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Addition of *Z*-Vinylic Higher Order Cyanocuprates to Enones Followed by *O*-Functionalization

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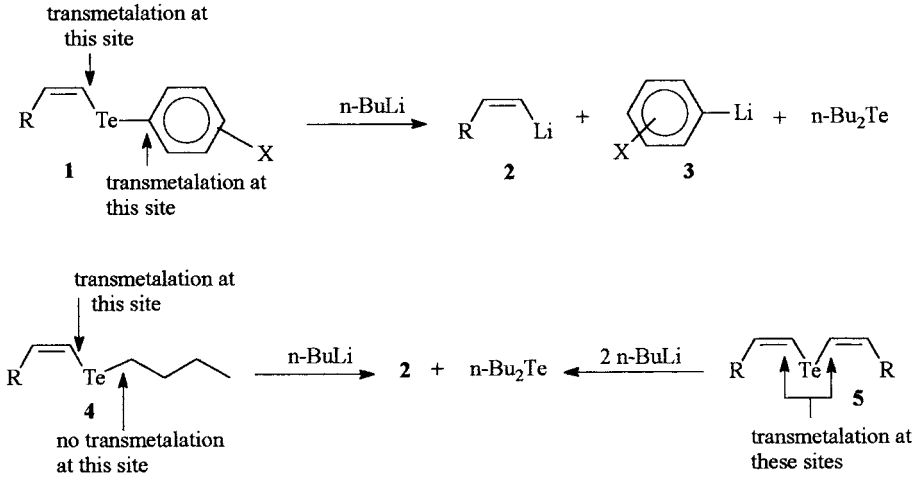
Abstract—Transmetalation reaction between *Z*-vinylic tellurides and higher order cyanocuprates generated the corresponding *Z*-vinylic cyanocuprates. Conjugate addition of these cuprates to enones followed by *O*-functionalization led to silyl enol ethers, vinyl phosphates and vinyl triflates. The vinyl triflates were transformed into highly unsaturated systems by coupling with alkynes or with *Z*-vinyl zinc chlorides under Pd (0) catalysis.

Introduction

In the course of recent years our laboratory has devoted efforts to find synthetic applications to *Z*-vinylic tellurides,[1] since these compounds can be easily prepared by hydrotelluration of alkynes.[1,2] In the majority of the cases the reaction occurs with high regioselectivity and with the exclusive formation of the *Z* isomer, which is sterically stable. To our knowledge no isomerization of vinylic tellurides during the isolation and purification processes was reported. In a seminal paper, Kauffmann,[3] in 1982, reported that phenyl vinyl telluride could be transformed into vinyl lithium and captured by electrophiles. The development of practical methods to prepare alkyl vinyl tellurides with high regio- and stereoselectivity led us[1,2b,4] and others[2c,5] to explore synthetically the pioneering observation made by Kauffmann. The early efforts in this area used aryl vinyl tellurides **1** as precursors of *Z*-vinyl lithiums **2**.[5a] However, we found that depending on the reaction time and conditions, mixtures of vinyl and aryl lithiums **3** can be formed,[4] as both species have the metallic counter ion associated to sp^2 carbanionic species, presenting similar stability. Therefore, we decided to use alkyl vinyl **4** or bis vinyl tellurides **5** for this purpose,[2b] since these precursors of vinyl organometallics do not present such drawback (Scheme 1).



Scheme 1.

Keywords: *Z*-vinylic tellurides; higher order cyanocuprates; conjugated addition; vinyl triflates; vinyl phosphates; silyl enol ethers.
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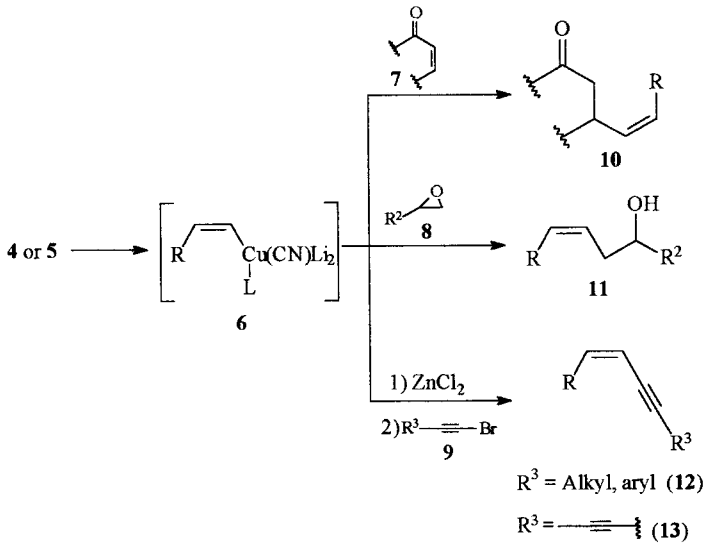
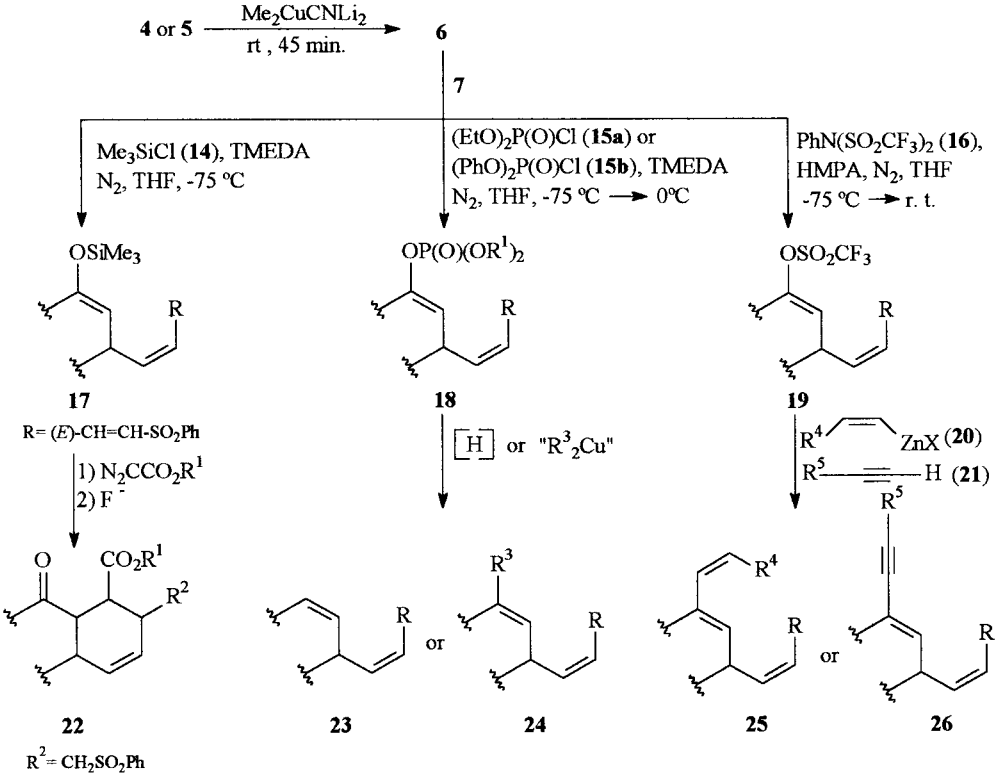


Scheme 2.

In view of the easier preparation of the butyl vinyl tellurides **4**[1,6] as compared to the bis vinylic tellurides **5**,[1,2a,6] we preferred the first to generate *Z*-vinylic organometallics. The preparation of *E*-vinylic organometallics by transmetalation reactions is a well-established methodology,[7] since most of the precursors of reactive vinyl organometallic species are obtained by hydrometallation of alkynes, which gives the *E* olefin through a *syn* addition.[8] As a consequence, the preparation of *Z*-vinyl organometallics (e.g. vinyl lithium and vinyl copper species) by a transmetalation reaction is not a trivial synthetic task. The discovery that the transmetalation of *Z*-vinylic tellurides occurs with total retention of the olefin geometry,[1,4,6,9] coupled with the easy preparation of these organo element intermediates through hydrotelluration of alkynes,[1,2,6] opened the perspective of using them to assemble more complex carbon skeletons.

As organocopper reagents are widely used organometallics to form carbon–carbon bonds, we investigated in detail the transformation of butyl vinyl tellurides **4** and bis vinyl tellurides **5** into higher order vinylcyanocuprates.[6,9] In order to demonstrate the scope and limitations of this methodology, the higher order vinyl cyanocuprates **6**, generated in this way, were reacted with a variety of electrophiles such as



Scheme 3.

α,β unsaturated ketones **7**,[6,9a,b,d] epoxides **8**[6,9c] and haloalkynes **9**,[10] giving rise to unsaturated systems of great synthetic interest, such as 4-vinylketones **10**, homoallylic alcohols **11**, *Z*-enynes **12** and *Z*-enediynes **13** (Scheme 2).

Results and Discussion

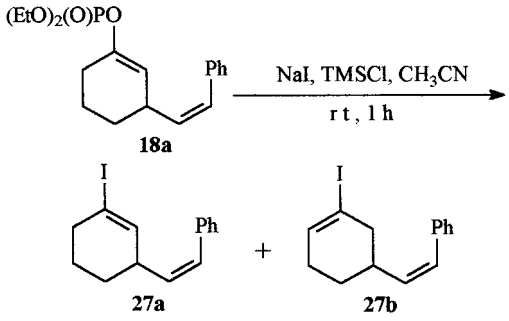
Among the synthetically useful reactions of organocopper reagents is the 1,4 addition to enones, followed by reaction with appropriate electrophiles leading to *O*-functionalization. In this work, we performed a systematic study of the 1,4 addition of higher order *Z*-vinylic cyanocuprates to enones followed by reaction with trimethylsilylchloride (**14**), diethyl-(**15a**) and diphenylphosphorochloridrate (**15b**) and *N*-phenyltrifluoromethanesulfonamide (**16**) (Scheme 3).

Among the vast spectrum of synthetic transformations possible to perform on the obtained systems, we mention the cyclopropanation of silyl enol ethers **17** followed by annulation to give **22**,[11] the reduction[12] or organometallic coupling[13] of vinyl phosphates **18** leading to unsaturated systems **23** or **24**, respectively. The coupling reactions of vinyl triflates **19**, with organo zinc compounds **20**[14] and with terminal alkynes **21**[14] catalyzed by Pd^0, were studied in this work.

Although the conjugated addition of cuprates to enones followed by enolate trapping with trialkylsilyl chlorides is a well known reaction,[15] we decided to investigate it using our reaction conditions, since the obtained silyl enol ethers **17** present a *Z* double bond strategically positioned to give substituted cyclohexenes **22** if submitted to the reaction sequence shown in Scheme 3.[11] The reaction was performed by addition of TMEDA (6 mmol) to a suspension of CuCN (2 mmol) in THF. To this clear solution cooled to −75°C was added MeLi (4 mmol) followed by heating to room temperature and addition of the vinylic telluride **4** (2 mmol) or **5** (1 mmol). After stirring for 45 min, the mixture was cooled again, to −75°C and the enone **7** was added. Addition of trimethylsilyl chloride (**14**), work up and purification by distillation gave **17a–e** in synthetically useful yields (Table 1).

Although less studied than the formation of silyl enol ethers **17**, the generation of vinyl phosphates **18** by conjugate addition of Gilman cuprates to enones followed by enolate trapping has been described.[15] Notwithstanding, the 1,4 addition of higher order cyanocuprates to enones followed by capture with phosphorochloridrates **15** has not yet been reported. As already mentioned (Scheme 3) vinyl phosphates are synthetically useful.[12,13,16] With this synthetic utility in mind we explored our vinylic telluride/higher order vinylic cyanocuprates methodology to prepare vinyl phosphates. The *Z*-vinyl cyanocuprate generated from the corresponding *Z*-vinylic telluride **4** (2 mmol) or **5** (1 mmol) was reacted with an enone **7** (2.2 mmol) at −75°C and to the resulting enolate was added diethyl- (**15a**) or diphenylphosphorochloridrates (**15b**) (3.2 mmol) in THF and TMEDA (6 mmol). The product was purified by silica gel chromatography to give the vinyl phosphates **18a–f** in good yields (Table 1).

In the search for synthetic applications for the vinyl phosphates obtained **18**, we attempted to assemble highly unsaturated systems by coupling them with *Z*-vinyl cyanocuprates **6** prepared from vinylic tellurides **4** or **5**. The reaction was, however, unsuccessful. Vinyl phosphate **18a** was transformed into the corresponding vinyl iodide by reaction with TMSCl/NaI in acetonitrile[16] in 60% yield. However, a 1:1 mixture of regioisomers **27a** and **27b** was formed (Eq. (1)). Finally, an interesting application for the vinyl phosphates of the type **18f** was found, which consists in their transformation into functionalized tetrasubstituted vinylic telluride **28** by reaction with lithium *n*-butyl tellurolate **29** (Scheme 4).[17]



(1)

Vinyl triflates are among the most synthetically explored derivatives of *O*-functionalization of enolate ions.[14] Few reports on the 1,4 addition of cuprates to enones followed by triflate formation do exist[14] and none of them deal with higher order cuprates. Recently, we demonstrated that our methodology of *Z* higher order vinyl cyanocuprate formation can be successfully applied to generate vinyl triflates.[18] In this paper we give a full account of this reaction. Initially we attempted to use triflic anhydride as the trifling agent. The yields were however low and did not exceed 30%. By changing triflic anhydride for triflic chloride only gummy unidentified products were obtained. The method of choice to prepare the vinyl triflates consisted in the preparation of the higher order vinyl cyanocuprate by addition of the appropriate *Z*-vinylic telluride **4** (2 mmol) to a solution of dimethyl cyanocuprate (2 mmol) at room temperature followed by the addition of the enone **7** (2.2 mmol) at −75°C. To the enolate formed was added *N*-phenyltrifluoromethanesulfonamide (**18**) (2.6 mmol) and HMPA (6.0 mmol). Work up and purification by flash silica gel chromatography gave the vinyl triflates **19a–g** with the yields shown in Table 1. The use of a co-solvent was crucial for the success of the reaction. In the reaction of telluride **4a** with enone **7a** in the absence of a co-solvent after 48 h a 40% yield of vinyl triflate **19a** was obtained; with DME and TMEDA as the co-solvent a 50% yield of **19a** was formed after 36 and 24 h, respectively; by using HMPA as the co-solvent, **19a** was obtained in 60% yield after 4 h. All compounds obtained were sufficiently stable to be purified by column chromatography.

In this case the construction of highly unsaturated conjugated systems by elaboration of the product of the 1,4 addition/electrophile capture was successful.

Our vinylic telluride transmetalation methodology proved to be a valuable method to generate *Z*-vinyl zinc chlorides.

Table 1. Products of the 1,4-addition of *Z*-vinylic cuprates to enones followed by *O*-functionalization

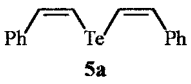
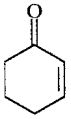
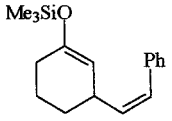
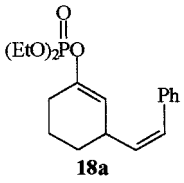
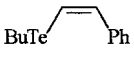
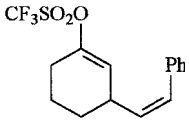
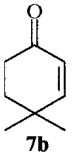
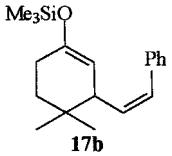
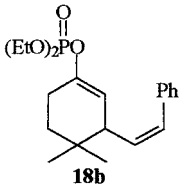
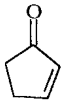
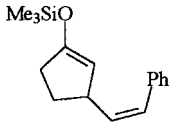
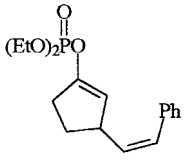
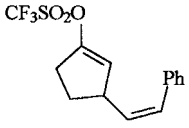
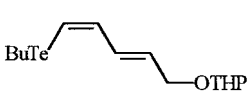
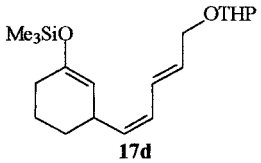
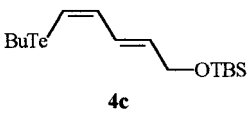
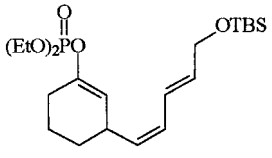
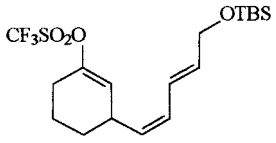
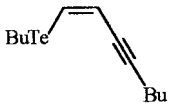
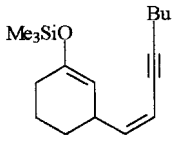
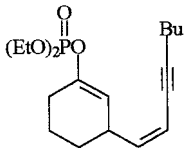
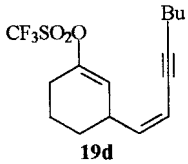
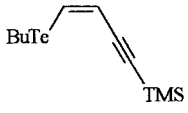
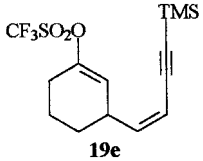
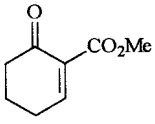
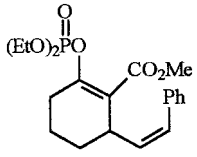
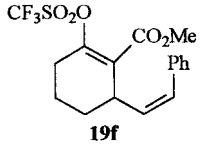
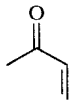
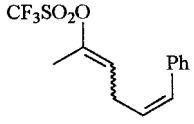
Entry	Telluride	Enone	Product	Yield (%)
1	 **5a**	 **7a**	 **17a**	85
2	**5a**	**7a**	 **18a**	85
3	 **4a**	**7a**	 **19a**	60
4	**5a**	 **7b**	 **17b**	72
5	**5a**	**7b**	 **18b**	90
6	**5a**	 **7c**	 **17c**	70
7	**5a**	**7c**	 **18c**	80
8	**4a**	**7c**	 **19b**	50
9	 **4b**	**7a**	 **17d**	65
10	 **4c**	**7a**	 **18d**	67

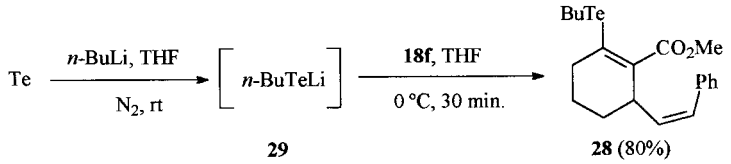
Table 1 (*continued*)

Entry	Telluride	Enone	Product	Yield (%)
11	**4c**	**7a**	 **19c**	65
12	 **4d**	**7a**	 **17e**	67
13	**4d**	**7a**	 **18e**	65
14	**4d**	**7a**	 **19d**	55
15	 **4c**	**7a**	 **19e**	65
16	**4a**	 **7d**	 **18f**	70
17	**4a**	**7d**	 **19f**	60
18	**4a**	 **7e**	 ***E*:*Z* (4:1)** **19g**	50

Organo zinc chlorides are useful intermediates for a number of synthetic transformations.[19] The *Z*-vinyl zinc chlorides were prepared by treating butyl *Z*-vinylic tellurides **4** (1.2 mmol) in THF with *n*-butyllithium (1.2 mmol) at −75°C and then adding a solution of $ZnCl_2$ (1.3 mmol) at the same temperature. The *Z*-vinyl zinc chlorides **30** formed in this way were added to a mixture of $Pd[P(Ph)_3]_4$ (0.1 mmol) and the enol triflate **19a** (1.0 mmol). The coupled products **25a–c** were obtained in good yields (Scheme 5).

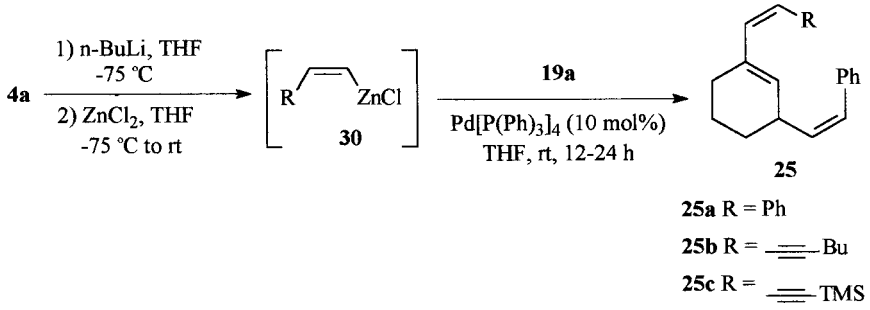
Sonogashira reaction on the obtained vinyl triflate **19a** gave the coupled products **26a–e** in good yields (Scheme 6).

In conclusion, the 1,4-addition of *Z*-vinyl cyanocuprates to enones followed by *O*-functionalization can be used to

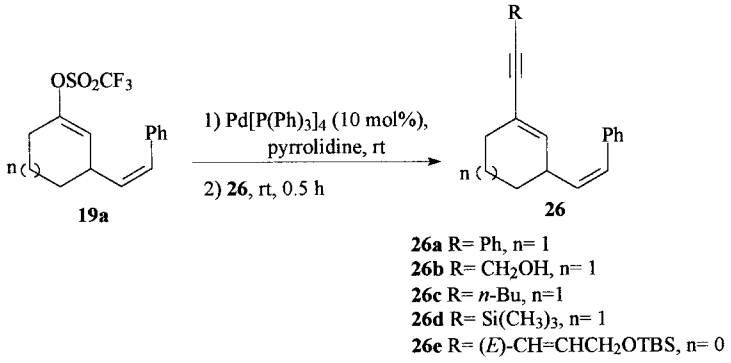


29 28 (80%)

Scheme 4.



Scheme 5.



Scheme 6.

assemble highly unsaturated systems, in the case of the vinyl triflates, the vinyl phosphates are precursors of functionalized tri- and tetrasubstituted *Z*-vinylic tellurides. The silyl enol ethers are being used in our laboratory in carbocyclization reactions.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DPX-300, Bruker DRX-500 or a Bruker AC-200 spectrometers using as internal standard tetramethylsilane and the central peak of $CDCl_3$ (77 ppm), respectively. Infrared spectra were recorded on a Perkin–Elmer 1600 spectrophotometer. Low resolution mass spectra were obtained on a Finnigan 4021 spectrometer or on a GC/MS-Hewlett–Packard 5988-8/5890 spectrometer, both operating at 70 eV. Elemental analysis was performed at the Microanalytical Laboratory of the Chemistry Institute, University of São Paulo. Column chromatography was carried out with Merck silica gel (230–400 mesh). Thin layer chromatography (TLC) was performed on silica gel F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods.[20] THF and diethyl ether were distilled from sodium/benzophenone under N_2, immediately before use. Elemental tellurium (200 mesh) was purchased from Aldrich and dried overnight in an oven at 100°C, CuCN was dried under vacuum in an *Abderhalden* apparatus over P_2O_5, at 70°C. The following reagents were prepared according to the literature procedures: butyl vinyl tellurides,[6] bis vinylic tellurides,[2a,6] dibutyl ditelluride,[6] *N*-phenyl trifluoromethanesulfonamide.[21] The remaining chemicals were obtained from commercial sources. All operations were carried out in dried glassware, under an inert atmosphere of dry and deoxygenated N_2. The IUPAC names were obtained using the ACD/Lab web service, version 3.5, at http://www.acdlabs.com/ilab.

General procedure for the 1,4 addition of higher order mixed cyanocuprates 6 to enones followed by *O*-functionalization by chlorotrimethylsilane (14)

Methyl lithium (4.0 mmol, 1.0 M in diethyl ether, 4.0 mL) was added to a suspension of CuCN (2.0 mmol, 0.18 g) in THF (10 mL) at −75°C. The reaction mixture was then stirred until a clear solution was obtained and allowed to warm to room temperature. The appropriate *Z*-vinylic telluride **4** (2.0 mmol) or **5** (1.0 mmol) was added and stirred for 45 min. The solution was cooled back to −75°C and the corresponding enone (2.2 mmol) was added. After 20 min, chlorotrimethylsilane **14** (2.6 mmol,

0.60 g) diluted in THF (5 mL) was added. The reaction mixture was stirred for 1 h, allowed to warm to room temperature and then treated with 1:1 solution of saturated aqueous NH_4Cl and NH_4OH (20 mL), extracted with ethyl acetate (3×20 mL), dried, evaporated and the residue was purified by Kugehlror distillation affording the silyl enol ethers **17**.

Trimethyl({3-[(*Z*)-2-phenylethenyl]-1-cyclohexen-1-yl}-oxy)silane (17a). Yield: 0.46 g (85%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.45–7.26 (m, 5H); 6.47 (d, J=11.5 Hz, 1H); 5.60 (dd, J=11.2, 10.8 Hz, 1H); 4.89–4.88 (m, 1H); 3.56–3.48 (m, 1H); 2.17–2.10 (m, 2H); 1.93–1.65 (m, 3H); 1.48–1.34 (m, 1H); 0.29 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 151.3, 137.5, 137.4, 128.6, 128.1, 127.5, 126.5, 107.3, 33.7, 29.6, 29.4, 21.4, 0.3. IR (cm^{-1}) (neat) 3414, 3015, 1594, 1582, 1487, 1449, 1335, 1294, 779, 695, 686, 503. LRMS *m/z* (rel. int.) 272 (67) (M^+), 257 (6), 244 (8), 195 (12), 181 (17), 153 (14), 128 (15), 115 (13), 91 (13), 73 (100). Anal. calcd for $C_{17}H_{24}OSi$: C, 74.96, H, 9.05. Found: C, 75.39, H, 9.23.

({4,4-Dimethyl-3-[(*Z*)-2-phenylethenyl]-1-cyclohexen-1-yl}-oxy)(trimethyl)silane (17b). Yield: 0.43 g (72%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.35–7.16 (m, 5H); 6.45 (d, J=11.6 Hz, 1H); 5.50 (t, J=11.4 Hz, 1H); 4.81–4.79 (m, 1H); 3.15–3.08 (m, 1H); 2.23–2.01 (m, 2H); 1.60–1.48 (m, 1H); 1.42–1.28 (m, 1H); 0.87 (s, 3H); 0.84 (s, 3H); 0.19 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 150.2, 137.8, 137.8, 128.8, 128.1, 126.4, 106.8, 43.1, 34.9, 31.8, 28.0, 27.7, 27.6, 23.4, 0.4. IR (cm^{-1}) (neat) 3012, 2958, 2922, 2896, 1662, 1600, 1449, 1253, 1197, 1167, 918, 884. LRMS *m/z* (rel. int.) 300 (17) (M^+), 244 (100), 229 (10), 181 (2), 153 (58), 128 (14), 91 (14), 73.(88). Anal. for $C_{19}H_{28}OSi$: C, 75.94, H, 9.39. Found: C, 76.33, H, 9.35.

Trimethyl({3-[(*Z*)-2-phenylethenyl]-1-cyclopenten-1-yl}-oxy)silane (17c). Yield: 0.36 g (70%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.31–7.20 (m, 5H); 6.33 (d, J=11.4 Hz, 1H); 5.55 (t, J=10.8 Hz, 1H); 4.63–4.56 (m, 1H); 3.85–3.72 (m, 1H); 2.46–2.11 (m, 3H); 1.75–1.54 (m, 1H); 0.22 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 156.0, 138.1, 137.5, 128.7, 128.4, 128.2, 128.1, 127.1, 126.5, 105.6, 40.4, 33.3, 29.6, 0.1. IR (cm^{-1}) (neat) 3061, 3005, 1746, 1643, 1344, 1310, 1253, 1187, 929, 869. LRMS *m/z* (rel. int.) 258 (50) (M^+), 243 (3), 181 (25), 155 (13), 128 (14), 91 (10), 73 (100). Anal. calcd for $C_{16}H_{22}OSi$: C, 74.38, H, 8.52. Found: C, 74.69, H, 8.30.

Trimethyl({3-[(1*Z*,3*E*)-5-(tetrahydro-2*H*-pyran-2-yloxy)-1,3-pentadienyl]-1-cyclohexen-1-yl}oxy)silane (17d). Yield: 0.43 g (65%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 6.57 (dd, J=11.2, 15.0 Hz, 1H); 5.93 (dd, J=10.8, 11.0 Hz, 1H); 5.77 (dt, J=6.4, 15.0 Hz, 1H); 5.28 (t, J=10.2 Hz, 1H); 4.66–4.64 (m, 2H); 4.28 (dd, J=6.4, 12.7 Hz, 1H); 4.02 (dd, J=6.4, 12.8 Hz, 1H); 3.88–3.83 (m, 1H); 3.54–3.48 (m, 1H); 3.30–3.20 (m, 1H); 1.99–1.52 (m, 12H); 0.18 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 151.0, 137.2, 129.3, 127.9, 126.3, 107.2, 97.7, 67.4, 62.0, 33.5, 30.5, 29.5, 29.2, 25.4, 21.4, 19.4, 0.2. IR (cm^{-1}) (neat) 2932, 2861, 1716, 1661, 1450, 1368, 1252, 1189, 1117, 986, 952, 906, 847. LRMS *m/z* (rel. int.) 336 (25) (M^+), 281 (7), 263 (4), 251 (31), 234 (7), 208 (52), 131 (6), 93 (21), 85 (41), 73 (100), 67 (13), 55 (18). Anal. calcd for $C_{19}H_{32}O_3Si$: C, 67.66, H, 9.77. Found: C, 67.55, H, 9.75.

Trimethyl({3-[(*Z*)-1-octen-3-ynyl]-1-cyclohexen-1-yl}oxy)-silane (17e). Yield: 0.37 g (67%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 5.61 (dd, J=10.1, 10.0 Hz, 1H); 5.33 (dt, J=10.6, 2.1 Hz, 1H); 4.69–4.67 (m, 1H); 3.34–3.24 (m, 1H); 2.30 (td, J=6.9, 2.0 Hz, 2H); 2.01–1.91 (m, 2H); 1.75–1.69 (m, 2H); 1.61–1.59 (m, 1H); 1.50 (quint., J=7.1 Hz, 2H); 1.40 (sext., J=7.3 Hz, 2H); 1.22–1.19 (m, 1H); 0.88 (t, J=7.2 Hz, 3H); 0.15 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 151.2, 146.6, 108.0, 106.8, 94.5, 77.1, 35.8, 30.9, 29.7, 28.4, 21.9, 21.4, 19.2, 13.5, 0.2. IR (cm^{-1}) (neat) 3018, 2959, 2934, 2863, 1719, 1661, 1456, 1367, 1252, 1201, 1188, 907, 847. LRMS *m/z* (rel. int.) 276 (5) (M^+), 233 (10), 219 (11), 191 (2), 143 (5), 129 (10), 91 (4), 73 (100). HRMS exact mass calcd for $C_{17}H_{28}OSi$: 276.19094. Found: 276.19054.

General procedure for the 1,4 addition of higher order mixed cyanocuprates 6 to enones followed by *O*-functionalization by diethylchlorophosphorochloridrate (15a)

Methyllithium (4.0 mmol, 1.0 M in THF/Cumene, 4.0 mL) was added to a suspension of CuCN (2.0 mmol, 0.18 g) in THF (10 mL) at −75°C. The reaction mixture was then stirred until a clear solution was obtained and allowed to warm to room temperature. The appropriate *Z*-vinylic telluride **4** (2.0 mmol) or **5** (1.0 mmol) was added and stirred for 45 min. The solution was cooled back to −75°C and the corresponding enone (2.2 mmol) was added. After 20 min, TMEDA (6.0 mmol, 0.70 mL) and diethylphosphorochloridrate **15a** (2.6 mmol, 0.46 g) in THF (5 mL) were added and the solution was allowed to warm to 0°C. The reaction mixture was stirred for 1 h and then treated with 1:1 solution of saturated aqueous NH_4Cl/NH_4OH (3×20 mL), extracted with ethyl acetate (3×20 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using a 3:1 hexane:ethyl acetate as eluent affording the vinyl phosphates **18**.

Diethyl 3-[(*Z*)-2-phenylethenyl]-1-cyclohexen-1-yl phosphate (18a). Yield: 0.57 g (85%), ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.41–7.24 (m, 5H); 6.42 (d, J=11.5 Hz, 1H); 5.50 (dd, J=11.4, 10.5 Hz, 1H); 5.37–5.27 (m, 1H); 4.15–4.10 (m, 4H); 3.49–3.44 (m, 1H); 2.27–2.22 (m, 2H); 1.82–1.32 (m, 4H); 1.37 (t, J=7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 148.6, 137.3, 135.6, 128.7, 128.6, 128.3, 126.8, 113.6, 64.2, 64.1, 33.5, 28.8, 27.6, 21.0, 16.2, 16.1. IR (cm^{-1}) (neat) 2985, 2936, 1677, 1446, 1368, 1273, 1141, 1098, 1029, 920, 702. LRMS *m/z* (rel. int.) 336 (26) (M^+), 307 (14), 279 (3), 251 (2), 199 (8), 182 (10), 167 (100), 154 (44), 91 (49), 81.(36), 77 (21), 65 (11). Anal. calcd for $C_{18}H_{25}PO_4$: C, 64.27, H, 7.44. Found: C, 63.95, H, 7.56.

4,4-Dimethyl-3-[(*Z*)-2-phenylethenyl]-1-cyclohexen-1-yl diethyl phosphate (18b). Yield: 0.65 g (90%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.35–7.20 (m, 5H); 6.50 (d, J=11.6 Hz, 1H); 5.49 (dd, J=11.4, 11.3 Hz, 1H); 5.31–5.31 (m, 1H); 4.15–4.10 (m, 4H); 3.20–3.15 (m, 1H); 2.25–2.10 (m, 2H); 1.67–1.46 (m, 2H); 1.34 (t, J=7.1 Hz,

6H); 0.88 (s, 3H); 0.85 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 147.3, 137.3, 132.3, 129.8, 128.5, 128.1, 126.5, 112.7, 64.1, 63.9, 42.8, 34.1, 31.7, 27.6, 25.4, 23.5, 16.1, 15.9. IR (cm^{-1}) (neat) 3449, 3056, 2983, 2937, 2911, 1737, 1656, 1446, 1343, 1277, 1219, 1167, 1034, 968, 701. LRMS *m/z* (rel. int.) 364 (13) (M^+), 308 (38), 251 (9), 231 (36), 175 (12), 154 (100), 128 (7), 91 (43), 81 (26). Anal. calcd for $C_{20}H_{29}PO_4$: C, 65.93, H 7.96. Found: C, 65.92, H, 7.75.

Diethyl 3-[(*Z*)-2-phenylethenyl]-1-cyclopenten-1-yl phosphate (18c). Yield: 0.51 g (80%), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.41–7.24 (m, 5H); 6.44 (d, J=11.5 Hz, 1H); 5.61 (t, J=10.8 Hz, 1H), 5.22–5.20 (m, 1H); 4.15–4.10 (m, 4H); 3.90–3.84 (m, 1H); 2.61–2.56 (m, 2H); 2.37–2.22 (m, 1H); 1.80–1.73 (m, 1H), 1.25 (t, J=7.1 Hz, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 150.8, 137.1, 128.6, 128.3, 128.2, 128.1, 126.6, 112.3, 64.4, 64.3, 40.1, 34.8, 31.3, 29.3, 26.9, 16.1, 15.9. IR (cm^{-1}) (neat) 2984, 2935, 2911, 1701, 1656, 1275, 1218, 1167, 1034, 968, 700. LRMS *m/z* (rel. int.) 322 (41) (M^+), 293 (8), 265 (4), 231 (4), 190 (8), 167 (100), 153 (42), 91 (41), 81 (39). Anal. calcd for $C_{17}H_{23}PO_4$: C, 63.35, H, 7.33. Found: C, 63.35, H, 7.14.

3-((1*Z*,3*E*)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-1,3-pentadienyl)-1-cyclohexen-1-yl diethyl phosphate (18d). Yield: 0.57 g (67%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 6.51 (dd, J=11.2, 15.1 Hz, 1H); 5.97 (dd, J=10.9, 11.0 Hz, 1H); 5.76 (dt, J=5.1, 15.1 Hz, 1H); 5.30–5.29 (m, 1H); 5.25 (dd, J=10.1, 10.3 Hz, 1H); 4.24 (d, J=5.1 Hz, 2H); 4.19–4.12 (m, 4H); 3.36–3.35 (m, 1H); 2.24–2.21 (m, 2H); 1.86–1.82 (m, 1H); 1.78–1.72 (m, 2H); 1.69–1.65 (m, 1H); 1.34 (t, J=7.1 Hz, 6H); 0.92 (s, 9H); 0.08 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 148.4, 134.4, 133.4, 127.6, 124.8, 113.8, 64.1, 63.6, 33.4, 28.8, 27.6, 27.5, 28.9, 25.2, 21.1, 18.4, 16.2, 16.1, 0.5, 0.2. IR (cm^{-1}) (neat) 3467, 2933, 2857, 1678, 1652, 1446, 1436, 1369, 1273, 1143, 1102, 1037, 968, 837, 778. LRMS *m/z* (rel. int.) 430 (8) (M^+), 373 (26), 285 (100), 257 (10), 197 (6), 155 (28), 73 (32). Anal. calcd for $C_{21}H_{39}PO_5Si$: C, 58.58, H, 9.13. Found: C, 58.24, H, 9.01.

Diethyl 3-[(*Z*)-1-octen-3-ynyl]-1-cyclohexen-1-yl phosphate (18e). Yield: 0.44 g (65%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 5.65 (dd, J=10.1, 10.0 Hz, 1H); 5.44 (dt, J=10.5, 1.9 Hz, 1H); 5.37–5.34 (m, 1H); 4.18–4.12 (m, 4H); 3.55–3.40 (m, 1H); 2.32 (td, J=6.9, 1.9 Hz, 2H); 2.22–2.12 (m, 2H); 1.84–1.79 (m, 2H); 1.67–1.81 (m, 2H); 1.52 (quint., J=7.0 Hz, 2H); 1.43 (sext., J=7.3 Hz, 2H); 1.35 (t, J=7.1 Hz, 6H); 0.92 (t, J=7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 148.3, 144.5, 113.0, 109.2, 95.1, 76.8, 64.1, 64.0, 35.5, 30.8, 27.7, 27.4, 21.8, 20.9, 19.1, 16.0, 15.9, 13.4. IR (cm^{-1}) (neat) 2982, 2957, 2933, 2865, 1678, 1368, 1273, 1147, 1030, 972, 932, 918. LRMS *m/z* (rel. int.) 340 (2) (M^+), 283 (24), 255 (8), 227 (13), 186 (40), 144 (73), 129 (100), 99 (43), 79 (12). HRMS exact mass calcd for $C_{18}H_{29}PO_4$: 340.18035. Found: 340.18066.

Methyl 2-[(diethoxyphosphoryl)oxy]-6-[(*Z*)-2-phenylethenyl]-1-cyclohexene-1-carboxylate (18f). Yield: 0.55 g (70%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.36–7.24 (m, 5H); 6.44 (d, J=11.5 Hz, 1H); 5.52 (dd, J=10.7, 11.4 Hz, 1H); 4.24–4.02 (m, 4H); 3.97–3.90 (m, 1H); 3.55 (s, 3H); 2.50–2.46 (m, 2H); 2.04–1.60 (m, 4H); 1.38–1.32 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 166.8, 151.7, 137.4, 133.6, 130.6, 130.2, 128.7, 128.4, 127.0, 119.5, 64.7, 51.5, 34.5, 28.8, 28.6, 19.9, 16.3. IR (cm^{-1}) (neat) 3055, 2986, 2946, 1726, 1670, 1276, 1032. LRMS *m/z* (rel. int.) 362 (100), 334 (14), 288 (7), 226 (92), 179 (38), 141 (21), 91 (27). Anal. calcd for $C_{20}H_{27}PO_6$: C, 60.91, H, 6.90. Found: C, 60.81, H, 7.13.

General procedure for the 1,4 addition of higher order mixed cyanocuprates 6 to enones followed by *O*-functionalization by *N*-phenyltrifluoromethanesulfonamide (16)

Methyl lithium (4.0 mmol, 1.0 M in THF/Cumene, 4.0 mL) was added to a suspension of CuCN (2.0 mmol, 0.18 g) in THF (10 mL) at −75°C. The reaction mixture was then stirred until a clear solution was obtained and allowed to warm to room temperature. The appropriate *Z*-vinyl butyl telluride **4** (2.0 mmol) was added and stirred for 45 min. The solution was cooled back to −75°C and the corresponding enone **7** (1.1 mmol) was added. After 20 min, HMPA (6.0 mmol, 0.6 mL) and *N*-phenyltrifluoromethanesulfonamide (**16**) (2.6 mmol, 0.6 g) in THF (5 mL) were added and the solution was allowed to warm to room temperature. The reaction mixture was stirred for 4 h and then treated with 1:1 solution of saturated aqueous NH_4Cl/NH_4OH (20 mL), extracted with ethyl acetate (3×20 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using hexane as eluent affording the vinyl triflates **19**.

3-[(*Z*)-2-Phenylethenyl]-1-cyclohexen-1-yl trifluoromethanesulfonate (19a). Yield: 0.39 g (60%), ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.36–7.19 (m, 5H); 6.49 (d, J=11.4 Hz, 1H); 5.64–5.63 (m, 1H); 5.46 (dd, J=11.4, 10.5 Hz, 1H); 3.46–3.60 (m, 1H); 2.33–2.31 (m, 2H); 1.98–1.63 (m, 3H); 1.48–1.35 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 149.9, 136.8, 133.3, 129.9, 128.5, 128.4, 127.1, 121.2, 118.4 (quart., J_{C-F}=318 Hz), 33.9, 28.2, 27.4, 21.0. IR (cm^{-1}) (neat) 3014, 2945, 1684, 1418, 1212, 1143, 900, 701. LRMS *m/z* (rel. int.) 332 (20) (M^+), 199 (26), 181 (71), 141 (79), 128 (68), 115 (50), 91 (100), 55 (64). Anal. calcd for $C_{15}H_{15}O_3SF_3$: C, 54.21, H, 4.55. Found: C, 54.11, H, 4.73.

3-[(*Z*)-2-Phenylethenyl]-1-cyclopenten-1-yl trifluoromethanesulfonate (19b). Yield: 0.31 g (50%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.35–7.20 (m, 5H); 6.46 (d, J=11.4 Hz, 1H); 5.55 (d, J=1.9 Hz, 1H); 5.52 (dd, J=10.5, 11.4 Hz, 1H); 3.91–3.90 (m, 1H); 2.69–2.59 (m, 2H); 2.34–2.29 (m, 1H); 1.86–1.79 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 150.1, 136.8, 132.8, 129.6, 128.6, 128.3, 127.0, 122.3, 118.6 (quart., J_{C-F}=318 Hz), 40.2, 31.1, 29.7. IR (cm^{-1}) (neat) 3024, 2958, 2937, 1684, 1419, 1208, 1144, 900. LRMS *m/z* (rel. int.): 318 (19) (M^+), 185 (35), 141 (100), 128 (79), 91 (41), 69 (25). Anal. calcd for $C_{14}H_{13}O_3SF_3$: C, 52.83, H, 4.09. Found: C, 52.86, H, 4.20.

3-((1*Z*,3*E*)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-1,3-pentadienyl)-1-cyclohexen-1-yl trifluoromethanesulfonate (19c). Yield: 0.55 g (65%), ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm)

6.54–6.45 (m, 1H); 6.03 (dd, J=11.0, 10.8 Hz, 1H); 5.80 (dt, J=15.1, 5.1 Hz, 1H); 5.58–5.57 (m, 1H); 5.22 (dd, J=17.0, 10.0 Hz, 1H); 4.25 (d, J=5.1 Hz, 2H); 3.47–3.42 (m, 1H); 2.34–2.32 (m, 2H); 1.96–1.70 (m, 4H); 0.92 (s, 9H); 0.08 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 196.7, 149.7, 134.4, 131.9, 128.7, 124.0, 121.4, 118.4 (quart., J_{C-F}=318 Hz), 63.4, 33.7, 28.2, 27.4, 25.9, 21.1, 18.4. IR (cm^{-1}) (neat) 2952, 2934, 2858, 1684, 1418, 1248, 1212, 1143, 837, 778, 610. LRMS *m/z* (rel. int.): 369 (4), 313 (4), 145 (100), 117 (70), 91 (68). Anal. calcd for $C_{18}H_{29}O_4SiSF_3$: C, 50.68, H, 6.85. Found: C, 50.79, H, 6.57.

3-[(*Z*)-1-Octen-3-ynyl]-1-cyclohexen-1-yl trifluoromethanesulfonate (19d). Yield: 0.37 g (55%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 5.64 (d, J=2.2 Hz, 1H); 5.61 (t, J=10.6 Hz, 1H); 5.50 (d, J=10.6 Hz, 1H); 3.59–3.56 (m, 1H); 2.38–2.29 (m, 4H); 1.91–1.77 (m, 3H); 1.50 (quint., J=7.1 Hz, 2H); 1.45–1.35 (m, 3H); 0.93 (t, J=7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 149.8, 142.2, 120.7, 118.0 (quart., J_{C-F}=318 Hz), 110.7, 96.3, 77.2, 35.9, 30.7, 27.4, 27.2, 21.9, 21.0, 19.2, 13,5. IR (cm^{-1}) (neat) 2906, 2869, 1659, 1424, 1213, 1142, 917, 700. LRMS *m/z* (rel. int.) 336 (3) (M^+), 203 (18), 147 (20), 105 (59), 91 (78), 55 (100). Anal. calcd for $C_{15}H_{19}O_3SF_3$: C, 53.56, H, 5.69. Found: C, 53.46, H, 5.76.

3-[(*Z*)-4-(Trimethylsilyl)-1-buten-3-ynyl]-1-cyclohexen-1-yl trifluoromethanesulfonate (19e). Yield: 0.45 g (65%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 5.70 (dd, J=10.7, 9.8 Hz, 1H); 5.63–5.61 (m, 1H); 5.50 (d, J=10.7 Hz, 1H); 3.58–3.50 (m, 1H); 2.40–2.30 (m, 2H); 1.80–1.70 (m, 3H); 1.39–1.36 (m, 1H); 0.16 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 149.9, 149.0, 120.3, 118.4 (quart., J_{C-F}= 318 Hz), 110.3, 100.8, 100.5, 41.4, 27.2, 27.0, 20.9. IR (cm^{-1}) (neat) 2958, 2152, 1686, 1418, 1250, 1212, 1143, 900, 844, 632. LRMS *m/z* (rel. int.): 352 (3) (M^+), 337 (5), 219 (35), 187 (12), 145 (29), 75 (56), 69 (100). Anal. calcd for $C_{14}H_{19}O_3SiSF_3$: C, 47.73, H, 5.39. Found: C, 47.42, H, 5.41.

Methyl 6-[(*Z*)-2-phenylethenyl]-2-{[(trifluoromethyl)sulfonyl]oxy}-1-cyclohexene-1-carboxylate (19f). Yield: 0.46 g (60%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.35–7.24 (m, 5H); 6.52 (d, J=10.0 Hz, 1H); 5.51 (t, J=10.0 Hz, 1H); 4.05–4.03 (m, 1H); 3.65 (s, 3H); 2.46–2.41 (m, 2H); 1.90–1.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 164.8, 150.6, 136.7, 131.5, 131.2, 128.4, 128.3, 127.1, 126.5, 119.6, 118.3 (quart., J_{C-F}=318 Hz), 51.9, 35.0, 28.2, 28.1, 19.7. IR (cm^{-1}) (neat) 3022, 2952, 1733, 1679, 1423, 1249, 1211, 1140, 1056, 911, 701, 618. LRMS *m/z* (rel. int.): 225 (100), 183 (3), 141 (17), 69 (15). Anal. calcd for $C_{17}H_{17}O_5SF_3$: C, 51.31, H, 4.39. Found: C, 51.44, H, 4.38.

(4*Z*)-1-Methyl-5-phenyl-1,4-pentadienyl trifluoromethanesulfonate (19g). Yield: 0.30 g (50%), ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.36–7.23 (m, 5H); 6.52 (d, J=11.5 Hz, 1H); 5.61–5.55 (m, 1H); 5.27 (t, J=7.2 Hz, 1H); 3.17 (t, J=7.2 Hz, 2H); 2.07 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 145.4, 136.6, 130.9, 128.6, 128.3, 128.3, 127.5, 127.0, 118.6 (quart., J_{C-F}=318 Hz), 25.3, 19.7. IR (cm^{-1}) (neat) 3020, 2955, 2930, 1680, 1420, 1245, 900. LRMS *m/z* (rel. int.) 157 (12), 129 (83), 115 (38), 91 (100), 77 (30), 69 (52). Anal. calcd for $C_{13}H_{13}O_3SF_3$: C, 50.68, H, 6.87. Found: C, 50.79, H, 6.57.

General procedure for the preparation of vinylic telluride 28 from enolphosphate 18f

To a suspension of tellurium powder (200 mesh, 0.254 g, 2.0 mmol) in THF (2 mL) at room temperature was added *n*-BuLi (1.4 M in hexanes, 0.7 mL, 2.0 mmol). The dark mixture turned a pale yellow clear solution, which was cooled to 0°C. The enolphosphate **18f** (0.54 g, 1.5 mmol) was then added dropwise. After 30 min, ethyl acetate (20 mL) was added and the organic layer was washed with brine (3×10 mL), dried with magnesium sulphate and the solvent was evaporated. The residue was purified by silica gel column chromatography eluting with a mixture of hexane/ethyl acetate (9:1). Compound **28** was isolated as yellow oil.

Methyl 6-[(*Z*)-2-phenylethenyl]-2-(butyl telluro)-1-cyclohexene-1-carboxylate (28). Yield: 0.68 g (80%), ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35–7.23 (m, 5H); 6.37 (d, J=11.4 Hz, 1H); 5.57 (dd, J=11.4, 10.8 Hz, 1H); 3.98 (m, 1H); 3.47 (s, 3H); 2.78–2.71 (m, 1H); 2.58–2.50 (m, 3H), 1.86–1.84 (m, 3H); 1.72–1.63 (m, 3H); 1.41 (sext., J=7.2 Hz, 2H); 0.95 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 169.5, 141.9, 138.1, 135.4, 128.7, 128.5, 128.3, 126.7, 51.7, 35.8, 33.4, 29.2, 25.6, 20.9, 13.7, 6.7. IR ν (cm^{-1}) (neat) 3007, 2953, 2930, 2870, 1715, 1678, 1435, 1273, 1255, 702. LRMS *m/z* (rel. int.) 426 (16), 371 (91), 181 (88), 91 (100), 57 (55). Anal. calcd for $C_{20}H_{26}O_2Te$: C, 56.39, H, 6.15. Found: C, 56.74, H, 6.50.

Transformation of the enolphosphate 18a into vinyl iodides 27a and 27b

To a mixture of the vinyl phosphate **18a** (3.30 g, 10.0 mmol), sodium iodide (4.50 g, 30.0 mmol) and acetonitrile (20 mL) under nitrogen and magnetic stirring, at room temperature, was added chlorotrimethylsilane (3.24 g, 30.0 mmol). After 15 min at room temperature the reaction was filtered, the solvent was evaporated and the residue was dissolved in CH_2Cl_2, washed with saturated aqueous solution of sodium bicarbonate and aqueous sodium thiosulfate. The aqueous phase was extracted twice with CH_2Cl_2. The organic extracts were dried with magnesium sulfate and evaporated. The residue was chromatographed on silica gel eluting with hexane. The product was isolated as a 1:1 mixture of **27a** and **b**.

1-Iodo-3-[(*Z*)-2-phenylethenyl]-1-cyclohexene (27a) and 1-iodo-5-[(*Z*)-2-phenylethenyl]-1-cyclohexene (27b). Yield: 1.92 g (60 %), ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.37–7.20 (m, 5 H); 6.45 (d, J=11.5 Hz, 1 H); 6.41 (d, J=11.5 Hz, 1H); 6.35–6.34 (m, 1H); 6.27–6.24 (m, 1H); 5.55–5.43 (m, 1H); 3.45–3.41 (m, 1H); 2.67–2.46 (m, 2H); 2.16–2.10 (m, 1H); 1.87–1.40 (m, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ (ppm) 139.4, 137.2, 136.9, 136.9, 135.5, 134.4, 128.9, 128.6, 128.5, 128.2, 126.8, 126.7, 98.2, 94.9, 45.2, 39.1, 38.5, 35.4, 27.9, 27.3, 23.6. LRMS *m/z* (rel. int.) 320 (62) (M^+), 219 (1), 183 (61), 155 (12), 141 (100), 91 (59), 77

(25), 65 (10), 51 (12). IR (cm^{-1}) (film) 3024, 3005, 2930, 2854, 1638, 1493, 1446, 1430, 794, 768, 736, 699. Anal. calcd for $C_{14}H_{15}I$: C, 54.21, H, 4.84. Found: C, 54.02, H, 4.82.

General procedure for the cross-coupling reaction between enol triflate 19a and *Z*-vinylic zinc chloride 30, catalyzed by $Pd[P(Ph)_3]_4$

n-Butyl lithium (1.2 mmol, 2.5 M in hexane, 0.40 mL) was added to a solution of the appropriate *Z*-vinyl butyl telluride **4** (1.2 mmol) in THF (5.0 mL) at −75°C and stirred for 45 min. After this time, $ZnCl_2$ (1.2 mmol, 1.0 M in THF, 1.20 mL) was added and the mixture was warmed up to room temperature. This solution was transferred via cannula to a previously prepared mixture of $Pd[P(Ph)_3]_4$ (10.0 mmol%, 0.1 mmol, 0.11 g) and the enol triflate **19a** (1.0 mmol, 0.33 g) in THF (5.0 mL). The reaction was monitored by TLC until all the starting material was consumed. The reaction times are described below. After this, CH_2Cl_2 (30.0 mL) was added and the organic phase was washed with brine (3×20.0 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using hexane as eluent.

1,3-bis[(*Z*)-2-Phenylethenyl]-1-cyclohexene (25a). Yield: 0.21 g (75%). *Reaction time:* 10 h, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.31–7.19 (m, 10H); 6.39 (d, J=11.5 Hz, 1H); 6.35 (d, J=12.2 Hz, 1H); 6.09 (d, J=12.2 Hz, 1H); 5.64–5.60 (m, 1H); 5.49–5.45 (dd, J=10.5, 11.5 Hz, 1H); 3.40–3.38 (m, 1H); 1.95–1.91 (m, 2H); 1.79–1.69 (m, 2H); 1.39–1.35 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 136.1, 133.3, 130.1, 129.0, 128.8, 128.3, 128.2, 128.1, 127.8, 126.5, 35.1, 29.2, 27.9, 21.3. LRMS *m/z* (rel. int.): 286 (100) (M^+), 195 (45), 167 (75), 128 (32), 91 (70). IR (cm^{-1}) (film) 3055, 2954, 2930, 2861, 1601, 1448, 1430, 1303, 853, 766, 699. Anal. calcd for $C_{22}H_{22}$: C, 92.26, H, 7.98. Found: C, 92.59, H, 8.03.

(*Z*)-1-{3-[(*Z*)-2-Phenylethenyl]-1-cyclohexen-1-yl}-1-octen-3-yne (25b). Yield: 0.22 g (75%). *Reaction time:* 24 h, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.34–7.22 (m, 5H); 6.43 (d, J=11.5 Hz, 1H); 6.05 (d, J=11.9 Hz, 1H); 5.84–5.82 (m, 1H); 5.50 (t, J=10.8 Hz, 1H); 5.35 (dt, J=2.2, 11.5 Hz, 1H); 3.51–3.45 (m, 1H); 2.66–2.63 (m, 1H); 2.35–2.31 (m, 2H); 1.84–1.82 (m, 2H); 1.55–1.51 (m, 4H); 1.44–1.39 (m, 3H); 0.90 (t, J=7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 141.1, 137.9, 136.6, 133.8, 129.2, 129.1, 128.8, 127.2, 126.3, 105.9, 96.7, 80.1, 35.8, 31.3, 29.5, 27.5, 22.5, 21.6, 19.9, 13.9. LRMS *m/z* (rel. int.): 233 (100), 205 (62), 141 (28), 129 (42), 91 (43). IR (cm^{-1}) (film) 3055, 3297, 3445, 1948, 1753, 1629, 1574, 1262, 862, 767. Anal. calcd for $C_{22}H_{26}$: C, 90.22, H, 9.77. Found: C, 90.34, H, 9.13.

Trimethyl((*Z*)-4-{3-[(*Z*)-2-phenylethenyl]-1-cyclohexen-1-yl}-3-buten-1-ynyl)silane (25c). Yield: 0.24 g (80%). *Reaction time:* 12 h, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.34–7.21 (m, 5H); 6.44 (d, J=11.4 Hz, 1H); 6.14 (d, J=12.1 Hz, 1H); 5.87 (m, 1H); 5.50 (dd, J=10.5, 11.3 Hz, 1H); 5.36 (d, J=12.1 Hz, 1H); 3.52–3.47 (m, 1H); 2.55–2.50 (m, 1H); 1.86–1.79 (m, 2H); 1.59–1.55 (m, 1H); 1.43–1.39 (m, 1H); 1.26–1.23 (m, 1H); 0.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 143.2, 137.6, 137.5, 135.7, 134.9, 128.7, 128.6, 128.2, 126.7, 104.8, 104.5, 100.4, 35.4, 29.1, 27.0, 21.1, 0.2. LRMS *m/z* (rel. int.): 306 (2) (M^+), 263 (1), 233 (29), 191 (11), 128 (9), 91 (14), 73 (100). IR (cm^{-1}) (film) 3009, 2957, 2932, 2138, 2097, 1946, 1613, 1493, 1447, 1406, 1250, 1000, 845, 761, 700, 635. Anal. calcd for $C_{21}H_{26}Si$: C, 82.29, H, 8.55. Found: C, 82.38, H, 8.27.

General procedure for the coupling reaction between enol triflate 19a and terminal alkynes 21, catalyzed by $Pd[P(Ph)_3]_4$

Enol triflate 19a, (1.0 mmol, 0.33 g) was added to a stirred suspension containing a mixture of $Pd[P(Ph)_3]_4$ (10.0 mmol%, 0.1 mmol, 0.11 g) and pyrrolidine (2.0 mL). The mixture was stirred for 15 min and the appropriate terminal alkyne **21** (1.2 mmol) was then added, dropwise, at room temperature. The reaction was monitored by TLC until all the starting material was consumed. The reaction times are described below. After this, CH_2Cl_2 (30.0 mL) was added and the organic phase was washed with brine (3×20.0 mL), dried, evaporated and the residue was purified by flash silica gel chromatography using hexane as eluent.

3-[(*Z*)-2-Phenylethenyl]-1-(2-phenylethynyl)-1-cyclohexene (26a). Yield: 0.21 g (75%). *Reaction time:* 30 min, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.43–7.23 (m, 10H); 6.45 (d, J=11.4 Hz, 1H); 6.10–6.09 (m, 1H); 5.50 (t, J=11.4 Hz, 1H); 3.48–3.46 (m, 1H); 2.25–2.24 (m, 2H); 1.84–1.81 (m, 2H); 1.61–1.41 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 137.2, 136.9, 135.0, 131.4, 128.9, 128.4, 128.3, 128.2, 126.8, 123.5, 121.6, 90.8, 87.6, 34.1, 29.2, 28.6, 21.2. LRMS *m/z* (rel. int.): 284 (72) (M^+), 241 (51), 178 (100), 165 (94), 128 (51), 115 (86), 91 (69), 77 (44). IR (cm^{-1}) (film) 3009, 2930, 2216, 1601, 1449, 770, 700. Anal. calcd for $C_{22}H_{20}$: C, 92.96, H, 7.04. Found: C, 92.44, H, 7.28.

3-{3-[(*Z*)-2-Phenylethenyl]-1-cyclohexen-1-yl}-2-propyn-1-ol (26b). Yield: 0.19 g (80%). *Reaction time:* 20 min, ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.36–7.20 (m, 5H); 6.43 (d, J=11.4 Hz, 1H); 6.01–5.95 (m, 1H); 5.45 (t, J=11.4 Hz, 1H); 4.36 (s, 2H); 3.40–3.39 (m, 1H); 2.13–2.11 (m, 2H); 1.80–1.76 (m, 3H); 1.57–1.37 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 137.2, 137.1, 134.8, 128.9, 128.5, 128.4, 126.7, 120.9, 86.9, 85.4, 51.3, 34.9, 28.8, 28.5, 21.0. LRMS *m/z* (rel. int.) 238 (40) (M^+), 205 (27), 154 (50), 128 (50), 115 (55), 91 (100). IR (cm^{-1}) (film) 3309, 3053, 3007, 2933, 2218, 1600, 1446, 1213, 1015, 701. Anal. calcd for $C_{17}H_{18}O$: C, 85.71, H, 7.56. Found: C, 85.11, H, 7.71.

1-(1-Hexynyl)-3-[(*Z*)-2-phenylethenyl]-1-cyclohexene (26c). Yield: 0.19 g (75%). *Reaction time:* 45 min, ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34–7.19 (m, 5H); 6.42 (d, J=11.4 Hz, 1H); 5.90–5.82 (m, 1H); 5.47 (dd, J=10.5, 11.4 Hz, 1H); 3.32–3.47 (m, 1H); 2.32–2.27 (m, 2H); 2.13–2.11 (m, 2H); 1.81–1.73 (m, 2H); 1.60–1.31 (m, 6H); 0.93–0.88 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 138.4, 135.5, 135.1, 128.6, 128.2, 126.7, 122.1, 88.4, 81.9, 34.9, 31.0, 29.5, 28.8, 21.9, 20.9, 19.0, 13.7. LRMS *m/z* (rel. int.): 264 (100) (M^+), 207 (41), 179 (61),

173 (10), 115 (37), 91 (93), 77 (16). IR (cm^{-1}) (film) 3025, 2957, 2931, 2860, 2837, 1449, 700. Anal. calcd for $C_{20}H_{24}$: C, 90.90, H, 9.09. Found: C, 90.87, H, 9.25.

Trimethyl(2-{3-[(*Z*)-2-phenylethenyl]-1-cyclohexen-1-yl}-ethynyl)silane (26d). Yield: 0.22 g (78%). *Reaction time:* 30 min, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.33–7.20 (m, 5H); 6.43 (d, J=11.5 Hz, 1H); 6.07–6.05 (m, 1H); 5.45 (dd, J=10.4, 11.5 Hz, 1H); 3.42–3.39 (m, 1H); 2.15–2.13 (m, 2H); 1.79–1.75 (m, 2H); 1.55–1.51 (m, 1H); 1.40–1.36 (m, 1H); 0.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 137.9, 137.2, 134.9, 128.9, 128.6, 128.2, 126.7, 121.6, 106.7, 91.8, 35.0, 28.8, 28.5, 20.7, 0.1. LRMS *m/z* (rel. int.) 280 (27) (M^+), 265 (17), 207 (18), 154 (28), 91 (21), 73 (100). IR (cm^{-1}) (film) 3444, 2958, 2930, 2141, 1445, 1250, 1168, 873, 846, 763, 702, 660, 531. Anal. calcd for $C_{19}H_{24}Si$: C, 81.36, H, 8.62. Found: C, 80.76, H, 8.78.

***tert*-Butyl(dimethyl)[((*E*)-5-{3-[(*Z*)-2-phenylethenyl]-1-cyclopenten-1-yl}-2-penten-4-ynyl)oxy] (26e).** Yield: 0.29 g (80%). *Reaction time:* 40 min, ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 7.34–7.22 (m, 5H); 6.41 (d, J=11.4 Hz, 1H); 6.19 (dt, J=15.7, 4.3 Hz, 1H); 5.91–5.90 (m, 2H); 5.50 (dd, J=11.4, 10.0 Hz, 1H); 3.95–4.02 (m, 1H); 2.56–2.44 (m, 2H); 2.24–2.20 (m, 1H); 1.73–1.66 (m, 1H); 0.91 (s, 9H); 0.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) 142.2, 139.8, 137.3, 134.9, 128.7, 128.6, 128.2, 126.8, 125.7, 108.8, 89.7, 86.6, 62.9, 44.9, 36.1, 31.8, 25.9, 18.3, −5.3. LRMS *m/z* (rel. int.) 364 (16) (M^+); 307 (38); 233 (38); 141 (100); 91 (19); 75 (59). IR (cm^{-1}) (film) 3007, 2953, 2931, 2857, 2186, 1600, 1466, 1377, 1255, 1129, 953, 838, 778. Anal. calcd for $C_{24}H_{32}OSi$: C, 79.16, H, 8.85. Found C, 79.59, H, 8.93.

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