Supporting Information

**Synthesis of Z-Alkenes from Rh(I) Catalyzed Olefin Isomerization of \( \beta,\gamma \)-Unsaturated Ketones**

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1. Experimental Procedures and Characterization Data

1.1 General Methods of Synthesis

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. THF, DME and toluene were distilled from sodium and benzophenone prior to use. CH$_3$CN and DCE were distilled from CaH$_2$ prior to use. Dichloroethane was distilled from P$_2$O$_5$ prior to use. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

NMR spectra were measured on Bruker ARX 400 ($^1$H at 400 MHz, $^{13}$C at 100 MHz) nuclear magnetic resonance spectrometers. Data or $^1$H-NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplet, ddd = doublet of doublet of doublets, tdd = triplet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for $^{13}$C-NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl$_3$: 77.0 ppm, C$_6$D$_6$: 128.0 ppm). Infrared spectra were recorded on Mettler-Toledo React IR iC10 system with a SiComp probe and are reported in wave numbers (cm$^{-1}$). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer (ESI) using FT-ICR analyzer. Gas chromatography analyses were carried out with Agilent series 6820 GC using columns J&K Scientific CATALOG 1251017.

Abbreviations:
- DCE = 1,2-dichloromethane
- DCM = dichloromethane
- DME = dimethoxyethane
- PE = petroleum ether
- EA = ethyl acetate
- TBS = tert-butyldimethylsilyl
- THF = tetrahydrofuran
- TLC = thin layer chromatography
- DMP = Dess–Martin periodinane
1.2 Synthesis of New Substrates

β,γ-unsaturated ketones (1 or 3) were prepared by following the reported procedure through allyl magnesium chloride addition to aldehydes/DMP oxidation.

A solution of allyl magnesium chloride in ether (4.1 mL, 1.7 M, 7.2 mmol) was added to a solution of aldehyde (S1, 5.0 mmol) in anhydrous THF (15 mL) at 0 °C. The resulting mixture was stirred for 30 min at room temperature and then concentrated in vacuum and dissolved in 15 mL Et₂O. 5 mL saturated NH₄Cl (aq) and 5 mL water were added at 0 °C to the above ether solution, and then the organic layer was separated. The aqueous layer was extracted with Et₂O, and the combined organic layers were washed with saturated brine, dried over Na₂SO₄, and concentrated in vacuum. The crude product was purified by a flash silica gel eluted with PE/EA to afford the crude product S2.

To a solution of crude S2 and NaHCO₃ (4 eq of crude S2) in CH₂Cl₂ (30 mL) at room temperature, DMP (1.4 eq of crude S2) was added. After 20 min of stirring, 5 mL saturated Na₂S₂O₃ (aq) and 10 mL water were added slowly at 0 °C. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (10 mL), and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/E) to give 1.

1-(4-chlorophenyl)but-3-en-1-one (1b)

White solid: Rᵣ (5% EA/PE) = 0.70, 75% yield. m.p. 41-44 °C

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 6.07 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 5.28 – 5.17 (m, 2H), 3.73 (dt, J = 6.7, 1.3 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 196.8, 139.7, 134.9, 130.7, 129.7, 129.0, 119.0, 43.4.

FT-IR (neat): ν 1687, 1590, 1400, 1211, 1091, 927 cm⁻¹


1-(2-chlorophenyl)but-3-en-1-one (1c)

Colorless oil: Rᵣ(5% EA/PE) = 0.70, 54% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.30-7.48 (m, 5H), 6.01 (ddt, J = 17.1, 10.3, 6.8 Hz, 1H), 5.25 – 5.16 (m, 2H), 3.74 (dt, J = 6.8, 1.3 Hz, 2H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 201.1, 139.1, 131.8, 130.9, 130.5, 130.2, 129.1, 126.9, 119.2, 47.5.

FT-IR (neat): $\nu$ 1702, 1661, 1594, 1434, 1296, 1065, 1006, 927 cm$^{-1}$


**1-(3-chlorophenyl)but-3-en-1-one (1d)**

\[
\text{\includegraphics[width=0.2\textwidth]{3-chlorophenyl-butenone.png}}
\]

Colorless oil: $R_f$ (5% EA/PE) = 0.70, 57% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (s, 1H), 7.84 (d, $J = 7.8$ Hz, 1H), 7.57 – 7.51 (m, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 6.07 (ddt, $J = 17.0$, 10.3, 6.7 Hz, 1H), 5.30 – 5.18 (m, 2H), 3.74 (d, $J = 6.7$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.7, 138.1, 135.0, 133.1, 130.5, 130.0, 128.4, 126.4, 119.1, 43.5.

FT-IR (neat): $\nu$ 1695, 1576, 1423, 1333, 1207, 916, 793 cm$^{-1}$


**1-(4-fluorophenyl)but-3-en-1-one (1e)**

\[
\text{\includegraphics[width=0.2\textwidth]{4-fluorophenyl-butenone.png}}
\]

Colorless oil: $R_f$ (5% EA/PE) = 0.70, 52% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.00 (dd, $J = 8.8$, 5.4 Hz, 2H), 7.14 (t, $J = 8.6$ Hz, 2H), 6.07 (ddt, $J = 17.0$, 10.3, 6.7 Hz, 1H), 5.29 – 5.17 (m, 2H), 3.74 (dt, $J = 6.7$, 1.3 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.41 (s), 165.79 (d, $J = 254.9$ Hz), 132.98 (d, $J = 3.0$ Hz), 130.94 (d, $J = 9.3$ Hz), 118.89 (s), 130.85 (s), 115.74 (d, $J = 21.9$ Hz), 43.39 (s).

FT-IR (neat): $\nu$ 1687, 1628, 1508, 1333, 1229, 1009 cm$^{-1}$

HRMS (ESI) calcd for C$_{10}$H$_{10}$FO [M+H$^+$]: 165.07102. Found: 165.07119.

**1-p-tolylbut-3-en-1-one (1f)**

\[
\text{\includegraphics[width=0.2\textwidth]{p-tolyl-butenone.png}}
\]

Colorless oil: $R_f$ (5% EA/PE) = 0.75, 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 6.08 (ddt, $J = 17.1$, 10.4, 6.7 Hz, 1H), 5.18-5.24 (m, 2H), 3.73 (d, $J = 6.7$ Hz, 2H), 2.41 (s, 3H).

FT-IR (neat): $\nu$ 1680, 1591, 1444, 890 cm$^{-1}$

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.7, 144.0, 134.1, 131.3, 129.3, 128.4, 118.6, 43.4, 21.6.

HRMS (ESI) calcd for [M+H$^+$]: 161.09664. Found: 161.09617
1-m-tolylbutil-3-en-1-one (1g)

![Chemical结构](attachment:image)

Colorless oil: $R_f(5\%\text{ EA/PE}) = 0.75$, 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 – 7.70 (m, 2H), 7.41 – 7.31 (m, 2H), 6.09 (ddt, $J = 17.1, 10.4, 6.7$ Hz, 1H), 5.25 – 5.22 (m, 1H), 5.18 – 5.24 (m, 2H), 3.75 (dt, $J = 6.7, 1.4$ Hz, 2H), 2.41 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.2, 138.4, 136.7, 133.9, 131.2, 128.5, 128.5, 125.5, 118.6, 43.5, 21.4.

FT-IR (neat): $\nu$ 1687, 1609, 1590, 1430, 1300, 924 cm$^{-1}$

HRMS (ESI) calcd for C$_{11}$H$_{12}$O [M+Na$^+$]: 183.07804. Found: 183.07818.

1-(4-methoxyphenyl)but-3-en-1-one (1h)

![Chemical结构](attachment:image)

White solid: $R_f(10\%\text{ EA/PE}) = 0.70$, 71% yield. m.p. 40–42 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 8.9$ Hz, 2H), 6.08 (ddt, $J = 17.1, 10.5, 6.7$ Hz, 1H), 5.18-5.21 (m, 2H), 3.87 (s, 3H), 3.71 (dt, $J = 6.7, 1.4$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.6, 163.6, 131.5, 130.6, 129.7, 118.5, 113.8, 55.5, 43.2.

FT-IR (neat): $\nu$ 1684, 1613, 1512, 1270, 1170, 1024 cm$^{-1}$

HRMS (ESI) calcd for C$_{11}$H$_{12}$O$_2$ [M+Na$^+$]: 199.07295. Found: 199.07306.

1-(3-methoxyphenyl)but-3-en-1-one (1i)

![Chemical结构](attachment:image)

Colorless oil: $R_f(5\%\text{ EA/PE}) = 0.75$, 64% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J = 7.7$ Hz, 1H), 7.51 – 7.47 (m, 1H), 7.37 (t, $J = 7.9$ Hz, 1H), 7.11 (dd, $J = 8.2, 2.6$ Hz, 1H), 6.08 (ddt, $J = 17.1, 10.4, 6.7$ Hz, 1H), 5.28 – 5.16 (m, 2H), 3.85 (s, 3H), 3.74 (dt, $J = 6.7, 1.3$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.8, 159.9, 138.0, 131.1, 129.6, 120.9, 119.6, 118.7, 112.6, 55.4, 43.6.

FT-IR (neat): $\nu$ 1687, 1583, 1486, 1438, 1248, 1028 cm$^{-1}$

HRMS (ESI) calcd for C$_{11}$H$_{12}$O$_2$ [M+Na$^+$]: 199.07295. Found: 199.07311.
1-(2-methoxyphenyl)but-3-en-1-one (1j)

Colorless oil: $R_f$ (5% EA/PE) = 0.70, 86% yield.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.86 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.03 (tdd, $J$ = 9.1, 4.2, 1.8 Hz, 1H), 6.70 (td, $J$ = 7.4, 1.9 Hz, 1H), 6.37 (dd, $J$ = 8.1, 5.3 Hz, 1H), 6.22 (ddt, $J$ = 17.5, 10.8, 6.8 Hz, 1H), 5.02-5.06 (m, 2H), 3.67 (dd, $J$ = 6.8, 1.3 Hz, 3H), 3.11 (d, $J$ = 6.2 Hz, 2H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 198.4, 158.6, 133.2, 133.1, 132.5, 130.8, 120.8, 117.3, 111.5, 54.7, 48.8.

FT-IR (neat): $\nu$ 1676, 1602, 1490, 1468, 1248, 1028 cm$^{-1}$

HRMS (ESI) calcd for C$_{11}$H$_{12}$NaO$_2$ [M+Na$^+$]: 199.07295. Found: 199.07312.

1-(3,4-dimethoxyphenyl)but-3-en-1-one (1k)

White solid: $R_f$ (20% EA/PE) = 0.40, 88% yield. m.p. 50-55°C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J$ = 8.4 Hz, 1H), 7.54 (d, $J$ = 0.9 Hz, 1H), 6.90 (d, $J$ = 8.4 Hz, 1H), 6.16-6.02 (m, 1H), 5.23 (s, 1H), 5.22-5.18 (m, 1H), 3.94 (s, 3H), 3.96 (s, 3H), 3.75-3.70 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 196.6, 153.4, 149.1, 131.5, 129.8, 123.0, 118.43, 110.4, 110.0, 56.1, 56.0, 43.2.

FT-IR (neat): $\nu$ 1674, 1596, 1517, 1419, 1244, 1022 cm$^{-1}$

HRMS (ESI) calcd for C$_{12}$H$_{15}$O$_3$ [M+H$^+$]: 207.10157. Found: 207.10178.

1-(biphenyl-4-yl)but-3-en-1-one (1l)

White solid: $R_f$ (5% EA/PE) = 0.75, 75% yield. m.p. 73-75°C.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ = 8.5 Hz, 2H), 7.62-7.67 (m, 4H), 7.38-7.49 (m, 3H), 6.11 (ddt, $J$ = 17.1, 10.5, 6.7 Hz, 1H), 5.28-5.25 (m, 1H), 5.23 (dd, $J$ = 9.3, 1.4 Hz, 1H), 3.79 (dt, $J$ = 6.7, 1.3 Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.7, 145.9, 139.9, 135.3, 131.1, 129.0, 128.9, 128.3, 127.3, 118.8, 43.5.

FT-IR (neat): $\nu$ 1680, 1609, 1400, 1333, 1196 cm$^{-1}$

HRMS (ESI) calcd for C$_{16}$H$_{15}$O [M+H$^+$]: 223.11174. Found: 223.11203.
1-(naphthalen-2-yl)but-3-en-1-one (1m)

Colorless oil: $R_f$ (5% EA/PE) = 0.75, 79% yield

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.60 (d, $J = 8.6$ Hz, 1H), 7.98 (d, $J = 8.2$ Hz, 1H), 7.88 (t, $J = 7.3$ Hz, 2H), 7.63 – 7.43 (m, 3H), 6.19 – 6.04 (m, 1H), 5.30 – 5.21 (m, 2H), 3.84 (d, $J = 6.8$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 202.0, 135.5, 134.0, 132.8, 131.2, 130.3, 128.4, 128.0, 127.8, 126.5, 125.8, 124.3, 118.8, 47.0.

FT-IR (neat): ν 1684, 1516, 1292, 1233, 1177, 1091, 927 cm$^{-1}$


dec-1-en-4-one (3a)

Colorless oil: $R_f$ (5% EA/PE) = 0.80, 46% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.92 (ddt, $J = 17.2$, 10.2, 7.0 Hz, 1H), 5.22 – 5.09 (m, 2H), 3.17 (d, $J = 7.0$ Hz, 2H), 2.43 (t, $J = 7.4$ Hz, 2H), 1.57 (dq, $J = 14.7$, 7.3 Hz, 2H), 1.26 – 1.28 (m, 6H), 0.88 (t, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 209.0, 135.5, 134.0, 132.8, 131.2, 130.3, 128.0, 127.8, 126.5, 125.8, 124.3, 118.6, 47.7, 42.4, 31.6, 28.9, 23.7, 22.8, 14.0.

FT-IR (neat): ν 1719, 1460, 700 cm$^{-1}$

HRMS (ESI) calcd for C$_{10}$H$_{12}$O $[\text{M+H}]^+$: 155.14304. Found: 155.14319.

1-phenylpent-4-en-2-one (3b)

Colorless oil: $R_f$ (5% EA/PE) = 0.75, 55% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.19-7.35 (m, 5H), 5.90 (ddt, $J = 17.2$, 10.2, 6.9 Hz, 1H), 5.09-5.19 (m, 2H), 3.72 (s, 2H), 3.21 (d, $J = 6.9$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 206.1, 134.0, 130.4, 129.5, 128.5, 127.1, 119.0, 49.6, 46.8.

FT-IR (neat): ν 1720, 1499, 1458, 1459, 1333, 1056, 700 cm$^{-1}$

HRMS (ESI) calcd for C$_{11}$H$_{12}$O $[\text{M+H}]^+$: 183.07804. Found: 183.07818.

1-phenylhex-5-en-3-one (3c)

Colorless oil: $R_f$ (5% EA/PE) = 0.75, 27% yield.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17-7.31 (m, 5H), 5.90 (ddt, $J =$ 17.2, 10.2, 7.0 Hz, 1H), 5.17 (dd, $J =$ 10.2, 1.1 Hz, 1H), 5.09-5.19 (m 1H), 3.15 (d, $J =$ 7.0 Hz, 2H), 2.94 – 2.85 (m, 2H), 2.82 – 2.74 (m, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 207.8, 141.0, 130.5, 128.5, 128.3, 126.1, 119.0, 47.9, 43.9, 29.7.

FT-IR (neat): $\nu$ 1718, 1499, 700 cm$^{-1}$

HRMS (ESI) calcd for C$_{12}$H$_{14}$NaO $[\text{M+Na}^+]$: 197.09369. Found: 197.09339.

1-cyclohexylbut-3-en-1-one (3d)

![1-cyclohexylbut-3-en-1-one](image)

Colorless oil: $R_f$(5% EA/PE) = 0. 80, 46% yield.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 5.97 (ddt, $J =$ 17.1, 10.2, 6.9 Hz, 1H), 5.02 (d, $J =$ 9.7 Hz, 1H), 4.95 (d, $J =$ 17.2 Hz, 1H), 2.82 (d, $J =$ 6.8 Hz, 2H), 1.96 (ddd, $J =$ 11.5, 7.4, 3.3 Hz, 1H), 1.65 – 1.49 (m, 4H), 1.45 – 1.54 (m, 1H), 1.31 – 1.15 (m, 2H), 1.43 – 1.14 (m, 3H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 209.0, 131.9, 117.5, 50.1, 45.3, 28.4, 26.0, 25.7.

FT-IR (neat): $\nu$ 2934, 2858, 1709, 1450, 1149 cm$^{-1}$


1-(tert-butyldimethylsilyloxy)hex-5-en-3-one (3e)

![1-(tert-butyldimethylsilyloxy)hex-5-en-3-one](image)

Colorless oil: $R_f$(5% EA/PE) = 0.75, 53% yield.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 5.86 (ddt, $J =$ 17.2, 10.2, 7.0 Hz, 1H), 4.97 (dd, $J =$ 10.2, 1.3 Hz, 1H), 4.89 (dd, $J =$ 17.2, 1.5 Hz, 1H), 3.43 (t, $J =$ 6.1 Hz, 2H), 2.74 (d, $J =$ 7.0 Hz, 2H), 2.14 (t, $J =$ 7.1 Hz, 2H), 1.74 – 1.66 (m, 2H), 0.93 (s, 9H), 0.02 – 0.01 (m, 6H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 206.1, 117.8, 135.1, 62.2, 47.5, 38.2, 26.9, 26.0, 18.3, -5.4.

FT-IR (neat): $\nu$ 2932, 2858, 2365, 1720, 1638, 1102, 668 cm$^{-1}$

HRMS (ESI) calcd for C$_{13}$H$_{26}$NaO$_2$Si $[\text{M+Na}^+]$: 265.15943. Found: 265.15941.

5-ethylhept-1-en-4-one (3f)

![5-ethylhept-1-en-4-one](image)

Colorless oil: $R_f$(5% EA/PE) = 0. 80, 24% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.93 (ddt, $J =$ 17.2, 10.2, 7.0 Hz, 1H), 5.26 – 5.05 (m, 2H), 3.19 (dt, $J =$ 7.0, 1.3 Hz, 2H), 2.39 (tt, $J =$ 7.9, 5.7 Hz, 1H), 1.70 – 1.56 (m, 2H), 1.54 – 1.38 (m, 2H), 0.86 (t, $J =$ 7.4 Hz, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 212.4, 130.8, 117.8, 135.1, 62.2, 47.5, 38.2, 26.9, 26.0, 18.3, 11.8.

FT-IR (neat): $\nu$ 2368, 1655, 1562 cm$^{-1}$

5-ethynon-1-en-4-one (3g)

\[
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.80, \ 36\% \text{ yield.}
\]

\[\text{H NMR (400 MHz, CDCl}_3) \delta 5.93 \text{ (ddt, } J = 17.2, 10.2, 7.0 \text{ Hz, 1H), } 5.22 - 5.07 \text{ (m, 2H), } 3.19 \text{ (d, } J = 7.0 \text{ Hz, 2H), } 2.51 - 2.39 \text{ (m, 1H), } 1.70 - 1.53 \text{ (m, 2H), } 1.38 - 1.46 \text{ (m, 2H), } 1.34 - 1.10 \text{ (m, 4H), } 0.85-0.89 \text{ (m, 6H)}\]

\[\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3) \delta 212.4, 130.8, 118.4, 53.5, 47.0, 30.9, 29.6, 24.5, 22.8, 13.9, 11.8\]

\[\text{FT-IR (neat): } \nu 2370, 1655, 1560, \text{ cm}^{-1}\]

\[\text{HRMS (ESI) calcd for C}_{11}\text{H}_{20}\text{NaO [M+Na}^+\text{]: } 191.14064. \text{ Found: } 191.14015.\]

5,9-dimethyldeca-1,8-dien-4-one (3h)

\[
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.80, \ 52\% \text{ yield.}
\]

\[\text{H NMR (400 MHz, CDCl}_3) \delta 5.93 \text{ (ddt, } J = 17.2, 10.2, 6.9 \text{ Hz, 1H), } 5.20 - 5.09 \text{ (m, 2H), } 5.06 \text{ (t, } J = 7.1 \text{ Hz, 1H), } 3.21 \text{ (d, } J = 6.9 \text{ Hz, 2H), } 2.56 - 2.61 \text{ (m, 1H), } 1.95 \text{ (q, } J = 7.4 \text{ Hz, 2H), } 1.77 - 1.69 \text{ (m, 1H), } 1.68 \text{ (s, 3H), } 1.59 \text{ (s, 3H), } 1.31 - 1.39 \text{ (m, 1H), } 1.08 \text{ (d, } J = 7.0 \text{ Hz, 3H)}\]

\[\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3) \delta 212.3, 132.3, 130.9, 123.7, 118.4, 46.0, 45.4, 32.9, 25.7, 25.7, 17.7, 16.3\]

\[\text{FT-IR (neat): } \nu 2938, 1718, 1460, 996 \text{ cm}^{-1}\]

\[\text{HRMS (ESI) calcd for C}_{12}\text{H}_{20}\text{NaO [M+Na}^+\text{]: } 203.14064. \text{ Found: } 203.14016.\]

2-phenylhex-5-en-3-one (3i)

\[
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.70, \ 41\% \text{ yield.}
\]

\[\text{H NMR (400 MHz, CDCl}_3) \delta 7.36 - 7.19 \text{ (m, 5H), } 5.83 \text{ (ddt, } J = 17.1, 10.2, 6.9 \text{ Hz, 1H), } 5.11 \text{ (dd, } J = 10.2, 1.4 \text{ Hz, 1H), } 5.00 \text{ (dd, } J = 17.1, 1.5 \text{ Hz, 1H), } 3.81 \text{ (q, } J = 6.9 \text{ Hz, 1H), } 3.11 \text{ (dd, } J = 6.9, 1.1 \text{ Hz, 2H), } 1.39 \text{ (d, } J = 7.0 \text{ Hz, 3H)}\]

\[\text{\textsuperscript{13}C NMR (101 MHz, CDCl}_3) \delta 208.5, 140.4, 130.8, 129.0, 128.0, 127.2, 118.6, 52.5, 45.9, 17.5\]

\[\text{FT-IR (neat): } \nu 1718, 1493, 1456, 702 \text{ cm}^{-1}\]

\[\text{HRMS (ESI) calcd for C}_{13}\text{H}_{14}\text{NaO [M+Na}^+\text{]: } 197.09369. \text{ Found: } 197.09328.\]

(E)-1-(4-chlorophenyl)hex-3-en-1-one (5)
A solution of S4 in ether (3.9 mL, 1 M, 3.9 mmol) was added to a solution of aldehyde (S3, 2.8 mmol, 281 mg) in anhydrous THF (10 mL) at 0 °C. The resulting mixture was stirred for 30 min at room temperature and then concentrated in vacuum and dissolved in 15 mL Et2O. 5 mL saturated NH4Cl (aq) and 5 mL water were added at 0 °C to the above ether solution, and the organic layer was separated. The aqueous layer was extracted with Et2O, and the combined organic layers were washed with saturated brine, dried over Na2SO4, and concentrated in vacuum. The crude product was purified by a flash silica gel eluted with PE/EA to afford the crude S5 (crude, yellow oil, 243 mg).

To a solution of crude S5 and NaHCO3 (4.6 mmol, 386 mg) in CH2Cl2 (5 mL) at room temperature, DMP (1.16 mmol, 682 mg) was added. After 20 min of stirring, 3 mL saturated Na2S2O3 (aq) and 5 mL water were added slowly at 0 °C. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH2Cl2, and the combined organic layers were washed with brine, dried over Na2SO4, and concentrated in vacuum. The crude product of S8 was purified by column chromatography on silica-gel (eluted with PE/EA = 30:1) to give S9, 140 mg, 22% yield for two steps, as a colorless oil (Rf (5% EA/PE) = 0.65).

1H NMR (400 MHz, CDCl3) δ 7.91 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 5.65 - 5.67 (m, 2H), 3.66 (d, J = 4.6 Hz, 2H), 2.07 (dd, J = 7.4, 4.3 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H).
13C NMR (101 MHz, CDCl3) δ 197.5, 139.5, 136.9, 135.0, 129.8, 128.9, 120.9, 42.5, 25.7, 13.5.
FT-IR (neat): ν1634, 1607, 1500, 904 cm⁻¹

(E)-1,6-diphenylhex-5-en-3-one (6)

A mixture of S6 (5.0 mmol, 670 mg) and indium powder (7.5 mmol, 861 mg) in H2O (5 mL) was added S7 (6.0 mmol, 118 mg) slowly at room temperature. The reaction mixtures were stirred for 12 hours at room temperature. Ethyl ether was added to dilute the reaction mixture, followed by 1 M HCl (4 mL) to quench the reaction. The reaction mixture was then extracted with ether. The combined organic layer was washed with saturated brine, and dried over anhydrous Na2SO4, filtered and the solvent was removed in vacuum. The crude product of S8 was purified by flash column chromatography to get 584 mg (44%) as an oil.

Under Ar, to a solution of crude S8 (1.94 mmol, 490 mg) in dry CH2Cl2 (30 mL) at room temperature, S6 (0.19 mmol, 38 mg) and Cu(OTf)2 (0.19 mmol, 68 mg) were added. After 4 h of stirring, the reaction mixture was concentrated in vacuum. The residue was purified by column
chromatography on silica-gel (eluted with PE/EA = 20:1) to give S9, 170 mg (35%) as a colorless oil.

To a solution of S9 (0.71 mmol, 170 mg), NaHCO₃ (2.84 mmol, 238 mg) in CH₂Cl₂ (8 mL) at room temperature, DMP (1.13 mmol, 481 mg) was added. After 20 min of stirring, 5 mL saturated Na₂S₂O₃ (aq) and 3 mL water were added slowly. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/EA = 30:1) to give 6, 70 mg (41%) as a colorless oil (Rf (5% EA/PE) = 0.60).

1H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 5H), 7.25 – 7.16 (m, 5H), 6.43 (d, J = 15.9 Hz, 1H), 6.27 (dt, J = 15.9, 7.1 Hz, 1H), 3.29 (d, J = 7.1 Hz, 2H), 2.94 – 2.88 (m, 2H), 2.85 – 2.79 (m, 2H).

13C NMR (101 MHz, CDCl₃) δ 207.7, 141.0, 136.9, 133.9, 128.6, 128.5, 128.4, 127.6, 126.3, 126.2, 121.9, 47.2, 44.0, 29.8.

FT-IR (neat): ν1673, 1510, 710 cm⁻¹


1-(4-chlorophenyl)-2-vinylpentan-1-one (7)

A mixture of S10 (3 mmol, 422 mg) and indium powder (4.5 mmol, 517 mg) in H₂O (5 mL) was added S11 (3.6 mmol, 587 mg) slowly at room temperature. The resulting reaction mixture was stirred for 16 hours at room temperature. Ethyl ether was added to dilute the reaction mixture followed by 1 M HCl (4 mL) to quench the reaction. The reaction mixture was extracted with ether. The combined organic layer was washed with saturated brine, and dried over anhydrous Na₂SO₄, filtered and the solvent was removed in vacuum. The crude product of S12 was purified by flash column chromatography to get S12 522 mg (78%) as a yellow oil.

To a solution of crude S12, NaHCO₃ (9.28 mmol, 780 mg) in CH₂Cl₂ (30 mL) at room temperature, DMP (3.28 mmol, 1.39 g) was added. After 20 min of stirring, 10 mL saturated Na₂S₂O₃ (aq) and 10 mL water were added slowly at 0 °C. The mixture was stirred for another 20 min and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂, and the combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuum. The residue was purified by column chromatography on silica-gel (eluted with PE/EA = 30:1) to give 7, 503 mg (95%) as a colorless oil (Rf (5% EA/PE) = 0.65).

1H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 5.95 – 5.82 (m, 1H), 5.17 (d, J = 1.8 Hz, 1H), 5.14 (d, J = 3.6 Hz, 1H), 3.96 - 4.02 (dd, J = 15.1, 7.5 Hz, 1H), 1.80-1.86 (m, 1H), 1.66 – 1.54 (m, 1H), 1.44 – 1.23 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).

13C NMR (101 MHz, CDCl₃) δ 199.9, 139.4, 136.9, 135.1, 129.9, 128.9, 117.7, 51.6, 34.2, 20.4, 14.0.

FT-IR (neat): ν1734, 1500, 702 cm⁻¹

**but-3-enenitrile (8)** was synthesized by reported method.

![But-3-enenitrile (8)](image)

**4-allyl-1,2-dimethoxybenzene (9)** is commercially available.

![4-allyl-1,2-dimethoxybenzene (9)](image)
1.3 Details for the Rh(I)-Catalyzed Olefin Isomerization of β,γ-unsaturated Ketones

**General procedure for Rh(I)-catalyzed olefin isomerization of β,γ-unsaturated ketones.**
Under Ar, a solution of ligand (dppm, 0.036 mmol) and [Rh(CO)_2Cl]_2 (0.015 mmol) in anhydrous solvent (DCE or DME, 1.5 mL) was stirred for 30 min at room temperature. Then β,γ-unsaturated ketone (0.3 mmol) was added and the reaction mixture was immersed in an oil bath at the indicated temperature (65 °C, 75 °C or 85 °C). When GC indicated the conversion of the starting material reached 85% ~ 100%, the reaction mixture was cooled to room temperature and concentrated. The crude mixture was submitted to flash column chromatography on silica gel to afford the mixture of β,γ-unsaturated ketones, Z- and E-α,β-unsaturated keto. The ratio was determined by integration of suitable 1H NMR signals and the reaction’s conversion and yields can be obtained. Pure E-α,β-unsaturated ketone can be obtained by further column chromatography (PE:EA = 150:1 ~ 100:1, except 1k which used PE:EA = 10:1) on silica gel. Meanwhile, part of pure Z-α,β-unsaturated ketone can also be obtained in this further chromatography. However, the remaining mixture containing Z-α,β-unsaturated ketone and the starting material cannot be separated completely. This is because the Rf values of Z-α,β-ketone and the starting material are very close, while the Rf value of E-α,β-unsaturated ketone is different from those of Z-α,β-unsaturated ketone and the starting material (and E-α,β-unsaturated ketone can be separated easier).

We found that, if the reaction scaled to 1.5 mmol, we can get a better separated yield. For example, in the case of isomerization of 1m, the pure Z-α,β-unsaturated ketone can be obtained by column chromatography in 73% yield. This suggests that the present isomerization reaction can be used for synthesis if a larger scale of the reaction can be carried out.

**Note 1:** In some cases, the amounts of E isomers from the isomerization reactions were too low to get their NMR data. Therefore, we synthesized these isomers by isomerizations of the unsaturated ketones using Al_2O_3 as the catalyst (see below for details).

**Note 2:** The Z/E ratio of the products usually decreased with time. Therefore, we stopped the reaction when the conversion reached to 85%-100%.

**Note 3:** Stereochemistry was determined by comparing the 1H NMR shift and the coupling constants. The α-H of carbonyl (in olefin) in E-isomers is significant in the lower field with larger chemical shift than the corresponding α-H of carbonyl (in olefin) in Z-isomers. The coupling constants of olefin in Z-α,β-unsaturated ketones are usually lower than coupling constants of olefin in E-α,β-unsaturated ketones, if both can be read from the NMR data. Using either one of the above two features we can then determine the relative ratios of Z and E isomers of our Rh-catalyzed isomerization reactions by comparing integrations of their characteristic proton signals.
1.3.1 Additional Details of Screening Reaction Conditions

\[ \text{Ph} \text{O} \text{C} \text{H} \text{O} \text{C} \text{Ph} \]

\[ \text{5 mol\% [Rh]} \]

\[ \text{AgX or L = 1.2 [Rh]} \]

\[ \text{Ph} \text{O} \text{C} \text{H} \text{O} \text{C} \text{Ph} \]

\[ \text{GC} \text{ Z} 2 \text{ - Z} 2 \text{ - E} \]

\[ \text{NMR} \text{ Z} 2 \text{ - Z} 2 \text{ - E} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Z/E Ratio</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Rh(CO)\text{Cl}_2, AgOTf, 75 °C, DCE, 18 h</td>
<td>0.8:1</td>
<td>84(^a)</td>
<td>55(^a)</td>
</tr>
<tr>
<td>2. Rh(PPh\text{3})\text{Cl}, 75 °C, DCE, 23 h</td>
<td>2.8:1</td>
<td>67(^a)</td>
<td>35(^a)</td>
</tr>
<tr>
<td>3. Rh(PPh\text{3})\text{Cl}, AgSbF\text{6}, 75 °C, DCE, 12 h</td>
<td>0.2:1</td>
<td>92(^a)</td>
<td>72(^a)</td>
</tr>
<tr>
<td>4. Rh(PPh\text{3})\text{Cl}, AgOTf, 75 °C, DCE, 12 h</td>
<td>0.1:1</td>
<td>82(^a)</td>
<td>62(^a)</td>
</tr>
<tr>
<td>5. [Rh(CO)\text{Cl}_2]_2, dppm, AgSbF\text{6}, 75 °C, DCE, 13 h</td>
<td>0.1:1</td>
<td>100(^a)</td>
<td>83(^a)</td>
</tr>
<tr>
<td>6. [Rh(CO)\text{Cl}_2]_2, dppm, 75 °C, Dioxane, 23 h</td>
<td>3.7:1</td>
<td>(75)(^b)</td>
<td>(47)(^b)</td>
</tr>
<tr>
<td>7. [Rh(CO)\text{Cl}_2]_2, dppm, 75 °C, DME, 23 h</td>
<td>4.3:1</td>
<td>(94)(^b)</td>
<td>(75)(^b)</td>
</tr>
<tr>
<td>8. [Rh(CO)\text{Cl}_2]_2, dppm, 75 °C, Toluene, 23 h</td>
<td>2.3:1</td>
<td>(95)(^b)</td>
<td>(60)(^b)</td>
</tr>
<tr>
<td>9. [Rh(CO)\text{Cl}_2]_2, L1, 75 °C, DCE, 23 h</td>
<td>1.2:1</td>
<td>98(^b)(100)(^b)</td>
<td>64(^b)(66)(^b)</td>
</tr>
<tr>
<td>10. [Rh(CO)\text{Cl}_2]_2, PPh\text{2}, 80 °C, DCE, 23 h</td>
<td>1.4:1</td>
<td>(92)(^b)</td>
<td>(75)(^b)</td>
</tr>
</tbody>
</table>

\(^a\) Determined by GC. \(^b\) Determined by NMR

1.3.2 The Spectroscopic Data of Z and E-Unsaturated Ketones

\[ \text{2a-Z}^3, \text{2a-E}^3, \text{2b-E}^3, \text{2c-E}^4, \text{2c-E}^5, \text{2f-E}^4, \text{2g-E}^5, \text{2h-E}^4, \text{2l-E}^5, \text{2m-E}^6, \text{4a-Z}^3, \text{4a-E}^3, \text{4d-Z}^5 \text{ and } \text{4d-E}^6 \text{ all are known molecules.} \]

In some cases, the amounts of E isomers from our isomerization reaction were too low to get the pure products. Therefore, we synthesized these isomers by isomerizations of the unsaturated ketones using Al\text{2}O\text{3} as the catalyst.\(^7\) These new compounds are: \text{2i-E}, \text{2j-E}, \text{4d-E}, \text{4e-E}, \text{4f-E}, \text{4g-E}, \text{4h-E} and \text{4i-E}. The general synthesis of these new compounds is given below.

**General procedure for isomerization of the β,γ-unsaturated ketones to the corresponding E-α,β-unsaturated ketones.**\(^7\) To an acetone solution (1 mL) of β,γ-unsaturated ketone (0.2 mmol), Al\text{2}O\text{3} (neutral, 0.15 g) was added, and the mixture was stirred at room temperature until TLC indicated the disappearance of the starting material. After filtration of the suspension, acetone was evaporated, and the crude mixture was submitted to flash column chromatography on silica gel to afford the E-α,β-unsaturated ketone.

(\text{Z})-1-(4-chlorophenyl)but-2-en-1-one (2b-Z)

\[
\text{Cl} \hspace{2cm} \text{O} \hspace{2cm} \text{C} \hspace{2cm} \text{H} \hspace{2cm} \text{O} \\
\]

Colorless oil: \( R_f (5\% \text{ EA/PE}) = 0.70 \), NMR yield of E and Z isomers, 85%

\(^1\text{H} \text{NMR} \ (400 \text{ MHz, C}_6\text{D}_6) \delta 7.35 \ (d, J = 8.6 \text{ Hz, 2H}), 6.80 \ (d, J = 8.6 \text{ Hz, 2H}), 6.13 \ (dq, J = 11.5, 1.7 \text{ Hz, 1H}), 5.72 \ (dq, J = 11.5, 7.2 \text{ Hz, 1H}), 1.82 \ (dd, J = 7.2, 1.8 \text{ Hz, 3H}).

\(^1\text{C} \text{NMR} \ (101 \text{ MHz, C}_6\text{D}_6) \delta 189.5, 143.9, 138.7, 137.2, 129.8, 128.8, 124.8, 16.0.

\text{FT-IR (neat): v} 1672, 1620, 1694, 1233, 1099, 1017 \text{ cm}^{-1}
HRMS (ESI) calcd for C_{10}H_{10}ClO [M+H^+]: 181.04147. Found: 181.04181.

(Z)-1-(2-chlorophenyl)but-2-en-1-one (2c-Z)

![Chemical structure](image)

Colorless oil: $R_f$(5% EA/PE) = 0.70, NMR yield of E and Z isomers, 93%

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.12 – 7.02 (m, 1H), 6.82 (dd, $J = 6.3$, 2.8 Hz, 1H), 6.61 – 6.46 (m, 2H), 6.16 (dd, $J = 11.4$, 1.1 Hz, 1H), 5.69 (dq, $J = 11.4$, 7.3 Hz, 1H), 1.82 (dd, $J = 7.3$, 0.9 Hz, 3H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 192.4, 144.1, 141.0, 131.1, 130.2, 129.6, 126.8, 16.0.

FT-IR (neat): $\nu$ 1676, 1616, 1430, 1270, 1222, 1076, 1013 cm$^{-1}$


(Z)-1-(3-chlorophenyl)but-2-en-1-one (2d-Z)

![Chemical structure](image)

Colorless oil: $R_f$(5% EA/PE) = 0.70, NMR yield of E and Z isomers, 75%

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ 7.66 (t, $J = 1.8$ Hz, 1H), 7.39 – 7.34 (m, 1H), 6.86 (dd, $J = 7.9$, 1.9, 0.8 Hz, 1H), 6.52 (t, $J = 7.9$ Hz, 1H), 6.06 (dd, $J = 11.5$, 1.7 Hz, 1H), 5.68 (dq, $J = 11.5$, 7.2 Hz, 1H), 1.80 (dd, $J = 7.3$, 1.8 Hz, 3H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) $\delta$ 189.3, 144.4, 134.8, 132.2, 129.9, 128.5, 126.3, 124.5, 16.0.

FT-IR (neat): $\nu$ 1672, 1616, 1576, 1445, 1222 cm$^{-1}$


(Z)-1-(4-fluorophenyl)but-2-en-1-one (2e-Z)

![Chemical structure](image)

Colorless oil: $R_f$(5% EA/PE) = 0.70, NMR yield of E and Z isomers, 79%

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (dd, $J = 8.8$, 5.5 Hz, 2H), 6.53 (t, $J = 8.7$ Hz, 2H), 6.24 (dd, $J = 11.5$, 1.7 Hz, 1H), 5.80 (dq, $J = 11.6$, 7.2 Hz, 1H), 1.88 (dd, $J = 7.2$, 1.8 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 187.99 (s), 164.21 (d, $J = 253.0$ Hz), 142.22 (s), 134.07 (d, $J = 2.9$ Hz), 129.70 (d, $J = 9.1$ Hz), 123.60 (s), 114.17 (d, $J = 21.8$ Hz), 14.74 (s).

FT-IR (neat): $\nu$ 1676, 1620, 1605, 1441, 1209, 1044 cm$^{-1}$

HRMS (ESI) calcd for C$_{10}$H$_9$FClO [M+H$^+$]: 165.07102. Found: 165.07123.
(Z)-1-p-tolylbut-2-en-1-one (2f-Z)

\[
\begin{array}{c}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.75, \text{ NMR yield of } E \text{ and } Z \text{ isomers, 80%} \\
^1H \text{ NMR (400 MHz, C}_6D_6) \delta 7.67 (d, J = 8.0 \text{ Hz}, 2H), 6.70 (d, J = 8.0 \text{ Hz}, 2H), 6.38 (dq, J = 11.5, 1.7 \text{ Hz}, 1H), 5.75 (dq, J = 11.5, 7.2 \text{ Hz}, 1H), 1.88 (dd, J = 7.2, 1.8 \text{ Hz}, 3H), 1.79 (s, 3H). \\
^{13}C \text{ NMR (101 MHz, C}_6D_6) \delta 189.3, 141.6, 141.4, 135.5, 128.0, 127.4, 124.1, 19.9, 14.8. \\
\text{FT-IR (neat): } \nu 1676, 1609, 1237, 1021 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for } C_{11}H_{13}O [M+H]^+: 161.09609. \text{ Found: 161.09618.}
\end{array}
\]

(Z)-1-m-tolylbut-2-en-1-one (2g-Z)

\[
\begin{array}{c}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.75, \text{ NMR yield of } E \text{ and } Z \text{ isomers, 65%} \\
^1H \text{ NMR (400 MHz, C}_6D_6) \delta 7.60 (s, 1H), 7.53 (d, J = 7.6 \text{ Hz}, 1H), 6.83 (t, J = 7.5 \text{ Hz}, 1H), 6.78 (d, J = 7.6 \text{ Hz}, 1H), 6.37 (dq, J = 11.5, 1.8 \text{ Hz}, 1H), 5.75 (dq, J = 11.5, 7.2 \text{ Hz}, 1H), 1.87 (dd, J = 7.2, 1.8 \text{ Hz}, 3H), 1.82 (s, 3H). \\
^{13}C \text{ NMR (101 MHz, C}_6D_6) \delta 189.9, 141.7, 136.9, 131.9, 127.8, 127.2, 124.5, 124.2, 19.7, 14.8. \\
\text{FT-IR (neat): } \nu 1676, 1617, 1240 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for } C_{11}H_{13}O [M+H]^+: 161.09609. \text{ Found: 161.09624.}
\end{array}
\]

(Z)-1-(4-methoxyphenyl)but-2-en-1-one (2h-Z)

\[
\begin{array}{c}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.70, \text{ NMR yield of } E \text{ and } Z \text{ isomers, 74%} \\
^1H \text{ NMR (400 MHz, CDCl}_3) \delta 8.00 (d, J = 8.9 \text{ Hz}, 2H), 6.72 (d, J = 8.9 \text{ Hz}, 2H), 6.65 (dq, J = 11.5, 1.7 \text{ Hz}, 1H), 6.03 (dq, J = 11.5, 7.2 \text{ Hz}, 1H), 3.24 (s, 3H), 2.16 (dd, J = 7.2, 1.7 \text{ Hz}, 3H). \\
^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 189.5, 163.1, 142.0, 132.1, 130.6, 125.3, 113.7, 54.6, 15.9. \\
\text{FT-IR (neat): } \nu 1684, 1613, 1270, 1222, 1170, 1024 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for } C_{11}H_{12}O_2 [M+Na]^+: 199.07295. \text{ Found: 199.09124.}
\end{array}
\]

(Z)-1-(3-methoxyphenyl)but-2-en-1-one (2i-Z)

\[
\begin{array}{c}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) = 0.70, \text{ NMR yield of } E \text{ and } Z \text{ isomers, 74%} \\
^1H \text{ NMR (400 MHz, CDCl}_3) \delta 8.00 (d, J = 8.9 \text{ Hz}, 2H), 6.72 (d, J = 8.9 \text{ Hz}, 2H), 6.65 (dq, J = 11.5, 1.7 \text{ Hz}, 1H), 6.03 (dq, J = 11.5, 7.2 \text{ Hz}, 1H), 3.24 (s, 3H), 2.16 (dd, J = 7.2, 1.7 \text{ Hz}, 3H). \\
^{13}C \text{ NMR (101 MHz, CDCl}_3) \delta 189.5, 163.1, 142.0, 132.1, 130.6, 125.3, 113.7, 54.6, 15.9. \\
\text{FT-IR (neat): } \nu 1684, 1613, 1270, 1222, 1170, 1024 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for } C_{11}H_{12}O_2 [M+Na]^+: 199.07295. \text{ Found: 199.09124.}
\end{array}
\]
Colorless oil: \( R_t(5\% \text{ EA/PE}) = 0.75 \), NMR yield of \( E \) and \( Z \) isomers, 67%

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.71 \) (s, 1H), 7.52 (d, \( J = 7.6 \) Hz, 1H), 7.10 (td, \( J = 7.9, 1.4 \) Hz, 1H), 6.93-6.96 (m 1H), 6.63 (d, \( J = 11.5 \) Hz, 1H), 6.08 – 5.97 (m, 1H), 3.35 (s, 3H), 2.13 (dt, \( J = 7.2, 1.4 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 190.6, 160.2, 143.1, 140.4, 129.4, 125.2, 120.9, 119.1, 112.5, 54.5, 15.9.

FT-IR (neat): \( \nu = 1669, 1583, 1270, 1207, 1028 \) cm\(^{-1}\)

HRMS (ESI) calcd for C\(_{11}\)H\(_{12}\)NO\(_2\) [M+Na\(^+\)]: 199.07295. Found: 199.07336.

\((E)-1-(3\text{-methoxyphenyl})\text{but-2-en-1-one} \) (2i-\(E\))

\(\text{OMe}\)

(from isomerization of the \(\beta,\gamma\)-unsaturated ketone by Al\(_2\)O\(_3\), see section 1.3.2)

Colorless oil: \( R_t(5\% \text{ EA/PE}) = 0.65 \), 67%

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.46\text{-}7.51 \) (m, 2H), 7.34\text{-}7.38 (m, 1H), 7.14\text{-}7.02 (m, 1H), 6.89 (dd, \( J = 15.3, 1.4 \) Hz, 1H), 3.85 (s, 3H), 1.99 (dd, \( J = 6.8, 0.6 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 190.4, 159.8, 145.1, 139.3, 129.5, 127.5, 121.1, 119.1, 112.8, 55.4, 18.6.

FT-IR (neat): \( \nu = 1674, 1569, 1439, 1296, 1035, 778 \) cm\(^{-1}\)

HRMS (ESI) calcd for C\(_{11}\)H\(_{13}\)O\(_2\) [M+H\(^+\)]: 177.09101. Found: 177.09128.

\((Z)-1-(2\text{-methoxyphenyl})\text{but-2-en-1-one} \) (2j-\(Z\))

\(\text{O}\)

\(\text{OMe}\)

Colorless oil: \( R_t(5\% \text{ EA/PE}) = 0.70 \), NMR yield of \( E \) and \( Z \) isomers, 66%

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \( \delta 7.82 \) (dd, \( J = 7.6, 1.6 \) Hz, 1H), 7.07 – 6.99 (m, 1H), 6.72-6.81 (s, 1H), 6.77 – 6.69 (m, 1H), 6.39 (d, \( J = 8.3 \) Hz, 1H), 5.95 (dq, \( J = 11.4, 7.3 \) Hz, 1H), 3.16 (s, 3H), 2.16 (dd, \( J = 7.3, 1.7 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, C\(_6\)D\(_6\)) \( \delta 192.5, 158.1, 141.3, 132.5, 131.1, 130.9, 129.8, 120.9, 111.6, 54.9, 16.2.

FT-IR (neat): \( \nu = 1669, 1583, 1270, 1207, 1028 \) cm\(^{-1}\)

HRMS (ESI) calcd for C\(_{11}\)H\(_{12}\)NO\(_2\) [M+Na\(^+\)]: 199.07295. Found: 199.07316.

\((E)-1-(2\text{-methoxyphenyl})\text{but-2-en-1-one} \) (2j-\(E\))

\(\text{O}\)

\(\text{OMe}\)

(from isomerization of the \(\beta,\gamma\)-unsaturated ketone by Al\(_2\)O\(_3\), see section 1.3.2)

Colorless oil: \( R_t(5\% \text{ EA/PE}) = 0.65 \), 56%

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta 7.48 \) (dd, \( J = 7.5, 1.5 \) Hz, 1H), 7.46 – 7.38 (m, 1H), 6.94-7.01 (m, 2H), 6.86 (dq, \( J = 13.6, 6.8 \) Hz, 1H), 6.67 – 6.71 (m, 1H), 3.85 (s, 3H), 1.93 (d, \( J = 6.8 \) Hz, 3H).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.6, 157.8, 144.2, 132.4, 132.3, 129.9, 129.2, 120.5, 111.5, 55.7, 18.4.

FT-IR (neat): ν 1657, 1620, 1486, 1437, 1324, 1244, 1026 cm$^{-1}$

HRMS (ESI) calcd for C$_{11}$H$_{13}$O$_2$ [M+H$^+$]: 177.09101. Found: 177.09125.

(Z)-1-(3,4-dimethoxyphenyl)but-2-en-1-one (2k-Z)

![Chemical structure]

yellow oil: $R_{f}$ (5% EA/PE) = 0.70, NMR yield of E and Z isomers, 90%

$^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.70 (d, $J$ = 1.4 Hz, 1H), 7.48 (dd, $J$ = 8.3, 1.9 Hz, 1H), 6.69 (dd, $J$ = 11.5, 1.8 Hz, 1H), 6.43 (d, $J$ = 8.3 Hz, 1H), 6.00 (dq, $J$ = 11.6, 7.2 Hz, 1H), 3.35 (s, 3H), 3.29 (s, 3H), 2.11 (dd, $J$ = 7.2, 1.4 Hz, 3H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) δ 189.8, 153.8, 150.0, 142.0, 132.3, 125.5, 122.7, 111.3, 110.4, 55.5, 55.2, 16.1.

FT-IR (neat): ν 1584, 1514, 1266, 1206, 1167, 1024 cm$^{-1}$

HRMS (ESI) calcd for C$_{12}$H$_{15}$O$_3$ [M+H$^+$]: 207.10157. Found: 207.10189.

(E)-1-(3,4-dimethoxyphenyl)but-2-en-1-one (2k-E)

![Chemical structure]

yellow oil: $R_{f}$ (5% EA/PE) = 0.70, NMR yield of E and Z isomers, 90%

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.62 – 7.54 (m, 2H), 7.12 – 7.03 (dq, $J$ = 13.4, 6.7 Hz, 1H), 6.98 – 6.87 (m, 2H), 3.95 (s, 6H), 2.00 (dd, $J$ = 6.7, 1.2 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 188.8, 153.8, 150.0, 142.0, 132.3, 125.5, 122.7, 111.3, 110.4, 55.2, 55.2, 16.1.

FT-IR (neat): ν 1584, 1514, 1266, 1206, 1167, 1024 cm$^{-1}$

HRMS (ESI) calcd for C$_{12}$H$_{15}$O$_3$ [M+H$^+$]: 207.10157. Found: 207.10175.

(Z)-1-(biphenyl-4-yl)but-2-en-1-one (2l-Z)

![Chemical structure]

White solid: $R_{f}$ (5% EA/PE) = 0.75, NMR yield of E and Z isomers, 82%. m.p. 51-55 °C.

$^1$H NMR (400 MHz, C$_6$D$_6$) δ 7.76 (d, $J$ = 8.3 Hz, 2H), 7.12-7.03 (m, 4H), 6.98 – 6.87 (m, 2H), 3.95 (s, 6H), 2.00 (dd, $J$ = 6.7, 1.2 Hz, 3H).

$^{13}$C NMR (101 MHz, C$_6$D$_6$) δ 198.8, 153.8, 150.0, 142.0, 132.3, 125.5, 122.7, 111.3, 110.4, 55.2, 55.2, 16.1.

FT-IR (neat): ν 1665, 1620, 1437, 1324, 1244, 1026 cm$^{-1}$

HRMS (ESI) calcd for C$_{16}$H$_{15}$O$_3$ [M+H$^+$]: 223.11174. Found: 223.11206.
(Z)-1-(naphthalen-2-yl)but-2-en-1-one (2m-Z)

![Structure of (Z)-1-(naphthalen-2-yl)but-2-en-1-one](image)

Colorless oil: \( R_f (5\% \text{ EA/PE}) = 0.70 \), NMR yield of E and Z isomers, 78%.

When we scaled our reaction to 1.5 mmol, we can get 94% conversion and 81% yield (by NMR), with the Z:E = 13:1. The isolated yield of 2m-Z is 73% in column chromatography (PE : EA = 120:1).

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \( \delta \) 8.68 (d, \( J = 8.6 \) Hz, 1H), 7.43 – 7.32 (m, 3H), 7.19 – 7.14 (m, 1H), 6.97 (t, \( J = 7.3 \) Hz, 1H), 6.20 (d, \( J = 11.5 \) Hz, 1H), 5.72 (dt, \( J = 11.5 \), 1.7 Hz, 1H), 1.83 (dd, \( J = 7.3, 1.7 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, C\(_6\)D\(_6\)) \( \delta \) 194.7, 142.9, 138.0, 134.2, 132.0, 130.8, 129.1, 128.5, 127.9, 126.4, 126.3, 124.5, 16.0.

FT-IR (neat): \( \nu \) 1672, 1616, 1434, 1237, 1128, 1106, 793 cm\(^{-1}\).


(Z)-1-phenylpent-3-en-2-one (4b-Z)

![Structure of (Z)-1-phenylpent-3-en-2-one](image)

Colorless oil: \( R_f (5\% \text{ EA/PE}) = 0.75 \), NMR yield of E and Z isomers, 88%

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.11 – 6.96 (m, 5H), 5.82 (dd, \( J = 11.3 \), 1.6 Hz, 1H), 3.35 (s, 2H), 1.96 (dd, \( J = 7.2, 1.7 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 195.9, 141.9, 133.8, 128.4, 127.5, 125.6, 125.6, 50.1, 14.4.

FT-IR (neat): \( \nu \) 1687, 1618, 1439, 1076, 700 cm\(^{-1}\).


(Z)-1-phenylhex-4-en-3-one (4c-Z)

![Structure of (Z)-1-phenylhex-4-en-3-one](image)

Colorless oil: \( R_f (5\% \text{ EA/PE}) = 0.75 \), NMR yield of E and Z isomers, 73%

\(^1\)H NMR (400 MHz, C\(_6\)D\(_6\)) \( \delta \) 7.17–7.21 (m, 2H), 7.08–7.13 (m, 3H), 5.82 – 5.70 (m, 2H), 2.90 (dd, \( J = 7.6 \) Hz, 2H), 2.44 (t, \( J = 7.6 \) Hz, 2H), 2.09 (d, \( J = 6.1 \) Hz, 3H).

\(^{13}\)C NMR (101 MHz, C\(_6\)D\(_6\)) \( \delta \) 198.9, 141.9, 141.6, 128.4, 127.5, 125.6, 125.6, 50.1, 14.4.

FT-IR (neat): \( \nu \) 1694, 1620, 1454 cm\(^{-1}\).


(Z)-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one (4e-Z)

![Structure of (Z)-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one](image)

Colorless oil: \( R_f (5\% \text{ EA/PE}) = 0.75 \), NMR yield of E and Z isomers, 67%
\( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 5.81 (dd, \( J = 11.4, 1.5 \text{ Hz}, 1 \text{H} \)), 5.74 – 5.64 (m, 1H), 3.47 (t, \( J = 6.2 \text{ Hz}, 2 \text{H} \)), 2.27 (t, \( J = 7.1 \text{ Hz}, 2 \text{H} \)), 2.01 (dd, \( J = 7.2, 1.6 \text{ Hz}, 3 \text{H} \)), 1.78 (p, \( J = 6.6 \text{ Hz}, 2 \text{H} \)), 0.93 (s, 9H), 0.00 (s, 6H).

\( ^13 \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 198.6, 140.3, 126.6, 61.0, 39.1, 25.9, 24.7, 17.1, 14.4, 0.0, -6.6.

FT-IR (neat): \( \nu \) 2932, 2860, 1698, 1257, 1102, 728 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{13}\)H\(_{26}\)NaO\(_2\)Si [M+Na\(^+\)]: 265.15943. Found: 265.15939.

\( \text{(E)} \)-1-(tert-butylidimethylsilyloxy)hex-4-en-3-one (4e-E)

\[
\text{TBSO} \overset{\text{-}}{\text{C}} \overset{\text{O}}{\text{CH}_3}
\]

(from isomerization of the \( \beta,\gamma \)-unsaturated ketone by Al\(_2\)O\(_3\), see section 1.3.2)

Colorless oil: \( R_f \) (5% EA/PE) = 0.70, 60%

\( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.82 (dq, \( J = 13.7, 6.8 \text{ Hz}, 1 \text{H} \)), 6.09 (dd, \( J = 15.8, 1.5 \text{ Hz}, 1 \text{H} \)), 3.59 (t, \( J = 6.1 \text{ Hz}, 2 \text{H} \)), 2.57 (t, \( J = 7.3 \text{ Hz}, 2 \text{H} \)), 1.86 (dd, \( J = 6.8, 1.4 \text{ Hz}, 3 \text{H} \)), 1.83 – 1.73 (m, 2H), 0.85 (s, 9H), -0.00 (s, 6H).

\( ^13 \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 200.4, 142.3, 132.1, 62.2, 36.2, 27.2, 25.9, 18.3, 18.2, -5.35.

FT-IR (neat): \( \nu \) 2134, 1702, 1560, 1257, 1102, 836 cm\(^{-1}\).

HRMS (ESI) calcd for C\(_{13}\)H\(_{26}\)NaO\(_2\)Si [M+Na\(^+\)]: 265.15943. Found: 265.15919.

\( \text{(Z)} \)-5-ethylhept-2-en-4-one (4f-Z)

\[
\overset{\text{O}}{\text{CH}} \overset{\text{-}}{\text{C}} \overset{\text{O}}{\text{CH}_3}
\]

Colorless oil: \( R_f \) (5% EA/PE) = 0.80, NMR yield of E and Z isomers, 69%

\( ^1 \)H NMR (400 MHz, C\(_6\)D\(_6\)) \( \delta \) 5.88 – 5.92 (m, 1H), 5.73 – 5.81 (m, 1H), 2.05 (dd, \( J = 7.1, 1.5 \text{ Hz}, 3 \text{H} \)), 2.13 – 2.09 (m, 1H), 1.53 – 1.62 (m, 2H), 1.35 – 1.23 (m, 2H), 0.78 (t, \( J = 7.4 \text{ Hz}, 6 \text{H} \)).

\( ^13 \)C NMR (101 MHz, C\(_6\)D\(_6\)) \( \delta \) 202.4, 140.9, 126.3, 54.8, 23.1, 10.6.

FT-IR (neat): \( \nu \) 1655, 1507, 1207 cm\(^{-1}\).


\( \text{(E)} \)-5-ethylhept-2-en-4-one (4f-E)

\[
\overset{\text{O}}{\text{CH}} \overset{\text{-}}{\text{C}} \overset{\text{O}}{\text{CH}_3}
\]

(from isomerization of the \( \beta,\gamma \)-unsaturated ketone by Al\(_2\)O\(_3\), see section 1.3.2)

Colorless oil: \( R_f \) (5% EA/PE) = 0.75, 65%

\( ^1 \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 6.82 (dq, \( J = 13.7, 6.9 \text{ Hz}, 1 \text{H} \)), 6.14 (dd, \( J = 15.6, 1.5 \text{ Hz}, 1 \text{H} \)), 2.46 (dq, \( J = 8.1, 5.6 \text{ Hz}, 1 \text{H} \)), 1.83 (dd, \( J = 6.9, 1.5 \text{ Hz}, 3 \text{H} \)), 1.63 – 1.50 (m, 2H), 1.46 – 1.33 (m, 2H), 0.77 (t, \( J = 7.4 \text{ Hz}, 6 \text{H} \)).

\( ^13 \)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 202.9, 141.2, 130.4, 51.8, 23.5, 17.2, 10.8.

FT-IR (neat): \( \nu \) 1655, 1560, 1262 cm\(^{-1}\).

(Z)-5-ethyl-2-en-4-one (4g-Z)

\[
\begin{align*}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) & = 0.80, \text{ NMR yield of } E \text{ and } Z \text{ isomers, 75\% } \\
^1\text{H NMR (400 MHz, C}_6\text{D}_6\text{)} & \delta 5.93 (dd, J = 11.4, 1.6 Hz, 1H), 5.78 (dq, J = 11.4, 7.2 Hz, 1H), 2.07 (dd, J = 7.2, 1.7 Hz, 3H), 1.69 – 1.55 (m, 2H), 1.39 – 1.25 (m, 2H), 1.26 – 1.11 (m, 4H), 0.85-0.80 (m, 6H). \\
^{13}\text{C NMR (101 MHz, C}_6\text{D}_6\text{)} & \delta 203.8, 142.2, 127.5, 54.6, 31.3, 29.9, 24.9, 23.1, 15.8, 14.0, 11.9. \\
\text{FT-IR (neat): } \nu 1655, 1560 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for C}_{11}\text{H}_{20}\text{O } [\text{M+Na}^+] : 191.14064. \text{ Found: 191.14015.}
\end{align*}
\]

(E)-5-ethyl-2-en-4-one(4g-E)

\[
\begin{align*}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) & = 0.75, 77\% \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)} & \delta 6.89 (dq, J = 20.8, 6.9 Hz, 1H), 6.21 (dd, J = 15.6, 1.6 Hz, 1H), 2.58 (tt, J = 8.2, 5.5 Hz, 1H), 1.49 (dd, J = 6.9, 1.5 Hz, 3H), 1.57-1.67 (m, 2H), 1.55 – 1.35 (m, 3H), 1.34 – 1.25 (m, 2H), 1.25 – 1.14 (m, 3H), 0.93 – 0.80 (m, 6H). \\
^{13}\text{C NMR (101 MHz, CDCl}_3\text{)} & \delta 204.0, 142.2, 121.3, 51.3, 31.3, 29.7, 24.9, 22.9, 18.3, 13.9, 11.9. \\
\text{FT-IR (neat): } \nu 2934, 1629, 1462, 970 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for C}_{11}\text{H}_{21}\text{O } [\text{M+H}^+] : 169.15865. \text{ Found: .169.15899.}
\end{align*}
\]

(Z)-5,9-dimethyldeca-2,8-dien-4-one (4h-Z)

\[
\begin{align*}
\text{Colorless oil: } R_f (5\% \text{ EA/PE}) & = 0.80, \text{ NMR yield of } E \text{ and } Z \text{ isomers, 70\% } \\
^1\text{H NMR (400 MHz, C}_6\text{D}_6\text{)} & \delta 5.71 (dd, J = 11.4, 1.5 Hz, 1H), 5.35 – 5.63 (m, 1H), 4.97 – 4.89 (m, 1H), 2.13-2.19 (m, 1H), 1.88 (dd, J = 7.1, 1.6 Hz, 3H), 1.79 (q, J = 7.4 Hz, 2H), 1.66 – 1.54 (m, 1H), 1.45 (s, 3H), 1.32 (s, 3H), 1.15 – 1.06 (m, 2H), 0.80 (d, J = 6.9 Hz, 3H). \\
^{13}\text{C NMR (101 MHz, C}_6\text{D}_6\text{)} & \delta 203.5, 142.4, 131.6, 127.1, 124.6, 46.5, 33.2, 30.1, 26.0, 25.7, 17.5, 16.2, 15.8. \\
\text{FT-IR (neat): } \nu 2919, 2815, 2283, 1692, 1622, 1331, 812 \text{ cm}^{-1} \\
\text{HRMS (ESI) calcd for C}_{12}\text{H}_{20}\text{NaO } [\text{M+Na}^+] : 203.14064. \text{ Found: 203.14023.}
\end{align*}
\]
(E)-5,9-dimethyldeca-2,8-dien-4-one (4h-E)

(from isomerization of the β,γ-unsaturated ketone by Al₂O₃, see section 1.3.2)

Colorless oil: Rᵣ (5% EA/PE) = 0.75, 52%

¹H NMR (400 MHz, CDCl₃) δ 6.81 (dq, J = 13.7, 6.8 Hz, 1H), 6.11 (dd, J = 15.6, 1.4 Hz, 1H), 5.00 (t, J = 7.1 Hz, 1H), 2.66 (d, J = 6.9 Hz, 1H), 1.93 – 1.86 (m, 2H), 1.83 (dd, J = 6.8, 1.3 Hz, 3H), 1.71 – 1.62 (m, 1H), 1.60 (s, 3H), 1.50 (s, 3H), 1.29 (td, J = 14.2, 7.3 Hz, 1H), 1.01 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 203.8, 142.2, 132.1, 130.6, 124.0, 43.2, 33.2, 25.7, 18.2, 17.7, 16.6.

FT-IR (neat): ν 2932, 1698, 1631, 1560, 1460, 1378, 974 cm⁻¹


(Z)-2-phenylhex-4-en-3-one (4i-Z)

Colorless oil: Rᵣ (5% EA/PE) = 0.70, NMR yield of E and Z isomers, 70%

¹H NMR (400 MHz, CDCl₃) δ 7.19 – 7.11 (m, 4H), 7.05 – 7.10 (m, 1H), 5.92 (dd, J = 11.4, 1.7 Hz, 1H), 5.71 (dq, J = 11.4, 7.2 Hz, 1H), 3.48 (q, J = 6.9 Hz, 1H), 2.10 (dd, J = 7.2, 1.6 Hz, 3H), 1.44 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 198.4, 141.5, 140.2, 127.7, 126.9, 125.8, 125.7, 52.5, 16.3, 14.5.

FT-IR (neat): ν 1698, 1565, 1460 cm⁻¹


(E)-2-phenylhex-4-en-3-one (4i-E)

(from isomerization of the β,γ-unsaturated ketone by Al₂O₃, see section 1.3.2)

Colorless oil: Rᵣ (5% EA/PE) = 0.65, 61%

¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.17 (m, 5H), 6.89 (dq, J = 13.8, 6.9 Hz, 1H), 6.10 (dd, J = 15.5, 1.6 Hz, 1H), 3.91 (q, J = 6.9 Hz, 1H), 1.79 (dd, J = 6.9, 1.6 Hz, 3H), 1.41 (d, J = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 199.4, 142.8, 140.9, 130.1, 125.9, 125.8, 125.7, 52.5, 16.3, 18.2, 17.8.

FT-IR (neat): ν 1698, 1631, 1452, 702 cm⁻¹

1.3.3 Additional Detail of Rh(I)-Catalyzed Olefin Isomerization of But-3-enenitrile (8).

Under Ar, a solution of dpmm (0.036 mmol, 13.8 mg) and [Rh(CO)\(_2\)Cl]\(_2\) (0.015 mmol, 5.6 mg) in CD\(_2\)Cl\(_2\) (1.5 mL) was stirred for 50 min at room temperature. Then but-3-enenitrile \(^8\) (0.3 mmol, 20.1 mg) was added and the reaction mixture was immersed in microwave at 85 °C. After 1 h, the reaction mixture was cooled to room temperature. The crude mixture was used for \(^1\)H NMR analysis directly, showing that no new product was observed.
1.4 References


2. NMR Spectra
1-(4-chlorophenyl)but-3-en-1-one (1b, mixture with trace of 2b-E)
1-(2-chlorophenyl)but-3-en-1-one (1c, mixture with trace of 2c-E)
1-(3-chlorophenyl)but-3-en-1-one (1d)
1-(4-fluorophenyl)but-3-en-1-one (1e)
1-p-tolylbut-3-en-1-one (1f,mixture with trace of 2f-E)
1-m-tolylbut-3-en-1-one (1g, mixture with trace of 2g-E)
1-(4-methoxyphenyl)but-3-en-1-one (1h)
1-(3-methoxyphenyl)but-3-en-1-one (1i)
1-(2-methoxyphenyl)but-3-en-1-one (1j)
1-(3,4-dimethoxyphenyl)but-3-en-1-one (1k)
1-(biphenyl-4-yl)but-3-en-1-one (II)
1-(naphthalen-2-yl)but-3-en-1-one (1m)
dec-1-en-4-one (3a)
1-phenylpent-4-en-2-one (3b)
1-phenylhex-5-en-3-one (3c)
1-cyclohexylbut-3-en-1-one (3d)
1-(tert-butyldimethylsilyloxy)hex-5-en-3-one (3e)
5-ethylhept-1-en-4-one (3f)
5-ethylnon-1-en-4-one (3g)
5,9-dimethyldeca-1,8-dien-4-one (3h)
2-phenylhex-5-en-3-one (3i)
(E)-1,6-diphenylhex-5-en-3-one (6)
1-(4-chlorophenyl)-2-vinylpentan-1-one (7)
(Z)-1-(4-chlorophenyl)but-2-en-1-one (2b-Z)
(Z)-1-(2-chlorophenyl)but-2-en-1-one (2c-Z)
(Z)-1-(3-chlorophenyl)but-2-en-1-one (2d-Z)
(Z)-1-(4-fluorophenyl)but-2-en-1-one (2e-Z)
(Z)-1-p-tolybut-2-en-1-one (2f-Z)
(Z)-1-m-tolybut-2-en-1-one(2g-Z)
(Z)-1-(4-methoxyphenyl)but-2-en-1-one (2h-Z)
(Z)-1-(3-methoxyphenyl)but-2-en-1-one (2i-Z)
\( (E)-1-(3\text{-}\text{methoxyphenyl})\text{but}-2\text{-en}-1\text{-one (2\text{-}E)} \)
(Z)-1-(2-methoxyphenyl)but-2-en-1-one (2j-Z)
(E)-1-(2-methoxyphenyl)but-2-en-1-one (2j-E)
(Z)-1-(3,4-dimethoxyphenyl)but-2-en-1-one(2k-Z)
\((E)-1-(3,4\text{-dimethoxyphenyl})\text{but-2-en-1-one (2k-E)}\)
(Z)-1-(biphenyl-4-yl)but-2-en-1-one (2l-Z) (mixture with minor $E$-isomer)
(Z)-1-(naphthalen-2-yl)but-2-en-1-one (2m-Z)
(Z)-1-phenylpent-3-en-2-one (4b-Z)
(Z)-1-phenylhex-4-en-3-one (4c-Z)
(Z)-1-(tert-butyldimethylsiloxy)hex-4-en-3-one (4e-Z)
(E)-1-(tert-butyldimethylsilyloxy)hex-4-en-3-one (4e-E)
(Z)-5-ethylhept-2-en-4-one (4f-Z) (mixture with minor E-isomer)
(E)-5-ethylhept-2-en-4-one (4f,E)
(Z)-5-ethylnon-2-en-4-one(4g-Z)
(E)-5-ethylnon-2-en-4-one(4g-E) (mixture with 3g)
(Z)-5,9-dimethyldeca-2,8-dien-4-one (4h-Z)
(E)-5,9-dimethyldeca-2,8-dien-4-one (4h-E)
(Z)-2-phenylhex-4-en-3-one (4i-Z)
(E)-2-phenylhex-4-en-3-one (4i-E)