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Annulation Reactions of Allene-Derived 1,3-Dipole with 3-Substituted-Chromones: Unusual Recognition of 4π-Component in 3-(*N*-arylimino-methyl)chromones through [4+3] Annulation

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Supporting Information

General:

Starting materials and reagents were purchased from commercial suppliers and used without further purification except for the following: Benzene was distilled over sodium and benzophenone under N_2 atmosphere. Hexane and ethyl acetate used in column chromatography were distlled before use. Ethyl 2,3-butadienoate was prepared by the method of Lang and Hansen.[1] 3-(*N*-aryliminomethyl)chromones were prepared by condensing the corresponding anilines with 3-Formylchromones using *p*-toluene-sulphonic acid in catalytic amount under azeptropic removal of water.[2]

All reactions were carried out under N_2 atm in oven-dried (150 °C, ≥ 7h) glassware. Degassing refers to the flow of dry N_2 (g) bubbling through reaction solvent for 10 min. The reactions were stirred with a Teflon covered stir bar. Concentration refers to the removal of solvent using an Eyela rotary evaporator followed by the use of vacuum pump at approximately 2 torr. Silica Gel column chromatography was performed using Acme Synthetic Chemicals (Mumbai, India) brand silica gel (60-120 mesh).

Bruker AC-200FT NMR spectrometer was used to measure ^{1}H NMR (200 MHz)

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1 Lang, R.W.; Hansen, H.J. *Helv. Chim.Acta.* **1980**, *63*, 438.

2 Baruah, A.K; Prajapati, D; Sandhu, J.S. *J. Chem. Soc. Perkin Trans 1*, **1987**, 1995.

spectra and ^{13}C NMR (50 MHz) spectra. Chemical shifts are reported in ppm as down field displacements from tetramethylsilane used as the internal standard. For **^{1}H-NMR** spectra the data is reported as follows: chemical shift, multiplicity [s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublets of doublet, dt = doublets of triplet(for dt the coupling values were measured by performing the decoupling experiments)], integration and coupling constants (Hz). **^{13}C-NMR** spectra were recorded with complete proton decoupling. Infrared spectra (**IR**) were measured on a Shimadzu DR 2001 in $CHCl_3$ solution or KBr pellets and are reported in wave numbers (cm^{-1}). Some bands are characterized as broad (br), strong (s), medium (m) or weak (w). Mass spectra were recorded on Shimadzu GCMS-QP-2000A spectrometer. Elemental analyses were performed at RSIC Chandigarh and are reported in percent atomic abundance.

All melting points are uncorrected and were measured in open glass-capillary.

General Procedure for the Reactions of 3-Formylchromones with Dipole A:

3-Formylchromone (**2**, 1.40 mmol), allenic ester (**1**, 1.70 mmol) and triphenylphosphine (0.20 mmol) in 60ml of dry benzene were taken in a 100ml round bottom flask and solution was degassed for 10 minutes. The solution was refluxed with constant stirring under nitrogen till all the chromone was consumed (tlc). Concentration, followed by silica gel chromatography (Hexane:EtOAc 40:1) yielded adduct (**3**) as light brown semisolids. The spectroscopic data of the 2,3-dihydro-2,3-cyclopentenochromones (**3**) is as follows:

3a,9a-Dihydro-1-ethoxycarbonyl-1-cyclopenteno[5,4-*b*]benzopyran-4-one(3a): Light-brown semisolid: **IR** ($CHCl_3$)/cm^{-1}: 1722(CO_2Et), 1684(C=O), 1642, 1616, 1592; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.31 (t, 3H, J = 7.13 Hz, OCH_2CH_3), 2.80-3.00 (m, 2H, C3-Hs), 3.08-3.26 (dt, 1H, J = 6.43, ~6.65 Hz, C3a-H), 4.30 (q, 2H, J = 7.13 Hz, OCH_2), 5.66 (d, 1H, J = 6.43 Hz, C9a-H), 6.92-6.98 (m, 2H, C8-,C6-Hs), 7.19 (t, 1H, J = 2.00 Hz, C2-H), 7.41 (dd, 1H, J = 7.55,1.60 Hz, C7-H), 7.84 (dd, 1H, J = 7.80,1.60 Hz, C5-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.37($-CH_3$), 35.82(C3), 47.90(C3a), 60.66($O\underline{C}H_2$), 81.61(C9a), 118.22(C8), 119.86(C4a), 121.53(C6), 127.81(C5), 136.26 (C7), 136.87(C1), 148.51(C2), 160.79(C8a), 162.82($-CO_2$), 191.89(C=O); **Mass m/z**: 260 (M^++2, 2), 259 (M^++1, 5), 258 (M^+, 15), 257 (M^+-1,4), 213 (13), 212 (20), 185 (20), 184 (15), 121 (100),

120 (60); **Analysis:** Calculated for ($C_{15}H_{14}O_4$) C 69.76, H 5.42%; Found C 69.78, H 5.39 %.

6-chloro-3a,9a-dihydro-1-ethoxycarbonyl-1-cyclopenteno[5,4-*b*]benzopyran-4-one (3b): Light-brown semisolid: **IR** ($CHCl_3$)/cm^{-1}: 1722(CO_2Et), 1684(C=O), 1636, 1611, 1585; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.32 (t, 3H, *J* = 7.11 Hz, OCH_2CH_3), 2.86-3.09 (m, 2H, C3-Hs), 3.15-3.30 (dt, 1H, *J* = 6.42, 7.57 Hz, C3a-H), 4.29 (q, 2H, *J* = 7.11 Hz, OCH_2), 5.64 (d, 1H, *J* = 6.42 Hz, C9a-H), 6.93 (d, 1H, *J* = 8.86 Hz, C8-Hs), 7.21 (t, 1H, *J* = 2.32 Hz, C2-H), 7.42 (dd, 1H, *J* = 6.52, 2.69 Hz, C7-H), 7.81(d, 1H, *J* = 2.60 Hz, C5-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.13(CH_3), 35.65(C3), 47.27(C3a), 60.64 (OCH_2), 81.79(C9a), 119.80(C8), 120.29(C4a), 126.06(C5), 126.18(C6), 135.79(C7), 135.88(C1), 148.57(C2), 158.98(C8a), 162.64(-CO_2), 191.02(C=O), **Analysis:** Calculated for ($C_{15}H_{13}O_4Cl$) C 61.64, H 4.45 %; Found C 61.65, H 4.42 %.

3a,9a-Dihydro-1-ethoxycarbonyl-6-methyl-1-cyclopenteno[5,4-*b*]benzopyran-4-one (3c): Light-brown semisolid: **IR** ($CHCl_3$)/cm^{-1}: 1722(CO_2Et), 1684(C=O), 1636, 1611, 1585; **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.35 (t, 3H, *J* = 7.11 Hz, OCH_2CH_3), 2.30 (s, 3H, Ar-CH_3), 2.88-2.99 (m, 2H, C3-Hs), 3.08-3.25 (dt, 1H, *J* = 6.38, ~7.99 Hz, C3a-H), 4.29 (q, 2H, *J* = 7.11 Hz, OCH_2), 5.64 (d, 1H, *J* = 6.38 Hz, C9a-H), 6.85 (d, 1H, *J* = 8.40 Hz, C8-Hs), 7.18 (t, 1H, *J* = 2.43 Hz, C2-H), 7.28 (dd, 1H, *J* = 6.32, 1.97 Hz, C7-H), 7.64 (d, 1H, *J* =1.96 Hz, C5-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.36(CH_3), 20.47(Ar-CH_3), 35.83(C3), 47.97(C3a), 60.72(OCH_2), 81.54(C9a), 118.28(C8), 119.56(C4a), 126.65(C5), 130.93(C6), 136.91(C1), 137.47(C7), 148.54(C2), 158.91(C8a), 162.90 (CO_2), 192.37 (C=O), **Mass** m/z: 274 (M^++2, 2), 273 (M^++1, 7), 272 (M^+, 55), 271 (M^+-1, 5), 227 (18), 226 (20), 200 (7), 199 (30), 198 (25), 136 (6), 135 (100), 134 (97); **Analysis**: Calculated for $C_{16}H_{16}O_4$ C 70.58, H 5.88 %; Found C 70.83, H 5.69 %.

General procedure for the reaction of dipole A with azadiene (4):

Azadiene (**4**, 0.71 mmol), allenic ester (**1**, 0.93 mmol) and triphenylphosphine (0.093 mmol) in 50ml of dry benzene was taken in a 100ml round bottom flask and the solution was bubbled with dry nitrogen for 10 minutes. The solution was refluxed with constant stirring under nitrogen till all the azadiene was consumed. Concentration, followed by

silica gel column chromatography (Hexane:EtOAc 40:1) yielded azepines (**5**) as colorless needles. The spectroscopic data of the azepines is as follows:

***N*-*p*-Methoxyphenyl-2,3-dihydro-4-ethoxycarbonyl-chromano[2,3-*b*]azepine-6-one (5a):** colourless needles; mp 118-119°C ; **UV** (MeOH)/nm : 214.4, 224.6, 244.0, 272.2 (sh), 302.9 (sh), 336.0; **IR** (KBr)/ cm^{-1}: 1699 (m), 1680 (s), 1628 (s), 1599 (m), 1499 (s), 1448 (m), 1431 (m) , 1390 (m), 1344 (m), 1315 (w), 1304 (w), 1288 (s), 1245 (s), 1199 (m), 1093 (m), 1054 (br), 1013 (m), 972 (m); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.35 (t, 3H, J = 7.10 Hz, OCH_2CH_3), 2.87 (distorted t, 2H, C3-Hs), 3.82 (distorted t, 2H, C2-Hs), 3.86 (s, 3H, OCH_3), 4.23 (q, 2H, J = 7.10 Hz, OCH_2), 6.93-6.99 (m, 3H, C10-,C2′,C6′-Hs), 7.14 (d, 2H, J = 8.86 Hz, C3′-H,C5′-Hs), 7.29-7.42 (m, 2H, C8-,C9-Hs), 8.17 (dd, 1H, J = 7.90, 1.81 Hz, C7-H), 8.44 (s, 1H, C5-H); **^{13}C NMR** ($CDCl_3$,50 MHz): 14.54(CH_3) , 30.55(C3), 52.99(C2), 55.51(OCH_3), 60.61(OCH_2), 99.74(C5a), 115.03(C3′), 116.48 (C10), 121.67(C8a), 124.81(C8), 125.38(C4), 126.61(C7), 127.53(C2′), 130.47(C5), 132.82(C9), 136.75(C1′), 153.06(C10a), 158.81(C4′), 162.04(C11a), 167.84 (CO_2), 176.67(C6); **Mass** *m/z* : 392 (M^++1, 1), 391 (M^+, 1.8). **Analysis:** Calculated for ($C_{23}H_{21}O_5N$) C 70.58, H 5.37, N 3.58 %; Found C 70.56, H 5.38, N 3.56%.

***N*-*p*-Chlorophenyl-2,3-dihydro-4-ethoxycarbonyl-chromano[2,3-*b*]azepine-6-one (5b):** colorless needles; mp 111-112°C ; **UV** (MeOH)/nm : 210.4, 223.2, 242.6, 271.8 (sh), 307.8 (sh), 333.8; **IR** (KBr)/ cm^{-1}: 1700 (sh), 1678 (s), 1635.5 (m), 1622 (s), 1584 (w), 1533 (s), 1490 (w), 1448 (m), 1425 (s), 1404 (br), 1367 (w), 1352 (m), 1311 (m), 1271 (s), 1238 (s), 1194 (m), 1155 (w), 1086 (m), 1065 (m), 1016 (m), 997 (br); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.35 (t, 3H, J = 7.10 Hz, $-CO_2CH_2CH_3$), 2.85 (distorted t, 2H, C2-Hs), 3.89 (distorted t, 2H, C2-Hs), 4.25 (q, 2H, J = 7.10 MHz, OCH_2), 6.96 (d, 1H, J = 8.52 Hz, C10-H), 7.20 (d, 2H, J = 9.20 Hz, C2′-,C6′-Hs), 7.27-7.35 (m, 2H, C8-,C9-Hs), 7.45 (d, 2H, J = 9.01 Hz, C3′-H, C5′-H), 8.17 (dd, 1H, J = 7.86, 1.72 Hz, C7-H), 8.39 (s, 1H, C5-H); **^{13}C NMR** ($CDCl_3$,50 MHz): δ 14.33(CH_3), 30.27(C3), 51.95(C2), 60.43(OCH_2), 100.26(C5a), 116.29(C10), 121.52(C6a), 124.74(C8), 125.73(C4), 126.25(C7), 127.30(C2′), 129.79 (C3′&C5), 132.84 (C9&C4′), 141.94(C1′), 152.76(C10a), 160.99(C11a), 167.25 (CO_2), 176.27(C6); **Mass** *m/z*: 398 (M^++3, 12), 397

(M^++2, 13), 395 (M^+, 42), 350 (10), 324 (35), 323 (32), 322 (100). **Analysis:** Calculated for ($C_{22}H_{18}O_4NCl$) C 66.83, H 4.55, N 3.54 %; Found C 66.90, H 4.60, N 3.57%.

***N*-*p*-Methoxyphenyl-2,3-dihydro-4-ethoxycarbonyl-8-methyl-chromano[2,3-b]azepine-6-one (5c):** colorless crystals; mp 139-140°C; **UV** (MeOH)/nm: 223.4(sh), 242.5, 248.5(sh), 257.4(sh), 278.0, 299.4, 333.5, 350.5(sh); **IR** (KBr)/ cm^{-1}: 1699 (CO_2Et), 1676 (sh), 1645(m), 1612(m), 1593(s), 1536(s), 1508(m); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.32 (t, 3H, J = 7.14 Hz, -$CO_2CH_2CH_3$), 2.41 (s, 3H, CH_3), 2.86 (distorted t, 2H, C3-Hs), 3.86 (overlapping distorted t & s, C2-Hs & OCH_3), 4.25 (q, 2H, J = 7.14 Hz, OCH_2), 6.83 (d, 1H, J = 8.39 Hz, C10-H), 6.94 (d, 2H, J = 8.85 Hz, C3′,C5′-Hs), 7.14 (d, 2H, J = 8.85 Hz, C2′,C6′-Hs,), 7.23 (dd, 1H, J = 8.39,1.39 Hz, C9-H), 7.96 (bs, 1H, C7-H), 8.43 (bs, 1H, C5-H); **^{13}C NMR** ($CDCl_3$,50 MHz): δ 14.54(CH_3), 20.94(Ar-CH_3), 30.52(C3), 52.90(C2), 55.46(OCH_3), 60.53(OCH_2), 99.70(C5a), 114.93(C3′), 116.22(C10), 121.51 (C6a), 125.1(C4), 126.12 (C7), 127.50(C2′), 130.60(C5), 133.82(C9), 134.49(C1′), 151.22(C10a), 158.70(C4′), 162.51(C11a), 167.63(CO_2), 176.88(C6); **Mass** *m/z*: 406 (M^++1, 20), 405 (M^+, 25), 333 (30), 332 (38), 58(100); **Analysis:** Calculated for $C_{24}H_{23}O_5N$: C 71.11%, H 5.67%, N 3.45%; Found : C 71.20%, H 5.59%, N 3.41%).

***N*-*p*-Chlorophenyl-2,3-dihydro-4-ethoxycarbonyl-8-methyl-chromano[2,3-*b*]-azepine-6-one (5d) :** colorless needles; mp 143-145°C ; **UV** (MeOH)/nm : 214.8, 226.4, 243.2, 254.3 (sh), 279.8 (sh), 304.9 (sh), 334.4, 351.5 (sh); **IR** (KBr)/ cm^{-1}: 1699 (sh), 1684 (s), 1618 (s), 1593 (m), 1499 (s), 1458 9m), 1419 (m), 1396 (m), 1365 (w), 1348 (m), 1315 (w), 1300 (w), 1268 (s), 1234 (s), 1190 (m), 1090 (m), 1068 (br), 1003 (m); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.37 (t, 3H, J = 7.10 Hz, OCH_2CH_3), 2.43 (s, 3H, Ar-Me), 2.87 (distorted t, 2H, C3-Hs), 3.88 (distorted t, 2H, C2-Hs), 4.26 (q, 2H, J = 7.10 Hz, OCH_2), 6.87 (d, 1H, J = 8.45 Hz, C10-H), 7.18 (d, 2H, J = 8.69 Hz, C2′-,C6′-Hs), 7.30 (dd, 1H, J = 8.70, 2.20 Hz, C9-H), 7.43 (d, 2H, J = 8.71 Hz, C3′-,C5′-Hs), 7.97 (bs, 1H, C7-H), 8.39 (s, 1H, C5-H); **^{13}C NMR** ($CDCl_3$,50 MHz): δ 14.37(CH_3), 20.81(Ar-CH_3), 30.29(C3), 51.85(C2), 60.44(OCH_2), 101.02(C5a), 116.06(C10), 121.23(C6a), 125.58 (C4), 125.90(C7), 127.23(C2′), 129.79(C3′), 129.90(C5), 132.71(C4′), 133.90(C9), 134.53(C8),

142.00(C1′), 151.02(C10a), 160.90(C11a), 167.35(CO_2), 176.42(C6); **Mass** *m/z*: 412 (M^++3, 2), 411 (M^++2, 10), 410 (M^++1, 8), 409 (M^+, 40), 366 (3), 365 (2), 364 (10), 339 (9), 338 (38), 337 (40), 336 (100). **Analysis:** Calculated for ($C_{23}H_{20}O_4NCl$) C 67.48, H 4.88, N 3.42 %; Found C 67.44, H 4.80, N 3.45%.

***N-p*-Methoxyphenyl-2,3-dihydro-4-ethoxycarbonyl-8-chloro-chromano[2,3-b]-azepine-6-one (5e) :** colorless needles; mp 145-146°C ; **UV** (MeOH)/nm : 218.2, 226.8 (sh), 249.0, 283.2, 303.9 (sh), 338.2; **IR** (KBr)/ cm^{-1}: 1701(m), 1685 (m), 1635 (w), 1622 (s), 1588 (s), 1580 (w), 1541 (m), 1490 (w), 1458 (m), 1437 (m), 1400 (m), 1385 (m), 1352 (br), 1306 (m), 1251 (s), 1190 (m), 1097 (m), 1066 (m), 1032 (m); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.38 (t, 3H, *J* = 7.12 Hz, OCH_2CH_3), 2.87 (distorted t, 2H, C3-Hs), 3.87 (overlapping distorted t & s,C2-Hs and OCH_3), 4.28 (q, 2H, *J* = 7.12 Hz, OCH_2), 6.95 (m, 3H, C10-,C2′-,C6′-Hs), 7.13-7.17 (d, 2H, *J* = 8.42 Hz, C3′-,C5′-Hs), 7.37 (dd, 1H, *J* = 8.69, 1.82 Hz, C9-H), 8.15 (bs, 1H, C7-H), 8.39 (s, 1H, C5-H); **^{13}C NMR** ($CDCl_3$,50 MHz): δ 14.61(CH_3) , 30.54(C3), 53.10(C2), 55.51(OCH_3), 60.70 (OCH_2), 99.70(C5a), 115.09(C3′), 118.12(C10), 123.01(C6a), 125.87(C4), 126.17(C7), 127.55(C2′), 130.17(C5), 130.76(C8), 132.88(C9), 136.55(C1′), 151.31(C10a), 158.96 (C4′), 161.65(C11a), 167.63(CO_2), 175.31(C6); **Mass** *m/z*: 427 (M^++2, 3), 425 (M^+, 12), 354 (5), 353 (10), 336 (3), 282 (6), 58 (100). **Analysis:** Calculated for ($C_{23}H_{20}O_5NCl$) C 64.94, H 4.70, N 3.29 %; Found C 64.99, H 4.71, N 3.26%.

***N-p*-Chlorophenyl-2,3-dihydro-4-ethoxycarbonyl-8-chloro-chromano[2,3-*b*]azepine-6-one (5f) :** colorless crystals; mp 161-162°C, **UV** (MeOH)/nm: 219.9(sh), 239.0, 248.5(sh), 258.0(sh), 265.7, 304.5, 337.5, 350.5(sh), **IR** (KBr)/cm^{-1}: 1699 (s,CO_2Et), 1678 (sh), 1645(w), 1624 (br), 1541(m), 1490(m), 1458(m), 1437(m), 1394(m), 1370(w), 1342(w), 1300(s), 1260(s), 1236(m), 1190(m), 1092(m); **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 1.32 (t, 3H, *J* = 7.13 Hz, OCH_2CH_3), 2.84 (distorted t, 2H, C3-Hs), 3.87 (distorted t, 2H, C2-Hs), 4.22 (q, 2H, *J* = 7.13, OCH_2), 6.90 (d, 1H, *J* = 8.88 Hz, C10-H), 7.17 (d, 2H, *J* = 8.84 Hz, C2-,C6-Hs), 7.37-7.46 (m, 3H, C9-, C3-,C5Hs), 8.05 (d, 1H, *J* = 2.55 Hz, C7-H), 8.35 (bs, 1H, C5-H); **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 14.33(CH_3), 30.31(C3), 52.22(C2), 60.80(OCH_2), 100.25(C5a), 118.10 (C10), 122.63(C6a), 125.80(C7), 126.37(C4), 127.36(C2′), 129.42(C5), 129.98 (C5&C4′), 130.75(C8), 133.09(C9), 141.71(C1′), 151.12

(C10a), 161.10 (C11a), 167.58(CO_2), 175.52(C6); **Mass** *m/z*: 433(M^++4, 2), 432(M^++3, 4), 431(M^++2, 12), 430(M^++1, 6), 429(M^+, 20), 386(5), 384 (6), 358 (10), 356 (13), 129 (5), 112 (8), 58 (100). **Analysis:** Calculated for ($C_{22}H_{17}O_4NCl_2$) C 61.53, H 3.96, N 3.26 %; Found C 61.52, H 3.98, N 3.26%.