Ring size effects in the C^2–C^6 biradical cyclisation of enyne–allenes and the relevance for neocarzinostatin

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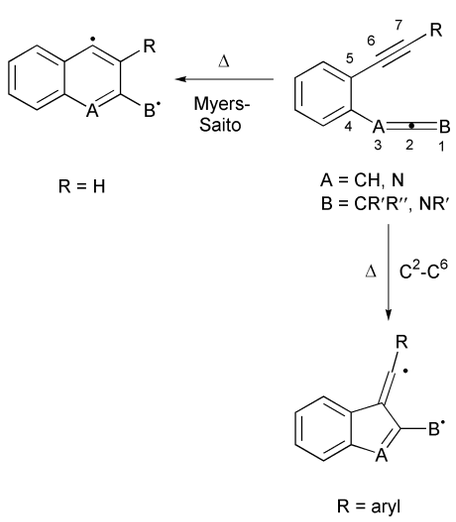
The regioselectivity of the thermal cyclisations of enyne–allenes **1** can be toggled as a function of the ring size of the cycloalkene. With a cyclopentene as the ene moiety the Myers–Saito (C^2–C^7) cycloaromatisation product is formed, whereas with six- and seven-membered cycloalkenes the novel C^2–C^6 cyclisation is observed. DFT calculations are used to rationalise these changes. The implications of these findings for alternative thermal biradical cyclisations of neocarzinostatin are discussed.

Introduction

Cycloaromatisations of enediynes[1] (*Bergman* cyclisation) and enyne–allenes[2] (*Myers–Saito* cyclisation, C^2–C^7) have received large interest over the last decade[3] 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 states[5] the novel C^2–C^6 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 studies[6] 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 (C^2–C^7) towards the C^2–C^6 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 C^2–C^6 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 biradical[6] in the C^2–C^6 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 C^2–C^6 cyclisation has recently moved into the focus of theoretical,[10] DNA cleavage,[11] and synthetic studies (*e.g.* towards the kinamycin[12] and the neocryptolepine[13] 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 examples[14] may indicate some effect. Herein, we would like to disclose[15] that the switch between the C^2–C^7 and the C^2–C^6 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 latter[16] are reacted using a Sonogashira coupling with two acetylides, either *n*BuC≡CMgBr or [$(PhC{\equiv}C)_2$-AlH_2]Na,[17] the second being prepared from phenylacetylene and SDDA ([Et_2AlH_2]Na). The resultant propargyl (prop-2-ynyl) alcohols **3a**–**f** were treated with $ClPPh_2$ thus providing the diphenylphosphane oxide substituted enyne–allenes[18] **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, ^{1}H NMR, ^{13}C 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 temperature[19] 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)

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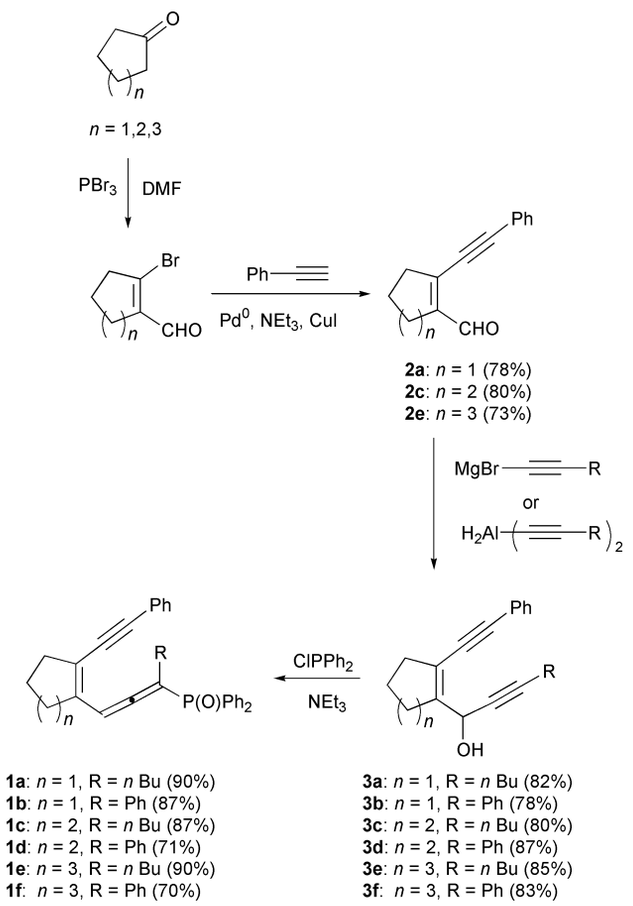
furnished the cyclisation products **4a** (15%) and **4b** (31%) (Scheme 3). In addition, some other follow-up products (**5a**, **6a** and **7b**) were found, which were structurally characterised using NMR techniques such as DEPT, H,H- and C,H-COSY and HMBC measurements.

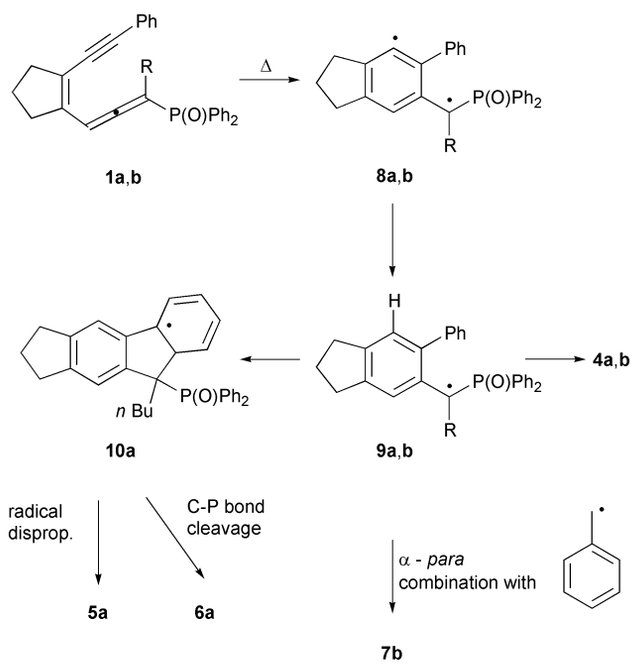
Products **4a**–**6a**, **4b**, **7b** can be explained directly from the intermediate Myers–Saito (C^2–C^7) biradical **8a,b** (Scheme 4). While the more reactive σ-radical site readily abstracts one hydrogen from toluene–cyclohexadiene to afford **9a,b**, the benzylic π-radical is less reactive and 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 = *n*Bu) may undergo a cyclisation to 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).

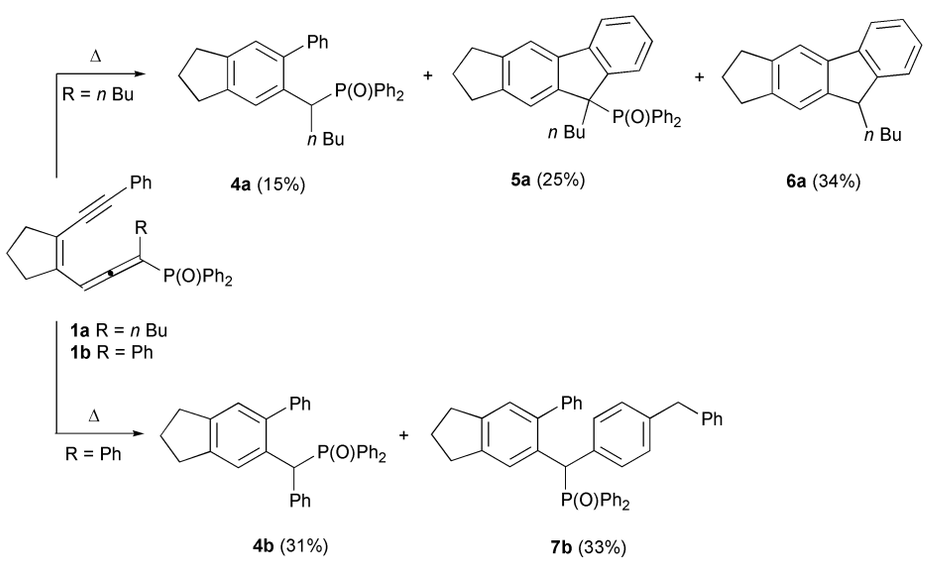
Thermolyses (5 min at 80 °C, DMSO, without 1,4-CHD) of the enyne–allenes **1c,e** also led to C^2–C^6 cyclisation products. Detailed investigations by ^{1}H NMR (see Experimental section) showed the intermediate formation of the ene products **12c,e** through intramolecular hydrogen transfer from **11c,e**. Unfortunately, **12c,e** are not stable enough to be isolated, as they contain a vinyl fulvene as a structural motif that is prone



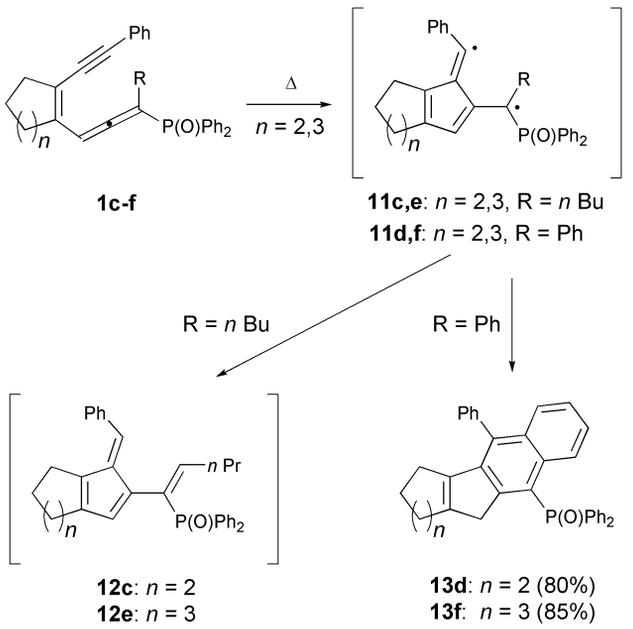
Scheme 2 Synthesis of the enyne–allenes **1a**–**f**.



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.

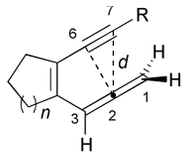
Calculations

Our original reasoning about the dramatic switch from the C^2–C^7 to the C^2–C^6 cyclisation as a function of the substituent at the alkyne terminus was based on the assumption that the transition state (TS) of the C^2–C^6 cyclisation would already show some biradical character. As a consequence, a phenyl group should stabilise the forming vinyl radical center[22] and thus the TS of the C^2–C^6 cyclisation could fall beneath that of the C^2–C^7 cycloaromatisation. Recent calculations by Engels[6c] and by Schreiner,[10a] however, have indicated clearly that the TS of the C^2–C^6 cyclisation possesses mainly a closed-shell electronic structure. Nevertheless, the calculations indicate a lower activation barrier for the C^2–C^6 than for the C^2–C^7 cyclisation (29 *vs.* 30 kcal mol^{-1}). The reason for that is a resonance stabilisation of the C^2–C^6 cyclisation TS as evidenced by a significant C^7–C^{phenyl} bond shortening (1.411 Å) when compared to the C^2–C^7 TS (1.454 Å).

Analogue quantum chemical calculations were now used to get an insight into ring size effects on the C^2–C^6 and C^2–C^7 cyclisations.[23] The geometries of all stationary points were optimised using analytical energy gradients within the density functional theory (DFT) approach[24] employing the B3LYP[25] 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 Gaussian98[28] 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. U*B3LYP) 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 performed[29] 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 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.

Table 1 Summary of the calculated data for the transition state energies $\Delta G^{\ddagger}$ (298 K) of C^2–C^6 and Myers–Saito (C^2–C^7) cyclisation of model compound **15**. The energies are given in kcal mol^{-1} with respect to those of the corresponding enyne–allenes[23]



15

	n	Substituent R	$\Delta G^{\ddagger}$ (C^2–C^6)	$\Delta G^{\ddagger}$ (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

Discussion

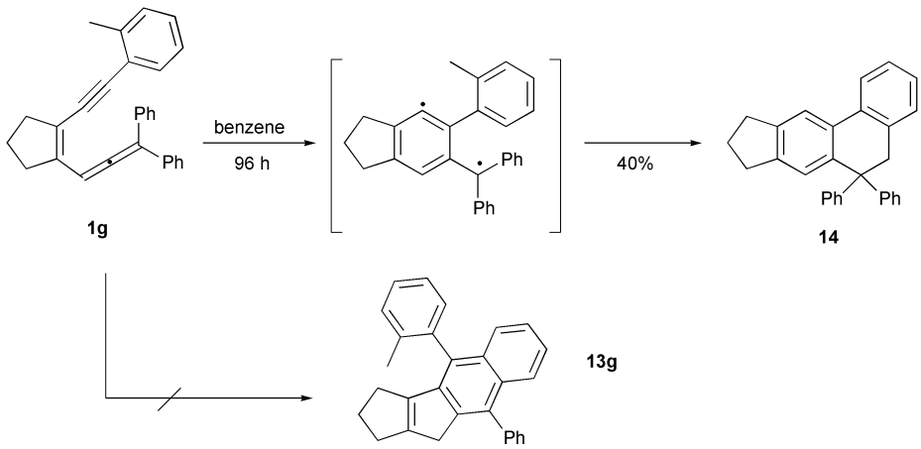
Ring strain effects and cyclisation mode

Knowing that aryl groups at the alkyne terminus redirect the course of enyne–allene cyclisations towards the C^2–C^6 mode a recent result of Wang *et al.*[14] was quite surprising. Thermolysis of the cyclopentene based enyne–allene **1g** only furnished the C^2–C^7 cyclisation product **14** and not **13g** (Scheme 6). Another example of the C^2–C^7 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 C^2–C^6 cyclisation is observed as controlled through the presence of a phenyl group at the acetylene terminus, but the Myers–Saito (C^2–C^7) 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 C^2–C^7 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(C^2–C^6) and d(C^2–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 C^2–C^7 ($\Delta d \approx 150$–165 pm) than for the C^2–C^6 ($\Delta d \approx 110$–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 $\Delta G^{\ddagger}$ with increasing ring size is stronger for the C^2–C^6 cyclisation



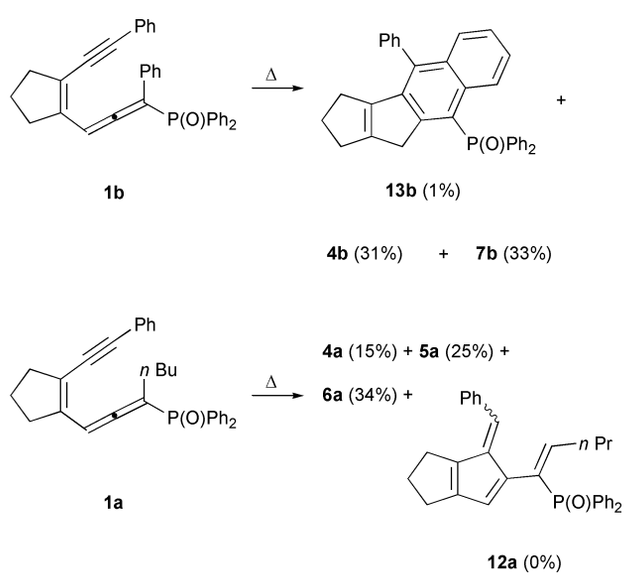
Scheme 6 Unexpected cyclisation pathway of enyne–allene **1g** as shown by Wang *et al.*[14]

Table 2 Structural data (from calculations) for enyne–allene **15** and the corresponding C^2–C^6 and C^2–C^7 transition states (TS)

		TS C^2–C^6			Enyne–allene			TS C^2–C^7		
Comp.	*n*	d^a (C^2–C^6)	ϕ^b	θ^c	d^a (C^2–C^6)	d^a (C^2–C^7)	θ^c	d^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(C^2–C^6) or d(C^2–C^7) is provided in pm. [b] Dihedral angle (in °) for C^3–C^2–C^1–H^1. [c] Dihedral angle (in °) for C^6–C^7–C^{Ph}–C^{Ph+1}.

(*ca.* 8 kcal mol^{-1}) than for the C^2–C^7 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; C^2–C^7 cyclisation is clearly favoured over C^2–C^6 cyclisation for all three calculated model compounds ($\Delta\Delta G^{\ddagger} = 6$–$9$ 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 C^2–C^7 cyclisation by approximately 5.5–6 kcal mol^{-1} while it decreases the one for C^2–C^6 cyclisation by 4 ± 0.5 kcal mol^{-1}. For **15e** and **15f** the C^2–C^6 cyclisation is now clearly favoured over C^2–C^7 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 C^2–C^6 cyclisation ($\Delta\Delta G^{\ddagger} = 0.6$ kcal mol^{-1}) the thermolysis of **1a,b** led to the formation of C^2–C^7 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 C^2–C^6 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).

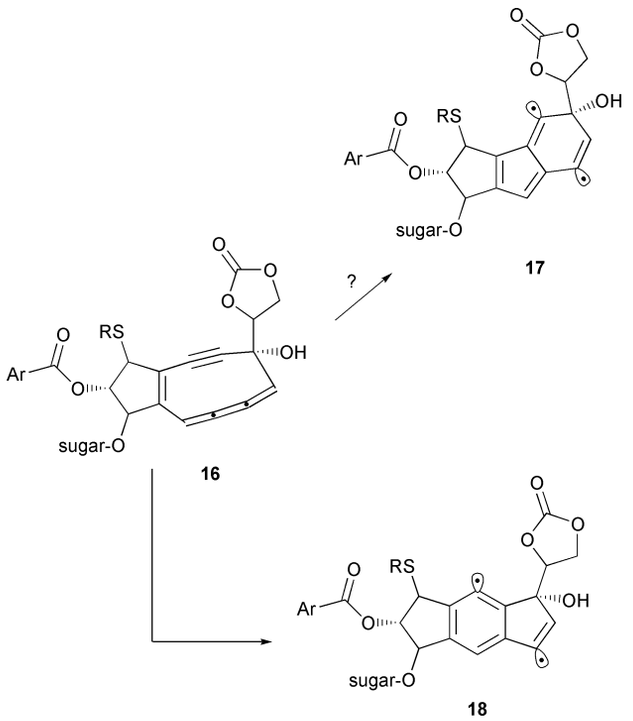


Scheme 7

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 C^2–C^6 biradical—by the kinetics of the follow-up reaction. Unfortunately, reliable theoretical calculations on the biradicals 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 C^2–C^7 (leading to **18**) over C^2–C^6 cyclisation (leading to biradical **17**). Calculations by Schreiner[10a] indicate that smaller cyclic enyne–allenes (8- and 9-membered systems) prefer kinetically the C^2–C^6 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 C^2–C^7 biradical mode in **19** has been evaluated recently using BPW91/cc-pVDZ quantum mechanical calculations[33] without addressing alternative pathways. Our *U*B3LYP DFT



Scheme 8

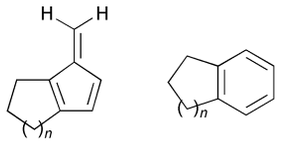
calculations on **19** now reveal that the C^2–C^6 cyclisation pathway ($\Delta G^{\ddagger} = 17.6$ kcal mol^{-1}) is kinetically favoured over the C^2–C^7 mode ($\Delta G^{\ddagger} = 20.8$ kcal mol^{-1}). As 68% of the products in the neocarzinostatin cycloaromatisation are derived from biradical **18**, one has to assume that nature uses the annulated cyclopentene ring in **16** to control the regioselectivity of the biradical cyclisations!

19 **20** (n = 1,2)

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 C^2–C^7 cyclisation of enyne–cumulenes,[33,34] while experimental investigations on neocarzinostatin models follow the natural bicyclic[7.3.0] system[35] 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 C^2–C^6 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 C^2–C^6 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 C^2–C^6 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 $\Delta\Delta G^{\ddagger}$ (C^2–C^6 *vs.* C^2–C^7) 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 C^2–C^6 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 (C^2–C^7) cyclisation to **18**, since in the parent 9-membered cyclic enyne–cumulene the C^2–C^6 biradical is kinetically favoured over the C^2–C^7 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. 6*b*. Compound **2a** was synthesised according to ref. 31*a*.

Compound 2c. To a mixture of cyclohexene–bromocarbaldehyde (5.00 g, 26.4 mmol) (prepared analogously to Arnold and Holý[16]) and phenylacetylene (3.10 g, 30.4 mmol) in triethylamine (100 cm^3) were added $PdCl_2(PPh_3)_2$ (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 cm^3) and *n*-pentane (200 cm^3). After filtration the aqueous layer was washed with *n*-pentane (2 × 100 cm^3). The combined organic layers were dried ($MgSO_4$) 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. $C_{15}H_{14}O$ requires C, 85.67; H, 6.72%); $\tilde{\nu}_{max}$(film)/cm^{-1} 3056, 2935, 2860, 2732, 2199, 1673, 1603, 1489, 1442, 758 and 689; δ_H(200 MHz; $CDCl_3$; Me_4Si) 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, C*H*O); δ_C(50 MHz; $CDCl_3$; Me_4Si) 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 cm^3), $PdCl_2(PPh_3)_2$ (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. $C_{16}H_{16}O$ requires 224.1201); $\tilde{\nu}_{max}$(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, C*H*O); 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 × 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. $C_{20}H_{22}O$ requires 278.1671); $\tilde{\nu}_{max}$(film)/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-$CH_2CH_2CH_2$), 2.22 (2 H, td, *J* 6.9, *J* 1.9, C≡CCH_2CH_2), 2.45 (1 H, s, O*H*), 2.62 (2 H, tt, *J* 8.0, *J* 2.3, cyclo-CH_2-CH_2-CH_2), 2.66 (2 H, tt, *J* 8.0, *J* 2.3, cyclo-CH_2-CH_2-CH_2), 5.52 (1 H, t, *J* 1.9, HOC*H*C≡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. $C_{22}H_{17}O$ ($M^+ - 1$) requires 297.1279); $\tilde{\nu}_{max}$(film)/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, $CH_2CH_2CH_2$), 2.65 (2 H, tt, *J* 7.6, *J* 2.2, $CH_2CH_2CH_2$), 2.70 (1 H, br s, O*H*), 2.77 (2 H, tt, *J* 7.6, *J* 2.2, $CH_2CH_2CH_2$), 5.79 (1 H, HOC*H*C≡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 °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 × 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. $C_{21}H_{24}O$ requires 292.1827); $\tilde{\nu}$(film)/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, $CH_2CH_2CH_3$), 1.50–1.72 (4 H, m, cyclo-CH_2CH_2), 2.20 (2 H, td, *J* 7.2, *J* 2.0, C≡CCH_2CH_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, O*H*), 5.72 (1 H, t, *J* 2.0, HOC*H*C≡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. $C_{23}H_{20}O$ requires 312.1514); $\tilde{\nu}$(film)/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, O*H*), 5.98 (1 H, s, HOC*H*C≡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 °C)–diethyl ether = 4 : 1) to furnish propargyl alcohol **3e** (750 mg, 85%) as a yellow oil (Found: 306.1977. $C_{22}H_{26}O$ requires 306.1983); $\tilde{\nu}$(film)/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, CH_2CH_2-CH_3), 1.74–1.87 (2 H, m, cyclo-CH_2), 2.06 (1 H, s, O*H*), 2.23 (2 H, td, *J* 7.0, *J* 1.8, C≡CCH_2), 2.46–2.51 (4 H, m, cyclo-CH_2), 5.71 (1 H, d, *J* 1.8, HOC*H*C≡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 °C)–diethyl ether = 4 : 1) afforded propargyl alcohol **3f** (783 mg, 83%) as a yellow oil (Found: 326.1663. $C_{24}H_{22}O$ requires 326.1670); $\tilde{\nu}$(film)/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, O*H*), 2.50–2.61 (4 H, m, cyclo-CH_2), 5.97 (1 H, s, HOC*H*C≡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 °C chlorodiphenylphosphane (192 mg, 870 μmol) was added dropwise during 15 min under vigorous stirring. After stirring at −80 °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 × 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)); $\tilde{\nu}$(film)/cm^{-1} 3078, 3059, 2958, 2928, 2870, 2852, 2186, 1925, 1488, 1438, 1194, 1117, 1101, 831, 760, 724, 701 and 692; δ_H(250 MHz; $CDCl_3$; Me_4Si) 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, CH_2CH_2-CH_3), 2.47–2.57 (2 H, m, C=C=CCH_2CH_2), 6.42 (1 H, td, *J* 11.0, *J* 3.2, C*H*C=C=C), 7.24–7.34 (3 H, m), 7.36–7.54 (8 H, m), 7.65–7.80 (4 H, m); δ_C(100 MHz; $CDCl_3$; Me_4Si) 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); δ_P(162 MHz; $CDCl_3$; H_3PO_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); $\tilde{\nu}$(film)/cm^{-1} 3057, 2957, 2840, 2197, 1913, 1719, 1708, 1596, 1490, 1438, 1176, 1119, 1098, 1071, 757, 726, 693 and 546; δ_H(250 MHz; $CDCl_3$; Me_4Si) 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, C*H*C=C=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); δ_C(100 MHz; $CDCl_3$; Me_4Si) 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); δ_P(162 MHz; $CDCl_3$; H_3PO_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); $\tilde{\nu}$(film)/cm^{-1} 3054, 2929, 2197, 1920, 1590, 1484, 1438, 1195, 1117, 754, 721 and 692; δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.85 (3 H, t, *J* 7.0, CH_2CH_3), 1.24–1.43 (4 H, m, $CH_2CH_2CH_3$), 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, C=C=CCH_2), 6.66 (1 H, dt, *J* 11.2, *J* 3.2, C*H*C=C=C), 7.29–7.34 (2 H, m), 7.36–7.52 (9 H, m), 7.63–7.83 (4 H, m); δ_C(63 MHz; $CDCl_3$; Me_4Si) 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); δ_P(162 MHz; $CDCl_3$; H_3PO_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); $\tilde{\nu}$(film)/cm^{-1} 3056, 2933, 2860, 2198, 1911, 1592, 1490, 1437, 1195, 1117, 737, 724 and 693; δ_H(200 MHz; $CDCl_3$; Me_4Si) 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, C*H*C=C=C), 7.21–7.40 (6 H, m), 7.44–7.55 (8 H, m), 7.65–7.72 (6 H, m); δ_C(50 MHz; $CDCl_3$; Me_4Si) 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); δ_P(162 MHz; $CDCl_3$; H_3PO_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%); $\tilde{\nu}$(film)/cm^{-1} 3056, 2927, 2853, 2184, 1919, 1591, 1488, 1194, 1117, 755, 722 and 690; δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.84 (3 H, t, *J* 7.3, CH_2CH_3), 1.06–1.42 (4 H, m, $CH_2CH_2CH_3$), 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, C=C=CCH_2), 6.67 (1 H, td, *J* 3.1, *J* 3.1, C*H*C=C=C), 7.26–7.32 (3 H, m), 7.37–7.48 (8 H, m), 7.62–7.82 (4 H, m); δ_C(63 MHz; $CDCl_3$; Me_4Si) 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); δ_P(162 MHz; $CDCl_3$; H_3PO_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 triethyamine (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); $\tilde{\nu}$(film)/cm^{-1} 3056, 2924, 2852, 2202, 1911, 1594, 1490, 1182, 1117, 759 and 694; δ_H(250 MHz; $CDCl_3$; Me_4Si) 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, C*H*C=C=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); δ_C(63 MHz; $CDCl_3$; Me_4Si) 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); δ_P(162 MHz; $CDCl_3$; H_3PO_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); $\tilde{\nu}$(film)/cm^{-1} 3056, 3023, 2955, 2932, 2861, 1480, 1437, 1185, 1116, 1101, 1072, 1028, 885, 722 and 698; δ_H(600 MHz; $CDCl_3$; Me_4Si) 0.72 (3 H, t, *J* 7.2, CH_2CH_3), 1.05–1.13 (3 H, m, $CH_2CH_2CH_3$), 1.22–1.28 (1 H, m, $CH_2CH_2CH_3$), 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. $C_{34}H_{29}OP$ requires 484.1956); $\tilde{\nu}$(film)/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, C*H*), 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. $C_{32}H_{31}OP$ requires 462.2113); $\tilde{\nu}$(film)/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_2), 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, $CH_2CH_2CH_3$), 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. $C_{20}H_{22}$ requires 262.1722); $\tilde{\nu}$(film)/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, $CH_2CH_2CH_3$), 2.01 (2 H, tt, *J* 7.3, *J* 7.3, cyclo-$CH_2CH_2CH_2$), 1.95–2.27 (2 H, m, $CHCH_2$-CH_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. $C_{41}H_{35}OP$ requires 574.2426); $\tilde{\nu}$(film)/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, $(Ph_2)P(O)CH$), 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. $C_{34}H_{27}OP$ requires 482.1800); $\tilde{\nu}$(film)/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-$CH_2CH_2CH_2$), 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. $C_{35}H_{29}OP$ requires 496.1947); $\tilde{\nu}$(film)/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. $C_{36}H_{31}OP$ requires 510.2112);

$\tilde{\nu}$(film)/cm^{-1} 3056, 2922, 1588, 1484, 1185, 1117, 758 and 695; δ_H(250 MHz; $CDCl_3$; Me_4Si) 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); δ_C(63 MHz; $CDCl_3$; Me_4Si) 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; δ_P(162 MHz; $CDCl_3$; H_3PO_4) 30.6 (s); *m*/*z* 510 (M^+, 100%), 433 (12), 201 (26).

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