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# **Graphical Abstract**

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# Synthesis of surface-active *N*-heterocyclic carbene ligand and its Pd-catalyzed aqueous Mizoroki–Heck reaction

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# Synthesis of surface-active *N*-heterocyclic carbene ligand and its Pd-catalyzed aqueous Mizoroki–Heck reaction

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ABSTRACT

A surface-active *N*-heterocyclic carbene (NHC) ligand with an octaethylene glycol monomethyl ether and n-dodecyl chain was synthesized. The NHC and its Pd complex behaved as a general surfactant, and hydrophobic oily substrates such as iodobenzene and styrene were emulsified in water, resulting in the acceleration of the Mizoroki–Heck reaction under heterogeneous conditions. Our results demonstrated that the reactive emulsion interface rendered by the surface-active NHC is effective for the aqueous Mizoroki–Heck reaction.

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### 1. Introduction

The use of water as a green solvent in chemical reactions is of significance as it is the most abundant, nontoxic, and environmentally friendly solvent.<sup>1</sup> Several reactions conducted in water exhibit efficiency higher than those obtained for reactions conducted in common organic solvents.<sup>2</sup> Multicomponent reactions, such as the Diels-Alder reaction and the Claisen rearrangement of hydrophobic compounds, have been found to be accelerated in water as compared to common organic solvents.<sup>3</sup> They are presented that insoluble reactants are vigorously stirred in an aqueous suspension for increasing the interfacial area. For improving the solubility of reactants, typically, phase-transfer catalysts, polymers, crown ethers, and surfactants are added into aqueous or multiphase media.<sup>4-7</sup> Among these additives, surfactants are one of the useful candidates because they not only solubilize reactants but also emulsify them for providing an interface between water and the reactants, which plays a role in accelerating the rate of the reaction.8

Lipshutz et al. have reported that the addition of surfactants, such as sodium dodecyl sulfate (SDS), polyoxyethanyl  $\alpha$ -tocopheryl sebacate, and DL- $\alpha$ -tocopherol methoxypolyethylene glycol succinate, together with hydrophobic organometallic <u>catalysts</u> in water facilitates several types of reactions including

cross-coupling reactions.<sup>9</sup> The enhancement of the reaction rate using micelles under pseudo-homogeneous conditions is primarily attributed to the increase in the local concentration of the reactants on the surface as well as inside the micelles.<sup>10</sup>

Surfactants also form emulsions, which are immiscible colloidal suspensions under heterogeneous conditions. The same rate enhancement is also observed for emulsions because they also contain dispersed oil and continuous water phases with a large interfacial area. Kobayashi et al. have reported a Lewis-acid–surfactant-combined catalyst (LASC), which forms emulsion droplets in the presence of oily substrates in water.<sup>11</sup> They have observed that several carbon–carbon bond-forming reactions, such as Aldol, allylation, and Mannich-type reactions, proceed under emulsion conditions. Excellent catalyst combined with a surfactant at the interface of emulsions, resulting in the formation of a reactive emulsion interface.

*N*-Heterocyclic carbene (NHC) ligands have attracted significant interest as the most attractive ligand for transitionmetal-catalyzed reactions in water.<sup>12-15</sup> As compared to conventional phosphine ligands, which are typically sensitive to water and air, NHCs exhibit superior bonding robustness.<sup>16</sup> Since the first report of a water-soluble sulfonate-functionalized NHC ligand, a number of hydrophilic-functionalized NHC ligands

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have been reported, with focus on increasing their solubilities in water.<sup>17</sup> Although the approach is successful, the NHCs are not expected to form a reactive interface in water as they remain in the aqueous phase even with the use of the surfactant; hence such systems are not completely utilized the potential of them. To the best of our knowledge, no studies have been reported on surface-active NHC ligands, even though such ligands are expected to exhibit dual functions as both a surfactant and ligand, which are soluble in water and form emulsions. Surface-active NHC can be expected to facilitate aqueous cross-coupling reactions, because the reaction commonly requires a hydrophilic base together with hydrophobic substrates; surface-active NHC should play a role to smoothly contact the reactants on the emulsion interface.

In this study, a surface-active NHC ligand having an oligoethylene glycol monomethyl ether and n-dodecyl chain **1** was synthesized, and its surface properties such as surface tension, micellization, and emulsification were evaluated. **1** was demonstrated to form a stable oil-in-water (O/W) emulsion with oily substrates, resulting in the acceleration of the Mizoroki–Heck reaction under heterogeneous conditions.

#### 2. Results and Discussion

#### 2.1. Synthesis

Although typical NHCs contain aryl substituents such as IPr, IMes, SiPr, and SiMes, which impart electronic and steric properties, an NHC with less bulky substituents such as an oligoethylene glycol monomethyl ether and n-dodecyl chain as the hydrophilic and hydrophobic parts, respectively, was synthesized; its structure was similar to that of the commonly used nonionic surfactants: octaethylene glycol monododecyl ether (C12EO8). As the nonionic nature of oligoethylene glycol also positively affects catalytic performance in cross-coupling reactions,<sup>18</sup> favorable activity would be expected for such a less sterically hindered NHC. Scheme 1 shows the synthesis of asymmetric N,N'-substituted imidazolium salt 1 with hydrophilic and hydrophobic parts by subsequent reactions of imidazole. First, imidazole was treated with 1-bromododecane in the presence of NaOH, affording 1-dodecylimidazole in 86% yield. Second, equimolar amounts of 1-dodecylimidazole and Br(CH<sub>2</sub>CH<sub>2</sub>O)<sub>8</sub>CH<sub>3</sub> were mixed under neat conditions at 100 °C, affording 1 in 62% yield. An analogous NHC precursor 2 having methyl and n-dodecyl substituents was also synthesized by treating 1-methylimidazole with 1-bromododecane. The MALDI-TOF MS spectrum of 1 exhibited a peak of m/z 603.46, corresponding to the  $[M - Br]^+$  fragment. A characteristic 2-H



Scheme 1. i) 1.0 equiv. bromododecane and 50% NaOH aq., ii) 1.0 equiv. Br(CH<sub>2</sub>CH<sub>2</sub>O)<sub>8</sub>CH<sub>3</sub>, 100 °C, iii) 0.5 equiv. Pd(OAc)<sub>2</sub>.

resonance at  $\delta = 10.46$  ppm was observed in the <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub>. A resonance was also observed at  $\delta =$ 137.3 ppm in the  ${}^{13}C{}^{1}H$  NMR spectrum, corresponding to the NCN carbon atom; this result further confirms the formation of 1. 1 is soluble in both water and organic solvents such as DMSO, DMF, acetone, chloroform, and CH2Cl2, indicative of its amphiphilic nature. Next, the formation of its Pd complex was confirmed by treating 0.5 equiv. of  $Pd(OAc)_2$  with 1 in water or THF; a clear, pale yellow solution was obtained. In the  ${}^{13}C{}^{1}H{}$ NMR spectrum, a characteristic 2-C resonance at  $\delta = 168.6$  ppm was observed. The chemical shift is well consistent with those of typical NHC-Pd complexes, where the value of Pd-C signals range from ca. 158–185 ppm.<sup>19</sup> It should be noted that there are no signal corresponding to free carbene signal above 200 ppm, indicating that carbene does not dissociate from Pd. Two sets of peaks at 123.6 and 122.4 ppm, were observed, corresponding to cis/trans and/or syn/anti isomers. A peak of m/z 1503.51 was observed in the MALDI-TOF MS spectrum, corresponding to a  $[M + H]^+$  fragment (calcd: 1503.91); this result also supports the formation of [PdBr<sub>2</sub>(NHC)<sub>2</sub>] (1-Pd). Peaks were also observed a peak of m/z 1104.73 and 1992.77, attributed to Pd oligomers.<sup>2</sup> These results **imply** that **1**-Pd is formed as a mixture.

#### 2.2. Surface properties

The surface activities of the designed NHC 1 in water were confirmed by the Wilhelmy plate method (Fig. 1 and Table 1). In Fig. 1, the surface tension of water decreased with increasing concentration of 1 from 72.2 to 27.6 mN/m, indicating that 1 behaves as a surfactant in water. Typically, it is believed that



**Fig.1.** Relationship between surface tension and concentration of **1** (square) and **1**-Pd prepared *in situ* (circle) at  $25 \,^{\circ}$ C.

**Table 1.** Surface properties of **1** and **1**-Pd prepared *in* situ at 25  $^{\circ}$ C.<sup>a)</sup>

Compound	CMC (M)	$\gamma_{CMC}$ (mN/m)	Averaged diameter (nm) <sup>b)</sup>
1	$3.9 \times 10^{-3}$	27.6	$2.5\pm0.3$
1-Pd	$1.2\times10^{^{-3}}$	33.2	$31.9\pm10.8$

<sup>a</sup>The activity coefficient was fixed as 1. <sup>b</sup>Average diameter of micelles was determined by DLS measurements.

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Table 2. Interfacial tension of	water-iodobenzene and
water-styrene interfaces at 25	°C <sup>a),b)</sup>

surface-active compound	Iodobenzene	Styrene	Styrene	
	(mN/m)	(mN/m)		
none	34.6	33.4		
1	5.6	4.5		
<b>1</b> -Pd <sup>c)</sup>	13.1	11.8		

<sup>a</sup>[surface-active compound] = 30 mM. <sup>b</sup>ref. 20 <sup>c</sup>1-Pd was prepared *in situ* and measured as a mixture.

when such a surface-active compound is adsorbed at the airwater interface, the alkyl chain is directed out of water, whereas the hydrophilic part is directed in water. When the interface is completely occupied by 1, the excess molecules of 1 start to aggregate into micelles in water. Dynamic light scattering (DLS) measurements of aqueous solution of 1 (10 mM) confirm the formation of micelles with a hydrodynamic diameter of  $2.5 \pm 0.3$ nm. Fig. 1 plots the surface tension versus concentration; the critical micelle concentration (CMC) of 1 was determined from this plot. The CMC obtained from the intersection of the two fitted lines was  $3.9 \times 10^{-3}$  M.<sup>21</sup> The addition of 0.5 eq. of  $Pd(OAc)_2$  to 1 produced 1-Pd as a mixture, which also exhibits an ability to decrease surface tension. NHC-Pd catalysts are known to form several isomers;12 hence, we also studied the surface activities of the mixture of 1-Pd. The CMC of 1-Pd was determined to be  $1.2 \times 10^{-3}$  M. The micelle size of 1-Pd was greater than that of 1, suggesting that the complexation of Pd with 1 promotes the association of molecules in water. The CMC values of **1** and **1**-Pd were less than that of SDS (8.3 mM) but greater than that of cetyltrimethylammonium bromide (CTAB, 0.9 mM).<sup>20</sup> The CMC of 1-Pd was less than that of 1, attributed to the shielding of electropositive repulsion between imidazolium moieties. The  $\gamma_{CMC}$  (33.2 mN/m) of 1-Pd was greater than that of 1 as the introduction of Pd between the hydrophilic and hydrophobic parts of 1 led to the increase of steric bulk at the air-water interface. Indeed, the micelle size of 1-Pd was relatively greater (31.9  $\pm$  10.8 nm) than that of 1. The solubility of hydrophobic substrates within the micelle of 1 was confirmed by <sup>1</sup>H NMR measurements (Fig. S-9). Iodobenzene and styrene, as oily compounds, were chosen as model substrates in this study because they are miscible with each other and are substrates most typically used in the Mizoroki-Heck reaction. In the absence of 1, iodobenene and styrene exhibited partial solubility in D<sub>2</sub>O below 0.23 and 0.77 mM, respectively. Mixing of 1 above the CMC (30 mM) led to the solubilization of the hydrophobic substrates within the micelles, thereby increasing solubility to 5.42 and 7.04 mM, respectively.

The interfacial tension between water and each substrate used in the cross-coupling reaction was investigated. <u>Iodobenzene and</u> styrene, as oily compounds, were chosen as model substrates in this study because they are miscible with each other and are the most typical substrates used in the Mizoroki Heck reaction. Table 2 shows the values of interfacial tension at the interfaces of water–iodobenzene and water–styrene in the absence or presence of surface-active compounds. In the absence of the surface-active compound, the interfacial tension of iodobenzene exhibited a high value of 34.6 mN/m; hence, they are immisible.<sup>22</sup> exhibit the ability to decrease interfacial tension. Indeed, surfaceactive NHC **1** and its Pd complex mixture (**1**-Pd) formed emulsions from the mixture of iodobenzene, styrene, and water, where Pd centers can align between the oil and water phases to form a reactive interface.

#### 2.3. Aqueous Mizoroki–Heck reactions

Next, 1 was applied for the aqueous Mizoroki-Heck reactions (Table 3). First, as a typical protocol, the reaction in DMF afforded with quantitative conversion after 24 h and the product was isolated in 95% yield (entry 1). Hence, we fixed the concentration of 1 above the CMC (30 mM) in water; then, the amounts of  $Pd(OAc)_2$  and 1 were also fixed to be 3.0 mol% for the substrates. The aqueous cross-coupling reaction of iodobenzene and styrene was conducted via in situ generation of 1-Pd (as a mixture) in the presence of  $NEt_3$  (Table 3, entry 2). The solution formed an O/W emulsion, and with the vigorous stirring of the emulsion at 70 °C for 24 h, stilbene was obtained with quantitative conversion and the product was isolated in 96% yield. By decreasing the amount of water, the conversion at 3 h gradually decreased (89% for 0.6 mL, 60% for 0.2 mL, 58% for 0.006 mL, and 20% without water, respectively). These results clearly demonstrate that surface-active NHC 1 retains its activity under aqueous condition and facilitates the Mizoroki–Heck reaction. In contrast, a reaction using a similar less bulky NHC ligand 2 without the hydrophilic octaethylene glycol moiety afforded stilbene in only 15% (entry 4). On the other hand, the catalytic performance of **2** in DMF was relatively low (52%) entry 3), while the significant difference of conversion between the reaction in organic and aqueous solvent were observed. Other control experiments using common NHC ligands such as 1,3dimethylimidazolium iodide (IDM, entry 5) and 1,3-bis(2,6diisopropylphenyl)imidazolium chloride (IPr, entry 6) provided stilbene only 33 and 85% yield, respectively. These results indicate that a conventional NHC and its Pd catalyst are not suitable for aqueous reactions.

**Table 3.** Scope of Mizoroki-Heck reactions between iodobenzene and styrene<sup>a</sup>)

	+	ligand		
$\checkmark$		NEt <sub>3,</sub>	70 ºC, 24 h <sup>ℂ</sup>	
entry	ligand	solvent <sup>b)</sup>	Conv. (%) <sup>c)</sup>	Yield (%) <sup>d)</sup>
1	1	DMF	>99	95
2	1	water	>99	96
3	2	DMF	60	52
4	2	water	17	15
5	IDM <sup>e)</sup>	water	46	33
6	IPr <sup>f)</sup>	water	93	85

<sup>a</sup>iodobenzene (0.54 mmol), styrene (0.78 mmol), NEt<sub>3</sub> (0.69 mmol), Pd(OAc)<sub>2</sub> (0.018 mmol), ligand, or surfactant (0.018 mmol) were mixed in a solvent for 24 h at 70 °C. <sup>b</sup>the amount of solvents were set to be 1mL for DMF and 0.6 mL for water. <sup>c</sup>Conversions after 24 h. <sup>d</sup>Isolated yields. <sup>e</sup>1,3-dimethylimidazolium iodide. <sup>f</sup>1,3-bis(2,6 diisopropylphenyl)imidazolium chloride.

For evaluating the catalytic performance of 1, the reaction profile was also studied (Fig. 2). From the results obtained, undoubtedly, 1 is found to be the most active, with total conversion occurring within 5 h, while 2 affords stilbene in 17%. When a surface-active compound such as SDS was added to 2 for forming O/W emulsions similar to the case of 1, a moderate conversion of 40% was observed for the mixture. Lipshutz et al. have reported that mixing the NHC-Pd catalyst and surfactant facilitates the aqueous Mizoroki-Heck reactions.9 In the case of the reaction in DMF, 1 affords stilbene 53% after 5 h and required 24 h to consume iodobenzene quantitatively (Fig. S-10). These results suggest that the alignment of the Pd centers at the interface of emulsions with a large reaction area plays a significant role for the reaction. Fig. 3 shows the visual appearance during the reaction. An hour after the reaction began, the mixture separated into a suspended aqueous phase, and the oil phase with a solid precipitate of stilbene was obtained. Finally, residual oil was completely consumed, and the solid part was separated by simple filtration, affording stilbene as the pure product. Unfortunately, the Pd catalyst generated in situ resulted in the formation of a mixture of isomers as well as Pd black after treatment at 70 °C for 24 h; thus, it exhibits low recyclability. Further approaches for synthesizing a more stable surface-active NHC-Pd catalyst have been conducted, which can be recycled after the reaction.

Given that **1** can efficiently catalyze aqueous Mizoroki-Heck reaction of iodobenzene and styrene, it was then utilized to



**Fig.2.** Concentration versus time profile for the Mizoroki– Heck reaction: triangle; **2**, square; mixture of **2** and SDS, circle; **1**.



**Fig.3.** Visual observation of the Mizoroki–Heck reaction: (a) mixture of the aqueous solution of **1**, iodobenzene, and styrene (t = 0), (b) after the addition of Pd(OAc)<sub>2</sub> and NEt<sub>3</sub>, t = 1 h, (c) t = 24 h.



<sup>a</sup>Reactions carried out at 70 °C for 24 h using aryl halide (1 equiv), olefin (2 equiv), triethylamine (3 equiv), **1** (3 mol%, 30mM), and Pd(OAc)<sub>2</sub> (3 mol%), <sup>b</sup>Isolated yield. <sup>c</sup>No reaction. <sup>d</sup>NMR yield.

expand the catalytic scope towards various aryl halides and olefins (Table 4). A reaction of bromobenzene with styrene (entry 1) afforded stilbenes in low yield (35%) and that of chlorobenzene did not proceeded (entry 2), likely due to the nature of substituent on the aromatic ring (I > Br >> Cl). Under the optimized condition, both electron-rich (entry 3) and electron-poor (entry 4) aryl iodides reacted with styrene leading to good yield (77 and 87%, respectively). Reactions between acrylates and aryl iodides were also performed, where acrylates are less reactive coupling partners relative to styrene. The coupling reactions of methyl acrylate with aryl iodides (entries 5 and 6) also provided methyl cinnamates in 91 and 89%, respectively.

#### 3. Conclusions

In this study, surface-active NHC ligand 1 bearing an octaethylene glycol monomethyl ether and n-dodecane chain was synthesized for the first time. 1 behaved as a typical surfactant, demonstrating the ability to decrease surface tension as well as to form micelles in water. Interestingly, the CMC value decreased after complexation with  $Pd(OAc)_2$ . Furthermore, 1 and 1-Pd decreased the interfacial tension of water-iodobenzene and water-styrene, thus providing their stable O/W emulsions. The utility of the catalyst thus developed was demonstrated in the aqueous Mizoroki-Heck reaction, affording stilbene, which was separated by simple filtration, in a conversion of greater than 99%. We revealed that the scope of our methodology can be extended to various aryl halides and olefins. All these observations imply that 1, exhibiting dual functions as a ligand and surfactant, is crucial for facilitating aqueous Mizoroki-Heck reaction. The operationally simple process without addition of unnecessary additional surfactants allows the reactions to take place under environmentally attractive conditions. Furthermore, the functionalization of NHC with the aim of exhibiting surface

activities demonstrates potential applications for not only the Mizoroki–Heck reactions but also various organometallic reactions.

#### 4. Experimental

#### 4.1. General

All reagents purchased from commercial sources were used without further purification. Ultrapure water was obtained using a Millipore (Milli Q) apparatus. NMR spectra were recorded in CDCl<sub>3</sub> on an NMR Avance III 400MHz NMR spectrometer (Bruker BioSpin K.K.) using tetramethylsilane (TMS) as the reference. All spectra were recorded at 298 K and analyzed using software. Matrix-assisted the Topspin 3.1 laser desorption/ionization time-of-flight mass spectra (MALDI-TOFMS) were recorded on an Autoflex series MALDI-TOF (Bruker Daltonics, USA), where 2,5-dihydroxybenzoic acid and sinapic acid were used as the matrices. HRMS spectra were recorded on a JMS-S3000 Spiral TOF system (JEOL, Japan) using NaI as the calibration standard. Dynamic light scattering (DLS) measurements were performed on a DLS-7000 instrument (Otsuka Electronics Co., Japan) using a wavelength of 488 nm and an Ar laser of 75 mW as the light source at 25 °C. The timedependent correlation function of the scattered light intensity was measured at a scattering angle of 30°. In this study, particle size distributions were determined by the histogram method. The purification of products was performed by silica-gel column chromatography using Wako gel C-200 (75-150 µm, Wako Pure Chemical Industries Co., Japan). TLC was performed using silica-gel 70F254 plates (Wako Pure Chemical Industries Co., Japan) and were visualized using UV light (254 nm) and I<sub>2</sub>. 1-Dodecylimidazole and octaethylene glycol monomethyl ether bromide were synthesized according to a previously reported method.<sup>23</sup>

#### 4.2. Synthesis of surface-active N-heterocyclic ligand 1/

1-Dodecylimidazole (0.532 g, 2.25 mmol) and octaethylene glycol monomethyl ether bromide (1.00 g, 2.24 mmol) were added into a test tube and charged with a stir bar. The mixture was stirred at 100 °C for 2 days. The crude product was purified by silica-gel chromatography ( $R_f = 0.49$ , CHCl<sub>3</sub>/acetone/MeOH = 6/2/2) to afford **1** (0.930 g, 1.36 mmol, 61%). Pale yellow oil; R<sub>f</sub>  $(Et_2O/CH_2Cl_2= 3/7)$  0.43;  $\delta_H$  (400 MHz CDC1<sub>3</sub>): 10.46 (1H, s, imidazole), 7.81 (1H, s, imidazole), 7.21 (1H, s, imidazole), 4.69 (2H, t, J 4.0 Hz, NCH<sub>2</sub>), 4.26 (2H, t, J 8.0 Hz, NCH<sub>2</sub>), 3.94 (2H, t, J = 4.0 Hz, CH<sub>2</sub>), 3.74–3.52 (28H, m, CH<sub>2</sub>), 3.39 (3H, s, CH<sub>3</sub>), 1.90 (2H, t, J 8.0 Hz, CH<sub>2</sub>), 1.44–1.15 (18H, m, CH<sub>2</sub>), 0.87 (3H, t, J 8.0 Hz, CH<sub>3</sub>); δ<sub>C</sub> (100 MHz, CDCl<sub>3</sub>) 137.3, 123.9, 121.1, 71.8, 70.4, 70.3, (2CH<sub>2</sub>), 70.2, 69.1, 59.0, 50.0, 49.6, 31.9, 30.3, 29.6, 29.5, 29.4, 29.3, 29.0, 26.3, 22.6, 14.1; m/z (MALDI-TOFMS) 603.46 ( $[M-Br]^+$ ); HRMS (MALDI-TOF):  $[M - Br]^+$ , found 603.4560. C<sub>32</sub>H<sub>63</sub>N<sub>2</sub>O<sub>8</sub> calculated 603.4584.

#### 4.3. Preparation of NHC-Pd complex 2

A 25 mL Schlenk flask was charged with palladium acetate (22.5 mg, 0.100 mmol), **1** (136.8 mg, 0.200 mmol), 5 mL water or THF, and a stir bar. The mixture was stirred at 45 °C for 24 h. The volatiles were removed *in vacuo*, and **1**-Pd was obtained as a mixture of isomers. Brown oil;  $\delta_{\rm H}$  (400 MHz CDC1<sub>3</sub>) 7.78 (1H, s, imidazole), 7.65 (1H, s, imidazole), 7.22 (1H, s, imidazole), 7.05 (1H, s, imidazole), 7.04 (1H, s, imidazole), 4.62 (2H, m, CH<sub>2</sub>), 4.43 (2H, m, CH<sub>2</sub>), 4.26 (2H, m, CH<sub>2</sub>), 4.03 (2H, m, CH<sub>2</sub>), 3.89 (2H, m, CH<sub>2</sub>), 3.61–3.82 (52H, CH<sub>2</sub>), 3.57 (4H, t, *J* 8.0 Hz, CH<sub>2</sub>), 3.39 (6H, s, CH<sub>3</sub>), 1.19-1.48 (36H, CH<sub>2</sub>), 0.84–0.94 (3H, s, CH<sub>3</sub>);

 $δ_{\rm C}$  (100 MHz, CDCl<sub>3</sub>) 168.6, 137.4, 123.6, 122.4, 120.9, 120.3, 70.4, 70.3, 70.1, 69.2, 58.9, 50.9, 50.8, 49.9, 49.6, 31.8, 30.8, 30.7, 30.2, 29.6, 29.5 (2C), 29.3 (2C), 29.0, 26.4, 26.2, 22.6, 14.0; *m/z* (MALDI-TOFMS) 1503.51 (MH<sup>+</sup>).

#### 4.4. Surface tension measurements

The surface tension of the solutions of **1** and **1**-Pd was determined by the Wilhelmy plate method at 25 °C using a DY-500 surface tension meter (Kyowa Kaimen Kagaku Co., Japan); its accuracy was intermittently checked using ultrapure water. The Pt plate was cleaned by flaming, and glassware was rinsed using tap and ultrapure water.

#### 4.5. Interfacial tension measurements

The interfacial tension of water–oil substrates was determined by the pendant-drop method at 25 °C; these measurements were carried out using an automatic interfacial tensiometer (DM500; Kyowa Interface Science, Japan) and drop shape analysis software (FAMAS ver. 2.01.19). Water-dissolved **1** or **1**-Pd was used as the drop phase, and the drop was formed at the tip of the syringe by forcing the solution out by using a set screw. For interfacial tension measurements of water–iodobenzene, a reverse needle was used because of the high density of the oil. Drop shape analysis was performed as follows: first, a drop profile was extracted from the drop image; second, a curve-fitting program was used to compare the experimental drop profile with the theoretical profile; finally, the corresponding interfacial tension value was obtained.<sup>24</sup>

#### 4.6. Light scattering measurements

The sizes of 1 and 1-Pd assemblies were evaluated by dynamic light scattering (DLS). A DLS-7000 (Otsuka Electronics CO., Japan) instrument was employed using a He-Ne laser (wavelength: 633 nm) at scattering angles of 30 and 90°. The aqueous solution was passed through a polyvinylidene difluoride (PVDF) membrane filter (0.45  $\mu$ m) three times. DLS intensity data were processed using the instrument software for obtaining the hydrodynamic diameter, polydispersity index, and mass diffusion coefficient (D) of the samples. D was derived from the decay time  $(\tau_c)$  of the intensity correlation function as D = $(2k_L^2 \tau_c)^{-1}$ , where  $k_L$  is the scattering wave vector. The hydrodynamic mass-diffusion coefficient  $D_0$  was obtained as the limit of D as  $k_L$  tended to zero.  $D_0$  was observed to obey the Stokes–Einstein relation,  $D_0 = kT/6\pi\eta R_H$ , where k is the Boltzmann constant, T is the absolute temperature,  $\eta$  is the viscosity of the solvent, and  $R_H$  is the hydrodynamic radius.<sup>2</sup>

# 4.7. General procedure for the aqueous Mizoroki–Heck reaction

NHC ligand (0.018 mmol), aryl halide (0.54 mmol), and olefin (0.78 mmol) were added to a test tube equipped with a stir bar and capped with a silicone septum.  $600 \ \mu\text{L}$  of water was then added and vortexed for several seconds. Pd(OAc)<sub>2</sub> (4.0 mg, 0.018 mmol) and triethylamine (95  $\mu$ L, 0.69 mmol) were added, and the mixture was vigorously stirred (1200 rpm) at 70 °C. Conversion was monitored by <sup>1</sup>H-NMR spectroscopy based on the signal intensities. After completion of the reaction, the mixture was cooled to room temperature and filtered, and the remaining solid was washed with ethyl acetate. After washing the ethyl acetate with brain, the organic phase was extracted and dried over MgSO<sub>4</sub>. The organic solvent was evaporated to obtain the crude product. For further purification it was purified through column chromatography (hexane/ethyl acetate).

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