

## New Efficient Nickel-Catalyzed Cross-Coupling Reaction between Two Csp<sup>3</sup> Centers

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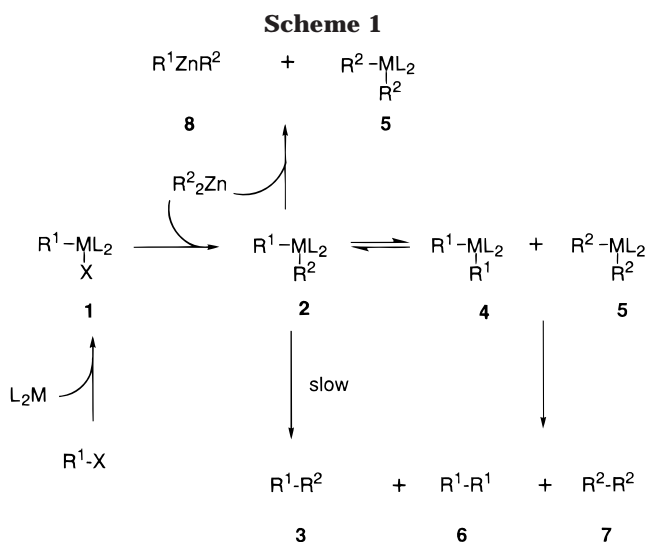
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The presence of a remote unsaturation (double bond, carbonyl group, cyano group) in an alkyl halide facilitates its cross-coupling reaction with various diorganozincs in the presence of Ni(acac)<sub>2</sub> (7.5–10 mol % in THF/NMP mixtures). These results were used to develop a new general cross-coupling reaction between functionalized diorganozincs and alkyl iodides using *m*- or *p*-trifluoromethylstyrene as a reaction promotor and Ni(acac)<sub>2</sub> as a catalyst (7.5–10 mol %; –35 °C, 5–10 h) leading to a broad range of polyfunctional cross-coupling products.

### Introduction

The cross-coupling reaction between an organometallic reagent R<sup>1</sup>M and an organic halide R<sup>2</sup>X is one of the most important methods for forming a new carbon–carbon bond.<sup>1</sup> Whereas cross-couplings between a Csp<sup>3</sup> center and either a Csp<sup>2</sup> or Csp center are well-known,<sup>1</sup> transition-metal-catalyzed cross-coupling reactions between Csp<sup>3</sup> centers are rare<sup>2</sup> and mostly only organocuprates<sup>3</sup> have been used for such C–C bond formation. This often requires the use of stoichiometric amounts of copper salts for the formation of the organocuprate R<sub>2</sub>CuLi and consequently often implies the loss of a nontransferred group R of R<sub>2</sub>CuLi.<sup>3</sup> Alternatively, copper-catalyzed cross-coupling of alkylmagnesium reagents displays a moderate chemoselectivity as a result of the high reactivity of the Grignard reagent.<sup>3,4</sup> Only recently, a chemoselective cross-coupling<sup>5</sup> reaction involving functionalized diorganozincs<sup>6</sup> (FG-R)<sub>2</sub>Zn in the presence of stoichiometric amounts of Me<sub>2</sub>Cu(CN)(MgCl)<sub>2</sub> has been developed.<sup>5</sup> However, the use of stoichiometric amounts of copper salts precludes large scale applications. There is the need for a transition-metal-catalyzed cross-coupling reaction between two Csp<sup>3</sup> centers.<sup>7</sup> The proposed catalytic cycle for such a catalysis (Scheme 1) first involves an oxidative addition of the transition metal catalyst (ML<sub>2</sub>; M = Ni or Pd) to a carbon–halide (X = I, Br) bond. Such a



reaction is well-known<sup>8</sup> and does not present a major problem. The resulting organometallic species **1** should also readily undergo a transmetalation with the zinc reagent R<sub>2</sub><sub>2</sub>Zn providing the key intermediate **2** (R<sup>1</sup>(R<sup>2</sup>)-ML<sub>2</sub>), which after reductive elimination should afford the desired cross-coupling product **3**. Unfortunately, contrary to a reductive elimination between two Csp<sup>2</sup> centers or a Csp<sup>3</sup> and Csp<sup>2</sup> center, the reductive elimination between two Csp<sup>3</sup> centers is slow. A competitive exchange reaction between the R<sup>1</sup> and R<sup>2</sup> groups occurs, affording the symmetrical organometallic species **4** (R<sup>1</sup><sub>2</sub>ML<sub>2</sub>) and **5** (R<sup>2</sup><sub>2</sub>ML<sub>2</sub>), which after reductive elimination furnish the homocoupling products **6** (R<sup>1</sup>-R<sup>1</sup>) and **7** (R<sup>2</sup>-R<sup>2</sup>). The key intermediate **2** can also undergo a further exchange reaction<sup>9</sup> with the zinc reagent R<sub>2</sub><sub>2</sub>Zn, providing the new zinc reagent **8** (R<sup>1</sup>ZnR<sup>2</sup>). To avoid most of these side reactions, a fast reductive elimination of **2** would be

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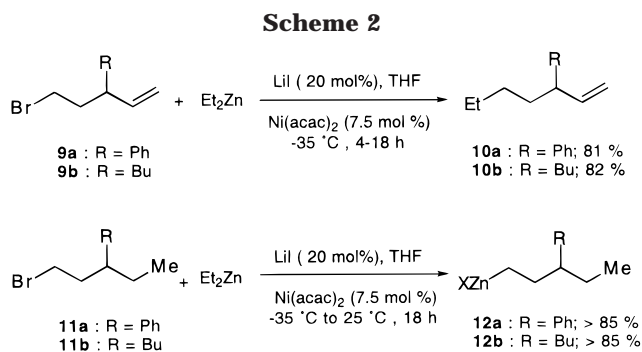
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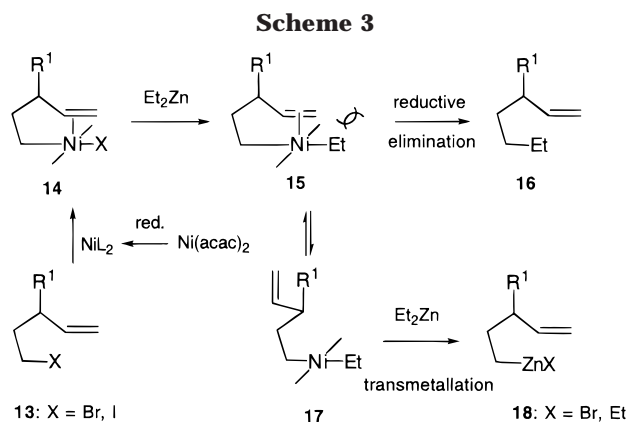


desirable. This elimination is especially difficult because of the high electron-donor ability of a Csp<sup>3</sup> center, which provides an electron-rich organometallic intermediate **2** less prone to reductively eliminate the two Csp<sup>3</sup> ligands. Mechanistic studies of Yamamoto<sup>10</sup> and Sustmann<sup>11</sup> indicate that the complexation of a Ni(II) or Pd(II) metallic center with an olefin bearing an electron-withdrawing substituent facilitates the reductive elimination. Herein, we wish to report a new nickel-catalyzed cross-coupling reaction between Csp<sup>3</sup> centers based on this principle, allowing the preparation of highly functionalized cross-coupling products.<sup>12</sup>

### Results and Discussion

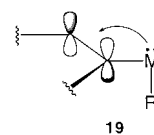
During the course of the study of radical cyclization reactions mediated by diethylzinc,<sup>9</sup> we have observed that the unsaturated organic bromides **9a,b** react with diethylzinc in the presence of catalytic amounts of Ni(acac)<sub>2</sub> (7.5 mol %) and LiI (20 mol %) in THF (−35 °C, 4–18 h), affording the corresponding cross-coupling products **10a,b** in 81–82% yield (Scheme 2).<sup>13</sup>

This behavior was surprising because in all the previously performed reactions between alkyl bromides or iodides with diethylzinc, the halogen–zinc exchange product (or cyclized organometallic product)<sup>9</sup> was obtained. We suspected that the remote double bond could act as an additional ligand for the nickel intermediates in the cross-coupling reaction.<sup>10,11</sup> The reduction of this double bond leads to the saturated alkyl bromides **11a,b**; these were submitted to the same reaction conditions (Ni(acac)<sub>2</sub> (7.5 mol %), LiI (20 mol %), −35 °C, 18 h) and negligible amounts of cross-coupling products were formed. Only the bromine–zinc exchange products **12a,b** were



obtained in over 85% yield as confirmed by iodolysis experiments of the crude reaction mixtures (Scheme 2). The absence of cross-coupling products clearly shows the importance of the double bond in the alkyl iodide for the course of the reaction. On the basis of the pioneering work of Yamamoto<sup>10</sup> and Sustmann,<sup>11</sup> we have proposed the following mechanistic scheme (Scheme 3).

The catalytically active species (L<sub>2</sub>Ni(0)) generated by the in situ reduction of Ni(acac)<sub>2</sub> undergoes an oxidative addition on the alkyl halide **13** (X = Br, I), producing a nickel(II) complex **14**, in which the double bond is complexed to the metal center. After ligand exchange with diethylzinc, the complex **15** is formed. The coordination of the double bond by nickel delocalizes the *d* electrons of the nickel into the π\*-antibonding orbitals of the double bond, resulting in a faster reductive elimination reaction leading to the desired cross-coupling product **16**. If a dissociation of the double bond occurs as a result of steric interactions (or if no double bond is present), a nickel(II) intermediate of type **17** results. This intermediate does not readily undergo a reductive elimination but rather can exchange further its organic ligands with diethylzinc. This transmetalation reaction results in the formation of the new zinc reagent **18**. It is formally the result of a halide–zinc exchange (**13** → **18**). This mechanistic scheme proves very useful to expand the scope of the reaction and may also explain why cross-couplings between Csp<sup>2</sup> centers are so efficient.<sup>1,2</sup> Thus, the higher electronegativity (and less donor ability) of Csp<sup>2</sup> centers promotes the reductive elimination, but also the presence of adjacent double bonds which are able to remove *d* electrons from palladium or nickel by transfer to the p\* orbitals (see **19**) may be responsible for the fast cross-coupling reaction.



Although other dialkylzincs react less readily in THF, a solvent change to a 2:1 mixture of THF and *N*-methylpyrrolidinone (NMP) sufficiently enhances the reaction rate so that a range of unsaturated iodides (**20a–d**)<sup>14</sup> undergo this nickel-catalyzed cross-coupling with good to excellent yields (Table 1). Thus, whereas **20a** requires a reaction time of 24 h for the cross-coupling

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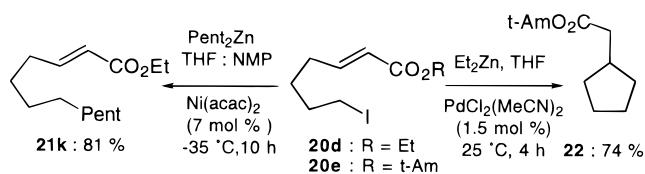
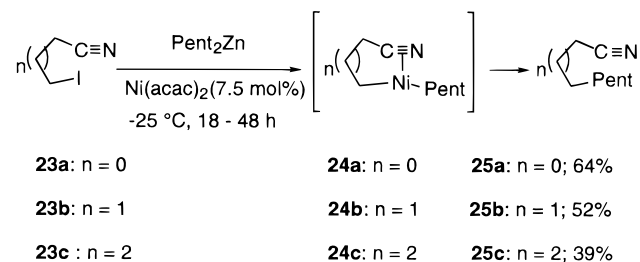
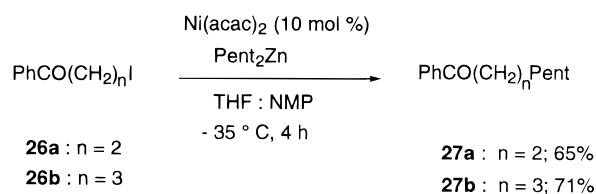
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**Table 1. Products 21a–k Obtained by the Nickel-Catalyzed Cross-Coupling of Dialkylzincs with Alkyl Iodides 20a–d in THF/NMP**

Entry	Iodoalkane of Type 20	R <sub>2</sub> Zn (R)	Product 21	Yield (%) <sup>a</sup>
1		Pent		80(73) <sup>b</sup>
2		Pent		72
3	<b>20a</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>		90(77) <sup>b</sup>
4	<b>20b</b>	PivO(CH <sub>2</sub> ) <sub>4</sub>		70(32) <sup>b</sup>
5		Pent		83
6		Et		84
7	<b>20c</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>		79
8	<b>20d</b>	AcO(CH <sub>2</sub> ) <sub>5</sub>		78
9	<b>20d</b>	PivO(CH <sub>2</sub> ) <sub>6</sub>		73
10	<b>20c</b>			65
11	<b>20d</b>	Pent		81

<sup>a</sup> Yield of analytically pure products <sup>b</sup> Reaction performed in THF.

reaction with dipentylzinc at  $-35\text{ }^{\circ}\text{C}$  in THF (73% isolated yield), the reaction of **20a** with dipentylzinc in THF/NMP (2:1) is complete within 3 h, leading to **21a** (80% isolated yield) (see entry 1 of Table 1). Similar results are observed with functionalized zinc reagents (see entries 3 and 4). A wide range of diorganozinc reagents obtained either by the iodine–zinc exchange reaction<sup>15</sup> or by a boron–zinc exchange<sup>16</sup> can be used for this cross-coupling reaction. The presence of a carbonyloxy substituent on the double bond facilitates further the cross-coupling reaction, and the substrates **20c** and **20d** afford the expected products of type **21** in good yields. Interestingly, palladium(0) complexes are less useful in this cross-coupling reaction. Thus, whereas the reaction of **20d** with dipentylzinc in the presence of Ni(acac)<sub>2</sub> (7 mol %) THF/NMP,  $-35\text{ }^{\circ}\text{C}$ , 10 h) only produces the cross-coupling product (**21k**), the corresponding reaction of the *tert*-amyl ester **20e**<sup>8e</sup> with diethylzinc and PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub> (1.5 mol %) as catalyst furnishes the cyclization product **22** (THF,  $25\text{ }^{\circ}\text{C}$ , 4 h, 74% isolated yield; Scheme 4).<sup>8e</sup> We

**Scheme 4****Scheme 5****Scheme 6**

have established that the presence of a double bond facilitates the cross-coupling reaction. To expand the scope of this reaction, we have now examined if a similar activation can be obtained with other unsaturated groups. Therefore, we have submitted the iodonitriles **23a–c**<sup>17</sup> to the cross-coupling reaction conditions with dipentylzinc (THF/NMP, Ni(acac)<sub>2</sub> (7.5 mol %),  $-25\text{ }^{\circ}\text{C}$ , 18–48 h), and we have obtained the cross-coupling products **25a–c** in 64–39% yield (Scheme 5).

The efficiency of the cross-coupling decreases with the chain length between the iodine and cyano group. This may be due to the better side-on complexation of the cyanide in the intermediate **24a** than in **24b** and **24c**. Alternatively, the cyano group may also influence the rate of the cross-coupling by an inductive effect that decreases with increasing values of  $n$ . Next, we have examined the case of keto-substituted alkyl iodides and have obtained fast rates of cross-coupling reactions with phenyl 2-iodoethyl ketone (**26a**)<sup>18</sup> and phenyl 3-iodopropyl ketone (**26b**)<sup>19</sup> leading to the desired cross-coupling products **27a,b**, respectively, in 65% and 71% yield (Scheme 6).

The crucial importance of the substituent at the carbonyl group is shown by using an alkyl 3-iodopropyl ketone instead of the corresponding aryl ketone. Thus, the reaction of butyl 3-iodopropyl ketone (**26c**) with dipentylzinc under our standard conditions provides the desired cross-coupling product (**27c**)<sup>20</sup> as well as considerable amounts of the iodine–zinc exchange product **28**

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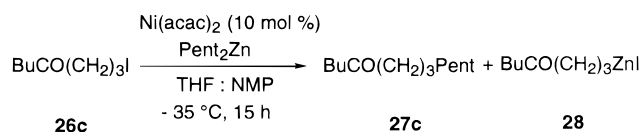
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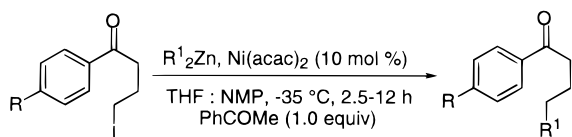
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## Scheme 7



PhCOMe (0 equiv) **27c** : 20% **28** : 57%  
 PhCOMe (1.0 equiv) **27c** : 71% **28** : < 5%

## Scheme 8



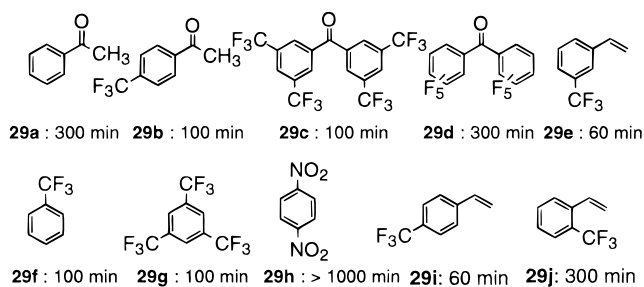
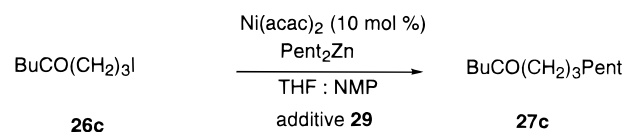
**26b** : R = H **27b** : R = H; R<sup>1</sup> = Pent; 88 %  
**26d** : R = OMe **27d** : R = OMe; R<sup>1</sup> = Bu; 71 %  
**26e** : R = CF<sub>3</sub> **27e** : R = CF<sub>3</sub>; R<sup>1</sup> = Pent; 92 %

(as proven by iodolysis and hydrolysis reactions). This result demonstrates the importance of the coordination of the nickel intermediate with an electron-poor unsaturation.<sup>21</sup> The addition of acetophenone (1 equiv) as an external ligand has a beneficial effect in this reaction. It accelerates considerably the rate of the reaction and completely suppresses the iodine–zinc side product **28** (less than 5% is formed). After workup, the cross-coupling product (**27c**) is obtained in 71% isolated yield (Scheme 7).

To evaluate the importance of the electron density of the arylcarbonyl group, we have treated several substituted aryl 3-iodopropyl ketones (**26b** (R = H),<sup>19</sup> **26d** (R = OMe), and **26e** (R = CF<sub>3</sub>)) with R<sup>1</sup><sub>2</sub>Zn (R<sup>1</sup> = Pent, Bu) (Ni(acac)<sub>2</sub> (10 mol %), PhCOMe (1 equiv), THF/NMP, –35 °C, 2.5–12 h) (Scheme 8).

The most efficient cross-coupling was obtained with the CF<sub>3</sub>-substituted alkyl iodide (**26e**). The reaction was complete after 2.5 h, affording the product **27e** in 92% yield. The unsubstituted substrate (**26b**, R = H) gave under these conditions the corresponding product (**27b**) in 88% yield, whereas the *p*-MeO-substituted starting alkyl iodide (**26d**) reacted very slowly (12 h reaction time), furnishing the cross-coupling product (**27d**) in only 71% isolated yield. Similarly, we have observed that several other cross-coupling reactions can be accelerated by the addition of an unsaturated molecule as promotor. Thus, the addition of an equivalent of ethyl crotonate to 5-iodopentanenitrile (**23c**) improves the yield of the cross-coupling product (**25c**) from 39% to 50%. Similarly, the reaction of dipentylzinc with 6-iodohexyl pivalate provides, in the presence of ethyl crotonate (1 equiv) and our standard reaction conditions, the cross-coupling product undecyl pivalate (**27f**) in 59% yield. Less than 30% yield is obtained in the absence of ethyl crotonate. Preliminary experiments have shown that styrene can also be used as promotor. On the basis of these results, we have examined in a more systematic way the nickel-catalyzed cross-coupling reaction between 1-iodo-4-octanone (**26c**) with dipentylzinc in the presence of 1 equiv of a cocatalyst or promotor (**29**), using the standard reaction conditions (Ni(acac)<sub>2</sub>, 10 mol %, THF/NMP, –35

## Scheme 9



°C). We have observed remarkable differences in reactivity and selectivity (Scheme 9).

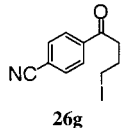
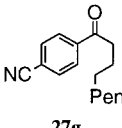
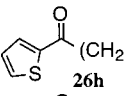
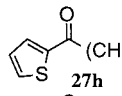
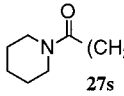
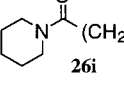
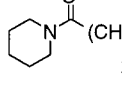
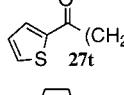
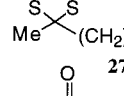
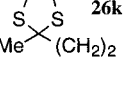
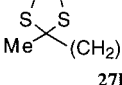
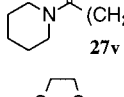
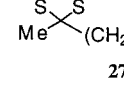

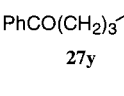

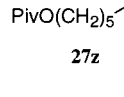
The presence of trifluoromethyl substituents increases the reaction rate (compare **29a** with **29b** and **29c**). However, perfluorinated benzophenone (**29d**) was less efficient than CF<sub>3</sub>-substituted additives, including the CF<sub>3</sub>-substituted benzenes<sup>21</sup> (**29f** and **29g**). Interestingly, 1,4-dinitrobenzene (**29h**) inhibits the cross-coupling reaction. Although various additives such as **29b,c** or **29f,g** led to fast reaction times, in all of these reactions the competitive formation of the iodine–zinc exchange product was observed. By using *m*-trifluoromethylstyrene (**29e**) or *p*-trifluoromethylstyrene (**29i**), considerably less iodine–zinc exchange product was observed and fast reaction times were obtained. Interestingly, *o*-trifluoromethylstyrene (**29j**) was far less active, showing that the complexation to the double bond may be less effective with **29j** as a result of steric hindrance. This indicates also that a complexation of the ligand to the nickel center is required and that electron transfer through space is not operating. It was possible to use substoichiometric amounts of the cocatalyst **29e** (20–50 mol %) with similar results. With these optimized reaction conditions, it was now possible to perform a variety of cross-coupling reactions (Table 2). All of these reactions were completed within a few hours at –35 °C. The presence of various functional groups was well tolerated. Some functional groups such as a thioether or a thioacetal have an accelerating effect as a result of a complexation of the nickel intermediates with the sulfur atom.<sup>22</sup> The cross-coupling with ester- or amide-functionalized iodoalkanes proceeds well with a range of functionalized zinc reagents, leading to polyfunctional products of type **27** (Table 2). The presence of a promotor influences also the chemoselectivity of the new carbon–carbon bond formation. Thus, the reaction of the iodo-ketone **26b** with diisopropylzinc (Ni(acac)<sub>2</sub>, 10 mol %, THF/NMP, –35 °C, 5 h) in the absence of acetophenone furnishes a mixture of the cross-coupling product **30** and the isomerized product **31** in the ratio 75:25. This isomerization can be mostly avoided by adding acetophenone **29a** (50 mol %), thereby leading to the desired product (**30**)<sup>23</sup> in 62% yield with only 3% of the isomer **31** (Scheme 10).

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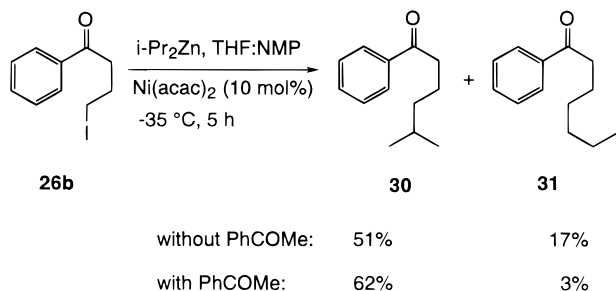
(22) For an excellent review on nickel-catalyzed reaction of thioketals, see: Luh, T.-Y. *Synlett* **1996**, 201–208.

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**Table 2. Products (27f–z) Obtained by Nickel-Catalyzed Cross-Coupling Reaction between Dialkylzincs and Polyfunctional Alkyl Iodides in the Presence of a Promotor**

Entry	Iodoalkane of type 26 (R)	R <sub>2</sub> Zn (R)	Product of type 27	Yield (%) <sup>a</sup>	Entry	Iodoalkane of type 26 (R)	R <sub>2</sub> Zn (R)	Product of type 27	Yield (%) <sup>a</sup>
1	PivO(CH <sub>2</sub> ) <sub>6</sub> <b>26f</b>	Pent	PivO(CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub> <b>27f</b>	59 <sup>h</sup>	12	<b>26c</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>	BuCO(CH <sub>2</sub> ) <sub>6</sub> OPiv <b>27q</b>	68 <sup>e</sup>
2	 <b>26g</b>	Pent	 <b>27g</b>	81 <sup>c</sup>	13	BnO <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> <b>26n</b>	Pent	BnO <sub>2</sub> C(CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> <b>27r</b>	76 <sup>d</sup>
3	 <b>26h</b>	Pent	 <b>27h</b>	67 <sup>g</sup>	14	<b>26i</b>	Pent	 <b>27s</b>	70 <sup>g</sup>
4	 <b>26i</b>	PivO(CH <sub>2</sub> ) <sub>4</sub>	 <b>27i</b>	64 <sup>g</sup>	15	<b>26h</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>	 <b>27t</b>	70 <sup>c</sup>
5	EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub> <b>26j</b>	Pent	EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub> <b>27j</b>	72 <sup>d</sup>	16	<b>26k</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>	 <b>27u</b>	70 <sup>b</sup>
6	 <b>26k</b>	Pent	 <b>27k</b>	78 <sup>d</sup>	17	<b>26i</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>	 <b>27v</b>	68 <sup>f</sup>
7	<b>26j</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>	EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>5</sub> OPiv <b>27l</b>	60 <sup>g</sup>	18	<b>26k</b>	PivO(CH <sub>2</sub> ) <sub>5</sub>	 <b>27w</b>	67 <sup>c</sup>
8	<b>26c</b>	EtO <sub>2</sub> C(CH <sub>2</sub> ) <sub>2</sub>	BuCO(CH <sub>2</sub> ) <sub>5</sub> CO <sub>2</sub> Et <b>27m</b>	58 <sup>g</sup>	19	<b>26b</b>		PhCO(CH <sub>2</sub> ) <sub>3</sub>  <b>27y</b>	66 <sup>g</sup>
9	PhS(CH <sub>2</sub> ) <sub>3</sub> <b>26l</b>	Pent	PhS(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub> <b>27n</b>	71 <sup>b</sup>	20	<b>26m</b>		PivO(CH <sub>2</sub> ) <sub>5</sub>  <b>27z</b>	74 <sup>f</sup>
10	PivO(CH <sub>2</sub> ) <sub>5</sub> <b>26m</b>	Pent	PivO(CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub> <b>27o</b>	78 <sup>c</sup>					
11	<b>26b</b>	PivO(CH <sub>2</sub> ) <sub>3</sub>	PhCO(CH <sub>2</sub> ) <sub>6</sub> OPiv <b>27p</b>	76 <sup>d</sup>					

<sup>a</sup> Isolated yields of analytically pure products. <sup>b</sup> Performed with **29e** (0.5 equiv). <sup>c</sup> Performed with **29e** (0.3 equiv). <sup>d</sup> Performed with **29e** (0.2 equiv). <sup>e</sup> Performed with **29a** (0.5 equiv). <sup>f</sup> Performed with **29e** (1.0 equiv). <sup>g</sup> Performed with **29a** (1.0 equiv). <sup>h</sup> Performed with ethyl crotonate (1.0 equiv).

**Scheme 10**

In summary, we have developed a new nickel-catalyzed cross-coupling reaction between polyfunctional primary iodoalkanes and primary diorganozincs using as best promotor *m*- or *p*-trifluoromethylstyrene (**29e** and **29i**). The cross-coupling reaction appears to have a large scope and further extensions are currently investigated.

**Experimental Section**

**General Considerations.** Unless otherwise indicated, all reactions were carried out under argon. Solvents (THF, toluene) were dried and freshly distilled over sodium/benzophenone. *N*-Methylpyrrolidone (NMP) was freshly distilled over CaH<sub>2</sub>.

Reactions were monitored by gas–liquid phase chromatography (GC) or thin-layer chromatography (TLC) of hydrolyzed

aliquots. Commercially available starting materials were used without further purification. Melting points are uncorrected.

**Starting Materials.** The following starting materials were prepared according to literature procedures: 5-iodo-3-phenyl-1-pentene (**20a**),<sup>14a</sup> (*E*)-ethyl 6-iodo-2-hexenoate (**20c**),<sup>14b</sup> (*E*)-ethyl 7-iodo-2-heptenoate (**20d**),<sup>14b</sup> (*E*)-*tert*-amyl 7-iodo-2-heptenoate (**20e**),<sup>8c</sup> 3-iodopropanenitrile (**23a**),<sup>17a</sup> 4-iodobutanenitrile (**23b**),<sup>17b</sup> 5-iodopentanenitrile (**23c**),<sup>17c</sup> 3-iodo-1-phenyl-1-propanone (**26a**),<sup>18</sup> 4-iodo-1-phenyl-1-butanone (**26b**),<sup>19</sup> 6-iodohexyl pivalate (**26f**),<sup>24</sup> 4-iodo-1-(2-thienyl)-1-butanone (**26h**),<sup>25</sup> ethyl 3-iodopropanoate (**26j**),<sup>26</sup> 2-(2-iodoethyl)-2-methyl-1,3-dithiolane (**26k**),<sup>27</sup> 3-iodopropyl phenyl sulfide (**26l**),<sup>28</sup> 5-iodopentyl pivalate (**26m**),<sup>24</sup> benzyl 3-iodopropanoate (**26n**),<sup>29</sup> 4-iodobutyl pivalate,<sup>30</sup> 3-iodopropyl pivalate,<sup>24</sup> 5-iodopentyl acetate,<sup>31</sup> 3-chloro-1-piperidino-1-propanone,<sup>32</sup> 4-(4-chlorobutanoyl)benzoxazole,<sup>33</sup> and 1-chloro-4-octanone.<sup>34</sup>

The diorganozinc reagents employed in cross-coupling reactions were prepared according to literature procedures.<sup>6</sup>

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**5-Bromo-3-phenyl-1-pentene (9a).** To an ice-cold solution of PPh<sub>3</sub> (2.62 g, 10 mmol) in toluene (15 mL) was added Br<sub>2</sub> (1.6 g, 10 mmol), and the reaction mixture was warmed to room temperature. After 30 h, the solution was cooled at 0 °C, and pyridine (0.79 g, 10 mmol) followed by 3-phenyl-4-pentenol (1.62 g, 10 mmol dissolved in toluene) was added. The reaction mixture was allowed to warm to room temperature and stirred for 3 h, before being poured into hexanes and filtered. The organic phase was washed with H<sub>2</sub>O and brine and dried (MgSO<sub>4</sub>). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/*t*-BuOMe 95:5) affording the desired product as a colorless oil (1.76 g, 78%). IR (neat): 3082, 3063, 1638, 701 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.39–7.24 (5H, m), 6.04–5.92 (1H, m), 5.20–5.12 (2H, m), 3.58 (1H, q, *J* = 7.5 Hz), 3.44–3.28 (2H, m), 2.37–2.19 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): δ 143.0, 141.0, 129.1, 128.1, 127.1, 115.6, 48.2, 38.4, 32.2. MS (EI): 225 (M<sup>+</sup>, 6), 117 (100). Anal. Calcd for C<sub>11</sub>H<sub>13</sub>Br: C, 58.69; H, 5.82. Found: C, 58.84; H, 5.97.

**5-Bromo-3-butyl-1-pentene (9b).** The procedure described above for the preparation of 1-bromo-3-phenyl-pent-4-ene (9a) was used, starting from 3-butyl-4-pentenol (1.42 g, 10 mmol). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording the desired product as a colorless oil (1.56 g, 76%). IR (neat): 3078, 2928, 1641, 640 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 5.46–5.34 (1H, m), 5.01–4.94 (2H, m), 3.41–3.21 (2H, m), 2.10–1.17 (9H, m), 0.82 (3H, t, *J* = 6.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 141.3, 115.7, 42.7, 37.8, 34.5, 32.0, 29.2, 22.7, 14.0. MS (EI): 205 (M<sup>+</sup>, 8), 162 (20), 148 (28), 54 (100). Anal. Calcd for C<sub>9</sub>H<sub>17</sub>Br: C, 52.70; H, 8.35. Found: C, 52.91; H, 8.32.

**5-Iodo-3-butyl-1-pentene (20b).** 3-Butyl-4-pentenol (1.58 g, 11.2 mmol) and MeI·2DCC<sup>35</sup> (7.39 g, 22.4 mmol) were dissolved in THF (125 mL), and the mixture was stirred at 35 °C for 8 h. The solvent was removed under reduced pressure, and the residue was dissolved in hexanes and washed with a 4:1 mixture of MeOH and H<sub>2</sub>O (60 mL). The aqueous phase was extracted with hexanes, and the combined organic fraction was washed with brine and dried (MgSO<sub>4</sub>). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording the product as a pale yellow oil (1.64 g, 58%). IR (neat): 3076, 2957, 1641, 917 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 5.45–5.36 (1H, m), 5.03–4.97 (2H, m), 3.22–3.14 (1H, m), 3.05–2.96 (1H, m), 2.05–1.16 (9H, m), 0.83 (3H, t, *J* = 6.7 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 141.3, 115.9, 45.0, 38.6, 34.4, 29.3, 22.8, 14.2, 5.4. MS (EI): 252 (M<sup>+</sup>, 3), 196 (25), 55 (100). Anal. Calcd for C<sub>9</sub>H<sub>17</sub>I: C, 42.87; H, 6.80. Found: C, 43.12; H, 6.90.

**1-Iodo-4-octanone (26c).** 1-Chloro-4-octanone<sup>34</sup> (5.85 g, 36 mmol) was treated with NaI (54 g, 360 mmol) in acetone (100 mL), and the mixture was refluxed overnight. The solvent was evaporated under reduced pressure and Et<sub>2</sub>O was added (100 mL). The organic layer was washed with an aqueous solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and the aqueous phase was extracted with Et<sub>2</sub>O. The combined organic fractions were dried (Na<sub>2</sub>SO<sub>4</sub>). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1) affording the product as a yellow oil (7.14 g, 78%). IR (neat): 2957, 1713, 1465 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.16 (2H, t, *J* = 6.6 Hz), 2.50 (2H, t, *J* = 6.9 Hz), 2.35 (2H, t, *J* = 7.3 Hz), 2.04–1.97 (2H, m), 1.54–1.44 (2H, m), 1.30–1.18 (2H, m), 0.84 (3H, t, *J* = 7.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 209.2, 42.6, 42.5, 27.0, 25.8, 22.2, 13.7, 6.5. MS (EI): 254 (M<sup>+</sup>, 100), 127 (52). Anal. Calcd for C<sub>8</sub>H<sub>15</sub>IO: C, 37.81; H, 5.94. Found: C, 37.80; H, 6.08.

**4-Iodo-1-(4-methoxyphenyl)butanone (26d).** The same procedure as described above has been used starting from

4-chloro-1-(4-methoxyphenyl)butanone (7.65 g, 36 mmol). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a yellow solid (mp 43 °C; 8.2 g, 75%). IR (neat): 2957, 1666, 1600, 1262 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.85–7.80 (2H, m), 6.84–6.79 (2H, m), 3.74 (3H, s), 3.19 (2H, t, *J* = 6.7 Hz), 2.94 (2H, t, *J* = 6.9 Hz), 2.16–2.07 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 196.7, 163.3, 130.0, 129.6, 113.5, 55.3, 38.4, 27.7, 6.8. MS (EI): 304 (M<sup>+</sup>, 0.7), 177 (28), 150 (23), 135 (100). M<sup>+</sup> calcd for C<sub>11</sub>H<sub>13</sub>IO<sub>2</sub>: 303.9960. Observed: 303.9961.

**4-Iodo-1-(4-trifluoromethylphenyl)butanone (26e).** In a three-necked 250 mL flask equipped with a stirring bar, a thermometer, and a gas inlet, dry MnCl<sub>2</sub> (5 g, 40 mmol)<sup>36</sup> and dry LiCl (3.4 g, 80 mmol) were dissolved in THF (100 mL) under argon. The reaction mixture was cooled at –60 °C, and a solution of 4-trifluoromethylphenylmagnesium bromide (1.7M in THF) (24 mL, 40 mmol) was carefully added by syringe. The reaction mixture was allowed to warm to 0 °C and after 10 min cooled again at –50 °C. 4-Chlorobutyl chloride (4.0 mL, 36 mmol) was added followed by CuCl (79 mg, 2 mol %). The reaction mixture was allowed to reach room temperature and stirred for 1 h before being poured into an ice-cold aqueous solution of NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O. The organic phase was dried (MgSO<sub>4</sub>), and the residue obtained after evaporation of the solvents was used in the next step without purification. The crude product was treated with NaI as described above and the residue obtained after the workup was purified by flash chromatography (hexanes/ether 20:1) affording the product as a yellow oil (8.5 g, 69%). IR (neat): 3066, 1692, 1326, 1169, 1130, 1066 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.97 (2H, d, *J* = 8.1 Hz), 7.62 (2H, d, *J* = 8.1 Hz), 3.25 (2H, t, *J* = 6.6 Hz), 3.07 (2H, t, *J* = 6.9 Hz), 2.21–2.10 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 197.3, 139.1, 134.2 (q, *J* = 32.6 Hz), 128.1, 125.4 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 271.0 Hz), 39.0, 27.0, 6.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 188 MHz): δ –63.2. MS (EI): 323 (1), 254 (2), 215 (29), 173 (100), 145 (27). M<sup>+</sup> calcd for C<sub>11</sub>H<sub>10</sub>IOF<sub>3</sub>: 322.9749. Observed: 322.9744.

**4-(4-Iodobutanoyl)benzotrile (26g).** The same procedure as described above for the preparation of 26c has been used starting from 4-(4-chlorobutanoyl)benzotrile<sup>33</sup> (7.47 g, 36 mmol). The crude product was purified by flash chromatography (hexanes/ether 10:1) affording the product as a yellow solid (mp 61 °C; 7.75 g, 72%). IR (neat): 3078, 2953, 2226, 1687 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.99 (2H, d, *J* = 8.1 Hz), 7.71 (2H, d, *J* = 8.1 Hz), 3.25 (2H, t, *J* = 6.5 Hz), 3.08 (2H, t, *J* = 6.8 Hz), 2.23–2.12 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 197.2, 139.6, 132.6, 128.4, 117.8, 116.5, 39.2, 27.1, 6.2. MS (EI): 299 (M<sup>+</sup>, 100), 172 (29). Anal. Calcd for C<sub>11</sub>H<sub>10</sub>INO: C, 44.17; H, 3.37; N, 4.68. Found: C, 44.05; H, 3.45; N, 4.53.

**3-Iodo-1-piperidino-1-propanone (26i).** The same procedure as described above has been used starting from 3-chloro-1-piperidino-1-propanone<sup>32</sup> (6.32 g, 36 mmol). The crude product was purified by flash chromatography (hexanes/ether 2:8) affording the product as a pale yellow oil (8.65 g, 90%). IR (neat): 2934, 2853, 1634, 1443 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.49 (2H, t, *J* = 5.5 Hz), 3.34–3.29 (4H, m), 2.88 (2H, t, *J* = 7.46 Hz), 1.63–1.43 (6H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 168.7, 46.3, 42.7, 37.4, 26.3, 25.4, 24.3, –1.6. MS (EI): 267 (M<sup>+</sup>, 25), 140 (100). Anal. Calcd for C<sub>8</sub>H<sub>14</sub>INO: C, 35.97; H, 5.28; N, 5.24. Found: C, 35.86; H, 5.12; N, 5.57.

**Ni(acac)<sub>2</sub>-Catalyzed Cross-Coupling between Dialkylzincs and Alkyl Iodides. Typical Procedure A. Preparation of (*E*)-Ethyl 12-Acetoxy-2-decenoate (21h).** A 50 mL two-necked flask equipped with an argon inlet and a rubber septum was charged with Ni(acac)<sub>2</sub> (0.116 g, 7.5 mol %). After the flask was cooled to –40 °C, THF (2.5 mL), NMP (1.5 mL), and 20c (1.69 g, 6 mmol) were added successively by syringe. The reaction mixture was cooled to –78 °C, and a solution of bis(5-acetoxyphenyl)zinc in THF (2 mL) prepared from 5-iodopentyl acetate (6.14 g, 24 mmol) and Et<sub>2</sub>Zn by an iodine–zinc

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exchange reaction was slowly added. The reaction mixture was allowed to warm to  $-35\text{ }^{\circ}\text{C}$  and was stirred for 15 h at this temperature. Excess of dialkylzinc was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  solution. After the usual workup, the resulting crude oil obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1–5:1) affording the desired product (1.33 g, 78% yield) as a colorless oil. IR (neat): 2935, 1730, 1660,  $1240\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.93–6.83 (1H, m), 5.72 (1H, d,  $J = 15.6$  Hz), 4.10 (2H, q,  $J = 7.0$  Hz), 3.97 (2H, t,  $J = 6.7$  Hz), 2.14 (2H, q,  $J = 7.3$  Hz), 1.96 (3H, s), 1.56–1.18 (17H, m).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  171.0, 166.6, 149.2, 121.3, 64.5, 60.0, 32.1, 29.3, 29.2, 29.1, 29.0, 28.6, 28.0, 25.9, 20.9, 14.2. MS (EI): 239 (6), 150 (59), 55 (100). Anal. Calcd for  $\text{C}_{16}\text{H}_{28}\text{O}_4$ : C, 67.57; H, 9.92. Found: C, 67.46; H, 10.12.

**Typical Procedure B. Preparation of 3-Phenyl-1-heptene (10a).**<sup>13a</sup>  $\text{LiI}$  (0.13 g, 20 mol %), dried under vacuum (2 h,  $100\text{ }^{\circ}\text{C}$ ), was dissolved in THF (7 mL) and cooled to  $-78\text{ }^{\circ}\text{C}$ .  $\text{Ni}(\text{acac})_2$  (96 mg, 7.5 mol %) and 1-bromo-3-phenyl-4-pentene (**9a**, 1.125 g, 5 mmol) were added followed by  $\text{Et}_2\text{Zn}$  (1 mL, 10 mmol). The reaction mixture was allowed to reach room temperature in 4 h, before being quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  solution and extracted with  $\text{Et}_2\text{O}$ . The organic phase was washed with brine and dried ( $\text{MgSO}_4$ ). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording the product as a colorless oil (0.7 g, 81% yield). The NMR data of the product fits the literature data.<sup>13a</sup>

**Typical Procedure C. In Presence of a Promotor. Preparation of Benzyl Octanoate (27r).**<sup>37</sup> A 25 mL two-necked flask equipped with an argon inlet and a rubber septum was charged with  $\text{Ni}(\text{acac})_2$  (0.128 g, 10 mol %), THF (3.4 mL), NMP (1.7 mL), *m*-trifluoromethylstyrene (0.172 g, 20 mol %), and **26n** (1.45 g, 5 mmol) at room temperature. The reaction mixture was cooled at  $-78\text{ }^{\circ}\text{C}$ , and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol) was carefully added. The reaction mixture was allowed to warm to  $-35\text{ }^{\circ}\text{C}$  and stirred for 2.5 h, before being poured into an ice-cold aqueous saturated solution of  $\text{NH}_4\text{Cl}$ . After the usual workup, the resulting crude oil obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the desired product (0.89 g, 76% yield) as a colorless oil. The NMR data of the product fits the literature data.<sup>37</sup>

**3-Butyl-1-heptene (10b).**<sup>13b</sup> The reaction was carried out according to typical procedure B starting from **9b** (1.03 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (96 mg, 7.5 mol %), and  $\text{Et}_2\text{Zn}$  (1 mL, 10 mmol). Reaction time was 18 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording the product as a colorless oil (0.63 g, 82% yield). The NMR data of the product fits the literature data.<sup>13b</sup>

**3-Phenyl-1-decene (21a).** The reaction was carried out according to typical procedure A starting from **20a** (5 mmol, 1.36 g),  $\text{Ni}(\text{acac})_2$  (96 mg, 7.5 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). Reaction time was 3 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording the product as a colorless oil (0.86 g, 80% yield). IR (neat): 3082, 3028, 2926, 1636,  $699\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.29–7.14 (5H, m), 5.98–5.86 (1H, m), 5.02–4.96 (2H, m), 3.20 (1H, q,  $J = 7.2$  Hz), 1.77–1.63 (2H, m), 1.22–1.16 (10H, m), 0.84 (3H, t,  $J = 6.4$  Hz).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  144.7, 142.5, 128.3, 127.5, 126.2, 113.8, 49.9, 35.4, 31.8, 29.5, 29.2, 27.5, 22.6, 14.1. MS (EI): 216 ( $\text{M}^+$ , 23), 117 (100). Anal. Calcd for  $\text{C}_{16}\text{H}_{24}$ : C, 88.82; H, 11.18. Found: C, 88.95; H, 11.30.

**3-Butyl-1-decene (21b).** The reaction was carried out according to typical procedure A, starting from **20b** (1.26 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (96 mg, 7.5 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes) affording the product as a colorless oil (0.71 g, 72% yield). Reaction time

was 3 h at  $-35\text{ }^{\circ}\text{C}$ . IR (neat): 3076, 2926, 1640, 1460, 995,  $960\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  5.48–5.40 (1H, m), 4.89–4.79 (2H, m), 1.88–1.84 (1H, m), 1.26–1.10 (21H, m), 0.82 (3H, t,  $J = 6.7$  Hz).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  144.3, 114.2, 44.6, 35.6, 35.3, 32.4, 30.3, 30.0, 29.9, 27.7, 23.4, 23.2, 14.6. MS (EI): 196 ( $\text{M}^+$ , 28), 168 (26), 154 (26), 70 (100). Anal. Calcd for  $\text{C}_{14}\text{H}_{28}$ : C, 85.63; H, 14.37. Found: C, 85.53; H, 14.35.

**6-Phenyl-7-octenyl Pivalate (21c).** The reaction was carried out according to typical procedure A, starting from **20a** (0.82 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (57 mg, 7.5 mol %), and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2 mL). Reaction time was 4 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/*t*-BuOMe 95:5) affording the product as a colorless oil (0.78 g, 90% yield). IR (neat): 3063, 3028, 2973, 1728, 1285,  $701\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.34–7.18 (5H, m), 6.02–5.90 (1H, m), 5.07–5.00 (2H, m), 4.04 (2H, t,  $J = 6.6$  Hz), 3.24 (q, 1H,  $J = 7.5$  Hz), 1.77–1.70 (2H, m), 1.63–1.57 (2H, m), 1.41–1.33 (4H, m), 1.19 (9H, s).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  178.6, 144.5, 142.4, 128.5, 127.6, 126.2, 114.0, 64.4, 49.9, 38.8, 35.4, 28.6, 27.3, 27.2, 26.0. MS (EI): 186 (28), 157 (33), 117 (100), 91 (40), 57 (72). Anal. Calcd for  $\text{C}_{19}\text{H}_{28}\text{O}_2$ : C, 79.12; H, 9.78. Found: C, 79.01; H, 9.92.

**6-Butyl-7-octenyl Pivalate (21d).** The reaction was carried out according to typical procedure A starting from **20b** (0.76 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (57 mg, 7.5 mol %), and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2 mL). Reaction time was 3 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/*t*-BuOMe 95:5) affording the product as a colorless oil (0.56 g, 70% yield). IR (neat): 3070, 2928, 1731, 1620, 1480, 1285,  $1156\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  5.50–5.38 (1H, m), 4.90–4.82 (2H, m), 3.97 (2H, t,  $J = 6.6$  Hz), 1.90–1.80 (1H, m), 1.59–1.50 (2H, m), 1.25–1.06 (21H, m), 0.81 (3H, t,  $J = 6.7$  Hz).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  178.5, 143.5, 113.7, 64.3, 43.9, 38.6, 34.8, 34.7, 29.3, 28.5, 27.1, 26.9, 25.8, 22.7, 14.0. MS (EI): 166 (5), 137 (32), 109 (50), 57 (100). Anal. Calcd for  $\text{C}_{17}\text{H}_{32}\text{O}_2$ : C, 76.06; H, 12.01. Found: C, 76.33; H, 12.30.

**(E)-Ethyl 2-Undecenoate (21e).**<sup>9b</sup> The reaction was carried out according to typical procedure A, starting from **20c** (1.34 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (96 mg, 7.5 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). Reaction time was 3 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 95:5) affording the product as a colorless oil (0.88 g, 83% yield). The NMR data of the product fits the literature data.<sup>9b</sup>

**(E)-Ethyl 2-Nonenoate (21f).**<sup>38</sup> The reaction was carried out according to typical procedure A starting from **20d** (1.41 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (96 mg, 7.5 mol %), and  $\text{Et}_2\text{Zn}$  (1 mL, 10 mmol). Reaction time was 3 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as a colorless oil (0.77 g, 84% yield). The NMR data of the product fits the literature data.<sup>38</sup>

**(E)-Ethyl 9-Pivaloxy-2-nonenoate (21g).** The reaction was carried out according to typical procedure A, starting from **20c** (0.80 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (57 mg, 7.5 mol %), and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 5 h at  $-35\text{ }^{\circ}\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/*t*-BuOMe 90:10) affording the product as a colorless oil (0.67 g, 79% yield). IR (neat): 2977, 1727, 1655, 1285,  $1159\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.93–6.83 (1H, m), 5.77 (1H, d,  $J = 15.7$  Hz), 4.12 (2H, q,  $J = 7.1$  Hz), 3.97 (2H, t,  $J = 6.5$  Hz), 2.13 (2H, q,  $J = 7.1$  Hz), 1.57–1.19 (11H, m), 1.12 (9H, s).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  178.5, 166.6, 148.9, 121.4, 64.2, 60.0, 38.7, 32.0, 28.7, 28.5, 27.9, 27.1, 25.7, 14.2. MS (EI): 238 (5), 136 (42), 109 (30), 57 (100). Anal. Calcd for  $\text{C}_{16}\text{H}_{28}\text{O}_4$ : C, 67.57; H, 9.92. Found: C, 67.90; H, 9.64.

**(E)-Ethyl 13-Pivaloxy-2-tridecenoate (21i).** The reaction was carried out according to typical procedure A, starting from

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**20d** (1.69 g, 6 mmol), Ni(acac)<sub>2</sub> (115 mg, 7.5 mol %), and bis-(6-pivaloxyhexyl)zinc (12 mmol) in THF (4 mL). Reaction time was 15 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a colorless oil (1.49 g, 73% yield). IR (neat): 2935, 1730, 1465, 1160 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 6.93–6.83 (1H, m), 5.73 (1H, d, 15.7 Hz), 4.09 (2H, q, *J* = 7.1 Hz), 3.96 (2H, t, *J* = 6.6 Hz), 2.11 (2H, t, *J* = 7.1 Hz), 1.56–1.49 (2H, m), 1.39–1.35 (2H, m), 1.28–1.17 (15H, m), 1.11 (9H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 178.5, 166.6, 149.3, 121.3, 64.4, 60.0, 38.7, 32.1, 29.43, 29.37, 29.32, 29.16, 29.09, 28.6, 28.0, 27.2, 25.9, 14.2. MS (EI): 341 (M<sup>+</sup>, 100). Anal. Calcd for C<sub>20</sub>H<sub>36</sub>O<sub>4</sub>: C, 70.54; H, 10.65. Found: C, 70.48; H, 10.61.

**(E)-Ethyl 6-(3-Oxocyclohexyl)-2-hexenoate (21j)**. The reaction was carried out according to typical procedure A, starting from **20c** (0.8 g, 3 mmol), Ni(acac)<sub>2</sub> (57 mg, 7.5 mol %), and bis(3-trimethylsilyloxy cyclohex-2-en-1-yl)zinc (7 mmol) in THF (2.5 mL). Reaction time was 12 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/*t*-BuOMe 75:25) affording the product as a colorless oil (0.46 g, 65% yield). IR (neat): 2926, 1723, 1656, 1145 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 7.00–6.87 (1H, m), 5.88 (1H, d, *J* = 15.7 Hz), 4.18 (2H, q, *J* = 7.1 Hz), 2.38–1.26 (18H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 213.0, 166.7, 148.9, 121.6, 60.2, 50.6, 42.1, 34.0, 32.4, 29.1, 28.1, 25.8, 25.0, 14.3. MS(EI): 238 (M<sup>+</sup>, 20), 141 (25), 98 (100). M<sup>+</sup> calcd for C<sub>14</sub>H<sub>22</sub>O<sub>3</sub>: 238.1644. Observed: 238.1643.

**(E)-Ethyl 2-Dodecenoate (21k)**.<sup>39</sup> The reaction was carried out according to typical procedure A, starting from **20d** (1.69 g, 6 mmol), Ni(acac)<sub>2</sub> (115 mg, 7.5 mol %), and Pent<sub>2</sub>Zn (2.4 mL, 12 mmol). Reaction time was 10 h at -40 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1) affording the product as a yellow oil (1.10 g, 81% yield). The NMR data of the product fits the literature data.<sup>39</sup>

**tert-Amyl Cyclopentyl Acetate (22)**.<sup>8e</sup> A three-necked flask equipped with a magnetic stirring bar, a thermometer, and a gas inlet was charged with PdCl<sub>2</sub>(MeCN)<sub>2</sub> (17 mg, 1.5 mol %) in THF (5 mL) and cooled at -78 °C. The iodide **20e** (1.38 g, 4.3 mmol) and Et<sub>2</sub>Zn (0.86 mL, 8.6 mmol, 2 equiv) were added. The reaction mixture was slowly (over 4 h) warmed to room temperature and quenched with water. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1) affording the product as a colorless oil (0.62 g, 74% yield). The NMR data of the product fits the literature data.<sup>8e</sup>

**Octanenitrile (25a)**.<sup>40</sup> The reaction was carried out according to typical procedure A, starting from **23a** (0.45 g, 2.5 mmol), Ni(acac)<sub>2</sub> (64 mg, 10 mol %), and Pent<sub>2</sub>Zn (1 mL, 5 mmol). Reaction time was 48 h at -25 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1–10:1) affording the product **25a** as a yellow oil (0.20 g, 64%). The NMR data of the product fits the literature data.<sup>40</sup>

**Nonanenitrile (25b)**.<sup>41</sup> The reaction was carried out according to typical procedure A, starting from **23b** (0.97 g, 5 mmol), Ni(acac)<sub>2</sub> (0.128 g, 10 mol %), and Pent<sub>2</sub>Zn (2 mL, 10 mmol). Reaction time was 48 h at -25 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1–10:1) affording the product **25b** as a colorless oil (0.36 g, 52% yield). The NMR data of the product fits the literature data.<sup>41</sup>

**Decanenitrile (25c)**.<sup>42</sup> The reaction was carried out according to typical procedure A starting from **23c** (1.04 g, 5 mmol), Ni(acac)<sub>2</sub> (0.128 g, 10 mol %), and Pent<sub>2</sub>Zn (2 mL, 10 mmol). Reaction time was 48 h at -25 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1–10:1) affording the product

**25c** as a colorless oil (0.30 g, 39% yield). The NMR data of the product fits the literature data.<sup>42</sup>

***n*-Octanophenone (27a)**.<sup>43</sup> The reaction was carried out according to typical procedure C, starting from **26a** (0.78 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), and Pent<sub>2</sub>Zn (1.2 mL, 6 mmol). Reaction time was 3 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a colorless oil (0.43 g, 71% yield). The NMR data of the product fits the literature data.<sup>43</sup>

***n*-Nonanophenone (27b)**.<sup>9b</sup> The reaction was carried out according to typical procedure C, starting from **26b** (0.82 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), acetophenone (0.36 g, 3 mmol), and Pent<sub>2</sub>Zn (1.2 mL, 6 mmol). Reaction time was 2.5 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a colorless oil (0.57 g, 88%). The NMR data of the product fits the literature data.<sup>9b</sup>

**5-Tridecanone (27c)**.<sup>20</sup> The reaction was carried out according to typical procedure C, starting from **26c** (0.76 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), *m*-trifluoromethylstyrene (0.103 g, 20 mol %), and Pent<sub>2</sub>Zn (1.2 mL, 6 mmol). Reaction time was 1 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1) affording the product as a colorless oil (0.44 g, 74%). The NMR data of the product fits the literature data.<sup>20</sup>

**1-(4-Methoxyphenyl)octanone (27d)**.<sup>44</sup> The reaction was carried out according to typical procedure C, starting from **26d** (0.91 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), acetophenone (0.36 g, 3 mmol), and Bu<sub>2</sub>Zn (1 mL, 6 mmol). Reaction time was 12 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a white solid (mp 44 °C; 0.50 g, 72%). The NMR data of the product fits the literature data.<sup>44</sup>

**1-(4-Trifluoromethylphenyl)nonanone (27e)**. The reaction was carried out according to typical procedure C, starting from **26e** (1 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), and Pent<sub>2</sub>Zn (1.2 mL, 6 mmol). Reaction time was 1 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1) affording the product as a solid (mp 36 °C; 0.78 g, 91% yield). IR (neat): 2955, 2926, 1695, 1330, 1170 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.94 (2H, d, *J* = 8.1 Hz), 7.59 (2H, d, *J* = 8.1 Hz), 2.88 (2H, t, *J* = 7.3 Hz), 1.66–1.62 (2H, m), 1.24–1.17 (10H, m), 0.79–0.74 (3H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 199.2, 139.6, 134.0 (q, *J* = 32.3 Hz), 128.2, 125.4 (q, *J* = 3.6 Hz), 123.5 (q, *J* = 270.9 Hz), 38.7, 31.7, 29.3, 29.1, 24.0, 22.5, 13.8. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 188 MHz): δ -63.4. MS (EI): 286 (M<sup>+</sup>, 4), 201 (12), 188 (100), 173 (62), 145 (22). M<sup>+</sup> calcd for C<sub>16</sub>H<sub>21</sub>OF<sub>3</sub>: 286.1542. Observed: 286.1544.

**Undecyl Pivalate (27f)**. The reaction was carried out according to typical procedure C, starting from **26f** (0.94 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), ethyl crotonate (68 mg, 20 mol %), and Pent<sub>2</sub>Zn (1.2 mL, 6 mmol). Reaction time was 15 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as a colorless oil (0.45 g, 59%). IR (neat): 2926, 2855, 1732, 1157 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.97 (2H, t, *J* = 6.6 Hz), 1.56–1.49 (2H, m), 1.38–1.18 (16H, m), 1.12 (9H, s), 0.82–0.78 (3H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 178.5, 64.4, 38.7, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 28.6, 27.2, 25.9, 22.6, 14.0. MS (EI): 256 (M<sup>+</sup>, 0.1), 154 (23), 103 (77), 57 (100). M<sup>+</sup> calcd for C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>: 256.2396. Observed: 256.2402.

**4-Nonanoylbenzotrile (27g)**. The reaction was carried out according to typical procedure C, starting from **26g** (0.90 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), acetophenone (0.36

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g, 3 mmol), and  $\text{Pent}_2\text{Zn}$  (1.2 mL, 6 mmol). Reaction time was 5 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the products as a white solid (mp  $36^\circ\text{C}$ ; 0.59 g, 81%). IR (neat): 2955, 2921, 2872, 2232, 1691, 1467, 837  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.79 (2H, d,  $J = 9.0$  Hz), 7.50 (2H, d,  $J = 9.0$  Hz), 2.73 (2H, t,  $J = 9.0$  Hz), 1.52–1.42 (2H, m), 1.10–1.00 (10H, m), 0.6 (3H, t,  $J = 6.66$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  198.6, 139.8, 132.2, 128.2, 117.7, 115.9, 38.6, 31.3, 29.1, 29.0, 28.9, 23.8, 22.4, 13.8. MS (EI): 243 ( $\text{M}^+$ , 3), 145 (100), 130 (52), 102 (30).  $\text{M}^+$  calcd for  $\text{C}_{16}\text{H}_{21}\text{NO}$ : 243.1631. Observed: 243.1624.

**2-Nonanoylthiophene (27h).** The reaction was carried out according to typical procedure C, starting from **26h** (0.84 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (77 mg, 10 mol %), acetophenone (0.18 g, 50 mol %), and  $\text{Pent}_2\text{Zn}$  (1.2 mL, 6 mmol). Reaction time was 8 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a yellow oil (0.45 g, 67%). IR (neat): 2955, 2926, 2854, 1664, 1417  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.78 (1H, dd,  $J = 1.1$  Hz,  $J = 3.8$  Hz), 7.68 (1H, dd,  $J = 1.1$  Hz,  $J = 5$  Hz), 7.20–7.17 (1H, m), 2.96 (2H, t,  $J = 6.0$  Hz), 1.89–1.76 (2H, m), 1.44–1.35 (10H, m), 0.96 (3H, t,  $J = 6.75$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  193.1, 144.3, 133.0, 131.4, 127.8, 39.2, 31.6, 29.2, 29.1, 28.9, 24.6, 22.5, 13.9. MS (EI): 224 ( $\text{M}^+$ , 4), 126 (100), 111 (95).  $\text{M}^+$  calcd for  $\text{C}_{13}\text{H}_{20}\text{S}$ : 224.1237. Observed: 224.1235.

**7-Oxo-7-piperidinoheptyl Pivalate (27i).** The reaction was carried out according to typical procedure C, starting from **26i** (1.33 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.43 g, 50 mol %), and bis(4-pivaloxybutyl)zinc (10 mmol) in THF (3 mL). Reaction time was 6 h at  $-30^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 2:8) affording the product as a yellow oil (0.95 g, 64% yield). IR (neat): 2935, 2857, 1727, 1645, 1435, 1157  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.97 (2H, t,  $J = 6.5$  Hz), 3.47 (2H, t,  $J = 5.35$  Hz), 3.32 (2H, t,  $J = 5.35$  Hz), 2.24 (2H, t,  $J = 7.6$  Hz), 1.58–1.42 (10H, m), 1.36–1.28 (4H, m), 1.12 (9H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  178.5, 171.2, 64.2, 46.6, 42.6, 38.7, 33.2, 29.0, 28.4, 27.1, 26.5, 25.7, 25.5, 25.2, 24.5. MS (EI): 113 (15), 95 (100). Anal. Calcd for  $\text{C}_{17}\text{H}_{31}\text{NO}_3$ : C, 68.65; N, 4.71; H, 10.50. Found: C, 68.53; N, 4.90; H, 10.70.

**Ethyl Octanoate (27j).** The reaction was carried out according to typical procedure C, starting from **26j** (1.14 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.172 g, 20 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). Reaction time was 4 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as a colorless oil (0.62 g, 72%). The NMR data of the product fits the literature data (Aldrich catalog).

**2-Heptyl-2-methyl-1,3-dithiolane (27k).** The reaction was carried out according to typical procedure C, starting from **26k** (1.37 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.172 g, 20 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). Reaction time was 1 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 30:1) affording the product as a colorless oil (0.85 g, 78%). IR (neat): 2955, 2925, 1457, 1375, 1276  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.39–3.25 (4H, m), 1.95–1.89 (2H, m), 1.75 (3H, s), 1.52–1.43 (2H, m), 1.30–1.28 (8H, m), 0.88 (3H, t,  $J = 6.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  67.0, 45.9, 39.7, 32.3, 31.8, 29.8, 29.2, 27.4, 22.6, 14.1. MS (EI): 218 ( $\text{M}^+$ , 18), 119 (100). Anal. Calcd for  $\text{C}_{11}\text{H}_{22}\text{S}_2$ : C, 60.49; H, 10.15. Found: C, 60.41; H, 10.37.

**Ethyl 6-Pivaloxyhexanoate (27l).** The reaction was carried out according to typical procedure C, starting from **26l** (0.68 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (77 mg, 10 mol %), acetophenone (0.36 g, 1 equiv) and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 4 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a colorless oil (0.44 g, 60%). IR (neat): 2960, 2827, 1732, 1481, 1286, 1159, 1035  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.04

(2H, q,  $J = 7.0$  Hz), 3.98 (2H, t,  $J = 6.5$  Hz), 2.23 (2H, t,  $J = 7.4$  Hz), 1.64–1.53 (4H, m), 1.37–1.27 (2H, m), 1.17 (3H, t,  $J = 7.0$  Hz), 1.11 (9H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz): 178.2, 173.2, 63.9, 60.0, 38.5, 34.0, 28.2, 27.0, 26.8, 25.4, 24.4, 14.1. MS (EI): 142 (31), 115 (36), 101 (23), 57 (100). Anal. Calcd for  $\text{C}_{13}\text{H}_{24}\text{O}_4$ : C, 63.90; H, 9.90. Found: C, 63.65; H, 10.05.

**Ethyl 7-Oxo-undecanoate (27m).** The reaction was carried out according to typical procedure C starting from **26c** (0.76 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (77 mg, 10 mol %), acetophenone (0.18 g, 50 mol %), and bis(2-carbethoxyethyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 8 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a colorless oil (0.40 g, 58%). IR (neat): 2957, 2935, 1736, 1715, 1180, 1033  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.04 (2H, q,  $J = 7.1$  Hz), 2.36–2.29 (4H, m), 2.22 (2H, t,  $J = 6.0$  Hz), 1.58–1.44 (6H, m), 1.27–1.15 (7H, m), 0.8 (3H, t,  $J = 6.0$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  210.8, 173.3, 59.9, 42.2, 42.1, 33.8, 28.4, 25.7, 24.4, 23.1, 22.1, 13.9, 13.5. MS (EI): 186 (11), 129 (59), 125 (54), 101 (31), 85 (97), 69 (49), 97 (100), 29 (75). Anal. Calcd for  $\text{C}_{13}\text{H}_{24}\text{O}_3$ : C, 68.38; H, 10.59. Found: C, 68.24; H, 10.65.

**Octyl Phenyl Sulfide (27n).**<sup>45</sup> The reaction was carried out according to typical procedure C, starting from **26l** (1.39 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.43 g, 50 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). Reaction time was 2 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 35:1) affording the product as a colorless oil (0.79 g, 71% yield). The NMR data of the product fits the literature data.<sup>45</sup>

**Decyl Pivalate (27o).** The reaction was carried out according to typical procedure C, starting from **26m** (1.49 g, 5 mmol),  $\text{Ni}(\text{acac})_2$  (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.172 g, 20 mol %), and  $\text{Pent}_2\text{Zn}$  (2 mL, 10 mmol). Reaction time was 1 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a colorless oil (0.95 g, 78% yield). IR (neat): 2957, 2928, 2856, 1732, 1157  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.97 (2H, t,  $J = 6.6$  Hz), 1.59–1.49 (2H, m), 1.33–1.19 (14H, m), 1.12 (9H, s), 0.8 (3H, t,  $J = 6.7$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  178.2, 64.1, 38.4, 31.6, 29.2, 29.0, 28.9, 28.4, 26.9, 25.9, 25.7, 22.4, 13.8. MS (EI): 140 (8), 103 (43), 57 (100). Anal. Calcd for  $\text{C}_{15}\text{H}_{30}\text{O}_2$ : C, 74.32; H, 12.47. Found: C, 74.35; H, 12.64.

**6-Benzoylhexyl Pivalate (27p).** The reaction was carried out according to typical procedure C, starting from **26b** (0.82 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (77 mg, 10 mol %), acetophenone (0.18 g, 50 mol %), and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 10 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a yellow oil (0.66 g, 76%). IR (neat): 2935, 2867, 1727, 1688, 1286, 1157  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.87–7.84 (2H, m), 7.48–7.33 (3H, m), 3.96 (2H, t,  $J = 6.6$  Hz), 2.87 (2H, t,  $J = 7.2$  Hz), 1.74–1.53 (4H, m), 1.36–1.30 (4H, m), 1.10 (9H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  200.0, 178.3, 136.9, 132.7, 128.4, 127.9, 64.1, 38.5, 38.2, 28.7, 28.3, 27.0, 25.5, 24.0. MS (EI): 290 ( $\text{M}^+$ , 1), 120 (100), 105 (95).  $\text{M}^+$  calcd for  $\text{C}_{18}\text{H}_{26}\text{O}_3$ : 290.1882. Found: 290.1890.

**7-Oxoundecyl Pivalate (27q).** The reaction was carried out according to typical procedure C starting from **26c** (0.76 g, 3 mmol),  $\text{Ni}(\text{acac})_2$  (77 mg, 10 mol %), acetophenone (0.18 g, 50 mol %), and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 8 h at  $-35^\circ\text{C}$ . The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a yellow oil (0.55 g, 68%). IR (neat): 2935, 2872, 1728, 1286  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.96 (2H, t,  $J = 6.6$  Hz), 2.35–2.29 (4H, m), 1.59–1.42 (6H, m), 1.33–1.16 (6H, m), 1.11 (9H, s), 0.82 (3H, t,  $J = 7.2$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):

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211.0, 178.4, 64.2, 42.5, 38.7, 28.8, 28.5, 27.2, 26.0, 25.8, 23.6, 22.3, 13.8. MS (EI): 270 (M<sup>+</sup>, 100), 228 (30). Anal. Calcd for C<sub>16</sub>H<sub>30</sub>O<sub>3</sub>: C, 71.06; H, 11.18. Found: 70.69; H, 11.36.

**1-Piperidino-1-octanone (27s).**<sup>46</sup> The reaction was carried out according to typical procedure C, starting from **26i** (1.33 g, 5 mmol), Ni(acac)<sub>2</sub> (0.128 g, 10 mol %), acetophenone (0.6 g, 5 mmol), and Pent<sub>2</sub>Zn (2 mL, 10 mmol). Reaction time was 4 h at -30 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 2:8) affording the product as a pale yellow oil (0.74 g, 70%). The NMR data of the product fits the literature data.<sup>46</sup>

**7-Oxo-7-(2-thienyl)heptyl Pivalate (27t).** The reaction was carried out according to typical procedure C, starting from **26h** (0.84 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), acetophenone (0.18 g, 50 mol %), and bis(3-pivaloxypropyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 18 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 10:1) affording the product as a yellow oil (0.62 g, 70%). IR (neat): 3060, 2955, 2862, 1669, 1602, 1255, 1179. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.62 (1H, dd, *J* = 3.0 Hz, *J* = 1.1 Hz), 7.53 (1H, dd, *J* = 5.0 Hz, 1.1 Hz), 7.03–7.00 (1H, m), 3.94 (2H, t, *J* = 6.5 Hz), 2.80 (2H, t, *J* = 7.3 Hz), 1.70–1.60 (2H, m), 1.58–1.49 (2H, m), 1.36–1.25 (4H, m), 1.08 (9H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 192.9, 178.2, 144.3, 133.2, 131.6, 127.9, 64.0, 38.7, 38.5, 28.7, 28.3, 27.0, 25.6, 24.5. MS (EI): 296 (M<sup>+</sup>, 1), 126 (100), 111 (86), 57 (41). M<sup>+</sup> calcd for C<sub>16</sub>H<sub>24</sub>SO<sub>3</sub>: 296.1443. Found: 296.1446.

**5-(2-Methyl-1,3-dithiolan-2-yl)pentyl Pivalate (27u).** The reaction was carried out according to typical procedure C, starting from **26k** (1.37 g, 5 mmol), Ni(acac)<sub>2</sub> (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.43 g, 50 mol %), and bis(3-pivaloxypropyl)zinc (10 mmol) in THF (3 mL). Reaction time was 6 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as colorless oil (1.01 g, 70%). IR (neat): 2957, 2931, 1728, 1284, 1157 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 75 MHz): δ 4.05 (2H, t, *J* = 6.51 Hz), 3.39–3.25 (4H, m), 1.96–1.90 (2H, m), 1.75 (3H, s), 1.70–1.50 (4H, m), 1.44–1.36 (2H, m), 1.13 (9H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 178.5, 66.7, 64.2, 45.7, 39.8, 38.7, 32.3, 28.5, 27.2, 27.0, 26.1. MS (EI): 119 (100). Anal. Calcd for C<sub>14</sub>H<sub>26</sub>S<sub>2</sub>O<sub>2</sub>: C, 57.88; H, 9.02. Found: C, 57.80; H, 9.04.

**6-Oxo-6-piperidinohexyl Pivalate (27v).** The reaction was carried out according to typical procedure C, starting from **26i** (1.33 g, 5 mmol), Ni(acac)<sub>2</sub> (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.86 g, 1 equiv), and bis(3-pivaloxypropyl)zinc (10 mmol) in THF (3 mL). Reaction time was 6 h at -30 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 2:8) affording the product as a pale yellow oil (0.96 g, 68%). IR (neat): 2937, 2858, 1726, 1635 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.98 (2H, t, *J* = 6.56 Hz), 3.47 (2H, t, *J* = 5.27), 3.32 (2H, t, *J* = 5.27 Hz), 2.26 (2H, t, *J* = 7.6 Hz), 1.63–1.30 (12H, m), 1.12 (9H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 178.3, 170.9, 64.0, 46.5, 42.5, 38.5, 33.0, 28.4, 27.0, 26.4, 25.7, 25.4, 24.9, 24.4. MS (EI): 283 (M<sup>+</sup>, 8), 182 (21), 140 (23), 127 (100). M<sup>+</sup> calcd for C<sub>16</sub>H<sub>29</sub>NO<sub>3</sub>: 283.2147. Observed: 283.2144.

**7-(2-Methyl-1,3-dithiolan-2-yl)heptyl Pivalate (27w).** The reaction was carried out according to typical procedure C, starting from **26k** (1.37 g, 5 mmol), Ni(acac)<sub>2</sub> (0.128 g, 10 mol %), *m*-trifluoromethylstyrene (0.258 g, 30 mol %), and bis(5-pivaloxypropyl)zinc (10 mmol) in THF (3 mL). The residue

obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as colorless oil (1.06 g, 67% yield). Reaction time was 7 h at -35 °C. IR (neat): 2956, 2930, 1728, 1284, 1157 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 4.05 (2H, t, *J* = 6.59 Hz), 3.39–3.26 (4H, m), 1.95–1.89 (2H, m), 1.75 (3H, s), 1.65–1.57 (2H, m), 1.55–1.48 (2H, s), 1.40–1.30 (6H, m), 1.13 (9H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 178.6, 66.9, 64.4, 45.8, 39.8, 38.8, 32.4, 29.6, 29.1, 28.6, 27.3, 27.2, 25.9. MS (EI): 318 (M<sup>+</sup>, 1), 119 (100), 57 (20), 41 (10), 28 (20). Anal. Calcd for C<sub>16</sub>H<sub>30</sub>O<sub>2</sub>S<sub>2</sub>: C, 60.32; H, 9.49. Found: C, 60.41; H, 9.26.

**5-[(1*S*,2*S*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]-1-phenyl-1-pentanone (27y).** The reaction was carried out according to procedure C, starting from **26b** (0.82 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), acetophenone (0.180 g, 50 mol %), and bis(myrtanyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 8 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as a colorless oil (0.56 g, 66%). IR (neat): 2932, 1687, 1598, 1467, 1219, 748, 734 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.86–7.82 (2H, m), 7.41–7.30 (3H, m); 2.83 (2H, t, *J* = 7.38 Hz), 2.22–2.18 (1H, m), 1.85–1.71 (6H, m), 1.65–1.58 (2H, m), 1.35–1.22 (5H, m), 1.07 (3H, s), 0.88 (3H, s), 0.76–0.67 (1H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 200.1, 137.0, 132.6, 128.3, 127.9, 46.3, 41.5, 41.3, 38.6, 38.4, 37.4, 33.7, 28.1, 27.7, 26.4, 24.5, 23.2, 22.4. MS (EI): 284 (M<sup>+</sup>, 1), 164 (26), 120 (34), 105 (100). Anal. Calcd for C<sub>20</sub>H<sub>28</sub>O: C, 84.45; H, 9.92. Found: C, 84.35; H, 10.07.

**6-[(1*S*,2*S*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]hexyl Pivalate (27z).** The reaction was carried out according to typical procedure C, starting from **26m** (0.89 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), *m*-trifluoromethylstyrene (0.516 g, 3 mmol), and bis(myrtanyl)zinc (6 mmol) in THF (2.5 mL). Reaction time was 8 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 15:1) affording the product as a colorless oil (0.68 g, 74%). IR (neat): 2923, 2858, 1732, 1480, 1159 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.97 (2H, t, *J* = 6.6 Hz), 2.27–2.21 (1H, m), 1.88–1.74 (6H, m), 1.56–1.51 (2H, m), 1.37–1.18 (m, 9H), 1.11 (9H, s), 1.09 (3H, s), 0.91 (3H, s), 0.8–0.76 (1H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 178.2, 64.2, 46.3, 41.45, 41.4, 39.1, 38.52, 38.50, 33.6, 29.4, 29.2, 28.4, 28.1, 27.8, 27.0, 26.4, 25.8. MS (EI): 308 (M<sup>+</sup>, 0.5), 163 (34), 123 (64), 95 (41), 82 (100). Anal. Calcd for C<sub>20</sub>H<sub>36</sub>O<sub>2</sub>: C, 77.86; H, 11.76. Found: C, 77.60; H, 11.61.

**5-Methyl-1-phenylhexanone (30).**<sup>23</sup> The reaction was carried out according to typical procedure C, starting from **26b** (0.82 g, 3 mmol), Ni(acac)<sub>2</sub> (77 mg, 10 mol %), acetophenone (0.36 g, 3 mmol), and *i*-Pr<sub>2</sub>Zn (1.5 mL of a 4 M solution in THF, 6 mmol). Reaction time was 5 h at -35 °C. The residue obtained after evaporation of the solvents was purified by flash chromatography (hexanes/ether 20:1) affording the product as a colorless oil (0.37 g, 65%). The ratio **30:31** was 95:5. The NMR data of the product fits the literature data.<sup>23</sup>

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**Supporting Information Available:** Experimental procedures and spectral data for unknown compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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