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Preparation of Polyfunctional Aryl and Alkenyl Zinc Halides from Functionalized Unsaturated Organolithiums and their Reactivity in Cross-Coupling and Conjugated Addition Reactions

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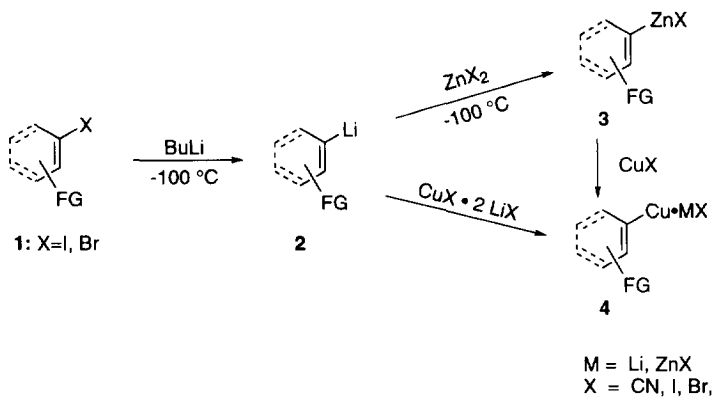
Dedicated to Professor Ei-ichi Negishi on the occasion of his 60th birthday and for his numerous contributions to organic and organometallic chemistry

Abstract: Functionalized aryl and alkenyl iodides undergo an iodine-lithium exchange at -90 to -80 °C providing polyfunctional organolithiums which are stable for a short time at these low temperatures and can be transmetalated to organozinc derivatives by the addition of zinc bromide. The resulting unsaturated organozinc halides can then be warmed up and are perfectly stable at 25 °C. They react directly with tosyl cyanide. In the presence of CuCN·2LiCl, they add in a Michael-fashion to alkylidenemalonates. In the presence of catalytic amounts of $Pd(dba)_2$ and TPP or TFP, they undergo readily a cross-coupling at 25 °C with aryl and alkenyl iodides. The Pd-catalyzed coupling of arylzinc bromides with aryl triflates could also be achieved by using dppf as a ligand and 60 °C as reaction temperature.

Introduction

Organozinc halides are useful organometallic intermediates in organic synthesis due to their broad functional group tolerance which allows the preparation of highly functionalized derivatives.[1] Furthermore, their excellent transmetalation ability allows to perform a number of high yield reactions with organic electrophiles in the presence of copper,[1,2] palladium[3] and titanium[4,5] salts. Whereas primary and secondary alkylzinc iodides are conveniently prepared by the direct insertion of commercially available zinc dust into alkyl iodides,[2] this procedure meets only little success with aryl and alkenyl iodides due to the higher energy of the Csp^2-I bond and to its higher stability. Furthermore, the direct zinc insertion to pure E- or Z-alkenyl iodides affords mixtures of E- and Z-alkenylzinc compounds.[6] The use of highly activated zinc powders[7,8] solves partly the problem but the scope of this approach seems somewhat limited. The preparation of activated zinc[7,8] on a large scale is not convenient

and a more straightforward approach to aryl and alkenyl zinc derivatives consists of using a halogen-lithium exchange reaction followed by a low temperature transmetalation with zinc salts.[9] Although alkyllithiums do not tolerate the presence of functionalities, *aryl-* and *alkenyl*-lithium compounds are far less reactive and tolerate a range of functional groups (nitrile, ester, chloride, nitro group) at low temperature.[9-11] Thus, we have found that various functionalized alkenyl and aryl halides **1** can be converted at low temperature (-100 to -80 °C) to the corresponding lithium reagent of type **2** by a halogen-lithium exchange.[12] The transmetalation of **2** to the corresponding organozinc compound of type **3** is readily achieved by the addition of a zinc halide.[9]



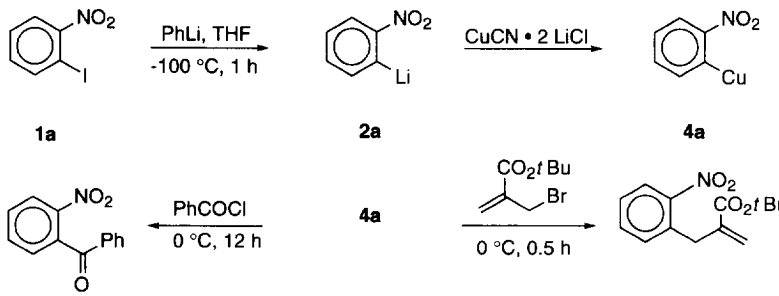
Scheme 1

The lithium reagent **2** has been converted by a transmetalation using the THF soluble copper salt CuX·2 LiX, to a functionalized aryl- or alkenyl-copper of type **4**.[9,13] Whereas the original lithium species **2** are stable only at low temperature and can only be reacted cleanly with reactive carbonyl compounds,[11] the newly formed zinc and copper compounds of type **3** and **4** are stable at 0 °C and are easy to use for further transformations. Herein we wish to describe the scope of this preparation method and demonstrate the synthetic utility of the zinc and copper reagents for performing cross-coupling reactions[14] and Michael additions.

Results and Discussion

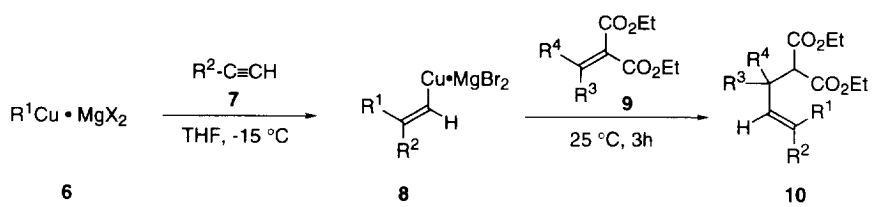
The treatment of various functionalized aryl halides (X = I or Br) and alkenyl iodides with *n*-BuLi (1.05 equiv of a ca. 1.6 M solution in hexanes) in a THF-ether-pentane mixture (4:1:1)[15] at -100 °C for 5 min affords soluble organolithium species which after an immediate treatment at -100 °C with a THF solution of ZnI_2 or $ZnBr_2$ provide the corresponding functionalized arylzinc halides of type **3**. These zinc reagents are stable for several days at rt in strong contrast to the lithium precursors. Interestingly, functional groups like an ester, nitrile, chloride, azide or even nitro are tolerated in this procedure. For the generation of *o*-lithionitrobenzene **2a**, the iodine-lithium exchange is best performed with phenyllithium according to Fréchet[11j] (Scheme 2). The addition of a THF solution of CuCN·2 LiCl (1 equiv) at -90 °C

to **2a** produces *o*-nitrophenylcopper **4a** which by the reaction with benzoyl chloride (0.7 equiv; 0 °C, 12 h) produces *o*-nitrobenzophenone **5a**[16] in 75 % yield and by allylation with *t*-butyl α-(bromomethyl)acrylate[17] (0.7 equiv; 0 °C, 0.5 h) gives the unsaturated ester **5b** in 79 % yield (Scheme 2).



Scheme 2

The reactivity of aryl and alkenyl copper species generated by an iodine-lithium exchange towards Michael acceptors such as ethyl propiolate, nitro olefins and alkylidenemalonates was first examined. Since aryl and alkenyl copper reagents are considerably less reactive than their alkyl-counterparts and since almost no addition reactions of alkenylcoppers to alkylidenemalonates was reported,[18] a preliminary study was performed by preparing alkenylcoppers via the carbocupration of alkynes (Scheme 3 and Table 1).[19]



Scheme 3

Table 1. Unsaturated malonic esters **10** prepared by the addition of pure *E*-alkenylcopper **8** to alkylidenemalonates **9**

entry	product **10**	R^1	R^2	R^3	R^4	yield (%)[a]
1	**a**	Et	Pent	Me	Me	60
2	**b**	Et	Pent	Me	H	80
3	**c**	Et	Pent	Pr	H	58
4	**d**	Et	Pent	*i*Pr	H	71
5	**e**	Bu	Pent	*i*Pr	H	68[b]
6	**f**	Et	Pent	Ph	H	90[b]
7	**g**	Bu	Dec	Ph	H	70
8	**h**	Et	Pent	H	H	67[c]
9	**i**	Bu	Dec	Me	H	58

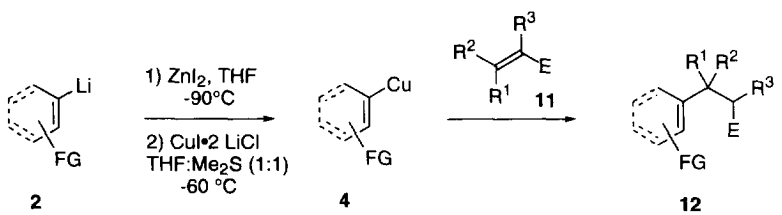
[a] Isolated yields of analytically pure products.

[b] Reaction performed in ether.

[c] Reaction performed in the presence of Me_3SiBr (1.2 equiv).

We found that the slow addition of an alkylmagnesium bromide to a suspension of CuI in ether at -35 °C provides a yellow precipitate of the copper reagent **6** which adds regio- and stereoselectively to terminal alkynes **7** (1.0 equiv, -35 °C, then -15 to -10 °C, 1.5 h) to give a dark-green solution of the alkenylcopper **8**. After the addition of the alkylidenemalonate **9** (1.0 equiv) in THF at -10 °C and warming up the resulting grey heterogeneous reaction mixture to rt for 3 h, the desired Michael adducts **10a-i** were obtained in good to excellent yields (Table 1). A complete retention of the double bond geometry of compounds **10** was found.

Attempts at improving the yields by adding Me_3SiCl[20] did not succeed but in the case of the addition to diethyl methylidenemalonate ($R^3 = R^4 = H$),[21] the addition of Me_3SiBr (1.2 equiv) lead to a substantial improvement (from 52 % without Me_3SiBr to 67 %; entry 8 of Table 1). After these encouraging results, we returned to the addition of functionalized aryl and alkenyl copper-zinc species **4** to Michael acceptors. We obtained especially good results by transmetalating the lithium reagent **2** first to the zinc compound **3**, then to the corresponding copper reagent by adding a THF-Me_2S solution (1:1) of CuI•2 LiI. This resulted in a relatively stable but sufficiently reactive alkenylcopper to add to various Michael acceptors **11** leading to the conjugated adducts **12** in satisfactory yields (Scheme 4 and Table 2). The presence of zinc salts had a beneficial stabilizing effect on the arylcopper species **4** as has been shown previously.[24]



Scheme 4

Table 2. Conjugate addition products **12a-m** obtained by the reaction of unsaturated copper-zinc species **4a-f** with Michael acceptors **11a-i**.

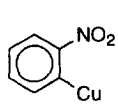
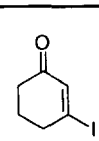
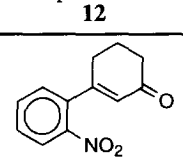
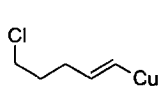
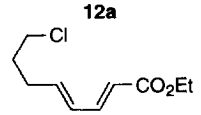
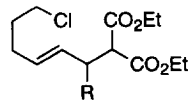
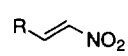
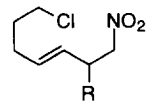
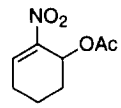
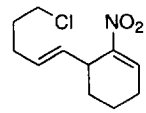
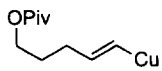
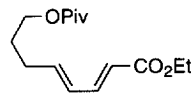
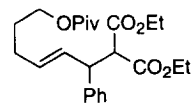
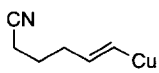
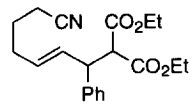
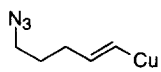
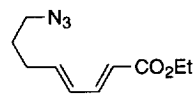
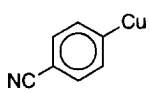
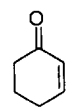
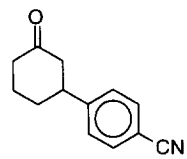
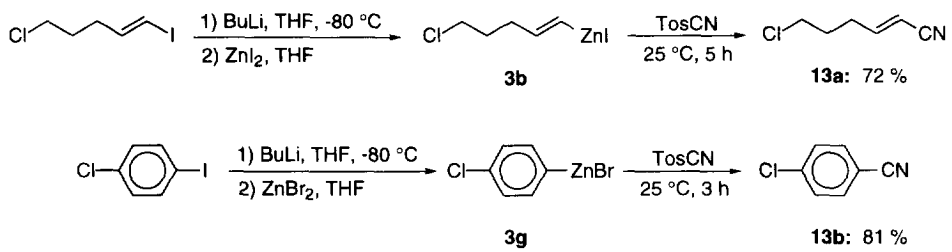
entry	unsaturated copper-zinc reagent **4**	electrophile **11**	product **12**	yield (%)
1	 **4a**	 **11a**	 **12a**	70
2	 **4b**	$HC{\equiv}C{-}CO_2Et$ **11b**	 **12b**	71

Table 2 (continued).

		R-CH=C(CO_2Et)$_2$		
3	**4b**	**11c** R = Ph	**12c** R = Ph	80
4	**4b**	**11d** R = c-Hex	**12d** R = c-Hex	71
				
5	**4b**	**11e** R = Pent	**12e** R = Pent	85
6	**4b**	**11f** R = i-Pr	**12f** R = i-Pr	88
7	**4b**	**11g** R = Ph	**12g** R = Ph	86
8	**4b**	 **11h**	 **12h**	86
9	 **4c**	HC≡C—CO_2Et **11b**	 **12i**	68
10	**4c**	Ph-CH=C(CO_2Et)$_2$ **11c**	 **12j**	76
11	 **4d**	Ph-CH=C(CO_2Et)$_2$ **11c**	 **12k**	82
12	 **4e**	HC≡C—CO_2Et **11b**	 **12l**	81
13	 **4f**	 **11i**	 **12m**	93

Thus the addition of *o*-nitrophenylcopper **4a** to 3-iodocyclohexenone[22] **11a** affords the addition-elimination product **12a** in 70 % yield (entry 1 of Table 2). Reactive acetylenic esters like ethyl propiolate **11b** add readily to functionalized alkenylcopper reagents providing stereomerically pure (E,E)-1,3-dienes (entries 2, 9, and 12). This last example provides an efficient way to the unsaturated azide **12l** which can

be used for the synthesis of pyrrolizidines.[23] The addition to alkylidenemalonates requires longer reaction times (25 °C, 1-5 h) and gives the 1,4-addition products **12c**, **12d**, **12j**, **12k** in 70-80 % yield (entries 3, 4, 10, 11 of Table 2). The conjugated addition to an unsaturated ketone like cyclohexenone proceeds well in the presence of Me_3SiCl[2,20] leading to the 3-arylcyclohexanone **12m** in 93 % yield (entry 13). Nitroolefins are excellent Michael acceptors and (E)-5-chloropentenylcopper **4b** adds to aliphatic and aromatic nitroolefins[24] in excellent yields. The very reactive nitro compound 6-acetoxy-1-nitrocyclohexene[25] **11h** adds the alkenylcopper **4b** at -60 °C leading to nitrodiene **12h** in 86 % yield (entry 8). The direct formation of C-C bonds with organozinc halides can be performed well only in a few cases. Tosyl cyanide[26] is a reactive reagent which couples rapidly with alkenyl and arylzinc halides providing respectively α,β-unsaturated and aromatic nitriles such as **13a** and **13b** in 72-81 % yield (Scheme 5).



Scheme 5

Although palladium cross-coupling reactions have been reported for mostly unfunctionalized organometallics,[2,3,7,27,28] we describe herein a very convenient procedure involving the iodine-lithium transmetalation sequence. Thus, the aryl or alkenylzinc halides **3** generated from the corresponding lithium reagent react with various unsaturated iodides and some bromides in the presence of catalytic amounts (4 mol %) of *bis*(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$)[29] and triphenylphosphine (TPP; 16 mol %). The reaction is complete within a few hours at 25 °C and produces the desired cross-coupling products **14** in excellent yields (Scheme 6 and Table 3).

Table 3. Functionalized cross-coupling products **14a-p** obtained by the palladium catalyzed coupling of unsaturated zinc halides **3** with organic iodides.

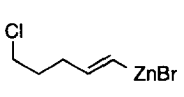
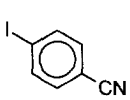
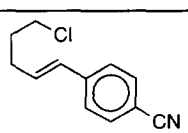
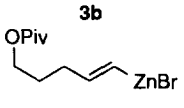
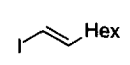
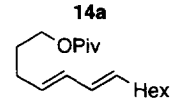
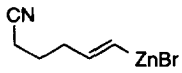
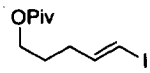
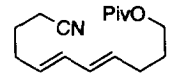
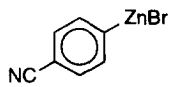
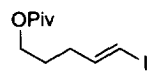
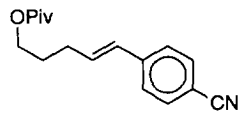
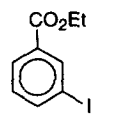
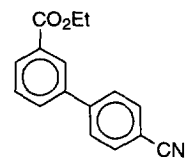
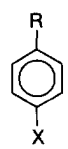
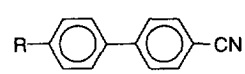
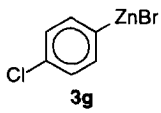
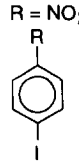
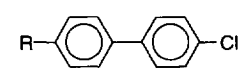
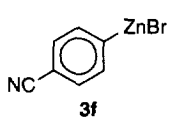
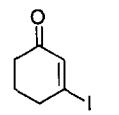
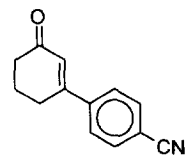
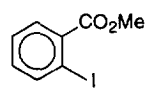
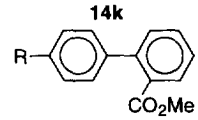
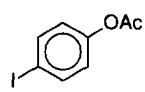
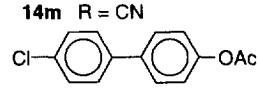
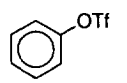
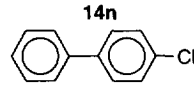
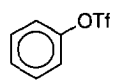
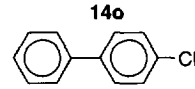
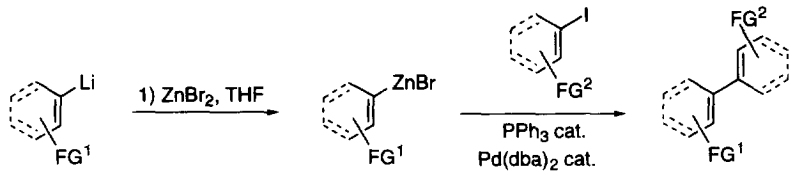
entry	unsaturated zinc reagent **3**	organic iodide	product **14**	yield (%)
1	 **3b**		 **14a**	74
2	 **3c**		 **14b**	72

Table 3 (continued).

3	 **3d**		 **14c**	86
4	 **3f**		 **14d**	81
5	**3f**		 **14e**	93
				
6	**3f**	X = I R = CO_2Et	**14f** R = CO_2Et	87
7	**3f**	X = I R = OAc	**14g** R = OAc	90
8	**3f**	X= Br R = NO_2	**14h** R = NO_2	69
	 **3g**			
9		X = I R = CO_2Et	**14i** R = CO_2Et	88
10		X = Br R = NO_2	**14j** R = NO_2	71
11	 **3f**		 **14k**	89
				
12	**3g**		**14l** R = Cl	79(83)
13	**3f**		**14m** R = CN	80(84)
14	**3g**		 **14n**	71
15	**3g**		 **14o**	92
16	**3f**		 **14p**	74

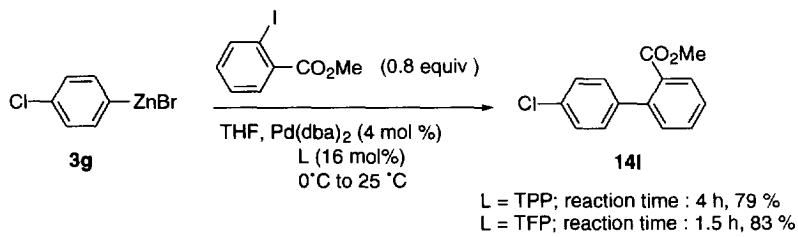
Yields in parentheses obtained by using TFP instead of TPP as ligand.



2 **3** **14**

Scheme 6

The polyfunctional dienes **14b** and **14c** (entries 2 and 3 of Table 3) were stereomerically pure (E,E)-products. The cross-coupling reaction to biphenyl proceeds uniformly well regardless of the nature of the substituent present in the aryl iodide. Furthermore, a significant reaction time shortening and yield improvement could be achieved by using *tris-o*-furylphosphine[30] (TFP) as a ligand instead of TPP. Thus the reaction of the zinc reagent **3g** with methyl *o*-iodobenzoate is complete within 1.5 h and affords the desired biphenyl **14l** in 83 % yield (entries 12-14 of Table 3) whereas a reaction time of 4 h and a yield of 79 % is obtained with TPP (Scheme 7).

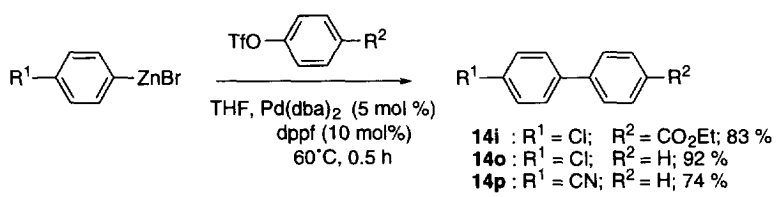


3g **14l**

L = TPP; reaction time : 4 h, 79 %
L = TFP; reaction time : 1.5 h, 83 %

Scheme 7

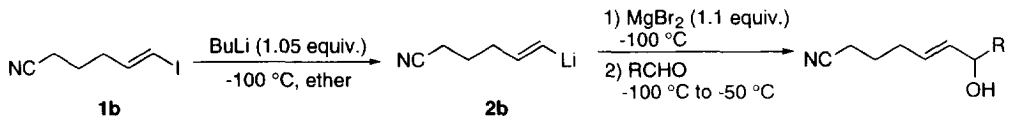
Attempts to extend this reaction to aryl triflates under our standard reaction conditions were disappointing. However, the use of 1,1'-*bis*(diphenylphosphino)ferrocene (dppf)[31] as ligand *and* a reaction temperature of 60 °C for 0.5 h lead to excellent results and provides the coupling products **14i, o, p** in 74-92 % yield (Scheme 8).



14i : R^1 = Cl; R^2 = CO_2Et; 83 %
14o : R^1 = Cl; R^2 = H; 92 %
14p : R^1 = CN; R^2 = H; 74 %

Scheme 8

Transmetalation of a functionalized alkenyllithium to a magnesium derivative is also of synthetic interest. Whereas the low temperature (-100 °C) addition of the alkenyllithium **2b** to an aldehyde proceeds only in low yield, the transmetalation of **2b** to the corresponding Grignard reagent ($MgBr_2$ in THF, -100 °C, 5 min), followed by aldehyde addition (0.9 equiv, -90 °C to -50 °C) cleanly furnishes the pure (E)-allylic alcohols **15a-b** in 71-77 % yield (Scheme 9).



1b **2b**

15a: R = c-Hex: 71 %
15b: R = $(CH_2)_3OPiv$: 77 %

Scheme 9

In summary, we have shown that low temperature halogen-lithium exchange followed by transmetalation with a zinc halide (X=I or Br) provides a very convenient preparation of stereochemically well defined polyfunctional alkenylzinc halides and functionalized arylzinc halides. Although, these unsaturated zinc compounds react only directly with tosyl cyanide a stoichiometric transmetalation to the corresponding copper compound allows to perform conjugate additions to a range of Michael acceptors providing a variety of polyfunctional adducts. The palladium(0) catalyzed cross-coupling reaction using aryl and alkenyl iodides or triflates allows the synthesis of polyfunctional biphenyls and 1,3-dienes.

Experimental

General methods. Unless otherwise indicated, all reactions were carried out under an argon atmosphere. Solvents (THF or ether) were dried and freshly distilled over sodium/benzophenone. Zinc dust (-325 mesh) was purchased from Aldrich or Riedel-de-Haën (Germany). Reactions were monitored by gas-chromatography (GC) analysis of reaction aliquots. Unless otherwise indicated, the reaction mixtures were worked up by pouring into a mixture of ether and sat. aqueous 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) and brine (20 mL), dried over $MgSO_4$ and filtered. The residue obtained after evaporation of the solvents was purified by flash-chromatography. Fourier transform 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 AC-300 (300 MHz (proton) and 75.5 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).

Starting materials. The following starting materials were prepared according to literature procedures: *t*-butyl α-(bromomethyl)acrylate,[17] diethyl methylidenemalonate,[21] 3-iodo-2-cyclohexen-1-one,[22] 6-acetoxy-1-nitrocyclohexene **11h**,[25] *bis*(dibenzylideneacetone)palladium(0),[29] (E)-1-nitroheptene **11e**,[32] (E)-3-methyl-1-nitrobutene **11f**, (E)-1-iodooctene.[33]

Preparation of the (E)-alkenyl iodides (1b-e).
5-Chloro-1-iodo-1-pentene (1b). A three-necked flask equipped with an addition funnel, a thermometer and an argon inlet was charged with 5-chloro-1-pentyne[34] and hexanes (15 mL). Diisobutylaluminium-hydride (9.25 mL, 52 mmol, 1.02 equiv) was added in such a way that the temperature remained below 30 °C. The reaction mixture was stirred 0.5 h at 30 °C and subsequently 6 h at 50 °C. After cooling to rt, the solvents were distilled off and dry THF (45 mL) was added. The reaction mixture was cooled to

-78 °C and a solution of iodine (15.5 g, 122 mmol, 2.4 equiv) in THF (20 mL) was added. The temperature was kept below -60 °C during the addition. The reaction mixture was stirred 1 h at this temperature and was warmed up to 0 °C and poured in hexanes (100 mL) and aqueous 1N HCl (100 mL). The aqueous phase was extracted twice with hexanes (2 x 50 mL) and the combined organic phases were washed successively with dilute NaOH (10 mL), aqueous $Na_2S_2O_3$ (20 mL), brine (3 x 50 mL) and dried over $MgSO_4$.The residue obtained by evaporation of the solvents was distilled under reduced pressure (bp_{10} 89-90 °C) affording the product **1b** as a colorless liquid (8.8 g, 38 mmol, 75 % yield). IR (neat): 2955 (s), 2948 (m), 2912 (m), 1588 (m), 1442 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.49 (dt, 1H, J = 14.3 Hz, 7.2 Hz), 6.10 (d, 1H, J = 14.3 Hz), 3.54 (t, 2H, J = 6.4 Hz), 2.27-2.20 (m, 2H), 1.91-1.82 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 144.6, 76.0, 43.8, 33.1, 31.1. MS (EI, 70 eV) m/e (rel int): 103 (26), 127 (12), 167 (26), 230 (25), 232 (8). Exact mass calcd. for $C_5H_8{}^{35}ClI$: 230.5126. Observed: 230.5121.

(E)-5-Iodo-4-pentenyl 2,2-dimethylpropionate (1c). An ether (10 mL) solution of (E)-pinacol[5-(pivaloxy)-1-pentenyl]boronate[35] prepared from 4-pentynyl 2,2-dimethylpropionate (1.68 g, 10 mmol) and pinacolborane[35] (1.27 g, 10 mmol) was treated with potassium *t*-butoxide (3.00 g, 30 mmol) in ether (50 mL) and the resulting reaction mixture was stirred at 0 °C for 10 min. An ether solution (10 mL) of iodine (5.08 g, 20 mmol) was added dropwise and the reaction mixture was stirred for an additional hour. After the usual workup (see above), the crude residue obtained after evaporation of the solvents was purified by chromatography (ether:hexanes 1:10) affording **1c** as a yellow oil (2.24 g, 76 % yield). IR (neat): 2935 (s), 2872 (s), 1727 (s), 1490 (s), 1398 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.52 (dt, J = 14.6 Hz, 7.3 Hz), 6.05 (d, 1H, J = 14.6 Hz), 4.07 (t, 2H, J = 6.9 Hz), 2.12 (q, 2H, J = 7.4 Hz), 1.75 (p, 2H, J = 7.5 Hz), 1.18 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.3, 145.0, 75.4, 63.1, 38.6, 32.4, 27.3, 27.1. MS (EI, 70 eV) m/e (rel int): 84 (29), 167 (10), 194 (100), 269 (2). Exact mass calcd. for $C_{10}H_{17}IO_2$: 296.0273. Observed: 296.0250.

(E)-6-Iodo-5-hexenenitrile (1d). Prepared as described for the preparation of **1c** starting from 5-hexynenitrile (0.93 g, 10 mmol) and pinacolborane[35] (1.27 g, 10 mmol). The product **1d** was obtained after flash-chromatography (ether:hexanes 5:95) as a pale yellow oil. IR (neat): 2936 (s), 2246 (m), 1609 (m), 1424 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.45 (dt, 1H, J = 14.4 Hz, 7.2 Hz), 6.16 (d, 1H, J = 14.4 Hz), 2.36 (t, 2H, J = 7.0 Hz), 2.24 (q, 2H, J = 7.2 Hz), 1.76 (p, 2H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 143.8, 119.1, 76.9, 34.6, 24.1, 16.3. MS (EI, 70 eV) m/e (rel int): 67 (100), 94 (48), 127 (16), 167 (40), 195 (15), 221 (21). Exact mass calcd. for C_6H_8N: 221.0691. Observed: 221.0687.

(E)-5-Azido-1-iodo-1-pentene (1e). A DMSO solution (25 mL) of 1,5-diiodo-1-pentyne[36] (8.05 g, 25 mmol) and sodium azide (3.25 g, 50 mmol) was stirred at rt for 6 h, then diluted with ether (200 mL) and washed with brine (2 x 200 mL). The organic phase was dried over $MgSO_4$ and the solvents were removed under vacuum. The residue was purified by flash-chromatography (hexane:ether 80:20) affording the azide **1e** as a red oil (4.66 g, 78 % yield). IR (neat): 2946 (s), 2930 (s), 2102 (m), 1635 (m), 1487 (s), 1222 (s), 1139 (s), 1003 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.49 (dt, 1H, J = 14.4 Hz, 7.2 Hz), 6.08 (dt, 1H, J = 14.4 Hz, 1.3 Hz), 3.30 (t, 2H, J = 6.7 Hz), 2.16 (dq, 2H, J = 1.3 Hz, 7.2 Hz), 1.70 (p, 2H, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75.7 MHz): δ 144.7, 75.5, 50.4, 32.9, 27.6. MS (CI, NH_3) m/e (rel int): 84 (7), 110 (100), 136 (40), 180 (2), 210 $[M-N_2+H]^+$ (5). Exact mass calcd. for $C_5H_8IN_3+NH_3$: 209.4780. Observed: 209.4779.

Preparation of the *o*-substituted nitrobenzene derivatives 5a-b.

2-Nitrobenzophenone (5a): A three-necked flask equipped with an argon inlet, a thermometer and an addition funnel was charged with THF (2.5 mL) at -100 °C. 2-Iodonitrobenzene **1a** (0.50 g, 2 mmol) in THF (3 mL) and PhLi (2.14 M, 0.96 mL, 2.05 mmol) were added simultaneously, keeping the temperature below -90 °C. The resulting dark brown solution of **2a** was stirred at -100 °C for 1 h and treated with a solution of LiCl (0.17 g, 4 mmol) and CuCN (0.18 g, 2 mmol) at -90 °C. After 10 min, benzoyl chloride (0.20 g, 1.4 mmol) was added and the reaction mixture stirred at 0 °C for 13 h. After usual workup, the residue obtained after evaporation of the solvents was purified by flash-chromatography (solvent gradient of 1 % to 2 % ethyl acetate in hexane) furnishing 238 mg (75 % yield) of a yellow solid, mp 97-99 °C (105-106 °C)[16]. IR (KBr): 3036 (w), 1670 (s), 1527 (s), 1354 (s), 765 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 8.25 (d, 1H, J = 8.2 Hz), 7.66-7.82 (m, 4H), 7.59 (t, 1H, J = 7.4 Hz), 7.43-7.51 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 193.2, 146.9, 136.1, 136.0, 134.0, 133.6, 130.5,

129.1, 128.8, 128.7, 124.3. MS (EI, 70 eV): m/z (rel int): 77 (95), 105 (100), 134 (55), 152 (12), 182 (1), 198 (1), 227 (M^+, 3). Exact mass calcd. for $C_{13}H_9NO_3$: 227.0582. Observed: 227.0581.

Preparation of 2-(2-carbo-*t*-butoxy-2-propenyl)-1-nitrobenzene (5b). To *o*-nitrophenylcopper **4a** prepared as described above from 2-iodo-1-nitrobenzene **1a**[16] (0.50 g, 2 mmol) was added *t*-butyl α-(bromomethyl)acrylate (0.31 g, 1.4 mmol) at -60 °C. The reaction mixture was stirred at -20 °C for 13 h and worked up as usually. The crude residue obtained after evaporation of the solvents was purified by flash-chromatography (ethyl acetate:hexane 2:98) affording the product **5b** as a yellow oil (291 mg, 79 % yield). IR (neat): 1712 (s), 1636 (m), 1527 (s), 1393 (m), 850 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.92 (d, 1H, J = 8.1 Hz), 7.53 (t, 1H, J = 7.5 Hz), 7.34-7.40 (m, 2H), 6.19 (s, 1H), 5.32 (s, 1H), 3.93 (s, 2H), 1.41 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 165.4, 149.6, 139.8, 134.0, 132.6, 131.9, 127.4, 125.6, 124.5, 80.9, 34.6, 27.8. MS (CI with NH_3): m/z (rel int) 94 (8), 136 (100), 153 (7), 162 (1), 179 (1), 209 (0.5), 225 (4), 234 (6), 265 (0.5), 281 ($[M+NH_4]^+$, 15). Exact mass calcd. for $C_{14}H_{17}NO_4NH_4$: 281.1501. Observed: 281.1507. Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.86; H, 6.51; N, 5.32. Observed: C, 63.50; H, 6.65; N, 5.30.

Preparation of alkenylcoppers (8) by the carbocupration of alkynes with alkylcoppers (6) and their conjugate addition to alkylidenemalonates (9) leading to the Michael-adducts (10a-i). Typical procedure: Preparation of (E)-diethyl 3-ethyl-1-phenyl-2-octenylmalonate (10f). A three-necked flask equipped with a thermometer, a gas inlet and an addition funnel was charged under argon with a suspension of CuI (10.1 g, 53 mmol) in Et_2O (50 mL). The reaction mixture was cooled to -35 °C and EtMgBr (27.3 mL, 53 mmol, 1.94 N solution in ether) was added over 30 min to form the alkenylcopper species as a precipitate. 1-Heptyne (4.80 g, 50 mmol) was added at -35 °C over 10 min and the reaction mixture was stirred at -15 °C for 1.5 h. The addition of a solution of diethyl benzylidenemalonate (12.41 g, 50 mmol) in THF (100 mL) at -10 °C and warming up of the reaction mixture to rt gave a suspension which after the usual work-up and distillation furnished 16.85 g (90 %) of the desired 1,4-adduct (E)-diethyl 3-ethyl-1-phenyl-2-octenylmalonate with complete retention of the double bond geometry (checked by ^{1}H- and ^{13}C-NMR spectroscopy and GC analysis).

Analytical data of the products 10a-i (Table 1)

(E)-Diethyl (3-ethyl-1,1-dimethyl-2-octenyl)malonate (10a). 5.87 g (60 % yield) of a colorless oil obtained from ethylmagnesium bromide (17.6 mL, 30 mmol, 1.70 M in ether), 1-heptyne (2.88 g, 30 mmol) and diethyl 1-methyl-ethylidenemalonate (6.00 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1740 (s), 1640 (s), 1460 (s), 1360 (s), 1035 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.22 (s, 1H), 4.15 (q, 4H, J = 7.3 Hz), 3.57 (s, 1H), 2.15 (q, 2H, J = 7.6 Hz), 1.92 (t, 2H, J = 7.0 Hz), 1.34 (s, 6H), 1.25 (t, 6H, J = 7.3 Hz), 1.33-1.24 (m, 6H), 0.99 (t, 3H, J = 7.6 Hz), 0.88 (t, 3H, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 168.2, 141.8, 131.3, 61.1, 60.7, 37.5, 37.2, 31.5, 28.3, 27.4, 23.4, 22.5, 14.0, 13.9, 12.8. Anal. Calcd. for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50. Found: C, 69.81; H, 10.73.

(E)-Diethyl (3-ethyl-1-methyl-2-octenyl)malonate (10b). 7.49 g (80 % yield) of a colorless oil obtained from ethylmagnesium bromide (17.6 mL, 30 mmol, 1.70 M in ether), 1-heptyne (2.88 g, 30 mmol) and diethyl ethylidenemalonate (5.58 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1735 (s), 1460 (s), 1360 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.92 (d, 1H, J = 8.8 Hz), 4.19 (q, 2H, J = 6.6 Hz), 4.05 (m, 2H), 3.18 (m, 1H), 2.20 (m, 1H), 1.94 (m, 4H), 1.20-1.08 (m, 6H), 1.27 (t, 3H, J = 6.4 Hz), 1.22 (t, 3H, J = 6.0 Hz), 1.02 (d, 3H, J = 6.6 Hz), 0.96 (t, 3H, J = 7.4 Hz), 0.88 (t, 3H, J = 7.4 H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 168.9, 168.8, 142.8, 125.7, 61.4, 61.3, 58.8, 36.6, 33.1, 31.8, 28.1, 23.4, 22.8, 19.9, 14.4, 13.7. Anal. Calcd. for $C_{18}H_{32}O_4$: C, 69.19; H, 10.32. Found: C, 69.26; H, 10.35.

(E) Diethyl (3-ethyl-1-propyl-2-octenyl)malonate (10c). 5.92 g (58 % yield) of a colorless oil obtained from ethylmagnesium bromide (17.6 mL, 30 mmol, 1.70 M in ether), 1-heptyne (2.88 g, 30 mmol) and diethyl propylidenemalonate (6.00 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1730 (s), 1660 (s), 1030 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.83 (d, 1H, J = 9.0 Hz), 4.20 (qd, 2H, J = 7.2, 3.0 Hz), 4.12 (qd, 2H, J = 7.2, 3.0 Hz), 3.23 (d, 1H, J = 9.6 Hz), 3.08 (m, 1H), 2.16 (m, 1H), 1.98 (m, 3H), 1.24 (m, 16H), 0.96 (t, 3H, J = 7.4 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ

168.7, 168.5, 143.9, 124.0, 61.1, 60.9, 57.7, 37.7, 36.0, 35.9, 31.6, 27.9, 23.5, 22.5, 20.2, 14.1, 12.9. Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.49; H, 10.61.

(E)-Diethyl (3-ethyl-1-isopropyl-2-octenyl)malonate (10d). 7.25 g (71 % yield) of a colorless oil obtained from ethylmagnesium bromide (17.6 mL, 30 mmol, 1.70 M in ether), 1-heptyne (2.88 g, 30 mmol) and diethyl isopropylidenemalonate (6.42 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1735 (s), 1655 (s), 1460 (s), 1360 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.94 (d, 1H, J = 10.5 Hz), 4.25-3.96 (m, 4H), 3.44 (d, 1H, J = 9.9 Hz), 3.04 (dt, 1H, J = 4.3 Hz, 10.5 Hz), 2.22-1.95 (m, 4H), 1.76 (m, 1H), 1.40-1.17 (m, 6H), 1.26 (t, 3H, J = 7.2 Hz), 1.22 (t, 3H, J = 7.2 Hz), 0.94 (t, 3H, J = 6.9 Hz), 0.88 (t, 3H, J = 6.9 Hz), 0.83 (d, 6H, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 160.7, 160.4, 144.9, 120.6, 61.1, 60.8, 55.8, 43.2, 36.3, 31.8, 30.2, 28.2, 23.1, 22.7, 21.5, 17.4, 14.5, 12.7. Anal. Calcd. for $C_{20}H_{36}O_4$: C, 70.55; H, 10.66. Found: C, 70.44; H, 10.63.

(E)-Diethyl (3-butyl-1-isopropyl-2-octenyl)malonate (10e). 7.31 g (68 % yield) of a colorless oil obtained from *n*-BuLi (18.8 mL, 30 mmol, 1.60 M in ether), 1-heptyne (2.88 g, 30 mmol) and diethyl isopropylidenemalonate (6.42 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1740 (s), 1655 (s), 1460 (s), 1360 (s), 1030 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.96, (d, 1H, J = 10.9 Hz), 4.18 (q, 2H, J = 7.3 Hz), 4.08 (m, 2H), 3.44 (d, 1H, J = 9.9 Hz), 3.04 (dt, 1H, J = 10.6 Hz, 4.3 Hz), 2.10 (m, 1H), 1.97 (m, 3H), 1.76 (m, 1H), 1.40-1.20 (m, 10H), 1.26 (t, 3H, J = 7.3 Hz), 1.22 (t, 3H, J = 7.3 Hz), 0.88 (t, 6H, J = 6.9 Hz), 0.82 (d, 6H, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 168.8, 168.5, 143.8, 120.5, 61.1, 60.9, 55.7, 43.0, 36.7, 31.6, 30.4, 30.1, 29.9, 28.1, 23.2, 22.5, 21.4, 17.2, 14.0. Anal. Calcd. for $C_{22}H_{40}O_4$: C, 71.70; H, 10.94. Found: C, 71.83; H, 11.19.

(E)-Diethyl (3-ethyl-1-phenyl-2-octenyl)malonate (10f). (see typical procedure). IR (neat): 1740 (s), 1655 (s), 1600 (s), 1450 (s), 1365 (s), 1025 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.18 (m, 1H), 7.16 (m, 4H), 5.28 (d, 1H, J = 10.5 Hz), 4.32 (t, 1H, J = 10.4 Hz), 4.16 (m, 2H), 3.86 (m, 2H), 3.74 (d, 1H, J = 10.5 Hz), 2.28 (m, 1H), 2.00 (m, 1H), 1.94 (m, 2H), 1.40-1.16 (m, 10H), 0.98 (t, 3H, J = 7.5 Hz), 0.90 (t, 3H, J = 7.5 Hz), 0.86 (t, 3H, J = 7.5 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 168.0, 167.7, 143.8, 142.3, 128.4, 127.8, 126.5, 123.4, 61.3, 61.1, 58.8, 44.1, 36.4, 31.6, 27.8, 23.3, 22.6, 14.1, 14.0, 13.8, 12.9. Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.71; H, 9.21.

(E)-Diethyl (3-butyl-1-phenyl-2-tridecenyl)malonate (10g). 9.92 g (70 % yield) of a colorless oil obtained from *n*-BuLi (18.8 mL 30 mmol, 1.60 M in ether), 1-dodecyne (4.98 g, 30 mmol) and diethyl phenylidenemalonate (7.44 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1745 (s), 1660 (s), 1605 (s), 1460 (s), 1360 (s), 1030 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.32 (m, 4H), 7.28 (m, 1H), 5.74 (d, 1H, J = 9.7 Hz), 4.92 (t, 1H, J = 9.5 Hz), 4.32-4.18 (m, 3H), 4.02-3.94 (m, 2H), 2.60 (m, 1H), 2.32 (m, 1H), 2.20 (m, 2H), 1.30 (m, 2H), 1.24 (m, 18H), 1.16 (t, 3H, J = 7.5 Hz), 1.08 (m, 6H), 0.84 (t, 3H, J = 7.5 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 167.8, 167.6, 142.5, 142.4, 128.4, 127.9, 126.5, 124.1, 61.1, 61.0, 59.9, 44.2, 37.0, 32.0, 30.5, 30.3, 29.7, 29.4, 28.3, 23.0, 22.7, 14.1, 13.8. Anal. Calcd. for $C_{30}H_{48}O_4$: C, 76.23; H, 10.23. Found: C, 76.22; H, 10.11.

(E)-Diethyl (3-ethyl-2-octenyl)malonate (10h). 5.99 g (67 % yield) of a colorless oil obtained from ethylmagnesium bromide (17.6 mL, 30 mmol, 1.70 M in ether), 1-heptyne (2.88 g, 30 mmol) and diethyl methylidenemalonate (5.16 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1740 (s), 1460 (s), 1360 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.00 (t, 1H, J = 7.2 Hz), 4.15 (q, 4H, J = 7.2 Hz), 3.33 (t, 1H, J = 7.1 Hz), 2.61 (t, 2H, J = 7.1 Hz), 2.02 (q, 2H, J = 7.2 Hz), 1.96 (t, 2H, J = 7.2 Hz), 1.40-1.19 (m, 6H), 1.26 (t, 6H, J = 7.2 Hz), 0.95 (t, 3H, J = 7.2 Hz), 0.88 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 169.3, 144.6, 118.8, 61.2, 52.5, 36.4, 31.5, 27.7, 27.1, 23.0, 22.5, 14.1, 13.1. Anal. Calcd. for $C_{17}H_{30}O_4$: C, 68.42; H, 10.13. Found: C, 68.36; H, 10.15.

(E)-Diethyl (3-butyl-1-methyl-2-tridecenyl)malonate (10i). 8.00 g (65 % yield) of a colorless oil obtained from *n*-BuLi (18.8 mL, 30 mmol, 1.60 M in ether), 1-dodecyne (4.98 g, 30 mmol) and diethyl ethylidenemalonate (7.44 g, 30 mmol). The crude product obtained after workup was purified by distillation. IR (neat): 1735 (s), 1455 (s), 1355 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.94 (d, 1H, J = 9.0 Hz), 4.15 (m, 4H), 3.18 (m, 1H), 2.1 (m, 1H), 1.92 (m, 4H), 1.38-1.18 (m, 26H), 1.03 (d, 3H, J = 6.0 Hz), 0.91 (t, 3H, J = 6.5 Hz), 0.88 (t, 3H, J = 6.5 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 168.6, 168.4, 141.1, 125.9, 61.1, 58.5, 36.7, 32.8, 31.8, 30.8, 29.9, 29.6, 29.5, 29.3, 28.2, 22.8, 22.6, 19.5, 14.5, 14.0. Anal. Calcd. for $C_{25}H_{46}O_4$: C, 73.12; H, 11.29. Found: 73.03; H, 11.38.

Conjugate addition of functionalized alkenyl and arylcoppers to Michael-acceptors leading to products of type 12. Typical procedure: Preparation of (2E,4E)-ethyl 8-pivaloxy-2,4-octadienoate (12i). A three-necked flask equipped with a thermometer, a gas inlet and an addition funnel was charged with (E)-5-iodo-5-pentenyl pivalate **1c** (0.74 g, 2.50 mmol) in a mixture of THF:ether:pentane (4:1:1; 12 mL), cooled to -100 °C (liq. N_2, ether bath) and *n*-BuLi (1.62 mL, 2.6 mmol, 1.60 M in hexanes) was added over 4 min. The resulting yellow solution was stirred for 3 min at -100 °C and a THF solution (5 mL) of ZnI_2 (0.83 g, 2.6 mmol) was added. After stirring for 10 min at -100 °C, a slurry of CuCN (0.23 g, 2.6 mmol) and LiCl (0.22 g, 5.2 mmol) in a mixture (10 mL) of THF and Me_2S (1:1) was added. The dark red solution was warmed to -60 °C and after 5 min was cooled back to -78 °C. Ethyl propiolate (0.20 g, 2.0 mmol) was added and the reaction mixture was warmed to -20 °C and stirred for 2 h. After the usual workup and evaporation of the solvents, the crude residue obtained was purified by flash-chromatography (hexane:ether, 19:1) yielding **12i** (360 mg, 68 %) as a clear oil (100 % *E,E* by GC analysis).

Analytical data of the products 12a-m (Table 2)

3-(2-Nitrophenyl)-2-cyclohexenone (12a): To *o*-nitrophenylcopper **4a** prepared as described above from 2-iodo-1-nitrobenzene **1a**[11j] (0.50 g, 2 mmol) was added 3-iodo-2-cyclohexenenone (0.35 g, 16 mmol) at -70 °C. The reaction mixture was stirred at 0 °C for 1.5 h and then 11 h at 20 °C. After the usual workup and flash-chromatography of the residue (solvent: hexane:ethyl acetate 19:1), the enone **12a** (243 mg, 70 % yield) was isolated as a yellow solid (mp 92-94 °C). IR (KBr): 1671 (s), 1601 (m), 1525 (s), 1347 (s), 790 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.11 (d, 1H, J = 8.1 Hz), 7.67 (t, 1H, J = 7.5 Hz), 7.55 (t, 1H, J = 7.8 Hz), 7.31 (d, 1H, J = 7.5 Hz), 5.98 (s, 1H), 2.51-2.54 (m, 4H), 2.18-2.26 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 198.3, 160.3, 146.5, 136.3, 133.6, 129.4, 129.3, 127.3, 124.6, 37.0, 30.5, 30.0. MS (CI with NH_3): m/z (rel int) 83 (7), 130 (8), 146 (9), 172 (8), 188 (39), 201 (18), 218 ($[M+H]^+$, 100). Exact mass calcd. for $C_{12}H_{11}NO_3H$: 218.0817. Observed: 218.0816.

(E,E)-Ethyl 8-chloro-2,4-octadienoate (12b). 285 mg (70 % yield) of a colorless oil obtained from (E)-5-chloro-1-iodo-1-pentene (580 mg, 2.5 mmol) and ethyl propiolate (200 mg, 2.0 mmol). Flash chromatography (3 % ether in hexane). IR (neat): 2982 (s), 2959 (s), 2939 (s), 1714 (s), 1644 (s), 1618 (s), 1445 (m), 1368 (s), 1303 (s), 1146 (s), 1001 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.29-7.20 (dd, 1H, J = 15.4 Hz, 10.7 Hz), 6.27-6.18 (dd, 1H, J = 15.4 Hz, 10.7 Hz), 6.11-6.02 (dt, 1H, J = 15.2 Hz, 6.8 Hz), 5.84-5.79 (d, 1H, J = 15.4 Hz), 4.23-4.16 (q, 2H, J = 7.2 Hz), 3.56-3.52 (t, 2H, J = 6.5 Hz), 2.38-2.31 (q, 2H, J = 7.3 Hz), 1.96-1.86 (p, 2H, J = 6.5 Hz), 1.31-1.27 (t, 3H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 167.0, 144.3, 141.7, 129.5, 120.0, 60.1, 44.0, 31.3, 29.9, 14.2. MS (EI, 70 eV): 84 (49), 97 (71), 125 (100), 157 (31), 167 (5), 174 (3), 202 (25). Exact mass calcd. for $C_{10}H_{15}{}^{35}ClO_2$: 202.0761. Observed: 202.0752.

(E)-Diethyl 2-(6-chloro-1-phenyl-2-hexenyl)malonate (12c). 1.41 g (80 % yield) of a colorless oil obtained from (E)-**1b** (1.15 g, 5 mmol) and diethyl phenylidenemalonate (1.48 g, 6 mmol, 1.2 equiv). Reaction time: 6 h, rt. The crude residue obtained after evaporation of the solvents was purified by flash-chromatography (hexane:ether 10:1). IR (neat): 3020 (w), 2940 (s), 1725 (s), 1580 (w,b), 1430 (s), 1370 (s), 1225 (s), 1250 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.24-7.10 (m, 5H), 5.64-5.56 (m, 1H), 5.49-5.40 (m, 1H), 4.12 (q, 2H, J = 7.1 Hz), 4.02-3.96 (m, 1H), 3.86 (q, 2H, J = 7.5 Hz), 3.72 (d, 1H, J = 11.0 Hz), 3.39 (t, 2H, J = 6.6 Hz), 2.06 (q, 2H, J = 6.9 Hz), 1.71 (q, 2H, J = 6.9 Hz), 1.20 (t, 3H, J = 7.1 Hz), 0.91 (t, 3H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.8, 167.4, 140.6, 131.1, 130.7, 128.4, 127.8, 126.8, 61.4, 61.2, 57.8, 48.8, 44.0, 31.8, 29.4, 14.1, 13.7. MS (EI, 70 eV): 91 (13), 115 (12), 129 (14), 193 (21), 201 (31), 279 (22). Anal. Calcd. for $C_{19}H_{25}ClO_4$: C, 64.67; H, 7.14. Found: C, 64.50; H, 7.06.

(E)-Diethyl 2-(6-chloro-1-cyclohexyl-2-hexenyl)malonate (12d). 1.51 g (71 % yield) of a colorless oil was obtained from (E)-**1b** (1.85 g, 8 mmol) and diethyl cyclohexylidenemalonate (1.52 g, 6 mmol). Reaction time: 8 h, rt. The crude residue was purified by flash-chromatography (hexane:ether 98:2). IR (neat): 2981 (s), 2850 (s), 1756 (s), 1724 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.40 (d, 2H, J = 5 Hz), 4.25-4.10 (m, 4H), 3.52 (q, 3H, J = 6 Hz), 2.60 (m, 1H), 2.13 (m, 2H), 1.82 (q, 2H, J = 6 Hz), 1.80-1.52 (m, 5H), 1.35 (q, 6H, J = 6 Hz), 1.40-0.85 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 168.5, 168.1, 131.9, 131.1, 60.9, 60.7, 54.6, 48.6, 43.9, 39.4, 32.2, 31.6, 29.4, 28.8, 26.4, 26.3, 13.9. MS (EI, 70 eV): 125 (63), 160 (38), 198 (16), 207 (22), 285 (17), 359 (MH+, 0.25). Exact mass calcd. for $C_{19}H_{31}O_4Cl$: 359.1989. Observed: 359.1982.

E)-1-Chloro-6-nitromethyl-4-undecene (12e). 0.98 g (85 % yield) of a clear oil was obtained from (E)-**1b** (1.84 g, 8 mmol) and (E)-1-nitro-1-heptene (0.71 g, 5 mmol). Reaction time: 5 h, 10 °C. The crude residue was purified by flash-chromatography (hexane:ether 5:1). IR (neat): 2950 (s), 1555 (s), 1380 (w), 1260 (s), 1010 (s), 795 (s), 680 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 5.48-5.38 (m, 1H), 5.22-5.13 (m, 1H), 4.31-4.16 (m, 2H), 3.43 (t, 2H, J = 6.5 Hz), 2.80-2.67 (m, 1H), 2.13-2.06 (m, 2H), 1.74 (q, 2H, J = 6.9 Hz), 1.20-1.29 (m, 8H), 0.80-0.83 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 132.5, 129.9, 80.3, 44.1, 42.1, 31.9, 31.8, 31.5, 29.4, 26.4, 22.4, 13.9. MS (EI, 70 eV): 146 (21), 144 (62), 109 (20), 95 (61), 81 (52). Anal. Calcd. for $C_{12}H_{22}ClNO_2$: C, 58.17; H, 8.84; N, 5.65. Found: C, 58.37; H, 8.85; N, 5.55.

(E)-8-Chloro-2-methyl-3-nitromethyl-4-octene (12f). 0.96 g (88 % yield) of a clear oil was obtained from (E)-3-methyl-1-nitro-1-butene (0.57 g, 5 mmol) and (E)-**1b** (1.95 g, 8.50 mmol). Reaction time: 8 h.The crude residue was purified by flash-chromatography (hexane:ether 5:1). IR (neat): 2950 (s), 1550 (s), 1435 (s), 1380 (s), 1285 (b), 970 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 5.46-5.36 (m, 1H), 5.28-5.19 (m, 1H), 4.41-4.16 (m, 2H), 3.43 (t, 2H, J = 6.6 Hz), 2.61-2.55 (m, 1H), 2.11 (q, 2H, J = 7.2 Hz), 1.74 (q, 2H, J = 6.8 Hz), 1.61 (s, 1H, J = 4.4 Hz), 0.87-0.82 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 133.6, 127.7, 79.1, 48.5, 44.2, 31.9, 29.9, 29.1, 20.5. MS (EI, 70 eV): 95 (26), 109 (14), 130 (16), 172 (18). Anal. Calcd. for $C_{10}H_{18}ClNO_2$: C, 54.66; H, 8.25; N, 6.37. Found: C, 54.74; H, 8.46; N, 6.39.

(E)-6-Chloro-1-nitromethyl-1-phenyl-2-hexene (12g). 1.09 g (86 % yield) of a clear oil was obtained from (E)-**1b** (1.84 g, 8 mmol) and nitrostyrene (0.74 g, 5 mmol). Reaction time: 8 h, 0 °C. The crude residue was purified by flash-chromatography (hexane:ether 5:1). IR (neat): 3040 (w), 2910 (s), 1550 (s,b), 1490 (w), 1425 (s), 1370 (s) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.39-7.22 (m, 5H), 5.73-5.54 (m, 2H), 4.63 (m, 2H), 4.17 (q, 1H, J = 7.8 Hz), 3.51 (t, 2H, J = 6.5 Hz), 2.21 (q, 2H, J = 6.9 Hz), 1.83 (q, 2H, J = 6.9 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 138.8, 132.5, 129.2, 129.1, 127.8, 127.5, 80.1, 47.3, 44.2, 31.8, 29.6. MS (EI, 70 eV): 103 (10), 104 (14), 115 (16), 117 (25), 118 (23), 128 (15), 129 (100), 130 (14), 143 (39), 206 (53), 208 (15). Anal. Calcd. for $C_{13}H_{16}ClNO_2$: C, 57.51; H, 7.00; N, 5.52. Found: C, 61.60; H, 6.92; N, 5.49.

(E)-6-(5-Chloropentenyl)-1-nitrocyclohexane (12h). 0.78 g (86 % yield) obtained from (E)-**1b** (1.84 g, 8 mmol) and 6-acetoxy-1-nitrocyclohexene[25] (0.92 g, 5 mmol). The crude product obtained after workup was purified by flash-chromatography (hexane:ether 5:1). IR (neat): 2930 (s), 1540 (m), 1510 (s), 1455 (w) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.26 (t, 1H, J = 4.1 Hz), 5.45-5.22 (m, 2H), 3.56 (s, 1H), 3.42 (t, 2H, J = 6.6 Hz), 2.35-2.21 (m, 2H), 2.12-2.03 (m, 2H), 1.77-1.65 (m, 4H), 1.59-1.49 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 151.3, 134.8, 130.8, 127.2, 130.9, 44.1, 35.7, 31.8, 29.3, 28.3, 24.8, 16.5. MS (EI, 70 eV): 77 (21), 79 (20), 91 (26). Anal. Calcd. for $C_{11}H_{16}ClNO_2$: C, 57.51; H, 7.02; N, 6.09. Found: C, 57.41; H, 6.99; N, 6.28.

(E,E)-Ethyl 8-pivaloxy-2,4-octadienoate (12i). 367 mg (68 %) of a colorless oil were obtained from (E)-5-iodo-4-pentenyl 2,2-dimethylpropanoate **1c** (740 mg, 2.5 mmol) and ethyl propiolate (200 mg, 2 mmol). Flash-chromatography (5 % ether in hexane). IR (neat): 2976 (s), 2937 (m), 1727 (s), 1645 (s), 1619 (m), 1480 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.28-7.20 (dd, 1H, J = 15.2 Hz, J = 9.9 Hz), 6.23-6.04 (m, 2H), 5.82-5.76 (d, 1H, J = 15.2 Hz), 4.21-4.14 (q, 2H, J = 7.4 Hz), 4.07-4.03 (t, 2H, J = 6.2 Hz), 2.29-2.21 (q, 2H, J = 7.0 Hz), 1.83-1.72 (p, 2H, J = 7.3 Hz), 1.30-1.25 (t, 3H, J = 7.6 Hz), 1.18 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.4, 167.0, 144.4, 142.3, 129.3, 120.2, 63.5, 60.1, 38.8, 29.4, 28.0, 27.2, 14.3. MS (EI, 70 eV): 57 (100), 120 (35), 137 (19), 166 (15), 223 (3), 268 (2). Exact mass calcd. for $C_{15}H_{24}O_4$: 268.1675. Observed: 268.1674.

Diethyl 6-pivaloxy-1-phenyl-2-hexenylmalonate (12j). 1.28 g (76 % yield) obtained from diethyl benzylidenemalonate (0.99 mg, 4 mmol) and the alkenyl iodide **1c** (1.78 g, 6 mmol). Reaction time: 5 h, rt. The crude product obtained after evaporation of the solvents was purified by flash-chromatography (hexane:ether 95:5); IR (neat): 2978 (s), 2937 (s), 2908 (s), 1761 (s), 1727 (s), 1420 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.30-7.15 (m, 5H), 5.60 (m, 2H), 4.19 (q, 2H, J = 7.2 Hz), 4.10-3.90 (m, 6H), 3.78 (d, 1H, J = 11 Hz), 2.03 (q, 2H, J = 6 Hz), 1.68 (q, 2H, J = 6 Hz), 1.27 (t, 3H, J = 7 Hz), 1.17 (s, 9H), 0.98 (t, 3H, J = 7 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.1, 167.6, 167.2, 140.5, 131.2, 130.4, 128.3, 127.7, 126.7, 63.3, 61.2, 61.0, 57.7, 48.7, 38.5, 28.6, 28.0, 27.0, 13.9, 13.5. MS (EI, 70 eV): 129 (21), 156 (100), 196 (5), 345 (1). Exact mass calcd. for $C_{24}H_{35}O_6$: 419.2434. Observed: 419.2426.

Diethyl 6-cyano-1-phenyl-2-hexenylmalonate (12k). 1.37 g (82 % yield) obtained from diethyl benzylidenemalonate (0.99 g, 4 mmol) and the alkenyl iodide **1d** (1.56 g, 6 mmol). Reaction time: 5 h, rt. The crude product obtained after evaporation of the solvents was purified by flash-chromatography (hexane:ether 95:5). IR (neat): 3030 (s), 2982 (s), 2964 (s), 2246 (s), 1754 (s), 1732 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.30 (m, 2H), 7.20 (m, 3H), 5.69 (dt, 1H, J = 1 Hz, 9 Hz), 5.48 (dt, 1H, J = 1 Hz, 9 Hz), 4.19 (q, 2H, J = 7.5 Hz), 4.06 (m, 1H), 3.94 (m, 2H), 3.78 (d, 1H, J = 11.5 Hz), 2.27 (t, 2H, J = 7 Hz), 2.14 (m, 2H), 1.69 (m, 2H, J = 7 Hz), 1.27 (t, 3H, J = 7 Hz), 0.99 (t, 3H, J = 7 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 167.4, 166.9, 140.1, 131.6, 129.7, 128.2, 127.4, 126.6, 119.1, 61.0, 60.8, 57.3, 48.4, 30.6, 24.4, 15.7, 13.7, 13.3. MS (EI, 70 eV): 143 (34), 184 (95), 201 (100), 224 (23), 251 (32), 270 (51), 297 (12), 343 (14). Exact mass calcd. for $C_{20}H_{25}O_4N$: 343.1784. Observed: 343.1778.

(E,E)-Ethyl 8-azido-2,4-octadienoate (12l). 342 mg (81 %) of a colorless sensitive oil were obtained from 5-azido-1-iodo-1-pentene **1e** (590 mg, 3 mmol) and ethyl propiolate (200 mg, 2 mmol). Flash-chromatography (10 % ether in hexane). IR (neat): 2964 (s), 2951 (m), 2098 (s), 1713 (s), 1643 (m), 1260 (s), 1136 (s), 1038 (m), 1005 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.29-7.20 (dd, 1H, J = 15.4 Hz, 10.4 Hz), 6.26-6.17 (dd, 1H, J = 15.2 Hz, J = 10.0 Hz), 6.12-6.02 (dt, 1H, J = 15.2 Hz, J = 6.8 Hz), 5.84-5.78 (d, 1H, J = 15.4 Hz), 4.23-4.16 (q, 2H, J = 7.1 Hz), 3.32-3.28 (t, 2H, J = 6.7 Hz), 2.31-2.24 (q, 2H, J = 7.0 Hz), 1.78-1.68 (p, 2H, J = 7.2 Hz), 1.32-1.27 (t, 3H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 167.0, 144.3, 141.8, 129.5, 120.2, 60.1, 50.7, 29.9, 27.9, 14.2. MS (EI): 138 (100), 142 (12), 167 (5), 181 (9), 209 (2). Exact mass calcd. for $C_{10}H_{15}N_3O_2$: 209.1728. Observed: 209.1739.

3-(4-Cyanophenyl)cyclohexanone (12m). 259 mg (93 % yield) of a yellow oil were obtained from 4-bromobenzonitrile **1f** (360 mg, 2 mmol) and 2-cyclohexenone (130 mg, 1.4 mmol). Flash-chromatography (solvent gradient of 5 % to 10 % to 20 % ethyl acetate in hexane). IR (neat): 2941 (s), 2867 (m), 2227 (s), 1711 (s), 1608 (s), 1506 (s), 1448 (m), 1418 (s), 1315 (m), 1225 (s), 834 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, 2H, J = 8.2 Hz), 7.33 (d, 2H, J = 8.2 Hz), 3.11-3.03 (m, 1H), 2.61-2.35 (m, 4H), 2.19-2.07 (m, 2H), 1.92-1.75 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 209.1, 149.3, 132.2, 127.2, 118.4, 110.2, 47.7, 44.2, 40.6, 31.9, 24.9. MS (EI, 70 eV): 77 (8), 96 (5), 102 (10), 116 (19), 129 (45), 143 (51), 156 (100), 171 (6), 199 (75). Exact mass calcd. for $C_{13}H_{13}NO$: 199.0997. Observed: 199.0986.

Cyanation of alkenylzinc derivatives. Typical procedure for the preparation of (E)-6-chloro-2-hexenenitrile (13a). A three-necked flask equipped with a thermometer, a gas inlet and an addition funnel was charged with (E)-5-chloro-1-iodo-1-pentene (1.38 g, 6.0 mmol) in THF (5 mL), cooled to -100 °C (liquid N_2 / ether bath). *n*-BuLi (3.9 mL, 6.3 mmol, 1.6 M in hexane) was added over 4 min. The resulting colorless solution was stirred for 3 min at -100 °C and a THF solution (5 mL) of ZnI_2 (1.91 g, 6.0 mmol) was added. After warming up to 0 °C for 2 min and cooling back to -78 °C, *p*-toluenesulfonyl cyanide (0.90 g, 5.0 mmol) in THF (5 mL) was added and the reaction mixture was warmed to rt and stirred for 3 h. After the usual workup and evaporation of the solvents, the crude residue obtained was purified by flash-chromatography (hexane:ether 10:1) yielding **13a** (466 mg, 72 %) as a clear oil (100 % E by GC analysis and ^{13}C-NMR analysis). IR (neat): 2960 (s), 2230 (s), 1630 (v), 1440 (v), 1205 (w), 1145 (w), 975 (s), 650 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.64 (dt, 1H, J = 8.2 Hz, 16.4 Hz), 5.35 (d, 1H, J = 16.3 Hz), 3.48 (t, 2H, J = 6.4 Hz), 2.39-2.31 (m, 2H), 1.91-1.82 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 153.9, 117.1, 100.9, 43.6, 30.2, 28.9. MS (EI, 70 eV): 66 (100), 67 (21), 80 (22), 129 (5). Anal. Calcd. for C_6H_8ClN: C, 55.61; H, 6.22; N, 10.80. Found: C, 55.73; H, 6.19; N, 10.52.

4-Chlorobenzonitrile (13b). 0.55 g (81 % yield) was obtained from 4-chloro-1-iodobenzene (1.19 g, 5 mmol) and *p*-toluenesulfonyl cyanide (0.90 g, 5 mmol). Reaction time: 4 h, rt. The crude product was purified by flash-chromatography (hexane:ether 10:1). IR (KBr): 3091 (s), 2226 (s), 1593 (m), 1484 (s), 1399 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, 2H, J = 10.8 Hz), 7.39 (d, 2H, J = 8.6 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 139.5, 133.4, 129.7, 117.9, 110.8. MS (EI, 70 eV): 102 (27), 137 (100), 139 (39). Anal. Calcd. for C_7H_4ClN. Calcd. C, 61.12; H, 2.93; N, 10.18. Found: C, 60.75; H, 3.22; N, 9.88.

Typical procedure for the cross-coupling between functionalized aryl or alkenylzinc halides and aryl or alkenyl iodides. Preparation of 4-(5-chloro-1-pentenyl)benzonitrile (14a). A three-necked flask equipped with a thermometer, a gas inlet and an addition funnel was charged with 4-bromobenzonitrile (1.09 g, 6 mmol) in THF (5 mL). The reaction mixture was cooled to -78 °C and *n*-BuLi (3.91 mL, 6.2 mmol, 1.6 M in hexane) was added over 4 min. A precipitate formed immediately and

the reaction mixture was stirred 30 min at this temperature. A THF solution (3 mL) of $ZnBr_2$ (1.35 g, 6 mmol) was slowly added and it was warmed up to 0 °C for 5 min. After cooling back to -20 °C, *bis*(dibenzylideneacetone)palladium(0) (0.13 g, 0.24 mmol, 4 mol %), TPP (0.25 g, 0.96 mmol, 16 mol %) and (E)-5-chloro-1-iodopentene **1b** (1.15 g, 5 mmol) in THF (5 mL) were added. The reaction mixture was stirred 5 h at 25 °C and diluted with ether (10 mL). The organic phase was worked up as described above leading to a crude product which was purified by flash-chromatography affording **14a** as a clear oil (0.76 g, 74 % yield).

Typical procedure for the coupling of functionalized arylzinc halides with aryl triflates. Preparation of 4-chlorobiphenyl (14o). To a solution of $Pd(dba)_2$ (163 mg, 0.3 mmol, 5 mol %) in THF (4 mL) was added dppf (125 mg, 0.3 mmol, 5 mol %) at 0 °C. After a few minutes, phenyl triflate (0.91 g, 4 mmol) was added, followed by a solution of 4-chlorophenylzinc bromide (6 mmol) in THF/hexane prepared as described above. The reaction mixture was heated to 60 °C for 1.5 h. After cooling to rt, the reaction mixture was worked up as usually and the crude residue obtained after evaporation of the solvents was purified by flash-chromatography (hexanes) affording **14o** as a clear oil (695 mg, 92 % yield).

Analytical data of the products (14a-p) of Table 3

(E)-4-(5-Chloro-1-pentenyl)benzonitrile (14a) (see the typical procedure above). IR (neat): 3020 (w), 2920 (s), 2220 (s), 1640 (m), 1600 (s), 1500 (m), 1440 (s), 1410 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.47 (d, 2H, J = 10 Hz), 7.31 (d, 2H, J = 10 Hz), 6.39-6.20 (m, 2H), 3.50 (t, 2H, J = 6.5 Hz), 2.32 (q, 2H, J = 7.0 Hz), 1.88 (q, 2H, J = 6.9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.0, 133.2, 132.9, 129.7, 126.2, 119.1, 119.1, 44.4, 31.0, 30.2. MS (EI, 70 eV): 115 (11), 116 (13), 129 (12), 142 (64), 205 (15). Anal. Calcd. for $C_{12}H_{12}ClN$: C, 70.07; H, 5.88; N, 6.81. Found: C, 69.88; H, 5.90; N, 6.72.

(E,E)-4,6-Tridecadienyl 2,2-dimethylpropionate (14b). 404 mg (72 % yield) of a colorless oil was obtained from 740 mg (E)-5-iodo-4-pentenyl 2,2-dimethylpropanoate **1c** (740 mg, 2.5 mmol) and (E)-1-iodo-1-hexene (480 mg, 2.3 mmol). Flash-chromatography (2 % ether in hexane). IR (neat): 3015 (m), 2958 (s), 2928 (s), 2855 (s), 1731 (s), 1480 (m), 1248 (s), 1156 (s), 987 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.03-5.94 (m, 2H), 5.63-5.49 (m, 2H), 4.08-4.03 (t, 2H, J = 6.5 Hz), 2.17-2.10 (q, 2H, J = 7.3 Hz), 2.08-2.01 (q, 2H, J = 7.0 Hz), 1.76-1.67 (p, 2H, J = 6.5 Hz), 1.44-1.26 (m, 8H), 1.19 (s, 9H), 0.90-0.86 (t, 3H, J = 6.7 Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.4, 133.0, 131.4, 130.3, 130.2, 63.7, 38.7, 32.5, 31.7, 29.3, 28.9, 28.8, 28.5, 27.2, 22.5, 13.9. MS (EI, 70 eV): 93 (100), 107 (39), 124 (46), 135 (11), 149 (6), 178 (67), 280 (1). Exact mass calcd. for $C_{18}H_{32}O_2$: 280.2402. Observed: 280.2392.

(E,E)-11-Pivaloxy-5,7-undecadienenitrile (14c). 573 mg (86 % yield) of a colorless oil were obtained from (E)-6-iodo-5-hexenenitrile **1d** (550 mg) and (E)-5-iodo-4-pentenyl 2,2-dimethylpropanoate **1c** (740 mg). Flash-chromatography (solvent gradient 5 %-20 % ether in hexane). IR (neat): 2677 (s), 2936 (s), 2247 (s), 1726 (s), 1480 (m), 1259 (s), 1159 (s), 990 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.05-5.92 (m, 2H), 5.60-5.51 (m, 1H), 5.49-5.40 (m, 1H), 4.04-3.99 (t, 2H, J = 6.5 Hz), 2.31-2.26 (t, 2H, J = 7.1 Hz), 2.21-2.14 (q, 2H, J = 7.1 Hz), 2.14-2.07 (q, 2H, J = 7.2 Hz), 1.75-1.64 (m, 4H), 1.15 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.2, 132.2, 131.9, 130.5, 129.1, 119.1, 63.5, 38.5, 31.0, 28.7, 28.2, 27.0, 24.9, 16.1. MS (EI, 70 eV): 93 (100), 107 (32), 120 (18), 133 (30), 146 (23), 161 (58), 263 (5). Exact mass calcd. for $C_{16}H_{25}NO_2$: 263.1885. Observed: 263.1902.

(E)-5-(4-Cyanophenyl)-4-pentenyl 2,2-dimethylpropanoate (14d). 306 mg (81 % yield) of an orange oil were obtained from 4-bromobenzonitrile **1f** (360 mg, 2.0 mmol) and 5-iodo-4-pentenyl pivalate (410 mg, 1.4 mmol). Flash-chromatography (2 % ethyl acetate in hexane). IR (neat): 2972 (s), 2936 (m), 2226 (s), 1725 (s), 1605 (s), 1481 (m), 1285 (s), 1159 (s), 970 (m), 734 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.57 (d, 2H, J = 8.1 Hz), 7.40 (d, 2H, J = 8.1 Hz), 6.40-6.38 (m, 2H), 4.11 (t, 2H, J = 6.4 Hz), 2.38-2.28 (m, 2H), 1.90-1.76 (m, 2H), 1.20 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 178.1, 142.0, 133.6, 132.1, (100), 169 (1), 180 (3), 289 $[M+NH_4]^+$(18). Exact mass calcd. for $C_{17}H_{21}NO_2NH_4$: 289.1916. Observed: 289.1915.

Ethyl 3-(4-cyanophenyl)benzoate (14e).[7] 374 mg (93 % yield) obtained from 4-bromobenzonitrile (365 mg, 2 mmol) and ethyl 3-iodobenzoate (440 mg, 1.6 mmol). Reaction time: 16 h, rt. The crude product was purified by flash-chromatography (ethyl acetate:hexane 3:97). IR (KBr): 2223 (m), 1606 (m), 1110 (s), 826 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 360 MHz): δ 8.27 (s, 1H), 8.10 (d, 1H, J = 7.8 Hz), 7.78 -7.71 (m, 5H), 7.56 (t, 1H, J = 7.8 Hz), 4.42 (q, 2H, J = 7.1 Hz), 1.42 (t, 3H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 90

MHz): δ 165.8, 144.2, 139.0, 132.4, 131.1, 129.3, 128.9, 127.9, 127.5, 118.4, 111.1, 61.0, 14.1. MS (EI, 70 eV): m/z (rel int): 151 (34), 178 (36), 206 (100), 223 (40), 236 (3), 251 (M+, 45). Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.58; H, 5.02; N, 5.36.

4-Cyano-4'-(carbethoxy)biphenyl (14f). 1.08 g (87 % yield) obtained from 4-bromobenzonitrile (1.09 g, 6 mmol) and ethyl 4-iodobenzoate (1.38 g, 5 mmol). The product was purified by crystallization in ethanol (mp 113-115 °C). IR (KBr): 3071 (w), 2991 (m), 2223 (s), 1706 (s), 1606 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.07 (d, 2H, J = 8.1 Hz), 7.66-7.53 (m, 6H), 4.34 (q, 2H, J = 7.1 Hz), 1.35 (t, 3H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 165.9, 144.3, 143.1, 132.5, 130.4, 130.1, 127.7, 127.0, 118.5, 111.6, 61.0, 14.2. MS (EI, 70 eV): 151 (16), 177 (15), 178 (18), 206 (100), 207 (19), 223 (26), 251 (44). Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.21; N, 5.57. Found: C, 76.33; H, 5.22; N, 5.61.

4-Acetoxy-4'-cyanobiphenyl (14g). 1.06 g (90 % yield) obtained from 4-bromobenzonitrile (1.09 g, 6 mmol) and 4-iodoacetoxybenzene (1.31 g, 5 mmol). Reaction time: 6 h, rt. The crude product was purified by crystallization in ethanol (mp 115-117 °C). IR (KBr): 3446 (w), 2226 (s), 1762 (s), 1605 (m), 1494 (s), 1362 (m), 1224 (s), 1204 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.70-7.55 (m, 6H), 7.19 (d, 2H, J = 8.7 Hz), 2.32 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 169.3, 151.2, 144.7, 136.8, 132.7, 128.3, 127.7, 122.4, 118.9, 111.1, 21.2. MS (EI, 70 eV): 27 (5), 43 (27), 140 (8), 166 (7), 195 (100), 196 (20), 237 (5). Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.99; H, 4.74; N, 5.70.

4-Cyano-4'-nitrobiphenyl (14h). 0.77 g (69 % yield) obtained from 4-bromobenzonitrile (1.09 g, 6 mmol) and 4-bromonitrobenzene (1.01 g, 5 mmol). The crude product was purified by crystallization in THF (mp 181-183 °C). IR (KBr): 3096 (m), 2925 (m), 2227 (s), 1602 (m), 1512 (s), 1348 (s) cm^{-1}. ^{1}H-NMR (DMSO-d_6, 300 MHz): δ 8.28 (d, 2H, J = 8.8 Hz), 7.99-7.92 (m, 6H). ^{13}C-NMR (DMSO-d_6, 75 MHz): δ 147.4, 144.5, 142.1, 132.9, 128.3, 127.9, 124.1, 118.5, 111.3. MS (EI, 70 eV): 67 (100), 91 (31), 129 (22), 143 (49), 206 (25), 208 (21). Anal. Calcd. for $C_{13}H_8N_2O_2$: C, 69.64; H, 3.60; N, 12.49. Found: C, 69.61; H, 3.55; N, 12.38.

4-Chloro-4'-(carbethoxy)biphenyl (14i). 0.57 g (88 % yield) obtained from 4-chloroiodobenzene (0.71 g, 3 mmol) and ethyl 4-iodobenzoate (0.69 g, 2.5 mmol). Reaction time: rt, 6 h. The crude product was purified by crystallization in ethanol (mp 71-73 °C). IR (KBr): 3058 (s), 2983 (s), 1714 (s), 1607 (m), 1478 (m), 1290 (s), 1277 (s), 1101 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.06 (d, 2H, J = 8.3 Hz), 7.61-7.40 (m, 6H), 4.36 (q, 2H, J = 7.1 Hz), 1.37 (t, 3H, J = 7.1 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.3, 144.2, 138.5, 134.3, 129.9, 129.6, 129.1, 128.5, 126.8, 61.0, 14.3. MS (EI, 70 eV): 152 (56), 153 (10), 183 (9), 215 (100), 216 (18), 217 (36), 222 (14), 224 (10), 232 (21), 234 (9), 260 (81), 261 (15), 262 (43). Anal. Calcd. for $C_{15}H_{13}ClO_2$: C, 69.10; H, 5.03. Found: C, 69.35; H, 5.09.

4-Chloro-4'-nitrobiphenyl (14j). 0.82 g (71 % yield) obtained from 4-chloroiodobenzene (1.43 g, 6 mmol) and 4-bromonitrobenzene (1.01 g, 5 mmol). The crude product was purified by crystallization in THF (mp 144-145 °C). IR (KBr): 3073 (w), 1596 (m), 1510 (s), 1477 (m). 1344 (s) cm^{-1}. ^{1}H-NMR (acetone-d_6, 300 MHz): δ 8.34 (d, 2H, J = 8.8 Hz), 7.96 (d, 2H, J = 9.0 Hz), 7.81 (d, 2H, J = 8.7 Hz), 7.57 (d, J = 8.7 Hz, 2H). ^{13}C-NMR (acetone-d_6, 75 MHz): δ 148.2, 146.7, 138.1, 135.5, 130.9, 130.0, 128.6, 124.8. MS (EI, 70 eV): 157 (68), 171 (26), 173 (24), 201 (94), 203 (100). Anal. Calcd. for $C_{12}H_8ClNO_2$: C, 61.69; H, 3.45; N, 5.99. Found: C, 61.61; H, 3.39; N, 5.76.

4-(3-Oxocyclohexenyl)benzonitrile (14k). 0.86 g (89 % yield) prepared from 4-bromobenzonitrile (1.09 g, 6 mmol) and 3-iodo-2-cyclohexen-1-one[22] (1.09 g, 5 mmol). The crude product was purified by crystallization in ethanol (mp 79-81 °C). IR (KBr): 3045 (w), 2952 (s), 2929 (s), 2223 (s), 1664 (s), 1603 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.62 (d, 2H, J = 8.6 Hz), 7.54 (d, 2H, J = 8.6 Hz), 6.33 (s, 1H), 2.69 (t, 2H, J = 6.0 Hz), 2.43 (t, 2H, J = 6.7 Hz), 2.11 (q, 2H, J = 6.3 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 198.9, 157.1, 143.2, 132.3, 127.8, 126.5, 118.1, 113.1, 37.0, 27.8, 22.5. MS (EI, 70 eV): 114 (8), 127 (7), 140 (22), 141 (35), 155 (7), 169 (100), 170 (14), 197 (49). Anal. Calcd. for $C_{13}H_{11}NO$: C, 79.17; H, 5.62; N, 7.10. Found: C, 79.11; H, 5.35; N, 7.05.

2-Carbomethoxy-4'-chlorobiphenyl (14l). 1.02 g (83 % yield) obtained from 4-choroiodobenzene (1.43 g, 6 mmol) and methyl 2-iodobenzoate (1.31 g, 5 mmol). Reaction time: 1.5 h, rt. Flash-chromatography (5 % ether in hexane). IR (neat): 3064 (m), 2950 (m), 1726 (s), 1287 (s), 1126 (s), 1088 (s), 834 (s), 764 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.87 (d, 1H, J = 7.7 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.44 (t, 1H, J =

7.5 Hz), 7.40-7.33 (m, 3H), 7.27 (d, 2H, J = 8.3 Hz), 3.69 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 168.7, 141.1, 139.9, 133.4, 131.4, 130.7, 130.1, 129.7, 128.2, 127.5, 52.0. MS (EI 70 eV): 76 (40), 152 (76), 215 (100), 246 (99). Anal. Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.50. Found: C, 67.93; H, 4.61.

2-Carbomethoxy-4'-cyanobiphenyl (14m). 0.83 g (84 % yield) obtained from 4-bromobenzonitrile (1.10 g, 6 mmol) and methyl 2-iodobenzoate (1.10 g, 4.2 mmol). Flash-chromatography (10 % ether in hexanes). IR (neat): 3065 (m), 2952 (m), 2228 (s), 1726 (s), 1290 (s), 1090 (s), 765 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.92 (d, 1H, J = 7.8 Hz), 7.67 (d, 2H, J = 8.2 Hz), 7.56 (t, 1H, J = 7.6 Hz), 7.47 (t, 1H, J = 7.6 Hz), 7.39 (d, 2H, J = 8.2 Hz), 7.30 (d, 1H, J = 7.8 Hz), 3.65 (s, 3H). ^{13}C-NMR (75 MHz): δ 168.0, 146.5, 141.1, 131.8, 130.6, 130.5, 130.2, 129.3, 128.3, 118.9, 111.2, 52.1. MS (EI, 70 eV): 151 (20), 178 (25), 206 (100), 237 (51). Anal. Calcd for $C_{15}H_{11}N_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.70; H, 4.75; N, 6.03.

4-Acetoxy-4'-chlorobiphenyl (14n). 0.73 g (71 % yield) obtained from 4-chloroiodobenzene (1.43 g, 6 mmol) and 4-acetoxy iodobenzene (1.10 g, 4.2 mmol). Flash-chromatography (15 % ether in hexane). (mp 108-110 °C). IR (neat): 3092 (w), 1750 (s), 1483 (s), 1205 (s), 1186 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.52 (d, 2H, J = 8.6 Hz), 7.46 (d, 2H, J = 8.7 Hz), 7.37 (d, 2H, J = 8.6 Hz), 7.14 (d, 2H, J = 8.6 Hz), 2.30 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 169.5, 150.5, 138.9, 137.8, 133.6, 129.0, 128.4, 128.1, 122.1, 21.1. MS (EI, 70 eV): 204 (100), 246 (12). Anal. Calcd for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.50. Found: C, 68.07; H, 4.40.

4-Chlorobiphenyl (14o). (see typical procedure) (mp 76-78 °C). IR (neat): 3058 (w), 3032 (w), 1479 (s), 1089 (m), 832 (s), 759 (s), 688 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.61-7.40 (m, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 139.9, 139.6, 133.3, 128.8, 128.7, 128.3, 127.5, 126.9. MS (EI, 70 eV): 76(22), 152 (46), 188 (100). Anal. Calcd. for $C_{12}H_9Cl$: C, 76.40; H, 4.81. Found: C, 76.30; H, 4.85.

4-Cyanobiphenyl (14p). 0.53 g (74 % yield) obtained from 4-bromobenzonitrile (1.10 g, 6 mmol) and phenyl trifluoromethylsulfonate[37] (0.90 g, 4 mmol). Flash-chromatography purification (5 % ethyl acetate in hexane), (mp 82-84 °C). IR (neat): 3077 (w), 2226 (s), 1605 (m), 1484 (m), 770 (s) 697 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.79-7.68 (m, 4H) 7.63-7.60 (m, 2H), 7.50-7.42 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.1, 118.8, 110.9. MS (EI, 70 eV): 179 (100). Anal. Calcd. for $C_{13}H_9N$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.31; H, 4.88; N, 7.95.

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