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Pd(0)-Catalysed Formation of Diarylated Dienes from Propargyl Carbonates and Organoboron and Organotin(IV) Reagents.

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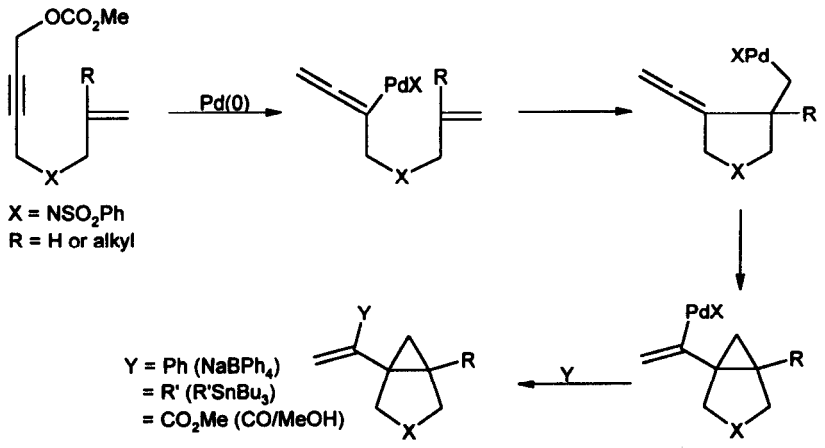
Abstract. The 1,1-dimethylbutyne-1,4-diol derivative **1** reacts with 2 mol. equiv. of organoboron ($NaBPh_4$ arylboronic acids) and organotin(IV) reagents to give 1,1-dimethyl-2,3-disubstituted butadienes in good yield via allenylpalladium(II) and vinylidene-π-allylpalladium(II) intermediates. Unsubstituted esters **6** and butyne dicarbonate **7** lead to symmetrical dienes **8**.

Keywords. Catalysis, allenylpalladium(II), π-allylpalladium(II), boronic acids, Stille coupling, Suzuki coupling.

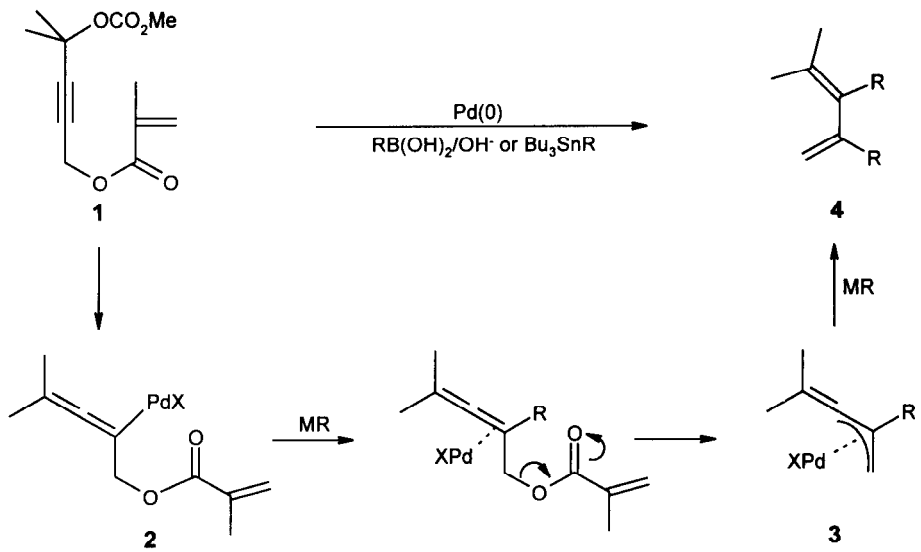
Propargyl carbonates provide a facile entry to allenylpalladium(II) species[1] which are versatile intermediates in a variety of Pd(0) catalysed processes.[2] We[3] and subsequently others[4] have utilised them to access hetero bicyclo [3.1.0]hexanes (Scheme 1).[2]



Scheme 1

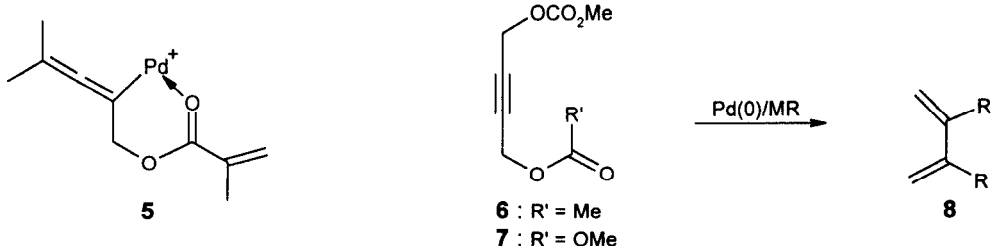
0040-4020/99/$ - see front matter
PII: S0040-4020(99)00831-5

In the context of our palladium catalysed cascade cyclisation-anion capture methodology[5] the allenylpalladium(II) species is attractive and versatile in that it can function as a dual starter and terminating species as illustrated in Scheme 1.[3,5] In pursuing these studies we encountered, serendipitously, a further useful process that occurs when the propargyl carbonate contains an additional potential leaving group (Scheme 2).



Scheme 2

In the case of the alkyne **1**, which has a methacryloyloxy substituent in addition to the carbonate moiety, the cyclopropanation does not occur when B or Sn(IV) anion capture agents are used. The products from these reactions are 1,3-dienes **4** which arise from reactions with two mol. eq. of the organoboron or Sn(IV) reagents. A plausible mechanism for diene formation (Scheme 2) involves initial formation of the allenylpalladium(II) species **2** followed by cross-coupling with the boron or tin reagent. Loss of the acryloyloxy group then generates π-allyl species **3** which reacts further with the boron or tin reagent to give **4**.



5

6 : R' = Me
7 : R' = OMe

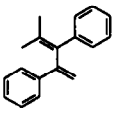
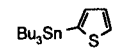
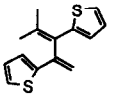
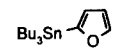
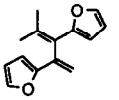
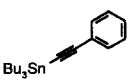
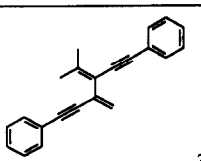
8

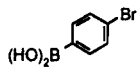
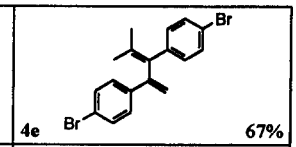
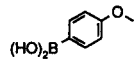
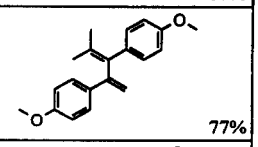
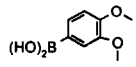
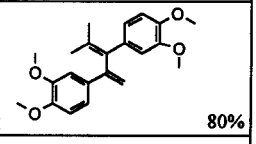
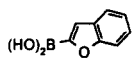
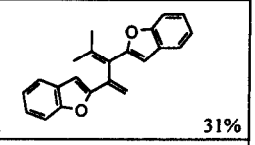
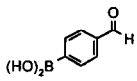
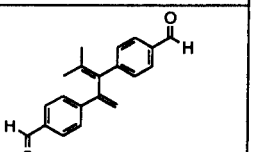
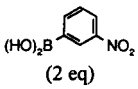
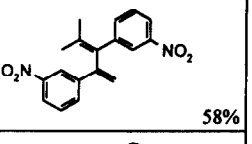
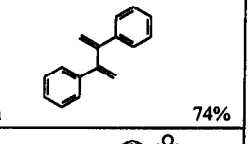
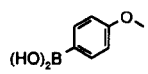
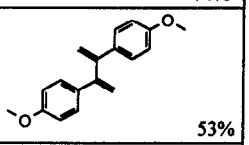
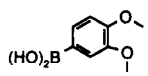
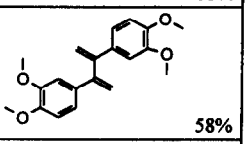
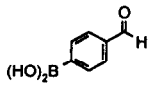
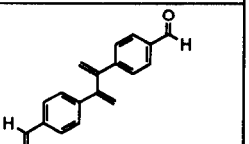
Scheme 3

Whereas in Scheme 1 5-exo trig cyclisation of the allenylpalladium(II) species is faster than cross-coupling the corresponding relative rates in Scheme 2 are reversed. This suggests a role for the acryloyloxy moiety in **2** in favouring cross-coupling over cyclisation. The complex **5**, which provides two vacant co-ordination sites allied with a cationic palladium centre, illustrates a possible basis for this rate reversal.

Simple esters like **6**[6] or carbonates **7**[7] undergo the same type of reaction and afford symmetrical dienes **8**, albeit in lower yields compared to reactions with the dimethyl substituted compound **1**. Tsuji et al. have reported a related carbonylation process **7** → **8** (50°C, 10 atm CO, EtOH; R = CO_2Et)[7] and π-allyl species analogous to **3** have been invoked in several other catalytic processes.[8] Our results, involving sodium tetraphenylborates, six boronic acids and three stannanes, are summarised in Table 1. The product dienes **4b** - **4j** generally exhibit low stability. They can be stored in solution in diethyl ether below 4°C for several weeks whilst the pure colourless or pale yellow dienes turn brown within hours. For this reason it was not possible to obtain full analytical data on all the products. In cases where elemental analysis was not available accurate mass measurements were made, apart from **4d** which proved the most unstable diene and for which only ^1H nmr data are presented. Several attempts were made to effect Diels-Alder reactions with **4a** and N-methylmaleimide (NMM) and N-phenyl-1,3,4-triazolin-2,5-dione (NPTAD). The Diels-Alder reaction with NMM failed to occur even at 140°C in xylene for 48 h. NPTAD reacts with the dienes even at low temperatures (-78°C to 25°C) to afford insoluble materials. The physical properties and spectroscopical data of **8a**[9], **8b**[10] and **8c**[11] are consistent with those previously reported in the literature.

Table 1. Formation of Dienes **4** and **8** from **1**, **6** or **7**, respectively, and Organoboron and $RSnBu_3$ Reagents.[a]

Entry	Procedure	B/Sn-reagent	Base/ Additive	Solvent	Temp. (°C)	Time (h)	Product/Yield
1	A	$NaBPh_4$ (1.3eq)	-	THF	65	2	 **4a** 93%
2	B	 (2.2 eq)	LiCl (2 eq)	THF	65	4	 **4b** 94%
3	B	 (2.2 eq)	LiCl (2 eq)	THF	65	4	 **4c** 90%
4	B	 (2.2 eq)	LiCl (2 eq)	THF	0→rt	5	 **4d** 37%

5	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	0→rt	4	 **4e** 67%
6	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	0→rt	4	 **4f** 77%
7	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	0→rt	5	 **4g** 80%
8	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	Rt, then 50	60, then 5	 **4h** 31%
9	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	0→rt	5	 **4l** 58%
10	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	70	15	 **4j** 58%
11	A	$NaBPh_4$ (1.3eq)	-	THF	65	4	 **8a** 74%
12	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	65	15	 **8b** 53%
13	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	65	15	 **8c** 58%
14	C	 (2 eq)	K_2CO_3 (4 eq)	Toluene/ Water	rt	15	 **8d** 42%

a. all reactions employed a catalytic system comprising 10 mol% $Pd(OAc)_2$ and 20 mol% PPh_3

EXPERIMENTAL SECTION ^{1}H-NMR spectra were recorded for deuterochloroform solutions at 250 MHz and ^{13}C-NMR spectra were recorded at 63 MHz on a Bruker AVANCE 250 spectrometer. Chemical shifts are reported in parts per million (d) downfield from tetramethylsilane as internal standard. Coupling constants are reported in hertz (Hz). Mass spectral data were recorded using a VG Autospec operating at 70 eV. Accurate molecular weights were determined using perfluorokerosine as internal standard. Microanalyses were obtained using a Carlo Erba elemental analyser MOD.1108. Flash chromatography was performed with Fischer Chemicals Matrex Silica 60 (35-70 mm). Thin-layer chromatography was performed on Merck TLC plastic sheets (silica gel 60 F_{254}). Tetrahydrofuran and toluene were dried over sodium with subsequent distillation. Petroleum ether (PE) refers to the fraction with bp 40-60°C.

2,3-Diphenyl-4-methyl-1,3-pentadiene (4a) (Procedure A). The propargyl carbonate **1** (240 mg, 1.0 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%) and $NaBPh_4$ (445 mg, 1.3 mmol) were mixed in dry THF (10 mL) and the mixture heated to 65°C for 2h. After cooling the solvent was evaporated and the residue purified by column chromatography eluting with 4:1 v/v petroleum ether – ethyl acetate to afford the product (218 mg, 93%) as a colourless oil (R_f = 0.69, PE/EtOAc 4:1). (Found: C, 92.1; H, 7.7; $C_{18}H_{18}$ requires: C, 92.3; H, 7.75%); ν_{max} (neat) 3080, 3060, 3030, 2910, 2850, 1595, 740, 700 cm^{-1}; δ_H 7.60-7.20(m, 10H, ArH), 5.67 and 5.15(2xd, J1.7Hz, 2H, $=CH_2$), 1.82 and 1.83(2xs, 6H, Me); δ_C 22.3 and 23.2(Me), 115.0($=CH_2$), 126.6, 127.0, 127.6, 127.7, 127.8, 128.2, 128.7, 129.2 and 129.8(CH), 132.5, 136.9, 140.4, 141.7 and 150.0(C); m/z(%): 234(M^+,60), 219(76), 204(38), 154(100).

2,3-Bis(2'-thiophenyl)-4-methyl-1,3-pentadiene (4b) (Procedure B). The propargyl carbonate **1** (240 mg, 1.0 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), LiCl (80 mg, 2.0 mmol) and the 2-(tributylstannyl)thiophene (0.70 mL, 2.2 mmol) were mixed in dry THF (10 mL) and the mixture heated to 65°C for 2h. After cooling the solvent was evaporated and the residue dissolved in EtOAc (10 mL) and stirred with a saturated aqueous KF-solution (5 mL) for 1 h. The mixture was filtered, the organic layer separated, dried over magnesium sulfate, concentrated and the residue purified by column chromatography eluting with 9:1 v/v petroleum ether – dichloromethane to afford the product (230 mg, 94%) as a pale yellow oil (R_f = 0.35, PE/CH_2Cl_2 9:1). (Found: C, 68.25; H, 5.6; $C_{14}H_{14}S_2$ requires: C, 68.25; H, 5.75%); ν_{max} (neat) 3155, 3110, 2910, 2850, 1485 cm^{-1}; δ_H 7.15-7.10 and 6.94-6.86(2xm, 6H, CH), 5.67 and 5.05(2xd, J0.8Hz, 2H, $=CH_2$), 2.04 and 1.86(2xs, 6H, Me); δ_C 22.6 and 23.7(Me), 113.6($=CH_2$), 124.8, 125.2, 125.6, 126.9, 127.0 and 127.8 (CH), 129.6, 134.5, 143.7, 143.8 and 144.8(C); m/z(%): 246(M^+,100), 231(67), 216(17).

2,3-Bis(2'-furyl)-4-methyl-1,3-pentadiene (4c) Prepared as above from propargyl carbonate **1** and 2-(tributylstannyl)furan. Column chromatography eluting with 95:5 v/v petroleum ether – dichloromethane afforded the product (193 mg, 90%) as a colourless oil (R_f = 0.60, PE/CH_2Cl_2 95:5). (Found: C, 78.4; H, 6.6; $C_{14}H_{14}O_2$ requires: C, 78.5; H, 6.6%); ν_{max} (neat) 3150, 3125, 2915, 2900, 730 cm^{-1}; δ_H 6.54(d, J3.3Hz, 1H, CH), 6.42(dd, J1.7, 3.3Hz, 1H, CH), 6.30(dd, J1.7, 3.3Hz, 1H, CH), 6.26(dd, J1.7, 3.3Hz, 1H, CH), 6.16(d,

J1.3Hz, 1H, CH), 6.03(d, J3.3Hz, 1H, CH), 5.38 and 5.03(2xd, J1.5Hz, 2H, $=CH_2$), 2.09 and 1.81(2xs, 6H, Me); δ_C 22.5 and 23.6(Me), 108.3, 109.1, 111.1 and 111.7(CH), 113.1($=CH_2$), 124.7, 135.0 and 137.3 (C), 141.3 and 142.5(CH), 154.3 and 154.7(C); m/z(%): 214(M^+,100), 199(25), 133(57).

2,3-Bis(phenylethynyl)-4-methyl-1,3-pentadiene (4d) The propargyl carbonate **1** (240 mg, 1.0 mmol), $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%) and LiCl (80 mg, 2.0 mmol) were mixed in dry THF (10 mL) and phenylethynyl tributyltin (0.77 mL, 2.2 mmol) was added dropwise with stirring at 0°C. The reaction mixture was allowed to warm to room temperature and then stirred for another 4 h. The solvent was evaporated and the residue dissolved in EtOAc (10 mL) and stirred with a saturated aqueous KF-solution (5 mL) for 1 h. After filtering, the layers were separated, the organic layer dried over magnesium sulfate, concentrated and the crude product purified by column chromatography eluting with petroleum ether to afford the product (105 mg, 37%) as a bright yellow unstable oil (R_f = 0.20, petroleum ether). δ_H 7.48-7.24(m, 10H, ArH), 5.80 and 5.66(2xd, J1.7Hz, 2H, $=CH_2$), 2.15 and 2.07(2xs, 6H, Me).

General procedure for reactions with boronic acids (Procedure C):

The boronic acid (2.0 mmol) was dissolved in toluene (5 mL), potassium carbonate (553 mg, 4.0 mmol) in water (1 mL) added and the mixture stirred at room temperature for 10 min then cooled to 0°C. The Propargyl derivative **1** (240 mg, 1.0 mmol), $Pd(OAc)_2$ (10 mol%) and PPh_3 (20 mol%) were added at 0°C and the mixture allowed to rise to room temperature and stirred for several hours. EtOAc (5 ml) was then added and the mixture was washed with saturated aqueous $NaHCO_3$, water and brine. The organic layer was separated, dried over magnesium sulfate, concentrated and the residue purified by column chromatography.

2,3-Bis(4'-bromophenyl)-4-methyl-1,3-pentadiene (4e) Obtained from the reaction of **1** with 4-bromobenzeneboronic acid (402 mg) at room temperature for 4h. Column chromatography eluting with 95:5 v/v petroleum ether – ethyl acetate afforded the product (263 mg, 67%) as a colourless oil (R_f = 0.35, PE/EtOAc 95:5). (Found: C, 54.85; H, 4.3; $C_{18}H_{16}Br_2$ requires: C, 55.15; H, 4.1%); ν_{max} (neat) 3050, 2960, 2840, 1610, 740, 705 cm^{-1}; δ_H 7.54-7.03(m, 8H, ArH), 5.66 and 5.16(2xd, J1.4Hz, 2H, $=CH_2$), 1.82 and 1.80(2xs, 6H, Me); δ_C 22.3 and 23.2(Me), 116.5($=CH_2$), 120.7 and 122.0(C), 128.6, 128.9, 131.4, 131.5, 131.7 and 132.5(CH), 133.9, 135.3, 139.0, 140.3 and 148.5(C); m/z(%): 392(M^+,20), 312(100), 232(65), 152(81).

2,3-Bis(4'-methoxyphenyl)-4-methyl-1,3-pentadiene (4f) Obtained from the reaction of **1** with 4-methoxybenzeneboronic acid (304 mg) at room temperature for 4h. Column chromatography eluting with 95:5 v/v petroleum ether – ethyl acetate afforded the product (226 mg, 77%) as a colourless oil (R_f = 0.26, PE/EtOAc 95:5). (Found: C, 81.65; H, 7.7; $C_{20}H_{22}O_2$ requires: C, 81.6; H, 7.55%); ν_{max} (neat) 3050, 2960, 2910, 2840, 1610, 740, 705 cm^{-1}; δ_H 7.36 and 7.35(2xd, J6.8Hz, 2H, ArH), 6.75 and 6.74(2xd, J6.8Hz, 2H, ArH), 6.79-6.73(m, 4H, ArH), 5.58 and 5.04(2xd, J1.7Hz, 2H, CH_2), 3.71 and 3.70 (2xs, 6H, OMe), 1.83(s, 6H, Me); δ_C 22.3 and 23.1(Me), 55.5 and 55.6(OMe), 113.3($=CH_2$), 113.5, 114.0, 128.1 and 130.8(CH), 132.9, 133.9, 134.3, 136.5, 149.4, 158.2 and 159.4(C); m/z(%): 294(M^+,100), 279(82), 264(26), 238(34), 173(100).

2,3-Bis(3',4'-dimethoxyphenyl)-4-methyl-1,3-pentadiene (4g) Obtained from the reaction of **1** with 3,4-dimethoxybenzeneboronic acid (364 mg) at room temperature for 5h. Column chromatography eluting with 3:1 v/v petroleum ether – ethyl acetate affords the product (255 mg, 72%) as a colourless oil (R_f = 0.29, PE/EtOAc 3:1). (Found: C, 74.4; H, 7.4; $C_{22}H_{26}O_4$ requires: C, 74.55; H, 7.4%); ν_{max} (neat) 3060, 3010, 2970, 2935, 2840, 735, 705 cm^{-1}; δ_H 7.01-6.71(m, 6H, ArH), 5.62 and 5.08(2xd, J1.6Hz, 2H, $=CH_2$), 3.84, 3.82, 3.81 and 3.80(4xs, 12H, OMe), 1.86 and 1.86(2xs, 6H, Me); δ_C 22.3 and 23.1(Me), 56.0 and 56.1(OMe), 110.1, 110.8, 111.1, 113.0, 113.5, 119.7, 122.2, 130.9, 131.9, 133.2, 134.5, 135.3 and 136.6($=CH_2$, CH and C), 147.4, 148.5, 148.9 and 149.5(C); m/z(%): 354(M^+,75), 339(20), 323(45), 305(15), 292(15), 203(100).

2,3-Bis(2'-benzo[b]furyl)-4-methyl-1,3-pentadiene (4h) Obtained from the reaction of **1** with 2-benzo[b]furaneboronic acid (324 mg) at room temperature for 60 h followed by heating at 50°C for 5 h. Column chromatography eluting with petroleum ether afforded the product (97 mg, 31%) as a yellow oil (R_f = 0.75, petroleum ether). ν_{max} (neat) 3070, 2975, 2910, 2860, 810, 740 cm^{-1}; δ_H 7.47-7.13(m, 8H, ArH), 7.11(d, J1.3Hz, 1H, CH), 7.10(d, J1.0Hz, 1H, CH), 6.46 and 6.20(2xd, J1.4Hz, 2H, $=CH_2$), 2.28 and 1.90(2xs, 6H, Me); δ_C 22.9 and 24.2(Me), 105.2, 105.9, 111.4(CH), 116.9(CH_2), 121.0, 121.5, 123.0, 123.1, 123.8 and 124.7(CH), 124.3(C), 125.0(CH), 129.1, 129.5, 137.3, 139.0, 154.9, 155.4, 155.8 and 156.9(C); HRMS (EI) *m/z* 314.1307 (M^+), $C_{22}H_{18}O_2$ requires 314.1307; m/z(%): 314(M^+,100), 299(45), 183(50).

2,3-Bis(4'-formylphenyl)-4-methyl-1,3-pentadiene (4i) Obtained from the reaction of **1** with 4-formylbenzeneboronic acid (300 mg) at room temperature for 5h. Column chromatography eluting with 4:1 v/v petroleum ether – ethyl acetate afforded the product (168 mg, 58%) as a yellow oil (R_f = 0.30, PE/EtOAc 4:1). ν_{max} (neat) 3060, 2835, 2745, 1700, 1605, 735 cm^{-1}; δ_H 9.94 and 9.92 (2xs, 2H, CHO), 7.77 and 7.75 (2xd, J6.5Hz, 4H, ArH), 7.55 and 7.38 (2xd, J8.2Hz, 4H, ArH), 5.88 and 5.37(2xd, J1.1Hz, 2H, $=CH_2$), 1.89 and 1.88(2xs, 6H, Me); δ_C 22.5 and 23.4(Me), 119.3(CH_2), 130.2, 130.3, 130.4 and 130.8(CH), 134.9, 135.3, 135.8, 146.0, 147.9 and 148.3(C), 192.1 and 192.2(CHO); HRMS (EI) *m/z* 290.1311 (M^+), $C_{20}H_{18}O_2$ requires 290.1307; m/z(%): 290(M^+, 100), 275(17), 261(36), 233(58), 219(49), 204(35), 171(52).

2,3-Bis(3'-nitrophenyl)-4-methyl-1,3-pentadiene (4j) Obtained from the reaction of **1** with 3-nitrobenzeneboronic acid (334 mg) at 70°C for 15h. Column chromatography eluting with 4:1 v/v petroleum ether – ethyl acetate afforded the product (188 mg, 58%) as a colourless oil (R_f = 0.55, PE/EtOAc 4:1). ν_{max} (neat) 3085, 2985, 2915, 2860, 1530, 1345 cm^{-1}; δ_H 8.22 and 8.09 (2xdd, J1.9, 2.0Hz, 2H, ArH), 7.70, 7.56, 7.46 and 7.40 (4xd, J7.7Hz, 4H, ArH), 5.91 and 5.44(2xs, 2H, $=CH_2$), 1.95 and 1.90(2xs, 6H, Me); δ_C 22.4 and 23.3(Me), 119.4(CH_2), 121.7, 122.0, 122.9, 124.5, 129.4, 129.9 and 132.8(CH), 133.8(C), 136.0(CH), 136.9, 141.4, 142.6, 146.9, 148.5 and 148.9(C); HRMS (EI) *m/z* 324.1110 (M^+), $C_{18}H_{16}N_2O_4$ requires 324.1110; m/z(%): 324(M^+,100), 307(80), 277(50), 263(65), 217(35), 202(62), 188(67), 115(57).

2,3-Diphenyl-1,3-butadiene (8a)[9] Prepared as described for **4a** from the butyne ester **6** (186 mg, 1 mmol) and $NaBPh_4$ (445 mg, 1.3 mmol) at 65°C for 4 h. Column chromatography eluting with petroleum ether

afforded the product (152 mg, 74%) as colourless crystals (mp. 48°C, lit.[8b] 47°C; R_f = 0.55, PE). δ_H 7.55-7.37(m, 10H, ArH), 5.52 and 5.30(2xd, J1.6Hz, 4H, $=CH_2$).

2,3-Bis(4'-methoxyphenyl)-1,3-butadiene (8b)[10] Prepared as described above from 7 (202 mg, 1.0 mmol) and 4-methoxybenzeneboronic acid (304 mg) at 65°C for 15h. Column chromatography eluting with 95:5 v/v petroleum ether – ethyl acetate afforded the product (140 mg, 53%) as colourless crystals (mp. 109°C, lit.[9] 109-110°C; R_f = 0.35, PE/EtOAc 95:5). δ_H 7.31 and 6.78(2xd, J8.7Hz, 8H, ArH), 5.47 and 5.23(2xd, J1.7Hz, 4H, $=CH_2$), 3.76(s, 6H, OMe).

2,3-Bis(3',4'-dimethoxyphenyl)-1,3-butadiene (8c)[11] Prepared as described above from 7 (202 mg, 1.0 mmol) and 3,4-dimethoxybenzeneboronic acid (364 mg) at 65°C for 15h. Column chromatography eluting with 3:1 v/v petroleum ether – ethyl acetate affords the product (190 mg, 58%) as colourless crystals (mp. 106°C, lit.[10] 106-108°C; R_f = 0.27, PE/EtOAc 3:1). δ_H 6.97-6.91(m, 4H, ArH), 6.74(d, J8.1Hz, 2H, ArH), 5.50 and 5.29(2xd, J1.5Hz, 2H, $=CH_2$), 3.84 and 3.82(2xs, 12H, OMe).

2,3-Bis(4'-formylphenyl)-1,3-butadiene (8d) Obtained from the reaction of 7 (202 mg, 1.0 mmol) with 4-formylbenzeneboronic acid (300 mg) at room temperature for 15h. Column chromatography eluting with 4:1 v/v petroleum ether – ethyl acetate afforded the product (110 mg, 42%) as colourless crystals (mp. 97°C, R_f = 0.20, PE/EtOAc 4:1). (Found: C, 82.5; H, 5.35; $C_{18}H_{14}O_2$ requires: C, 82.4; H, 5.35%); ν_{max} (nujol) 3055, 1700, 1605, 735, 705 cm^{-1}; δ_H 9.96 (s, 2H, CHO), 7.79 and 7.52 (2xd, J8.1Hz, 8H, ArH), 5.73 and 5.51(2xs, 4H, $=CH_2$); δ_C 119.6(CH_2), 128.4 and 130.3(CH), 136.0, 146.0, and 148.6(C), 192.1(CHO); m/z(%): 262(M^+, 5), 234(28), 205(100), 159(27), 115(37), 77(39).

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