



# Synthesis and cross-coupling reactions of tetraalkylammonium organotrifluoroborate salts

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Received 21 September 2001; revised 15 October 2001; accepted 22 October 2001

**Abstract**—Treatment of organoboronic acids with hydrofluoric acid generates an in situ tetracoordinate hydronium organotrifluoroborate species which undergoes counterion exchange with tetra-*n*-butylammonium hydroxide. The resultant tetraalkylammonium salts are as air and moisture stable as their potassium organotrifluoroborate counterparts with the added advantage of being readily soluble in organic media. They were found to undergo Pd-catalyzed Suzuki–Miyaura cross-couplings with a variety of aryl- and alkenylhalides under mild conditions. Their Pd-catalyzed cross-coupling with acid halides is also possible for the generation of ketones. © 2001 Published by Elsevier Science Ltd.

The Pd-catalyzed cross-coupling reaction between organoboron compounds and organohalides or triflates, commonly referred to as the Suzuki–Miyaura reaction, provides a powerful and general method for carbon–carbon bond formation.<sup>1</sup> The availability of reagents and mild reaction conditions contribute to the versatility of the reaction. Additional advantages of the Suzuki–Miyaura reaction include the tolerance of a broad range of functional groups and the generation of easily removable, nontoxic, inorganic by-products. In addition, the reaction tolerates the presence of water. These advances have made the Suzuki–Miyaura reaction suitable for both industrial processes and laboratory syntheses, including combinatorial and total synthesis applications.

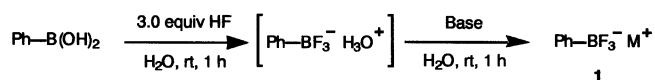
Potassium organotrifluoroborate salts offer an air and moisture stable alternative to commonly used organoboron compounds. These salts can be stored under normal atmospheric conditions for extended periods without noticeable degradation or decomposition as compared to some of their boronic acid, boronate ester, and haloborane counterparts. The first synthetic use of potassium organotrifluoroborate salts was Vedejs' work in the synthesis of oxazaborolidinones.<sup>2</sup> Our own use of the salts includes their Rh(I)-catalyzed additions to aldehydes and  $\alpha,\beta$ -unsaturated ketones,<sup>3a</sup> and their use for allylation and crotylation of aldehydes

using Lewis acid catalysis.<sup>3b,c</sup> In the case of the Rh(I)-catalyzed additions, it was found that the trifluoroborate salts reacted more effectively than their boronic acid counterparts, which may be attributed to the tetracoordinate borate undergoing transmetallation more rapidly. Furthermore, Wright and co-workers tentatively proposed that CsF promoted Suzuki–Miyaura cross-coupling of boronic acids may occur via in situ generation of a trifluoroborate anion followed by transmetallation to Pd.<sup>4</sup> Genêt and co-workers have previously reported that potassium aryltrifluoroborate salts undergo Pd-catalyzed cross-coupling reactions with arenediazonium tetrafluoroborates under mild conditions, but appeared to be unreactive towards halogen functionalities on the substrates.<sup>5</sup> This limitation was directly observed by Fu and co-workers in their study of  $P(t\text{-Bu})_3$ /Pd-catalyzed Suzuki–Miyaura cross-couplings.<sup>6</sup> Our interest in transmetallation reactions with the trifluoroborate salts has prompted us to investigate further their utility in Suzuki–Miyaura type cross-couplings. We were interested in both establishing optimal conditions under which the coupling to aryl- and alkenylhalides was possible, and determining whether the organotrifluoroborate was the active species in the transmetallation step. During the course of this study, Molander and Ito reported the Pd-catalyzed cross-couplings of potassium alkyltrifluoroborates with alkenyltriflates.<sup>7</sup>

The potassium organotrifluoroborate salts are formed via treatment of the corresponding boronic acids with  $\text{KHF}_2$ .<sup>2a</sup> Although the  $\text{K}^+$  salts have been synthetically useful, they have the limitation of being insoluble in

**Keywords:** counterion exchange; organotrifluoroborate salts; Suzuki–Miyaura cross-coupling; palladium; transmetallation.

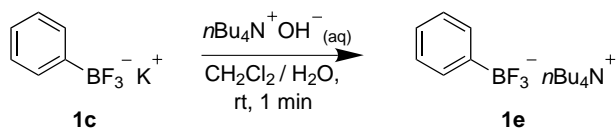
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**Table 1.** Synthesis of phenyltrifluoroborate salts with a variety of counterions

Entry	Base	Product	M <sup>+</sup>	Yield (%)
1	LiOH	<b>1a</b>	Li <sup>+</sup>	60
2	NaOH	<b>1b</b>	Na <sup>+</sup>	83
3	KOH	<b>1c</b>	K <sup>+</sup>	90
4	Cs <sub>2</sub> CO <sub>3</sub>	<b>1d</b>	Cs <sup>+</sup>	Quant.
5	<i>n</i> Bu <sub>4</sub> N <sup>+</sup> OH <sup>-</sup>	<b>1e</b>	<i>n</i> Bu <sub>4</sub> N <sup>+</sup>	95
6	<i>n</i> Bu <sub>4</sub> P <sup>+</sup> OH <sup>-</sup>	<b>1f</b>	<i>n</i> Bu <sub>4</sub> P <sup>+</sup>	90

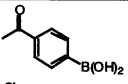
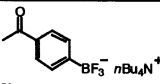
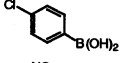
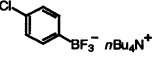
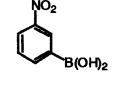
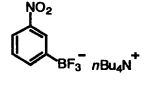
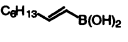
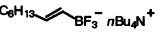
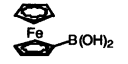
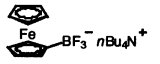
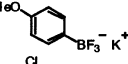
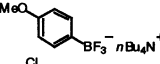
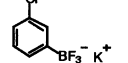
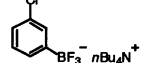
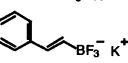
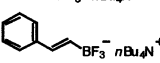
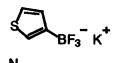
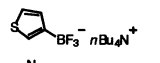

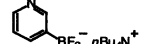
organic media, and require polar solvents like MeCN and H<sub>2</sub>O at elevated temperatures for dissolution. Our explorations of alternative methods<sup>8</sup> of generating trifluoroborates without KHF<sub>2</sub> led to the discovery that reaction of 3 equiv. of HF with a boronic acid gave the corresponding trifluoroborate species in solution, as observed by <sup>1</sup>H, <sup>11</sup>B, and <sup>19</sup>F NMR. Unsurprisingly, all attempts to isolate the solid trifluoroborate salt with a hydronium counterion resulted in decomposition. Treatment of the reaction mixture with a base resulted in a counterion exchange to produce isolable organotrifluoroborate salts with various counterions (Table 1).<sup>9</sup> The species generated by reaction with LiOH was soluble in the aqueous layer, but slow evaporation of the aqueous solvent gave the crystalline solid **1a**. Compounds **1b–d** containing an inorganic counterion were insoluble in the aqueous reaction mixture and readily precipitated out of solution. Compounds **1e**<sup>10</sup> and **1f** ‘oiled out’ of the aqueous reaction mixture and were isolated by extracting with CH<sub>2</sub>Cl<sub>2</sub>. Evaporation of the organic solvent gave the corresponding crystalline solids. Compounds **1e** and **1f** are readily soluble in a wide range of polar and nonpolar organic solvents.

Counterion exchange can also be achieved by treating the salts containing an inorganic counterion with tetra-*n*-butylammonium (TBA<sup>+</sup>) hydroxide (Scheme 1). Counterion exchange reactions on potassium organotrifluoroborate salts have been previously observed; however, the reaction has been reported to be slow with reaction times ranging from 18 h<sup>2b</sup> to several weeks.<sup>11</sup> Under our protocol the reaction is nearly instantaneous and the products are isolated and purified with ease. One equiv. of an aqueous solution of *n*Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup> (1.54 M) is added to a suspension of the K<sup>+</sup> salt (e.g. **1c**), the mixture is shaken, the layers immediately separated, and the organic phase dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo to give the purified TBA<sup>+</sup> salt (e.g. **1e**).

**Scheme 1.**

The scope of these counterion exchange protocols was explored by generating a number of tetra-*n*-butylammonium organotrifluoroborate salts from their boronic acid (Table 2, entries 1–6), potassium trifluoroborate (Table 2, entries 7–9), or lithium organoboronate derivatives (Table 2, entry 10). The latter example was generated directly from 3-bromopyridine by reaction with *n*BuLi and B(O*i*Pr)<sub>3</sub>. This procedure thus constitutes a method for the formation of trifluoroborate salts directly from their halide precursors. All of the TBA<sup>+</sup> compounds produced were found to be readily soluble in both polar and nonpolar organic solvents. X-Ray crystal structures were obtained of the tetra-*n*-butylammonium phenyl- (Table 1, entry 5)<sup>12a</sup> and ferrocenyltrifluoroborate (Table 2, entry 5)<sup>12b</sup> compounds.

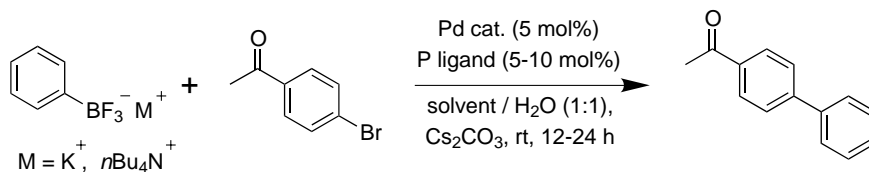
**Table 2.** Tetra-*n*-butylammonium organotrifluoroborate salts via a counterion exchange

Entry	Boron Reagent	Conditions <sup>a</sup>	Product	Yield (%)
1		A		quant.
2		A		97
3		A		97
4		A		95
5		A		80
6		B		92
7		B		97
8		B		90
9		B		95
10		A		90

a) Conditions A: i) 3.0 equiv. HF, H<sub>2</sub>O, rt, 1 h. ii) 1.0 equiv. *n*Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>, H<sub>2</sub>O, rt, 1 h. Conditions B: 1.0 equiv. *n*Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>, H<sub>2</sub>O, rt, 1 h.

Our attention then turned to studying the synthetic utility of these salts in cross-coupling reactions. Both the K<sup>+</sup> and the TBA<sup>+</sup> salts were examined in parallel in our optimization experiments (Scheme 2). The nature of the Pd catalyst (Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>, Pd<sub>2</sub>(dba)<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>), the phosphine ligand (PPh<sub>3</sub>, dppb, dppe, dppf, 2-(di-*t*-butyl-phosphino)biphenyl), and the organic cosolvent used (toluene, xylenes, DMA, DME, NMP) were investigated.

The use of water as a cosolvent was found to be essential in order for the reaction to proceed. Reactions performed in the absence of water showed low conversion in the case of the TBA<sup>+</sup> salts, and no reaction in the case of the K<sup>+</sup> salts. This is consistent with Molander's conditions for the cross-coupling of alkyltri-



Scheme 2.

fluoroborates with alkenyltriflates which also employed water.<sup>7</sup> The TBA<sup>+</sup> salts gave yields often 25–50% greater than their K<sup>+</sup> counterparts in the biphasic solvent systems under the same conditions. The organic phase was necessary to dissolve the arylhalides, while the more polar K<sup>+</sup> salts were soluble only in the aqueous phase. Addition of 10 mol% of a phase-transfer catalyst such as tetra-*n*-butylammonium iodide to the K<sup>+</sup> salts gave comparable yields to those of the TBA<sup>+</sup> salts under otherwise identical conditions. The K<sup>+</sup> salts also underwent cross-coupling reactions with water as the only solvent, using water soluble/stable arylhalides. Optimal conditions were achieved for the Pd-catalyzed cross-coupling of the TBA<sup>+</sup> salts with aryl- and alkenylbromides and aryl iodides (Table 3). The cross-coupling reactions were carried out under an open atmosphere using 1.25 equiv. of the borate to 1 equiv. of the aryl- or alkenylhalide in the presence of 5 mol% Pd(OAc)<sub>2</sub>, 5 mol% dppb, and 1.25 equiv. of Cs<sub>2</sub>CO<sub>3</sub> dissolved in a 1:1 mixture of DME:water.<sup>13</sup> The reaction was found to be tolerant of a wide range of functionalities including electron rich, electron poor, and sterically hindered substrates. While bromides and iodides coupled with ease, chlorides did not show any reactivity under these conditions, with no trace of the diphenylated product observed in Table 3, entry 4, even when 2.5 equiv. of the borate was used.

The nature of the borate was also examined (Table 4). These conditions allow for the convenient synthesis of a range of polysubstituted biaryls (Table 4, entries 1–4), arylated alkenes (Table 4, entries 5 and 6), and functionalized heterocycles (Table 4, entries 7–9).

We have begun a mechanistic investigation into the reaction of the organotrifluoroborate salts. Wright observed that CsF could be substituted for a base in Suzuki–Miyaura cross-couplings of organoboronic acids.<sup>4</sup> It was hypothesized that the CsF displaced the hydroxyls of the boronic acid to form an organotrifluoroborate, in situ, which then undergoes transmetalation to Pd. To test this theory, we ran parallel reactions under Wright's conditions with both PhB(OH)<sub>2</sub> and Cs<sup>+</sup>PhBF<sub>3</sub><sup>-</sup> (Scheme 3). While the control experiment with the boronic acid occurred as stated in the literature, the experiment with the trifluoroborate gave no reaction. Upon addition of 1 equiv. of Cs<sub>2</sub>CO<sub>3</sub> to the reaction, a similar yield of the cross-coupled product was isolated. Thus, the boron species that participates in the transmetalation step is not an organotrifluoroborate species. This is in accordance with the observations made by Fu and co-workers in comparing the reactivity of K<sup>+</sup>*o*-tolylBF<sub>3</sub><sup>-</sup> versus *o*-

tolyB(OH)<sub>2</sub> and KF under the same conditions.<sup>6</sup> From these results, we conclude that one or more hydroxyl groups must still be attached to the boron of the tetracoordinate species which undergoes the transmetalation (i.e. RBF<sub>2</sub>(OH)<sup>-</sup> or RBF(OH)<sub>2</sub>), these species forming on hydrolysis of the trifluoroborate salts with Cs<sub>2</sub>CO<sub>3</sub>/DME/H<sub>2</sub>O. In fact, this is consistent with Matos and Soderquist's mechanistic study which describes a hydroxyborate species participating in a four-centered hydroxo-μ<sub>2</sub>-bridged transition state at the

Table 3. Pd-Catalyzed cross-coupling of PhBF<sub>3</sub><sup>-</sup> nBu<sub>4</sub>N<sup>+</sup> with various arylbromides and iodides

Entry	Arylhalide	Temp (°C)	Time (h)	Product	Yield (%)
1		rt	12	<b>3a</b>	90
2		50	24	<b>3b</b>	79
3		50	24	<b>3c</b>	79
4		50	12	<b>3d</b>	96
5		rt	12	<b>3e</b>	93
6		50	24	<b>3f</b>	85
7		50	24	<b>3g</b>	93
8		rt	12	<b>3h</b>	91
9		rt	12	<b>3i</b>	quant.
10		rt	12	<b>3a</b>	92
11		50	24	<b>3b</b>	82
12		50	24	<b>3j</b>	76
13		rt	12	<b>3k</b>	97
14		50	24	<b>3l</b>	55

**Table 4.** Pd-catalyzed cross-coupling of  $\text{RBF}_3^- \text{nBu}_4\text{N}^+$  with various arylbromides

$\text{R}^1-\text{BF}_3^- \text{nBu}_4\text{N}^+$ (4) + $\text{R}^2-\text{Br}$ (5)		$\xrightarrow[\text{Cs}_2\text{CO}_3, \text{DME} / \text{H}_2\text{O} (1:1), 50^\circ\text{C}, 24 \text{ h}]{\text{Pd}(\text{OAc})_2 (5 \text{ mol}\%), \text{dppb} (5 \text{ mol}\%)}$	$\text{R}^1-\text{R}^2$ (6)	
Entry	Borate	Bromide	Product	Yield (%)
1				75
2				78
3				60
4				92
5				55
6				87
7				91
8				88
9				69

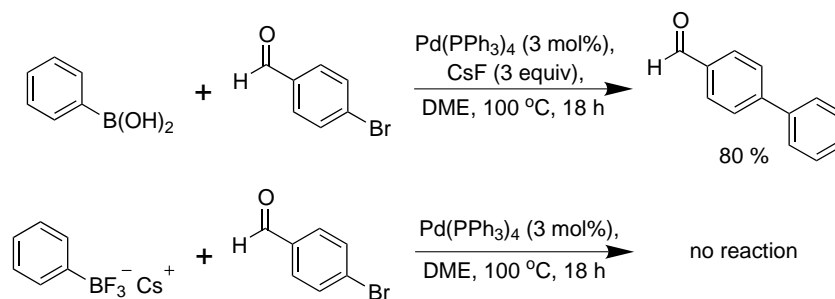
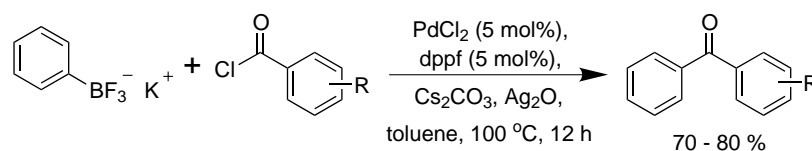
transmetallation step.<sup>14</sup> This effect may be operative in Molander's Pd-catalyzed cross-couplings of alkyltrifluoroborates,<sup>7</sup> and in the Rh(I)-catalyzed addition of aryl- and alkenyltrifluoroborates to aldehydes and

$\alpha,\beta$ -unsaturated carbonyl compounds.<sup>3a</sup> We believe this concept is generally applicable to fluoride ion promoted, transition metal catalyzed cross-couplings that involve transmetallation from boron in the catalytic cycle.

Continuing with the theme of cross-coupling reactions, we have begun preliminary studies in the Pd-catalyzed couplings of organotrifluoroborates with acid halides (Scheme 4). It has previously been reported that acid chlorides can undergo cross-couplings with sodium tetraphenylborates,<sup>15</sup> arylboronic acids,<sup>15,16</sup> and trialkylboranes.<sup>17</sup> Attempts at the cross-couplings following previous protocols of using only a Pd catalyst and an inorganic base<sup>15-17</sup> gave none of the desired product.

Deng and co-workers had reported that  $\text{Ag}_2\text{O}$  can be used to enhance the effectiveness of cross-coupling reactions.<sup>18</sup> Addition of 1 equiv. of  $\text{Ag}_2\text{O}$  to the reaction mixture did indeed provide the desired ketone. An optimization study was performed examining the nature of the Pd catalyst and ligand system, the base, the solvent, and the Ag additive. Interestingly, while the  $\text{K}^+$  salts gave moderate to good yields under these conditions, the  $\text{TBA}^+$  did not give any of the desired ketone products.

In summary, tetraalkylammonium organotrifluoroborate salts are readily prepared using a counterion exchange protocol. These salts are soluble in organic solvents and undergo Pd-catalyzed cross-coupling reactions with a variety of functionalized aryl- and alkenylhalides under mild conditions and ambient temperatures. The active species in the transmetallation step is not however the organotrifluoroborate anion. Also, potassium organotrifluoroborate salts will undergo  $\text{Ag}_2\text{O}$  assisted cross-couplings with acid halides at elevated temperatures.

**Scheme 3.****Scheme 4.**

### Acknowledgements

T.D.Q. gratefully acknowledges the receipt of an Ontario Graduate Scholarship in Science and Technology (OGSST), and thanks Dr. A. N. Thadani for his advice in working with trifluoroborate salts. We would like to thank Dr. A. J. Lough for his work in X-ray crystallography, and Dr. A. B. Young for mass spectrometric analysis.

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- Acylamino difluoroborane analogues of amino acids have been synthesized by treating the corresponding boronic acids with an excess of HF. See: Kinder, D. H.; Katzenellenbogen, J. A. *J. Med. Chem.* **1985**, *28*, 1917–1925.
- Representative procedure as used for the synthesis of **1e**: To a solution of PhB(OH)<sub>2</sub> (0.52 g, 4.27 mmol) in MeOH (ca. 1 mL) was added a solution of HF (2.65 mL, 5.0 M, 13.3 mmol) via a polypropylene syringe with vigorous stirring over 1 min at rt. The reaction mixture was then cooled to 0°C and a solution of *n*Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup> (2.76 mL, 1.54 M, 4.27 mmol) was slowly added over 5 min. The reaction was warmed to rt and stirred for another 1 h. The biphasic reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL), the layers separated, and the aqueous phase further extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo to afford 1.57 g of the pale yellow, crystalline solid **1e** (4.06 mmol, 95%).  
*Tetra-*n*-butylammonium phenyltrifluoroborate (1e)*: mp = 74°C (CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.51 (2H, d, *J* = 6.5 Hz), 7.15–7.00 (3H, m), 2.90–2.80 (8H, m), 1.40–1.18 (16H, m), 0.89 (12H, t, *J* = 7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 131.6, 126.4, 125.3, 57.6, 23.3, 19.1, 13.3 (one signal absent); <sup>11</sup>B NMR (CDCl<sub>3</sub>, 160 MHz) δ 3.30 (br s); <sup>19</sup>F NMR (CDCl<sub>3</sub>, 282 MHz) δ -142.03 (br s); IR (film) ν 3449, 2964, 2876, 1636, 1487, 1431, 1382, 1269, 1192, 1071, 950, 908, 751, 706, 598 cm<sup>-1</sup>; LRMS (FAB): *m/z* = 145 (100), 144 (25), 91 (22), 34 (10); HRMS (FAB): *m/z* calcd. for (C<sub>6</sub>H<sub>5</sub>BF<sub>3</sub>)<sup>-</sup> = 145.0436, found = 145.0449.
- An alternative synthesis of *n*Bu<sub>4</sub>N<sup>+</sup>PhBF<sub>3</sub><sup>-</sup> from PhBF<sub>2</sub> and TBAF has been reported. See: Wang, C.; Mo, Y.; Jang, M.; Janzen, A. F. *Can. J. Chem.* **1993**, *71*, 525–528.
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- (a) Quach, T. D.; Batey, R. A.; Lough, A. J. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2001**, *E57*, o688–o689; (b) Quach, T. D.; Batey, R. A.; Lough, A. J. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2001**, *E57*, m320–m321.
- Representative procedure as used for the synthesis of **6f**: *n*Bu<sub>4</sub>N<sup>+</sup>C<sub>6</sub>H<sub>13</sub>CH=CHBF<sub>3</sub><sup>-</sup> (0.53 g, 1.25 mmol), 4-BrC<sub>6</sub>H<sub>4</sub>COCH<sub>3</sub> (0.20 g, 1.00 mmol), dppb (21 mg, 0.050 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.41 g, 1.25 mmol) were suspended in DME (5 mL). Water (5 mL) was then added to the stirred reaction mixture, along with the Pd(OAc)<sub>2</sub> catalyst (11 mg, 0.050 mmol). The reaction was stirred at 50°C for 24 h, then transferred to a separatory funnel, diluted with water (30 mL), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). The combined organic layers were dried (MgSO<sub>4</sub>), filtered, and concentrated in vacuo to afford the crude product mixture. The product (**6f**) was isolated by column chromatography (eluting with hexanes:EtOAc 9:1 ~ 3:1) as an oil (0.20 g, 0.87 mmol, 87%).  
*1-(4-Acetylphenyl)-1-octene (6f)*: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 7.87 (2H, d, *J* = 8.5 Hz), 7.79 (2H, d, *J* = 8.5 Hz), 6.44–6.30 (2H, m), 2.55 (3H, s), 2.26–2.18 (2H, m), 1.52–1.24 (8H, m), 0.89 (3H, t, *J* = 7.5 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 197.6, 142.8, 135.5, 134.6, 129.0, 128.8, 126.0, 33.3, 31.8, 29.2, 29.0, 26.6, 22.7, 14.2; IR (film) ν 2926, 2855, 1682, 1648, 1602, 1563, 1466, 1410, 1357, 1268, 1181, 1111, 1074, 1013, 966, 855, 809, 724, 705, 592 cm<sup>-1</sup>; LRMS (EI): *m/z* = 231 (21), 230 (89), 216 (16), 215 (77), 147 (22), 146 (67), 145 (16), 134 (19), 131 (100), 117 (24), 115 (37), 91 (14); HRMS (EI): *m/z* calcd. for (C<sub>16</sub>H<sub>22</sub>O)<sup>+</sup> = 230.1671, found = 230.1675.
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