DOI: 10.1002/ejoc.200701216

Palladium-Catalysed Cross-Coupling Reactions of Triorganoindium Reagents with Alkenyl Halides

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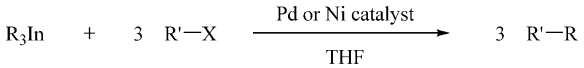
Keywords: Indium / Cross-coupling / Palladium / Homogeneous catalysis / Haloalkenes / Stereoselective reactions

The regio- and stereoselectivity of the palladium-catalysed cross-coupling reactions of indium organometallics with stereodefined 1-haloalkenes and 1,1-dihaloalkenes have been studied. Triorganoindium reagents (R_3In; R = alkyl, alkenyl, aryl and alkynyl) can be stereospecifically coupled with stereodefined alkenyl iodides in good yields and short reaction times under palladium catalysis. Additionally, the palladium-catalysed cross-coupling reaction of R_3In (90 mol-%) with 1,1-dibromo-1-alkenes gave dicoupling products in high yields. When the reaction was performed with 40 mol-% of aryl-, vinyl- and alkynylindium derivatives, *trans*-selective monosubstitution products were obtained in moderate to good yields. These selective couplings were performed with $[Pd_2dba_3]/P(2\text{-furyl})_3$ (1:1, 2 mol-%) at 0 °C or, for 1,1-dibromo-1-alkenes with an aromatic group in the β-position, $[Pd(DPEPhos)Cl_2]$ (2 mol-%) at room temperature as the catalytic system. The resulting (*Z*)-monobromoalkenes can be further functionalized by cross-coupling reaction with various R_3In (R = alkyl, aryl and alkynyl) in the presence of $[Pd(tBu_3P)_2]$ as catalyst, at room temperature, to provide trisubstituted olefins in good yields.

Introduction

During the last few years, indium organometallics have been shown to be useful reagents in metal-catalysed cross-coupling reactions.[1,2] In this reaction, triorganoindium reagents can be efficiently coupled with organic halides and triflates under palladium or nickel catalysis (Scheme 1). The main features of indium reagents in these cross-coupling reactions are their high efficiency, versatility and chemoselectivity, all three organic groups attached to the metal atom can be efficiently transferred to the electrophile, and a wide variety of carbon groups (sp^3, sp^2, sp) can be transferred from the metal atom. Additionally, the reaction can also be performed under aqueous conditions[3] and, more recently, the first asymmetric cross-coupling reaction using organoindium reagents has been reported.[4]



R = alkyl, vinyl, aryl, alkynyl
R' = aryl, vinyl, benzyl, acyl
X = Cl, Br, I, OTf

Scheme 1. Palladium- or nickel-catalysed cross-coupling of indium organometallics with organic electrophiles.

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Metal-catalysed cross-coupling reactions using alkenyl halides provide a unique methodology for the regio- and stereoselective synthesis of substituted alkenes, a structural functionality of great importance in organic chemistry. This reaction can be performed with different transition-metal complexes as catalysts, (phosphane)palladium complexes being the most useful in terms of chemical yields and stereoselectivity. As nucleophilic partners, the main organometallic reagents have been studied,[5] but the utility of indium organometallics remains unexplored. In this article we report our findings on the regio- and stereoselectivity of the palladium-catalysed cross-coupling reactions of triorganoindium reagents with stereodefined 1-haloalkenes and 1,1-dihaloalkenes.

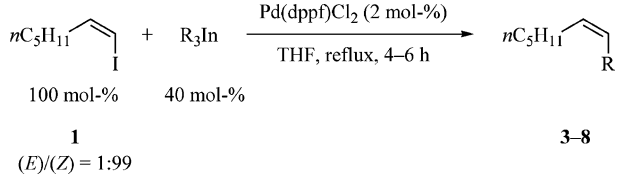
Results and Discussion

Stereoselectivity in Palladium-Catalysed Cross-Coupling Reactions of R_3In with 1-Iodoalkenes

Our research started by studying the reactivity and stereoselectivity of triorganoindium reagents with stereodefined 1-iodoalkenes. For this purpose we prepared both stereoisomers of 1-iodohept-1-ene. The (*Z*) isomer **1** was prepared from hept-1-yne with high stereoselectivity [(*E*)/(*Z*) = 1:99],[6] and (*E*)-1-iodohept-1-ene [**2**, (*E*)/(*Z*) = 92:8] was prepared from hexanal.[7] In our initial experiments we found that the reaction of (*Z*)-1-iodohept-1-ene (**1**) with triphenylindium (40 mol-%) in the presence of a catalytic amount of several palladium complexes afforded, after

heating at reflux (4–6 h) in THF, the coupling product **3** in good yields (72–82%) with retention of the alkene configuration. The best result was obtained by using 2 mol-% of [Pd(dppf)Cl_2] (82% yield, (*E*)/(*Z*) = 4:96; Table 1, Entry 1).

Table 1. Palladium-catalysed cross-coupling of indium organometallics with (*Z*)-1-iodohept-1-ene (**1**).



Entry	R	Product	Yield [%][a]	(*E*)/(*Z*)[b]
1	Ph	**3**	82	4:96
2	Me	**4**	80	1:99
3	*n*Bu	**5**	90	1:99
4	CH_2=CH	**6**	75	1:99
5	PhC≡C	**7**	72	1:99
6	Me_3SiC≡C	**8**	99	5:95

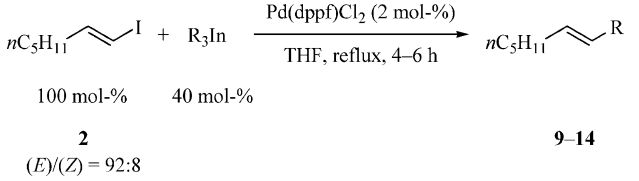
[a] Isolated yield. [b] Determined by GC.

The palladium cross-coupling reaction of (*Z*)-1-iodohept-1-ene (**1**) with trialkylindium reagents, such as trimethyl- and tri-*n*-butylindium, also took place with retention of stereochemistry, affording the coupling products **4** and **5** in good yields (80–90%) and with excellent stereoselectivities [(*E*)/(*Z*) = 1:99; Table 1, Entries 2 and 3). Interestingly, the reaction of **1** with trivinylindium afforded diene **6** in good yield and stereoselectivity [75%, (*E*)/(*Z*) = 1:99; Table 1, Entry 4]. The reaction with the alkynylindium reagents derived from phenylacetylene and (trimethylsilyl)-acetylene also proceeded with high efficiency [72–99% yield, (*E*)/(*Z*) up to 1:99; Table 1, Entries 5 and 6). Overall, these results show organoindium reagents to be useful reagents in the synthesis of stereodefined dienes and enynes. Additionally, the isolated yields obtained by using only 40 mol-% of R_3In imply that more than one group of the triorganoindium reagents is transferred to the electrophile during the cross-coupling reaction.

The reactivity of (*E*)-1-iodohept-1-ene (**2**) with the previous triorganoindium reagents was also studied; the results are summarized in Table 2. As previously, we observed that aryl- (phenyl-), alkyl-, vinyl- and alkynylindium organometallics reacted with **2** in good yield (78–90%) with retention of configuration [(*E*)/(*Z*) ratio from 91:9 to 97:3]. Interestingly, in these reactions the (*E*)/(*Z*) ratio of the coupling product was slightly higher than that of the initial iodoalkene (97:3 vs. 92:8; Table 2, Entries 1, 5 and 6), a result that can be attributed to the higher reactivity of the (*E*) isomer of the initial iodoalkene or to isomerization during the cross-coupling reaction.

These results demonstrate that triorganoindium reagents can be coupled under palladium catalysis with alkenyl iodides in good yields and high stereoselectivity with retention of the stereochemistry of the alkenyl iodide. Additionally, the versatility of indium organometallics and their efficiency (only 40 mol-%) is also evidenced by using aryl-, alkyl-, vinyl- and alkynylindium derivatives.

Table 2. Palladium-catalysed cross-coupling of indium organometallics with (*E*)-1-iodohept-1-ene (**2**).



Entry	R	Product	Yield [%][a]	(*E*)/(*Z*)[b]
1	Ph	**9**	78	97:3
2	Me	**10**	87	91:9
3	*n*Bu	**11**	80	91:9
4	CH_2=CH	**12**	90	91:9
5	PhC≡C	**13**	81	97:3
6	Me_3SiC≡C	**14**	86	97:3

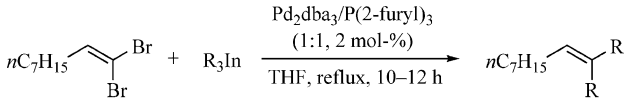
[a] Isolated yield. [b] Determined by GC.

Palladium-Catalysed Cross-Coupling Reactions of R_3In with 1,1-Dibromo-1-alkenes

The 1,1-dihalo-1-alkene functionality is an attractive bidentate electrophile for palladium-catalysed cross-coupling reactions. In these substrates, the two halogen atoms linked to one alkenyl carbon atom increases its reactivity towards palladium(0) complexes. These easily prepared compounds[8] have already been used for the stereoselective synthesis of (*Z*)-haloalkenes by *trans*-selective coupling, and for the synthesis of trisubstituted alkenes by double or stepwise cross-coupling reactions.

In our research, we first explored the double palladium-catalysed cross-coupling reactions of triorganoindium reagents with 1,1-dibromonon-1-ene (**15**; Table 3). Under the reaction conditions previously developed, we found that the reaction of 90 mol-% of Ph_3In with dibromide **15** (2 mol-% of [Pd(dppf)Cl_2], reflux, 4 h) gave the doubly cross-coupled product **16** in low yield (40%) accompanied by 18% of the monocoupling product. After some screening we found that the yield can be improved by using [Pd_2dba_3] and P(2-furyl)$_3$ (1:1, 2 mol-%) as the catalytic system (72%; Table 3, Entry 1). Under these conditions, the reaction of alkyl- (methyl- and *n*-butyl-) and alkynyl- [phenylethynyl-, (trimethylsilyl)ethynyl-]indium organometallics with dibromide **15** afforded the corresponding doubly cross-coupled products, dimethyl- and di-*n*-butylalkenes **17** and **18** and enediynes **19** and **20** in good yields (73–90%; Table 3, Entries 2–5). Cross-conjugated enediynes are an interesting class of compounds which have recently received considerable attention given their applications in materials science.[9] They can be prepared from 1,1-dihalo-1-alkenes by cross-coupling reactions with alkynes under Sonogashira conditions[10] and with alkynyl trifluoroborates,[11] affording in some cases low yields and a mixture of reaction products. In comparison, the low loading of catalyst necessary with R_3In is also remarkable.

Table 3. Palladium-catalysed double cross-coupling of indium organometallics with **15**.



100 mol-% 90 mol-%

15 **16–20**

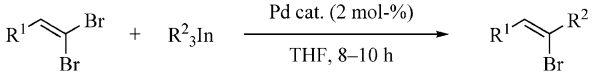
Entry	R	Product	Yield [%][a]
1	Ph	**16**	72
2	Me	**17**	79
3	*n*Bu	**18**	84
4	PhC≡C	**19**	73
5	$Me_3SiC{\equiv}C$	**20**	90

[a] Isolated yield.

trans-Selective monosubstitution and stepwise cross-coupling reactions between 1,1-dihalo-1-alkenes and indium organometallics have also been studied. The Pd-catalysed cross-coupling of 1,1-dihalo-1-alkenes is largely *trans*-selective, attributed to steric effects exerted by carbon substituents which favour oxidative addition to the palladium atom *trans* to carbon substituents in the β-position. Unfortunately, disubstitution is sometimes an undesirable side-reaction. This has been explained by the persistence of the usually transitory (olefin)palladium(0) complex generated in the reductive elimination step which favours subsequent oxidative insertion into the carbon–halogen bond.[12]

In this reaction, several organometallics, such as Grignard[13] and zinc[12,14] reagents, organotin[15] and boron derivatives,[16] and terminal alkynes,[17] had already been used as nucleophilic counterparts. The reactivity is a function of the nucleophile, the nature of the halide and the alkene substituent at the β-position. In β-alkyl-substituted 1,1-dibromoalkenes, *trans*-selective monosubstitution can be satisfactorily performed by using different nucleophiles; but when an aryl group is placed at the β-position, the disubstitution reaction becomes an important side-reaction. In our case, we observed that the reaction of triphenylindium (40 mol-%) with 1,1-dibromonon-1-ene (**15**; Table 4) using $[Pd(Ph_3P)_2Cl_2]$, $[Pd(Ph_3P)_4]$ or $[Pd(dppf)Cl_2]$ as the catalyst resulted in the formation of the dicoupling product as the major one. Careful examination of different palladium complexes and reaction conditions led to the discovery that the best results for the monocoupling reaction with R_3In were obtained with $[Pd_2dba_3]$ and P(2-furyl)$_3$ (1:1, 2 mol-%) as the catalyst system at 0 °C for 8–10 h. Under these conditions, the reaction of Ph_3In with **15** afforded the monocoupling product **22** in 55% yield accompanied by 18% of the dicoupling product (Table 4, Entry 1). The reaction of trialkynylindium reagents, such as tris[(trimethylsilyl)ethynyl]- and tris(phenylethynyl)indium, with **15** improved the yields, affording the bromoenynes **23** and **24** in 76 and 70% yields, respectively (Table 4, Entries 2 and 3). Unfortunately, when the same reaction conditions were applied to trialkyl- or trivinylindium reagents, the dicoupling compounds were obtained as the major products.[18]

Table 4. Palladium-catalysed *trans*-selective cross-coupling of indium organometallics with 1,1-dibromo-1-alkenes.



100 mol-% 40 mol-%

15: $R^1 = nC_7H_{15}$
21: R^1 = Ph

22–28

Entry	1,1-Dibromoalkene	R^2	Product	Yield [%][a]
1	**15**	Ph	**22**	55[b]
2	**15**	$Me_3SiC{\equiv}C$	**23**	76[b]
3	**15**	PhC≡C	**24**	70[b]
4	**21**	Ph	**25**	57[c]
5	**21**	CH_2=CH	**26**	69[c]
6	**21**	$Me_3SiC{\equiv}C$	**27**	62[c]
7	**21**	PhC≡C	**28**	77[c]

[a] Isolated yield. [b] Reaction performed with $[Pd_2dba_3]$/P(2-furyl)$_3$ (1:1, 2 mol-%) as the catalyst system at 0 °C. [c] Reaction performed with $[Pd(DPEphos)Cl_2]$ (2 mol-%) as the catalyst system at room temperature.

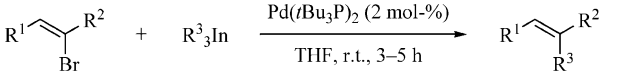
The *trans*-selective cross-coupling reaction was also tested by using β,β-dibromostyrene (**21**) as the electrophile. In this case the reactions of different triorganoindium compounds using the previous catalytic system ($[Pd_2dba_3]$/P(2-furyl)$_3$, 1:1, 2 mol-%, 0 °C) afforded the dicoupling products as the major compounds in the reaction mixture. In a new search, we obtained the best results by using $[Pd(DPEphos)Cl_2]$ (2 mol-%)[19] at room temperature for 8–10 h. Under these conditions, phenyl-, vinyl- and alkynylindium organometallics reacted with **21** to afford the monosubstituted products **25**–**28** in moderate to good yields (57–77%, Table 4, Entries 4–7). Remarkably, the reaction of **21** with trivinylindium afforded the bromodiene **26** in a good yield of 69%. As for **15**, these reaction conditions were unsuccessful with trialkylindium compounds (methyl, *n*-butyl), giving a mixture of mono- and dicoupling products alongside some unreacted dibromide.

Internal monobromides **22**–**28**, prepared by *trans*-selective monosubstitution of 1,1-dibromo-1-alkenes, are suitable substrates for a new palladium-catalysed cross-coupling reaction. Nevertheless, this reaction has been useful only when the second coupling reaction is performed with alkyl nucleophiles[12a,14,16b] or when alkenyl chlorides are employed as electrophiles.[12b,13]

The cross-coupling reaction of organoindium reagents using the previously developed catalytic systems ($[Pd_2dba_3]$/P(2-furyl)$_3$, $[Pd(DPEphos)Cl_2]$, 0 °C to room temp.) afforded low yields of the coupling products and, in some cases, (*E*)/(*Z*) isomerization of the double bond was observed.[20] Negishi et al. also observed isomerization in the palladium-catalysed cross-coupling of 3-bromo-3-alken-1-ynes (such as **23**, **24**, **27** and **28**) with organozinc reagents.[12a] In these reactions, they observed that the isomerization was influenced by the ligands in the palladium catalyst and that the best results were obtained when $[Pd(tBu_3P)_2]$ was used as the catalyst.

In our case, we also found that organoindium reagents can be coupled with internal monobromides in the presence of $[Pd(tBu_3P)_2]$[21] at room temperature for 3–5 h without detectable isomerization. For instance, bromide **22** reacted with tris[(trimethylsilyl)ethynyl]indium to afford enyne **29** in 50% yield (Table 5, Entry 1). The bromoenynes **23**, **24** and **27** also can be coupled with alkyl-, aryl- and alkynylindium organometallics in the presence of $[Pd(tBu_3P)_2]$ as catalyst to afford cross-coupled products efficiently (62–99%; Table 5, Entries 2–7) and without detectable (*E*)/(*Z*) isomerization of the double bond.[22] These results show that a variety of indium reagents (alkyl, aryl and alkynyl) can be used in the second step of the stepwise coupling sequence with 1,1-dibromo-1-alkenes, demonstrating the efficiency of these organometallics in cross-coupling reactions.

Table 5. Palladium-catalysed cross-coupling of indium organometallics with (*Z*)-bromoalkenes.



100 mol-% 60 mol-%

29–35

Entry	Alkenyl bromide	R^1	R^2	R^3	Product	Yield [%][a]
1	**22**	nC_7H_{15}	Ph	$Me_3SiC{\equiv}C$	**29**	50
2	**23**	nC_7H_{15}	$Me_3SiC{\equiv}C$	Me	**30**	70
3	**24**	nC_7H_{15}	$PhC{\equiv}C$	Ph	**31**	62
4	**24**	nC_7H_{15}	$PhC{\equiv}C$	$Me_3SiC{\equiv}C$	**32**	80
5	**27**	Ph	$Me_3SiC{\equiv}C$	Ph	**33**	99
6	**27**	Ph	$Me_3SiC{\equiv}C$	*n*Bu	**34**	69
7	**27**	Ph	$Me_3SiC{\equiv}C$	$PhC{\equiv}C$	**35**	87

[a] Isolated yield.

Conclusions

We have shown that the palladium-catalysed cross-coupling reaction of indium(III) organometallics with stereodefined alkenyl iodides proceeds stereospecifically in good yields and short reaction times for alkyl-, alkenyl-, aryl- and alkynylindium reagents. Additionally, the palladium-catalysed cross-coupling reaction of triorganoindium compounds (90 mol-%) with 1,1-dibromo-1-alkenes afforded the dicoupling products in high yields. The reaction of 40 mol-% of aryl-, vinyl- and alkynylindium reagents with 1,1-dibromo-1-alkenes in the presence of a palladium catalyst afforded the *trans*-selective monosubstitution products in moderate to good yields. The resulting (*Z*)-monobromoalkenes can be further coupled with other indium organometallics in the presence of a palladium catalyst. In this reaction, the use of $[Pd(tBu_3P)_2]$ as the catalyst at room temperature provided the coupling product in good yields and without isomerization of the double bond.

In all of these reactions, the indium organometallics showed a high atom economy as they transfer to the electrophile all of the carbon groups attached to the metal atom. The procedure developed in this study should be useful for the synthesis of stereodefined and trisubstituted alkenes. These results, although comparable to those obtained using other organometallics in cross-coupling reactions, confirm triorganoindium reagents as a useful alternative.

Experimental Section

General Methods: All reactions were conducted in flame-dried glassware under a positive pressure of argon. Reaction temperatures refer to external bath temperatures. Tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone. (*Z*)-1-Iodohept-1-ene [**1**; (*E*)/(*Z*) = 1:99] was prepared from hept-1-yne by iodination (*n*BuLi, I_2) and then hydroboration reduction (9-BBN-H, HOAc).[6,23] (*E*)-1-Iodohept-1-ene [**2**; (*E*)/(*Z*) = 92:8] was prepared from hexanal according to the Takai procedure.[7,24] 1,1-Dibromo-1-alkenes were prepared from their corresponding aldehydes according to the method of Corey and Fuchs.[8b,25] $[Pd(Ph_3P)_4]$[26] and $[Pd(DPEphos)Cl_2]$[19] were prepared according to literature procedures. All other commercially available reagents were used as received. Liquid reagents or reagent solutions were added by syringe or cannula. Organic extracts were dried with anhydrous Na_2SO_4, filtered and concentrated using a rotary evaporator at aspirator pressure (20–30 Torr). Thin-layer chromatography was carried out on silica gel 60 F_{254} (layer thickness 0.2 mm), and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid or *p*-anisaldehyde reagent followed by heating. Flash chromatography was performed on silica gel 60 (230–400 mesh). NMR spectra were recorded with a Bruker Avance 300 spectrometer in $CDCl_3$ using the residual solvent signal at δ = 7.26 (^{1}H) or 77.0 (^{13}C) ppm as the internal standard. DEPT was used to assign carbon types. Low-resolution electron-impact mass spectra were recorded with a Thermo Finnigan Trace MS spectrometer at 70 eV. High-resolution mass spectra were measured with a Thermo Finnigan MAT 95XP spectrometer. Gas chromatography analyses were performed with an HP 6890 gas chromatograph using an HP-1 capillary column (30 m × 0.32 mm × 0.25 μm) with N_2 as carrier gas (2 mL/min) and equipped with an FID detector (300 °C). The temperature indicated in GC analyses refers to the oven temperature.

Triorganoindium Reagents: Triorganoindium compounds were prepared according to previously published methods[1c] by treatment of the corresponding organolithium or Grignard reagent (3 equiv.) with $InCl_3$ (1.1 equiv.) in dry THF at –78 °C and warming to room temperature. In this procedure triphenyl-, trimethyl-, tributyl-, tris[(trimethylsilyl)ethynyl]- and tris(phenylethynyl)indium were prepared from the corresponding organolithium reagents, and trivinylindium was prepared from vinylmagnesium bromide. Commercially available organolithium and Grignard solutions were used as received. (Trimethylsilyl)ethynyl- and (phenylethynyl)lithium were prepared prior to use by metallation of (trimethylsilyl)acetylene and phenylacetylene, respectively, with *n*BuLi in dry THF at –78 °C and warming to room temperature.

General Procedure. Palladium-Catalysed Cross-Coupling Reaction of Alkenyl Halides with Triorganoindium Reagents: A solution of R_3In (0.4 mmol, ca. 0.1 M in THF) was slowly added to a solution of the alkenyl halide (1 mmol) and the palladium catalyst ($[Pd(dppf)Cl_2]$, 0.02 mmol, unless otherwise stated) in dry THF (4 mL). The resulting mixture was heated at reflux under argon until the starting material had been consumed (4–6 h, TLC test), and the reaction was then quenched by the addition of a few drops of MeOH. The mixture was concentrated under reduced pressure, and Et_2O was added (15 mL). The organic phase was washed with

aqueous HCl (5%, 15 mL), saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexanes) to afford the cross-coupling products.

Procedure A. Double Palladium-Catalysed Cross-Coupling Reaction of 1,1-Dibromo-1-alkene 15 with Triorganoindium Reagents: The general procedure was applied using 90 mol-% of R_3In, [Pd_2dba_3/P(2-furyl)$_3$ (1:1, 2 mol-%) as the catalytic system and by heating the reaction mixture at reflux for 10–12 h.

Procedure B. *trans*-Selective Palladium-Catalysed Cross-Coupling Reaction of 1,1-Dibromo-1-alkenes with Triorganoindium Reagents: According to the general procedure, [Pd_2dba_3]/P(2-furyl)$_3$ (1:1, 2 mol-%) was used as the catalytic system for coupling reactions at room temp. and [Pd(DPEphos)Cl_2] (2 mol-%) for reactions at 0 °C. The reactions were carried out over 8–10 h.

Procedure C. Palladium-Catalysed Cross-Coupling Reaction of (*Z*)-Alkenyl Bromides 22–24 and 27 with Triorganoindium Reagents: The general procedure was applied using 60 mol-% of R_3In, [Pd-(tBu$_3$P)$_2$] (2 mol-%) as the catalyst and by performing the reactions at room temp. for 3–5 h.

[(*Z*)-Hept-1-enyl]benzene (3):[27] According to the general procedure, the reaction of **1** (220 mg, 0.982 mmol) with triphenylindium (0.39 mmol) afforded **3** [140 mg, 82%, (*E*)/(*Z*) = 4:96]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.80–0.92 (m, 3 H), 1.23–1.44 (m, 6 H), 2.33 (dq, J = 8.3, 1.4 Hz, 2 H), 5.68 (dt, J = 11.7, 7.3 Hz, 1 H), 6.41 (d, J = 11.7 Hz, 1 H), 7.17–7.37 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.6 (CH_2), 29.1 (CH_2), 31.6 (CH_2), 33.0 (CH_2), 125.9 (2× CH), 126.7 (CH), 128.1 (CH), 128.5 (2× CH), 128.7 (CH), 138.0 (C) ppm. MS (EI): *m*/*z* (%) = 174 (4) $[M]^+$, 117 (100) $[M - C_4H_9]^+$. GC [180 °C (2 min) up to 250 °C at 10 °C/min]: t_R = 4.0 min.

(*Z*)-Oct-2-ene (4):[28] According to the general procedure, the reaction of **1** (243 mg, 1.084 mmol) with trimethylindium (0.43 mmol) afforded **4** [97 mg, 80%, (*E*)/(*Z*) = 1:99]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.80–0.87 (m, 3 H), 1.30–1.43 (m, 6 H), 1.6 (d, J = 5.3 Hz, 3 H), 2.05–2.12 (m, 2 H), 5.41–5.46 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 19.2 (CH_3), 22.9 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 33.4 (CH_2), 123.5 (CH), 132.0 (CH) ppm. GC (200 °C): t_R = 5.2 min.

(*Z*)-Undec-5-ene (5):[29] According to the general procedure, the reaction of **1** (238 mg, 1.062 mmol) with tri-*n*-butylindium (0.42 mmol) afforded **5** [147 mg, 90%, (*E*)/(*Z*) = 1:99]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.80–0.99 (m, 6 H), 1.30 (m, 10 H), 2.01–2.05 (m, 4 H), 5.36 (t, J = 9.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.0 (2× CH_3), 22.6 (2× CH_2), 26.8 (CH_2), 29.4 (CH_2), 31.5 (2× CH_2), 129.8 (2× CH) ppm. GC (180 °C): t_R = 4.7 min.

(*Z*)-Nona-1,3-diene (6):[30] According to the general procedure, the reaction of **1** (215 mg, 0.959 mmol) with trivinylindium (0.38 mmol) afforded **6** [89 mg, 75%, (*E*)/(*Z*) = 1:99]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, J = 6.9 Hz, 3 H), 1.27–1.45 (m, 6 H), 2.09 (dd, J = 7.7, 6.9 Hz, 2 H), 5.09 (d, J = 10.0 Hz, 1 H), 5.19 (dd, J = 16.9, 2.0 Hz, 1 H), 5.43–5.52 (m, 1 H), 6.00 (t, J = 10.9 Hz, 1 H), 6.59–6.72 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.0 (CH_3), 22.5 (CH_2), 27.7 (CH_2), 29.3 (CH_2), 31.4 (CH_2), 116.6 (CH_2), 129.1 (CH), 132.4 (CH), 133.1 (CH) ppm. GC (80 °C): t_R = 9.1 min.

[(*Z*)-Non-3-en-1-ynyl]benzene (7):[31] According to the general procedure, the reaction of **1** (240 mg, 1.071 mmol) with tris(phenylethynyl)indium (0.43 mmol) afforded **7** [153 mg, 72%, (*E*)/(*Z*) = 1:99]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.94 (t, J = 11.2 Hz, 3 H), 1.23–1.52 (m, 6 H), 2.40 (dq, J = 7.3, 1.0 Hz, 2 H), 5.68 (dd, J = 9.3, 1.4 Hz, 1 H), 5.99 (dt, J = 10.0, 3.9 Hz, 1 H), 7.32–7.37 (m, 3 H), 7.42–7.56 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.5 (CH_2), 28.6 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 87.5 (C), 93.0 (C), 109.1 (CH), 123.8 (C), 128.3 (2× CH), 131.4 (2× CH), 144.5 (CH) ppm. MS (EI): *m*/*z* (%) = 202 (5) $[M - H]^+$, 132 (22) $[M - C_5H_5]^+$, 102 (100). GC [120 °C (2 min) up to 200 °C at 10 °C/min]: t_R = 4.4 min.

Trimethyl[(*Z*)-non-3-en-1-ynyl]silane (8):[32] According to the general procedure, the reaction of **1** (261 mg, 1.165 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.47 mmol) afforded **8** [224 mg, 99%, (*E*)/(*Z*) = 5:95]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.20 (s, 9 H), 0.84–0.90 (m, 3 H), 1.25–1.33 (m, 6 H), 2.32 (q, J = 6.8 Hz, 2 H), 5.50 (d, J = 11.2 Hz, 1 H), 5.96 (dt, J = 7.3, 3.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.1 (3× CH_3), 13.9 (CH_3), 22.3 (CH_2), 28.3 (CH_2), 30.1 (CH_2), 31.2 (CH_2), 102.1 (2× C), 109.0 (CH), 145.6 (CH) ppm. MS (EI): *m*/*z* (%) = 194 (6) $[M]^+$, 179 (82) $[M - CH_3]^+$, 73 (100). GC (200 °C): t_R = 4.7 min.

[(*E*)-Hept-1-enyl]benzene (9):[27] According to the general procedure, the reaction of **2** (230 mg, 1.026 mmol) with triphenylindium (0.41 mmol) afforded **9** [139 mg, 78%, (*E*)/(*Z*) = 97:3]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.83–0.92 (m, 3 H), 1.24–1.36 (m, 6 H), 2.23 (q, J = 6.8 Hz, 2 H), 6.27 (dt, J = 16.1, 6.3 Hz, 1 H), 6.41 (d, J = 16.1 Hz, 1 H), 7.17–7.39 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.2 (CH_3), 22.7 (CH_2), 29.2 (CH_2), 31.6 (CH_2), 33.1 (CH_2), 126.0 (2× CH), 126.8 (CH), 128.6 (2× CH), 129.8 (CH), 131.4 (CH), 138.1 (C) ppm. MS (EI): *m*/*z* (%) = 174 (4) $[M]^+$, 117 (100) $[M - C_4H_9]^+$. GC [180 °C (2 min) up to 250 °C at 10 °C/min]: t_R = 4.2 min.

(*E*)-Oct-2-ene (10):[33] According to the general procedure, the reaction of **2** (224 mg, 1.000 mmol) with trimethylindium (0.40 mmol) afforded **10** [98 mg, 87%, (*E*)/(*Z*) = 91:9]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.20 (s, 9 H), 0.89 (t, J = 6.8 Hz, 3 H), 1.24–1.44 (m, 6 H), 2.10 (q, J = 7.1 Hz, 2 H), 5.47–5.52 (m, 1 H), 6.22–6.27 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 19.2 (CH_3), 22.9 (CH_2), 29.7 (CH_2), 32.0 (CH_2), 33.4 (CH_2), 125.2 (CH), 132.2 (CH) ppm. GC (200 °C): t_R = 5.3 min.

(*E*)-Undec-5-ene (11):[29] According to the general procedure, the reaction of **2** (232 mg, 1.035 mmol) with tri-*n*-butylindium (0.41 mmol) afforded **11** [128 mg, 80%, (*E*)/(*Z*) = 91:9]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.80–0.96 (m, 6 H), 1.21–1.44 (m, 10 H), 2.07–2.14 (m, 4 H), 5.38–5.49 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.2 (2× CH_3), 22.3 (CH_2), 22.6 (2× CH_2), 29.8 (CH_2), 32.4 (CH_2), 32.7 (2× CH_2), 130.4 (2× CH) ppm. GC (180 °C): t_R = 4.9 min.

(*E*)-Nona-1,3-diene (12):[30] According to the general procedure, the reaction of **2** (210 mg, 0.937 mmol) with trivinylindium (0.37 mmol) afforded **12** [105 mg, 90%, (*E*)/(*Z*) = 91:9]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, J = 6.9 Hz, 3 H), 1.29–1.46 (m, 6 H), 2.09 (dd, J = 14.4, 7.3 Hz, 2 H), 4.96 (d, J = 10.1 Hz, 1 H), 5.09 (dd, J = 10.1, 1.3 Hz, 1 H), 5.65–5.79 (m, 1 H), 6.05 (dd, J = 15.5, 10.2 Hz, 1 H), 6.32 (dt, J = 16.9, 10.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.0 (CH_3), 22.5 (CH_2), 28.9 (CH_2), 31.4 (CH_2), 32.5 (CH_2), 114.5 (CH_2), 130.8 (CH), 135.6 (CH), 137.4 (CH) ppm. MS (EI): *m*/*z* (%) = 124 (15) $[M]^+$, 109 (21) $[M - CH_3]^+$, 67 (100). HRMS (EI): calcd. for C_9H_{16} 124.1247; found 124.1240. GC (80 °C): t_R = 9.0 min.

[(*E*)-Non-3-en-1-ynyl]benzene (13):[31] According to the general procedure, the reaction of **2** (216 mg, 0.963 mmol) with tris(phenyl-

ethynyl)indium (0.39 mmol) afforded **13** [155 mg, 81%, (*E*)/(*Z*) = 97:3]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, *J* = 7.2 Hz, 3 H), 1.35–1.49 (m, 6 H), 2.41 (q, *J* = 8.3 Hz, 2 H), 5.68 (d, *J* = 10.8 Hz, 1 H), 5.99 (dt, *J* = 10.8, 7.4 Hz, 1 H), 7.28–7.34 (m, 2 H), 7.41–7.46 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3) 22.5 (CH_2), 28.6 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 87.5 (C), 93.0 (C), 109.0 (CH), 123.8 (C), 128.3 (2× CH), 131.4 (2× CH), 144.5 (CH) ppm. MS (EI): *m*/*z* (%) = 202 (5) $[M]^+$, 129 (100) $[M - C_5H_{11}]^+$. GC [120 °C (2 min) up to 200 °C at 10 °C/min]: t_R = 4.6 min.

Trimethyl[(*E*)-non-3-en-1-ynyl]silane (14):[34] According to the general procedure, the reaction of **2** (224 mg, 1.000 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.40 mmol) afforded **14** [167 mg, 86%, (*E*)/(*Z*) = 97:3]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.20 (s, 9 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 1.24–1.44 (m, 6 H), 2.10 (q, *J* = 7.1 Hz, 2 H), 5.47–5.52 (m, 1 H), 6.22–6.27 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.1 (3× CH_3), 14.1 (CH_3), 22.5 (CH_2), 28.4 (CH_2), 31.3 (CH_2), 33.1 (CH_2), 92.5 (C), 104.3 (C), 109.6 (CH), 146.5 (CH) ppm. MS (EI): *m*/*z* (%) = 194 (10) $[M]^+$, 73 (100). GC (200 °C): t_R = 4.9 min.

1,1-Diphenylnon-1-ene (16):[35] According to procedure A, the reaction of **15** (280 mg, 0.986 mmol) with triphenylindium (0.89 mmol) afforded **16** (198 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, *J* = 6.9 Hz, 3 H), 1.27–1.54 (m, 10 H), 2.13 (q, *J* = 7.4 Hz, 2 H), 6.11 (t, *J* = 7.4 Hz, 1 H), 7.12–7.50 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.6 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.7 (CH_2), 30.0 (CH_2), 31.8 (CH_2), 126.7 (CH), 126.8 (CH), 127.2 (2× CH), 128.04 (2× CH), 128.08 (2× CH), 130.0 (2× CH), 130.4 (CH), 140.4 (C), 141.4 (C), 142.9 (C) ppm. MS (EI): *m*/*z* (%) = 278 (37) $[M]^+$, 193 (100).

2-Methyldec-2-ene (17):[36] According to procedure A, the reaction of **15** (289 mg, 1.018 mmol) with trimethylindium (0.92 mmol) afforded **17** (124 mg, 79%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.89 (t, *J* = 5.9 Hz, 3 H), 1.18–1.25 (m, 10 H), 1.60 (s, 3 H), 1.69 (s, 3 H), 1.97 (m, 2 H), 5.12 (t, *J* = 14.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.4 (CH_3), 17.8 (CH_3), 22.7 (CH_2), 25.8 (CH_3), 28.2 (CH_2), 29.9 (CH_2), 30.5 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 125.1 (CH), 131.2 (C) ppm.

5-Butyltridec-5-ene (18):[37] According to procedure A, the reaction of **15** (287 mg, 1.011 mmol) with tri-*n*-butylindium (0.91 mmol) afforded **18** (202 mg, 84%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.89 (m, 9 H), 1.33 (m, 18 H), 1.93–2.00 (m, 6 H), 5.10 (t, *J* = 13.6 Hz,1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 13.76 (CH_3), 13.79 (2× CH_3), 22.3 (CH_2), 22.4 (CH_2), 22.6 (CH_2), 27.4 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 29.5 (CH_2), 29.9 (CH_2), 30.3 (CH_2), 30.5 (CH_2), 31.6 (CH_2), 36.4 (CH_2), 124.5 (CH), 139.3 (C) ppm. MS (EI): *m*/*z* (%) = 238 (20) $[M]^+$, 69 (100).

[3-(Phenylethynyl)undec-3-en-1-ynyl]benzene (19): According to procedure A, the reaction of **15** (280 mg, 0.986 mmol) with tris(phenylethynyl)indium (0.90 mmol) afforded **19** (235 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, *J* = 6.9 Hz, 3 H), 1.29–1.55 (m, 10 H), 2.49 (q, *J* = 7.4 Hz, 2 H), 6.50 (t, *J* = 7.7 Hz, 1 H), 7.31–7.40 (m, 6 H), 7.49–7.55 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.6 (CH_2), 28.6 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 31.0 (CH_2), 31.8 (CH_2), 84.9 (C), 86.5 (C), 87.5 (C), 92.8 (C), 105.6 (C), 123.07 (C), 123.09 (C), 128.20 (CH), 128.24 (2× CH), 128.28 (2× CH), 128.4 (CH), 131.60 (2× CH), 131.62 (2× CH), 149.7 (CH) ppm. MS (EI): *m*/*z* (%) = 326 (14) $[M]^+$, 255 (15) $[M - C_5H_{11}]^+$, 115 (100). HRMS (EI): calcd. for $C_{25}H_{26}$ 326.2029; found 326.2030.

Trimethyl{3-[(trimethylsilyl)ethynyl]undec-3-en-1-ynyl}silane (20): According to procedure A, the reaction of **15** (285 mg, 1.004 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.90 mmol) afforded **20** (288 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.20 (s, 9 H), 0.22 (s, 9 H), 0.89 (t, *J* = 7.4 Hz, 3 H), 1.19–1.42 (m, 10 H), 2.34 (q, *J* = 7.4 Hz, 2 H), 6.42 (t, *J* = 7.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.1 (6× CH_3), 14.1 (CH_3), 22.6 (CH_2), 28.3 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 30.8 (CH_2), 31.8 (CH_2), 91.4 (C), 98.3 (C), 99.8 (C), 102.5 (C), 105.8 (C), 152.2 (CH) ppm. MS (EI): *m*/*z* (%) = 318 (8) $[M]^+$, 303 (13) $[M - CH_3]^+$, 105 (100). HRMS (EI): calcd. for $C_{19}H_{34}Si_2$ 318.2194; found 318.2192.

[(*Z*)-1-Bromonon-1-enyl]benzene (22): According to procedure B, the reaction of **15** (284 mg, 1.000 mmol) with triphenylindium (0.40 mmol) afforded **22** (155 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, *J* = 6.6 Hz, 3 H), 1.28–1.55 (m, 10 H), 2.38 (q, *J* = 7.1 Hz, 2 H), 6.22 (t, *J* = 7.1 Hz, 1 H), 7.26–7.37 (m, 3 H), 7.52–7.55 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.6 (CH_2), 28.4 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 32.5 (CH_2), 125.2 (C), 127.5 (2× CH), 128.2 (3× CH), 132.0 (CH), 140.2 (C) ppm. MS (EI): *m*/*z* (%) = 282 (12) $[M]^+$ (^{81}Br), 280 (13) $[M]^+$ (^{79}Br), 105 (100). HRMS (EI): calcd. for $C_{15}H_{21}Br$ 280.0821; found 280.0826.

[(*Z*)-3-Bromoundec-3-en-1-ynyl]trimethylsilane (23): According to procedure B, the reaction of **15** (280 mg, 0.986 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.40 mmol) afforded **23** (226 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.21 (s, 9 H), 0.89 (t, *J* = 6.6 Hz, 3 H), 1.21–1.56 (m, 10 H), 2.21 (q, *J* = 7.1 Hz, 2 H), 6.34 (t, *J* = 7.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.3 (3× CH_3), 14.1 (CH_3), 22.6 (CH_2), 27.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 32.0 (CH_2), 94.5 (C), 102.2 (C), 102.4 (C), 141.5 (CH) ppm. MS (EI): *m*/*z* (%) = 299 (1) $[M - H]^+$ (^{79}Br), 125 (100). HRMS (EI): calcd. for $C_{14}H_{25}SiBr$ 300.0903; found 300.0907.

[(*Z*)-3-Bromoundec-3-en-1-ynyl]benzene (24): According to procedure B, the reaction of **15** (280 mg, 0.986 mmol) with tris(phenylethynyl)indium (0.40 mmol) afforded **24** (211 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.93 (t, *J* = 7.1 Hz, 3 H), 1.21–1.52 (m, 10 H), 2.30 (q, *J* = 7.1 Hz, 2 H), 6.39 (t, *J* = 7.1 Hz, 1 H), 7.33–7.37 (m, 3 H), 7.45–7.50 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.1 (CH_3), 22.6 (CH_2), 28.0 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 32.1 (CH_2), 87.7 (C), 88.9 (C), 102.4 (C), 122.2 (C), 128.3 (2× CH), 128.7 (CH), 131.6 (2× CH), 140.6 (CH) ppm. MS (EI): *m*/*z* (%) = 306 (10) $[M]^+$ (^{81}Br), 304 (10) $[M]^+$ (^{79}Br), 129 (100). HRMS (EI): calcd. for $C_{17}H_{21}Br$ 304.0821; found 304.0824.

1,1′-[(*Z*)-1-Bromoethene-1,2-diyl]bisbenzene (25):[15] According to procedure B, the reaction of **21** (261 mg, 0.997 mmol) with triphenylindium (0.40 mmol) afforded **25** (147 mg, 57%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.80 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 124.1 (C), 127.8 (2× CH), 128.0 (CH), 128.2 (2× CH), 128.3 (2× CH), 128.7 (CH), 129.2 (2× CH), 129.9 (CH), 136.3 (C), 141.0 (C) ppm. MS (EI): *m*/*z* (%) = 260 (20) $[M]^+$ (^{81}Br), 258 (21) $[M]^+$ (^{79}Br), 178 (100) $[M - HBr]^+$. HRMS (EI): calcd. for $C_{14}H_{11}Br$ 258.0039; found 258.0041.

[(*Z*)-2-Bromobuta-1,3-dienyl]benzene (26):[38] According to procedure B, the reaction of **21** (260 mg, 0.993 mmol) with trivinylindium (0.40 mmol) afforded **26** (143 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.35 (d, *J* = 10.4 Hz, 1 H), 5.75 (d, *J* = 16.2 Hz, 1 H), 6.53 (dd, *J* = 16.2, 10.4 Hz, 1 H), 7.00 (s, 1 H), 7.30–7.42 (m, 3 H), 7.71 (d, *J* = 7.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 119.0 (CH_2), 123.9 (C), 128.1 (2× CH), 128.3 (CH), 129.5 (2× CH), 132.3 (CH), 135.6 (C), 137.1 (CH) ppm. MS (EI): *m*/*z* (%) = 209 (6) $[M]^+$ (^{81}Br), 207 (6) $[M]^+$

(^{79}Br), 129 (100). HRMS (EI): calcd. for $C_{10}H_9Br$ 207.9882; found 207.9888.

[(*Z*)-3-Bromo-4-phenylbut-3-en-1-ynyl]trimethylsilane (27):[12a] According to procedure B, the reaction of **21** (290 mg, 1.107 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.44 mmol) afforded **27** (192 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.26 (s, 9 H), 7.29 (s, 1 H), 7.32–7.42 (m, 3 H), 7.66–7.69 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.3 (3× CH_3), 96.9 (C), 100.0 (C), 103.7 (C), 128.3 (2× CH), 129.0 (CH), 129.2 (2× CH), 134.8 (C), 137.3 (CH) ppm. MS (EI): *m*/*z* (%) = 280 (24) $[M]^+$ (^{81}Br), 278 (24) $[M]^+$ (^{79}Br), 263 (11) $[M - CH_3]^+$ (^{79}Br), 183 (100). HRMS (EI): calcd. for $C_{13}H_{15}BrSi$ 278.0121; found 278.0123.

[(*Z*)-2-Bromo-4-phenylbut-1-en-3-ynyl]benzene (28):[12a] According to procedure B, the reaction of **21** (293 mg, 1.119 mmol) with tris(phenylethynyl)indium (0.45 mmol) afforded **28** (244 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.75 (m, 11 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 89.2 (C), 91.1 (C), 100.1 (C), 122.0 (C), 128.3 (2× CH), 128.4 (2× CH), 128.9 (CH), 129.0 (CH), 129.3 (2× CH), 131.7 (2× CH), 135.0 (C), 136.6 (CH) ppm. MS (EI): *m*/*z* (%) = 284 (24) $[M]^+$ (^{81}Br), 282 (25) $[M]^+$ (^{79}Br), 202 (100) $[M - HBr]^+$. HRMS (EI): calcd. for $C_{16}H_{11}Br$ 282.0039; found 282.0035.

Trimethyl[(*Z*)-3-phenylundec-3-en-1-ynyl]silane (29): According to procedure C, the reaction of **22** (265 mg, 0.942 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.57 mmol) afforded **29** (141 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.26 (s, 9 H), 0.84–0.92 (m, 3 H), 1.30–1.54 (m, 10 H), 2.50 (q, *J* = 7.4 Hz, 2 H), 6.45 (t, *J* = 7.4 Hz, 1 H), 7.25–7.36 (m, 3 H), 7.59 (d, *J* = 7.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.1 (3× CH_3), 14.1 (CH_3), 22.7 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.3 (CH_2), 31.8 (CH_2), 100.2 (C), 102.4 (C), 123.5 (C), 125.9 (2× CH), 127.3 (CH), 128.3 (2× CH), 138.0 (C), 140.0 (CH) ppm. MS (EI): *m*/*z* (%) = 298 (49) $[M]^+$, 283 (12) $[M - CH_3]^+$, 185 (100). HRMS (EI): calcd. for $C_{20}H_{30}Si$ 298.2111; found 298.2106.

Trimethyl[(*E*)-3-methylundec-3-en-1-ynyl]silane (30): According to procedure C, the reaction of **23** (268 mg, 0.889 mmol) with trimethylindium (0.53 mmol) afforded **30** (147 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.18 (s, 9 H), 0.89 (t, *J* = 7.1 Hz, 3 H), 1.26–1.36 (m, 10 H), 1.78 (s, 3 H), 2.07 (q, *J* = 7.4 Hz, 2 H), 5.94 (dt, *J* = 7.4, 1.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.2 (3× CH_3), 14.2 (CH_3), 17.2 (CH_3), 22.8 (CH_2), 28.6 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 32.0 (CH_2), 89.9 (C), 108.9 (C), 117.7 (C), 139.9 (CH) ppm. MS (EI): *m*/*z* (%) = 236 (19) $[M]^+$, 97 (91), 83 (100). HRMS (EI): calcd. for $C_{15}H_{28}Si$ 236.1955; found 236.1947.

[(*E*)-1-(Phenylethynyl)non-1-enyl]benzene (31): According to procedure C, the reaction of **24** (243 mg, 0.796 mmol) with triphenylindium (0.48 mmol) afforded **31** (149 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, *J* = 7.0 Hz, 3 H), 1.28–1.60 (m, 10 H), 2.60 (q, *J* = 7.3 Hz, 2 H), 6.50 (t, *J* = 7.5 Hz, 1 H), 7.29–7.40 (m, 6 H), 7.53–7.57 (m, 2 H), 7.67–7.70 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 14.2 (CH_3), 22.7 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 29.8 (CH_2), 31.9 (CH_2), 87.3 (C), 91.6 (C), 123.5 (C), 123.8 (C), 127.4 (2× CH), 128.0 (CH), 128.28 (CH), 128.35 (2× CH), 128.94 (2× CH), 131.6 (2× CH), 137.8 (C), 140.9 (CH) ppm. MS (EI): *m*/*z* (%) = 302 (19) $[M]^+$, 204 (100) $[M - C_7H_{14}]^+$. HRMS (EI): calcd. for $C_{23}H_{26}$ 302.2029; found 302.2032.

Trimethyl[(*Z*)-3-(phenylethynyl)undec-3-en-1-ynyl]silane (32): According to procedure C, the reaction of **24** (280 mg, 0.917 mmol) with tris[(trimethylsilyl)ethynyl]indium (0.55 mmol) afforded **32** (237 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.25 (s, 9 H), 0.90 (t, *J* = 6.9 Hz, 3 H), 1.31–1.56 (m, 10 H), 2.47 (m, 2 H), 6.46 (t, *J* = 8.0 Hz, 1 H), 7.34 (m, 3 H), 7.49–7.57 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.1 (3× CH_3), 14.1 (CH_3), 22.6 (CH_2), 28.5 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 30.9 (CH_2), 31.8 (CH_2), 84.7 (C), 91.3 (C), 92.9 (C), 102.8 (C), 105.7 (C), 123.1 (C), 128.2 (2× CH), 128.4 (CH), 131.6 (2× CH), 150.8 (CH) ppm. MS (EI): *m*/*z* (%) = 322 (16) $[M]^+$, 249 (8) $[M - C_3H_9Si]^+$, 73 (100). HRMS (EI): calcd. for $C_{22}H_{30}Si$ 322.2111; found 322.2111.

[(*E*)-3,4-Diphenylbut-3-en-1-ynyl]trimethylsilane (33): According to procedure C, the reaction of **27** (264 mg, 0.946 mmol) with triphenylindium (0.57 mmol) afforded **33** (259 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.40 (s, 9 H), 7.22 (m, 3 H), 7.32 (m, 3 H), 7.44 (m, 3 H), 7.53 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.0 (3× CH_3), 94.5 (C), 107.6 (C), 124.2 (C), 127.7 (CH), 127.8 (CH), 128.1 (2× CH), 128.4 (2× CH), 129.1 (2× CH), 129.3 (2× CH), 136.0 (C), 137.33 (CH), 137.36 (C) ppm. MS (EI): *m*/*z* (%) = 276 (70) $[M]^+$, 261 (42) $[M - CH_3]^+$, 245 (100). HRMS (EI): calcd. for $C_{19}H_{20}Si$ 276.1329; found 276.1326.

[(*E*)-3-Butyl-4-phenylbut-3-en-1-ynyl]trimethylsilane (34): According to procedure C, the reaction of **27** (206 mg, 0.738 mmol) with tri-*n*-butylindium (0.44 mmol) afforded **34** (131 mg, 69%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.26 (s, 9 H), 0.93 (t, *J* = 7.5 Hz, 3 H), 1.39 (dt, *J* = 7.5, 7.2 Hz, 2 H), 1.64 (tt, *J* = 7.8, 7.5 Hz, 2 H), 2.40 (t, *J* = 7.8 Hz, 2 H), 6.93 (s, 1 H), 7.26–7.33 (m, 3 H), 7.36 (t, *J* = 7.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 0.05 (3× CH_3), 13.9 (CH_3), 22.4 (CH_2), 30.6 (CH_2), 30.9 (CH_2), 93.8 (C), 107.8 (C), 125.6 (C), 127.2 (CH), 128.2 (2× CH), 128.8 (2× CH), 136.63 (CH), 136.68 (C) ppm. MS (EI): *m*/*z* (%) = 256 (25) $[M]^+$, 241 (22) $[M - CH_3]^+$, 183 (54) $[M - C_3H_9Si]^+$, 73 (100). HRMS (EI): calcd. for $C_{17}H_{24}Si$ 256.1642; found 256.1650.

[(*E*)-3-Benzylidene-5-phenylpenta-1,4-diynyl]trimethylsilane (35): According to procedure C, the reaction of **27** (227 mg, 0.813 mmol) with tris(phenylethynyl)indium (0.49 mmol) afforded **35** (213 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.29 (s, 9 H), 7.15 (s, 1 H), 7.34–7.44 (m, 6 H), 7.55 (m, 2 H), 7.93 (dd, *J* = 8.7, 1.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = –0.1 (3× CH_3), 86.7 (C), 93.3 (C), 94.7 (C), 103.2 (C), 104.2 (C), 122.9 (C), 128.4 (4× CH), 128.7 (CH), 129.1 (2× CH), 129.2 (CH), 131.6 (2× CH), 135.6 (C), 144.1 (CH) ppm. MS (EI): *m*/*z* (%) = 300 (100) $[M]^+$, 285 (53) $[M - CH_3]^+$. HRMS (EI): calcd. for $C_{21}H_{20}Si$ 300.1329; found 300.1331.

Acknowledgments

We are grateful to the Ministerio de Educación y Ciencia (Spain, BQU2003-00301 and CTQ2006-06166), the Xunta de Galicia (PGIDIT04PXIC10308PN), and FEDER for financial support. R. R. thanks the Xunta de Galicia for an "Isidro Parga Pondal" contract.

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Received: December 21, 2007
Published Online: February 22, 2008

