Supporting Information For

Regio- and stereoselective multisubstituted olefin synthesis via hydro/carboalumination of alkynes and subsequent iron-catalysed cross-coupling reaction with alkyl halides

Shintaro Kawamura, Ryosuke Agata, and Masaharu Nakamura*

Department of Hydrocarbon Chemistry, Graduate School of Engineering and International Research Center for Elements Science, Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in dry reaction vessels under a positive pressure of argon gas. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a PFA tube. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). The TLC plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of p-anisaldehyde, followed by heating on a hot plate. The organic solutions were concentrated using rotary evaporation at ca. 30 mmHg. Flash column chromatography was performed on SilliCycle SiliaFlash Irregular Silica Gels F60 Silica (spherical, 40–63 μm), Merck silica gel 60 (spherical, 140–325 mesh), and Wakogel® 60N (fractured, 38–100 μm) as described by Still et al.1

Instrumentation. The proton nuclear magnetic resonance (1H NMR) and carbon NMR (13C NMR), were recorded on a JEOL ECS-400NR (392 MHz) NMR spectrometer. The proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the residual proton signal of CHCl3 (δ 7.26). The 13C NMR spectra were recorded at 98.5 MHz. The chemical shifts of the carbon atoms are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the carbon resonance of CDCl3 (δ 77.16). The data are presented as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, and br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (in italics). High-resolution mass spectra (HRMS) were obtained in fast atom bombardment (FAB) ionization or electron ionization (EI) mode on a JEOL JMS-700 mass spectrometer. IR spectra were

recorded on a PerkinElmer Spectrum One FT-IR Spectrometer, and characteristic IR absorptions are reported in cm\(^{-1}\).

**Solvent.** The anhydrous tetrahydrofuran (THF) and 1,2-dichloroethane used were purchased from the Wako Chemical Co. and distilled from benzophenone ketyl and P\(_2\)O\(_5\) respectively under argon (at atmospheric pressure) immediately before use. Water contents of the solvents were determined using a Karl-Fischer moisture titrator (MCU-610 or MKC-610, Kyoto Electronics Company) and found to be < 15 ppm.

**Materials.** The chemical reagents used were purchased from Wako Pure Chemical Industries, Ltd (Wako), Tokyo Chemical Industry Co. Ltd, Aldrich Inc., and other commercial suppliers. Florisil\textsuperscript{®} (100–200 mesh) was purchased from Nacalai Tesque Inc. FeCl\(_2\)-SciOPP complexes were synthesized according to the literature,\(^2\) and dissolved in THF at 0 °C prior to use. Diisobutylaluminum hydride (neat) was supplied from Tosoh Finechem Corporation, and dissolved in hexane at 0 °C prior to use.

**GC analysis.** The yield (using undecane as an internal standard) was determined for the crude product using GLC analysis on a Shimadzu GC-2010 Plus analyser equipped with an FID detector and a capillary column, ZB-1MS (10 m \(\times\) 0.1 mm i.d., film thickness = 0.1 \(\mu\)m).

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Additional Data of the effect of KF in the cross coupling reaction (supplement to Scheme 3)

Effect of KF on the product yield in the reactions with various alkenylaluminium reagents

Table S1. The reaction of various alkenyl aluminum reagents

<table>
<thead>
<tr>
<th>entry</th>
<th>organoaluminium reagent</th>
<th>coupling product</th>
<th>product yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>with KF&lt;sup&gt;b,c&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>i-But&lt;sub&gt;2&lt;/sub&gt;Al-H, Hex</td>
<td>4ab</td>
<td>91 (99% E)</td>
</tr>
<tr>
<td>2</td>
<td>i-But&lt;sub&gt;2&lt;/sub&gt;Al-H, Et</td>
<td>4bb</td>
<td>86 (E/Z = 97:3)</td>
</tr>
<tr>
<td>3</td>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;Al-Me, Hex</td>
<td>4cb</td>
<td>86 (99% E)</td>
</tr>
<tr>
<td>4</td>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;Al-Me, Et</td>
<td>4db</td>
<td>19 (E/Z = 70:30)</td>
</tr>
</tbody>
</table>

<sup>a</sup>See the experimental section in this SI for details of the reaction conditions for each entries.<br><sup>b</sup>Isolated yield.<br><sup>c</sup>The ratio of stereoisomers was determined by GLC analysis. The yields were determined by <sup>1</sup>H NMR analysis, using 1,1,2,2-tetrachloroethane as an internal standard.

Effect of the amount of KF on the product yield and selectivity

The effect of the amount of KF on the reaction of 1-bromodecane 3a with alkenyl aluminum reagent 1a was examined (Table S2). While 3 equivalents of KF to the alkenyl aluminium gave the virtually same result with the reaction of 1.5 equivalents of KF (entry 1), a catalytic amount (20 mol%) of KF led to a decrease in the conversion (20% yield) as well as the lower product selectivity (entry 3). Addition of 18-crown-6 to increase the solubility of KF in THF but did not improve the yield and the product selectivity.

Table S2. Effect of the amount of KF in the reaction

<table>
<thead>
<tr>
<th>entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>additive</th>
<th>4aa (E/Z)</th>
<th>GC yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>1-decane (%)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>RSM&lt;sup&gt;a&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KF (3.0 equiv)</td>
<td>78 (99% E)</td>
<td>10</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>KF (1.5 equiv)</td>
<td>76 (99% E)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>KF (20 mol %)</td>
<td>20 (99% E)</td>
<td>10</td>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>KF (1.5 equiv) + 18-crown-6 (1.5 equiv)</td>
<td>30 (99% E)</td>
<td>26</td>
<td>16</td>
<td>22</td>
</tr>
</tbody>
</table>

<sup>a</sup>For reaction conditions, see Table 1.<br><sup>b</sup>Yields and stereoisomeric ratio were determined by GLC analysis, using undecane as an internal standard.<br><sup>c</sup>Recovery of starting material 3a.<br><sup>d</sup>Isolated yield.
**Reaction with iron fluoride**

The combination of an iron fluoride (Na$_2$Fe$_2$F$_6$) and TMS-SciOPP was used as a precatalyst instead of FeCl$_2$(TMS-SciOPP) to study the catalytic competency of ferrate species, which is supposed to form in the presence of excess fluoride anion source (Scheme S1). The ferrate precatalyst was found ineffective and no cross-coupling product was obtained under the similar conditions of the reaction with FeCl$_2$(TMS-SciOPP), suggesting that the presence of excess fluoride anion may impair the reactivity of iron catalyst through the formation of ferrate species.

**Scheme S1.** Iron-catalyzed cross coupling of alkenyl aluminum reagents prepared by zirconium-mediated carbometalation in the presence of iron fluoride

![Scheme S1 diagram]

**Effect of KF in the Negishi coupling of alkenyl aluminium reagents**

The effect of KF in the conventional palladium-catalyzed Negishi coupling of alkenyl aluminum 1b with 4-tolyl iodide 3k was examined (Scheme S2). The typical Negishi coupling, where alkenyl aluminium is converted to the corresponding zinc reagent by transmetallation, proceeded readily at room temperature in the presence of a catalytic amount of Pd(PPh$_3$)$_4$ to afford the desired coupling product 4bk in high yield. Addition of KF, instead of ZnCl$_2$, resulted in substantial decrease of the catalytic activity as the reaction proceeded at higher temperature (60 °C) along with the formation of side product 7. The cross coupling reaction without any additive also proceeded at 60 °C to give the alkenylation product in 18% yield. These results suggest that KF enhances the transmetalation by forming higher reactive alkenylaluminium species but causes non-selective transfer of organic ligands on the organoaluminum reagent (e.g., alkyl vs. alkenyl) to decrease the cross-coupling selectivity.

**Scheme S2.** Effect of KF addition on the conventional Pd-catalyzed Negishi coupling

![Scheme S2 diagram]
19F NMR analysis of a mixture of alkenylaluminum and KF

A mixture of alkenyl aluminum 1a and KF in THF-d8 at 60 °C was analyzed with 19F NMR; however, no significant change in the signal was observed, and only a very weak broad signal (ca. 5%) was detected at –164.9 ppm, which suggested the formation of organoaluminate, albeit in a small amount (Figure S1).3

![19F NMR spectrum of a mixture of 1a and KF in THF-d8 at 60 °C](image)

Figure S1. 19F NMR spectrum of a mixture of 1a and KF in THF-d8 at 60 °C

Because the coupling reaction did not take place in the absence of KF, we tentatively consider that the organoaluminate species generated in situ is responsible for the transmetalation of alkenyl group form aluminium to iron to facilitate the coupling reaction. However, the details are not clear at the present stage and additional study is requisite for further discussion of the reaction mechanism.

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(3) Harrison and Beach reported the chemical shift of the 19F NMR signal derived from K[(Et3Al)2F] to lie at δF = –160.6 ppm: J. J. Harrison, D. L. Beach, D. C. Young, K. S. Seshadri and J. D. Nelligan, Organometallics., 1987, 6, 343.
Screening of catalysts

**Table S3. Screening of iron catalysts**

<table>
<thead>
<tr>
<th>entry&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fe catalyst</th>
<th>GC yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>diom&lt;sup&gt;c,d&lt;/sup&gt; (%)</th>
<th>RSM&lt;sup&gt;c,d&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10 (&gt;99% E)</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;(tmdea)</td>
<td>2 (&gt;99% E)</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;(dppbz)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;(SciOPP)</td>
<td>65 (&gt;99% E)</td>
<td>22</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>FeCl&lt;sub&gt;2&lt;/sub&gt;(TMS-SciOPP)</td>
<td>76 (&gt;99% E)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>none</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup>For reaction conditions, see Table 1, entry 3. <sup>b</sup>Yields and stereoisomeric ratio were determined by GLC analysis, using undecane as an internal standard. <sup>c</sup>Yield of hexadeca-7,9-diene was determined based on the starting 1-bromodecane 3a. <sup>d</sup>Recovery of starting material 3a. *Isolated yield.

**Figure S2.** Structures of the iron complexes used as the cross-coupling catalysts
Procedure for the screening of the additives (Table 1)

1-Octyne (92.2 mg, 0.84 mmol) was added to a solution of diisobutylaluminum hydride (0.75 mL, 0.75 mmol) at 0 °C. The reaction mixture was stirred at 50–60 °C for overnight, and then, dried in vacuo to remove solvent. To the residue, 0.50 mL of THF was added at 0 °C, followed by additives (0.75–1.50 mmol), 1-bromodecane (110.6 mg, 0.50 mmol) and a THF solution of FeCl2(TMS-SciOPP) (0.25 mL, 0.03 mmol) in that order. The coupling reaction was carried out at 60 °C for 3 h. After cooling the mixture to ambient temperature, an aliquot of the reaction mixture was taken to determine the yield of the products by GLC analysis using undecane as an internal standard.

Typical procedures for the reactions shown in Scheme 3 and Table 2

· General procedure A (hydroalumination/cross-coupling reactions);

**synthesis of (E)-octadec-7-ene (4aa)**

1-Octyne (184 mg, 1.70 mmol) was added to a 1.00 M solution of diisobutylaluminum hydride (1.50 mL, 1.50 mmol) at 0 °C. The reaction mixture was stirred at 50–60 °C for 12 h, and then, dried in vacuo. To the residue, 1.00 mL of THF was added at 0 °C, followed by potassium fluoride (87.2 mg, 1.50 mmol), 1-bromodecane (221 mg, 1.00 mmol) and a 0.10 M THF solution of FeCl2(TMS-SciOPP) (0.50 mL, 0.05 mmol) in that order. The coupling reaction was conducted at 60 °C for 3 h. After cooling the mixture to ambient temperature, aqueous HCl (1 N, 4 mL) were added at 0 °C. The aqueous layer was extracted with ethyl acetate three times (2 mL × 3). The combined organic extracts were filtered using a pad of Florisil®. After removal of the solvent in vacuo, the crude product was purified using chromatography on a silica gel to obtain the desired compound (192 mg, 76% yield, 98% purity on GC analysis) as a colourless oil.

**1H NMR (391.8 MHz, CDCl3)**

- 0.87 (t, J = 6.7 Hz, 6H, -CH2CH3), 1.08–1.50 (m, 24H, overlap), 1.97, (dt, J = 4.0, 5.8 Hz, 4H, -C=CCH2-), 5.38 (t, J = 4.0 Hz, 2H, -CH=CH-)

**13C NMR (98.5 MHz, CDCl3)**

- 14.3 (2C), 22.8 (2C), 22.9 (2C), 29.0, 29.3, 29.5, 29.7, 29.8 (2C), 31.9, 32.1, 32.8 (2C), 130.5 (2C)

**IR (neat, cm⁻¹)**

- 2956, 2921, 2852, 1466, 1378, 965, 721

**Elemental analysis**


(4) The reagent can be stocked in a refrigerator for several days and available for the reaction without loss of the yield and selectivity of the desired product.
General procedure B (carbometalation/cross-coupling reaction); synthesis of \((E)-(2\text{-methyloct-1-en-1-yl})\)cycloheptane (4cb)

1-Octyne (110 mg, 1.00 mmol) was added to a mixture of trimethylaluminum (1.87 mL, 1.07 M, 2.00 mmol) in hexane and zirconocene dichloride (146 mg, 0.50 mmol) in 3 mL of 1,2-dichloroethane at 0 °C. The reaction mixture was stirred at room temperature for 24 h, and then, dried \textit{in vacuo}. To the residue, 1.00 mL of THF was added at 0 °C, followed by potassium fluoride (58.1 mg, 1.00 mmol), bromocycloheptane (119 mg, 0.67 mmol) and a 0.10 M THF solution of FeCl$_2$(TMS-SciOPP) (0.33 mL, 0.03 mmol) in that order. The coupling reaction was carried out at 60 °C for 3 h. After cooling the mixture to ambient temperature, aqueous HCl (1 N, 4 mL) were added. The aqueous layer was extracted with ethyl acetate three times (2 mL × 3). The combined organic extracts were filtered using a pad of Florisil®. After removal of the solvent \textit{in vacuo}, the crude product was purified using chromatography on a silica gel to obtain the desired compound (191 mg, 86% yield, 98% purity on GC analysis) as a colourless oil.

$^1$H NMR (391.8 MHz, CDCl$_3$)

0.90 (t, $J = 7.2$ Hz, 3H, -CH$_2$CH$_3$), 1.04–1.78 (m, 24H, overlap), 1.93 (m, 1H, -C=CCH$_2$-), 2.32 (m, 1H, -(CH$_2$)$_2$CHC=C-), 5.05 (d, $J = 9.0$ Hz, 1H, -CH=CCH$_3$)

$^{13}$C NMR (98.5 MHz, CDCl$_3$)

14.3, 16.1, 22.8, 26.7 (2C), 28.1, 28.6 (2C), 29.0, 31.9, 35.5 (2C), 38.7, 39.8, 132.0, 132.1

IR (neat, cm$^{-1}$)

2955, 2922, 2852, 1458, 1378, 883, 724

Elemental analysis

Anal. calcd. for C$_{16}$H$_{30}$, C, 86.40; H, 13.60. Found C, 86.73; H, 13.93

Synthesis of \((E)\)-oct-1-en-1-ylcycloheptane (4ab)

The reaction was carried out according to the general procedure A using 3b-Br (177 mg, 1.00 mmol). The titled compound (190 mg, 91% yield) was obtained as a colorless oil after silica gel column chromatography.

$^1$H NMR (391.8 MHz, CDCl$_3$)

0.88 (t, $J = 6.7$ Hz, 3H, -CH$_2$CH$_3$), 1.10–1.78 (m, 20H, overlap), 1.95 (dt, $J = 6.7$, 7.0 Hz, 2H, -C=CCH$_2$-), 2.87 (m, 1H, -(CH$_2$)$_2$CHC=C-), 5.35 (m, 2H, -CH=CH-)

$^{13}$C NMR (98.5 MHz, CDCl$_3$)

14.3, 22.8, 26.4 (2C), 28.6 (2C), 29.0, 29.8, 31.9, 32.8, 35.2 (2C), 43.0, 127.2, 137.4

IR (neat, cm$^{-1}$)

2961, 2921, 2853, 1458, 1373, 1066, 907, 844, 751

Elemental analysis

Anal. calcd. for C$_{15}$H$_{28}$, C, 86.46; H, 13.54. Found C, 86.16; H, 13.59
Synthesis of (E)-hex-3-en-3-ylcycloheptane (4bb)

The reaction was carried out according to the general procedure A using 3-hexyne (1.70 mmol, 140 mg) and 3b-Br (177 mg, 1.00 mmol). The titled compound (155 mg, 86% yield) was obtained as a colorless oil after silica gel column chromatography.

\[ \text{C-H NMR (391.8 MHz, CDCl}_3\text{)} \]

- 0.95 (t, \( J = 7.2 \text{ Hz}, 3 \text{H, -CH}_2\text{C}_3\text{H}_3 \))
- 0.96 (t, \( J = 7.2 \text{ Hz}, 3 \text{H, CH}_3\text{C}(\text{C}_8\text{H}_{17})\text{C}=-\text{C} \))
- 1.10–1.80 (m, 12H, overlap)
- 1.99 (m, 5H, -(CH)_2CH=CH=C-)

\[ \text{C-13 NMR (98.5 MHz, CDCl}_3\text{)} \]

14.5, 14.9, 21.0, 23.1, 27.4 (2C), 28.1 (2C), 35.0 (2C), 47.6, 124.0, 147.6

Elemental analysis

Anal. calcd. for C_{13}H_{24}, C, 86.58; H, 13.42. Found C, 86.40; H, 13.59

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Synthesis of (4-methylhex-3-en-3yl)cycloheptane (4db)

The reaction was carried out according to the general procedure B. The carboalumination using 3-hexyne (2.01 mmol, 169 mg) and the coupling reaction of 3b-Br (118 mg, 0.67 mmol) were conducted for 50 ºC for 24 h and at 80 °C for 36 h respectively. The titled compound (25.2 mg, 19% yield, \( E/Z = 70/30 \)) was obtained as a colorless oil after silica gel column chromatography. The stereochemistry of the isomers was analogized from that of the starting alkenylaluminum reagent.\(^5\)

\[ \text{H NMR (391.8 MHz, CDCl}_3\text{)} \]

\( E/Z \) mixture: 0.92–0.99 (m, 6H, -CH_3)
- 1.38–1.74 (m, 15H, overlap)
- 1.95–2.05 (m, 4H, CH_3CH_2C=CHCH_2CH_3)
- 2.48–2.59 (m, 1H, -C=CH-)

\[ \text{C-13 NMR (98.5 MHz, CDCl}_3\text{)} \]

\( E/Z \) mixture: 13.3, 13.8, 15.1, 16.0, 17.3, 18.1, 21.7, 21.9, 27.2, 27.4, 28.0 (4C), 28.1 (4C), 33.7 (2C), 34.0 (2C), 43.4, 43.9, 128.1, 128.2, 140.1, 140.2

IR (neat, cm\(^{-1}\))

2961, 2923, 2854, 1455, 1374, 1059, 786

Elemental analysis

Anal. calcd. for C_{14}H_{26}, C, 86.52; H, 13.48. Found C, 86.41; H, 13.52

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Synthesis of (E)-9-methylheptadec-7-ene (4ac)

The reaction was carried out according to the general procedure A using 3c (177 mg, 1.00 mmol). The titled compound (217 mg, 86% yield) was obtained as a colorless oil after silica gel column chromatography.

\[ \text{H NMR (391.8 MHz, CDCl}_3\text{)} \]

0.87 (t, J = 6.7 Hz, 6H, -CH₂CH₃), 0.93 (d, J = 6.7 Hz, 3H, -CHCH₃), 1.10–1.14 (m, 22H, overlap), 1.95 (q, J = 6.7 Hz, 2H, -C=CHCH₂-, 2.02 (m, 1H, CH₃CHC≡C-), 5.22 (dd, J = 6.7, 15.3 Hz, 1H, -C=CHCH₂-), 5.32 (dt, J = 6.7, 15.3 Hz, 1H, CH₃CHCH=C-)

¹³C NMR (98.5 MHz, CDCl₃)
14.3 (2C), 21.1, 22.8, 22.9, 27.5, 29.0, 29.5, 29.8 (2C), 30.0, 31.9, 32.1, 32.8, 36.9, 37.4, 128.6, 136.6

IR (neat, cm⁻¹)
2956, 2922, 2853, 1457, 1377, 966, 722

Elemental analysis

**Synthesis of (E)-undec-4-enenitrile (4ad)**

![Chemical Structure](image)

The reaction was carried out according to the general procedure A using 3d (190 mg, 1.00 mmol). The titled compound (199 mg, 90% yield) was obtained as a colorless oil after silica gel column chromatography.

¹¹H NMR (391.8 MHz, CDCl₃)
0.87 (t, 5.7 Hz, 3H, -CH₂CH₃), 1.10–1.50 (m, 9H, overlap), 1.43 (quint, J = 7.2 Hz, 2H, NC(CH₂)₂CH₂CH₂-), 1.64 (quint, J = 7.2 Hz, 2H, NCCH₂CH₂CH₂-), 1.97 (m, 4H, -CH₂CH≡CHCH₂-), 2.32 (t, J = 7.2 Hz, 2H, NCCH₂CH₂-), 5.36 (m, 2H, -CH=CH-)

¹³C NMR (98.5 MHz, CDCl₃)
14.2, 17.3, 22.8, 25.5, 28.3, 28.6, 29.0, 29.3, 29.7, 31.9, 32.5, 32.7, 120.0, 129.9, 131.0

IR (neat, cm⁻¹)
2923, 2854, 2247, 1643, 1378, 967, 724

Elemental analysis
Anal. calcd. for C₁₅H₂₇N, C, 81.38; H, 12.29; N, 6.33.
Found C, 81.10; H, 12.19; N, 6.54

**Synthesis of 4-((E)-oct-1-en-1-yl)cyclohexyl acetate (4ae)**

![Chemical Structure](image)

The reaction was carried out according to the general procedure A for 6 h using 3e (222 mg, 1.01 mmol). The titled compound (trans-isomer 72.4 mg; cis-isomer 51.5 mg, 49% yield) was obtained as a colorless oil after GPC using toluene as the eluent.

¹¹H NMR (391.8 MHz, CDCl₃)
trans-isomer: 0.88 (t, J = 7.1 Hz, 3H, -CH₂CH₃), 1.13–1.42 (m, 12H, overlap), 1.74–1.80 (m, 2H, -OCH(CH₂CH₂)₂-), 1.85–2.00 (m, 5H, overlap), 2.03 (s, 3H, -COCH₃), 4.65 (tt, J = 4.7, 10.6 Hz, 1H, -OCH(CH₂CH₂)₂-), 5.30 (dd, J = 5.9, 15.5 Hz, 1H, -CHCH=CHCH₂-), 5.39 (dt, 5.8, 15.5 Hz, 1H, -CHCH=CHCH₂-);
cis-isomer: 0.88 (t, $J = 7.1$ Hz, 3H, -CH$_2$CH$_3$), 1.28–1.38 (m, 14H, overlap), 1.80–1.86 (m, 2H, -OCH(CH$_2$CH$_2$)$_2$), 1.96–2.03 (m, 3H, -CHCH=CHCH$_2$), 2.05 (s, 3H, -COCH$_3$), 4.94–5.00 (m, 1H, -OCH(CH$_2$CH$_2$)$_2$), 5.39–5.41 (m, 2H, -CHCH=CHCH$_2$)  

$^{13}$C NMR (98.5 MHz, CDCl$_3$)  
trans-isomer: 14.2, 21.6, 22.8, 28.9, 29.7, 31.1 (2C), 31.5 (2C), 31.9, 32.7, 39.8, 73.3, 129.0, 134.7, 170.8  
cis-isomer: 14.2, 21.6, 22.8, 27.8 (2C), 28.9, 29.4 (2C), 29.7, 31.9, 32.8, 39.1, 70.1, 128.9, 135.0, 170.8  

IR (neat, cm$^{-1}$)  
trans-isomer: 2925, 2856, 1734, 1452, 1369, 1237, 1031, 968, 733  
cis-isomer: 2926, 2856, 1736, 1445, 1368, 1239, 1034, 966, 733  

HRMS (FAB)  

cis-isomer: m/z [M]$^+$ calcd for C$_{16}$H$_{28}$O$_2$: 252.2089; found: 252.2089.  

Synthesis of (E)-non-2-en-1-ylcyclopentane (4af)  
The reaction was carried out according to the general procedure A for 6 h using 3f (163 mg, 1.00 mmol). The titled compound (89.3 mg, 46% yield) was obtained as a colorless oil after GPC using toluene as the eluent.  

$^1$H NMR (391.8 MHz, CDCl$_3$)  
0.88 (t, $J = 7.5$ Hz, 3H, -CH$_2$CH$_3$), 1.07–1.16 (m, 2H, -CH$_2$CH$_2$CH-(^Pent)), 1.26–1.35 (m, 8H, overlap), 1.45–1.52 (m, 2H, -CH$_2$CH$_2$CH-(^Pent)), 1.56–1.63 (m, 2H, -CH$_2$CH$_2$CH-(^Pent)), 1.67–1.75 (m, 2H, -CH$_2$CH$_2$CH-(^Pent)), 1.75–1.87 (m, 1H, -CH$_2$CH$_2$CH-(^Pent)), 1.95–1.99 (m, 4 H, -CH$_2$CH=CHCH$_2$), 5.38–5.40 (m, 2H, -CH=CH-)  

$^{13}$C NMR (98.5 MHz, CDCl$_3$)  
14.3, 22.8, 25.3 (2C), 29.0, 29.8, 31.9, 32.4 (2C), 32.8, 39.2, 40.3, 129.8, 131.0  

IR (neat, cm$^{-1}$)  
2952, 2924, 2855, 1453, 1243, 966  

HRMS (EI)  
m/z [M]$^+$ calcd for C$_{14}$H$_{26}$: 194.2035; found: 194.2027.  

Synthesis of (E)-dodeca-1,5-diene (4ag)  
The reaction was carried out according to the general procedure A at 80 ºC for 6 h using 3g (137 mg, 1.01 mmol). The titled compound (27.9 mg, 17% yield) was obtained as a colorless oil after silica gel column chromatography using pentane as the eluent and GPC using chloroform as the eluent.  

$^1$H NMR (391.8 MHz, CDCl$_3$)
0.88 (t, J = 7.1 Hz, 3H, -CH\textsubscript{2}CH\textsubscript{3}), 1.25–1.36 (m, 8H, overlap), 1.94–1.99 (m, 2H, CH\textsubscript{2}=HCC\textsubscript{2}H\textsubscript{2}CH\textsubscript{2}--), 2.03–2.12 (m, 4H, -CH\textsubscript{2}CH\textsubscript{2}CH=CHCH\textsubscript{2}CH\textsubscript{2}--), 4.94 (m, 1H, CH\textsubscript{2}=CH--), 5.00 (m, 1H, CH\textsubscript{2}=CH--), 5.35–5.46 (m, 2H, -CH\textsubscript{2}CH=CHCH\textsubscript{2}--), 5.81 (ddt, J = 16.9, 9.8, 5.8 Hz, 1H, CH\textsubscript{2}=CCH\textsubscript{2}--)

\textsuperscript{13}C NMR (98.5 MHz, CDCl\textsubscript{3})

14.3, 22.8, 29.0, 29.7, 31.9, 32.2, 32.7, 34.0, 114.6, 129.5, 131.1, 138.7

IR (neat, cm\textsuperscript{-1})

2958, 2924, 2854, 1641, 1452, 1378, 966, 910

Synthesis of \((E)-(2\text{-phenylprop-1-en-1-yl})\text{cycloheptane} (4eb)\)

The reaction was carried out according to the general procedure B using ethynylbenzene (105 mg, 1.02 mmol) and 3b–Br (87.9 mg, 0.50 mmol). The titled compound (52.6 mg, 49% yield) was obtained as a colorless oil after silica gel column chromatography.

\textsuperscript{1}H NMR (391.8 MHz, CDCl\textsubscript{3})

1.34–1.79 (m, 12H, -CH\textsubscript{2}-- (c\text{Hep})), 2.03 (s, 3H, -CH=CPhCH\textsubscript{3}), 2.48–2.57 (m, 1H, -CH\textsubscript{2}CH=CHCH\textsubscript{2}--), 5.71 (d, J = 9.0 Hz, 1H, -CHCH=CPh(CH\textsubscript{3})), 7.20 (t, J = 7.8 Hz, 1H, Ph (4-position)), 7.29 (t, J = 7.8 Hz, 2H, Ph (3-position)), 7.38 (d, J = 1.2 Hz, 2H, Ph (2-position))

\textsuperscript{13}C NMR (98.5 MHz, CDCl\textsubscript{3})

15.9, 26.7 (2C), 28.6 (2C), 35.1 (2C), 39.4, 125.8 (2C), 126.5, 128.2 (2C), 131.6, 135.7, 144.3

IR (neat, cm\textsuperscript{-1})

2917, 2851, 1598, 1494, 1458, 1444, 1379, 1027, 880

Elemental analysis

Anal. calcd. for C\textsubscript{16}H\textsubscript{22}, C, 89.65; H, 10.35. Found C, 89.38; H, 10.45

HRMS (FAB)

[M]\textsuperscript{+} calcd for C\textsubscript{16}H\textsubscript{22}: 214.1722; found: 214.1720

Synthesis of \((E)-1,1\text{,}0\text{-dichloro-5-methyldec-5-ene} (4fh)\)

The reaction was carried out according to the general procedure B using 6-chloro-1-hexyne (117 mg, 1.00 mmol) and 3h (171 mg, 0.67 mmol). The titled compound (119 mg, 78% yield) was obtained as a colorless oil after silica gel column chromatography.

\textsuperscript{1}H NMR (391.8 MHz, CDCl\textsubscript{3})

1,43–1.60 (m, 7H, overlap), 1.74 (m, 4H, ClCH\textsubscript{2}CH\textsubscript{2}--), -CH\textsubscript{2}CH\textsubscript{2}Cl), 1.94 (m, 4H, -CH\textsubscript{2}CH\textsubscript{2}CH=CH(CH\textsubscript{3})CH\textsubscript{2}--), 3.52 (t, J = 6.8 Hz, 4H, ClCH\textsubscript{2}CH\textsubscript{2}--), -CH\textsubscript{2}CH\textsubscript{2}Cl), 5.11 (t, J = 7.0 Hz, 1H, -CH=CH(CH\textsubscript{3})--)

\textsuperscript{13}C NMR (98.5 MHz, CDCl\textsubscript{3})
Elemental analysis

Anal. calcd. for C<sub>11</sub>H<sub>20</sub>Cl, C, 59.20; H, 9.03. Found C, 59.10; H, 8.79

**Synthesis of (E)-1-bromo-4-(8-chloro-4-methyloct-3-en-1-yl)benzene (4fi)**

The reaction was carried out according to the general procedure B using 6-chloro-1-hexyne (117 mg, 1.00 mmol) and 3i (157 mg, 0.67 mmol). The titled compound (160 mg, 76% yield) was obtained as a colorless oil after silica gel column chromatography.

**1H NMR (391.8 MHz, CDCl<sub>3</sub>)**

1.45–1.58 (m, 5H, -CH=C(C<sub>2</sub>H<sub>3</sub>)CH<sub>2</sub> ), 1.68 (quint, J = 6.7 Hz, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>),

1.98 (t, J = 7.2 Hz, 2H, -CH=C(CH<sub>3</sub>)CH<sub>2</sub>), 2.28 (dt, J = 7.2, 7.6 Hz, 2H, -CH<sub>2</sub>CH=C(CH<sub>3</sub>) ), 2.59 (t, J = 7.6 Hz, 2H, ArCH<sub>2</sub>), 3.52 (t, J = 6.7 Hz, 2H, -CH<sub>2</sub>Cl),

5.12 (t, J = 7.2 Hz, 1H, -CH=C(CH<sub>3</sub>) ), 7.03 (d, J = 8.5 Hz, 2H, Ar (3-position)), 7.37 (d, J = 8.5 Hz, 2H, Ar (2-position))

**13C NMR (98.5 MHz, CDCl<sub>3</sub>)**

15.9, 25.1, 29.8, 32.1, 35.6, 38.9, 45.2, 119.5, 123.8, 130.4 (2C), 131.4 (2C), 135.7, 141.3

Elemental analysis

Anal. calcd. for C<sub>15</sub>H<sub>20</sub>ClBr, C, 57.07; H, 6.39. Found C, 57.29; H, 6.56

**Synthesis of 2-chloro-5-(3-methyl-2-propylhex-2-en-1-yl)pyridine (4gj)**

The reaction was carried out according to the general procedure B. The carboalumination using 4-octyne (0.75 mmol, 82.1 mg) and the coupling reaction of 3j (80.1 mg, 0.49 mmol) were conducted for 60 ºC for 24 h and at 80 °C for 15 h respectively. The titled compound (89.6 mg, 72% yield, E/Z = 64/36) was obtained as a brown oil after silica gel column chromatography hexane/EtOAc (10/1). Stereochemistry of isomers was determined by a NOE correlation.

**1H NMR (391.8 MHz, CDCl<sub>3</sub>)**

E/Z mixture:

0.84–0.94 (m, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.25–1.37 (m, 2H, -C=C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.39–1.49 (m, 2H, CH<sub>3</sub>CH=CHC=C(CH<sub>3</sub>)- ), 1.70 (s, 3H, -C=C(CH<sub>3</sub>)-[{(E)-product}]), 1.72 (s, 3H, -C=C(CH<sub>3</sub>)-[{(Z)-product}]),

1.88–1.95 (m, 2H, CH<sub>3</sub>CH=CHC=C(CH<sub>3</sub>)- ), 2.04–2.10 (m, 2H, -C=C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>), 3.36 (s, 2H, ArCH<sub>2</sub>C=C-), 7.21 (d, J = 8.2 Hz, 1H, Ar (3-position)),

7.40 (d, J = 8.2 Hz, 1H, Ar (4-position)), 8.17 (s, 1H, Ar ([{(E)-product}], 6-position)), 8.18 (s, 1H, Ar ([{(Z)-product}, 6-position])

**13C NMR (98.5 MHz, CDCl<sub>3</sub>)**

E/Z mixture: 14.2 (2C), 14.3, 14.4, 18.2, 18.7, 21.7, 21.8 (2C), 22.2, 33.9, 34.2 (2C), 34.3, 36.4, 36.9, 123.9 (2C), 129.7, 130.0, 132.6 (2C), 135.6, 135.7, 138.8, 138.9, 148.9 (2C) 149.8, 149.9
IR (neat, cm$^{-1}$)

\[E/Z\] mixture: 2957, 2930, 2870, 1583, 1563, 1456, 1379, 1102, 812

Elemental analysis

Anal. calcd. for C\textsubscript{15}H\textsubscript{22}ClN, C, 71.55; H, 8.81. Found C, 71.35; H, 9.01

HRMS (FAB)

m/z [M+H]$^+$ calcd for C\textsubscript{15}H\textsubscript{23}ClN: 252.1519; found: 252.1517
$^1$H and $^{13}$C NMR spectra of the compounds

\[
\text{Dec} \xrightarrow{\text{H}} \text{Hex}
\]

4aa

\[X : \text{parts per Million : } 1\text{H}\]

\[X : \text{parts per Million : } 13\text{C}\]