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Synthesis of 2-Substituted Cyclohexene Derivatives through Cross-Coupling Reactions via π -Allylmetal Intermediate Using N-Heterocyclic Carbenes (NHCs) as Ligands

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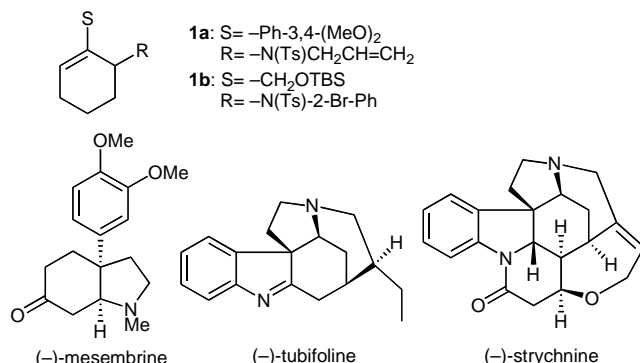
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Abstract: a Pd- or a Ni-catalyzed cross-coupling of 2-substituted cyclohexenes, which are generally less reactive than those having no substituent at the C-2 position, with organotin reagents (Migita-Kosugi-Stille coupling) or with Grignard reagents (Kumada-Tamao-Corriu coupling) using NHC as a ligand was investigated. It was found that NHCs are effective as ligands for these reactions, giving the corresponding cross-coupling products in good yields.

Key Words: N-heterocyclic carbene (NHC), cross-coupling, Migita-Kosugi-Stille reaction, Kumada-Tamao-Corriu reaction, palladium, nickel

Cyclohexene derivatives **1**, having a substituent at the C-2 position on the alkene, are useful synthetic intermediates for various natural products.¹ We have already reported syntheses of natural products from cyclohexene derivatives, including the synthesis of (–)-mesembrine from **1a**^{1a} and the syntheses of (–)-tubifoline^{1d,f} and (–)-strychnine^{1e,f} from **1b**, respectively (Scheme 1).

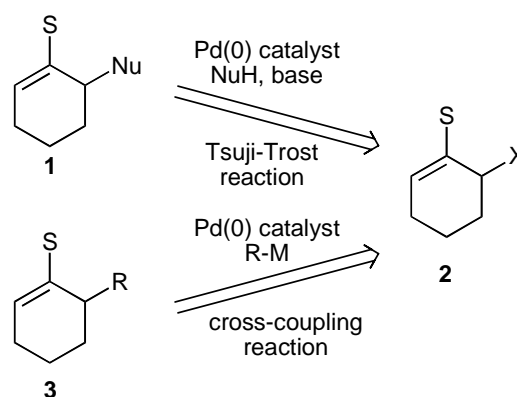
Scheme 1. Synthetic Utility of 2-Substituted Cyclohexenes



In the previous syntheses, the desired 2-substituted cyclohexene derivatives **1a** and **1b** were synthesized via a Pd-catalyzed Tsuji-Trost reaction of allylic substrate **2** and nucleophiles in the presence of a base (Scheme 2).²

The versatility of 2-substituted cyclohexenes as a useful synthon prompted us to develop an alternative route to synthesize such compounds **3** via a cross-coupling reaction of **2** and organometallic reagent (R-M). Cross-coupling reactions are widely used to form carbon-carbon bonds in the field of synthetic organic chemistry.³ Recently, N-heterocyclic carbenes (NHCs) have been found to be very effective as ligands for various cross-coupling reactions.⁴ Thus, we decided to investigate the utility of NHCs for cross-coupling reaction between 2-substituted allylic substrate **2** and organometallic reagents.

Scheme 2. Synthetic Route for 2-Substituted Cyclohexenes



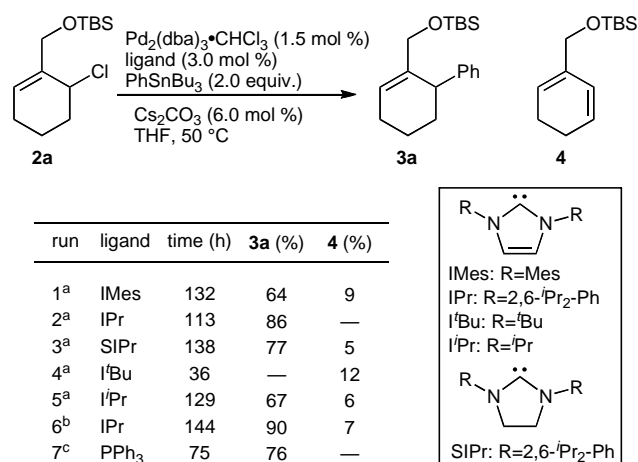
Although there have been a number of studies on transition metal-catalyzed cross-coupling reaction using NHC ligands between an sp^2 carbon center in the substrate (e.g., aryl halide, vinyl halide) and various organometallic reagents, examples of the reaction between allylic substrates and organometallic reagents are limited. In addition, our previous studies on Pd-catalyzed Tsuji-Trost reaction of 2-substituted allylic substrates **2** revealed that the reactivity of **2** is relatively low due to the bulkiness of the C-2 substituent, compared to those having no substituent at C-2 position. Thus, we herein report a Pd-catalyzed cross-coupling of **2** with organotin reagent (Migita-Kosugi-Stille coupling)⁵ and a Ni-catalyzed cross-coupling of **2** with Grignard reagent (Kumada-Tamao-Corriu coupling)⁶ using NHC as a ligand.

Migita-Kosugi-Stille Coupling Reaction of 2-Substituted Cyclohexene with Organotin Reagents Catalyzed by Pd-NHC Complexes

Initially, we investigated the cross-coupling reaction of 2-substituted cyclohexene derivative **2a** with PhSnBu₃ using various Pd-NHC complexes generated in situ from Pd₂dba₃•CHCl₃ (1.5 mol %) and various imidazolium salts as precursors of NHC in the presence of Cs₂CO₃ (Table 1). A THF solution of Pd₂(dba)₃•CHCl₃ (1.5 mol %), PPh₃ (3.0 mol %), and IMes•HCl (3.0 mol %) was stirred at 50 °C for 10 min. To this Pd(PPh₃)(NHC) catalyst solution were added a THF solution of **2a** and PhSnBu₃, and the mixture was stirred at 50 °C for 132 hours. After the usual work-up, the desired coupling product **3a** was obtained in 64% yield along with β -eliminated product **4** in 9% yield (run 1). The use of IPr and the use of SIPr under similar conditions improved

the yields of **3a** to 86% and to 77%, respectively (runs 2 and 3). NHCs having an alkyl substituent on nitrogen in the imidazole ring such as *t*Bu or *i*Pr were less effective for the coupling reaction (runs 4 and 5). Cross-coupling reaction using a Pd-IPr catalyst prepared from Pd₂(dba)₃•CHCl₃ (1.5 mol %), IPr•HCl (3.0 mol %), and Cs₂CO₃ in the absence of PPh₃ gave the best result, providing **3a** in 90% yield (run 6). On the other hand, the reaction of **2a** with PhSnBu₃ using PPh₃ instead of NHCs gave **3a** in 76% yield (run 7), indicating that the NHC ligand is superior to a phosphorous ligand in this reaction system.

Table 1. Cross-Coupling Reaction of **2a** with PhSnBu₃



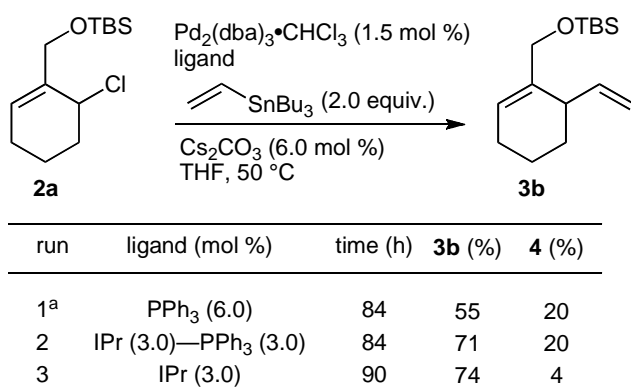
^a Reactions were carried out using Pd(PPh₃)(NHC) complex generated in situ from Pd₂(dba)₃•CHCl₃ (1.5 mol %), imidazolium salts (3.0 mol %), and PPh₃ (3.0 mol %) in the presence of Cs₂CO₃ (6.0 mol %) in THF at 50 °C for 10 min.

^b Pd-IPr complex generated in situ from Pd₂(dba)₃•CHCl₃ (1.5 mol %) and IPr•HCl (3.0 mol %), and Cs₂CO₃ (6.0 mol %) was used.

^c In the absence of Cs₂CO₃.

Next, the reactions of **2a** with vinyl stannane were investigated, and the results are shown in Table 2. The reaction of **2a** with (CH₂=CH)SnBu₃ using PPh₃ gave the desired product **3b** in 55% yield along with β-eliminated product **4** in 20% yield (run 1). In this reaction system, the use of NHCs gave superior results. Thus, the reaction using a mixed ligand complex, Pd(PPh₃)(NHC), formed from Pd₂(dba)₃•CHCl₃ (1.5 mol %), PPh₃ (3.0 mol %), and IMes•HCl (3.0 mol %) in the presence of Cs₂CO₃, produced **3b** in 71% yield.

Table 2. Cross-Coupling Reaction of **2a** with Vinyl Stannane

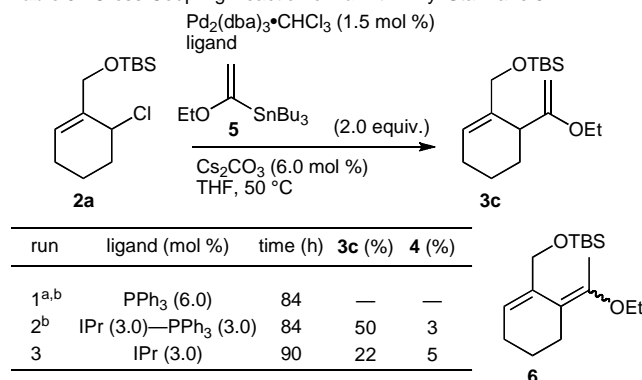


^a Reactions were carried out in the absence of Cs₂CO₃.

In the reaction of **2a** with vinyl stannane using a Pd-IPr catalyst prepared from Pd₂(dba)₃•CHCl₃, IPr•HCl, and Cs₂CO₃ in the absence of PPh₃, the yield of **3b** was improved to 74%.

The reaction of **2a** with a functionalized vinyl stannane **5** would provide the coupling product **3c**, which could be converted into methyl ketone derivatives and should be a useful synthon. In the reaction of **2a** with **5** using PPh₃ as a ligand, however, the desired product **3c** was not obtained, only isomerized product **6** being obtained in 25% yield. On the other hand, the reaction using a mixed ligand complex, Pd(PPh₃)(NHC), gave the desired product **3c** in 50% yield along with β-eliminated product **4** (3%) and **6** (8%). The use of Pd-IPr was less effective in this reaction system, giving **3c** in 22% yield. Although the yield of **3c** was still modest, these results suggest the superiority of NHCs to a phosphorous ligand in Migita-Kosugi-Stille coupling reaction of 2-substituted cyclohexenes.

Table 3. Cross-Coupling Reaction of **2a** with Vinyl Stannane **5**



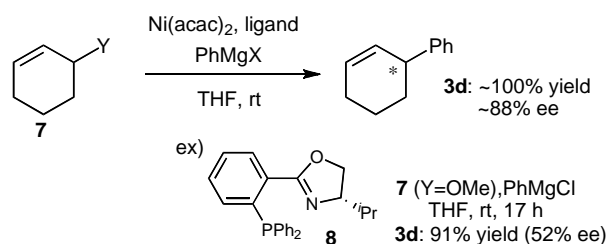
^a Reactions were carried out in the absence of Cs₂CO₃.

^b By-product **6** was also obtained in 25% (run 1) or 8% (run 2).

Kumada-Tamao-Corriu Coupling Reaction of 2-Substituted Cyclohexene with Grignard Reagent Catalyzed by Ni-NHC Complexes

Next, we turned our attention to the synthesis of 2-substituted cyclohexenes through a Ni-catalyzed Kumada-Tamao-Corriu coupling reaction. Recently, Uemura and co-workers have reported an asymmetric Kumada-Tamao-Corriu coupling reaction of simple cyclohexene derivatives **7** with Grignard reagents using Ni complexes (Scheme 3).⁷

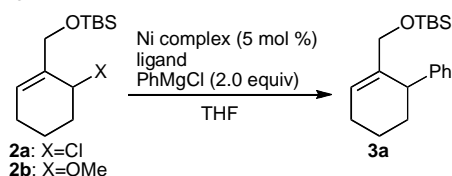
Scheme 3. Asymmetric Kumada-Tamao-Corriu Coupling Reaction of Non-Substituted Cyclohexene Derivatives Reported by Uemura



In their study, the yield and enantiomeric excess of **3d** varied up to 100% yield and 88% ee, depending on the

reaction conditions and the properties of ligands. For instance, the reaction of **7** (Y=OMe) with PhMgCl using Ni(acac)₂ (5 mol %) and chiral ligand **8** gave the product **3d** in 91% yield and 52% ee. However, the reaction of the corresponding 2-substituted cyclohexene derivative **2b** with PhMgCl under the same conditions did not give the coupling product **3a** at all, indicating a low reactivity of 2-substituted cyclohexene substrate toward this cross-coupling reaction (Table 4, run 1).

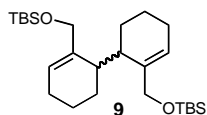
Table 4. Ni-Catalyzed Cross-Coupling of 2-Substituted Cyclohexenes **2** with PhMgCl



run	substrate	catalyst, ligand (mol %)	conditions	3a (%)	9 (%)
1 ^a	2b	Ni(acac) ₂ , 8 (10)	rt, 17 h	—	—
2 ^a	2b	Ni(acac) ₂ , PPh ₃ (20)	rt, 17 h	—	—
3 ^{a,b}	2b	Ni(cod) ₂ , IPr (5)-PPh ₃ (5)	rt, 48 h	—	—
4	2a	Ni(cod) ₂ , PPh ₃ (10)	rt, 2 h	38	35
5 ^b	2a	Ni(cod) ₂ , IPr (5)-PPh ₃ (5)	rt, 2 h	48	37
6 ^b	2a	Ni(cod) ₂ , IPr (5)	rt, 1.5 h	82	4

^a The starting material **2b** was recovered in 84% (run 1), 82% (run 2), or 87% (run 3).

^b The reaction was carried out in the presence of Cs₂CO₃ (6 mol %).



Thus, combinations of catalyst and ligand were screened in the reaction of **2a** or **2b** with PhMgCl, and the results are summarized in Table 4. The reaction of **2b** with PhMgCl in the presence of Ni(acac)₂ (5 mol %) and PPh₃ (20 mol %) also gave no desired product **3a** (run 2). The use of a mixed ligand complex, Ni(IPr)(PPh₃), which was generated in situ from Ni(cod)₂ (5 mol %), IPr·HCl (5 mol %), and PPh₃ (5 mol %) in the presence of Cs₂CO₃ (6.0 mol %), was not effective in this reaction (run 3). On the other hand, the substrate **2a** was found to be more reactive toward this reaction than **2b**, and the reaction of **2a** with PhMgCl in the presence of Ni(cod)₂ (5 mol %) and PPh₃ (20 mol %) gave the desired product **3a** in 38% yield along with the dimer **9** in 35% yield (run 4). The use of a mixed ligand complex slightly improved the yield of **3a** to 48%, but a significant amount of the dimer **9** was also obtained (run 5). On the other hand, the use of Ni-IPr complex, generated in situ from Ni(cod)₂ (5 mol %) and IPr·HCl (5 mol %) in the presence of Cs₂CO₃ (6 mol %), gave the best result, giving **3a** in 82% yield and also suppressing the formation of **9** (run 6).

In summary, a Pd- or Ni-catalyzed cross-coupling of 2-substituted cyclohexene derivatives **2** with organotin reagent (Migita-Kosugi-Stille coupling) or with Grignard reagent (Kumada-Tamao-Corriu coupling) was investigated using NHC as a ligand. Although 2-substituted cyclohexenes **2** are generally less reactive as substrates toward these types of cross-coupling reactions due to the bulkiness of the C2-substituent, compared to those having no substituent at the C2 position, it was

found that NHCs are effective as ligands for these reactions and can suppress the formation of by-products such as a β-eliminated product for Migita-Kosugi-Stille coupling and a dimeric product for Kumada-Tamao-Corriu coupling.

All manipulations were performed under an argon atmosphere. THF was purified using Glass Contour Solvent Purification System, and all other solvents and reagents were purified when necessary by standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh), and flash chromatography on silica gel (Meck, 230-400 mesh) with the indicated solvent as eluent. IR spectra were obtained on a Jasco FT/IR-460 plus, and ¹H NMR and ¹³C NMR spectroscopy were carried out on a Jeol EX270 or a Jeol AL400 NMR spectrometer. Mass spectra were obtained on a Jeol JMS-700TZ for LRMS (EI) and HRMS (EI), and a Shimadzu GCMS-QP5050A for LCMS (EI).

1-*tert*-Butyldimethylsilyloxymethyl-6-chloro-1-cyclohexene (**2a**)

To a solution of 2-(*tert*-butyldimethylsilyloxymethyl)-cyclohex-2-enol^{1d} (410 mg, 1.7 mmol) in CH₂Cl₂ (3.5 mL) were added ¹Pr₂NEt (0.4 mL, 2.5 mmol) and methanesulfonyl chloride (0.2 mL, 2.5 mmol), and the mixture was stirred at 0 °C for 2 hours then at room temperature for 3 hours. To the mixture was added sat. NH₄Cl aqueous solution at 0 °C, and the solution was extracted with CH₂Cl₂. The combined organic layer was washed with sat. NaCl aqueous solution, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane-EtOAc, 19/1) to give **2a** (400 mg, 90%) as a colorless oil.

IR (neat) 2953, 1742, 838, 777 cm⁻¹.

¹H NMR (270 MHz, CDCl₃) δ=5.85 (m, 1 H), 4.68 (m, 1 H), 4.22-4.29 (m, 1 H), 4.05-4.12 (m, 1 H), 1.54-2.19 (m, 6 H), 0.92 (s, 9 H), 0.09 (s, 3 H), 0.08 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ=136.8, 127.1, 64.7, 55.2, 32.3, 26.1, 24.9, 18.6, 17.4, -5.0; LRMS (EI) *m/z* 259 [M-1]⁺, 225 [M-Cl]⁺, 203 [M-Bu]⁺; HRMS (EI) Calcd for C₉H₁₆ClOSi [M-Bu]⁺: 203.0659; Found: 203.0649.

1-*tert*-Butyldimethylsilyloxymethyl-6-methoxy-1-cyclohexene (**2b**)

To a suspension of NaH (60% dispersion in mineral oil, 160 mg, 4.0 mmol) in THF (2.5 mL) were successively added a solution of 2-(*tert*-butyldimethylsilyloxymethyl)-cyclohex-2-enol (485 mg, 2.0 mmol) in THF (2.5 mL) and methyl iodide (1.3 mL, 20 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 hours. To the mixture was added sat. NH₄Cl aqueous solution, and the solution was extracted with Et₂O. The combined organic layer was washed with sat. NaCl aqueous solution, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane-Et₂O, 40/1) to give **2b** (497 mg, 97%) as a colorless oil.

¹H NMR (270 MHz, CDCl₃) δ=5.83 (m, 1 H), 4.21-4.27 (m, 1 H), 4.03-4.09 (m, 1 H), 3.76 (m, 1 H), 3.35 (s, 3 H), 1.54-2.19 (m, 6 H), 0.91 (s, 9 H), 0.08 (s, 3 H), 0.07 (s, 3 H).

Typical Procedure for Migita-Kosugi-Stille Coupling of **2a** with PhSnBu₃ using Pd-IPr catalyst (Table 1, run 6)

A solution of Pd₂(dba)₃·CHCl₃ (4.8 mg, 0.0047 mmol), IPr·HCl (3.9 mg, 0.0094 mmol), and Cs₂CO₃ (6.0 mg, 0.019 mmol) in

degassed THF (3 mL) was stirred at 50 °C for 10 min to generate in situ Pd-IPr complex. To the catalyst solution were added a solution of **2a** (81 mg, 0.31 mmol) in THF (3 mL) and PhSnBu₃ (0.2 mL, 0.62 mmol), and the mixture was stirred at 50 °C for 144 hours. The mixture was filtered through a pad of Celite, and the filtrate was concentrated. The residue was purified by column chromatography on KF/SiO₂⁸ (hexane) to give **3a** (85 mg, 90%) as a colorless oil.

IR (neat) 3060, 2929, 1601 cm⁻¹

¹H NMR (270 MHz, CDCl₃) δ=7.15-7.27 (m, 5 H), 5.97 (m, 1 H), 3.86 (m, 2 H), 3.44 (m, 1 H), 1.45-2.14 (m, 6 H), 0.84 (s, 9 H), -0.07 (s, 3 H), -0.08 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ=145.7, 138.6, 129.2, 128.8, 126.6, 124.8, 66.5, 41.7, 32.9, 26.5, 25.6, 19.2, 19.0, -4.9.

LRMS (EI) *m/z* 302 [M]⁺, 287 [M-Me]⁺, 245 [M-^tBu]⁺.

HRMS (EI) Calcd for C₁₉H₃₀OSi: 302.2066; Found: 302.2054.

1-*tert*-Butyldimethylsilyloxymethyl-6-vinyl-1-cyclohexene (**3b**)

IR (neat) 2930, 1634, 913, 836 cm⁻¹.

¹H NMR (270 MHz, CDCl₃) δ=5.69-5.82 (m, 2 H), 5.02 (broad s, 1 H), 4.96 (m, 1 H), 3.99 (m, 2 H), 2.78 (m, 1 H), 2.03 (m, 2 H), 1.53-1.76 (m, 4 H), 0.90 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ=141.0, 137.4, 122.6, 114.6, 65.6, 39.4, 29.1, 26.2, 25.2, 19.1, 18.6, -4.9.

LRMS (EI) *m/z* 252 [M]⁺, 237, 219, 195, 75.

HRMS (EI) Calcd for C₁₅H₂₈OSi: 252.1909; Found: 252.1897.

1-*tert*-Butyldimethylsilyloxymethyl-6-(1-ethoxyvinyl)-1-cyclohexene (**3c**)

IR (neat) 2931, 1649, 1068 cm⁻¹.

¹H NMR (270 MHz, CDCl₃) δ=5.82 (m, 1 H), 4.05 (m, 2 H), 3.93 (d, *J* = 1.6 Hz, 1 H), 3.80 (d, *J* = 1.6 Hz, 1 H), 3.69 (m, 2 H), 2.82 (m, 1 H), 1.47-2.04 (m, 6 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 0.90 (s, 9 H), 0.04 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃) δ=163.9, 136.4, 123.7, 82.2, 65.7, 62.7, 40.6, 27.4, 26.2, 25.0, 18.9, 18.7, 14.7, -5.08.

LRMS (EI) *m/z* 296 [M]⁺, 267, 239, 75.

HRMS (EI) Calcd for C₁₇H₃₂O₂Si: 296.2172; Found: 296.2174.

Typical Procedure for Kumada-Tamao-Corriu Coupling of **2a** with PhMgCl using Ni-IPr catalyst (Table 4, run 6)

A solution of Ni(cod)₂ (4.3 mg, 0.016 mmol), IPr•HCl (6.7 mg, 0.016 mmol), and Cs₂CO₃ (11.0 mg, 0.032 mmol) in degassed THF (3 mL) was stirred at room temperature for 1 hour to generate in situ Ni-IPr complex. To the catalyst solution were added a solution of **2a** (81 mg, 0.31 mmol) in THF (3 mL) and PhMgCl (1.7 M THF solution, 0.36 mL, 0.62 mmol), and the mixture was stirred at room temperature for 1.5 hours. To the mixture was added sat. NH₄Cl aqueous solution at 0 °C, and the solution was extracted with EtOAc. The combined organic layer was washed with sat. NaCl aqueous solution, and dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane) to give **3a** (77 mg, 82%) as a colorless oil along with the dimer **9** (2.6 mg, 4%).

2,2'-bis(*tert*-butyldimethylsilyloxy)methyl-1,1'-bi(cyclohex-2-ene) (**9**)

¹H NMR (270 MHz, CDCl₃) δ=5.78-5.84 (m, 2 H), 4.04-4.14 (m, 4 H), 2.46-2.53 (m, 2 H), 1.23-1.78 (m, 12 H), 0.91 (s, 9 H), 0.89 (m, 9 H), 0.03 (s, 6 H), 0.01 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃) δ=139.8, 138.1, 123.9, 122.9, 65.7, 38.3, 36.1, 27.7, 26.2, 25.4, 25.3, 24.2, 22.5, 22.2, 18.6, -4.99.

LRMS (EI) *m/z* 450 [M]⁺, 393 [M-^tBu]⁺, 318 [M-OTBDMS]⁺.

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