Supporting Information for

Iridium-Catalyzed Enantioselective Allylation of Silyl Enol Ethers Derived from Ketones and α,β-Unsaturated Ketones

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List of Supporting Information

1. General Experimental Details

All reactions were conducted under an atmosphere of nitrogen using dried glassware, and all reactions solvents were purified and dried according to standard methods prior to use. The phosphoramidite ligands **(*S*)-L**, **(*R*)-L**, **(*rac*)-L** were prepared according to published procedures.[1] All allylic alcohols were prepared by the addition reaction of the corresponding aldehyde with vinylmagnesium bromide (1.0 M in THF) at 0 °C, and purification of the crude products by flash column chromatography (gradient elution: petroleum ether/Et_2OAc = 50/1 to 5/1) to provide the products. All silyl enol ethers were prepared by reaction of the corresponding ketones with Lithium bis(trimethylisilyl)amide (1.0 M in THF/Ethylbenzene) and trimethyl chlorosilane under in situ-quench conditions at -78 °C and purified by column flash chromatography (petroleum ether/Et_2OAc = 99/1) to provide the products. All other starting materials, reagents were purchased from commercial sources and were used without further purification.

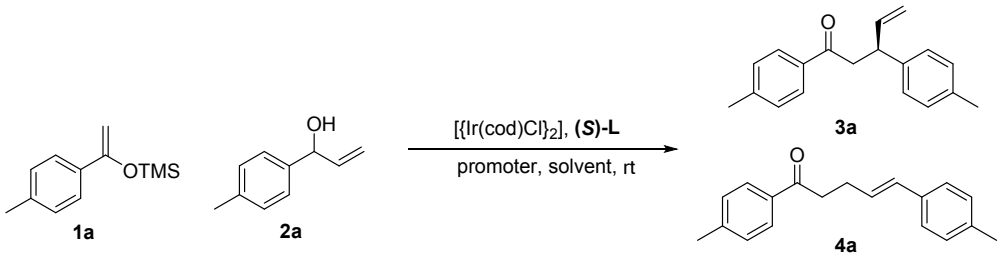
Chromatographic purification of products was accomplished using forced-flow chromatography on 200-300 mesh silica gel. The TLC glass plates were performed on 0.20 mm or 1.0 mm (preparative) silica gel GF254 plates, and visualized with UV light (254 nm) or $KMnO_4$.

^1H and ^{13}C NMR spectra were acquired on Bruker AM-400 or DRX-600 NMR spectrometer. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were

used as internal standards. Chemical shifts (δ) were given in ppm with reference to residual solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.2)]. Data for ^{1}H NMR were recorded as follows: chemical shift (d, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ^{13}C NMR were reported in terms of chemical shift (d, ppm). Infrared spectra were recorded on a BRUKER Tensor-27 Fourier-Transform Infrared spectrometer, the peaks were reported as absorption maxima (n, cm^{-1}). High resolution mass spectral data were obtained at the mass spectrometry service operated at the Waters Auto Spec Premier P776 spectrometer for electron impact ionization (EI) and Agilent 6540 Q-TOF spectrometer for electrospray ionization (ESI) and were reported as (m/z). Optical rotations were measured with Jasco P-1020 Polarimeter. Melting points were measured on a WRX-5A melting point apparatus.

2. Optimization Studies

General Procedure for Optimization of Ir-Catalyzed Allylation of Ketone Silyl Enol Ether[1]



1a 2a 3a 4a

[{Ir(cod)Cl}$_2$] and **(*S*)-L** were added to a 10 ml nitrogen-filled round-bottom flask with solvent and stirred for 15 minutes. Then the allylic alcohol **2a**, the silyl enolate **1a** and acidic promoter were sequentially added. The resulting orange mixture was stirred at room temperature. The reaction progress was monitored by TLC. After the reaction ended, the mixture was filtered through a short pad of silica gel with CH_2Cl_2, concentrated in vacuo, and analyzed with ^{1}H NMR to determine the ratio of branched (**3a**) to linear (**4a**) products. Purification of the crude product was performed by preparative TLC (petroleum ether/Et_2OAc = 20/1) to provide the product. Enantiomeric excess was determined by HPLC analysis (Chiralpak AD-H).

2.1 Acid and Solvent Screening

Reaction Conditions: **1a** (30.9 mg, 0.15 mmol, 1.5 equiv), **2a** (14.8 mg, 0.1 mmol, 1.0 equiv), $[Ir(cod)Cl]_2$ (2.04 mg, 3 μmol, 0.03 equiv), **(*S*)-L** (6.08 mg, 12 μmol, 0.12 equiv), promoters (10 μmol, 0.1 equiv), solvent (0.4 ml, 0.25 M).

Table S1

Entry	Promoter	Solvent	Time (h)	Yield (%)	b:l (**3a:4a**)	*ee* (%)
1	$Zn(OTf)_3$	DME	12	78	>50:1	80
2	$Sc(OTf)_3$	DME	2.5	81	>50:1	89
3	$Yb(OTf)_3$	DME	8.5	76	>50:1	76
4	$Bi(OTf)_3$	DME	2.5	70	>50:1	60
5	TFA (0.2 equiv)	DME	2	30	>50:1	>99.5
6	$BF_3{\cdot}Et_2O$	DME	13	60	>50:1	85
7	$P(O)(OBu)_2OH$	DME	1	<5	—	—
8	$Zn(OTf)_3$	DCE	4	73	>50:1	63
9	$In(OTf)_3$	DCE	2	60	>50:1	80
10	$Sc(OTf)_3$	DCE	3	83	>50:1	96
11	$Sc(OTf)_3$	Toluene	3	70	>50:1	91
12	$Sc(OTf)_3$	1,4-dioxane	2	75	>50:1	83
13	$Sc(OTf)_3$	CH_3CN	2.5	35	15:1	82
14	$Sc(OTf)_3$	THF	2	73	>25:1	86

2.2 Concentration Screening

Reaction Conditions: **1a** (30.9 mg, 0.15 mmol, 1.5 equiv), **2a** (14.8 mg, 0.1 mmol, 1.0 equiv), $[Ir(cod)Cl]_2$ (2.04 mg, 3 μmol, 0.03 equiv), **(*S*)-L** (6.08 mg, 12 μmol, 0.12 equiv), $Sc(OTf)_3$ (4.92 mg, 10 μmol, 0.1 equiv), DCE.

Table S2

Entr	Concentratio	Time	Yield	b:l	***ee***

y	n (mmol/ml)	(h)	(%)	(**3a:4a**)	(%)
1	0.125	3	68	>50:1	88
2	0.25	3	83	>50:1	96
3	0.5	2	76	>50:1	94

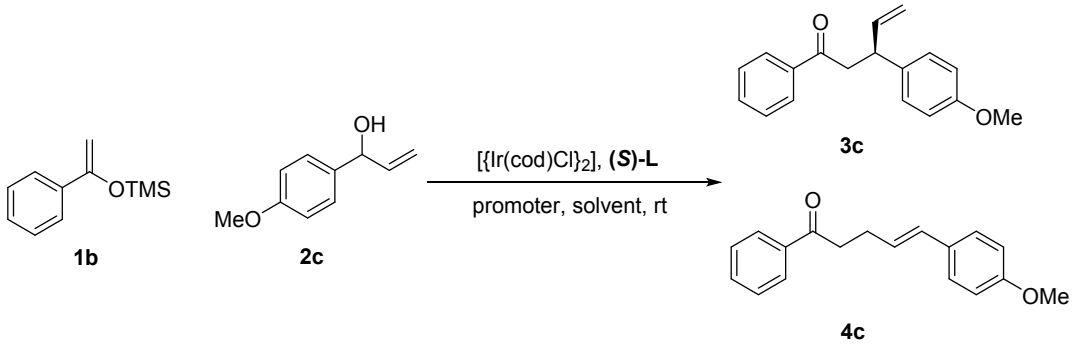
2.3 Effect of Compound 1a Amount

Reaction Conditions: **1a**, **2a** (14.8 mg, 0.1 mmol, 1.0 equiv)**,** [{Ir(cod)Cl}$_2$] (2.04 mg, 3 μmol, 0.03 equiv), **(*S*)-L** (6.08 mg, 12 μmol, 0.12 equiv), , Sc(OTf)$_3$ (4.92 mg, 10 μmol, 0.1 equiv), DCE (0.4 ml, 0.25 M).

Table S3

Entry	**1a** (equiv)	Yield (%)	**ee** (%)
1	2.5	82	93
2	1.5	83	96
3	1.0	78	94

2.4 Optimization of the Reaction Conditions for the Ratio of Branched (3c) to Linear (4c) Products



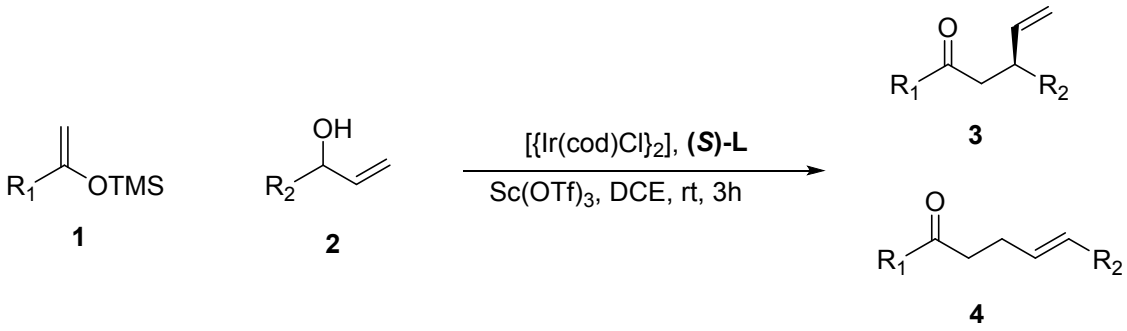
Reaction Conditions: **1b** (28.8 mg, 0.15 mmol, 1.5 equiv), **2c** (16.4 mg, 0.1 mmol, 1.0 equiv), [Ir(cod)Cl]$_2$ (2.04 mg, 3 μmol, 0.03 equiv), **(*S*)-L** (6.08 mg, 12 μmol, 0.12 equiv), promoters (10 μmol, 0.1 equiv), solvent (0.4 ml, 0.25 M).

Table S4

Entry	Solvent	Promoter	T (°C)	b:l（**3c:4c**）	t（h）
1	DCE	$Sc(OTf)_3$	23	4.5:1	3
2	DME	$Sc(OTf)_3$	23	3.3:1	3
3	Tol	$Sc(OTf)_3$	23	4.6:1	3
4	1.4-dioxane	$Sc(OTf)_3$	23	2:3	3
5	DCE	$BF_3{\cdot}Et_2O$ (0.5 equiv)	23	1.5:1	0.5
6	DCE	$Bi(OTf)_3$	23	2:1	0.5
7	DCE	$Sc(OTf)_3$	23	2:1	2
8	DCE	$Sc(OTf)_3$	23	—	—
9	DCE	$Sc(OTf)_3$	0	5:1	>10

3. Synthesis and Characterization of Products

3.1 General Procedure of Ir-Catalyzed Allylation of Ketone Silyl Enol Ether

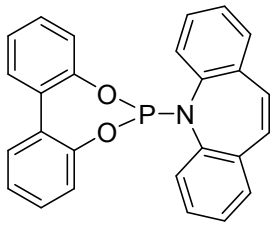


[{Ir(cod)Cl}$_2$] (2.04 mg, 3 μmol, 0.03 equiv) and **(*S*)-L** (6.08 mg, 12 μmol, 0.12 equiv) were added to a 10 ml nitrogen-filled round-bottom flask with DME (0.4 ml, 0.25 M) and stirred for 15 minutes. Then the allylic alcohol **2** (0.1 mmol), the silyl enolate **1 (**0.15 mmol**)** and $Sc(OTf)_3$ (4.92 mg, 10 μmol, 0.1 equiv) were sequentially added. The resulting orange mixture was stirred 3 hours at room temperature. The reaction mixture was filtered through a short pad of silica gel with CH_2Cl_2, concentrated in vacuo, and analyzed with ^{1}H NMR to determine the ratio of branched **3** to linear **4** products. Purification of the crude product was performed by preparative TLC (petroleum ether/Et_2OAc = 20/1) to provide the product. Enantiomeric excess was

determined by HPLC analysis (Chiralpak AD-H or Chiralcel OD-H).

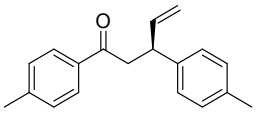
Preparation of Racemic Standards[1]

Racemic products were acquired by using the above procedure with racemic ligand **(*rac*)-L** (4.88 mg, 12 μmol, 0.12 eq) instead of **(*S*)-L**.



(*rac*)-L

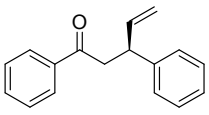
(*S*)-1,3-(di-*p*-tolylpent)-4-en-1-one (3a)



3a

Isolated as colorless oil (21.9 mg, 83% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.14 (q, *J* = 8.0 Hz, 4H), 6.04 (ddd, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.09 – 4.97 (m, 2H), 4.10 (t, *J* = 7.0 Hz, 1H), 3.41 (dd, *J* = 16.4, 7.8 Hz, 1H), 3.32 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 143.8, 141.0, 140.2, 136.0, 134.7, 129.2, 128.2, 127.6, 114.5, 44.2, 44.0, 21.6, 21.0; IR (KBr): 3085, 3004, 2922, 2854, 1680, 1635, 1608, 1513, 1409, 1383, 1361, 1262, 1181, 1112, 1038, 813, 584, 527 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{21}O$ $[M+H]^+$ 265.1587, found 265.1586; $[\alpha]^{23}_D$ = +6.9 (c = 1.22, $CHCl_3$); 96% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 8.64 min; t_2 = 11.68 min (major)].

(*S*)-1,3-diphenylpent-4-en-1-one (3b)[2]

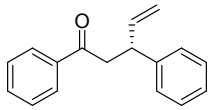


3b

Isolated as colorless oil (17.3mg, 73% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.14 (m, 5H), 6.05 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.12 – 4.94 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 1H), 3.40 (qd, *J* = 16.6, 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 143.2, 140.7, 137.2, 133.0, 128.6, 128.1, 127.7, 126.6, 114.7, 44.6, 44.1; IR (neat): 3061, 3028, 2978, 2920, 1687, 1598, 1493, 1449, 1361, 1260, 1206, 1076, 990,

918, 751, 699, 526 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{17}O$ $[M+H]^+$: 237.1274, found: 237.1274; $[\alpha]^{23}_D$ = +1.8 (c = 0.93, $CHCl_3$); 94% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 6.34 min; t_2 = 7.03 min (major)]. Lit [2]: $\alpha]^{20}_D$ = +1.2 (c = 0.85, $CHCl_3$), 96% ee.

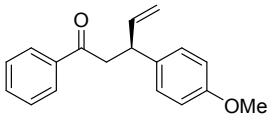
(*R*)-1,3-diphenylpent-4-en-1-one (3b')[2]



3b'

From a second experiment, employing **(*R*)-L**, 17.5 mg (74% yield) of the enantiomer of the title compound were isolated: $[\alpha]^{22}_D$ = -1.5 (c = 2.11, $CHCl_3$); 91% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 6.31 min (major); t_2 = 7.00 min]. Lit [2]: $[\alpha]^{20}_D$ = -1.6 (c = 3.14, $CHCl_3$), 95% ee.

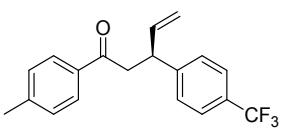
(*S*)-3-(4-methoxyphenyl)-1-phenylpent-4-en-1-one (3c)[2]



3c

Isolated as colorless oil (19.9 mg, 75% yield)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.87 – 6.82 (m, 2H), 6.03 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.05 (d, *J* = 10.3 Hz, 1H), 5.01 (d, *J* = 17.2 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 3.41 (dd, *J* = 16.5, 7.6 Hz, 1H), 3.34 (dd, *J* = 16.5, 6.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.4, 158.2, 141.0, 137.1, 135.1, 133.0, 128.7, 128.6, 128.1, 114.4, 113.9, 55.2, 44.1, 43.7; IR (neat): 3061, 3002, 2957, 2918, 2836, 1686, 1611, 1512, 1448, 1359, 1302, 1249, 1179, 1036, 993, 917, 831, 756, 692, 537 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{19}O_2$ $[M+H]^+$ 267.1380, found 267.1400; $[\alpha]^{20}_D$ = -4.2 (c = 0.95, $CHCl_3$); 94% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 96/4, 1.0 ml/min, t_1 = 9.54 min; t_2 = 12.22 min (major)]. Lit [2]: $\alpha]^{20}_D$ = -3.2 (*c* = 1.17, $CHCl_3$), 96% ee.

(*S*)-1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (3d)

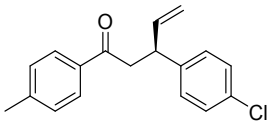


3d

Isolated as colorless oil (16.5 mg, 52% yield)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.24 (s, 2H), 6.02 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.14 – 4.96 (m, 2H), 4.21 (q, *J* = 7.0 Hz, 1H), 3.47 – 3.33 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.3, 147.3, 144.1, 139.9, 134.4, 129.3, 128.1, 125.5, 115.4, 44.2, 43.5, 21.6; IR (neat): 3087, 3060, 3004, 2983, 2921, 1684, 1608, 1416, 1327, 1261, 1165, 1124, 1069, 1018, 922, 840, 809, 755, 606 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{18}F_3O$ $[M+H]^+$ 319.1304, found 319.1302; $[\alpha]^{23}_D$ = +6.1 (c = 0.83, $CHCl_3$); >99% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 96/4, 1.0 ml/min, t_1 = 6.67 min; t_2 = 9.01 min (major)].

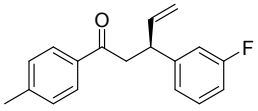
(*S*)-3-(4-chlorophenyl)-1-(p-tolyl)pent-4-en-1-one (3e)



3e

Isolated as colorless oil (20.7 mg, 73% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.15 (m, 6H), 6.00 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.12 – 4.97 (m, 2H), 4.11 (q, *J* = 6.9 Hz, 1H), 3.38 (dd, *J* = 16.6, 7.2 Hz, 1H), 3.30 (dd, *J* = 16.7, 7.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 144.0, 141.7, 140.4, 134.6, 132.2, 129.3, 129.2, 128.7, 128.2, 115.0, 43.9, 43.7, 21.6; IR (neat): 3082, 3031, 3003, 2922, 1683, 1607, 1491, 1409, 1358, 1258, 1204, 1181, 1092, 1015, 995, 920, 827, 757, 521 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}ClO$ $[M+H]^+$ 285.1041, found 285.1041; $[\alpha]^{23}_D$ = +9.3 (c = 1.21, $CHCl_3$); 93% ee [(Chiralpak AD-H) hexane/i-PrOH (230 nm, 30 °C) = 99/1, 1.0 ml/min, t_1 = 11.62 min; t_2 = 13.91 min (major)].

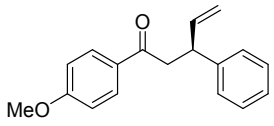
(*S*)-3-(3-fluorophenyl)-1-(p-tolyl)pent-4-en-1-one (3f)



3f

Isolated as colorless oil (14.2 mg, 53% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.21 (m, 3H), 7.04 (d, *J* = 7.7 Hz, 1H), 7.01 – 6.84 (m, 2H), 6.01 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.13 – 4.99 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 1H), 3.45 – 3.27 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 164.1, 161.7, 145.9, 145.8, 144.0, 140.1, 134.5, 130.0, 129.9, 129.3, 128.2, 123.5, 123.4, 115.1, 114.7, 114.5, 113.5, 113.3, 44.2, 43.6, 21.6; IR (KBr): 3083, 3003, 2957, 2919, 2851, 1683, 1610, 1487, 1448, 1359, 1261, 1181, 810, 786, 698 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}FO$ $[M+H]^+$ 269.1336, found 269.1337; $[\alpha]^{22}_D$ = +4.5 (c = 0.92, $CHCl_3$); >99.5% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 99.4/0.6, 0.7 ml/min, t_1 = 21.60 min (major)].

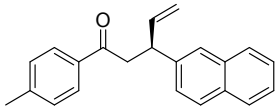
(*S*)-1-(4-methoxyphenyl)-3-phenylpent-4-en-1-one (3g)



3g

Isolated as colorless oil (19.7 mg, 74% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.34 – 7.22 (m, 4H), 7.27 – 7.15 (m, 1H), 6.95 – 6.88 (m, 2H), 6.05 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.10 – 4.97 (m, 2H), 4.13 (q, *J* = 7.0 Hz, 1H), 3.86 (s, 3H), 3.34 (qd, *J* = 16.4, 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 163.5, 143.3, 140.8, 130.4, 130.2, 128.6, 127.7, 126.5, 114.7, 113.7, 55.5, 44.7, 43.7; IR (KBr): 3079, 3028, 3005, 2923, 1676, 1636, 1601, 1511, 1419, 1312, 1258, 1172, 1028, 990, 834, 702, 599 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{19}O_2$ $[M+H]^+$ 267.1380, found 267.1383; $[\alpha]^{22}_D$ = +4.9 (c = 0.81, $CHCl_3$); 99% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 16.63 min; t_2 = 21.11 min (major)].

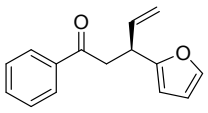
(*S*)-3-(naphthalen-2-yl)-1-(p-tolyl)pent-4-en-1-one (3h)



3h

Isolated as colorless oil (21.1 mg, 70% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.75 (m, 5H), 7.70 (d, *J* = 1.8 Hz, 1H), 7.50 – 7.38 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.12 (ddd, *J* = 17.1, 10.4, 6.07 Hz, 1H), 5.15 – 5.02 (m, 2H), 4.31 (q, *J* = 6.9 Hz, 1H), 3.57 – 3.38 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 143.9, 140.7, 140.6, 134.6, 133.6, 132.3, 129.3, 128.2, 127.7, 127.6, 126.3, 126.0, 125.5, 114.9, 44.6, 43.8, 21.6; IR (KBr): 3055, 2962, 2916, 2850, 1681, 1606, 1444, 1409, 1353, 1262, 1181, 1097, 1020, 807, 749, 478 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}O$ $[M+H]^+$ 301.1587, found 301.1587; $[\alpha]^{22}_D$ = +16.9 (c = 0.85, $CHCl_3$); 96% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 10.48 min; t_2 = 11.68 min (major)].

(*S*)-3-(furan-2-yl)-1-phenylpent-4-en-1-one (3i)[2]

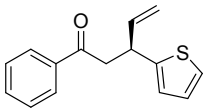


3i

Isolated as colorless oil (16.5 mg, 73% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.61 – 7.52 (m, 1H), 7.46 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.32 (d, *J* = 1.9 Hz, 1H), 6.28 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.07 (d, *J* = 3.2 Hz, 1H), 6.05 – 5.91 (m, 1H), 5.16 – 5.06 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 1H), 3.49 (dd, *J* = 16.8, 6.3 Hz, 1H), 3.32 (dd, *J* = 16.8, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 155.9, 141.4, 137.8, 137.0, 133.2, 128.6, 128.1, 116.2, 110.2, 105.4, 41.9, 38.5; IR (neat): 3084, 3063, 3005, 2981, 2923, 1688, 1597, 1504, 1449, 1410, 1357, 1274, 1210, 1075, 1011, 922, 755, 739, 691 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}O_2$ $[M+H]^+$ 227.1067, found 227.1069; $[\alpha]^{23}_D$ = +40.9 (c = 0.80, $CHCl_3$); 94% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 6.96 min; t_2 = 7.86 min (major)]. Lit [2]: $\alpha]^{20}_D$ = +55.8 (*c* = 1.1, $CHCl_3$), 96% ee.

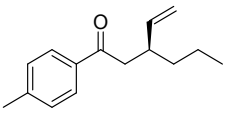
(*S*)-1-phenyl-3-(thiophen-2-yl)pent-4-en-1-one (3j)



3j

Isolated as pale yellow oil(16.9 mg, 70% yield)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.57 (s, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.16 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.04 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.16 – 5.08 (m, 2H), 4.45 (q, *J* = 7.1 Hz, 1H), 3.50 – 3.39 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.7, 146.8, 140.0, 137.0, 133.2, 128.6, 128.1, 126.8, 124.0, 123.7, 115.4, 44.9, 39.9; IR (neat): 3068, 3004, 2919, 1687, 1639, 1597, 1448, 1408, 1352, 1273, 1209, 1181, 989, 921, 850, 757, 691, 599 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{15}OS$ $[M+H]^+$ 243.0838, found 243.0840; $[\alpha]^{23}_D$ = +21.2 (c = 0.96, $CHCl_3$); 91% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 96/4, 1.0 ml/min, t_1 = 6.95 min; t_2 = 7.35 min (major)].

(*S*)-1-(p-tolyl)-3-vinylhexan-1-one (3k)

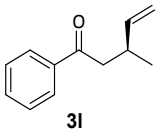


3k

Isolated as colorless oil (14.9 mg, 69% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 2H), 7.24 (s, 2H), 5.68 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H), 5.03 – 4.92 (m, 2H), 2.94 (d, *J* = 6.9 Hz, 2H), 2.75 (h, *J* = 7.3 Hz, 1H), 2.41 (s, 3H), 1.50 – 1.21 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 143.7, 141.7, 134.9, 129.2, 128.3, 114.6, 43.8, 39.7, 36.9, 21.6, 20.3, 14.1; IR (neat): 3029, 2958, 2927, 2871, 1684, 1607, 1455, 1410, 1357, 1286, 1181, 995, 915, 807, 602 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{21}O$ $[M+H]^+$ 217.1587, found 217.1585; $[\alpha]^{22}_D$ = -14.1 (c = 0.58, $CHCl_3$); 99% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) =

99/1, 1.0 ml/min, t_1 = 5.72 min (major); t_2 = 6.34 min].

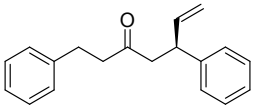
(*S*)-3-methyl-1-phenylpent-4-en-1-one (3l)



3l

Isolated as as colorless oil (12.4 mg, 71% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.63 – 7.51 (m, 1H), 7.46 (dd, *J* = 8.4, 6.9 Hz, 2H), 5.85 (ddd, *J* = 16.9, 10.3, 6.3 Hz, 1H), 5.10 – 4.89 (m, 2H), 3.13 – 2.97 (m, 1H), 2.91 (dq, *J* = 9.4, 7.0, 5.7 Hz, 2H), 1.10 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 143.1, 137.3, 133.0, 128.6, 128.1, 113.0, 45.2, 33.6, 19.8; IR(neat): 3082, 3066, 2963, 2928, 1687, 1598, 1449, 1358, 1278, 1210, 1000, 916, 753, 691, 576 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{15}O$ $[M+H]^+$ 175.1117, found 175.1119; $[\alpha]^{25}_D$ = -2.7 (c = 0.55, $CHCl_3$); >99% ee [(Chiralpak AD-H) hexane/i-PrOH (230 nm, 30 °C) = 99.5/0.5, 0.8 ml/min, t_1 = 14.59 min (major); t_2 = 15.56 min].

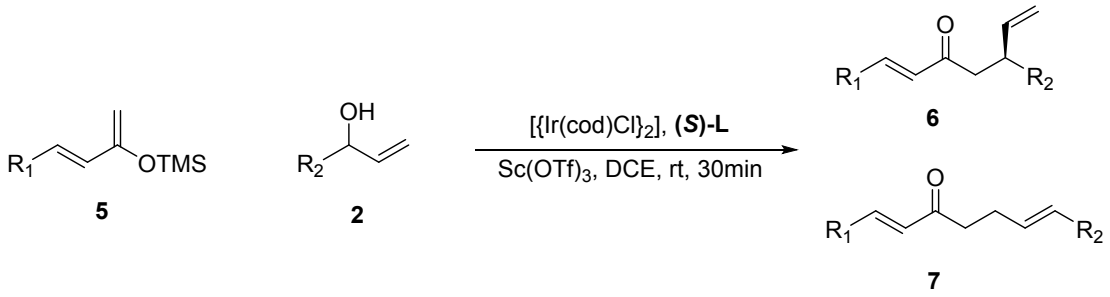
(*S*)-1,5-diphenylhept-6-en-3-one (3m)[2]



3m

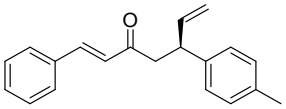
Isolated as colorless oil (15.8 mg, 60% yield)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.28 – 7.18 (m, 3H), 7.20 – 7.15 (m, 3H), 7.13 – 7.08 (m, 2H), 5.95 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.04 (dt, *J* = 10.3, 1.4 Hz, 1H), 4.99 (dd, *J* = 17.1, 1.5 Hz, 1H), 3.92 (q, *J* = 7.3 Hz, 1H), 2.88 – 2.75 (m, 4H), 2.74 – 2.65 (m, 1H), 2.61 (ddd, *J* = 17.2, 8.9, 6.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.2, 142.8, 141.0, 140.5, 128.6, 128.4, 128.3, 127.6, 126.6, 126.0, 114.6, 48.3, 45.1, 44.5, 29.4; IR (KBr): 3062, 3028, 2919, 2850, 1715, 1637, 1603, 1495, 1453, 1408, 1368, 1155, 1089, 1031, 919, 754, 701, 507, 466 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{20}OK$ $[M+K]^+$ 303.1146, found 303.1145; $[\alpha]^{23}_D$ = -13.0 (c = 0.72, $CHCl_3$); 99% ee [(Chiralpak AD-H) hexane/i-PrOH (210 nm, 30 °C) = 98:2, 1.0 ml/min, t_1 = 6.77 min; t_2 = 7.23 min (major)]. Lit [2]: $\alpha]^{20}_D$ = -9.2 (*c* = 1.1, $CHCl_3$), 94% ee.

3.2 General Procedure for Ir-Catalyzed Allylation of α, β-Unsaturated Ketone Silyl Enol Ether



[{Ir(cod)Cl}$_2$] (2.04 mg, 3 μmol, 0.03 equiv) and **(*S*)-L** (6.08 mg, 12 μmol, 0.12 equiv) were added to a 10 ml nitrogen-filled round-bottom flask with DME (0.4 ml, 0.25 M) and stirred for 15 minutes. Then the allylic alcohol **2** (0.1 mmol), the silyl enolate **5 (**0.15 mmol**)** and Sc(OTf)$_3$ (9.84 mg, 20 μmol, 0.2 equiv) were sequentially added. The resulting orange mixture was stirred 30min at room temperature. The reaction mixture was filtered through a short pad of silica gel with CH_2Cl_2, concentrated in vacuo, and analyzed with ^{1}H NMR to determine the ratio of branched **6** to linear **7** products. Purification of the crude product was performed by preparative TLC (petroleum ether/Et_2OAc = 20/1) to provide the product. Enantiomeric excess was determined by HPLC analysis (Chiralpak AD-H or Chiralcel OD-H).

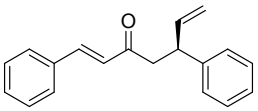
(*S,E*)-1-phenyl-5-(p-tolyl)hepta-1,6-dien-3-one (6a)[3]



6a

Isolated as colorless oil (20.6 mg, 75% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 3H), 7.39 (q, *J* = 3.6 Hz, 3H), 7.18 – 7.00 (m, 4H), 6.69 (d, *J* = 16.2 Hz, 1H), 6.01 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.10 – 4.97 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 1H), 3.07 (qd, *J* = 15.9, 7.3 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 142.7, 140.8, 140.0, 136.1, 134.5, 130.5, 129.3, 128.9, 128.3, 127.6, 126.4, 114.5, 46.4, 44.4, 21.0; IR (neat): 3081, 3024, 3005, 2978, 2922, 2865, 1690, 1662, 1610, 1576, 1513, 1449, 1411, 1331, 1176, 1085, 989, 917, 815, 747, 691, 563, 522 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{21}O$ $[M+H]^+$ 277.1587, found 277.1588; $[\alpha]^{24}_D$ = +14.5 (c = 1.23, $CHCl_3$); 92% ee [(Chiralpak AD-H) hexane/i-PrOH (230 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 11.06 min; t_2 = 13.45 min (major)]. Lit [3]: $[\alpha]^{25}_D$ = -20.9 (c = 1.25, $CHCl_3$), 95% ee (**6a**′).

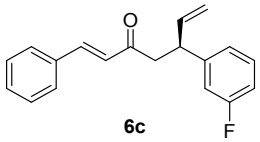
(*S,E*)-1,5-diphenylhepta-1,6-dien-3-one (6b)[3]



6b

Isolated as white solid oil (18.3 mg, 70% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.44 (m, 3H), 7.41 – 7.36 (m, 3H), 7.34 – 7.16 (m, 5H), 6.70 (d, *J* = 16.2 Hz, 1H), 6.03 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.22 – 4.88 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 1H), 3.09 (qd, *J* = 15.9, 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 143.0, 142.8, 140.6, 134.5, 130.5, 128.9, 128.6, 128.3, 127.7, 126.6, 126.4, 114.7, 46.3, 44.8; IR (KBr): 3082, 3028, 3003, 2977, 2922, 1687, 1646, 1610, 1494, 1450, 1333, 1203, 1177, 1074, 987, 920, 748, 701, 586, 524 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{19}O$ $[M+H]^+$ 263.1430, found 263.1435; $[\alpha]^{25}_D$ = +11.5 (c = 0.90, $CHCl_3$); 92% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 11.65 min; t_2 = 13.18 min (major)]; mp: 74-75°C. Lit [3]: $[\alpha]^{25}_D$ = -16.5 (c = 1.12, $CHCl_3$), 96% ee (**6b**′).

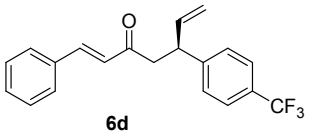
(*S,E*)-5-(3-fluorophenyl)-1-phenylhepta-1,6-dien-3-one (6c)[3]



6c

Isolated as colorless oil (16.0 mg, 57% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 3H), 7.40 (q, *J* = 3.7 Hz, 3H), 7.35 – 7.21 (m, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 7.00 – 6.81 (m, 2H), 6.71 (d, *J* = 16.2 Hz, 1H), 5.99 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.14 – 4.99 (m, 2H), 4.06 (q, *J* = 7.1 Hz, 1H), 3.08 (qd, *J* = 16.2, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 164.2, 161.7, 145.7, 145.6, 143.0, 140.0, 134.4, 130.6, 130.1, 130.0, 129.0, 128.3, 126.2, 123.5, 123.4, 115.2, 114.7, 114.5, 113.6, 113.4, 46.0, 44.3; IR(neat): 3082, 3029, 3006, 2956, 2922, 1690, 1662, 1612, 1490, 1449, 1360, 1330, 1256, 1175, 1075, 978, 921, 786, 746, 694, 551, 461 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{18}FO$ $[M+H]^+$ 281.1336, found 281.1337; $[\alpha]^{25}_D$ = +17.3 (c = 0.74, $CHCl_3$); >99.5% ee [(Chiralcel OD-H) hexane/i-PrOH (254 nm, 30 °C) = 95/5, 1.0 ml/min, t_1 = 11.77 min (major)]. Lit [3]: $[\alpha]^{25}_D$ = -25.8 (c = 1.20, $CHCl_3$), 97% ee (**6c**′).

(*S,E*)-1-phenyl-5-(4-(trifluoromethyl)phenyl)hepta-1,6-dien-3-one (6d)[3]

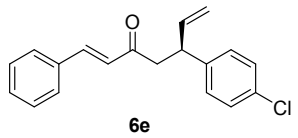


6d

Isolated as colorless oil (18.5 mg, 56% yield)
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 5H), 7.42 – 7.35 (m, 5H), 6.70 (d, *J* = 16.1 Hz, 1H), 6.01 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.15 – 5.04 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 1H), 3.16 (dd, *J* = 16.4, 7.1 Hz, 1H), 3.08 (dd, *J* = 16.4, 7.3 Hz, 1H)； ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.6, 147.1, 143.1, 139.8, 134.2, 130.7, 129.0, 128.3, 128.1, 126.0, 125.5, 125.5, 115.5, 45.9, 44.3； IR (neat): 3083, 3043, 3006, 2983, 2923, 1691, 1662, 1613, 1417, 1327, 1166, 1123, 1069, 1018, 978, 921, 842, 750, 690, 605 cm^{-1}; HRMS (ESI):

m/z calcd for $C_{20}H_{18}F_3O$ $[M+H]^+$ 331.1304, found 331.1308; $[\alpha]^{25}_D$ = +22.2 (c = 0.87, $CHCl_3$); >99.5% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_2 = 14.16 (major)]. Lit [3]: $[\alpha]^{25}_D$ = -23.9 (c = 1.00, $CHCl_3$), 95% ee (**6b**′).

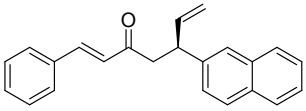
(*S,E*)-5-(4-chlorophenyl)-1-phenylhepta-1,6-dien-3-one (6e)



6e

Isolated as white solid (22.5 mg, 76% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 3H), 7.39 (p, *J* = 3.7 Hz, 3H), 7.34 – 7.23 (m, 2H), 7.22 – 7.13 (m, 2H), 6.69 (d, *J* = 16.2 Hz, 1H), 5.99 (ddd, *J* = 17.0, 10.3, 6.6 Hz, 1H), 5.16 – 4.96 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.07 (qd, *J* = 16.2, 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 143.0, 141.5, 140.2, 134.3, 132.3, 130.6, 129.1, 129.0, 128.7, 128.3, 126.2, 115.1, 46.1, 43.9; IR (KBr): 3082, 3061, 3042, 3004, 2978, 2921, 1689, 1636, 1609, 1576, 1492, 1408, 1333, 1176, 1091, 1014, 987, 921, 828, 751, 692, 521 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{18}ClO$ $[M+H]^+$ 297.1041, found 297.1034; $[\alpha]^{24}_D$ = +24.8 (c = 1.09, $CHCl_3$); 96% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 0.7 ml/min, t_1 = 20.23 min; t_2 = 24.29 min (major)]; mp: 68-69 °C.

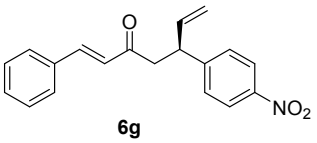
(*S,E*)-5-(naphthalen-2-yl)-1-phenylhepta-1,6-dien-3-one (6f)[3]



6f

Isolated as colorless oil (24.0mg, 77% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 3H), 7.70 (s, 1H), 7.64 – 7.32 (m, 9H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.11 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.17 – 5.06 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 1H), 3.29 – 3.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 142.9, 140.5, 140.5, 134.4, 133.6, 132.4, 130.5, 128.9, 128.3, 128.3, 127.7, 127.6, 126.3, 126.3, 126.1, 126.0, 125.6, 115.0, 46.3, 44.8; IR (KBr): 3056, 2922, 1687, 1657, 1610, 1449, 1331, 1172, 1075, 982, 820, 749, 692, 478 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{21}O$ $[M+H]^+$ 313.1587, found 313.1591; $[\alpha]^{24}_D$ = +36.2 (c = 1.33, $CHCl_3$); 93% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 0.7 ml/min, t_1 = 24.75 min; t_2 = 29.53 min (major)]. Lit [3]: $[\alpha]^{25}_D$ = -45.1 (c = 1.20, $CHCl_3$), 97% ee (**6f**′).

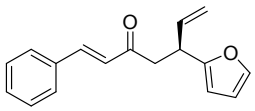
(*S,E*)-5-(4-nitrophenyl)-1-phenylhepta-1,6-dien-3-one (6g)



6g

Isolated as pale yellow oil (11.6 mg, 38% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 7.96 (m, 2H), 7.59 – 7.47 (m, 3H), 7.46 – 7.35 (m, 5H), 6.71 (d, *J* = 16.2 Hz, 1H), 6.00 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1H), 5.25 – 4.99 (m, 2H), 4.19 (q, *J* = 7.0 Hz, 1H), 3.15 (qd, *J* = 16.7, 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 150.7, 146.7, 143.3, 139.2, 134.2, 130.8, 129.0, 128.7, 128.4, 125.9, 123.8, 116.0, 45.8, 44.2; IR(neat): 3082, 3062, 3027, 2957, 2919, 2850, 1690, 1661, 1608, 1518, 1450, 1346, 1175, 1110, 1081, 990, 923, 855, 749, 692 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{18}NO_3$ $[M+H]^+$ 308.1281, found 308.1282; $[\alpha]^{24}_D$ = +58.1 (c = 0.58, $CHCl_3$); 100% ee [(Chiralcel OD-H) hexane/i-PrOH (254 nm, 30 °C) = 90/10, 1.0 ml/min, t_2 = 22.98 min (major)].

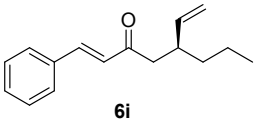
(*S,E*)-5-(furan-2-yl)-1-phenylhepta-1,6-dien-3-one (6h)[3]



6h

Isolated as colorless oil (18.9 mg, 75% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.48 (m, 3H), 7.45 – 7.29 (m, 4H), 6.72 (d, *J* = 16.2 Hz, 1H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.07 (d, *J* = 3.1 Hz, 1H), 5.95 (ddd, *J* = 17.3, 9.9, 7.3 Hz, 1H), 5.20 – 5.02 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 1H), 3.18 (dd, *J* = 16.1, 6.6 Hz, 1H), 3.02 (dd, *J* = 16.1, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 155.8, 143.0, 141.5, 137.7, 134.4, 130.6, 129.0, 128.3, 126.2, 116.1, 110.2, 105.5, 44.0, 38.7; IR (KBr): 3085, 3029, 3004, 2926, 1719, 1687, 1629, 1612, 1450, 1402, 1335, 1260, 1179, 1087, 991, 752, 695, 559 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_2K$ $[M+K]^+$ 291.0782, found 291.0791; $[\alpha]^{23}_D$ = +53.9 (c = 0.92, $CHCl_3$); 93% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 98/2, 1.0 ml/min, t_1 = 12.97 min; t_2 = 13.97 min (major)]. Lit [3]: $[\alpha]^{25}_D$ = -49.4 (c = 1.20, $CHCl_3$), 96% ee (**6h**').

(*S,E*)-1-phenyl-5-vinyloct-1-en-3-one (6i)

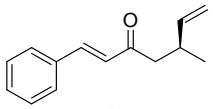


6i

Isolated as colorless oil (14.4 mg, 63%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 3H), 7.36 – 7.42 (m, 3H), 6.74 (d, *J* = 16.1 Hz, 1H), 5.66 (ddd, *J* = 17.5, 10.3, 7.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 2.67 (s, 3H), 1.46 – 1.25 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 142.5, 141.5, 134.6, 130.4, 128.9, 128.3, 126.6, 114.7, 46.4, 39.7, 36.9, 20.2, 14.0; IR(neat): 3079, 3028, 2958, 2872, 1690, 1660, 1611, 1495, 1450, 1331, 1180, 1070, 992, 915, 748, 691, 558, 483 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1587, found

229.1582; $[\alpha]^{25}_{D}$ = -21.4 (c = 0.84, $CHCl_3$); >99.5% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 98.5/1.5, 1.0 ml/min, t_1 = 8.23 min (major)].

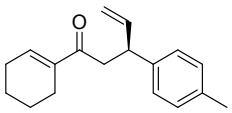
(*S,E*)-5-methyl-1-phenylhepta-1,6-dien-3-one (6j)[3]



6j

Isolated as colorless oil (13.6 mg, 68%)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 3H), 7.40 (p, *J* = 3.9 Hz, 3H), 6.75 (d, *J* = 16.2 Hz, 1H), 5.83 (ddd, *J* = 17.1, 10.4, 6.7 Hz, 1H), 5.09 – 4.93 (m, 2H), 2.90 – 2.67 (m, 2H), 2.60 (dd, *J* = 15.4, 7.5 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 143.0, 142.6, 134.5, 130.5, 129.0, 128.3, 126.5, 113.1, 47.5, 33.8, 19.8; IR(neat): 3082, 3029, 2961, 2926, 1689, 1611, 1451, 1332, 1280, 1180, 1079, 997, 798, 751, 693, 463 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{17}O$ $[M+H]^+$ 201.1274, found 201.1270; $[\alpha]^{25}_{D}$ = -4.4 (c = 0.75, $CHCl_3$); >99.5% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 98.5/1.5, 0.8 ml/min, t_1 = 11.11 min (major)]. Lit [3]: $[\alpha]^{25}_{D}$ = +5.9 (c = 1.33, $CHCl_3$), 94% ee (**6j'**).

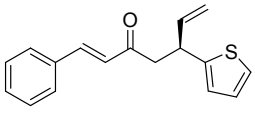
(*S*)-1-(cyclohex-1-en-1-yl)-3-(p-tolyl)pent-4-en-1-one (6k)



6k

Isolated as colorless oil (19.1 mg, 75% yield)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 6.86 (td, *J* = 3.8, 1.9 Hz, 1H), 5.97 (ddd, *J* = 17.1, 10.4, 6.8 Hz, 1H), 5.06 – 4.93 (m, 2H), 3.95 (q, *J* = 7.0 Hz, 1H), 3.13 – 2.93 (m, 2H), 2.31 (s, 3H), 2.25 – 2.13 (m, 4H), 1.66 – 1.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 141.2, 140.4, 139.8, 139.6, 135.9, 129.2, 127.6, 114.2, 44.5, 42.6, 26.1, 23.1, 21.9, 21.5, 21.0; IR (KBr): 3083, 3050, 3004, 2920, 2851, 1711, 1673, 1638, 1514, 1450, 1409, 1382, 1260, 1181, 1112, 1075, 1021, 919, 817, 639, 524 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{18}H_{22}O$ $[M]^+$ 254.1671, found 254.1676; $[\alpha]^{25}_{D}$ = +12.0 (c = 0.94, $CHCl_3$); 91% ee [(Chiralpak AD-H) hexane/i-PrOH (230 nm, 30 °C) = 99/1, 1.0 ml/min, t_1 = 6.83 min; t_2 = 8.55 min (major)].

(*S,E*)-1-phenyl-5-(thiophen-2-yl)hepta-1,6-dien-3-one (6l)

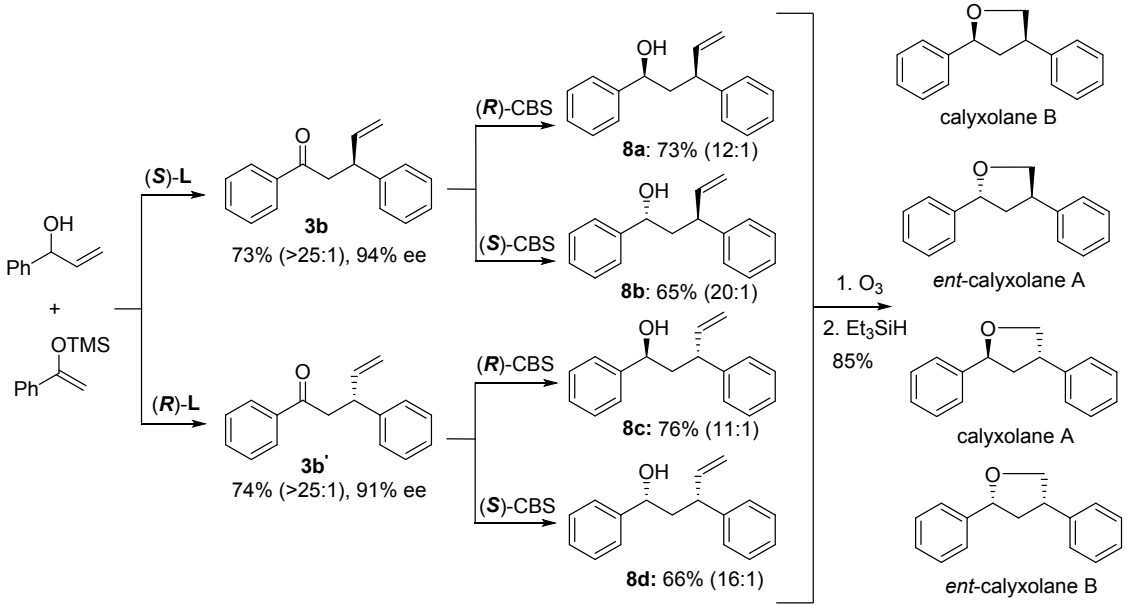


6l

Isolated as pale yellow oil (19.8 mg, 74% yield)

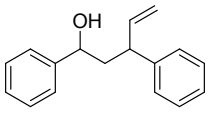
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.43 (m, 3H), 7.44 – 7.36 (m, 3H), 7.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.97 – 6.83 (m, 2H), 6.73 (d, *J* = 16.2 Hz, 1H), 6.03 (ddd, *J* = 17.2, 10.2, 7.2 Hz, 1H), 5.19 – 5.06 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 1H), 3.22 – 3.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 146.7, 143.0, 140.0, 134.4, 130.6, 129.0, 128.4, 126.8, 126.3, 124.1, 123.7, 115.4, 47.2, 40.1; IR(neat): 3080, 3063, 3027, 3004, 2978, 2957, 2924, 1689, 1660, 1610, 1576, 1495, 1449, 1331, 1279, 1174, 1077, 979, 920, 749, 693 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{17}OS$ $[M+H]^+$ 269.0995, found 269.0999; $[\alpha]^{25}_D$ = +31.7 (c = 1.62, $CHCl_3$); 94% ee [(Chiralpak AD-H) hexane/i-PrOH (254 nm, 30 °C) = 97/3, 1.0 ml/min, t_1 = 12.71 min; t_2 = 14.02 min (major)].

4. Synthesis of calyxolane A, B and ent-calyxolane A, B



Calyxolane A and B were first isolated from the marine sponge *Calyx podatypa* in 1997.

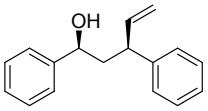
1,3-diphenylpent-4-en-1-ol (8):



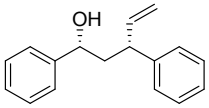
8

A flame dried 25 ml round bottom flask charged with ***(R) or (S)***-CBS (1.0 *M* in toluene) (380 µl, 0.38 mmol, 3.0 equiv) and THF (5 ml), then the solution was cooled to 0 °C under a stream of N_2 and BH_3·THF (1.0 M in THF) (250 µl, 0.25 mmol, 2.0 equiv)was added. The reaction mixture was stirred for 5 minutes. **3b or 3b'** (30 mg, 0.13 mmol, 1.0 eq) was added dropwise via a syringe. After 20 minutes of stirring, the reaction mixture was quenched with H_2O and allowed to warm up to room temperature, and extracted with Et_2O (3 × 15 ml).The organic layer were combined, dried over Na_2SO_4

and concentrated in vacuo. The product was purified by flash column chromatography on silica gel (eluting with petroleum ether/Et_2OAc = 20/1 to 5/1) to give **8** as a colorless oil. Diastereoselectivity of **8** was determined by analysis of ^1H NMR spectra.

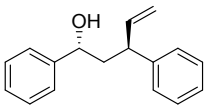


8a

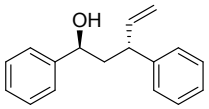


8d

^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 6H), 7.31 – 7.17 (m, 4H), 6.09 – 5.94 (m, 1H), 5.11 – 5.00 (m, 2H), 4.50 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.55 (q, *J* = 7.5 Hz, 1H), 2.23 (ddd, *J* = 13.8, 9.0, 6.3 Hz, 1H), 2.06 (ddd, *J* = 13.7, 9.0, 4.5 Hz, 1H), 1.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.4, 142.2, 128.6, 128.5, 127.8, 127.6, 126.5, 125.8, 114.2, 72.2, 46.4, 44.5; IR(neat): 3082, 3062, 3029, 2918, 1637, 1601, 1493, 1453, 1414, 1326, 1055, 1025, 999, 915, 754, 701, 602, 548 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{18}ONa$ $[M+Na]^+$ 261.1250, found 261.1256; $[\alpha]^{23}_D$ = -1.0 (c = 0.47 $CHCl_3$) (**8a**); $[\alpha]^{23}_D$ =+0.1 (c = 0.68, $CHCl_3$) (**8d**).



8b



8c

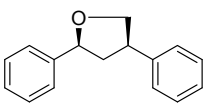
^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 7H), 7.24 – 7.17 (m, 3H), 5.96 (ddd, *J* = 18.0, 10.2, 7.9 Hz, 1H), 5.19 – 4.99 (m, 2H), 4.66 (ddd, *J* = 8.6, 5.2, 3.5 Hz, 1H), 3.45 (q, *J* = 7.7 Hz, 1H), 2.32 – 2.15 (m, 1H), 2.09 (ddd, *J* = 13.8, 8.5, 5.2 Hz, 1H), 1.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 143.9, 141.5, 128.6, 128.5, 127.7, 127.6, 126.4, 126.1, 114.9, 72.4, 46.4, 44.5; IR (KBr): 3083, 3062, 3028, 2919, 1636, 1601, 1493, 1453, 1414, 1328, 1057,1023, 917, 747, 700, 601, 530 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{18}ONa$ $[M+Na]^+$ 261.1250, found 261.1256; $[\alpha]^{23}_D$ = +44.5 (c = 0.58, $CHCl_3$) (**8b**); $[\alpha]^{23}_D$ = -45.7 (c = 0.49, $CHCl_3$) (**8c**).

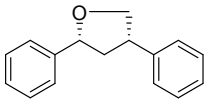
Calyxolane A, B and ent-calyxolane A, B[4]

a) Ozone was bubbled through a solution of **8** (**8a, 8b, 8c or 8d**) (20 mg, 84 μmol, 1.0 equiv) and DCM (5 ml) that had been cooled to -78 °C. The reaction was closely monitored via TLC（petroleum ether/Et_2OAc = 5/1） until complete consumption of starting material was observed. At that time, dimethylsulfide (200 μl) was added, then the reaction was warmed to room temperature and continued to stir for 10 hours. After completion of the reaction, as determined by TLC, the solvent were evaporated in vacuo and a crude product of was obtained without further purification.

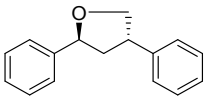
b) Triethylsilane (16 μl, 0.10 mmol, 1.2 equiv) was added slowly into a solution of above-mentioned crude product in dichloromethane (1ml) at -78 °C. Boron trifluoride etherate (48%) (33 μl, 0.13 mmol, 1.5 equiv) was then added dropwise into a reaction mixture and it was stirred at room temperature for 3 hours. The reaction mixture was poured on ice-water and extracted with Et_2O. The organic layer were combined, dried over Na_2SO_4 and concentrated in vacuo. The product was

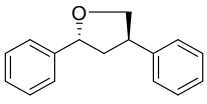
purified by flash column chromatography on silica gel (eluting with petroleum ether/Et_2OAc = 50/:1 to 10/1) to give the product as a colorless oil.


calyxolane B


ent-calyxolane B

^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 10H), 5.08 (dd, *J* = 10.2, 5.7 Hz, 1H), 4.37 (t, *J* = 8.2 Hz, 1H), 4.02 (t, *J* = 8.5 Hz, 1H), 3.65 (m, 1H), 2.76 (ddd, *J* = 12.7, 7.3, 5.7 Hz, 1H), 2.02 (dt, *J* = 12.4, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 141.7, 128.6, 128.4, 127.4, 127.3, 126.7, 125.7, 81.9, 75.1, 46.0, 43.7; IR (neat): 3049, 3027, 2958, 2920, 2844, 1637, 1440, 1250, 1091, 1015, 787, 688 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{16}H_{16}O$ $[M]^+$ 224.1201, found 224.1202; $[\alpha]^{23}_D$ = -44.2 (c = 0.43, $CHCl_3$) (calyxolane B); lit [4]: $[\alpha]^{22}_D$ = 0 (c = 0.4, $CHCl_3$) (calyxolane B); $[\alpha]^{24}_D$ = +52.5 (c = 0.58, $CHCl_3$) (ent-calyxolane B).


calyxolane A


ent-calyxolane A

^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 10H), 5.24 (dd, *J* = 7.8, 5.8 Hz, 1H), 4.47 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.95 (t, *J* = 8.2 Hz, 1H), 3.54 (m, 1H), 2.48 (dt, *J* = 12.6, 7.7 Hz, 1H), 2.34 (ddd, *J* = 12.6, 8.3, 5.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.0, 128.7, 128.4, 127.4, 127.2, 126.6, 125.5, 80.6, 75.2, 44.4, 42.7; IR (neat): 3055, 3020, 2950, 2914, 2844, 1675, 1442, 1252, 1097, 1013, 794, 752, 689 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{16}H_{16}O$ $[M]^+$ 224.1201, found 224.1202; $[\alpha]^{23}_D$ = +23.3 (c = 0.35, $CHCl_3$) (calyxolane A); lit [4]: $[\alpha]^{22}_D$ = +34.6 (c = 0.3, $CHCl_3$) (calyxolane A); $[\alpha]^{22}_D$ = -39.9 (c = 0.42, $CHCl_3$) (ent-calyxolane A).

References

(1) Hamilton, J. Y.; Hauser, N.; Sarlah, D.; Carreira, E. M. *Angew. Chem. Int. Ed*. **2014,** *53*, 10759.
(2) Graening, T; Hartwig, J. F. *J. Am. Chem. Soc*. **2005,** *127*, 17192.
(3) Chen, M.; Hartwig, J. F. *Angew. Chem. Int. Ed*. **2014**, *53*, 8691.
(4) Abimael D. R.; Oscar, M. C; Omayra, L. P. *J. Nat. Prod*. **1997**, *60*, 915.