Domino Metathesis Involving ROM-RCM of Substituted Norbornenes. Rapid Access to Densely Functionalized Tricyclic Bridged and Condensed Ring systems

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Experimental Section:

All reactions were carried out under a blanket of Ar. Melting points were taken in open capillaries in sulfuric acid bath and are uncorrected. Petroleum ether refers to the fraction having bp 60-80° C. A usual work up of the reaction mixture consists of extraction with ether, washing with brine, drying over anhydrous Na₂SO₄, and removal of the solvent in vacuo. Column chromatography was carried out with silica gel (60-120 mesh). Peak position in ¹H and ¹³C NMR spectra are indicated in ppm downfield from internal TMS in δ units. NMR spectra were taken in CDCl₃ at 300 MHz for ¹H and 75 MHz for ¹³C. ¹³C peaks assignment is based on DEPT experiment. IR spectra were recorded as neat for liquid and in KBr for solids.

Methyl 3-(bicyclo[2.2.1]hept-5-en-2-yl)-3-oxopropanoate 2. A 100 mL three necked round bottomed flask is equipped with a mechanical stirrer, reflux condenser and a pressure equalizing dropping funnel bearing a nitrogen inlet. The flask is flushed with nitrogen and charged with dimethyl carbonate (9.3 mL, 110.29 mmol), THF (25mL) and sodium hydride (3.3 g, 138.1 mmol). The suspension is stirred and heated at reflux temperature and the ketone **1** (6 g, 44.12 mmol) in THF (15mL) was added drop wise over a period of 30 min. The mixture was stirred and heated at reflux for another 1 h, cooled in an ice bath for 10 min and hydrolyzed by slowly adding 12 mL 3(M) aqueous acetic acid. The contents of the flask were poured into 20 mL aqueous sodium chloride and the aqueous mixture was extracted with 3x 100 mL portion of CHCl₃. The organic layer was dried and the solvent was removed under reduced pressure. The compound was purified by column chromatography ether- petroleum ether (1:6) as eluent to afford the β – keto ester **2** (5.6 g, 60%) as a colorless viscous liquid: IR (neat) $\nu_{\max}$ 1708 cm⁻¹, 1747 cm⁻¹; ¹H NMR δ 1.32 (1H, d, *J* = 8.0 Hz), 1.38- 1.52 (2H, m), 1.73-1.81 (1H, m), 2.91 (1H, br s), 3.15 (1H, m), 3.23 (1H, br s), 3.46 (2H, d, *J* = 3.42 Hz), 3.71 (3H, s), 5.85 (1H, dd, *J* = 5.4, 2.6 Hz), 6.16 (1H, dd, *J* = 5.4, 2.9 Hz); ¹³C NMR δ 27.6 (CH₂), 42.7 (CH), 45.9 (CH), 48.3 (CH₂), 49.9 (CH₂), 52.0 (CH), 52.2 (OCH₃), 131.2 (CH), 138.2 (CH), 167.7 (COOMe), 202.8 (CO); HRMS (ESI) *m/z* (M + Na)⁺ calcd for C₁₁H₁₄O₃Na : 217.0841, found: 217.0850.

Synthesis of the compound 3. To a magnetically stirred suspension of NaH (0.300 g, 12.9 mmol, 60% in oil, freed from adhering oil by repeated washing with petroleum

ether) in dry THF (6 mL) at 0°C was added dropwise a solution of the compound **2** (1.25 g, 6.44 mmol) in THF (10 mL) under N₂ atmosphere. To this mixture was added HMPA (0.5 mL) followed by allyl bromide (1.4 mL, 13.9 mmol) drop wise. After stirring for an additional 12 h at rt, the reaction mixture was cooled at 0°C and quenched by adding cold water (2 mL). Usual work up of the reaction mixture followed by column chromatography using ether-petroleum ether (1:9) as eluent afforded the diallyl derivative **3** (1.46 g, 83%); IR (neat) $\nu_{\max}$ 1708.0, 1747 cm⁻¹; ¹H NMR δ 1.19 – 1.24 (2H, m), 1.36 (1H, d, J = 8.2 Hz), 1.65-1.79 (1H, m), 2.63 (4H, d, J = 10.4 Hz), 2.86 (1H, br s), 2.94 (1H, br s), 3.14 -3.19 (1H, m), 3.71 (3H, s), 5.02 – 5.09 (4H, m), 5.41 – 5.60 (2H, m), 5.78 (1H, dd, J = 5.5, 2.8 Hz), 6.19 (1H, dd, J = 5.5, 3.1 Hz), ¹³C NMR δ 31.9 (CH₂), 35.65 (CH₂), 35.7 (CH₂), 42.9 (CH), 47.1 (CH), 47.9 (CH), 50.2 (CH₂), 52.1 (OMe), 63.3 (C), 119.1 (CH₂), 131.3 (CH), 132.1 (CH), 132.4 (CH), 137.4 (CH), 172.1 (COOMe), 207.4 (CO); HRMS (ESI) m/z (M⁺ Na)⁺ calcd for C₁₇H₂₂O₃Na :297.1467, found: 297.1459.

Synthesis of the compound 4. A solution of the ketone **3** (1.5 g, 5.47 mmol) in THF (6 mL) was added drop wise to a magnetically stirred solution of LDA [prepared from diisopropyl amine (1.9 mL, 13.67 mmol) in anhydrous THF (5 mL) and n-BuLi (5.7 mL, 13.67 mmol, 2.4 M in hexane)] at -78 °C. The reaction mixture was then slowly raised to -30 °C and stirred at that temperature for 1 h. The reaction mixture was then again cooled to -78 °C and to it HMPA (1.5 mL) was added followed by addition of allyl bromide (1.5 mL, 13.67 mmol). The reaction mixture was allowed to attain rt and stirred for 2 h. After quenching with saturated aqueous NH₄Cl solution (1 mL), the reaction mixture was worked up in the usual way to afford after column chromatography [ether-petroleum ether 1:9] the ketone **4** (1.12 g, 65%); IR: $\nu_{\max}$ 1685, 1732 cm⁻¹; ¹H NMR δ 1.31 (1H, dd, J = 9, 1.8 Hz); 1.39 (1H, dd, J = 12.3, 3.6 Hz); 1.51 (1H, d, J = 9 Hz); 1.78 (1H, dd, J = 12.3, 2.4 Hz); 2.26 (1H, dd, J = 15, 7.8 Hz); 2.39 (1H, dd, J = 9, 3 Hz); 2.44-2.56 (2H, m); 2.62 (1H, dd, J = 14.1, 7.2 Hz); 2.79 (1H, br s); 2.93 (1H, dd, J = 15, 6.6 Hz); 3.11 (1H, br s); 3.69 (3H, s); 4.94 – 5.01 (6H, d, J = 16.9 Hz); 5.46 – 5.59 (2H, m); 5.68 – 5.73 (1H, m); 5.96 (1H, dd, J = 5.6, 2.9 Hz); 6.07 (1H, dd, J = 5.4, 3 Hz); HRMS (ESI) m/z (M + H)⁺ calcd for C₂₀H₂₇O₃ :315.1960, found: 315.1955.

Metathesis of the compound 4. Synthesis of the bridged tricyclic ketone 8. A magnetically stirred solution of the compound **4** (70 mg, 0.223mmol) in dry

dichloromethane (15ml) at -78 °C was saturated by purging ethylene through it. After 30 min Grubbs' catalyst **7** (18 mg, 0.022 mmol, 10 mol %) was added to it. After 2h the reaction was found to be complete (TLC) and the solvent was removed under vacuum. The residual mass was charged on to a column of silica gel (60 – 120 mesh) containing a bed of neutral alumina on top of silica gel and chromatographed (15% ether – hexane) to afford the compound **8** (38 mg, 59%); m.p. 79-80 °C; IR: $\nu_{\max}$ = 1737.7, 1687.6 cm^{-1} ; ^1H NMR δ 1.48 (1H, ddd, J = 13.4, 8.3, 4.7 Hz), 1.71 (1H, dd, J = 13.4, 7.1 Hz), 1.91 (1H, dd, J = 13.2, 11.4 Hz), 2.09 (1H, d, J = 14.1 Hz), 2.27-2.41 (m, 2H), 2.45-2.56 (m, 2H), 2.59-2.70 (m, 2H), 2.96 (1H, ddd, J = 14.4, 6.3, 1.2 Hz), 3.20-3.23 (1H m), 3.73 (3H, s, COOMe), 4.89 (1H, dt, J = 10.8, 0.75 Hz), 4.99 (1H, dt, J = 17.1, 1.4 Hz), 5.46 (1H, ddd, J = 9.9, 4.5, 1.8 Hz) 5.71-5.86 (2H, m), 5.89-5.93 (2H, m), ^{13}C NMR δ = 31.7 (CH_2), 32.6 (CH_2), 35.2 (CH_2), 38.8 (CH_2), 39.6 (CH), 41.9 (CH_2), 42.4 (CH), 52.3 (OCH_3), 64.77(C), 64.81(C), 113.2 (CH_2), 128.9 (CH), 129.6 (CH), 129.8 (CH), 138.2 (CH), 142.7 (CH), 174.0 (COOMe), 211.0 (CO); HRMS (ESI) m/z ($\text{M} + \text{H}$)⁺ calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_3$: 287.1647, found 287.1641 m/z and a fraction (20 mg) having an inseparable mixture of several components as revealed by the presence of several COOMe signals in its ^1H NMR spectrum.

Methyl 2-allylbicyclo[2.2.1]hept-5-ene-2-carboxylate 11. Following the procedure used for allylation of the ester **3**, the ester **10** (4 g, 26.32 mmol) was treated with LDA [prepared from diisopropylamine (9.2 mL, 65.79 mmol) in THF (10 mL) and *n*-BuLi (28.6 mL, 65.79 mmol, 2.3 M in hexane)], HMPA (2 mL) and allyl bromide (8.4 mL, 78.96 mmol) to afford the ester **11** (3.97 g, 78%) as a colorless liquid; IR: (neat): $\nu_{\max}$ 1737 cm^{-1} ; ^1H NMR δ 1.31-1.56 (3H, m), 1.86 (1H, dd, J = 12, 2.7 Hz), 2.33 (1H, dd, J = 13.7, 7.5 Hz), 2.84 (2H, br s), 3.57 (3H, s), 4.97 – 5.03 (2H, m), 5.64-5.75 (1H, m), 5.96 (1H, dd, J = 5.7, 3 Hz), 6.14 (1H, dd, J = 5.6, 2.9 Hz); ^{13}C NMR δ 35.6 (CH_2); 42.6 (CH); 44.5 (CH_2); 47.0 (CH_2); 5.01 (CH); 51.3 (OCH_3); 54.7 (C); 116.9 (CH_2); 134.5 (CH); 134.6 (CH); 138.4 (CH); 176.2 (COOMe); HRMS (ESI) m/z ($\text{M} + \text{Na}$)⁺ calcd. for $\text{C}_{12}\text{H}_{16}\text{NaO}_2$: 215.1048, found 215.1055 m/z .

2-Allylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde 12. To a stirred suspension of LiAlH_4 (1.78 g, 46.88 mmol) in diethyl ether (15 mL) at 0°C was added drop wise a solution of the norbornene ester **11** (4.5 g, 23.4 mmol) in diethyl ether (15 mL). After stirring at that

temperature for 1h the reaction mixture was quenched by sequential addition of water (1.8 mL), aqueous NaOH solution (15%, 1.8 mL) and water (5.4 mL) and allowed to attain rt. After stirring for 15 min, the white solid formed was filtered off after washing it thoroughly with diethyl ether. Removal of solvent in vacuo followed by column chromatography using ether-petroleum ether (1:5) as eluent afforded the corresponding alcohol (3.4 g, 90%) as a colorless viscous liquid; IR: $\nu_{\max}$ 3367 cm^{-1} ; ^1H NMR δ 1.36-1.48 (2H, m), 1.59 (2H, d, J = 8.7 Hz), 2.29 (1H, dd, J = 13.8, 7.1 Hz), 2.46 (1H, dd, J = 13.9, 7.7 Hz), 2.62- 2.63 (1H, m), 2.78-2.79 (1H, m), 3.25 (1H, dd, J = 10.8, 4.2 Hz), 3.37 (1H, dd, J = 10.8, 3.4 Hz), 5.03-5.14 (2H, m), 5.86- 5.97 (1H, m), 6.0-6.1 (2H, m); ^{13}C NMR δ 34.8 (CH_2), 41.7 (CH_2), 42.5 (CH), 47.3 (CH_2), 47.29 (C), 48.2 (CH), 67.5 (CH_2), 116.7 (CH_2), 135.1(CH), 136.4 (CH), 136.8 (CH), HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^+$ calcd. for $\text{C}_{11}\text{H}_{16}\text{NaO}$: 187.1099, found 187.1095 m/z . The hydroxy compound thus obtained was oxidized as follows.

To a magnetically stirred cold (-78°C) solution of oxalyl chloride (2.7 mL, 31.09 mmol) in dichloromethane (10 mL) was added a solution of DMSO (3.67 mL, 31.09 mmol) in dichloromethane (5 mL). A solution of the above alcohol (3.4 g, 20.73 mmol) in dichloromethane (1 mL) was added to this mixture and stirred for 45 min. Triethylamine (11.6 mL, 82.9 mmol) was then added to it drop wise. The reaction mixture was allowed to attain rt. It was then cooled to 0°C and quenched by adding water. Usual work-up of the reaction mixture followed by column chromatography using ether: petroleum ether (1:19) as eluent afforded the aldehyde **12** (2.35 g, 70%) as a colorless liquid; IR: $\nu_{\max}$ 1720 cm^{-1} ; ^1H NMR δ 1.47-1.76 (3H, m), 2.34-2.43 (2H, m), 2.59 - 2.61 (1H, m), 2.86 (1H, br s), 2.92 (1H, br s), 4.97 - 5.07 (2H, m), 5.63- 5.77 (1H, m), 6.04 (1H, dd, J = 5.2, 2.8 Hz), 6.18 (1H, dd, J = 5.5, 2.8 Hz), 9.42 (1H, s); ^{13}C NMR δ 33.9 (CH_2), 40.8 (CH_2), 43.2 (CH), 47.3 (CH_2), 49.9 (CH), 58.6 (C), 117.6 (CH_2), 133.5 (CH), 134.1 (CH), 138.7 (CH), 205.7 (CHO), HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^+$ calcd. for $\text{C}_{11}\text{H}_{14}\text{NaO}$: 185.0942, found 185.0939.

1-(2-Allylbicyclo[2.2.1]hept-5-en-2-yl)pent-4-en-1-one 13. To a magnetically stirred solution of 4-butenyl magnesium bromide [prepared from 4-bromo-1- butene (1.75 mL, 17.28 mmol) in THF (10 mL) and magnesium turnings (476 mg, 19.9 mmol)] was added a solution of the aldehyde **12** (1.4 g, 8.6 mmol) in THF (10 mL at 0°C . Stirring was

continued for 1 h. On cooling to 0 °C the reaction mixture was quenched by adding water (1 mL) and filtered. Organic phase was washed with brine (3x6 mL) and dried. Removal of solvent in vacuo followed by column chromatography using ether-petroleum ether (1:5) as eluent afforded the addition product (1.26 g, 67%) as a mixture of two diastereomers; IR: $\nu_{\max}$ 3378 cm^{-1} ; ^1H NMR (for the mixture) δ 1.26-1.33 (2H, m), 1.34-1.43 (2H, m), 1.52-1.65 (4H, m), 2.26-2.35 (2H, m), 2.48-2.56 (2H, m), 2.78 (1H, br s), 2.93 (1H, br s), 3.17 (1H, t, $J = 6.2$ Hz), 4.93 – 5.14 (4H, m), 5.82 (1H, m), 6.1-6.19 (3H, m); ^{13}C NMR δ 31.5 (CH_2), 31.9 (CH_2), 32.9 (CH_2), 33.1(CH_2), 35.7 (CH_2), 37.1 (CH_2), 40.7, (CH_2) 40.8 (CH_2), 42.4 (CH), 42.9 (CH), 46.8 (CH_2), 47.9 (CH_2), 47.6 (CH), 50.3 (CH), 50.2 (C), 50.9 (C), 78.7 (CHOH), 79.6 (CH-OH), 114.6 (CH_2), 114.8 (CH_2), 116.3 (CH_2), 116.5 (CH_2), 134.3 (CH), 135.2 (CH), 137.1 (CH), 137.4 (CH), 137.8 (CH), 137.8 (CH); 138.5 (CH), 138.8 (CH); HRMS (ESI) m/z ($M + \text{Na}$) $^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{ONa}$: 241.1568, found: 241.1560. To a magnetically stirred and cooled (0 °C) solution of the mixture of the addition products obtained as above (400 mg, 2.31 mmol) in acetone (2 mL) was added drop wise Jones reagent¹ (1mL) till the color of the reagent persisted. After stirring at that temperature for an additional 30 min, the reaction mixture was diluted with water (2 mL), extracted with diethyl ether (2x 10 mL). Combined organic layer was washed subsequently with 2% aqueous NaOH solution (5 mL), brine (5 mL) and dried. Removal of the solvent in vacuo followed by column chromatography using ether-petroleum ether (1: 9) as eluent afforded the ketone **13** (421 mg, 85%); IR: $\nu_{\max}$ 1705 cm^{-1} ; ^1H NMR δ 1.44-1.49 (2H, m), 1.63 (1H, d, $J = 8.7$ Hz), 1.96 (1H, dd, $J = 12.1$, 2.6 Hz), 2.24- 2.51 (4H, m), 2.59- 2.62 (2H, m), 2.85 (1H, br s), 2.88 (1H, br s), 4.94- 5.06 (4H, m), 5.61 (1H, m), 5.80 (1H, m), 5.93 (1H, dd, $J = 5.7$, 2.8 Hz); 6.13 (1H, dd, $J = 5.6$, 3.0 Hz); ^{13}C NMR δ 27.8 (CH_2), 34.0 (CH_2), 38.9 (CH_2), 42.8 (CH), 43.9 (CH_2), 47.3 (CH_2), 50.3 (CH), 60.7 (C), 114.9 (CH_2), 117.1 (CH_2), 133.8 (CH), 134.2 (CH), 137.7 (CH), 138.6 (CH), 211.6 (CO); HRMS (ESI) m/z ($M + \text{Na}$) $^+$ calcd for $\text{C}_{15}\text{H}_{20}\text{ONa}$: 239.1412, found: 239.1417.

2-Allyl-1-(2-allylbicyclo[2.2.1]hept-5-en-2-yl)pent-4-en-1-one 14. A solution of the ketone **13** (262 mg, 1.2 mmol) in THF (3 mL) was added drop wise to a magnetically stirred solution of LDA [prepared from diisopropylamine (0.25 mL, 1.8 mmol) in

¹ Bowden, K.; Halsall, T. G.; Jones, E. R. H.; Weedon, B. C. L. J. Chem. Soc. 1946, 39 – 45.

anhydrous THF (3 mL) and n-BuLi (1.2 mL, 1.8 mmol, 1.5 M in hexane] at -78°C . The reaction mixture was then slowly raised to -30°C and stirred at that temperature for 1 h. The reaction mixture was then again cooled to -78°C and to it HMPA (0.2 mL) was added followed by addition of allyl bromide (0.2 mL, 1.82 mmol). The reaction mixture was allowed to attain rt and stirred for 2 h. After quenching with saturated aqueous NH_4Cl solution (1 mL), the reaction mixture was worked up in the usual way to afford after column chromatography [ether-petroleum ether 1:19) the ketone **14** (227 mg, 73%); IR: ν_{max} 1697 cm^{-1} ; ^1H NMR δ 1.56-1.60 (2H, m), 1.80 (1H, dd, $J = 12.0, 1.7\text{ Hz}$), 1.96 - 2.07 (2H, m), 2.09- 2.31 (3H, m), 2.50 (2H, d, $J = 7.05\text{ Hz}$), 2.69 (1H, m), 2.84 (1H, br s), 2.94 (1H, br s), 4.97 – 5.05 (6H, m), 5.59 – 5.74 (3H, m), 6.02 – 6.09 (2H, m); ^{13}C NMR δ 35.4 (CH_2), 35.5 (CH_2), 35.6 (CH_2), 42.7 (CH), 43.6 (CH_2), 46.8 (CH_2), 47.8 (CH), 49.0 (CH), 61.8 (C) 117.3 (CH_2), 117.3 (CH_2), 117.7 (CH_2), 134.6 (CH), 135.9 (CH), 136.3 (CH), 137.3 (CH), 137.5 (CH), 215.5 (CO); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{18}\text{H}_{24}\text{ONa}$:279.1725, found: 179.1732.

Metathesis of the compound 14. Synthesis of the bridged tricyclic ketone 15.

Following the procedure described for metathesis of the compound **5**, the compound **14** (100 mg, 0.39 mmol) in DCM (15 mL) with the catalyst **7** (20 mg, 0.024 mmol) afforded the tricyclic compound **15** (54 mg, 60%): IR: ν_{max} 1699 cm^{-1} ; ^1H NMR δ 1.46-1.54 (2H, m), 1.64 (2H, d, $J = 8.6\text{ Hz}$), 1.93 (2H, dd, $J = 12.1, 2.6\text{ Hz}$), 2.41-2.55 (3H, m), 2.67 (1H, dd, $J = 14.6, 7.1\text{ Hz}$), 2.85 (1H, br s), 2.91 (1H, br s), 3.48 (1H, m), 4.99 – 5.05 (2H, m), 5.55-5.66 (3H, m), 5.96 (1H, dd, $J = 5.6, 3.0\text{ Hz}$), 6.12 (1H, dd, $J = 5.7, 2.8\text{ Hz}$); ^{13}C NMR δ 33.8 (CH_2), 38.1 (CH_2), 38.8 (CH_2), 42.8 (CH), 43.2 (CH_2), 45.2 (CH), 47.2 (CH_2), 49.9 (CH), 61.6 (C); 117.3 (CH_2), 128.3 (CH), 129.2 (CH), 134.6 (CH), 138.2 (CH), 216.9 (CO); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{16}\text{H}_{20}\text{ONa}$: 251.1412, found: 251.1406.

Methyl 2-(1-hydroxyallyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate 16. A solution of the methyl ester **10** (1.7 g, 11.18 mmol) in THF (10 mL) was added drop wise to a magnetically stirred solution of LDA [prepared from diisopropyl amine (3.1 mL, 22.4 mmol) in anhydrous THF (10 mL) and n-BuLi (15.9 mL, 22.4 mmol), 1.4 M in hexane] at -78°C . The reaction mixture was then slowly raised to -30°C and stirred at that temperature for 1 h. The reaction mixture was then again cooled to -78°C and to it

HMPA (1 mL) was added followed by acrolein (2.3 mL, 33.5 mmol) drop wise. The reaction mixture was allowed to stir for 1 h at -78°C . After quenching with saturated aqueous NH_4Cl solution (1 mL), the reaction mixture was worked up in the usual way to afford after column chromatography (ether-petroleum ether 1:4) one diastereoisomer (R_f 0.3) of the mixture the hydroxy-esters **16** (600mg, 42 %); IR: ν_{max} 1720, 3483 cm^{-1} ; ^1H NMR δ 1.39-1.45 (1H, m), 1.67 (1H, d, $J = 8.8$ Hz), 1.80 (1H, dd, $J = 12.3, 2.7$ Hz), 2.01 (1H, dd, $J = 12.4, 3.5$ Hz), 2.47 (1H, br s OH), 2.88 (1H, m), 2.94 (1H, m), 3.61 (3H, s), 4.17 (1H, m), 5.17- 5.28 (2H, m), 5.91 – 6.03 (1H, m), 6.06 (1H, dd, $J = 5.6, 2.9$ Hz), 6.21 (1H, dd, $J = 5.6, 3.0$ Hz); ^{13}C NMR δ 34.9 (CH_2), 42.2 (CH), 46.7 (CH_2), 47.7 (CH), 51.4 (CH), 60.1 (C), 79.0 (CH), 116.3 (CH_2), 135.7 (CH), 137.6 (CH), 139.0 (CH), 175.0 (COOMe); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{Na}$:231.0997, found: 231.0987 and the other diastereoisomer (R_f 0.35) (600 mg, 42%); IR: ν_{max} 1718, 3478 cm^{-1} ; ^1H NMR δ 0.83 (1H, dd, $J = 12.3, 2.5$ Hz), 1.29 (1H, d, $J = 8.7$ Hz), 1.42 (1H, d, $J = 8.7$ Hz), 2.44 (1H, dd, $J = 12.3, 3.9$ Hz), 2.87 (1H, br s), 3.19 (1H, d, $J = 10.4$ Hz), 3.24 (1H, br s), 3.57 (1H, br s OH), 3.68 (3H, s), 5.05 – 5.25 (2H, m), 5.70 – 5.81 (1H, m), 6.19 – 6.25 (2H, m); ^{13}C NMR δ 32.8 (CH_2), 42.1 (CH), 47.0 (CH_2), 49.8 (CH), 52 (CH), 59.6 (C), 77.4 (CH_3), 115.1 (CH_2), 133.7 (CH), 137.4 (CH), 138.9 (CH), 179.4 (COOMe); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{Na}$:231.099, found: 231.0985.

Methyl 2-(1-(methoxymethoxy)allyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate 17. To a magnetically stirred solution of the alcohol **16** (with R_f 0.3) (500 mg, 2.4 mmol) in dimethoxymethane (0.26 mL, 2.9 mmol) and dry DCM (2 mL), $\text{BF}_3 \cdot \text{OEt}_2$ (0.34 mL, 2.9 mmol) was added drop wise at 0°C . After complete addition, the reaction mixture was stirred for 30 min at 0°C . After quenching with aqueous saturated NaHCO_3 solution, the reaction mixture was worked up in the usual way to afford after column chromatography (ether-petroleum ether 1:9) The norbornene derivative **17** (0.91 g, 80%); IR(neat): ν_{max} 1741 cm^{-1} ; ^1H NMR δ 1.36 (1H, dd, $J = 8.6, 1.4$ Hz), 1.72 (1H, d, $J = 8.4$ Hz), 1.78 (1H, dd, $J = 12.2, 3.5$ Hz), 2.01 (1H, dd, $J = 12.3, 2.7$ Hz), 2.86 (1H, br s), 2.92 (1H, br s), 3.37 (3H, s), 3.6 (3H, s), 4.15 (1H, d, $J = 9$ Hz), 4.48 (1H, d, $J = 6.9$ Hz), 4.68 (1H, d, $J = 6.5$ Hz), 5.15-5.29 (2H, m), 5.76-5.88 (1H, m), 5.92 (1H, dd, $J = 5.4, 3$ Hz), 6.22 (1H, dd, $J = 5.4, 3$ Hz); ^{13}C NMR δ 34.5 (CH_2), 42.3 (CH), 47.1 (CH_2), 49.2 (CH), 51.4 (OCH_3),

55.8 (OCH₃ of MOM), 58.6 (C), 83.5 (CH), 93.3 (OCH₂), 119.5 (CH₂), 134.6 (CH), 135.3 (CH), 139.9 (CH), 174.4 (CO); HRMS (ESI) *m/z* (M + Na)⁺ calcd for C₁₄H₂₀O₄Na :275.1259, found: 275.1257.

2-(1-(Methoxymethoxy)allyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde 18. Following the procedure described for reduction of the ester **11**, the ester **17** (400 mg, 1.695 mmol) in dry ether (15 mL) was reduced with LiAlH₄ (128.8 mg, 3.4 mmol) to afford the hydroxy compound (0.807 g, 85%); IR: $\nu_{\max}$ 3417 cm⁻¹; ¹H NMR δ 1.22 (1H, d, *J* = 12.3 Hz), 1.39 (1H, d, *J* = 8.1 Hz), 1.66 (1H, d, *J* = 8.6 Hz), 1.72 (1H, dd, *J* = 12.3, 3.7 Hz), 2.64 (1H, br s), 2.89 (1H, br s), 3.03 (1H, br s OH), 3.41 (3H, s), 3.65 (2H, d, *J* = 10.9 Hz), 4.16 (1H, d, *J* = 8.3 Hz), 4.53 (1H, d, *J* = 6.8 Hz), 4.71 (1H, d, *J* = 6.8 Hz), 5.22-5.37 (2H, m), 5.92 – 6.01 (1H, m), 6.04 (1H, dd, *J* = 5.8, 2.9 Hz), 6.20 (1H, dd, *J* = 5.6, 2.9 Hz); ¹³C NMR δ 34.4 (CH₂), 43.2 (CH), 46.7 (CH), 47.0 (CH₂), 51.5 (C), 56.4 (CH₃), 67.9 (CH₂), 87.0 (CH), 94.3 (CH₂), 119.9 (CH₂), 135.4 (CH), 135.9 (CH), 138.5 (CH); HRMS (ESI) *m/z* (M + Na)⁺ calcd for C₁₃H₂₀O₃Na :247.1310, found: 247.1301. A solution of the above hydroxy compound (300 mg, 1.34 mmol) in dry DCM (5 mL) was oxidized with oxalyl chloride (0.29 mL, 3.35 mmol), DMSO (0.32 mL, 4.69 mmol) and triethylamine (0.56 mL, 4.02 mmol) according to the procedure described for preparation of the aldehyde **12**, to afford the aldehyde **18** (247 mg, 83%) as a light yellow oil; IR: $\nu_{\max}$ 1720 cm⁻¹; ¹H NMR δ 1.4 (1H, d, *J* = 7.8 Hz), 1.69 (1H, d, *J* = 8.7 Hz), 1.80 (1H, dd, *J* = 12.3, 3.3 Hz), 1.93 (1H, d, *J* = 12 Hz), 2.93 (1H, br s), 3.05 (1H, br s), 3.37 (3H, s), 4.22 (1H, d, *J* = 8.7 Hz), 4.47 (1H, d, *J* = 6.9 Hz), 4.67 (1H, d, *J* = 7.4 Hz), 5.25- 5.40 (2H, m), 5.83- 5.95 (1H, m), 6.02 (1H, m), 6.20 (1H, m); ¹³C NMR δ 34.5 (CH₂), 43.1 (CH), 47.1 (CH), 47.8 (CH₂), 56.3 (CH₃), 62.9 (C), 84.3 (CH), 93.9 (CH₂), 120.7 (CH₂), 134.6 (CH), 134.8 (CH), 139.9 (CH), 205.3 (CHO); HRMS (ESI) *m/z* (M + Na)⁺ calcd for C₁₃H₁₈O₃Na :245.1154, found: 245.1149.

1-(2-(1-(Methoxymethoxy)allyl)bicyclo[2.2.1]hept-5-en-2-yl)pent-4-en-1-one 19. Following the procedure described for the preparation of the compound **13**, the aldehyde **18** (247 mg, 1.13 mmol) in dry THF (5 mL) was treated with butenyl magnesium bromide [prepared from 4-bromo butene (0.23 mL, 2.3 mmol) in THF (10 mL) and magnesium turnings (54 mg, 2.25 mmol)] to afford the hydroxy compound as a 1:1 mixture. Column chromatography of the mixture gave one isomer of the alcohol (101 mg,

33%); IR: $\nu_{\max}$ 3446 cm^{-1} ; ^1H NMR δ 1.36 (1H, d, J = 8.7 Hz), 1.59- 1.76 (4H, m), 1.81 (1H, dd, J = 12.3, 3.8 Hz), 1.99 - 2.08 (2H, m), 2.35 – 2.37 (1H, m), 2.65 (1H, br s), 2.91 (1H, br s), 3.08 (1H, t, J = 10.1 Hz), 3.41 (3H, s), 4.31 (1H, d, J = 9.1 Hz), 4.52 (1H, d, J = 7.0 Hz), 4.67 (1H, d, J = 6.9 Hz), 4.95-5.07 (2H, m), 5.14-5.33 (2H, m), 5.94-5.96 (1H, m), 5.97 (1H, m), 6.01-6.06 (1H, m), 6.24 (1H, dd, J = 5.48, 3 Hz). ^{13}C NMR δ 31.9 (CH₂), 35.3 (CH₂), 37.8 (CH₂), 42.7 (CH), 46.8 (CH₂), 48.4(CH), 52.8(C), 56.1 (CH₃), 80.2 (CH), 90.1 (CH), 93.7 (CH₂), 114.5 (CH₂), 119.6 (CH₂), 134.3 (CH), 135.6 (CH), 138.9 (CH), 139.0 (CH); and the other isomer (100mg, 33%); ^1H NMR δ 1.35 (1H, d, J = 9.3 Hz), 1.51 (1H, dd, J = 3.9, 8.2 Hz), 1.54-1.74 (3H, m), 2.0-2.1 (2H, m), 2.31-2.34 (1H, m), 2.77 (1H, br s), 3.11 (1H br s), 3.18 (1H, t, J = 9.5 Hz), 3.42 (3H, s), 4.34 (1H, d, J = 8.6 Hz), 4.54 (1H, d, J = 6.9 Hz), 4.74 (1H, d, J = 6.9 Hz), 4.91 – 5.04 (2H, m), 5.15-5.31 (2H, m), 5.81-5.93 (2H, m), 6.14 (1H, dd, J = 5.6, 2.9 Hz), 6.31 (1H, dd, J = 5.5, 3 Hz); ^{13}C NMR δ 31.9 (CH₂), 32.9 (CH₂), 33.6 (CH₂), 42.9 (CH), 46.8 (CH), 48.2 (CH₂), 53.9 (C), 57.1 (CH₃), 79.6 (CH), 85.0 (CH), 94.7 (CH₂), 114.7 (CH₂), 118.97 (CH₂), 137.5 (CH), 137.6 (CH), 137.9(CH), 139.5(CH); HRMS (ESI) m/z ($M + \text{Na}$)⁺ calcd for C₁₇H₂₆O₃Na :301.1780, found: 301.1773. The mixture of the hydroxy compounds obtained as above (300 mg, 1.08 mmol) in acetone (3 mL) was treated with Jones reagent¹ (0.8 mL) to afford the ketone **19** (0.774 g, 78%); IR: $\nu_{\max}$ 1699 cm^{-1} ; ^1H NMR δ 1.36 (1H, dd, J = 8.7, 1.8 Hz), 1.71 (1H, d, J = 8.7 Hz), 1.93 (2H, d, J = 9 Hz), 2.20-2.38 (3H, m), 2.53-2.59 (1H, m), 2.89 (1H, m), 3.0 (1H,m), 3.40 (3H, s), 4.11 (1H, d, J = 8.7 Hz), 4.47 (1H, d, J = 6.9 Hz), 4.66 (1H, d, J = 7.7 Hz), 4.92- 5.04 (1H, m), 5.14-5.32 (2H, m), 5.68- 5.77 (1H, m), 5.95 (1H, dd, J = 5.6, 2.9 Hz), 6.17 (1H, dd, J = 5.6, 2.9 Hz); ^{13}C NMR δ 27.8 (CH₂), 34.4 (CH₂), 42.3 (CH), 42.5 (CH₂), 46.7 (CH₂), 55.9 (CH₃), 64.2 (C), 84.5 (CH), 93.5 (CH₂), 114.7 (CH₂), 119.6 (CH₂), 135.8 (CH), 137.9 (CH), 138.9 (CH), 212.1 (CO); HRMS (ESI) m/z ($M + \text{Na}$)⁺ calcd for C₁₇H₂₄O₃Na :299.1623, found: 299.1628.

2-Allyl-1-(2-(1-(methoxymethoxy)allyl)bicyclo[2.2.1]hept-5-en-2-yl)pent-4-en-1-one
20. A solution of the ketone **21** (140 mg, 0.51 mmol) in THF (1.5 mL) was added drop wise to a magnetically stirred solution of LDA [prepared from diisopropylamine (0.14 mL, 1.02 mmol) in anhydrous THF (1 mL) and n-BuLi (0.73 mL, 1.02 mmol), 1.4 M in hexane] at -78°C. The reaction mixture was then slowly raised to -30°C and stirred at that

temperature for 1h. The reaction mixture was then again cooled to -78°C and to it was added HMPA (0.1 mL) followed by addition of a solution of allyl bromide (0.05 mL, 0.51 mmol). The reaction mixture was allowed to attain -30°C and stirred for 2h followed by quenching with NH_4Cl (0.5 mL). Usual work up of the reaction mixture followed by column chromatography (ether-petroleum ether 1:49) afforded the compound **20** (69 mg, 60%) as an yellow oil; IR: ν_{max} 1698 cm^{-1} , ^1H NMR δ 1.36 – 1.37 (2H, m); 1.56 (2H, dd, $J = 12.6, 3.4\text{ Hz}$); 1.78 – 1.87 (2H, m), 2.13 – 2.34 (3H, m); 2.74 – 2.80 (2H, m), 3.39 (3H, s), 4.13 (1H, d, $J = 8.4\text{ Hz}$), 4.51 (1H, d, $J = 6.7\text{ Hz}$), 4.67 (1H, d, $J = 7.0\text{ Hz}$), 4.91 – 5.05 (3H, m), 6.03 – 6.06 (1H, m), 6.15 – 6.17 (1H, m); ^{13}C NMR δ 34.2 (CH_2), 34.8 (CH_2), 35.3 (CH_2), 42.7 (CH), 47.6 (CH_2), 48.1 (CH), 48.4 (CH), 56.4 (CH_3), 65.8 (C), 83.9 (CH), 94.1(CH_2), 116.9 (CH_2), 116.93 (CH_2), 120 (CH_2), 134.9 (CH), 135.9 (CH), 136.5 (CH), 139.5 (CH), 140.8 (CH), 215.3 (CO); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{20}\text{H}_{28}\text{O}_3\text{Na}$:339.1936, found: 339.1944.

Synthesis of the bridged tricyclic ketone 21. Following the procedure described for metathesis of the compound **5**, the compound **20** (70mg, 0.222 mmol) in DCM (15 mL) with the catalyst **7** (9 mg, 0.011 mmol) afforded the tricyclic compound **21** (45 mg, 70%): IR: ν_{max} 1697 cm^{-1} ; ^1H NMR δ 1.40 (1H, dd, $J = 12.6, 3.6\text{ Hz}$), 1.50 (1H, d, $J = 8.7\text{ Hz}$), 1.70 (1H, d, $J = 8.7\text{ Hz}$), 1.93 (1H, dd, $J = 12.6, 2.7\text{ Hz}$), 2.33-2.37 (2H, m), 2.41-2.48 (2H, m), 2.54- 2.57 (1H, m), 2.81(1H, br s), 3.42 (3H, s), 3.71 (1H, m), 4.10 (1H, d, $J = 8.1\text{ Hz}$), 4.52 (1H, d, $J = 6.6\text{ Hz}$), 4.69 (1H, d, $J = 6.6\text{ Hz}$), 5.19 – 5.28 (2H, m), 5.42 – 5.48 (1H, m), 5.58 – 5.63 (2H, m), 6.01 (1H, dd, $J = 5.7, 2.7\text{ Hz}$), 6.18 (1H, dd, $J = 5.7, \text{ Hz}$); ^{13}C NMR δ 34.6 (CH_2), 39.1 (CH_2), 39.7 (CH_2), 42.6 (CH), 47.0 (CH), 47.16 (CH_2), 47.22 (CH), 56.1 (CH), 65.7 (C), 83.3 (CH_3), 93.8 (CH_2), 119.8 (CH_2), 128.9 (CH), 129.2 (CH), 134.1(CH), 134.6 (CH), 140.2 (CH), 217.9 (CO); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^{+}$ calcd for $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}$:311.1623, found: 311.1628.

1-(2Allylbicyclo[2.2.1]hept-5-en-2-yl)but-3-en-1-one 26. A solution of allyl bromide (3.49 mL, 32.92 mmol) in THF (20 mL) was added drop wise to a stirred suspension of commercial zinc dust (1.44 g, 21.95 mmol) in THF (10 mL) at rt, and the mixture was stirred for 1h to produce a clear solution. A solution of the aldehyde **12** (3 g, 18.29 mmol) in THF (20 mL) was added drop wise to this solution at rt and stirred for 1 h. The reaction mixture was then cooled to 0°C and quenched by addition of a few drops of

water. Usual work up of the reaction mixture followed by column chromatography using ether-petroleum ether (1:6) as eluent afforded the allyl addition product (0.856 g, 68%) as a mixture of the two diastereomers; IR: $\nu_{\max}$ 3447 cm^{-1} ; ^1H NMR (for the mixture) δ 1.27 – 1.29 (1H, m), 1.33- 1.35 (1H, m), 1.39- 1.44 (2H, m), 2.18- 2.38 (2H, m), 2.42-2.46 (2H, m), 2.52 (1H, br s), 2.79-2.93 (1H, m), 3.23- 3.27 (1H, m), 5.02 – 5.13 (4H, m), 5.78-5.84 (1H, m), 5.98-6.01 (1H, m), 6.09-6.17 (2H, m); ^{13}C NMR (for the mixture) δ 35.9 (CH_2), 36.9 (CH_2), 38.3 (CH_2), 38.4 (CH_2), 40.5 (CH_2), 40.54 (CH_2), 42.4 (CH), 42.9 (CH), 46.8 (CH_2), 47.8 (CH_2), 47.8(CH), 49.7 (CH), 50.3(C), 50.4 (C); 78.6 (CH), 79.1 (CH), 116.1 (CH_2), 116.2 (CH_2), 116.87 (CH_2), 116.9 (CH_2), 134.2 (CH), 135.4 (CH), 136.4 (CH), 136.5 (CH), 136.9 (CH), 137.7 (CH), 137.7 (CH), 138.3 (CH); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^+$ calcd for $\text{C}_{14}\text{H}_{20}\text{ONa}$:227.1412, found:227.1418. The hydroxy compound thus obtained (1.5 g, 7.35 mmol) in acetone (5.6 mL), was oxidized with Jones reagent¹ (2 ml) to afford the ketone **26** (0.832 g, 84 %) as a colorless liquid. IR: $\nu_{\max}$ 1706 cm^{-1} ; ^1H NMR δ 1.44-1.51 (2H, m), 1.63 (1H, d, J = 8.7 Hz), 1.96 (1H, dd, J = 12.1, 2.6 Hz), 2.40 (2H, dd, J = 14.3, 6.9 Hz), 2.65 (2H, dd, J = 14.3, 7.5 Hz), 2.85 – 2.89 (1H, m), 3.16 – 3.20 (1H,m), 4.99- 5.16 (4H, m), 5.61 (1H, m), 5.84- 5.89 (1H, m), 5.91-5.95 (1H, m), 6.13 (1H, dd, J = 5.6, 3 Hz); ^{13}C NMR δ 33.8 (CH_2), 42.7 (CH), 43.4 (CH_2), 44.2 (CH_2), 47.2 (CH_2), 50.2 (CH), 61.1 (C), 117.2 (CH_2), 117.6 (CH_2), 131.5 (CH), 133.7 (CH), 134.01 (CH), 138.6 (CH), 210.1 (CO); HRMS (ESI) m/z ($\text{M} + \text{Na}$) $^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{ONa}$:225.1255, found: 225.1259.

1-(2-Allylbicyclo[2.2.1]hept-5-en-2-yl)-2-vinylpent-4-en-1-one 27. Following the procedure used for allylation of the compound **13**, the ketone **26** (500 mg, 2.48 mmol) was treated with LDA [prepared from diisopropyl amine (0.52 mL, 3.71 mmol) in anhydrous THF (5 mL) and $n\text{BuLi}$ (2.3 mL, 3.71 mmol) 1.6 M in hexane] and HMPA (0.2 mL) to afford the ketone **27** (0.779 g, 65%) as colorless oil. IR: $\nu_{\max}$ 1706 cm^{-1} ; ^1H NMR δ 1.42-1.52 (2H, m), 1.61 (1H, d, J = 8.7 Hz), 1.87 (1H, dd, J = 12.1, 2.4 Hz), 2.15- 2.29 (2H, m), 2.49 (1H, dd, J = 14.9, 6.8 Hz), 2.64 (1H, dd, J = 14.8, 7.2 Hz), 2.83 (1H, br s), 2.9 (1H, br s), 3.38 (1H, m), 4.97- 5.13 (6H, m), 5.55 – 5.71 (3H, m), 5.97 – 5.99 (1H, m), 6.05 – 6.08 (1H, m); ^{13}C NMR δ 34.1 (CH_2), 36.5 (CH_2), 42.3 (CH), 43.0 (CH_2), 46.8 (CH_2), 49.1 (CH_2), 54.0 (CH), 61.7 (C), 116.6 (CH_2), 117.0 (CH_2), 117.4 (CH_2),

134.2 (CH), 135.5 (CH), 135.8 (CH), 137.3 (CH), 137.5 (CH), 212.5 (CO); HRMS (ESI) m/z (M + Na)⁺ calcd for C₁₇H₂₂ONa :265.1568, found: 265.1566.

Synthesis of the bridged tricyclic ketone 28. Following the procedure described for metathesis of compound **5**, the compound **27** (80mg, 0.33 mmol) in DCM (15 mL) with the catalyst **7** (10 mg, 0.012 mmol) afforded the tricyclic compound **28** (28 mg, 40%): IR: $\nu_{\max}$ 1701. cm⁻¹; ¹H NMR δ 1.44 -1.48 (1H, m), 1.59-1.67 (3H, m), 2.14 (2H, dd, J = 2.6, 11.9 Hz), 2.24-2.35 (2H, m), 2.56-2.60 (1H, m), 2.86-2.98 (1H, m), 3.66 (1H, m), 5.05 (2H, dd, J = 13.6, 2.2 Hz), 5.80-5.88 (3H, m), 5.97 – 6.06 (1H, m), 6.16 (1H, dd, J = 5.64, 3 Hz); ¹³C NMR δ 33.7 (CH₂), 36.4 (CH₂), 37.03 (CH₂), 42.8 (CH), 46.8 (CH₂), 49.7 (CH), 52.4 (CH), 62.1 (C), 115.05 (CH₂), 128.2 (CH), 129.9 (CH), 132.9 (CH), 137.3 (CH), 139.13 (CH), 213.1 (CO); HRMS (ESI) m/z (M + Na)⁺ calcd for C₁₅H₁₈ONa : 237.1255, found: 237.1250.

1-(Bicyclo[2.2.1]hept-5-en-2-yl)prop-2-en-1-one 32. The aldehyde **31** (3 g, 24.6 mmol) in dry THF (15 mL) was treated with vinyl magnesium bromide [prepared from vinyl bromide (3.3 g, 31 mmol) in THF (40 mL) and magnesium turnings (1.8 g, 73.77 mmol)] to afford the vinyl addition product (3.2 g, 85%) as a 1:1 diastereomeric mixture; IR: $\nu_{\max}$ 3450 cm⁻¹; ¹H NMR (for the mixture) δ 1.19-1.22 (1H, m), 1.35-1.43 (1H, m), 1.65 – 1.72 (1H, m), 1.85-1.86 (1H, m); 2.01-2.12 (1H, m), 2.22 (OH br s), 2.71-2.80 (1H, m), 3.02 (1H, br s), 3.36-3.45 (1H, m), 4.99 – 5.17 (2H, m), 5.75 – 5.88 (1H, m), 5.99-6.02 (1H, m), 6.12-6.13 (1H, m); ¹³C NMR (for the mixture) δ 29.2 (CH₂), 29.8 (CH₂), 42.2 (CH), 42.7 (CH), 43.9 (CH), 44.6 (CH), 45.3 (CH), 46.3 (CH), 49.3 (CH₂), 49.6 (CH₂), 76.9 (CH), 78.0 (CH), 114.7 (CH₂), 114.9 (CH₂), 132.1(CH), 132.6 (CH), 137.7 (CH), 137.8 (CH), 140.7 (CH), 140.8 (CH); HRMS (ESI) m/z (M + Na)⁺ calcd for C₁₀H₁₄ONa :173.0942, found: 173.0935. The above alcohol (500 mg, 3.33 mmol) in acetone (5 mL) was treated with Jones reagent¹ (1.2 mL) to afford the ketone **32** (346 mg, 70%): IR: $\nu_{\max}$ 1697 cm⁻¹; ¹H NMR δ 1.29 (1H, d, J = 8.1 Hz), 1.39 (1H, dd, J = 1.4, 7.8 Hz), 1.44-1.50 (1H, m), 1.71-1.78 (1H, m), 2.85 (1H, br s), 3.16-3.21 (2H, m), 5.65 (1H, dd, J = 10.5, 1.1 Hz), 5.74 (1H, dd, J = 5.4, 2.5 Hz), 6.07 (1H, dd, J = 5.5, 3.0 Hz), 6.16 (1H, dd, J = 17.5, 1.10 Hz), 6.40 (1H, dd, J = 17.5, 10.5 Hz); ¹³C NMR δ 28.3 (CH₂), 43.2 (CH), 46.5 (CH), 50.1 (CH), 50.2 (CH₂), 127.7 (CH₂), 131.9 (CH), 136.1 (CH), 137.8 (CH), 200.9 (CO); HRMS (ESI) m/z (M + H)⁺ calcd for C₁₀H₁₃O :149.0966, found: 149.0975.

Diels-Alder reaction of the enone 32. To a solution of the enone **32** (200 mg, 1.35 mmol) in dry DCM (10 mL) freshly distilled cyclopentadiene (445 mg, 6.75 mmol) was added drop wise in ice-cold condition. Stirring was continued for 1 h in 0 °C and 13 h at rt. The solvent was removed under reduced pressure and the white residue was purified by column chromatography (ether – petroleum ether 1:19) to afford an inseparable mixture of the adducts **33** and **34** (220 mg, 76%) as a white solid, mp 112-118 °C IR: $\nu_{\max}$ 1695 cm^{-1} ; ^1H NMR (for the mixture) δ 1.29-1.36 (2H, m), 1.37-1.46 (2H, m), 1.49-1.55 (1H, m), 1.65-1.85 (2H, m), 2.89 (1H, br s), 3.03-3.14 (2H, m), 3.22 – 3.31 (2H, m), 5.77- 5.90 (2H, m), 6.10-6.14 (2H, m); ^{13}C NMR (for the mixture) δ 27.6 (CH_2), 28.9 (CH_2), 42.7 (CH), 42.9 (CH), 45.8 (CH), 46.5 (CH), 49.9(CH_2), 50.1 (CH_2), 50.3 (CH), 51.1 (CH), 131.1(CH), 132.3 (CH), 137.3 (CH), 137.9 (CH), 210.8 (CO), 212.2 (CO); HRMS (ESI) m/z ($M + \text{Na}$) $^+$ calcd for $\text{C}_{15}\text{H}_{18}\text{ONa}$:237.1255, found: 237.1254.

Metathesis of the mixture of the compounds 33 and 34. Synthesis of the tricyclic compounds 35 & 36. Following the procedure described for metathesis of the compound **5**, the inseparable mixture of the compounds **33** and **34** (83mg, 0.39 mmol) in DCM (15 mL) with the catalyst **7** (16 mg, 0.019 mmol) afforded a mixture of the tricyclic compounds **35** and **36**. Column chromatography of this mixture gave the pure ketone **35** (22 mg, 23%); IR: $\nu_{\max}$ 1697.2 cm^{-1} ; ^1H NMR δ 1.48 (2H, dd, $J = 23.2, 11.3$ Hz), 1.89 (2H, dd, $J = 22.2, 10.5$ Hz), 1.98-2.16 (4H, m), 2.50-2.62 (2H, m), 2.92-3.0 (2H, m), 3.32 (2H, dd, $J = 8.5, 18.4$ Hz), 4.97-5.10 (4H, m), 5.62 (2H, d, $J = 2.8$ Hz), 5.84-5.95 (2H, m); ^{13}C NMR δ 35.1 (CH_2), 40.7 (CH_2), 41.1 (CH), 44.2 (CH), 54.1 (CH), 114.0 (CH_2), 132.4 (CH), 141.8 (CH), 211.8 (CO); HRMS (ESI) m/z ($M + \text{Na}$) $^+$ calcd for $\text{C}_{17}\text{H}_{22}\text{ONa}$: 265.1568, found: 265.1585, and the pure ketone **36** (57mg, 45%); IR: $\nu_{\max}$ 1703 cm^{-1} ; ^1H NMR δ 1.25-1.32 (2H, m), 1.41-1.46 (2H, m), 1.78-1.87 (2H, m), 1.90-1.98 (2H, m), 2.47-2.58 (2H, m), 2.88-2.92 (1H, m), 2.95-3.05 (2H, m), 3.21-3.24 (1H, m), 3.32-3.40 (1H, m), 4.86-5.04 (4H, m), 5.51-5.63 (1H, m), 5.69 (1H, dd, $J = 5.4, 2.6$ Hz), 5.74-5.89 (1H, m), 6.14 (1H, dd, $J = 5.4, 3.0$ Hz); ^{13}C NMR δ 26.9 (CH_2), 34.9 (CH_2), 39.6 (CH_2), 43.0 (CH), 43.9 (CH), 46.3 (CH), 47.7 (CH), 50.2 (CH_2), 52.9 (CH), 53.5 (CH), 113.4 (CH_2), 115.2 (CH_2), 130.9 (CH), 137.9 (CH), 139.6 (CH), 142.2 (CH), 212.5 (CO); HRMS (ESI) m/z ($M + \text{Na}$) $^+$ calcd for $\text{C}_{17}\text{H}_{22}\text{ONa}$: 265.1568, found: 265.1564.

X-Ray crystal data for compound 8

See (fig 1) and Crystal data: Refined formula $C_{18}H_{22}O_3$, Formula weight $M_r = 286.36$, Crystal system Triclinic, Space group P-1 (No. 2), $a = 10.2279(13)$, $b = 10.6309(13)$, $c = 15.3920(19)$ Å, $\alpha = 80.421(2)^\circ$, $\beta = 71.857(2)^\circ$, $\gamma = 89.308(2)^\circ$, Volume (V) = $1566.8(3)$ Å³, No of the formula units in the unit cell $Z = 2$, Calculated density $\rho_{\text{calcd}} = 1.214$ g cm⁻³, linear absorption coefficient $\mu(\text{Mo-K}\alpha) = (0.081\text{mm}^{-1})$, radiation and wavelength MoK α ($\lambda = 0.71073$ Å), temperature of measurement $T = 298$ K, $F(000) = 616$, $\theta_{\text{min}} = 2.1^\circ$, $\theta_{\text{max}} = 28.3^\circ$, no. of measured reflection 9414, no. of independent reflection 6894, $R_{\text{int}} = 0.020$, $R_1 = 0.0590$, $wR2 = 0.1872$, residual electron density max and min $-0.15, 0.28$ e Å⁻³. The structure was solved by direct methods (SHELXS-97) and refined by full- matrix least squares using SHELXL-97 with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were partly refined with isotropic thermal parameters, and partly placed in calculated position.