Supporting Information for Cobalt-Catalyzed Cross-Coupling of Alkynyl Grignard Reagents with Alkenyl Triflates

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General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA500 (1H, 500 MHz; 13C, 125 MHz) spectrometer or a JEOL JNM FX-400 (1H, 400 MHz; 13C, 100 MHz) spectrometer using tetramethylsilane as an internal standard. High-resolution mass spectra (ESI, APCI or APPI) were obtained with a Bruker Daltonics microTOF-Q spectrometer. Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-908 equipped with JAIGEL-1H and -2H using chloroform as an eluent. Unless otherwise noted, reagents were commercially available and used without further purification. Tetrahydrofuran was purified by passing through a alumina/catalyst column system (GlassContour Co.).

Cobalt-Catalyzed Coupling of Alkynylmagnesium Bromides with Alkenyl Triflates (Table 2): A General Procedure. To an alkyne (0.50 mmol) placed in a 20 mL Schlenk tube was added ethylmagnesium bromide (ca. 1.0 M THF solution, 0.45 mmol) at room temperature, and it was stirred for 30 min. To the mixture was added THF (0.50 mL), Co(acac)₃ (2.7 mg, 7.5 µmol) and an alkenyl triflate (0.25 mmol). After stirring at the temperature for the time both specified in Table 2, a 0.1 M HCl aqueous solution (10 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (10 mL), and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC or column chromatography (SiO₂) gave the corresponding enyne. Further purification with GPC was required in some cases.

In the coupling of triethylsilylethynylmagnesium bromide (1f) with 1-octen-2-yl triflate (2g), the alkyne-derived products were surveyed. Thus, triethylsilylacetylene (0.090 mL, 0.50 mmol), ethylmagnesium bromide (0.97 M, 0.48 mL, 0.47 mmol) and 2g (65 mg, 0.25 mmol) were subjected to the general procedure described above. 1H NMR analysis using nitromethane as an internal standard showed that the crude product contains 0.25 mmol of coupling product 3fg and 0.10 mmol of triethylsilylacetylene. The crude product was separated by preparative recycling GPC into two fractions. The first fraction is consisting of polymeric compounds (8.2 mg corresponding to 0.058 mmol of triethylsilylacetylene unit), the 1H NMR of which shows two major sets of broadened peaks at regions of Et₃Si group. The lower molecular weight fraction mainly contains 3fg and 1,4-bis(triethylsilyl)-1,3-butadiyne, the amount of which was estimated to be 0.040 mmol in comparison with that (0.25 mmol as estimated above) of 3fg.

2-Hexyl-1-decen-3-yne (3aa). A colorless oil. 1H NMR (400 MHz, CDCl₃) δ 0.88 (t, J = 7.2 Hz, 3 H), 0.89 (t, J = 6.8 Hz, 3 H), 1.16–1.45 (m, 12 H), 1.45–1.58 (m, 4 H), 2.11 (t, J = 7.6 Hz, 2 H), 2.30 (t, J = 7.2 Hz, 2
H), 5.11 (d, J = 1.6 Hz, 1 H), 5.20 (d, J = 1.6 Hz, 1 H).

**6-Pentadecen-8-yne (3ab).** A colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.88 (t, J = 7.1 Hz, 3 H), 0.89 (t, J = 6.9 Hz, 3 H), 1.20–1.45 (m, 12 H), 1.51 (quint, J = 7.3 Hz, 2 H), 2.07 (q, J = 7.1, 2 H), 2.28 (t, J = 6.3 Hz, 2 H), 5.45 (d, J = 15.9 Hz 1 H), 6.04 (dt, J = 15.9, 7.1 Hz, 1 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.99, 14.04, 19.4, 22.47, 22.54, 28.5, 28.6, 28.8, 31.3, 31.4, 32.9, 79.2, 88.7, 109.8, 143.4. HRMS (APPI) Calcd for C$_{13}$H$_{26}$: M$^+$, 206.202902. Found: $m/z$ 206.202898.

**1-(1-Octynyl)cyclopentene (3ac).** A colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (t, J = 6.8 Hz, 3 H), 1.21–1.44 (m, 6 H), 1.53 (quint, J = 7.2 Hz, 2 H), 1.87 (quint, J = 7.6 Hz, 2 H), 2.31 (t, J = 7.2 Hz, 2 H), 2.35–2.48 (m, 4 H), 5.93 (t, J = 2.0 Hz, 1 H).

**1-(1-Octynyl)cyclohexene (3ad).** A colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89 (t, J = 6.4 Hz, 3 H), 1.16–1.40 (m, 4 H), 1.39 (quint, J = 7.0 Hz, 2 H), 1.51 (quint, J = 7.2 Hz, 2 H), 1.50–1.70 (m, 4 H), 1.96–2.20 (m, 4 H), 2.28 (t, J = 7.0 Hz, 2 H), 6.00 (bs, 1 H).

**1-(1-Octynyl)cycloheptene (3ae).** A colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89 (t, J = 6.8 Hz, 3 H), 1.20–1.43 (m, 6 H), 1.44–1.61 (m, 6 H), 1.67–1.78 (m, 2 H), 2.15 (q, J = 6.0 Hz, 2 H), 2.28 (t, J = 7.0 Hz, 2 H), 2.23–2.34 (m, 2 H), 6.19 (t, J = 6.6 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 19.4, 22.5, 26.5, 26.6, 28.6, 28.9, 29.0, 31.3, 32.2, 34.6, 83.9, 87.4, 127.3, 138.1. Anal. Calcd for C$_{15}$H$_{34}$: C, 88.16; H, 11.84. Found: C, 88.39; H, 12.05.

**1-(1-Octynyl)-3,4-dihyronaphthalene (3af).** A pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.91 (t, J = 6.8 Hz, 3 H), 1.22–1.39 (m, 4 H), 1.47 (quint, J = 7.5 Hz, 2 H), 1.61 (quint, J = 7.3 Hz, 2 H), 2.27 (td, J = 8.0, 4.8 Hz, 2 H), 2.42 (t, J = 7.0 Hz, 2 H), 2.78 (t, J = 8.0 Hz, 2 H), 6.36 (t, J = 4.8 Hz, 1 H), 7.09 (d, J = 6.8 Hz, 1 H), 7.16 (td, J = 7.4, 1.5 Hz, 1 H), 7.22 (td J = 7.4, 1.5 Hz, 1 H), 7.57 (d, J = 7.2 Hz, 1 H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.1, 19.4, 22.6, 23.5, 27.3, 28.6, 28.9, 31.4, 78.2, 91.2, 122.0, 125.0, 126.5, 127.2, 127.4, 133.2, 133.9, 135.2. Anal. Calcd for C$_{18}$H$_{22}$: C, 90.70; H, 9.30. Found: C, 90.54; H, 9.51.

**2-(1-Octynyl)-3,4-dihyronaphthalene (3ag).** A pale yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90 (t, J = 7.0 Hz, 3 H), 1.23–1.48 (m, 6 H), 1.57 (quint, J = 7.2 Hz, 2 H), 2.37 (t, J = 7.2 Hz, 2 H), 2.41 (td, J = 8.4, 1.6 Hz, 2 H), 2.82 (t, J = 8.4 Hz, 2 H), 6.68 (bs, 1 H), 7.00 (d, J = 6.4 Hz, 1 H), 7.06–7.17 (m, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.0, 19.6, 22.5, 27.7, 28.2, 28.6, 28.8, 31.4, 81.9, 92.7, 122.0, 126.0, 126.5, 127.2, 127.3, 131.7, 134.0, 134.6. Anal. Calcd for C$_{18}$H$_{32}$: C, 90.70; H, 9.30. Found: C, 90.62; H, 9.32.
2,3-Dimethyl-2-tridecen-4-yne (3bh). A pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 6.9\) Hz, 3 H), 1.20–1.35 (m, 8 H), 1.36–1.46 (m, 2 H), 1.48–1.58 (m, 2 H), 1.71 (s, 3 H), 1.78 (s, 3 H), 1.91 (s, 3 H), 2.33 (t, \(J = 7.0\) Hz, 2 H).

1-(tert-Butoxycarbonyl)-4-(1-octynyl)-3,4-didehydroperipiperidine (3ai). A colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 6.8\) Hz, 3 H), 1.21–1.58 (m, 8 H), 1.46 (s, 9 H), 2.21 (bs, 2 H), 2.29 (t, \(J = 7.2\) Hz, 2 H), 3.48 (t, \(J = 5.6\) Hz, 2 H), 3.93 (bs, 2 H), 5.90 (bs, 1 H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 14.0, 19.2, 22.5, 28.3, 28.39, 28.45, 28.48, 28.7, 29.6, 31.23, 31.27, 79.7, 80.6, 83.5, 89.5, 93.0, 154.7. HRMS (ESI) Calcd for C\(_{19}\)H\(_{29}\)NO\(_2\)\+: [M–H+Li]\(^+\), 297.227498. Found: \(m/z\) 297.227375.

6-Methylidene-1-tetradeac-7-yne (3aj). A pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 7.0\) Hz, 3 H), 1.24–1.36 (m, 4 H), 1.40 (quint, \(J = 7.4\) Hz, 2 H), 1.53 (quint, \(J = 7.3\) Hz, 2 H), 1.62 (quint, \(J = 7.5\) Hz, 2 H), 2.07 (q, \(J = 7.2\) Hz, 2 H), 2.15 (t, \(J = 7.5\) Hz, 2 H), 2.30 (t, \(J = 7.1\) Hz, 2 H), 4.94–4.98 (m, 1 H), 5.02 (dq, \(J = 17.1, 1.8\) Hz, 1 H), 5.13 (d, \(J = 1.7\) Hz, 1 H), 5.22 (d, \(J = 1.7\) Hz, 1 H), 5.81 (ddt, \(J = 17.1, 10.3, 6.7\) Hz, 1 H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 14.0, 19.3, 22.5, 27.3, 28.5, 28.7, 31.3, 32.9, 36.9, 80.9, 90.3, 114.6, 119.6, 132.0, 138.6. HRMS (APCI) Calcd for C\(_{12}\)H\(_{24}\): [M+H]\(^+\), 205.195077. Found: \(m/z\) 205.194914.

1-Dodec-3-yne (3bk). A pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 7.0\) Hz, 3 H), 1.21–1.43 (m, 10 H), 1.53 (quint, \(J = 7.2\) Hz, 2 H), 2.30 (td, \(J = 7.2, 2.2\) Hz, 2 H), 5.37 (dd, \(J = 11.3, 2.2\) Hz, 1 H), 5.54 (dd, \(J = 17.4, 2.2\) Hz, 1 H), 5.78 (ddt, \(J = 17.4, 11.3, 2.2\) Hz, 1 H).

2-Ethynyl-3,4-dihydronaphthalene (3cg). A colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.45 (t, \(J = 8.2\) Hz, 2 H), 2.85 (t, \(J = 8.2\) Hz, 2 H), 3.13 (s, 1 H), 6.85 (bs, 1 H), 7.01–7.06 (m, 1 H), 7.08–7.20 (m, 3 H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 27.42, 27.44, 78.9, 85.0, 120.0, 126.5, 126.6, 127.5, 127.9, 133.3, 134.7, 134.9. HRMS (APCI) Calcd for C\(_{12}\)H\(_10\): [M+H]\(^+\), 155.085527. Found: \(m/z\) 155.085814.

2-(3,3-Dimethyl-1-butynyl)-3,4-dihydronaphthalene (3dg). A pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 1.28 (s, 9 H), 2.40 (t, \(J = 8.3\) Hz, 2 H), 2.81 (t, \(J = 8.3\) Hz, 2 H), 6.67 (bs, 1 H), 6.99 (d, \(J = 7.0\) Hz, 1 H), 7.04–7.17 (m, 3 H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 27.7, 28.1, 28.3, 31.1, 80.4, 100.7, 122.0, 126.0, 126.5, 127.1, 127.3, 131.7, 134.0, 134.7. Anal. Calcd for C\(_{16}\)H\(_{18}\): C, 91.37; H, 8.63. Found: C, 91.33; H, 8.80.

2-Hexyl-4-phenyl-1-buten-3-yne (3ea). A pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 6.9\) Hz, 2 H), 1.25–1.39 (m, 6 H), 1.59 (quint, \(J = 5.6\) Hz, 2 H), 1.61 (m, 8 H), 2.21 (bs, 2 H), 2.29 (t, \(J = 7.2\) Hz, 2 H), 3.45–3.48 (m, 2 H), 3.93 (bs, 2 H), 5.92 (bs, 1 H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 14.0, 19.3, 22.5, 27.3, 28.5, 28.7, 31.3, 32.9, 36.9, 80.9, 90.3, 114.6, 119.6, 132.0, 138.6. HRMS (APCI) Calcd for C\(_{18}\)H\(_{24}\): [M+H]\(^+\), 205.195077. Found: \(m/z\) 205.194914.

2-Hexyl-4-phenyl-1-buten-3-yne (3ea). A pale yellow oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.89 (t, \(J = 6.9\) Hz, 2 H), 1.25–1.39 (m, 6 H), 1.59 (quint, \(J = 5.6\) Hz, 2 H), 1.61 (m, 8 H), 2.21 (bs, 2 H), 2.29 (t, \(J = 7.2\) Hz, 2 H), 3.45–3.48 (m, 2 H), 3.93 (bs, 2 H), 5.92 (bs, 1 H). \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 14.0, 19.3, 22.5, 27.3, 28.5, 28.7, 31.3, 32.9, 36.9, 80.9, 90.3, 114.6, 119.6, 132.0, 138.6. HRMS (APCI) Calcd for C\(_{18}\)H\(_{24}\): [M+H]\(^+\), 205.195077. Found: \(m/z\) 205.194914.
temperature. After addition of CuI (1.2 mg, 6.3 µmol), the mixture was stirred at 60 °C for 6 h.

\[ \text{CDCl}_6 \]

The palladium-catalyzed coupling of 3al with phenylacetylene followed the literature procedure with slight modification. A mixture of PdCl₂(PPh₃)₂ (17.5 mg, 0.0249 mmol), PPh₃ (3.3 mg, 0.013 mmol), phenylacetylene (75.2 mg, 0.736 mmol), 3al (168 mg, 0.530 mmol), and triethylamine (110 mg, 1.09 mmol) in THF (2.0 mL) was stirred for 20 min at room temperature. After addition of CuI (1.2 mg, 6.3 µmol), the mixture was stirred at 60 °C for 6 h. The solvent was evaporated, and the residue was treated with pentane. Filtration through Celite, evaporation of the solvent, and purification with PTLC (SiO₂, hexane/EtOAc = 87/13) gave 2-(1-octynyl)-6-phenylethynyl-3,4-dihydropyran (4: 169 mg, 94%).

\[ \text{Supplementary Material (ESI) for Chemical Communications} \]
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MHz, CDCl$_3$ $\delta$ 0.91 (t, $J = 6.9$ Hz, 3 H), 1.24–1.42 (m, 4 H), 1.43 (quint, $J = 7.2$ Hz, 2 H), 1.57 (quint, $J = 7.3$ Hz, 2 H), 2.38 (t, $J = 7.2$ Hz, 2 H), 2.42 (t, $J = 8.2$ Hz, 2 H), 2.82 (t, $J = 8.2$ Hz, 2 H), 6.67 (bs, 1 H), 6.97 (d, $J = 7.9$ Hz, 1 H), 7.24–7.37 (m, 5 H), 7.51 (d, $J = 8.0$ Hz, 2 H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 14.0, 19.7, 22.5, 27.5, 28.2, 28.6, 28.8, 31.4, 81.9, 89.7, 89.9, 93.7, 121.7, 123.2, 123.4, 125.9, 128.1, 128.3, 129.9, 130.4, 131.3, 131.6, 134.1, 134.6. HRMS (APCI) Calcd for C$_{24}$H$_{26}$: [M+K]$^+$, 353.166609. Found: $m/z$ 353.166646.

**Stoichiometric Reactions of Co(acac)$_3$, an AlkynylMagnesium Bromide and an Alkenyl Triflate (Scheme 5).** To triethylsilylacetylene (0.44, 0.55 or 0.88 mmol) placed in a 20 mL Schlenk tube was added ethylmagnesium bromide (0.93 M THF solution, 0.40, 0.50 or 0.80 mmol) at room temperature, and it was stirred for 30 min. To the mixture was added THF (0.80 mL) and Co(acac)$_3$ (35.6 mg, 0.100 mmol). After stirring at 20 °C for 10 min, 2-(trifluoromethanesulfonyloxy)-3,4-dihydronaphthalene (2g: 27.8 mg, 0.100 mmol) was added and the stirring was continued for 2 h. A 0.1 M HCl aqueous solution (10 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (10 mL) and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by $^1$H NMR using nitromethane as an internal standard.

**References**