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The effect of CO on the reaction of (tributyltin)lithium with alkyl and aryl bromides

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Abstract

The reaction of (tributyltin)lithium with alkyl and aryl bromides in THF was studied in the presence of CO and of *p*-dinitrobenzene under several reaction conditions. The observed results indicate that electron transfer is involved in the substitution reaction. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Lithium; Carbon monoxide; Electron transfer; Substitution

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1. Introduction

In the last few years, several mechanistic studies have been reported on the trialkylstannylation of organic halides [1–3]. The most recent studies, carried out using bridged bicyclic halides [1,2] and cyclizable probes [3] as a way of distinguishing between polar and radical pathways, are controversial.

Three basic mechanistic pathways have been proposed for the reaction of alkyl halides with trialkyltin alkali–metal compounds: (a) a classic S_N2 substitution of the alkyl halide with a trialkyltin anion as the nucleophile (mainly observed with primary halides) [4,5], (b) substitution by an electron transfer (ET)-initiated $S_{RN}1$ process [3,6] and (c) substitution by halogen–metal exchange (HME; only established for polyhalogenated compounds and for alkyl and aryl iodides) ([1]b,[4]). In many cases, the observed distribution of products was interpreted as the result of different apportionments between two or three pathways [1,2,4] (albeit a mainly carbanionic mechanism was reported for the case of Me_3SnNa ([1]a), while in other cases the authors seem to favor an almost exclusively radical pathway [3]). Evidence has recently been presented that establishes that even the formation of carbene-derived products in the reaction of geminal dihalides with trimethyltinsodium is in fact preceded by a radical intermediate [3].

Previous studies were based on the trapping of intermediates with carbanion and/or radical traps [2], or other ways of trapping the intermediates [7], the formation of rearranged products [3,6,8] and a variety of stereochemical studies [9,10]. The present approach is based on the use of carbon monoxide as a good one-electron acceptor, as it has been described in previous studies carried out with phenyllithium [11]. The reaction of organotin compounds with carbon monoxide is a well-known reaction that has been successfully used for the synthesis of carbonyl-functionalized compounds [12]. Taking into account the reagents and reaction conditions, those reactions were usually written as classical polar reactions. However, recent research has been reported describing the generation of radicals from trialkyltin hydride and azo-bis-isobutyronitrile (AIBN) [13,14] as an efficient method for the preparation of acylstannyl compounds.

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Table 1
Reaction between Bu_3SnLi and organic bromides, RBr, in the presence of CO, in THF at 0°C[a]

Entry	RBr	Reaction conditions	% Composition of the reaction mixture				% RBr conversion into Bu_3SnR
			RBr[b]	Bu_4Sn[c]	Bu_3Sn[c]	Bu_6Sn_2	
1[e]	c-$C_6H_{11}Br$	—	31	30	35	26	43
2[f]		CO	45	43	20	36	24
3[g]	C_6H_5Br	—	30	14	51	9	68
4[h]		CO	50	17	31	33	35

[a] Initial $[Bu_3SnLi]$ 0.4–0.5 M; [b] % recovered; [c] % yields based on $[Bu_3SnLi]_i$; [d] % yield of Bu_3SnR based on $[RBr]_i$; [e] $[Bu_3SnLi]$:[c-$C_6H_{11}Br$], 1:0.9; [f] $[Bu_3SnLi]$:[c-$C_6H_{11}Br$], 1:0.85; [g] $[Bu_3SnLi]$:$[C_6H_5Br]$, 1:0.81; [h] $[Bu_3SnLi]$:$[C_6H_5Br]$, 1:0.88.

Most of the synthetic and mechanistic studies on the stannylation of organic halides were carried out using triorganotinsodium ([1]a,[2–6,8–10]) and, only in a few cases, comparison with triorganotinlithium was reported ([1]b). We have recently reported the role of aggregation effects in the reaction of organolithium compounds with CO [15]: although the information on the aggregation state of organostannyl alkali–metal compounds is currently very scarce [16], the possibility of aggregates should be borne in mind. In spite of the fact that usually only the tin substitution products are reported, it is likely that some information could be also provided by a careful examination of most of the tin products in the reaction mixture. Therefore, in the present paper, as an additional mechanistic clue, the yields of Bu_3SnR and of other unsubstituted Bu_nSn_m are given to account for the fate of the stannyl reagent.

2. Results and discussion

2.1. The nature of the reagent

Taking into account the fact that usually the reactions of organotin compounds lead to complex reaction mixtures [17], several methods of preparation described in the literature were tried and in each case the presence of by-products was carefully tested. Tributyltinlithium can be prepared through the reaction in THF of: hexabutylditin and metallic lithium [1]; tetrabutyltin and lithium metal [18]; tributyltinchloride and lithium metal [19]; or hexabutyltin and lithium dispersion at 0° (as described for the preparation of Me_3SnNa) [20]. The best results (highest yield of reagent and smaller amounts of by-products) were obtained from the reaction of tributyltinchloride and lithium metal. Several ratios of $[Bu_3SnCl]$:[Li] were tested, 1:2,1:3, 1:5, 1:12 and 1:15. For ratios where the excess of [Li] was $<1:5$, the yield of the reagent was low and a significant amount of Bu_6Sn_2 was obtained. For [Li] excess $>1:5$, the yield of the reagent was good, but a significant amount of the disubstitution product (Bu_2SnR_2) was observed in the reactions with RX. Details of the preparation and quantitative analysis of the reagent are given in Section 2.3. Since some small amounts of Bu_6Sn_2 (and sometimes Bu_4Sn) are almost unavoidable in the preparation of Bu_3SnLi, discussion of the yields of these organotin compounds will be made on the basis of relative differences; in all cases, a control determination of the reaction in the absence of any additive was carried out each time.

We have examined the reaction of Bu_3SnLi with an alkyl halide and an aromatic halide in the presence of CO in THF at 0°C. The results are summarized in Table 1. With cyclohexyl bromide, **1**, the yield of substitution product is decreased from 35% to 20% (entries 1 and 2) in the presence of CO in the same time period. Moreover, the amounts of by-products, Bu_4Sn and Bu_6Sn_2, have slightly increased and also the amount of recovered cyclohexyl bromide. In the reaction of Bu_3SnLi with bromobenzene (entries 3 and 4) a similar decrease in the yield of substitution product was observed, while the yield of Bu_6Sn_2 significantly increased (from 9% to 33%) as has the amount of unreacted bromobenzene. These results indicate that CO interferes with the substitution reaction. CO is an inert gas toward any polar reaction, while it was previously reported that CO is an excellent one-electron acceptor in the reactions of aryllithium compounds. In spite of previous reports that radicals were not involved in the reactions of primary halides with Bu_3SnLi [21], Ashby and coworkers [6] have provided evidence that the reactions of primary alkyl bromides with Bu_3SnNa proceeds via an ET pathway to a significant extent. On the other hand, in kinetic studies of the reactions of trialkyltinlithiums with aliphatic chlorides in THF, Kuivila reported that while the 1-butyl chloride reacted by an S_N2 pathway, geminal dichlorides such as CH_2Cl_2 and Me_2CCl_2 reacted by electron transfer processes [5].

The effect of CO observed in the present work is interpreted as a competition in the first electron transfer step (measured by k_1), in which Bu_3SnLi transfers one electron to the organic bromide, giving a radical cation–radical anion pair. CO would operate as a good one-electron acceptor, competing with the organic halide for the transferred electron (Eqs. (1) and (2)). It

Table 2
Reaction between Bu_3SnLi and bromobenzene in the presence of CO and/or PDNB, in THF at 0°C[a]

Entry	Reaction conditions	% Composition of thereaction mixture				% C_6H_5Br conversion into Bu_3SnR[d]
		C_6H_5Br[b]	Bu_4Sn[c]	Bu_3SnR[c]	Bu_6Sn_2[c]	
1[e]	—	30	14	51	9	68
2[f,g]	PDNB	50	10	28	46	33
3[h,g]	CO/PDNB	45	9	10	46	13
4[i]	—	0	16	57	7	83
5[i]	CO	21	13	41	17	60
6[i]	PDNB[k]	87	14	0	55	0
7[j]	CO/PDNB[l]	82	19	0	80	0

[a] Initial $[Bu_3SnLi]$ 0.4–0.5 M; [b] % recovered; [c] % yields based on $[Bu_3SnLi]_i$; [d] % yield of Bu_3SnR based on $[C_6H_5Br]_i$; [e] $[Bu_3SnLi]:[C_6H_5Br]$, 1:0.81; [f] $[Bu_3SnLi]:[C_6H_5Br]$, 1:1.02; [g] $[Bu_3SnLi]:[PDNB]$, 1:0.1; [h] $[Bu_3SnLi]:[C_6H_5Br]$, 1:0.88; [i] $[Bu_3SnLi]:[C_6H_5Br]$, 1:0.76 (quenching with Ac_2O); [j] $[Bu_3SnLi]:[C_6H_5Br]$, 1:0.81 and $[Bu_3SnLi]:[PDNB]$, 1:1; [k] 57% PDNB recovered; [l] 90% PDNB recovered.

can be observed that for PhBr, in which the radical anion would be more stabilized, the yield of substitution product is higher than for cyclohexyl bromide. The radical ions formed in the first step give the organic free radicals, $R^\bullet$ and $Bu_3Sn^\bullet$ by diffusion out of the solvent cage. $R^\bullet$ reacts with fresh Bu_3SnLi to start the $S_{RN}1$ radical chain.

$$Bu_3SnLi + RBr \underset{ET}{\overset{k_1}{\rightarrow}} [(Bu_3SnLi)^{+\bullet}, (RBr)^{-\bullet}] \qquad (1)$$

$$Bu_3SnLi + CO \underset{ET}{\overset{k_{CO}}{\rightarrow}} [(Bu_3SnLi)^{+\bullet}, (CO)^{-\bullet}] \qquad (2)$$

Although Eq. (1) is usually written as the anion Bu_3Sn^- giving the free radicals $Bu_3Sn^\bullet$ and $R^\bullet$, it is preferred to write it as a radical ion pair in view of the differential effect observed for the counter-ion in the few reactions where both, Na and Li organotin compounds, were studied ([1]a,[2]). Solvent effects seem to suggest that the lithium atom is in the co-ordination sphere; thus, the addition of electron donors and of 18-crown-6 ether, has a significant effect on the reaction of Me_3SnLi with 2-bromooctane [22]. The effect of the viscosity of the solvent has also been studied, and the findings are consistent with the formation of a radical anion–radical cation pair, and diffusion out of the solvent cage increases as the viscosity of the solvent decreases [6,10].

If the above interpretation is correct, a known radical anion scavenger such as *p*-dinitrobenzene (PDNB) would trap the radical anion, and thus slow down the substitution reaction. It can be observed from Table 2 (entry 2) that PDNB produces a significant decrease in the yield of Bu_3SnPh; 50% of bromobenzene is recovered unreacted and, moreover, the yield of Bu_6Sn_2 has increased from 9% to 46%. When the reaction was carried out in the presence of both CO and PDNB (entry 3), the yield of substitution product was only 10%, while formation of Bu_6Sn_2, a likely coupling product of $Bu_3Sn^\bullet$, was significant. When the reaction was carried out with the Bu_3SnLi in a slight excess and quenched with acetic anhydride, no unreacted bromobenzene was observed in the absence of a radical trap (entry 4), while 20% of bromobenzene was recovered when CO was present (entry 5) and no substitution product was detected in the presence of *p*-dinitrobenzene (PDNB) (entry 6) or in the presence of both CO/PDNB (entry 7).

The effects of temperature and of the reaction of structurally different organic bromides with Bu_3SnLi was then examined. Table 3 summarizes the results of the reactions with cyclohexyl, phenyl, allyl and benzyl bromide with Bu_3SnLi in THF at 50°C. By comparison with the results in Table 1, it can be observed that, as expected for an ET reaction, the temperature has no effect on the yield of the substitution product (entries 1 and 2 of Tables 1 and 2). For the reaction of PhBr, a slight decrease is observed, probably due to the smaller [PhBr]. As was found at 0°C, the formation of the substitution product is slowed down in the presence of CO. However, a new feature appeared, namely the significative increase in the amount of Bu_4Sn (entries 1–4), which will be discussed below. Since its yield is almost unaffected by the presence of CO or PDNB it could suggest that the formation of Bu_4Sn is not involved in the reaction with RX.

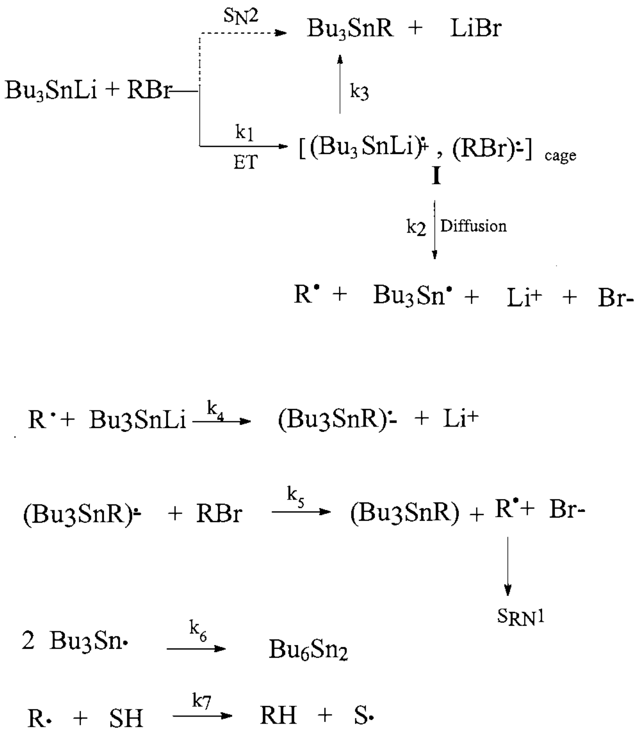
All the above results can be interpreted by the reaction scheme shown (Scheme 1). The first slow step (k_1) would be the electron transfer from Bu_3SnLi to the organic halide to form a radical cation–radical anion pair, I. Although a parallel S_N2 reaction is not excluded, the evidence indicates that radicals are strongly involved in the whole mechanisms. Reaction within the cage (measured by k_3) could produce the substitution product but diffusion of the radicals out of the cage (k_2) is favoured in solvents of relatively low viscosity. The organic radical, $R^\bullet$, could react with unreacted Bu_3SnLi (k_4), giving the $(Bu_3SnR)^{-\bullet}$, which by further attack on the organic halide would give the substitution products and a fresh $R^\bullet$. Further formation of Bu_3SnR could occur by propagation of a radical chain $S_{RN}1$ mechanisms.

Table 3
Reaction between Bu_3SnLi and organic bromides, RBr, in the presence of CO, in THF at 50°C[a]

Entry	Halide	Reaction conditions	% Composition of the reaction mixture				% RBr conversion into Bu_3SnR[d]
			RBr[b]	Bu_4Sn[c]	Bu_3SnR[c]	Bu_6Sn_2[c]	
1[e]	c-$C_6H_{11}Br$	—	30	58	35	5	53
2		CO	33	50	22[f]	10	32
3[g]	C_6H_5Br	—	23	55	30[h]	8	76
4		CO	42	43	22[i]	32	57
5[j]	C_3H_5Br	—		41	41	31	
6		CO		44	32	31	
7[k]	$C_6H_5CH_2Br$	—	3	18	60[l]	17	63
8		CO	10	21	44[m]	22	46

[a] Initial $[Bu_3SnLi]$ 0.4–0.5 M; [b] % recovered; [c] % yields based on $[Bu_3SnLi]$; [d] % yield of Bu_3SnR based on $[RBr]_i$; [e] $[Bu_3SnLi]$:$C_6H_{11}Br]$, 1:0.87; [f] $Bu_2Sn(c\text{-}C_6H_{11})_2$ 9%; [g] $[Bu_3SnLi]$:$[C_6H_5Br]$, 1:0.60; [h] Bu_2SnPh_2 3%; [i] Bu_2SnPh_2 6%; [j] $[Bu_3SnLi]$:$[C_3H_5Br]$, 1:0.9, the % unreacted C_3H_5Br could not be determined by GC under the present conditions; [k] $[Bu_3SnLi]$:$[C_6H_5CH_2Br]$, 1:1; [l] toluene 11%; [m] toluene 9%.

In the presence of CO, ET to this good one-electron acceptor (measured by k_6) would compete with k_1, resulting in a lower production of $R^{\bullet}$ and a consequent decrease in the yield of the substitution product, Bu_3SnR. The relatively high $[Bu_3Sn^{\bullet}]$ compared with $[R^{\bullet}]$ leads the reaction toward the production of higher yields of the coupling products, Bu_6Sn_2 (k_6). Termination of the radical chain by proton abstraction by the solvent is indicated by reaction k_7. With most of the organic halides studied, the hydrocarbon was not detected by GC (probably owing to their volatility). However, in the case of benzyl bromide, toluene was detected in significant amounts (entries 7 and 8 in Table 3). In the presence of CO, the yield of toluene is slightly lower than that in the absence of CO, which is consistent with the above proposed reaction (Scheme 1). The effect of [PDNB] is also suggestive. It can be observed from Table 2 that a significant decrease in the conversion of C_6H_5Br is observed in the presence of PDNB (entries 1–3). However, the production of Bu_3SnPh is only completely inhibited when a 1:1 reagent:scavenger ratio is used (entries 6 and 7). This shows that if the $S_{RN}1$ chain exists, it is not very long.



Scheme 1. The reaction scheme of (tributyltin)lithium with alkyl and aryl bromides.

Variable amounts of Bu_4Sn are observed as an additional by-product in all cases, but it is especially high in the reactions carried out at 50°C (Table 3). Although, in principle, it could be assumed to arise from a side reaction when preparing the reagent, it is clear that its proportion in the reaction mixture varies according to the reaction conditions, and it is especially high in the reactions carried out at 50°C. A possible explanation for the formation of Bu_4Sn could be the partial decomposition of the substrate and further reactions as shown by Eqs. (3) and (4).

$$Bu_3SnLi \rightarrow Bu^{\bullet} + (Bu_2SnLi)^{\bullet} \tag{3}$$

$$Bu_3SnLi + Bu^{\bullet} + SH \rightarrow Bu_4Sn + Li^{+} + (SH)^{\bullet} \tag{4}$$

Although compounds with Bu entities < 3 have been detected only as traces in some reaction mixtures, it is likely that species like $(Bu_2SnLi)^{\bullet}$ could also react with the solvent, giving volatile compounds as well as with $R^{\bullet}$ (or RBr) giving disubstitution products (Eqs. (5) and (6)). Partial decomposition of the products to $(Bu_2SnR)^{\bullet}$ could also occur (although only to a minor extent), which by further reaction would give rise to the disubstitution product Bu_2SnR_2, which was observed in small amounts (9, 3 and 6%, for entries 2–4, respectively) when the reaction was carried out at 50°C (Table 3).

$$(Bu_2SnLi)^{\bullet} + R^{\bullet} \rightarrow Bu_2RSnLi \tag{5}$$

$$Bu_2RSnLi + RBr \rightarrow Bu_2R_2Sn + Li^+ + Br^- \quad (6)$$

Decomposition of Bu_3SnLi has been observed on standing and it is known that it increases with temperature. This explanation is consistent with the observation that with a more reactive alkyl bromide such as $C_6H_5CH_2Br$ (entries 7 and 8) less decomposition of the substrate is observed.

For the reactions with 1-bromopropene, in which stabilization of the radical anion is also possible, the amount of substitution product is similar to PhBr. In the case of benzyl bromide (entries 7 and 8), the increased yield may be due to the slightly higher [$PhCH_2Br$]. It is worthwhile noting that in this case toluene was also present in the reaction mixture in 11 and 9%, respectively (entries 7 and 8). This is a clear indication of the presence of the $PhCH_2^{\bullet}$ radical, that abstracts a proton from the solvent giving the hydrocarbon. Similar results were not observed in the previous reactions, probably due to the more volatile nature of the corresponding hydrocarbon. In all cases, the yield of substitution product decreased while formation of the by-products has increased.

2.2. Conclusions

The observed inhibition in the production of the substitution product in the reaction of tributyltinlithium with organic bromides, when CO is present, indicates that electron transfer is involved in the substitution mechanism and that CO is a good one-electron acceptor competitor in that reaction. This conclusion is confirmed by the effect of radical scavengers and the yields of by-products arising from radical couplings and hydrogen abstraction from the solvent.

2.3. Experimental

2.3.1. Materials

Tetrahydrofuran and hexane were purified as previously described [23] and distilled from sodium benzophenone ketyl immediately prior to use. Tributyltinchloride (Merck) was used as-received. All halides were distilled prior to use.

2.3.2. General procedures

All reactions were carried out in a nitrogen-inert atmosphere. Solutions and solvents were transferred by syringes, under a stream of inert gas. Quantitative GC analyses were performed using a Hewlett Packard HP 5890 series II plus gas chromatograph equipped with a flame ionization detector and a HP-5 column; *n*-decane was used as an internal reference in all cases. A typical procedure employed a N_2 flow rate of 1.5 ml min^{-1} and a temperature programing from 70°C (held for 5 min) to 250 or 270°C (held for 10 min) at 10°C min^{-1}. The injection port was kept at 270°C, and the detector at 300°C. All product yields were obtained by GC. NMR spectra were recorded in $CDCl_3$ solution with tetramethylsilane as reference, using a Brucker 200 spectrometer. Mass spectra were recorded using a BG Trio-2 mass spectrometer. The isolation of the compounds was made by reverse-phase chromatography, using CH_2Cl_2 and CH_3CN as eluents.

2.3.3. Lithium Tributyltin

Bu_3SnLi was synthesized by a modification of a method described in Ref. ([18]b). Lithiumtributyltin was prepared by cutting lithium wire (25 mmol) into small pieces into a flask containing boiling THF (16 ml), the flask was capped with a nonair stopper and kept at 0°C. Tributyltinchloride (2 ml, 5 mmol) was syringed into the flask and kept for 4 h at 0°C. The mixture was then kept at 4–6°C until used. The concentration of the solution of Bu_3SnLi was typically 0.35–0.45 M. This determination was made by Gilman's double titration method. The total amount of tin present was determined by quenching a 1-ml aliquot of the solution of Bu_3SnLi with excess *n*-butyl chloride at 0°C and CG analyses of the reaction mixture.

2.3.4. Reaction of halides with lithium tributyltin in the presence of CO

A vial containing a Teflon-coated stirring bar was capped with a nonair stopper, it was evacuated and filled with dry nitrogen alternatively several times, and then put into a bath at the appropriate temperature, with vigorous magnetic stirring. A solution of Bu_3SnLi in THF was added by a syringe, the solution was exposed to CO at ca. 1013 mbar for 30 min. Then aliquots of the halide in THF solution was added by a syringe during 90 min, under a CO atmosphere. The reaction was quenched by treating the reaction mixture with NH_4Cl (10%). When the radical trap PDNB was used (typically 10 mol%) it was added to the vial prior to the addition of Bu_3SnLi.

2.3.5. Bu_4Sn

EM; m/z (relative intensity): 291 (M^+-57) (46), 289 (34), 235 (72), 233 (55), 177 (93), 179 (100), 119 (36), 121 (45). ^{1}H-NMR ($CDCl_3$, δ ppm): 1.60–1.40 (m, 6H), 1.30–1.15 (m, 12H), 1.00–0.75 (m, 9H). ^{13}C-NMR ($CDCl_3$, δ ppm): 29.8, 27.4, 13.7, 8.8.

2.3.6. Bu_6Sn_2

EM; m/z (relative intensity): 525 (M^+-57) (16), 523 (14), 467 (16), 465 (14), 355 (46), 353 (43), 295 (21), 293 (20), 291(20), 239 (28), 235 (39), 179 (89), 177 (100), 121 (49), 119 (52). ^{1}H-NMR ($CDCl_3$, δ ppm): 1.55–1.51 (m, 12H), 1.50–1.35 (m, 12H), 1.30–1.15 (m, 12H), 1.00–0.75 (m, 19H). ^{13}C-NMR ($CDCl_3$, δ ppm): 28.8, 27.4, 13.7, 8.5.

2.3.7. $Bu_3SnC_6H_5$

EM; m/z (relative intensity): 311 (M^+-57) (64), 309 (49), 255 (80), 253 (61), 197 (100), 195 (89), 120 (30). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.50–7.49 (m, 2H), 7.35–7.33 (m, 3H), 1.62–1.60 (m, 6H), 1.41–1.38 (m, 6H), 1.15–1.12 (m, 6H), 0.98–0.80 (m, 9H). ^{13}C-NMR ($CDCl_3$, δ ppm): 142.0, 136.0, 127.0, 29.1, 27.4, 13.7, 9.6.

2.3.8. $Bu_3SnCH_2C_6H_5$

EM; m/z (relative intensity): 325 (M^+-57) (5), 291 (41), 289 (30), 235 (57), 233 (45), 179 (100), 177 (94), 121 (51), 119 (45), 91 (54). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.24–7.20 (m, 2H), 7.16–7.01 (m, 3H), 2.35 (s, 2H), 1.60–1.22 (m, 12H), 0.99 0.82 (m, 15H). ^{13}C-NMR ($CDCl_3$, δ ppm): 128.3, 127.0, 122.9, 29.1, 27.3, 18.2, 13.64, 9.36.

2.3.9. $Bu_3SnC_6H_{11}$

EM; m/z (relative intensity): 317 (M^+-57) (17), 315 (13), 291 (34), 289 (24), 261 (33), 259 (24), 235 (57), 233 (45), 179 (100), 177 (90), 121 (51), 119 (42). ^{1}H-NMR ($CDCl_3$, δ ppm): 1.40–1.20 (m, 23H), 1.05–0.70 (m, 15H). ^{13}C-NMR ($CDCl_3$, δ ppm): 30.6, 29.3, 29.08, 27.6, 25.6, 13.6, 10.0, 7.8.

2.3.10. $Bu_3SnC_3H_5$

EM; m/z (relative intensity): 275 (M^+-57) (10), 235 (57), 233 (40), 179 (100), 177 (90), 121 (50), 119 (47). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.02–5.88 (m, 1H), 4.84–4.63 (m, 2H), 1.81–1.77 (m, 1H), 1.60–1.40 (m, 6H), 1.35–1.10 (m, 12H), 1.10–0.60 (m, 10H). ^{13}C-NMR ($CDCl_3$, δ ppm): 138.1, 109.1, 30.6, 29.1, 27.3, 13.6, 9.13.

2.3.11. $C_6H_5CH_2CH_2C_6H_5$

EM; m/z (relative intensity): 182 (M^+) (17), 91 (100), 77 (4). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.18–7.16 (m, 8H), 7.12–7.09 (m, 12H), 2.57–2.60 (m, 4H). ^{13}C-NMR ($CDCl_3$, δ ppm): 144.2, 128.5, 127.9, 125.7, 28.9.

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