Iron-Catalyzed Arylmagnesiation of Aryl(alkyl)acetylenes in the Presence of an *N*-Heterocyclic Carbene Ligand

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Supporting Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. THF was purified by passing through a neutral alumina column under nitrogen. 1-Hexyne (Wako Chemicals), phenylacetylene (Wako Chemicals), 4-methyl-1-pentyne (TCI), 3-methyl-1-butyne (Wako Chemicals), 3-butyne-1-ol (Aldrich), iodomethane (Wako Chemical), 2-iodoaniline (Wako Chemicals), 3-iodoaniline (Wako Chemicals), 4-iodoaniline (Wako Chemicals), 1-chloro-4-iodobenzene (TCI), 2-bromoanisole (TCI), 3-bromoanisole (TCI), 4-bromoanisole (TCI), 4-bromotoluene (Wako Chemicals), 1-bromo-3,5-dimethylbenzene (Wako Chemicals), 1-bromo-4-fluorobenzene (Wako Chemicals), 1-bromonaphthalene (TCI), 1-phenyl-1-butyne (Wako Chemicals), Mg (Wako Chemicals), 1,2-dibromomethane (TCI), Et₃N (Wako Chemicals), D₂O (Cambridge Isotope Laboratories, Inc.), allyl bromide (TCI), benzyl bromide (TCI), ZnCl₂ (Wako Chemicals), I₂ (Wako Chemicals), CuI (Wako Chemicals), and iodobenzene (TCI) were used as received.

Fe(acac)₃,¹ NiCl₂(PPh₃)₂,² Pd(PPh₃)₄,³ and IPr⁴ were synthesized following the literature procedures.

All other chemicals and solvents were purchased from Aldrich, Wako Chemicals, TCI, or Kanto Chemicals and used as received.

II. Preparation of Substrates

General Procedure for the Preparation of Aryl(alkyl)acetylenes

1-Alkyne (22 mmol) was added to a solution of aryl iodide (20 mmol), Pd(PPh₃)₄ (232 mg, 0.20 mmol), and CuI (174 mg, 1.8 mmol) in Et₃N (30 mL) at 60 °C. The resulting mixture was stirred at 60 °C for 12-24 h, passed through a pad of silica gel with EtOAc, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford the corresponding alkynes as an oil.

General Procedure for the Preparation of Arylmagnesium Bromides

Aryl bromide solution (5 mmol in THF (3 mL)) was added dropwise to a suspension of Mg activated by 1,2-dibromoethane in THF (1.5 mL) at room temperature. The reaction mixture was stirred at room temperature for 2 h. The concentration was determined by acid-base titration with methyl orange (typically 0.88-1.11 M).

¹ Charles, R. G.; Pawlikowski, M. A. *J. Phys. Chem.* **1958**, 62, 440.

² Venanzi, L. M. *J. Chem. Soc.* **1958**, 719.

³ Couison, D. R. *Inorg. Synth.* **1972**, 13, 121.

⁴ Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, 606, 49.

III. Catalytic Reactions

A Typical Procedure for the Arylmagnesiation of Alkynes (entry 1 in Table 1).

A solution of Fe(acac)₃ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL) was stirred at room temperature for 5 min. 1-Phenyl-1-hexyne (**1a**, 31.6 mg, 0.200 mmol) and 4-methoxyphenylmagnesium bromide (**2m**, 0.38 mL, 0.40 mmol; 1.06 M solution in THF) were added, and the mixture was stirred at 60 °C for 16 h. The reaction was quenched with water (80 μL), passed through a pad of silica gel with Et₂O, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/Et₂O (95/5) to give product (**3am**, 48.7 mg, 0.183 mmol; 91% yield).

General Procedure for Table 2.

A solution of Fe(acac)₃ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL) was stirred at room temperature for 5 min. An alkyne (**1**, 0.20 mmol) and ArMgBr (**2**, 0.36- 0.46 mL, 0.40 mmol; 0.88-1.11 M solution in THF) were added, and the mixture was stirred at 60 °C for 16 h. The reaction was quenched with water (80 μL), passed through a pad of silica gel with Et₂O, and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/Et₂O (95/5) to give product **3**.

3am. 2-(4-Methoxyphenyl)-1-phenyl-1-hexene (Colorless oil. 91% yield; entry 1)

(*E*)-**3am**; ¹H NMR (CDCl₃): δ 7.39 (d, ³J_{HH} = 8.2 Hz, 2H), 7.35 (t, ³J_{HH} = 7.6 Hz, 2H), 7.30 (d, ³J_{HH} = 8.2 Hz, 2H), 7.22 (t, ³J_{HH} = 7.1 Hz, 1H), 6.90 (d, ³J_{HH} = 8.5 Hz, 2H), 6.64 (s, 1H), 3.82 (s, 3H), 2.67 (t, ³J_{HH} = 7.9 Hz, 2H), 1.41 (quint, ³J_{HH} = 7.6 Hz, 2H), 1.32 (sextet, ³J_{HH} = 7.3 Hz, 2H), 0.85 (t, ³J_{HH} = 7.1 Hz, 3H). The NOE was observed at ortho protons of 4-methoxyphenyl group (13%) and ortho protons of phenyl group (10%) on irradiation at 6.64 ppm (=CH-). For (*Z*) isomer, olefin proton appears at 6.39 ppm. ¹³C NMR (CDCl₃): δ 159.1, 142.9, 138.7, 135.7, 128.9, 128.3, 127.8, 126.9, 126.4, 113.9, 55.4, 31.2, 30.0, 22.9, 14.0. Anal. Calcd for C₁₉H₂₂O: C, 85.67; H, 8.32. Found: C, 85.58; H, 8.41.

3bm. 2-(4-Methoxyphenyl)-1-phenyl-1-butene (Colorless oil. 91% yield; entry 2)

(*E*)-**3bm**; ¹H NMR (CDCl₃): δ 7.40 (d, ³J_{HH} = 8.4 Hz, 2H), 7.35 (t, ³J_{HH} = 7.6 Hz, 2H), 7.31 (d, ³J_{HH} = 7.0 Hz, 2H), 7.23 (t, ³J_{HH} = 7.2 Hz, 1H), 6.90 (d, ³J_{HH} = 8.5 Hz, 2H), 6.64 (s, 1H), 3.82 (s, 3H), 2.71 (q, ³J_{HH} = 7.5 Hz, 2H), 1.06 (t, ³J_{HH} = 7.5 Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.39 ppm. ¹³C NMR (CDCl₃): δ 159.1, 144.0, 138.7, 135.2, 128.8, 128.4, 127.8, 126.5, 126.5, 113.9, 55.4, 23.3, 13.7. Anal. Calcd for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.73; H, 7.67.

3cm. 2-(4-Methoxyphenyl)-1-phenyl-4-methyl-1-pentene (Colorless oil. 87% yield; entry 3)

(*E*)-**3cm**; ^1H NMR (CDCl_3): δ 7.37 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 7.33 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.30 (d, $^3J_{\text{HH}} = 6.7$ Hz, 2H), 7.22 (t, $^3J_{\text{HH}} = 6.6$ Hz, 1H), 6.89 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.67 (s, 1H), 3.82 (s, 3H), 2.58 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 1.69 (heptet, $^3J_{\text{HH}} = 6.8$ Hz, 1H), 0.81 (d, $^3J_{\text{HH}} = 6.4$ Hz, 6H). For (*Z*) isomer, olefin proton appears at 6.37 ppm. ^{13}C NMR (CDCl_3): δ 159.0, 142.3, 138.7, 136.1, 129.1, 128.5, 128.3, 127.9, 126.4, 113.8, 55.4, 38.7, 27.3, 22.6. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67; H, 8.32. Found: C, 85.70; H, 8.38.

3dm. 2-(4-Methoxyphenyl)-1-phenyl-3-methyl-1-butene (Colorless oil. 84% yield; entry 4)

(*E*)-**3dm**; ^1H NMR (CDCl_3): δ 7.35 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.32 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 7.25-7.19 (m, 1H), 7.21 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.87 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.33 (s, 1H), 3.82 (s, 3H), 3.27 (heptet, $^3J_{\text{HH}} = 6.9$ Hz, 1H), 1.05 (d, $^3J_{\text{HH}} = 7.0$ Hz, 6H). For (*Z*) isomer, olefin proton appears at 6.37 ppm. ^{13}C NMR (CDCl_3): δ 158.6, 149.5, 138.3, 135.1, 130.1, 129.1, 129.0, 128.3, 126.5, 113.1, 55.4, 29.5, 22.1. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$: C, 85.67; H, 7.99. Found: C, 85.97; H, 8.13.

3an. 2-(4-Methylphenyl)-1-phenyl-1-hexene (Colorless oil. 93% yield; entry 5)

(*E*)-**3an**; ^1H NMR (CDCl_3): δ 7.35 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.33 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.30 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.22 (t, $^3J_{\text{HH}} = 6.8$ Hz, 1H), 6.90 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.67 (s, 1H), 2.68 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 2.36 (s, 3H), 1.41 (quint, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.31 (sextet, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.40 ppm. ^{13}C NMR (CDCl_3): δ 143.4, 140.4, 138.6, 137.0, 129.2, 128.9, 128.3, 127.5, 126.6, 126.5, 31.1, 30.0, 23.0, 21.2, 14.0. Anal. Calcd for $\text{C}_{19}\text{H}_{22}$: C, 91.14; H, 8.86. Found: C, 91.35; H, 8.82.

3en. 1-(4-Methoxyphenyl)-2-(4-methylphenyl)-1-hexene (Pale yellow oil. 80% yield; entry 6)

(*E*)-**3en**; ^1H NMR (CDCl_3): δ 7.34 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.25 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 7.15 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.89 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.61 (s, 1H), 3.81 (s, 3H), 2.68 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 2.36 (s, 3H), 1.41 (quint, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.33 (sextet, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 0.85 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.33 ppm. ^{13}C NMR (CDCl_3): δ 158.3, 142.0, 140.6, 136.8, 130.2, 130.1, 129.2, 127.1, 126.5, 113.8, 55.4, 31.1, 30.0, 23.0, 21.2, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.83; H, 8.90.

3fn. 1-(3-Methoxyphenyl)-2-(4-methylphenyl)-1-hexene (Colorless oil. 87% yield; entry 7)

(*E*)-**3fn**; ^1H NMR (CDCl_3): δ 7.35 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.26 (t, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.16 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 6.90 (d, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 6.86 (s, 1H), 6.79 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 6.64 (s, 1H), 3.80 (s, 1H), 2.69 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 2.36 (s, 3H), 1.41 (quint, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.32 (sextet, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.37 ppm. ^{13}C NMR (CDCl_3): δ 159.6, 143.6, 140.3, 140.0, 137.0, 129.3, 129.2, 127.4, 126.6, 121.5, 114.3, 112.2, 55.3, 31.2, 30.2, 23.0, 21.2, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.54; H, 8.71.

3gn. 1-(2-Methoxyphenyl)-2-(4-methylphenyl)-1-hexene (Colorless oil. 75% yield; entry 8)

(*E*)-**3gn**; ^1H NMR (CDCl_3): δ 7.38 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 7.28 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H), 7.24 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.16 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 6.96 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 6.88 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 6.72 (s, 1H), 3.80 (s, 1H), 2.64 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 2.36 (s, 3H), 1.39 (quint, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 1.30 (sextet, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 0.83 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.59 ppm. ^{13}C NMR (CDCl_3): δ 157.7, 142.8, 140.3, 130.6, 129.8, 129.1, 129.0, 128.1, 126.7, 123.2, 120.2, 110.6, 55.5, 31.2, 30.1, 23.0, 21.2, 14.0. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.89; H, 8.65.

3hm. 1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-1-hexene (Colorless oil. 69% yield; entry 9)

(*E*)-**3hm**; ^1H NMR (CDCl_3): δ 7.38 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 7.31 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 7.22 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 6.90 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.57 (s, 1H), 3.83 (s, 3H), 2.63 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 1.39 (quint, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.31 (sextet, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 0.85 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.33 ppm. ^{13}C NMR (CDCl_3): δ 159.2, 143.6, 137.1, 135.3, 130.2, 129.7, 128.5, 127.8, 125.6, 113.9, 55.5, 31.1, 30.0, 22.9, 14.0. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{ClO}$: C, 75.86; H, 7.04. Found: C, 75.97; H, 7.15.

3eo. 2-(3,5-Dimethylphenyl)-1-(4-methoxyphenyl)-1-hexene (Pale yellow oil. 73% yield; entry 10)

(*E*)-**3eo**; ^1H NMR (CDCl_3): δ 7.24 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 7.05 (s, 2H), 6.91 (s, 1H), 6.89 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.59 (s, 1H), 3.81 (s, 3H), 2.66 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 2.33 (s, 6H), 1.41 (quint, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 1.33 (sextet, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 0.86 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.30 ppm. ^{13}C NMR (CDCl_3): δ 158.3, 143.7, 142.5, 137.8, 131.2, 130.1, 128.8, 127.4, 124.6, 113.8, 55.4, 31.2, 30.2, 23.0, 21.6, 14.1. Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}$: C, 85.67; H, 8.90. Found: C, 85.40; H, 8.70.

3ap. 2-(3-Methoxyphenyl)-1-phenyl-1-hexene (Colorless oil. 75% yield; entry 11)

(*E*)-**3ap**; ^1H NMR (CDCl_3): δ 7.38-7.02 (m, 7H), 7.00 (s, 1H), 6.84 (dd, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 2.4$ Hz, 1H), 6.70 (s, 1H), 3.84 (s, 3H), 2.68 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 1.42 (quint, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.32 (sextet, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 0.85 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.41 ppm. ^{13}C NMR (CDCl_3): δ 159.8, 145.0, 143.4, 138.4, 129.4, 129.1, 128.9, 128.4, 126.7, 119.3, 112.8, 112.5, 55.4, 31.1, 30.2, 22.9, 14.0. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67; H, 8.32. Found: C, 85.76; H, 8.39.

3aq. 2-(2-Methoxyphenyl)-1-phenyl-1-hexene (Colorless oil. 59% yield; entry 12)

(*E*)-**3aq**; ^1H NMR (CDCl_3): δ 7.36-7.33 (m, 4H), 7.29-7.20 (m, 3H), 6.95 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 6.89 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 6.45 (s, 1H), 3.82 (s, 3H), 2.70 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 1.32-1.22 (m, 4H), 0.79 (t, $^3J_{\text{HH}} = 6.9$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.47 ppm. ^{13}C NMR (CDCl_3): δ 157.0, 143.3, 138.3, 133.7, 130.6, 129.2, 129.1, 128.3, 128.2, 126.4, 120.6, 110.9, 55.6, 30.9, 30.8, 22.9, 14.0. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67; H, 8.32. Found: C, 85.46; H, 8.29.

3er. 2-(4-Fluorophenyl)-1-(4-methoxyphenyl)-1-hexene (Colorless oil. 73% yield; entry 13)

(*E*)-**3er**; ^1H NMR (CDCl_3): δ 7.39 (dd, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HF}} = 5.5$ Hz, 2H), 7.24 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 7.02 (dd, $^3J_{\text{HH}} = 8.5$ Hz, $^3J_{\text{HF}} = 8.5$ Hz, 2H), 6.90 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.57 (s, 1H), 3.82 (s, 3H), 2.66 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 1.43-1.27 (m, 4H), 0.85 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.37 ppm. ^{13}C NMR (CDCl_3): δ 162.2 (d, $^1J_{\text{CF}} = 244.9$ Hz), 158.5, 141.2, 139.5 (d, $^4J_{\text{CF}} = 3.1$ Hz), 130.2, 130.1, 128.2 (d, $^3J_{\text{CF}} = 8.3$ Hz), 127.8, 115.2 (d, $^2J_{\text{CF}} = 21.7$ Hz), 113.9, 55.4, 31.0, 30.2, 22.9, 14.0. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{FO}$: C, 80.25; H, 7.44. Found: C, 80.16; H, 7.56.

3es. 1-(4-Methoxyphenyl)-2-(1-naphthyl)-1-hexene (yellow oil. 69% yield; entry 14)

(*E*)-**3es**; ^1H NMR (CDCl_3): δ 8.10-8.05 (m, 1H), 7.88-7.83 (m, 1H), 7.77 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.49-7.41 (m, 3H), 7.38-7.32 (m, 3H), 6.94 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 6.46 (s, 1H), 3.83 (s, 3H), 2.74 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 1.38 (quint, $^3J_{\text{HH}} = 7.7$ Hz, 2H), 1.27 (sextet, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 0.79 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H). For (*Z*) isomer, olefin proton appears at 6.63 ppm. ^{13}C NMR (CDCl_3): δ 158.5, 142.9, 141.4, 134.0, 132.0, 130.7, 130.1, 130.0, 128.4, 127.1, 126.1, 125.8, 125.7, 125.5, 125.4, 113.9, 55.4, 33.4, 30.9, 23.0, 14.0. Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{O}$: C, 87.30; H, 7.64. Found: C, 87.54; H, 7.66.

Procedure for the Iron-Catalyzed Arylmagnesiation and Deuteration

A solution of $\text{Fe}(\text{acac})_3$ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL) was stirred at room temperature for 5 min. 1-Phenyl-1-hexyne (**1a**, 31.6 mg, 0.200 mmol) and 4-methoxyphenylmagnesium bromide (**2m**, 0.38 mL, 0.40 mmol; 1.06 M solution in THF) were added, and the mixture was stirred at 60 $^\circ\text{C}$ for 16 h. After quenching with deuterium oxide (80 μL), the reaction mixture was passed through a pad of silica gel with Et_2O , and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/ Et_2O (95/5) to give product (**3am-d**, 49.2 mg, 0.184 mmol; 92% yield).

3am-d. 1-Deuterio-2-(4-methoxyphenyl)-1-phenyl-1-hexene (Colorless oil)

(*E*)-**3am-d**; ^1H NMR (CDCl_3): δ 7.39 (dd, $^3J_{\text{HH}} = 8.8$ Hz and $^4J_{\text{HH}} = 1.8$ Hz, 2H), 7.37-7.32 (m, 2H), 7.32-7.28 (m, 2H), 7.22 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 6.90 (dd, $^3J_{\text{HH}} = 8.5$ Hz and $^4J_{\text{HH}} = 1.8$ Hz, 2H), 3.82 (s, 3H), 2.67 (t, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 1.42 (quint, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 1.32 (sextet, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 0.85 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H). For (*Z*) isomer, allylic proton appears at 2.46 ppm (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 159.1, 142.8, 138.6, 135.7, 128.9, 128.3, 127.8, 126.6 (t, $^1J_{\text{CD}} = 23.2$ Hz), 126.4, 113.9, 55.4, 31.2, 30.0, 22.9, 14.0. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{DO}$: C, 85.35; H, 8.67. Found: C, 85.55; H, 8.44.

Procedure for Equation 1

A solution of $\text{Fe}(\text{acac})_3$ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL) was stirred at room temperature for 5 min. 4-Methoxy-1-phenyl-1-butyne (**4**, 32.0 mg, 0.200 mmol) and 4-methylphenylmagnesium bromide (**2n**, 0.40 mL, 0.40 mmol; 1.00 M solution in THF) were added, and the mixture was stirred at 60 $^\circ\text{C}$ for 16 h. The reaction was quenched with water (80 μL), passed through a pad of silica gel with Et_2O , and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/ Et_2O (95/5) to give the hydroarylation products (**5** and **6**, 40.8 mg, 0.161 mmol; 81% yield).

5. (*E*)- and (*Z*)-4-Methoxy-1-2-(4-methylphenyl)-phenyl-1-butene (Colorless oil)

(*E*)-**5**; ^1H NMR (CDCl_3): δ 7.40-7.32 (m, 6H), 7.26-7.21 (m, 1H), 7.22 (d, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 6.77 (s, 1H), 3.43 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 3.27 (s, 3H), 3.01 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (CDCl_3): δ 139.8, 138.1, 137.8, 137.2, 129.3, 129.2, 128.9, 128.6, 128.4, 126.5, 71.3, 58.7, 30.8, 21.2. (*Z*)-**5**; ^1H NMR (CDCl_3): δ 7.13-7.02 (m, 7H), 6.94 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 6.47 (s, 1H), 3.42 (t, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 3.30 (s, 3H), 2.75 (td, $^3J_{\text{HH}} = 7.0$ Hz and $^4J_{\text{HH}} = 1.2$ Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (CDCl_3): δ 139.8, 139.0, 137.5, 136.8, 129.6, 129.4, 127.9, 127.8, 126.8, 126.3, 71.1, 58.7, 40.9, 21.4. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$: C, 85.67; H, 7.99. Found: C, 85.87; H, 7.96.

Procedures for Equation 2

To a solution of $\text{Fe}(\text{acac})_3$ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL), 1-phenyl-1-hexyne (**1a**, 31.6 mg, 0.200 mmol) and 4-methoxyphenylmagnesium bromide (**2m**, 0.38 mL, 0.40 mmol; 1.06 M solution in THF) were added, and the mixture was stirred at 60 $^\circ\text{C}$ for 16 h. Then allyl bromide (73 mg, 0.60 mmol) was added and the resulting mixture was further stirred at 60 $^\circ\text{C}$ for 2 h. The mixture was passed through a pad of silica gel with Et_2O , and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/ Et_2O (95/5) to give the product (**7**, 47.8 mg, 0.156 mmol; 78% yield).

7. 5-(4-Methoxyphenyl)-4-phenyl-1,4-nonadiene (Pale yellow oil)

(*E*)-**7**; ^1H NMR (CDCl_3): δ 7.33 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 7.24 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.19 (dd, $^3J_{\text{HH}} = 8.2$ Hz and $^4J_{\text{HH}} = 1.2$ Hz, 2H), 7.15 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.90 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 5.62 (ddt, $^3J_{\text{HH}} = 17.0$ Hz, $^3J_{\text{HH}} = 10.0$ Hz and $^3J_{\text{HH}} = 6.7$ Hz, 1H), 4.83 (dd, $^3J_{\text{HH}} = 10.0$ Hz and $^2J_{\text{HH}} = 2.1$ Hz, 1H), 4.80 (dd, $^3J_{\text{HH}} = 17.0$ Hz and $^2J_{\text{HH}} = 2.1$ Hz, 1H), 3.83 (s, 3H), 2.93 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 2.14 (t, $^3J_{\text{HH}} = 7.6$ Hz, 2H), 1.20-1.06 (m, 4H), 0.70 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H). For (*Z*) isomer, allylic proton appears at 3.30 ppm (d, $^3J_{\text{HH}} = 6.1$ Hz, 2H) and 2.52 ppm (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 158.3, 142.9, 139.4, 136.8, 135.7, 134.9, 129.8, 129.0, 128.0, 126.4, 115.3, 113.6, 55.3, 40.5, 35.4, 30.9, 22.6, 14.0. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}$: C, 86.23; H, 8.55. Found: C, 85.97; H, 8.41.

1-Phenyl-1-hexyne (**1a**, 31.6 mg, 0.200 mmol) and 4-methoxyphenylmagnesium bromide (**2m**, 0.38 mL, 0.40 mmol; 1.06 M solution in THF) were added to a solution of $\text{Fe}(\text{acac})_3$ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL). After stirring at 60 $^\circ\text{C}$ for 16 h, ZnCl_2 (73 mg, 0.60 mmol) was added and the mixture was stirred at room temperature for 5 min, and then I_2 (152 mg, 0.599 mmol) was added. The resulting mixture was further stirred at room temperature for 2 h, passed through a pad of silica gel with Et_2O , and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/ Et_2O (95/5) to give the alkenyl iodide (**8**, 71.4 mg, 0.182 mmol; 91% yield).

8. 1-Iodo-2-(4-methoxyphenyl)-1-phenyl-1-hexene (Pale yellow oil)

(*E*)-**8**; ^1H NMR (CDCl_3): δ 7.36-7.32 (m, 4H), 7.27-7.23 (m, 1H), 7.17 (d, $^3J_{\text{HH}} = 7.9$ Hz, 2H), 6.93 (d, $^3J_{\text{HH}} = 8.5$ Hz, 2H), 3.84 (s, 3H), 2.30 (t, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 1.20 (quint, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 1.11 (sextet, $^3J_{\text{HH}} = 7.5$ Hz, 2H), 0.70 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). For (*Z*) isomer, allylic proton appears at 2.79 ppm (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H). ^{13}C NMR (CDCl_3): δ 158.9, 150.0, 144.6, 138.5, 129.5, 128.7, 128.4, 127.8, 113.7, 97.7, 55.3, 35.4, 30.7, 22.3, 13.8. Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{IO}$: C, 58.17; H, 5.40. Found: C, 58.40; H, 5.54.

Procedure for Equation 3

A solution of $\text{Fe}(\text{acac})_3$ (3.5 mg, 9.9 μmol) and IPr (15.6 mg, 40.0 μmol) in THF (1.0 mL) was stirred at room temperature for 5 min, and 4-methoxy-1-phenyl-1-butyne (**4**, 32.0 mg, 0.200 mmol) and 4-methylphenylmagnesium bromide (**2n**, 0.40 mL, 0.40 mmol; 1.00 M solution in THF) were added. The mixture was stirred at 60 $^\circ\text{C}$ for 16 h before a suspension of $\text{NiCl}_2(\text{PPh}_3)_2$ (6.5 mg, 9.9 μmol) and iodobenzene (122 mg, 0.598 mmol) in THF (0.5 mL) was added. The mixture was further stirred at 60 $^\circ\text{C}$ for 16 h, and it was passed through a pad of silica gel with Et_2O , and concentrated under vacuum. The residue was purified by silica gel preparative TLC with Hexane/ Et_2O (95/5) to give the product (**9**, 47.0 mg, 0.143 mmol; 72% yield).

9. 4-Methoxy-2-(4-methylphenyl)-1,1-diphenyl-1-butene (White solid)

^1H NMR (CDCl_3): δ 7.33 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.28 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 7.24 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.04-6.93 (m, 7H), 6.89 (d, $^3J_{\text{HH}} = 7.0$ Hz, 2H), 3.31 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 3.20 (s, 3H), 2.75 (t, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (CDCl_3): δ 143.3, 143.2, 141.0, 139.0, 136.7, 136.0, 130.8, 129.7, 129.5, 128.8, 128.3, 127.5, 126.8, 125.9, 71.4, 58.6, 36.1, 21.3. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}$: C, 87.76; H, 7.37. Found: C, 87.46; H, 7.37.