

Design of Polyaromatic Hydrocarbon-Supported Tin Reagents: A New Family of Tin Reagents Easily Removable from Reaction **Mixtures**

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We report in this paper the preparation and use of stannanes **11**, **12a**, and **12b**, compounds whose 3-pyrenylpropyl side chain affinity for activated carbon simplifies tin removal and product isolation. Our pyrene-supported reagents can be used for radical reductions and cyclizations (11), radical and cationic allylations (12a), and Stille couplings (12b) in much the same way as tributyltin derivatives.

Introduction

The usefulness of tin reagents in chemistry is broadly acknowledged, and to date, most radical reactions are still conducted using tin hydrides despite the problems of separation, tin toxicity, and tin disposal. Indeed, radical chemists have been addressing the problem of purification of radical reaction mixtures for more than 10 years. The methods using tin hydride substitutes such as silanes or thiols, for example, as well as special workup procedures allowing for removal of tin have been reviewed by Studer and Amrein recently.¹

The fashionable technique to overcome difficulties associated with the removal of excess reagent and reagent-derived side products in general is to use a polymer-supported reagent.² However, such supported reagents are usually insoluble, and therefore, reactions have to be performed under heterogeneous conditions. Furthermore, although such tin reagents have been synthesized and used with some success,³⁻¹³ most of the

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reactions require excesses of reagents on resin support and up to 3-4 equiv of AIBN.

As for our concern, we prospected for alternative soluble tin hydrides that might allow easy removal of tin residues from reaction mixtures. Regarding liquid-phase supported reagents, the innovation lies mostly with the way reagent-derived side products are separated. A few of these tin reagents designed with modified alkyl chains have been reported previously. The methods of Breslow,^{14,15} Gaston,¹⁶ Vedejs,¹⁷ Yoshida,¹⁸ and Collum¹⁹ all use the side chain of a modified tin reagent as a water-,¹⁴⁻¹⁶ acid-,^{17,18} or base-soluble¹⁹ handle for purification of reaction mixtures. Polar pyridylstannane described by Clive could be easily separated by chromatography when radical reduction led to nonpolar compounds,²⁰ and the second method of Clive uses a lipophilic tin hydride unstable under basic and acidic conditions.²¹ Once decomposed, the tin residues may be removed by extraction with water. The method of Bergbreiter²² and Enholm²³ and the method of Curran²⁴ all attach the molecule of interest to a solubility control device to remove the undesired material from the reaction mixtures. In the former cases,

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tin is linked to soluble polymeric supports that can precipitate upon cooling or addition of organic cosolvents. In the latter case, a fluorous phase soluble unit allows for selective liquid—liquid extraction of the undesired fluorous reagent derived side products from reaction mixtures.

With the handle concept in mind, we sought a group that would have a strong affinity for activated carbon, strong enough to allow separation on demand.²⁵ Such a group should be soluble in organic solvents to allow for immediate use of standard radical chemistry solutionphase procedures. Herein, we describe our work on the use of polyaromatic hydrocarbons (PAHs) as soluble supports for tin reagents and demonstrate how undesired side products can be efficiently removed from reaction mixtures by simple treatment with activated carbon.

Results and Discussion

At first, we concentrated our efforts on the use of Ramage's 17H-tetrabenzo[a, c, g, i]fluorenyl (Tbf) moiety as a polyaromatic tag. Originally, the tetrabenzofluorenylmethyl oxycarbonyl group (Tbfmoc) was designed as an Fmoc-related protecting group and its affinity for charcoal has been used in the purification of peptides, proteins, and oligonucleotides.^{26–29} Later on, Tbf was also used as an anchor group for solution phase supported organic synthesis, and this work was illustrated by the preparation of the quinolone antibacterial ciprofloxacin.³⁰ With regard to supported synthesis, the authors recommended to choose a 10-carbon alkyl chain as a spacer between the Tbf moiety and the substrate to limit any steric effects which the bulky Tbf group may impart.

Preparation and alkylation of Tbf has been very well described³⁰ and can be easily reproduced. In the synthesis of Tbf, two regioisomers may be obtained, one with an endo double bond and the other one with an exo double bond. The former is the kinetic isomer, and the latter is the thermodynamic one. Rearrangement occurs spontaneously upon heating in the rotary evaporator, but both isomers react in the same way and give the same product in the alkylation reaction. 10-Bromodec-1-ene and 1,10-dibromodecane were treated with Tbf carbanion. This gave the desired products **1a** and **1b**, respectively, in good yields. Unfortunately, many efforts to incorporate tin starting from **1a** or **1b** remained unsuccessful (Scheme 1).

For example, attempted radical addition of Bu₂SnHCl, generated in situ by mixing an equimolar amount of dibutyltin dihydride and dibutyltin dichloride, resulted in no reaction, while we successfully accomplished this transformation with simple alkenes (vide infra).³¹ Starting material **1a** was also recovered unchanged upon attempted palladium-catalyzed addition of dibutylphen-

SCHEME 1^a



^a Reagents and conditions: (a) tetrabutylammonium hydroxide, dioxane; R-Br, dioxane, 95 °C (**1a**, 80%; **1b**, 62%); (b) NaI (15 equiv), acetone, 50 °C, 12 h (98%, **1c/1b** = 9/1); (c) Bu₂SnHCl, AIBN, CH₂Cl₂; (d) Bu₂SnHPh, Pd(OH)₂/C; (e) Bu₂SnHLi, THF.

SCHEME 2^a



^{*a*} Reagents and conditions: (a) Bu_2SnHPh (1.5 equiv), $Pd(OH)_2/C$ (17%); (b) TsCl, pyridine (88%); (c) Tbf/tetrabutylammonium hydroxide, dioxane (46%); (d) I_2 , BuOH; NaBH₄.

yltin hydride (Lautens' procedure).³² Finally, halides substitutions with Bu₂SnHLi³³ starting either from **1b** or **1c** were also unsuccessful and led to decomposition upon forcing conditions. Apparently, the presence of the Tbf group on one side seems to preclude addition at the other end of the alkyl chain, even with a 10-carbon spacer. Even the Finkelstein reaction with NaI on **1b** proved unexpectedly slow and was not completed after 12 h at reflux in the presence of a large excess of salt. In addition, attempted transformation of **1c** into the related alkyllithium with *t*-BuLi³⁴ resulted in extensive decomposition of the starting material. A new route to the desired tin hydride was sought, which would not require incorporation of tin after ω -alkylation with the Tbf carbanion.

1-Decen-10-ol was regioselectively hydrostannated with the tin moiety placed at the terminus following Lautens' procedure (Scheme 2).³² However, the yield of hydrostannation was low and the purification was very tedious when the reaction was conducted with Bu₂SnHPh. The five-step route to the Tbf-supported tin hydride eventually led to the preparation of the desired compound **4** in a very small amount and proved very difficult to scaleup.

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 a Reagents and conditions: (a) Bu_2SnHCl, AIBN, CH_2Cl_2; NaBH_3CN, t-BuOH, reflux (56%).

Owing to the difficulties associated with the preparation of a Tbf-supported tin hydride on large scale, we sought other polyaromatic hydrocarbons with good affinity for activated carbon. We found that pyrene is known to exhibit strong affinity for other large aromatic systems such as carbon nanotubes³⁵⁻³⁷ or activated carbon.^{38,39} Besides, while our work was in progress, Warmus and Da Silva's report confirmed the good potential of pyrene as a soluble support for the preparation of a pyrene-supported scavenger reagent for electrophiles.⁴⁰ When we decided to start working with pyrene, we first evaluated the relative affinity of alkylpyrenes, alkylphenanthrenes and alkyl-Tbf for activated carbon. It was found that alkylpyrenes were always adsorbed faster and more efficiently than the corresponding alkylphenanthrenes or alkyl-Tbf.

Stannane **6** can be prepared straightforwardly following the route summarized in Scheme 3. Allylpyrenylmethyl ether **5** is readily available on large scale starting from commercially available pyrenemethanol. It can be regioselectively hydrostannated in the presence of dibutyltin hydrochloride under radical conditions, and the resulting trialkyltin chloride can be reduced in situ to generate the desired tin hydride **6** in 56% unoptimized yield over two steps.

We discovered that pyrene-supported tin hydride **6** successfully reduces alkyl halides under radical conditions. Unfortunately, removal of the resulting tin halides from crude reaction mixtures was not satisfactory. Indeed, the workup with activated carbon (2 g of carbon per mmol of tin) did not yield tin-free material, and we observed that product recovery became complicated and low yielding if much larger quantities of carbon were used in reaction workup. Instead, we envisioned dropping the relative proportion of aliphatic carbons in our supported tin hydride.

Therefore, stannane **11** was designed with the smallest possible alkyl substituents on tin, i.e., methyl groups, and with the shortest possible spacer between the tin and the pyrene moiety. Aryltin hydrides (no spacer) are sensitive and their reactivity is tempered by the delocalization of tin-centered radical into the π -system,⁴¹ and arylmethyl-(one-carbon spacer)⁴² or 2-arylethyltin hydrides (two-

^a Reagents and conditions: (a) $(EtO)_2(O)PCH_2CO_2Et/NaH$ (88%); (b) NaBH₄/CoCl₂ (94%); (c) LiAlH₄ (96%); (d) PPh₃/I₂/imidazole (77%); (e) methanesulfonyl chloride, NEt₃ (85%); (f) Me₆Sn₂/MeLi (quant from 8a, 73% from 8b); (g) I₂/CHCl₃ then NaBH₄/MeOH (67%).

carbon spacer)¹¹ are not very stable over time and under radical conditions. The choice of a three-carbon spacer appeared to be the best balance between a good similarity with tributyltin hydride, good stability, and the minimal number of aliphatic carbons.

Stannane 11 may be prepared in a straightforward manner from commercially available pyrene carboxaldehyde 7 following the route summarized in Scheme 4. Wittig-Horner olefination followed by reduction of the double bond with NaBH₄/CoCl₂⁴³ yielded ester **8**. Iodide **9** was obtained in two steps from **7** by reduction with LiAlH₄ and transformation of the resulting primary alcohol with I₂/PPh₃. Alternatively, the alcohol was also transformed into its methanesulfonic ester; this route was found more convenient on larger scale because the mesylate can be purified by crystallization. Substitution of the primary iodide or mesylate in 9 with trimethylstannyllithium⁴⁴ afforded tetraalkylstannane **10** in very good yield. Treatment of 10 with exactly 1 equiv of I2 replaces one methyl group selectively. The desired tin hydride was finally obtained as a white solid after reduction with sodium borohydride. Compound 11 is reasonably stable since it was recovered unchanged after several months at -15 °C (freezer).

Reagent **11** may be used for tin hydride mediated radical reactions in much the same way as tributyltin hydride. We have evaluated its performance in the reduction of various alkyl halides, as exemplified in Table 1.

Yields are comparable to those obtained with tributyltin hydride mediated reactions, and workup with activated carbon is quite straightforward and afforded essentially pure products in all cases (see the Experimental Section). Indeed, integration of the ¹H NMR spectra allowed us to evaluate the amount of residual tin derivative which was found always to be below 2 mol % and not even detectable in some samples (Table 1, entries 1, 2, 5, and 6). Product of typical free radical

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^{*a*} Standard procedure: **11** (1.2 equiv), AIBN, benzene, reflux. ^{*b*} Catalytic procedure: NaBH₃CN, **11** (0.1 equiv), tBuOH, reflux. ^{*c*} Only traces (<2%) of uncylized product were detected from the ¹H NMR spectrum of the crude reaction mixture. ^{*d*} Photochemical initiation: **11**, AIBN, benzene, *hv*, room temperature. ^{*e*} Measured by ICP-MS analysis.

reduction depicted in entry 4 was tested for tin pollution using ICP-MS analysis. Before any further purification, we obtained 0.31% of elemental tin in the sample resulting from treatment with activated carbon. If tin impurity is the pyrene-supported tin iodide, then the relative proportion product/tin derivative is 168:1 (99.4:0.6). We can conclude from this measurement that treatment with activated carbon is able to remove more than 99% of tin byproducts.

Unfortunately, reagent recovery from activated carbon is low-yielding.²⁵ On the other hand, we were pleased to discover that the use of a catalytic amount of 11 following the procedure described by Stork successfully reduced methyl 2-bromo-2-phenylacetate (entry 1).⁴⁵ In addition, attempted classical cyclizations of an aryl radical led to the expected benzodihydrofuran in good yields (entries 5 and 6). The photochemically activated cyclization reaction was also successful (entry 6). Considering how small the relative proportion of uncyclized product was in these reactions, we wondered what might be the rate constant of radical reduction with **11** as compared to that with tributyltin hydride. Indeed, the same radical reaction (entry 5) conducted with tributyltin hydride under the same experimental conditions also led to the formation of cyclized product containing only trace amount of allyl-phenyl ether. Although the very low relative proportion of uncyclized product does not allow for accurate measurement of the reduction rate of the aryl radical, we hypothesized that the order of reactivity of Me₃SnH, 11 and Bu_3SnH with alkyl radicals is $Me_3SnH < 11 <$ Bu₃SnH. Therefore, since Me₃SnH will react in general about 0.4 times as fast as Bu₃SnH,⁴⁶ we concluded that the rate constant of reduction with 11 must be in most cases within the same order of magnitude than that with tributyltin hydride.





^a Reagents and conditions: (a) I_2 , CDCl₃; (b) allyl-MgBr, THF (**12a**, 92% for two steps); (c) PhLi, THF (**12b**, 62% for two steps).

 TABLE 2.
 Allylations with 12a and Stille Couplings with 12b

Entry	Substrate	Reaction conditions	Product	lsolated Yield (%)	Sn content (% w/w)
1	Br Ph CO ₂ Me	12a , AIBN benzene, reflux	Ph CO ₂ Me	86%	0.37
2	Br	12a , AIBN benzene, reflux		86%	0.77
3	NC	12a , BF ₃ .OEt _{2,} CH ₂ Cl ₂	OH NC	≈ 90%	0.20
4	MeO	12b, PdCl ₂ (dppf), CD ₃ OD, NBu ₃	MeO Ph	59%	
5	HO	12b , PdCl ₂ (dppf), CD ₃ OD, NBu ₃	HO	74%	
6	NO ₂	12b , PdCl ₂ (dppf), CD ₃ OD, NBu ₃	Ph NO ₂	95%	

Our success in the design and use of pyrene-supported tin hydride **11** prompted us to investigate related tin reagents such as allyltrialkyltin for use in radical,⁴⁷ or cationic allylations,⁴⁸ or aryltrialkyltin for use in Stille coupling.⁴⁸ Such stannanes may be prepared straightforwardly from **10** by treatment with 1 equiv of iodine, followed by trapping of the intermediate tin iodide with the desired organometallic reagent (Scheme 5).

We were pleased to discover that radical and cationic allylations with **12a** give good yields in the desired products (Table 2, entries 1–3) and, more importantly, that these products could be purified by treatment with activated carbon. It can be seen from Table 2 that the palladium-catalyzed Stille couplings with aryl iodides were also successful (entries 4–6). In all these reactions, ¹³C NMR and ¹H NMR indicated no contamination by tin byproducts (<2 mol %). This observation was further confirmed by ICP-MS analysis, which provided the same very low values for tin pollution as that obtained for radical reduction.

In conclusion, we have reported in this paper the preparation and use of stannanes **11**, **12a**, and **12b**, compounds whose 3-pyrenylpropyl side chain simplifies tin removal and product isolation. Although further

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purification may be compulsory if the radical reaction product is meant for biological assays, the purification method with activated carbon is very fast and efficient. It gives satisfying results for organic chemistry purposes. Our work provides a prototype for rendering a tin reagent pyrene-supported and pyrene may now be regarded as a viable alternative to reticulated polystyrene.

Experimental Section

¹H NMR spectra were recorded at 200 or 300 MHz and ¹³C NMR spectra at 75.5 or 100.6 MHz as indicated. Chemical shifts (δ) are in ppm downfield from tetramethylsilane, and coupling constants (*J*) are in Hz (s stands for singlet, d for doublet, t for triplet, q for quadruplet, quint for quintuplet, and m for multiplet). Satellite signals in NMR refer to distinguishable signals obtained for ¹¹⁷Sn and ¹¹⁹Sn (spin = ¹/₂), the natural abundance of which is 7.7 and 8.6%, respectively. All solvents were dried and distilled by standard techniques. Activated carbon was purchased from Aldrich (Darco KB-B, 27,810-6).

3-Pyren-1-ylpropionic Acid Ethyl Ester (8). Sodium hydride (0.15 mol) was added portionwise to a solution of triethylphosphonoacetate (28.5 g, 0.127 mol) in THF (300 mL) at 0 °C. The mixture was stirred for 1 h at 0 °C. 1-Pyrenecarboxaldehyde (20.93 g, 0.091 mol) in THF (150 mL) was slowly added. The resulting solution was stirred for one night at room temperature. The mixture was diluted with a 10% HCl solution, extracted three times with toluene, washed with water, dried (MgSO₄), and concentrated. The desired 3-pyren-1-ylacrylic acid ethyl ester (22.3 g, 81% yield) precipitated upon trituration of the crude mixture in MeOH. Spectral data were identical to those previously described in the literature (CAS Registry No.: 82979-68-8):⁴⁹ ¹H NMR (CDCl₃, 300 MHz) δ 1.41 (t, 3H, J = 7.2), 4.36 (q, 2H, J = 7.2), 7.70 (d, 1H, J = 15.7), 8.20-8.30 (m, 8H), 8.47 (d, 1H, J = 9.3), 8.81 (d, 1H, J = 15.7); $^{13}\mathrm{C}$ NMR (CDCl₃, 75.5 MHz) δ 14.8, 61.0, 120.7, 122.9, 124.2, 124.6, 125.0, 125.3, 125.4, 126.2, 126.4, 126.7, 127.7, 128.7, 128.9, 130.1, 131.1, 131.7, 133.0, 167.5.

Sodium borohydride (5.6 g, 0.148 mol) was added to a solution of the α , β -unsaturated ester (22.26 g, 0.074 mol) and cobalt chloride hexahydrate (5.87 g, 0.024 mol) dissolved in a mixture of MeOH and THF 7/4 (550 mL). The solution was stirred for 48 h at room temperature. After concentration, the residue was diluted with a 1 N aqueous HCl, and the aqueous layer was extracted three times with toluene. The combined organic fractions were washed with water, dried (MgSO₄), and concentrated. Compound 8 (21.47 g, 96% yield) was precipitated by trituration of the crude residue in MeOH. Spectral data were identical to those previously described in the literature (CAS Registry No.: 83671-44-7):50 1H NMR (CDCl₃, 300 MHz) δ 1.36 (t, 3H, J = 7.2), 2.82 (t, 2H, J = 7.7), 3.68 (t, 2H, J=7.7), 4.25 (q, 2H, J=7.2), 7.86 (d, 1H, J=7.9), 7.95-8.28 (m, 7H), 8.27 (\hat{d} , 1H, J = 9.3); ¹³C NMR (CDCl₃, 75.5 MHz) δ 15.0, 29.5, 37.0, 61.4, 123.7, 125.6, 125.7, 125.8, 125.9, 126.7, 127.6, 127.8, 128.3, 128.4, 129.4, 130.9, 131.6, 132.2, 135.4, 173.8

3-Pyren-1-ylpropan-1-ol. To a solution of ester **8** (21.47 g, 0.071 mol) in THF (200 mL) was added AlLiH₄ (3.76 g, 0.099 mol). The solution was stirred for 4 h at room temperature. After dilution with toluene, the reaction mixture was carefully hydrolyzed with 1 N aqueous HCl. The aqueous phase was extracted twice with toluene, and the combined organic layers were washed with brine and dried (MgSO₄). The solution was concentrated to give the desired primary alcohol (18.49 g, 100% yield). Spectral data were identical to those previously de-

scribed in the literature (CAS Registry No.: 61098-94-0);⁵¹ ¹H NMR (CDCl₃, 300 MHz) δ 2.10 (m, 2H), 3.42 (t, 2H, J = 7.6), 3.76 (t, 2H, J = 6.3), 7.87 (d, 1H, J = 7.9), 7.94–8.18 (m, 7H), 8.29 (d, 1H, J = 9.4); ¹³C NMR (CDCl₃, 75.5 MHz) δ 30.4, 35.3, 63.1, 124.1, 125.6, 125.7, 125.7, 125.8, 125.9, 126.6, 127.4, 128.0, 128.1, 128.3, 129.5, 130.7, 131.7, 132.2, 137.0.

1-(3-Iodopropyl)pyrene (9a). Iodine (1.35 g, 5.32 mmol) was added to a solution of PPh3 (1.395 g, 5.32 mmol) and imidazole (362 mg, 5.32 mmol) in dichloromethane (8 mL) at 0 °C. After 20 min stirring, 3-pyren-1-ylpropan-1-ol (1 g, 3.8 mmol) dissolved in dichloromethane (5 mL) was added. The resulting solution was stirred for 3 h at room temperature, diluted with water, washed successively with a 1 N aqueous Na₂S₂O₃ solution and brine, and then dried with MgSO₄. The solvent was removed in vacuo, and the crude material was subjected to column chromatography on silica gel (pentane/ dichloromethane, 95:5) to give 9a (1.09 g, 77% yield): ¹H NMR (CDCl₃, 300 MHz) δ 2.37 (quint, 2H, J = 7.2), 3.35 (t, 2H, J =7.2), 3.45 (t, 2H, J = 7.2), 7.90 (d, 1H, J = 7.9), 7.94–8.20 (m, 7H), 8.29 (d, 1H, J = 9.4); ¹³C NMR (CDCl₃, 75.5 MHz) δ 7.6, 34.7, 35.9, 123.9, 125.6, 125.7, 125.8, 125.9, 125.9, 126.7, 127.6, 128.2, 128.3, 129.5, 130.9, 131.7, 132.2, 135.4; MS (FAB+, NBA matrix) *m*/*z* 370 (M⁺, 100), 215 (PyreneCH₂⁺, 75);. HRMS calcd for C₁₉H₁₅I⁺ (M⁺) 370.0219, found 370.0231.

Methanesulfonic Acid 3-Pyren-1-ylpropyl Ester (9b). To a solution of 3-pyren-1-ylpropan-1-ol (7.0 g, 26.6 mmol) and triethylamine (3.54 g, 34.9 mmol) in dichloromethane (100 mL) at -10 °C was added methanesulfonyl chloride (3.69 g, 32.2 mmol). The reaction mixture was allowed to warm slowly to room temperature and was then diluted with water, washed with 1 N aqueous HCl and brine, and dried with MgSO4. Pure **9b** (7.62 g, 85% yield) solidified by trituration of the crude residue with MeOH: ¹H NMR (CDCl₃, 300 MHz) δ 2.32 (m, 2H), 3.50 (t, 2H, J = 7.4), 4.32 (t, 2H, J = 6.2), 7.87 (d, 1H, J = 7.9), 7.96–8.19 (m, 7H), 8.25 (d, 1H, J = 9.3); ¹³C NMR (CDCl₃, 75.5 MHz) δ 29.6, 31.3, 37.8, 69.7, 123.3, 125.3, 123.3, 125.5, 126.4, 127.3, 127.7, 127.9, 128.1, 129.1, 130.6, 131.2, 131.8, 134.8.

Trimethyl(3-pyren-1-ylpropyl)stannane (10). Methyllithium (9.4 mL, 15 mmol) was added dropwise to a solution of hexamethylditin (3.11 mL, 15 mmol) in dry and degassed THF (30 mL) at –40 °C. The reaction mixture was allowed to warm slowly to -20 °C (45 min) and was then cooled to -80°C. The iodide (3.72 g, 10 mmol) was added in one portion, and the reaction mixture was allowed to warm to room temperature overnight. Alumina was added, the solvent was evaporated, and the desired product 10 was obtained after alumina column chromatography (hexane) (4.08 g, quant). Alternatively, we found accidentally that nice crystals may be obtained from recrystallization in hexane (reflux to -20 °C). The same procedure applied to 9b (3.70 g, 10.9 mmol) instead of 9a also yielded the desired tetraalkylstannane (3.25 g, 73% yield): ¹H NMR (CDCl₃, 300 MHz) δ 0.10 (s, 9H) (satellite signals: (d, ${}^{2}J_{H-Sn} = 51$), (d, ${}^{2}J_{H-Sn} = 52$)), 1.00 (m, 2H), 2.05 (m, 2H), 3.35 (pseudo t, 2H, J = 7.7), 7.87 (d, 1H, J = 7.7), 8.01 (t, 1H, J = 7.7), 8.03 (AB spectrum, 2H, J = 8.9), 8.08-8.18 (m, 4H), 8.29 (d, 1H, J=9.5); ¹³C NMR (CDCl₃, 75.5 MHz) δ -9.4 (satellite signals: (d, ${}^{1}J_{C-Sn} = 321$), (d, ${}^{1}J_{C-Sn} = 307$)), 12.1 (satellite signals: (d, ${}^{1}J_{C-Sn} = 356$), (d, ${}^{1}J_{C-Sn} = 341$)), 30.2 (satellite signals: (d, ${}^{3}J_{C-Sn} = 18$), 38.9 (satellite signals: $(d, {}^{2}J_{C-Sn} = 63), 124.3, 125.4, 125.5, 125.6, 125.9, 126.6, 127.3,$ 127.9, 128.2, 128.3, 129.4, 130.5, 131.7, 132.3, 137.7; MS (FAB+, NBA matrix) m/z 408 (M⁺, 2.3, tin isotopic pattern), 393 and 391 (Pyrene(CH₂)₃SnMe₂⁺, 67 and 52%, respectively, tin isotopic pattern), 215 (PyreneCH₂⁺, 100); HRMS calcd for $C_{22}H_{24}^{120}Sn^+$ (M⁺) 408.0904, found 408.0913.

Dimethyliodo(3-pyren-1-ylpropyl)stannane. Iodine (405 mg, 1.6 mmol) was added in one portion at 0 °C to a solution of **10** (650 mg, 1.6 mmol) in CHCl₃ (10 mL). The reaction

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mixture was allowed to warm slowly to room temperature overnight. After evaporation of the solvent, ¹H NMR showed that the expected product was formed in nearly quantitative yield. The tin iodide was pure enough and was therefore used without further purification: ¹H NMR (CDCl₃, 300 MHz) δ 0.85 (s, 6H) (satellite signals: (d, $^2J_{\rm H-Sn}=54$), (d, $^2J_{\rm H-Sn}=52$)), 1.57 (m, 2H), 2.20 (m, 2H), 3.42 (pseudo t, 2H, J=7.6), 7.87 (d, 1H, J=7.9), 7.99 (t, 1H, J=7.6), 8.03 (s, 2H), 8.09–8.19 (m, 4H), 8.28 (d, 1H, J=9.3); ¹³C NMR (CDCl₃, 75.5 MHz) δ -1.5 (satellite signals: (d, $^1J_{\rm C-Sn}=322$), (d, $^1J_{\rm C-Sn}=307$)), 18.3 (satellite signals: (d, $^1J_{\rm C-Sn}=368$), (d, $^1J_{\rm C-Sn}=351$)), 29.8 (satellite signals: (d, $^3J_{\rm C-Sn}=24$)), 37.7 (satellite signals: (d, $^2J_{\rm C-Sn}=75$)), 124.2, 125.6, 125.7, 125.8, 125.8, 125.9, 126.7, 127.6, 128.2, 128.3, 129.5, 130.8, 131.7, 132.3, 137.6; HRMS calcd for C₂₁H₂₁I¹²⁰Sn⁺ (M⁺) 519.9714, found 519.9717.

Dimethyl(3-pyren-1-ylpropyl)stannane (11). The crude iodide (1.6 mmol) was dissolved in methanol (40 mL) and placed under argon at 0 °C. Sodium borohydride (61 mg, 1.6 mmol) was added, and after 30 min, the reaction mixture was dissolved in EtOAc (40 mL) and water (20 mL). The aqueous layer was discarded, and the organic phase was further washed three times with water and dried (MgSO₄). The solvent was removed in vacuo, and the crude material was subjected to flash column chromatography on neutral Al₂O₃ (pentane) to give **11** (420 mg, 67%): ¹ \hat{H} NMR (C₆D₆, 300 MHz) δ 0.20 (s, 6H) (satellite signals: (d, ${}^{2}J_{H-Sn} = 57$), (d, ${}^{2}J_{H-Sn} = 53$)), 1.02 (m, 2H), 2.08 (m, 2H), 3.29 (t, 2H, J = 7.4), 4.98 (broad. s, 1H), 7.81 (d, 1H, J = 7.9), 7.86 (t, 1H, J = 7.4), 7.92 (AB spectrum, 2H, J = 9.1), 7.98-8.08 (m, 4H), 8.29 (d, 1H, J = 9.3); ¹³C NMR (C₆D₆, 75.5 MHz) δ –12.0 (satellite signals: (d, ${}^{1}J_{C-Sn} = 326$), (d, ${}^{1}J_{C-Sn} = 318$)), 10.2 (satellite signals: (d, ${}^{1}J_{C-Sn} = 376$),(d, ${}^{1}J_{C-Sn} = 359$)), 30.6 (satellite signals: (d, ${}^{3}J_{C-Sn} = 20$), 38.6 (satellite signals: (d, ${}^{2}J_{C-Sn} = 58$)), 124.3, 125.6, 125.7, 125.8, 126.3, 126.4, 126.6, 127.5, 128.1, 128.5, 129.8, 130.9, 132.0, 132.5, 137.3; MS (FAB+, NBA matrix) m/z 393 ($[M - H]^+$, 56, tin isotopic pattern), 379 and 377 (Pyrene-(CH₂)₃SnMeH⁺, 25 and 16, respectively, tin isotopic pattern), 215 (PyreneCH₂⁺, 100); HRMS calcd for $C_{21}H_{21}^{120}Sn^+$ ([M -H]⁺) 393.0669, found 393.0651.

General Procedure for Radical Reduction (11 Stoichiometric/AIBN/Benzene). Under inert atmosphere, a solution of substrate (0.2 mmol), **11** (1.2 equiv), and AIBN (0.1 equiv) in dry degassed benzene (1–2 mL) was stirred under reflux for 1 h (TLC monitoring). The mixture was cooled and evaporated. Methanol/dichloromethane 3/2 (4 mL) was added to the residue immediately followed by activated carbon (800 mg). The suspension was stirred for 30 min (the adsorption of pyrene derivatives was monitored by UV spectroscopy of the supernatant). After filtration, the activated carbon was washed with MeOH and the combined filtrates were evaporated, allowing isolation of the radical reaction product in essentially pure form.

Allyldimethyl(3-pyren-1-yl-propyl)stannane (12a). Intermediate tin iodide (dimethyliodo(3-pyren-1-ylpropyl)stannane) was prepared prior to being needed in the same way as described for the synthesis of tin hydride 11. Crude tin iodide (2.39 mmol) was dissolved in dry degassed THF (10 mL), and the solution was placed under argon at -78 °C. Allylmagnesium bromide (4.78 mL of a 1.0 M solution in diethyl ether, 4.78 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight. After dilution with toluene, the reaction mixture was hydrolyzed with water and extracted twice with toluene. The combined organic fractions were washed with brine and dried (MgSO₄). The solvent was removed in vacuo, and the crude material was subjected to flash column chromatography on neutral Al₂O₃ (pentane) to give **12a** (950 mg, 92%): ¹H NMR (C₆D₆, 300 MHz) δ 0.15 (s, 6H) (satellite signals: (d, ${}^{2}J_{H-Sn} = 49$), (d, ${}^{2}J_{H-Sn} = 51$)), 1.00 (m, 2H), 1.80 (d, 2H, J = 8.6), 2.07 (m, 2H), 3.29 (pseudo t, 2H, J = 7.6), 4.84 (bd, 1H, J = 10.0), 4.97 (bd, 1H, $\hat{J} = 10.0$), 6.00 (ddt, 1H, J = 17.0, 10.0, 8.6), 7.82 (d, 1H, J = 17.07.7), 7.85 (t, 1H, J = 7.6), 7.90 (AB spectrum, 2H, J = 9.0), 7.98–8.06 (m, 4H), 8.29 (d, 1H, J = 9.3); ¹³C NMR (C₆D₆, 75.5 MHz) δ –11.3 (satellite signals: (d, ¹J_{C-Sn} = 310), (d, ¹J_{C-Sn} = 297)), 10.9 (satellite signals: (d, ¹J_{C-Sn} = 330), (d, ¹J_{C-Sn} = 345)), 17.6 (satellite signals: (d, ¹J_{C-Sn} = 283), (d, ¹J_{C-Sn} = 271)), 29.7 (satellite signals: (d, ³J_{C-Sn} = 19)), 38.5 (satellite signals: (d, ²J_{C-Sn} = 61)), 110.2 (satellite signals: (d, ²J_{C-Sn} = 49)), 123.9, 125.2, 125.3, 125.4, 125.9, 126.0, 126.2, 127.1, 127.7, 127.8, 128.0, 129.4, 130.5, 131.6, 132.1, 137.0, 137.8; MS (FAB+, NBA matrix) *m*/*z* 435 (MH⁺, 2.3, tin isotopic pattern), 393 (Pyrene(CH₂)₃SnMe₂⁺, 100, tin isotopic pattern), 215 (PyreneCH₂⁺, 55%); HRMS: calcd for C₂₄H₂₇¹²⁰Sn⁺ (MH⁺) 435.1135, found 435.1138.

General Procedure for Radical Allylation (Table 2, Entries 1 and 2). Under inert atmosphere, a solution of substrate (0.2 mmol), 12a (2 equiv), and AIBN (0.1 equiv) in dry degassed benzene (200 μ L) was stirred under reflux for 5 h (after 2 h, an additional portion of AIBN (0.1 equiv) was added). The mixture was cooled and evaporated. Methanol/ dichloromethane 3/2 (4 mL) was added to the residue immediately followed by activated carbon (800 mg). The suspension was stirred for 30 min (the adsorption of pyrene derivatives was monitored by UV spectroscopy). After filtration, the activated carbon was washed with MeOH and the combined filtrates were evaporated, allowing isolation of the radical reaction product in pure form.

General Procedure for Electrophilic Allylation. Under inert atmosphere, a solution of substrate (0.1 mmol) and 12a (2 equiv) in dry dichloromethane (2 mL) under argon was cooled to -78 °C. Boron trifluoride etherate (1 equiv) was added dropwise. The reaction mixture was allowed to warm to room temperature overnight. After dilution with an aqueous solution of sodium carbonate, the reaction was extracted twice with dichloromethane, and the combined organic fractions were washed with brine and dried (MgSO₄). After concentration, methanol/dichloromethane 3/2 (4 mL) was added to the residue immediately followed by activated carbon (800 mg). The suspension was stirred for 30 min (the adsorption of pyrene derivatives was monitored by UV spectroscopy). After filtration, the activated carbon was washed with MeOH and the combined filtrates were evaporated, allowing isolation of the allylation reaction product in pure form.

Dimethylphenyl(3-pyren-1-ylpropyl)stannane (12b). Iodine (203 mg, 0.8 mmol) was added in one portion to a 0 °C cooled solution of trimethylstannane (326 mg, 0.8 mmol) in CDCl₃ (10 mL). The reaction mixture was allowed to warm slowly to room temperature overnight. ¹H NMR showed that the expected iodide was formed in nearly quantitative yield. CDCl₃ was evaporated, the crude tin iodide was dissolved in dry and degassed THF (4 mL), and the solution was cooled to -80 °C. A PhLi solution (prepared by adding BuLi (1.4 M, 1.15 mL, 1.6 mmol) over PhI (179 μ L, 1.6 mmol) in THF (2.5 mL) at -80 °C and stirring for 30 min) was added dropwise to the tin iodide solution. The reaction mixture was allowed to warm to room temperature overnight, neutral alumina was added, and the THF was evaporated. Column chromatography over neutral alumina (hexane) allowed isolation of the desired product 12b as a viscous colorless oil (233 mg, 62%): $\,^1\!H$ NMR (CDCl₃, 200 MHz) δ 0.48 (s, 6H) (satellite signals: (d, ²J_{H-Sn} = 53), (d, ${}^{2}J_{H-Sn} = 51$)), 1.29 (m, 2H), 2.16 (m, 2H), 3.40 (broad t, 2H, J = 7.7), 7.35-7.46 (m, 3H), 7.51-7.60 (m, 2H), 7.87 (d, 1H, J = 7.8), 8.07 (s, 2H), 7.99-8.28 (superimposed m, 6H); ¹³C NMR (CDCl₃, 100.6 MHz) δ –10.2 (satellite signals: (d, ${}^{1}J_{C-Sn} = 334$), (d, ${}^{1}J_{C-Sn} = 320$)), 11.8 (satellite signals: (d, ${}^{1}J_{C-Sn} = 368$), (d, ${}^{1}J_{C-Sn} = 351$)), 29.6 (satellite signals: (d, ${}^{3}J_{C-Sn} = 19)$), 38.4 (satellite signals: (d, ${}^{2}J_{C-Sn} = 62)$), 123.9, 125.0, 125.1, 125.2, 125.5, 126.2, 126.9, 127.5, 127.8, 127.9, 128.6, 128.7, 129.1, 130.2, 131.3, 131.9, 136.5 (satellite signals: (d, ${}^{2}J_{C-Sn} = 34$), 137.1, 142.2; MS (FAB+, NBA matrix) m/z 470 (C₂₇H₂₆¹²⁰Sn⁺ (M⁺), 10, isotopic pattern of tin), 455 and 453 ($C_{26}H_{23}^{120}$ Sn, 55, and $C_{26}H_{23}^{118}$ Sn, 45, respectively, isotopic pattern of tin $(M^+ - CH_3)$), 393 and 391 $(C_{21}H_{20}^{120}Sn$, 50, and $C_{21}H_{20}^{118}$ Sn, 38, respectively, isotopic pattern of tin $(M^+-Ph),\,227$ and 225 $(C_8 H_{10}^{120} Sn,\,100,\,and\,C_8 H_{10}^{118} Sn,\,68,\,$ respectively, isotopic pattern of tin $(M^+-[pyrene-(CH_2)_3]));\,HRMS$ calcd for $C_{27} H_{27}^{120} Sn$ (MH^+) 470.1056, found 470.1052.

General Procedure for Stille Couplings (Table 2, Entries 4–6). A mixture of stannane 12b (1.5 equiv) and aryl iodide (50 μ mol) was thoroughly degassed by repeated vacuum/ nitrogen cycles. Methanol- d_4 (6 equiv), tributylamine (2 equiv), and PdCl₂(dppf) (0.1 equiv) were then successively added, and the reaction mixture was sealed and heated at 60 °C for 12 h. At the end of the reaction, ¹H NMR of the crude mixture (CDCl₃) showed complete disappearance of the starting material. The crude reaction mixture was diluted with MeOH/CH₂- Cl_2 (3/2, 1 mL) and treated with activated carbon (200 mg). After 30 min, charcoal was removed by filtration over Celite and was washed with MeOH. Evaporation gave the desired product tin-free, but still containing high-boiling tributyl-amine, which could be easily removed by chromatography.

Supporting Information Available: Experimental procedures and spectral data (¹H NMR, ¹³C NMR and HRMS) for compounds **1a–c**, **2**, **3**, **5**, and **6** and all compounds described in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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