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PAPER

The thermal C^2–C^6/[2 + 2] cyclisation of enyne-allenes: Reversible diradical formation†‡

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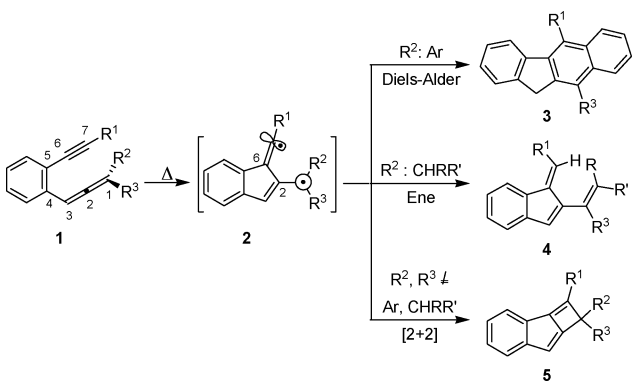
New enyne-allenes, structurally designed toward the thermal C^2–C^6/[2 + 2] cyclisation mode, were prepared and characterised, one of them even by X-ray crystallography. The mechanism of their transformation to formal [2 + 2] cycloadducts was interrogated by trapping experiments and DFT computations. The results support a stepwise mechanism that involves the reversible formation of the C^2–C^6 diradical intermediate.

The (benzo)fulvene diradical **2**,[1,2] generated in the thermal C^2–C^6 cyclisation of enyne-allene **1**, is well known to undergo intramolecular follow-up processes, such as formal ene[3,4] and Diels–Alder[5,6] (DA) cycloadditions, depending on the nature of the substituents at the allene terminus. With R^2 and/or R^3 being aryl substituents the reaction furnished benzofluorene **3** along the DA pathway whereas with R^2 and/or R^3 being CHRR′ benzofulvenes **4** were obtained (Scheme 1).[7] In contrast, the involvement of **2** in the formal [2 + 2] cycloaddition of **1** affording **5** has not been investigated.



Scheme 1 Various products arising from the thermal C^2–C^6 cyclisation of enyne-allenes.

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† This paper is dedicated to the commemoration of the late Athel L. J. Beckwith for his numerous insightful and valuable contributions to the field of radical chemistry.

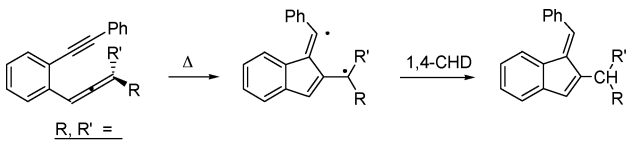
‡ Electronic supplementary information (ESI) available: Experimental details, ^{1}H and ^{13}C-NMR spectra of all new compounds. Crystal data and structure refinement details for **6c** and cartesian coordinates of all stationary points of **6d**. See DOI: 10.1039/c0ob01275k

§ C. Vavilala deceased on 18 February 2010. We will remember him for his friendship and many scientific stimuli.

The first example of a [2 + 2] cycloaddition[8] was reported by Gillmann[9] in the thermolysis of an enyne-allene with a TMS group at the alkyne terminus and two hydrogens at the allene terminal. Despite excess amounts of 1,4-cyclohexadiene (1,4-CHD), the C^2–C^6 diradical was not intercepted by hydrogen abstraction. Nevertheless, a stepwise mechanism *via* the C^2–C^6 diradical was proposed by Gillmann, a suggestion taken over later by Wang, who designed a number of ingenious examples along the [2 + 2] reaction channel.[10]

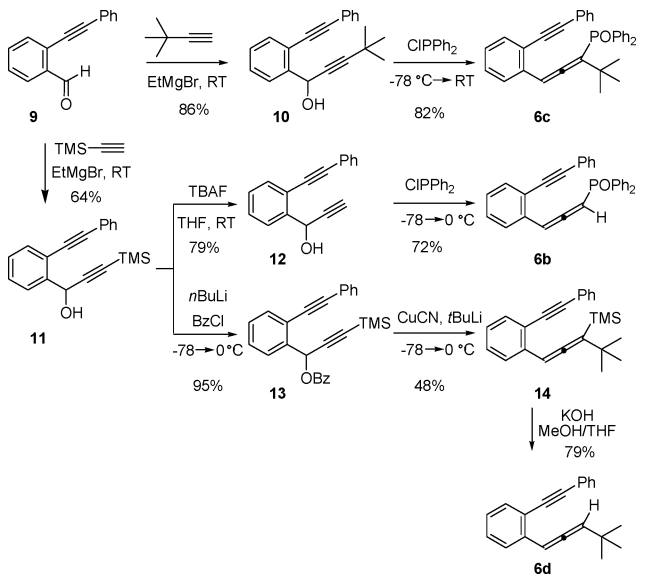
Basically all C^2–C^6/[2 + 2] reactions of enyne-allenes known as of today command absence of aryl and alkyl groups at the allene terminus. Such substituent pattern may be seen as a hint to the intermediacy of **2** also in the [2 + 2] cycloaddition mode, as the competing DA and ene reactions of **2** exhibit activation barriers of less than 9 and 3 kcal mol^{-1}, respectively.[11]

In the present paper we address the intermediacy of the C^2–C^6 diradical in the [2 + 2] cycloaddition in more detail. It is important, however, to note that not all enyne-allenes structurally designed toward a [2 + 2] route undergo this cycloaddition. For example, thermolysis of **6a** in the presence of 1,4-CHD furnished 11% of **8a** (Scheme 2),[1d] visibly arising by trapping of the corresponding diradical intermediate **7a** through hydrogen abstraction. Equally, there is evidence for the intermediacy of **7b** in the thermal cyclisation of **6b**, by both product study and DNA strand cleavage.[5a] Thus, to clarify the intermediacy of the C^2–C^6 diradical in the [2 + 2] channel, we reinvestigated **6b** and complemented the series by adding **6c–6d**. The results of our experimental and computational study strongly support a stepwise diradical mechanism with a reversible C^2–C^6 cyclisation.



Scheme 2 Trapping of the C^2–C^6 diradical **7** with 1,4-CHD.

6b was prepared along a literature procedure,[5a] while **6c** was obtained in two steps starting with the Grignard addition of *tert*-butylacetylene to 2-(2-phenylethynyl)benzaldehyde (**9**) (Scheme 3).[12] The resultant propargyl alcohol **10** was reacted with chlorodiphenyl phosphine, affording **6c** in 82% yield. Its solid state structure, the second one of the enyne-allene family,[13] was unambiguously determined by X-ray crystallography.



Scheme 3 Synthesis of enyne-allenes **6b–6d**.

In the solid state, enyne-allene **6c** is present in the s-*trans* conformation (C2–C1–C15–C16 dihedral angle = 169.3°) that unlike the thermally reactive s-*cis* conformation does not allow for cyclisation (Fig. 1).[14] The lengths of the allene double bonds, C15–C16 and C16–C17, are d_{CC} = 130.3(4) and 131.5(4) pm and therefore well in line with those of regular allenes.[15]

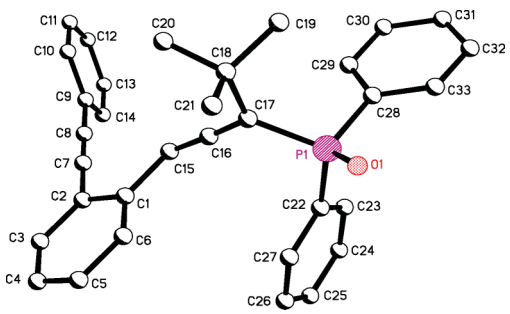


Fig. 1 X-ray structure of enyne-allene **6c**.¶

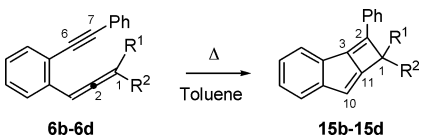
To prepare enyne-allene **6d**, propargyl alcohol **11** was first protected with benzoyl chloride followed by treatment with *t*-BuLi in the presence of CuCN providing enyne-allene **14** in moderate yield (48%). Removal of the TMS group was carried out in 1 M KOH solution, affording enyne-allene **6d** in 79% yield (Scheme 3).

The thermolysis of enyne-allenes **6b–6d** was performed in dry toluene under nitrogen. All compounds underwent C^2–C^6 cyclisation to [2 + 2] cycloadducts in moderate (**15b** and **15d**) to good (**15c**) yields (Scheme 4). The reaction conditions are listed in Table 1.

Table 1 Thermolysis conditions for enyne-allenes **6b–6d** (solvent: toluene) and product yields

Enyne-allene	R^1	R^2	1,4-CHD[a]	Temp. [°C]	Time [h]	Product (Yield [%])
6b	$POPh_2$	H	—	111	4	**15b** (24)
6c	$POPh_2$	*t*Bu	—	150[b]	5	**15c** (72)[c]
6c	$POPh_2$	*t*Bu	100 eq.	160[b]	42.5	**15c** (67)
6d	*t*Bu	H	—	111	8	**15d** (26)

[a] 1,4-CHD = 1,4-cyclohexadiene. [b] In sealed tube. [c] At 29% conversion.



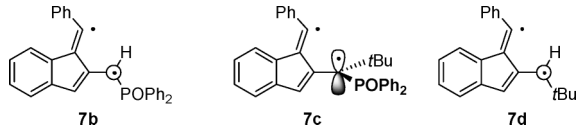
Scheme 4 Thermolysis of enyne-allenes **6b–6d** (for R^1,R^2 see Table 1).

Thermolysis of **6b** in toluene (111 °C, 4 h), but in absence of 1,4-CHD, furnished the corresponding [2 + 2] cycloadduct **15b** in 24% yield. It was identified from its doublet at 5.39 ppm with a coupling constant of 9.9 Hz (for 1-H) and by a singlet at 5.93 ppm (for 10-H) in the ^{1}H-NMR. The ^{13}C-NMR shows a characteristic doublet at 51.1 ppm for C-1with a carbon phosphorous coupling constant $J_{C,P}$ = 70 Hz. As the thermal reaction of **6b** in presence of 1,4-CHD had earlier led to **8b**,[5a] diradical **7b** (Scheme 2) is a likely precursor to both products. Notably, the thermolysis of **6c** in toluene afforded 72% of the [2 + 2] cycloadduct **15c**, whose ^{13}C-NMR shows the expected doublet at 72.0 ppm for C-1 with a coupling constant $J_{C,P}$ = 64 Hz. In contrast to the situation with **6b**, however, thermolysis of **6c** in presence of 100 equiv. of 1,4-CHD did not furnish a single trace of the putative trapping product **8c**, as analysed by ^{1}H and ^{13}C-NMR, excluding any major follow-up reaction of **7c** *via* hydrogen abstraction. In lieu thereof, the [2 + 2] cycloadduct **15c** was isolated in 67% yield (Scheme 4 and Table 1)

To investigate whether the combined steric effects of the *t*Bu and $POPh_2$ subunits are responsible for the high [2 + 2] cycloaddition yield, we turned our attention to **6d** that is an analogue of **6b** with the *t*Bu replacing the $POPh_2$ group. The thermal cyclisation of **6d** was performed in refluxing toluene for 8 h affording **15d** (26%), the latter being identified by characteristic singlets at 4.40 ppm (1-H) and 6.08 ppm (10-H) in the ^{1}H NMR and a distinct ^{13}C NMR resonance at 61.6 ppm (C-1).

The low yields of **15b** (24%) and **15d** (26%) together with their low total product balances (representing otherwise an untraceable and complex mixture) as well as the high yield for **15c** may actually be taken as evidence for the involvement of a reactive intermediate, whose follow-up reaction is heavily controlled by steric effects. Indeed, intermediates **7b** and **7d** may readily adopt a planar conformation (Scheme 5), which is surely precluded for **7c**. Hence, the preferred conformation of **7c** is well biased to furnish

¶ **X-ray data collection and structure determinations**. X-ray single-crystal diffraction data for **6c** was collected on a STOE IPDS one-circle image plate diffractometer. The structure was solved using the SHELXL-97 crystallographic software package and refined by the full-matrix least-squares technique.[21] The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The non-H atoms were refined with anisotropic thermal parameters. The crystal parameters, data collection, and refinement results are summarised in Table S1 (ESI‡). Selected bond lengths and angles are listed in Table S2 (ESI‡).



Scheme 5 Preferred conformations of diradicals **7b–7d**.

15c effortlessly, while that of **7b** and **7d** allows for a variety of follow-up radical processes.

The sum of all experimental findings thus presents convincing facts for the involvement of the reactive diradical **7**, as it is a reasonable intermediate for the [2 + 2] cycloadducts **15**, the hydrogenation products **8** and the unidentified side products.

To shed more light on the mechanism of the thermal C^2–C^6/[2 + 2] cyclisation of enyne-allenes, we performed DFT calculations[16] with an unrestricted broken-spin-symmetry ((BS)-(U)BLYP/6-31G(d))[17] on **6d** (Fig. 2). Pure DFT functionals, like BLYP, in combination with a 6-31G(d) basis set were demonstrated by Schreiner to provide high chemical accuracy and reasonable computational costs in Bergman and Myers-Saito diradical reactions.[18]

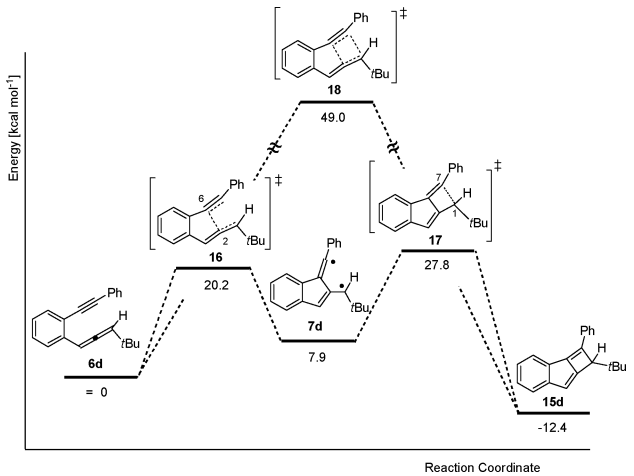


Fig. 2 Potential energy curve obtained from (BS)-(U)BLYP/6-31G(d) level calculations for the C^2–C^6/[2 + 2] cyclisation of **6d**. (Electronic energies including unscaled zpe are relative to the starting material **6d**).

The DFT results show an overall downhill process of 12.4 kcal mol^{-1} for the two-step transformation **6d** → **7d** → **15d**. **16**, the transition state (TS) to diradical **7d**, is characterised by bond formation between C2 and C6 (δ_{CC} = 194.3 pm), whereas transition state **17** still shows the C1–C7 bond formation in the cyclobutene ring at an initial stage (δ_{CC} = 263.7 pm). In **17**, the C2–C6 bond has already shortened to 146.7 pm, which is close to that in **15d** (δ_{CC} = 145.4 pm). In comparison to the stepwise [2 + 2] cycloaddition of hepta-1,2-dien-6-yne the barrier of the diradical formation is substantially lowered, while that of the final ring closure is much higher.[19]

Unlike ene[3,4,20] and DA[5] reactions of enyne-allenes *via* the C^2–C^6 diradical, the [2 + 2] ring closure transition state **17** has a significantly higher energy than **16**, the transition state of the initial diradical cyclisation.[2b] As hydrogen incorporation was not always seen during thermolysis in the presence of 1,4-CHD, the possibility of a concerted mechanism was also taken into consideration. However, **18**, the TS for the concerted process **6d** → **15d**, is located 21 kcal mol^{-1} above the rate-determining TS **17** of the stepwise variant. The high activation energy for TS **18** thus excludes any concerted mechanism and presents a particularly clear-cut case of a stepwise intramolecular [2 + 2] cycloaddition of allene-ynes.[19]

In summary, the present experimental and computational results suggest that the thermal C^2–C^6/[2 + 2] cyclisation of enyne-allenes proceeds *via* a stepwise pathway. In contrast to the ene and DA pathway of enyne-allenes, formation of the C^2–C^6 diradical is not rate determining in the [2 + 2] cycloaddition. As a consequence, we would expect that upon mild thermolysis the chiral enyne-allenes **6a–6d**, if prepared in an optical active form, should undergo partial racemisation *via* the benzofulvene diradical. Moreover, the deep shallow minimum about diradical **7d** indicates that non-statistical dynamic effects can reliably be excluded in the [2 + 2] pathway, quite in contrast to the situation of enyne-allenes following the thermal ene reaction pathway.[4,20]

Experimental Section

The preparation of all precursors for enyne-allenes **6c–6d** is described in the ESI‡. **6b** was prepared as described in the literature.[5a]

4,4-Dimethyl-3-(diphenylphosphinoyl)-1-[2-(phenylethynyl)-phenyl]-pent-1,2-diene (6c). To a solution of **10** (740 mg, 2.56 mmol) and NEt_3 (311 mg, 3.08 mmol) in THF (20 mL) at –78 °C was added chlorodiphenylphosphine (679 mg, 3.08 mmol) in THF (5 mL) over 15 min. The reaction mixture was stirred for 1 h at the same temperature and then allowed to slowly warm up to RT. After stirring for 1 h, it was hydrolysed with water and extracted with ethyl acetate. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. After purification by column chromatography (silica gel, n-hexane/ethyl acetate = 3 : 2, R_f 0.34) **6c** was isolated in 82% yield (994 mg, 2.10 mmol) as white solid. Mp: 38–40 °C. IR (KBr, cm^{-1}) 3057, 2962, 2213, 1936, 1599, 1494, 1438, 1190, 1116, 813, 756. ^{1}H-NMR (400 MHz, C_6D_6) δ 1.50 (s, 9H), 6.80–6.84 (m, 1H), 6.88–7.02 (m, 11H), 7.30 (d, J = 7.8 Hz, 1H), 7.36–7.39 (m, 3H), 7.87–7.96 (m, 4H). ^{13}C-NMR (100 MHz, C_6D_6) δ 31.0 (d, $J_{C,P}$ = 2.6 Hz), 38.0 (d, $J_{C,P}$ = 5.1 Hz), 87.9, 94.9, 96.0 (d, $J_{C,P}$ = 14 Hz), 113.0 (d, $J_{C,P}$ = 92 Hz), 121.5 (d, $J_{C,P}$ = 2.6 Hz), 123.5, 126.5 (d, $J_{C,P}$ = 1.7 Hz), 127.4, 127.9, 128.2, 128.4 (d, $J_{C,P}$ = 1.7 Hz), 128.7 (d, $J_{C,P}$ = 1.7 Hz), 131.3 (d, $J_{C,P}$ = 2.6 Hz), 131.5 (d, $J_{C,P}$ = 2.6 Hz), 131.7, 131.8, 131.9, 132.0, 132.8, 135.0 (d, $J_{C,P}$ = 102 Hz), 135.1 (d, $J_{C,P}$ = 104 Hz), 135.3 (d, $J_{C,P}$ = 6.8 Hz), 209.4 (d, $J_{C,P}$ = 6.8 Hz); HRMS-EI (m/z) for $C_{33}H_{29}OP$ $[M]^+$ calcd. 472.196, found 472.196.

4,4-Dimethyl-1-[2-(phenylethynyl)phenyl]-penta-1,2-diene (6d). To a solution of **14** (100 mg, 290 µmol) in 5 mL of methanol was added 10 mL of 1 N KOH and 5 mL of THF. The reaction mixture was stirred for 4 h at room temperature. After extraction with diethyl ether (3 × 15 mL) the organic phase was washed with water. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. After purification by column chromatography (silica gel, n-pentane, R_f 0.44) **6d** was isolated in 79% yield (62 mg, 228 µmol) as viscous yellow oil. IR (KBr, cm^{-1}) 3058, 3031, 2960, 2901, 2864, 2215, 1947, 1599, 1494, 1445, 1363, 1248, 882, 756. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 9H), 5.52 (d, J = 6.4 Hz, 1H), 6.88 (td, J = 7.6, 1.1 Hz), 6.96–6.99 (m, 3H), 7.05 (td, J = 7.6, 1.1 Hz, 1H), 7.30 (d, J = 6.4 Hz, 1H), 7.40–7.44 (m, 2H), 7.52 (dd, J = 7.6, 1.1 Hz, 1H), 7.67 (d, J = 7.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 30.3, 32.8, 88.4,

94.8, 95.1, 107.2, 121.6, 123.8, 126.3, 126.8, 128.4, 128.6, 128.8, 131.9, 132.8, 137.3, 203.8. HRMS-EI (m/z) for $C_{21}H_{20}$ $[M]^+$ calcd 272.157, found 272.157.

2-Phenyl-1-diphenylphosphinoyl-1*H*-cyclobuta[a]indene (15b). 6b[5a] (50.0 mg, 120 µmol) was dissolved in dry toluene (30 mL) and, after degassing, the resulting solution was refluxed for 4 h. After removal of toluene under reduced pressure and purification by chromatography (preparative TLC, silica gel 60 F_{254}, n-hexane/ethyl acetate = 1 : 1, R_f 0.34) **15b** was isolated in 24% yield (12.0 mg, 28.8 µmol) as a dark yellow solid. Mp: >194 °C decomposition; IR (KBr, cm^{-1}) 3053, 2953, 2923, 2857, 1621, 1547, 1437, 1385, 1180, 1157, 1119, 1102, 1070, 1029, 755, 726, 693. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.39 (d, $J_{H,P}$ = 9.9 Hz, 1H), 5.93 (s, 1H), 7.08 (td, J = 7.5, 1.7 Hz), 7.18–7.24 (m, 4H), 7.32–7.44 (m, 4H), 7.51–7.62 (m, 6H), 7.87–7.95 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 51.1 (d, $J_{C,P}$ = 70 Hz), 113.9, 122.0, 123.8, 124.2, 128.0 (d, $J_{C,P}$ = 12 Hz, 2 × C), 128.7 (d, $J_{C,P}$ = 12 Hz, 2 × C), 128.8 (2 × C), 128.9, 129.1 (2 × C), 129.6, 129.7 (d, $J_{C,P}$ = 113 Hz, 2 × C), 131.2 (d, $J_{C,P}$ = 9.4 Hz, 2 × C), 131.7 (d, $J_{C,P}$ = 8.6 Hz, 2 × C), 131.8 (d, $J_{C,P}$ = 2.6 Hz), 132.0 (d, $J_{C,P}$ = 2.6 Hz), 132.8, 133.4, 138.4 (d, $J_{C,P}$ = 6.0 Hz), 144.7 (d, $J_{C,P}$ = 6.8 Hz), 147.2 (d, $J_{C,P}$ = 14 Hz), 151.5. HRMS-EI (m/z) for $C_{29}H_{21}OP$ $[M]^+$ calcd. 416.133, found 416.133.

1-*t*-Butyl-2-phenyl-1-diphenylphosphinoyl-1*H*-cyclobuta[a]-indene (15c). To a degassed solution of **6c** (250 mg, 529 µmol) in dry toluene (40 mL) was added 100 equiv. of 1,4-CHD (4.47 mL, 52.9 mmol). The resulting solution was heated up to 160 °C for 42.5 h in a sealed vessel. After removal of toluene under reduced pressure and purification by column chromatography (silica gel, n-hexane/ethyl acetate = 3 : 2, R_f 0.65) **15c** was isolated in 67% yield (168 mg, 356 µmol) as orange solid. Mp: 216–218 °C; IR (KBr, cm^{-1}) 3061, 2973, 2928, 2867, 1592, 1537, 1477, 1438, 1368, 1175, 1153, 1107, 761, 697. ^{1}H-NMR (400 MHz, C_6D_6) δ 1.32 (s, 9H), 6.31 (s, 1H), 6.60–6.62 (m, 3H), 6.91 (td, J = 7.3, 1.1 Hz, 1H), 6.98–7.06 (m, 3H), 7.10–7.20 (m, 4H), 7.30 (d, J = 7.5 Hz, 1H), 7.36 (d, J = 7.3 Hz, 1H), 7.99–8.04 (m, 2H), 8.53–8.59 (m, 4H). ^{13}C-NMR (100 MHz, C_6D_6) δ 30.4 (d, $J_{C,P}$ = 4.3 Hz, 3 × C), 39.7 (d, $J_{C,P}$ = 2.6 Hz), 72.0 (d, $J_{C,P}$ = 64 Hz), 116.2, 122.3, 124.4, 124.8, 127.6, 127.7, 128.6 (d, $J_{C,P}$ = 11 Hz, 2 × C), 128.9 (2 × C), 129.2, 129.6, 130.3, 130.6 (2 × C), 130.9 (d, $J_{C,P}$ = 2.6 Hz), 131.4, 131.5, 132.5 (d, $J_{C,P}$ = 8.6 Hz, 2 × C), 134.4 (d, $J_{C,P}$ = 98 Hz), 134.7, 135.8 (d, $J_{C,P}$ = 87 Hz), 144.1 (d, $J_{C,P}$ = 3.4 Hz), 148.2 (d, $J_{C,P}$ = 13 Hz), 151.6 (2 × C), 152.6 (d, $J_{C,P}$ = 4.3 Hz). Anal. calcd. for $C_{33}H_{29}OP$ (472.56): C, 83.87; H, 6.19. Found: C, 83.36; H, 6.46.

1-*t*-Butyl-2-phenyl-1*H*-cyclobuta[a]indene (15d). 6d (50.0 mg, 184 µmol) was dissolved in dry toluene (40 mL) and, after degassing, the resulting solution was refluxed for 8 h. After removal of toluene under reduced pressure and purification by chromatography (preparative TLC, silica gel 60 F_{254}, n-hexane, R_f 0.62) **15d** was isolated in 26% yield (13 mg, 47.7 µmol) as red waxy solid. IR (KBr, cm^{-1}) 3063, 2958, 2903, 2867, 1711, 1676, 1596, 1547, 1460, 1436, 1364, 1180, 754, 696. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 9H), 4.40 (s, 1H), 6.08 (s, 1H), 7.10 (td, J = 7.5, 1.1 Hz, 1H), 7.25 (td, J = 7.5, 1.1 Hz, 1H), 7.29–7.32 (m, 1H), 7.36–7.40 (m, 1H), 7.45–7.49 (m, 2H), 7.66 (dd, J = 7.5, 1.1 Hz, 1H), 7.71–7.74 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 28.6 (3 × C), 33.9, 61.6, 111.0, 121.4, 123.3, 123.5, 128.3 (2 × C), 128.5 (2 × C), 128.6, 129.3, 129.4, 135.0, 146.2, 148.3, 149.9, 152.8. HRMS-EI (m/z) for $C_{21}H_{20}$ $[M]^+$ calcd 272.157, found 272.157.

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