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1-Bromo-2-(diphenylphosphinoyl)ethyne and 1-bromo-2-(*p*-tolylsulfinyl) ethyne: versatile reagents eventually leading to benzocyclotrimers

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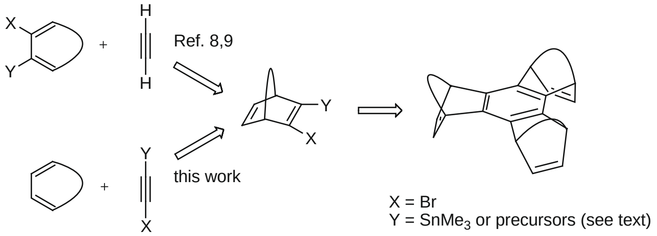
ABSTRACT

The title compounds form Diels–Alder cycloadducts with a number of dienes, which can be transformed into *vic*-bromo(trimethylstannyl)olefins, ultimate precursors for the synthesis of benzocyclotrimers via copper-mediated cyclotrimerization. The overall result is a formal condensation of three diatomic carbons with three dienes.

Benzocyclotrimers are useful scaffolds in supramolecular applications,[1] such as complexation of fullerene,[2] chiral recognition of ammonium salts[3] and gas hosting in molecular capsule.[4] Furthermore, one of these cup-shaped compounds is the crucial precursor for the synthesis of the smallest, non planar fragment of fullerene, that is, sumanene.[5] These and further applications call for general and effective synthetic methodologies. In principle, the Diels–Alder cycloaddition is the most valuable reaction for the synthesis of suitable substrates for the cyclotrimerization provided that the functional groups needed to activate the dienophile are convertible into halogen (bromine) and metal (trimethyltin) moieties which are needed to promote cyclotrimerization.[1–3,5–7] In fact, copper(I) 2-thiophenecarboxylate (CuTC)-mediated cyclotrimerization of *vic*-bromo(trimethyltin)olefins is still the most reliable method to prepare benzocyclotrimers with a wide range of shapes and functional groups.[6,8] In an alternative strategy, we have proved that these two functionalities can be introduced in the diene rather than in the dienophile (Scheme 1).[8,9]

Both sulfoxide and phosphine oxide groups can efficiently activate triple bonds for Diels–Alder reactions.[10,11] In addition, when treated with organometallic reagents they can act as leaving groups in olefins bearing vicinal halogens.[12,13] For these reasons, 1-bromo-2-(diphenylphosphinoyl)ethyne and 1-bromo-2-(*p*-tolylsulfinyl)ethyne can be regarded as synthetic equivalents of 1-bromo-2-(trimethyltin)ethyne.



Scheme 1. Possible strategies for the synthesis of precursors of benzocyclotrimers.

The synthesis of 1-bromo-2-(*p*-tolylsulfinyl)ethyne **1** turned out to be low yielding and troublesome,[14] such as the cycloaddition reaction was tested with 1,3-cyclopentadiene only providing the expected cycloadducts in good yield as a separable 1:1 mixture of diastereomers.[15] The latter underwent facile substitution at sulfur with phenylmagnesiumbromide. The resulting organomagnesium derivative was treated with trimethyltinchloride to afford 2-bromo-3-(trimethyltin)bicyclo[2.2.1]hepta-2,5-diene **3**[7b,16] in good yields (Scheme 2).

In order to overcome the poor stability of **1**, 1-bromo-2-(diphenylphosphinoyl)ethyne was synthesized. Commercially available trimethylsilylethyne or sodium acetylide was converted into intermediate diphenylphosphinoylethyne (DPE) in good yields.[17] The

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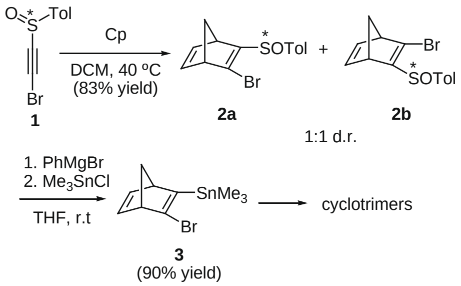
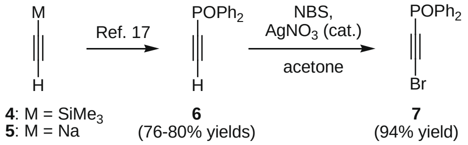
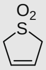
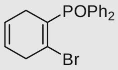
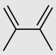
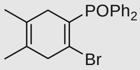
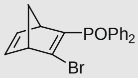
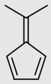
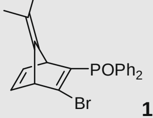
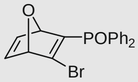
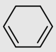
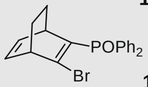
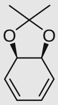
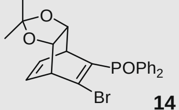
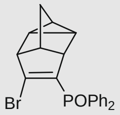
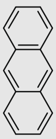
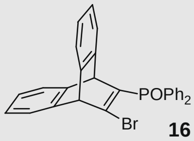


Scheme 2. Synthesis of norbornadiene benzocyclotrimers, via cycloaddition of bromo sulfinyl alkyne **1** and sulfinyl replacement.

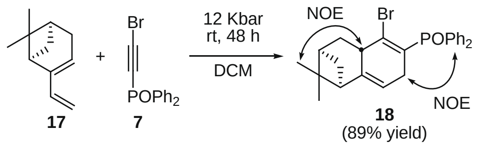


Scheme 3. Synthesis of dienophile **7**.

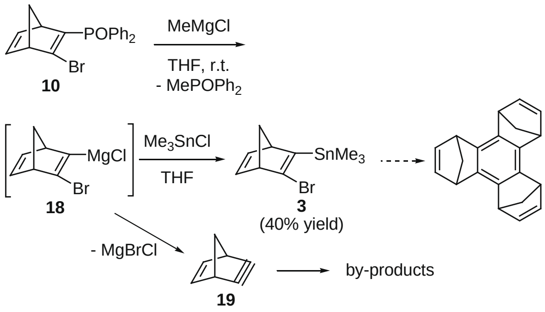
Table 1
Cycloaddition of **7** with 1,3-dienes

Entry	Diene	Cycloadduct	Yield[a] (%)
1		 **8**	27[b]
2		 **9**	48[b]
3		 **10**	80
4		 **11**	53
5		 **12**	27
6		 **13**	22[c]
7		 **14**	94
8		 **15**	34
9		 **16**	72

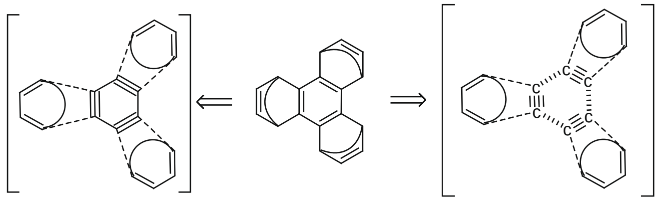
[a] Isolated yields.
[b] Aromatization occurred.
[c] Aromatization occurred via retro Diels–Alder.



Scheme 4. High-pressure Diels–Alder reaction of (−)-nopadiene with **7**.



Scheme 5. Possible paths of organometallic intermediate generated by **10**.



Scheme 6. Alternative disconnections for benzocyclotrimers: tribenzyne cycloaddition (left), versus cyclo-condensation of diatomic carbon (right).

bromination of DPE was achieved with *N*-bromosuccinimide in the presence of catalytic amounts of silver(I) nitrate,[18] to afford **7** in good yield and reasonable purity after a simple filtration over basic alumina (Scheme 3).[19]

The cycloaddition of **7** was tested with a number of dienes under standard conditions at 120 °C, affording the expected products in variable yields (Table 1).[20] Nevertheless in the case of cyclopentadiene, when milder conditions (80 °C) were applied for a prolonged time (24 h), a nearly quantitative amount of cycloadduct was obtained.

Other 1,3-dienes (1,3,5,7-cyclooctatetraene, α-phellandrene, naphthalene, 1*H*-pyrrol-*N*-(*t*-butyl)carbamate, 1-tosyl-1*H*-pyrrole and nopadiene) failed to afford the expected cycloadducts, because of concomitant decomposition. In order to avoid the isomerization, nopadiene **17**[21] was reacted with the dienophile at rt under high pressure conditions (12 kbar)[22] for 48 hours, to obtain cycloadduct **18** in very good yield as a single stereo- and regio-isomer, as demonstrated by NOESY experiments (Scheme 4).[23]

The cycloadduct **10** was treated with various Grignard reagents[24] in THF, followed by quenching with trimethyltinchloride: when methyl magnesiumchloride was used the desired precursor **3** was obtained, although in modest yield (Scheme 5).

The poor yield can be imputed to the long reaction time required for the complete consumption of the starting phosphine oxide: during this time the resulting *vic*-bromo(chloromagnesium)olefin can decompose with elimination of the dihalomagnesium salt, leading to the formation of the very reactive strained alkyne **19**.[25] Furthermore, when the reaction was carried out in the presence of a catalytic amount of nickel(II) dichloro[1,2-bis(diphenylphosphino)ethane], a small amount of *syn*- and *anti*-cyclotrimers was observed in the reaction mixture. Under these conditions nickel can either mediate the coupling between organomagnesium species with halides[26] or stabilize the strained alkyne by complexation.[27]

In conclusion, in this Letter we describe the use of two different dienophiles for the synthesis of cycloadducts that can be converted to precursors of functionalized cyclotrimers. The overall path is such that the dienophile can be regarded as a synthetic equivalent of diatomic carbon, or it can resemble a cycloaddition of cyclohexatriene with three dienes (Scheme 6).

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14. Obtained according to the reported methodology for 1-bromo-2-(phenylsulfinyl)ethyne: Hori, I.; Oishi, T. *Tetrahedron Lett.* **1979**, *42*, 4087-4090. An analytical sample of 1-bromo-2-(*p*-tolylsulfinyl)ethyne (**1**) was obtained by FC on silica-gel (eluant Et$_2$O/hexanes 3:7): pale yellow oil stable for several months in CDCl$_3$ solution in refrigerator, which rapidly polymerizes when concentrated. ^{1}H NMR (CDCl$_3$, 200 MHz, TMS) δ 7.68 (2H, d, J = 7.0 Hz); 7.36 (2H, d, J = 7.0 Hz); 2.44 (3H, s); ^{13}C NMR (CDCl$_3$, 50 MHz, TMS) δ 142.9, 140.2, 130.2, 125.1, 78.2, 66.8, 21.4; IR (film) ν 3056, 2925, 2130, 1089, 1059, 809, 537; GC–MS (EI, 70 eV): *m/z* 194–196 (13), 155 (54), 139 (100), 91 (31), 65 (40).
15. Diastereomers of 2-bromo-3-(phenylsulfinyl)-bicyclo[2.2.1]hepta-2,5-diene **2a** and **2b** were separated by flash-chromatography (eluant 6:4 diethylether/hexanes). *First eluant*: colourless oil (44% yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ (ppm): 7.55 (2H, d, J = 8.3 Hz), 7.34 (2H, d, J = 8.3 Hz), 6.92 (1H, dd, J = 5.0 and 3.0 Hz), 6.84 (1H, dd, J = 5.0 and 3.0 Hz), 3.70 (1H, br s), 3.65 (1H, br s), 2.44 (3H, s), 2.04 (1H, dt, J = 6.6 and 1.8 Hz), 1.99 (1H, dd, J = 6.6 and 1.4 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz) δ (ppm): 153.0, 143.4, 142.9, 141.09, 140.1, 129.9, 129.7, 124.0, 72.0, 60.1, 50.1, 21.4; MS (70 eV): *m/z* 260–262 ($\mathrm{M^{+}}$–SO, 24), 229 (50), 181 (56), 166 (55), 89 (91), 77 (100%). *Second eluate:* colourless oil, (39% yield). ^{1}H NMR (CDCl$_3$, 300 MHz) δ (ppm): 7.35 (2H, d, J = 8.2 Hz), 7.28 (2H, d, J = 8.2 Hz), 6.50 (1H, dd, J = 3.2 and 4.7 Hz), 6.01 (1H, dd, J = 3.2 and 4.7 Hz), 3.82 (1H, br s), 3.71 (1H, br s), 2.41 (3H, s), 2.34 (1H, dt, J = 6.7 and 1.5 Hz), 2.07 (1H, dd, J = 6.7 and 1.7 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz) δ (ppm): 153.0, 142.4, 141.0, 140.9, 137.8, 136.3, 129.7, 124.0, 70.8, 60.1, 48.3; MS (70 eV): *m/z*: 260–262 ($\mathrm{M^{+}}$–SO, 25), 229 (51), 181 (57), 166 (56), 89 (89), 77 (100%).
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19. An analytical sample of 1-bromo-2-(diphenylphosphinoyl)ethyne (**7**) was obtained by FC on silica-gel (eluant AcOEt/hexanes 6:4): mp 67 °C. ^{1}H NMR (CDCl$_3$, 200 MHz, TMS) δ 7.91–7.75 (4H, Ar, m), 7.36–7.42 (6H, Ar, m); ^{13}C NMR (CDCl$_3$, 50 MHz, TMS) δ 132.2 (Ar, J_{PCipso} = 122.8 Hz), 132.4 (Ar, J_{CPpara} = 3.0 Hz), 130.9 (Ar, J_{CPmeta} = 11.4 Hz), 128.7 (Ar, J_{CPortho} = 13.7 Hz), 76.4 ($\mathrm{C{\equiv}C}$, J_{CP} = 161.0 Hz), 69.2 ($\mathrm{C{\equiv}C}$, J_{CP} = 26.2 Hz); ^{31}P NMR (CDCl$_3$, 80 MHz, H$_3$PO$_4$) δ 9.17; IR (KBr) ν 3058, 2141, 1200. GC–MS (EI, 70 eV) *m/z* 306–304 (8), 225 (100), 178 (24), 77 (23%).
20. *General cycloaddition procedure.* In a screw-capped Pyrex test tube, a solution of **7** (915 mg, 3.0 mmol), diene (1 equiv for entry 4; 1.2 equiv for entry 7; 1.5 equiv for entries 5, 6, 9; 2.0 equiv for entries 2, 3, 8; 4.0 equiv for entry 1) and hydroquinone (5 mg) in toluene (1 mL) was purged with argon, sealed and heated at 120 °C for 18 h. The mixture was purified by flash-chromatography (eluant 1:1 AcOEt/hexanes). 1-Bromo-2-(diphenylphosphinoyl)cyclohexa-1,4-diene (**8**). Waxy solid. ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ (ppm): 7.85–7.63 (4H, m), 7.60–7.30 (6 H, m), 5.74–5.47 (2H, m), 3.39–3.23 (2H, m), 2.82–2.66 (2H, m); ^{31}P NMR (81 MHz, CHCl$_3$, H$_3$PO$_4$) δ (ppm): 29.7; ^{13}C NMR (50 MHz, CHCl$_3$, TMS) δ (ppm): 135.9 (d, J = 10.6 Hz), 134.5 (d, J = 24.8 Hz), 133.9 (d, J = 104.0 Hz), 133.4 (d, J = 2.4 Hz), 131.9 (d, J = 2.8 Hz), 131.7 (d, J = 10.0 Hz), 128.6 (d, J = 12.4 Hz), 123.0 (d, J = 8.8 Hz), 122.7 (d, J = 1.3 Hz), 39.6 (d, J = 7.7 Hz), 33.0 (d, J = 10.2 Hz); IR (KBr) ν 1187 (PO) cm^{-1}; *m/z* (EI, 70 eV): 358–360 ($\mathrm{M^{+}}$, 20), 359–357 ($\mathrm{M^{+}}$–H, 55), 357–355 (80), 277 (80), 199 (90), 152 (97), 77 (100%). 1-Bromo-2-(diphenylphosphinoyl)-4,5-dimethylcyclohexa-1,4-diene (**9**). Waxy solid. ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ (ppm): 7.84–7.67 (4H, m), 7.60–7.38 (6 H, m), 3.28–3.13 (2H, m), 2.81–2.64 (2H, m), 1.60 (3H, s), 1.52 (3H, s); ^{31}P NMR (81 MHz, CHCl$_3$, H$_3$PO$_4$) δ (ppm): 29.1; ^{13}C NMR (50 MHz, CHCl$_3$, TMS) δ (ppm): 133.2 (d, $J_{\text{C–P}}$ = 20.5 Hz), 131.8 (d, $J_{\text{C–P}}$ = 2.8 Hz), 131.7 (d, $J_{\text{C–P}}$ = 10.0 Hz), 131.0 (d, $J_{\text{C–P}}$ = 9.6 Hz), 129.9 (d, $J_{\text{C–P}}$ = 93.6 Hz), 128.5 (d, $J_{\text{C–P}}$ = 12.4 Hz), 122.5 (d, $J_{\text{C–P}}$ = 6.4 Hz), 122.4 (d, $J_{\text{C–P}}$ = 0.8 Hz), 46.0 (d, $J_{\text{C–P}}$ = 8.0 Hz), 39.0 (d, $J_{\text{C–P}}$ = 9.2 Hz), 17.7, 17.5; IR (KBr) ν 1199 ($\mathrm{P{=}O}$) cm^{-1}; *m/z* (EI, 70 eV): 388–386 ($\mathrm{M^{+}}$, 25), 385–388 ($\mathrm{M^{+}}$–H, 85), 305–307 (80), 227 (80), 201 (100), 77 (97%). 2-Bromo-3-(diphenylphosphinoyl)bicyclo[2.2.1]hepta-2,5-diene (**10**). Oil. ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ (ppm): 7.76–7.37(10 H, series of m), 6.86 (1H, dd, J = 4.9 and 3.0 Hz), 6.76 (1H, dd, J = 4.9 and 3.0 Hz), 3.95 (1H, br s), 3.75 (1H, br s), 2.42 (1H, dt, J = 6.7 and 1.8 Hz), 2.07(1H, br d, J = 6.7 Hz); ^{31}P NMR (81 MHz, CHCl$_3$, H$_3$PO$_4$) δ (ppm): 24.1; ^{13}C NMR (50 MHz, CHCl$_3$, TMS) δ (ppm): 151.1 (d, $J_{\text{C–P}}$ = 4.4 Hz), 142.9 (d, $J_{\text{C–P}}$ = 0.8 Hz), 141.5 (d, $J_{\text{C–P}}$ = 112.8 Hz), 140.0 (d, $J_{\text{C–P}}$ = 2.0 Hz), 132.4 (d, $J_{\text{C–P}}$ = 38.9 Hz), 132.0 (d, $J_{\text{C–P}}$ = 2.8 Hz), 131.9 (d, $J_{\text{C–P}}$ = 2.8 Hz), 131.6 (d, $J_{\text{C–P}}$ = 10.4 Hz, two overlapping C), 130.2 (d, $J_{\text{C–P}}$ = 38.5 Hz), 128.5 (d, $J_{\text{C–P}}$ = 12.4 Hz), 128.4 (d, $J_{\text{C–P}}$ = 12.4 Hz), 72.3 (d, $J_{\text{C–P}}$ = 4.4 Hz), 63.0 (d, $J_{\text{C–P}}$ = 9.3 Hz), 55.1 (d, $J_{\text{C–P}}$ = 8.8 Hz); IR (film) ν 1182 ($\mathrm{P{=}O}$) cm^{-1}; *m/z* (EI, 70 eV): 370–372 ($\mathrm{M^{+}}$, 3), 369–371 ($\mathrm{M^{+}}$–H, 4), 355–307 (8), 291 (100), 201 (50), 77 (70%). 2-Bromo-3-(diphenylphosphinoyl)-7-isopropylidenebicyclo[2.2.1]hepta-2,5-diene (**11**). Colourless crystals mp = 102–103 °C (dec); ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ (ppm): 7.27–7.32 (10H, series of m), 6.89 (1H, ddd, J = 4.3, 3.0 and 1.2 Hz), 6.79 (1H, dd, J = 4.3 and 3.0 Hz), 4.30–4.21 (1H, m), 4.18–4.11 (1H, m), 1.45 (3H, s), 1.35 (3H, s); ^{31}P NMR (81 MHz, CHCl$_3$, H$_3$PO$_4$) δ (ppm): 24.1; ^{13}C NMR (50 MHz, CHCl$_3$, TMS) δ (ppm): 160.2 (d, $J_{\text{C–P}}$ = 5.2 Hz), 149.5 (d, $J_{\text{C–P}}$ = 4.8 Hz), 142.3 (d, $J_{\text{C–P}}$ = 1.2 Hz), 141.3 (d, $J_{\text{C–P}}$ = 110.8 Hz), 140.0 (d, $J_{\text{C–P}}$ = 2.0 Hz), 132.3 (d, $J_{\text{C–P}}$ = 9.6 Hz), 131.91 (d, $J_{\text{C–P}}$ = 2.8 Hz), 131.89 (d, $J_{\text{C–P}}$ = 2.8 Hz), 131.6 (d, $J_{\text{C–P}}$ = 10.4 Hz), 131.4 (d, $J_{\text{C–P}}$ = 10.4 Hz), 130.2 (d, $J_{\text{C–P}}$ = 9.2 Hz), 128.42 (d, $J_{\text{C–P}}$ = 12.4 Hz), 128.38 (d, $J_{\text{C–P}}$ = 12.8 Hz), 99.2, 62.5 (d, $J_{\text{C–P}}$ = 7.6 Hz), 55.3 (d, $J_{\text{C–P}}$ = 9.2 Hz), 18.4, 18.1; IR (KBr.) ν 1198 ($\mathrm{P{=}O}$) cm^{-1}; *m/z* (EI, 70 eV): 410–412 ($\mathrm{M^{+}}$, 7), 409–411 ($\mathrm{M^{+}}$–H, 15), 201 (25), 141 (75), 57 (100%). 2-Bromo-3-(diphenylphosphinoyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene (**12**). Colourless crystals mp = 125–127 °C (dec); ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ (ppm): 7.78–7.39 (10 H, series of m), 7.16 (1H, dd, J = 5.4 and 1.8 Hz), 7.06 (1H, dd, J = 5.4 and 1.8 Hz), 5.69 (1H, br q, J = 1.5 Hz), 5.37–5.34 (1H, m); ^{31}P NMR (81 MHz, CHCl$_3$, H$_3$PO$_4$) δ (ppm): 21.9; ^{13}C NMR (50 MHz, CHCl$_3$, TMS) δ (ppm): 151.6 (d, $J_{\text{C–P}}$ = 4.0 Hz), 144.6 (d, $J_{\text{C–P}}$ = 0.8 Hz), 142.8 (d, $J_{\text{C–P}}$ = 113.2 Hz), 140.5 (d, $J_{\text{C–P}}$ = 1.6 Hz), 132.4 (d, $J_{\text{C–P}}$ = 3.2 Hz, two overlapping C), 131.7 (d, $J_{\text{C–P}}$ = 10.4 Hz), 131.5 (d, $J_{\text{C–P}}$ = 10.4 Hz), 130.7 (d, $J_{\text{C–P}}$ = 110.8 Hz), 130.2 (d, $J_{\text{C–P}}$ = 110.8 Hz), 128.8 (d, $J_{\text{C–P}}$ = 12.8 Hz), 128.7 (d, $J_{\text{C–P}}$ = 12.8 Hz), 90.5 (d, $J_{\text{C–P}}$ = 9.2 Hz), 87.2 (d, $J_{\text{C–P}}$ = 11.6 Hz); IR (KBr) ν 1186 ($\mathrm{P{=}O}$) cm^{-1}; *m/z* (EI, 70 eV): 355–357 ($\mathrm{M^{+}}$–O, 10), 280–282 (15), 133 (60), 95 (65), 76 (100%). 2-Bromo-3-(diphenylphosphinoyl)bicyclo[2.2.2]octa-2,5-diene (**13**). Colourless crystals mp = 130–4 °C (dec); ^{1}H NMR (200 MHz, CDCl$_3$, TMS) δ (ppm): 7.78–7.30 (10 H, series of m), 6.40–6.30 (2H, m), 4.16–4.00 (1H, m), 3.96–3.82 (1H, m), 1.50–1.20 (4H, m); ^{31}P NMR (81 MHz, CHCl$_3$, H$_3$PO$_4$) δ (ppm): 26.4; ^{13}C NMR (50 MHz, CHCl$_3$, TMS) δ (ppm): 138.8 (d, $J_{\text{C–P}}$ = 2.8 Hz), 135.5 (d, $J_{\text{C–P}}$ = 106.0 Hz), 133.8 (d, $J_{\text{C–P}}$ = 3.6 Hz), 132.8 (d, $J_{\text{C–P}}$ = 2.0 Hz), 131.8 (d, $J_{\text{C–P}}$ = 108.0 Hz), 131.7 (d, $J_{\text{C–P}}$ = 3.2 Hz), 131.6 (d, $J_{\text{C–P}}$ = 2.8 Hz), 131.5 (d, $J_{\text{C–P}}$ = 107.2 Hz), 131.5 (d, $J_{\text{C–P}}$ = 10.4 Hz), 131.4 (d,

$J_{\mathrm{C-P}} = 10.4$ Hz), 128.3 (d, $J_{\mathrm{C-P}} = 12.8$ Hz, two overlapping C), 51.2 (d, $J_{\mathrm{C-P}} = 7.2$ Hz), 41.7 (d, $J_{\mathrm{C-P}} = 8.4$ Hz), 24.9 (d, $J_{\mathrm{C-P}} = 1.6$ Hz), 24.6 (d, $J_{\mathrm{C-P}} = 2.0$ Hz); IR (KBr) ν 1190 (P=O) $\mathrm{cm^{-1}}$; *m/z* (EI, 70 eV): 358–356 ($M^+ - C_2H_4$, 55), 357–355 (70), 277 (60), 199 (85), 183 (70), 152 (100), 77 (97%). 8-Bromo-9-(diphenylphosphinoyl)-4,4-dimethyl-3,5-dioxatricyclo[5.2.2.0^{2,6}]undeca-8,10-diene (**14**). Colourless crystals mp = 153–155 °C (dec.) (Et_2O). ^1H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 7.77–7.40 (10 H, series of m), 6.43 (1H, *pseudo*-t, $J = 6.3$ Hz), 6.33 (1H, *pseudo*-t, $J = 6.3$ Hz), 4.51 (1H, dd, $J = 6.9$ and 3.5 Hz), 4.31 (1H, dd, $J = 6.9$ and 3.5 Hz), 4.20–4.07 (2H, m), 1.29 (3H, s), 1.25 (3H, s); ^{31}P NMR (81 MHz, $CHCl_3$, H_3PO_4) δ (ppm): 26.3; ^{13}C NMR (50 MHz, $CHCl_3$, TMS) δ (ppm): 139.2 (d, $J_{\mathrm{C-P}} = 3.2$ Hz), 134.6 (d, $J_{\mathrm{C-P}} = 104.2$ Hz), 131.3 (d, $J_{\mathrm{C-P}} = 108.4$ Hz), 131.2 (d, $J_{\mathrm{C-P}} = 108.0$ Hz), 132.19 (d, $J_{\mathrm{C-P}} = 2.9$ Hz), 132.17 (d, $J_{\mathrm{C-P}} = 2.8$ Hz), 131.7 (d, $J_{\mathrm{C-P}} = 11.5$ Hz), 131.5 (d, $J_{\mathrm{C-P}} = 11.1$ Hz), 131.4 (d, $J_{\mathrm{C-P}} = 3.4$ Hz), 131.0 (d, $J_{\mathrm{C-P}} = 1.9$ Hz), 128.8 (d, $J_{\mathrm{C-P}} = 12.8$ Hz), 128.7 (d, $J_{\mathrm{C-P}} = 12.5$ Hz), 113.6, 78.0 (d, $J_{\mathrm{C-P}} = 3.0$ Hz), 77.5 (d, $J_{\mathrm{C-P}} = 2.9$ Hz), 56.6 (d, $J_{\mathrm{C-P}} = 7.1$ Hz), 46.6 (d, $J_{\mathrm{C-P}} = 8.0$ Hz), 25.7, 25.6; IR (KBr) ν 1189 (P=O) $\mathrm{cm^{-1}}$; *m/z* (EI, 70 eV): 358–356 ($M^+ - C_5H_8O_2$, 27), 357–355 ($M^+ - C_5H_9O_2$, 70), 277 (30), 199 (60), 152 (70), 77 (100%). 8-Bromo-9-(diphenylphosphinoyl)tetracyclo [4.3.0.^{2,4}0^{3,7}]non-8-ene (**15**). Colourless crystals mp = 130–3 °C; ^1H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 7.80–7.62 (4H, m), 7.60–7.37(6 H, m), 2.97–2.88 (2H, m), 2.37 (1H, br s), 1.84–1.76 (1H, m), 1.70–1.62 (1H, m), 1.57 (2H, br s), 1.49–1.41 (1H, m); ^{31}P NMR (81 MHz, $CHCl_3$, H_3PO_4) δ (ppm): 23.4; ^{13}C NMR (50 MHz, $CHCl_3$, TMS) δ (ppm): 140.9 (d, $J_{\mathrm{C-P}} = 2.4$ Hz), 136.7 (d, $J_{\mathrm{C-P}} = 110.0$ Hz), 134.0 (d, $J_{\mathrm{C-P}} = 65.8$ Hz), 132.0 (d, $J_{\mathrm{C-P}} = 75.5$ Hz), 131.8 (d, $J_{\mathrm{C-P}} = 3.2$ Hz, two overlapping C), 131.6 (d, $J_{\mathrm{C-P}} = 10.4$ Hz), 131.5 (d, $J_{\mathrm{C-P}} = 10.4$ Hz), 131.2 (d, $J_{\mathrm{C-P}} = 62.6$ Hz), 128.4 (d, $J_{\mathrm{C-P}} = 13.6$ Hz, two overlapping C), 61.0 (d, $J_{\mathrm{C-P}} = 9.6$ Hz), 56.8 (d, $J_{\mathrm{C-P}} = 4.8$ Hz), 53.8 (d, $J_{\mathrm{C-P}} = 8.8$ Hz), 32.4, 26.7, 23.8 (d, $J_{\mathrm{C-P}} = 0.8$ Hz), 23.4 (d, $J_{\mathrm{C-P}} = 2.8$ Hz); IR (KBr) ν 1194 (P=O) $\mathrm{cm^{-1}}$; *m/z* (EI, 70 eV): 398–396 (M^+, 7), ($M^+ - H$, 17), 317 (28), 201 (100), 115 (60), 77 (50%). **11-**Bromo-12-(diphenylphosphinoyl)-9,10-dihydro-9,10-ethenylantracene (**16**). Colourless crystals mp = 130–132 °C (dec); ^1H NMR (200 MHz, $CDCl_3$, TMS) δ (ppm): 7.60–7.32 (12H, m), 7.14–6.94 (8 H, m), 5.34–5.25 (2H, m); ^{31}P NMR (81 MHz, $CHCl_3$, H_3PO_4) δ (ppm): 28.0; ^{13}C NMR (50 MHz, $CHCl_3$, TMS) δ (ppm): 146.2 (d, $J_{\mathrm{C-P}} = 2.8$ Hz), 143.2 (d, $J_{\mathrm{C-P}} = 2.8$ Hz), 143.1 (d, $J_{\mathrm{C-P}} = 2.0$ Hz), 138.8 (d, $J_{\mathrm{C-P}} = 103.6$ Hz), 132.1 (d, $J_{\mathrm{C-P}} = 2.8$ Hz), 131.8 (d, $J_{\mathrm{C-P}} = 10.4$ Hz), 131.1 (d, $J_{\mathrm{C-P}} = 108.8$ Hz), 128.5 (d, $J_{\mathrm{C-P}} = 12.4$ Hz), 125.7, 125.2, 123.6, 123.4, 64.3 (d, $J_{\mathrm{C-P}} = 7.2$ Hz), 55.0 (d, $J_{\mathrm{C-P}} = 8.8$ Hz); IR (KBr) ν 1184 (P=O) $\mathrm{cm^{-1}}$; *m/z* (EI, 70 eV): 484–482 (M^+, 1), 403 ($M^+ - Br$, 7), 201 (30), 178 (100%).

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23. A solution of **7** (1.04 g, 3.4 mmol) and nopadiene (666 mg, 4.5 mmol) in DCM was placed in a 3 mL screw-capped Teflon capsule that was submitted to 12 Kbar pressure for 48 hours at r.t. The volatile materials were removed, and the residue was recrystallized from AcOEt to afford 1.39 g (89% yield) of 5-bromo-6-(diphenylphosphinoyl)-9,9-dimethyl-1,2,3,4,4a,7-hexahydro-1,3-methanonaphthalene (**18**) as colourless crystals, mp = 184–185 °C. $[\alpha]_D^{22}$ −12 (*c* 1.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 7.68–7.76 (4H, series of m), 7.41–7.56 (6H, series of m), 5.31 (1H, m), 3.75 (1H, m), 2.48–2.82 (4H, series of m), 2.08–2.38 (3H, series of m), 1.27 (3H, s), 0.97 (3H, s), 0.90 (1H, d, $J = 8.9$ Hz); ^{31}P NMR (122 MHz, $CDCl_3$, H_3PO_4) δ (ppm): 30.6; ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ (ppm): 143.7 (d, $J = 1.5$ Hz), 143.3, 132.6 (d, $J = 106.2$ Hz), 132.3 (d, $J = 105.0$ Hz), 132.1 (d, $J = 3.4$ Hz), 132.0 (d, $J = 3.4$ Hz), 131.7 (d, $J = 9.7$ Hz), 131.6 (d, $J = 9.9$ Hz), 128.6 (d, $J = 101.2$ Hz), 128.5 (d, $J = 12.3$ Hz), 128.4 (d, $J = 12.3$ Hz), 115.4 (d, $J = 9.0$ Hz), 51.1, 42.3, 40.2 (d, $J = 7.9$ Hz), 39.5, 35.7, 34.0, 33.8 (d, $J = 10.6$ Hz), 27.0, 23.2; IR (KBr) ν 1187 (P=O) $\mathrm{cm^{-1}}$.
24. PhMgBr furnished no products, presumably because of steric hindrance. Me_2 Mg/MgI_2 in THF furnished only 10–15% yields of **3**.
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