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Synthesis of *cis*-vinyltrimethylstannanes and *cis*-vinylpinacolboronates in a two-step highly regio and stereoselective process

Paul Malek Mirzayans, Rebecca H. Pouwer, Craig M. Williams *, Paul V. Bernhardt

School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, 4072, Queensland, Australia

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ABSTRACT

A highly efficient two-step regio and stereoselective method for the synthesis of both *cis*-vinyltrimethylstannanes and *cis*-vinylpinacolboronates is described. This method takes advantage of the known lithium/tellurium exchange pathway providing a versatile alternative to known literature methods. The methodology presented demonstrates compatibility, for example, with substrates bearing oxygen functionality in comparison to previously reported methods of *cis*-selective hydrostannylation (i.e., $ZrCl_4$).

1. Introduction

The ability to synthesize conjugated systems bearing a variety of functionality in a highly stereo-selective fashion is of central importance to synthetic organic chemistry. An excellent illustration of the need to drive the development of such methodology can be found in the relative under-use of the 6π-electrocyclisation of 1,3-(*Z*)-5-hexatrienes in strategic synthesis.[1,2] Though not the sole factor, synthetic difficulties in obtaining the requisite 1,3-(*Z*)-5-hexatrienes in reliable yield and with high stereo-control have certainly limited the utility of such a reaction. To date, *cis*-vinylstannane and *cis*-vinylboronate reagents have played a major role in the construction of *Z*-conjugated systems via transition metal catalyzed cross coupling reactions, i.e., the Stille[3] and Suzuki[4] reactions, respectively.[5] Unfortunately, methods to access *cis*-vinylstannanes and *cis*-vinylboronates are not numerous and frequently have problems associated with poor stereoselectivity and functional group tolerance. Over the decades *cis*-vinylstannanes have been most commonly synthesized by radical,[6] Lewis acid,[7] and transition metal[8] mediated hydrostannylation of alkynes, hydrozirconation[9] of stannyl alkynes, and by the transmetallation of vinyl metallic substrates.[10] The use of the Lewis acid catalyst $ZrCl_4$ in the hydrostannylation of alkynes has found considerable popularity,[7b] mainly due to the reaction proceeding in an entirely *cis*-selective fashion. Compatibility of $ZrCl_4$ with oxygen containing functionality, however, is poor (i.e., Lewis acid coordination), although this can be remedied with introduction of bulky substituents on oxygen (i.e., TBDMS).[7b] This solution, however, has not proven to be a general method in order to circumvent the problem.[5] To date, only a few methods have been reported to tolerate oxygen functionality in the synthesis of *cis*-vinylstannanes. Unfortunately, most of these methods suffer from limitations, e.g., high cost,[9] substrate dependence in order to exhibit high (*Z*)-stereoselectivity,[11,12] and loss of stereochemistry in isolated cases.[7a] In the case of *cis*-vinylboronates, a limited number of synthetic methods are available which have seen varying degrees of utilization. For example, 1) hydrogenation,[13] hydroboration[14] or hydrozirconation[15] of 1-alkynylboranes; 2) hydroboration[16] of acetylenes and 1-alkynylbromides[17]; and 3) Peterson type olefination of aldehydes.[18,19] Furthermore, in the case of di- and tri-stannylation and boration, the high control over stereochemistry is often lost.[7c,20]

Considering that the hydrotelluration of alkynes occurs in a highly selective *anti* fashion to give *cis*-vinyltellurides that are not susceptible to isomerisation,[21] and also undergo transmetalation to give *cis*-vinyl metallated species (i.e., lithium, copper, zinc, magnesium, aluminium, calcium, and sodium) with retention of configuration,[22] we wondered whether this pre-existing methodology could be translated into a new synthetic method for *cis*-vinylstannanes and *cis*-vinylboronates. A vital pre-requisite of any new methodolgy in this area, in addition to being practical, reliable and stereoselective, would be accommodation of oxygen functionality. Results of these endeavours are now reported herein.[23]

2. Results and discussion

A variety of alkynes (i.e., **1**) (Table 1, **25**–**34**) were treated with dibutyl ditelluride **2** and sodium borohydride under standard conditions[21,22] to give *cis*-vinyltellurides (i.e., **3**) in 58–94% yield (Table 1, **35**–**43**) (Scheme 1). For all conjugated alkynes, the *cis*-vinyltellurides were obtained with excellent regio- and stereo-selectivity. Isolated terminal alkyne **34** (Table 1, Entry 10), however, suffered loss of regioselectivity yielding 1,2- and 2,2-disubstituted vinylic tellurides **44** and **45**, in favour of the 1,2-disubstituted vinylic telluride **44**, as

* Corresponding author.
E-mail address: c.williams3@uq.edu.au (C.M. Williams).

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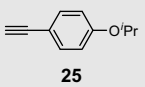
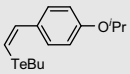
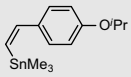
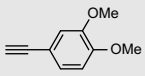
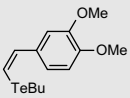
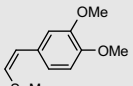
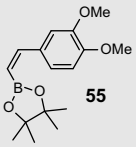
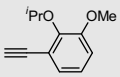
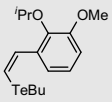
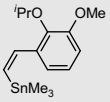
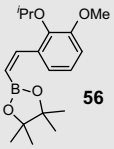
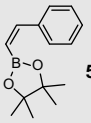
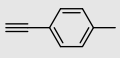
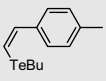
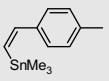
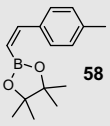
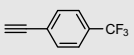
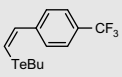
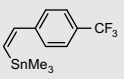
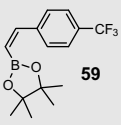
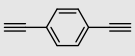
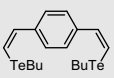
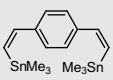
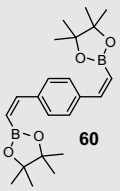
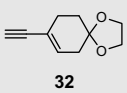
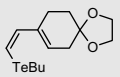
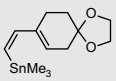
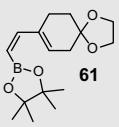
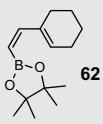
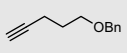
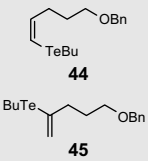
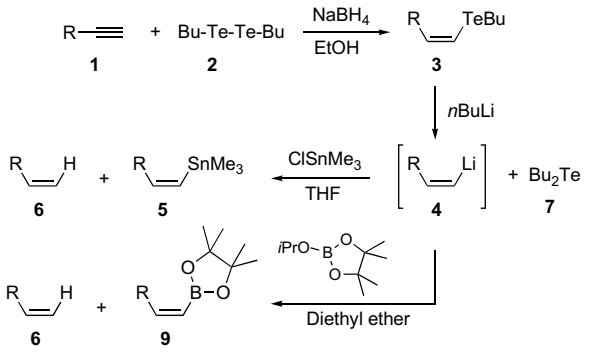
previously documented for isolated alkynes.[21,24,25] Unfortunately, in our case, an inseparable mixture was obtained. Efficient methodology to circumvent this problem, however, has been reported to regioselectively give the 1,2-disubstituted *cis*-vinylic tellurides by hydroboration or hydrometallation of 1-alkynyltellurides.[26]

The *cis*-vinyltellurides **3** were facilely transmetallated with *n*-butyllithium in anhydrous tetrahydrofuran (THF) to the corresponding vinyl lithium intermediate **4**, and subsequently quenched with trimethyltin chloride to afford the *cis*-vinyl stannanes (i.e., **5**) in 40–68% yield without any detectable amount of *trans*-vinyl stannanes (Table 1, **46**–**54**) (Scheme 1) (See Fig. 1A for the X-ray crystal structure of compound **52**, which has crystallographic inversion symmetry). Purification of the *cis*-vinylstannanes posed a challenge as dibutyltelluride **7** was very difficult to remove by distillation or by column chromatography when certain non-polar and/or low molecular weight *cis*-vinyltrimethylstannanes **5** were

Table 1
cis-Vinylbutyltellurides, *cis*-vinyltrimethylstannanes and *cis*-vinylpinacolboronates

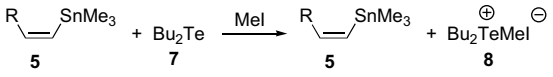
Entry	Acetylene	R–Te–Bu	Yield (%)	$RSnMe_3$	Yield (%)	RB (pin)	Yield (%)
1	 **25**	 **35**	67	 **46**	46	—	—
2	 **26**	 **36**	71	 **47**	68	 **55**	65
3	 **27**	 **37**	84	 **48**	60	 **56**	54
4	 **28**	 **38**	61	 **49**	50	 **57**	65
5	 **29**	 **39**	78	 **50**	68	 **58**	72
6	 **30**	 **40**	94	 **51**	61	 **59**	70
7	 **31**	 **41**	80	 **52**	40	 **60**	22
8	 **32**	 **42**	82	 **53**	64	 **61**	72
9	 **33**	 **43**	58	 **54**	50	 **62**	75
10	 **34**	 **44** **45**	42	—	—	—	—



Scheme 1.

being produced. An efficient method was devised which capitalized on the known reactivity of dibutyl telluride **7** with methyl iodide to give methyl di-*n*-butyltelluronium iodide **8** under catalysed ($AgNO_3$, $AgBF_4$)[27] and non-catalysed conditions.[28] When excess methyl iodide (6 equiv) was added to the reaction mixture after trimethyltin chloride, it selectively reacted with the dibutyl telluride **7** affording telluronium salt **8**, which could be readily removed by trituration, followed by column chromatography (Scheme 2). Initial transmetallation investigations involving tributyltin chloride were shown to proceed smoothly to afford the tributylvinylstannane derivatives, however, purification by distillation proved difficult so the study focused on trimethylstannanes.

Treatment of the *cis*-vinyltellurides **3** with *n*-butyllithium, followed by *iso*-propoxypinacolboronate afforded the desired *cis*-vinylboronates in 22–75% yield, again without any detectable amount of the *trans*-isomer (Table 1, compounds **55**–**62**) (Scheme 1). Reactions were performed in diethyl ether based on results obtained



Scheme 2.

by Brown[29] and Stefani[30] et al., however, for comparison when THF was used in the case of **60**, the same result was obtained. Owing to the higher polarity of the *cis*-vinylboranes, column chromatography was sufficient for removal of the dibutyl telluride **7**. Methyl iodide was used, in this case, in order to scavenge for isopropoxide. [See Figure 1 (B–D) for X-ray crystal structure analysis of compounds **55**, **59** and **60**]. Interestingly, in some cases, trace amounts of *cis*-vinyltellurides **3** were recovered, regardless of conditions. This proved to be most significant for the synthesis of *cis*-vinylpinacolboronate **56**, from which 25% of the *cis*-vinyltelluride **37** was recovered.

Recently, a mechanistic study of the synthesis of potassium *trans*-vinyltrifluoroborate salts, from *cis*-vinyltellurides via *cis*-vinylboronates, has been reported by Stefani et al.[30] In view of the historically characteristic *cis*-selectivity of the tellurium–lithium exchange, a free radical pathway has been proposed to account for the *trans*-selectivity of this system (Scheme 3). It was suggested that the loss of stereochemistry was caused by a *n*-butyl radical **11**, generated from the homolytic cleavage of dibutyl telluride **7**, caused by lithium species present in the reaction medium. Attack of the anionic complex **10** by **11**, generates boronate **12** and a vinyl radical **13**, isomerisation of which affords radical **14** leading to the *trans*-selectivity observed.

In the view of our results, we were led to consider an ionic mechanism to account for the retention of cis-selectivity in our system. We postulated that substitution of butyl lithium for hexyl lithium, in the tellurium–lithium exchange reaction, would generate a butyl-hexyltelluride **18**, which in turn could give a butyl **11** or hexyl **24** radical in a free radical approach. By analogy to Scheme 3 (*n*-$BuBF_3K$ salt **16**) these

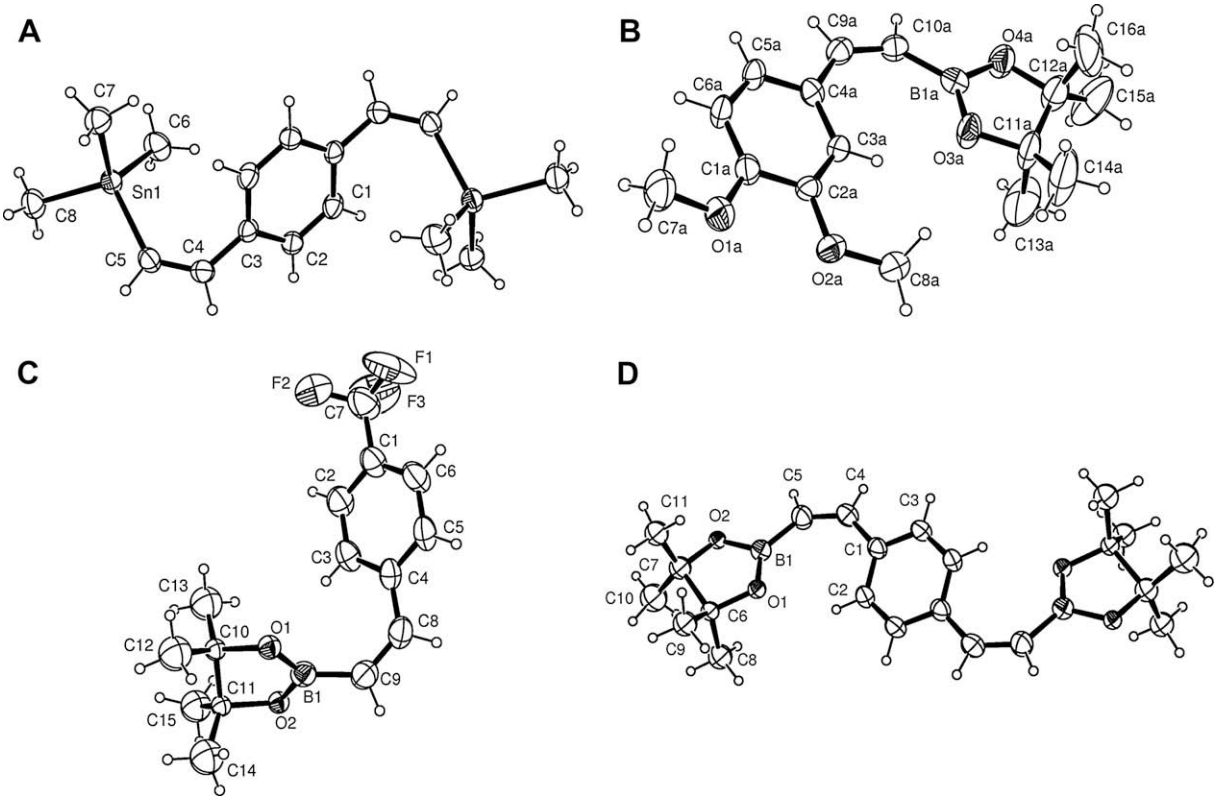
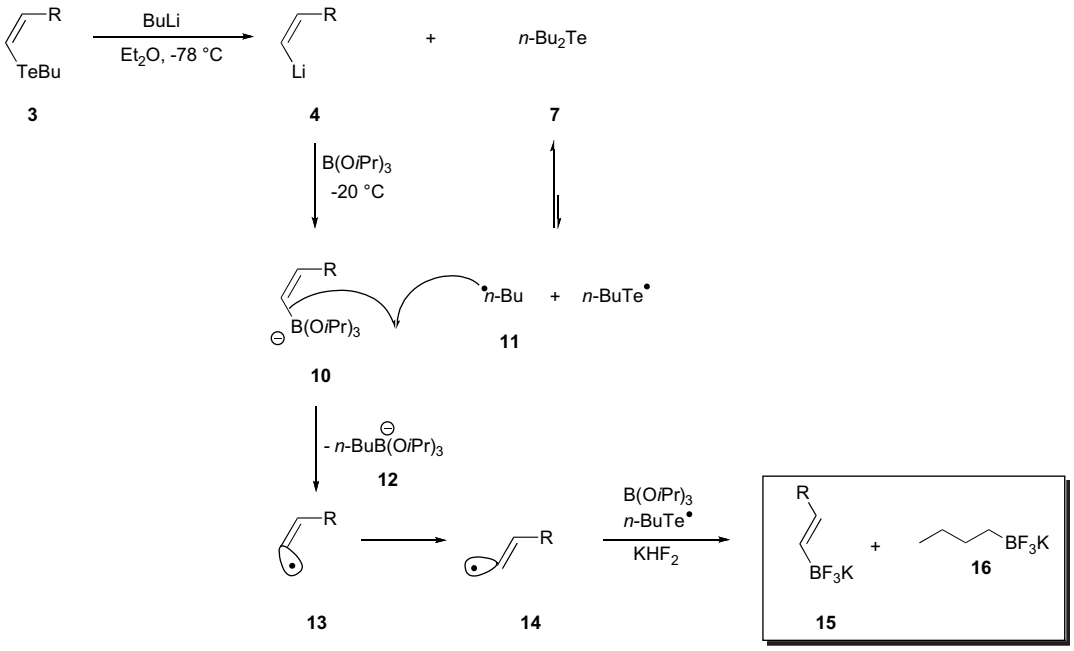


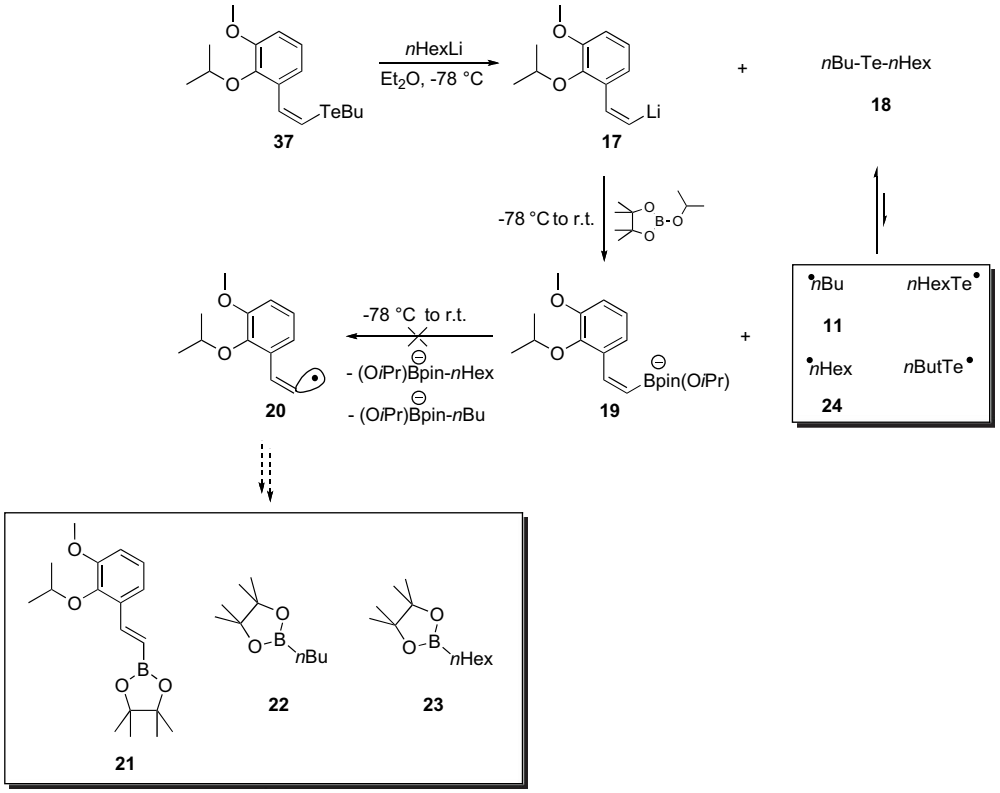
Figure 1. ORTEP views of crystallographically characterized compounds **52** (A), **55** (B, one of the two independent molecules shown), **59** (C) and **60** (D), (30% probability ellipsoids). For the structures of **59** and **60** which exhibiting disorder in the boronic ester and/or $-CF_3$ groups, a single conformation is shown (see Electronic Supplementary data for diagrams showing all contributors to disorder).



Scheme 3.

radical species would give rise to a mixture of *n*-butyl and *n*-hexylpinacolboronates **22** and **23** respectively (Scheme 4).

However, when carrying out the reaction using hexyl lithium and *Z*-β-(butyltelluro)-2-isopropoxy-3-methoxystyrene (**37**) under standard conditions, vinylboronate **56** and butyl-hexyl-telluride **18** were observed by GC–MS to be the major products. As expected, rather than a mixture of **22**, **23** and **21** only a small amount of *n*-hexylpinacolboronate **23**, believed to be formed by the direct addition of hexyl lithium to *iso*-propoxypinacolboronate, was observed along with small amounts of the corresponding alkene, starting material **37**, and hexane. Interestingly, trace amounts of dihexyltelluride and *Z*-β-(hexyltelluro)-2-isopropoxy-3-methoxystyrene were also observed. It should be noted that in addition to the different boronate used in our system, boronates were added at −78 °C as compared to −20 °C in the synthesis of potassium *trans*-vinyltrifluoroborate salts[30] (Scheme 4). Although radicals cannot be ruled out, our results suggest that such a pathway is not in effect under our reaction conditions, hence, the preserved *cis*-selectivity in our system.



Scheme 4.

The bis-systems (i.e., **52** and **60**), derived from 1,4-diethynylbenzene **31**, were of particular interest for application to the construction of conjugated polyenes via tandem bis-Stille or -Suzuki reactions. Distannane **52** was isolated in moderate yield with complete retention of stereochemical integrity. [see X-ray crystal structure analysis (Fig. 1A)] Excellent stereo-control was again obtained in the case of the bis-boronate **60** [see X-ray crystal structure analysis (Fig. 1D)], but the yield was much lower and could not be improved by standard variations in conditions.

Compound **55** crystallized with two independent molecules, with no significant differences in the unit cell (Fig. 1B). The structures of compounds **59** and **60**, however, were plagued by disorder of the boronic ester groups. As shown in ESI Fig. S1, the 5-membered rings were disordered between three different puckered conformations. In addition, the trifluoromethyl group in **59** was disordered between two rotamers. The lack of H-bond donors and the presence of the bulky methyl groups attached to the five-membered rings enables the boronic ester groups to adopt a number of conformations without disturbing the overall packing within the structure. The disorder lowered the precision of the structures of compounds **59** and **60** as a consequence. Compound **60** (like **52**) also has crystallographic inversion symmetry.

In conclusion, a new versatile method for the synthesis of *cis*-vinyltrimethylstannanes and *cis*-vinylpinacolboronates in a two-step, highly regio- and stereoselective manner has been disclosed, which builds on the well known tellurium–lithium metal exchange protocol. In the case of *cis*-vinyltrimethylstannanes, this method offers advantages over other popular methods when oxygen functionality is required. *cis*-Vinyl tellurides offer increasing potential as synthetic reagents,[31] and further work in this area is currently underway.

3. Experimental section

3.1. General experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV400 (400.13 MHz; 100.62 MHz), AV300 (300.13 MHz; 75.47 MHz) and DRX500 (500.13 MHz; 125.76 MHz) instruments in deuteriochloroform ($CDCl_3$). Coupling constants are given in Hz and chemical shifts are expressed as δ values in ppm. Hydrogen–tin couplings are reported when possible and are in accordance with what has been previously reported for similar compounds.[32] High resolution electron impact ionization (HREIMS) accurate mass measurements were recorded on a Finnigan MAT 900XL-TRAP (EI 70 eV) using perfluorokerosene-H as reference calibrant. High resolution electrospray ionisation (HRESIMS) accurate mass measurements were recorded in positive mode on a Bruker MicrOTOF-Q (quadrupole—Time of Flight) instrument with a Bruker ESI source using sodium formate as a reference calibrant. IR spectra were measured on a Perkin–Elmer FT-IR spectrometer (Spectrum 2000) with a Smiths detection (DuraSampler*IR* II). Microanalyses were performed by the University of Queensland Microanalytical Service. Column chromatography was undertaken on silica gel (Flash Silica gel 230–400 mesh) or active neutral aluminium oxide (Brockman grade 1) with distilled solvents. All reagents and solvents were distilled according to Perin and Armarego, 'Purification of laboratory chemicals', 3rd ed. prior to use. Tetrahydrofuran was freshly distilled from a sodium/benzophenone still. Melting points were determined on a Stuart SMP11 Melting Point apparatus and are uncorrected. Dibutyl ditelluride can be purchased from ACROS chemical company, however, it was readily prepared, see below. Vinyltellurides were placed under vacuum with gentle stirring overnight prior to use. Toxicity and pharmacology information of organotellurium compounds has been reported.[33] Fine chemicals were purchased from the Aldrich Chem. Co. hexyl lithium was prepared according to literature procedure.[34]

Crystallographic data for structures **52**, **55**, **59** and **60** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 708676–708679) and may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk.

3.2. Dibutyl ditelluride (2)

To a suspension of tellurium powder (3 g, 23.5 mmol, 200 mesh) in anhydrous tetrahydrofuran (30 mL) at 0 °C under an argon atmosphere was added *n*-butyllithium (15.9 mL, 1.48 M in hexanes, 23.5 mmol) drop-wise. The reaction was stirred for 35 min at 0 °C and an additional 15 min at rt after which time the mixture was poured into an Erlenmeyer flask containing water (60 mL). After stirring for 20 min under air the organic phase was separated and the aqueous phase was extracted with ethyl acetate. The combined organic phase was washed with saturated ammonium chloride solution, brine, dried over magnesium sulphate, and filtered through a plug of Celite. The solvent was removed in vacuo to yield the title compound (3.96 g, 91%) as a red oil. ^{1}H NMR (300 MHz) δ ppm 0.91 (t, J=7.3 Hz, 6H), 1.40 (m_c, 4H), 1.63–1.75 (m, 4H), 3.09 (m_c, 4H). ^{1}H NMR and all other spectroscopic data were identical to that previously reported.[22b]

3.3. General procedure for the preparation of *cis*-vinyltellurides

The procedure described for the preparation of *Z*-β-(butyltelluro)-4-trifluoromethylstyrene (**40**) is representative. Dibutylditelluride (540 mg, 1.46 mmol) and 1-ethynyl-4-(trifluoromethyl)benzene (**30**) (0.454 mL, 2.78 mmol) were suspended in anhydrous ethanol (8 mL) under an argon atmosphere. Sodium borohydride (110 mg, 2.92 mmol) was added portion-wise and the solution became yellow in colour. The reaction was then heated to reflux, and further portions of sodium borohydride were added to keep the mixture yellow in colour. After 3 h, the reaction was quenched by the addition of water (3 mL) and 10% sodium hydroxide solution (3 mL). The mixture was extracted with petroleum ether and the combined organic phase was washed with brine and dried over magnesium sulfate. The solvent was removed in vacuo and the residue was purified by silica gel column chromatography (petroleum ether) to yield the title compound (932 mg, 94%) as a yellow oil. ^{1}H NMR (400 MHz) δ ppm 0.92 (t, J=7.4 Hz, 3H), 1.40 (m_c, 2H), 1.77–1.86 (m, 2H), 2.76 (m_c, 2H), 7.19 (d, J=10.9 Hz, 1H), 7.33–7.38 (m, 2H), 7.39 (d, J=10.9 Hz, 1H), 7.59 (d, J=8.2 Hz, 2H). ^{13}C NMR (100 MHz) 9.6, 13.4, 24.9, 33.9, 109.0, 124.2 (q, $^1J_{CF}$=271.9 Hz), 125.3 (q, $^3J_{CF}$=3.8 Hz), 127.7, 128.9 (q, $^2J_{CF}$=32.5 Hz), 135.5, 142.4. HRMS (EI) Calculated for $C_{13}H_{15}F_3Te$: $M^{+\bullet}$ 358.0183. Found: 358.0195. IR ν (cm^{-1}) 2960, 2929, 2873, 1614, 1404, 1321, 1162, 1113, 1065, 847.

3.4. *Z*-β-(Butyltelluro)-4-isopropoxystyrene (35)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 20 h. Purification by silica gel column chromatography (15:1, petroleum ether/diethyl ether) yielded the title compound (35 mg, 67%) as a yellow oil. ^{1}H NMR (300 MHz) δ ppm 0.91 (t, J=7.3 Hz, 3H), 1.32 (d, J=6.1 Hz, 6H), 1.40 (m_c, 2H), 1.74–1.86 (m, 2H), 2.71 (m_c, 2H), 4.53 (sept., J=6.1 Hz, 1H), 6.79 (d, J=10.7 Hz, 1H), 6.82–6.90 (m, 2H), 7.14–7.22 (m, 2H), 7.30 (d, J=10.7 Hz, 1H). ^{13}C NMR (125 MHz) 8.9, 13.4, 22.1, 25.0, 30.9, 34.0, 69.9, 102.1, 115.6, 129.0, 131.5, 136.5, 157.1. HRMS (EI) Calculated for $C_{15}H_{22}OTe$: $M^{+\bullet}$ 348.0727. Found: 348.0734. IR ν (cm^{-1}) 2974, 2926, 2871, 1605, 1563, 1504, 1297, 1244, 1180, 1108, 953, 835.

3.5. *Z*-β-(Butyltelluro)-3,4-dimethoxystyrene (36)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 18 h. Purification by silica gel column chromatography (5:1, petroleum ether/diethyl ether) yielded the title compound (543 mg, 71%) as a yellow oil. ^{1}H NMR (300 MHz) δ ppm 0.91 (t, J=7.3 Hz, 3H), 1.40 (m_c, 2H), 1.75–1.87 (m, 2H), 2.73 (m_c, 2H), 3.87 (s, 3H), 3.89 (s, 3H), 6.79–6.88 (m, 3H), 6.83 (d, J=10.6 Hz, 1H), 7.30 (d, J=10.6 Hz, 1H). ^{13}C NMR (75 MHz) 9.0, 13.4, 25.0, 34.0, 55.9, 103.0, 110.4, 111.0, 120.6, 132.2, 136.5, 148.3, 148.8. HRMS (ESI) Calculated for $C_{14}H_{20}O_2TeNa^+$: 373.0418. Found: 373.0418. IR ν (cm^{-1}) 2855, 2927, 2834, 1593, 1509, 1460, 1257, 1235, 1169, 1134, 1024.

3.6. *Z*-β-(Butyltelluro)-2-isopropoxy-3-methoxystyrene (37)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 5.5 h. Purification by silica gel column chromatography (25:1, petroleum ether/diethyl ether) yielded the title compound (360 mg, 84%) as a yellow oil. ^{1}H NMR (400 MHz) δ ppm 0.90 (t, J=7.4 Hz, 3H), 1.24 (d, J=6.2 Hz, 6H), 1.38 (m_c, 2H), 1.73–1.82 (m, 2H), 2.67 (m_c, 2H), 3.82 (s, 3H), 4.34 (sept., J=6.2 Hz, 1H), 6.83 (dd, J=8.1, 1.5 Hz, 1H), 6.86–6.90 (m, 1H), 6.95 (d, J=10.7 Hz, 1H), 7.02 (t, J=7.9 Hz, 1H), 7.53 (d, J=10.7 Hz, 1H). ^{13}C NMR (100 MHz) 8.2, 13.4, 22.5, 24.9, 34.0, 55.8, 75.6, 106.2, 111.9, 119.3, 123.2, 133.9, 134.5, 144.7, 153.1. HRMS (EI) Calculated for $C_{16}H_{24}O_2Te$: $M^{+\cdot}$ 378.0833. Found: 378.0838. IR ν (cm^{-1}) 2960, 2927, 1588, 1569, 1471, 1449, 1378, 1276, 1256, 1213, 1106, 1067, 933, 779.

3.7. *Z*-β-(Butyltelluro)styrene[35] (38)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 2.5 h. Purification by silica gel column chromatography (petroleum ether) yielded the title compound (343 mg, 61%) as a yellow oil. ^{1}H NMR (400 MHz) δ ppm 0.91 (t, J=7.4 Hz, 3H), 1.40 (m_c, 2H), 1.76–1.85 (m, 2H), 2.72 (m_c, 2H), 6.98 (d, J=10.8 Hz, 1H), 7.20–7.28 (m, 3H), 7.32–7.37 (m, 2H), 7.37 (d, J=10.8 Hz, 1H). ^{13}C NMR (100 MHz) 9.0, 13.4, 25.0, 34.0, 105.3, 127.3, 127.6, 128.4, 136.9, 139.0. IR ν (cm^{-1}) 2956, 2925, 2870, 1597, 1492, 1442, 1329, 1247, 1167, 769, 696.

3.8. *Z*-β-(Butyltelluro)-4-methylstyrene (39)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 5.5 h. Purification by silica gel column chromatography (petroleum ether) yielded the title compound (638 mg, 78%) as a yellow oil. ^{1}H NMR (300 MHz) δ ppm 0.91 (t, J=7.3 Hz, 3H), 1.39 (m_c, 2H), 1.73–1.87 (m, 2H), 2.32 (s, 3H), 2.71 (m_c, 2H), 6.90 (d, J=10.7 Hz, 1H), 7.15 (s, 4H), 7.34 (d, J=10.7 Hz, 1H). ^{13}C NMR (75 MHz) 8.9, 13.4, 21.3, 25.0, 34.0, 104.0, 127.5, 129.0, 136.2, 136.8, 137.1. IR ν (cm^{-1}) 3019, 2956, 2924, 2869, 1587, 1507, 1458, 1330, 1181, 1167, 817.

3.9. 1,4-Bis[(*Z*)-2-(butyltelluro)vinyl]benzene (41)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 4.5 h. Purification by silica gel column chromatography (250:1, petroleum ether/diethyl ether) yielded the title compound (361 mg, 80%) as a yellow solid, mp 34–36 °C. ^{1}H NMR (500 MHz) δ ppm 0.92 (t, J=7.4 Hz, 6H), 1.40 (m_c, 4H), 1.77–1.85 (m, 4H), 2.73 (m_c, 4H), 6.99 (d, J=10.8 Hz, 2H), 7.26 (s, 4H), 7.35 (d, J=10.8 Hz, 2H). ^{13}C NMR (125 MHz) 9.3, 13.4, 25.0, 34.0, 105.5, 127.6, 136.4, 137.8. HRMS (EI) Calculated for $C_{18}H_{26}Te_2$: $M^{+\cdot}$ 502.0153. Found: 502.0180. Anal. Calcd for $C_{18}H_{26}Te_2$: C, 43.45; H, 5.27. Found: C, 43.43; H, 5.13. IR ν (cm^{-1}) 3019, 2951, 2922, 2868, 2837, 1581, 1505, 1460, 1403, 1338, 1304, 1246, 1187, 1161, 827.

3.10. (*Z*)-[2-(1,4-Dioxaspiro[4,5]dec-7-en-8-yl)-vinyl]butyltelluride (42)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 20 h. Purification by silica gel column chromatography (14:1, petroleum ether/diethyl ether) yielded the title compound (3.0 g, 82%) as a red/yellow oil. ^{1}H NMR (400 MHz) δ ppm 0.90 (t, J=7.4 Hz, 3H), 1.37 (m_c, 2H), 1.72–1.82 (m, 4H), 2.33–2.39 (m, 2H), 2.43 (m_c, 2H), 2.63 (m_c, 2H), 3.96–3.97 (m, 4H), 5.53 (m_c, 1H), 6.52 (d, J=10.7 Hz, 1H), 6.78 (d, J=10.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 8.8, 13.4, 25.0, 26.7, 30.8, 33.9, 35.9, 64.4, 101.2, 107.7, 125.0, 136.8, 138.3. MS (EI): m/z 352 (21), 350 (19), 348 (12), 295 (27), 293 (25), 291 (16), 251 (14), 249 (13), 209 (39), 207 (37), 205 (21), 166 (11), 165 (100), 99 (15), 93 (16), 91 (14), 79 (40), 77 (18). HRMS (EI) Calculated for $C_{14}H_{22}O_2Te$: $M^{+\cdot}$ 352.0681. Found: 352.0681. IR ν (cm^{-1}) 2955, 2925, 2873, 1629, 1566, 1460, 1446, 1429, 1367, 1321, 1248, 1109, 1058, 947, 867.

3.11. *Z*-(2-Cyclohexenyl-1-ethenyl)butyltelluride[36] (43)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 6 h. Purification by silica gel column chromatography (petroleum ether) yielded the title compound (282 mg, 58%) as a yellow/orange oil. ^{1}H NMR (400 MHz) δ ppm 0.90 (t, J=7.3 Hz, 3H), 1.38 (m_c, 2H), 1.53–1.68 (m, 4H), 1.72–1.82 (m, 2H), 2.07–2.14 (m, 2H), 2.14–2.20 (m, 2H), 2.62 (m_c, 2H), 5.63 (m_c, 1H), 6.45 (d, J=10.6 Hz, 1H), 6.73 (dd, J=10.6, 0.7 Hz, 1H). ^{13}C NMR (75 MHz) 8.6, 13.4, 22.1, 22.5, 25.0, 25.5, 27.6, 34.0, 99.9, 128.2, 137.5, 139.6. IR ν (cm^{-1}) 2924, 1565, 1435, 1324, 1247, 1165, 848.

3.12. *Z*-β-(Butyltelluro)-5-benzyloxy-1-pentenyl (44) and 2-butyltelluro-5-benzyloxy-1-pentenyl (45)

The title compound was prepared as indicated in the representative procedure. The reaction was quenched after 21 h. Purification by silica gel column chromatography (20:1, petroleum ether/diethyl ether) yielded an inseparable mixture of α and β-vinyltellurides in the ratio 1:1.6 (392 mg, 42%) as a yellow oil. ^{1}H NMR (400 MHz) δ ppm 0.91 (t, J=7.4 Hz, 6H), 1.38 (m_c, 4H), 1.68–1.87 (m, 8H), 2.09–2.16 (m, 2H), 2.41 (br t, J=7.5 Hz, 2H), 2.66 (m_c, 2H), 2.73 (m_c, 2H), 3.48 (t, J=6.3 Hz, 2H), 3.48 (t, J=6.5 Hz, 2H), 4.49 (s, 2H), 4.49 (s, 2H), 5.37 (t, J=0.6 Hz, 1H), 5.88 (t, J=1.5 Hz, 1H), 6.17 (dt, J=6.9, 9.3 Hz, 1H), 6.57 (dt, J=1.2, 9.3 Hz, 1H), 7.24–7.30 (m, 5H), 7.31–7.36 (m, 5H). ^{13}C NMR (100 MHz) 6.0, 6.4, 13.4, 24.9, 25.2, 28.8, 29.5, 32.3, 33.7, 34.2, 39.3, 69.1, 69.6, 72.9 (m), 103.2, 122.8, 126.6, 127.5 (m), 127.6 (m), 128.3, 138.5, 138.6, 139.6. IR ν (cm^{-1}) 2956, 2927, 2855, 1599, 1101, 733, 696, 617.

3.13. Methyl di-*n*-butyltelluronium iodide (8)

Methyl di-*n*-butyltelluronium iodide was isolated as a white amorphous solid, mp 93–95 °C (lit. 94 °C[37]). ^{1}H NMR (400 MHz) δ ppm 0.97 (t, J=7.3 Hz, 6H), 1.47 (m_c, 4H), 1.74–1.87 (m, 4H), 2.32–2.41 (m, 3H), 3.05 (m_c, 4H). ^{13}C NMR (100 MHz) 5.7, 13.5, 24.6, 26.7, 27.9. IR ν (cm^{-1}) 2958, 2930, 2869, 1460, 1380, 1178, 1091, 897, 843, 772, 700.

3.14. General procedure for the preparation of *cis*-vinylstannanes

The procedure described for the preparation of *Z*-β-(trimethylstannyl)-3,4-dimethoxystyrene (**47**) is representative. To a solution of *Z*-β-(butyltelluro)-3,4-dimethoxystyrene (**36**) (136 mg, 0.391 mmol)

in anhydrous tetrahydrofuran (4 mL) at −78 °C under an argon atmosphere was added *n*-butyllithium (0.319 mL, 1.35 M in hexanes, 0.430 mmol) drop-wise. The reaction was stirred for 10 min before a solution of trimethyltin chloride (0.496 mL, 1 M in THF, 0.496 mmol) was added drop-wise. The reaction was stirred for a further 30 min at −78 °C then allowed to warm to 0 °C over 2 h. After reaching 0 °C the reaction mixture was shielded from light, placed in an ice bath, and MeI (0.146 mL, 2.35 mmol) was added drop-wise after which time the ice bath was removed. After stirring for 4 h at rt the solvent was removed in vacuo and the resulting crude oil was triturated with petroleum ether/diethyl ether (4:1), the combined organic phase was concentrated and purified on a plug of neutral Al_2O_3 (10:1, petroleum ether/diethyl ether) to yield the title compound (87 mg, 68%) as a colourless oil. ^{1}H NMR (400 MHz) δ ppm 0.10 (s, 9H, $^2J_{SnH}$=52.7 Hz/55.1 Hz), 3.87 (s, 3H), 3.87 (s, 3H), 6.07 (d, J=13.6 Hz, 1H, $^2J_{SnH}$=61.6 Hz/64.5 Hz),[38] 6.77–6.79 (m, 1H), 6.80–6.82 (m, 2H), 7.49 (d, J=13.6 Hz, 1H, $^3J_{SnH}$=144.1 Hz/150.8 Hz). ^{13}C NMR (100 MHz) −8.1, −8.1 (d, $^1J_{SnC}$=338.8 Hz/354.7 Hz), 55.9 (m), 110.2, 110.8, 120.1, 131.4, 134.0, 146.9, 148.6 (m). HRMS (ESI) Calculated for $C_{13}H_{20}O_2SnNa^+$: 351.0377. Found: 351.0377. IR ν (cm^{-1}) 2961, 2835, 1600, 1572, 1508, 1461, 1259, 1237, 1130, 1027, 764.

3.15. *Z*-β-(Trimethylstannyl)-4-isopropoxystyrene (46)

The title compound was prepared as indicated in the representative procedure with the following exception. The reaction was allowed to reach rt over a period of 2 h, the solvent was removed in vacuo and the crude mixture was purified on a short plug of silica treated with TEA (petroleum ether, 1% TEA) to yield the title compound (43 mg, 46%) as a colourless oil. ^{1}H NMR (400 MHz) δ ppm 0.08 (s, 9H, $^2J_{SnH}$=52.7 Hz/55.2 Hz), 1.32 (d, J=6.1 Hz, 6H), 4.53 (sept., J=6.1 Hz, 1H), 6.04 (d, J=13.6 Hz, 1H, $^2J_{SnH}$=62.8 Hz/65.7 Hz), 6.79–6.84 (m, 2H), 7.13–7.18 (m, 2H), 7.49 (d, J=13.6 Hz, 1H, $^3J_{SnH}$=145.0 Hz/151.8 Hz). ^{13}C NMR (100 MHz) −8.1, 22.0, 69.9, 115.6, 128.4, 131.2, 133.6, 146.7, 157.4. HRMS (EI) Calculated for $C_{13}H_{19}OSn$: $[M-Me]^+$ 311.0452. Found: 311.0449. IR ν (cm^{-1}) 2976, 2918, 1606, 1504, 1295, 1243, 1119, 954, 841, 766.

3.16. *Z*-β-(Trimethylstannyl)-2-isopropoxy-3-methoxystyrene (48)

The title compound was prepared as indicated in the representative procedure with the following exception. The reaction was allowed to reach rt over a period of 2 h, the solvent was removed in vacuo and the crude mixture was purified on a short plug of silica treated with TEA (25:1, petroleum ether/diethyl ether, 1% TEA) to yield the title compound (92 mg, 60%) as a colourless oil. ^{1}H NMR (500 MHz) δ ppm 0.02 (s, 9H, $^2J_{SnH}$=52.9 Hz/55.1 Hz), 1.24 (d, J=6.2 Hz, 6H), 3.81 (s, 3H), 4.40 (sept., J=6.2 Hz, 1H), 6.18 (d, J=13.6 Hz, 1H, $^2J_{SnH}$=67.9 Hz/71.0 Hz), 6.79–6.85 (m, 2H), 6.95 (t, J=7.9 Hz, 1H), 7.68 (d, J=13.6 Hz, 1H, $^3J_{SnH}$=145.0 Hz/151.8 Hz). ^{13}C NMR (125 MHz) −8.1, −8.1 (d, $^1J_{SnC}$=338.9 Hz/354.4 Hz), 22.5, 55.8, 75.2, 111.9, 120.2, 123.2, 133.6, 136.5, 144.3, 144.9, 152.8. HRMS (ESI) Calculated for $C_{15}H_{24}O_2SnNa^+$: 379.0696. Found: 379.0690 IR ν (cm^{-1}) 2974, 1567, 1471, 1452, 1372, 1274, 1215, 1108, 1069, 769, 746.

3.17. *Z*-β-(Trimethylstannyl)styrene[39] (49)

The title compound was prepared as indicated in the representative procedure with the following exception. After stirring for 4 h at rt the reaction was quenched by the addition of saturated aqueous $NaHCO_3$. The organic phase was diluted with Et_2O separated and dried over $MgSO_4$. The solvent was removed in vacuo and the crude mixture was purified on a plug of neutral Al_2O_3 (petroleum ether) to yield the title compound (65 mg, 50%) as a colourless oil. ^{1}H NMR (300 MHz) δ ppm 0.06 (s, 9H, $^2J_{SnH}$=53.0 Hz/55.4 Hz), 6.18 (d, J=13.6 Hz, 1H, $^2J_{SnH}$=62.7 Hz/65.4 Hz), 7.19–7.35 (m, 5H), 7.57 (d, J=13.6 Hz, 1H). ^{13}C NMR (75 MHz) −8.1, 127.3 (m), 128.2, 133.8, 141.1, 147.3.

3.18. *Z*-β-(Trimethylstannyl)-4-methylstyrene (50)

The title compound was prepared as indicated in the representative procedure with the following exception. The resulting crude oil was triturated with petroleum ether, purified on a plug of neutral Al_2O_3 (petroleum ether) to yield the title compound (119 mg, 68%) as a colourless oil. ^{1}H NMR (400 MHz) δ ppm 0.07 (s, 9H, $^2J_{SnH}$=53.2 Hz/55.2 Hz), 2.32 (s, 3H), 6.11 (d, J=13.6 Hz, 1H, $^2J_{SnH}$=63.1 Hz/65.4 Hz),[40] 7.10 (d, J=8.1 Hz, 2H), 7.14 (d, J=8.1 Hz, 2H), 7.52 (d, J=13.6 Hz, 1H, $^3J_{SnH}$=144.5 Hz/151.0 Hz). ^{13}C NMR (100 MHz) −8.1, 21.2, 127.2, 128.9, 132.5, 137.1, 138.2, 147.2. IR ν (cm^{-1}) 2967, 2918, 1590, 1562, 1508, 1450, 1188, 1113, 821, 761, 733. HRMS (EI) Calculated for $C_{11}H_{15}{}^{118}Sn$: $[M-Me]^+$ 265.0190. Found: 265.0196.

3.19. *Z*-β-(Trimethylstannyl)-4-trifluoromethylstyrene (51)

The title compound was prepared as indicated in the representative procedure with the following exception. The resulting crude oil was triturated with petroleum ether. Purified on a plug of neutral Al_2O_3 (petroleum ether) to yield the title compound (118 mg, 61%) as a colourless oil. ^{1}H NMR (400 MHz) δ ppm 0.07 (s, 9H, $^2J_{SnH}$=53.1 Hz/55.5 Hz), 6.34 (d, J=13.8 Hz, 1H, $^2J_{SnH}$=58.2 Hz/60.9 Hz), 7.31–7.36 (m, 2H), 7.53–7.58 (m, 2H), 7.56 (d, J=13.4 Hz, 1H, $^3J_{SnH}$=137.2 Hz/143.4 Hz). ^{13}C NMR (100 MHz) −8.1, −8.1 (d, $^1J_{SnC}$=342.0 Hz/358.1 Hz), 124.2 (q, $^1J_{CF}$=271.9 Hz), 125.2 (q, $^3J_{CF}$=3.8 Hz), 127.5, 129.3 (q, $^2J_{CF}$=32.4 Hz), 136.9, 136.9 (d, $^1J_{SnC}$=394.7 Hz/413.3 Hz), 144.6 (m), 145.8. IR ν (cm^{-1}) 2974, 1619, 1323, 1163, 1123, 1065, 856, 767. HRMS (EI) Calculated for $C_{11}H_{12}F_3Sn$: $[M-Me]^+$ 265.0190. Found: 265.0196.

3.20. 1,4-Bis[(*Z*)-2-(trimethylstannyl)vinyl]benzene (52)

The title compound was prepared as indicated in the representative procedure with the following exception. The resulting crude oil was triturated with petroleum ether, purified on a plug of silica treated with TEA (petroleum ether, 1% TEA) to yield the title compound (40 mg, 40%) as white crystals, mp 53–55 °C. ^{1}H NMR (300 MHz) δ ppm 0.09 (s, 18H, $^2J_{SnH}$=52.9 Hz/55.4 Hz), 6.18 (d, J=13.7 Hz, 2H, $^2J_{SnH}$=61.3 Hz/64.1 Hz), 7.20 (s, 4H), 7.54 (d, J=13.7 Hz, 2H, $^3J_{SnH}$=142.6 Hz/149.3 Hz). ^{13}C NMR (75 MHz) −8.0, 127.2, 133.7, 140.2, 146.9. HRMS (EI) Calculated for $C_{15}H_{23}{}^{118}SnSn$: $[M-Me]^+$ 440.9929.[41] Found: 440.9827. IR ν (cm^{-1}) 2969, 2912, 1577, 1501, 1400, 1336, 1185, 857, 760, 721.

3.21. (*Z*)-[2-(1,4-Dioxaspiro[4,5]dec-7-en-8-yl)-vinyl]trimethylstannane (53)

The title compound was prepared as indicated in the representative procedure with the following exception. The reaction was allowed to reach rt over a period of 2 h and quenched by the addition of saturated aqueous $NaHCO_3$. The organic phase was diluted with Et_2O separated and dried over $MgSO_4$. The solvent was removed in vacuo and the crude mixture was purified by silica column chromatography, treated with TEA (20:1, petroleum ether/diethyl ether, 1% TEA) to yield the title compound (120 mg, 64%) as a colourless oil. ^{1}H NMR (400 MHz) δ ppm 0.14 (s, 9H, $^2J_{SnH}$=52.5 Hz/54.9 Hz), 1.77 (tt, J=6.6, 0.8 Hz, 2H), 2.25–2.31 (m, 2H), 2.32–2.36 (m, 2H), 3.97 (s, 4H), 5.55 (m_c, 1H), 5.78 (d, J=13.5 Hz, 1H, $^2J_{SnH}$=63.4 Hz/66.1 Hz), 6.93 (dd, J=13.5, 0.8 Hz, 1H). ^{13}C NMR (100 MHz) −7.5, 26.1, 30.9, 36.0, 64.4, 107.8, 124.2,

129.2, 139.0, 148.9. HRMS (EI) Calculated for $C_{13}H_{22}O_2Sn$: $M^{+\bullet}$ 330.0636. Found: 330.0634. IR ν (cm^{-1}) 2953, 2880, 1634, 1563, 1423, 1368, 1107, 1059, 1044, 871, 766, 719.

3.22. *Z*-(2-Cyclohexenyl-1-ethenyl)trimethylstannane (54)

The title compound was prepared as indicated in the representative procedure with the following exception. The reaction was allowed to reach rt over a period of 2 h and quenched by the addition of saturated aqueous $NaHCO_3$. The organic phase was diluted with Et_2O, separated, and dried over $MgSO_4$. The solvent was removed in vacuo and the crude mixture was purified by silica column chromatography, treated with TEA (*n*-pentane, 1% TEA) to yield the title compound (60 mg, 50%) as a colourless oil. ^1H NMR (400 MHz) δ ppm 0.13 (s, 9H, $^2J_{SnH}$=52.4 Hz/54.9 Hz), 1.51–1.68 (m, 4H), 2.00–2.13 (m, 4H), 5.64–5.69 (m, 1H), 5.72 (d, J=13.4 Hz, 1H, $^2J_{SnH}$=66.9 Hz/69.7 Hz), 6.90 (dd, J=13.4 Hz, 0.8 Hz, 1H). ^{13}C NMR (100 MHz) −7.4, 22.2, 22.6, 25.6, 27.1, 127.2, 128.0, 139.7, 150.3. IR ν (cm^{-1}) 2927, 1633, 1562, 1436, 1187, 1133, 920, 764, 722.

3.23. General procedure for the preparation of *cis*-vinylboronates

The procedure described for the preparation of (*Z*)-2-[2-(1,4-dioxaspiro[4.5]dec-7-en-8-yl)vinyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**61**) is representative. To a solution of (*Z*)-[2-(1,4-dioxaspiro[4,5]dec-7-en-8-yl)-vinyl]butyltelluride (**42**) (107 mg, 0.306 mmol) in anhydrous diethyl ether (5 mL) at −78 °C under an argon atmosphere was added *n*-butyllithium (0.220 mL, 1.53 M in hexanes, 0.336 mmol) drop-wise. The reaction was stirred for 15 min before a solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.121 mL, 0.612 mmol) was added drop-wise. The reaction was stirred for a further 30 min at −78 °C then allowed to warm to rt over 2 h. After reaching rt the reaction mixture was shielded from light, placed in an ice bath, and MeI (1.83 mmol, 0.114 mL) was added drop-wise after which the ice bath was removed. After stirring for 30 min at rt the reaction mixture was diluted with diethyl ether and filtered through a plug of cotton using suction filtration. The solvent was removed in vacuo and the resulting crude oil was purified by silica column chromatography (5:1, petroleum ether/diethyl ether) to yield the title compound (64 mg, 72%) as a colourless oil. ^1H NMR (300 MHz) δ ppm 1.26 (s, 12H), 1.78 (tt, J=6.6, 0.8 Hz, 2H), 2.33–2.39 (m, 2H), 2.47–2.55 (m, 2H), 3.96 (s, 4H), 5.22 (dd, J=14.9, 0.5 Hz, 1H), 5.71 (m_c, 1H), 6.65 (d, J=15.1 Hz, 1H). ^{13}C NMR (75 MHz) 24.8, 25.2, 30.9, 36.2, 64.4, 83.4, 107.8, 128.6, 137.4, 148.5. HRMS (ESI) Calculated for $C_{16}H_{25}BO_4Na^+$: 315.1738. Found: 315.1745. IR ν (cm^{-1}) 2979, 2930, 2885, 1634, 1600, 1255, 1142, 1111, 1059, 1045, 871, 692, 671.

3.24. (*Z*)-2-(3,4-Dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (55)

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (5:1, petroleum ether/diethyl ether) yielded the title compound (72 mg, 65%) as white crystals, mp 49–51 °C. ^1H NMR (400 MHz) δ ppm 1.28 (s, 12H), 3.87 (s, 3H), 3.91 (s, 3H), 5.43 (d, J=15.1 Hz, 1H), 6.78 (d, J=8.3 Hz, 1H), 6.97–7.02 (m, 1H), 7.11 (d, J=15.1 Hz, 1H), 7.71 (d, J=2.0 Hz, 1H). ^{13}C NMR (100 MHz) 24.9, 55.8, 83.4, 110.3, 111.4, 123.3, 131.5, 148.5, 149.1, 149.2. HRMS (ESI) Calculated for $C_{16}H_{23}BO_4Na^+$: 313.1582. Found: 313.1572. Anal. Calcd for $C_{16}H_{23}BO_4$: C, 66.23; H, 7.99. Found: C, 66.20; H, 8.08. IR ν (cm^{-1}) 3131, 3096, 2976, 2933, 2836, 1614, 1598, 1244, 1136, 1025, 876, 822, 673.

3.25. (*Z*)-2-(3-Methoxy-2-isopropoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (56)

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (15:1, petroleum ether/diethyl ether) yielded the title compound (46 mg, 54%) as a colourless oil. ^1H NMR (500 MHz) δ ppm 1.23 (s, 12H), 1.24 (d, J=6.2 Hz, 6H), 3.81 (s, 3H), 4.36 (sept., J=6.2 Hz, 1H), 5.59 (d, J=14.9 Hz, 1H), 6.82 (dd, J=8.1, 1.5 Hz, 1H), 6.92 (t, J=8.0 Hz, 1H), 7.19 (dd, J=7.7, 1.4 Hz, 1H), 7.44 (d, J=14.9 Hz, 1H). ^{13}C NMR (100 MHz) 22.5, 24.8, 55.8, 75.7, 83.2, 112.2, 121.7, 122.6, 134.0, 144.3, 145.3, 152.8. HRMS (ESI) Calculated for $C_{18}H_{27}BO_4Na^+$: 341.1895. Found: 341.1891. IR ν (cm^{-1}) 2977, 2934, 2837, 1619, 1574, 1441, 1253, 1142, 785, 671.

3.26. (*Z*)-4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane (57)[42]

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (30:1, petroleum ether/diethyl ether) yielded the title compound (153 mg, 65%) as a colourless oil. ^1H NMR (500 MHz) δ ppm 1.27 (s, 12H), 5.57 (d, J=14.9 Hz, 1H), 7.20 (d, J=14.9 Hz, 1H), 7.22–7.31 (m, 3H), 7.50–7.53 (m, 2H). ^{13}C NMR (125 MHz) 24.8, 83.5, 127.9, 128.0, 128.6, 138.5, 148.1. IR ν (cm^{-1}) 3058, 3028, 2980, 2933, 1619, 1495, 1255, 1141, 742, 692, 672.

3.27. (*Z*)-4,4,5,5-Tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (58)

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (20:1, petroleum ether/diethyl ether) yielded the title compound (100 mg, 72%) as a colourless oil. ^1H NMR (500 MHz) δ ppm 1.28 (s, 12H), 2.32 (s, 3H), 5.50 (d, J=14.9 Hz, 1H),[43] 7.09 (d, J=7.9 Hz, 2H), 7.16 (d, J=14.9 Hz, 1H), 7.43 (d, J=8.1 Hz, 2H). ^{13}C NMR (125 MHz) 21.3, 24.8, 83.4, 128.6 (m), 135.6, 137.9, 148.2. IR ν (cm^{-1}) 2979, 2928, 2869, 1618, 1513, 1371, 1254, 1142, 836, 671. HRMS (ESI) Calculated for $C_{15}H_{21}BO_2Na^+$: 267.1533. Found: 267.1531.

3.28. (*Z*)-4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (59)

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (20:1, petroleum ether/diethyl ether) yielded the title compound (167 mg, 70%) as white crystals, mp 58–60 °C. ^1H NMR (400 MHz) δ ppm 1.27 (s, 12H), 5.71 (d, J=14.9 Hz, 1H), 7.20 (d, J=14.9 Hz, 1H), 7.52–7.56 (m, 2H), 7.60–7.64 (m, 2H). ^{13}C NMR (100 MHz) 24.8, 83.7, 124.2 (q, $^1J_{CF}$=272.2 Hz), 124.8 (q, $^3J_{CF}$=3.7 Hz), 128.8, 129.7 (q, $^2J_{CF}$=32.4 Hz), 141.8, 146.6. Anal. Calcd for $C_{15}H_{18}F_3BO_2$: C, 60.43; H, 6.09. Found: C, 60.56; H, 6.25. IR ν (cm^{-1}) 3051, 2986, 2933, 2871, 1616, 1574, 1319, 1260, 1163, 1136, 1110, 1065, 845, 670.

3.29. 1,4-Bis[(*Z*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]benzene (60)

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (15:1, petroleum ether/diethyl ether) yielded the title compound (10 mg, 22%) as white needles, mp 122–126 °C. ^1H NMR (400 MHz) δ ppm 1.28 (s, 24H), 5.56 (d, J=14.9 Hz, 2H), 7.16 (d, J=14.9 Hz, 2H), 7.50 (s, 4H). ^{13}C NMR (100 MHz) 24.8, 83.5, 128.4, 138.1, 147.8. Anal. Calcd for $C_{22}H_{32}B_2O_4$: C, 69.15; H, 8.44. Found: C, 68.89; H, 8.63. IR ν (cm^{-1}) 3093, 2980, 2934, 1613, 1513, 1446, 1248, 1136, 848, 670.

3.30. (*Z*)-2-(1-Cyclohexenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (62)

The title compound was prepared as indicated in the representative procedure. Purification by silica gel column chromatography (30:1, petroleum ether/diethyl ether) yielded the title compound (118 mg, 75%) as a colourless oil. ^{1}H NMR (400 MHz) δ ppm 1.26 (s, 12H), 1.53–1.66 (m, 4H), 2.07–2.15 (m, 2H), 2.21–2.27 (m, 2H), 5.15 (d, J=14.9 Hz, 1H), 5.81 (m_c, 1H), 6.62 (d, J=14.9 Hz, 1H). ^{13}C NMR (100 MHz) 22.1, 22.4, 24.8, 26.0, 26.3, 83.3, 132.1, 138.0, 149.8. IR ν (cm^{-1}) 2979, 2929, 2860, 2833, 1629, 1599, 1255, 1141, 847, 671.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.092.

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