# Triarylalkenes from the site-selective reductive cross-coupling of benzophenones and aldehydes

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#### 1. General experimental information

The first half of the reaction up to the addition of MeOH was carried out in a glove box while the second part can be conducted without any special precautions. Glassware was flame-dried, and aldehydes dried/distilled prior to use. THF and Et<sub>2</sub>O were freshly distilled over Na/benzophenone under nitrogen. tBuOOH was dried with an azeotrope distillation of water and benzene from a commercial water solution of the peroxide. LiOEt and tBuOK were both used as a commercially available 1M solution in THF. All the carbonyl compounds except ketone **C** are commercially available and were purchased from Sigma Aldrich. Ketone bis-(4-octyloxy-phenyl)-methanone (Ketone **C**) was prepared according to the literature procedure.<sup>1</sup> NMR spectra were recorded on a JEOL (400YH magnet) Resonance 400 MHz spectrometer. Chemical shifts  $\delta$  are reported in ppm and coupling constants *J* in Hz. <sup>1</sup>H NMR and <sup>13</sup>C NMR chemical shifts are referenced to the residual protic solvent signal and <sup>31</sup>P NMR spectra externally to 85% H<sub>3</sub>PO<sub>4</sub>(aq). High-resolution mass spectra (HR-MS) were recorded on a Thermo Scientific Orbitrap LTQ XL spectrometer.

#### 2. Preparation of PhPTMS<sub>2</sub>

To the solution of 1 g (0.009 mol) of PhPH<sub>2</sub> in 25 ml of diethyl ether 2.2 eq. (0.02 mol, 12.5 ml of 1.6M solution) of MeLi in diethylether was added dropwise at  $-10^{\circ}$ C. The resulting yellow solution was stirred at r.t. for 3h and then refluxed for additional 1h during which precipitation occurred. To the resulting suspension, 2.5 eq. (2.5 g, 0.023 mol, 2.9 ml) of freshly distilled TMSCl was added dropwise at  $-78^{\circ}$ C. The reaction mixture was warmed up to r.t and stirred for additional 10h during which the color of the suspension changed from yellow to colorless and a large amount of an off-white precipitate formed. If the color of the solution after 10h was still yellowish, additional TMSCl was added to completely transform all lithium salts into trimethylsilyl derivatives. Even traces of the lithium salts can cause decomposition of crude product during the distillation attempt! Solvent and remaining TMSCl were removed in vacuum and the residue was subjected to careful distillation. The product is obtained as colorless liquid with b.p. 82°C at 0.1 mm. Hg. Yield: 2.17 g, 95 %. All NMR data identical to those reported in the literature.<sup>2</sup>

#### 3. Preparation of PhP(Li)TMS

To a solution of PhP(TMS)<sub>2</sub> (1eq, 1.07 g, 4.21 mmol) in 25 mL of dry THF a solution of LiOEt (1eq, 1M in THF) at room temperature was added. The reaction mixture was stirred at ambient temperature for 4 hours until full conversion of the starting material to the lithium salt was achieved. PhP(Li)TMS has surprisingly the same <sup>31</sup>P chemical shift (-153 ppm) of the starting material. The solvent was removed under reduced pressure to afford a yellow solid. Dry Et<sub>2</sub>O was added and the yellow solution was stored in the glove box until further use for up to one week without visible changes. Assuming quantitative conversion, the molarity of the solution is estimated to 0.168 M (4.21 mmol of PhP(Li)TMS dissolved in 25 mL of dry Et<sub>2</sub>O).

#### 4. General procedure for coupling of two carbonyl compound

To the solution of the ketone **A-G** (1 eq.) in diethyl ether, the stock solution of PhP(Li)TMS (1 eq.) was added at r.t. at once. Color change was observed in most of the cases. After 2-3 min, the reaction mixture was quenched by the addition of MeOH (ca 0.3 ml). After this, reaction mixture was taken out of the glove box and a solution of tBuOOH in benzene (1.25 eq.) was added. After this, the solvent was removed to yield crude compounds **A-G** as white powders. At this stage a sample of the crude can be taken to determine the crude yield of **3** (see section 5 for details). Crude compounds **3A-G** are suspended in THF and 1 or 0.9 eq. (see the procedure for the specific compound) of aldehydes **a-f** are added at r.t. Addition of 1.5 eq. of tBuOK (1M solution in the THF was used) results in a color change from colorless to yellow which fades with time. The reaction can be monitored by <sup>31</sup>P NMR spectroscopy where the disappearance of the characteristic phosphinate signal (+41 ppm) is observed. For specific conditions, please check the experimental section on the compound of interest in section 6. After this, the reaction mixture is diluted with diethyl ether and brine, the layers separated, and the aqueous layer extracted with diethyl ether (3×25 ml). The combined organic phases are washed with brine (50 ml) and dried over MgSO4. After solvent removal *in vacuo*, the crude alkenes are chromatographed on silica gel using a solvent gradient from pure heptane to 5% ethyl acetate to afford pure final products.

#### 5. Determination of crude yield of compounds A-G



Figure S1. <sup>1</sup>H NMR of the crude **3A** with internal standard – cyclohexene in CDCl<sub>3</sub>.

Determination of crude yields (conversions): a sample of crude product of known mass is dissolved in 1 ml of a CDCl<sub>3</sub> stock solution of cyclohexene (0.039 M) and added to a NMR tube. Integration of the benzylic proton

peak of the product in the <sup>1</sup>H NMR spectrum against the reference peak of cyclohexene (5.67 ppm, set as 1.00 reference integral value) allows the calculation of the product concentration in the sample. With this concentration and the known mass of the crude product, the total mass of the product in the crude reaction mixture can be calculated. Conversions are calculated relative to the amount of used lithium phenyl(trimethylsilyl)phosphanide. An example is shown in Figure S1 for the crude product compound **3A**.

In the specific example the total mass of crude product is: m(crude product) = 1212 mg. 16 mg were taken and dissolved in 1 ml of CDCl<sub>3</sub> stock solution of cyclohexene for the crude yield determination. Consequently, the mass factor is:

1212 mg/16 mg = 75.75

Integration of the benzylic protons (d at 4.45 ppm) gives a value of  $2 \times 0.35 = 0.7$  relative to the signal of the two olefinic protons in cyclohexene (Figure S1). With a concentration of the cyclohexene stock solution of 0.039 M, the concentration of the product for the NMR tube is calculated as:

c(product NMR tube) =  $0.7 \times 0.039$  M = 0.0273 M

With the NMR sample volume being 1 ml, n(product NMR tube) = 0.0273 mmol. Multiplication with the mass factor gives the total amount of product in the crude reaction mixture:

 $n(product) = 75.75 \times 0.0273 \text{ mmol} = 2.068 \text{ mmol}.$ 

From the amount of used starting material, quantitative yield would correspond to 2.22 mmol. 2.068 mmol : 2.22 mmol results in 94% crude yield (conversion).

	Carbonyl	Yield of <b>3</b>	δ <sup>31</sup> P, ppm
a		94 %	41.3
b	P F	63 %	41.4
с	OctylO OctylO	Quant.	41.7
d	O Br	n.a.	40.9 , 40.5
e	O	n.a.	41.41 , 41.38
f		≤5 %	46.6 , 45.6
g	OMe	41 %	47.4 , 45.9

Table S1. Crude yields of compounds **3A-G** and their chemical shifts

#### 6. Details on preparation and characterization of alkenes

#### Ethene-1,1,2-triyltribenzene



Scale: stock solution of PhP(Li)TMS (0.4 mmol, 1 eq.), 73 mg (0.4 mmol, 1 eq.) benzophenone, solution of tBuOOH in benzene (0.5 mmol; 1.25 eq.), 42 mg (0.4 mmol, 1 eq.) benzaldehyde and 0.6 ml of a 1 M solution of tBuOK (in THF, 1.5 eq.).

Yield: 64 mg, 63%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34 – 7.29 (m, 7H, Ph), 7.29 – 7.26 (m, 1H, Ph), 7.22 – 7.18 (m, 2H, Ph), 7.13 – 7.08 (m, 3H, Ph), 7.05 – 7.00 (m, 2H, Ph), 6.96 (s, 1H, CH=) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 143.4, 142.6, 140.4, 137.4, 130.4, 129.6, 128.7, 128.2, 128.0, 127.6, 127.5, 127.4, 126.8 ppm.

#### (2-(4-bromophenyl)ethene-1,1-diyl)dibenzene



Scale: stock solution of PhP(Li)TMS (0.4 mmol, 1 eq.), 73 mg (0.4 mmol, 1 eq.) benzophenone, solution of tBuOOH in benzene (0.5 mmol; 1.25 eq.), 74 mg (0.4 mmol, 1 eq.) p-bromobenzaldehyde and 0.6 ml of a 1 M solution of tBuOK (in THF, 1.5 eq.).

Yield: 90 mg, 67%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35 – 7.28 (m, 8H, Ph), 7.23 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, PhBr), 7.19 – 7.15 (m, 2H, Ph), 6.88 (s, 1H, CH=), 6.87 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.0 Hz, 2H, PhBr) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 143.4, 143.1, 139.9, 136.3, 131.1, 131.0, 130.2, 128.8, 128.2, 127.7, 127.6, 127.6, 126.8, 120.5 ppm.

#### (2-(4-methoxyphenyl)ethene-1,1-diyl)dibenzene



Scale: stock solution of PhP(Li)TMS (0.4 mmol, 1 eq.), 73 mg (0.4 mmol, 1 eq.) benzophenone, solution of tBuOOH in benzene (0.5 mmol; 1.25 eq.), 54 mg (0.4 mmol, 1 eq.) p-methoxybenzaldehyde and 0.6 ml of a 1 M solution of tBuOK (in THF, 1.5 eq.).

Yield: 66 mg, 58%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.37 - 7.26$  (m, 8H, Ph), 7.25 - 7.20 (m, 2H, Ph), 6.96 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, PhOMe), 6.93 (s, 1H, CH=), 6.68 (d, 3*J*<sub>HH</sub> = 8.9 Hz, 2H, PhOMe), 3.75 (s, 3H, OMe) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 158.4, 143.6, 140.6, 140.6, 130.8, 130.4, 130.0, 128.7, 128.1, 127.6, 127.4, 127.3, 127.2, 113.4, 55.1 ppm.

## 2-(2,2-diphenylvinyl)thiophene



Scale: stock solution of PhP(Li)TMS (0.4 mmol, 1 eq.), 73 mg (0.4 mmol, 1 eq.) benzophenone, solution of tBuOOH in benzene (0.5 mmol; 1.25 eq.), 45 mg (0.4 mmol, 1 eq.) thiophene aldehyde and 0.6 ml of a 1 M solution of tBuOK (in THF, 1.5 eq.).

Yield: 87 mg, 79%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.52 - 7.43$  (m, 3H, Ph, CH=), 7.37 - 7.21 (m, 8H, Ph), 7.06 - 7.00 (m, 1H, thiophene), 6.93 (dd, J = 3, 1 Hz, 1H, thiophene), 6.87 (dd, J = 5.0, 3 Hz, 1H, thiophene) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 141.8, 141.3, 139.8, 139.4, 130.3, 129.3, 128.9, 128.3, 128.0, 127.3, 126.7, 126.2, 126.2, 120.9 ppm.

## (2-(4-nitrophenyl)ethene-1,1-diyl)dibenzene



Scale: For the reaction was used a solution of PhP(Li)TMS containing 0.63 mmol (1 eq.) of compound, 116 mg (1 eq.) benzophenone, a solution of tBuOOH in benzene containing 0.79 mmol (1.25 eq.) of peroxide, 86 mg (0.9 eq.) *para*-nitrobenzaldehyde and 0.95 ml (1 M solution in THF, 1.5 eq.) tBuOK.

Yield: 93 mg, 54%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.97 (d, *J* = 9 Hz, 2H, PhNO<sub>2</sub>), 7.38 – 7.31 (m, 8H, Ph), 7.18 – 7.14 (m, 2H, Ph), 7.12 (d, *J* = 9 Hz, 2H, PhNO<sub>2</sub>), 6.98 (s, 1H, CH=) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ =147.0, 145.9, 144.3, 142.4, 139.3, 130.1, 130.0, 128.9, 128.5, 128.4, 128.2, 127.8, 125.7, 123.3 ppm.

#### 4,4'-(2-phenylethene-1,1-diyl)bis(fluorobenzene)



Scale: For the reaction was used a solution of PhP(Li)TMS containing 0.5 mmol (1 eq.) of compound, 109 mg (1 eq.) p-fluorobenzophenone, a solution of tBuOOH in benzene containing 0.63 mmol (1.25 eq.) of peroxide, 48 mg (0.9 eq.) benzealdehyde and 0.75 ml (1 M solution in THF, 1.5 eq.) tBuOK.

Yield: 73 mg, 56%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.29 – 7.22 (m, 2H, Ar), 7.18 – 7.10 (m, 5H, Ar), 7.05 – 6.96 (m, 6H, Ar), 6.89 (s, 1H, CH=) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -114.1 (m), -114.5 (m) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 162.5$  (d, J = 247 Hz), 162.3 (d, J = 247 Hz), 140.5, 139.4 (d, J = 3 Hz), 137.1, 136.0 (d, J = 3.5 Hz), 132.1 (d, J = 8 Hz), 129.5 (d, J = 5 Hz), 129.2 (d, J = 8 Hz), 128.4, 128.1, 126.9, 115.7 (d, J = 21 Hz), 115.1 (d, J = 20 Hz) ppm.

4,4'-(2-(4-bromophenyl)ethene-1,1-diyl)bis(fluorobenzene)



Scale: For the reaction were used a solution of PhP(Li)TMS containing 0.5 mmol (1 eq.) of compound, 109 mg (1 eq.) p-fluorobenzophenone, a solution of tBuOOH in benzene containing 0.63 mmol (1.25 eq.) of peroxide, 83 mg (0.9 eq.) p-bromobenzealdehyde and 0.75 ml (1 M solution in THF, 1.5 eq.) tBuOK.

Yield: 82 mg, 49%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.26 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.5 Hz, 2H, PhBr), 7.28 – 7.22 (m, 2H, PhF), 7.14 – 7.08 (m, 2H, PhF), 7.03 (dm, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, PhF), 6.99 (dm, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, PhF), 6.86 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.5 Hz, 2H, PhBr), 6.80 (s, 1H, CH=) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -114.1 (m), -113.6 (m) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 162.6 (d, *J* = 248 Hz), 162.4 (d, *J* = 248 Hz), 141.3, 139.1 (d, *J* = 3 Hz), 136.0, 135.6 (d, *J* = 4 Hz), 132.0 (d, *J* = 8 Hz), 131.2, 131.0, 129.2 (d, *J* = 8 Hz), 127.0, 120.8, 115. 9 (d, *J* = 21 Hz), 115.2 (d, *J* = 22 Hz) ppm.

HRMS: C<sub>20</sub>H<sub>13</sub>BrF<sub>2</sub>, [M]<sup>+</sup>, calc. 370.01632, obs. 370.01584.

## 4,4'-(2-(4-methoxyphenyl)ethene-1,1-diyl)bis(fluorobenzene)



Scale: For the reaction was used a solution of PhP(Li)TMS containing 0.5 mmol (1 eq.) of compound, 109 mg (1 eq.) p-fluorobenzophenone, a solution of tBuOOH in benzene containing 0.63 mmol (1.25 eq.) of peroxide, 61 mg (0.9 eq.) p-methoxybenzealdehyde and 0.75 ml (1 M solution in THF, 1.5 eq.) tBuOK.

Yield: 48 mg, 33%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.25 - 7.21$  (m, 2H, PhF), 7.17 - 7.12 (m, 2H, PhF), 7.01 (ddm,  $J_{HF} = 17$ ,  ${}^{3}J_{HH} = 9$  Hz, 2H, PhF), 6.99 (ddm,  $J_{HF} = 17$ ,  ${}^{3}J_{HH} = 9$  Hz, 2H, PhF), 6.9 (dm,  ${}^{3}J_{HH} = 9$  Hz, 2H, PhOMe), 6.83 (s, 1H HC=), 6.68 (d,  ${}^{3}J_{HH} = 9$  Hz, 2H, PhOMe), 3.75 (s, 3H, OMe) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -115.0 (m), -114.4 (m) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 162.4$  (d, J = 247 Hz), 162.3 (d, J = 247 Hz), 158.6, 139.7 (d, J = 3 Hz), 138.6, 136.4 (d, J = 4 Hz), 132.2 (d, J = 8 Hz), 130.8, 129.8, 129.1 (d, J = 8 Hz), 128.0, 115.9 (d, J = 21 Hz), 115.2 (d, J = 21 Hz), 113.6, 55.3 ppm.

2-(2,2-bis(4-fluorophenyl)vinyl)thiophene



Scale: For the reaction was used a solution of PhP(Li)TMS containing 0.5 mmol (1 eq.) of compound, 109 mg (1 eq.) p-fluorobenzophenone, a solution of tBuOOH in benzene containing 0.63 mmol (1.25 eq.) of peroxide, 50 mg (0.9 eq.) thiophene aldehyde and 0.75 ml (1 M solution in THF, 1.5 eq.) tBuOK.

Yield: 64 mg, 48%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.29 - 7.19$  (m, 4H, PhF), 7.22 (s, 1H, CH=), 7.19 - 7.13 (m, 2H, PhF), 7.07 - 7.04 (m, 1H, thiophene), 7.01 - 6.95 (m, 2H, PhF), 6.95 - 6.92 (m, 1H, thiophene), 6.90 - 6.86 (m, 1H, thiophene) ppm.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -114.6 (m), -113.4 (m) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 163.0$  (d, J = 247 Hz), 162.4 (d, J = 248 Hz), 141.0, 138.0 (d, J = 4 Hz), 137.8, 135.1 (d, J = 4 Hz), 132.2 (d, J = 8 Hz), 129.3, 128.4 (d, J = 8 Hz), 126.4, 121.3 (d, J = 2 Hz), 116.6 (d, J = 21 Hz), 115.3 (d, J = 22 Hz) ppm.

HRMS:  $C_{18}H_{12}SF_2$ ,  $[M]^+$ , calc. 298.06223, obs. 298.06199.

4,4'-(2-(4-methoxyphenyl)ethene-1,1-diyl)bis((octyloxy)benzene) OctylO OMe OOctyl

Scale: For the reaction was used a solution of PhP(Li)TMS containing 0.34 mmol (1 eq.) of compound, 150 mg (1 eq.) bis(4-(octyloxy)phenyl)methanone, a solution of tBuOOH in benzene containing 0.43 mmol (1.25 eq.) of peroxide, 42 mg (0.9 eq.) p-methoxybenzealdehyde and 0.51 ml (1 M solution in THF, 1.5 eq.) tBuOK. Reaction mixture was refluxed for 24h to achieve complete disappearance of **3C**.

Yield: 40 mg, 23%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.21 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, Ph), 7.09 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ph), 6.96 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ph), 6.84 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ph), 6.81 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, Ph), 6.75 (s, 1H, CH=), 6.66 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, Ph), 4.00 - 3.91 (m, 4H, OCH<sub>2</sub>), 3.74 (s, 3H, OMe), 1.85 - 1.70 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.50 - 1.40 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.35 - 1.22 (m, 16H, -CH<sub>2</sub>-), 0.93 - 0.81 (m, 6H, CH<sub>2</sub>CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 158.6, 158.4, 158.0, 140.0, 136.4, 132.8, 131.5, 130.6, 130.6, 128.6, 125.5, 114.5, 114.1, 113.4, 68.0, 68.0, 31.8, 31.8, 29.4, 29.4, 29.3, 29.3, 29.25, 29.2, 26.1, 26.0, 26.0, 22.7, 22.65, 14.1 ppm.

HRMS: C<sub>37</sub>H<sub>50</sub>O<sub>3</sub>, [M]<sup>+</sup>, calc. 542.37545, obs. 542.37321.

#### 4,4'-(2-(4-bromophenyl)ethene-1,1-diyl)bis((octyloxy)benzene)



Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.4 mmol (1 eq.) of compound, 175 mg (1 eq.) bis(4-(octyloxy)phenyl)methanone, a solution of tBuOOH in benzene containing 0.6 mmol (1.25 eq.) of peroxide, 67 mg (0.9 eq.) p-bromobenzealdehyde and 0.6 ml (1 M solution in THF, 1.5 eq.) tBuOK. Reaction mixture was refluxed for 16h to achieve complete disappearance of **3C**.

Yield: 98mg, 46%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.22$  (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 2H, Ph), 7.22 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ph), 7.05 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, 2H, Ph), 6.87 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 1H), 6.83 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.4 Hz, 2H, Ph), 6.81 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ph), 6.71 (s, 1H, CH=), 3.95 (dd, *J* = 12, 6 Hz, 2H, OCH<sub>2</sub>), 3.95 (dd, *J* = 12, 6 Hz, 2H, OCH<sub>2</sub>), 1.83 – 1.72 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.49 – 1.43 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.37 – 1.21 (m, 16H, -CH<sub>2</sub>-), 0.92 – 0.82 (m, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 159.0, 158.7, 142.8, 136.9, 135.8, 132.0, 131.5, 131.0, 130.9, 128.8, 124.5, 119.9, 114.6, 114.1, 68.1, 68.0, 31.82, 31.81, 29.4, 29.35, 29.32, 29.3, 29.24, 29.23, 26.1, 26.0, 22.66, 22.65, 14.11, 14.09 ppm.

HRMS: C<sub>36</sub>H<sub>47</sub>O<sub>2</sub>Br, [M]<sup>+</sup>, calc. 590.27539, obs. 590.27496.

1-bromo-4-(2-(4-methoxyphenyl)-2-phenylvinyl)benzene



Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.68 mmol (1 eq.) of compound, 143 mg (1 eq.) (4-methoxyphenyl)(phenyl)methanone, a solution of tBuOOH in benzene containing 0.85 mmol (1.25 eq.) of peroxide, 112 mg (0.9 eq.) p-bromobenzealdehyde and 1 ml (1 M solution in THF, 1.5 eq.) tBuOK. Reaction mixture was stirred for 12h to achieve complete disappearance of **3D**.

Yield: 136 mg, 61%. The compound was isolated as a mixture of E and Z isomers in a ratio of E:Z = 1:0.65. The isomer ratio was determined based on the ratio of the characteristic peaks of the OMe protons in the <sup>1</sup>H NMR spectrum of the isolated product.

Major E

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.34 - 7.28$  (m, 5H, Ph, overlapping with Z isomer), 7.27 - 7.20 (m, 2H, Ar, overlapping with Z isomer), 7.09 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, Ar), 6.91 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 2H, Ar), 6.86 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, Ar), 6.81 (s, 1H, HC=), 3.83 (s, 3H, OMe) ppm.

Minor Z

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.34 – 7.28 (m, 5H, Ph overlapping with E isomer), 7.27 – 7.20 (m, 4H, Ar, overlapping with E isomer), 7.18 – 7.15 (m, 2H, Ph), 6.84 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.8 Hz, 2H, Ar), 6.80 (s, 1H, HC=), 3.81 (s, 3H, OMe) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for mixture of E and Z isomers: δ = 159.4, 159.1, 143.4, 143.1, 142.9, 140.1, 136.6, 136.5, 135.6, 132.0, 131.5, 131.1, 131.0, 131.01, 130.9, 130.2, 128.8, 128.7, 128.2, 127.7, 127.6, 126.4, 125.1, 120.3, 120.2, 114.1, 113.6, 55.3, 55.2 ppm.

4,4'-(1-phenylethene-1,2-diyl)bis(methoxybenzene)



Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.68 mmol (1 eq.) of compound, 143 mg (1 eq.) (4-methoxyphenyl)(phenyl)methanone, a solution of tBuOOH in benzene containing 0.85 mmol (1.25 eq.) of peroxide, 83 mg (0.9 eq.) p-methoxybenzealdehyde and 1 ml (1 M solution in THF, 1.5 eq.) tBuOK. Reaction mixture was stirred for 12h to achieve complete disappearance of **3D**.

Yield: 84 mg, 44%. The compound was isolated as a mixture of E and Z isomers in a ratio of E:Z = 1:0.74. The isomer ratio was determined based on the ratio of the characteristic peaks of the OMe protons in the <sup>1</sup>H-NMR spectrum of the isolated product.

Major E isomer:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.28 (m, 5H, Ph, overlapping with Z isomer), 7.13 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ar), 7.00 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, Ar), 6.88 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7 Hz, 2H, Ar), 6.86 (s, 1H, CH=), 6.69 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, Ar), 3.84 (s, 3H, OMe), 3.76 (s, 3H, OMe) ppm.

Minor Z isomer:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 7.36 - 7.29$  (m, 3H, Ph, overlapping with E isomer), 7.28 - 7.20 (m, 4H, Ph+Ar), 6.93 (d,  ${}^{3}J_{\text{HH}} = 8.9$  Hz, 2H, Ar), 6.84 (s, 1H, CH=), 6.84 (d,  ${}^{3}J_{\text{HH}} = 8.8$  Hz, 2H, Ar), 6.66 (d,  ${}^{3}J_{\text{HH}} = 8.9$  Hz, 2H, Ar), 3.81 (s, 3H, OMe), 3.74 (s, 3H, OMe) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for mixture of E and Z isomers: δ = 159.0, 158.8, 158.2, 158.1, 144.0, 140.8, 140.3, 140.1, 136.2, 132.8, 131.6, 130.7, 130.6, 130.4, 130.3, 130.25, 128.7, 128.5, 128.1, 127.5, 127.3, 127.2, 127.1, 126.0, 114.1, 113.5, 113.4, 113.36, 55.3, 55.2, 55.13, 55.11 ppm.

HRMS: C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>, [M]<sup>+</sup>, calc. 316.14578, obs. 316.14539.

#### 4,4'-(1-phenylethene-1,2-diyl)bis(bromobenzene)

Br

Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.68 mmol (1 eq.) of compound, 176 mg (1 eq.) (4-bromophenyl)(phenyl)methanone, a solution of tBuOOH in benzene containing 0.85 mmol (1.25 eq.) of peroxide, 112 mg (0.9 eq.) p-bromobenzealdehyde and 1 ml (1 M solution in THF, 1.5 eq.) tBuOK. The reaction mixture was stirred for 12h to achieve complete disappearance of **3D**.

Yield: 99 mg, 39%. The compound was isolated as a mixture of E and Z isomers in a ratio of E:Z = 1:0.82. The isomer ratio was determined based on the ratio of the well separated aromatic peaks in the <sup>1</sup>H-NMR spectrum of the isolated product.

Major E isomer:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz, 2H, Ar), 7.35 – 7.25 (m, 7H, Ph+Ar, overlapping with Ph of the Z isomer), 7.05 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz, 2H, Ar), 6.89 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 2H, Ar), 6.88 (s, 1H, CH=) ppm.

Minor Z isomer:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 2H, Ar), 7.35 – 7.26 (m, 3H, Ph, overlapping with Ph of E isomer), 7.24 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz, 2H, Ar), 7.16 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 2H, Ar), 7.15 – 7.12 (m, 2H, Ph), 6.86 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz, 2H, Ar), 6.85 (s, 1H, CH=) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for mixture of E and Z isomers :  $\delta = 142.6$ , 142.3, 142.2, 142.0, 139.4, 138.9, 135.97, 135.96, 132.1, 132.0, 131.4, 131.3, 131.2, 131.02, 131.0, 130.2, 129.3, 128.9, 128.3, 128.0, 127.9, 127.6, 127.4, 127.2, 121.8, 121.78, 120.9, 120.8 ppm.

#### 1-bromo-4-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene



Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.68 mmol (1 eq.) of compound, 176 mg (1 eq.) (4-bromophenyl)(phenyl)methanone, a solution of tBuOOH in benzene containing 0.85 mmol (1.25 eq.) of peroxide, 83 mg (0.9 eq.) p-methoxybenzaldehyde and 1 ml (1 M solution in THF, 1.5 eq.) tBuOK. The reaction mixture was stirred for 12h to achieve complete disappearance of **3D**.

Yield: 78 mg, 36%. The compound was isolated as mixture of E and Z isomers in a ratio of E:Z = 1:0.71. The isomer ratio was determined based on the ratio of the characteristic peaks of the OMe groups in the <sup>1</sup>H NMR spectrum of the isolated product.

Major E isomer:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.45 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz, 2H, Ar), 7.35 – 7.25 (m, 5H, Ph, overlapping with Ph of the Z isomer), 7.09 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.3 Hz, 2H, Ar), 6.96 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, Ar), 6.90 (s, 1H, CH=), 6.70 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, Ar), 3.76 (s, 3H, OMe) ppm.

#### Minor Z isomer:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.40 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.5 Hz, 2H, Ar), 7.35 – 7.24 (m, 3H, Ph, overlapping with the Ph of E isomer), 7.19 – 7.15 (m, 2H, Ph), 7.15 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.5 Hz, 2H, Ar), 6.93 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, Ar), 6.88 (s, 1H, HC=), 6.66 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.9 Hz, 2H, Ar), 3.74 (s, 3H, OMe) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for mixture of E and Z isomers:  $\delta = 143.1$ , 142.6, 140.1, 139.6, 139.4, 139.38, 132.3, 131. 9, 131.2, 130.82, 130.79, 130.3, 129.7, 129.66, 129.0, 128.8, 128.26, 128.25, 128.0, 127.5, 127.43, 127.42, 121.3, 121.2, 113.6, 113. 5, 55.18, 55.15 ppm.

HRMS:  $C_{21}H_{17}OBr$ ,  $[M]^+$ , calc. 364.04573, obs. 364.04534.

#### (E)-buta-1,3-diene-1,1,4-triyltribenzene



Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.3 mmol (1 eq.) of compound, 53 mg (1 eq.) benzophenone, a solution of tBuOOH in benzene containing 0.38 mmol (1.25 eq.) of peroxide, 34 mg (0.9 eq.) *trans*-cinnamon aldehyde and 0.45ml (1 M solution in THF, 1.5 eq.) tBuOK.

Yield: 25 mg, 34%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47 – 7.37 (m, 3H, Ph), 7.36 – 7.24 (m, 11H, Ph), 7.20 (m, 1H, Ph), 6.96 – 6.85 (m, 2H, CH=), 6.81 – 6.68 (m, 1H, CH=) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.1, 142.3, 139.8, 137.5, 133.9, 130.6, 128.6, 128.3, 128.2, 128.2, 127.6, 127.5, 127.5, 127.1, 126.4 ppm.

#### (3-methylbut-1-ene-1,1-diyl)dibenzene



Procedure: For the reaction was used a solution of PhP(Li)TMS containing 0.3 mmol (1 eq.) of compound, 53 mg (1 eq.) benzophenone, a solution of tBuOOH in benzene containing 0.38 mmol (1.25 eq.) of peroxide, 19 mg (0.9 eq.) *iso*-propylaldehyde and 0.45ml (1 M solution in THF, 1.5 eq.) of tBuOK.

Yield: 14 mg, 24%

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.38 – 7.33 (m, 2H, Ph), 7.32 – 7.27 (m, 2H, Ph), 7.24 – 7.22 (m, 1H, Ph), 7.22 – 7.14 (m, 5H, Ph), 5.88 (d, <sup>3</sup>*J*<sub>HH</sub> = 10 Hz, 1H, CH=), 2.50 – 2.36 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.00 (d, <sup>3</sup>*J*<sub>HH</sub> = 7 Hz, 6H, CH<sub>3</sub>) ppm.

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 142.8, 140.6, 139.2, 137.4, 129.9, 128.2, 128.1, 127.2, 126.9, 126.8, 28.8, 23.3 ppm.

# 7. Figures of NMR spectra NMR of PV intermediates









NMRs of alkene

## Ethene-1,1,2-triyltribenzene





(2-(4-bromophenyl)ethene-1,1-diyl)dibenzene





(2-(4-methoxyphenyl)ethene-1,1-diyl)dibenzene





## 2-(2,2-diphenylvinyl)thiophene





(2-(4-nitrophenyl)ethene-1,1-diyl)dibenzene





#### 4,4'-(2-phenylethene-1,1-diyl)bis(fluorobenzene)





4,4'-(2-(4-bromophenyl)ethene-1,1-diyl)bis(fluorobenzene)





4,4'-(2-(4-methoxyphenyl)ethene-1,1-diyl)bis(fluorobenzene)





## 2-(2,2-bis(4-fluorophenyl)vinyl)thiophene

7.28 7.7.22 7.7.20 7.7.7.20 7.7.70 7.7.70 7.7.70 7.7.70 7.7.70 7.7.70 7.7.70 7.7.70 7.7.70 7.7.70 7





-350



4,4'-(2-(4-methoxyphenyl)ethene-1,1-diyl)bis((octyloxy)benzene)





4,4'-(2-(4-bromophenyl)ethene-1,1-diyl)bis((octyloxy)benzene)





## 1-bromo-4-(2-(4-methoxyphenyl)-2-phenylvinyl)benzene





## 4,4'-(1-phenylethene-1,2-diyl)bis(methoxybenzene)



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## 4,4'-(1-phenylethene-1,2-diyl)bis(bromobenzene)





## 1-bromo-4-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene





# (E)-buta-1,3-diene-1,1,4-triyltribenzene





# (3-methylbut-1-ene-1,1-diyl)dibenzene





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