Rhodium-Catalyzed Isomerization of α -Arylpropargyl Alcohols to Indanones: Involvement of an Unexpected Reaction Cascade

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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 distilled over benzophenone ketyl under nitrogen.

Trimethylsilylacetylene (Aldrich), triethylsilylacetylene (Aldrich), 1-hexyne (Aldrich), 3-methyl-1-butyne (Wako Chemicals), benzaldehyde (Wako Chemicals), *p*-tolualdehyde (Wako Chemicals), *p*-anisaldehyde (Nacalai Tesque), *o*-tolualdehyde (TCI), *m*-tolualdehyde (Nacalai Tesque), *m*-chlorobenzaldehyde (Wako Chemicals), *n*-BuLi (Kanto Chemicals; 1.60 M solution in hexane), and 1,4-bis(diphenylphosphino)butane (TCI) were used as received. $\text{RhCl}(\text{PPh}_3)_3$ ¹ and $\text{RhH}(\text{PPh}_3)_4$ ² 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. Synthesis of Substrates

The yields have not been optimized.

1-Phenyl-3-trimethylsilyl-2-propyn-1-ol (**1a**) (CAS 89530-34-7)

n-BuLi (3.94 mL, 6.30 mmol; 1.60 M solution in hexane) was added to a solution of trimethylsilylacetylene (933 μL , 6.60 mmol) in THF (18 mL) at $-50\text{ }^\circ\text{C}$ and the mixture was stirred for 25 min. Benzaldehyde (610 μL , 6.00 mmol) was then added to this, and the resulting solution was stirred for 1 h at room temperature. The reaction was quenched with water, poured into NaCl (aqueous, saturated), and extracted with Et_2O . The organic layer was dried over MgSO_4 , filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with Et_2O /hexane=1/3 to afford 1-phenyl-3-trimethylsilyl-2-propyn-1-ol as a colorless oil (1.20 g, 5.85 mmol; 97% yield).

¹H NMR (CDCl_3): δ 7.55 (d, $^3J_{\text{HH}} = 7.2\text{ Hz}$, 2H), 7.39 (t, $^3J_{\text{HH}} = 7.3\text{ Hz}$, 2H), 7.33 (t, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 1H), 5.46 (d, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1H), 2.18 (d, $^3J_{\text{HH}} = 6.3\text{ Hz}$, 1H), 0.21 (s, 9H).

¹ Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

² Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 58.

1-Phenyl-3-triethylsilyl-2-propyn-1-ol (1b) (CAS 70975-28-9 for (*R*), 70975-27-8 for (*S*))

This was synthesized using triethylsilylacetylene instead of trimethylsilylacetylene, following the procedure for compound **1a**. Colorless oil, 98% yield.

^1H NMR (CDCl_3): δ 7.56 (d, $^3J_{\text{HH}} = 7.4$ Hz, 2H), 7.38 (t, $^3J_{\text{HH}} = 6.9$ Hz, 2H), 7.32 (t, $^3J_{\text{HH}} = 7.1$ Hz, 1H), 5.47 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H), 2.20 (d, $^3J_{\text{HH}} = 6.5$ Hz, 1H), 1.01 (t, $^3J_{\text{HH}} = 7.8$ Hz, 9H), 0.64 (q, $^3J_{\text{HH}} = 7.9$ Hz, 6H).

Deuterated compounds **4**, **5**, and **7** were synthesized in the same way using corresponding deuterated benzaldehydes (α -deuterobenzaldehyde: CAS 3592-47-0, pentadeuterobenzaldehyde: CAS 14132-51-5, 2-deuterobenzaldehyde: CAS 66154-03-8).

1-(*p*-Tolyl)-3-triethylsilyl-2-propyn-1-ol (1c)

This was synthesized using triethylsilylacetylene and *p*-tolualdehyde instead of trimethylsilylacetylene and benzaldehyde, following the procedure for compound **1a**. Colorless oil, 94% yield.

^1H NMR (CDCl_3): δ 7.45 (d, $^3J_{\text{HH}} = 8.0$ Hz, 2H), 7.18 (d, $^3J_{\text{HH}} = 8.1$ Hz, 2H), 5.43 (d, $^3J_{\text{HH}} = 6.5$ Hz, 1H), 2.35 (s, 3H), 2.12 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H), 1.00 (t, $^3J_{\text{HH}} = 7.9$ Hz, 9H), 0.63 (q, $^3J_{\text{HH}} = 8.0$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 138.2, 137.6, 129.2, 126.7, 106.4, 88.8, 64.9, 21.1, 7.4, 4.3. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.87; H, 9.49.

1-(*p*-Anisyl)-3-triethylsilyl-2-propyn-1-ol (1d)

This was synthesized using triethylsilylacetylene and *p*-anisaldehyde instead of trimethylsilylacetylene and benzaldehyde, following the procedure for compound **1a**. Colorless oil, 95% yield.

^1H NMR (CDCl_3): δ 7.49 (d, $^3J_{\text{HH}} = 8.8$ Hz, 2H), 6.91 (d, $^3J_{\text{HH}} = 8.7$ Hz, 2H), 5.42 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H), 3.82 (s, 3H), 2.07 (d, $^3J_{\text{HH}} = 6.4$ Hz, 1H), 1.01 (t, $^3J_{\text{HH}} = 7.8$ Hz, 9H), 0.63 (q, $^3J_{\text{HH}} = 8.1$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 159.6, 132.9, 128.2, 113.9, 106.5, 88.7, 64.6, 55.3, 7.4, 4.3. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Si}$: C, 69.51; H, 8.75. Found: C, 69.42; H, 8.86.

1-(*o*-Tolyl)-3-triethylsilyl-2-propyn-1-ol (1e)

This was synthesized using triethylsilylacetylene and *o*-tolualdehyde instead of trimethylsilylacetylene and benzaldehyde, following the procedure for compound **1a**. Colorless oil, 99% yield.

^1H NMR (CDCl_3): δ 7.69-7.65 (m, 1H), 7.25-7.21 (m, 2H), 7.19-7.15 (m, 1H), 5.62 (d, $^3J_{\text{HH}} = 6.0$ Hz, 1H), 2.45 (s, 3H), 2.04 (d, $^3J_{\text{HH}} = 6.0$ Hz, 1H), 1.00 (t, $^3J_{\text{HH}} = 7.9$ Hz, 9H), 0.63 (q, $^3J_{\text{HH}} = 7.8$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 138.2, 136.2, 130.7, 128.4, 126.6, 126.1, 106.0, 89.0, 65.8, 18.9, 7.4, 4.3. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.65; H, 9.38.

1-(*m*-Tolyl)-3-triethylsilyl-2-propyn-1-ol (**1f**)

This was synthesized using triethylsilylacetylene and *m*-tolualdehyde instead of trimethylsilylacetylene and benzaldehyde, following the procedure for compound **1a**. Colorless oil, 96% yield.

^1H NMR (CDCl_3): δ 7.39 (s, 1H), 7.36 (d, $^3J_{\text{HH}} = 7.6$ Hz, 1H), 7.27 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.14 (d, $^3J_{\text{HH}} = 7.4$ Hz, 1H), 5.43 (d, $^3J_{\text{HH}} = 6.5$ Hz, 1H), 2.37 (s, 3H), 2.14 (d, $^3J_{\text{HH}} = 6.5$ Hz, 1H), 1.01 (t, $^3J_{\text{HH}} = 7.9$ Hz, 9H), 0.64 (q, $^3J_{\text{HH}} = 7.8$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 140.4, 138.2, 129.0, 128.4, 127.5, 123.8, 106.3, 89.0, 65.1, 21.4, 7.4, 4.3. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.85; H, 9.54.

1-(*m*-Chlorophenyl)-3-triethylsilyl-2-propyn-1-ol (**1g**)

This was synthesized using triethylsilylacetylene and *m*-chlorobenzaldehyde instead of trimethylsilylacetylene and benzaldehyde, following the procedure for compound **1a**. Pale yellow oil, 98% yield.

^1H NMR (CDCl_3): δ 7.60-7.55 (m, 1H), 7.46-7.42 (m, 1H), 7.33-7.28 (m, 2H), 5.44 (d, $^3J_{\text{HH}} = 6.3$ Hz, 1H), 2.19 (d, $^3J_{\text{HH}} = 6.3$ Hz, 1H), 1.01 (t, $^3J_{\text{HH}} = 7.8$ Hz, 9H), 0.64 (q, $^3J_{\text{HH}} = 7.9$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 142.4, 134.4, 129.8, 128.4, 127.0, 124.8, 105.4, 89.9, 64.4, 7.4, 4.2. Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{ClOSi}$: C, 64.14; H, 7.54. Found: C, 63.87; H, 7.25

Phenyl triethylsilylethynyl ketone (**6**)

This was prepared by the literature procedure for the synthesis of phenyl

trimethylsilylethynyl ketone,³ starting with triethylsilylacetylene, in 85% yield. Colorless oil.

¹H NMR (CDCl₃): δ 8.16 (d, ³J_{HH} = 7.1 Hz, 2H), 7.61 (t, ³J_{HH} = 7.5 Hz, 1H), 7.49 (t, ³J_{HH} = 7.9 Hz, 2H), 1.08 (t, ³J_{HH} = 7.9 Hz, 9H), 0.75 (q, ³J_{HH} = 7.6 Hz, 6H). ¹³C NMR (CDCl₃): δ 177.4, 136.5, 134.0, 129.4, 128.4, 102.0, 98.5, 7.2, 3.8. Anal. Calcd for C₁₅H₂₀OSi: C, 73.71; H, 8.25. Found: C, 73.33; H, 8.26.

1-Phenyl-2-heptyn-1-ol (CAS 2108-51-2)

This was synthesized using 1-hexyne instead of trimethylsilylacetylene, following the procedure for compound **1a**. Colorless oil, 96% yield.

¹H NMR (CDCl₃): δ 7.54 (d, ³J_{HH} = 7.4 Hz, 2H), 7.37 (t, ³J_{HH} = 6.9 Hz, 2H), 7.31 (t, ³J_{HH} = 7.3 Hz, 1H), 5.45 (d, ³J_{HH} = 6.1 Hz, 1H), 2.27 (td, ³J_{HH} = 7.1 Hz and ⁴J_{HH} = 2.0 Hz, 2H), 2.15 (bs, 1H), 1.56-1.49 (m, 2H), 1.47-1.38 (m, 2H), 0.92 (t, ³J_{HH} = 7.3 Hz, 3H).

1-Phenyl-4-methyl-2-pentyn-1-ol (CAS 5923-01-3)

This was synthesized using 3-methyl-1-butyne instead of trimethylsilylacetylene, following the procedure for compound **1a**. Colorless oil, 92% yield.

¹H NMR (CDCl₃): δ 7.54 (d, ³J_{HH} = 7.3 Hz, 2H), 7.37 (t, ³J_{HH} = 7.7 Hz, 2H), 7.32 (t, ³J_{HH} = 7.3 Hz, 1H), 5.45 (d, ³J_{HH} = 4.6 Hz, 1H), 2.65 (septet of d, ³J_{HH} = 6.8 Hz and ⁴J_{HH} = 1.8 Hz, 1H), 2.15 (bs, 1H), 1.21 (d, ³J_{HH} = 6.8 Hz, 6H).

RhCl(dppb)(PPh₃)

A solution of RhCl(PPh₃)₃ (1.02 g, 1.10 mmol) and dppb (469 mg, 1.10 mmol) in CH₂Cl₂ (25 mL) was stirred for 1 h at room temperature. The solution was concentrated under vacuum (until ca. 5 mL in volume) and hexane (50 mL) was added to form an orange-yellow precipitate. After stirring for 1 h at room temperature, the precipitate was collected by filtering off the solvent, washed with hexane, and dried under vacuum to afford RhCl(dppb)(PPh₃) as a yellow solid (676 mg, 0.82 mmol; 74% yield).

¹H NMR (C₆D₆): δ 8.08 (t, *J* = 7.3 Hz, 4H), 7.67 (t, *J* = 8.9 Hz, 4H), 7.48 (t, *J* = 9.3 Hz, 6H), 7.25-7.12 (m, 6H), 7.05-6.93 (m, 3H), 6.89 (q, *J* = 6.6 Hz, 6H), 6.80 (t, *J* = 7.6 Hz, 6H), 2.14-2.09 (m, 2H), 1.96 (bs, 2H), 1.84-1.73 (m, 2H), 1.18-1.08 (m, 2H). ³¹P{¹H} NMR (C₆D₆): δ 54.3 (ddd, ¹J_{RhP} = 185 Hz, ²J_{PP(cis)} = 48 Hz, and ²J_{PP(cis)} = 35 Hz), 32.2 (ddd, ²J_{PP(trans)} = 362 Hz, ¹J_{RhP} = 137 Hz, and ²J_{PP(cis)} = 35 Hz), 24.6 (ddd, ²J_{PP(trans)} = 360 Hz, ¹J_{RhP} = 137 Hz, and ²J_{PP(cis)} = 48 Hz). Anal. Calcd for C₄₆H₄₃ClP₃Rh: C, 66.80; H, 5.24. Found: C, 66.42; H, 5.32.

³ Logue, M. W.; Moore, G. L. *J. Org. Chem.* **1975**, *40*, 131.

III. Catalytic Isomerization Reactions

Procedure for Equation 1.

Propargyl alcohol **1a** (61.3 mg, 0.30 mmol) was added to a solution of $\text{RhCl}(\text{PPh}_3)_3$ (27.8 mg, 30 μmol) in THF (7.5 mL) at room temperature. KOH (0.15 mL, 90 μmol ; 0.6 M in H_2O) was then added to it and the resulting solution was stirred for 62 h at 60 $^\circ\text{C}$. The reaction 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 PTLC with Et_2O /hexane = 1/3 to afford indanone **2a** as a white solid (44.7 mg, 0.22 mmol; 73% yield).

^1H NMR (CDCl_3): δ 7.74 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.54 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H), 7.37 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.28 (t, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 2.87 (dd, $^2J_{\text{HH}} = 19.4$ Hz and $^3J_{\text{HH}} = 8.5$ Hz, 1H), 2.79-2.76 (m, 1H), 2.57 (dd, $^2J_{\text{HH}} = 19.3$ Hz and $^3J_{\text{HH}} = 2.0$ Hz, 1H), 0.02 (s, 9H). ^{13}C NMR (CDCl_3): δ 207.1, 158.6, 136.0, 134.3, 125.8, 125.6, 123.9, 39.5, 28.7, -3.2. Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{OSi}$: C, 70.53; H, 7.89. Found: C, 70.23; H, 7.71.

General Procedure for Table 1.

Propargyl alcohol **1** (0.40 mmol) was added to a solution of $\text{RhCl}(\text{PPh}_3)_3$ (18.5 mg, 20 μmol) in THF (5 mL) at room temperature. KOH (0.10 mL, 60 μmol ; 0.6 M in H_2O) was then added to it and the resulting solution was stirred for 48 h at 60 $^\circ\text{C}$. The reaction 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 PTLC with Et_2O /hexane = 1/3 to afford indanone **2**.

Entry 1. Pale yellow oil. 92% yield.

^1H NMR (CDCl_3): δ 7.73 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.53 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 7.36 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.27 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 2.91 (d, $^3J_{\text{HH}} = 10.0$ Hz, 1H), 2.87 (dd, $^2J_{\text{HH}} = 18.1$ Hz and $^3J_{\text{HH}} = 8.5$ Hz, 1H), 2.62 (d, $^2J_{\text{HH}} = 18.2$ Hz, 1H), 0.89 (t, $^3J_{\text{HH}} = 7.8$ Hz, 9H), 0.58 (q, $^3J_{\text{HH}} = 8.0$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 207.2, 159.0, 136.2, 134.3, 125.73, 125.68, 124.0, 39.4, 25.3, 7.3, 2.3. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{OSi}$: C, 73.11; H, 9.00. Found: C, 72.79; H, 9.20.

Entry 2. Pale yellow oil. 87% yield.

^1H NMR (CDCl_3): δ 7.62 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 7.14 (s, 1H), 7.08 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 2.89-2.81 (m, 2H), 2.63-2.56 (m, 1H), 2.43 (s, 3H), 0.89 (t, $^3J_{\text{HH}} = 8.0$ Hz, 9H), 0.58 (q, $^3J_{\text{HH}} = 7.9$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 206.6, 159.6, 145.4, 134.0, 127.1, 126.0, 123.8, 39.6, 25.1, 22.1, 7.3, 2.4. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.86; H, 9.33.

Entry 3. Pale yellow oil. 90% yield.

^1H NMR (CDCl_3): δ 7.67 (d, $^3J_{\text{HH}} = 8.5$ Hz, 1H), 6.82 (dd, $^3J_{\text{HH}} = 8.4$ Hz and $^4J_{\text{HH}} = 2.1$ Hz, 1H), 6.79 (d, $^4J_{\text{HH}} = 1.7$ Hz, 1H), 3.87 (s, 3H), 2.90-2.76 (m, 2H), 2.63-2.56 (m, 1H), 0.90 (t, $^3J_{\text{HH}} = 8.2$ Hz, 9H), 0.59 (q, $^3J_{\text{HH}} = 7.9$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 205.3, 165.0, 161.9, 129.7, 125.6, 113.3, 109.2, 55.5, 39.6, 25.4, 7.3, 2.4. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Si}$: C, 69.51; H, 8.75. Found: C, 69.23; H, 8.84.

Entry 4. Pale yellow oil. 84% yield.

^1H NMR (CDCl_3): δ 7.36 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H), 7.16 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 6.99 (d, $^3J_{\text{HH}} = 7.3$ Hz, 1H), 2.89-2.81 (m, 2H), 2.62 (s, 3H), 2.62-2.55 (m, 1H), 0.88 (t, $^3J_{\text{HH}} = 8.1$ Hz, 9H), 0.57 (q, $^3J_{\text{HH}} = 7.9$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 208.1, 159.8, 139.1, 133.7, 133.6, 127.6, 123.1, 40.1, 24.8, 18.4, 7.3, 2.4. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.59; H, 9.39.

Entry 5. 10 mol % catalyst was used. Pale yellow oil. 76% yield, >20/1 regioselectivity.

Major isomer: ^1H NMR (CDCl_3): δ 7.53 (s, 1H), 7.35 (d, $^3J_{\text{HH}} = 7.9$ Hz, 1H), 7.25 (d, $^3J_{\text{HH}} = 7.8$ Hz, 1H), 2.90-2.82 (m, 2H), 2.65-2.57 (m, 1H), 2.38 (s, 3H), 0.89 (t, $^3J_{\text{HH}} = 8.0$ Hz, 9H), 0.57 (q, $^3J_{\text{HH}} = 7.7$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 207.2, 156.3, 136.3, 135.7, 135.5, 125.3, 123.9, 39.7, 24.8, 20.8, 7.3, 2.4. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.49; H, 9.32.

Entry 6. 10 mol % catalyst was used. Pale yellow oil. 74% yield, 10/1 regio-selectivity.

Major isomer: ^1H NMR (CDCl_3): δ 7.69 (d, $^4J_{\text{HH}} = 2.0$ Hz, 1H), 7.48 (dd, $^3J_{\text{HH}} = 8.2$ Hz and $^4J_{\text{HH}} = 2.1$ Hz, 1H), 7.30 (d, $^3J_{\text{HH}} = 8.2$ Hz, 1H), 2.91 (dd, $^2J_{\text{HH}} = 17.9$ Hz and $^3J_{\text{HH}} = 8.5$ Hz, 1H), 2.86 (d, $^3J_{\text{HH}} = 9.0$ Hz, 1H), 2.65 (d, $^2J_{\text{HH}} = 17.7$ Hz, 1H), 0.89 (t, $^3J_{\text{HH}} = 7.9$ Hz, 9H), 0.57 (q, $^3J_{\text{HH}} = 7.9$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 205.6, 157.1, 137.6, 134.3, 132.1, 126.8, 123.8, 39.9, 25.2, 7.3, 2.3. Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{ClOSi}$: C, 64.14; H, 7.54. Found: C, 63.87; H, 7.25.

Procedure for Equation 6.

Alkynone **6** (48.7 mg, 0.20 mmol) was added to a solution of $\text{RhH}(\text{PPh}_3)_4$ (277 mg, 0.24 mmol) in THF (30 mL) at room temperature. H_2O (0.60 mL) was then added to it and the resulting solution was stirred for 26 h at 60 °C. The reaction 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 PTLC with Et_2O /hexane = 1/3 to afford indanone **2b** as a pale yellow oil (22.1 mg, 89 μmol ; 45% yield).

Procedure for Equation 8.

Propargyl alcohol (0.20 mmol) was added to a solution of $\text{RhCl}(\text{dppb})(\text{PPh}_3)$ (16.5 mg, 20 μmol) in THF (5.0 mL) at room temperature. KOH (0.10 mL, 60 μmol ; 0.6 M in H_2O) was then added to it and the resulting solution was stirred for 21 h at 50 °C. The reaction 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 PTLC with Et_2O /hexane = 1/3 to afford indanone.

Pale yellow oil. 66% yield. (CAS 50438-03-4)

^1H NMR (CDCl_3): δ 7.73 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.60 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H), 7.51 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.37 (t, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 3.39-3.32 (m, 1H), 2.85 (dd, $^2J_{\text{HH}} = 19.1$ Hz and $^3J_{\text{HH}} = 7.6$ Hz, 1H), 2.36 (dd, $^2J_{\text{HH}} = 19.1$ Hz and $^3J_{\text{HH}} = 3.3$ Hz, 1H), 1.95-1.89 (m, 1H), 1.54-1.32 (m, 5H), 0.92 (t, $^3J_{\text{HH}} = 6.9$ Hz, 3H).

Pale yellow oil. 67% yield. (CAS 22531-07-3)

^1H NMR (CDCl_3): δ 7.73 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.59 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 7.49 (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H), 7.37 (t, $^3J_{\text{HH}} = 7.2$ Hz, 1H), 3.43-3.39 (m, 1H), 2.66 (dd, $^2J_{\text{HH}} = 19.0$

Hz and $^3J_{\text{HH}} = 7.7$ Hz, 1H), 2.46 (dd, $^2J_{\text{HH}} = 19.1$ Hz and $^3J_{\text{HH}} = 3.0$ Hz, 1H), 2.27 (septet of d, $^3J_{\text{HH}} = 6.8$ Hz and $^3J_{\text{HH}} = 4.1$ Hz, 1H), 1.02 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H), 0.67 (d, $^3J_{\text{HH}} = 6.8$ Hz, 3H).

IV. ^1H NMR Spectra