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SUPPLEMENTARY MATERIAL TO

Facile and rapid synthesis of diverse xanthene derivatives using Lanthanum(III) chloride/chloroacetic acid as an efficient and reusable catalytic system under solvent-free conditions

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*9,10-dihydro-9,9-dimethyl-12-phenyl-8*H-*benzo[a]xanthen-11(12*H*)-one* (***5a***). IR (KBr, ν / cm^{-1}): 3072, 2960, 1664 (C=O), 1624, 1424, 1359. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm) 0.98 (3H, *s*, CH_3), 1.14 (3H, *s*, CH_3), 2.21–2.36 (2H, *m*, CH_2), 2.59 (2H, *s*, CH_2), 5.73 (1H, *s*, CH), 7.05–7.21 (3H, *m*, arom.), 7.34––7.47 (5H, *m*, arom.), 7.75-8.03 (3H, *m*, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 7.18, 29.30, 34.71, 41.42, 50.89, 109.46, 114.27, 117.05, 117.70, 123.69, 124.91, 126.25, 127.01, 128.07, 128.24, 128.43, 128.84, 129.77, 131.40, 131.49, 144.74, 147.73, 197.02.

9*,10-dihydro-12-(4-hydroxyphenyl)-9,9-dimethyl-8*H-*benzo[*a*]xanthen--11(12*H*)-one* (**5b**). IR (KBr, ν / cm^{-1}): 3354 (OH), 3059, 3022, 2954, 2869, 1651(C=O), 1594, 1466, 1373. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.99 (3H, *s*, CH_3), 1.13 (3H, *s*, CH_3), 2.22–2.36 (2H, *m*, CH_2), 2.59 (2H, *s*, CH_2), 4.83 (1H, *s*, OH), 5.66 (1H, *s*, CH), 6.61–6.67 (2H, *m*, arom.), 7.14–7.21 (2H, *m*, arom.), 7.32–7.47 (3H, *m*, arom.), 7.69–8.00 (3H, *m*, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 27.17, 29.26, 33.87, 41.41, 50.90, 109.47, 114.43, 115.19, 117.02, 117.62, 123.73, 124.91, 126.98, 128.39, 128.77, 129.57, 131.51, 137.00, 147.62, 154.01, 162.32, 197.67**.**

*12-phenyl-9,10-dihydro-8*H-*benzo[*a*]xanthen-11(12*H*)-one* (***5c***). IR (KBr, ν / / cm^{-1}): 3063, 2967, 2895, 1652(C=O), 1595, 1369. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.98–2.10 (2H, *m*, CH_2), 2.30–2.52 (2H, *m*, CH_2), 2.64–2.80 (2H, *m*, CH_2), 5.76 (1H, *s*, CH), 7.09 (1H, *t*, J = 7 Hz, arom.), 7.18 (2H, *t*, J = 8 Hz, arom.), 7.35–7.42 (3H, *m*, arom.), 7.43–7.46 (2H, *m*, arom.), 7.78–7.81 (2H, *m*, arom.), 7.99 (1H, *d*, J = 8 Hz, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 27.28, 27.75, 34.64, 37.06, 115.56, 116.98, 117.71, 123.71, 124.89, 126.56,

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127.00, 128.28, 128.38, 128.50, 128.64, 131.39, 131.49, 150.09, 145.04, 147.78, 147.78, 165.63, 197.11.

*9,10-dihydro-12-(3-nitrophenyl)-8*H-*benzo[*a*]xanthen-11(12*H*)-one* (***5d***). IR (KB ν / cm^{-1}): 3064, 2954, 2891, 1647(C=O), 1595, 1375. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.95–2.13 (2H, *m*, CH_2), 2.35–2.47 (2H, *m*, CH_2), 2.69–2.85 (2H, *m*, CH_2), 5.86 (1H, *s,* CH), 7.37–7.48 (4H, *m*, arom.), 7.81–7.86 (4H, *m*, arom.), 7.95–8.11 (2H, *m*, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.25, 27.75, 34.72, 36.91, 114.40, 116.01, 117.16, 121.61, 122.52, 123.16, 123.33, 125.20, 127.36, 128.69, 129.08, 131.61, 134.95, 135.99, 146.99, 147.83, 197.10.

*9,10-dihydro-12-(4-nitrophenyl)-8*H-*benzo[*a*]xanthen-11(12*H*)-one* (***5e***). IR (KBr, ν / cm^{-1}): 3106, 3068, 2946, 2887, 1651 (C=O), 1593, 1455. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.93–2.15 (2H, *m*, CH_2), 2.35–2.52 (2H, *m*, CH_2), 2.68––2.83 (2H, *m*, CH_2), 5.86 (1H, *s*, CH), 7.38–7.54 (5H, *m*, arom.), 7.82–7.85 (3H, *m*, arom.), 8.05–8.12 (2H, *m*, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.23, 27.78, 34.83, 36.95, 114.25, 116.05, 117.04, 123.15, 123.46, 123.68, 125.25, 127.40, 128.67, 129.44, 129.65, 131.01, 131.57, 143.35, 147.77, 152.13, 196.99.

*9-phenyl-3,4,5,6,7,9-hexahydro-1*H-*xanthene-1,8(2*H*)-dione* (***6a***). IR (KBr, ν / cm^{-1}): 3050, 2953, 2885, 1673 (C=O), 1621, 1429. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.96–2.05 (4H, *m*, CH_2), 2.29–2.41 (4H, *m*, CH_2), 2.54–2.70 (4H, *m*, CH_2), 4.83 (1H, *s*, CH), 7.12–7.33 (5H, *m*, arom.). ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.30, 27.16, 31.62, 36.96, 116.91, 126.42, 128.38, 144.37, 163.91, 196.55.

*9-(4-chlorophenyl)-3,4,6,7-tetrahydro-2*H-*xanthen-1,8(5*H*,9*H*)-dione* (***6b***). IR (KBr, ν / cm^{-1}): 3086, 3052, 2958, 2893, 1667 (C=O), 1616, 1459. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.92–2.10 (4H, *m*, CH_2), 2.29–2.42 (4H, *m*, CH_2), 2.54–2.70 (4H, *m*, CH_2), 4.78 (1H, *s*, CH), 7.18–7.28 (4H, *m*, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.28, 27.13, 31.29, 36.91, 116.49, 128.24, 129.81, 132.09, 142.94, 164.10, 196.56.

*9-(4-hydroxyphenyl)-3,4,5,6,7,9-hexahydro-1*H-*xanthene-1,8(2H)-dione* (***6c***). IR (KBr, ν / cm^{-1}): 3378 (OH), 3022, 2949, 2920, 2867, 1661 (C=O), 1609, 1446. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.98–2.08 (4H, *m*, CH_2), 2.29–2.44 (4H, *m*, CH_2), 2.53–2.70 (4H, *m*, CH_2), 4.26 (1H, *s*, –OH), 4.76 (1H, *s*, CH), 6.66 (2H, *d*, J = 8.4 Hz, arom.), 7.16 (2H, *d*, J = 8.4 Hz, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.31, 27.14, 30.79, 36.98, 115.08, 117.07, 129.52, 136.58, 154.23, 163.86, 196.94.

*9-(*p*-tolyl)-3,4,5,6,7,9-hexahydro-1*H-*xanthen-1,8(2*H*)-dione* (***6d***). IR (KBr, ν / cm^{-1}): 3012, 2949, 2919, 2867, 1661 (C=O), 1609, 1446. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.44–1.47 (4H, *m*, CH_2), 2.11 (3H, *s*, CH_3), 2.14–2.22 (4H, *m*, CH_2), 2.63–2. 80 (4H, *m*, CH_2), 4.88 (1H, *s*, CH), 7.42 (2H, *d*, J = 7 Hz, arom.), 7.49 (2H, *d*, J = 7 Hz, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.61,

26.40, 27.62, 30.92, 36.14, 118.71, 129.35, 129.65, 129.98, 130.32, 130.78, 130.88, 130.98, 197.04.

*3,4,6,7-tetrahydro-9-(4-nitrophenyl)-2*H*-xanthen-1,8(5*H*,9*H*)-dione (**6e**)*. IR (KBr, ν / cm^{-1}): 3022, 2949, 2920, 2867, 1661 (C=O), 1609, 1446. ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.98–2.10 (4H, *m*, CH_2), 2.35–2.52 (4H, *m*, CH_2), 2.64––2.80 (4H, *m*, CH_2), 4.76 (1H, *s*, CH), 7.42 (2H, *d*, *J* = 8 Hz, arom.), 7.48–7.70 (2H, *m*, arom.); ^{13}C-NMR ($CDCl_3$, 100 MHz, δ / ppm): 20.62, 27.62, 30.63, 36.17, 116.16, 127.96, 129.22, 129.98, 130.98, 145.69, 157.76, 195.41.

*9-(3-nitrophenyl)-3,4,5,6,7,9-hexahydro-1*H*-xanthen-1,8(2*H*)-dione (**6f**)*. IR (KBr, ν / cm^{-1}): 3031, 2922, 1664 (CO), 1595. ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 1.61–1.78 (4H, *m*, CH_2), 2.06–2.19 (4H, *m*, $2CH_2$), 4.72 (1H, *s*, CH), 7.55 (1H, *t*, *J* = 7 Hz, 1H, arom.), 7.72–7.75 (1H, *m*, arom.), 7.97–8.16 (2H, *m*, arom.); ^{13}C-NMR (DMSO-d_6, 100 MHz, δ / ppm): 21.10, 26.18, 32.36, 36.54, 113.54, 121.47, 129.35, 148.02, 153.32, 167.37, 196.04.

*3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione (**6g**)*. IR (KBr, ν / cm^{-1}): 3029, 2988, 1669 (CO), 1596. ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.68 (6H, *s*, CH_3), 0.85 (6H, *s*, CH_3), 1.73 (2H, d, *J* = = 17.4 Hz), 1.97 (2H, *d*, *J* = 16.0 Hz), 2.15 (4H, *dd*, J_1 = 15.9 Hz, J_2 = 3.6 Hz), 5.01 (1H, *s*), 7.20–7.30 (4H, *m*, arom.), 7.47 (1H, *d*, *J* = 6.9 Hz, arom.); ^{13}C-NMR (DMSO-d_6, 100 MHz, δ / ppm): 26.40, 29.63, 32.47, 41.37, 50.00, 113.55, 126.26, 128.00, 128.42, 135.33, 141.31, 146.68, 150.5, 167.41, 195.6.

*9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1*H*-xanthen--1,8(2*H*)-dione (**6h**)*. IR (KBr, ν / cm^{-1}): 3031, 2989, 1670 (CO), 1596. ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 0.67 (6H, *s*, CH_3), 0.85 (6H, *s*, CH_3), 1.76 (2H, *d*, *J* = 17.4 Hz), 1.99 (2H, *d*, *J* = 16.0 Hz), 2.17 (4H, *dd*, J_1 = 15.9 Hz, J_2 = 3.6 Hz), 5.11 (1H, *s*), 7.54–7.56 (2H, *d*, *J* = 7 Hz, arom.), 8.05–8.07 (2H, *d*, *J* = 6.9 Hz, arom.); ^{13}C-NMR (DMSO-d_6, 100 MHz, δ / ppm): 26.45, 29.59, 32.55, 41.34, 49.80, 112.66, 122.57, 130.26, 134.77, 136.51, 147.86, 148.61, 151.30, 167.34, 195.59.

*11-Phenyl-10*H*-di-indeno[1,2-*b*:2',1'-*e*]pyran-10,12(11*H*)-dione (**7a**)*. IR (KBr, cm^{-1}): 3066, 2945, 2841, 1699 (C=O), 1608; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm) 4.66 (1H, *s*, CH), 7.03–7.05 (1H, *m*, Ar-H), 7.10–7.18 (2H, *m*, Ar-H), 7.47–7.60 (3H, *m*, Ar-H), 7.84–7.94 (3H, *m*, Ar-H), 8.03–8.07 (2H, *m*, Ar-H), 8.49 (2H, *d*, *J* = 6.8 Hz, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 47.01, 122.08, 123.37, 124.30, 125.68, 128.82, 130.93, 133.23, 134.18, 135.26, 136.65, 147.04, 196.78.

*11-(4-Chlorophenyl)-10*H*-di-indeno[1,2-*b*:2',1'-*e*]pyran-10,12(11*H*)-dione (**7b**)*. Anal. calcd. for $C_{25}H_{13}ClO_3$: C, 75.67; H, 3.30 %. Found: C, 75.48; H, 3.32 %; IR (KBr, cm^{-1}): 3062, 2950, 29021, 1689 (C=O), 1608; ^{1}H-MR (400 MHz, DMSO-d_6, δ / ppm) 5.13 (1H, *s*, CH), 6.79 (4H, *t*, *J* = 8.0 Hz, Ar-H), 6.96 (1H, *d*, *J* = 8.0 Hz, Ar-H), 7.15 (1H, *d*, *J* = 6.8 Hz, Ar-H), 7.59 (2H, *t*, *J* = 7.6 Hz,

Ar-H), 7.75 (1H, *d*, *J* = 8.0 Hz, Ar-H), 8.08 (2H, *d*, *J* = 8.0 Hz, Ar-H), 8.11 (1H, *d*, *J* = 2.5 Hz, Ar-H); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 40.8, 111.9, 116.1, 120.9, 121.9, 129.1, 129.6, 131.0, 134.2, 147.3, 148.3, 151.8, 157.8, 195.1.