Rhodium-Catalyzed Addition of Arylzinc Reagents to Aryl Alkynyl Ketones: Synthesis of β,β -Disubstituted Indanones

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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.

Dichloromethane and 1,2-dichloroethane were distilled over CaH_2 under nitrogen. THF and toluene were distilled over benzophenone ketyl under nitrogen.

MnO_2 (Sigma-Aldrich Japan), allyl bromide (TCI), 1,1'-bis(diphenylphosphino)ferrocene (Fluka), 1,3-bis(diphenylphosphino)propane (Kanto Chemicals), 1,4-bis(diphenylphosphino)butane (TCI), and triphenylphosphine (Wako Chemicals) were used as received. $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$,¹ $[\text{RhCl}(\text{cod})]_2$,² and ligand **7**³ were synthesized following the literature procedures.

α -Arylpropargyl alcohols (precursors of aryl alkynyl ketones) were synthesized from the corresponding terminal alkynes and aromatic aldehydes following the procedure described in the literature.⁴ Arylzinc chlorides were prepared following the literature procedure.⁵

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

¹ Cramer, R. *Inorg. Synth.* **1974**, *15*, 16.

² Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

³ Hayashi, T.; Kanehira, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1988**, *53*, 113.

⁴ Shintani, R.; Okamoto, K.; Hayashi, T. *J. Am. Chem. Soc.* **2005**, *127*, asap.

⁵ Shintani, R.; Tokunaga, N.; Doi, H.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 6240.

II. Synthesis of Substrates

The yields have not been optimized.

1-Phenyl-2-heptyn-1-one (1a) (CAS 18998-78-2)

1-Phenyl-2-heptyn-1-ol (790 mg, 4.20 mmol) was added to a suspension of MnO_2 (3.65 g, 42.0 mmol) in dichloromethane (30 mL) at 0 °C, and the resulting mixture was stirred for 2 h at 0 °C. After filtered through celite/ MgSO_4 , the solvent was removed under vacuum. The residue was passed through a pad of silica gel with Et_2O to afford 1-phenyl-2-heptyn-1-one as a colorless oil (782 mg, 4.20 mmol; 100% yield).

^1H NMR (CDCl_3): δ 8.14 (dd, $^3J_{\text{HH}} = 8.0$ Hz and $^4J_{\text{HH}} = 1.0$ Hz, 2H), 7.59 (tt, $^3J_{\text{HH}} = 7.4$ Hz and $^4J_{\text{HH}} = 1.2$ Hz, 1H), 7.47 (t, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 2.51 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 1.69-1.64 (m, 2H), 1.55-1.47 (m, 2H), 0.97 (t, $^3J_{\text{HH}} = 7.5$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 178.5, 137.2, 134.0, 129.8, 128.7, 97.0, 79.9, 30.1, 22.3, 19.1, 13.7.

1-Phenyl-2-nonyn-1-one (1b) (CAS 56517-81-8)

This was synthesized from 1-phenyl-2-nonyn-1-ol, following the procedure for compound **1a**. Colorless oil, 89% yield.

^1H NMR (CDCl_3): δ 8.14 (dd, $^3J_{\text{HH}} = 8.1$ Hz and $^4J_{\text{HH}} = 0.7$ Hz, 2H), 7.59 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.47 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 2.50 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 1.68 (quint, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 1.51-1.45 (m, 2H), 1.36-1.31 (m, 4H), 0.91 (t, $^3J_{\text{HH}} = 6.9$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 178.5, 137.2, 134.0, 129.8, 128.7, 97.1, 79.9, 31.4, 28.9, 28.0, 22.7, 19.4, 14.2.

1-Phenyl-5-methyl-2-hexyn-1-one (1c) (CAS 65236-44-4)

This was synthesized from 1-phenyl-5-methyl-2-hexyn-1-ol, following the procedure for compound **1a**. Colorless oil, 100% yield.

^1H NMR (CDCl_3): δ 8.14 (dd, $^3J_{\text{HH}} = 8.2$ Hz and $^4J_{\text{HH}} = 1.5$ Hz, 2H), 7.59 (tt, $^3J_{\text{HH}} = 7.3$ Hz and $^4J_{\text{HH}} = 1.2$ Hz, 1H), 7.48 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H), 2.41 (d, $^3J_{\text{HH}} = 6.4$ Hz, 2H), 2.02 (septet, $^3J_{\text{HH}} = 6.6$ Hz, 1H), 1.09 (d, $^3J_{\text{HH}} = 6.7$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 178.4, 137.2, 134.0, 129.7, 128.7, 96.0, 80.8, 28.5, 28.0, 22.3.

1-(*p*-Tolyl)-2-heptyn-1-one (1d) (CAS 38395-06-1)

This was synthesized from 1-(*p*-tolyl)-2-heptyn-1-ol, following the procedure for compound **1a**. Colorless oil, 95% yield.

^1H NMR (CDCl_3): δ 8.03 (d, $^3J_{\text{HH}} = 8.2$ Hz, 2H), 7.27 (d, $^3J_{\text{HH}} = 8.4$ Hz, 2H), 2.50 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H), 2.43 (s, 3H), 1.69-1.63 (m, 2H), 1.55-1.47 (m, 2H), 0.97 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 178.2, 145.1, 134.9, 129.9, 129.4, 96.5, 80.0, 30.1, 22.3, 22.0, 19.1, 13.7.

1-(*p*-Methoxyphenyl)-2-heptyn-1-one (**1e**) (CAS 93845-81-9)

This was synthesized from 1-(*p*-methoxyphenyl)-2-heptyn-1-ol, following the procedure for compound **1a**. The crude material was chromatographed on silica gel with Et_2O /hexane = 1/5. Colorless oil, 70% yield.

^1H NMR (CDCl_3): δ 8.11-8.10 (m, 2H), 6.95-6.94 (m, 2H), 3.88 (s, 3H), 2.49 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 1.69-1.63 (m, 2H), 1.54-1.47 (m, 2H), 0.96 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 177.2, 164.5, 132.1, 130.6, 113.9, 96.1, 79.9, 55.8, 30.1, 22.3, 19.1, 13.7.

1-(*p*-Fluorophenyl)-2-heptyn-1-one (**1f**)

This was synthesized from 1-(*p*-fluorophenyl)-2-heptyn-1-ol, following the procedure for compound **1a**. Colorless oil, 89% yield.

^1H NMR (CDCl_3): δ 8.18-8.14 (m, 2H), 7.17-7.12 (m, 2H), 2.50 (t, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 1.69-1.64 (m, 2H), 1.54-1.47 (m, 2H), 0.97 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 176.8, 166.5 (d, $^1J_{\text{CF}} = 255.8$ Hz), 133.7 (d, $^4J_{\text{CF}} = 3.1$ Hz), 132.4 (d, $^3J_{\text{CF}} = 9.3$ Hz), 115.9 (d, $^2J_{\text{HH}} = 22.2$ Hz), 97.3, 79.6, 30.0, 22.3, 19.1, 13.7. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{FO}$: C, 76.45; H, 6.42. Found: C, 76.36; H, 6.41.

1-(*o*-Tolyl)-2-heptyn-1-one (**1g**)

This was synthesized from 1-(*o*-tolyl)-2-heptyn-1-ol, following the procedure for compound **1a**. The crude material was chromatographed on silica gel with Et_2O /hexane = 1/5. Colorless oil, 65% yield.

^1H NMR (CDCl_3): δ 8.18 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.42 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 7.31 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.24 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 2.62 (s, 3H), 2.47 (t, $^3J_{\text{HH}} = 7.1$ Hz, 2H),

1.67-1.62 (m, 2H), 1.53-1.46 (m, 2H), 0.96 (t, $^3J_{\text{HH}} = 7.4$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 180.2, 140.5, 136.1, 133.4, 132.8, 132.2, 125.9, 95.6, 81.4, 30.1, 22.3, 22.1, 19.1, 13.7. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C, 83.96; H, 8.05. Found: C, 84.04; H, 8.09.

III. Catalytic Reactions

Procedure for Table 1, entry 1.

1-Phenyl-2-heptyn-1-one **1a** (37.3 mg, 0.20 mmol) was added to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.9 mg, 20 μmol Rh) and dppf (12.2 mg, 22 μmol) in 1,2-dichloroethane (10 mL). PhZnCl (625 μL , 0.30 mmol; 0.48 M in THF) was then added to it and the resulting solution was stirred for 7 h at 25 $^\circ\text{C}$. The reaction was quenched with water (30 μL) and passed through a pad of silica gel with Et_2O . The solvent was removed under vacuum and the residue was purified by silica gel preparative TLC with Et_2O /hexane = 1/4.5 to afford indanone **2a** as a pale yellow oil (42.1 mg, 0.16 mmol; 80% yield).

^1H NMR (CDCl_3): δ 7.78 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.60 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 7.42 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 7.33 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.31-7.27 (m, 2H), 7.23-7.18 (m, 3H), 2.96 (d, $^2J_{\text{HH}} = 19.1$ Hz, 1H), 2.92 (d, $^2J_{\text{HH}} = 19.0$ Hz, 1H), 2.27 (ddd, $^2J_{\text{HH}} = 13.6$ Hz and $^3J_{\text{HH}} = 12.5$ and 4.3 Hz, 1H), 2.15 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.2 Hz, 1H), 1.34-1.26 (m, 2H), 1.25-1.16 (m, 1H), 0.92-0.85 (m, 1H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.0, 161.0, 147.2, 137.0, 135.1, 128.7, 127.9, 126.7, 126.5, 126.4, 123.6, 53.1, 50.1, 40.0, 27.3, 23.4, 14.1. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: C, 86.32; H, 7.63. Found: C, 86.61; H, 7.66.

General Procedure for Table 2.

Aryl alkynyl ketone **1** (0.20 mmol) was added to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.9 mg, 20 μmol Rh) and dppf (12.2 mg, 22 μmol) in 1,2-dichloroethane (10–15 mL). PhZnCl (625 μL , 0.30 mmol; 0.48 M in THF) was then added to it and the resulting solution was stirred for 7–19 h at 25 $^\circ\text{C}$. The reaction was quenched with water (30 μL) and passed through a pad of silica gel with Et_2O . The solvent was removed under vacuum and the residue was purified by silica gel preparative TLC with Et_2O /hexane to afford indanone **2**.

Entry 2. Pale yellow oil. 84% yield.

^1H NMR (CDCl_3): δ 7.78 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.60 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 7.42 (t, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.34-7.27 (m, 3H), 7.23-7.18 (m, 3H), 2.96 (d, $^2J_{\text{HH}} = 19.1$ Hz, 1H), 2.92 (d, $^2J_{\text{HH}} = 19.0$ Hz, 1H), 2.27 (ddd, $^2J_{\text{HH}} = 13.5$ Hz and $^3J_{\text{HH}} = 12.0$ and 4.2 Hz, 1H), 2.14 (ddd, $^2J_{\text{HH}} = 13.5$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.6 Hz, 1H), 1.31-1.17 (m, 7H), 0.92-0.85 (m, 1H), 0.84 (t, $^3J_{\text{HH}} = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.1, 161.1, 147.2, 137.0, 135.1, 128.7, 128.0, 126.7, 126.6, 126.4, 123.6, 53.1, 50.2, 40.3, 31.8, 30.0, 25.1, 22.8, 14.2. Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}$: C, 86.26; H, 8.27. Found: C, 86.08; H, 8.36.

Entry 3. Pale yellow oil. 75% yield.

^1H NMR (CDCl_3): δ 7.78 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.60 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.43-7.40 (m, 2H), 7.29-7.23 (m, 4H), 7.18 (t, $^3J_{\text{HH}} = 6.9$ Hz, 1H), 3.04 (d, $^2J_{\text{HH}} = 19.1$ Hz, 1H), 2.98 (d, $^2J_{\text{HH}} = 18.9$ Hz, 1H), 2.33 (dd, $^2J_{\text{HH}} = 14.1$ Hz and $^3J_{\text{HH}} = 4.6$ Hz, 1H), 2.10 (dd, $^2J_{\text{HH}} = 14.0$ Hz and $^3J_{\text{HH}} = 6.6$ Hz, 1H), 1.51-1.45 (m, 1H), 0.89 (d, $^3J_{\text{HH}} = 6.7$ Hz, 3H), 0.59 (d, $^3J_{\text{HH}} = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.1, 161.0, 147.7, 137.0, 134.9, 128.7, 128.0, 126.8, 126.6, 126.5, 123.6, 53.2, 50.2, 48.9, 25.5, 25.4, 24.4. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}$: C, 86.32; H, 7.63. Found: C, 86.58; H, 7.84.

Entry 4. Pale yellow oil. 74% yield.

^1H NMR (CDCl_3): δ 7.67 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.31-7.27 (m, 2H), 7.24-7.18 (m, 4H), 7.09 (s, 1H), 2.94 (d, $^2J_{\text{HH}} = 18.9$ Hz, 1H), 2.89 (d, $^2J_{\text{HH}} = 18.9$ Hz, 1H), 2.41 (s, 3H), 2.28 (td, $J_{\text{HH}} = 13.3$ Hz and $^3J_{\text{HH}} = 4.1$ Hz, 1H), 2.12 (td, $J_{\text{HH}} = 13.3$ Hz and $^3J_{\text{HH}} = 4.4$ Hz, 1H), 1.36-1.27 (m, 2H), 1.25-1.15 (m, 1H), 0.94-0.84 (m, 1H), 0.85 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 205.6, 161.7, 147.4, 146.3, 134.8, 129.3, 128.7, 126.7, 126.5, 126.4, 123.4, 53.3, 49.8, 39.8, 27.3, 23.4, 22.5, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29; H, 7.97. Found: C, 86.04; H, 8.03.

Entry 5. Pale yellow oil. 63% yield.

^1H NMR (CDCl_3): δ 7.72 (d, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 7.31-7.27 (m, 2H), 7.24-7.18 (m, 3H), 6.94 (dd, $^3J_{\text{HH}} = 8.5$ Hz and $^4J_{\text{HH}} = 2.2$ Hz, 1H), 6.69 (d, $^4J_{\text{HH}} = 2.2$ Hz, 1H), 3.83 (s, 3H), 2.93 (d, $^2J_{\text{HH}} = 18.9$ Hz, 1H), 2.88 (d, $^2J_{\text{HH}} = 18.8$ Hz, 1H), 2.28 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.2 Hz, 1H), 2.11 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.4$ and 4.4 Hz, 1H), 1.38-1.27 (m, 2H), 1.25-1.16 (m, 1H), 0.94-0.86 (m, 1H), 0.85 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 204.2, 165.7, 164.1, 147.3, 130.5, 128.7, 126.6, 126.5, 125.3, 115.6, 109.7, 55.9, 53.3, 49.9, 39.6, 27.2, 23.4, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$: C, 81.60; H, 7.53. Found: C, 81.43; H, 7.49.

Entry 6. Pale yellow oil. 68% yield.

^1H NMR (CDCl_3): δ 7.78 (dd, $^3J_{\text{HH}} = 8.4$ Hz and $^4J_{\text{HF}} = 5.4$ Hz, 1H), 7.32-7.29 (m, 2H), 7.23-7.20 (m, 3H), 7.11 (td, $^3J = 8.5$ Hz and $^4J_{\text{HH}} = 2.2$ Hz, 1H), 6.96 (dd, $^3J_{\text{HF}} = 8.8$ Hz and $^4J_{\text{HH}} = 2.2$ Hz, 1H), 2.97 (d, $^2J_{\text{HH}} = 19.2$ Hz, 1H), 2.93 (d, $^2J_{\text{HH}} = 19.2$ Hz, 1H), 2.28 (ddd, $^2J_{\text{HH}} = 13.7$ Hz and $^3J_{\text{HH}} = 12.2$ and 4.2 Hz, 1H), 2.12 (ddd, $^2J_{\text{HH}} = 13.6$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.4 Hz, 1H), 1.39-1.26 (m, 2H), 1.25-1.16 (m, 1H), 0.94-0.85 (m, 1H), 0.86 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 204.0, 167.5 (d, $^1J_{\text{CF}} = 256.3$ Hz), 164.2 (d, $^3J_{\text{CF}} = 8.8$ Hz), 146.5, 133.4 (d, $^4J_{\text{CF}} = 2.1$ Hz), 128.9, 126.8, 126.5, 125.9 (d, $^3J_{\text{CF}} = 10.9$ Hz), 116.4 (d, $^2J_{\text{CF}} = 23.7$ Hz), 112.9 (d, $^1J_{\text{CF}} = 22.2$ Hz), 53.2, 50.0 (d, $^4J_{\text{CF}} = 2.1$ Hz), 39.7, 27.2, 23.3, 14.1. HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{19}\text{FONa}$ ($\text{M} + \text{Na}^+$) 305.1312, found 305.1309.

Entry 7. Pale yellow oil. 77% yield.

^1H NMR (CDCl_3): δ 7.43 (t, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 7.30-7.27 (m, 2H), 7.23-7.17 (m, 3H), 7.13 (t, $^3J_{\text{HH}} = 8.3$ Hz, 2H), 2.94 (d, $^2J_{\text{HH}} = 19.1$ Hz, 1H), 2.90 (d, $^2J_{\text{HH}} = 19.6$ Hz, 1H), 2.69 (s, 3H), 2.27 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.2 Hz, 1H), 2.12 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.4 Hz, 1H), 1.38-1.28 (m, 2H), 1.24-1.17 (m, 1H), 0.95-0.88 (m, 1H), 0.85 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 207.0, 161.9, 147.6, 138.6, 134.4, 134.3, 129.7, 128.7, 126.7, 126.4, 123.7, 53.5, 49.3, 40.0, 27.3, 23.4, 18.7, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29; H, 7.97. Found: C, 86.22; H, 8.05.

General Procedure for Table 3.

1-Phenyl-2-heptyn-1-one **1a** (37.3 mg, 0.20 mmol) was added to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.9 mg, 20 μmol Rh) and dppf (12.2 mg, 22 μmol) in 1,2-dichloroethane (10–15 mL). ArZnCl (0.30 mmol; 0.48–0.79 M in THF) was then added to it and the resulting solution was stirred for 7–17 h at 25 $^\circ\text{C}$. The reaction was quenched with water (30 μL) and passed through a pad of silica gel with Et_2O . The solvent was removed under vacuum and the residue was purified by silica gel preparative TLC with Et_2O /hexane to afford indanone **2**.

Entry 2. Pale yellow oil. 81% yield.

^1H NMR (CDCl_3): δ 7.77 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.59 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.40 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.32 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.13 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 6.82 (d, $^3J_{\text{HH}} = 8.6$ Hz, 2H), 3.77 (s, 3H), 2.94 (d, $^2J_{\text{HH}} = 19.0$ Hz, 1H), 2.88 (d, $^2J_{\text{HH}} = 18.9$ Hz, 1H), 2.24 (td, $J_{\text{HH}} = 13.3$ Hz and $^3J_{\text{HH}} = 4.1$ Hz, 1H), 2.12 (td, $J_{\text{HH}} = 13.3$ Hz and $^3J_{\text{HH}} = 4.2$ Hz, 1H), 1.36-1.25 (m, 2H), 1.23-1.15 (m, 1H), 0.92-0.84 (m, 1H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.2, 161.3, 158.1, 139.3, 136.9, 135.1, 127.9, 127.7, 126.3, 123.5, 114.0, 55.4, 53.2, 49.5, 40.2, 27.3, 23.4, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$: C, 81.60; H, 7.53. Found: C, 81.35; H, 7.53.

Entry 3. Pale yellow solid. 72% yield.

^1H NMR (CDCl_3): δ 7.78 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.61 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.43 (t, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.31 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.17 (dd, $^3J_{\text{HH}} = 8.9$ Hz and $^4J_{\text{HF}} = 5.2$ Hz, 2H), 6.97 (t, $^3J = 8.6$ Hz, 2H), 2.95 (d, $^2J_{\text{HH}} = 19.1$ Hz, 1H), 2.86 (d, $^2J_{\text{HH}} = 19.0$ Hz, 1H), 2.24 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.4 Hz, 1H), 2.13 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.4 Hz, 1H), 1.36-1.25 (m, 2H), 1.22-1.13 (m, 1H), 0.92-0.82 (m, 1H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 205.7, 161.5 (d, $^1J_{\text{CF}} = 245.4$ Hz), 160.7, 143.1 (d, $^4J_{\text{CF}} = 3.0$ Hz), 137.0, 135.2, 128.3 (d, $^3J_{\text{CF}} = 8.3$ Hz), 128.1, 126.2, 123.7, 115.5 (d, $^2J_{\text{CF}} = 20.7$ Hz), 53.2, 49.7, 40.2, 27.3, 23.3, 14.1. Anal. Calcd for $\text{C}_{19}\text{H}_{19}\text{FO}$: C, 80.82; H, 6.78. Found: C, 80.63; H, 6.85.

Entry 4. Pale yellow oil. 74% yield.

^1H NMR (CDCl_3): δ 7.78 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.60 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H), 7.41 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H), 7.34 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 6.84 (s, 1H), 6.82 (s, 2H), 2.92 (s, 2H), 2.26 (s, 6H), 2.26 (td, $J_{\text{HH}} = 12.9$ Hz and $^3J_{\text{HH}} = 4.2$ Hz, 1H), 2.13 (td, $J_{\text{HH}} = 12.9$ Hz and $^3J_{\text{HH}} = 4.4$ Hz, 1H), 1.35-1.26 (m, 2H), 1.32-1.13 (m, 1H), 0.89-0.81 (m, 1H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.4, 161.3, 147.2, 138.2, 136.9, 135.1, 128.2, 127.8, 126.4, 124.5, 123.5, 53.1, 49.9, 40.0, 27.3, 23.4, 21.7, 14.1. HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{ONa}$ ($\text{M}+\text{Na}^+$) 315.1719, found 315.1721.

Entry 5. Pale yellow oil. 77% yield.

^1H NMR (CDCl_3): δ 7.83 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.80-7.73 (m, 4H), 7.62 (t, $^3J_{\text{HH}} = 6.9$ Hz, 1H), 7.49-7.43 (m, 3H), 7.36 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.27-7.24 (m, 1H), 3.02 (s, 2H), 2.40 (td, $J_{\text{HH}} = 12.9$ Hz and $^3J_{\text{HH}} = 4.3$ Hz, 1H), 2.27 (td, $J_{\text{HH}} = 12.9$ Hz and $^3J_{\text{HH}} = 4.3$ Hz, 1H), 1.40-1.31 (m, 2H), 1.30-1.21 (m, 1H), 0.96-0.87 (m, 1H), 0.87 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.0, 161.0, 144.4, 137.1, 135.2, 133.4, 132.1, 128.7, 128.2, 128.1, 127.6, 126.5, 126.4, 126.1, 125.6, 124.7, 123.7, 52.9, 50.2, 39.9, 27.3, 23.4, 14.2. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{22}\text{ONa}$ ($\text{M}+\text{Na}^+$) 337.1563, found 337.1562.

Entry 6. Pale yellow oil. 53% yield.

^1H NMR (CDCl_3): δ 7.79 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H), 7.59 (t, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 7.45-7.41 (m, 2H), 7.26 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.20-7.15 (m, 2H), 7.12-7.10 (m, 1H), 3.01 (d, $^2J_{\text{HH}} = 19.3$ Hz, 1H), 2.92 (d, $^2J_{\text{HH}} = 19.3$ Hz, 1H), 2.25-2.16 (m, 2H), 1.87 (s, 3H), 1.32-1.23 (m, 2H), 1.15-1.06 (m, 1H), 0.81 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H), 0.76-0.68 (m, 1H). ^{13}C NMR (CDCl_3): δ 206.2, 161.6, 143.8, 137.3, 136.7, 135.0, 133.3, 127.8, 127.2, 127.1, 126.3, 125.9, 123.7, 51.2, 49.9, 41.3, 27.0, 23.3, 22.0, 14.1. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29; H, 7.97. Found: C, 86.02; H, 7.92.

Procedure for Equation 2.

Substrate **4** (38.3 mg, 0.20 mmol) was added to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.9 mg, 20 μmol Rh) and dppf (12.2 mg, 22 μmol) in 1,2-dichloroethane (10 mL). PhZnCl (625 μL , 0.30 mmol; 0.48 M in THF) was then added to it and the resulting solution was stirred for 17 h at 25 $^\circ\text{C}$. The reaction was quenched with water (30 μL) and passed through a pad of silica gel with Et_2O . The solvent was removed under vacuum and the residue was purified by silica gel preparative TLC with Et_2O /hexane = 1/5 to afford indanone **5** as a colorless oil (41.8 mg, 0.16 mmol; 78% yield).

^1H NMR (CDCl_3): δ 7.31-7.27 (m, 2H), 7.23-7.18 (m, 3H), 2.95 (bs, 0.73H), 2.92 (bs, 0.27H), 2.27 (ddd, $^2J_{\text{HH}} = 13.6$ Hz and $^3J_{\text{HH}} = 12.5$ and 4.3 Hz, 1H), 2.15 (ddd, $^2J_{\text{HH}} = 13.4$ Hz and $^3J_{\text{HH}} = 12.3$ and 4.2 Hz, 1H), 1.34-1.26 (m, 2H), 1.25-1.16 (m, 1H), 0.92-0.85 (m, 1H), 0.84 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 206.1, 160.9, 147.18 (minor) and 147.16 (major), 136.9, 134.6 (t, $^1J_{\text{CD}} = 25.3$ Hz), 128.7, 127.4 (t, $^1J_{\text{CD}} = 25.3$ Hz), 126.6, 126.5, 125.9 (t, $^1J_{\text{CD}} = 24.8$ Hz), 123.1 (t, $^1J_{\text{CD}} = 24.2$ Hz), 52.8 (t, $^1J_{\text{CD}} = 20.5$ Hz; minor) and 52.7 (t, $^1J_{\text{CD}} = 20.7$ Hz; major), 50.0, 39.99 (major) and 39.98 (minor),

27.3, 23.3, 14.1. ^2H NMR (CHCl_3): δ 7.83 (bs, 1H), 7.65 (bs, 1H), 7.46 (bs, 1H), 7.38 (bs, 1H), 2.92 (bs, 1H).

Procedure for Equation 3.

1-Phenyl-2-heptyn-1-one **1a** (37.3 mg, 0.20 mmol) was added to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.9 mg, 20 μmol Rh) and dppf (12.2 mg, 22 μmol) in 1,2-dichloroethane (12 mL). PhZnCl (625 μL , 0.30 mmol; 0.48 M in THF) was then added to it and the resulting solution was stirred for 17 h at 25 $^\circ\text{C}$. The reaction mixture was cooled to 0 $^\circ\text{C}$ and allyl bromide (51.9 μL , 0.60 mmol) was added dropwise to it. After stirring for 6 h at 25 $^\circ\text{C}$, the mixture was directly passed through a pad of silica gel with Et_2O and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with Et_2O /hexane = 1/8 to afford allylated indanone **6** as a pale yellow oil (36.4 mg, 0.12 mmol; 60% yield; d.r. = 2.1/1). HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{24}\text{ONa}$ ($\text{M}+\text{Na}^+$) 327.1719, found 327.1720.

Major diastereomer: ^1H NMR (CDCl_3): δ 7.82 (d, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.59 (t, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.43 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 7.32-7.21 (m, 3H), 7.19-7.15 (m, 1H), 6.96 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2H), 5.78-5.66 (m, 1H), 4.88 (d, $^3J_{\text{HH}} = 9.6$ Hz, 1H), 4.75 (dd, $^3J_{\text{HH}} = 16.9$ Hz and $^4J_{\text{HH}} = 1.5$ Hz, 1H), 2.82 (dd, $^3J_{\text{HH}} = 7.8$ and 6.2 Hz, 1H), 2.36 (dt, $^2J_{\text{HH}} = 13.7$ Hz and $^3J_{\text{HH}} = 4.7$ Hz, 1H), 2.35-2.28 (m, 2H), 1.67-1.60 (m, 1H), 1.40-1.32 (m, 1H), 1.27-1.17 (m, 2H), 1.06-0.96 (m, 1H), 0.87 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 207.3, 159.3, 144.1, 136.78, 136.77, 135.1, 128.3, 128.2, 127.8, 126.7, 126.1, 123.5, 116.1, 57.8, 54.0, 38.0, 32.9, 26.9, 23.5, 14.2.

Minor diastereomer: ^1H NMR (CDCl_3): δ 7.81 (d, $^3J_{\text{HH}} = 6.2$ Hz, 1H), 7.57 (t, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.43 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 7.32-7.21 (m, 5H), 7.19-7.15 (m, 1H), 5.78-5.66 (m, 1H), 5.03 (dd, $^3J_{\text{HH}} = 16.4$ Hz and $^4J_{\text{HH}} = 1.4$ Hz, 1H), 4.90 (d, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 2.84-2.79 (m, 2H), 2.33-2.26 (m, 1H), 2.22 (dt, $^2J_{\text{HH}} = 13.1$ Hz and $^3J_{\text{HH}} = 4.4$ Hz, 1H), 1.90 (dt, $^2J_{\text{HH}} = 12.9$ Hz and $^3J_{\text{HH}} = 4.1$ Hz, 1H), 1.67-1.60 (m, 1H), 1.40-1.32 (m, 2H), 0.80 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3H), 0.75-0.66 (m, 1H). ^{13}C NMR (CDCl_3): δ 206.1, 160.0, 146.3, 137.3, 136.5, 134.4, 128.5, 128.0, 127.9, 126.7, 126.6, 123.3, 115.9, 63.7, 53.8, 35.7, 30.0, 27.7, 23.3, 14.1.

Procedure for Equation 4.

1-Phenyl-2-heptyn-1-one **1a** (18.6 mg, 0.10 mmol) was added to a solution of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (1.9 mg, 9.8 μmol Rh) and ligand **7** (6.6 mg, 11 μmol) in 1,2-dichloroethane (6 mL). PhZnCl (313 μL , 0.15 mmol; 0.48 M in THF) was then added to it and the resulting solution was stirred for 13 h at 25 $^\circ\text{C}$. The reaction was quenched with water (30 μL) and passed through a pad of silica gel with Et_2O . The solvent was removed under vacuum and the residue was purified by silica gel preparative TLC with Et_2O /hexane = 1/5 to afford indanone **2a** as a pale yellow oil (17.1 mg, 64.7 μmol ; 65% yield). The ee was determined using a Daicel Chiralcel OJ-H column with hexane : 2-propanol = 95 : 5, flow = 0.3 mL/min. Retention times: 34.6 min [(+)-enantiomer], 37.1 min [(-)-enantiomer]. 54% ee. $[\alpha]_{\text{D}}^{20} +8.3$ (c 0.62, CHCl_3).