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Telomerisation of Buta-1,3-diene and Methanol: Superiority of Chromanyl-Type Phosphines in the Dow Process for the Industrial Production of 1-MOD**

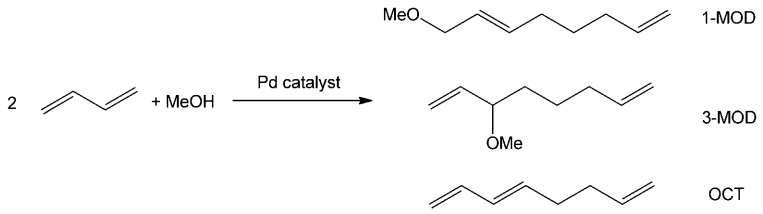
Mathieu J.-L. Tschan,[a] Hélène Launay,[b] Henk Hagen,[b] Jordi Benet-Buchholz,[a] and Piet W. N. M. van Leeuwen*[a]

Abstract: Butadiene and methanol were telomerised in the presence of palladium catalysts with ligands containing 8-diphenylphosphinochromane-like substituents at phosphorus. MonoXantphos and monoSPANphos afforded the most active, stable and selective catalysts known to date under commercially relevant production conditions for 1-methoxyocta-2,7-diene, the precursor to oct-1-ene.

Keywords: carbenes · ligand design · palladium · phosphane ligands · telomerisation

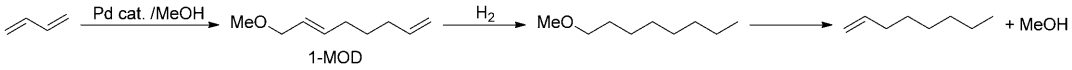
Introduction

The telomerisation of 1,3-dienes with nucleophiles has been studied extensively in both academic and industrial laboratories.[1] The telomerisation of buta-1,3-diene (Bd) with methanol is the key step of the commercial route developed by the Dow Chemical Company (Dow) to produce oct-1-ene (Scheme 1).[2] The process came on stream in Tarragona in 2007 and is based on the use of a crude C4 cut (containing 50 wt% of buta-1,3-diene). The telomerisation product, 1-methoxyocta-2,7-diene (1-MOD),[3] is fully hydrogenated to 1-methoxyoctane in the next step. Subsequent thermal cracking of 1-methoxyoctane gives oct-1-ene, the desired product, together with methanol that can be recycled.



Scheme 2. Telomerisation of buta-1,3-diene.

Apart from 1-MOD, two main byproducts—3-methoxyocta-1,7-diene (3-MOD) and octa-1,3,7-triene (OCT, Scheme 2) are formed. At high temperatures the thermal Diels–Alder adduct vinylcyclohexene is also obtained. The catalytic system currently used in the commercial process is based on Pd/PPh_3 and gives moderate results under typical conditions in terms of activity, selectivity and stability:[4] the best-performing catalyst under laboratory conditions is an N-heterocyclic carbene (NHC)Pd complex reported by Beller and co-workers.[5a,b]



Scheme 1. Simplified view of the Dow process.

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[**] 1-MOD = 1-methoxyocta-2,7-diene

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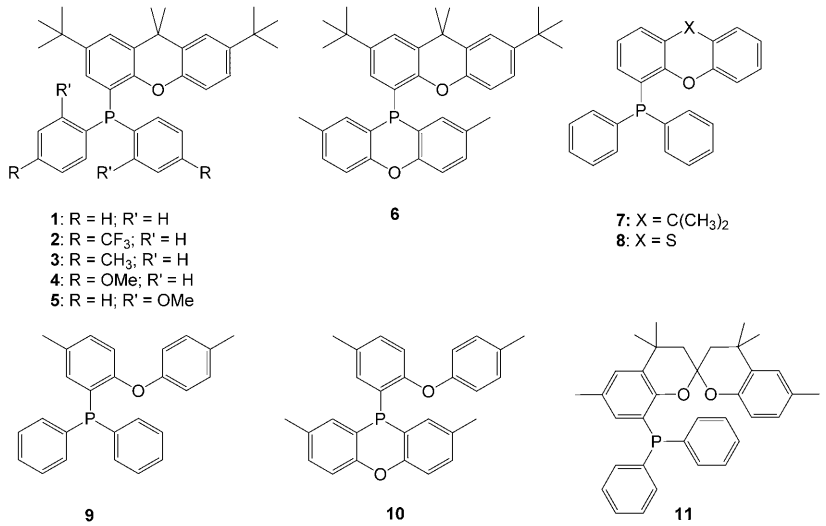
Results and Discussion

We recently reported bulky phosphines that efficiently catalysed the telomerisation of butadiene with methanol.[6] Phosphine **1** is a new, efficient ligand for the telomerisation of buta-1,3-diene with methanol under commercial production conditions.[6] This excellent result prompted us to investigate the electronic and steric effects of bulky phosphine ligands on the selectivity, productivity, activity and stability of the catalyst for the telomerisation of buta-1,3-diene with methanol. A new range of bulky phosphines (**2**–**11**) was thus de-



veloped, with a focus on the chromane substituent and related fragments.

Ligand synthesis: Phosphines **2–6** were prepared by the same method as reported for **1**,[6] from 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene by selective bromination, lithiation and phosphorylation. Phosphines **10** and **11** were prepared by the same strategy. The synthesis thus proceeds through the formation of two new monobrominated compounds: the 2-bromo-di-*p*-tolyl ether (**12**) and 8-bromo-4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (**13**).

The bromo ether (**12**) is obtained as a di-*p*-tolyl ether/**12**/2,2′-dibromo-di-*p*-tolyl ether mixture (5:80:15) by treatment of di-*p*-tolyl ether with *N*-bromosuccinimide (NBS). In the same manner, the 8-bromo-4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (**13**) is obtained as a mixture of the starting material, compound **13** and the dibromo compound (20:65:15) by treatment of the 4,4,4′,4’,6,6′-hexamethylspiro-2,2′-bichroman (SPAN) backbone with NBS.

The bromo compound mixtures, which give backbone/monophosphine/diphosphine mixtures after lithiation/phosphorylation, were used without further purification, because in our hands it remains easier to separate the phosphine product mixtures. In the cases of **7–9**, one-pot, one-step syntheses—direct lithiation of the backbone at room temperature followed by phosphorylation as reported for the synthesis of DPEphos and xantphos derivatives[7]—were investigated.

Non-optimised overall yields were 45% for phosphines **2** and **3**, 52% for **6**, around 20% for **4** and **5** and 37% for **11**. Phosphines **7–9** were obtained pure in 21–45% yields. The yields are moderate for all ligands, due to the difficulty of selective monofunctionalisation of a symmetrical backbone (e.g., concomitant formation of the corresponding diphosphines).

Crystals of **11** suitable for X-ray diffraction analysis were obtained. The molecular structure of **11** shows the niche formed by the ligand, in which the palladium catalyst nicely fits (Figure 1).[8]

Catalytic experiments: All phosphines were tested in the telomerisation of buta-1,3-diene with MeOH under commercial (Dow) production conditions (90°C, NaOMe/Pd (molar) = 5, Pd/Bd = 0.0025 mol%, crude C4). Different temperatures (60–100°C) and different methanol/butadiene ratios (2, 2.6 wt/wt, 3.4, 4.4 mol/mol, respectively) were used in particular cases, because higher MeOH/butadiene ratios increase 1-MOD selectivity.[5c]

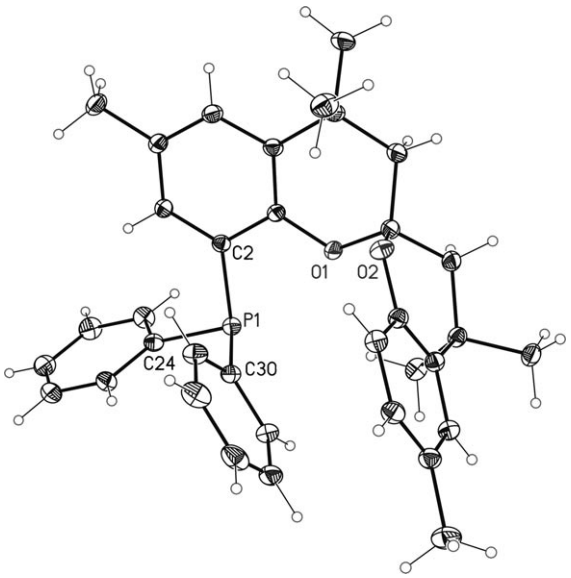


Figure 1. ORTEP plot (thermal ellipsoids shown at 50% probability level) of compound **11**. Selected distances (Å) and angles (°): P1–C2: 1.8390(8); P1–C24: 1.8376(9); P1–C30: 1.8337(9). C2-P1-C24: 101.94(4); C2-P1-C30: 100.40(4); C24-P1-C30: 102.89(4).

No differences were observed with use of well-defined L-Pd^0-diolefin complexes or Pd^{II}/ligand precatalysts,[6,5a,b] so catalytic reactions were carried out with a phosphine/Pd^{II} precatalyst. All phosphines were tested and compared with **1** and PPh_3 to study structure–reactivity relationships of the phosphine for the telomerisation reaction.

The performances of **2–11** are presented in Table 1. Almost all of the new ligands gave more productive and selective catalysts than PPh_3, up to 10 and 11% respectively. It seems not to be a straightforward matter to find general rules relating to the influence of steric/electronic properties of the ligand, because the two factors are always subtly associated. It appears that for a similar ligand type, a phosphine

Table 1. Catalytic results obtained for the ligands **1**–**11** at 90 °C over 2.5 h.[a]

	Ligand	Conv. Bd [%]	1-MOD [%]	3-MOD [%]	OCT [%]	Chemo. [%][c]	Pd loss [%][b]
1	PPh_3	85	82	5	13	87	17
2	**1**	93	89	5	6	94	6
3	**2**	75	77	5	18	82	17
4	**3**	93	90	5	5	95	14
5	**4**	91	90	5	5	95	14
6	**5**	95	93	4	3	97	22
7	**6**	83	91	5	4	96	10
8	**7**	92	87	5	8	92	22
9	**8**	86	83	5	12	88	25
10	**9**	87	87	5	8	92	41
11	**10**	93	88	5	7	93	23
12	**11**	94	88	6	6	94	8

[a] Reaction conditions: Pd (0.0025 mol% vs. Bd), NaOMe (0.0125 mol% vs. butadiene), ligand/Pd 2:1, MeOH/Bd 2.6, wt/wt. [b] Measurement error ±5% absolute. [c] Chemoselectivity (%) = (1-MOD + 3-MOD)/(1-MOD + 3-MOD + OCT) × 100.

that is less basic than **1** gives a less productive catalyst and/or is less active (cf. **1** with **2** (p-CF_3) and **6** (POP); Table 1, entries 2, 3, 7 and Figure 2) and also gives a less chemoselective catalyst (cf. **1** with **2**). More basic ligands thus give higher chemoselectivity (cf. **3**, **4**, **5**; Table 1, entries 4, 5, 6, respectively,). A positive influence of the o-MeO substituents in **5** on catalyst selectivity, activity and productivity is highlighted.[6,9]

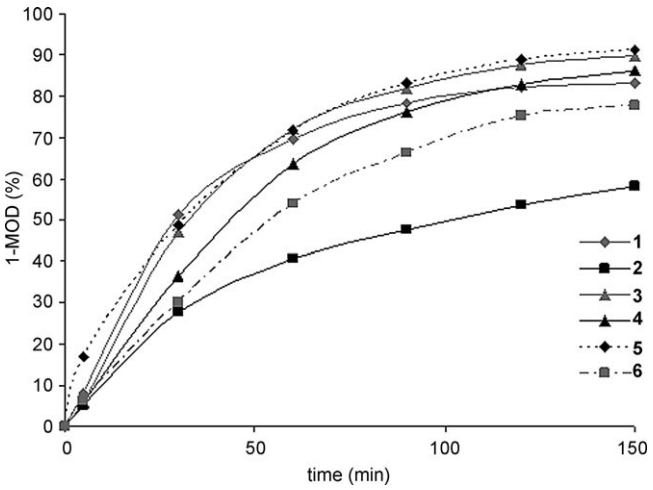


Figure 2. Formation of 1-MOD (% yield) over time:[a] influence of electronic properties. Reaction conditions: cf. Table 1.

High activity (Figure 2), high conversion and high selectivity (95 and 93%, respectively; Table 1, entry 6) for 1-MOD was thus achieved with **5** as the ligand at 90 °C under commercial production conditions. More basic ligands led to increases in Pd loss because the phosphine is more easily oxidised during the catalysis.

Decreasing the steric bulk of the xanthene backbone influenced the stability of the catalyst, as expressed in Pd loss, whereas selectivity and productivity decreased only slightly (cf. **7**, **8**). Higher Pd loss, up to 41%, was observed with use of a less bulky and less rigid backbone (cf. **9**, **10**), which also gave a slightly lower selectivity. Catalyst selectivity and productivity dropped when phosphine **8** was used, probably because of the presence of the sulfur atom.

MonoSPANphos **11** performed similarly to **1** in terms of productivity, selectivity and stability at 90 °C (Table 2). Interestingly, ligand **11** exhibited a remarkable activity at low temperature and it was studied in detail (Table 2). Compound **11** should thus permit higher selectivity and productivity to be obtained and energy to be saved relative to **1** or PPh_3. Moreover, to highlight the excellent performances of **1** and **11** for the telomerisation, they were compared with IMes (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, used as its IMesHCl salt), an N-heterocyclic carbene reported by Beller and co-workers,[5a,b] under suitable production conditions (crude C4, low amounts of promoter). The results are presented in Table 2 (results obtained for **1** were reported previously).[6]

Table 2. Catalytic results obtained for **11**.[a]

	L (L/Pd)	Pd/Bd [10^{-6} mol]	t [h]	T [°C]	Base/Pd [mol]	Conv. Bd [%]	1-MOD sel. [%][b]	Pd loss [%][c]
1	**1** (2)	25	2.5	60	5	36	94	2
2	**1** (2)	25	2.5	75	5	67	93	–
3	**1** (2)	25	2.5	90	5	93	89	6
4	**11** (2)	25	2.5	60	5	71	94	0
5	**11** (2)	25	2.5	75	5	82	91	–
6	**11** (2)	25	2.5	90	5	94	88	8
7	IMesHCl (1)	25	2.5	90	5	32	86	23
8	IMesHCl (1)	25	2.5	90	100	87	97	45
9	IMesHCl (1)	25	2.5	90	1000	93	96	77

[a] Reaction conditions: MeOH/Bd: 2.6 wt/wt. [b] 1-MOD selectivity (%) is 1-MOD/(1-MOD + 3-MOD + OCT) × 100. Measurement error ±5% absolute.

Surprisingly, at 90 °C, the ligands **1** and **11** form more productive catalysts than IMes and the last compound shows a lower selectivity than reported previously (Table 2, entries 3, 6, 7).[5a,c] Obviously, activity and productivity cannot be compared with the reported values because [Bd] in the medium is lower than that in our work (higher MeOH/Bd ratio, crude C4, impurities). To achieve excellent performances with an NHC ligand, a high NaOMe/Pd ratio is required—from 100 to 1000 (Table 2, entries 8 and 9; Figure 3)—probably due to poor precatalyst formation at low base concentrations,[10] but such conditions are not viable industrially. Moreover, under such conditions the loss of palladium is very important, up to 77% (Table 2, entry 9).

At 60 °C, the ligand **11** is highly superior to **1** and IMes, showing a turn-over number (TON) of 26696 after 2.5 h and a selectivity for 1-MOD of 94% (Table 2, entries 4 and 1). As shown in Figure 3, the presence of more equivalents of NaOMe significantly increased the rate of formation of 1-

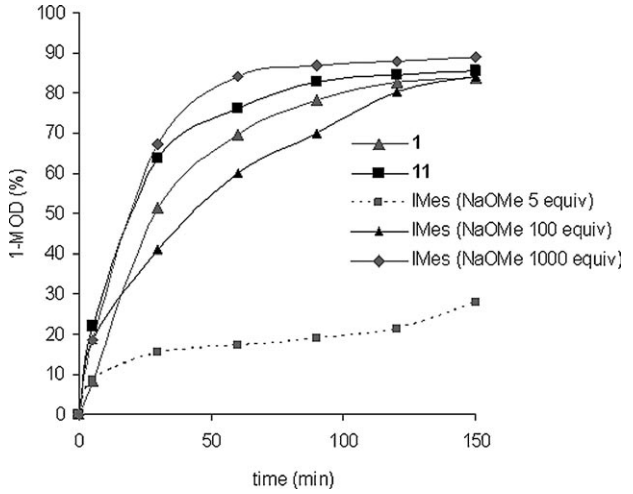


Figure 3. Formation of 1-MOD (% yield) over time (Pd (0.0025 mol%), MeOH/Bd = 2.6, NaOMe (5 equiv vs. Pd)); comparison of IMes, **11** and **1**.

MOD in the case of IMes ligand; a similar effect was observed for PPh_3 (see the Supporting Information), so the kinetic profiles (Figure 3) of IMes with NaOMe (1000 equiv vs. Pd) and of **1** or **11** with NaOMe (5 equiv vs. Pd) are not comparable.[11] IMes performed less well than **11** in the presence of 5 or even 100 equiv of NaOMe, giving rates intermediate between those of **1** and **11**. The attractive feature of the NHC ligand is that, under suitable conditions, the 1-MOD selectivity does not depend on reaction temperature and remains constant at ≈96%.

The formation of 1-MOD versus time at different temperatures for **11** and **1** is shown in Figure 4 at a MeOH/Bd ratio of 2 (2.6 is reported in the Supporting Information). In the case of **11**, the 1-MOD formation rate is significantly higher than in that of **1** (Figure 4). The initial rate at 60 °C for **11** is similar to that of **1** at 90 °C. With regard to the activity of the catalyst, an impressive turn-over frequency (TOF_{max}; 5 min) of 170000 h^{-1} (30 min; 52000 h^{-1}) is observed at 90 °C with **11** (conversion of Bd = 35 and 65%, respectively); compound **1** exhibits a TOF_{max} of 40000 h^{-1} (for **1**, TOF (5 min) ≈ TOF (30 min)) only at 90 °C (TOFs are calculated with respect to butadiene).

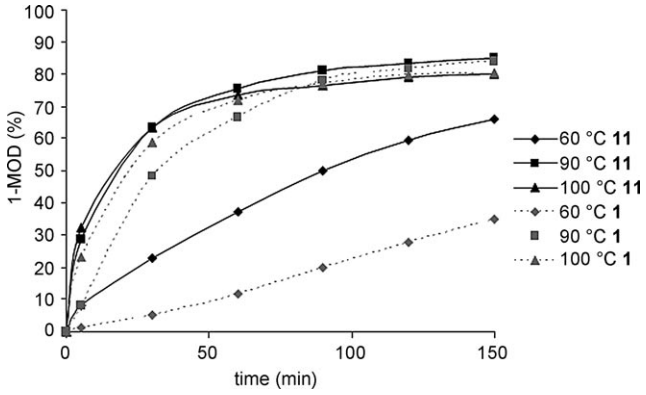


Figure 4. Formation of 1-MOD (% yield) over time (Pd (0.0025 mol%), MeOH/Bd = 2); comparison of the ligands **11** and **1**.

Conclusion

In summary, we have studied the steric and electronic effects of phosphines on the telomerisation of butadiene and methanol. It appears that the presence of chromanyl-like moieties such as xanthene or bischromane backbones (SPANphos) in phosphine ligands is exceptionally well suited for the telomerisation, especially with regard to selectivity, activity and productivity/stability of the catalyst. The ligand **5** gives rise to 95% Bd conversion and 93% selectivity for 1-MOD at 90 °C and is the best ligand of the monoXantphos series. Under industrial production conditions, monoXantphos **1** and monoSPANphos **11**, especially, are better ligands than IMes even at 90 °C. To the best of our knowledge, **11** is the most active ligand at low temperature for this reaction. The moderate steric bulk of the substituent and the weakly coordinating nature of the chromanyl oxygen atom are believed to be responsible for this performance.

Experimental Section

General procedures: All reactions were carried out under argon with use of Schlenk techniques. Deuterated chloroform was distilled over calcium hydride under argon prior to use. All chlorodiphenylphosphine derivatives were purchased from Alfa Aesar and used as received. Di-*p*-tolyl ether, 9,9-dimethylxanthene, and phenoxathiine were purchased from Aldrich and used without further purifications. 4,4,4′,4′,6,6′-Hexamethylspiro-2,2′-bichroman was prepared by a previously described method.[12] 4-Bromo-2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (impure) was prepared by the reported method.[6a] NMR spectra were recorded with a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm, and were calibrated with the aid of the residual ^1H and ^{13}C resonances of the deuterated solvents. Coupling constants (J) are expressed in Hz. Mass spectra and X-ray structure analyses were carried out at the Research Support Unit of the ICIQ (Tarragona, Spain). Analyses of the catalytic reactions were performed with a GC-FID and HP-5 (5% phenyl methyl siloxane; 30 m × 320 μm × 0.25 μm) capillary column. Elemental analyses were performed at the Unidade de Análise Elemental of the Universidade de Santiago de Compostela (Spain).

Synthesis of 4-(bis-*p*-trifluoromethylphenylphosphino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (2): *n*BuLi (2.5 M in hexane, 1.24 mL, 1.1 equiv) was added slowly at −78 °C to a solution of 4-bromo-2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (1,13 g, 2.8 mmol) in THF (30 mL), and the mixture was allowed to stir at −78 °C for 2 h. A solution of chloro-bis-*p*-trifluoromethylphenylphosphine (1 g, 2.8 mmol in 15 mL of THF) was added dropwise to the reaction mixture at −78 °C, and the mixture was allowed to stir for 2 h at −78 °C and overnight at RT. The solvent was evaporated under vacuum and dichloromethane (or diethyl ether, 20 mL) and degassed water (10 mL) were then added. The organic layer was recovered and dried with $MgSO_4$. Evaporation of the solvent afforded a white solid. The product was purified by column chromatography over silica gel with use of a gradient elution from hexane to hexane/CH_2Cl_2 (8:1) and was obtained from the third fraction as a white solid (55%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 7.61$ (m, 4H; H arom.), 7.50 (m, 5H; H arom.), 7.40 (d, $J = 2.3$ Hz, 1H; H arom.), 7.10 (dd, $J = 2.3$, 8.5 Hz, 1H; H arom.), 6.75 (dd, $J = 2.3$, 7.0 Hz, 1H; H arom.), 6.46 (d, $J = 8.5$ Hz, 1H; H arom.), 1.67 (s, 6H; CH_3), 1.32 (s, 9H; $C(CH_3)$), 1.20 ppm (s, 9H; $C(CH_3)$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 150.3$ (d, $J_{P,C} =$

11.6 Hz), 148.0, 146.0, 145.7 (d, $J_{P,C}=3.6$ Hz), 141.4 (d, $J_{P,C}=15.0$ Hz), 133.9 (d, $J_{P,C}=20.3$ Hz), 131.0, 130.0 (d, $J_{P,C}=1.4$ Hz), 129.3, 129.2 (d, $J_{P,C}=10.2$ Hz), 125.1 (m), 124.5, 124.3, 124.0 (d, $J_{F,C}=270.0$ Hz) 122.0, 121.2 (d, $J_{P,C}=13.4$ Hz), 115.5, 34.8, 34.6, 34.34, 31.8, 31.5 31.4 ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): $\delta=-62.87$ ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-9.03$ ppm; elemental analysis calcd (%) for $C_{37}H_{37}F_6OP$: C 69.15, H 5.80; found: C 69.35, H 5.89.

Synthesis of 4-(bis-*p*-tolylphosphino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (3): The same procedure as described for the synthesis of **2** was followed (chloro-bis-*p*-tolylphosphine, 0.696 g, 2.8 mmol in 15 mL of THF). The product was purified by column chromatography over silica gel with use of a gradient elution from hexane to hexane/CH_2Cl_2 (10:3) and obtained as a white solid from the third fraction (56%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.40$ (dd, $J=2.3$, 12.9 Hz, 2H; H arom.), 7.29 (m, 4H; H arom.), 7.15 (m, 4H; H arom.), 7.09 (dd, $J=2.3$, 8.5 Hz, 1H; H arom.), 6.72 (dd, $J=2.3$, 5.8 Hz, 1H; H arom.), 6.58 (d, $J=8.5$ Hz, 1H), 2.32 (s, 6H; $CH_{3\,tolyl}$), 1.65 (s, 6H; CH_3), 1.31 (s, 9H; $C(CH_3)$), 1.17 ppm (s, 9H; $C(CH_3)$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=$ 150.1 (d, $J_{P,C}=13.0$ Hz), 148.3, 145.4, 145.1 (d, $J_{P,C}=2.3$ Hz), 138.5, 133.9 (d, $J_{P,C}=19.7$ Hz), 131.8 (d, $J_{P,C}=10.9$ Hz), 129.4, 129.2 (d, $J_{P,C}=2.2$ Hz), 129.1, 129.1, 128.9 (d, $J_{P,C}=4.9$ Hz), 124.0, 123.3, 121.9, 115.9, 34.5, 34.4, 34.4, 31.8, 31.5, 31.4, 31.3 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-12.06$ ppm; elemental analysis calcd (%) for $C_{37}H_{43}OP$: C 83.11, H 8.11; found: C 82.95, H 8.16.

Synthesis of 4-(bis-*p*-methoxyphenylphosphino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (4): The same procedure as described for the synthesis of **2** was followed (chloro-bis-*p*-methoxyphenylphosphine, 0.785 g, 2.8 mmol in 15 mL of THF). The product was purified by column chromatography over silica gel with use of a gradient elution from hexane to hexane/CH_2Cl_2 (1:1) and obtained as a white solid (28%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.40$–7.30 (m, 6H; H arom.), 7.08 (dd, $J=$ 2.3, 8.5 Hz, 1H; H arom.), 6.89 (dd, $J=0.8$, 8.7 Hz, 4H; H arom.), 6.68 (dd, $J=2.2$, 5.6 Hz, 1H; H arom.), 6.57 (d, $J=8.5$ Hz, 1H), 3.82 (s, 6H; OCH_3), 1.65 (s, 6H; CH_3), 1.31 (s, 9H; $C(CH_3)$), 1.17 ppm (s, 9H; $C(CH_3)$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=160.1$, 150.0 (d, $J_{P,C}=$ 13.7 Hz), 148.3, 145.4, 145.1 (d, $J_{P,C}=1.4$ Hz), 135.4 (d, $J_{P,C}=21.7$ Hz), 129.5, 129.3 (d, $J_{P,C}=1.4$ Hz), 128.6 (d, $J_{P,C}=4.2$ Hz), 127.8 (d, $J_{P,C}=$ 5.9 Hz), 124.5 (d, $J_{P,C}=13.0$ Hz), 124.1, 123.0, 121.8, 115.9, 114.0 (d, $J_{P,C}=$ 8.4 Hz), 55.2, 34.7, 34.5, 34.4, 31.8, 31.5, 31.4 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-13.62$ ppm; elemental analysis calcd (%) for $C_{37}H_{43}O_3P$: C 78.42, H 7.65; found: C 78.67, H 7.72.

Synthesis of 4-(bis-*o*-methoxyphenylphosphino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (5): The same procedure as described for the synthesis of **2** was followed (chloro-bis-*o*-methoxyphenylphosphine, 0.785 g, 2.8 mmol in 15 mL of THF). The product was purified by column chromatography over silica gel with use of a hexane/CH_2Cl_2 gradient elution (8:2 to 1:1) and was obtained as a white solid (20%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.38$–7.30 (m, 4H), 7.07 (dd, $J=2.3$, 8.5 Hz, 1H), 6.93–6.90 (m, 2H), 6.83 (m, 4H), 6.73 (dd, $J=2.3$, 5.8 Hz, 1H), 6.61 (d, $J=8.5$ Hz, 1H), 3.77 (s, 6H), 1.65 (s, 6H), 1.31 (s, 9H), 1.16 ppm (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=161.5$ (d, $J_{P,C}=16.8$ Hz), 150.6 (d, $J_{P,C}=13.8$ Hz), 148.6, 145.1, 144.7 (d, $J_{P,C}=2.2$ Hz), 134.1 (d, $J_{P,C}=1.4$ Hz), 129.9, 129.6, 129.2 (d, $J_{P,C}=6.3$ Hz), 128.8 (d, $J_{P,C}=1.3$ Hz), 124.7 (d, $J_{P,C}=12.7$ Hz), 123.9, 122.7, 122.3 (d, $J_{P,C}=15.0$ Hz), 121.7, 120.9, 116.1, 110.0 (d, $J_{P,C}=1.5$ Hz), 55.7, 34.7, 34.5, 34.4, 31.7, 31.6, 31.4 ppm; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-32.38$ ppm; elemental analysis calcd (%) for $C_{37}H_{43}O_3P$: C 78.42, H 7.65; found: C 78.14, H 7.59.

Synthesis of 4-(2,7-dimethylphenoxaphosphino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (6): The same procedure as described for the synthesis of **2** was used (chloro-2,7-dimethylphenoxaphosphine, 0.735 g, 2.8 mmol in 15 mL of THF). The product was purified by column chromatography over silica gel with use of a gradient elution from hexane to hexane/CH_2Cl_2 (5:1) and obtained as a white solid from the third fraction (58%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.51$ (br dd, $J=1.9$, 10.7 Hz, 2H; H arom.), 7.38 (d, $J=2.3$ Hz, 1H; H arom.), 7.29 (m, 2H; H arom.), 7.20 (d, $J=8.5$ Hz, 1H; H arom.), 7.16 (br dd, $J=2$, 8.5 Hz, 2H; H arom.), 7.09 (d, $J=8.3$ Hz, 2H; H arom.) 6.65 (dd, $J=2.3$, 7.4 Hz, 1H; H arom.), 2.33 ($CH_{3\,POP}$) 1.59 (s, 6H; CH_3), 1.36 (s, 9H; $C(CH_3)$), 1.16 ppm (s, 9H; $C(CH_3)$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=$ 154.4, 149.8 (d, $J_{P,C}=9.5$ Hz), 148.1, 145.5, 144.7 (d, $J_{P,C}=3.0$ Hz), 135.8, 135.5, 132.3 (d, $J_{P,C}=9.3$ Hz), 131.5, 128.9 (d, $J_{P,C}=9.3$ Hz), 128.1 (d, $J_{P,C}=$ 9.0 Hz), 125.3 (d, $J_{P,C}=21$ Hz), 124.2, 123.9, 122.5, 117.2, 117.1 (d, $J_{P,C}=$ 2.1 Hz), 115.6, 34.4, 34.4, 34.3, 32.5, 31.59, 31.3, 20.6 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-60.50$ ppm; elemental analysis calcd (%) for $C_{37}H_{41}O_2P$: C 80.99, H 7.53; found: C 80.95, H 7.50.

Synthesis of compounds 7–9: *n*BuLi (1.6 M in hexane, 1.2 equiv, 6 mmol, 3.75 mL) was added dropwise at room temperature to a stirred solution of the backbone (5 mmol; 9,9-dimethylxanthene (1.05 g), phenoxathiin (1.013 g), di-*p*-tolyl ether (0.991 g)) and TMEDA (1.2 equiv, 6 mmol, 0.697 g, 0.899 mL) in THF (50 mL), and the mixture was stirred for 16 h. Chlorodiphenylphosphine (1 equiv, 5 mmol, 1.103 g, 0.897 mL) was then added at room temperature and the mixture was stirred for 16 h more. After 16 h, solvent was evaporated to dryness and diethyl ether or CH_2Cl_2 (≈30 mL) was added, followed by water (10 mL). The organic layer was recovered and dried over $MgSO_4$ and the solvent was evaporated to dryness. The pure products **7**, **8** and **9** were obtained in 21, 41 and 45% yields, respectively, after purification by column chromatography over silica gel (eluent: CH_2Cl_2/hexane 2:10 v/v).

4-(Diphenylphosphino)-9,9-dimethylxanthene (7): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.46$–7.34 (m, 12H), 7.09–6.98 (m, 3H), 6.63 (m, 2H), 1.64 ppm (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=152.3$ (d, $J_{P,C}=14.3$ Hz), 150.5, 136.5 (d, $J_{P,C}=10$ Hz), 134.0 (d, $J_{P,C}=20.1$ Hz), 131.4 (d, $J_{P,C}=2.7$ Hz), 130.4, 130.3, 128.8, 128.5 (d, $J_{P,C}=7.0$ Hz), 127.2, 126.5, 125.3, 125.1 (d, $J_{P,C}=14.4$ Hz), 123.3, 123.2, 116.6, 34.4, 31.5 ppm; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-11.72$ ppm; elemental analysis calcd (%) for $C_{27}H_{23}OP$: C 82.21, H 5.88; found: C 82.56, H 5.98.

4-(Diphenylphosphino)phenoxathiin (8): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.42$–7.32 (m, 10H), 7.14 (m, 1H), 7.08 (m, 1H), 6.94 (m, 3H), 6.54 (ddd, $J=1.5$, 4.2, 7.6 Hz, 1H), 6.27 ppm (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=153.5$ (d, $J_{P,C}=14.7$ Hz), 151.9, 135.9 (d, $J_{P,C}=10.4$ Hz), 134.1 (d, $J_{P,C}=20.4$ Hz), 131.5 (d, $J_{P,C}=3.0$ Hz), 129.0, 128.6 (d, $J_{P,C}=7.4$ Hz), 127.8 (d, $J_{P,C}=16.7$ Hz), 127.5, 127.4, 126.5, 124.6, 124.5, 118.0 ppm; ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-11.38$ ppm; elemental analysis calcd (%) for $C_{37}H_{43}O_3P$: C 74.98, H 4.46; found: C 74.76, H 4.35.

2-(Diphenylphosphino)-di-*p*-tolyl ether (9): ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.45$–7.36 (m, 10H; H arom.), 7.10 (d, $J=8.3$ Hz; H arom.), 7.06 (d, $J=8.4$ Hz, 2H; H arom.), 6.78–6.73 (m, 3H; H arom.), 6.65 (dd, $J=2.3$, 4.7 Hz, 1H), 2.32 (s, 3H; CH_3), 2.23 ppm (s, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=157.6$ (d, $J_{P,C}=16.5$ Hz), 154.7, 136.5 (d, $J_{P,C}=10.8$ Hz), 134.2, 134.0 (d, $J_{P,C}=19.8$ Hz), 132.6, 132.5, 130.8, 129.9, 128.4, 128.6, 128.3, 118.9, 117.38, 20.8, 20.7 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-12.99$ ppm; elemental analysis calcd (%) for $C_{26}H_{23}OP$: C 81.66, H 6.06; found: C 81.72, H 6.14.

Synthesis of 2-(2,7-dimethylphenoxaphosphino)-di-*p*-tolyl ether (10): *n*BuLi (1.6 M in hexane, 1.2 equiv, 2.2 mL) was added dropwise at −78 °C to a solution of 2-bromo-di-*p*-tolyl ether **15** (80%, 1 g, 2.9 mmol) in THF (30 mL) and the mixture was stirred at −78 °C for 2 h. Chloro-2,7-dimethylphenoxaphosphine (3.48 mmol, 0.913 g) in THF (15 mL) was then added dropwise at −78 °C and the mixture was stirred for 2 h at −78 °C and for 2 h at RT. Solvent was evaporated to dryness and diethyl ether or CH_2Cl_2 (≈30 mL) was added, followed by water (10 mL). The organic layer was recovered and dried over $MgSO_4$ and the solvent was evaporated to dryness. The pure product was obtained in 70% yield after purification by column chromatography over silica gel (eluent: from hexane to CH_2Cl_2/hexane 2:10 v/v). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta=7.39$ (br d, $J=10.5$ Hz, 2H; H arom.), 7.19–7.07 (m, 6H; H arom.), 6.95 (br d, $J=8.3$ Hz; H arom.), 6.76 (m, 2H; H arom.), 6.64 (ddd, $J=8.2$, 4.1, 1.8 Hz, 1H; H arom.), 6.50 (m, 1H; H arom.), 2.37 (s, 3H; CH_3), 2.27 (s, 6H; $CH_{3\,POP}$), 2.15 ppm (s, 3H; CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): $\delta=156.8$ (d, $J_{P,C}=15.5$ Hz), 155.2, 154.6, 136.1, 135.7, 132.6 (m), 132.5, 132.3, 131.5, 130.6, 130.5 (d, $J_{P,C}=25$ Hz), 130.0, 118.5, 118.0 (d, $J_{P,C}=1.4$ Hz), 117.3, 117.1 (d, $J_{P,C}=3.0$ Hz), 20.8, 20.7 20.5 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 °C): $\delta=-62.51$ ppm; elemental analysis calcd (%) for $C_{28}H_{25}O_2P$: C 79.23, H 5.94; found: C 79.10, H 5.92.

Synthesis of 8-diphenylphosphino-4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (11) (mono-SPANphos): A solution of 8-bromo-4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (**16**, 65%, 2.2 g, containing 3.44 mmol of **16**) in THF (40 mL) was cooled to −78 °C. *n*BuLi (2.5 M in hexane, 1.9 mL) was then added slowly. The mixture was stirred at −78 °C for 1 h and $ClPPh_2$ (0.9 mL) was added. The mixture was stirred at −78 °C for 1 h and at RT for 1 h. The solvent was then evaporated and degassed water was added. The product was extracted with CH_2Cl_2. The organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave crude product (2.2 g), which was purified by column chromatography on silica gel (eluent gradient from hexane to CH_2Cl_2/hexane 2:5). The product was isolated as a white solid from the third fraction (1 g, 1.92 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.36 (m, 3H; H arom.), 7.21–7.15 (m, 3H; H arom.), 7.13–7.09 (m, 1H; H arom.), 7.05–6.95 (m, 4H; H arom), 6.83 (brs, 1H; H arom.), 6.71 (brd, J = 8.2 Hz, 1H), 6.44 (d, J = 8.2 Hz, 1H), 6.25 (dd, J = 1.9, 4.0 Hz, 1H), 2.24 (s, 3H; CH_3 arom.), 2.15 (s, 3H; CH_3 arom.), 2.10–2.00 (m, 3H; CH_2), 1.89 (d, J = 14.1 Hz, 1H), 1.69 (s, 3H; CH_3), 1.48 (s, 3H; CH_3), 1.38 (s, 3H; CH_3), 1.25 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.9 (d, $J_{P,C}$ = 16.7 Hz), 147.9, 137.7 (d, $J_{P,C}$ = 11.4 Hz), 136.3 (d, $J_{P,C}$ = 10.7 Hz), 134.2 (d, $J_{P,C}$ = 19.8 Hz), 133.2 (d, $J_{P,C}$ = 19.0 Hz), 132.4, 130.9 (d, $J_{P,C}$ = 2.3 Hz), 130.3, 130.3, 130.0, 128.1, 128.0 (d, $J_{P,C}$ = 6.6 Hz), 127.8 (d, $J_{P,C}$ = 6.6 Hz), 127.6, 127.4, 126.5, 124.5 (d, $J_{P,C}$ = 13.1 Hz), 116.8, 97.8, 46.9, 46.8, 33.0 32.8, 32.3, 31.8 (d, $J_{P,C}$ = 8.9 Hz), 31.6, 30.8 (d, $J_{P,C}$ = 1.7 Hz), 30.1, 20.9, 20.8 ppm; ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 °C): δ = −13.05 ppm; elemental analysis calcd (%) for $C_{35}H_{37}O_2P$: C 80.74, H 7.16; found: C 80.53, H 7.09.

Synthesis of 2-bromo-di-*p*-tolyl ether (12): Di-*p*-tolyl ether (5.0 g, 25.2 mmol) and NBS (5.5 g, 31 mmol) were dissolved in DMF (150 mL) and the mixture was stirred at RT for 2 days. The conversion was monitored by GC/MS. If necessary, more NBS can be added. After one day, a mixture containing the monobromo compound, the dibromo compound and the starting material, in an 80:15:5 ratio, had been formed. The solvent was evaporated to dryness and the solid was washed with water and extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and concentrated to dryness. The obtained solid was washed with ethanol to give a white solid (4.5 g, containing a mixture of the monobromo compound, the dibromo compound and the starting material 80:15:5). The mixture was used without further purification to prepare the phosphine.

Synthesis of 8-bromo-4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (13): 4,4,4′,4′,6,6′-hexamethylspiro-2,2′-bichroman (2 g, 5.9 mmol) and NBS (1.05 g, 5.9 mmol) were dissolved in DMF (100 mL) and stirred at RT for 1 day. The conversion was monitored by GC/MS. If necessary, more NBS can be added. After two days, a mixture of the monobromo compound, the dibromo compound and the starting material in a 65:15:20 ratio had been formed. The solvent was evaporated to dryness and the solid was washed with water and extracted with diethyl ether. The diethyl ether solution was dried over $MgSO_4$ and evaporated to dryness. The obtained solid was washed with ethanol to give a white solid (2 g, containing a mixture of the monobromo compound, the dibromo compound and the starting material 65:15:20). The mixture was used without further purification to prepare the phosphine.

Pre-catalyst solution: The catalyst was prepared with palladium acetyl acetonate ($Pd(acac)_2$) plus two molar equivalents of the phosphine. One molar equivalent of acetic acid may be added to increase storage stability. The catalyst was prepared in methanol by dissolving all three components such that the palladium concentration in methanol equalled about 500 ppm.

Catalytic reaction: Each reaction was carried in a 1 L Parr reactor made from electropolished stainless steel. For each reaction, the autoclave of the Parr reactor was filled with specified amounts of methanol (MeOH/Bd ratio 2 or 2.6 by weight, 3.4 or 4.4 by mol), promoter (sodium methoxide, at a promoter to palladium molar ratio of 5:1) and inhibitor (diethyl hydroxyl amine, approximately 20 parts by weight per million parts by weight (ppm) based on total weight of methanol plus crude C4 load). The autoclave was closed and purged twice with low-pressure nitrogen (6 bar or 600 kPa) to substantially remove oxygen contained in the autoclave. A stainless steel sample cylinder was filled with a crude C4 stream containing approximately 50 weight percent of buta-1,3-diene, based upon total crude C4 stream weight and pressure. The content was added to the autoclave with low-pressure nitrogen (6 bar or 600 kPa). The temperature in the autoclave was raised to the desired work temperature (90 °C unless otherwise indicated).

An amount of the catalyst solution was weighed, such that the palladium concentration in the reactor after addition of all raw materials was 10 ppm based on total weight of raw materials, into a dry box, and the catalyst solution was then placed in a stainless steel sample cylinder. The catalyst solution was added to the autoclave with use of high-pressure nitrogen (19 bar to 20 bar, or 1900 kPa to 2000 kPa). After catalyst addition, the reaction began, producing the final product. Samples were taken from the autoclave at set times (five minutes after catalyst addition and at 30-minute intervals thereafter), and gas and liquid phases of the samples were analysed by GC (internal standard *m*-xylene).

Palladium precipitation measurement: Palladium precipitation in the reactor was determined by measurement of palladium concentration in the liquid phase after the reaction and comparison of that with a theoretical number based on total amount of palladium added and total liquid volume, which includes liquids added at the beginning of the reaction and liquids formed due to the butadiene conversion. Palladium concentration in the liquid was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

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[8] Crystals of **11** suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution of **11** in CH_2Cl_2 at low temperature (−25 °C). Crystal data for **11** at 100 K: $C_{36}H_{39}Cl_2O_2P_1$; 605.54 g mol^{-1}; triclinic; $P\bar{1}$; $a=11.4134(4)$, $b=12.0574(4)$, $c=13.3831(5)$ Å; $\alpha=65.6340(10)$, $\beta=76.4820(10)$, $\gamma=67.9480(10)°$; $V=1548.15(9)$ Å^3; $Z=2$, $\rho_{calcd}=1.299$ Mg m^{-3}; $R_1=0.0420$ (0.0541); $wR2=0.1156$ (0.1257); for 3164 reflections with $I>2\sigma(I)$ (for 11819 reflections (R_{int}: 0.0314) with a total measured of 43206 reflections); goodness-of-fit on $F^2=1.055$; largest diff. peak (hole) = 0.742 (−0.612) e Å^{-3}. CCDC-794329 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[10] A ratio of 1:1 for Pd/NHC or Pd/(NHC)HCl is optimal for this catalytic system when a low amount of base is used; an excess of (NHC)HCl is even detrimental.

[11] The amount of NaOMe also increased the initial rate of the reaction in the case of PPh_3 (by more than two times, see the Supporting Information). The influence of the amount of NaOMe on the systems of **1** and **11**, was not investigated, but it should be similar to that on PPh_3.

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