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A Nickel-Catalyzed Carbozincation of Aryl-Substituted Alkynes

Thomas Stüdemann, Malika Ibrahim-Ouali and Paul Knochel*

Fachbereich Chemie der Philipps-Universität Marburg

Hans-Meerwein-Straße, D – 35032 Marburg, Germany

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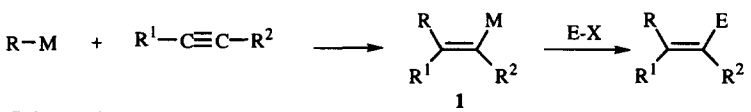
Abstract: *The addition of dialkylzincs or diphenylzinc to substituted phenylacetylenes in the presence of catalytic amounts of Ni(acac)$_2$ in THF : NMP mixtures produces syn-carbozincation products with good to excellent regio- and stereoselectivity. After quenching with an electrophile (iodine, acyl chloride, allyl bromide) tetrasubstituted olefines are obtained in good to satisfactory yields. An intramolecular version of the reaction is possible using a terminal triple bond bearing an iodine at a remote position. More substituted iodo-alkynes furnish only reductive elimination products. An application to a stereoselective synthesis of (Z)-tamoxifen (Z : E > 99 : 1) has been developed.*

The addition of organometallics (RM) to alkynes (carbometalation)[1] constitutes an excellent method for the preparation of alkenyl organometallics of type **1** which after a reaction with an electrophilic reagent (E-X) provide tri- or tetrasubstituted olefines (Scheme 1).



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Scheme 1

Of special interest are carbometalation reactions which are regio- and stereoselective. Under those, the carbocupration and zirconium mediated carboalumination are highly useful carbometalation procedures and only a few carbozincations of alkynes have been reported.[1,2] Herein, we wish to report a new nickel catalyzed addition of various dialkyl- and diarylzincs to alkynes.[3,4] Remarkably this addition proceeds with a high (> 99 %) *syn*-stereoselectivity and allows a regioselective addition to substituted phenylacetylenes. 1,2-Diphenylacetylene adds dipentylzinc in a THF : NMP mixture (1:3) at –35 °C for 18 h in the presence of Ni(acac)$_2$ (ca. 25 mol %) affording only (*Z*)-1,2-diphenylheptene **2a** in 76 % yield (*Z* : *E* > 99 : 1). With diethylzinc, a similar addition occurs leading to (*Z*)-1,2-diphenylbutene **2b** (*Z* : *E* > 98 : 2). In this case, the product is contaminated with a small amount (2 %) of (*Z*)-stilbene **3** obtained presumably via a hydronickelation. The intermediate EtNiX undergoes a particularly favorable β-hydride elimination furnishing a nickel hydride (HNiX) which adds to the triple bond and gives after hydrolysis the reduction product **3** (Scheme 2).

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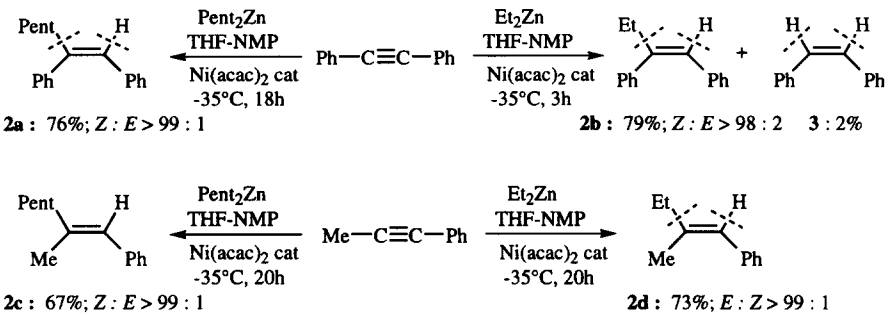
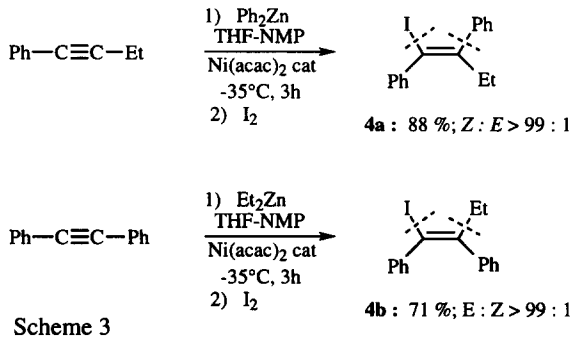


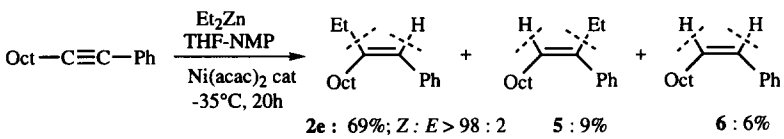
Scheme 2

With a less bulky alkyne like 1-phenyl-1-propyne, the *syn*-addition compounds **2c** and **2d** are the only products obtained as pure (*Z*)-isomers. Interestingly, it is possible to add diphenylzinc[5] to substituted phenylacetylenes. Thus, the addition of Ph_2Zn to 1-phenyl-1-butyne proceeds with complete stereoselectivity and regioselectivity providing after iodolysis the alkenyl iodide **4a** in 88 % yield and $Z : E > 99 : 1$. In this reaction, the diphenylzinc used was added as an etheral solution of sublimed arylzinc reagent[5]. Attemps to generate Ph_2Zn *in situ* using PhLi and $ZnCl_2$ (0.5 equiv) or using PhMgBr and $ZnCl_2$ led to unsatisfactory results. (*E*)-1-iodo-1,2-diphenylbutene (**4b**) has been prepared for demonstrating the stereoselectivity of the *syn*-carbometalation. Thus, the reaction of 1,2-diphenylacetylene with diethylzinc followed by an iodolysis furnishes (*E*)-1-iodo-1,2-diphenylbutene (**4b**) in 73 % yield ($Z : E > 99 : 1$; Scheme 3). No (*Z*)-alkenyl iodide (**4b**) was contained in the crude reaction mixture of **4a** (checked by ^{13}C NMR spectroscopy) showing that the stereoselectivity is better than 99 %.



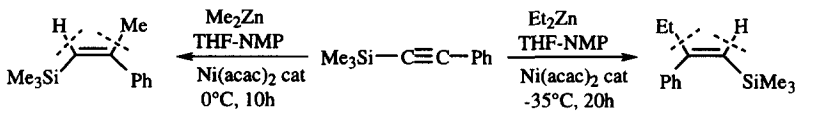
Scheme 3

With substituted phenylacetylenes bearing longer alkyl chains, a lower regioslectivity is observed. Thus, the nickel catalyzed addition of diethylzinc to 1-phenyl-1-decyne affords besides the expected (*Z*)-2-ethyl-1-phenyldecene **2e** (69 % isolated yield; $Z : E > 98 : 2$), the regioisomeric addition product (*Z*)-3-phenyl-3-dodecene **5** with 9 % yield as well as the hydrometalation product (*Z*)-1-phenyldecene **6** with 6 % yield (Scheme 4).



Scheme 4

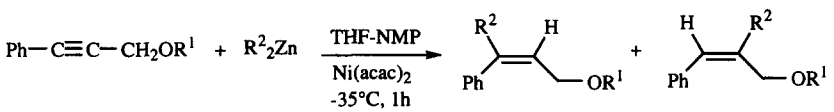
With silylated phenylacetylene[6] the opposite regioisomer is obtained selectively, e.g. the organic group adds at the α-position to the phenyl ring. The addition of diethylzinc to trimethylsilylphenylacetylene gives only (*Z*)-2-phenyl-1-trimethylsilylbutene (**2f**) in 82 % yield (-35 °C, 20 h; *E* : *Z* = 99 : 1).[7] Interestingly, the addition of dimethylzinc to this alkyne occurs as well furnishing (*Z*)-2-methyl-2-phenyl-1-trimethylsilylethene (**2g**) in 64 % yield (0 °C, 10 h; *Z* : *E* = 98 : 2; Scheme 5). It should be noticed that methylcuprates undergo additions to alkynes only with difficulty.[8]



2g : 64%; *E* : *Z* > 98 : 2 **2f** : 82%; *E* : *Z* = 99 : 1

Scheme 5

The addition to phenyl substituted propargylic ethers **7a-b** has also been examined. These reactive alkynes add dialkylzincs with excellent stereoselectivity furnishing *Z*-β-disubstituted allylic ethers **8a-d** after hydrolysis. The reactions are complete within 1 h at –35 °C (Scheme 6).

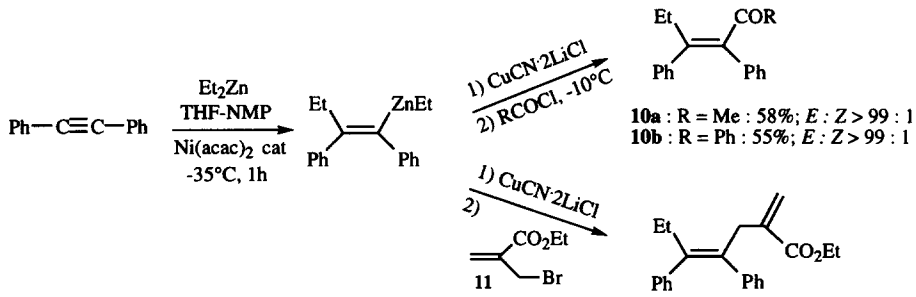


		major	minor	yield
7a : R^1 = Bn	R^1 = Bn; R^2 = Et	**8a** : 100%	**9a** : 0%	56%
7b : R^1 = OTIPS	R^1 = OTIPS; R^2 = Et	**8b** : 95%	**9b** : 5%	73%
	R^1 = OTIPS; R^2 = i-Pr	**8c** : 90%	**9c** : 10%	68%
	R^1 = OTIPS; R^2 = Ph	**8d** : 90%*	**9d** : 10%*	64%

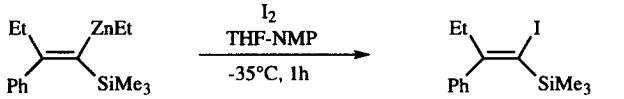
(*) isolated as the corresponding alcohol

Scheme 6

Small amounts of the regioisomeric carbometalation products **9a-d** are also formed. The mixed alkenylalkylzincs obtained after the carbometalation step can be trapped by several types of electrophiles. For example, the addition product of diethylzinc to 1,2-diphenylacetylene affords, after addition of the THF soluble salt CuCN·2LiCl[9] and acetyl chloride or benzoyl chloride, the *E*-unsaturated ketones **10a-b** in 58 % and 55 % overall yield (*E* : *Z* > 99 : 1). Reacting the same alkenylzinc intermediate with ethyl (2-bromomethyl)acrylate (**11**)[10] provides the skipped dienyl ester **12** in 71 % yield (*E* : *Z* > 98 : 2). Similarly, the iodolysis of various alkenylzincs like **13** obtained by nickel catalyzed carbozincation furnishes the corresponding alkenyl iodide **14** with satisfactory yield and stereoselectivity (Scheme 7 and 8).



Scheme 7

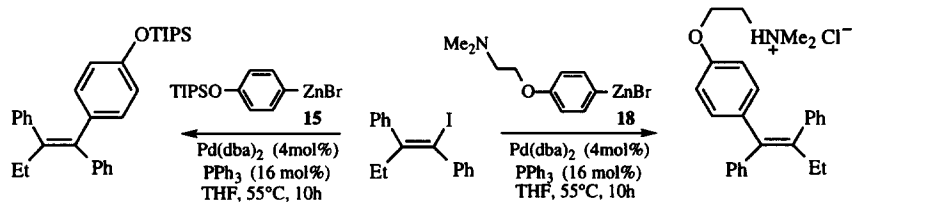


13

14 : 61%; E : Z = 97 : 3

Scheme 8

Although palladium catalyzed cross-coupling reactions are possible with the intermediate alkenylzinc derivatives, better results are obtained by reacting the isolated alkenyl iodides obtained after iodolysis. For example, the reaction of the alkenyl iodide **4a** with 4-triisopropylsiloxyphenylzinc bromide (**15**)[11] in the presence of Pd(dba)2 (4 mol % dba = dibenzylideneacetone)[12] and PPh3 (16 mol %) in THF (55 °C, 10 h) provides the expected cross-coupling product **16** (81 %; *Z* : *E* > 99 : 1); Scheme 9.



16 : 81%; *Z* : *E* > 99 : 1

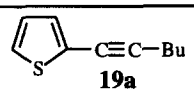
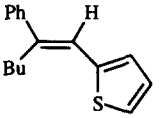
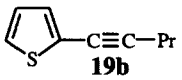
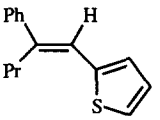
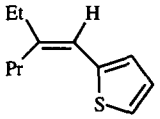
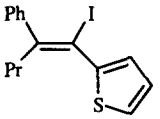
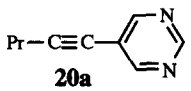
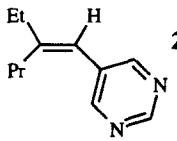
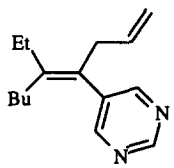
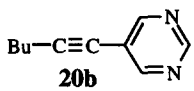
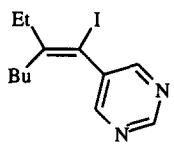
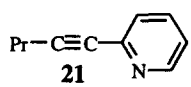
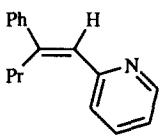
17 : (*Z*)-tamoxifen-hydrochloride 75%; *Z* : *E* > 99 : 1

Scheme 9

This method has been used to prepare (*Z*)-tamoxifen-hydrochloride (**17**), an anti-estrogenic anticancer drug that is effective for the treatment of metastatic breast cancer[13] starting from **4a** and performing the cross-coupling with the polyfunctional arylzinc bromide **18** at 55 °C for 10 h. After acidic workup, (*Z*)-tamoxifen-hydrochloride (**17**) is isolated in 75 % yield (*Z* : *E* > 99 : 1).

This carbozincation can also be applied efficiently to alkynes bearing heterocyclic substituents. Thus, 2-thienyl, 5-pyrimidyl, 2-pyridyl substituted alkynes **19a-h**, **20a-b** and **21** add diethylzinc or diphenylzinc with complete regio- and stereoselectivity affording after quenching with an electrophile the tri- or tetra-substituted alkenes **22a-h** in satisfactory to good yields (35-77 %; see Table 1).

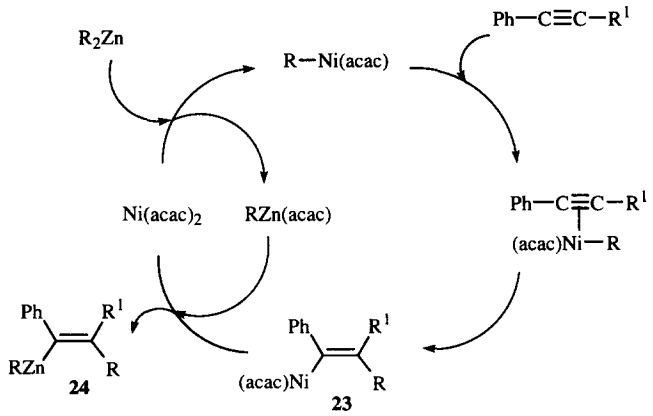
Table 1. Substituted heterocyclic alkenes **22a-i** obtained by the nickel catalyzed carbozincation of disubstituted heterocyclic acetylenes **19-21** followed by trapping with an electrophile.

entry	Alkyne	R_2Zn (R)	electrophile	product **22**	yield (%)[a]	E:Z ratio
1	 **19a**	Ph	H_2O	 **22a**	67	> 99:1
2	 **19b**	Ph	H_2O	 **22b**	64	> 99:1
3	**19b**	Et	H_2O	 **22c**	63	< 1:99
4	**19b**	Ph	I_2	 **22d**	58	> 99:1
5	 **20a**	Et	H_2O	 **22e**	77	< 1:99
6	**20a**	Et	allyl bromide[b]	 **22g**	35	< 1:99
7	 **20b**	Et	I_2	 **22f**	64	< 1:99
8	 **21**	Ph	H_2O	 **22h**	67	> 99:1

[a]Isolated yield of analytically pure product. [b]The quenching with allyl bromide is performed in the presence of CuCN·2LiCl

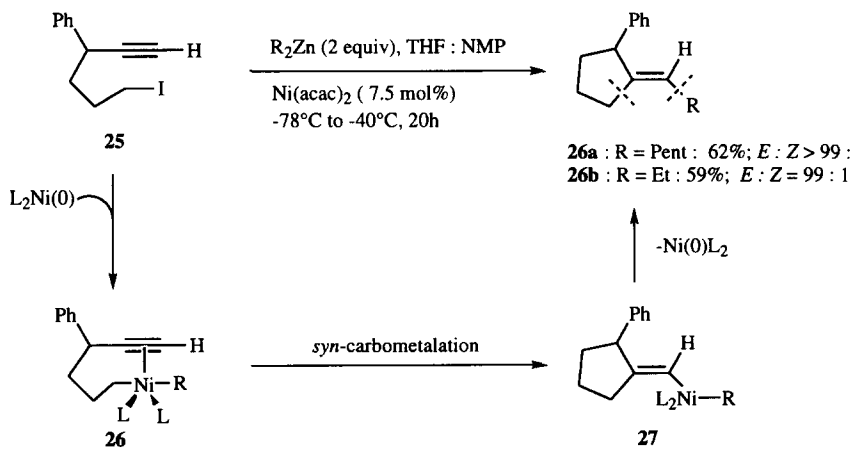
The mechanism of the carbozincation can best be rationalized by assuming that the zinc reagent R_2Zn undergoes a transmetalation with $Ni(acac)_2$ and generates an alkylnickel RNi(acac) which complexes the substituted phenylacetylene and undergoes a carbonickelation reaction affording the alkenylnickel intermediate

23 (Scheme 10). By subsequent transmetalation with RZn(acac) the carbozincation product **24** is obtained. The observed regioselectivity of the carbometalation may be the result of steric and electronic factors.



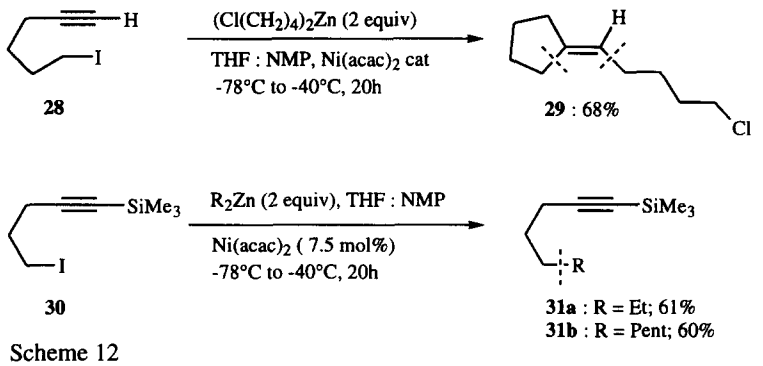
Scheme 10

Efforts were made to extend this carbometalation reaction to its intramolecular version. In this case, the intermediate nickel species undergoing the carbonickelation step is generated by an oxidative addition. Thus, the iodoalkyne **25** was prepared and treated with dipentylzinc in THF : NMP in the presence of Ni(acac)2 (7.5 mol %) in THF : NMP at -40 °C for 20 h resulting in the exclusive formation of **26a** in 62 % yield as one stereoisomer (*E* : *Z* > 99 : 1). Performing the reaction with diethylzinc results in the formation of **26b** in 59 % yield (*E* : *Z* = 99 : 1). These results may be explained by assuming that diethylzinc reacts with Ni(acac)2 generating a nickel(0) species which undergoes an oxidative addition to **25** providing a nickel(II) complex which coordinates to the triple bond. After carbonickelation leading to the alkenylnickel **27**, a reductive elimination occurs furnishing the products **26a-b** (Scheme 11).



Scheme 11

The labeling phenyl group of **25** demonstrates that a *syn*-carbometalation[14] has occurred. This reaction can be accomplished using zinc organometallics bearing some functional groups. Thus $Zn((CH_2)_4Cl)_2$ adds to the alkyne **28** ($Ni(acac)_2$, 7.5 mol %; THF : NMP, -40 °C, 20 h) leading to exo-alkylidenylcyclopentane **29** in 68 % yield. Interestingly, with the silyl-substituted iodoalkyne **30**, no carbonickelation occurred due to the shorter chain lenght of this substrate leading only to the reductive elimination[15] products **31a** and **31b** (Scheme 12).



Scheme 12

In summary, we have shown that various substituted phenylacetylenes undergo a highly stereoselective *syn*-carbozincation reaction by treatment with dialkylzincs or diphenylzinc in the presence of catalytic amounts of $Ni(acac)_2$ leading to useful trisubstituted aryl or heteroaryl olefines. By quenching with an electrophile, tetrasubstituted olefines can be obtained with high stereoselectivity. The intramolecular version of the reaction is possible using a terminal alkyne.

Experimental Section

General methods. Unless otherwise indicated, all reactions were carried out under an argon atmosphere. Solvents (THF or NMP) were dried and freshly distilled over respectively sodium/benzophenone and CaH_2. Reactions were monitored by gas-chromatography (GC) analysis of worked up reaction aliquots. Unless otherwise indicated, the reaction mixtures were worked up as follows: the reaction mixture was poured into a mixture of ethyl acetate or diethyl ether and sat. aq. NH_4Cl. The two phase mixture was filtered to remove insoluble salts and the two layers were separated. The combined organic extracts were washed with water (50 mL), sat. aq. NaCl (20 mL), dried over $MgSO_4$ and filtered. The residue obtained after evaporation of the solvents was purified by flash-chromatography. Fourier transformation infrared spectra (FT-IR) were recorded on a Nicolet 5 DXB spectrometer. Proton and carbon nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Bruker AX 200 and AC 300 (200, 300 MHz, proton) and (50, 75 MHz, carbon). Mass spectra (MS) and exact mass calculations were recorded on a VG-70-250 S mass spectrometer. The ionization methods used were desorption chemical ionization (CI) and electron impact ionization (EI, 70 eV).

Starting materials. The following starting materials were prepared according to literature procedures: ethyl (2-bromomethyl)acrylate (**11**) ,[10] dipentylzinc,[16] dimethylzinc,[16] diphenylzinc,[5] 4-triisopropylsiloxyphenylzinc

bromide,[11] 1-phenyl-1-decyne,[17] 2-phenyl-1-trimethylsilylacetylene,[18], 4-[3-dimethylamino-1-oxapropyl]-1-iodobenzene,[19] 1-thienyl-2-pentyne (**19b**),[20] 1-thienyl-2-hexyne (**19a**),[20] 6-iodo-3-phenyl-1-hexyne **25**,[21] 6-iodo-1-hexyne **28**,[22] 5-iodo-1-trimethylsilylpentyne (**30**).[23]

Preparation of 1-phenyl-3-benzyloxy-1-propyne (7a). To a solution of 3-phenyl-2-propyn-1-ol (5 g, 37.8 mmol, 1 equiv) and benzyl bromide (7.1 g, 4.95 mL, 41.6 mmol, 1.1 equiv) in DMF (50 mL) was added NaH (1.25 g, 80 % suspension in oil, 41.6 mmol, 1.1 equiv) at –20 °C. The reaction mixture was slowly warmed to rt and was quenched with sat. aq. NH_4Cl solution (100 mL). The aqueous layer was extracted with ether (3 x 50 mL) and the combined organic layer was dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash-chromatography (ether : hexane 1 : 25) affording the benzyl ether (**7a**) as a clear oil (8 g, 36.9 mmol, 95 % yield). IR (neat): 3963 (s), 2854 (s), 1490 (m), 1089 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44-7.23 (m, 10 H), 4.63 (s, 2H), 3.39 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.5, 131.7, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 122.6, 86.4, 85.0, 71.5, 57.8. MS (EI): 222 (M^+, 8), 193 (23), 116 (73), 115 (100), 114 (8), 105 (36), 91 (45), 7 (13). Exact mass calcd. for $C_{16}H_4O$: 222.1045. Observed: 222.1045.

Preparation of 1-phenyl-3-triisopropylsiloxypropyne (7b). To a solution of imidazole (3.4 g 50 mmol, 2.2 equiv) and triisopropylsilyl chloride (TIPSCl, 4.8 g, 5.32 mL, 25 mmol, 1.1 equiv) in DMF (10 mL) was slowly added 3-phenyl-2-propyn-1-ol (3.0 g, 22.6 mmol, 1 equiv). The reaction mixture was stirred for 12 h at rt and was quenched with a sat. aq. NH_4Cl solution (10 mL). The organic layer was successively washed with sat. aq. $NaHCO_3$ (10 mL) and brine (5 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash-chromatography (ether : hexane 1 : 25) affording the silyl ether **7b** as a clear oil (6.25 g, 22.6 mmol, 92 % yield). IR (neat): 2944 (s), 2893 (s), 1092 (m), 1069 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.42-7.38 (m, 2H), 7.35-7.31 (m, 3H), 4.60 (s, 2H); 1.20-1.02 (m, 21H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.6, 128.2, 128.0, 123.1, 88.0, 84.5, 52.5, 17.9, 12.0. MS (EI): 288 (M^+, 0.1), 247 (5), 246 (17), 245 (71), 216 (19), 215 (71), 204 (20), 203 (100), 187 (32), 173 (41), 159 (28), 115 (73), 94 (42). Anal. Calcd. for C: 74.94; H: 9.78. Found C: 75.30, H: 10.14.

Preparation of 5-pyrimidyl-1-hexyne (20b).[24] A 250 mL-three-necked flask equipped with a septum and an argon inlet was charged with $PdCl_2(PPh_3)_2$ (70 mg, 0.2 mmol, 1.0 mol %) and was flushed with argon. 5-Bromopyrimidine (3.17 g, 20 mmol) and 1-hexyne (1.64 g, 20 mmol) and Et_2NH (120 mL) were successively added. Finally CuI (38 mg, 0.2 mmol, 1 mol %) was added and the reaction mixture was stirred for 20 h at rt. The solvent was evaporated and the residue was extracted with ether. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash-chromatography (hexane : ethyl acetate 9 : 1) affording the alkyne **20b** (2.58 g, 16 mmol, 80 % yield) as a yellowish oil. IR (neat): 3041 (w), 2959 (m), 2235 (m), 1540 (m), 1412 (s), 1184 (m), 721 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.00 (s, 1H), 8.64 (s, 2H), 2.36 (t, J = 7.0 Hz, 2H), 1.57-1.32 (m, 4H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) : δ 158.6, 156.1, 120.5, 98.1, 74.0, 30.4, 22.0, 19.1, 13.5. MS (EI): 160 (M^+, 81), 145 (100), 131 (22), 118 (78), 104 (39), 91 (45), 63 (52). Exact mass calcd. for $C_{10}H_{12}N_2$: 160.1003. Observed: 160.1001.

5-Pyrimidyl-1-pentyne (20a).[24] 2.24 g, 77 % yield obtained using the same procedure as for the preparation of **20b** with 5-bromopyrimidine (3.17 g, 20 mmol), 1-pentyne (1.36 g, 20 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (38 mg, 0.2 mmol) and Et_2NH (120 mL). IR (neat): 3041 (w), 2965 (m), 2241 (w), 1539 (m), 1412 (s), 1186 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.00 (s, 1H), 8.64 (s, 2H), 2.34 (t, J = 7.0 Hz, 2 H), 1.56 (hex, J = 7.3 Hz, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 158.6, 156.1, 120.4, 97.8, 74.1, 21.7, 21.3, 13.4. MS (EI): 146 (M^+, 100), 131 (21), 118 (52), 104 (35), 91 (54), 63 (66). Exact mass calcd. for $C_9H_{10}N_2$: 146.0843. Observed: 146.0844.

2-Pyridyl-1-pentyne (21).[24] 2.43 g, 84 % yield obtained using the same procedure as for the preparation of **20b** and **20a** with 2-bromopyridine (3.16 g, 20 mmol), 1-pentyne (1.36 g, 20 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol), CuI (38 mg, 0.2 mmol) and Et_2NH (120 mL). IR (neat): 3051 (w), 2964 (m),. 2239 (m), 1583 (s), 1465 (s), 1427 (s), 1269 (m), 779 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.26 (dd, J = 4.7 Hz, 0.6 Hz, 1H), 7.12 (dt, J = 7.7 Hz, 1.7 Hz, 1H), 7.10 (d, J = 7.7 Hz, 1H), 6.92-6.88 (m, 1H), 2.16 (t, J = 7.0 Hz, 2H), 1.40 (hex, J = 7.3 Hz, 2H), 0.80 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.6, 143.9, 135.9, 126.6, 122.1, 90.7, 80.5, 21.8, 21.2, 13.4. MS (EI): 145 (M^+, 35), 130 (54), 117 (100), 89 (18), 63 (13). Exact mass calcd. for $C_{10}H_{11}N$: 145.0891. Observed: 145.0892.

Typical procedure A for the nickel catalyzed carbozincation of substituted phenylacetylenes followed by the quenching with an electrophile. Preparation of (Z)-ethyl 2-(2,3-diphenyl-2-pentenyl)acrylate (12). $Ni(acac)_2$ (320 mg, 1.25 mmol, 25 %) and 1,2-diphenylacetylene (0.89 g, 5 mmol, 1 equiv) were dissolved in THF (3.8 mL) and NMP (1.3 mL) at –40 °C under argon. Diethylzinc (1.0 mL, 10 mmol, 2 equiv) was carefully added via syringe at –78 °C. The reaction mixture was allowed to warm to –35 °C and stirred for 2.5 h. Meanwhile a mixture of CuCN (1.79 g, 20 mmol, 4 equiv) and LiCl (1.69 g, 40 mmol, 8 equiv) was dried in vacuo at 130 °C for 2 h and then dissolved in THF (10 mL). The solution was cooled to –60 °C and added by syringe to the reaction mixture at –78 °C. The resulting dark solution was warmed to 0 °C for a few minutes and then again cooled to –78 °C. Ethyl (2-bromomethyl)acrylate **11**[10] (4.82 g, 25 mmol, 5 equiv) was added, and the reaction mixture warmed to 25 °C and worked up. The crude product was purified by flash-chromatography (hexane : ether 20 : 1) affording the ester **12** (1.13 g, 3.53 mmol, 71 % yield, $Z:E > 99:1$) as a white powder (mp = 73°C). IR (KBr): 3058 (w), 1713 (s), 1260 (s), 1164 (m), 698 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.17-7.03 (m, 10H), 6.30 (d, J = 1.5 Hz, 1H), 4.26 (q , J = 7.0 Hz, 2H), 3.70 (s, 2H), 2.63 (q, J = 7.5 Hz, 2H), 3.70 (s, 2H), 2.63 (q, J = 7.5 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.2, 143.2, 142.6, 142.5, 138.1, 132.9, 129.8, 129.7, 127.6, 127.4, 125.9, 125.7, 125.2, 60.7, 36.0, 27.8, 14.2, 12.9. MS (EI): 320 (M^+, 38). 207 (100), 169 (20), 129 (65), 91 (82). Anal. calcd. for C: 82.46, H: 7.54. Found C: 82.45, H: 7.69.

(Z)-1,2-Diphenyl-1-heptene (2a): 1.33 g, 76 % yield obtained via **typical procedure A** using 1,2-diphenylacetylene (1.24 g, 7 mmol), $Ni(acac)_2$ (449 mg, 1.74 mmol), dipentylzinc (3.8 mL, 28 mmol), THF (5.3 mL) and NMP (1.8 mL). Reaction conditions: 18 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3035 (w), 2940 (m), 1600 (m), 1490 (m), 1440 (m), 915 (w), 660 (m), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47-7.12 (m, 10 H), 6.65 (s, 1H), 2.70 (dt, J = 7.6 Hz, 1.0 Hz, 2H), 1.68-1.44 (m, 6H), 1.11-1.02 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.5, 141.4, 137.5, 129.0, 128.5,

128.4, 127.7, 126.6, 126.2, 126.0, 40.7, 31.4, 27.6, 22.5, 14.0; MS (EI): 250 (M^+, 95), 193 (75), 179 (44), 115 (79), 103 (18), 91 (100). Anal. calcd. for C: 91.14 H: 8.85. Found C: 90.91, H: 9.20.

(*Z*)-1,2-Diphenyl-1-butene (2b): 1.15 g, 79 % yield obtained via **typical procedure A** using 1,2-diphenylacetylene (1.24 g, 7 mmol). $Ni(acac)_2$ (456 mg, 1.77 mmol), diethylzinc (2.8 mL, 28 mmol), THF (5.3 mL) and NMP (1.8 mL). Reaction conditions: 3 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3035 (m), 2960 (m), 1595 (m), 1490 (m), 1460 (m), 865 (w), 765 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.44-7.10 (m, 10H), 6.61 (s, 1H). 2.68 (dq, *J* = 7.4 Hz, 1.3 Hz, 2H), 1.24 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.0, 141.6, 137.7, 129.1, 128.7, 128.6, 127.9, 126.9, 126.2, 125.3, 33.7, 13.1. MS (EI): 208 (M^+, 100), 179 (36), 115 (48), 91 (28). Anal. calcd. for C: 92.25, H: 7.74. Found C: 92.39, H: 7.80.

(*E*)-2-Methyl-1-phenyl-1-heptene (2c): 0.89 g, 67 % yield obtained via **typical procedure A** using 1-phenyl-1-propyne (0.81 g, 7 mmol), $Ni(acac)_2$ (449 mg, 1.75 mmol), dipentylzinc (5.8 mL, 28 mol), THF (5.3 mL) and NMP (1.8 mL). Reaction conditions: 20 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3030 (w), 2920 (s), 1650 (m), 1600 (m), 1380 (m), 915 (m), 750 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.19 (m, 5H), 6.29 (s, 1H), 2.21 (dt, *J* = 7.5 Hz, 0.5 Hz, 2H), 1.88 (d, *J* = 1.2 Hz, 3H), 1.59-1.50 (dq, *J* = 7.5 Hz, 0.5 Hz, 2H), 1.42-1.30 (m, 4H), 0.95 (t, 3 = 6.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.3, 138.7, 128.8, 127.9, 125.7, 124.7, 40.7, 31.5, 27.7, 22.6, 17.7, 14.0. MS (EI): 188 (M^+, 37), 131 (100), 91 (38), 55 (19). Anal. calcd. for C: 89.29, H: 10.70. Found C: 89.32, H: 10.91.

(*E*)-2-Methyl-1-phenyl-1-butene (2d): 0.74 g, 73 % yield obtained via **typical procedure A** using 1-phenyl-1-propyne (0.81 g, 7 mmol), $Ni(acac)_2$ (359 mg, 1.4 mmol), diethylzinc (2.8 mL, 28 mmol), THF (5.3 mL) and NMP (1.8 mL). Reaction conditions: 15 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3035 (w), 2960 (m), 1595 (m), 1490 (m), 1445 (m), 860 (m), 740 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46-7.30 (m, 5H), 6.41 (s, 1H), 2.32 (dq, *J* = 7.4 Hz, 1.0 Hz, 2H), 2.00 (d, J = 1.27 Hz, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.7, 138.8, 128.9, 128.0, 125.9, 123.7, 33.4, 17.7, 12.8. MS (EI): 146 (M^+, 45), 131 (100), 91 (33). Anal. calcd. for C: 90.35, H: 9.64. Found C: 90.12, H: 9.76.

(*Z*)-2-Ethyl-1-phenyl-1-decene (2e): 0.84 g, 69 % yield obtained via **typical procedure A** using 1-phenyl-1-decyne (1.07 g, 5 mmol), $Ni(acac)_2$ (320 g, 1.3 mmol), diethylzinc (1.0 mL, 10 mmol), THF (3.8 mL) and NMP (1.3 mL). Reaction conditions: 20 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3025 (w), 2935 (s), 1495 (w), 1449 (m), 940 (w), 860 (m), 755 (m), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.30-7.09 (m, 5H), 6.17 (s, 1H), 2.22-2.12 (m, 4H), 1.47-1.23 (m, 14H), 1.08 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.3, 138.7, 128.6, 127.9, 125.7, 123.6, 31.8, 30.7, 29.9, 29.7, 29.3, 29.1, 28.2, 22.5, 14.0, 12.8. MS (EI): 244 (M^+, 55), 145 (94), 131 (44), 117 (100), 104 (32), 91 (64). Anal. calcd. for C: 88.45, H: 11.54. Found C: 88.39, H: 11.69.

(Z)-2-Phenyl-1-trimethylsilyl-1-butene (2f) : 1.18 g, 82 % yield obtained via **typical procedure A** using 1-phenyl-2-trimethylsilylacetylene (1.22 g, 7 mmol), $Ni(acac)_2$ (359 mg, 1.39 mmol), diethylzinc (2.8 mL, 28 mmol, THF (5.3 mL) and NMP (1.8 mL). Reaction conditions: 20 h at-35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3045 (w), 2960 (m), 1595 (m), 1490 (m), 1440 (m), 1260 (s), 855 (s), 755, 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.16 (m, 5H), 5.60 (t, J = 1.4 Hz, 1H), 2.45 (dq, J = 7.4 Hz, 1.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.1, 144.3, 127.8, 127.6, 126.6, 125.1, 35.2, 12.5, 0.0. MS (EI): 204 (M^+, 16), 189 (82), 135 (100), 73 (63), 59 (29). Anal calcd. for C: 76.39 H: 9.86. Found C: 76.14 H: 10.05.

(Z)-2-Phenyl-1-trimethylsilyl-1-propene (2g): 0.85 g, 64 % yield obtained via **typical procedure A** using 1-phenyl-2-trimethylsilylacetylene (1.22 g, 7 mmol), $Ni(acac)_2$ (449 mg, 1.74 mmol), dimethylzinc (2.0 mL, 28 mmol), THF (5.3 mL), NMP (1.8 mL). Reaction conditions: 10 h at 0°C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3045 (w), 2960 (m), 1595 (m), 1490 (m), 1440 (m), 1260 (s), 855 (s), 755 (s), 690 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.56-7.55 (m, 2H). 7.41-7.32 (m, 3H), 6.02 (s, 1H), 2.30 (d, J = 0.6 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 151.6, 144.3, 128.0, 127.2, 125.4, 20.8, 0.0; MS (EI): 190 (M^+, 17), 175 (71), 135 (100), 73 (26). Anal. calcd. for C: 75.71, H: 9.53. Found C: 75.73, H: 9.58.

(Z)-1-Iodo-1,2-diphenyl-1-butene (4a): 1.47 g, 88 % yield (mp = 124 °C) obtained via **typical procedure A** using 1-phenyl-1-butyne (0.65 g, 5 mmol), $Ni(acac)_2$ (380 mg, 1.48 mmol), diphenylzinc (5.0 mL of a solution in diethyl ether (4.0 M, 20 mmol), THF (3.8 mL), NMP (1.3 mL) and iodine (15.2 g, 60 mmol) in THF (10 mL). Reaction conditions: 4 h at –35 °C, addition of the solution of iodine in THF at –78 °C, 5 min at –10 °C, workup with a solution of $Na_2S_2O_3$. Purification by chromatography (hexanes). IR (KBr): 3076 (w), 3051 (w), 1440 (m), 1097 (w), 841 (m), 759 (m), 694 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.30 (m, 10H), 2.42 (q, J = 7.5 Hz, 2H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 151.5, 145.8, 144.3, 128.5, 128.4, 128.3, 128.2, 127.7, 127.3, 97.4, 29.0, 13.3; MS (EI): 334 (M^+, 22), 207 (94), 178 (27), 129 (100), 91 (53). Anal. calcd. for C: 57.50, H: 4.52. Found C: 57.52, H: 4.62.

(E)-1-Iodo-1,2-diphenyl-1-butene (4b): 1.18 g, 71 % yield obtained via **typical procedure A** using 1,2-diphenylacetylene (0.89 g, 5 mmol), $Ni(acac)_2$ (320 mg, 1.25 mmol), diethylzinc (1.0 mL, 10 mmol), THF (3.8 mL), NMP (1.3 mL) and iodine (10.1 g, 40 mmol) in THF (10 mL). Reaction conditions: 3 h at -35 °C, addition of the solution of iodine in THF at -78 °C, 5 min at -10 °C, workup with an aq. solution of $Na_2S_2O_3$. Purification by chromatography (hexanes). IR (neat): 3077 (m), 3056 (m), 2930 (m), 1598 (m), 1488 (m), 1441 (m), 1078 (m), 1036 (m), 762 (m), 733 (m), 694 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.14-7.00 (m, 10H), 2.87 (q, J = 7.5 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.2, 144.5, 139.6, 129.8, 129.0, 127.7, 127.5, 126.9, 126.5, 98.9, 38.6, 11.8. MS (EI): 334 (M+, 14), 207 (98), 178 (38), 129 (100), 91 (48). Anal calcd. for C: 57.50, H: 4.52; Found C: 57.40, H: 4.24.

(Z)-1-Benzyloxy-3-phenyl-2-pentene (8a): 320 mg, 56 % yield obtained via **typical procedure A** using **7a** (500 mg, 2.25 mmol) with Et_2Zn (550 mg, 0.46 mL, 2 eq) and $Ni(acac)_2$ (140 mg, 0.54 mmol). Reaction conditions: -78 °C to –35 °C, 1 h then usual workup. Purification by flash chromatography (ether : hexane 1 :

25-1 : 9). IR (neat): 3033 (s), 2876 (s), 1453 (m), 1384 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.32-7.00 (m, 10H), 5.61 (dt, *J* = 6.8 Hz, 1H), 4.33 (s, 2H), 3.85 (dd, *J* = 7 Hz, 2H), 2.33 (9, *J* = 7.5 Hz, 2H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 146.1, 139.4, 137.4, 127.3, 127.1, 127.0, 126.8, 126.7, 126.6, 121.0, 71.1, 66.6, 30.8, 11.7; MS (EI): 252 (M^+, 0.1), 239 (1), 162 (8), 135 (22), 117 (22), 106 (8), 105 (100), 91 (5), 77 (25), 28 (31). Exact mass calcd. for $C_{18}H_{20}O$: 252.1514. Observed: 252.1516.

(*Z*)-1-Triisopropylsiloxy-3-phenyl-2-pentene (8b): 700 mg, 73 % yield obtained via **typical procedure A** using **7b** (864 mg, 3 mmol) with Et_2Zn (740 mg, 0.61 mL, 6.0 mmol) and $Ni(acac)_2$ (190 mg, 0.75 mmol). Reaction conditions: -78 °C to –35 °C, 0.5 h then usual workup. The crude reaction mixture was purified by flash-chromatography (hexanes). IR (neat): 2961 (s), 2942 (s), 1463 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.33-7.15 (m, 3H), 7.10-7.01 (m, 2H), 5.56 (dt, 1H, *J* = 6.5 Hz, 1H), 4.06 (dt, 2H, *J* = 6.5 Hz, 1H), 2.40-2.23 (m, 2H), 1.01-0.87 (m, 24H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 144.2, 141.0, 128.6, 128.3, 127.2, 126.1, 61.5, 32.0, 18.4, 13.2, 12.4. MS (EI): 318 (M^+, 1), 275 (79), 145 (29), 131 (100), 109 (14), 103 (60), 91 (12). Anal. calcd. for C: 75.40, H: 10.76; Found: C: 75.25, H: 10.63.

(*Z*)-1-Triisopropylsiloxy-3-phenyl-4-methyl-2-pentene (8c): 680 mg, 68 % yield obtained via **typical procedure A** using **7b** (864 mg, 3 mmol) with diisopropylzinc (6.40 M in ether, 1.5 mL) and $Ni(acac)_2$ (190 mg, 0.75 mmol). Reaction conditions: -78°C to –35 °C, 1 h then usual workup. Purification by flash-chromatography (hexanes). IR (neat): 3062 (s), 3028 (s), 2926 (m), 1493 (s), 1453 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.31-7.14 (m, 3H), 7.06-7.00 (m, 2H), 5.45 (dt, 1H, *J* = 6.5 Hz, 1H), 4.01 (dd, 2H, *J* = 6.5 Hz, 1H), 2.62-2.46 (m, 1H), 1.02-0.80 (m, 27 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.9, 140.4, 128.4, 127.6, 126.5, 124.5, 61.2, 35.3, 21.5, 17.8, 11.8; MS (EI): 332 (M^+, 4), 290 (26), 289 (100), 159 (11), 131 (31), 117 (31), 75 (22), 43 (23). Exact mass calcd. for $C_{31}H_{36}OSi$: 332.2535. Observed: 332.2534.

3,3-Diphenylprop-2-en-1-ol (8d): 1-Triisopropylsiloxy-3,3-diphenyl-2-pentene (366 mg, 1 mmol) obtained via **typical procedure A** using **7b** (288 mg, 1 mmol) with $Ni(acac)_2$ (64 mg, 25 mol%) and Ph_2Zn (1.32 M, 4.5 mL, 2.0 mmol), was treated with Bu_4NF (1.1 mL of a 1 M solution in THF , 1.1 mmol) at 0 °C for 0.5 h. The solution was further stirred for 0.5 h at 25°C, and sat. aq. NH_4Cl (5 mL) was added. The aqueous phase was extracted with ether (3 x 5 mL), the combined organic layer was dried over $MgSO_4$, and the solvents were evaporated. The crude residue was purified by flash-chromatography (ether : hexane 1 : 9), affording the alcohol **8d** (135 mg, 64 % yield). IR (neat): 3434 (w), 2921 (m), 2852 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 7.40-7.10 (m, 10H), 6.28 (t, J = 7 Hz, 1H), 4.24 (d, 7Hz, 1H), 1.76-1.70 (bs, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 147.7, 144.0, 139.0, 129.7, 128.2, 128.1, 127.6, 127.5, 60.6. MS (EI): 210 (M^+, 100), 192 (23), 167 (80), 165 (27), 105 (41), 103 (52) , 91 (36), 28 (41). Exact mass calcd. for $C_{14}H_{15}O$: 210.1040. Observed: 210.1043.

(*E*)-3,4-Diphenyl-3-hexen-2-one (10a): 0.73 g, 58 % yield (mp = 92 °C) obtained by **typical procedure A** using 1,2-diphenylacetylene (0.89 g, 5 mmol), $Ni(acac)_2$ (320 mg, 1.75 mmol), diethylzinc (1.0 mL, 10 mmol), THF (3.8 mL), NMP (1.3 mL), CuCN (1.79 g, 20 mmol), LiCl (1.69 g, 40 mmol) and acetyl chloride (2.0 mL, 28 mmol) in THF (10 mL). Reaction conditions: 3 h at –35 °C, transmetalation: -78 °C to 0 °C, addition of acetyl chloride at –78 °C, 3 h at –35 °C, then usual workup. Purification by chromatography (hexane : diethyl

ether 40 : 1 to 20 : 1). IR (KBr): 3077 (w), 3020 (m), 1687 (ss), 1486 (m), 1443 (m), 1350 (m), 1186 (m), 771 (s), 760 (ss), 573 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.15-6.95 (m, 10H), 2.63 (q, J = 7.5 Hz, 2H), 2.16 (s, 3H), 1.04 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 204.3, 146.9, 140.3, 140.2, 137.3, 130.0, 129.1, 128.2, 127.8, 127.0, 126.9, 30.5, 29.2, 13.3. MS (EI): 250 (M^+, 100), 207 (43), 178 (31), 129 (83), 91 (53), 43 (62). Anal. calcd. for C: 86.36, H: 7.24. Found. C: 86.61,. H: 6.97.

(*E*)-1,2,3-Triphenyl-2-penten-1-one (10b): 0.86 g, 55 % yield obtained by **typical procedure A** using 1,2-diphenylacetylene (0.89 g, 5 mmol), $Ni(acac)_2$ (320 mg, 1.75 mmol), diethylzinc (1.0 mL, 10 mmol), THF (3.8 mL), NMP (1.3 mL), CuCN (1.79 g, 20 mmol), LiCl (1.69 g, 40 mmol) and benzoyl chloride (3.25 mL, 28 mmol) in THF (10 mL). Reaction conditions: 3 h at –35 °C, transmetalation: -78 °C to 0 °C, addition of benzoyl chloride at –78 °C, 1 h at –35 °C, usual workup. Purification by chromatography (hexane : diethyl ether 20 : 1). IR (neat): 3058 (w), 2970 (m), 1665 (ss), 1597 (m), 1449 (m), 1261 (s), 762 (s), 699 (ss) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.06-8.05 (m, 2H), 7.47-7.38 (m, 3H), 7.18-7.16 (m, 5H), 7.04-6.99 (m, 5H), 2.42 (q, J = 7.5 Hz, 2H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 198.2, 144.2, 139.7, 137.4, 136.7, 136.6, 133.3, 129.8, 129.6, 129.4, 128.7, 128.2, 128.1, 126.9, 29.6, 12.9; MS (EI): 312 (M^+, 67), 297 (31), 178 (18), 129 (19), 105 (69), 84 (100). Exact mass calcd. for $C_{23}H_{20}O$: 312.15045. Observed: 312.1535.

(*E*)-1-Iodo-2-phenyl-1-trimethylsilyl-1-butene (14): 1.40 g, 61 % yield obtained via **typical procedure A** using 1-phenyl-2-trimethylsilylacetylene (1.22 g, 7 mmol), $Ni(acac)_2$ (449 mg, 1.74 mmol), diethylzinc (2.8 mL, 28 mmol), THF (5.3 mL), NMP (1.8 mL), iodine (9.90 g, 39 mmol) in THF (15 mL). Reaction conditions: 30 h, at –35 °C, addition of the solution of iodine in THF at -78°C, 5 min at -10°C, workup with an aq. solution of $Na_2S_2O_3$. Purification by chromatography (hexanes). IR (neat): 3045 (w), 2960 (m), 1595 (m), 1490 (m), 1440 (m), 1250 (s), 865 (ss), 765 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.30 (m, 3H), 7.12-7.09 (m, 2H), 2.75 (q, J = 7.4 Hz, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 161.3, 141.7, 128.4, 127.8, 127.3, 110.3, 41.2, 11.0, 0.0. MS (EI): 330 (M^+, 4), 315 (3), 203 (23), 185 (25), 73 (100). Exact mass calcd. for $C_{13}H_{19}SiI$: 330.03030. Observed: 330.03010.

(*E*)-2-Phenyl-1-thienyl-1-hexene (22a): 0.29 g, 67 % yield obtained via **typical procedure A** using **19a** (0.29 g, 1.76 mmol), $Ni(acac)_2$ (113 mg, 0.44 mmol), diphenylzinc (3.0 mL) of a solution in diethyl ether (2.38 M), 7.0 mmol) THF (2.0 mL) and NMP (1.0 mL). Reaction conditions: 18 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3059 (w), 2956 (m), 1597 (w), 1466 (m), 1426 (w), 854 (w), 761 (m), 696 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.62-7.12 (m, 8H), 6.97 (s, 1H), 3.04-2.99 (m, 2H), 1.70-1.51 (m, 4H), 1.06 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.4, 141.7, 141.2, 128.5, 127.9, 127.3, 127.0, 126.6, 125.0, 121.0, 31.5, 30.6, 23.1, 14.1. MS (EI): 242 (M^+, 100), 199 (63), 165 (25), 154 (43), 115 (32), 91 (31). Exact mass calcd. for $C_{16}H_{18}S$: 242.1126. Observed: 242.1123.

(*E*)-2-Phenyl-1-thienyl-1-pentene (22b): 0.74 g, 64 % yield obtained via **typical procedure A** using **19b** (0.75 g, 5 mmol), Ni (acac)$_2$ (321 mg, 1.25 mmol), diphenylzinc (8.5 mL of a solution in diethyl ether (2.38 M), 20 mmol) THF (2 mL) and NMP (2 mL). Reaction conditions: 24 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3060 (w), 2959 (m), 1597 (w), 1467 (m), 854 (w), 762 (m), 696 (s) cm^{-1};

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63-7.59 (m, 2H), 7.51-7.38 (m, 4H), 7.19-7.16 (m, 2H), 7.01 (s, 1H), 3.05-3.00 (m, 2H), 1.74 (dhex, *J* = 7.3 Hz, 2.7 Hz, 2H), 1.16 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.3, 141.5, 141.1, 128.5, 127.9, 127.2, 127.0, 126.5, 125.0, 121.2, 33.6, 21.8, 14.3. MS (EI): 228 (M^+, 50), 199 (67), 115 (24), 84 (100). Exact mass calcd. for $C_{15}H_{16}S$: 228.0974. Observed: 228.0973.

(*Z*)-2-Ethyl-1-thienyl-1-pentene (22c): 0.45 g, 63 % yield obtained via **typical procedure A** using **19b** (0.60 g, 4 mmol), $Ni(acac)_2$ (257 mg, 1 mmol), diethylzinc (1.0 mL, 10 mmol). THF (3.0 mL) and NMP (1.0 mL). Reaction conditions: 7.5 h at –35 °C, then usual workup. Purification by chromatography (hexanes). IR (neat): 3069 (w), 2961 (s), 1677 (w), 1458 (m), 1431 (w), 1241 (w), 1048 (w), 855 (m), 690 cm^{-1}; ^{13}C NMR ($CDCl_3$, 75 MHz): 7.23-7.21 (m, 1H), 7.05-7.02 (m, 1H), 6.96-6.95 (m, 1H), 6.43 (s, 1H), 2.47-2.42 (m, 2H), 2.26 (dq, *J* = 7.4 Hz, 1.2 Hz, 2H), 1.68-1.55 (m, 2H), 1.17 (t, *J* = 7.4 Hz, 3H). 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.7, 141.4, 126.1, 123.8, 117.1, 34.2, 30.9, 21.4, 14.5, 13.0. MS (EI): 180 (M^+, 93), 151 (100), 137 (48), 123 (19), 97 (35). Exact mass calcd. for $C_{11}H_{16}S$: 180.0970. Observed: 180.0972.

(*E*)-1-Iodo-2-phenyl-1-thienyl-1-pentene (22d): 0.77 g, 58 % yield obtained via **typical procedure A** using **19b** (0.56 g, 3.73 mmol), $Ni(acac)_2$ (239 mg, 0.93 mmol), diphenylzinc (6.3 mL of a solution in diethyl ether (2.38 M), 15 mmol), THF (2 mL), NMP (2 mL) and iodine (11.4 g, 45 mmol) in THF (10 mL). Reaction conditions: 24 h at -35 °C, addition of the solution of iodine in THF at -78 °C, 5 min at -10 °C, workup with an aq. solution of $Na_2S_2O_3$. Purification by chromatography (hexanes). IR (neat): 302 (m), 2959 (s), 1489 (s), 1462 (s), 1228 (s), 1107 (s), 792 (s), 705 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47–7.05 (m, 8H), 2.60–2.55 (m, 2H), 1.43 (hex, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H); ^{1}H NMR ($CDCl_3$, 75 MHz): δ 153.8, 146.5, 146.3, 128.5, 128.1, 127.6, 127.5, 126.9, 126.0, 87.9, 38.5, 22.0, 13.9. MS (EI): 354 (M^+ 25), 227 (100), 184 (17), 154 (29), 143 (43), 128 (25), 117 (45), 97 (67). Exact mass calcd. for $C_{15}H_{15}S$ = 353.9944. Observed: 353.9939.

(*Z*)-2-Ethyl(-1-(5-pyrimidyl)-1-pentene (22e): 0.68 g, 77 % yield obtained via **typical procedure A** using **20a** (0.73 g, 5 mmol), $Ni(acac)_2$ (321 mg, 1.25 mmol), diethylzinc (2.0 mL, 20 mmol), THF (3.8 mL) and NMP (1.3 mL). Reaction conditions: 48 h at -35 °C, workup with an aq. solution of $Na_2S_2O_3$. Purification by chromatography (hexane : ethyl acetate 9 : 1). IR (neat): 3040 (w), 2962 (s), 1647 (m), 1549 (s), 1458 (m), 1411 (s), 728 (s), 631 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.88 (s, 1H), 8.43 (s, 2H), 5.96 (s, 1H), 2.13-2.01 (m, 4H), 1.41-1.29 (d hex, *J* = 7.3 Hz, 2.0 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.9, 155.7, 150.2, 132.0, 116.3, 32.9, 29.8, 21.3, 13.8, 12.3. MS (EI): 176 (M^+, 78), 147 (100), 133 (49), 120 (45), 107 (26), 83 (26), 77 (21). Exact mass calcd. for $C_{11}H_{16}N_2$: 176.1313. Observed: 176.1314.

(*Z*)-2-Ethyl-1-iodo-1-(5-pyrimidyl)-1-pentene (22f): 0.29 g, 64 % yield obtained via **typical procedure A** using **20a** (0.22 g, 1.5 mmol), $Ni(acac)_2$ (96 mg, 0.37 mmol), diethylzinc (0.6 mL, 6 mmol), THF (2 mL), NMP (1 mL) and iodine (4.50 g, 18 mmol) in THF (5 mL). Reaction conditions: 48 h at -35 °C, addition of the solution of iodine in THF at -78 °C, 5 min at -10 °C, workup with an aq. solution of $Na_2S_2O_3$. Purification by chromatography (hexane : ethyl acetate 9 : 1). IR (neat): 3038 (w), 2964 (s), 1566 (m), 1463 (m), 1408 (s), 1184

(m), 863 (m), 726 (m), 630 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.00 (s, 1H), 8.53 (s, 2H), 2.40 (q, *J* = 7.6 Hz, 2H), 2.01-1.94 (m, 2H), 1.34 (hex, *J* = 7.4 Hz, 2H), 1.05 (t, *J* = 7.6 Hz, 3H), 0.71 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.7, 156.3, 153.6, 138.6, 85.0, 34.2, 34.0, 21.7, 13.6, 11.7. MS (EI): 302 (M^+, 30), 175 (100), 133 (47), 119 (33), 107 (71), 91 (29), 77 (19), 69 (38), 55 (36). Exact mass calcd. for $C_{11}H_{15}N_2I$: 302.0283. Observed: 302.0280.

(*Z*)-5-Ethyl-4-(5-pyrimidyl)-1,4-nonadiene (22g): 0.40 g, 35 % yield obtained via **typical procedure A** using **20b** (0.8 g, 5 mmol), $Ni(acac)_2$ (321 mg, 1.25 mmol), diethylzinc (2.0 mL, 20 mmol), THF (3.8 mL), NMP (1.3 mL), CuCN (3.58g, 40 mmol), LiCl (3.39 g, 80 mmol) and allyl bromide (7.25 g, 60 mmol) in THF (12 mL). Reaction conditions: 48 h at -35 °C, transmetallation: -78 °C to 0 °C, addition of allyl bromide at -78 °C, 5 min at 25°C, then usual workup. Purification by chromatography (hexane : ethyl acetate 9 : 1). IR (neat): 3079 (w), 2960 (s), 1695 (m), 1551 (m), 1459 (m), 1411 (s), 915 (w), 732 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.02 (bs, 1H), 8.43 (bs, 2H), 5.66-5.53 (dq, *J* = 6.4 Hz, 2.6 Hz, 1H), 4.93-4.82 (m, 2H), 3.00 (d, *J* = 6.4 Hz, 2H), 2.17 (q, *J* = 7.6 Hz, 2H), 1.78 (t, *J* = 7.5 Hz, 2H), 1.27-1.17 (m, 2H), 1.14-1.02 (m, 2H), 1.04-1.00 (t, J = 7.6 Hz, 3H), 0.70 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.8, 156.4, 144.0, 134.8, 125.8, 116.5, 38.4, 32.4, 31.1, 24.2, 22.7, 13.8, 13.4. MS (EI): 230 (M^+, 100), 145 (73), 133 (35), 107 (25), 93 (35), 77 (24). Exact mass calcd. for $C_{15}H_{22}N_2$: 230.1782. Observed: 230.1783.

(*E*)-2-Phenyl-1-(2-pyridyl)-1-pentene (22h): 0.64 g, 67 % yield obtained via **typical procedure A** using **21** (0.62 g, 4.27 mmol), $Ni(acac)_2$ (230 mg, 0.89 mmol), diphenylzinc (8.5 mL of a solution in diethyl ether (0.5 M), 4.25 mmol), THF (3.8 mL) and NMP (1.3 mL). Reaction conditions: 20 h at -35 °C, then usual workup. Purification by chromatography (hexane : ethyl acetate 9 : 1). IR (neat): 3056 (w), 2959 (m), 1627 (m), 1584 (s), 1493 (m), 1445 (m), 760 (m), 698 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.68 (d, *J* = 3.4 Hz, 1H), 7.66 (dt, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.58-7.55 (m, 2H), 7.44-7.30 (m, 4H), 7.13 (dt, *J* = 5.0 Hz, 1.7 Hz, 1H), 6.78 (s, 1H), 3.11 (t, *J* = 7.6 Hz, 2H), 1.56 (hex, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.2, 149.2, 147.5, 143.3, 135.9, 128.3, 127.4, 127.3, 126.7, 124.3, 121.0, 32.4, 22.0, 14.1. MS (EI): 223 (M^+, 100), 208 (90), 194 (44), 93 (22). Exact mass calcd. for $C_{16}H_{17}N$: 223.1363. Observed: 223.1361.

Cross-coupling of the alkenyl iodide 4a with an arylzinc bromide. Preparation of Z-tamoxifen-hydrochloride (17). A three-necked-flask was charged with 1-iodo-4-dimethylaminoethoxybenzene (4.39 g, 4.8 mmol) in THF (5 mL) was cooled to –78 °C. N-Butyllithium (3.6 mL, 4.96 mmol, 1.38 M solution in hexane) was dropwise added and the reaction mixture was stirred for 15 min at –78 °C, warmed to –40 °C and $ZnBr_2$ (1.08 g, 4.8 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to 0 °C and a solution of (*Z*)-1-iodo-1,2-diphenyl-1-butene **4a** (1.47 g, 4.40 mmol), $Pd(dba)_2$ (92 mg, 0.16 mmol) and PPh_3 (0.17 g, 0.64 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to 25 °C and heated at 55 °C for 10 h. After the usual workup and evaporation of the solvents, the crude product was dissolved in ether. An etheral solution of HCl (20 mL) was added. The solvent was evaporated and the crude residue was purified by recrystallization from hexane : ethyl acetate (1 : 1) affording (*Z*)-tamoxifen hydrochloride (**17**) (1.22 g, 75 % yield, mp = 189 °C). IR(KBr): 3454 (bs), 3047 (w), 3028 (w), 1604 (m), 1507 (m), 1237 (s), 697 (m) cm^{-1}; ^1H NMR (d_6-DMSO, 300 MHz): δ 10.38 (bs, 1H), 7.37-7.09 (m, 10H), 6.68 (dd, *J* = 33 Hz, 9 Hz, 4H),

4.17 (m, 2H), 3.36 (m, 2H), 2.73 (s, 6H), 2.33 (q, J = 7.5 Hz, 2H), 0.81 (t, J = 7.5 Hz, 3H); ^{13}C NMR (d_6 -DMSO, 75 MHz): δ 155.4, 143.1, 141.6, 140.9, 137.7, 135.6, 131.3, 129.3, 128.8, 128.2, 127.9, 126.6, 126.1, 113.6, 62.1, 55.2, 42.7, 28.4, 13.2. MS (EI): 371 (M^+-[HCl], 5)), 277 (1), 72 (22), 58 (100). Exact mass calcd. for $C_{26}H_{29}ON$: 371.21908. Observed: 371.22488.

(*Z*)-1,2-Diphenyl-1-(4-triisopropylsiloxyphenyl)-1-butene (16): 1.10 g, 81 % yield was obtained using the same procedure as used for the preparation of **17** with **4a** (1.0 g, 3 mmol), $Pd(dba)_2$ (78 mg, 0.14 mmol), PPh_3 (150 mg, 0.57 mmol) in THF (5 ml), 1-iodo-4-triisopropylsilyloxybenzene (1.35 g, 3.6 mmol), N-butyllithium (2.48 mL of a solution in hexane (1.5 M), 3.7 mmol) and $ZnBr_2$ (0.81 g, 3.6 mmol) in THF (6 mL). Reaction conditions: 10 h at 55 °C, usual workup. Purification by chromatography (hexanes). IR (neat): 3056 (w), 3028 (m), 2944 (m), 1603 (m), 1506 (s), 1463 (m), 1264 (s), 912 (m), 883 (m), 724 (m), 702 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.47-7.38 (m, 5H), 7.28-7.26 (m, 5H), 6.80 (dd, J = 57 Hz, 8.6 Hz, 4H), 2.64 (q, J = 7.5 Hz), 1.45-1.14 (m, 21 H), 1.08 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.2, 143.8, 142.5, 141.4, 138.7, 136.2, 131.9, 129.8, 129.5, 128.1, 127.9, 126.6, 126.0, 119.1, 28.9, 18.0, 13.7, 12.7. MS (EI): 456 (M^+, 100), 413 (23), 207 (46), 178 (23), 129 (81), 105 (23), 91 (43). Anal calcd. for C: 81.52, H: 8.82. Found C: 81.14, H: 9.25.

Intramolecular nickel catalyzed carbozincation. Preparation of (*E*)-2-phenyl-1-hexylidenylcyclopentane (26a) : $Ni(acac)_2$ (96 mg, 0.37 mmol, 7 mol %) was dissolved in THF (3.8 mL) and NMP (1.3 mL) at -40 °C under argon and 1-iodo-4-phenyl-5-hexyne (**25**) (1.41 g, 5 mmol, 1 equiv) was added. At -78 °C, $Pent_2Zn$ (2.0 mL, 10 mmol, 2 equiv) was carefully added by syringe. The reaction mixture was stirred for 30 h at -40 °C. After the usual workup, the solvents were evaporated, and the crude residue was purified by chromatography (hexanes) to give the cyclized product (**26a**) (0.74 g, 3.24 mmol, 62 % yield: $E : Z > 99 : 1$) as a colorless oil. IR (neat): 3030 (w), 2925 (s), 1610 (w), 1490 (m), 1460 (m), 770 (m), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29-7.13 (m, 5H), 4.90-4.83 (m, 1H), 3.49-3.47 (m, 1H), 2.42-2.34 (m, 2H), 2.11-1.83 (m, 4H), 1.70-1.61 (m, 2H), 1.32-1.19 (m, 6H), 0.85 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.3, 145.8, 128.5, 128.2, 125.8, 123.5, 51.6, 36.8, 31.7, 29.7, 29.6, 29.2, 24.7, 22.6, 14.1. MS (EI): 228 (M^+, 40), 173 (44), 158 (47), 143 (44), 129 (57), 117 (74), 91 (100). Anal. calcd. for C: 89.40, H: 10.59; Found C: 89.35, H: 10.48.

(*E*)-2-Phenyl-1-propylidenylcyclopentane (26b): 0.59 g, 62 % yield was obtained using the same procedure as used for the preparation of **26a** with **25** (1.41 g, 5 mmol), $Ni(acac)_2$ (96 mg, 0.37 mmol), diethylzinc (1.0 mL, 10 mmol), THF (3.8 mL) and NMP (1.3 mL). Reaction conditions: 20 h at -40 °C, usual workup. Purification by chromatography (hexanes). IR (neat): 3035 (w), 2962 (s) 1600 (w), 1495 (m), 1465 (m), 1030 (w), 760 (m), 695 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.24 (m, 5H), 5.00-4.93 (m, 1H), 3.59-3.56 (m, 1H), 2.62-2.38 (m, 2H), 2.26-1.90 (m, 4H), 1.86-1.68 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.6, 145.5, 128.3, 128.0, 125.7, 51.3, 36.5, 29.2, 24.5, 22.7, 13.8. MS (EI): 186 (M^+, 66), 157 (100), 143 (38), 129 (66), 115 (39), 91 (70). Exact mass calcd. for $C_{14}H_{18}$: 186.14375. Observed: 186.14085.

5-Chloropentylidenylcyclopentane (29): 0.70 g, 68 % yield was obtained using the same procedure as used for the preparation of **26a-b** with **28** (1.24 g, 6 mmol), $Ni(acac)_2$ (116 mg, 0.45 mmol), di(4-chlorobutyl)zinc[25] (12 mmol in THF (1.0 mL)), THF (4.5 mL) and NMP (1.5 mL). Reaction conditions: 24 h at -40 °C, usual

workup. Purification by chromatography (hexanes). IR (neat): 2935 (s), 1440 (m), 920 (w), 740 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.19-5.12 (m, 1H), 3.46 (t, J = 6.8 Hz, 2H), 2.16-2.07 (m, 4H), 1.93-1.91 (m, 2H), 1.74-1.69 (m, 2H), 1.62-1.23 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.6, 119.2, 44.9, 33.4, 32.1, 28.6, 28.5, 26.8, 26.3, 26.2. MS (EI): 172 (M^+, 13), 95 (100), 82 (39), 67 (87), 41 (36). Exact mass calcd. for $C_{10}H_{17}Cl$: 172.09974. Observed: 172.10184.

Alkylation of 1-trimethylsilyl-5-iodopentyne (30) with organozincs. Preparation of 1-trimethylsilyl-1-heptyne (31a). [26] A 50 mL-three-necked flask equipped with an argon inlet, an internal thermometer and a rubber septum was charged with $Ni(acac)_2$ (192 mg, 0.75 mmol) and was flushed with argon. At -40 °C THF (7.5 mL), NMP (2.5 mL) and **30** were successively added via syringe. At -78 °C diethylzinc (2.0 mL, 20 mmol) was carefully added via syringe. The mixture was allowed to stir for 20 h at -35 °C. It was worked up with an ice cold solution of aq. NH_4Cl and then extracted with diethyl ether. The organic layer was dried ($MgSO_4$) and the solvents were distilled off. The crude product was purified by chromatography (hexanes) affording **31a** (1.02 g, 6.1 mmol, 61 %) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.20 (t, J = 7.0 Hz, 2H), 1.53 (q, J = 7.0 Hz, 2H), 1.43-1.27 (m, 4H), 0.93-0.88 (m, 3H), 0.00 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 107. 5, 84.0, 30.8, 28.1, 21.9, 19.6, 13.7, 0.0.

1-Trimethylsilyl-1-decyne (31b): 1.26 g, 60 % yield was obtained using the same procedure as used for the preparation of **31a** with **30** [23] (2.66 g, 10 mmol), $Ni(acac)_2$ (192 mg, 0.75 mmol), dipentylzinc (4.15 mL, 20 mmol), THF (7.5 mL) and NMP (2.5 mL). Reaction conditions: 48 h at -35 °C, usual workup. Purification by chromatography (hexanes). IR (neat): 2945 (s), 2190 (m), 1460 (m), 1260 (s), 865 (ss), 770 (s), 695 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 2.13 (t, J = 7.0 Hz, 2H), 1.46-1.13 (m, 12H), 0.82-0.79 (m, 3H), 0.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 107.5, 84.0, 31.6, 28.9, 28.8, 28.6, 28.4, 22.4, 19.6, 13.8, 0.0. MS (EI): 195 (M^+-[CH_3], 65), 73 (100), 59 (40), 28 (84). Exact mass calcd. for $C_{12}H_{23}Si$: 195.15629. Observed: 195.15689.

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