Supplementary Information

High degree of chemoselectivities recorded during the Reformatsky reaction on coumarinyl phenyl ketones and formyl coumarins

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NMR: Chemical shift in ppm. Splitting pattern and probable assessment in parentheses. (5 -25).

5. PMR: 1.22(3H, t, J=7Hz, CO2CH2CH3) 3.78(3H, s, 7-OMe), 4.10(2H, q, J=7Hz, CO2CH2CH3), 5.07(1H, d, J=1.0Hz, CH-CO2Et), 6.72(1H, d, J= 8 Hz,6-H), 6.96(1H, dd, J =10 Hz, 3-H), 7.28(1H, d, J=8Hz 5-H), 7.38-7.62(3H, compl. 3'-H,4'-H, 5'-H,), 7.70(1H, d, J=10Hz, 4-H), 7.88(2H, dd, J=8Hz,,2Hz, 2'-H,3'-H).

6. PMR: 1.17(3H, t, J=7Hz, CO2CH2Me), 2.24(3H,d, J=1.0Hz, 4-Me), 3.75(3H, s, 7-OMe) 4.03(2H, q, J=7Hz, CO2CH2CH3), 4.92(1H, d, J=1 Hz, CHCO2Et), 6.72(1H, d, J=8Hz, 6-H), 7.37(1H, d, J=8Hz, 5-H) 7.34-7.44(3H, compl., 3'-H, 4'-H,5'-H) 7.52(1H, quint, J=1.0Hz, 3-H), 7.80(2H, dd, J=8Hz& 2Hz, 2'-H,6'-H).

COSY, 2D(^{1}H vs^{1}H), strong cross peak: 1'-CO2CH2Me with 1'-CO2CH2CH3,1'-CH3 4- CH3 with 3-H ,1'+CO2CH2Me,; 5-H ; with 6-H; 6'-H3'-H, 5'-H, 3'-H& 5'-HH 2'-H6'-H&4'-H.
NOE studies: Irradiation of 1"-CO2CH2Me enhancement (30%) of the signal of 1"-CO2CH2CH3 & 3-H, , irradiation of 1"-CO2CH2CH3 enhancement of signal of 1"-CO2CH2ME & 3-H, irradiating of 1"-CH3, 4- CH3 noe enhancement in 2'-H, 6-H, & 3-H, 4-H respectively.

7. P.M.R ; 1.24(3H, t, J=7Hz, CO2CH2Me); 1.36(3H, s, 1"-Me); 3.79(3H, s, 7-OMe), 4.13(2H, q, J=7Hz, CO2CH2Me), 6.72(1H d, J=8.5Hz, 6-H), 6.77(1H, d, J=10.3Hz, 3-H), 7.22(1H, d, J=8.5Hz, 5-H), 7.45(2H, t, J=7Hz, 3'-H, &,5'-H), 7.58(1H, tt, J=7 & 1.4Hz4'-H), 7.72(1H, d, J=10.3Hz, 4-H,) 7.88(2H, dd, J=7 &1.4Hz, 2'-H, 6'-H).

^{13}C NMR : 156.7(C-2), 106.3(C-3), 128.3(C-4), 116.4(C-4a), 127.7(C-5), 118.2(C-6), 158.6(C-7), 114.6(C-8), 151.6(C-8a), 193.5(8-C=O), 137.4(C-1'), 129.8(C-2'), 128.7(C-3'), 133.7(C-4'), 56.1(7-OMe), 103.0(C-1''), 168.0(C-2''), 59.8(C-4''), 14.1(C-5''), 10.8(1'')- CH_3

Cross Peaks [δ ^{1}H vs. δ ^{1}H] observed COSY of alkylidenechromene derivatives

Protons attached on, chemical shifts (δ)	Protons attached on, chemical shifts (δ)

1''-CO_2CH_2Me (4.13)	1''-$CO_2CH_2CH_3$ (1.24) & 1''-CH_3 (1.36)
1''-CH_3 (1.36)	3-H (6.77) & 4-H (7.71)
6-H (6.71)	5-H (7.22) & 7-OCH_3 (3.79)
4-H (7.71)	3-H (6.77) & 1''-CH_3 (1.36)
3'-H & 5'-H (7.45)	2'-H, 6'-H (7.88) & 4'-H (7.58)
3-H (6.77)	1''-CH_3 (1.36) & 4-H (7.73)

8. P.M.R: 1.24(3H, t, J=7Hz, CO2CH2Me); 1.34(3H, s, 1"-Me), 2.23(3H, s, 4-Me), 3.80(3H, s, 7-OMe), 4.12(2H, q, J=7Hz, CO2CH2Me), 6.75(1H, d, J=8.7Hz, 6-H) 7.37(1H, d, J=8.7Hz, 5-H), 7.44(2H, t, J=6.4Hz, 3'-H, 5-H), 7.56(1H, tt, J=7 ,1.5Hz,4'-H,),7.65(1H, br.q, J=1.0Hz, 3-H), 7.88(2H, dd, J=7,&1.5 Hz, 2'-H, 6'-H)

^{13}C NMR : 157.2(C-2), 106.0(C-3), 133.5(C-4), 115.8(C-4a), 125(C-5), 116.6(C-6), 158.5(C-7), 114.4(C-8), 150.6(C-8a), 193.7(8-C=O), 137(C-1'), 129.5(C-2'), 129.2(C-3'), 133.7(C-4'), 56.0(7-OMe), 18.4(4-Me), 103.2(C-1''), 168.6(C-2''), 59.7(C-3''), 14.2(C-5''), 10.5(1''-Me)

Cross Peaks [δ ^1H vs. δ ^1H] observed COSY of alkylidenechromene derivatives

Protons attached on, chemical shifts (δ)	Protons attached on, chemical shifts (δ)
4-CH_3 (2.23)	1''-CO_2CH_2Me (1.24) & 3-H (7.65)
1''-CO_2CH_2Me (4.13) & 5-H (7.37)	1''-$CO_2CH_2CH_3$ (1.24) & 6-H (6.75)
2'-H & 6-H (7.8)	3'-H, 5'-H (7.44)
3'-H & 5'-H (7.44)	2'-H, 6'-H (7.88) & 4'-H (7.56)

NOE data of alkylidenechromene

Irradiated at the signal with chemical shift (δ)	NOE enhancement observed for the signal with chemical shift (δ)

1''-CO_2CH_2Me (4.13)	1''-$CO_2CH_2CH_3$ (1.24) & 3-H (7.65)
1''-$CO_2CH_2CH_3$ (1.24)	1''-CO_2CH_2Me (4.12) & 3-H (7.65)
1''-CH_3 (1.34)	2'-H & 6'-H (7.88)
4-CH_3 (2.23)	3-H (7.65) & 5-H (7.37)

9. P.M.R:.50(3H, t, J=7.4Hz, 1"-CH2Me); 1.24(3H, t, J=7Hz, CO2CH2Me,), 1.90((2H, q, J=7.4Hz, 1"CH2Me), 3.79(3H, s,7-OMe), 4.14(2H, q, J=7Hz, CO2CH2Me) 6.73(1H, d, J=8.5Hz, 6-H), 6.78(1H, d, J=10.3Hz, 3-H), 7.22(1H, d, J=8.5Hz, 5-H) 7.46(2H, t, J=8Hz, 3'-H& 5'-H), 7.58(1H, tt., J=7.3& 1.4Hz, 4'-H), 7.90(2H, dd, J=6.7 & 1.1Hz, 2'-H, 6'-H).

^{13}C NMR : 150.6(C-2), 106.3(C-3), 129.2(C-4), 116.3(C-4a), 127.9(C-5), 118.3(C-6), 158.5(C-7), 114.6(C-8), 150.9(C-8a), 193.5(8-C=O), 137.5(C-1'), 129.5(C-2'), 128.7(C-3'), 133.8(C-4'), 56.1(7-OMe), 109.5(C-1''), 168.1(C-2''), 59.7(C-3''), 14.2(C-5''), 19.2(1''- $\underline{C}H_2Me$), 12.4(1''-$CH_2\underline{C}H_3$)

Cross Peaks [δ ^1H vs. δ ^1H] observed COSY of alkylidenechromene derivatives

Protons attached on, chemical shifts (δ)	Protons attached on, chemical shifts (δ)
1''-CH_2Me	1'-CH_2CH_3 (0.50)
1''-CO_2CH_2Me (4.14)	1''-$CO_2CH_2CH_3$ (1.24)
6-H (6.72)	5-H (7.32)
4-H (7.69)	3-H (6.78)
3'-H & 5'-H (7.46)	2'-H & 6'-H (7.90)

NOE data of alkylidenechromene

Irradiated at the signal with chemical shift (δ)	NOE enhancement observed for the signal with chemical shift (δ)
1''-CO_2CH_2Me (4.34)	1''-$CO_2CH_2CH_3$ (1.24) & 4-H (7.36)
1''-CH_2Me (1.90)	1''-CH_2CH_3 (0.50), 2'-H & 6'-H (7.90), 4'-H

	(7.58)
7-OCH_3 ()	6-H (6.72) & 2'-H, 6'-H (7.90)

10. P.M.R: ,0.47(3H, t, J=7.4Hz, 1"-CH2Me) 1.24(3H, t, J=7Hz, CO2CH2Me), 1.88(2H q, J=74Hz, 1"-CH2Me), 2.23(3H, d, J=1Hz 4-Me), 3.80(3H, d, 7-OMe), 4.13(2H, q,J=7Hz, CO2CH2Me), 6.73(1H, d, J=8.7Hz 6-H), 7.32(1H, d, J=8.7Hz, 5-H), 7.44(2H,t, J=7.7Hz, 3'-H, 5'-H), 7.56(1H, tt, J=6.5 &1.3Hz, 4'-H), 7.62(1H, br.q, J=1.2Hz, 3-H 7.86(2H, dd, J=7.8 & 2.0Hz, 2'-H, 6'-H)Jz

11. P.M.R: 1.16(3H, t, J=8Hz, CO2CH2Me), 1.22(12H, s, 4-Me of two Me2CO2Et,) 2.56(1H, dd, J=16&8Hz, 3-Ha), 2.82(1H,dd , J=16 & 4Hz, 3-Hb), 3.30(1H, dd, J=4& 8 Hz, 4-H), 3.70(3H, s, 7-OMe), 4.08(2H, q, J=8Hz, CO2CH2Me), 6.68(2H, d J=8Hz ,6-H), 7.22(1H, d, H=8Hz, 5-H), 7.48(3H, compl.t, J=8Hz, 3'-H, 4'-H, 5'-H)7.80(2H, dd, J=8 & 2Hz, 2'-H, &6-H).

12. P.M.R: 1.20(6H, t, J=7Hz, 2 Me of two CO2CH2Me), 1.24(12H, s, 4 Me of two CMe2CO2Et), 3.81(3H, s, OMe), 4.05(2H, qJ=7Hz, CO2CH2Me), 4.08(2H, q, J=7Hz, CO2CH2Me), 6.36(1H, d, J=8Hz 2"-H), 6.77(1H, d, J=9Hz, 4-H), 7.00(1H, d, J=8Hz, 1"-H), 7.06(1H, d, J=9Hz, 5-H) 7.38-7.64(3H, compl., 3'-H, 4'+H & 5'-H).7.86(2H, dd, J=8&2 Hz, 2'-H, 6'-H), 11.1(1H, s, exchangeable with D2O, OH).

13. P.M.R: 1.08(6H, t, J=8Hz, two CO2CH2Me 1.25(6H, s, 4-C(Me)2CO2Et), 1.55(9H, s 7-OMe), 3.90(4H, q, J=8Hz, CO2CH2Me) 4.55(1H, s, 3-H), 6.72(1H, d, J=8Hz, 6-H) 7.36(1H, d, J=8Hz, 5-H), 7.50(3H, compl. 3-H, 4'-H & 5'-H), 7.87(2H, dd, J=7 &2 Hz, 2'-H & 6'-H).

14. P.M.R: 1.02(3H, t, J=7Hz, CO2CH2Me), 2.87 &3.50(each 1H, d, J=16Hz, 2'-Hb,2'-Ha), 3.97(3H, s, OMe), 4.02(2H, q, J=7Hz, CO2CH2Me), 5.14(1H, d, J=1Hz,1'-H), 5.50(1H, s, 1'-OH), 6.88 & 7.37(each, 1H, d, J=9Hz, 6-H, 5-H), 6.20(each 1H, d, J=9Hz, 3-H, 4-H)

^{13}C NMR;159.2(C-2), 108.6(C-3), 121.4 C-4), 115.1(C-4a), 124.4(C-5), 112.6((C-6), 1.59.8(C-7), 122.4(C-8),114.8(C-4a) ,56.8(7-OMe),.74.5(C-1'), 47.4((C-2'), 171.4(C-3'), 60.1((C-4'),

15. P.M.R: 1.08(3H, t, J=7Hz, 2'-CO2CH2Me), 2.35(3H, d, J=1Hz, 4-Me), 2.87 & 3.53(each 1H, d, J=16Hz, 2'-Hb, 2'-Ha), 3.97(3H, s, OMe), 4.00(2H, q, J=7Hz, 2'-CO2 CH2CH3), 5.19(1H, d. J=1Hz, 1'-H), 5.70(s, 1'-OH), 6.13(1H, q, J=7Hz, 3-H), 6.92 & 7.52(each 1H, d, J=9Hz, 6-H, 5-H).

^{13}CNMR: 160(C-2), 108.1((C-3), 144.2(C-4) 127.9((C-5), 113.0(C-6), 159.9((C-7), 121.3(C-8), 152.2(C-9)., 113.7(C-10),.19.2 (C-4a), 56.7(7-OMe), 74.1(C -1'), 47.3(C-2'), 171(.3(C-3'), 60.1(C-4'), 14.1 (4-Me) .

16. P.M.R: 1.28 & 4.18(3H, t, &2H, q, J=7Hz, 2'-CO2CH2 CH3), 3.85(3H, s, OMe), 6.18 &7.58(each 1H, d J=10Hz, 3-H, 4-H) 6.58 & 6.18(each1H, d, J=10Hz, 6-H, 5-H), 8.02(1H, d, J=16Hz, 1'-H), 7.70(1H,d, H=16Hz, 2'-H).

NOE observed for unsaturated ester compound (16) for irradiating 1" CO2CH2Me(4.13) enhancement of methylene proton (20%) .

^{13}CNMR : 157.9(C-2), 111.9(C-3), 149.2(C-4) 124.0(C-5), 105.9(C-6), 158.5(C-7)115.9(C-8), 136.0(C-8a), 136.0(C-4a), 56.4(OMe) 135(C-1'), 107.0(C-2'), 168.3(C-3'), 59.8(C-4'), 14.1(4-Me).

Cross Peaks [δ ^{1}H vs. δ ^{1}H] observed COSY of unsaturated ester(16).

Protons attached on, chemical shifts (δ)	Protons attached on, chemical shifts (δ)
2''-CO_2CH_2Me (4.14)	2''-$CO_2CH_2CH_3$ (1.20)
6-H (6.58)	5-H (6.18)
4-H (7.58)	3-H (6.13), 5-H (6.18)
1'-H (8.02)	2'-H (6.98), 2'-CO_2CH_2Me (4.13)
2'-H (6.98)	2'-$CO_2CH_2CH_3$ ()

NOE data of unsaturated ester (16).

Irradiated at the signal with chemical shift (δ)	NOE enhancement observed for the signal with chemical shift (δ)
2'-CO_2CH_2Me (4.13)	2'-$CO_2CH_2CH_3$ (4.13)
2''-CO_2CH_2Me (1.28)	2''-CH_3 (6.98) & 1'-H (8.02)
1'-H (8.02)	7-OCH_3 (3.85) & 6-H (6.58)

17. P.M.R : 1.37 & 4.00(3H, t, J*=7Hz, & 2H, q, J=7Hz, 2'-CO2CH2CH3), 2.47(3H, d,J=0.5Hz, 4-Me), ,3.90(3H, s, OMe), 6.14(1H, d, J=0.5Hz, 3-H), 6.57(1H, d,J=18Hz, 2'-H), 6.91 & 7.54(each, 1H, d, J=8Hz, 6-H, 5-H), 7.95(1H, d, J=18Hz,1'-H).

^{13}C.NMR : 159.5(C-2), 117.5(C-3), 149.8 (C-4), 125.5(C-5), 112.5(C-6) 160.4(C-7) 115.2(C-8), 136.0(C-8a), 118.5(C-4a), 19.2(4-Me), 36.6((7-OMe), 132.2(C-1') 135.8(C-2'), 167.0((C'-3'), 61.5((C-4') 14.5(2'-Me), 14.1((4'-Me) .

HMQC & HMBC of compound(17)

Cross peaks [δ ^{1}H vs. ^{13}C] observed in HMQC

Entry No.	Protons(numbered) attached on; chemical shifts(δ)	Carbon (numbered) attached on ; chemical shifts(δ)
1	$CO_2CH_2CH_3$(1.08)	$CO_2CH_2CH_3$(60.1)
2	$COCH_2Me$(4.00)	$COCH_2Me$(14.5)
3	CH_aH_bCO2Et(3.53)	CH_aH_bCO2Et(47.3)

Cross peaks [δ ^{1}H vs. δ ^{13}C] observed in HMBC

Entry No.	Protons (numbered) attached on ; chemical shifts(δ)	Chemical shift (δ) carbon attached/bond having relation as	
		2-bond	3-bond
1	8-C(OH)C$\underline{H}_2$ (3.53)	C-8	C-7
2	8-C$\underline{H}$(OH)CH_2 (5.19)	C-2, C-8	C-7, 2-CO
3	3-H(6.13)	C-4, C-2	4-Me
4	6-H(6.92)	C-7	C-8, C-4a
5	5-H(7.52)	C-6, C-4a	C-4, C-7

18. PMR 1.90(3H, s, 2'-Me), 1.35 &4.19(2H, q, &, 3H, t, J=7Hz, 2'- CO2CH2CH3), 3.83(3H, s, 7-OMe), 6.70 & 7.10(each, 1H,d, J=8Hz, 3-H,5-H), 6.60(1H,d,J=17,2'-H) 7.38 & 6.18 (1 H, d, J= 10Hz, 4 -H, 3-H) 8.00(1H , d, J=17Hz, 1'-H) J=16Hz, 1'-H).

19. PMR:1..20(3H,.t, J=7Hz, 2'-CO2CH2Me), 1.80(3H, d, J=1Hz, 2'-H) 2.48(3H, d, J=.5 Hz, 4-Me), 3.80(3H, s, OMe), 4.20(2H, q, J=7Hz, 2-CO2CH2CH3), 6.74 & 7..27 (each 1H, d, J=7Hz, 6-H, 5-H), 6.57(1H,d,J 17,Hz, 2'- H, 7.70(1H, d, J=0.5Hz, -H).7.96(1 H, d, J=17Hz, 1'-H).

20. PMR: 1.48(3H, s, 2'-Me), 1.80(3H, s, 2 Me), 3.85(3H, s, 7-OMe), 6.71 &7.12 (each 1H, d, J=9Hz, 6-H, 5-H,), 6.60(1H d, J=9Hz, 4-H), 7.72(1H, d, J=9Hz, 1'-H)

21. PMR; 1.43(3H, s, 2'-Me), 1.78(1H, s, 2'-Me) 2.37(3H, d, J=1.0Hz, 4+Me), 3.85(3H, s, 7-OMe), 6.08(1H, q,, J=1Hz, 3-H), 6.84&H 7.45(each 1H, d, J=9Hz, 6-H, 5-H). 7.98(1H, s, 1'-H).

25. PMR: 2.08(3H, s, 2'-Me) 3.80(3H, s, 5- OMe), 2.26(3H, d,J=0.5Hz, 4-Me), 5.11 & 5.18(each1H, s, 3'-H,), 7.85 & 6.42(each1H, d, J=17Hz, 1'-H, 3-H), 7.66 & 6.60(each1H, d, J=8Hz,7-H, 6-H)

26. PMR,:1.21(3H, t, J =7Hz, CO2CH2Me), 2.21(3H, d, J= 0.5 Hz, 4- Me), 3.90(3H, s, 5-OMe), 4.02(2H, q, J=7Hz, CO2CH2Me),5.95 & 7.36(each, 1H, d d, J=12 Hz, 2'-H, 3'-H), 6.38 &7.11(each 1H,d, J=8Hz 6-H, 7-H).

27. PMR: 1.03 & 1.30(each 3H, d, J=5.5Hz, CHMe2). 2.15(3H, d, J=0.5Hz 4- Me .3.90(3H, s, 5-OMe), 4.96(1H, sept.J=5.5 CO2CH2Me2), 5.83 & 7.80(. each 1H,d, J=13Hz, 2'-H, 3'-H), 6.38 &7.39(each 1H,d, J=8Hz, 6-H,7-H)