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Ionic Liquid Supported Organotin Reagents: Green Tools for Stille Cross-Coupling Reactions with Brominated Substrates

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Efficiency of ionic liquid supported organotin reagents in Stille cross-coupling reactions involving aryl bromides has been investigated. In a general manner, products were isolated with good yields by using a very simple catalytic system without the need of solvent, ligand, or additives. The organotin compounds were recycled without loss of activity and the contamination by tin was limited and controlled ([Sn] < 3 ppm).

Introduction

Amongst the palladium-catalyzed cross-coupling methods, the Stille reaction of organostannanes with organic electrophiles represents a versatile method for carbon–carbon bond formation.[1] Indeed, this transformation is one of the most general and selective Pd-catalyzed cross-coupling reactions for the synthesis of complex molecules because of its broad scope and high tolerance towards many functional groups.[2] However, the use of organotin reagents has been avoided for the synthesis of pharmacologically active substances due to their toxicity and the difficulties of removing residues from the products. As a result, ongoing efforts have been devoted to solve these problems by using solid-phase synthetic methods,[3,4] phosphonium-grafted organotins,[5] Stille couplings catalytic in tin,[6] and other modified organotin reagents.[7]

Convenient access to biaryl compounds is receiving currently a great deal of attention due to the prominence of this scaffold in biological and naturally occurring molecules.[8] As a part of our ongoing research program dealing with potentialities of TSILs (task-specific ionic liquids), and particularly organotin reagents supported on ionic liquids,[9] we previously reported an exploration of their scope of the Stille reaction involving aryl iodide substrates.[9a,9d] High yields of biaryl products were obtained under low-temperature, solvent-free, ligand-free conditions, with simple purification techniques. Moreover, the products were isolated with minimal amount of tin (<6 ppm). This result prompted us to investigate the scope and limits of organotin reagents supported on ionic liquid in the Stille reaction with brominated substrates.

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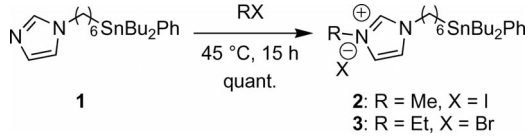
Results and Discussion

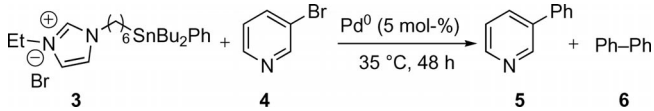
Starting from imidazole derivative **1**,[9a] new room-temperature ionic liquid (RTIL) **3** (R = Et, X = Br) was easily synthesized in a similar manner to that used for ionic liquid **2** (R = Me, X = I; Scheme 1).



Scheme 1. Synthesis of ionic liquids **2** and **3**.

The reactivity of compound **3** in Stille cross-coupling reactions has been evaluated with different palladium precatalysts (5 mol-%) and by using bromopyridine **4** as a benchmark substrate. It should be noted that this heteroaromatic substrate was chosen to differentiate desired product **5** from biphenyl byproduct **6**.[9a] Results are summarized in Table 1.

Table 1. Precatalyst effect on Stille cross-coupling reactions.



3 **4** **5** **6**

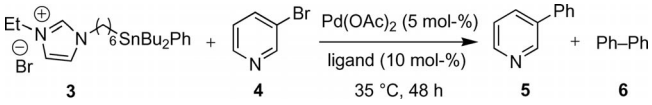
Entry	Pd^0	Conv. [%][a]	**5**[a] [%]	**6**[a] [%]
1	$[Pd_2(dba)_3{\cdot}CHCl_3]$	0	–	–
2	$[PdCl_2]$	0	–	–
3	$[Pd(PPh_3)_4]$	0	–	–
4	[Pd/C]	0	–	–
5	$[Pd_2(dba)_3]$	11	64	36
6	$[Pd\{P(tBu)_3\}_2]$	20	46	54
7	$[Pd(OAc)_2]$	93	65	35

[a] Determined by GC.

As an initial assay, conditions previously used for aryl iodide substrates {e.g., 48 h, 35 °C, **2** (2 equiv.), and $[Pd_2(dba)_3{\cdot}CHCl_3]$ as precatalyst} were applied. No conversion was observed with this catalytic system (Table 1, Entry 1). Moreover, the use of $[PdCl_2]$ (Table 1, Entry 2), $[Pd(PPh_3)_4]$ (Table 1, Entry 3), and [Pd/C] (Table 1, Entry 4) did not allow the formation of the desired compound. When using $[Pd_2(dba)_3]$ (Table 1, Entry 5) or $[Pd\{P(t\text{Bu})_3\}_2]$[10] (Table 1, Entry 6) the reaction proceeded with only 11–20% conversion, generating a high proportion of biphenyl product **6**. The highest conversion (93%) was observed when using $[Pd(OAc)_2]$ as the precatalyst with a 65:35 ratio of 3-phenylpyridine (**5**) and biphenyl byproduct **6** (Table 1, Entry 7).

To enhance the selectivity in favor of 3-phenylpyridine (**5**), we decided to examine the influence of several ligands with $[Pd(OAc)_2]$ as the precatalyst (Table 2). Addition of phosphane ligands such as P(*o*-tolyl)$_3$ and PPh_3 (Table 2, Entries 2 and 3), led to a loss of catalytic activity, as only 25% conversion were measured after a reaction time of 48 h. The use of ancillary ligands $AsPh_3$ or P(*t*Bu)$_3$ (Table 2, Entries 4 and 5) afforded conversions of 49 and 82%, respectively. These results clearly highlight that our catalytic system does not require the addition of a ligand.

Table 2. Ligand effect on Stille cross-coupling reactions.



3 4 5 6

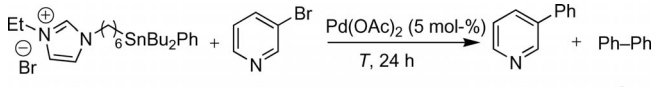
Entry	Ligand	Conv. [%][a]	**5**[a] [%]	**6**[a] [%]
1	none	93	65	35
2	P(*o*-tolyl)$_3$	25	21	79
3	PPh_3	25	53	47
4	$AsPh_3$	49	58	42
5	P(*t*Bu)$_3$	82	48	52

[a] Determined by GC.

To further optimize the reaction conditions, the Stille cross-coupling transformation was performed in the presence of copper(I)[11] (CuI, CuBr, CuCl) and a fluoride source[12] (CsF, NaF, KF) (classical conditions for Stille cross-coupling reactions often require these types of additives).[13] Once again, no improvement in terms of catalytic activity was noticed.

Temperature effect was also investigated by using 3-bromopyridine (**4**), ionic liquid **3**, and $[Pd(OAc)_2]$ precatalyst (Table 3). After 24 h of reaction at 35 °C, only 69% conversion was observed with a **5/6** ratio similar to that obtained after a reaction time of 48 h at the same temperature (Table 3, Entry 1). It is noteworthy that an increase in temperature to 100 °C led to full conversion. More interestingly, the proportion of **5** increased from 68 to 93% (Table 3, Entry 2). Finally, only 21% conversion were reached when applying a temperature of 150 °C (Table 3, Entry 3). Of note, under these reaction conditions, no degradation of ionic liquid **3** was observed. However, at this temperature, formation of droplets on neck of the flask was noticed. This could be the result of the condensation of compound **4**, which, as a consequence, would not remain in the reaction mixture and would explain the decrease in the reactivity.

Table 3. Temperature effect on Stille cross-coupling reactions.



3 4 5 6

Entry	*T* [°C]	Conv. [%][a]	**5** [%][a]	**6** [%][a]
1	35	69	68	32
2	100	100	93	7
3	150	21	79	21

[a] Determined by GC.

In summary, we showed after this optimization part that a very simple catalytic system ($[Pd(OAc)_2]$ at 100 °C) without need of solvent, ligand, or additives represented the most effective conditions.

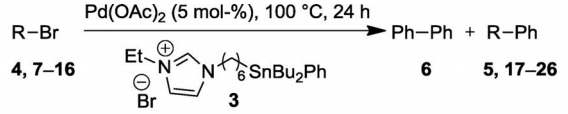
To perform a thorough evaluation of the activity of our system, we decided to investigate the Stille cross-coupling reaction with various brominated substrates. Results are depicted in Table 4.

Reactivity of hetreoaryl and aryl bromide substrates diversely substituted has been evaluated in Stille cross-coupling reactions using ionic liquid **3**. For instance, heteroaryl derivatives such as 3-bromopyridine (**4**), 5-bromo-2-(trifluoromethyl)pyridine (**7**), and 3-bromoisoquinoline (**8**) turned out to be good candidates for this transformation (Table 4, Entries 1, 2 and 3). The coupling with 4-bromoacetophenone (**9**) proceeded in good yield (Table 4, Entry 4), whereas benzaldehyde **10** and benzonitrile **11** exhibited moderate reactivities (Table 4, Entries 5 and 6). Reactions involving naphthyl as well as styrenyl and benzothiophene derivatives afforded good results in spite of difficulties concerning their isolation (Table 4, Entries 7–11). Indeed, contrary to Wang's report,[14] isolation of 2-phenylnaphthalene (**23**; Table 4, Entry 8) by flash chromatography failed because of its similar polarity with biphenyl byproduct **6**.

To provide a greater versatility to our methodology, we were concerned by the transfer of other groups than phenyl. Thus, five new organotin reagents supported on ionic liquid (**28**–**32**) bearing, respectively, vinyl, allyl, anisole, fluorobenzene, and thiophene moieties have been straightforwardly synthesized. These compounds have been isolated with good yields after reaction of Grignard reagents with derivative **27** (Scheme 2).

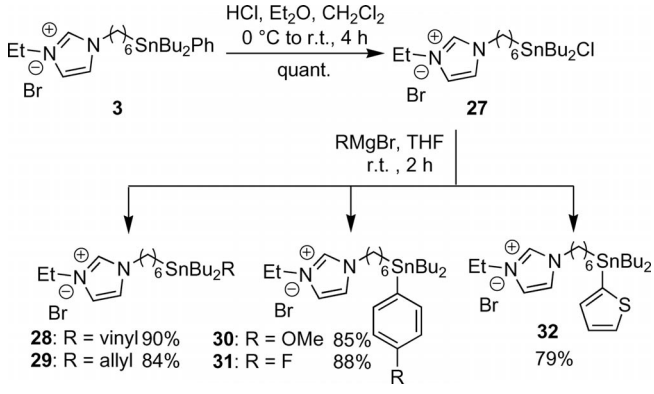
To determine the best catalytic system, new methodology was employed, which required the use of vinylstannane **28** and bromoacetophenone **9** at 80 °C for 15 h (Table 5). By using catalysts such as $[Pd(OAc)_2]$, $[Pd_2(dba)_3{\cdot}CHCl_3]$, and $[Pd_2(dba)_3]$ (Table 5, Entries 1–3), almost no coupling products were detected. Interestingly, by using $[Pd(PPh_3)_4]$, total

Table 4. Stille cross-coupling reactions with phenyl stannane.



Entry	RBr	RPh	RPh[a]/**6** [%][b]	Yield RPh [%]
1	 **4**	 **5**	93/7	78
2	 **7**	 **17**	88/12	85[c]
3	 **8**	 **18**	98/2	83
4	 **9**	 **19**	86/14	69
5	 **10**	 **20**	68/32	56
6	 **11**	 **21**	72/28	70
7	 **12**	 **22**	71/29	–[d]
8	 **13**	 **23**	88/12	–[d]
9	 **14**	 **24**	86/8	–[d,e]
10	 **15**	 **25**	85/15	–[d,f]
11	 **16**	 **26**	87/13	–[d]

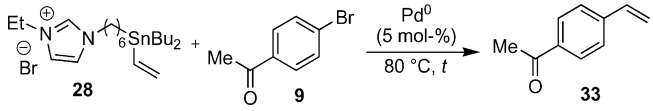
[a] Full conversion. [b] Determined by GC. [c] 8 h. [d] Inseparable products. [e] Conversion of 94% and 6% of R–R was formed. [f] 80 °C.



Scheme 2. Synthesis of vinyl, allyl, aryl, and heteroaryl RTILs.

conversion was observed after 5 h of heating at 80 °C. These reaction conditions in hand, various brominated substrates were investigated in the Stille cross-coupling reaction.

Table 5. Precatalyst effect on Stille cross-coupling reactions.

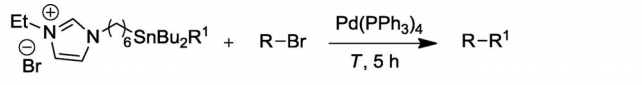


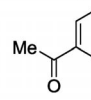
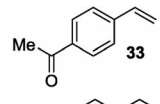
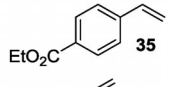
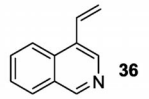
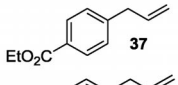
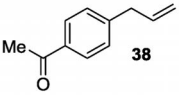
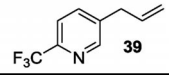
Entry	Pd^0	*t* [h]	Conv. [%][a]
1	$[Pd(OAc)_2]$	15	4
2	$[Pd_2(dba)_3{\cdot}CHCl_3]$	15	6
3	$[Pd_2(dba)_3]$	15	3
4	$[Pd(PPh_3)_4]$	15	100
5	$[Pd(PPh_3)_4]$	5	100

[a] Determined by GC.

After optimization, it was found that the use of $[Pd(PPh_3)_4]$ in conjunction with only 1 equiv. of ionic liquid **28** or **29** constituted the best system for this application. Both allylation and vinylation products were isolated with good yields after 5 h of reaction. Several cross-coupling partners bearing various functionalities were examined. The results depicted in Table 6 clearly indicate a good tolerance of our catalytic system towards esters, ketones, and nitrogen-containing heteroaromatic substrates.

Table 6. Stille cross-coupling reaction with vinyl- and allylstannanes.

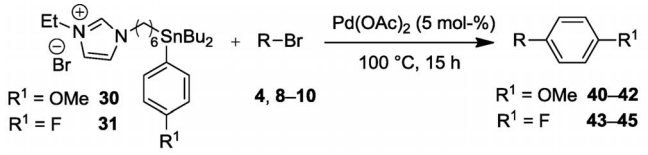


Entry	IL	RBr	R–R^1	*T* [°C]	Yield [%]
1[a]	**28**	 **9**	 **33**	80	67
2[a]	**28**	 **34**	 **35**	80	80
3[a]	**28**	 **8**	 **36**	100	52
4[b]	**29**	 **34**	 **37**	80	86
5[b]	**29**	 **9**	 **38**	80	78
6[b]	**29**	 **7**	 **39**	110	55

[a] $Pd(PPh_3)_4$: 2 mol-%. [b] $Pd(PPh_3)_4$: 5 mol-%.

Aryl–aryl or aryl–heteroaryl cross-coupling reactions using arylstannanes **30** and **31** were investigated. The results are summarized in Table 7. Reactions between anisol-containing stannane **30** bearing an electron-donating substituent ($MeOC_6H_4$; Table 7, Entries 1–3) and heteroaryl or aryl bromides were carried out in the presence of $[Pd(OAc)_2]$ at 100 °C for 15 h. As a general trend, coupling products were isolated in good yields (63–82%). Fluorine-containing compounds represent versatile building blocks in medicinal chemistry.[15] Indeed, cross-coupling reactions between fluorinated tin reagent **31** and various aryl and heteroaryl bromides were examined (Table 7, Entries 4–6) and the expected products were isolated with good yields in the range of 70%.

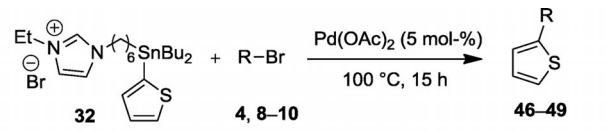
Table 7. Stille cross-coupling reaction with aryl stannanes **30** and **31**.



Entry	IL	RBr	R–R[1]	Yield [%]
1	**30**	**4**	**40**	68
2	**30**	**9**	**41**	82
3	**30**	**10**	**42**	63
4	**31**	**4**	**43**	66
5	**31**	**9**	**44**	68
6	**31**	**8**	**45**	71

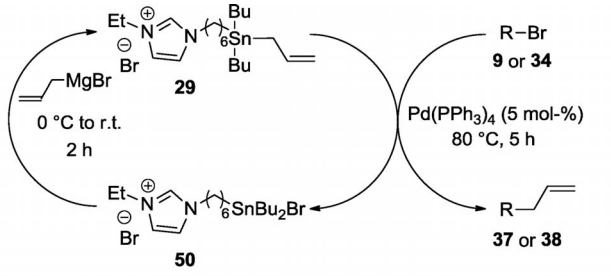
The reactivity of thiophene-containing organotin reagent **32** was tested in the Stille reaction with various brominated substrates (Table 8). Products were obtained in very good yields (75–80%). Interestingly, the coupling reaction was successfully performed in the presence of bromoquinoline **8** (Table 8, Entry 4); the heteroaryl product was obtained with a yield of 80%.

Table 8. Stille cross-coupling reaction with thiophenstannane.



Entry	RBr	Product	Yield [%]
1	**4**	**46**	79
2	**9**	**47**	75
3	**10**	**48**	78
4	**8**	**49**	80

Table 9. Recycling of the tin compound.



Run	RBr	R–	Yield [%]	Yield **29** [%][b]
1	**34**	**37**	86	75
2[a]	**34**	**37**	82[c]	67
3[a]	**9**	**38**	70	68
4[a]	**9**	**38**	76	67
6[a]	**34**	**37**	76	69

[a] Recovered tin reagent **29** from the previous cycle. [b] Yield over 2 steps. [c] ICP-MS: 2.4 ppm.

Benefiting from the intrinsic properties of ILs, we proposed to recycle our organotin-supported reagent. Indeed, halogenotin-supported ionic liquid **50**, obtained after Stille reaction, could be easily separated from product **37** or **38** by extraction with ethyl ether. After addition of allylmagnesium bromide in THF, ionic liquid **29** can be regenerated in two steps with good yield. Thus, organotin compound **29** could be recycled five times with different bromide substrates **9** and **34** without loss of reactivity (Table 9).

It is noteworthy that ICP-MS analysis confirmed that contamination by tin in the coupling product was avoided ([Sn] < 3 ppm).

Conclusions

In conclusion, new diversely substituted organotin reagents supported on ionic liquid turned out to be useful tools for Stille cross-coupling reactions involving brominated substrates. We have shown that these transformations could be performed without solvents or additives by using commercially available precatalysts. Organotin compound was recycled five times with good yield and reused in Stille cross-coupling reactions without loss of reactivity. Moreover, it is noteworthy that contamination by tin was limited. Further applications of organotin reagents on ionic liquids are currently under investigation in our laboratory.

Experimental Section

1-{6-[Dibutyl(phenyl)stannyl]hexyl}-3-ethyl-1*H*-imidazol-3-ium Bromide (3): To imidazole derivative **1**[9d] (5.35 g, 11.60 mmol) in a sealed tube was added bromoethane (9 mL, 110.60 mmol). The mixture was stirred for 17 h at 45 °C then concentrated under reduced pressure to give ionic liquid **3** (6.61 g, quant.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.34 (s, 1 H, 2-H), 7.68 (s, 1 H, 3-H or 4-H), 7.47–7.43 (m, 2 H, $H_{arom.}$), 7.42 (s, 1 H, 3-H or 4-H), 7.35–7.25 (m, 3 H, $H_{arom.}$), 4.43 (q, *J* = 7.2 Hz, 2 H, 5-H), 4.28 (t, *J* = 7.6 Hz, 2 H, 7-H), 2.00–1.80 (m, 2 H, 8-H), 1.60 (t, *J* = 7.2 Hz, 3 H, 6-H), 1.57–1.47 (m, 6 H, 10-H and 15-H), 1.38–1.27 (m, 8 H, 9-H, 11-H and 14-H), 1.10–0.97 (m, 6 H, 12-H and 13-H), 0.88 (t, *J* = 7.2 Hz, 6 H, 16-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.6 (17-C), 136.4 (2-C), 136.3 (*J* = 15 Hz, 18-C), 127.9 (*J* = 20 Hz, 19-C), 127.9 (*J* = 6 Hz, 20-C), 122.1 (3-C or 4-C), 121.9 (3-C or 4-C), 49.9 (7-C), 45.1 (5-C), 33.6 (*J* = 28 Hz, 11-C), 30.2 (8-C), 28.9 (*J* = 10 Hz, 15-C), 27.2 (*J* = 28 Hz, 14-C), 26.5 (*J* = 10 Hz, 10-C), 25.6 (9-C), 15.6 (6-C), 13.6 (16-C), 9.5 (*J* = 170 Hz, 12-C), 9.4 (*J* = 170 Hz, 13-C) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –43.8 ppm. HRMS (ESI): calcd. for $C_{25}H_{43}N_2Sn$ [M – Br]$^+$ 491.2443; found 491.2456.

1-[6-(Dibutylchlorostannyl)hexyl]-3-ethyl-1*H*-imidazol-3-ium Bromide (27): To a solution of ionic liquid **3** (1.092 g, 1.916 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added a solution of HCl (2 M in Et_2O, 1.05 mL, 2.107 mmol). The mixture was stirred for 4 h at room temperature, then treated with H_2O. The organic layer was extracted with CH_2Cl_2, dried with $MgSO_4$, filtered, and concentrated under reduced pressure to yield ionic liquid **27** (1.006 g, quant.) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.05 (s, 1 H, 2-H), 7.59 (s, 1 H, 3-H or 4-H), 7.59 (s, 1 H, 3-H or 4-H), 4.41 (q, *J* = 7.6 Hz, 2 H, 5-H), 4.34 (t, *J* = 7.2 Hz, 2 H, 7-H), 2.05–1.85 (m, 2 H, 8-H), 1.80–1.65 (m, 6 H, 10-H and 15-H), 1.62 (t, *J* = 7.6 Hz, 3 H, 6-H), 1.50–1.30 (m, 14 H, 9-H, 11-H, 12-H, 13-H, and 14-H), 0.90 (t, *J* = 7.2 Hz, 6 H, 16-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9 (2-C), 122.4 (3-C or 4-C), 121.8 (3-C or 4-C), 49.8 (7-C), 45.2 (5-C), 32.0 (*J* = 34 Hz, 11-C), 29.6 (8-C), 28.2 (*J* = 12 Hz, 15-C), 26.8 (*J* = 37 Hz, 14-C), 25.2 (*J* = 13 Hz, 10-C), 24.9 (9-C), 21.9 (*J* = 194 Hz, 13-C), 21.4 (*J* = 190 Hz, 12-C), 15.5 (6-C), 13.7 (16-C) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = +54.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{38}ClN_2Sn$ [M – Br]$^+$ 449.1740; found 449.1739.

General Procedure for the Synthesis of Ionic Liquids 28–32: To a solution of ionic liquid **27** (3.76 g, 7.11 mmol) in THF (100 mL) at room temperature was added a solution of the Grignard reagent (30.5 mL, 21.33 mmol). After 2 h at room temperature, the solution was quenched with H_2O. The organic layer was then extracted with CH_2Cl_2, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to afford ionic liquids **28**–**32**.

1-{6-[Dibutyl(vinyl)stannyl]hexyl}-3-ethyl-1*H*-imidazol-3-ium Bromide (28): Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1 H, 2-H), 7.50 (s, 1 H, 3-H or 4-H), 7.34 (s, 1 H, 3-H or 4-H), 6.42 (dd, *J* = 20.8, 14.0 Hz, 1 H, 17-H), 6.12 (dd, *J* = 3.6, 14.0 Hz, 1 H, 18-H_{cis}), 5.63 (dd, *J* = 3.6, 20.8 Hz, 1 H, 18-H_{trans}), 4.39 (q, *J* = 7.6 Hz, 2 H, 5-H), 4.28 (t, *J* = 7.2 Hz, 2 H, 7-H), 1.88–1.75 (m, 2 H, 8-H), 1.58 (t, *J* = 7.6 Hz, 3 H, 6-H), 1.50–1.40 (m, 6 H, 10-H and 15-H), 1.35–1.20 (m, 10 H, 9-H, 11-H, 12-H and 14-H), 1.00–0.75 (m, 4 H, 13-H), 0.87 (t, *J* = 7.2 Hz, 6 H, 16-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0 (*J* = 188 Hz, 17-C), 137.3 (2-C), 133.9 (18-C), 121.9 (3-C or 4-C), 121.9 (3-C or 4-C), 50.2 (7-C), 45.4 (5-C), 33.7 (*J* = 28 Hz, 11-C), 30.4 (8-C), 29.1 (*J* = 10 Hz, 15-C), 27.3 (*J* = 26 Hz, 14-C), 26.7 (*J* = 10 Hz, 10-C), 25.9 (9-C), 15.7 (6-C), 13.8 (16-C), 9.3 (*J* = 170 Hz, 12-C), 9.3 (*J* = 170 Hz, 13-C) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –51.4 ppm. HRMS (ESI): calcd. for $C_{21}H_{41}N_2Sn$ [M – Br]$^+$ 441.2286; found 441.2304.

1-{6-[Dibutyl(allyl)stannyl]hexyl}-3-ethyl-1*H*-imidazol-3-ium Bromide (29): Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.42 (s, 1 H, 2-H), 7.78 (s, 1 H, 3-H or 4-H), 7.54 (s, 1 H, 3-H or 4-H), 5.92 (ddt, *J* = 8.4, 10.0, 16.8 Hz, 1 H, 18-H), 4.77 (dd, *J* = 2.0, 16.8 Hz, 1 H, 19-H_{trans}), 4.63 (dd, *J* = 2.0, 10.0 Hz, 1 H, 19-H_{cis}), 4.47 (q, *J* = 7.2 Hz, 2 H, 5-H), 4.35 (t, *J* = 7.2 Hz, 2 H, 7-H), 1.97–1.86 (m, 2 H, 8-H), 1.76 (d, *J* = 8.4 Hz, 2 H, 17-H), 1.62 (t, *J* = 7.6 Hz, 3 H, 6-H), 1.55–1.42 (m, 6 H, 10-H and 15-H), 1.40–1.22 (m, 8 H, 9-H, 11-H, and 14-H), 0.89 (t, *J* = 7.2 Hz, 6 H, 16-H), 0.92–0.77 (m, 6 H, 12-H and 13-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.8 (*J* = 22 Hz, 18-C), 136.3 (2-C), 122.1 (3-C or 4-C), 121.9 (3-C or 4-C), 109.1 (*J* = 22 Hz, 19-C), 49.9 (7-C), 45.0 (5-C), 33.6 (*J* = 27 Hz, 11-C), 30.2 (8-C), 28.9 (*J* = 10 Hz, 15-C), 27.0 (*J* = 26 Hz, 14-C), 26.5 (*J* = 10 Hz, 10-C), 25.7 (9-C), 15.9 (*J* = 123 Hz, 17-C), 15.6 (6-C), 13.5 (16-C), 8.9 (*J* = 156 Hz, 12-C), 8.8 (*J* = 153 Hz, 13-C) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –18.9 ppm. HRMS (ESI): calcd. for $C_{22}H_{43}N_2Sn$ [M – Br]$^+$ 455.2443; found 455.2453.

1-{6-[Dibutyl(4-methoxyphenyl)stannyl]hexyl}-3-ethyl-1*H*-imidazol-3-ium Bromide (30): Yield: 85%. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.51 (s, 1 H, 2-H), 7.45 (s, 1 H, 3-H or 4-H), 7.36 (d, *J* = 8.6 Hz, 2 H, $H_{arom.}$), 7.28 (s, 1 H, 3-H or 4-H), 6.90 (d, *J* = 8.6 Hz, 2 H, $H_{arom.}$), 4.44 (q, *J* = 7.5 Hz, 2 H, 5-H), 4.29 (t, *J* = 7.5 Hz, 2 H, 7-H), 3.80 (s, 3 H, 21-H), 1.70–1.95 (m, 2 H, 8-H), 1.60 (t, *J* = 7.5 Hz, 3 H, 6-H), 1.40–1.60 (m, 6 H, 10-H and 15-H), 1.20–1.40 (m, 8 H, 9-H, 11-H, and 14-H), 0.95–1.10 (m, 6 H, 12-H and 13-H), 0.88 (t, *J* = 7.1 Hz, 6 H, 16-H) ppm. ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 159.5 (20-C), 137.3 (J = 20 Hz, 19-C), 136.2 (2-C), 131.5 (J = 203 Hz, 17-C), 122.0 (3-C or 4-C), 121.9 (3-C or 4-C), 113.7 (J = 22 Hz, 18-C), 57.8 (21-C), 49.8 (7-C), 45.0 (5-C), 33.5 (J = 28 Hz, 11-C), 30.1 (8-C), 28.9 (J = 10 Hz, 15-C), 27.2 (J = 28 Hz, 14-C), 26.5 (J = 10 Hz, 10-C), 25.6 (9-C), 15.5 (6-C), 13.5 (16-C), 9.4 (J = 165 Hz, 12-C), 9.3 (J = 165 Hz, 13-C) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –41.9 ppm. HRMS (ESI): calcd. for $C_{26}H_{45}N_2OSn$ $[M - Br]^+$ 521.2548; found 521.2582.

1-{6-[Dibutyl(4-fluorophenyl)stannyl]hexyl}-3-ethyl-1*H*-imidazol-3-ium Bromide (31): Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.32 (s, 1 H, 2-H), 7.72 (s, 1 H, 3-H or 4-H), 7.46 (s, 1 H, 3-H or 4-H), 7.32 (dd, J = 8.5 Hz, $J_{H,F}$ = 8.5 Hz, 2 H, $H_{arom.}$), 6.9 (dd, J = 8.5 Hz, $J_{H,F}$ = 8.5 Hz, 2 H, $H_{arom.}$), 4.38 (q, J = 7.1 Hz, 2 H, 5-H), 4.24 (t, J = 7.7 Hz, 2 H, 7-H), 1.70–1.90 (m, 2 H, 8-H), 1.52 (t, J = 7.1 Hz, 3 H, 6-H), 1.35–1.50 (m, 6 H, 10-H and 15-H), 1.15–1.35 (m, 8 H, 9-H, 11-H, and 14-H), 0.85–1.10 (m, 6 H, 12-H and 13-H), 0.80 (t, J = 7.1 Hz, 6 H, 16-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, $J_{C,F}$ = 250 Hz, 20-C), 137.6 (d, $J_{C,F}$ = 6 Hz, J = 18 Hz, $C_{arom.}$), 136.3 (17-C), 136.2 (2-C), 122.1 (3-C or 4-C), 121.9 (3-C or 4-C), 114.9 (d, $J_{C,F}$ = 19 Hz, J = 22 Hz, $C_{arom.}$), 49.8 (5-C), 45.0 (7-C), 33.5 (J = 28 Hz, 11-C), 30.1 (8-C), 28.8 (J = 10 Hz, 15-C), 27.1 (J = 28 Hz, 14-C), 26.4 (J = 10 Hz, 10-C), 25.6 (9-C), 15.5 (6-C), 13.5 (16-C), 9.5 (J = 165 Hz, 12-C), 9.4 (J = 165 Hz, 13-C) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –114.7 ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): = δ–40.5 (d, $J_{Sn,F}$ = 8.1 Hz) ppm. HRMS (ESI): calcd. for $C_{25}H_{42}N_2FSn$ $[M - Br]^+$ 509.2349; found 509.2386.

1-{6-[Dibutyl(thiophen-2-yl)stannyl]hexyl}-3-ethyl-1*H*-imidazol-3-ium Bromide (32): Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.47 (s, 1 H, 2-H), 7.64 (d, J = 4.7 Hz, 1 H, 20-H), 7.63 (s, 1 H, 3-H or 4-H), 7.40 (s, 1 H, 3-H or 4-H), 7.26 (dd, J = 3.0, 4.7 Hz, 1 H, 19-H), 7.18 (d, J = 3.0 Hz, 1 H, 18-H), 4.44 (q, J = 7.5 Hz, 2 H, 5-H), 4.30 (t, J = 7.5 Hz, 2 H, 7-H), 1.80–1.95 (m, 2 H, 8-H), 1.60 (t, J = 7.5 Hz, 3 H, 6-H), 1.50–1.60 (m, 6 H, 10-H and 15-H), 1.25–1.40 (m, 8 H, 9-H, 11-H, and 14-H), 1.00–1.15 (m, 6 H, 12-H and 13-H), 0.89 (t, J = 7.1 Hz, 6 H, 16-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.1 (2-C), 135.5 (17-C), 134.9 (J = 13 Hz, 19-C), 130.3 (20-C), 127.6 (J = 20 Hz, 18-C), 122.1 (3-C or 4-C), 121.8 (3-C or 4-C), 49.6 (7-C), 44.8 (5-C), 33.2 (J = 28 Hz, 11-C), 29.9 (8-C), 28.6 (J = 10 Hz, 15-C), 26.9 (J = 28 Hz, 14-C), 26.1 (J = 10 Hz, 10-C), 25.4 (9-C), 15.4 (6-C), 13.3 (16-C), 10.5 (J = 165 Hz, 12-C), 10.5 (J = 165 Hz, 13-C) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$): δ = –40.0 ppm. HRMS (ESI): calcd. for $C_{23}H_{41}N_2SSn$ $[M - Br]^+$ 497.2007; found 497.2021.

General Procedure for Recycling Tin Compound 29: To a solution of ionic liquid **29** (950 mg, 1.780 mmol) was added $Pd(PPh_3)_4$ (102 mg, 5 mol-%) and aryl bromide **9** or **34** (290 μL, 1.780 mmol). The mixture was stirred for 5 h at 80 °C. Ionic liquid **50** (1.076 g) was separated from product **37** or **38** by extraction with ether. The organic layer was concentrated, and the crude product was purified by silica gel flash column chromatography to afford allyl compound **37** or **38** (290 mg, 86%). Ionic liquid **29** was heated (70 °C) under high vacuum. After cooling to room temperature, allylmagnesium bromide (1 M in Et_2O, 5.6 mL, 3.228 mmol) was added in THF (30 mL) at room temperature. The mixture was stirred for 2 h at room temperature, then treated with H_2O. The organic layer was extracted with CH_2Cl_2, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to afford ionic liquid **29** (710 mg, 75% in two steps) as a yellow oil.

Supporting Information (see footnote on the first page of this article): Experimental details and copies of the ^{1}H and ^{13}C NMR spectra.

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