NHC-catalysed annulation of enals to tethered dienones: efficient synthesis of bicyclic dienes†

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Homoenolates generated from α,β-unsaturated aldehydes using NHC catalysis underwent facile addition to dibenzylidene cyclohexanone to afford bicyclic cyclopentenes as single diastereomers.

Introduction

In recent years, nucleophilic heterocyclic carbenes (NHCs)[1] have emerged as important ligands[2] to metals, building blocks[3] for heterocycles and catalysts[4] in organic synthesis. Although the catalytic activity of NHCs has found wide ranging applications, their unique ability in transforming enals into d_3 nucleophiles, *viz*, homoenolates,[5,6] by the process of conjugate umpolung has received the most attention. *Inter alia*, homoenolates have been engaged in the synthesis of lactones,[7] spirolactones,[8] lactams,[9] pyrazolidinones,[10] pyridazinones,[11] cyclopentenes[12] and other cyclopentanoids.[13] In the course of our work in this area, we chanced upon a facile annulation of dibenzylidene cyclopentanone to spirocyclopentanone derivatives as a single diastereomer.[13a] (Scheme 1).

These results were in sharp contrast to the formation of a mixture (1 : 1) of cyclopentanone and cyclopentene derivatives in a similar annulation involving acyclic dienones.[13a] In view of the interesting result obtained with dibenzylidene cyclopentanone, it was obligatory to investigate the reaction employing other tethered dienones. As a logical first step, it was decided to extend the studies to dibenzylidene cyclohexanone and analogues. The results of the studies constitute the subject matter of this paper.

Results and discussion

Our studies were initiated by exposing dibenzylidene cyclohexanone **5a** to the homoenolate from 4-methoxycinnamaldehyde generated *in situ* by the addition of a catalytic amount of IMes, formed from the corresponding imidazolium chloride and DBU in dichloromethane. The reaction mixture after the usual work up and chromatography afforded a colorless viscous liquid, which was characterised as the cyclopentene **6a** (Scheme 2).

The structure of the product **6a** was assigned by the usual spectroscopic analysis. The characteristic olefinic proton signal of the cyclopentene ring displayed its resonance signal at δ 5.83 as a singlet while the methoxy proton signal was discernible at δ 3.69. ^{13}C NMR as well as mass spectral data were also in good agreement with the proposed structure.[14] Conclusive evidence for the structure and relative stereochemistry of **6a** was ascertained from the single crystal X-ray data (Fig. 1) of **8**,[15] obtained by the

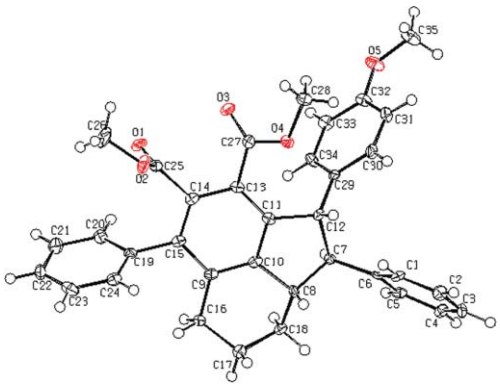
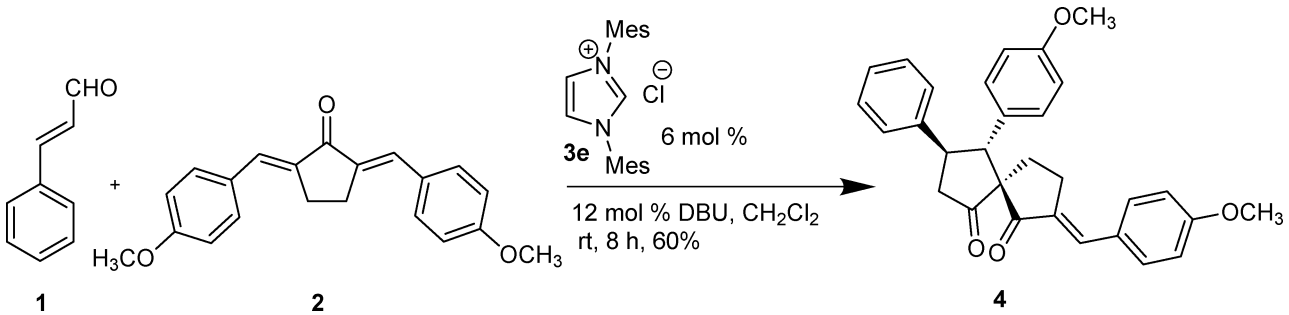


Fig. 1 ORTEP diagram of **8**.



Scheme 1 Reaction of cinnamaldehyde with dibenzylidene cyclopentanone.

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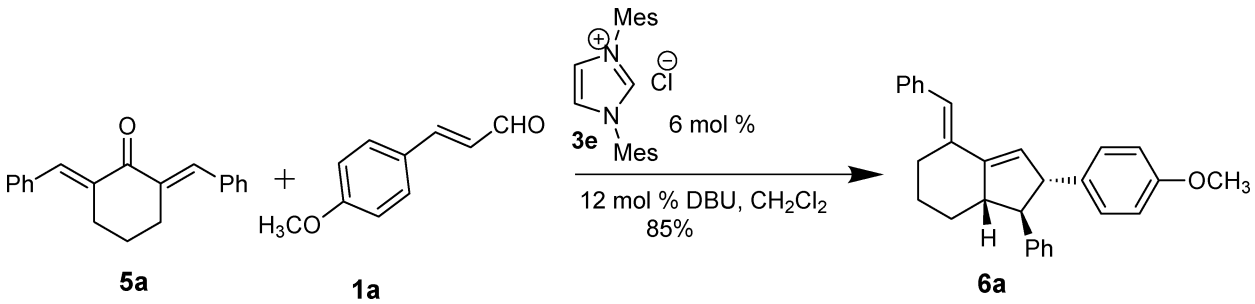
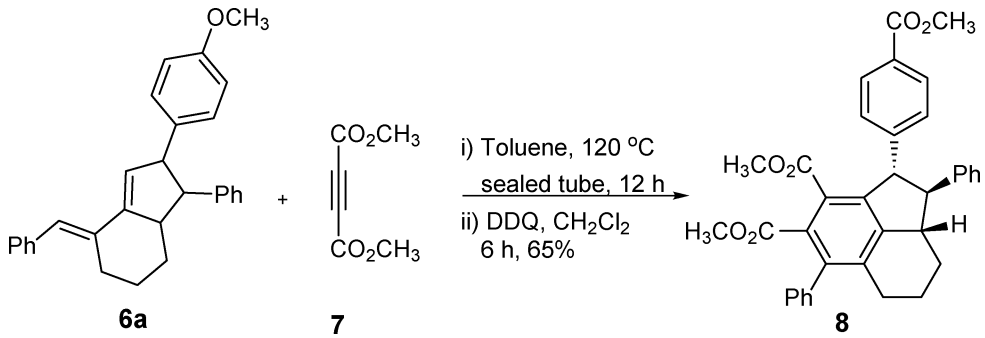
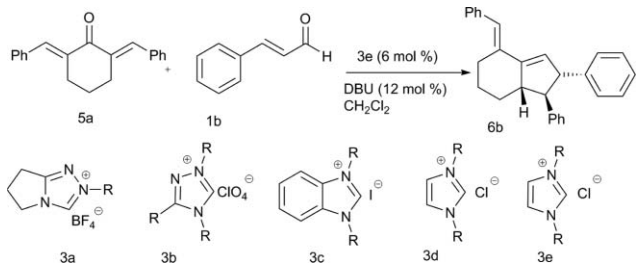


Scheme 2



Scheme 3

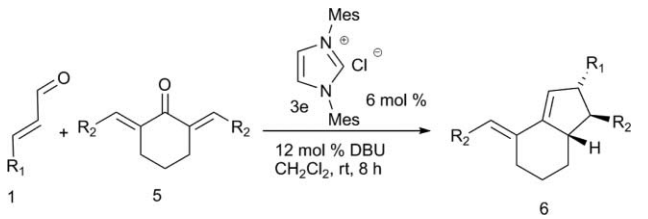
Table 1 Catalyst screening



Entry	Catalyst	Conditions	Yield (%)[a]
1	**3a**	DCM, rt, 8 h	—
2	**3b**	DCM, rt, 8 h	—
3	**3c**	DCM, rt, 8 h	18
4	**3d**	DCM, rt, 8 h	29
5	**3e**	DCM, rt, 8 h	80

[a] Isolated yield **3a**: R = pentaflourophenyl, **3b**: R = phenyl, **3c**: R = ethyl, **3d**: R = 2, 6-diisopropylphenyl, **3e**: R = 2,4,6-trimethylphenyl

Table 2 Substrate scope



Entry	R_1	R_2	Product	Yield (%)[a]
1	phenyl	phenyl	**6b**	80
2	4-MP[b]	4-chlorophenyl	**6c**	82
3	phenyl	4-fluorophenyl	**6d**	85
4	4-MP[b]	4-bromophenyl	**6e**	75
5	phenyl	4-bromophenyl	**6f**	77
6	phenyl	3,4-dichlorophenyl	**6g**	72
7	4-MP[b]	3,4-dichlorophenyl	**6h**	71
8	4-MP[b]	4-fluorophenyl	**6i**	79
9	4-MP[b]	4-methoxyphenyl	**6j**	51
10	4-MP[b]	4-methylphenyl	**6k**	77

[a] Isolated yield. [b] Methoxyphenyl.

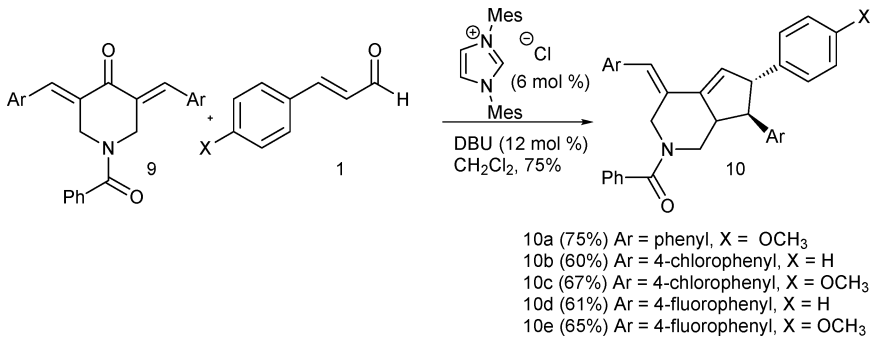
Diels–Alder reaction of **6a** with DMAD followed by aromatization (Scheme 3).

A number of commonly used NHC catalysts were screened to assess their utility in optimising the reaction involving cinnamaldehyde, and the results are summarized in Table 1. Triazolium catalysts were found to be ineffective in this reaction while imidazolium catalysts **3c** and **3d** afforded the product in low yield. Among the various catalysts screened, **3e** was found to give the best results in dichloromethane at room temperature.

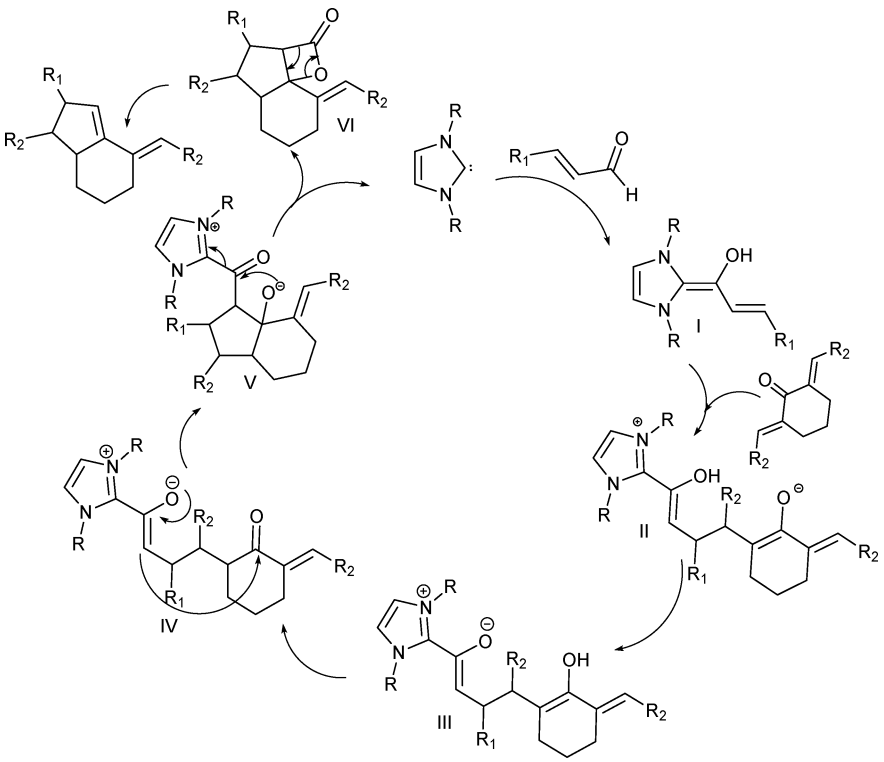
The reaction was performed with a number of dibenzylidene cyclohexanones and the results are presented in Table 2.

Subsequently, we investigated the potential of this annulation towards *N*-benzoyl-3,5-dibenzylidene piperidone and analogous dienones. The reaction proceeded well, and interestingly only one diastereomer is formed in each case. The structure of the products is established by the usual spectroscopic methods. The reaction is of a general nature and the results are presented in Scheme 4.

A mechanistic pathway for the cyclopentene formation is presented in Scheme 5. Evidently, the homoenolate annulation of dibenzylidene cyclohexanone reported herein proceeds *via* a pathway divergent from that reported earlier[13a] for the reaction involving dibenzylidene cyclopentanone. The divergence may be attributed to the different reactivities of the two enolates involved. The cyclohexanone enolate formed by the addition of



Scheme 4 Reaction with *N*-benzoyl-3,5-dibenzylidenepiperidone.



Scheme 5 Plausible mechanistic pathway to the formation of bicyclic cyclopentene.

homoenolate to dibenzylidene cyclohexanone, being less reactive than the one derived from cyclopentanone, presumably isomerises to a second enolate III/IV which endures a Claisen–Dieckmann type cyclization to afford V. The latter is ideally set up to undergo a second cyclization to deliver a β-lactone VI, which then fragments *via* a retro [2 + 2] process to lose CO_2 and deliver the cyclopentene (Scheme 5).

Conclusion

In conclusion, the novel homoenolate annulation strategy for the synthesis of cyclopentenes, reported by us previously,[12a] has been exploited in the construction of bicyclic cyclopentenes. It offers a viable protocol for the formation of bicyclic cyclopentenes from dibenzylidene cyclohexanones. The formation of a single diastereomer is noteworthy. It is reasonable to assume that the diene systems formed in the present reaction may find application in the synthesis of complex polycyclic frameworks.

Experimental

General

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz on a Bruker DPX-300 MHz NMR spectrometer. Chemical shifts (δ) are reported relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. Coupling constants (J) are reported in Hertz (Hz). Mass spectra were recorded under EI/HRMS or FAB using JEOL JMS 600H mass spectrometer. IR spectra were recorded on a Nicolet Impact 400D FT-IR spectrophotometer. Gravity column chromatography was performed using

100–200 mesh silica gel and mixtures of petroleum ether–ethyl acetate were used for elution.

General procedure for the synthesis of bicyclic cyclopentenes

DBU (12 mol%) was added to a suspension of the carbene precursor—1,3-dimesityl imidazolium chloride (IMesCl) (6 mol%), enal (1 mmol) and dibenzylidenecyclohexanone derivative (0.50 mmol) in dry dichloromethane and the resulting solution was stirred for 12 h. The reaction mixture was then passed through a short pad of Celite®. After the removal of the solvent by distillation under vacuum using a rotary evaporator, the residue was subjected to column chromatography on a silica gel (60–120 mesh) column using 95 : 5 petroleum ether–ethyl acetate solvent mixtures to afford the bicyclic cyclopentene derivatives.

(1*S*,2*S*,*E*)-4-Benzylidene-2-(4-methoxyphenyl)-1-phenyl-2,4,5,6,7,7a-hexahydro-1*H*-indene (6a). **IR** (film) ν_{max}: 3025, 2927, 1603, 1487, 1440, 1331, 1125 cm^{-1}; **^{1}H NMR**: δ 7.31–7.27 (m, 4H), 7.23–7.20 (m, 2H), 7.18–7.13 (m, 4H), 6.98 (d, 2H, J = 8.5 Hz), 6.77 (bs, 1H), 6.72 (d, 2H, J = 8.5 Hz), 5.83 (s, 1H), 3.98 (t, 1H, J = 6.0 Hz), 3.69 (s, 3H), 2.95 (d, 1H, J = 15.0 Hz), 2.83–2.81 (m, 2H), 2.26 (t, 1H, J = 13.5 Hz), 1.92 (d, 1H, J = 11.0 Hz), 1.81 (d, 1H, J = 12.0 Hz), 1.36–1.25 (m, 2H) ppm; **^{13}C NMR**: δ 158.1, 146.4, 142.5, 137.5, 136.7, 129.4, 128.4, 128.2, 128.1, 126.5, 126.3, 125.6, 123.9, 113.6, 65.5, 57.6, 55.0, 53.7, 32.3, 29.3, 26.9, 25.5 ppm; **LRMS-FAB** calcd. for $C_{29}H_{28}O$ (M+H)$^+$: 393.22, found: 393.41

(1*S*,2*S*,*E*)-4-Benzylidene-1,2-diphenyl-2,4,5,6,7,7a-hexahydro-1*H*-indene (6b). IR (film) ν_{max}: 3026, 2926, 1600, 1494, 1450 cm^{-1}; **^{1}H NMR**: δ 7.31–7.06 (m, 15H), 6.78 (s, 1H), 5.87 (s, 1H), 4.06–4.03 (m, 1H), 2.99–2.85 (m, 3H), 2.29–2.25 (m, 1H), 1.97–1.81 (m, 2H), 1.42–1.27 (m, 2H) ppm; **^{13}C NMR**: δ 146.6, 144.6, 142.5, 137.4, 136.7, 129.4, 128.5, 127.7, 126.5, 125.2, 124.0, 65.3, 58.4, 53.8, 32.3, 29.7, 25.7. ppm; **FAB-LRMS** for $C_{28}H_{26}$: calcd. (M+H)$^+$: 363.20, found: 363.13.

(1*S*,2*S*,*E*)-4-(4-Chlorobenzylidene)-1-(4-chlorophenyl)-2-(4-methoxyphenyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene (6c). **IR** (film) ν_{max}: 3028, 2933, 1599, 1488, 1437, 1333, 1126 cm^{-1}; **^{1}H NMR**: δ 7.28 (d, 2H, J = 6.5 Hz), 7.21–7.19 (m, 4H), 7.07 (d, 2H, J = 8.5 Hz), 6.96 (d, 2H, J = 8.5 Hz), 6.74 (d, 2H, J = 8.5 Hz), 6.69 (d, 1H, J = 2.0 Hz), 5.83 (s, 1H), 3.92–3.89 (m, 1H), 3.73 (s, 3H), 2.88 (d, 1H, J = 15.0 Hz), 2.80–2.77 (m, 2H), 2.26–2.18 (m, 1H), 1.92–1.82 (m, 2H), 1.38–1.27 (m, 2H) ppm; **^{13}C NMR**: δ 158.2, 146.0,140.8, 137.2, 136.2, 135.8, 132.3, 132.1, 130.7, 129.4, 128.4, 128.3, 125.9, 122.9, 113.7, 64.9, 57.7, 55.1, 53.5, 32.1, 29.7, 29.2, 26.9, 25.4 ppm; **LRMS-FAB** for $C_{29}H_{26}Cl_2O$: (M+H)$^+$ calcd.: 461.15, found: 461.33

(1*S*,2*S*,*E*)-4-(4-Fluorobenzylidene)-1-(4-fluorophenyl)-2-phenyl-2,4,5,6,7,7a-hexahydro-1*H*-indene (6d). **IR** (film) ν_{max}: 3035, 2957, 1597, 1483, 1428, 1328, 1128 cm^{-1}; **^{1}H NMR**: δ 7.24–7.22 (m, 2H), 7.20 (d, 2H, J = 7.5 Hz), 7.17–7.08 (m, 3H), 7.06 (d, 2H, J = 8.0 Hz), 7.00 (t, 2H, J = 8.5 Hz), 6.93 (t, 2H, J = 8.5 Hz), 6.72 (d, 1H, J = 2.0 Hz), 5.83 (s, 1H), 3.96 (d, 1H, J = 9.5 Hz), 2.89 (d, 1H, J = 15.0 Hz), 2.87–2.78 (m, 2H), 2.25–2.19 (m, 1H), 1.93–1.83 (m, 2H), 1.39–1.23 (m, 2H) ppm; **^{13}C NMR**: δ 162.5, 162.4, 160.6, 160.5, 146.4, 144.3, 137.9, 136.4, 133.4, 133.9, 131.0, 130.9, 129.6, 129.4, 129.3, 128.6, 128.6, 128.3, 127.4, 126.4, 125.3, 123.0, 115.2, 115.1, 115.0, 114.9, 64.7, 58.6, 53.7, 32.1, 29.1, 26.9, 25.5 ppm; **LRMS-FAB** for $C_{28}H_{24}F_2$: (M+H)$^+$ calcd. (M+H)$^+$: 399.19, found: 399.37

(1*S*,2*S*,*E*)-4-(4-Bromobenzylidene)-1-(4-bromophenyl)-2-(4-methoxyphenyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene (6e). **IR** (film) ν_{max}: 3041, 2935, 1579, 1479, 1429, 1325, 1118 cm^{-1}; **^{1}H NMR**: δ 7.44 (d, 2H, J = 6.5 Hz), 7.36 (d, 2H, J = 6.5 Hz), 7.15 (d, 2H, J = 8.5 Hz), 7.03 (d, 2H, J = 9.0 Hz), 6.97 (d, 2H, J = 6.5 Hz), 6.75 (d, 2H, J = 9.5 Hz), 6.67 (d, 1H, J = 2.5 Hz), 5.84 (s, 1H), 3.92–3.89 (m, 1H), 3.75 (s, 3H), 2.88 (d, 1H, J = 15.0 Hz), 2.79–2.77 (m, 2H), 2.22 (t, 1H, J = 13.0 Hz), 1.91 (d, 1H, J = 10.5 Hz), 1.86–1.83 (m, 1H), 1.38–1.25 (m, 2H) ppm; **^{13}C NMR**: δ 158.3, 146.1, 141.4, 137.3, 136.2, 136.1, 131.4, 131.2, 131.0, 129.8, 128.3, 125.9, 122.9, 120.5, 120.2, 113.7, 65.0, 57.7, 55.1, 53.5, 32.1, 29.2, 25.4 ppm; **LRMS-FAB** for $C_{29}H_{26}Br_2O$: (M+H)$^+$ calcd.: 549.05, found: 549.24, 551.17

(1*S*,2*S*,*E*)-4-(4-Bromobenzylidene)-1-(4-bromophenyl)-2-phenyl-2,4,5,6,7,7a-hexahydro-1*H*-indene (6f). **IR** (film) ν_{max}: 3036, 2944, 1568, 1475, 1422, 1318, 1115 cm^{-1}; **^{1}H NMR**: δ 7.27 (d, 2H, J = 6.5 Hz), 7.21–7.12 (m, 7H), 7.07–7.03 (m, 4H), 6.69 (d, 1H, J = 2.0 Hz), 5.85 (s, 1H), 3.95 (d, 1H, J = 9.0 Hz), 2.88 (d, 1H, J = 14.5 Hz), 2.83–2.77 (m, 2H), 2.24–2.18 (m, 1H), 1.91–1.81 (m, 2H), 1.37–1.25 (m, 2H) ppm; **^{13}C NMR**: δ 146.3, 144.1, 140.8, 137.2, 135.8, 132.4, 132.1, 130.7, 129.6, 129.4, 128.7, 128.5, 128.3, 127.4, 127.1, 126.5, 125.6, 122.9, 64.8, 58.5, 53.6, 32.1, 29.2, 26.9, 25.4 ppm; **LRMS-FAB** for $C_{28}H_{24}Br_2$: (M+H)$^+$ calcd. 519.03, found: 519.41, 521.17

(1*S*,2*S*,*E*)-4-(3, 4-Dichlorobenzylidene)-1-(3, 4-dichlorophenyl)-2-phenyl-2,4,5,6,7,7a-hexahydro-1*H*-indene (6g). **IR** (film) ν_{max}: 3032, 2943, 1581, 1468, 1423, 1322, 1121 cm^{-1}; **^{1}H NMR**: δ 7.39–7.36 (m, 2H), 7.32–7.28 (m, 2H), 7.25–7.17 (m, 3H), 7.10 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.07–7.05 (m, 2H), 6.96 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.0), 6.64 (d, 1H, J = 2.5 Hz), 5.86 (s, 1H), 3.97 (d, 1H, J = 9.5 Hz), 2.89–2.78 (m, 3H), 2.27–2.21 (m, 1H), 1.95–1.87 (m, 1H), 1.92 (d, 1H, J = 11.0 Hz), 1.81 (d, 1H, J = 12.0 Hz), 1.40–1.25 (m, 2H) ppm; **^{13}C NMR**: δ 145.9, 143.6, 142.7, 138.2, 137.3, 132.4, 132.3, 131.1, 130.5, 130.4, 130.3, 130.1, 129.7, 128.7, 128.5, 127.5,,127.4, 126.7, 125.9, 122.0, 64.4, 58.5, 53.6, 32.1, 29.1, 25.3 ppm; **LRMS-FAB** for $C_{28}H_{22}Cl_4$: (M+H)$^+$ calcd.: 499.06, found: 499.32, 501.27

(1*S*,2*S*,*E*)-4-(3,4-Dichlorobenzylidene)-1-(3,4-dichlorophenyl)-2-(4-methoxyphenyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene (6h). **IR** (film) ν_{max}: 2951, 1775, 1723, 1699, 1685, 1652, 1607, 1216, 1066, 1030, 843, 774 cm^{-1}; **^{1}H NMR**: δ 7.32–7.29 (m, 2H), 7.25–7.21 (m, 2H), 7.03 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.91–6.88 (m, 3H), 6.69 (dd, 2H, J_1 = 7.0 Hz), 6.56 (d, 1H, J = 2.0 Hz), 5.76 (s, 1H), 3.85–3.83 (m, 1H), 3.69 (s, 3H), 2.79 (d, 1H, J = 14.5 Hz), 2.72–2.69 (m, 2H), 2.23–2.11 (m, 1H), 1.87–1.79 (m, 2H), 1.35–1.18 (m, 2H) ppm; **^{13}C NMR**: δ 158.4, 145.6, 142.8, 138.3, 137.3, 135.7, 132.4, 132.3, 131.1, 130.5, 130.4, 130.3, 130.1, 129.8, 128.7, 128.3, 128.0, 127.6, 126.4, 121.9, 114.2, 113.9, 64.6, 57.7, 55.2, 53.5, 32.1, 29.2, 26.9, 25.4 ppm; **LRMS-FAB** for $C_{29}H_{24}Cl_4O$: (M+H)$^+$ calcd.: 529.07, found: 529.47, 531.24

(1*S*,2*S*,*E*)-4-(4-Fluorobenzylidene)-1-(4-fluorophenyl)-2-(4-methoxyphenyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene (6i). **IR** (film) ν_{max}: 2951, 1775, 1723, 1699, 1685, 1652, 1607, 1216, 1066, 1030,

843, 774 cm^{-1}; **^{1}H NMR**: δ 7.26–7.23 (m, 2H), 7.11–7.08 (m, 2H), 7.02–6.91 (m, 6H), 6.76–6.71 (m, 3H), 5.82 (s, 1H), 3.90 (d, 1H, J = 9.0 Hz), 3.74 (s, 3H), 2.88 (d, 1H, J = 15.0 Hz), 2.83–2.77 (m, 2H), 2.25–2.19 (m, 1H), 1.93–1.83 (m, 2H), 1.39–1.26 (m, 2H) ppm; **^{13}C NMR**: δ 162.5, 162.4, 160.6, 160.5, 158.2, 146.1, 138.0, 136.5, 136.4, 133.5, 133.4, 131.0, 130.9, 129.4, 129.3, 128.3, 125.6, 122.9, 115.2, 115.1, 115.0, 114.9, 113.7, 64.8, 57.9, 55.1, 53.6, 32.1, 29.1, 25.5 ppm; **LRMS-FAB** calcd. for $C_{29}H_{26}F_2O$: calcd. $(M+H)^+$: 429.21, found: 429.27

(1*S*,2*S*,*E*)-4-(4-Methoxybenzylidene)-1,2-bis(4-methoxyphenyl)-2,4,5,6,7,7a-hexahydro-1*H*-indene (6j). **IR** (film) ν_{max}: 3025, 2927, 1603, 1487, 1440, 1331, 1125 cm^{-1}; **^{1}H NMR**: δ 7.22 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 9 Hz, 2H), 6.84 (d, J = 9 Hz, 2H), 6.78–6.72 (m, 5H), 5.81 (s, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 2.92 (m, 1H), 2.76 (m, 2H), 2.23 (m, 1H), 1.92 (d, J = 11 Hz, 1H), 1.82 (d, J = 13 Hz, 1H) ppm; **^{13}C NMR**: δ 158.2, 158.1, 146.5, 136.8, 135.1, 134.5, 130.7, 130.2, 128.9, 128.4, 125.2, 123.5, 113.6, 113.5, 64.9, 57.6, 55.1, 55.0, 53.6 ppm; **LRMS-FAB** calcd. for $C_{31}H_{32}O_3$ $(M+H)^+$: 453.33, found: 453.46

(1*S*,2*S*,*E*)-4-(4-Methoxyphenyl)-4-(4-methylbenzylidine)-1-*p*-tolyl-2,4,5,6,7,7a-hexahydro-1*H*-indene (6k). **IR** (film) ν_{max}: 3025, 2927, 1604, 1487, 1443, 1331, 1127 cm^{-1}; **^{1}H NMR**: δ 7.10 (d, J = 8 Hz, 3H), 7.02 (d, J = 8 Hz, 3H), 6.96– 6.89 (m, 7H), 6.65 (s, 1H), 5.73 (s, 1H), 3.89–3.87 (m, 1H), 3.62 (s, 3H), 2.87– 2.85 (d, J = 15 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H), 2.16–2.15 (m, 1H), 1.85–1.83 (d, J = 10.5 Hz, 2H), 1.74–1.71 (m, 1H) ppm; **^{13}C NMR**: δ 157.9, 146.6, 139.4, 136.9, 136.0, 135.5, 134.6, 129.8, 129.6, 129.4, 129.0, 128.9, 128.7, 128.3, 127.9,127.3, 125.3, 123.8, 113.5,65.1, 57.5, 55.0, 53.7, 34.6, 32.2, 29.2, 26.9, 25.5, 25.2, 22.6, 21.8, 21.7, 21.2, 21.0 ppm; **LRMS-FAB** calcd. for $C_{31}H_{32}O$ $(M+H)^+$: 421.25, found: 421.53

(1*S*,2*S*,8a*S*)-Dimethyl-2-(4-methoxyphenyl)-1,5-diphenyl-1,2,6,7,8,8a-hexahydroacenaphthylene-3,4-dicarboxylate 8. **Mp**: 155-157 °C; IR (KBr) ν_{max}: 3026, 2945, 1722, 1593, 1489, 1448, 1355, 1298, 1168 cm^{-1}. **^{1}H NMR**: δ 7.40–7.07 (m, 10 H), 6.77 (d, 2H, J = 8.4 Hz), 6.66 (d, 2H, J = 8.5 Hz), 4.61 (d, 1H, J = 10.4 Hz), 3.71 (s, 3H), 3.39 (s, 3H), 3.26–3.19 (m, 1H), 3.11 (s, 3H), 3.01–2.93 (m, 2H), 2.63–2.38 (m, 2H), 2.03–1.99 (m, 2H), 1.65–1.62 (m, 1H), 1.37–1.25 (m, 1H) ppm; **^{13}C NMR**: δ 168.8, 167.0, 157.8, 145.6, 142.6, 140.1, 138.4, 137.9, 135.4, 134.9, 133.4, 129.4, 128.6, 128.4, 128.3, 128.0, 127.7, 127.4, 126.8, 125.3, 113.5, 67.1, 58.4, 55.0, 51.9, 51.5, 48.2, 27.1, 26.5, 23.3 ppm. **HRMS** (EI) for $C_{35}H_{32}O_5$: calcd. (M^+): 532.2250, found: 532.2239

(*Z*)-(4-Benzylidene-6,7-diphenyl-3,4-dihydro-1*H*-cyclopenta[*c*]-pyridin-2(6*H*,7*H*,7a*H*)-yl)(phenyl)methanone (10a). **IR** (film) ν_{max}: 3003, 2985, 1626, 1492, 1442, 1213, 907 cm^{-1}; **^{1}H NMR**: δ 7.25–7.18 (m, 15H), 7.10–7.08 (m, 5H), 6.93 (s, 1H), 6.05 (s, 1H), 4.78 (bs, 1H), 4.11 (d, 1H, J = 7.3 Hz), 3.92 (d, 1H, J = 14.8 Hz), 3.28 (bs, 1H), 2.93–2.89 (m, 2H), 1.52 (bs, 1H) ppm; **^{13}C NMR**: δ 170.1, 143.5, 142.9, 140.7, 135.7, 133.3, 129.4, 128.8, 128.5, 128.4, 128.2, 127.9, 127.5, 127.4, 126.8, 126.6, 125.4, 123.8, 62.1, 58.9, 51.6, 48.5, 26.9 ppm; **LRMS-FAB** calcd. for $C_{34}H_{29}NO$ $(M+H)^+$: 468.23, found: 468.38

(*Z*)-(4-(4-Chlorobenzylidene)-7-(4-chlorophenyl)-6-phenyl-3,4-dihydro-1*H*-cyclopenta[*c*]pyridin-2(6*H*,7*H*,7a*H*)-yl)(phenyl) methanone (10b). **IR** (film) ν_{max}: 2999, 1628, 1491, 1433, 1261, 1093, 1018 cm^{-1}; **^{1}H NMR**: δ 7.33–7.04 (m, 17H), 6.88–6.81 (m, 2H), 6.01 (s, 1H), 4.75 (bs, 1H), 4.01 (bs, 1H), 3.86 (d, 1H, J = 15.5 Hz), 3.23 (bs, 1H), 2.88–2.81 (bs, 2H), 1.28–1.22 (m, 1H) ppm; **^{13}C NMR**: δ 170.1, 142.9, 142.6, 139.0, 135.3, 134.1, 133.3, 132.6, 131.9, 130.0, 129.5, 129.1, 128.7, 128.6, 128.1, 127.8, 127.4, 126.9, 126.8, 126.7, 126.6, 124.2, 123.8, 61.5, 59.0, 51.2, 48.0, 26.8 ppm; **LRMS-FAB** calcd. for $C_{34}H_{27}Cl_2NO$ $(M+H)^+$: 536.16, found: 536.25

(*Z*)-(4-(4-Chlorobenzylidene)-7-(4-chlorophenyl)-6-(4-methoxyphenyl)-3,4-dihydro-1*H*-cyclopenta[*c*]pyridin-2(6*H*,7*H*,7a*H*)-yl)-(phenyl)methanone (10c). **IR** (film) ν_{max}: 3007, 1613, 1488, 1432, 1257, 1095, 980 cm^{-1}; **^{1}H NMR**: δ 7.28–7.03 (m, 13H), 6.86–6.77 (m, 5H), 5.96 (s, 1H), 4.71–4.66 (m, 1H), 3.94 (bs, 1H), 3.83 (d, 1H, J = 14.5 Hz), 3.80 (s, 3H), 3.19 (bs, 1H), 2.90–2.74 (m, 2H), 1.23 (bs, 1H) ppm; **^{13}C NMR**: δ 170.2, 158.5, 142.3, 139.1, 136.3, 135.3, 134.9, 134.1, 133.3, 132.5, 132.1, 130.0, 129.6, 129.0, 128.6, 128.4, 126.7, 124.1, 114.4, 114.2, 113.8, 112.1, 61.7, 60.2, 58.3, 51.0, 48.3, 26.9 ppm; **LRMS-FAB** calcd. for $C_{35}H_{29}Cl_2NO_2$ $(M+H)^+$: 566.17, found: 566.29

(*Z*)-(4-(4-Fluorobenzylidene)-7-(4-fluorophenyl)-6-phenyl-3, 4-dihydro-1*H*-cyclopenta[*c*]pyridin-2(6*H*,7*H*,7a*H*)-yl)(phenyl)methanone (10d). **IR** (film) ν_{max}: 3019, 2987, 1622, 1498, 1425, 1254, 1166, 935 cm^{-1}; **^{1}H NMR**: δ 7.35–7.12 (m, 14H), 7.08–6.95 (m, 5H), 6.03 (s, 1H), 4.85–4.70 (m, 1H), 4.04 (bs, 1H), 3.87 (d, 1H, J = 15.5 Hz), 3.25 (bs, 1H), 2.99–2.83 (m, 2H), 1.29–1.25 (m, 1H) ppm; **^{13}C NMR**: δ 170.1, 162.9, 162.7, 160.9, 160.7, 143.4, 142.7, 136.2, 135.7, 135.3, 133.3, 131.7, 130.5, 129.5, 129.2, 128.8, 128.5, 127.9, 127.7, 127.4, 127.0, 126.7, 125.3, 124.3, 123.8, 115.4, 115.2, 61.4, 59.1, 51.3, 48.0, 25.3 ppm; **LRMS-FAB** calcd. for $C_{34}H_{27}F_2NO$ $(M+H)^+$: 504.22, found: 504.41

(*Z*)-(4-(4-Fluorobenzylidene)-7-(4-fluorophenyl)-6-(4-methoxyphenyl)-3,4-dihydro-1*H*-cyclopenta[*c*]pyridin-2(6*H*,7*H*,7a*H*)-yl)(phenyl)methanone (10e). **IR** (film) ν_{max}: 3049, 2991, 1616, 1506, 1433, 1244, 1168, 904 cm^{-1}; **^{1}H NMR**: δ 7.25–6.81 (m, 15H), 6.78 (d, 2H, J = 8.6 Hz), 5.99 (s, 1H), 4.73 (bs, 1H), 3.97 (d, 1H, J = 8.3 Hz), 3.87 (d, 1H, J = 15.7 Hz), 3.77 (s, 3H), 3.21 (bs, 1H), 2.87 (bs, 2H), 1.26 (bs, 1H) ppm; **^{13}C NMR**: δ 170.1, 162.8, 162.6, 160.8, 160.7, 142.3, 136.2, 135.1, 131.7, 130.4, 129.9, 129.5, 129.1, 128.8, 128.3, 128.2, 127.9, 127.7, 126.71 124.1, 115.3, 115.2, 114.1, 114.0, 113.9, 61.5, 58.3, 55.0, 51.1, 48.3, 26.8 ppm; **LRMS-FAB** calcd. for $C_{35}H_{29}F_2NO_2$ $(M+H)^+$: 534.23, found: 534.35

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14 An isolated example (entry 1, Table 2) was reported by us previously. In this case direct evidence for the assigned structure of the diene (**6b**) was obtained by ^{1}H NOE studies (see supplementary information in ref. 13a cited above).
15 Crystal structure of compound **8** have been deposited at the Cambridge Crystallographic Centre and allocated reference no. CCDC 777238†.

