An Improved Synthesis of Fluorinated Imidoylsilanes

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Abstract: A practical and efficient method for the preparation of fluorinated imidoylsilanes is described. The key step involves finely controlled activation of C–Cl and C–Br bonds in fluorinated imidoyl chlorides and bromides, respectively.

Key words: magnesium, fluorine, imines, umpolung, imidoylsilane

Fluorinated acyl anions and their equivalents are highly useful synthons for the nucleophilic introduction of fluorinated acyl groups into organic molecules.[1–6] Fluorinated acylsilanes **1**[3,4] and imidoylsilanes **2**[7] have been regarded as versatile intermediates in the synthesis of fluorinated ketones and their derivatives (Figure 1).

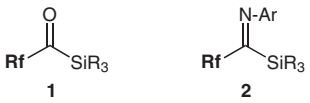
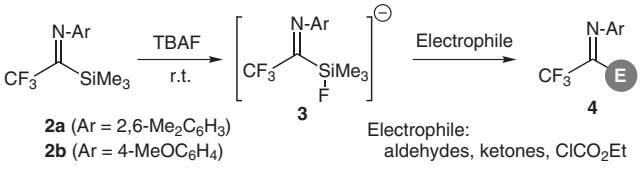


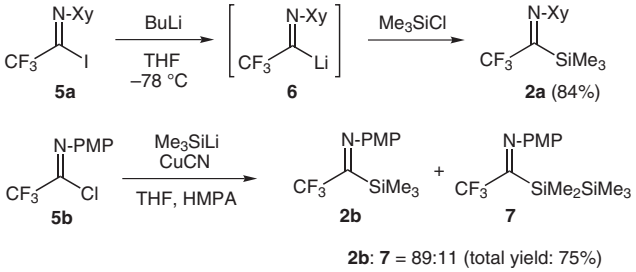
Figure 1

Previously, we demonstrated several examples of trifluoroacetimidoylsilanes **2** acting as useful carbanion sources.[7] Upon treatment with TBAF, imidoylsilanes **2** underwent C–C bond-forming reactions with carbon electrophiles such as aldehydes, ketones, and chloroformate to afford functionalized imines **4** in good yields (Scheme 1). A key feature of this methodology is the mildness of the reaction conditions (room temperature), which was attributed to the thermal stability of pentavalent silicates **3**, whereas the corresponding imidoyl lithium agents require low temperature conditions (below –60 °C) due to their poor thermal stability.



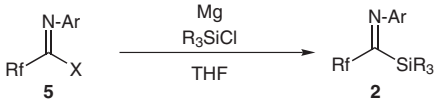
Scheme 1

Despite their usefulness, there have been only two methods described for the preparation of trifluoroacetimidoylsilanes **2**: (a) the reaction of the trifluoroacetimidoyl lithium species with chlorotrimethylsilane by iodine–lithium exchange of the corresponding trifluoroacetimidoyl iodides and (b) the reaction of trifluoroacetimidoyl chlorides with silyl cuprate reagents (Scheme 2). The limitation of the former method (via iodine–lithium exchange) is the range of applicable substrates. In general, imidoyl lithium species are not thermally stable at higher temperatures due to the existence of an equilibrium between an imidoyl anion and an aminocarbene species.[8] This protocol worked well only for trifluoroacetimidoyl iodides endowed with bulky aromatic substituents such as a 2,6-dimethylphenyl (Xy) group on the nitrogen atoms of the imine moieties, which prevents the isomerization of imidoyl lithium agents to the corresponding carbenes.



Scheme 2

Moreover, the latter method (nucleophilic silylation) required significant amounts of toxic HMPA as an additive to give trimethylsilyl lithium; in addition, small amounts of the byproduct disilane **7** were observed. Therefore, an efficient method for the preparation of fluorinated imidoylsilanes is required. Herein, we present Mg-promoted selective activation of imidoyl carbon–halogen bonds,[9,10] which provides a practical method to prepare fluorinated imidoylsilanes **2** (Scheme 3).



Scheme 3

A Mg/TMSCl system[11,12] is considered to be useful for the reductive dehalogenation of fluorinated imidoyl halides. When imidoyl chloride **5b** was treated with an excess amount of magnesium metal (4 equiv) and TMSCl (4 equiv) in THF at 0 °C, selective formation of bis(silyl)enamine **8**[12] was observed and the desired imidoylsilane **2b** was not detected (Table 1, entry 1).

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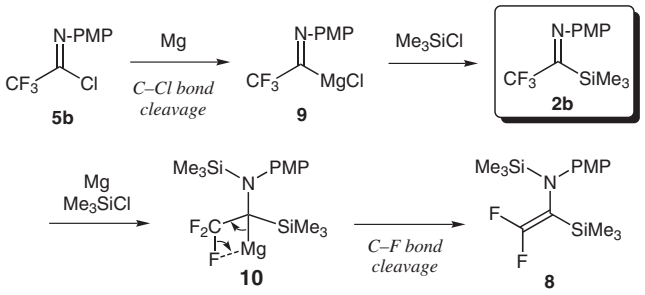
A plausible mechanism for the formation of difluoroenamine **8** is shown in Scheme 4. Initially, the reductive cleavage of the C–Cl bond of the imidoyl chloride **5b** took place to generate imidoyl magnesium species **9**, which reacted with TMSCl to provide the imidoylsilane **2b**. Subsequent two-electron reduction of the resultant imidoylsilane **2b** afforded defluorinated product **8**.



Scheme 4

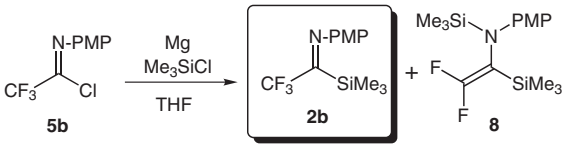
Focusing on the selective synthesis of **2b**, further reduction involving C–F bond cleavage should be avoided. Upon treatment with a reduced amount of magnesium metal (1 equiv), the formation of imidoylsilane **2b** was observed (Table 1, entry 2). Conducting the reaction at a low temperature (–40 °C) for 30 minutes, further reduction was suppressed and the desired imidoylsilane **2b** was obtained selectively (Table 1, entry 3), however, the conversion of the starting imidoyl chloride **5b** was low. In order to increase the chemical yield of **2b** under low temperature conditions, a technique to activate the surface of metallic magnesium would be important. When the reaction was carried out at –40 °C in the presence of a catalytic amount of ethyl bromide,[13] the chemical conversion of imidoyl chloride **5b** was dramatically improved to provide **2b** and **8** in 52% and 25% yields, respectively (Table 1, entry 5). At lower temperatures (–75 °C), overreduction of imidoylsilane **2b** was prevented, resulting in the selective formation of **2b** in 73% isolated yield (Table 1, entry 6).

Other examples of the selective synthesis of imidoylsilanes **2** are given in Table 2. Difluoromethyl, perfluoroalkyl and pentafluoroethyl imidoylsilanes **2** were obtained in moderate to good yields (Table 2, entries 2–7). For the synthesis of perfluoroalkylated imidoylsilanes **2d** and **2e**, the use of the corresponding imidoyl bromides (**5d′** and **5e**) as substrates was important (Table 2, entries 3–6). When imidoyl chloride **5d** was employed, the desired imidoylsilane **2d** was produced in only 40% yield (Table 2, entry 3). However, the corresponding bromide **5d′** smoothly underwent selective monosilylation at –60 °C to provide pentafluoroethyl imidoylsilane **2d** in 96% yield (Table 2, entry 4). On the whole, while the desired reactions proceeded sluggishly under low temperature conditions (below –50 °C), both remarkable enhancement in the reactivity and high reproducibility were obtained when a catalytic amount of ethyl bromide was employed (Table 2, entries 1, 6, and 7).

Furthermore, synthesis of imidoylsilanes with other alkylsilyl groups was examined. As shown in Scheme 5, chlorotriethylsilane (TESCl) provided the corresponding TES-derivative **2g** in 63% yield upon reacting with trifluoroacetimidoyl bromide **5b′** (Rf = CF_3, X = Br). However, the use of more bulky silanes such as TBDMSCl, TBDMS-OTf, and TIPSCl were unsuccessful. The present silylation of the imidoyl magnesium seems to be affected by the steric bulkiness of trialkylsilyl reagents.

In summary, we have described a convenient synthesis of fluorinated imidoylsilanes, which are the stable versions of fluorinated acyl anion equivalents. Finely controlled reductive cleavage of carbon–halogen bonds expands the scope of these building blocks in synthetic organic chemistry.

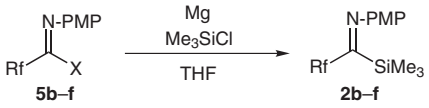
Table 1 Mg-Promoted Reductive Silylation of Imidoyl Chloride **5b**



Entry	Mg (equiv)	TMSCl (equiv)	Additive	Conditions	Yield (%)[a]	
					2b	**8**
1	4	4	–	0 °C, 30 min	0	85
2	1	4	–	0 °C, 30 min	12	20
3	2	4	–	–40 °C, 30 min	37	–
4	3	4	–	–75 °C, 30 min	**5b** recovered	
5	3	4	EtBr (0.05 equiv)[b]	–40 °C, 2.5 h	52	25
6	3.5	2	EtBr (0.05 equiv)[b]	–75 °C, 2.5 h	73[c]	–

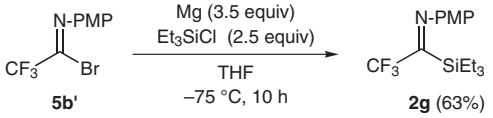
[a] Determined by ^{19}F NMR spectroscopy.
[b] A catalytic amount of EtBr (0.05 equiv) was added prior to each reaction.
[c] Isolated yield.

Table 2 Synthesis of Imidoylsilanes **2**



Entry	**5**			Mg	Me_3SiCl	Conditions	**2**	Yield (%)[a]
	Rf	X		(equiv)	(equiv)			
1[b]	CF_3	Cl	**5b**	3.5	2	–75 °C, 2.5 h	**2b**	73
2	CF_2H	Cl	**5c**	8	4	0 °C, 1 h	**2c**	77
3	C_2F_5	Cl	**5d**	4	2	–75 °C, 1 h	**2d**	40
4	C_2F_5	Br	**5d′**	4	2	–60 °C, 2.5 h	**2d**	96
5	C_3F_7	Br	**5e**	4	2	–60 °C, 11 h	**2e**	5[c]
6[b]	C_3F_7	Br	**5e**	4	2	–60 °C, 5 h	**2e**	63
7[b]	C_6F_5	Cl	**5f**	2	8	–70 °C, 1.5 h	**2f**	79

[a] Isolated yields.
[b] Reaction was performed in the presence of EtBr (cat.).
[c] Most of the starting material **5e** remained.



Scheme 5

^1H and ^{19}F NMR spectra were recorded at 200 and 188 MHz, respectively, in $CDCl_3$. The chemical shifts are reported in ppm relative to $CHCl_3$ (7.26 ppm for ^1H NMR) and C_6F_6 (0 ppm for ^{19}F NMR). Coupling constants are reported in Hz. All air- and/or water-sensitive reactions were carried out under an argon atmosphere with anhydrous, freshly distilled solvents using standard syringe/cannula/septa techniques. THF was distilled from Na-benzophenone ketyl. All other reagents and solvents were employed without further purification. Column chromatography was carried out with Merck silica gel (Kieselgel 60, 230–400 mesh). IR spectra were recorded on a Hitachi 270-30 spectrometer. A Perkin-Elmer Series II CHNS/O Analyzer 2400 was employed for elemental analyses. GC/MS analyses were performed on a Hewlett-Packard HP5971A. The starting imidoyl halides **5** were prepared from the corresponding fluorinated carboxylic acid, *p*-anisidine, PPh_3, Et_3N, and CX_4 (X = Cl, Br).[14]

_N_-(4-Methoxyphenyl)-_N_-[2,2,2-trifluoro-1-(trimethylsilyl)ethylidene]amine (2b)

To a suspension of Mg (173 mg, 7.1 mmol) and EtBr (8 μL, 0.1 mmol) in freshly distilled THF (15 mL) were added TMSCl (0.54 mL, 4.2 mmol) and **5b** (505 mg, 2.1 mmol) at –75 °C under an argon atmosphere. The reaction mixture was stirred at –75 °C for 2.5 h. A solution of Et_3N (10%) in hexane (10 mL) was added to the residue. Then, the mixture was decanted to remove residual Mg, the organic layer was washed with ice-cold H_2O (20 mL), and dried over Na_2SO_4. Column chromatography (hexane–EtOAc, 40:1) afforded **2b** (410.5 mg, 73%) as a pale-yellow oil.

IR (neat): 2968, 1506 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 9 H), 3.81 (s, 3 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 6.87 (d, *J* = 9.0 Hz, 2 H).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 93.1 (s, 3 F).

GC-MS: *m*/*z* (%) = 275 (20) [M^+], 206 (100), 133 (8), 73 (72).

Anal. Calcd for $C_{12}H_{16}F_3NOSi$: C, 52.35; H, 5.86; N, 5.09. Found: C, 52.55; H, 5.87; N, 5.44.

_N_-(4-Methoxyphenyl)-_N_-[2,2-difluoro-1-(trimethylsilyl)ethylidene]amine (2c)

To a suspension of Mg (293 mg, 12.0 mmol) in freshly distilled THF (15 mL) were added TMSCl (0.77 mL, 6.0 mmol) and **5c** (311 mg, 1.4 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h. Then, the majority of the THF was removed under reduced pressure; filtration of the residue through a pad of Celite followed by Kugelrohr distillation afforded **2c** as a white solid (277 mg, 77%); bp 90 °C (13 mmHg); mixture of *E*/*Z* isomers.

IR (KBr): 2968, 1504 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.09 (s, 9 H), 3.80 (s, 3 H), 5.93 (t, J_{HF} = 57.1 Hz, 1 H), 6.69 (d, *J* = 8.5 Hz, 2 H), 6.86 (d, *J* = 8.5 Hz, 2 H).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 46.9 (d, J_{HF} = 57.1 Hz, 2 F, major isomer), 47.8 (d, J_{HF} = 57.1 Hz, 2 F, minor isomer).

GC-MS: *m*/*z* (%) = 257 (7) [M^+], 206 (64), 73 (100).

Anal. Calcd for $C_{12}H_{17}F_2NOSi$: C, 56.00; H, 6.66; N, 5.44. Found: C, 56.35; H, 6.90; N, 5.46.

_N_-(4-Methoxyphenyl)-_N_-[2,2,3,3,3-pentafluoro-1-(trimethylsilyl)propylidene]amine (2d)

To a suspension of Mg (51 mg, 2.1 mmol) in freshly distilled THF (6 mL) were added TMSCl (0.15 mL, 1.2 mmol) and **5d′** (165 mg, 0.50 mmol) at –60 °C under an argon atmosphere. The reaction mixture was stirred at –60 °C for 2.5 h. A solution of Et_3N in hexane (10%; 10 mL) was added to the residue. The mixture was decanted to remove the residual Mg, the organic layer was washed with ice-cold H_2O (10 mL), and dried over Na_2SO_4. Column chromatography (hexane–EtOAc, 50:1) afforded **2d** (155 mg, 96%) as a yellow oil.

IR (neat): 2964, 1504 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.05 (s, 9 H), 3.80 (s, 3 H), 6.66 (d, *J* = 9.0 Hz, 2 H), 6.86 (d, *J* = 9.0 Hz, 2 H).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 50.7 (s, 2 F), 81.8 (s, 3 F).

GC-MS: *m*/*z* (%) = 325 (5) [M$^+$], 252 (2), 206 (57), 107 (3), 92 (10), 73 (100).

Anal. Calcd for $C_{13}H_{16}F_5NOSi$: C, 47.99; H, 4.96; N, 4.31. Found: C, 48.22; H, 5.31; N, 4.61.

_N_-[2,2,3,3,4,4,4-Heptafluoro-1-(trimethylsilyl)butylidene]-_N_-(4-methoxyphenyl)amine (2e)

To a suspension of Mg (44 mg, 1.8 mmol) and EtBr (2 μL, 0.026 μmol) in freshly distilled THF (5 mL) were added TMSCl (0.13 mL, 1.0 mmol) and **5e** (192 mg, 0.50 mmol) at –60 °C under an argon atmosphere. The reaction mixture was stirred at –60 °C for 5 h. A solution of Et_3N in hexane (10%; 10 mL) was added to the residue. The mixture was decanted to remove the residual Mg, the organic layer was washed with ice-cold H_2O (10 mL), and dried over Na_2SO_4. Column chromatography (hexane–EtOAc, 50:1) afforded **2e** (118 mg, 63%) as a yellow oil.

IR (neat): 2968, 1504 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 9 H), 3.81 (s, 3 H), 6.66 (d, *J* = 8.9 Hz, 2 H), 6.87 (d, *J* = 8.9 Hz, 2 H).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 37.5 (s, 2 F), 53.5 (s, 2 F), 82.1 (s, 3 F).

GC-MS: *m*/*z* (%) = 375 (2) [M$^+$], 206 (59), 133 (4), 73 (100).

Anal. Calcd for $C_{14}H_{16}F_7NOSi$: C, 44.80; H, 4.30; N, 3.73. Found: C, 44.73; H, 4.44; N, 3.96.

_N_-(4-Methoxyphenyl)-_N_-[pentafluorophenyl(trimethylsilyl)methylene]amine (2f)

To a suspension of Mg (99 mg, 4.1 mmol) and EtBr (8 μL, 0.1 μmol) in freshly distilled THF (16 mL) were added TMSCl (2.1 mL, 16 mmol) and **5e** (672 mg, 2.0 mmol) at –70 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 1.5 h. The majority of the THF was removed under reduced pressure; filtration of the residue through a pad of Celite followed by Kugelrohr distillation afforded **2e** as a pale-yellow solid (532 mg, 79%): bp 140 °C (13.5 mmHg).

IR (KBr): 2968, 1502 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.26 (s, 9 H), 3.73 (s, 3 H), 6.60 (d, *J* = 9.0 Hz, 2 H), 6.72 (d, *J* = 9.0 Hz, 2 H).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 0.79–1.06 (m, 2F), 7.93 (t, *J* = 21.1 Hz, 1 F), 22.7 (d, *J* = 17.3 Hz, 2 F).

GC-MS: *m*/*z* (%) = 373 (15) [M$^+$], 300 (22), 206 (26), 73 (100).

Anal. Calcd for $C_{17}H_{16}F_5NOSi$: C, 54.68; H, 4.32; N, 3.75. Found: C, 54.32; H, 4.15; N. 3.64.

_N_-(4-Methoxyphenyl)-_N_-[2,2,2-trifluoro-1-(triethylsilyl)ethylidene]amine (2g)

To a suspension of Mg (169 mg, 7.0 mmol) in freshly distilled THF (4 mL) were added TMSCl (0.591 mL, 4.0 mmol) and **5b′** (562 mg, 2.0 mmol) at –75 °C under an argon atmosphere. The reaction mixture was stirred at –75 °C for 10 h. A solution of Et_3N in hexane (10%; 5 mL) was added to the residue. The mixture was decanted to remove residual Mg, the organic layer was washed with ice-cold H_2O (10 mL), and dried over Na_2SO_4. Purification by Kugelrohr distillation afforded **2g** (247 mg, 63%) as a pale-yellow oil; bp 150 °C (3 mmHg).

IR (neat): 2964, 1502 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.53 (q, *J* = 8.1 Hz, 6 H), 0.87 (t, *J* = 8.1 Hz, 9 H), 3.82 (s, 3 H), 6.71 (d, *J* = 9.0 Hz, 2 H), 6.86 (d, *J* = 9.0 Hz, 2 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = 93.1 (s, 3 F).

GC-MS: *m*/*z* (%) = 317 (10) [M$^+$], 248 (100), 115 (39), 87 (97), 77 (32), 59 (40).

Anal. Calcd for $C_{15}H_{22}F_3NOSi$: C, 56.76; H, 6.99; N, 4.41. Found: C, 56.74; H, 7.18; N, 4.04.

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References

(1) (a) Ichikawa, J.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1989**, *30*, 1641. (b) Ichikawa, J.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1989**, *30*, 5437. (c) Ichikawa, J.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1989**, *30*, 6379. (d) Ichikawa, J.; Moriya, T.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1991**, 961. (e) Ichikawa, J.; Hamada, S.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1992**, *33*, 337. (f) Okada, Y.; Minami, T.; Yamamoto, T.; Ichikawa, J. *Chem. Lett.* **1992**, 547. (g) Ichikawa, J.; Minami, T.; Sonoda, T.; Kobayashi, H. *Tetrahedron Lett.* **1992**, *33*, 3779. (h) Ichikawa, J.; Ikeura, C.; Minami, T. *Synlett* **1992**, 739. (i) Ichikawa, J.; Yonemaru, S.; Minami, T. *Synlett* **1992**, 833.

(2) (a) Patel, S. T.; Percy, J. M.; Wilkens, R. D. *Tetrahedron* **1995**, *51*, 9201. (b) Howarth, J. A.; Owton, W.; Percy, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 757. (c) Howarth, J. A.; Owton, W.; Percy, J. M.; Rock, M. H. *Tetrahedron* **1995**, *51*, 10289. (d) Crowley, P. J.; Howarth, J. A.; Owton, W.; Percy, J. M.; Stansfield, K. *Tetrahedron Lett.* **1996**, *37*, 5975. (e) Crowley, P. J.; Percy, J. M.; Stansfield, K. *Tetrahedron Lett.* **1996**, *37*, 8233. (f) Crowley, P. J.; Percy, J. M.; Stansfield, K. *Tetrahedron Lett.* **1996**, *37*, 8237. (g) Balnaves, A. S.; Gelbrich, T.; Hursthouse, M. B.; Light, M. E.; Palmer, M. J.; Percy, J. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2525. (h) DeBoos, G. A.; Fullbrook, J. J.; Owton, W. M.; Percy, J. M.; Thomas, A. C. *Synlett* **2000**, 963. (i) DeBoos, G. A.; Fullbrook, J. J.; Percy, J. M. *Org. Lett.* **2001**, *3*, 2859. (j) Garayt, M. R.; Percy, J. M. *Tetrahedron Lett.* **2001**, *42*, 6377. (k) Cox, L. R.; DeBoos, G. A.; Fullbrook, J. J.; Percy, J. M.; Spencer, N. S.; Tolley, M. *Org. Lett.* **2003**, *5*, 337.

(3) (a) Jin, F.; Jiang, B.; Xu, Y. *Tetrahedron Lett.* **1992**, *33*, 1221. (b) Jin, F.; Xu, Y.; Huang, W. *J. Chem. Soc., Perkin Trans. 1* **1993**, 795. (c) Jin, F.; Xu, Y. *J. Fluorine Chem.* **1993**, *62*, 207. (d) Jin, F.; Xu, Y.; Huang, W. *J. Chem. Soc., Chem Commun.* **1993**, 814.

(4) Bordeau, M.; Clavel, P.; Barba, A.; Berlande, M.; Biran, C.; Roques, N. *Tetrahedron Lett.* **2003**, *44*, 3741.

(5) (a) Higashiya S., Lim D. S., Ngo S. C., Toscano P. J., Welch J. T.; Abstracts of Papers, 222nd National Meeting of the American Chemical Society, Chicago IL, Aug 26–30, 2001; American Chemical Society: Washington D.C., **2001**; ORGN 41 (b) Ngo, S. C.; Chung, W. J.; Lim, D. S.; Shigashiya, S.; Welch, J. T. *J. Fluorine Chem.* **2002**, *117*, 207. (c) Chung, W. J.; Higashiya, S.; Oba, Y.; Welch, J. T. *Tetrahedron* **2003**, *59*, 10031. (d) Chung, W. J.; Welch, J. T. *J. Fluorine Chem.* **2004**, *125*, 543. (e) Chung, W. J.; Ngo, S. C.; Higashiya, S.; Welch, J. T. *Tetrahedron Lett.* **2004**, *45*, 5403.

(6) (a) Watanabe, H.; Yamashita, F.; Uneyama, K. *Tetrahedron Lett.* **1993**, *34*, 1941. (b) Tamura, K.; Yan, F.-Y.; Sakai, T.; Uneyama, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 300. (c) Watanabe, H.; Yan, F.-Y.; Sakai, T.; Uneyama, K. *J. Org. Chem.* **1994**, *59*, 758.
(7) Uneyama, K.; Noritake, C.; Sadamune, K. *J. Org. Chem.* **1996**, *61*, 6055.
(8) A carbene-type intermediate has been proposed for benzoyl lithium, see: (a) Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Nudelman, N. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 8118. (b) Nudelman, N. S.; Vitale, A. A. *J. Org. Chem.* **1981**, *46*, 4625. (c) Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. (d) Aminocarbene structure: Butters, M. *Comprehensive Organic Functional Group Transformations*, Vol. 5; Katrizky, A. R.; Meth-Cohn, O.; Rees, C. W.; Moody, C. J., Eds.; Pergamon Press: Oxford, **1995**, 783–804.
(9) Preparation of (non-fluorinated) imidoylsilanes from imidoyl chlorides: (a) Bourgeois, P. *J. Organomet. Chem.* **1974**, *76*, C1. (b) Niznik, G. E.; Morrison, W. H.; Walborsky, H. M. *J. Org. Chem.* **1974**, *39*, 600.
(10) Generation of (non-fluorinated) imidoyl lithiums from the corresponding imidoyl chlorides: Alonso, E.; Ramón, D. J.; Yus, M. *Tetrahedron* **1998**, *54*, 12007.
(11) (a) Amii, H.; Kobayashi, T.; Hatamoto, Y.; Uneyama, K. *Chem. Commun.* **1999**, 1323. (b) Amii, H.; Kobayashi, T.; Uneyama, K. *Synthesis* **2000**, 2001. (c) Mae, M.; Amii, H.; Uneyama, K. *Tetrahedron Lett.* **2000**, *41*, 7893. (d) Amii, H.; Kobayashi, T.; Terasawa, H.; Uneyama, K. *Org. Lett.* **2001**, *3*, 3103. (e) Amii, H.; Hatamoto, Y.; Seo, M.; Uneyama, K. *J. Org. Chem.* **2001**, *66*, 7216. (f) Hata, H.; Kobayashi, T.; Amii, H.; Uneyama, K.; Welch, J. T. *Tetrahedron Lett.* **2002**, *43*, 6099.
(12) Kobayashi, T.; Nakagawa, T.; Amii, H.; Uneyama, K. *Org. Lett.* **2003**, *5*, 4297.
(13) (a) Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic Press: London, **1995**. (b) Pearson, D. E.; Cowan, D.; Beckler, J. D. *J. Org. Chem.* **1958**, *24*, 504. (c) Garst, J. F.; Ungvary, F.; Batlaw, R.; Lawrence, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 6697.
(14) Tamura, K.; Mizukami, H.; Maeda, K.; Watanabe, H.; Uneyama, K. *J. Org. Chem.* **1993**, *58*, 32.