

Ring size effects in the C²–C⁶ biradical cyclisation of enyne–allenes and the relevance for neocarcinostatin

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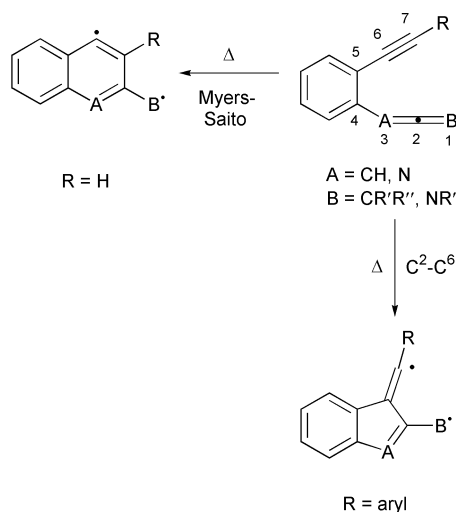
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The regioselectivity of the thermal cyclisations of enyne–allenes **1** can be toggled as a function of the ring size of the cycloalkene. With a cyclopentene as the ene moiety the Myers–Saito (C²–C⁷) cycloaromatisation product is formed, whereas with six- and seven-membered cycloalkenes the novel C²–C⁶ cyclisation is observed. DFT calculations are used to rationalise these changes. The implications of these findings for alternative thermal biradical cyclisations of neocarcinostatin are discussed.

Introduction

Cycloaromatisations of enediynes¹ (Bergman cyclisation) and enyne–allenes² (Myers–Saito cyclisation, C²–C⁷) have received large interest over the last decade³ since the intervening biradicals constitute key intermediates in the *mode of action* of natural enediyne antitumor antibiotics.⁴ However, while the above cyclisations may be regarded as electrocyclic reactions leading to aromatic biradicals *via* in-plane aromatic transition states⁵ the novel C²–C⁶ cyclisation of enyne–allenes (Scheme 1)⁶



Scheme 1

leads to an intermediate benzofulvene biradical in a 5-*exo-dig* fashion reminiscent of the regioselectivity of mono radical cyclisations. Our studies⁶ have shown that the proper choice of substituents R at the alkyne terminus allows the regioselectivity of thermal enyne–allene biradical cyclisations to be steered away from the Myers–Saito (C²–C⁷) towards the C²–C⁶ pathway. Moreover, the switch from R = H towards R = aryl likewise led to analogue regiocontrol of the biradical cyclisations of enyne–carbodiimides and enyne–ketenimines.^{7–9}

In many examples described so far the C²–C⁶ reaction proceeds in rather high yields, in particular when compared to other thermal biradical cyclisations. As ample mechanistic

evidence has been presented for the intermediate benzofulvene biradical⁶ in the C²–C⁶ cyclisation, it is the intramolecular follow-up reaction of the biradical intermediate to formal ene and Diels–Alder type products that renders this process so efficient. In contrast, intermolecular trapping of the benzofulvene biradical is synthetically rather unsatisfying.^{6c}

As the novel C²–C⁶ cyclisation has recently moved into the focus of theoretical,¹⁰ DNA cleavage,¹¹ and synthetic studies (e.g. towards the kinamycin¹² and the neocryptolepine¹³ family), it seemed to be important to learn more about the various factors controlling the regioselectivity of a thermal biradical cyclisation. Up to now the influence of ring size effects on the regioselectivity has not been investigated systematically, although a few isolated examples¹⁴ may indicate some effect. Herein, we would like to disclose¹⁵ that the switch between the C²–C⁷ and the C²–C⁶ cyclisation can be initiated simply by ring size effects.

Results

Preparation of cyclic enyne–allenes **1a–f**

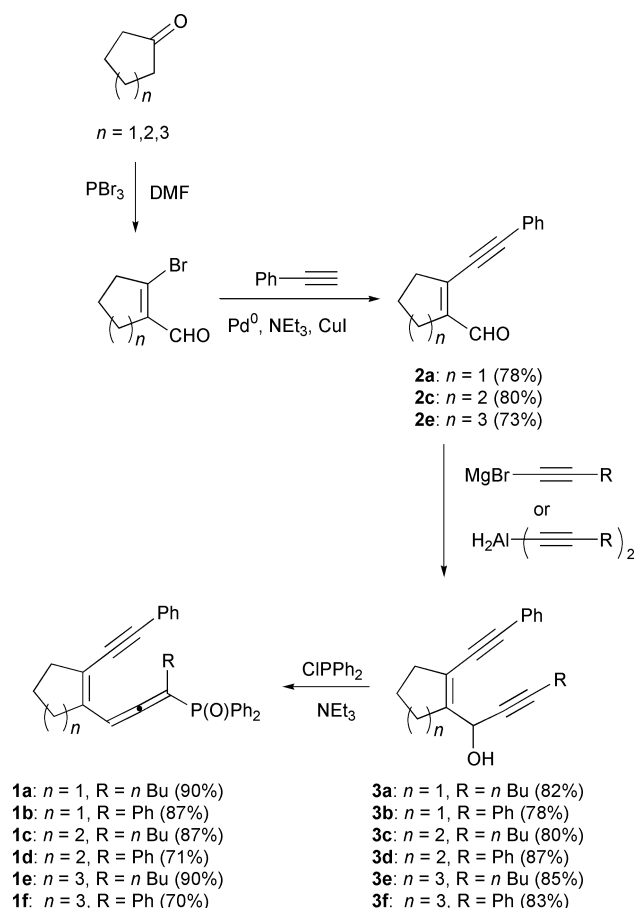
Enyne–allenes **1a–f** are available in a four-step synthesis from the corresponding cycloalkanones *via* the cycloalkene carbaldehydes. The latter¹⁶ are reacted using a Sonogashira coupling with two acetylides, either *n*BuC≡CMgBr or [(PhC≡C)₂–AlH₂]Na,¹⁷ the second being prepared from phenylacetylene and SDDA ([Et₂AlH₂]Na). The resultant propargyl (prop-2-ynyl) alcohols **3a–f** were treated with ClPPh₂ thus providing the diphenylphosphane oxide substituted enyne–allenes¹⁸ **1a–f** after a [2,3]-sigmatropic rearrangement (Scheme 2). Enyne–allenes were isolated by column chromatography or HPLC. The structures were identified by IR, ¹H NMR, ¹³C NMR and high resolution mass spectrometry. During isolation of enyne–allene **1f** the follow-up product **13f** was also obtained.

Thermolysis of **1a–f**

Enyne–allenes **1a–f** experience thermal cyclisation over a wide temperature range as demonstrated by the onset temperature¹⁹ from DSC experiments (**1a**: 145 °C, **1b**: 110 °C, **1c**: 92 °C, **1d**: 70 °C, **1e**: 61 °C, **1f**: 40 °C). Thermolyses of enyne–allene **1a** in toluene and of **1b** in mesitylene at reflux temperature in the presence of an excess of cyclohexa-1,4-diene (1,4-CHD)

furnished the cyclisation products **4a** (15%) and **4b** (31%) (Scheme 3). In addition, some other follow-up products (**5a**, **6a** and **7b**) were found, which were structurally characterised using NMR techniques such as DEPT, H,H- and C,H-COSY and HMBC measurements.

Products **4a–6a**, **4b**, **7b** can be explained directly from the intermediate Myers–Saito (C^2-C^7) biradical **8a,b** (Scheme 4). While the more reactive σ -radical site readily abstracts one hydrogen from toluene–cyclohexadiene to afford **9a,b**, the benzylic π -radical is less reactive and additionally shielded to some extent against intermolecular reactions. Hence, only some of the **9a,b** undergoes a second hydrogen abstraction to **4a,b**. Alternatively, radical **9a** ($R = nBu$) may undergo a cyclisation to

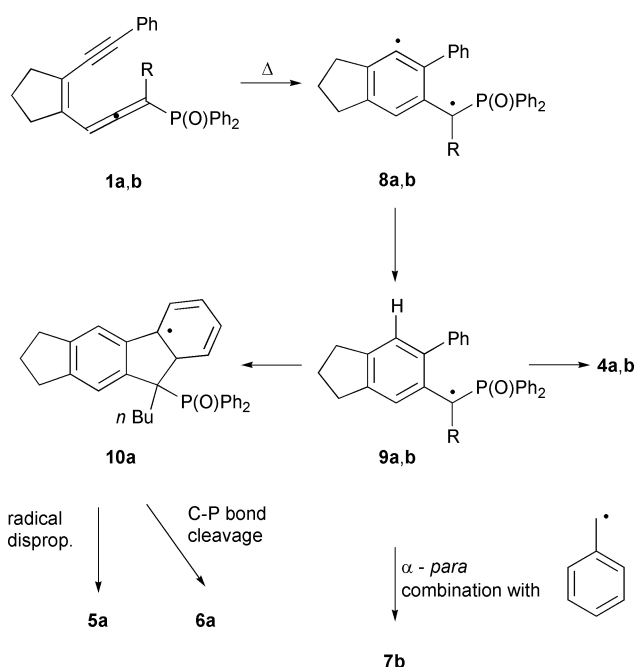


Scheme 2 Synthesis of the enyne-allenes **1a–f**.

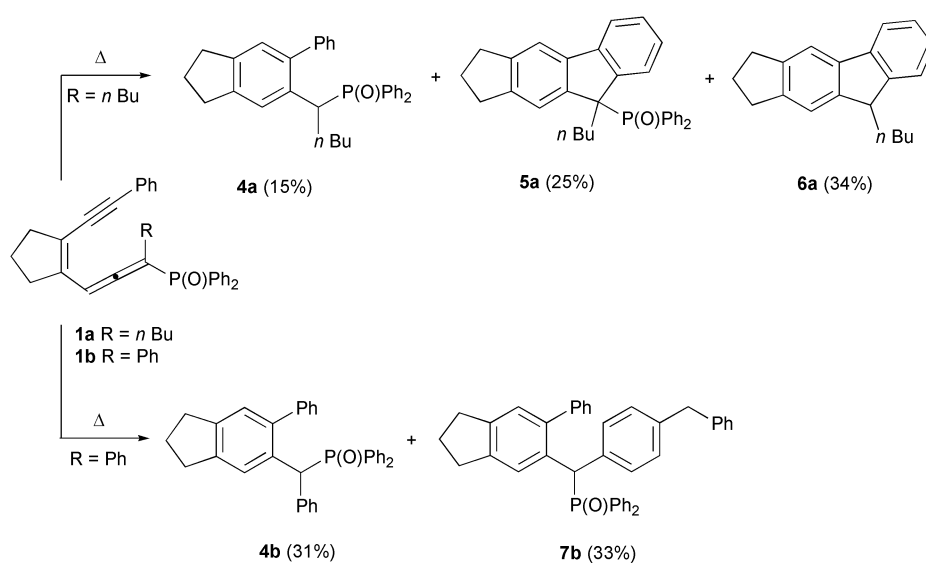
the radical **10a**, because it can be stabilised either through hydrogen donation to another radical or through C–P bond cleavage (a phenylogous β -fragmentation). For the benzylic radical **9b** cyclisation is less of an option because it is a less reactive benzhydryl radical, but it can nevertheless combine in the *para* position with benzyl radicals (from the solvent) to form the α ,*para* combination product whose rearrangement furnishes **7b** (Scheme 4).

In contrast, thermolysis of enyne-allenes **11d,f** afforded the C^2-C^6 cyclisation products, as demonstrated by formation of the formal Diels–Alder products **13d** (80%, 110 °C, 3 h, 20 eq. of 1,4-CHD) and **13f** (85%, 110 °C, 3 h, 20 eq. of 1,4-CHD). These products are exactly those that we expect from an intermediate fulvene biradical **11d,f** after intramolecular ring closure (Scheme 5).

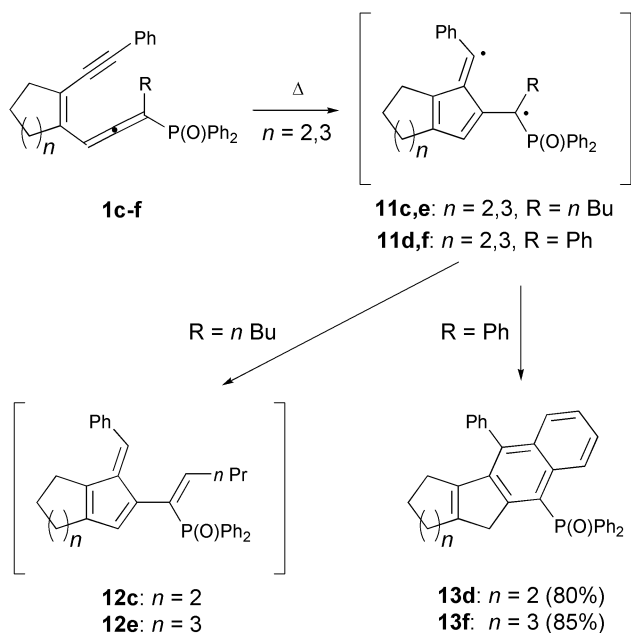
Thermolyses (5 min at 80 °C, DMSO, without 1,4-CHD) of the enyne-allenes **1c,e** also led to C^2-C^6 cyclisation products. Detailed investigations by 1H NMR (see Experimental section) showed the intermediate formation of the ene products **11c,e** through intramolecular hydrogen transfer from **11c,e**. Unfortunately, **11c,e** are not stable enough to be isolated, as they contain a vinyl fulvene as a structural motif that is prone



Scheme 4 Thermolyses of enyne-allenes **1a,b**.



Scheme 3



Scheme 5 Thermolysis of enyne-allenes **1c-f**.

to dimerisations or polymerisations.^{20,21} Indeed, prolonged heating caused decomposition of **12c,e** to unidentifiable products. Even when using different conditions for the thermolysis (various temperatures, flash pyrolysis, different solvents) complex mixtures were always furnished.

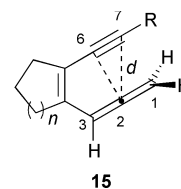
Calculations

Our original reasoning about the dramatic switch from the C²–C⁷ to the C²–C⁶ cyclisation as a function of the substituent at the alkyne terminus was based on the assumption that the transition state (TS) of the C²–C⁶ cyclisation would already show some biradical character. As a consequence, a phenyl group should stabilise the forming vinyl radical center²² and thus the TS of the C²–C⁶ cyclisation could fall beneath that of the C²–C⁷ cycloaromatisation. Recent calculations by Engels^{6c} and by Schreiner,^{10a} however, have indicated clearly that the TS of the C²–C⁶ cyclisation possesses mainly a closed-shell electronic structure. Nevertheless, the calculations indicate a lower activation barrier for the C²–C⁶ than for the C²–C⁷ cyclisation (29 vs. 30 kcal mol^{–1}). The reason for that is a resonance stabilisation of the C²–C⁶ cyclisation TS as evidenced by a significant C⁷–C^{phenyl} bond shortening (1.411 Å) when compared to the C²–C⁷ TS (1.454 Å).

Analogue quantum chemical calculations were now used to get an insight into ring size effects on the C²–C⁶ and C²–C⁷ cyclisations.²³ The geometries of all stationary points were optimised using analytical energy gradients within the density functional theory (DFT) approach²⁴ employing the B3LYP²⁵ hybrid functional in conjunction with the 6-31G(d)²⁶ basis set. Optimised stationary points were characterised as minima or transition states by the computation of the corresponding vibrational frequencies. The influence of nuclear motion and temperature effects were incorporated in the standard approach.²⁷ All calculations were performed with the Gaussian98²⁸ package.

Former studies^{6c,d,10a} showed, that DFT is sufficiently accurate to describe the barriers of activation correctly if a spatial and spin unrestricted ansatz (e.g. UB3LYP) is employed and no or only small spin contamination occurs for the transition states along the biradical pathways. In order to test for the biradical nature of the transition states, an additional check of the stability of the wavefunctions was performed²⁹ and the wavefunction as well as the geometry were reoptimised if an instability was encountered. This additional check of the wavefunction is necessary since in many cases the simple use of

Table 1 Summary of the calculated data for the transition state energies ΔG^\ddagger (298 K) of C²–C⁶ and Myers–Saito (C²–C⁷) cyclisation of model compound **15**. The energies are given in kcal mol^{–1} with respect to those of the corresponding enyne-allenes²³



	<i>n</i>	Substituent R	ΔG^\ddagger (C ² –C ⁶)	ΔG^\ddagger (C ² –C ⁷)
15a	1	H	+34.1	+25.0
15b	2	H	+27.8	+22.3
15c	3	H	+26.6	+20.6
15d	1	Ph	+30.3	+30.9
15e	2	Ph	+24.2	+28.1
15f	3	Ph	+22.2	+26.1

the unrestricted approach does not reveal an existing instability of the closed shell solution possibly found. Corrections to the pure singlet state were not performed since all optimised stationary points under consideration possess no or only minor spin contamination ($\langle S^2 \rangle \leq 0.2$). The computational results on the enyne-allenes and the transition states of both biradical cyclisations are depicted in Tables 1 and 2.

Discussion

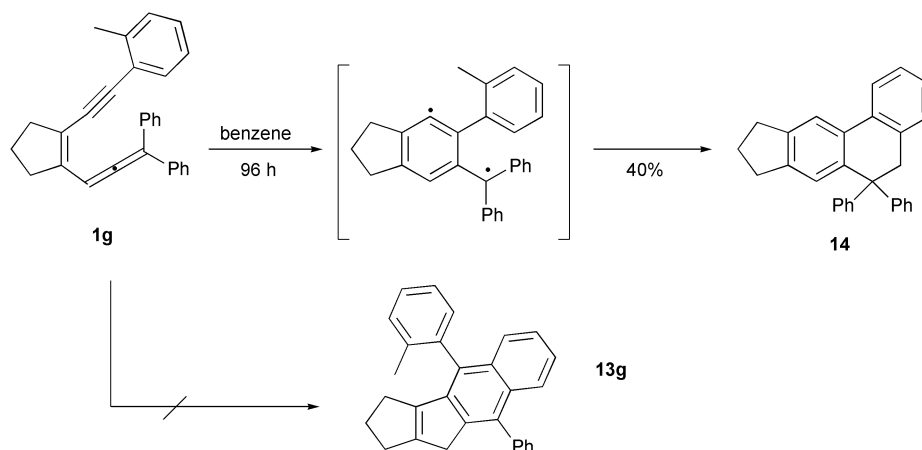
Ring strain effects and cyclisation mode

Knowing that aryl groups at the alkyne terminus redirect the course of enyne-allene cyclisations towards the C²–C⁶ mode a recent result of Wang *et al.*¹⁴ was quite surprising. Thermolysis of the cyclopentene based enyne-allene **1g** only furnished the C²–C⁷ cyclisation product **14** and not **13g** (Scheme 6). Another example of the C²–C⁷ cyclisation of a cyclopentene based enyne-allene derivative with an attached aryl group at the acetylene terminus was presented by Nakatani *et al.* in the biradical cyclisation of enyne-ketenes.³⁰

A much more detailed picture now emerges from our experimental results on the thermolyses of enyne-allenes **1a-f** which are summarised in Schemes 3 and 5. Accordingly, with cyclohexene and cycloheptene derived enyne-allenes the novel C²–C⁶ cyclisation is observed as controlled through the presence of a phenyl group at the acetylene terminus, but the Myers–Saito (C²–C⁷) cycloaromatisation is the predominant pathway for the cyclopentene based enyne-allenes. Obviously, the aryl group at the alkyne cannot override a particular ring size effect that for a 5-membered ring prefers the C²–C⁷ cyclisation.

To understand this ring size effect we have carried out calculations on the two competing biradical cyclisations using enyne-allene **15** as a model. Neither the distances $d(\text{C}^2\text{--C}^6)$ and $d(\text{C}^2\text{--C}^7)$ nor the dihedral angles ϕ and θ (Table 2) reveal a clear trend with ring size in enyne-allene **15** or with transition state free energies (Table 1) for both cyclisation modes. This is quite in contrast to Nicolaou's postulate (revised later by Maier) relating the corresponding *cd*-distance in enediynes with their thermal activation barriers.^{3a} It is clear, however, that the geometrical reorganisation along *d* when going from the enyne-allene to the transition state is much larger for the C²–C⁷ ($\Delta d \approx 150\text{--}165$ pm) than for the C²–C⁶ ($\Delta d \approx 110\text{--}120$ pm) cyclisation.

The energetics, as summarised in Table 1, are more informative indicating that the size of the embedded cycloalkene unit has a remarkable leverage on the transition state energy of the two cyclisation modes. For both hydrogen and phenyl substituents at the alkyne (i.e. for **15a-c** vs. **15d-f**) the decrease of ΔG^\ddagger with increasing ring size is stronger for the C²–C⁶ cyclisation



Scheme 6 Unexpected cyclisation pathway of enyne-allene **1g** as shown by Wang *et al.*¹⁴

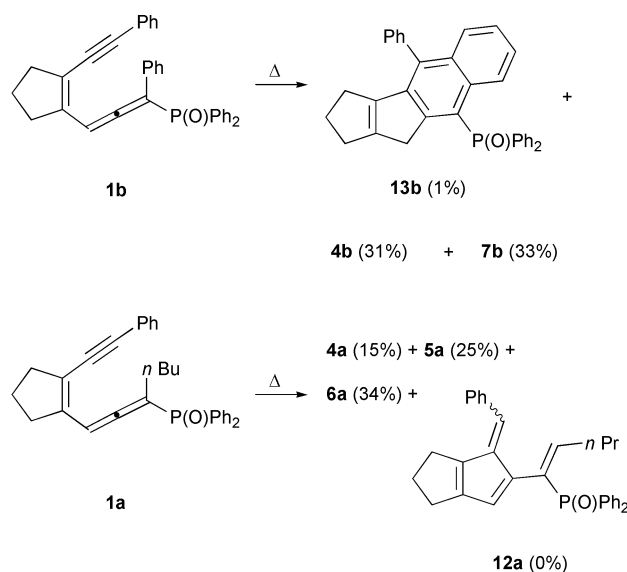
Table 2 Structural data (from calculations) for enyne-allene **15** and the corresponding C²–C⁶ and C²–C⁷ transition states (TS)

Comp.	<i>n</i>	TS C ² –C ⁶			Enyne-allene			TS C ² –C ⁷		
		<i>d</i> ^a (C ² –C ⁶)	ϕ ^b	θ ^c	<i>d</i> ^a (C ² –C ⁶)	<i>d</i> ^a (C ² –C ⁷)	θ ^c	<i>d</i> ^a (C ² –C ⁷)	ϕ ^b	θ ^c
15a	1	192.0	12.1		318.5	373.8		208.4	39.4	
15b	2	190.6	13.6		303.0	355.6		205.7	43.5	
15c	3	191.9	14.0		300.6	354.3		208.0	43.2	
15d	1	193.7	18.1	56.5	319.0	375.1	0.1	207.3	39.5	61.4
15e	2	192.8	19.2	65.5	302.6	356.0	2.2	204.1	42.7	61.3
15f	3	194.2	20.9	62.9	300.6	355.2	17.2	206.3	41.8	61.6

^a The distance *d*(C²–C⁶) or *d*(C²–C⁷) is provided in pm. ^b Dihedral angle (in °) for C³–C²–C¹–H¹. ^c Dihedral angle (in °) for C⁶–C⁷–C^{Ph}–C^{Ph}+1.

(*ca.* 8 kcal mol^{−1}) than for the C²–C⁷ cyclisation (*ca.* 5 kcal mol^{−1}). For R = H (**15a–c**) ring size effects are too small to cause a change in the regioselectivity of the cyclisation for systems; C²–C⁷ cyclisation is clearly favoured over C²–C⁶ cyclisation by all three calculated model compounds ($\Delta\Delta G^\ddagger = 6\text{--}9$ kcal mol^{−1}) as corroborated by a few experimental results from the literature.³¹ A different situation is found for the phenyl substituted systems. In agreement with earlier calculations^{6c} the phenyl group increases the barrier for the C²–C⁷ cyclisation by approximately 5.5–6 kcal mol^{−1} while it decreases the one for C²–C⁶ cyclisation by 4 ± 0.5 kcal mol^{−1}. For **15e** and **15f** the C²–C⁶ cyclisation is now clearly favoured over C²–C⁷ cyclisation by about 4 kcal mol^{−1}, in good agreement with the observed experimental data for **1c–f**. For the cyclopentenyne-allene **15d** both cyclisations have a similar activation free energy. However, while the calculated data slightly favour the C²–C⁶ cyclisation ($\Delta\Delta G^\ddagger = 0.6$ kcal mol^{−1}) the thermolysis of **1a,b** led to the formation of C²–C⁷ cyclisation products. This close energetic situation as obtained through the calculations led us to carefully reinvestigate the products from the thermolysis of **1a** and **1b**. Indeed for **1b** we could identify as a minor side product **13b** from the C²–C⁶ pathway among a large excess of Myers–Saito products (**4b**, **7b**). Compound **13b** was unequivocally identified by its spectral data and by comparison with analogous systems. Despite major efforts, only **4a**, **5a**, and **6a** but no **12a** could be detected in the thermolysis of **1a**, but this may be due to the aforementioned thermal lability of vinylfulvenes (Scheme 7).

At this point, the calculations on **15d** and the experimental results on **1a,b** show some minor deviation in the regioselectivity of the biradical cyclisation. This discrepancy may simply be related to the fact that different systems are being used for the experimental and the theoretical investigation. On the other hand, one might argue that for the five-membered ring system the product distribution is no longer exclusively controlled by the kinetic competition of the two biradical cyclisations, but—because of the unfavourable thermodynamics of the C²–C⁶ biradical—by the kinetics of the follow-up reaction. Unfortunately, reliable theoretical calculations on the biradicals

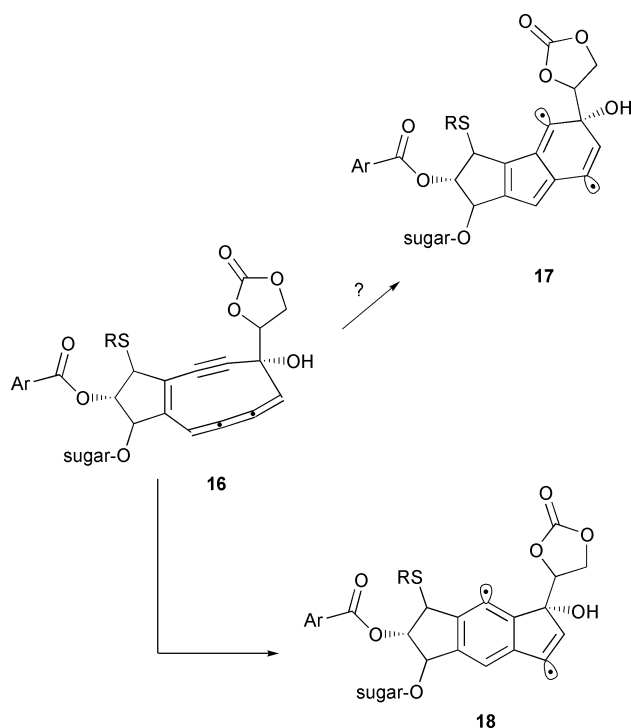


Scheme 7

and their follow-up reactions are too time consuming as density function theory would not be adequate any more.

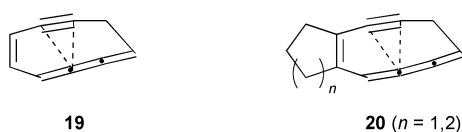
Finally, after knowing about ring size effects it seemed reasonable to ask whether the neocarzinostatin chromophore uses the cyclopentene unit to favour C²–C⁷ (leading to **18**) over C²–C⁶ cyclisation (leading to biradical **17**). Calculations by Schreiner^{10a} indicate that smaller cyclic enyne-allenes (8- and 9-membered systems) prefer kinetically the C²–C⁶ cyclisation pathway and one could imagine that this preference also should be valid for the cyclic 9-membered enyne-cumulene **16** as found at the heart of the neocarzinostatin cycloaromatisation (Scheme 8).³²

The C²–C⁷ biradical mode in **19** has been evaluated recently using BPW91/cc-pVDZ quantum mechanical calculations³³ without addressing alternative pathways. Our UB3LYP DFT



Scheme 8

calculations on **19** now reveal that the C²–C⁶ cyclisation pathway ($\Delta G^\ddagger = 17.6 \text{ kcal mol}^{-1}$) is kinetically favoured over the C²–C⁷ mode ($\Delta G^\ddagger = 20.8 \text{ kcal mol}^{-1}$). As 68% of the products in the neocarzinostatin cycloaromatisation are derived from biradical **18**, one has to assume that nature uses the annulated cyclopentene ring in **16** to control the regioselectivity of the biradical cyclisations!



Further calculations, in particular with regard to the cyclisation modes of **20** with $n = 1, 2$, are currently under way in our laboratories to clarify this point of interest. So far, calculations from other groups have solely focused on the straightforward C²–C⁷ cyclisation of enyne-cumulenes,^{33,34} while experimental investigations on neocarzinostatin models follow the natural bicyclic[7.3.0] system³⁵ or—because of thermal stability—operate with increased ring size of the larger ring.³⁶ At present, no experimental data on the parent nine-membered enyne-[3]cumulene are available to prove or disprove an alternative C²–C⁶ cyclisation. But it is clear from literature reports on related systems that competitive biradical cyclisations may be quite reasonable options.^{31c,34,37}

The kinetically controlled switch in the regioselectivity between the Myers–Saito and the C²–C⁶ cyclisation as a function of the ring size is most likely due to ring strain that already materialises partly in the transition state and that is substantial in the biradicals. To estimate the differential strain in the Myers–Saito vs. the C²–C⁶ biradicals depending on the ring size we have determined the relative energy differences $\Delta\Delta E$ (**21–22**) employing DFT.³⁸ The data in Table 3 reveal clearly a parallel trend for both the differential activation data and $\Delta\Delta E$ (**21–22**). In both sets of data an increase is observed when going from the unstrained systems **b,c** (with 6- and 7-membered rings) to **a** (5-membered ring). Since the increase is much more pronounced for $\Delta\Delta E$ (**21–22**) than for $\Delta\Delta G^\ddagger$ (C²–C⁶ vs. C²–C⁷) only a part of the strain in the biradicals is already found in the transition states.

Table 3 Comparison of differential energies for **21a–c** vs. **22a–c** and of the differential free activation energies for **15a–c**

		21a–c	22a–c
	n	$\Delta\Delta G^\ddagger$ (C ² –C ⁶ vs. C ² –C ⁷) for 15a–c	$\Delta\Delta E$ (21–22)
a	1	9.1	+38.5
b	2	5.5	+32.8
c	3	6.0	+33.3

Conclusion

Ring size effects can be used to control the regioselectivity of thermal enyne–allene cyclisations, allowing either the Myers–Saito (with cyclopentenyne–allenes) or C²–C⁶ cyclisation products (with larger cycloalkenyne–allenes) to be accessed. This toggle is in line with calculations on the DFT level. Neocarzinostatin also seems to make use of the annulated cyclopentene ring to control its Myers–Saito (C²–C⁷) cyclisation to **18**, since in the parent 9-membered cyclic enyne-cumulene the C²–C⁶ biradical is kinetically favoured over the C²–C⁷ cyclisation.

Experimental

Preamble

All J values are given in Hz. SDDA = sodium diethyldihydroaluminate. In almost all cases purification was achieved by standard column chromatography; in such cases only the solvent (mixture) is provided. For details about the equipment used please consult ref. 6b. Compound **2a** was synthesised according to ref. 31a.

Compound 2c. To a mixture of cyclohexene–bromocarbaldehyde (5.00 g, 26.4 mmol) (prepared analogously to Arnold and Holý¹⁶) and phenylacetylene (3.10 g, 30.4 mmol) in triethylamine (100 cm³) were added PdCl₂(PPh₃)₂ (278 mg, 396 μmol) and CuI (125 mg, 655 μmol). After stirring the black solution for 16 h at room temperature it was quenched with a mixture of saturated aqueous ammonium chloride (200 cm³) and n -pentane (200 cm³). After filtration the aqueous layer was washed with n -pentane (2 × 100 cm³). The combined organic layers were dried (MgSO₄) and evaporated under reduced pressure to furnish a brown oil. After purification by column chromatography (silica gel, n -pentane–diethyl ether = 10 : 1) carbaldehyde **2c** (4.45 g, 80%) was isolated as a brown oil (Found: C, 85.93; H, 6.95. C₁₅H₁₄O requires C, 85.67; H, 6.72%); $\tilde{\nu}_{\text{max}}$ (film)/cm^{−1} 3056, 2935, 2860, 2732, 2199, 1673, 1603, 1489, 1442, 758 and 689; δ_{H} (200 MHz; CDCl₃; Me₄Si) 1.63–1.64 (4 H, m), 2.20–2.30 (2 H, m), 2.40–2.50 (2 H, m), 7.28–7.45 (3 H, m), 7.40–7.45 (2 H, m), 10.28 (1 H, s, CHO); δ_{C} (50 MHz; CDCl₃; Me₄Si) 21.5, 22.3, 22.5, 32.7, 86.7, 98.9, 122.7, 128.9, 129.9, 135.1, 140.4, 143.0, 193.3.

Compound 2e. Analogously to **2c** a mixture of cycloheptene–bromocarbaldehyde (2.00 g, 9.85 mmol), phenylacetylene (1.14 g, 11.2 mmol) in triethylamine (35 cm³), PdCl₂(PPh₃)₂ (104 mg, 148 μmol), and CuI (46.6 mg, 244 μmol) were allowed to react. After stirring the black solution for 72 h at room temperature it was worked up as described above. The purification of the remaining brown oil *via* column chromatography on silica gel with a mixture of petroleum ether–diethyl ether (10 : 1) afforded the carbaldehyde **2e** (1.62 g, 73%) as a yellow oil (Found: 224.1197. C₁₆H₁₆O requires 224.1201); $\tilde{\nu}_{\text{max}}$ (film)/cm^{−1}

3055, 2922, 2850, 2189, 1669, 1599, 1588, 1489, 757 and 670; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 1.40–1.50 (2 H, m), 1.68–1.74 (2 H, m), 1.80–1.83 (2 H, m), 2.52–2.57 (2 H, m), 2.68–2.73 (2 H, m), 7.33–7.37 (2 H, m), 7.45–7.47 (1 H, m), 7.49–7.50 (2 H, m) 10.30 (1 H, s, CHO); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 24.4, 25.8, 25.9, 32.4, 37.6, 87.8, 100.4, 122.5, 128.6, 129.3, 131.8, 145.9, 148.7, 192.4; m/z 224 (M^+ , 64%), 195 (30), 167 (100).

Compound 3a. At room temperature a solution of hex-1-yne (452 mg, 5.50 mmol) in dry diethyl ether (5 cm^3) was added to a solution of ethylmagnesium bromide (prepared from ethyl bromide (600 mg, 5.51 mmol) and magnesium turnings (134 mg, 5.51 mmol) in dry diethyl ether (5 cm^3)) and heated under reflux for 3 h. Carbaldehyde **2a** (800 mg, 4.08 mmol) dissolved in diethyl ether (5 cm^3) was added to the Grignard solution at room temperature and stirred at this temperature for 16 h. It was then quenched with aqueous saturated ammonium chloride (10 cm^3). After extraction of the aqueous layer with diethyl ether (3 \times 10 cm^3) the combined organic layers were dried (MgSO_4), filtered and concentrated to furnish a brown oil, which was purified by column chromatography (silica gel, *n*-pentane–dichloromethane–diethyl ether = 5 : 5 : 1). Propargyl alcohol **3a** (930 mg, 82%) was afforded as a yellow oil (Found: 278.1666. $\text{C}_{20}\text{H}_{22}\text{O}$ requires 278.1671); $\tilde{\nu}_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3374, 3080, 3049, 2956, 2933, 2871, 2274, 2219, 1596, 1489, 1442, 1379, 1124, 1009, 954, 756, 732 and 691; δ_{H} (200 MHz; CDCl_3 ; Me_4Si) 0.90 (3 H, t, J 7.1, CH_2CH_3), 1.30–1.57 (4 H, m), 1.94 (2 H, quintet, J 8.0, cyclo- $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.22 (2 H, td, J 6.9, J 1.9, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 2.45 (1 H, s, OH), 2.62 (2 H, tt, J 8.0, J 2.3, cyclo- $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 2.66 (2 H, tt, J 8.0, J 2.3, cyclo- $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 5.52 (1 H, t, J 1.9, $\text{HOCHC}\equiv\text{C}$), 7.26–7.32 (3 H, m), 7.42–7.46 (2 H, m); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 13.4, 18.3, 21.8, 22.1, 30.5, 31.3, 36.8, 60.0, 78.6, 84.4, 86.2, 94.8, 120.6, 123.1, 128.0, 128.1, 131.3, 149.0.

Compound 3b. As described above for the synthesis of **3a** phenylacetylene (562 mg, 5.50 mmol) in dry diethyl ether (5 cm^3) was allowed to react with ethylmagnesium bromide, prepared from ethyl bromide (600 mg, 5.51 mmol) and magnesium turnings (134 mg, 5.51 mmol) in dry diethyl ether (5 cm^3), and the resulting Grignard reagent was treated with **2a** (800 mg, 4.08 mmol), dissolved in dry diethyl ether (5 cm^3). After work-up, purification by column chromatography (silica gel, *n*-pentane–dichloromethane–diethyl ether = 5 : 5 : 1) furnished propargyl alcohol **3b** as an orange oil (953 mg, 78%) (Found: 297.1272. $\text{C}_{22}\text{H}_{17}\text{O}$ ($\text{M}^+ - 1$) requires 297.1279); $\tilde{\nu}_{\text{max}}(\text{film})/\text{cm}^{-1}$ 3347, 3056, 2955, 2849, 2223, 2196, 1597, 1490, 1442, 1177, 1036, 990, 932, 756, 733 and 690; δ_{H} (200 MHz; CDCl_3 ; Me_4Si) 1.98 (2 H, quintet, J 7.6, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.65 (2 H, tt, J 7.6, J 2.2, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.70 (1 H, br s, OH), 2.77 (2 H, tt, J 7.6, J 2.2, $\text{CH}_2\text{CH}_2\text{CH}_2$), 5.79 (1 H, $\text{HOCHC}\equiv\text{C}$), 7.28–7.32 (6 H, m), 7.44–7.50 (4 H, m); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 22.1, 31.3, 36.9, 60.3, 84.4, 85.3, 87.6, 95.2, 121.4, 122.4, 123.0, 128.1, 128.2 (2 C), 128.3, 131.4, 131.7, 148.2.

Compound 3c. Hex-1-yne (2.75 cm^3 , 22.5 mmol) was added dropwise to a solution of 2 M SDDA (5.25 cm^3 , 10.5 mmol) in toluene (25 cm^3). The mixture was stirred for 3 h at ambient temperature until gas evolution stopped. At 0 $^\circ\text{C}$ a mixture of **2c** (1.85 g, 8.77 mmol) in toluene (5 cm^3) was added slowly. After stirring at room temperature for 3 h the reaction mixture was quenched with saturated aqueous ammonium chloride (40 cm^3). After the aqueous layer had been extracted with ethyl acetate (4 \times 40 cm^3), the combined organic layers were dried (MgSO_4), filtered and concentrated. Purification by column chromatography (silica gel, *n*-pentane–diethyl ether = 8 : 1) afforded propargyl alcohol **3c** (2.06 g, 80%) as a red oil (Found: 292.1826. $\text{C}_{21}\text{H}_{24}\text{O}$ requires 292.1827); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3373, 3055, 2930, 2860, 2302, 2276, 1597, 1483, 1442, 755 and 690; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 0.88 (3 H, t, J 7.0, CH_2CH_3), 1.31–1.47

(4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.50–1.72 (4 H, m, cyclo- CH_2CH_2), 2.20 (2 H, td, J 7.2, J 2.0, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 2.11–2.31 (2 H, m, cyclo- CH_2), 2.32–2.40 (2 H, m, cyclo- CH_2), 2.70 (1 H, s, OH), 5.72 (1 H, t, J 2.0, $\text{HOCHC}\equiv\text{C}$), 7.24–7.28 (3 H, m), 7.38–7.41 (2 H, m); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 14.0, 18.9, 22.4, 22.5, 22.7, 23.9, 30.6, 31.1, 64.7, 79.1, 86.6, 88.5, 93.6, 118.0, 123.8, 128.4, 128.7, 131.8, 144.4; m/z 292 (M^+ , 8%), 275 (14), 211 (100).

Compound 3d. As described for **3c**, phenylacetylene (2.47 cm^3 , 22.5 mmol) was allowed to react with a 2 M SDDA solution in toluene (5.25 cm^3 , 10.5 mmol) and with **2c** (1.85 g, 8.77 mmol) in toluene (5 cm^3). After work-up the remainder was purified by column chromatography (silica gel, *n*-pentane–diethyl ether = 4 : 1) to afford propargyl alcohol **3d** (2.4 g, 87%) as a red oil (Found: 312.1503. $\text{C}_{23}\text{H}_{20}\text{O}$ requires 312.1514); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3374, 3079, 2930, 2848, 2212, 2202, 1597, 1571, 1487, 754 and 690; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 1.71 (4 H, br s, cyclo- CH_2), 2.33 (2 H, br s, cyclo- CH_2), 2.47 (2 H, br s, cyclo- CH_2), 2.83 (1 H, s, OH), 5.98 (1 H, s, $\text{HOCHC}\equiv\text{C}$), 7.29–7.32 (6 H, m), 7.41–7.48 (4 H, m); δ_{C} (50 MHz; CDCl_3 ; Me_4Si) 22.6, 24.2, 27.4, 30.7, 65.1, 85.9, 88.5, 88.7, 94.0, 118.9, 123.1, 123.8, 128.6, 128.7, 128.8, 128.9, 131.9, 132.3, 143.7; m/z 312 (M^+ , 43%), 295 (37), 294 (100).

Compound 3e. As described above for **3c**, hex-1-yne (850 mm^3 , 7.44 mmol) was allowed to react with 2 M SDDA (1.74 cm^3 , 3.47 mmol) in toluene (10 cm^3) and to this mixture was added **2e** (650 mg, 2.9 mmol). After stirring for 17 h at ambient temperature and work-up the residue was purified by column chromatography (petroleum (bp 40–60 $^\circ\text{C}$)–diethyl ether = 4 : 1) to furnish propargyl alcohol **3e** (750 mg, 85%) as a yellow oil (Found: 306.1977. $\text{C}_{22}\text{H}_{26}\text{O}$ requires 306.1983); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3390, 3054, 2924, 2851, 2275, 2220, 1596, 1480, 755 and 690; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 0.90 (3 H, t, J 7.0, CH_2CH_3), 1.36–1.50 (4 H, m, cyclo- CH_2), 1.51–1.67 (4 H, m, $\text{CH}_2\text{CH}_2\text{-CH}_3$), 1.74–1.87 (2 H, m, cyclo- CH_2), 2.06 (1 H, s, OH), 2.23 (2 H, td, J 7.0, J 1.8, $\text{C}\equiv\text{CCH}_2$), 2.46–2.51 (4 H, m, cyclo- CH_2), 5.71 (1 H, d, J 1.8, $\text{HOCHC}\equiv\text{C}$), 7.28–7.30 (2 H, m), 7.32–7.35 (1 H, m), 7.41–7.44 (2 H, m); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 13.6, 18.3, 21.9, 26.2, 27.2, 28.8, 30.7, 32.5, 34.9, 65.3, 79.0, 86.4, 89.5, 93.8, 123.3, 123.6, 128.0, 128.3, 131.3, 149.4; m/z 306 (M^+ , 67%), 289 (100), 229 (28).

Compound 3f. As described above for the synthesis of **3c**, phenylacetylene (820 mm^3 , 7.44 mmol) was allowed to react with 2 M SDDA (1.74 cm^3 , 3.47 mmol) in toluene (10 cm^3) and with **2e** (650 mg, 2.90 mmol). After stirring for 17 h at ambient temperature it was worked up as described before. Purification (silica gel, petroleum (bp 40–60 $^\circ\text{C}$)–diethyl ether = 4 : 1) afforded propargyl alcohol **3f** (783 mg, 83%) as a yellow oil (Found: 326.1663. $\text{C}_{24}\text{H}_{22}\text{O}$ requires 326.1670); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3375, 3054, 2922, 2850, 2226, 2195, 1596, 1569, 1480, 754 and 690; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 1.63–1.68 (4 H, m, cyclo- CH_2CH_2), 1.79–1.83 (2 H, m, cyclo- CH_2), 2.24 (1 H, s, OH), 2.50–2.61 (4 H, m, cyclo- CH_2), 5.97 (1 H, s, $\text{HOCHC}\equiv\text{C}$), 7.30–7.34 (6 H, m), 7.43–7.48 (4 H, m); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 26.1, 27.2, 29.0, 32.5, 35.0, 65.6, 85.5, 88.1, 89.4, 94.1, 122.7, 123.5, 124.1, 128.1, 128.2, 128.3, 128.5, 131.4, 131.8, 148.7; m/z 326 (M^+ , 81%), 308 (100), 249 (12).

Compound 1a. Propargyl alcohol **3a** (218 mg, 783 μmol) and triethylamine (87.6 mg, 866 μmol) were dissolved in THF (10 cm^3). After cooling to $-80\text{ }^\circ\text{C}$ chlorodiphenylphosphane (192 mg, 870 μmol) was added dropwise during 15 min under vigorous stirring. After stirring at $-80\text{ }^\circ\text{C}$ for another 10 minutes the suspension was allowed to warm up slowly to room temperature (2 h). Then water (10 cm^3) and dichloromethane (10 cm^3) were added, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (2 \times 10 cm^3). The combined organic layers were dried (MgSO_4), filtered and con-

centrated *in vacuo*. Purification of the residue (silica gel, diethyl ether) afforded enyne-allene **1a** (326 mg, 90%) as a yellow oil that crystallised on standing (Found: 462.2110. $C_{32}H_{31}OP$ requires 462.2113); mp 98 °C (differential scanning calorimetry (DSC)); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3078, 3059, 2958, 2928, 2870, 2852, 2186, 1925, 1488, 1438, 1194, 1117, 1101, 831, 760, 724, 701 and 692; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.84 (3 H, t, J 7.2, CH_2CH_3), 1.25–1.39 (2 H, m, cyclo- CH_2), 1.44–1.57 (2 H, m, cyclo- CH_2), 1.70–1.90 (2 H, m, cyclo- CH_2), 1.95–2.39 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.47–2.57 (2 H, m, $\text{C}=\text{C}=\text{CCH}_2\text{CH}_2$), 6.42 (1 H, td, J 11.0, J 3.2, $\text{CHC}=\text{C}=\text{C}$), 7.24–7.34 (3 H, m), 7.36–7.54 (8 H, m), 7.65–7.80 (4 H, m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.7, 22.3, 22.4, 28.0 (d, J 5.7), 30.6 (d, J 5.7), 33.3, 37.0, 85.4 (d, J 2.9), 93.3 (d, J 14.3), 96.5 (d, J 1.9), 101.3 (d, J 99.2), 121.5 (d, J 4.8), 123.3, 128.1, 128.1 (d, J 12.4), 128.2, 128.3 (d, J 12.4), 131.3, 131.5 (d, J 9.5), 131.5 (d, J 9.5), 131.7 (d, J 2.9), 131.8 (d, J 103.0), 131.9 (d, J 2.9), 131.9 (d, J 105.0), 141.7 (d, J 9.5), 211.6 (d, J 5.7); $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 28.6 (s).

Compound 1b. Propargyl alcohol **3b** was reacted as described for **1a**. Accordingly, **3b** (273 mg, 915 μmol), triethylamine (102 mg, 1.01 mmol), both dissolved in THF (15 cm^3), were treated with chlorodiphenylphosphane (222 mg, 1.01 mmol). After purification (silica gel, diethyl ether) enyne-allene **1b** was isolated as a yellow oil (385 mg, 87%) which crystallised on standing (Found: 481.1716. $C_{34}H_{26}OP$ ($M - 1$) requires 481.1721); mp 56 °C (DSC); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3057, 2957, 2840, 2197, 1913, 1719, 1708, 1596, 1490, 1438, 1176, 1119, 1098, 1071, 757, 726, 693 and 546; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.69–1.95 (2 H, m, CH_2), 2.08–2.20 (2 H, m, CH_2), 2.48–2.57 (2 H, m, CH_2), 6.56 (1 H, d, J 10.7, $\text{CHC}=\text{C}=\text{C}$), 7.14–7.30 (6 H, m), 7.33–7.52 (8 H, m), 7.59–7.62 (2 H, m), 7.68–7.81 (4 H, m); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 22.5, 33.3, 37.0, 85.2 (d, J 2.8), 94.2 (d, J 12.8), 97.0, 103.9 (d, J 99.2), 122.9 (d, J 4.8), 123.1, 127.8, 128.2 (d, J 12.4), 128.2, 128.3, 128.3 (d, J 11.4), 128.3 (d, J 4.8), 128.6, 131.3, 131.6 (d, J 9.5), 131.7 (d, J 9.5), 131.8 (d, J 2.9), 132.0 (d, J 2.9), 132.1 (d, J 106.8), 132.1 (d, J 105.9), 132.1 (d, J 5.7), 140.5 (d, J 8.6), 215.1 (d, J 4.8); $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 28.9 (s).

Compound 1c. As described above for **1a**, propargyl alcohol **3c** (400 mg, 1.36 mmol) was allowed to react with chlorodiphenylphosphane (356 mg, 1.64 mmol) and triethylamine (271 mg, 1.64 mmol). Purification of the crude product (silica gel, petroleum (bp 40–60 °C)–acetone = 4 : 1) afforded the enyne-allene **1c** (565 mg, 87%) as a yellow oil (Found: 476.2258. $C_{33}H_{33}OP$ requires 476.2258); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3054, 2929, 2197, 1920, 1590, 1484, 1438, 1195, 1117, 754, 721 and 692; $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.85 (3 H, t, J 7.0, CH_2CH_3), 1.24–1.43 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.47–1.55 (4 H, m, cyclo- CH_2), 1.62–1.75 (1 H, br s, cyclo- CH_2), 1.90–2.05 (1 H, br s, cyclo- CH_2), 2.18–2.30 (2 H, m, cyclo- CH_2), 2.35 (2 H, tdd, J 17.6, J 7.7, J 3.2, $\text{C}=\text{C}=\text{CCH}_2$), 6.66 (1 H, dt, J 11.2, J 3.2, $\text{CHC}=\text{C}=\text{C}$), 7.29–7.34 (2 H, m), 7.36–7.52 (9 H, m), 7.63–7.83 (4 H, m); $\delta_{\text{C}}(63 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.2, 22.4, 22.7, 22.8, 26.9, 28.5, 31.0, 31.1, 89.5, 95.0, 99.0 (d, J 14.2), 102.6 (d, J 99.1), 118.3, 123.9, 128.5 (d, J 11.3), 128.7, 128.9, 132.1 (d, J 4.5), 132.3 (d, J 105.9), 132.4, 134.8 (d, J 12.2), 136.4, 210.3 (d, J 5.7); $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 29.1 (s).

Compound 1d. As described above for **1a**, the enediyne **3d** (360 mg, 1.15 mmol) was brought to reaction with chlorodiphenylphosphane (338 mg, 1.54 mmol) and triethylamine (158 mg, 1.53 mmol). Purification of the crude product (silica gel, petroleum (bp 40–60 °C)–acetone–dichloromethane = 5 : 1 : 2) afforded enyne-allene **1d** (410 mg, 71%) as a yellow oil (Found: 496.1944. $C_{35}H_{29}OP$ requires 496.1945); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3056, 2933, 2860, 2198, 1911, 1592, 1490, 1437, 1195, 1117, 737, 724 and 693; $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.55 (4 H, br s, CH_2), 1.70 (1 H, br s, CH_2), 2.02 (1 H, br s, CH_2), 2.24 (2 H, br s,

CH_2), 6.85 (1 H, d, J 10.6, $\text{CHC}=\text{C}=\text{C}$), 7.21–7.40 (6 H, m), 7.44–7.55 (8 H, m), 7.65–7.72 (6 H, m); $\delta_{\text{C}}(50 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 22.3, 22.6, 27.0, 31.0, 89.3, 95.3, 99.9 (d, J 11.7), 105.5 (d, J 99.1), 119.1, 127.5, 127.6, 127.9, 128.0, 128.3 (d, J 11.7), 128.6, 128.7, 131.3 (d, J 12.4), 131.7 (d, J 5.1), 132.0, 132.1 (d, J 108.4), 132.4, 135.5, 214.4 (d, J 4.8); $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 28.6 (s).

Compound 1e. As described for **1a**, propargyl alcohol **3e** (200 mg, 654 μmol) was reacted with chlorodiphenylphosphane (173 mg, 788 μmol) and triethylamine (79 mg, 784 μmol). After stirring for 30 min at 0 °C and 1 h at ambient temperature standard work-up was followed. The purification (silica gel, petroleum (bp 40–60 °C)–ethyl acetate = 1 : 1) afforded **1e** (290 mg, 90%) as a yellow oil (Found: C, 83.01; H, 7.05. $C_{34}H_{35}OP$ requires C, 83.22; H, 7.20%); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3056, 2927, 2853, 2184, 1919, 1591, 1488, 1194, 1117, 755, 722 and 690; $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.84 (3 H, t, J 7.3, CH_2CH_3), 1.06–1.42 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.43–1.70 (6 H, m, cyclo- CH_2), 2.10–2.18 (2 H, m, cyclo- CH_2), 2.26–2.43 (4 H, cyclo- CH_2 , $\text{C}=\text{C}=\text{CCH}_2$), 6.67 (1 H, td, J 3.1, J 3.1, $\text{CHC}=\text{C}=\text{C}$), 7.26–7.32 (3 H, m), 7.37–7.48 (8 H, m), 7.62–7.82 (4 H, m); $\delta_{\text{C}}(63 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 13.9, 22.4, 26.0, 26.4, 28.1, 30.4, 30.6, 33.4, 35.1, 90.8, 95.6, 100.0 (d, J 14.3), 102.5 (d, J 99.6), 123.2, 127.9, 128.1 (d, J 12.2), 128.4, 131.1, 131.5 (d, J 9.2), 131.7, 131.8 (d, J 3.1), 131.9 (d, J 103.7), 142.4, 210.7 (d, J 5.7); $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 30.7 (s).

Compound 1f. As described above for **1a**, propargyl alcohol **3f** (200 mg, 612 μmol) was treated with chlorodiphenylphosphane (162 mg, 739 μmol) and triethylamine (75.0 mg, 741 μmol). After stirring for 30 min at 0 °C and for 1 h at ambient temperature the work-up followed that described above. Purification (silica gel, petroleum (bp 40–60 °C)–ethyl acetate = 1 : 1) afforded enyne-allene **1f** (218 mg, 70%) as a pale-red oil (Found: 510.2105. $C_{36}H_{31}OP$ requires 510.2112); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3056, 2924, 2852, 2202, 1911, 1594, 1490, 1182, 1117, 759 and 694; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.18–1.39 (2 H, m, CH_2), 1.44–1.79 (4 H, CH_2), 2.10–2.27 (2 H, CH_2), 2.36–2.49 (2 H, CH_2), 6.85 (1 H, d, J 10.4, $\text{CHC}=\text{C}=\text{C}$), 7.19–7.37 (6 H, m), 7.39–7.53 (8 H, m), 7.55–7.65 (2 H, m), 7.72–7.81 (4 H, m); $\delta_{\text{C}}(63 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 26.0, 28.9, 29.6, 33.3, 34.9, 86.4, 92.9, 105.4 (d, J 98.8), 109.9 (d, J 105.2), 124.3, 127.3, 127.8, 128.0, 128.2, 128.3, 128.5, 128.6 (d, J 12.2), 131.1, 131.3 (d, J 95.5), 131.6 (d, J 9.2), 131.8, 131.9, 139.1, 210.7 (d, J 5.7); $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 28.9 (s).

Thermolysis of enyne-allenes **1a–f**

All enyne-allenes were thermolysed in toluene or mesitylene in the presence of 20 equivalents of the cyclohexa-1,4-diene. For solvent, duration, temperature and yields see Table 4. After several hours the solvent was removed under reduced pressure and the mixture was purified by column chromatography if necessary.³⁸

Compound 4a. Column chromatography on silica gel with petroleum (bp 40–60 °C)–ethyl acetate (1 : 1) as eluent provided the cyclisation product **4a** as a yellow oil (Found: 464.2270. $C_{32}H_{33}OP$ requires 464.2269); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3056, 3023, 2955, 2932, 2861, 1480, 1437, 1185, 1116, 1101, 1072, 1028, 885, 722 and 698; $\delta_{\text{H}}(600 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.72 (3 H, t, J 7.2, CH_2CH_3), 1.05–1.13 (3 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.22–1.28 (1 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.72–1.79 (1 H, m, CHCH_2CH_2), 2.12–2.17 (3 H, m, cyclo- CH_2 , CHCH_2CH_2), 2.85–2.94 (2 H, cyclo- CH_2), 2.95–3.00 (m, 1H, cyclo- CH_2), 3.05–3.10 (1 H, m, cyclo- CH_2), 3.62 (1 H, ddd, J 11.4, J 8.1, J 3.2, CHCH_2CH_2), 6.00 (2 H, br s), 6.87 (1 H, s), 7.01 (2 H, dd, J 11.1, J 7.1), 7.14–7.17 (2 H, m), 7.20–7.29 (2 H, br s), 7.28 (1 H, t, J 7.3), 7.35 (1 H, t, J 7.4), 7.44–7.47 (2 H, m), 7.52 (1 H, t, J 7.4), 7.57 (2 H, dd, J 11.0,

Table 4 Reaction conditions and products of thermolyses of enyne-allenes **1a–f**

Enyne-allene	Conditions	Products
1a	20 eq. 1,4-CHD, mesitylene, reflux, 1 h	4a (15%), 5a (25%), 6a (34%)
1b	20 eq. 1,4-CHD, toluene, reflux, 18 h	4b (31%), 7b (33%), 13b (1%)
1c	20 eq. 1,4-CHD, toluene, reflux, 5 min	[12c] ³⁹
1d	20 eq. 1,4-CHD, toluene, reflux, 3 h	13d (80%)
1e	20 eq. 1,4-CHD, toluene, reflux, 5 min	[12e] ³⁹
1f	20 eq. 1,4-CHD, toluene, reflux, 3 h	13f (85%)

J 7.8), 7.77 (1 H, s); δ_{C} (151 MHz; CDCl_3 ; Me_4Si) 13.7, 22.5, 25.5, 30.0 (d, *J* 12.6), 30.3 (d, *J* 1.1), 32.6, 32.8, 41.6 (d, *J* 67.7), 124.5 (d, *J* 4.6), 125.5 (d, *J* 1.7), 126.6, 127.7, 127.7 (d, *J* 11.5), 128.5 (d, *J* 11.5), 129.6, 131.1 (d, *J* 2.9), 131.2 (d, *J* 102.7), 131.4 (d, *J* 5.7), 131.5 (d, *J* 9.2), 131.5 (d, *J* 8.0), 131.6, 132.9 (d, *J* 97.5), 141.3 (d, *J* 7.5), 141.7 (d, *J* 1.2), 142.7 (d, *J* 2.9), 143.9 (d, *J* 2.3); δ_{P} (162 MHz; CDCl_3 ; H_3PO_4) 34.8 (s).

Compound 4b. Column chromatography (silica gel, dichloromethane–diethyl ether = 20 : 1) afforded product **4b** as colourless oil (Found: 484.1946. $\text{C}_{34}\text{H}_{29}\text{OP}$ requires 484.1956); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3057, 3026, 2951, 2844, 1599, 1493, 1479, 1437, 1265, 1201, 1178, 1117, 1072, 1030, 998, 920, 888, 733 and 698; δ_{H} (600 MHz; CDCl_3 ; Me_4Si) 2.02–2.09 (2 H, m, CH_2), 2.78–2.87 (2 H, m, cyclo- CH_2), 2.93–3.03 (2 H, m, cyclo- CH_2), 4.79 (1 H, d, *J* 9.5, CH), 6.88 (2 H, br s), 6.92 (1 H, m), 7.09 (1 H, t, *J* 7.2), 7.11–7.14 (2 H, m), 7.19–7.22 (2 H, m), 7.24–7.26 (2 H, m), 7.28–7.32 (3 H, m), 7.33–7.37 (5 H, m), 7.40 (1 H, t, *J* 7.4), 7.44 (2 H, dd, *J* 11.0, *J* 7.6), 8.37 (1 H, s); δ_{C} (151 MHz; CDCl_3 ; Me_4Si) 25.3, 32.4, 32.8, 48.7 (d, *J* 65.4), 125.8, 126.1 (d, *J* 5.7), 126.5 (d, *J* 2.3), 127.0, 127.9, 127.9 (d, *J* 11.5), 128.1 (d, *J* 11.5), 128.1 (d, *J* 2.3), 129.6, 130.0 (d, *J* 5.7), 131.1 (d, *J* 2.3), 131.2 (d, *J* 2.3), 131.2 (d, *J* 8.6), 131.3 (d, *J* 9.2), 132.2 (d, *J* 99.1), 132.2 (d, *J* 4.0), 132.6 (d, *J* 97.0), 136.9 (d, *J* 5.2), 140.4 (d, *J* 8.6), 141.8, 142.9 (d, *J* 1.7), 144.0 (d, *J* 1.1); δ_{P} (162 MHz; CDCl_3 ; H_3PO_4) 32.4 (s).

Compound 5a. Column chromatography (silica gel, petroleum (bp 40–60 °C)–ethyl acetate = 1 : 1) furnished product **5a** as a pale yellow oil (Found: 462.2121. $\text{C}_{32}\text{H}_{31}\text{OP}$ requires 462.2113); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3059, 3011, 2954, 2864, 1439, 1314, 1179, 1110, 1027, 999, 911, 730, 698 and 643; δ_{H} (600 MHz; CDCl_3 ; Me_4Si) 0.41–0.53 (2 H, m, cyclo- CH_3), 0.64 (3 H, t, *J* 7.4, CH_2CH_3), 1.12 (2 H, qt, *J* 7.4, *J* 7.5, CH_2CH_3), 2.09 (2 H, tt, *J* 7.5, *J* 7.4, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.60–2.66 (1 H, cyclo- CH_2), 2.69–2.76 (1 H, cyclo- CH_2), 2.81–2.90 (2 H, m, cyclo- CH_2), 2.92 (2 H, t, *J* 7.4, CCH_2CH_2), 7.00 (1 H, s), 7.13 (1 H, t, *J* 7.5), 7.19–7.27 (5 H, m), 7.28 (1 H, d, *J* 7.5), 7.30–7.35 (3 H, m), 7.36–7.43 (3 H, m), 7.43 (1 H, s), 7.51 (1 H, d, *J* 7.5); δ_{C} (151 MHz; CDCl_3 ; Me_4Si) 13.7, 22.8, 24.8 (d, *J* 10.2), 25.5, 31.3 (d, *J* 1.5), 32.6, 32.7, 58.2 (d, *J* 61.5), 115.4 (d, *J* 1.5), 119.1 (d, *J* 1.5), 121.7 (d, *J* 2.9), 125.6 (d, *J* 2.9), 126.1 (d, *J* 2.4), 127.5 (2 C, d, *J* 10.7), 127.6 (d, *J* 1.9), 130.2 (d, *J* 95.0), 130.3 (d, *J* 95.0), 131.3 (2 C, d, *J* 2.9), 132.1 (d, *J* 7.8), 132.2 (d, *J* 8.2), 140.6 (d, *J* 4.9), 141.3 (d, *J* 1.9), 142.4 (d, *J* 4.9), 143.3 (d, *J* 2.4), 143.4 (d, *J* 2.4), 144.1 (d, *J* 2.4); δ_{P} (162 MHz; CDCl_3 ; H_3PO_4) 33.0 (s).

Compound 6a. Column chromatography (silica gel, petroleum (bp 40–60 °C)–ethyl acetate = 1 : 1) gave product **6a** as a colourless oil that is not stable standing in air for a long time (Found: 262.1723. $\text{C}_{20}\text{H}_{22}$ requires 262.1722); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3010, 2955, 2928, 2857, 1606, 1452, 1317, 1260, 1096, 1022, 875, 803, 740 and 700; δ_{H} (250 MHz; C_6D_6 ; Me_4Si) 0.80 (3 H, t, *J* 6.7, CH_2CH_3), 1.05–1.27 (4 H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.01 (2 H, tt, *J* 7.3, *J* 7.3, cyclo- $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.95–2.27 (2 H, m, CHCH_2CH_2), 2.90 (4 H, t, *J* 7.3, cyclo- CH_2), 3.94 (1 H, t, *J* 5.7, CHCH_2CH_2), 7.31 (1 H, t, *J* 7.3), 7.37 (1 H, s), 7.40 (1 H, t, *J* 7.3), 7.49 (1 H, d, *J* 7.3), 7.65 (1 H, s), 7.81 (1 H, d, *J* 7.3); δ_{C} (63 MHz; C_6D_6 ; Me_4Si) 14.0, 23.4, 26.2, 27.9, 32.9, 33.1, 33.3,

47.4, 116.1, 119.7, 120.5, 124.6, 126.5, 127.2, 140.2, 142.1, 143.1, 143.5, 146.5, 148.2.

Compound 7b. Column chromatography (silica gel, dichloromethane–diethyl ether = 20 : 1) gave product **7b** as a colourless oil (Found: 574.2416. $\text{C}_{41}\text{H}_{35}\text{OP}$ requires 574.2426); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3058, 3026, 2949, 2846, 1712, 1598, 1482, 1437, 1314, 1270, 1180, 1114, 1028, 997, 910, 730 and 698; δ_{H} (600 MHz; CDCl_3 ; Me_4Si) 2.02–2.08 (2 H, m, cyclo- CH_2), 2.80–2.84 (2 H, m, cyclo- CH_2), 2.92–3.00 (2 H, cyclo- CH_2), 3.86 (2 H, s, ArCH_2Ph), 4.76 (1 H, d, *J* 9.7, $(\text{Ph}_2)\text{P}(\text{O})\text{CH}$), 6.90 (2 H, br s), 6.91 (1 H, s), 6.95 (2 H, d, *J* 8.0), 7.08 (2 H, d, *J* 7.0), 7.16–7.21 (5 H, m), 7.24 (2 H, t, *J* 6.7), 7.28–7.37 (8 H, m), 7.39 (1 H, m), 7.41–7.44 (2 H, m), 8.35 (1 H, s); δ_{C} (151 MHz; CDCl_3 ; Me_4Si) 25.4, 32.5, 32.9, 41.4, 48.3 (d, *J* 65.4), 125.8, 125.9, 126.1 (d, *J* 5.2), 127.0, 127.8, 127.9 (d, *J* 11.5), 128.0 (d, *J* 11.5), 128.3, 128.8 (d, *J* 1.7), 128.8, 129.7, 130.1 (d, *J* 5.7), 131.1 (d, *J* 2.9), 131.2 (d, *J* 2.9), 131.3 (d, *J* 8.6), 131.4 (d, *J* 9.2), 132.3 (d, *J* 98.1), 132.3 (d, *J* 3.4), 132.4 (d, *J* 96.9), 134.6 (d, *J* 5.2), 139.2 (d, *J* 2.3), 140.4 (d, *J* 8.6), 141.1, 141.8, 142.9 (d, *J* 1.7), 144.0 (d, *J* 1.7); δ_{P} (162 MHz; CDCl_3 ; H_3PO_4) 32.6 (s).

Compounds 12c,e. The thermolysis was followed by ^1H NMR. After 5 min (d_6 -DMSO, 80 °C) signals could be observed that are indicative of **12c** and **12e** as judged by characteristic signals of similar cyclisation products.^{6,11} After prolonged heating **12c** and **12e** finally decomposed. **12c**: δ_{H} (200 MHz; CDCl_3 ; Me_4Si) 5.53 (1 H, d, *J* 3.5), 6.48 (1 H, s). **12e**: δ_{H} (200 MHz; CDCl_3 ; Me_4Si) 5.68 (1 H, d, *J* 3.5), 6.62 (1 H, s).

Compound 13b. Column chromatography (silica gel, dichloromethane–diethyl ether = 5 : 1) furnished Diels–Alder product **13b** as a yellow fluorescent oil (Found: 482.1800. $\text{C}_{34}\text{H}_{27}\text{OP}$ requires 482.1800); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3057, 2961, 2928, 2862, 1937, 1747, 1707, 1597, 1490, 1438, 1262, 1183, 1113, 1026, 801, 756, 726 and 697; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 1.84 (2 H, br s, cyclo- CH_2), 2.11 (2 H, tt, *J* 7.4, *J* 6.9, cyclo- $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.41 (2 H, t, *J* 6.9, cyclo- CH_2), 3.23 (2 H, s, CH_2), 7.15 (1 H, t, *J* 7.6), 7.23–7.30 (2 H, m), 7.34–7.38 (2 H, m), 7.41–7.58 (9 H, m), 7.72–7.81 (4 H, m), 8.27 (1 H, d, *J* 8.5); δ_{P} (162 MHz; CDCl_3 ; H_3PO_4) 30.6 (s).

Compound 13d. Column chromatography (silica gel, petroleum (bp 40–60 °C)–acetone = 2 : 1) gave Diels–Alder product **13d** as a yellow fluorescent oil (Found: 496.1956. $\text{C}_{35}\text{H}_{29}\text{OP}$ requires 496.1947); $\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3054, 2918, 1591, 1482, 1165, 1119, 821, 733 and 691; δ_{H} (250 MHz; CDCl_3 ; Me_4Si) 1.61–1.80 (4 H, br s, cyclo- CH_2), 2.57–2.65 (2 H, br s, cyclo- CH_2), 2.81–2.90 (2 H, m, cyclo- CH_2), 3.32 (2 H, s, CH_2), 6.97–7.22 (4 H, m), 7.28–7.58 (8 H, m), 7.63–7.89 (4 H, m), 7.91–7.98 (2 H, m), 8.08 (1 H, d, *J* 9.1); δ_{C} (63 MHz; CDCl_3 ; Me_4Si) 23.2, 24.3, 26.5, 30.1, 45.2, 123.2, 124.8, 125.2, 126.9, 127.5, 128.2, 128.9 (d, *J* 12.1), 129.4, 129.5, 130.6, 130.9, 131.8 (d, *J* 2.9), 132.1, 132.7, (d, *J* 11.4), 134.5 (d, *J* 69.8), 136.1 (d, *J* 102.2), 140.1, 143.2, 144.9, 151.1; δ_{P} (162 MHz; CDCl_3 ; H_3PO_4) 33.4 (s); *m/z* 496 (M^+ , 100%), 295 (100).

Compound 13f. Column chromatography (silica gel, petroleum (bp 40–60 °C)–acetone = 3 : 1) gave product **13f** as a red fluorescent oil (Found: 510.2112. $\text{C}_{36}\text{H}_{31}\text{OP}$ requires 510.2112);

$\tilde{\nu}(\text{film})/\text{cm}^{-1}$ 3056, 2922, 1588, 1484, 1185, 1117, 758 and 695; $\delta_{\text{H}}(250 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 1.17–1.44 (2 H, m, cyclo- CH_2), 1.49–1.85 (4 H, m, cyclo- CH_2), 2.13–2.22 (2 H, m, cyclo- CH_2), 2.28–2.42 (2 H, m, cyclo- CH_2), 3.45 (2 H, s, CH_2), 7.09–7.20 (1 H, m), 7.30–7.56 (11 H, m), 7.69–7.84 (4 H, m), 7.89–7.97 (2 H, m), 8.13 (1 H, m); $\delta_{\text{C}}(63 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$ 26.7, 27.2, 30.0, 30.4, 31.3, 44.7, 124.7, 125.2, 125.7, 127.1, 127.8, 128.3, 129.0 (d, J 12.2), 129.3, 129.6, 130.2, 130.9, 132.1 (d, J 3.2), 132.2, 132.3, (d, J 10.7), 135.0 (d, J 70.2), 135.3 (d, J 102.2), 139.5, 143.6, 145.0, 150.8; $\delta_{\text{P}}(162 \text{ MHz}; \text{CDCl}_3; \text{H}_3\text{PO}_4)$ 30.6 (s); m/z 510 (M^+ , 100%), 433 (12), 201 (26).

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