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Tetrahedron
Tetrahedron 63 (2007) 8801–8809

The coupling of butylvinyltellurides with organometallic reagents catalysed by nickel complexes

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Received 23 March 2007; revised 7 June 2007; accepted 12 June 2007
Available online 22 June 2007

Abstract—Vinylic tellurides couple efficiently with sp, sp^2 and sp^3 hybridised organometallic compounds (Li, MgX and Zn species) in the presence of dichloro-bis(triphenylphosphine)nickel(II) as catalyst.

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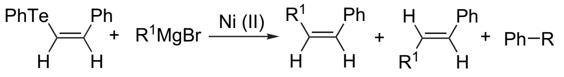
1. Introduction

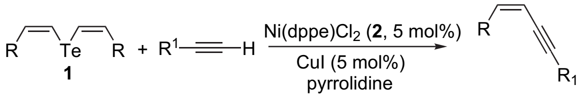
Over the last two decades, organic tellurium compounds have been the focus of intensive study and a number have proven to be valuable synthetic intermediates.[1] A full investigation into the toxicity of these compounds has been carried out,[2] and the allegation that they possess somewhat unpleasant odours and are generally unstable to light and air has been shown not to be totally correct.[3] In this context, dialkyl tellurides, which have long been considered unsuitable for synthetic purposes, have recently been prepared as stable, non-noxious compounds presenting significant synthetic potential.[4]

The vinylic tellurides constitute a class of organic tellurium compounds that is most often employed in organic synthesis.[1] The method of choice for the preparation of the vinylic tellurides is by hydrotelluration of an alkyne,[1,5] a unique anti-hydrometallation reaction that proceeds via a free radical process leading to the exclusive formation of product with the *Z*-configuration.[6] In view of this stereoselectivity, various vinylic tellurides have already been employed successfully in the synthesis of biologically active compounds.[4,7] Some of these synthetic routes[4a,7b,d] have utilised the most explored property of the vinylic tellurides, namely, their transformation into reactive organometallic compounds by a tellurium/metal exchange reaction,[8] whilst others involved coupling of vinylic tellurides with cuprates[7a,9] or with monosubstituted alkynes promoted by palladium(II) chloride.[7c] This latter reaction has been developed considerably since it was first described in 1999,[10] and its use in the assembly of several unsaturated systems has been reported.[11] The mechanism of the reaction has recently been investigated.[12]

In view of the high price of palladium compounds, a number of other elements have been considered as potential catalysts for the coupling of vinylic tellurides and alkynes. Nickel compounds are known to be efficient catalysts in coupling reactions,[13] as was aptly demonstrated by the pioneering work of Uemura et al.[14] on the coupling of phenylvinyltellurides with Grignard reagents promoted by Ni(II) complexes (Scheme 1). More recently, Silveira et al.[15] reported that dichloro-bis(triphenylphosphine)nickel(II) ($Ni(PPh_3)_2Cl_2$) (**2**) and CuI catalyse the reaction of bis-vinylic tellurides **1** with monosubstituted alkynes in the presence of pyrrolidine to give enynes in good yield and with retention of the *Z* double bond geometry (Scheme 2).



Scheme 1.



Scheme 2.

In the present work, the coupling of vinylic tellurides with sp, sp^2 and sp^3 hybridised organometallic compounds in the presence of dichloro-bis(triphenylphosphine)nickel(II) ($Ni(PPh_3)_2Cl_2$) or dichloro-(1,2-bis(diphenylphosphino)-ethane)nickel(II) ($Ni(dppe)Cl_2$) as catalyst has been studied.

Keywords: Coupling reaction; Tellurides; Nickel complexes; Catalysis; Organometallic reagents.

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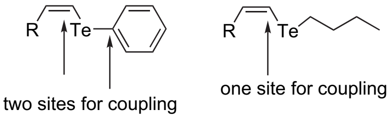
0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.06.057

2. Results and discussion

As an extension to our previous studies,[15] the aim of the present work was to prepare *Z*-enediynes, which are structural moieties that are present in various important bioactive natural products.[16] However, bis-enynic tellurides are not available through the hydrotelluration of diynes since, under the conditions used to prepare bis-vinylic tellurides,[8e] diyne substrates yield tellurophenes instead.[17] For this reason, butyltelluroenynes, which are readily prepared by hydrotelluration of diynes with di-*n*-butylditelluride/$NaBH_4$,[5,8c] were employed as vinylic tellurides in the coupling reaction. Surprisingly, these compounds did not couple with monosubstituted alkynes under the conditions shown in Scheme 2.

As an alternative procedure, alkynoates were employed as substrates instead of alkynes in the coupling reaction. It was anticipated that in the case of the butylvinyltellurides **3**, the by-products observed by Uemura et al.[14] (Scheme 1) would not be formed, since only the sp^2 carbon is expected to react[18] (Scheme 3). A preliminary study was performed in order to determine the most appropriate conditions for the chosen coupling reaction,[19] and the results are summarised in Table 1. The highest yield of product was obtained when 2.5 equiv of the lithium acetylide **4** and 5 mol % of $Ni(dppe)Cl_2$ (**2**) were employed (Table 1, entry 3).



Scheme 3.

In order to establish the range and limitations of the coupling procedure, a number of vinylic tellurides and alkynes were subjected to the reaction conditions shown in Table 1 (entry 3), and the results are presented in Table 2. In all cases, the formation of dibutylditelluride and the diyne resulting from the homocoupling of the starting lithium acetylide was observed. The vinylic tellurides **3a**, **3c**, **3d** and **3e** gave good yields of coupling products (Table 2, entries 1, 2, and 5–9), whilst **3b** gave only traces of product. This suggests that steric effects can influence the course of the reaction since the carbinol carbon of **3b** bears a large substituent. Additionally, the protecting group of telluride **3e** was lost during the coupling reaction and the deprotected alcohol **5i** was formed in quantitative yield (Table 2, entry 9).

With the aim of synthesising functionalised enynes, vinylic telluride **3f** was submitted to the coupling reaction under the established conditions. The product of this reaction was, however, compound **6** derived from the coupling of **3f** with the lithium alkynoate and subsequent addition of lithium alkynoate to the ester group (Scheme 4). In order to overcome this problem, the lithium alkynoate **4a** was transformed into the zinc alkynoate **7** by reaction with $ZnCl_2$. Coupling of **3f** with **7** gave the desired product **5j** but as a mixture of *Z* and *E* enynes in which the *E* isomer was the major component (Scheme 4).

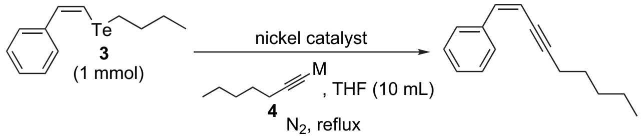
The above strategy was applied to the coupling of telluride **3g**, in which the double bond cannot isomerise, and this gave rise to the formation of coupling products **5k** and **5l** in good yields (Scheme 5). This result demonstrates that the methodology can be applied successfully to functionalised substrates provided that the double bond of the coupling product cannot undergo inversion of configuration.

In order to extend the coupling methodology to sp^2 hybridised carbanions, vinylic tellurides **3a** and **3c** were treated, respectively, with 2-furfurylzinc (**8a**) and 2-thienylzinc (**8b**) according to Scheme 6. The coupling products **9a** and **9b** were formed in good yields, but whilst **9a** was obtained as a 95:5 diastereomeric mixture of the *Z* and *E* olefins, **9b** was present as a single isomer.

We have recently demonstrated that arylbutyltellurides can be transformed into arylcuprates[20] and aryllithium compounds,[21] respectively, through tellurium/copper and tellurium/lithium exchange reactions. Using the latter exchange reaction, 4-methoxyphenyllithium **10**[21] was prepared, diethyl zinc or $ZnCl_2$ added in order to form the expected organometallic species **11–14** (Scheme 7),[22] which were then reacted with vinylic telluride **3a**. In the case of the zinc compound **11**, a 35% yield of the olefin **15** was formed after 24 h reflux. Under similar reaction conditions, the zincate **12** reacted with **3a** to form a complex mixture of unidentified products. When the diorganozinc **13** was reacted with **3a**, a complex mixture of products was also formed, but in this case compound **15** and 1-phenyl-1-hexene could be identified. Finally, the coupling products **15** and **16** were obtained in good yields when the diarylzinc **14** was reacted with **3a** (Scheme 8).

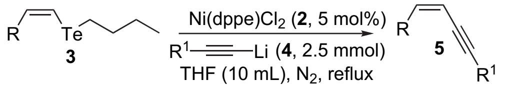
The formation of 1-phenyl-1-hexene when telluride **3a** was allowed to react with the organozinc **13**, led us to investigate

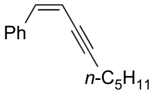
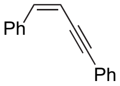
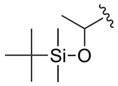
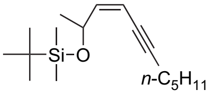
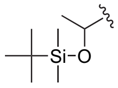
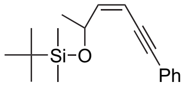
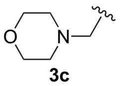
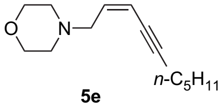
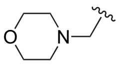
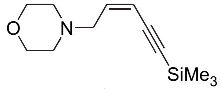
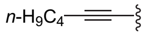
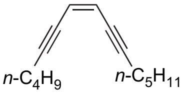
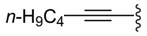
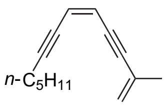
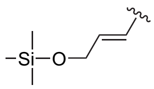
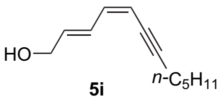
Table 1. Optimisation of the conditions for the coupling reaction



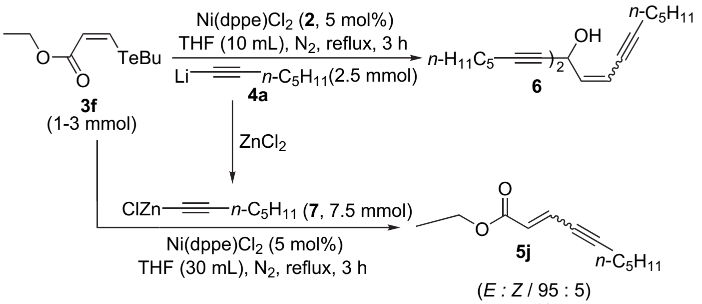
Entry	M=metal (mmol)	Nickel catalyst (mol%)	Temperature	Time (h)	Isolated yield (%)
1	MgBr (2.5)	$Ni(PPh_3)_2Cl_2$ (5.0)	Reflux	4	70
2	Li (2.5)	$Ni(PPh_3)_2Cl_2$ (5.0)	Reflux	3	90
3	Li (2.5)	$Ni(dppe)Cl_2$ (5.0)	Reflux	3	100
4	Li (1.5)	$Ni(dppe)Cl_2$ (5.0)	Reflux	3	87
5	Li (1.5)	$Ni(dppe)Cl_2$ (1.0)	Reflux	24	Traces
6	Li (2.5)	$Ni(dppe)Cl_2$ (5.0)	Room temperature	72	Traces

Table 2. Coupling reaction of *Z*-vinylic tellurides and lithium acetylides with Ni(dppe)Cl_2 catalyst



Entry	R	R^1	Product	Reaction time (h)	Isolated yield (%)
1	Ph **3a**	n-C_5H_{11} **4a**	 **5a**	3	100
2	Ph **3a**	Ph **4b**	 **5b**	12	93
3	 **3b**	n-C_5H_{11} **4a**	 **5c**	12	Traces
4	 **3b**	Ph **4b**	 **5d**	12	Traces
5	 **3c**	n-C_5H_{11} **4a**	 **5e**	7	100
6	 **3c**	Me_3Si **4c**	 **5f**	4	64
7	 **3d**	n-C_5H_{11} **4a**	 **5g**^{a}	5	97
8	 **3d**	 **4d**	 **5h**	5	75
9	 **3e**	n-C_5H_{11} **4a**	 **5i**	12	100

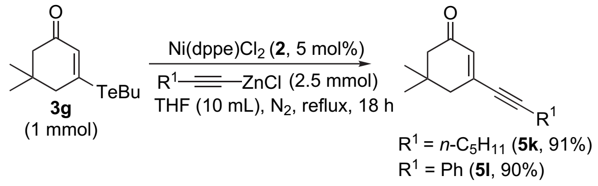
[a] Configuration determined by IR.



(*E* : *Z* / 95 : 5)
78%

Scheme 4.

the coupling reaction of dialkylzinc compounds with the vinylic tellurides **3a**, **3c** and **3g**. When vinylic telluride **3a** was reacted for 3 h under reflux with bis(n-butyl)zinc in the presence of Ni(dppe)Cl_2, a mixture of the *Z* and *E* isomers of the olefin **17** was formed. It is worth mentioning that no change in the isomeric ratio of **17** was observed after 24 h



Scheme 5.

reflux in THF. After 3 h under reflux, vinylic telluride **3c** reacted with bis(n-butyl)zinc in the presence of Ni(dppe)Cl_2 to give the coupling product **18** as a single stereoisomer in 60% yield. Reaction of diethyl zinc with the telluroenone **3g** gave 51% of the coupling product **19** after 3 h under reflux (Scheme 9). The lower yields of the coupling reaction with alkylzinc compounds can be attributed to a tellurium/zinc exchange[23] leading, after work up, to the corresponding detellurated products that could be detected and identified in the crude reaction mixture by GC–MS analysis.

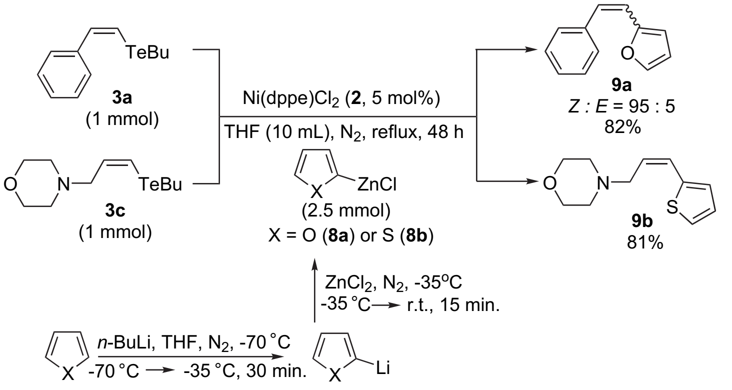
3. Conclusion

The coupling reaction of vinylic tellurides with organometallic compounds promoted by Ni(dppe)Cl_2 provides a viable alternative to the similar coupling reaction employing the more expensive palladium compounds as catalyst.

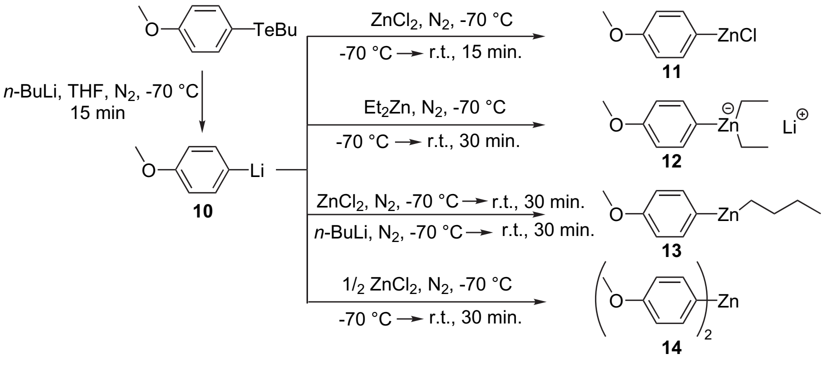
4. Experimental

4.1. Materials and general procedures

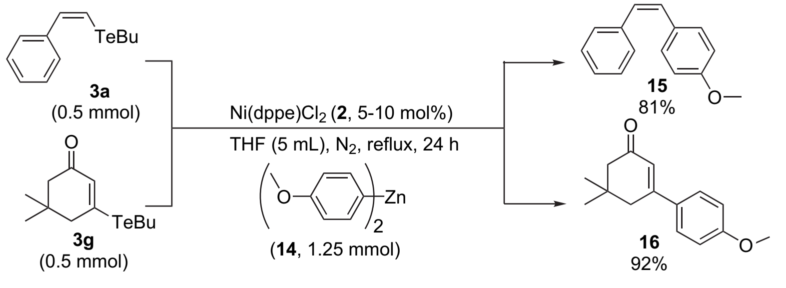
Tellurium powder (−200 mesh) and standard chemicals were obtained from commercial sources. All reagents and



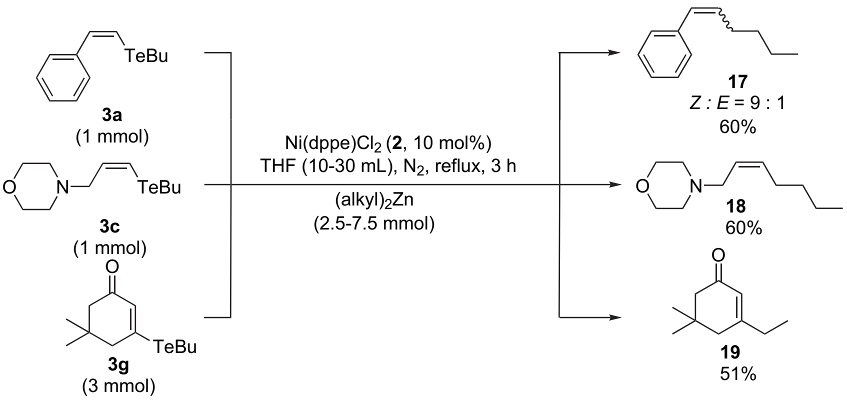
Scheme 6.



Scheme 7.



Scheme 8.



Scheme 9.

solvents were purified and dried prior to use according to the published methods.[24] THF was distilled from sodium/benzophenone under N_2 immediately before use,[24] whilst *n*-BuLi was titrated using 1,10-phenanthroline.[25] Nitrogen gas used in the reactions was deoxygenated and dried as described in the literature,[8b,24] and all operations were carried out in flame-dried glassware. The following reagents were prepared according to the literature procedures: $Ni(PPh_3)_2Cl_2$,[26] $Ni(dppe)Cl_2$,[27] butyl(*Z*-(styryl))tellane (**3a**),[8b] ((*Z*)-4-(butyltellanyl)but-3-en-2-yloxy)(*tert*-butyl)dimethylsilane (**3b**),[12] 4-((*Z*)-3-(butyltellanyl)allyl)morpholine (**3c**),[8b] butyl((*Z*)-oct-1-en-3-ynyl)tellane (**3d**),[28] ((2*E*,4*Z*)-5-(butyltellanyl)penta-2,4-dienyloxy)trimethylsilane (**3e**),[29] (*Z*)-ethyl 3-(butyltellanyl)acrylate (**3f**),[30] 3-(butyltellanyl)-5,5-dimethylcyclohex-2-enone (**3g**)[31] and butyl-(4-methoxyphenyl)tellane.[21] All the organic tellurium compounds presented analytical data that were in agreement with those reported in the literature. Column chromatographic separations were carried out using Merck silica gel 60 (0.063–0.200 mm). IUPAC names were verified using ChemDraw Ultra (version 8.0) software.

4.2. Instrumentation

^1H and ^{13}C NMR spectra were obtained using a Bruker AC-200 (^1H, 200 MHz; ^{13}C, 50 MHz) or a Varian INOVA 300 (^1H, 300 MHz; ^{13}C, 75 MHz) spectrometer. All spectra were measured in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Low resolution mass spectra were recorded on a Shimadzu CG-17A/CGMS-QP5050A spectrometer, whilst high resolution spectra were measured on a VG Autospec instrument. Near-IR spectra were determined on Bomem MB-100 or MB-Series spectrometers. Melting points were measured using a Büchi B-545 apparatus. Elemental analyses were performed on a Perkin Elmer 2400 CNH analyser at the Microanalytical Laboratory of the Institute of Chemistry, University of São Paulo, SP, Brazil.

4.3. Coupling reaction between tellurides and metal acetylides using nickel complexes as catalysts

4.3.1. Preparation of hept-1-ynylmagnesium bromide.[32] Hept-1-yne (0.240 g, 2.5 mmol) was added dropwise by syringe to a 15 mL two-necked round-bottomed flask, equipped with a reflux condenser, rubber septum, magnetic stirrer/hot plate and silicone oil bath, and containing ethylmagnesium bromide (2.5 mL of a 1 mol L^{-1} solution in THF, 2.5 mmol) at 50 °C under an atmosphere of N_2. The reaction mixture was stirred for 1 h at 50 °C following which the magnesium reagent was ready for use.

4.3.2. Preparation of lithium acetylides.[32] The appropriate alkyne (2.75 mmol) and THF (2.5 mL) were added by syringe to a 15 mL two-necked round-bottomed flask, equipped with a rubber septum and magnetic stirrer, and maintained under a N_2 atmosphere at -70 °C. *n*-BuLi (1.92 mL of a 1.3 mol L^{-1} solution in hexane, 2.5 mmol) was added dropwise at -70 °C, and the reaction mixture stirred at this temperature for 10 min after which the lithium reagent was ready for use.

4.3.3. Preparation of alkynylzinc chloride.[33] $ZnCl_2$ (2.5 mL of a 1.0 mol L^{-1} solution in THF, 2.5 mmol) was added in a single portion to the appropriate lithium acetylide (2.5 mmol; prepared as described above) maintained at -70 °C under a N_2 atmosphere. The reaction mixture was warmed to room temperature and then stirred for 20 min following which the zinc reagent was ready for use.

4.3.4. Coupling reaction. The nickel complex (0.05 mmol), appropriate telluride (1 mmol), THF (10 mL) and the appropriate metal alkynoate (2.5 mmol, prepared as described above) were added by syringe to a 50 mL two-necked round-bottomed flask equipped with a reflux condenser, rubber septum, magnetic stirrer/hot plate and silicone oil bath. The reaction mixture was refluxed under an atmosphere of N_2 for the time indicated in Tables 1 and 2 or in Schemes 4 and 5. The reaction was quenched with brine (50 mL) and the resulting mixture extracted with ethyl acetate (3×50 mL). The extracts were dried over $MgSO_4$, filtered, the solvent evaporated under reduced pressure and the residue purified by column chromatography over silica gel using an appropriate eluent.

4.3.5. 1-((*Z*)-Non-1-en-3-ynyl)benzene (5a) [CAS Registry Number 172368-35-3]. Product eluted with pentane, quantitative yield 0.198 g (100%). The spectral data agreed with those from the literature.[10]

4.3.6. (*Z*)-1,4-Diphenylbut-1-en-3-yne (5b) [CAS Registry Number 13343-78-7]. Product eluted with hexane, yield

0.190 g (93%). The spectral data agreed with those from the literature.[15]

4.3.7. 4-((*Z*)-Dec-2-en-4-ynyl)morpholine (5e). Product eluted with ethyl acetate, quantitative yield 0.221 g (100%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.89 (dt, J=11.0, 7.0 Hz, 1H), 5.63 (d, J=11.0 Hz, 1H), 3.72 (t, J=4.8 Hz, 4H), 3.25 (dd, J=6.8, 1.1 Hz, 2H), 2.49 (t, J=4.8 Hz, 4H), 2.34 (td, J=6.8, 1.9 Hz, 2H), 1.55 (quint, J=7.0 Hz, 2H), 1.44–1.25 (m, 4H), 0.91 (t, J=7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.9, 112.9, 96.1, 76.6, 66.8, 57.5, 53.4, 30.9, 28.3, 22.0, 19.3, 13.8; near-IR (film) cm^{-1} 3027 (w), 2958 (s), 2932 (s), 2857 (s), 2800 (m), 2215 (w), 1619 (w), 1454 (m), 1326 (m), 1291 (m), 1119 (s); LRMS *m/z* (relative intensity) 221 [M$^+$] (1.7%), 206 (3.8%), 192 (12.6%), 178 (18.3%), 164 (100.0%), 150 (27.4%), 134 (25.4%), 120 (82.5%), 106 (35.6%), 91 (49.2%), 77 (73.9%), 56 (63.3%). Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.62; H, 10.48; N, 6.10.

4.3.8. 4-((*Z*)-5-(Trimethylsilyl)pent-2-en-4-ynyl)morpholine (5f). Product eluted with ethyl acetate/hexane (8:2), yield 0.142 g (64%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.04 (dt, J=11.0, 7.0 Hz, 1H), 5.68 (dt, J=11.0, 1.3 Hz, 1H), 3.73 (t, J=4.8 Hz, 4H), 3.29 (dd, J=7.0, 1.3 Hz, 2H), 2.52 (t, J=4.6 Hz, 4H), 0.20 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.7, 112.8, 101.1, 100.6, 66.8, 57.6, 53.5, −0.1; near-IR (film) cm^{-1} 3028 (w), 2960 (s), 2897 (m), 2855 (m), 2810 (m), 2148 (m), 1453 (m), 1326 (m), 1251 (s), 1119 (s), 846 (s); LRMS *m/z* (relative intensity) 223 [M$^+$] (0.4%), 208 (2.8%), 194 (8.3%), 180 (5.9%), 167 (19.8%), 150 (24.1%), 135 (4.2%), 123 (15.7%), 109 (9.3%), 86 (12.8%), 73 (100.0%), 59 (38.7%). Anal. Calcd for $C_{12}H_{21}NOSi$: C, 64.52; H, 9.48; N, 6.27. Found: C, 64.47; H, 9.42; N, 6.53.

4.3.9. (*Z*)-Pentadeca-7-en-5,9-diyne (5g). Product eluted with hexane, yield 0.196 g (97%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.65 (s, 2H), 2.32 (t, J=6.4 Hz, 4H), 1.50–1.18 (m, 10H), 0.89–0.80 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 118.8, 97.7, 97.6, 78.3, 78.3, 31.0, 30.7, 28.3, 22.2, 21.8, 19.7, 19.4, 13.8, 13.5; near-IR (film) cm^{-1} 3026 (w), 2958 (s), 2932 (s), 2861 (m), 2216 (w), 1577 (w), 1463 (w), 1326 (w), 745 (m); LRMS *m/z* (relative intensity) 202 (42.4%), 187 (2.2%), 173 (3.5%), 159 (6.5%), 145 (26.8%), 131 (65.8%), 117 (77.5%), 105 (44.1%), 91 (100.0%), 77 (44.0%), 63 (22.5%), 51 (25.8%). Mass Calcd for $C_{15}H_{22}$: 202.1692. Found: 202.1721.

4.3.10. (*Z*)-2-Methyldodeca-1,5-dien-3,7-diyne (5h). Product eluted with hexane, yield 0.129 g (75%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.86 (d, J=10.5 Hz, 1H), 5.79 (dt, J=10.5, 1.7 Hz, 1H), 5.35 (d, J=0.9 Hz, 1H), 5.28 (quint$_{ap}$, J=1.7 Hz, 1H), 2.42 (td, J=7.0, 1.7 Hz, 2H), 1.95 (d, J=1.3 Hz, 3H), 1.64–1.38 (m, 4H), 0.92 (t, J=7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 126.9, 122.3, 120.1, 118.1, 99.2, 97.3, 86.2, 78.3, 30.7, 23.3, 21.9, 19.5, 13.5; near-IR (film) cm^{-1} 3097 (w), 3025 (w), 2959 (s), 2931 (s), 2868 (s), 2219 (w), 2191 (w), 1679 (w), 1610 (w), 1458 (m), 1399 (w), 897 (s), 745 (s); LRMS *m/z* (relative intensity) 172 (81.3%), 157 (4.6%), 142 (31.1%), 128 (100.0%), 115 (74.9%), 102 (8.2%), 91 (28.4%), 77 (32.4%), 63 (24.0%), 51 (29.4%). Mass Calcd for $C_{13}H_{16}$: 172.1252. Found: 172.1232.

4.3.11. (2*E*,4*Z*)-Dodeca-2,4-dien-6-yn-1-ol (5i) [CAS Registry Number 157554-21-7]. Product eluted with hexane/ethyl acetate (8:2), quantitative yield 0.178 g (100%). The spectral data agreed with those from the literature.[34]

4.3.12. (*Z*)-8-(Hept-1-ynyl)heptadeca-9-en-6,11-diyn-8-ol (6). Yield 73% (by GC); analyses of crude material—^{1}H NMR (200 MHz, $CDCl_3$) δ 6.81 (d, J=10.1 Hz, 1H), 6.53 (d, J=10.5 Hz, 1H); near-IR (film) cm^{-1} 3399 (m, broad), 3056 (w), 2957 (s), 2930 (s), 2859 (s), 2228 (m), 1462 (m), 1378 (m), 1180 (m), 728 (m); LRMS *m/z* (relative intensity) 340 [M$^+$] (0.5%), 244 (27.3%), 229 (2.6%), 215 (7.5%), 201 (100.0%), 188 (5.9%), 173 (22.3%), 159 (15.1%), 145 (47.6%), 131 (96.6%), 115 (42.9%), 105 (21.1%), 91 (40.3%), 77 (36.2%), 55 (49.5%).

4.3.13. Ethyl dec-2-en-4-ynoate (5j). Reaction scale 3 mmol, product eluted with hexane followed by ethyl acetate, yield (after horizontal distillation) 0.455 g (78%). GC analysis of the purified product showed it to be a 95:5 mixture of the *E* and *Z* isomers of **5j**, respectively. (*E*)-**5j** [CAS Registry Number 66901-42-6]: The spectral data agreed with those from the literature.[35] (*Z*)-**5j**: Identified in the mixture by LRMS *m/z* (relative intensity) 194 [M$^+$] (1.9%), 179 (0.7%), 166 (35.9%), 149 (22.2%), 137 (13.3%), 123 (47.0%), 109 (100.0%), 91 (20.6%), 81 (69.6%), 65 (28.8%), 55 (48.9%), and by a low intensity doublet at δ 6.01 with J=11.4 Hz in the ^{1}H NMR (200 MHz, $CDCl_3$).

4.3.14. 3-(Hept-1-ynyl)-5,5-dimethylcyclohex-2-enone (5k). Product eluted with hexane/ethyl acetate (9:1), yield 0.198 g (91%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.14 (s, 1H), 2.39 (t, J=6.8 Hz, 2H), 2.30 (d, J=1.8 Hz, 2H), 2.24 (s, 2H), 1.57 (quint, J=6.9 Hz, 2H), 1.45–1.25 (m, 4H), 1.05 (s, 6H), 0.91 (t, J=7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.8, 142.1, 130.3, 101.7, 80.4, 60.0, 50.8, 44.5, 33.3, 30.8, 27.8, 27.8, 21.9, 19.1, 13.7; near-IR (film) cm^{-1} 3048 (w), 2958 (s), 2934 (s), 2869 (s), 2218 (s), 1667 (s), 1596 (s), 1465 (m), 1355 (s), 1277 (s); LRMS *m/z* (relative intensity) 218 [M$^+$] (21.5%), 203 (14.5%), 189 (5.8%), 175 (18.2%), 162 (34.2%), 147 (34.1%), 134 (37.0%), 119 (100.0%), 106 (47.2%), 91 (68.8%), 77 (44.0%), 65 (21.2%), 55 (37.3%). Anal. Calcd for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.29; H, 10.15.

4.3.15. 5,5-Dimethyl-3-(2-phenylethynyl)cyclohex-2-enone (5l). Product eluted with hexane/ethyl acetate (9:1), yield 0.201 g (90%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.51–7.45 (m, 2H), 7.40–7.32 (m, 3H), 6.30 (t, J=1.7 Hz, 1H), 2.43 (d, J=1.3 Hz, 2H), 2.29 (s, 2H), 1.09 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 198.9, 141.2, 132.0, 131.4, 129.5, 128.5, 122.1, 99.4, 88.7, 51.1, 44.4, 33.8, 28.1; near-IR (film) cm^{-1} 3058 (w), 2958 (s), 2872 (m), 2823 (w), 2199 (m), 1665 (s), 1593 (s), 1359 (s), 1277 (s), 759 (s), 691 (s); LRMS *m/z* (relative intensity) 224 [M$^+$] (63.1%), 209 (15.8%), 181 (19.0%), 168 (100.0%), 139 (62.6%), 126 (9.5%), 114 (8.3%), 98 (2.5%), 89 (9.6%), 77 (9.2%), 63 (9.9%), 55 (9.2%). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.39; H, 7.40.

4.4. Coupling reaction between vinylic tellurides and aromatic zinc reagents or zincate catalysed by Ni(dppe)Cl$_2$

4.4.1. Preparation of 2-furanyl (8a) or 2-thienylzinc chloride (8b).[36] Furan or thiophene (2.5 mmol) and THF (7.5 mL) were added by syringe to a 15 mL two-necked round-bottomed flask, equipped with a rubber septum and magnetic stirrer, and maintained under a N_2 atmosphere at −70 °C. *n*-BuLi (1.92 mL of a 1.3 mol L^{-1} solution in hexane, 2.5 mmol) was added drop-wise at −70 °C, the reaction mixture was warmed to −35° and stirred for 15 min. ZnCl$_2$ (2.5 mL of a 1.0 mol L^{-1} solution in THF, 2.5 mmol) was added to the mixture, the whole warmed to room temperature and stirred for 15 min following which the zinc reagent was ready for use.

4.4.2. Preparation of 4-methoxyphenyllithium (10).[21] Butyl(4-methoxyphenyl)tellane (1.25–2.5 mmol) and THF (2.5–5.0 mL) were added by syringe to a 15 mL two-necked round-bottomed flask, equipped with a rubber septum and magnetic stirrer, and maintained under a N_2 atmosphere at −70 °C. *n*-BuLi (0.92–1.92 mL of a 1.3 mol L^{-1} solution in hexane, 1.25–2.5 mmol) was added in a single portion at −70 °C and the reaction mixture stirred for 20 min after which the lithium reagent was ready for use.

4.4.3. Preparation of 4-methoxyphenylzinc chloride (11).[33] ZnCl$_2$ (1.25 mL of a 1.0 mol L^{-1} solution in THF, 1.25 mmol) was added in a single portion to 4-methoxyphenyllithium (1.25 mmol, prepared as described above) maintained under a N_2 atmosphere at −70 °C. The reaction mixture was warmed to room temperature and stirred for 30 min after which the zinc reagent was ready for use.

4.4.4. Preparation of 4-methoxyphenyldiethyl lithium zincate (12).[23] Et$_2$Zn (1.25 mL of a 1.0 mol L^{-1} solution in THF, 1.25 mmol) was added in a single portion to 4-methoxyphenyllithium (1.25 mmol, prepared as described above) maintained under a N_2 atmosphere at −70 °C. The reaction mixture was warmed to room temperature and stirred for 30 min following which the zincate was ready for use.

4.4.5. Preparation of 4-methoxyphenyl-*n*-butylzinc (13).[37] ZnCl$_2$ (1.25 mL of a 1.0 mol L^{-1} solution in THF, 1.25 mmol) was added in a single portion to 4-methoxyphenyllithium (1.25 mmol, prepared as described above) maintained under a N_2 atmosphere at −70 °C. The reaction mixture was warmed to room temperature, stirred for 30 min, cooled again to −70 °C and *n*-BuLi (0.96 mL of a 1.3 mol L^{-1} solution in hexane, 1.25 mmol) was added. Finally, the mixture was warmed to room temperature and stirred for 30 min after which the zinc reagent was ready for use.

4.4.6. Preparation of bis(4-methoxyphenyl)zinc (14).[23] ZnCl$_2$ (1.25 mL of a 1.0 mol L^{-1} solution in THF, 1.25 mmol) was added in a single portion to 4-methoxyphenyllithium (2.5 mmol, prepared as described above) maintained under a N_2 atmosphere at −70 °C. The reaction mixture was warmed to room temperature and stirred for 30 min after which the zinc reagent was ready for use.

4.4.7. Coupling reaction. Ni(dppe)Cl$_2$ (0.05–0.10 mmol, see Schemes 6 and 8), the appropriate telluride (0.5–1 mmol), THF (5–10 mL) and the appropriate zinc reagent or zincate (1.25–2.5 mmol, prepared as described above) were added by syringe to a 50 mL two-necked round-bottomed flask equipped with a reflux condenser, rubber septum, magnetic stirrer/hot plate and silicone oil bath. The reaction mixture was refluxed under an atmosphere of N_2 for the time indicated in Schemes 6 and 8. The reaction was quenched with brine (50 mL) and the resulting mixture extracted with ethyl acetate (3×50 mL). The extracts were dried over MgSO$_4$, filtered, the solvent evaporated under reduced pressure and the residue purified by column chromatography over silica gel using an appropriate eluent.

4.4.8. 2-Styrylfuran (9a). Reaction scale 1 mmol, product eluted with hexane, yield 0.140 g (82%). GC analysis of the purified product showed it to be a 95:5 mixture of the *Z* and *E* isomers of **9a**, respectively. (*Z*)-**9a** [CAS Registry Number 18138-87-9]: The spectral data agreed with those from the literature.[36] (*E*)-**9a** [CAS Registry Number 21676-00-6]: Identified in the mixture by LRMS *m*/*z* (relative intensity) 170 [M$^+$] (100.0%), 155 (1.4%), 141 (94.3%), 115 (58.8%), 102 (4.7%), 89 (10.3%), 77 (9.2%), 70 (20.2%), 63 (22.1%), 55 (33.7%), 51 (20.9%), 40 (95.7%), and by two low intensity doublets at δ 7.05 and 6.89 both with J=16.2 Hz in the ^{1}H NMR (200 MHz, CDCl$_3$).

4.4.9. 4-((*Z*)-3-(Thiophen-2-yl)allyl)morpholine (9b). Reaction scale 1 mmol, product eluted with hexane/ethyl acetate (7:3), yield 0.169 g (81%), mp 39–41 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.29 (d, J=4.4 Hz, 1H), 7.04–7.00 (m, 2H), 6.67 (d, J=11.9 Hz, 1H), 5.67 (dt, J=11.8, 6.1 Hz, 1H), 3.74 (t, J=4.6 Hz, 4H), 3.37 (dd, J=6.6, 1.8 Hz, 2H), 2.54 (t, J=4.4 Hz, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 139.9, 128.0, 126.8, 126.8, 125.8, 123.9, 66.9, 57.1, 53.7; near-IR (KBr) cm^{-1} 3100 (w), 2968 (w), 2936 (w), 2897 (w), 2855 (w), 2786 (w), 2686 (w), 2648 (w), 1629 (w), 1449 (m), 1292 (s), 1112 (s); LRMS *m*/*z* (relative intensity) 209 [M$^+$] (26.4%), 178 (1.3%), 164 (1.8%), 150 (7.9%), 135 (4.8%), 123 (73.5%), 112 (100.0%), 100 (7.7%), 97 (12.6%), 86 (15.8%), 79 (22.5%), 77 (14.1%), 56 (42.3%), 45 (47.7%). Anal. Calcd for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69. Found: C, 63.11; H, 6.94; N, 7.21.

4.4.10. (*Z*)-1-Methoxy-4-styrylbenzene (15) [CAS Registry Number 1657-53-0]. Reaction scale 0.5 mmol, product eluted with hexane, yield 0.085 g (81%). The spectral data agreed with those from the literature.[38]

4.4.11. 3-(4-Methoxyphenyl)-5,5-dimethylcyclohex-2-enone (16) [CAS Registry Number 29339-44-4]. Reaction scale 0.5 mmol, product eluted with hexane, yield 0.106 g (92%), mp 43–45 °C. The spectral data agreed with those from the literature.[39]

4.5. Coupling reaction between vinylic tellurides and bis(alkyl)zinc reagents catalysed by Ni(dppe)Cl$_2$

4.5.1. Preparation of bis(*n*-butyl)zinc.[23] ZnCl$_2$ (2.5 mL of a 1.0 mol L^{-1} solution in THF, 2.5 mmol) was added by syringe to a 15 mL two-necked round-bottomed flask, equipped with a rubber septum and magnetic stirrer, and maintained under a N_2 atmosphere at $-70\ ^{\circ}C$. *n*-BuLi (3.85 mL of a $1.3\ mol\,L^{-1}$ solution in hexane, 5 mmol) was added dropwise at $-70\ ^{\circ}C$, the reaction mixture warmed to room temperature and stirred for 15 min after which the zinc reagent was ready for use.

4.5.2. Coupling reaction. Ni(dppe)Cl_2 (0.053 g, 0.10 mmol), the appropriate telluride (1 mmol), THF (10 mL) and the appropriate zinc reagent (2.5 mmol, prepared as described above or purchased from Aldrich Chemical Co.) were added by syringe to a 50 mL two-necked round-bottomed flask equipped with a reflux condenser, rubber septum, magnetic stirrer/hot plate and silicone oil bath. The reaction mixture was refluxed under an atmosphere of N_2 for 3 h and quenched with brine (50 mL). The solid residues were filtered off over Celite and silica gel and washed several times with ethyl acetate. The aqueous phase was extracted with ethyl acetate (3×50 mL) and the bulked extracts dried over $MgSO_4$, filtered, the solvent evaporated under reduced pressure and the residue purified by column chromatography over silica gel using an appropriate eluent.

4.5.3. 1-(Hex-1-enyl)benzene (17). The product eluted with hexane, the residue obtained after column chromatography was dissolved in ethyl acetate (30 mL) and the extract washed with 1% aqueous NaClO (30 mL) and H_2O (2×50 mL), yield 0.096 g (60%). GC analysis of the purified product showed it to be a 9:1 mixture of the *Z* and *E* isomers of **17**, respectively. (*Z*)-**17** [CAS Registry Number 15325-54-9]: The spectral data agreed with those from the literature.[8b] (*E*)-**17** [CAS Registry Number 6111-82-6]: Identified in the mixture by LRMS *m/z* (relative intensity) 160 [M^+] (26.6%), 131 (3.1%), 117 (100.0%), 104 (68.7%), 91 (31.8%), 77 (10.0%), 65 (7.3%), 51 (10.2%).[40]

4.5.4. 4-((*Z*)-Hept-2-enyl)morpholine (18) [CAS Registry Number 144758-48-5]. The product eluted with hexane and then ethyl acetate, yield 0.110 g (60%); ^1H NMR (200 MHz, $CDCl_3$) δ 5.58 (dtd, J=11.0, 7.0, 1.3 Hz, 1H), 5.44 (dtd, J=11.0, 7.0, 1.0 Hz, 1H), 3.72 (t, J=4.8 Hz, 4H), 3.01 (d, J=6.6 Hz, 2H), 2.46 (t, J=4.4 Hz, 4H), 2.07 (quint, J=6.6 Hz, 2H), 1.37–1.30 (m, 4H), 0.90 (t, J=6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 133.6, 125.1, 66.8, 55.3, 53.5, 31.6, 27.1, 22.1, 13.8; near-IR (film) cm^{-1} 3015 (w), 2959 (m), 2929 (m), 2856 (m), 2802 (m), 1456 (m), 1293 (m), 1119 (s); LRMS *m/z* (relative intensity) 183 [M^+] (5.4%), 154 (0.4%), 140 (2.2%), 126 (9.5%), 110 (11.0%), 100 (13.6%), 96 (8.3%), 87 (100.0%), 81 (10.2%), 67 (9.0%), 57 (44.5%), 55 (39.1%).

4.5.5. 3-Ethyl-5,5-dimethylcyclohex-2-enone (19) [CAS Registry Number 28017-78-9]. Reaction scale 3 mmol, yield (after horizontal distillation) 0.234 g (51%). The spectral data agreed with those from the literature.[41]

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