Facile, Regioselective [4+2] Cycloaddition Involving 1-Aryl-4-phenyl-1-azadienes and Allenic esters: An Efficient Route to Novel substituted 1-Aryl-4-phenyl-1,4-dihydropyridines

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SUPPORTING INFORMATION

General:

Starting materials and reagents were purchased from commercial suppliers and purified/distilled/crystallized before use. Benzene was distilled over sodium and benzophenone under N_2 atmosphere. Hexane, Pet. ether and ethyl acetate used in column chromatography were distlled before use; Pet. ether employed was the fraction boiling in the range of 40-60°C. Allenic esters were prepared by the method of Lang and Hansen and characterized spectroscopically.[1] Azadienes were also prepared according to literature method and characterized spectroscopically.[2]

All reactions were carried out under N_2 atm. in oven-dried (150 °C, ≥ 7h) glassware. The reactions were stirred with a Teflon covered stir bar. Solvents were removed 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 (100-200 mesh and 230-400 mesh for flash chromatography).

Bruker AC-200FT NMR spectrometer was used to record ^{1}H NMR (200 MHz) 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 = doublet of doublet, ddd= doublet of doublet of doublet, dt = doublets of triplet(some of the coupling constant values were measured by performing the decoupling experiments)], integration and coupling constants (Hz). **^{13}C-NMR** spectra were recorded with complete proton decoupling, off-resonance

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

2 (a) Brady, W.T.; Sheih, C.H. *J.Org. Chem.* **1983**, 48, 2499. (b) Anteuis, N.; Bruyn, A.De.; Sandhu, J.S., *J.Magn.Reson.* **1972**, 8,7

and DEPT. Infrared spectra (**IR**) were measured on a Shimadzu DR 2001 spectrometer in $CHCl_3$ solution and are reported in wave numbers (cm^{-1}). Mass spectra were recorded on Shimadzu GCMS-QP-2000A spectrometer. Elemental analyses were performed at RSIC, Chandigarh and are reported in percent atomic abundance.

General Procedure for reaction of 1-aryl-4-Phenyl- 1-aza -1,3-butadienes (1) with Allenic esters (2) at high temperature:

A solution of Azadiene (**1**, 1.00 mmol) and allenic ester (**2**, 1.10mmol) in dry benzene (20 ml) was refluxed under an atmosphere of nitrogen till the azadiene was completely consumed (tlc, Table 1). Solvent was removed under vacuum and the formed cycloadducts were purified by flash column chromatography (silica gel 230-400 mesh, eluent EtOAc : Hexane 1:100)[3].

The physical and spectroscopic data for various dihydropyridines (**4a-n**) are as follows:

1,4-Diphenyl-3-ethoxycarbonyl-2-Methyl-1,4-dihydropyridine

4a: Light-brown semisolid; **UV**(MeOH)/nm : 238.0, 256.16, 271.60, 293.3 ; **IR**($CHCl_3$)/cm^{-1} : 1688 (CO_2Et), 1607, 1593, 1449, 1448, 1376, 1286, 1244, 1098 ; **^{1}HNMR**($CDCl_3$, 200 MHz) : δ 1.12 (t, 3H, *J*=7.10 Hz, -OCH_2CH_3), 2.14 (s, CH_3), 3.99 (q, 2H, *J*=7.10 Hz, -OCH_2-), 4.64 (d, 1H, *J*=5.36 Hz, C4-H), 4.78 (dd, 1H, *J*=7.40, 5.36 Hz, C5-H), 6.11 (d, 1H, *J*=7.46 Hz, C6-H), 7.07-7.42 (m,10H, Ar-Hs) ; **^{13}C NMR**($CDCl_3$, 50 MHz) : δ 14.25(CH_2CH_3), 18.53(C2-CH_3), 40.24(C4), 58.82(OCH_2-), 102.31(C3), 107.49(C5), 125.90(CH), 126.96(CH), 127.44(CH), 128.22(CH), 128.70(CH), 129.13 (CH), 129.35(CH), 143.90(q, arm.), 147.02(q, arom.), 148.26 (C2), 167.54(-CO_2-). **Mass**(m/z) : 321 (28, M^+, +2), 320 (25,M^+, +1) 319 (87, M^+), 307.0 (!2), 306 17), 305 (71), 244 (5), 243 (9): **Analysis**: Calculated for $C_{21}H_{21}NO_2$; C 78.95, H 6.64, N 4.38%; Found: C 78.99, H 6.68, N4.33%.

1,4-Diphenyl-3-ethoxycarbonyl-2-ethyl-1,4-dihydropyridine

4b: Light-yellow semisolid; **UV**(MeOH)/nm : 238.0, 256.6, 290.0, 335.0 ; **IR**($CHCl_3$)/cm^{-1} : 1692 (CO_2Et), 1602, 1593, 1568, 1512, 1499, 1451, 1380, 1290, 1247, 1123 ; **^{1}H NMR**.($CDCl_3$, 200 MHz) : δ 0.96 (t, 3H, *J*=7.34 Hz, -CH_2CH_3) 1.10 (t,3H, *J*=7.09 Hz -OCH_2CH_3), 2.52-2.74 (m, 2H, -CH_2CH_3), 4.03 (q, 2H, *J*=7.09 Hz, -OCH_2-), 4.64 (d,1H, *J*=5.61 Hz, C4-H), 4.98 (dd, 1H, *J*=7.53, 5.61 Hz, C5-H), 6.10 (d, 1H, *J*=7.53 Hz, C6-H), 7.12-7.52 (m, 10H, Ar-Hs) ; **^{13}CNMR**($CDCl_3$, 200 MHz) : δ 13.48 (CH_2CH_3), 14.16 (OCH_2CH_3), 22.91 (CH_2), 39.95 (C4), 59.11 (OCH_2), 101.64 (C3), 107.50 (C5), 125.96 (CH), 127.93 (CH), 128.03 (CH), 128.17 (CH), 128.19 (CH), 129.70 (CH), 129.85 (CH), 142.80 (q. arom.), 148.13 (q, Arom.), 150.30 (C2), 168.01 (CO_2-). **Mass**(m/z) : 335 (2, M^+, +2) 334 (8, M^+,+1), 333 (36, M^+), 305 (5), 304 (24), 261 (10), 260 (47), 258 (5), 257 (18), 256

[3] The separated pure products resisted all attempts at crystallization and semisolids obtained in certain cases were not amenable to melting point determination.

(100), 229 (9), 228 (46), 77 (43); **Analysis**: Calculated for $C_{22}H_{23}NO_2$: C 79.25, H 6.96, N 4.20%; Found: C 79.22, H 6.94, N 4.22%.

1,4-Diphenyl-3-ethoxycarbonyl-2-propyl-1,4-dihydropyridine

4c: Yellowish semisolid; **UV**(MeOH)/nm: 238.3, 258.3, 298.3, 340 ; **IR**($CHCl_3$)/cm^{-1}: 1688 (CO_2Et), 1624, 1599, 1569, 1495, 1457, 1252, 1175, 1093 ; **^{1}H NMR**($CDCl_3$, 200 MHz) : δ 0.63 (t, 3H, *J*=7.20 Hz,-$CH_2CH_2CH_3$), 1.18 (t, 3H, *J*=7.11 Hz, OCH_2CH_3), 1.30-1.41 (m, 2H, $CH_2CH_2CH_3$), 2.39-2.59 (m, 2H, $CH_2CH_2CH_3$), 3.93 (q, 2H, *J*=7.11 Hz, -OCH_2-), 4.57 (d, 1H, *J*=5.61 Hz, C4-H), 4.88(dd, 1H, *J*=7.42, 5.61 Hz, C5-H), 6.00 (d, 1H, *J*=7.42 Hz, C6-H), 6.97-7.36 (m,10H, Ar-Hs) ; **^{13}C NMR**($CDCl_3$, 50 MHz) : δ 13.04(-CH_3), 14.03 (-CH_3), 22.5 (-CH_2-), 31.48 ((-CH_2-), 40.07 (C4), 59.02 (-O-CH_2-), 101.09 (C3), 107.46 (C5), 124.74 (CH), 127.31 (CH), 127.93 (CH), 128.14 (CH), 128.32 (CH), 129.08 (CH), 130.50 (CH), 143.69 (q, arom.), 148.44 (q. arom.), 152.35 (C2), 167.67 (CO_2). **Mass**(m/z) : 349 (5,M^+, +2), 348 (25, M^+, +1), 347 (83, M^+), 320 (1), 319 (6), 318 (230, 276 (5), 275 (110, 274 (45), 272 (5), 271 (19), 270 (100), 244 (11), 243 (11), 242 (39), 214 (4), 213 (17), 167 (4), 168 (10), 77 (249), 58 (11). **Analysis**: Calculated for $C_{23}H_{25}NO_2$: C 79.51 H 7.25, N 4.03 %; Found C 79.56, H 7.28, N 3.99%.

3-Ethoxycarbonyl-2-methyl-4-phenyl-1-*p*-tolyl-1,4-dihydropyridine

4d: Light-yellow semisolid; **UV**(MeOH)/nm: 236.4, 265.4, 338.0; **IR**($CHCl_3$)/cm^{-1}: 1692(-CO_2-Et), 1615, 1600, 1552, 1460, 1385, 1265, 11190, 1100, 1040; **^{1}H NMR**($CDCl_3$, 200 MHz) : δ 1.06(t, 3H, *J*=7.08 Hz, -OCH_2CH_3), 2.07(s, 3H, C2-Me), 2.32(s, 3H, Ar-Me), 3.92(q, 2H, *J*=7.11 Hz, -OCH_2-), 4.59(d, 1H, *J*=5.42 Hz, C4-H), 4.89(dd, 1H, *J*=7.63, 5.42 Hz, C5-H), 6.05 (d, 1H, *J*=7.63 Hz, C6-H), 6.89-2.42(m, 9H, arom.-Hs); **^{13}C NMR**($CDCl_3$, 50 MHz) δ 14.38(-CH_3), 18.78(C2-Me), 21.44(Ar-Me), 40.29(C4), 59.28(-OCH_2-), 101.86(C3), 107.49(C5), 119.50(CH), 124.69(CH), 126.12(CH), 127.61(CH), 128.30(CH), 129.38(C6), 138.49(q, arom.), 143.81(q, arom.), 146.42(q, arom.), 148.58(C2), 168.21(-CO_2-); **Mass**(m/z) : 335 (8, M^+ +2), 334 (15, M^+ +1), 333 (43, M^+), 320 (8), 319(24), 318(76), 285(23), 256(25), 242(64), 77(79): **Analysis**: Calculated for $C_{22}H_{23}NO_2$: C 79.25, H 6.95, N 4.20%; Found: C 79.29, H 6.98, N 4.18%.

3-Ethoxycarbonyl-2-ethyl-4-phenyl-1-*p*-tolyl-1,4-dihydropyridine

4e: Brownish semisolid: **UV**(MeOH)/nm: 237.0, 264.0, 340.0; **IR**($CHCl_3$)/cm^{-1}: 1690 (CO_2Et), 1612, 1602, 1593, 1560, 1520, 1500, 14560, 1440, 1380, 1305, 1250, 1200, 1120, 1076; **^{1}H NMR**.($CDCl_3$, 200 MHz) : δ 0.97 (t, 3H, *J*=6.24 Hz, -CH_2CH_3) 1.09 (t,3H, *J*=7.08 Hz -OCH_2CH_3), 2.32(s, 3H, Ar-Me), 2.58-2.77 (m, 2H, -CH_2CH_3), 3.93 (q, 2H, *J*=7.08 Hz, -OCH_2-), 4.54 (d,1H, *J*=5.24 Hz, C4-H), 5.00 (dd, 1H, *J*=7.54, 5.24 Hz, C5-H), 5.98 (d, 1H, *J*=7.54 Hz, C6-H), 7.02-7.57 (m, 9H, Ar-Hs) ; **Mass**(m/z): 348(6, M^+ +1), 347(24, M^+), 333(40), 319(33), 314(24), 313(35), 295(20), 272(32),

260(14), 256(22), 149(37), 94(14), 92(100), 91(20); **Analysis**: Calculated for $C_{23}H_{25}NO_2$: C 79.51, H 7.25, N 4.03%; Found: C 79.47, H7.22, N4.09%.

1-*p*-Anisyl-3-ethoxycarbonyl-2-methyl-4-phenyl-1,4-dihydropyridine

4f: UV(MeOH)/nm: 237.3, 257.5, 343.0; **IR**($CHCl_3$)/cm^{-1}: 1684 (CO2Et), 1510, 1242, 1111, 1076, 1034; **^{1}H NMR** ($CDCl_3$,200MHz): δ 1.05 (t, 3H, *J*=7.11Hz, OCH_2CH_3), 2.06 (s, 3H, CH_3), 3.76(s, 3H, OCH_3), 3.94 (q, 2H, *J*=7.11 Hz, -OCH_2-), 4.58 (d, 1H, *J*=5.44 Hz, C4-H), 4.88(dd, 1H, *J*=7.60, 5.44 Hz, C5-H), 5.99(d, 1H, *J*=7.60 Hz, C6-H), 6.83 (d, 2H, J = 8.84 Hz, C3′- & C5′-Hs), 7.04 (d, 2H, J = 8.88 Hz, C2′- & C6′-Hs), 7.13-7.31 (m, 5H, Ar-Hs). **^{13}C NMR**($CDCl_3$, 50 MHz): δ 14.28 (-CH_3), 18.44 (C2-CH_3), 40.30 (C4), 55.35 (OCH_3), 59.16 (OCH_2), 101.26 (C3), 107.27 (C5), 114.68 (CH), 126.03 (CH), 127.51 (CH), 128.24 (CH), 128.82 (CH), 129.61(C6), 136.71 (C1′), 148.68(C2), 148.25 (q, arom.), 158.69 (C4′), 168.51 (-CO_2). **Mass** : (m/z) : 351 (15, M^+,+2) 350 (29, M^+,+1), 349 (83, M^+),336 (11), 335 (33), 322 (6), 321(25), 320 (86), 306 (26), 305 (10), 304 (50), 378 (5), 372 (8), 276 (42), 274 (40), 273 (9), 272 (100); **Analysis**: Calculated for $C_{22}H_{23}NO_3$: C 75.62, H 6.63, N 4.01; Found: C 75.66, H 6.68, N 3.98%.

1-*p*-Anisyl-3-ethoxycarbonyl-2-ethyl-4-phenyl-1,4-dihydropyridine

4g: Yellowish semisolid; **UV**(MeOH)/nm: 242.0, 262.5, 343.0; **IR** ($CHCl_3$)/cm^{-1}: 1690(CO_2Et), 1610, 1565, 1510, 1400, 1380, 1300, 1248, 1185, 1100, 1030 : **^{1}H NMR**($CDCl_3$, 200 MHz): δ 0.98 (t, 3H, *J*=6.88 Hz, -CH_2CH_3), 1.12 (t, 3H, *J*=7.10 Hz, -OCH_2CH_3), 2.58-2.68 (m, 2H, CH_2CH_3), 3.84 (s, 3H, -OCH_3), 4.02 (q, 2H, *J*=7.10 Hz, OCH_2-), 4.61(d, 1H, *J*=5.50 Hz, C4-H), 4.92 (dd, 1H, *J*=7.38, 5.50 Hz, C5-H) 5.94 (d, 1H, *J*=7.38 Hz, C6-H), 6.87 (d, 2H, *J*=8.44 Hz, C3′ & C5′-Hs), 7.16 (d, 2H, J=8.72 Hz, C2′ & C6′-Hs), 7.24-7.37 (m, 5H, Ar-Hs). **^{13}C NMR** ($CDCl_3$, 50 MHz) : δ 13.62 (-CH_2CH_3), 14.25 (-OCH_2CH_3), 23.46 (CH_2), 44.09 (C4), 54.75 (-OCH_3), 59.19 (-OCH_2-),101.43 (C3), 106.80 (C5), 113.91 (CH), 125.71 (CH), 126.95 (CH), 128.25 (CH), 128.56(CH), 130.02 (C6), 136.53 (C1′), 148.84 (q, arom.), 150.09(C2), 159.63 (C4′), 167.21(CO_2) ; **Mass**(m/z): 363 (6, M^+), 349 (8), 348(25), 290 (8), 287 (10), 286 (15), 258 (8), 252 (6), 151 (5), 149 (15), 131 (5), 129 (5), 58(100); **Analysis**: Calculated for $C_{23}H_{25}NO3$: C 76.01, H 6.93, N 3.85%; Found C 76.02, H6.93, N3.84%.

1-*p*-Anisyl-3-ethoxycarbonyl-4-phenyl-2-propyl-1,4-dihydropyridine

4h: Yellow semisolid; **UV**(MeOH)/nm: 238.4, 263, 341.2; **IR** ($CHCl_3$)/cm^{-1} : 1692, 1615, 1521, 1474, 1449, 1303.3, 1256.2, 1187.9, 1111, 1083.3. ;**^{1}H NMR**($CDCl_3$,200 MHz): δ 0.72 (t, 3H, *J*=7.20 Hz, $CH_2CH_2CH_3$), 1.12 (t, 3H, *J*=7.09 Hz, OCH_2CH_3), 1.33-1.49 (m, 2H, $CH_2CH_2CH_3$), 2.49-2.58 (m, 2H, $CH_2CH_2CH_3$), 3.83 (s, OCH_3), 3.99 (q, 2H, *J*=7.09 Hz, OCH_2CH_3), 4.63 (d, 1H, *J*=5.50 Hz, C4-H), 4.93 (dd, 1H, *J*=7.50, 5.50 Hz, C5-H), 6.01(d, 1H, *J*=7.50 Hz, C6-H), 6.95 (d, 2H, *J*=9.0

Hz, C3′ & C5′-Hs), 7.13 (d, 2H, *J*=8.68 Hz, C2′ & C6′-Hs), 7.24-7.41(5H, arom-Hs). **^{13}C NMR** ($CDCl_3$, 50 MHz) : δ 13.71 (-CH_3), 14.05 (-OCH_2CH_3), 23.46 (-CH_2-), 33.26(-CH_2-), 40.12(C4), 55.25 (-OCH_3), 59.14 (-OCH_2-), 100.91 (C3), 107.31(C5), 114.72 (CH), 126.31 (CH), 127.69 (CH), 128.15 (CH), 128.35 (CH), 129.22 (C6), 136.37 (C1′), 148.79 (q, arom.), 151.63(C2), 159.70 (C4′), 168.01 (-CO_2-). **Mass**(m/z) : 377 (10, M^+), 362 (15), 361 (10), 360 (20), 348 (90), 334 (10), 304 (20), 300 (20), 290 (10), 288 (10), 286 (10), 274 (15), 272 (10); **Analysis**: Calculated for $C_{24}H_{27}NO_3$: C 76.36, H 7.21, N 3.71%; Found: C 76.41, H 7.27, N3.68%.

1-*p*-Chlorophenyl-3-ethoxycarbonyl-2-methyl 4-phenyl-1,4-dihydropyridine

4i: Yellowish semisolid; **UV** (MeOH)/nm: 238.3, 260.3, 293.3, 341.6 ; **IR**($CHCl_3$)/cm^{-1} : 1687.9, 1683.7, 1572.5, 1457.1, 1393.0 , 1384.3, 1290.4, 1260.4, 1222.0 1205.0, 1175.0, 1119.5, 1098.1, 1038.3, 1034.0, 1021.0, 987.0; **^{1}H NMR**($CDCl_3$, 200 MHz): δ 1.30(t, 3H, *J*=7.18 Hz, OCH_2CH_3), 2.13 (s, CH_3), 4.02 (q, 2H, *J*=7.09 Hz, OCH_2CH_3), 4.66 (d, 1H, *J*=5.80 Hz, C4-H), 4.99 (dd, 1H, *J*=7.64, 5.80 Hz, C5-H), 6.09 (d, 1H, *J*=7.64 Hz, C6-H), 7.14 (d, 2H, J=8.8 Hz, Ar-Hs), 7.20-7.28 (m, 5H, Ar-Hs), 7.37 (d, 2H, J=8.8 Hz, Ar-Hs),. **^{13}CNMR** ($CDCl_3$, 50 MHz) : δ 14.42 (-CH_3), 18.29 (C2-Me), 40.48 (C4), 59.53 (_OCH_2-), 103.08 (C3), 106,14 (C5), 126.37 (CH), 127.66 (CH), 128.49 (CH), 128.99 (CH), 129.43 (CH), 129.92 (CH), 134.60(C4′), 142.90 (C1′), 147.04 (C2), 148.26 (q, arom.), 168.43 (-CO_2-). **Mass** (m/z): 355 (12, M^++2), 354 (8, M^+ +1), 353 (32, M^+), 326 (8), 325 (5), 324 (25), 282 (15), 281 (10), 280 (43), 278 (38), 277 (18), 276 (100), 250 (17), 249 (8), 248 (50), 169 (28); **Analysis**: Calculated for $C_{21}H_{20}ClNO_2$: C 71.28, H 5.70, N 3.96%; Found: C 71.36, II 5.73, N 3.88%.

1-*p*-Chlorophenyl-3-ethoxycarbonyl-2-ethyl 4-phenyl-1,4-dihydropyridine

4j: Yellowish semisolid; **UV**(MeOH)/nm : 338.3, 258.3, 291.6, 338.3; **IR**($CHCl_3$)/cm^{-1}: 1696, 1618, 1606, 1500, 1457, 1376, 1243, 1098, 832, 760. **^{1}H NMR**($CDCl_3$, 200 MHz) : δ 0.97 (t, 3H, *J*=7.28 Hz, -CH_2CH_3), 1.13 (t, 3H, *J*=7.12 Hz, -OCH_2CH_3), 2.49-2.77 (m, 2H, CH_2CH_3), 4.02 (q, 2H, *J*=7.12 Hz, -OCH_2-), 4.63 (d, 1H, *J*=5.56 Hz, C4-H), 4.99 (dd, 1H, *J*=7.50, 5.56 Hz, C5-H), 6.04 (d, 1H, *J*=7.50 Hz, C6-H), 7.20 (d, 2H, *J*=8.56 Hz, Ar-Hs), 7.24-7.38 (m, 5H, Ar-Hs), 7.38 (d, 2H, *J*=8.60 Hz, Ar-Hs); **^{13}CNMR**($CDCl_3$, 50 MHz): 13.48 (-CH_3), 14.15 (-CH_3), 22.89(-CH_2), 40.01 (C4), 59.29 (-OCH_2-), 101.38 (C3), 107.91 (C5), 126.10 (CH), 127.32 (CH), 128.89 (CH), 129.33 (CH), 129.43 (CH), 129.69 (CH), 133.30 (C4′), 142.14 (C1′), 148.18 (q. arom.), 151.29 (C2), 167.68 (CO_2). **Mass**(m/z) : 369 (10, M^+, +2), 368 (8, M^+, +1), 367 (25,M^+), 340 (22), 339 (10), 338 (44), 171 (23), 155 (54), 127 (100); **Analysis**: Calculated for $C_{22}H_{22}ClNO_2$: C 71.83, H 6.03, N 3.81%; found: C 71.85, H 6. 06, N 3.83%.

1-*p*-Chlorophenyl-3-ethoxycarbonyl-4-phenyl-2-propyl-1,4-dihydropyridine

4k: Yellowish semisolid; **UV**(MeOH)/nm: 240.0, 265.5, 291.5, 340.0. **IR**($CHCl_3$))/cm^{-1}:)/cm^{-1}: 1689, 1610, 1598.7, 1547.0, 1499.0, 1491.0, 1401.0, 1371.0, 1247.0 ,1234.0, 1200.0, 1162.0, 1098.0. **^{1}H NMR**($CDCl_3$,200 MHz): δ 0.75 (t,3H, *J*=7.22 Hz, -$CH_2CH_2CH_3$), 1.14 (t,3H, *J*=7.10 Hz, -OCH_2CH_3), 1.33-1.48 (m, 2H, -$CH_2CH_2CH_3$), 2.45-2.60 (m, 2H, -$CH_2CH_2CH_3$), 4.02 (q, 2H, *J*=7.10 Hz -OCH_2-), 4.65 (d, 1H, *J*=5.52 Hz, C4-H), 4.99 (dd, 1H, *J*=7.51 Hz, C5-H), 6.05 (d, 1H, *J*=7.51 Hz, C6-H), 7.18 (d, 2H, J=8.56 Hz, Ar-Hs), 7.24-7.34 (m, 5H, Ar-Hs), 7.39 (d, 2H, J= 8.62 Hz, Ar-Hs). **^{13}C NMR** ($CDCl_3$, 50MHz): 13.96 (-CH_3), 14.48 (-CH_3), 22.46 (-CH_2-), 31.30 (-CH_2-), 39.96 (C4), 59.11 (-OCH_2-), 101.50 (C3), 107.80 (C5), 125.98 (CH), 127.22 (CH), 128.14 (CH), 128.73 (CH), 129.29 (CH), 129.54 (CH), 133.07 (C4′), 142.15 (C1′), 148.01 (q, arom.), 153.70 (C2), 168.01 (-CO_2-). **Mass**(m/z) : 383 (18,M^+,+2), 382 (18, M^+, +1), 381 (50, M^+), 369 (13), 368 (10), 367 (24), 352 (15), 310 (9), 309 (5), 308 (12), 172 (5), 171 (44); **Analysis**: Calculated for $C_{23}H_{24}ClNO_2$: C= 72.34, H=6.33, N= 3.67%; Found: C 72.34, H 6. 34, N 3.78%.

3-Ethoxycarbonyl-1-*p*-fluorophenyl-2-methyl-4-phenyl-1,4-dihydropyridine

4l: Yellowish semisolid; **UV**(MeOH)/nm : 238.3, 256.6, 287.0, 336.3 ; **IR**($CHCl_3$)/cm^{-1}: 1692 (CO_2Et), 1625, 1619, 1568, 1550, 1517, 1478, 1457, 1375, 1235, 1222, 1213, 1098, 1021 ; **^{1}H NMR**($CDCl_3$,200 MHz) : δ 1.13 (t, 3H, *J*=7.10 Hz, -OCH_2CH_3), 2.13 (s, CH_3), 4.02(q, 2H, *J*=7.10 Hz, -OCH_2CH_3), 4.67 (d, 1H, *J*=5.42 Hz, C4-H), 4.98 (dd, 1H, *J*=7.63 Hz, C5-H), 6.08 (d, 1H, *J*=7.63, 5.42 Hz, C6-H), 7.04 -7.34 (m, 9H, Ar-Hs). **^{13}CNMR**($CDCl_3$, 50 MHz) : 14.25 (-CH_3), 18.52 (C2-Me), 40.29 (C4), 59.38 (-OCH_2-), 102.19 (C3), 107.68 (C5), 116.48 (C3′,C5′, $J_{C,F}$=22.4 Hz), 126.19 (CH), 127.51 (CH), 128.34 (CH), 129.31 (CH), 129.49 (CH), 139.86 (C1′), 147.48(C2), 148.34 (q, arom.), 161.55 (C4′, $J_{C,F}$= 246.1 Hz), 168.52(CO_2) ; **Mass**(m/z) : 339 (4, M^+, +2), 338 (20,M^+, +1), 337 (94, M^+), 324 (4), 323 (10), 309 (7), 308 (27), 265 (11), 264 (470, 263 (6), 261 (9), 260 (100), 233 (12), 232 (62), 172 (10), 171 (45), 96 (10), 95 (18); **Analysis**: Calculated for $C_{21}H_{20}FNO_2$: C 74.76, H5.91, N 4.15%; Found: C 74.79, H 5.93, N 4.09%.

3-Ethoxycarbonyl-2-ethyl-1-*p*-fluorophenyl-4-phenyl-1,4-dihydropyridine

4m: Yellowish semisolid; **UV**(MeOH)/nm : 238.3, 258.3, 290.0, 337.0 ; **IR**($CHCl_3$)/cm^{-1} : 1687 (CO_2Et), 1564, 1517, 1239, 1196, 1021 ; **^{1}H NMR**($CDCl_3$, 200 MHz) : δ 0.89 (t, 3H, *J*=7.28 Hz, -CH_2CH_3), 1.04 (t, 3H, *J*=7.10 Hz, -OCH_2CH_3), 2.42-2.62 (m, -CH_2CH_3), 3.93(q, 2H, *J*=7.10 Hz, -OCH_2-), 4.54 (d, 1H, *J*=5.40 Hz, C5-H), 4.87 (dd, 1H, J=7.54, 5.40 Hz, C5-H), 5.93 (d,1H, *J*=7.54 Hz, C6-H), 7.02-7.31 (m, 9H, Ar-Hs). **^{13}CNMR**($CDCl_3$, 200 MHz) : δ 13.62 (-CH_3), 14.48(-CH_3), 22.78 (-CH_2-), 40.13 (C4), 59.29 (-OCH_2-), 101.16 (C3), 107.87 (C5), 116.50 (C3′,C5′, $J_{C,F}$= 22.65 Hz), 126.19 (CH), 127.44 (CH), 128.37 (CH), 129.71 (CH), 129.90 (CH), 139.06 (C1′), 148.46 (q,

arom.), 152.64 (C2), 160.91 (C4′, $J_{C,F}$= 246.6 Hz), 167.65 (-CO_2-) ; **Mass**(m/z) : 352 (8, M^+, +1) 351 (23, M^+), 323 (14), 322 (41), 309 (8), 308 (14), 279 (4), 278 (13), 276 (2), 275 (40, 274 (21), 246 (4), 245 (12), 171 (32); **Analysis**: Calculated for $C_{22}H_{22}FNO_2$; C 75.19, H 6.31, N 3.99%; Found: C 75.32, H 6.33, N4.02%.

3-Ethoxycarbonyl-1-*p*-fluorophenyl-4-phenyl-2-propyl-1,4-dihydropyridine

4n: Yellowish semisolid; **UV**(MeOH)/nm : 236, 256.4, 290.0, 338.6; **IR**($CHCl_3$)/cm^{-1}: 1688 (CO_2Et), 1624, 1513, 1470, 1452, 1376, 1243, 1217, 1162, 1098, 1029, 1021.0 ; **^{1}H NMR**($CDCl_3$, 200 MHz) : δ 0.73 (t, 3H, *J*=7.25 Hz, -$CH_2CH_2CH_3$), 1.08 (t, 3H, *J*=7.14 Hz, -OCH_2CH_3), 1.32-1.44 (m, 2H, -$CH_2CH_2CH_3$), 2.48-2.60 (m, 2H, -$CH_2CH_2CH_3$), 4.02 (q, 2H, *J*=7.14 Hz, -OCH_2-), 4.65 (d, 1H, *J*=5.54 Hz, C4-H), 4.97 (dd, 1H, *J*=7.46, 5.54 Hz, C5-H), 6.03 (d,1H, *J*=7.5 Hz, C6-H), 7.03-7.31(m, 9H, Ar-Hs) ; **^{13}CNMR**($CDCl_3$, 50 MHz) : δ 13.72 (-CH_3), 14.00 (-CH_3), 22.48 (-CH_2-), 31.48 (-CH_2-), 40.02 (C4), 61.01 (_OCH_2-), 101.21 (C3), 107.58 (C5), 116.71(C3′,C5′, $J_{C,F}$=22.35 Hz), 126.00(CH), 127.69(CH), 128.21(CH), 129.65(CH), 129.83(CH), 139.60 (C1′), 148.33 (q, arom.), 153.23 (C2), 161.48(C4′, $J_{C,F}$= 246.7 Hz), 167.86 (-CO_2-). **Mass** (m/z) : 367 (2,M^+, +2), 366 (10, M^+, +1), 365 (38, M^+), 338 (10), 337 (9), 336 (27), 294 (9), 293 (120, 292 (50), 200 (7), 289 (21), 2889100), 262 (14), 261 (11), 260 (48), 172(6),171 (33); **Analysis**: Calculated for $C_{22}H_{24}FNO_2$; C 75.59, H 6.62, N 3.83%; Found: C 75.64, H 6.64, N 3.80%.

General Procedure for reaction of 1-aryl-4-Phenyl-1-aza-1,3-butadiene (1) with Allenic esters (2) at room temperature:

A solution of Azadiene (**1**, 1.00 mmol) and allenic ester (**2**, 1.10 mmol) in dry benzene (20 ml) was stirred at room temperature under an atmosphere of nitrogen till the azadiene was completely consumed (tlc, Table 2). The solvent was evaporated under vacuum and a ^{1}H NMR of the crude product was recorded in $CDCl_3$. The products were separated by flash column chromatography using 230-400 mesh silica gel (1% EtOAc in Hexane as eluent). The obtained (2+2) adducts gave following spectroscopic data:

2-Ethoxycarbonylmethylidene-3-methyl-4-styryl-1-tolylazetidine

5a: Yellow semisolid; **IR**($CHCl_3$)/cm^{-1} : 1705 (-CO_2Et), 1632, 1620, 1601, 1590 (s), 1495, 1468, 1372, 1243, 1128, 1099, 1051, 978; **^{1}H NMR** ($CDCl_3$, 200 MHz) : δ 1.30 (t, 3H, *J*=7.12 Hz, -CH_3), 1.59 (d, 3H, *J*=6.98 Hz, C3-Me), 2.32 (s, 3H, Ar-CH_3), 3.41(split q, 1H, *J*=6.98, 2.4 Hz), 4.15 (q, 2H, *J*=7.12 Hz, -$CO_2CH_2CH_3$), 4.56 (dd, 1H, *J*=7.56 and 2.44 Hz, C4-H), 5.34 (d, 1H, *J*=0.91 Hz, C7-H), 6.35 (dd,1H, *J*=14.0 and 7.56 Hz, C5-H), 6.80 (bd, 1H, *J*=14 Hz, C6-H), 7.42-7.05 (m, 9H, arom Hs); **Analysis** : Calculated for $C_{23}H_{25}O_2N$: C 79.51, H7.25, N 4.03%; Found: C 79.56, H 7.18, N 4.01%.

1-*p*-Chlorophenyl-2-ethoxycarbonylmethylidene-3-methyl-4-styrylzetidine

5b: Yellowish semisolid; **IR**($CHCl_3$)/cm^{-1} : 1705, 1628, 1594, 1500, 1453, 1372, 1239, 1132, 1098, 1047, 978 ; **^{1}HNMR** ($CDCl_3$, 200 MHz) : δ 1.27 (t, 3H, *J*=7.1 Hz, -OCH_2CH_3), 1.57 (d, *J*=7.0 Hz, C3-Me), 3.39 (split q, 1H, *J*=5.2, ~2.0 Hz, C3-H), 4.14 (q, 2H, *J*=5.79 Hz, -OCH_2CH_3), 4.49 (dd, 1H, *J*=6.78, 2.12 Hz, C4-H), 5.29 (b s, 1H, C7-H), 6.26 (dd, 1H, *J*=15.80, 6.78 Hz, C5-H), 6.68 (d, 1H, *J*=15.87 Hz, C6-H), 6.98 (d, 2H, *J*=8.83 Hz, Ar-Hs), 7.19-7.38 (m, 7H, Ar-Hs). **^{13}CNMR**($CDCl_3$, 50 MHz) : δ 14.63 (-CH_3), 16.10(-CH_3), 44.54 (C3), 59.02 (-OCH_2-), 71.1 (C4), 85.7 (C7), 117.7 (CH), 126.7 (CH), 126.8 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 129.30 (CH), 134.16 (q, arom.), 135.7 (q, arom.),138.54(q, arom.), 145.82(C2), 164.6 (CO_2Et) ; **Mass**(m/z) : 367 (13, M^+), 296 (20), 295 (13), 294 (40), 284 (24), 283 (73), 259 (25); **Analysis :** Calculated for $C_{22}H_{22}ClNO_2$ C 71.83, H 6.03, N 3.81%; Found: C 71.91, H 6.08, N 3.78%.

1-*p*-Chlorophenyl-2-ethoxycarbonylmethylidene-3-ethyl-4-styrylzetidine

5c: Yellowish semisolid; IR($CHCl_3$)/cm^{-1} : 1705 (-CO_2Et), 1626, 1601, 1594, 1497, 1477, 1392, 1250, 1129, 1100, 1040, 970; **^{1}HNMR** ($CDCl_3$, 200 MHz) : δ 0.93 (t, 3H, *J*=7.20 Hz, -CH_2CH_3), 1.18 (t, 3H, *J*=7.10 Hz, -OCH_2CH_3), 1.54 (m, C3-CH_2-), 3.24 (bt, 1H, C3-H), 4.13 (q, 2H, *J*=7.10 Hz, -OCH_2CH_3), 4.62 (dd, 1H, *J*=8.34, 2.15 Hz,C4-H), 5.29 (bs, C7-H), 6.25 (dd, 1H, *J*=15.68, 6.87 Hz, C5-H), 6.70 (d, 1H, *J*=15.68 Hz, C6-H), 6.92 (d, 2H, *J*=8.87Hz, Ar-Hs), 7.21-7.58 (m, 7H, Ar-Hs). **Mass** (m/z): 382 (M^++1, 2.3), 381 (M^+, 12), 353(5), 311 (15), 310(52); **Analysis :** Calculated for ($C_{23}H_{24}ClNO_2$) C 72.34, H 6.33, N 3.67%; Found: C 72.28, H 6.30, N 3.70%.

1-*p*-Chlorophenyl-2-ethoxycarbonylmethylidene-4-styrylazetidine

5d: Yellowish semisolid; **IR**($CHCl_3$)/cm^{-1} : 1705(-CO_2Et), 1632, 1615, 1594, 1501, 1479, 1469, 1135, 1109, 1050, 983; **^{1}HNMR** ($CDCl_3$, 200 MHz) : δ 1.29(t, 3H, *J*=7.10Hz, -OCH_2CH_3), 3.15 (dt, *J*=17.10, ~2.31 Hz, C3-H), 3.64 (ddd, 1H, 17.10, 9.68, 2.59 Hz, C3-H), 4.15 (q, 2H, *J*=7.10 Hz, -OCH_2CH_3), 4.37-4.43(m, 1H, Hz,C4-H), 5.34 (dist. t, 1H, C7-H), 6.30 (dd, 1H, *J*=15.72, 6.75 Hz, C5-H), 6.72 (d, 1H, *J*=15.72 Hz, C6-H), 6.99 (d, 2H, J=8.80 Hz, Ar-Hs), 7.22-7.40(m, 7H, Ar-Hs). **Mass** (m/z): 355(0.20, M^++2), 354(0.50, M^++1), 353(0.45, M^+), 324(0.30), 278(3.50), 279(5), 240(42), 167(35), 149(100); **Analysis :** Calculated for ($C_{21}H_{20}ClNO_2$) C 71.28, H 5.70, N 3.96%; Found: C 71.32, H5.74, N 3.98%.

2-Ethoxycarbonylmethylidene-3-methyl-1-phenyl-4-styryl-azetidine

5e: Yellowish semisolid; **IR**($CHCl_3$)/cm^{-1} : 1705 (s), 1626 (br), 1601 (sh), 1590 (s), 1497 (m), 1470 (m), 1372 (m), 1250 (br), 1129 (m), 1100 (w), 1040 (m), 970 (m). **^{1}HNMR** ($CDCl_3$, 200 MHz) : δ 1.29 (t, 3H, *J*=7.10 Hz, -OCH_2CH_3), 1.58 (d, *J*=6.62 Hz, C3-CH_3), 3.24 (sq, 1H, C3-H), 4.19 (q, 2H, *J*=7.10 Hz, -OCH_2CH_3), 4.49 (dd, 1H, *J*=7.50, 2.05 Hz,C4-H), 5.38 (s, 1H, C1'-H), 6.31 (dd, 1H,

J=15.90, 7.50 Hz, C5-H), 6.72 (d, 1H, *J*=15.90 Hz, C6-H), 7.06-7.40 (m, 10H, Ar-Hs). **Mass** (m/z): 334(1, M^++1), 333(4, M^+), 304(3), 279(4), 260(7), 258(8), 206(25), 167(22), 149(70), 58(100); **Analysis :** Calculated for ($C_{22}H_{23}NO_2$) C 79.25, H 6.95, N 4.20%; Found: C 79.22, H 6.88, N 4.24%.

1-*p*-Anisyl-2-ethoxycarbonylmethylidene-3-methyl-4-styrylzetidine

5f: (2+2) adduct, R=OMe, R_1=Me) IR($CHCl_3$)/cm^{-1} : 1705 (s), 1626 (br), 1601 (sh), 1590 (s), 1497 (m), 1470 (m), 1372 (m), 1250 (br), 1129 (m), 1100 (w), 1040 (m), 970 (m). **^{1}HNMR** ($CDCl_3$, 200 MHz) : δ 1.28 (t, 3H, *J*=7.09Hz, -OCH_2CH_3), 1.58 (d, *J*=6.60 Hz, C3-CH_3), 3.21 (split q, 1H, C3-H), 4.17 (q, 2H, *J*=7.09 Hz, -OCH_2CH_3), 4.51 (dd, 1H, *J*=7.26, 2.10 Hz,C4-H), 5.25 (b s, 1H, C7-H), 6.30 (dd, 1H, *J*=15.92, 7.26 Hz, C5-H), 6.71 (d, 1H, *J*=15.92 Hz, C6-H), 6.85 (d, 2H, J=8.50 Hz, Ar-Hs), 7.02 (d, 2H, J = 8.63 Hz, Ar-Hs), 7.19-7.40(m, 5H, Ar-Hs); **^{13}CNMR**($CDCl_3$, 50 MHz) : δ 14.15(-CH_3), 15.95(-CH_3), 44.42(C3), 55.42(-OCH_3), 59.72(-OCH_2-), 71.09(C4), 82.98(C7), 114.56(CH), 118.33(CH), 125.99(CH), 126.61(CH), 128.63(CH), 129.22(CH), 130.04(CH), 133.81(q, arom.), 143.01(C1′), 148.81(C2), 159.45(C4′), 168.12(-CO_2-); **Mass** (m/z): 365(4, M^++2), 364(3.7, M^++1), 363(12, M^+), 290(47), 286(20), 236(75), 122(40), 115(70), 58(100); **Analysis :** Calculated for($C_{23}H_{25}NO_3$) C 76.01, H 6.93, N 3.85%; Found: C 75.98, H 6.89, N3.91%.

General Procedure for conversion of azetidines (5) to cyclohexenones(3):

The azetidines (**5**, 0.25 to 0.4 mmole) were stirred with silica gel in $CHCl_3$ (10 ml) till whole of **5** was consumed. The solution was filtered and the product (**3**) was again separated column chromatographically using silica 100-200 mesh and EtOAc: Hexane (1:100) as eluent. Cylohexenones (**3a-c**) were characterized spectroscopically;[4] compound **3a** gave following data:

3a: Light yellow viscous material; **UV**(MeOH)/nm : 330, 280, 230 ; **IR**($CHCl_3$)/cm^{-1} : 1732, 1675, 1580, 1500, 1440, 1275, 1260, 1180, 1150 ; **^{1}HNMR**($CDCl_3$, 200MHz) : δ 1.17 (t, 3H, *J*= 7.10 Hz, -$CO2CH_2CH_3$), 2.60(m, 2H, C_4-Hs), 3.75-3.60 (m, 2H, C_5 and C_6-Hs), 4.02 (q, 2H, *J*=7.10 Hz, -CO_2CH_2-), 6.45(d, 1H, *J*= 8.15 Hz, C2-H), 6.80(m, 1H, C3-H), 7.13-7.15(m 5H arom-Hs); **Mass**(m/z): 245 (42, M^+, +1), 244 (100, M^+), 216(40), 171(70), 131(10), 98 (80), 77 (20).

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[4] Gandhi, R.P.; Ishar, M.P.S.; Wali, A. *Tetrahedron Lett.* **1987**, 6679.