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Preparation of optically pure cross-conjugated cyclopentadienones

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Abstract—The synthesis of optically pure cross-conjugated cyclopentadienones is readily achieved in two steps via a one-pot alkylcuprate addition/aldol condensation/dehydration sequence using racemic or enantioenriched *endo*-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-1-ones followed by microwave-mediated Lewis acid-catalysed *retro* Diels–Alder reaction. An alternative route involving a modified Baylis–Hillman protocol followed by conjugate addition with alkylcuprates and a retro Diels–Alder reaction was also investigated.
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1. Introduction

Recent reports of the potent biological properties exhibited by many prostanoid compounds containing a cross-conjugated cyclopentadienone unit has heightened our interest in the synthesis of this important structural motif.[1]

The clavulone series of marine natural products **1**,[2] the unsaturated prostaglandin (PG) $\Delta^{12,14}$-15-deoxy-PG-J_2 **2**,[3] the related C-18 chromomoric acid **3**[4] and the potential anticancer agent TEI-9826 **4**[5] all contain the 5-alkylidene-cyclopent-2-enone unit (Fig. 1). In addition, similar compounds have recently been implicated in the development and progression of atherosclerosis.[6]

In general there exists a number of approaches to cross-conjugated dienone-containing ring structures **D** from enones **A** that involve the formation of a β-hydroxy alkylated species **C**, their further derivatisation and subsequent β-elimination (Scheme 1).

In many of these cases, the β-hydroxy alkylated moiety of **C** can be obtained by either trapping the enolate **B** (resulting from conjugate addition) with a suitable aldehyde[6b,7] or through conjugate addition to an α-alkoxy alkylated enone **F** (derived from seleno enolate **E**) using alkylcuprates, as reported by Noyori.[8]

Although the enolate trapping route has enjoyed considerable popularity in the synthesis of structures of type **C**, Noyori's pathway has not been employed to the same extent, probably due to the greater number of steps involved, as well as the potential hazards from handling toxic selenide reagents and intermediates. Interestingly, Noyori's procedure had notable mechanistic similarities with the Baylis–Hillman reaction and, in particular, with a recently reported variant involving mild cooperative catalysis (from tributylphosphine as a Lewis base with phenol as a Brønsted acid) to give α-methylene-β-hydroxy enones **F** via enolate **G** and adduct **H** (Scheme 2).[9]

We surmised that a novel synthetic sequence that comprised a mechanistically similar and higher yielding Baylis–Hillman reaction as its key step, circumventing the disadvantages of Noyori's method, might offer a more efficient approach to cross-conjugated cyclopentadienones.

2. Results and discussion

We chose to conduct the modified Baylis–Hillman reaction on racemic *endo*-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-1-one **5**[10] to give β-hydroxy alkylated enones which we wished to derivatise (e.g. by acetoxylation) and finally perform an alkylcuprate conjugate addition to give an exocyclic alkene, after spontaneous β-elimination. Lewis acid-catalysed *retro* Diels–Alder would then release the corresponding cross-conjugated cyclopentadienone (Scheme 3).

Keywords: Microwave-promoted reactions; *retro*-Diels–Alder reaction; 4-Alkyl 5-alkyli-denecyclopent-2-enones; Baylis–Hillman reaction.
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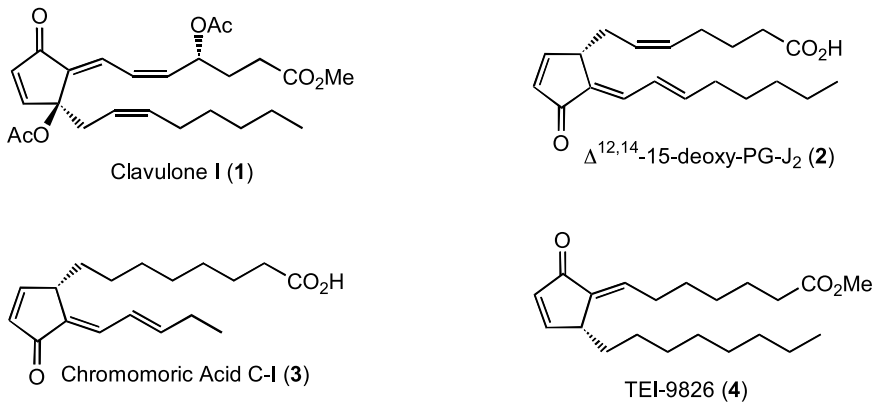


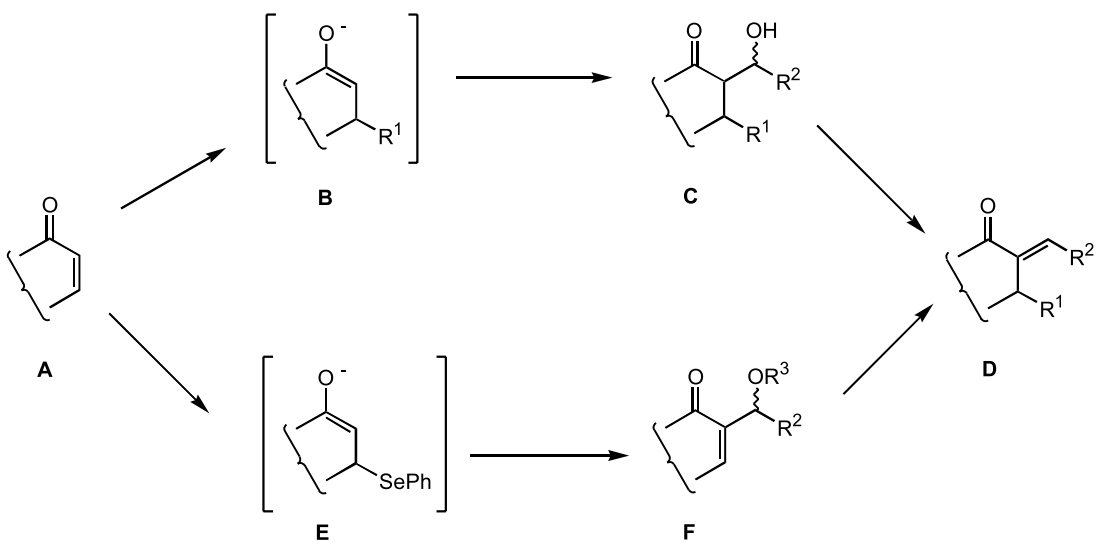
Figure 1. Alkylidenecyclopentenones of biological interest.

The Baylis–Hillman adducts **6**–**10** were easily prepared, usually in high yield (87–93%) after stirring a mixture of racemic enone, phenol, tributylphosphine and aldehyde in THF at room temperature for 24 h. The corresponding acetates **11**–**15** were prepared in the standard manner (47–97% yield).

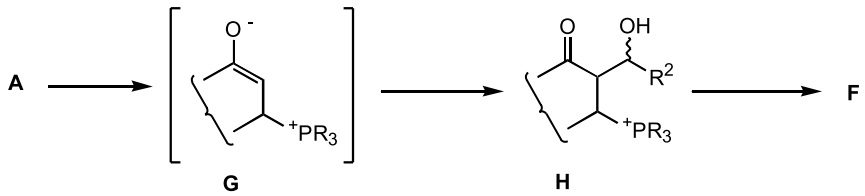
The key conjugate addition/elimination tandem reaction worked well for the isopropyl compound **11**, furnishing the alkylated products **16** and **17** as the only isolable compounds in 57 and 59% yield, respectively. However, the procedure was not as satisfactory for other substrates. For example, when the compound **12** was used as starting material in a reaction with dimethylcuprate, the desired compound **18** was formed (34%) in admixture with the bis-alkylated product **25** (28%). Reaction of **12** with butylcyanocuprate was even more complex furnishing the bis-alkylated product **26** (7%) as well as the required product **19** which was not separated from the isomer **27** (42% yield; ratio **19**:**27** 9:1 by NMR spectroscopy). Similarly addition of methylcyanocuprate to the acetoxy-enone **13** was not regioselective, the desired product **20** (61%) being contaminated with the (separable) isomer **28** (19%).

Clearly continuing with this strategy with its unpredictable overall yields and, more significantly, the often-observed poor regioselectivity, was not appealing. Our attention turned to a one-pot alkylcuprate addition/aldol condensation/dehydration procedure which had literature precedent[4d] and, we felt, could be applied with more confidence to racemic and enantioenriched *endo*-3a,4,7,7a-tetrahydro-4,7-methano-inden-1-one **5** in order to access a range of target compounds. Indeed cross-conjugated cyclopentenedione precursors have been obtained from **5** previously.[11] However the required intermediate was obtained only after isolation of the aldol and subsequent acid-catalysed rearrangement, generating a mixture of *Z*- and *E*-geometrical isomers (Scheme 4). More recently cross-conjugated cyclopentadienones have been accessed from enone **29** using a one-pot conjugate addition/Peterson olefination sequence followed by a *retro* Diels–Alder reaction.[12]

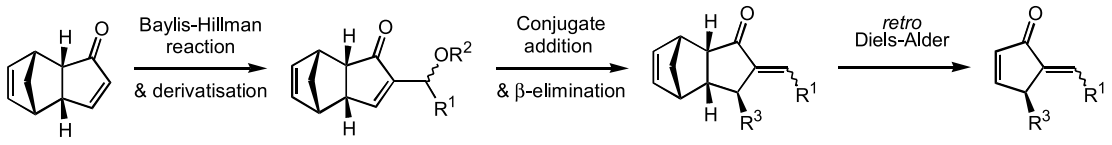
Both enantioenriched (+)-**5** and (−)-**5** were available in high yield and on a multi-gram scale.[13] The enantiomers underwent facile chemo- and diastereoselective 1,4-conjugate addition with an alkylcuprate; aldehyde quench of the intermediate enolate and spontaneous dehydration upon



Scheme 1. Approaches towards β-hydroxy alkylated species.



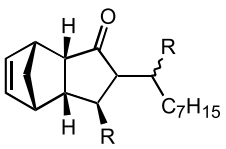
Scheme 2. An approach comprising the modified Baylis–Hillman reaction.

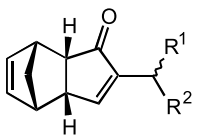


6 R^1=$CHMe_2$; R^2=H
7 R^1=C_7H_{15}; R^2=H
8 R^1=$CH(CH_2)_2$; R^2=H
9 R^1=Ph; R^2=H
10 R^1=CH_2Ph; R^2=H
11 R^1=$CHMe_2$; R^2=Ac
12 R^1=C_7H_{15}; R^2 = Ac
13 R^1=$CH(CH_2)_2$; R^2=Ac
14 R^1=Ph; R^2=Ac
15 R^1=Bn; R^2=Ac

16 R^1=$CHMe_2$; R^3=Me
17 R^1=$CHMe_2$; R^3=C_4H_9
18 R^1=C_7H_{15}; R^3=Me
19 R^1=C_7H_{15}; R^3=C_4H_9
20 R^1=$CH(CH_2)$; R^3=Me
21 R^1=$CHMe_2$; R^3=C_8H_{17}
22 R^1=Ph; R^3=Me
23 R^1=Ph; R^3=C_8H_{17}
24 R^1=*p*-F.C_6H_4; R^3=Me

Scheme 3. Baylis–Hillman adducts and cross-conjugated cyclopentadienones derived from (±)-*endo* enone **5**.



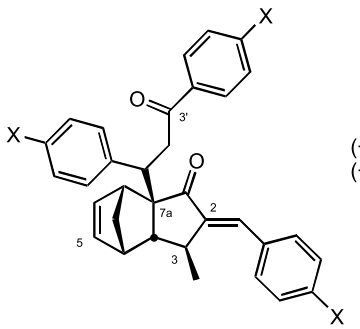


25 R=Me
26 R=C_4H_9

27 R^1=C_4H_9; R^2=C_7H_{15}
28 R^1=Me; R^2=$CH(CH_2)_2$

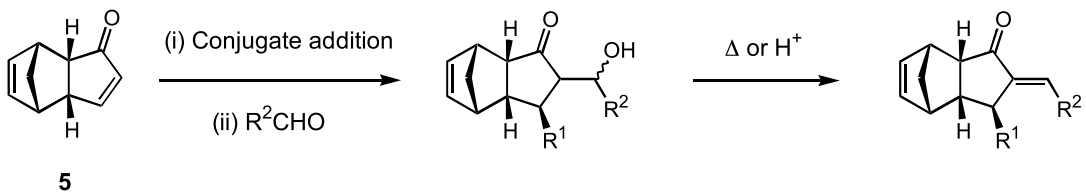
work-up furnished the desired products (Table 1). Generally, the one-pot three component coupling proceeded smoothly giving good or very good yields of *exo*-cyclic enones. Entries 1–4 and 10, demonstrated that the reaction exhibited exclusively *E*-selectivity, whilst the remainder (entries 5–8) provided the same isomer in very high purity (>95%). It is possible that the small contamination by the *Z*-isomer may have been due to photolytic and or thermally induced isomerisation. Differentiation between *E*- and *Z*-isomers of compounds **32**–**36** was possible using ^{1}H NMR spectroscopic techniques and was in accordance with literature precedent.[4d]

In a few cases the one-pot strategy provided some unexpected by-products. In addition to the desired *exo*-cyclic enones (+)-**22** and (+)-**24** (entries 5 and 10 respectively), more polar compounds were also isolated (15% yield in each case). After NMR spectroscopic and high resolution mass spectrometric analysis the compounds were assigned the structures of the tri-aryl species (+)-**30** and (+)-**31**.



(+) **30** (X= H)
(+) **31** (X= F)

Previously, it has been reported that Lewis acid-catalysed *retro* Diels–Alder reactions involving *exo*-cyclic enones similar to **16**, **21**–**24** were achievable only with reaction times of between 1 and 24 h duration.[12] It was found that a



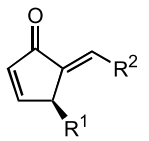
Scheme 4. Synthesis of cross-conjugated cyclopentadienone precursors.

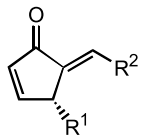
Table 1. Synthesis of some *exo*-cyclic enones by one-pot conjugate addition/aldol condensation/dehydration

Entry	Substrate	Cuprate reagent	Aldehyde	Product (yield, %)[a] (*E*/*Z* ratio)[b]
1	(+)-**5**	Me_2CuLi	Me_2CHCHO	(+)-**16** (76) (100:0)
2	(−)-**5**	Me_2CuLi	Me_2CHCHO	(−)-**16** (60) (100:0)
3	(+)-**5**	Oct_2CuLi	Me_2CHCHO	(+)-**21** (61) (100:0)
4	(−)-**5**	Oct_2CuLi	Me_2CHCHO	(−)-**21** (54) (100:0)
5	(+)-**5**	Me_2CuLi	PhCHO	(+)-**22** (64) (97:3)
6	(−)-**5**	Me_2CuLi	PhCHO	(−)-**22** (75) (92:8)
7	(+)-**5**	Oct_2CuLi	PhCHO	(+)-**23** (57) (92:8)
8	(−)-**5**	Oct_2CuLi	PhCHO	(−)-**23** (83) (99:2)
9	(±)-**5**	Me_2CuLi	*p*-F.C_6H_4CHO	(±)-**24** (83) (99:1)
10	(+)-**5**	Me_2CuLi	*p*-F.C_6H_4CHO	(+)-**24** (55) (100:0)

[a] Yield following purification by flash column chromatography.
[b] Ratio determined by ^{1}H NMR spectroscopy of the crude reaction mixture.

considerable enhancement of the reaction rate was possible, for the *exo*-cyclic enones **16**, **21**–**24**, when the [4+2]-cycloreversion step was carried out in a microwave reactor (SmithCreator, ~20 W).





(+)-**32** R^1=Me; R^2=$CHMe_2$ (-)-**32** R^1=Me; R^2=$CHMe_2$
(+)-**33** R^1=C_8H_{17}; R^2=$CHMe_2$ (-)-**33** R^1=C_8H_{17}; R^2=$CHMe_2$
(-)-**34** R^1=Me; R^2=Ph (+)-**34** R^1=Me; R^2=Ph
(+)-**35** R^1=C_8H_{17}; R^2=Ph (-)-**35** R^1=C_8H_{17}; R^2=Ph
(-)-**36** R^1=Me; R^2=*p*-F.C_6H_4 (+)-**36** R^1=Me; R^2=*p*-F.C_6H_4

Thus microwave-mediated reactions of *exo*-cyclic enones **16**, **21**–**24** were performed in DCM in sealed glass vials at 60 °C with $MeAlCl_2$ as Lewis acid catalyst and an excess of maleic anhydride as a cyclopentadiene trap.[13] In most cases, the reaction was stopped after 25 min. Continued irradiation eroded the yields of products **32**–**36** which were generally very respectable (Table 2). In contrast to earlier reports,[12] little significant change in the *E*/*Z* isomer ratios was observed.

Table 2. Synthesis of some optically active cross-conjugated cyclopentadienones **32**–**36**

Entry	Substrate	Product (yield %)[a] (*E*/*Z* ratio)[b]
1	(+)-**16**	(+)-**32** (63)* (98:2)
2	(−)-**16**	(−)-**32** (83)* (97:3)
3	(+)-**21**	(+)-**33** (84)* (100:0)
4	(−)-**21**	(−)-**33** (65)* (94:6)
5	(+)-**22**	(−)-**34** (74) (97:3)
6	(−)-**22**	(+)-**34** (69) (97:3)
7	(+)-**23**	(+)-**35** (82)* (99:1)
8	(−)-**23**	(−)-**35** (62)* (98:2)
9	(±)-**24**	(±)-**36** (83) (96:4)
10	(+)-**24**	(−)-**36** (91) (100:0)

[a] Yield following purification by flash column chromatography and taking into account recovered starting material (10–20%) where indicated (*).
[b] Estimated by ^{1}H NMR spectroscopy.

3. Conclusions

We have combined a one-pot three-component coupling procedure on racemic and enantioenriched substrate **5** with a facile microwave-mediated *retro* Diels–Alder reaction to give optically pure cross-conjugated cyclopentadienones in two steps. Significantly the initial alkylcuprate conjugate addition reaction proceeds with high diastereoselectivity and the condensation with very high *E*-selectivity; the overall yield for the whole process is 50% or greater in the vast majority of the cases studied.

4. Experimental

4.1. General

Starting materials were purchased from commercial sources and were used without further purification. ^{1}HNMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a Bruker AMX400 spectrometer. ^{13}C NMR assignments were made using DEPT experiments. Infra red spectroscopy was performed on a Perkin–Elmer Paragon 1000 FT1R machine. Optical rotation measurements were recorded using an Optical Activity, Polar 2001 polarimeter at 589 nm and are quoted in units of 10^{-1} deg cm^2 g^{-1}. Flash column chromatography was performed using silica gel-ICN 32-63, 60 Å.

4.2. Baylis–Hillman reaction representative procedure

4.2.1. (±)-2-(1-Hydroxy-octyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one 7. Phenol (0.2 equiv.) and *n*-tributylphosphine (0.4 equiv.) was added to a stirring solution of enone **5** (1.0 g, 6.91 mmol) and *n*-octylaldehyde (1.5 equiv.) in anhydrous THF (6.2 cm^3) at room temperature under nitrogen stream. After 5–8 days at this temperature, flash silica (4.5 g) was added and the solvent removed in vacuo to afford crude product, pre-absorbed on silica. Purification using flash column chromatography (SiO_2), eluting with *n*-hexane/2-butanone, (9:1) afforded the allylic alcohol **7** (1.63 g, 86%) as a transparent pale yellow oil; R_f 0.24 (SiO_2, *n*-hexane/diethyl ether, 2:1); δ_H (400 MHz, $CDCl_3$) 7.10 (1H, d, *J*=2.6 Hz, H_3), 5.91 (1H, dd, *J*=5.6, 2.9 Hz, $H_{5/6}$), 5.79 (1H, m, $H_{6/5}$), 4.20 (1H, s, 2C*H*(OH) *n*-hep), 3.27 (2H, m), 2.91 (2H, m), 1.75 (1H, m), 1.75 (1H, d, *J*=8.5 Hz, 4-C*H*H-7), 1.62 (1H, d, *J*=8.5 Hz, 4-CH*H*-7), 1.26 (1H, s, 1CH(OH)(CH_2)$_6$Me), 0.87 (3H, t, *J*=6.7 Hz, 1CH(OH)(CH_2)$_6$*Me*); δ_C (100 MHz, $CDCl_3$) 210.9 (s, C_1), 158.1 (d, C_3), 150.9 (s, C_2), 133.0 (d, $C_{5/6}$), 132.7 ($C_{6/5}$), 68.7 (2*C*H(OH) *n*-hep), 53.1 (t, 4-CH_2-7), 52.0 (d), 45.89, 45.5, 44.5, 36.6 (t, 2CH(OH)(*C*H_2)$_6$Me), 32.1, 29.7, 29.6, 25.8, 23.0, 14.4 (q, 2CH(OH)(CH_2)$_6$*Me*); *m*/*z* (CI/NH_3) 275 (MH^+, 100%), 257 ([$MH-H_2O$]$^+$, 97), 144 (29); (HRMS: found MH^+, 275.2011. $C_{18}H_{27}O_2^+$ requires 275.2018).

4.2.2. (±)-2-(1-Hydroxy-2-methylpropyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one 6. (1.32 g, 87%), a transparent pale yellow oil; R_f 0.25 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 7.07 (1H, d, *J*=2.5 Hz, H_3), 5.94 (1H, dd, *J*=5.5, 2.8 Hz, $H_{5/6}$), 5.80 (1H, dd, *J*=5.5, 3.0 Hz, $H_{6/5}$), 3.99 (1H, d, *J*=5.8 Hz, 2C*H*(OH) *i*-prop), 3.34 (1H, m), 3.22 (1H, m), 2.97 (1H, m),

2.88 (1H, t, J=4.8 Hz), 1.87–1.75 (1H, m), 1.64–1.57 (1H, m), 0.89 (3H, d, J=6.8 Hz, 2CH(OH)CH*Me*Me), 0.83 (3H, d, J=6.8 Hz, 2CH(OH)CHMe*Me*); δ_C (100 MHz, $CDCl_3$) 211.1 (s, C_1), 159.5 (d, C_3), 149.3 (s, C_2), 133.2 (d, $C_{5/6}$), 133.0 ($C_{6/5}$), 74.9 (2*C*H(OH) *i*-prop), 53.2 (t, 4-CH_2–7), 52.0 (d), 46.1, 45.5, 44.6, 33.6, 19.3 (q, 2CH(OH)CH-*Me*Me), 17.9 (2CH(OH)CHMe*Me*); *m/z* (CI/NH_3) 219 (MH^+, 100%), 201 ($[MH-H_2O]^+$, 75), 137 (42.3); (HRMS: found MH^+, 219.1393. $C_{14}H_{19}O_2^+$ requires 219.1385).

4.2.3. (±)-2-(Cyclopropyl-hydroxy-methyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one 8. (3.44 g, 93%), a transparent yellow oil; R_f 0.17 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 7.20 (1H, d, J=2.6 Hz, H_3), 5.92 (1H, dd, J=5.3, 2.7 Hz, H_6), 5.80 (1H, dd, J=5.3, 3.0 Hz, H_5), 3.67 (1H, d, J=8.1 Hz, 2C*H*(OH) cycloprop), 3.33 (1H, m, H_{3a}), 3.22 (1H, m, H_7), 3.12 (1H, br. s, 2CH(OH) cycloprop), 2.97 (1H, m, H_4), 2.89 (1H, t, J=5.12 Hz, H_{7a}), 1.75 (1H, dd, J=8.4, 1.4 Hz, 4-C*H*H-7), 1.62 (1H, d, J=8.4 Hz, 4-CH*H*-7), 1.07–0.94 (1H, m, 2CH(OH) *cycloprop*), 0.57–0.42 (2H, m, 2CH(OH) *cycloprop*), 0.38–0.33 (1H, m, 2CH(OH) *cycloprop*), 0.27–0.21 (1H, m, 2CH(OH) *cycloprop*); δ_C (100 MHz, $CDCl_3$) 210.9 (s, C_1), 158.4 (d, C_3), 150.3 (s, C_2), 132.9 (d, C_6), 132.7 (C_5), 72.2 (2*C*H(OH) cycloprop), 51.9 (C_{7a}), 45.9 (C_{3a}), 45.5 (C_7), 44.4 (C_4), 17.0 (2CH(OH) *cycloprop*), 3.5 (t, 2CH(OH) *cycloprop*), 2.5 (2CH(OH) *cycloprop*); *m/z* (CI/NH_3) 234 ($[MH+NH_3]^+$, 3.7%), 216 ($[MH+NH_3-H_2O]^+$, 74.4), 199 (100); (HRMS: found $MH+NH_3^+$, 234.1498. $C_{14}H_{20}NO_2^+$ requires 234.1494).

4.2.4. (±)-2-(1-Hydroxy-phenyl-methyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one 9. (0.73 g, 89%), an off-white crystalline solid; R_f 0.28 (SiO_2, *n*-hexane/diethyl ether, 1:1); ν_{max} (film)/cm^{-1} 3355 (OH), 1664.9 (CO); δ_H (400 MHz, $CDCl_3$) 7.34–7.31 (5H, m, 2CH(OH)*Ph*), 6.94 (1H, d, J=1.9 Hz, H_3), 5.90 (1H, dd, J=5.6, 2.9 Hz, $H_{5/6}$), 5.76 (1H, dd, J=5.6, 3.0 Hz, $H_{6/5}$), 5.42 (1H, s, 2C*H*(OH)Ph), 3.45 (1H, s, 2CH(*OH*)Ph), 3.29 (1H, m, H_{3a}), 3.22 (1H, m, $H_{4/7}$), 2.93 (1H, m, $H_{7/4}$), 2.89 (1H, t, J=5.1 Hz, H_{7a}), 1.74 (1H, dt, J=8.5, 1.7 Hz, 4-C*H*H-7), 1.60 (1H, d, J=8.5 Hz, 4-CH*H*-7); δ_C (100 MHz, $CDCl_3$) 210.7 (s, C_1), 159.7 (d, C_3), 150.7 (s, C_2), 141.9 (2CH(OH)*Ph*), 133.0 (d, C_6), 132.9 (C_5), 128.8 (2d, 2CH(OH)*Ph*), 128.1 (d, 2CH(OH)*Ph*), 126.8 (2d, 2CH(OH)*Ph*), 70.6 (d, 2*C*H(OH)Ph), 53.1 (t, 4-CH_2-7), 52.0 (d, C_{3a}), 45.9 (C_{7a}), 45.6 (C_4), 44.5 (C_7); *m/z* (CI/NH_3) 504 (7.0%), 487 (8.8), 270 ($[MH+NH_3]^+$, 7.9), 252 (44.8), 235 (100), 207 (35.7), 169 (13.8); (HRMS: found $MH+NH_3^+$, 270.1498. $C_{17}H_{20}NO_2^+$ requires 270.1501).

4.2.5. (±)-2-(1-Hydroxy-2-phenyl-ethyl)-3a,4,7,7a-tetrahydro-4,7-methano inden-1-one 10. (0.51 g, 56%), a yellow crystalline solid; R_f 0.24 (SiO_2, *n*-hexane/diethyl ether, 1:1); δ_H (250 MHz, $CDCl_3$) 7.27–7.16 (6H, m, 2CH(OH)CH_2*Ph*, H_3), 5.83 (1H, dd, J=5.5, 3.1 Hz, $H_{5/6}$), 5.66 (1H, dd, J=5.5, 3.1 Hz, $H_{6/5}$), 4.44 (1H, m, 2C*H*(OH)CH_2Ph), 4.30 (1H, br. s, 2CH(O*H*)CH_2Ph), 3.22 (1H, m, H_{3a}), 3.15 (1H, m, $H_{4/7}$), 2.96 (1H, dd, J=13.7, 4.1 Hz, 2CH(OH)C*H*HPh), 2.90 (1H, m, $H_{7/4}$), 2.83 (1H, t, J=5.1 Hz, H_{7a}), 2.68 (1H, dd, J=13.7, 8.2 Hz, 2CH(OH)CH*H*Ph), 1.69 (1H, d, J=8.6 Hz, 4-C*H*H-7), 1.59 (1H, m, 4-CH*H*-7); δ_C (100 MHz, $CDCl_3$) 213.9 (s, C_1), 163.4 (d, C_3), 155.9 (s), 143.4, 137.5 (d, $C_{5/6}$), 136.9 ($C_{6/5}$), 134.4 (2d, 2CH(OH)CH_2*Ph*), 132.8, 130.9 (d, 2CH(OH)CH_2*Ph*), 72.7 (2*C*H(OH)CH_2Ph), 57.3 (t, 4-CH_2-7), 56.5 (d), 56.5, 50.1, 49.7, 48.7, 47.2 (t, 1CH(OH)*C*H_2Ph); *m/z* (CI/NH_3) 387 (100%), 369 (58.1), 351 (18.0), 266 ($[MH+NH_3-H_2O]^+$, 7.3), 249 ($[MH-H_2O]^+$, 26.9), 194 (17.4), 91 (26.4); (HRMS: found MH^+, 267.1391. $C_{18}H_{19}O_2^+$ requires 267.1385).

4.3. Acetylation of Baylis–Hillman products representative procedure

4.3.1. (±)-Acetic acid 1-(1-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-2-yl)-octyl ester 12. Acetic anhydride (11 equiv.) was added to a solution of allylic alcohol **7** (0.25 g, 0.91 mmol) in freshly distilled pyridine (1.6 cm^3) and stirred at room temperature for 17 h under nitrogen atmosphere. Water (8 cm^3) and ethyl acetate (8 cm^3) were added, the aqueous layer separated and extracted further with ethyl acetate (3×8 cm^3). The combined organic layers were washed with 10% $NaHCO_3$ solution (8 cm^3), water (8 cm^3), dried ($MgSO_4$) and solvent removed in vacuo to afford crude acetate. Purification using flash column chromatography (SiO_2), eluting with *n*-hexane/2-butanone (9:1) gave allylic acetate **12** (0.21 g, 72%) as a transparent amber oil; R_f 0.46 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 7.11 (1H, d, J=2.5 Hz, H_3), 5.91 (1H, m, $H_{5/6}$), 5.71 (1H, m, $H_{6/5}$), 5.34 (1H, m, 2C*H*(OAc) *n*-hep), 3.31–3.28 (1H, m), 3.21 (1H, m), 2.94 (1H, m), 2.84 (1H, m), 2.03 (3H, s, 2CH(OCO*Me*) *n*-hep), 1.74–1.58 (4H, m, 2CH(OAc)(CH_2)$_6$Me), 1.24 (10H, m, 2CH(OAc)(CH_2)$_6$-Me), 0.86 (3H, m, 2CH(OAc)(CH_2)$_6$*Me*); δ_C (100 MHz, $CDCl_3$) 207.5 (s, C_1), 169.9 (2CH(O*CO*Me) *n*-hep), 158.8 (d, C_3), 148.0 (s, C_2), 132.7 (d, $C_{5/6}$), 132.3 ($C_{6/5}$), 69.7 (2*C*H(OAc) *n*-hep), 52.5 (t, 4-CH_2-7), 53.0 (d), 45.5, 45.2, 44.2, 33.0 (t, 2CH(OAc)(CH_2)$_6$Me), 31.8, 29.2, 29.1, 25.2, 22.6, 21.1 (q, 2CH(OCO*Me*) *n*-hep), 14.1 (2CH(OAc)(CH_2)$_6$*Me*); *m/z* (CI/NH_3) 334 ($[MH+NH_3]^+$, 30.7%), 317 (MH^+, 93.4), 274 (3.3), 257 (100), 144 (21.9); (HRMS: found MH^+, 317.2116. $C_{20}H_{29}O_3^+$ requires 317.2117).

4.3.2. (±)-Acetic acid 2-methyl-1-(1-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-2-yl)-propyl ester 11. (0.25 g, 83%), a transparent pale yellow oil; R_f 0.49 (SiO_2, *n*-hexane/2-butanone, 4:1); ν_{max} (film)/cm^{-1} 3061, 2966, 2934, 2873, 1738, 1703, 1627; δ_H (400 MHz, $CDCl_3$) 7.11 (1H, d, J=2.5 Hz, H_3), 5.91 (1H, m, $H_{5/6}$), 5.70 (1H, m, $H_{6/5}$), 5.15 (1H, d, J=6.3 Hz, 2C*H*(OAc) *i*-prop), 3.31 (1H, m), 3.22 (1H, m), 2.94 (1H, m), 2.85 (1H, m), 2.12 (1H, m, 2CH(OAc)C*H*Me_2), 2.03 (3H, s, 2CH(OAc) *i*-prop), 1.75 (1H, m, 4-C*H*H-7), 1.60 (1H, m, 4-CH*H*-7), 0.84 (3H, s, 2CH(OH)CH*Me*Me), 0.83 (3H, 2CH(OH)CHMe*Me*); δ_C (100 MHz, $CDCl_3$) 207.5 (s, C_1), 170.0 (2CH(O*CO*Me) *i*-prop), 160.0 (d, C_3), 147.1 (s, C_2), 132.9 (d, $C_{5/6}$), 132.4 ($C_{6/5}$), 74.1 (2*C*H(OAc) *i*-prop), 52.5 (t, 4-CH_2-7), 51.6 (d), 45.6, 45.2, 44.2, 30.3 (2CH(OAc)*C*HMe_2), 21.0 (q, 2CH(OCO*Me*) *i*-prop), 18.7 (2CH(OH)CH*Me*Me), 17.5 (2CH(OH)CHMe*Me*); *m/z* (CI/NH_3) 278 ($[MH+NH_3]^+$, 16.1%), 261 (MH^+, 71.4), 201 (100); (HRMS: found MH^+, 261.1485. $C_{16}H_{21}O_3^+$ requires 261.1491); Found: C, 73.7; H, 7.8%, $C_{16}H_{20}O_3$ requires C, 73.8; H, 7.7%.

4.3.3. (±)-Acetic acid cyclopropyl-(1-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-2-yl)-methyl ester 13. (4.56 g, 97%), a transparent pale brown oil; R_f 0.35 (SiO_2, *n*-hexane/Et_2O, 1:1); δ_H (400 MHz, $CDCl_3$) 7.19 (1H, d, *J*=2.6 Hz, H_3), 5.90 (1H, dd, *J*=5.6, 2.9 Hz, $H_{5/6}$), 5.72 (1H, dd, *J*=5.6, 3.0 Hz, $H_{6/5}$), 4.78 (1H, d, *J*=8.9 Hz, 2C*H*(OAc) cycloprop), 3.31 (1H, m), 3.22 (1H, m), 2.96 (1H, m), 2.86 (1H, t, *J*=5.0 Hz), 2.03 (3H, s, 2CH(OCO*Me*) cycloprop), 1.74 (1H, dt, *J*=8.4, 1.7 Hz, 4-C*H*H-7), 1.60 (1H, d, *J*=8.4 Hz, 4-CH*H*-7), 1.24–1.16 (1H, m, 2CH(OAc) *cycloprop*), 0.55–0.44 (2H, m, 2CH(OAc) *cycloprop*), 0.39–0.28 (2H, m, 2CH(OAc) *cycloprop*); δ_C (100 MHz, $CDCl_3$) 207.7 (s, C_1), 170.3 (2CH(O*CO*Me) cycloprop), 159.4 (C_2), 148.0 (d, C_3), 133.0 ($C_{5/6}$), 132.6 ($C_{6/5}$), 73.1 (t, 2CH(OAc) cycloprop), 52.8 (4-CH_2-7), 51.7 (d), 45.9, 45.6, 44.9, 21.5 (2CH(OAc) *cycloprop*), 14.6 (q, 2CH(OCO*Me*) cycloprop), 4.3 (t, 2CH(OAc) *cycloprop*), 2.9 (2CH(OAc) *cycloprop*); *m/z* (CI/NH_3) 276 ([MH+NH_3]$^+$, 11.0%), 259 (MH^+, 13.3), 216 (100), 199 (94.5), 164 (16.4), 147 (20.3), 135 (9.6); (HRMS: found MH^+, 259.1329. $C_{16}H_{18}O_3^+$ requires 259.1334).

4.3.4. (±)-Acetic acid (1-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-2-yl)-phenyl-methyl ester 14. (0.74 g, 93%), an off-white crystalline solid; R_f 0.34 (SiO_2, *n*-hexane/diethyl ether, 1:1); δ_H (400 MHz, $CDCl_3$) 7.33–7.22 (5H, m, 2CH(OCOMe)*Ph*), 7.19 (1H, m, H_3), 6.38 (1H, dd, *J*=5.2, 2.9 Hz, $H_{5/6}$), 5.91 (1H, dd, *J*=5.2, 2.5 Hz, $H_{6/5}$), 3.30–3.27 (1H, m, $H_{3a/7a}$), 3.18 (1H, m, $H_{4/7}$), 2.95 (1H, m, $H_{7/4}$), 2.80 (1H, t, *J*=4.9 Hz, $H_{7a/3a}$), 2.05 (3H, s, 2CH(OCO*Me*)Ph), 1.71 (1H, d, *J*=8.4 Hz, 4-C*H*H-7), 1.56 (1H, d, *J*=8.4 Hz, 4-CH*H*-7); δ_C (100 MHz, $CDCl_3$) 207.0 (s, C_1), 169.8 (2CH(O*CO*Me)Ph), 159.1 (d, C_3), 148.4 (s, C_2), 138.6 (2CH(OCOMe)*Ph*), 133.0 (d, $C_{5/6}$), 132.7 ($C_{6/5}$), 128.8 (2d, 2CH(OCOMe)*Ph*), 128.5, 127.4 (d, 2CH(OCOMe)*Ph*), 70.7 (2*C*H(OCOMe)Ph), 52.9 (t, 4-CH_2-7), 51.8 (d, $C_{3a/7a}$), 46.0 ($C_{4/7}$), 45.6 ($C_{7/4}$), 44.6 ($C_{7a/3a}$), 21.4 (q, 2CH(OCO*Me*)Ph); *m/z* (ES$^+$) 413 (5.0%), 408 (5.0), 333 ([M+K]$^+$, 5.6), 317 ([M+Na]$^+$, 100), 301 (29.4), 251 (36.9); (HRMS: found M+Na^+, 317.1160. $C_{19}H_{18}O_3^{23}Na$ requires 317.1154); Found: C, 77.5; H, 6.2%, $C_{19}H_{18}O_3$ requires C, 77.5; H, 6.2%.

4.3.5. (±)-Acetic acid-1-(1-oxo-3a,4,7,7a-tetrahydro-1*H*-4,7-methano-inden-2-yl)-2-phenyl-ethyl ester 15. (0.27 g, 47%), a transparent pale yellow oil; R_f 0.22 (SiO_2, *n*-hexane/diethyl ether, 2:1); ν_{max} (film)/cm^{-1} 3469, 3062, 3029, 2979, 2936, 2869, 1742, 1698; δ_H (400 MHz, $CDCl_3$) 7.27–7.12 (5H, m, 2CH(OAc)CH_2*Ph*), 7.01 (1H, d, *J*=2.4 Hz, H_3), 5.86 (1H, dd, *J*=5.6, 2.8 Hz, $H_{5/6}$), 5.61 (1H, m, 2C*H*(OAc)CH_2Ph), 5.54 (1H, dd, *J*=5.6, 2.9 Hz, $H_{6/5}$), 3.24–3.20 (2H, m), 3.10 (1H, dd, *J*=14.0, 5.5 Hz, 2CH(OAc)C*H*HPh), 2.92 (1H, m, 2CH(OAc)CH*H*Ph), 2.88 (1H, m), 2.84 (1H, t, *J*=5.1 Hz), 1.98 (3H, s, 2CH(OCO*Me*)CH_2Ph), 1.70 (1H, dt, *J*=8.4, 1.6 Hz, 4-C*H*H-7), 1.56 (1H, d, *J*=8.4 Hz, 4-CH*H*-7); δ_C (100 MHz, $CDCl_3$) 207.8 (s, C_1), 170.0 (2CH(O*CO*Me)Ph), 160.1 (d, C_3), 147.2 (s, C_2), 137.3 (2CH(OCOMe)CH_2*Ph*), 133.0 (d, $C_{5/6}$), 132.6 ($C_{6/5}$), 129.9 (2d, 2CH(OCOMe)CH_2*Ph*), 128.5, 126.9 (d, 2CH(OCOMe)*Ph*), 70.5 (2*C*H(OCOMe)CH_2Ph), 52.8 (t, 4-CH_2-7), 52.0 (d, $C_{3a/7a}$), 45.9 ($C_{4/7}$), 45.5 ($C_{7/4}$), 44.4 ($C_{7a/3a}$), 39.3 (t, 2CH(OAc)*C*H_2Ph), 21.3 (q, 2CH(OCO*Me*)CH_2Ph); *m/z* (CI/NH_3) 326 ([MH+NH_3]$^+$, 15.1%), 309 ([MH]$^+$, 48.8), 249 (100); (HRMS: found MH^+, 309.1491. $C_{20}H_{21}O_3^+$ requires 309.1491) as well as its elimination product (0.23 g, 48%) as white crystalline solid; R_f 0.54 (SiO_2, *n*-hexane/diethyl ether, 1:1); ν_{max} (film)/cm^{-1} 3061, 3028, 2978, 2940, 2869, 1748, 1697, 910, 734; δ_H (400 MHz, $CDCl_3$) 7.45–7.30 (2H, m, 2C*H*CH*Ph*), 7.29–7.16 (5H, m, H_3, 2CHCH*Ph*), 6.65 (1H, d, *J*=16.4 Hz, 2CHC*H*Ph), 5.94 (1H, dd, *J*=5.6, 3.0 Hz, $H_{5/6}$), 5.80 (1H, dd, *J*=5.6, 2.8 Hz, $H_{6/5}$), 3.33 (1H, m, $H_{3a/7a}$), 3.26 (1H, m, $H_{4/7}$), 2.98 (1H, m, $H_{7/4}$), 2.94 (1H, t, *J*=5.1 Hz, $H_{7a/3a}$), 1.76 (1H, dt, *J*=8.4, 1.7 Hz, 4-C*H*H-7), 1.62 (1H, d, *J*=8.4 Hz, 4-CH*H*-7); δ_C (100 MHz, $CDCl_3$) 208.7 (CO, C_1), 158.8 (CH, C_3), 144.0 (R_4C, C_2), 137.6 (2CHCH*Ph*), 133.1 (CH), 133.0, 128.9, 128.3, 127.0, 118.7 (2CH*C*HPh), 53.1 (R_2CH_2, 4-CH_2-7), 52.4 (R_3CH), 45.9 (2R_3CH), 45.1; *m/z* (CI/NH_3) 266 ([MH+NH_3]$^+$, 22.9%), 249 ([MH]$^+$, 100); (HRMS: found MH^+, 249.1275. $C_{18}H_{17}O^+$ requires 249.1279).

4.4. Alkylcuprate addition and acetate elimination representative procedure

4.4.1. (±)-2-(*E*)-Octylidene-3-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one 18 and (±)-2-(1-methyloctyl)-3-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one 25. 1.4 M Methyllithium in diethyl ether (3.3 equiv.) was added to a suspension of anhydrous copper (I) iodide (1.7 equiv.) in diethyl ether (1.6 cm^3) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to warm to −40 °C and stirred for 30 min. The alkylcuprate reagent was added dropwise to a stirring solution of acetate **12** (53 mg, 0.17 mmol) in anhydrous diethyl ether (0.17 cm^3) at −78 °C and the reaction allowed to warm to room temperature. After 12.5 h at room temperature, saturated aqueous NH_4Cl solution (0.75 cm^3) was added and the reaction mixture extracted with diethyl ether (3×0.75 cm^3). The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo to afford crude product. Preparative thin layer chromatography (SiO_2) eluting with *n*-hexane/2-butanone (5:1) gave the methylated adduct **18** (15.8 mg, 34%) as a pale yellow transparent oil; R_f 0.56 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 6.94 (1H, d, *J*=2.7 Hz, 2C*Hn*-hep), 5.87 (1H, dd, *J*=5.5, 2.7 Hz, $H_{5/6}$), 5.73 (1H, dd, *J*=5.5, 2.9 Hz, $H_{6/5}$), 3.25–3.22 (1H, m), 3.20 (1H, m), 2.92 (1H, m), 2.89 (1H, t, *J*=5.1 Hz), 2.38 (1H, m, H_3), 1.74–1.71 (1H, dt, *J*=8.3, 1.8 Hz, 4-C*H*H-7), 1.61–1.59 (1H, m, 4-CH*H*-7), 1.41–1.09 (12H, m, 2CH(CH_2)$_6$Me), 0.98 (3H, d, *J*=6.9 Hz, 3*Me*), 0.87 (3H, t, *J*=6.8 Hz, 2CH(CH_2)$_3$*Me*); δ_C (100 MHz, $CDCl_3$) 209.6 (s, C_1), 155.9 (d, 2*C*H *n*-hep), 154.7 (s, C_2), 132.5 (d, $C_{5/6}$), 132.4 ($C_{6/5}$), 52.6 (t, 4-CH_2-7), 51.1 (d), 49.0, 45.2, 44.2, 35.9 (t, 2CH(*C*H_2)$_6$Me), 31.9, 31.8, 29.6, 29.3, 27.1, 22.1, 19.6 (q, 3Me), 14.1 (2CH(CH_2)$_6$*Me*); *m/z* (CI/NH_3) 303 (0.5%), 290 ([MH+NH_3]$^+$, 0.9), 273 (MH^+, 100), 173 (26.4); (HRMS: found MH^+, 273.2224. $C_{19}H_{19}O^+$ requires 273.2218) and the bis-alkylated adduct **25** (13.9 mg, 28%) as a pale yellow transparent oil; R_f 0.66 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 6.14 (1H, dd, *J*=5.6, 3.0 Hz, $H_{5/6}$), 6.04 (1H, dd, *J*=5.6, 3.0 Hz, $H_{6/5}$), 3.13 (1H, m), 3.03 (1H, m), 2.97–2.92 (1H, m), 2.48–2.43 (1H, m), 1.95 (1H, dt, *J*=11.8, 2.8 Hz), 1.67–1.55 (3H, m), 1.40 (1H, d, *J*=8.1 Hz), 1.29–1.20 (12H, m, 2CHMe(CH_2)$_6$Me), 1.17 (3H, d, *J*=6.6 Hz, 2CH*Men*-hep), 0.87 (3H, t, *J*=6.6 Hz, 2CHMe(CH_2)$_3$*Me*), 0.83 (3H, d, *J*=6.8 Hz, 3*Me*); δ_C

(100 MHz, $CDCl_3$) 218.3 (s, C_1), 137.1 (d, $C_{5/6}$), 135.7 ($C_{6/5}$), 65.1 (d), 55.1, 52.3 (t, 4-CH_2-7), 48.0 (d), 45.5, 44.7, 35.7, 34.5, 31.9 (t, 2CH(CH_2)$_6$Me), 31.6, 29.8, 29.4, 28.0, 22.7, 21.8 (q), 16.8, 14.1; *m/z* (CI/NH_3) 306 ([MH+NH_3]$^+$, 20.7%), 289 (MH^+, 6.3), 240 (37.6), 223 (100), 96 (20), 60 (15.5); (HRMS: found MH+NH_3^+, 306.2799. $C_{20}H_{36}NO^+$ requires 306.2797).

4.4.2. (±)-2-(2-(*E*)-Methylpropylidene)-3-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one 16. (50.7 mg, 57%), a pale yellow transparent oil; R_f 0.50 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 6.06 (1H, dd, *J*=10.5, 2.1 Hz, 2C*Hi*-prop), 5.95 (2H, m, H_5, H_6), 3.23 (1H, m), 3.06 (1H, m), 3.00 (1H, m), 2.52 (1H, m), 1.47 (1H, dt, *J*=8.3, 1.7 Hz, 4-C*H*H-7), 1.37 (1H, d, *J*=8.3 Hz, 4-CH*H*-7), 1.11 (3H, d, *J*=7.3 Hz, 3Me), 1.00 (3H, d, *J*=7.3 Hz, 2CHCH*Me*Me), 0.95 (3H, d, *J*=6.6 Hz, 2CHCHMe*Me*); δ_C (100 MHz, $CDCl_3$) 209.7 (s, C_1), 143.2 (C_2), 142.8 (d), 136.1, 133.0, 53.3 (d),51.4 (t, 4-CH_2-7), 47.4 (d), 47.1, 46.9, 35.0, 28.5, 23.4 (q, 3Me), 22.1 (2CHCH*Me*Me), 21.9 (2CHCHMe*Me*); *m/z* (CI/NH_3) 234 ([MH+NH_3]$^+$, 3.1%), 217 (MH^+, 16.8), 168 (23.7), 151 (100); (HRMS: found MH^+, 217.1595. $C_{15}H_{21}O^+$ requires 217.1592).

4.4.3. (±)-2-(2-(*E*)-Methylpropylidene)-3-butyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one 17. (28.2 mg, 59%) as a transparent pale yellow oil; R_f 0.54 (SiO_2, *n*-hexane/2-butanone, 4:1); δ_H (400 MHz, $CDCl_3$) 6.07 (1H, dd, *J*=10.7, 2.1 Hz, 2C*Hi*-prop), 5.95 (2H, m, H_5, H_6), 3.23 (1H, m), 3.00 (1H, m), 2.96 (1H, m), 2.51 (1H, m), 2.43–2.34 (2H, m), 1.41–1.31 (8H, m, 4-CH_2-7 and 3(CH_2)$_3$Me), 1.00 (3H, d, *J*=6.6 Hz, 2CH(OH)CH*Me*Me), 0.95 (3H, d, *J*=6.5 Hz, 2CH(OH)CHMe*Me*), 0.90 (3H, t, *J*=6.6 Hz, 3(CH_2)$_3$*Me*); δ_C (100 MHz, $CDCl_3$) 210.4 (s, C_1), 143.3 (d, 2*C*H *i*-prop), 142.5 (s, C_2), 136.3 (d, $C_{5/6}$), 133.8 ($C_{6/5}$), 54.2, 51.9 (t, 4-CH_2-7), 47.9 (d), 44.6, 40.8, 37.4 (t), 29.4, 29.0 (d), 23.3 (t), 22.3 (2q, 2CH*Me*$_2$), 14.5 (q, 3(CH_2)$_3$*Me*); *m/z* (CI/NH_3) 278 (3.6%), 259 (MH^+, 11.3), 210 (25.2), 193 (100); (HRMS: found MH^+, 259.2060. $C_{18}H_{27}O^+$ requires 259.2062).

4.5. Alkyl cyanocuprate addition and elimination representative procedure

4.5.1. (±)-2-(*E*)-Octylidene-3-butyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one 19 and (±)-2-(1-butyl-octyl)-3-butyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one 26. 2.5 M *n*-Butyllithium in diethyl ether (1.2 equiv.) was added to a suspension of anhydrous copper (I) cyanide (1.2 equiv.) in diethyl ether (3.1 cm^3) at −78 °C under nitrogen atmosphere. The reaction mixture was allowed to warm to −40 °C and stirred for 40 min. The alkyl cyanocuprate reagent was added dropwise to a stirring solution of acetate **12** (0.5 g, 1.58 mmol) in anhydrous diethyl ether (1.6 cm^3) at −78 °C. After 45 min at this temperature, saturated aqueous NH_4Cl solution (2.5 cm^3) was added and the reaction mixture extracted with diethyl ether (3×4 cm^3). The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo to afford a yellow opalescent oil. Purification by flash column chromatography (SiO_2), eluting with *n*-hexane/diethyl ether (9:1 and 4:1), gave an inseparable mixture (9:1) of the 3-butylated adduct **19** and its *exo*-butylated regioisomer **27** (0.21 g, 42%) as a transparent pale yellow oil; R_f 0.43 (SiO_2, *n*-hexane/diethyl ether, 4:1); ν_{max} (film)/cm^{-1} 2958, 2927, 2857, 1712, 1639; δ_H (400 MHz, $CDCl_3$) 6.31 (1H, m, 2C*Hn*-hep), 5.98 (2H, m, H_5, H_6), 3.26 (1H, m), 3.04 (1H, m), 2.99 (1H, m), 2.55 (1H, m), 2.43 (1H, m), 2.08 (2H, m), 1.51 (1H, m, 4-C*H*H-7), 1.43 (1H, d, *J*=8.1 Hz, 4-CH*H*-7), 1.39–1.25 (15H, m, 2CH(CH_2)$_6$Me, 3(CH_2)$_3$Me), 0.95–0.89 (6H, m, 2CH(CH_2)$_6$*Me*, 3(CH_2)$_3$*Me*); δ_C (100 MHz, $CDCl_3$) 209.8 (s, C_1), 143.9 (C_2), 137.6 (d, 2*C*H *n*-hep), 136.2 ($C_{5/6}$), 133.9 ($C_{6/5}$), 54.2, 51.9 (t, 4-*C*H_2-7), 47.9 (d), 47.8, 44.6, 40.8, 36.8 (t), 32.2, 29.8, 29.7, 29.5, 29.4, 29.0, 23.3, 23.0, 14.5 (q, 2CH(CH)$_6$*Me*), 14.5 (3(CH_2)$_3$*Me*); *m/z* (CI/NH_3) 315 (MH^+, 19.4%), 249 (100); (HRMS: found MH^+, 315.2681. $C_{22}H_{35}O^+$ requires 315.2688) as well as the bis-alkylated adduct **26** (38.3 mg, 7%) as a transparent pale yellow oil; R_f 0.59 (SiO_2, *n*-hexane/diethyl ether, 4:1); ν_{max} (film)/cm^{-1} 2924, 2854, 1733, 1466, 1229, 731; δ_H (400 MHz, $CDCl_3$) 6.13 (1H, dd, *J*=5.5, 2.9 Hz, $H_{5/6}$), 6.04 (1H, dd, *J*=5.5, 2.9 Hz, $H_{6/5}$), 3.13 (1H, m), 2.99 (1H, m), 2.97–2.92 (1H, m), 2.54–2.49 (1H, m), 2.15 (1H, dt, *J*=11.8, 2.4 Hz), 1.67–1.61 (1H, m), 1.59–1.50 (3H, m), 1.45–1.09 (24H, m), 0.95 (3H, t, *J*=6.8 Hz), 0.89 (6H, m); δ_C (75.5 MHz, $CDCl_3$) 218.9 (s, C_1), 137.3 (d, $C_{5/6}$), 135.8 ($C_{6/5}$), 61.0, 55.1, 52.59 (t, 4-CH_2-7), 47.4 (d), 46.2, 44.5, 40.5, 36.9, 36.65 (t), 32.2, 31.8, 31.5, 30.5, 29.9, 29.8, 29.2, 28.1, 22.8, 22.7, 14.0 (q), 13.9, 13.89; *m/z* (CI/NH_3) 390 (MH+NH_3^+, 18.2%), 373 (MH^+, 14.2), 324 (21.0), 138 (26.2); (HRMS: found MH^+, 373.3462. $C_{26}H_{45}O^+$ requires 373.3470).

4.5.2. (±)-2-(*E*)-Cyclopropylmethylene-3-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one 20 and 2-(1-cyclopropyl-ethyl)-3a,4,7,7a-tetrahydro-4,7-methano-inden-1-one 28. Methylated enone **20** (0.25 g, 61%), a pale yellow transparent oil; R_f 0.36 (SiO_2, *n*-hexane/Et_2O, 2:1); δ_H (400 MHz, $CDCl_3$) 6.02 (1H, dd, *J*=5.7, 3.0 Hz, H_6), 5.96 (1H, dd, *J*=5.7, 2.9 Hz, H_5), 5.71 (1H, dd, *J*=11.0, 2.2 Hz, 2C*H* cycloprop), 3.23 (1H, m, H_4), 3.08 (1H, m, H_7), 3.01 (1H, m, H_{3a}), 2.61 (1H, m, H_3), 2.43 (1H, m, H_{7a}), 1.48 (1H, dt, *J*=8.3, 1.8 Hz, 4-C*H*H-7), 1.44–1.36 (2H, m, 4-CH*H*-7, 2CH *cycloprop*), 1.20 (3H, d, *J*=7.3 Hz, 3*Me*), 0.99–0.90 (2H, m, 2CH *cycloprop*), 0.63–0.58 (2H, m, 2CH *cycloprop*); δ_C (100 MHz, $CDCl_3$) 208.1 (s, C_1), 143.6 (C_2), 142.3 (d, 2*C*H cycloprop), 136.0 (C_5), 133.5 (C_6), 53.8 (d, C_{3a}), 51.4 (t, 4-CH_2-7), 47.2 (d, C_4), 46.9 (C_7), 46.9 (C_{7a}), 35.2 (C_3), 22.3 (q, 3*Me*), 12.3 (d, 2CH *cycloprop*), 9.5 (t, 2CH *cycloprop*), 8.8 (2CH *cycloprop*); *m/z* (CI/NH_3) 429 (2.4%), 363 (4.7), 232 ([MH+NH_3]$^+$, 1.3), 215 (MH^+, 34.6), 149 (100); (HRMS: found MH^+, 215.1441. $C_{15}H_{19}O_3^+$ requires 215.1436); and its regioisomer **28** (77.3 mg, 19%) as a pale yellow transparent oil; R_f 0.49 (SiO_2, *n*-hexane/diethyl ether, 2:1); ν_{max} (film)/cm^{-1} 3062, 2962, 2931, 2870, 1698, 1621; δ_H (400 MHz, $CDCl_3$) 7.04 (1H, d, *J*=2.6 Hz, H_3), 5.84 (1H, dd, *J*=5.5, 2.9 Hz, $H_{5/6}$), 5.72 (1H, dd, *J*=5.5, 2.9 Hz, $H_{6/5}$), 3.23 (1H, m), 3.18 (1H, m), 2.90 (1H, m), 2.79 (1H, t, *J*=5.1 Hz), 1.71 (1H, d, *J*=8.4 Hz, 4-C*H*H-7), 1.58 (1H, d, *J*=8.4 Hz, 4-CH*H*-7), 1.05 (3H, d, *J*=7.0 Hz, 2CHCH*Me* cycloprop), 0.66 (1H, m, 2CHCHMe *cycloprop*), 0.39 (1H, m), 0.20 (1H, m), 0.03-(-0.02) (2H, m); *m/z* (CI/NH_3) 232 ([MH+NH_3]$^+$, 0.6%), 215 (MH^+, 100); (HRMS: found MH^+, 215.1441. $C_{15}H_{19}O^+$ requires 215.1436).

4.6. Alkyl cuprate addition/aldol condensation/dehydration representative procedure

4.6.1. (+)-2-(*E*)-Isobutylidene)-3(*S*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (+)-16. 1.6 M Methyl lithium in diethyl ether (2.4 equiv.) was added to a stirring suspension of copper (I) iodide (1.2 equiv.) in anhydrous diethyl ether (6 cm^3) at −78 °C under nitrogen stream. After 3.0 h stirring at this temperature, a solution of (+)-enone (+)-**5** (0.2 g, 0.37 mmol) in diethyl ether (3 cm^3) was added dropwise over 5 min at −78 °C and stirred for 1.5 h. Whereupon, a solution of freshly distilled isobutyraldehyde (3.0 equiv.) was added, the reaction mixture stirred at −78 °C for 2 h and then allowed to warm to 0 °C overnight. The reaction was quenched with saturated aqueous NH_4Cl (9 cm^3), aqueous ammonia (2–3 drops) added and the reaction mixture extracted with diethyl ether (3×15 cm^3). The combined organic layers were washed with saturated aqueous NaCl (3×7 cm^3), dried ($MgSO_4$) and the solvent removed in vacuo to afford crude enone as a dark green transparent oil. Purification using flash column chromatography (SiO_2), eluting with *n*-hexane/acetone, (38:1) afforded the (+)-**16** (0.23 g, 76%) as a transparent pale yellow oil; R_f 0.50 (SiO_2, *n*-hexane/acetone, 4:1); $[\alpha]_D^{24}$ 2.89 (*c* 2.27 $CHCl_3$); δ_H (400 MHz, CD_2Cl_2) 5.91 (1H, d, *J*=2.1 Hz, 2C*Hi*-prop), 5.88 (1H, m, H_6), 5.81 (1H, dd, *J*=5.7, 2.9 Hz, H_5), 3.08 (1H, m, H_4), 2.97 (1H, br. s, H_7), 2.87 (1H, dd, *J*=8.8, 4.8 Hz, H_{3a}), 2.47–2.41 (1H, m, H_3), 2.39–2.29 (2H, m, H_{7a}, 2CHC*H*Me_2), 1.36 (1H, dt, *J*=8.1, 1.8 Hz, 4-C*H*H-7), 1.29 (1H, d, *J*=8.1, 1.4 Hz, 4-CH*H*-7), 1.02 (3H, d, *J*=7.2 Hz, 3Me), 0.91 (3H, d, *J*=6.7 Hz, 2CHCH*Me*Me), 0.87 (3H, d, *J*=6.5 Hz, 2CHCHMe*Me*); δ_C (100 MHz, CD_2Cl_2) 209.5 (s, C_1), 144.2 (C_2), 142.9 (d, 2*C*H *i*-prop), 136.6 (C_5), 134.2 (C_6), 54.2 (C_{3a}), 52.0 (t, 4-CH_2-7), 48.1 (d, C_4), 47.9 (C_7), 47.6 (2CH*C*HMe$_2$), 35.7 (C_3), 29.1 (C_{7a}), 23.9 (q, 3Me), 22.6 (2CHCH*Me*Me), 22.4 (2CHCHMe*Me*); *m/z* (CI/NH_3) 234 ($[MH+NH_3]^+$, 2.6%), 217 (MH^+, 8.9), 168 ($[MH+NH_3-C_5H_6]^+$, 15.3), 151 ($[MH-C_5H_6]^+$, 100.0), 66 (C_5H_6, 5.8); (HRMS: found MH^+, 217.1592. $C_{15}H_{21}O^+$ requires 217.1597).

4.6.2. (−)-2-(*E*)-Isobutylidene)-3(*R*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (−)-16. (0.14 g, 60%), a transparent pale brown oil; R_f 0.55 (SiO_2, *n*-hexane/acetone, 4:1); $[\alpha]_D^{22}=-3.13$ (*c* 6.90 $CHCl_3$); δ_H (400 MHz, CD_2Cl_2) 6.03 (1H, d, *J*=2.1 Hz, 2C*Hi*-prop), 6.00 (1H, m, H_6), 5.93 (1H, dd, *J*=5.6, 2.8 Hz, H_5), 3.20 (1H, m, H_4), 3.08 (1H, m, H_7), 2.98 (1H, dd, *J*=8.6, 4.8 Hz, H_{3a}), 2.55 (1H, m, H_3), 2.51–2.40 (2H, m, H_{7a}, 2CHC*H*Me_2), 1.47 (1H, dt, *J*=8.2, 1.6 Hz, 4-C*H*H-7), 1.40 (1H, d, *J*=8.2 Hz, 4-CH*H*-7), 1.14 (3H, d, *J*=7.3 Hz, 3Me), 1.03 (3H, d, *J*=6.7 Hz, 2CHCH*Me*Me), 0.95 (3H, d, *J*=6.7 Hz, 2CHCHMe*Me*); δ_C (100 MHz, CD_2Cl_2) 209.5 (s, C_1), 144.2 (C_2), 142.8 (d, 2*C*H *i*-prop), 136.6 (C_5), 134.2 (C_6), 54.2 (C_{3a}), 52.0 (t, 4-CH_2-7), 48.1 (d, C_4), 47.9 (C_7), 47.6 (2CH*C*HMe$_2$), 35.7 (C_3), 29.1 (C_{7a}), 23.9 (q, 3Me), 22.6 (2CHCH*Me*Me), 22.4 (2CHCHMe*Me*); *m/z* (CI/NH_3) 234 ($[MH+NH_3]^+$, 1.0%), 217 (MH^+, 5.4), 168 ($[MH+NH_3-C_5H_6]^+$, 6.7), 151 ($[MH-C_5H_6]^+$, 100), 91 (6.7), 66 (C_5H_6, 13.7); (HRMS: found MH^+, 217.1602. $C_{15}H_{21}O^+$ requires 217.1592).

4.6.3. (+)-2-(*E*)-Isobutylidene-3(*S*)-octyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one (+)-21. (0.26 g, 61%) as a very pale yellow transparent oil; R_f 0.38 (SiO_2, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{21}$ 2.39 (*c* 8.49 $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 6.07 (1H, dd, *J*=10.7, 2.1 Hz, 2C*Hi*-prop), 5.97 (1H, d, *J*=5.6, 3.0 Hz, $H_{5/6}$), 5.93 (1H, dd, *J*=5.6, 2.9 Hz, $H_{6/5}$), 3.32 (1H, m, $H_{4/7}$), 3.01 (1H, br. s, $H_{7/4}$), 2.96 (1H, dd, *J*=8.7, 4.8 Hz, $H_{3a/7a}$), 2.51 (1H, ddd, *J*=8.7, 4.1, 1.4 Hz, $H_{7a/3a}$), 2.43–2.36 (2H, m, H_3, 2CHC*H*Me_2), 1.47 (1H, d, *J*=8.2 Hz, 4-C*H*H-7), 1.40 (1H, d, *J*=8.2 Hz, 4-CH*H*-7), 1.37–1.27 (14H, m, 3(CH_2)$_7$Me), 1.00 (3H, d, *J*=6.6 Hz, 2CHCH*Me*Me), 0.96 (3H, d, *J*=6.6 Hz, 2CHCHMe*Me*), 0.88 (3H, t, *J*=6.7 Hz, 3(CH_2)$_7$*Me*); δ_C (100 MHz, CD_2Cl_2) 210.5 (s, C_1), 143.3 (d, 2*C*H *i*-prop), 142.5 (s, C_2), 136.3 (d, C_6), 133.8 (C_5), 54.2 (C_{7a}), 51.9 (t, 4-CH_2-7), 47.9 (2d, C_4, C_7), 44.6 (C_{3a}), 40.8 (C_3), 37.7 (t, 3(*C*H_2)$_7$Me), 32.3, 30.2, 29.6, 29.7, 29.0 (d, 2CH*C*HMe$_2$), 27.2 (t, 3(CH_2)$_7$Me), 23.0, 22.3 (2q, 2CHCH*Me*$_2$), 14.5 (q, 3(CH_2)$_7$*Me*); *m/z* (CI/NH_3) 332 ($[MH+NH_3]^+$, 0.5%), 315 (MH^+, 4.0), 287 (0.3), 266 (4.1), 249 ($[MH+NH_3-C_5H_6]^+$, 100), 150 (4.0), 66 (C_5H_6, 3.7); (HRMS: found MH^+, 315.2689. $C_{22}H_{35}O^+$ requires 315.2688).

4.6.4. (−)-2-(*E*)-Isobutylidene)-3(*R*)-octyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (−)-21. (0.23 g, 54%), a very pale yellow transparent oil; R_f 0.38 (SiO_2, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{27}$ −2.27 (*c* 8.34 $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 6.06 (1H, dd, *J*=10.6, 2.0 Hz, 2C*Hi*-prop), 5.96 (1H, d, *J*=5.6, 3.0 Hz, $H_{5/6}$), 5.93 (1H, dd, *J*=5.6, 2.8 Hz, $H_{6/5}$), 3.22 (1H, m, $H_{4/7}$), 3.00 (1H, m, $H_{7/4}$), 2.95 (1H, dd, *J*=8.7, 4.8 Hz, $H_{3a/7a}$), 2.50 (1H, ddd, *J*=8.7, 4.1, 1.8 Hz, $H_{7a/3a}$), 2.43–2.34 (2H, m, H_3, 2CHC*H*Me_2), 1.48 (1H, dt, *J*=8.3, 1.6 Hz, 4-C*H*H-7), 1.39 (1H, m, 4-CH*H*-7), 1.43–1.21 (14H, m, 3(*C*H_2)$_7$Me), 1.00 (3H, d, *J*=6.5 Hz, 2CHCH*Me*Me), 0.96 (3H, d, *J*=6.7 Hz, 2CHCHMe*Me*), 0.88 (3H, t, *J*=6.7 Hz, 3(CH_2)$_7$*Me*); δ_C (100 MHz, $CDCl_3$) 210.3 (s, C_1), 143.3 (d, 2*C*H *i*-prop), 142.5 (s, C_2), 136.3 (d, C_6), 133.7 (C_5), 54.2 (C_{7a}), 51.8 (t, 4-CH_2-7), 47.9 (d, C_4), 47.8 (C_7), 44.7 (C_{3a}), 40.8 (C_3), 37.7 (t, 3(*C*H_2)$_7$Me), 32.3, 30.2, 29.9, 26.6, 29.0 (d, 2CH*C*HMe$_2$), 27.1 (t, 3(*C*H_2)$_7$Me), 23.0, 22.30 (q, 2CHCH*Me*Me), 22.98 (2CHCHMe*Me*), 14.3 (q, 3(CH_2)$_7$*Me*); *m/z* (CI/NH_3) 315 (MH^+, 3.9%), 266 ($[MH+NH_3-C_5H_6]^+$, 4.8), 249 ($[MH-C_5H_6]^+$, 100), 163 (7.4), 150 (10), 135 (7.4), 121 (3.5), 107 (5.7), 91 (7.1), 66 (C_5H_6, 15.8); (HRMS: found MH^+, 315.2692. $C_{22}H_{35}O^+$ requires 315.2688).

4.6.5. (+)-2-(*E*)-Benzylidene-3(*S*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (+)-(22) and (+)-7a(*S*)-(1,3-bisphenyl-3-oxo-propyl)-2-(*E*)-benzylidene-3(*S*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one (+)-30. Methylated enone (+)-**22** (0.22 g, 64%), a pale yellow crystalline solid; R_f 0.43 (SiO_2, *n*-hexane:diethyl ether, 2:1); δ_H (400 MHz, $CDCl_3$) 7.50 (2H, d, *J*=7.3 Hz, 2CH*Ph*), 7.38–7.29 (3H, m, 2CH*Ph*), 7.07 (1H, d, *J*=1.9 Hz, 2C*H*Ph), 5.98 (2H, m, H_5, H_6), 3.30 (1H, m, H_4), 3.11 (1H, m, H_7), 3.08–3.02 (2H, m, H_3, H_{3a}), 2.56 (1H, ddd, *J*=8.7, 4.1, 1.3 Hz, H_{7a}), 1.50 (1H, m, 4-C*H*H-7), 1.42 (1H, d, *J*=8.2 Hz, 4-CH*H*-7), 1.18 (3H, d, *J*=7.1 Hz, 3*Me*); δ_C (100 MHz, $CDCl_3$) 210.3 (s, C_1), 144.8 (2CH*Ph*), 136.7 (d, $C_{5/6}$), 135.4 (s, C_2), 133.8 (d, $C_{6/5}$),

132.7 (2C*H*Ph), 130.8 (2CH*Ph*), 129.5 (2CH*Ph*), 129.1 (2CH*Ph*), 52.9 (C_{3a}), 51.8 (t, 4-CH_2-7), 48.0 (d, C_4), 47.5 ($C_{7/7a}$), 47.5 ($C_{7a/7}$), 36.64 (C_3), 21.2 (q, 3Me); *m/z* (CI/NH_3) 502 (3.0%), 435 (4.2), 268 ($[MH+NH_3]^+$, 2.4), 251 (MH^+, 36.1), 222 (5.6), 202 ($[MH+NH_3-C_5H_6]^+$, 6.1), 185($[MH-C_5H_6]^+$, 100), 156 (7.9), 141 (4.3), 115 (3.2), 91 (4.1), 66 (C_5H_6, 4.3); (HRMS: found MH^+, 251.1434. $C_{18}H_{19}O^+$ requires 251.1436), and the 7a(*S*)-alkylated by-product, (+)-**30** (108 mg, 15%) as a transparent pale yellow oil; R_f 0.18 (SiO_2, *n*-hexane/acetone, 9:1); δ_H (400 MHz, $CDCl_3$) 7.84 (2H, d, *J*=7.2 Hz, 2CH*Ph*), 7.51 (2H, m, 1′/3′*Ph*), 7.43–7.48 (3H, m, 1′/3′*Ph*), 7.30–7.39 (4H, m, 1′/3′*Ph*), 7.25 (2H, m, 1′/3′*Ph*), 7.16 (2H, m, 2C*H*Ph, 1′/3′*Ph*), 6.07 (1H, dd, *J*=5.6, 2.7 Hz, H_6), 5.97 (1H, dd, *J*=5.6, 3.0 Hz, H_5), 3.91 (1H, dd, *J*=10.3, 3.2 Hz, $H_{1'}$), 3.79 (1H, dd, *J*=10.5, 4.9 Hz, 1′C*H*HCOPh), 3.54 (1H, dd, *J*=16.7, 3.3 Hz, 1′CH*H*COPh), 3.03 (1H, br. s, H_4), 3.00 (1H, m, H_3), 2.91 (1H, br. s, H_7), 2.44 (1H, dd, *J*=3.8, 1.0 Hz, H_{3a}), 1.61 (1H, d, *J*=8.6 Hz, 4-C*H*H-7), 1.36 (1H, d, *J*=8.6 Hz, 4-CH*H*-7), 1.16 (3H, d, *J*=7.2 Hz, 3*Me*); δ_C (100 MHz, $CDCl_3$) 211.0 (s, C_1), 198.8 ($C_{3'}$), 145.1 (2CH*Ph*), 141.8 (3′CO*Ph*), 138.6 (d, C_5), 137.7 (s, 1′*Ph*), 135.9 (d, C_6), 135.4 (s, C_2), 133.7 (d, 2*C*HPh), 133.2 (1′/3′*Ph*), 131.0 (2d, 2CH*Ph*), 130.4 (d, 1′/3′*Ph*), 129.7 (2CH*Ph*), 129.1 (2d, 2CH*Ph*), 128.9 (1′/3′*Ph*), 128.5, 128.4, 127.1 (d, 1′/3′*Ph*), 64.9 (s, C_{7a}), 54.6 (d, C_{3a}), 51.2 (C_7), 4.3 (t, 4-CH_2-7), 48.5 (d, C_4), 47.4 ($C_{1'}$), 41.4 (t, $C_{2'}$), 36.4 (d, C_3), 20.6 (q, 3Me); *m/z* (ES^+) 939 ($[2M+Na]^+$, 57.8%), 518 (10.2), 481 ($[M+Na]^+$, 100), 415 (9.6); (HRMS: found $M+Na^+$, 481.216. $C_{33}H_{30}O_2Na^+$ requires 481.2144).

4.6.6. (−)-2-(*E*)-Benzylidene-3(*R*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (−)-22. (0.13 g, 75%) as a transparent pale yellow oil; R_f 0.51 (SiO_2, *n*-hexane/Et_2O, 2:1); δ_H (400 MHz, $CDCl_3$) 7.51 (2H, d, *J*=7.2 Hz, 2CH*Ph*), 7.40–7.30 (3H, m, 2CH*Ph*), 7.08 (1H, d, *J*=2.1 Hz, 2C*H*Ph), 5.99 (2H, m, H_5, H_6), 3.30 (1H, m, H_4), 3.13 (1H, m, H_7), 3.08 (1H, dd, *J*=8.6, 4.8 Hz, H_{3a}), 3.06 (1H, m, H_3), 2.57 (1H, ddd, *J*=8.6, 4.0, 1.3 Hz, H_{7a}), 1.51 (1H, dt, *J*=8.2, 1.6 Hz, 4-C*H*H-7), 1.43 (1H, d, *J*=8.2 Hz, 4-CH*H*-7), 1.18 (3H, d, *J*=7.3 Hz, 3*Me*); δ_C (100 MHz, $CDCl_3$) 210.6 (s, C_1), 144.7 (2CH*Ph*), 136.7 (d, $C_{5/6}$), 135.4 (s, C_2), 133.8 (d, $C_{6/5}$), 132.7 (2C*H*Ph), 130.9 (2CH*Ph*), 129.6 (2CH*Ph*), 129.1 (2CH*Ph*), 52.9 (C_{3a}), 51.8 (t, 4-CH_2-7), 48.0 (d, C_4), 47.5 ($C_{7/7a}$), 47.5 ($C_{7a/7}$), 36.7 (C_3), 21.2 (q, 3Me); *m/z* (EI) 250 (M^+, 53.2%), 222 (8.6), 185 (88.5), 183 (100), 165 (16.3), 156 (33.6), 147 (37.9), 129 (25.5), 128 (32.3), 115 (57.5), 91 ($[M-PhCH_2]^+$, 47.2), 66 (92.8); (HRMS: found M^+, 250.1360. $C_{18}H_{19}O^+$ requires 250.1358).

4.6.7. (+)-2-(*E*)-Benzylidene-3(*S*)-octyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one (+)-23. (0.27 g, 57%) as a transparent yellow oil; R_f 0.36 (SiO_2, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{22}$ 1.13 (*c* 8.33 $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.48 (2H, dd, *J*=7.3, 1.4 Hz, 2CH*Ph*), 7.39–7.30 (3H, m, 2CH*Ph*), 7.09 (1H, d, *J*=2.1 Hz, 2C*H*Ph), 5.98 (2H, m, H_5, H_6), 3.30 (1H, m, H_7), 3.07 (1H, m, H_4), 3.03 (1H, dd, *J*=8.6, 4.8 Hz, H_{7a}), 2.89 (1H, d, *J*=8.1 Hz, H_3), 2.67 (1H, ddd, *J*=8.1, 4.0, 1.3 Hz, H_{3a}), 1.52 (1H, m, 4-C*H*H-7), 1.47 (1H, m, 4-CH*H*-7), 1.50–1.24 (12H, m, 3(CH_2)$_7$Me), 0.87 (3H, t, *J*=6.8 Hz, 3(CH_2)$_7$*Me*); δ_C (100 MHz, $CDCl_3$) 210.6 (s, C_1), 143.9 (C_2), 136.6 (d, C_6), 135.6 (s, 2CH*Ph*), 133.9 (d, C_5), 132.8 (2*C*HPh), 130.8 (2d, 2CH*Ph*), 129.50 (d, 2CH*Ph*), 129.0 (2d, 2CH*Ph*), 53.4 (C_{7a}), 51.9 (t, 4-CH_2-7), 48.1 (d, C_7), 48.0 (C_4), 45.0 (C_{3a}), 42.3 (C_3), 34.8 (t, 3(*C*H_2)$_7$Me), 32.2, 30.0, 29.9, 29.6, 27.6, 23.0, 14.5 (q, 3(CH_2)$_7$*Me*); *m/z* (CI/NH_3) 349 (MH^+, 9.7%), 320 (1.3), 283 ($[MH-C_5H_6]^+$, 48.9), 169 (4.1), 141 (10.4), 128 (3.3), 115 (9.8), 91 (11.1), 66 (C_5H_6, 100), 55 (5.5); (HRMS: found MH^+, 349.25394. $C_{25}H_{33}O^+$ requires 349.25314).

4.6.8. (−)-2-(*E*)-Benzylidene-3(*R*)-octyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one (−)-23. (0.40 g, 83%) as a transparent pale yellow oil; R_f 0.31 (SiO_2, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{24}$ −0.87 (*c* 12.09 $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.48 (2H, dd, *J*=8.6, 1.5 Hz, 2CH*Ph*), 7.39–7.32 (3H, m, 2CH*Ph*), 7.09 (1H, d, *J*=2.2 Hz, 2C*H*Ph), 5.99 (2H, m, H_5, H_6), 3.30 (1H, m, H_7), 3.07–3.06 (1H, m, H_4), 3.03 (1H, dd, *J*=8.7, 4.8 Hz, H_{7a}), 2.90 (1H, d, *J*=8.1 Hz, H_3), 2.67 (1H, ddd, *J*=8.1, 4.0, 1.3 Hz, H_{3a}), 1.62–1.18 (12H, m, 3(CH_2)$_7$Me), 1.52 (1H, m, 4-C*H*H-7), 1.47 (1H, m, 4-CH*H*-7), 0.88 (3H, t, *J*=6.7 Hz, 3(CH_2)$_7$*Me*); δ_C (100 MHz, $CDCl_3$) 210.5 (s, C_1), 143.9 (C_2), 136.6 (d, C_6), 135.6 (s, 2CH*Ph*), 133.9 (d, C_5), 132.8 (2*C*HPh), 130.8 (2d, 2CH*Ph*), 129.50 (d, 2CH*Ph*), 129.0 (2d, 2CH*Ph*), 53.4 (C_{7a}), 51.9 (t, 4-CH_2-7), 48.1 (d, C_7), 48.0 (C_4), 45.1 (C_{3a}), 42.3 (C_3), 34.8 (t, 3(*C*H_2)$_7$Me), 32.2, 30.0, 29.9, 29.6, 27.6, 23.0, 14.5 (q, 3(CH_2)$_7$*Me*); *m/z* (CI/NH_3) 349 (MH^+, 11.4%), 320 (2.9), 300 (9.3), 284 ($[MH-C_5H_6]^+$, 70.9), 169 (16.9), 155 (10.8), 141 (22.9), 115 (12.8), 91 (12.6), 66 (C_5H_6, 16.3); (HRMS: found MH^+, 349.25362. $C_{25}H_{33}O^+$ requires 349.25314).

4.6.9. (±)-2-(4-(*E*)-Fluorobenzylidene)-3(*R*/*S*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (±)-24. (0.15 g, 83%), a pale yellow crystalline solid; R_f 0.47 (SiO_2, *n*-hexane/Et_2O, 2:1); δ_H (400 MHz, CD_2Cl_2) 7.42 (2H, m, 2CH*Ph*·*p*-F), 6.99 (2H, m, 2CH*Ph*·*p*-F), 6.89 (1H, d, *J*=2.1 Hz, 2C*H*Ph·*p*-F), 5.89 (1H, dd, *J*=5.6, 2.8 Hz, H_6), 5.85 (1H, dd, *J*=5.6, 2.7 Hz, H_5), 3.15 (1H, m, H_4), 3.02 (1H, m, H_7), 2.94 (1H, m, H_{3a}), 2.90 (1H, dd, *J*=14.3, 7.1 Hz, H_3), 2.47 (1H, ddd, *J*=8.6, 4.0, 1.4 Hz, H_{7a}), 1.39 (1H, m, 4-C*H*H-7), 1.34 (1H, m, 4-CH*H*-7), 1.07 (3H, d, *J*=7.1 Hz, 3*Me*); δ_C (100 MHz, CD_2Cl_2) 209.9 (s, C_1), 163.7 (sd, $J_{C,F}$=249.0 Hz, 2CH*Ph*·*p*-F), 145.1 (sd, $J_{C,F}$=2.3 Hz, C_2), 136.9 (d, C_5), 134.2 (C_6), 133.1 (dd, $J_{C,F}$=8.3 Hz, 2CH*Ph*·*p*-F), 132.2 (sd, $J_{C,F}$=3.2 Hz, 2CH*Ph*·*p*-F), 131.2 (d, 2*C*HPh·*p*-F), 116.4 (dd, $J_{C,F}$=21.7 Hz, 2CH*Ph*·*p*-F), 53.2 (C_{3a}), 52.6 (t, 4-CH_2-7), 48.4 (d, C_4), 48.0 (C_7), 47.9 (C_{7a}), 36.8 (C_3), 21.2 (q, 3Me); *m/z* (CI/NH_4) 286 ($[MH+NH_4]^+$, 1.5%), 269 (MH^+, 31.2), 240 (3.9), 220 (7.7), 203 ($[MH-C_5H_6]^+$, 100); (HRMS: found MH^+, 269.1333. $C_{18}H_{18}OF^+$ requires 269.1342).

4.6.10. (+)-2-(4-(*E*)-Fluorobenzylidene)-3(*S*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methanoinden-1-one (+)-24 and (+)-7a(*S*)-[1,3-bis-(4-fluoro-phenyl)-3-oxo-propyl]-2-(4-(*E*)-fluorobenzylidene)-3(*S*)-methyl-2,3,3a,4,7,7a-hexahydro-4,7-methano-inden-1-one (+)-31. Methylated enone (+)-**24** (0.20 g, 55%) as a transparent pale yellow oil; R_f 0.29 (SiO_2, *n*-hexane/acetone, 9:1); $[\alpha]_D^{20}$ 0.89 (*c* 8.50, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.49 (2H, m, 2CH*Ph*·*p*-F), 7.06 (2H, m, 2CH*Ph*·*p*-F), 7.03 (1H, d, *J*=2.0 Hz, 2C*H*Ph·*p*-F), 5.99 (2H, m, H_6, H_5), 3.30 (1H, m, H_4), 3.12 (1H, m, H_7), 3.07 (1H, dd, *J*=8.6, 4.8 Hz, H_{3a}), 3.00 (1H, m, H_3), 2.57 (1H, ddd,

J=8.7, 4.1, 1.4 Hz, H_{7a}), 1.51 (1H, m, 4-C*H*H-7), 1.43 (1H, m, 4-CH*H*-7), 1.17 (3H, d, J=7.3 Hz, 3*Me*); δ_C (100 MHz, $CDCl_3$) 210.1 (s, C_1), 163.3 (sd, $J_{C,F}$=250.0 Hz, 2CH*Ph·p*-F), 144.3 ($J_{C,F}$=2.9 Hz, C_2), 136.7 (d, C_5), 133.7 (C_6), 132.7 (dd, $J_{C,F}$=8.1 Hz, 2CH*Ph·p*-F), 131.6 (sd, $J_{C,F}$=3.6 Hz, 2CH*Ph·p*-F), 131.4 (d, 2C*H*Ph·*p*-F), 116.3 (dd, $J_{C,F}$=21.2 Hz, 2CH*Ph·p*-F), 52.9 (d, C_{3a}), 51.8 (t, 4-CH_2-7), 48.0 (d, C_4), 47.5 (C_7, C_{7a}), 36.5 (C_3), 21.0 (q, 3Me); *m/z* (CI/NH_4) 286 ($[MH+NH_4]^+$, 1.5%), 269 (MH^+, 34.7), 240 (6.5), 220 (6.1), 203 ($[MH-C_5H_6]^+$, 100), 174 (10.5), 66 (7.5); (HRMS: found MH^+, 269.1343. $C_{18}H_{18}OF^+$ requires 269.1342), and the 7a(*S*)-alkylated by-product (+)-**31** (108 mg, 15%) as a transparent pale yellow oil; R_f 0.18 (SiO_2, *n*-hexane/acetone, 9:1); $[\alpha]_D^{18}$ 0.44 (*c* 6.65, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 7.85 (2H, m, 3′*Ph·p*-F), 7.51 (2H, m, *Ph·p*-F), 7.43 (2H, m, *Ph·p*-F), 7.14 (1H, d, J=2.2 Hz, 2C*H*Ph·*p*-F), 7.11–7.02 (4H, m, *Ph·p*-F), 6.95 (2H, m, *Ph·p*-F), 6.08 (1H, dd, J=5.6, 2.9 Hz, $H_{5/6}$), 5.97 (1H, dd, J=5.6, 3.0 Hz, $H_{6/5}$), 3.85 (1H, dd, J=10.6, 3.3 Hz, $H_{1'}$), 3.66 (1H, m, 1′C*H*HCOPh·*p*-F), 3.42 (1H, dd, J=16.7, 3.3 Hz, 1′CH*H*COPh.p-F), 3.08 (1H, br. s, H_4), 2.96 (1H, dd, J=14.3, 7.3 Hz, H_3), 2.84 (1H, br. s, H_7), 2.41 (1H, dd, J=4.0, 1.3 Hz, H_{3a}), 1.63 (1H, m, 4-C*H*H-7), 1.39 (1H, m, 4-CH*H*-7), 1.17 (3H, d, J=7.3 Hz, 3*Me*); δ_C (100 MHz, $CDCl_3$) 210.4 (s, C_1), 196.7 ($C_{3'}$), 165.7 (sd, $J_{C,F}$=253.4 Hz, *Ph·p*-F), 163.3 ($J_{C,F}$=250.4 Hz, *Ph·p*-F), 161.8 ($J_{C,F}$=244.4 Hz, *Ph·p*-F), 144.2 ($J_{C,F}$=2.3 Hz, *Ph·p*-F), 138.0 (d, $C_{5/6}$), 137.7 (sd, $J_{C,F}$=12.7 Hz, *Ph·p*-F), 135.7 (d, $C_{6/5}$), 133.6 (sd, $J_{C,F}$=9.6 Hz, *Ph·p*-F), 132.6 (dd, $J_{C,F}$=8.8 Hz, *Ph·p*-F), 132.4 (d, 2*C*HPh·*p*-F), 131.4 (dd, $J_{C,F}$=7.2 Hz, *Ph·p*-F), 131.1 (sd, $J_{C,F}$=12.7 Hz, *Ph·p*-F), 130.6 (dd, $J_{C,F}$=8.8 Hz, *Ph·p*-F), 115.9 ($J_{C,F}$=21.6 Hz, *Ph·p*-F), 115.6, 115.0 ($J_{C,F}$=20.8 Hz, *Ph·p*-F), 64.5 (s, C_{7a}), 54.7 (d, C_{3a}), 50.9 (C_7), 48.8 (t, 4-CH_2-7), 47.6 (d, C_4), 46.7 ($C_{1'}$), 41.1 (t, $C_{2'}$), 35.9 (d, C_3), 20.2 (q, 3Me); δ_F (376 MHz, $CDCl_3$) −105.7 (Ph·*p*-*F*), −110.4, −116.5; *m/z* (ES$^+$) 1047 ($[2M+Na]^+$, 3.7%), 551 (4.4), 535 ($[M+Na]^+$, 100), 469 ($[M-C_5H_6]^+$, 87.0), 449 (3.1), 413 (4.4), 331 (3.4); (HRMS: found $M+Na^+$, 535.1843. $C_{33}H_{27}O_2F_3Na^+$ requires 535.1861).

4.7. Microwave assisted *retro* Diels–Alder reaction: representative procedure

4.7.1. (+)-5-(*E*)-Isobutylidene-4(*S*)-methyl-cyclopent-2-enone (+)-32. To a stirring solution of (+)-**16** (0.22 g, 1.02 mmol) and maleic anhydride (5.0 equiv.) in anhydrous DCM (5.1 cm^3) was added 1.0 M methyl aluminiumdichloride in hexanes (0.5 equiv.) at room temperature under a nitrogen stream. The mixture was heated at 60 °C for 30 min in a microwave (Smith-Creator), and cooled to room temperature under a nitrogen stream. Flash silica (0.94 g) was added and the solvent removed in vacuo to afford pre-absorbed crude product. Purification by flash column chromatography (SiO_2), eluting with *n*-hexane/diethyl ether (5:1), gave recovered enone (+)-**16** (32 mg, 14%) as a pale yellow transparent oil and an inseparable mixture (98:2) of *E*- and *Z*-isomers of dienone (+)-**32** (81.8 mg, 54%) as a transparent yellow oil; R_f 0.31 (SiO_2, *n*-hexane/diethyl ether, 2:1); δ_H (400 MHz, CD_2Cl_2) 7.37 (1H, dd, J=5.9, 2.6 Hz, H_3), 6.19 (1H, d, J=10.7 Hz 5C*Hi*-prop), 6.13 (1H, dd, J=5.9, 1.7 Hz, H_2), 3.40 (1H, m, H_4), 2.59 (1H, m, 5CHC*H*Me_2), 1.18 (3H, d, J=7.2 Hz, 4Me), 1.00 (3H, d, J=6.7 Hz, 5CHCH*Me*Me), 0.98 (3H, d, J=6.6 Hz, 5CHCHMe*Me*); δ_C (100 MHz, CD_2Cl_2) 197.4 (s, C_1), 164.2 (d, C_3), 142.0 (5*C*H *i*-prop), 137.7 (s, C_5), 134.5 (d, C_2), 39.0 (d, C_4), 29.3 (5CHC*H*Me_2), 22.6 (q, 5CHCH*Me*Me), 22.6 (5CHCHMe*Me*), 19.4 (4*Me*); *m/z* (CI/NH_3) 233 (5.2%), 220 (12.3), 205 (19.9), 168 ($[MH+NH_3]^+$, 7.0), 151 (MH^+, 100); (HRMS: found MH^+, 151.1120. $C_{10}H_{15}O^+$ requires 151.1123).

4.7.2. (−)-5-(*E*)-Isobutylidene-4(*R*)-methyl-cyclopent-2-enone (−)-32. (69.7 mg, 73%), a transparent yellow oil; R_f 0.32 (SiO_2, *n*-hexane/diethyl ether, 2:1); $[\alpha]_D^{22}$ −10.52 (*c* 4.44 $CHCl_3$); δ_H (250 MHz, CD_2Cl_2) 7.40 (1H, ddd, J=5.8, 2.4, 1.1 Hz, H_3), 6.25 (1H, dt, J=10.6, 1.0 Hz 5C*Hi*-prop), 6.19 (1H, dd, J=5.8, 1.7 Hz, H_2), 3.47 (1H, m, H_4), 2.65 (1H, m, 5CHC*H*Me_2), 1.23 (3H, d, J=7.2 Hz, 4Me), 1.05 (3H, d, J=6.5 Hz, 5CHCH*Me*Me), 1.03 (3H, d, J=6.5 Hz, 5CHCHMe*Me*); δ_C (100 MHz, CD_2Cl_2) 197.4 (s, C_1), 164.2 (d, C_3), 142.0 (5*C*H *i*-prop), 136.7 (s, C_5), 134.5 (d, C_2), 39.0 (C_4), 28.7 (5CHC*H*Me_2), 22.7 (q, 5CHCH*Me*Me), 22.6 (5CHCHMe*Me*), 19.4 (4*Me*); *m/z* (CI/NH_3) 168 ($[MH+NH_3]^+$, 7.4%), 151 (MH^+, 100); (HRMS: found MH^+, 151.1123. $C_{10}H_{15}O^+$ requires 151.1123).

4.7.3. (+)-5-(*E*)-Isobutylidene-4(*S*)-octyl-cyclopent-2-enone (+)-33. (94.2 mg, 74%) a transparent pale yellow oil; R_f 0.28 (SiO_2, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{22}$ 1.70 (*c* 4.65 $CHCl_3$); δ_H (400 MHz, CD_2Cl_2) 7.46 (1H, dd, J=6.0, 2.5 Hz, H_3), 6.19 (1H, m, H_2), 6.17 (1H, dd, J=1.4 Hz, 5CH *i*-prop), 3.42 (1H, m, H_4), 2.58 (1H, m, 5CHC*H*Me_2), 1.75 (1H, m, 4C*H*H$(CH_2)_6$Me), 1.45 (1H, m, 4CH*H*$(CH_2)_6$Me), 1.26–1.12 (12H, m, 4CH_2(C$H_2)_6$Me), 0.98 (6H, m, 5CHCHMe_2), 0.79 (3H, t, J=6.5 Hz, 4$(CH_2)_7$*Me*); δ_C (100 MHz, CD_2Cl_2) 197.8 (s, C_1), 162.8 (d, C_3), 141.9 (5*C*H *i*-prop), 136.4 (s, C_5), 135.3 (d, C_2), 44.0 (C_4), 33.7 (t, 4*C*$H_2(CH_2)_6$Me), 32.6 (4CH_2(*C*$H_2)_6$Me), 30.6, 30.2, 29.3 (d, 5CH*C*HMe_2), 26.6 (t, 4CH_2(*C*$H_2)_6$Me), 23.4, 22.7 (q, 5CHCH*Me*Me), 22.5 (5CHCHMe*Me*), 14.7 (4$(CH_2)_7$*Me*); *m/z* (CI/NH_3) 266 ($[MH+NH_3]^+$, 2.0%), 249 (MH^+, 100), 163 (4.0), 150 (5.8), 135 (3.7), 121 (2.3), 107 (3.7), 91 (2.2); (HRMS: found MH^+, 249.2222. $C_{17}H_{29}O^+$ requires 249.2218).

4.7.4. (−)-5-(*E*)-Isobutylidene-4(*R*)-octyl-cyclopent-2-enone (−)-33. (95 mg, 60%) a transparent pale yellow oil; R_f 0.28 (SiO_2, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{24}$ −1.76 (*c* 4.35 $CHCl_3$); δ_H (400 MHz, CD_2Cl_2) 7.56 (1H, ddd, J=6.0, 2.7, 1.0 Hz, H_3), 7.47 (0.06H, dd, J=6.0, 2.6 Hz, *Z*-isomer H_3), 6.31–6.27 (2H, m, H_2, 5C*Hi*-prop), 6.23 (0.06H, m, *Z*-isomer H_2), 5.83 (0.06H, d, J=9.8 Hz, *Z*-isomer 5C*Hi*-prop), 3.93 (0.06H, m, *Z*-isomer H_4), 3.53 (1H, m, H_4), 3.28 (0.06H, m, *Z*-isomer 5CHC*H*Me_2), 2.69 (1H, m, 5CHC*H*Me_2), 1.86 (1H, m, 4C*H*H$(CH_2)_6$Me), 1.55 (1H, m, 4CH*H*$(CH_2)_6$Me), 1.29 (12H, m, 4CH_2(C$H_2)_6$Me), 1.10 (3H, d, J=6.7 Hz, 5CHCH*Me*Me), 1.08 (3H, d, J=6.8 Hz, 5CHCHMe*Me*), 1.03 (0.18 Hz, d, J=2.1 Hz, *Z*-isomer 5CHCH*Me*Me), 1.02 (0.18 Hz, d, J=2.1 Hz, *Z*-isomer 5CHCHMe*Me*), 0.90 (3H, t, J=6.8 Hz, 4$(CH_2)_7$*Me*); δ_C (100 MHz, CD_2Cl_2) 197.65 (s, C_1), 162.7 (d, C_3), 161.3 (*Z*-isomer C_3), 147.1 (*Z*-isomer 5*C*H *i*-prop), 141.9 (5*C*H *i*-prop), 136.7 (*Z*-isomer C_2), 136.4 (s, C_5), 135.3 (d, C_2), 46.2 (*Z*-isomer C_4), 44.0 (C_4), 34.3 (t, *Z*-isomer 4*C*$H_2(CH_2)_6$Me), 33.7 (4*C*$H_2(CH_2)_6$Me), 32.6 (4CH_2(*C*$H_2)_6$Me), 30.5, 30.5 (*Z*-isomer 4CH_2(*C*$H_2)_6$Me), 30.2 (4CH_2(*C*$H_2)_6$Me), 30.0,

29.2 (d, 5CH*C*HMe$_2$), 26.6 (t, 4CH$_2$(*C*H$_2$)$_6$Me), 26.3 (d, *Z*-isomer 5CHC*H*Me$_2$), 23.4 (t, 4(*C*H$_2$)$_7$Me), 23.0 (q, *Z*-isomer 5CHCH*Me*Me), 22.9 (*Z*-isomer 5CHCHMe*Me*), 22.7 (q, 5CHCH*Me*Me), 22.4 (5CHCHMe*Me*), 14.6 (4(CH$_2$)$_7$*Me*); *m/z* (CI/NH$_3$) 266 ([MH+NH$_3$]$^+$, 3.8%), 249 (MH$^+$, 100), 163 (4.3), 149 (6.1), 135 (4.6), 121 (3.0), 107 (4.8), 91 (3.0); (HRMS: found MH$^+$, 249.2219. $C_{17}H_{29}O^+$ requires 249.2218).

4.7.5. (−)-5-(*E*)-Benzylidene-4(*S*)-methyl-cyclopent-2-enone (−)-34. (54.5 mg, 74%) as a transparent pale yellow oil; R_f 0.34 (SiO$_2$, *n*-hexane/ethyl acetate, 3:1); $[\alpha]_D^{21}$ −0.61 (*c* 5.34 CHCl$_3$); δ_H (400 MHz, CD$_2$Cl$_2$) 7.53 (1H, ddd, *J*=5.9, 2.7, 1.0 Hz, H$_3$), 7.48 (2H, d, *J*=7.2 Hz 5CH*Ph*), 7.34–7.25 (3H, m, 5CH*Ph*), 7.21 (1H, m, 5C*H*Ph), 6.27 (1H, dd, *J*=5.9, 1.9 Hz, H$_2$), 3.86 (1H, m, H$_4$), 1.10 (3H, d, *J*=7.2 Hz, 4Me); δ_C (100 MHz, CD$_2$Cl$_2$) 197.7 (s, C$_1$), 164.9 (d, C$_3$), 139.4 (s, 5CH*Ph*), 135.6 (C$_5$), 134.1 (d, C$_2$), 131.8 (5*C*HPh), 131.4 (2d, 5CH*Ph*), 129.9 (d, 5CH*Ph*), 129.5 (2d, 5CH*Ph*), 39.6 (d, C$_4$), 16.9 (q, 4Me); *m/z* (CI/NH$_3$) 185 (MH$^+$, 100%), 202 ([MH+NH$_3$]$^+$, 2.4); (HRMS: found MH$^+$, 185.0969. $C_{13}H_{13}O^+$ requires 185.0967).

4.7.6. (+)-5-(*E*)-Benzylidene-4(*R*)-methyl-cyclopent-2-enone (+)-34. (62.0 mg, 69%) as a transparent pale yellow oil; R_f 0.33 (SiO$_2$, *n*-hexane/ethyl acetate, 3:1); $[\alpha]_D^{18}$ 0.88 (*c* 5.02 CHCl$_3$); δ_H (400 MHz, CD$_2$Cl$_2$) 7.53 (1H, ddd, *J*=5.9, 2.6, 0.8 Hz, H$_3$), 7.47 (2H, d, *J*=7.3 Hz, 5CH*Ph*), 7.34 (2H, t, *J*=7.0 Hz, 5CH*Ph*), 7.29 (1H, d, *J*=7.1 Hz, 5CH*Ph*), 7.35 (1H, br. s, 5C*H*Ph), 6.27 (1H, dd, *J*=5.9, 1.9 Hz, H$_2$), 3.85 (1H, m, H$_4$), 1.10 (3H, d, *J*=7.2 Hz, 4Me); δ_C (100 MHz, CD$_2$Cl$_2$) 197.7 (s, C$_1$), 164.9 (d, C$_3$), 139.4 (s, 5CH*Ph*), 135.6 (C$_5$), 134.1 (d, C$_2$), 131.8 (5*C*HPh), 131.4 (2d, 5CH*Ph*), 130.0 (d, 5CH*Ph*), 129.5 (2d, 5CH*Ph*), 39.6 (d, C$_4$), 16.9 (q, 4Me); *m/z* (CI/NH$_3$) 202 ([MH+NH$_3$]$^+$, 3.0%), 185 (MH$^+$, 100); (HRMS: found MH$^+$, 185.0967. $C_{13}H_{13}O^+$ requires 185.0967).

4.7.7. (+)-5-(*E*)-Benzylidene-4(*S*)-octyl-cyclopent-2-enone (+)-35. (91 mg, 56%) as a transparent pale yellow oil; *E*-isomer; R_f 0.26 (SiO$_2$, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{22}$ 0.61 (*c* 6.07 CHCl$_3$); δ_H (400 MHz, CD$_2$Cl$_2$) 7.63 (1H, ddd, *J*=6.0, 2.7, 1.0 Hz, H$_3$), 7.47–7.44 (2H, m, 5CH*Ph*), 7.36–7.25 (4H, m, 5CH*Ph*, 5C*H*Ph), 6.31 (1H, dd, *J*=6.0, 1.9 Hz, H$_2$), 3.84 (1H, m, H$_4$), 1.79–1.70 (1H, m, 4C*H*H(CH$_2$)$_6$Me), 1.33–1.25 (1H, m, 4CH*H*(CH$_2$)$_6$Me), 1.23–1.05 (12H, m, 4CH$_2$(C*H*$_2$)$_6$Me), 0.77 (3H, t, *J*=7.0 Hz, 4(CH$_2$)$_7$Me); δ_C (100 MHz, CD$_2$Cl$_2$) 197.7 (s, C$_1$), 163.2 (d, C$_3$), 138.3 (s, 5CH*Ph*), 135.8 (C$_5$), 134.9 (d, C$_2$), 131.7 (5*C*HPh), 131.2 (2d, 5CH*Ph*), 129.9 (d, 5CH*Ph*), 129.4 (2d, 5CH*Ph*), 44.7 (d, C$_4$), 32.6 (t, 4(*C*H$_2$)$_7$Me), 31.0, 30.3, 30.1, 29.9, 26.8, 23.4, 14.6 (q, 4(CH$_2$)$_7$*Me*); *m/z* (CI/NH$_3$) 300 ([MH+NH$_3$]$^+$, 11.5%), 283 (MH$^+$, 100), 195 (6.2), 186 (8.3), 169 (4.7), 156 (5.9), 141 (8.6), 128 (5.0), 115 (5.8), 91 (6.9); (HRMS: found MH$^+$, 283.2070. $C_{20}H_{27}O^+$ requires 283.2062); *Z*-isomer; R_f 0.36 (SiO$_2$, *n*-hexane/ethyl acetate, 9:1); δ_H (400 MHz, CDCl$_3$) 7.98 (2H, dd, *J*=8.3, 1.6 Hz, 5CH*Ph*), 7.48 (1H, dd, *J*=6.0, 2.6 Hz, H$_3$), 7.44–7.32 (3H, m, 5CH*Ph*), 6.76 (1H, br. s, 5CH*Ph*), 6.34 (1H, dd, *J*=6.0, 1.8 Hz, H$_2$), 3.47 (1H, m, H$_4$), 1.89–1.81 (1H, m, 4C*H*H(CH$_2$)$_6$Me), 1.66–1.56 (1H, m, 4CH*H*(CH$_2$)$_6$Me), 1.43–1.23 (12H, m, 4CH$_2$(C*H*$_2$)$_6$Me), 0.88 (3H, t, *J*=6.5 Hz, 4(CH$_2$)$_7$Me); δ_C (100 MHz, CDCl$_3$) 196.0 (s, C$_1$), 160.1 (d, C$_3$), 138.0 (s, C$_5$), 137.2 (d, C$_2$), 136.5 (5*C*HPh), 134.8 (s, 5CH*Ph*), 131.2 (2d, 5CH*Ph*), 129.8 (d, 5CH*Ph*), 128.4 (2d, 5CH*Ph*), 47.7 (d, C$_4$), 34.4 (t, 4(*C*H$_2$)$_7$Me), 32.2, 30.2, 29.8, 29.6, 26.6, 23.0, 14.4 (q, 4(CH$_2$)$_7$*Me*); *m/z* (CI/NH$_3$) 300 ([MH+NH$_3$]$^+$, 1.4%), 283 (MH$^+$, 100), 225 (6.7), 211 (9.5), 199 (6.7), 183 (20.6), 169 (32.5), 156 (35.0), 141 (60.8), 128 (24.6), 115 (36.5), 91 (26.2), 55 (11.2); (HRMS: found MH$^+$, 283.2065. $C_{20}H_{27}O^+$ requires 283.2062).

4.7.8. (−)-5-(*E*)-Benzylidene-4(*R*)-octyl-cyclopent-2-enone (−)-35. (0.15 g, 54%) as a transparent pale yellow oil; R_f 0.23 (SiO$_2$, *n*-hexane/ethyl acetate, 9:1); $[\alpha]_D^{22}$ −0.48 (*c* 4.67 CHCl$_3$); δ_H (400 MHz, CDCl$_3$) 7.69 (1H, ddd, *J*=6.0, 2.7, 0.8 Hz, H$_3$), 7.52 (2H, dd, *J*=7.2, 1.4 Hz, 5CH*Ph*), 7.43–7.34 (4H, m, 5CH*Ph*, 5C*H*Ph), 6.45 (1H, dd, *J*=6.0, 1.9 Hz, H$_2$), 3.92 (1H, m, H$_4$), 1.87–1.79 (1H, m, 4C*H*H(CH$_2$)$_6$Me), 1.43–1.33 (1H, m, 4CH*H*(CH$_2$)$_6$Me), 1.31–1.08 (12H, m, 4CH$_2$(C*H*$_2$)$_6$Me), 0.86 (3H, t, *J*=6.8 Hz, 4(CH$_2$)$_7$Me); δ_C (100 MHz, CDCl$_3$) 197.9 (s, C$_1$), 162.8 (d, C$_3$), 137.6 (s, 5CH*Ph*), 135.2 (C$_5$), 134.8 (d, C$_2$), 132.0 (5*C*HPh), 130.8 (2d, 5CH*Ph*), 129.6 (d, 5CH*Ph*), 129.1 (2d, 5CH*Ph*), 44.7 (d, C$_4$), 32.2 (t, 4(*C*H$_2$)$_7$Me), 30.6, 29.8, 29.6, 29.5, 26.4, 23.0, 14.4 (q, 4(CH$_2$)$_7$*Me*); *m/z* (CI/NH$_3$) 300 ([MH+NH$_3$]$^+$, 5.7%), 283 (MH$^+$, 100), 186 (3.0), 169 (4.5), 156 (3.5), 141 (6.7), 128 (2.9), 115 (4.5), 91 (4.3); (HRMS: found MH$^+$, 283.2070. $C_{20}H_{27}O^+$ requires 283.2062).

4.7.9. (±)-5-(4-(*E*)-Fluorobenzylidene)-4(*R*/*S*)-methyl-cyclopent-2-enone (±)-36. (96.9 mg, 86%) as a transparent pale yellow oil; R_f 0.35 (SiO$_2$, *n*-hexane/ethyl acetate, 3:1); δ_H (400 MHz, CD$_2$Cl$_2$) 7.52 (1H, ddd, *J*=5.9, 2.5, 0.8 Hz, H$_3$), 7.47 (2H, m, 5CH*Ph*·*p*-F), 7.21 (1H, m, 5C*H*Ph·*p*-F), 7.04 (2H, m, 5CH*Ph*·*p*-F), 6.27 (1H, dd, *J*=5.9, 1.9 Hz, H$_2$), 3.81 (1H, m, H$_4$), 1.10 (3H, d, *J*=7.2 Hz, 4Me); δ_C (100 MHz, CD$_2$Cl$_2$) 197.5 (s, C$_1$), 164.6 (d, C$_3$), 163.8 (sd, $J_{C,F}$=250.0 Hz, 5CH*Ph*·*p*-F), 139.1 ($J_{C,F}$=1.6 Hz, C$_5$), 134.1 (d, C$_2$), 133.23 (dd, $J_{C,F}$=8.4 Hz, 5CH*Ph*·*p*-F), 131.9 (sd, $J_{C,F}$=3.2 Hz, 5CH*Ph*·*p*-F), 130.5 (d, 5*C*HPh·*p*-F), 116.5 (dd, $J_{C,F}$=21.6 Hz, 5CH*Ph*·*p*-F), 39.5 (C$_4$), 16.9 (q, 4Me); *m/z* (CI/NH$_3$) 220 ([MH+NH$_3$]$^+$, 3.7%), 203 (MH$^+$, 100); (HRMS: found MH$^+$, 203.0873. $C_{13}H_{12}OF^+$ requires 203.0872).

4.7.10. (−)-5-(4-(*E*)-Fluorobenzylidene)-4(*S*)-methyl-cyclopent-2-enone (−)-36. (0.14 g, 91%) as a transparent yellow oil; R_f 0.31 (SiO$_2$, *n*-hexane/ethyl acetate, 3:1); $[\alpha]_D^{22}$ −0.87 (*c* 7.50, CHCl$_3$); δ_H (400 MHz, CD$_2$Cl$_2$) 7.51 (1H, m, H$_3$), 7.45 (2H, m, 5CH*Ph*·*p*-F), 7.21 (1H, br. s, 5C*H*Ph·*p*-F), 7.03 (2H, m, 5CH*Ph*·*p*-F), 6.26 (1H, dd, *J*=5.9, 1.8 Hz, H$_2$), 3.80 (1H, m, H$_4$), 1.08 (3H, d, *J*=7.2 Hz, 4Me); δ_C (100 MHz, CD$_2$Cl$_2$) 197.5 (s, C$_1$), 164.6 (d, C$_3$), 163.8 (sd, $J_{C,F}$=250.0 Hz, 5CH*Ph*·*p*-F), 139.1 ($J_{C,F}$=2.4 Hz, C$_5$), 134.1 (d, C$_2$), 133.2 (dd, $J_{C,F}$=8.8 Hz, 5CH*Ph*·*p*-F), 131.9 (sd, $J_{C,F}$=3.2 Hz, 5CH*Ph*·*p*-F), 130.5 (d, 5*C*HPh·*p*-F), 116.5 (dd, $J_{C,F}$=3.2 Hz, 5CH*Ph*·*p*-F), 39.4 (d, C$_4$), 16.9 (q, 4Me); *m/z* (CI/NH$_3$) 220 ([MH+NH$_3$]$^+$, 3.7%), 203 (MH$^+$, 100), 174 (9.4), 159 (6.6), 133 (4.9); (HRMS: found MH$^+$, 203.0877. $C_{13}H_{12}OF^+$ requires 203.0872).

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