Supporting Information for

Catalytic Enantioselective Synthesis of Acyclic Quaternary Centers: Palladium-Catalyzed Decarboxylative Allylic Alkylation of Fully Substituted Acyclic Enol Carbonates.

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Materials and Methods

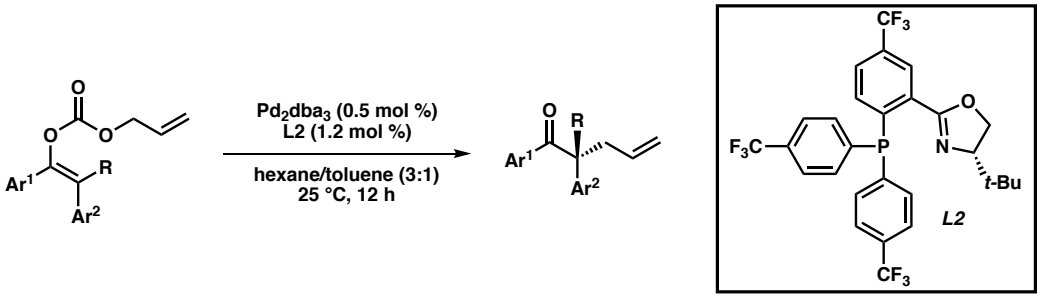
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+). Absolute configuration of **2b** was determined by comparison of the optical rotation to literature reported value,[2] and all other products are assigned by analogy.

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Ligands **L1**,[3] **L2**,[4] and **L4**[5] and trisubstituted ketones[6] were prepared by known methods.

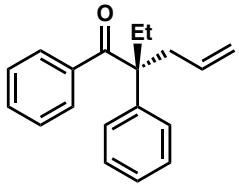
List of Abbreviations:

ee – enantiomeric excess, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, IPA – isopropanol

General Procedure for Pd-Catalyzed Allylic Alkylation Reactions

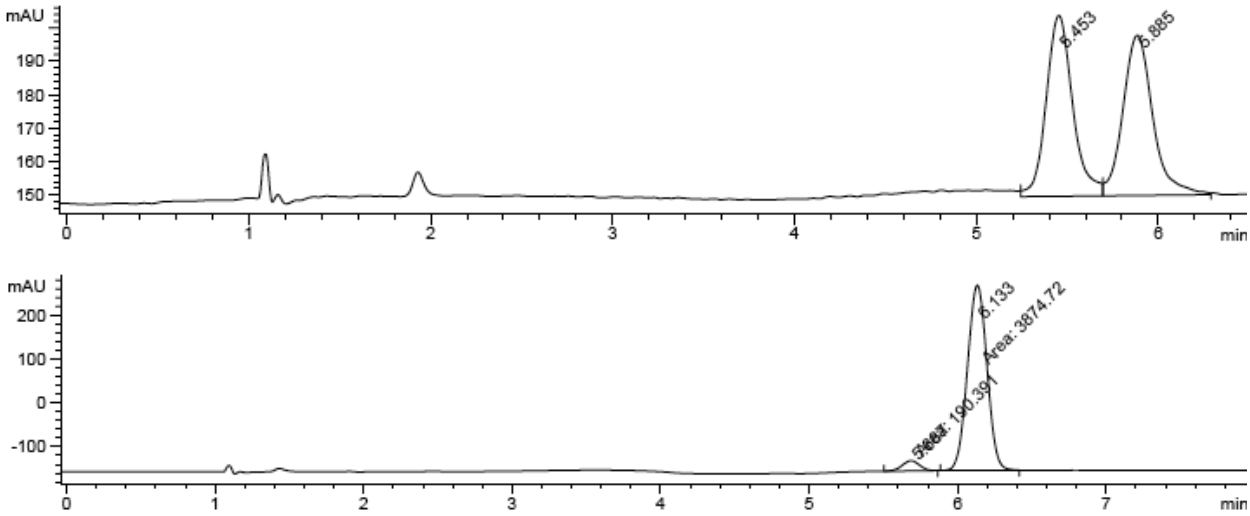


In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (1.8 mg/mL) and **L2** (2.8 mg/mL) in toluene was stirred for 30 minutes at 25 °C, then 0.5 mL of the resulting catalyst solution was added to a one dram vial containing allyl enol carbonate substrate (0.2 mmol) dissolved in hexanes (1.5 mL). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and stirred at 25 °C for 12 h. The crude reaction mixture was concentrated then purified by silica gel flash chromatography to provide the desired alkylation product.



(*R*)-2-ethyl-1,2-diphenylpent-4-en-1-one (2a)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (51.1 mg, 97% yield); 91% ee, $[\alpha]_D^{25}$ –107.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 5H), 7.31–7.25 (m, 3H), 7.24–7.17 (m, 2H), 5.38 (dddd, *J* = 16.8, 10.3, 8.2, 6.5 Hz, 1H), 5.03–4.85 (m, 2H), 2.91–2.72 (m, 2H), 2.16 (qd, *J* = 7.4, 3.3 Hz, 2H), 0.69 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 142.7, 137.3, 133.6, 131.8, 129.5, 129.0, 128.1, 127.1, 127.0, 118.3, 58.2, 39.3, 26.9, 8.0; IR (Neat Film, NaCl) 3065, 2973, 2940, 2879, 1675, 1597, 1578, 1496, 1446, 1227, 1182, 1142, 1004, 917, 839, 764, 714, 702, 654 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{21}O$ $[M+H]^+$: 265.1587, found 265.1577; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 5.33, major = 5.76.



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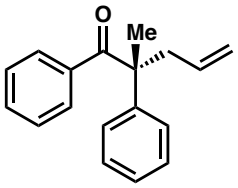
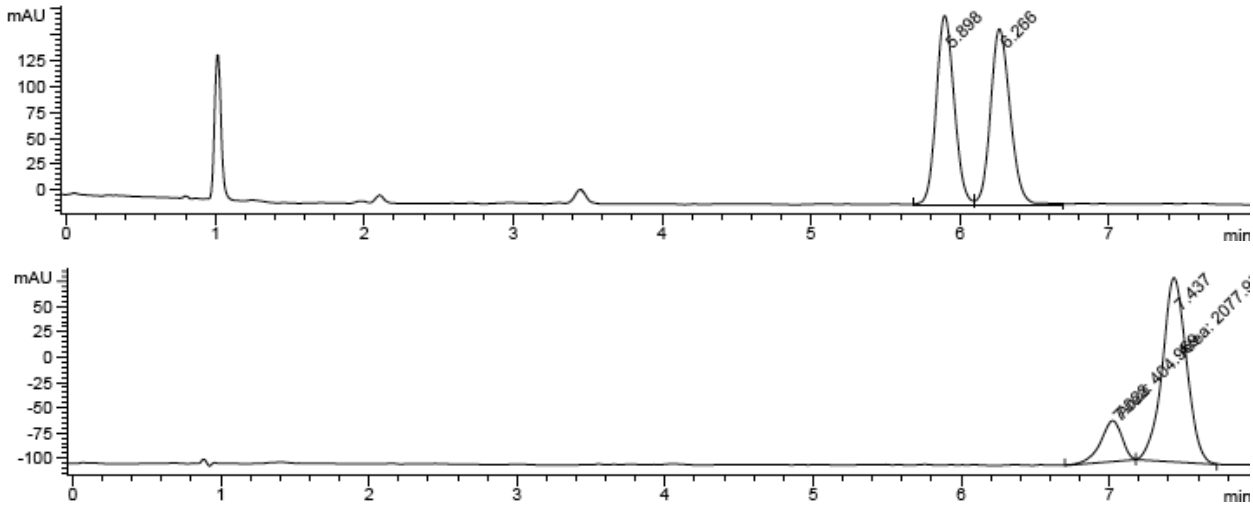


(*R*)-2-methyl-1,2-diphenylpent-4-en-1-one (2b)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (48.3 mg, 96% yield); 67% ee, $[a]_D^{25}$ –111.9 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.40–7.33 (m, 3H), 7.33–7.27 (m, 3H), 7.24–7.18 (m, 2H), 5.51 (dddd, *J* = 17.0, 10.2, 7.7, 6.9 Hz, 1H), 5.08–4.87 (m, 2H), 2.89–2.71 (m, 2H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 143.6, 136.9, 134.1, 131.8, 129.7, 129.1, 128.1, 127.1, 126.4, 118.5, 54.4, 44.8, 23.8; IR (Neat Film, NaCl) 3065, 3024, 2977, 2935, 1677, 1638, 1597, 1578, 1496, 1446, 1376, 1240, 1182, 1139, 1078, 1028, 1001, 970, 917, 762, 716, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found 251.1418; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 7.02, major = 7.44.



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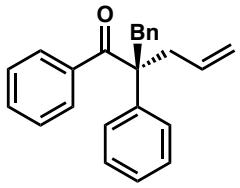
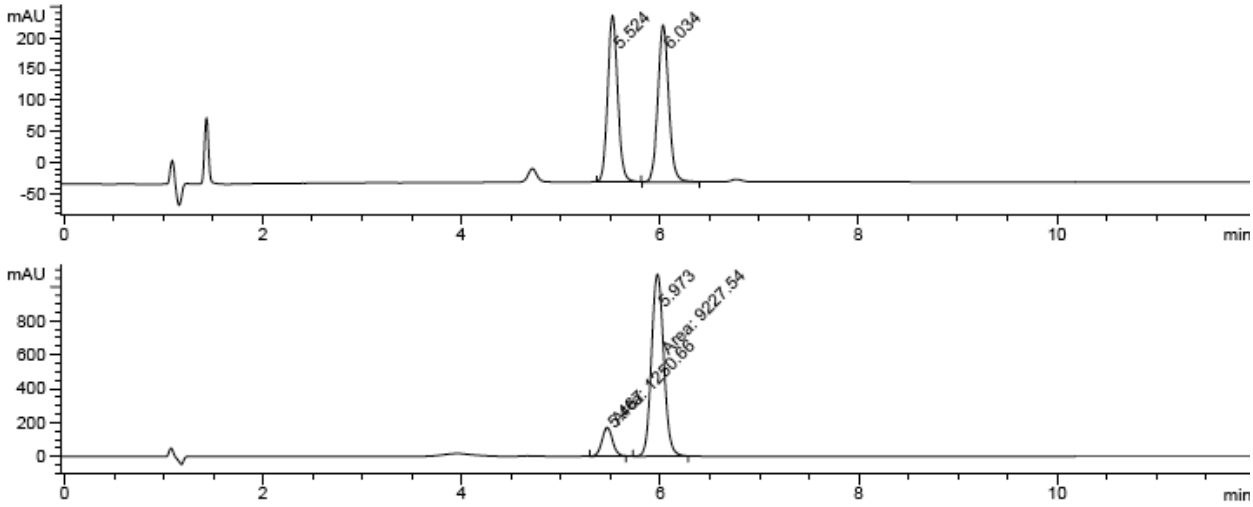


(*S*)-2-benzyl-1,2-diphenylpent-4-en-1-one (2c)

Purified by column chromatography (3% Et_2O in hexanes) to provide a white solid (64.9 mg, 99% yield); 76% ee, $[\alpha]_D^{25}$ +102.5 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.40 (m, 2H), 7.37–7.23 (m, 4H), 7.23–7.13 (m, 2H), 7.12–6.97 (m, 5H), 6.58–6.49 (m, 2H), 5.64 (ddt, J = 17.2, 10.2, 7.1 Hz, 1H), 5.07–4.97 (m, 1H), 4.84 (dd, *J* = 17.0, 1.8 Hz, 1H), 3.41–3.26 (m, 2H), 2.90–2.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 142.2, 137.2, 137.1, 133.2, 131.9, 130.9, 129.9, 129.0, 128.1, 127.6, 127.4, 127.3, 126.3, 119.4, 59.0, 42.1, 37.9; IR (Neat Film, NaCl) 3062, 1674, 1597, 1579, 1496, 1446, 1269, 1216, 1180, 1078, 1026, 912, 768, 722, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{23}O$ $[M+H]^+$: 327.1743, found 327.1748; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 5.47, major = 5.97.



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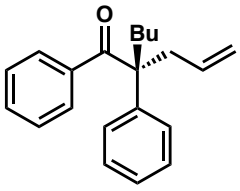
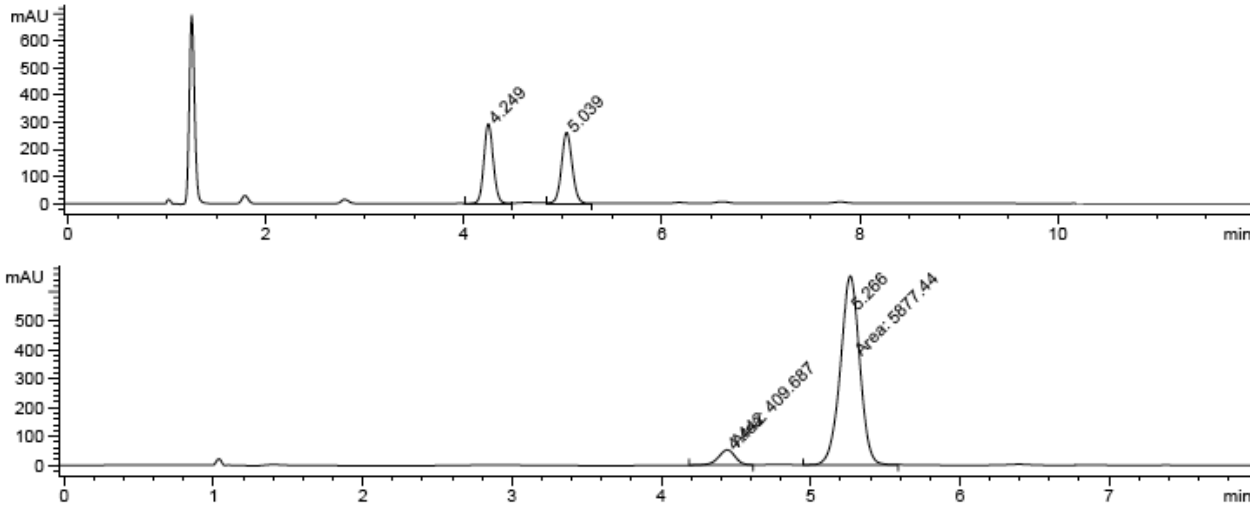
2	5.973	MM	0.1431	9227.54004	1075.06592	88.0642



(*R*)-2-allyl-1,2-diphenylhexan-1-one (2d)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (58.2 mg, 99% yield); 87% ee, $[\alpha]_D^{25}$ –112.6 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.41–7.28 (m, 5H), 7.28–7.20 (m, 3H), 7.16 (dd, *J* = 8.2, 7.0 Hz, 2H), 5.35 (dddd, *J* = 16.8, 10.3, 7.9, 6.7 Hz, 1H), 4.98–4.80 (m, 2H), 2.92–2.67 (m, 2H), 2.06 (dt, *J* = 9.9, 4.9 Hz, 2H), 1.23–0.99 (m, 3H), 0.96–0.78 (m, 1H), 0.71 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 142.8, 137.3, 133.7, 131.7, 129.5, 129.0, 128.0, 127.1, 126.9, 118.3, 57.8, 40.0, 33.8, 25.6, 23.2, 13.9; IR (Neat Film, NaCl) 3064, 2956, 2871, 2861, 1676, 1639, 1597, 1578, 1496, 1466, 1446, 1254, 1240, 1212, 1181, 1144, 1001, 918, 764, 720, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{25}O$ $[M+H]^+$: 293.1900, found 293.1898; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.44, major = 5.27.



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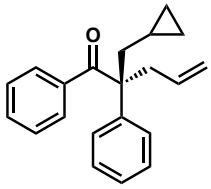
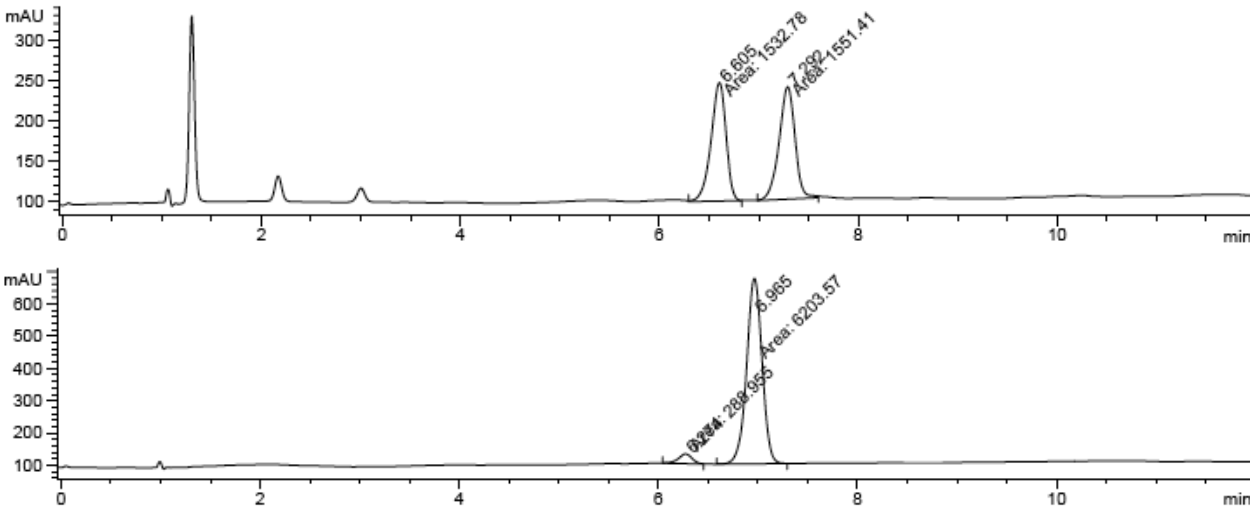
2	5.266	MM	0.1498	5877.43555	653.93146	93.4837



(*S*)-2-(cyclopropylmethyl)-1,2-diphenylpent-4-en-1-one (2e)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (56.5 mg, 97% yield); 91% ee, $[\alpha]_D^{25}$ –57.6 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 7.37–7.33 (m, 3H), 7.30–7.25 (m, 3H), 7.22–7.17 (m, 2H), 5.42 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.04–4.80 (m, 2H), 3.04 (dt, *J* = 7.2, 1.3 Hz, 2H), 2.16 (dd, *J* = 14.1, 6.1 Hz, 1H), 2.03 (dd, *J* = 14.1, 7.0 Hz, 1H), 0.49–0.38 (m, 1H), 0.36–0.22 (m, 2H), -0.09 (dtd, *J* = 8.4, 5.0, 3.7 Hz, 1H), –0.18 – -0.27 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 143.1, 137.1, 133.8, 131.8, 129.8, 129.0, 128.1, 127.1, 126.9, 118.5, 58.8, 40.1, 39.3, 5.9, 4.9, 4.5; IR (Neat Film, NaCl) 3075, 3003, 2936, 1676, 1639, 1597, 1579, 1496, 1446, 1273, 1221, 1181, 1151, 1019, 919, 762, 719, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{23}O$ $[M+H]^+$: 291.1743, found 291.1743; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 6.27, major = 6.97.



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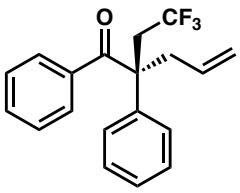
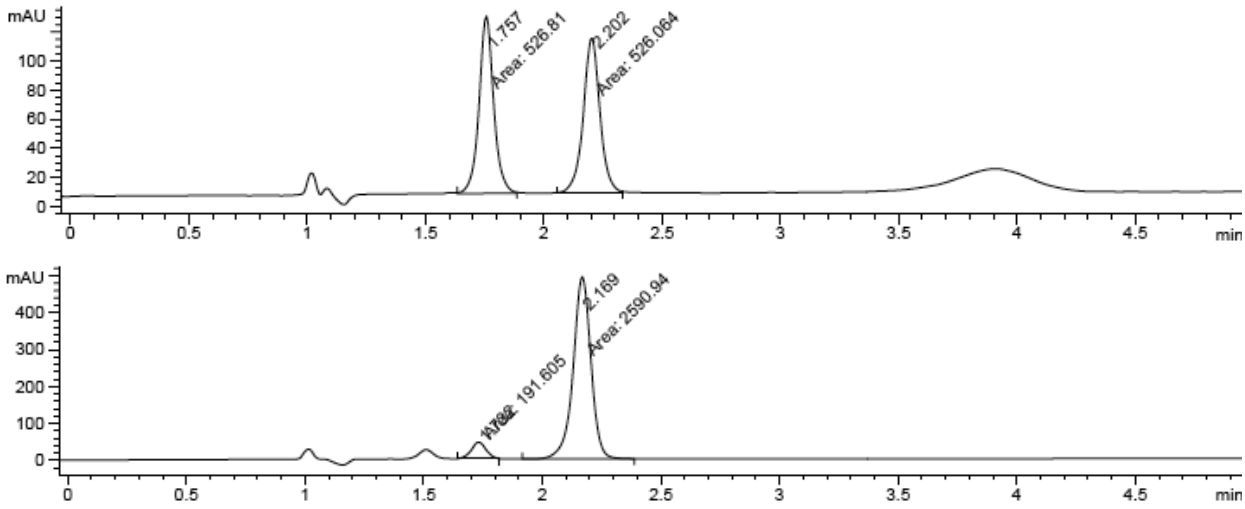
2	6.965	MM	0.1801	6203.56738	573.93951	95.5494



(*S*)-1,2-diphenyl-2-(2,2,2-trifluoroethyl)pent-4-en-1-one (2f)

Purified by preparative TLC (10% Et_2O in hexanes) to provide a colorless oil (57.1 mg, 90% yield); 86% ee, $[a]_D^{25}$ +78.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49–7.31 (m, 8H), 7.24–7.18 (m, 2H), 5.45 (ddt, *J* = 17.3, 10.2, 7.3Hz, 1H), 5.08 (ddt, *J* = 10.2, 1.9, 1.0 Hz, 1H), 4.96 (dq, *J* = 17.0, 1.5 Hz, 1H), 3.27–3.16 (m, 1H), 3.15 – 2.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 139.8, 136.4, 132.1, 131.8, 129.7, 129.4, 128.3, 128.0, 126.8 (q, *J* = 272.9 Hz), 126.7, 120.6, 55.5 (d, *J* = 1.5 Hz), 39.1 (q, *J* = 26.7 Hz), 38.5 (d, *J* = 1.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –58.4 (t, *J* = 11.1 Hz); IR (Neat Film, NaCl) 3067, 3027, 2985, 1678, 1642, 1598, 1579, 1498, 1371, 1272, 1260, 1219, 1202, 1184, 1142, 1118, 1087, 1045, 1025, 982, 926, 765, 727, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{18}F_3O$ $[M+H]^+$: 319.1304, found 319.1293; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 1.73, major = 2.17.



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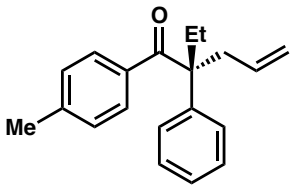
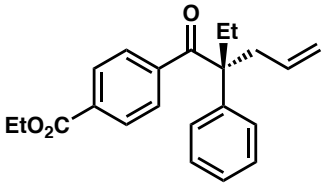
2	2.169	MM	0.0873	2590.93604	494.61243	93.1140



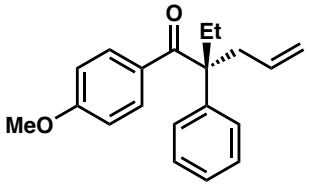
(*R*)-2-ethyl-2-phenyl-1-(*p*-tolyl)pent-4-en-1-one (2g)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (52.1 mg, 94% yield); 90% ee, $[\alpha]_D^{25}$ –99.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.31 (m, 4H), 7.31–7.21 (m, 3H), 7.04–6.97 (m, 2H), 5.38 (dddd, *J* = 16.7, 10.2, 8.3, 6.4 Hz, 1H), 4.99–4.88 (m, 2H), 2.87 (ddt, *J* = 14.2, 8.3, 1.0 Hz, 1H), 2.78 (ddt, *J* = 14.2, 6.3, 1.4 Hz, 1H), 2.28 (s, 3H), 2.20–2.11 (m, 2H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 143.1, 142.4, 134.4, 133.7, 129.7, 128.9, 128.8, 127.0, 127.0, 118.2, 58.1, 39.5, 27.0, 21.6, 8.0; IR (Neat Film, NaCl) 3063, 3026, 2973, 2879, 1673, 1640, 1606, 1496, 1446, 1230, 1182, 1001, 916, 824, 774, 740, 704 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O$ $[M+H]^+$: 279.1743, found 279.1754; SFC Conditions(for cross-metathesis product, see pg S33): 5% IPA, 2.5 mL/min, Chiralcel OB-H column, λ = 210 nm, t_R (min): minor = 4.14, major = 4.95.



ethyl (*R*)-4-(2-ethyl-2-phenylpent-4-enoyl)benzoate (2h)

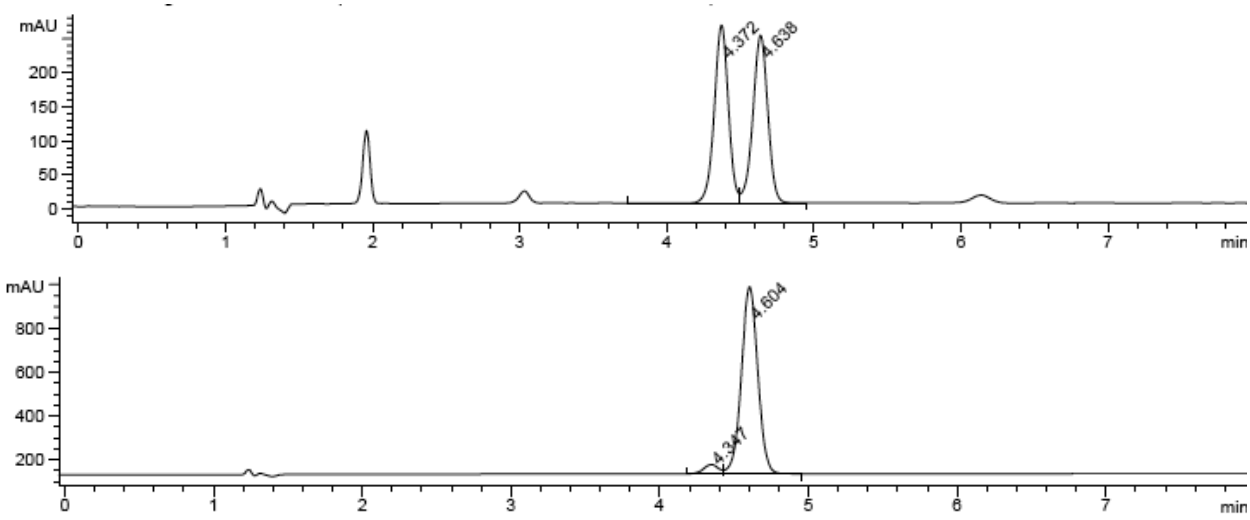
Purified by column chromatography (5% Et_2O in hexanes) to provide a white solid (66.4 mg, 99% yield); 90% ee, $[\alpha]_D^{25}$ –79.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 2H), 7.45–7.34 (m, 4H), 7.33–7.24 (m, 3H), 5.44–5.30 (m, 1H), 5.07–4.83 (m, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.83 (dt, *J* = 7.6, 1.2 Hz, 2H), 2.14 (qq, *J* = 14.4, 7.3, 6.9 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 165.9, 142.1, 140.9, 133.2, 132.9, 129.3, 129.3, 129.1, 127.4, 127.0, 118.5, 61.4, 58.4, 39.0, 26.7, 14.4, 7.9; IR (Neat Film, NaCl) 3076, 2977, 2940, 2879, 1722, 1581, 1649, 1599, 1580, 1570, 1495, 1462, 1446, 1404, 1367, 1312, 1276, 1225, 1180, 1107, 1017, 1001, 918, 833, 788, 767, 727, 703 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798, found 337.1786; SFC Conditions(for cross-metathesis product, see pg S34): 7% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 9.38, major = 10.31.



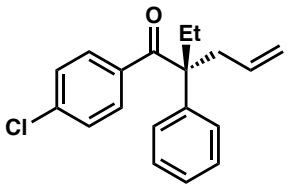
(*R*)-2-ethyl-1-(4-methoxyphenyl)-2-phenylpent-4-en-1-one (2i)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (58.4 mg, 99% yield); 91% ee, $[\alpha]_D^{25}$ –91.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.45 (m, 2H), 7.38–7.31 (m, 2H), 7.26 (tt, *J* = 6.5, 1.1 Hz, 4H), 6.69 (d, *J* = 9.0 Hz, 1H), 5.38 (dddd, *J* = 16.8, 10.3, 8.3, 6.3 Hz, 1H), 5.03–4.85 (m, 2H), 3.76 (s, 3H), 2.87 (ddt, *J* = 14.2, 8.3, 1.0 Hz, 1H), 2.77 (ddt, *J* = 14.2, 6.4, 1.4 Hz, 1H), 2.19–2.12 (m, 2H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 162.3, 143.4, 133.8, 132.0, 129.7, 128.9, 126.9, 118.1, 113.2, 57.9, 55.4, 39.6, 27.2, 8.0; IR (Neat Film, NaCl) 3075, 3004, 2971, 2938, 2839, 1667, 1600, 1574, 1508, 1496, 1459, 1445, 1417, 1307, 1258, 1238, 1174, 1142, 1033, 998, 916, 837, 778, 750, 703 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1688;

SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 4.35, major = 4.60.

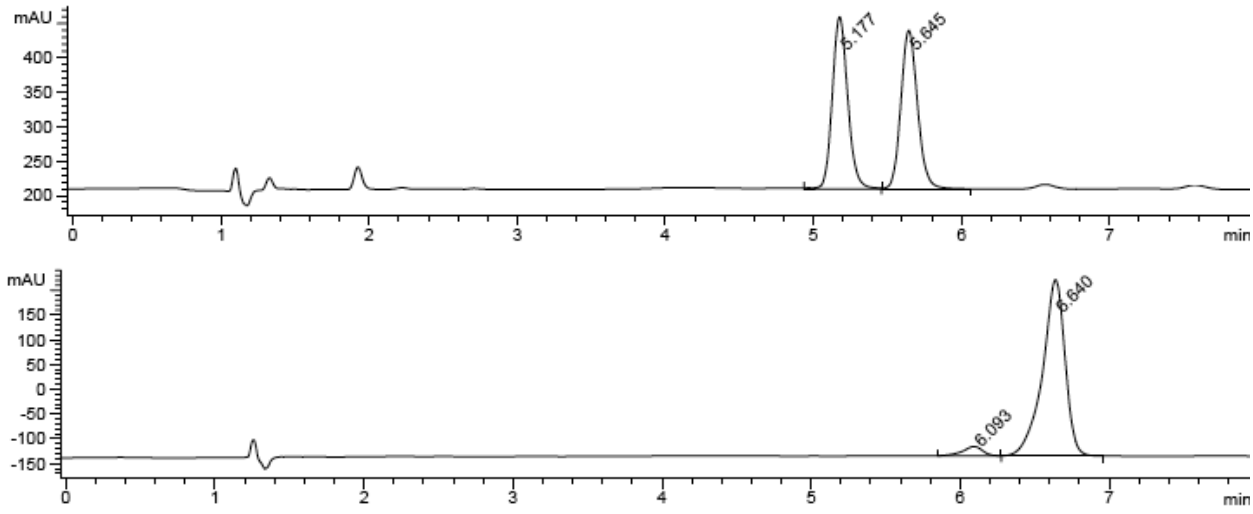


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.347	BV	0.1049	298.80319	43.10856	4.3440
2	4.604	VB	0.1198	6579.75732	854.97278	95.6560

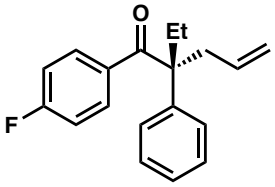


(*R*)-1-(4-chlorophenyl)-2-ethyl-2-phenylpent-4-en-1-one (2j)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (57.1 mg, 96% yield); 91% ee, $[a]_D^{25}$ –91.3 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.31–7.27 (m, 1H), 7.27–7.23 (m, 2H), 7.19–7.15 (m, 2H), 5.36 (dddd, *J* = 16.8, 10.2, 8.2, 6.4 Hz, 1H), 5.00–4.87 (m, 2H), 2.86–2.76 (m, 2H), 2.23–2.04 (m, 2H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 142.5, 138.1, 135.4, 133.3, 131.0, 129.1, 128.4, 127.3, 126.9, 118.5, 58.2, 39.2, 26.9, 8.0; IR (Neat Film, NaCl) 3074, 2973, 2940, 2878, 1677, 1640, 1586, 1486, 1446, 1398, 1225, 1178, 1093, 1001, 917, 827, 775, 744, 703 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}ClO$ $[M+H]^+$: 299.1197, found 299.1201; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 6.09, major = 6.64.

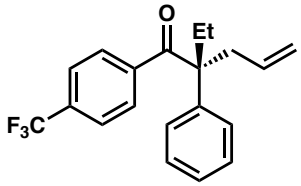


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.093	BV	0.1413	182.94630	19.17632	4.6398
2	6.640	VB	0.1571	3760.03101	356.24255	95.3602



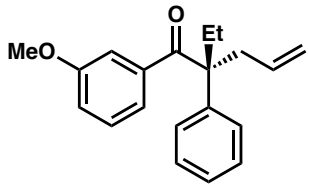
(*R*)-2-ethyl-1-(4-fluorophenyl)-2-phenylpent-4-en-1-one (2k)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (54.1 mg, 96% yield); 91% ee, $[\alpha]_D^{25}$ –111.7 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.43 (m, 2H), 7.40–7.31 (m, 2H), 7.32–7.23 (m, 3H), 6.91–6.82 (m, 2H), 5.37 (dddd, *J* = 16.8, 10.2, 8.2, 6.4 Hz, 1H), 5.00–4.87 (m, 2H), 2.91–2.72 (m, 2H), 2.27–1.97 (m, 2H), 0.69 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz) δ –107.1 (tt, *J* = 8.5, 5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 164.7 (d, *J* = 253.6 Hz), 142.7, 133.4, 133.3 (d, *J* = 3.3 Hz), 132.2 (d, *J* = 8.9 Hz), 129.1, 127.2, 126.9, 118.4, 115.1 (d, *J* = 21.5 Hz), 58.1, 39.3, 27.0, 8.0; IR (Neat Film, NaCl) 3076, 2973, 2940, 1677, 1639, 1598, 1504, 1446, 1231, 1158, 1143, 1000, 917, 841, 777, 747, 704 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}FO$ $[M+H]^+$: 283.1493, found 283.1479; SFC Conditions (on cross-metathesis pdt, see pg S35): 5% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 7.43, major = 8.03.



(*R*)-2-ethyl-2-phenyl-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (2l)

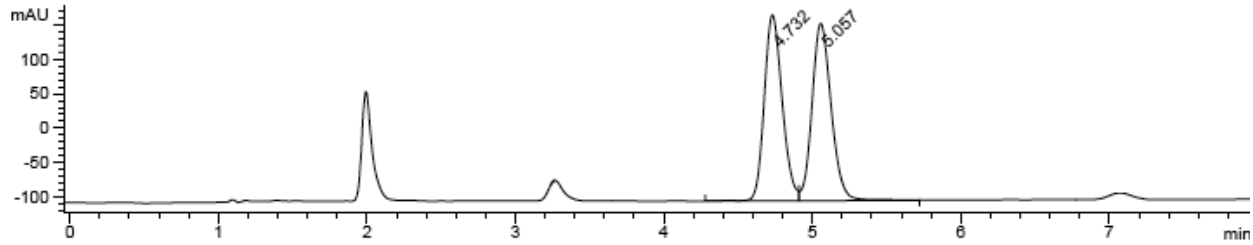
Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (65.5 mg, 99% yield); 90% ee, $[\alpha]_D^{25}$ –95.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 4H), 7.41–7.36 (m, 2H), 7.34–7.29 (m, 1H), 7.29–7.25 (m, 2H), 5.37 (ddt, *J* = 17.0, 10.2, 7.3 Hz, 1H), 5.02 4.87 (m, 2H), 2.83 (dt, *J* = 7.3, 1.2 Hz, 2H), 2.26–2.05 (m, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz) δ –63.2 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 141.9, 140.3, 133.1, 133.1 (q, *J* = 32.6 Hz) 129.7, 129.2, 127.5, 126.9, 125.1 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5) 118.6, 58.4, 39.0, 26.7, 7.9; IR (Neat Film, NaCl) 3078, 2974, 2942, 2880, 1683, 1641, 1599, 1580, 1494, 1461, 1446, 1407, 1326, 1227, 1170, 1131, 1069, 1016, 1001, 918, 849, 834, 781, 754, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}F_3NO$ $[M+NH_4]^+$: 350.1726, found 350.1723; SFC Conditions (on cross-metathesis pdt, see pg S36): 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.47, major = 5.90.

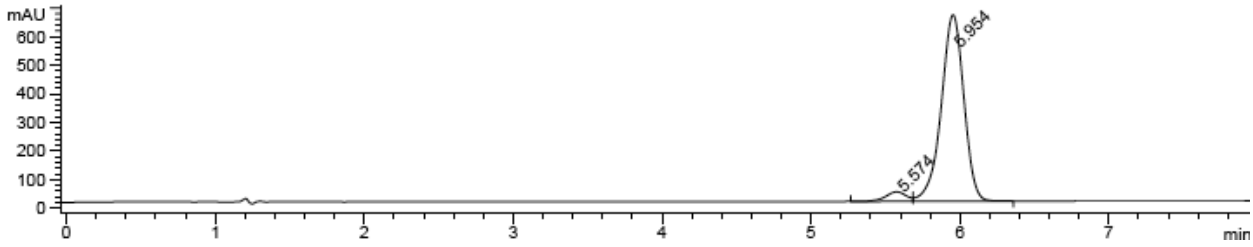


(*R*)-2-ethyl-1-(3-methoxyphenyl)-2-phenylpent-4-en-1-one (2m)

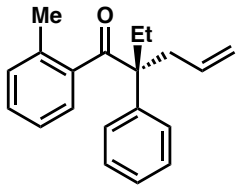
Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (55.9 mg, 95% yield); 91% ee, $[\alpha]_D^{25}$ –89.4 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.34 (m, 2H), 7.31–7.26 (m, 3H), 7.09 (ddd, *J* = 8.2, 7.4, 0.7 Hz, 1H), 7.00–6.96 (m, 2H), 6.90 (ddd, *J* = 8.2, 2.5, 1.2 Hz, 1H), 5.38 (dddd, *J* = 16.8, 10.3, 8.2, 6.4 Hz, 1H), 5.04–4.87 (m, 2H), 3.62 (s, 3H), 2.98–2.74 (m, 2H), 2.16 (q, *J* = 7.5 Hz, 2H), 0.70 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 159.1, 142.8, 138.5, 133.6, 129.0, 129.0, 127.1, 127.0, 122.1, 118.4, 118.3, 113.9, 58.2, 55.3, 39.2, 26.9, 8.0; IR (Neat Film, NaCl) 3074, 2970, 2940, 1677, 1640, 1596,

1580, 1487, 1462, 1446, 1425, 1318, 1288, 1258, 1206, 1180, 1046, 917, 790, 773, 738, 703 cm^{1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1681; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): minor = 5.57, major = 5.95.





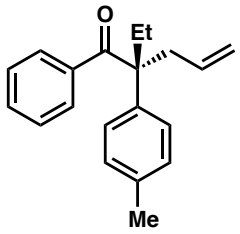
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.574	BV	0.1488	324.44357	33.57056	4.4862
2	5.954	VB	0.1635	6907.67090	652.32867	95.5138



(*R*)-2-ethyl-2-phenyl-1-(*o*-tolyl)pent-4-en-1-one (2n)

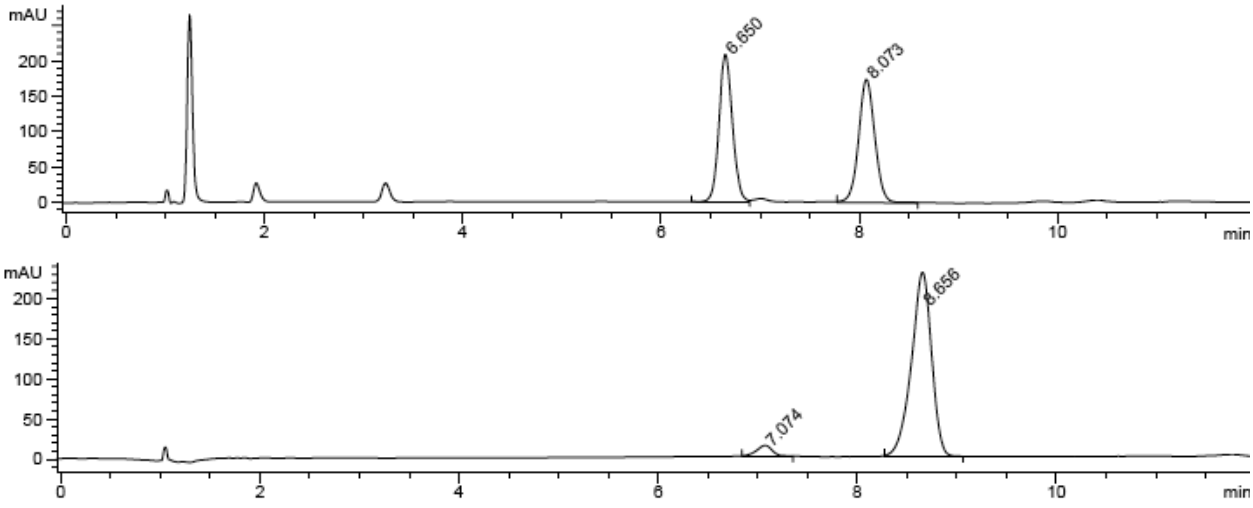
Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (53.0 mg, 95% yield); 73% ee, $[\alpha]_D^{25}$ –62.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.24 (m, 4H), 7.22–7.15 (m, 1H), 7.11–7.04 (m, 2H), 6.74 (dtd, *J* = 8.6, 4.0, 0.7 Hz, 1H), 6.54 (dt, *J* = 7.8, 1.0 Hz, 1H), 5.35 (dddd, *J* = 16.9, 10.3, 7.9, 6.6 Hz, 1H), 4.92–4.75 (m, 2H), 2.75 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 2H), 2.26 (s, 3H), 2.14–1.87 (m, 2H), 0.62 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 141.9, 138.3, 138.1, 133.7, 131.9, 130.0, 128.9, 127.6, 127.1, 127.0, 124.6, 118.2, 58.7, 38.5, 26.7, 21.1, 7.9; IR (Neat Film, NaCl) 3061, 2972, 2939, 2879, 1680, 1640, 1599, 1493, 1456, 1446, 1381, 1287, 1226, 1121, 997, 916, 847, 764, 755, 734, 702, 652 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O$ $[M+H]^+$: 279.1743, found 279.1746; SFC

Conditions (on cross metathesis pdt, see pg S37): 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 5.74, major = 6.49.

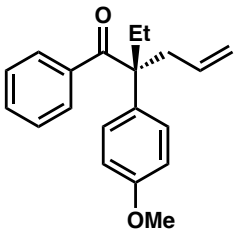


(*R*)-2-ethyl-1-phenyl-2-(*p*-tolyl)pent-4-en-1-one (2o)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (53.5 mg, 96% yield); 91% ee, $[\alpha]_D^{25}$ –107.3 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44–7.41 (m, 2H), 7.37–7.33 (m, 1H), 7.23–7.18 (m, 2H), 7.17 (s, 4H), 5.38 (dddd, *J* = 16.8, 10.2, 8.2, 6.4 Hz, 1H), 5.01–4.84 (m, 2H), 2.92–2.74 (m, 2H), 2.35 (s, 3H), 2.20–2.03 (m, 2H), 0.68 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 139.5, 137.5, 136.7, 133.8, 131.7, 129.7, 129.5, 128.0, 126.8, 118.1, 57.8, 39.2, 26.9, 21.2, 8.0; IR (Neat Film, NaCl) 3069, 2973, 2878, 1676, 1640, 1597, 1578, 1514, 1446, 1228, 1182, 1143, 1020, 1004, 914, 815, 779, 734, 708, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O$ $[M+H]^+$: 279.1743, found 279.1733; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 7.07, major = 8.66.

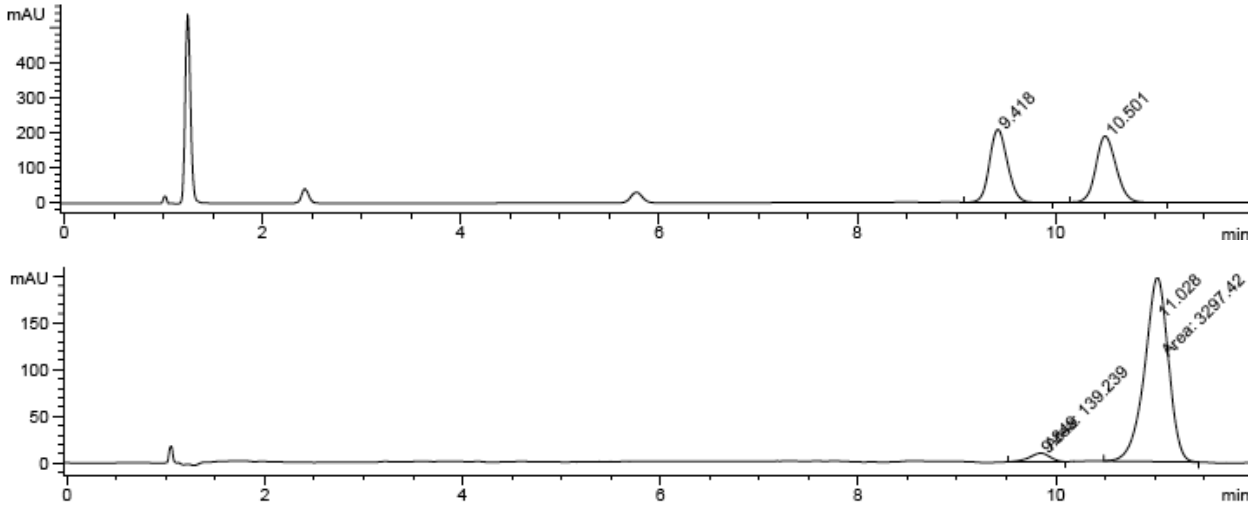


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.074	BB	0.1685	158.56238	13.75147	4.6612
2	8.656	BB	0.2128	3243.18799	229.55760	95.3388

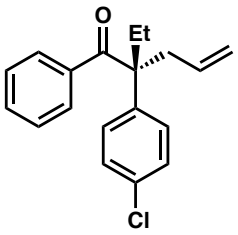


(*R*)-2-ethyl-2-(4-methoxyphenyl)-1-phenylpent-4-en-1-one (2p)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (59.0 mg, 99% yield); 92% ee, $[\alpha]_D^{25}$ –109.6 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.45–7.31 (m, 3H), 7.24–7.16 (m, 4H), 6.94–6.87 (m, 2H), 5.39 (dddd, *J* = 16.9, 10.3, 8.0, 6.6 Hz, 1H), 5.04–4.80 (m, 2H), 3.81 (s, 3H), 2.80 (ddt, *J* = 6.7, 5.7, 1.2 Hz, 2H), 2.26–2.01 (m, 2H), 0.68 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 158.6, 137.5, 134.5, 133.7, 131.6, 129.5, 128.1, 128.0, 118.1, 114.3, 57.4, 55.3, 39.3, 26.9, 8.0; IR (Neat Film, NaCl) 3069, 2970, 2836, 1674, 1639, 1609, 1578, 1513, 1262, 1445, 1295, 1251, 1229, 1182, 1143, 1035, 1004, 915, 827, 781, 741, 709, 693 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1683; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 9.85, major = 11.03

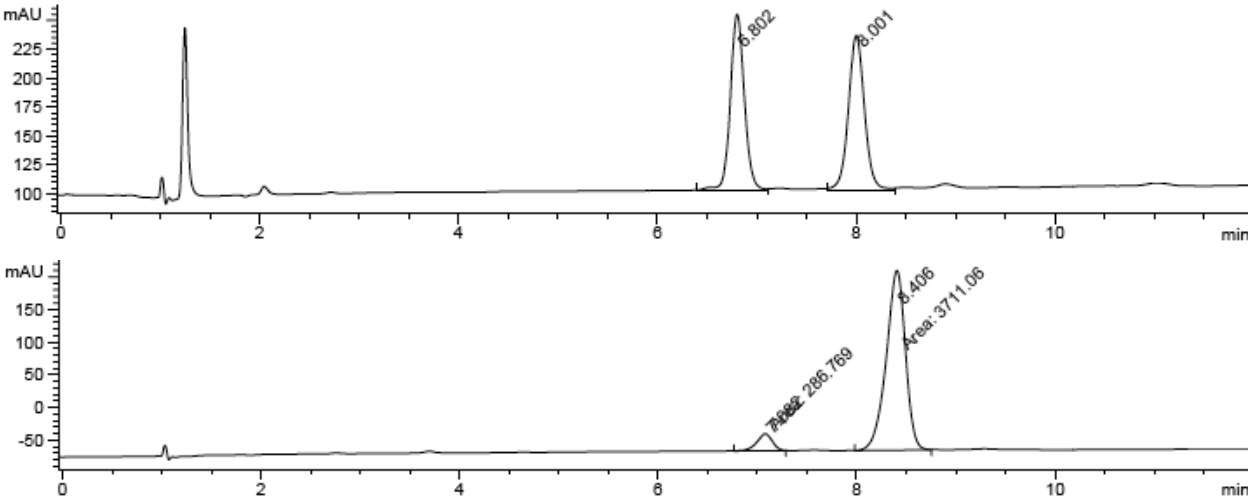


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.849	MM	0.2431	139.23929	9.54773	4.0516
2	11.028	MM	0.2785	3297.41772	197.36160	95.9484

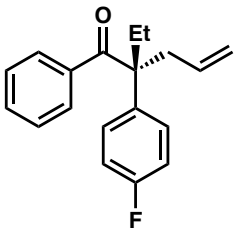


(*R*)-2-(4-chlorophenyl)-2-ethyl-1-phenylpent-4-en-1-one (2q)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (59.1 mg, 99% yield); 86% ee, $[\alpha]_D^{25}$ –92.7 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.44–7.40 (m, 2H), 7.40–7.36 (m, 1H), 7.36–7.32 (m, 2H), 7.25–7.19 (m, 4H), 5.36 (dddd, *J* = 16.8, 10.2, 8.3, 6.4 Hz, 1H), 5.02–4.84 (m, 2H), 2.89–2.67 (m, 2H), 2.13 (q, *J* = 7.4 Hz, 2H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 141.4, 136.9, 133.1, 133.0, 132.0, 129.5, 129.2, 128.3, 128.2, 118.7, 57.8, 39.3, 27.0, 8.0; IR (Neat Film, NaCl) 3071, 2972, 2940, 2879, 1676, 1596, 1492, 1446, 1402, 1227, 1181, 1096, 1014, 1004, 917, 821, 784, 725, 691 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}ClO$ $[M+H]^+$: 299.1197, found 299.1187; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 7.08, major = 8.41.

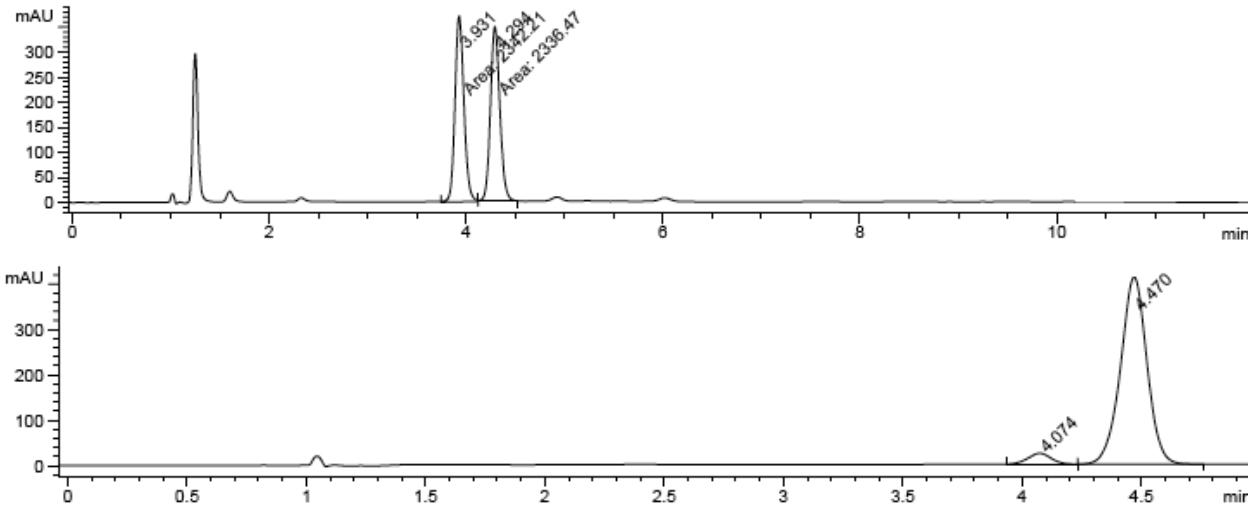


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.082	MM	0.1840	286.76880	25.97683	7.1731
2	8.406	MM	0.2248	3711.05859	275.17242	92.8269



(*R*)-2-ethyl-2-(4-fluorophenyl)-1-phenylpent-4-en-1-one (2r)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (55.3 mg, 98% yield); 90% ee, $[\alpha]_D^{25}$ –104.7 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.43–7.35 (m, 3H), 7.26–7.19 (m, 4H), 7.09–7.03 (m, 2H), 5.36 (dddd, *J* = 16.8, 10.2, 8.2, 6.4 Hz, 1H), 5.05–4.84 (m, 2H), 2.90–2.71 (m, 2H), 2.14 (q, *J* = 7.4 Hz, 2H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz) δ –115.6 (tt, *J* = 8.4, 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 161.9 (d, *J* = 246.2 Hz), 138.5 (d, *J* = 3.4 Hz), 137.1, 133.3, 131.9, 129.5, 128.5 (d, *J* = 7.9 Hz), 128.1, 118.5, 115.9 (d, *J* = 21.2 Hz), 57.7, 39.4, 27.1, 8.0; IR (Neat Film, NaCl) 3073, 2974, 2880, 1675, 1598, 1510, 1446, 1230, 1164, 1004, 917, 829, 816, 782, 737, 707, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}FO$ $[M+H]^+$: 283.1493, found 283.1491; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.07, major = 4.47.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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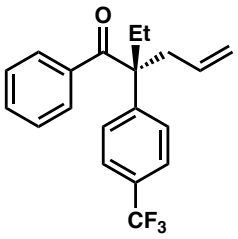
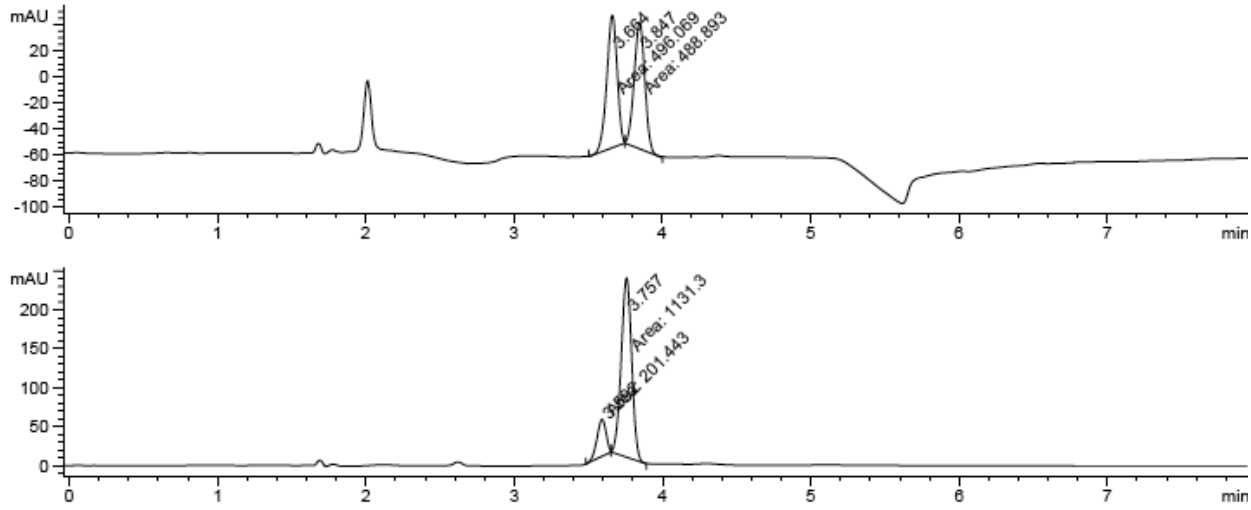
2	4.470	VB	0.1182	3194.52808	413.07336	95.0223

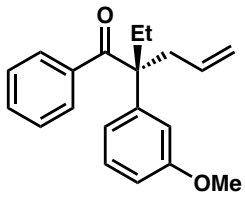


(*R*)-2-ethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (2s)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (65.7 mg, 99% yield); 70% ee, $[\alpha]_D^{25}$ –57.1 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 (m, 2H), 7.45–7.35 (m, 5H), 7.25–7.20 (m, 2H), 5.35 (dddd, *J* = 16.8, 10.2, 8.3, 6.5 Hz, 1H), 5.05–4.85 (m, 2H), 3.01–2.71 (m, 2H), 2.19 (q, *J* = 7.4 Hz, 2H), 0.71 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz) δ –62.5 (s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.2, 147.1 (d, *J* = 1.4 Hz), 136.6, 132.8, 132.2, 129.5, 129.3 (q, *J* = 32.9 Hz), 128.3, 127.3, 125.9 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.1 Hz) 118.9, 58.3, 39.4, 27.1, 8.0; IR (Neat Film, NaCl) 3075, 2975, 2942, 1678, 1641, 1617, 1597, 1579, 1447, 1411, 1328, 1228, 1168, 1127, 1070, 1017, 920, 828, 712, 656 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}F_3O$ $[M+H]^+$: 333.1461, found 333.1455; SFC Conditions: 5% IPA, 3.0 mL/min, Chiralpak AD-H column (2 columns combined), λ = 210 nm, t_R (min): minor = 3.59, major = 3.76.

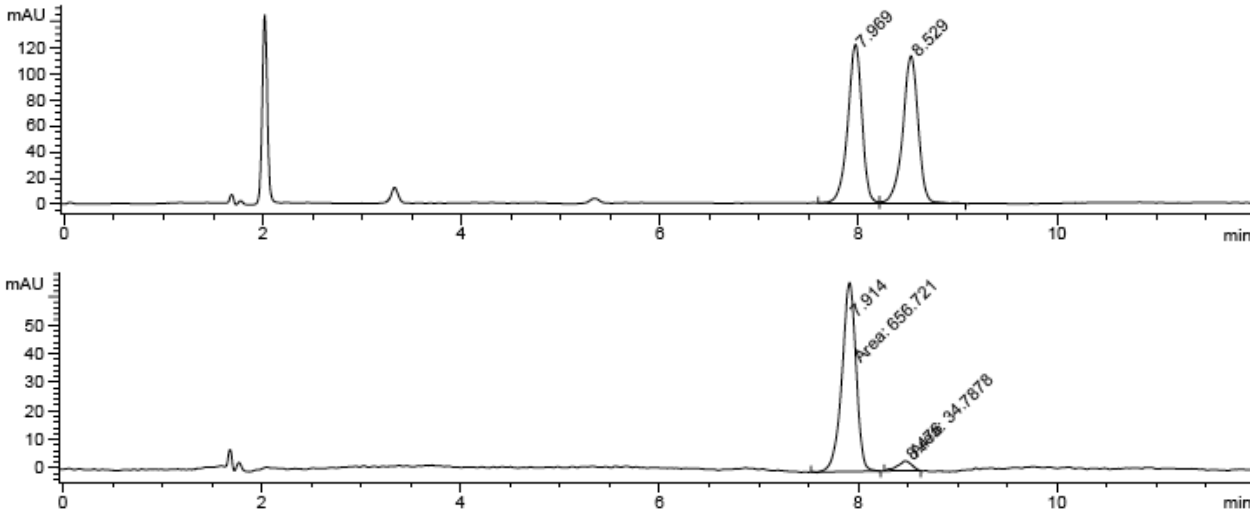


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.592	MM	0.0701	201.44276	47.86584	15.1149
2	3.757	MM	0.0817	1131.30029	230.90933	84.8851

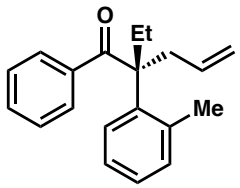


(*R*)-2-ethyl-2-(3-methoxyphenyl)-1-phenylpent-4-en-1-one (2t)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (56.1 mg, 95% yield); 90% ee, $[\alpha]_D^{25}$ –103.0 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.48–7.42 (m, 2H), 7.39–7.33 (m, 1H), 7.31–7.27 (m, 1H), 7.25–7.17 (m, 2H), 6.90–6.79 (m, 3H), 5.38 (dddd, *J* = 16.8, 10.3, 8.0, 6.6 Hz, 1H), 5.02–4.82 (m, 2H), 3.78 (s, 3H), 2.90–2.70 (m, 2H), 2.25–2.04 (m, 2H), 0.68 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 160.1, 144.4, 137.3, 133.6, 131.8, 129.9, 129.4, 128.1, 119.5, 118.2, 113.1, 112.0, 58.1, 55.3, 39.2, 26.9, 8.0; IR (Neat Film, NaCl) 3070, 2971, 2939, 2878, 2835, 1676, 1640, 1598, 1581, 1487, 1462, 1446, 1433, 1292, 1261, 1229, 1168, 1050, 1004, 917, 776, 727, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O_2$ $[M+H]^+$: 295.1693, found 295.1683; SFC Conditions: 5% IPA, 3.0 mL/min, Chiralpak AD-H column (2 columns combined), λ = 210 nm, t_R (min): minor = 7.91, major = 8.48.

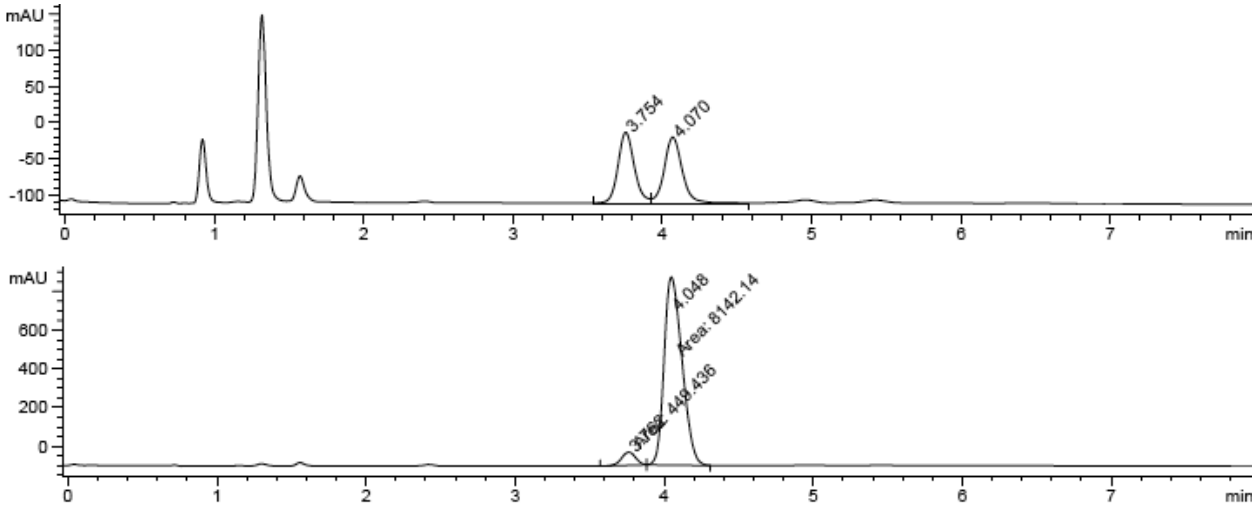


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.914	MM	0.1651	656.72083	66.31249	94.9693
2	8.476	MM	0.1650	34.78777	3.51379	5.0307



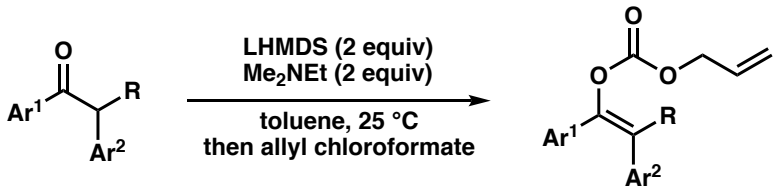
(*R*)-2-ethyl-1-phenyl-2-(*o*-tolyl)pent-4-en-1-one (2u)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (55.9 mg, 99% yield); 90% ee, $[\alpha]_D^{25}$ –100.6 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.63–7.58 (m, 2H), 7.51–7.48 (m, 1H), 7.41–7.35 (m, 1H), 7.33–7.28 (m, 1H), 7.22–7.16 (m, 3H), 7.07–7.02 (m, 1H), 5.34 (ddt, *J* = 17.5, 10.3, 7.4 Hz, 1H), 5.06–4.84 (m, 2H), 2.93–2.86 (m, 2H), 2.28 (dt, *J* = 14.8, 7.4 Hz, 1H), 2.14 (dt, *J* = 13.9, 7.3 Hz, 1H), 2.09 (s, 3H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 141.4, 136.7, 133.9, 132.7, 132.3, 129.1, 128.1, 127.1, 126.6, 126.4, 118.2, 57.9, 37.3, 26.6, 21.1, 8.1; IR (Neat Film, NaCl) 3068, 2975, 2879, 1674, 1639, 1596, 1578, 1487, 1446, 1384, 1225, 1181, 1136, 1059, 1004, 915, 841, 760, 733, 710, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}O$ $[M+H]^+$: 279.1743, found 279.1736; SFC Conditions: 5% IPA, 3.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 3.76, major = 4.05.

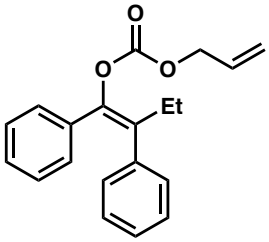


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.762	MM	0.1098	449.43604	68.19579	5.2311
2	4.048	MM	0.1396	8142.14111	972.34613	94.7689

General Procedure for Preparation of Allyl Enol Carbonate Substrates



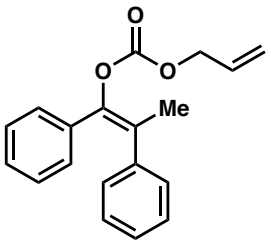
To a flame-dried flask was added LHMDS (335 mg, 2 mmol) followed by toluene (3.0 mL) and N,N-dimethylethylamine (0.213 mL), and the resulting mixture stirred at 25 °C for 5 minutes. A solution of ketone (1 mmol) in toluene (2.0 mL) was then added, and the reaction stirred at 25 °C for an additional 30 minutes. The flask was then submerged in a room temperature water bath, and allyl chloroformate (0.217 mL, 2 mmol) was added neat, and the reaction continued until no starting material remained by TLC (typically less than 30 minutes). The crude reaction mixture was diluted with Et_2O and quenched with water. The layers were separated, and the aqueous layer was extracted with Et_2O twice. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel flash chromatography to afford the desired enol carbonate. The *E/Z* ratio of enol carbonates was determined by ^{1}H NMR and is >95:5 unless stated otherwise.



(*E*)-allyl (1,2-diphenylbut-1-en-1-yl) carbonate (1a)

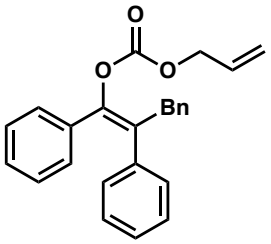
Run on 2.0 mmol scale. Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (586.3 mg, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.17 (m, 3H), 7.14–7.10 (m, 7H), 5.93 (ddt, J = 17.2, 10.5, 5.7 Hz, 1H), 5.40–5.22 (m, 2H), 4.64 (dt, J = 5.7, 1.4 Hz, 2H), 2.58 (q, J = 7.5 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 142.9, 138.9, 135.1, 133.3, 131.3, 129.5, 128.9, 128.2, 127.8, 127.8, 127.0, 119.0, 68.9, 26.0,

12.2; IR (Neat Film, NaCl) 3083, 3057, 2972, 2936, 2875, 1756, 1651, 1600, 1577, 1493, 1445, 1364, 1257, 1220, 1122, 1091, 1075, 1044, 988, 858, 766, 697 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{24}NO_3$ $[M+NH_4]^+$: 326.1751, found 326.1756.



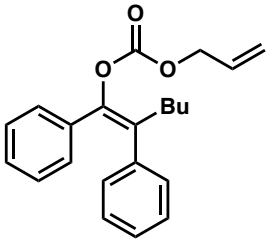
(*E*)-allyl (1,2-diphenylprop-1-en-1-yl) carbonate (1b)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (210.3 mg, 71% yield, 81:17 *E/Z* ratio); ^1H NMR major isomer (300 MHz, $CDCl_3$) δ 7.46–7.34 (m, 1H), 7.23–7.17 (m, 2H), 7.17–7.09 (m, 7H), 5.94 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.44–5.23 (m, 2H), 4.65 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR major isomer (100 MHz, $CDCl_3$) δ 153.1, 143.6, 140.4, 135.1, 131.4, 129.1, 128.6, 128.4, 128.0, 127.4, 127.3, 127.2, 119.2, 69.0, 19.2; IR (Neat Film, NaCl) 3082, 3057, 3024, 2992, 2947, 1759, 1493, 1444, 1381, 1364, 1229, 1122, 1030, 966, 777, 765, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}NO_3$ $[M+NH_4]^+$: 312.1594, found 312.1583.



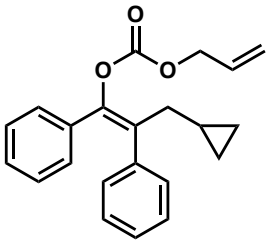
(*E*)-allyl (1,2,3-triphenylprop-1-en-1-yl) carbonate (1c)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (305.8 mg, 83% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.25–7.09 (m, 13H), 7.04–6.98 (m, 2H), 5.90 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.46–5.15 (m, 2H), 4.61 (dt, *J* = 5.8, 1.4 Hz, 2H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 144.4, 138.8, 138.6, 134.9, 131.3, 130.3, 129.7, 129.1, 128.4, 128.2, 128.1, 128.0, 127.2, 126.2, 119.3, 69.1, 39.1; IR (Neat Film, NaCl) 3027, 1760, 1601, 1495, 1444, 1364, 1227, 1118, 1030, 971, 776, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{26}NO_3$ $[M+NH_4]^+$: 388.1907, found 388.1898.



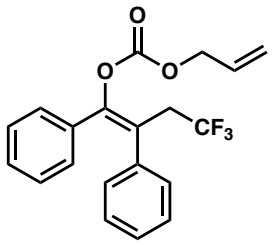
(*E*)-allyl (1,2-diphenylhex-1-en-1-yl) carbonate (1d)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (301.3 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.16 (m, 3H), 7.15–7.09 (m, 7H), 5.92 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.40–5.23 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.59–2.47 (m, 2H), 1.38–1.28 (m, 4H), 0.98–0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 143.4, 139.2, 135.2, 132.2, 131.4, 129.5, 129.0, 128.3, 127.9, 127.8, 127.1, 119.1, 69.0, 32.6, 29.6, 22.7, 14.0; IR (Neat Film, NaCl) 3082, 3057, 3024, 2957, 2930, 2861, 1760, 1493, 1444, 1380, 1364, 1292, 1240, 1227, 1207, 1122, 1000, 964, 772, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{28}NO_3$ $[M+NH_4]^+$: 354.2064, found 354.2047.



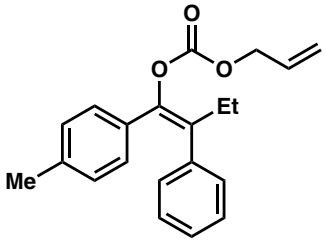
(*E*)-allyl (3-cyclopropyl-1,2-diphenylprop-1-en-1-yl) carbonate (1e)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (299.4 mg, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.09 (m, 10H), 5.92 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.39–5.22 (m, 2H), 4.63 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.47 (d, *J* = 6.9 Hz, 2H), 0.78–0.67 (m, 1H), 0.41–0.31 (m, 2H), 0.13 – -0.03 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 143.3, 139.6, 135.1, 131.9, 131.4, 129.6, 129.0, 128.2, 127.9, 127.0, 119.2, 69.0, 37.5, 9.6, 4.7; IR (Neat Film, NaCl) 3079, 3003, 2950, 1760, 1491, 1444, 1364, 1292, 1247, 1222, 1127, 1056, 1018, 972, 936, 826, 771, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{26}NO_3$ $[M+NH_4]^+$: 352.1907, found 352.1903.



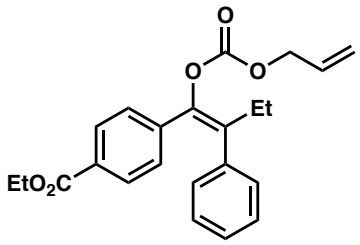
(*E*)-allyl (4,4,4-trifluoro-1,2-diphenylbut-1-en-1-yl) carbonate (1f)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (299.0 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 3H), 7.19–7.11 (m, 7H), 5.90 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.44–5.21 (m, 2H), 4.62 (dt, *J* = 5.8, 1.4 Hz, 2H), 3.40 (q, *J* = 10.3 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.1 (t, *J* = 10.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 148.5, 137.7, 134.1, 131.0, 129.6, 129.1, 128.8, 128.6, 128.1, 127.8, 125.7 (q, *J* = 278.5 Hz), 120.6 (q, *J* = 2.6 Hz), 119.6, 69.4, 37.3 (q, *J* = 30.0 Hz); IR (Neat Film, NaCl) 3085, 3059, 3026, 1764, 1651, 1494, 1446, 1258, 1224, 1136, 1110, 1056, 972, 956, 940, 777, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{21}F_3NO_3$ $[M+NH_4]^+$: 380.1468, found 380.1455.



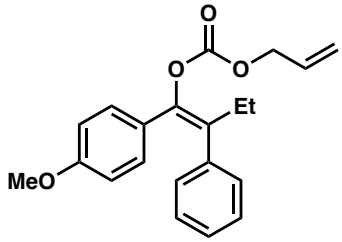
(*E*)-allyl (2-phenyl-1-(*p*-tolyl)but-1-en-1-yl) carbonate (1g)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (291.6 mg, 90% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.17 (m, 3H), 7.16–7.10 (m, 2H), 7.04–6.98 (m, 2H), 6.96–6.89 (m, 2H), 5.93 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.42–5.23 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 143.1, 139.2, 137.7, 132.7, 132.2, 131.5, 129.6, 128.8, 128.7, 128.3, 127.0, 119.2, 69.0, 26.1, 21.4, 12.3; IR (Neat Film, NaCl) 3082, 3055, 3026, 2972, 2875, 1760, 1650, 1511, 1491, 1443, 1308, 1291, 1258, 1226, 1184, 1122, 1089, 1045, 988, 946, 929, 862, 826, 784, 768, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_3$ $[M+NH_4]^+$: 340.1907, found 340.1896.



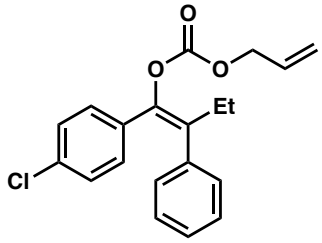
ethyl (*E*)-4-(1-(((allyloxy)carbonyl)oxy)-2-phenylbut-1-en-1-yl)benzoate (1h)

Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (291.2 mg, 77% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.74 (m, 2H), 7.25–7.15 (m, 5H), 7.14–7.05 (m, 2H), 5.92 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.48–5.20 (m, 2H), 4.64 (dt, *J* = 5.8, 1.4 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 153.2, 142.0, 139.7, 138.5, 135.4, 131.2, 129.5, 129.4, 129.2, 128.8, 128.5, 127.5, 119.4, 69.2, 61.0, 26.3, 14.4, 12.2; IR (Neat Film, NaCl) 3081, 3057, 2978, 2937, 2876, 1761, 1718, 1609, 1444, 1407, 1366, 1276, 1224, 1180, 1125, 1108, 1045, 1022, 990, 947, 860, 769, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{28}NO_5$ $[M+NH_4]^+$: 398.1962, found 398.1952.



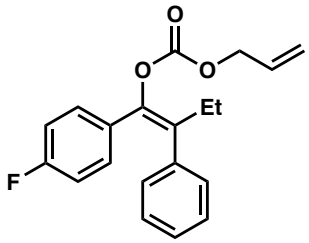
(*E*)-allyl (1-(4-methoxyphenyl)-2-phenylbut-1-en-1-yl) carbonate (1i)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (254.3 mg, 75% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.16 (m, 3H), 7.16–7.10 (m, 2H), 7.09–7.01 (m, 2H), 6.72–6.58 (m, 2H), 5.94 (ddt, *J* = 17.3, 10.5, 5.7 Hz, 1H), 5.49–5.20 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.72 (s, 3H), 2.55 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 153.4, 142.9, 139.2, 132.1, 131.5, 130.3, 129.6, 128.3, 127.6, 127.0, 119.2, 113.3, 69.0, 55.2, 26.0, 12.3; IR (Neat Film, NaCl) 2970, 2936, 1760, 1651, 1609, 1576, 1511, 1462, 1443, 1364, 1294, 1252, 1226, 1176, 1123, 1044, 1014, 988, 946, 862, 836, 784, 767, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_4$ $[M+NH_4]^+$: 356.1856, found 356.1845.



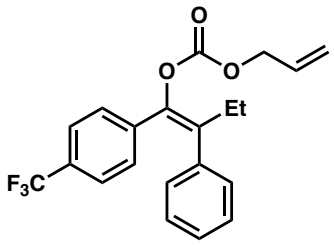
(*E*)-allyl (1-(4-chlorophenyl)-2-phenylbut-1-en-1-yl) carbonate (1j)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (310.0 mg, 90% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.14–7.00 (m, 6H), 6.04–5.82 (m, 1H), 5.45–5.24 (m, 2H), 4.64 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 141.9, 138.6, 134.2, 133.7, 133.6, 131.3, 130.3, 129.5, 128.5, 128.2, 127.4, 119.4, 69.2, 26.1, 12.2; IR (Neat Film, NaCl) 3081, 3057, 2972, 2936, 2875, 1760, 1649, 1594, 1490, 1443, 1364, 1292, 1275, 1257, 1224, 1180, 1123, 1092, 1045, 1015, 989, 946, 930, 860, 835, 768, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}ClNO_3$ $[M+NH_4]^+$: 360.1361, found 360.1372.



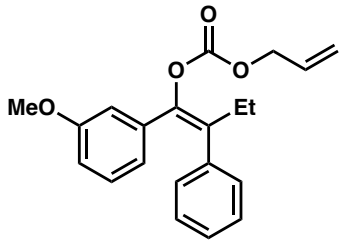
(*E*)-allyl (1-(4-fluorophenyl)-2-phenylbut-1-en-1-yl) carbonate (1k)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil which solidifies in a freezer (303.7 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.18 (m, 3H), 7.10 (ddq, *J* = 5.3, 4.6, 2.9 Hz, 4H), 6.85–6.74 (m, 2H), 5.93 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.50–5.14 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz) δ –113.3 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 248.1 Hz), 153.3, 142.1, 138.8, 133.6, 131.3, 131.3, 130.9 (d, *J* = 8.3 Hz), 129.5, 128.4, 127.2, 119.3, 115.0 (d, *J* = 21.6 Hz), 69.1, 26.0, 12.2; IR (Neat Film, NaCl) 3081, 3058, 3024, 2973, 2937, 2876, 1760, 1651, 1605, 1444, 1364, 1292, 1259, 1225, 1159, 1122, 1096, 1045, 989, 946, 930, 864, 842, 809, 785, 767, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}FNO_3$ $[M+NH_4]^+$: 344.1656, found 344.1659.



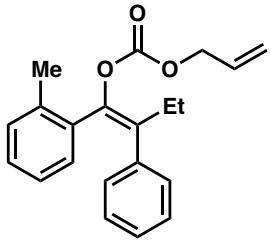
(*E*)-allyl (2-phenyl-1-(4-(trifluoromethyl)phenyl)but-1-en-1-yl) carbonate (1l)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil which solidifies in a freezer (354.0 mg, 94% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.33 (m, 2H), 7.25–7.19 (m, 5H), 7.15–7.06 (m, 2H), 5.93 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.48–5.15 (m, 2H), 4.65 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz) δ –62.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 141.6, 138.8, 138.3, 135.6, 131.2, 129.6 (q, *J* = 32.4 Hz), 129.4, 129.1, 128.6, 127.6, 124.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.6 Hz), 119.5, 69.3, 26.3, 12.1; IR (Neat Film, NaCl) 3083, 2059, 3025, 2975, 2938, 2878, 1760, 1651, 1618, 1577, 1492, 1444, 1408, 1365, 1327, 1292, 1260, 1226, 1168, 1127, 1068, 1046, 1018, 989, 946, 931, 847, 782, 769, 702, 613 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{23}F_3NO_3$ $[M+NH_4]^+$: 394.1625, found 394.1608



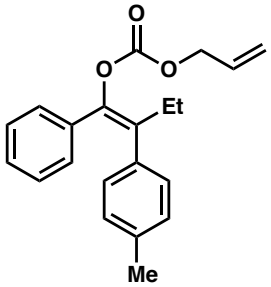
(*E*)-allyl (1-(3-methoxyphenyl)-2-phenylbut-1-en-1-yl) carbonate (1m)

Purified by column chromatography (10% Et_2O in hexanes) to provide a colorless oil (320.2 mg, 95% yield); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.18 (m, 3H), 7.17–7.11 (m, 2H), 7.04 (ddd, *J* = 8.2, 7.7, 0.4 Hz, 1H), 6.78–6.59 (m, 3H), 5.94 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.47–5.20 (m, 2H), 4.65 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.51 (s, 3H), 2.56 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 153.4, 142.8, 139.1, 136.3, 133.5, 131.4, 129.5, 128.9, 128.4, 127.2, 121.1, 119.2, 114.5, 114.0, 69.1, 55.1, 26.2, 12.2; IR (Neat Film, NaCl) 2970, 2937, 1760, 1600, 1580, 1486, 1464, 1454, 1444, 1428, 1364, 1323, 1288, 1234, 1204, 1178, 1120, 1043, 994, 948, 892, 863, 784, 769, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_4$ $[M+NH_4]^+$: 356.1856, found 356.1844



(*E*)-allyl (2-phenyl-1-(*o*-tolyl)but-1-en-1-yl) carbonate (1n)

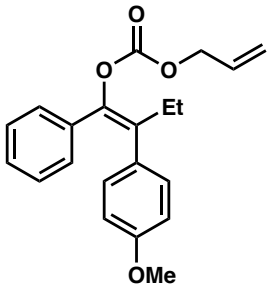
Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (299.3 mg, 93% yield, 80:20 *E/Z* ratio); ^{1}H NMR major isomer (300 MHz, $CDCl_3$) δ 7.41–7.28 (m, 1H), 7.21 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16–7.06 (m, 4H), 7.04 – 6.97 (m, 3H), 5.91 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.41 – 5.22 (m, 2H), 4.60 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.62 (q, *J* = 7.5 Hz, 2H), 2.18 (s, 3H), 1.02 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR major isomer (100 MHz, $CDCl_3$) δ 153.1, 142.9, 138.5, 137.5, 134.4, 134.3, 131.5, 131.5, 130.0, 129.0, 128.5, 127.9, 126.9, 125.2, 119.2, 68.9, 25.1, 20.0, 12.9; IR (Neat Film, NaCl) 3022, 2971, 1758, 1493, 1457, 1443, 1380, 1364, 1292, 1258, 1225, 1131, 1044, 988, 946, 862, 769, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_3$ $[M+NH_4]^+$: 340.1907, found 340.1892.



(*E*)-allyl (1-phenyl-2-(*p*-tolyl)but-1-en-1-yl) carbonate (1o)

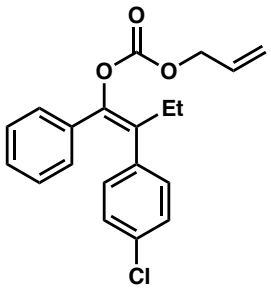
Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (295.7 mg, 92% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.11 (m, 5H), 7.03–6.99 (m, 4H), 5.93 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.41–5.24 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 2.30 (s, 3H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 142.7, 136.8, 135.9, 135.3, 133.3, 131.4, 129.4, 129.1, 129.0, 127.9, 127.8, 119.2, 69.0, 26.1, 21.3, 12.3; IR (Neat Film, NaCl) 3024, 2971, 2935, 2874, 1760, 1512, 1292, 1445, 1364, 1291, 1258, 1224,

1122, 1044, 988, 946, 928, 818, 778, 697 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{23}O_3$ $[M+H]^+$: 323.1642, found 323.1630.



(*E*)-allyl (2-(4-methoxyphenyl)-1-phenylbut-1-en-1-yl) carbonate (1p)

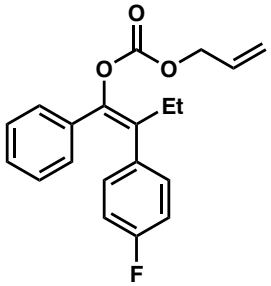
Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (295.0 mg, 87% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.16–7.11 (m, 5H), 7.07–7.00 (m, 2H), 6.78–6.71 (m, 2H), 5.93 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.40–5.23 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.77 (s, 3H), 2.55 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 153.4, 142.6, 135.4, 132.9, 131.4, 131.1, 130.7, 129.0, 127.9, 127.7, 119.2, 113.8, 69.0, 55.3, 26.1, 12.3; IR (Neat Film, NaCl) 2970, 1758, 1650, 1608, 1574, 1511, 1493, 1462, 1444, 1364, 1289, 1245, 1223, 1177, 1122, 1044, 987, 831, 778, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591, found 339.1574.



(*E*)-allyl (2-(4-chlorophenyl)-1-phenylbut-1-en-1-yl) carbonate (1q)

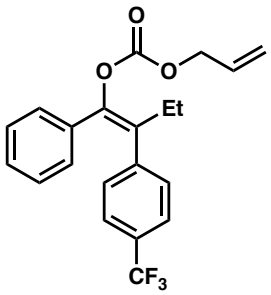
Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil which solidifies in a freezer (315.0 mg, 92% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.20–7.10 (m, 7H), 7.07–7.02 (m, 2H), 5.92 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.46–5.19 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 143.5, 137.5, 134.8, 133.0, 132.2, 131.3, 131.0, 129.1, 128.6, 128.1, 128.1, 119.3, 69.1,

25.9, 12.2; IR (Neat Film, NaCl) 2973, 2936, 1760, 1490, 1445, 1364, 1292, 1256, 1224, 1123, 1090, 1043, 988, 947, 928, 861, 828, 774, 697 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}ClO_3$ $[M+H]^+$: 343.1095, found 343.1087.



(*E*)-allyl (2-(4-fluorophenyl)-1-phenylbut-1-en-1-yl) carbonate (1r)

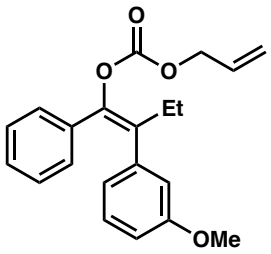
Purified by column chromatography (6% Et_2O in hexanes) to provide a colorless oil (305.7 mg, 94% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.16–7.10 (m, 5H), 7.10–7.05 (m, 2H), 6.93–6.85 (m, 2H), 5.92 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.46–5.16 (m, 2H), 4.64 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.56 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –115.1 (tt, *J* = 8.8, 5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, *J* = 246.2 Hz), 153.3, 143.3, 135.0, 134.8 (d, *J* = 3.4 Hz), 132.4, 131.4, 131.2 (d, *J* = 7.9 Hz), 129.0, 128.0, 119.3, 115.4 (d, *J* = 21.4 Hz), 69.1, 26.0, 12.2; IR (Neat Film, NaCl) 2973, 2936, 1759, 1602, 1508, 1445, 1364, 1292, 1259, 1222, 1158, 1122, 1043, 988, 945, 835, 767, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}FO_3$ $[M+H]^+$: 327.1391, found 327.1396.



(*E*)-allyl (1-phenyl-2-(4-(trifluoromethyl)phenyl)but-1-en-1-yl) carbonate (1s)

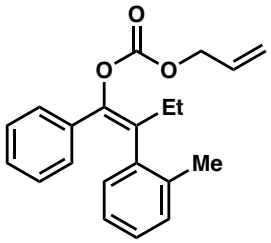
Purified by column chromatography (8% Et_2O in hexanes) to provide a white solid (359.9 mg, 96% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49–7.44 (m, 2H), 7.25–7.22 (m, 2H), 7.19–7.08 (m, 5H), 5.93 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.49–5.22 (m, 2H), 4.65 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.60 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.5 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 144.0, 143.0 (d, *J* = 1.6 Hz), 134.6, 132.2, 131.3, 130.0, 129.2

(q, J = 32.2 Hz), 129.1, 128.4, 128.1, 125.3 (q, J = 3.8 Hz), 124.2 (q, J = 272.1 Hz), 119.4, 69.2, 25.9, 12.2; IR (Neat Film, NaCl) 2975, 2939, 1760, 1616, 1446, 1406, 1365, 1326, 1260, 1225, 1166, 1125, 1109, 1067, 1044, 988, 947, 930, 839, 779, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{23}F_3NO_3$ $[M+NH_4]^+$: 394.1625, found 394.1612.



(*E*)-allyl (2-(3-methoxyphenyl)-1-phenylbut-1-en-1-yl) carbonate (1t)

Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (288.3 mg, 85% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 7.18–7.05 (m, 6H), 6.77–6.62 (m, 3H), 5.93 (ddt, J = 17.2, 10.5, 5.7 Hz, 1H), 5.43–5.21 (m, 2H), 4.64 (dt, J = 5.7, 1.4 Hz, 2H), 3.66 (s, 3H), 2.56 (q, J = 7.5 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 153.3, 143.0, 140.3, 135.2, 133.3, 131.4, 129.3, 128.9, 127.9, 122.1, 119.2, 115.0, 113.0, 69.1, 55.2, 26.0, 12.3; IR (Neat Film, NaCl) 2970, 1759, 1598, 1577, 1486, 1463, 1446, 1427, 1260, 1225, 1180, 1120, 1048, 988, 780, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_4$ $[M+NH_4]^+$: 356.1856, found 356.1845.

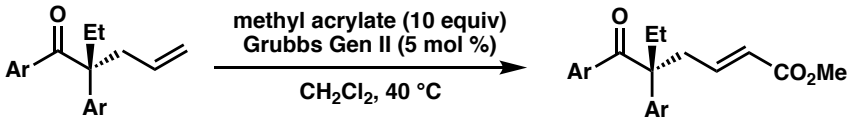


(*E*)-allyl (1-phenyl-2-(*o*-tolyl)but-1-en-1-yl) carbonate (1u)

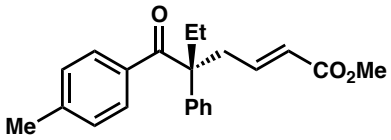
Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (225.3 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–7.04 (m, 9H), 5.96 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.47–5.19 (m, 2H), 4.68 (dq, J = 5.7, 1.2 Hz, 2H), 2.67–2.41 (m, 2H), 2.13 (d, J = 0.6 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 142.7, 138.1, 136.2, 135.2, 132.3, 131.4, 130.3, 129.7, 127.8, 127.8, 127.4, 125.8, 119.1, 69.0, 26.2, 19.6, 11.6; IR (Neat

Film, NaCl) 2970, 1758, 1494, 1444, 1363, 1259, 1222, 1132, 1088, 1044, 987, 918, 858, 762, 730, 694 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_3$ $[M+NH_4]^+$: 340.1907, found 340.1912.

Derivatization of Alkylation Products

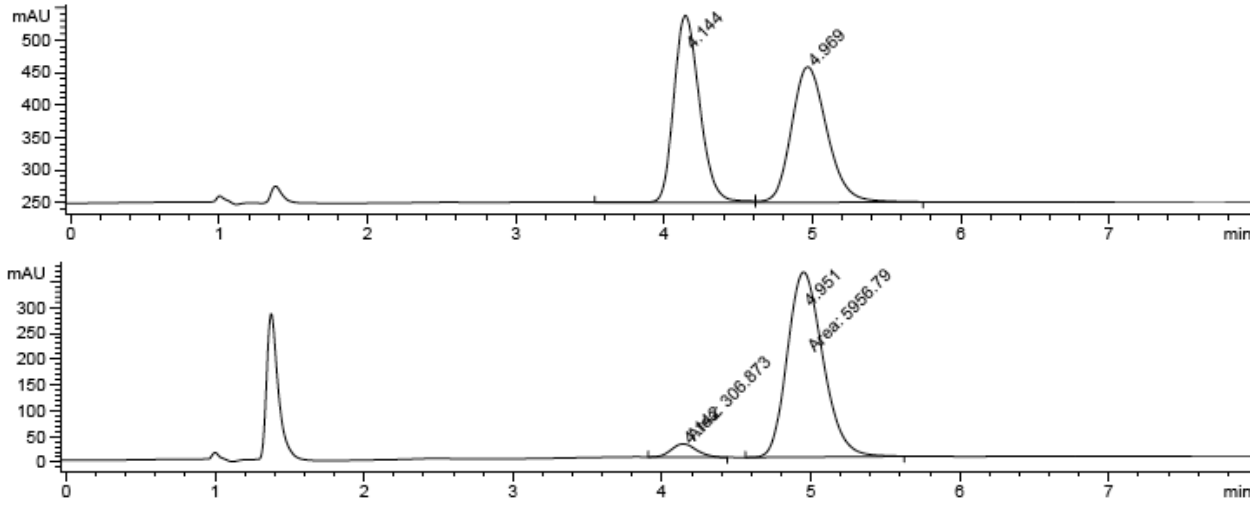


To an oven dried vial was added the alpha-quaternary ketone (0.1 mmol) followed by CH_2Cl_2 (1.0 mL) and methyl acrylate (1.0 mmol, 90 μL). The resulting solution was stirred for five minutes at ambient temperature then treated with a solution of Grubb's second generation catalyst (4.2 mg) in 500 μL CH_2Cl_2. The reaction was then heated to 40 °C and stirred for five hours. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography to obtain the desired product.



methyl (*R*,*E*)-5-(4-methylbenzoyl)-5-phenylhept-2-enoate (SI1)

Purified by column chromatography (4% Et_2O in hexanes) to provide a white solid (25.4 mg, 76% yield; 90% ee, $[\alpha]_D^{25}$ –117.37 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.32 (m, 4H), 7.32–7.24 (m, 3H), 7.04–6.99 (m, 2H), 6.56 (ddd, *J* = 15.5, 9.0, 6.4 Hz, 1H), 5.71 (ddd, *J* = 15.5, 1.7, 1.1 Hz, 1H), 3.67 (s, 3H), 2.99 (ddd, *J* = 14.5, 9.1, 1.2 Hz, 1H), 2.86 (ddt, *J* = 14.6, 6.4, 1.3 Hz, 1H), 2.29 (s, 3H), 2.27–2.12 (m, 2H), 0.72 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 166.6, 145.1, 142.7, 142.3, 133.9, 129.7, 129.2, 128.9, 127.4, 126.8, 124.0, 58.2, 51.6, 38.8, 26.9, 21.6, 8.2; IR (Neat Film, NaCl) 2970, 2949, 1724, 1672, 1606, 1495, 1446, 1435, 1335, 1270, 1199, 1183, 1167, 1140, 1036, 1000, 969, 854, 821, 773, 740, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798, found 337.1785; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel OB-H column, λ = 210 nm, t_R (min): minor = 4.14, major = 4.95.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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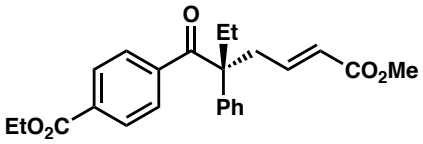
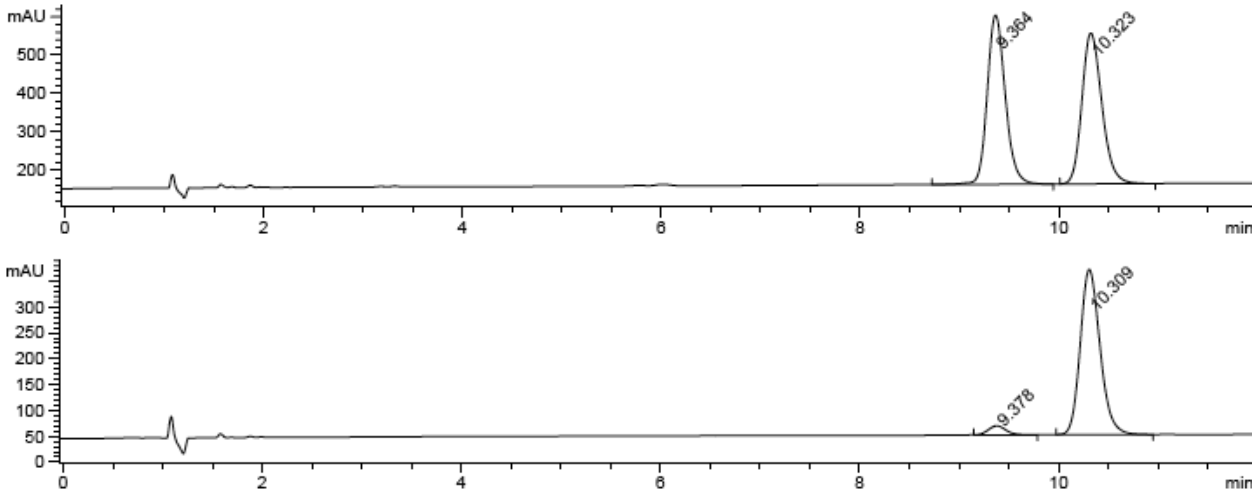
2	4.951	MM	0.2771	5956.78760	358.28424	95.1007

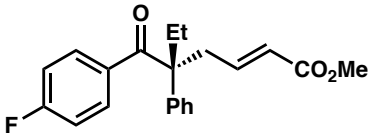


ethyl (*R*,*E*)-4-(2-ethyl-6-methoxy-6-oxo-2-phenylhex-4-enoyl)benzoate (6)

Purified by column chromatography (7% Et_2O in hexanes) to provide a white solid (34.8 mg, 88% yield; 90%, $[\alpha]_D^{25}$ –113.62 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.85 (m, 2H), 7.45–7.36 (m, 4H), 7.35–7.27 (m, 3H), 6.54 (ddd, *J* = 15.5, 8.9, 6.5 Hz, 1H), 5.71 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.67 (s, 3H), 3.02–2.82 (m, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 166.5, 165.8, 144.4, 141.3, 140.3, 133.2, 129.4, 129.4, 129.3, 127.8, 126.8, 124.2, 61.4, 58.5, 51.6, 38.4, 26.5, 14.4, 8.2; IR (Neat Film, NaCl) 2974, 1723, 1681, 1657, 1495, 1446, 1436, 1337, 1312, 1276, 1228, 1199, 1170, 1106, 1020, 1001, 867, 839, 768, 729, 703 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{27}O_5$ $[M+H]^+$: 395.1853, found 395.1870; SFC Conditions: 7% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 9.38, major = 10.31.

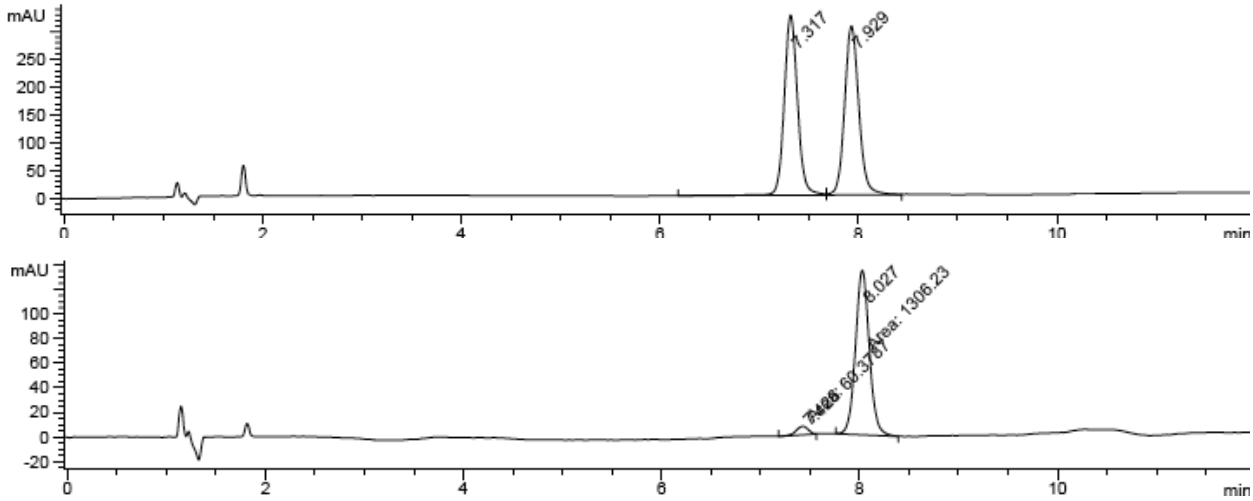


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.378	BB	0.1959	228.93370	18.06382	4.9015
2	10.309	BB	0.2142	4441.78662	319.39063	95.0985

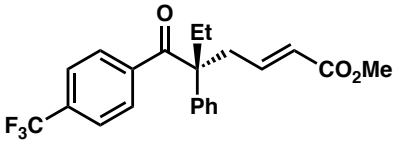


methyl (*R*,*E*)-5-(4-fluorobenzoyl)-5-phenylhept-2-enoate (SI2)

Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (28.4 mg, 83% yield; 91% ee, $[\alpha]_D^{25}$ –136.18 (*c* 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50–7.43 (m, 2H), 7.42–7.29 (m, 3H), 7.27–7.20 (m, 2H), 6.94–6.83 (m, 2H), 6.54 (ddd, *J* = 15.5, 9.1, 6.5 Hz, 1H), 5.71 (ddd, *J* = 15.6, 1.7, 1.2 Hz, 1H), 3.67 (s, 3H), 3.08–2.80 (m, 2H), 2.18 (q, *J* = 7.4 Hz, 2H), 0.72 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –106.5 (tt, *J* = 8.4, 5.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 166.6, 164.8 (d, *J* = 254.4 Hz), 144.7, 141.9, 132.8 (d, *J* = 3.2 Hz), 132.2 (d, *J* = 9.0 Hz), 129.4, 127.7, 126.7, 124.2, 115.3 (d, *J* = 21.6 Hz), 58.3, 51.6, 38.7, 26.9, 8.2; IR (Neat Film, NaCl) 2970, 2950, 1724, 1676, 1656, 1598, 1504, 1435, 1336, 1271, 1232, 1199, 1158, 1001, 848, 748, 703 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}FO_3$ $[M+H]^+$: 341.1548, found 348.1534; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 7.43, major = 8.03.

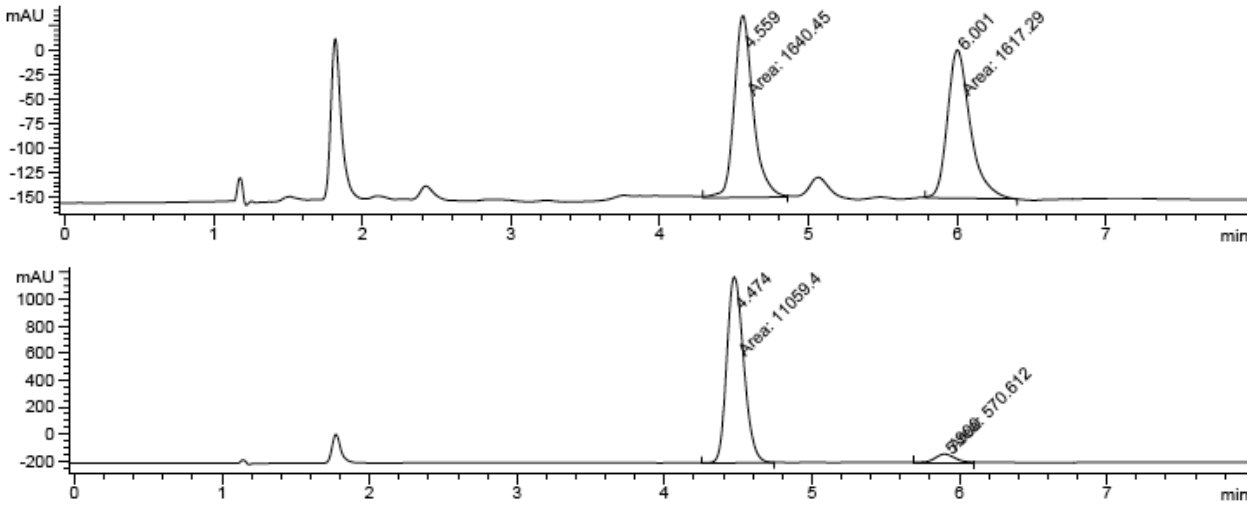


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.426	MM	0.1427	60.37870	7.05324	4.4181
2	8.027	MM	0.1626	1306.22778	133.85184	95.5819

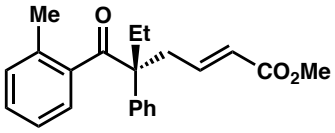


methyl (*R*,*E*)-5-phenyl-5-(4-(trifluoromethyl)benzoyl)hept-2-enoate (SI3)

Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (32.2 mg, 82% yield) containing 6% dimethyl fumarate as an impurity; 90% ee, $[\alpha]_D^{25}$ –116.94 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 4H), 7.43–7.37 (m, 2H), 7.36–7.31 (m, 1H), 7.29–7.26 (m, 2H), 6.54 (ddd, *J* = 15.5, 9.0, 6.4 Hz, 1H), 5.78–5.66 (m, 1H), 3.67 (s, 3H), 3.04–2.81 (m, 2H), 2.27–2.10 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.3 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 166.5, 144.3, 141.2, 139.7, 133.3 (q, *J* = 32.7 Hz), 129.7, 129.5, 127.9, 126.8, 125.3 (q, *J* = 3.7 Hz), 124.3, 123.6 (d, *J* = 272.8 Hz), 58.5, 51.6, 38.4, 26.5, 8.2; IR (Neat Film, NaCl) 2972, 2952, 1725, 1682, 1657, 1446, 1407, 1326, 1272, 1227, 1199, 1169, 1131, 1068, 1001, 858, 755, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{25}F_3NO_3$ $[M+NH]^+$: 408.1781, found 408.1771; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 4.47, minor = 5.90.

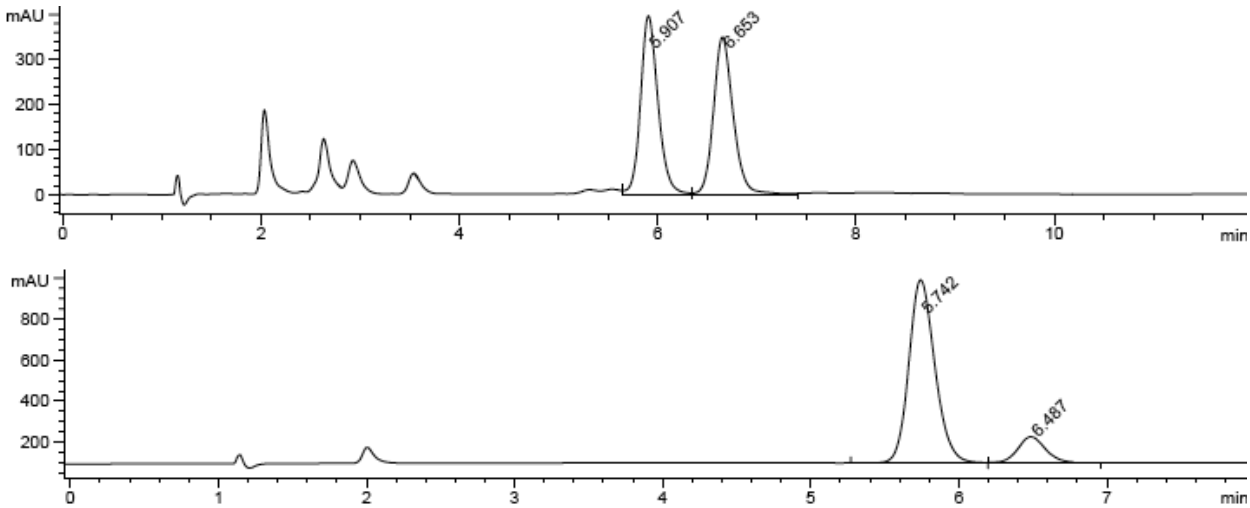


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.474	MM	0.1334	1.10594e4	1381.80981	95.0936
2	5.900	MM	0.1528	570.61169	62.23502	4.9064

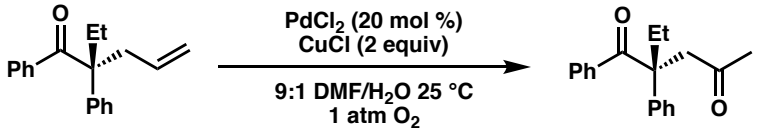


methyl (*R*,*E*)-5-(2-methylbenzoyl)-5-phenylhept-2-enoate (SI4)

Purified by column chromatography (7% Et_2O in hexanes) to provide a colorless oil (25.8 mg, 77% yield); 73% ee, $[\alpha]_D^{25}$ –66.93 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 7.20 (dd, *J* = 4.1, 1.0 Hz, 2H), 6.90–6.81 (m, 1H), 6.65–6.55 (m, 2H), 5.72 (dt, *J* = 15.6, 1.4 Hz, 1H), 3.68 (s, 3H), 3.07–2.88 (m, 2H), 2.37 (s, 3H), 2.13 (q, *J* = 7.4 Hz, 2H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 166.6, 144.9, 141.2, 138.2, 137.7, 132.1, 130.3, 129.2, 127.6, 127.5, 126.8, 124.8, 124.0, 58.8, 51.6, 37.7, 26.7, 21.1, 8.1; IR (Neat Film, NaCl) 3059, 3022, 2970, 2950, 1725, 1681, 1656, 1494, 1446, 1436, 1337, 1269, 1229, 1197, 1170, 1036, 995, 763, 734, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{25}O_3$ $[M+H]^+$: 337.1798, found 337.1813; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 5.74, minor = 6.49.



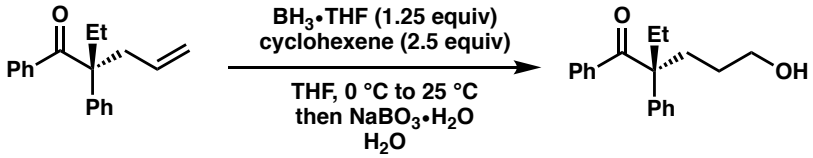
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.742	BV	0.1888	1.09209e4	892.03528	86.7234
2	6.487	VB	0.2009	1671.90112	127.57262	13.2766



(*R*)-2-ethyl-1,2-diphenylpentane-1,4-dione (3)

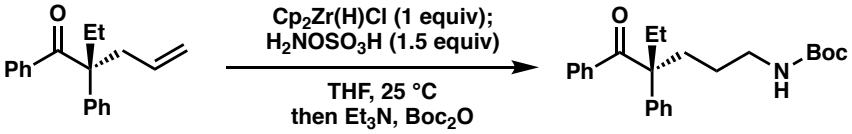
To a 20 mL vial containing alpha quaternary ketone **2a** (0.2 mmol, 52.8 mg) dissolved in 5 mL of 9:1 DMF/H_2O was added $PdCl_2$ (0.04 mmol, 7.1 mg) and CuCl (0.4 mmol, 39.6 mg), and the vial sealed with a Teflon-lined septum cap. The vial was then quickly evacuated and backfilled three times with a balloon of O_2, and then stirred at 25 °C under a balloon of O_2 for 16 h. The crude reaction was then diluted with EtOAc, followed by water and brine. The layers were separated, and the aqueous layer extracted with EtOAc twice. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel flash chromatography (20% Et_2O in hexanes) to afford the desired product as a white, waxy solid in a 14:1 ketone/aldehyde ratio (47.4 mg, 85% yield); $[\alpha]_D^{25}$ –87.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR of ketone (500 MHz, $CDCl_3$) δ 7.43–7.27 (m, 8H), 7.23–7.16 (m, 2H), 3.32 (d, *J* = 16.2 Hz, 1H), 3.18 (d, *J* = 16.2 Hz, 1H), 2.59–2.46 (m, 1H), 2.28–2.17 (m, 1H), 1.82 (s, 3H), 0.72 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR of ketone (100 MHz, $CDCl_3$) δ 207.3, 202.7, 141.4, 137.5, 131.5, 129.2, 129.2, 128.0, 127.5, 126.9, 57.0, 47.5, 31.8, 27.2, 8.7; IR (Neat Film, NaCl) 3059, 2971, 2940, 2880, 1716, 1682, 1598, 1579, 1495, 1462, 1446, 1415, 1361, 1260, 1229, 1214, 1180, 1033,

1003, 986, 913, 783, 764, 716, 703, 646 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1536, found 281.1534.



(*R*)-2-ethyl-5-hydroxy-1,2-diphenylpentan-1-one (4)

To a one dram vial was added a 1 M solution of BH_3•THF (0.25 mmol, 250 μL) and the vial cooled to 0 °C. Cyclohexene (0.5 mmol, 51 μL) was then added neat, dropwise and the mixture stirred at 0 °C for 1 h. A solution of alpha quaternary ketone **2a** (0.2 mmol, 52.8 mg) in 1.0 mL THF was then added, and the reaction was allowed to warm to room temperature and stirred for 4 h. Water (500 μL) was then added to the vial followed by $NaBO_3$•$4H_2O$ (1 mmol, 153.9 mg) and the resulting mixture stirred vigorously for 18 h. The crude reaction was diluted with Et_2O and water, and the layers separated. The aqueous layer was extracted with Et_2O twice, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by preparative TLC (30% acetone in hexanes) to afford the desired product as a colorless oil (42.2 mg, 75% yield); $[\alpha]_D^{25}$ –11.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.32 (m, 5H), 7.31–7.26 (m, 3H), 7.22–7.15 (m, 2H), 3.52 (td, *J* = 6.6, 2.4 Hz, 2H), 2.22–2.09 (m, 4H), 1.32–1.23 (m, 2H), 0.69 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 142.9, 137.2, 131.8, 129.4, 129.0, 128.1, 127.1, 127.0, 63.4, 58.1, 30.5, 27.1, 27.0, 8.1; IR (Neat Film, NaCl) 3336 (br) ,3059, 2965, 2878, 1673, 1597, 1578, 1495, 1446, 1383, 1229, 1180, 1060, 1004, 913, 761, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{23}O_2$ $[M+H]^+$: 283.1693, found 283.1688.

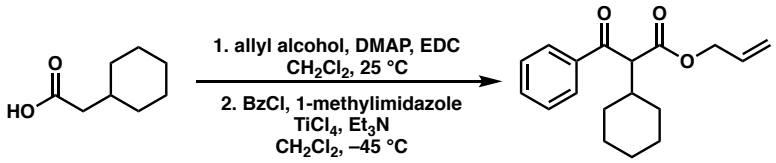


***tert*-butyl (*R*)-(4-benzoyl-4-phenylhexyl)carbamate (5)**

In a nitrogen-filled glovebox, ketone **2a** (0.1 mmol, 26.4 mg) was added to a one dram vial followed by THF (1 mL). $Cp_2Zr(H)Cl$ was then added (0.1 mmol, 25.7 mg) and the resulting suspension stirred at room temperature for 30 minutes, at which point the reaction became a

homogeneous yellow solution. Hydroxylamine-*O*-sulfonic acid was then added (0.15 mmol, 17.0 mg) and the vial removed from the glovebox and stirred at room temperature for 1 hr. Et_3N (0.3 mmol, 42 μL) was then added followed by Boc_2O (0.3 mmol, 69 μL) and the reaction continued for 2 hr and then filtered through a plug of silica. The crude product was purified via preparative TLC (12% Et_2O in hexanes) to afford the desired product at a viscous colorless oil (83% yield, 31.5 mg): $[\alpha]_D^{25}$ 24.5 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.46–7.36 (m, 5H), 7.33 (td, *J* = 6.7, 1.1 Hz, 3H), 7.29–7.19 (m, 2H), 4.41 (s, 1H), 3.21–2.96 (m, 2H), 2.16 (dq, *J* = 42.9, 9.0, 8.2 Hz, 4H), 1.46 (s, 9H), 1.22 (ddd, *J* = 10.1, 6.6, 2.9 Hz, 1H), 0.73 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 155.9, 142.8, 137.2, 131.8, 129.4, 129.0, 128.1, 127.1, 127.0, 79.1, 58.1, 41.0, 31.4, 28.5, 26.9, 24.1, 8.1; IR (Neat Film, NaCl) 3377 (br), 2972, 1701, 1676, 1597, 1578, 1516, 1446, 1391, 1365, 1270, 1248, 1173, 761, 732, 703; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{32}NO_3$ $[M+H]^+$: 382.2377, found 382.2375.

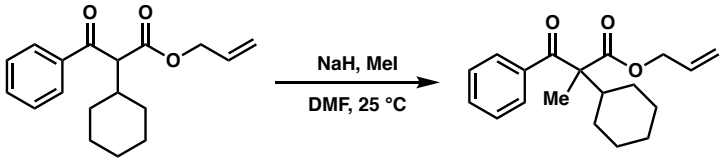
Preliminary Investigation of Fully Alkyl Quaternary Stereocenters



allyl 2-cyclohexyl-3-oxo-3-phenylpropanoate (SI5)

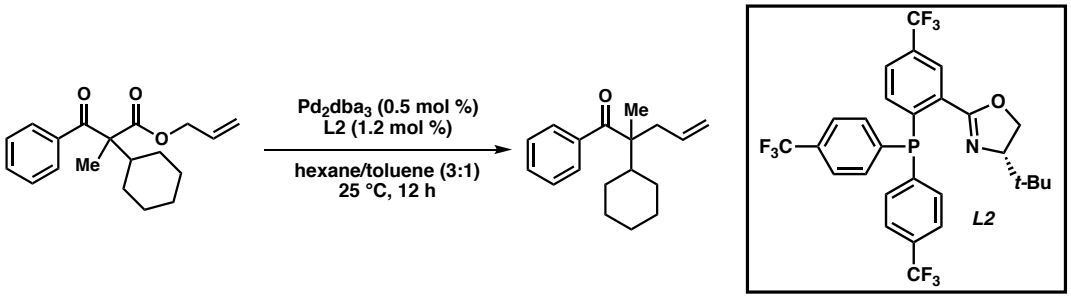
To a flame-dried flask containing cyclohexaneacetic acid (10 mmol, 1.4220 g), DMAP (1 mmol, 122 mg), and EDC-HCl (11 mmol, 2.1087 g) was added CH_2Cl_2 (30 mL) and the resulting mixture stirred for 10 minutes at 25 °C. Allyl alcohol (10 mmol, 680 μL) was then added and the reaction continued at 25 °C for 1 h, then diluted with water and extracted with CH_2Cl_2. The combined organic layers were washed with brine, then dried with Na_2SO_4. The crude product was filtered through a plug of silica and concentrated to a colorless oil (1.5733 g, 86% crude yield) which was then transferred to a flame-dried flask containing benzoyl chloride (8.61 mmol, 1.0 mL) dissolved in 40 mL CH_2Cl_2. The reaction was cooled to –45 °C and 1-methylimidazole (10.34 mmol, 824 μL) was added followed by sequential slow addition of $TiCl_4$ (30.15 mmol, 3.31 mL) over 20 minutes and Et_3N (34.5 mmol, 4.8 mL) over 1 h. The resulting mixture was stirred for 1 h at –45 °C then slowly quenched with water. The aqueous layer was extracted with Et_2O and the combined organic layers washed with water then brine, and dried over Na_2SO_4. The crude product was purified by silica gel flash chromatography (10% Et_2O in hexanes) to

afford the desired product as a colorless oil (2.2396 g, 78% yield over two steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04–7.96 (m, 2H), 7.62–7.53 (m, 1H), 7.51–7.40 (m, 2H), 5.81 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.28–5.07 (m, 2H), 4.57 (ddt, *J* = 5.8, 2.9, 1.4 Hz, 2H), 4.21 (d, *J* = 9.6 Hz, 1H), 2.46–2.33 (m, 1H), 1.76 (tdt, *J* = 8.6, 3.5, 1.7 Hz, 1H), 1.66 (dddd, *J* = 12.9, 8.6, 4.2, 2.5 Hz, 4H), 1.40–1.24 (m, 2H), 1.23–1.06 (m, 2H), 1.01–0.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 168.7, 137.2, 133.6, 131.7, 128.8, 128.6, 118.6, 65.8, 60.5, 38.5, 31.5, 31.0, 26.2, 26.1, 26.0; IR (Neat Film, NaCl) 2927, 2852, 1736, 1686, 1596, 1448, 1284, 1239, 1199, 1154, 1128, 990, 928, 670 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{26}NO_3$ $[M+NH_4]^+$: 304.1907, found 304.1913.



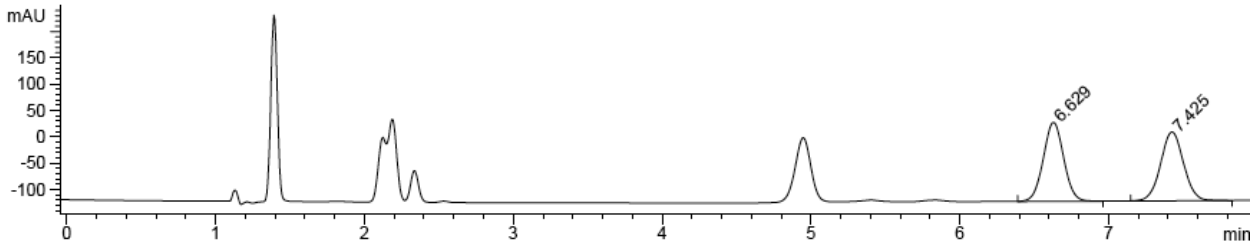
allyl 2-cyclohexyl-2-methyl-3-oxo-3-phenylpropanoate (SI6)

To a flame-dried flask containing NaH (2 mmol, 80 mg, 60% dispersion in mineral oil) and DMF (6 mL) was added beta-ketoester **SI5** (1 mmol, 286.4 mg) neat at 25 °C, and the resulting suspension stirred for 30 minutes. MeI (2 mmol, 125 μL) was then added and the reaction continued at 25 °C for 1.5 h. The reaction was quenched with saturated NH_4Cl and diluted with water and Et_2O. The aqueous layer was extracted with Et_2O and the combined organic layers dried over $MgSO_4$. The crude product was purified by silica gel flash chromatography (6% Et_2O in hexanes) to afford the desired product as a colorless oil (240.6 mg, 80%) containing some of the undesired *O*-alkylated product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82–7.73 (m, 2H), 7.56–7.44 (m, 1H), 7.43–7.34 (m, 2H), 5.68 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.22–5.08 (m, 2H), 4.60–4.49 (m, 2H), 2.46 (tt, *J* = 11.9, 2.7 Hz, 1H), 1.87–1.64 (m, 5H), 1.64–1.49 (m, 1H), 1.46 (s, 3H), 1.42–1.22 (m, 2H), 1.19–0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 173.3, 136.7, 132.3, 131.3, 128.4, 128.3, 118.7, 65.6, 60.9, 42.6, 28.6, 28.0, 26.8, 26.8, 26.5, 17.7; IR (Neat Film, NaCl) 2930, 2853, 2360, 1734, 1684, 1447, 1258, 1233, 1186, 1153, 1121, 1081, 964, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}O_3$ $[M+H]^+$: 301.1798, found 301.1787.



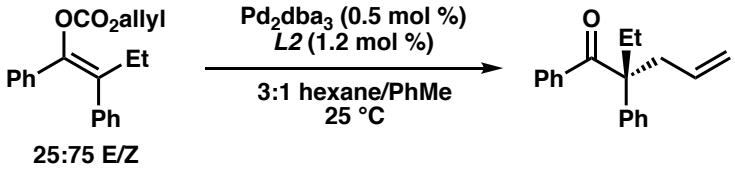
2-cyclohexyl-2-methyl-1-phenylpent-4-en-1-one (SI7)

In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (1.8 mg/mL) and **L2** (2.8 mg/mL) in toluene was stirred for 30 minutes at 25 °C, then 0.5 mL of the resulting catalyst solution was added to a one dram vial containing beta-ketoester **SI6** (0.2 mmol) dissolved in hexanes (1.5 mL). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and stirred at 25 °C for 12 h. The crude reaction mixture was concentrated then purified by preparative TLC to provide the desired alkylation product as a colorless oil (27.0 mg, 53% yield); 37% ee, $[\alpha]_D^{25}$ – 7.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.58 (m, 2H), 7.49–7.32 (m, 3H), 5.77–5.53 (m, 1H), 5.13–4.87 (m, 2H), 2.72 (dd, *J* = 13.9, 6.6 Hz, 1H), 2.40–2.19 (m, 1H), 2.00 (tt, *J* = 11.3, 2.9 Hz, 1H), 1.84–1.56 (m, 4H), 1.48 (dt, *J* = 9.1, 3.2 Hz, 1H), 1.35–1.03 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 140.3, 134.5, 130.8, 128.2, 127.6, 118.0, 55.3, 45.5, 42.2, 28.8, 27.5, 27.1, 27.0, 26.7, 18.5; IR (Neat Film, NaCl) 2929, 2853, 1672, 1446, 1379, 1216, 1002, 967, 916, 772, 723, 694 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{25}O$ $[M+H]^+$: 257.1900, found 257.1894; SFC Conditions : 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 6.16, minor = 6.92.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.159	VV	0.1531	2831.57959	282.05585	68.4086
2	6.916	VB	0.1606	1307.63428	126.53262	31.5914

Enantioselectivity Time Course Measurement



entry	time (min)	ee
1	10	89.5
2	20	89.3
3	30	89.2
4	60	89.8
5	120	89.7
6	180	89.6

In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (1.8 mg/mL) and **L2** (2.8 mg/mL) in toluene was stirred for 30 minutes at 25 °C, then 2.5 mL of the resulting catalyst solution was added to a vial containing 25:75 E/Z enol carbonate **1a** (1.0 mmol) dissolved in hexanes (7.5 mL). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and stirred at 25 °C. At the indicated time intervals, 250 μL of the reaction mixture was removed, filtered through a plug of silica, and purified by preparative TLC (10% Et_2O in hexanes). Analysis by chiral SFC showed that the ee of the product is initially high, and remains constant throughout the course of the reaction.

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