

Rapid methylation on carbon frameworks useful for the synthesis of ¹¹CH₃-incorporated PET tracers: Pd(0)-mediated rapid coupling of methyl iodide with an alkenyl tributylstannane leading to a 1-methylalkene

(Rapid methylation on carbon frameworks for PET tracer synthesis: Part 7)

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Supplementary data

General remarks

Methyl iodide (Nacalai) was distilled before used. (*E*)-2-heptene (Aldrich), (*Z*)-2-heptene (AVOCAD), 1-methylcyclohexene (Nacalai), 3-Methyl-2-buten-1-ol (Aldrich), 3-methyl-2-butenal (TCI), 2,5-dimethyl-2,4-hexadiene (TCI), (*E*)- β -methylstyrene (TCI), (*Z*)- β -methylstyrene (TCI), (2*E*,4*E*)-2,4-hexadienoic acid methyl ester (TCI), 3-methyl-2-cyclohexene-1-one (Wako), *n*-nonane (TCI), *n*-heptane (Nacalai), *n*-decane (Nacalai), tris(dibenzylideneacetone)dipalladium(0) (Aldrich), di- μ -chlorobis[(η -allyl)palladium(II)] (Wako), tetrakis(triphenylphosphine)palladium(0) (Aldrich), palladium(II) chloride (Wako), triphenylphosphine (Nacalai), tri-*t*-butylphosphine (Kanto), tri-*o*-tolylphosphine (Aldrich), di-*t*-butylmethylphosphine (Strem), copper chloride (Wako), copper bromide (Wako), copper iodide (Wako), tetramethylammonium fluoride (Aldrich), potassium carbonate (Wako), cesium carbonate (Wako), cesium fluoride (Aldrich), hydrate tetrahydrofuran (THF, Wako) and hydrate *N,N*-dimethylformamide (DMF, Kanto) were commercial grade.

All reaction were performed under Ar with Schlenk techniques. Yields of the reaction were determined by GLC analysis. GLC analysis was performed on a Shimadzu GCMS-QP5050A; capillary column, TC-5, 60 m x 0.25 mm i.d., $d_f = 0.25$ mm, GL Science Inc.; carrier gas: He, flow rate: 0.8 mL/min, injector temperature: 280 °C, detector temperature 250 °C, on a Shimadzu GC-2010 instrument equipped with a flame ionization detector; capillary column, TC-1701, 60 m

x 0.25 mm i.d., df = 0.25 mm, GL Science Inc.; carrier gas: He, flow rate: 0.4 mL/min, injector temperature: 280 °C, detector temperature: 280 °C, on a Shimadzu GC-2010 instrument equipped with a flame ionization detector; capillary column, TC-WAX, 60 m x 0.25 mm i.d., df = 0.25 mm, GL Science Inc.; carrier gas: He, flow rate: 0.4 mL/min, injector temperature: 280 °C, detector temperature: 280 °C, on a Shimadzu GC-17A instrument equipped with a flame ionization detector; capillary column, TC-5, 60 m x 0.25 mm i.d., df = 0.25 mm, GL Science Inc.; carrier gas: N₂, flow rate: 0.6 mL/min, injector temperature: 280 °C, detector temperature: 280 °C.

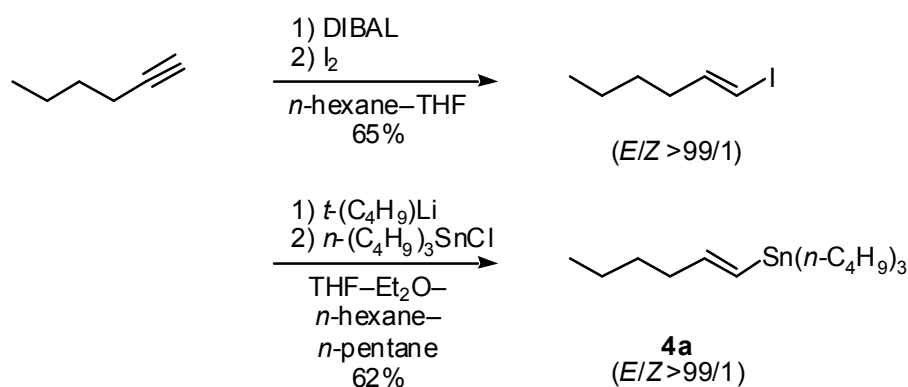
¹H- and ¹³C NMR spectra were obtained with JEOL AL-400 spectrometer. CDCl₃ (Acros) was used as solvent for obtaining NMR spectra. Chemical shift (δ) are given in parts per million (ppm) downfield from (CH₃)₄Si (for ¹H NMR) or solvent (¹³C NMR) as internal references with coupling constant (*J*) in Hz. The abbreviations s, d, t, q, and m signify singlet, doublet, triplet, quartet, and multiplet, respectively.

Synthetic method and characterization of alkenyl tributylstannanes and the corresponding 1-methylalkenes

Tributyl-(*E*)-1-hexenylstannane (**4a**)

Registry Number: 124582-25-8

¹H NMR (CDCl₃, 400 MHz) δ 5.95 (dt, *J* = 5.8, 19 Hz, 1H, C=CH), 5.84 (d, *J* = 19 Hz, 1H, C=CH), 2.14 (m, 2H, CH₂), 1.44–1.56 (m, 6H, 3CH₂), 1.25–1.39 (m, 10H, 5CH₂), 0.83–0.91 (m, 18H, 3CH₂, 4CH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 149.81, 126.89 (t, *J*_{Sn(119)-C} = 398 Hz, *J*_{Sn(117)-C} = 380 Hz), 37.63 (t, *J*_{Sn-C} = 62.6 Hz), 31.14, 29.15 (t, *J*_{Sn-C} = 19.6 Hz), 27.29 (t, *J*_{Sn-C} = 52.6 Hz), 22.18, 13.97, 13.70, 9.37 (t, *J*_{Sn(119)-C} = 338 Hz, *J*_{Sn(117)-C} = 322 Hz).

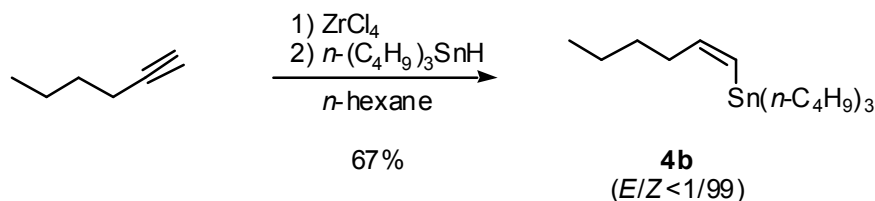


- ref. G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, 1967, **89**, 2753–2754.
 J. J. Eisch and J. E. Galle, *J. Organomet. Chem.*, 1988, **341**, 293–313.

Tributyl-(*Z*)-1-hexenylstannane (**4b**)

Registry Number: 127020-46-6

^1H NMR (CDCl_3 , 400 MHz) δ 6.51 (dt, $J = 7.2, 12.4$ Hz, $J_{\text{Sn-H}} = 142.4$ Hz, 1H, C=CH), 5.84 (d, $J = 12.4$ Hz, $J_{\text{Sn(119)-H}} = 85.8$ Hz, $J_{\text{Sn(117)-H}} = 60.9$ Hz, 1H, C=CH), 2.14 (dt, $J = 6.8, 7.2$ Hz, 2H, CH_2), 1.46–1.55 (m, 6H, 3CH_2), 1.26–1.37 (m, 10H, 5CH_2), 0.78–0.97 (m, 18H, $3\text{CH}_2, 4\text{CH}_3$); ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.83, 127.12 (t, $J_{\text{Sn(119)-C}} = 388$ Hz, $J_{\text{Sn(117)-C}} = 372$ Hz), 36.45 (t, $J_{\text{Sn-C}} = 37.2$ Hz), 31.69, 28.78 (t, $J_{\text{Sn-C}} = 19.6$ Hz), 26.90 (t, $J_{\text{Sn-C}} = 55.8$ Hz), 22.09, 13.60, 13.23, 9.76 (t, $J_{\text{Sn(119)-C}} = 336$ Hz, $J_{\text{Sn(117)-C}} = 320$ Hz).

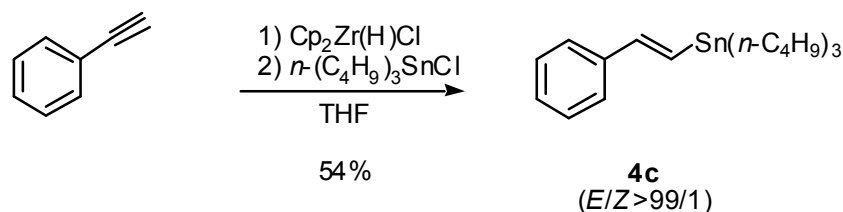


- ref. N. Asao, J.-X. Liu, T. Sudoh and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4568–4571.

Tributyl-(*E*)-(2-phenylethenyl)stannane (**4c**)

Registry Number: 66680-88-4

^1H NMR (CDCl_3 , 400 MHz) δ 7.41 (d, $J = 7.6$ Hz, 2H, Ar), 7.31 (t, $J = 7.6$ Hz, 2H, Ar), 7.21 (t, $J = 7.6$ Hz, 1H, Ar), 6.86 (s, $J_{\text{Sn-H}} = 40$ Hz, 64 Hz, 2H, CH=CH), 1.47–1.60 (m, 6H, 3CH_2), 1.29–1.38 (m, 6H, 3CH_2), 0.89–0.96 (m, 15H, $3\text{CH}_2, 3\text{CH}_3$); ^{13}C NMR (CDCl_3 , 100 MHz) δ 146.05 (t, $J_{\text{Sn-C}} = 11.4$ Hz), 138.81 (t, $J_{\text{Sn-C}} = 62.6$ Hz), 129.44 (t, $J_{\text{Sn(119)-C}} = 374$ Hz, $J_{\text{Sn(117)-C}} = 358$ Hz), 128.42, 127.46, 125.95, 29.13 (t, $J_{\text{Sn-C}} = 21.4$ Hz), 27.30 (t, $J_{\text{Sn-C}} = 54.2$ Hz), 13.70, 9.57 (t, $J_{\text{Sn(119)-C}} = 342$ Hz, $J_{\text{Sn(117)-C}} = 326$ Hz).

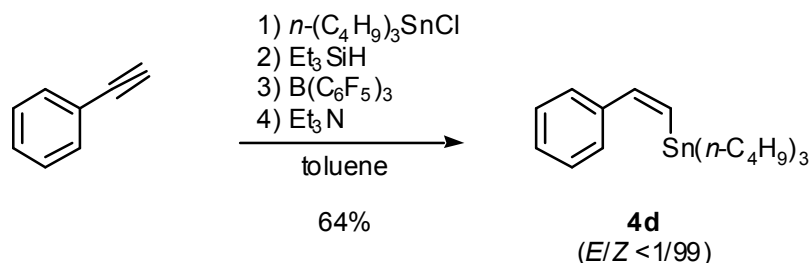


ref. S. Kim and K. H. Kim, *Tetrahedron Lett.*, 1995, **36**, 3725–3728.

Tributyl-(Z)-(2-phenylethenyl)stannane (4d)

Registry Number 66680-87-3

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.61 (d, $J = 13.6$ Hz, $J_{\text{Sn}(119)\text{-H}} = 146$ Hz, $J_{\text{Sn}(117)\text{-H}} = 120$ Hz, 1H, C=CH), 7.21-7.32 (m, 5H, Ar), 6.19 (d, $J = 13.6$ Hz, $J_{\text{Sn}(119)\text{-H}} = 70.0$ Hz, $J_{\text{Sn}(117)\text{-H}} = 42.5$ Hz, 1H, C=CH), 1.36–1.46 (m, 6H, 3CH₂), 1.19 (m, 6H, 3CH₂), 0.73–0.95 (m, 15H, 3CH₂, 3CH₃); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 147.38 (t, $J_{\text{Sn-C}} = 6.6$ Hz), 141.50 (t, $J_{\text{Sn-C}} = 26.2$ Hz), 132.84 (t, $J_{\text{Sn}(119)\text{-C}} = 356$ Hz, $J_{\text{Sn}(117)\text{-C}} = 340$ Hz), 128.13, 127.26, 127.08, 29.06 (t, $J_{\text{Sn-C}} = 19.6$ Hz), 27.25 (t, $J_{\text{Sn-C}} = 56.0$ Hz), 13.68, 10.83 (t, $J_{\text{Sn}(119)\text{-C}} = 342$ Hz, $J_{\text{Sn}(117)\text{-C}} = 326$ Hz).

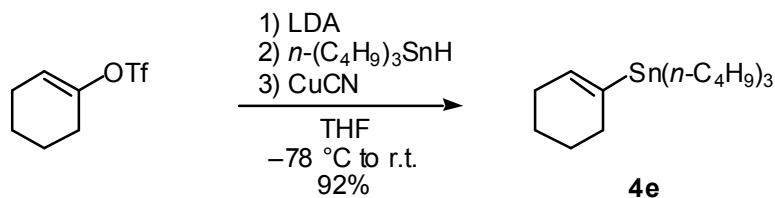


ref. V. Gevorgyan, J.-X. Liu and Y. Yamamoto, *Chem. Commun.*, 1998, 37–38.

Tributyl-(1-cyclohexenyl)stannane (4e)

Registry Number: 100073-20-9

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 5.78 (m, $J_{\text{Sn-H}} = 68.8$ Hz, 1H, C=CH), 2.14 (br, 2H, CH₂), 2.06 (br, 2H, CH₂), 1.61 (br, 4H, 2CH₂), 1.25–1.35 (m, 6H, 3CH₂), 1.44–1.51 (m, 6H, 3CH₂), 0.78–0.90 (m, 15H, 3CH₂, 3CH₃); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 140.54 (t, $J_{\text{Sn}(119)\text{-C}} = 416$ Hz, $J_{\text{Sn}(117)\text{-C}} = 396$ Hz), 137.23 (t, $J_{\text{Sn-C}} = 23.0$ Hz), 31.95 (t, $J_{\text{Sn-C}} = 36.2$ Hz), 29.25 (t, $J_{\text{Sn-C}} = 19.8$ Hz), 27.46 (t, $J_{\text{Sn-C}} = 54.4$ Hz), 23.79 (t, $J_{\text{Sn-C}} = 31.2$ Hz), 22.77 (t, $J_{\text{Sn-C}} = 6.6$ Hz), 13.74, 8.84 (t, $J_{\text{Sn}(119)\text{-C}} = 326$ Hz, $J_{\text{Sn}(117)\text{-C}} = 310$ Hz).

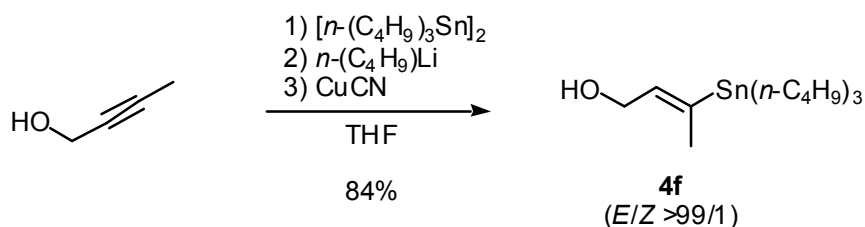


ref. S. R. Gilbertson, C. A. Challener, M. E. Bos and W. D. Wulff, *Tetrahedron Lett.*, 1988, **29**, 4795–4798.

Tributyl-(*E*)-(3-hydroxy-1-methyl-1-propenyl)stannane (**4f**)

Registry Number: 124607-17-6

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 5.75 (tq, $J = 1.8, 5.8$ Hz, $J_{\text{Sn-H}} = 68.4$ Hz, 1H, C=CH), 4.25 (dd, $J = 5.8, 5.8$ Hz, 2H, CH_2), 1.88 (d, $J = 1.8$ Hz, $J_{\text{Sn-H}} = 45.6$ Hz, 3H, CH_3), 1.44–1.52 (m, 6H, 3CH_2), 1.26–1.35 (m, 6H, 3CH_2), 1.21 (t, $J = 5.8$ Hz, 1H, OH), 0.81–0.97 (m, 15H, $3\text{CH}_2, 3\text{CH}_3$); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 142.30 (t, $J_{\text{Sn}(119)\text{-C}} = 392$ Hz, $J_{\text{Sn}(117)\text{-C}} = 374$ Hz), 139.23 (t, $J_{\text{Sn-C}} = 24.6$ Hz), 58.75 (t, $J_{\text{Sn-C}} = 59.2$ Hz), 29.06 (t, $J_{\text{Sn-C}} = 19.8$ Hz), 27.34 (t, $J_{\text{Sn-C}} = 54.4$ Hz), 19.32 (t, $J_{\text{Sn-C}} = 37.8$ Hz), 13.62, 9.01 (t, $J_{\text{Sn}(119)\text{-C}} = 328$ Hz, $J_{\text{Sn}(117)\text{-C}} = 314$ Hz).



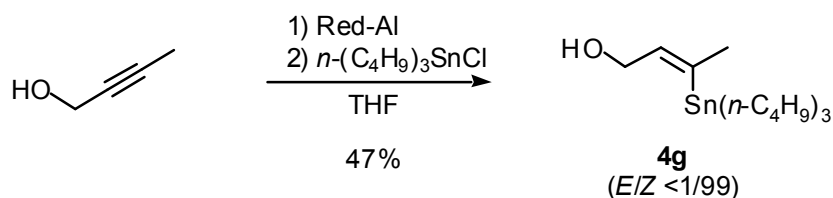
ref. J.-F. Betzer, F. Delalogue, B. Muller, A. Pancrazi and J. Prunet, *J. Org. Chem.*, 1997, **62**, 7768–7780.

Tributyl-(*Z*)-(3-hydroxy-1-methyl-1-propenyl)stannane (**4g**)

Registry Number: 121882-41-5

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 6.27 (tq, $J = 1.7, 6.2$ Hz, $J_{\text{Sn-H}} = 124.6$ Hz, 1H, C=CH), 4.02 (dd, $J = 6.2$ Hz, 2H, CH_2), 1.95 (d, $J = 1.7$ Hz, $J_{\text{Sn-H}} = 40.5$ Hz, 3H, CH_3), 1.44–1.52 (m, 6H, 3CH_2), 1.26–1.36 (m, 6H, 3CH_2), 1.13 (t, $J = 6.2$ Hz, 1H, OH), 0.85–0.96 (m, 15H, $3\text{CH}_2, 3\text{CH}_3$); $^{13}\text{C NMR}$

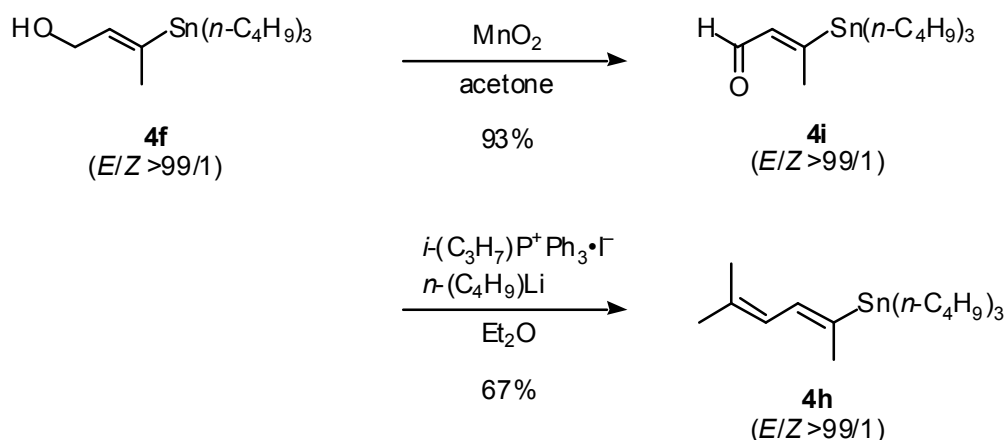
NMR (CDCl₃, 100 MHz) δ 144.96 (t, $J_{\text{Sn}(119)\text{-C}} = 366$ Hz, $J_{\text{Sn}(117)\text{-C}} = 348$ Hz), 139.64 (t, $J_{\text{Sn-C}} = 25.0$ Hz), 65.34 (t, $J_{\text{Sn-C}} = 36.0$ Hz), 29.36 (t, $J_{\text{Sn-C}} = 20.0$ Hz), 27.54 (t, $J_{\text{Sn-C}} = 58.0$ Hz), 27.11 (t, $J_{\text{Sn-C}} = 42.0$ Hz), 13.77, 10.26 (t, $J_{\text{Sn}(119)\text{-C}} = 332$ Hz, $J_{\text{Sn}(117)\text{-C}} = 318$ Hz).



ref. G. Evano, J. V. Schaus, and J. S. Panek, *Org. Lett.*, 2004, **6**, 525–528.

Tributyl-(*E*)-(1,4-dimethyl-1.3-pentadienyl)stannane (**4h**)

To a solution of isopropyltriphenylphosphonium iodide (4.32 g, 10.0 mmol) in diethyl ether (30 mL) was added *n*-BuLi (1.60 M *n*-hexane solution, 6.25 mL, 10.0 mmol) at 0 °C, and the mixture was stirred for 30 min at room temperature. To this was added (*2E*)-3-(tributylstannyl)-2-butenal (3.62 g, 10.0 mmol) in diethyl ether (15 mL) by canular at 0 °C, and the mixture was stirred for 1.5 h. To this was added water (100 mL) and the mixture was extracted with diethyl ether. The combined organic extracts were washed with brine, dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by reversed-phase flushed chromatography (CH₃CN/CH₂Cl₂ = 15/1) to give stannane **4h** (2.57 g, 66.8%): Light yellow oil; reversed-phase TLC $R_f = 0.31$ (CH₃CN/CH₂Cl₂ = 4/1); ¹H NMR (CDCl₃, 400 MHz) δ 6.36 (d, $J = 11$ Hz, $J_{\text{Sn}(119)\text{-H}} = 81.2$ Hz, $J_{\text{Sn}(117)\text{-H}} = 58.0$ Hz, C=CH), 6.17 (d, $J = 11$ Hz, 1H, C=CH), 1.97 (s, 3H, $J_{\text{Sn-H}} = 46.9$ Hz, CH₃), 1.82 (s, 3H, CH₃), 1.78 (s, 3H, CH₃), 1.46–1.52 (m, 6H, 3CH₂), 1.26–1.36 (m, 6H, 3CH₂), 0.81–0.97 (m, 15H, 3CH₂, 3CH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 140.14, 135.38 (t, $J_{\text{Sn-C}} = 32.8$ Hz), 134.33, 120.09, 29.21 (t, $J_{\text{Sn-C}} = 19.8$ Hz), 27.42 (t, $J_{\text{Sn-C}} = 54.4$ Hz), 26.33, 19.58, 18.04, 13.71, 9.21 (t, $J_{\text{Sn}(119)\text{-C}} = 328$ Hz, $J_{\text{Sn}(117)\text{-C}} = 316$ Hz).



ref. B. Dominguez, Y. Pazos and A. R. de Lera, *J. Org. Chem.*, 2000, **65**, 5917–5925.

T. Shinada, N. Sekiya, N. Bojkova and K. Yoshihara, *Tetrahedron*, 1999, **55**, 3675–3686.

Tributyl-(*E*)-(2-formyl-1-methylethenyl)stannane (**4i**)

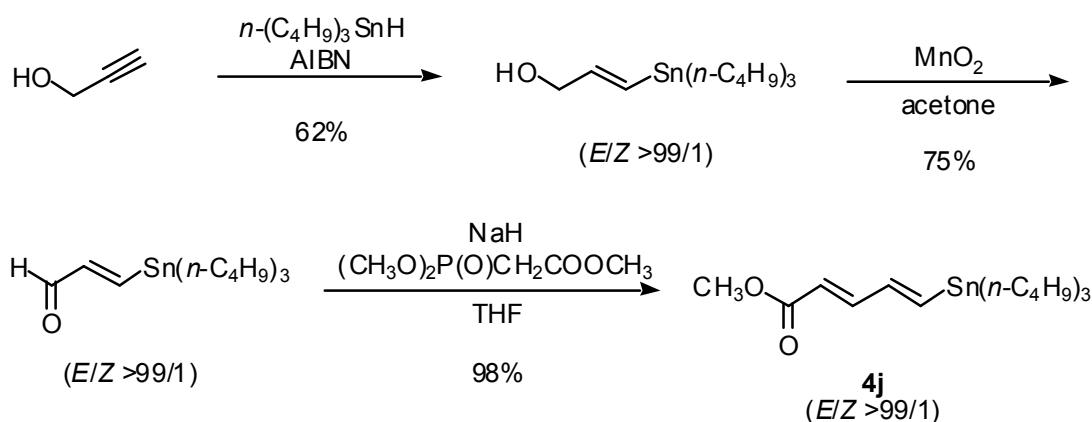
Registry Number: 256518-22-6

^1H NMR (CDCl_3 , 400 MHz) δ 10.0 (d, $J = 8.4$ Hz, 1H, CHO), 6.21 (dq, $J = 2.0, 8.4$ Hz, $J_{\text{Sn}(119)\text{-H}} = 67.7$ Hz, $J_{\text{Sn}(117)\text{-H}} = 52.2$ Hz, 1H, C=CH), 2.45 (d, $J = 2.0$ Hz, $J_{\text{Sn-H}} = 43.5$ Hz, 3H, CH_3), 1.46–1.54 (m, 6H, 3 CH_2), 1.27–1.36 (m, 6H, 3 CH_2), 0.89–0.99 (m, 15H, 3 CH_2 , 3 CH_3); ^{13}C NMR (CDCl_3 , 100 MHz) δ 187.29 (t, $J_{\text{Sn-C}} = 59.0$ Hz), 174.21 (t, $J_{\text{Sn}(119)\text{-C}} = 308$ Hz, $J_{\text{Sn}(117)\text{-C}} = 294$ Hz), 139.80 (t, $J_{\text{Sn-C}} = 23.0$ Hz), 28.87 (t, $J_{\text{Sn-C}} = 21.0$ Hz), 27.21 (t, $J_{\text{Sn-C}} = 56.0$ Hz), 20.64 (t, $J_{\text{Sn-C}} = 28.0$ Hz), 13.53, 9.21 (t, $J_{\text{Sn}(119)\text{-C}} = 334$ Hz, $J_{\text{Sn}(117)\text{-C}} = 320$ Hz).

Tributyl-(2*E*,4*E*)-(4-methoxycarbonyl-1,3-butadienyl)stannane (**4j**)

Registry Number: 221652-69-3

^1H NMR (CDCl_3 , 400 MHz) δ 7.19 (dd, $J = 10.1, 15.4$ Hz, 1H, C=CH), 6.81 (d, $J = 18.6$ Hz, 1H, C=CH), 6.64 (dd, $J = 10.1, 18.6$ Hz, 1H, C=CH), 5.80 (d, $J = 15.4$ Hz, 1H, C=CH), 3.74 (s, 3H, OCH_3), 1.47–1.55 (m, 6H, 3 CH_2), 1.26–1.35 (m, 6H, 3 CH_2), 0.88–1.05 (m, 15H, 3 CH_2 , 3 CH_3); ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.77, 147.45 (t, $J_{\text{Sn}(119)\text{-C}} = 338$ Hz, $J_{\text{Sn}(117)\text{-C}} = 326$ Hz), 146.56 (t, $J_{\text{Sn-C}} = 70.8$ Hz), 144.11, 119.31, 51.44, 28.98 (t, $J_{\text{Sn-C}} = 19.8$ Hz), 27.17 (t, $J_{\text{Sn-C}} = 54.4$ Hz), 13.60, 9.58 (t, $J_{\text{Sn}(119)\text{-C}} = 346$ Hz, $J_{\text{Sn}(117)\text{-C}} = 330$ Hz).

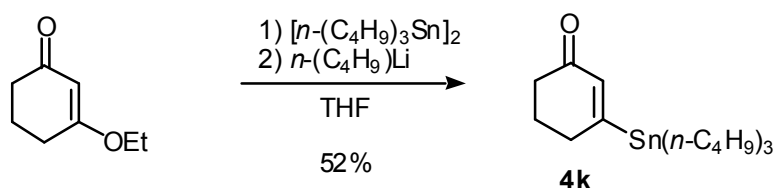


- ref. G. Oddon and D. Uguen, *Tetrahedron Lett.*, 1998, **39**, 1153–1156.
 B. Dominguez, Y. Pazos and A. R. de Lera, *J. Org. Chem.*, 2000, **65**, 5917–5925.
 K. Tanaka, H. Mori, M. Yamamoto and S. Katsumura, *J. Org. Chem.*, 2001, **66**, 3099–3110.

Tributyl-(2-cyclohex-3-enonyl)stannane (4k)

Registry Number: 71106-31-5

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 6.17–6.31 (m, $J_{\text{Sn-H}} = 56.0$ Hz, 1H, C=CH), 2.47–2.51 (m, 2H, CH_2), 2.39–2.42 (m, 2H, CH_2), 1.96–2.02 (m, 2H, CH_2), 1.46–1.53 (m, 6H, 3 CH_2), 1.26–1.35 (m, 6H, 3 CH_2), 0.87–1.06 (m, 15H, 3 CH_2 , 3 CH_3); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 196.72 (t, $J_{\text{Sn-C}} = 51.0$ Hz), 174.78 (t, $J_{\text{Sn}(119)\text{-C}} = 296$ Hz, $J_{\text{Sn}(117)\text{-C}} = 284$ Hz), 138.76 (t, $J_{\text{Sn-C}} = 16.6$ Hz), 38.10, 32.74 (t, $J_{\text{Sn-C}} = 26.4$ Hz), 28.88 (t, $J_{\text{Sn-C}} = 19.8$ Hz) 27.17 (t, $J = 54.2$ Hz), 23.63 (t, $J_{\text{Sn-C}} = 28.0$ Hz), 13.59, 9.17 (t, $J_{\text{Sn}(119)\text{-C}} = 336$ Hz, $J_{\text{Sn}(117)\text{-C}} = 320$ Hz).

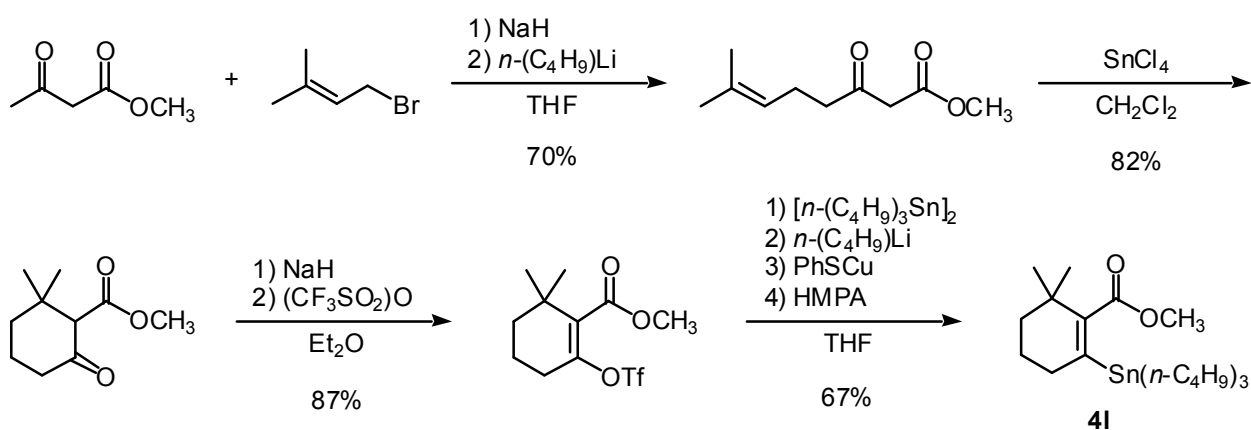


- ref. E. Laborde, L. E. Lesheski and J. S. Kiely, *Tetrahedron Lett.*, 1990, **31**, 1837–1840.

Tributyl-(3,3-dimethyl-2-methoxycarbonylcyclohexenyl)stannane (4l)

To a solution of ($n\text{-Bu}_3\text{Sn}$) $_2$ (8.60 mL, 17.0 mmol) in THF (170 mL) was added $n\text{-BuLi}$ (1.59

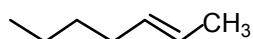
M hexane solution, 10.7 mL, 17.0 mmol) at 0 °C, and the mixture was stirred for 15 min. To this was added phenylthiocopper(I) (2.93 g, 17.0 mmol) at -20 °C, and the mixture was stirred for 15 min. To this was added 6,6-dimethyl-2-trifluoromethanesulfonyloxy-1-cyclohexene-1-carboxylic acid methyl ester (3.57 g, 11.3 mmol) in THF (10 mL) by canular at -20 °C, and the mixture was stirred for 1 h. To this was added HMPA (3.93 mL, 22.6 mmol) at the same temperature, and the mixture was allowed to warm up to 0 °C and stirred for 10 h. To the mixture was added saturated aqueous NH₄Cl solution and stirred for 15 min. The mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 100/0~60/1~50/1~40/1) to give stannane **4I** (3.49 g, 67.6%): colorless oil; TLC *R*_f = 0.78 (*n*-hexane/EtOAc = 30/1); ¹H NMR (CDCl₃, 400 MHz) δ 3.70 (s, 3H, OCH₃), 2.27-2.35 (m, 2H, CH₂), 1.58-1.64 (m, 2H, CH₂), 1.42-1.52 (m, 8H, 4CH₂), 1.24-1.37 (m, 6H, 3CH₂), 1.18 (s, 6H, 2CH₃), 0.81-0.94 (m, 15H, 3CH₂, 3CH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 170.44, 157.78, 145.77, 51.12, 40.29, 34.76, 34.58, 29.18 (t, *J*_{Sn-C} = 19.8 Hz), 28.75, 27.4 (t, *J*_{Sn-C} = 57.6 Hz), 19,90 (t, *J*_{Sn-C} = 32.8 Hz), 13.76, 11.14 (t, *J*_{Sn(119)-C} = 350 Hz, *J*_{Sn(117)-C} = 334 Hz).



ref. F.-W. Sum and L. Weiler, *Can. J. Chem.*, 1979, **57**, 1431-1441.

E. Piers and H. L. A. Tse, *Can. J. Chem.*, 1993, **71**, 983-994.

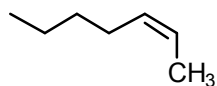
(*E*)-2-Heptene (**5a**)



Registry Number: 97797-33-6; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min,

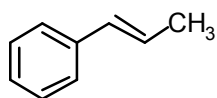
retention time 6.1 min (*n*-nonane: 8.8 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 10.6 min (*n*-nonane: 16.6 min).

(Z)-2-Heptene (5b)



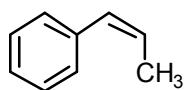
Registry Number: 97797-35-8; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 6.2 min (*n*-nonane: 8.8 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 10.8 min (*n*-nonane: 16.6 min).

(E)-*b*-Methylstyrene (5c)



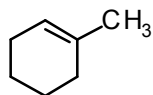
Registry Number: 873-66-5; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 17.0 min (*n*-heptane: 6.9 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 23.6 min (*n*-heptane: 10.8 min).

(Z)-*b*-Methylstyrene (5d)



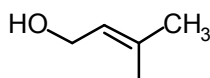
Registry Number: 766-90-5; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 9.6 min (*n*-heptane: 5.6 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 22.0 min (*n*-heptane : 10.8 min).

1-Methylcyclohexene (5e)



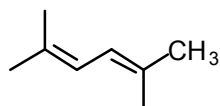
Registry Number: 591-49-1; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 6.7 min (*n*-nonane: 9.0 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 13.1 min (*n*-nonane: 17.2 min).

3-Methyl-2-buten-1-ol (5fg)



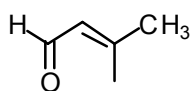
Registry Number: 556-82-1; condition A, B, C, D: Shimadzu GC-2010, column TC-WAX, initial column temperature 150 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 15 min, retention time 9.6min (*n*-decane: 8.5 min).

2,5-Dimethyl-2,4-hexadiene (5h)



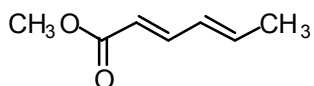
Registry Number: 764-13-6; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 8.3 min (*n*-heptene 5.2 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 16.5 min (*n*-heptane: 10.3 min).

3-Methyl-2-butenal (5i)



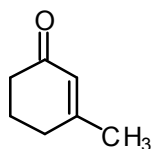
Registry Number: 107-86-6; condition A, B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 15.9 min (*n*-nonane: 15.5 min).

(2E,4E)-2,4-Hexadienoic acid methyl ester (5j)



Registry Number: 689-89-4; condition A: Shimadzu GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 14.2 min (*n*-nonane: 9.4 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 23.3 min (*n*-nonane: 15.6 min).

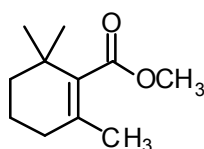
3-Methyl-2-cyclohexene-1-one (5k)



Registry Number: 1193-18-6; condition A, B, C, D: Shimadzu GC-17A, column TC-5, initial column temperature 80 °C, final 100 °C, temperature rate 5 °C/min from 10 min to 14 min, retention time 18.0 min (*n*-nonane: 11.2 min).

6,6-Dimethyl-2-methyl-1-cyclohexene-1-carboxylic acid methyl ester (5l)

Registry Number: 49815-58-9



To a solution of 6,6-dimethyl-2-trifluoromethanesulfonyloxy-1-cyclohexene-1-carboxylic acid methyl ester (158 mg, 499 μmol) in 1,4-dioxane was added trimethylboroxine (50% w.t. THF solution, 124 mg, 493 μmol), Pd[(PPh₃)₄] (57.7 mg, 49.9 μmol), and K₂CO₃ (207 mg, 1.50 mmol), and the mixture was stirred at 100 °C for 2 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 60/1~40/1) to give methylated product **5l** (65.0 mg, 71.3%): colorless oil; TLC *R_f* = 0.46 (*n*-hexane/EtOAc = 30/1); ¹H NMR (CDCl₃, 400 MHz) δ 3.74 (s, 3H, OCH₃), 1.98 (t, *J* = 6.4 Hz, 2H, CH₂), 1.63–1.69 (m, 5H, CH₂, CH₃), 1.43–1.46 (m, 2H, CH₂), 1.08 (s, 6H, 2CH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 170.40, 134.45, 133.63, 50.82, 38.19, 32.90, 31.05, 28.28, 21.28, 18.67; GLC analysis condition

A: GCMS-QP5050A, column TC-5, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 21.1 min (*n*-nonane 9.4 min); condition B, C, D: Shimadzu GC-2010, column TC-1701, initial column temperature 80 °C, final 200 °C, temperature rate 10 °C/min from 10 min to 22 min, retention time 28.9 min (*n*-nonane: 15.6 min).