Copper(II)-Catalyzed Highly Regio- and Stereoselective Hydrosilylation of Unactivated Internal Alkynes with Silylborate in Water

Qing-Qing Xuan,\textsuperscript{a,b} Chuan-Li Ren,\textsuperscript{a,b} Li Liu,\textsuperscript{a} \textsuperscript{*} Dong Wang,\textsuperscript{a} and Chao-Jun Li \textsuperscript{c} \textsuperscript{*}

\textsuperscript{a} Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. \textsuperscript{b} University of Chinese Academy of Sciences, Beijing 100049, China. \textsuperscript{c} Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A0B8

Supplementary Information

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1. General methods

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used without further purification. Internal alkynes were prepared according to original or modified literature procedures. All reactions were carried out under N₂ atomosphere, unless otherwise noted. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, h= heptet, m= multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). IR spectra were recorded on a Bruker tensor 27 infrared spectrometer. Melting points were measured on Beijing Tech X-4 apparatus without correction. Mass spectra were obtained using electrospray ionization (APCI) mass spectrometer. Column chromatography was performed using silica gel (200-300 mesh). TLC was performed on glass-backed silica plates.

2. Experimental section

2.1 The Preparation of Internal Alkynes

The internal alkynes were synthesized from methyl propiolate acid and an aryl halide following the literature procedure (eq s1).¹

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General procedure:
A mixture of Pd(PPh₃)₂Cl₂ (0.0343 mmol), 1,4-bis(diphenylphosphanyl)butane (0.0701 mmol), 4-halosubstituted benzene (3.04 mmol), 2-butynoic acid (3.00 mmol), base (6.0 mmol), and DMSO (6.0 mL) was stirred at 80-110 °C. After 2-24 h, the reaction mixture was poured into a saturate aqueous solution of NH₄Cl and was extracted with CH₂Cl₂. The combined CH₂Cl₂ extracts were washed with H₂O, dried over Na₂SO₄, and filtered. The filtrate was concentrated in vacuo, and the resulting residue was purified using silicagel column chromatography.
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2.2 General Procedure for the Reaction of Internal Alkynes 1 with Me₂PhSiBpin 2.

Ligand L₉ (0.003mmol, 0.5mg), and Cs₂CO₃ were added to a Schlenk tube, which was evacuated and backfilled with N₂. Then 1ml solution of Cu(OTf)₂ (0.9mg/ml), Me₂PhSiBpin (0.15mmol, 40µl) and internal alkyne 1a (0.1mmol,12.6µl) were added via syringe, and the reaction mixture was stirred for 20h at room temperature. Then the reaction solution was extracted with ether for 3 times, the organic layer was combined and dried over Na₂SO₄. Next, the organic solvent was
evaporated and the residue was subjected to flash column chromatography on silica gel with petroleum ether as eluent to afford the desired product 3a.

2.3 The screening of copper source.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu-salt</th>
<th>Yield(%)</th>
<th>β/α</th>
</tr>
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<tr>
<td>1</td>
<td>CuOTf</td>
<td>65</td>
<td>88/12</td>
</tr>
<tr>
<td>2</td>
<td>CuOAc</td>
<td>22</td>
<td>83/17</td>
</tr>
<tr>
<td>3*d</td>
<td>Cu(OTf)₂</td>
<td>75</td>
<td>92/8</td>
</tr>
</tbody>
</table>

*a General procedure: A mixture of 1a (1.0 equiv), 2 (1.5 equiv), ligand (3~6 mol%), base (10 mol%) and Cu(OTf)₂ (2.5 mol%) in water (1 mL) was stirred under N₂ at room temperature.  
*b The yields of 3a were determined by ¹H NMR analysis.  
*c The ratio (β/α) was determined by ¹H NMR analysis.  
*d The reaction was carried out under air.

**Colourless oil.**

(1)-(4-fluorophenyl)prop-1-en-2-yl)dimethyl(phenyl)silane (β-3a)

![Chemical structure](image)

1H NMR (400 MHz, CDCl₃) δ: 7.57-7.56(d, J=4Hz, 2H), 7.36-7.26(m, 7H), 7.24-7.20(t, J=8Hz, 1H), 1.94(s, 3H), 0.43(s, 6H).  
13C NMR (100MHz, CDCl₃) δ: 137.99, 137.41, 137.4, 137.3, 133.2, 128.2, 128.1, 127.2, 126.9, 125.7, 15.8, -4.3. IR νmax (KBr, film, cm⁻¹): 1594, 1427, 1243, 823. HRMS (APCI): calcld for C₁₇H₂₀Si[M+H]⁺ 253.14070, found: 253.14055.

(1,2-diphenylvinyl)dimethyl(phenyl)silane (β-3b)

![Chemical structure](image)

1H NMR (400 MHz, CDCl₃) δ: 7.55-7.53(t, J=4Hz, 2H), 7.36-7.35(d, J=4Hz, 3H), 7.36-7.14(m, 3H), 7.08-7.06(t, J=4Hz, 3H), 6.94-6.88(m, 4H), 6.82(s, 1H), 0.39(s, 6H).  
13C NMR (100MHz, CDCl₃) δ: 144.1, 141.4, 138.3, 136.8, 133.4, 128.6, 128.2, 127.6, 127.0, 126.8, 127.7, 126.3, 124.8, -3.9. IR νmax (KBr, film, cm⁻¹): 1593, 1426, 1246, 968, 823. HRMS (APCI): calcld for C₂₂H₂₂Si[M⁺]⁺ 314.14853, found: 314.14835.

(1)-(4-fluorophenyl)prop-1-en-2-yl)dimethyl(phenyl)silane (β-3c)

![Chemical structure](image)

1H NMR (400 MHz, CDCl₃) δ: 7.57-7.54(m, 2H), 7.38-7.36(m,3H), 7.28-7.25(m, 3H), 7.04-7.06(t, J=10Hz, 2H), 1.92-1.91(d, J=4Hz, 3H), 0.43(s, 6H).  
13C NMR (100MHz, CDCl₃) δ: 140.6, 137.3, 137.1, 136.8, 133.4, 133.2, 129.8(d, JCF=160Hz), 129.7, 126.93, 114(d, JCF=21.2Hz), 15.7, -4.3. IR νmax (KBr, film, cm⁻¹): 1596, 1422, 1360, 1263, 908. HRMS (APCI): calcld for C₁₇H₁₉FSi[M⁺]⁺ 271.13128, found: 271.13103.

(2)-(dimethyl(phenyl)silyl)prop-1-en-1-yl)benzonitrile (β-3d)

![Chemical structure](image)

colourless oil. **Yield 95%.**  
1H NMR (400 MHz, CDCl₃) δ: 7.62-7.60(d, J=8Hz, 2H), 7.56-7.53(m, 2H), 7.39-7.38(t, J=2Hz, 4H), 7.36(s, 1H), 6.760-6.757(d, J=1.2Hz, 1H), 1.934-1.929(d, J=1.5Hz, 3H), 0.45(s, 3H).
6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 142.0, 141.9, 136.8, 136.0, 133.1, 130.9, 128.7, 128.4, 127.0, 118.2, 109.1, 15.9, -4.5. IR $\nu_{max}$ (KBr, film, cm$^{-1}$): 2242, 1591, 1422, 1202, 1029, 834. HRMS (APCI): calede for C$_{18}$H$_{19}$NSi [M+H]$^+$ 278.13595, found: 278.13571.

(E)-4-[2-(dimethyl(phenyl)silyl)prop-1-en-1-yl]benzonitrile (β-3e)

(E)-dimethyl(phenyl)(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)silane (β-3f)

(E)-dimethyl(phenyl)(1-(2-(trifluoromethyl)phenyl)prop-1-en-2-yl)silane (β-3g)

(E)-1-(2-methoxyphenyl)prop-1-en-2-yl(dimethyl)silane (β-3h)

(E)-dimethyl(phenyl)(1-3-(trifluoromethyl)phenyl)prop-1-en-2-yl)silane (β-3i)

(E)-dimethyl(phenyl)(1-phenylhex-1-en-2-yl)silane (β-3j)
HRMS (APCI): calcd for C_{20}H_{26}Si [M+H]^+ 295.18765, found: 295.18710.

(E)-dimethyl(1-(naphthalen-2-yl)prop-1-en-2-yl)(phenyl)silane (β-3k)

White solid. Yield 92%. M.p. 56-58°C. 1H NMR (400 MHz, CDCl3) δ: 7.81-7.78(m, 3H), 7.75(s, 1H), 7.61-7.58(dd, J=2.8Hz, J=3.2Hz, 2H), 7.45-7.43(m, 3H), 7.39-7.37(t, J=4Hz, 3H), 6.95(s, 1H), 2.023-2.019(d, J=1.6Hz, 3H), 0.47(s, 6H).

IR ν\_max (KBr, film, cm\(^{-1}\))): 1634, 1427, 1243, 894, 789, 753. HRMS (APCI): calcd for C_{30}H_{36}Si [M+H]^+ 352.14819, found: 352.14853.

(E)-dimethyl(1-(naphthalen-1-yl)prop-1-en-2-yl)(phenyl)silane (β-3l)

colourless oil. Yield 89%. 1H NMR (400 MHz, CDCl3): 7.92-7.79(t, J=6Hz, 1H), 7.86-7.83(m, J=4Hz, 2H), 7.76-7.74(m, J=8Hz, 1H), 7.65-7.64(t, J=2Hz, 2H), 7.49-7.46(m, 2H), 7.44-7.42(d, J=8Hz, 1H), 7.40-7.39(t, J=2Hz, 3H), 7.33-7.31(t, J=4Hz, 1H), 7.24(s, 1H), 1.78(s, 3H), 0.52(s, 6H).

IR ν\_max (KBr, film, cm\(^{-1}\))): 1634, 1423, 1247, 1120, 843. HRMS (APCI): calcd for C_{32}H_{38}Si [M+H]^+ 320.14853, found: 320.14818.

(E)-dimethyl(1-(phenanthren-9-yl)prop-1-en-2-yl)(phenyl)silane (β-3m)

White solid. Yield 91%. M.p. 80-82°C. 1H NMR (400 MHz, CDCl3): 8.77-8.75(d, J=8Hz, 1H), 8.72-8.70(d, J=8Hz, 1H), 8.05-8.03(m, 1H), 7.90-7.88(m, 1H), 7.74-7.71(m, 2H), 7.70-7.66(m, 2H), 7.64-7.61(m, 3H), 7.30(s, 1H), 1.894-1.890(d, J=1.6Hz, 3H), 0.597(s, 6H).

IR ν\_max (KBr, film, cm\(^{-1}\))): 1698, 1574, 1457, 1029, 893. HRMS (APCI): calcd for C_{25}H_{24}Si [M+H]^+ 352.16418, found: 352.16388.

(E)-2-(2-(dimethyl(phenyl)silyl)prop-1-en-1-yl)pyridine (β-3n)

Yellow oil. Yield 87%. 1H NMR (400 MHz, CDCl3): 8.62-8.61(d, J=4Hz, 1H), 7.66-7.62(td, J=1.6 Hz, J=1.2 Hz, 1H), 7.58-7.56(dd, J=2 Hz, J=3.4 Hz, 2H), 7.37-7.36(m, 3H), 7.30-7.28(d, J=8Hz, 1H), 7.11-7.09(q, J=4.4Hz, 1H), 6.87(s, 1H), 2.092-2.089(d, J=1.2Hz, 3H), 0.461(s, 6H).

IR ν\_max (KBr, film, cm\(^{-1}\))): 1594, 1432, 1193, 1009, 873. HRMS (APCI): calcd for C_{16}H_{19}NSi [M+H]^+ 254.13595, found: 254.13580.

(E)-dimethyl(phenyl)(1-(thiophen-2-yl)prop-1-en-2-yl)silane (β-3o)

Yellow oil. Yield 94%. 1H NMR (400 MHz, CDCl3): 7.55-7.53(m, 2H), 7.37-7.35(dd, J=2Hz, J=1.6Hz, 3H), 7.299-7.287(d, J=5.2Hz, 1H), 7.06-7.02(m, 2H), 6.936-6.933(d, J=1.2Hz, 3H), 0.42(s, 6H).

IR ν\_max (KBr, film, cm\(^{-1}\))): 142.7, 138.7, 137.9, 137.5, 133.2, 128.0, 127.8, 126.8, 126.1, 125.7, 31.1, 29.6, 22.1, 12.9, -3.3. HRMS (APCI): calcd for C_{21}H_{22}Si [M+H]^+ 295.18765, found: 295.18710.

\( [M]^{+} \)
4.3. IR $\nu_{\text{max}}$ (KBr, film, cm$^{-1}$): 1592, 1426, 1126, 1111, 868. HRMS (APCI): calcd for C$_{13}$H$_{18}$Si[M+H]$^+$ 259.09712, found: 259.09690.

$(E)$-(2-(dimethyl(phenyl)silyl)vinyl)trimethylsilane ($\beta$-3p)

**TMS$\xrightarrow{\text{SiMe}_2\text{Ph}}$ colourless oil. yield 95%.** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.56-7.53(dd, $J=2.8$Hz, $J=3.6$Hz, 2H), 7.39-7.38(t, $J=2$Hz, 3H), 6.73(s, 2H), 0.37(s, 6H), 0.1(s, 9H). $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$: 152.1, 147.1, 137.9, 132.9, 127.9, 126.8, -2.5, -3.8. IR $\nu_{\text{max}}$ (KBr, film, cm$^{-1}$): 1594, 1452, 1243, 867, 823. HRMS (APCI): calcd for C$_{13}$H$_{22}$Si[M+H]$^+$ 235.13328, found: 235.13307.

$(E)$-dimethyl(phenyl)(1-phenylprop-1-en-2-yl-1-d)silane ($\beta$-4a)

**colourless oil. yield 96%.** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.56-7.55(t, $J=2$Hz, 2H), 7.37-7.35(t, $J=4$Hz, 3H), 7.33-7.30(t, $J=6$Hz, 4H), 7.22-7.19(m, 1H), 1.94(s, 3H), 0.43(s, 6H). $^{13}$C NMR (100MHz, CDCl$_3$) $\delta$: 137.3, 137.3, 137.2, 133.2, 128.2, 128.1, 127.2, 126.9, 125.8, 124.5, 15.8, -4.3. IR $\nu_{\text{max}}$ (KBr, film, cm$^{-1}$): 2596, 1584, 1426, 1019, 833. HRMS (APCI): calcd for C$_{17}$H$_{19}$DSi[M+H]$^+$ 254.14705, found: 254.14698.

NOESY spectrum of β-3a
NOESY spectrum of β-3n