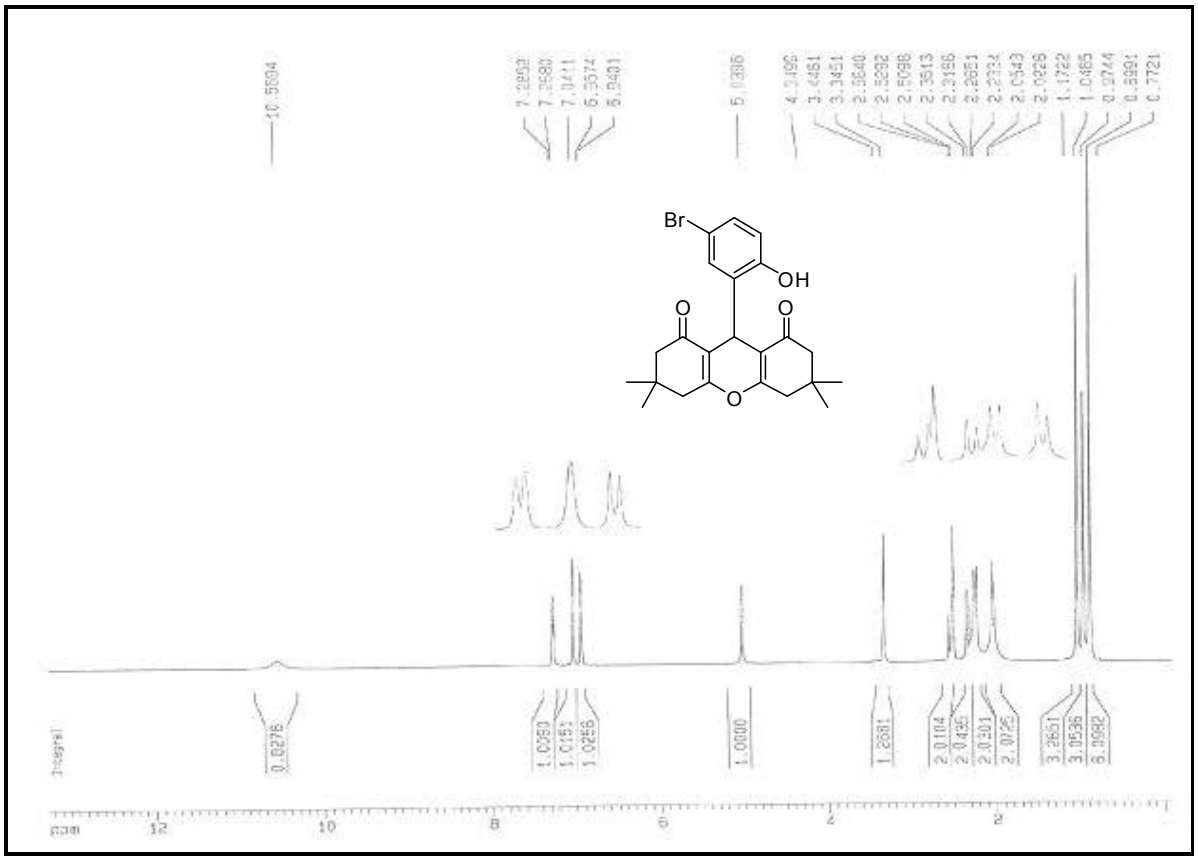


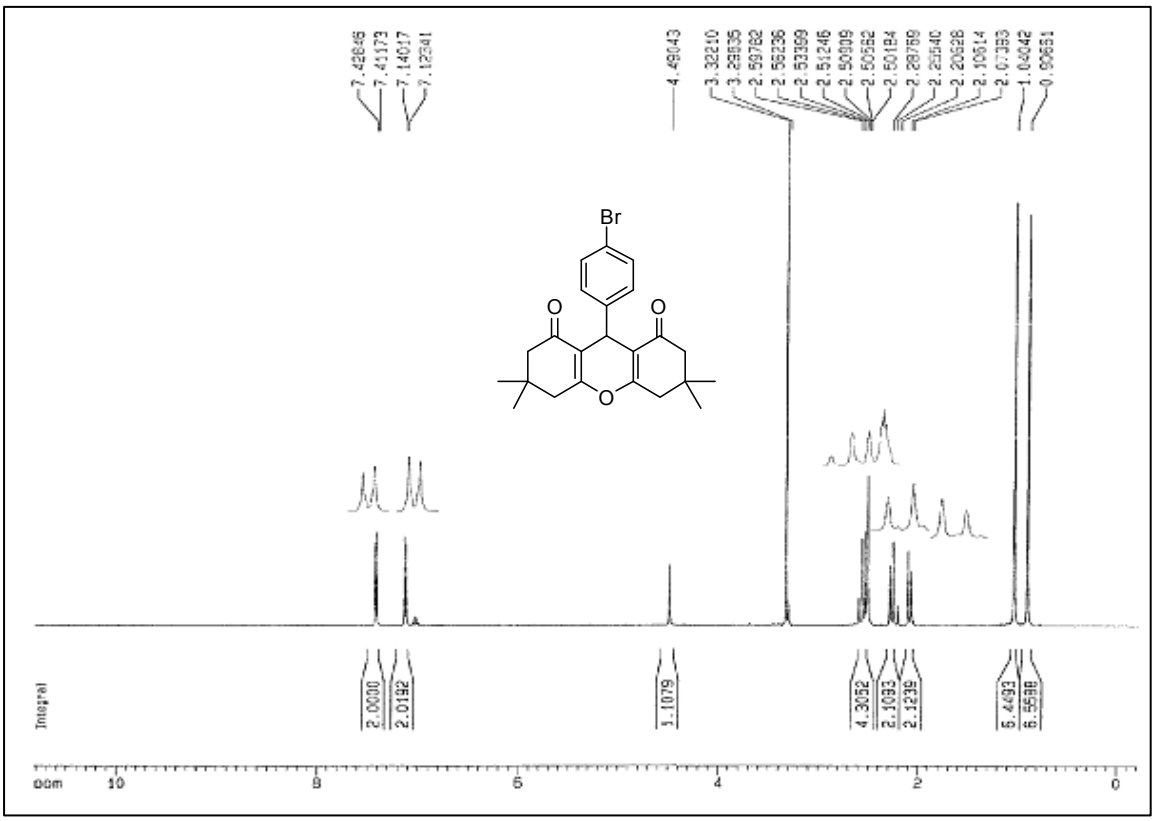


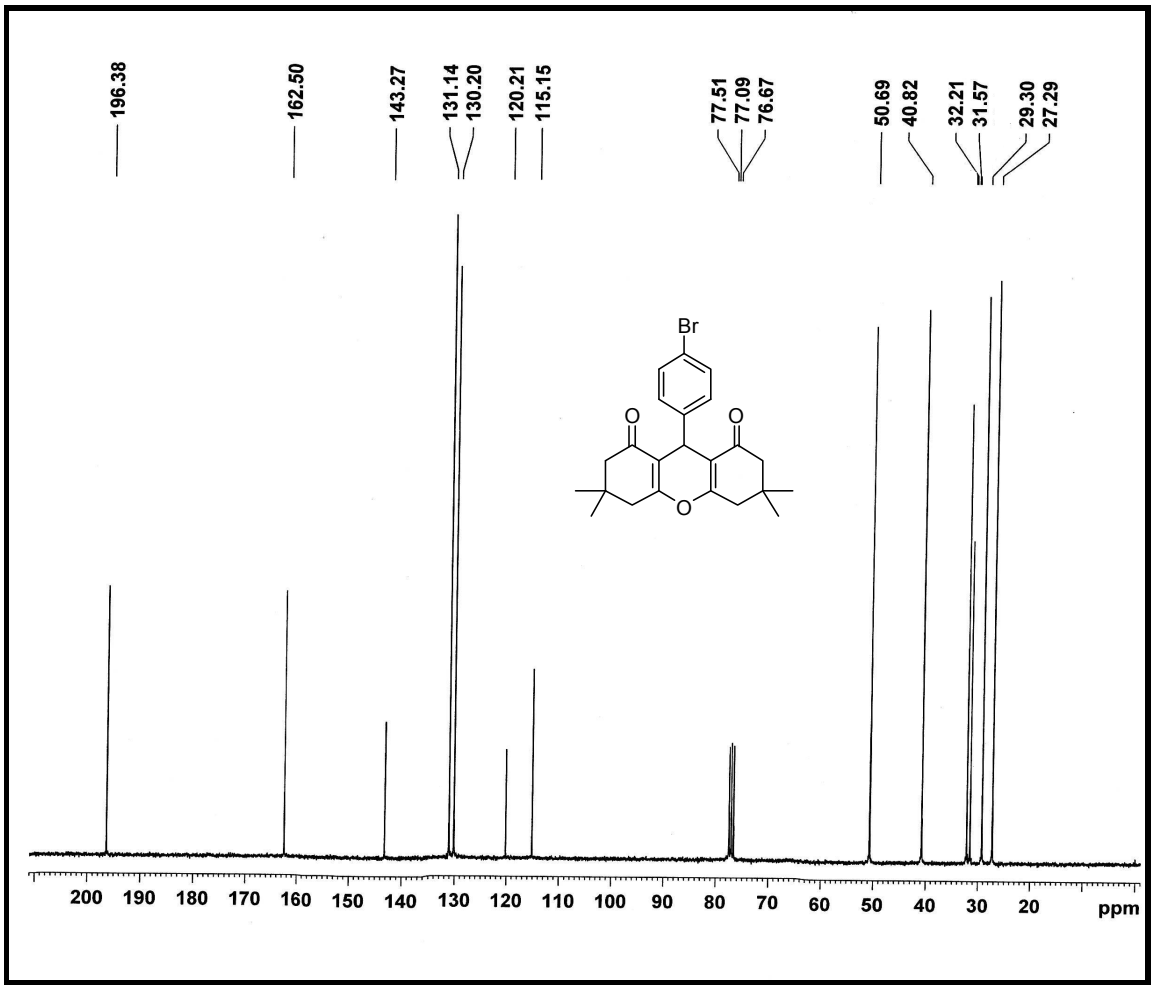
3,3,6,6-Tetramethyl-9(5-bromo-2-hydroxyphenyl)-1,8-dioxo-octahydroxanthene (1i)



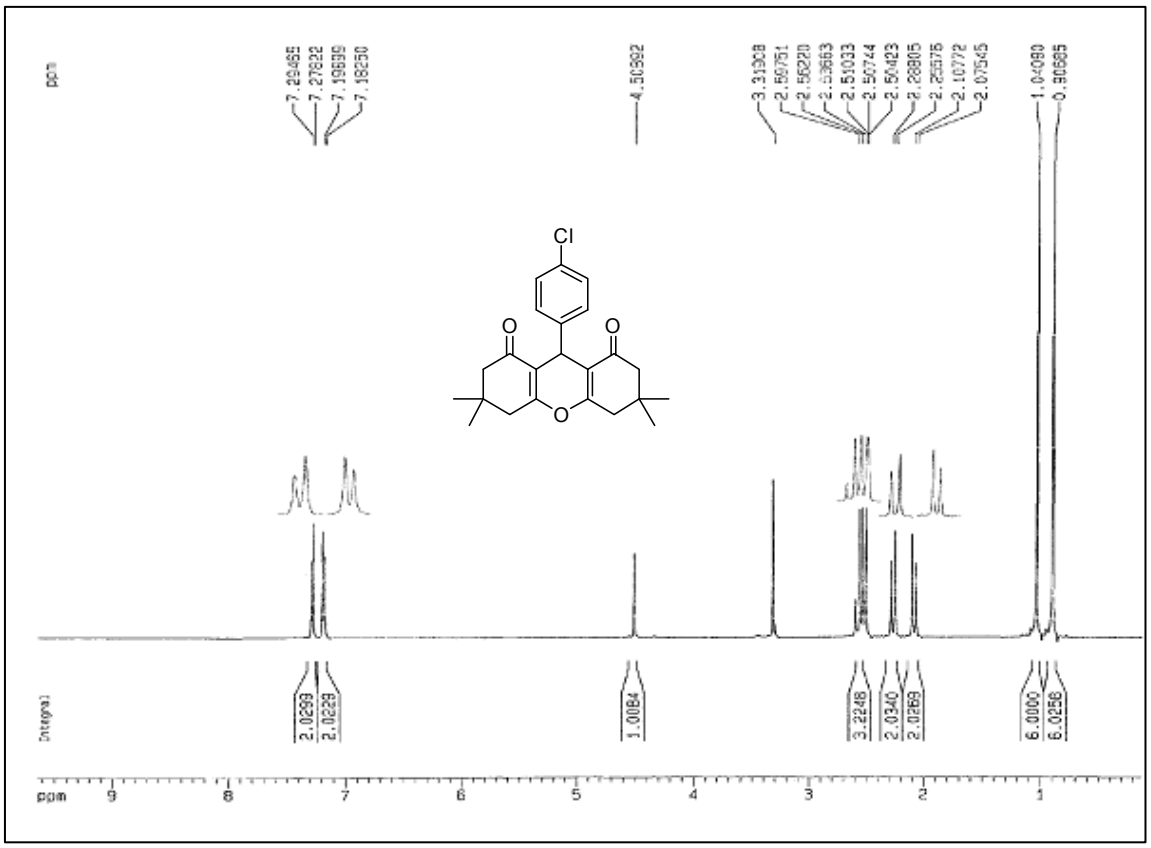
b

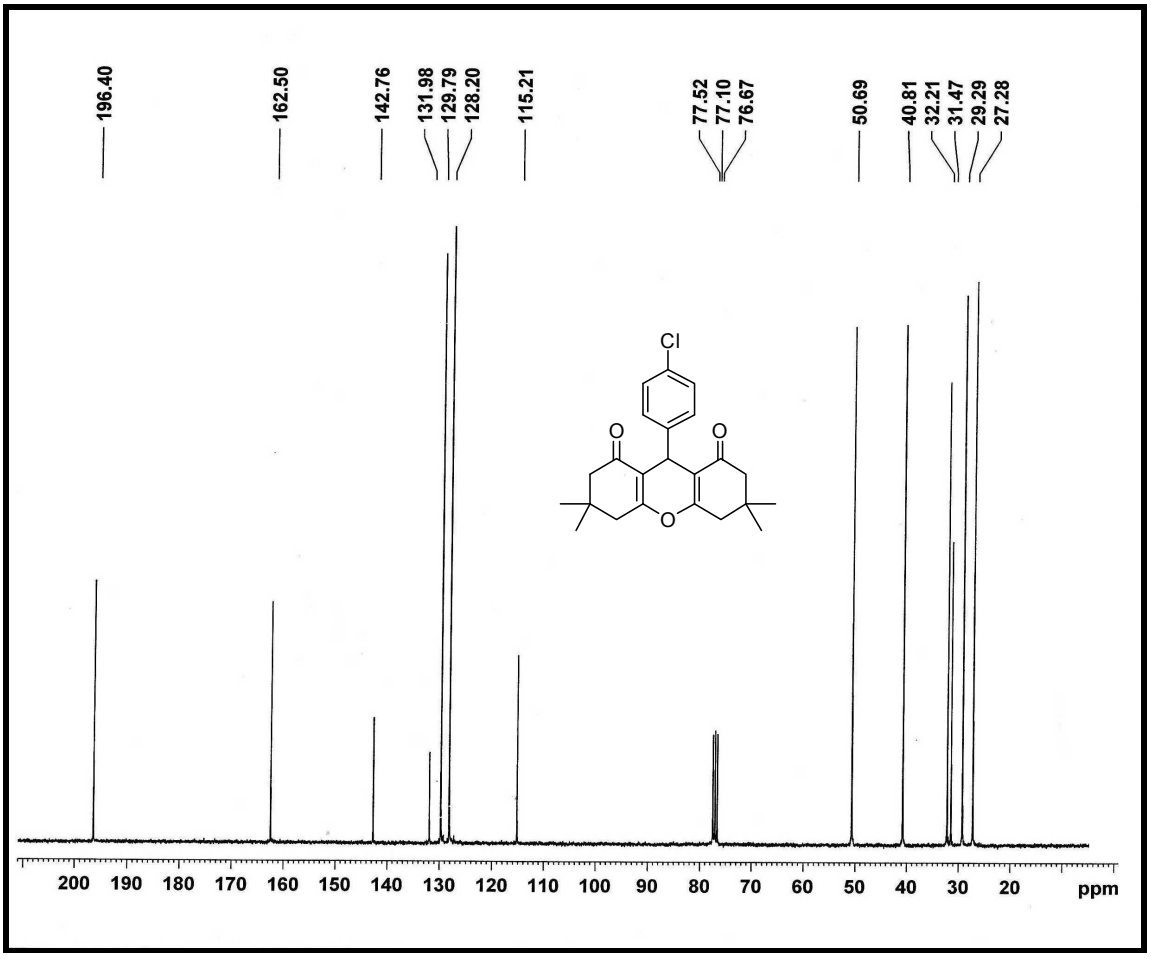
3,3,6,6-Tetramethyl-9-(4-bromophenyl)-1,8-dioxo-octahydroxanthene (1J)





3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene (1k)





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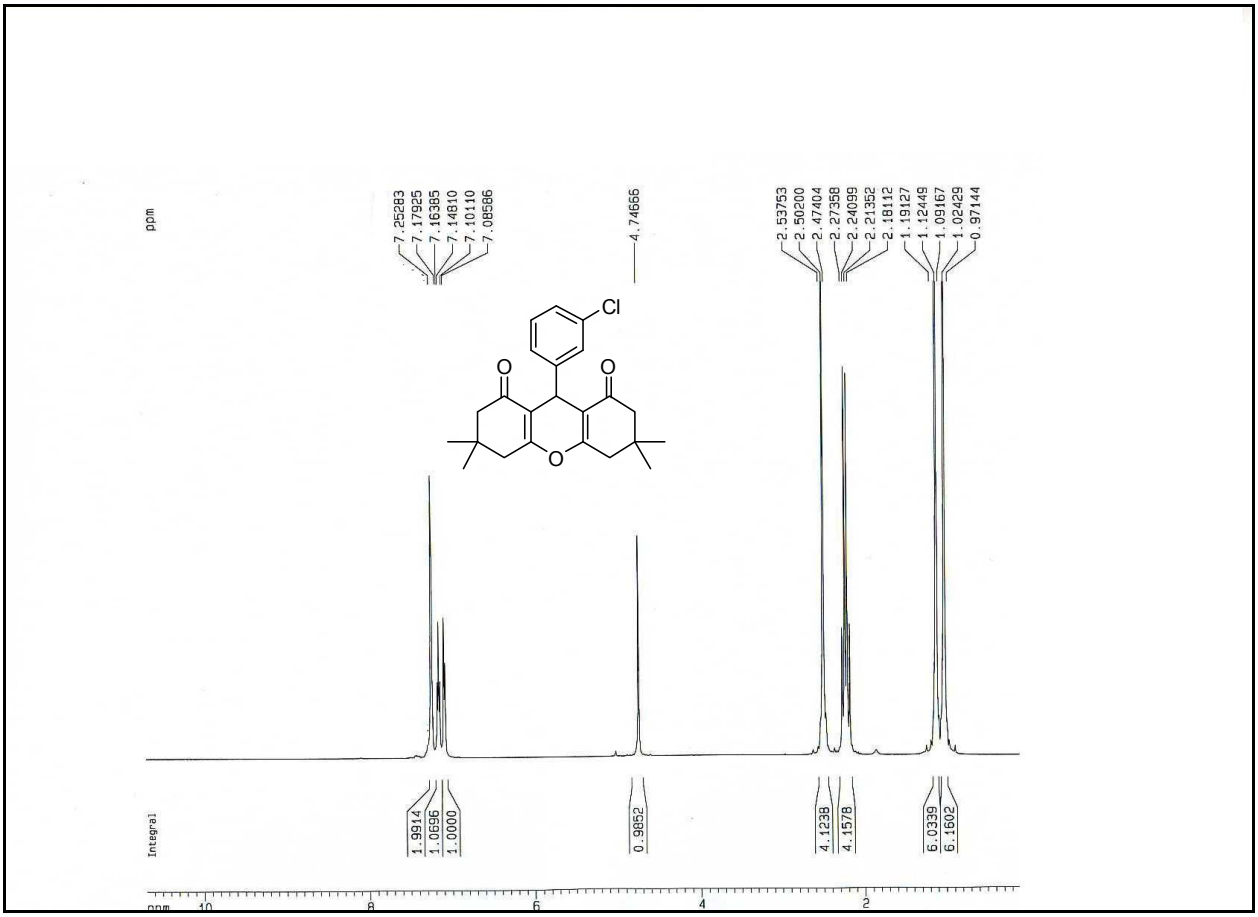

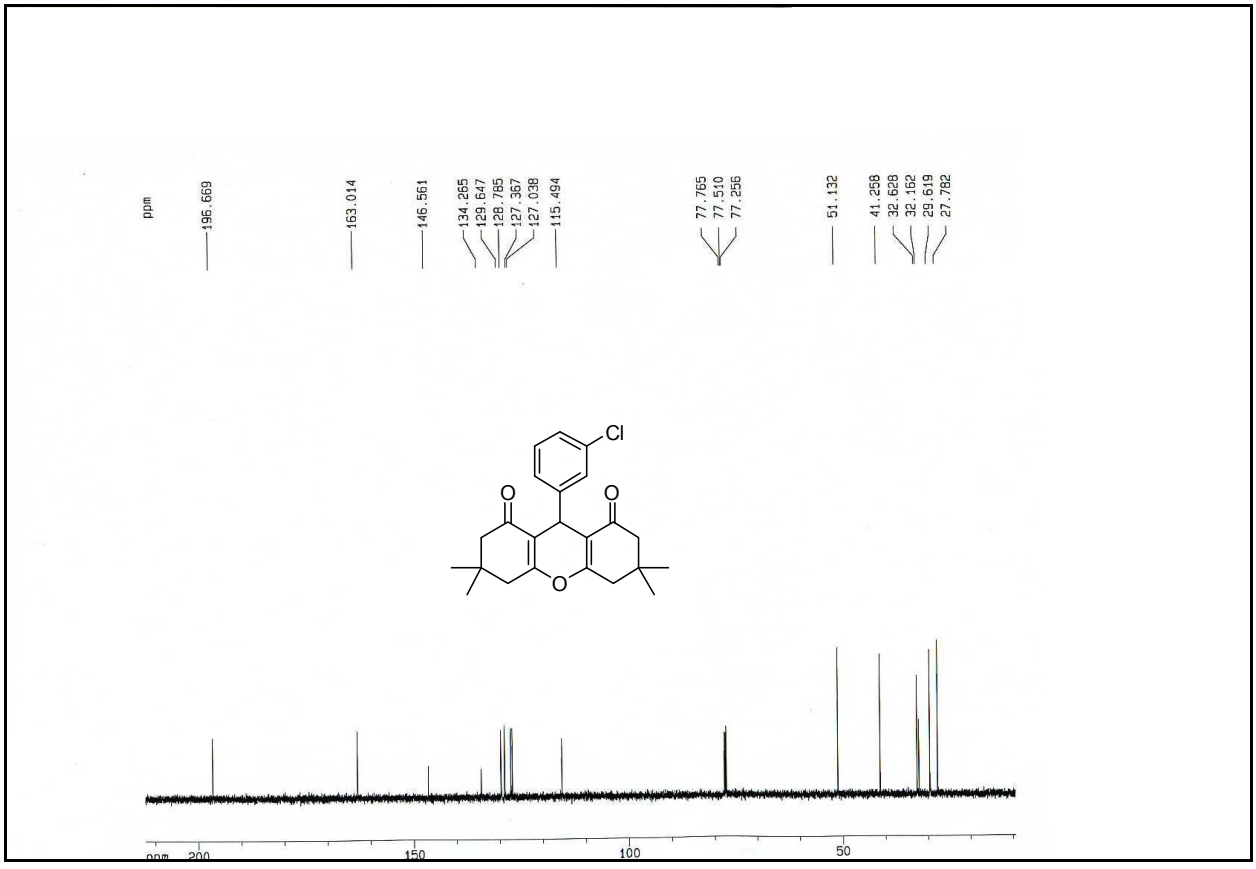

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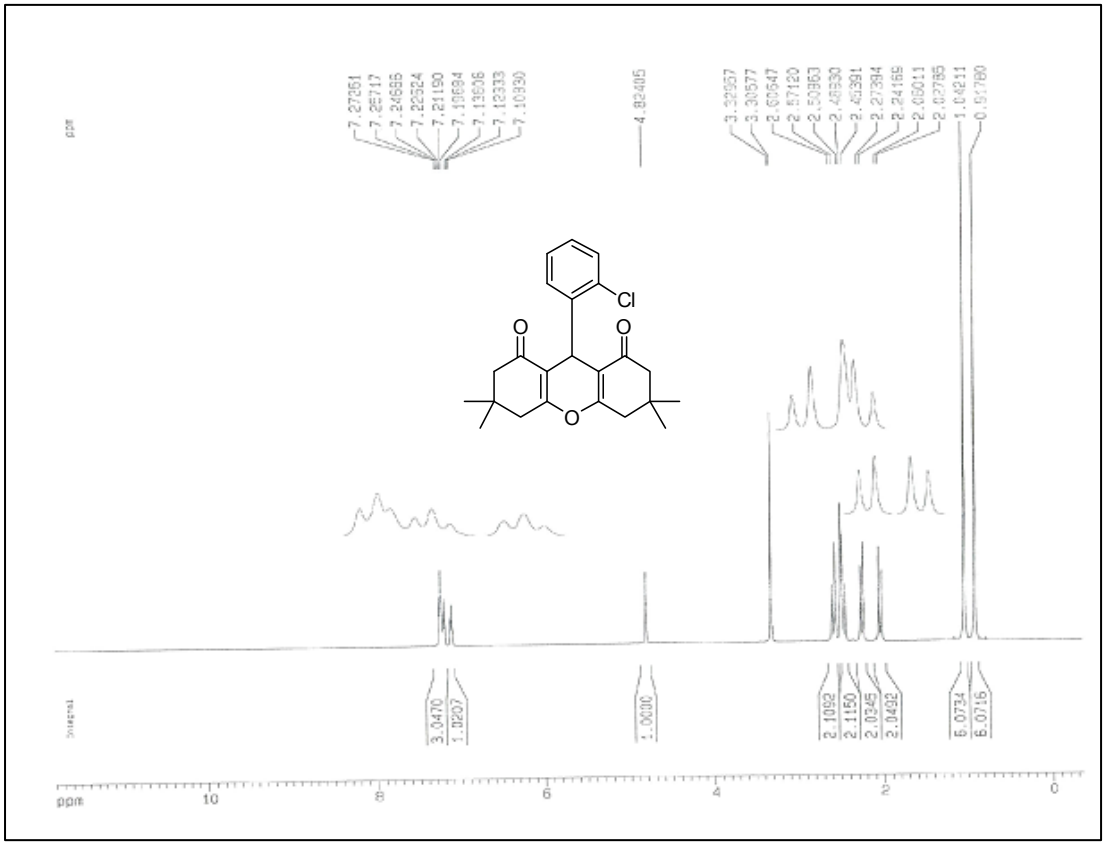
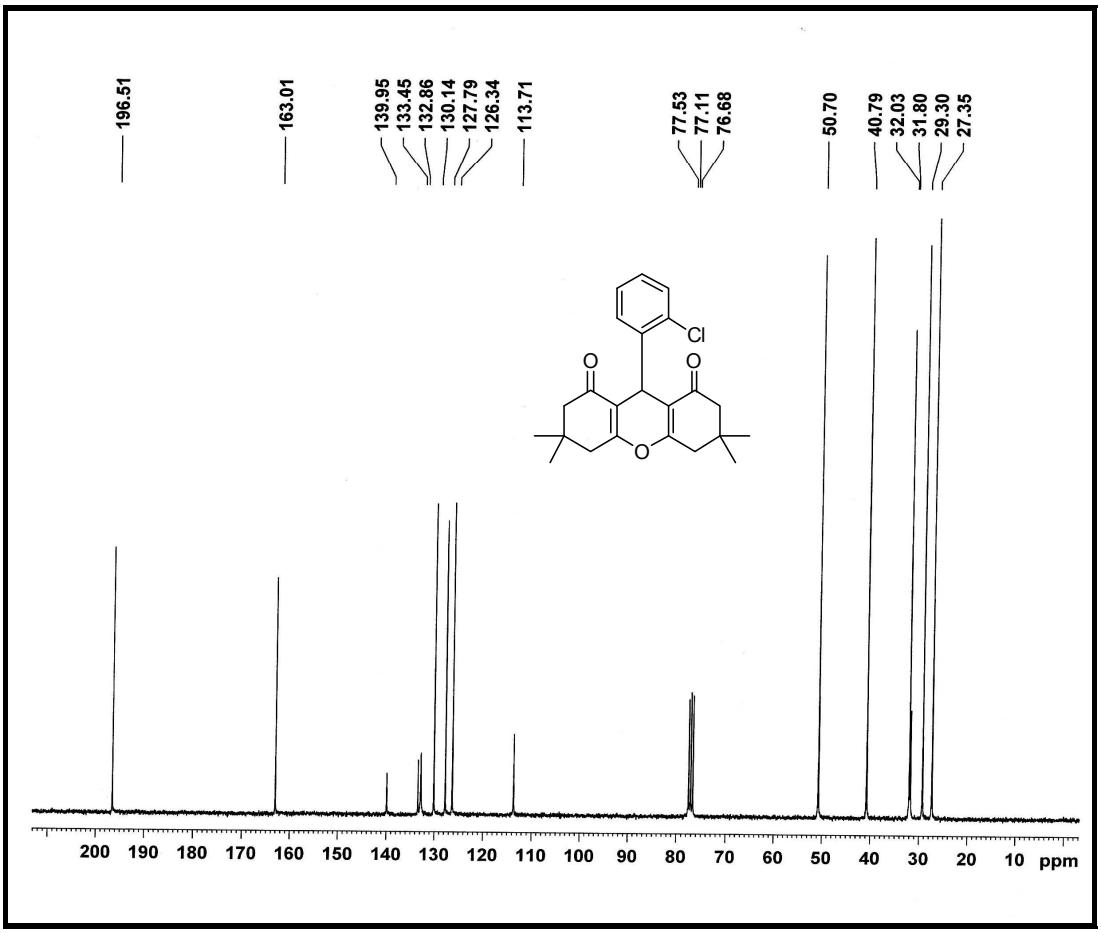
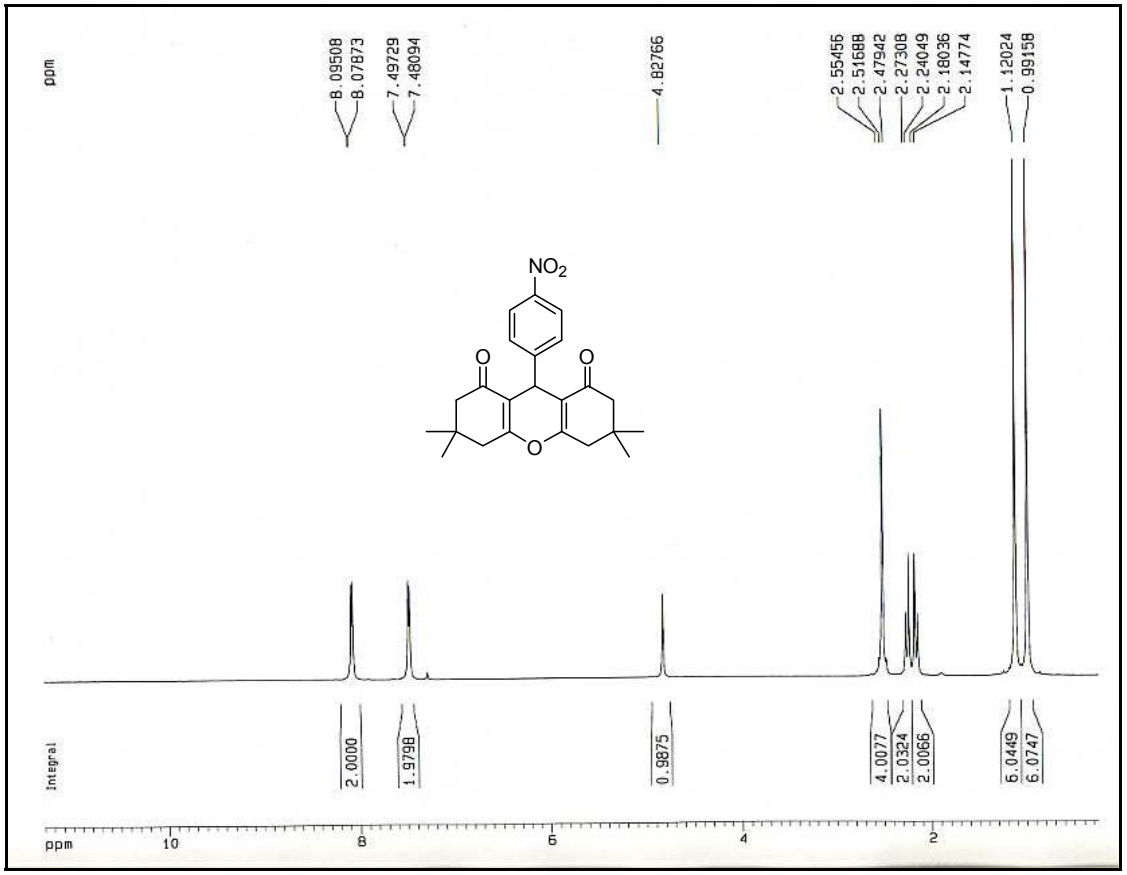
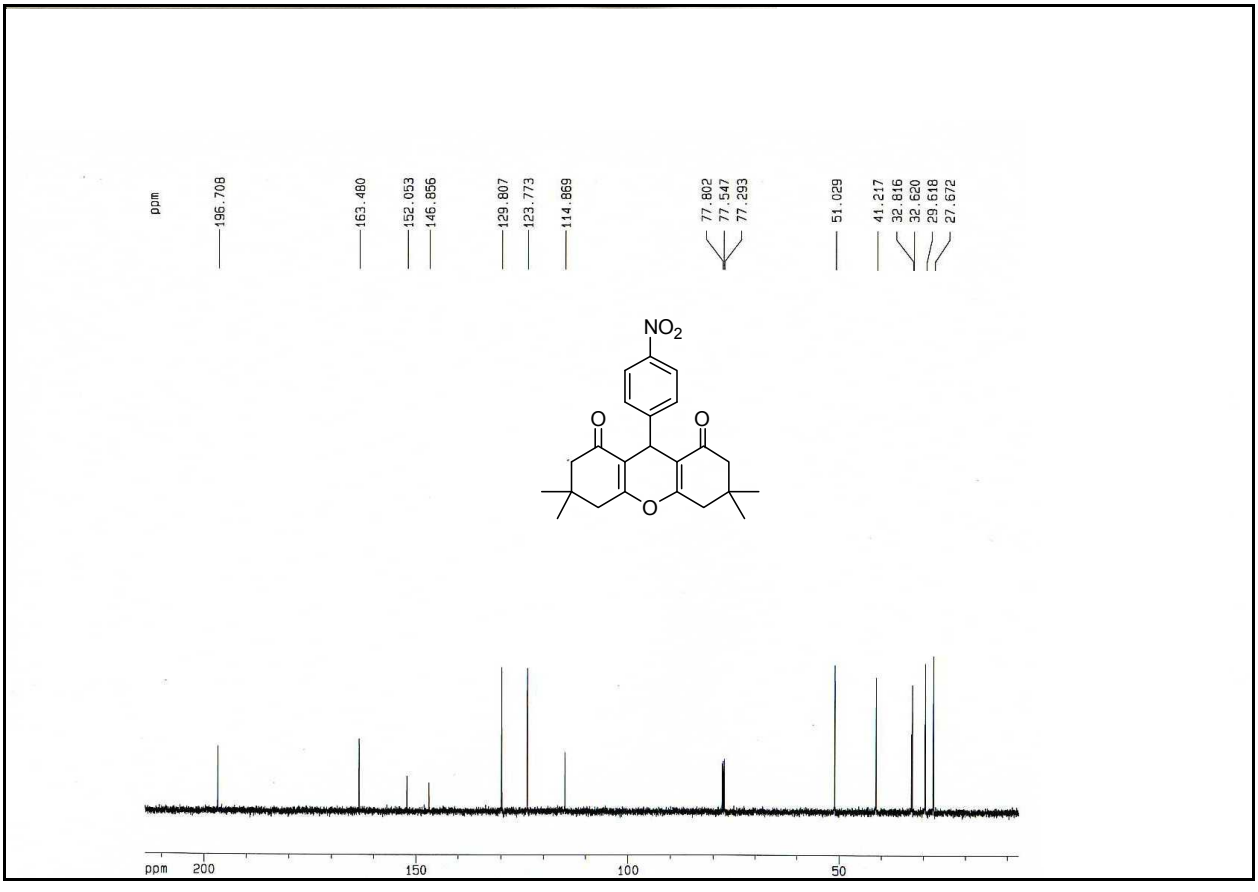




3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene (1n)





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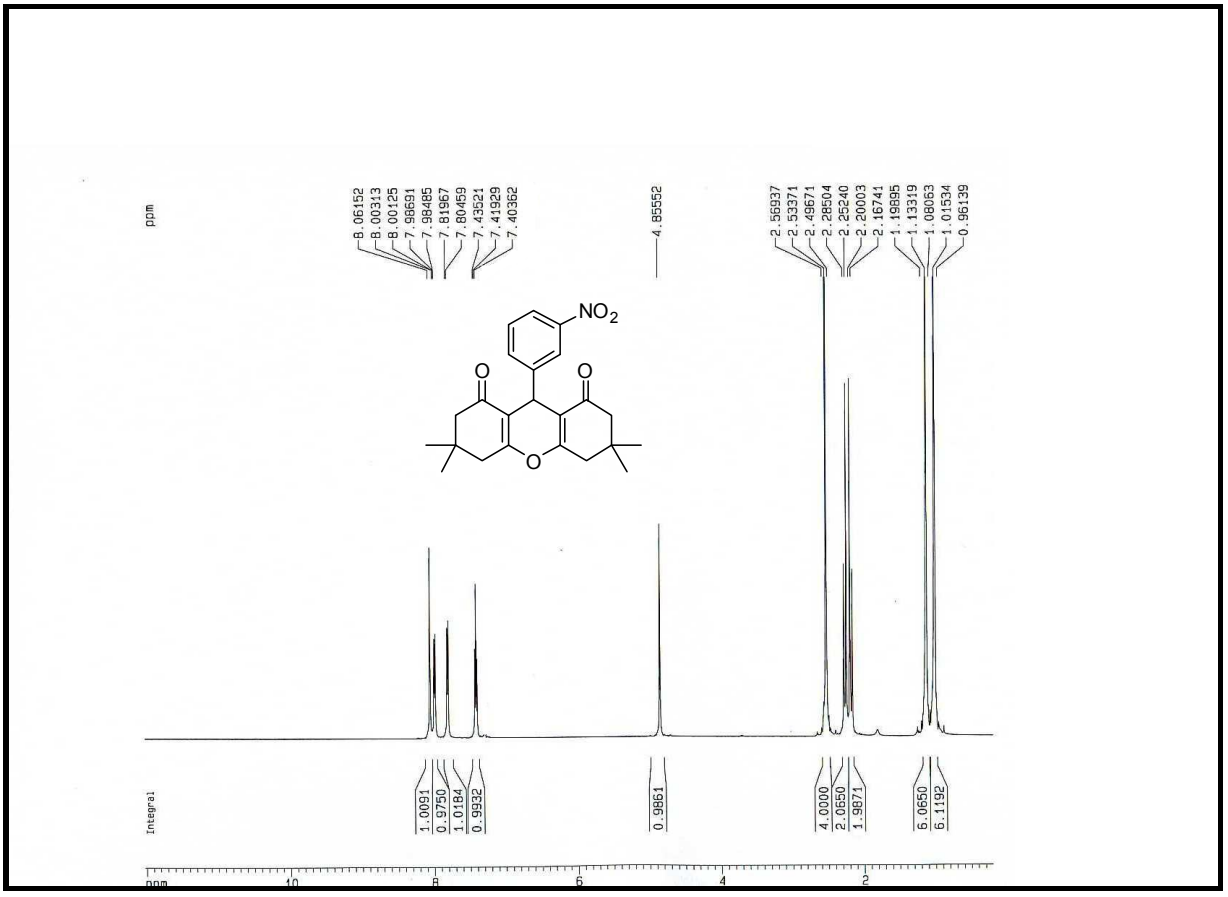

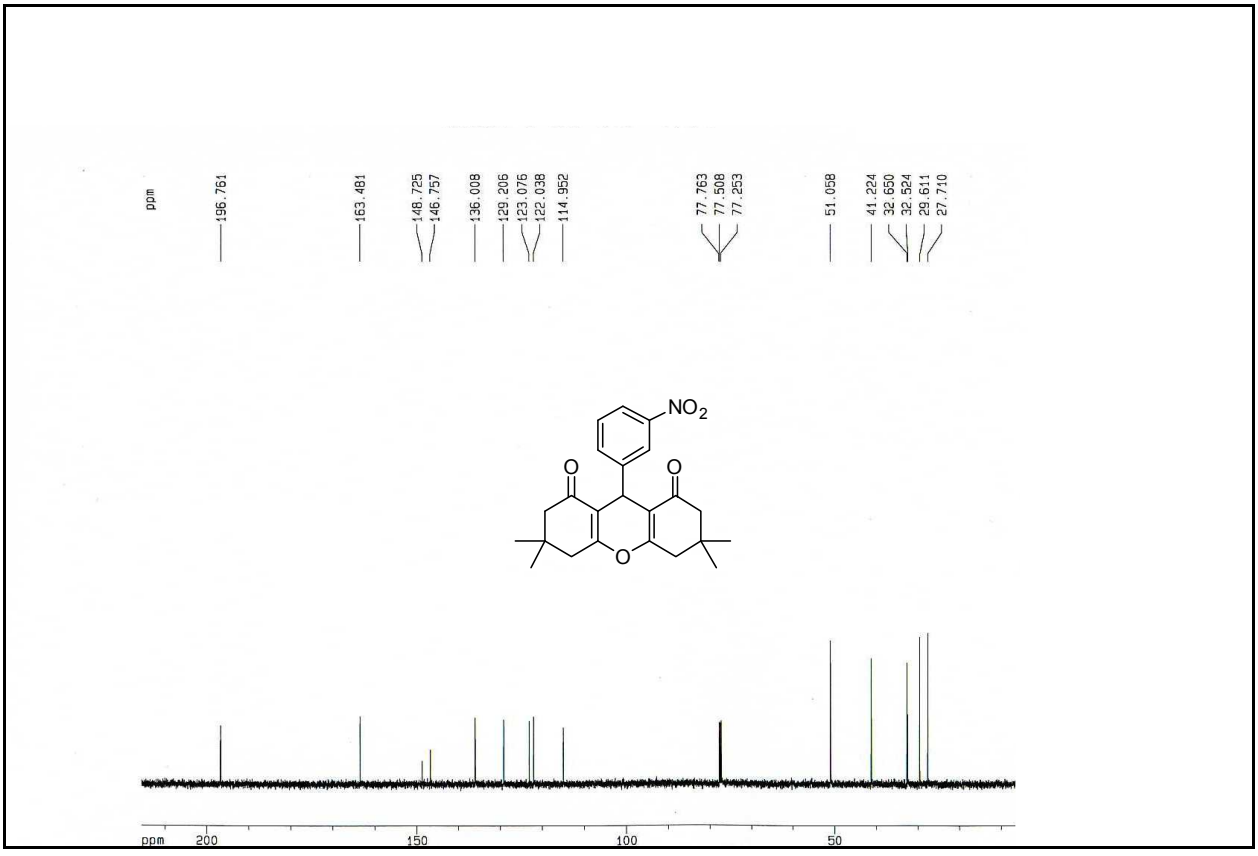

3,3,6,6-Tetramethyl-9-(4-cyanophenyl)-1,8-dioxo-octahydroxanthene (1p)