

Supporting Information:

General procedure for dipolar addition of allenic ester/ketone to tropone.

A solution of allenic ester/ketone (**1**, R = OEt, Me, Ph, Bz, CH₂PhpOMe, 1.87 mmol), triphenylphosphine (0.20 mmol) and tropone (**2**, 1.56 mmol) in dry benzene (40 ml) was stirred at room temperature under an atmosphere of nitrogen, till all tropone was consumed (Table 1) and the solution turned reddish in color. Solvent was evaporated in vacuo and the products were separated by flash column chromatography (silica gel 230-400 mesh, eluent Hexane: Ethyl acetate 40:1). In case of allenic ester **8**, the solution of allene, phosphine and tropone was refluxed in dry benzene under inert atmosphere for 14 h and products were separated as described before.

Selected data for some products.

6a: colorless needles; mp 51-52°C, ¹H NMR (CDCl₃, 200 MHz): δ 1.30 (t, 3H, *J* = 7.08 Hz, CH₃), 2.98-2.91 (m, 1H, C1-H), 3.30 (ddd, 1H, *J* = 19.68, 4.99, 2.19 Hz, C10-Ha), 3.70 (ddd, 1H, *J* = 19.68, 11.10, 2.20 Hz, C10-Hb), 4.18(q, 2H, *J* = 7.08 Hz, OCH₂), 5.03(dd, 1H, *J* = 9.45, 4.75 Hz, C2-H), 5.50 (t, 1H, *J* = 2.19 Hz, C1'-H), 5.88 (d, 1H, *J* = 5.84 Hz, C6-H), 6.17-6.08 (m, 1H), 6.45-6.28 (m, 2H); ¹³C NMR (CDCl₃, 50 MHz): δ 14.42 (CH₃), 35.98 (CH₂, C10), 37.27 (CH, C1), 61.25 (OCH₂), 93.38 (C1'), 98.85 (C6), 123.18 (CH), 126.31 (CH), 127.31 (CH), 127.75 (CH), 150.31 (C7), 167.50 (C=O), 173.25 (C9); IR (neat)ν = 1701(CO₂Et), 1680, 1641, 1551, 1474, 1405, 1375, 1342, 1260 cm⁻¹; Mass *m/z*: 219 (M⁺+1,

10), 218 (M^+ , 18), 217 (M^+-1 , 20), 58 (100); elemental analysis calculated for $C_{13}H_{14}O_3$: C 71.55%, H 6.42%; found C 71.40%, H 6.28%.

6b: colorless needles; mp 49-50°C; 1H NMR ($CDCl_3$, 200 MHz): δ 2.19 (s, 3H, CH_3), 2.97-2.87 (m, 1H, C1-H), 3.30 (ddd, 1H, $J = 20.18, 4.99, 1.88$ Hz, C10-Ha), 3.68 (ddd, 1H, $J = 20.17, 11.10, 1.95$ Hz, C10-Hb), 5.01 (dd, 1H, $J = 9.45, 3.59$ Hz, C2-H), 5.87 (d, 1H, $J = 5.57$ Hz, C6-H), 5.96 (t, 1H, $J = 1.81$ Hz, C1'-H), 6.07-6.14 (m, 1H), 6.27-6.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 31.28 (CH_3), 36.81 (C10), 37.18 (C1), 99.23 (C6), 100.99 (C1'), 123.23 (CH), 126.53 (CH), 127.28 (CH), 127.61 (CH), 150.41 (C7), 173.01 (C9), 196.97 (C=O); IR (neat): $\nu = 1688$ (C=O), 1666, 1547, 1423, 1380, 1239, 1166, 1145 cm^{-1} ; Mass m/z : 189 ($M^++1,4$), 188 (M^+ , 17), 187 (M^+-1 , 22), 58 (100); elemental analysis calculated for $C_{12}H_{12}O_2$: C 76.59%, H 6.38%; Found C 76.70%, H 6.49%.

6c: semisolid; 1H NMR ($CDCl_3$, 200 MHz): δ 2.98-3.03 (m, 1H, C1-H), 3.45 (ddd, 1H, $J = 20.18, 4.89, 1.85$ Hz, C10-Ha), 3.85 (ddd, 1H, $J = 20.18, 11.10, 1.99$ Hz, C10-Hb), 5.05 (dd, 1H, $J = 9.45, 3.60$ Hz, C2-H), 5.92 (d, 1H, $J = 5.60$ Hz, C6-H), 6.11-6.35 (m, 1H), 6.41-6.47 (m, 2H), 7.42-7.56 (m, 3H, Ar-Hs), 7.92 (dd, 2H, $J = 7.20, 1.00$ Hz, Ar-Hs); IR (neat): $\nu = 1688$ (C=O), 1658, 1607, 1594, 1457.

7a: semisolid (16%); 1H NMR ($CDCl_3$, 200 MHz): δ 1.28 (t, 3H, $J = 7.13$ Hz, OCH_2CH_3), 2.65 (ddd, 1H, $J = 18.49, 5.81, 1.19$ Hz, C9-H), 2.71-2.91 (m, 1H, C9-H), 3.39 (broad t, 1H, $J = 5.4$ Hz, C1-H), 3.98 (broad, 1H, C6-H), 4.17(q, 2H, $J = 7.13$ Hz, OCH_2), 5.35 (dd, 1H, $J =$

10.62, 5.95 Hz, C2-H), 5.89-5.96 (m, 3H, C3-, C4- & C5-Hs), 7.04 (m, 1H, C8-H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 14.12 (CH_3), 35.05, (CH_2 , C9), 50.71 (CH), 50.93 (CH), 60.61 (OCH_2), 124.14 (CH), 124.43 (CH), 126.06 (CH), 128.24 (CH), 130.32 (q, C7), 135.38 (CH), 164.62 (CO_2 -), 203.49 (C=O); IR (neat): ν = 1722 & 1720 (overlapping, C=O & CO_2Et), 1658, 1440, 1376, 1244, 1218, 1167, 1090 cm^{-1} ; Mass m/z : 220 ($\text{M}^+ + 2$, 2), 219 ($\text{M}^+ + 1$, 5), 218 (M^+ , 60), 217 ($\text{M}^+ - 1$, 10), 117(100); elemental analysis calculated for $\text{C}_{13}\text{H}_{14}\text{O}_3$: C 71.55%, H 6.42%; found C 71.54%, H 6.47%.

9: semisolid; ^1H NMR (CDCl_3 , 200 MHz): δ 1.31 (t, 3H, J = 7.09 Hz, CH_3), 1.85 (distorted t, 3H, J ~ 1.50 Hz, $\text{C1}'\text{-CH}_3$), 2.83-2.90 (m, 1H, C1-H), 3.29 (ddd, 1H, J = 19.65, 4.96, 1.48 Hz, C10-Ha), 3.59 (ddd, 1H, J = 19.65, 11.10, 1.50 Hz, C10-Hb), 4.17 (q, 2H, J = 7.09 Hz, OCH_2), 4.97 (dd, 1H, J = 9.41, 3.40 Hz, C2-H), 5.83 (d, 1H, J = 6.00 Hz, C6-H), 6.03-6.11 (m, 1H), 6.21-6.41 (m, 2H); ^{13}C NMR (CDCl_3 , 50 MHz): δ 14.39 (OCH_2CH_3), 36.57 ($\text{C1}'\text{-CH}_3$), 37.88 (C1), 59.77 (OCH_2), 98.38 (C6), 101.80 (C1'), 123.33 (CH), 125.91 (CH), 127.13 (CH), 127.92 (CH), 150.93 (C7), 166.88 (CO_2), 167.00 (C9); IR (neat): ν = 1700 (CO_2Et), 1640, 1557, 1474, 1410, 1390; Mass m/z : 232 (M^+ , 25), 185 (30), 159 (27), 56 (100).