Supporting Information

Synthesis of Polysubstituted Enynes through Iron-Catalyzed Carbomagnesiation of Conjugated Diynes

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1. Materials and Methods

**General.** All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under an atmosphere of nitrogen or argon. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Gas-liquid chromatographic (GLC) analysis was performed on a Shimadzu 14A or 14B machine equipped with glass capillary column HR-1 (0.25-mm i.d. × 25 m). Flash silica gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140–325 mesh) as described by Still. 1 Gel permeation column chromatography was performed on a Japan Analytical Industry LC-908 (eluent: chloroform) with JAIGEL 1H and 2H polystyrene columns. NMR spectra were measured on JEOL ECX-400, JEOL ECA-500 spectrometers and reported in parts per million from tetramethylsilane. 1H NMR spectra in CDCl₃ were referenced internally to tetramethylsilane as a standard, and 13C NMR spectra to the solvent resonance. Mass spectra (GC MS) are taken at SHIMADZU Parvum 2 gas chromatograph mass spectrometer. High resolution (HR MS) mass spectra were acquired by atmospheric pressure ionization (APCI) or electrospray ionization (ESI) using a time-of-flight mass analyzer on JEOL JMS-T100LC (AccuTOF) spectrometer with a calibration standard of polyethylene glycol (MW 400). The melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and were uncorrected.

**Materials.** Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used after appropriate purification before use. Diethyl ether was purchased from Kanto Chemical Co., Inc. and purified by a solvent purification system (GlassContour)2 equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. The water content of the solvent was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 25 ppm. Iron(II) chloride (99.9%, beads) was purchased from Aldrich Inc. and used as received. Grignard reagents were purchased

from Aldrich Inc. or prepared from the corresponding halides and magnesium turnings in anhydrous diethyl ether, and titrated prior to use.
2. Preparation of Substrates

1,4-Bis(trimethylsilyl)-1,3-butadiyne was purchased from Aldrich Inc. and 5,7-Dodecadiyne was purchased from TCI and they were used as received. Other diynes were prepared according to the literature procedure.\textsuperscript{3} The compound data was in good agreement with the literature: 1,4-diphenyl-1,3-butadiyne,\textsuperscript{4} 1-trimethylsilyl-4-phenyl-1,3-butadiyne.\textsuperscript{5}

3. Investigation of the Key Reaction Parameters

3.1 Effect of Ligand

<table>
<thead>
<tr>
<th>entry</th>
<th>Ligand (mol%)</th>
<th>GC Yield(%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>Phen (5)</td>
<td>20</td>
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<td>3</td>
<td>dtbpy (5)</td>
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<tr>
<td>4</td>
<td>TMEDA (5)</td>
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<tr>
<td>5</td>
<td>P(n-Bu)_3 (10)</td>
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<td>6</td>
<td>dppe (5)</td>
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<tr>
<td>7</td>
<td>dppbz (5)</td>
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<tr>
<td>8</td>
<td>xantphos (5)</td>
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</tr>
<tr>
<td>9</td>
<td>IPr (10)</td>
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</table>

Yield was estimated by GC in the presence of n-tridecane

3.2 Effect of Solvent

<table>
<thead>
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<th>entry</th>
<th>Solvent</th>
<th>GC Yield(%)</th>
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<tbody>
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<tr>
<td>2</td>
<td>Hexane</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>Benzene</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>NEt_3</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>THF</td>
<td>13</td>
</tr>
</tbody>
</table>

Estimated by GC in the presence of n-tridecane
3.3 Effect of Catalyst

\[
\text{PhMgBr (1.2 equiv)} \quad \text{FeCl}_2 \text{ (10 mol \%)} \quad \text{Et}_2\text{O (0.2 M)} \quad \text{rt, 3 h}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>GC Yield(%)</th>
</tr>
</thead>
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<tr>
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</tr>
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<td>2</td>
<td>Fe(acac)_2</td>
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<td>3</td>
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<tr>
<td>4</td>
<td>FeCl_2 (99.9 %)</td>
<td>71</td>
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<tr>
<td>5</td>
<td>FeCl_3</td>
<td>25</td>
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<tr>
<td>6</td>
<td>FeF_3</td>
<td>5</td>
</tr>
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<td>7</td>
<td>Fe(OTf)_2</td>
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<td>8</td>
<td>Fe(OAc)_2</td>
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<td>Mn(OAc)_2</td>
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<td>11</td>
<td>Ni(acac)_2</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>Co(acac)_2</td>
<td>5</td>
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</table>

Estimated by GC in the presence of n-tridecane

3.4 Poor Substrates

- 31% yield (GC), two isomers (41:59)
- 19% yield (GC), two isomers (48:52)
- 33% yield (GC), two isomers (40:60)
4. Iron-catalyzed Carbomagnesiation of Conjugated Diynes

General Procedure for Iron-Catalyzed Carbomagnesiation of Conjugated Diynes (Scheme 1)

In an oven-dried Schlenk tube, FeCl₂ (5.0 mg, 0.040 mmol) was added to a solution of 1,4-bis(trimethylsilyl)-1,3-butadiyne (78 mg, 0.40 mmol) in Et₂O (1.6 mL). After 15 minutes, a solution of phenylmagnesium bromide in Et₂O (0.35 mL, 1.46 mol/L, 0.48 mmol) was added to the reaction mixture at room temperature, and the resulting mixture was stirred at room temperature for an additional 3 hours, then H₂O (3.0 mL) was added. The organic phase was extracted with ethyl acetate (3 × 5 ml), then the mixture was passed over a pad of Florisil. The volatiles were removed in vacuo to obtain an oily brown residue. The crude mixture was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless oil in 68% yield (74 mg). GC analysis and ¹H NMR analysis of the crude product indicated that only one isomer was obtained.

(Z)-1-Phenyl-1,4-bis(trimethylsilyl)but-1-en-3-yne: ¹H NMR (500 MHz, CDCl₃): δ 7.29–7.21 (m, 3H), 7.05–7.03 (m, 2H), 6.14 (s, 1H), 0.25–0.22 (m, 18H); ¹³C NMR (125 MHz, CDCl₃): 159.8, 145.1, 128.0, 126.7, 126.4, 122.0, 104.9, 100.5, -0.3, -0.4. GC MS (EI) m/z (relative intensity): 272 (27), 257 (52), 199 (17), 155 (16), 73 (100).

The compound data do not agree with those reported in the literature.⁶ We argue that the structure assignment proposed here is correct and the data reported in the literature is erroneous based on the following:

1) The stereochemistry was confirmed by NOE measurement (see the chart in section 5). The vinyl C–H interacted with phenyl’s aromatic C–H, in agreement with the proposed (Z) stereochemistry.

2) The regiochemistry was determined by protodesilylation of the product with TBAF⁷ to produce the known (E)-4-phenylbut-3-en-1-yne. The compound data was in

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good agreement with the literature.\(^8\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.40–7.35 \) (m, 2H), \(7.33–7.30 \) (m, 3H), \(7.06–7.03 \) (d, \(J = 16.4\) Hz, 1H), \(6.15–6.12, \) (dd, \(J = 16.3\) Hz, 2.3 Hz, 1H), \(3.05 \) (d, \(J = 2.3\) Hz, 1H).

![Chemical structure](image)

\((Z)\)-1-(4-Fluorophenyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (Table 1, entry 2)

\[\text{F} \quad \text{Me}_3\text{Si} \quad \text{Ph} \quad \text{SiMe}_3 \]

The general procedure was applied to 1,4-bis(trimethylsilyl)-1,3-butadiyne (77 mg, 0.40 mmol) in diethyl ether (1.52 mL) and 4-fluorophenyl magnesium bromide (0.48 mL, 1.00 mol/l, 0.48 mmol) in diethyl ether. The crude product was purified by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, colorless oil, in 69% yield (80 mg).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.01–6.95 \) (m, 4H), \(6.12 \) (s, 1H), \(0.26–0.19 \) (m, 18H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(161.7 \) (d, \(J = 244\) Hz), \(158.7, 141.0 \) (d, \(J = 3.0\) Hz), \(128.2 \) (d, \(J = 7.2\) Hz), \(122.3 \) (d, \(J = 1.2\) Hz), \(114.8 \) (d, \(J = 21\) Hz), \(104.7, 100.8, –0.3, -0.5.\) GC MS (EI) \(m/z\) (relative intensity): 290 (19), 275 (28), 155 (38), 73 (100).

\((Z)\)-1-(4-Methoxyphenyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (Table 1, entry 3)

![Chemical structure](image)

The general procedure was applied to 1,4-bis(trimethylsilyl)-1,3-butadiyne (78 mg, 0.40 mmol) in diethyl ether (0.4 mL) and 4-methoxyphenylmagnesium bromide (1.6 mL, 0.30 mol/l, 0.48 mmol) in diethyl ether.


and benzene. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to afford the title compound as a single isomer, yellow solid, in 83% yield (100 mg). Mp: 67–68 °C.

\(^1\)H NMR (500 MHz, CDCl$_3$): \(\delta\) 7.00–6.98 (m, 2H), 6.83–6.81 (m, 2H), 6.12 (m, 1H), 3.79 (s, 3H), 0.26–0.21 (m, 18H); \(^{13}\)C NMR (125 MHz, CDCl$_3$): 159.2, 158.4, 137.5, 127.9, 121.3, 113.4, 105.2, 100.2, 55.2, –0.30. GC MS (EI) \(m/z\) (relative intensity): 302 (44), 287 (26), 155 (48), 132 (48), 73 (100).

\((Z)-1-(4\text{-Methylphenyl})-1,4\text{-bis}(\text{trimethylsilyl})\text{but-1-en-3-yne (Table 1, entry 4)}\)

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \equiv \\
\text{SiMe}_3 & \quad \equiv 
\end{align*}
\]

The general procedure was applied to 1,4-bis(trimethylsilyl)-1,3-butadiyne (80 mg, 0.41 mmol) in diethyl ether (1.30 mL) and 4-methylphenyl magnesium bromide (0.70 mL, 0.69 mol/l, 0.48 mmol) in diethyl ether. The crude product was purified by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, colorless oil, in 69% yield (80 mg).

\(^1\)H NMR (500 MHz, CDCl$_3$): \(\delta\) 7.10–7.08 (m, 2H), 6.95–6.93 (m, 2H), 6.12 (s, 1H), 2.33 (m, 3H), 0.26–0.22 (m, 18H); \(^{13}\)C NMR (125 MHz, CDCl$_3$): 159.7, 142.2, 136.1, 128.7, 126.6, 121.6, 105.1, 100.3, 21.1, –0.31, -0.36. GC MS (EI) \(m/z\) (relative intensity): 286 (21), 271 (32), 173 (30), 155 (43), 73 (100).

\((Z)-1-(2,4,6\text{-Trimethylphenyl})-1,4\text{-bis}(\text{trimethylsilyl})\text{but-1-en-3-yne (Table 1, entry 5)}\)

\[
\begin{align*}
\text{Me}_3\text{Si} & \quad \equiv \\
\text{SiMe}_3 & \quad \equiv 
\end{align*}
\]

The general procedure was applied to 1,4-bis(trimethylsilyl)-1,3-butadiyne (80 mg, 0.41 mmol) in diethyl ether (1.50 mL) and 2-mesitylmagnesium bromide (0.48 mL, 1.00 mol/l, 0.48 mmol) in diethyl ether. The crude product was
purified by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, yellow oil, in 65% yield (84 mg).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.82 (s, 2H), 5.97 (s, 1H), 2.26 (s, 3H), 2.09 (s, 6H), 0.23 (s, 9H), 0.17 (s, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$): 161.8, 141.5, 135.4, 134.0, 128.2, 128.1, 122.1, 105.1, 99.9, 21.2, 21.1, 0.01, -0.73. GC MS (EI) $m/z$ (relative intensity): 314 (15), 299 (8), 226 (18), 144 (33), 125 (38), 73 (100).

1,1,4-Triphenylbut-1-en-3-yne (Table 1, entry 6)

\[
\begin{align*}
\text{Ph} & \equiv \text{Ph} \\
\text{Ph} & \equiv \text{Ph}
\end{align*}
\]

The general procedure was applied to 1,4-diphenyl-1,3-butadiyne (79 mg, 0.40 mmol) in diethyl ether (1.65 mL) and phenylmagnesium bromide in diethyl ether (0.35 mL, 1.46 mol/L, 0.48 mmol) The crude product was purified by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, yellow solid, in 62% yield (68 mg). The compound data was in good accordance with the literature.\textsuperscript{9} Mp: 102–103 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.55–7.53 (m, 2H), 7.42–7.37 (m, 3H), 7.33 (s, 5H), 7.29–7.25 (m, 5H), 6.24 (s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$): 152.7, 141.4, 139.2, 131.4, 130.2, 128.32, 128.30, 128.24, 128.16, 128.03, 128.00, 127.8, 123.6, 107.1, 93.7, 89.2.

GC MS (EI) $m/z$ (relative intensity): 280 (100), 202 (35), 77 (39).

(Z)-1-Methyl-1,4-diphenylbut-1-en-3-yne (Table 1, entry 7)

\[
\begin{align*}
\text{NH} & \equiv \text{NH} \\
\text{NH} & \equiv \text{NH}
\end{align*}
\]

The general procedure was applied to 1,4-bis(trimethylsilyl)-1,3-butadiyne (78 mg, 0.40 mmol) in diethyl ether (1.70 mL) and methylmagnesium

bromide in diethyl ether (0.27 mL, 1.78 mol/l, 0.48 mmol). GC and GC MS analysis indicated the presence of two isomers in the crude reaction mixture in 90:10 ratio. The \(^1\)H NMR spectrum of the isomer mixture is shown in section 5. The crude product was purified two times by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, white solid, in 48% yield (41 mg).

Data for the major isomer:

Mp: 86–87 °C.

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.50–7.48 (m, 4H), 7.38–7.26 (m, 6H), 6.12 (d, \(J = 1.2\) Hz, 1H), 2.41 (d, \(J = 1.2\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 148.3, 140.9, 131.3, 128.4, 128.3, 128.1, 128.0, 125.5, 123.7, 106.6, 95.2, 88.2, 18.7. GC MS (EI) \(m/z\) (relative intensity): 218 (100), 202 (81), 115 (28), 77 (52).

\((E)\)-5-Phenylbut-5-en-7-yne (Table 1, entry 8)

\[
\begin{array}{c}
\text{Ph} \\
\text{n-Bu} \\
\text{n-Bu}
\end{array}
\]

The general procedure was applied to 5,7-dodecadiyne (54 mg, 0.33 mmol) in diethyl ether (1.4 mL) and phenylmagnesium bromide in diethyl ether (0.27 mL, 1.46 mol/l, 0.40 mmol). GC and GC MS analysis indicated the presence of two isomers in the crude reaction mixture in 88:12 ratio. The crude product was purified two times by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, colorless oil, in 66% yield (52 mg).

Data for the major isomer:

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.38–7.25 (m, 5H), 5.76–5.75 (t, \(J = 2.3\) Hz, 1H), 2.78–2.75 (m, 2H), 2.43–2.40 (m, 2H), 1.60–1.32 (m, 8H), 0.96–0.88 (m, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): 152.2, 140.6, 128.3, 127.6, 125.9, 107.3, 95.7, 78.9, 31.8, 31.0, 30.5, 22.6, 22.0, 19.4, 13.9, 13.6. GC MS (EI) \(m/z\) (relative intensity): 240 (19), 155 (34), 141 (100), 91 (24).

\(1,1\)-Diphenyl-4-trimethylsilylbut-1-en-3-yne (Table 1, entry 9)

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{TMS}
\end{array}
\]
The general procedure was applied to 1-trimethylsilyl-4-phenyl-1,3-butyadiyne (59 mg, 0.30 mmol) in diethyl ether (1.67 mL) and phenylmagnesium bromide in diethyl ether (0.33 mL, 1.46 mol/L, 0.48 mmol). The crude product was purified by column chromatography on silica gel (hexane 100%) to afford the title compound as a single isomer, yellow oil, in 64% yield (53 mg). The compound data was in good accordance with the literature.10

1H NMR (500 MHz, CDCl3): δ 7.50–7.48 (m, 2H), 7.36–7.24 (m, 8H), 6.01 (s, 1H), 0.12 (s, 9H); 13C NMR (125 MHz, CDCl3): 154.0, 141.4, 138.8, 130.1, 128.4, 128.3, 128.2, 128.1, 127.6, 107.0, 104.3, 99.4, -0.28. GC MS (EI) m/z (relative intensity): 276 (63), 261 (100), 245 (49), 215 (31).

(Z)-2-Allyl-1-phenyl-1,4-bis(trimethylsilyl)but-1-en-3-yne (Scheme 1)

In an oven-dried Schlenk tube, FeCl2 (5.0 mg, 0.04 mmol) was added to a solution of 1,4-diphenyl-1,3-butyadiyne (79 mg, 0.40 mmol) in diethyl ether (1.6 mL). After 15 minutes, a solution of phenylmagnesium bromide in diethyl ether (0.35 mL, 1.46 mol/L, 0.48 mmol) was added to the reaction mixture at room temperature, and the resulting mixture was stirred at room temperature for an additional 3 hours. Next allyl bromide (0.05 mL, 0.60 mmol) was added to the reaction mixture at room temperature, and the resulting mixture was stirred at room temperature for an additional 12 hours, then H2O (3.0 mL) was added. The organic phase was extracted with ethyl acetate (3 × 5 ml), and the mixture was passed over a pad of Florisil. The volatiles were removed in vacuo to obtain an oily brown residue. The crude mixture was purified by column chromatography (hexane 100%) to afford the desired compound as a single isomer, yellow oil, in 57% yield (72 mg).

1H NMR (500 MHz, CDCl3): δ 7.29–7.26 (m, 2H), 7.18–7.15 (m, 1H), 6.85–6.84 (m, 2H), 5.82–5.77 (m, 1H), 4.98–4.91 (m, 2H), 2.72–2.71 (m, 2H), 0.27–0.13 (m, 18H);

$^{13}$C NMR (125 MHz, CDCl$_3$): 154.2, 143.6, 136.3, 132.2, 128.7, 127.6, 126.3, 116.4, 107.6, 99.5, 40.4, 0.49, 0.00. GC MS (EI) $m/z$ (relative intensity): 239 (2, M–TMS), 223 (12), 209 (11), 183 (19), 73 (100).

**1,1,2,4-Tetraphenylbut-1-en-3-yne (eq 1)**

![Chemical Structure](image)

In an oven-dried Schlenk tube, FeCl$_2$ (5.0 mg, 0.04 mmol) was added to a solution of 1,4-diphenyl-1,3-butadiyne (80 mg, 0.40 mmol) in diethyl ether (1.6 mL). After 15 minutes, a solution of phenylmagnesium bromide in diethyl ether (0.35 mL, 1.46 mol/L, 0.48 mmol) was added to the reaction mixture at room temperature, and the resulting mixture was stirred at room temperature for an additional 3 hours. Next PdCl$_2$(PPh$_3$)$_2$ (28 mg, 0.04 mmol) and PhI (0.05 mL, 98 mg, 0.48 mmol) were added, and the mixture was stirred for 12 hours. H$_2$O (3.0 mL) was added, the organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of florisil. The volatiles were removed *in vacuo* to obtain an oily brown residue. The crude mixture was purified by column chromatography (hexane 100%) to afford the desired compound as a single isomer, yellow solid, in 46% yield (66 mg). The compound data was in good accordance with the literature.$^{11}$ Mp: 124–126 °C.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.57–7.56 (m, 2H), 7.38–7.32 (m, 5H), 7.25–7.11 (m, 11H), 7.02–7.01 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): 148.9, 142.7, 141.4, 139.6, 131.3, 131.1, 130.5, 130.0, 128.2, 127.93, 127.89, 127.87, 127.8, 127.6, 127.2, 127.0, 123.6, 121.5, 92.9, 92.4. GC MS (EI) $m/z$ (relative intensity): 356 (100), 279 (80), 178 (41).

**(Z)-1,4-Bis(trimethylsilyl)-1-phenyl-2-(((E)-styryl)but-1-en-3-yne (eq 2)**

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In an oven-dried Schlenk tube, FeCl₂ (5.0 mg, 0.04 mmol) was added to a solution of 1,4-diphenyl-1,3-butadiyne (79 mg, 0.40 mmol) in diethyl ether (1.6 mL). After 15 minutes, a solution of phenylmagnesium bromide in diethyl ether (0.35 mL, 1.46 mol/L, 0.48 mmol) was added to the reaction mixture at room temperature, and the resulting mixture was stirred at room temperature for an additional 3 hours, then NiCl₂(dppe) (21 mg, 0.04 mmol) and β-bromostyrene (0.8 mL, 77 mg, 0.60 mmol) were added. After stirring at room temperature for an additional 12 hours, H₂O was added. The organic phase was extracted with ethyl acetate (3 × 5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed in vacuo to obtain an oily brown residue. The crude mixture was purified by column chromatography (hexane 100%) to afford the desired compound as yellow solid in 43% yield (66 mg) containing a small amount of isomer (< 5%). Mp: 85–88 °C

\[ ^1H \text{NMR (500 MHz, CDCl}_3\text{): } \delta 7.34–7.31 (m, 2H), 7.26–7.19 (m, 6H), 7.10–7.06 (d, } J = 15.8 \text{ Hz, 1H), 6.93–6.92 (m, 2H), 6.61–6.57 (d, } J = 15.7 \text{ Hz, 1H), 0.31 (s, 9H), 0.19 (s, 9H); } ^{13}\text{C NMR (125 MHz, CDCl}_3\text{): } 155.3, 142.5, 137.1, 132.5, 131.0, 128.5, 128.0, 127.7, 127.4, 126.9, 126.4, 125.9, 103.6, 100.8, -0.25, -0.64. GC MS (EI) m/z (relative intensity): 374 (14), 285 (22), 271 (17), 155 (28), 73 (100).\]

\((E)-2\text{-Iodo-1,4-bis(trimethylsilyl)-1-phenylbut-1-en-3-yne (eq 3)}\)

In an oven-dried Schlenk tube, FeCl₂ (5.0 mg, 0.04 mmol) was added to a solution of 1,4-diphenyl-1,3-butadiyne (79 mg, 0.40 mmol) in diethyl ether (1.6 mL). After 15 minutes, a solution of phenylmagnesium bromide in diethyl ether (0.35 mL, 1.46 mol/L, 0.48 mmol) was added to the reaction mixture at room temperature, and...
the resulting mixture was stirred at room temperature for an additional 3 hours, then ZnCl₂ (65 mg) was added. After 30 minutes, I₂ (122 mg) was added, and the resulting mixture was stirred at room temperature for an additional 12 hours, then H₂O (3 mL) was added. The organic phase was extracted with ethyl acetate (3 × 5 ml), and the mixture was passed over a pad of Florisil. The volatiles were removed in vacuo to obtain an oily brown residue. The crude mixture was purified by column chromatography (hexane 100%) to afford the desired compound as a single isomer, yellow oil, in 49% yield (79 mg). Mp: 45–47 °C.

¹H NMR (500 MHz, CDCl₃): δ 7.35–7.32 (m, 2H), 7.26–7.25 (m, 1H), 6.84–6.82 (m, 2H), 0.25–0.17 (m, 18H); ¹³C NMR (125 MHz, CDCl₃): 164.4, 148.7, 128.8, 127.2, 126.6, 107.1, 101.5, 86.4, 0.08, 0.00 GC MS (EI) m/z (relative intensity): 271 (22), 183 (66), 73 (100).
5. $^1$H and $^{13}$C NMR Spectra

$^1$H NMR and $^{13}$C NMR of (Z)-1-Phenyl-1,4-bis(trimethylsilyl)but-1-en-3-yne (Scheme 1)
NOE measurement of (Z)-1-Phenyl-1,4-bis(trimethylsilyl)but-1-en-3-yne (Scheme 1)
Crude $^1$H NMR and of (E)-4-phenylbut-3-en-1-yne
$^1$H NMR and $^{13}$C NMR of (Z)-1-(4-Fluorophenyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (Table 1, entry 2)
$^1$H NMR and $^{13}$C NMR of (Z)-1-(4-Methoxyphenyl)-1,4-bis(trimethylsilyl) but-1-en-3-yne (Table 1, entry 3)
$^1$H NMR and $^{13}$C NMR of (Z)-1-(4-Methylphenyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (Table 1, entry 4)
$^1$H NMR and $^{13}$C NMR of (Z)-1-(2,4,6-trimethylphenyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (Table 1, entry 5)
$^1$H NMR and $^{13}$C NMR of 1,1,4-Triphenylbut-1-en-3-yne (Table 1, entry 6)
$^1$H NMR and $^{13}$C NMR of (Z)-1-Methyl-1,4-diphenylbut-1-en-3-yne (Table 1, entry 7)
Crude $^1$H NMR of (Z)-1-Methyl-1,4-diphenylbut-1-en-3-yne (Table 1, entry 8)
$^1$H NMR and $^{13}$C NMR of (E)-5-Phenylbut-5-en-7-yne (Table 1, entry 7)
$^1$H NMR and $^{13}$C NMR of 1,1-Diphenyl-4-trimethylsilylbut-1-en-3-yne (Table 1, entry 9)
$^1$H NMR and $^{13}$C NMR of (Z)-2- Allyl-1 -phenyl-1,4-bis(trimethylsilyl)but-1-en-3-yne (Scheme 1)
$^1$H NMR and $^{13}$C NMR of 1,1,2,4-Tetraphenylbut-1-en-3-yne (eq 1)
$^1$H NMR and $^{13}$C NMR of (Z)-1,4-bis(trimethylsilyl)-1-phenyl-2-((E)-styryl)but-1-en-3-yne (eq 2)
$^1$H NMR and $^{13}$C NMR of (E)-2-Iodo-1,4-bis(trimethylsilyl)-1-phenylbut-1-en-3-yne (eq 3)