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Palladium-catalysed reactions of 6-halogeno-1,1′-binaphthyl derivatives. A detailed investigation of structure/reactivity and structure/selectivity relationships

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ABSTRACT

Five 6-halogeno-binaphthyl derivatives of different structure were synthesised starting from 2,2′-dihydroxy-1,1′-binaphthyl **1**. Several new 6-substituted binaphthyl compounds were obtained via the palladium-catalysed reactions of these derivatives. The reactivity of 6-iodo derivatives was much greater in most cases. In cross-coupling reactions the 6-bromo compounds were converted into the products using longer reaction times and/or higher temperatures. The reactivity difference between the two types of substrates was especially marked in aminocarbonylation and Heck reactions.

1. Introduction

Asymmetric synthesis remains a challenge to synthetic chemists as the demand for enantiomerically pure compounds continues to increase. Optically active 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) and its derivatives are among the most widely used ligands for both stoichiometric and catalytic asymmetric reactions.[1]

Accordingly, a great variety of functionalised BINOL or BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) derivatives have been prepared, especially to enable the attachment of the binaphthyl core to various supports.[2] Many of these heterogenisation methods incorporate a palladium-catalysed coupling reaction of halogeno-BINOL derivatives as the key step.[3–6] Both di- and mono-halogenated BINOL derivatives were successfully used as substrates in these reactions. According to the literature, BINOL and its derivatives can be halogenated at the 6,6′-,[7] 3,3′-[8] and 5,5′-[9] positions. There are several reports on the synthesis of 6-bromo-,[3,10–12] 3-iodo-[4] and 6-iodo BINOL derivatives.[13] The iodo derivatives are usually synthesised by multistep methods involving deiodination of a diiodo derivative,[4] or halogen exchange of a bromo compound.[13]

Recently, we have developed a high-yielding procedure for selective monoiodination of BINOL (Scheme 1) and have shown that 6-iodo-2,2′-dipivaloyloxy-1,1′-binaphthyl (**4**) is a highly reactive substrate for palladium-catalysed functionalisation under very mild reaction conditions.[14]

Deactivation of one of the naphthol rings via monoester formation is a prerequisite of selective monohalogenation of BINOL.[3,12,14] After the halogenation step, compound **3** was converted into the dipivaloyloxy derivative **4**,[14] because the incorporation of electron-withdrawing groups into the aromatic ring of aryl halides warrants high reactivity in palladium-catalysed reactions. At the same time, although aryl halides bearing electron-donating groups are known to be less reactive substrates in palladium-catalysed couplings, there are some examples for the successful conversion of halogenophenol derivatives[15] and even for the Heck reaction of 6-bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl.[3]

Based on these findings, the applicability of **3** as substrate in various palladium-catalysed couplings was also investigated. Although **3** could be converted into the coupling products, the reactions took place with poor selectivity. Because of the great importance of such couplings in the immobilisation of BINOL derivatives, a more detailed investigation of the effect of the protecting and leaving groups on the outcome of the palladium-catalysed reactions has been carried out.

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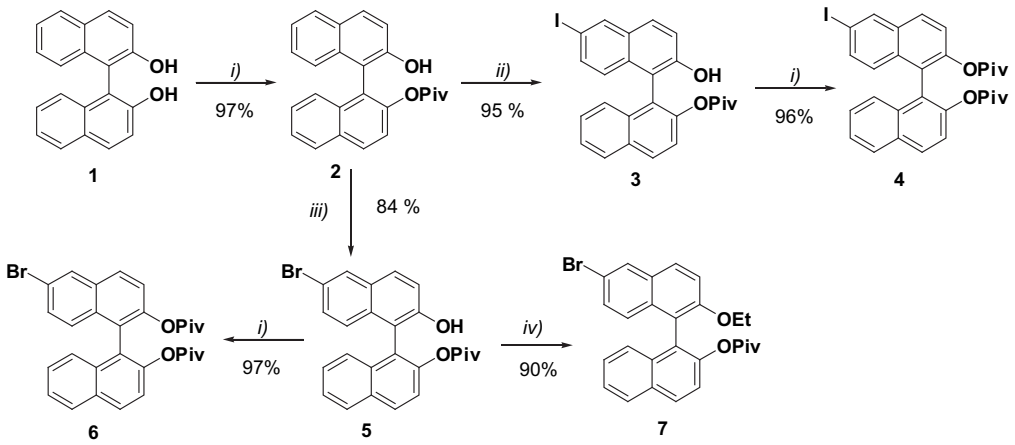


Scheme 1. Synthesis of 6-halogeno-1,1′-binaphthyl derivatives. Reaction conditions: (i) $(CH_3)_3CCOCl$, Et_3N, CH_3CN, 1 h, 0 °C, then 4 h at rt; (ii) Ag_2SO_4, I_2, EtOH, 12 h, rt; (iii) Br_2, CH_3CN, 0 °C, 3 h; (iv) EtBr, K_2CO_3, acetone, reflux, 18 h.

2. Results and discussion

Five 6-halogeno-binaphthyl derivatives of different structure were synthesised starting from 2,2′-dihydroxy-1,1′-binaphthyl **1** (Scheme 1). Selective monoiodination leading to compounds **3** and **4** was reported in our previous paper.[14] The bromo-derivatives, 6-bromo-2,2′-dipivaloyloxy-1,1′-binaphthyl (**6**) and 6-bromo-2-ethoxy-2′-pivaloyloxy-1,1′-binaphthyl (**7**) were obtained by derivatisation of the known 6-bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl **5**.

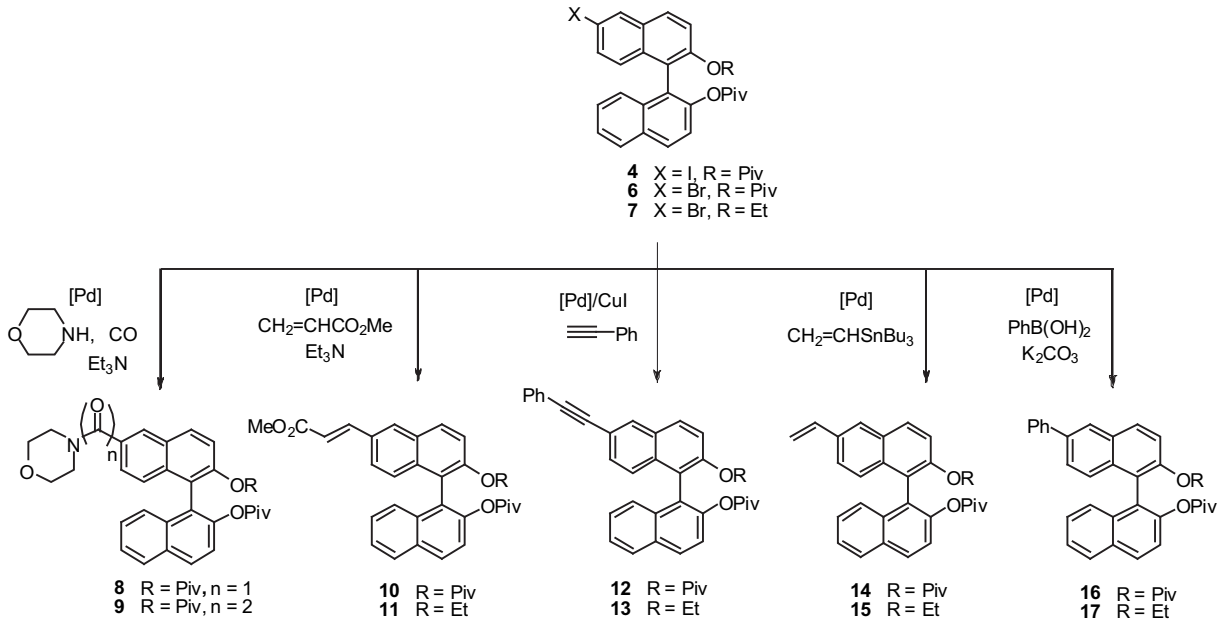
Compounds **3**–**7** were used as substrates in various palladium-catalysed coupling and carbonylation reactions (Schemes 2 and 3, Table 1). The reactions were followed by GC.

Except for the Suzuki coupling (entries 15 and 16), the iodo derivative **4** gave uniformly better results than the corresponding bromo compound **6**. The reactivity difference between the two substrates was especially marked in the aminocarbonylation (entries 1 and 2) and Heck reactions (entries 3 and 4). In the Sonogashira and Stille couplings, the products could be obtained in good yields starting from compound **6** (entries 8 and 13), but the use of the iodo derivative **4** made it possible to carry out the reactions at lower temperature and reactions were completed in shorter reaction times (entries 6, 7 and 11, 12).

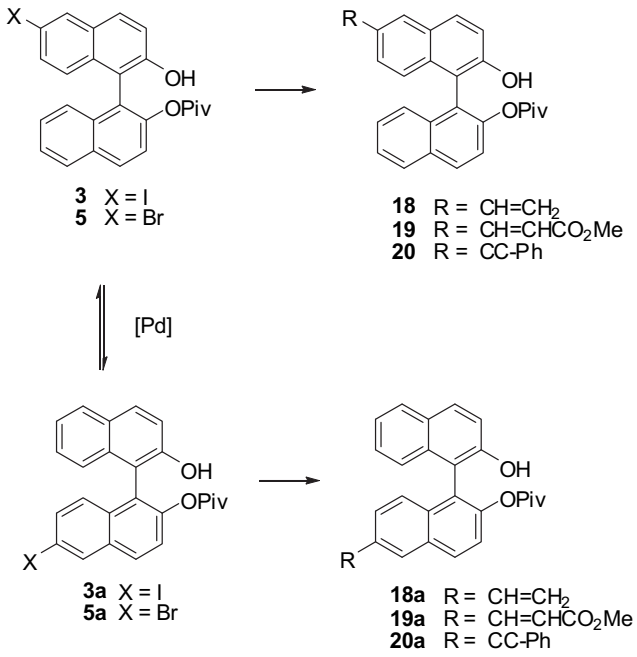
The other substrate with the bromo leaving group **7** gave comparable results with the bromo derivative **6**. In the Heck reaction, the reactivities of both compounds were low (entries 4 and 5). In Stille and Sonogashira couplings the conversion of **7** (entries 9 and 14) was lower than that of **6** under the same reaction conditions (entries 8 and 13). In the Suzuki coupling, the phenyl derivatives **16** and **17** could be produced in good yields starting from **6** and **7**, respectively (entries 16 and 17).

All of the reactions were completely selective except for the aminocarbonylation, when a double carbonylation accompanied the formation of the amide product **8**. The products **8** and **10**–**17** were isolated by column chromatography and their structures were proved by ^1H, ^{13}C NMR and MS. The formation of the side product of the aminocarbonylation, ketoamide **9**, was confirmed by the GC–MS measurements of the reaction mixtures.[16]

Heck and cross-coupling reactions of 6-halogeno-BINOL derivatives with one unprotected OH group (**3**, **5**) were also investigated (Table 2). Conversions were lower in Stille (entries 1 and 4) and Heck couplings (entries 5–7) than those obtained in the



Scheme 2. Palladium-catalysed reactions of 6-halogeno-1,1′-binaphthyl derivatives **4**, **6**, **7**.



Scheme 3. Formation of isomeric products in the Stille, Heck and Sonogashira couplings of **3** and **5**.

reactions of the corresponding dipivaloyl derivatives **4** and **6** (Table 1, entries 11–13 and 3 and 4) and comparable in the Sonogashira coupling (compare entry 8 in Table 2 and entry 6 in Table 1). The iodo compound **3** was more reactive in each case than the corresponding bromo derivative **5**.

Table 1
Palladium-catalysed coupling and carbonylation reactions of **4**, **6** and **7.**

Entry	Products	Substrate	Temp [°C]	Time [h]	Yield[a] [%]
1[b]	**8**+**9**	**4**	100	2	92 (**8**/**9**=94/6)
2[b]	**8**+**9**	**6**	100	2 (12)	16 (23)[g] (**8**/**9**=90/10)
3[c]	**10**	**4**	100	2	100
4[c]	**10**	**6**	100	2	21
5[c]	**11**	**7**	100	2 (24)	22 (89)
6[d]	**12**	**4**	60	2	100
7[d]	**12**	**4**	rt	0.5	100
8[d]	**12**	**6**	60	2 (8)	50 (81)[g]
9[d]	**13**	**7**	60	2	36
11[e]	**14**	**4**	100	2	100
12[e]	**14**	**4**	60	2	100
13[e]	**14**	**6**	100	2 (4)	60 (100)[g]
14[e]	**15**	**7**	100	4	75
15[f]	**16**	**4**	60	2	92
16[f]	**16**	**6**	60	2	93
17[f]	**17**	**7**	60	2	92

[a] Determined by GC.
[b] $Pd(OAc)_2$ (5 mol %), 10 mol % PPh_3, substrate/morpholine/Et_3N=1/5/2 in DMF under a CO atmosphere.
[c] $Pd(OAc)_2$ (5 mol %), 10 mol % PPh_3, substrate/methyl acrylate/Et_3N=1/2.5/2 in DMF.
[d] $PdCl_2(PPh_3)_2$ (5 mol %), 5 mol % CuI, substrate/phenylacetylene/Et_3N=1/2.5/2 in DMF.
[e] $Pd(PPh_3)_4$ (2 mol %), substrate/CH_2=$CHSnBu_3$=1/1.1, in DMF.
[f] $Pd(PPh_3)_4$ (5 mol %) substrate/$PhB(OH)_2$/K_2CO_3=1/2/5 in THF/H_2O (1:1).
[g] Yield obtained after heating the reaction mixture for the total time given in parenthesis in the previous column.

Stille coupling of **3** resulted in a 65% conversion of the substrate in 4 h (Table 2, entry 1). Surprisingly, the formation of two products (**18**, **18a**) with almost identical mass spectra was observed in 52/48 ratio. At the same time, an isomerisation of the unreacted starting material was also observed. Beside the peak corresponding to the iodo compound **3**, the signal of another component with a similar mass spectrum appeared in chromatograms obtained by GC and GC–MS.

The main steps of Stille coupling involve oxidative addition of the halide, transmetallation and reductive elimination. It can be assumed that in the presence of the palladium catalyst, an isomerisation of the BINOL halide takes place prior to the transmetallation step. As in most cases transmetallation is the rate determining step of Stille coupling, the extent of isomerisation might be reduced by accelerating this step by the use of less donating ligands, or by an excess of the organometallic reagent.[17] Indeed, the products were obtained as a 70/30 mixture of two isomers in the presence of the $Pd_2(dba)_3{\cdot}CHCl_3/AsPh_3$ catalyst system (entry 2). However, the selectivity of the reaction could not be improved further by increasing the ratio of the organometallic reagent (entry 3). Isolation of the two products by column chromatography was attempted but complete separation could not be achieved. Mixtures with 95/5 and 35/65 product ratios were obtained from the reactions carried out using the conditions described in entries 2 and 1, respectively. The main product was identified as 6-vinyl-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl **18** using 2D NMR techniques ($^1H-^1H$ COSY, HSQC and HMBC). Fig. 1 shows the regions of aromatic/olefinic protons of **18** (below) and the 35/65 product mixture (above). Unfortunately, the exact position of the vinyl substituent in **18a** could not be determined from the 2D NMR spectra of the latter sample because of the overlap of the signals of the two isomers.

Similar isomerisation was observed in the Sonogashira and Heck reactions of **3** and also in the palladium-catalysed reactions of **5**. Although an acceleration in the Heck reaction of **5** was observed using *o*-tolyl-phosphine (entry 7) instead of PPh_3 (entry 6) but isomerisation could not be suppressed.

According to GC–MS measurements, an isomer of **5** was obtained in 36% yield upon heating it at 100 °C in DMF in the presence of the $Pd(OAc)_2$/2 PPh_3 catalyst for half an hour. Although the two isomers could not be separated, the ^1H NMR spectrum of the mixture showed that the isomer had a very similar substitution pattern to that of **5** (Fig. 2) with a doublet (J=2 Hz) at 8.11 ppm. The pattern of the signal and the coupling constant corresponds to

Table 2
Palladium-catalysed coupling reactions of **3** and **5** with vinyltributylstannane, methyl acrylate or phenylacetylene.

Entry	Product	Substrate	Catalyst (mol % Pd)	Temp [°C]	Time [h]	Conv.[a] [%]	Distribution of isomers[a] (%)	
							Product	Substrate
1[b]	**18**+**18a**	**3**	$Pd(PPh_3)_4$ (2)	100	4	65	52/48	55/45 (**3**/**3a**)
2[b]	**18**+**18a**	**3**	$Pd_2(dba)_3{\cdot}CHCl_3$+4 $AsPh_3$ (5)	100	4	100	70/30	—
3[c]	**18**+**18a**	**3**	$Pd_2(dba)_3{\cdot}CHCl_3$+4 $AsPh_3$ (5)	100	4	100	65/35	—
4[b]	**18**+**18a**	**5**	$Pd(PPh_3)_4$ (2)	100	4	25	64/36	65/35 (**5**/**5a**)
5[d]	**19**+**19a**	**3**	$Pd(OAc)_2$+2PPh_3 (5)	100	2	63	56/44	60/40 (**3**/**3a**)
6[d]	**19**+**19a**	**5**	$Pd(OAc)_2$+2PPh_3 (5)	100	12	39	53/47	55/45 (**5**/**5a**)
7[d]	**19**+**19a**	**5**	$Pd(OAc)_2$+2P(*o*-Tol)$_3$ (5)	100	2	41	56/44	52/48 (**5**/**5a**)
8[e]	**20**+**20a**	**3**	$PdCl_2(PPh_3)_2$/CuI (5)	60	2	100	57/43	—

[a] Determined by GC.
[b] Substrate/CH_2=$CHSnBu_3$=1/1.1, in DMF.
[c] Substrate/CH_2=$CHSnBu_3$=1/1.65, in DMF.
[d] Substrate/methyl acrylate/Et_3N=1/2.5/2 in DMF.
[e] CuI (5 mol %), substrate/phenylacetylene/Et_3N=1/2.5/2 in DMF.

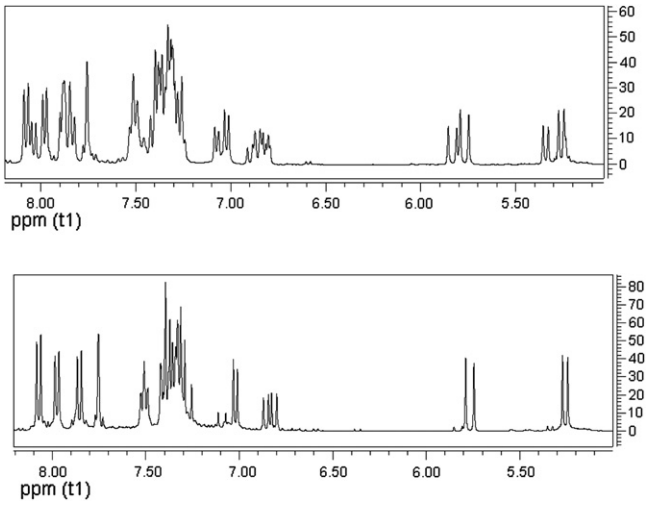


Fig. 1. Regions of aromatic/olefinic protons of ^{1}H NMR spectra of 18/18a mixtures (below: **18**/**18a**=95/5, above: **18**/**18a**=35/65).

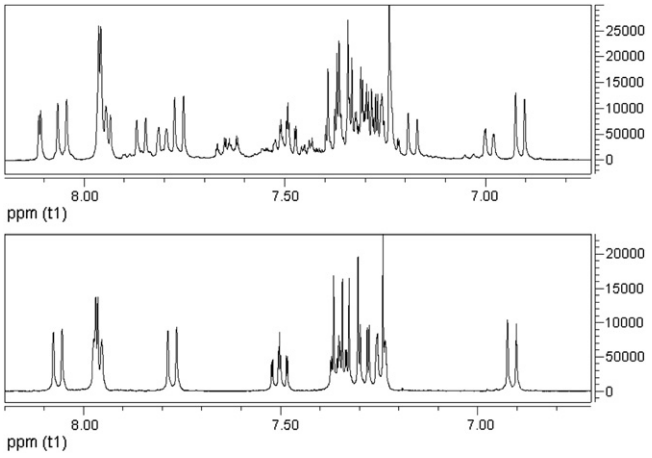


Fig. 2. Regions of aromatic protons of ^{1}H NMR spectra of **5** (below) and that of the reaction mixture after isomerisation in the presence of $Pd(OAc)_2$/PPh_3 (above).

a coupling with only one proton in the *meta* position. That means that the bromo substituent of the isomer can only be attached to the 7, 6′ or 7′ positions of the binaphthyl core.

Uozumi reported that the Heck reaction of **5** and butyl acrylate afforded the coupling product in 87% yield in the presence of the $Pd(OAc)_2$/P(*o*-Tol)$_3$ catalytic system after heating for 36 h at 130 °C.[3] Although there is no mention of isomerisation in this paper, the coupling product was found to give complicated NMR spectra with overlapping signals, despite the fact that it was analytically pure. Upon hydrolysis of the pivaloyl group, the product gave satisfactory NMR spectra corresponding to a 6-substituted 2,2-dihydroxy compound.[3]

Based on these observations, the mixture obtained by the palladium-catalysed isomerisation of **5** was reacted with pivaloyl chloride. Pivaloylation resulted in the formation of a single compound that was found to be identical with **6** according to the ^{1}H NMR spectrum of the reaction mixture. Similarly, pivaloylation of isomeric mixtures of products obtained by the Stille (**18**/**18a**), Heck (**19**/**19a**) and Sonogashira reactions (**20**/**20a**) led to products identical with compounds **14**, **10** and **12**, respectively.

These observations support the assumption that in the coupling reactions of **3** and **5**, an isomerisation of the substrates to **3a** and **5a** takes place prior to transmetallation, leading to the formation of a mixture of 6- and 6′-substituted 2-hydroxy-2-pivaloyloxy-1,1′-binaphthyl derivatives (Scheme 3).

There are two possible explanations for this isomerisation: (i) a 6→6′ palladium migration of palladium after the oxidative addition step or (ii) the migration of the pivaloyl group to the OH oxygen of the 6-substituted naphthyl ring.

However, both of these explanations have some weaknesses. A well-known and interesting aspect of the chemistry of aryl coupling is that it can take place at an arene position different from that of the original C–Pd bond.[18] Various aryl to aryl,[19] aryl to benzylic[20] and vinylic to aryl[21] palladium migrations have been described in the literature for biaryl compounds[19] or naphthalene derivatives.[20] Although according to DFT/B3LYP calculations of Dedieu,[22] various 1→*n* aryl-to-aryl palladium shifts (*n*=3–6) are feasible, to the best of our knowledge, no such migrations involving binaphthyl derivatives have been reported before.

On the other hand, although acyl-transfer under acidic, basic or even neutral conditions is a known reaction in e.g., carbohydrate chemistry, the pivaloyl group is generally regarded as less prone to such migrations.[23] Besides, according to our own results, other 2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl derivatives without a halide group, such as 6-nitro-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl,[14] do not undergo isomerisation in the presence of a palladium catalyst under similar conditions.

3. Conclusions

6-Iodo-1,1′-binaphthyl derivatives were shown to be excellent substrates for the palladium-catalysed functionalisation of the binaphthyl core. Reactivities of 6-bromo derivatives were comparable only in Suzuki couplings. The reactivity difference between the two types of substrates was especially marked in aminocarbonylation and Heck reactions. Coupling reactions of 2,2′-

dipivaloyloxy and 2-ethoxy-2′-pivaloyloxy derivatives were completely selective. However, an isomerisation of the substrates was found to take place when using 2-hydroxy-2′-pivaloyloxy derivatives as substrates.

4. Experimental

4.1. General

Gas chromatographic analyses were performed on an HP 4890D instrument with FID, using a 30 m, 0.32 mm ID, 0.25 μm SPB 1 column. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Inova 400 spectrometer at 400.13 MHz and 100.62 MHz, respectively. Mass spectra of were recorded on an HP-5971A MSD connected to an HP-5890/II gas chromatograph. Elemental analyses were measured on a 1108 Carlo Erba apparatus.

Compounds **2**, **5**[3] and **3**, **4**, **6**[14] were obtained as described previously.

*4.1.1. 6-Bromo-2-ethoxy-2′-pivaloyloxy-1,1′-binaphthyl (**7**).* 6-Bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**5**) (6.7 mmol, 3.01 g) and K_2CO_3 (13.4 mmol, 1.85 g) were dissolved in acetone (30 mL) under argon. In an inert atmosphere 13.4 mmol (1.46g) EtBr was added and the mixture was refluxed for 18 h. The solvent was removed in vacuo and the residue was dissolved in $CHCl_3$ (30 mL). The solution was washed with saturated $Na_2S_2O_3$ (30 mL) and brine (30 mL) and then dried over Na_2SO_4. After evaporation of the solvent, the product was purified by column chromatography (silica, *n*-hexane/EtOAc=6/1) to give 3.10 g of **7** (97% yield) as a yellow solid. [Found: C, 67.88; H 5.35, $C_{27}H_{25}BrO_3$ requires C, 67.93; H, 5.28%]; R_f (toluene) 0.60; ν_{max} (KBr) 1748, 1115 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 7.99–8.04 (m, 2H), 7.96 (d, *J* 8.2 Hz, 1H), 7.87 (d, *J* 8.9 Hz, 1H), 7.46–7.51 (m, 3H), 7.26–7.35 (m, 3H), 7.05 (d, *J* 9.1 Hz, 1H), 4.07 (q, *J* 7.0 Hz, 2H), 1.11 (t, *J* 7.0 Hz, 3H), 0.80 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.4, 154.6, 147.0, 133.6, 132.5, 131.7, 130.0, 129.7, 129.6, 129.1, 128.8, 128.2, 127.4, 126.5, 126.0, 125.4, 124.7, 122.0, 118.9, 117.5, 116.0, 65.1, 38.7, 26.6, 14.9; *m*/*z* (EI) 476/478 (53, M$^+$), 392/394 (100), 364/366 (28), 284 (24), 255 (26), 226 (33), 57 (56).

*4.1.2. 6-(Morpholino-carbonyl)-2,2′-dipivaloyloxy-1,1′-binaphthyl (**8**).* A solution of 6-iodo-2,2′-pivaloyloxy-1,1′-binaphthyl (**4**) (290 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and morpholine (218 μL, 2.5 mmol) was dissolved in 5 mL DMF under argon. Triethylamine (139 μL, 1 mmol) was added and the atmosphere was changed to carbon monoxide. The mixture was heated at 100 °C for 4 h, then the solvent was removed in vacuo. The residue was dissolved in chloroform (20 mL) and washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The product was purified by chromatography (silica, toluene, toluene/EtOAc=8/1) to give 235 mg of **8** (83%) as a light yellow solid. [Found: C, 74.22; H, 6.51; N, 2.41, $C_{35}H_{37}NO_6$ requires C, 74.05; H, 6.57; N, 2.47%]; R_f (toluene/EtOAc=8/1) 0.81; ν_{max} (KBr) 1750, 1634, 1100 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 8.00 (d, *J* 1.3 Hz, 1H), 7.98 (d, *J* 8.8 Hz, 1H), 7.96 (d, *J* 8.9 Hz, 1H), 7.90 (dd, *J* 8.1, 1.2 Hz, 1H), 7.48–7.61 (m, 2H), 7.44 (d, *J* 8.9 Hz, 1H), 7.37 (d, *J* 8.8 Hz, 1H), 7.27–7.33 (m, 3H), 3.47–3.74 (m, 8H), 0.74 (s, 9H), 0.72 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.2, 176.1, 170.1, 148.0, 146.9, 133.8, 133.2, 132.2, 131.4, 130.7, 129.6, 129.4, 127.9, 127.2, 126.7, 126.5, 125.7, 125.6, 124.9, 123.9, 123.0, 122.9, 121.8, 66.8, 66.3, 45.8, 40.4, 38.6, 38.5, 26.3, 26.2; *m*/*z* (EI) 567 (7, M$^+$), 483 (29), 399 (70), 313 (90), 57 (100).

4.2. General procedure for the Heck reactions of 4, 6 and 7

A solution of the 6-halogeno-1,1′-binaphthyl derivative (**4**, **6** or **7**) (0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and methyl acrylate (112 μL, 1.25 mmol) was dissolved in 5 mL DMF under argon. Triethylamine (139 μL, 1 mmol) was added and the mixture was heated at 100 °C for 2–24 h. Then the solvent was removed in vacuo. The residue was dissolved in chloroform (20 mL) and washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The products were purified by chromatography (silica, toluene).

*4.2.1. 6-((E)-(1-Methoxycarbonyl)-ethen-2-yl)-2,2′-dipivaloyloxy-1,1′-binaphthyl (**10**).* Yield: 256 mg (95%, starting from **4**), white solid. [Found: C, 75.69; H, 6.28, $C_{34}H_{34}O_6$ requires C, 75.82; H, 6.36%]; R_f (toluene) 0.18; ν_{max} (KBr) 1750, 1721, 1115 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 7.97 (d, *J* 8.8 Hz, 1H), 7.96 (d, *J* 1.5 Hz, 1H), 7.95 (d, *J* 8.9 Hz, 1H), 7.90 (dd, *J* 8.1, 1.2 Hz, 1H), 7.82 (d, *J* 16.0 Hz, 1H), 7.43–7.50 (m, 2H), 7.41 (d, *J* 8.9 Hz, 1H), 7.36 (d, *J* 8.8 Hz, 1H), 7.23–7.33 (m, 3H), 6.48 (d, *J* 16.0 Hz, 1H), 3.80 (s, 3H), 0.73 (s, 9H), 0.72 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.2, 176.1, 167.3, 148.1, 146.9, 144.5, 134.5, 134.4, 134.3, 133.2, 131.6, 131.4, 131.2, 129.7, 129.6, 129.4, 127.9, 126.8, 126.7, 125.7, 125.6, 124.2, 122.8, 121.8, 118.1, 51.7, 38.6, 38.5, 26.3, 26.2; *m*/*z* (EI) 538 (11, M$^+$), 454 (38), 370 (95), 57 (100).

*4.2.2. 6-((E)-(1-Methoxycarbonyl)-ethen-2-yl)-2-ethoxy-2′-pivaloyloxy-1,1′-binaphthyl (**11**).* Yield 152 mg (63%), white solid. [Found: C, 77.31; H 6.42, $C_{31}H_{30}O_5$ requires C, 77.16; H, 6.27%]; R_f (toluene) 0.12; ν_{max} (KBr) 1749, 1716, 1115 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 7.96 (d, *J* 8.8 Hz, 1H), 7.93 (d, *J* 9.0 Hz, 1H), 7.92 (dd, *J* 8.3, 1.2 Hz, 1H), 7.90 (d, *J* 1.8 Hz, 1H), 7.79 (d, *J* 16.0 Hz, 1H), 7.43 (ddd, *J* 8.3, 6.4, 1.6 Hz, 1H), 7.39 (dd, *J* 8.9, 1.8 Hz, 1H), 7.38 (d, *J* 9.0 Hz, 1H), 7.37 (d, *J* 8.8 Hz, 1H), 7.24–7.28 (m, 2H), 7.10 (d, *J* 8.9 Hz, 1H), 6.42 (d, *J* 16.0 Hz, 1H), 4.05 (q, *J* 7.1 Hz, 2H), 1.09 (t, *J* 7.1 Hz, 3H), 0.73 (s, 9H); *m*/*z* (EI) 482 (70, M$^+$), 398 (100), 370 (17), 57 (35).

4.3. General procedure for the Sonogashira coupling of 4, 6 and 7

A solution of the 6-halogeno-1,1′-binaphthyl derivative (**4**, **6** or **7**) (0.5 mmol), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and phenylacetylene (137 μL, 1.25 mmol) was dissolved in 5 mL DMF under argon. Triethylamine (139 μL, 1 mmol) was added and the mixture was heated at 60 °C for 2 h. Then the solvent was removed in vacuo. The residue was dissolved in chloroform (20 mL) and washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The products were purified by chromatography (silica, toluene).

*4.3.1. 6-((1-Phenyl)-ethyn-2-yl)-2,2′-dipivaloyloxy-1,1′-binaphthyl (**12**).* Yield: 268 mg (97%, starting from **4**), light orange solid. [Found: C, 82.11; H, 6.09, $C_{38}H_{34}O_4$ requires C, 82.28; H, 6.18%]; R_f (toluene) 0.58; ν_{max} (KBr) 1751, 1116 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 8.11 (d, *J* 1.4 Hz, 1H), 7.96 (d, *J* 8.9 Hz, 1H), 7.92 (d, *J* 9.1 Hz, 1H), 7.90 (d, *J* 8.9 Hz, 1H), 7.52–7.56 (m, 2H), 7.45 (ddd, *J* 1.4, 6.5, 8.1 Hz, 1H), 7.25–7.41 (m, 9H), 0.75 (s, 9H), 0.72 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.3, 176.2, 147.7, 147.0, 133.4, 132.9, 131.7, 131.5, 131.4, 131.1, 129.4, 129.3, 129.1, 128.4, 128.3, 128.0, 126.8, 126.3, 125.9, 125.7, 123.9, 123.3, 123.2, 122.8, 121.9, 120.5, 90.1, 89.6, 38.7, 26.4, 26.3; *m*/*z* (EI): 554 (3, M$^+$), 470 (20), 386 (61), 57 (100).

*4.3.2. 6-((1-Phenyl)-ethyn-2-yl)-2-ethoxy-2′-pivaloyloxy-1,1′-binaphthyl (**13**).* Yield: 239 mg (96%), light orange solid. [Found: C, 84.49; H, 6.12, $C_{35}H_{30}O_3$ requires C, 84.31; H, 6.06%]; R_f (toluene) 0.48; ν_{max} (KBr) 1748, 1114 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 8.06 (d, *J* 1.3 Hz, 1H), 7.99 (d, *J* 8.9 Hz, 1H), 7.95 (d, *J* 8.3 Hz, 1H), 7.92 (d, *J* 9.2 Hz, 1H), 7.54–7.58 (m, 2H), 7.25–7.49 (m, 9H), 7.12 (d, *J* 8.8 Hz, 1H), 4.06 (q, *J* 6.9 Hz, 2H), 1.10 (t, *J* 6.9 Hz, 3H), 0.78 (s, 9H); δ_C

(100.62 MHz, $CDCl_3$) 176.3, 155.1, 147.0, 133.7, 133.5, 131.6, 131.3, 129.7, 129.0, 129.0, 128.5, 128.4, 128.2, 128.1, 126.4, 126.3, 126.1, 125.6, 125.4, 124.9, 123.5, 122.0, 118.7, 118.2, 115.5, 90.0, 89.3, 65.0, 38.7, 26.5, 14.8; *m*/*z* (EI): 498 (100, M^+), 414 (96), 368 (30), 281 (63), 57 (39).

4.4. General procedure for the Stille coupling of 4, 6 and 7

In a typical reaction, a solution of the 6-halogeno-1,1′-binaphthyl derivative (**4**, **6** or **7**) (0.5 mmol), $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol) and vinyltributylstannane (161 μL, 0.55 mmol) was dissolved in 5 mL DMF under argon. The mixture was heated at 100 °C for 2–4 h, then the solvent was removed in vacuo. The residue was dissolved in toluene (20 mL), 10 mL of saturated aqueous solution of KF was added and the mixture was stirred overnight. The organic phase was dried over Na_2SO_4 and concentrated. The products were purified by chromatography (silica, toluene).

*4.4.1. 6-Vinyl-2,2′-dipivaloyloxy-1,1′-binaphthyl (**14**).* Yield: 180 mg (75%), light yellow solid. [Found: C, 79.78; H, 6.91, $C_{32}H_{32}O_4$ requires C, 79.97; H, 6.71%]; R_f (toluene) 0.51; ν_{max} (KBr) 1750, 1108 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 7.95 (d, *J* 8.9 Hz, 1H), 7.92 (d, *J* 8.9 Hz, 1H), 7.90 (d, *J* 8.2 Hz, 1H), 7.81 (d, *J* 1.4 Hz, 1H), 7.41–7.46 (m, 2H), 7.37 (d, *J* 8.9 Hz, 1H), 7.36 (d, *J* 8.9 Hz, 1H), 7.25–7.31 (m, 2H), 7.23 (d, *J* 8.6 Hz, 1H), 6.85 (dd, *J* 11.0, 17.0 Hz, 1H), 5.80 (dd, *J* 0.6, 17.0 Hz, 1H), 5.30 (dd, *J* 0.6, 11.0 Hz, 1H), 0.75 (s, 9H), 0.73 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.4, 176.3, 147.1, 147.0, 136.6, 134.7, 133.4, 133.1, 131.6, 131.5, 129.3, 129.2, 128.2, 127.9, 127.8, 126.7, 126.3, 126.2, 126.0, 125.6, 124.0, 122.3, 121.9, 114.4, 38.7, 26.4, 26.3; *m*/*z* (EI): 480 (9, M^+), 396 (33), 312 (86), 57 (100).

*4.4.2. 6-Vinyl-2-ethoxy-2′-pivaloyloxy-1,1′-binaphthyl (**15**).* Yield: 151 mg (71%), light yellow solid. [Found: C, 81.83; H, 6.72, $C_{29}H_{28}O_3$ requires C, 82.05; H, 6.65%]; R_f (toluene) 0.50; ν_{max} (KBr) 1750, 1114 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 7.95 (d, *J* 8.8 Hz, 1H), 7.91 (d, *J* 8.2 Hz, 1H), 7.88 (d, *J* 8.9 Hz, 1H), 7.71 (d, *J* 1.6 Hz, 1H), 7.33–7.45 (m, 2H), 7.38 (d, *J* 8.8 Hz, 1H), 7.34 (d, *J* 8.9 Hz, 1H), 7.25–7.27 (m, 2H), 7.06 (d, *J* 8.9 Hz, 1H), 6.81 (dd, *J* 18.2, 10.9 Hz, 1H), 5.74 (d, *J* 18.2 Hz, 1H), 5.23 (d, *J* 10.9 Hz, 1H), 4.01 (q, *J* 7.0 Hz, 2H), 1.06 (t, *J* 7.0 Hz, 3H), 0.73 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.4, 154.5, 146.9, 136.8, 133.7, 133.6, 132.8, 131.6, 129.8, 129.0, 128.8, 128.1, 126.4, 126.3, 126.2, 126.1, 125.7, 125.3, 123.8, 122.0, 118.7, 115.3, 113.3, 65.0, 38.6, 26.5, 14.9; *m*/*z* (EI): 424 (88, M^+), 340 (100), 312 (39), 294 (23), 57 (21).

4.5. General procedure for the Suzuki coupling of 4, 6 and 7

A solution of the 6-halogeno-1,1′-binaphthyl derivative (**4**, **6** or **7**) (0.5 mmol), $Pd(PPh_3)_4$ (28.9 mg, 0.025 mmol), phenylboronic acid (122 mg, 1.0 mmol) and K_2CO_3 (345 mg, 2.5 mmol) was dissolved in THF/H_2O=1/1 mixture (5 mL) under argon. The mixture was heated at 100 °C for 2 h, then the solvent was removed in vacuo. The residue was dissolved in chloroform (20 mL) and washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The products were purified by chromatography (silica, toluene).

*4.5.1. 6-Phenyl-2,2′-dipivaloyloxy-1,1′-binaphthyl (**16**).* Yield: 225 mg (85%), brownish yellow powder. [Found: C, 81.61; H, 6.37, $C_{36}H_{34}O_4$ requires C, 81.48; H, 6.46%]; R_f (toluene) 0.48; ν_{max} (KBr) 1750, 1117 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 8.10 (d, *J* 1.9 Hz, 1H), 8.01 (d, *J* 8.8 Hz, 1H), 7.97 (d, *J* 8.9 Hz, 1H), 7.91 (d, *J* 8.3 Hz, 1H), 7.67–7.71 (m, 2H), 7.57 (dd, *J* 1.9, 8.8 Hz, 1H), 7.42–7.48 (m, 3H), 7.40 (d, *J* 8.8 Hz, 1H), 7.39 (d, *J* 8.9 Hz, 1H), 7.31–7.37 (m, 4H), 0.75 (s, 9H), 0.73 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 176.3, 176.2, 147.0, 146.9, 140.6, 138.1, 133.4, 132.6, 131.7, 131.4, 129.4, 129.2, 128.8, 127.8, 127.4, 127.2, 126.7, 126.6, 126.2, 126.0, 125.6, 125.5, 123.6, 123.5, 122.3, 121.9, 38.6, 38.5, 26.4, 26.3; *m*/*z* (EI) 530 (10, M^+), 446 (31), 362 (87), 57 (100).

*4.5.2. 6-Phenyl-2-ethoxy-2′-pivaloyloxy-1,1′-binaphthyl (**17**).* Yield: 197 mg (83%), yellow powder. [Found: C, 83.66; H, 6.21, $C_{33}H_{30}O_3$ requires C, 83.52; H, 6.37%]; R_f (toluene) 0.42; ν_{max} (KBr) 1748, 1111 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 8.04 (d, *J* 1.9 Hz, 1H), 7.98 (d, *J* 9.0 Hz, 2H), 7.93 (d, *J* 8.3 Hz, 1H), 7.66–7.71 (m, 2H), 7.50 (dd, *J* 8.8 Hz, 1.9 Hz, 1H), 7.39–7.47 (m, 5H), 7.28–7.36 (m, 3H), 7.21 (d, *J* 8.8 Hz, 1H), 4.05 (q, *J* 7.0 Hz, 2H), 1.08 (t, *J* 7.0 Hz, 3H), 0.76 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 175.3, 153.4, 145.9, 140.0, 135.1, 132.7, 132.1, 130.6, 128.9, 128.2, 127.8, 127.7, 127.0, 126.1, 126.0, 125.2, 125.1, 125.0, 124.9, 124.4, 124.3, 124.2, 121.0, 117.5, 114.5, 64.0, 37.6, 25.5, 13.8; *m*/*z* (EI): 474 (98, M^+), 390 (100), 362 (35), 344 (32), 57 (30).

4.6. Stille coupling of 3 in the presence of the $Pd_2(dba)_3 \cdot CHCl_3/AsPh_3$ catalyst

A solution of 6-iodo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**3**) (248 mg, 0.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (12.9 mg, 0.0125 mmol), $AsPh_3$ (30 mg, 0.1 mmol) and vinyltributylstannane (161 μL, 0.55 mmol) was dissolved in 5 mL DMF under argon. The mixture was heated at 100 °C for 4 h, then the solvent was removed in vacuo. The residue was dissolved in toluene (20 mL), 10 mL of saturated aqueous solution of KF was added and the mixture was stirred overnight. The organic phase was dried over Na_2SO_4 and concentrated. The residue was purified by chromatography (silica, toluene) to give 101 mg of **18**/**18a**=95/5 mixture (51%).[24]

*4.6.1. 6-Vinyl-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**18**).* (Obtained as a 95/5 mixture of **18** and **18a**) as a light yellow solid. [Found: C, 81.62; H, 6.25, $C_{27}H_{24}O_3$ requires C, 81.79; H, 6.10%]; R_f (toluene) 0.11; ν_{max} (KBr) 3410, 1750, 1122 cm^{-1}; δ_H (400.13 MHz, $CDCl_3$) 8.07 (d, *J* 8.9 Hz, 1H), 7.97 (d, *J* 8.2 Hz, 1H), 7.85 (d, *J* 9.0 Hz, 1H), 7.75 (br s, 1H), 7.51 (ddd, *J* 1.3, 6.5, 8.2 Hz, 1H), 7.28–7.44 (m, 5H), 7.02 (d, *J* 8.8 Hz, 1H), 6.83 (dd, *J* 10.9, 17.6 Hz, 1H), 5.77 (d, *J* 17.6 Hz, 1H), 5.26 (d, 10.9 Hz, 1H), 4.85 (br s, 1H), 0.81 (s, 9H); δ_C (100.62 MHz, $CDCl_3$) 177.9, 152.0, 148.3, 136.8, 133.5, 133.4, 132.8, 132.2, 130.7, 130.4, 129.0, 128.3, 127.5, 126.4, 126.2, 125.6, 124.9, 124.1, 122.9, 121.8, 118.6, 114.4, 113.3, 38.8, 26.5; *m*/*z* (EI) 396 (30, M^+), 312 (95), 252 (14), 239 (16), 57 (100).

In another experiment, the mixture obtained by the Stille coupling of **3** was dissolved in toluene and washed with saturated KF. The organic phase was dried over Na_2SO_4 and concentrated. Et_3N (139 μL, 1 mmol) was added and the mixture was dissolved in MeCN (6 mL) under argon. The solution was cooled to 0 °C and pivaloyl chloride (93 μL, 0.75 mmol) was added. The solution was stirred for 1 h at 0 °C and then for 4 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in $CHCl_3$ (10 mL), washed with 5% HCl (2×10 mL), saturated $NaHCO_3$ (10 mL) and brine (10 mL) and then dried over Na_2SO_4. Removal of the solvent gave a single product identical with **14** according to GC–MS and ^1H NMR.

4.7. General procedure for the Heck reaction of 3 and 5

A solution of 6-iodo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**3**) or 6-bromo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**5**) (0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (13.1 mg, 0.05 mmol) and methyl acrylate (112 μL, 1.25 mmol) was dissolved in 5 mL DMF under argon. Triethylamine (139 μL, 1 mmol) was added and the mixture was heated at 100 °C. The mixture was analysed by GC and GC–MS.[25]

The GC analysis of the reaction mixture obtained by the Heck reaction of **3** showed complete conversion of the substrate after 6 h. Then the solvent was removed in vacuo. The residue was dissolved

in chloroform (20 mL) and washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The residue and Et_3N (139 μL 1 mmol) was dissolved in MeCN (6 mL) under argon. The solution was cooled to 0 °C and pivaloyl chloride (93 μL, 0.75 mmol) was added. The solution was stirred for 1 h at 0 °C and then for 4 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in $CHCl_3$ (10 mL), washed with 5% HCl (2×10 mL), saturated $NaHCO_3$ (10 mL) and brine (10 mL) and then dried over Na_2SO_4. Removal of the solvent gave a single product identical with **10** according to GC–MS and ^{1}H NMR.

4.8. Sonogashira coupling of 3

A solution of 6-iodo-2-hydroxy-2′-pivaloyloxy-1,1′-binaphthyl (**3**) (248 mg, 0.5 mmol), $PdCl_2(PPh_3)_2$ (17.5 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol) and phenylacetylene (137 μL, 1.25 mmol) was dissolved in 5 mL DMF under argon. Triethylamine (139 μL, 1 mmol) was added and the mixture was heated at 60 °C for 2 h. The mixture was analysed by GC and GC–MS.[26] Then the solvent was removed in vacuo. The residue was dissolved in chloroform (20 mL) and washed twice with 5% HCl (20 mL), saturated $NaHCO_3$ (20 mL), brine (20 mL), dried over Na_2SO_4 and concentrated. The residue and Et_3N (139 μL 1 mmol) was dissolved in MeCN (6 mL) under argon. The solution was cooled to 0 °C and pivaloyl chloride (93 μL, 0.75 mmol) was added. The solution was stirred for 1 h at 0 °C and then for 4 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in $CHCl_3$ (10 mL), washed with 5% HCl (2×10 mL), saturated $NaHCO_3$ (10 mL) and brine (10 mL) and then dried over Na_2SO_4. Removal of the solvent gave a single product identical with **12** according to GC–MS and ^{1}H NMR.

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References and notes

1. Brunel, J. M. *Chem. Rev.* **2005**, *105*, 857–897.
2. (a) Trindade, A. F.; Gois, P. M. P.; Afonso, C. A. M. *Chem. Rev.* **2009**, *109*, 418–514; (b) Framery, E.; Andrioletti, B.; Lemaire, M. *Tetrahedron: Asymmetry* **2010**, *21*, 1110–1124.
3. Hocke, H.; Uozumi, Y. *Tetrahedron* **2003**, *59*, 619–630.
4. Meng, Y.; Slaven, W. T., IV; Wang, D.; Liu, T. J.; Chow, H. F.; Li, C. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3693–3707.
5. (a) Hocke, H.; Uozumi, Y. *Tetrahedron* **2004**, *60*, 9297–9306; (b) Wu, L.; Zheng, L.; Zong, L.; Xu, J.; Cheng, Y. *Tetrahedron* **2008**, *64*, 2651–2657; (c) Yuan, X. Y.; Li, H. Y.; Hodge, P.; Kilner, M.; Tastard, C. Y.; Zhang, Z. P. *Tetrahedron: Asymmetry* **2006**, *17*, 2401–2407; (d) Hu, Q. S.; Vitharana, D.; Zheng, X. F.; Wu, C.; Kwan, C. M. S.; Pu, L. *J. Org. Chem.* **1996**, *61*, 8370–8377.
6. Shi, L.; Wang, X.; Sandoval, C. A.; Wang, Z.; Li, H.; Wu, J.; Yu, L.; Ding, K. *Chem.—Eur. J.* **2009**, *15*, 9855–9867.
7. (a) Ishitani, H.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2000**, *122*, 8180–8186; (b) Deussen, H. J.; Hendrickx, E.; Boutton, C.; Krog, D.; Clays, K.; Bechgaard, K.; Persoons, A.; Bjørnholm, T. *J. Am. Chem. Soc.* **1996**, *118*, 6841–6852.
8. (a) Balaraman, E.; Swamy, K. C. K. *Tetrahedron: Asymmetry* **2007**, *18*, 2037–2048; (b) Yamashita, Y.; Ishitani, H.; Shimizu, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2002**, *124*, 3292–3302.
9. Zhang, S.; Liu, Y.; Huang, H.; Zheng, L.; Wu, L.; Cheng, Y. *Synlett* **2008**, 853–856.
10. Jayaprakash, D.; Sasai, H. *Tetrahedron: Asymmetry* **2001**, *12*, 2589–2595.
11. Regnouf de Vains, J. B. *Tetrahedron Lett.* **2001**, *42*, 6507–6509.
12. Cai, D.; Larsen, R. D.; Reider, P. J. *Tetrahedron Lett.* **2002**, *43*, 4055–4057.
13. Ma, L.; White, P. S.; Lin, W. *J. Org. Chem.* **2002**, *67*, 7577–7586.
14. Fehér, C.; Urbán, B.; Ürge, L.; Darvas, F.; Bakos, J.; Skoda-Földes, R. *Tetrahedron Lett.* **2010**, *51*, 3629–3632.
15. Duque Estrada, G. O.; de Douza, A. L. F.; Mendes da Silva, J. F.; Antunes, O. A. C. *Catal. Commun.* **2008**, *9*, 1734–1738.
16. MS of **9** (*m*/*z* (rel int. %)): 595 (10) (M^+), 511 (25), 427 (55), 285 (10), 57 (100).
17. Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73–78.
18. Chiusoli, G. P.; Catellani, M.; Costa, M.; Motti, E.; Della Ca', N.; Maestri, G. *Coord. Chem. Rev.* **2010**, *254*, 456–469.
19. (a) Karig, G.; Moon, M. T.; Thasana, N.; Gallagher, T. *Org. Lett.* **2002**, *4*, 3115–3118; (b) Campo, M. A.; Zhang, H.; Yao, T.; Ibdah, A.; McCulla, R. D.; Huang, Q.; Zhao, J.; Jenks, W. S.; Larock, R. C. *J. Am. Chem. Soc.* **2007**, *129*, 6298–6307.
20. Kesharwani, T.; Larock, R. C. *Tetrahedron* **2008**, *64*, 6090–6102.
21. Zhao, J.; Larock, R. C. *Org. Lett.* **2005**, *7*, 701–704.
22. Mota, A. J.; Dedieu, A. *Organometallics* **2006**, *25*, 3130–3142.
23. Bérces, A.; Whitfield, D. M.; Nukada, T.; Do Santos, I.; Obuchowska, A.; Krepinsky, J. J. *Can. J. Chem.* **2004**, *82*, 1157–1171.
24. MS of **18a** (*m*/*z* (rel int. %)): 396 (22) (M^+), 312 (90), 252 (15), 239 (17), 57 (100).
25. MS of **19** (*m*/*z* (rel int. %)): 454 (4) (M^+), 370 (15), 286 (32), 57 (100). MS of **19a** (*m*/*z* (rel int. %)): 454 (7) (M^+), 370 (18), 286 (30), 57 (100).
26. MS of **20** (*m*/*z* (rel int. %)): 470 (50) (M^+), 386 (100), 281 (23), 57 (25). MS of **20a** (*m*/*z* (rel int. %)): 470 (55) (M^+), 386 (100), 281 (26), 57 (35).