

Effect of immobilization on catalytic characteristics of saturated Pd-N-heterocyclic carbenes in Mizoroki–Heck reactions

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Abstract

A saturated Pd-N-heterocyclic complex was immobilized on an amorphous silica. The complex itself is of very high thermal stability. However, TEM observations, hot filtration, reusability, and poisoning tests all revealed that the complex acted only as a precatalyst to highly active Pd species in Mizoroki–Heck reactions when immobilized. The complex appears more stable when used under homogeneous reaction conditions. The immobilized complex afforded high turnover numbers, 10^4 – 10^5 . The higher turnover frequencies were realized at the lower Pd concentrations, which is a characteristic property of ligand-free Pd catalyzed reactions.

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1. Introduction

Since their first introduction by Öfele and Wanzlick [1], N-heterocyclic carbenes (NHCs) have become universally accepted ligands in organometallic and inorganic coordination chemistries. Due to their being strong σ -donors and low π -acceptors, NHCs have even been proposed as replacements for the more commonly used phosphane ligands in palladium catalyzed coupling reactions, because they resemble organophosphanes [2]. Furthermore, NHCs are easily acquired, non-toxic and exhibit high thermal stability when compared with phosphanes [3]. These properties have been exploited in a broad range of catalytic applications [4].

As a catalyst, Pd is very important in the pharmaceutical industry; however, because of its expense and toxicity, it is particularly important to reduce both its loss and presence

in the product solution, respectively. To this end, immobilization of Pd-catalysts onto a support allows heterogeneous catalyst with decreased leaching of Pd to the solution. When an NHC is complexed with a metal, it exhibits extraordinary thermal stability, making it a reasonable candidate for immobilization. Likewise, due to the stability of the metal complex, it is presumed that the metal will remain in its immobilized state when anchored to a support prior to reaction making it be less likely to leach into solution [3c,5].

According to the proposed reaction mechanism for coupling reactions involving haloarenes, the oxidative Pd addition to haloarenes is believed to be the rate-determining step with the activity of catalyst being determined by the electron density on palladium. Therefore, in the paper presented here, the use of saturated NHCs was preferred because of their electron-donating ability as compared with their unsaturated counterparts.

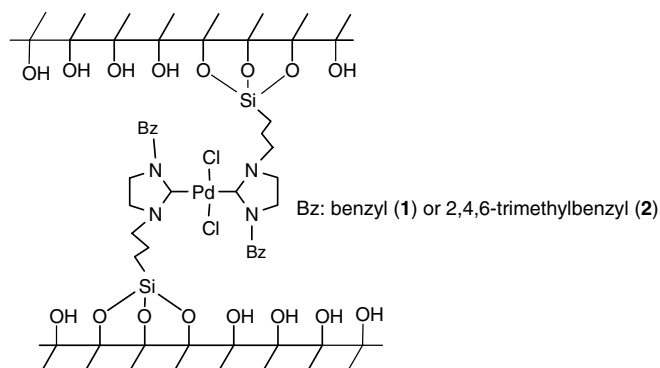
In contrast to view that metals of NHCs are less likely to leach into solution, results will be shown here which

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indicate that immobilization of a thermally stable Pd–NHC complex [5e], led to the liberation of Pd into solution, thus giving rise to highly reactive Pd species during Mizoroki–Heck (M–H) reactions.

2. Results and discussion

The amorphous silica supported Pd–NHC complexes, **1** and **2**, were the catalysts tested in this study. The molar N/C ratio of the samples indicated that no ethoxy group remained after anchoring the complex.



Initial trials were performed to determine the optimal base type for the coupling reaction of bromobenzene with styrene over catalyst **2** (0.066 mmol Pd/g silica) with a Pd concentration of 0.5% in DMF solvent at 140 °C. Catalyst **2** demonstrated very low activity with NaOAc and Cs₂CO₃ (Table 1). Na₂CO₃ was somewhat more effective than K₃PO₄.

The catalysts were tested for their recyclabilities for M–H reactions involving styrene. For each cycle, the amounts

Table 1
The effect of base on M–H reactions of bromobenzene with styrene over catalyst **2**^a

| Base | Time (h) | Conversion (%) | Yield (%) <i>trans</i> |
|------------------------------------|----------|----------------|------------------------|
| CH ₃ CO ₂ Na | 14 | 40 | 25 |
| Na ₂ CO ₃ | 7 | 87 | 78 |
| Cs ₂ CO ₃ | 18 | 46 | 12 |
| K ₃ PO ₄ | 14 | >99 | 70 |

^a With 0.066 mmol Pd/g silica.

Table 2
Recyclability test of the immobilized complex **2** for M–H reaction^a

| Aryl halide/cycle | <i>trans</i> -Yield % (time, h) | | | | | | | | | |
|--|---------------------------------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|-----------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 4-CH ₃ C ₆ H ₄ I | 87 (7.3) | 85 (6.8) | 88 (6.6) | 91 (7.5) | 89 (8) | 88 (7.4) | 88 (10.5) | 88 (11.5) | 90 (11.3) | 86 (14.3) |
| 4-CH ₃ COC ₆ H ₄ Br | 95 (2) | 95 (3) | 96 (4) | 96 (4.7) | 93 (7.3) | 83 (11.2) | 93 (18) | 65 (28.5) | – | – |

^a Reaction conditions. 4 mmol aryl halide, 4.8 mmol styrene, 6 mmol Na₂CO₃, 10 ml DMF, 0.5% Pd, 140 °C, with 0.066 mmol Pd/g silica.

of solvent and reagents were adjusted depending on the amount of catalyst that had been recovered from the previous run. The results are presented in Table 2.

The immobilized complex **2** (catalyst **2**) appears to be reusable for 10 cycles for the reaction of 4-iodotoluene; however, longer reaction periods are required for reactions after the sixth cycle. A reaction period of 7–8 h seems to be sufficient for the first six cycles, nevertheless, it took nearly 14 h to obtain high yield formation for the tenth cycle.

The first cycle showed a higher rate of reaction for 4-bromoacetophenone as compared to 4-iodotoluene; however, longer reaction times were required progressively for each subsequent cycle to attain the *trans*-coupling product at yields greater than 90%. While *trans*-coupling product formation was achieved at yields of 95%, after 2 h for the reaction of 4-bromoacetophenone with styrene during its first use, it took, however, 18 h to obtain the same amount of yield during its seventh use, and only 64% product formation could be achieved after 28.5 h when the catalyst had been used for the eighth time, indicating that the catalyst underwent gradual deactivation at each cycle. Trends were also similar with the immobilized complex **1**.

Atomic absorption spectrometry (AAS) analyses revealed no detectable amounts of Pd within the filtrates after the reactions. However, a significant amount of Pd was determined in a solution recovered upon hot filtration: The reaction solution of 2 mmol 4-bromoacetophenone with styrene which had been performed under standard conditions was recovered upon hot filtration under dry N₂ atmosphere after 15 min of reaction, where the conversion and *trans*-yields were 16% and 9%, respectively. Further AAS analysis revealed the presence of 3.6 ppm Pd in the solution, this being about 3.4% of the Pd charged initially. Moreover, the reaction proceeded to give a 39% conversion and to yield 34% of the *trans*-coupling product when the base was added to the filtrate and heated for an additional 3.75 h. Though these results do not rule out the possibility that the anchored complex might have been involved in the reaction in a heterogeneous way, it is evident that the catalyst released Pd species into the solution that were capable of catalyzing the reaction.

TEM analyses revealed the presence of Pd particles on the silica support of the used catalysts which were recovered after the first and eight runs with 4-bromoacetophenone and styrene (Fig. 1). After its first use, the Pd agglomerates were considerably large, extending to diameters as large as 90 nm, with an average size of 36.7 nm. Nevertheless, the catalyst after the eighth run contained a higher quantity

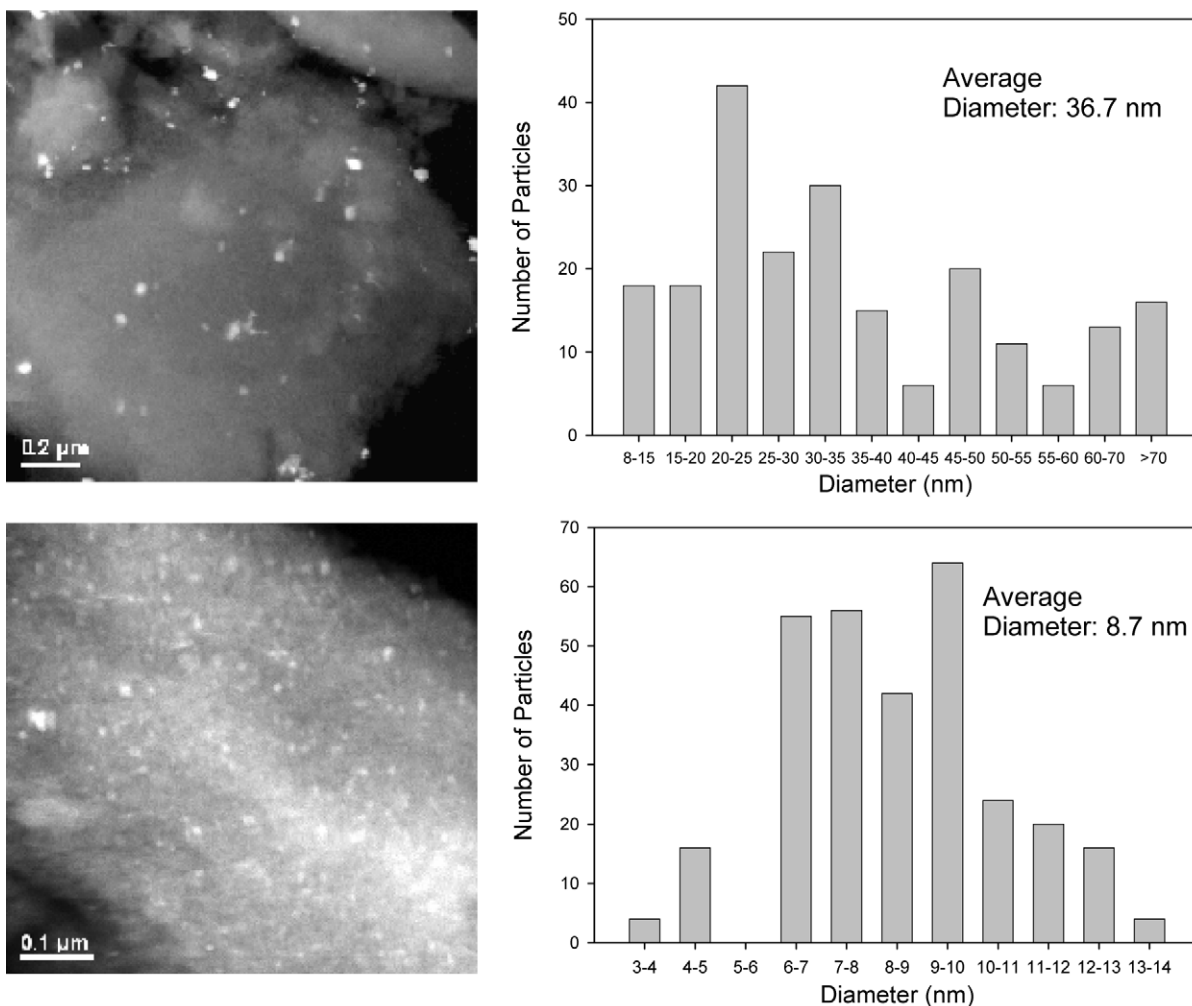


Fig. 1. The TEM micrographs with histograms of palladium particle sizes of catalyst **2** recovered from the reaction of 4-bromoacetophenone with styrene after the first run (upper figure) and the eight run (lower figure). Bright spots in the images are due to the contrast from Pd.

of particles with smaller average size (8.7 nm), and the particles were located less distant with respect to each other on the silica when compared to those of the former catalyst. These results seem to demonstrate that the immobilized complex decomposed gradually at each cycle, however, it was not possible to be certain whether the loss in activity is due to the complex decomposition or the consumption of a source of the soluble active Pd species (i.e., whether the M–H reaction is catalyzed by free or immobilized palladium). On the other hand, it was surprising somewhat, for us, that Pd dissociated from the complex, because it was previously determined that complex **2** was stable up to 250 °C during heat treatment [5e].

In an effort to determine the relative fraction of the M–H reaction that was catalyzed by the leached Pd from an immobilized Pd–SCS pincer complex, You et al. performed an M–H reaction in the presence of an insoluble cross-linked poly(vinylpyridine) polymer (PVPy) [6]. PVPy strongly coordinates to soluble Pd(II) species, but it is incapable of interacting with solid Pd. They found that the reaction was completely inhibited in the presence of PVPy, supporting the hypothesis that the reaction had been cata-

lyzed by only soluble Pd species leached from the solid catalyst.

The same methodology was applied herein. Fig. 2 compares the effect of PVPy addition on the conversion kinetics

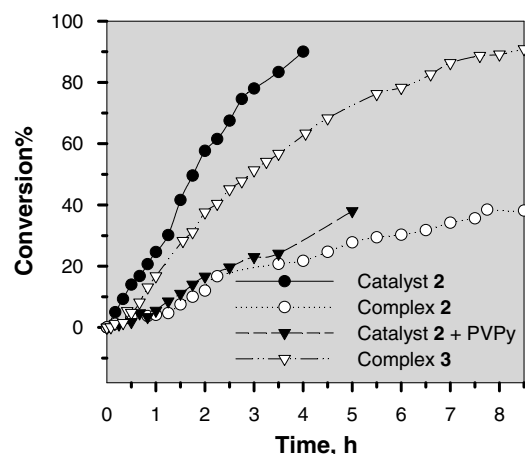


Fig. 2. Conversion kinetics of the M–H reactions of 4-bromoacetophenone and styrene. Pd: 0.05%, with 0.013 mmol Pd/g silica for catalyst **2**.

for the reaction of 4-bromoacetophenone. Yet, these reactions were performed at a lower Pd concentration, 0.05%, than those of the recyclability tests, since the higher Pd concentration could mask various stages of the reaction (e.g., an induction period).

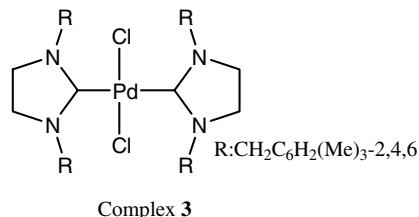
In the absence of PVPy, the conversion was 90% after 4 h of reaction and no induction period was observable from the conversion curve (Fig. 2). However, in the presence of PVPy, the activity of the catalyst was significantly reduced to give only 28% of conversion after 5 h of reaction. This difference demonstrated that the reaction was catalyzed mainly by the dissolved Pd.

For comparison, a homogeneous reaction was performed over complex **2**. Interestingly, the kinetic profile of the homogeneous reaction was very similar to that of the reaction performed over immobilized complex–PVPy combination (Fig. 2). This similarity may imply that probably a similar type of Pd species catalyzed the reactions in both reaction media. It has been shown previously that PVPy supported Pd nano-clusters can catalyze the M–H reaction [7]. Then, the M–H catalysis should have taken place either on the surface of Pd aggregates or via the ligand-immobilized Pd with the catalyst **2**–PVPy combination.

The Hg poisoning test is a popular method to probe the catalyst for its status in a reaction (homogeneous or heterogeneous) [4c,4e,8]. Metallic mercury deteriorates the activity of the colloidal Pd by forming an amalgam. The addition of Hg (300 equiv.) to the reaction medium, either in the presence of free complex or catalyst **2**, completely prohibited the M–H reaction of 4-bromoacetophenone and styrene. A negative result for the mercury test can confirm a homogeneous catalytic system [4c,4e,8a,8c], and a positive result can essentially confirm a reaction proceeding through the Pd(0)–Pd(II) cycle, but does not warrant heterogeneous colloidal Pd catalysis [8c].

Under homogeneous conditions (with complex **2**), the solution turned from a light yellow to a yellow-orange color towards the end of the reaction, and no palladium black formation was observed, whereas the solid catalyst turned to gray, consistent with the formation of Pd aggregates. In the former case, NHC ligands should have been available to coordinate with Pd, preventing Pd black formation, but on the other hand, lowering Pd activity by confining it. Immobilization of the palladium complexes may restrict them from adopting the most stable geometries required for efficient reaction [9]. This would place high strain to temporary structures and, therefore, lead to decomposition of the complex. The less strongly coordinated Pd species would effectively catalyze the reaction until they precipitate to the less active agglomerates on the silica surface. In conclusion, the above experiments show that the reactions over the immobilized Pd–NHC complex were catalyzed predominantly by dissolved Pd species. Nevertheless by saying this, we do not mean that there would be no contribution of the immobilized complex, and/or by other Pd species to the overall activity of the catalyst.

Fig. 2 also illustrates the kinetic profile for the reaction catalyzed by another type of Pd–NHC complex (complex **3**) in which all nitrogen atoms of pentacyclic rings of NHC ligands are functionalized by 2,4,6-trimethylbenzyl groups [10]:



It is apparent that though this catalyst afforded the reaction in higher reaction rates than did complex **2** under homogeneous protocol, however, it is less active than the immobilized complex **2**.

M–H reactions were also performed at low Pd concentrations to realize the limits of this catalytic system. The overall silica content of each reaction medium was brought to 300 mg upon addition of silica that contained no Pd originally. This enabled us to recover the catalyst more effectively, otherwise it would have been impractical to recover the very small amounts of catalyst used for the studies performed at low Pd concentrations.

As can be seen in Table 3, catalyst **2** showed high activities when used also in lower proportions for the M–H reactions with styrene. Interestingly, the reactions of 4-iodoanisole proceeded at comparable rates over the both palladium concentration of 0.05% and 0.5% (entries 1 and 2). Very high turnover numbers (TON) and turnover frequencies (TOF), which were calculated on the basis of *trans*-coupling product formation, were achieved for iodo- and bromoarenes. Higher TOF values were obtained at lower catalyst concentrations. TON values were as high as 166,000 and 19,000, and TOF values of ≈ 6900 and ≈ 1200 h⁻¹ were obtained with excellent yield of *trans*-coupling products from the reactions of 4-iodoanisole and 4-bromoacetophenone with styrene, respectively, and a good yield (66%) was obtained at a very high TON value (66,000) for the reaction using 4-bromoacetophenone (Table 3, entries 1–11), whereas the total TON and TOF values were only 1422 and 18 h⁻¹, respectively, for 4-bromoacetophenone after eight consecutive runs were conducted.

Catalyst **2**, which was subjected to the M–H reaction of 4-bromoacetophenone at a Pd concentration of 0.005%, showed reduced activity during second use of the catalyst, giving 48% of the *trans*-coupling product after 38 h of reaction time (Table 2, entry 10).

The sterically congested 2-iodoanisole required comparatively longer reaction times (Table 3, entry 6). Another activated aryl bromide, 4-bromonitrobenzene afforded relatively lower *trans*-coupling products at a Pd concentration of 0.005%, giving rise to 78% *trans*-coupling product with a TON value of 15,600 (Table 2, entry 12). As a model

Table 3
The M–H reactions of aryl halides with styrene over the catalyst **2**^a

| Entry | Aryl halide | Pd (%) | Time (h) | Conversion (%) | Yield (%) <i>trans</i> | TON ^b | TOF ^b (h ⁻¹) |
|-------|---|----------------------|----------|----------------|------------------------|------------------|-------------------------------------|
| 1 | 4-CH ₃ OC ₆ H ₄ I ^c | 5 × 10 ⁻¹ | 6 | 98 | 83 | 166 | 28 |
| 2 | 4-CH ₃ OC ₆ H ₄ I | 5 × 10 ⁻² | 5.3 | >99 | 82 | 1640 | 309 |
| 3 | 4-CH ₃ OC ₆ H ₄ I ^d | 5 × 10 ⁻³ | 14.5 | 100 | 82 | 16,400 | 1131 |
| 4 | 4-CH ₃ OC ₆ H ₄ I ^{d,e} | 5 × 10 ⁻³ | 22 | 50 | 44 | 8800 | 400 |
| 5 | 4-CH ₃ OC ₆ H ₄ I ^f | 5 × 10 ⁻⁴ | 24 | 94 | 83 | 166,000 | 6917 |
| 6 | 2-CH ₃ OC ₆ H ₄ I ^c | 5 × 10 ⁻¹ | 23 | 96 | 90 | 180 | 8 |
| 7 | 4-CH ₃ COC ₆ H ₄ Br ^c | 5 × 10 ⁻¹ | 2 | >99 | 95 | 190 | 85 |
| 8 | 4-CH ₃ COC ₆ H ₄ Br | 5 × 10 ⁻² | 4 | 90 | 87 | 1740 | 450 |
| 9 | 4-CH ₃ COC ₆ H ₄ Br ^f | 5 × 10 ⁻³ | 15 | 99 | 93 | 18,600 | 1240 |
| 10 | 4-CH ₃ COC ₆ H ₄ Br ^{e,f} | 5 × 10 ⁻³ | 38 | 54 | 48 | 9600 | 253 |
| 11 | 4-CH ₃ COC ₆ H ₄ Br ^f | 1 × 10 ⁻³ | 37 | 77 | 66 | 66,000 | 1784 |
| 12 | 4-NO ₂ C ₆ H ₄ Br ^d | 5 × 10 ⁻³ | 22 | 93 | 78 | 15,600 | 709 |
| 13 | 3-BrC ₆ H ₅ N | 5 × 10 ⁻² | 16 | >99 | 87 | 1740 | 109 |
| 14 | 3-BrC ₆ H ₅ N | 1 × 10 ⁻² | 35 | 82 | 60 | 6000 | 171 |
| 15 | C ₆ H ₅ Br | 5 × 10 ⁻¹ | 7 | 87 | 78 | 156 | 22 |
| 16 | C ₆ H ₅ Br | 5 × 10 ⁻² | 15 | 84 | 59 | 1180 | 79 |
| 17 | C ₆ H ₅ Br | 1 × 10 ⁻² | 8 | 57 | 28 | 2800 | 350 |
| 18 | 4-CH ₃ C ₆ H ₄ Br | 5 × 10 ⁻¹ | 10.7 | 69 | 63 | 126 | 12 |
| 19 | 4-CH ₃ C ₆ H ₄ Br | 5 × 10 ⁻² | 15 | 73 | 64 | 1280 | 85 |
| 20 | 4-CH ₃ C ₆ H ₄ Br | 1 × 10 ⁻² | 9 | 35 | 29 | 2900 | 322 |
| 21 | 4-CH ₃ OC ₆ H ₄ Br | 5 × 10 ⁻¹ | 5 | 23 | 19 | 38 | 7.6 |
| 22 | 4-CH ₃ OC ₆ H ₄ Br ^f | 5 × 10 ⁻² | 6 | 15 | 14 | 280 | 47 |
| 23 | 4-CH ₃ COC ₆ H ₄ Cl | 5 × 10 ⁻¹ | 19 | 28 | 15 | 30 | 2 |

^a [Styrene]/[aryl halide] = 1.2, [Na₂CO₃]/[aryl halide] = 1.5, with 0.013 mmol Pd/g silica, 4 mmol aryl halide, 10 ml DMF, 140 °C, under inert atmosphere, sufficient amount of silica was added to the reaction medium to contain 300 mg of silica overall.

^b TON = [*trans*-yield]/[Pd], TOF = TON/h.

^c The catalyst contained 0.066 mmol Pd/g silica, with no additional silica.

^d 6.7 mmol aryl halide.

^e Second use.

^f 20 mmol aryl halide, 15 mL DMF.

molecule to hetero-aryl halide compounds, 3-bromopyridine was also converted effectively, yielding 87% and 60% *trans*-coupling product for Pd concentrations of 0.05% and 0.01%, respectively (Table 3, entries 13–14).

Non-activated bromoarenes, bromobenzene, and 4-bromotoluene gave moderate to high coupling yields at Pd concentrations of 0.5% and 0.05% (entries 15–22). Catalyst **2** was, however, low in its activity towards M–H reactions of 4-bromoanisole and 4-chloroacetophenone (Table 2, entries 21–23). Nevertheless, it should be noted that *trans*-coupling formation was approximately comparable and ceased at the fifth and sixth h of reaction of 4-bromoanisole for Pd concentrations of both 0.5% and 0.05%, respectively.

1,1-Diarylethene was the major isomeric by-product of the M–H reactions when styrene was used as an olefin source. Its formation varied between 3% and 6% for reactions involving bromoarenes, while iodoarenes gave higher yields of this isomeric product, (10–12%). *cis*-Coupling isomer formation was generally observed at yields of less than 1%.

Reactions with low Pd amounts were also performed with butyl acrylate as an olefin reagent. As expected, the catalyst was more active with this olefin (Table 4). The reaction was more selective to *trans*-coupling product with

acrylate reagent than with styrene (total isomeric products were usually <1%). The higher TOF values with the lower catalyst amounts were also a characteristic trend for the coupling reaction of this reagent with aryl halides. Catalyst **2** gave high coupling product formation with extremely high TONs for all the activated aryl bromides employed, being as high as 500,000; 700,000; and 840,000 for 4-bromobenzonitrile; 4-nitrobromobenzene; and 4-bromoacetophenone, respectively (Table 4, entries 1–12). However, the catalyst was air-sensitive; the *trans*-coupling product formation was 63% after 9 h of reaction of 4-bromoacetophenone in air versus 95% after 6.8 h in an inert atmosphere.

For butyl acrylate, the catalyst was ineffective during second use under low Pd concentrations (Table 4, entry 5). Catalyst **2** was also very active for the reactions involving either 3-bromopyridine or 2-bromonaphthalene, yielding very high coupling products with low Pd concentrations (Table 4, entries 13–15). A moderate coupling product formation was obtained for Pd-catalyzed M–H reaction involving bromobenzene and 4-bromotoluene (Table 4, entries 16–19).

de Vries and Reetz pointed out that the irreversible correlation of TOF values with Pd concentrations is an indication for the presence of an equilibrium between less active

Table 4
The M–H reactions of aryl halides with butyl acrylate over the catalyst **2**^a

| Entry | Aryl halide | Pd (%) | Time (h) | Conversion (%) | Yield (%) <i>trans</i> | TON ^b | TOF ^b (h ⁻¹) |
|-------|---|----------------------|----------|----------------|------------------------|------------------|-------------------------------------|
| 1 | 4-CH ₃ COC ₆ H ₄ Br ^c | 5 × 10 ⁻³ | 2.5 | 100 | 98 | 19,600 | 7840 |
| 2 | 4-CH ₃ COC ₆ H ₄ Br ^d | 5 × 10 ⁻⁴ | 6.8 | 97 | 95 | 190,000 | 27,941 |
| 3 | 4-CH ₃ COC ₆ H ₄ Br ^{d,e} | 5 × 10 ⁻⁴ | 9 | 69 | 63 | 126,000 | 14,000 |
| 4 | 4-CH ₃ COC ₆ H ₄ Br ^d | 2 × 10 ⁻⁴ | 12 | 73 | 68 | 340,000 | 28,333 |
| 5 | 4-CH ₃ COC ₆ H ₄ Br ^{d,f} | 2 × 10 ⁻⁴ | 28 | 30 | 12 | 60,000 | 2143 |
| 6 | 4-CH ₃ COC ₆ H ₄ Br ^g | 1 × 10 ⁻⁴ | 28 | 87 | 84 | 840,000 | 30,000 |
| 7 | 4-NO ₂ C ₆ H ₄ Br ^h | 5 × 10 ⁻⁴ | 24 | 77 | 74 | 148,000 | 6167 |
| 8 | 4-NO ₂ C ₆ H ₄ Br ^d | 2 × 10 ⁻⁴ | 24 | 78 | 71 | 355,000 | 14,792 |
| 9 | 4-NO ₂ C ₆ H ₄ Br ^d | 1 × 10 ⁻⁴ | 25 | 77 | 70 | 700,000 | 28,000 |
| 10 | 4-CNC ₆ H ₄ Br ^d | 5 × 10 ⁻⁴ | 22 | 98 | 96 | 192,000 | 8727 |
| 11 | 4-CNC ₆ H ₄ Br ^d | 2 × 10 ⁻⁴ | 24 | 89 | 80 | 400,000 | 16,667 |
| 12 | 4-CNC ₆ H ₄ Br ^d | 1 × 10 ⁻⁴ | 24 | 53 | 50 | 500,000 | 20,833 |
| 13 | 3-BrC ₆ H ₅ N ⁱ | 1 × 10 ⁻² | 16 | 99 | 98 | 9800 | 613 |
| 14 | 3-BrC ₆ H ₅ N ^c | 5 × 10 ⁻³ | 28 | 81 | 80 | 16,000 | 571 |
| 15 | 2-Bromonaphthalene ^c | 5 × 10 ⁻³ | 20 | 97 | 94 | 18,000 | 940 |
| 16 | C ₆ H ₅ Br ⁱ | 5 × 10 ⁻² | 7.8 | 74 | 64 | 1280 | 164 |
| 17 | C ₆ H ₅ Br ⁱ | 1 × 10 ⁻² | 9 | 64 | 54 | 5400 | 600 |
| 18 | C ₆ H ₅ Br ^c | 5 × 10 ⁻³ | 20 | 39 | 31 | 6200 | 310 |
| 19 | 4-CH ₃ C ₆ H ₄ Br ⁱ | 5 × 10 ⁻² | 11 | 52 | 48 | 960 | 82 |

^a [butyl acrylate]/[aryl halide] = 1.2; [Na₂CO₃]/[aryl halide] = 1.5, with 0.013 mmol Pd/g silica, under inert atmosphere, sufficient amount of silica was added to the reaction medium to contain 300 mg of silica overall.

^b TON = [*trans*-yield]/[Pd], TOF = TON/h.

^c 6.67 mmol aryl halide, 10 mL DMF.

^d 20 mmol aryl halide, 15 mL DMF.

^e Under air.

^f Second use.

^g 40 mmol, 20 mL DMF.

^h 10 mmol aryl halide, 10 mL DMF.

ⁱ 4 mmol aryl halide, 10 mL DMF.

Pd aggregates and highly active Pd species, lowering the Pd-to-aryl halide ratio shifts the equilibrium in favor of the latter species [11].

Various supported Pd catalysts [12], some pincer complexes [6,13], palladacycles [6a,11a], and simple Pd compounds [11a,14] were also shown to act as Pd reservoirs when used for M–H reactions.

Our results are also consistent with previously reported results of various supported unsaturated Pd–NHC complexes. Schwarz et al. demonstrated that a polymer supported N-heterocyclic dicarbene chelate complex of palladium was recyclable up to 15 times for the M–H reaction of 4-bromoacetophenone with styrene at a Pd concentration of 0.15%, while its activity gradually decreased after the fifth use when the Pd concentration was 0.02% in the reaction medium [3c]. Moreover, several other types of polymer bounded Pd–NHC complexes also revealed lower activities in subsequent uses for M–H [5a] and Suzuki reactions [5b].

In agreement with the reports by You et al. [6], where immobilized Pd–SCS complexes were shown to act as catalyst precursors rather than as true heterogeneous catalysts, this study, also revealed that even thermally stable complexes, such as NHC ligated metals, may decompose during a reaction process. In fact, there have been numerous reports that claimed immobilized metal complexes as reusable heterogeneous catalysts; however, for most of

these reports, true active state of metal which catalyzed the reaction is unknown.

A catalyst, such as the one used in this study, that delivers metal to the reaction solution, would not be favored. However, possibly the complete recovery of Pd at the end reactions may be an advantage of the catalyst used here. If metal recovery is one of the most important criteria in choosing a catalyst, it would be more preferable to use a better accessible, lower cost catalyst such as a metal oxide, zeolite or carbon supported metals, provided that the process works at high TONs and TOFs, and that the catalyst leaves no remnants of metal within the end product [12,15], since the transition metal contamination is highly regulated in the pharmaceutical industry.

3. Conclusion

Silica anchored saturated Pd–N-heterocyclic carbenes were tested for their catalytic behavior in M–H reactions of aryl halides. Activity of the Pd–NHC complex was greatly promoted upon immobilization, functioning at very high TONs and TOFs. This is related to the decomposition of the immobilized complex to give rise to the highly active Pd species, which precipitates onto the silica surface at the end of the reaction. Pd–NHC complex seems to be highly stable when used at homogeneous procedures. However, it lost its stability upon immobilization, probably due to

its restricted mobility in adopting stable geometries of temporary structures in a reaction cycle.

4. Experimental section

Diethyl ether (J.T. Baker) was distilled under nitrogen from sodium benzophenone ketyl just before use. DMF (J.T. Baker) was dried over molecular sieve 4A. Chloroform (Riedel-de Haën, extra pure) was dried by refluxing with anhydrous CaCl_2 . All other reagents which were obtained from commercial sources were used without further purification. All the syntheses of the 1,3-disubstituted imidazolium salts and the Pd–NHC complexes were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. Amorphous silica was synthesized as reported earlier [16]. Accordingly, to a 3 N, 500 mL solution of H_2SO_4 was added sodium silicate solution (5% NaOH, 13.5% SiO_2 , Riedel-de Haën) at a flow rate of 10 mL min^{-1} by means of a peristaltic pump until a pH of 3.65 was attained. Gelation occurred in 5 min after addition of the silicate solution was completed. The synthesized silica was washed with water until the solution conductivity showed no change. The BET surface area was $490 \text{ m}^2/\text{g}$; the single point total pore volume was $0.75 \text{ cm}^3/\text{g}$. Average pore diameter by BET was 61 \AA .

4.1. Synthesis of 1-benzyl or 1-(2,4,6-trimethylbenzyl)-3-(propyltriethoxysilane)-imidazolium chloride

The preparation of the imidazolium salts were readily accomplished by the quarternization of 1-(3-triethoxysilylpropyl)-2-imidazoline (imeo). To a 5 mL of DMF solution of imeo (3.99 g, 14.78 mmol) was added 14.79 mmol of benzyl chloride or 2,4,6-trimethylbenzyl chloride and the resulting mixture was stirred at room temperature (RT) for 24 h. Diethyl ether (20 mL) was added to obtain a white crystalline solid. The product was filtered, washed with Et_2O ($2 \times 15 \text{ mL}$) and dried under vacuum. The salt was colorless, hygroscopic and freely soluble in CHCl_3 , but insoluble in hexane or diethyl ether. The structural characterizations for this sample are given elsewhere [17].

4.2. Synthesis of bis[1-(benzyl or 2,4,6-trimethylbenzyl)-3-(propyltriethoxysilane)-imidazolidin-2-ylidene]dichloropalladium(II) complexes

To a CH_2Cl_2 (10 mL) solution of the 1.0 mmol corresponding imidazolium salt synthesized, 0.5 mmol Ag_2O was added. After stirring the mixture for 48 h at RT, 0.13 g (0.53 mmol) of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ was added and it was further stirred for 48 h at RT. The precipitated AgCl was separated from the mixture by filtration. The complex was recrystallized from ether, giving 62% yield. Analytical calculation for $\text{C}_{38}\text{H}_{64}\text{Cl}_2\text{N}_4\text{PdSi}_2$: C, 50.367.12%; N, 6.18%. Found: C, 48.8%; H, 6.8%; N, 6.1% for the benzyl substituted complex (complex 1). The structural elucidation of the complex was established through X-ray crystal-

lography technique (Fig. 3). The characterization of the 2,4,6-trimethylbenzyl substituted complex (complex 2) is given elsewhere [5e].

4.3. Anchoring of Pd–NHC complexes

A dry CHCl_3 solution (20 mL/g silica) which contained Pd–NHC complex in an amount furnishing 0.2 or 1 wt% Pd with respect to the silica amount was added drop wise to the amorphous silica which was evacuated overnight at $120 \text{ }^\circ\text{C}$ previous to the anchoring process. The resulting suspension was refluxed for 24 h under inert atmosphere while being magnetically stirred. After filtration, it was washed with CH_2Cl_2 thoroughly. AAS analysis of the sample showed a palladium loading of 0.013 mmol or $0.066 \text{ mmol g}^{-1}$, respectively.

4.4. Characterization of the catalysts

Specific surface areas of the catalysts and the pure support material were measured using a static process by means of a Micrometrics ASAP 2010 instrument using nitrogen at 77 K. The specific surface area was calculated by the BET method and average pore diameters and pore size distributions were calculated from the adsorption branch of the isotherm using the Barrett, Joyner and Helenda (BJH) method. All samples were degassed overnight at 423 K. Elemental analyses of samples were done by the Scientific and Technical Research Council of Turkey using a LECO CHNS-932 instrument. The palladium content of the catalysts was determined by AAS (Solaar AA Spectrometer Thermo Elemental). The samples (20 mg) were digested in a mixture of HNO_3 (65%, 3 mL), HF (40%, 2 mL) and HClO_4 (65%, 1 mL) using an Ethos Plus Microwave Labstation furnace. TEM observations were performed using a JEM-2010F field emission transmission microscope operated in the scanning mode at 200 kV and a high angle annular dark field detector was utilized.

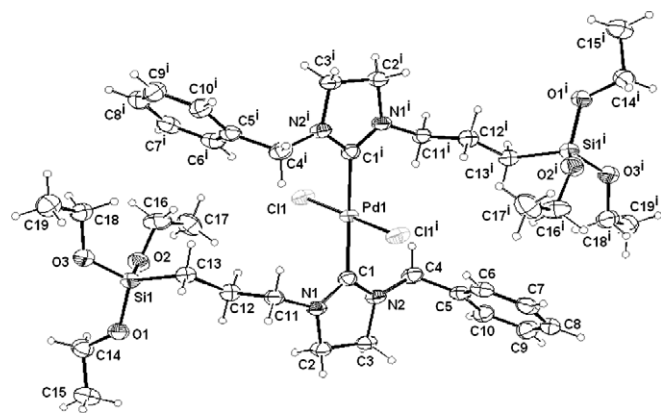


Fig. 3. X-ray structure of complex 1. Selected bond distances (\AA) and angles ($^\circ$): Pd1–C1 2.031, Pd–Cl1 2.311; C1–Pd1–Cl1 $90.71(7)$, C1–Pd1–Cl1' 89.29 .

4.5. Typical procedure for the Heck reactions

Aryl halide, olefin, base and hexadecane (as an internal standard) and DMF were introduced into a 3-necked round bottomed flask which was equipped with a condenser and a septum and contained the catalyst which was predried at 110 °C for 2 h under vacuum. The reactor was then placed in a preheated oil bath at 140 °C and vigorously stirred during the reaction under inert atmosphere. Small amounts of samples were periodically withdrawn by syringe during the reaction, diluted in CH₂Cl₂ and analyzed by GC. The course of the reaction was followed until no further increase in the yield was observed. After cooling to room temperature, the catalyst was recovered by filtering through a membrane filter with 0.2 μm porosity.

All products are known compounds and products were analyzed by GC and GC/MS and isolated by column chromatography on silica gel.

In order to remove adsorbed organic substrates and bases, the catalyst was first washed with CH₂Cl₂ and then with CH₃OH for NaOAc or with water for other bases after the reaction. For the recycling studies, the recovered catalyst was dried at 110 °C under vacuum for at least 2 h and reused without further treatment. A small sample of the reaction solution was collected for GC analysis and the remaining solution was kept for Pd analysis. The filtrate was digested in a Teflon vessel in the presence of H₂O₂ and HNO₃ (conc.) after all the organic solvent was completely evaporated for AAS analysis.

4.5.1. 4-Nitro-*trans*-stilbene

Hexane:DCM (2:1); yellow plates; m.p.: 156–157 °C; purity: >99%; ¹H NMR (400 MHz, CDCl₃) δ: 8.21 (d, 2H, *J* = 9.2 Hz), 7.61 (d, 2H, *J* = 9.2 Hz), 7.52 (d, 2H, *J* = 7.2 Hz), 7.28–7.42 (m, 3H), 7.24 (d, 1H, *J* = 16 Hz), 7.12 (d, 1H, *J* = 16.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 147.2, 143.9, 136.4, 133.5, 129.1, 129.0, 127.2, 127.0, 126.5, 124.3; MS: 225 (M⁺), 178.

4.5.2. 4-Acetyl-*trans*-stilbene

Hexane:DCM (4:1); white plates; m.p.: 138.7–144.8 °C; purity: >99%; ¹H NMR (400 MHz, CDCl₃) δ: 7.92 (d, 2H, *J* = 8.0 Hz), 7.55 (d, 2H, *J* = 8.0 Hz), 7.50 (d, 2H, *J* = 8.0 Hz), 7.24–7.38 (m, 3H), 7.19 (d, 1H, *J* = 16.4 Hz), 7.04 (d, 1H, *J* = 16.4 Hz), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 196.6, 142.1, 136.9, 136.3, 131.7, 129.0, 129.0, 128.5, 127.7, 127.0, 126.7, 26.6; MS: 222 (M⁺), 207, 178.

4.5.3. 4-Methoxy-*trans*-stilbene

Hexane:DCM (4:1); pale yellow plates; m.p.: 135.4–137.1 °C; purity: >99%; ¹H NMR (400 MHz, CDCl₃) δ: 7.37 (d, 2H, *J* = 7.2 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.23 (t, 2H, *J* = 7.2 Hz), 7.12 (t, 1H, *J* = 6.8 Hz), 6.95 (d, 1H, *J* = 16.0 Hz), 6.85 (d, 1H, *J* = 16.4 Hz), 6.78 (d, 2H, *J* = 8.4 Hz), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 159.4, 137.8, 130.3, 128.7, 128.4, 127.8, 127.2, 126.8, 126.4, 114.2, 55.2; MS: 210 (M⁺), 165.

4.5.4. 2-Methoxy-*trans*-stilbene

Hexane:DCM (9:1); pale yellow plates; m.p.: 59.5–65.5 °C; >99%; ¹H NMR (400 MHz, CDCl₃) δ: 7.46 (d, 1H, *J* = 8.0 Hz), 7.40 (d, 2H, *J* = 7.2 Hz), 7.35 (d, 1H, *J* = 16.8 Hz), 7.21 (t, 2H, *J* = 7.6 Hz), 7.06–7.13 (m, 2H), 6.97 (d, 1H, *J* = 16.4 Hz), 6.83 (t, 1H, *J* = 7.6 Hz), 6.74 (d, 1H, *J* = 8.0 Hz), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 157.2, 138.3, 129.3, 128.8, 127.6, 126.9, 126.8, 126.7, 123.9, 121.0, 111.1, 55.6; MS: 210 (M⁺).

4.5.5. 4-Methyl-*trans*-stilbene

Hexane; white plates; m.p.: 117–118 °C; purity >99%; ¹H NMR (400 MHz, CDCl₃) δ: 7.38 (d, 2H, *J* = 8.4 Hz), 7.29 (d, 2H, *J* = 8.0 Hz), 7.23 (t, 2H, *J* = 7.6 Hz), 7.12 (t, 1H, *J* = 6.4 Hz), 7.043 (d, 2H, *J* = 8.0 Hz), 6.97 (d, 1H, *J* = 16.5 Hz), 6.93 (d, 1H, *J* = 16.3 Hz), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 137.7, 137.3, 134.8, 129.5, 128.8, 128.7, 127.9, 127.5, 126.6, 126.6, 21.5; MS: 194 (M⁺), 179, 178.

4.5.6. *trans*-3-Styrylpyridine

Hexane:ether (2:3); pale yellow plates; m.p.: 78.6–81.6 °C; purity: >99%; ¹H NMR (400 MHz, CDCl₃) δ: 8.62 (s, 1H), 8.38 (d, 1H, *J* = 4.8 Hz), 7.70 (d, 1H, *J* = 8.4 Hz), 7.40 (d, 2H, *J* = 7.2 Hz), 7.26 (t, 2H, *J* = 7.2 Hz), 7.12–7.20 (m, 2H), 7.05 (d, 1H, *J* = 16.4 Hz), 6.95 (d, 1H, *J* = 16.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 148.7, 148.6, 136.8, 133.0, 132.6, 131.0, 128.9, 128.3, 126.8, 125.0, 123.5; MS: 181 (M⁺).

4.5.7. *trans*-4-Nitrocinnamic acid butyl ester

Hexane; yellow plates; m.p.: 59.6–64.4 °C; purity: 97.3%; ¹H NMR (400 MHz, CDCl₃) δ: 8.24 (d, 2H, *J* = 8.8 Hz), 7.65–7.71 (m, 3H), 6.55 (d, 1H, *J* = 16 Hz), 4.23 (t, 2H, *J* = 6.8 Hz), 1.68 (quint, 2H, *J* = 7.6 Hz), 1.43 (sixet, 2H, *J* = 7.6 Hz), 0.96 (t, 3H, *J* = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 166.3, 148.7, 141.8, 140.8, 128.8, 124.4, 122.9, 65.1, 30.9, 19.4, 13.9; MS: 249 (M⁺), 194, 176, 130.

4.5.8. *trans*-4-Acetylcinnamic acid butyl ester

Hexane:ethyl acetate (gradient elution, 8:2 and 6:4); colorless, oily; 99.1%; ¹H NMR (400 MHz, CDCl₃) δ: 7.93 (d, 2H, *J* = 8.8 Hz), 7.64 (d, 1H, *J* = 16 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 6.47 (d, 1H, *J* = 16 Hz), 4.19 (t, 2H, *J* = 7.2 Hz), 2.57 (s, 3H), 1.70 (quint, 2H, *J* = 7.2 Hz), 1.42 (sixet, 2H, *J* = 7.2 Hz), 0.96 (t, 3H, *J* = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃) δ: 196.3, 166.2, 143.0, 139.0, 138.2, 129.0, 128.2, 121.1, 64.6, 31.0, 26.6, 19.4, 14.0; MS: 246 (M⁺), 231, 190, 175, 131, 115.

4.5.9. *trans*-3-(3-Pyridinyl)acrylic acid butyl ester

Hexane:ethyl acetate (2:1); oily; colorless; purity: 99.1%; ¹H NMR (400 MHz, CDCl₃) δ: 8.72 (s, 1H), 8.60 (m, 1H), 7.82 (d, 1H, *J* = 8.4 Hz), 7.64 (d, 1H, *J* = 16 Hz), 7.31 (m, 1H), 6.49 (d, 1H, *J* = 16.4 Hz), 4.2 (t, 2H, *J* = 6.6 Hz), 1.67 (quint, 2H, *J* = 7.2 Hz), 1.41 (sixet, 2H, *J* = 7.2 Hz), 0.94

(t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.6, 150.9, 149.7, 140.9, 134.6, 130.6, 124.0, 120.9, 64.9, 30.9, 21.2, 19.4, 13.9; MS: 205 (M^+), 190, 176, 150, 132, 121, 104, 77.

4.5.10. *trans*-4-Methyl-cinnamic acid butyl ester

Hexane:ethyl acetate (12:1); oily; colorless; purity: 97%; ^1H NMR (400 MHz, CDCl_3) δ : 7.66 (d, 1H, $J = 16$ Hz), 7.42 (d, 2H, $J = 8.4$ Hz), 7.19 (d, 2H, $J = 8.4$ Hz), 6.39 (d, 1H, $J = 16$ Hz), 4.20 (t, 2H, $J = 6.4$ Hz), 2.37 (s, 3H), 1.68 (quint, 2H, $J = 6$ Hz), 1.45 (sixet, 2H, $J = 7.2$ Hz), 0.97 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.5, 144.8, 140.8, 132.0, 129.8, 128.3, 117.5, 64.5, 31.0, 21.7, 19.4, 14.0; MS: 218 (M^+), 162, 145, 115, 91.

4.5.11. *trans*-Cinnamic acid butyl ester

Hexane:DCM (7:3); oily; colorless; purity: 98.7%; ^1H NMR (400 MHz, CDCl_3) δ : 7.69 (d, 1H, $J = 16$ Hz), 7.52 (m, 2H), 7.38 (m, 3H), 6.44 (d, 1H, $J = 16$ Hz), 4.22 (t, 2H, $J = 6.8$ Hz), 1.71 (quint, 2H, $J = 7.2$ Hz), 1.44 (sixet, 2H, $J = 7.2$ Hz), 0.97 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.3, 144.7, 134.8, 130.4, 129.1, 128.3, 118.6, 64.6, 31.0, 19.4, 13.5; MS: 204 (M^+) 148, 131, 103, 77.

4.5.12. *trans*-3-(2-Naphthyl)-propenoic acid butyl ester

Hexane:ethyl acetate (11:1); white plates; m.p.: 56.6–64 °C; purity: 98.8%; ^1H NMR (400 MHz, CDCl_3) δ : 7.93–7.49 (m, 8H), 6.56 (d, 1H, $J = 16$ Hz), 4.25 (t, 2H, $J = 6.6$), 1.71 (quint, 2H, $J = 7.2$ Hz), 1.44 (sixet, 2H, $J = 7.2$ Hz), 0.97 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.4, 144.8, 134.5, 133.6, 132.3, 130.0, 128.9, 128.8, 128.0, 127.4, 126.9, 123.8, 118.7, 64.7, 31.1, 19.5, 14.0; MS: 254 (M^+), 198, 181, 152.

4.5.13. *trans*-4-Cyanocinnamic acid butyl ester

Hexane:ethyl acetate (14:1); white plate; m.p.: 43.5–46.9; purity: >99% ^1H NMR (400 MHz, CDCl_3) δ : 7.67–7.58 (m, 5H), 6.51 (d, 1H, $J = 16$ Hz), 4.22 (t, 2H, $J = 6.6$ Hz), 1.68 (quint, 2H, $J = 7.2$ Hz), 1.43 (sixet, 2H, $J = 7.4$ Hz), 0.96 (t, 3H, $J = 7.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.4, 142.3, 139.0, 132.8, 128.6, 122.2, 118.5, 113.6, 65.0, 30.9, 19.4, 13.9; MS: 229 (M^+), 173, 156, 128.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.03.012](https://doi.org/10.1016/j.jorganchem.2006.03.012).

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