Supporting Information

1,4-Reduction of α,β–Unsaturated Ketones through Rhodium(III)-Catalyzed Transfer Hydrogenation

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1. General Remarks

$^1$H-NMR spectra were recorded on a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and calibrated with CDCl$_3$ ($\delta = 77.00$ ppm). Mass spectra were recorded using an Agilent 5975 GC-MS and Bruker APEX IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Chalcones were easily synthesized according to the reported methods.$^1$

2. Typical Procedure

To an oven-dried vial, chalcone 1 (0.20 mmol, 1.0 equiv), $[(\text{Cp*RhCl}_2)_2]$ (0.006 mmol, 3.0 mol %), and isopropanol (1.0 mL) were added. The vial was charged with N$_2$ and sealed immediately. The mixture was stirred at 100 °C, and the progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was cooled down to room temperature, filtered through a celite pad, and washed with ethyl acetate. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel or preparative thin-layer chromatography to obtain the desired products 2 (petroleum ether : ethyl acetate = 100:1).

3. Synthesis and Characterization of Substrates

1) 1,3-Diphenylpropan-1-one (2a)$^2$

The reaction of chalcone (1a, 0.2 mmol, 41.6 mg), $[(\text{Cp*RhCl}_2)_2]$ (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 39.5 mg (94%) of 2a as an solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.96$ (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.8$ Hz, 2H), 7.34-7.17 (m, 5H), 3.31 (t, $J = 7.8$ Hz, 2H), 3.07 (t, $J = 7.8$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 199.2, 141.3, 136.8, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1$ ppm; IR (KBr): $\nu_{\text{max}} = 3440, 1682, 1602, 1506, 1448, 1209, 744, 702, 689$ cm$^{-1}$.
2) 1-(2-Hydroxyphenyl)-3-phenylpropan-1-one (2b)³

The reaction of 1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1b, 0.2 mmol, 44.8 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 130 °C for 12 h afforded 40.9 mg (90%) of 2b as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 12.32 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.6 (t, J = 7.8 Hz, 1H), 7.34-7.20 (m, 5H), 6.98 (d, J = 8.4 Hz, 1H), 6.88 (t, J = 7.6 Hz, 1H), 3.33 (t, J = 7.6 Hz, 2H), 3.07 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 205.3, 162.4, 140.7, 136.3, 129.8, 128.6, 128.4, 126.3, 119.2, 118.9, 118.5, 40.0, 30.0 ppm; IR (KBr): vₘₓ = 3028, 1639, 1614, 1581, 1487, 1447, 1305, 1259, 1198, 1157, 979, 751, 699 cm⁻¹.

3) 1-(2-Aminophenyl)-3-phenylpropan-1-one (2c)⁴

The reaction of 1-(2-aminophenyl)-3-phenylprop-2-en-1-one (1c, 0.2 mmol, 44.6 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 130 °C for 12 h afforded 34.1 mg (76%) of 2c as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.73 (d, J = 8.0 Hz, 1H), 7.34-7.17 (m, 6H), 6.69-6.60 (m, 2H), 6.29 (br, 2H), 3.28 (t, J = 7.6 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 201.5, 150.3, 141.5, 134.3, 131.0, 128.5, 128.4, 126.0, 117.7, 117.3, 115.8, 41.0, 30.5 ppm; IR (KBr): vₘₓ = 3402, 1652, 1615, 1577, 1448, 1202, 1158, 975, 751 cm⁻¹.

4) 1-(4-Fluorophenyl)-3-phenylpropan-1-one (2d)²

The reaction of 1-(4-fluorophenyl)-3-phenylprop-2-en-1-one (1d, 0.2 mmol, 45.2 mg),
[(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 41.9 mg (92%) of 2d as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 8.02-7.94 (m, 2H), 7.34-7.18 (m, 5H), 7.16-7.08 (m, 2H), 3.28 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 197.6, 165.7 (J_C-F = 253.2 Hz), 141.1, 133.2 (J_C-F = 2.9 Hz), 130.6 (J_C-F = 9.3 Hz), 128.5, 128.4, 126.2, 115.7 (J_C-F = 21.8 Hz), 40.4, 30.0 ppm; ¹⁹F NMR (377 MHz, CDCl₃): δ = -105.21 (s); IR (KBr): ν_max = 3441, 1681, 1597, 1506, 1243, 1204, 848, 701 cm⁻¹.

5) 1-(4-Chlorophenyl)-3-phenylpropan-1-one (2e)²

![Structure 2e](image)

The reaction of 1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (1e, 0.2 mmol, 48.2 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 44.7 mg (91%) of 2e as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.90 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 7.33-7.17 (m, 5H), 3.28 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 7.7 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 198.0, 141.0, 139.5, 135.1, 129.4, 128.9, 128.5, 128.4, 126.2, 40.4, 30.0 ppm; IR (KBr): ν_max = 3437, 1682, 1587, 1397, 1204, 1094, 979, 847, 779, 745, 696 cm⁻¹.

6) 1-(4-Bromophenyl)-3-phenylpropan-1-one (2f)²

![Structure 2f](image)

The reaction of 1-(4-bromophenyl)-3-phenylprop-2-en-1-one (1f, 0.2 mmol, 57.4 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 33.1 mg (57%) of 2f as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.82 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.34-7.19 (m, 5H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 198.2, 141.0, 135.4, 131.9, 129.5, 128.5, 128.4, 126.2, 40.4, 30.0 ppm; IR (KBr): ν_max = 3442, 1683, 1582,
1396, 1203, 1071, 978, 779, 745, 699 cm$^{-1}$.

7) 3-Phenyl-1-(p-tolyl)propan-1-one (2g)$^5$

![Image of 3-Phenyl-1-(p-tolyl)propan-1-one]

The reaction of 3-phenyl-1-(p-tolyl)prop-2-en-1-one (1g, 0.2 mmol, 44.4 mg), [(Cp*RhCl$_2$)$_2$] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 42.1 mg (94%) of 2g as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.86$ (d, $J = 8.4$ Hz, 2H), 7.33-7.17 (m, 7H), 3.27 (t, $J = 7.7$ Hz, 2H), 3.06 (t, $J = 7.7$ Hz, 2H), 2.40 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 19.8, 143.8, 141.4, 134.3, 129.2, 128.5, 128.4, 128.1, 126.0, 40.3, 30.2, 21.6$ ppm; IR (KBr): $\nu_{\text{max}} = 3435, 1674, 1605, 1494, 1451, 1384, 1201, 1193, 971, 775, 743, 701$ cm$^{-1}$.

8) 1-(4-Methoxyphenyl)-3-phenylpropan-1-one (2h)$^2$

![Image of 1-(4-Methoxyphenyl)-3-phenylpropan-1-one]

The reaction of 1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (1h, 0.2 mmol, 47.6 mg), [(Cp*RhCl$_2$)$_2$] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 43.7 mg (91%) of 2h as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.95$ (d, $J = 8.8$ Hz 2H), 7.33-7.18 (m, 5H), 6.93 (d, $J = 8.8$ Hz 2H), 3.87 (s, 3H), 3.25 (t, $J = 7.8$ Hz, 2H), 3.06 (t, $J = 7.8$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 197.8, 163.4, 141.4, 130.3, 129.9, 128.5, 128.4, 126.1, 113.7, 55.4, 40.1, 30.3$ ppm; IR (KBr): $\nu_{\text{max}} = 3436, 1670, 1602, 1576, 1442, 1261, 1211, 1178, 1028, 978, 841, 782, 740, 699$ cm$^{-1}$.

9) 3-Phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (2i)$^2$
The reaction of 3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1i, 0.2 mmol, 55.2 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 45.1 mg (81%) of 2i as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 8.05 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.34-7.19 (m, 5H), 3.33 (t, J = 7.6 Hz, 2H), 3.08 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 198.2, 140.8, 139.3, 134.3 (q, J_C-F = 32.3 Hz), 128.6, 128.4, 128.3, 126.3, 125.7 (q, J_C-F = 3.6 Hz), 123.5 (q, J_C-F = 271.1 Hz), 40.7, 29.8 ppm; ¹⁹F NMR (377 MHz, CDCl₃): δ = -63.0 (s); IR (KBr): ν_max = 3440, 1685, 1412, 1332, 1169, 1132, 1120, 1086, 1016, 837, 786, 694 cm⁻¹.

10) 1-(4-Nitrophenyl)-3-phenylpropan-1-one (2j)⁶

The reaction of 1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (1j, 0.2 mmol, 50.6 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 30.1 mg (59%) of 2j as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 8.30 (d, J = 8.4 Hz 2H), 8.10 (d, J = 8.8 Hz, 2H), 7.36-7.19 (m, 5H), 3.36 (t, J = 7.6 Hz, 2H), 3.09 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 197.6, 150.2, 141.1, 140.6, 129.0, 128.6, 128.4, 126.4, 123.9, 41.0, 29.8 ppm; IR (KBr): ν_max = 3438, 1686, 1521, 1345, 1196, 1107, 1067, 978 cm⁻¹.

11) 3-Phenyl-1-(thiophen-2-yl)propan-1-one (2k)⁵

The reaction of 3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (1k, 0.2 mmol, 42.8
mg), \[
(Cp*RhCl_2)_2 \] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 130 °C for 12 h afforded 37.2 mg (86%) of \( 2k \) as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.72-7.67 \) (m, 1H), 7.65-7.60 (m, 1H), 7.34-7.19 (m, 5H), 7.15-7.09 (m, 1H), 3.24 (t, \( J = 8.0 \) Hz, 2H), 3.08 (t, \( J = 8.0 \) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 192.2, 144.1, 141.0, 133.5, 131.8, 128.5, 128.4, 128.1, 126.2, 41.1, 30.3 \) ppm; IR (KBr): \( \nu_{\text{max}} = 3446, 3354, 3016, 2945, 2857, 1684, 1424, 1284, 1045, 931 \) cm\(^{-1}\).

12) \( \text{1-Phenyl-3-\(p\)-tolyl)propan-1-one (2l)} \)

The reaction of 1-phenyl-3-(\(p\)-tolyl)propan-2-en-1-one (1l, 0.2 mmol, 44.4 mg), \[
(Cp*RhCl_2)_2 \] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 39.9 mg (89%) of \( 2l \) as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.97 \) (d, \( J = 8.0 \) Hz 2H), 7.57 (t, \( J = 7.6 \) Hz, 1H), 7.46 (t, \( J = 7.6 \) Hz, 2H), 7.22 (d, \( J = 8.0 \) Hz, 2H), 7.12 (d, \( J = 8.0 \) Hz, 2H), 3.30 (t, \( J = 7.6 \) Hz, 2H), 3.04 (t, \( J = 7.6 \) Hz, 2H), 2.33 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 199.3, 138.1, 136.8, 135.6, 133.0, 129.2, 128.6, 128.3, 128.0, 40.6, 29.7, 21.0 \) ppm; IR (KBr): \( \nu_{\text{max}} = 3438, 1683, 1516, 1447, 1207, 795, 747, 692 \) cm\(^{-1}\).

13) \( \text{1-Phenyl-3-\(m\)-tolyl)propan-1-one (2m)} \)

The reaction of 1-phenyl-3-(\(m\)-tolyl)propan-2-en-1-one (1m, 0.2 mmol, 44.4 mg), \[
(Cp*RhCl_2)_2 \] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 40.8 mg (91%) of \( 2m \) as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.98 \) (d, \( J = 7.6 \) Hz, 2H), 7.57 (t, \( J = 7.2 \) Hz, 1H), 7.47 (t, \( J = 7.6 \) Hz, 2H), 7.21 (t, \( J = 7.6 \) Hz, 1H), 7.10-7.01 (m, 3H), 3.31 (t, \( J = 7.6 \) Hz, 2H), 3.04 (t, \( J = 7.6 \) Hz, 2H), 2.35 (s, 3H);
$^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 199.3, 141.2, 138.1, 136.7, 133.0, 129.2, 128.6,$
$128.4, 128.0, 126.8, 125.3, 40.5, 30.0, 21.4$ ppm; IR (KBr): $\nu_{\text{max}} = 3443, 1683, 1448,$
$1359, 1293, 1206, 776, 746, 702, 691$ cm$^{-1}$.

14) 1-Phenyl-3-(o-tolyl)propan-1-one ($2n$)$^2$

![Image of 1-Phenyl-3-(o-tolyl)propan-1-one](image)

The reaction of 1-phenyl-3-(o-tolyl)prop-2-en-1-one ($1n$, 0.2 mmol, 44.4 mg),
[(Cp*RhCl$_2$)$_2$] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h
afforded 43.0 mg (96%) of $2n$ as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.97$ (d, $J$
$= 7.2$ Hz, 2H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.46 (t, $J = 7.2$ Hz, 2H), 7.23-7.10 (m, 4H),
3.25 (t, $J = 7.0$ Hz, 2H), 3.06 (t, $J = 7.0$ Hz, 2H), 2.35 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100
MHz): $\delta = 199.3, 139.4, 136.8, 136.0, 133.1, 130.3, 128.7, 128.6, 128.0, 126.3, 126.2,$
39.1, 27.5, 19.3 ppm; IR (KBr): $\nu_{\text{max}} = 3442, 1682, 1493, 1450, 1363, 1207, 974, 753,$
691 cm$^{-1}$.

15) 3-(3,5-Dimethylphenyl)-1-phenylpropan-1-one ($2o$)$^7$

![Image of 3-(3,5-Dimethylphenyl)-1-phenylpropan-1-one](image)

The reaction of 3-(3,5-dimethylphenyl)-1-phenylprop-2-en-1-one ($1o$, 0.2 mmol, 47.2
mg), [(Cp*RhCl$_2$)$_2$] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 130 °C for
12 h afforded 40.9 mg (86%) of $2o$ as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.98$
(d, $J = 8.4$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.49-7.25 (m, 2H), 6.89 (s, 2H), 6.87 (s,
1H), 3.30 (t, $J = 7.8$ Hz, 2H), 3.00 (t, $J = 7.8$ Hz, 2H), 2.31 (s, 6H); $^{13}$C NMR (CDCl$_3$, 100
MHz): $\delta = 199.3, 166.8, 141.2, 138.0, 136.7, 133.0, 128.5, 128.0, 127.7, 126.2,$
40.6, 29.9, 21.3 ppm; IR (KBr): $\nu_{\text{max}} = 3440, 1677, 1606, 1448, 1362, 1277, 1207,$
975, 845, 746, 698, 692 cm$^{-1}$.
16) 3-(4-Fluorophenyl)-1-phenylpropan-1-one (2p)$^2$

![2p](image)

The reaction of 3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (1p, 0.2 mmol, 45.2 mg), $\text{[Cp}^*\text{RhCl}_2\text{]}_2$ (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 42.4 mg (93%) of 2p as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.95 (d, $J$ = 7.6 Hz, 2H), 7.57 (t, $J$ = 7.2 Hz, 1H), 7.50-7.40 (m, 2H), 7.25-7.17 (m, 2H), 7.01-6.93 (m, 2H), 3.29 (t, $J$ = 7.6 Hz, 2H), 3.05 (t, $J$ = 7.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 199.0, 161.3 ($J_{C-F}$ = 242.4 Hz), 136.8 ($J_{C-F}$ = 3.1 Hz), 136.7, 133.1, 129.8 ($J_{C-F}$ = 7.8 Hz), 128.6, 128.0, 115.2 ($J_{C-F}$ = 21.1 Hz), 40.4, 29.2 ppm; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ = -117.25 (s); IR (KBr): $\nu_{max}$ = 3443, 1682, 1601, 1509, 1446, 1360, 1292, 1215, 1205, 1157, 834, 746, 691, 538 cm$^{-1}$.

17) 3-(4-Chlorophenyl)-1-phenylpropan-1-one (2q)$^2$

![2q](image)

The reaction of 3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (1q, 0.2 mmol, 48.5 mg), $\text{[Cp}^*\text{RhCl}_2\text{]}_2$ (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 41.6 mg (85%) of 2q as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.95 (d, $J$ = 8.0 Hz, 2H), 7.57 (t, $J$ = 7.2 Hz, 1H), 7.50-7.43 (m, 2H), 7.26 (d, $J$ = 8.0 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 3.29 (t, $J$ = 7.2 Hz, 2H), 3.04 (t, $J$ = 7.6 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 198.8, 139.7, 136.6, 133.2, 131.8, 129.8, 128.6, 128.5, 128.0, 40.1, 29.3 ppm; IR (KBr): $\nu_{max}$ = 3439, 1669, 1492, 1448, 1269, 1210, 1094, 1015, 825, 778, 741, 687, 677, 485 cm$^{-1}$.

18) 3-(4-Bromophenyl)-1-phenylpropan-1-one (2r)$^2$
The reaction of 3-(4-bromophenyl)-1-phenylprop-2-en-1-one (1r, 0.2 mmol, 57.4 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 56.6 mg (98%) of 2r as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.95 (d, J = 7.6 Hz, 2H), 7.59-7.51 (m, 1H), 7.50-7.32 (m, 2H), 7.16-7.05 (m, 2H), 3.28 (t, J = 7.2 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 198.8, 140.2, 136.7, 133.2, 131.5, 130.2, 128.6, 128.0, 119.8, 40.0, 29.4 ppm; IR (KBr): νmax = 3439, 1669, 1487, 1446, 1425, 1270, 1210, 1073, 1011, 823, 776, 766, 740, 687, 480 cm⁻¹.

19) 3-(4-Methoxyphenyl)-1-phenylpropan-1-one (2s)²

The reaction of 3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (1s, 0.2 mmol, 47.6 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 45.1 mg (94%) of 2s as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.96 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.50-7.40 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 3.27 (t, J = 7.6 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 199.4, 158.0, 136.8, 133.3, 133.0, 129.3, 128.6, 128.0, 113.9, 55.2, 40.7, 29.2 ppm; IR (KBr): νmax = 3447, 1681, 1464, 1403, 1236, 1203, 1179, 1033, 825, 744, 692, 549 cm⁻¹.

20) 3-(4-Hydroxyphenyl)-1-phenylpropan-1-one (2t)⁶

The reaction of 3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (1t, 0.2 mmol, 44.8 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 120 °C for
12 h afforded 42.1 mg (93%) of 2t as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.96\) (d, \(J = 7.6\) Hz, 2H), 7.56 (t, \(J = 7.2\) Hz, 1H), 7.50-7.40 (m, 2H), 7.11 (d, \(J = 7.6\) Hz, 2H), 6.78 (d, \(J = 7.6\) Hz, 2H), 5.21 (s, 1H), 3.28 (t, \(J = 7.6\) Hz, 2H), 3.00 (t, \(J = 7.6\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 199.8, 154.0, 136.7, 133.1, 129.5, 128.6, 128.0, 115.3, 40.7, 29.3\) ppm; IR (KBr): \(\nu_{\max} = 3421, 1677, 1612, 1595, 1515, 1446, 1291, 1261, 1216, 1202, 745, 690, 547\) cm\(^{-1}\).

21) 4-(3-Oxo-3-phenylpropyl)benzonitrile (2u)\(^6\)

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\text{O} \quad \begin{array}{c}
\text{CN} \\
\text{Ph} \\
\text{Ph}
\end{array}
\]

The reaction of 4-(3-oxo-3-phenylprop-1-en-1-yl)benzonitrile (1u, 0.2 mmol, 46.6 mg), [(Cp*RhCl\(_2\))] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 33.8 mg (72%) of 2u as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.95\) (d, \(J = 7.6\) Hz, 2H), 7.64-7.51 (m, 3H), 7.47 (t, \(J = 7.6\) Hz, 2H), 7.37 (d, \(J = 8.0\) Hz, 2H), 3.33 (t, \(J = 7.4\) Hz, 2H), 3.14 (t, \(J = 7.4\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 198.2, 147.0, 136.4, 133.3, 132.3, 129.3, 128.7, 127.9, 119.0, 110.0, 39.4, 29.9\) ppm; IR (KBr): \(\nu_{\max} = 3428, 2220, 1678, 1606, 1448, 1438, 1213, 828, 747, 690, 556\) cm\(^{-1}\).

22) 1-Phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (2v)\(^2\)

\[
\text{CF}_3 \quad \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

The reaction of 1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1v, 0.2 mmol, 55.2 mg), [(Cp*RhCl\(_2\))] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 52.8 mg (95%) of 2v as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.04-7.90\) (m, 2H), 7.64-7.53 (m, 3H), 7.54-7.45 (m, 2H), 7.43-7.31 (m, 2H), 3.40-3.28 (m, 2H), 3.20-3.08 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 198.5, 145.4, 136.6, 133.2, 128.8, 128.6, 128.3, 128.0, 125.4\) (q, \(J_{C,F} = 3.4\) Hz), 124.3 (q, \(J_{C,F} = 270.5\) Hz), 39.8, 29.7 ppm; \(^{19}\)F NMR (377 MHz, CDCl\(_3\) : \(\delta = -62.33\) (s); IR (KBr):
\[ \nu_{\text{max}} = 3444, 1678, 1328, 1160, 1116, 1105, 1069, 829, 747, 691, 662, 595 \text{ cm}^{-1}. \]

23) 3-(4-Nitrophenyl)-1-phenylpropan-1-one (2w)\(^8\)

The reaction of 3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (1w, 0.2 mmol, 50.6 mg), [(Cp*RhCl\(_2\))]\(_2\) (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 45.9 mg (90%) of 2w as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.15 \text{ (d, } J = 8.0 \text{ Hz, 2H), } 7.95 \text{ (d, } J = 7.6 \text{ Hz, 2H), } 7.58 \text{ (t, } J = 7.2 \text{ Hz, 1H), } 7.51-7.38 \text{ (m, 4H), } 3.36 \text{ (t, } J = 7.4 \text{ Hz, 2H), } 3.19 \text{ (t, } J = 7.4 \text{ Hz, 2H); } ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz): } \delta = 198.1, 149.2, 146.4, 136.4, 133.4, 129.3, 128.7, 127.9, 123.7, 39.4, 29.6 \text{ ppm; IR (KBr): } \nu_{\text{max}} = 3439, 1682, 1597, 1511, 1450, 1344, 1291, 1208, 1110, 976, 854, 743, 692 \text{ cm}^{-1}. \]

24) 1-Phenyl-3-(thiophen-2-yl)propan-1-one (2x)\(^2\)

The reaction of 1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (1x, 0.2 mmol, 42.8 mg), [(Cp*RhCl\(_2\))]\(_2\) (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 130 °C for 12 h afforded 34.6 mg (80%) of 2x as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.98 \text{ (d, } J = 8.0 \text{ Hz, 2H), } 7.57 \text{ (t, } J = 7.6 \text{ Hz, 1H), } 7.52-7.42 \text{ (m, 2H), } 7.14 \text{ (d, } J = 4.8 \text{ Hz, 1H), } 6.96-6.90 \text{ (m, 1H), } 6.89-6.85 \text{ (m, 1H), } 3.38 \text{ (t, } J = 7.1 \text{ Hz, 2H), } 3.30 \text{ (t, } J = 7.1 \text{ Hz, 2H); } ^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz): } \delta = 198.6, 143.8, 136.8, 133.2, 128.6, 128.0, 126.8, 124.7, 123.4, 40.5, 24.1 \text{ ppm; IR (KBr): } \nu_{\text{max}} = 3424, 1682, 1447, 1362, 1297, 1207, 972, 748, 739, 706, 692 \text{ cm}^{-1}. \]

25) Chroman-4-one (2y)\(^9\)

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The reaction of 4H-chromen-4-one (1y, 0.2 mmol, 29.2 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 26.9 mg (91%) of 2y as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.95-7.86 (m, 1H), 7.50-7.43 (m, 1H), 7.07-6.96 (m, 2H), 4.54 (t, J = 6.4 Hz, 2H), 2.82 (t, J = 6.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 191.9, 161.8, 136.0, 127.1, 121.4, 121.3, 117.9, 67.0, 37.8 ppm; IR (KBr): ν_max = 3440, 1685, 1602, 1578, 1479, 1461, 1332, 1321, 1230, 1257, 1220, 1147, 1033, 1018, 767, 665, 557, 507 cm⁻¹.

26) Propiophenone (2z)¹⁰

The reaction of 1-phenylprop-2-en-1-one (1z, 0.2 mmol, 26.4 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 19.6 mg (73%) of 2z as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.99-7.94 (m, 2H), 7.58-7.51 (m, 1H), 7.48-7.42 (m, 2H), 3.01 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 200.8, 136.8, 132.8, 128.5, 127.9, 31.7, 8.2 ppm; IR (KBr): ν_max = 3433, 2923, 1683, 1645, 1449, 1384, 1261, 1076, 1025, 749, 697 cm⁻¹.

27) 2-Methyl-3,4-dihydronaphthalen-1(2H)-one (2a')¹⁰

The reaction of 2-methylene-3,4-dihydronaphthalen-1(2H)-one (1a’, 0.2 mmol, 31.6
mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 21.4 mg (67%) of 2a′ as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 8.03 (d, J = 8.0 Hz, 1H), 7.49-7.42 (m, 1H), 7.33-7.20 (m, 2H), 3.10-2.94 (m, 2H), 2.66-2.53 (m, 1H), 2.24-2.13 (m, 1H), 1.95-1.82 (m, 1H), 1.27 (d, J = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 200.8, 144.2, 133.0, 132.3, 128.7, 127.3, 126.5, 42.6, 31.3, 28.8, 15.4 ppm; IR (KBr): v_max = 2931, 1685, 1602, 1455, 1375, 1358, 1323, 1267, 1228, 968, 907, 739 cm⁻¹.

28) 4-Phenylbutan-2-one (2b′)⁵

The reaction of 4-phenylbut-3-en-2-one (1b′, 0.2 mmol, 29.2 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 24 h afforded 20.1 mg (68%) of 2b′ as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.34-7.26 (m, 2H), 7.22-7.15 (m, 3H), 2.90 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.14 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 208.0, 140.9, 128.4, 128.2, 126.1, 45.1, 30.1, 29.6 ppm; IR (KBr): v_max = 3413, 3027, 2926, 1717, 1603, 1497, 1453, 1359, 1162, 1030, 750, 699, 502 cm⁻¹.

29) 1-Phenylbutan-1-one (2c′)¹¹

The reaction of 1-phenylbut-2-en-1-one (1c′, 0.2 mmol, 29.2 mg), [(Cp*RhCl₂)₂] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 20.1 mg (68%) of 2c′ as a solid; ¹H NMR (CDCl₃, 400 MHz): δ = 7.99-7.93 (m, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.50-7.40 (m, 2H), 2.95 (t, J = 7.2 Hz, 2H), 1.83-1.71 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 200.4, 137.1, 132.8, 128.5, 128.0, 40.5, 17.7, 13.9 ppm; IR (KBr): v_max
\[ x = 2962, 2932, 1686, 1597, 1448, 1369, 1274, 1213, 1002, 753, 735, 691, 569 \text{ cm}^{-1}. \]

30) 1,4-Diphenylbutane-1,4-dione (2d')

![2d']

The reaction of 1,4-diphenylbut-2-ene-1,4-dione (1d', 0.2 mmol, 47.2 mg), [(Cp*RhCl)_2] (0.006 mmol, 4.2 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 30.9 mg (65%) of 2d' as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.05\) (d, \(J = 8.0\) Hz, 4H), 7.59 (t, \(J = 7.6\) Hz, 2H), 7.51-7.45 (m, 4H), 3.48 (s, 4H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 198.7, 136.7, 133.2, 128.6, 128.1, 32.5\); IR (KBr): \(\nu_{\text{max}} = 3440, 1677, 1593, 1446, 1354, 1223, 1180, 991, 776, 737, 694, 554 \text{ cm}^{-1}\).

31) 1-Phenylpentane-1,4-dione (2e')

![2e']

The reaction of 1-phenylpent-2-ene-1,4-dione (1e', 0.2 mmol, 34.8 mg), [(Cp*RhCl\(_2\))] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 29.9 mg (85%) of 2e' as a solid; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 7.98\) (d, \(J = 7.6\) Hz, 2H), 7.56 (t, \(J = 7.2\) Hz, 1H), 7.50-7.40 (m, 2H), 3.28 (t, \(J = 7.0\) Hz, 2H), 2.89 (t, \(J = 7.0\) Hz, 2H), 2.26 (s, 3H); \(^1^3\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 207.3, 198.5, 136.6, 133.1, 128.5, 128.0, 37.0, 32.4, 30.1\); IR (KBr): \(\nu_{\text{max}} = 2911, 1715, 1683, 1596, 1448, 1359, 1211, 1161, 1001, 995, 744, 690, 552, 490 \text{ cm}^{-1}\).

32) Methyl 4-oxo-4-phenylbutanoate (2f')

![2f']
The reaction of methyl-4-oxo-4-phenylbut-2-enoate (1f', 0.2 mmol, 38.0 mg), [(Cp*RhCl$_2$)$_2$] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 16.1 mg (42%) of 2f' as a solid; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 8.00-7.95 (m, 2H), 7.57 (t, $J$ = 7.2 Hz, 1H), 7.50-7.40 (m, 2H), 3.71 (s, 3H), 3.33 ($t$, $J$ = 6.6 Hz, 2H), 2.77 (t, $J$ = 6.6 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 198.0, 173.4, 136.5, 133.2, 128.6, 128.0, 51.8, 33.4, 28.0; IR (KBr): $\nu_{max}$ = 2952, 1739, 1686, 1597, 1449, 1438, 1358, 1221, 1167, 1001, 949, 750, 691, 558 cm$^{-1}$.

33) 1-Phenyl-3-(4-vinylphenyl)propan-1-one (2g')

The reaction of 1-phenyl-3-(4-vinylphenyl)propen-2-en-1-one (1g', 0.2 mmol, 46.9 mg), [(Cp*RhCl$_2$)$_2$] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 24.1 mg (51%) of 2g' as a solid. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.97 (d, $J$ = 5.6 Hz, 2H), 7.56 (t, $J$ = 5.8 Hz, 1H), 7.48-7.44 (m, 2H), 7.36 (d, $J$ = 6.6 Hz, 2H), 7.22 (d, $J$ = 6.6 Hz, 2H), 6.70 (dd, $J$ = 14, 8.8 Hz, 1H), 5.72 (d, $J$ = 14 Hz, 1H), 5.21 (d, $J$ = 8.8 Hz, 1H), 3.30 (t, $J$ = 12.2 Hz, 2H), 3.07 (t, $J$ = 12.2 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 126 MHz): $\delta$ = 199.2, 140.9, 136.8, 136.5, 135.5, 133.1, 128.6, 128.0, 126.3, 113.2, 40.3, 29.8 ppm. IR (KBr): $\nu_{max}$ = 1680, 1630, 1600, 1579, 1508, 1448, 1206, 974, 742, 688 cm$^{-1}$. HRMS m/z (ESI) calcd for C$_{17}$H$_{16}$O$^+$ (M+H)$^+$ 237.12739, found 237.12741274.

34) Ethyl 3-phenylpropanoate (4)$^{14}$
The reaction of ethyl cinnamate (3, 0.2 mmol, 35.2 mg), [(Cp*RhCl2)] (0.006 mmol, 3.7 mg), in isopropanol (1.0 mL) under 100 °C for 12 h afforded 27.9 mg (79%) of 4 as a solid. \(^1\)H NMR (CDCl₃, 400 MHz): \(\delta = 7.32-7.27\) (m, 2H), 7.24-7.19 (m, 3H), 4.13 (q, \(J = 5.7\) Hz, 2H), 2.96 (t, \(J = 6.2\) Hz, 2H), 2.63 (t, \(J = 6.2\) Hz, 2H), 1.24 (t, \(J = 5.7\) Hz, 3H). \(^{13}\)C NMR (CDCl₃, 126 MHz): \(\delta = 172.9, 140.5, 128.4, 128.3, 126.2, 60.4, 35.9, 30.9, 14.2.\)

4. References


5. NMR Spectra
2i