Supporting Information

Manganese(III)-Mediated Oxidative Annulation with Methylenecyclopropanes with β -Dicarbonyl Compounds

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General remarks. ^1H -NMR spectra were recorded on a 300 MHz spectrometer in CDCl_3 using tetramethylsilane as the internal standard. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA^+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points are uncorrected. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel.

General Reaction Procedure for the Manganese(III)-Based Oxidative Annulation of 2,4-Pentanedione with Methylenecyclopropane 1.

Under an argon atmosphere, MCP **1** (0.50 mmol), 2,4-pentanedione (1.50 mmol) and $\text{Mn}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ (1.1 mmol) were dissolved in 5.0 mL of acetic acid. The reaction mixture was stirred at room temperature for 12 hrs. The reaction solution was diluted with ether (20 mL) and washed with water, saturated NaHCO_3 solution, brine and water. The organic layers were dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to give **2a** as a colorless solid.

1-(6-Methyl-4,4-diphenyl-5-oxa-spiro[2.4]hept-6-en-7-yl)ethanone (2a). a colorless solid, yield: 60%. mp: 106-108 $^\circ\text{C}$; IR (thin film): ν 3011, 1638, 1611, 1498, 1446, 1390, 1234 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.23 (t, $J = 4.8$ Hz, 2H, CH_2), 1.57 (t, $J = 4.8$ Hz, 2H, CH_2), 2.24 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 7.25-7.35 (m, 10H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.0, 17.0, 30.7, 32.9, 94.8, 117.0, 127.7, 127.8, 141.7, 165.3, 193.3; MS (EI) m/z : 304 (M^+) (35), 261 (27), 213 (21), 204 (23), 189 (20), 165 (21), 43 (100); Anal. calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_3$ requires C, 82.86; H, 6.62; found: C, 82.76; H, 6.85%.

The crystal data of **2a** has been deposited in CCDC with number 232276. Empirical Formula: $C_{21}H_{20}O_2$; Formula Weight: 304.37; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.290 x 0.288 x 0.213 mm; Crystal System: Monoclinic; Lattice Type: Primitive; Lattice Parameters: $a = 10.1025(11)\text{\AA}$, $b = 12.1715(12)\text{\AA}$, $c = 13.6175(14)\text{\AA}$, $\alpha = 90^\circ$, $\beta = 99.925(2)^\circ$, $\gamma = 90^\circ$, $V = 1649.4(3)\text{\AA}^3$; Space group: $P2(1)/n$; $Z = 4$; $D_{calc} = 1.226\text{ g/cm}^3$; $F_{000} = 648$; Diffractometer: Rigaku AFC7R; Residuals: R ; R_w : 0.0511, 0.0854.

Table 1. Crystal data and structure refinement for cd23453.

Identification code	cd23453
Empirical formula	C21 H20 O2
Formula weight	304.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 10.1025(11) Å alpha = 90 deg. b = 12.1715(12) Å beta = 99.925(2) deg. c = 13.6175(14) Å gamma = 90 deg.
Volume	1649.4(3) Å ³
Z, Calculated density	4, 1.226 Mg/m ³
Absorption coefficient	0.077 mm ⁻¹
F(000)	648
Crystal size	0.290 x 0.288 x 0.213 mm
Theta range for data collection	2.26 to 28.29 deg.
Limiting indices	-13<=h<=10, -11<=k<=16, -18<=l<=18
Reflections collected / unique	9910 / 3836 [R(int) = 0.0633]
Completeness to theta = 28.29	93.4 %
Absorption correction	Sadabs
Max. and min. transmission	1.00000 and 0.48127
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3836 / 1 / 289
Goodness-of-fit on F ²	0.851
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.0854
R indices (all data)	R1 = 0.1022, wR2 = 0.1013
Extinction coefficient	0.0037(7)
Largest diff. peak and hole	0.241 and -0.132 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23453. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	9455(1)	6102(1)	1954(1)	44(1)
O(2)	6254(2)	5288(1)	-766(1)	70(1)
C(1)	8889(2)	5001(1)	2118(1)	38(1)
C(2)	8126(2)	4736(1)	1073(1)	41(1)
C(3)	7326(3)	3702(2)	860(2)	59(1)
C(4)	8586(3)	3840(2)	447(2)	59(1)
C(5)	7777(2)	5851(1)	632(1)	41(1)
C(6)	8632(2)	6564(1)	1158(2)	42(1)
C(7)	8932(3)	7755(2)	1045(3)	63(1)
C(8)	6782(2)	6054(2)	-262(2)	51(1)
C(9)	6361(3)	7208(2)	-571(2)	70(1)
C(10)	7995(2)	5205(1)	2896(1)	39(1)
C(11)	6605(2)	5250(2)	2673(2)	47(1)
C(12)	5853(3)	5509(2)	3403(2)	56(1)
C(13)	6473(3)	5709(2)	4363(2)	62(1)
C(14)	7854(3)	5670(2)	4591(2)	65(1)
C(15)	8604(3)	5424(2)	3875(2)	55(1)
C(16)	10044(2)	4232(1)	2488(1)	39(1)
C(17)	9787(2)	3234(2)	2920(2)	47(1)
C(18)	10814(3)	2493(2)	3209(2)	52(1)
C(19)	12098(3)	2728(2)	3085(2)	57(1)
C(20)	12374(2)	3712(2)	2666(2)	57(1)
C(21)	11343(2)	4463(2)	2372(2)	49(1)

Table 3. Bond lengths [Å] and angles [deg] for cd23453.

O(1)-C(6)	1.369(2)
O(1)-C(1)	1.4885(19)
O(2)-C(8)	1.223(2)
C(1)-C(16)	1.514(2)
C(1)-C(10)	1.527(3)
C(1)-C(2)	1.531(2)
C(2)-C(3)	1.497(3)
C(2)-C(5)	1.501(2)
C(2)-C(4)	1.506(3)
C(3)-C(4)	1.487(3)
C(3)-H(1)	1.00(2)
C(3)-H(2)	0.97(2)
C(4)-H(3)	0.968(19)
C(4)-H(4)	1.01(2)
C(5)-C(6)	1.341(2)
C(5)-C(8)	1.460(3)
C(6)-C(7)	1.493(3)
C(7)-H(5)	0.95(3)
C(7)-H(6)	0.918(17)
C(7)-H(7)	0.94(3)
C(8)-C(9)	1.507(3)
C(9)-H(8)	1.02(2)
C(9)-H(9)	0.97(2)
C(9)-H(10)	0.96(2)
C(10)-C(11)	1.387(3)
C(10)-C(15)	1.394(3)
C(11)-C(12)	1.388(3)
C(11)-H(11)	0.970(17)
C(12)-C(13)	1.371(3)
C(12)-H(12)	1.022(19)
C(13)-C(14)	1.376(3)
C(13)-H(13)	0.99(2)
C(14)-C(15)	1.367(3)
C(14)-H(14)	0.96(2)
C(15)-H(15)	0.96(2)
C(16)-C(21)	1.377(3)
C(16)-C(17)	1.393(2)
C(17)-C(18)	1.380(3)
C(17)-H(16)	0.986(17)
C(18)-C(19)	1.367(3)
C(18)-H(17)	1.004(19)
C(19)-C(20)	1.375(3)
C(19)-H(18)	0.988(19)
C(20)-C(21)	1.392(3)
C(20)-H(19)	0.98(2)
C(21)-H(20)	0.958(19)
C(6)-O(1)-C(1)	106.99(13)
O(1)-C(1)-C(16)	108.21(14)
O(1)-C(1)-C(10)	104.27(13)
C(16)-C(1)-C(10)	112.53(15)
O(1)-C(1)-C(2)	101.29(13)
C(16)-C(1)-C(2)	114.52(15)
C(10)-C(1)-C(2)	114.61(16)
C(3)-C(2)-C(5)	126.94(17)
C(3)-C(2)-C(4)	59.37(15)
C(5)-C(2)-C(4)	120.13(18)
C(3)-C(2)-C(1)	121.74(17)
C(5)-C(2)-C(1)	103.11(14)
C(4)-C(2)-C(1)	121.59(17)
C(4)-C(3)-C(2)	60.63(14)
C(4)-C(3)-H(1)	118.9(11)
C(2)-C(3)-H(1)	118.3(11)
C(4)-C(3)-H(2)	118.8(13)

C(2)-C(3)-H(2)	114.8(11)
H(1)-C(3)-H(2)	114.7(16)
C(3)-C(4)-C(2)	60.00(15)
C(3)-C(4)-H(3)	120.3(12)
C(2)-C(4)-H(3)	116.7(11)
C(3)-C(4)-H(4)	120.0(12)
C(2)-C(4)-H(4)	117.5(11)
H(3)-C(4)-H(4)	112.6(17)
C(6)-C(5)-C(8)	128.54(18)
C(6)-C(5)-C(2)	106.67(16)
C(8)-C(5)-C(2)	124.51(17)
C(5)-C(6)-O(1)	113.82(15)
C(5)-C(6)-C(7)	134.2(2)
O(1)-C(6)-C(7)	111.94(18)
C(6)-C(7)-H(5)	111.0(15)
C(6)-C(7)-H(6)	114.6(17)
H(5)-C(7)-H(6)	126(2)
C(6)-C(7)-H(7)	104.8(17)
H(5)-C(7)-H(7)	85(2)
H(6)-C(7)-H(7)	109(2)
O(2)-C(8)-C(5)	120.64(19)
O(2)-C(8)-C(9)	118.6(2)
C(5)-C(8)-C(9)	120.7(2)
C(8)-C(9)-H(8)	108.9(14)
C(8)-C(9)-H(9)	108.9(13)
H(8)-C(9)-H(9)	105.5(19)
C(8)-C(9)-H(10)	113.1(14)
H(8)-C(9)-H(10)	109(2)
H(9)-C(9)-H(10)	111.0(19)
C(11)-C(10)-C(15)	117.8(2)
C(11)-C(10)-C(1)	123.48(17)
C(15)-C(10)-C(1)	118.64(18)
C(10)-C(11)-C(12)	120.7(2)
C(10)-C(11)-H(11)	118.8(11)
C(12)-C(11)-H(11)	120.5(11)
C(13)-C(12)-C(11)	120.5(2)
C(13)-C(12)-H(12)	121.1(11)
C(11)-C(12)-H(12)	118.4(11)
C(12)-C(13)-C(14)	119.2(2)
C(12)-C(13)-H(13)	117.6(12)
C(14)-C(13)-H(13)	123.2(12)
C(15)-C(14)-C(13)	120.8(2)
C(15)-C(14)-H(14)	120.1(13)
C(13)-C(14)-H(14)	119.1(13)
C(14)-C(15)-C(10)	121.1(2)
C(14)-C(15)-H(15)	122.4(12)
C(10)-C(15)-H(15)	116.5(12)
C(21)-C(16)-C(17)	118.53(19)
C(21)-C(16)-C(1)	122.04(17)
C(17)-C(16)-C(1)	119.37(18)
C(18)-C(17)-C(16)	120.3(2)
C(18)-C(17)-H(16)	120.1(10)
C(16)-C(17)-H(16)	119.6(10)
C(19)-C(18)-C(17)	120.7(2)
C(19)-C(18)-H(17)	123.6(11)
C(17)-C(18)-H(17)	115.7(11)
C(18)-C(19)-C(20)	119.9(2)
C(18)-C(19)-H(18)	123.1(12)
C(20)-C(19)-H(18)	117.0(12)
C(19)-C(20)-C(21)	119.7(2)
C(19)-C(20)-H(19)	122.7(11)
C(21)-C(20)-H(19)	117.5(11)
C(16)-C(21)-C(20)	120.9(2)
C(16)-C(21)-H(20)	121.0(12)
C(20)-C(21)-H(20)	118.0(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23453.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	46(1)	31(1)	53(1)	2(1)	0(1)	-7(1)
O(2)	78(1)	71(1)	54(1)	2(1)	-11(1)	-9(1)
C(1)	44(1)	26(1)	42(1)	1(1)	4(1)	-5(1)
C(2)	49(1)	34(1)	38(1)	0(1)	2(1)	-2(1)
C(3)	73(2)	41(1)	56(2)	-1(1)	-10(1)	-13(1)
C(4)	81(2)	48(1)	45(2)	-13(1)	1(1)	10(1)
C(5)	45(1)	38(1)	39(1)	3(1)	5(1)	-1(1)
C(6)	44(1)	32(1)	51(1)	5(1)	9(1)	3(1)
C(7)	58(2)	34(1)	93(2)	10(1)	4(2)	-5(1)
C(8)	51(1)	59(1)	43(1)	5(1)	8(1)	1(1)
C(9)	79(2)	66(2)	59(2)	12(1)	-3(2)	21(2)
C(10)	44(1)	30(1)	43(1)	-1(1)	4(1)	1(1)
C(11)	49(1)	39(1)	51(1)	5(1)	5(1)	3(1)
C(12)	53(2)	46(1)	73(2)	6(1)	20(1)	7(1)
C(13)	78(2)	44(1)	69(2)	-5(1)	32(2)	11(1)
C(14)	76(2)	69(2)	50(2)	-18(1)	13(1)	7(1)
C(15)	53(2)	59(1)	50(1)	-13(1)	4(1)	4(1)
C(16)	46(1)	34(1)	36(1)	-4(1)	4(1)	1(1)
C(17)	51(1)	39(1)	48(1)	1(1)	3(1)	-2(1)
C(18)	68(2)	38(1)	47(1)	3(1)	-1(1)	4(1)
C(19)	62(2)	54(2)	53(2)	-2(1)	1(1)	19(1)
C(20)	48(2)	67(2)	56(2)	5(1)	10(1)	11(1)
C(21)	50(1)	47(1)	49(1)	5(1)	7(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23453.

	x	y	z	U(eq)
H(1)	7315(18)	3172(16)	1415(15)	60(6)
H(2)	6470(20)	3791(15)	420(15)	68(7)
H(3)	9390(20)	3445(15)	735(14)	60(7)
H(4)	8540(20)	3992(15)	-285(16)	68(7)
H(5)	9860(30)	7860(20)	1020(20)	117(11)
H(6)	8230(20)	8159(19)	711(18)	121(11)
H(7)	9160(30)	8020(20)	1700(20)	124(12)
H(8)	7120(20)	7578(19)	-854(18)	93(9)
H(9)	5610(20)	7177(16)	-1115(17)	79(8)
H(10)	6150(20)	7647(18)	-29(18)	87(9)
H(11)	6165(17)	5099(13)	1995(14)	45(5)
H(12)	4830(20)	5539(14)	3208(14)	62(6)
H(13)	5890(20)	5860(15)	4865(15)	66(7)
H(14)	8290(20)	5782(15)	5272(17)	72(7)
H(15)	9570(20)	5399(15)	4013(15)	67(7)
H(16)	8861(18)	3054(13)	3004(13)	45(5)
H(17)	10554(19)	1797(16)	3523(14)	64(6)
H(18)	12860(20)	2215(15)	3272(14)	64(6)
H(19)	13270(20)	3906(15)	2545(14)	63(7)
H(20)	11554(19)	5126(16)	2052(15)	64(7)

Table 6. Torsion angles [deg] for cd23453.

C(6)-O(1)-C(1)-C(16)	146.26(15)
C(6)-O(1)-C(1)-C(10)	-93.75(16)
C(6)-O(1)-C(1)-C(2)	25.53(18)
O(1)-C(1)-C(2)-C(3)	-177.77(18)
C(16)-C(1)-C(2)-C(3)	66.0(3)
C(10)-C(1)-C(2)-C(3)	-66.2(2)
O(1)-C(1)-C(2)-C(5)	-27.36(18)
C(16)-C(1)-C(2)-C(5)	-143.54(16)
C(10)-C(1)-C(2)-C(5)	84.23(17)
O(1)-C(1)-C(2)-C(4)	111.1(2)
C(16)-C(1)-C(2)-C(4)	-5.1(3)
C(10)-C(1)-C(2)-C(4)	-137.3(2)
C(5)-C(2)-C(3)-C(4)	106.5(2)
C(1)-C(2)-C(3)-C(4)	-110.5(2)
C(5)-C(2)-C(4)-C(3)	-117.6(2)
C(1)-C(2)-C(4)-C(3)	110.7(2)
C(3)-C(2)-C(5)-C(6)	169.1(2)
C(4)-C(2)-C(5)-C(6)	-118.4(2)
C(1)-C(2)-C(5)-C(6)	20.8(2)
C(3)-C(2)-C(5)-C(8)	-16.5(3)
C(4)-C(2)-C(5)-C(8)	55.9(3)
C(1)-C(2)-C(5)-C(8)	-164.86(19)
C(8)-C(5)-C(6)-O(1)	-178.96(19)
C(2)-C(5)-C(6)-O(1)	-4.9(2)
C(8)-C(5)-C(6)-C(7)	-2.1(4)
C(2)-C(5)-C(6)-C(7)	172.0(3)
C(1)-O(1)-C(6)-C(5)	-13.9(2)
C(1)-O(1)-C(6)-C(7)	168.54(19)
C(6)-C(5)-C(8)-O(2)	166.0(2)
C(2)-C(5)-C(8)-O(2)	-7.0(3)
C(6)-C(5)-C(8)-C(9)	-15.4(4)
C(2)-C(5)-C(8)-C(9)	171.6(2)
O(1)-C(1)-C(10)-C(11)	104.05(18)
C(16)-C(1)-C(10)-C(11)	-138.90(17)
C(2)-C(1)-C(10)-C(11)	-5.7(2)
O(1)-C(1)-C(10)-C(15)	-71.86(19)
C(16)-C(1)-C(10)-C(15)	45.2(2)
C(2)-C(1)-C(10)-C(15)	178.35(16)
C(15)-C(10)-C(11)-C(12)	0.2(3)
C(1)-C(10)-C(11)-C(12)	-175.72(17)
C(10)-C(11)-C(12)-C(13)	-1.0(3)
C(11)-C(12)-C(13)-C(14)	1.2(3)
C(12)-C(13)-C(14)-C(15)	-0.6(4)
C(13)-C(14)-C(15)-C(10)	-0.1(3)
C(11)-C(10)-C(15)-C(14)	0.3(3)
C(1)-C(10)-C(15)-C(14)	176.47(19)
O(1)-C(1)-C(16)-C(21)	-18.1(2)
C(10)-C(1)-C(16)-C(21)	-132.82(18)
C(2)-C(1)-C(16)-C(21)	94.0(2)
O(1)-C(1)-C(16)-C(17)	164.79(16)
C(10)-C(1)-C(16)-C(17)	50.1(2)
C(2)-C(1)-C(16)-C(17)	-83.1(2)
C(21)-C(16)-C(17)-C(18)	-1.0(3)
C(1)-C(16)-C(17)-C(18)	176.17(17)
C(16)-C(17)-C(18)-C(19)	0.6(3)
C(17)-C(18)-C(19)-C(20)	-0.1(3)
C(18)-C(19)-C(20)-C(21)	0.1(3)
C(17)-C(16)-C(21)-C(20)	0.9(3)
C(1)-C(16)-C(21)-C(20)	-176.15(18)
C(19)-C(20)-C(21)-C(16)	-0.5(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd23453 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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1-(6-Methyl-4,4-di-p-tolyl-5-oxa-spiro[2.4]hept-6-en-7-yl)ethanone (2b).

a colorless white solid, yield: 72%. mp: 112-114 °C; IR (thin film): ν 3003, 2923, 1638, 1608, 1512, 1445, 1388, 1236, 1185 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.02 (t, $J = 4.5$ Hz, 2H, CH_2), 1.35 (t, $J = 4.5$ Hz, 2H, CH_2), 2.02 (s, 3H, CH_3), 2.06 (s, 6H, CH_3), 2.13 (s, 3H, CH_3), 6.98 (d, $J = 8.1$ Hz, 4H, ArH), 7.01 (d, $J = 8.1$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 8.9, 17.0, 21.0, 30.6, 32.9, 94.0, 116.2, 127.6, 128.4, 137.3, 138.8, 165.3, 193.2; MS (EI) m/z : 332 (M^+) (35), 289 (150), 232 (14), 227 (25), 215 (14), 202 (14), 43 (100); Anal. calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_2$ requires C, 83.10; H, 7.28; found: C, 82.88; H, 7.27%.

1-[4,4-Bis(4-methoxyphenyl)-6-methyl-5-oxa-spiro[2.4]hept-6-en-7-yl]ethanone (2c).

a colorless oil, yield: 53%. IR (thin film): ν 3002, 2933, 1609, 1512, 1463, 1442, 1389, 1302, 1250, 1176, 1114, 1035 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.02 (t, $J = 5.1$ Hz, 2H, CH_2), 1.35 (t, $J = 4.5$ Hz, 2H, CH_2), 2.04 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 3.61 (s, 6H, OCH_3), 6.94 (d, $J = 8.5$ Hz, 4H, ArH), 7.07 (d, $J = 8.5$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.6, 17.0, 30.6, 33.1, 55.1, 94.7, 113.0, 117.0, 129.0, 134.0, 159.0, 165.4, 193.3; MS (EI) m/z : 364 (M^+) (34), 321 (15), 293 (13), 243 (67), 201 (8), 121 (12), 43 (100); HRMS (EI): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_2$ requires 364.1675, found: 364.1639.

Acetic acid (5-acetyl-6-methyl-3,4-dihydro-2H-pyran-4-yl)-bis(4-methoxyphenyl)methyl ester (3c).

a yellowish oil, yield: 23%. IR (thin film): ν 2933, 1737, 1670, 1611, 1463, 1443, 1512, 1463, 1443, 1385, 1368, 1303, 1250, 1179, 1035 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 1.53-1.65 (m, 2H, CH_2), 1.90 (s, 3H, CH_3), 2.266 (s, 3H, CH_3), 2.274 (s, 3H, CH_3), 3.55-3.72 (m, 2H, CH_2), 3.778 (s, 3H, OCH_3), 3.781 (s, 3H, OCH_3), 3.93 (t, $J = 6.0$ Hz, 1H, CH_2), 6.82 (d, $J = 8.7$ Hz, 2H, ArH), 6.84 (d, $J = 8.7$ Hz, 2H, ArH), 7.19 (d, $J = 8.7$ Hz, 2H, ArH), 7.38 (d, $J = 8.7$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 15.9, 21.0, 29.2, 31.0, 46.0, 55.2, 62.3, 94.7, 113.3, 119.6, 127.5, 127.8, 132.8, 136.6, 158.6, 159.0, 165.6, 170.9, 193.5; MS (EI) m/z : 424 (M^+) (6), 381 (31), 364 (70), 321 (99), 303 (34), 279 (41), 243 (53), 226 (59), 135 (53), 43 (100); HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{28}\text{O}_6$ requires 424.1886, found: 424.1911.

1-[4,4-Bis(4-chlorophenyl)-6-methyl-5-oxa-spiro[2.4]hept-6-en-7-yl]ethanone (2d).

a colorless solid, yield: 55%. mp: 109-111 °C; IR (thin film): ν 3000, 2933, 1641, 1614, 1491, 1389, 1231, 1094, 1014 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.20 (dd, $J = 6.6, 3.8$ Hz, 2H, CH_2), 1.58 (t, $J = 6.6, 3.8$ Hz, 2H, CH_2), 2.23 (s, 3H, CH_3), 2.27 (s, 6H, CH_3), 7.16 (d, $J = 9.0$ Hz, 4H, ArH), 7.20 (d, $J = 9.0$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 8.9, 16.8, 30.6, 32.8, 93.7, 116.8, 128.1, 129.0, 134.0, 139.7, 164.8, 193.2; MS (EI) m/z : 372 (M^+) (40), 329 (19), 247 (32), 215 (28), 189 (20), 43 (100); HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{18}\text{Cl}_2\text{O}_2$ requires 372.0684, found: 372.0681.

1-[4,4-Bis(4-fluorophenyl)-6-methyl-5-oxa-spiro[2.4]hept-6-en-7-yl]ethanone (2e).

a colorless oil, yield: 77% IR (thin film): ν 3293, 1639, 1612, 1508, 1388, 1230, 1159, 1101, 1012 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.11 (dd, $J = 6.9, 4.5$ Hz, 2H, CH_2), 1.50 (dd, $J = 6.9, 4.5$ Hz, 2H, CH_2), 2.15 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 6.91 (dd, $J = 8.7$ Hz, $J_{\text{H-F}} = 8.7$ Hz, 4H, ArH), 7.21 (dd, $J = 8.7$ Hz, $J_{\text{H-F}} = 5.4$ Hz, 4H, ArH); ^{19}F NMR (CDCl_3 , TMS, 282 MHz): δ -114.5; ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.0, 16.9, 30.6, 33.0, 93.9, 114.7 (d, $J = 24.6$ Hz), 116.9, 129.4 (d, $J = 2.1$ Hz), 137.4 (d, $J = 12.6$ Hz), 160.6, 164.4 (d, $J = 246.3$ Hz), 193.3; MS (EI) m/z : 340 (M^+) (23), 297 (12), 231 (15), 201 (9), 84 (13), 43 (100); HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{18}\text{F}_2\text{O}_2$ requires 340.1275, found: 340.1227.

1-[4-(4-Methoxyphenyl)-6-methyl-4-phenyl-5-oxa-spiro[2.4]hept-6-en-7-yl]ethanone (2f).

a yellow oil, yield: 67%. For **2f**: IR (thin film): ν 3001, 2931, 1637, 1610, 1512, 1446, 1389, 1302, 1252, 1234, 1176, 1035 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.06-0.16 (m, 1H, CH_2), 0.27-0.36 (m, 1H, CH_2), 1.38-1.47 (m, 1H, CH_2), 1.60-1.73 (m, 1H, CH_2), 2.24 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.81 (s, 3H, CH_3), 6.83 (d, $J = 9.1$ Hz, 2H, ArH), 7.25-7.32 (m, 7H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 8.72, 9.24, 17.0, 30.6, 33.0, 55.1, 94.7, 113.0, 116.9, 127.5, 127.7, 127.8, 129.2, 134.1, 141.6, 159.0, 165.3, 193.3; MS (EI) m/z : 334 (M^+) (48), 291 (24), 264 (21), 234 (24), 213 (51), 202 (18), 121 (20), 43 (100); HRMS (EI): calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_3$ requires 334.1569, found: 334.1549.

1-[4-(4-Ethoxyphenyl)-4,6-dimethyl-5-oxa-spiro[2.4]hept-6-en-7-yl]ethanone (2h).

For compound 2h. a yellowish oil, yield: 50%. IR (thin film): ν 2927, 1673, 1609, 1512, 1478, 1379, 1301, 1244, 1179, 1147, 1117, 1087, 1049 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ -0.13-0.06 (m, 1H, CH_2), 0.48-0.55 (m, 1H, CH_2), 1.03-1.11 (m, 1H, CH_2), 1.41 (t, $J = 6.9$ Hz, 3H, CH_3), 1.53-1.60 (m, 1H, CH_2), 1.61 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.02 (q, $J = 6.9$ Hz, 2H, OCH_2), 6.84 (d, $J = 8.1$ Hz, 2H, ArH), 7.19 (d, $J = 8.1$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 6.5, 10.5, 14.8, 16.9, 23.5, 30.7, 36.3, 63.3, 90.3, 113.9, 115.6, 126.6, 134.1, 158.2, 166.1, 193.5; MS (EI) m/z : 286 (M^+) (52), 271 (18), 243 (13), 216 (12), 151 (23), 115 (13), 43 (100); HRMS (EI): calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_3$ requires 286.1569, found: 286.1592.

General Reaction Procedure for the Manganese(III)-Based Oxidative Annulation of 1,3-Cyclohexanedione with Methylene cyclopropane 1a. Under an argon atmosphere, MCP **1a** (0.50 mmol), 1,3-cyclohexanedione (0.55 mmol) and $\text{Mn}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ (1.1 mmol) were dissolved in 4.0 mL of acetic acid. The reaction mixture was stirred at room temperature for 10~12 hrs. The reaction solution was diluted with ether (20 mL) and washed with water, saturated NaHCO_3 solution, brine and water. The organic layers were dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to give **4a** as a colorless solid.

Compound 4a.

a colorless solid, yield: 79%. mp: 153-155 °C; IR (thin film): ν 2948, 1628, 1492, 1446, 1423, 1408, 1367, 1237, 1180, 1072, 1008 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.36 (dd, J = 6.6, 5.1 Hz, 2H, CH_2), 1.54 (dd, 6.6, 5.1 Hz, 2H, CH_2), 2.01 (tt, J = 6.6, 6.6 Hz, 2H, CH_2), 2.32 (t, J = 6.6 Hz, 2H, CH_2), 2.43 (t, J = 6.6 Hz, 2H, CH_2), 7.25-7.40 (m, 10H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.5, 21.6, 24.4, 31.2, 37.3, 97.6, 115.7, 127.5, 128.0, 141.2, 174.3, 194.5; MS (EI) m/z : 316 (M^+) (100), 288 (15), 260 (14), 239 (19), 225 (25), 202 (33), 189 (22), 165 (25), 105 (19); Anal. calcd. for $\text{C}_{22}\text{H}_{20}\text{O}_2$ requires C, 83.51; H, 6.37; found: C, 83.45; H, 6.41%.

Compound 4b.

a slight yellow oily compound. yield: 72%. IR (thin film): ν 2948, 1628, 1492, 1446, 1423, 1408, 1367, 1237, 1180, 1072, 1008 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.26 (dd, $J = 6.6, 4.8$ Hz, 2H, CH_2), 1.44 (dd, 6.6, 5.1 Hz, 2H, CH_2), 1.92 (tt, $J = 6.9, 6.3$ Hz, 2H, CH_2), 2.23 (t, $J = 6.9$ Hz, 2H, CH_2), 2.26 (s, 6H, CH_3), 2.34 (t, $J = 6.3$ Hz, 2H, CH_2), 7.04 (d, $J = 8.1$ Hz, 4H, ArH), 7.13 (d, $J = 8.1$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.4, 21.0, 21.6, 24.4, 31.2, 37.3, 97.7, 115.7, 127.4, 128.6, 137.6, 138.4, 174.4, 194.5; MS (EI) m/z : 344 (M^+) (6), 88(11), 86 (65), 84 (100), 51 (7), 49 (28), 47 (21); HRMS (MALDI): calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_2$ requires 344.1776, found: 344.1774.

Compound 4c.

a slight yellow oily compound. yield: 44%. IR (thin film): ν 2949, 1625, 1511, 1408, 1367, 1302, 1252, 1178, 1074, 1034, 1007 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.33 (dd, $J = 6.6, 4.8$ Hz, 2H, CH_2), 1.51 (dd, 6.6, 4.8 Hz, 2H, CH_2), 2.01 (tt, $J = 6.3, 6.3$ Hz, 2H, CH_2), 2.31 (t, $J = 6.3$ Hz, 2H, CH_2), 2.42 (t, $J = 6.3$ Hz, 2H, CH_2), 3.81 (s, 6H, OCH_3), 6.84 (d, $J = 8.7$ Hz, 4H, ArH), 7.25 (d, $J = 8.7$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.4, 21.6, 24.4, 31.4, 37.3, 55.2, 97.7, 113.2, 115.7, 128.9, 133.6, 159.1, 174.4, 194.5; MS (EI) m/z : 376 (M^+) (46), 361(4), 348 (8), 277 (7), 255 (100), 135 (12), 84 (8), 49 (6); HRMS (MALDI): calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_4$ requires 376.1675, found: 376.1655.

4-[Bis(4-methoxyphenyl)methylene]-2,3,4,6,7,8-hexahydrochromen-5-one (5c).

a slight yellow oily compound. yield: 25%, IR (thin film): ν 2925, 1707, 1667, 1607, 1510, 1250, 1179, 1028 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 1.93 (dd, $J = 6.6, 6.6$ Hz, 2H, CH_2), 2.24 (t, $J = 6.6$ Hz, 2H, CH_2), 2.60 (t, $J = 6.6$ Hz, 2H, CH_2), 2.84 (t, $J = 8.1$ Hz, 2H, CH_2), 3.27 (t, $J = 8.1$ Hz, 2H, CH_2), 3.80 (s, 6H, CH_3), 6.82 (d, $J = 8.4$ Hz, 4H, ArH), 7.12 (d, $J = 8.4$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 17.9, 33.1, 38.3, 39.1, 40.0, 55.2, 63.8, 113.1, 129.6, 131.6, 135.6, 158.0, 187.1, 195.7, 199.0; MS (EI) m/z : 376 (M^+) (53), 361 (6), 348 (9), 255 (100), 225 (12), 135 (14); HRMS (MALDI): calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_4$ requires 2376.1675, found: 376.1653.

Compound 4d.

a colorless solid, yield: 87%. mp: 140-142 °C; IR (thin film): ν 2948, 1631, 1592, 1407, 1365, 1234, 1178, 1094, 1073, 1009 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.02 (dd, $J = 6.6, 5.1$ Hz, 2H, CH_2), 1.25 (dd, 6.6, 5.1 Hz, 2H, CH_2), 1.70 (tt, $J = 6.4, 6.2$ Hz, 2H, CH_2), 2.01 (t, $J = 6.4$ Hz, 2H, CH_2), 2.11 (t, $J = 6.2$ Hz, 2H, CH_2), 6.93 (d, $J = 9.0$ Hz, 4H, ArH), 6.99 (d, $J = 9.0$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.31, 21.5, 24.2, 31.0, 37.2, 96.4, 115.5, 128.2, 128.8, 134.1, 139.3, 173.9, 194.3; MS (EI) m/z : 384 (M^+) (100), 356 (17), 273 (18), 259 (56), 224 (36), 215 (44), 202 (31), 187 (19), 139 (35), 125 (22), 112 (13), 55 (19); HRMS (MALDI): calcd. for $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{O}_2$ requires 384.0684, found: 384.0728.

4-[Bis(4-chlorophenyl)methylene]-2,3,4,6,7,8-hexahydrochromen-5-one (5d).

a slight yellow oily compound. yield: 6%. IR (thin film): ν 3345, 2935, 1741, 1631, 1515, 1391, 1302, 1243, 1186, 1045 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 1.94 (dd, $J = 6.5, 6.3$ Hz, 2H, CH_2), 2.26 (t, $J = 6.5$ Hz, 2H, CH_2), 2.62 (t, $J = 6.3$ Hz, 2H, CH_2), 2.86 (t, $J = 8.4$ Hz, 2H, CH_2), 3.31 (t, $J = 8.4$ Hz, 2H, CH_2), 7.11 (d, $J = 8.7$ Hz, 4H, ArH), 7.27 (d, $J = 8.7$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 17.8, 29.7, 33.1, 38.7, 39.2, 40.0, 63.7, 128.1, 129.8, 132.6, 141.2, 184.9, 195.5, 198.8; MS (EI) m/z : 384 (M^+) (7), 275 (12), 139 (44), 111 (32), 84 (76), 71 (81), 57 (100), 43 (71); HRMS (MALDI): calcd. for $\text{C}_{22}\text{H}_{19}\text{Cl}_2\text{O}_2$ ($\text{M}^+ + 1$) requires 385.0757, found: 385.0720.

Compound 4e.

a colorless solid, yield: 71%. mp: 180-182 °C; IR (thin film): ν 2926, 1631, 1605, 1509, 1408, 1366, 1234, 1160, 1074, 1009 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.32 (dd, $J = 6.6, 4.8$ Hz, 2H, CH_2), 1.55 (dd, 6.6, 4.8 Hz, 2H, CH_2), 2.02 (tt, $J = 6.3, 6.2$ Hz, 2H, CH_2), 2.35 (t, $J = 6.3$ Hz, 2H, CH_2), 2.43 (t, $J = 6.3$ Hz, 2H, CH_2), 7.02 (d, $J = 8.7$ Hz, $J_{\text{H-F}} = 8.7$ Hz, 4H, ArH), 7.30 (dd, $J = 8.7$ Hz, $J_{\text{H-F}} = 5.4$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.4, 21.6, 24.3, 31.3, 37.3, 96.7, 115.0 (d, $J = 21.1$ Hz), 115.6, 129.3 (d, $J = 8.6$ Hz), 137.0 (d, $J = 2.8$ Hz), 162.4 (d, $J = 246.1$ Hz), 174.2, 194.5; MS (EI) m/z : 352 (M^+) (100), 324 (15), 296 (12), 281 (12), 251 (25), 243 (52), 201 (29), 123 (34); Anal. calcd. for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{O}_2$ requires C, 74.99; H, 5.15; found: C, 74.99; H, 5.11%.

4-[Bis(4-fluorophenyl)methylene]-2,3,4,6,7,8-hexahydrochromen-5-one (5c).

a slight yellow oily compound. yield: 11%. IR (thin film): ν 2925, 2853, 1709, 1668, 1601, 1508, 1230, 1161 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 1.93 (dd, $J = 6.3, 6.3$ Hz, 2H, CH_2), 2.24 (t, $J = 6.3$ Hz, 2H, CH_2), 2.61 (t, $J = 6.3$ Hz, 2H, CH_2), 2.87 (t, $J = 8.4$ Hz, 2H, CH_2), 3.30 (t, $J = 8.4$ Hz, 2H, CH_2), 6.98 (dd, $J = 8.4$ Hz, $J_{\text{H-F}} = 8.4, 8.4$ Hz, 4H, ArH), 7.15 (dd, $J = 8.4$ Hz, $J_{\text{H-F}} = 5.4$ Hz, 4H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 17.5, 33.1, 38.6, 39.2, 40.0, 114.6 (d, $J = 21.1$ Hz), 115.4, 130.1 (d, $J = 8.6$ Hz), 135.2, 138.7 (d, $J = 2.8$ Hz), 162.1 (d, $J = 246.1$ Hz), 185.8, 198.9, 201.2; MS (EI) m/z : 352 (M^+) (100), 324 (14), 281 (12), 251 (24), 243 (54), 201 (61), 123 (56), 71 (24); HRMS (MALDI): calcd. for $\text{C}_{22}\text{H}_{18}\text{F}_2\text{O}_2$ requires 352.1275, found: 352.1287.

Compound 4f.

a slight yellow oily compound. yield: 65%. IR (thin film): ν 2931, 1627, 1511, 1408, 1367, 1252, 1178, 1073 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.19-0.27 (m, 1H, CH_2), 0.42-0.50 (m, 1H, CH_2), 1.34-1.42 (m, 1H, CH_2), 1.65-1.72 (m, 1H, CH_2), 2.00 (tt, $J = 6.3, 6.3$ Hz, 2H, CH_2), 2.31 (t, $J = 6.3$ Hz, 2H, CH_2), 2.42 (t, $J = 6.3$ Hz, 2H, CH_2), 3.79 (s, 3H, OCH_3), 6.84 (d, $J = 8.7$ Hz, 2H, ArH), 7.27-7.31 (m, 7H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.09, 9.67, 21.6, 24.3, 29.6, 31.3, 37.2, 55.1, 97.6, 113.1, 115.6, 127.1, 127.8, 127.9, 129.1, 133.6, 141.1, 159.2, 174.3, 194.4; MS (EI) m/z : 346 (M^+) (100), 318 (18), 255 (23), 225 (67), 202 (21), 189 (20), 165 (16), 121 (19); HRMS (MALDI): calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_3$ requires 346.1569, found: 346.1578.

4-[(4-Methoxyphenyl)phenylmethylene]-2,3,4,6,7,8-hexahydrochromen-5-one (5f).

a slight yellow oily compound. yield: 7%. IR (thin film): ν 2925, 1723, 1609, 1511, 1460, 1372, 1252, 1189, 1088, 1033 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 1.90-2.11 (m, 2H, CH_2), 2.20-2.50 (m, 2H, CH_2), 2.58-2.68 (m, 2H, CH_2), 2.82-2.94 (m, 2H, CH_2), 3.24-3.35 (m, 2H, CH_2), 3.75 (s, 3H, OCH_3), 6.81-6.87 (m, 2H, ArH), 7.11-7.40 (m, 7H, ArH); MS (EI) m/z : 346 (M^+) (77), 318 (14), 271 (24), 247 (35), 235 (39), 225 (41), 210 (51), 165 (45), 135 (58), 85 (64), 71 (80), 57 (100); HRMS (MALDI): calcd. for $\text{C}_{23}\text{H}_{22}\text{O}_3$ requires 346.1569, found: 346.1588.

Compound 4g.

For compound **4g**, a slight yellow oily compound, yield: 40%. IR (thin film): ν 2979, 2938, 1628, 1513, 1409, 1369, 1247, 1182, 1047, 1003 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0-0.07 (m, 1H, CH_2), 0.62-0.70 (m, 1H, CH_2), 1.05-1.23 (m, 1H, CH_2), 1.41 (t, $J = 6.9$ Hz, 3H, CH_3), 1.48-1.55 (m, 1H, CH_2), 1.66 (s, 3H, CH_3), 2.02-2.13 (m, 2H, CH_2), 2.29-2.36 (m, 2H, CH_2), 2.50-2.56 (m, 2H, CH_2), 4.01 (q, $J = 6.9$ Hz, 2H, OCH_2), 6.85 (d, $J = 8.7$ Hz, 2H, ArH), 7.18 (d, $J = 8.7$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 6.8, 10.2, 14.8, 21.7, 23.6, 24.4, 34.3, 37.3, 63.3, 93.2, 113.9, 114.5, 126.0, 126.6, 133.9, 158.3, 175.0, 194.8; MS (EI) m/z : 298 (M^+) (43), 269 (100), 241 (9), 163 (7), 128 (7); HRMS (MALDI): calcd. for $\text{C}_{19}\text{H}_{22}\text{O}_3$ requires 298.1569, found: 298.1555.

Acetic acid 1-(4-ethoxyphenyl)-1-(5-oxo-3,4,5,6,7,8-hexahydro-2H-chromen-4-yl)ethyl ester (5g-1).

a slight yellow oily compound, yield: 12%. IR (thin film): ν 2935, 1741, 1631, 1515, 1391, 1243, 1186, 1045 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.82-0.94 (m, 2H, CH_2), 1.23 (s, 3H, CH_3), 1.16-1.24 (m, 2H, CH_2), 1.40 (t, $J = 6.9$ Hz, 3H, CH_3), 1.94 (s, 3H, CH_3), 2.00-2.06 (m, 2H, CH_2), 2.40-2.51 (m, 2H, CH_2), 2.86 (d, $J = 17.7$ Hz, 1H, CH_2), 3.48 (d, $J = 17.7$ Hz, 1H, CH_2), 4.02 (q, $J = 6.9$ Hz, CH), 4.36 (m, 1H, CH), 6.86 (d, $J = 9.0$ Hz, 2H, ArH), 7.30 (d, $J = 9.0$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 10.7, 14.8, 20.9, 22.1, 22.2, 28.1, 29.7, 36.6, 63.3, 79.4, 83.3, 109.0, 114.3, 126.9, 130.9, 158.6, 168.8, 169.1, 197.7; MS (EI) m/z : 298 ($\text{M}^+ - \text{HOAc}$) (31), 269 (100), 257 (5), 241 (4), 163 (8), 149 (9), 121 (12), 43 (26); HRMS (MALDI): calcd. for $\text{C}_{21}\text{H}_{27}\text{O}_5$ ($\text{M}^+ + 1$) requires 359.1853, found: 359.1843.

4-[1-(4-Ethoxyphenyl)-1-hydroxy-ethyl]-2,3,4,6,7,8-hexahydrochromen-5-one (5g-2).

a slight yellow oily compound, yield: 12%. IR (thin film): ν 2950, 2920, 1738, 1633, 1513, 1456, 1395, 1376, 1247 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 1.40 (t, J = 6.9 Hz, 3H, CH_3), 1.93 (s, 3H, CH_3), 1.94-2.10 (m, 2H, CH_2), 2.10-2.20 (m, 2H, CH_2), 2.21-2.40 (m, 2H, CH_2), 2.40-2.46 (m, 2H, CH_2), 3.32 (t, J = 6.3 Hz, 1H, CH), 4.01 (q, J = 6.9 Hz, 2H, CH_2), 4.23 (t, J = 6.6 Hz, 2H, CH_2), 6.85 (d, J = 8.7 Hz, 2H, ArH), 7.22 (d, J = 8.7 Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 14.8, 21.0, 21.5, 23.5, 24.2, 29.1, 36.9, 46.8, 63.3, 63.4, 94.3, 114.3, 116.1, 125.3, 138.2, 158.2, 171.0, 175.9, 195.4; MS (EI) m/z : 298 ($\text{M}^+ - \text{H}_2\text{O}$) (100), 283 (47), 269 (47), 255 (1), 199 (14), 165 (18), 149 (24), 121 (19), 43 (57); HRMS (MALDI): calcd. for $\text{C}_{19}\text{H}_{25}\text{O}_4$ ($\text{M}^+ + 1$) requires 317.1747, found: 317.1712.

Compound 4h.

a slight yellow oily compound, yield: 30%. IR (thin film): ν 2927, 1753, 1628, 1514, 1455, 1427, 1411, 1372, 1250, 1174, 1066, 1034, 1004 cm^{-1} ; ^1H NMR (CDCl_3 , TMS, 300 MHz): δ 0.22-0.29 (m, 1H, CH_2), 0.42-0.49 (m, 1H, CH_2), 0.78-0.88 (m, 1H, CH_2), 1.53-1.60 (m, 1H, CH_2), 2.08 (tt, $J = 6.6, 6.6$ Hz, 2H, CH_2), 2.34 (t, $J = 6.6$ Hz, 2H, CH_2), 2.53 (t, $J = 6.6$ Hz, 2H, CH_2), 3.81 (s, 3H, CH_3), 5.44 (s, 1H, CH), 6.89 (d, $J = 8.4$ Hz, 2H, ArH), 7.18 (d, $J = 8.4$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3 , TMS, 75 MHz): δ 9.43, 10.3, 21.8, 24.3, 29.0, 37.3, 55.2, 91.3, 113.8, 114.8, 128.7, 129.7, 159.9, 176.7, 194.7; MS (EI) m/z : 270 (M^+) (87), 255 (67), 242 (22), 227 (23), 199 (17), 85 (40), 71 (57), 57 (93), 43 (100); HRMS (MALDI): calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_3$ requires 270.1256, found: 270.1251.