Homogeneous Catalysis

DOI: 10.1002/anie.200702528

Ni-Catalyzed Cascade Formation of C(sp^3)–C(sp^3) Bonds by Cyclization and Cross-Coupling Reactions of Iodoalkanes with Alkyl Zinc Halides**

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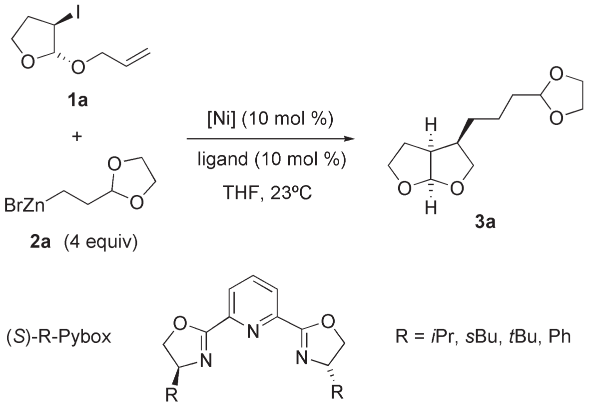
The development of methods for the formation of C(sp^3)–C(sp^3) bonds has become a topic of major interest.[1] In the last few years, advances in metal-catalyzed cross-coupling reactions of alkyl electrophiles (halides and tosylates) with alkyl metal derivatives have been reported.[2,3] The first report on a general and functional-group-tolerant alkyl–alkyl coupling reaction was published by Knochel and co-workers, who used di(alkyl)zinc reagents and alkyl iodides in a nickel-catalyzed process. This achievement constituted a milestone in this type of transformation.[4,5] Di(alkyl) zinc derivatives have been used extensively as nucleophiles in many reactions, including cross-coupling reactions for the formation of other types of C–C bonds.[6] In subsequent studies the reaction was extended to the more stable and convenient alkyl zinc halides.[7] More recently, Fu and co-workers reported nickel-catalyzed alkyl–alkyl coupling reactions of alkyl zinc halides with secondary iodides and bromides,[8] as well as the first catalytic asymmetric cross-coupling reaction of alkyl electrophiles.[9] Three-component coupling reactions of alkyl halides, dienes, and organomagnesium or organozinc reagents have also been reported.[10] Alkyl–alkyl Negishi cross-coupling reactions can also be catalyzed by palladium complexes with heterocyclic carbene ligands.[11]

Certain cross-coupling reactions of alkyl electrophiles with alkyl zinc halides seem to follow a radical pathway.[12–16] Vicic and co-workers reported the synthesis and catalytic activity of radical nickel(I) complexes containing terdentate nitrogen-based ligands in Negishi coupling reactions.[17] Although the precise mechanism is not fully understood, square-planar alkyl–nickel(I) complexes have been proposed as the active species.[18] Cobalt-catalyzed radical cyclizations of olefin-containing halo ketals followed by coupling with Grignard reagents have been developed by Oshima and co-workers.[19–21] We reasoned that radical reactions of alkyl iodides catalyzed by nickel complexes could give rise to transformations involving the formation of several alkyl–alkyl bonds in a single operation, in which 5-hexenyl radicals would undergo cyclization.[22] Herein we report our results on the nickel-catalyzed cyclization of alkyl halides containing an alkene group which takes place with a subsequent cross-coupling reaction with alkyl zinc bromides.

We first studied the nickel-catalyzed reaction of iodoacetal **1a** with commercially available organozinc derivative **2a** (4 equiv; Scheme 1). Under the conditions described by Vicic and co-workers (terpyridine and [Ni(cod)$_2$] (cod = cycloocta-1,5-diene) as the catalytic system) the cyclization and coupled derivative **3a** was isolated in 24% yield as a racemic single diasteroeomer. The yield was lower (19%) when bipyridine was used. Other Ni precursors (NiBr$_2$, [Ni(acac)$_2$ (acac = acetylacetone), NiCl$_2$) gave poorer results. A higher yield was observed (57%) when the air and moisture-stable blue complex [Ni(py)$_4$Cl$_2$][23] (py = pyridine) was used as the catalyst together with terpyridine. We tried some other nitrogen-based terdentate ligands based on the pybox skeleton. The di-*sec*-butyl derivative gave the best results (79%), which is in accord with the results previously observed by Fischer and Fu in simple cross-coupling reactionss.[9] The homocoupled compound derived from the alkyl zinc bromide was isolated in approximately 10% yield (relative to the starting nucleophile) in most cases. The use of lower amounts of the nucleophile led to lower yields.



Scheme 1. Ni-catalyzed cyclization/cross-coupling reaction.

In the absence of added ligands or in presence of *o*-phenanthroline, **4** was obtained in variable yields along with its reduction product **5**, in which iodine had been replaced by

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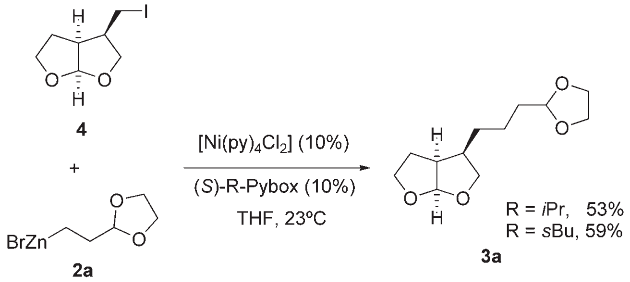
[**] We thank the Ministerio de Educación y Ciencia for financial support under project CTQ2004-02040/BQU and the MAE-AECI for a fellowship to V.B.P. We also thank the Centro de Computación Científica-UAM for computation time.

Supporting information for this article (including experimental data for new compounds, as well as atomic coordinates and energies for the calculated stationary points) is available on the WWW under http://www.angewandte.org or from the author.

hydrogen, probably abstracted from the solvent. Formation of this compound further supports a radical mechanism, since the reaction of **1a** with BEt_3 has been reported to give **4**.[24] This compound cannot be discarded as a reaction intermediate in the formation of **3a**, since it afforded the coupling product when subjected to the reaction conditions (Scheme 2).



Scheme 2. Cross-coupling of **4** affords the coupling product **3a**.

We have shown that $[Ni(py)_4Cl_2]$ is also an effective catalyst in simple alkyl–alkyl coupling reactions, and constitutes a more convenient Ni source. A variety of alkyl iodides, both primary (Table 1, entries 1 and 5) and secondary (entries 2, 3, and 4), afforded the desired coupling derivatives in moderate to good yields. Cyclization from citronellyl iodide (**6e**; Table 1, entry 5) was not observed.

The reaction of **6a** with **2a** in the presence of terpyridine afforded **7a** in 63 % yield, and thus is as effective as when (*S*)-(*s*Bu)-Pybox is used as the ligand in the reaction. The electronic structure of alkyl–nickel(I)–terpyridine complexes, which have been proposed as the actual catalysts, has previously been reported.[17a] This prompted us to calculate the structure of the model methyl–nickel(I) complex containing Me-Pybox for comparison. Optimization at the DFT level shows a square-planar structure, typical of Ni^{II} complexes, with the singly occupied molecular orbital delocalized on the ligand, as previously reported for the analogous complex with terpyridine (Figure 1). Therefore, complex **I** is better described as a Ni^{II} complex with a coordinated anionic terdentate ligand.[25]

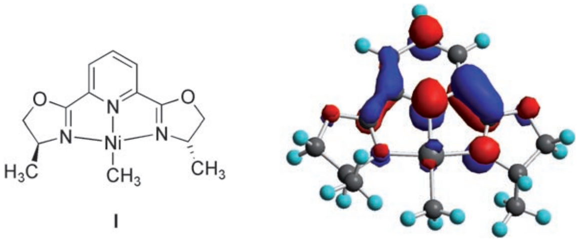
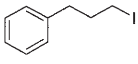
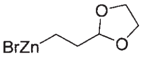
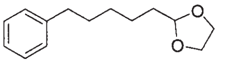
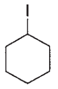
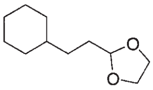
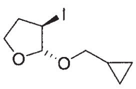
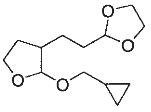
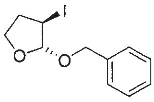
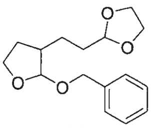
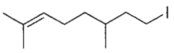
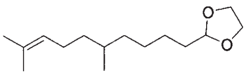


Figure 1. Optimized structure of complex **I** showing the ligand-centered singly occupied molecular orbital.

The cyclization and cross-coupling reaction is general and can be extended to a wide variety of substrates with different functional groups. Thus, compound **1a** gave good results with other organozinc reagents (Table 2, entries 2 and 3) and afforded only one diastereomer. The six-membered-ring derivative **1b** gave better yields in the reactions of several alkyl zinc bromides, although minor amounts of diastereomers of the main compounds were observed in the ^1H MNR spectra. The stereoisomers could not be separated by column chromatography, but were characterized by GC-MS. The five-membered-ring iodoacetal **1c** (Table 2, entries 7 and 8) again afforded only one stereoisomer. In contrast, the reaction of ether **1d** was not stereoselective (Table 2, entries 9 and 10) and the two possible C-3 epimers were obtained in roughly equimolar amount. Exocyclic halide **1e** was less prone to cyclization, and the expected product was obtained in 46 % yield (Table 2, entry 11) together with the derivative resulting from the cross-coupling reaction of the iodoalkene with the zinc reagent without previous cyclization (36 %). In all cases, the bicyclic products show *cis* fusion.[26]

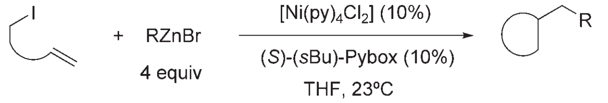
Malonate derivative **1f** also gave the expected compound (Table 2, entry 12), although some direct coupling product without cyclization was obtained (13 %). Especially interesting are the results obtained with substrate **1g** (Table 2, entries 13 and 14), since they open up further applications for the synthesis of compounds

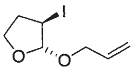
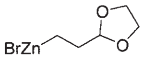
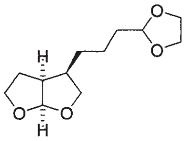
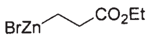
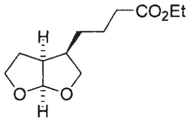
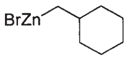
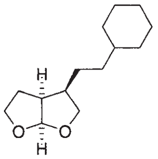
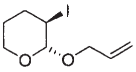
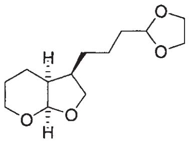
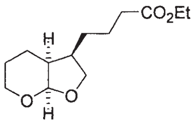
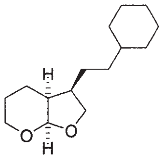
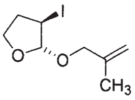
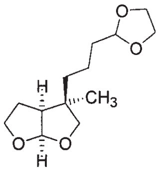
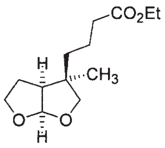
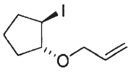
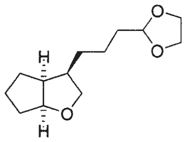
Table 1: Nickel-catalyzed cross-coupling reactions of alkyl iodides.[a]

Entry	Substrate	RZnBr	Product	*t* [h]	Yield [%]
1	 **6a**	 **2a**	 **7a**	11	69
2	 **6b**		 **7b**	11	74
3	 **6c**		 **7c**	6	79[b,c] (92:8)
4	 **6d**		 **7d**	16	72[b]
5	 **6e**		 **7e**	8	76

[a] Conditions: $[Ni(py)_4Cl_2]$ (10 mol%), (*S*)-(*s*Bu)-Pybox (10 mol%), THF, 23 °C. [b] Relative stereochemistry was not determined. [c] 64 % yield using (*S*)-(*i*Pr)-Pybox as ligand.

Table 2: Nickel-catalyzed formation of two alkyl–akyl bonds by radical cyclization and Negishi cross-coupling.



Entry	Substrate	RZnBr	Product	*t* [h]	Yield [%]
1	 **1a**	 **2a**	 **3a**	7	79
2	**1a**	 **2b**	 **3a'**	13	65
3	**1a**	 **2c**	 **3a''**	15	60
4	 **1b**	**2a**	 **3b**	8	83 (92:8)[a]
5	**1b**	**2b**	 **3b'**	16	94 (97:3)[a]
6	**1b**	**2c**	 **3b''**	8	81 (93:7)[a]
7	 **1c**	**2a**	 **3c**	8	64
8	**1c**	**2b**	 **3c'**	15	68
9	 **1d**	**2a**	 **3d**	9	76 (64:36)[b,c]

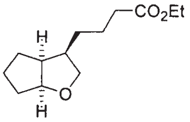
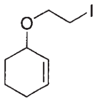
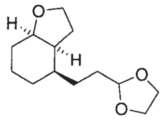
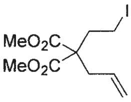
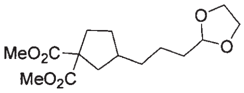
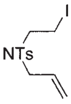
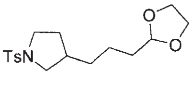
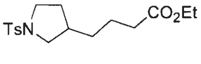
containing a pyrrolidine ring. Ketone and nitrile functional groups are also compatible with the reaction conditions, which widens the scope of the reaction. Thus, the reaction of 6-iodo-2-hexanone and 5-iodopentanenitrile with 3-pentylzinc bromide under the standard conditions afforded the desired coupling products in approximately 65% yield. Nevertheless, the presence of inseparable by-products has precluded isolation of the pure compounds. Experimental data and spectra can be found in the Supporting Information.[27]

Experiments and calculations were performed to obtain mechanistic information about this process. Thus, the reaction of the *cis* stereoisomer of **1d** (**9**) under the standard reaction conditions led to **3d'** with the same yield and stereoselectivity (Scheme 3), thus indicating the presence of a common reaction intermediate for both isomers, presumably the same secondary radical.

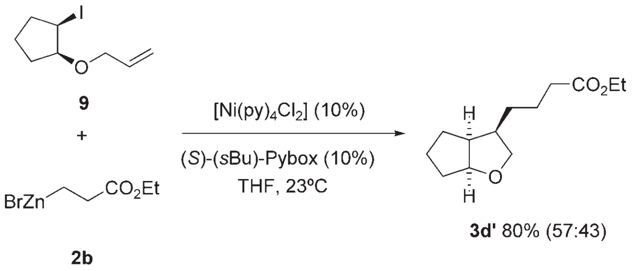
When the reaction of **1a**, **6a**, or **6b** was performed in the presence of 1.1 equiv of the radical inhibitor TEMPO (2,2,6,6-tetramethyl-1-piperidinoxy (free radical)), the formal coupling product of this reagent with the radical derived from **2a** was obtained (**8**, ca. 60%) together with recovered haloalkane (ca. 90%). TEMPO may react with the alkyl–$Ni^I(L_3)$ complex formed by transmetalation with the organozinc compound leading to the product and Ni^0 (Scheme 4). Comproportion with a dialkyl–nickel(II) derivative could regenerate the active catalyst, as proposed.[17a] Nevertheless, we have not been able to ascertain the necessary oxidation step that has to take place to explain the observed yields of **8** and the amount of recovered halide.

On the other hand, the reaction in the presence of di-*tert*-butylated hydroxytoluene (BHT) led to similar yields for simple cross-coupling reactions of alkyl iodides **6a**, **6b**, and **6d** (65, 72, and 71%, respectively). In contrast, partial inhibi-

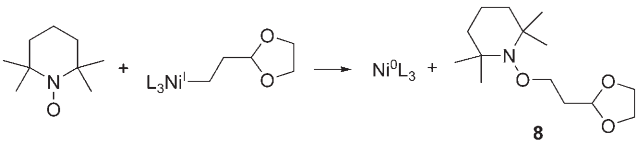
Table 2: (Continued)

Entry	Substrate	RZnBr	Product	*t* [h]	Yield [%]
10	**1d**	**2b**	 **3d'**	13	81 (57:43)[b,c]
11	 **1e**	**2a**	 **3e**	11	46[d]
12	 **1f**	**2a**	 **3f**	7	63[e]
13	 **1g**	**2a**	 **3g**	16	83
14	**1g**	**2b**	 **3g'**	19	66

[a] Measured by GC-MS. The minor isomer has the opposite configuration at C3. [b] The relative configuration shown corresponds to the major isomer. The minor one is the C3 epimer [c] Isomers were separated by flash chromatography. [d] The coupling product without cyclization is formed in 36% yield (isolated yields). [e] The coupling product without cyclization is formed in 13% yield (the compounds could not be separated. Yields are calculated from the ^{1}H NMR spectrum of the mixture).



Scheme 3. Reaction of the *cis* stereoisomer of **1d** gives the same isomeric ratio.



Scheme 4. Possible mechanism for the formation of **8**.

tion was observed for the cascade reaction of **1a**. The yields were variable, thus indicating partial inhibition, but were not reproducible.

The competition between cross-coupling reactions with or without previous cyclization in some cases (Table 2, entries 11 and 12), together with the plausible radical nature of the intermediate species, led us to explore the coupling reactions of several radical clocks.[28] The results are summarized in Table 3.

Taking into account the reaction rates for cyclization (Table 3, entries 1–3) or ring opening (Table 3, entries 4 and 5) for the radicals generated from the corresponding iodides, it can be deduced that the key C–C coupling reaction has a rate comparable to a unimolecular reaction and took place in the range 0.9×10^7–$6.7\times10^7\,\mathrm{s}^{-1}$. Since a bimolecular process actually takes place, the intrinsic reactivity of the intermediates species must be even higher. Therefore, the formation of the C–C bond is not the rate-limiting step.

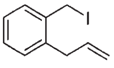
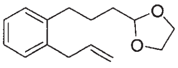
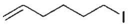
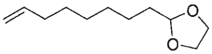
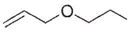
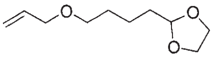
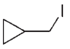
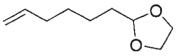
We have performed calculations to get insight into the formation of radicals from Ni^{I} complexes. Thus, the reaction of model methyl-Ni^{I}(terpyridine) (**II**) with 2-iodopropane proceeds through transition state **TS1** (Scheme 5).

The activation free energy is only 5.1 kcal mol^{-1} from an association complex in which the iodide ion interacts with the Ni atom along the axis perpendicular to the coordination plane at 3.53 Å.[29] The reaction is exoergic (-7.3 kcal mol^{-1}) and affords the free-radical and square-pyramidal Ni^{II} complex **III**. Although the calculation level does not allow fully quantitative conclusions to be drawn, the activation energy is in accord with a reaction taking place at room temperature.

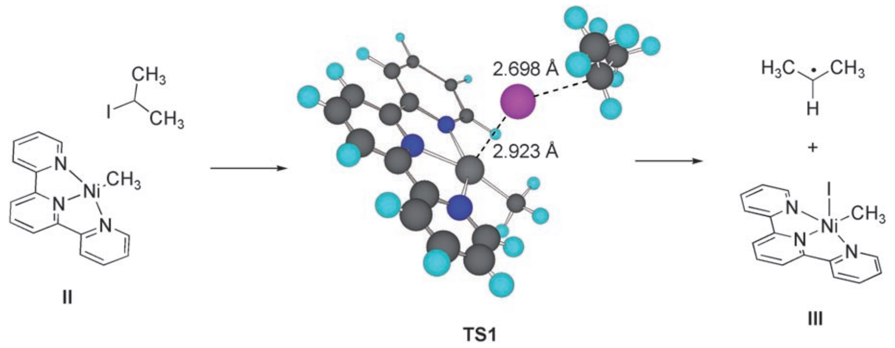
We have also calculated the transition state for the reaction of **II** with 2-iodopropane to give radicaloid iodo and a dialkyl-nickel(II) complexes containing methyl and isopropyl groups as carbon ligands which would presumably evolve by reductive elimination. This transition state (not shown; see the Supporting Information) is 10.2 kcal mol^{-1} less stable than **TS1**, and therefore this alternative pathway can be discarded.

A plausible mechanism for the cyclization/coupling reaction is shown in Scheme 6. Our experimental and computational results, which are in accord with the previous proposal for simple coupling reactions, suggest that free radicals (**A**) are readily formed from alkyl iodides, and that in some cases they last long enough to cyclize to intermediates **B**. If cyclization is slow, a faster coordination to the Ni^{II} complex to give dialkyl–nickel(III) intermediates **E** would take place. This species would then undergo reductive elimination to give the coupling product with regeneration of the Ni^{I} active species. The effect of BHT is not clear, since it only prevents the reaction of **1a**, but not simple cross-coupling reactions. Since reduced products have not been detected in the reaction of **1a** in the presence of BHT, our hypothesis is that this reagent decomposes intermediate Ni^{II} complexes **C** when the radical takes time to cyclize instead of rapidly coordinating to

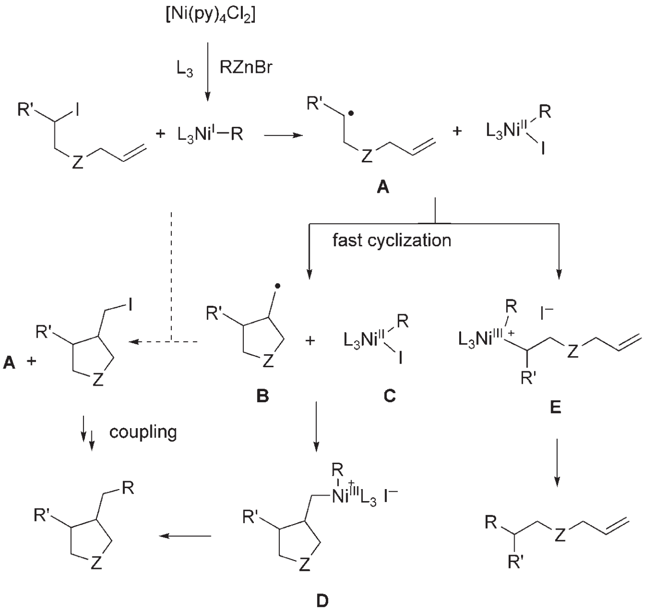
Table 3: Ni-catalyzed cross-coupling reactions of radical-clock precursors with RZnBr ([Ni(py)$_4$Cl$_2$] (10 mol%), (*S*)-(*sec*-Bu)-Pybox (10 mol%), THF, 23 °C).

Entry	Substrate	RZnBr	Product	k [s^{-1}][a]	t [h]	Yield [%][b]
1	 **10a**	**2a**	 **11a**	0.1	3	82
2	 **10b**	**2a**	 **11b**	2.3×10^5	20	41[b]
3	 **10c**	**2a**	 **11c**	9×10^6	11	25[b]
4	 **10d**	**2a**	 **11d**	6.7×10^7	5	63
5	**10d**	**2b**	 **11d'**	6.7×10^7	4	59

[a] Cyclization or ring-opening rate of the radical formed from **10a–d** after homolytic cleavage of the C–I bond. See Ref. [28]. [b] The low yields are probable due to the formation of volatile compounds resulting from H abstraction from the solvent.



Scheme 5. Calculated transition state (DFT level) for the reaction of alkyl–nickel(I) complex with 2-iodopropane.



Scheme 6. Possible mechanistic pathways for the nickel-catalyzed cyclization/coupling reaction.

the Ni center. Alternatively, radical **B** could react with the starting iodide to give **A** plus rearranged compounds such as **4**, which would subsequently couple to the organozinc reagent (Scheme 6, dashed lines).

In summary, we have shown that two different alkyl–alkyl bonds can be formed from alkyl iodides and organozinc reagents in a process that is triggered by the formation of radicals in the reaction of iodides with Ni^I complexes. The key C(sp^3)–C(sp^3) bond formation is a fast process, which can even compete with cyclization of carbon radicals. [Ni(py)$_4$Cl$_2$] is a convenient precatalyst for these transformations. Our calculations show that the reaction of alkyl–nickel(I) complexes with iodoalkanes is fast and affords free radicals, in accord with the experimental observations. The wide scope and functional-group compatibility of this reaction would allow the development of novel approaches to the synthesis of complex molecules based on C(sp^3)–C(sp^3) bond disconnections.

Received: June 11, 2007
Revised: August 30, 2007

Keywords: C–C coupling · density functional calculations · homogeneous catalysis · nickel · radical reactions

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[26] The reaction of the bromide analogue of **1a** with **2a** also led to **3a** in 57 % yield. The reactivity of bromides, chlorides, fluorides, and tertiary iodides is under investigation.

[27] The presence of heteroatoms in the substrate is not necessary for the reaction to take place. Thus, we have performed the cross-coupling reaction of 1-iodo-3-phenylpropane with 3-pentylzinc bromide under the standard conditions, which afforded the expected product in approximately 60 % yield. Moreover, the reaction of 1-(but-3-enyl)-2-iodocyclopentane with the same organozinc compound gave the corresponding cyclization/cross-coupling derivative in about 70 % yield. Again in these cases, these low polarity compounds could not be separated from by-products by column chromatography. Experimental details can be found in the Supporting Information.

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