Supporting Information for

Iron-catalyzed carbolithiation of alkynes having no heteroatoms

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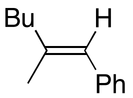
General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL JNM LA500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz) using tetramethylsilane (^{1}H and ^{13}C) as an internal standard. GC spectra were taken on Hewlett-Packard HP6890. GC-MS spectra were taken on Shimazu GCMS-QP5050A. High-resolution mass spectra were obtained with a Bruker Daltonics microTOF-Q spectrometer (APCI and ESI). 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. Diethyl ether was purified by passing through an alumina/catalyst column system (GlassContour Co.). Isobutyl-, 3,5-xylyl- and phenyllithiums were prepared from the corresponding halides by halogen–lithium exchange using *t*-BuLi (2 equiv).

Iron-Catalyzed Alkyllithiation of Alkynes (Table 2).

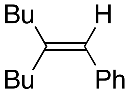
Method A: A solution of $FeCl_3$ (3.7 mg, 23 μmol), PPh_3 (11.8 mg, 45 μmol), and *N,N,N',N'*-tetramethylethylenediamine (TMEDA: 13.6 μL, 90 μmol) in diethyl ether (1.7 mL) was placed in a 20 mL Schlenk tube and stirred for 10 min at –20 °C. To this solution was added successively an alkyne (0.45 mmol) and a solution of an alkyllithium (0.68 mmol), and the mixture was stirred at –20 °C. After the time specified in Table 2, methanol (0.20 mL) was added and stirring was continued for 5 min. H_2O (10 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2) gave the corresponding alkyllithiation products, whose isomer ratio was determined by GC and ^{1}H NMR. The product was further purified by GPC if necessary.

Method B: To a solution of $FeCl_3$ (3.2 mg, 20 μmol), PPh_3 (10.5 mg, 40 μmol), and an alkyne (0.60 mmol) in diethyl ether (1.0 mL) placed in a 20 mL Schlenk tube was added Zn powder (5.2 mg, 80 μmol) at room temperature and the reaction mixture was stirred for 10 min. To this solution was added successively *N,N,N',N'*-tetramethylethylenediamine (TMEDA: 12.0 μL, 80 μmol) and a solution of an alkyllithium (0.40 mmol), and the mixture was stirred at –20 °C. After the time specified in Table 2, methanol (0.20 mL) was added and stirring was continued for 5 min. H_2O (1.0 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2) gave the corresponding butyllithiation products, whose isomer ratio was determined by GC and ^{1}H NMR. The product was further purified if necessary.

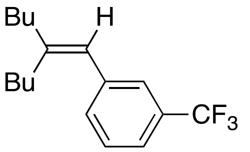


(*E*)-2-Methyl-1-phenyl-1-hexene (5a, entry 9 of Table 1, cf. Method B in Table 2).[1] A colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3 H), 1.36 (sext, *J* = 7.4 Hz, 2 H), 1.49 (quint, *J* = 7.8 Hz, 2 H), 1.85 (d, *J* = 1.3 Hz, 3 H), 2.17 (t, *J* = 7.6 Hz, 2 H), 6.26 (s, 1

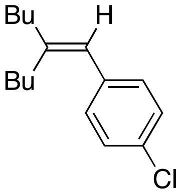
H), 7.17 (t, J = 7.3 Hz, 1 H), 7.23 (d, J = 7.4 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 2 H).



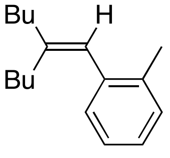
2-Butyl-1-phenyl-1-hexene (entries 1 and 7 of Table 2).[2] A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.31 (sext, J = 7.3 Hz, 2 H), 1.37 (sext, J = 7.5 Hz, 2 H), 1.40–1.53 (m, 4 H), 2.16 (t, J = 7.6 Hz, 2 H), 2.22 (t, J = 8.1 Hz, 2 H), 6.25 (s, 1 H), 7.16 (t, J = 7.4 Hz, 1 H), 7.19 (d, J = 7.4 Hz, 2 H), 7.29 (t, J = 7.4 Hz, 2 H).



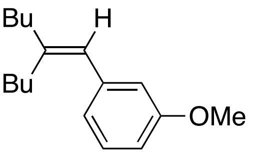
2-Butyl-1-[3-(trifluoromethyl)phenyl]-1-hexene (entry 2 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.88 (t, J = 7.4 Hz, 3 H), 0.95 (t, J = 7.4 Hz, 3 H), 1.31 (sext, J = 7.3 Hz, 2 H), 1.37 (sext, J = 7.5 Hz, 2 H), 1.41–1.54 (m, 4 H), 2.14–2.22 (m, 4 H), 6.26 (s, 1 H), 7.35 (d, J = 7.6 Hz, 1 H), 7.40 (t, J = 7.6 Hz, 1 H), 7.43 (d, J = 7.6 Hz, 1 H), 7.44 (s, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.0, 14.2, 22.7, 23.0, 30.5, 30.6, 30.6, 37.1, 122.65 (q, $^3J_{\text{C–F}}$ = 3.8 Hz), 123.5, 124.5 (q, $^1J_{\text{C–F}}$ = 272.0 Hz), 125.5 (q, $^3J_{\text{C–F}}$ = 4.0 Hz), 128.6, 130.6 (q, $^2J_{\text{C–F}}$ = 31.9 Hz), 132.0, 139.6, 146.1. HRMS (APCI) Calcd for $C_{17}H_{23}F_3$: M$^+$, 284.1746. Found: m/z 284.1756.



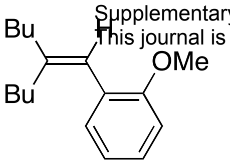
2-Butyl-1-(4-chlorophenyl)-1-hexene (entry 3 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.88 (t, J = 7.3 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.29 (sext, J = 7.4 Hz, 2 H), 1.36 (sext, J = 7.5 Hz, 2 H), 1.38–1.52 (m, 4 H), 2.14 (t, J = 7.9 Hz, 2 H), 2.18 (t, J = 7.9 Hz, 2 H), 6.18 (s, 1 H), 7.11 (d, J = 8.3 Hz, 2 H), 7.25 (d, J = 8.3 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.1, 14.2, 22.7, 23.0, 30.5, 30.59, 30.62, 37.1, 123.7, 128.3, 130.1, 131.6, 137.4, 144.9. HRMS (APCI) Calcd for $C_{16}H_{23}Cl$: M$^+$, 250.1483. Found: m/z 250.1479.



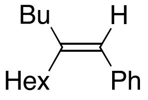
2-Butyl-1-(2-methylphenyl)-1-hexene (entry 4 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.85 (t, J = 7.3 Hz, 3 H), 0.99 (t, J = 7.4 Hz, 3 H), 1.25 (sext, J = 7.4 Hz, 2 H), 1.35–1.48 (m, 4 H), 1.54 (quint, J = 7.5 Hz, 2 H), 2.09 (t, J = 7.8 Hz, 2 H), 2.22 (t, J = 7.5 Hz, 2 H), 2.25 (s, 3 H), 6.23 (s, 1 H), 7.10–7.21 (m, 4 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.1, 14.2, 20.1, 22.7, 22.8, 30.2, 30.52, 30.55, 36.2, 124.2, 125.4, 126.3, 129.4, 129.7, 136.5, 138.3, 143.2. HRMS (APCI) Calcd for $C_{17}H_{26}$: M$^+$, 230.2029. Found: m/z 230.2021.



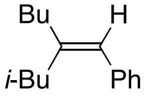
2-Butyl-1-(3-methoxyphenyl)-1-hexene (entry 5 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (t, J = 7.3 Hz, 3 H), 0.96 (t, J = 7.3 Hz, 3 H), 1.33 (sext, J = 7.4 Hz, 2 H), 1.38 (sext, J = 7.5 Hz, 2 H), 1.42–1.56 (m, 4 H), 2.17 (t, J = 7.6 Hz, 2 H), 2.24 (t, J = 8.0 Hz, 2 H), 3.81 (s, 3 H), 6.24 (s, 1 H), 6.75 (d, J = 7.7 Hz, 1 H), 6.76 (s, 1 H), 6.81 (d, J = 7.7 Hz, 1 H), 7.22 (t, J = 7.7 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.1, 14.2, 22.7, 23.1, 30.6, 30.70, 30.74, 37.1, 55.3, 111.6, 114.2, 121.4, 124.7, 129.1, 140.3, 144.4, 159.5. HRMS (APCI) Calcd for $C_{17}H_{27}O$: [M+H]$^+$, 247.2056. Found: m/z 247.2053.



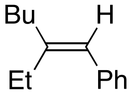
2-Butyl-1-(2-methoxyphenyl)-1-hexene (entry 6 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.85 (t, J = 7.3 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.27 (sext, J = 7.4 Hz, 2 H), 1.38 (sext, J = 7.4 Hz, 2 H), 1.42 (quint, J = 7.7 Hz, 2 H), 1.51 (quint, J = 7.6 Hz, 2 H), 2.16 (t, J = 7.8 Hz, 2 H), 2.19 (t, J = 7.6 Hz, 2 H), 3.81 (s, 3 H), 6.26 (s, 1 H), 6.85 (d, J = 8.2 Hz, 1 H), 6.90 (t, J = 7.4 Hz, 1 H), 7.15 (d, J = 7.4 Hz, 1 H), 7.18 (t, J = 7.8 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.1, 14.2, 22.7, 23.0, 30.6, 30.7, 30.8, 36.7, 55.6, 110.6, 120.1, 120.3, 127.4, 127.9, 130.3, 143.8, 157.3. HRMS (APCI) Calcd for $C_{17}H_{27}O$: [M+H]$^+$, 247.2056. Found: m/z 247.2054.



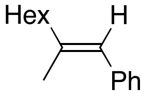
(*Z*)-2-Butyl-1-phenyl-1-octene (entry 8 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.87 (t, J = 7.0 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.20–1.34 (m, 6 H), 1.37 (sext, J = 7.4 Hz, 2 H), 1.40–1.52 (m, 4 H), 2.16 (t, J = 7.7 Hz, 2 H), 2.21 (t, J = 8.0 Hz, 2 H), 6.25 (s, 1 H), 7.14–7.21 (m, 3 H), 7.29 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.05, 14.06, 22.57, 22.63, 28.3, 29.5, 30.5, 30.7, 31.7, 37.0, 124.7, 125.7, 128.0, 128.6, 138.8, 143.9. HRMS (APCI) Calcd for $C_{18}H_{28}$: M$^+$, 244.2186. Found: m/z 244.2188.



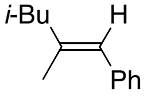
(*Z*)-2-Isobutyl-1-phenyl-1-hexene (entry 9 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.82 (d, J = 6.7 Hz, 6 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.37 (sext, J = 7.3 Hz, 2 H), 1.48 (quint, J = 7.4 Hz, 2 H), 1.83 (nonet, J = 7.2 Hz, 1 H), 2.11–2.18 (m, 2 H), 2.13 (d, J = 7.2 Hz, 2 H), 6.33 (s, 1 H), 7.14–7.22 (m, 3 H), 7.28 (t, J = 7.6 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 14.0, 22.5, 22.6, 26.4, 30.5, 36.9, 39.1, 125.7, 125.9, 127.9, 128.9, 139.0, 142.6. HRMS (APCI) Calcd for $C_{16}H_{24}$: M$^+$, 216.1873. Found: m/z 216.1866.



(*E*)-2-Ethyl-1-phenyl-1-hexene (entry 10 of Table 2).[3] A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.94 (t, J = 7.3 Hz, 3 H), 1.07 (t, J = 7.6 Hz, 3 H), 1.37 (sext, J = 7.3 Hz, 2 H), 1.49 (quint, J = 7.4 Hz, 2 H), 2.17 (t, J = 7.7 Hz, 2 H), 2.25 (q, J = 7.6 Hz, 2 H), 6.24 (s, 1 H), 7.17 (t, J = 7.4 Hz, 1 H), 7.21 (t, J = 7.3 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 2 H).



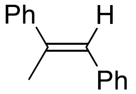
(*E*)-2-Methyl-1-phenyl-1-octene (entry 11 of Table 2).[4] A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.24–1.38 (m, 6 H), 1.51 (quint, J = 7.5 Hz,, 2 H), 1.85 (d, J = 1.4 Hz, 3 H), 2.16 (t, J = 7.7 Hz, 2 H), 6.26 (s, 1 H), 7.17 (t, J = 7.3 Hz, 1 H), 7.23 (t, J = 7.2 Hz, 2 H), 7.30 (t, J = 7.6 Hz, 2H).



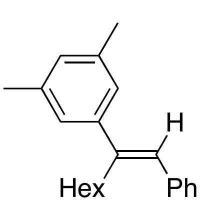
(*E*)-2,4-Dimethyl-1-phenyl-1-pentene (entry 12 of Table 2). A colorless oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.92 (d, J = 6.6 Hz, 6 H), 1.83 (d, J = 1.4 Hz,, 3 H), 1.86 (nonet, J = 6.6 Hz, 1 H), 2.03 (dd, J = 7.3, 0.8 Hz, 2 H), 6.24 (s, 1 H), 7.17 (t, J = 7.4 Hz, 1 H), 7.24 (d, J = 7.5 Hz, 2 H), 7.31 (t, J = 7.7 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 17.7, 22.5, 26.4, 50.5, 125.8, 126.1, 128.0, 128.8, 138.3, 138.7. HRMS (APCI) Calcd for $C_{13}H_{18}$: M$^+$, 174.1403. Found: m/z 174.1411.

Aryllithiation of Alkynes Catalyzed Cooperatively by Iron and Copper Complexes (Scheme 1). To a solution of Fe(acac)$_3$ (7.1 mg, 20 μmol), CuBr (5.7 mg, 40 μmol), PBu$_3$ (40 μL, 0.16 mmol), and an alkyne

(0.40 mmol) in diethyl ether (1.0 mL) placed in a 20 mL Schlenk tube was added a solution of an aryllithium (0.80 mmol) at room temperature. After the reaction mixture was stirred at 30 °C for the time specified in Scheme 1, methanol (0.20 mL) was added and stirring was continued for 5 min. H_2O (10 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2) gave the corresponding aryllithiation products, whose isomer ratio was determined by GC and ^1H NMR. The product was further purified by GPC if necessary.

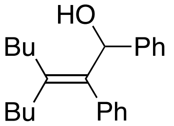


(*E*)-1,2-Diphenyl-1-propene (8a).[5] A white solid. ^1H NMR (500 MHz, $CDCl_3$) δ 2.29 (d, *J* = 1.4 Hz, 3 H), 6.84 (d, *J* = 1.4 Hz, 1 H), 7.22–7.32 (m, 2 H), 7.34–7.41 (m, 6 H), 7.51–7.55 (m, 2 H).

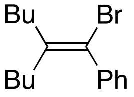


(*E*)-1-Phenyl-2-(3,5-xylyl)-1-octene (8b).[6] A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.1 Hz, 3 H), 1.16–1.34 (m, 6 H), 1.37–1.45 (m, 2 H), 2.34 (s, 6 H), 2.66 (t, *J* = 8.0 Hz, 2 H), 6.65 (s, 1 H), 6.93 (s, 1 H), 7.06 (s, 2 H), 7.23 (t, *J* = 7.2 Hz, 1 H), 7.30 (d, *J* = 7.1 Hz, 2 H), 7.35 (t, *J* = 7.5 Hz, 2 H).

Butyllithiation of 1-Phenyl-1-hexyne Followed by Reaction with Electrophiles (Scheme 2). A solution of $FeCl_3$ (3.2 mg, 20 µmol), PPh_3 (10.5 mg, 40 µmol), and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA: 12.0 µL, 80 µmol) in diethyl ether (1.0 mL) was placed in a 20 mL Schlenk tube and stirred for 10 min at –20 °C. To this solution was added successively 1-phenyl-1-hexyne (**2c**: 63.3 mg, 0.40 mmol) and a hexane solution of butyllithium (**1a**: 1.60 M. 0.38 mL, 0.60 mmol), and the mixture was stirred for 1.5 h at –20 °C. After an electrophile (amount specified in Scheme 2) was added and stirring was continued for the time specified in Scheme 2. H_2O (10 mL) was added and the resulting mixture was extracted with diethyl ether (10 mL x 3). The combined organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by purification with PTLC (SiO_2) gave the corresponding product. The product was further purified by GPC if necessary.



3-Butyl-1,2 -diphenyl-2-hepten-1-ol (11). A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 0.72 (t, *J* = 7.3 Hz, 3 H), 0.98 (t, *J* = 7.3 Hz, 3 H), 1.04–1.15 (m, 2 H), 1.21–1.36 (m, 2 H), 1.37–1.52 (m, 2 H), 1.53–1.63 (m, 2 H), 1.70 (d, *J* = 7.5 Hz, 1 H), 1.76–1.88 (m, 2 H), 2.26–2.36 (m, 1 H), 2.42–2.51 (m, 1 H), 5.96 (d, *J* = 7.5 Hz, 1 H), 6.65–6.84 (m, 2 H), 7.12–7.18 (m, 3 H), 7.18–7.23 (m, 3 H), 7.24–7.29 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 14.1, 22.7, 23.1, 30.78, 30.83, 31.7, 32.9, 71.9, 125.8, 126.5, 126.7, 127.6, 127.9, 130.6, 137.2, 138.0, 140.3, 143.0. HRMS (ESI) Calcd for $C_{23}H_{30}ONa$: $[M+Na]^+$, 345.2189. Found: m/z 345.2184.



1-Bromo-2-butyl-1-phenyl-1-hexene (12). A colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 0.77 (t, *J* = 7.3 Hz, 3 H), 0.98 (t, *J* = 7.3 Hz, 3 H), 1.15 (sext, *J* = 7.4 Hz, 2 H), 1.34 (quint, *J* = 7.6 Hz, 2 H), 1.42 (sext, *J* = 7.3 Hz, 2 H), 1.53 (quint, *J* = 7.7 Hz, 2 H), 2.00 (t, *J* = 7.9 Hz, 2 H), 2.38 (t, *J* = 8.0 Hz, 2 H), 7.23–7.28 (m, 3 H), 7.30–7.35 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.8, 14.0, 22.4, 22.8, 29.7, 30.6, 32.7, 35.3, 117.6, 127.6, 128.1, 129.1, 141.5, 142.0. HRMS (APCI) Calcd for $C_{17}H_{23}Br$: M^+, 294.0978. Found: m/z 294.0973.

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