Synthesis of *N,N*-Dimethyl-2-(tributylstannyl)methyl-5-substituted Benzylamines as a Quinodimethane Precursor by the Reaction of *N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-substituted Benzylammonium Salts with Lithium Diisopropylamide

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Reaction of *N,N*-dimethyl-*N*-(tributylstannyl)methyl-4-substituted benzylammonium salts **2** with lithium diisopropylamide (LDA) gave *N,N*-dimethyl-2-(tributylstannyl)methyl-5-substituted benzylamines **3** as the main products. Treatment of **3** with iodomethane followed by tetrabutylammonium fluoride (TBAF) in the presence of dimethyl fumarate gave the corresponding dimethyl *trans*-1,2,3,4-tetrahydro-6-substituted naphthalene-2,3-dicarboxylates **15** in good yields.

Key words ammonium ylide; quinodimethane; destannylation; sigmatropic rearrangement; isotoluene

In our previous studies of regioselective *N*-alkylidene formation by fluoride ion-induced desilylation of [1-(trimethylsilyl)alkyl]ammonium salts,¹⁾ we reported that the base-induced destannylation of [(tributylstannyl)methyl]ammonium salts could be useful in synthetic organic chemistry.²⁾ For example, the treatment with butyllithium of *N,N*-dimethyl-*N*-[(tributylstannyl)methyl]benzylammonium salt **2a** gave a Sommelet-Hauser rearrangement product **4a**, and the treatment with lithium diisopropylamide (LDA) afforded *N,N*-dimethyl-2-[(tributylstannyl)methyl]benzylamine **3a** as the main product, respectively (Chart 1). A quaternized salt **13a** of **3a** could be used as an *ortho*-quinodimethane precursor (Chart 3). To assess the generality of the quinodimethane reaction, we examined the synthesis of 2-[(tributylstannyl)methyl]benzylamines with various *para* substituents in detail.

Results and Discussion

Eight *N,N*-dimethyl-*N*-(tributylstannyl)methyl-4-substituted benzylammonium salts **2a–h** were prepared by reacting 4-substituted benzyl halides **1** with tributyl(dimethylaminomethyl)tin (Chart 1). The reaction of the *N,N*-dimethyl-*N*-[(tributylstannyl)methyl]benzylammonium salt **2a** with an equimolar amount of LDA at 0°C in tetrahydrofuran (THF) gave a mixture of *N,N*-dimethyl-2-[(tributylstannyl)methyl]benzylamine **3a**, *N,N*-dimethyl-2-methylbenzylamine **4a** and *N*-methyl-*N*-(tributylstannyl)methyl-2-[(tributylstannyl)methyl]benzylamine³⁾ **11a** (Chart 2, Table 1, entry 1).

A similar reaction of the 4-methylbenzylammonium **2b** or 4-methoxybenzylammonium salt **2c** gave *N*-methyl-*N*-(tributylstannyl)methyl-5-(methyl or methoxy)-2-methylbenzylamine **12b, c** as a new by-product together with the expected products **3b, c**, **4b, c** and **11b, c**. In the reaction of the 4-fluorobenzylammonium **2d**, 4-chlorobenzylammonium **2e** and 4-(trifluoromethyl)benzylammonium **2f** salts, the formation of **11d–f** and **12d–f** decreased, while *N,N*-dimethyl-3-(fluoro or chloro)-2-tributylstannyl-6-[(tributylstannyl)methyl]benzylamine **7d, e** was formed as another by-product (entries 4, 5). In contrast, the reaction of the 2-cyanobenzylammonium salt **2g** gave a complex mixture and that of the 2-nitrobenzylammonium salt **2h** yielded only 4,4'-dinitrobenzyl and tributyl(dimethylaminomethyl)tin.

2-Substituted 5-methylene-6-[methyl(tributylstannyl)methyl]aminomethyl]cyclohexa-1,3-dienes **10**, which are [2,3] sigmatropic rearrangement products of the ylide **9**, are possible precursors of **11** and **12** (Chart 2). Thus, for the ylides **5a–c** with *para*-electron-releasing substituents ($\sigma_p < 0$), isomerization to the methylide **9** is important. The presence of a *para*-electron-withdrawing group (**2d, e**, $0 < \sigma_p < 0.22$) is favorable for the synthesis of **3**, while the

Table 1. Reaction of *N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-substituted Benzylammonium Hexafluorophosphates **2** with LDA at 0°C for 2 h in THF

Entry	R	Total yield ^{b)} (%)	Product ratio ^{a)}				
			3	4	7	11	12
1	2a H	95	65	10	0	25	0
2	2b Me	95	42	32	0	22	4
3	2c OMe	88	25	32	0	24	19
4	2d F	92	62	15	23	0	0
5	2e Cl	92	95	3	1	1	0
6	2f CF ₃	29 ^{c)}	90	0	0	10	0
7	2g CN	—	Complex mixture				
8	2h NO ₂	0 ^{d)}	0	0	0	0	0

a) Ratio of the products determined by HPLC analysis at 275 nm. b) Yields determined by integration of the ¹H signals in the 270-MHz NMR spectrum, using an internal standard (phthalide). c) Ammonium salt **2f** (55%) was recovered. d) 4,4'-Dinitrobenzyl (39%) and tributyl(dimethylaminomethyl)tin (75%) were obtained.

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Chart 2

Chart 3

presence of stronger electron-withdrawing groups (**2f–h**, $\sigma_p > 0.54$) is not favorable. By-products **7** and **11**, which have two tributylstannyl groups, may be formed by the reaction of isotoluene intermediates (**6**, **10**) with the stannyl radical generated by the conversion of **6** to **4**. The low yield of **3f** was a result of the formation of the benzylide **8f**, which was recovered as **2f** (55%) from the aqueous work-up.

When **3a–e** were quaternized with iodomethane to *N,N,N*-trimethyl-2-(tributylstannyl)methyl-5-substituted benzylammonium iodides **13** and treated with tributylammonium fluoride (TBAF) in the presence of dimethyl fumarate, dimethyl *trans*-1,2,3,4-tetrahydro-6-substituted naphthalene-2,3-dicarboxylates⁴⁾ **15** were obtained in yields of 60–70% (Chart 3). Thus, compounds **13** are useful for the synthesis of naphthalenes with dienophiles (Diels–Alder reaction).

Experimental

All reactions were carried out in nitrogen. THF was distilled from sodium and benzophenone. All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. ¹H-NMR and ¹³C-NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. MS were measured on a JEOL JMS SX-102A spectrometer. UV spectra were recorded on a Shimadzu UV-240 spectrophotometer.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-substituted Benzylammonium Hexafluorophosphates (**2**)** General Procedure: A solution of 4-substituted benzyl halides **1** (20 mmol) and tributyl(dimethylamino)-

methyltin⁵⁾ (7.7 g, 22 mmol) in acetone (20 ml) was stirred at room temperature for 2 h and the solvent was removed under reduced pressure. The residue was washed with hexane, and dissolved in MeOH (5 ml). This solution was mixed with 4 M aqueous NH₄PF₆ (10 ml), and after 0.5 h the mixture was extracted with CHCl₃ (3 × 50 ml). The CHCl₃ layer was dried (MgSO₄) and concentrated to give the ammonium salts **2**.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-methylbenzylammonium Hexafluorophosphate (**2a**):** Yield 89%, colorless crystals, mp 73–74 °C. ¹H-NMR (270 MHz; CDCl₃) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.99–1.54 (18H, m), 3.00 (6H, s), 3.16 (2H, t, $J = 12.0$ Hz), 4.45 (2H, s), 7.41–7.50 (5H, m). IR (KBr) cm⁻¹: 1460, 840. Anal. Calcd for C₂₂H₄₄F₆NPSn: C, 45.23; H, 7.25; N, 2.40. Found: C, 45.08; H, 7.17; N, 2.37.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-methylbenzylammonium Hexafluorophosphate (**2b**):** Yield 85%, colorless crystals, mp 68–71 °C. ¹H-NMR (270 MHz; CDCl₃) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.96–1.54 (18H, m), 2.38 (3H, s), 2.99 (6H, s), 3.13 (2H, t, $J = 12.0$ Hz), 4.40 (2H, s), 7.23 (2H, d, $J = 7.9$ Hz), 7.33 (2H, d, $J = 7.9$ Hz). IR (KBr) cm⁻¹: 1480, 830. Anal. Calcd for C₂₃H₄₄F₆NPSn: C, 46.18; H, 7.41; N, 2.34. Found: C, 46.08; H, 7.41; N, 2.48.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-methoxybenzylammonium Hexafluorophosphate (**2c**):** Yield 92%, colorless crystals, mp 73–75 °C. ¹H-NMR (400 MHz; CDCl₃) δ : 0.90 (9H, t, $J = 7.3$ Hz), 1.07–1.52 (18H, m), 2.97 (6H, s), 3.10 (2H, t, $J = 12.1$ Hz), 3.83 (3H, s), 4.39 (2H, s), 6.94 (2H, d, $J = 8.8$ Hz), 7.37 (2H, d, $J = 8.8$ Hz). IR (KBr) cm⁻¹: 1520, 1260, 830. Anal. Calcd for C₂₃H₄₄F₆NOPSn: C, 44.97; H, 7.22; N, 2.28. Found: C, 44.78; H, 7.29; N, 2.37.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-fluorobenzylammonium Hexafluorophosphate (**2d**):** Yield 93%, colorless crystals, mp 119–121 °C. ¹H-NMR (270 MHz; CDCl₃) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.98–1.63 (18H, m), 3.06 (6H, s), 3.13 (2H, t, $J = 11.6$ Hz), 4.65 (2H, s), 7.73 (2H, d, $J = 8.4$ Hz), 8.28 (2H, d, $J = 8.4$ Hz). IR (KBr) cm⁻¹: 1530, 1350, 830. Anal. Calcd for C₂₂H₄₁F₇NPSn: C, 43.88; H, 6.86; N, 2.33. Found: C, 43.73; H, 6.97; N, 2.38.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-chlorobenzylammonium Hexafluorophosphate (**2e**):** Yield 86%, colorless crystals, mp 141–144 °C. ¹H-NMR (270 MHz; CDCl₃) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.94–1.54 (18H, m), 2.99 (6H, s), 3.09 (2H, t, $J = 11.5$ Hz), 4.47 (2H, s), 7.42 (4H, s). IR (KBr) cm⁻¹: 1480, 840. Anal. Calcd for C₂₂H₄₁ClF₆NPSn: C, 42.67; H, 6.83; N, 2.23. Found: C, 42.48; H, 6.64; N, 2.34.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-(trifluoromethyl)benzylammonium Hexafluorophosphate (**2f**):** Yield 92%, colorless crystals, mp 143–144 °C. ¹H-NMR (270 MHz; CDCl₃) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.99–1.57 (18H, m), 2.99 (6H, s), 3.12 (2H, t, $J = 12.0$ Hz), 4.46 (2H, s), 7.12 (2H, t, $J = 8.4$ Hz), 7.50 (2H, dd, $J = 5.1, 8.4$ Hz). IR (KBr) cm⁻¹: 1320, 1130, 830. Anal. Calcd for C₂₃H₄₁F₉NPSn: C, 42.35; H, 6.34; N, 2.15. Found: C, 42.17; H, 6.25; N, 2.40.

***N,N*-Dimethyl-*N*-(tributylstannyl)methyl-4-cyanobenzylammonium Hexafluorophosphate (**2g**):** Yield 91%, colorless crystals, mp 83–84 °C. ¹H-NMR (270 MHz; CDCl₃) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.97–1.51 (18H,

m), 3.05 (6H, s), 3.11 (2H, t, $J = 11.7$ Hz), 4.61 (2H, s), 7.66 (2H, d, $J = 8.3$ Hz), 7.77 (2H, d, $J = 8.3$ Hz). IR (KBr) cm^{-1} : 2220, 1460, 840. *Anal.* Calcd for $\text{C}_{23}\text{H}_{41}\text{F}_6\text{N}_2\text{P}\text{Sn}$: C, 45.34; H, 6.78; N, 4.60. Found: C, 45.30; H, 6.79; N, 4.79.

N,N-Dimethyl-*N*-(tributylstannyl)methyl-4-nitrobenzylammonium Hexafluorophosphate (**2h**): Yield 90%, colorless crystals, mp 82–83 °C. $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.89 (9H, t, $J = 7.3$ Hz), 0.98–1.63 (18H, m), 3.06 (6H, s), 3.13 (2H, t, $J = 11.6$ Hz), 4.65 (2H, s), 7.73 (2H, d, $J = 8.4$ Hz), 8.28 (2H, d, $J = 8.4$ Hz). IR (KBr) cm^{-1} : 1530, 1350, 830. *Anal.* Calcd for $\text{C}_{23}\text{H}_{41}\text{F}_6\text{N}_2\text{O}_2\text{P}\text{Sn}$: C, 41.99; H, 6.57; N, 4.45. Found: C, 41.80; H, 6.56; N, 4.72.

Reaction of 2a with LDA A solution of **2a** (1.07 g, 2 mmol) in THF (10 ml) was treated with an LDA solution⁶¹ (2 ml, 2 mmol) at 0 °C, and the mixture was stirred for 2 h, then poured into water (20 ml) and extracted with Et_2O (3×50 ml). The ethereal extract was dried (MgSO_4), filtered and concentrated under reduced pressure. The residue was chromatographed on a silica gel column (Et_2O –hexane, 1:10) to yield *N,N*-dimethyl-2-[(tributylstannyl)methyl]benzylamine²¹ **3a**, *N,N*-dimethyl-2-methylbenzylamine⁷¹ **4a** and *N*-methyl-*N*-(tributylstannyl)methyl-2-[(tributylstannyl)methyl]benzylamine **11a**. The yields were determined from the integrated $^1\text{H-NMR}$ values of the mixture by using an internal standard (phthalide, 134 mg, 1 mmol), and the ratios were calculated from the results of HPLC analysis (corrected based on the molar absorptivities of all of the compounds at 275 nm) (Table 1, entry 1).

11a: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.72–0.93 (30H, m), 1.18–1.60 (24H, m), 2.16 (3H, s), 2.44 (2H, t, $J = 29.1$ Hz), 2.59 (2H, t, $J = 10.3$ Hz), 3.26 (2H, s), 6.93–7.15 (4H, m). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 8.8–29.3 (25C), 46.2, 46.6, 64.6, 122.4, 126.9, 128.1, 129.8, 134.5, 143.1. IR (film) cm^{-1} : 2930, 1460, 750. UV λ_{max} (hexane) nm (log ϵ): 238 (4.10). *Anal.* Calcd for $\text{C}_{34}\text{H}_{67}\text{NSn}_2$: C, 56.15; H, 9.29; N, 1.93. Found: C, 56.17; H, 9.31; N, 1.81.

Reaction of 2b with LDA In a manner similar to that described above, a solution of **2b** (1.10 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol) and the mixture was worked up to yield *N,N*-dimethyl-5-methyl-2-[(tributylstannyl)methyl]benzylamine **3b**, *N,N*-dimethyl-2,5-dimethylbenzylamine⁸¹ **4b**, *N*-methyl-*N*-(tributylstannyl)methyl-5-methyl-2-[(tributylstannyl)methyl]benzylamine **11b** and *N*-methyl-*N*-(tributylstannyl)methyl-2,5-dimethylbenzylamine **12b** (entry 2).

3b: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.70–0.88 (15H, m), 1.18–1.46 (12H, m), 2.23 (6H, s), 2.26 (3H, s), 2.36 (2H, t, $J = 29.4$ Hz), 3.24 (2H, s), 6.84–6.95 (3H, m). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.7 (3C, t, $J = 156$ Hz), 13.7 (3C), 15.0, 20.8, 27.4 (3C, t, $J = 28$ Hz), 29.1 (3C), 45.7 (2C), 62.7, 127.7, 128.1, 130.6, 132.0, 133.8, 139.7. IR (film) cm^{-1} : 2910, 1460, 1020. UV λ_{max} (hexane) nm (log ϵ): 242 (4.16). *Anal.* Calcd for $\text{C}_{23}\text{H}_{43}\text{NSn}$: C, 61.08; H, 9.58; N, 3.10. Found: C, 60.97; H, 9.56; N, 3.03.

11b: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.64–1.00 (30H, m), 1.21–1.64 (24H, m), 2.17 (3H, s), 2.26 (3H, s), 2.38 (2H, br s), 2.60 (2H, t, $J = 10.2$ Hz), 3.22 (2H, s), 6.83–6.96 (3H, m). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.8–29.4 (26C), 46.3, 46.7, 64.4, 127.5, 128.0, 130.4, 131.9, 134.2, 139.5. IR (film) cm^{-1} : 2920, 1460. UV λ_{max} (hexane) nm (log ϵ): 240 (4.25). *Anal.* Calcd for $\text{C}_{35}\text{H}_{69}\text{NSn}_2$: C, 56.71; H, 9.38; N, 1.89. Found: C, 56.42; H, 9.62; N, 1.73.

12b: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.77–0.95 (15H, m), 1.23–1.58 (12H, m), 2.16 (3H, s), 2.29 (3H, s), 2.30 (3H, s), 2.56 (2H, t, $J = 10.9$ Hz), 3.32 (2H, s), 6.94–7.07 (3H, m). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 10.0 (3C, t, $J = 150$ Hz), 13.7 (3C), 18.7, 20.9, 27.4 (3C, t, $J = 27$ Hz), 29.2 (3C), 46.3, 46.4, 64.0, 127.4, 130.0, 130.3, 134.0, 134.8, 137.4. IR (film) cm^{-1} : 2910, 1460, 800. UV λ_{max} (hexane) nm (log ϵ): 276 (3.01). *Anal.* Calcd for $\text{C}_{33}\text{H}_{43}\text{NSn}$: C, 61.08; H, 9.58; N, 3.10. Found: C, 61.11; H, 9.74; N, 2.84.

Reaction of 2c with LDA Similarly, a solution of **2c** (1.23 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol) and the mixture was worked up to yield *N,N*-dimethyl-5-methoxy-2-[(tributylstannyl)methyl]benzylamine **3c**, *N,N*-dimethyl-5-methoxy-2-methylbenzylamine⁹¹ **4c**, *N*-methyl-*N*-(tributylstannyl)methyl-5-methoxy-2-[(tributylstannyl)methyl]benzylamine **11c** and *N*-methyl-*N*-(tributylstannyl)methyl-5-methoxy-2-methylbenzylamine **12c** (entry 3).

3c: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.69–0.88 (15H, m), 1.18–1.46 (12H, m), 2.23 (6H, s), 2.33 (2H, t, $J = 28.0$ Hz), 3.24 (2H, s), 3.77 (3H, s), 6.66 (1H, dd, $J = 3.0, 8.3$ Hz), 6.76 (1H, d, $J = 2.6$ Hz), 6.89 (1H, d, $J = 8.3$ Hz). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.9 (3C, t, $J = 166$ Hz), 13.7 (3C), 14.2, 27.4 (3C, t, $J = 27$ Hz), 29.2 (3C), 45.7 (2C),

55.3, 62.8, 112.6, 115.4, 128.9, 134.9, 135.1, 155.7. IR (film) cm^{-1} : 2910, 1500, 1460, 1260, 1050. UV λ_{max} (hexane) nm (log ϵ): 245 (4.22), 293 (3.47). *Anal.* Calcd for $\text{C}_{23}\text{H}_{43}\text{NOSn}$: C, 58.99; H, 9.25; N, 2.99. Found: C, 58.66; H, 9.44; N, 2.99.

11c: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.71–0.99 (30H, m), 1.21–1.58 (24H, m), 2.17 (3H, s), 2.34 (2H, t, $J = 29.0$ Hz), 2.58 (2H, t, $J = 10.6$ Hz), 3.23 (2H, s), 3.76 (3H, s), 6.65 (1H, dd, $J = 3.0, 8.3$ Hz), 6.80 (1H, d, $J = 3.0$ Hz), 6.86 (1H, d, $J = 8.3$ Hz). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.7–29.4 (25C), 46.3, 46.6, 55.3, 64.5, 112.5, 114.9, 128.8, 134.6, 135.6, 155.8. IR (film) cm^{-1} : 2910, 1490, 1460, 1260, 1040. UV λ_{max} (hexane) nm (log ϵ): 242 (4.22), 292 (3.40). *Anal.* Calcd for $\text{C}_{35}\text{H}_{69}\text{NOSn}_2$: C, 55.51; H, 9.18; N, 1.85. Found: C, 55.32; H, 9.23; N, 1.71.

12c: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.80–0.95 (15H, m), 1.23–1.68 (12H, m), 2.17 (3H, s), 2.26 (3H, s), 2.55 (2H, t, $J = 10.4$ Hz), 3.32 (2H, s), 3.78 (3H, s), 6.69 (1H, dd, $J = 2.6, 8.3$ Hz), 6.88 (1H, d, $J = 2.6$ Hz), 7.03 (1H, d, $J = 8.3$ Hz). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 10.0 (3C, t, $J = 149$ Hz), 13.7 (3C), 18.2, 27.4 (3C, t, $J = 27$ Hz), 29.2 (3C), 46.3 (2C), 55.2, 64.2, 111.9, 115.0, 129.0, 130.8, 138.8, 157.6. IR (film) cm^{-1} : 2910, 1490, 1460, 1240, 1040. UV λ_{max} (hexane) nm (log ϵ): 277 (3.39). *Anal.* Calcd for $\text{C}_{23}\text{H}_{43}\text{NOSn}$: C, 58.99; H, 9.25; N, 2.99. Found: C, 58.78; H, 9.22; N, 2.98.

Reaction of 2d with LDA Similarly, a solution of **2d** (1.20 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol) and the mixture was worked up to yield *N,N*-dimethyl-5-fluoro-2-[(tributylstannyl)methyl]benzylamine **3d**, *N,N*-dimethyl-5-fluoro-2-methylbenzylamine⁹¹ **4d** and *N,N*-dimethyl-3-fluoro-2-tributylstannyl-6-[(tributylstannyl)methyl]benzylamine **7d** (entry 4).

3d: a colorless oil $^1\text{H-NMR}$ (400 MHz; CDCl_3) δ : 0.75–0.88 (15H, m), 1.20–1.44 (12H, m), 2.24 (6H, s), 2.33 (2H, t, $J = 28.4$ Hz), 3.24 (2H, s), 6.79 (1H, td, $J = 2.9, 8.4$ Hz), 6.87–6.93 (2H, m). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.8 (3C, t, $J = 159$ Hz), 13.6 (3C), 14.6, 27.4 (3C, t, $J = 28$ Hz), 29.0 (3C), 45.7 (2C), 62.4, 113.6 (d, $J_{\text{F-C}} = 33$ Hz), 116.1 (d, $J_{\text{F-C}} = 21$ Hz), 129 (d, $J_{\text{F-C}} = 10$ Hz), 135.8 (d, $J_{\text{F-C}} = 6$ Hz), 138.3 (d, $J_{\text{F-C}} = 3$ Hz), 159.4 (d, $J_{\text{F-C}} = 241$ Hz). IR (film) cm^{-1} : 2920, 1480, 1460, 1250, 1090. UV λ_{max} (hexane) nm (log ϵ): 233 (4.05), 283 (3.24). *Anal.* Calcd for $\text{C}_{22}\text{H}_{40}\text{FNSn}$: C, 57.92; H, 8.84; N, 3.07. Found: C, 57.72; H, 8.92; N, 3.08.

7d: a colorless oil $^1\text{H-NMR}$ (400 MHz; CDCl_3) δ : 0.73–1.07 (30H, m), 1.18–1.55 (24H, m), 2.12 (6H, s), 2.37 (2H, t, $J = 28.2$ Hz), 3.28 (2H, s), 6.68–6.93 (2H, m). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.8–29.1 (25C), 45.1 (2C), 61.9, 112.6 (d, $J_{\text{F-C}} = 29$ Hz), 128.2 (d, $J_{\text{F-C}} = 42$ Hz), 130.1 (d, $J_{\text{F-C}} = 7$ Hz), 138.3 (d, $J_{\text{F-C}} = 13$ Hz), 141.8 (d, $J_{\text{F-C}} = 13$ Hz), 164.6 (d, $J_{\text{F-C}} = 230$ Hz). IR (film) cm^{-1} : 2920, 1440, 1220, 1120. UV λ_{max} (hexane) nm (log ϵ): 291 (3.40). *Anal.* Calcd for $\text{C}_{34}\text{H}_{66}\text{FNSn}_2$: C, 54.79; H, 8.93; N, 1.88. Found: C, 54.50; H, 8.92; N, 1.76.

Reaction of 2e with LDA Similarly, a solution of **2e** (1.24 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol) and the mixture was worked up to yield *N,N*-dimethyl-5-chloro-2-[(tributylstannyl)methyl]benzylamine **3e**, *N,N*-dimethyl-5-chloro-2-methylbenzylamine¹⁰¹ **4e** and a mixture of *N,N*-dimethyl-3-chloro-2-tributylstannyl-6-[(tributylstannyl)methyl]benzylamine **7e** and *N*-methyl-*N*-(tributylstannyl)methyl-5-chloro-2-[(tributylstannyl)methyl]benzylamine **11e** (entry 5).

3e: a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) δ : 0.74–0.90 (15H, m), 1.18–1.46 (12H, m), 2.23 (6H, s), 2.35 (2H, t, $J = 29.4$ Hz), 3.23 (2H, s), 6.89 (1H, d, $J = 8.3$ Hz), 7.05 (1H, dd, $J = 2.3, 8.3$ Hz), 7.15 (1H, d, $J = 2.3$ Hz). $^{13}\text{C-NMR}$ (67.8 MHz; CDCl_3) δ : 9.8 (3C, t, $J = 158$ Hz), 13.6 (3C), 15.1, 27.3 (3C, t, $J = 28$ Hz), 29.0 (3C), 45.6 (2C), 62.3, 65.8, 126.9, 128.0, 129.3, 129.5, 135.8, 141.8. IR (film) cm^{-1} : 2900, 1480, 1460, 1090. UV λ_{max} (hexane) nm (log ϵ): 246 (4.08). *Anal.* Calcd for $\text{C}_{23}\text{H}_{40}\text{ClNSn}$: C, 55.90; H, 8.53; N, 2.96. Found: C, 55.65; H, 8.61; N, 2.85.

Mixture of **7e** and **11e** (1:1): a colorless oil $^1\text{H-NMR}$ (270 MHz; CDCl_3) **7e**: δ : 2.12 (6H, s), 2.39 (2H, br s), 3.30 (2H, s); **11e**: δ : 2.18 (3H, s), 2.36 (2H, br s), 2.53 (2H, br s), 3.22 (2H, s); others: δ : 0.69–0.93 (60H, m), 1.04–1.53 (48H, m), 6.82–7.19 (5H, m). IR (film) cm^{-1} : 2920, 1460, 1080. UV λ_{max} (hexane) nm (log ϵ): 245 (4.22). *Anal.* Calcd for $\text{C}_{34}\text{H}_{66}\text{ClNSn}_2$: C, 53.61; H, 8.73; N, 1.84. Found: C, 53.49; H, 8.79; N, 1.69.

Reaction of 2f with LDA Similarly, a solution of **2f** (1.30 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol) and the mixture was worked up. The $^1\text{H-NMR}$ spectrum of the ethereal extract showed the presence of **2f** (soluble in Et_2O), *N,N*-dimethyl-5-trifluoromethyl-2-[(tributylstannyl)methyl]benzylamine **3f** and *N*-meth-

yl-*N*-(tributylstannyl)methyl-5-trifluoromethyl-2-[(tributylstannyl)methyl]benzylamine **11f**. Compounds **3f** and **11f** were isolated on a silica gel column (Et₂O–hexane, 1:10) (entry 6).

3f: a colorless oil ¹H-NMR (270 MHz; CDCl₃) δ: 0.73–0.88 (15H, m), 1.18–1.46 (12H, m), 2.23 (6H, s), 2.46 (2H, t, *J* = 29.0 Hz), 3.30 (2H, s), 7.05 (1H, d, *J* = 8.3 Hz), 7.32 (1H, d, *J* = 8.3 Hz), 7.40 (1H, s). ¹³C-NMR (67.8 MHz; CDCl₃) δ: 10.0 (3C, t, *J* = 160 Hz), 13.6 (3C), 16.3, 27.3 (3C, t, *J* = 28 Hz), 29.0 (3C), 45.7 (2C), 62.4, 123.8 (d, *J*_{F–C} = 4 Hz), 124.9 (d, *J*_{F–C} = 33 Hz), 124.7 (q, *J*_{F–C} = 271 Hz), 126.5 (d, *J*_{F–C} = 4 Hz), 128.2, 134.4, 148.1. IR (film) cm^{–1}: 2910, 1320, 1120. UV λ_{max} (hexane) nm (log ε): 257 (3.95). *Anal.* Calcd for C₂₃H₄₀F₃NSn: C, 54.57; H, 7.96; N, 2.77. Found: C, 54.57; H, 8.15; N, 2.67.

11f: a colorless oil ¹H-NMR (270 MHz; CDCl₃) δ: 0.71–0.99 (30H, m), 1.28–1.58 (24H, m), 2.19 (3H, s), 2.47 (2H, t, *J* = 29.7 Hz), 2.53 (2H, t, *J* = 10.9 Hz), 3.29 (2H, s), 7.03 (1H, d, *J* = 7.9 Hz), 7.30 (1H, d, *J* = 7.9 Hz), 7.44 (1H, s). ¹³C-NMR (67.8 MHz; CDCl₃) δ: 10.0–29.2 (25C), 46.2, 46.4, 64.2, 123.5 (d, *J*_{F–C} = 4 Hz), 125.0 (d, *J*_{F–C} = 32 Hz), 124.8 (q, *J*_{F–C} = 271 Hz), 126.2 (d, *J*_{F–C} = 4 Hz), 128.1, 135.0, 147.7. IR (film) cm^{–1}: 2910, 1320, 1160, 1120, 1080. UV λ_{max} (hexane) nm (log ε): 248 (4.44). *Anal.* Calcd for C₃₅H₆₆F₃NSn₂: C, 52.86; H, 8.36; N, 1.76. Found: C, 52.68; H, 8.37; N, 1.77.

Reaction of 2g with LDA Similarly, a solution of **2g** (1.22 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol). The product was a complex mixture.

Reaction of 2h with LDA Similarly, a solution of **2h** (1.26 g, 2 mmol) in THF (10 ml) was allowed to react with an LDA solution (2 ml, 2 mmol) and the mixture was worked up to yield 4,4'-dinitrotribenzyl and tributyl(dimethylaminomethyl)tin.

Dimethyl trans-1,2,3,4-Tetrahydro-6-substituted Naphthalene-2,3-dicarboxylates (15) General Procedure: A mixture of **3** (1 mmol) and iodomethane (710 mg, 5 mmol) in MeCN (15 ml) was stirred at room temperature for 1 h. The excess iodomethane and about 10 ml of MeCN were distilled off. Dimethyl fumarate (288 mg, 2 mmol) and tetrabutylammonium fluoride (TBAF) (3 ml, 3 mmol, 1 M in MeCN) were added to the resulting solution of *N,N,N*-trimethyl-2-[(tributylstannyl)methyl]-5-substituted benzylammonium iodides **13**. The mixture was stirred at room temperature for 24 h and poured into water (50 ml). The precipitated crystals (fluorotributyltin) were filtered off on Celite and the filtrate was extracted with Et₂O (3 × 50 ml). The ethereal extract was dried (MgSO₄), and concentrated under reduced pressure. The residue was chromatographed on preparative silica gel TLC (AcOEt–hexane, 1:2).

Dimethyl *trans*-1,2,3,4-Tetrahydronaphthalene-2,3-dicarboxylate (**15a**): Yield 66%, colorless crystals, mp 39–40 °C [lit.¹¹⁾ mp 44–44.5 °C].

Dimethyl *trans*-1,2,3,4-Tetrahydro-6-methylnaphthalene-2,3-dicarboxylate (**15b**): Yield 68%, colorless crystals, mp 71–72 °C. ¹H-NMR (270 MHz; CDCl₃) δ: 2.29 (3H, s), 2.88–3.14 (6H, m), 3.73 (3H, s), 3.74 (3H, s), 6.91–7.00 (3H, m). IR (KBr) cm^{–1}: 1740, 1440, 1180, 1000. MS *m/z* (rel. int. %): 262 (M⁺, 34), 202 (95), 143 (100). *Anal.* Calcd for C₁₅H₁₈O₄: C, 68.69; H, 6.92. Found: C, 68.47; H, 7.03.

Dimethyl *trans*-1,2,3,4-Tetrahydro-6-methoxynaphthalene-2,3-di-

carboxylate (**15c**): Yield 60%, colorless crystals, mp 90–91 °C. ¹H-NMR (400 MHz; CDCl₃) δ: 2.84–3.13 (6H, m), 3.73 (3H, s), 3.74 (3H, s), 3.77 (3H, s), 6.63 (1H, d, *J* = 2.4 Hz), 6.72 (1H, dd, *J* = 2.4, 8.5 Hz), 7.00 (1H, d, *J* = 8.5 Hz). IR (KBr) cm^{–1}: 1720, 1440, 1310, 1260, 1200, 1150. MS *m/z* (rel. int. %): 278 (M⁺, 31), 218 (52), 159 (100). *Anal.* Calcd for C₁₅H₁₈O₅: C, 64.74; H, 6.52. Found: C, 64.81; H, 6.63.

Dimethyl *trans*-6-Fluoro-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (**15d**): Yield 65%, colorless crystals, mp 77–78 °C. ¹H-NMR (270 MHz; CDCl₃) δ: 2.87–3.16 (6H, m), 3.73 (3H, s), 3.74 (3H, s), 6.78–6.88 (2H, m), 7.05 (1H, dd, *J* = 5.5, 7.7 Hz). IR (KBr) cm^{–1}: 1740, 1720, 1500, 1220, 1200, 1000. MS *m/z* (rel. int. %): 266 (M⁺, 9), 206 (39), 147 (100). *Anal.* Calcd for C₁₄H₁₅FO₄: C, 63.15; H, 5.68. Found: C, 62.94; H, 5.64.

Dimethyl *trans*-6-Chloro-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylate (**15e**): Yield 70%, colorless crystals, mp 100–102 °C. ¹H-NMR (270 MHz; CDCl₃) δ: 2.88–3.14 (6H, m), 3.73 (3H, s), 3.74 (3H, s), 7.01–7.13 (3H, m). IR (KBr) cm^{–1}: 1730, 1740, 1440, 1200, 1000. MS *m/z* (rel. int. %): 282 (M⁺, 23), 222 (88), 163 (100). *Anal.* Calcd for C₁₄H₁₅ClO₄: C, 59.48; H, 5.35. Found: C, 59.41; H, 5.39.

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References and Notes

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